Supporting Information

# Overcoming the Necessity of γ-substitution in δ-C(sp$^3$)–H Arylation: Pd-Catalyzed Derivatization of α-Amino Acids

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## Experimental procedures and data

**General Methods.** The corresponding starting materials were synthetized using oven-dried glassware under argon atmosphere containing a teflon-coated stirrer bar and dry septum. All reactions were performed at ambient pressure in oven-dried pressure tube, sealed with a Teflon-lined screw cap.

All general reagents were obtained from usual commercial sources and were used, except when noted, without further purification. Amino acid and iodoarene derivatives were purchased from Aldrich Chemical Co., TCI or Fluorochem and used without further purification. $Pd(OAc)_2$ and silver acetate were purchased from Aldrich Chemical Co.

Solvents were purified by standard procedures prior to use. All other compounds are commercially available and were used without further purification.

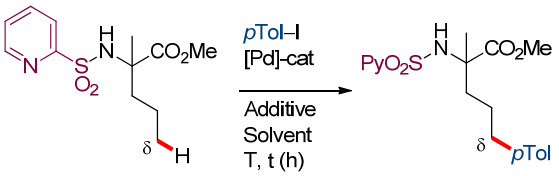
Flash column chromatography was performed using 230-400 mesh ultra-pure silica gel. NMR-spectra were obtained on 300 and 500 MHz spectrometers, chloroform-d as solvent, with proton and carbon resonances at 300/500 MHz and 75/126 MHz, respectively. $^{13}C$ NMR experiments are $^{1}H$ decoupled.

Infrared experiments were carried out in an *Agilent Cary 630 FTIR* spectrometer. Mass spectral data were acquired on a VG *AutoSpec mass* spectrometer. The isotopes considered in the HRMS analysis was $^{79}Br$ and $^{35}Cl$ respectively. Melting points were determined in a *Büchi Melting Point* apparatus. Optical rotations were measured at 20 °C or 25 °C on an *Anton Paar Modular Compact Polarimeter* (MCP 150) using a 10 cm cell with the solvent and concentration stated, at 589 nm (sodium lamp).

The 2-pyridylsulfonyl chloride was synthesized from 2-mercaptopyridine following the procedure described in the literature.[1]

## 1. Additional information

### 1.1. Optimization studies for the derivatization of 1b (Table S1)




**1b** **4b**

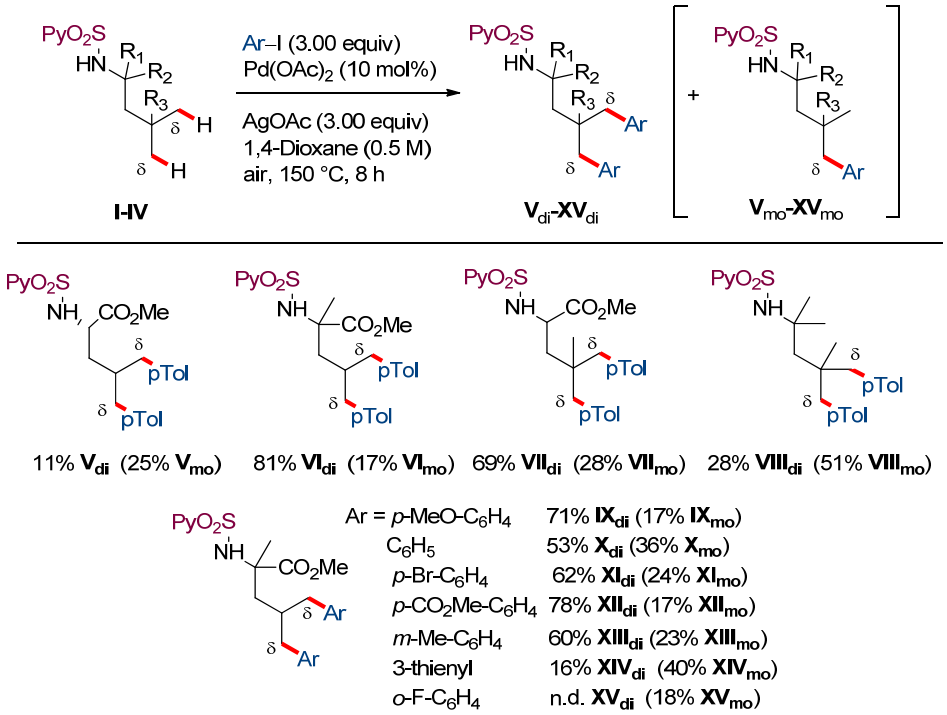
| Entry | *p*Tol–I (equiv) | Additives (equiv) | Solvent | 4b (%)[a] |
|---|---|---|---|---|
| **1** | 5.00 | AgOAc (3.00) | HFIP | 42 |
| **2** | 5.00 | AgOAc (1.50) | HFIP | 29 |
| **3** | 3.00 | AgOAc (3.00) | HFIP | 34 |
| **4** | 3.00 | AgOAc (3.00) | 1,4-Dioxane | 49 |
| **5**[b] | 3.00 | AgOAc (3.00) | 1,4-Dioxane | 58 |
| **6**[b,c] | 3.00 | AgOAc (3.00) | 1,4-Dioxane | – |
| **7**[b] | 3.00 | - | 1,4-Dioxane | – |
| **8**[b] | 3.00 | NaOAc (3.00) | 1,4-Dioxane | – |
| **9**[b] | 3.00 | AgOTFA (3.00) | 1,4-Dioxane | 15 |
| **10**[b] | 3.00 | AgOTFA+NaOAc (3.00+3.00) | 1,4-Dioxane | 20 |
| **11**[b,d] | 3.00 | AgOAc (3.00) | 1,4-Dioxane | 66 |

*Reaction conditions:* *N*–$SO_2$Py-DL-α-Me-Nva **1b** (0.20 mmol, 1.00 equiv), $Pd(OAc)_2$ (10 mol%, 0.02 mmol), Additive, Solvent (anh.) (1.0 M), 150 °C, 16 (h), Argon. [a] Isolated yields. [b] Solvent (0.50 M). [c] Without $Pd(OAc)_2$. [d] With $Pd(OAc)_2$ (15 mol%) HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol.

**Table S1.** Optimization studies for the derivatization of **1b**

We started our investigations by subjecting the *N*–$SO_2$Py-α-methyl-norvaline derivative **1b** to a modified protocol of our previously described arylation conditions.[2] The reaction conditions consisted in 5.00 equiv of 4-iodotoluene, 10 mol% of $Pd(OAc)_2$ and 3.00 equiv of AgOAc, with HFIP as solvent at 150 °C for 16 h. To our surprise, the δ-arylated product could be isolated in a 42% yield (entry 1) with complete regioselectivity even in the presence of the typically more reactive methylene γ-C($sp^3$)–H bonds, recovering the remaining starting material unaltered. Lower amounts of AgOAc or 4-iodotoluene (entries 2 and 3, respectively) were translated in a decrease of the δ-arylated product yield. However, the yield increased up to a 49% (entry 4) when using 1,4-dioxane instead of HFIP. Lower concentrations of solvent increased the yield up to a 58% (entry 5). Control experiments showed that both the palladium and the silver salts were essential components of the catalyst system (entries 6-8). Thus, the formation of the δ-arylated product **4b** was not detected in the absence of the Pd source (entry 6). The same outcome was observed in the absence of silver, even when an external base was present in the system (entries 7 and 8, respectively). In addition, lower yields were obtained when AgOTFA was used, as well as when using a combination of AgOTFA and NaOAc (entries 9 and 10, respectively). Finally, the yield increased up to a 66% when using 15 mol% of $Pd(OAc)_2$ (entry 11).

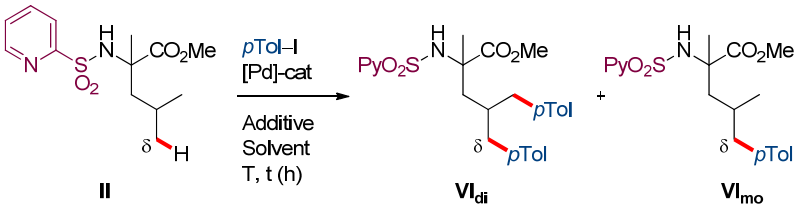
## 1.2. δ-Arylation of substrates with branching at γ-position




**Scheme S1.** δ-Arylation of substrates with branching at γ-position.

This method was shown to be also suitable for α-AAs having γ-substitution. For example, the simple leucine derivative **I** underwent δ-arylation with high selectivity, although the reaction could not be stopped at the mono-arylation stage and a mixture of mono- and diarylation products was obtained in modest yield (11% of $\mathbf{V_{di}}$ and 25% of $\mathbf{V_{mo}}$). The presence of a tetra-substituted carbon at either α- or γ-position led to a dramatic increase in reactivity and a greater diarylation ratio, as illustrated by the formation of the diarylated α-methyl leucine derivative $\mathbf{VI_{di}}$ (81%) [$\mathbf{VI_{mo}}$ (17%)], and product $\mathbf{VII_{di}}$ (69%) [$\mathbf{VII_{mo}}$ (28%)]. The 2,4,4-trimethylpentan-2-amine derivative **IV**, with fully substituted carbons at both α- and γ-position provided mainly the mono δ-arylation product with moderate selectivity [$\mathbf{VIII_{mo}}$ (51%) and $\mathbf{VIII_{di}}$ (28%)]. It was found, however, that the reactivity or the mono/disubstitution selectivity was marginally affected by the electronic properties of the aryl iodide partner upon exploring a range of *para*- and *meta*-substituted aryl iodides in the arylation of α-methyl leucine derivative **II**, (products **IX-XIII**, 83-95%), yet 3-iodothiophene displayed diminished reactivity, better monoarylation selectivity was observed [$\mathbf{XIV_{mo}}$ (40%) and $\mathbf{XIV_{di}}$ (16%)]. *Ortho*-substitutents resulted in reduced reactivity ($\mathbf{XV_{mo}}$, 18%). These results highlight that this method is complementary in scope to earlier methods by Maiti[3] and Yu[4] favoring monoarylation at δ-position in substrates branched at γ-carbons holding di- or trimethyl moieties.

### 1.3. Optimization studies for the derivatization of II (Table S2)



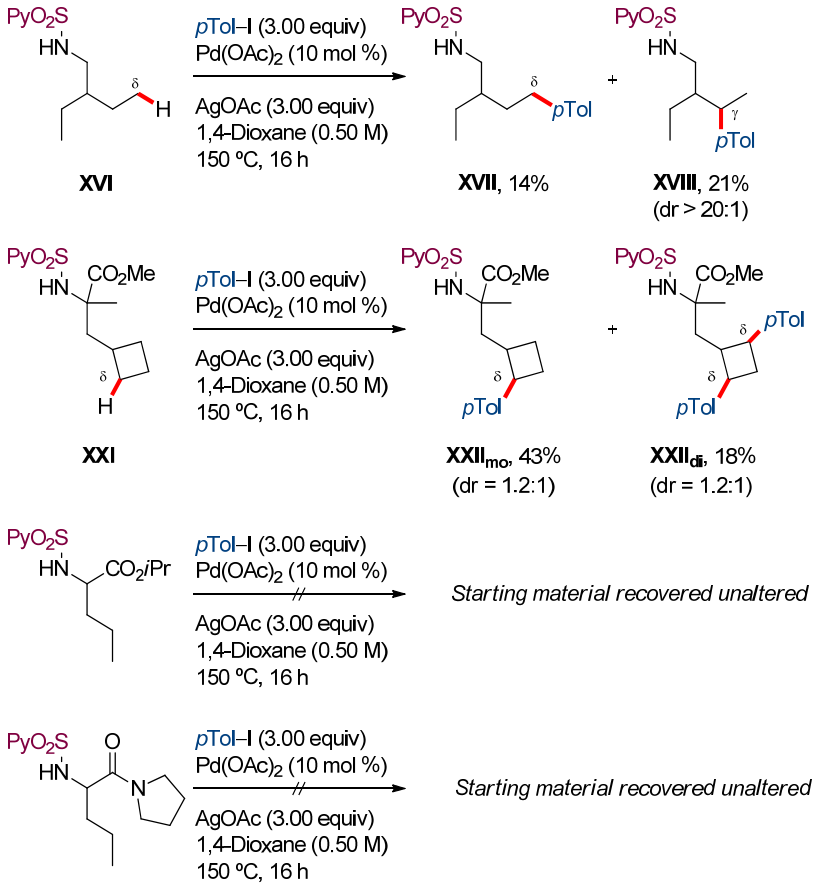

| Entry | *p*Tol–I (equiv) | Additives (equiv) | $VI_{di}$ (%) [a] | $VI_{mo}$ (%) [a] |
|---|---|---|---|---|
| **1** | 3.00 | AgOAc (3.00) | 81 | 17 |
| **2** | 2.00 | AgOAc (3.00) | 61 | 39 |
| **3** | 1.20 | AgOAc (3.00) | 22 | 46 |
| **4** | 1.20 | AgOAc (2.00) | 13 | 43 |
| **5** | 1.20 | AgOAc (1.20) | 13 | 41 |
| **6** | 2.00 | AgOAc (1.20) | 15 | 44 |
| **7**[b] | 2.00 | AgOAc (1.20) | 8 | 39 |
| **8**[c] | 2.00 | AgOAc (1.20) | – | – |

*Reaction conditions: N*–$SO_2$Py-α-Me-Leu **II** (0.20 mmol, 1.00 equiv), $Pd(OAc)_2$ (10 mol%, 0.02 mmol), Additive, 1,4-dioxane (anh.) (0.5 M), T °C, 16 (h), Argon. [a] Determined by $^1$H NMR of the crude mixture. [b] T = 130 °C. [c] T = 110 °C.

**Table S2.** Optimization studies for the derivatization of **II**.

In order to evaluate the selectivity of the system towards the monoarylation versus the diarylation, substrate *N*–$SO_2$Py-α-methyl-leucine **II** was used as model substrate. Starting from the previously optimized conditions, a quantitative conversion was observed obtaining the diarylated product $\mathbf{VI_{di}}$ in 81% yield along with 17% of the monoarylated derivative $\mathbf{VI_{mo}}$ (entry 1). Therefore, we initially attempted to favor the monoarylation by just lowering the amount of the aryl iodide partner. Obtaining the best result on using 1.20 equiv of 4-iodotoluene (entry 3): 22% of $\mathbf{VI_{di}}$ along with 46% of $\mathbf{VI_{mo}}$ (entry 3). Nonetheless, the conversion was slower. In principle, we attempt to improve it by decreasing the amount of the silver salt (entries 4-5). However, the conversion decreased although the selectivity towards the monoarylated product slightly improved. This result was not modified on increasing the amount of aryl iodide to 2.00 equiv (entry 6), even when decreasing the reaction temperature to 130 °C (entry 7). No reactivity was observed at 110 °C (entry 8).

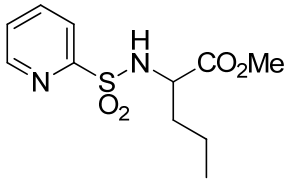
## 1.4. Other substrates tested

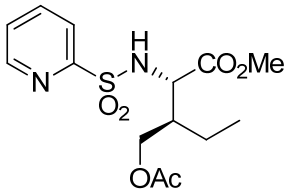



**Scheme S2.** δ-Arylation of amine **XVI** and aminoacid **XXI**.

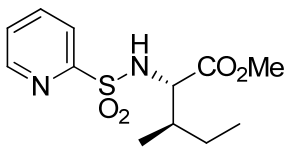
## 2. Synthesis of starting materials

### 2.1. Typical procedure for the synthesis of the *N*–$SO_2$Py protected amino acid derivatives 8, 9, 45-47, I and II

**Synthesis of (*rac*)-methyl 2-(pyridine-2-sulfonamido)pentanoate (8).**[2]  In a 100 mL round bottom flask, DL-Norvaline methyl ester hydrochloride (553 mg, 3.30 mmol, 1.00 equiv) was introduced and next flushed with argon. Anhydrous $CH_3CN$ (50.0 mL) and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) (2.70 mL, 18.0 mmol, 6.00 equiv) were then added. The mixture was placed in a 0 °C bath (ice-water) and 2-pyridylsulfonyl chloride (533 mg, 3.00 mmol, 1.00 equiv) was added dropwise. The mixture was stirred for 18 h at room temperature. The solvent was then removed under reduced pressure and the resulted crude product was dissolved in EtOAc and washed with 1 M HCl. The organic phase was then washed with water, brine, dried over $Na_2SO_4$, filtered, and concentrated *in vacuo*. The resulted residue was purified by flash column chromatography (cyclohexane:EtOAc 3:1) to give **8** as a white solid; yield: 688 mg (84%); mp = 97-98 °C. **$^1$H NMR (500 MHz, $CDCl_3$, δ):** 8.64 (ddd, *J* = 4.6, 1.5, 0.8 Hz, 1H), 7.97 (dt, *J* = 7.9, 0.9 Hz, 1H), 7.90 (td, *J* = 7.7, 1.7 Hz, 1H), 7.48 (ddd, *J* = 7.6, 4.7, 1.1 Hz, 1H), 5.46 (d, *J* = 9.0 Hz, 1H), 4.30 (ddd, *J* = 8.9, 8.0, 5.2 Hz, 1H), 3.59 (s, 3H), 1.80 – 1.73 (m, 1H), 1.68 – 1.61 (m, 1H), 1.47 – 1.35 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$, δ):** 172.5, 158.0, 149.8, 138.2, 126.8, 121.9, 56.7, 52.5, 35.8, 18.4, 13.6. **HRMS-ESI (*m/z*):** calcd. for $C_{11}H_{16}N_2O_4SNa$ $(M+Na)^+$: 295.0723; Found: 295.0723.

**(2*S**,3*R**)-Methyl 3-(acetoxymethyl)-2-(pyridine-2-sulfonamido)pentanoate (9).**  Compound **9** was prepared following the typical procedure from DL-γ-acetyl-*allo*-isoleucine methyl ester hydrochloride (791 mg, 3.30 mmol, 1.10 equiv) to give **9** as a colorless oil; yield: 857 mg (83%). **$^1$H NMR (300 MHz, $CDCl_3$, δ):** 8.63 (ddd, *J* = 4.7, 1.7, 0.9 Hz, 1H), 7.98 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.90 (td, *J* = 7.7, 1.7 Hz, 1H), 7.47 (ddd, *J* = 7.5, 4.7, 1.3 Hz, 1H), 5.44 (d, *J* = 9.6 Hz, 1H), 4.51 (dd, *J* = 9.6, 3.4 Hz, 1H), 4.06 – 4.04 (m, 2H), 3.59 (s, 3H), 2.27 – 2.18 (m, 1H), 1.97 (s, 3H), 1.59 – 1.50 (m, 1H), 1.46 – 1.31 (m, 1H), 1.02 (t, *J* = 7.4 Hz, 3H).**$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 172.0, 170.8, 158.1, 149.8, 138.2, 126.9, 121.9, 63.3, 57.3, 52.6, 42.8, 21.4, 20.9, 11.6. **HRMS-ESI (*m/z*):** calcd. for $C_{14}H_{20}N_2O_6SNa$ $(M+Na)^+$: 367.0934; Found: 367.0935.

**(2*S**,3*R**)-Methyl 3-methyl-2-(pyridine-2-sulfonamido)pentanoate (XIX).**

**Step 1. Protection of the acid group.** To a suspended mixture of DL-allo-isoleucine  (2.00 g, 15.2 mmol, 1.00 equiv) in MeOH (30.5 mL) at 0 °C, thionyl chloride (1.22 mL, 16.7 mmol, 1.10 equiv) was added dropwise under argon atmosphere. Once the thionyl chloride was added, the solution was refluxed for 3 h. After this time, the volatiles were removed *in vacuo* affording the pure aminoester hydrochloride, which was used without further purification.

**Step 2. Protection of the amino group**. The previously synthetized methyl ester hydrochloride (600 mg, 3.30 mmol, 1.10 equiv) was submitted to the conditions of the general protocol for the synthesis of *N*–$SO_2$Py protected amino acid derivatives, to give **XIX** as a white solid; yield: 3.92 g (90%); mp = 111-112 °C. **$^1$H NMR (300 MHz, $CDCl_3$, δ):** 8.59 (d, *J* = 4.6 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.85 (td, *J* = 7.7, 1.6 Hz, 1H), 7.44 (ddd, *J* = 7.4, 4.7, 1.2 Hz, 1H), 5.47 (d, *J* = 9.9 Hz, 1H), 4.29 (dd, *J* = 9.9, 4.1 Hz, 1H), 3.52 (s, 3H), 1.88 – 1.75 (m, 1H), 1.56 – 1.42 (m, 1H), 1.30 – 1.15 (m, 1H), 0.90 (t, *J* = 7.4 Hz, 3H), 0.80 (d, *J* = 6.9 Hz, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 172.2, 157.9, 149.7, 138.1, 126.7, 121.8, 60.2, 52.3, 38.2, 26.0, 14.3, 11.5. **HRMS-ESI (*m/z*):** calcd. for $C_{12}H_{19}N_2O_4S$ $(M+H)^+$: 287.1060; Found: 287.1060.

**(2*S*,3*S*)-Methyl 3-methyl-2-(pyridine-2-sulfonamido)pentanoate ((+)-XX).** Compound (+)-**XX** was prepared following the typical procedure from L-isoleucine methyl ester hydrochloride (600 mg, 3.30 mmol, 1.10 equiv) to give (+)-**XX** as a white solid; yield: 664 mg (77%); mp = 98-100 °C. **$^1$H NMR (300 MHz, $CDCl_3$, δ):** 8.61 (ddd, *J* = 4.7, 1.5, 0.9 Hz, 1H), 7.94 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.87 (td, *J* = 7.7, 1.7 Hz, 1H), 7.45 (ddd, *J* = 7.5, 4.7, 1.3 Hz, 1H), 5.47 (d, *J* = 9.6 Hz, 1H), 4.17 (dd, *J* = 9.6, 5.3 Hz, 1H), 3.54 (s, 3H), 1.89 – 1.76 (m, 1H), 1.50 – 1.36 (m, 1H), 1.24 – 1.09 (m, 1H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 171.9, 157.9, 149.8, 138.1, 126.8, 121.9, 61.4, 52.2, 38.7, 24.7, 15.5, 11.4. **HRMS-ESI (*m/z*):** calcd. for $C_{12}H_{19}N_2O_4S$ $(M+H)^+$: 287.1060; Found: 287.1052. **$[\alpha]_D^{25}$:** +25 (*c* = 1.0; $CH_2Cl_2$).

**(*S*)-Methyl 4-methyl-2-(pyridine-2-sulfonamido)pentanoate ((+)-I).** Compound (+)-**I** was prepared following the typical procedure from L-Leucine methyl ester hydrochloride (600 mg, 3.30 mmol, 1.10 equiv) to give (+)-**I** as a white solid; yield: 604 mg (70%); mp = 81-83 °C. **$^1$H NMR (300 MHz, $CDCl_3$, δ):** 8.65 – 8.63 (m, 1H), 7.97 (d, *J* = 7.9 Hz, 1H), 7.89 (td, *J* = 7.7, 1.6 Hz, 1H), 7.47 (ddd, *J* = 7.4, 4.7, 1.2 Hz, 1H), 5.32 (d, *J* = 9.5 Hz, 1H), 4.35 – 4.27 (m, 1H), 3.56 (s, 3H), 1.84 (n, *J* = 6.7 Hz, 1H), 1.57 – 1.52 (m, 2H), 0.94 (d, *J* = 6.5 Hz, 3H), 0.92 (d, *J* = 6.6 Hz, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 172.9, 158.0, 149.9, 138.1, 126.8, 121.9, 55.6, 52.5, 42.8, 24.4, 22.9, 21.6. **HRMS-ESI (*m/z*):** calcd. for $C_{12}H_{19}N_2O_4S$ $(M+H)^+$: 287.1060; Found: 287.1058. **$[\alpha]_D^{25}$:** +3 (*c* = 1.0; $CH_2Cl_2$).

**(*rac*)-Methyl 2,4-dimethyl-2-(pyridine-2-sulfonamido)pentanoate (II).**

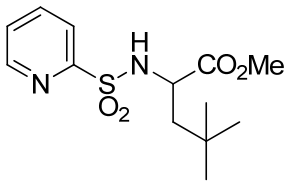
**Step 1. Protection of the acid group.** To a suspended mixture of DL-α-methyl-leucine (2.21 g, 15.2 mmol, 1.00 equiv) in MeOH (30.5 mL) at 0 °C, thionyl chloride (1.22 mL, 16.7 mmol, 1.10 equiv) was added dropwise under argon atmosphere. Once the thionyl chloride was added, the solution was refluxed for 16 h. After this time, the volatiles were removed *in vacuo* affording the pure aminoester hydrochloride, which was used without further purification.

**Step 2. Protection of the amino group**. The previously synthetized methyl ester hydrochloride (646 mg, 3.30 mmol, 1.10 equiv) was submitted to the conditions of the general protocol for the synthesis of *N*–$SO_2$Py protected amino acid derivatives, to give **II** as a white solid; yield: 542 mg (60%); mp = 82-84 °C. **$^1$H NMR (300 MHz, $CDCl_3$, δ):**

8.71 – 8.69 (m, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.88 (td, *J* = 7.7, 1.7 Hz, 1H), 7.46 (ddd, *J* = 7.6, 4.7, 1.2 Hz, 1H), 5.98 (s, 1H), 3.70 (s, 3H), 2.02 (dd, *J* = 14.0, 4.7 Hz, 1H), 1.89 – 1.76 (m, 1H), 1.70 – 1.62 (m, 1H), 1.36 (s, 3H), 0.91 (d, *J* = 6.6 Hz, 3H), 0.80 (d, *J* = 6.6 Hz, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 174.6, 159.8, 150.1, 138.1, 126.5, 121.4, 62.6, 53.0, 48.5, 24.3, 24.2, 22.7. **HRMS-ESI (*m/z*):** calcd. for $C_{13}H_{20}N_2O_4SNa$ ($M+H^+$): 323.1036; Found: 323.1037.

**(*rac*)-Methyl 4,4-dimethyl-2-(pyridine-2-sulfonamido)pentanoate (III).**

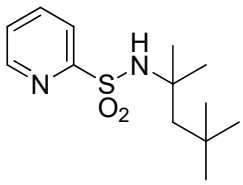
**Step 1. Protection of the acid group.** To a suspended mixture of DL-neopentylglycine



(2.21 g, 15.2 mmol, 1.00 equiv) in MeOH (30.5 mL) at 0 °C, thionyl chloride (1.22 mL, 16.7 mmol, 1.10 equiv) was added dropwise under argon atmosphere. Once the thionyl chloride was added, the solution was refluxed for 16 h. After this time, the volatiles were removed *in vacuo* affording the pure aminoester hydrochloride, which was used without further purification.

**Step 2. Protection of the amino group**. The previously synthetized methyl ester hydrochloride (646 mg, 3.30 mmol, 1.10 equiv) was submitted to the conditions of the general protocol for the synthesis of *N*–$SO_2$Py protected amino acid derivatives, to give **47** as a white solid; yield: 793 mg (88%). **$^1$H NMR (300 MHz, $CDCl_3$, δ):** 8.65 (ddd, *J* = 4.7, 1.7, 0.9 Hz, 1H), 7.97 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.89 (td, *J* = 7.7, 1.7 Hz, 1H), 7.47 (ddd, *J* = 7.5, 4.7, 1.3 Hz, 1H), 5.19 (d, *J* = 10.1 Hz, 1H), 4.36 (ddd, *J* = 10.2, 8.5, 4.3 Hz, 1H), 3.51 (s, 3H), 1.66 (dd, *J* = 14.4, 4.3 Hz, 1H), 1.51 (dd, *J* = 14.4, 8.5 Hz, 1H), 1.00 (s, 9H). **$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 173.2, 157.9, 149.9, 138.1, 126.8, 122.0, 54.9, 52.4, 47.1, 31.0, 29.7. **HRMS-ESI (*m/z*):** calcd. for $C_{13}H_{20}N_2O_4SNa$ ($M+Na)^+$: 323.1036; Found: 323.1037.

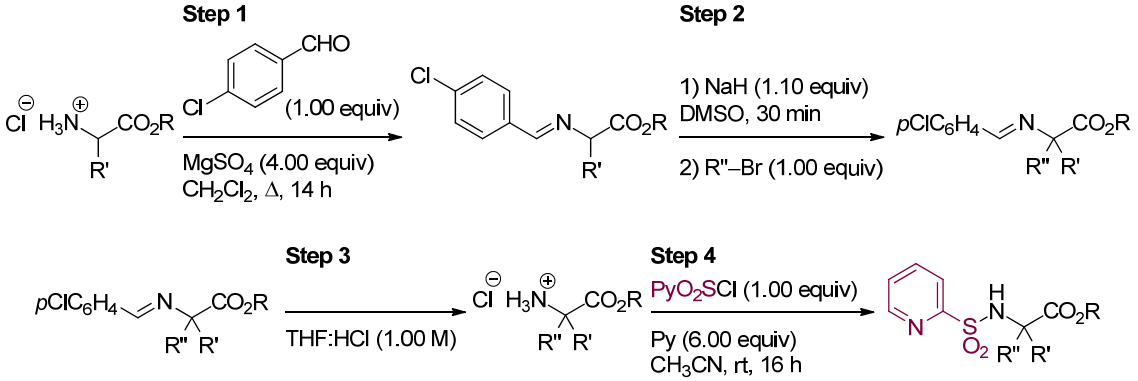
***N*-(2,4,4-Trimethylpentan-2-yl)pyridine-2-sulfonamide (IV).** Compound **IV** was



prepared following the typical procedure from *tert*-octylamine (0.53 mL, 3.30 mmol, 1.10 equiv) to give **IV** as a colorless oil; yield: 682 mg (84%). **$^1$H NMR (300 MHz, $CDCl_3$, δ):** 8.69 (ddd, *J* = 4.7, 1.5, 0.8 Hz, 1H), 8.00 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.87 (td, *J* = 7.7, 1.7 Hz, 1H), 7.45 (ddd, *J* = 7.6, 4.7, 1.1 Hz, 1H), 4.94 (bs, 1H), 1.55 (s, 2H), 1.22 (s, 6H), 1.00 (s, 9H). **$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 160.2, 149.9, 138.1, 126.3, 121.6, 58.9, 55.5, 31.8, 31.7, 29.6. **HRMS-ESI (*m/z*):** calcd. for $C_{26}H_{44}N_4O_4S_2Na$ ($2M+Na)^+$: 563.2696; Found: 563.2707.

## 2.2. Synthesis of α,α'-disubstituted *N*–$SO_2$Py amino ester derivatives[5]

### General procedure

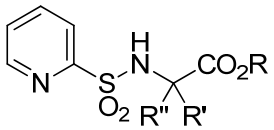



**Step 1. Synthesis of 4-chlorobenzylidene imine ester derivatives.** To a 50.0 mL round bottom flask, 4-chlorobenzaldehyde (2.11 g, 15 mmol, 1.00 equiv), amino acid alkyl ester hydrochloride (15.0 mmol, 1.00 equiv) and $MgSO_4$ (7.22 g, 60 mmol, 4.00 equiv) were added. The flask was then sealed with a rubber septum and filled with argon. Under positive argon pressure, $Et_3N$ (3.86 mL, 52.5 mmol, 3.50 equiv) and $CH_2Cl_2$ (15.0 mL) were added. Then, the reaction was heated under reflux for 14 h. After that time, the reaction was cooled to room temperature, filtered, washed with water and brine, dried over $MgSO_4$ and filtered. The solvent was eliminated *in vacuo* affording the corresponding imines which were used without further purification due to its instability.

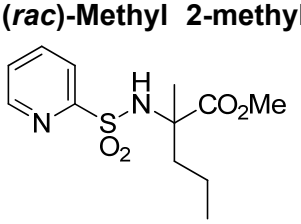
**Step 2. α-Alkylation of imine derivatives.** In a 100 mL vessel NaH in mineral oil (219 mg, 5.50 mmol, 1.10 equiv) was weighed and washed with hexane. Then, a solution of the previously synthetized imine derivatives (5.00 mmol, 1.00 equiv) in dry dimethylsulfoxide (10.0 mL) was added under positive argon pressure. After 30 min stirring, the corresponding alkylbromide (5.00 mmol, 1.00 equiv) was added *via* syringe and the resulting mixture was left under stirring for another 16 h. After that time, the crude mixture was diluted with brine and $Et_2O$. The organic phase was separated, and the aqueous phase was extracted three times with $Et_2O$. The combination of the organic phases was dried over $MgSO_4$, filtered and the solvent was eliminated *in vacuo*, affording the corresponding α,α'-disubstituted imine derivatives which were used without further purification.

**Step 3. Deprotection of the α,α'-disubstituted imine derivatives.** The previously synthetized imine derivatives (5.00 mmol, 1.00 equiv) were dissolved in THF (7.50 mL) and at 0 °C, a HCl 1 M aqueous solution (7.50 mL) was added. The resulting mixture was left under stirring for 90 min. After that time, Et2O (10.0 mL) was added and the organic solvent was extracted. Then, and the organic phase was washed with $H_2O$. The combined aqueous solvent was removed *in vacuo* and the resulting crude aminoester hydrochloride was used without further purification.

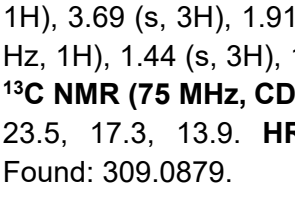
**Step 4. Protection of the amino group.** The protection of the amino group was carried out following the general protocol for the synthesis of *N*–$SO_2$Py protected amino acid derivatives, and the resulting crude *N*–$SO_2$Py amino ester derivative was purified by flash column chromatography (heptane:EtOAc 4:1). All the experimental data, global yields and characterization of the synthetized products are described below.



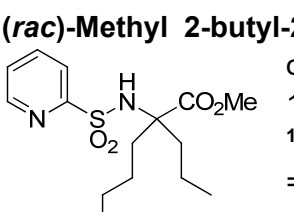

**(*rac*)-Methyl 2-methyl-2-(pyridine-2-sulfonamido)pentanoate (1b).** Compound **1b** was obtained from DL-norvaline methyl ester hydrochloride and iodomethane as a white solid; yield: 1.25 g (87%); mp = 86-87 °C. **$^1$H NMR (300 MHz, $CDCl_3$, δ):** 8.70 (ddd, *J* = 4.7, 1.6, 0.9 Hz, 1H), 7.99 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.89 (td, *J* = 7.7, 1.7 Hz, 1H), 7.46 (ddd, *J* = 7.6, 4.7, 1.2 Hz, 1H), 5.83 (s, 1H), 3.69 (s, 3H), 1.91 (ddd, *J* = 13.8, 12.1, 4.5 Hz, 1H), 1.70 (ddd, *J* = 13.8, 12.0, 4.8 Hz, 1H), 1.44 (s, 3H), 1.36 – 1.21 (m, 1H), 1.16 – 1.01 (m, 1H), 0.79 (t, *J* = 7.3 Hz, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 174.0, 159.5, 150.0, 138.1, 126.5, 121.5, 63.2, 53.0, 41.8, 23.5, 17.3, 13.9. **HRMS-ESI (*m/z*):** calcd. for $C_{12}H_{18}N_2O_4SNa$ (M+Na$^+$): 309.0879; Found: 309.0879.




**(*rac*)-Methyl 2-butyl-2-(pyridine-2-sulfonamido)pentanoate (5).** Compound **5** was obtained from DL-norvaline methyl ester hydrochloride and 1-bromobutane as a colorless oil; yield: 740 mg (45%). **$^1$H NMR (300 MHz, $CDCl_3$, δ):** 8.72 (d, *J* = 4.7 Hz, 1H), 8.01 (d, *J* = 7.9 Hz, 1H), 7.89 (td, *J* = 7.7, 1.7 Hz, 1H), 7.47 (ddd, *J* = 7.6, 4.7, 1.0 Hz, 1H), 5.94 (s, 1H), 3.72 (s, 3H), 2.08 – 1.98 (m, 2H), 1.74 – 1.62 (m, 2H), 1.18 – 1.02 (m, 4H), 0.93 – 0.84 (m, 2H), 0.77 (t, *J* = 7.1 Hz, 3H), 0.64 (t, *J* = 7.3 Hz, 3H).**$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 173.5, 159.6, 150.1, 138.0, 126.4, 121.5, 67.9, 53.0, 39.7, 37.5, 31.5, 23.7, 22.5, 17.3, 13.7. **HRMS-ESI (*m/z*):** calcd. for $C_{16}H_{26}N_2O_5SNa$ (M+Na$^+$): 365.1505; Found: 365.1504.



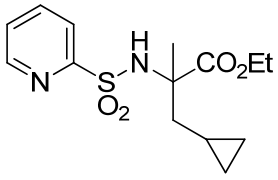

**(*rac*)-Methyl 2-propyl-2-(pyridine-2-sulfonamido)pentanoate (6).** Compound **6** was obtained from DL-norvaline methyl ester hydrochloride and 1-bromopropane as a white solid; yield: 802 mg (51%); mp = 81-83 °C. **$^1$H NMR (300 MHz, $CDCl_3$, δ):** 8.73 – 8.70 (m, 1H), 8.01 (d, *J* = 7.9 Hz, 1H), 7.89 (td, *J* = 7.7, 1.7 Hz, 1H), 7.47 (ddd, *J* = 7.6, 4.7, 1.1 Hz, 1H), 5.94 (s, 1H), 3.71 (s, 3H), 2.02 (ddd, *J* = 14.1, 12.3, 4.1 Hz, 2H), 1.67 (ddd, *J* = 14.1, 12.1, 4.9 Hz, 2H), 1.21 – 1.04 (m, 2H), 0.96 – 0.81 (m, 2H), 0.63 (t, *J* = 7.3 Hz, 6H). **$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 173.5, 159.5, 150.1, 138.1, 126.5, 121.5, 67.9, 53.0, 39.6, 17.3, 13.7. **HRMS-ESI (*m/z*):** calcd. for $C_{14}H_{22}N_2O_4SNa$ (M+Na$^+$): 337.1192; Found: 337.1191.




**(*rac*)- 4-Ethyl 1-methyl 2-propyl-2-(pyridine-2-sulfonamido)succinate (7).** Compound **7** was obtained from DL-norvaline methyl ester hydrochloride and ethyl iodoacetate as a colorless oil; yield: 844 mg (47%). **$^1$H NMR (300 MHz, $CDCl_3$, δ):** 8.66 (d, *J* = 3.9 Hz, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.87 (td, *J* = 7.7, 1.6 Hz, 1H), 7.45 (ddd, *J* = 7.4, 4.7, 1.1 Hz, 1H), 6.17 (s, 1H), 3.96 – 3.82 (m, 2H), 3.72 (s, 3H), 3.34 (d, *J* = 17.3 Hz, 1H), 2.89 (d, *J* = 17.3 Hz, 1H), 2.09 (ddd, *J* = 13.6, 12.7, 4.0 Hz, 1H), 1.67 – 1.57 (m, 1H), 1.27 – 1.12 (m, 4H), 1.00 – 0.83 (m, 1H),

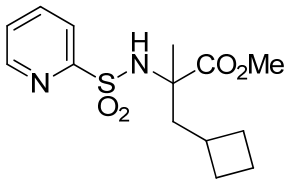
0.66 (t, *J* = 7.3 Hz, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 172.3, 169.8, 159.2, 150.0, 138.1, 126.5, 121.6, 64.2, 60.8, 53.3, 42.2, 39.7, 16.9, 14.1, 13.6. **HRMS-APCI (*m/z*):** calcd. for $C_{15}H_{23}N_2O_6S$ ($M+H^+$): 359.1271; Found: 359.1270.

**(*rac*)-Methyl 3-cyclopropyl-2-methyl-2-(pyridine-2-sulfonamido)propanoate (43).**



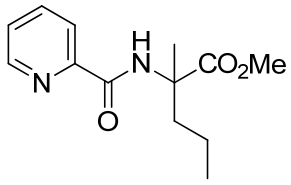
Compound **43** was obtained from DL-alanine ethyl ester hydrochloride and (bromomethyl)cyclopropane as a colorless oil; yield: 467 mg (30%). **$^1$H NMR (500 MHz, $CDCl_3$, δ):** 8.70 (d, *J* = 4.7 Hz, 1H), 8.00 (d, *J* = 7.9 Hz, 1H), 7.89 (td, *J* = 7.8, 1.6 Hz, 1H), 7.46 (ddd, *J* = 7.5, 4.7, 0.9 Hz, 1H), 5.97 (s, 1H), 4.21 – 4.08 (m, 2H), 2.01 (dd, *J* = 14.1, 6.0 Hz, 1H), 1.57 (dd, *J* = 14.2, 7.4 Hz, 1H), 1.46 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H), 0.69 – 0.62 (m, 1H), 0.46 – 0.37 (m, 2H), 0.13 – 0.09 (m, 1H), 0.01 – -0.04 (m, 1H). **$^{13}$C NMR (126 MHz, $CDCl_3$, δ):** 173.5, 159.6, 150.0, 138.1, 126.5, 121.6, 63.4, 62.1, 44.8, 23.1, 14.2, 6.0, 4.3, 4.2. **HRMS-ESI (*m/z*):** calcd. for $C_{14}H_{20}N_2O_4SNa$ ($M+Na^+$): 335.1036; Found: 335.1039.

**(*rac*)-Methyl 3-cyclobutyl-2-methyl-2-(pyridine-2-sulfonamido)propanoate (XXI).**



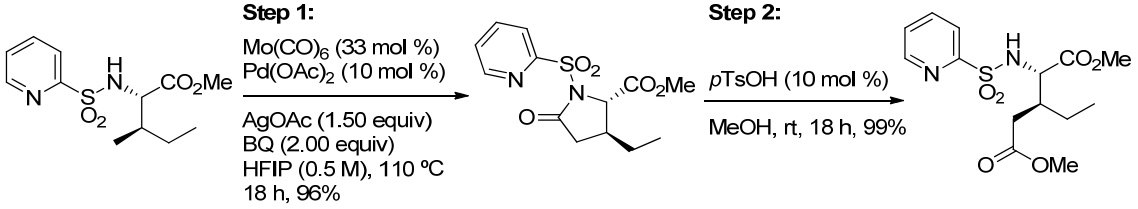
Compound **XXI** was obtained from DL-alanine methyl ester hydrochloride and (bromomethyl)cyclobutane as a white solid; yield: 980 mg (63%); mp = 100-101 °C. **$^1$H NMR (500 MHz, $CDCl_3$, δ):** 8.69 (ddd, *J* = 4.7, 1.7, 0.9 Hz, 1H), 7.97 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.88 (td, *J* = 7.7, 1.7 Hz, 1H), 7.46 (ddd, *J* = 7.6, 4.7, 1.1 Hz, 1H), 5.84 (s, 1H), 3.65 (s, 3H), 2.36 – 2.27 (m, 1H), 2.05 (dd, *J* = 14.1, 6.1 Hz, 1H), 1.92 – 1.85 (m, 2H), 1.84 – 1.79 (m, 1H), 1.79 – 1.76 (m, 1H), 1.71 – 1.60 (m, 2H), 1.56 – 1.49 (m, 1H), 1.38 (s, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$, δ):** 173.9, 159.5, 150.0, 138.1, 126.5, 121.5, 62.4, 52.8, 46.9, 31.6, 29.4, 29.1, 23.2, 19.1. **HRMS-ESI (*m/z*):** calcd. for $C_{14}H_{21}N_2O_4S$ ($M+H^+$): 313.1222; Found: 313.1220.

**(*rac*)-Methyl 2-methyl-2-(picolinamido)pentanoate (1a).** Compound **1a** was obtained from DL-norvaline methyl ester hydrochloride and iodomethane. Instead of following the general procedure for the protection of the amino group, the procedure was as it follows: A 50.0 mL round-bottomed flask was immersed in a 0 °C bath (ice-water) was charged with picolinic acid (616 mg, 5.00 mmol, 1.00 equiv) and $CH_2Cl_2$ (10.0 mL). To the stirred suspension was added dropwise oxalyl chloride (0.47 mL, 5.50 mmol, 1.10 equiv) over a 15 min period followed by addition of DMF (0.10 mL, catalytic amount) in one portion, producing a rust-red color and the evolution of a gas. The mixture was kept in the cooling bath for 1 h and then allowed to warm to room temperature. After gas evolution ceased, the mixture was again cooled to 0 °C and TMEDA (4.50 mL, 30.0 mmol, 6.00 equiv) was added dropwise over a 15 min period. The reaction mixture was then added to a round bottomed flask with the previously synthetized amino ester hydrochloride and was left under stirring at room temperature for 16 h. Removal of solvent *in vacuo* gave the crude product as a brown oil that was extracted with $H_2O$-$CH_2Cl_2$. The organic phases were combined, concentrated under reduced pressure and purified by chromatography (cyclohexane:EtOAc 6:1) to give **1a** as a colorless oil; yield: 962 mg (77%). **$^1$H NMR (300 MHz, $CDCl_3$, δ):** 8.72 (s, 1H), 8.54 (d, *J* = 4.8 Hz, 1H), 8.12 (dd, *J* = 7.8, 0.8 Hz, 1H), 7.80 (td, *J* = 7.7, 1.6 Hz, 1H), 7.39 (dd, *J* = 7.6, 4.8 Hz, 1H), 3.76 (s, 3H), 2.30 – 2.20 (m, 1H), 1.93 – 1.83 (m, 1H), 1.68 (s, 3H), 1.39 – 1.26 (m, 1H), 1.24 – 1.09 (m, 1H), 0.88 (t, *J* = 7.3 Hz, 3H). **$^{13}$C NMR (75 MHz,**



**$CDCl_3$, δ):** 174.8, 163.4, 150.2, 148.2, 137.3, 126.2, 121.9, 60.2, 52.7, 39.4, 23.0, 17.6, 14.1.

### 2.3. Synthesis of (2*S**,3*S**)-dimethyl 3-ethyl-2-(pyridine-2-sulfonamido) pentanedioate (10)

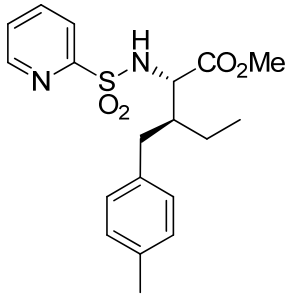



**Step 1. Synthesis of (2*S**,3*S**)-methyl 3-ethyl-5-oxo-1-(pyridin-2-ylsulfonyl) pyrrolidine-2-carboxylate (XXIII).**[6] An oven-dried Ace Pressure tube was charged with (2*S**,3*R**)-methyl 3-methyl-2-(pyridine-2-sulfonamido)pentanoate (**XIX**) (286 mg, 1.00 mmol, 1.00 equiv), AgOAc (250 mg, 1.50 mmol, 1.50 equiv), 1,4-benzoquinone (BQ) (216 mg, 2.00 mmol, 2.00 equiv), molybdenumhexacarbonyl (88.0 mg, 0.33 mmol, 0.33 equiv) and $Pd(OAc)_2$ (22.4 mg, 0.10 mmol, 0.10 equiv). The tube was sealed with a rubber septum and flushed with argon. Under positive pressure of argon, HFIP (2.00 mL) was added *via* syringe. The septum was then replaced by a Teflon-lined scew cap and the mixture was stirred at 110 °C for 18 h. After that time, the reaction mixture was cooled to room temperature, diluted with EtOAc, filtered through a short pad of Celite® and concentrated *in vacuo*. The resulting crude mixture was diluted with $CH_2Cl_2$, washed with NaOH 0.5 M, dried over $Na_2SO_4$ and concentrated *in vacuo*. The crude mixture was used in the next step without further purification.

**Step 2. Synthesis of (2*S**,3*S**)-dimethyl 3-ethyl-2-(pyridine-2-sulfonamido) pentanedioate (10).**[7] In a 10.0 mL vessel, (2*S**,3*S**)-methyl 3-ethyl-5-oxo-1-(pyridin-2-ylsulfonyl)pyrrolidine-2-carboxylate **XXIII** (188 mg, 0.60 mmol, 1.00 equiv) and *p*-toluenesulfonic acid (11.4 mg, 0.06 mmol, 0.10 equiv) were added. MeOH (1.00 mL) was added *via* syringe and the resulting mixture was stirred at room temperature for 18 h. Then, the solvent was removed *in vacuo* and the crude mixture was purified by column chromatography (heptane:EtOAc 2:1) to give **10** as a colorless oil; yield: 204 mg (99%). **$^1$H NMR (300 MHz, $CDCl_3$, δ):** 8.60 (ddd, *J* = 4.7, 1.4, 0.9 Hz, 1H), 7.93 (dt, *J* = 6.9, 0.9 Hz, 1H), 7.87 (td, *J* = 7.7, 1.7 Hz, 1H), 7.45 (ddd, *J* = 7.4, 4.7, 1.3 Hz, 1H), 5.64 (d, *J* = 9.7 Hz, 1H), 4.37 (dd, *J* = 9.7, 4.1 Hz, 1H), 3.61 (s, 3H), 3.54 (s, 3H), 2.41 – 2.22 (m, 3H), 1.62 – 1.48 (m, 1H), 1.41 – 1.29 (m, 1H), 0.94 (t, *J* = 7.4 Hz, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 173.0, 171.8, 157.9, 149.8, 138.1, 126.8, 121.9, 58.6, 52.5, 51.8, 40.0, 34.5, 24.2, 11.2. **HRMS-ESI (*m/z*):** calcd. for $C_{14}H_{20}N_2O_6SNa$ ($M+Na^+$): 367.0934; Found: 367.0934.

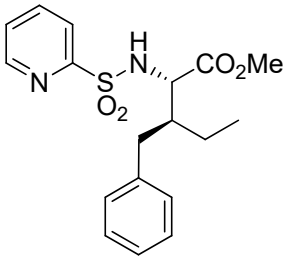
## 2.4. Typical procedure for the Pd-catalyzed γ-arylation of *N*–$SO_2$Py protected amino acid derivatives[8]

**(2*S**,3*S**)-Methyl 3-(4-methylbenzyl)-2-(pyridine-2-sulfonamido)pentanoate (11).** An



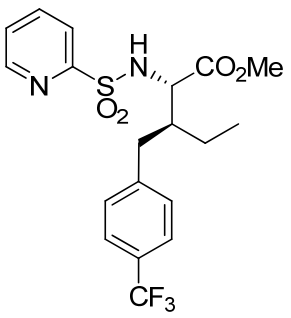
oven-dried pressure tube was charged with $Pd(OAc)_2$ (5.61 mg, 0.025 mmol, 10 mol %), AgOAc (41.7 mg, 0.25 mmol), 4-iodotoluene (54.5 mg, 0.25 mmol, 1.00 equiv), DL-*allo*-isoleucine derivative **XIX** (71.6 mg, 0.25 mmol, 1.00 equiv) and HFIP (0.25 mL). The tube was sealed with a screw cap and then placed in an oil bath at 150 °C for 6 h. After the reaction time was completed, the reaction mixture was diluted with EtOAc, filtered through a short pad of Celite®, and concentrated *in vacuo*. The residue was purified by flash column chromatography (30:1 $CH_2Cl_2$:$Et_2O$) to obtain **11** as a white solid; yield: 67.9 mg (72%); mp = 96-97 °C. **$^1$H NMR (300 MHz, $CDCl_3$, δ):** 8.63 – 8.61 (m, 1H), 7.91 (d, *J* = 7.7 Hz, 1H), 7.85 (td, *J* = 7.6, 1.7 Hz, 1H), 7.44 (ddd, *J* = 7.4, 4.7, 1.4 Hz, 1H), 7.05 (d, *J* = 7.9 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 5.53 (d, *J* = 9.5 Hz, 1H), 4.43 (dd, *J* = 9.5, 3.5 Hz, 1H), 3.47 (s, 3H), 2.57 – 2.41 (m, 2H), 2.29 (s, 3H), 2.14 – 2.03 (m, 1H), 1.59 – 1.45 (m, 1H), 1.40 – 1.26 (m, 1H), 0.94 (t, *J* = 7.3 Hz, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 172.1, 157.8, 149.8, 138.0, 136.3, 135.7, 129.1, 129.1, 126.7, 121.9, 58.2, 52.4, 45.5, 35.4, 22.9, 21.1, 11.6. **HRMS-ESI (*m/z*):** calcd. for $C_{19}H_{25}N_2O_4S$ ($M+H^+$): 377.1535; Found: 377.1530.

**(2*S**,3*S**)-Methyl 3-benzyl-2-(pyridine-2-sulfonamido)pentanoate (12b).** Compound



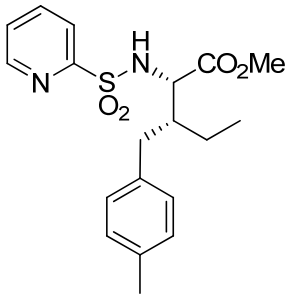
**12b** was prepared following the general protocol from DL-*allo*-isoleucine derivative **XIX** (71.6 mg, 0.25 mmol, 1.00 equiv) and iodobenzene (28.0 µL, 0.25 mmol, 1.00 equiv) to give **12b** as a yellow oil; yield: 63.6 mg (70%); **$^1$H NMR (300 MHz, $CDCl_3$, δ):** 8.60 (d, *J* = 4.6 Hz, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.83 (td, *J* = 7.6, 1.6 Hz, 1H), 7.43 (ddd, *J* = 7.3, 4.7, 1.3 Hz, 1H), 7.25 – 7.21 (m, 2H), 7.18 – 7.14 (m, 1H), 7.13 – 7.07 (m, 2H), 5.60 (d, *J* = 9.5 Hz, 1H), 4.42 (dd, *J* = 9.5, 3.5 Hz, 1H), 3.46 (s, 3H), 2.61 – 2.46 (m, 2H), 2.16 – 2.06 (m, 1H), 1.61 – 1.46 (m, 1H), 1.39 – 1.25 (m, 1H), 0.94 (t, *J* = 7.3 Hz, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 172.0, 157.8, 149.8, 139.5, 138.0, 129.2, 128.4, 126.7, 126.2, 121.9, 58.2, 52.4, 45.4, 35.9, 23.0, 11.5. **HRMS-ESI (*m/z*):** calcd. for $C_{18}H_{23}N_2O_4S$ ($M+H^+$): 363.1379; Found: 363.1380.

**(2*S**,3*S**)-Methyl 2-(pyridine-2-sulfonamido)-3-(4-(trifluoromethyl)benzyl)-pentanoate (13).** Compound **13** was prepared following the general protocol from DL-*allo*-isoleucine derivative **XIX** (71.6 mg, 0.25 mmol, 1.00 equiv) and 4-iodobenzotrifluoride (36.7 µL, 0.25 mmol, 1.00 equiv) to give **13** as a yellow solid; yield: 77.4 mg (72%); mp = 128-131 °C. **$^1$H NMR (300 MHz, $CDCl_3$, δ):** 8.61 – 8.58 (m, 1H), 7.89 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.84 (td, *J* = 7.3, 1.7 Hz, 1H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.45 – 7.41 (m, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 5.80 (d, *J* = 9.2 Hz, 1H), 4.36 (dd, *J* = 9.2, 3.7 Hz, 1H), 3.48 (s, 3H), 2.69 – 2.55 (m, 2H), 2.18 – 2.07 (m, 1H), 1.62 – 1.47 (m, 1H), 1.34 – 1.20 (m, 1H), 0.94 (t, *J* = 7.3 Hz, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 171.8, 157.7, 149.8, 143.9 (q, *J* = 1.2 Hz), 138.1, 129.6, 128.6 (q, *J* = 32.3 Hz), 126.8, 125.3 (q, *J* = 3.7 Hz), 124.3 (q, *J* = 271.8 Hz),



122.0, 58.1, 52.4, 45.3, 35.7, 22.9, 11.4. **HRMS-ESI (*m/z*):** calcd. for $C_{19}H_{22}F_3N_2O_4S$ ($M+H^+$): 431.1247; Found: 431.1247.

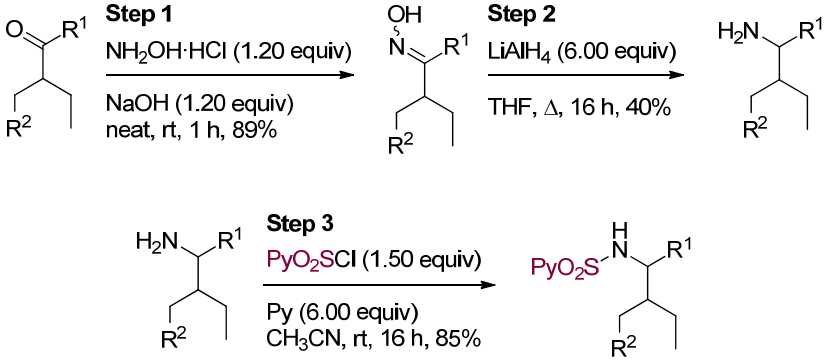
**(2*S*,3*R*)-Methyl 3-(4-methylbenzyl)-2-(pyridine-2-sulfonamido)pentanoate** [(+)-**25**]**.**




Compound (+)-**25** was prepared following the general protocol from L-isoleucine derivative **XX** (71.6 mg, 0.25 mmol, 1.00 equiv) and 4-iodotoluene (54.5 mg, 0.25 mmol, 1.00 equiv) to give **25** as a yellow solid; yield: 50.8 mg (54%); mp = 95-97 °C. **$^1$H NMR (300 MHz, $CDCl_3$, δ):** 8.63 (ddd, *J* = 4.7, 1.6, 0.9 Hz, 1H), 7.96 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.87 (td, *J* = 7.7, 1.7 Hz, 1H), 7.46 (ddd, *J* = 7.4, 4.7, 1.3 Hz, 1H), 7.10 (bs, 4H), 5.37 (d, *J* = 9.8 Hz, 1H), 4.34 (dd, *J* = 9.8, 3.6 Hz, 1H), 3.51 (s, 3H), 2.71 (dd, *J* = 14.0, 7.7 Hz, 1H), 2.56 (dd, *J* = 14.0, 6.5 Hz, 1H), 2.32 (s, 3H), 2.11 – 2.01 (m, 1H), 1.38 – 1.28 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 172.2, 158.0, 149.9, 138.1, 136.8, 135.7, 129.3, 129.2, 126.8, 121.9, 58.6, 52.4, 46.0, 36.0, 22.1, 21.2, 11.7. **HRMS-ESI (*m/z*):** calcd. for $C_{19}H_{25}N_2O_4S$ ($M+H^+$): 377.1535; Found: 377.1536. **$[\alpha]_D^{20}$:** +49 (*c* = 1.0; $CH_2Cl_2$).

## 2.5. Synthesis of aliphatic amines via reductive amination

### General procedure




### *N*-(2-Ethylbutyl)pyridine-2-sulfonamide (XVI):

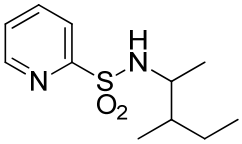
**Step 1. Synthesis of 2-ethylbutanal oxime (XXIV).**[9] Sodium hydroxide (2.40 g, 60.0 mmol, 1.20 equiv) was triturated in a mortar and mixed then with hydroxylamine hydrochloride (4.17 g, 60.0 mmol, 1.20 equiv) with a high emission of water fume. Once a paste was formed, 2-ethylbutanal was added (6.15 mL, 50.0 mmol, 1.00 equiv). The trituration was continued in 10 min interval after 5 min of rest in each for 1 h. The crude mixture was dissolved in $CH_2Cl_2$ and washed with water, brine, dried over $Na_2SO_4$ and filtered. The solvent was then removed *in vacuo* affording the pure oxime **XXIV** as a colorless oil; yield: 5.13 g (89%). The oxime was used in the next step without further purification.

**Step 2. Synthesis of 2-ethylbutylamine (XXV).**[10] In a 250 mL round bottomed flask was added $LiAlH_4$ (1.14 g, 30.0 mmol, 6.00 equiv) and sealed with a rubber septum. It was then evacuated and flushed with argon. Under positive argon pressure, anhydrous THF (125 mL) was added. To the formed suspension, 2-ethylbutanal oxime **XXIV** (0.66 mL, 5.00 mmol, 1.00 equiv) was added dropwise and left under reflux for 16 h. After that time, the reaction mixture was cooled to 0 °C and water (50.0 mL) was added. $Et_2O$ (50.0 mL) was then added and the aqueous phase was extracted with $Et_2O$ (2 x 50.0 mL). The organic phases were dried over $Na_2SO_4$, filtered and the solvent was removed *in vacuo* at low temperature, to give 2-ethylbutylamine **XXV** as a colorless liquid; yield: 101 mg (40%). The amine was used in the next step without further purification.

**Step 3. Synthesis of *N*-(2-ethylbutyl)pyridine-2-sulfonamide (XVI).** The protection of the amino group was carried out following the general protocol for the synthesis of *N*–$SO_2$Py protected amino acid derivatives, which could be obtained after isolation by flash column chromatography (heptane:EtOAc 4:1); yield: 414 mg (85%). **$^1$H NMR (300 MHz, $CDCl_3$, δ):** 8.70 (d, *J* = 4.6 Hz, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.91 (td, *J* = 7.7, 1.6 Hz, 1H), 7.49 (ddd, *J* = 7.5, 4.7, 1.1 Hz, 1H), 4.98 (s, 1H), 2.96 – 2.92 (m, 2H), 1.34 – 1.26 (m, 5H), 0.81 (t, *J* = 7.1 Hz, 6H). **$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 157.6, 150.1, 138.1, 126.7, 122.4, 46.0, 41.0, 23.5, 10.8. **HRMS-ESI (*m/z*):** calcd. for $C_{11}H_{19}N_2O_2S$ ($M+H^+$): 243.1161; Found: 243.1165.

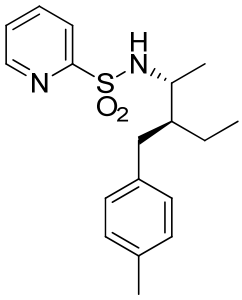
**Synthesis of *N*-((2*R**,3*S**)-3-(4-methylbenzyl)pentan-2-yl)pyridine-2-sulfonamide (14).**

**Step 1. Synthesis of *N*-(3-Methylpentan-2-yl)pyridine-2-sulfonamide (XXVI).**



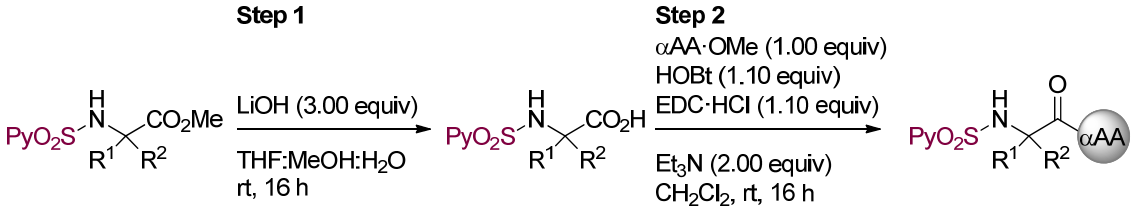
Compound **XXVI** was synthetized from 3-methyl-2-pentanone following the general procedure for the synthesis of aliphatic amines via reductive amination, giving compound **XXVI**, as a 1:1 mixture of diasteromers, as a colorless oil, which was used in the next step without further purification.

**Step 2. Synthesis of *N*-((2*R**,3*S**)-3-(4-methylbenzyl)pentan-2-yl)pyridine-2-sulfonamide (14).**



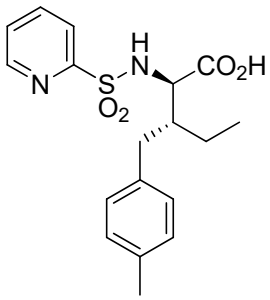
Compound **14** was synthetized following the general protocol for the Pd-catalyzed γ-arylation of *N*–$SO_2$Py protected amino acid derivatives from *N*-(3-methylpentan-2-yl)pyridine-2-sulfonamide (**XXVI**) (60.6 mg, 0.25 mmol, 1.00 equiv) and 4-iodotoluene (54.5 mg, 0.25 mmol, 1.00 equiv), giving compound **14** as a yellow oil; yield: 20.9 mg (25%). **$^1$H NMR (500 MHz, $CDCl_3$, δ):** 8.68 (d, *J* = 4.7 Hz, 1H), 7.87 (d, *J* = 7.2 Hz, 1H), 7.84 (td, *J* = 7.5, 1.3 Hz, 1H), 7.48 – 7.45 (m, 1H), 7.03 (d, *J* = 7.7 Hz, 2H), 6.93 (d, *J* = 7.9 Hz, 2H), 4.78 (d, *J* = 7.9 Hz, 1H), 3.45 – 3.39 (m, 1H), 2.50 – 2.42 (m, 2H), 2.31 (s, 3H), 1.61 – 1.54 (m, 1H), 1.44 – 1.36 (m, 1H), 1.23 – 1.18 (m, 1H), 1.03 (d, *J* = 6.8 Hz, 3H), 0.82 (t, *J* = 7.4 Hz, 3H).**$^{13}$C NMR (126 MHz, $CDCl_3$, δ):** 158.0, 150.2, 138.1, 137.3, 135.5, 129.2, 128.9, 126.6, 122.4, 51.4, 47.2, 35.7, 21.8, 21.2, 17.8, 11.8. **HRMS-ESI (*m/z*):** calcd. for $C_{18}H_{24}N_2O_2SNa$ ($M+Na^+$): 355.1451; Found: 355.1457.

## 2.6. Synthesis of dipeptide 45[8]




### Step 1. Hydrolysis of the ester group

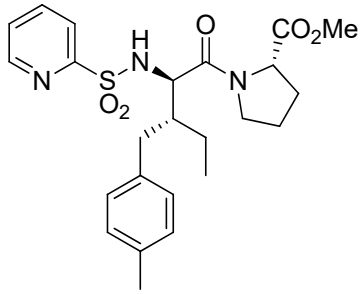
**(2*R*,3*R*)-3-(4-Methylbenzyl)-2-(pyridine-2-sulfonamido)pentanoic acid (XXVII).** An



oven dried, nitrogen flushed 10.0 mL vessel was charged with (2*R*,3*R*)-methyl 3-ethyl-2-(pyridine-2-sulfonamido)-4-(*p*-tolyl) butanoate (**11**) (113 mg, 0.30 mmol, 1.00 equiv), LiOH·$H_2O$ (37.8 mg, 0.90 mmol, 3.00 equiv) and a 3:1:1 mixture of THF:MeOH:$H_2O$ (2.00 mL). Next, the corresponding mixture was heated to 60 °C for 24 h. After that time, the reaction was allowed to reach room temperature and 1 M HCl was added until pH ≈ 2 (a solid could be observed). EtOAc or $CH_2Cl_2$ (10.0 mL) was added to dissolve this solid and the organic phase was washed with water (10.0 mL), brine (10.0 mL), dried over $Na_2SO_4$, filtered and the solvent was eliminated *in vacuo* to obtain **XXVII** as a white oil. The crude carboxylic acid was used in the next step without further purification.

### Step 2. Amidation of the carboxyl group

**Synthesis of methyl *N*-($SO_2$Py)-γ-*p*-tolyl-L-*allo*-isoleucinyl-prolinate (45).** In a

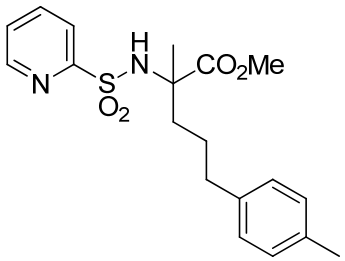


10.0 mL round bottom flask, (2*R*,3*R*)-3-(4-Methylbenzyl)-2-(pyridine-2-sulfonamido)pentanoic acid (**XXVII**) (362 mg, 1.00 mmol, 1.00 equiv), proline methyl ester hydrochloride (166 mg, 1.00 mmol, 1.00 equiv), HOBt·$H_2O$ (135 mg, 1.10 mmol, 1.10 equiv) and EDC·HCl (192 mg, 1.10 mmol, 1.10 equiv) were suspended in anhydrous $CH_2Cl_2$ (5.00 mL). Then, $Et_3N$ (0.28 mL, 2.00 mmol, 2.00 equiv) was added via syringe, and the solution was left stirring at room temperature for 24 h. The reaction mixture was then diluted with EtOAc and washed with an aqueous solution of citric acid 0.5 M (3 x 10.0 mL), $NaHCO_3$ (sat.) (3 x 10.0 mL) and brine (20.0 mL). The organic phase was dried over $Na_2SO_4$, filtered and the solvent was eliminated *in vacuo*. The residue was purified by flash column chromatography (cyclohexane-EtOAc 1:1) to obtain the dipeptide **45**, as a 86:14 mixture of diasteromers, as yellow solid; yield: 420 mg (97%); mp = 93-97 °C. **$^1$H NMR (300 MHz, $CDCl_3$, δ):** 8.76 – 8.74 (m, 1H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.85 (td, *J* = 7.7, 1.7 Hz, 1H), 7.45 (ddd, *J* = 7.5, 4.7, 1.2 Hz, 1H), 7.05 (d, *J* = 7.8 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 5.76 (d, *J* = 8.6 Hz, 1H), 4.83 (dd, *J* = 8.6, 1.9 Hz, 1H), 4.20 (dd, *J* = 8.0, 3.0 Hz, 1H), 3.85 – 3.78 (m, 1H), 3.58 (s, 3H), 3.53 – 3.44 (m, 1H), 2.71 (dd, *J* = 14.0, 3.0 Hz, 1H), 2.39 – 2.34 (m, 1H), 2.30 (s, 3H), 2.16 – 1.93 (m, 4H), 1.74 – 1.62 (m, 2H), 1.54 – 1.43 (m, 1H), 1.01 (t, *J* = 7.1 Hz, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 172.1, 170.1, 158.4, 150.7, 138.0, 137.4, 135.5, 129.1, 129.0, 126.4, 121.3, 59.2, 57.0, 52.1, 46.6,

45.5, 34.3, 29.3, 24.8, 23.0, 21.1, 12.0. **HRMS-ESI (*m/z*):** calcd. for $C_{24}H_{32}N_3O_5S$ ($M+H^+$): 474.2057; Found: 474.2056. **$[\alpha]_D^{20}$:** -18 (*c* = 1.0; $CH_2Cl_2$).

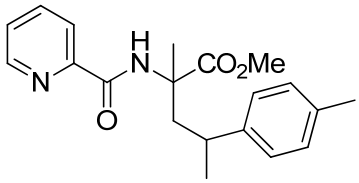
### 3. General protocol for the Pd-catalyzed δ-C($sp^3$)–H arylation of amine and amino acid derivatives

**(*rac*)-Methyl 2-methyl-2-(pyridine-2-sulfonamido)-5-(*p*-tolyl)pentanoate (4b).** An



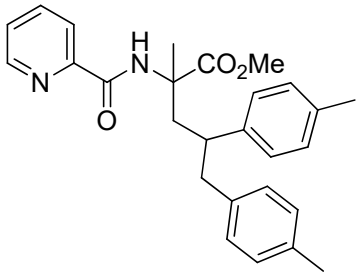
oven-dried, argon flushed, pressure tube was charged with $Pd(OAc)_2$ (4.48 mg, 0.02 mmol, 0.10 equiv), AgOAc (100 mg, 0.60 mmol, 3.00 equiv), 4-iodotoluene (131 mg, 0.60 mmol, 3.00 equiv) and methyl 2-methyl-2-(pyridine-2-sulfonamido)pentanoate (**1b**) (57.2 mg, 0.20 mmol, 1.00 equiv). Then, 1,4-dioxane (0.40 mL) was added *via* syringe. The pressure tube was sealed with a screw cap and finally placed in an oil bath at 150 °C for 16 h. The reaction mixture was then removed from the oil bath and allowed reach room temperature. The mixture was then diluted with EtOAc, filtered through a short pad of Celite® and concentrated *in vacuo*. The residue was purified by flash column chromatography ($CH_2Cl_2$:$Et_2O$ 30:1) to afford **4b** as a colorless oil; yield: 43.8 mg (58%). The starting material **1b** was recovered unaltered by flash column chromatography (23.8 mg, 0.08 mmol, 42%). **$^1$H NMR (300 MHz, $CDCl_3$, δ):** 8.69 (ddd, *J* = 4.7, 1.6, 0.9 Hz, 1H), 7.99 (dt, *J* = 7.8, 0.9 Hz, 1H), 7.88 (td, *J* = 7.7, 1.7 Hz, 1H), 7.45 (ddd, *J* = 7.6, 4.7, 1.2 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 5.83 (s, 1H), 3.65 (s, 3H), 2.51 – 2.39 (m, 2H), 2.31 (s, 3H), 2.03 – 1.93 (m, 1H), 1.81 – 1.71 (m, 1H), 1.67 – 1.61 (m, 1H), 1.42 (s, 3H), 1.38 – 1.32 (m, 1H). **$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 173.8, 159.5, 150.1, 138.5, 138.1, 135.5, 129.1, 128.3, 126.5, 121.5, 63.1, 53.0, 39.2, 35.1, 25.7, 23.4, 21.1. **$^{13}$C NMR-DEPT-135 (75 MHz, $CDCl_3$, δ):** positive peaks: 150.1, 138.1, 129.1, 128.3, 126.5, 121.5; negative peaks: 39.2, 35.1, 25.7. **HRMS-ESI (*m/z*):** calcd. for $C_{19}H_{24}N_2O_4SNa$ ($M+Na^+$): 399.1349; Found: 399.1347.

**(*rac*)-Methyl 2-methyl-2-(picolinamido)-4-(*p*-tolyl)pentanoate (2a).** Compound **2a**



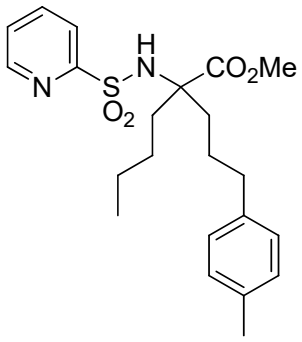
was prepared following the general protocol from (*rac*)-methyl 2-methyl-2-(picolinamido)pentanoate (**1a**) (50.1 mg, 0.20 mmol, 1.00 equiv) to give **2a** as a colorless oil; yield: 34.9 mg (51%). **$^1$H NMR (300 MHz, $CDCl_3$, δ):** 8.95 (s, 1H), 8.57 (ddd, *J* = 4.7, 1.6, 0.8 Hz, 1H), 8.14 (d, *J* = 7.8 Hz, 1H), 7.83 (td, *J* = 7.7, 1.7 Hz, 1H), 7.42 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1H), 7.03 (bs, 4H), 3.30 (s, 3H), 2.82 – 2.68 (m, 2H), 2.41 – 2.33 (m, 1H), 2.26 (s, 3H), 1.68 (s, 3H), 1.21 (d, *J* = 6.9 Hz, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 174.6, 163.4, 150.4, 148.3, 142.9, 137.3, 135.6, 129.0, 127.6, 126.1, 121.8, 59.8, 52.3, 44.1, 36.1, 24.5, 24.2, 21.1.

Along product **2a**, product **3a** was also isolated.



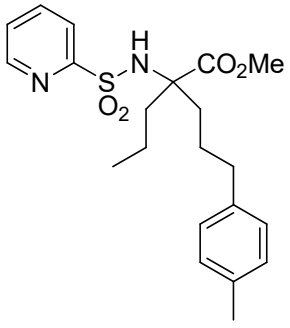
**(*rac*)-Methyl 2-methyl-2-(picolinamido)-4,5-di-*p*-tolylpentanoate (3a).** Compound **3a** was isolated as a colorless oil; yield: 30.8 mg (36%). **$^1$H NMR (300 MHz, $CDCl_3$, δ):** 8.45 (s, 1H), 8.39 (ddd, *J* = 4.7, 1.6, 0.9 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.71 (td, *J* = 7.7, 1.7 Hz, 1H), 7.31 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1H), 7.03 – 6.90 (m, 6H), 6.77 (d, *J* = 7.9 Hz, 2H), 3.58 (s, 3H), 2.87 – 2.76 (m, 2H), 2.73 – 2.65 (m, 1H), 2.28 (s, 3H), 2.23 – 2.15 (m, 2H), 1.98 (s, 3H), 1.62 (s, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 174.6, 163.0, 150.1, 147.7, 141.6, 137.2, 136.7, 135.5, 135.2, 129.1, 128.9, 128.9, 127.7, 125.7, 121.6, 60.5, 52.5, 44.9, 44.8, 40.6, 23.8, 21.1, 20.9.

**(*rac*)-Methyl 2-(pyridine-2-sulfonamido)-2-(3-(*p*-tolyl)propyl)hexanoate (15).**



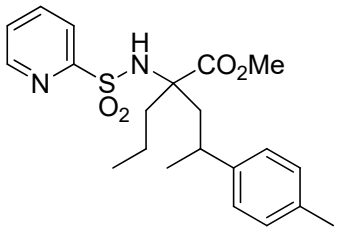
Compound **15** was prepared following the general protocol from methyl 2-propyl-2-(pyridine-2-sulfonamido)hexanoate (**5**) (65.7 mg, 0.20 mmol, 1.00 equiv) to give **15** as a colorless oil; yield: 34.8 mg (42%). The starting material **5** was recovered unaltered by flash column chromatography (33.3 mg, 51%). **$^1$H NMR (300 MHz, $CDCl_3$, δ):** 8.71 (ddd, *J* = 4.7, 1.6, 0.8 Hz, 1H), 8.01 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.88 (td, *J* = 7.7, 1.7 Hz, 1H), 7.45 (ddd, *J* = 7.6, 4.7, 1.1 Hz, 1H), 7.05 (d, *J* = 7.8 Hz, 2H), 6.91 (d, *J* = 7.9 Hz, 2H), 5.93 (s, 1H), 3.68 (s, 3H), 2.33 – 2.28 (m, 4H), 2.13 (ddd, *J* = 13.9, 12.4, 4.1 Hz, 1H), 2.01 (ddd, *J* = 14.1, 12.2, 3.9 Hz, 1H), 1.75 (ddd, *J* = 13.9, 12.3, 4.5 Hz, 1H), 1.67 (ddd, *J* = 14.0, 12.1, 4.5 Hz, 1H), 1.61 – 1.51 (m, 2H), 1.19 – 1.12 (m, 1H), 1.09 – 1.06 (m, 2H), 1.02 – 0.96 (m, 1H), 0.90 – 0.85 (m, 1H), 0.76 (t, *J* = 7.3 Hz, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 173.4, 159.6, 150.2, 138.6, 138.0, 135.4, 129.1, 128.2, 126.5, 121.5, 67.9, 53.1, 37.5, 37.2, 34.9, 31.5, 25.7, 23.6, 22.5, 21.1. **HRMS-ESI (*m/z*):** calcd. for $C_{22}H_{30}N_2O_4SNa$ ($M+Na^+$): 455.1975; Found: 455.1975.

**(*rac*)-Methyl 2-propyl-2-(pyridine-2-sulfonamido)-5-(*p*-tolyl)pentanoate (16).**



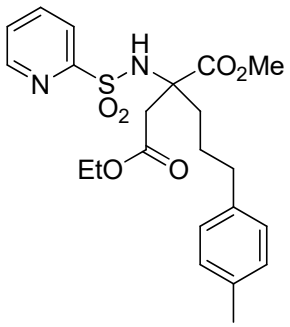
Compound **16** was prepared following the general protocol from methyl 2-propyl-2-(pyridine-2-sulfonamido)pentanoate (**6**) (62.9 mg, 0.20 mmol, 1.00 equiv) to give **16** as a colorless oil; yield: 21.5 mg (26%). The starting material **6** was recovered unaltered by flash column chromatography (33.4 mg, 53%). **$^1$H NMR (300 MHz, $CDCl_3$, δ):** 8.71 (d, *J* = 4.7 Hz, 1H), 8.02 (d, *J* = 7.9 Hz, 1H), 7.89 (td, *J* = 7.8, 1.7 Hz, 1H), 7.46 (ddd, *J* = 7.6, 4.7, 1.0 Hz, 1H), 7.05 (d, *J* = 7.9 Hz, 2H), 6.91 (d, *J* = 7.9 Hz, 2H), 5.94 (s, 1H), 3.67 (s, 3H), 2.34 – 2.28 (m, 5H), 2.18 – 1.96 (m, 2H), 1.82 – 1.61 (m, 3H), 1.19 – 1.06 (m, 2H), 0.92 – 0.81 (m, 1H), 0.62 (t, *J* = 7.3 Hz, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 173.3, 159.5, 150.1, 138.6, 138.1, 135.4, 129.1, 128.2, 126.5, 121.5, 67.9, 53.0, 39.6, 37.2, 34.9, 25.7, 21.1, 17.3, 13.7. **HRMS-ESI (*m/z*):** calcd. for $C_{21}H_{28}N_2O_4SNa$ ($M+Na^+$): 427.1662; Found: 427.1663.

Along product **16**, product **γ-16** was also isolated.



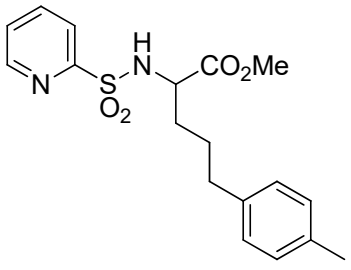
**(2*S*,3*S*)-Methyl 2-propyl-2-(pyridine-2-sulfonamido)-4-(*p*-tolyl)pentanoate (γ-16).** Compound **γ-16** was isolated as a colorless oil; yield: 12.5 mg (16%). **$^1$H NMR (500 MHz, $CDCl_3$, δ):** 8.74 (ddd, *J* = 4.7, 1.6, 0.8 Hz, 1H), 8.05 (d, *J* = 7.9 Hz, 1H), 7.90 (td, *J* = 7.8, 1.7 Hz, 1H), 7.48 (ddd, *J* = 7.6, 4.7, 1.1 Hz, 1H), 7.03 (bs, 4H), 6.14 (s, 1H), 3.02 – 2.94 (m, 4H), 2.46 (dd, *J* = 14.4, 2.6 Hz, 1H), 2.27 (s, 3H), 2.20 (dd, *J* = 14.4, 10.9 Hz, 1H), 1.90 (ddd, *J* = 14.1, 12.4, 3.8 Hz, 1H), 1.54 (ddd, *J* = 14.1, 12.4, 5.1 Hz, 1H), 1.10 (d, *J* = 7.1 Hz, 3H), 0.72 – 0.64 (m, 1H), 0.63 – 0.55 (m, 1H), 0.40 (t, *J* = 7.3 Hz, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$, δ):** 172.4, 159.7, 150.2, 142.4, 138.1, 135.7, 128.8, 128.1, 126.5, 121.4, 66.8, 52.3, 46.3, 40.3, 35.5, 24.5, 21.1, 16.8, 13.4. **HRMS-APCI (*m/z*):** calcd. for $C_{21}H_{29}N_2O_4S$ ($M+H^+$): 405.1843; Found: 408.1852.

**(*rac*)-4-Ethyl 1-methyl 2-(pyridine-2-sulfonamido)-2-(3-(*p*-tolyl)propyl)succinate (17).**

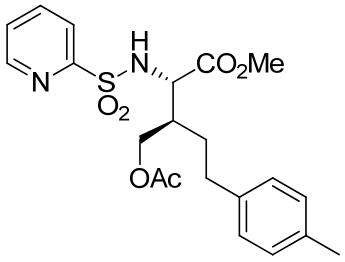


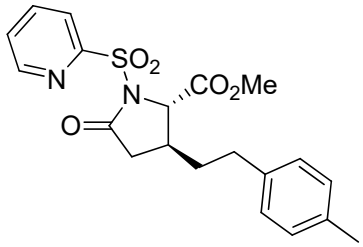
Compound **17** was prepared following the general protocol from 4-ethyl 1-methyl 2-propyl-2-(pyridine-2-sulfonamido) succinate (**7**) (71.7 mg, 0.20 mmol, 1.00 equiv) to give **17** as a white solid; yield: 50.5 mg (56%). The starting material **7** was recovered unaltered by flash column chromatography (28.7 mg, 40%); mp = 78-82 °C. **$^1$H NMR (500 MHz, $CDCl_3$, δ):** 8.66 (ddd, *J* = 4.7, 1.6, 0.8 Hz, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.88 (td, *J* = 7.7, 1.8 Hz, 1H), 7.44 (ddd, *J* = 7.7, 4.7, 1.0 Hz, 1H), 7.05 (d, *J* = 7.8 Hz, 2H), 6.92 (d, *J* = 7.9 Hz, 2H), 6.16 (s, 1H), 3.96 – 3.92 (m, 1H), 3.89 – 3.85 (m, 1H), 3.70 (s, 3H), 3.35 (d, *J* = 17.3 Hz, 1H), 2.89 (d, *J* = 17.3 Hz, 1H), 2.40 – 2.33 (m, 2H), 2.30 (s, 3H), 2.25 – 2.18 (m, 2H), 1.74 – 1.68 (m, 1H), 1.65 – 1.60 (m, 1H), 1.15 (t, *J* = 7.1 Hz, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$, δ):** 172.2, 169.7, 159.2, 150.0, 138.4, 138.1, 135.5, 129.1, 128.2, 126.5, 121.6, 64.2, 60.9, 53.3, 42.2, 37.3, 34.8, 29.8, 25.2, 21.1. **HRMS-APCI (*m/z*):** calcd. for $C_{22}H_{29}N_2O_6S$ ($M+H^+$): 449.1741; Found: 449.1743.

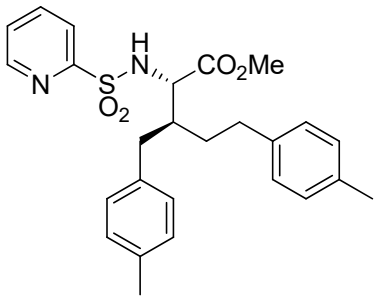
**(*rac*)-Methyl 2-(pyridine-2-sulfonamido)-5-(*p*-tolyl)pentanoate (18).** Compound **18** was prepared following the general protocol from methyl 2-(pyridine-2-sulfonamido)pentanoate (**8**) (54.5 mg, 0.20 mmol, 1.00 equiv) to give **18** as a colorless oil; yield: 11.7 mg (16%). The starting material **8** was recovered unaltered by flash column chromatography (33.9 mg, 62%).



**$^1$H NMR (500 MHz, $CDCl_3$, δ):** 8.62 (ddd, *J* = 4.7, 1.7, 0.9 Hz, 1H), 7.96 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.89 (td, *J* = 7.7, 1.7 Hz, 1H), 7.46 (ddd, *J* = 7.6, 4.7, 1.2 Hz, 1H), 7.08 (d, *J* = 7.8 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 5.35 (d, *J* = 9.0 Hz, 1H), 4.36 – 4.31 (m, 1H), 3.59 (s, 3H), 2.64 – 2.51 (m, 2H), 2.31 (s, 3H), 1.85 – 1.79 (m, 1H), 1.75 – 1.64 (m, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$, δ):** 172.4, 158.1, 149.9, 138.5, 138.2, 135.5, 129.2, 128.4, 126.8, 121.9, 56.8, 52.6, 34.8, 33.3, 26.9, 21.1. **HRMS-ESI (*m/z*):** calcd. for $C_{18}H_{22}N_2O_4SNa$ ($M+Na^+$): 385.1192; Found: 385.1195.

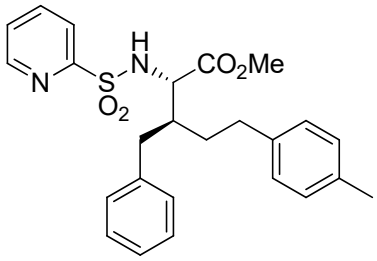
**(2*S**,3*R**)-Methyl 3-(acetoxymethyl)-2-(pyridine-2-sulfonamido)-5-(*p*-tolyl) pentanoate (19).**  Compound **19** was prepared following the general protocol from (2*S**,3*R**)-methyl 3-(acetoxymethyl)-2-(pyridine-2-sulfonamido)pentanoate (**9**) (68.9 mg, 0.20 mmol, 1.00 equiv) to give **19** as a colorless oil; yield: 52.0 mg (60%). The starting material **9** was recovered unaltered by flash column chromatography (21.1 mg, 31%). **$^1$H NMR (300 MHz, $CDCl_3$, δ):** 8.62 (d, *J* = 6.1 Hz, 1H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.89 (td, *J* = 7.7, 1.7 Hz, 1H), 7.46 (ddd, *J* = 7.5, 4.7, 1.2 Hz, 1H), 7.10 (bs, 4H), 5.48 (d, *J* = 9.6 Hz, 1H), 4.60 (dd, *J* = 9.6, 3.3 Hz, 1H), 4.12 – 3.98 (m, 2H), 3.58 (s, 3H), 2.80 (ddd, *J* = 13.8, 9.9, 5.9 Hz, 1H), 2.63 (ddd, *J* = 13.7, 9.8, 6.2 Hz, 1H), 2.41 – 2.32 (m, 4H), 1.96 (s, 3H), 1.92 – 1.81 (m, 1H), 1.65 – 1.53 (m, 1H). **$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 171.8, 170.9, 158.1, 149.8, 138.3, 138.2, 135.6, 129.3, 128.5, 126.9, 121.9, 63.4, 57.3, 52.6, 40.4, 32.6, 30.2, 21.1, 20.8. **HRMS-APCI (*m/z*):** calcd. for $C_{21}H_{27}N_2O_6S$ ($M+H^+$): 435.1584; Found: 435.1594.

**(2*S**,3*R**)-Methyl 3-(4-methylphenethyl)-5-oxo-1-(pyridin-2-ylsulfonyl)pyrrolidine-2-carboxylate (20).**  Compound **20** was prepared following the general protocol from (2*S**,3*S**)-dimethyl 3-ethyl-2-(pyridine-2-sulfonamido) pentanedioate (**10**) (68.9 mg, 0.20 mmol, 1.00 equiv) to give **20** as a white solid; yield: 45.2 mg (56%). The starting material **10** was recovered as γ-lactam by flash column chromatography (23.2 mg, 37%); mp = 47-49 °C. **$^1$H NMR (300 MHz, $CDCl_3$, δ):** 8.64 (d, *J* = 5.4 Hz, 1H), 8.23 (d, *J* = 7.9 Hz, 1H), 7.96 (td, *J* = 7.8, 1.7 Hz, 1H), 7.54 (ddd, *J* = 7.7, 4.7, 1.0 Hz, 1H), 7.11 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 2H), 4.84 (d, *J* = 2.7 Hz, 1H), 3.85 (s, 3H), 2.80 (dd, *J* = 17.4, 8.5 Hz, 1H), 2.71 – 2.66 (m, 2H), 2.47 – 2.37 (m, 1H), 2.33 (s, 3H), 2.13 (dd, *J* = 17.5, 3.2 Hz, 1H), 2.05 – 1.93 (m, 1H), 1.80 – 1.68 (m, 1H). **$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 172.8, 170.9, 155.9, 150.1, 138.2, 137.4, 136.0, 129.4, 128.4, 128.0, 124.4, 65.6, 53.1, 37.2, 36.5, 36.4, 32.5, 21.1. **HRMS-APCI (*m/z*):** calcd. for $C_{20}H_{23}N_2O_5S$ ($M+H^+$): 403.1322; Found: 403.1332.

**(2*S**,3*S**)-Methyl 3-(4-methylbenzyl)-2-(pyridine-2-sulfonamido)-5-(*p*-tolyl) pentanoate (21).**  Compound **21** was prepared following the general protocol from (2*S**,3*S**)-methyl 3-(4-methylbenzyl)-2-(pyridine-2-sulfonamido)pentanoate (**11**) (75.3 mg, 0.20 mmol, 1.00 equiv) to give **21** as a colorless oil; yield: 65.2 mg (70%). **$^1$H NMR (300 MHz, $CDCl_3$, δ):** 8.62 – 8.61 (m, 1H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.86 (td, *J* = 7.7, 1.6 Hz, 1H), 7.44 (ddd, *J* = 7.4, 4.7, 1.2 Hz, 1H), 7.08 – 7.01 (m, 6H), 6.95 (d, *J* = 8.0 Hz, 2H), 5.42 (d, *J* = 9.4 Hz, 1H), 4.54 (dd, *J* = 9.4, 3.3 Hz, 1H), 3.48 (s, 3H), 2.85 – 2.76 (m, 1H), 2.60 – 2.46 (m, 3H), 2.31 (s, 3H), 2.30 (s, 3H), 2.27 – 2.21 (m, 1H), 1.92 – 1.79 (m, 1H), 1.63 – 1.51 (m, 1H). **$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 172.0, 157.9, 149.9, 138.8, 138.1, 136.0, 135.8, 135.3, 129.1, 129.1, 129.0, 128.5, 126.8, 122.0, 58.6, 52.5, 43.2, 35.7, 32.8, 32.2, 21.1. **$^{13}$C NMR-DEPT-135 (75 MHz, $CDCl_3$, δ):** positive peaks: 149.9, 138.1, 129.1, 129.1, 129.0, 128.5, 126.8, 122.0, 58.6,

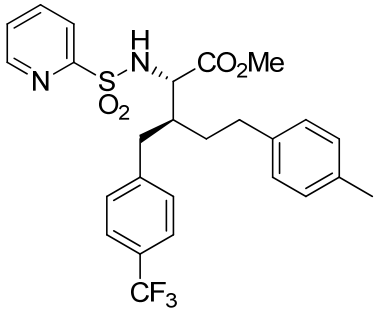
52.5, 43.2, 21.1; negative peaks: 35.7, 32.8, 32.2. **HRMS-ESI (*m/z*):** calcd. for $C_{26}H_{30}N_2O_4SNa$ ($M+Na^+$): 489.1818; Found: 489.1821.

**(2*S**,3*S**)-Methyl 3-benzyl-2-(pyridine-2-sulfonamido)-5-(*p*-tolyl)pentanoate (22).**



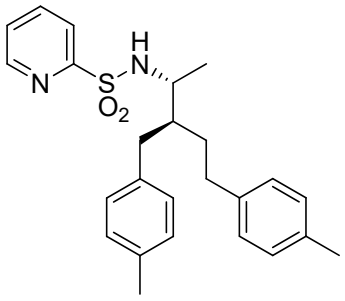
Compound **22** was prepared following the general protocol from (2*S**,3*S**)-methyl 3-benzyl-2-(pyridine-2-sulfonamido)pentanoate (**12b**) (72.5 mg, 0.20 mmol, 1.00 equiv) to give **22** as a colorless oil; yield: 58.7 mg (65%). The starting material **12b** was recovered unaltered by flash column chromatography (28.5 mg, 39%). **$^1$H NMR (300 MHz, $CDCl_3$, δ):** 8.61 (ddd, *J* = 4.7, 1.6, 1.0 Hz, 1H), 7.93 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.89 (td, *J* = 7.5, 1.7 Hz, 1H), 7.45 (ddd, *J* = 7.4, 4.7, 1.4 Hz, 1H), 7.24 – 7.17 (m, 3H), 7.12 – 7.00 (m, 6H), 5.38 (d, *J* = 9.3 Hz, 1H), 4.54 (dd, *J* = 9.3, 3.3 Hz, 1H), 3.47 (s, 3H), 2.80 (ddd, *J* = 13.6, 10.6, 5.3 Hz, 1H), 2.64 – 2.46 (m, 3H), 2.33 – 2.25 (m, 4H), 1.94 – 1.81 (m, 1H), 1.63 – 1.51 (m, 1H). **$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 171.9, 157.9, 149.9, 139.2, 138.8, 138.1, 135.3, 129.3, 129.1, 128.5, 128.5, 126.8, 126.4, 122.0, 58.6, 52.5, 43.2, 36.2, 32.8, 32.3, 21.1. **HRMS-ESI (*m/z*):** calcd. for $C_{25}H_{28}N_2O_4SNa$ ($M+Na^+$): 475.1662; Found: 475.1666.

**(2*S**,3*S**)-Methyl 2-(pyridine-2-sulfonamido)-5-(*p*-tolyl)-3-(4-(trifluoromethyl) benzyl)pentanoate (23).**



Compound **23** was prepared following the general protocol from (2*S**,3*S**)-methyl 2-(pyridine-2-sulfonamido)-3-(4-(trifluoromethyl)benzyl) pentanoate (**13**) (86.1 mg, 0.20 mmol, 1.00 equiv) to give **23** as a yellow solid; yield: 54.3 mg (52%). The starting material **13** was recovered unaltered by flash column chromatography (36.2 mg, 42%); mp = 57-59 °C. **$^1$H NMR (500 MHz, $CDCl_3$, δ):** 8.60 (ddd, *J* = 4.7, 1.5, 0.9 Hz, 1H), 7.92 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.87 (td, *J* = 7.7, 1.7 Hz, 1H), 7.49 – 7.45 (m, 3H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 7.9 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 5.43 (d, *J* = 9.0 Hz, 1H), 4.49 (dd, *J* = 9.0, 3.4 Hz, 1H), 3.51 (s, 3H), 2.83 – 2.77 (m, 1H), 2.69 – 2.59 (m, 2H), 2.55 – 2.49 (m, 1H), 2.31 (s, 3H), 2.29 – 2.25 (m, 1H), 1.94 – 1.87 (m, 1H), 1.55 – 1.48 (m, 1H). **$^{13}$C NMR (126 MHz, $CDCl_3$, δ):** 171.8, 157.8, 149.9, 143.5, 138.4, 138.2, 135.5, 129.6, 129.2, 128.8 (q, *J* = 32.4 Hz), 128.5, 126.9, 125.4 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 271.6 Hz), 122.0, 58.4, 52.7, 43.0, 36.0 32.7, 32.0, 21.1. **HRMS-APCI (*m/z*):** calcd. for $C_{26}H_{28}N_2O_4F_3S$ ($M+H^+$): 521.1716; Found: 521.1726.

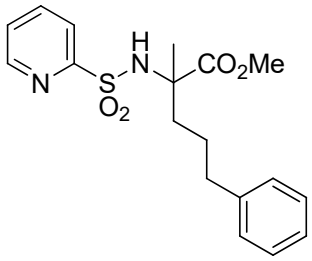
***N*-((2*R**,3*S**)-3-(4-Methylbenzyl)-5-(*p*-tolyl)pentan-2-yl)pyridine-2-sulfonamide (24).**



Compound **24** was prepared following the general protocol from *N*-((2*R**,3*S**)-3-(4-methylbenzyl)pentan-2-yl)pyridine-2-sulfonamide (**14**) (66.5 mg, 0.20 mmol, 1.00 equiv) to give **24** as a colorless oil; yield: 47.1 mg (56%). The starting material **14** was recovered unaltered by flash column chromatography (25.1 mg, 38%). **$^1$H NMR (500 MHz, $CDCl_3$, δ):** 8.65 (ddd, *J* = 4.7, 1.6, 0.9 Hz, 1H), 7.86 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.83 (td, *J* = 7.4, 1.7 Hz, 1H), 7.44 (ddd, *J* = 7.4, 4.7, 1.4 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 2H), 7.03 (d, *J* = 7.8 Hz, 2H), 6.98 (d, *J* = 7.9 Hz, 2H), 6.92 (d, *J* = 7.9 Hz, 2H), 4.73 (d, *J* = 8.0 Hz, 1H), 3.50 – 3.44 (m, 1H), 2.57 – 2.44

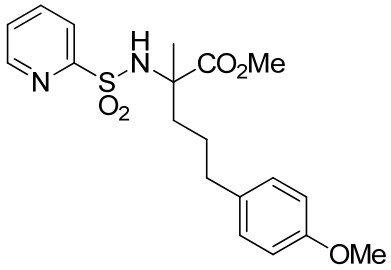
(m, 4H), 2.31 (s, 3H), 2.31 (s, 3H), 1.78 – 1.72 (m, 1H), 1.71 – 1.66 (m, 1H), 1.49 – 1.42 (m, 1H), 1.02 (d, *J* = 6.8 Hz, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$, δ):** 158.0, 150.2, 139.1, 137.9, 137.0, 135.6, 135.4, 129.2, 129.2, 128.9, 128.3, 126.6, 122.3, 51.5, 45.0, 36.1, 33.2, 31.3, 21.2 21.1, 17.7.

**(*rac*)-Methyl 2-methyl-5-phenyl-2-(pyridine-2-sulfonamido)pentanoate (26).**



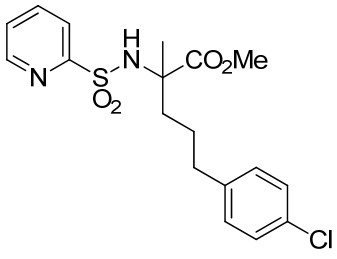
Compound **26** was prepared following the general protocol from (*rac*)-methyl 2-methyl-2-(pyridine-2-sulfonamido) pentanoate (**1b**) (57.2 mg, 0.20 mmol, 1.00 equiv) and iodobenzene (67.1 µL, 0.60 mmol, 3.00 equiv) to give **26** as a colorless oil; yield: 37.2 mg (51%). The starting **1b** material was recovered unaltered by flash column chromatography (26.5 mg, 46%). **$^{1}$H NMR (300 MHz, $CDCl_3$, δ):** 8.69 (dd, *J* = 4.6, 0.5 Hz, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.91 (td, *J* = 7.7, 1.7 Hz, 1H), 7.45 (ddd, *J* = 7.5, 4.7, 1.1 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.17 (t, *J* = 7.3 Hz, 2H), 7.09 (d, *J* = 6.9 Hz, 2H), 5.84 (s, 1H), 3.65 (s, 3H), 2.55 – 2.44 (m, 2H), 2.05 – 1.95 (m, 1H), 1.82 – 1.72 (m, 1H), 1.71 – 1.61 (m, 1H), 1.42 (s, 3H), 1.39 – 1.35 (m, 1H). **$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 173.8, 159.5, 150.1, 141.6, 138.1, 128.5, 128.4, 126.5, 126.1, 121.5, 63.1, 53.1, 39.2, 35.5, 25.6, 23.4. **HRMS-APCI (*m/z*):** calcd. for $C_{18}H_{23}N_2O_4S$ ($M+H^+$): 363.1373; Found: 363.1380.

**(*rac*)-Methyl 5-(4-methoxyphenyl)-2-methyl-2-(pyridine-2-sulfonamido)pentanoate (27).**



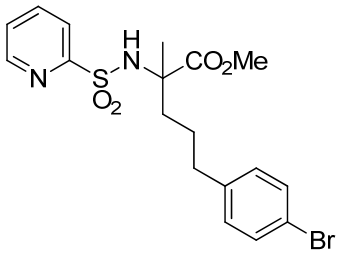
Compound **27** was prepared following the general protocol from (*rac*)-methyl 2-methyl-2-(pyridine-2-sulfonamido)pentanoate (**1b**) (57.2 mg, 0.20 mmol, 1.00 equiv) and 4-iodoanisole (140 mg, 0.60 mmol, 3.00 equiv) to give **27** as a white solid; yield: 41.7mg (53%). The starting material **1b** was recovered unaltered by flash column chromatography (23.8 mg, 42%); mp = 106-107 °C. **$^{1}$H NMR (500 MHz, $CDCl_3$, δ):** 8.69 (d, *J* = 4.7 Hz, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.89 (td, *J* = 7.7, 1.7 Hz, 1H), 7.46 (ddd, *J* = 7.6, 4.7, 0.9 Hz, 1H), 7.00 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 5.83 (s, 1H), 3.78 (s, 3H), 3.66 (s, 3H), 2.49 – 2.38 (m, 2H), 2.00 – 1.94 (m, 1H), 1.78 – 1.71 (m, 1H), 1.66 – 1.62 (m, 1H), 1.42 (s, 3H), 1.37 – 1.32 (m, 1H). **$^{13}$C NMR (126 MHz, $CDCl_3$, δ):** 173.8, 159.5, 158.0, 150.0, 138.1, 133.7, 129.3, 126.5, 121.6, 113.9, 63.2, 55.4, 53.0, 39.2, 34.6, 25.9, 23.4. **HRMS-APCI (*m/z*):** calcd. for $C_{19}H_{25}N_2O_5S$ ($M+H^+$): 393.1479; Found: 393.1487.

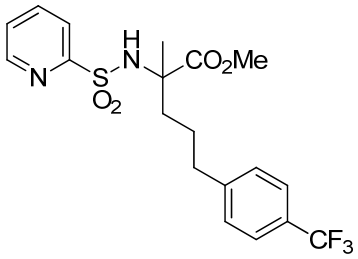
**(*rac*)-Methyl 5-(4-chlorophenyl)-2-methyl-2-(pyridine-2-sulfonamido)pentanoate (28).**

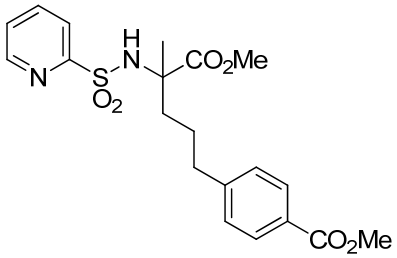


Compound **28** was prepared following the general protocol from (*rac*)-methyl 2-methyl-2-(pyridine-2-sulfonamido)pentanoate (**1b**) (57.2 mg, 0.20 mmol, 1.00 equiv) and 1-chloro-4-iodobenzene (143 mg, 0.60 mmol, 3.00 equiv) to give **28** as a white solid; yield: 56.3 mg (71%). The starting material **1b** was recovered unaltered by flash column chromatography (11.6 mg, 20%); mp = 89-92 °C. **$^{1}$H NMR (300 MHz, $CDCl_3$, δ):** 8.68 (d, *J* = 4.7 Hz, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.89 (td, *J* = 7.7, 1.7 Hz, 1H), 7.46 (ddd, *J* = 7.6, 4.7, 1.1 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.3 Hz, 2H), 5.90 (s, 1H), 3.66 (s, 3H), 2.51 – 2.45 (m, 2H),

2.05 – 1.96 (m, 1H), 1.80 – 1.71 (m, 1H), 1.69 – 1.64 (m, 1H), 1.40 (s, 3H), 1.37 – 1.32 (m, 1H). **$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 173.8, 159.5, 150.0, 140.0, 138.1, 131.8, 129.8, 128.6, 126.6, 121.5, 63.1, 53.1, 38.9, 34.8, 25.5, 23.5. **HRMS-APCI (*m/z*):** calcd. for $C_{18}H_{22}N_2O_4SCl$ ($M+H^+$): 397.0983; Found: 397.0994.

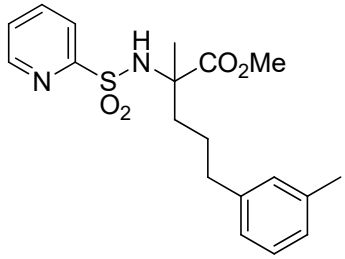
**(*rac*)-Methyl 5-(4-bromophenyl)-2-methyl-2-(pyridine-2-sulfonamido)pentanoate (29).**  Compound **29** was prepared following the general protocol from (*rac*)-methyl 2-methyl-2-(pyridine-2-sulfonamido)pentanoate (**1b**) (57.2 mg, 0.20 mmol, 1.00 equiv) and 1-bromo-4-iodobenzene (170 mg, 0.60 mmol, 3.00 equiv) to give **29** as a yellow solid; yield: 40.8 mg (46%). The starting material **1b** was recovered unaltered by flash column chromatography (23.0 mg, 39%); mp = 96-97 °C. **$^{1}$H NMR (500 MHz, $CDCl_3$, δ):** 8.68 (d, *J* = 4.7 Hz, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.89 (td, *J* = 7.7, 1.7 Hz, 1H), 7.46 (ddd, *J* = 7.5, 4.7, 1.0 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 2H), 6.97 (d, *J* = 8.3 Hz, 2H), 5.89 (s, 1H), 3.66 (s, 3H), 2.52 – 2.41 (m, 2H), 2.03 – 1.97 (m, 1H), 1.78 – 1.72 (m, 1H), 1.71 – 1.64 (m, 1H), 1.40 (s, 3H), 1.37 – 1.33 (m, 1H). **$^{13}$C NMR (126 MHz, $CDCl_3$, δ):** 173.8, 159.5, 150.0, 140.6, 138.1, 131.5, 130.2, 126.6, 121.5, 119.8, 63.1, 53.1, 38.9, 34.9, 25.4, 23.5. **HRMS-APCI (*m/z*):** calcd. for $C_{18}H_{22}N_2O_4SBr$ ($M+H^+$): 441.0478; Found: 441.0488.

**(*rac*)-Methyl 2-methyl-2-(pyridine-2-sulfonamido)-5-(4-trifluoromethyl) phenyl)pentanoate (30).**  Compound **30** was prepared following the general protocol from (*rac*)-methyl 2-methyl-2-(pyridine-2-sulfonamido)pentanoate (**1b**) (57.2 mg, 0.20 mmol, 1.00 equiv) and 4-iodobenzotrifluoride (88.2 μL, 0.60 mmol, 3.00 equiv) to give **30** as a yellow oil; yield: 47.2 mg (55%). The starting material **1b** was recovered unaltered by flash column chromatography (15.8 mg, 28%). **$^{1}$H NMR (300 MHz, $CDCl_3$, δ):** 8.68 (d, *J* = 4.5 Hz, 1H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.89 (td, *J* = 7.7, 1.6 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.46 (ddd, *J* = 7.5, 4.7, 1.0 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 5.93 (s, 1H), 3.66 (s, 3H), 2.63 – 2.52 (m, 2H), 2.08 – 2.00 (m, 1H), 1.83 – 1.72 (m, 2H), 1.46 – 1.37 (m, 4H). **$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 173.7, 159.4, 150.0, 145.8, 138.2, 128.7, 128.5 (q, *J* = 32.4 Hz), 126.6, 125.4 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 271.8 Hz), 121.5, 63.1, 53.1, 38.9, 35.3, 25.4, 23.5. **HRMS-APCI (*m/z*):** calcd. for $C_{19}H_{22}N_2O_4SF_3$ ($M+H^+$): 431.1247; Found: 431.1254.

**(*rac*)-Methyl 4-(5-methoxy-4-methyl-5-oxo-4-(pyridine-2-sulfonamido)pentyl) benzoate (31).**  Compound **31** was prepared following the general protocol from (*rac*)-methyl 2-methyl-2-(pyridine-2-sulfonamido)pentanoate (**1b**) (57.2 mg, 0.20 mmol, 1.00 equiv) and methyl 4-iodobenzoate (157 mg, 0.60 mmol, 3.00 equiv) to give **31** as a white solid; yield: 56.3 mg (67%). The starting material **1b** was recovered unaltered by flash column chromatography (21.1 mg, 29%); mp = 123-125 °C. **$^{1}$H NMR (300 MHz, $CDCl_3$, δ):** 8.68 (d, *J* = 4.6 Hz, 1H), 7.99 – 7.85 (m, 4H), 7.45 (ddd, *J* = 7.5, 4.7, 1.1 Hz, 1H), 7.16 (d, *J* = 8.2 Hz, 2H), 5.90 (s, 1H), 3.90 (s, 3H), 3.66 (s, 3H), 2.65 – 2.48 (m, 2H), 2.07 – 1.95 (m, 1H), 1.81 – 1.67 (m, 2H), 1.45 – 1.36 (m, 4H). **$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 173.7,

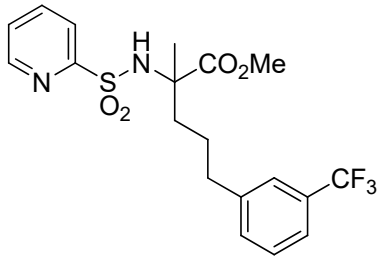
167.2, 159.4, 150.04 147.1, 138.1, 129.8, 128.5, 128.1, 126.6, 121.5, 63.1, 53.1, 52.1, 38.9, 35.5, 25.3, 23.5. **HRMS-APCI (*m/z*):** calcd. for $C_{20}H_{25}N_2O_6S$ ($M+H^+$): 421.1428; Found: 421.1441.

**(*rac*)-Methyl 2-methyl-2-(pyridine-2-sulfonamido)-5-(*m*-tolyl)pentanoate (32).**



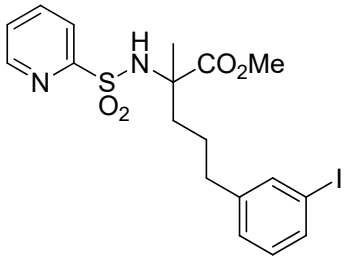
Compound **32** was prepared following the general protocol from (*rac*)-methyl 2-methyl-2-(pyridine-2-sulfonamido)pentanoate (**1b**) (57.2 mg, 0.20 mmol, 1.00 equiv) and 3-iodotoluene (77.0 μL, 0.60 mmol, 3.00 equiv) to give **32** as a white solid; yield: 40.3 mg (53%). The starting material **1b** was recovered unaltered by flash column chromatography (24.2 mg, 42%); mp = 75-78 °C. **$^1$H NMR (300 MHz, $CDCl_3$, δ):** 8.69 (dd, *J* = 4.6, 0.6 Hz, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.89 (td, *J* = 7.8, 1.7 Hz, 1H), 7.46 (ddd, *J* = 7.5, 4.7, 1.1 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 7.4 Hz, 1H), 6.90 – 6.87 (m, 2H), 5.84 (s, 1H), 3.66 (s, 3H), 2.51 – 2.40 (m, 2H), 2.32 (s, 3H), 2.05 – 1.95 (m, 2H), 1.81 – 1.72 (m, 1H), 1.42 (s, 3H), 1.40 – 1.36 (m, 1H). **$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 173.8, 159.5, 150.0, 141.6, 138.1, 138.0, 129.2, 128.4, 126.8, 126.5, 125.4, 121.5, 63.2, 53.0, 39.3, 35.4, 25.7, 23.4, 21.5. **HRMS-APCI (*m/z*):** calcd. for $C_{19}H_{25}N_2O_4S$ ($M+H^+$): 377.1530; Found: 377.1536.

**(*rac*)-Methyl 2-methyl-2-(pyridine-2-sulfonamido)-5-(3-trifluoromethyl) phenyl)pentanoate (33).**



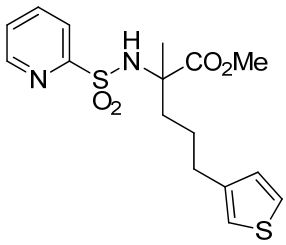
Compound **33** was prepared following the general protocol from (*rac*)-methyl 2-methyl-2-(pyridine-2-sulfonamido)pentanoate (**1b**) (57.2 mg, 0.20 mmol, 1.00 equiv) and 3-iodobenzotrifluoride (86.5 μL, 0.60 mmol, 3.00 equiv) to give **33** as a white solid; yield: 53.6 mg (62%). The starting material **1b** was recovered unaltered by flash column chromatography (20.0 mg, 35%); mp = 93-96 °C. **$^1$H NMR (500 MHz, $CDCl_3$, δ):** 8.69 (d, *J* = 4.7 Hz, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.89 (td, *J* = 7.8, 1.7 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.31 (s, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 5.91 (s, 1H), 3.67 (s, 3H), 2.62 – 2.51 (m, 2H), 2.08 – 2.02 (m, 1H), 1.81 – 1.75 (m, 1H), 1.75 – 1.66 (m, 1H), 1.42 (s, 3H), 1.40 – 1.35 (m, 1H). **$^{13}$C NMR (126 MHz, $CDCl_3$, δ):** 173.8, 159.5, 150.1, 142.5, 138.2, 131.9, 130.8 (q, *J* = 32.0 Hz), 128.9, 126.6, 125.0 (q, *J* = 3.7 Hz), 124.4 (q, *J* = 272.2 Hz), 123.0 (q, *J* = 3.8 Hz), 121.5, 63.1, 53.2, 38.8, 35.3, 25.5, 23.7. **HRMS-APCI (*m/z*):** calcd. for $C_{19}H_{22}N_2O_4SF_3$ ($M+H^+$): 431.1247; Found: 431.1255.

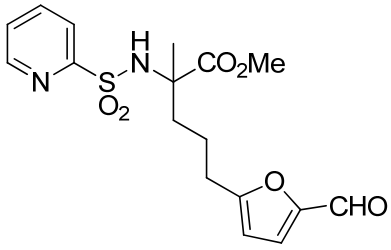
**(*rac*)-Methyl 5-(3-iodophenyl)-2-methyl-2-(pyridine-2-sulfonamido)pentanoate (34).**

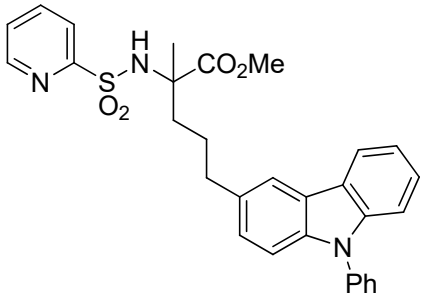


Compound **34** was prepared following the general protocol from (*rac*)-methyl 2-methyl-2-(pyridine-2-sulfonamido)pentanoate (**1b**) (57.2 mg, 0.20 mmol, 1.00 equiv) and 1,3-diiodobenzene (198 mg, 0.60 mmol, 3.00 equiv) to give **34** as a yellow oil; yield: 72.5 mg (74%). **$^1$H NMR (500 MHz, $CDCl_3$, δ):** 8.69 (ddd, *J* = 4.7, 1.7, 0.9 Hz, 1H), 7.99 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.89 (td, *J* = 7.7, 1.7 Hz, 1H), 7.51 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.47 (ddd, *J* = 7.6, 4.7, 1.1 Hz, 1H), 7.42 (t, *J* = 1.5 Hz, 1H), 7.06 (d, *J* = 7.7 Hz, 1H), 6.99 (t, *J* = 7.7 Hz, 1H), 5.91 (s, 1H), 3.68 (s, 3H), 2.49 – 2.37 (m, 2H), 2.03 – 1.97 (m, 1H), 1.79 – 1.73 (m, 1H), 1.68 – 1.59 (m, 1H), 1.41 (s, 3H), 1.37 – 1.30 (m, 1H). **$^{13}$C NMR (126 MHz, $CDCl_3$, δ):** 173.8, 159.4, 150.1, 144.1,

138.2, 137.4, 135.2, 130.2, 127.7, 126.6, 121.5, 94.5, 63.1, 53.2, 38.8, 35.0, 25.5, 23.6. **HRMS-ESI (*m/z*):** calcd. for $C_{18}H_{22}N_2O_4SI$ ($M+H^+$): 489.0340; Found: 489.0346.

**(*rac*)-Methyl 2-methyl-2-(pyridine-2-sulfonamido)-5-(thiophen-3-yl)pentanoate (35).**  Compound **35** was prepared following the general protocol from (*rac*)-methyl 2-methyl-2-(pyridine-2-sulfonamido)pentanoate (**1b**) (57.2 mg, 0.20 mmol, 1.00 equiv) and 3-iodothiophene (61.0 μL, 0.60 mmol, 3.00 equiv) to give **35** as a yellow oil; yield: 14.8 mg (20%). The starting material **1b** was recovered unaltered by flash column chromatography (44.8 mg, 78%). **$^1$H NMR (500 MHz, $CDCl_3$, δ):** 8.69 (ddd, *J* = 4.7, 1.7, 0.9 Hz, 1H), 7.99 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.89 (td, *J* = 7.7, 1.7 Hz, 1H), 7.46 (ddd, *J* = 7.6, 4.7, 1.1 Hz, 1H), 7.23 (dd, *J* = 4.9, 3.0 Hz, 1H), 6.88 – 6.87 (m, 1H), 6.86 (dd, *J* = 4.9, 1.3 Hz, 1H), 5.87 (s, 1H), 3.67 (s, 3H), 2.52 (t, *J* = 7.5 Hz, 2H), 2.04 – 1.98 (m, 1H), 1.80 – 1.74 (m, 1H), 1.72 – 1.64 (m, 1H), 1.42 (s, 3H), 1.40 – 1.35 (m, 1H). **$^{13}$C NMR (126 MHz, $CDCl_3$, δ):** 173.8, 159.5, 150.0, 142.0, 138.2, 128.1, 126.6, 125.5, 121.5, 120.3, 63.2, 53.1, 39.1, 29.9, 24.9, 23.5. **HRMS-ESI (*m/z*):** calcd. for $C_{16}H_{20}N_2O_4S_2Na$ ($M+Na^+$): 391.0757; Found: 391.0765.

**(*rac*)-Methyl 5-(5-formylfuran-2-yl)-2-methyl-2-(pyridine-2-sulfonamido) pentanoate (36).**  Compound **36** was prepared following the general protocol from (*rac*)-methyl 2-methyl-2-(pyridine-2-sulfonamido)pentanoate (**1b**) (57.2 mg, 0.20 mmol, 1.00 equiv) and 5-iodofuran-2-carbaldehyde (133 mg, 0.60 mmol, 3.00 equiv) to give **36** as a yellow oil; yield: 45.4 mg (60%). The starting material **1b** was recovered unaltered by flash column chromatography (18.5 mg, 32%). **$^1$H NMR (500 MHz, $CDCl_3$, δ):** 9.52 (s, 1H), 8.70 (ddd, *J* = 4.7, 1.7, 0.9 Hz, 1H), 7.99 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.90 (td, *J* = 7.7, 1.7 Hz, 1H), 7.48 (ddd, *J* = 7.6, 4.7, 1.1 Hz, 1H), 7.16 (d, *J* = 3.5 Hz, 1H), 6.25 (d, *J* = 3.5 Hz, 1H), 5.97 (s, 1H), 3.71 (s, 3H), 2.64 (t, *J* = 7.2 Hz, 2H), 2.13 – 2.08 (m, 1H), 1.85 – 1.75 (m, 2H), 1.52 – 1.45 (m, 1H), 1.40 (s, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$, δ):** 177.1, 173.7, 162.8, 159.4, 152.0, 150.1, 138.2, 126.7, 121.5, 109.1, 63.0, 53.4, 38.6, 28.1, 23.8, 22.3. **HRMS-ESI (*m/z*):** calcd. for $C_{17}H_{20}N_2O_6SNa$ ($M+Na^+$): 403.0934; Found: 403.0941.

**(*rac*)-Methyl 2-methyl-5-(9-phenyl-9*H*-carbazol-3-yl)-2-(pyridine-2-sulfonamido) pentanoate (37).**  Compound **37** was prepared following the general protocol from (*rac*)-methyl 2-methyl-2-(pyridine-2-sulfonamido)pentanoate (**1b**) (57.2 mg, 0.20 mmol, 1.00 equiv) and 3-iodo-*N*-phenylcarbazole (88.2 μL, 0.60 mmol, 3.00 equiv) to give **37** as a brown oil; yield: 52.9 mg (50%). The starting material **1b** was recovered unaltered by flash column chromatography (14.0 mg, 25%). **$^1$H NMR (500 MHz, $CDCl_3$, δ):** 8.68 (ddd, *J* = 4.7, 1.6, 0.8 Hz, 1H), 8.12 (d, *J* = 7.7 Hz, 1H), 7.99 (dt, *J* = 7.9, 0.9 Hz, 1H), 7.88 – 7.85 (m, 2H), 7.62 – 7.59 (m, 2H), 7.57 – 7.54 (m, 2H), 7.48 – 7.45 (m, 1H), 7.43 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 1H), 7.41 – 7.39 (m, 2H), 7.31 (d, *J* = 8.3 Hz, 1H), 7.29 – 7.26 (m, 1H), 7.14 (dd, *J* = 8.4, 1.7 Hz, 1H), 5.90 (s, 1H), 3.65 (s, 3H), 2.76 – 2.64 (m, 2H), 2.08 – 2.03 (m, 1H), 1.86 – 1.75 (m, 2H), 1.54 – 1.47

(m, 1H), 1.45 (s, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$, δ):** 173.9, 159.4, 150.0, 141.2, 139.6, 138.1, 138.0, 133.2, 130.0, 127.4, 127.1, 126.6, 126.5, 126.0, 123.5, 123.3, 121.5, 120.3, 119.9, 119.7, 109.9, 109.7, 63.2, 53.0, 53.0, 39.2, 35.5, 26.3, 23.4. **HRMS-ESI (*m/z*):** calcd. for $C_{30}H_{29}N_3O_4SNa$ ($M+Na^+$): 550.1771; Found: 550.1777.

**(2*S**,3*S**)-Methyl 3-(4-methylbenzyl)-5-phenyl-2-(pyridine-2-sulfonamido) pentanoate (38).** Compound **38** was prepared following the general protocol from (2*R**,3*R**)-methyl 3-(4-methylbenzyl)-2-(pyridine-2-sulfonamido)pentanoate (**11**) (75.3 mg, 0.20 mmol, 1.00 equiv) and iodobenzene (67.1 µL, 0.60 mmol, 3.00 equiv) to give **38** as a colorless oil; yield: 56.3 mg (62%). **$^1$H NMR (300 MHz, $CDCl_3$, δ):** 8.61 (ddd, *J* = 4.7, 1.6, 0.9 Hz, 1H), 7.92 (dt, *J* = 7.7, 1.2 Hz, 1H), 7.86 (td, *J* = 7.6, 1.7 Hz, 1H), 7.45 (ddd, *J* = 7.5, 4.7, 1.4 Hz, 1H), 7.25 – 7.22 (m, 2H), 7.19 – 7.12 (m, 3H), 7.04 (d, *J* = 7.8 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 5.37 (d, *J* = 9.4 Hz, 1H), 4.55 (dd, *J* = 9.4, 3.3 Hz, 1H), 3.48 (s, 3H), 2.84 (ddd, *J* = 13.6, 10.8, 5.4 Hz, 1H), 2.60 – 2.48 (m, 3H), 2.33 – 2.22 (m, 4H), 1.94 – 1.81 (m, 1H), 1.65 – 1.58 (m, 1H). **$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 172.0, 157.9, 149.9, 141.9, 138.1, 136.0, 135.9, 129.2, 129.1, 128.6, 128.4, 126.8, 125.9, 122.0, 58.6, 52.5, 43.2, 35.7, 33.3, 32.1, 21.2. **HRMS-ESI (*m/z*):** calcd. for $C_{25}H_{28}N_2O_4SNa$ ($M+Na^+$): 475.1662; Found: 475.1666.

**(2*S**,3*S**)-Methyl 3-(4-methylbenzyl)-2-(pyridine-2-sulfonamido)-5-(4-(trifluoro methyl)phenyl)pentanoate (39).** Compound **39** was prepared following the general protocol from (2*R**,3*R**)-methyl 3-(4-methylbenzyl)-2-(pyridine-2-sulfonamido)pentanoate (**11**) (75.3 mg, 0.20 mmol, 1.00 equiv) and 4-iodobenzotrifluoride (88.2 µL, 0.60 mmol, 3.00 equiv) to give **39** as a yellow oil; yield: 59.0 mg (57%). The starting material **11** was recovered unaltered by flash column chromatography (22.7 mg, 30%). **$^1$H NMR (500 MHz, $CDCl_3$, δ):** 8.61 (d, *J* = 4.6 Hz, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.89 (td, *J* = 7.7, 1.6 Hz, 1H), 7.49 – 7.45 (m, 3H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 7.8 Hz, 2H), 6.93 (d, *J* = 7.9 Hz, 2H), 5.41 (d, *J* = 9.4 Hz, 1H), 4.61 (dd, *J* = 9.4, 3.1 Hz, 1H), 3.50 (s, 3H), 2.94 (ddd, *J* = 14.0, 11.2, 5.1 Hz, 1H), 2.61 – 2.53 (m, 2H), 2.44 (dd, *J* = 13.8, 8.9 Hz, 1H), 2.30 (s, 3H), 2.27 – 2.23 (m, 1H), 1.95 – 1.87 (m, 1H), 1.64 – 1.60 (m, 1H). **$^{13}$C NMR (126 MHz, $CDCl_3$, δ):** 171.9, 158.0, 149.8, 146.1, 138.2, 136.0, 135.8, 129.2, 129.1, 129.0 (q, *J* = 34.7 Hz), 129.0, 126.9, 125.3 (q, *J* = 3.8 Hz), 124.5 (q, *J* = 271.7 Hz), 122.0, 58.6, 52.6, 43.1, 35.7, 33.1, 31.8, 21.1. **HRMS-ESI (*m/z*):** calcd. for $C_{26}H_{27}F_3N_2O_4SNa$ ($M+Na^+$): 543.1536; Found: 543.1541.

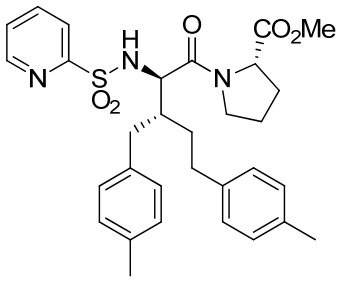
**(8*R*,9*S*,13*S*,14*S*)-14-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl 4-((3*R*,4*S*)-5-methoxy-3-(4-methylbenzyl)-5-oxo-4-(pyridine-2-sulfonamido)pentyl)benzoate ((+)-40).** Compound (+)-**40** was prepared following the general protocol from (2*S*,3*R*)-methyl 3-(4-methylbenzyl)-2-(pyridine-2-sulfonamido)pentanoate ((+)-**25**) (75.3 mg, 0.20 mmol, 1.00 equiv) and estronyl 4-iodobenzoate (300 mg, 0.60 mmol, 3.00 equiv) to give (+)-**40** as a white solid; yield: 90.0 mg (60%). The starting material (+)-**25** was recovered unaltered by flash column chromatography (9.1 mg, 12%); mp = 99-105 °C. **$^1$H NMR (500 MHz, $CDCl_3$, δ):** 8.61 (ddd, *J* = 4.7, 1.5, 0.8 Hz, 1H), 8.06 (d, *J* = 8.3 Hz, 2H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.88 (td, *J* = 7.7, 1.7 Hz, 1H), 7.47 (ddd, *J* = 7.5, 4.7, 1.2 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.18 (d, *J* = 8.3 Hz, 2H), 7.11 – 7.07 (m, 4H), 6.97 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.94 (d, *J* = 2.5 Hz, 1H), 5.49 (d, *J* = 9.7 Hz, 1H), 4.40 (dd, *J* = 9.7, 3.7 Hz, 1H), 3.49 (s, 3H), 2.94 – 2.93 (m, 3H), 2.81 (dd, *J* = 14.0, 7.4 Hz, 1H), 2.61 (dd, *J* = 14.1, 6.9 Hz, 1H), 2.54 – 2.49 (m, 2H), 2.45 – 2.41 (m, 1H), 2.33 (s, 3H), 2.19 – 2.12 (m, 2H), 2.09 – 2.04 (m, 2H), 2.01 – 1.96 (m, 2H), 1.70 – 1.30 (m, 4H), 1.56 – 1.47 (m, 4H), 0.92 (s, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$, δ):** 220.9, 171.9, 165.5, 157.9, 149.8, 149.0, 147.9, 138.2, 137.5, 136.2, 136.0, 130.4, 129.3, 129.2, 128.7, 127.6, 126.9, 126.6, 121.9, 121.8, 119.0, 59.0, 52.5, 50.6, 48.1, 44.3, 43.3, 38.2, 36.4, 36.0, 33.2, 31.7, 30.6, 29.6, 26.5, 25.9, 21.7, 22.0, 14.0.**HRMS-ESI (*m/z*):** calcd. for $C_{44}H_{48}N_2O_7SNa$ ($M+Na^+$): 771.3074; Found: 771.3079. **$[\alpha]_D^{25}$:** +102 (*c* = 1.0; $CH_2Cl_2$).

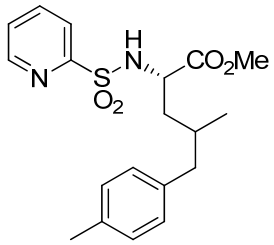
**(3*S*,8*S*,9*S*,10*R*,13*R*,14*R*,17*R*)-10-Methyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*] phenanthren-3-yl 4-((3*R*,4*S*)-5-methoxy-3-(4-methylbenzyl)-5-oxo-4-(pyridine-2-sulfonamido) pentyl)benzoate ((+)-41).** Compound (+)-**41** was prepared following the general protocol from (2*S*,3*R*)-methyl 3-(4-methylbenzyl)-2-(pyridine-2-sulfonamido)pentanoate ((+)-**25**) (75.3 mg, 0.20 mmol, 1.00 equiv) and cholesteroyl 4-iodobenzoate (362 mg, 0.60 mmol, 3.00 equiv) to give (+)-**41** as a yellow solid; yield: 90.1 mg (53%). The starting material (+)-**25** was recovered unaltered by flash column chromatography (13.3 mg, 18%); mp = 93-94 °C. **$^1$H NMR (500 MHz, $CDCl_3$, δ):** 8.60 (ddd, *J* = 4.7, 1.6, 0.9 Hz, 1H), 7.94 – 7.86 (m, 4H), 7.46 (ddd, *J* = 7.5, 4.7, 1.2 Hz, 1H), 7.11 – 7.05 (m, 6H), 5.44 (d, *J* = 9.7 Hz, 1H), 5.41 (d, *J* = 3.4 Hz, 1H), 4.88 – 4.80 (m, 1H), 4.37 (dd, *J* = 9.7, 3.6 Hz, 1H), 3.46 (s, 3H), 2.79 (dd, *J* = 14.0, 7.5 Hz, 1H), 2.70 – 2.65 (m, 1H), 2.63 – 2.58 (m, 1H), 2.46 – 2.44 (m, 2H), 2.32 (s, 3H), 2.14 – 2.08 (m, 1H), 2.03 – 1.97 (m, 4H), 1.93 – 1.89 (m, 1H), 1.88 – 1.80 (m, 1H), 1.77 – 1.71 (m, 1H), 1.65 – 1.43 (m, 10H), 1.38 – 1.32 (m, 3H), 1.21 – 1.09 (m, 10H), 1.03 – 0.97 (m, 4H), 0.92 (d, *J* = 6.5 Hz,

3H), 0.88 – 0.86 (m, 6H), 0.69 (s, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$, δ):** 171.9, 166.1, 157.9, 149.8, 146.9, 139.8, 138.2, 136.2, 136.0, 129.8, 129.3, 129.3, 128.4, 126.9, 122.9, 121.9, 74.6, 58.9, 56.8, 56.3, 52.5, 50.2, 43.2, 42.5, 39.9, 39.7, 38.4, 37.2, 36.8, 36.4, 36.3, 35.9, 33.1, 32.1, 32.0, 30.6, 28.4, 28.2, 28.0, 24.4, 24.0, 23.0, 22.7, 21.2, 19.5, 18.9, 12.0. **HRMS-ESI (*m/z*):** calcd. for $C_{53}H_{72}N_2O_6SNa$ ($M+Na^+$): 887.5003; Found: 887.5003. **$[\alpha]_D^{25}$:** +24 (*c* = 1.0; $CH_2Cl_2$).

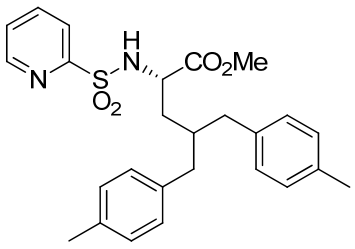
**((1*S*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 4-((3*R*,4*S*)-5-methoxy-3-(4-methylbenzyl)-5-oxo-4-(pyridine-2-sulfonamido)pentyl)benzoate ((+)-42).** Compound (+)-**42** was prepared following the general protocol from (2*S*,3*R*)-methyl 3-(4-methylbenzyl)-2-(pyridine-2-sulfonamido)pentanoate ((+)-**25**) (75.3 mg, 0.20 mmol, 1.00 equiv) and menthyl 4-iodobenzoate (232 mg, 0.60 mmol, 3.00 equiv) to give (+)-**42** as a white solid; yield: 68.7 mg (54%). The starting material (+)-**25** was recovered unaltered by flash column chromatography (29.3 mg, 39%); mp = 68-71 °C. **$^1$H NMR (500 MHz, $CDCl_3$, δ):** 8.60 (ddd, *J* = 4.7, 1.6, 0.9 Hz, 1H), 7.94 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.89 (td, *J* = 7.6, 1.6 Hz, 1H), 7.46 (ddd, *J* = 7.5, 4.7, 1.2 Hz, 1H), 7.12 – 7.07 (m, 6H), 5.45 (d, *J* = 9.7 Hz, 1H), 4.91 (td, *J* = 10.9, 4.4 Hz, 1H), 4.38 (dd, *J* = 9.7, 3.6 Hz, 1H), 3.46 (s, 3H), 2.80 (dd, *J* = 14.0, 7.4 Hz, 1H), 2.69 – 2.64 (m, 1H), 2.62 – 2.58 (m, 2H), 2.32 (s, 3H), 2.14 – 2.10 (m, 2H), 1.97 – 1.93 (m, 1H), 1.74 – 1.72 (m, 2H), 1.66 – 1.62 (m, 1H), 1.58 – 1.52 (m, 3H), 1.12 – 1.07 (m, 2H), 0.93 – 0.91 (m, 6H), 0.79 (d, *J* = 6.9 Hz, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$, δ):** 171.9, 166.2, 157.9, 149.8, 146.9, 138.2, 136.2, 136.0, 129.8, 129.3, 129.3, 128.8, 128.5, 126.9, 121.9, 74.8, 59.0, 52.5, 47.4, 43.3, 41.1, 36.4, 34.5, 33.1, 31.6, 30.6, 26.7, 23.8, 22.2, 21.2, 20.9, 16.7. **HRMS-APCI (*m/z*):** calcd. for $C_{36}H_{47}N_2O_6S$ ($M+H^+$): 635.3149; Found: 635.3163. **$[\alpha]_D^{25}$:** +11 (*c* = 7.5; $CH_2Cl_2$).

**(*rac*)-Ethyl 2-methyl-2-(pyridine-2-sulfonamido)-3-(2-(*p*-tolyl)cyclopropyl) propanoate (44).** Compound **44** was prepared following the general protocol from (*rac*)-methyl 3-cyclopropyl-2-methyl-2-(pyridine-2-sulfonamido) propanoate (**43**) (62.5 mg, 0.20 mmol, 1.00 equiv) to give **44** as an 80:20 mixture of diasteromers. The starting material **43** was recovered unaltered by flash column chromatography (22.9 mg, 36%). Colorless oil; yield: 48.2 mg (60%). **$^1$H NMR (300 MHz, $CDCl_3$, δ):** 8.67 – 8.65 (m, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.87 (td, *J* = 7.6, 1.7 Hz, 1H), 7.42 (ddd, *J* = 7.3, 4.7, 1.4 Hz, 1H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.03 (d, *J* = 7.9 Hz, 2H), 5.84 (s, 1H), 3.68 (dq, *J* = 10.7, 7.2 Hz, 1H), 3.38 (dq, *J* = 10.7, 7.2 Hz, 1H), 2.50 – 2.40 (m, 2H), 2.37 (m, 2H), 2.28 (s, 3H) , 2.10 – 2.03 (m, 1H), 1.28 (s, 3H), 1.06 (t, *J* = 7.2 Hz, 3H), 0.67 – 0.62 (m, 1H). **$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 173.0, 159.9, 149.9, 140.5, 138.0, 136.1, 130.2, 128.8, 126.3, 121.3, 62.8, 61.9, 50.0, 24.0, 22.2, 21.1, 13.8, 13.0, 12.8. **HRMS-ESI (*m/z*):** calcd. for $C_{21}H_{26}N_2O_4SNa$ ($M+Na^+$): 425.1505; Found: 425.1505.

**(*S*)-Methyl 1-((2*R*,3*R*)-3-(4-methylbenzyl)-2-(pyridine-2-sulfonamido)-5-(*p*-tolyl) pentanoyl)pyrrolidine-2-carboxylate ((–)-46).**  Compound (–)-**46** was prepared following the general protocol from (–)-**45** (94.7 mg, 0.20 mmol, 1.00 equiv) to give (–)-**46** as yellow solid; yield: 37.4 mg (33%). The starting material (–)-**45** was recovered unaltered by flash column chromatography (38.8 mg, 41%); mp = 58-62 °C. **$^1$H NMR (500 MHz, $CDCl_3$, δ):** 8.80 – 8.79 (m, 1H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.91 (td, *J* = 7.8, 1.7 Hz, 1H), 7.50 (ddd, *J* = 7.6, 4.8, 1.0 Hz, 1H), 7.09 – 7.06 (m, 6H), 6.94 (d, *J* = 7.9 Hz, 2H), 5.87 (d, *J* = 8.5 Hz, 1H), 4.91 (dd, *J* = 8.5, 2.4 Hz, 1H), 4.18 (dd, *J* = 8.2, 3.2 Hz, 1H), 3.75 – 3.69 (m, 1H), 3.62 (s, 3H), 3.23 – 3.18 (m, 1H), 2.96 – 2.91 (m, 1H), 2.75 (dd, *J* = 14.0, 3.9 Hz, 1H), 2.58 (ddd, *J* = 13.8, 9.4, 6.7 Hz, 1H), 2.42 (dd, *J* = 14.0, 9.4 Hz, 1H), 2.35 (s, 3H), 2.34 (s, 3H), 2.11 – 2.04 (m, 2H), 1.94 – 1.88 (m, 2H), 1.85 – 1.81 (m, 1H), 1.80 – 1.73 (m, 2H). **$^{13}$C NMR (126 MHz, $CDCl_3$, δ):** 172.1, 169.9, 158.4, 150.6, 138.6, 138.1, 137.1, 135.6, 135.3, 129.2, 129.1, 129.0, 128.7, 126.5, 121.4, 59.1, 57.7, 52.1, 46.5, 42.3, 34.6, 32.6, 31.5, 29.2, 24.7, 21.2, 21.1. **HRMS-APCI (*m/z*):** calcd. for $C_{31}H_{38}N_3O_5S$ ($M+H^+$): 564.2527; Found: 564.2540. **$[\alpha]_D^{25}$:** –27 (*c* = 1.0; $CH_2Cl_2$).

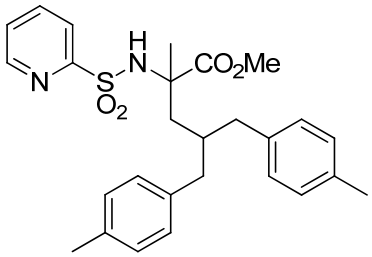
**(2*S*)-Methyl 4-methyl-2-(pyridine-2-sulfonamido)-5-(*p*-tolyl)pentanoate ((+)-$V_{mo}$).**  Compound (+)-**V** was prepared following the general protocol from (*S*)-methyl 4-methyl-2-(pyridine-2-sulfonamido)pentanoate ((+)-**I**) (57.3 mg, 0.20 mmol, 1.00 equiv) to give (+)-**V** as 73:23 mixture of diastereomers as a yellow solid; yield: 18.9 mg (25%). The starting material (+)-**I** was recovered unaltered by flash column chromatography (32.5 mg, 57%); mp = 100-101 °C. **$^1$H NMR (500 MHz, $CDCl_3$, δ):** 8.63 (ddd, *J* = 4.7, 1.7, 0.9 Hz, 1H), 7.98 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.90 (td, *J* = 7.7, 1.7 Hz, 1H), 7.47 (ddd, *J* = 7.6, 4.7, 1.1 Hz, 1H), 7.07 (d, *J* = 7.9 Hz, 2H), 7.04 (d, *J* = 8.1 Hz, 2H), 5.34 (d, *J* = 9.5 Hz, 1H), 4.44 (td, *J* = 9.0, 5.8 Hz, 1H), 3.57 (s, 3H), 2.79 (dd, *J* = 13.3, 5.0 Hz, 1H), 2.31 (s, 3H), 2.26 (dd, *J* = 13.3, 8.9 Hz, 1H), 2.01 – 1.95 (m, 1H), 1.74 (ddd, *J* = 13.4, 7.4, 5.8 Hz, 1H), 1.57 – 1.53 (m, 1H), 0.87 (d, *J* = 6.7 Hz, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$, δ):** 172.7, 158.0, 149.9, 138.2, 137.2, 135.4, 129.4, 129.0, 126.8, 121.9, 55.4, 52.5, 41.8, 41.0, 31.3, 21.2, 19.6. **HRMS-APCI (*m/z*):** calcd. for $C_{19}H_{25}N_2O_4S$ ($M+H^+$): 377.1530; Found: 377.1541. **$[\alpha]_D^{25}$:** +6 (*c* = 1.0; $CH_2Cl_2$).

Along product (+)-$V_{mo}$, product (–)-$V_{di}$ was also isolated.



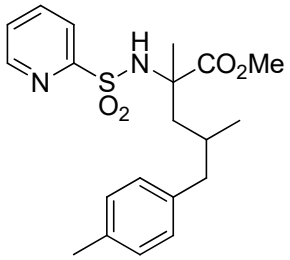
**(*S*)-Methyl 4-(4-methylbenzyl)-2-(pyridine-2-sulfonamido)-5-(*p*-tolyl)pentanoate ((–)-$V_{di}$).** Colorless oil; yield: 10.0 mg (11%). **$^1$H NMR (500 MHz, $CDCl_3$, δ):** 8.61 (ddd, *J* = 4.7, 1.6, 0.9 Hz, 1H), 7.95 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.89 (td, *J* = 7.7, 1.7 Hz, 1H), 7.46 (ddd, *J* = 7.6, 4.7, 1.2 Hz, 1H), 7.12 – 7.08 (m, 4H), 7.05 (d, *J* = 7.7 Hz, 2H), 6.95 (d, *J* = 7.9 Hz, 2H), 5.03 (d, *J* = 9.8 Hz, 1H), 4.48 – 4.43 (m, 1H), 3.52 (s, 3H), 2.89 (dd, *J* = 13.5, 4.5 Hz, 1H), 2.72 – 2.67 (m, 1H), 2.45 – 2.40 (m, 1H), 2.32 (s, 3H), 2.31 – 2.26 (m, 5H), 1.56 – 1.51 (m, 2H). **$^{13}$C NMR (126 MHz, $CDCl_3$, δ):** 172.7, 158.1, 149.8, 138.1, 137.1, 136.9, 135.5, 129.5,

129.2, 129.1, 126.8, 121.9, 55.2, 52.5, 39.3, 39.1, 37.8, 36.9, 21.2, 21.1. **HRMS-APCI (*m/z*):** calcd. for $C_{26}H_{31}N_2O_4S$ ($M+H^+$): 467.1999; Found: 467.2011. **$[\alpha]_D^{25}$:** –18 (*c* = 7.5; $CH_2Cl_2$).

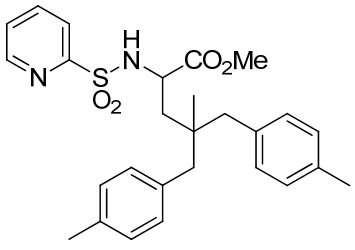


**(*rac*)-Methyl 2-methyl-4-(4-methylbenzyl)-2-(pyridine-2-sulfonamido)-5-(*p*-tolyl)pentanoate ($VI_{di}$).** Compound $VI_{di}$ was prepared following the general protocol from (*rac*)-methyl 2,4-dimethyl-2-(pyridine-2-sulfonamido)pentanoate (**II**) (60.1 mg, 0.20 mmol, 1.00 equiv) to give $VI_{di}$ as a colorless oil; yield: 77.7 mg (81%). **$^1$H NMR (300 MHz, $CDCl_3$, δ):** 8.67 (d, *J* = 4.7 Hz, 1H), 7.90 (dt, *J* = 7.4, 1.4 Hz, 1H), 7.89 (td, *J* = 7.2, 1.6 Hz, 1H), 7.45 (ddd, *J* = 7.1, 4.7, 1.6 Hz, 1H), 7.11 – 7.02 (m, 6H), 6.96 (d, *J* = 8.0 Hz, 2H), 5.50 (s, 1H), 3.48 (s, 3H), 2.65 (dd, *J* = 13.7, 6.5 Hz, 1H), 2.52 – 2.43 (m, 2H), 2.38 – 2.34 (m, 1H), 2.31 (s, 3H), 2.31 (s, 3H), 2.10 – 2.02 (m, 1H), 1.94 (dd, *J* = 14.4, 5.3 Hz, 1H), 1.76 (dd, *J* = 14.4, 5.0 Hz, 1H), 1.31 (s, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 174.0, 159.7, 149.9, 138.0, 137.3, 135.6, 129.4, 129.3, 129.2, 129.1, 126.4, 121.3, 62.6, 52.8, 43.1, 40.8, 40.4, 38.1, 23.2, 21.2, 21.1. **HRMS-ESI (*m/z*):** calcd. for $C_{27}H_{32}N_2O_4SNa$ ($M+Na^+$): 503.1975; Found: 503.1972.

Along product $VI_{di}$, product $VI_{mo}$ was also isolated.

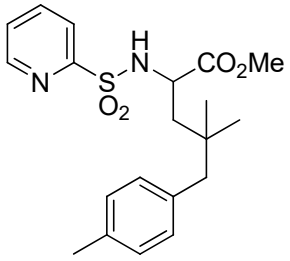


**(*rac*)-Methyl 2,4-dimethyl-2-(pyridine-2-sulfonamido)-5-(*p*-tolyl)pentanoate ($VI_{mo}$).** Yellow solid; mp = 100-103 °C; yield: 13.4 mg (17%). **$^1$H NMR (300 MHz, $CDCl_3$, δ):** 8.68 (d, *J* = 4.8 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.91 – 7.85 (m, 1H), 7.45 (ddd, *J* = 7.4, 4.7, 1.0 Hz, 1H), 7.07 (d, *J* = 7.8 Hz, 2H), 6.98 (d, *J* = 7.9 Hz, 2H), 5.86 (s, 1H), 3.61 (s, 3H), 2.46 (dd, *J* = 13.4, 5.8 Hz, 1H), 2.31 – 2.22 (m, 4H), 1.99 – 1.90 (m, 1H), 1.86 – 1.77 (m, 2H), 1.36 (s, 3H), 0.92 (d, *J* = 6.4 Hz, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 174.2, 159.7, 150.0, 138.1, 137.5, 135.5, 129.2, 129.1, 126.5, 121.4, 62.8, 52.9, 46.3, 43.7, 31.6, 23.5, 21.2, 21.1. **HRMS-APCI (*m/z*):** calcd. for $C_{20}H_{27}N_2O_4S$ ($M+H^+$): 391.1686; Found: 391.1690



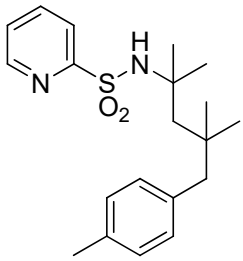
**(*rac*)-Methyl 4-methyl-4-(4-methylbenzyl)-2-(pyridine-2-sulfonamido)-5-(*p*-tolyl)pentanoate ($VII_{di}$).** Compound $VII_{di}$ was prepared following the general protocol from (*rac*)-Methyl 4,4-dimethyl-2-(pyridine-2-sulfonamido)pentanoate (**III**) (60.1 mg, 0.20 mmol, 1.00 equiv) to give $VII_{di}$ as a colorless oil; yield: 66.3 mg (69%). **$^1$H NMR (500 MHz, $CDCl_3$, δ):** 8.62 (ddd, *J* = 4.7, 1.6, 0.8 Hz, 1H), 7.96 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.89 (td, *J* = 7.7, 1.7 Hz, 1H), 7.46 (ddd, *J* = 7.6, 4.7, 1.1 Hz, 1H), 7.08 – 7.03 (m, 6H), 6.96 (d, *J* = 8.0 Hz, 2H), 5.14 (d, *J* = 10.3 Hz, 1H), 4.55 (ddd, *J* = 10.2, 8.8, 3.8 Hz, 1H), 3.50 (s, 3H), 2.71 (d, *J* = 13.3 Hz, 1H), 2.66 (d, *J* = 13.3 Hz, 1H), 2.61 (d, *J* = 13.3 Hz, 1H), 2.58 (d, *J* = 13.3 Hz, 1H), 2.33 (s, 3H), 2.32 (s, 3H), 1.69 (dd, *J* = 14.6, 3.9 Hz, 1H), 1.53 (dd, *J* = 14.6, 8.7 Hz, 1H), 0.94 (s, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$, δ):** 173.1, 157.8, 149.8, 138.2, 135.7, 135.7, 134.9, 134.9, 131.0, 130.9, 128.7, 126.8, 122.0, 54.3, 52.5, 46.1, 46.1, 42.2, 38.1, 23.8, 21.2, 21.1. **HRMS-ESI (*m/z*):** calcd. for $C_{27}H_{32}N_2O_4SNa$ ($M+Na^+$): 503.1975; Found: 503.1975.

Along product **VII$_{di}$**, product **VII$_{mo}$** was also isolated.



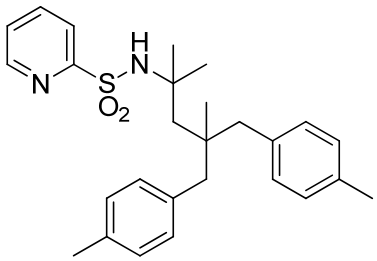
**(*rac*)-Methyl 4,4-dimethyl-2-(pyridine-2-sulfonamido)-5-(*p*-tolyl)pentanoate (VII$_{mo}$).** Colorless oil; yield: 22.0 mg (28%). **$^1$H NMR (500 MHz, CDCl$_3$, δ):** 8.63 (ddd, *J* = 4.7, 1.7, 0.9 Hz, 1H), 7.97 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.89 (td, *J* = 7.7, 1.7 Hz, 1H), 7.47 (ddd, *J* = 7.6, 4.7, 1.2 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 5.27 (d, *J* = 10.2 Hz, 1H), 4.44 (ddd, *J* = 10.2, 8.5, 4.1 Hz, 1H), 3.51 (s, 3H), 2.56 (d, *J* = 13.2 Hz, 1H), 2.52 (d, *J* = 13.2 Hz, 1H), 2.32 (s, 3H), 1.68 (dd, *J* = 14.4, 4.1 Hz, 1H), 1.54 (dd, *J* = 14.4, 8.5 Hz, 1H), 0.98 (s, 3H), 0.96 (s, 3H). **$^{13}$C NMR (126 MHz, CDCl$_3$, δ):** 173.1, 157.82 149.8, 138.2, 135.6, 135.2, 130.7, 128.6, 126.8, 122.0, 54.5, 52.4, 48.6, 45.4, 34.6, 26.8, 26.7, 21.1. **HRMS-ESI (*m/z*):** calcd. for $C_{40}H_{52}N_4O_8S_2Na$ (2M+Na$^+$): 803.3119; Found: 803.3122.

***N*-(2,4,4-Trimethyl-5-(*p*-tolyl)pentan-2-yl)pyridine-2-sulfonamide (VIII$_{mo}$).**



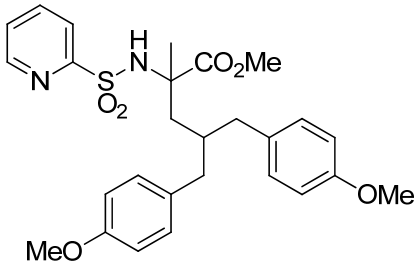
Compound **VIII$_{mo}$** was prepared following the general protocol from *N*-(2,4,4-trimethylpentan-2-yl)pyridine-2-sulfonamide (**IV**) (54.1 mg, 0.20 mmol, 1.00 equiv) to give **VIII$_{mo}$** as a colorless oil; yield: 36.6 mg (51%). **$^1$H NMR (300 MHz, CDCl$_3$, δ):** 8.71 – 8.69 (m, 1H), 8.02 (d, *J* = 7.8 Hz, 1H), 7.89 (td, *J* = 7.7, 1.6 Hz, 1H), 7.46 (ddd, *J* = 7.6, 4.7, 0.9 Hz, 1H), 7.07 (d, *J* = 7.9 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 4.91 (bs, 1H), 2.52 (s, 2H), 2.32 (s, 3H), 1.63 (s, 2H), 1.26 (s, 6H), 1.02 (s, 6H). **$^{13}$C NMR (75 MHz, CDCl$_3$, δ):** 160.2, 149.9, 138.2, 135.6, 135.5, 130.9, 128.5, 126.4, 121.7, 58.9, 54.5, 51.2, 35.5, 29.3, 28.0, 21.1. **HRMS-ESI (*m/z*):** calcd. for $C_{20}H_{28}N_2O_2SNa$ (M+Na$^+$): 383.1769; Found: 383.1761.

Along product **VIII$_{mo}$**, product **VIII$_{di}$** was also isolated.



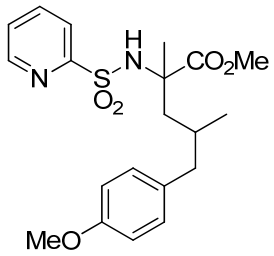
***N*-(2,4-Dimethyl-4-(4-methylbenzyl)-5-(*p*-tolyl)pentan-2-yl)pyridine-2-sulfonamide (VIII$_{di}$).** Colorless oil; yield: 25.4 mg (28%). **$^1$H NMR (300 MHz, CDCl$_3$, δ):** 8.68 (ddd, *J* = 4.7, 1.6, 0.8 Hz, 1H), 8.00 (dt, *J* = 7.9, 0.9 Hz, 1H), 7.88 (td, *J* = 7.7, 1.7 Hz, 1H), 7.45 (ddd, *J* = 7.6, 4.7, 1.1 Hz, 1H), 7.06 (d, *J* = 7.9 Hz, 4H), 6.98 (d, *J* = 8.0 Hz, 4H), 4.86 (bs, 1H), 2.75 (d, *J* = 13.1 Hz, 2H), 2.58 (d, *J* = 13.1 Hz, 2H), 2.32 (s, 6H), 1.65 (s, 2H), 1.28 (s, 6H) , 1.00 (s, 3H). **$^{13}$C NMR (75 MHz, CDCl$_3$, δ):** 160.2, 150.0, 138.1, 135.6, 135.4, 131.0, 128.6, 126.4, 121.7, 58.9, 51.6, 47.9, 38.9, 30.2, 24.5, 21.1. **HRMS-ESI (*m/z*):** calcd. for $C_{27}H_{34}N_2O_2SNa$ (M+Na$^+$): 473.2233; Found: 473.2232.

**(*rac*)-Methyl 4-(4-methoxybenzyl)-5-(4-methoxyphenyl)-2-methyl-2-(pyridine-2-sulfonamido)pentanoate (IX$_{di}$).** Compound **IX$_{di}$** was prepared following the general protocol from (*rac*)-methyl 2,4-dimethyl-2-(pyridine-2-sulfonamido)pentanoate (**II**) (60.1 mg, 0.20 mmol, 1.00 equiv) and 4-iodoanisole (140 mg, 0.60 mmol, 3.00 equiv) to give **IX$_{di}$** as a yellow solid; yield: 72.7 mg (71%); mp = 110-116 °C. **$^1$H NMR (500 MHz,**



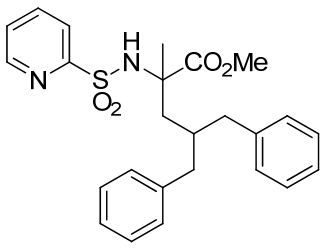
**$CDCl_3$, δ):** 8.66 (ddd, *J* = 4.7, 1.6, 0.9 Hz, 1H), 7.91 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.86 (td, *J* = 7.7, 1.7 Hz, 1H), 7.45 (ddd, *J* = 7.4, 4.7, 1.3 Hz, 1H), 7.05 (d, *J* = 8.6 Hz, 2H), 6.99 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 5.54 (s, 1H), 3.78 (s, 3H), 3.78 (s, 3H), 3.50 (s, 3H), 2.62 (dd, *J* = 13.8, 6.5 Hz, 1H), 2.49 – 2.42 (m, 2H), 2.33 (dd, *J* = 13.7, 7.1 Hz, 1H), 2.03 – 1.98 (m, 1H), 1.93 (dd, *J* = 14.4, 5.4 Hz, 1H), 1.75 (dd, *J* = 14.5, 5.1 Hz, 1H), 1.29 (s, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$, δ):** 174.0, 159.6, 158.1, 158.0, 149.8, 138.0, 132.5, 132.5, 130.4, 130.3, 126.4, 121.3, 113.9, 113.9, 62.6, 55.4, 55.4, 52.8, 43.1, 40.3, 39.9, 38.4, 23.2. **HRMS-APCI (*m/z*):** calcd. for $C_{27}H_{33}N_2O_4S$ ($M+H^+$): 513.2054; Found: 513.2057.

Along product **$IX_{di}$**, product **$IX_{mo}$** was also isolated.

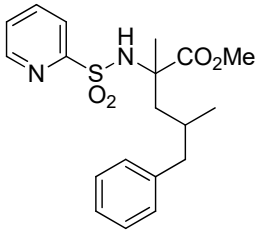



**(*rac*)-Methyl 5-(4-methoxyphenyl)-2,4-dimethyl-2-(pyridine-2-sulfonamido)pentanoate ($IX_{mo}$).** Colorless oil; yield: 14.0 mg (17%). **$^1$H NMR (500 MHz, $CDCl_3$, δ):** 8.68 (ddd, *J* = 4.7, 1.6, 0.9 Hz, 1H), 7.97 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.88 (td, *J* = 7.7, 1.7 Hz, 1H), 7.45 (ddd, *J* = 7.6, 4.7, 1.1 Hz, 1H), 7.01 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 5.86 (s, 1H), 3.79 (s, 3H), 3.62 (s, 3H), 2.44 (dd, *J* = 13.5, 6.0 Hz, 1H), 2.25 (dd, *J* = 13.5, 7.9 Hz, 1H), 1.96 – 1.92 (m, 1H), 1.83 – 1.78 (m, 2H), 1.35 (s, 3H), 0.92 (d, *J* = 6.5 Hz, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$, δ):** 174.2, 159.6, 158.0, 150.0, 138.1, 132.8, 130.2, 126.5, 121.4, 113.8, 62.8, 55.4, 53.0, 46.2, 43.2, 31.7, 23.5, 21.1. **HRMS-ESI (*m/z*):** calcd. for $C_{20}H_{26}N_2O_5SNa$ ($M+Na^+$): 429.1455; Found: 429.1453.

**(*rac*)-Methyl 2-methyl-4-benzyl-5-phenyl-2-(pyridine-2-sulfonamido)pentanoate ($X_{di}$).** Compound **$X_{di}$** was prepared following the general protocol from (*rac*)-methyl 2,4-dimethyl-2-(pyridine-2-sulfonamido)pentanoate (**II**) (60.1 mg, 0.20 mmol, 1.00 equiv) and iodobenzene (67.1 µL, 0.60 mmol, 3.00 equiv) to give **$X_{di}$** as a yellow solid; yield: 48.1 mg (53%); mp = 103-106 °C. **$^1$H NMR (500 MHz, $CDCl_3$, δ):** 8.66 (ddd, *J* = 4.7, 1.6, 0.9 Hz, 1H), 7.93 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.86 (td, *J* = 7.7, 1.7 Hz, 1H), 7.45 (ddd, *J* = 7.5, 4.7, 1.1 Hz, 1H), 7.30 – 7.27 (m, 3H), 7.26 – 7.24 (m, 1H), 7.21 – 7.17 (m, 2H), 7.15 (d, *J* = 7.0 Hz, 2H), 7.07 (d, *J* = 7.0 Hz, 2H), 5.66 (s, 1H), 3.47 (s, 3H), 2.77 (dd, *J* = 13.7, 6.4 Hz, 1H), 2.56 – 2.49 (m, 2H), 2.40 (dd, *J* = 13.6, 7.3 Hz, 1H), 2.14 – 2.07 (m, 1H), 2.00 (dd, *J* = 14.4, 5.6 Hz, 1H), 1.80 (dd, *J* = 14.4, 5.0 Hz, 1H), 1.29 (s, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$, δ):** 173.9, 159.6, 149.9, 140.5, 140.5, 138.1, 129.5, 129.4, 128.5, 128.5, 126.4, 126.2, 121.3, 62.6, 52.9, 43.0, 41.1, 40.8, 38.3, 23.2. **HRMS-APCI (*m/z*):** calcd. for $C_{25}H_{29}N_2O_4S$ ($M+H^+$): 453.1843; Found: 453.1840.




Along product **$X_{di}$**, product **$X_{mo}$** was also isolated.




**(*rac*)-Methyl 2,4-dimethyl-5-phenyl-2-(pyridine-2-sulfonamido)pentanoate ($X_{mo}$).** yellow solid; mp = 108-110 °C; mixture of diasteromers 91:9; yield: 27.0 mg (36%). **$^1$H NMR (500 MHz, $CDCl_3$, δ):** 8.68 (ddd, *J* = 4.7, 1.6, 0.8 Hz, 1H), 7.97 (dt, *J* = 7.9, 0.9 Hz, 1H), 7.88 (td, *J* = 7.7, 1.7 Hz, 1H), 7.45 (ddd, *J* = 7.6, 4.7, 1.1 Hz, 1H), 7.26 (t, *J* = 7.4 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 6.9 Hz, 2H), 5.91 (s, 1H), 3.60 (s, 3H),

2.51 (dd, *J* = 13.2, 6.0 Hz, 1H), 2.30 (dd, *J* = 13.3, 8.1 Hz, 1H), 2.00 – 1.96 (m, 1H), 1.89 – 1.81 (m, 2H), 1.35 (s, 3H), 0.94 (d, *J* = 6.5 Hz, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$, δ):** 174.2, 159.6, 150.0, 140.7, 138.1, 129.3, 128.4, 126.5, 126.1, 121.4, 62.8, 53.0, 46.2, 44.1, 31.6, 23.6, 21.1. **HRMS-APCI (*m/z*):** calcd. for $C_{19}H_{25}N_2O_4S$ ($M+H^+$): 377.1530; Found: 377.1529.

**(*rac*)-Methyl 4-(4-bromobenzyl)-5-(4-bromophenyl)-2-methyl-2-(pyridine-2-sulfonamido)pentanoate ($XI_{di}$).** Compound **$XI_{di}$** was prepared following the general protocol from (*rac*)-methyl 2,4-dimethyl-2-(pyridine-2-sulfonamido)pentanoate (**II**) (60.1 mg, 0.20 mmol, 1.00 equiv) and 1-bromo-4-iodobenzene (170 mg, 0.60 mmol, 3.00 equiv) to give **$XI_{di}$** as a white solid; yield: 75.5 mg (62%); mp = 179-181 °C. **$^1$H NMR (500 MHz, $CDCl_3$, δ):** 8.66 (ddd, *J* = 4.7, 1.6, 0.9 Hz, 1H), 7.93 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.88 (td, *J* = 7.7, 1.7 Hz, 1H), 7.45 (ddd, *J* = 7.5, 4.7, 1.2 Hz, 1H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 5.92 (s, 1H), 3.49 (s, 3H), 2.79 (dd, *J* = 13.8, 5.8 Hz, 1H), 2.47 (dd, *J* = 13.9, 7.1 Hz, 1H), 2.41 (dd, *J* = 13.6, 6.4 Hz, 1H), 2.35 (dd, *J* = 13.7, 6.8 Hz, 1H), 2.05 – 2.01 (m, 2H), 1.78 – 1.73 (m, 1H), 1.26 (s, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$, δ):** 174.0, 159.5, 150.0, 139.3, 139.3, 138.1, 131.6, 131.5, 131.2, 131.1, 126.6, 121.3, 120.1, 120.0, 62.6, 53.1, 42.6, 40.6, 39.9, 38.4, 23.5. **HRMS-APCI (*m/z*):** calcd. for $C_{25}H_{27}N_2O_4Br_2S$ ($M+H^+$): 611.0034; Found: 611.0032.

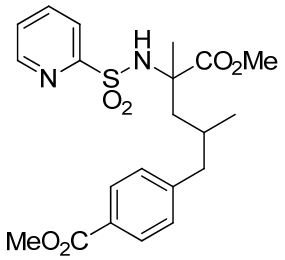
Along product **$XI_{di}$**, product **$XI_{mo}$** was also isolated.

**(*rac*)-Methyl 5-(4-bromophenyl)-2,4-dimethyl-2-(pyridine-2-sulfonamido)pentanoate ($XI_{mo}$).** White solid; mp = 110-112 °C mixture of diasteromers 94:6; yield: 22.0 mg (24%). **$^1$H NMR (300 MHz, $CDCl_3$, δ):** 8.68 (d, *J* = 4.7 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.88 (td, *J* = 7.7, 1.6 Hz, 1H), 7.46 (ddd, *J* = 7.5, 4.7, 1.1 Hz, 1H), 7.38 (d, *J* = 8.3 Hz, 2H), 6.97 (d, *J* = 8.3 Hz, 2H), 5.96 (s, 1H), 3.62 (s, 3H), 2.47 (dd, *J* = 13.3, 5.8 Hz, 1H), 2.24 (dd, *J* = 13.3, 8.1 Hz, 1H), 2.05 – 1.96 (m, 1H), 1.86 – 1.76 (m, 2H), 1.34 (s, 3H), 0.92 (d, *J* = 6.4 Hz, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 174.2, 159.6, 150.0, 139.7, 138.1, 131.4, 131.0, 126.5, 121.3, 119.9, 62.7, 53.0, 46.0, 43.3, 31.6, 23.7, 21.0. **HRMS-APCI (*m/z*):** calcd. for $C_{19}H_{24}N_2O_4BrS$ ($M+H^+$): 455.0635; Found: 455.0639.

**(*rac*)-Dimethyl 4,4'-(2-(3-methoxy-2-methyl-3-oxo-2-(pyridine-2-sulfonamido)propyl)propane-1,3-diyl)dibenzoate ($XII_{di}$).** Compound **$XII_{di}$** was prepared following the general protocol from (*rac*)-methyl 2,4-dimethyl-2-(pyridine-2-sulfonamido)pentanoate (**II**) (60.1 mg, 0.20 mmol, 1.00 equiv) and methyl 4-iodobenzoate (157 mg, 0.60 mmol, 3.00 equiv) to give **$XII_{di}$** as a colorless oil; yield: 88.9 mg (78%). **$^1$H NMR (300 MHz, $CDCl_3$, δ):** 8.66 (d, *J* = 4.4 Hz, 1H), 7.96 – 7.84 (m, 6H), 7.45 (ddd, *J* = 7.3, 4.7, 1.4 Hz, 1H), 7.21 (d, *J* = 8.3 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 5.96 (s, 1H), 3.89 (s, 3H), 3.89 (s, 3H), 3.47 (s, 3H), 2.93 (dd, *J* = 13.7, 6.0 Hz, 1H), 2.57 (dd, *J* = 13.7, 7.5 Hz, 1H), 2.50 – 2.48 (m, 2H), 2.20 – 2.04 (m, 2H), 1.79 (dd, *J* = 14.2, 4.8 Hz, 1H),

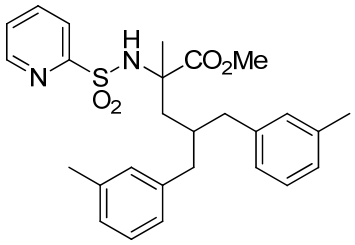
1.24 (s, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 174.0, 167.2, 167.1, 159.5, 150.0, 145.9, 138.2, 129.9, 129.8, 129.5, 129.4, 128.3, 128.3, 126.6, 121.3, 62.6, 53.1, 52.2, 52.1, 42.7, 41.3, 40.6, 38.4, 23.6. **HRMS-ESI (*m/z*):** calcd. for $C_{29}H_{32}N_2O_8SNa$ ($M+Na^+$): 591.1772; Found: 591.1772.

Along product **XII$_{di}$**, product **XII$_{mo}$** was also isolated.

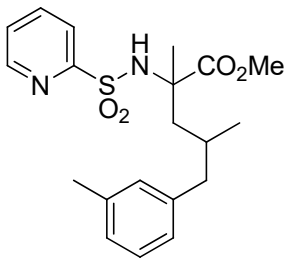


**(*rac*)-Methyl 4-(5-methoxy-2,4-dimethyl-5-oxo-4-(pyridine-2-sulfonamido)pentyl)benzoate (XII$_{mo}$).** Colorless oil; mixture of diasteromers 92:8; yield: 14.6 mg (17%). **$^1$H NMR (300 MHz, $CDCl_3$, δ):** 8.67 (d, *J* = 4.1 Hz, 1H), 7.98 – 7.85 (m, 4H), 7.45 (ddd, *J* = 7.5, 4.7, 1.1 Hz, 1H), 7.16 (d, *J* = 8.2 Hz, 2H), 6.00 (s, 1H), 3.90 (s, 3H), 3.61 (s, 3H), 2.57 (dd, *J* = 13.2, 5.9 Hz, 1H), 2.33 (dd, *J* = 13.2, 8.2 Hz, 1H), 2.02 (dd, *J* = 13.6, 6.1 Hz, 1H), 1.94 – 1.78 (m, 2H), 1.34 (s, 3H), 0.92 (d, *J* = 6.4 Hz, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 174.1, 167.2, 159.6, 150.0, 146.3, 138.2, 129.7, 129.3, 128.1, 126.5, 121.4, 62.7, 53.0, 52.1, 46.1, 43.9, 31.5, 23.7, 21.0. **HRMS-APCI (*m/z*):** calcd. for $C_{21}H_{27}N_2O_6S$ ($M+H^+$): 435.1584; Found: 435.1586.

**(*rac*)-Methyl 2-methyl-4-(3-methylbenzyl)-2-(pyridine-2-sulfonamido)-5-(*m*-tolyl)pentanoate (XIII$_{di}$).** Compound **XIII$_{di}$** was prepared following the general protocol from (*rac*)-methyl 2,4-dimethyl-2-(pyridine-2-sulfonamido)pentanoate (**II**) (60.1 mg, 0.20 mmol, 1.00 equiv) and 3-iodotoluene (77.0 μL, 0.60 mmol, 3.00 equiv) to give **XIII$_{di}$** as a colorless oil; yield: 57.5 mg (60%). **$^1$H NMR (500 MHz, $CDCl_3$, δ):** 8.67 (ddd, *J* = 4.7, 1.6, 0.9 Hz, 1H), 7.90 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.86 (td, *J* = 7.7, 1.7 Hz, 1H), 7.45 (ddd, *J* = 7.5, 4.7, 1.3 Hz, 1H), 7.19 – 7.13 (m, 2H), 7.01 – 6.98 (m, 2H), 6.95 – 6.93 (m, 2H), 6.88 – 6.87 (m, 2H), 5.47 (s, 1H), 3.49 (s, 3H), 2.66 (dd, *J* = 13.7, 6.8 Hz, 1H), 2.52 – 2.44 (m, 2H), 2.38 – 2.35 (m, 1H), 2.33 (s, 3H), 2.31 (s, 3H), 2.15 – 2.07 (m, 1H), 1.94 (dd, *J* = 14.5, 5.3 Hz, 1H), 1.77 (dd, *J* = 14.4, 5.1 Hz, 1H), 1.32 (s, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$, δ):** 173.9, 159.7, 149.9, 140.4, 140.4, 138.1, 138.0, 138.0, 130.2, 130.2, 128.4, 128.4, 127.0, 127.0, 126.5, 126.4, 126.4, 121.3, 62.6, 52.8, 43.3, 41.4, 41.0, 38.6, 37.9, 23.2, 21.6. **HRMS-APCI (*m/z*):** calcd. for $C_{27}H_{33}N_2O_4S$ ($M+H^+$): 481.2156; Found: 481.2165.

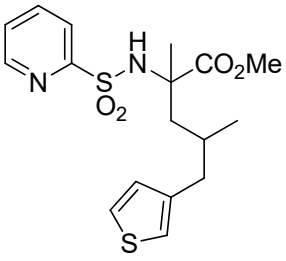


Along product **XIII$_{di}$**, product **XIII$_{mo}$** was also isolated.

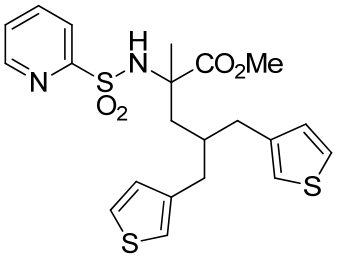


**(*rac*)-Methyl 2,4-dimethyl-2-(pyridine-2-sulfonamido)-5-(*m*-tolyl)pentanoate (XIII$_{mo}$).** Colorless oil; mixture of diasteromers 94:6; yield: 18.1 mg (23%). **$^1$H NMR (500 MHz, $CDCl_3$, δ):** 8.69 (ddd, *J* = 4.7, 1.6, 0.9 Hz, 1H), 7.97 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.88 (td, *J* = 7.7, 1.7 Hz, 1H), 7.45 (ddd, *J* = 7.6, 4.7, 1.1 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.91 (s, 1H), 6.89 (d, *J* = 7.5 Hz, 1H), 5.88 (s, 1H), 3.61 (s, 3H), 2.47 (dd, *J* = 13.2, 6.0 Hz, 1H), 2.32 (s, 3H), 2.26 (dd, *J* = 13.3, 8.1 Hz, 1H), 1.98 – 1.94 (m, 1H), 1.89 – 1.80 (m, 2H), 1.36 (s, 3H), 0.93 (d, *J* = 6.5 Hz, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$, δ):** 174.2, 159.7, 150.0, 140.6, 138.1, 137.9, 130.1, 128.3, 126.9, 126.5, 126.4, 121.4,

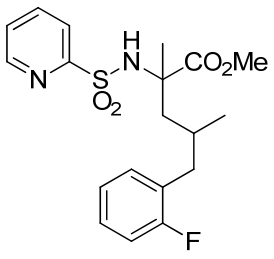
62.8, 52.9, 46.3, 44.0, 31.5, 23.5, 21.6, 21.2. **HRMS-ESI (*m/z*):** calcd. for $C_{20}H_{26}N_2O_4SNa$ ($M+Na^+$): 413.1505; Found: 413.1506.

**(*rac*)-Methyl 2,4-dimethyl-2-(pyridine-2-sulfonamido)-5-(thiophen-3-yl)pentanoate (XIV$_{mo}$).**  Compound **XIV$_{mo}$** was prepared following the general protocol from (*rac*)-methyl 2,4-dimethyl-2-(pyridine-2-sulfonamido)pentanoate (**II**) (60.1 mg, 0.20 mmol, 1.00 equiv) and 3-iodothiophene (61.0 μL, 0.60 mmol, 3.00 equiv) to give **XIV$_{mo}$** as a 84:16 mixture of diasteromers as a colorless oil; yield: 30.7 mg (40%). The starting material **II** was recovered unaltered by flash column chromatography (8.4 mg, 14%). **$^1$H NMR (300 MHz, $CDCl_3$, δ):** 8.68 (ddd, *J* = 4.7, 1.7, 0.9 Hz, 1H), 7.94 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.88 (td, *J* = 7.7, 1.7 Hz, 1H), 7.46 (ddd, *J* = 7.6, 4.7, 1.2 Hz, 1H), 7.27 – 7.26 (m, 1H), 7.25 – 7.24 (m, 1H), 6.99 – 6.98 (m, 1H), 6.93 (dd, *J* = 4.9, 1.3 Hz, 1H), 6.92 – 6.91 (m, 1H), 6.86 (dd, *J* = 4.9, 1.3 Hz, 1H), 5.71 (s, 1H), 3.57 (s, 3H), 2.72 (dd, *J* = 14.2, 6.2 Hz, 1H), 2.62 (dd, *J* = 14.2, 7.0 Hz, 1H), 2.53 (dd, *J* = 14.2, 7.0 Hz, 1H), 2.44 (dd, *J* = 14.2, 6.6 Hz, 1H), 2.17 – 2.10 (m, 1H), 2.01 (dd, *J* = 14.5, 5.2 Hz, 1H), 1.78 (dd, *J* = 14.4, 5.4 Hz, 1H), 1.33 (s, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 174.1, 159.6, 150.0, 140.9, 138.1, 128.7, 126.5, 125.4, 121.4, 121.4, 62.7, 53.0, 46.2, 38.4, 30.9, 23.4, 21.3. **HRMS-APCI (*m/z*):** calcd. for $C_{17}H_{23}N_2O_4S_2$ ($M+H^+$): 383.1094; Found: 383.1091.

Along product **XIV$_{mo}$**, product **XIV$_{di}$** was also isolated.

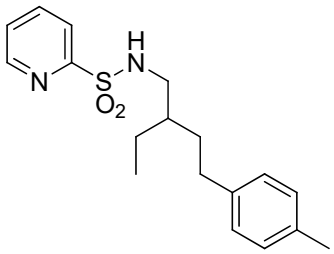


**(*rac*)-Methyl 2-methyl-2-(pyridine-2-sulfonamido)-5-(thiophen-3-yl)-4-(thiophen-3-ylmethyl)pentanoate (XIV$_{di}$).** Colorless oil; yield: 14.7 mg (16%). **$^1$H NMR (500 MHz, $CDCl_3$, δ):** 8.68 (ddd, *J* = 4.7, 1.7, 0.9 Hz, 1H), 7.94 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.88 (td, *J* = 7.7, 1.7 Hz, 1H), 7.46 (ddd, *J* = 7.6, 4.7, 1.2 Hz, 1H), 7.27 – 7.26 (m, 1H), 7.25 – 7.24 (m, 1H), 6.93 (dd, *J* = 4.9, 1.3 Hz, 1H), 6.86 (dd, *J* = 4.9, 1.3 Hz, 1H), 5.71 (s, 1H), 3.57 (s, 3H), 2.72 (dd, *J* = 14.2, 6.2 Hz, 1H), 2.62 (dd, *J* = 14.2, 7.0 Hz, 1H), 2.53 (dd, *J* = 14.2, 7.0 Hz, 1H), 2.44 (dd, *J* = 14.2, 6.6 Hz, 1H), 2.17 – 2.10 (m, 1H), 2.01 (dd, *J* = 14.5, 5.2 Hz, 1H), 1.78 (dd, *J* = 14.4, 5.4 Hz, 1H), 1.33 (s, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$, δ):** 174.0, 159.6, 149.9, 140.6, 140.4, 138.1, 128.9, 128.7, 126.5, 125.7, 125.6, 121.9, 121.7, 121.3, 62.6, 53.0, 43.4, 36.7, 35.5, 35.1, 23.3. **HRMS-APCI (*m/z*):** calcd. for $C_{21}H_{25}N_2O_4S_4$ ($M+H^+$): 465.0971; Found: 465.0971.

**(*rac*)-Methyl 5-(2-fluorophenyl)-2,4-dimethyl-2-(pyridine-2-sulfonamido)pentanoate (XV$_{mo}$).**  Compound **XV$_{mo}$** was prepared following the general protocol from (*rac*)-methyl 2,4-dimethyl-2-(pyridine-2-sulfonamido)pentanoate (**II**) (60.1 mg, 0.20 mmol, 1.00 equiv) and 2-fluoroiodobenzene (70.0 μL, 0.60 mmol, 3.00 equiv) to give **XV$_{mo}$** as a 78:22 mixture of diasteromers as a colorless oil; yield: 14.3 mg (18%). The starting material **II** was recovered unaltered by flash column chromatography (37.2 mg, 62%). **$^1$H NMR (500 MHz, $CDCl_3$, δ):** 8.68 (ddd, *J* = 4.7, 1.7, 0.8 Hz, 1H), 7.98 (dt, *J* = 7.9, 0.9 Hz, 1H), 7.88 (td, *J* = 7.8, 1.7 Hz, 1H), 7.45 (ddd, *J* = 7.6, 4.7, 1.1 Hz, 1H), 7.19 – 7.15 (m, 1H), 7.11 (td, *J* = 7.5, 1.8 Hz, 1H), 7.05 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.01 – 6.97 (m, 1H), 5.93 (s, 1H), 3.63 (s, 3H), 2.55 (dd, *J* = 13.3, 5.8

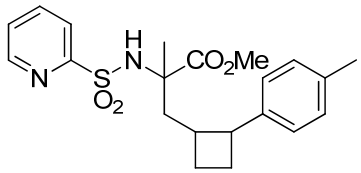
Hz, 1H), 2.37 (dd, *J* = 13.2, 8.3 Hz, 1H), 2.03 (dd, *J* = 13.8, 6.4 Hz, 1H), 1.90 – 1.81 (m, 2H), 1.35 (s, 3H), 0.96 (d, *J* = 6.5 Hz, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$, δ):** 174.2, 161.4 (d, *J* = 244.6 Hz), 159.7, 150.0, 138.1, 131.7 (d, *J* = 5.0 Hz), 127.9 (d, *J* = 8.1 Hz), 126.5, 124.0 (d, *J* = 3.5 Hz), 121.4, 115.3 (d, *J* = 22.4 Hz), 115.3 (d, *J* = 22.6 Hz), 62.9, 53.0, 46.3, 37.2, 30.8, 23.5, 21.0. **HRMS-ESI (*m/z*):** calcd. for $C_{19}H_{23}FN_2O_4SNa$ ($M+Na^+$): 417.1255; Found: 417.1253.

**(*rac*)-*N*-(2-Ethyl-4-(*p*-tolyl)butyl)pyridine-2-sulfonamide (XVII).** Compound **XVII** was



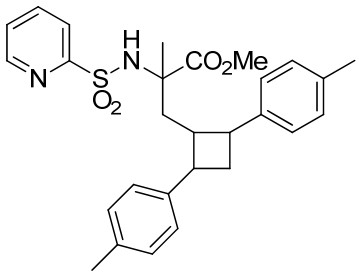
prepared following the general protocol from *N*-(2-ethylbutyl)pyridine-2-sulfonamide (**XVI**) (48.5 mg, 0.20 mmol, 1.00 equiv) to give **XVII** in a 40:60 mixture of δ- and γ-arylation products (**XVII** and **XVIII** respectively); yield: 23.4 mg (35%). **$^1$H NMR (500 MHz, $CDCl_3$, δ):** 8.73 – 8.67 (m, 1H), 8.01 – 7.96 (m, 1H), 7.92 – 7.87 (m, 1H), 7.51 – 7.46 (m, 1H), 7.08 – 6.97 (m, 4H), 4.72 (s, 1H), 3.00 (t, *J* = 6.0 Hz, 1H), 2.54 – 2.51 (m, 1H), 2.31 (s, 3H), 1.48 – 1.26 (m, 6H), 0.84 (t, *J* = 7.4 Hz, 3H). **HRMS-APCI (*m/z*):** calcd. for $C_{18}H_{25}N_2O_2S$ ($M+H^+$): 333.1631; Found: 333.1638.

**(*rac*)-Methyl 2-methyl-2-(pyridine-2-sulfonamido)-3-(2-(*p*-tolyl)cyclobutyl) propanoate ($XXII_{mo}$).**



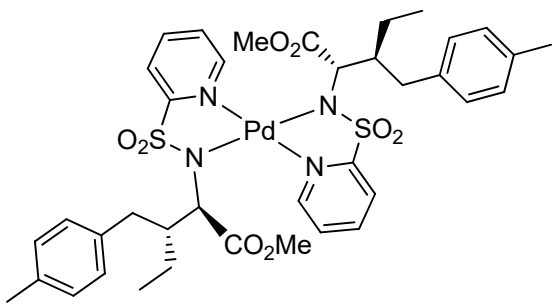
Compound $XXII_{mo}$ was prepared following the general protocol from (*rac*)-methyl 3-cyclobutyl-2-methyl-2-(pyridine-2-sulfonamido)propanoate (**XXI**) (62.5 mg, 0.20 mmol, 1.00 equiv) to give $XXII_{mo}$ as a 55:45 mixture of diasteromers as a colorless oil; yield: 34.3 mg (43%). The starting material **XXI** was recovered unaltered by flash column chromatography (19.8 mg, 32%). **$^1$H NMR (300 MHz, $CDCl_3$, δ):** 8.69 – 8.65 (m, 1H), 7.97 – 7.81 (m, 2H), 7.47 – 7.42 (m, 1H), 7.13 – 7.03 (m, 4H), 5.70 – 5.48 (m, 1H), 3.61 – 3.53 (m, 3H), 3.05 – 2.94 (m, 0.5H), 2.75 – 2.62 (m, 0.5H), 2.34 – 2.31 (m, 3H), 2.27 – 2.13 (m, 2H), 2.08 – 1.88 (m, 2H), 1.72 – 1.60 (m, 2H), 1.33 – 1.30 (m, 3H). **HRMS-APCI (*m/z*):** calcd. for $C_{21}H_{27}N_2O_4S$ ($M+H^+$): 403.1686; Found: 403.1688.

Along product $XXII_{mo}$, product $XXII_{di}$ was also isolated.



**(*rac*)-Methyl 3-(2,4-di-*p*-tolylcyclobutyl)-2-methyl-2-(pyridine-2-sulfonamido)propanoate ($XXII_{di}$).** White solid; mp = 144-147 °C mixture of diasteromers 55:45; yield: 17.8 mg (18%). **$^1$H NMR (500 MHz, $CDCl_3$, δ):** 8.62 – 8.61 (m, 1H), 7.84 – 7.74 (m, 2H), 7.43 – 7.39 (m, 1H), 7.22 – 7.07 (m, 8H), 5.36 (s, 0.5H), 4.51 (s, 0.5H), 3.81 – 3.75 (m, 1H), 3.38 – 3.32 (m, 3H), 3.11 – 2.94 (m, 2H), 2.72 – 2.56 (m, 2H), 2.34 – 2.33 (m, 6H), 1.26 (s, 3H), 1.23 – 1.18 (m, 2H). **HRMS-APCI (*m/z*):** calcd. for $C_{28}H_{33}N_2O_4S$ ($M+H^+$): 493.2156; Found: 493.2162.

## 4. Synthesis of $Pd^{II}$ complex A[6]




An oven-dried, Ar flushed 10.0 mL vessel was charged with (2*S**,3*S**)-methyl 3-(4-methylbenzyl)-2-(pyridine-2-sulfonamido)-pentanoate **11** (75.3 mg, 0.20 mmol, 1.00 equiv) and $Pd(OAc)_2$ (44.9 mg, 0.20 mmol, 1.00 equiv). The reaction vessel was sealed with a Teflon lined cap, then evacuated and flushed with argon three times. Under argon atmosphere, 1,4-dioxane (0.80 mL) was added *via* syringe and the reaction mixture was warmed up to 110 °C for 1 h. After that time, solvent was removed *in vacuo*, and the crude mixture was purified by flash column chromatography (cyclohexane:EtOAc 2:1) to give **Complex A** as a yellow solid; yield: 36.2 mg (42%).

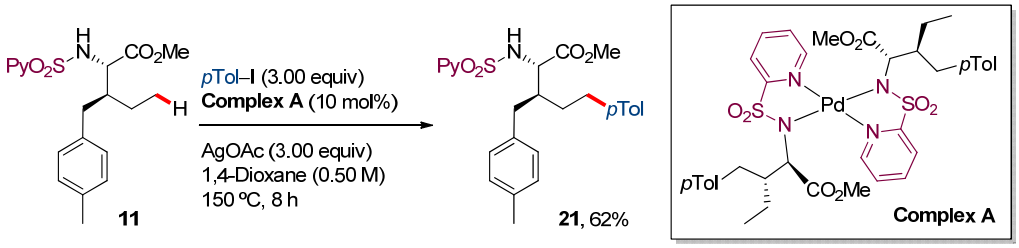
The spectroscopic data is similar to the previously reported information for a similar complex. CCDC Repository No. CCDC 1908969.

**$^1$H NMR (300 MHz, $CDCl_3$, δ):** 8.83 (d, *J* = 3.5 Hz, 1H), 7.88 (t, *J* = 7.0 Hz, 1H), 7.59 (d, *J* = 7.3 Hz, 1H), 7.36 – 7.32 (m, 1H), 7.11 (d, *J* = 7.1 Hz, 2H), 6.85 (d, *J* = 6.7 Hz, 2H), 3.74 (s, 3H), 3.26 – 3.17 (m, 2H), 2.76 (d, *J* = 12.3 Hz, 1H), 2.31 – 2.22 (m, 4H), 1.14 – 1.05 (m, 1H), 0.72 – 0.59 (m, 1H), 0.29 (t, *J* = 6.4 Hz, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$, δ):** 172.3, 162.7, 152.4, 140.0, 137.3, 134.6, 129.7, 129.0, 126.4, 123.3, 62.3, 51.9, 49.3, 35.9, 23.8, 21.2, 11.0.

## 5. Mechanistic studies

### 5.1. Stoichiometric and catalytic studies with the isolated $Pd^{II}$ complex A

#### 5.1.1. Using $Pd^{II}$ Complex A as catalyst

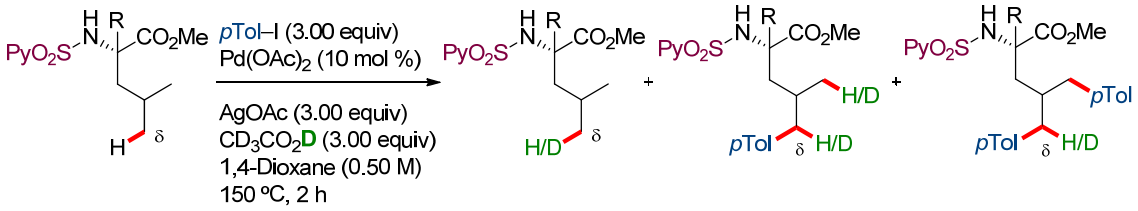



**General procedure.** An oven-dried, argon flushed, pressure tube was charged with **Complex A** (17.1 mg, 0.02 mmol, 0.10 equiv), AgOAc (100 mg, 0.30 mmol, 3.00 equiv), 4-iodotoluene (131 mg, 0.60 mmol, 3.00 equiv) and (2*S**,3*S**)-methyl 3-(4-methylbenzyl)-2-(pyridine-2-sulfonamido)pentanoate **11** (60.2 mg, 0.20 mmol, 1.00 equiv). Then, 1,4-dioxane (0.40 mL) was added *via* syringe. The pressure tube was sealed with a screw cap and finally placed in an oil bath at 150 °C for 8 h. The reaction mixture was then removed from the oil bath and allowed to cool to room temperature. The mixture was then diluted with EtOAc, filtered through a short pad of Celite® and concentrated *in vacuo*. The residue was analyzed by $^1$H NMR, yielding **21** in a 62% yield.

### 5.2. H/D exchange experiments using deuterium donor species

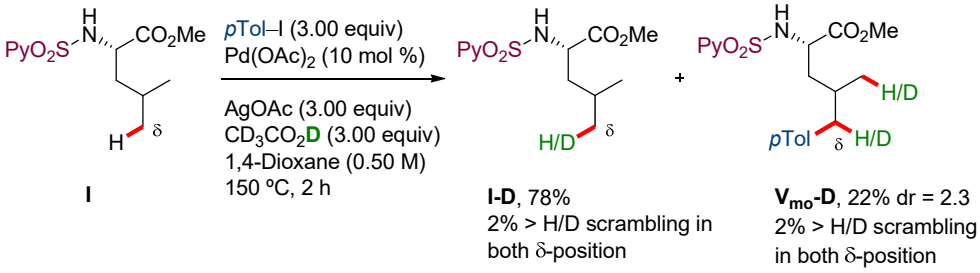
#### 5.2.1. Standard reaction using $CD_3CO_2D$ as deuterium source

These studies were performed in identical parallel reactions, stopped each of them after at 2 h at 150 °C.




**General procedure.** An oven-dried, argon flushed, pressure tube was charged with $Pd(OAc)_2$ (4.48 mg, 0.02 mmol, 0.10 equiv), AgOAc (100 mg, 0.60 mmol, 3.00 equiv), 4-iodotoluene (131 mg, 0.60 mmol, 3.00 equiv) and the corresponding *N*–$SO_2$Py aminoester derivative (0.20 mmol, 1.00 equiv). Then, 1,4-dioxane (0.40 mL) and $CD_3CO_2D$ (34.0 µL, 0.60 mmol, 3.00 equiv) were added *via* syringe. The sealed tube was then sealed with screw cap and finally placed in an oil bath at 150 °C for 2 h. The reaction mixture was then removed from the oil bath and cooled to room temperature. The mixture was then diluted with EtOAc, filtered through a short pad of Celite® and concentrated *in vacuo*. The residue was purified by flash column chromatography ($CH_2Cl_2$:$Et_2O$ 30:1) to afford the pure starting material and the pure δ-arylated derivatives (the corresponding yields and deuterium percentage are shown in the schemes).

### 5.2.1.1. H/D scrambling in *N*-$SO_2$Py L-Leucine derivative (I)



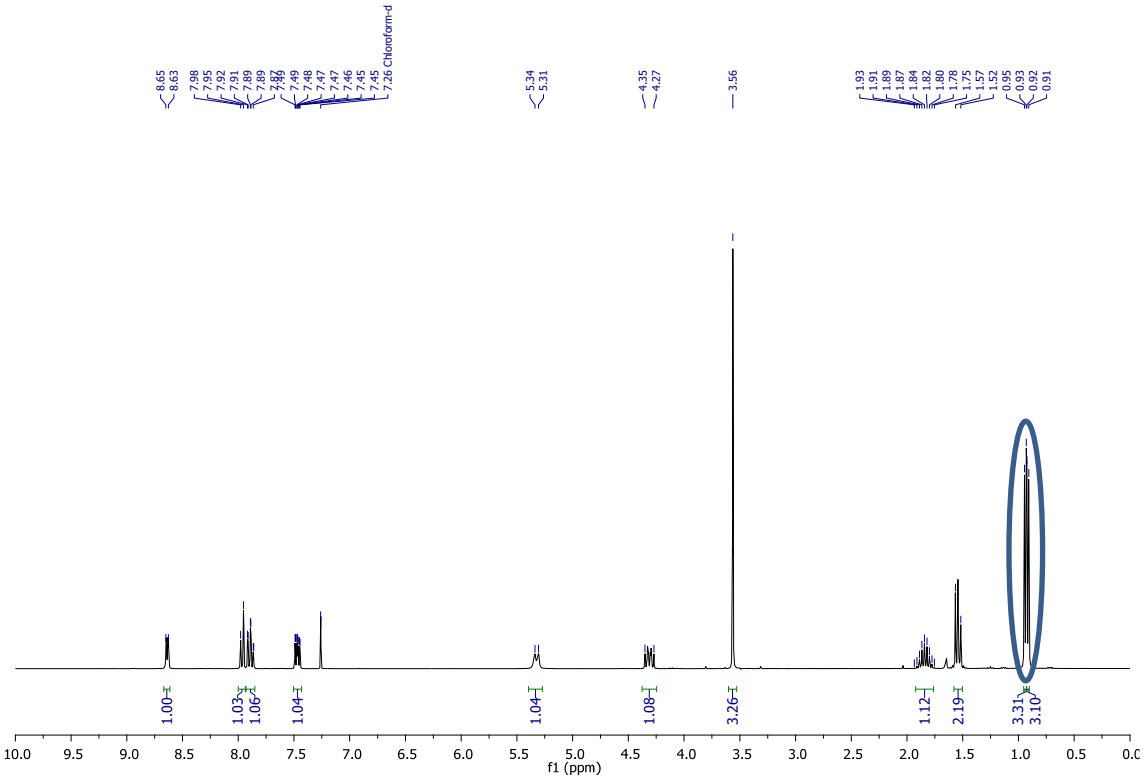

In the **I-D** spectra, the integration of both doublets at 0.95 - 0.91 ppm (signals corresponding to both methyl groups) was 6.29 instead of 6.41 (2% > H/D scrambling).

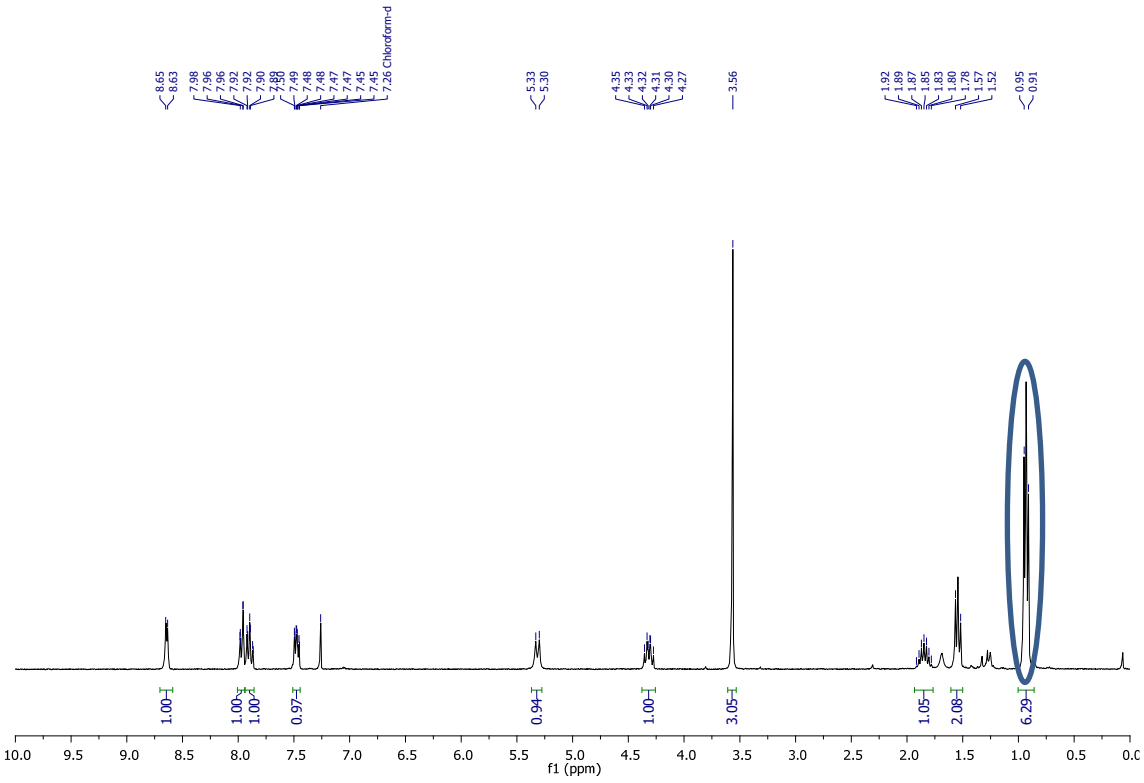
In the **$V_{mo}$-D** spectra, the integration of the doublet at 0.88 - 0.85 ppm (corresponding to the free methyl group) was 3.60 instead of 3.18 (2% > H/D scrambling).

The signals of the other H presented in the molecule remain unaltered, without H/D scrambling in any other position.

## Spectra of I and I-D

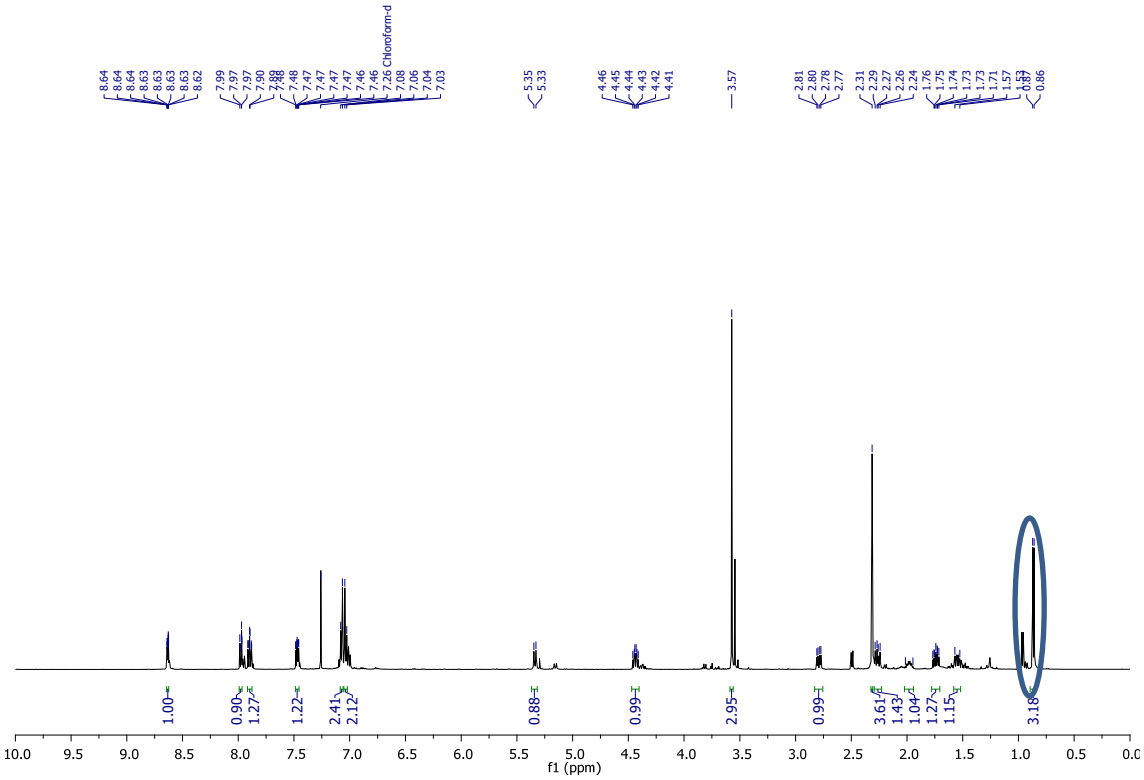
$^1$H NMR ($CDCl_3$, 300 MHz)

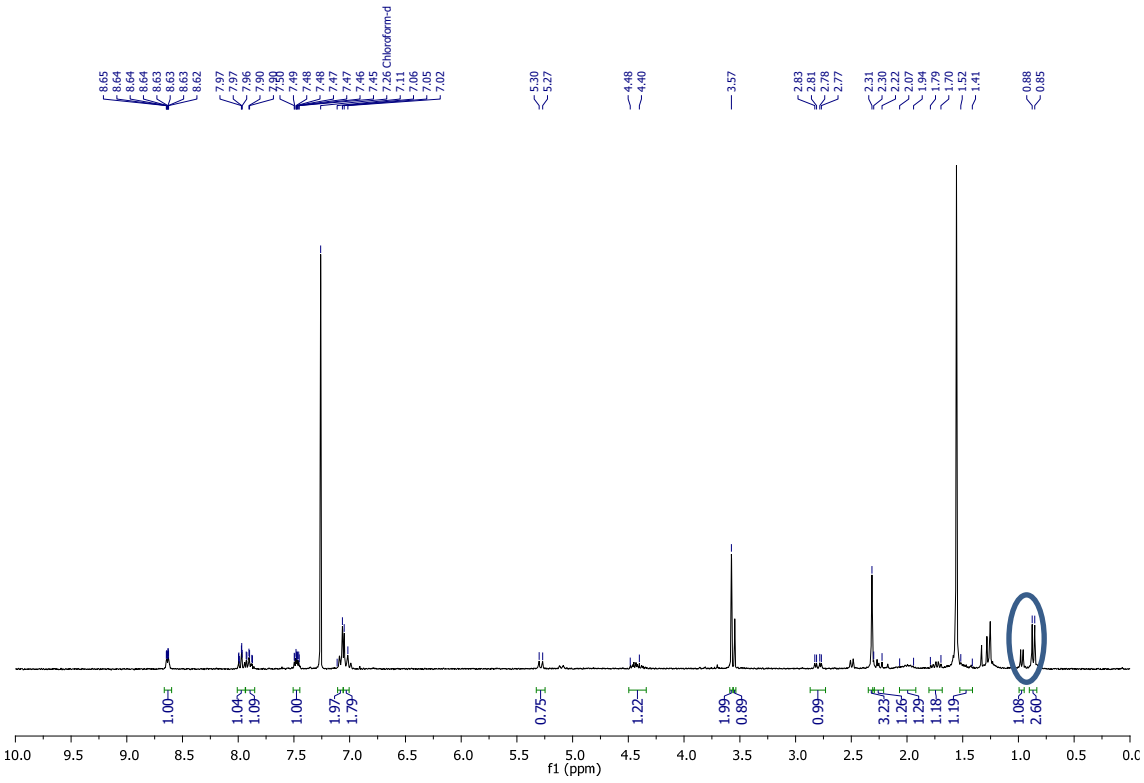


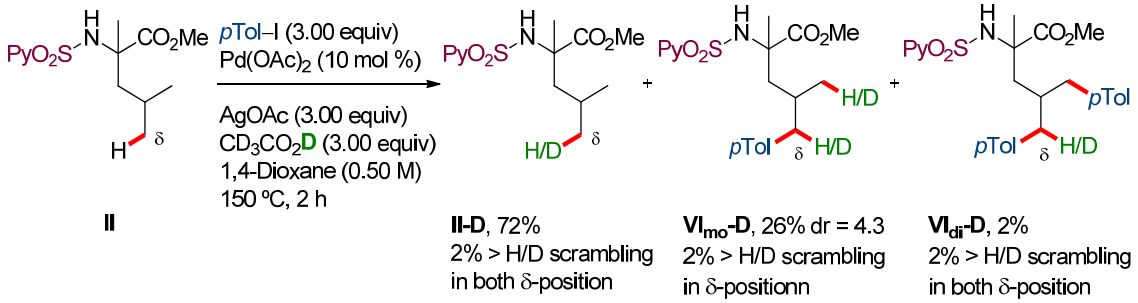
## Spectra of $V_{mo}$ and $V_{mo}$-D

$^1$H NMR ($CDCl_3$, 300 MHz)



### 5.2.1.2. H/D scrambling in *N*-$SO_2$Py α-Me-Leucine derivative (II)




**II**

**II-D**, 72%
2% > H/D scrambling in both δ-position

**VI$_{mo}$-D**, 26% dr = 4.3
2% > H/D scrambling in δ-positionn

**VI$_{di}$-D**, 2%
2% > H/D scrambling in both δ-position

In the **II-D** spectra, the integration of both doublets at 0.90 - 0.88 and 0.79 - 0.77 ppm (signals corresponding to both methyl groups) was 3.24 and 3.18 instead of 3.31 and 3.25 ppm respectively (2% > H/D scrambling in both cases).

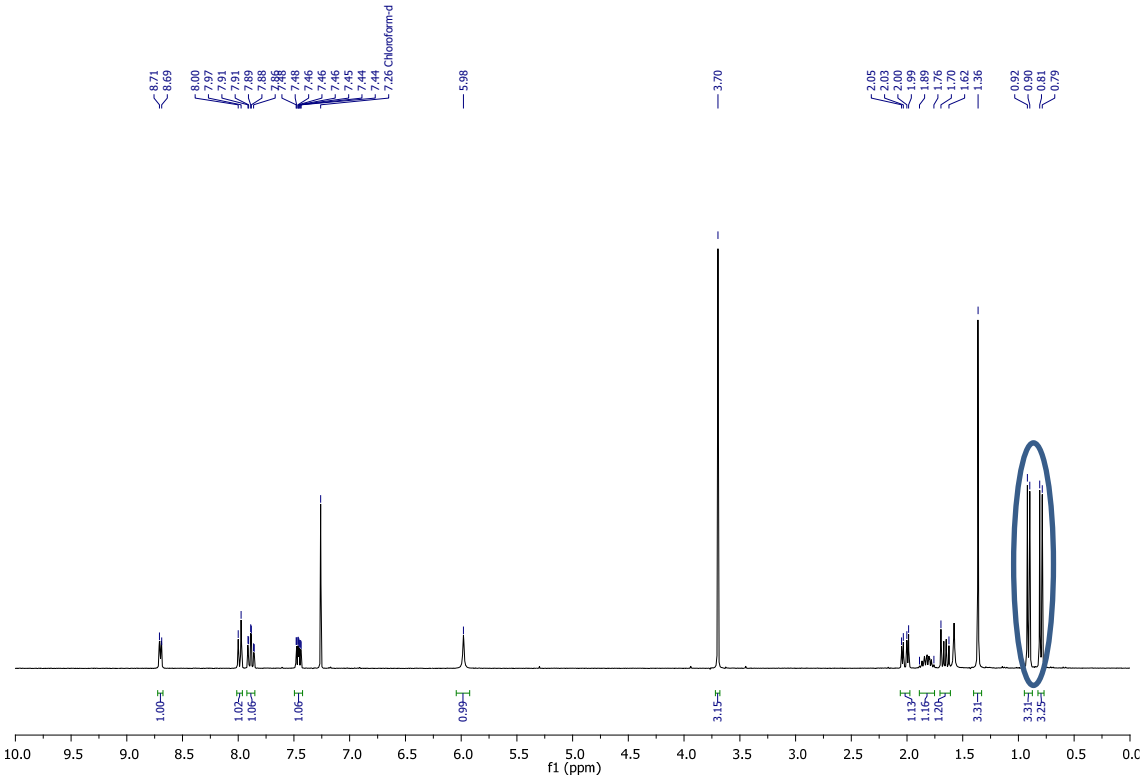
In the **VI$_{mo}$-D** spectra, the integration of the doublet at 0.93-0.91 ppm (corresponding to the free methyl group) was 3.19 instead of 2.98 (2% > H/D scrambling).

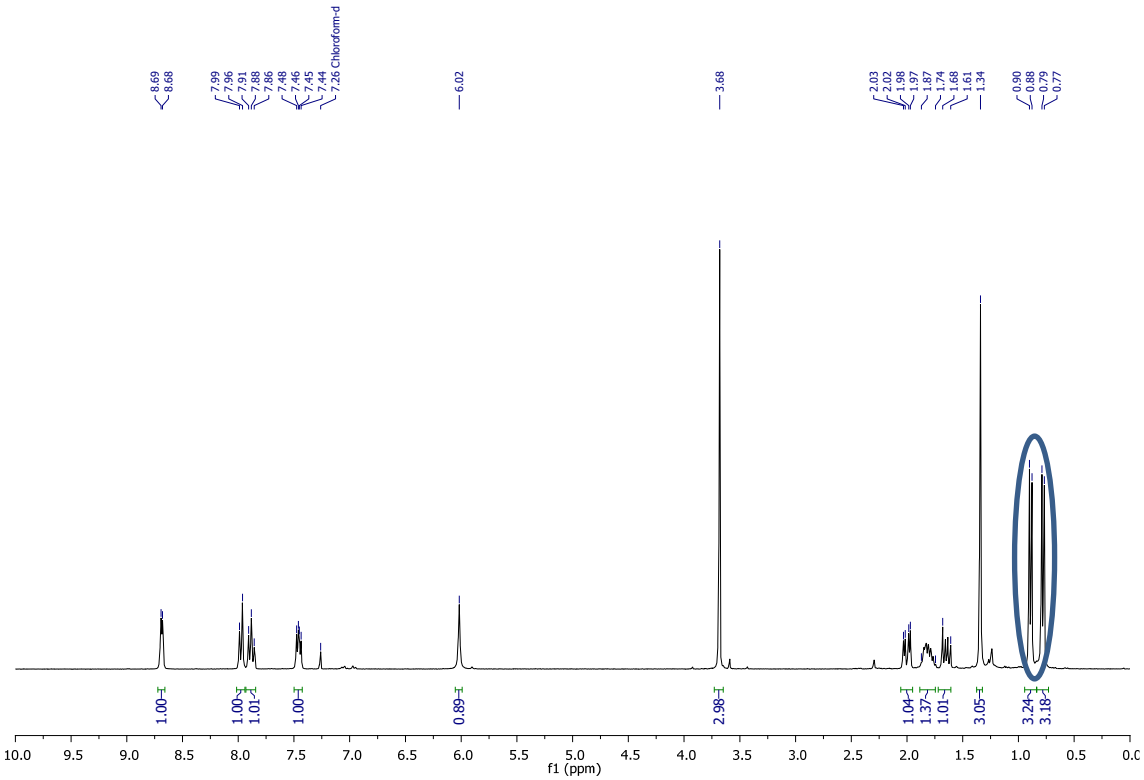
In the **VI$_{di}$-D** spectra, the integration of the signals corresponded to the benzylic H, the multiplets at 2.67-2.64, 2.62-2.52 and 2.43-2.38 ppm were 1.32, 2.40 and 1.31, respectively, instead of 1.17, 2.41 and 1.29 (2% > H/D scrambling).

The signals of the other H presented in the molecule remained unaltered, without H/D scrambling in any other position.

## Spectra of II and II-D

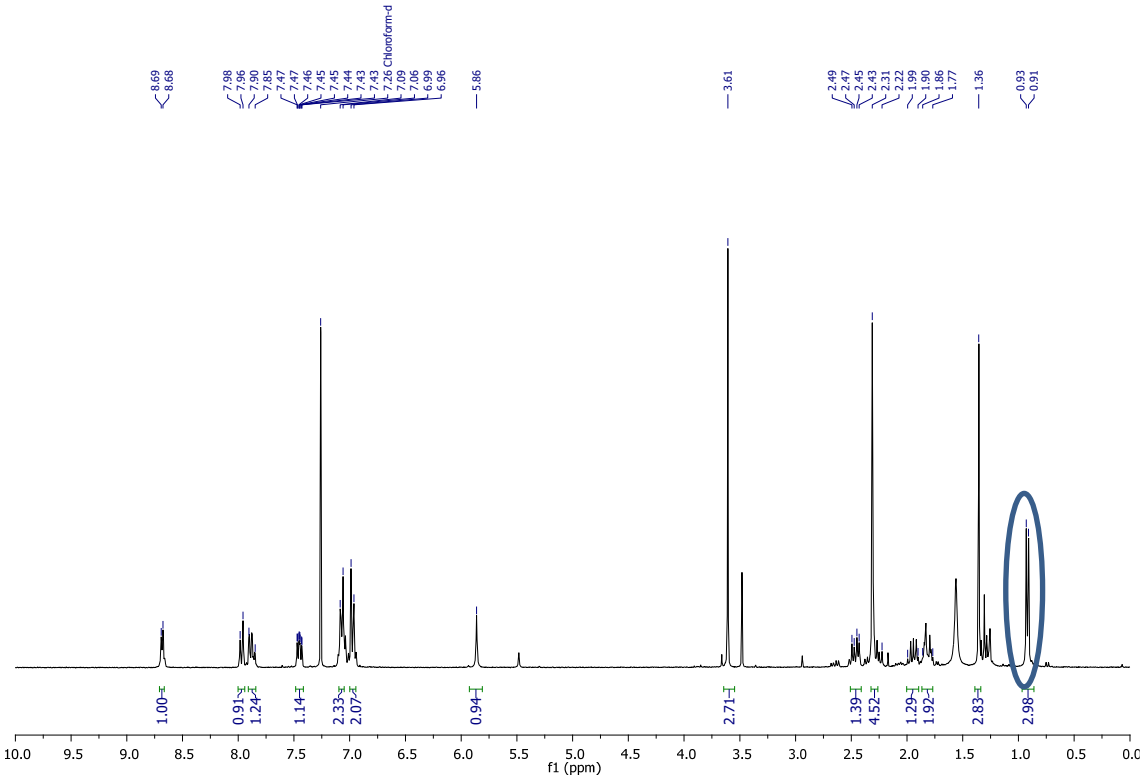
$^1$H NMR ($CDCl_3$, 300 MHz)

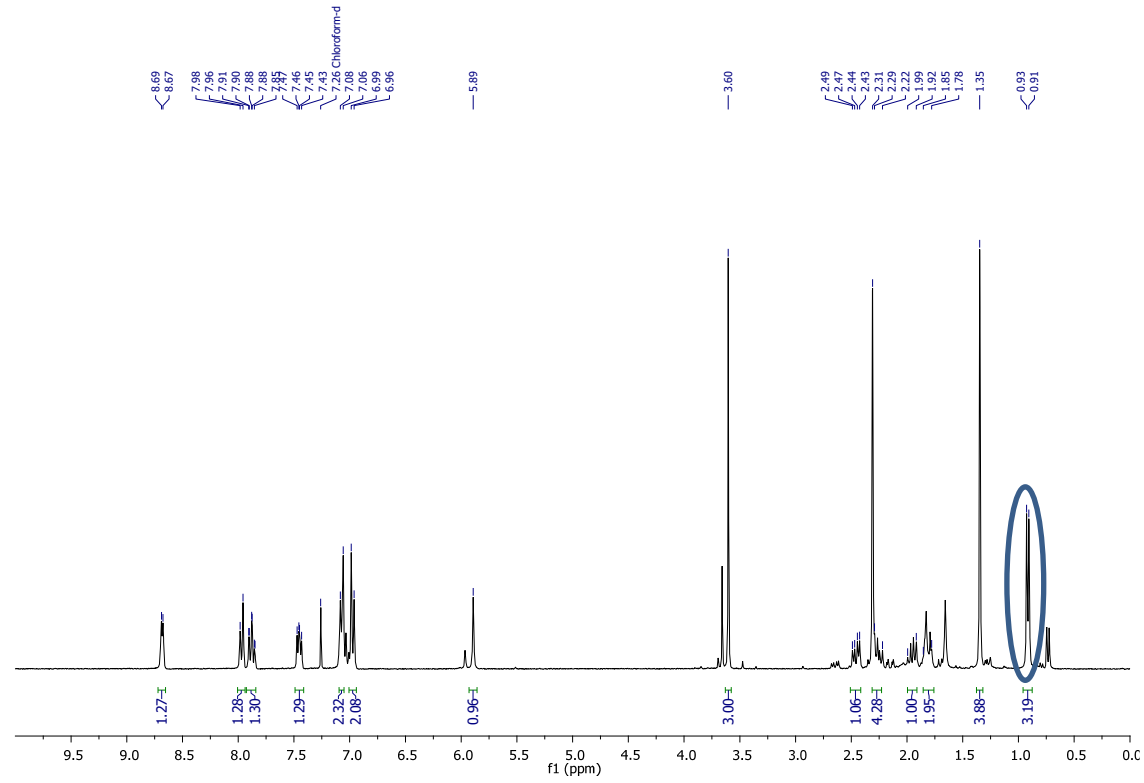


## Spectra of $VI_{mo}$ and $VI_{mo}$-D

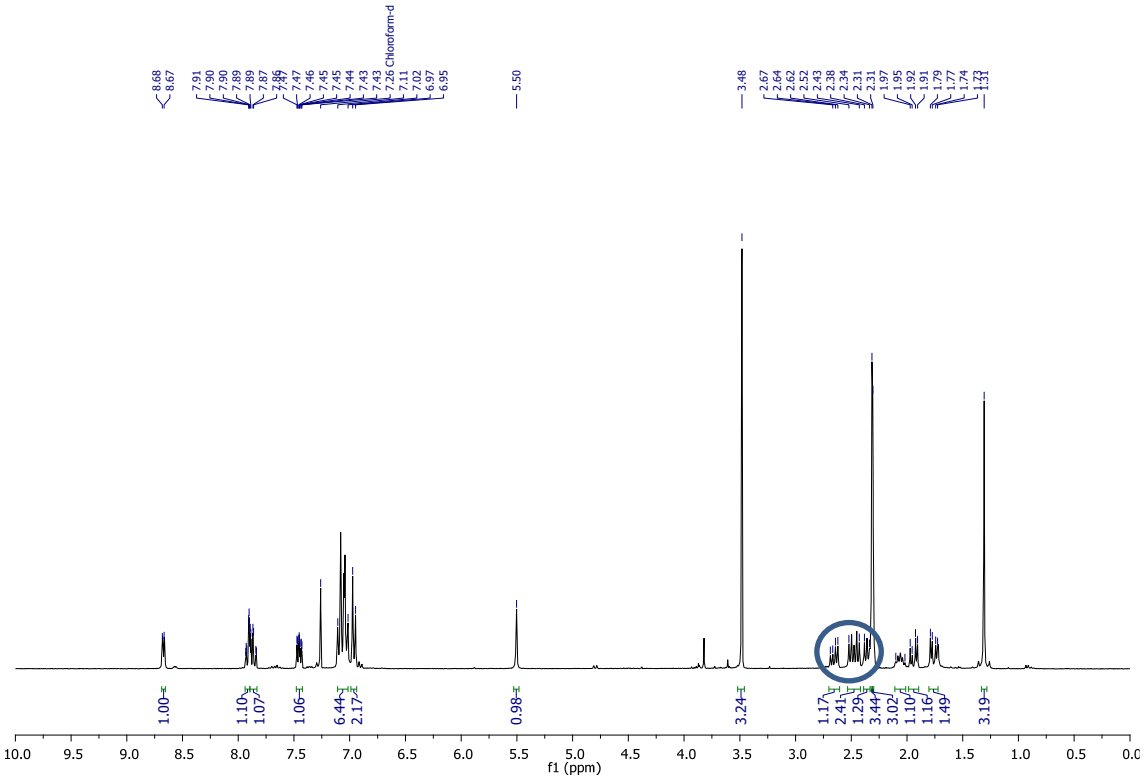
$^1H$ NMR ($CDCl_3$, 300 MHz)

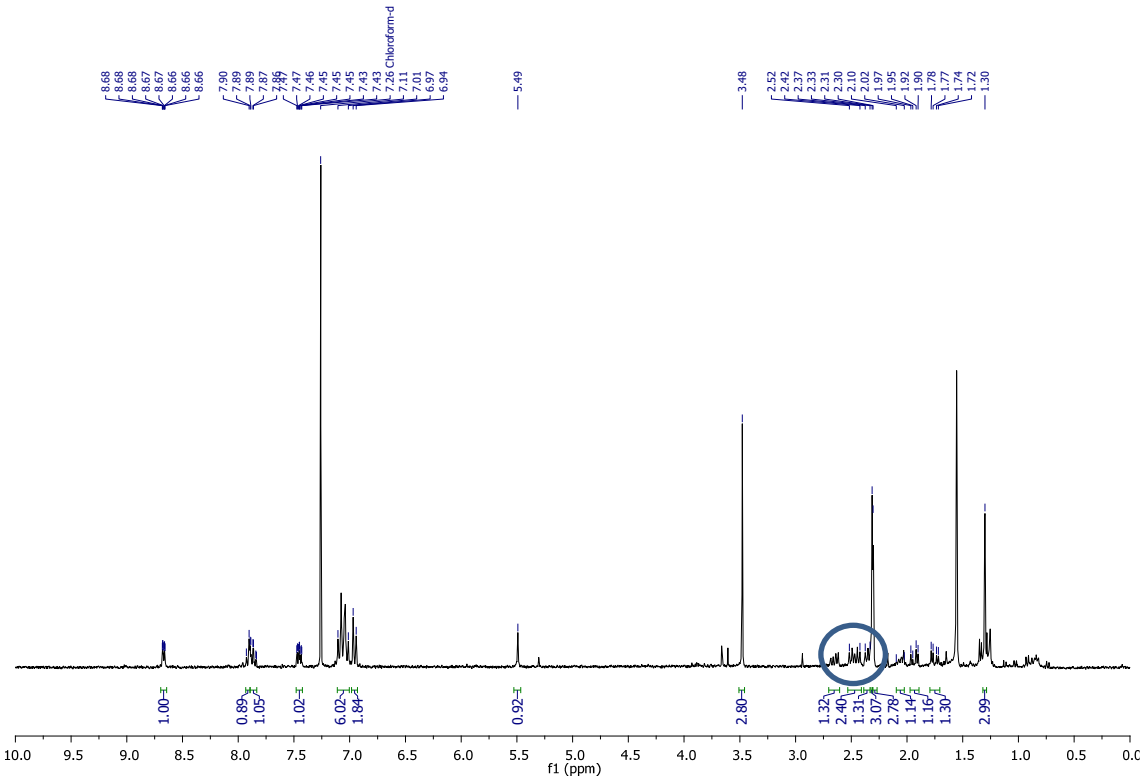


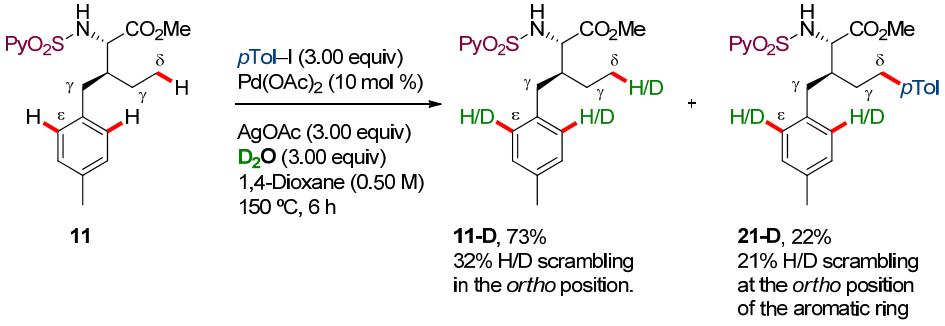
## Spectra of $VI_{di}$ and $VI_{di}$-D

$^1H$ NMR ($CDCl_3$, 300 MHz)



### 5.2.2. Arylation reaction of 11 using $D_2O$ as deuterium source




**General procedure.** An oven-dried, argon flushed, pressure tube was charged with $Pd(OAc)_2$ (4.48 mg, 0.02 mmol, 0.10 equiv), AgOAc (100 mg, 0.60 mmol, 3.00 equiv), 4-iodotoluene (131 mg, 0.60 mmol, 3.00 equiv) and (2*S**,3*S**)-methyl 3-(4-methylbenzyl)-2-(pyridine-2-sulfonamido)pentanoate **11** (75.3 mg, 0.20 mmol, 1.00 equiv). Then, 1,4-dioxane (0.40 mL) and $D_2O$ (12.0 µL, 0.60 mmol, 3.00 equiv) were added *via* syringe. The sealed tube was sealed with a screw cap and finally placed in an oil bath at 150 °C for 6 h. The reaction mixture was then removed from the oil bath and allowed to cool to room temperature. The mixture was then diluted with EtOAc, filtered through a short pad of Celite® and concentrated *in vacuo*. The residue was purified by flash column chromatography (cyclohexane:EtOAc 3:1) to afford **11-D** in 70% yield (52.9 mg) and **21-D** in 23% yield (21.4 mg).

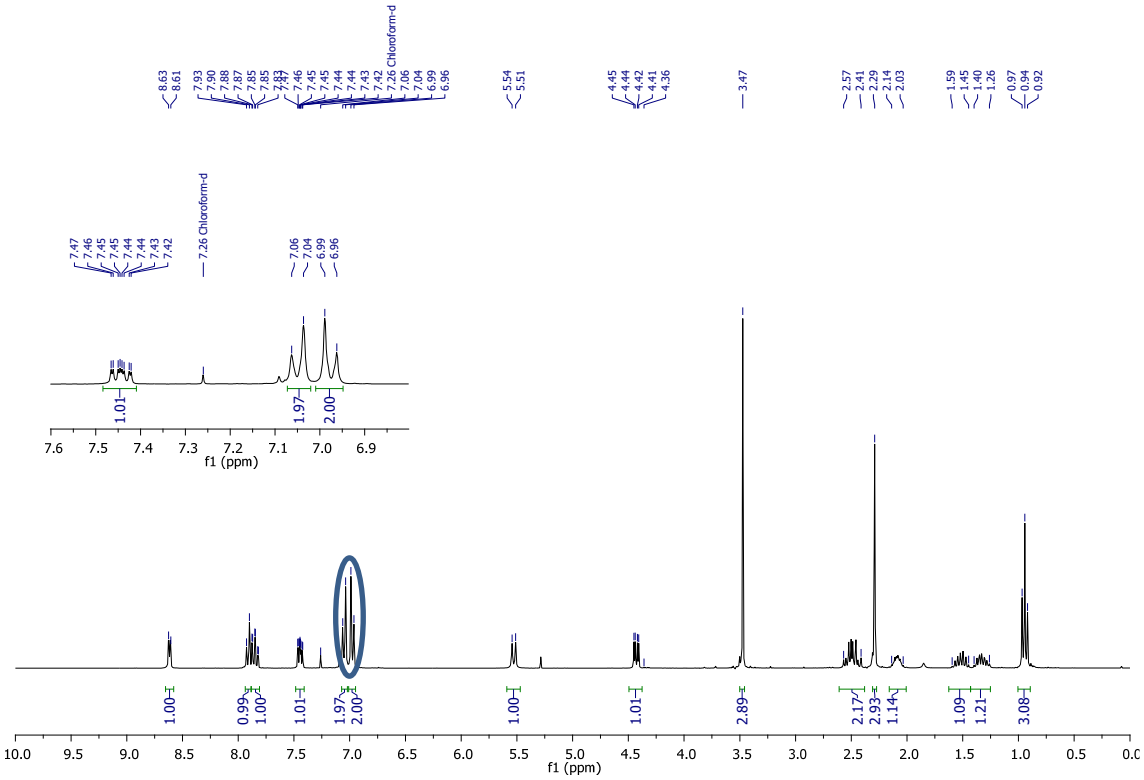
In the **11-D** spectra, the integration of the doublet at 6.99 - 6.97 ppm (corresponding to the *o*-phenyl positions) was 1.35 instead of 2.00 (32% H/D scrambling). The integration of the triplet at 0.97 - 0.92 ppm (corresponding to the free methyl group) was 3.11 instead of 3.08 ppm, which means that there is not H/D scrambling in delta position. The integration of the multiplet at 2.57 - 2.41 ppm was 2.18 instead of 2.29 ppm, which means that there is not H/D scrambling at γ-benzylic position. The integration of the multiplets at 1.59 - 1.45 and 1.40 - 1.26 ppm were 1.12 and 1.28 instead of 1.09 and 1.21 ppm respectively, which means that there is not H/D scrambling at γ-methylenic position.

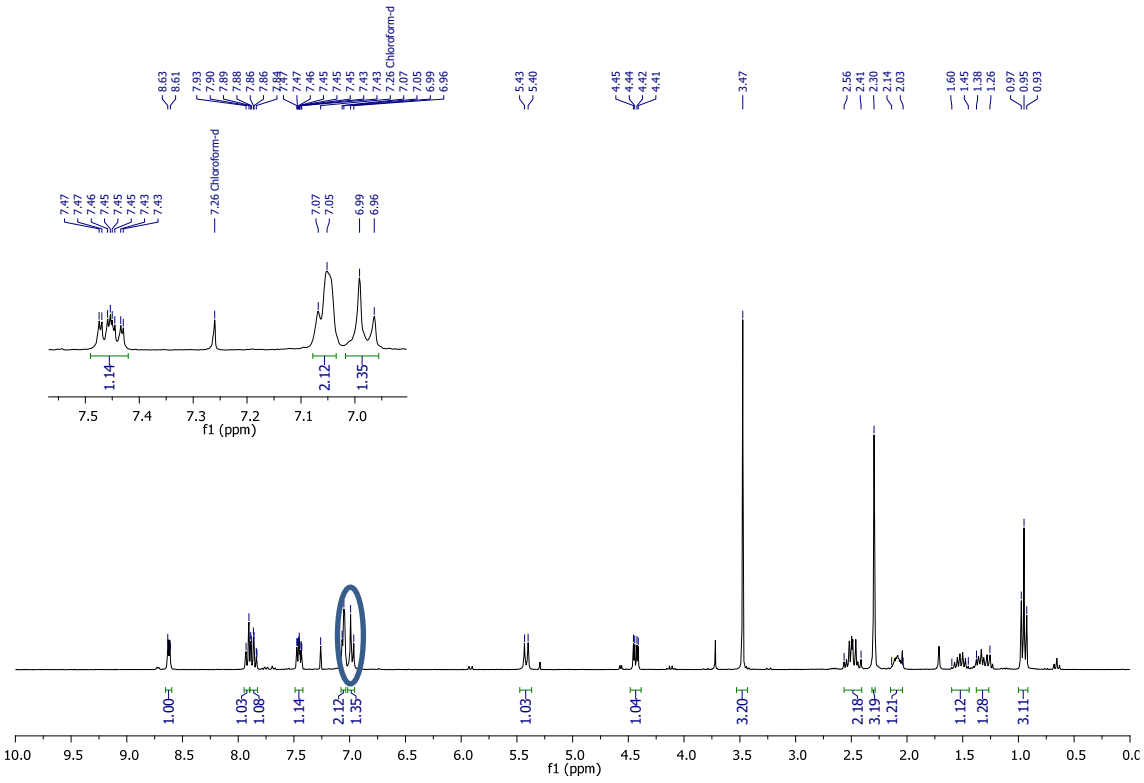
In the **21-D** spectra, deuteration at δ-methylene position was determined by the integration of the multiplet at 2.85-2.76 ppm. Its value was 1.02 in the spectra **21-D** instead of 1.15, resulting in not H/D scrambling at δ position. The integration of the multiplet at 2.60-2.46 ppm was 3.37 instead of 3.47 ppm, resulting in not H/D scrambling at γ-benzylic position. The integration of the doublet at 6.96-6.93 ppm was 1.63 instead of 2.20, which means that there is a 26% of H/D scrambling at *ortho*-phenyl positions.

The signals of the other H presented in the molecule remained unaltered, without H/D scrambling in any other position.

## Spectra of 11 and 11-D

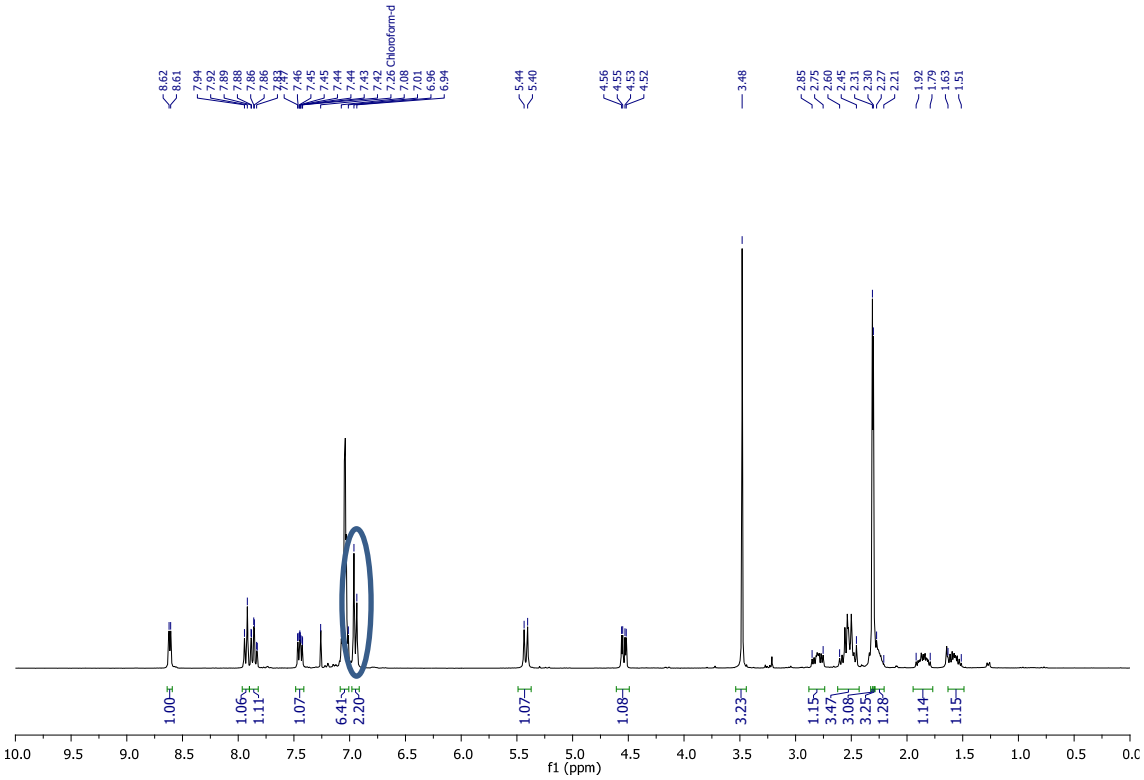
$^1$H NMR ($CDCl_3$, 300 MHz)

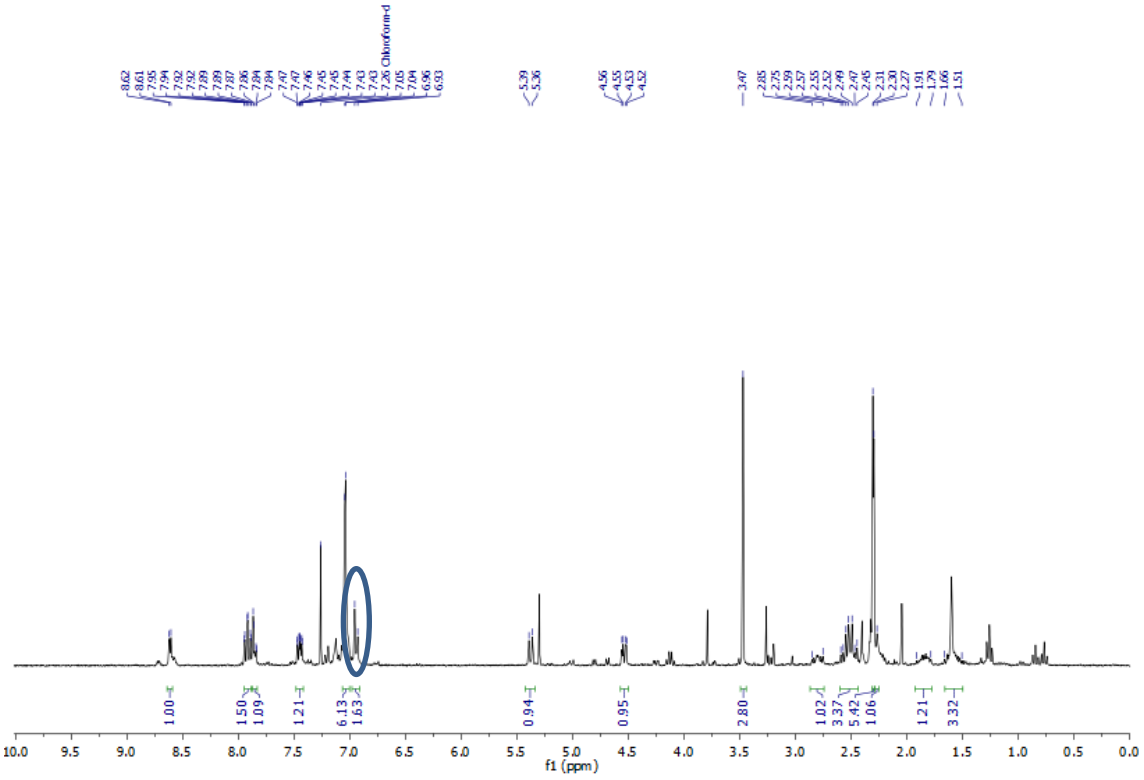


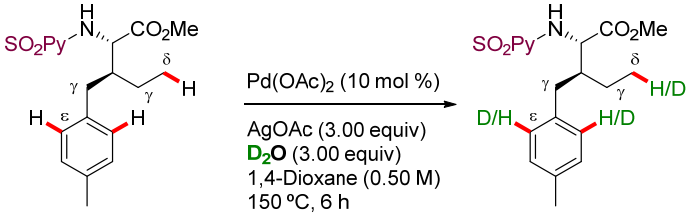
**Spectra of 21 and 21-D**

$^1$H NMR ($CDCl_3$, 300 MHz)



### 5.2.3. H/D Scrambling experiment in the absence of iodoarene




**11**

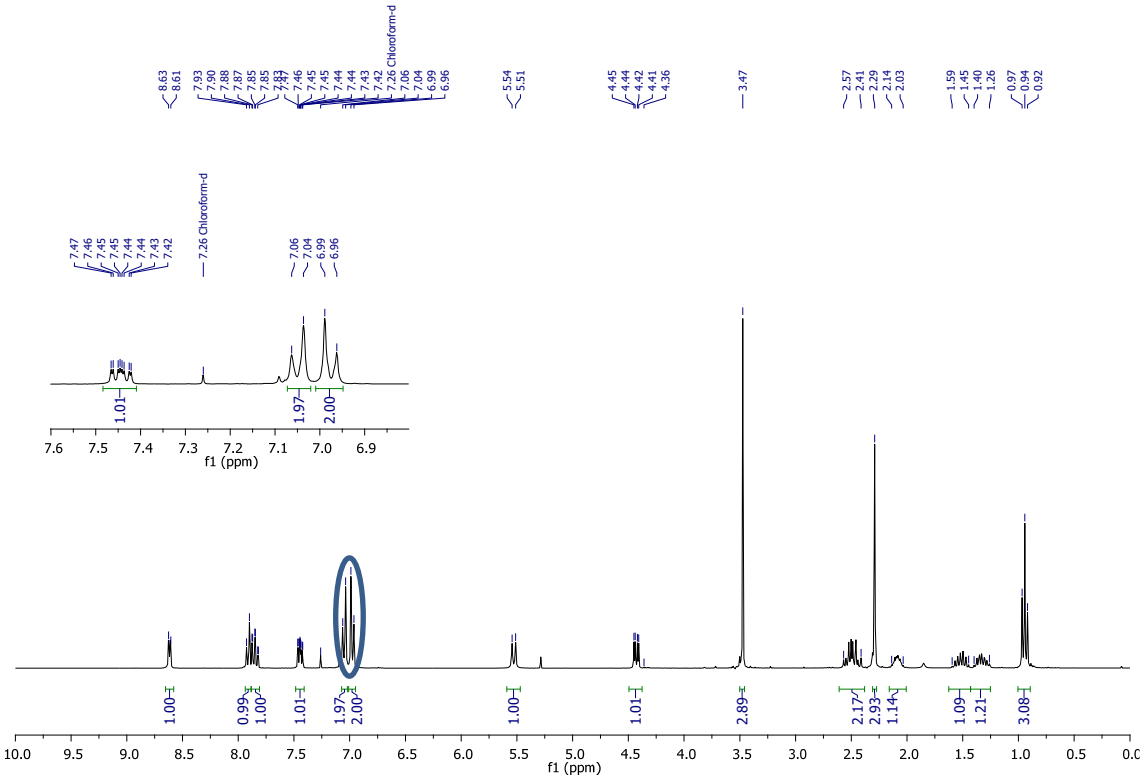
**11-D**, 99%
60% H/D scrambling in the *ortho* position.

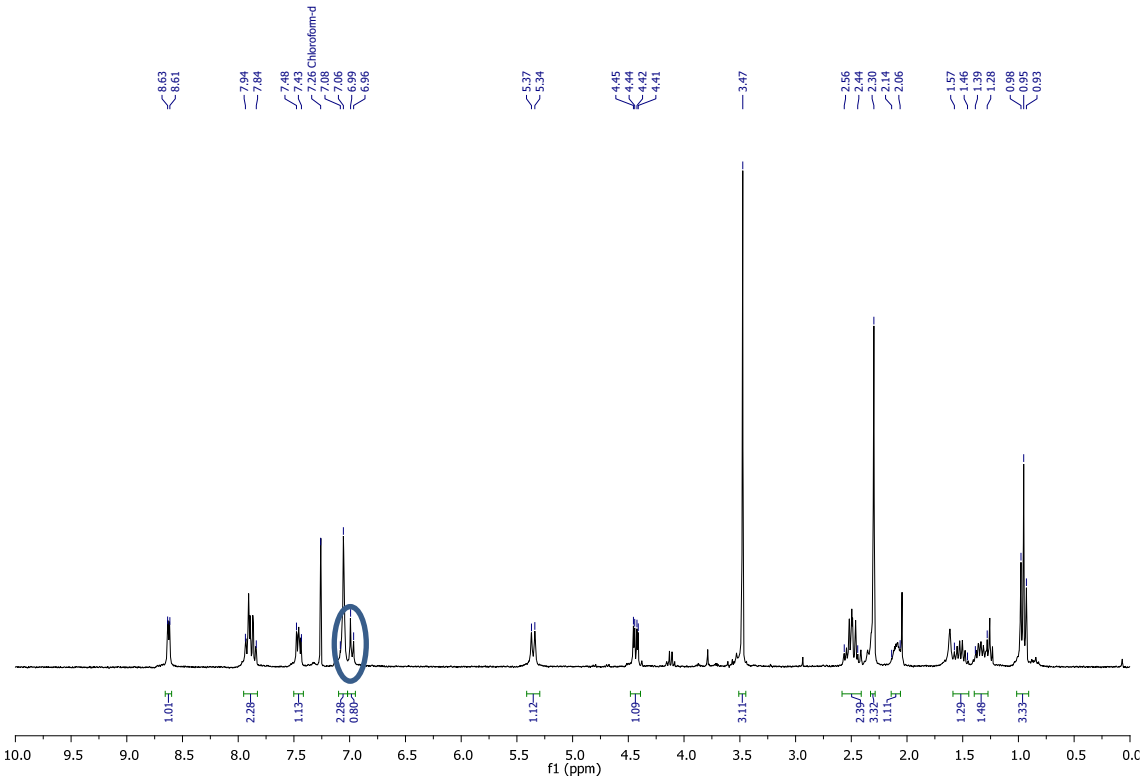
**General procedure.** An oven-dried, argon flushed, pressure tube was charged with $Pd(OAc)_2$ (4.48 mg, 0.02 mmol, 0.10 equiv), AgOAc (100 mg, 0.60 mmol, 3.00 equiv) and (2*S**,3*S**)-methyl 3-(4-methylbenzyl)-2-(pyridine-2-sulfonamido)pentanoate **11** (75.3 mg, 0.20 mmol, 1.00 equiv). Then, 1,4-dioxane (0.40 mL) and $D_2O$ (12.0 µL, 0.60 mmol, 3.00 equiv) were added *via* syringe. The sealed tube was sealed with a screw cap and finally placed in an oil bath at 150 °C for 6 h. The reaction mixture was then removed from the oil bath and allowed to cool to room temperature. The mixture was then diluted with EtOAc, filtered through a short pad of Celite® and concentrated *in vacuo*. The residue was purified by flash column chromatography (cyclohexane:EtOAc 3:1) to afford **11-D** in 99% yield (74.9 mg).

In the **11-D** spectra, the integration of the doublet at 6.99 - 6.97 ppm (corresponding to the *o*-phenyl positions) was 0.80 instead of 2.00 (60% H/D scrambling). The integration of the triplet at 0.97 - 0.92 ppm (corresponding to the free methyl group) was 3.33 instead of 3.08 ppm, which means that there is not H/D scrambling in delta position. The integration of the multiplet at 2.57 - 2.41 ppm was 2.39 instead of 2.29 ppm, which means that there is not H/D scrambling at γ-benzylic position. The integration of the multiplets at 1.59 - 1.45 and 1.40 - 1.26 ppm were 1.29 and 1.43 instead of 1.09 and 1.21 ppm respectively, which means that there is not H/D scrambling at γ-methylenic position.

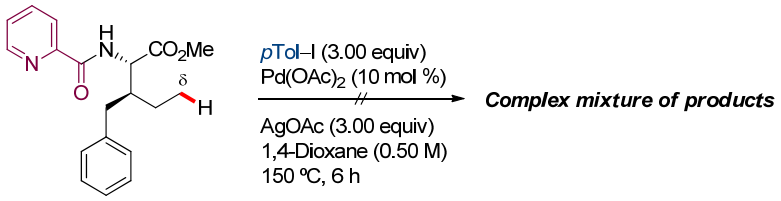
## Spectra of 11 and 11-D

$^1$H NMR ($CDCl_3$, 300 MHz)



### 5.3. Arylation reaction of compound 12a



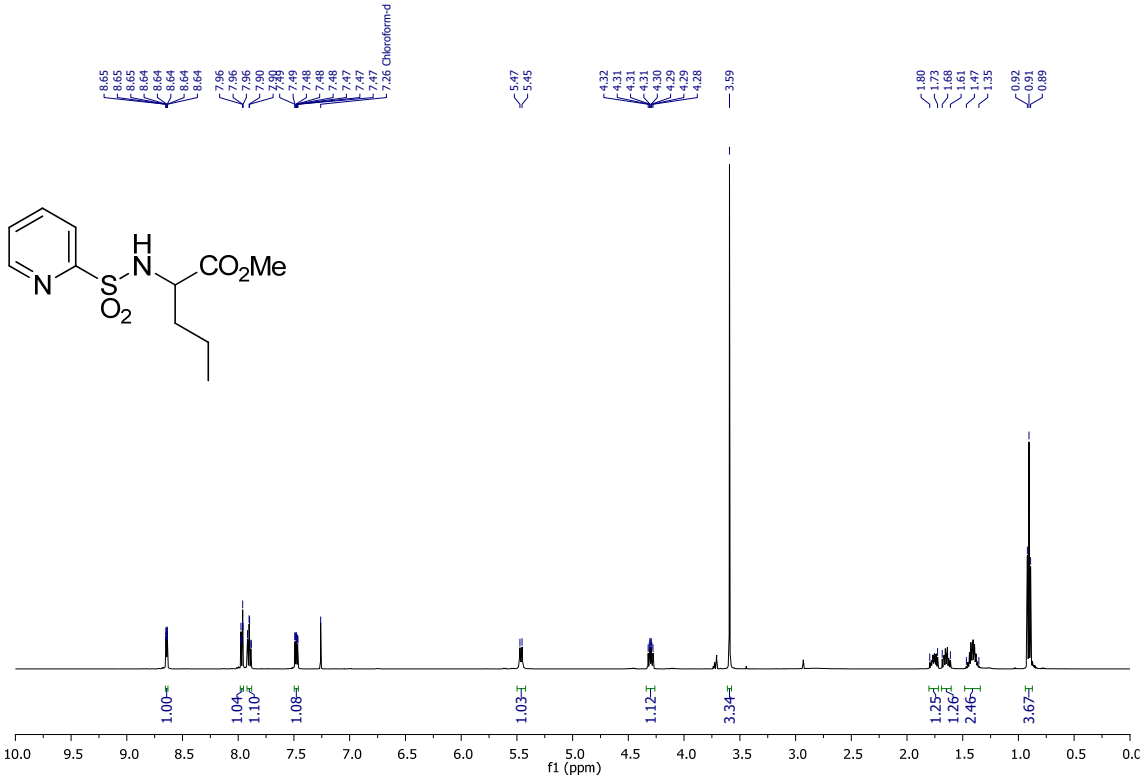

**12a**

**General procedure.** An oven-dried, argon flushed, pressure tube was charged with $Pd(OAc)_2$ (4.48 mg, 0.02 mmol, 0.10 equiv), AgOAc (100 mg, 0.60 mmol, 3.00 equiv), 4-iodotoluene (131 mg, 0.60 mmol, 3.00 equiv) and (2*S**,3*S**)-methyl 3-(4-benzyl)-2-(picolinamido)pentanoate **12a** (68.0 mg, 0.20 mmol, 1.00 equiv). Then, 1,4-dioxane (0.40 mL) was added *via* syringe. The sealed tube was sealed with a screw cap and finally placed in an oil bath at 150 °C for 6 h. The reaction mixture was then removed from the oil bath and allowed to cool to room temperature. The mixture was then diluted with EtOAc, filtered through a short pad of Celite® and concentrated *in vacuo*. The residue was analyzed by $^1$H NMR and a complex mixture of products was observed in the spectra. Any attempt of product isolation was unsuccessful.

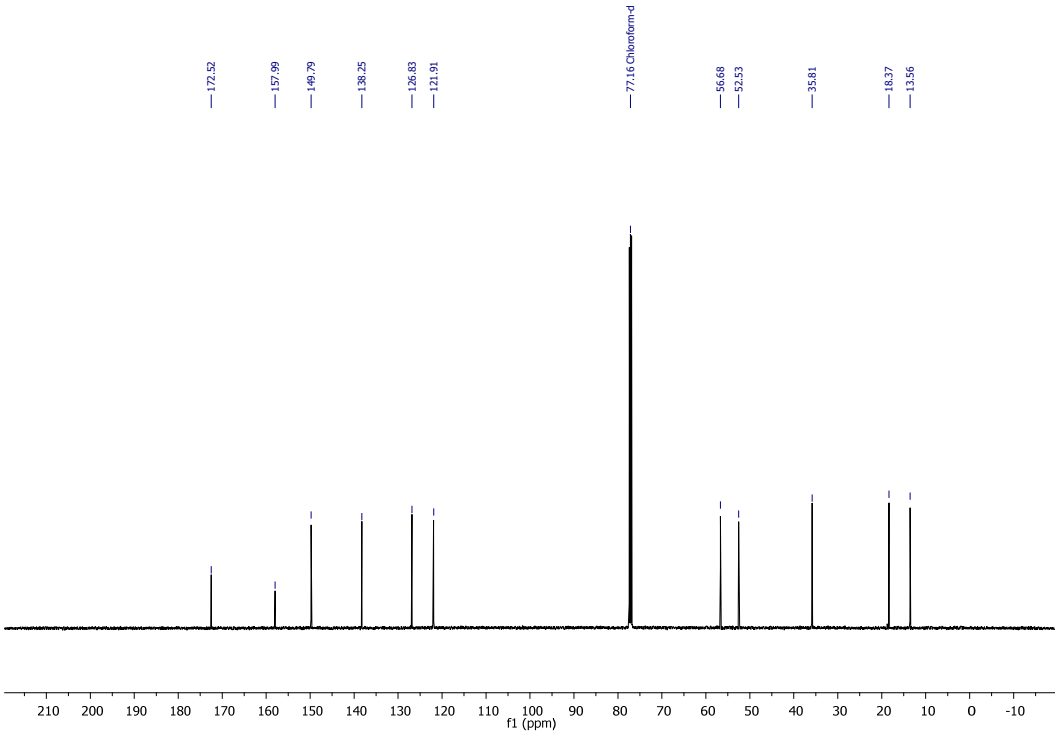
## 6. NMR Spectra

### (*rac*)-Methyl 2-(pyridine-2-sulfonamido)pentanoate (8)

$^{1}$H NMR ($CDCl_3$, 500 MHz)

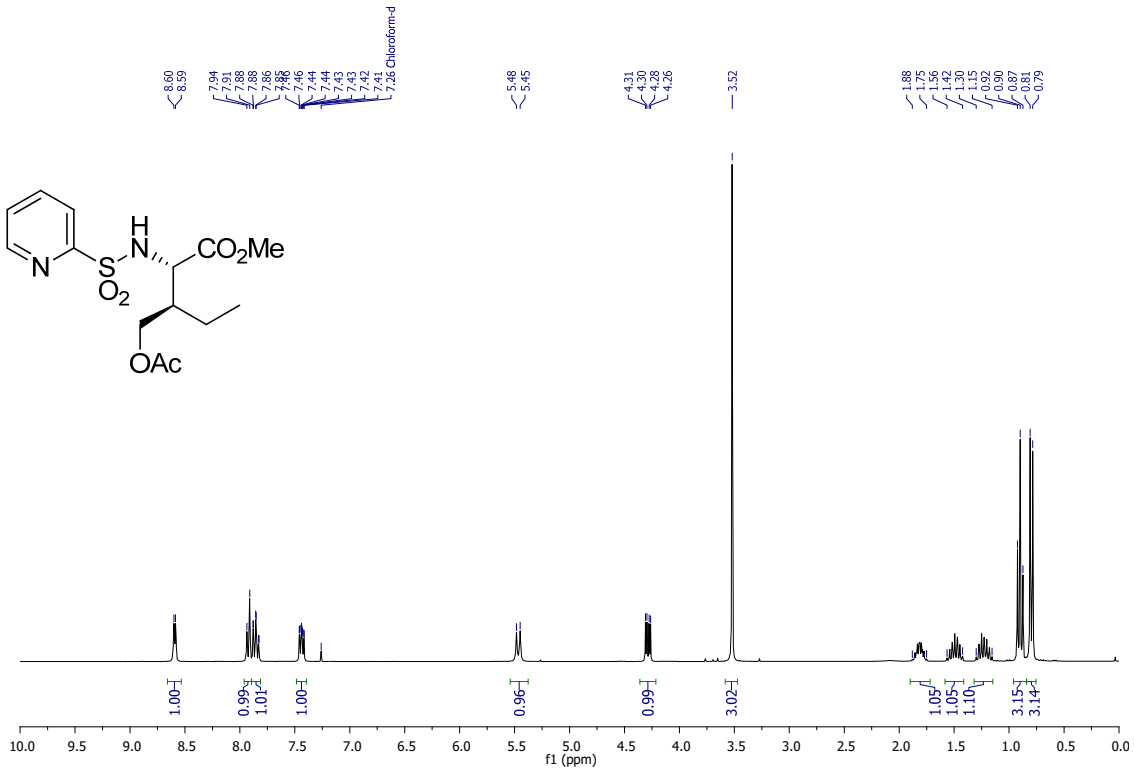



$^{13}$C NMR ($CDCl_3$, 126 MHz)

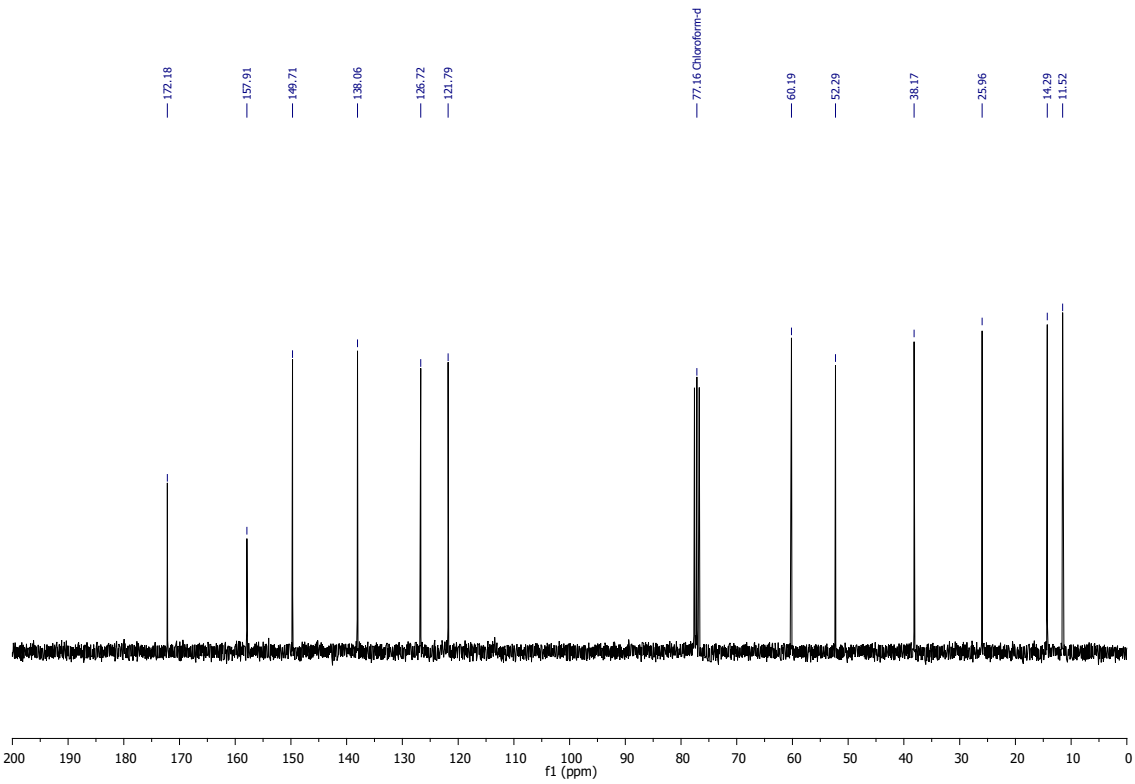


**(2*S**,3*R**)-Methyl 3-(acetoxymethyl)-2-(pyridine-2-sulfonamido)pentanoate (9)**

$^{1}$H NMR ($CDCl_3$, 300 MHz)

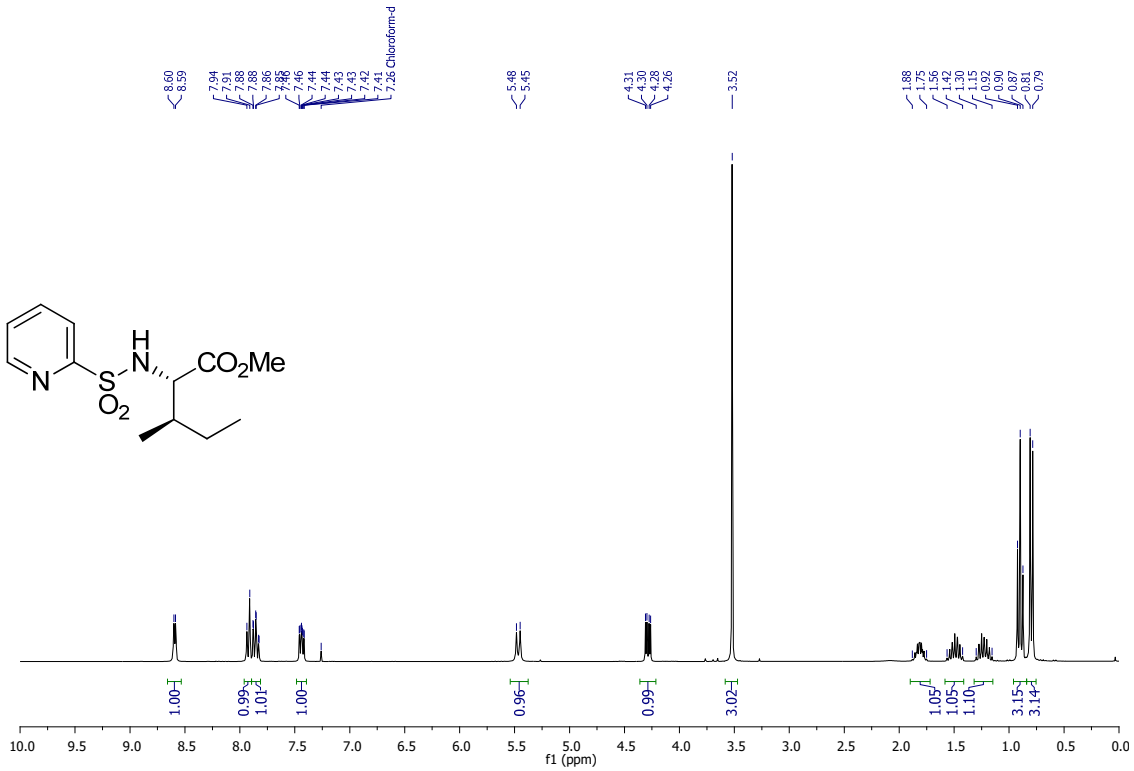



$^{13}$C NMR ($CDCl_3$, 75 MHz)

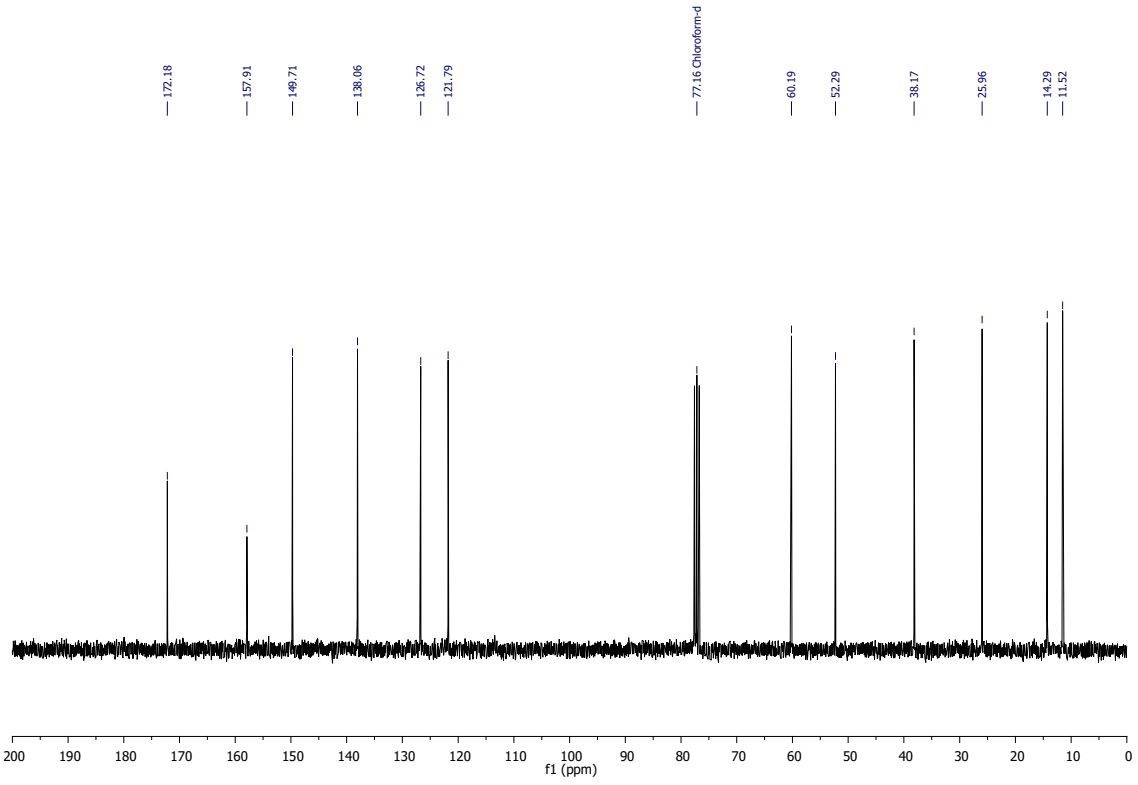


**(2*S**,3*R**)-Methyl 3-methyl-2-(pyridine-2-sulfonamido)pentanoate (XIX)**

$^{1}$H NMR ($CDCl_3$, 300 MHz)

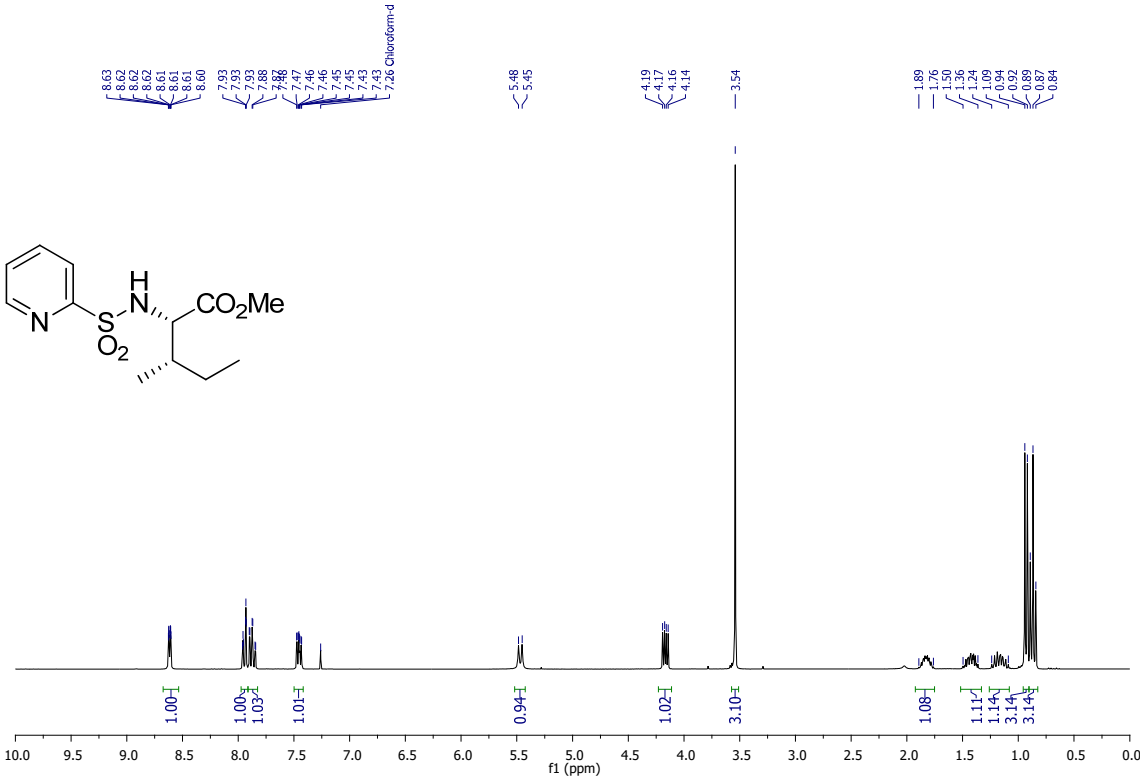



$^{13}$C NMR ($CDCl_3$, 75 MHz)

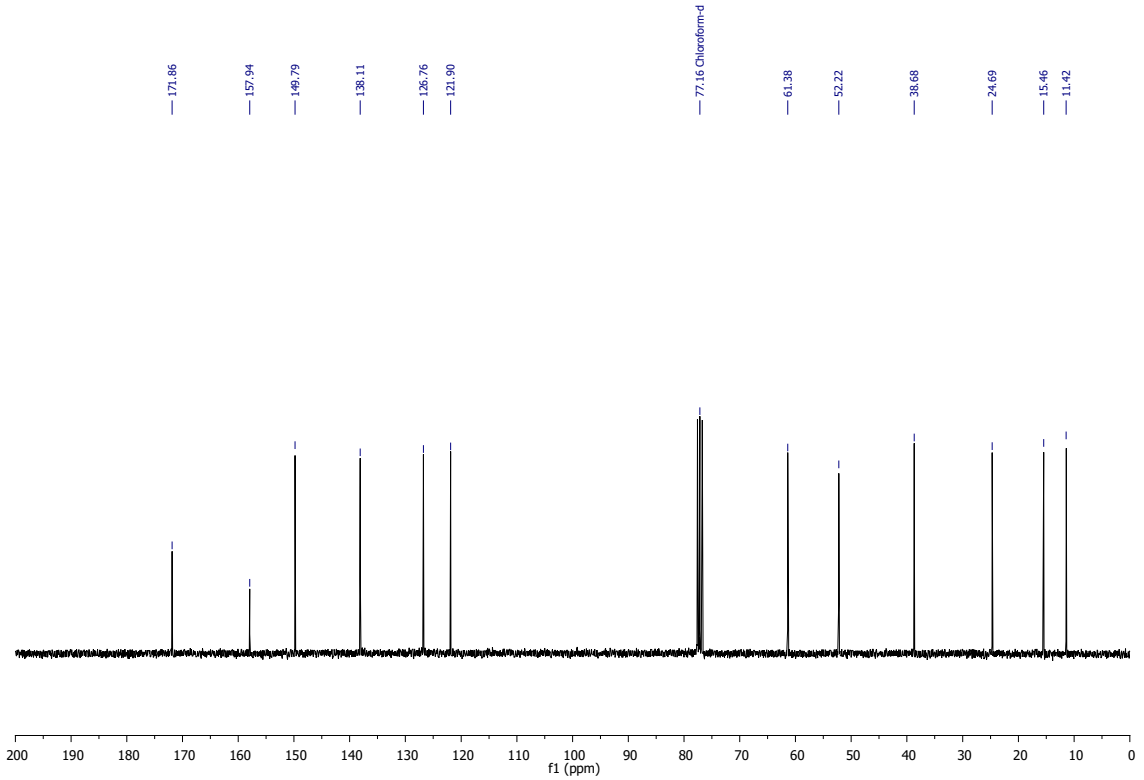


**(2*S*,3*S*)-Methyl 3-methyl-2-(pyridine-2-sulfonamido)pentanoate ((+)-XX)**

$^{1}$H NMR ($CDCl_3$, 300 MHz)

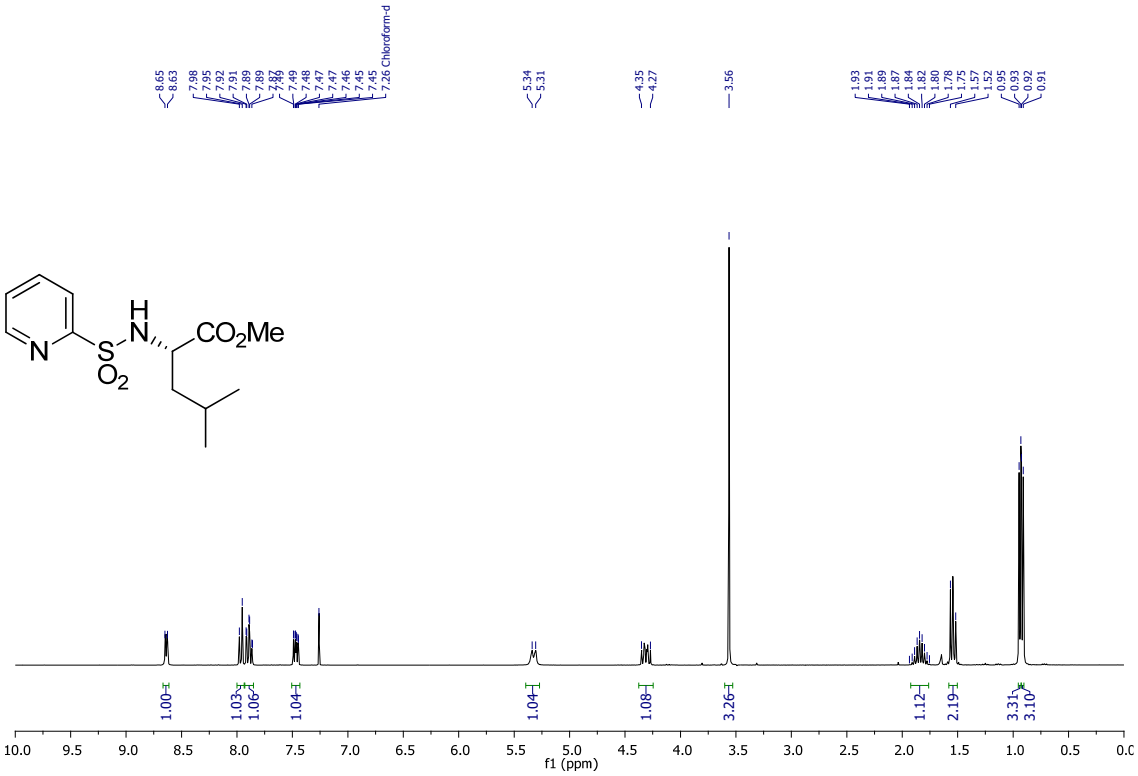



$^{13}$C NMR ($CDCl_3$, 75 MHz)

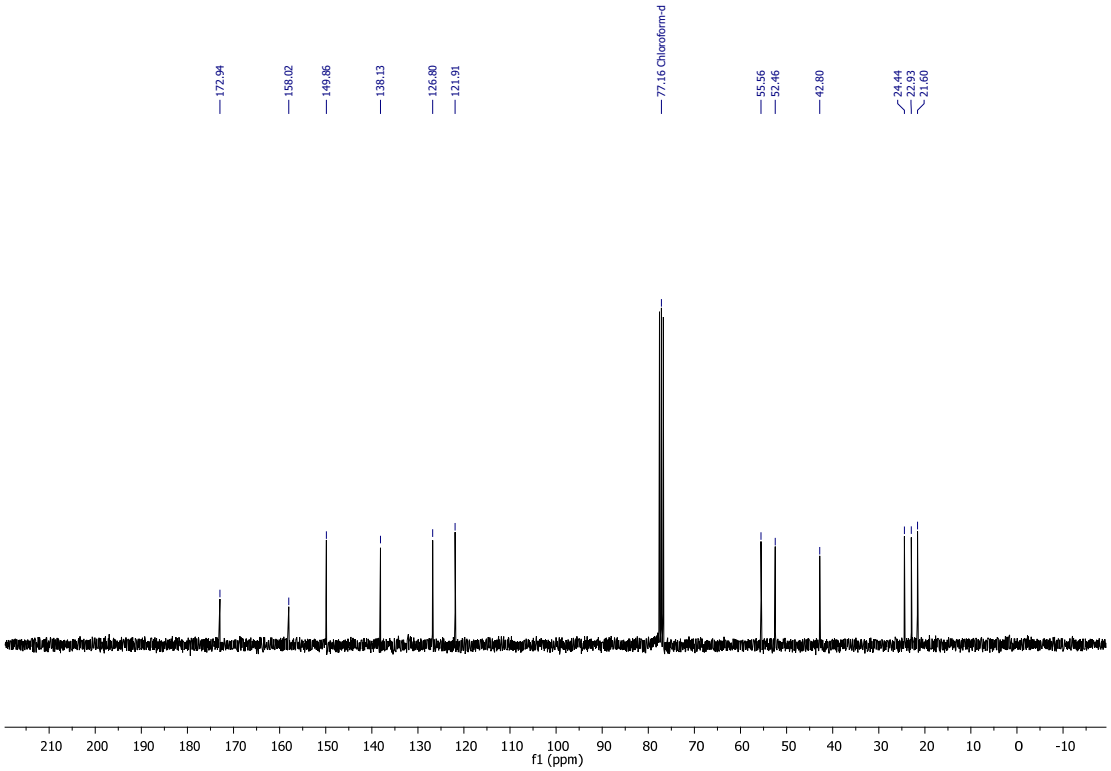


**(*S*)-Methyl 4-methyl-2-(pyridine-2-sulfonamido)pentanoate ((+)-I)**

$^{1}$H NMR ($CDCl_3$, 300 MHz)

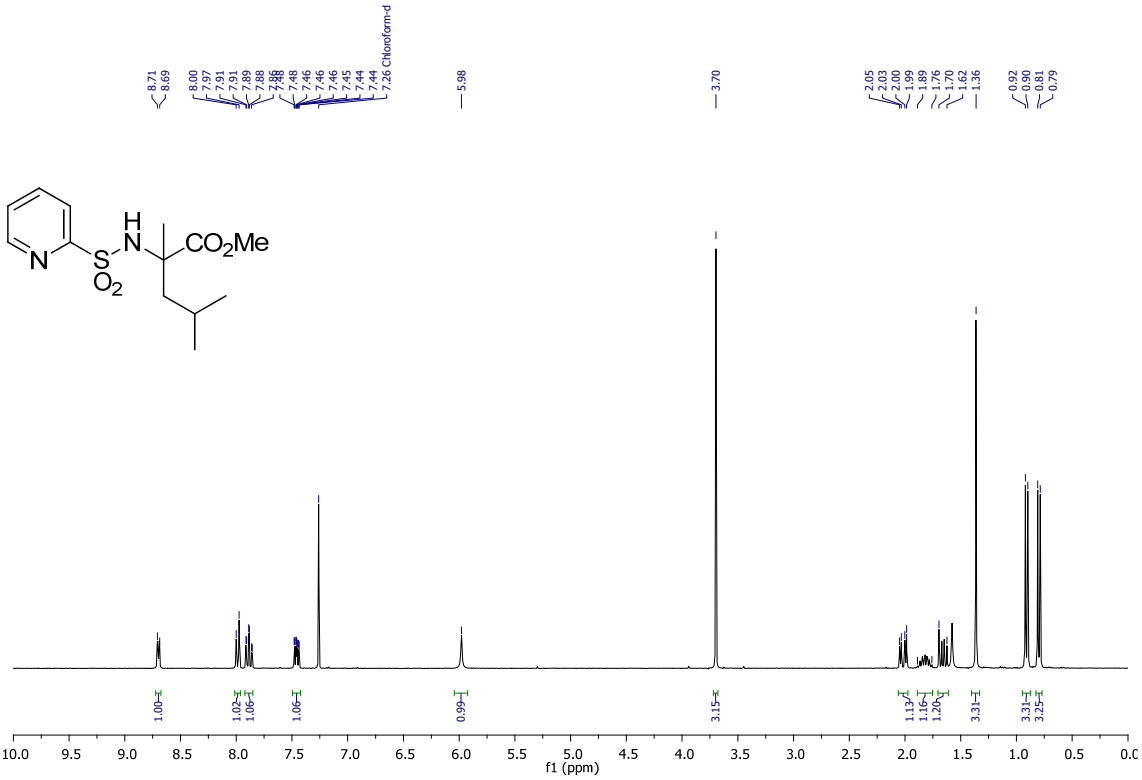



$^{13}$C NMR ($CDCl_3$, 75 MHz)

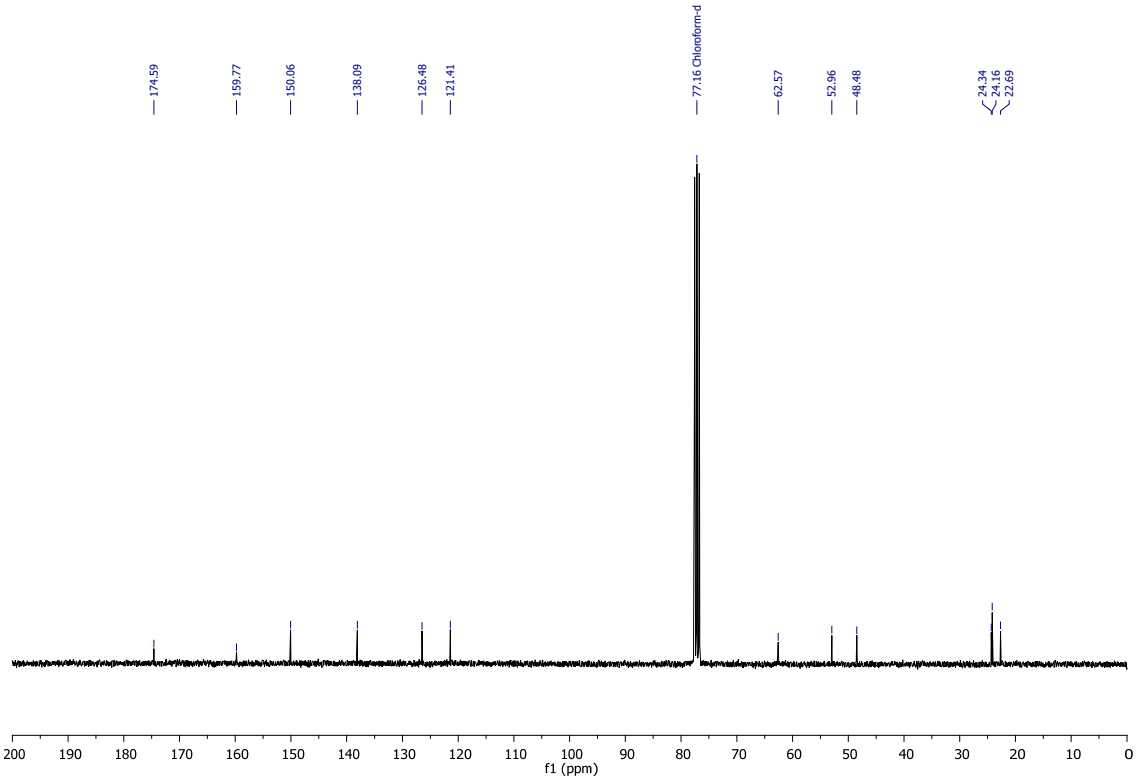


**(*rac*)-Methyl 2,4-dimethyl-2-(pyridine-2-sulfonamido)pentanoate (II)**

$^{1}$H NMR ($CDCl_3$, 300 MHz)

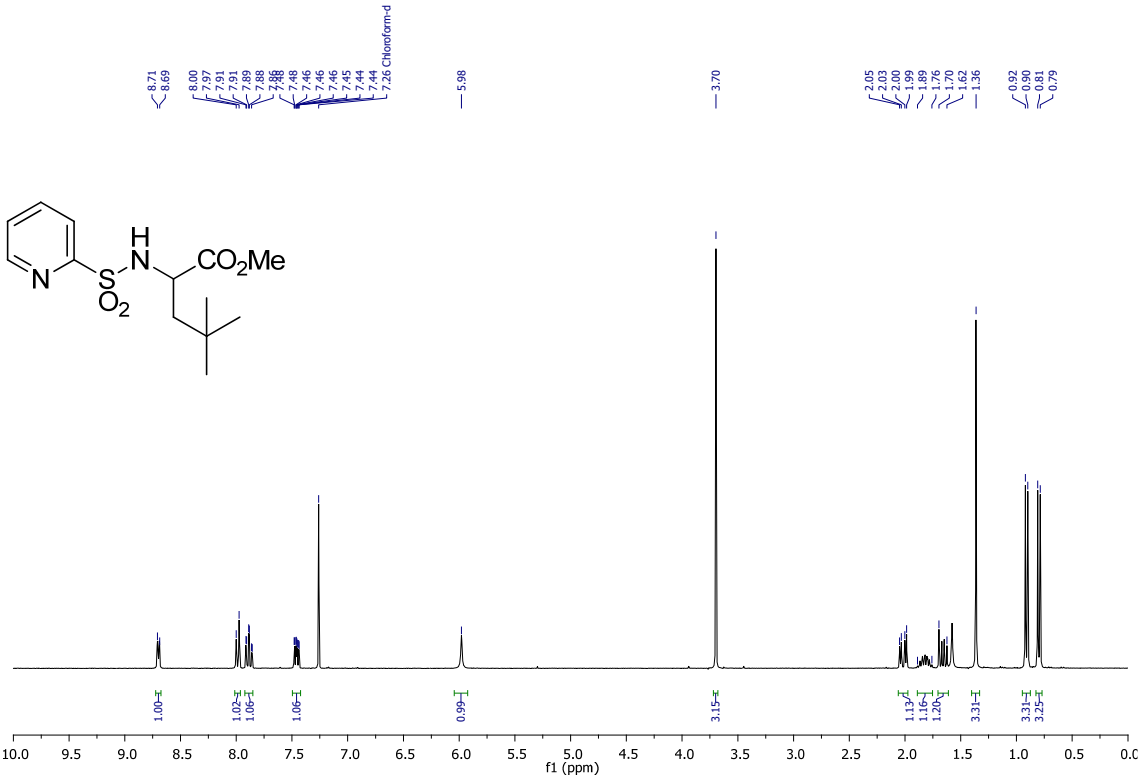



$^{13}$C NMR ($CDCl_3$, 75 MHz)

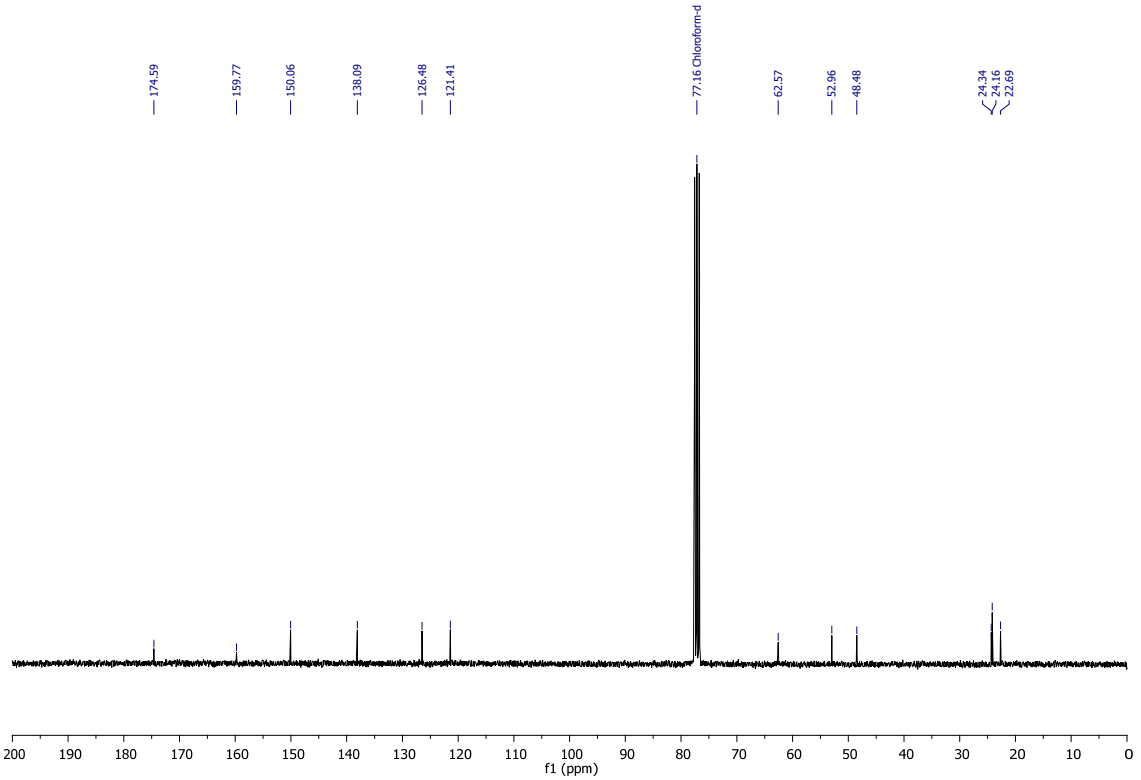


**(*rac*)-Methyl 4,4-dimethyl-2-(pyridine-2-sulfonamido)pentanoate (III)**

$^{1}$H NMR ($CDCl_3$, 300 MHz)

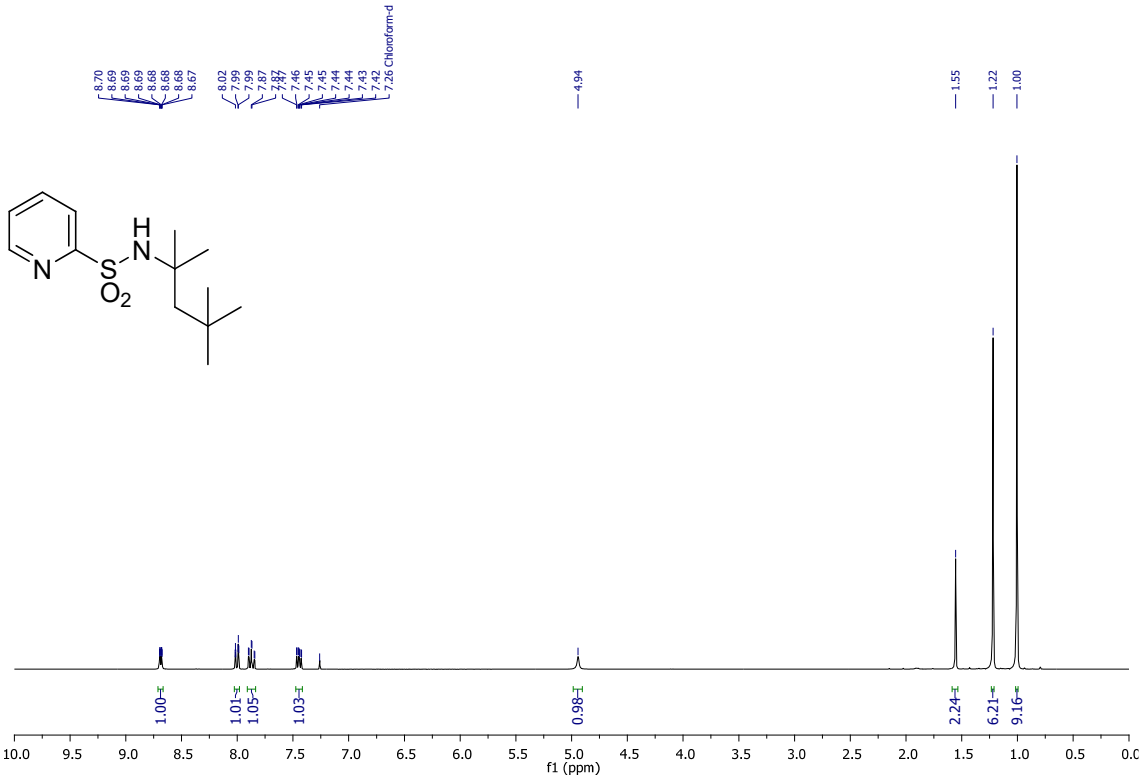



$^{13}$C NMR ($CDCl_3$, 75 MHz)

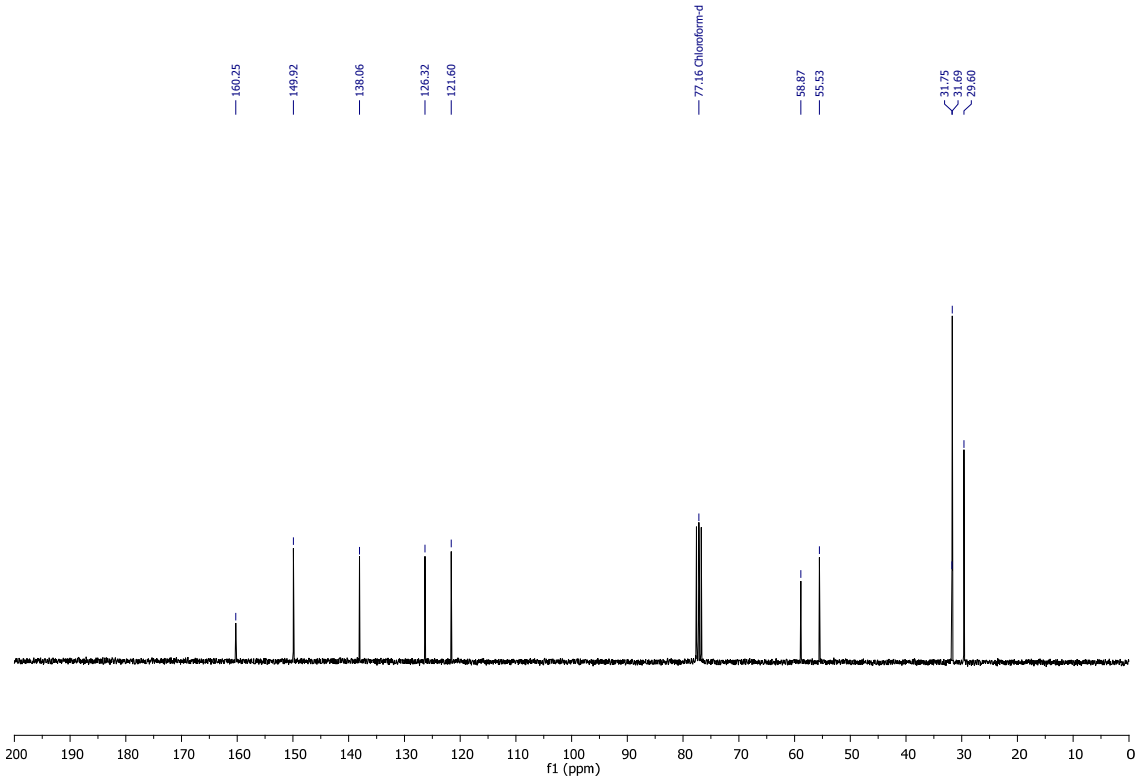


## *N*-(2,4,4-Trimethylpentan-2-yl)pyridine-2-sulfonamide (IV)

$^{1}$H NMR ($CDCl_3$, 300 MHz)

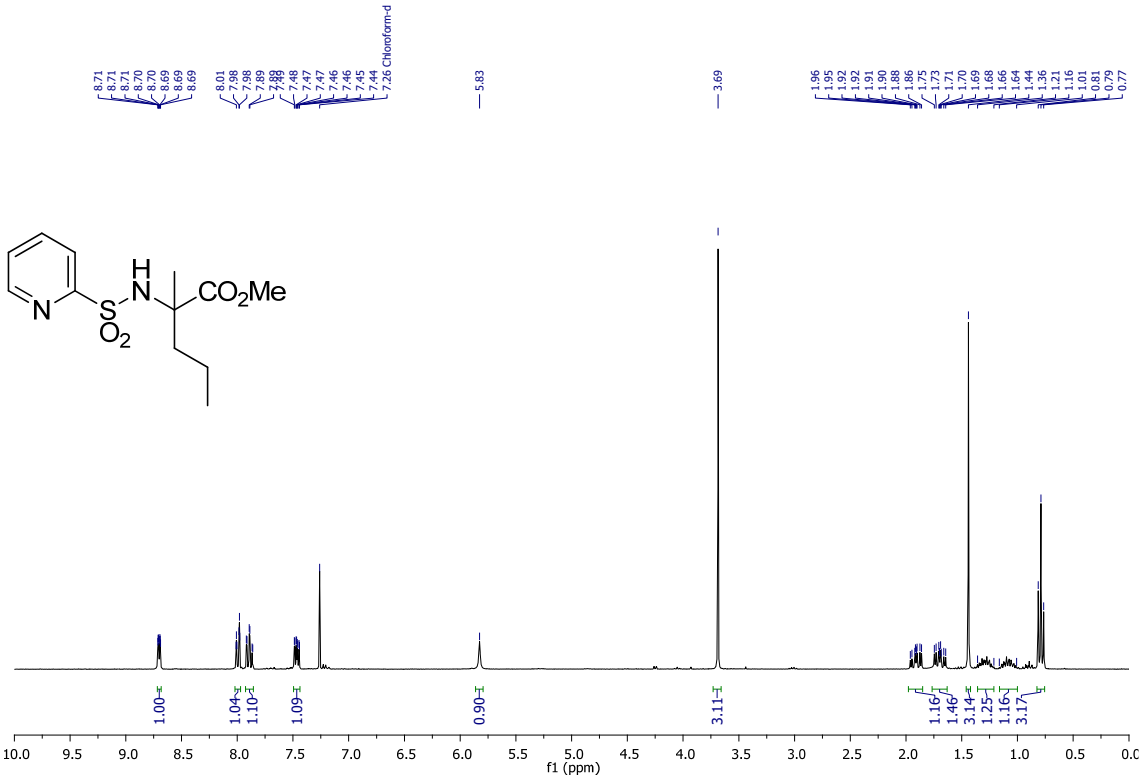



$^{13}$C NMR ($CDCl_3$, 75 MHz)

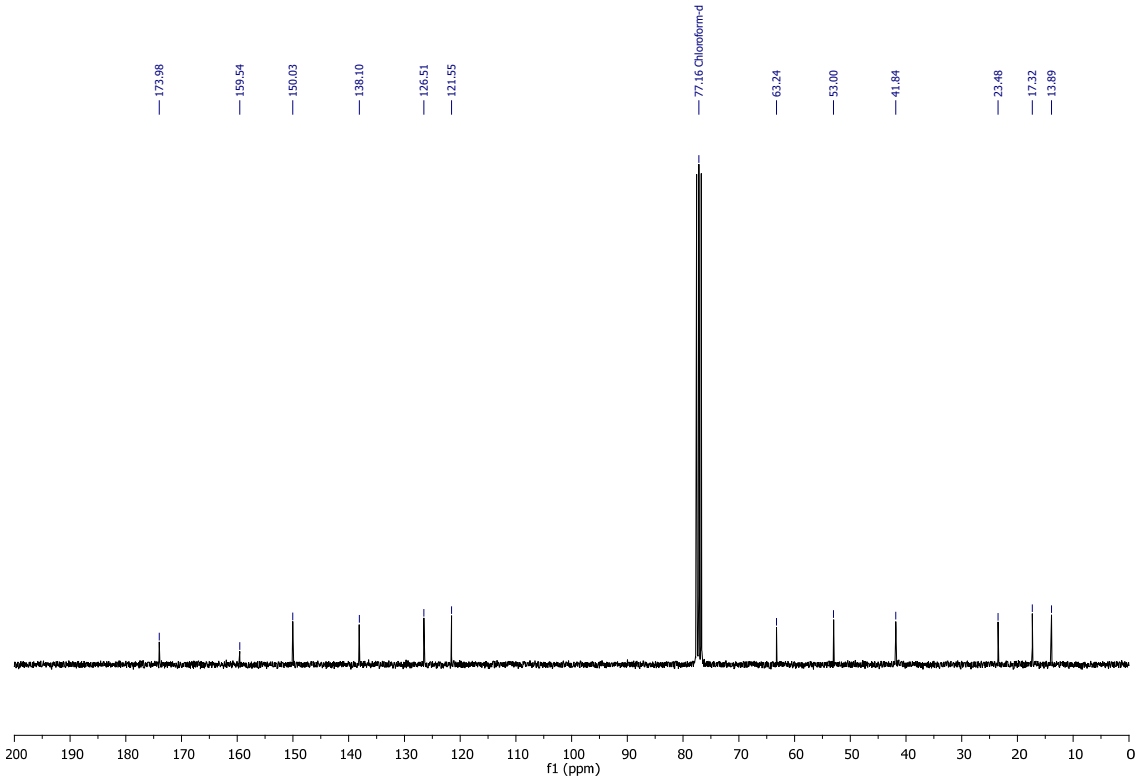


## (*rac*)-Methyl 2-methyl-2-(pyridine-2-sulfonamido)pentanoate (1b)

$^{1}$H NMR ($CDCl_3$, 300 MHz)

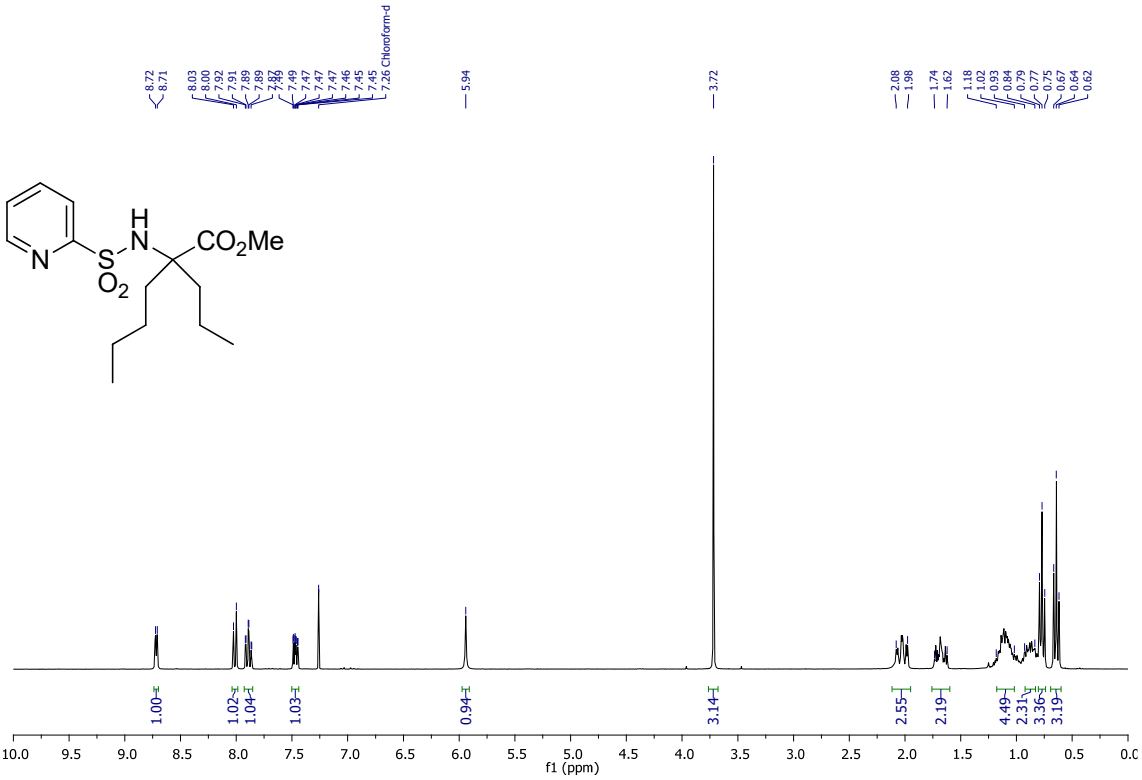



$^{13}$C NMR ($CDCl_3$, 75 MHz)

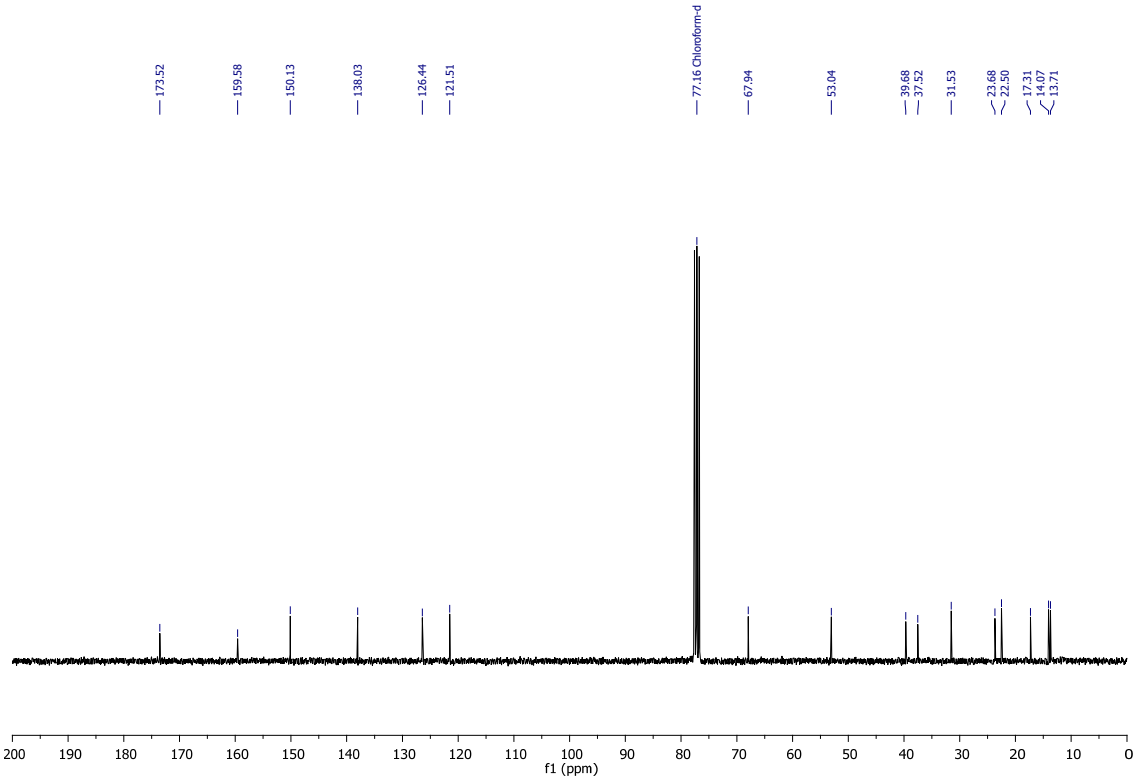


## (*rac*)-Methyl 2-butyl-2-(pyridine-2-sulfonamido)pentanoate (5)

$^1$H NMR ($CDCl_3$, 300 MHz)

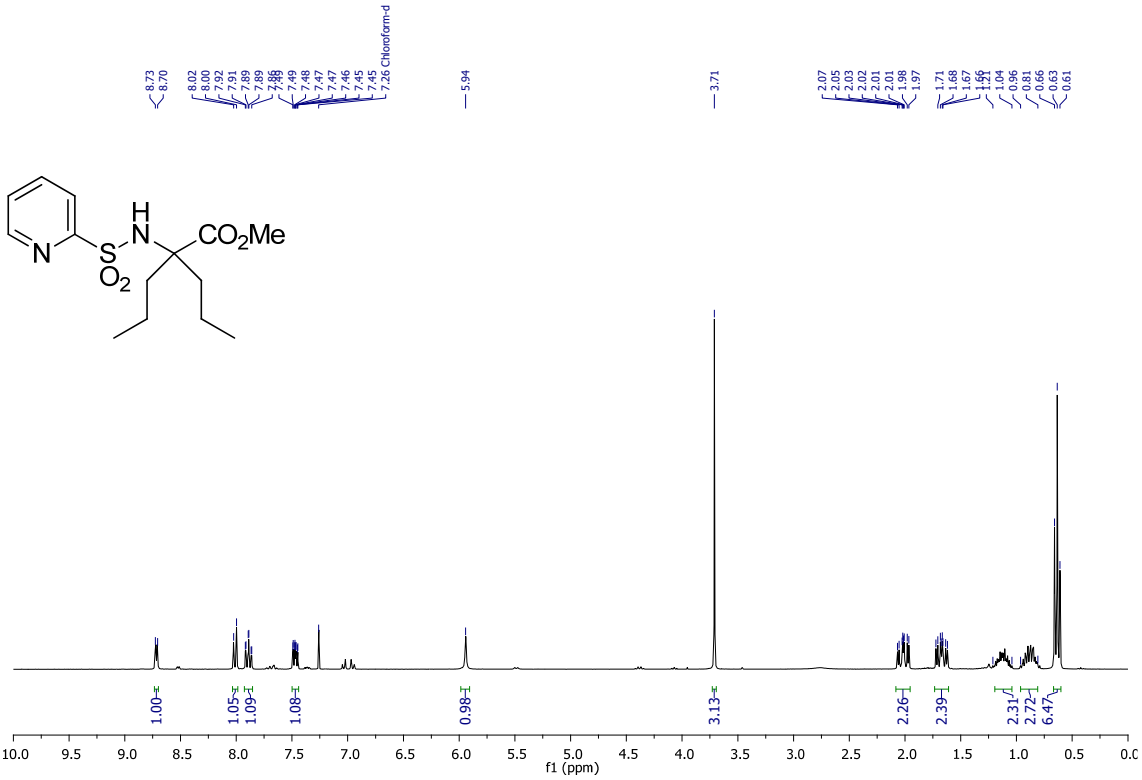



$^{13}$C NMR ($CDCl_3$, 75 MHz)

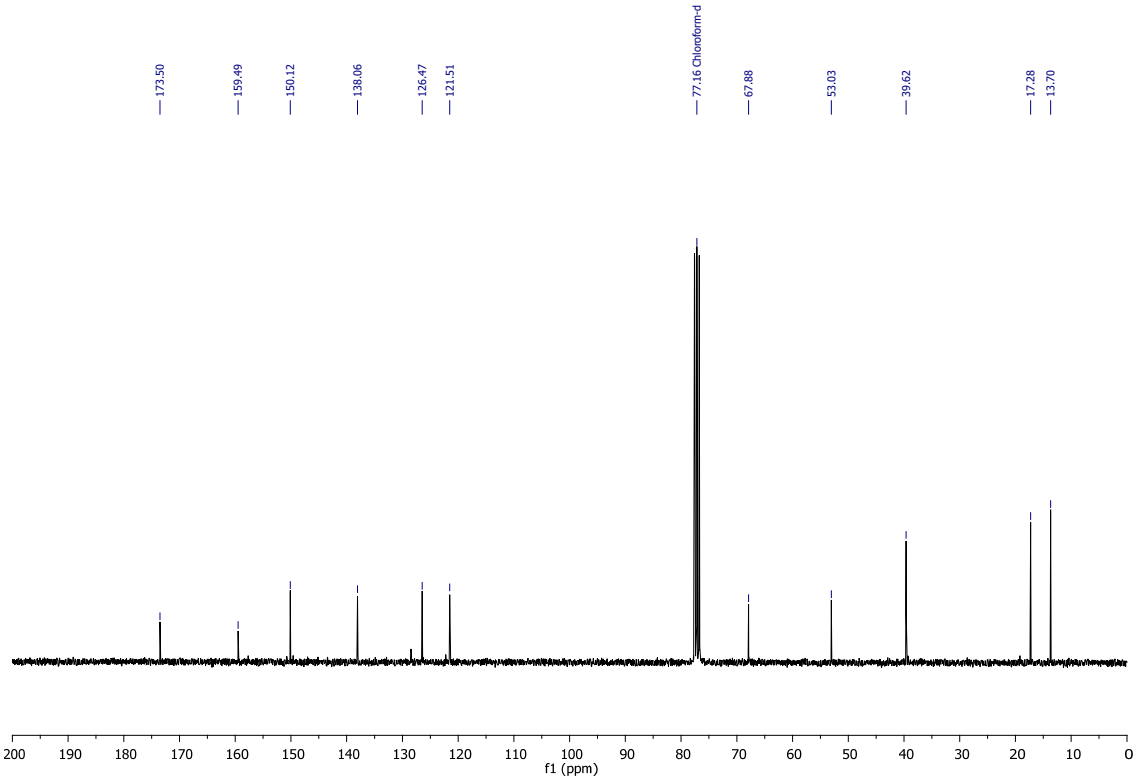


## (*rac*)-Methyl 2-propyl-2-(pyridine-2-sulfonamido)pentanoate (6)

$^{1}$H NMR ($CDCl_3$, 300 MHz)

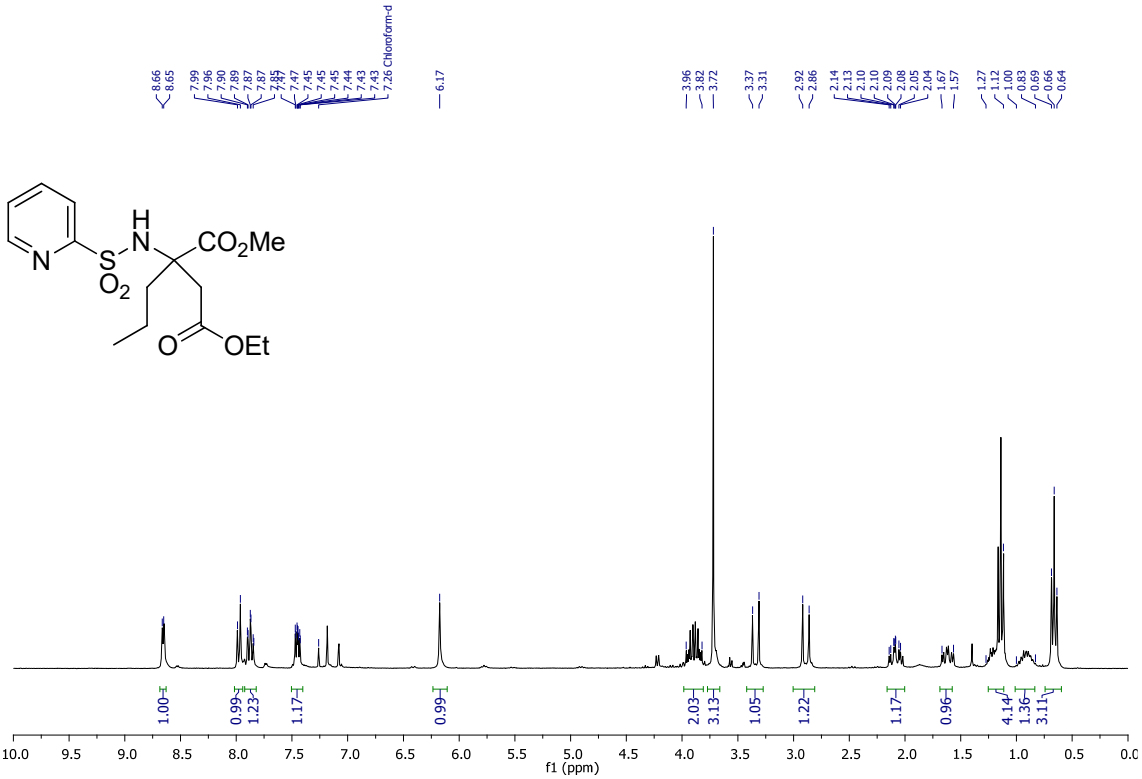



$^{13}$C NMR ($CDCl_3$, 75 MHz)

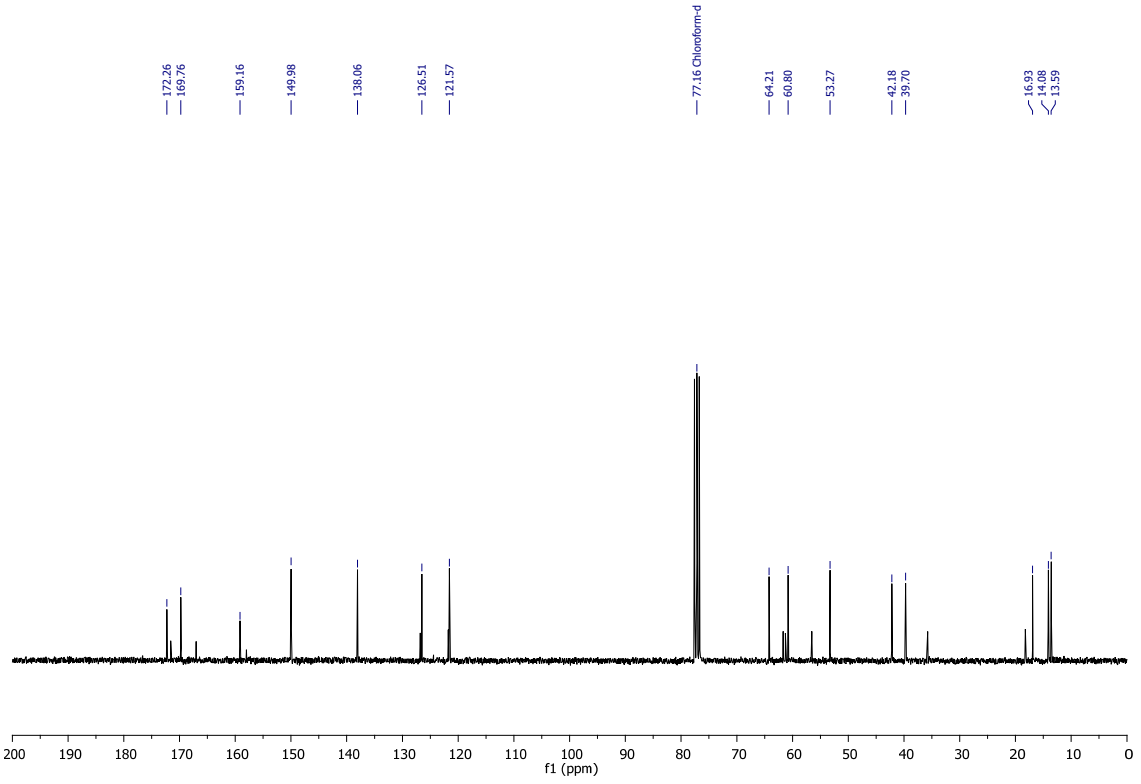


## (*rac*)- 4-Ethyl 1-methyl 2-propyl-2-(pyridine-2-sulfonamido)succinate (7)

$^{1}$H NMR ($CDCl_3$, 300 MHz)

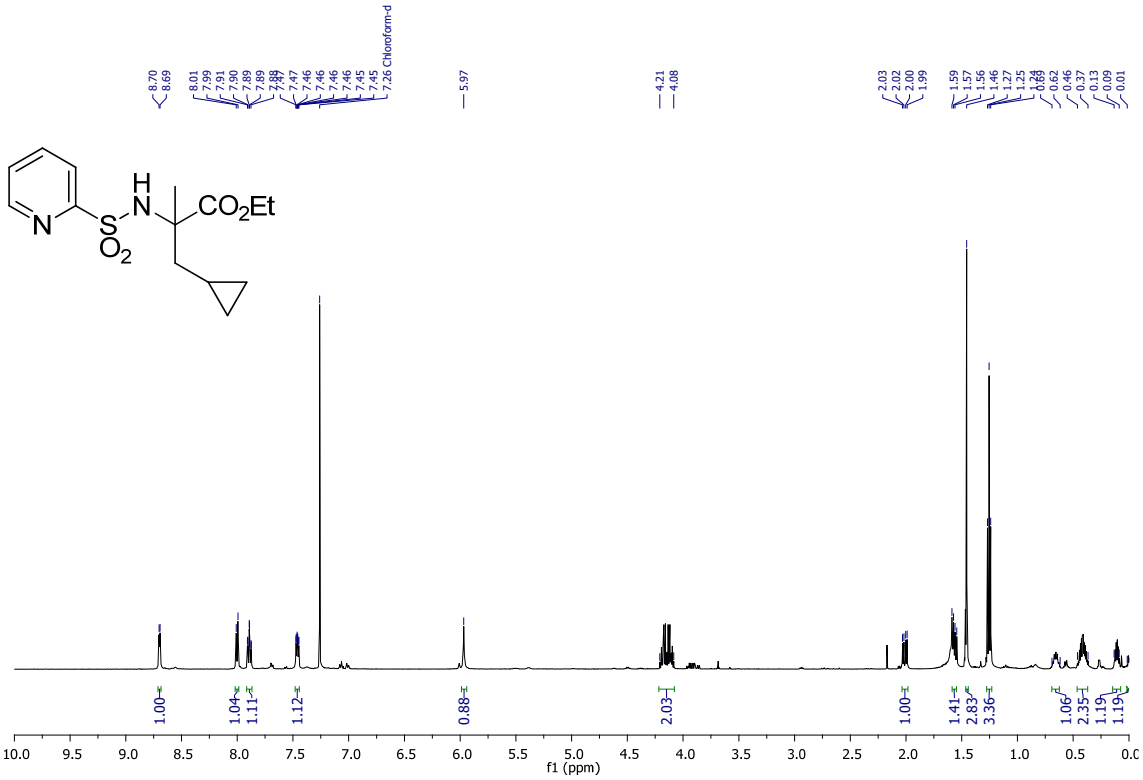



$^{13}$C NMR ($CDCl_3$, 75 MHz)

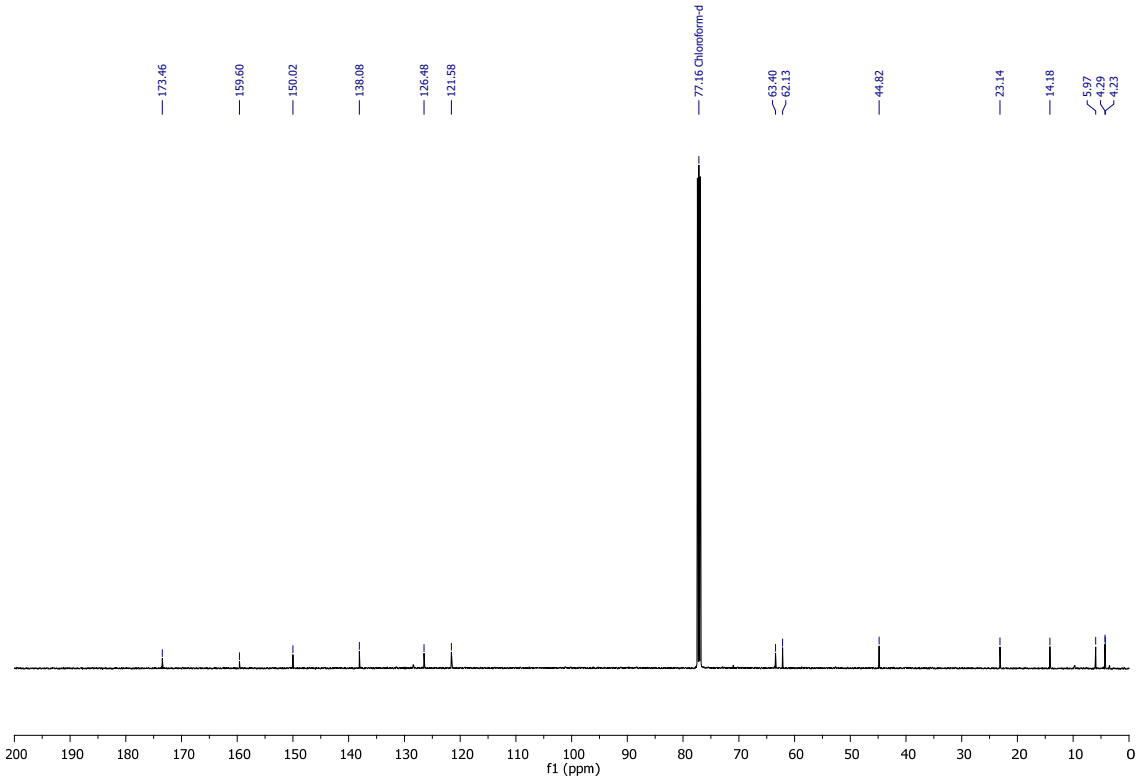


**(*rac*)-Methyl 3-cyclopropyl-2-methyl-2-(pyridine-2-sulfonamido)propanoate (43)**

$^{1}$H NMR ($CDCl_3$, 500 MHz)

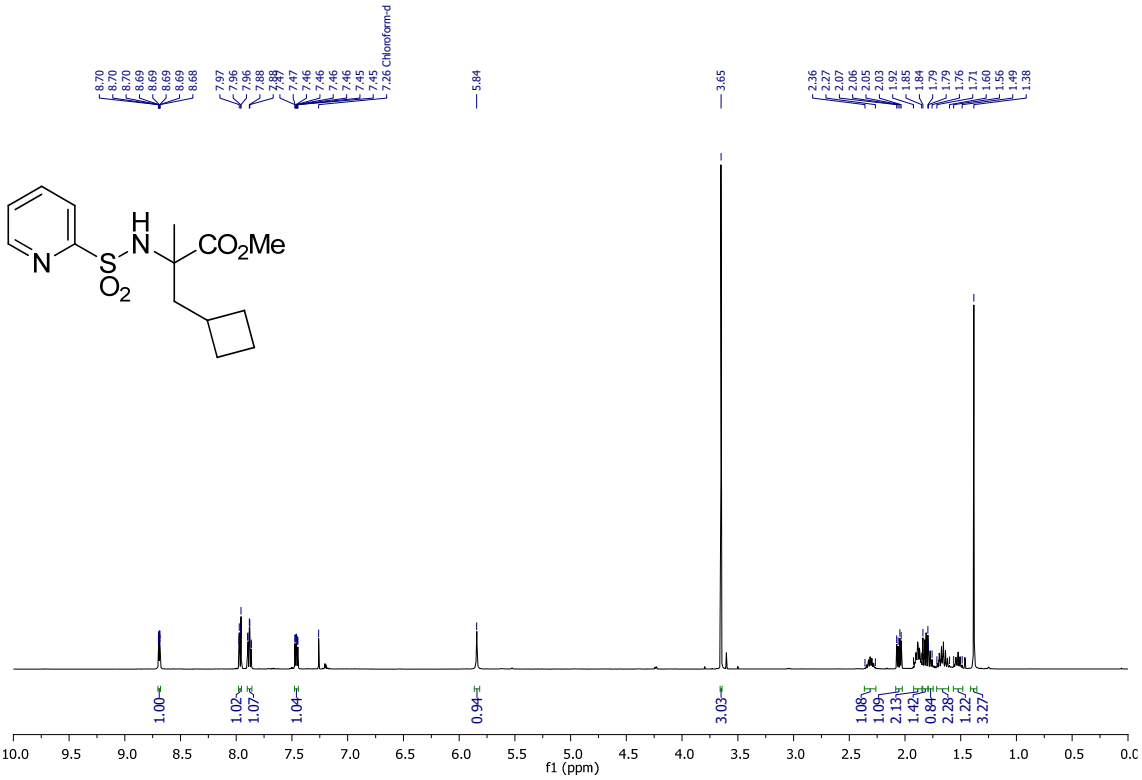



$^{13}$C NMR ($CDCl_3$, 126 MHz)

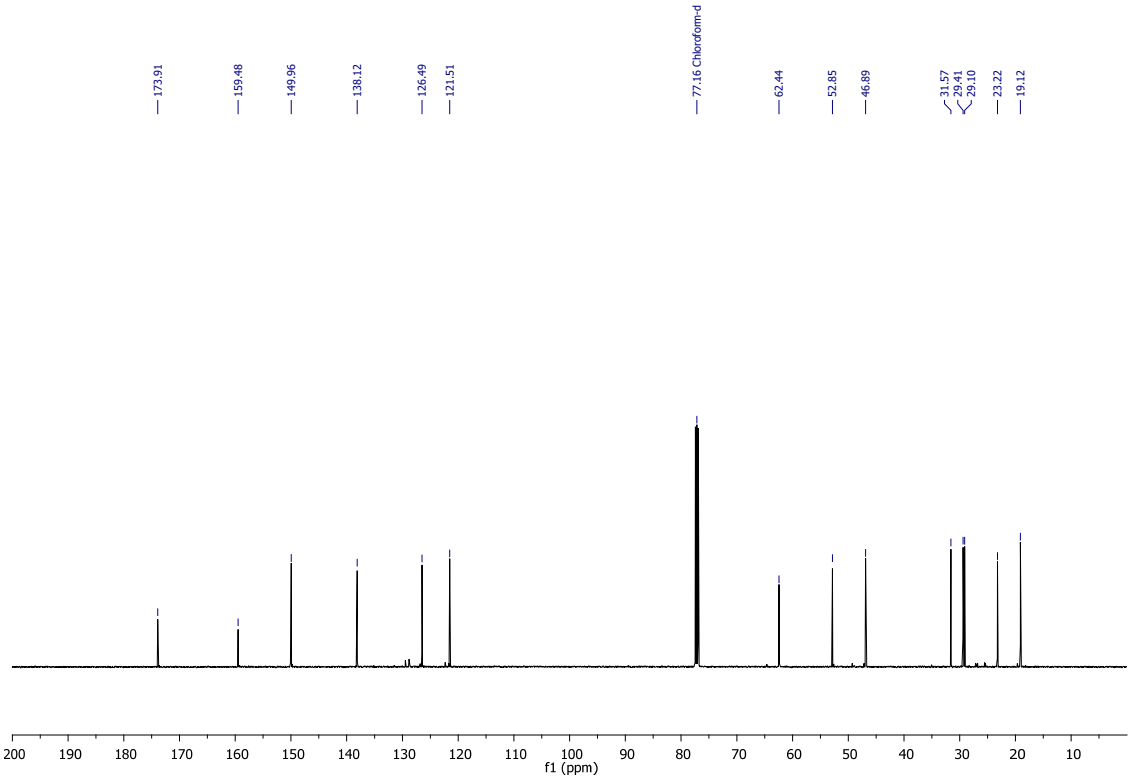


**(*rac*)-Methyl 3-cyclobutyl-2-methyl-2-(pyridine-2-sulfonamido)propanoate (XXI)**

$^{1}$H NMR ($CDCl_3$, 500 MHz)

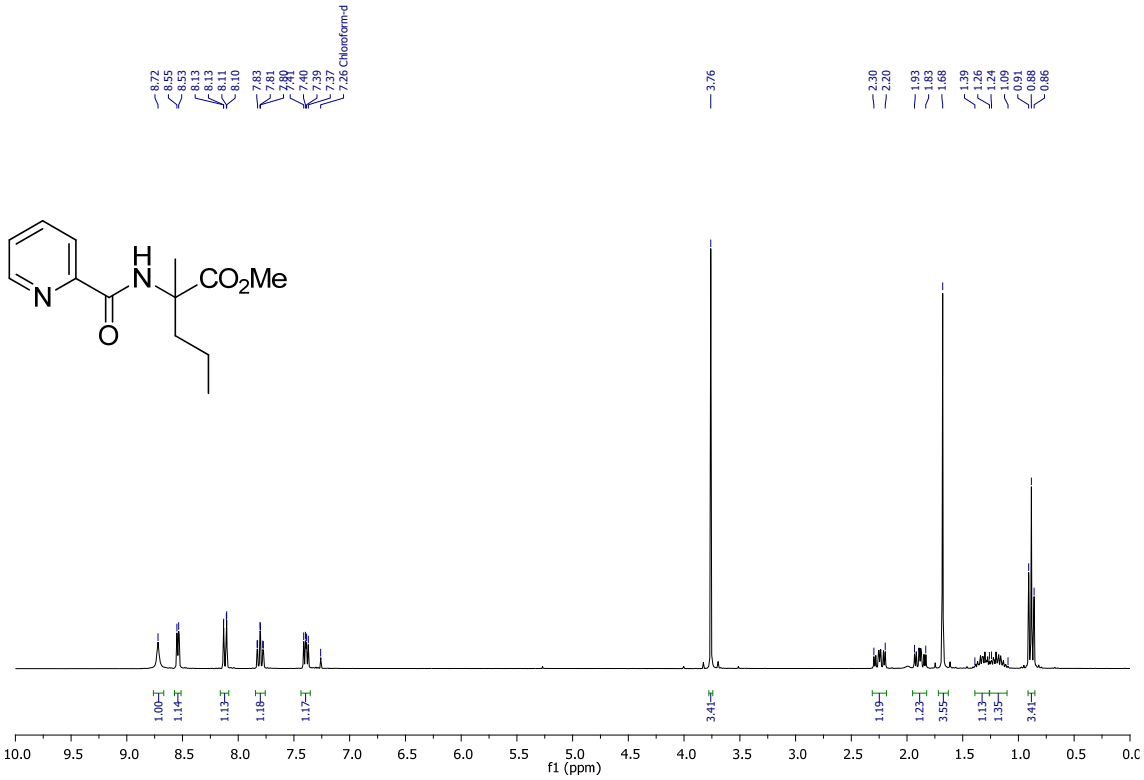



$^{13}$C NMR ($CDCl_3$, 126 MHz)

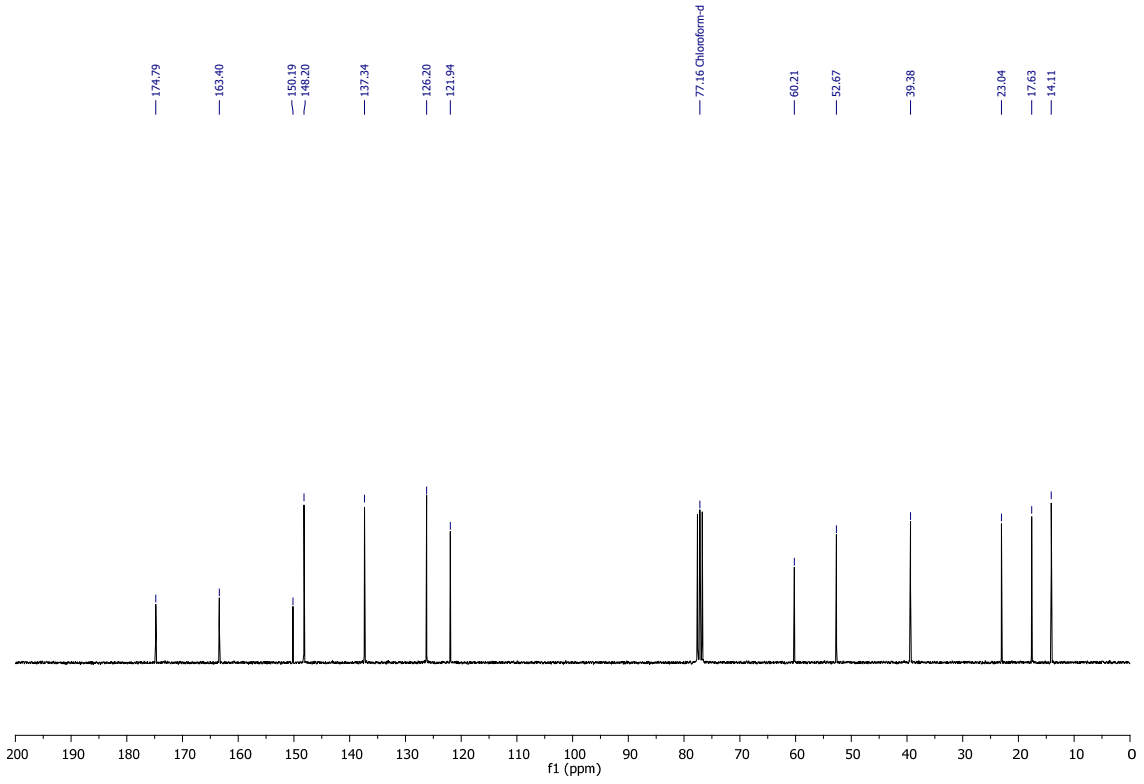


## (*rac*)-Methyl 2-methyl-2-(picolinamido)pentanoate (1a)

$^{1}$H NMR ($CDCl_3$, 300 MHz)

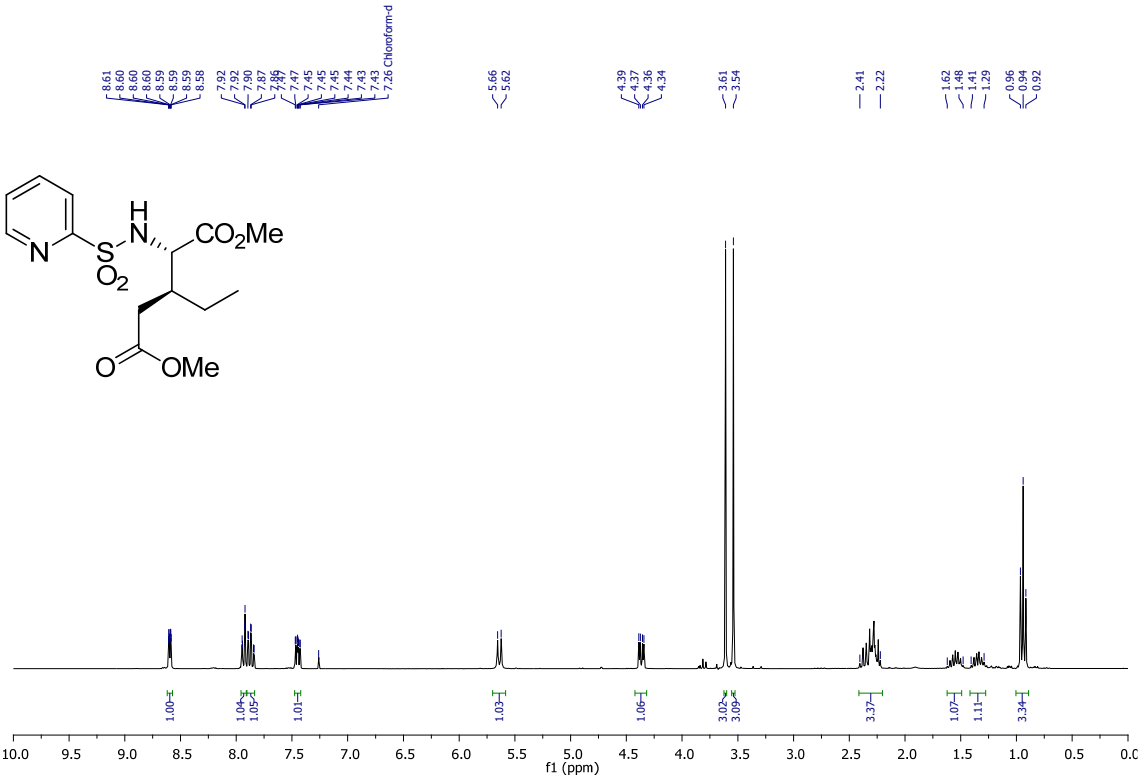



$^{13}$C NMR ($CDCl_3$, 75 MHz)

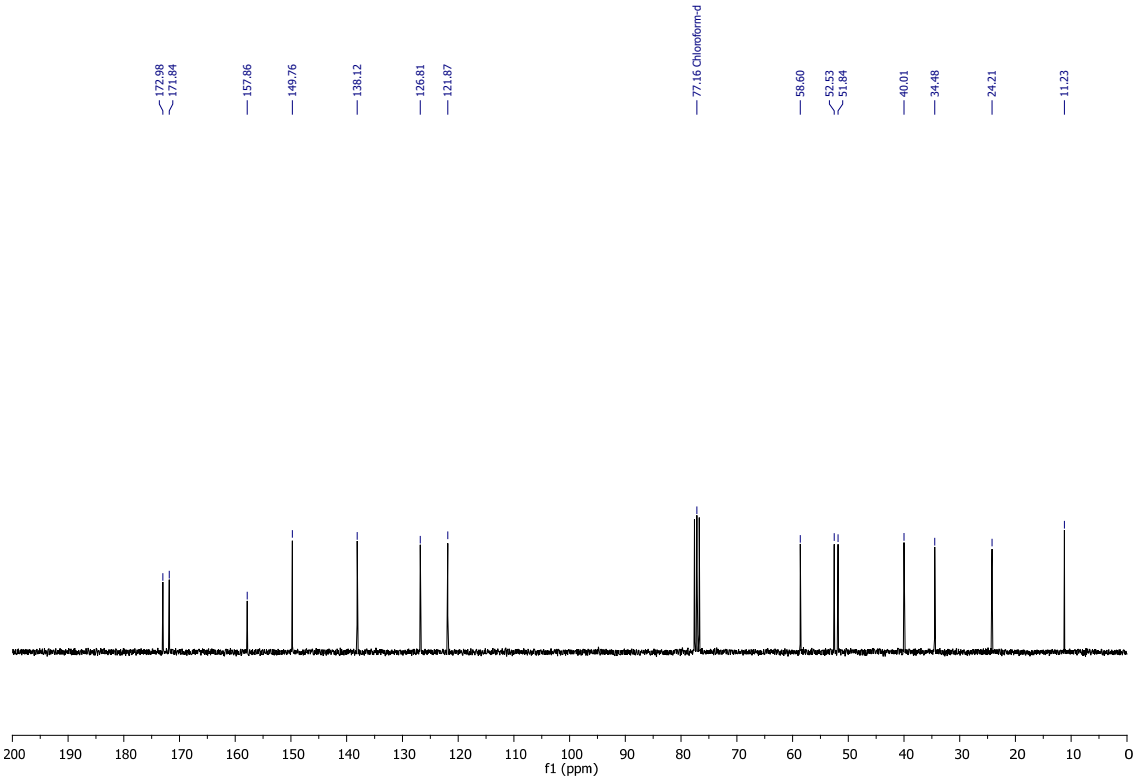


**(2*S**,3*S**)-Dimethyl 3-ethyl-2-(pyridine-2-sulfonamido) pentanedioate (10)**

$^{1}$H NMR ($CDCl_3$, 300 MHz)

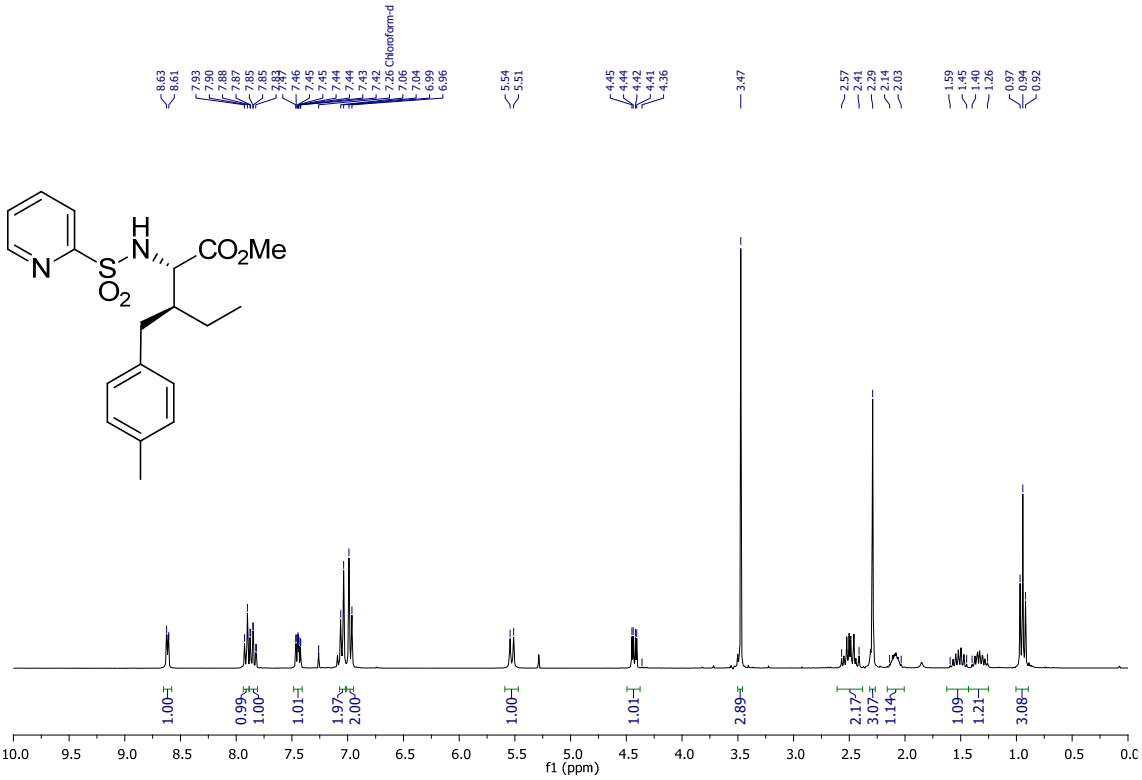



$^{13}$C NMR ($CDCl_3$, 75 MHz)

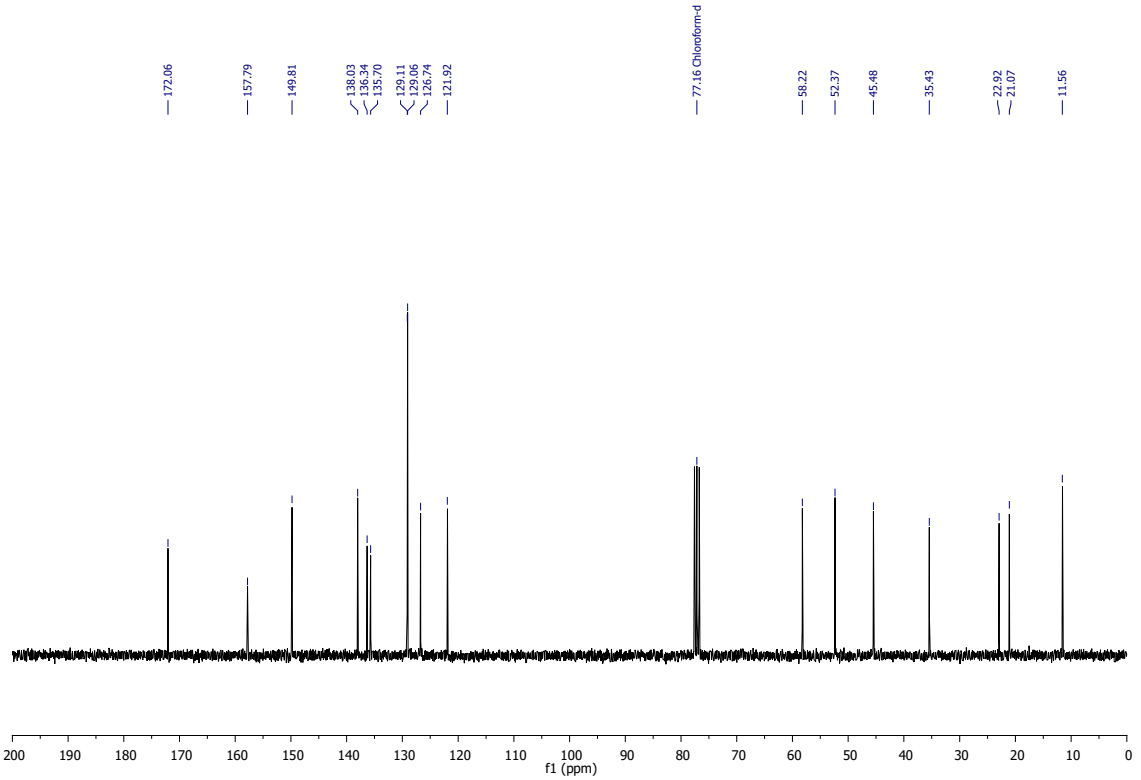


**(2*S**,3*S**)-Methyl 3-(4-methylbenzyl)-2-(pyridine-2-sulfonamido)pentanoate (11)**

$^{1}$H NMR ($CDCl_3$, 300 MHz)

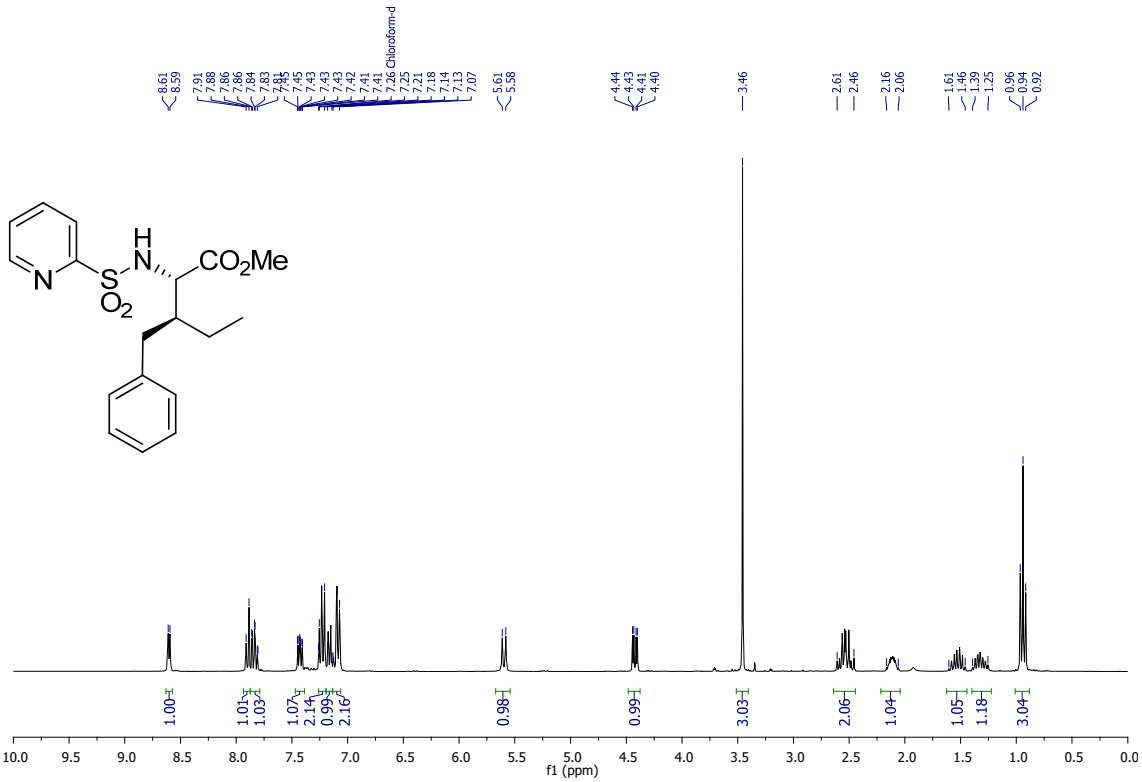



$^{13}$C NMR ($CDCl_3$, 75 MHz)

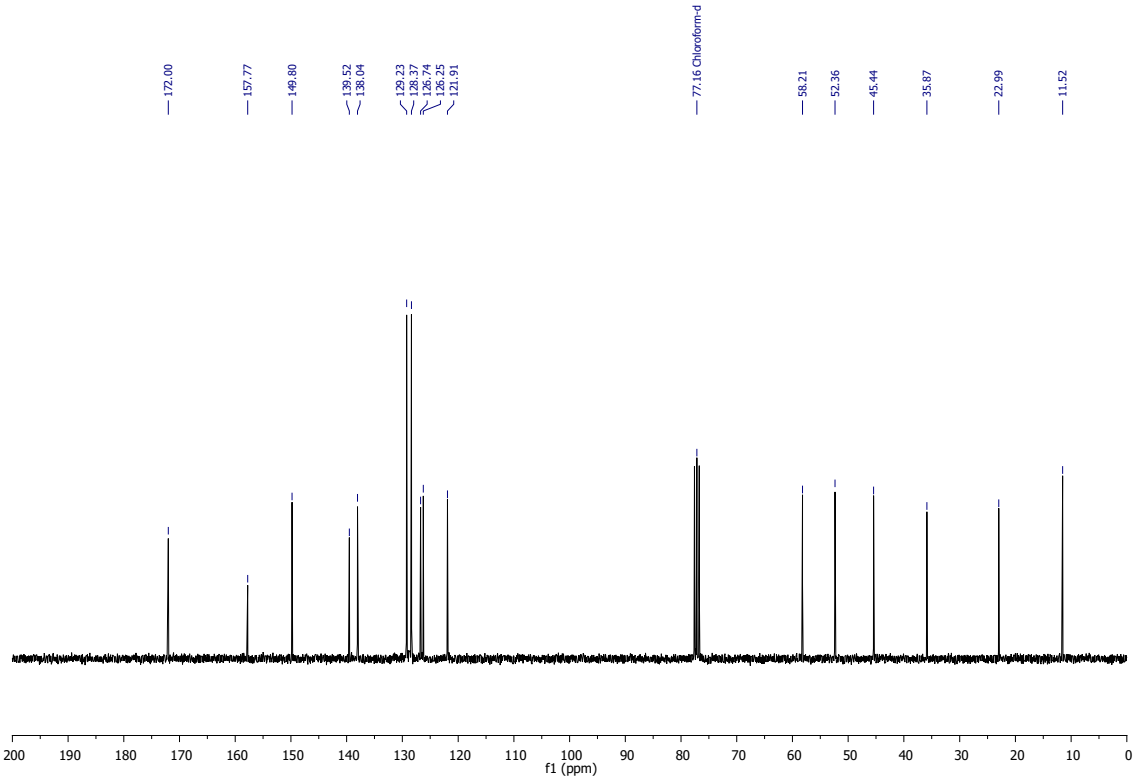


**(2*S**,3*S**)-Methyl 3-benzyl-2-(pyridine-2-sulfonamido)pentanoate (12b)**

$^{1}$H NMR ($CDCl_3$, 300 MHz)

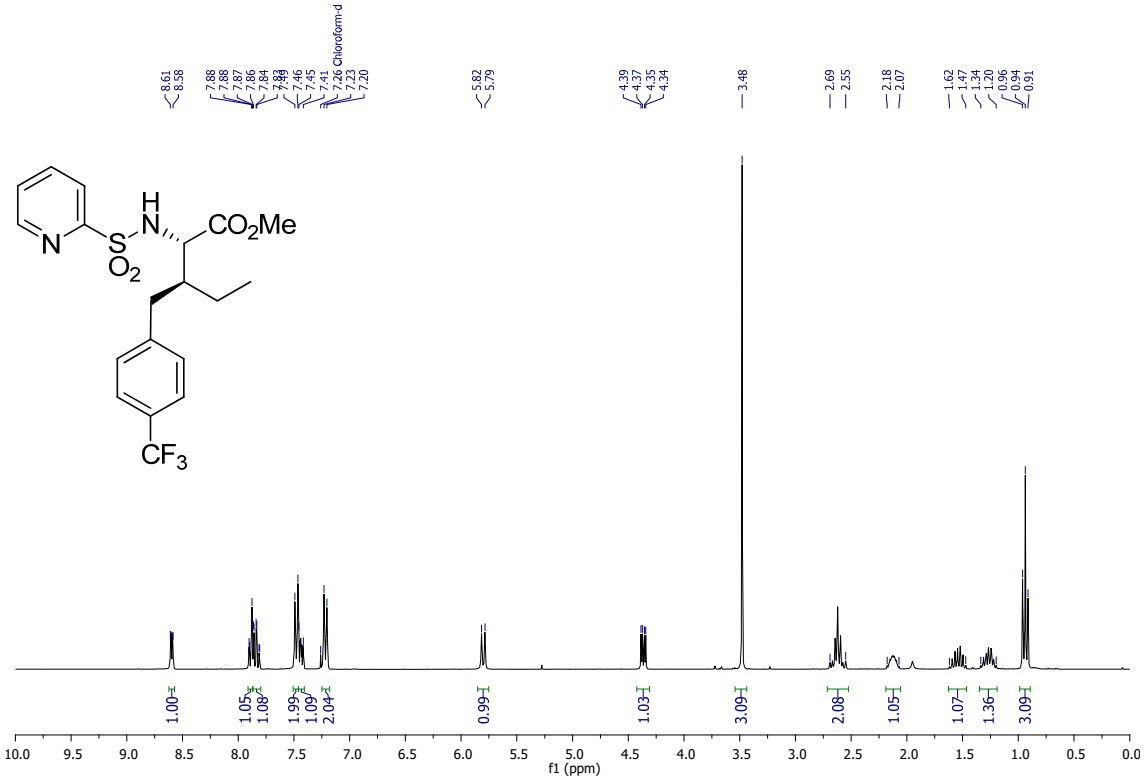



$^{13}$C NMR ($CDCl_3$, 75 MHz)

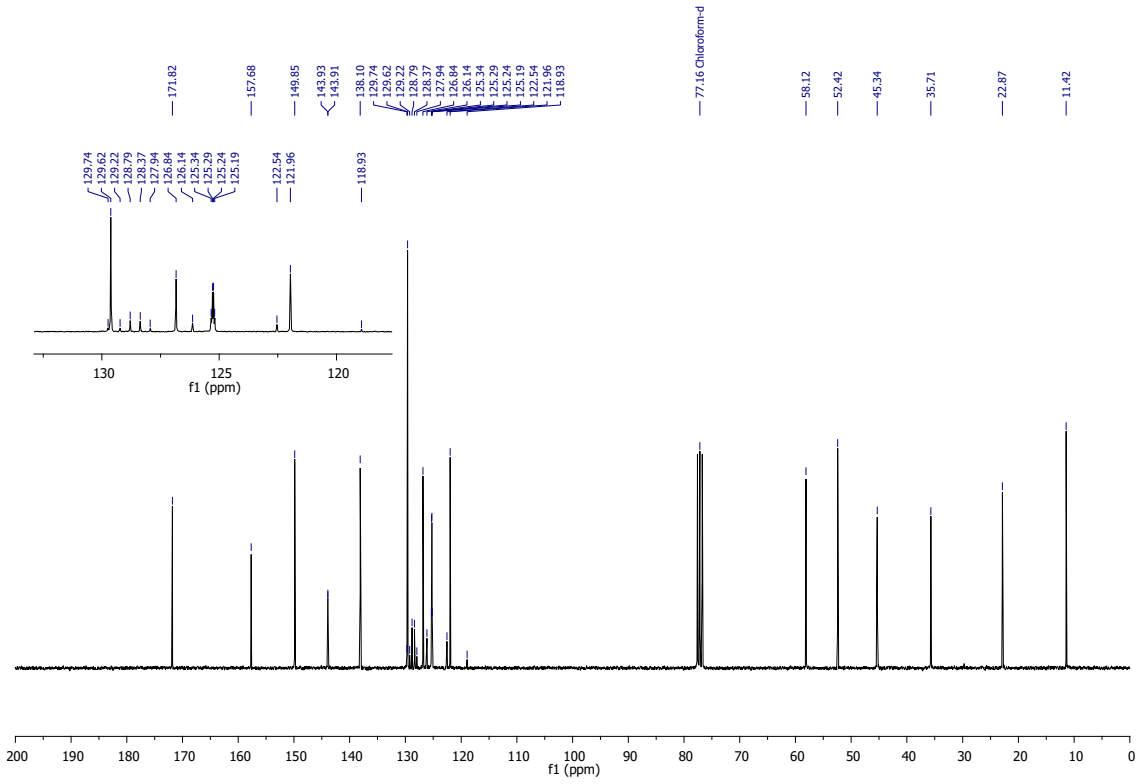


**(2*S**,3*S**)-Methyl 2-(pyridine-2-sulfonamido)-3-(4-(trifluoromethyl)benzyl) pentanoate (13)**

$^{1}$H NMR ($CDCl_3$, 300 MHz)

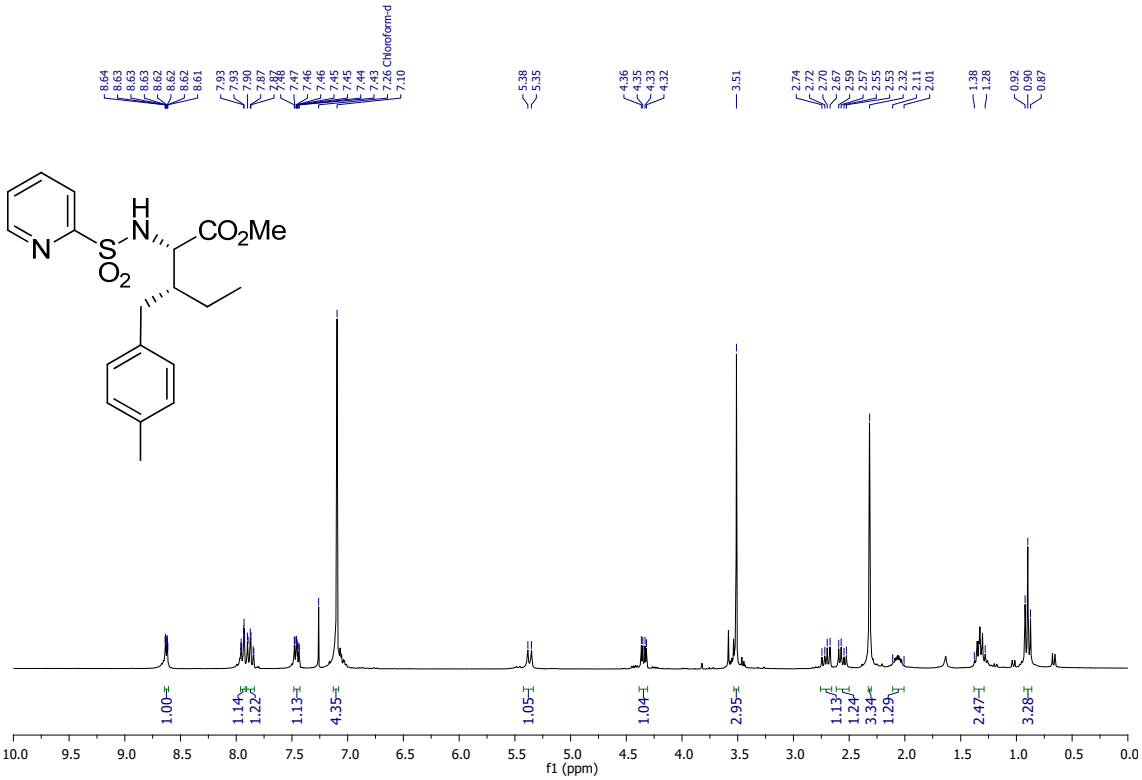



$^{13}$C NMR ($CDCl_3$, 75 MHz)

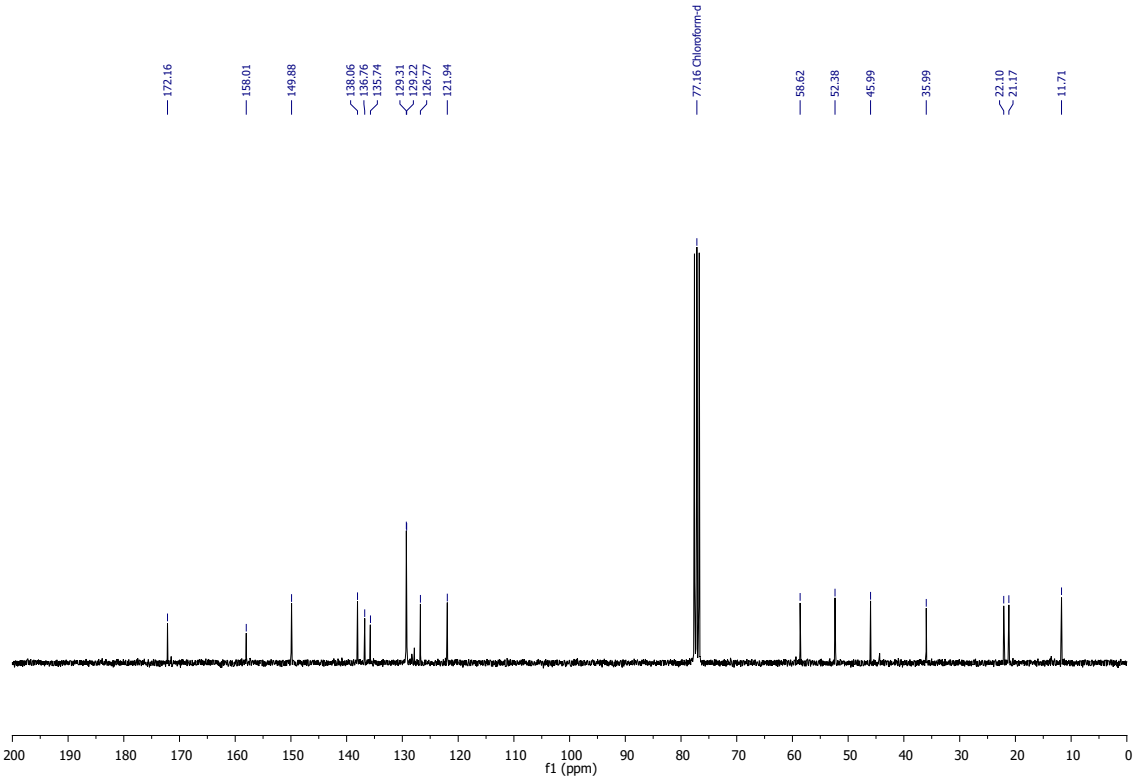


**(2*S*,3*R*)-Methyl 3-(4-methylbenzyl)-2-(pyridine-2-sulfonamido)pentanoate (25)**

$^{1}$H NMR ($CDCl_3$, 300 MHz)

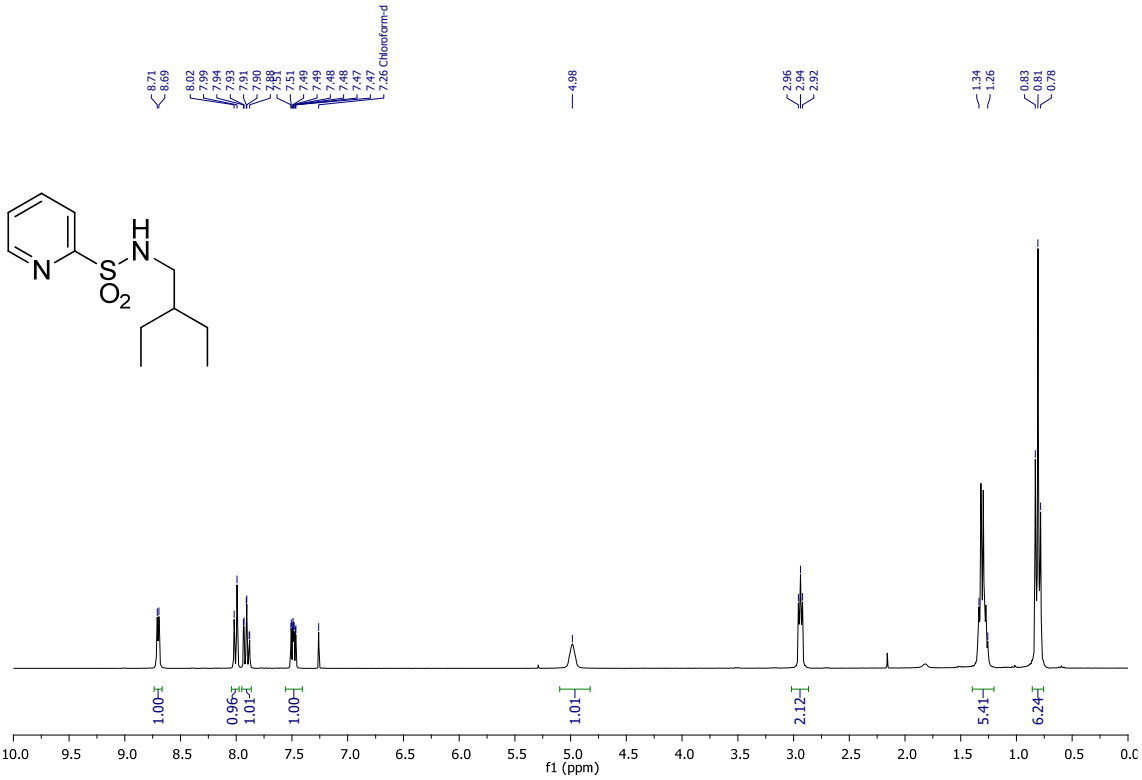



$^{13}$C NMR ($CDCl_3$, 75 MHz)

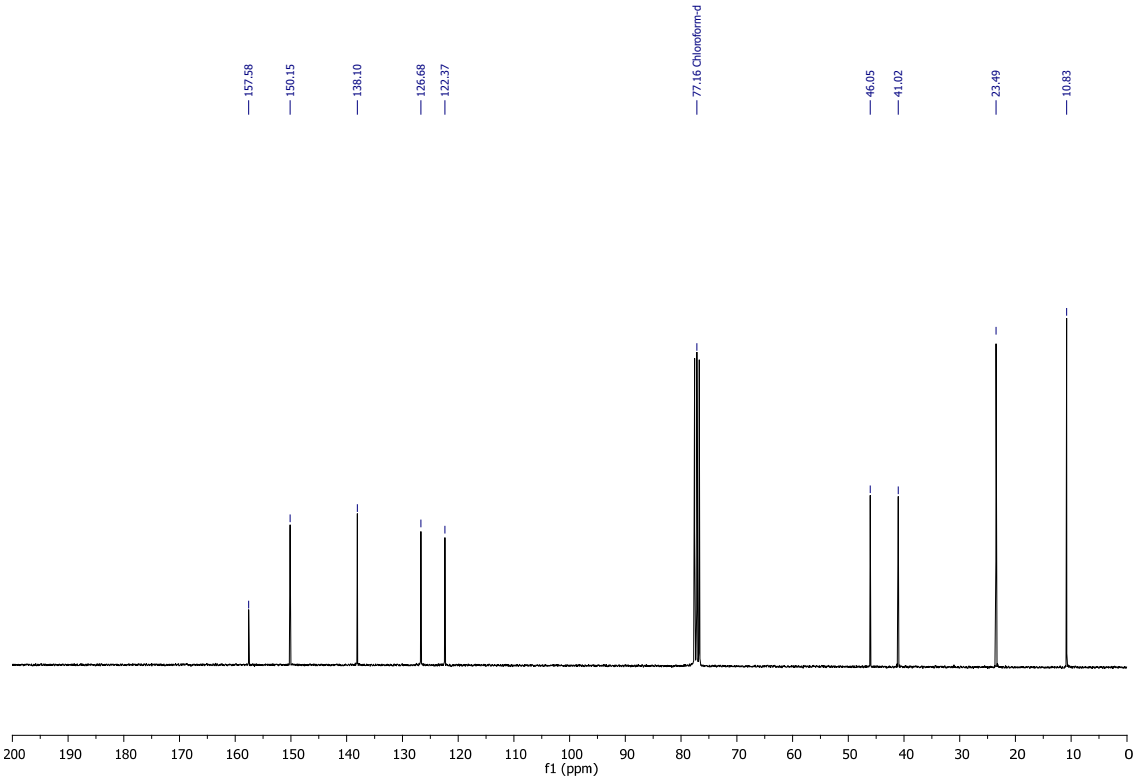


## *N*-(2-Ethylbutyl)pyridine-2-sulfonamide (XVI)

$^{1}$H NMR ($CDCl_3$, 300 MHz)

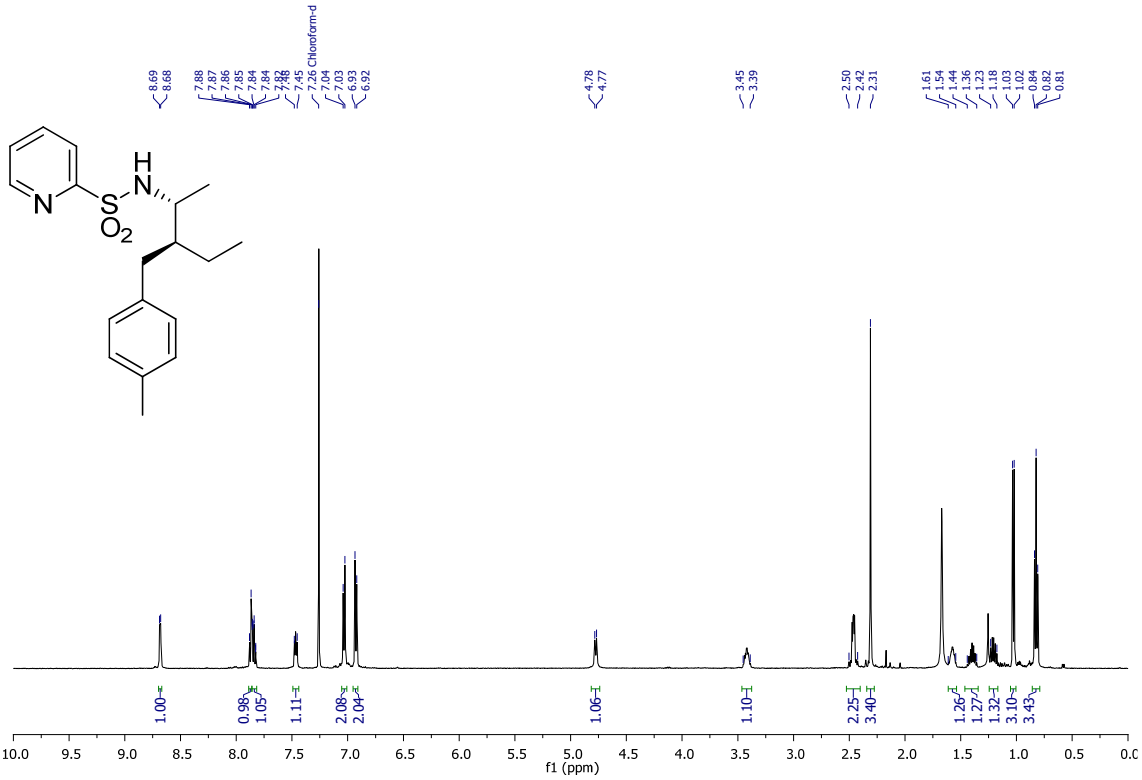



$^{13}$C NMR ($CDCl_3$, 75 MHz)

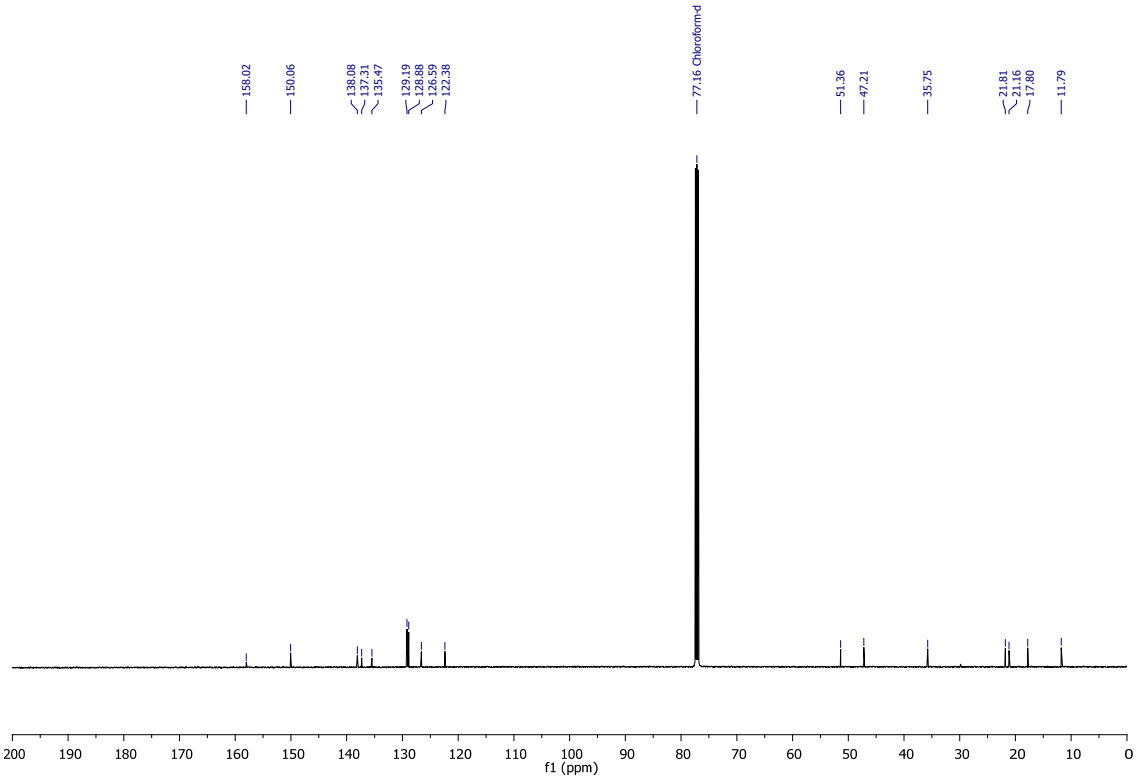


## *N*-((2*R**,3*S**)-3-(4-Methylbenzyl)pentan-2-yl)pyridine-2-sulfonamide (14)

$^{1}$H NMR ($CDCl_3$, 500 MHz)

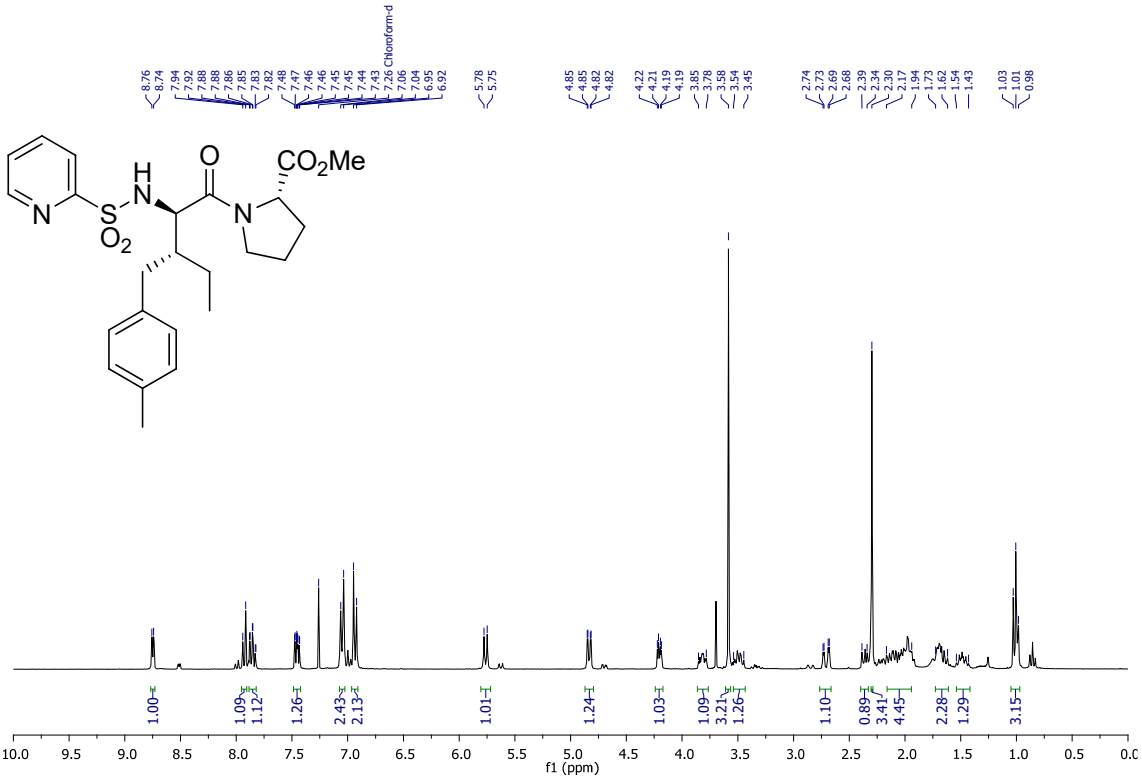



$^{13}$C NMR ($CDCl_3$, 126 MHz)

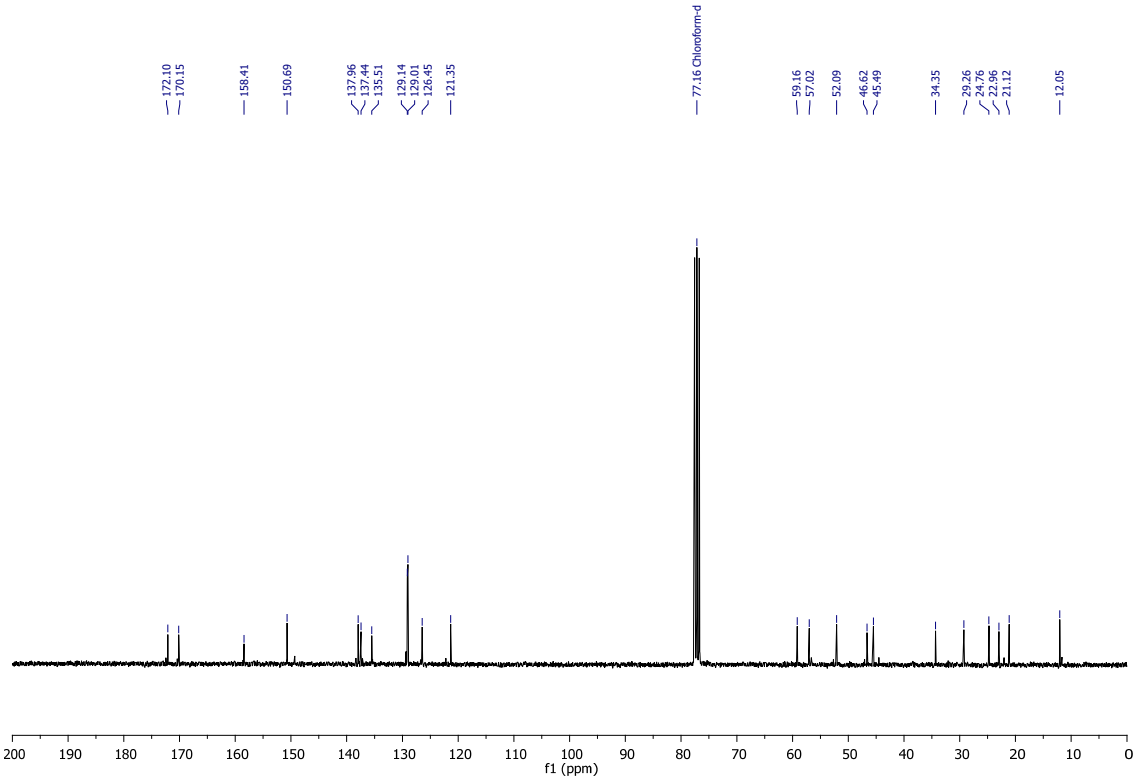


**Methyl *N*-($SO_2$Py)-γ-*p*-tolyl-L-*allo*-isoleucinyl-prolinate ((–)-45)**

$^1$H NMR ($CDCl_3$, 300 MHz)

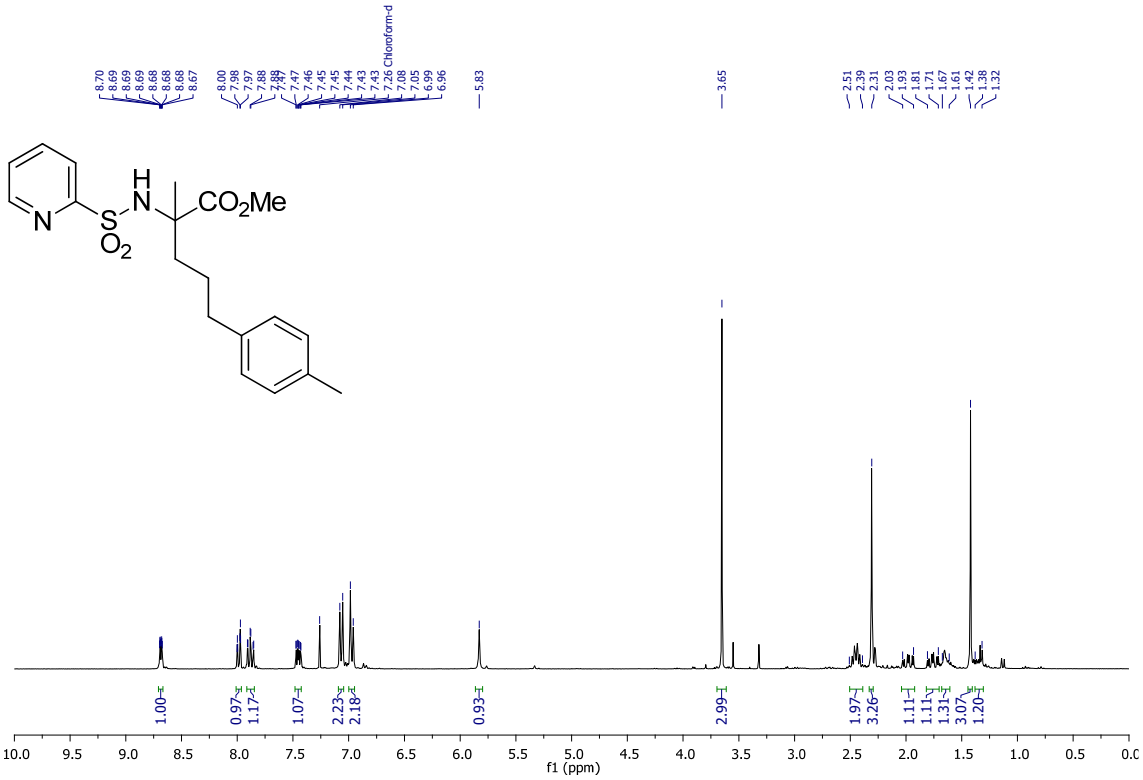



$^{13}$C NMR ($CDCl_3$, 75 MHz)

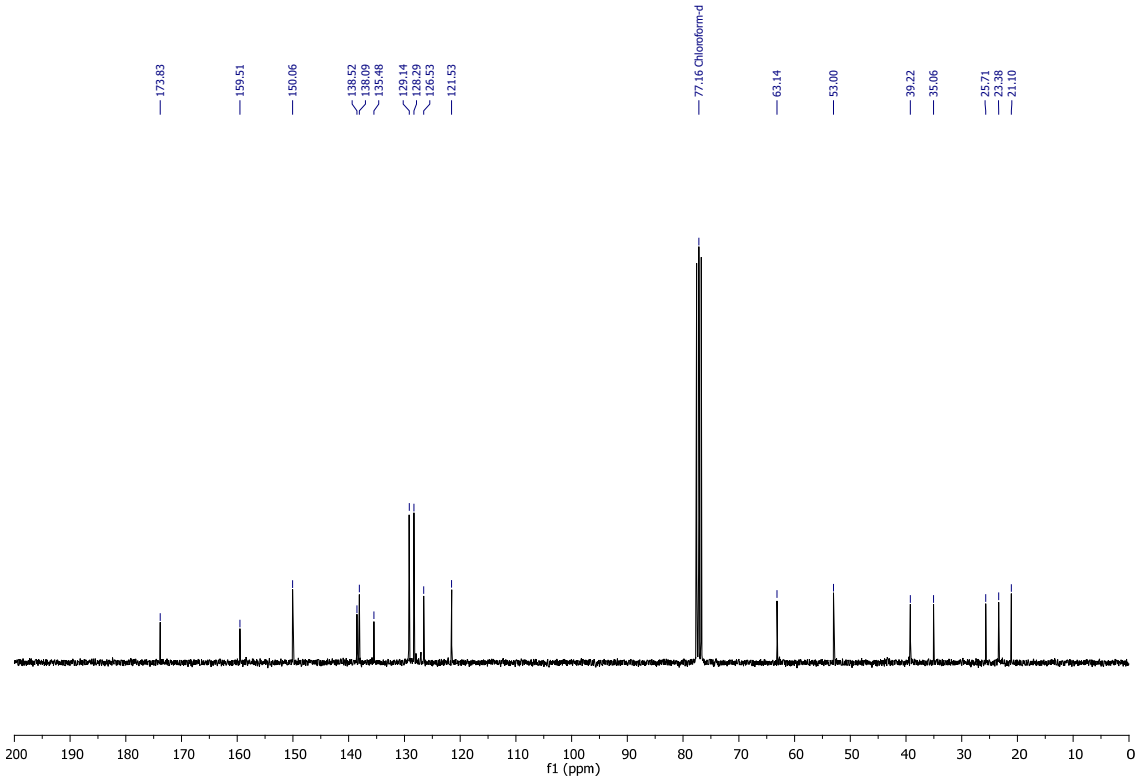


**(*rac*)-Methyl 2-methyl-2-(pyridine-2-sulfonamido)-5-(*p*-tolyl)pentanoate (4b)**

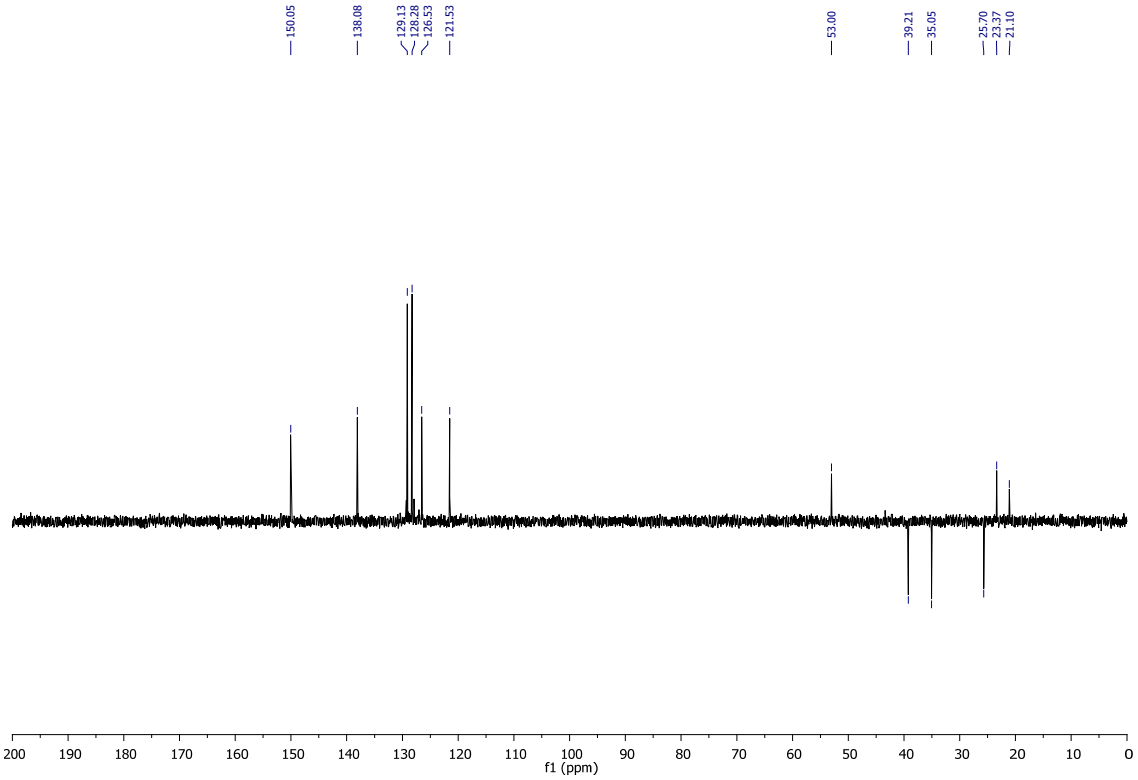
$^{1}$H NMR ($CDCl_3$, 300 MHz)




$^{13}$C NMR ($CDCl_3$, 75 MHz)

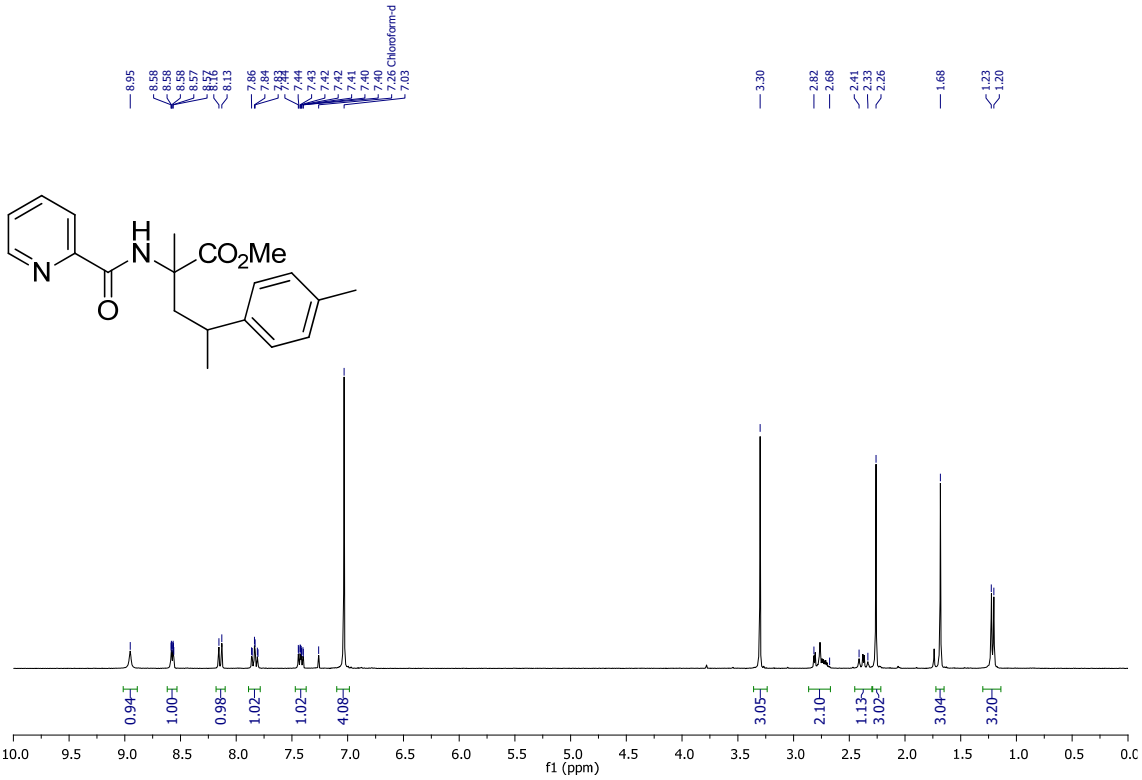


$^{13}$C NMR-DEPT-135 ($CDCl_3$, 75 MHz)

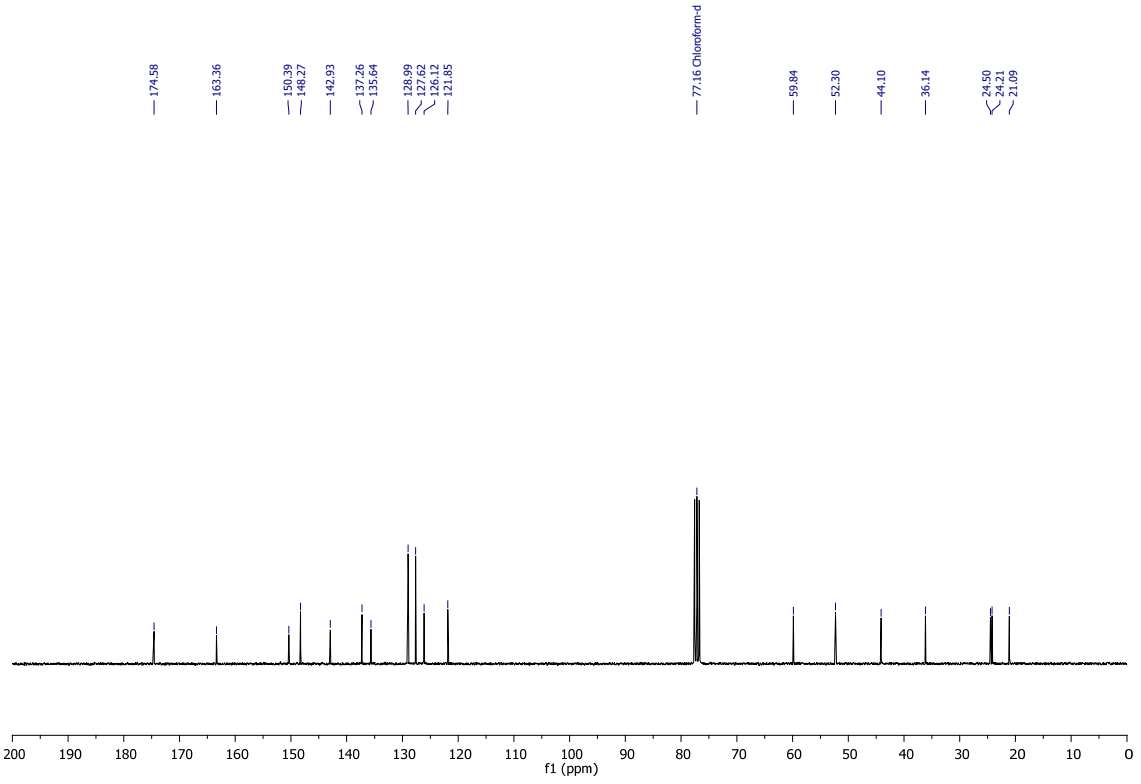


## (*rac*)-Methyl 2-methyl-2-(picolinamido)-4-(*p*-tolyl)pentanoate (2a)

$^{1}$H NMR ($CDCl_3$, 300 MHz)

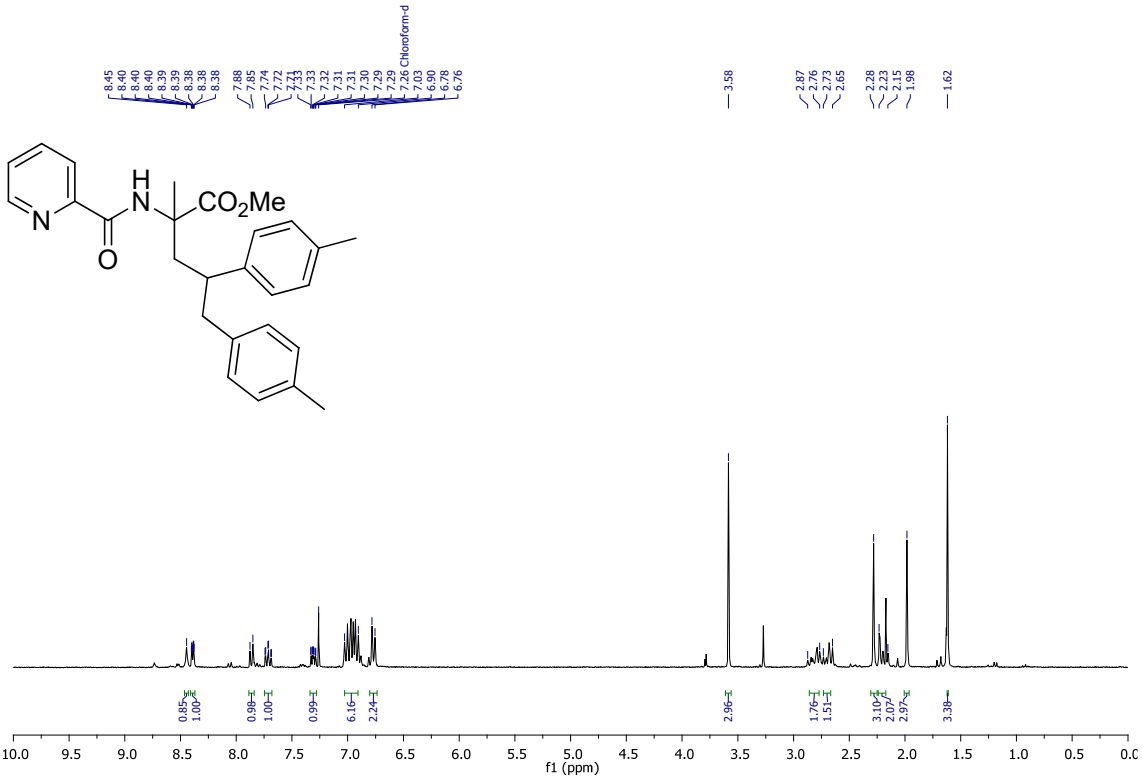



$^{13}$C NMR ($CDCl_3$, 75 MHz)

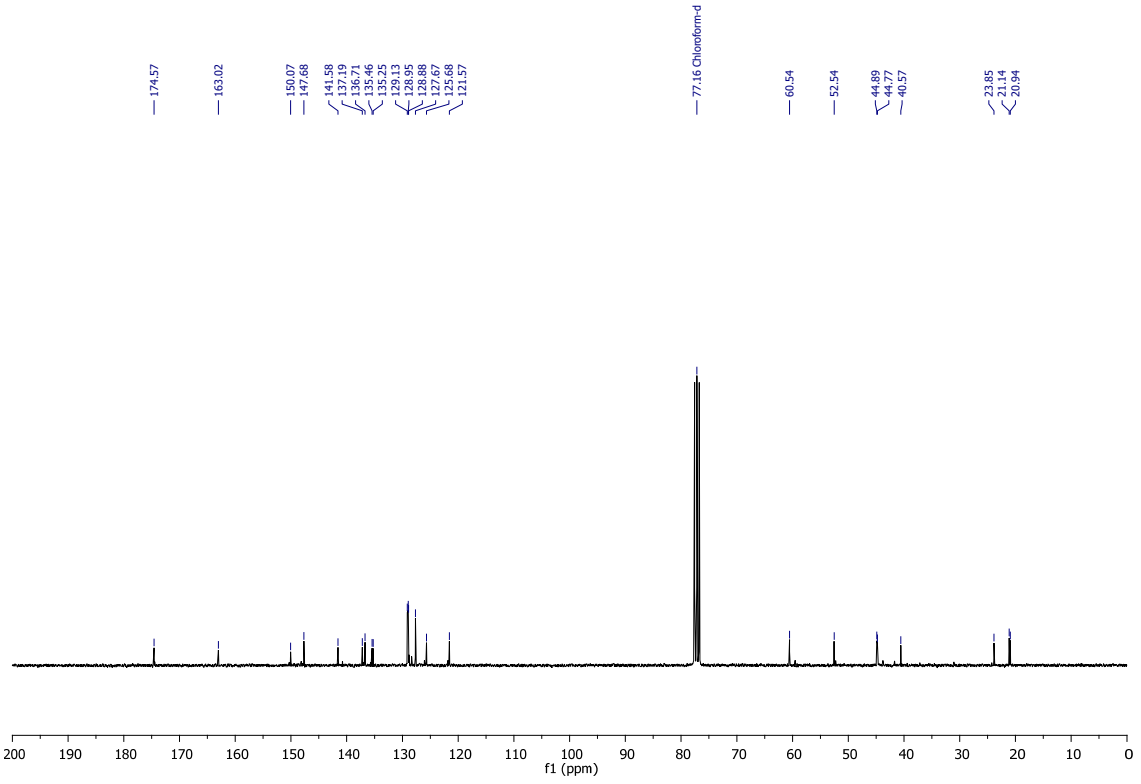


## (*rac*)-Methyl 2-methyl-2-(picolinamido)-4,5-di-*p*-tolylpentanoate (3a)

$^1$H NMR ($CDCl_3$, 300 MHz)

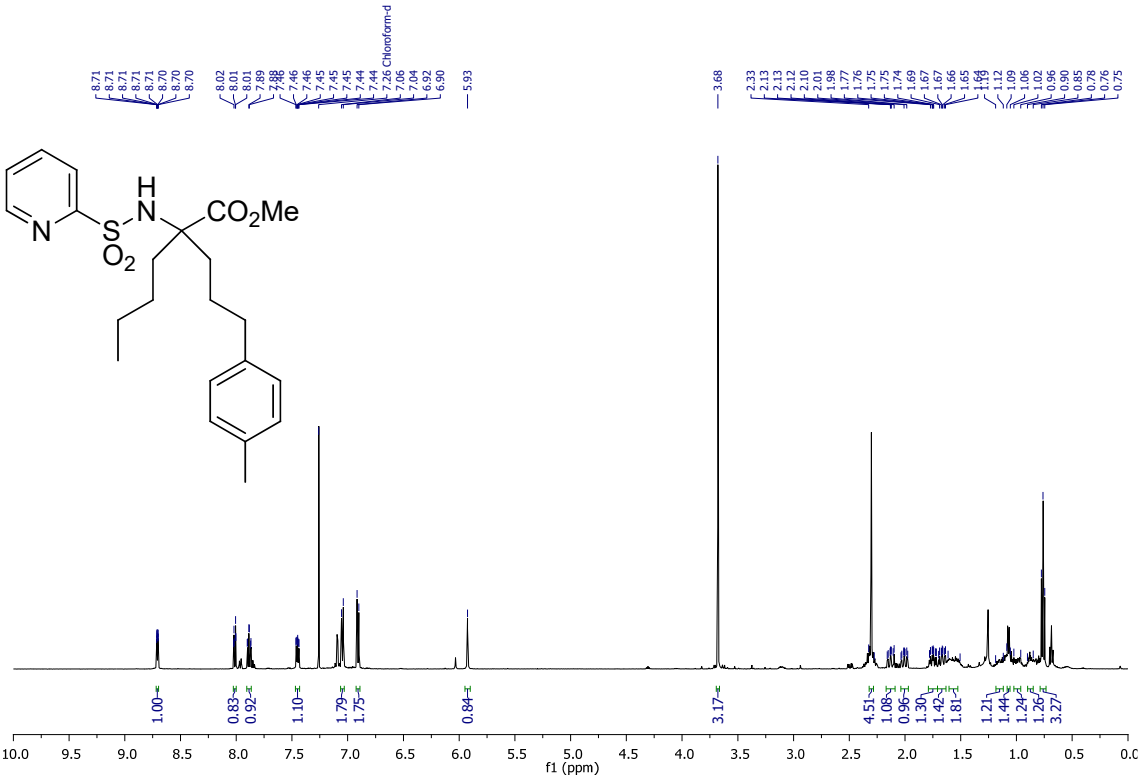



$^{13}$C NMR ($CDCl_3$, 75 MHz)

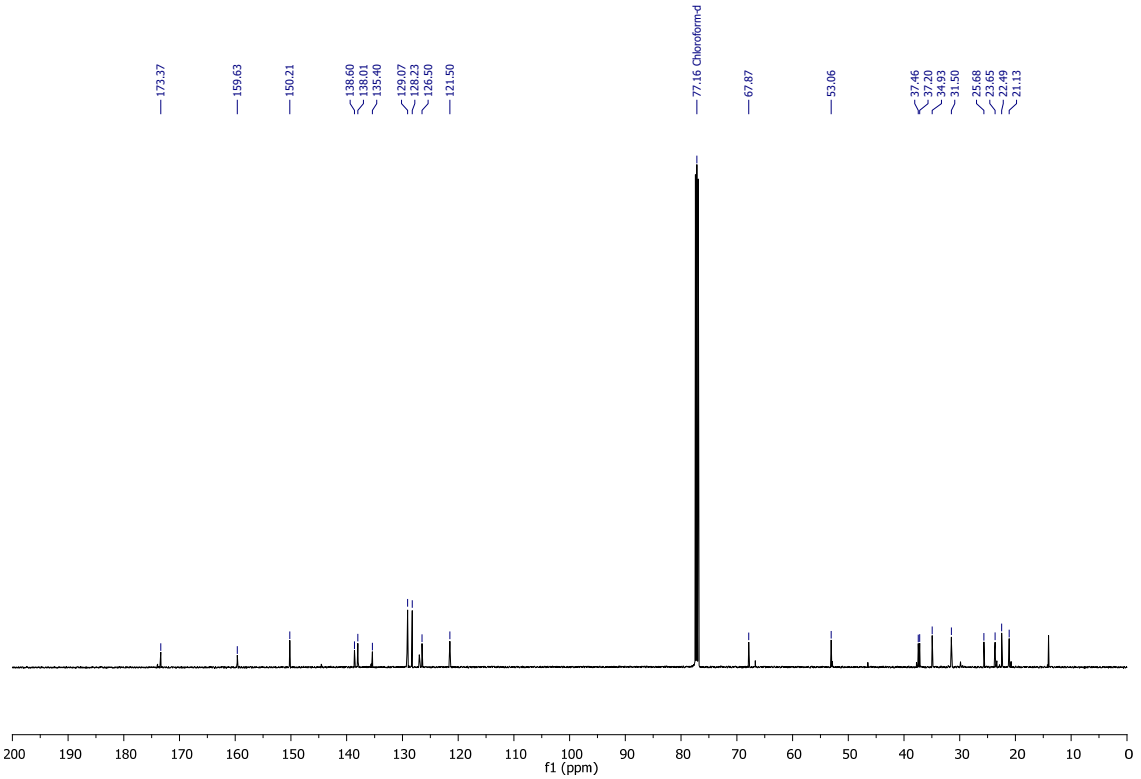


**(*rac*)-Methyl 2-(pyridine-2-sulfonamido)-2-(3-(*p*-tolyl)propyl)hexanoate (15)**

$^{1}$H NMR ($CDCl_3$, 300 MHz)

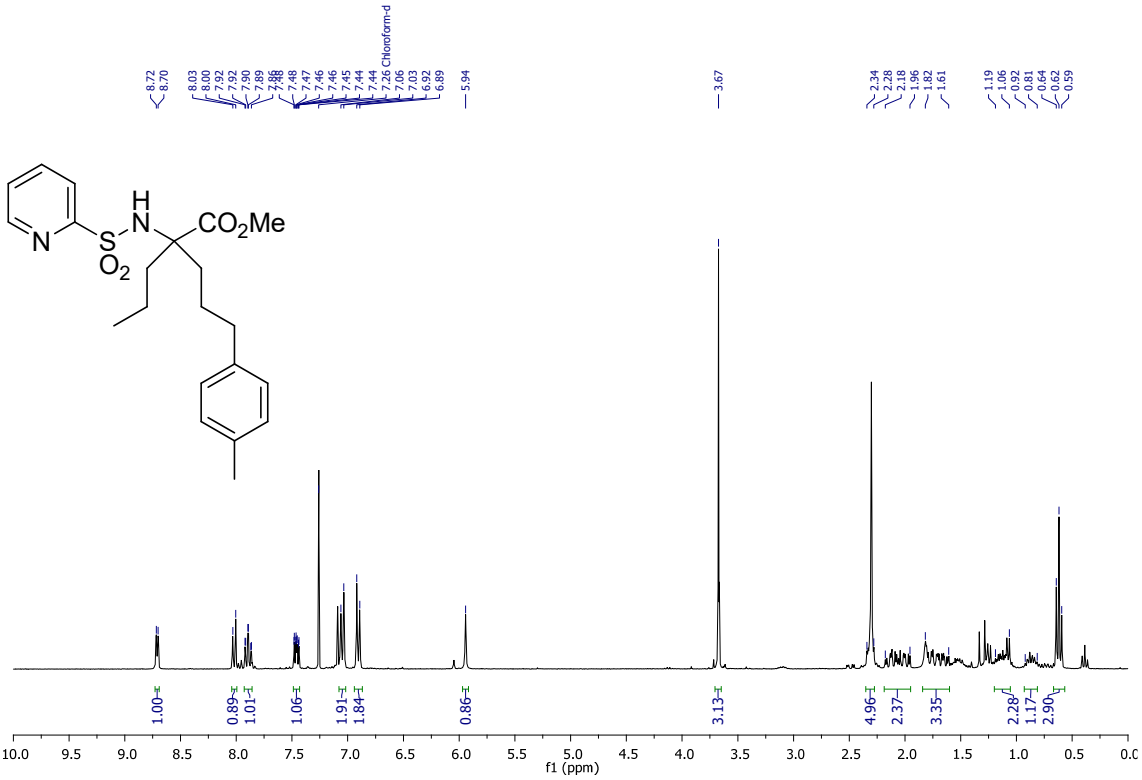



$^{13}$C NMR ($CDCl_3$, 75 MHz)

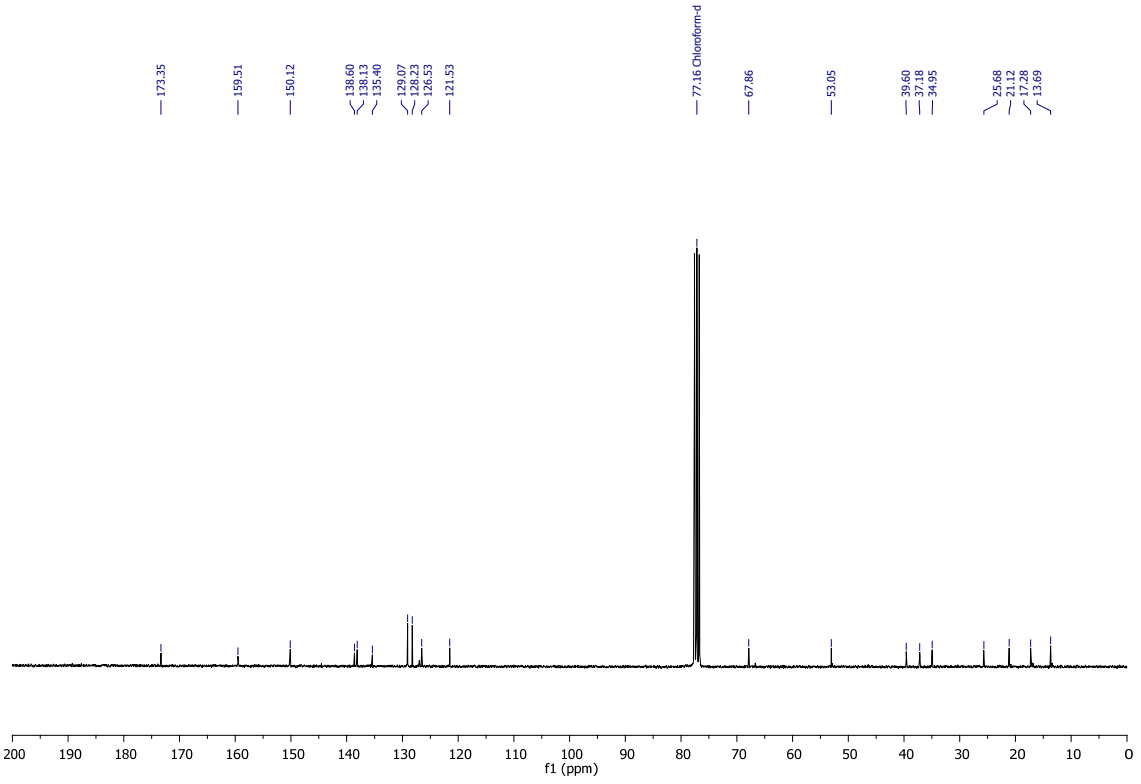


**(*rac*)-Methyl 2-propyl-2-(pyridine-2-sulfonamido)-5-(*p*-tolyl)pentanoate (16)**

$^{1}$H NMR ($CDCl_3$, 300 MHz)

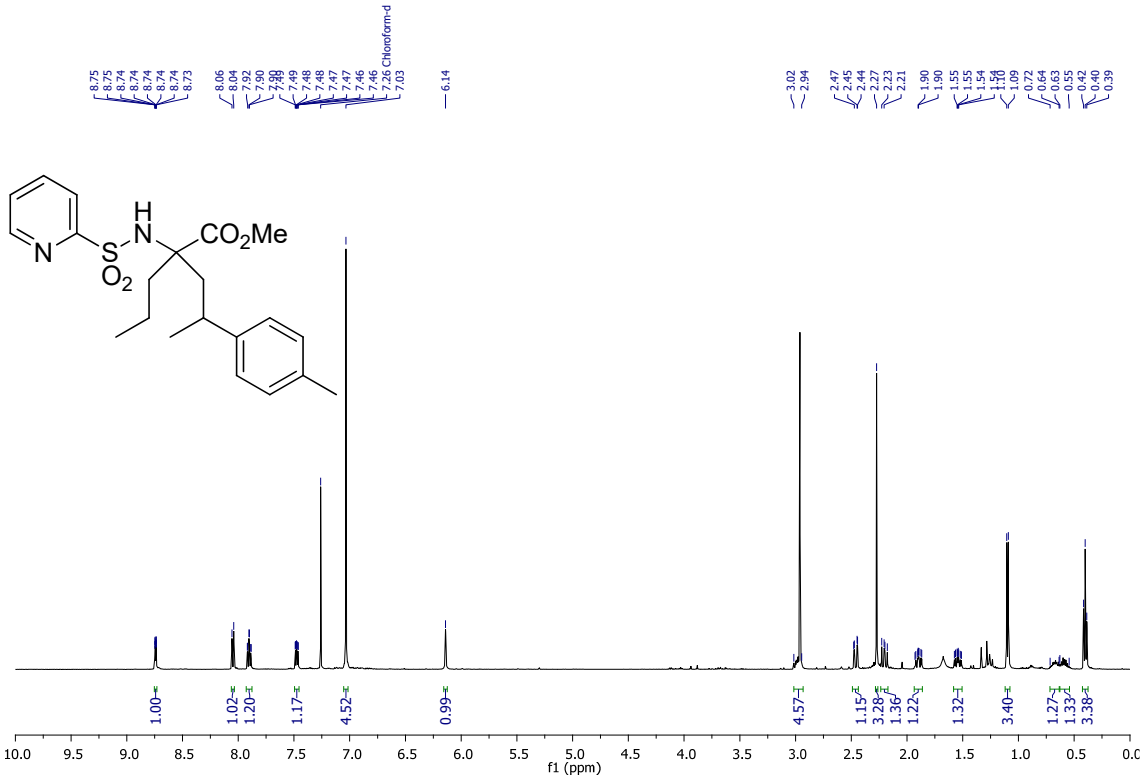



$^{13}$C NMR ($CDCl_3$, 75 MHz)

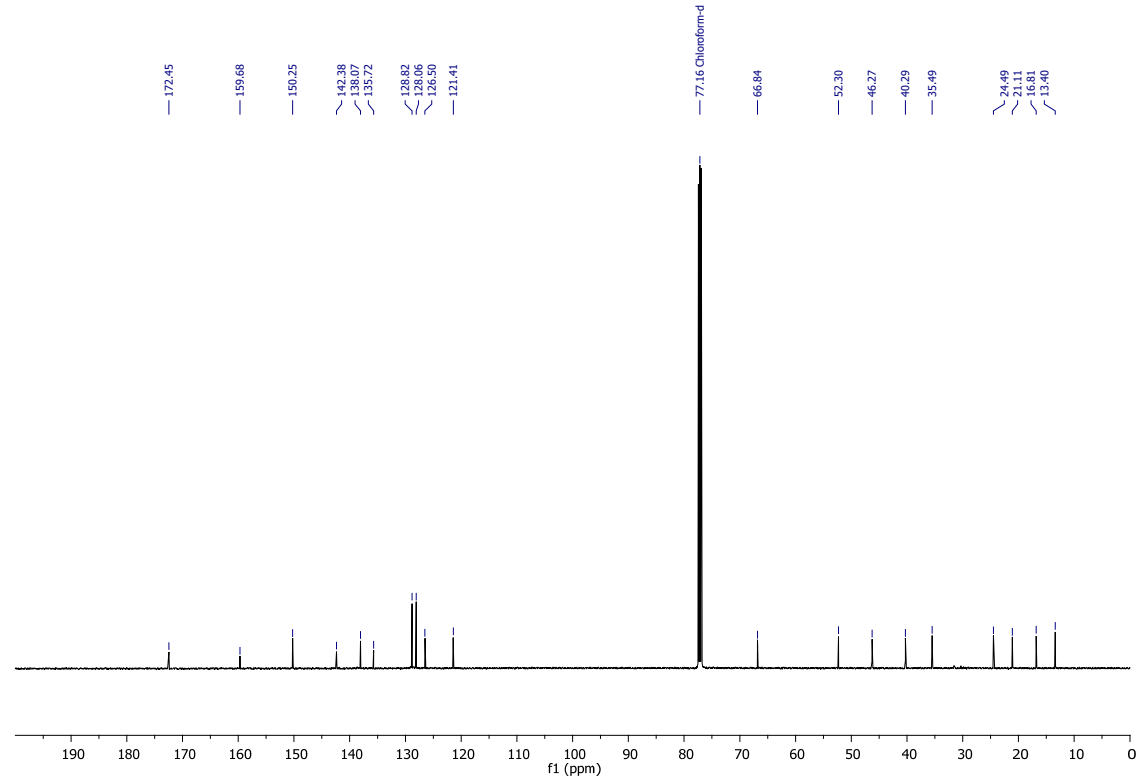


**(2*S*,3*S*)-Methyl 2-propyl-2-(pyridine-2-sulfonamido)-4-(*p*-tolyl)pentanoate (γ-16)**

$^{1}$H NMR ($CDCl_3$, 500 MHz)

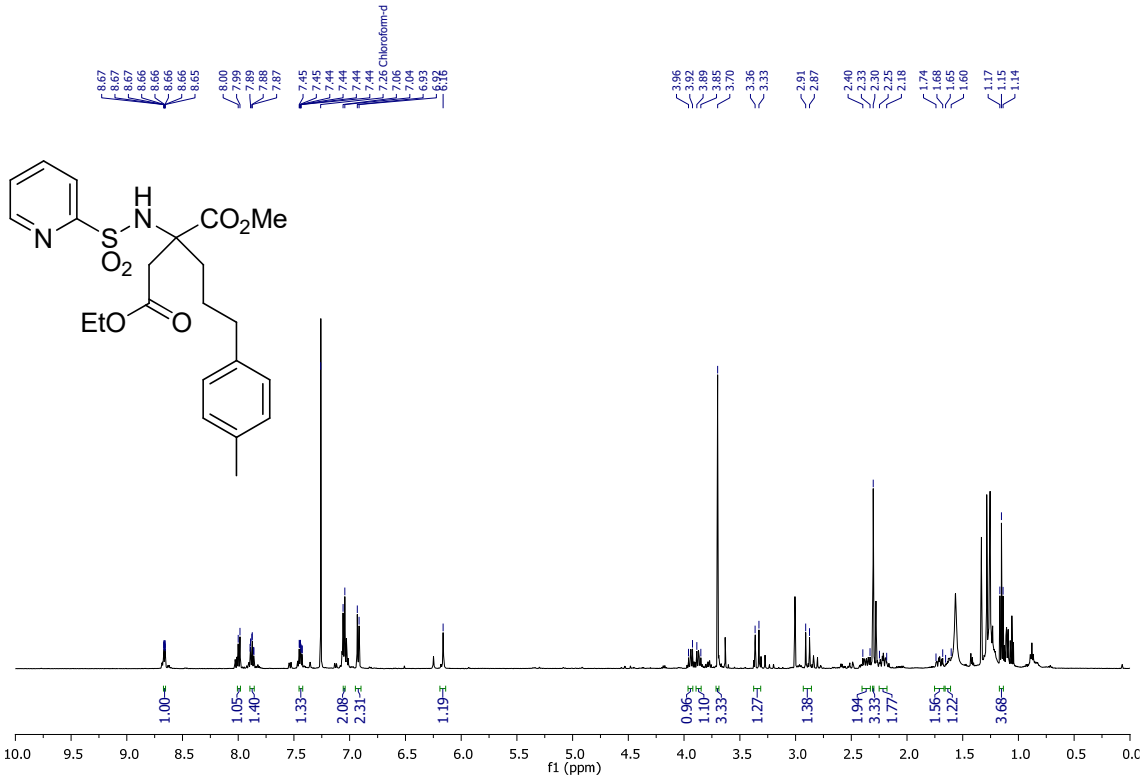



$^{13}$C NMR ($CDCl_3$, 126 MHz)

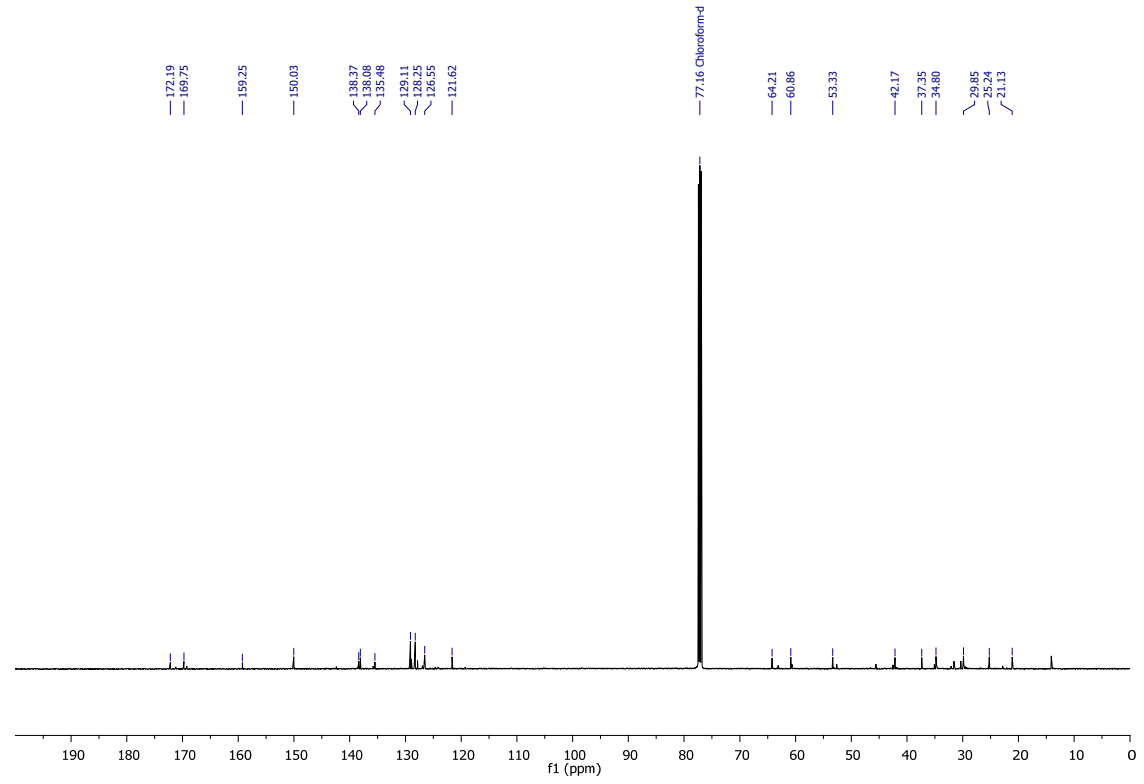


**(*rac*)-4-Ethyl 1-methyl 2-(pyridine-2-sulfonamido)-2-(3-(*p*-tolyl)propyl)succinate (17)**

$^{1}$H NMR ($CDCl_3$, 500 MHz)

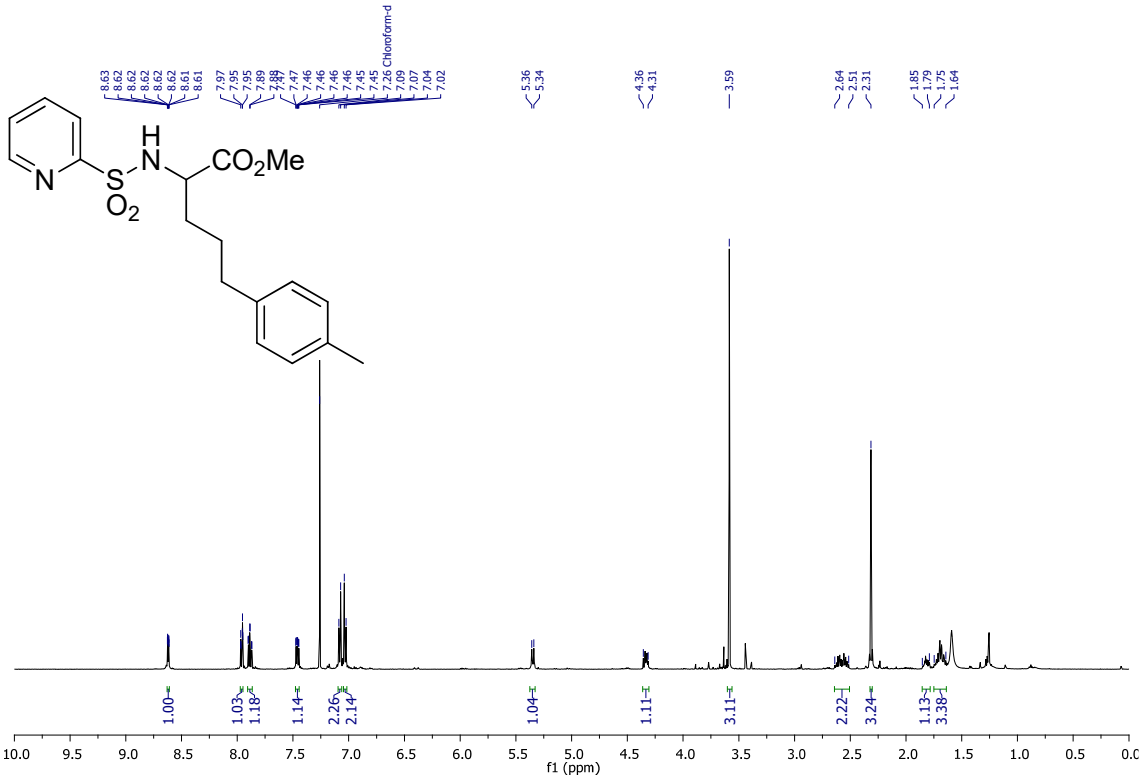



$^{13}$C NMR ($CDCl_3$, 126 MHz)

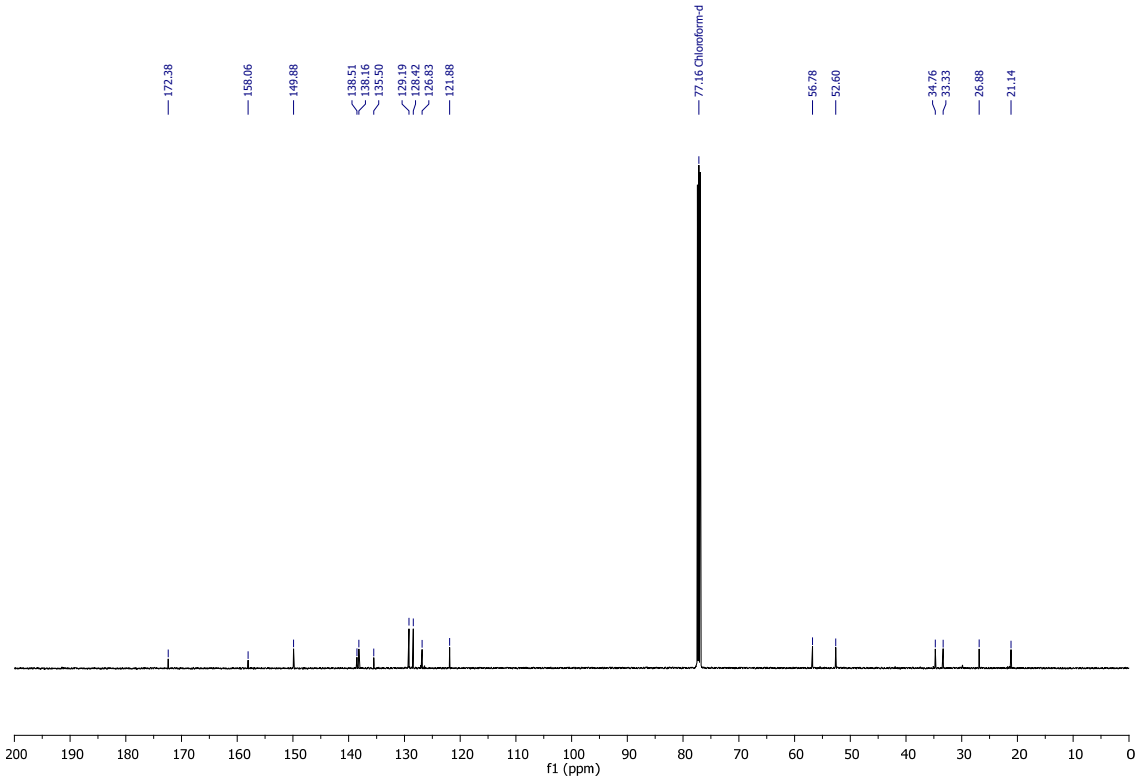


## (*rac*)-Methyl 2-(pyridine-2-sulfonamido)-5-(*p*-tolyl)pentanoate (18)

$^{1}$H NMR ($CDCl_3$, 500 MHz)

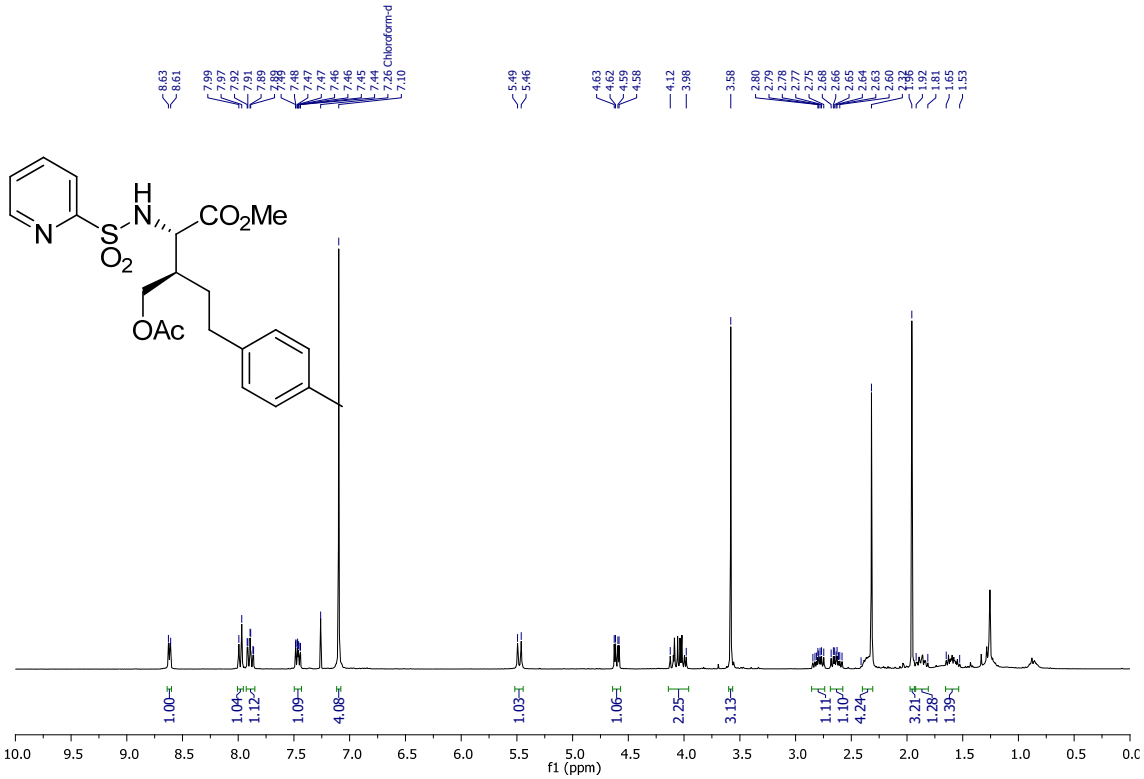



$^{13}$C NMR ($CDCl_3$, 126 MHz)

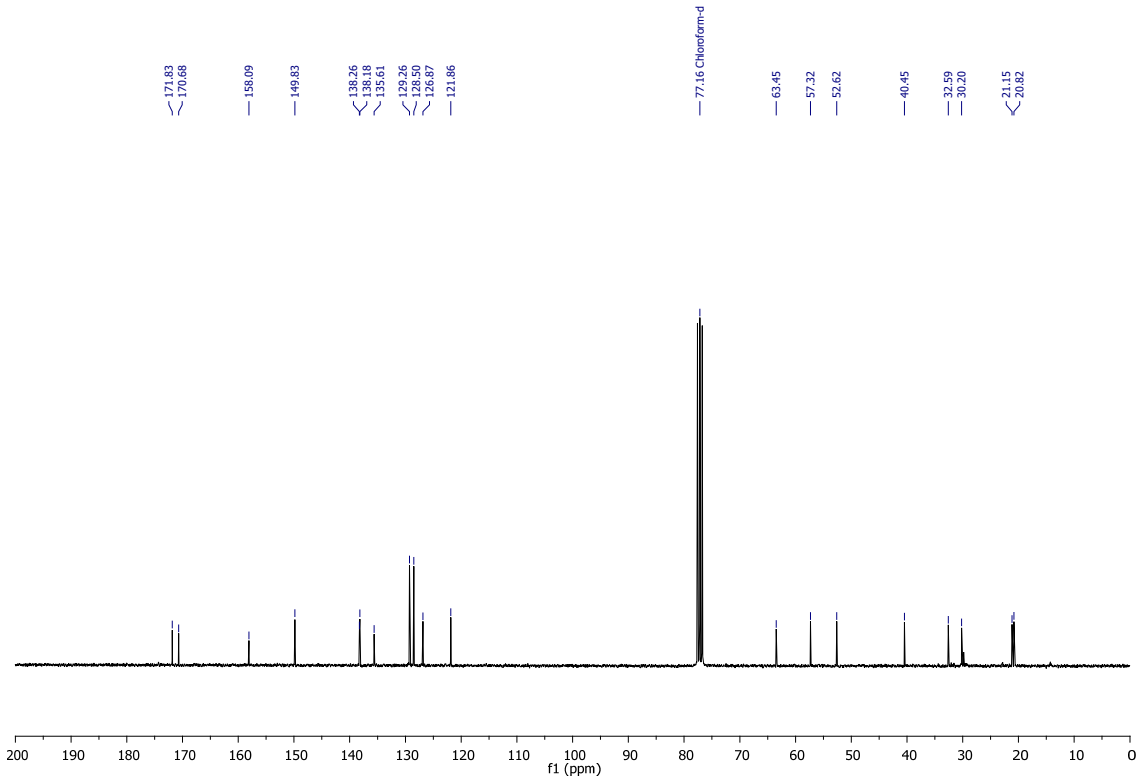


**(2*S**,3*R**)-Methyl 3-(acetoxymethyl)-2-(pyridine-2-sulfonamido)-5-(*p*-tolyl) pentanoate (19)**

$^{1}$H NMR ($CDCl_3$, 300 MHz)

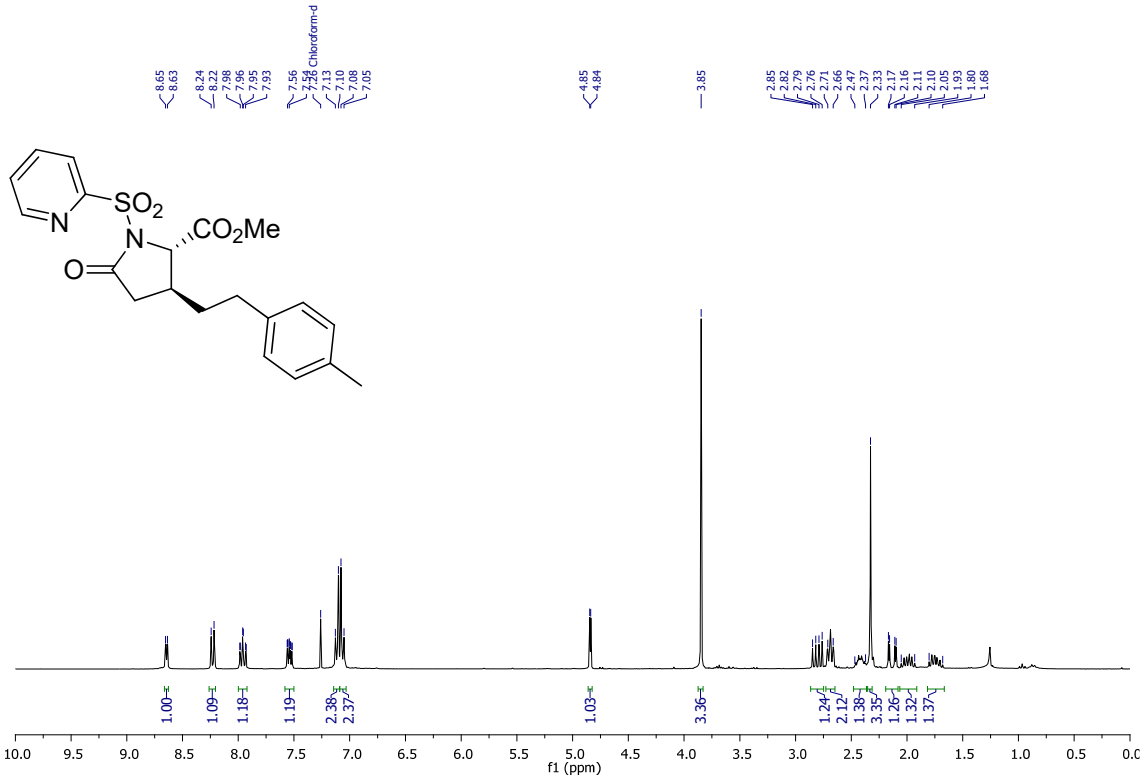



$^{13}$C NMR ($CDCl_3$, 75 MHz)

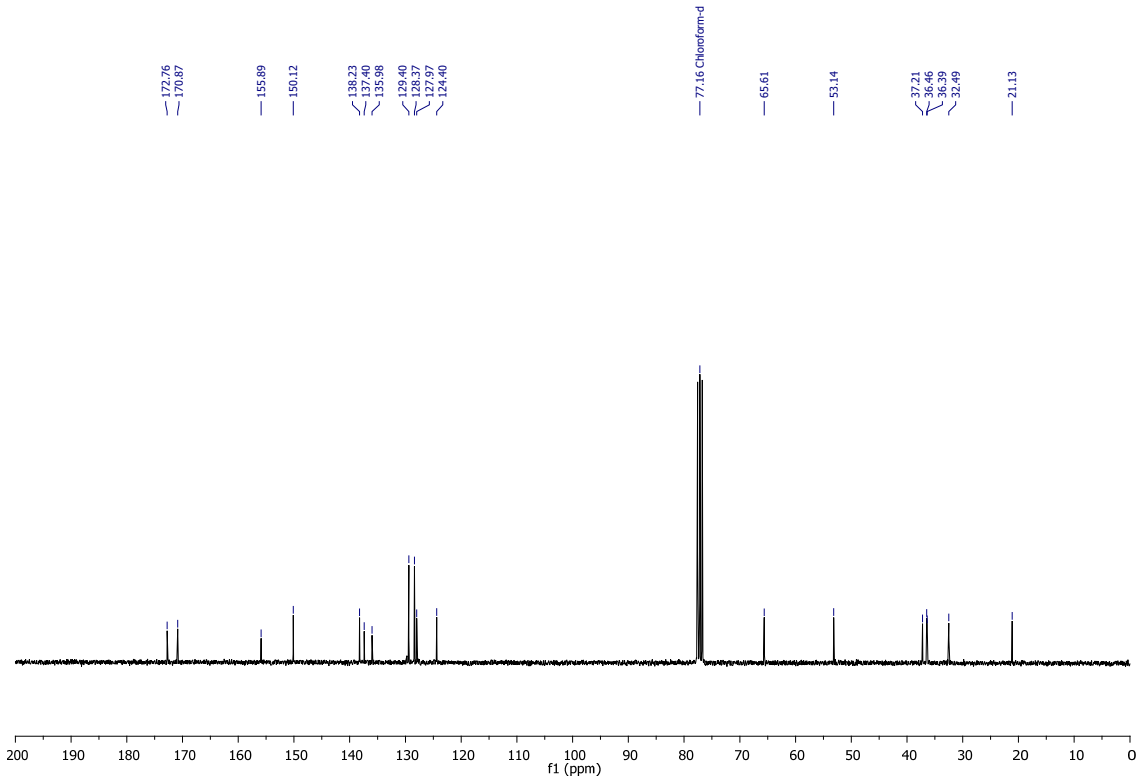


**(2*S**,3*R**)-Methyl 3-(4-methylphenethyl)-5-oxo-1-(pyridin-2-ylsulfonyl)pyrrolidine-2-carboxylate (20)**

$^{1}$H NMR ($CDCl_3$, 300 MHz)

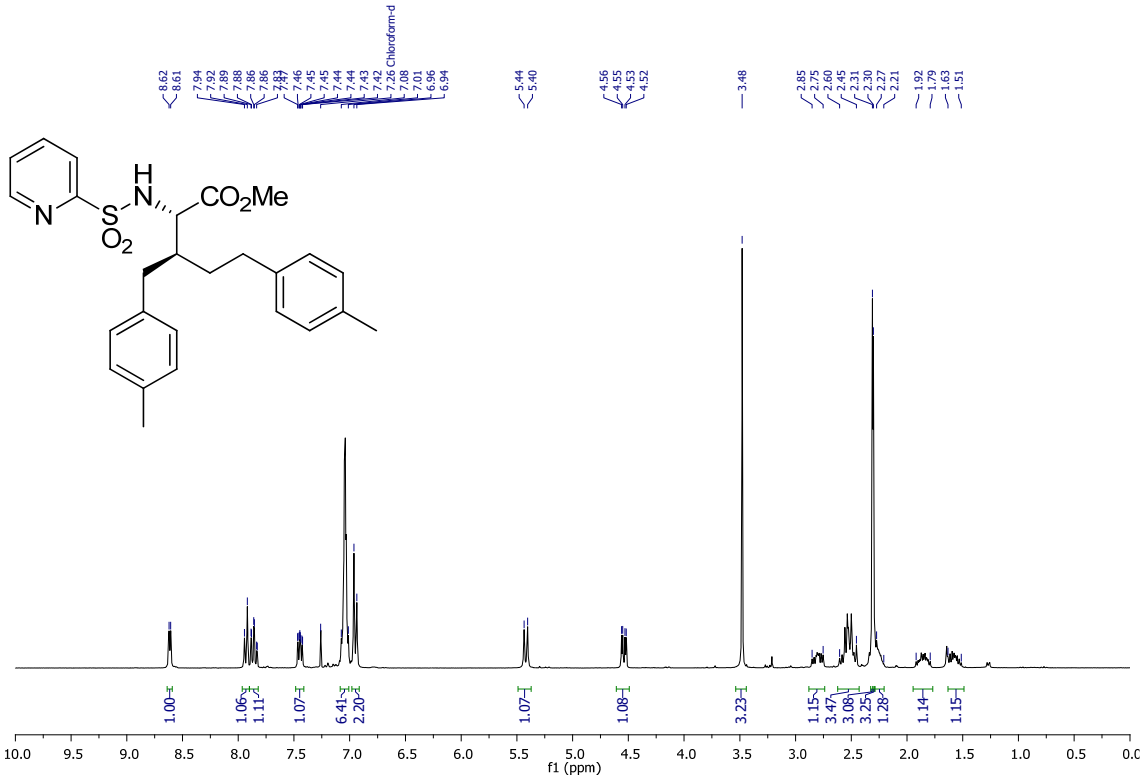



$^{13}$C NMR ($CDCl_3$, 75 MHz)

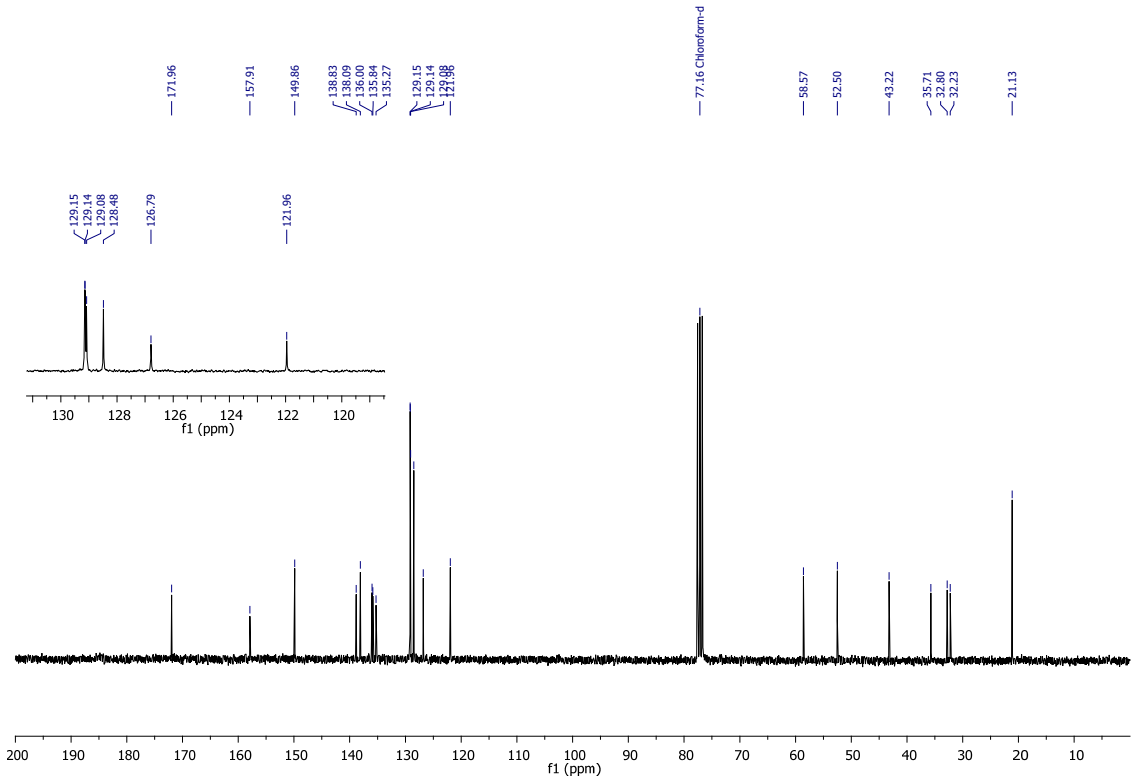


**(2*S**,3*S**)-Methyl 3-(4-methylbenzyl)-2-(pyridine-2-sulfonamido)-5-(*p*-tolyl) pentanoate (21)**

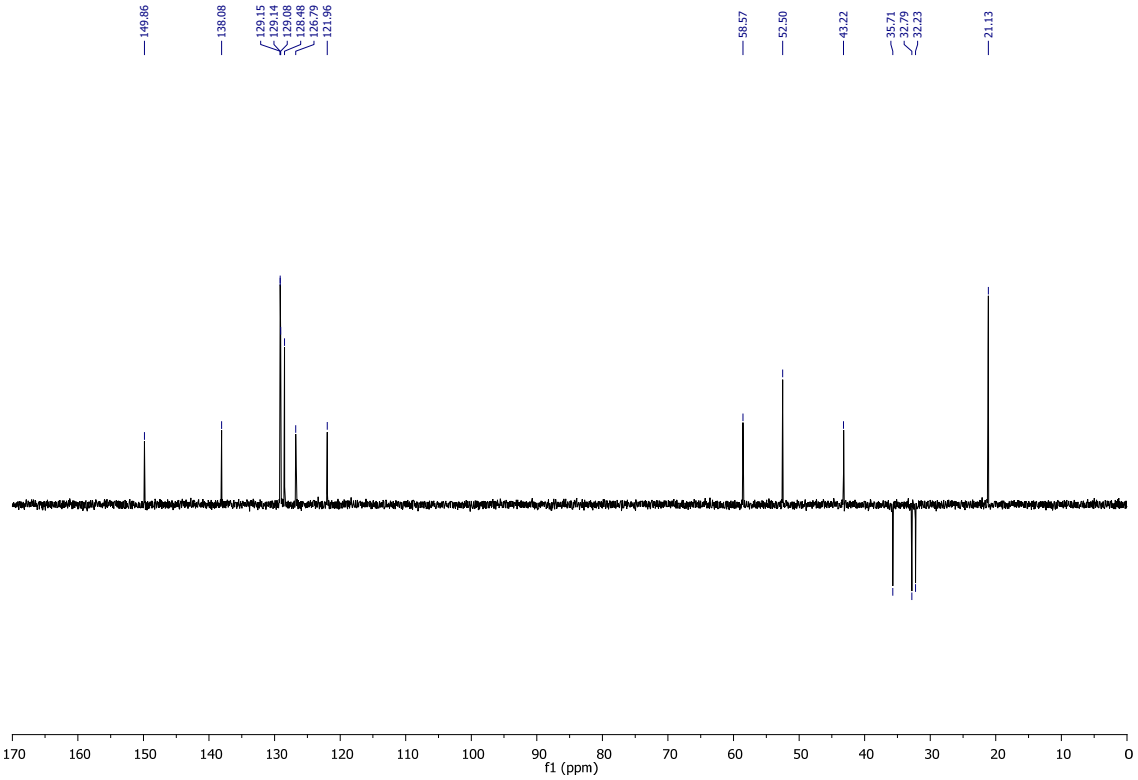
$^{1}$H NMR ($CDCl_3$, 300 MHz)




$^{13}$C NMR ($CDCl_3$, 75 MHz)

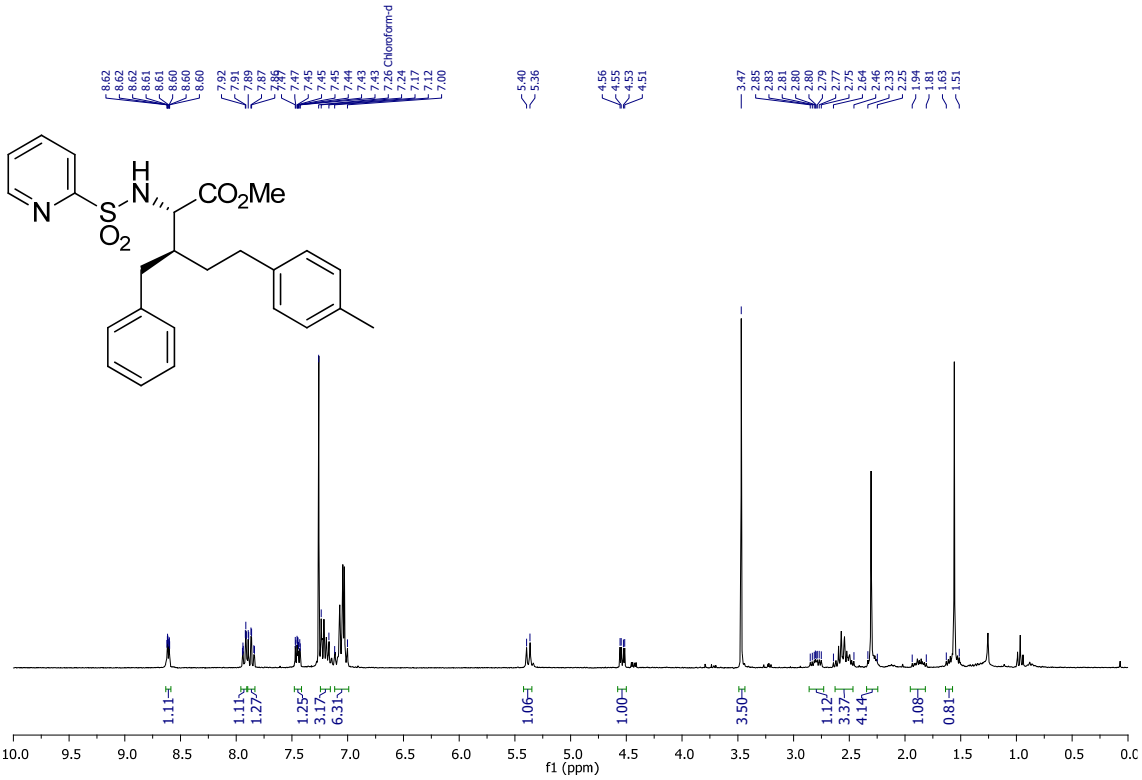


$^{13}$C NMR-DEPT-135 ($CDCl_3$, 75 MHz)

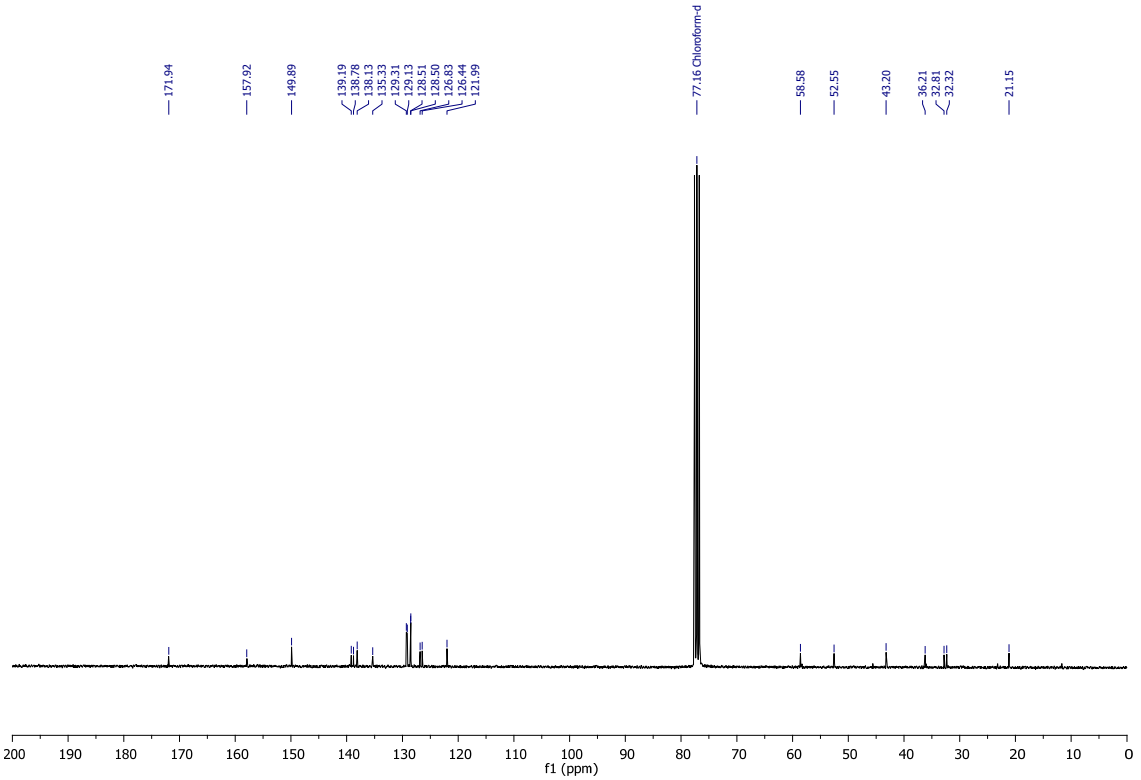


**(2*S**,3*S**)-Methyl 3-benzyl-2-(pyridine-2-sulfonamido)-5-(*p*-tolyl)pentanoate (22)**

$^{1}$H NMR ($CDCl_3$, 300 MHz)

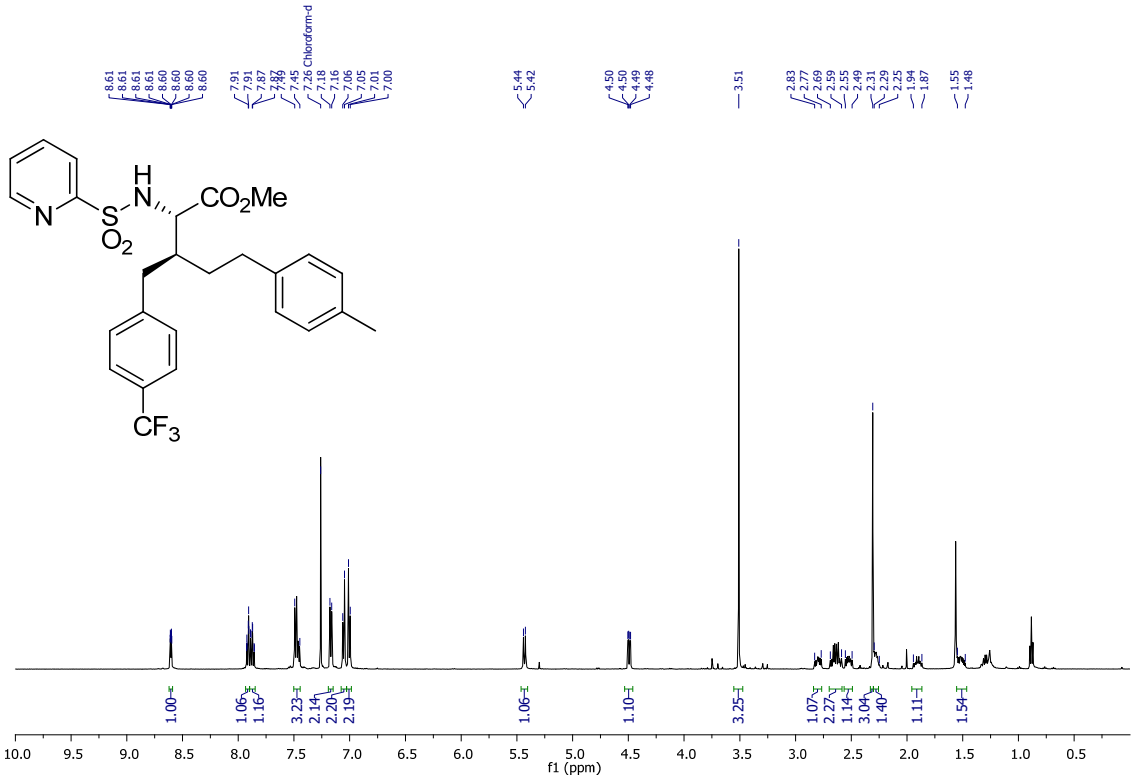



$^{13}$C NMR ($CDCl_3$, 75 MHz)

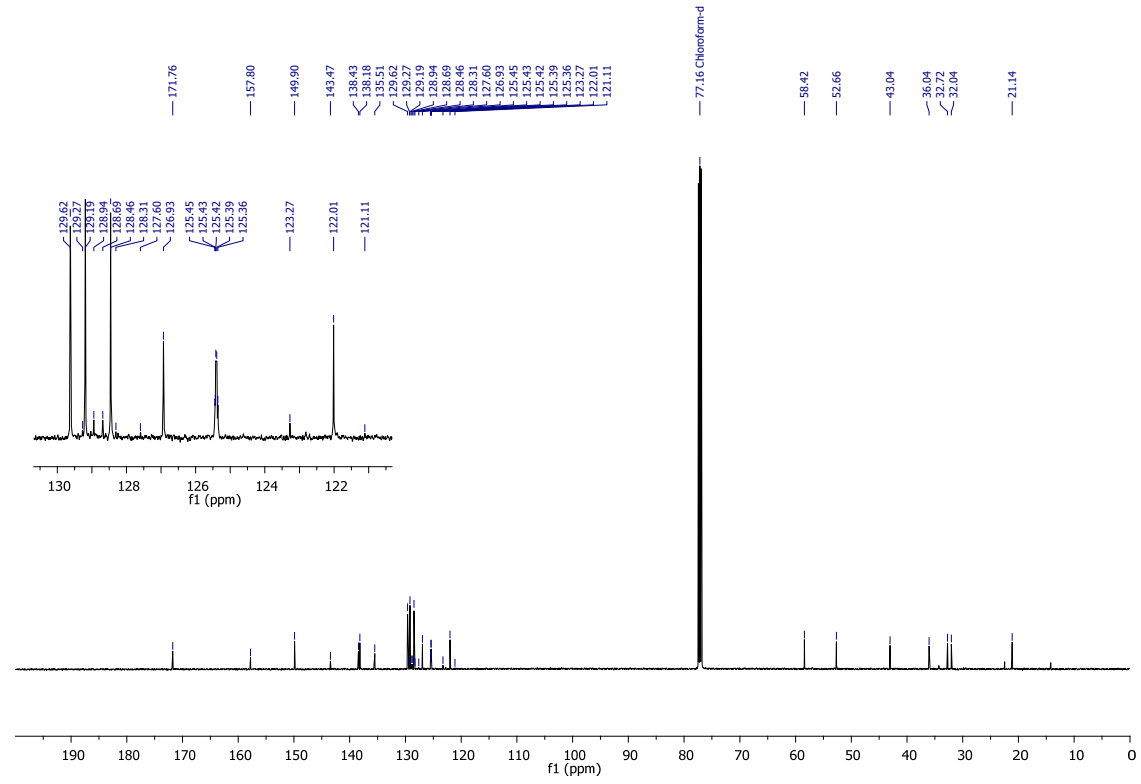


**(2*S**,3*S**)-Methyl 2-(pyridine-2-sulfonamido)-5-(*p*-tolyl)-3-(4-(trifluoromethyl) benzyl)pentanoate (23)**

$^{1}$H NMR ($CDCl_3$, 500 MHz)

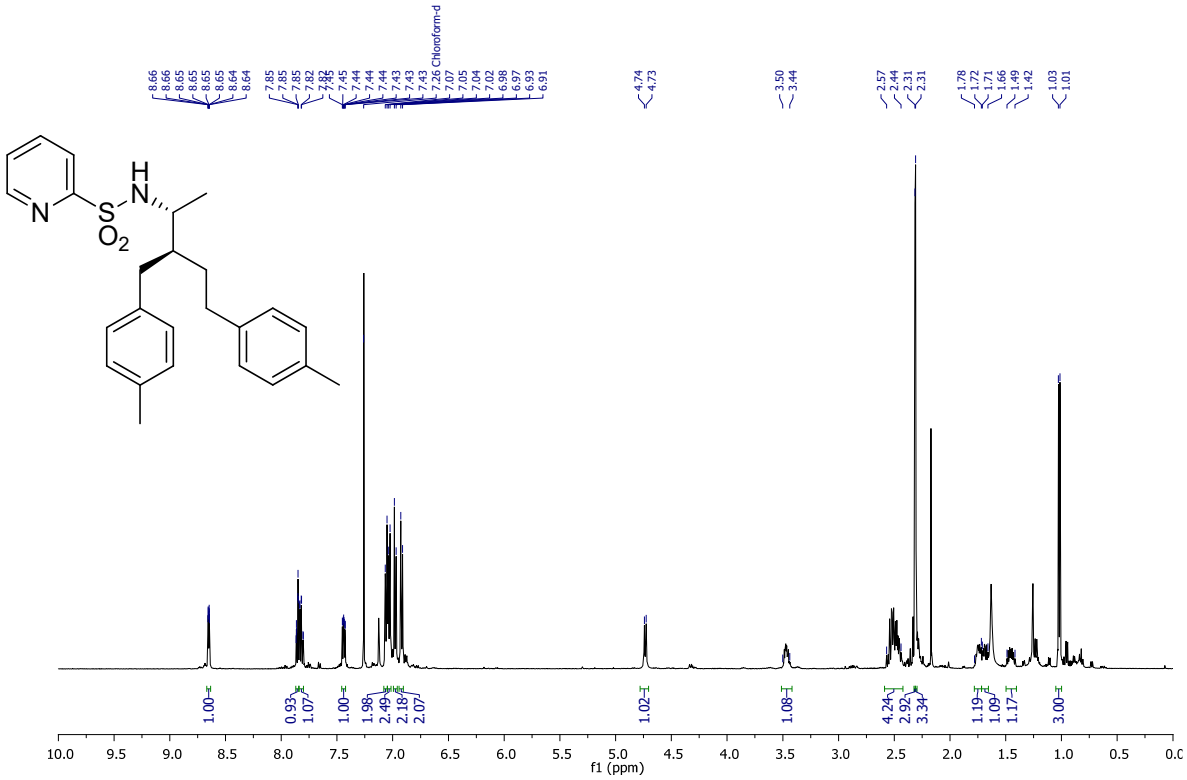



$^{13}$C NMR ($CDCl_3$, 126 MHz)

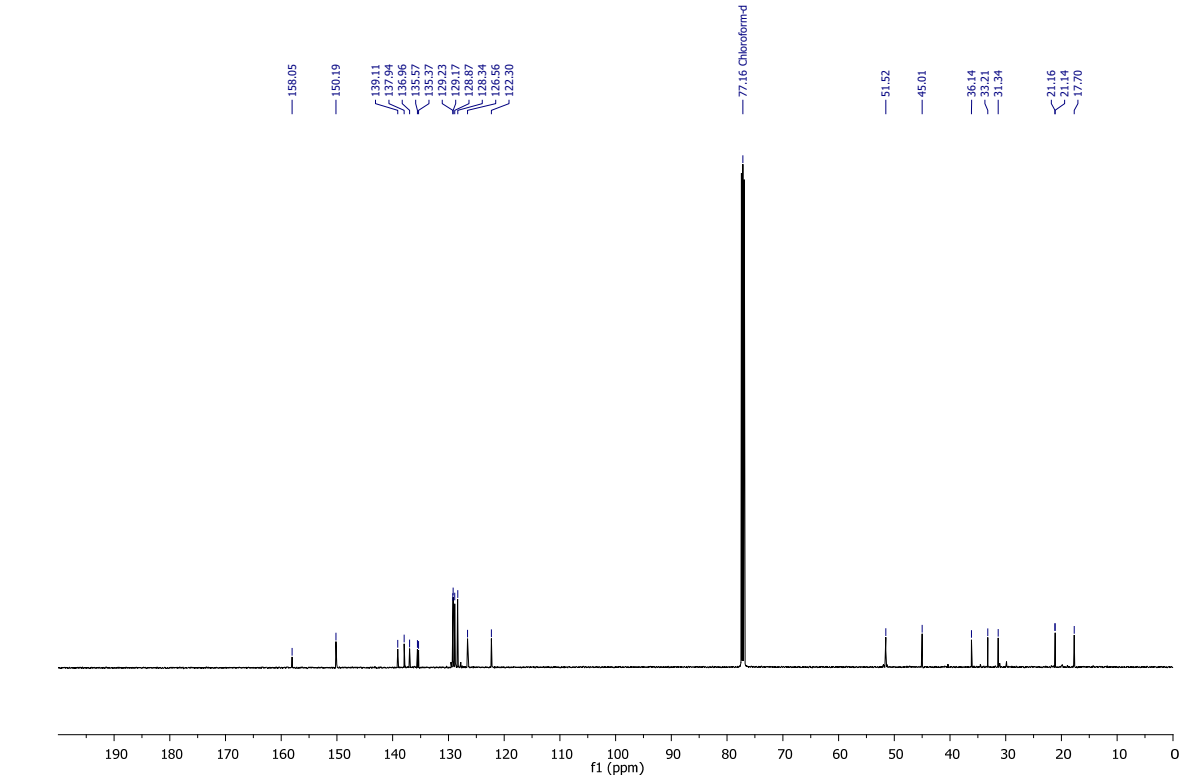


***N*-((2*R**,3*S**)-3-(4-Methylbenzyl)-5-(*p*-tolyl)pentan-2-yl)pyridine-2-sulfonamide (24)**

$^{1}$H NMR ($CDCl_3$, 500 MHz)

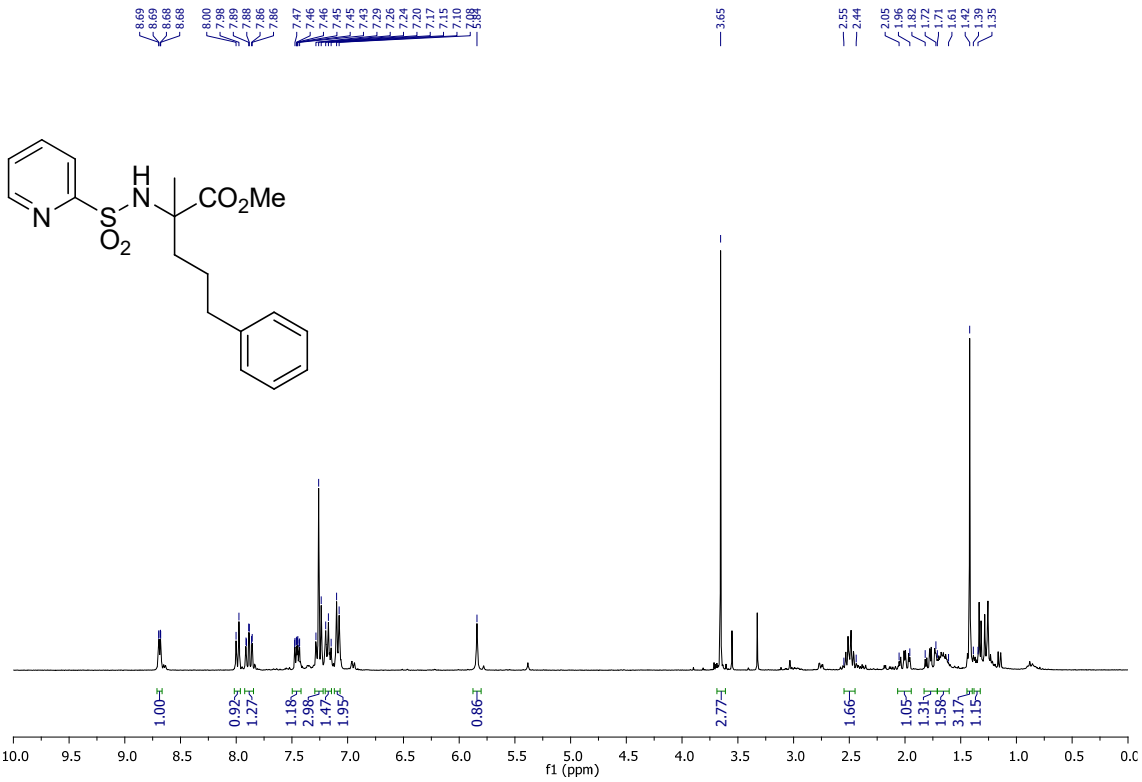



$^{13}$C NMR ($CDCl_3$, 126 MHz)

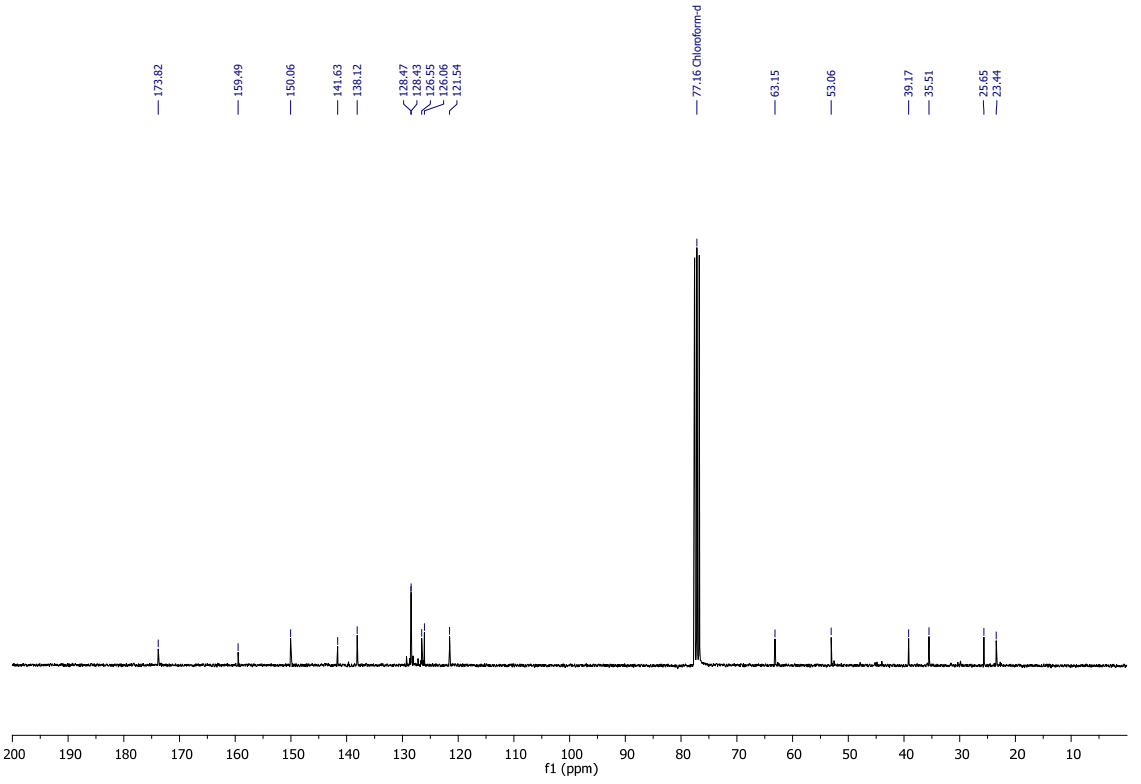


**(*rac*)-Methyl 2-methyl-5-phenyl-2-(pyridine-2-sulfonamido)pentanoate (26)**

$^{1}$H NMR ($CDCl_3$, 300 MHz)

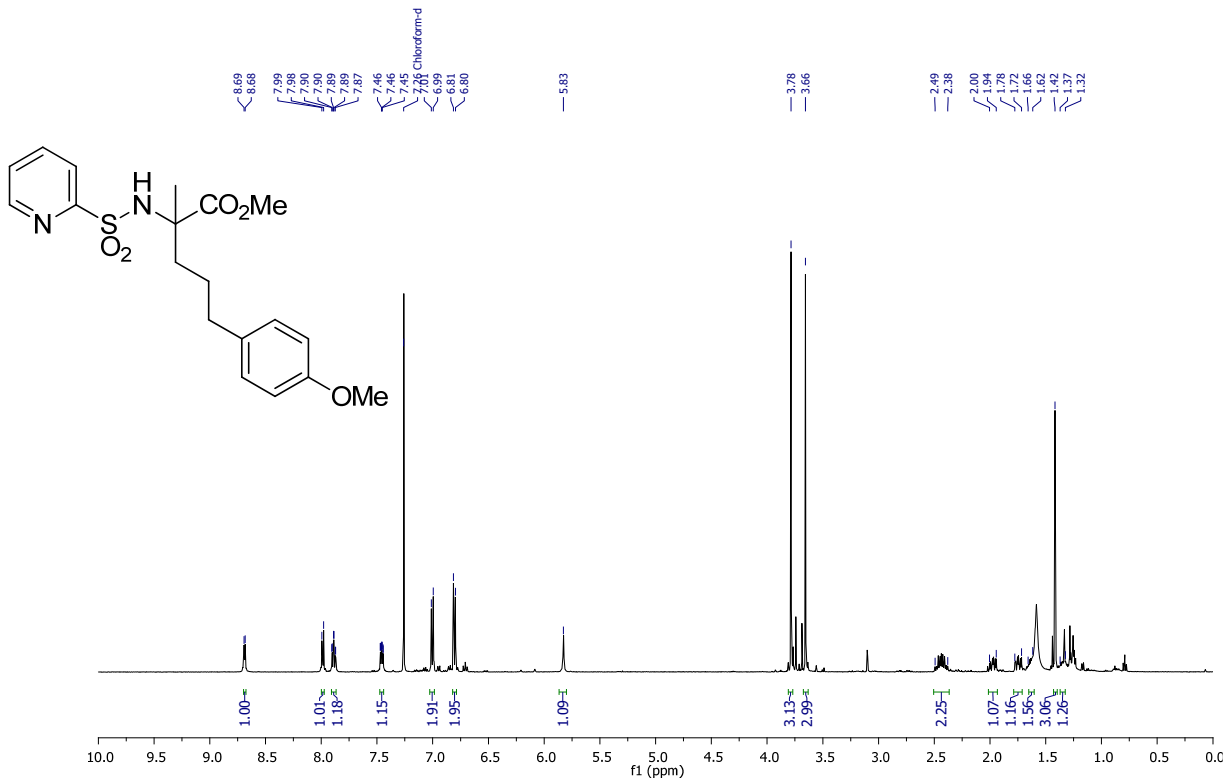



$^{13}$C NMR ($CDCl_3$, 75 MHz)

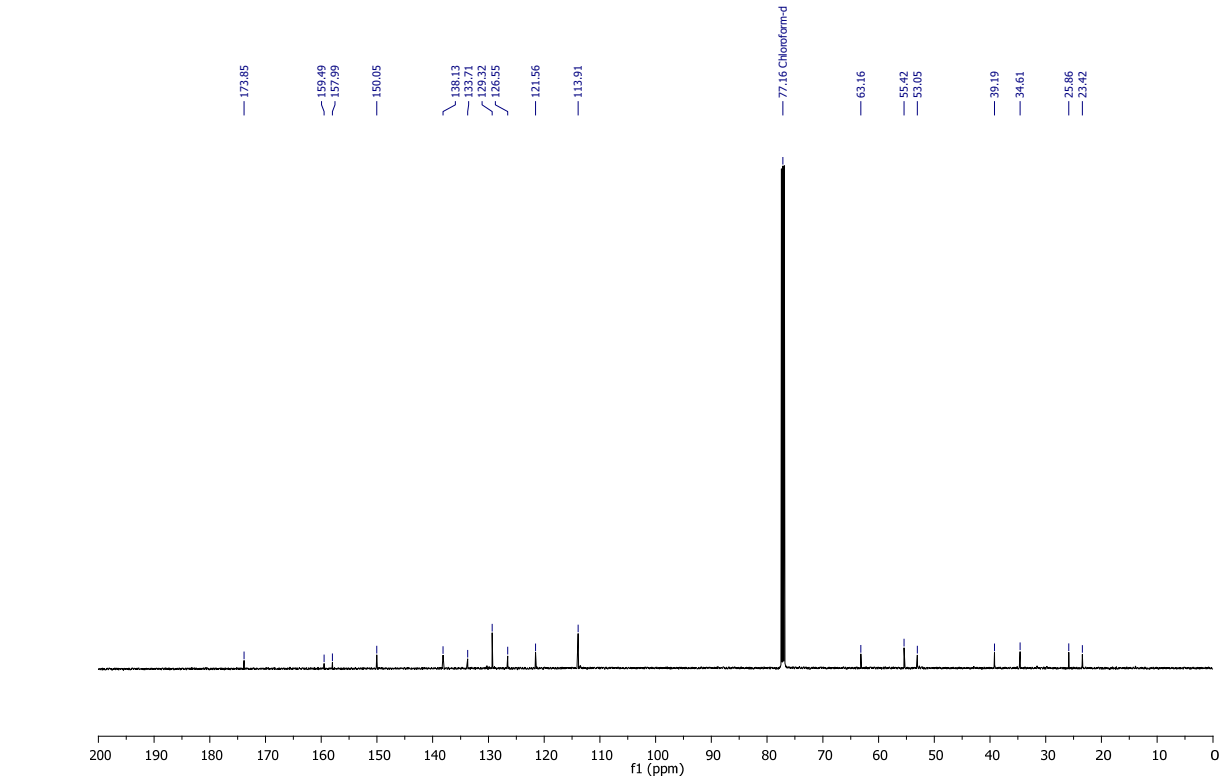


**(*rac*)-Methyl 5-(4-methoxyphenyl)-2-methyl-2-(pyridine-2-sulfonamido)pentanoate (27)**

$^{1}$H NMR ($CDCl_3$, 500 MHz)

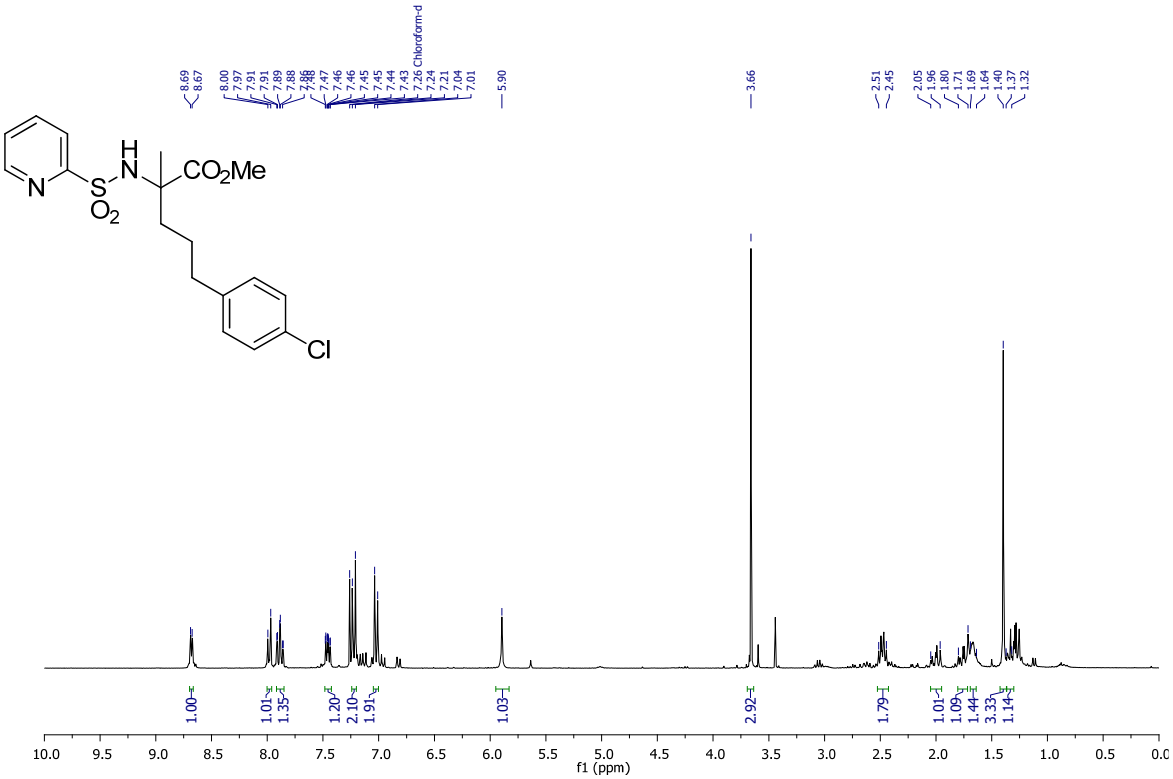



$^{13}$C NMR ($CDCl_3$, 126 MHz)

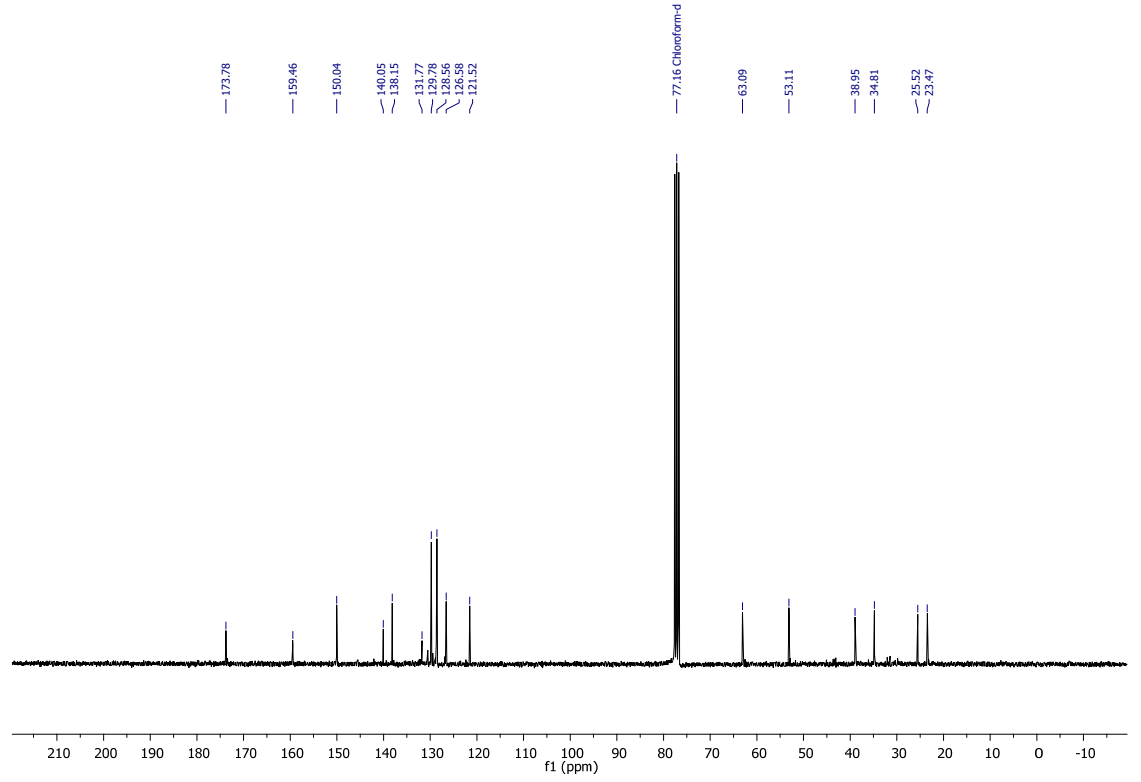


**(*rac*)-Methyl 5-(4-chlorophenyl)-2-methyl-2-(pyridine-2-sulfonamido)pentanoate (28)**

$^{1}$H NMR ($CDCl_3$, 300 MHz)

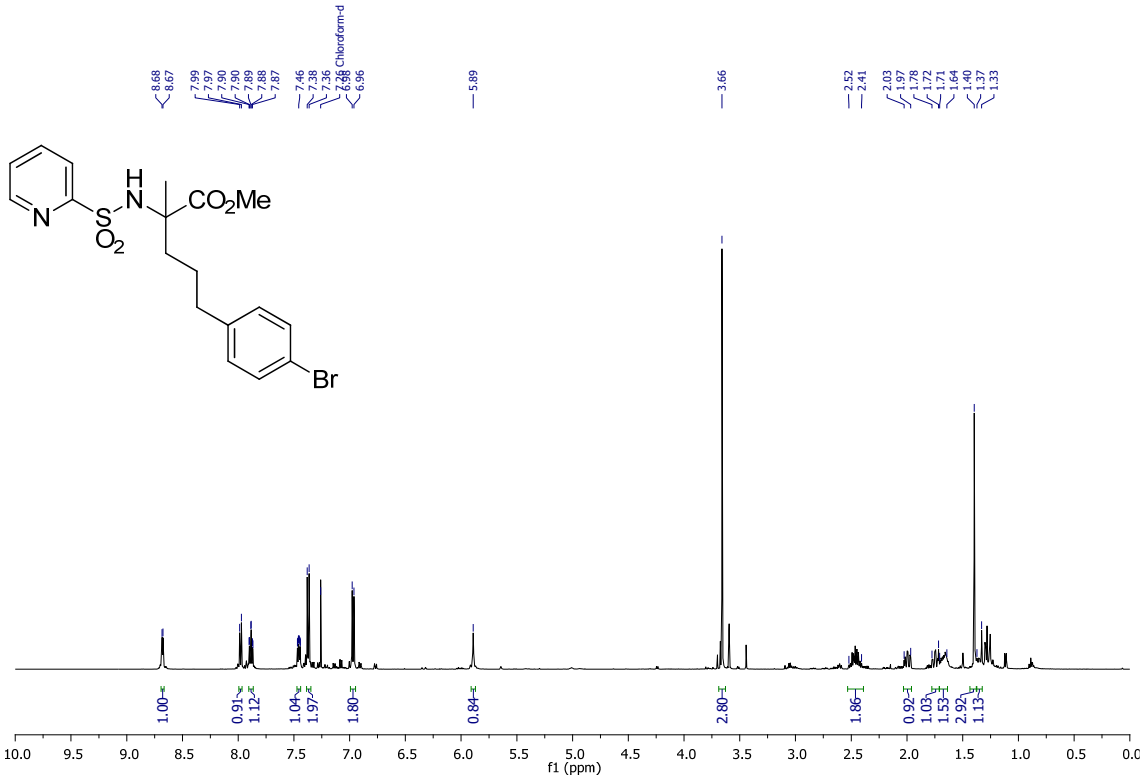



$^{13}$C NMR ($CDCl_3$, 75 MHz)

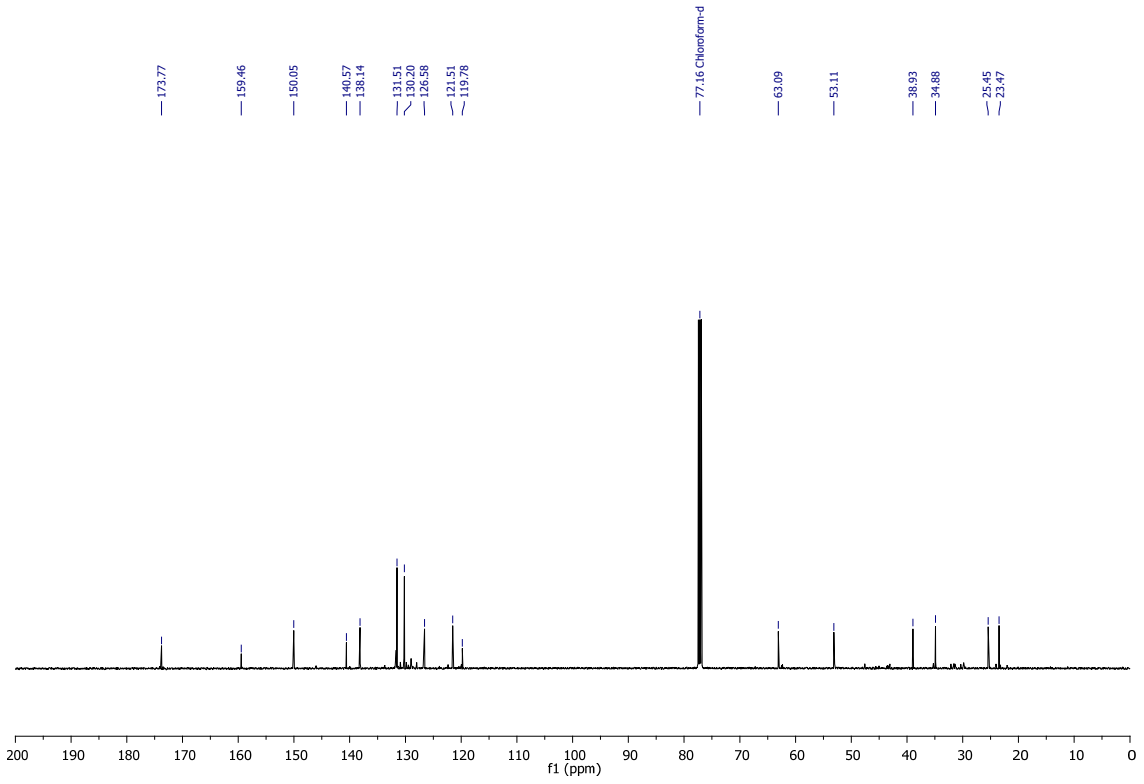


**(*rac*)-Methyl 5-(4-bromophenyl)-2-methyl-2-(pyridine-2-sulfonamido)pentanoate (29)**

$^{1}$H NMR ($CDCl_3$, 500 MHz)

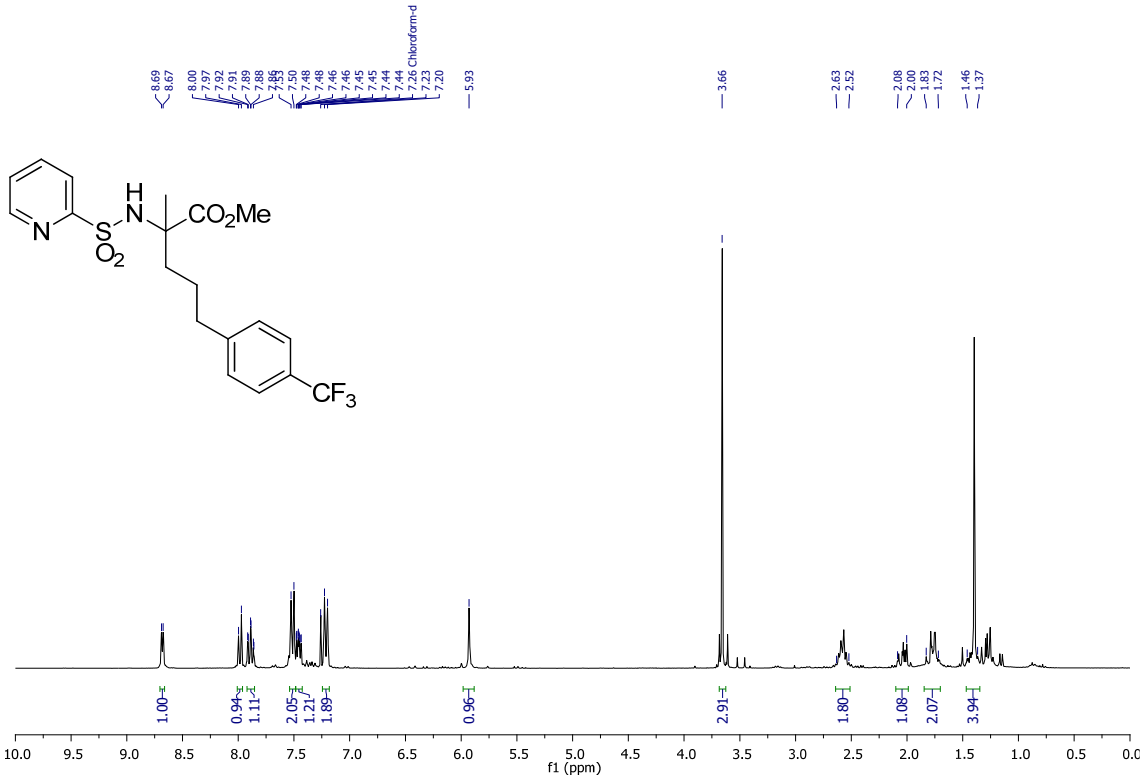



$^{13}$C NMR ($CDCl_3$, 126 MHz)

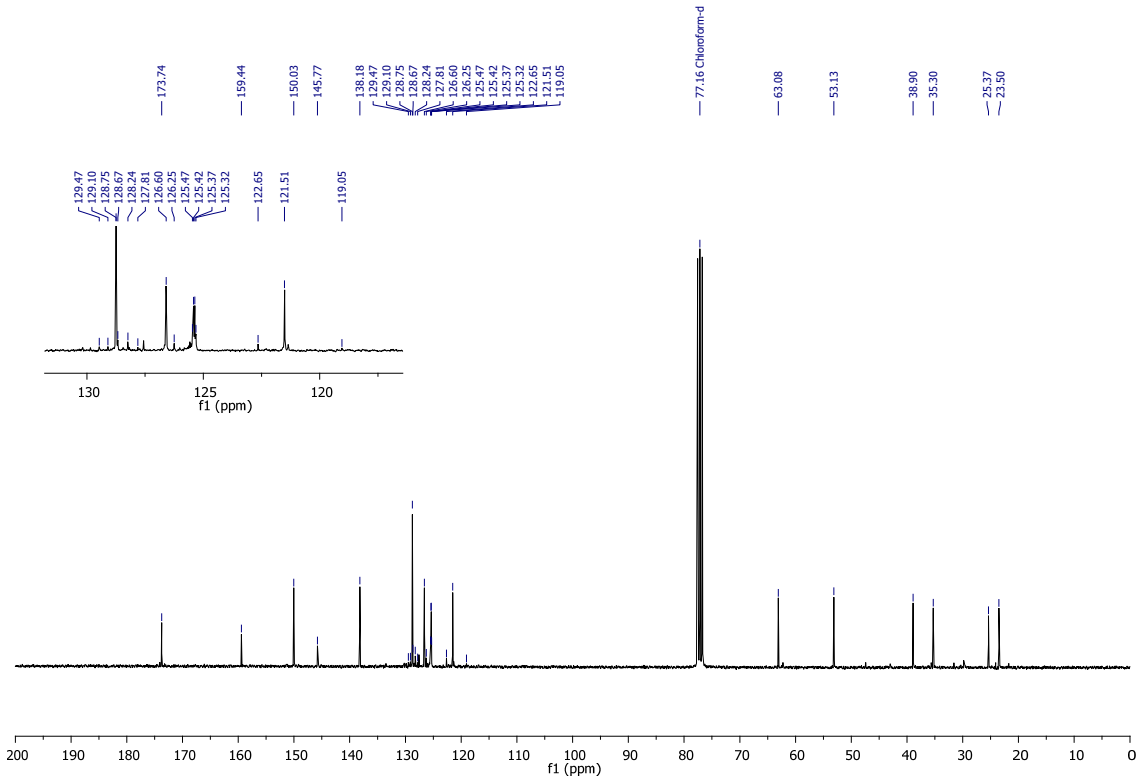


**(*rac*)-Methyl 2-methyl-2-(pyridine-2-sulfonamido)-5-(4-trifluoromethyl) phenyl)pentanoate (30)**

$^{1}$H NMR ($CDCl_3$, 300 MHz)

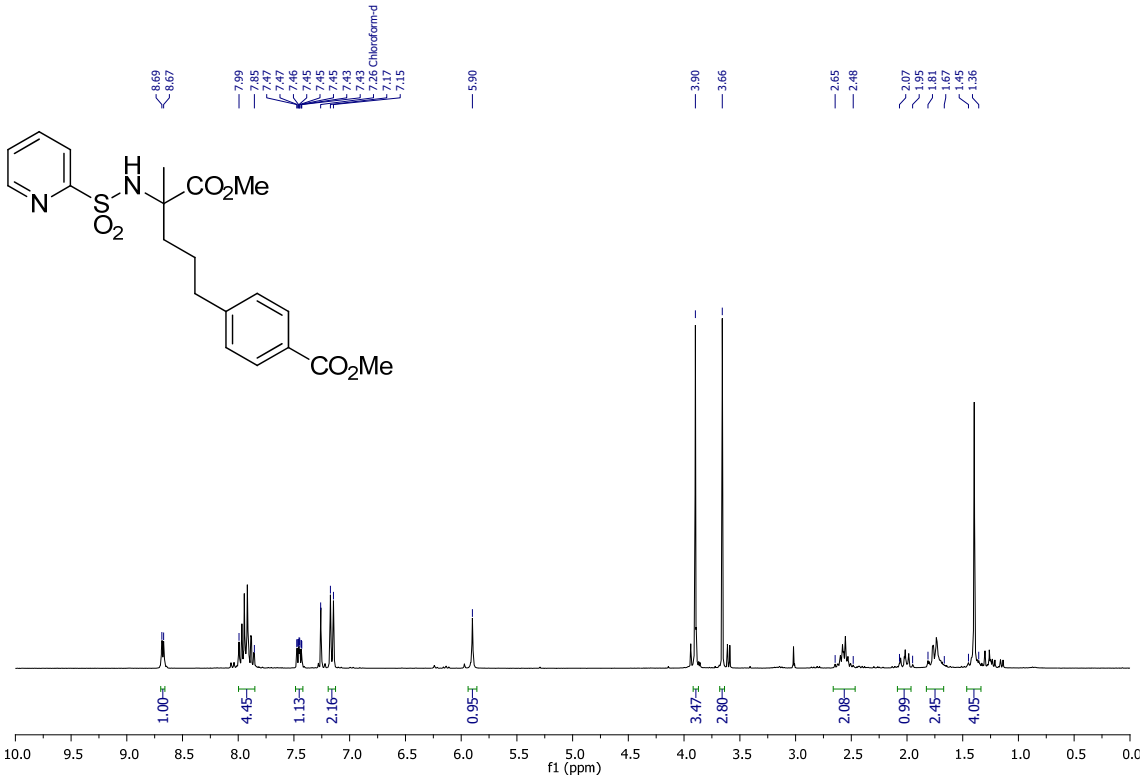



$^{13}$C NMR ($CDCl_3$, 75 MHz)

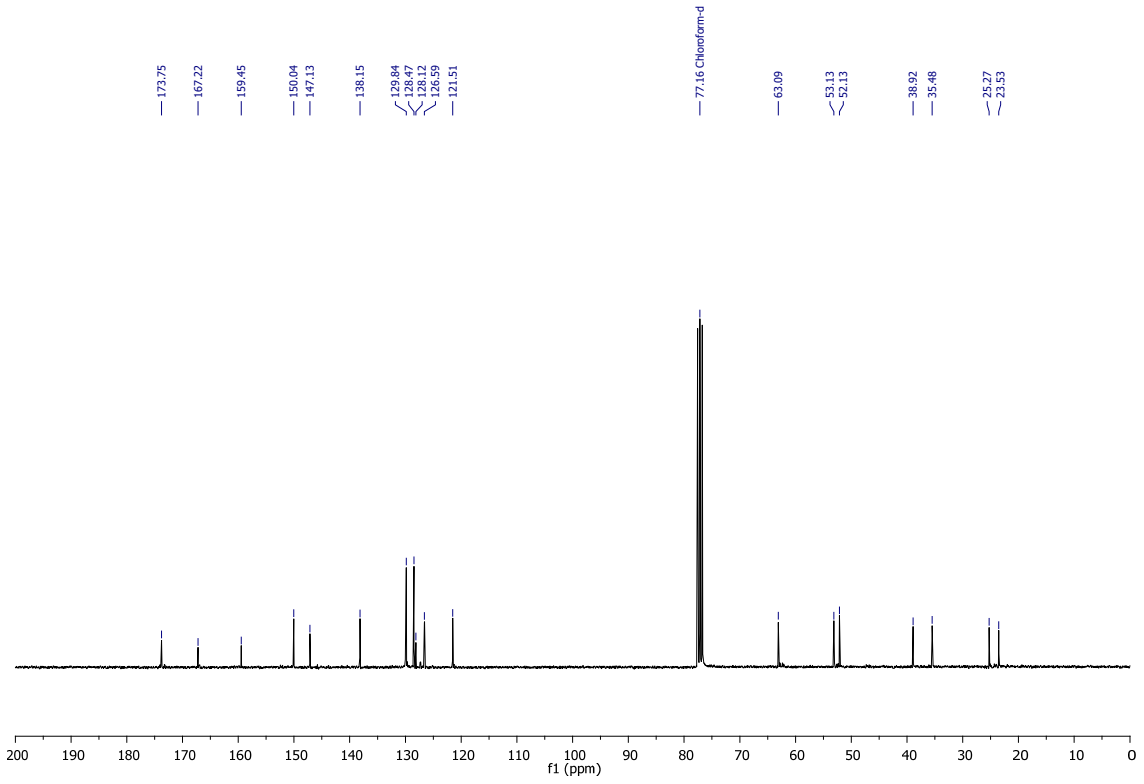


**(*rac*)-Methyl 4-(5-methoxy-4-methyl-5-oxo-4-(pyridine-2-sulfonamido)pentyl) benzoate (31)**

$^{1}$H NMR ($CDCl_3$, 300 MHz)

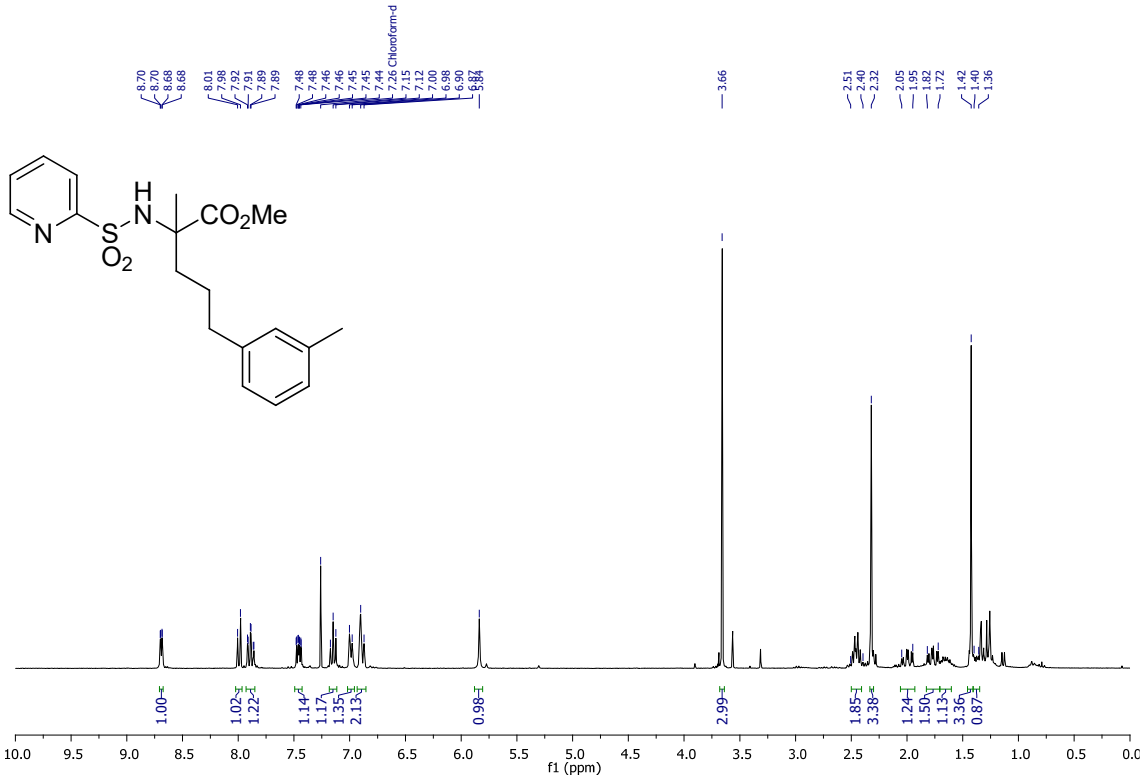



$^{13}$C NMR ($CDCl_3$, 75 MHz)

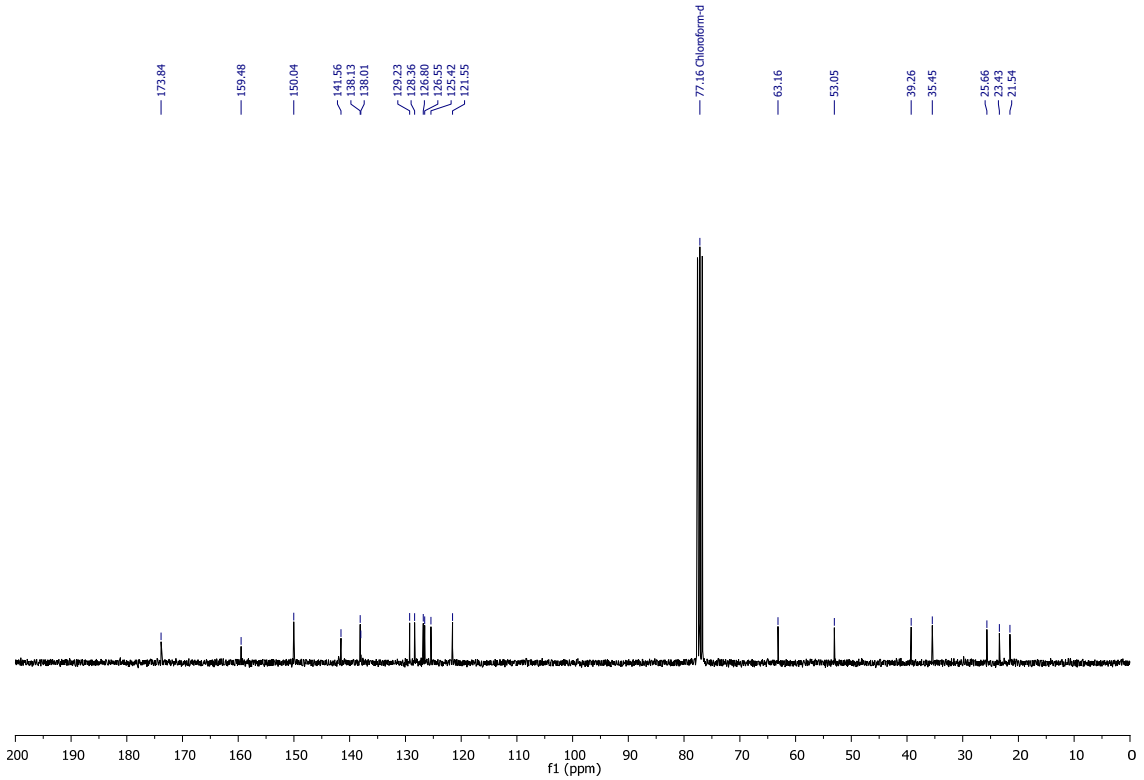


**(*rac*)-Methyl 2-methyl-2-(pyridine-2-sulfonamido)-5-(*m*-tolyl)pentanoate (32)**

$^{1}$H NMR ($CDCl_3$, 300 MHz)

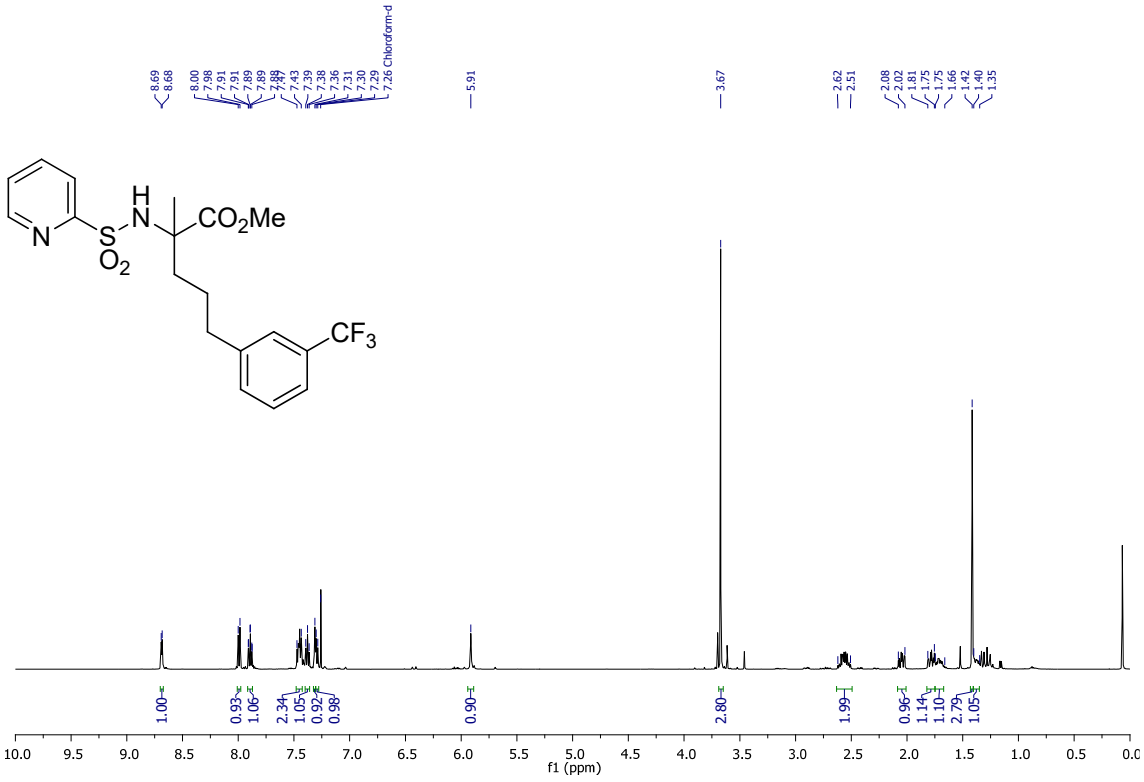



$^{13}$C NMR ($CDCl_3$, 75 MHz)

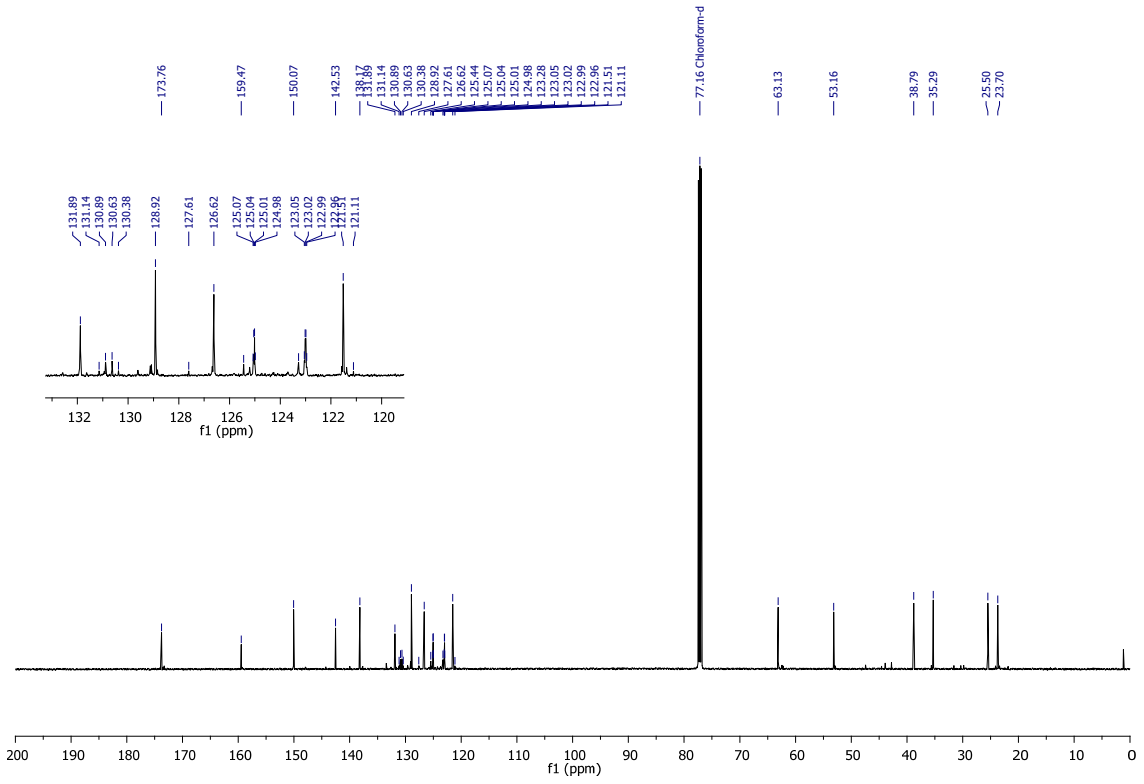


**(*rac*)-Methyl 2-methyl-2-(pyridine-2-sulfonamido)-5-(3-trifluoromethyl) phenyl)pentanoate (33)**

$^{1}$H NMR ($CDCl_3$, 500 MHz)

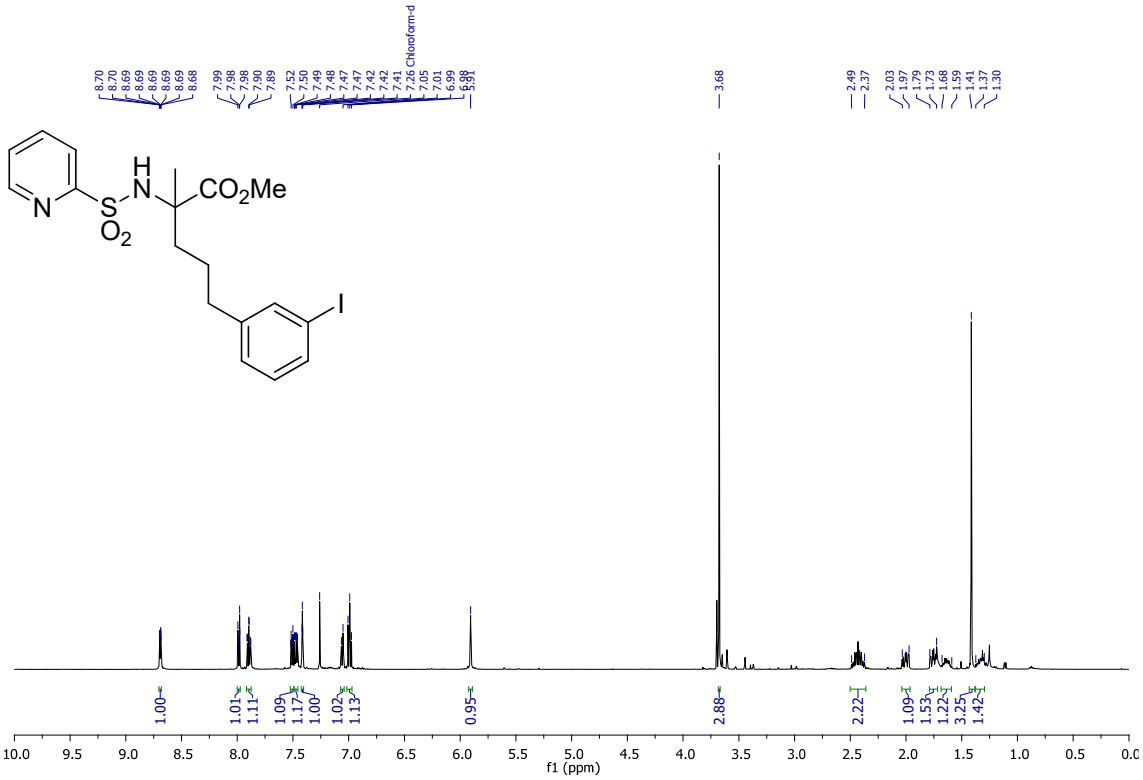



$^{13}$C NMR ($CDCl_3$, 126 MHz)

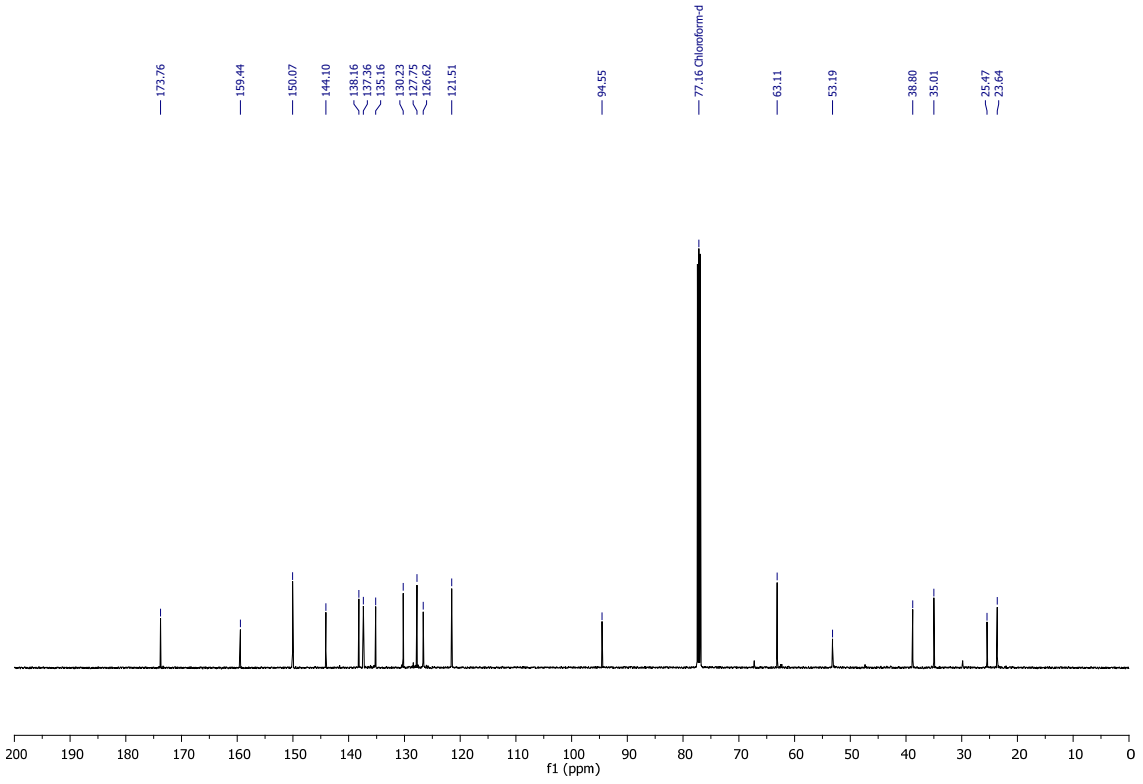


**(*rac*)-Methyl 5-(3-iodophenyl)-2-methyl-2-(pyridine-2-sulfonamido)pentanoate (34)**

$^{1}$H NMR ($CDCl_3$, 500 MHz)

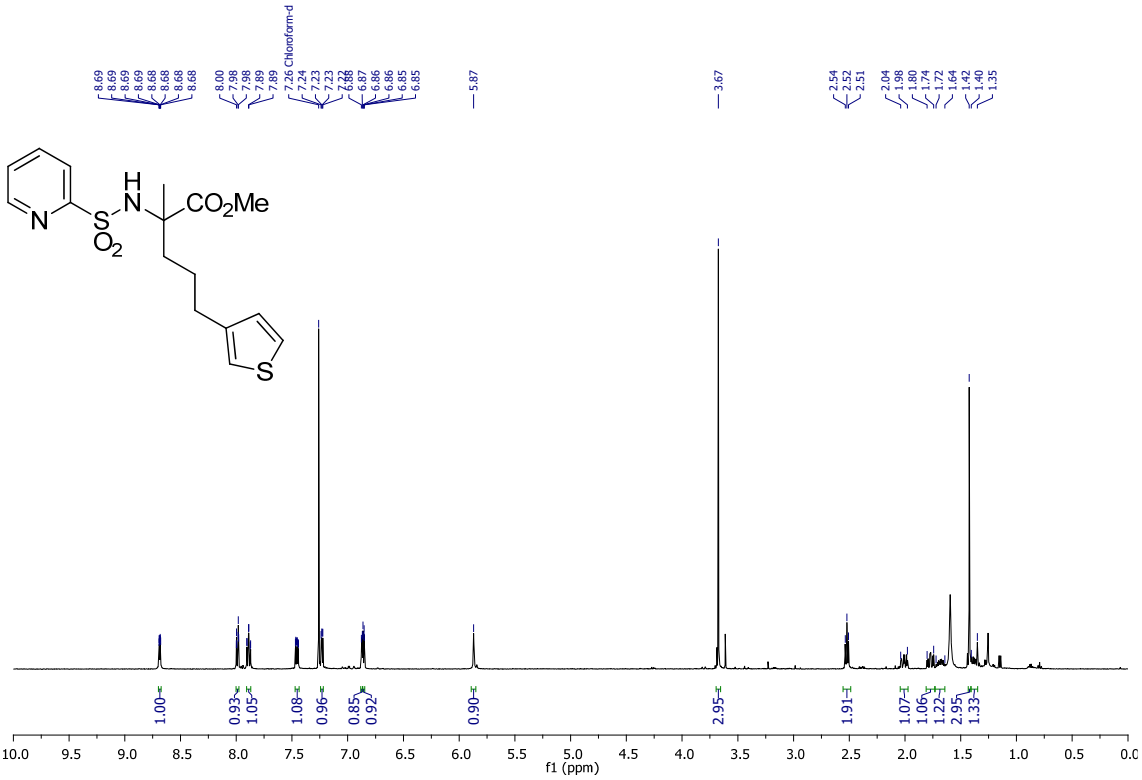



$^{13}$C NMR ($CDCl_3$, 126 MHz)

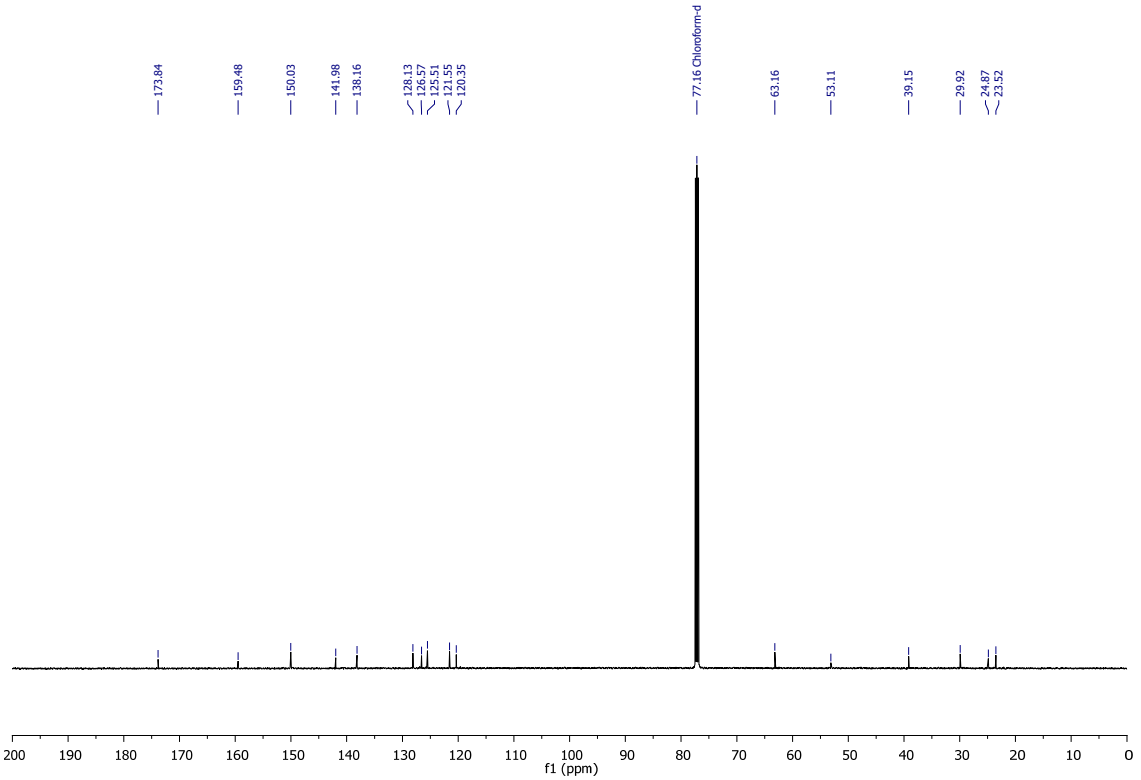


**(*rac*)-Methyl 2-methyl-2-(pyridine-2-sulfonamido)-5-(thiophen-3-yl)pentanoate (35)**

$^{1}$H NMR ($CDCl_3$, 500 MHz)

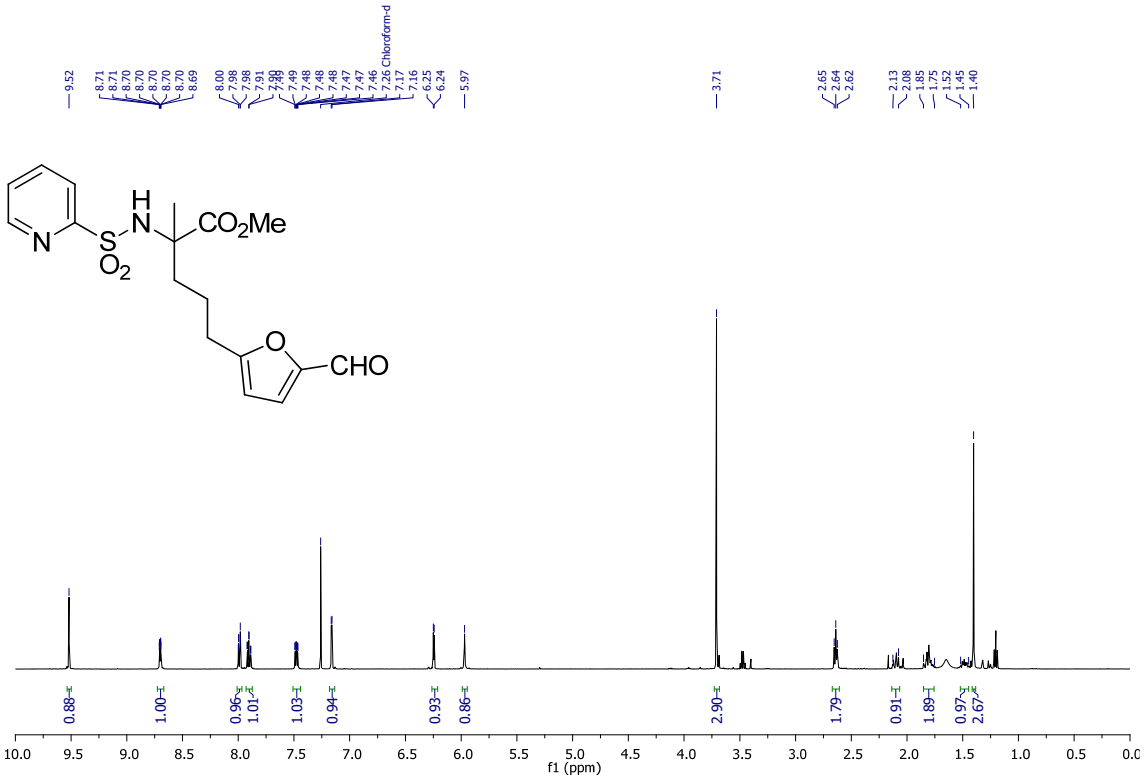



$^{13}$C NMR ($CDCl_3$, 126 MHz)

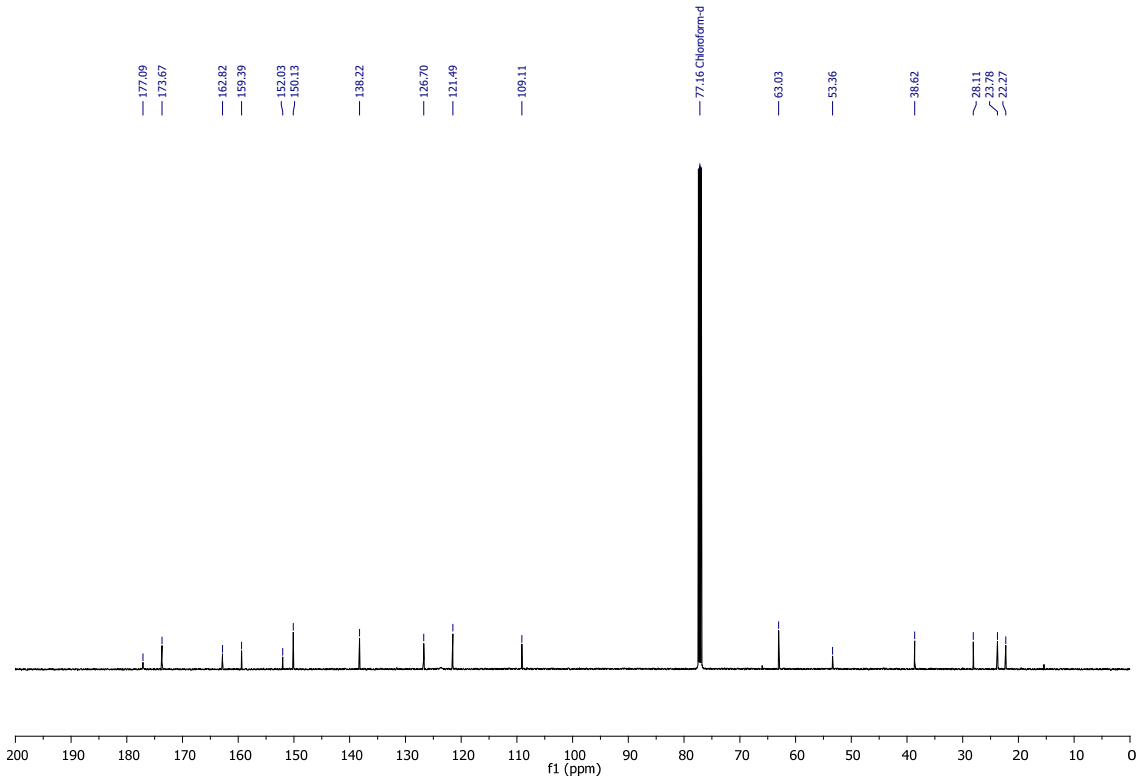


**(*rac*)-Methyl 5-(5-formylfuran-2-yl)-2-methyl-2-(pyridine-2-sulfonamido) pentanoate (36)**

$^{1}$H NMR ($CDCl_3$, 500 MHz)

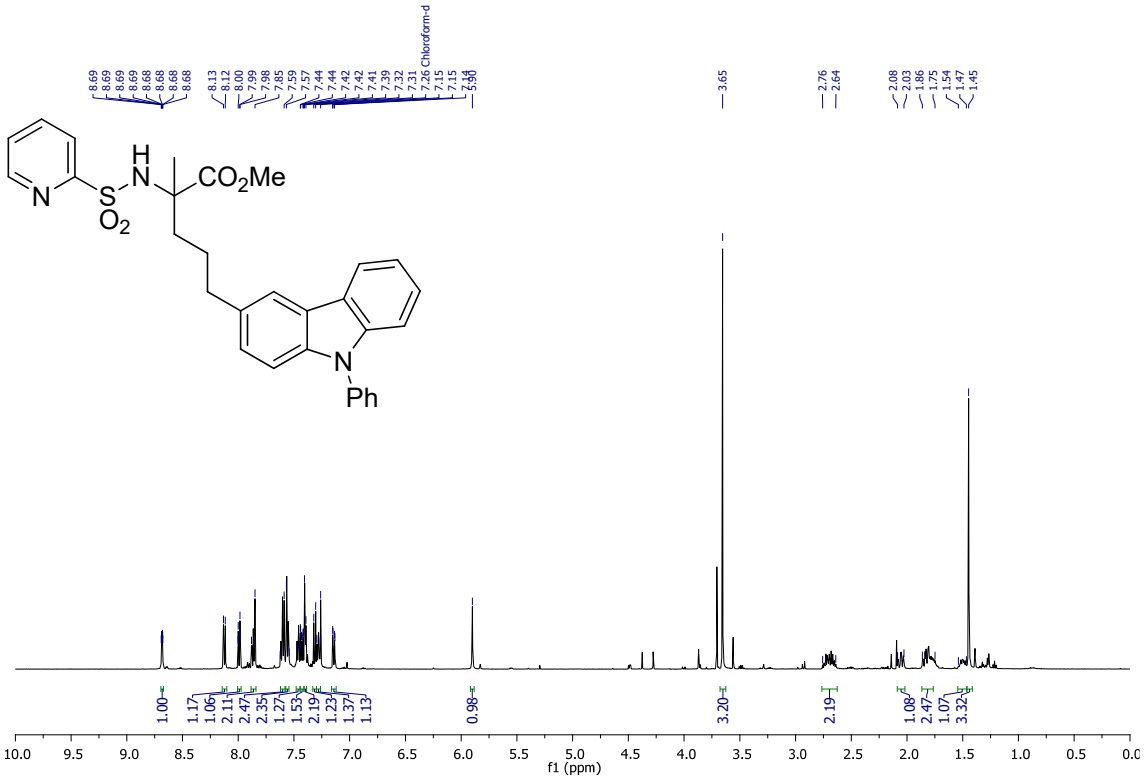



$^{13}$C NMR ($CDCl_3$, 126 MHz)

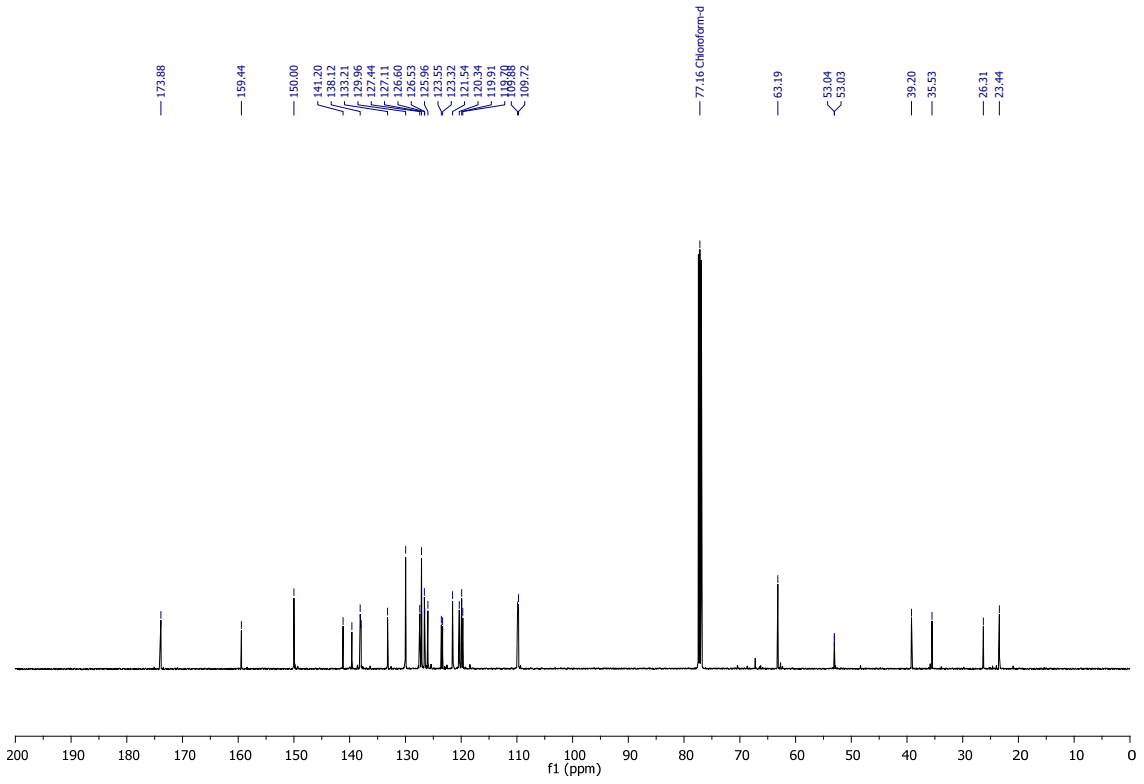


**(*rac*)-Methyl 2-methyl-5-(9-phenyl-9*H*-carbazol-3-yl)-2-(pyridine-2-sulfonamido) pentanoate (37)**

$^{1}$H NMR ($CDCl_3$, 500 MHz)

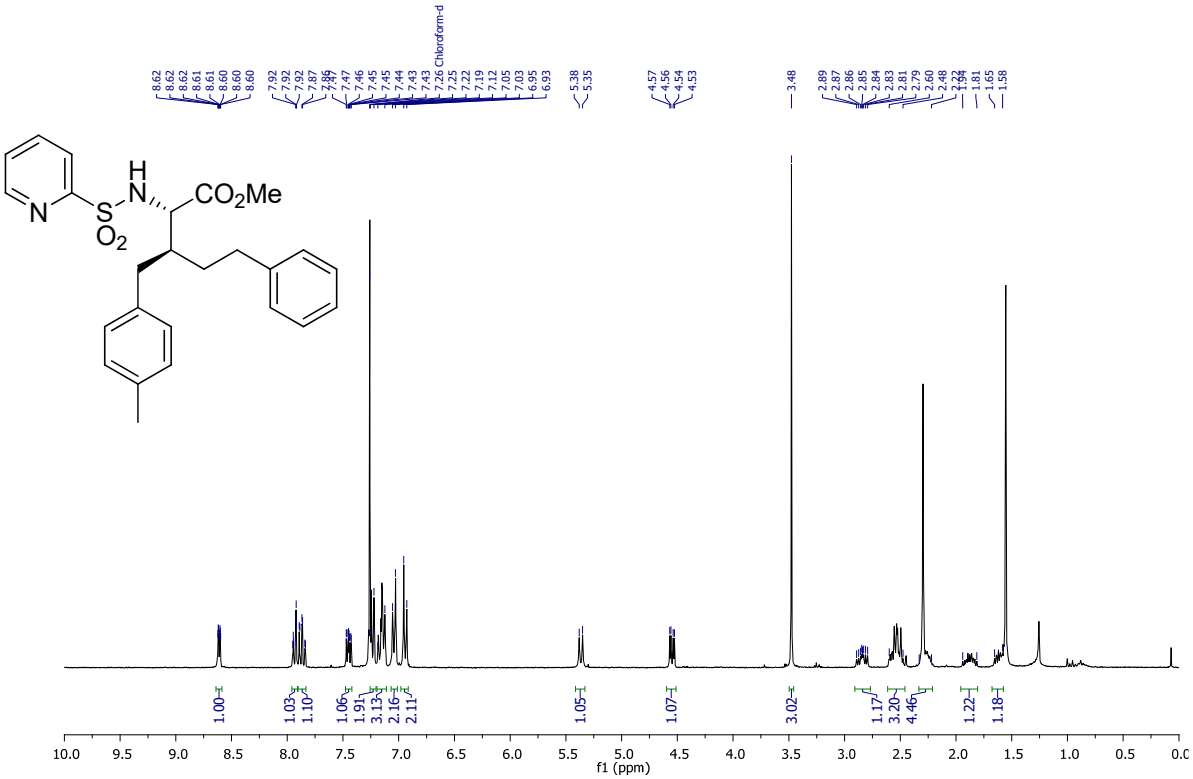



$^{13}$C NMR ($CDCl_3$, 126 MHz)

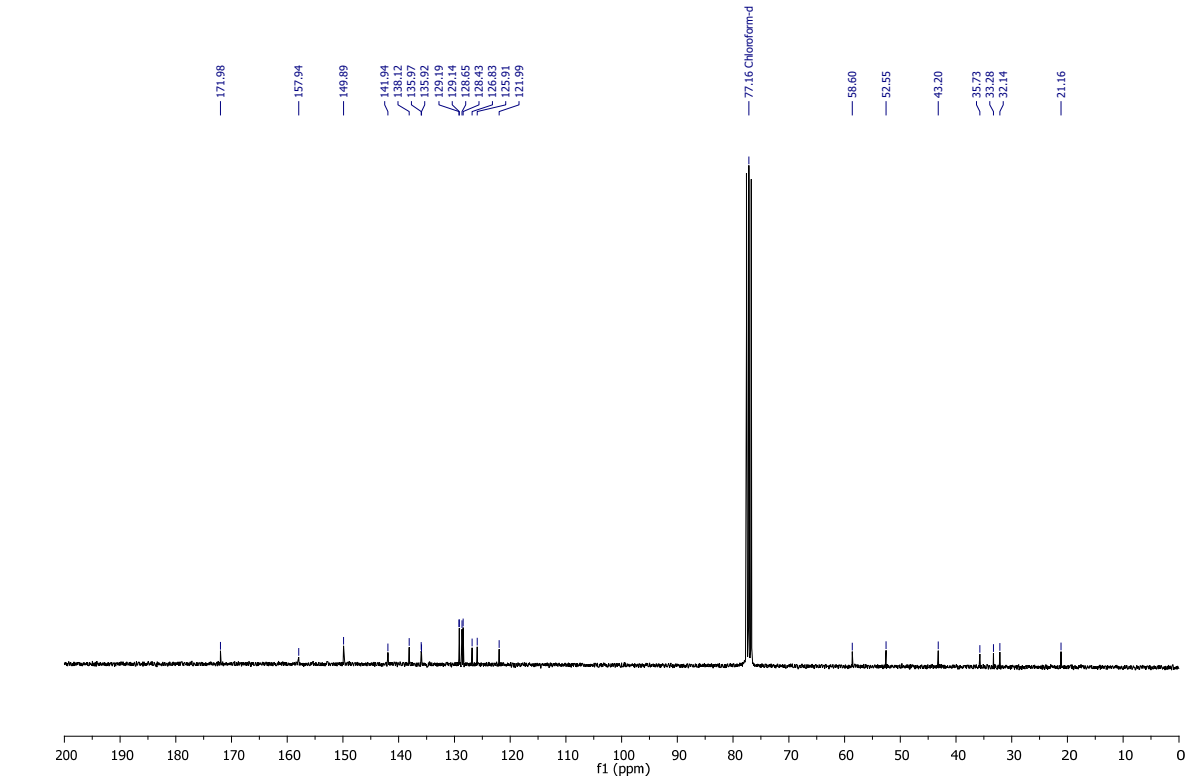


**(2*S**,3*S**)-Methyl 3-(4-methylbenzyl)-5-phenyl-2-(pyridine-2-sulfonamido) pentanoate (38)**

$^{1}$H NMR ($CDCl_3$, 300 MHz)

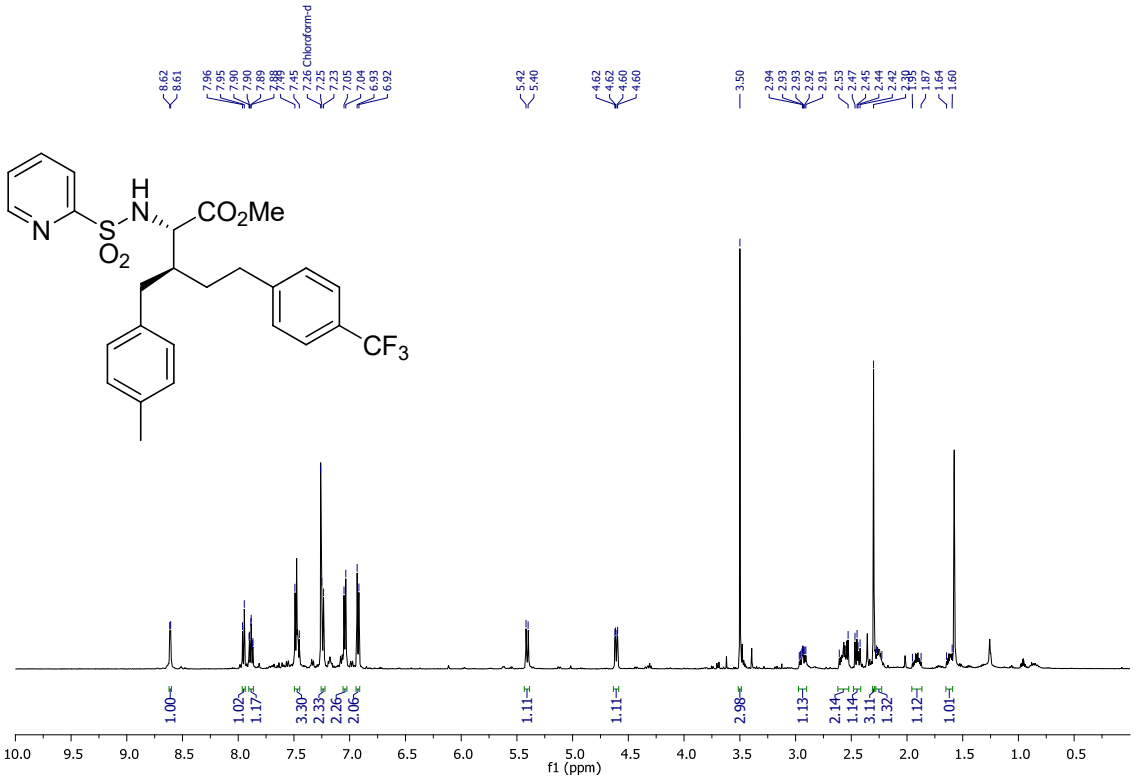



$^{13}$C NMR ($CDCl_3$, 75 MHz)

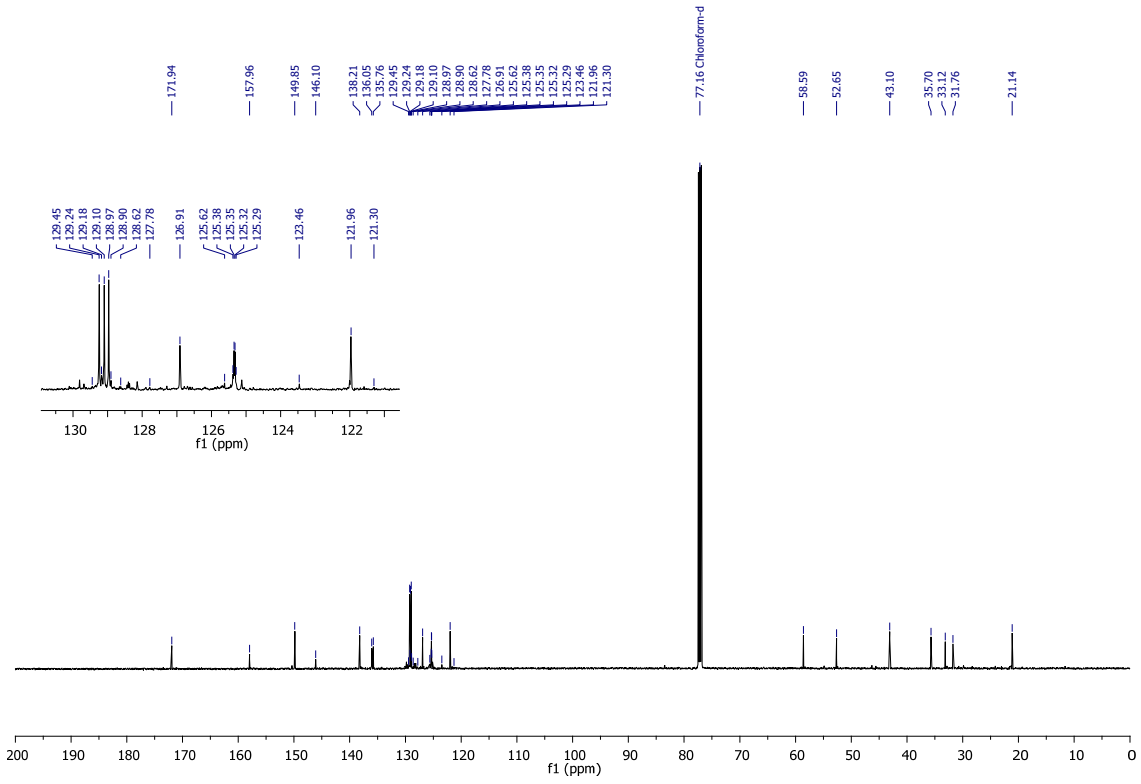


**(2*S**,3*S**)-Methyl 3-(4-methylbenzyl)-2-(pyridine-2-sulfonamido)-5-(4-(trifluoro methyl)phenyl)pentanoate (39)**

$^{1}$H NMR ($CDCl_3$, 500 MHz)

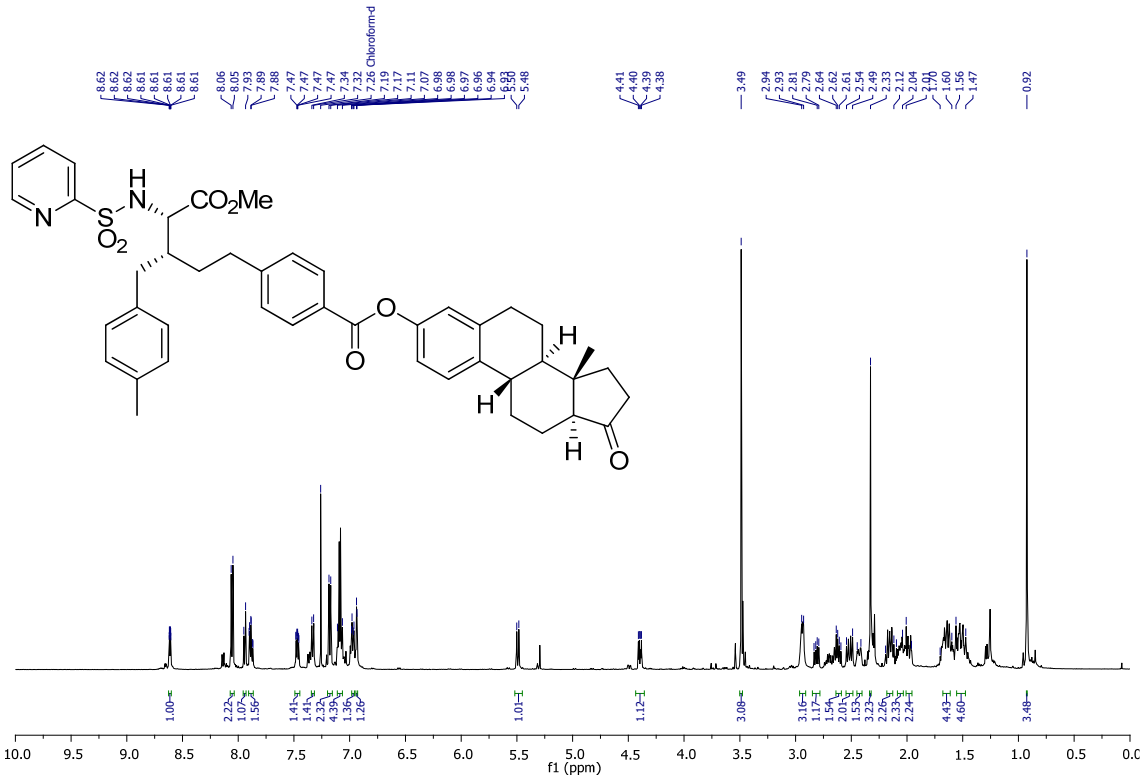



$^{13}$C NMR ($CDCl_3$, 126 MHz)

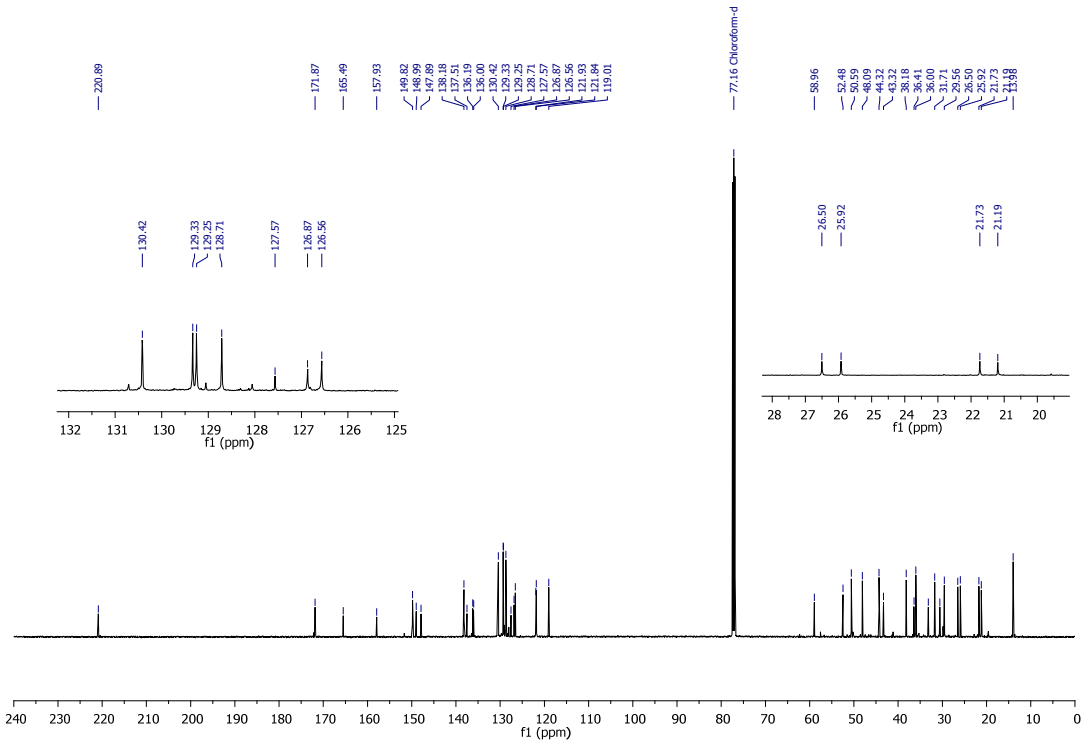


**(8*R*,9*S*,13*S*,14*S*)-14-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl 4-((3*R*,4*S*)-5-methoxy-3-(4-methylbenzyl)-5-oxo-4-(pyridine-2-sulfonamido)pentyl)benzoate ((+)-40)**

$^{1}$H NMR ($CDCl_3$, 300 MHz)

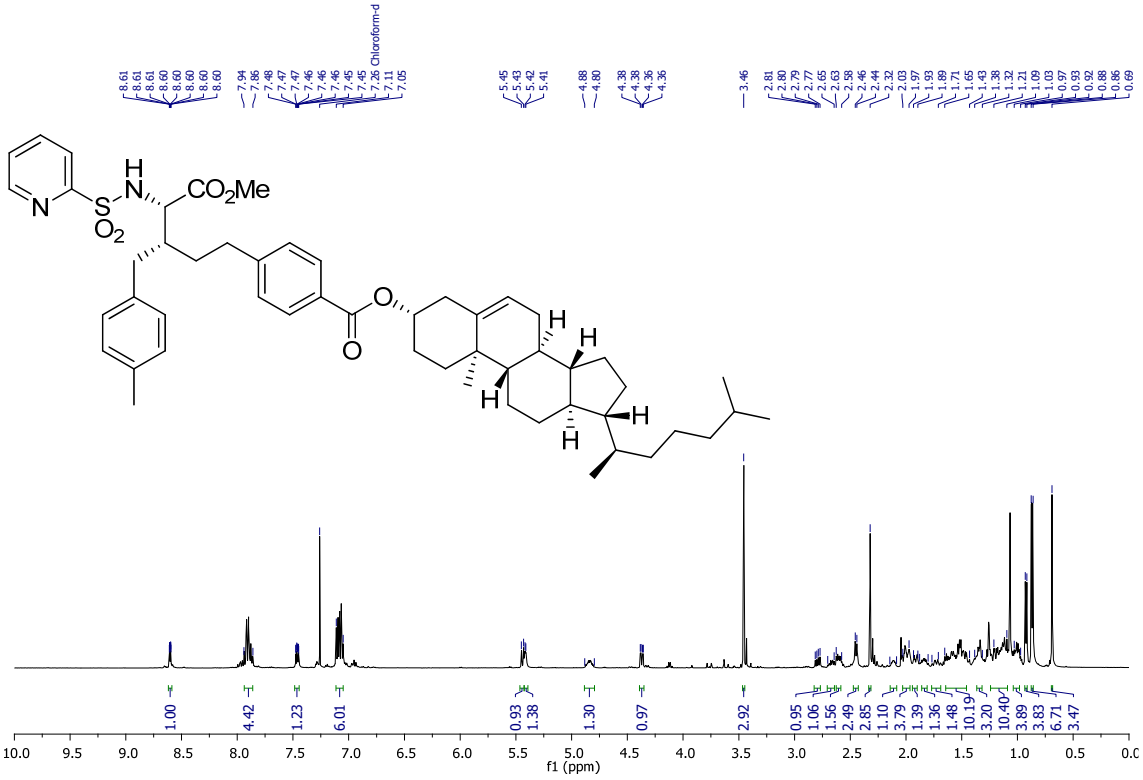



$^{13}$C NMR ($CDCl_3$, 75 MHz)

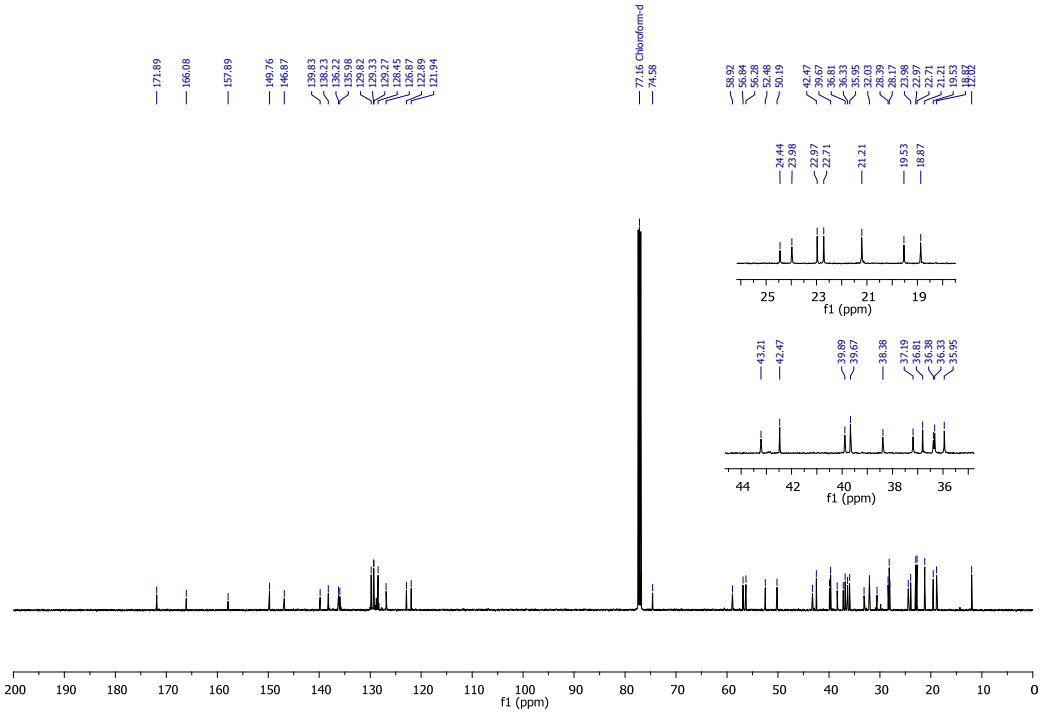


**(3*S*,8*S*,9*S*,10*R*,13*R*,14*R*,17*R*)-10-Methyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*] phenanthren-3-yl 4-((3*R*,4*S*)-5-methoxy-3-(4-methylbenzyl)-5-oxo-4-(pyridine-2-sulfonamido)pentyl)benzoate ((+)-41)**

$^{1}$H NMR ($CDCl_3$, 500 MHz)

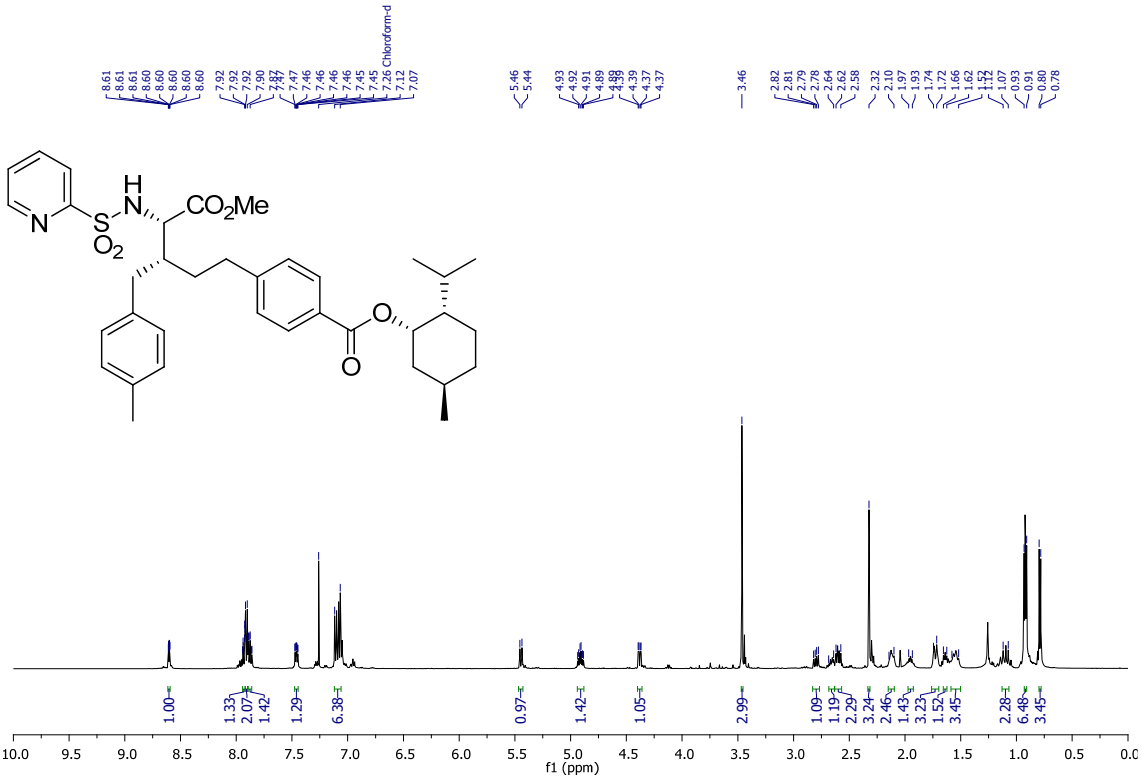



$^{13}$C NMR ($CDCl_3$, 126 MHz)

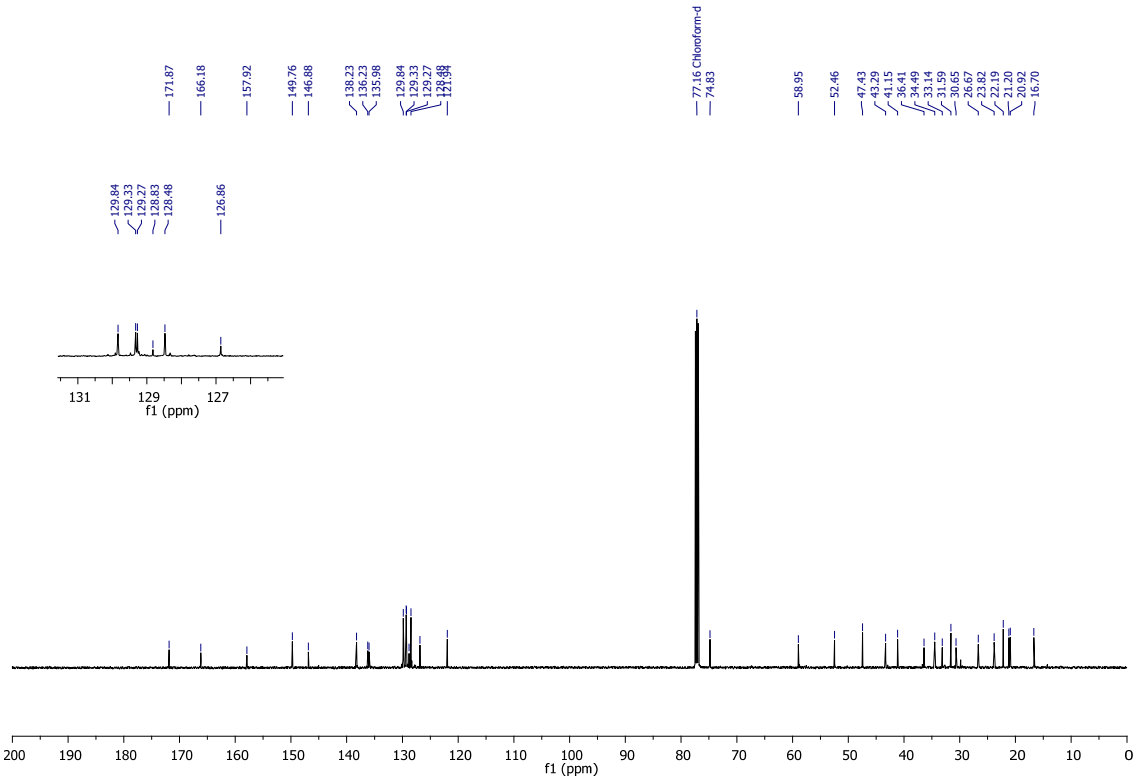


**((1*S*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 4-((3*R*,4*S*)-5-methoxy-3-(4-methylbenzyl)-5-oxo-4-(pyridine-2-sulfonamido)pentyl)benzoate ((+)-42)**

$^{1}$H NMR ($CDCl_3$, 500 MHz)

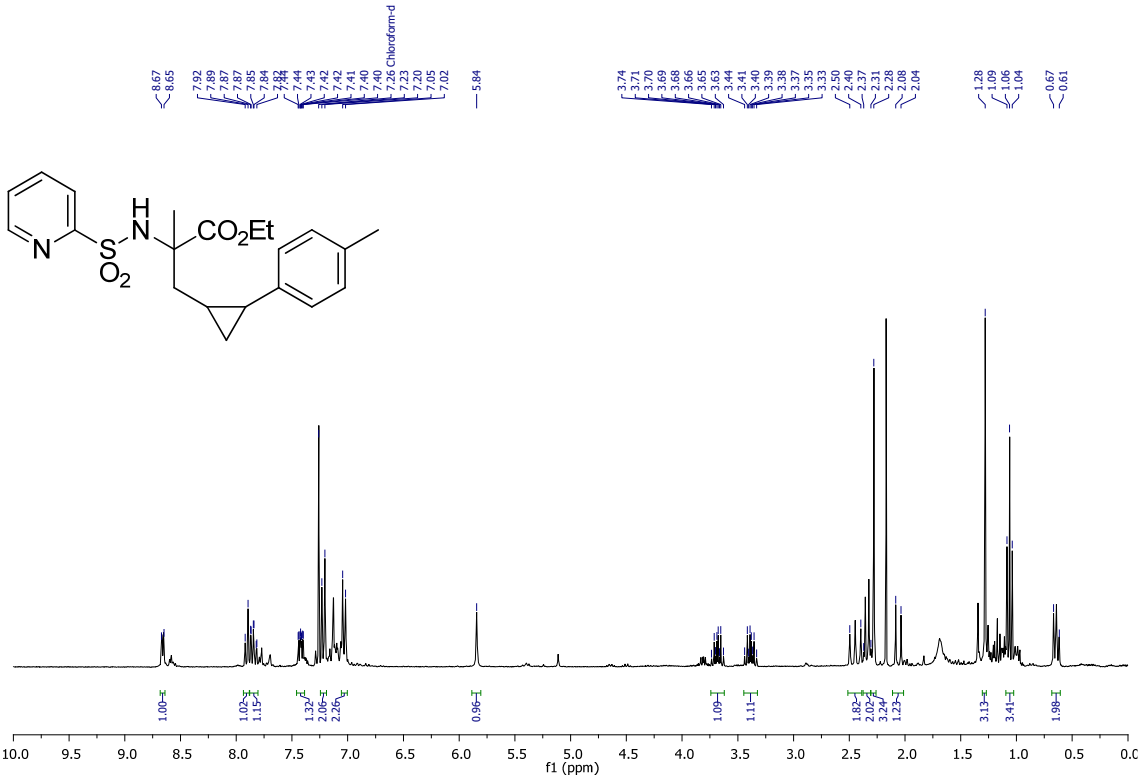



$^{13}$C NMR ($CDCl_3$, 126 MHz)

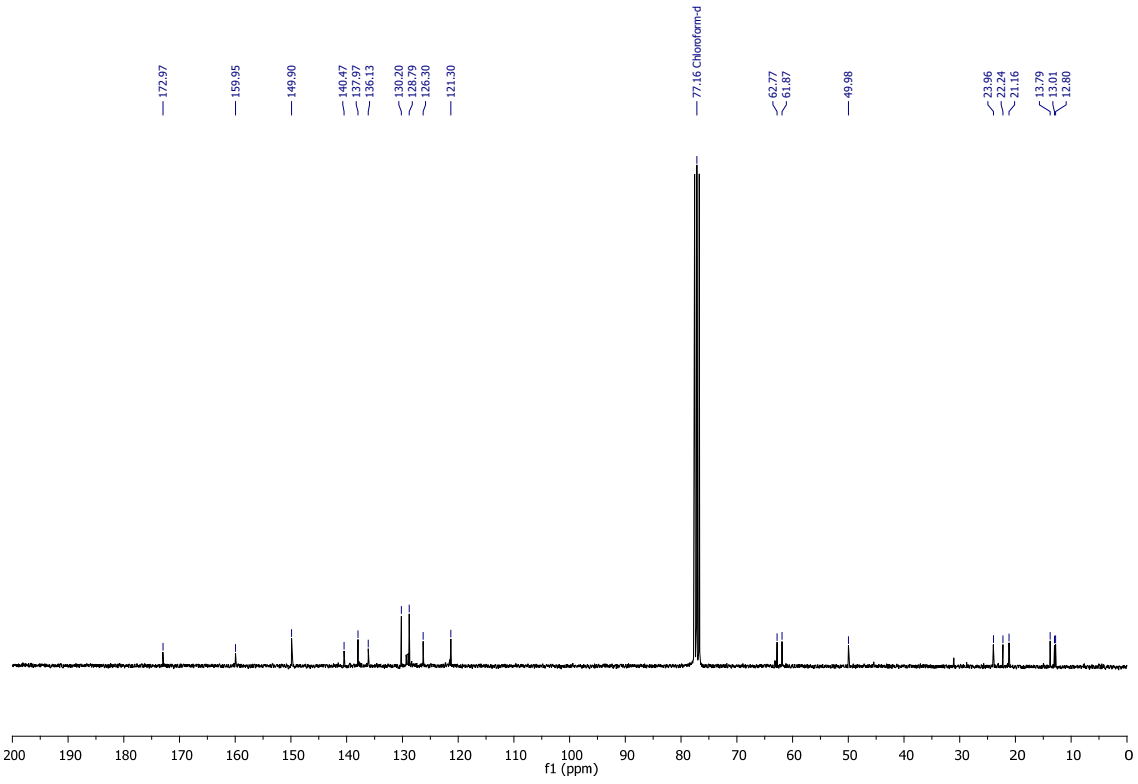


**(*rac*)-Ethyl 2-methyl-2-(pyridine-2-sulfonamido)-3-(2-(*p*-tolyl)cyclopropyl) propanoate (44)**

$^{1}$H NMR ($CDCl_3$, 300 MHz)

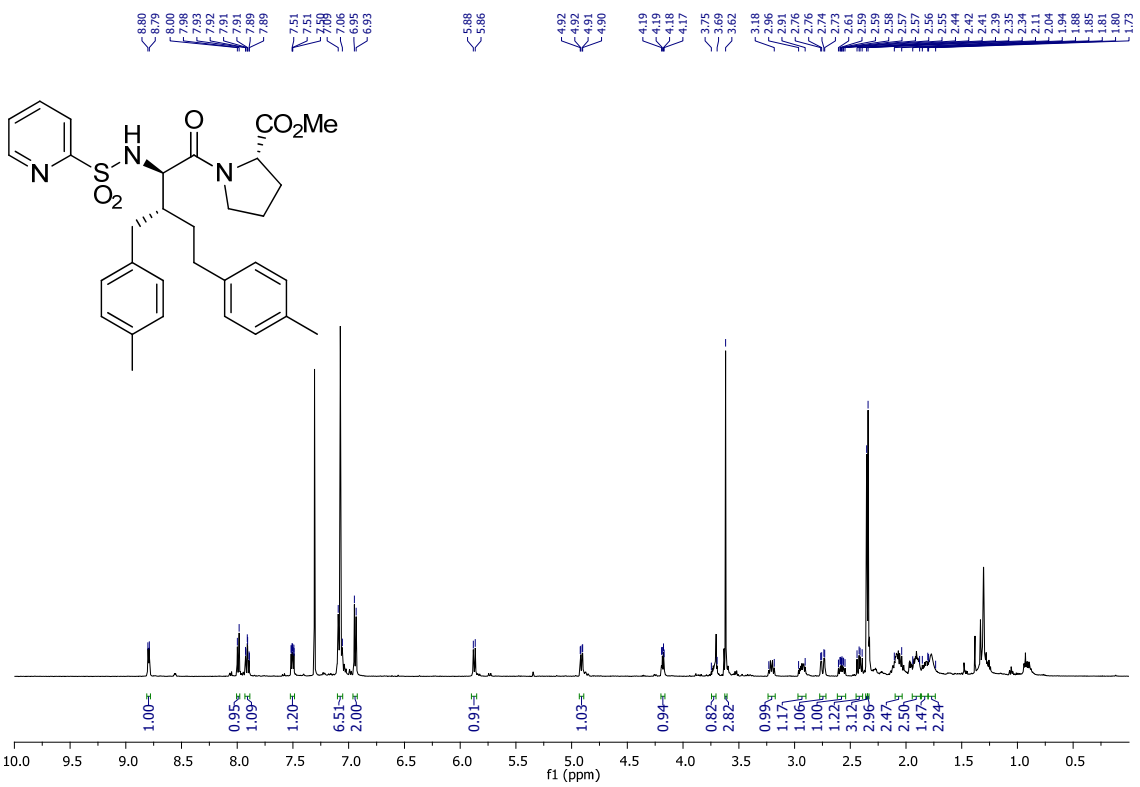



$^{13}$C NMR ($CDCl_3$, 75 MHz)

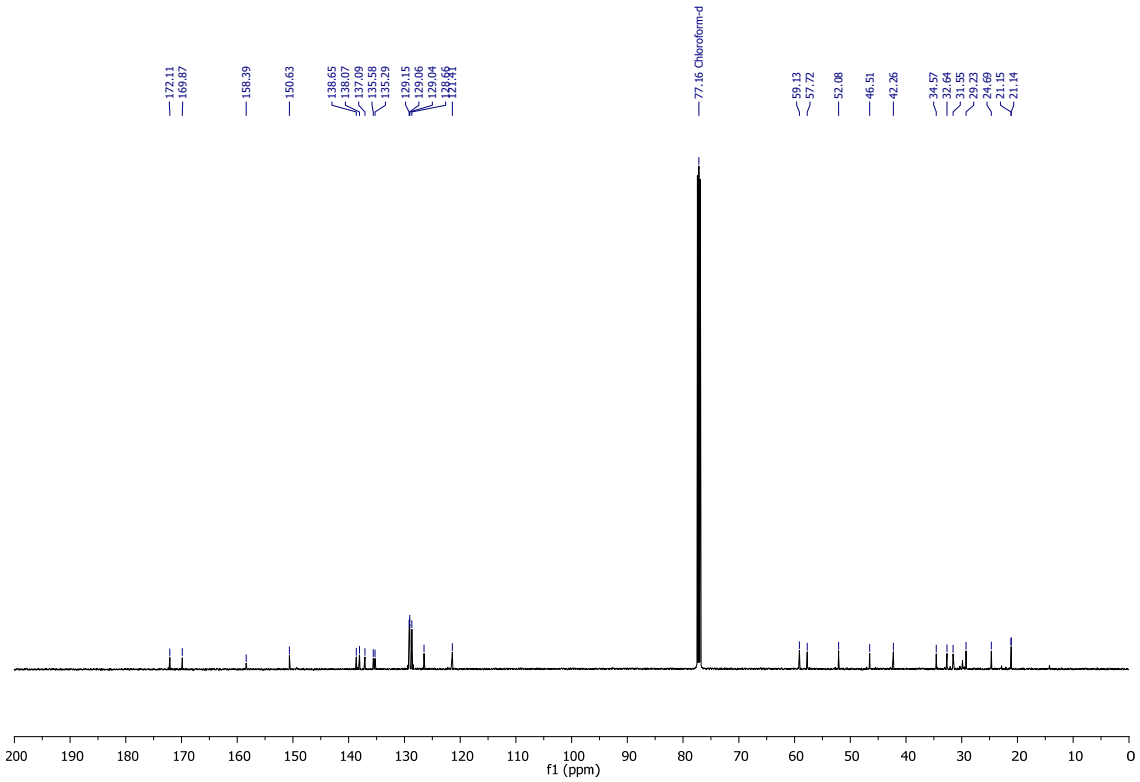


**(*S*)-Methyl 1-((2*R*,3*R*)-3-(4-methylbenzyl)-2-(pyridine-2-sulfonamido)-5-(*p*-tolyl) pentanoyl)pyrrolidine-2-carboxylate ((–)-46)**

$^{1}$H NMR ($CDCl_3$, 500 MHz)

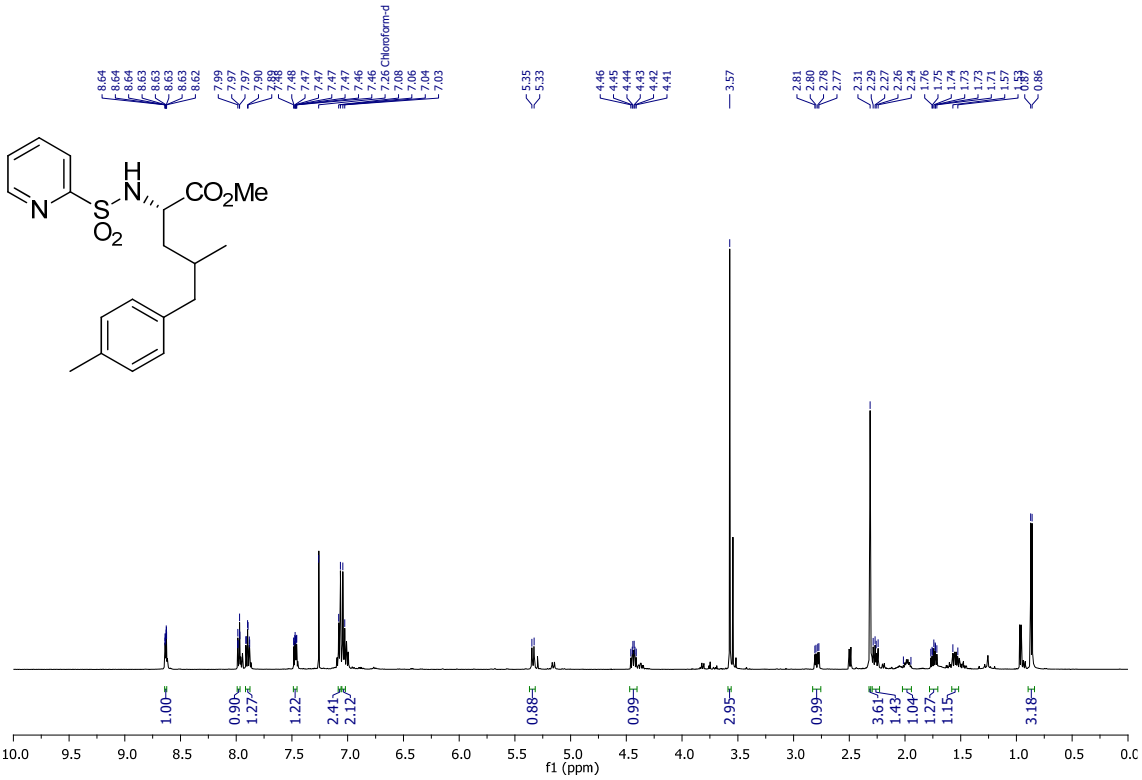



$^{13}$C NMR ($CDCl_3$, 126 MHz)

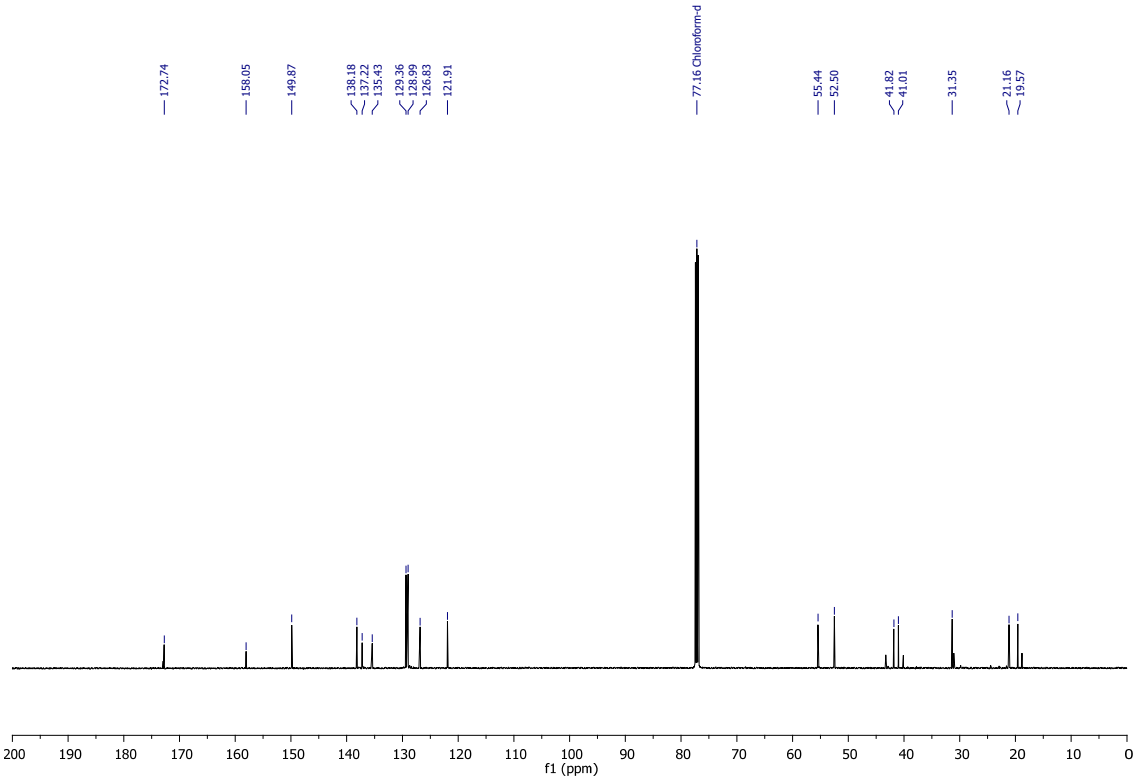


**(2*S*)-Methyl 4-methyl-2-(pyridine-2-sulfonamido)-5-(*p*-tolyl)pentanoate (V)**

$^{1}$H NMR ($CDCl_3$, 500 MHz)

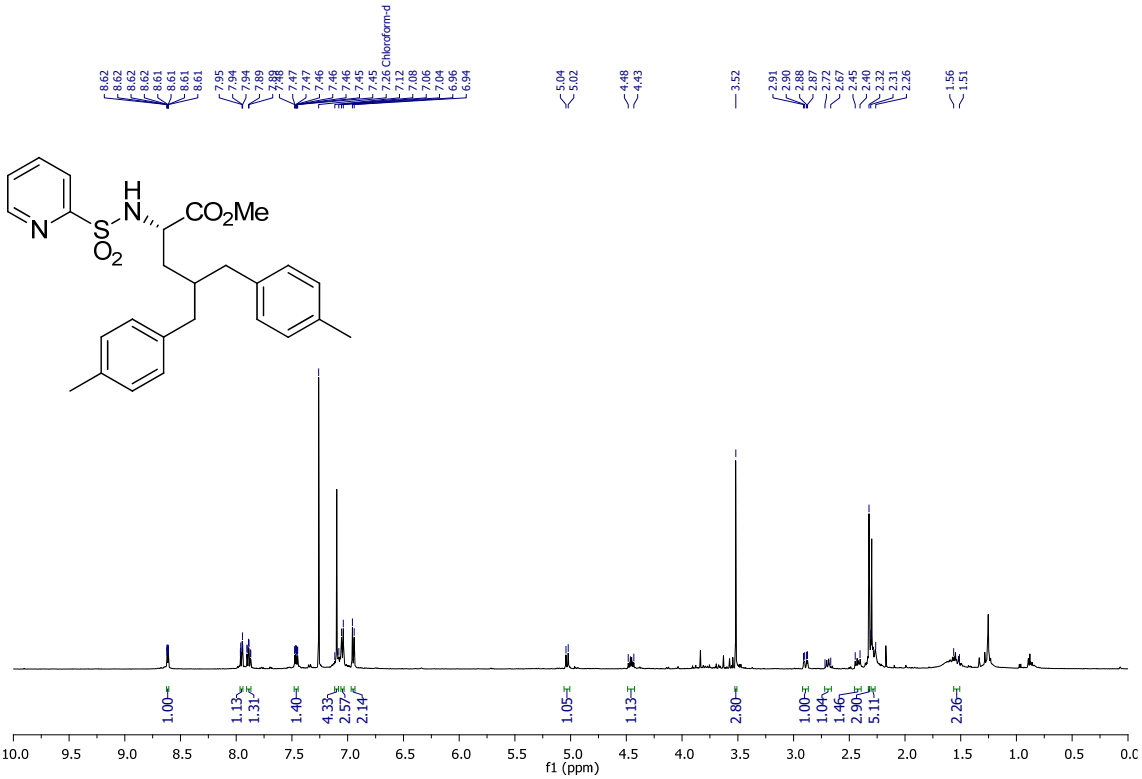



$^{13}$C NMR ($CDCl_3$, 126 MHz)

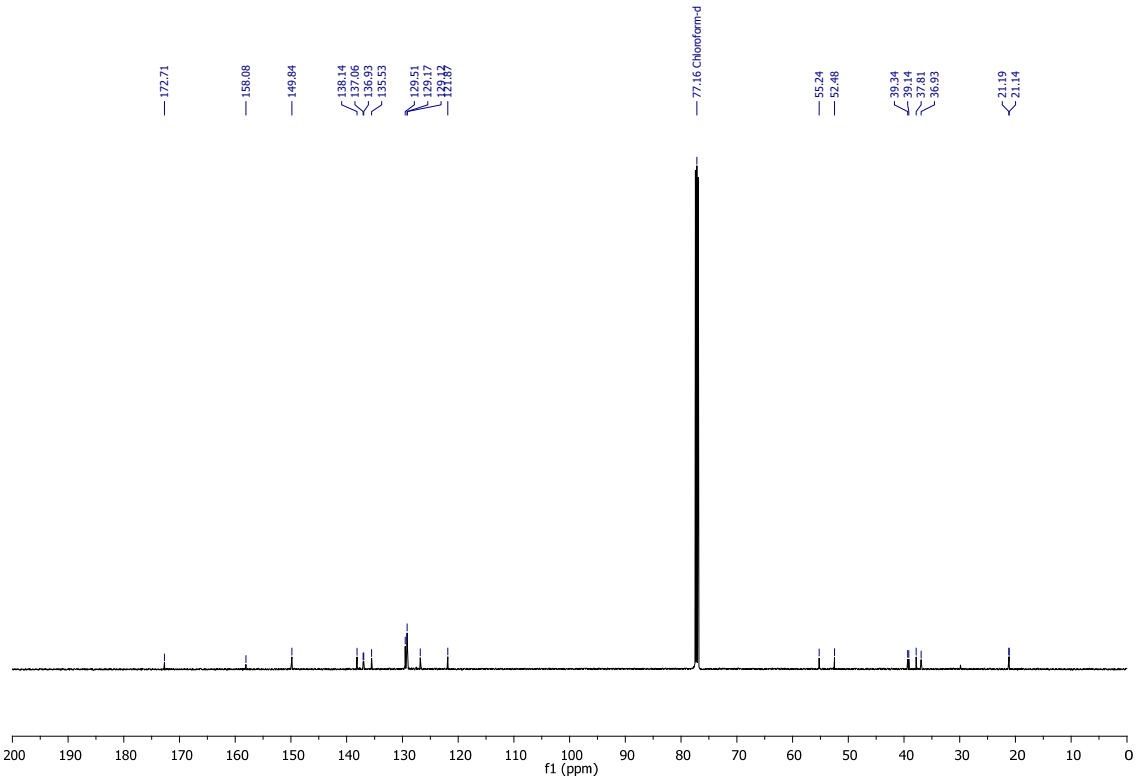


**(*S*)-Methyl 4-(4-methylbenzyl)-2-(pyridine-2-sulfonamido)-5-(*p*-tolyl)pentanoate ($V_{di}$)**

$^1$H NMR ($CDCl_3$, 500 MHz)

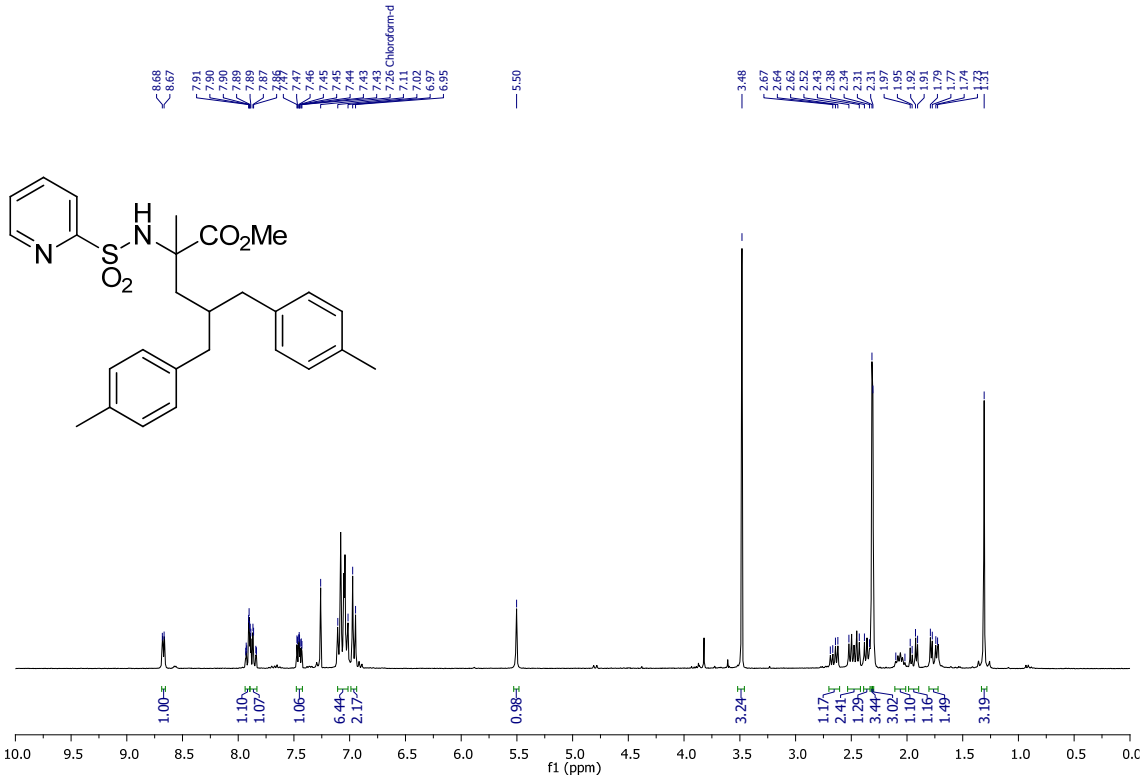



$^{13}$C NMR ($CDCl_3$, 126 MHz)

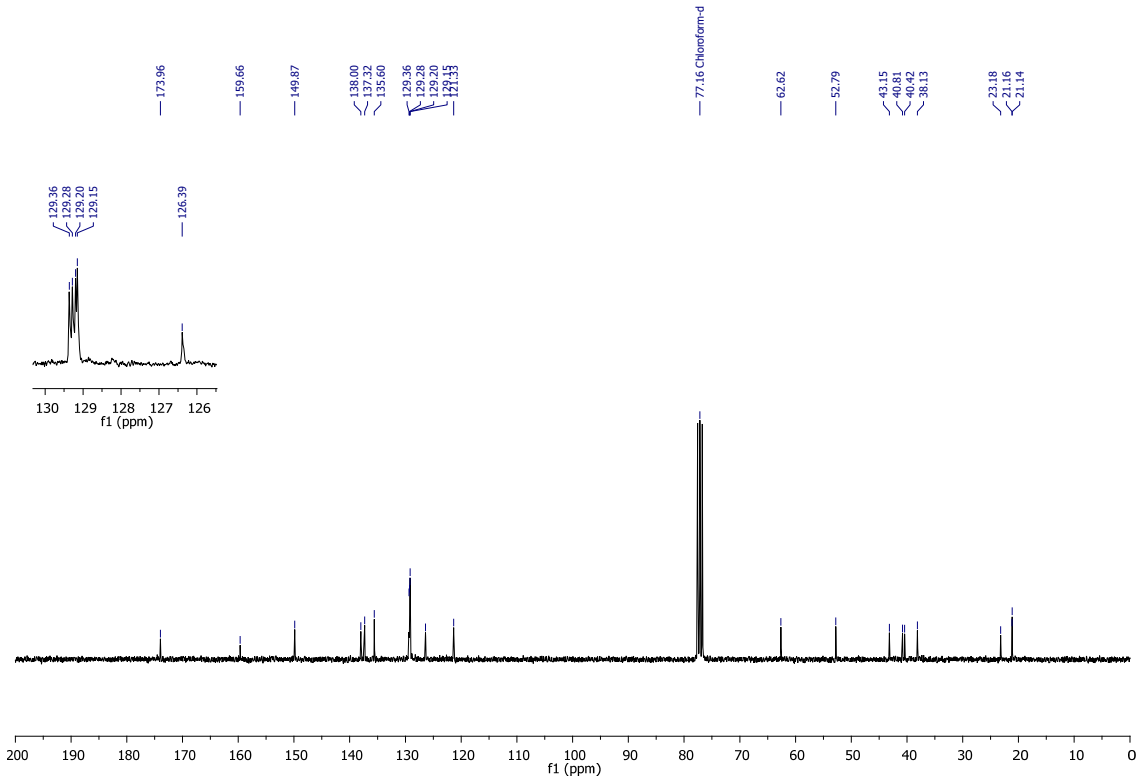


**(*rac*)-Methyl 2-methyl-4-(4-methylbenzyl)-2-(pyridine-2-sulfonamido)-5-(*p*-tolyl)pentanoate (VI)**

$^1$H NMR ($CDCl_3$, 300 MHz)

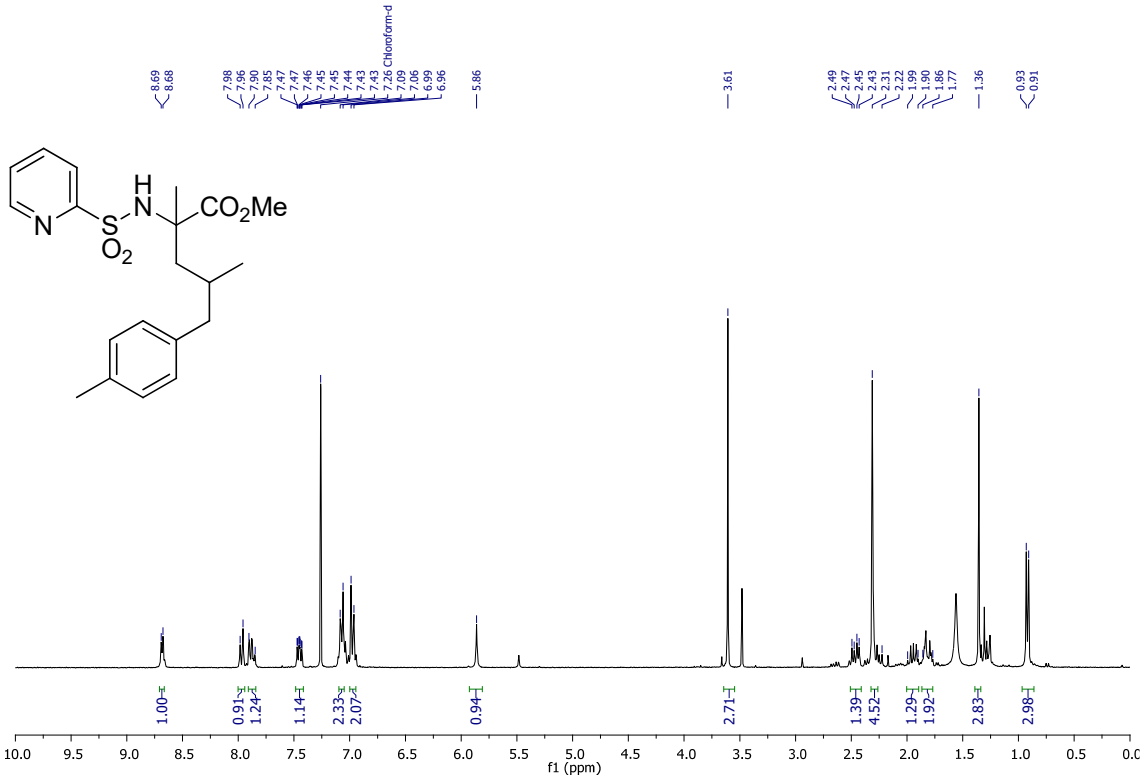



$^{13}$C NMR ($CDCl_3$, 75 MHz)

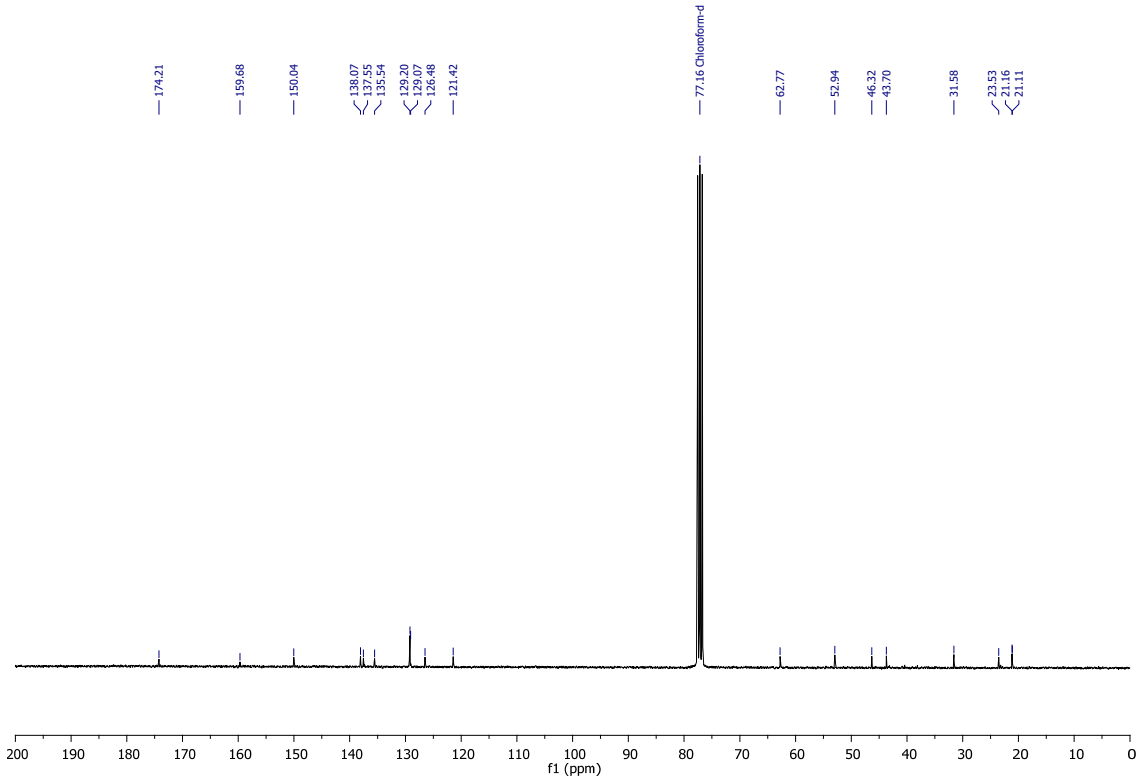


**(*rac*)-Methyl 2,4-dimethyl-2-(pyridine-2-sulfonamido)-5-(*p*-tolyl)pentanoate ($VI_{mo}$)**

$^1$H NMR ($CDCl_3$, 300 MHz)

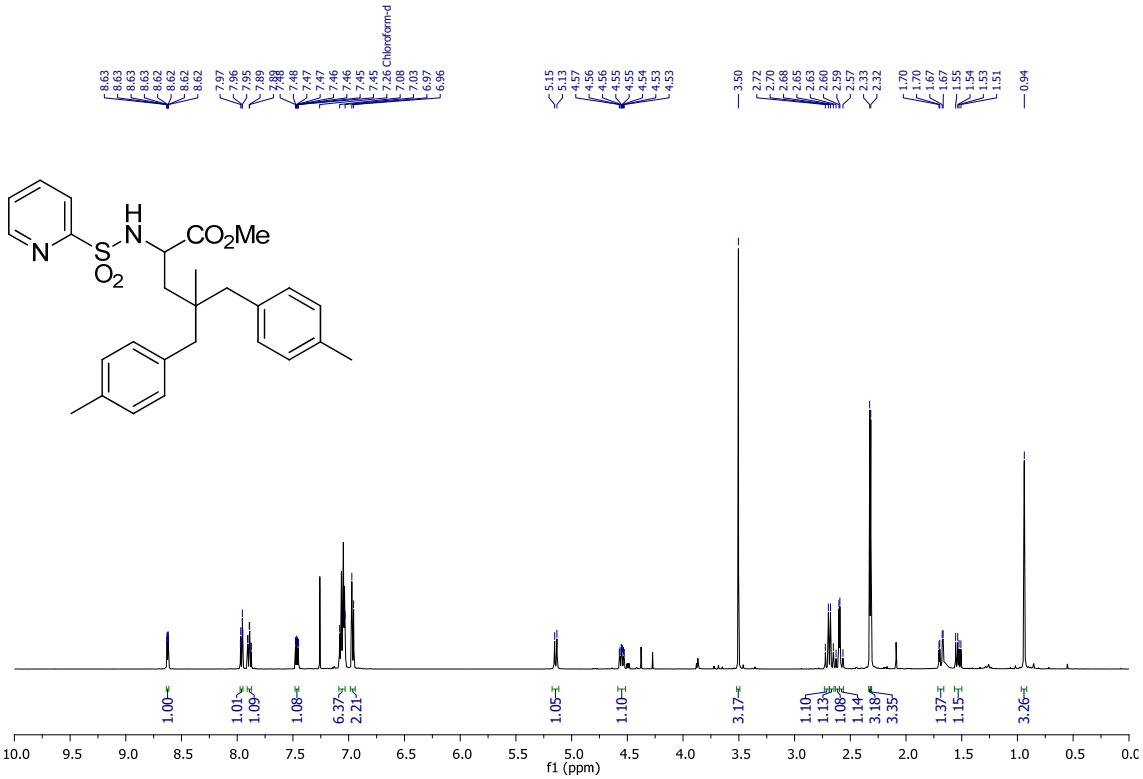



$^{13}$C NMR ($CDCl_3$, 75 MHz)

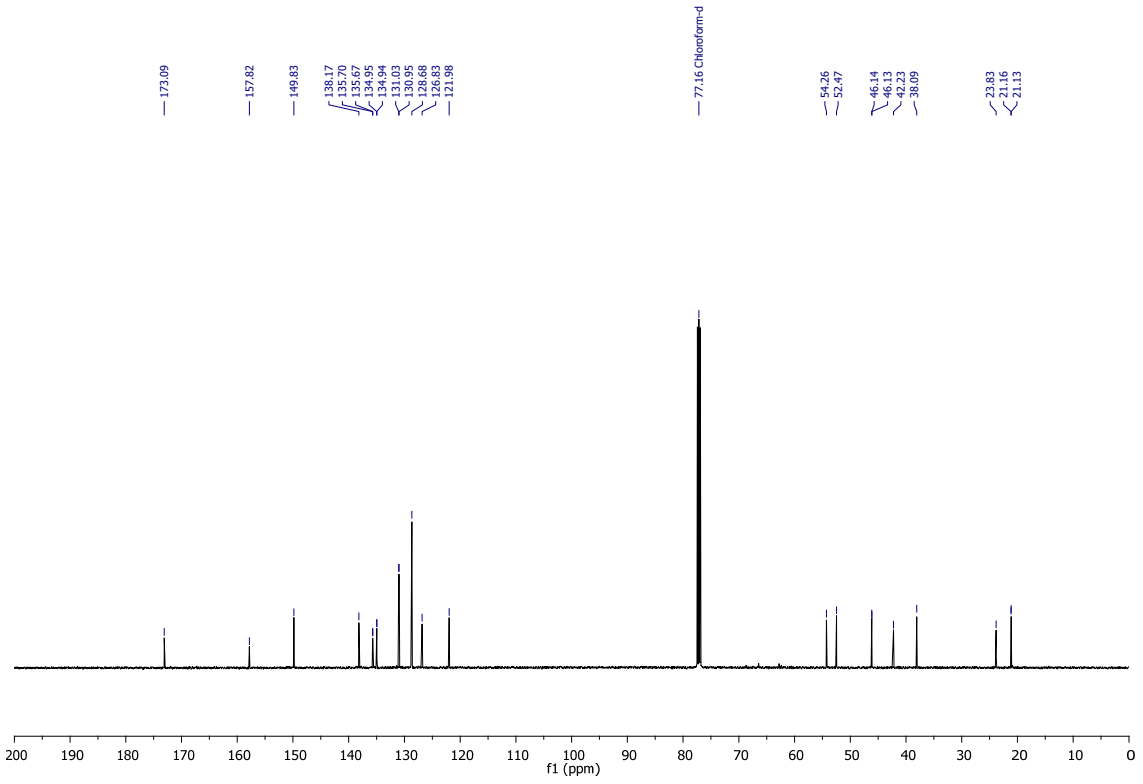


**(*rac*)-Methyl 4-methyl-4-(4-methylbenzyl)-2-(pyridine-2-sulfonamido)-5-(*p*-tolyl)pentanoate (VII)**

$^{1}$H NMR ($CDCl_3$, 500 MHz)

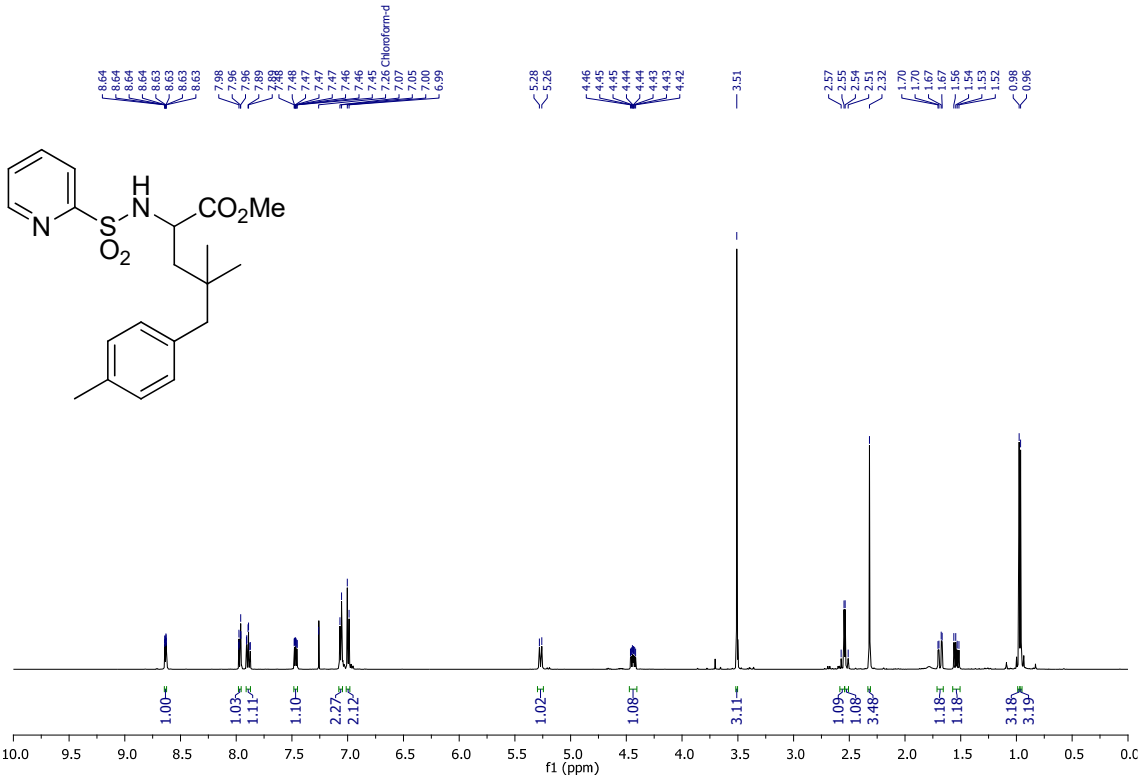



$^{13}$C NMR ($CDCl_3$, 126 MHz)

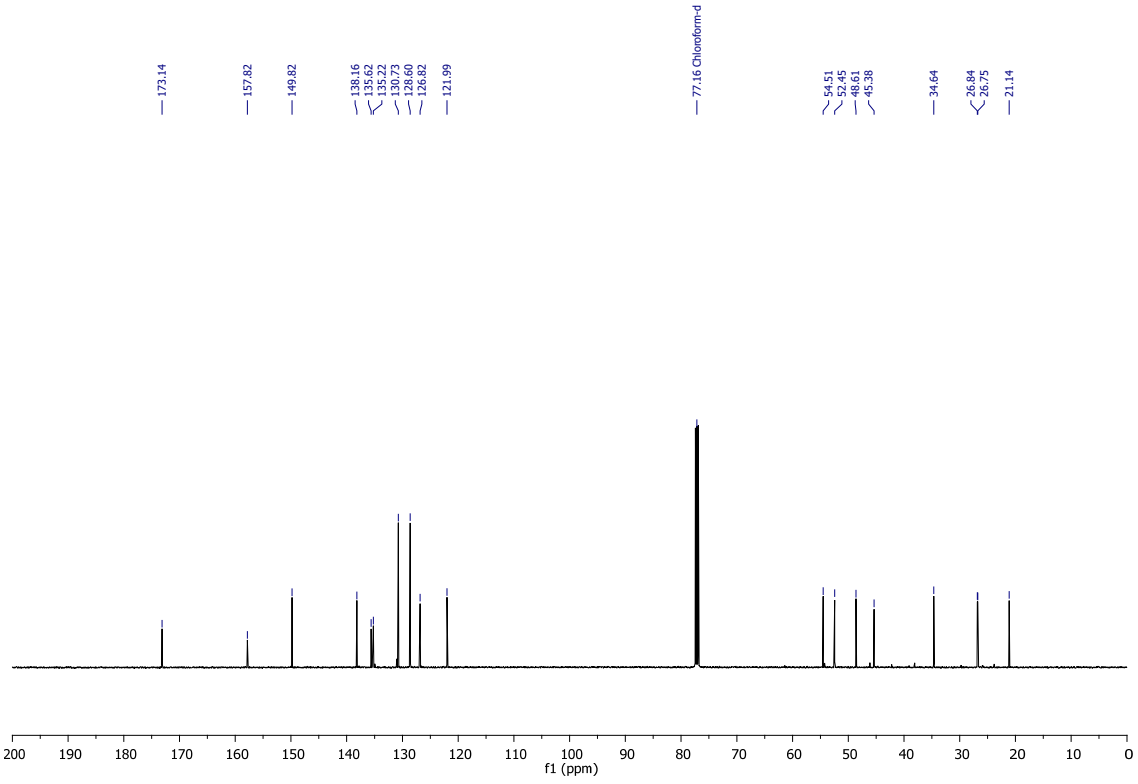


**(*rac*)-Methyl 4,4-dimethyl-2-(pyridine-2-sulfonamido)-5-(*p*-tolyl)pentanoate (VII$_{mo}$)**

$^{1}$H NMR ($CDCl_3$, 500 MHz)

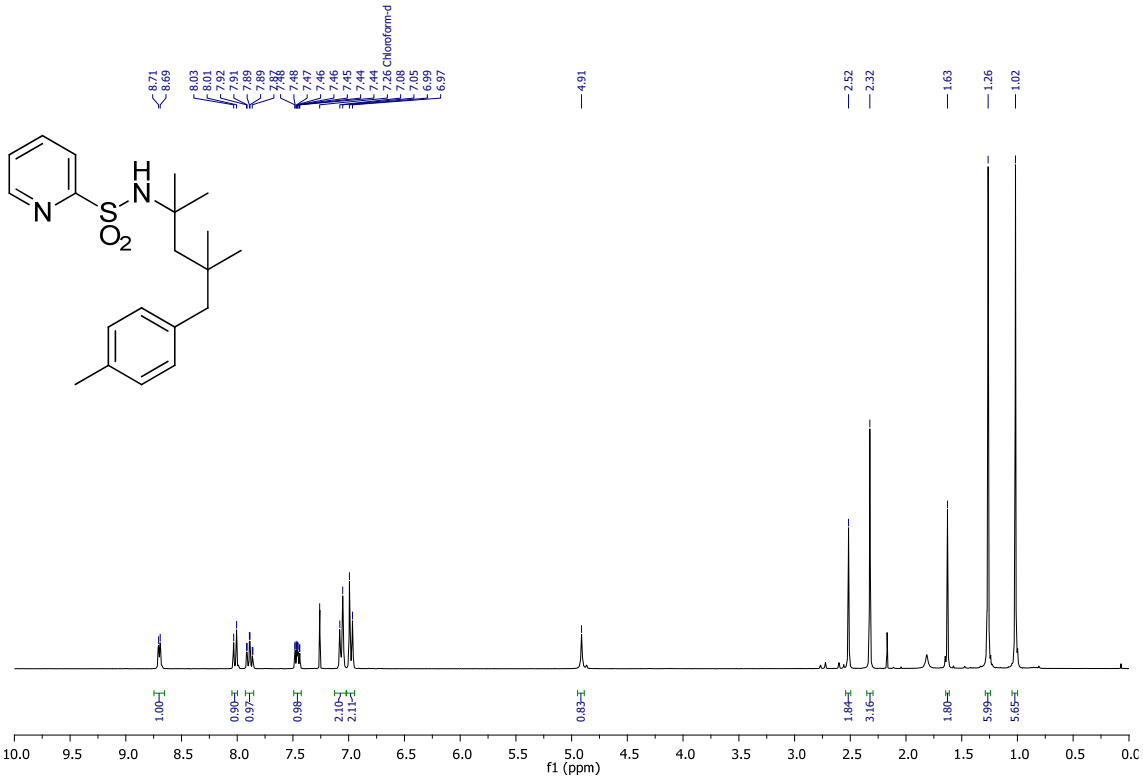



$^{13}$C NMR ($CDCl_3$, 126 MHz)

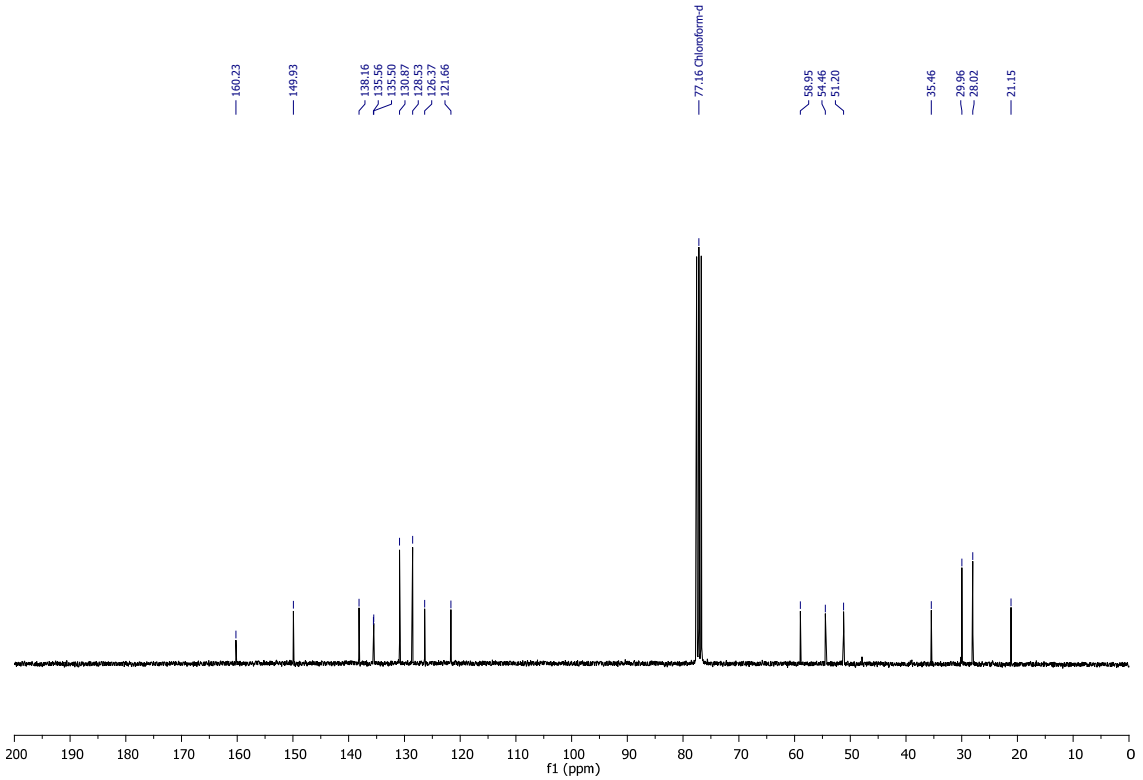


## *N*-(2,4,4-Trimethyl-5-(*p*-tolyl)pentan-2-yl)pyridine-2-sulfonamide (VIII)

$^{1}$H NMR ($CDCl_3$, 300 MHz)

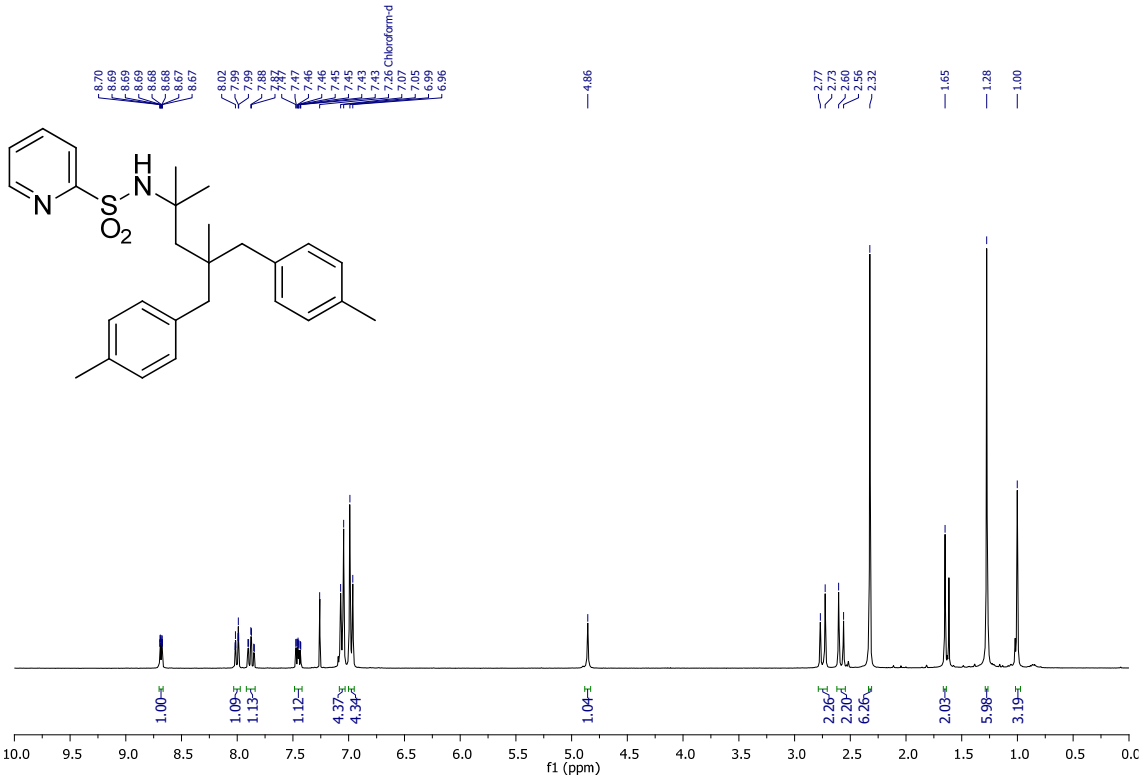



$^{13}$C NMR ($CDCl_3$, 75 MHz)

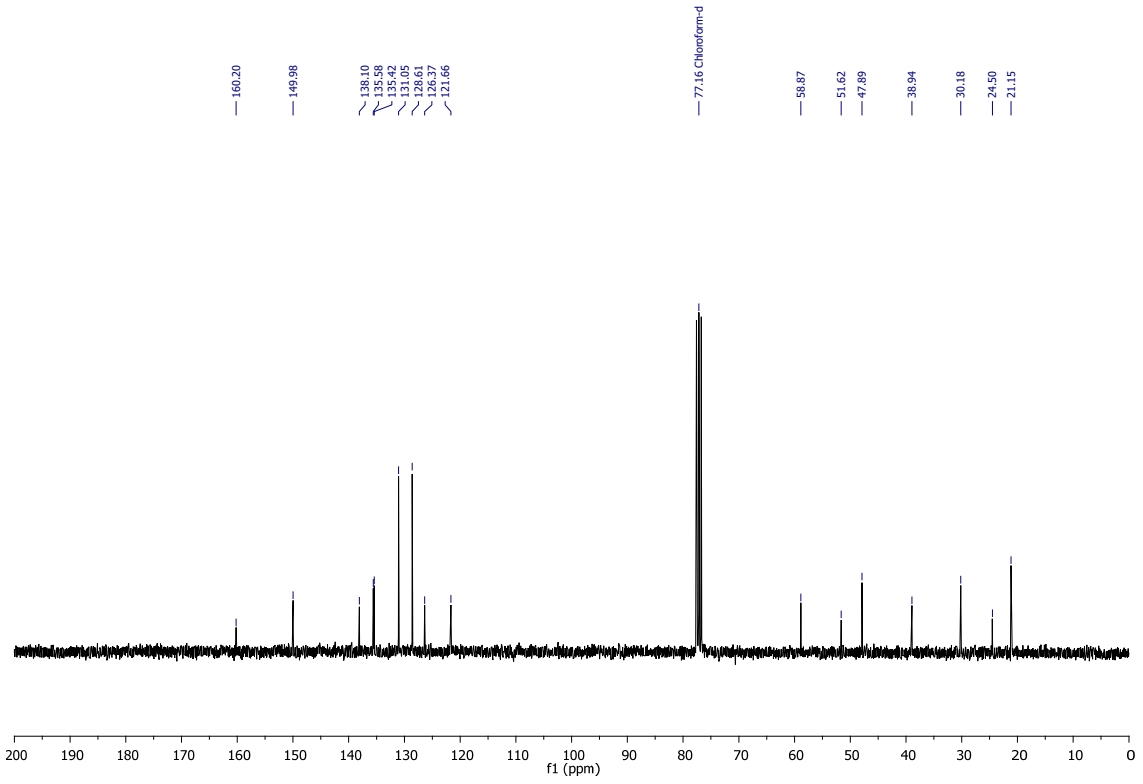


**_N_-(2,4-Dimethyl-4-(4-methylbenzyl)-5-(_p_-tolyl)pentan-2-yl)pyridine-2-sulfonamide ($VIII_{di}$)**

$^1H$ NMR ($CDCl_3$, 300 MHz)

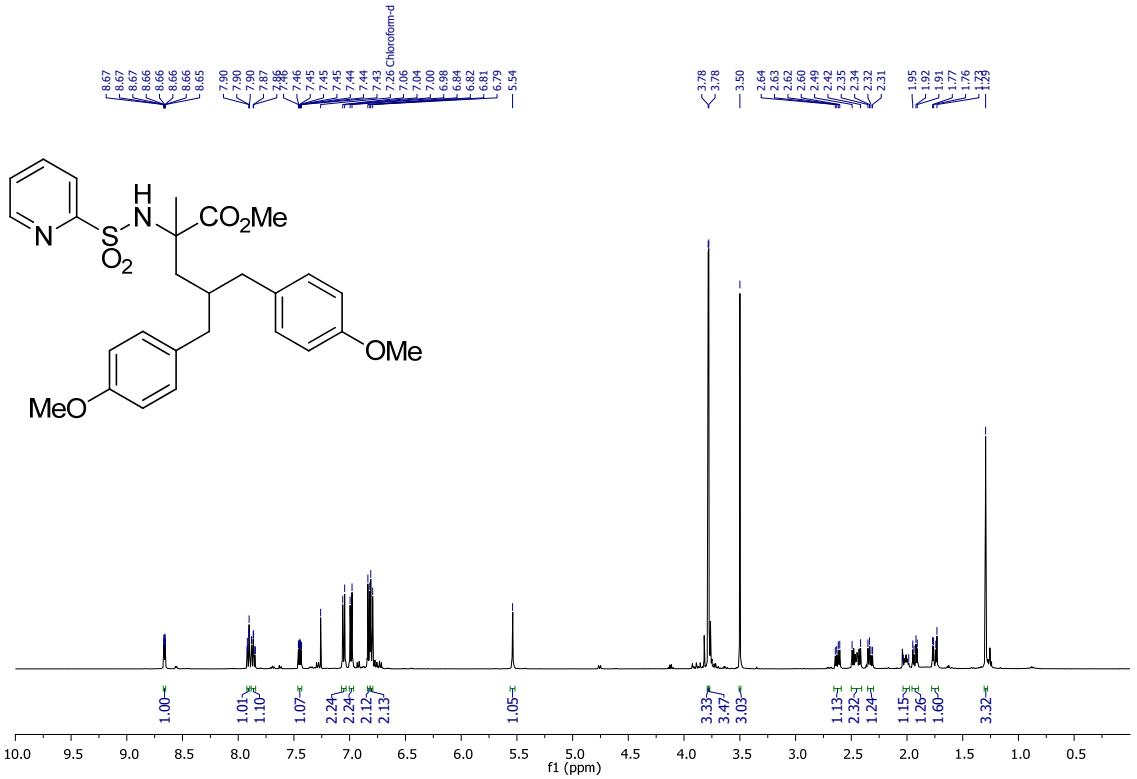



$^{13}C$ NMR ($CDCl_3$, 75 MHz)

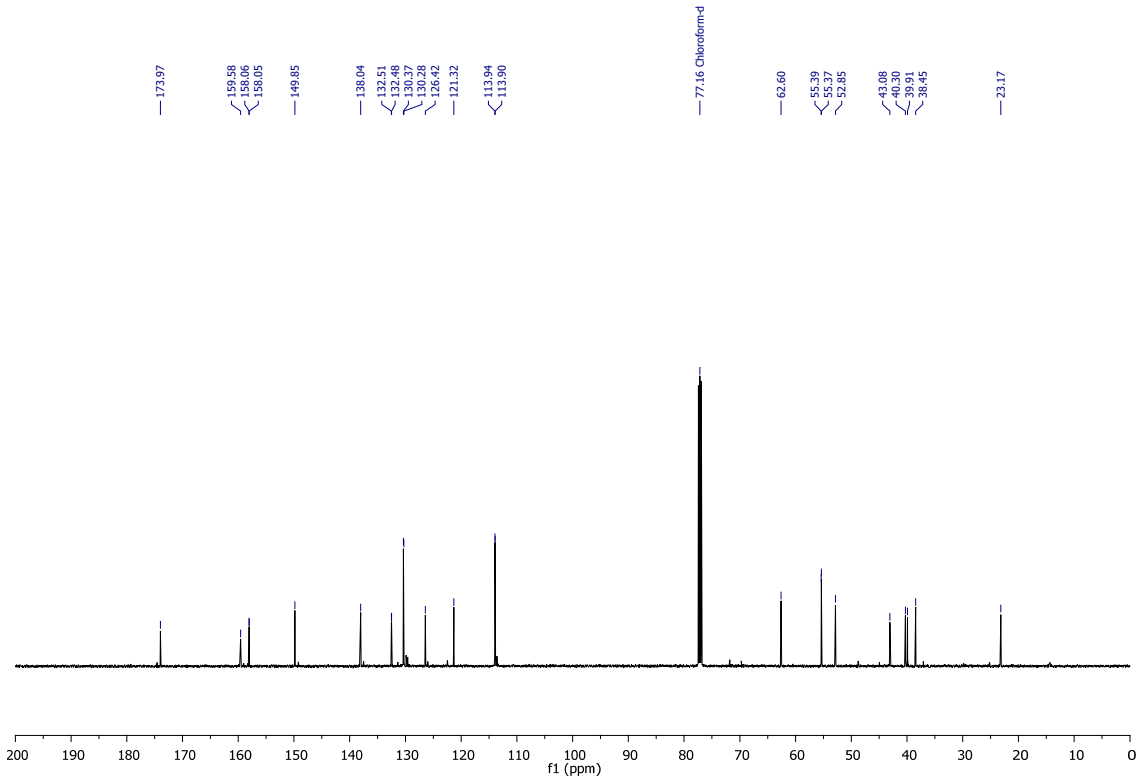


**(*rac*)-Methyl 4-(4-methoxybenzyl)-5-(4-methoxyphenyl)-2-methyl-2-(pyridine-2-sulfonamido)pentanoate (IX)**

$^{1}$H NMR ($CDCl_3$, 500 MHz)

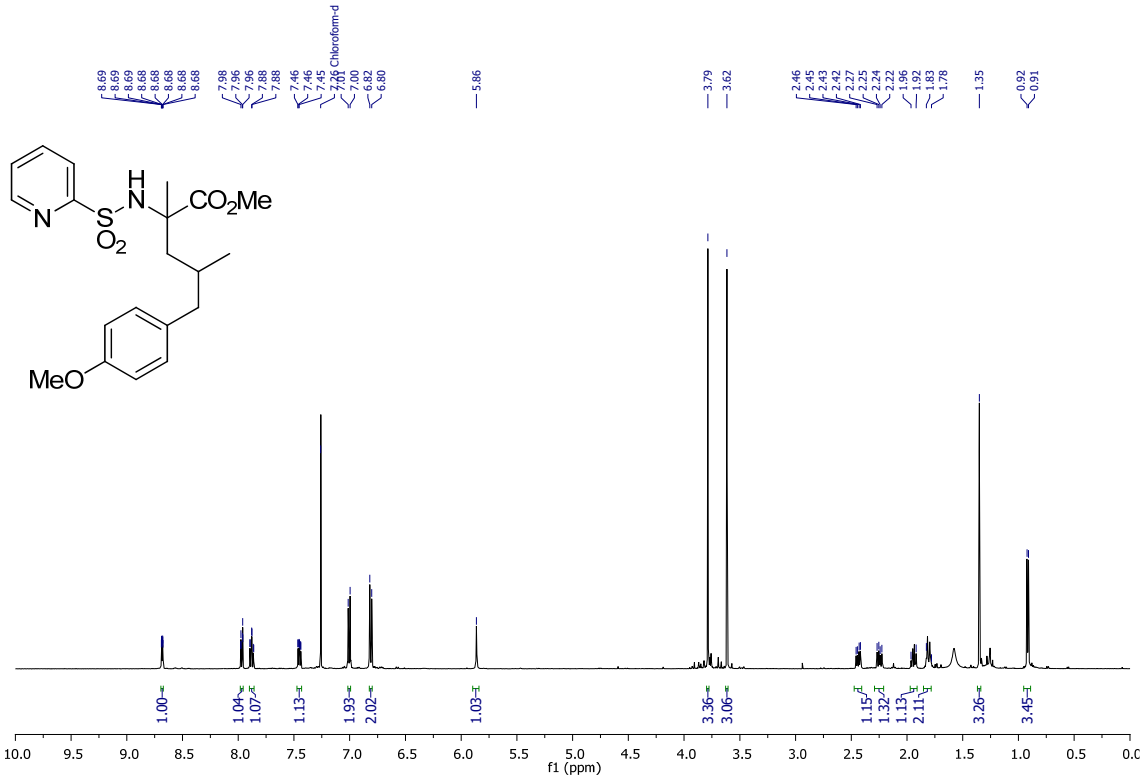



$^{13}$C NMR ($CDCl_3$, 126 MHz)

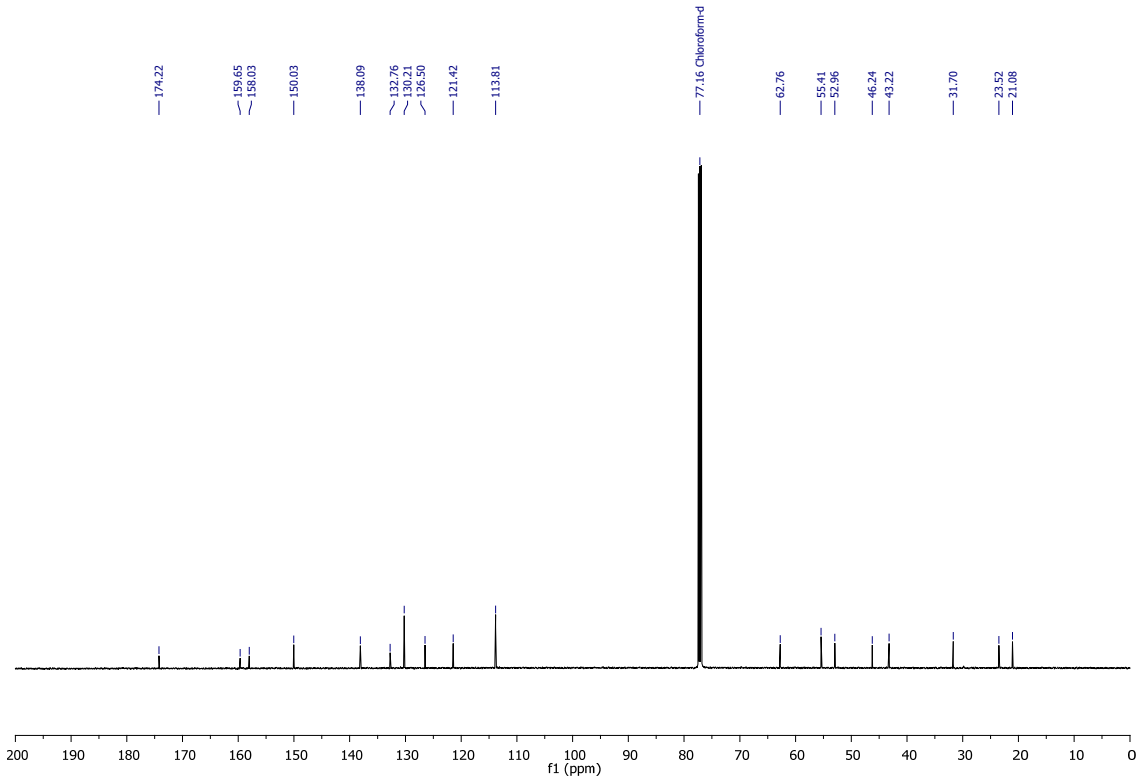


**(*rac*)-Methyl 5-(4-methoxyphenyl)-2,4-dimethyl-2-(pyridine-2-sulfonamido)pentanoate ($IX_{mo}$)**

$^{1}H$ NMR ($CDCl_3$, 500 MHz)

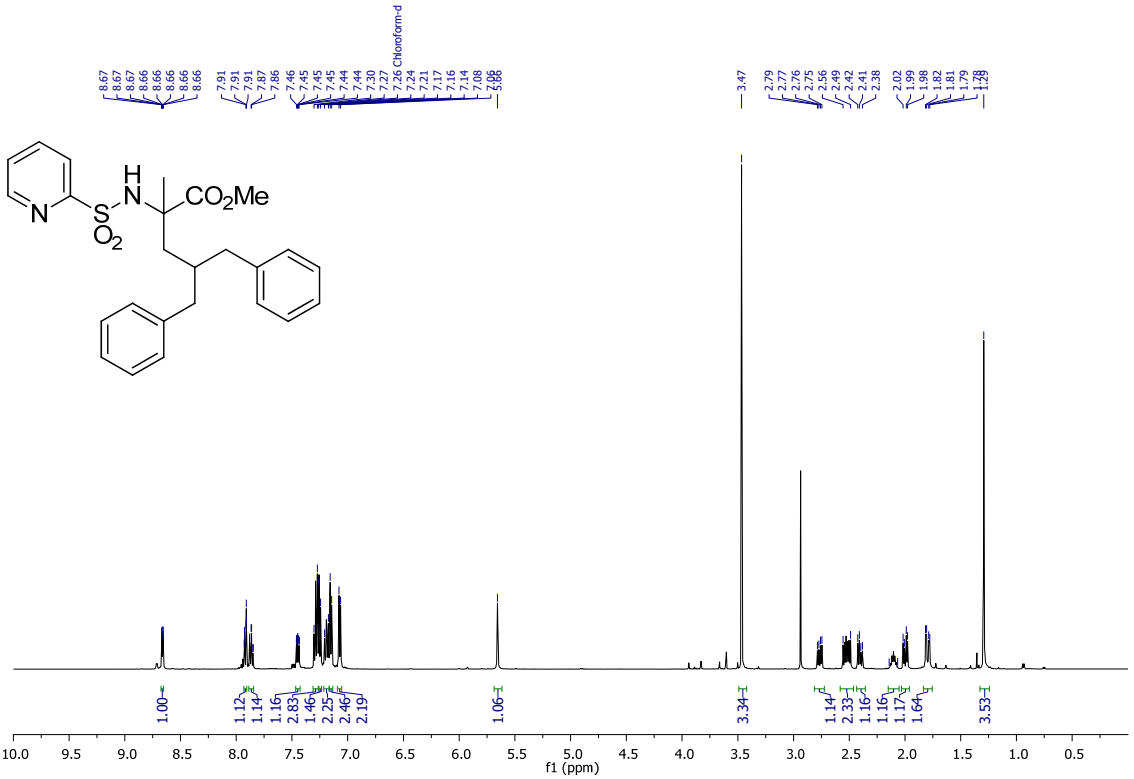



$^{13}C$ NMR ($CDCl_3$, 126 MHz)

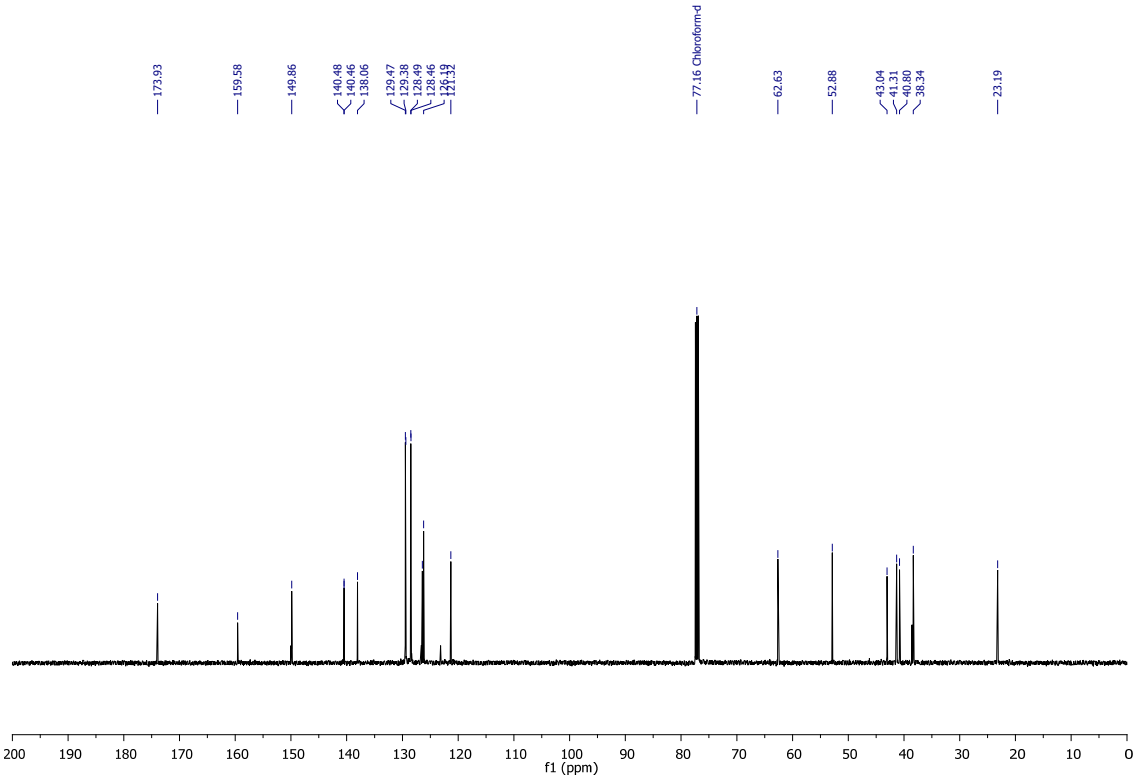


**(*rac*)-Methyl 2-methyl-4-benzyl-5-phenyl-2-(pyridine-2-sulfonamido)pentanoate (X)**

$^{1}$H NMR ($CDCl_3$, 500 MHz)

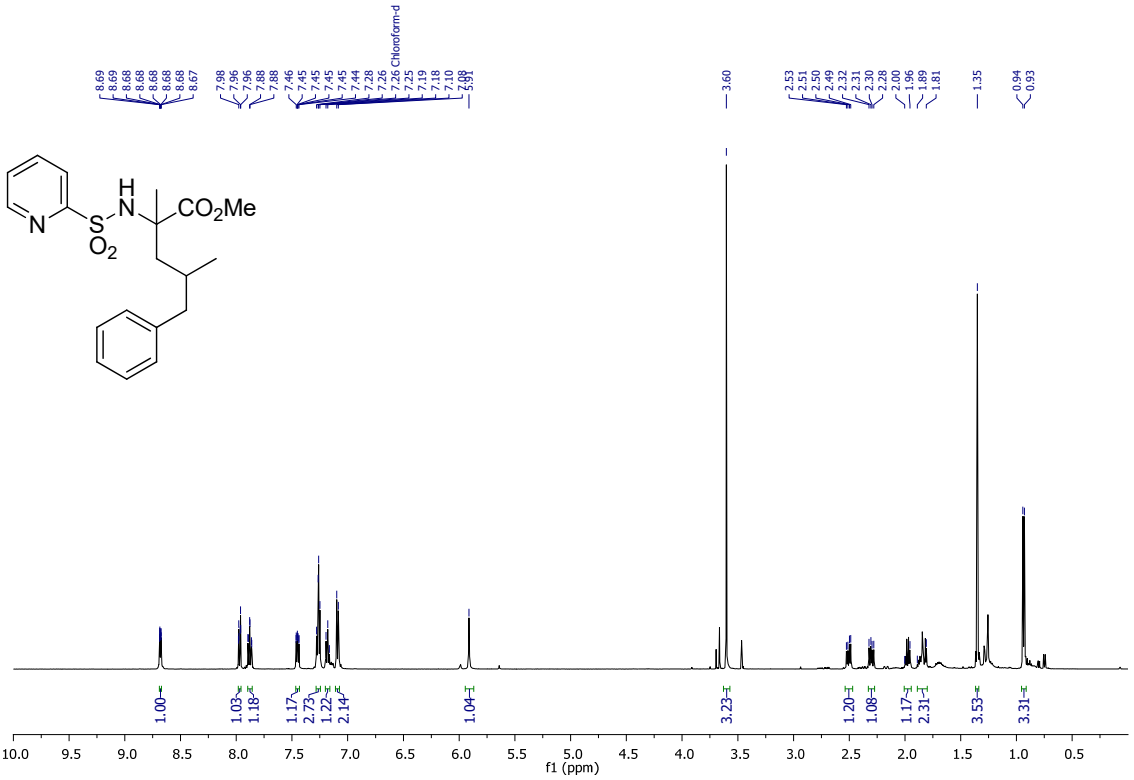



$^{13}$C NMR ($CDCl_3$, 126 MHz)

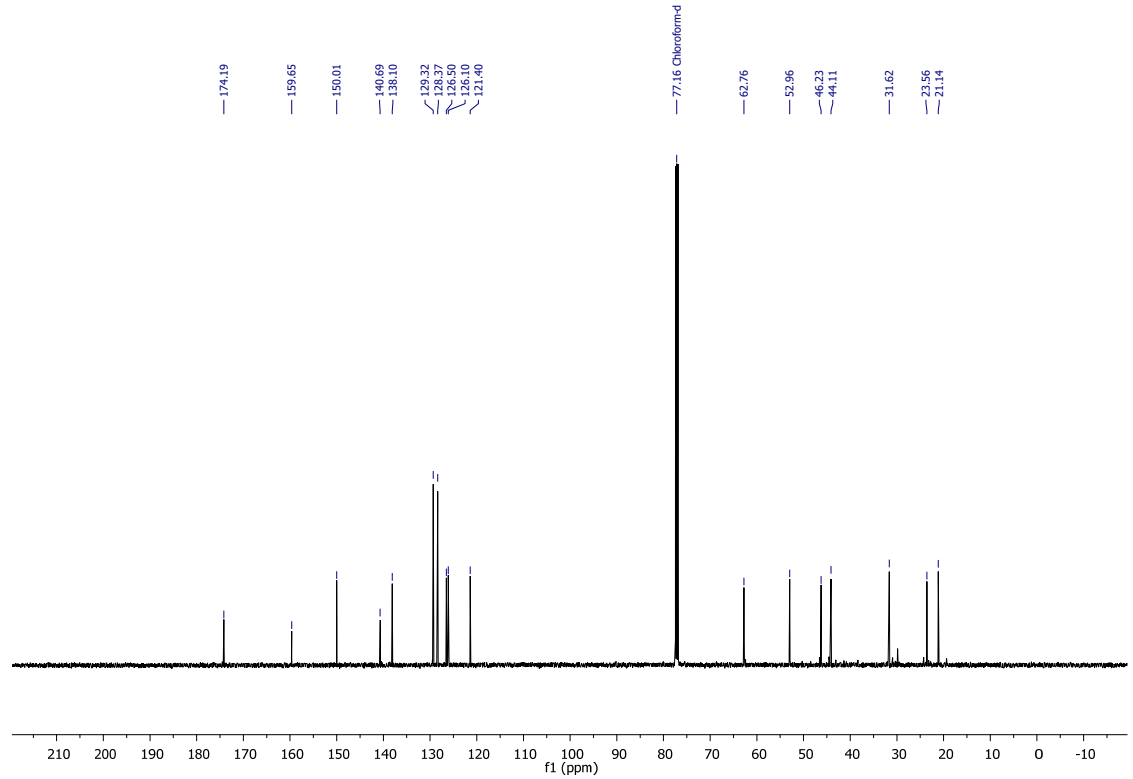


**(*rac*)-Methyl 2,4-dimethyl-5-phenyl-2-(pyridine-2-sulfonamido)pentanoate ($X_{mo}$)**

$^1$H NMR ($CDCl_3$, 500 MHz)

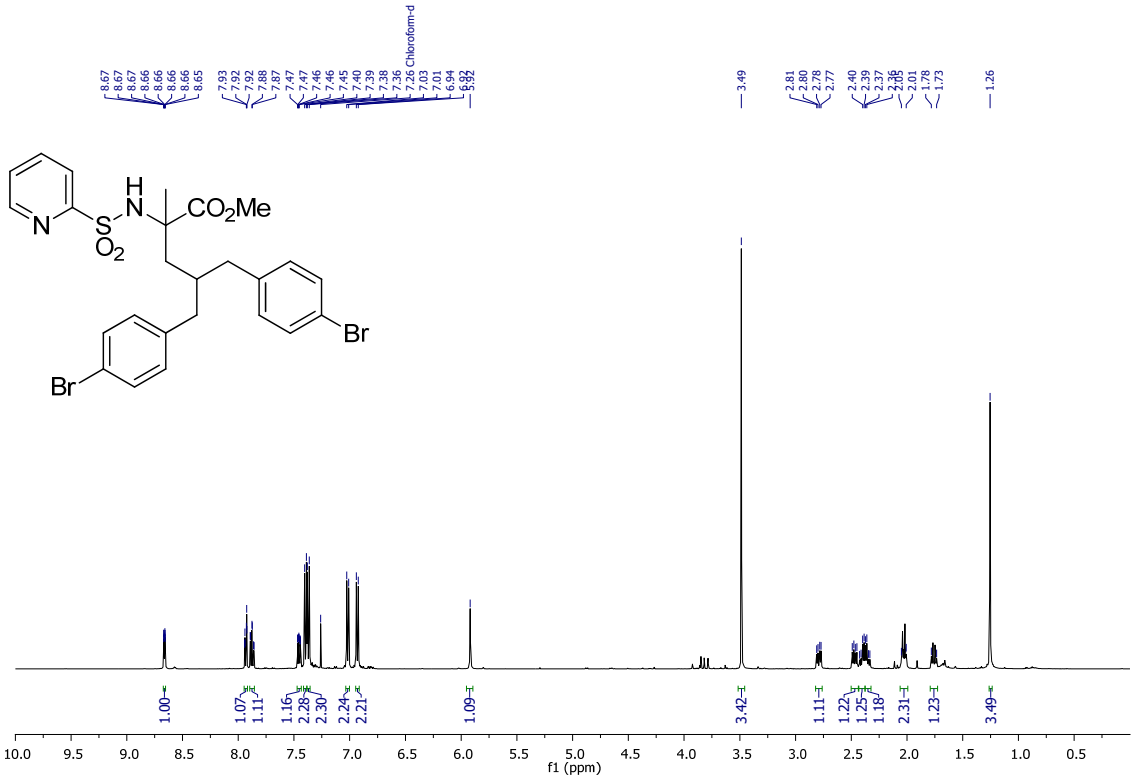



$^{13}$C NMR ($CDCl_3$, 126 MHz)

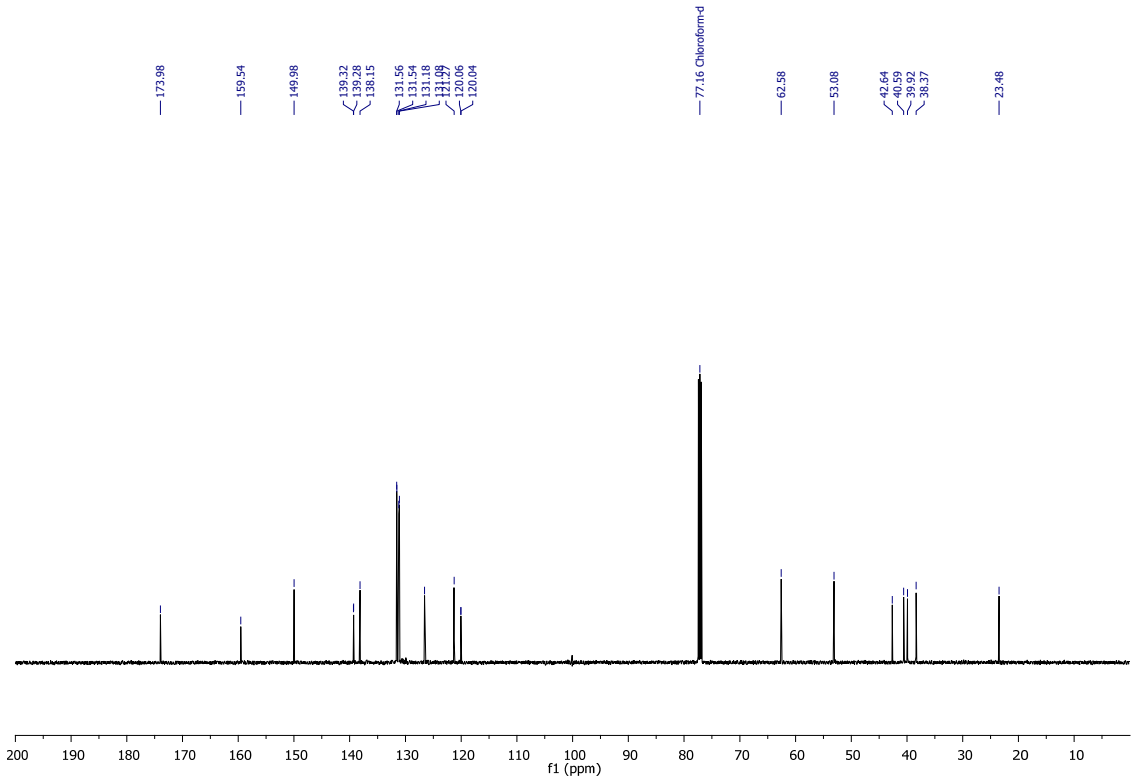


**(*rac*)-Methyl 4-(4-bromobenzyl)-5-(4-bromophenyl)-2-methyl-2-(pyridine-2-sulfonamido)pentanoate (XI)**

$^{1}$H NMR ($CDCl_3$, 500 MHz)

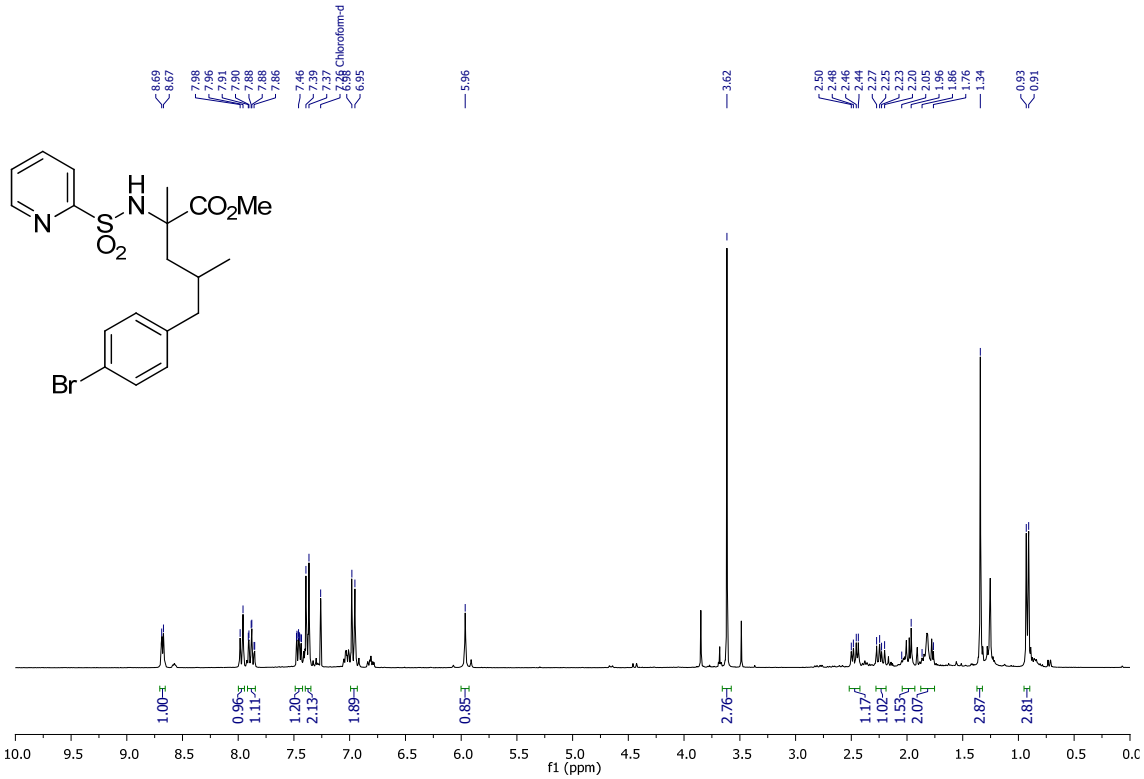



$^{13}$C NMR ($CDCl_3$, 126 MHz)

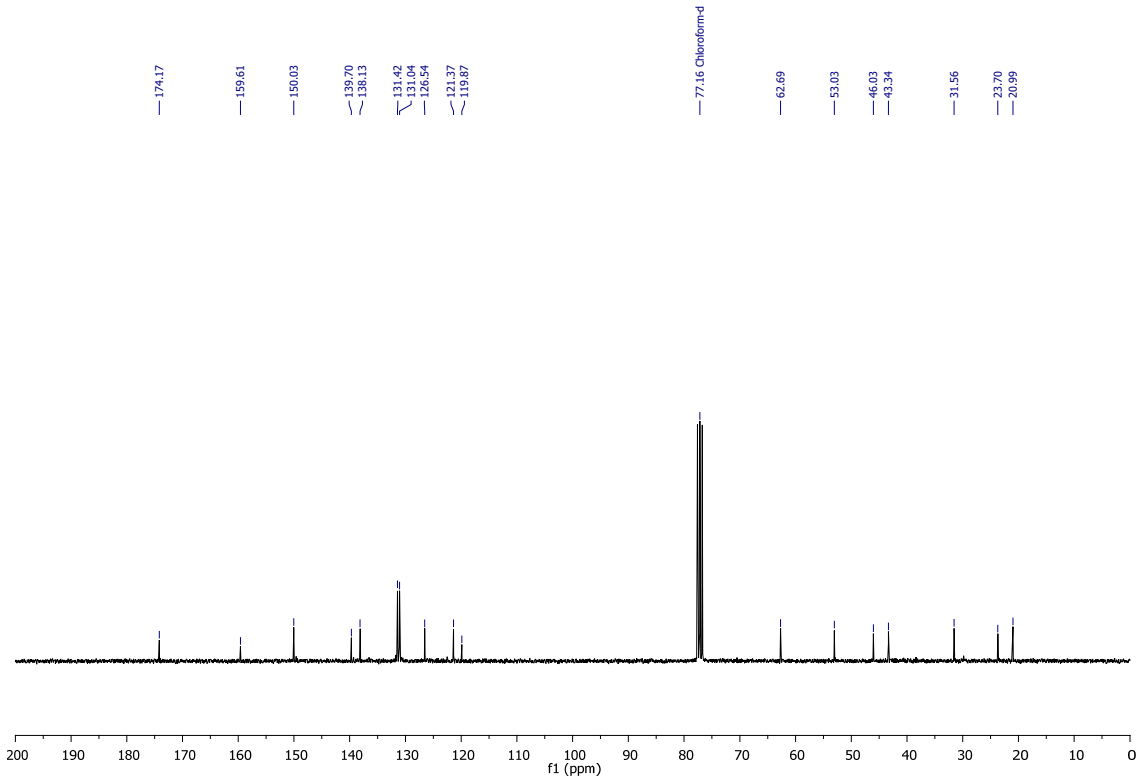


**(*rac*)-Methyl 5-(4-bromophenyl)-2,4-dimethyl-2-(pyridine-2-sulfonamido) pentanoate ($XI_{mo}$)**

$^{1}H$ NMR ($CDCl_3$, 300 MHz)

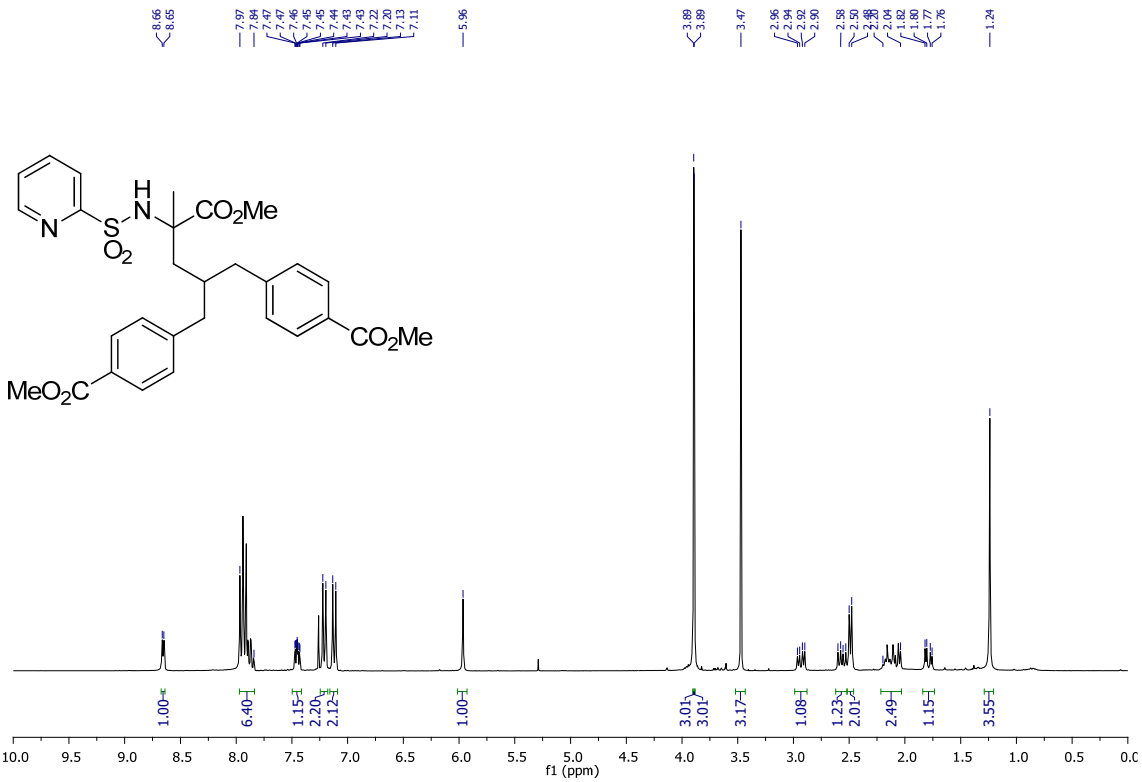



$^{13}C$ NMR ($CDCl_3$, 75 MHz)

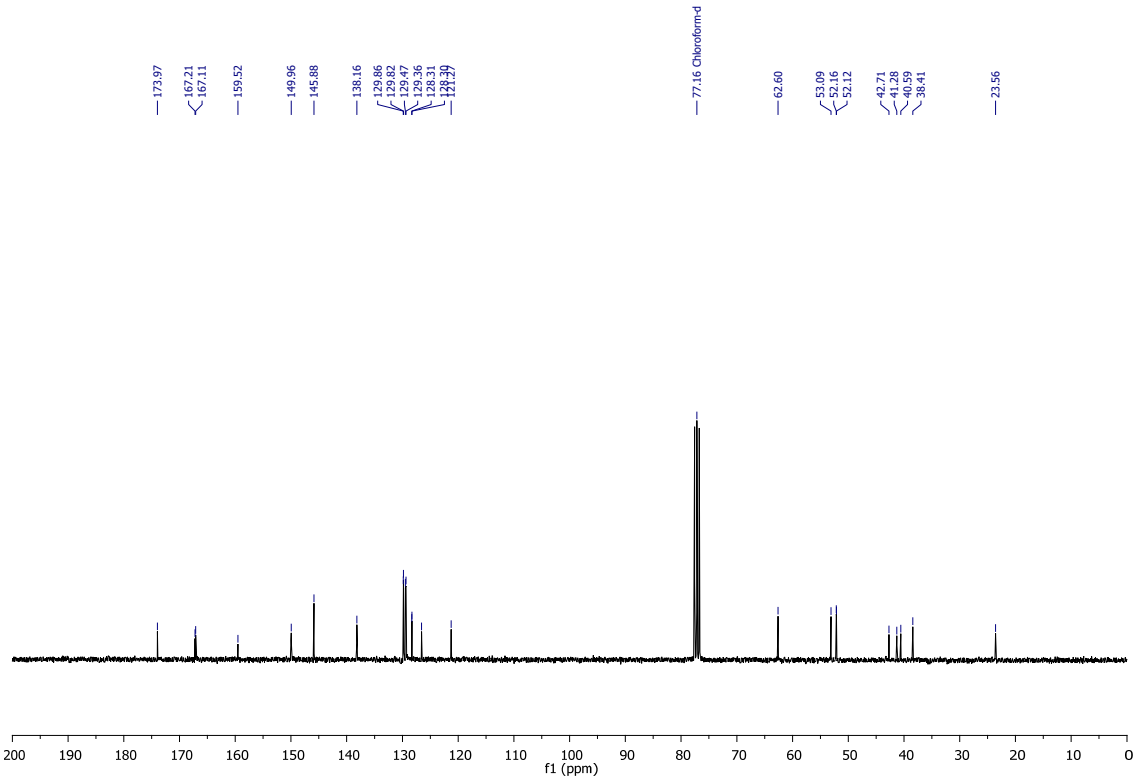


**(*rac*)-Dimethyl 4,4'-(2-(3-methoxy-2-methyl-3-oxo-2-(pyridine-2-sulfonamido)propyl)propane-1,3-diyl)dibenzoate (XII)**

$^{1}$H NMR ($CDCl_3$, 300 MHz)

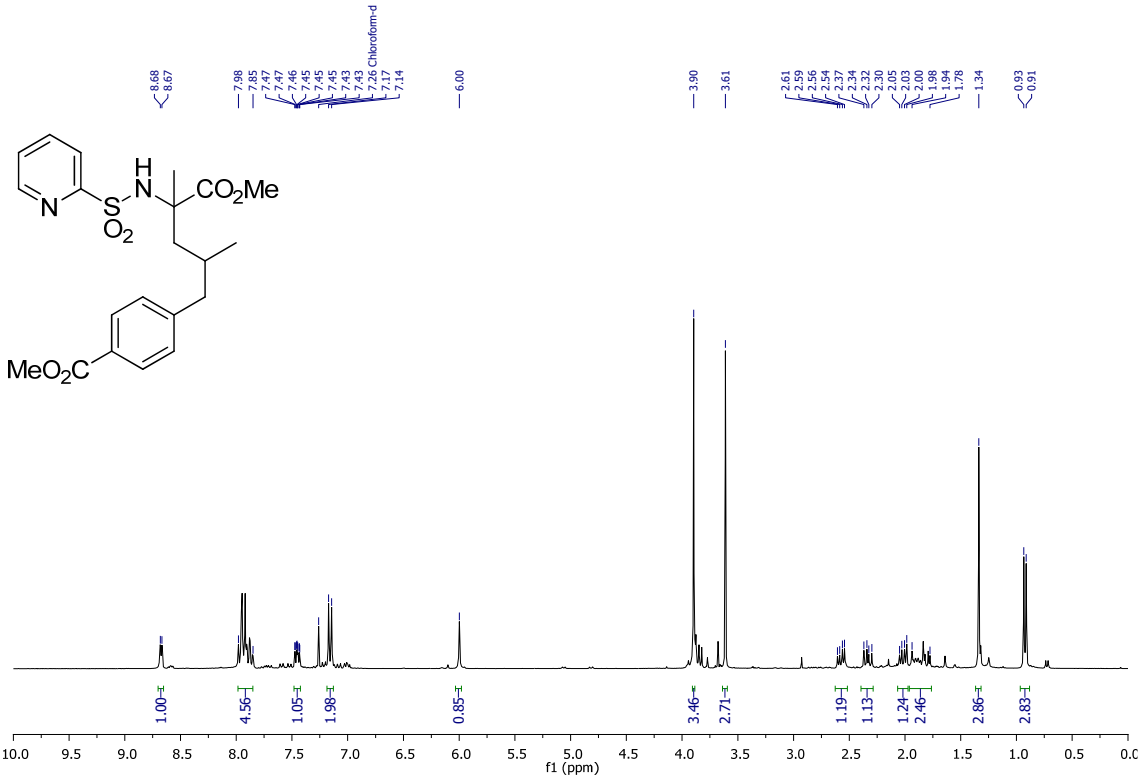



$^{13}$C NMR ($CDCl_3$, 75 MHz)

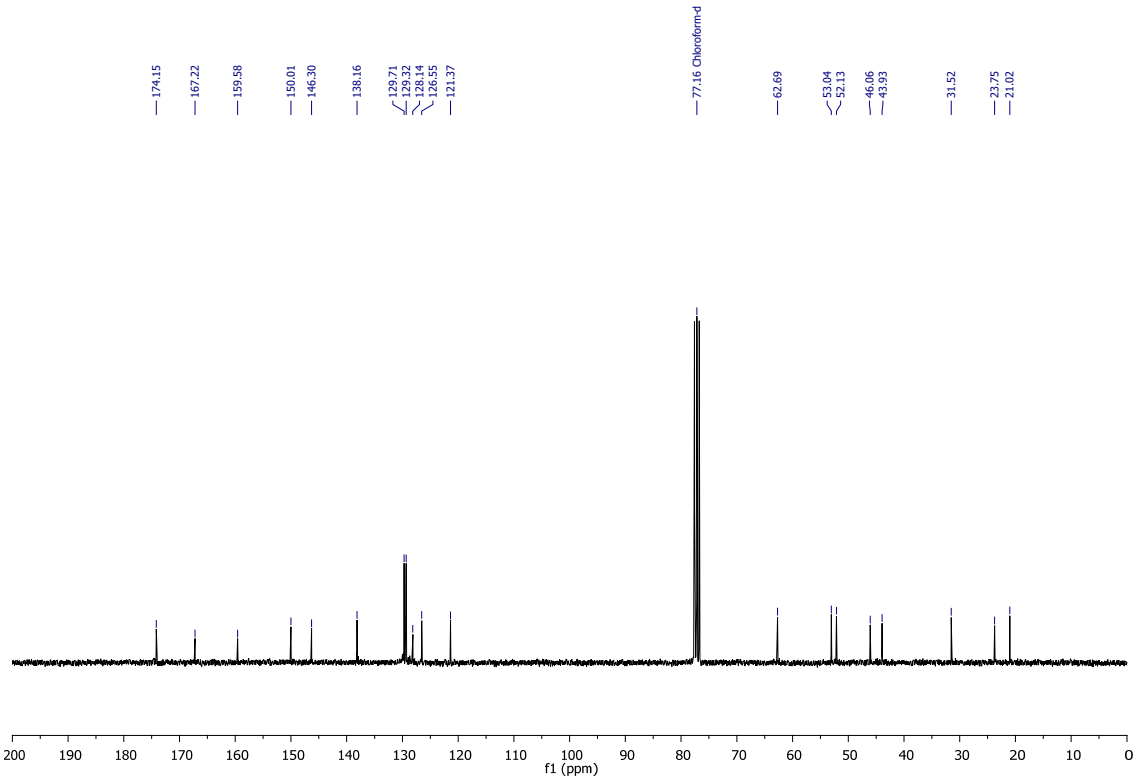


**(*rac*)-Methyl 4-(5-methoxy-2,4-dimethyl-5-oxo-4-(pyridine-2-sulfonamido)pentyl)benzoate ($XII_{mo}$)**

$^1$H NMR ($CDCl_3$, 300 MHz)

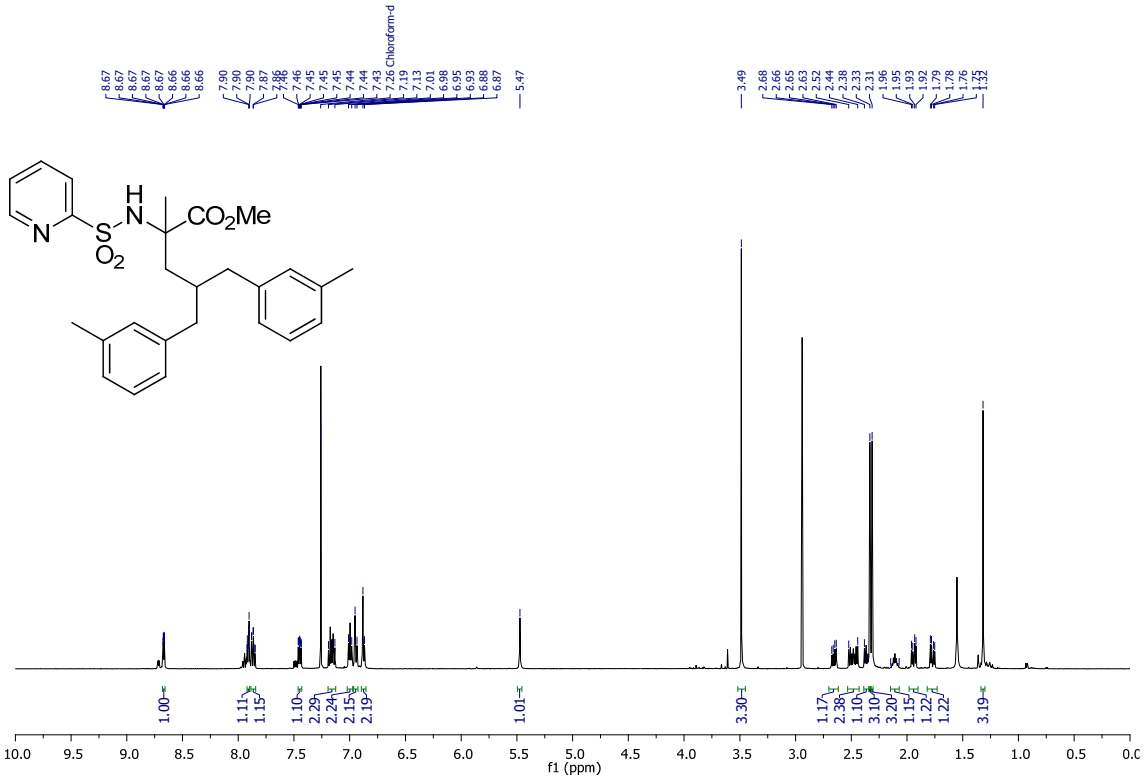



$^{13}$C NMR ($CDCl_3$, 75 MHz)

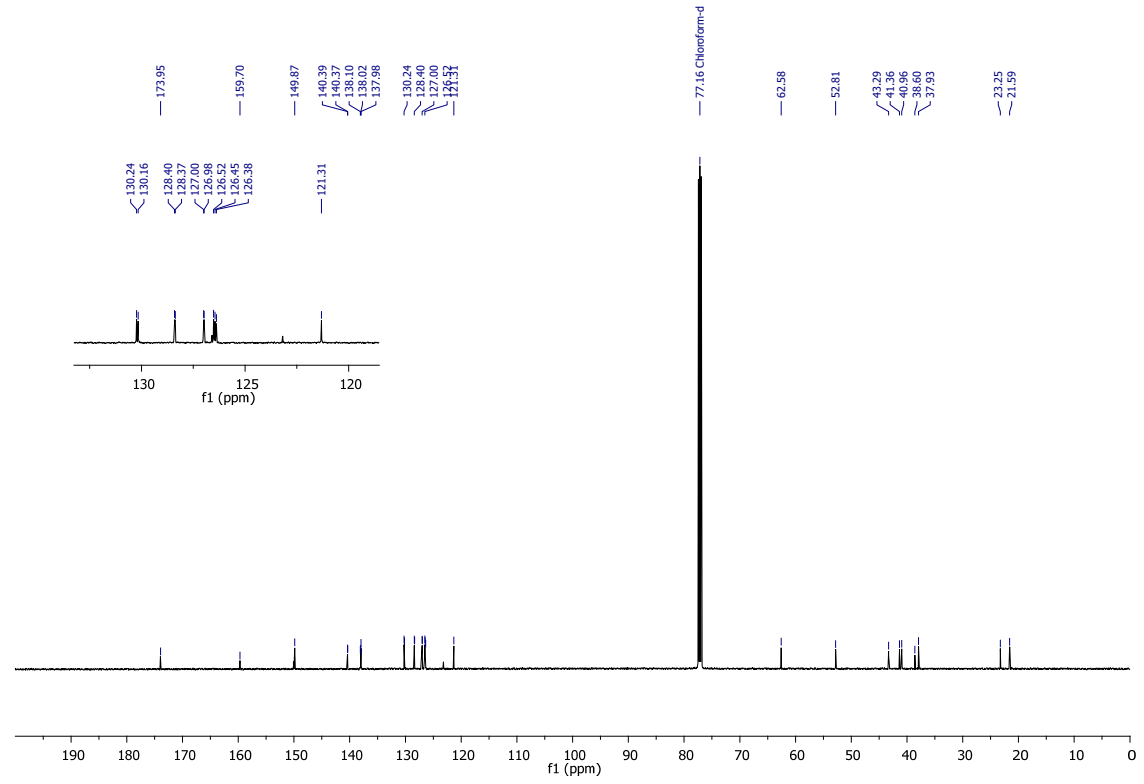


**(*rac*)-Methyl 2-methyl-4-(3-methylbenzyl)-2-(pyridine-2-sulfonamido)-5-(*m*-tolyl)pentanoate (XIII)**

$^1$H NMR ($CDCl_3$, 500 MHz)

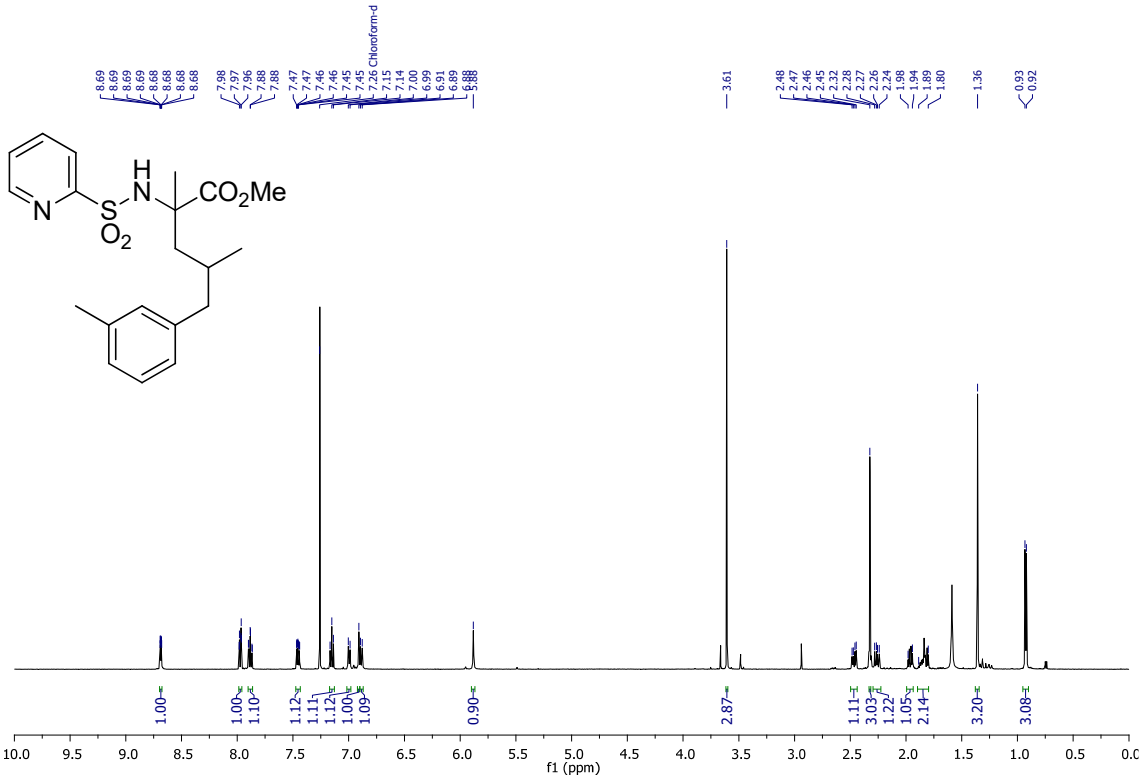



$^{13}$C NMR ($CDCl_3$, 126 MHz)

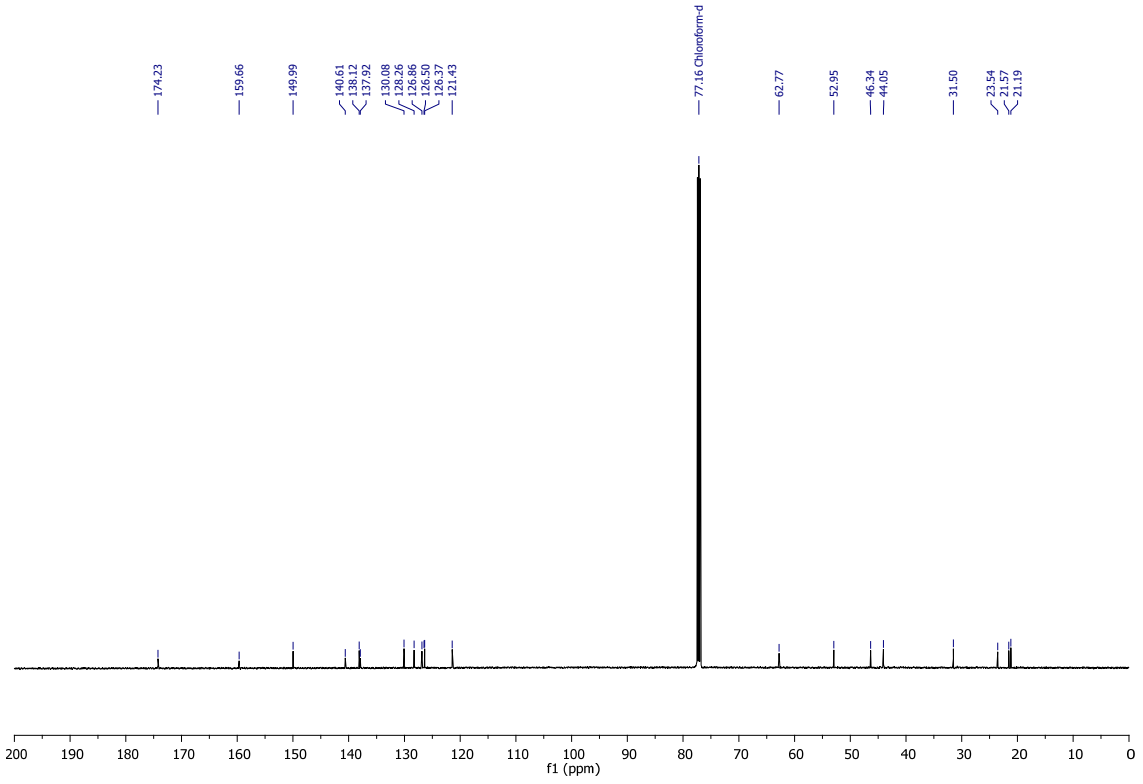


**(*rac*)-Methyl 2,4-dimethyl-2-(pyridine-2-sulfonamido)-5-(*m*-tolyl)pentanoate (XIII$_{mo}$)**

$^{1}$H NMR ($CDCl_3$, 500 MHz)

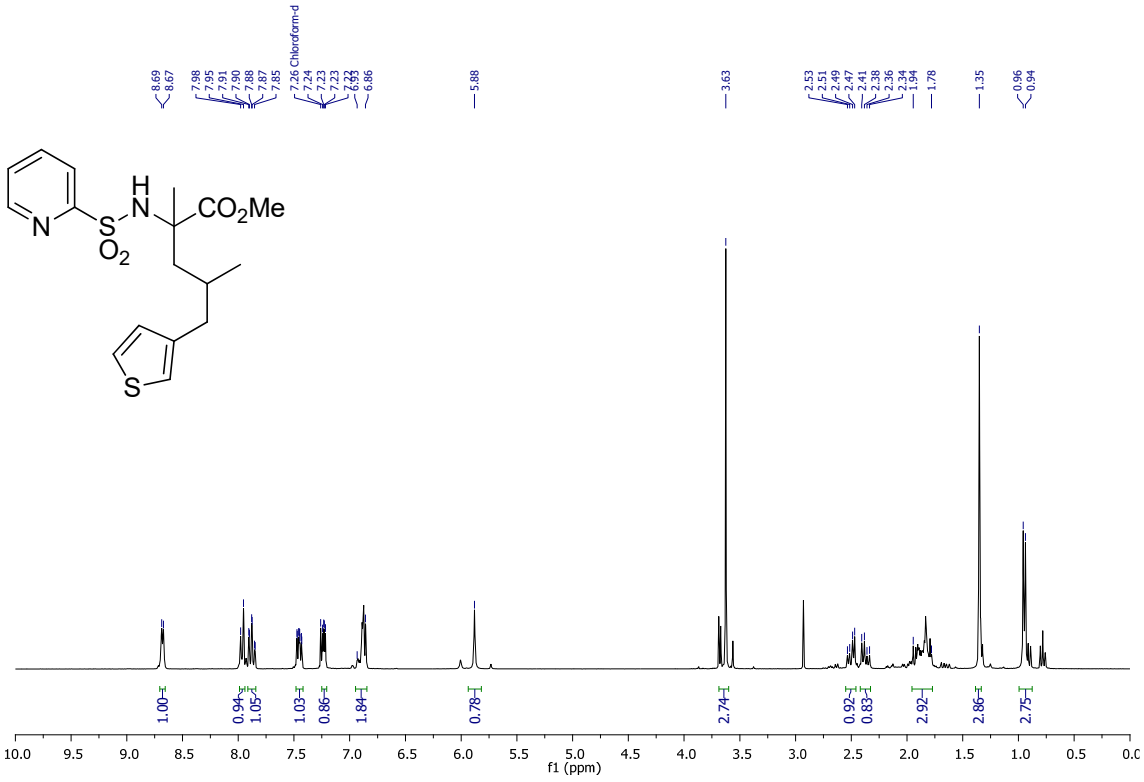



$^{13}$C NMR ($CDCl_3$, 126 MHz)

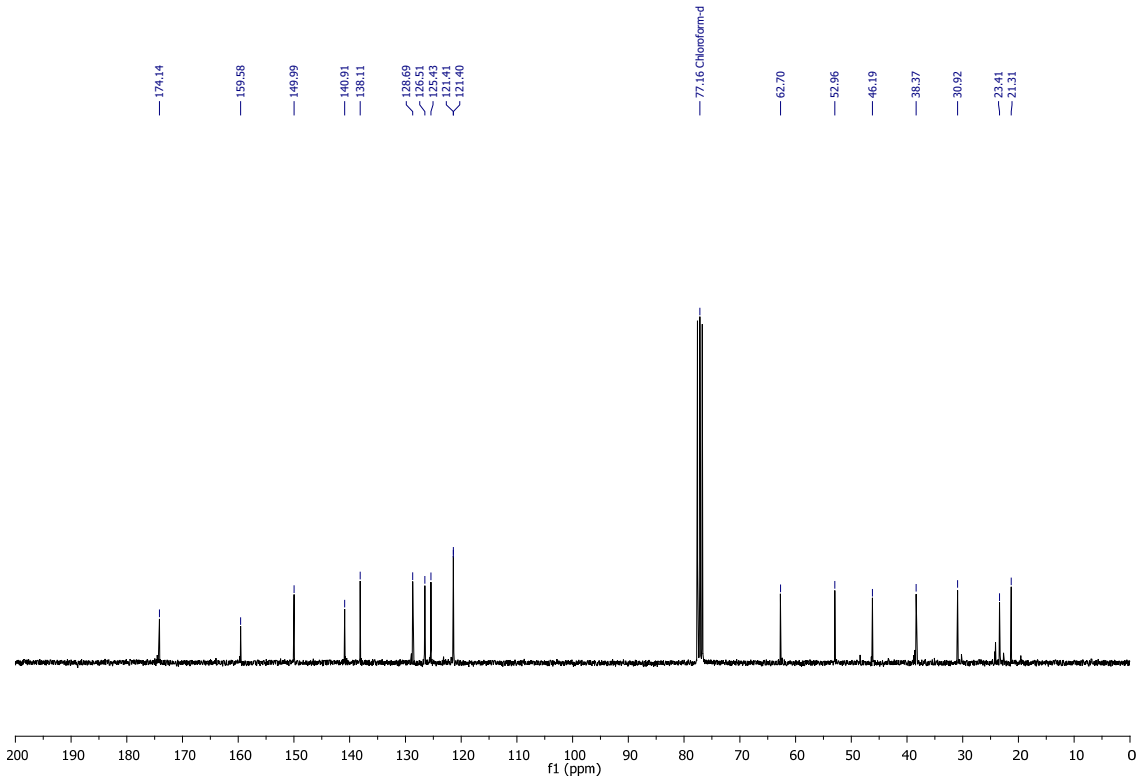


**(*rac*)-Methyl 2,4-dimethyl-2-(pyridine-2-sulfonamido)-5-(thiophen-3-yl)pentanoate (XIV)**

$^{1}$H NMR ($CDCl_3$, 300 MHz)

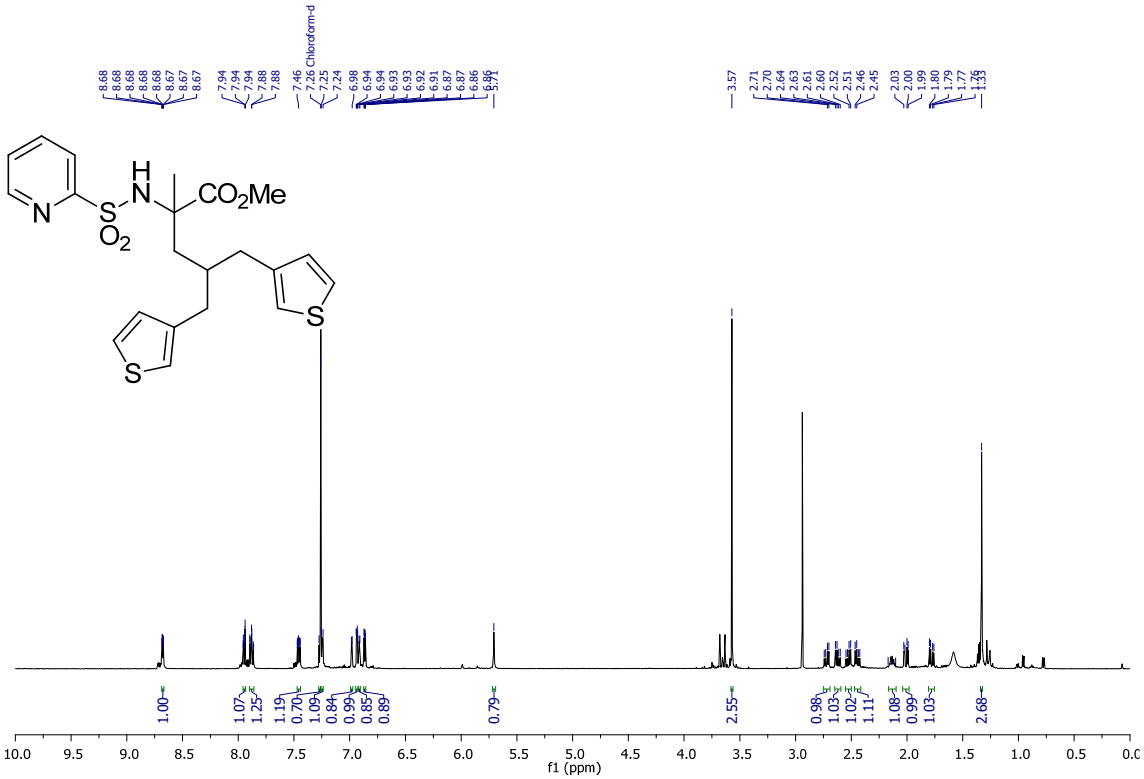



$^{13}$C NMR ($CDCl_3$, 75 MHz)

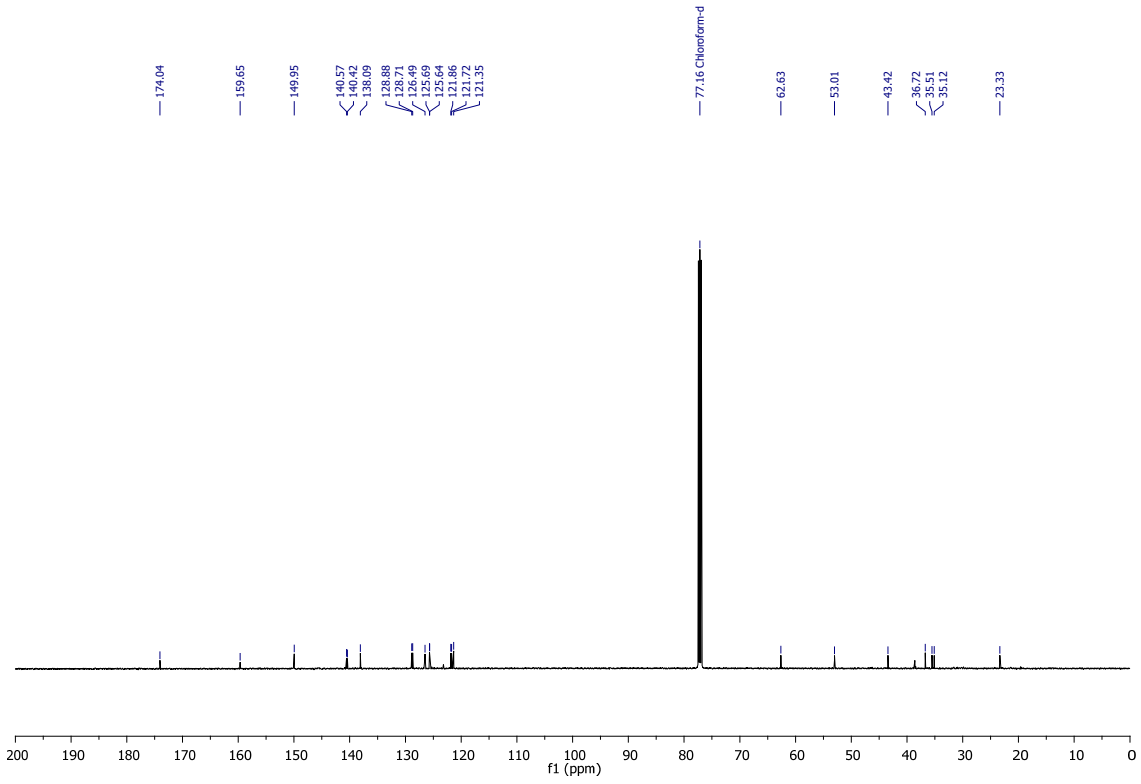


**(*rac*)-Methyl 2-methyl-2-(pyridine-2-sulfonamido)-5-(thiophen-3-yl)-4-(thiophen-3-ylmethyl)pentanoate ($XIV_{di}$)**

$^1H$ NMR ($CDCl_3$, 500 MHz)

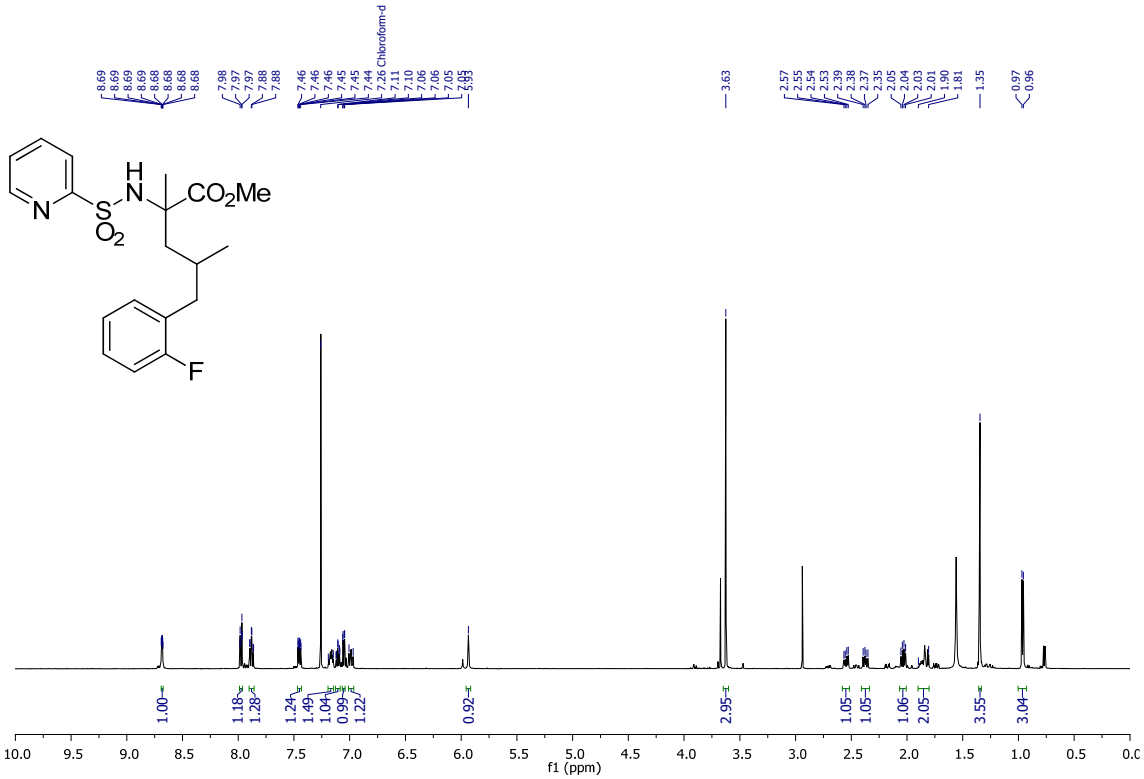



$^{13}C$ NMR ($CDCl_3$, 126 MHz)

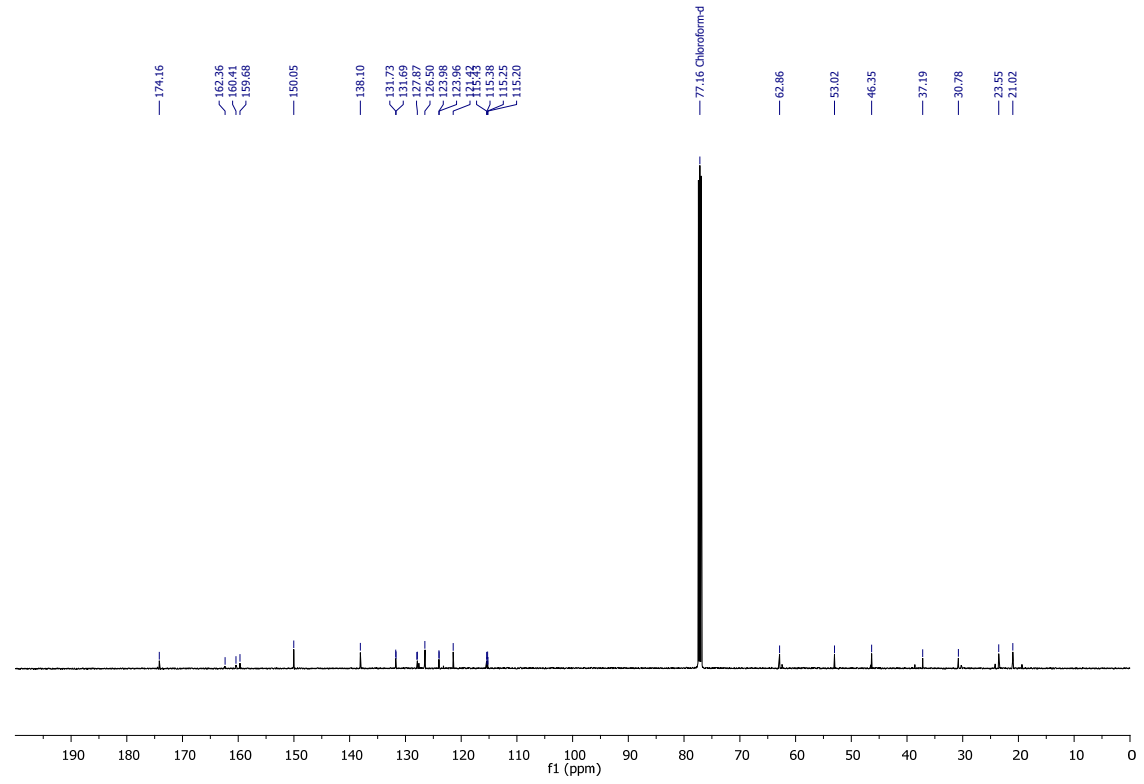


**(*rac*)-Methyl 5-(2-fluorophenyl)-2,4-dimethyl-2-(pyridine-2-sulfonamido)pentanoate (XV)**

$^{1}$H NMR ($CDCl_3$, 500 MHz)



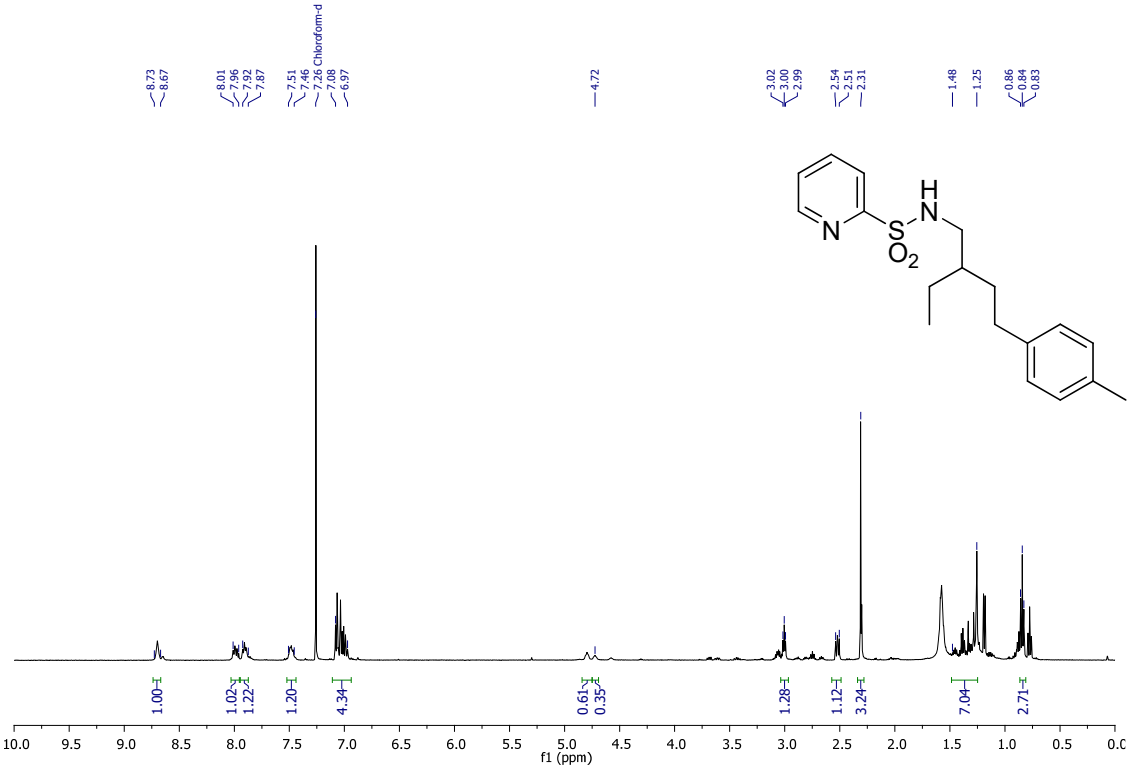

$^{13}$C NMR ($CDCl_3$, 126 MHz)



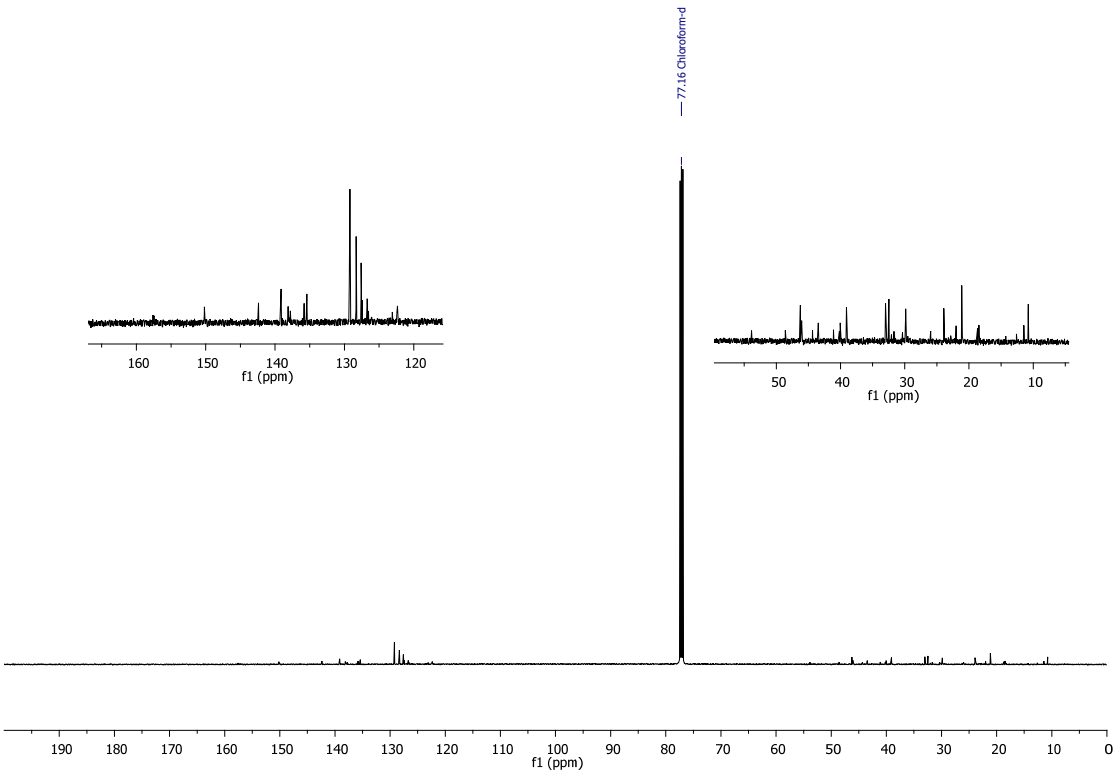
**(*rac*)-*N*-(2-Ethyl-4-(*p*-tolyl)butyl)pyridine-2-sulfonamide (XVII)**

The images below correspond to mixture of **XVII** and **XVIII** in a 40:60 ratio

$^{1}$H NMR ($CDCl_3$, 500 MHz)

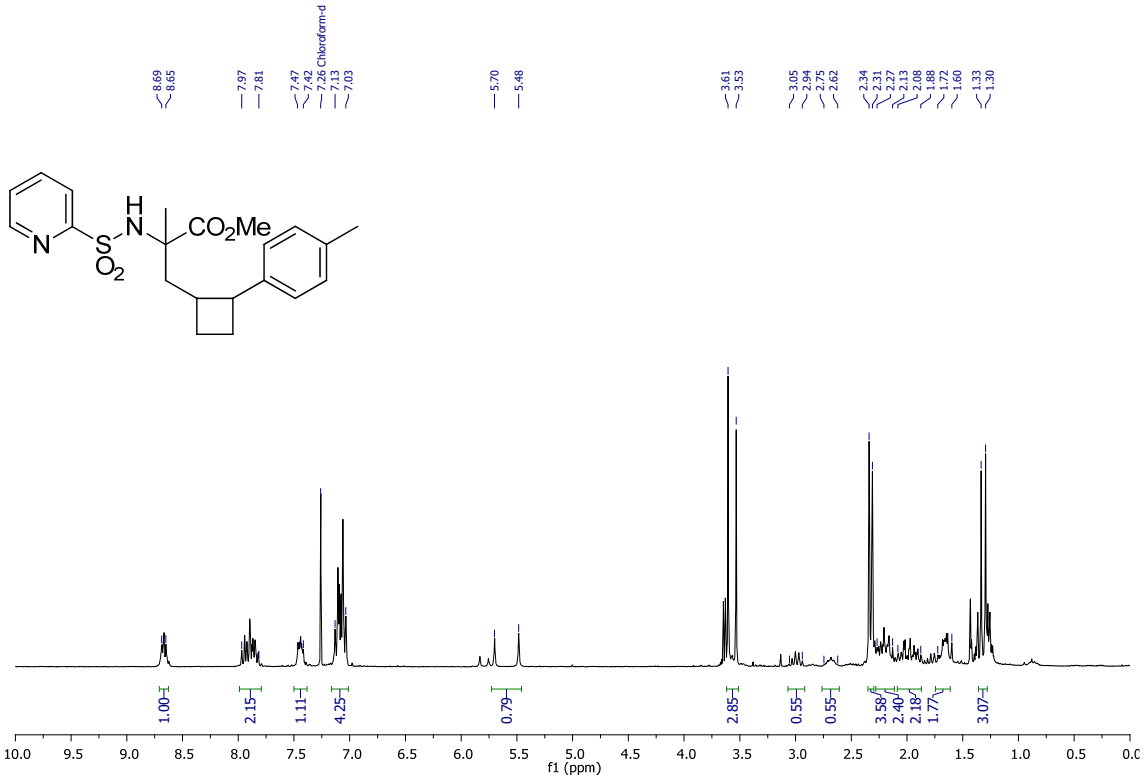



$^{13}$C NMR ($CDCl_3$, 126 MHz)

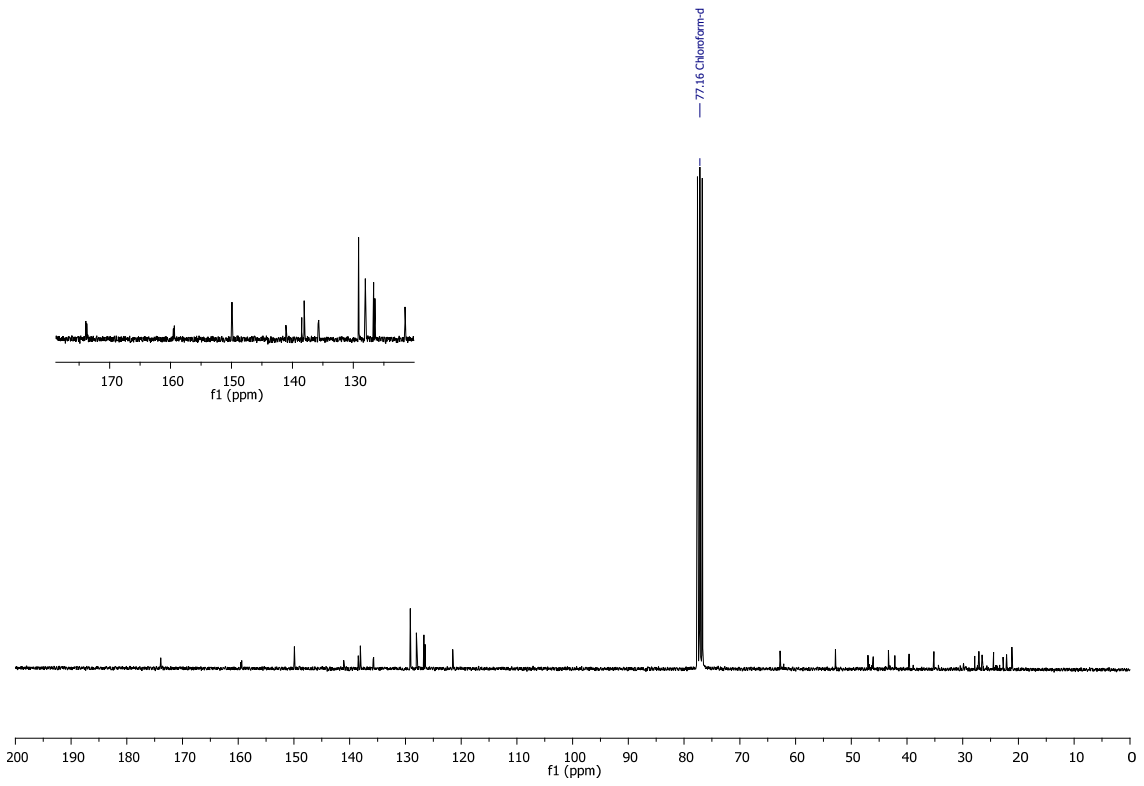


**(*rac*)-Methyl 2-methyl-2-(pyridine-2-sulfonamido)-3-(2-(*p*-tolyl)cyclobutyl) propanoate (XXII)**

$^{1}$H NMR ($CDCl_3$, 300 MHz)

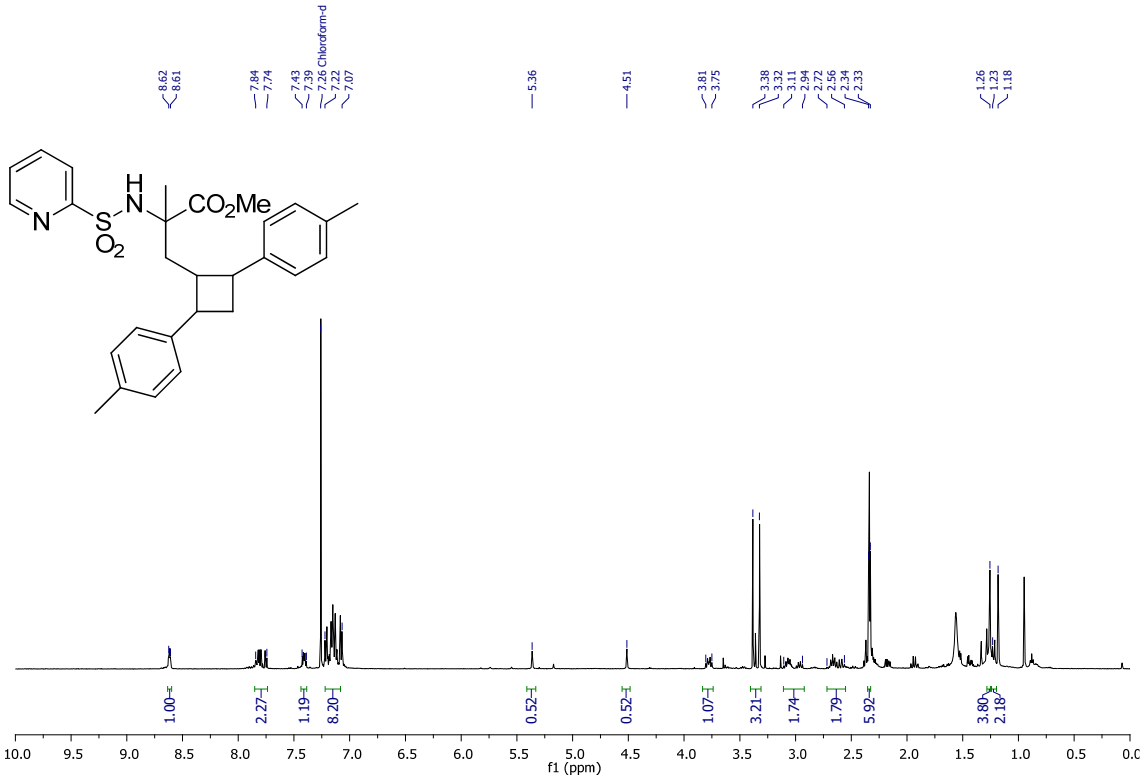



$^{13}$C NMR ($CDCl_3$, 75 MHz)

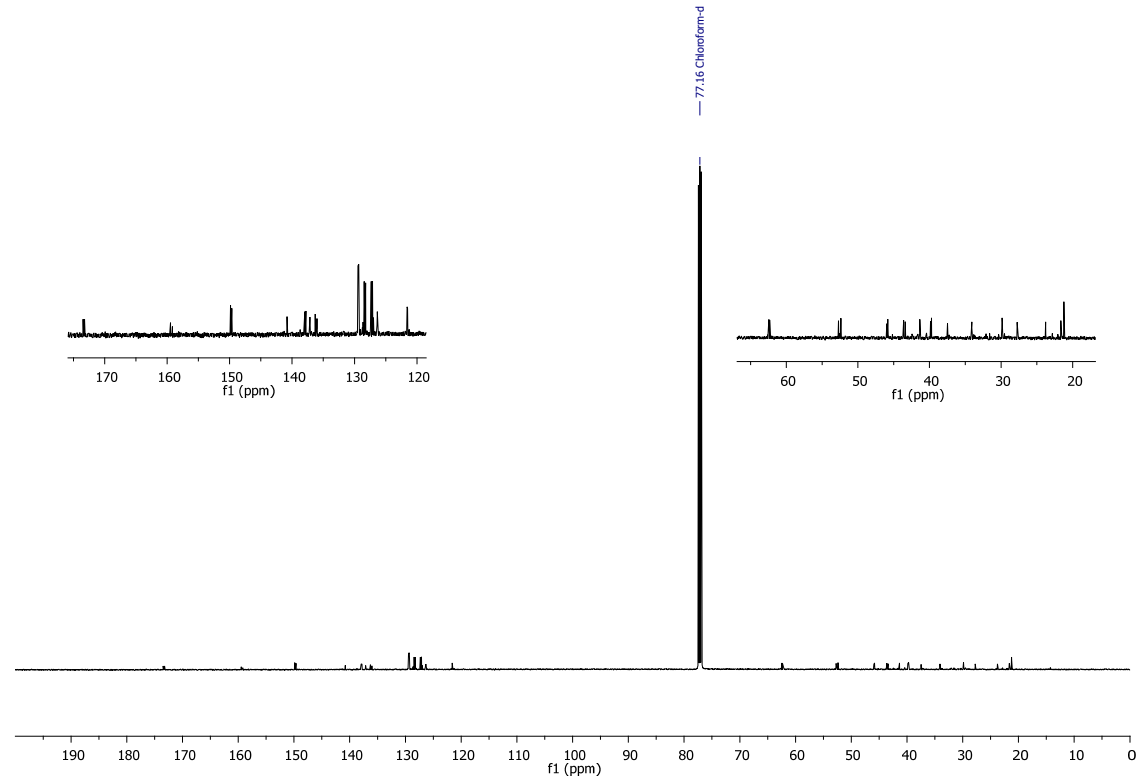


**(*rac*)-Methyl 3-(2,4-di-*p*-tolylcyclobutyl)-2-methyl-2-(pyridine-2-sulfonamido)propanoate ($XXII_{di}$)**

$^1$H NMR ($CDCl_3$, 500 MHz)

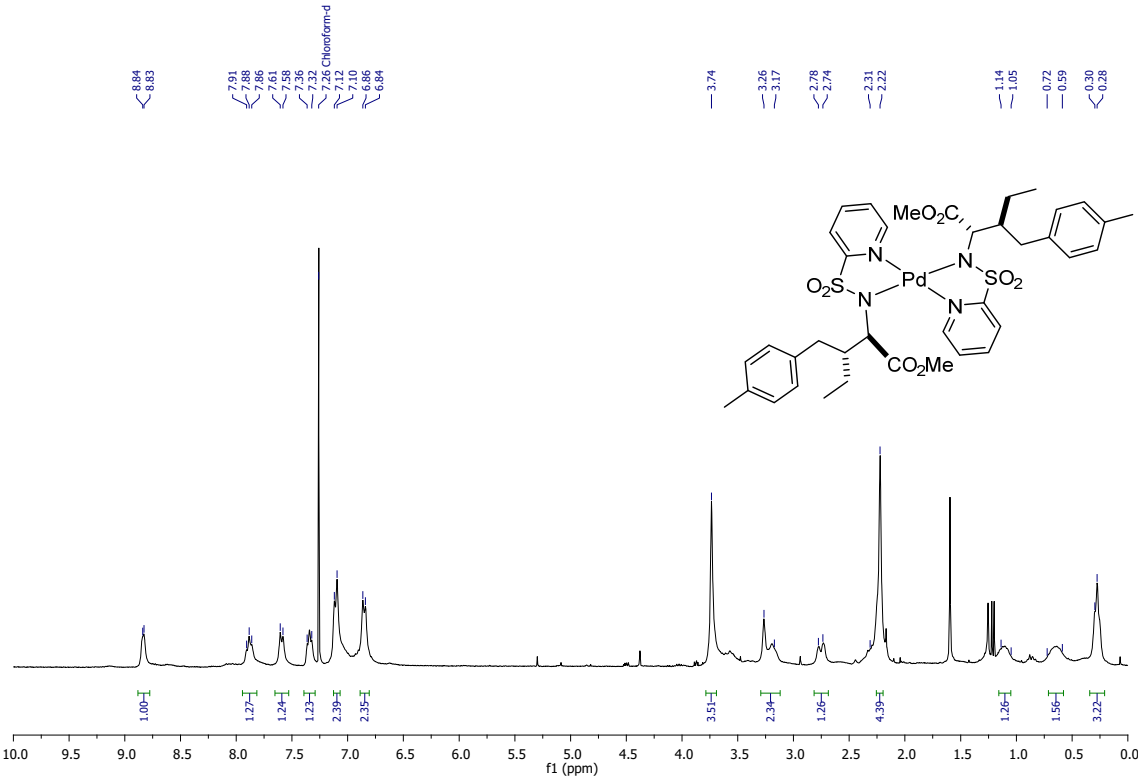



$^{13}$C NMR ($CDCl_3$, 126 MHz)

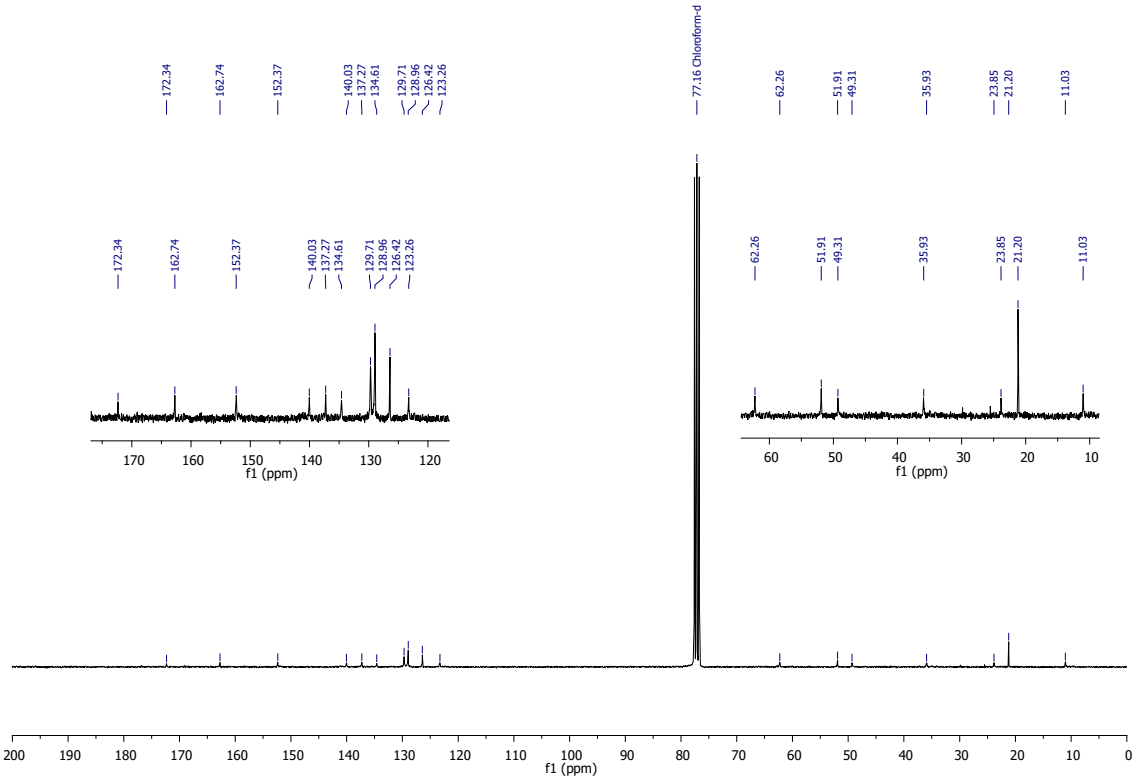


## Complex A

$^{1}$H NMR ($CDCl_3$, 300 MHz)




$^{13}$C NMR ($CDCl_3$, 75 MHz)



## 7. Theoretical calculation

### 7.1 Computational details

Theoretical calculations were performed with Gaussian 09.[9] Geometries were optimized using the B3LYP-D3[10] functional in the gas phase. A mixed basis set of LANL2DZ(f) for Pd and LANL2DZ(d) for I with 6-31G(d) for all other atoms was used in geometry optimizations (BS1). The LANL2DZ basis set was supplemented with an f-type polarization function (exponent 1.472 for Pd),[11] and a d-type polarization function (exponent 0.289 for I).[12] Harmonic frequencies were calculated at the same level to characterize the stationary points and to determine the zero-point energies (ZPE). Single points were calculated with the M06 functional[13] and a mixed basis set of SDD for Pd and I with 6-311++G(d,p) for all other atoms (BS2). Solvation was introduced implicitly in all cases through the SMD[14] model, with 1,4-dioxane as the solvent. The reported free energies include zero-point energies and thermal corrections calculated at 298 K with B3LYP-D3/LANL2DZ(d,f)-6-31G(d). Natural charges were calculated at the M06/SDD-6-311++G(d,p) level by means of the Natural Bond Orbital (NBO) analysis of Weinhold et al.[15]

## 7.2. Computational data for the C–H activation step of diverse substrates and model structures.

### 7.2.1. Substrate 12b.

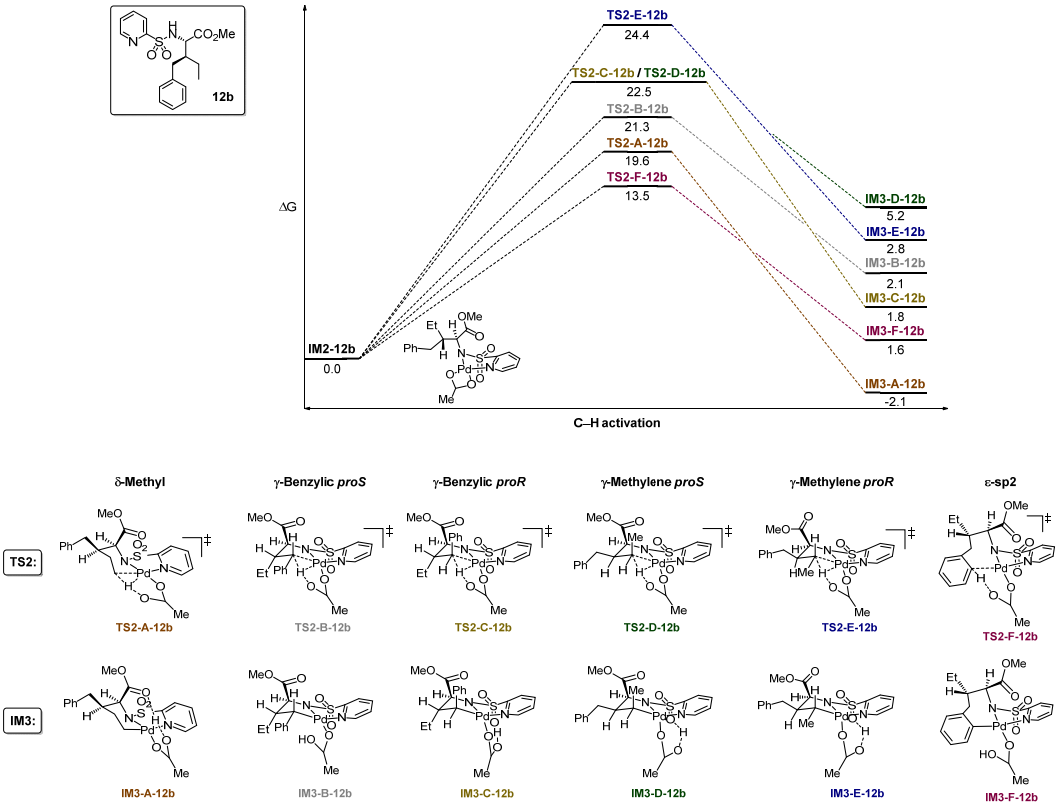



**Figure S1**. Energy profiles for the C–H activation step in different positions of substrate **12b**. Relative G values (kcal mol$^{-1}$, at 298 K in 1,4-dioxane) are respect to **IM2-12b** (that is 3.7 kcal mol$^{-1}$ less stable than $Pd_3(OAc)_6$).

## 7.2.2. Model structure for picolinamide derivative of γ-phenyl-*allo*-isoleucine (12a).

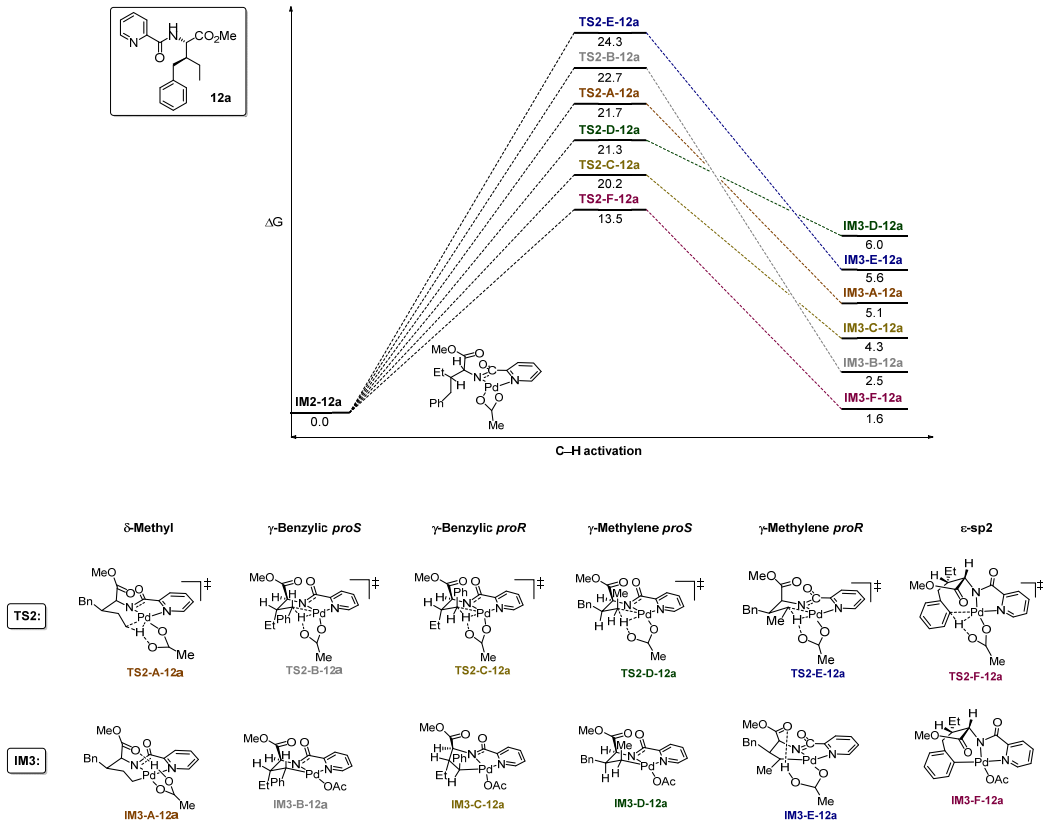



**Figure S2**. Energy profiles for the C–H activation step in different positions of model structure **12a**. Relative G values (kcal mol$^{-1}$, at 298 K in 1,4-dioxane) are respect to **IM2-12a** (that is 0.1 kcal mol$^{-1}$ more stable than $Pd_3(OAc)_6$). Since this step is reversible in all cases, only the pathways affording the most stable **IM3** intermediates for each position have been represented.

## 7.2.3. Model structure $14_{Ph}$

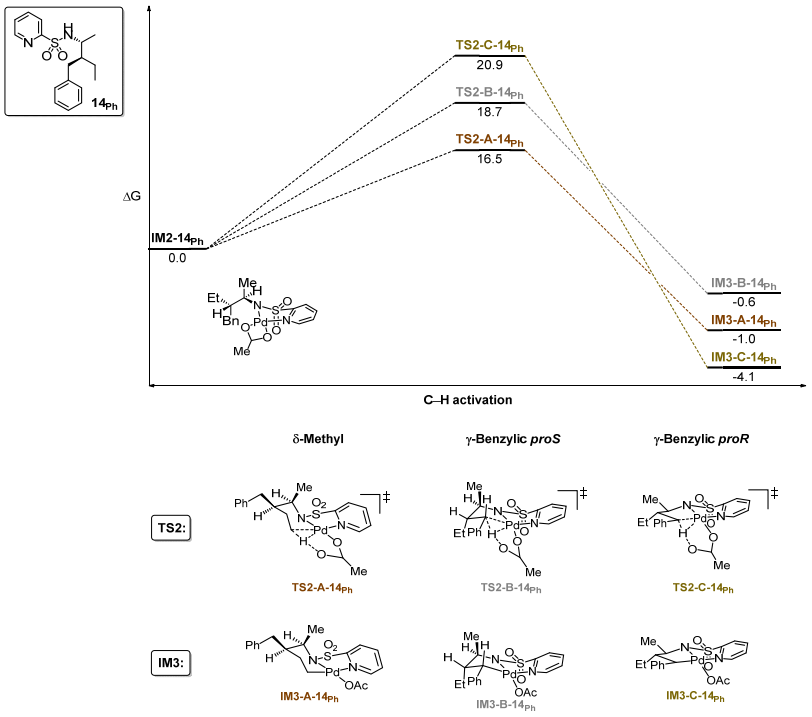



**Figure S3**. Energy profiles for the cleavage of δ-methyl and γ-benzylic bonds of model structure **$14_{Ph}$**. Relative G values (kcal $mol^{-1}$, at 298 K in 1,4-dioxane) are respect to **IM2-$14_{Ph}$** (that is 4.6 kcal $mol^{-1}$ less stable than $Pd_3(OAc)_6$). Since this step is irreversible in all cases, only the pathways with the lowest energy barrier for each position have been represented.

### 7.2.4. Substrate XVI

Substrate **XVI** showed a lower reactivity and afforded a mixture of products (δ:γ = 1:1.5, see scheme S2). This lack of selectivity could be related to the lower number of substituents on the palladacycle, reducing steric interactions and allowing γ-palladacycles become as stable as the δ one (see figure S4).

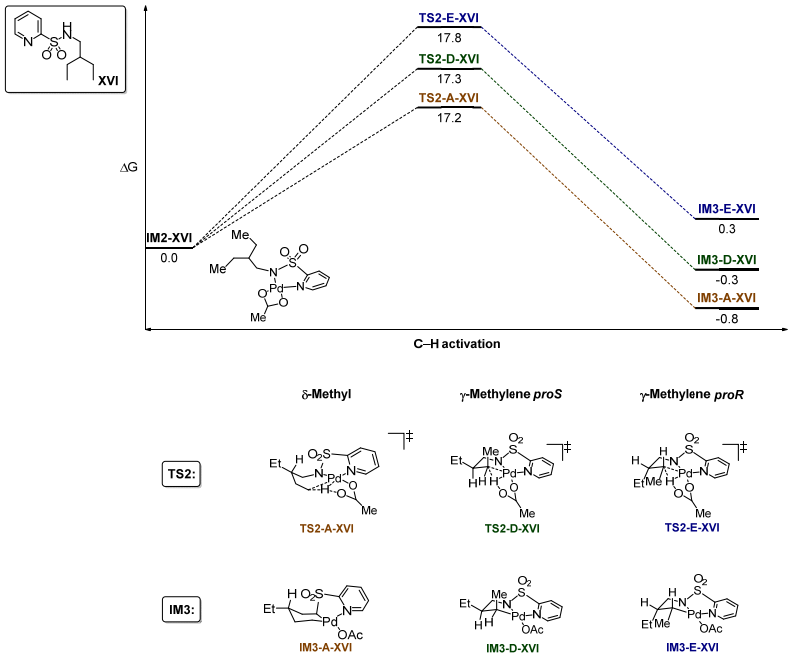
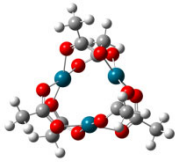



**Figure S4**. Energy profiles for the cleavage of δ-methyl and γ-methylene C–H bonds of substrate **XVI**. Relative G values (kcal $mol^{-1}$, at 298 K in 1,4-dioxane) are respect to **IM2-XVI** (that is 5.7 kcal $mol^{-1}$ less stable than $Pd_3(OAc)_6$). Since intermediates **IM3** are similar in energy to **IM2** in all cases, only the pathways with the lowest energy barrier for each position have been represented.

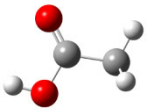
## 7.3. Cartesian coordinates (Å) and energies (hartrees) of all the optimized structures.



**$Pd_3(OAc)_6$**

E(B3LYP/BS1) = -1751.378039
H(correction) = 0.35177662
G(correction) = 0.24515262
E(M06/BS2) = -1754.449857
Imaginary frequencies: 0

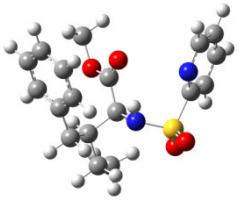
| | | | | |
|---|---|---|---|---|
| 46 | 0 | -1.61118 | 0.92426 | -0.00545 |
| 8 | 0 | -2.31509 | 0.003 | 1.66137 |
| 8 | 0 | -2.64737 | -0.34102 | -1.22557 |
| 8 | 0 | -1.15697 | 1.97807 | -1.68071 |
| 8 | 0 | -1.03048 | 2.44704 | 1.22427 |
| 6 | 0 | -2.2771 | -1.24774 | 1.86621 |
| 6 | 0 | -2.22443 | -1.35021 | -1.86424 |
| 6 | 0 | -0.05937 | 2.58056 | -1.87752 |
| 6 | 0 | 0.04663 | 2.58172 | 1.87624 |
| 8 | 0 | -1.59278 | -2.11218 | 1.2441 |
| 6 | 0 | -3.18058 | -1.77661 | 2.96087 |
| 8 | 0 | -1.15815 | -2.00338 | -1.65838 |
| 6 | 0 | -3.09611 | -1.81481 | -3.01234 |
| 8 | 0 | 1.01818 | 2.45122 | -1.22524 |
| 6 | 0 | -0.02104 | 3.57263 | -3.02126 |
| 8 | 0 | 1.14696 | 1.98419 | 1.67966 |
| 6 | 0 | 0.00377 | 3.574 | 3.01966 |
| 46 | 0 | 0.00466 | -1.85413 | 0.00027 |
| 1 | 0 | -3.456 | -0.97525 | 3.64866 |
| 1 | 0 | -4.09204 | -2.16959 | 2.49568 |
| 1 | 0 | -2.68811 | -2.59489 | 3.49076 |
| 1 | 0 | -4.12943 | -1.90992 | -2.66649 |
| 1 | 0 | -3.07918 | -1.05084 | -3.79684 |
| 1 | 0 | -2.73928 | -2.76516 | -3.41136 |
| 46 | 0 | 1.6064 | 0.93173 | 0.00496 |
| 1 | 0 | -0.99537 | 3.64496 | -3.50612 |
| 1 | 0 | 0.27889 | 4.55129 | -2.63363 |
| 1 | 0 | 0.7394 | 3.25621 | -3.74202 |
| 1 | 0 | 0.97873 | 3.65379 | 3.50205 |
| 1 | 0 | -0.30473 | 4.55019 | 2.63257 |
| 1 | 0 | -0.75232 | 3.25193 | 3.74252 |
| 8 | 0 | 1.60325 | -2.10526 | -1.24349 |
| 8 | 0 | 1.1679 | -1.99637 | 1.65935 |
| 8 | 0 | 2.31509 | 0.01337 | -1.66134 |
| 8 | 0 | 2.64936 | -0.32742 | 1.22556 |
| 6 | 0 | 2.28351 | -1.23767 | -1.86564 |
| 6 | 0 | 2.23099 | -1.33803 | 1.86506 |
| 6 | 0 | 3.19016 | -1.76242 | -2.95964 |
| 6 | 0 | 3.10437 | -1.79731 | 3.01398 |
| 1 | 0 | 3.46062 | -0.96024 | -3.64846 |
| 1 | 0 | 4.10412 | -2.14907 | -2.49399 |
| 1 | 0 | 2.70278 | -2.58443 | -3.48842 |
| 1 | 0 | 3.08313 | -1.03281 | 3.79787 |
| 1 | 0 | 2.75216 | -2.74914 | 3.41357 |
| 1 | 0 | 4.13837 | -1.88743 | 2.6688 |



**AcOH**

E(B3LYP/BS1) = -229.084787
H(correction) = 0.06753313
G(correction) = 0.03485013
E(M06/BS2) = -229.036494
Imaginary frequencies: 0

| | | | | |
|---|---|---|---|---|
| 6 | 0 | -0.09321 | 0.12693 | 0.00003 |
| 8 | 0 | -0.64567 | 1.20345 | -0.00004 |
| 8 | 0 | -0.77624 | -1.04813 | -0.00003 |
| 1 | 0 | -1.72264 | -0.81115 | -0.00008 |
| 6 | 0 | 1.39641 | -0.10952 | 0.00005 |
| 1 | 0 | 1.68118 | -0.69217 | 0.88223 |
| 1 | 0 | 1.6812 | -0.69225 | -0.88207 |
| 1 | 0 | 1.91636 | 0.84853 | 0.00001 |



**12b**

E(B3LYP/BS1) = -1057.752373
H(correction) = 0.40929378
G(correction) = 0.32771378
E(M06/BS2) = -1507.261378
Imaginary frequencies: 0

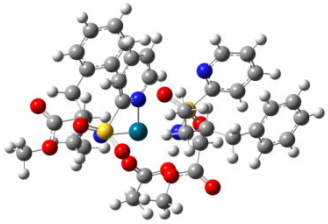
| | | | | |
|---|---|---|---|---|
| 1 | 0 | 0.56853 | 1.19938 | 1.16276 |
| 6 | 0 | -0.19238 | 0.86563 | 0.45041 |
| 6 | 0 | -0.58643 | -0.53911 | 0.90985 |
| 8 | 0 | -0.39154 | -1.55527 | 0.27933 |
| 8 | 0 | -1.13294 | -0.50591 | 2.13872 |
| 6 | 0 | -1.5681 | -1.78186 | 2.64525 |
| 1 | 0 | -1.97815 | -1.57744 | 3.63469 |
| 1 | 0 | -0.72445 | -2.47427 | 2.71083 |
| 1 | 0 | -2.33198 | -2.201 | 1.98551 |
| 7 | 0 | 0.40803 | 0.80386 | -0.88661 |
| 1 | 0 | 0.14613 | -0.04258 | -1.39413 |
| 16 | 0 | 2.0612 | 1.05674 | -1.03648 |
| 8 | 0 | 2.34853 | 1.11146 | -2.46588 |
| 8 | 0 | 2.409 | 2.15634 | -0.12706 |
| 6 | 0 | 2.81134 | -0.44833 | -0.34995 |
| 6 | 0 | 3.78959 | -2.76493 | 0.62791 |
| 7 | 0 | 2.47857 | -1.56445 | -0.9897 |
| 6 | 0 | 3.62037 | -0.37284 | 0.78067 |
| 6 | 0 | 4.12459 | -1.57735 | 1.27631 |
| 6 | 0 | 2.96343 | -2.70772 | -0.49971 |
| 1 | 0 | 3.83468 | 0.58628 | 1.23741 |
| 1 | 0 | 4.76429 | -1.5853 | 2.15431 |
| 1 | 0 | 2.67695 | -3.61449 | -1.02728 |
| 1 | 0 | 4.15642 | -3.72225 | 0.98501 |
| 6 | 0 | -1.34182 | 1.91209 | 0.49658 |
| 1 | 0 | -1.85826 | 1.76057 | 1.45277 |

| | | | | |
|---|---|---|---|---|
| 6 | 0 | -0.7756 | 3.34505 | 0.46425 |
| 1 | 0 | -1.62082 | 4.03611 | 0.34533 |
| 1 | 0 | -0.15072 | 3.45737 | -0.43041 |
| 6 | 0 | 0.02996 | 3.74618 | 1.70483 |
| 1 | 0 | 0.97149 | 3.19248 | 1.77057 |
| 1 | 0 | -0.54249 | 3.5753 | 2.62559 |
| 1 | 0 | 0.28945 | 4.80981 | 1.66445 |
| 6 | 0 | -2.35888 | 1.72543 | -0.65355 |
| 1 | 0 | -3.15088 | 2.47297 | -0.51419 |
| 1 | 0 | -1.85963 | 1.9685 | -1.59773 |
| 6 | 0 | -2.97498 | 0.34632 | -0.74048 |
| 6 | 0 | -4.05623 | -2.25207 | -0.85015 |
| 6 | 0 | -2.68496 | -0.5081 | -1.81115 |
| 6 | 0 | -3.82908 | -0.11928 | 0.27017 |
| 6 | 0 | -4.3669 | -1.40525 | 0.21769 |
| 6 | 0 | -3.21549 | -1.79775 | -1.86629 |
| 1 | 0 | -2.03027 | -0.15948 | -2.6069 |
| 1 | 0 | -4.06801 | 0.53282 | 1.10726 |
| 1 | 0 | -5.03267 | -1.74531 | 1.00729 |
| 1 | 0 | -2.9687 | -2.44731 | -2.70163 |
| 1 | 0 | -4.4712 | -3.25556 | -0.8905 |

**IM1-12b**

E(B3LYP/BS1) = -3141.087215
H(correction) = 0.80033677
G(correction) = 0.66445377
E(M06/BS2) = -3141.281423
Imaginary frequencies: 0

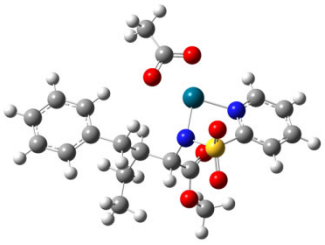
| | | | | |
|---|---|---|---|---|
| 6 | 0 | 1.10141 | 2.86548 | 0.20941 |
| 1 | 0 | 0.31267 | 2.81519 | 0.9501 |
| 6 | 0 | 1.87676 | 4.00016 | -0.01685 |
| 7 | 0 | 1.29422 | 1.75108 | -0.50992 |
| 1 | 0 | 1.70878 | 4.88723 | 0.58361 |
| 6 | 0 | 2.86939 | 3.96747 | -0.99713 |
| 6 | 0 | 2.24251 | 1.71807 | -1.46155 |
| 46 | 0 | 0.24761 | 0.00185 | -0.25958 |
| 1 | 0 | 3.49296 | 4.83839 | -1.17619 |
| 6 | 0 | 3.06326 | 2.79921 | -1.73827 |
| 16 | 0 | 2.32693 | 0.11309 | -2.33464 |
| 7 | 0 | -0.80011 | -1.76149 | -0.06004 |
| 1 | 0 | 3.83069 | 2.70371 | -2.49835 |
| 7 | 0 | 1.92666 | -0.90713 | -1.09966 |
| 8 | 0 | 1.2324 | 0.12069 | -3.31548 |
| 8 | 0 | 3.71808 | -0.02922 | -2.78494 |
| 6 | 0 | -0.69685 | -2.81221 | -0.88786 |
| 6 | 0 | -1.74533 | -1.7506 | 0.8964 |
| 6 | 0 | 3.04666 | -1.081 | -0.14506 |
| 1 | 0 | 0.09307 | -2.75143 | -1.62883 |
| 6 | 0 | -1.57076 | -3.8932 | -0.77437 |
| 16 | 0 | -1.72407 | -0.21129 | 1.87527 |
| 6 | 0 | -2.66863 | -2.76827 | 1.0561 |
| 1 | 0 | 3.5238 | -0.11919 | 0.07661 |
| 6 | 0 | 4.17747 | -1.95308 | -0.68486 |
| 6 | 0 | 2.54471 | -1.65837 | 1.2106 |
| 1 | 0 | -1.47279 | -4.72956 | -1.4579 |
| 6 | 0 | -2.57391 | -3.86537 | 0.19536 |
| 7 | 0 | -1.44542 | 0.88225 | 0.65827 |
| 8 | 0 | -0.52957 | -0.26738 | 2.73133 |
| 8 | 0 | -3.04721 | -0.11629 | 2.50663 |
| 1 | 0 | -3.45065 | -2.66705 | 1.79906 |
| 8 | 0 | 3.77381 | -2.85072 | -1.5974 |
| 8 | 0 | 5.31671 | -1.87261 | -0.26951 |
| 1 | 0 | 1.61039 | -1.13123 | 1.43662 |
| 6 | 0 | 2.22413 | -3.16179 | 1.13908 |
| 6 | 0 | 3.52822 | -1.29937 | 2.35016 |
| 1 | 0 | -3.28699 | -4.68011 | 0.27293 |
| 6 | 0 | -2.61288 | 0.98181 | -0.26302 |
| 6 | 0 | 4.82062 | -3.66033 | -2.15616 |
| 1 | 0 | 1.74768 | -3.36995 | 0.17534 |
| 1 | 0 | 3.15988 | -3.73796 | 1.14478 |
| 1 | 0 | 3.16094 | -1.75987 | 3.27437 |
| 1 | 0 | 4.50977 | -1.73404 | 2.13453 |
| 6 | 0 | 3.64371 | 0.19817 | 2.54552 |
| 6 | 0 | -3.7675 | 1.87585 | 0.28428 |
| 6 | 0 | -2.20531 | 1.44956 | -1.65547 |
| 1 | 0 | -3.03902 | -0.00919 | -0.44969 |
| 1 | 0 | 5.56081 | -3.02633 | -2.65163 |
| 1 | 0 | 4.33034 | -4.31397 | -2.8782 |
| 1 | 0 | 5.31501 | -4.24587 | -1.37545 |
| 6 | 0 | 4.77309 | 0.89956 | 2.10141 |
| 6 | 0 | 2.58131 | 0.91978 | 3.11174 |
| 6 | 0 | -5.08554 | 1.54957 | -0.46549 |
| 1 | 0 | -3.89958 | 1.56971 | 1.32499 |
| 6 | 0 | -3.41856 | 3.37343 | 0.27345 |
| 8 | 0 | -2.72713 | 1.02549 | -2.66738 |
| 8 | 0 | -1.27083 | 2.41492 | -1.65121 |
| 1 | 0 | 5.58441 | 0.34864 | 1.63159 |
| 6 | 0 | 4.84657 | 2.28951 | 2.22914 |
| 6 | 0 | 2.65626 | 2.30673 | 3.2452 |
| 1 | 0 | 1.68362 | 0.39729 | 3.42903 |
| 1 | 0 | -4.98139 | 1.8197 | -1.52258 |
| 1 | 0 | -5.88119 | 2.17977 | -0.0511 |
| 6 | 0 | -5.48312 | 0.09094 | -0.34054 |
| 1 | 0 | -2.38022 | 3.48128 | 0.60916 |
| 1 | 0 | -3.44959 | 3.75766 | -0.75523 |
| 6 | 0 | -0.79553 | 2.82535 | -2.95017 |
| 1 | 0 | 5.73046 | 2.81672 | 1.87866 |
| 6 | 0 | 3.79027 | 2.99686 | 2.80637 |
| 1 | 0 | 1.82606 | 2.84725 | 3.69377 |
| 6 | 0 | -5.95813 | -0.41232 | 0.87891 |
| 6 | 0 | -5.31834 | -0.79937 | -1.41182 |
| 1 | 0 | -0.07551 | 3.62008 | -2.75033 |
| 1 | 0 | -0.31036 | 1.98178 | -3.44635 |
| 1 | 0 | -1.62334 | 3.19624 | -3.55944 |
| 1 | 0 | 3.84924 | 4.07736 | 2.91327 |
| 1 | 0 | -6.06911 | 0.25981 | 1.72596 |
| 6 | 0 | -6.2698 | -1.76466 | 1.02473 |
| 6 | 0 | -5.62711 | -2.15452 | -1.2694 |
| 1 | 0 | -4.91241 | -0.42753 | -2.34845 |
| 1 | 0 | -6.64116 | -2.13233 | 1.97808 |
| 6 | 0 | -6.10656 | -2.64203 | -0.05151 |
| 1 | 0 | -5.49184 | -2.82788 | -2.11219 |
| 1 | 0 | -6.35632 | -3.69471 | 0.05821 |
| 6 | 0 | 1.31011 | -3.63811 | 2.27443 |
| 1 | 0 | 1.01618 | -4.68397 | 2.12855 |
| 1 | 0 | 1.80082 | -3.56801 | 3.25129 |
| 1 | 0 | 0.40025 | -3.02938 | 2.32589 |
| 6 | 0 | -4.33056 | 4.2174 | 1.17085 |
| 1 | 0 | -5.37544 | 4.18594 | 0.84154 |
| 1 | 0 | -4.29732 | 3.8596 | 2.20727 |
| 1 | 0 | -4.01892 | 5.26826 | 1.16871 |



**TS1-12b**

E(B3LYP/BS1) = -3370.171700
H(correction) = 0.86461866
G(correction) = 0.71586966
E(M06/BS2) = -3370.299847
Imaginary frequencies: -1055.90

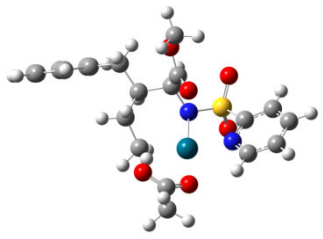
| | | | | |
|---|---|---|---|---|
| 6 | 0 | -0.20947 | 2.14356 | 0.87376 |
| 1 | 0 | 0.38232 | 2.19799 | -0.02627 |
| 6 | 0 | -0.35444 | 3.2372 | 1.72782 |
| 7 | 0 | -0.81009 | 0.97589 | 1.14058 |
| 1 | 0 | 0.13927 | 4.16731 | 1.47122 |
| 6 | 0 | -1.15426 | 3.1262 | 2.8616 |
| 6 | 0 | -1.60828 | 0.8766 | 2.22371 |
| 46 | 0 | -0.8091 | -0.70312 | -0.0756 |
| 1 | 0 | -1.29017 | 3.97226 | 3.52871 |
| 6 | 0 | -1.81294 | 1.91855 | 3.10975 |
| 16 | 0 | -2.53343 | -0.69087 | 2.27192 |
| 7 | 0 | 2.6367 | 2.45881 | -0.39917 |
| 1 | 0 | -2.49829 | 1.78073 | 3.93859 |
| 7 | 0 | -2.73169 | -0.89997 | 0.63962 |
| 8 | 0 | -1.63504 | -1.73227 | 2.78581 |
| 8 | 0 | -3.78918 | -0.39171 | 2.97295 |
| 6 | 0 | 3.5435 | 3.35024 | 0.01502 |
| 6 | 0 | 3.04532 | 1.52738 | -1.25283 |
| 6 | 0 | -3.70954 | 0.03529 | 0.04754 |
| 1 | 0 | 3.19121 | 4.09859 | 0.72145 |
| 6 | 0 | 4.86881 | 3.34356 | -0.42443 |
| 16 | 0 | 1.76074 | 0.41458 | -1.92303 |
| 6 | 0 | 4.34229 | 1.40598 | -1.74642 |
| 1 | 0 | -3.52761 | 1.06732 | 0.3725 |
| 6 | 0 | -5.15381 | -0.24611 | 0.46034 |
| 6 | 0 | -3.59684 | 0.01842 | -1.50466 |
| 1 | 0 | 5.56607 | 4.09335 | -0.06445 |
| 6 | 0 | 5.27276 | 2.35377 | -1.31867 |
| 7 | 0 | 1.28977 | -0.73309 | -0.73554 |
| 8 | 0 | 2.42986 | -0.30838 | -3.01229 |
| 8 | 0 | 0.56492 | 1.22632 | -2.19143 |
| 1 | 0 | 4.598 | 0.61272 | -2.43671 |
| 8 | 0 | -5.39468 | -1.53615 | 0.7268 |
| 8 | 0 | -6.00264 | 0.62433 | 0.47641 |
| 1 | 0 | -2.52054 | 0.05332 | -1.71921 |
| 6 | 0 | -4.15107 | -1.27548 | -2.12556 |
| 6 | 0 | -4.21046 | 1.30585 | -2.10324 |
| 1 | 0 | 6.29796 | 2.30297 | -1.66677 |
| 6 | 0 | 2.41987 | -1.29097 | 0.08283 |
| 6 | 0 | -6.72931 | -1.82867 | 1.16788 |
| 1 | 0 | -3.84808 | -2.11238 | -1.49034 |
| 1 | 0 | -5.24964 | -1.24631 | -2.11735 |
| 1 | 0 | -4.17904 | 1.22281 | -3.19573 |
| 1 | 0 | -5.26369 | 1.3772 | -1.81313 |
| 6 | 0 | -3.45913 | 2.54985 | -1.67596 |
| 6 | 0 | 2.73542 | -0.55334 | 1.42102 |
| 6 | 0 | 2.17986 | -2.77241 | 0.38346 |
| 1 | 0 | 3.31594 | -1.27147 | -0.5426 |
| 1 | 0 | -6.94334 | -1.2883 | 2.09411 |
| 1 | 0 | -6.75024 | -2.90536 | 1.33794 |
| 1 | 0 | -7.46004 | -1.54128 | 0.40631 |
| 6 | 0 | -3.99759 | 3.43994 | -0.73611 |
| 6 | 0 | -2.17178 | 2.7979 | -2.17449 |
| 6 | 0 | 4.11886 | -0.99505 | 1.98036 |
| 1 | 0 | 2.78078 | 0.51335 | 1.1793 |
| 6 | 0 | 1.66661 | -0.76168 | 2.5157 |
| 8 | 0 | 3.05879 | -3.60931 | 0.39006 |
| 8 | 0 | 0.91042 | -2.99729 | 0.73578 |
| 1 | 0 | -4.97889 | 3.23282 | -0.31617 |
| 6 | 0 | -3.27636 | 4.56403 | -0.32435 |
| 6 | 0 | -1.44656 | 3.91566 | -1.76163 |
| 1 | 0 | -1.72121 | 2.1025 | -2.87652 |
| 1 | 0 | 4.09506 | -2.08078 | 2.12563 |
| 1 | 0 | 4.21848 | -0.55292 | 2.97761 |
| 6 | 0 | 5.34092 | -0.63001 | 1.16671 |
| 1 | 0 | 0.67952 | -0.87452 | 2.07018 |
| 1 | 0 | 1.85533 | -1.71461 | 3.0276 |
| 6 | 0 | 0.53529 | -4.33384 | 1.10487 |
| 1 | 0 | -3.71211 | 5.24732 | 0.40058 |
| 6 | 0 | -2.00173 | 4.80884 | -0.84096 |
| 1 | 0 | -0.44587 | 4.07519 | -2.15404 |
| 6 | 0 | 6.08443 | 0.51693 | 1.47547 |
| 6 | 0 | 5.78513 | -1.44968 | 0.11566 |
| 1 | 0 | -0.48 | -4.24064 | 1.48801 |
| 1 | 0 | 0.56921 | -4.98375 | 0.22532 |
| 1 | 0 | 1.2146 | -4.72062 | 1.8684 |
| 1 | 0 | -1.44384 | 5.68755 | -0.52532 |
| 1 | 0 | 5.76012 | 1.15667 | 2.29363 |
| 6 | 0 | 7.24052 | 0.83911 | 0.7626 |
| 6 | 0 | 6.92787 | -1.11755 | -0.61501 |
| 1 | 0 | 5.2422 | -2.36505 | -0.10721 |
| 1 | 0 | 7.81181 | 1.7245 | 1.03126 |
| 6 | 0 | 7.66362 | 0.02538 | -0.29106 |
| 1 | 0 | 7.25573 | -1.76616 | -1.42314 |
| 1 | 0 | 8.56579 | 0.27141 | -0.84535 |
| 6 | 0 | -3.64666 | -1.51892 | -3.55164 |
| 1 | 0 | -4.02097 | -2.47279 | -3.94116 |
| 1 | 0 | -3.96439 | -0.73367 | -4.24723 |
| 1 | 0 | -2.55118 | -1.55548 | -3.56713 |
| 6 | 0 | 1.62203 | 0.37308 | 3.5425 |
| 1 | 0 | 2.57499 | 0.4964 | 4.0712 |
| 1 | 0 | 1.38642 | 1.32843 | 3.05902 |
| 1 | 0 | 0.84887 | 0.17678 | 4.29276 |
| 8 | 0 | -1.27303 | -2.36707 | -1.23395 |
| 6 | 0 | -0.48542 | -3.00245 | -1.99171 |
| 8 | 0 | 0.74112 | -2.7126 | -2.17401 |
| 1 | 0 | 1.02338 | -1.71028 | -1.51386 |
| 6 | 0 | -1.04793 | -4.17665 | -2.75655 |
| 1 | 0 | -0.31967 | -4.99172 | -2.77384 |
| 1 | 0 | -1.99162 | -4.50428 | -2.31803 |
| 1 | 0 | -1.22559 | -3.86433 | -3.79178 |



**IM2-12b**

E(B3LYP/BS1) = - 1862.406536
H(correction) = 0.45780604
G(correction) = 0.36228204
E(M06/BS2) = -1863.023280
Imaginary frequencies: 0

| | | | | |
|---|---|---|---|---|
| 46 | 0 | -0.83269 | 1.38787 | -0.076 |
| 7 | 0 | -2.78924 | 0.81077 | 0.00591 |
| 7 | 0 | -0.49008 | -0.4395 | -0.92526 |
| 8 | 0 | -0.77367 | 3.3159 | 0.78274 |
| 6 | 0 | -3.14203 | -0.27492 | -0.69761 |
| 6 | 0 | -3.67209 | 1.3832 | 0.83946 |
| 6 | 0 | 0.14826 | -1.49451 | -0.12287 |
| 16 | 0 | -1.82302 | -0.88154 | -1.7882 |
| 6 | 0 | 0.49238 | 3.33881 | 0.61133 |
| 6 | 0 | -4.39624 | -0.85737 | -0.59853 |
| 1 | 0 | -3.32052 | 2.25302 | 1.3842 |
| 6 | 0 | -4.95734 | 0.86918 | 0.98607 |
| 6 | 0 | 1.57592 | -1.04997 | 0.30349 |
| 1 | 0 | 0.23752 | -2.38603 | -0.74943 |
| 6 | 0 | -0.69264 | -1.87694 | 1.09901 |
| 8 | 0 | -1.97309 | -2.34163 | -1.86762 |
| 8 | 0 | -1.93016 | -0.05655 | -2.99272 |
| 8 | 0 | 1.03784 | 2.3192 | 0.06333 |
| 6 | 0 | 1.32647 | 4.50808 | 1.03977 |
| 6 | 0 | -5.32286 | -0.26831 | 0.26246 |
| 1 | 0 | -4.61374 | -1.74936 | -1.17574 |
| 1 | 0 | -5.65093 | 1.35178 | 1.66592 |
| 6 | 0 | 2.40522 | -0.70148 | -0.95923 |
| 6 | 0 | 2.2714 | -2.08541 | 1.21564 |
| 1 | 0 | 1.46804 | -0.13011 | 0.89266 |
| 8 | 0 | -1.33163 | -1.10021 | 1.78309 |
| 8 | 0 | -0.64072 | -3.19906 | 1.3412 |
| 1 | 0 | 0.69209 | 5.31395 | 1.41311 |
| 1 | 0 | 2.02016 | 4.18757 | 1.8248 |
| 1 | 0 | 1.92455 | 4.8574 | 0.19229 |
| 1 | 0 | -6.31672 | -0.69232 | 0.37135 |
| 1 | 0 | 2.41533 | -1.56641 | -1.63408 |
| 1 | 0 | 1.88651 | 0.10054 | -1.49218 |
| 6 | 0 | 3.82509 | -0.28148 | -0.6446 |
| 1 | 0 | 3.23176 | -1.65243 | 1.51705 |
| 1 | 0 | 1.69002 | -2.20244 | 2.13931 |
| 6 | 0 | 2.5175 | -3.46698 | 0.59685 |
| 6 | 0 | -1.36671 | -3.64841 | 2.49734 |
| 6 | 0 | 4.07918 | 0.92815 | 0.02138 |
| 6 | 0 | 4.91464 | -1.09172 | -0.98925 |
| 1 | 0 | 3.04934 | -4.11006 | 1.30739 |
| 1 | 0 | 1.58011 | -3.96749 | 0.3368 |
| 1 | 0 | 3.13407 | -3.39842 | -0.30507 |
| 1 | 0 | -0.9847 | -3.16518 | 3.40126 |
| 1 | 0 | -1.2098 | -4.72629 | 2.54026 |
| 1 | 0 | -2.43028 | -3.4165 | 2.3924 |
| 6 | 0 | 5.38363 | 1.3061 | 0.34027 |
| 1 | 0 | 3.24388 | 1.57422 | 0.27464 |
| 6 | 0 | 6.2224 | -0.7146 | -0.67416 |
| 1 | 0 | 4.73779 | -2.02649 | -1.51643 |
| 6 | 0 | 6.46168 | 0.48558 | -0.00379 |
| 1 | 0 | 5.56138 | 2.2481 | 0.85404 |
| 1 | 0 | 7.05223 | -1.35879 | -0.95412 |
| 1 | 0 | 7.47769 | 0.78216 | 0.24373 |



. **TS2-A-12b**

E(B3LYP/BS1) = -1862.360751

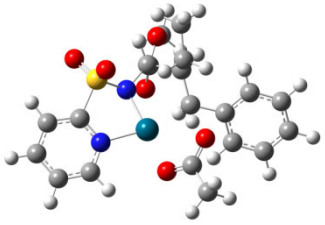
H(correction) = 0.45152676

G(correction) = 0.35773976

E(M06/BS2) = -1862.987550

Imaginary frequencies: -1315.71

| | | | | |
|---|---|---|---|---|
| 6 | 0 | 1.87433 | 1.09468 | 0.04302 |
| 1 | 0 | 2.85662 | 1.54856 | -0.13778 |
| 1 | 0 | 1.61528 | 1.34089 | 1.08296 |
| 6 | 0 | 2.05157 | -0.42672 | -0.08997 |
| 1 | 0 | 2.26423 | -0.64597 | -1.14456 |
| 6 | 0 | 0.76397 | -1.24986 | 0.20406 |
| 1 | 0 | 1.0252 | -2.3045 | 0.07186 |
| 6 | 0 | 0.85453 | 1.72515 | -0.91993 |
| 1 | 0 | 1.16942 | 2.73695 | -1.21517 |
| 1 | 0 | 0.8063 | 1.18956 | -1.87363 |
| 7 | 0 | -0.25868 | -0.89217 | -0.77195 |
| 46 | 0 | -1.20652 | 0.91887 | -0.61478 |
| 6 | 0 | 0.26984 | -1.1131 | 1.65043 |
| 8 | 0 | -0.67754 | -0.45046 | 2.02357 |
| 8 | 0 | 1.02852 | -1.84582 | 2.48997 |
| 6 | 0 | 3.25966 | -0.92367 | 0.74434 |
| 1 | 0 | 3.24823 | -2.02056 | 0.7627 |
| 1 | 0 | 3.14573 | -0.60141 | 1.78502 |
| 6 | 0 | 4.58539 | -0.44179 | 0.19551 |
| 6 | 0 | 5.31061 | 0.57548 | 0.82856 |
| 6 | 0 | 5.10515 | -0.99449 | -0.98438 |
| 6 | 0 | 6.52023 | 1.03242 | 0.29957 |
| 1 | 0 | 4.92219 | 1.01354 | 1.74536 |
| 6 | 0 | 6.31216 | -0.5425 | -1.51725 |
| 1 | 0 | 4.55675 | -1.78892 | -1.48659 |
| 6 | 0 | 7.02463 | 0.47484 | -0.87623 |
| 1 | 0 | 7.06735 | 1.82262 | 0.80734 |
| 1 | 0 | 6.69895 | -0.98611 | -2.4311 |
| 1 | 0 | 7.96594 | 0.82705 | -1.28957 |
| 16 | 0 | -1.31361 | -2.05189 | -1.24531 |
| 8 | 0 | -1.60472 | -1.91214 | -2.67532 |
| 8 | 0 | -0.96732 | -3.37216 | -0.69289 |
| 6 | 0 | -2.84904 | -1.52244 | -0.43515 |
| 6 | 0 | -3.83592 | -2.41774 | -0.04678 |
| 7 | 0 | -2.96784 | -0.19549 | -0.29489 |
| 6 | 0 | -5.0098 | -1.89699 | 0.49729 |
| 1 | 0 | -3.66556 | -3.48182 | -0.16787 |
| 6 | 0 | -4.09605 | 0.31186 | 0.22738 |
| 6 | 0 | -5.14399 | -0.51307 | 0.62792 |
| 1 | 0 | -5.80854 | -2.56045 | 0.81586 |
| 1 | 0 | -4.12804 | 1.3915 | 0.31729 |
| 1 | 0 | -6.04289 | -0.07145 | 1.04476 |
| 6 | 0 | -1.67808 | 3.60416 | 0.25511 |
| 8 | 0 | -2.29894 | 2.68158 | -0.362 |
| 8 | 0 | -0.44112 | 3.54368 | 0.5305 |
| 1 | 0 | 0.00129 | 2.49606 | -0.13972 |
| 6 | 0 | -2.44714 | 4.83212 | 0.67945 |
| 1 | 0 | -2.3941 | 4.92764 | 1.76884 |
| 1 | 0 | -1.97323 | 5.72008 | 0.25 |
| 1 | 0 | -3.48839 | 4.77192 | 0.36014 |
| 6 | 0 | 0.66237 | -1.77612 | 3.87889 |
| 1 | 0 | 1.37551 | -2.41403 | 4.40157 |
| 1 | 0 | 0.72616 | -0.74612 | 4.24132 |
| 1 | 0 | -0.35882 | -2.14003 | 4.02209 |



**TS2-B-12b**

E(B3LYP/BS1) = -1862.357725
H(correction) = 0.45129855
G(correction) = 0.35715355
E(M06/BS2) = -1862.984242
Imaginary frequencies: -1365.48

| | | | | |
|---|---|---|---|---|
| 46 | 0 | -0.45053 | -0.81962 | -0.2309 |
| 7 | 0 | -1.08805 | 1.09374 | -0.08907 |
| 7 | 0 | -2.49214 | -1.23547 | -0.4112 |
| 8 | 0 | 0.12765 | -2.8276 | -0.34951 |
| 6 | 0 | -0.07092 | 2.11084 | 0.18815 |
| 16 | 0 | -2.48786 | 1.17889 | 0.76244 |
| 6 | 0 | -3.29878 | -0.22255 | -0.06389 |
| 6 | 0 | -3.01875 | -2.35474 | -0.93249 |
| 6 | 0 | 1.04854 | -3.08652 | 0.49217 |
| 6 | 0 | 1.20476 | 1.43876 | 0.78151 |
| 1 | 0 | -0.43777 | 2.87154 | 0.88285 |
| 6 | 0 | 0.29871 | 2.82156 | -1.11306 |
| 8 | 0 | -3.23744 | 2.40588 | 0.45487 |
| 8 | 0 | -2.37922 | 0.79221 | 2.18311 |
| 6 | 0 | -4.67411 | -0.25771 | -0.24102 |
| 1 | 0 | -2.30974 | -3.13746 | -1.18061 |
| 6 | 0 | -4.39181 | -2.48045 | -1.13098 |
| 8 | 0 | 1.64034 | -2.19497 | 1.17572 |
| 6 | 0 | 1.48975 | -4.51888 | 0.66279 |
| 6 | 0 | 1.5523 | 0.22712 | -0.11449 |
| 8 | 0 | 0.2454 | 2.34463 | -2.22507 |
| 8 | 0 | 0.77656 | 4.05622 | -0.84701 |
| 6 | 0 | -5.22851 | -1.41579 | -0.78848 |
| 1 | 0 | -5.26957 | 0.60446 | 0.03883 |
| 1 | 0 | -4.79059 | -3.39607 | -1.55432 |
| 1 | 0 | 1.34257 | -1.03097 | 0.60358 |
| 1 | 0 | 0.79205 | -5.20542 | 0.18111 |
| 1 | 0 | 2.48223 | -4.62871 | 0.21152 |
| 1 | 0 | 1.58427 | -4.75031 | 1.72706 |
| 6 | 0 | 1.24607 | 4.7909 | -1.99033 |
| 1 | 0 | -6.30056 | -1.48666 | -0.94631 |
| 1 | 0 | 2.06223 | 4.25322 | -2.48188 |
| 1 | 0 | 1.594 | 5.74852 | -1.60174 |
| 1 | 0 | 0.43518 | 4.93736 | -2.70928 |
| 6 | 0 | 1.00372 | 1.06158 | 2.26395 |
| 1 | 0 | 0.09013 | 0.46431 | 2.36008 |
| 1 | 0 | 1.82942 | 0.40697 | 2.56747 |
| 6 | 0 | 0.92363 | 2.26379 | 3.20872 |
| 1 | 0 | 0.03712 | 2.87608 | 3.01037 |
| 1 | 0 | 0.8545 | 1.92986 | 4.24951 |
| 1 | 0 | 1.80759 | 2.90815 | 3.11784 |
| 1 | 0 | 2.02084 | 2.17433 | 0.72001 |
| 6 | 0 | 3.00644 | -0.17478 | -0.23603 |
| 6 | 0 | 3.99508 | 0.22994 | 0.67028 |
| 6 | 0 | 3.38079 | -1.0091 | -1.30327 |
| 6 | 0 | 5.32184 | -0.17527 | 0.50398 |
| 1 | 0 | 3.73914 | 0.86736 | 1.50977 |
| 6 | 0 | 4.7006 | -1.42099 | -1.46455 |
| 1 | 0 | 2.61871 | -1.33641 | -2.0081 |
| 6 | 0 | 5.68129 | -1.0038 | -0.55878 |
| 1 | 0 | 6.07459 | 0.15677 | 1.21442 |
| 1 | 0 | 4.96727 | -2.06235 | -2.30082 |
| 1 | 0 | 6.71313 | -1.32098 | -0.68275 |
| 1 | 0 | 1.24454 | 0.43402 | -1.1463 |

**TS2-C-12b**

E(B3LYP/BS1) = -1862.356641
H(correction) = 0.45111168
G(correction) = 0.35756168
E(M06/BS2) = -1862.982763
Imaginary frequencies: -1319.51

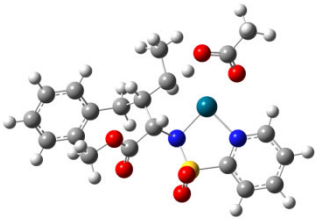
| | | | | |
|---|---|---|---|---|
| 46 | 0 | 0.58643 | 0.79138 | 0.24944 |
| 7 | 0 | 0.6428 | -1.1865 | 0.00051 |
| 7 | 0 | 2.49236 | 0.6612 | -0.61901 |
| 8 | 0 | 0.70656 | 2.8749 | 0.24258 |
| 6 | 0 | -0.57195 | -1.92342 | 0.30583 |
| 16 | 0 | 2.11226 | -1.81609 | 0.32015 |
| 6 | 0 | 3.02741 | -0.56862 | -0.63137 |
| 6 | 0 | 3.1314 | 1.66905 | -1.23367 |
| 6 | 0 | -0.08513 | 3.45837 | 1.05089 |
| 6 | 0 | -1.30307 | -1.18743 | 1.44494 |
| 1 | 0 | -0.34761 | -2.95189 | 0.61243 |
| 6 | 0 | -1.41407 | -2.048 | -0.97265 |
| 8 | 0 | 2.28052 | -3.13377 | -0.30905 |
| 8 | 0 | 2.58303 | -1.66114 | 1.71013 |
| 6 | 0 | 4.21944 | -0.86677 | -1.27428 |
| 1 | 0 | 2.64577 | 2.63693 | -1.17894 |
| 6 | 0 | 4.33992 | 1.45917 | -1.894 |
| 8 | 0 | -0.91604 | 2.83411 | 1.772 |
| 6 | 0 | -0.04724 | 4.96519 | 1.13226 |
| 6 | 0 | -1.53789 | 0.32575 | 1.115 |
| 8 | 0 | -1.08904 | -1.68587 | -2.07836 |
| 8 | 0 | -2.59289 | -2.64208 | -0.68782 |
| 6 | 0 | 4.8871 | 0.17467 | -1.92036 |
| 1 | 0 | 4.58803 | -1.88674 | -1.26747 |
| 1 | 0 | 4.833 | 2.29141 | -2.38474 |
| 1 | 0 | -0.87246 | 1.53988 | 1.38691 |
| 1 | 0 | 0.82668 | 5.36402 | 0.61523 |
| 1 | 0 | -0.95731 | 5.36279 | 0.6696 |
| 1 | 0 | -0.047 | 5.27591 | 2.18045 |
| 1 | 0 | -1.97066 | 0.68978 | 2.06138 |
| 6 | 0 | -3.51742 | -2.72055 | -1.78674 |
| 1 | 0 | 5.82162 | -0.01426 | -2.4402 |
| 1 | 0 | -3.77823 | -1.71474 | -2.12567 |
| 1 | 0 | -4.39633 | -3.23254 | -1.39312 |
| 1 | 0 | -3.08083 | -3.28336 | -2.61638 |
| 6 | 0 | -2.59675 | 0.60189 | 0.05804 |
| 6 | 0 | -2.30826 | 1.07325 | -1.22804 |
| 6 | 0 | -3.9443 | 0.36983 | 0.38464 |
| 6 | 0 | -3.32474 | 1.30481 | -2.15816 |
| 1 | 0 | -1.27404 | 1.24143 | -1.5145 |
| 6 | 0 | -4.96367 | 0.59485 | -0.53867 |
| 1 | 0 | -4.19377 | 0.006 | 1.37923 |
| 6 | 0 | -4.65665 | 1.06758 | -1.81816 |
| 1 | 0 | -3.06929 | 1.66438 | -3.15121 |
| 1 | 0 | -5.99706 | 0.40733 | -0.2584 |
| 1 | 0 | -5.44844 | 1.24879 | -2.54023 |
| 6 | 0 | -0.57174 | -1.33753 | 2.79427 |
| 1 | 0 | 0.40838 | -0.85052 | 2.74531 |

| | | | | |
|---|---|---|---|---|
| 1 | 0 | -1.15824 | -0.79099 | 3.54572 |
| 6 | 0 | -0.38526 | -2.78659 | 3.25558 |
| 1 | 0 | 0.36164 | -3.31031 | 2.64995 |
| 1 | 0 | -0.02749 | -2.81385 | 4.2904 |
| 1 | 0 | -1.32634 | -3.34931 | 3.20757 |
| 1 | 0 | -2.29775 | -1.64117 | 1.55144 |

**TS2-D-12b**

E(B3LYP/BS1) = -1862.352063
H(correction) = 0.45149533
G(correction) = 0.35559033
E(M06/BS2) = -1862.980833
Imaginary frequencies: -1332.55

| | | | | |
|---|---|---|---|---|
| 46 | 0 | 0.89425 | 0.88194 | -0.23376 |
| 7 | 0 | 0.88748 | -1.09728 | 0.1173 |
| 7 | 0 | 2.96703 | 0.66741 | 0.04178 |
| 8 | 0 | 1.15331 | 2.9071 | -0.68059 |
| 6 | 0 | -0.38947 | -1.80447 | 0.18027 |
| 16 | 0 | 2.00125 | -1.52307 | 1.24549 |
| 6 | 0 | 3.34544 | -0.49389 | 0.59249 |
| 6 | 0 | 3.9009 | 1.52898 | -0.3922 |
| 6 | 0 | 0.12345 | 3.62306 | -0.46754 |
| 6 | 0 | -1.51682 | -0.74544 | 0.28094 |
| 1 | 0 | -0.46309 | -2.44089 | 1.06976 |
| 6 | 0 | -0.51485 | -2.75147 | -1.02057 |
| 8 | 0 | 2.387 | -2.93619 | 1.11269 |
| 8 | 0 | 1.72529 | -1.01833 | 2.6031 |
| 6 | 0 | 4.67339 | -0.87237 | 0.72574 |
| 1 | 0 | 3.5254 | 2.44998 | -0.82391 |
| 6 | 0 | 5.25842 | 1.23571 | -0.28423 |
| 8 | 0 | -0.99045 | 3.13999 | -0.10807 |
| 6 | 0 | 0.23242 | 5.11759 | -0.65407 |
| 6 | 0 | -1.29733 | 0.50696 | -0.61112 |
| 6 | 0 | -2.92796 | -1.36432 | 0.09071 |
| 1 | 0 | -1.45827 | -0.39073 | 1.31746 |
| 8 | 0 | -0.02452 | -2.60497 | -2.11639 |
| 8 | 0 | -1.28302 | -3.81319 | -0.68513 |
| 6 | 0 | 5.64949 | 0.01756 | 0.27573 |
| 1 | 0 | 4.91151 | -1.83767 | 1.15895 |
| 1 | 0 | 5.99078 | 1.95067 | -0.64359 |
| 1 | 0 | -0.85953 | 1.7894 | -0.17178 |
| 1 | 0 | 1.23268 | 5.40059 | -0.98445 |
| 1 | 0 | -0.51204 | 5.44334 | -1.38716 |
| 1 | 0 | -0.00279 | 5.61358 | 0.29299 |
| 1 | 0 | -2.18783 | 1.11731 | -0.38894 |
| 1 | 0 | -3.05012 | -1.70186 | -0.94431 |
| 1 | 0 | -2.99325 | -2.26451 | 0.7132 |
| 6 | 0 | -4.03593 | -0.40172 | 0.4545 |
| 6 | 0 | -1.50769 | -4.76459 | -1.73824 |
| 1 | 0 | 6.70186 | -0.23736 | 0.35821 |
| 6 | 0 | -4.80658 | 0.22793 | -0.53161 |
| 6 | 0 | -4.28653 | -0.08723 | 1.79843 |
| 1 | 0 | -2.01419 | -4.28883 | -2.58339 |
| 1 | 0 | -2.13434 | -5.54336 | -1.30241 |
| 1 | 0 | -0.55764 | -5.18091 | -2.08417 |
| 6 | 0 | -5.79898 | 1.14909 | -0.188 |
| 1 | 0 | -4.62672 | -0.00587 | -1.57858 |
| 6 | 0 | -5.27633 | 0.83125 | 2.14678 |
| 1 | 0 | -3.69864 | -0.56952 | 2.5767 |
| 6 | 0 | -6.03635 | 1.45418 | 1.15285 |
| 1 | 0 | -6.38535 | 1.62674 | -0.96867 |
| 1 | 0 | -5.45641 | 1.05997 | 3.19395 |
| 1 | 0 | -6.80777 | 2.17029 | 1.4229 |
| 6 | 0 | -1.30131 | 0.32429 | -2.13582 |
| 1 | 0 | -2.2553 | -0.10339 | -2.47456 |
| 1 | 0 | -1.19633 | 1.30122 | -2.62178 |
| 1 | 0 | -0.50464 | -0.3312 | -2.48998 |

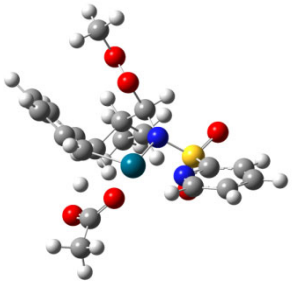


**TS2-E-12b**

E(B3LYP/BS1) = -1862.351681
H(correction) = 0.45172048
G(correction) = 0.35738448
E(M06/BS2) = -1862.979497
Imaginary frequencies: -1459.79

| | | | | |
|---|---|---|---|---|
| 7 | 0 | 0.20829 | -0.7542 | -0.31474 |
| 6 | 0 | -0.86641 | -0.22652 | 0.55806 |
| 16 | 0 | 0.81615 | -2.24755 | 0.15511 |
| 46 | 0 | 1.61348 | 0.72414 | -0.29099 |
| 6 | 0 | -1.40529 | 1.05988 | -0.12877 |
| 1 | 0 | -0.47385 | 0.04712 | 1.54528 |
| 6 | 0 | -2.00388 | -1.21095 | 0.81739 |
| 8 | 0 | 0.45011 | -3.33784 | -0.75266 |
| 8 | 0 | 0.67212 | -2.45125 | 1.60902 |
| 6 | 0 | 2.59872 | -2.00668 | -0.16014 |
| 6 | 0 | -0.233 | 1.9147 | -0.66819 |
| 8 | 0 | -2.25941 | -2.19781 | 0.16657 |
| 8 | 0 | -2.72104 | -0.77934 | 1.87202 |
| 7 | 0 | 3.06626 | -0.75413 | -0.21618 |
| 6 | 0 | 3.42355 | -3.12103 | -0.27349 |
| 1 | 0 | -0.00097 | 1.56975 | -1.68552 |
| 6 | 0 | -3.89836 | -1.54859 | 2.17772 |
| 6 | 0 | 4.38722 | -0.54106 | -0.36527 |
| 6 | 0 | 4.79264 | -2.90961 | -0.41986 |
| 1 | 0 | 2.98205 | -4.11123 | -0.25653 |
| 1 | 0 | -4.62641 | -1.45367 | 1.36919 |
| 1 | 0 | -4.29215 | -1.12209 | 3.10089 |
| 1 | 0 | -3.63766 | -2.60113 | 2.316 |
| 1 | 0 | 4.69355 | 0.49844 | -0.40624 |
| 6 | 0 | 5.28232 | -1.60056 | -0.46026 |
| 1 | 0 | 5.47057 | -3.7535 | -0.5066 |
| 1 | 0 | 6.34215 | -1.39888 | -0.57358 |
| 6 | 0 | -0.61276 | 3.40311 | -0.83493 |
| 1 | 0 | 0.21117 | 3.97518 | -1.27365 |
| 1 | 0 | -1.47502 | 3.4912 | -1.50865 |
| 1 | 0 | -0.87771 | 3.87215 | 0.11771 |
| 1 | 0 | -1.93072 | 1.62613 | 0.64859 |
| 6 | 0 | -2.38803 | 0.73819 | -1.29165 |
| 1 | 0 | -2.3609 | 1.57324 | -2.00315 |
| 1 | 0 | -1.99436 | -0.13337 | -1.82637 |
| 6 | 0 | -3.83936 | 0.50896 | -0.91299 |
| 6 | 0 | -4.51081 | -0.65367 | -1.3119 |
| 6 | 0 | -4.55823 | 1.48071 | -0.20132 |
| 6 | 0 | -5.86375 | -0.83881 | -1.01577 |
| 1 | 0 | -3.9606 | -1.42919 | -1.83575 |
| 6 | 0 | -5.90596 | 1.29601 | 0.10736 |

| | | | | |
|---|---|---|---|---|
| 1 | 0 | -4.05816 | 2.39454 | 0.11236 |
| 6 | 0 | -6.56641 | 0.13442 | -0.30285 |
| 1 | 0 | -6.36376 | -1.74945 | -1.33549 |
| 1 | 0 | -6.44263 | 2.06105 | 0.66282 |
| 1 | 0 | -7.61754 | -0.00986 | -0.06701 |
| 6 | 0 | 2.59468 | 3.17979 | 0.67943 |
| 8 | 0 | 3.02061 | 2.27776 | -0.10465 |
| 8 | 0 | 1.3909 | 3.22715 | 1.10191 |
| 1 | 0 | 0.73152 | 2.38813 | 0.38958 |
| 6 | 0 | 3.53867 | 4.26487 | 1.13245 |
| 1 | 0 | 3.18938 | 5.22638 | 0.74168 |
| 1 | 0 | 3.51911 | 4.32933 | 2.22444 |
| 1 | 0 | 4.55317 | 4.06996 | 0.78263 |



**TS2-F-12b**

E(B3LYP/BS1) = -1682.380727
H(correction) = 0.45155600
G(correction) = 0.35988800
E(M06/BS2) = -1862.999488
Imaginary frequencies: -1245.86

| | | | | |
|---|---|---|---|---|
| 46 | 0 | 0.74577 | 0.74953 | -0.00924 |
| 7 | 0 | 0.02395 | -1.16698 | -0.13763 |
| 7 | 0 | 2.58066 | -0.20943 | -0.45532 |
| 16 | 0 | 1.10697 | -2.22334 | 0.46374 |
| 6 | 0 | -1.33542 | -1.63668 | -0.34702 |
| 6 | 0 | 2.57966 | -1.54172 | -0.33797 |
| 6 | 0 | 3.65923 | 0.40754 | -0.9628 |
| 8 | 0 | 0.888 | -3.58678 | -0.05085 |
| 8 | 0 | 1.38025 | -2.06588 | 1.90532 |
| 6 | 0 | -2.26611 | -1.55065 | 0.90532 |
| 1 | 0 | -1.28819 | -2.69769 | -0.63206 |
| 6 | 0 | -1.89901 | -0.94918 | -1.59752 |
| 6 | 0 | 3.64199 | -2.34127 | -0.73604 |
| 1 | 0 | 3.59898 | 1.48879 | -1.02088 |
| 6 | 0 | 4.77475 | -0.3143 | -1.38109 |
| 6 | 0 | -2.11368 | -0.19518 | 1.64051 |
| 6 | 0 | -2.02348 | -2.7339 | 1.86376 |
| 1 | 0 | -3.29488 | -1.62591 | 0.53313 |
| 8 | 0 | -1.29767 | -0.21438 | -2.3472 |
| 8 | 0 | -3.18267 | -1.32744 | -1.80401 |
| 6 | 0 | 4.76293 | -1.70706 | -1.27266 |
| 1 | 0 | 3.56915 | -3.41781 | -0.62846 |
| 1 | 0 | 5.63073 | 0.21097 | -1.79113 |
| 1 | 0 | -1.13123 | -0.16595 | 2.12339 |
| 1 | 0 | -2.87366 | -0.14009 | 2.4279 |
| 6 | 0 | -2.27203 | 0.97119 | 0.70119 |
| 1 | 0 | -1.02581 | -2.64857 | 2.30907 |
| 1 | 0 | -2.02065 | -3.66219 | 1.27743 |
| 6 | 0 | -3.81188 | -0.73385 | -2.94938 |
| 1 | 0 | 5.61697 | -2.29142 | -1.60234 |
| 6 | 0 | -3.55161 | 1.30789 | 0.23843 |
| 6 | 0 | -1.14916 | 1.68414 | 0.21329 |
| 1 | 0 | -3.83612 | 0.35441 | -2.84227 |
| 1 | 0 | -4.82312 | -1.14236 | -2.97313 |
| 1 | 0 | -3.27036 | -0.9905 | -3.86429 |
| 1 | 0 | -4.41339 | 0.76588 | 0.62127 |
| 6 | 0 | -3.73076 | 2.30024 | -0.72424 |
| 6 | 0 | -1.35835 | 2.68675 | -0.76592 |
| 6 | 0 | -2.62798 | 2.9912 | -1.23965 |
| 1 | 0 | -4.73314 | 2.53873 | -1.07204 |
| 1 | 0 | -0.50055 | 3.24152 | -1.13731 |
| 1 | 0 | -2.7661 | 3.76141 | -1.99345 |
| 6 | 0 | -3.0725 | -2.85226 | 2.97602 |
| 1 | 0 | -2.90969 | -3.76279 | 3.56332 |
| 1 | 0 | -3.03353 | -2.00649 | 3.67153 |
| 1 | 0 | -4.08795 | -2.89847 | 2.56136 |
| 6 | 0 | 1.39414 | 3.30051 | 1.16753 |
| 8 | 0 | 1.73718 | 2.58199 | 0.17344 |
| 6 | 0 | 2.27642 | 4.46998 | 1.53952 |
| 1 | 0 | 1.68279 | 5.38918 | 1.52584 |
| 1 | 0 | 2.63842 | 4.32943 | 2.56314 |
| 1 | 0 | 3.12139 | 4.55589 | 0.85503 |
| 8 | 0 | 0.35036 | 3.1037 | 1.86283 |
| 1 | 0 | -0.36583 | 2.2338 | 1.17708 |

**IM3-A-12b**

E(B3LYP/BS1) = -1862.398491
H(correction) = 0.45707636
G(correction) = 0.36238836
E(M06/BS2) = -1863.026797
Imaginary frequencies: 0

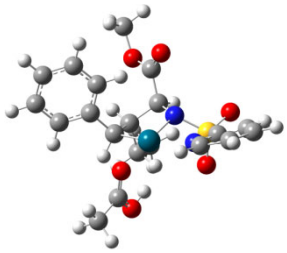
| | | | | |
|---|---|---|---|---|
| 6 | 0 | 1.85438 | 1.0259 | -0.27811 |
| 1 | 0 | 2.84499 | 1.44831 | -0.50556 |
| 1 | 0 | 1.57637 | 1.42968 | 0.70581 |
| 6 | 0 | 2.02717 | -0.49957 | -0.17431 |
| 1 | 0 | 2.2884 | -0.87768 | -1.17147 |
| 6 | 0 | 0.72155 | -1.26375 | 0.18894 |
| 1 | 0 | 0.96616 | -2.32846 | 0.22648 |
| 6 | 0 | 0.87103 | 1.49748 | -1.34359 |
| 1 | 0 | 0.82131 | 2.59286 | -1.3828 |
| 1 | 0 | 1.14003 | 1.11205 | -2.33399 |
| 7 | 0 | -0.27564 | -1.0348 | -0.84954 |
| 46 | 0 | -1.0264 | 0.87335 | -1.01154 |
| 6 | 0 | 0.25153 | -0.88425 | 1.59875 |
| 8 | 0 | -0.38928 | 0.10828 | 1.91914 |
| 8 | 0 | 0.66218 | -1.78093 | 2.50448 |
| 6 | 0 | 3.1716 | -0.87526 | 0.80138 |
| 1 | 0 | 3.16088 | -1.96141 | 0.95799 |
| 1 | 0 | 2.97953 | -0.42233 | 1.78284 |
| 6 | 0 | 4.53609 | -0.45184 | 0.30327 |
| 6 | 0 | 5.21356 | 0.63724 | 0.86545 |
| 6 | 0 | 5.14227 | -1.13649 | -0.76024 |
| 6 | 0 | 6.46165 | 1.03546 | 0.3805 |
| 1 | 0 | 4.75708 | 1.17864 | 1.69117 |
| 6 | 0 | 6.38785 | -0.74306 | -1.24901 |
| 1 | 0 | 4.63042 | -1.98664 | -1.2065 |
| 6 | 0 | 7.05294 | 0.34621 | -0.67922 |
| 1 | 0 | 6.97088 | 1.88315 | 0.83191 |
| 1 | 0 | 6.84139 | -1.28837 | -2.07264 |
| 1 | 0 | 8.02435 | 0.65269 | -1.05785 |
| 16 | 0 | -1.44414 | -2.16506 | -1.03782 |
| 8 | 0 | -1.78987 | -2.29324 | -2.45731 |
| 8 | 0 | -1.17141 | -3.37259 | -0.2353 |
| 6 | 0 | -2.92909 | -1.39764 | -0.29981 |

| | | | | |
|---|---|---|---|---|
| 6 | 0 | -3.90699 | -2.17123 | 0.31648 |
| 7 | 0 | -3.02154 | -0.07098 | -0.44573 |
| 6 | 0 | -5.04801 | -1.52281 | 0.78869 |
| 1 | 0 | -3.75556 | -3.24006 | 0.41884 |
| 6 | 0 | -4.12035 | 0.54959 | 0.00744 |
| 6 | 0 | -5.16131 | -0.13999 | 0.62592 |
| 1 | 0 | -5.8379 | -2.08662 | 1.27689 |
| 1 | 0 | -4.1453 | 1.62624 | -0.13393 |
| 1 | 0 | -6.03455 | 0.39936 | 0.97814 |
| 6 | 0 | -1.56169 | 3.40232 | 0.42978 |
| 8 | 0 | -1.7073 | 2.92794 | -0.70419 |
| 8 | 0 | -1.10316 | 2.74101 | 1.4742 |
| 1 | 0 | -0.88332 | 1.78734 | 1.27237 |
| 6 | 0 | -1.90305 | 4.8341 | 0.73786 |
| 1 | 0 | -2.59729 | 4.87844 | 1.58275 |
| 1 | 0 | -0.99204 | 5.36419 | 1.03584 |
| 1 | 0 | -2.33848 | 5.31062 | -0.14041 |
| 6 | 0 | 0.31623 | -1.50377 | 3.87414 |
| 1 | 0 | 0.73968 | -2.32483 | 4.45236 |
| 1 | 0 | 0.74047 | -0.5466 | 4.19001 |
| 1 | 0 | -0.77029 | -1.46863 | 3.99013 |

**IM3-B-12b**

E(B3LYP/BS1) = -1862.391282
H(correction) = 0.45693733
G(correction) = 0.36203033
E(M06/BS2) = -1863.019797
Imaginary frequencies: 0

| | | | | |
|---|---|---|---|---|
| 46 | 0 | 0.12036 | 0.73119 | -0.3008 |
| 7 | 0 | 1.315 | -0.88775 | -0.06721 |
| 7 | 0 | 2.06333 | 1.82512 | -0.29468 |
| 8 | 0 | -1.16597 | 2.46798 | -0.48452 |
| 6 | 0 | 0.62725 | -2.16068 | 0.18579 |
| 16 | 0 | 2.61387 | -0.54132 | 0.86914 |
| 6 | 0 | 3.07403 | 1.02063 | 0.05955 |
| 6 | 0 | 2.35227 | 3.02045 | -0.82962 |
| 6 | 0 | -1.91292 | 2.72419 | 0.46865 |
| 6 | 0 | -0.83809 | -1.83044 | 0.60019 |
| 1 | 0 | 1.11289 | -2.74388 | 0.97463 |
| 6 | 0 | 0.63555 | -3.02011 | -1.07662 |
| 8 | 0 | 3.7059 | -1.50776 | 0.6637 |
| 8 | 0 | 2.29694 | -0.18219 | 2.26929 |
| 6 | 0 | 4.41323 | 1.35019 | -0.10398 |
| 1 | 0 | 1.49885 | 3.62972 | -1.11146 |
| 6 | 0 | 3.66534 | 3.44861 | -1.01842 |
| 8 | 0 | -1.86521 | 2.07507 | 1.61954 |
| 6 | 0 | -2.9891 | 3.76202 | 0.39494 |
| 6 | 0 | -1.32488 | -0.75959 | -0.39669 |
| 8 | 0 | 0.7078 | -2.6243 | -2.21803 |
| 8 | 0 | 0.47552 | -4.32206 | -0.74334 |
| 6 | 0 | 4.71068 | 2.59785 | -0.65356 |
| 1 | 0 | 5.17709 | 0.63652 | 0.18427 |
| 1 | 0 | 3.85834 | 4.42465 | -1.45126 |
| 1 | 0 | -1.19017 | 1.35179 | 1.53338 |
| 1 | 0 | -2.76796 | 4.47263 | -0.40215 |
| 1 | 0 | -3.92279 | 3.23762 | 0.15687 |
| 1 | 0 | -3.11177 | 4.26975 | 1.35417 |
| 6 | 0 | 0.38632 | -5.23016 | -1.85287 |
| 1 | 0 | 5.74358 | 2.89972 | -0.80035 |
| 1 | 0 | -0.46623 | -4.97603 | -2.48991 |
| 1 | 0 | 0.25729 | -6.22022 | -1.41389 |
| 1 | 0 | 1.29924 | -5.19088 | -2.45391 |
| 6 | 0 | -0.85782 | -1.4138 | 2.09159 |
| 1 | 0 | 0.02178 | -0.79601 | 2.30187 |
| 1 | 0 | -1.73356 | -0.78807 | 2.2939 |
| 6 | 0 | -0.87212 | -2.61444 | 3.0441 |
| 1 | 0 | -0.0107 | -3.27054 | 2.87312 |
| 1 | 0 | -0.83183 | -2.28669 | 4.08848 |
| 1 | 0 | -1.77897 | -3.21827 | 2.91132 |
| 1 | 0 | -1.4582 | -2.73582 | 0.48926 |
| 6 | 0 | -2.76064 | -0.34559 | -0.39814 |
| 6 | 0 | -3.71002 | -0.75943 | 0.55376 |
| 6 | 0 | -3.21523 | 0.48962 | -1.44161 |
| 6 | 0 | -5.03664 | -0.32578 | 0.49052 |
| 1 | 0 | -3.42593 | -1.44411 | 1.34416 |
| 6 | 0 | -4.53535 | 0.92661 | -1.50534 |
| 1 | 0 | -2.50389 | 0.80759 | -2.19932 |
| 6 | 0 | -5.45636 | 0.52859 | -0.52902 |
| 1 | 0 | -5.74479 | -0.66467 | 1.24246 |
| 1 | 0 | -4.85024 | 1.57007 | -2.32339 |
| 1 | 0 | -6.48852 | 0.86533 | -0.57575 |
| 1 | 0 | -1.06295 | -1.07172 | -1.41519 |

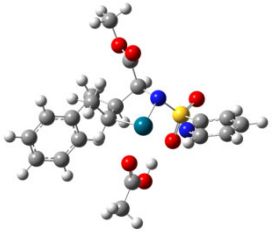


**IM3-C-12b**

E(B3LYP/BS1) = -1862.387781
H(correction) = 0.45659833
G(correction) = 0.35805933
E(M06/BS2) = -1863.016248
Imaginary frequencies: 0

| | | | | |
|---|---|---|---|---|
| 46 | 0 | 0.39746 | 0.78034 | -0.08736 |
| 7 | 0 | 0.54959 | -1.21575 | 0.08155 |
| 7 | 0 | 2.48695 | 0.53198 | -0.9157 |
| 8 | 0 | 0.23408 | 2.94591 | -0.09163 |
| 6 | 0 | -0.62928 | -1.90826 | 0.60776 |
| 16 | 0 | 2.0253 | -1.58117 | 0.6772 |
| 6 | 0 | 2.9717 | -0.67341 | -0.58333 |
| 6 | 0 | 3.16471 | 1.26748 | -1.80816 |
| 6 | 0 | 0.43501 | 3.51208 | 0.98807 |
| 6 | 0 | -1.46505 | -0.90072 | 1.43462 |
| 1 | 0 | -0.33391 | -2.75673 | 1.23808 |
| 6 | 0 | -1.3919 | -2.55835 | -0.55263 |
| 8 | 0 | 2.32644 | -3.0174 | 0.55868 |
| 8 | 0 | 2.3636 | -0.92615 | 1.96269 |
| 6 | 0 | 4.13587 | -1.21012 | -1.11615 |
| 1 | 0 | 2.72902 | 2.23066 | -2.05674 |
| 6 | 0 | 4.35136 | 0.8221 | -2.38969 |
| 8 | 0 | 0.79038 | 2.87246 | 2.09312 |
| 6 | 0 | 0.28716 | 4.99408 | 1.16745 |
| 6 | 0 | -1.4477 | 0.51334 | 0.75895 |
| 8 | 0 | -1.01127 | -2.6588 | -1.6964 |
| 8 | 0 | -2.57435 | -3.04827 | -0.11517 |
| 6 | 0 | 4.84129 | -0.43738 | -2.03979 |
| 1 | 0 | 4.45196 | -2.20287 | -0.81553 |
| 1 | 0 | 4.86974 | 1.44903 | -3.10765 |
| 1 | 0 | 0.85534 | 1.9016 | 1.88363 |

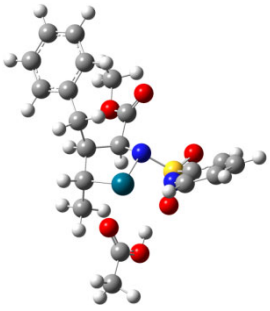
| | | | | |
|---|---|---|---|---|
| 1 | 0 | 0.05849 | 5.4622 | 0.21021 |
| 1 | 0 | -0.52042 | 5.19019 | 1.88093 |
| 1 | 0 | 1.20657 | 5.4109 | 1.59001 |
| 1 | 0 | -1.53378 | 1.25885 | 1.56032 |
| 6 | 0 | -3.4034 | -3.63707 | -1.12958 |
| 1 | 0 | 5.75696 | -0.81553 | -2.48498 |
| 1 | 0 | -3.69253 | -2.87835 | -1.86319 |
| 1 | 0 | -4.28192 | -4.01736 | -0.60694 |
| 1 | 0 | -2.87482 | -4.4464 | -1.64066 |
| 6 | 0 | -2.51841 | 0.81271 | -0.25329 |
| 6 | 0 | -2.54916 | 0.24423 | -1.54124 |
| 6 | 0 | -3.55082 | 1.70394 | 0.09026 |
| 6 | 0 | -3.58339 | 0.53589 | -2.43048 |
| 1 | 0 | -1.75046 | -0.41587 | -1.85806 |
| 6 | 0 | -4.58552 | 1.99886 | -0.79844 |
| 1 | 0 | -3.54632 | 2.16328 | 1.07691 |
| 6 | 0 | -4.60939 | 1.4111 | -2.06437 |
| 1 | 0 | -3.57893 | 0.08342 | -3.41905 |
| 1 | 0 | -5.37249 | 2.68759 | -0.50077 |
| 1 | 0 | -5.41255 | 1.63848 | -2.76038 |
| 6 | 0 | -0.92584 | -0.78486 | 2.87581 |
| 1 | 0 | 0.11934 | -0.45258 | 2.84653 |
| 1 | 0 | -1.49953 | 0.00474 | 3.38059 |
| 6 | 0 | -1.02429 | -2.07059 | 3.70346 |
| 1 | 0 | -0.3539 | -2.85258 | 3.3297 |
| 1 | 0 | -0.74028 | -1.87946 | 4.74429 |
| 1 | 0 | -2.04553 | -2.47193 | 3.6986 |
| 1 | 0 | -2.50257 | -1.25445 | 1.49104 |



**IM3-D-12b**

E(B3LYP/BS1) = -1862.385014
H(correction) = 0.45645966
G(correction) = 0.36044066
E(M06/BS2) = -1863.013184
Imaginary frequencies: 0

| | | | | |
|---|---|---|---|---|
| 46 | 0 | -0.81956 | -0.47059 | -0.88685 |
| 7 | 0 | -0.93709 | 1.26425 | 0.22554 |
| 7 | 0 | -3.07265 | -0.48138 | -0.41621 |
| 8 | 0 | -0.53883 | -2.56094 | -1.38755 |
| 6 | 0 | 0.38022 | 1.87884 | 0.46979 |
| 16 | 0 | -1.72753 | 0.73017 | 1.55272 |
| 6 | 0 | -3.25412 | 0.24057 | 0.69776 |
| 6 | 0 | -4.15748 | -0.9051 | -1.07817 |
| 6 | 0 | -0.39499 | -3.32689 | -0.42446 |
| 6 | 0 | 1.45668 | 0.76413 | 0.35797 |
| 1 | 0 | 0.42797 | 2.33014 | 1.46854 |
| 6 | 0 | 0.56186 | 3.0282 | -0.51939 |
| 8 | 0 | -2.04446 | 1.79491 | 2.51803 |
| 8 | 0 | -1.18453 | -0.53652 | 2.1462 |
| 6 | 0 | -4.49744 | 0.58031 | 1.2124 |
| 1 | 0 | -3.96947 | -1.47804 | -1.98124 |
| 6 | 0 | -5.45256 | -0.6251 | -0.64036 |
| 8 | 0 | -0.48443 | -2.99218 | 0.84783 |
| 6 | 0 | -0.08084 | -4.78468 | -0.62247 |
| 6 | 0 | 1.18432 | -0.14502 | -0.86905 |
| 6 | 0 | 2.91992 | 1.25487 | 0.47065 |
| 1 | 0 | 1.25965 | 0.14058 | 1.23864 |
| 8 | 0 | -0.01423 | 3.18261 | -1.57182 |
| 8 | 0 | 1.50704 | 3.88207 | -0.0579 |
| 6 | 0 | -5.62378 | 0.12941 | 0.52119 |
| 1 | 0 | -4.55859 | 1.18198 | 2.11228 |
| 1 | 0 | -6.3042 | -0.98863 | -1.20597 |
| 1 | 0 | -0.69626 | -2.02953 | 1.01222 |
| 1 | 0 | -0.07652 | -5.02421 | -1.68578 |
| 1 | 0 | 0.9002 | -5.00204 | -0.18662 |
| 1 | 0 | -0.81668 | -5.39857 | -0.09402 |
| 1 | 0 | 1.65505 | -1.11912 | -0.68659 |
| 1 | 0 | 3.17612 | 1.88354 | -0.38778 |
| 1 | 0 | 2.9989 | 1.90206 | 1.35392 |
| 6 | 0 | 3.90121 | 0.10643 | 0.58292 |
| 6 | 0 | 1.81706 | 4.98008 | -0.93112 |
| 1 | 0 | -6.62005 | 0.36822 | 0.88177 |
| 6 | 0 | 4.85595 | -0.13461 | -0.41255 |
| 6 | 0 | 3.86163 | -0.75886 | 1.68721 |
| 1 | 0 | 2.18109 | 4.61307 | -1.89551 |
| 1 | 0 | 2.59158 | 5.55279 | -0.41987 |
| 1 | 0 | 0.92964 | 5.59599 | -1.10149 |
| 6 | 0 | 5.74179 | -1.21076 | -0.31693 |
| 1 | 0 | 4.90875 | 0.53007 | -1.2717 |
| 6 | 0 | 4.74244 | -1.83555 | 1.7877 |
| 1 | 0 | 3.13477 | -0.58494 | 2.47769 |
| 6 | 0 | 5.6863 | -2.0675 | 0.78312 |
| 1 | 0 | 6.47454 | -1.37747 | -1.10245 |
| 1 | 0 | 4.69514 | -2.49163 | 2.65323 |
| 1 | 0 | 6.37395 | -2.90553 | 0.86078 |
| 6 | 0 | 1.61762 | 0.36295 | -2.24146 |
| 1 | 0 | 2.70906 | 0.49919 | -2.27589 |
| 1 | 0 | 1.36771 | -0.37404 | -3.01389 |
| 1 | 0 | 1.14669 | 1.31051 | -2.51081 |

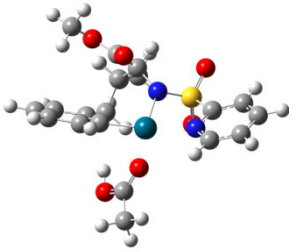


**IM3-E-12b**

E(B3LYP/BS1) = -1862.389485
H(correction) = 0.45650398
G(correction) = 0.36078398
E(M06/BS2) = -1863.017427
Imaginary frequencies: 0

| | | | | |
|---|---|---|---|---|
| 7 | 0 | -0.02676 | 0.6197 | 0.30252 |
| 6 | 0 | 1.12958 | 0.03753 | 1.01234 |
| 16 | 0 | -1.08664 | 1.44431 | 1.24679 |
| 46 | 0 | -1.25605 | -0.79432 | -0.53802 |
| 6 | 0 | 1.46579 | -1.27933 | 0.26931 |
| 1 | 0 | 0.8943 | -0.22719 | 2.05175 |
| 6 | 0 | 2.30309 | 1.01296 | 1.05774 |
| 8 | 0 | -0.50932 | 2.60319 | 1.93874 |
| 8 | 0 | -1.96099 | 0.55434 | 2.08107 |
| 6 | 0 | -2.16161 | 2.02465 | -0.09436 |
| 6 | 0 | 0.14856 | -2.08811 | 0.16538 |
| 8 | 0 | 2.41206 | 2.03581 | 0.42421 |
| 8 | 0 | 3.24184 | 0.53344 | 1.90305 |
| 7 | 0 | -2.54279 | 1.07117 | -0.95534 |
| 6 | 0 | -2.56382 | 3.35014 | -0.16884 |
| 1 | 0 | 0.25154 | -2.88115 | -0.58782 |
| 6 | 0 | 4.46766 | 1.28355 | 1.95079 |
| 6 | 0 | -3.3678 | 1.41488 | -1.9533 |

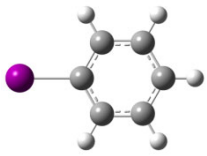
| | | | | |
|---|---|---|---|---|
| 6 | 0 | -3.42886 | 3.70002 | -1.20797 |
| 1 | 0 | -2.19465 | 4.06328 | 0.55964 |
| 1 | 0 | 4.96423 | 1.24994 | 0.97817 |
| 1 | 0 | 5.07965 | 0.79554 | 2.71044 |
| 1 | 0 | 4.26874 | 2.32365 | 2.22364 |
| 1 | 0 | -3.64606 | 0.61756 | -2.6361 |
| 6 | 0 | -3.8387 | 2.71894 | -2.1122 |
| 1 | 0 | -3.77327 | 4.72464 | -1.31297 |
| 1 | 0 | -4.50678 | 2.95522 | -2.93391 |
| 6 | 0 | -0.3164 | -2.69205 | 1.48904 |
| 1 | 0 | -1.20152 | -3.32123 | 1.34569 |
| 1 | 0 | 0.4721 | -3.33176 | 1.91739 |
| 1 | 0 | -0.56726 | -1.93041 | 2.23503 |
| 1 | 0 | 2.18611 | -1.84205 | 0.88186 |
| 6 | 0 | 2.09821 | -1.04336 | -1.12725 |
| 1 | 0 | 1.93887 | -1.95726 | -1.71575 |
| 1 | 0 | 1.54891 | -0.24705 | -1.64048 |
| 6 | 0 | 3.58305 | -0.73029 | -1.13328 |
| 6 | 0 | 4.06761 | 0.46773 | -1.67261 |
| 6 | 0 | 4.51102 | -1.65531 | -0.63152 |
| 6 | 0 | 5.43872 | 0.73327 | -1.71735 |
| 1 | 0 | 3.36179 | 1.2089 | -2.0349 |
| 6 | 0 | 5.8802 | -1.392 | -0.66421 |
| 1 | 0 | 4.15626 | -2.59504 | -0.21351 |
| 6 | 0 | 6.35075 | -0.19531 | -1.21259 |
| 1 | 0 | 5.79093 | 1.67082 | -2.13979 |
| 1 | 0 | 6.5808 | -2.12306 | -0.2685 |
| 1 | 0 | 7.41758 | 0.01039 | -1.24372 |
| 6 | 0 | -3.634 | -2.36176 | 0.1447 |
| 8 | 0 | -2.8199 | -2.28381 | -0.78591 |
| 8 | 0 | -3.63503 | -1.62022 | 1.23552 |
| 1 | 0 | -2.8985 | -0.94755 | 1.28942 |
| 6 | 0 | -4.75268 | -3.36756 | 0.12583 |
| 1 | 0 | -4.626 | -4.06278 | 0.96267 |
| 1 | 0 | -5.71119 | -2.85871 | 0.26758 |
| 1 | 0 | -4.74707 | -3.91469 | -0.81687 |



**IM3-F-12b**

E(B3LYP/BS1) = -1862.398518
H(correction) = 0.45721964
G(correction) = 0.36341764
E(M06/BS2) = -1863.021897
Imaginary frequencies: 0

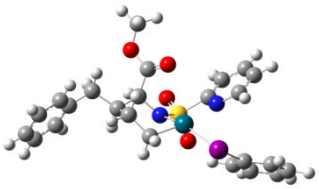
| | | | | |
|---|---|---|---|---|
| 46 | 0 | 0.62776 | 0.76867 | -0.05171 |
| 7 | 0 | 0.16126 | -1.21168 | -0.22705 |
| 7 | 0 | 2.6671 | 0.00304 | -0.33404 |
| 16 | 0 | 1.29827 | -2.13961 | 0.4752 |
| 6 | 0 | -1.14301 | -1.80324 | -0.49094 |
| 6 | 0 | 2.76038 | -1.32625 | -0.22318 |
| 6 | 0 | 3.72741 | 0.69175 | -0.78078 |
| 8 | 0 | 1.25771 | -3.52419 | -0.02918 |
| 8 | 0 | 1.43835 | -1.94092 | 1.93246 |
| 6 | 0 | -2.10245 | -1.85461 | 0.73972 |
| 1 | 0 | -0.98153 | -2.84113 | -0.82018 |
| 6 | 0 | -1.71848 | -1.10857 | -1.73634 |
| 6 | 0 | 3.89881 | -2.04691 | -0.55988 |
| 1 | 0 | 3.59391 | 1.76646 | -0.85384 |
| 6 | 0 | 4.91779 | 0.0593 | -1.13401 |
| 6 | 0 | -2.0334 | -0.54985 | 1.56817 |
| 6 | 0 | -1.81829 | -3.08957 | 1.62155 |
| 1 | 0 | -3.11882 | -1.95674 | 0.34376 |
| 8 | 0 | -1.07585 | -0.49526 | -2.55817 |
| 8 | 0 | -3.04983 | -1.31188 | -1.84488 |
| 6 | 0 | 5.0015 | -1.33103 | -1.0269 |
| 1 | 0 | 3.89586 | -3.12683 | -0.46271 |
| 1 | 0 | 5.75503 | 0.64734 | -1.49507 |
| 1 | 0 | -1.04272 | -0.48858 | 2.03003 |
| 1 | 0 | -2.76742 | -0.61442 | 2.37854 |
| 6 | 0 | -2.31262 | 0.68394 | 0.74018 |
| 1 | 0 | -0.85369 | -2.97176 | 2.12785 |
| 1 | 0 | -1.71866 | -3.9689 | 0.97143 |
| 6 | 0 | -3.67531 | -0.64716 | -2.95376 |
| 1 | 0 | 5.91334 | -1.85058 | -1.30685 |
| 6 | 0 | -3.63895 | 1.13024 | 0.60671 |
| 6 | 0 | -1.29542 | 1.3541 | 0.02864 |
| 1 | 0 | -3.54851 | 0.43473 | -2.85798 |
| 1 | 0 | -4.73086 | -0.91664 | -2.89803 |
| 1 | 0 | -3.24041 | -0.97936 | -3.90061 |
| 1 | 0 | -4.42288 | 0.61012 | 1.15385 |
| 6 | 0 | -3.96958 | 2.20354 | -0.21713 |
| 6 | 0 | -1.64053 | 2.43756 | -0.80244 |
| 6 | 0 | -2.96358 | 2.8629 | -0.92843 |
| 1 | 0 | -5.00428 | 2.52568 | -0.30279 |
| 1 | 0 | -0.86504 | 2.95066 | -1.36654 |
| 1 | 0 | -3.20656 | 3.70011 | -1.57839 |
| 6 | 0 | -2.90986 | -3.36689 | 2.66293 |
| 1 | 0 | -2.70657 | -4.3027 | 3.19581 |
| 1 | 0 | -2.97364 | -2.57284 | 3.4153 |
| 1 | 0 | -3.89605 | -3.45841 | 2.18932 |
| 6 | 0 | 1.03999 | 3.5482 | 1.05343 |
| 8 | 0 | 1.38697 | 2.77595 | 0.14855 |
| 6 | 0 | 1.77449 | 4.82645 | 1.336 |
| 1 | 0 | 1.10415 | 5.67487 | 1.16266 |
| 1 | 0 | 2.07071 | 4.85224 | 2.3894 |
| 1 | 0 | 2.65116 | 4.90465 | 0.69315 |
| 8 | 0 | 0.00934 | 3.33872 | 1.84497 |
| 1 | 0 | -0.48107 | 2.5347 | 1.52351 |



**IPh**

E(B3LYP/BS1) = -243.035352
H(correction) = 0.09715182
G(correction) = 0.05857982
E(M06/BS2) = -242.903810
Imaginary frequencies: 0

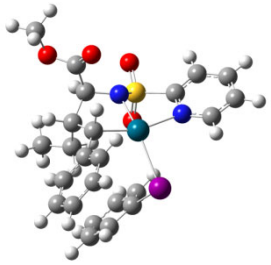
| | | | | |
|---|---|---|---|---|
| 6 | 0 | -1.25276 | -1.21602 | -0.00001 |
| 6 | 0 | -0.56451 | 0.00007 | -0.00003 |
| 6 | 0 | -1.25279 | 1.21603 | 0.00001 |
| 6 | 0 | -2.64962 | 1.20752 | 0. |
| 6 | 0 | -3.3505 | -0.00001 | -0.00001 |
| 6 | 0 | -2.6495 | -1.20758 | 0.00001 |
| 1 | 0 | -0.71136 | -2.15579 | 0. |
| 1 | 0 | -0.71155 | 2.15589 | 0.00001 |
| 1 | 0 | -3.18661 | 2.15186 | 0.00001 |
| 1 | 0 | -4.43654 | -0.00011 | 0. |
| 1 | 0 | -3.18656 | -2.15189 | 0.00003 |
| 53 | 0 | 1.55756 | 0. | 0. |



**IM4-A-12b**

E(B3LYP/BS1) = -1876.337592
H(correction) = 0.48623685
G(correction) = 0.38302985
E(M06/BS2) = -1876.889212
Imaginary frequencies: 0

| | | | | |
|---|---|---|---|---|
| 6 | 0 | 2.50228 | -1.0087 | -0.56938 |
| 1 | 0 | 3.30642 | -1.75977 | -0.61123 |
| 1 | 0 | 2.37932 | -0.64334 | -1.5995 |
| 6 | 0 | 2.99998 | 0.13997 | 0.32598 |
| 1 | 0 | 3.02733 | -0.22899 | 1.35975 |
| 6 | 0 | 2.0195 | 1.34705 | 0.38077 |
| 1 | 0 | 2.43757 | 2.08 | 1.07844 |
| 6 | 0 | 1.23264 | -1.71291 | -0.10073 |
| 1 | 0 | 1.0178 | -2.5865 | -0.72866 |
| 1 | 0 | 1.30328 | -2.02932 | 0.94563 |
| 7 | 0 | 0.74637 | 0.86286 | 0.88192 |
| 46 | 0 | -0.37663 | -0.48176 | -0.23748 |
| 6 | 0 | 1.89261 | 2.05299 | -0.97494 |
| 8 | 0 | 1.01873 | 1.86561 | -1.79746 |
| 8 | 0 | 2.89897 | 2.93366 | -1.15897 |
| 6 | 0 | 4.43408 | 0.57933 | -0.06162 |
| 1 | 0 | 4.6752 | 1.50752 | 0.47101 |
| 1 | 0 | 4.46663 | 0.82549 | -1.12931 |
| 6 | 0 | 5.47506 | -0.47193 | 0.25662 |
| 6 | 0 | 6.07271 | -1.23779 | -0.75242 |
| 6 | 0 | 5.84727 | -0.71767 | 1.58659 |
| 6 | 0 | 7.01347 | -2.22401 | -0.4453 |
| 1 | 0 | 5.79722 | -1.05829 | -1.78941 |
| 6 | 0 | 6.78565 | -1.70081 | 1.89941 |
| 1 | 0 | 5.39578 | -0.12881 | 2.38243 |
| 6 | 0 | 7.37258 | -2.45929 | 0.88263 |
| 1 | 0 | 7.4653 | -2.80652 | -1.24421 |
| 1 | 0 | 7.06177 | -1.87356 | 2.93648 |
| 1 | 0 | 8.10491 | -3.22491 | 1.12461 |
| 16 | 0 | -0.2684 | 1.91013 | 1.59931 |
| 8 | 0 | -1.05717 | 1.20067 | 2.62237 |
| 8 | 0 | 0.39005 | 3.18422 | 1.93997 |
| 6 | 0 | -1.50138 | 2.28882 | 0.31426 |
| 6 | 0 | -2.04413 | 3.55992 | 0.17464 |
| 7 | 0 | -1.86051 | 1.24019 | -0.43468 |
| 6 | 0 | -3.02756 | 3.74194 | -0.79811 |
| 1 | 0 | -1.68887 | 4.36379 | 0.80959 |
| 6 | 0 | -2.80356 | 1.41971 | -1.3687 |
| 6 | 0 | -3.41743 | 2.65319 | -1.57966 |
| 1 | 0 | -3.48097 | 4.71804 | -0.94599 |
| 1 | 0 | -3.06426 | 0.54475 | -1.9556 |
| 1 | 0 | -4.17706 | 2.75344 | -2.34795 |
| 6 | 0 | 2.8894 | 3.62996 | -2.41605 |
| 1 | 0 | 3.75657 | 4.29059 | -2.39228 |
| 1 | 0 | 2.96504 | 2.92335 | -3.24788 |
| 1 | 0 | 1.96701 | 4.2072 | -2.52554 |
| 6 | 0 | -3.34599 | -0.86772 | 1.47626 |
| 6 | 0 | -3.72749 | -1.58024 | 0.34015 |
| 6 | 0 | -5.06377 | -1.7353 | -0.02846 |
| 6 | 0 | -6.04717 | -1.14858 | 0.77355 |
| 6 | 0 | -5.69009 | -0.41785 | 1.9092 |
| 6 | 0 | -4.34473 | -0.27858 | 2.25541 |
| 1 | 0 | -2.30587 | -0.72912 | 1.74793 |
| 1 | 0 | -5.34093 | -2.29075 | -0.91853 |
| 1 | 0 | -7.09254 | -1.26033 | 0.49885 |
| 1 | 0 | -6.46014 | 0.04468 | 2.52012 |
| 1 | 0 | -4.04613 | 0.2993 | 3.12488 |
| 53 | 0 | -2.21132 | -2.40836 | -0.92618 |



**IM4-B-12b**

E(B3LYP/BS1) = -1876.334681
H(correction) = 0.48650612
G(correction) = 0.38470212
E(M06/BS2) = -1876.886807
Imaginary frequencies: 0

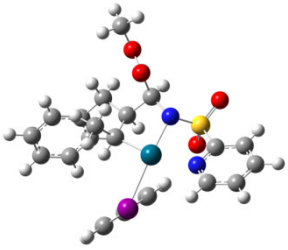
| | | | | |
|---|---|---|---|---|
| 46 | 0 | -0.35884 | -0.32118 | -0.71769 |
| 7 | 0 | -1.94631 | 0.76169 | 0.02836 |
| 7 | 0 | -1.90064 | -2.00007 | -0.66618 |
| 6 | 0 | -1.63425 | 2.13945 | 0.43255 |
| 16 | 0 | -2.79746 | -0.16154 | 1.0736 |
| 6 | 0 | -2.99816 | -1.60603 | -0.00636 |
| 6 | 0 | -1.97619 | -3.10982 | -1.41437 |
| 6 | 0 | -0.08292 | 2.25732 | 0.53929 |
| 1 | 0 | -2.09115 | 2.40499 | 1.39136 |
| 6 | 0 | -2.17009 | 3.11935 | -0.60778 |
| 8 | 0 | -4.1277 | 0.40894 | 1.35083 |
| 8 | 0 | -2.04035 | -0.67297 | 2.24314 |
| 6 | 0 | -4.21462 | -2.27429 | -0.05797 |
| 1 | 0 | -1.06627 | -3.39301 | -1.93501 |
| 6 | 0 | -3.14737 | -3.85863 | -1.52182 |
| 6 | 0 | 0.47432 | 1.57794 | -0.72601 |
| 8 | 0 | -2.36145 | 2.89331 | -1.78162 |
| 8 | 0 | -2.34248 | 4.33734 | -0.04284 |
| 6 | 0 | -4.28528 | -3.43064 | -0.83579 |
| 1 | 0 | -5.06264 | -1.87989 | 0.49077 |
| 1 | 0 | -3.16251 | -4.75271 | -2.13644 |
| 6 | 0 | -2.76734 | 5.37311 | -0.94276 |
| 1 | 0 | -5.21505 | -3.98734 | -0.90821 |
| 1 | 0 | -2.02999 | 5.51791 | -1.7382 |
| 1 | 0 | -2.85821 | 6.27362 | -0.3341 |
| 1 | 0 | -3.72864 | 5.11585 | -1.39661 |
| 6 | 0 | 0.3659 | 1.65379 | 1.89187 |
| 1 | 0 | -0.26525 | 0.79402 | 2.12583 |
| 1 | 0 | 1.37679 | 1.24953 | 1.8173 |
| 6 | 0 | 0.30186 | 2.66409 | 3.04035 |
| 1 | 0 | -0.70371 | 3.08879 | 3.14943 |
| 1 | 0 | 0.56328 | 2.18606 | 3.9911 |
| 1 | 0 | 0.99557 | 3.49979 | 2.87935 |
| 1 | 0 | 0.20668 | 3.32186 | 0.5209 |
| 6 | 0 | 1.92147 | 1.67597 | -1.05783 |
| 6 | 0 | 2.92643 | 2.07572 | -0.15873 |
| 6 | 0 | 2.32102 | 1.3635 | -2.37592 |
| 6 | 0 | 4.26798 | 2.12027 | -0.5481 |
| 1 | 0 | 2.66818 | 2.37148 | 0.85012 |
| 6 | 0 | 3.65504 | 1.3993 | -2.76394 |
| 1 | 0 | 1.55753 | 1.07214 | -3.09431 |
| 6 | 0 | 4.64345 | 1.77095 | -1.84487 |
| 1 | 0 | 5.02081 | 2.43632 | 0.17015 |
| 1 | 0 | 3.9277 | 1.14485 | -3.78503 |

| | | | | |
|---|---|---|---|---|
| 1 | 0 | 5.68789 | 1.80221 | -2.14321 |
| 1 | 0 | -0.10147 | 1.90969 | -1.59871 |
| 53 | 0 | 1.85704 | -1.95923 | -0.84382 |
| 6 | 0 | 2.4882 | -0.75556 | 3.86644 |
| 6 | 0 | 1.30037 | -1.36476 | 3.45618 |
| 6 | 0 | 3.50823 | -0.51848 | 2.94266 |
| 6 | 0 | 1.12438 | -1.74914 | 2.12552 |
| 1 | 0 | 0.48528 | -1.51927 | 4.15648 |
| 6 | 0 | 3.3511 | -0.88712 | 1.6029 |
| 1 | 0 | 4.42802 | -0.03093 | 3.25394 |
| 6 | 0 | 2.15978 | -1.50398 | 1.22412 |
| 1 | 0 | 0.17738 | -2.16673 | 1.80528 |
| 1 | 0 | 4.12426 | -0.66754 | 0.87549 |
| 1 | 0 | 2.61294 | -0.45171 | 4.90184 |

**IM4-C-12b**

E(B3LYP/BS1) = -1876.335344
H(correction) = 0.48630735
G(correction) = 0.38182035
E(M06/BS2) = -1876.887027
Imaginary frequencies: 0

| | | | | |
|---|---|---|---|---|
| 46 | 0 | -0.03652 | 0.12904 | -0.55314 |
| 7 | 0 | 1.39729 | 1.25093 | 0.36029 |
| 7 | 0 | -0.50756 | 2.1403 | -1.50473 |
| 6 | 0 | 2.27915 | 0.54083 | 1.28938 |
| 16 | 0 | 0.73274 | 2.66328 | 0.8238 |
| 6 | 0 | 0.07283 | 3.12649 | -0.80573 |
| 6 | 0 | -1.067 | 2.44248 | -2.68444 |
| 6 | 0 | 1.56821 | -0.75442 | 1.75315 |
| 1 | 0 | 2.51385 | 1.16448 | 2.16166 |
| 6 | 0 | 3.64325 | 0.31962 | 0.62769 |
| 8 | 0 | 1.74744 | 3.65183 | 1.2267 |
| 8 | 0 | -0.45997 | 2.54727 | 1.70194 |
| 6 | 0 | 0.1401 | 4.4441 | -1.23904 |
| 1 | 0 | -1.52564 | 1.61485 | -3.21718 |
| 6 | 0 | -1.06296 | 3.73775 | -3.20073 |
| 6 | 0 | 0.72858 | -1.38918 | 0.59355 |
| 8 | 0 | 4.02324 | 0.79752 | -0.41686 |
| 8 | 0 | 4.41027 | -0.48332 | 1.40073 |
| 6 | 0 | -0.44555 | 4.75246 | -2.46764 |
| 1 | 0 | 0.64669 | 5.18174 | -0.62659 |
| 1 | 0 | -1.52898 | 3.93845 | -4.15979 |
| 1 | 0 | -0.13697 | -1.88066 | 1.05135 |
| 6 | 0 | 5.707 | -0.78838 | 0.86379 |
| 1 | 0 | -0.41746 | 5.76915 | -2.84869 |
| 1 | 0 | 5.6049 | -1.34379 | -0.07354 |
| 1 | 0 | 6.20127 | -1.40093 | 1.61877 |
| 1 | 0 | 6.2733 | 0.12786 | 0.67539 |
| 6 | 0 | 1.3807 | -2.37095 | -0.33146 |
| 6 | 0 | 2.43864 | -2.03816 | -1.20081 |
| 6 | 0 | 0.89927 | -3.69347 | -0.36668 |
| 6 | 0 | 3.00301 | -2.9952 | -2.04352 |
| 1 | 0 | 2.80133 | -1.01879 | -1.24445 |
| 6 | 0 | 1.46167 | -4.65115 | -1.21042 |
| 1 | 0 | 0.07227 | -3.97071 | 0.28342 |
| 6 | 0 | 2.5219 | -4.30726 | -2.05175 |
| 1 | 0 | 3.8162 | -2.70847 | -2.70577 |
| 1 | 0 | 1.07121 | -5.66588 | -1.21045 |
| 1 | 0 | 2.96248 | -5.05009 | -2.71152 |
| 6 | 0 | 0.63323 | -0.46616 | 2.9477 |
| 1 | 0 | -0.11137 | 0.28028 | 2.64881 |
| 1 | 0 | 0.08152 | -1.38968 | 3.16886 |
| 6 | 0 | 1.34591 | -0.00163 | 4.2216 |
| 1 | 0 | 1.79722 | 0.99017 | 4.10462 |
| 1 | 0 | 0.63612 | 0.06869 | 5.05358 |
| 1 | 0 | 2.14105 | -0.69944 | 4.51314 |
| 1 | 0 | 2.32147 | -1.48285 | 2.08115 |
| 53 | 0 | -2.28933 | -1.24272 | -1.24273 |
| 6 | 0 | -4.47328 | -0.44136 | 3.0854 |
| 6 | 0 | -4.85427 | -1.52995 | 2.2977 |
| 6 | 0 | -3.48199 | 0.43201 | 2.6345 |
| 6 | 0 | -4.24547 | -1.75539 | 1.05966 |
| 1 | 0 | -5.62303 | -2.21551 | 2.64361 |
| 6 | 0 | -2.86348 | 0.23049 | 1.39744 |
| 1 | 0 | -3.16808 | 1.27922 | 3.23737 |
| 6 | 0 | -3.25782 | -0.86757 | 0.63348 |
| 1 | 0 | -4.53512 | -2.60783 | 0.45384 |
| 1 | 0 | -2.08336 | 0.91204 | 1.07493 |
| 1 | 0 | -4.946 | -0.27771 | 4.04964 |

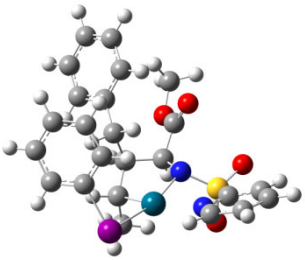


**IM4-D-12b**

E(B3LYP/BS1) = -1876.332260
H(correction) = 0.48637325
G(correction) = 0.38422325
E(M06/BS2) = -1876.884511
Imaginary frequencies: 0

| | | | | |
|---|---|---|---|---|
| 46 | 0 | 0.95018 | 0.1983 | -0.74793 |
| 7 | 0 | 1.5613 | -1.49062 | 0.27277 |
| 7 | 0 | 3.05292 | 0.87627 | -0.17922 |
| 6 | 0 | 0.49807 | -2.48898 | 0.4756 |
| 16 | 0 | 2.28183 | -0.95743 | 1.64031 |
| 6 | 0 | 3.49981 | 0.13284 | 0.84197 |
| 6 | 0 | 3.90338 | 1.73686 | -0.75558 |
| 6 | 0 | -0.85717 | -1.74833 | 0.33436 |
| 1 | 0 | 0.55307 | -2.94275 | 1.47278 |
| 6 | 0 | 0.70693 | -3.63828 | -0.51065 |
| 8 | 0 | 3.02103 | -2.02311 | 2.34051 |
| 8 | 0 | 1.43527 | -0.08106 | 2.49114 |
| 6 | 0 | 4.79766 | 0.19445 | 1.33385 |
| 1 | 0 | 3.5035 | 2.31856 | -1.58081 |
| 6 | 0 | 5.22264 | 1.88202 | -0.32816 |
| 6 | 0 | -0.83937 | -0.7842 | -0.87691 |
| 6 | 0 | -2.11567 | -2.64729 | 0.38977 |
| 1 | 0 | -0.87842 | -1.10647 | 1.22396 |
| 8 | 0 | 1.3423 | -3.61242 | -1.5395 |
| 8 | 0 | 0.04869 | -4.73985 | -0.07381 |
| 6 | 0 | 5.67656 | 1.0955 | 0.73187 |
| 1 | 0 | 5.08937 | -0.45647 | 2.15044 |
| 1 | 0 | 5.87612 | 2.59276 | -0.82331 |
| 1 | 0 | -1.63409 | -0.04681 | -0.72278 |
| 1 | 0 | -2.10795 | -3.35973 | -0.44078 |
| 1 | 0 | -2.06849 | -3.25083 | 1.30597 |
| 6 | 0 | -3.39882 | -1.84133 | 0.35992 |
| 6 | 0 | 0.12679 | -5.88151 | -0.94204 |

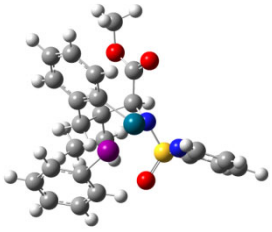
| | | | | |
|---|---|---|---|---|
| 1 | 0 | 6.70131 | 1.17938 | 1.08186 |
| 6 | 0 | -4.32907 | -2.00663 | -0.6738 |
| 6 | 0 | -3.6722 | -0.88647 | 1.35108 |
| 1 | 0 | -0.28795 | -5.64472 | -1.92651 |
| 1 | 0 | -0.45859 | -6.66235 | -0.45516 |
| 1 | 0 | 1.16625 | -6.19813 | -1.06545 |
| 6 | 0 | -5.49798 | -1.24319 | -0.7222 |
| 1 | 0 | -4.13422 | -2.74228 | -1.45108 |
| 6 | 0 | -4.83587 | -0.11978 | 1.30621 |
| 1 | 0 | -2.96231 | -0.73082 | 2.15954 |
| 6 | 0 | -5.75469 | -0.29417 | 0.26808 |
| 1 | 0 | -6.2049 | -1.38992 | -1.53495 |
| 1 | 0 | -5.01992 | 0.62009 | 2.07967 |
| 1 | 0 | -6.66173 | 0.30368 | 0.23271 |
| 6 | 0 | -0.98287 | -1.38651 | -2.27047 |
| 1 | 0 | -1.93734 | -1.92881 | -2.3564 |
| 1 | 0 | -1.00276 | -0.59288 | -3.02653 |
| 1 | 0 | -0.17594 | -2.07774 | -2.521 |
| 53 | 0 | -0.16815 | 2.57702 | -1.43107 |
| 6 | 0 | -1.38383 | 2.63558 | 0.3379 |
| 6 | 0 | -0.90069 | 2.0608 | 1.5132 |
| 6 | 0 | -2.64064 | 3.23362 | 0.26001 |
| 6 | 0 | -1.71651 | 2.09666 | 2.64778 |
| 1 | 0 | 0.06683 | 1.57291 | 1.56563 |
| 6 | 0 | -3.43572 | 3.26164 | 1.40917 |
| 1 | 0 | -3.00402 | 3.6606 | -0.66867 |
| 6 | 0 | -2.97579 | 2.6977 | 2.60077 |
| 1 | 0 | -1.34943 | 1.64399 | 3.56445 |
| 1 | 0 | -4.41982 | 3.7195 | 1.36226 |
| 1 | 0 | -3.60145 | 2.7207 | 3.48869 |



**IM4-E-12b**

E(B3LYP/BS1) = -1876.331996
H(correction) = 0.48637313
G(correction) = 0.38310113
E(M06/BS2) = -1876.88196
Imaginary frequencies: 0

| | | | | |
|---|---|---|---|---|
| 7 | 0 | 0.05615 | 1.66843 | -0.25303 |
| 6 | 0 | -1.21585 | 1.63621 | -0.98896 |
| 16 | 0 | 0.95469 | 3.03287 | -0.41712 |
| 46 | 0 | 1.28648 | 0.05902 | -0.56317 |
| 6 | 0 | -1.51343 | 0.138 | -1.25409 |
| 1 | 0 | -1.15624 | 2.14322 | -1.96064 |
| 6 | 0 | -2.34014 | 2.29734 | -0.19324 |
| 8 | 0 | 0.28106 | 4.22947 | 0.11227 |
| 8 | 0 | 1.6084 | 3.15803 | -1.7385 |
| 6 | 0 | 2.26312 | 2.5717 | 0.76582 |
| 53 | 0 | 2.46805 | -2.38831 | -0.51778 |
| 6 | 0 | -0.2266 | -0.49066 | -1.83136 |
| 8 | 0 | -2.34632 | 2.51601 | 0.99529 |
| 8 | 0 | -3.38187 | 2.54516 | -1.01828 |
| 7 | 0 | 2.67847 | 1.29673 | 0.74067 |
| 6 | 0 | 2.80208 | 3.5404 | 1.60386 |
| 1 | 0 | -0.32874 | -1.58346 | -1.83579 |
| 6 | 0 | -4.56972 | 3.03785 | -0.37598 |
| 6 | 0 | 3.67412 | 0.93725 | 1.56338 |
| 6 | 0 | 3.84316 | 3.16147 | 2.45168 |
| 1 | 0 | 2.39469 | 4.54508 | 1.58461 |
| 1 | 0 | -4.96721 | 2.28312 | 0.3076 |
| 1 | 0 | -5.27742 | 3.23622 | -1.18206 |
| 1 | 0 | -4.35125 | 3.95329 | 0.18079 |
| 1 | 0 | 3.97103 | -0.10689 | 1.5183 |
| 6 | 0 | 4.2895 | 1.83896 | 2.43025 |
| 1 | 0 | 4.29506 | 3.88551 | 3.12347 |
| 1 | 0 | 5.09422 | 1.50439 | 3.0768 |
| 1 | 0 | 0.24897 | -4.50173 | -1.18332 |
| 6 | 0 | -0.03453 | -4.13124 | -0.20415 |
| 6 | 0 | 0.75195 | -3.19553 | 0.46582 |
| 6 | 0 | -1.21428 | -4.57047 | 0.40572 |
| 6 | 0 | 0.39914 | -2.69321 | 1.7186 |
| 6 | 0 | -1.59083 | -4.07617 | 1.65534 |
| 1 | 0 | -1.84184 | -5.29176 | -0.1099 |
| 6 | 0 | -0.78234 | -3.14413 | 2.31004 |
| 1 | 0 | 1.00801 | -1.94157 | 2.20835 |
| 1 | 0 | -2.51784 | -4.40686 | 2.11362 |
| 1 | 0 | -1.07794 | -2.74611 | 3.2763 |
| 6 | 0 | 0.15954 | 0.00271 | -3.22349 |
| 1 | 0 | 1.02743 | -0.54482 | -3.608 |
| 1 | 0 | -0.67206 | -0.15938 | -3.92976 |
| 1 | 0 | 0.40988 | 1.06851 | -3.2379 |
| 1 | 0 | -2.31175 | 0.07529 | -2.00953 |
| 6 | 0 | -1.97687 | -0.62445 | 0.01545 |
| 1 | 0 | -1.71427 | -1.68023 | -0.12154 |
| 1 | 0 | -1.39445 | -0.2742 | 0.87286 |
| 6 | 0 | -3.45752 | -0.554 | 0.33303 |
| 6 | 0 | -3.91158 | -0.06817 | 1.56575 |
| 6 | 0 | -4.40902 | -1.02351 | -0.585 |
| 6 | 0 | -5.27423 | -0.05117 | 1.87449 |
| 1 | 0 | -3.1909 | 0.32931 | 2.27355 |
| 6 | 0 | -5.77144 | -1.00003 | -0.28694 |
| 1 | 0 | -4.07729 | -1.41354 | -1.54507 |
| 6 | 0 | -6.21039 | -0.51468 | 0.94826 |
| 1 | 0 | -5.60282 | 0.33515 | 2.8361 |
| 1 | 0 | -6.49082 | -1.36438 | -1.01619 |
| 1 | 0 | -7.27131 | -0.49715 | 1.18403 |

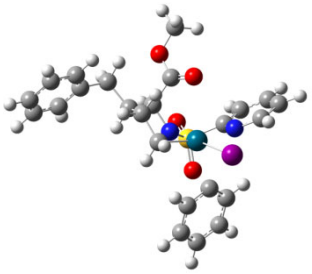


**IM4-F-12b**

E(B3LYP/BS1) = -1876.339053
H(correction) = 0.48662314
G(correction) = 0.38580714
E(M06/BS2) = -1876.886879
Imaginary frequencies: 0

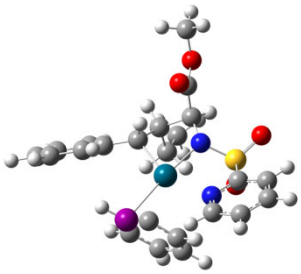
| | | | | |
|---|---|---|---|---|
| 46 | 0 | -0.55251 | 0.00673 | -0.7996 |
| 7 | 0 | 0.25767 | 1.73111 | 0.04267 |
| 7 | 0 | -2.44834 | 1.18712 | -0.57654 |
| 16 | 0 | -0.76302 | 2.34091 | 1.14372 |
| 6 | 0 | 1.66438 | 2.10167 | 0.11747 |
| 6 | 0 | -2.2811 | 2.29339 | 0.15768 |
| 6 | 0 | -3.58701 | 1.051 | -1.27161 |
| 8 | 0 | -0.45954 | 3.74902 | 1.4595 |
| 8 | 0 | -1.0713 | 1.4424 | 2.28227 |
| 6 | 0 | 2.50499 | 1.30432 | 1.16614 |

| | | | | |
|---|---|---|---|---|
| 1 | 0 | 1.72408 | 3.1659 | 0.39411 |
| 6 | 0 | 2.21669 | 2.05977 | -1.31699 |
| 6 | 0 | -3.21417 | 3.31967 | 0.23341 |
| 1 | 0 | -3.68268 | 0.13939 | -1.85351 |
| 6 | 0 | -4.58847 | 2.01982 | -1.25517 |
| 6 | 0 | 2.17566 | -0.20614 | 1.14581 |
| 6 | 0 | 2.3271 | 1.88932 | 2.583 |
| 1 | 0 | 3.55624 | 1.43262 | 0.88448 |
| 8 | 0 | 1.54955 | 2.07386 | -2.32683 |
| 8 | 0 | 3.5673 | 2.05977 | -1.32458 |
| 6 | 0 | -4.39536 | 3.17493 | -0.49436 |
| 1 | 0 | -2.99747 | 4.19266 | 0.83883 |
| 1 | 0 | -5.49374 | 1.87042 | -1.83414 |
| 1 | 0 | 1.16746 | -0.34707 | 1.54252 |
| 1 | 0 | 2.85951 | -0.72107 | 1.82839 |
| 6 | 0 | 2.29061 | -0.82838 | -0.22573 |
| 1 | 0 | 1.29903 | 1.72914 | 2.92501 |
| 1 | 0 | 2.47108 | 2.97696 | 2.53395 |
| 6 | 0 | 4.16599 | 1.94864 | -2.62567 |
| 1 | 0 | -5.15389 | 3.95194 | -0.47004 |
| 6 | 0 | 3.51562 | -1.38347 | -0.63406 |
| 6 | 0 | 1.22982 | -0.81594 | -1.14296 |
| 1 | 0 | 3.87162 | 1.00351 | -3.09011 |
| 1 | 0 | 5.243 | 1.97296 | -2.45407 |
| 1 | 0 | 3.85748 | 2.77913 | -3.26686 |
| 1 | 0 | 4.34457 | -1.39113 | 0.07148 |
| 6 | 0 | 3.69209 | -1.90658 | -1.91348 |
| 6 | 0 | 1.40328 | -1.33645 | -2.43107 |
| 6 | 0 | 2.62924 | -1.88253 | -2.81982 |
| 1 | 0 | 4.65034 | -2.33134 | -2.20181 |
| 1 | 0 | 0.58483 | -1.31075 | -3.14724 |
| 1 | 0 | 2.74944 | -2.28464 | -3.82296 |
| 6 | 0 | 3.29497 | 1.30408 | 3.61924 |
| 1 | 0 | 3.20554 | 1.83452 | 4.57419 |
| 1 | 0 | 3.09211 | 0.245 | 3.81453 |
| 1 | 0 | 4.33732 | 1.38914 | 3.28538 |
| 53 | 0 | -1.73858 | -2.49735 | -0.71602 |
| 6 | 0 | -0.82517 | -2.59249 | 1.22221 |
| 6 | 0 | 0.20794 | -3.50303 | 1.43251 |
| 6 | 0 | -1.21307 | -1.66143 | 2.18335 |
| 6 | 0 | 0.86538 | -3.48076 | 2.66607 |
| 1 | 0 | 0.51275 | -4.19649 | 0.65688 |
| 6 | 0 | -0.53234 | -1.64803 | 3.40294 |
| 1 | 0 | -1.97109 | -0.91541 | 1.98228 |
| 6 | 0 | 0.49921 | -2.55641 | 3.64701 |
| 1 | 0 | 1.6773 | -4.17975 | 2.84629 |
| 1 | 0 | -0.79727 | -0.89452 | 4.13764 |
| 1 | 0 | 1.02993 | -2.53302 | 4.59453 |
| 6 | 0 | 2.13315 | -0.73604 | -0.70144 |
| 1 | 0 | 2.95791 | -1.44361 | -0.88149 |
| 1 | 0 | 1.95349 | -0.2355 | -1.6633 |
| 6 | 0 | 2.62253 | 0.28399 | 0.34004 |
| 1 | 0 | 2.72929 | -0.2408 | 1.29859 |
| 6 | 0 | 1.58998 | 1.40879 | 0.62991 |
| 1 | 0 | 2.00806 | 2.05065 | 1.41106 |
| 6 | 0 | 0.92072 | -1.55107 | -0.28958 |
| 1 | 0 | 0.70499 | -2.34968 | -1.00518 |
| 1 | 0 | 1.01359 | -1.95592 | 0.72097 |
| 7 | 0 | 0.35779 | 0.79389 | 1.10639 |
| 46 | 0 | -0.74757 | -0.37348 | -0.25344 |
| 6 | 0 | 1.37027 | 2.28748 | -0.60647 |
| 8 | 0 | 0.53046 | 2.09533 | -1.46573 |
| 8 | 0 | 2.24472 | 3.31018 | -0.64802 |
| 6 | 0 | 4.0058 | 0.86679 | -0.0428 |
| 1 | 0 | 4.23654 | 1.69952 | 0.63315 |
| 1 | 0 | 3.95728 | 1.29648 | -1.05061 |
| 6 | 0 | 5.11258 | -0.16308 | 0.02263 |
| 6 | 0 | 5.66541 | -0.71471 | -1.1401 |
| 6 | 0 | 5.58963 | -0.60997 | 1.26371 |
| 6 | 0 | 6.66498 | -1.68819 | -1.06887 |
| 1 | 0 | 5.30831 | -0.37708 | -2.11064 |
| 6 | 0 | 6.58742 | -1.58143 | 1.34095 |
| 1 | 0 | 5.17389 | -0.18829 | 2.17657 |
| 6 | 0 | 7.12873 | -2.1253 | 0.17276 |
| 1 | 0 | 7.08097 | -2.10271 | -1.98358 |
| 1 | 0 | 6.94544 | -1.91201 | 2.31256 |
| 1 | 0 | 7.90728 | -2.88121 | 0.23123 |
| 16 | 0 | -0.67312 | 1.73259 | 1.95593 |
| 8 | 0 | -1.48303 | 0.88482 | 2.83901 |
| 8 | 0 | -0.00528 | 2.93379 | 2.49046 |
| 6 | 0 | -1.85622 | 2.337 | 0.70772 |
| 6 | 0 | -2.3344 | 3.64141 | 0.73937 |
| 7 | 0 | -2.22309 | 1.43297 | -0.20807 |
| 6 | 0 | -3.25553 | 4.01998 | -0.23793 |
| 1 | 0 | -1.9755 | 4.32129 | 1.50385 |
| 6 | 0 | -3.10189 | 1.80271 | -1.14958 |
| 6 | 0 | -3.64827 | 3.08501 | -1.19644 |
| 1 | 0 | -3.65588 | 5.02979 | -0.25452 |
| 1 | 0 | -3.35982 | 1.04422 | -1.88181 |
| 1 | 0 | -4.35674 | 3.34083 | -1.9775 |
| 6 | 0 | 2.13967 | 4.17044 | -1.7959 |
| 1 | 0 | 2.91323 | 4.92763 | -1.66622 |
| 1 | 0 | 2.30343 | 3.60315 | -2.71669 |
| 1 | 0 | 1.14929 | 4.63243 | -1.83527 |
| 6 | 0 | -1.48984 | -3.22737 | 0.97709 |
| 6 | 0 | -2.12853 | -2.07206 | 0.52313 |
| 6 | 0 | -3.12014 | -1.42902 | 1.26341 |
| 6 | 0 | -3.4083 | -1.91444 | 2.54106 |
| 6 | 0 | -2.75573 | -3.04239 | 3.0382 |
| 6 | 0 | -1.80405 | -3.69806 | 2.25278 |
| 1 | 0 | -0.75325 | -3.73389 | 0.36554 |
| 1 | 0 | -3.62195 | -0.54967 | 0.8817 |
| 1 | 0 | -4.14178 | -1.39066 | 3.14687 |
| 1 | 0 | -2.98965 | -3.41272 | 4.03185 |
| 1 | 0 | -1.29699 | -4.58321 | 2.62771 |
| 53 | 0 | -2.26489 | -1.89838 | -1.87674 |



**TS3-A-12b**

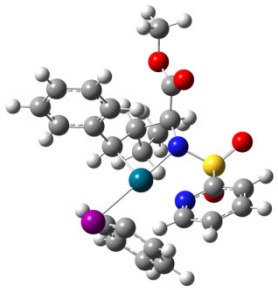
E(B3LYP/BS1) = -1876.320385
H(correction) = 0.48515087
G(correction) = 0.38598487
E(M06/BS2) = -1876.872954
Imaginary frequencies: -162.55



**TS3-B-12b**

E(B3LYP/BS1) = -1876.316604
H(correction) = 0.48536377
G(correction) = 0.38544477
E(M06/BS2) = -1876.867958
Imaginary frequencies: -162.42

| | | | | |
|---|---|---|---|---|
| 46 | 0 | -0.1174 | -0.34967 | -0.36536 |
| 7 | 0 | -1.57582 | 1.07112 | -0.01886 |
| 7 | 0 | -2.14452 | -1.68352 | -0.45093 |
| 6 | 0 | -1.13907 | 2.4511 | 0.18986 |
| 16 | 0 | -2.78233 | 0.51862 | 0.938 |
| 6 | 0 | -3.18652 | -0.96233 | -0.02164 |
| 6 | 0 | -2.39973 | -2.81263 | -1.12718 |
| 6 | 0 | 0.37758 | 2.3837 | 0.51074 |
| 1 | 0 | -1.67173 | 2.93973 | 1.01063 |
| 6 | 0 | -1.38672 | 3.28209 | -1.06729 |
| 8 | 0 | -3.94058 | 1.42905 | 0.90453 |
| 8 | 0 | -2.34108 | 0.03031 | 2.26162 |
| 6 | 0 | -4.51597 | -1.30647 | -0.23376 |
| 1 | 0 | -1.53056 | -3.36526 | -1.46938 |
| 6 | 0 | -3.69819 | -3.25401 | -1.38272 |
| 6 | 0 | 0.99165 | 1.44125 | -0.53904 |
| 8 | 0 | -1.41639 | 2.86931 | -2.20566 |
| 8 | 0 | -1.50119 | 4.5881 | -0.73993 |
| 6 | 0 | -4.77299 | -2.48695 | -0.93163 |
| 1 | 0 | -5.30163 | -0.65423 | 0.13083 |
| 1 | 0 | -3.85489 | -4.1765 | -1.93219 |
| 6 | 0 | -1.66553 | 5.48621 | -1.84986 |
| 1 | 0 | -5.79521 | -2.79895 | -1.12512 |
| 1 | 0 | -0.80607 | 5.42497 | -2.5242 |
| 1 | 0 | -1.7425 | 6.48261 | -1.41333 |
| 1 | 0 | -2.57183 | 5.23921 | -2.40985 |
| 6 | 0 | 0.55422 | 1.96294 | 1.98985 |
| 1 | 0 | -0.17504 | 1.18264 | 2.22982 |
| 1 | 0 | 1.53062 | 1.49717 | 2.1328 |
| 6 | 0 | 0.3976 | 3.13605 | 2.96179 |
| 1 | 0 | -0.57858 | 3.62458 | 2.85834 |
| 1 | 0 | 0.48128 | 2.79162 | 3.99826 |
| 1 | 0 | 1.16751 | 3.90112 | 2.79581 |
| 1 | 0 | 0.8308 | 3.38061 | 0.37755 |
| 6 | 0 | 2.46715 | 1.36436 | -0.66997 |
| 6 | 0 | 3.36567 | 1.94441 | 0.24676 |
| 6 | 0 | 3.01376 | 0.72251 | -1.80015 |
| 6 | 0 | 4.74555 | 1.85158 | 0.0592 |
| 1 | 0 | 2.99269 | 2.48617 | 1.10736 |
| 6 | 0 | 4.38853 | 0.61878 | -1.98313 |
| 1 | 0 | 2.33761 | 0.28775 | -2.53038 |
| 6 | 0 | 5.26497 | 1.17711 | -1.04674 |
| 1 | 0 | 5.41547 | 2.31027 | 0.78181 |
| 1 | 0 | 4.77833 | 0.10716 | -2.85888 |
| 1 | 0 | 6.33963 | 1.09782 | -1.18606 |
| 1 | 0 | 0.55604 | 1.63421 | -1.52563 |
| 53 | 0 | 1.3877 | -2.48789 | -1.11064 |
| 6 | 0 | 1.59826 | -1.47729 | 3.85023 |
| 6 | 0 | 0.41382 | -2.02592 | 3.35501 |
| 6 | 0 | 2.56671 | -0.99953 | 2.96394 |
| 6 | 0 | 0.18334 | -2.10006 | 1.97906 |
| 1 | 0 | -0.34902 | -2.39532 | 4.03408 |
| 6 | 0 | 2.35125 | -1.04248 | 1.58547 |
| 1 | 0 | 3.50002 | -0.58581 | 3.33706 |
| 6 | 0 | 1.13778 | -1.55137 | 1.11936 |
| 1 | 0 | -0.73584 | -2.52665 | 1.59922 |
| 1 | 0 | 3.09925 | -0.67189 | 0.89739 |
| 1 | 0 | 1.77072 | -1.43345 | 4.92166 |



**TS3-C-12b**

E(B3LYP/BS1) = - 1876,316030
H(correction) = 0.48502741
G(correction) = 0.38400441
E(M06/BS2) = -1876.8682108
Imaginary frequencies: -165.34

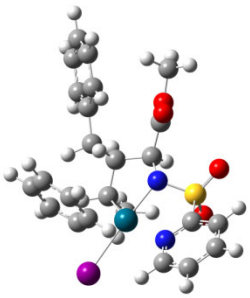
| | | | | |
|---|---|---|---|---|
| 46 | 0 | -0.39204 | -0.19811 | -0.18206 |
| 7 | 0 | 0.876 | 1.40241 | 0.04744 |
| 7 | 0 | -1.46407 | 1.38353 | -1.53785 |
| 6 | 0 | 2.04778 | 1.23273 | 0.90924 |
| 16 | 0 | 0.03059 | 2.79727 | 0.18754 |
| 6 | 0 | -0.95847 | 2.60502 | -1.32173 |
| 6 | 0 | -2.23334 | 1.19615 | -2.61981 |
| 6 | 0 | 1.84628 | -0.07766 | 1.70423 |
| 1 | 0 | 2.14391 | 2.06225 | 1.62216 |
| 6 | 0 | 3.34068 | 1.3255 | 0.08911 |
| 8 | 0 | 0.89413 | 3.97949 | 0.03552 |
| 8 | 0 | -0.9351 | 2.80301 | 1.30686 |
| 6 | 0 | -1.18351 | 3.69419 | -2.15402 |
| 1 | 0 | -2.60919 | 0.18726 | -2.7623 |
| 6 | 0 | -2.52984 | 2.22907 | -3.50858 |
| 6 | 0 | 1.12242 | -1.15484 | 0.84378 |
| 8 | 0 | 3.44127 | 1.72854 | -1.04635 |
| 8 | 0 | 4.39698 | 0.93766 | 0.83995 |
| 6 | 0 | -1.994 | 3.49629 | -3.27263 |
| 1 | 0 | -0.71918 | 4.64657 | -1.92356 |
| 1 | 0 | -3.1599 | 2.03496 | -4.37038 |
| 1 | 0 | 0.6598 | -1.87328 | 1.52277 |
| 6 | 0 | 5.66816 | 0.98854 | 0.17197 |
| 1 | 0 | -2.19777 | 4.31711 | -3.9541 |
| 1 | 0 | 5.66972 | 0.31057 | -0.68676 |
| 1 | 0 | 6.40285 | 0.67133 | 0.91299 |
| 1 | 0 | 5.88064 | 2.00339 | -0.17544 |
| 6 | 0 | 1.88995 | -1.91354 | -0.19271 |
| 6 | 0 | 2.45487 | -1.32237 | -1.33975 |
| 6 | 0 | 2.03463 | -3.30419 | -0.02992 |
| 6 | 0 | 3.16152 | -2.09106 | -2.26372 |
| 1 | 0 | 2.31774 | -0.26538 | -1.52913 |
| 6 | 0 | 2.7414 | -4.0724 | -0.95324 |
| 1 | 0 | 1.58537 | -3.78587 | 0.83554 |
| 6 | 0 | 3.31301 | -3.46702 | -2.07488 |
| 1 | 0 | 3.58705 | -1.60931 | -3.14011 |
| 1 | 0 | 2.84242 | -5.14363 | -0.79893 |
| 1 | 0 | 3.86245 | -4.06313 | -2.79863 |
| 6 | 0 | 1.04136 | 0.21402 | 2.9889 |

| | | | | |
|---|---|---|---|---|
| 1 | 0 | 0.12852 | 0.76278 | 2.72695 |
| 1 | 0 | 0.7142 | -0.7414 | 3.41779 |
| 6 | 0 | 1.82785 | 0.98574 | 4.05351 |
| 1 | 0 | 2.11877 | 1.9854 | 3.7107 |
| 1 | 0 | 1.22014 | 1.12114 | 4.9551 |
| 1 | 0 | 2.74377 | 0.45271 | 4.33765 |
| 1 | 0 | 2.82207 | -0.48922 | 1.99739 |
| 53 | 0 | -1.99706 | -2.28116 | -0.78461 |
| 6 | 0 | -3.2713 | 0.06416 | 3.53593 |
| 6 | 0 | -2.43236 | -1.05241 | 3.54527 |
| 6 | 0 | -3.56726 | 0.69789 | 2.32841 |
| 6 | 0 | -1.86838 | -1.52602 | 2.36003 |
| 1 | 0 | -2.20889 | -1.56466 | 4.47738 |
| 6 | 0 | -3.02671 | 0.23224 | 1.12805 |
| 1 | 0 | -4.21701 | 1.56793 | 2.30832 |
| 6 | 0 | -2.13644 | -0.84278 | 1.1714 |
| 1 | 0 | -1.22869 | -2.39986 | 2.36779 |
| 1 | 0 | -3.26114 | 0.72469 | 0.19374 |
| 1 | 0 | -3.70071 | 0.43111 | 4.46339 |

**TS3-D-12b**

E(B3LYP/BS1) = -1876.315857
H(correction) = 0.48518494
G(correction) = 0.38557994
E(M06/BS2) = -1876.870182
Imaginary frequencies: -165.57

| | | | | |
|---|---|---|---|---|
| 46 | 0 | -0.70285 | -0.29075 | -0.57574 |
| 7 | 0 | -0.81292 | 1.68104 | 0.04452 |
| 7 | 0 | -2.96007 | -0.20464 | -0.10721 |
| 6 | 0 | 0.47479 | 2.35966 | 0.25571 |
| 16 | 0 | -1.8784 | 1.83721 | 1.28199 |
| 6 | 0 | -3.26481 | 0.93072 | 0.53394 |
| 6 | 0 | -3.96056 | -0.93647 | -0.61926 |
| 6 | 0 | 1.57126 | 1.27726 | 0.06812 |
| 1 | 0 | 0.57769 | 2.75507 | 1.27327 |
| 6 | 0 | 0.60481 | 3.57202 | -0.67146 |
| 8 | 0 | -2.30431 | 3.23567 | 1.46674 |
| 8 | 0 | -1.49917 | 1.0844 | 2.49596 |
| 6 | 0 | -4.56278 | 1.39881 | 0.69932 |
| 1 | 0 | -3.66285 | -1.84053 | -1.14258 |
| 6 | 0 | -5.29678 | -0.56009 | -0.49166 |
| 6 | 0 | 1.19343 | 0.30488 | -1.06505 |
| 6 | 0 | 3.02741 | 1.8027 | -0.03485 |
| 1 | 0 | 1.52029 | 0.69603 | 0.99676 |
| 8 | 0 | 0.03006 | 3.76115 | -1.71835 |
| 8 | 0 | 1.5021 | 4.44334 | -0.15013 |
| 6 | 0 | -5.60119 | 0.62805 | 0.17544 |
| 1 | 0 | -4.72798 | 2.34052 | 1.21072 |
| 1 | 0 | -6.07638 | -1.18382 | -0.91659 |
| 1 | 0 | 1.84743 | -0.56852 | -1.03127 |
| 1 | 0 | 3.18469 | 2.30523 | -0.99563 |
| 1 | 0 | 3.17623 | 2.56297 | 0.74002 |
| 6 | 0 | 4.0115 | 0.66811 | 0.14389 |
| 6 | 0 | 1.74754 | 5.61545 | -0.94385 |
| 1 | 0 | -6.63211 | 0.95361 | 0.27971 |
| 6 | 0 | 4.58232 | 0.01439 | -0.95596 |
| 6 | 0 | 4.30244 | 0.1866 | 1.4286 |
| 1 | 0 | 2.13441 | 5.33837 | -1.92914 |
| 1 | 0 | 2.48527 | 6.19725 | -0.39013 |
| 1 | 0 | 0.82449 | 6.18669 | -1.07557 |
| 6 | 0 | 5.41122 | -1.0965 | -0.78076 |
| 1 | 0 | 4.36822 | 0.37489 | -1.95945 |
| 6 | 0 | 5.13493 | -0.91857 | 1.61012 |
| 1 | 0 | 3.86297 | 0.68032 | 2.29263 |
| 6 | 0 | 5.68837 | -1.56888 | 0.50362 |
| 1 | 0 | 5.84036 | -1.59147 | -1.64801 |
| 1 | 0 | 5.35455 | -1.27047 | 2.61517 |
| 1 | 0 | 6.33403 | -2.43174 | 0.64232 |
| 6 | 0 | 1.12739 | 0.84424 | -2.48611 |
| 1 | 0 | 2.0996 | 1.27696 | -2.77331 |
| 1 | 0 | 0.91426 | 0.03433 | -3.19157 |
| 1 | 0 | 0.37717 | 1.62877 | -2.60542 |
| 53 | 0 | -0.5259 | -2.83984 | -1.41238 |
| 6 | 0 | -0.023 | -2.04276 | 0.80511 |
| 6 | 0 | -1.03428 | -2.15371 | 1.76076 |
| 6 | 0 | 1.32984 | -2.08161 | 1.14941 |
| 6 | 0 | -0.67075 | -2.20139 | 3.10838 |
| 1 | 0 | -2.0773 | -2.15537 | 1.47206 |
| 6 | 0 | 1.66636 | -2.13647 | 2.50309 |
| 1 | 0 | 2.10981 | -2.04446 | 0.39926 |
| 6 | 0 | 0.67292 | -2.18891 | 3.48345 |
| 1 | 0 | -1.4525 | -2.23505 | 3.86153 |
| 1 | 0 | 2.71791 | -2.13046 | 2.77463 |
| 1 | 0 | 0.94513 | -2.22505 | 4.53413 |

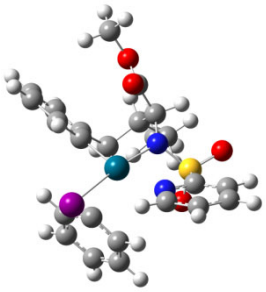


**TS3-E-12b**

E(B3LYP/BS1) = -1876.309953
H(correction) = 0.48491719
G(correction) = 0.38391919
E(M06/BS2) = -1876.863271
Imaginary frequencies: -164.91

| | | | | |
|---|---|---|---|---|
| 7 | 0 | -0.33439 | 1.35943 | -0.18021 |
| 6 | 0 | -1.5828 | 1.21057 | -0.94787 |
| 16 | 0 | 0.36147 | 2.84204 | -0.36397 |
| 46 | 0 | 1.09633 | -0.09953 | -0.51642 |
| 6 | 0 | -1.7082 | -0.29231 | -1.28946 |
| 1 | 0 | -1.55496 | 1.76194 | -1.89638 |
| 6 | 0 | -2.7873 | 1.72382 | -0.15917 |
| 8 | 0 | -0.46202 | 3.9279 | 0.18911 |
| 8 | 0 | 0.92343 | 3.04471 | -1.71861 |
| 6 | 0 | 1.78833 | 2.61674 | 0.73884 |
| 53 | 0 | 3.074 | -1.86136 | -0.92883 |
| 6 | 0 | -0.34093 | -0.74904 | -1.84344 |
| 8 | 0 | -2.83989 | 1.89355 | 1.03537 |
| 8 | 0 | -3.82402 | 1.90649 | -1.00527 |
| 7 | 0 | 2.42197 | 1.44069 | 0.6701 |
| 6 | 0 | 2.22051 | 3.68515 | 1.51664 |
| 1 | 0 | -0.29425 | -1.84113 | -1.89569 |
| 6 | 0 | -5.07079 | 2.25782 | -0.3802 |
| 6 | 0 | 3.56314 | 1.29502 | 1.35855 |
| 6 | 0 | 3.39964 | 3.52151 | 2.24369 |
| 1 | 0 | 1.63594 | 4.59805 | 1.53897 |

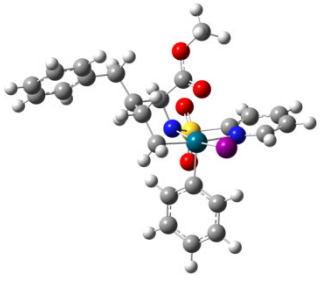
| | | | | |
|---|---|---|---|---|
| 1 | 0 | -5.41002 | 1.44241 | 0.26311 |
| 1 | 0 | -5.77326 | 2.41827 | -1.19902 |
| 1 | 0 | -4.95479 | 3.16798 | 0.21445 |
| 1 | 0 | 4.05877 | 0.33357 | 1.25475 |
| 6 | 0 | 4.08983 | 2.31123 | 2.15445 |
| 1 | 0 | 3.7765 | 4.32748 | 2.86657 |
| 1 | 0 | 5.01764 | 2.14958 | 2.69333 |
| 1 | 0 | 0.3527 | -3.50714 | -0.56799 |
| 6 | 0 | 0.47008 | -3.13609 | 0.44302 |
| 6 | 0 | 1.29391 | -2.03964 | 0.71098 |
| 6 | 0 | -0.21146 | -3.74218 | 1.49952 |
| 6 | 0 | 1.51729 | -1.60191 | 2.01984 |
| 6 | 0 | -0.0552 | -3.27646 | 2.80635 |
| 1 | 0 | -0.86922 | -4.5814 | 1.29034 |
| 6 | 0 | 0.81137 | -2.21186 | 3.06039 |
| 1 | 0 | 2.19529 | -0.78657 | 2.23339 |
| 1 | 0 | -0.59305 | -3.74926 | 3.6225 |
| 1 | 0 | 0.94918 | -1.84554 | 4.07404 |
| 6 | 0 | 0.05262 | -0.13538 | -3.18202 |
| 1 | 0 | 0.97823 | -0.58078 | -3.55989 |
| 1 | 0 | -0.74004 | -0.33051 | -3.92348 |
| 1 | 0 | 0.19946 | 0.94843 | -3.12632 |
| 1 | 0 | -2.44948 | -0.39945 | -2.09592 |
| 6 | 0 | -2.1663 | -1.16561 | -0.09715 |
| 1 | 0 | -1.87504 | -2.19756 | -0.32443 |
| 1 | 0 | -1.60222 | -0.88294 | 0.79709 |
| 6 | 0 | -3.65303 | -1.1649 | 0.20545 |
| 6 | 0 | -4.12236 | -0.86333 | 1.48995 |
| 6 | 0 | -4.58961 | -1.52147 | -0.77582 |
| 6 | 0 | -5.48518 | -0.92286 | 1.79004 |
| 1 | 0 | -3.41334 | -0.55383 | 2.25167 |
| 6 | 0 | -5.95318 | -1.57235 | -0.4856 |
| 1 | 0 | -4.24905 | -1.76623 | -1.77954 |
| 6 | 0 | -6.40699 | -1.27666 | 0.80273 |
| 1 | 0 | -5.82575 | -0.68166 | 2.79367 |
| 1 | 0 | -6.66082 | -1.84816 | -1.26336 |
| 1 | 0 | -7.46847 | -1.31888 | 1.0324 |



**TS3-F-12b**

E(B3LYP/BS1) = -1876.319953
H(correction) = 0.48553539
G(correction) = 0.38852839
E(M06/BS2) = -1876.865766
Imaginary frequencies: -171.70

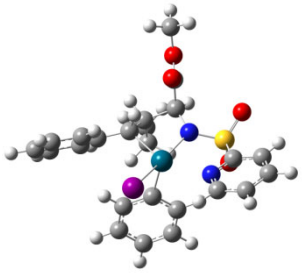
| | | | | |
|---|---|---|---|---|
| 46 | 0 | -0.50177 | -0.25867 | -0.41423 |
| 7 | 0 | 0.73848 | 1.43049 | -0.36565 |
| 7 | 0 | -2.06384 | 1.43037 | -0.77489 |
| 16 | 0 | -0.0005 | 2.67188 | 0.38445 |
| 6 | 0 | 2.19037 | 1.48084 | -0.46864 |
| 6 | 0 | -1.55796 | 2.64514 | -0.53334 |
| 6 | 0 | -3.23794 | 1.35265 | -1.42053 |
| 8 | 0 | 0.66606 | 3.95553 | 0.09906 |
| 8 | 0 | -0.38775 | 2.39106 | 1.78231 |
| 6 | 0 | 2.9514 | 1.01141 | 0.81247 |
| 1 | 0 | 2.48369 | 2.52471 | -0.65607 |
| 6 | 0 | 2.58226 | 0.75472 | -1.76393 |
| 6 | 0 | -2.17235 | 3.83295 | -0.9101 |
| 1 | 0 | -3.61167 | 0.3517 | -1.60602 |
| 6 | 0 | -3.93708 | 2.48585 | -1.83304 |
| 6 | 0 | 2.28858 | -0.24267 | 1.4267 |
| 6 | 0 | 3.06714 | 2.14857 | 1.84911 |
| 1 | 0 | 3.96607 | 0.7455 | 0.49479 |
| 8 | 0 | 1.82606 | 0.46709 | -2.66488 |
| 8 | 0 | 3.91088 | 0.52314 | -1.81032 |
| 6 | 0 | -3.39442 | 3.74587 | -1.57655 |
| 1 | 0 | -1.68611 | 4.77681 | -0.69091 |
| 1 | 0 | -4.8826 | 2.3735 | -2.35312 |
| 1 | 0 | 1.30782 | 0.03239 | 1.82382 |
| 1 | 0 | 2.89356 | -0.58241 | 2.27387 |
| 6 | 0 | 2.1717 | -1.36293 | 0.42066 |
| 1 | 0 | 2.08205 | 2.36265 | 2.27807 |
| 1 | 0 | 3.38372 | 3.06448 | 1.33315 |
| 6 | 0 | 4.36093 | -0.21081 | -2.9611 |
| 1 | 0 | -3.91168 | 4.64615 | -1.89538 |
| 6 | 0 | 3.24916 | -2.2532 | 0.26655 |
| 6 | 0 | 1.08064 | -1.50251 | -0.44758 |
| 1 | 0 | 3.89978 | -1.20212 | -2.97079 |
| 1 | 0 | 5.44308 | -0.29124 | -2.8506 |
| 1 | 0 | 4.10401 | 0.31815 | -3.88294 |
| 1 | 0 | 4.10435 | -2.14898 | 0.93151 |
| 6 | 0 | 3.25279 | -3.23931 | -0.71707 |
| 6 | 0 | 1.08096 | -2.4744 | -1.45303 |
| 6 | 0 | 2.16569 | -3.3458 | -1.58607 |
| 1 | 0 | 4.09882 | -3.91546 | -0.80835 |
| 1 | 0 | 0.25199 | -2.55222 | -2.14681 |
| 1 | 0 | 2.15327 | -4.10128 | -2.3676 |
| 6 | 0 | 4.06014 | 1.8481 | 2.97848 |
| 1 | 0 | 4.16961 | 2.71674 | 3.63754 |
| 1 | 0 | 3.73461 | 1.00709 | 3.60106 |
| 1 | 0 | 5.05297 | 1.60357 | 2.57914 |
| 53 | 0 | -2.41568 | -2.19761 | -0.50144 |
| 6 | 0 | -1.32061 | -1.21251 | 1.48336 |
| 6 | 0 | -0.51673 | -2.13839 | 2.15191 |
| 6 | 0 | -2.03111 | -0.21661 | 2.1503 |
| 6 | 0 | -0.35254 | -1.98945 | 3.5294 |
| 1 | 0 | -0.0101 | -2.92688 | 1.61165 |
| 6 | 0 | -1.83814 | -0.08271 | 3.52807 |
| 1 | 0 | -2.67961 | 0.46557 | 1.61706 |
| 6 | 0 | -1.00258 | -0.96086 | 4.21769 |
| 1 | 0 | 0.29187 | -2.68548 | 4.05966 |
| 1 | 0 | -2.34261 | 0.72478 | 4.05018 |
| 1 | 0 | -0.86295 | -0.85006 | 5.28899 |



**IM5-A-12b**

E(B3LYP/BS1) = -1876.347488
H(correction) = 0.48743773
G(correction) = 0.38950673
E(M06/BS2) = -1876.889938
Imaginary frequencies: 0

| | | | | |
|---|---|---|---|---|
| 6 | 0 | 2.20441 | -0.77476 | -0.47291 |
| 1 | 0 | 3.08766 | -1.43089 | -0.43525 |
| 1 | 0 | 2.08635 | -0.49846 | -1.52843 |
| 6 | 0 | 2.51778 | 0.46958 | 0.37855 |
| 1 | 0 | 2.64933 | 0.14847 | 1.41985 |
| 6 | 0 | 1.34208 | 1.48759 | 0.43463 |
| 1 | 0 | 1.67852 | 2.38121 | 0.96556 |
| 6 | 0 | 1.0289 | -1.61027 | -0.00808 |
| 1 | 0 | 0.87273 | -2.49677 | -0.61879 |
| 1 | 0 | 1.09993 | -1.88061 | 1.04384 |
| 7 | 0 | 0.20982 | 0.87815 | 1.14811 |
| 46 | 0 | -0.71876 | -0.49225 | -0.15113 |
| 6 | 0 | 0.94073 | 1.87184 | -0.98091 |
| 8 | 0 | 0.14584 | 1.20542 | -1.64073 |
| 8 | 0 | 1.55137 | 2.95013 | -1.45807 |
| 6 | 0 | 3.82281 | 1.16194 | -0.08637 |
| 1 | 0 | 3.9384 | 2.10074 | 0.47039 |
| 1 | 0 | 3.73344 | 1.43994 | -1.1435 |
| 6 | 0 | 5.0492 | 0.29956 | 0.11698 |
| 6 | 0 | 5.66975 | -0.3491 | -0.95796 |
| 6 | 0 | 5.57178 | 0.10951 | 1.40439 |
| 6 | 0 | 6.78325 | -1.16779 | -0.7552 |
| 1 | 0 | 5.27685 | -0.21071 | -1.96286 |
| 6 | 0 | 6.68335 | -0.70688 | 1.61235 |
| 1 | 0 | 5.10328 | 0.61079 | 2.249 |
| 6 | 0 | 7.29319 | -1.34925 | 0.53131 |
| 1 | 0 | 7.25163 | -1.66146 | -1.60261 |
| 1 | 0 | 7.07629 | -0.83892 | 2.61702 |
| 1 | 0 | 8.16039 | -1.98405 | 0.69141 |
| 16 | 0 | -0.86764 | 1.9343 | 1.83532 |
| 8 | 0 | -1.4784 | 1.30027 | 3.00382 |
| 8 | 0 | -0.27237 | 3.27764 | 1.95623 |
| 6 | 0 | -2.22091 | 2.10305 | 0.62072 |
| 6 | 0 | -2.98524 | 3.26524 | 0.59483 |
| 7 | 0 | -2.44641 | 1.05403 | -0.17237 |
| 6 | 0 | -4.05538 | 3.31482 | -0.2984 |
| 1 | 0 | -2.73205 | 4.09094 | 1.25035 |
| 6 | 0 | -3.47012 | 1.10326 | -1.03617 |
| 6 | 0 | -4.30595 | 2.21538 | -1.12193 |
| 1 | 0 | -4.68272 | 4.1999 | -0.35313 |
| 1 | 0 | -3.59181 | 0.23117 | -1.67131 |
| 1 | 0 | -5.12721 | 2.21773 | -1.83096 |
| 6 | 0 | 1.23415 | 3.30843 | -2.82285 |
| 1 | 0 | 1.82869 | 4.19684 | -3.03217 |
| 1 | 0 | 1.49796 | 2.49066 | -3.49797 |
| 1 | 0 | 0.16653 | 3.522 | -2.91442 |
| 6 | 0 | -0.91521 | -1.63282 | 2.57851 |
| 6 | 0 | -1.55814 | -1.55947 | 1.34523 |
| 6 | 0 | -2.83243 | -2.0937 | 1.15867 |
| 6 | 0 | -3.45816 | -2.73668 | 2.23325 |
| 6 | 0 | -2.82051 | -2.84096 | 3.46923 |
| 6 | 0 | -1.55378 | -2.28362 | 3.63887 |
| 1 | 0 | 0.03676 | -1.14492 | 2.74188 |
| 1 | 0 | -3.34015 | -2.02768 | 0.20594 |
| 1 | 0 | -4.44912 | -3.1595 | 2.08766 |
| 1 | 0 | -3.31232 | -3.34409 | 4.2973 |
| 1 | 0 | -1.05662 | -2.32999 | 4.60421 |
| 53 | 0 | -1.58521 | -1.99905 | -2.21975 |

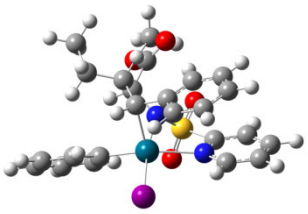


**IM5-B-12b**

E(B3LYP/BS1) = -1876.334945
H(correction) = 0.48722013
G(correction) = 0.38616013
E(M06/BS2) = -1876.875728
Imaginary frequencies: 0

| | | | | |
|---|---|---|---|---|
| 46 | 0 | -0.10615 | -0.43348 | -0.22274 |
| 7 | 0 | -1.36338 | 1.13241 | 0.15866 |
| 7 | 0 | -2.30416 | -1.49705 | -0.26495 |
| 6 | 0 | -0.81303 | 2.48097 | 0.16181 |
| 16 | 0 | -2.84471 | 0.91254 | 0.81352 |
| 6 | 0 | -3.29715 | -0.64466 | 0.00295 |
| 6 | 0 | -2.61709 | -2.69226 | -0.7851 |
| 6 | 0 | 0.6848 | 2.30591 | 0.51359 |
| 1 | 0 | -1.28429 | 3.13326 | 0.90324 |
| 6 | 0 | -0.99243 | 3.13343 | -1.21134 |
| 8 | 0 | -3.76366 | 1.96821 | 0.35725 |
| 8 | 0 | -2.81291 | 0.61932 | 2.26028 |
| 6 | 0 | -4.64027 | -0.91135 | -0.2365 |
| 1 | 0 | -1.77679 | -3.34292 | -1.00527 |
| 6 | 0 | -3.93622 | -3.06543 | -1.04405 |
| 6 | 0 | 1.24603 | 1.22676 | -0.4311 |
| 8 | 0 | -1.04762 | 2.54619 | -2.27022 |
| 8 | 0 | -1.01072 | 4.47428 | -1.08977 |
| 6 | 0 | -4.96153 | -2.15866 | -0.77302 |
| 1 | 0 | -5.38839 | -0.15764 | -0.01698 |
| 1 | 0 | -4.14584 | -4.04472 | -1.46143 |
| 6 | 0 | -1.11767 | 5.20279 | -2.32639 |
| 1 | 0 | -5.99636 | -2.41537 | -0.97994 |
| 1 | 0 | -0.27005 | 4.97479 | -2.97912 |
| 1 | 0 | -1.11805 | 6.25662 | -2.04698 |
| 1 | 0 | -2.04467 | 4.93882 | -2.84245 |
| 6 | 0 | 0.78008 | 2.07309 | 2.04548 |
| 1 | 0 | -0.11989 | 1.54179 | 2.37098 |
| 1 | 0 | 1.60557 | 1.40475 | 2.2931 |
| 6 | 0 | 0.91826 | 3.38987 | 2.81505 |
| 1 | 0 | 0.10434 | 4.08467 | 2.57373 |
| 1 | 0 | 0.89228 | 3.21405 | 3.89564 |
| 1 | 0 | 1.86319 | 3.89525 | 2.57677 |
| 1 | 0 | 1.22843 | 3.233 | 0.26982 |
| 6 | 0 | 2.70751 | 1.01164 | -0.51242 |
| 6 | 0 | 3.61747 | 1.41166 | 0.48637 |
| 6 | 0 | 3.23565 | 0.45058 | -1.69396 |
| 6 | 0 | 4.98993 | 1.23007 | 0.32004 |
| 1 | 0 | 3.26202 | 1.88001 | 1.39452 |
| 6 | 0 | 4.60311 | 0.2632 | -1.85814 |
| 1 | 0 | 2.5536 | 0.14432 | -2.48024 |
| 6 | 0 | 5.48856 | 0.64609 | -0.8458 |
| 1 | 0 | 5.6705 | 1.54819 | 1.10504 |
| 1 | 0 | 4.97866 | -0.18134 | -2.77529 |
| 1 | 0 | 6.55795 | 0.4987 | -0.9696 |
| 1 | 0 | 0.85096 | 1.37342 | -1.44201 |
| 53 | 0 | 1.08963 | -2.46057 | -1.48328 |
| 6 | 0 | 1.50156 | -1.91241 | 4.04908 |
| 6 | 0 | 0.14155 | -1.73357 | 3.79725 |
| 6 | 0 | 2.42838 | -1.6947 | 3.02819 |

| | | | | |
|---|---|---|---|---|
| 6 | 0 | -0.30431 | -1.33093 | 2.53069 |
| 1 | 0 | -0.59133 | -1.88932 | 4.58449 |
| 6 | 0 | 2.0048 | -1.29307 | 1.75624 |
| 1 | 0 | 3.49034 | -1.84476 | 3.20564 |
| 6 | 0 | 0.64381 | -1.10371 | 1.54153 |
| 1 | 0 | -1.35941 | -1.15613 | 2.36822 |
| 1 | 0 | 2.72912 | -1.13978 | 0.96798 |
| 1 | 0 | 1.83772 | -2.22325 | 5.03449 |



**IM5-C-12b**

E(B3LYP/BS1) = -1876.349734
H(correction) = 0.48737387
G(correction) = 0.38904887
E(M06/BS2) = -1876.888664
Imaginary frequencies: 0

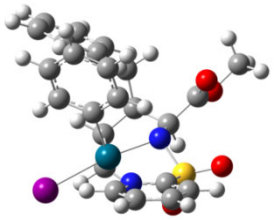
| | | | | |
|---|---|---|---|---|
| 46 | 0 | 0.61381 | 0.52685 | 0.35551 |
| 7 | 0 | -1.23077 | -0.37685 | 0.41256 |
| 7 | 0 | 1.12251 | -1.66205 | 1.02198 |
| 6 | 0 | -2.26116 | 0.20842 | -0.43759 |
| 16 | 0 | -1.4257 | -1.25955 | 1.76249 |
| 6 | 0 | 0.05958 | -2.28995 | 1.53667 |
| 6 | 0 | 2.25462 | -2.35094 | 0.83883 |
| 6 | 0 | -1.57225 | 0.49088 | -1.80198 |
| 1 | 0 | -2.63617 | 1.14559 | -0.01136 |
| 6 | 0 | -3.44101 | -0.7602 | -0.59737 |
| 8 | 0 | -2.60058 | -2.14458 | 1.69025 |
| 8 | 0 | -1.20008 | -0.48397 | 2.99601 |
| 6 | 0 | 0.05311 | -3.6328 | 1.88713 |
| 1 | 0 | 3.08087 | -1.79061 | 0.41343 |
| 6 | 0 | 2.34939 | -3.7052 | 1.16135 |
| 6 | 0 | -0.03218 | 0.39389 | -1.71984 |
| 8 | 0 | -3.43525 | -1.73759 | -1.31624 |
| 8 | 0 | -4.4731 | -0.38097 | 0.16656 |
| 6 | 0 | 1.23351 | -4.35361 | 1.69028 |
| 1 | 0 | -0.85031 | -4.08378 | 2.28195 |
| 1 | 0 | 3.28023 | -4.23523 | 0.98956 |
| 1 | 0 | 0.48021 | 1.26966 | -2.11447 |
| 6 | 0 | -5.54513 | -1.3376 | 0.2653 |
| 1 | 0 | 1.27735 | -5.40896 | 1.94356 |
| 1 | 0 | -5.94868 | -1.56591 | -0.7247 |
| 1 | 0 | -6.30012 | -0.86598 | 0.89431 |
| 1 | 0 | -5.16485 | -2.25032 | 0.73071 |
| 6 | 0 | 0.61996 | -0.87301 | -2.0885 |
| 6 | 0 | -0.03879 | -2.11735 | -1.96842 |
| 6 | 0 | 1.95516 | -0.85404 | -2.544 |
| 6 | 0 | 0.62974 | -3.29617 | -2.28074 |
| 1 | 0 | -1.06465 | -2.15786 | -1.62004 |
| 6 | 0 | 2.61595 | -2.03537 | -2.86209 |
| 1 | 0 | 2.47766 | 0.09532 | -2.60798 |
| 6 | 0 | 1.95672 | -3.26155 | -2.72329 |
| 1 | 0 | 0.11487 | -4.24681 | -2.17594 |
| 1 | 0 | 3.64494 | -2.00258 | -3.20836 |
| 1 | 0 | 2.47449 | -4.1866 | -2.96297 |
| 6 | 0 | -2.05001 | 1.81649 | -2.41938 |
| 1 | 0 | -1.81312 | 2.64597 | -1.74572 |
| 1 | 0 | -1.48953 | 1.99332 | -3.34743 |
| 6 | 0 | -3.55188 | 1.80546 | -2.73315 |
| 1 | 0 | -4.155 | 1.68495 | -1.82559 |
| 1 | 0 | -3.85602 | 2.74534 | -3.20596 |
| 1 | 0 | -3.80888 | 0.98464 | -3.41388 |
| 1 | 0 | -1.87821 | -0.31145 | -2.48221 |
| 53 | 0 | 3.14303 | 1.36817 | 0.28445 |
| 6 | 0 | -1.18446 | 4.9512 | 0.83421 |
| 6 | 0 | -0.27118 | 4.72601 | -0.19789 |
| 6 | 0 | -1.53726 | 3.90349 | 1.68589 |
| 6 | 0 | 0.28485 | 3.45644 | -0.38624 |
| 1 | 0 | 0.02113 | 5.53902 | -0.85784 |
| 6 | 0 | -0.99421 | 2.62562 | 1.50432 |
| 1 | 0 | -2.24265 | 4.06845 | 2.49639 |
| 6 | 0 | -0.0884 | 2.41165 | 0.46014 |
| 1 | 0 | 1.00978 | 3.30065 | -1.17788 |
| 1 | 0 | -1.28174 | 1.81766 | 2.17061 |
| 1 | 0 | -1.61434 | 5.939 | 0.97655 |

**IM5-D-12b**

E(B3LYP/BS1) = -1876.338881
H(correction) = 0.48695924
G(correction) = 0.38562524
E(M06/BS2) = -1876.882241
Imaginary frequencies: 0

| | | | | |
|---|---|---|---|---|
| 46 | 0 | -0.61512 | -0.52696 | -0.31181 |
| 7 | 0 | -0.81114 | 1.44905 | 0.14773 |
| 7 | 0 | -2.97535 | -0.39592 | -0.05476 |
| 6 | 0 | 0.41003 | 2.23187 | 0.35633 |
| 16 | 0 | -2.1363 | 1.9476 | 0.99304 |
| 6 | 0 | -3.37378 | 0.84382 | 0.25024 |
| 6 | 0 | -3.88451 | -1.26313 | -0.52324 |
| 6 | 0 | 1.59019 | 1.24044 | 0.16969 |
| 1 | 0 | 0.47724 | 2.63825 | 1.3723 |
| 6 | 0 | 0.45971 | 3.43121 | -0.60103 |
| 8 | 0 | -2.47972 | 3.33322 | 0.63778 |
| 8 | 0 | -2.08567 | 1.60913 | 2.42787 |
| 6 | 0 | -4.67868 | 1.29757 | 0.10254 |
| 1 | 0 | -3.50526 | -2.24806 | -0.77885 |
| 6 | 0 | -5.22437 | -0.91125 | -0.68681 |
| 6 | 0 | 1.26428 | 0.14807 | -0.86383 |
| 6 | 0 | 2.96486 | 1.90552 | -0.08854 |
| 1 | 0 | 1.6693 | 0.73035 | 1.13349 |
| 8 | 0 | 0.02963 | 3.47432 | -1.73061 |
| 8 | 0 | 1.10814 | 4.45424 | -0.00603 |
| 6 | 0 | -5.62447 | 0.38919 | -0.37612 |
| 1 | 0 | -4.9224 | 2.32603 | 0.34481 |
| 1 | 0 | -5.93121 | -1.64307 | -1.0635 |
| 1 | 0 | 1.95552 | -0.68774 | -0.76805 |
| 1 | 0 | 2.95951 | 2.43065 | -1.05022 |
| 1 | 0 | 3.12153 | 2.66958 | 0.68272 |
| 6 | 0 | 4.07711 | 0.87779 | -0.05738 |
| 6 | 0 | 1.25533 | 5.63729 | -0.81068 |
| 1 | 0 | -6.65768 | 0.69585 | -0.5101 |
| 6 | 0 | 4.76925 | 0.5216 | -1.22078 |
| 6 | 0 | 4.38893 | 0.2099 | 1.13675 |
| 1 | 0 | 1.81987 | 5.41421 | -1.72081 |
| 1 | 0 | 1.79446 | 6.35088 | -0.18711 |
| 1 | 0 | 0.2733 | 6.02911 | -1.08843 |
| 6 | 0 | 5.74323 | -0.47991 | -1.19824 |

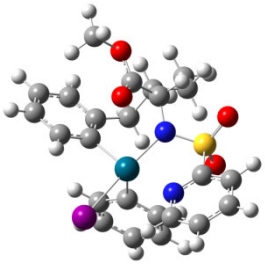
| | | | | |
|---|---|---|---|---|
| 1 | 0 | 4.54144 | 1.03029 | -2.15475 |
| 6 | 0 | 5.3586 | -0.79213 | 1.16376 |
| 1 | 0 | 3.86089 | 0.47063 | 2.05117 |
| 6 | 0 | 6.03833 | -1.14278 | -0.00622 |
| 1 | 0 | 6.26731 | -0.74294 | -2.11319 |
| 1 | 0 | 5.58503 | -1.29815 | 2.09871 |
| 1 | 0 | 6.79254 | -1.92466 | 0.01286 |
| 6 | 0 | 1.09685 | 0.55149 | -2.31674 |
| 1 | 0 | 2.0383 | 1.00293 | -2.66542 |
| 1 | 0 | 0.90214 | -0.32339 | -2.94258 |
| 1 | 0 | 0.31455 | 1.30014 | -2.46188 |
| 53 | 0 | -0.48975 | -2.90559 | -1.48488 |
| 6 | 0 | 0.06529 | -1.33927 | 1.42471 |
| 6 | 0 | -0.81573 | -1.23575 | 2.49395 |
| 6 | 0 | 1.31671 | -1.93577 | 1.55404 |
| 6 | 0 | -0.40941 | -1.72212 | 3.74397 |
| 1 | 0 | -1.78144 | -0.75879 | 2.39621 |
| 6 | 0 | 1.70599 | -2.40997 | 2.8114 |
| 1 | 0 | 1.98664 | -2.05135 | 0.71219 |
| 6 | 0 | 0.84736 | -2.30386 | 3.90647 |
| 1 | 0 | -1.08683 | -1.62592 | 4.58816 |
| 1 | 0 | 2.68389 | -2.8725 | 2.91765 |
| 1 | 0 | 1.15472 | -2.67596 | 4.87986 |



**IM5-E-12b**

E(B3LYP/BS1) = -1876.334758
H(correction) = 0.48724085
G(correction) = 0.38624985
E(M06/BS2) = -1876.875353
Imaginary frequencies: 0

| | | | | |
|---|---|---|---|---|
| 7 | 0 | 0.43201 | 1.57538 | -0.0904 |
| 6 | 0 | -0.8087 | 2.08993 | -0.70113 |
| 16 | 0 | 1.77963 | 2.2899 | -0.76182 |
| 46 | 0 | 0.7236 | -0.44725 | -0.46203 |
| 6 | 0 | -1.8624 | 0.9526 | -0.74819 |
| 1 | 0 | -0.64708 | 2.415 | -1.73686 |
| 6 | 0 | -1.32749 | 3.29346 | 0.08446 |
| 8 | 0 | 1.85493 | 3.72645 | -0.47255 |
| 8 | 0 | 1.95812 | 1.83971 | -2.16293 |
| 6 | 0 | 3.03989 | 1.42924 | 0.21285 |
| 53 | 0 | 1.38356 | -2.93731 | -1.21295 |
| 6 | 0 | -1.18556 | -0.33786 | -1.26386 |
| 8 | 0 | -1.04104 | 3.58403 | 1.22048 |
| 8 | 0 | -2.22533 | 3.96568 | -0.6712 |
| 7 | 0 | 2.88094 | 0.10393 | 0.25613 |
| 6 | 0 | 4.09328 | 2.10832 | 0.80599 |
| 1 | 0 | -1.72664 | -1.23354 | -0.95496 |
| 6 | 0 | -2.83606 | 5.09819 | -0.02814 |
| 6 | 0 | 3.78774 | -0.63455 | 0.90375 |
| 6 | 0 | 5.04503 | 1.33603 | 1.47872 |
| 1 | 0 | 4.14634 | 3.18926 | 0.74089 |
| 1 | 0 | -3.38286 | 4.78268 | 0.86542 |
| 1 | 0 | -3.51662 | 5.52374 | -0.76621 |
| 1 | 0 | -2.07404 | 5.82675 | 0.26145 |
| 1 | 0 | 3.60518 | -1.70489 | 0.91114 |
| 6 | 0 | 4.89374 | -0.05055 | 1.52521 |
| 1 | 0 | 5.89234 | 1.81343 | 1.96202 |
| 1 | 0 | 5.61546 | -0.67649 | 2.03937 |
| 1 | 0 | -0.81885 | -2.80578 | 0.86526 |
| 6 | 0 | -0.55752 | -2.12141 | 1.66092 |
| 6 | 0 | 0.10801 | -0.92533 | 1.40408 |
| 6 | 0 | -0.88383 | -2.43189 | 2.98754 |
| 6 | 0 | 0.43201 | -0.02711 | 2.41872 |
| 6 | 0 | -0.56167 | -1.55551 | 4.02408 |
| 1 | 0 | -1.39411 | -3.36869 | 3.19648 |
| 6 | 0 | 0.09 | -0.3558 | 3.73595 |
| 1 | 0 | 0.88778 | 0.92838 | 2.19527 |
| 1 | 0 | -0.82346 | -1.80281 | 5.04903 |
| 1 | 0 | 0.32666 | 0.34682 | 4.53058 |
| 6 | 0 | -0.89756 | -0.32635 | -2.76113 |
| 1 | 0 | -0.54423 | -1.29811 | -3.11157 |
| 1 | 0 | -1.83024 | -0.08457 | -3.29432 |
| 1 | 0 | -0.15803 | 0.43324 | -3.04583 |
| 1 | 0 | -2.58908 | 1.24814 | -1.5183 |
| 6 | 0 | -2.67746 | 0.76792 | 0.55405 |
| 1 | 0 | -2.03788 | 0.40704 | 1.36051 |
| 1 | 0 | -3.04784 | 1.75028 | 0.86933 |
| 6 | 0 | -3.86467 | -0.15225 | 0.34932 |
| 6 | 0 | -4.91337 | 0.23135 | -0.50145 |
| 6 | 0 | -3.94854 | -1.39572 | 0.98681 |
| 6 | 0 | -6.00445 | -0.60849 | -0.72108 |
| 1 | 0 | -4.87679 | 1.20327 | -0.99011 |
| 6 | 0 | -5.03993 | -2.24118 | 0.76968 |
| 1 | 0 | -3.15622 | -1.6978 | 1.66353 |
| 6 | 0 | -6.06938 | -1.85322 | -0.08821 |
| 1 | 0 | -6.80652 | -0.29093 | -1.38245 |
| 1 | 0 | -5.08407 | -3.20291 | 1.27453 |
| 1 | 0 | -6.91802 | -2.51005 | -0.25923 |



**IM5-F-12b**

E(B3LYP/BS1) = -1876.333052
H(correction) = 0.48723768
G(correction) = 0.38941468
E(M06/BS2) = -1876.870339
Imaginary frequencies: 0

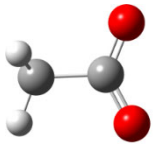
| | | | | |
|---|---|---|---|---|
| 46 | 0 | -0.48994 | -0.34308 | -0.23943 |
| 7 | 0 | 0.65115 | 1.41221 | -0.29303 |
| 7 | 0 | -2.16412 | 1.30689 | -0.65873 |
| 16 | 0 | -0.08211 | 2.80186 | 0.14644 |
| 6 | 0 | 2.07573 | 1.48257 | -0.58505 |
| 6 | 0 | -1.69858 | 2.55972 | -0.62507 |
| 6 | 0 | -3.40015 | 1.10845 | -1.14518 |
| 8 | 0 | -0.36486 | 2.9029 | 1.59098 |
| 8 | 0 | 0.55098 | 3.96189 | -0.50538 |
| 6 | 0 | 2.98249 | 1.17007 | 0.64168 |
| 1 | 0 | 2.30899 | 2.50864 | -0.90294 |
| 6 | 0 | 2.33519 | 0.6545 | -1.85017 |
| 6 | 0 | -2.40496 | 3.66808 | -1.07777 |
| 1 | 0 | -3.74173 | 0.07973 | -1.16225 |
| 6 | 0 | -4.19324 | 2.15581 | -1.61117 |
| 6 | 0 | 2.44237 | -0.04185 | 1.43329 |
| 6 | 0 | 3.11659 | 2.41244 | 1.54539 |
| 1 | 0 | 3.97582 | 0.91925 | 0.25077 |
| 8 | 0 | 1.4763 | 0.24063 | -2.60163 |

| | | | | |
|---|---|---|---|---|
| 8 | 0 | 3.6518 | 0.49491 | -2.06829 |
| 6 | 0 | -3.68583 | 3.45488 | -1.58579 |
| 1 | 0 | -1.94584 | 4.64931 | -1.03501 |
| 1 | 0 | -5.18546 | 1.94426 | -1.99551 |
| 1 | 0 | 1.49427 | 0.2344 | 1.89889 |
| 1 | 0 | 3.14044 | -0.27673 | 2.24256 |
| 6 | 0 | 2.2941 | -1.25519 | 0.54763 |
| 1 | 0 | 2.13883 | 2.65815 | 1.97668 |
| 1 | 0 | 3.40149 | 3.26916 | 0.91993 |
| 6 | 0 | 3.99231 | -0.30063 | -3.21881 |
| 1 | 0 | -4.27544 | 4.28832 | -1.95635 |
| 6 | 0 | 3.41415 | -2.09605 | 0.39955 |
| 6 | 0 | 1.17062 | -1.53707 | -0.24231 |
| 1 | 0 | 3.59035 | -1.31019 | -3.10191 |
| 1 | 0 | 5.0822 | -0.31943 | -3.24658 |
| 1 | 0 | 3.58892 | 0.14895 | -4.13003 |
| 1 | 0 | 4.29348 | -1.88644 | 1.00474 |
| 6 | 0 | 3.43434 | -3.15272 | -0.50447 |
| 6 | 0 | 1.18674 | -2.57434 | -1.18025 |
| 6 | 0 | 2.31832 | -3.38323 | -1.30827 |
| 1 | 0 | 4.31578 | -3.78269 | -0.58837 |
| 1 | 0 | 0.33907 | -2.7583 | -1.825 |
| 1 | 0 | 2.31245 | -4.19143 | -2.03482 |
| 6 | 0 | 4.14687 | 2.25326 | 2.66998 |
| 1 | 0 | 4.2777 | 3.19806 | 3.20904 |
| 1 | 0 | 3.84073 | 1.50017 | 3.40418 |
| 1 | 0 | 5.12593 | 1.95592 | 2.27248 |
| 53 | 0 | -2.27304 | -2.31988 | -0.64188 |
| 6 | 0 | -0.8232 | -0.76191 | 1.74132 |
| 6 | 0 | -1.50695 | 0.22781 | 2.43082 |
| 6 | 0 | -0.37614 | -1.93035 | 2.35353 |
| 6 | 0 | -1.69622 | 0.06284 | 3.81013 |
| 1 | 0 | -1.85965 | 1.12828 | 1.95142 |
| 6 | 0 | -0.57813 | -2.07278 | 3.72982 |
| 1 | 0 | 0.1097 | -2.71369 | 1.7891 |
| 6 | 0 | -1.23118 | -1.07846 | 4.46025 |
| 1 | 0 | -2.20778 | 0.84608 | 4.36269 |
| 1 | 0 | -0.22822 | -2.9775 | 4.21996 |
| 1 | 0 | -1.38473 | -1.19809 | 5.52909 |

**I$^-$**

E(B3LYP/BS1) = -11.472110
H(correction) = 0.00236006
G(correction) = -0.01684794
E(M06/BS2) = -11.531936
Imaginary frequencies: 0

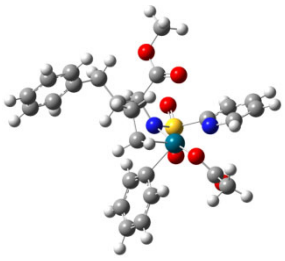
| | | | | |
|---|---|---|---|---|
| 53 | 0 | 0. | 0. | 0. |



**AcO$^-$**

E(B3LYP/BS1) = -228.500416
H(correction) = 0.05366011
G(correction) = 0.02083411
E(M06/BS2) = -228.520873
Imaginary frequencies: 0

| | | | | |
|---|---|---|---|---|
| 6 | 0 | 0.2207 | 0.00205 | 0.0001 |
| 8 | 0 | 0.81309 | -1.10615 | -0.00008 |
| 8 | 0 | 0.69076 | 1.16865 | -0.00006 |
| 6 | 0 | -1.3543 | -0.05949 | 0.00006 |
| 1 | 0 | -1.74935 | 0.4677 | 0.88092 |
| 1 | 0 | -1.74932 | 0.46781 | -0.88075 |
| 1 | 0 | -1.73048 | -1.0908 | -0.00001 |

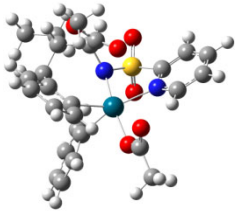


**TS4-A-12b**

E(B3LYP/BS1) = -2093.387070
H(correction) = 0.54099682
G(correction) = 0.43703082
E(M06/BS2) = -2093.876395
Imaginary frequencies: -275.44

| | | | | |
|---|---|---|---|---|
| 6 | 0 | -1.72667 | 0.08331 | -1.12786 |
| 1 | 0 | -2.64489 | 0.33111 | -1.68329 |
| 1 | 0 | -1.14459 | -0.58432 | -1.77045 |
| 6 | 0 | -2.13744 | -0.64321 | 0.16831 |
| 1 | 0 | -2.35473 | 0.11185 | 0.93444 |
| 6 | 0 | -0.98947 | -1.50372 | 0.75843 |
| 1 | 0 | -1.3632 | -1.9643 | 1.67782 |
| 6 | 0 | -1.04756 | 1.43448 | -0.93401 |
| 1 | 0 | -0.66342 | 1.87397 | -1.85394 |
| 1 | 0 | -1.75443 | 2.11186 | -0.46475 |
| 7 | 0 | 0.13737 | -0.63613 | 1.09703 |
| 46 | 0 | 0.9829 | 0.61624 | -0.32387 |
| 6 | 0 | -0.62513 | -2.65019 | -0.19166 |
| 8 | 0 | 0.19382 | -2.58728 | -1.08754 |
| 8 | 0 | -1.35655 | -3.74886 | 0.06855 |
| 6 | 0 | -3.42254 | -1.48414 | -0.03997 |
| 1 | 0 | -3.57759 | -2.11653 | 0.84253 |
| 1 | 0 | -3.28201 | -2.16841 | -0.88493 |
| 6 | 0 | -4.64353 | -0.62112 | -0.27389 |
| 6 | 0 | -5.23728 | -0.52556 | -1.53887 |
| 6 | 0 | -5.18866 | 0.1318 | 0.77685 |
| 6 | 0 | -6.34262 | 0.30203 | -1.75322 |
| 1 | 0 | -4.83084 | -1.10775 | -2.36319 |
| 6 | 0 | -6.29209 | 0.95871 | 0.56884 |
| 1 | 0 | -4.74424 | 0.0642 | 1.76783 |
| 6 | 0 | -6.8727 | 1.0477 | -0.69966 |
| 1 | 0 | -6.7886 | 0.36131 | -2.7426 |
| 1 | 0 | -6.70155 | 1.53155 | 1.39673 |
| 1 | 0 | -7.73293 | 1.69113 | -0.86296 |
| 16 | 0 | 1.36017 | -1.33035 | 1.95027 |
| 8 | 0 | 1.98785 | -0.31963 | 2.80351 |
| 8 | 0 | 0.9502 | -2.62849 | 2.5116 |
| 6 | 0 | 2.56552 | -1.69445 | 0.63756 |
| 6 | 0 | 3.47128 | -2.7411 | 0.73078 |
| 7 | 0 | 2.49894 | -0.87669 | -0.41821 |
| 6 | 0 | 4.35143 | -2.93265 | -0.33411 |
| 1 | 0 | 3.46177 | -3.38076 | 1.60625 |
| 6 | 0 | 3.33475 | -1.06063 | -1.4484 |
| 6 | 0 | 4.27973 | -2.08267 | -1.43916 |
| 1 | 0 | 5.07884 | -3.7387 | -0.30584 |
| 1 | 0 | 3.21817 | -0.37804 | -2.28028 |
| 1 | 0 | 4.94167 | -2.20697 | -2.28936 |
| 6 | 0 | -1.10172 | -4.87811 | -0.78531 |

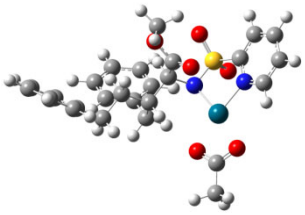
| | | | | |
|---|---|---|---|---|
| 1 | 0 | -1.77164 | -5.66476 | -0.43798 |
| 1 | 0 | -1.30897 | -4.62488 | -1.8291 |
| 1 | 0 | -0.05812 | -5.19151 | -0.69554 |
| 6 | 0 | -0.20085 | 2.25129 | 1.85391 |
| 6 | 0 | 0.14812 | 2.36028 | 0.50188 |
| 6 | 0 | 0.50638 | 3.59976 | -0.04254 |
| 6 | 0 | 0.55826 | 4.72368 | 0.78133 |
| 6 | 0 | 0.23872 | 4.62109 | 2.13765 |
| 6 | 0 | -0.13883 | 3.38569 | 2.66633 |
| 1 | 0 | -0.47018 | 1.29039 | 2.27051 |
| 1 | 0 | 0.74902 | 3.68083 | -1.09497 |
| 1 | 0 | 0.85502 | 5.6802 | 0.35898 |
| 1 | 0 | 0.28352 | 5.49855 | 2.77683 |
| 1 | 0 | -0.38186 | 3.29299 | 3.72147 |
| 6 | 0 | 2.97549 | 2.18262 | -1.6863 |
| 8 | 0 | 1.77561 | 1.67038 | -1.87852 |
| 8 | 0 | 3.68595 | 1.9745 | -0.71103 |
| 6 | 0 | 3.40068 | 3.10448 | -2.82351 |
| 1 | 0 | 4.47925 | 3.27004 | -2.78351 |
| 1 | 0 | 3.1098 | 2.69522 | -3.79547 |
| 1 | 0 | 2.89157 | 4.06902 | -2.70601 |



**TS4-F-12b**

E(B3LYP/BS1) = -2093.391717
H(correction) = 0.54071735
G(correction) = 0.43834535
E(M06/BS2) = -2093.871086
Imaginary frequencies: -205.89

| | | | | |
|---|---|---|---|---|
| 46 | 0 | 0.59689 | -0.56807 | -0.22194 |
| 7 | 0 | -0.3619 | 1.23573 | -0.62604 |
| 7 | 0 | 2.38254 | 0.76471 | -0.18957 |
| 16 | 0 | 0.61064 | 2.05906 | -1.66132 |
| 6 | 0 | -1.10367 | 2.01326 | 0.37264 |
| 6 | 0 | 2.20924 | 1.92952 | -0.82621 |
| 6 | 0 | 3.50282 | 0.58154 | 0.5261 |
| 8 | 0 | 0.73547 | 1.28255 | -2.90087 |
| 8 | 0 | 0.26593 | 3.48773 | -1.7192 |
| 6 | 0 | -2.62302 | 1.80918 | 0.1748 |
| 1 | 0 | -0.90131 | 3.07986 | 0.20195 |
| 6 | 0 | -0.55844 | 1.77343 | 1.7865 |
| 6 | 0 | 3.13303 | 2.96253 | -0.81636 |
| 1 | 0 | 3.57009 | -0.34477 | 1.0822 |
| 6 | 0 | 4.4935 | 1.56254 | 0.58601 |
| 6 | 0 | -2.9748 | 0.31626 | -0.0156 |
| 6 | 0 | -3.10035 | 2.64335 | -1.02977 |
| 1 | 0 | -3.12728 | 2.1768 | 1.07564 |
| 8 | 0 | 0.60026 | 1.50681 | 2.03085 |
| 8 | 0 | -1.48917 | 1.96336 | 2.73711 |
| 6 | 0 | 4.31217 | 2.76486 | -0.09545 |
| 1 | 0 | 2.91066 | 3.88439 | -1.34189 |
| 1 | 0 | 5.38366 | 1.37993 | 1.17849 |
| 1 | 0 | -2.69224 | 0.0168 | -1.02374 |
| 1 | 0 | -4.06205 | 0.20792 | 0.05033 |
| 6 | 0 | -2.34775 | -0.60878 | 0.99558 |
| 1 | 0 | -2.53862 | 2.33278 | -1.92008 |
| 1 | 0 | -2.82939 | 3.69298 | -0.85504 |
| 6 | 0 | -1.04978 | 1.70631 | 4.08385 |
| 1 | 0 | 5.06787 | 3.54401 | -0.0547 |
| 6 | 0 | -3.07227 | -0.85774 | 2.17694 |
| 6 | 0 | -1.09014 | -1.22951 | 0.88043 |
| 1 | 0 | -0.72495 | 0.66675 | 4.17432 |
| 1 | 0 | -1.91993 | 1.89475 | 4.71321 |
| 1 | 0 | -0.22408 | 2.37033 | 4.35273 |
| 1 | 0 | -4.04495 | -0.38263 | 2.28062 |
| 6 | 0 | -2.58976 | -1.66687 | 3.19866 |
| 6 | 0 | -0.60378 | -2.07148 | 1.88878 |
| 6 | 0 | -1.3438 | -2.27613 | 3.05197 |
| 1 | 0 | -3.18291 | -1.8266 | 4.09488 |
| 1 | 0 | 0.36567 | -2.53639 | 1.80607 |
| 1 | 0 | -0.93546 | -2.91091 | 3.83331 |
| 6 | 0 | -4.60484 | 2.55324 | -1.30585 |
| 1 | 0 | -4.89394 | 3.25054 | -2.09994 |
| 1 | 0 | -4.90362 | 1.54973 | -1.62807 |
| 1 | 0 | -5.18902 | 2.80525 | -0.41131 |
| 6 | 0 | -0.75788 | -1.84597 | -1.19978 |
| 6 | 0 | -1.26084 | -1.23997 | -2.35454 |
| 6 | 0 | -0.7465 | -3.23707 | -1.06656 |
| 6 | 0 | -1.76739 | -2.04873 | -3.37935 |
| 1 | 0 | -1.2091 | -0.16962 | -2.49245 |
| 6 | 0 | -1.26706 | -4.02552 | -2.09121 |
| 1 | 0 | -0.33902 | -3.70282 | -0.18021 |
| 6 | 0 | -1.78268 | -3.43542 | -3.24911 |
| 1 | 0 | -2.13486 | -1.5754 | -4.28582 |
| 1 | 0 | -1.2692 | -5.10654 | -1.97865 |
| 1 | 0 | -2.18566 | -4.05562 | -4.04506 |
| 8 | 0 | 1.76542 | -2.25259 | -0.21776 |
| 6 | 0 | 2.54971 | -2.61063 | 0.76196 |
| 8 | 0 | 2.61869 | -2.06651 | 1.86585 |
| 6 | 0 | 3.41131 | -3.81486 | 0.39855 |
| 1 | 0 | 3.96854 | -4.15175 | 1.27487 |
| 1 | 0 | 2.78518 | -4.62465 | 0.01126 |
| 1 | 0 | 4.10923 | -3.53674 | -0.39893 |

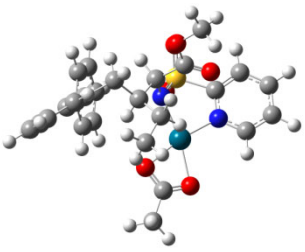


**IM6-A-12b**

E(B3LYP/BS1) = -2093.463622
H(correction) = 0.54403602
G(correction) = 0.43554302
E(M06/BS2) = -2093.950574
Imaginary frequencies: 0

| | | | | |
|---|---|---|---|---|
| 6 | 0 | -2.5219 | 0.41794 | -0.17513 |
| 1 | 0 | -2.98459 | -0.53278 | -0.4668 |
| 1 | 0 | -2.37893 | 0.97809 | -1.10506 |
| 6 | 0 | -1.1601 | 0.1494 | 0.49318 |
| 1 | 0 | -0.73296 | 1.1155 | 0.7933 |
| 6 | 0 | -0.17339 | -0.512 | -0.51097 |
| 1 | 0 | -0.60297 | -1.46925 | -0.82032 |
| 6 | 0 | -3.50626 | 1.22235 | 0.69672 |
| 1 | 0 | -3.72941 | 0.67724 | 1.62065 |
| 1 | 0 | -3.03156 | 2.16523 | 0.99918 |
| 7 | 0 | 1.10939 | -0.77438 | 0.15551 |
| 46 | 0 | 2.16632 | 0.7806 | 0.9487 |
| 6 | 0 | 0.0131 | 0.33435 | -1.7723 |
| 8 | 0 | 0.83065 | 1.22629 | -1.90161 |
| 8 | 0 | -0.84042 | -0.0319 | -2.74394 |
| 6 | 0 | -1.26663 | -0.70944 | 1.78734 |

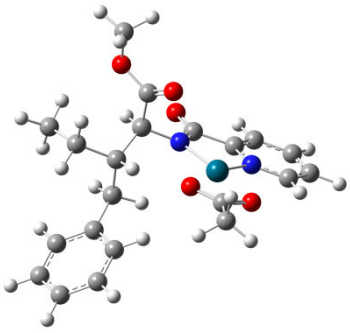
| | | | | |
|---|---|---|---|---|
| 1 | 0 | -1.93585 | -0.18869 | 2.48086 |
| 1 | 0 | -0.28482 | -0.72464 | 2.26366 |
| 6 | 0 | -1.75128 | -2.12704 | 1.56716 |
| 6 | 0 | -3.12054 | -2.43172 | 1.53836 |
| 6 | 0 | -0.83533 | -3.17205 | 1.36743 |
| 6 | 0 | -3.5656 | -3.73238 | 1.29521 |
| 1 | 0 | -3.84666 | -1.64308 | 1.72093 |
| 6 | 0 | -1.27649 | -4.47323 | 1.12058 |
| 1 | 0 | 0.22872 | -2.9598 | 1.40574 |
| 6 | 0 | -2.64304 | -4.75818 | 1.07891 |
| 1 | 0 | -4.63194 | -3.94424 | 1.27863 |
| 1 | 0 | -0.54797 | -5.26398 | 0.96216 |
| 1 | 0 | -2.98633 | -5.77137 | 0.88659 |
| 16 | 0 | 2.13172 | -1.81593 | -0.60342 |
| 8 | 0 | 2.87754 | -2.59012 | 0.39299 |
| 8 | 0 | 1.49368 | -2.49465 | -1.74053 |
| 6 | 0 | 3.34597 | -0.65557 | -1.29514 |
| 6 | 0 | 4.08042 | -0.90551 | -2.44439 |
| 7 | 0 | 3.47848 | 0.47138 | -0.58149 |
| 6 | 0 | 5.0015 | 0.05938 | -2.85299 |
| 1 | 0 | 3.91102 | -1.82559 | -2.99291 |
| 6 | 0 | 4.36006 | 1.40782 | -0.96756 |
| 6 | 0 | 5.14638 | 1.22819 | -2.10168 |
| 1 | 0 | 5.59682 | -0.09522 | -3.74797 |
| 1 | 0 | 4.41262 | 2.29778 | -0.34931 |
| 1 | 0 | 5.85094 | 2.00044 | -2.39046 |
| 6 | 0 | -0.75451 | 0.72284 | -3.96396 |
| 1 | 0 | -1.51094 | 0.29822 | -4.62406 |
| 1 | 0 | -0.95606 | 1.78141 | -3.77568 |
| 1 | 0 | 0.24223 | 0.62266 | -4.40276 |
| 6 | 0 | -5.01532 | 2.73066 | -0.67997 |
| 6 | 0 | -4.79494 | 1.50252 | -0.04406 |
| 6 | 0 | -5.77929 | 0.50955 | -0.15268 |
| 6 | 0 | -6.95205 | 0.73777 | -0.87277 |
| 6 | 0 | -7.16072 | 1.9687 | -1.50052 |
| 6 | 0 | -6.18774 | 2.96501 | -1.40203 |
| 1 | 0 | -4.26123 | 3.51159 | -0.60523 |
| 1 | 0 | -5.61941 | -0.45247 | 0.33008 |
| 1 | 0 | -7.7042 | -0.04397 | -0.94256 |
| 1 | 0 | -8.07485 | 2.14959 | -2.05976 |
| 1 | 0 | -6.34196 | 3.92701 | -1.88443 |
| 6 | 0 | 1.95053 | 2.34275 | 2.83134 |
| 8 | 0 | 1.06708 | 1.44615 | 2.6098 |
| 8 | 0 | 2.94972 | 2.40809 | 2.03411 |
| 6 | 0 | 1.83267 | 3.26371 | 4.00827 |
| 1 | 0 | 2.37561 | 4.19214 | 3.8176 |
| 1 | 0 | 0.78017 | 3.46561 | 4.22174 |
| 1 | 0 | 2.27234 | 2.77508 | 4.88584 |



**IM6-F-12b**

E(B3LYP/BS1) = -2093.469557
H(correction) = 0.54317569
G(correction) = 0.43866669
E(M06/BS2) = -2093.952012
Imaginary frequencies: 0

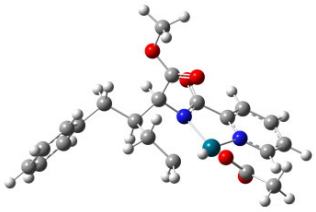
| | | | | |
|---|---|---|---|---|
| 46 | 0 | 1.26964 | -1.38043 | 0.04211 |
| 7 | 0 | 0.69461 | 0.46451 | -0.56888 |
| 7 | 0 | 3.15476 | -0.5897 | 0.10164 |
| 16 | 0 | 1.89499 | 1.10093 | -1.4894 |
| 6 | 0 | -0.04554 | 1.38938 | 0.2945 |
| 6 | 0 | 3.34436 | 0.57933 | -0.52838 |
| 6 | 0 | 4.14883 | -1.12432 | 0.829 |
| 8 | 0 | 2.02942 | 0.35343 | -2.74414 |
| 8 | 0 | 1.85534 | 2.57006 | -1.50818 |
| 6 | 0 | -1.25506 | 0.66049 | 0.96614 |
| 1 | 0 | -0.44393 | 2.17404 | -0.35396 |
| 6 | 0 | 0.82164 | 2.07784 | 1.3471 |
| 6 | 0 | 4.53652 | 1.28241 | -0.46287 |
| 1 | 0 | 3.93104 | -2.06937 | 1.31541 |
| 6 | 0 | 5.37992 | -0.48551 | 0.941 |
| 6 | 0 | -2.50502 | 1.58709 | 1.05729 |
| 6 | 0 | -0.89236 | 0.03089 | 2.32744 |
| 1 | 0 | -1.48435 | -0.15543 | 0.28067 |
| 8 | 0 | 1.9324 | 1.73644 | 1.69945 |
| 8 | 0 | 0.16189 | 3.1252 | 1.8816 |
| 6 | 0 | 5.57459 | 0.7358 | 0.2906 |
| 1 | 0 | 4.62088 | 2.233 | -0.97769 |
| 1 | 0 | 6.16501 | -0.93926 | 1.53589 |
| 1 | 0 | -2.36304 | 2.44716 | 0.39658 |
| 1 | 0 | -2.57627 | 2.00549 | 2.06776 |
| 6 | 0 | -3.81486 | 0.90002 | 0.70626 |
| 1 | 0 | -0.79593 | 0.82405 | 3.08249 |
| 1 | 0 | 0.09677 | -0.44002 | 2.2518 |
| 6 | 0 | 0.8601 | 3.83069 | 2.9209 |
| 1 | 0 | 6.52431 | 1.25596 | 0.37391 |
| 6 | 0 | -4.83595 | 0.82211 | 1.66159 |
| 6 | 0 | -4.03165 | 0.31084 | -0.56252 |
| 1 | 0 | 1.07044 | 3.16349 | 3.76199 |
| 1 | 0 | 0.1933 | 4.63717 | 3.22731 |
| 1 | 0 | 1.80337 | 4.23266 | 2.54097 |
| 1 | 0 | -4.67606 | 1.27752 | 2.63672 |
| 6 | 0 | -6.03837 | 0.1628 | 1.40207 |
| 6 | 0 | -5.23623 | -0.3642 | -0.80674 |
| 6 | 0 | -6.23679 | -0.44286 | 0.16208 |
| 1 | 0 | -6.80934 | 0.11846 | 2.16694 |
| 1 | 0 | -5.38606 | -0.81927 | -1.78244 |
| 1 | 0 | -7.16413 | -0.96671 | -0.05426 |
| 6 | 0 | -1.89985 | -1.022 | 2.79984 |
| 1 | 0 | -1.57549 | -1.4715 | 3.7462 |
| 1 | 0 | -2.89558 | -0.59588 | 2.95263 |
| 1 | 0 | -1.9895 | -1.8173 | 2.05223 |
| 6 | 0 | -3.00506 | 0.36434 | -1.64539 |
| 6 | 0 | -2.41502 | -0.8185 | -2.11728 |
| 6 | 0 | -2.59158 | 1.58656 | -2.1962 |
| 6 | 0 | -1.41589 | -0.77675 | -3.08889 |
| 1 | 0 | -2.7045 | -1.76701 | -1.67429 |
| 6 | 0 | -1.59404 | 1.6275 | -3.17185 |
| 1 | 0 | -3.05927 | 2.50804 | -1.85888 |
| 6 | 0 | -0.99767 | 0.44575 | -3.61578 |
| 1 | 0 | -0.94064 | -1.69829 | -3.41312 |
| 1 | 0 | -1.27397 | 2.58365 | -3.57717 |
| 1 | 0 | -0.18943 | 0.47988 | -4.33787 |
| 8 | 0 | 1.43639 | -3.40254 | 0.65834 |
| 6 | 0 | 0.17255 | -3.5334 | 0.51668 |
| 8 | 0 | -0.49366 | -2.52136 | 0.10779 |
| 6 | 0 | -0.5258 | -4.81858 | 0.84627 |
| 1 | 0 | -1.06426 | -4.69591 | 1.79324 |
| 1 | 0 | -1.26269 | -5.04779 | 0.0714 |
| 1 | 0 | 0.19571 | -5.63206 | 0.9436 |



**IM2-12a**

E(B3LYP/BS1) = -1427.195380
H(correction) = 0.45653583
G(correction) = 0.36304783
E(M06/BS2) = -1427.806673
Imaginary frequencies: 0

| | | | | |
|---|---|---|---|---|
| 46 | 0 | 1.21836 | 0.80082 | -0.54129 |
| 7 | 0 | 2.85793 | 0.65694 | 0.62371 |
| 7 | 0 | 0.80548 | -0.92956 | 0.39918 |
| 8 | 0 | 1.43527 | 2.6045 | -1.61062 |
| 6 | 0 | 2.88558 | -0.42965 | 1.41954 |
| 6 | 0 | 3.85233 | 1.55818 | 0.65416 |
| 6 | 0 | -0.32008 | -1.79388 | 0.06889 |
| 6 | 0 | 0.28978 | 2.42299 | -2.15136 |
| 6 | 0 | 3.94215 | -0.65527 | 2.29383 |
| 1 | 0 | 3.75232 | 2.40454 | -0.01768 |
| 6 | 0 | 4.93868 | 1.39329 | 1.50902 |
| 6 | 0 | -1.67027 | -1.02391 | 0.04064 |
| 1 | 0 | -0.36334 | -2.58323 | 0.82374 |
| 6 | 0 | -0.05571 | -2.44032 | -1.29079 |
| 8 | 0 | -0.37121 | 1.38271 | -1.82012 |
| 6 | 0 | -0.25529 | 3.38604 | -3.16426 |
| 6 | 0 | 4.98297 | 0.27062 | 2.34085 |
| 1 | 0 | 3.91063 | -1.55151 | 2.90354 |
| 1 | 0 | 5.7307 | 2.13441 | 1.51646 |
| 6 | 0 | -1.88736 | -0.29565 | 1.38851 |
| 6 | 0 | -2.86662 | -1.91817 | -0.3514 |
| 1 | 0 | -1.58409 | -0.25924 | -0.73692 |
| 8 | 0 | 0.44459 | -1.88252 | -2.24422 |
| 8 | 0 | -0.47649 | -3.72338 | -1.31587 |
| 1 | 0 | 0.25009 | 4.35068 | -3.08344 |
| 1 | 0 | -0.08756 | 2.97882 | -4.16812 |
| 1 | 0 | -1.33351 | 3.50033 | -3.02405 |
| 1 | 0 | 5.82134 | 0.12189 | 3.015 |
| 1 | 0 | -2.01796 | -1.03054 | 2.19191 |
| 1 | 0 | -0.97446 | 0.26154 | 1.62678 |
| 6 | 0 | -3.05983 | 0.65865 | 1.35389 |
| 1 | 0 | -3.75401 | -1.27476 | -0.384 |
| 1 | 0 | -2.72034 | -2.28153 | -1.37633 |
| 6 | 0 | -3.1436 | -3.11626 | 0.56583 |
| 6 | 0 | -0.3302 | -4.39375 | -2.57876 |
| 6 | 0 | -3.00488 | 1.81103 | 0.55335 |
| 6 | 0 | -4.2246 | 0.41412 | 2.09119 |
| 1 | 0 | -4.03943 | -3.65139 | 0.23036 |
| 1 | 0 | -2.31225 | -3.8278 | 0.55846 |
| 1 | 0 | -3.31931 | -2.80472 | 1.60171 |
| 1 | 0 | -0.89691 | -3.87349 | -3.35662 |
| 1 | 0 | -0.72212 | -5.39946 | -2.42384 |
| 1 | 0 | 0.7225 | -4.43015 | -2.8728 |
| 6 | 0 | -4.08319 | 2.69364 | 0.49918 |
| 1 | 0 | -2.1139 | 2.0025 | -0.0404 |
| 6 | 0 | -5.30672 | 1.29666 | 2.03985 |
| 1 | 0 | -4.2833 | -0.47655 | 2.71299 |
| 6 | 0 | -5.23914 | 2.44089 | 1.24393 |
| 1 | 0 | -4.0226 | 3.58206 | -0.12501 |
| 1 | 0 | -6.20111 | 1.08883 | 2.62198 |
| 1 | 0 | -6.07895 | 3.12966 | 1.2024 |
| 6 | 0 | 1.72755 | -1.38298 | 1.28083 |
| 8 | 0 | 1.70786 | -2.43354 | 1.9285 |

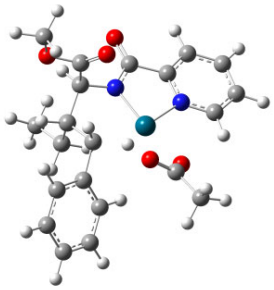


**TS2-A-12a**

E(B3LYP/BS1) = -1427.146472
H(correction) = 0.45008325
G(correction) = 0.35893025
E(M06/BS2) = -1427.768025
Imaginary frequencies: -1385.86

| | | | | |
|---|---|---|---|---|
| 6 | 0 | 1.76104 | 1.00161 | 0.35551 |
| 1 | 0 | 2.69014 | 1.52701 | 0.09903 |
| 1 | 0 | 1.6816 | 1.03622 | 1.45031 |
| 6 | 0 | 1.91825 | -0.45594 | -0.10644 |
| 1 | 0 | 1.857 | -0.47318 | -1.20374 |
| 6 | 0 | 0.77658 | -1.3924 | 0.36812 |
| 1 | 0 | 1.05882 | -2.42076 | 0.12256 |
| 6 | 0 | 0.59562 | 1.75749 | -0.28215 |
| 1 | 0 | 0.77962 | 2.84001 | -0.22418 |
| 1 | 0 | 0.56452 | 1.57791 | -1.36625 |
| 7 | 0 | -0.48832 | -1.10831 | -0.28286 |
| 46 | 0 | -1.3642 | 0.71088 | -0.33032 |
| 6 | 0 | 0.59443 | -1.32986 | 1.88986 |
| 8 | 0 | -0.23461 | -0.66667 | 2.47516 |
| 8 | 0 | 1.51134 | -2.09579 | 2.52116 |
| 6 | 0 | 3.30606 | -1.02285 | 0.29181 |
| 1 | 0 | 3.31693 | -2.10049 | 0.08456 |
| 1 | 0 | 3.44485 | -0.91964 | 1.37332 |
| 6 | 0 | 4.44821 | -0.3589 | -0.44626 |
| 6 | 0 | 5.29834 | 0.55355 | 0.19133 |
| 6 | 0 | 4.6642 | -0.63033 | -1.80552 |
| 6 | 0 | 6.33322 | 1.18147 | -0.50626 |
| 1 | 0 | 5.14596 | 0.77327 | 1.24571 |
| 6 | 0 | 5.69568 | -0.00696 | -2.50745 |
| 1 | 0 | 4.01667 | -1.34148 | -2.31464 |
| 6 | 0 | 6.53479 | 0.90355 | -1.85904 |
| 1 | 0 | 6.98153 | 1.886 | 0.00852 |
| 1 | 0 | 5.84786 | -0.23405 | -3.55958 |
| 1 | 0 | 7.34005 | 1.38905 | -2.40393 |
| 6 | 0 | -2.72965 | -1.76652 | -0.81367 |
| 6 | 0 | -3.70063 | -2.70844 | -1.13905 |
| 7 | 0 | -3.01444 | -0.45153 | -0.77051 |
| 6 | 0 | -4.98806 | -2.26681 | -1.43804 |
| 1 | 0 | -3.41488 | -3.75435 | -1.13694 |
| 6 | 0 | -4.25129 | -0.01217 | -1.04676 |
| 6 | 0 | -5.26914 | -0.89854 | -1.39003 |
| 1 | 0 | -5.76637 | -2.97775 | -1.70014 |
| 1 | 0 | -4.39689 | 1.06072 | -0.98105 |
| 1 | 0 | -6.26091 | -0.51788 | -1.61072 |
| 6 | 0 | -2.16025 | 3.22859 | 0.7075 |
| 8 | 0 | -2.52311 | 2.46225 | -0.24069 |
| 8 | 0 | -1.07846 | 3.07085 | 1.35663 |
| 1 | 0 | -0.40263 | 2.17947 | 0.65876 |
| 6 | 0 | -3.05237 | 4.38689 | 1.08431 |
| 1 | 0 | -3.37298 | 4.26506 | 2.12414 |

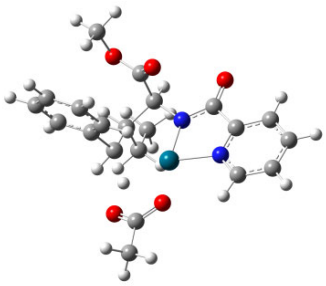
| | | | | |
|---|---|---|---|---|
| 1 | 0 | -2.48086 | 5.31826 | 1.0259 |
| 1 | 0 | -3.92402 | 4.43851 | 0.43043 |
| 6 | 0 | 1.44838 | -2.06954 | 3.95719 |
| 1 | 0 | 2.25334 | -2.72153 | 4.29805 |
| 1 | 0 | 1.59059 | -1.05098 | 4.3302 |
| 1 | 0 | 0.47921 | -2.43974 | 4.30286 |
| 6 | 0 | -1.3299 | -2.16473 | -0.421 |
| 8 | 0 | -1.06488 | -3.35764 | -0.23583 |



**TS2-B-12a**

E(B3LYP/BS1) = -1427.145054
H(correction) = 0.44981697
G(correction) = 0.35812597
E(M06/BS2) = -1427.765593
Imaginary frequencies: -1308.47

| | | | | |
|---|---|---|---|---|
| 46 | 0 | -0.52078 | -0.67293 | -0.1351 |
| 7 | 0 | -1.23224 | 1.10468 | 0.31091 |
| 7 | 0 | -2.50572 | -1.16068 | 0.19174 |
| 8 | 0 | 0.06178 | -2.62704 | -0.6196 |
| 6 | 0 | -0.31253 | 2.20777 | 0.23039 |
| 6 | 0 | -3.26387 | -0.08035 | 0.48258 |
| 6 | 0 | -3.05657 | -2.38023 | 0.11625 |
| 6 | 0 | 0.98382 | -2.63544 | -1.5018 |
| 6 | 0 | 1.0519 | 1.6679 | 0.7141 |
| 1 | 0 | -0.65017 | 3.04098 | 0.85443 |
| 6 | 0 | -0.20956 | 2.73342 | -1.20408 |
| 6 | 0 | -4.62917 | -0.19825 | 0.71242 |
| 1 | 0 | -2.3775 | -3.18998 | -0.12974 |
| 6 | 0 | -4.41886 | -2.56943 | 0.34066 |
| 8 | 0 | 1.53862 | -1.58201 | -1.93098 |
| 6 | 0 | 1.46768 | -3.96782 | -2.01968 |
| 6 | 0 | 1.51952 | 0.48482 | -0.21799 |
| 8 | 0 | -0.64949 | 2.19401 | -2.19409 |
| 8 | 0 | 0.49297 | 3.88877 | -1.22519 |
| 6 | 0 | -5.21511 | -1.46185 | 0.6426 |
| 1 | 0 | -5.1856 | 0.70575 | 0.93514 |
| 1 | 0 | -4.84003 | -3.56718 | 0.2762 |
| 1 | 0 | 1.14387 | -0.58619 | -1.06143 |
| 1 | 0 | 0.74838 | -4.75888 | -1.8011 |
| 1 | 0 | 1.65786 | -3.90401 | -3.09385 |
| 1 | 0 | 2.4181 | -4.20022 | -1.52528 |
| 6 | 0 | 0.69735 | 4.45681 | -2.5297 |
| 1 | 0 | -6.2799 | -1.58429 | 0.81891 |
| 1 | 0 | 1.25242 | 3.76248 | -3.16758 |
| 1 | 0 | 1.26917 | 5.37103 | -2.36652 |
| 1 | 0 | -0.26216 | 4.68115 | -3.00404 |
| 6 | 0 | 1.02437 | 1.32003 | 2.21514 |
| 1 | 0 | 0.35822 | 0.46514 | 2.38226 |
| 1 | 0 | 2.0278 | 0.98957 | 2.50148 |
| 6 | 0 | 0.60019 | 2.48484 | 3.11692 |
| 1 | 0 | -0.45918 | 2.73524 | 2.99359 |
| 1 | 0 | 0.75404 | 2.22713 | 4.17077 |
| 1 | 0 | 1.18684 | 3.38805 | 2.90587 |
| 1 | 0 | 1.79769 | 2.46424 | 0.57788 |
| 6 | 0 | 2.78887 | -0.16159 | 0.29925 |
| 6 | 0 | 2.75515 | -1.29549 | 1.12312 |
| 6 | 0 | 4.03589 | 0.39121 | -0.02228 |
| 6 | 0 | 3.93312 | -1.85816 | 1.61519 |
| 1 | 0 | 1.79509 | -1.74272 | 1.36701 |
| 6 | 0 | 5.21701 | -0.16542 | 0.47186 |
| 1 | 0 | 4.08 | 1.26544 | -0.66838 |
| 6 | 0 | 5.16974 | -1.29362 | 1.29305 |
| 1 | 0 | 3.88467 | -2.73938 | 2.24994 |
| 1 | 0 | 6.17379 | 0.2788 | 0.20939 |
| 1 | 0 | 6.08812 | -1.73187 | 1.67456 |
| 1 | 0 | 1.74544 | 0.96745 | -1.18047 |
| 6 | 0 | -2.55194 | 1.25432 | 0.5298 |
| 8 | 0 | -3.15976 | 2.30232 | 0.76108 |

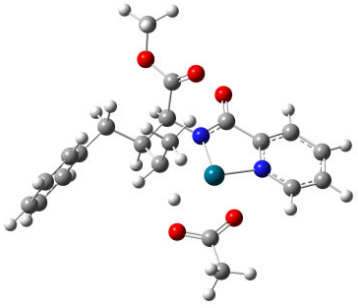


**TS2-C-12a**

E(B3LYP/BS1) = -1427.149583
H(correction) = 0.44979349
G(correction) = 0.3588325
E(M06/BS2) = -1427.770292
Imaginary frequencies: -1318.63

| | | | | |
|---|---|---|---|---|
| 46 | 0 | 0.84189 | 0.61774 | 0.29244 |
| 7 | 0 | 0.65958 | -1.33746 | 0.47383 |
| 7 | 0 | 2.68371 | 0.02597 | -0.44605 |
| 8 | 0 | 1.28664 | 2.64312 | -0.01018 |
| 6 | 0 | -0.6593 | -1.8579 | 0.72771 |
| 6 | 0 | 2.83002 | -1.3163 | -0.46727 |
| 6 | 0 | 3.66811 | 0.82511 | -0.88198 |
| 6 | 0 | 0.53725 | 3.45315 | 0.61919 |
| 6 | 0 | -1.36588 | -0.85607 | 1.6575 |
| 1 | 0 | -0.59537 | -2.84458 | 1.2015 |
| 6 | 0 | -1.40719 | -2.07845 | -0.59651 |
| 6 | 0 | 3.99443 | -1.9095 | -0.94007 |
| 1 | 0 | 3.468 | 1.89012 | -0.83543 |
| 6 | 0 | 4.86404 | 0.29609 | -1.36289 |
| 8 | 0 | -0.43412 | 3.07659 | 1.34177 |
| 6 | 0 | 0.79899 | 4.93413 | 0.4884 |
| 6 | 0 | -1.37153 | 0.59687 | 1.0737 |
| 8 | 0 | -0.94454 | -1.9081 | -1.70118 |
| 8 | 0 | -2.66573 | -2.50231 | -0.36025 |
| 6 | 0 | 5.02849 | -1.09111 | -1.3922 |
| 1 | 0 | 4.04502 | -2.9929 | -0.94326 |
| 1 | 0 | 5.64543 | 0.96476 | -1.70848 |
| 1 | 0 | -0.55771 | 1.75967 | 1.18014 |
| 1 | 0 | 1.73066 | 5.12135 | -0.04733 |
| 1 | 0 | -0.03506 | 5.39224 | -0.05414 |
| 1 | 0 | 0.83286 | 5.38903 | 1.48251 |
| 1 | 0 | -1.80089 | 1.17078 | 1.91141 |
| 6 | 0 | -3.49203 | -2.64315 | -1.52948 |
| 1 | 0 | 5.9507 | -1.52617 | -1.76651 |
| 1 | 0 | -3.60819 | -1.67455 | -2.02241 |
| 1 | 0 | -4.45414 | -3.00574 | -1.16541 |
| 1 | 0 | -3.04837 | -3.35754 | -2.22835 |
| 6 | 0 | -2.32812 | 0.81398 | -0.09125 |
| 6 | 0 | -1.90888 | 1.07113 | -1.40195 |
| 6 | 0 | -3.7114 | 0.75673 | 0.1535 |
| 6 | 0 | -2.8317 | 1.26007 | -2.43364 |

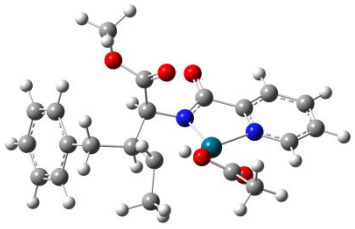
| | | | | |
|---|---|---|---|---|
| 1 | 0 | -0.84599 | 1.10466 | -1.6232 |
| 6 | 0 | -4.63879 | 0.94044 | -0.87069 |
| 1 | 0 | -4.06385 | 0.56439 | 1.16474 |
| 6 | 0 | -4.20061 | 1.19554 | -2.17363 |
| 1 | 0 | -2.47486 | 1.45146 | -3.44205 |
| 1 | 0 | -5.70239 | 0.89045 | -0.65152 |
| 1 | 0 | -4.91977 | 1.3434 | -2.97503 |
| 6 | 0 | -0.75821 | -0.86666 | 3.0751 |
| 1 | 0 | 0.28709 | -0.5384 | 3.02449 |
| 1 | 0 | -1.29149 | -0.11373 | 3.67168 |
| 6 | 0 | -0.83932 | -2.21972 | 3.78991 |
| 1 | 0 | -0.197 | -2.97084 | 3.31723 |
| 1 | 0 | -0.51513 | -2.12488 | 4.8324 |
| 1 | 0 | -1.8654 | -2.60878 | 3.792 |
| 1 | 0 | -2.41558 | -1.16709 | 1.7422 |
| 6 | 0 | 1.64868 | -2.12893 | 0.007 |
| 8 | 0 | 1.65266 | -3.35997 | -0.04597 |



**TS2-D-12a**

E(B3LYP/BS1) = -1427.146797
H(correction) = 0.45010973
G(correction) = 0.35882573
E(M06/BS2) = -1427.768546
Imaginary frequencies: -1331.74

| | | | | |
|---|---|---|---|---|
| 46 | 0 | 1.04991 | -0.80528 | 0.06337 |
| 7 | 0 | 0.96137 | 1.06151 | -0.57507 |
| 7 | 0 | 3.07245 | -0.45718 | -0.26566 |
| 8 | 0 | 1.39135 | -2.78676 | 0.6591 |
| 6 | 0 | -0.28036 | 1.79476 | -0.52066 |
| 6 | 0 | 3.31709 | 0.80937 | -0.66481 |
| 6 | 0 | 4.08098 | -1.32421 | -0.10027 |
| 6 | 0 | 0.37356 | -3.53871 | 0.5523 |
| 6 | 0 | -1.41803 | 0.74471 | -0.47788 |
| 1 | 0 | -0.40035 | 2.40975 | -1.42097 |
| 6 | 0 | -0.2699 | 2.78382 | 0.6553 |
| 6 | 0 | 4.61067 | 1.25325 | -0.91286 |
| 1 | 0 | 3.79887 | -2.31922 | 0.22732 |
| 6 | 0 | 5.40163 | -0.94771 | -0.3377 |
| 8 | 0 | -0.76976 | -3.11182 | 0.204 |
| 6 | 0 | 0.52122 | -5.00946 | 0.86128 |
| 6 | 0 | -1.14988 | -0.45601 | 0.47348 |
| 6 | 0 | -2.80819 | 1.39183 | -0.24093 |
| 1 | 0 | -1.43428 | 0.32255 | -1.49118 |
| 8 | 0 | 0.3723 | 2.67679 | 1.67627 |
| 8 | 0 | -1.09566 | 3.82201 | 0.40164 |
| 6 | 0 | 5.66897 | 0.36023 | -0.74946 |
| 1 | 0 | 4.74284 | 2.28479 | -1.2206 |
| 1 | 0 | 6.19928 | -1.66972 | -0.19763 |
| 1 | 0 | -0.67921 | -1.77519 | 0.13789 |
| 1 | 0 | 1.55299 | -5.2544 | 1.11699 |
| 1 | 0 | -0.14065 | -5.26804 | 1.69416 |
| 1 | 0 | 0.19855 | -5.59473 | -0.0054 |
| 1 | 0 | -2.03049 | -1.09616 | 0.30208 |
| 1 | 0 | -2.86295 | 1.79965 | 0.77376 |
| 1 | 0 | -2.90284 | 2.25156 | -0.91513 |
| 6 | 0 | -3.94978 | 0.42718 | -0.47268 |
| 6 | 0 | -1.1691 | 4.81246 | 1.44018 |
| 1 | 0 | 6.6905 | 0.67806 | -0.9375 |
| 6 | 0 | -4.68404 | -0.10371 | 0.59552 |
| 6 | 0 | -4.27767 | 0.01756 | -1.77377 |
| 1 | 0 | -1.52565 | 4.36577 | 2.37314 |
| 1 | 0 | -1.87161 | 5.56484 | 1.08001 |
| 1 | 0 | -0.18394 | 5.25414 | 1.61325 |
| 6 | 0 | -5.71489 | -1.02013 | 0.37423 |
| 1 | 0 | -4.44636 | 0.20529 | 1.61078 |
| 6 | 0 | -5.30581 | -0.8969 | -2.00077 |
| 1 | 0 | -3.7209 | 0.42417 | -2.61568 |
| 6 | 0 | -6.02874 | -1.4204 | -0.92527 |
| 1 | 0 | -6.27178 | -1.41969 | 1.21785 |
| 1 | 0 | -5.54554 | -1.1992 | -3.01698 |
| 1 | 0 | -6.83045 | -2.13278 | -1.10034 |
| 6 | 0 | -1.13087 | -0.18446 | 1.98561 |
| 1 | 0 | -2.08923 | 0.23485 | 2.32248 |
| 1 | 0 | -0.98697 | -1.12783 | 2.52489 |
| 1 | 0 | -0.34325 | 0.50846 | 2.28503 |
| 6 | 0 | 2.11803 | 1.71776 | -0.79957 |
| 8 | 0 | 2.24196 | 2.91204 | -1.08552 |

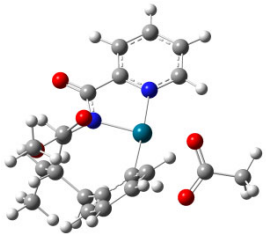


**TS2-E-12a**

E(B3LYP/BS1) = -1427.144512
H(correction) = 0.45004412
G(correction) = 0.3591591
E(M06/BS2) = -1427.764177
Imaginary frequencies: -1333.41

| | | | | |
|---|---|---|---|---|
| 46 | 0 | 1.46511 | -0.4099 | -0.32184 |
| 7 | 0 | 0.10126 | 0.96952 | 0.01219 |
| 7 | 0 | 2.63523 | 1.29393 | -0.51863 |
| 8 | 0 | 3.06056 | -1.74687 | -0.58782 |
| 6 | 0 | -1.18019 | 0.49109 | 0.4765 |
| 6 | 0 | 1.95347 | 2.41954 | -0.21161 |
| 6 | 0 | 3.9311 | 1.35374 | -0.85455 |
| 6 | 0 | 2.92403 | -2.7887 | 0.13058 |
| 6 | 0 | -1.45172 | -0.78825 | -0.34649 |
| 1 | 0 | -1.96255 | 1.23624 | 0.3049 |
| 6 | 0 | -1.11489 | 0.19377 | 1.97996 |
| 6 | 0 | 2.56845 | 3.66559 | -0.23423 |
| 1 | 0 | 4.40711 | 0.40265 | -1.06971 |
| 6 | 0 | 4.60598 | 2.57184 | -0.90967 |
| 8 | 0 | 1.87487 | -3.04149 | 0.79745 |
| 6 | 0 | 4.05581 | -3.78832 | 0.1745 |
| 6 | 0 | -0.31635 | -1.85314 | -0.20635 |
| 6 | 0 | -2.84528 | -1.40772 | -0.06097 |
| 1 | 0 | -1.45112 | -0.44597 | -1.38923 |
| 8 | 0 | -0.13115 | -0.18868 | 2.57513 |
| 8 | 0 | -2.31647 | 0.37272 | 2.57323 |
| 6 | 0 | 3.9134 | 3.74359 | -0.59472 |
| 1 | 0 | 1.97348 | 4.53086 | 0.03722 |
| 1 | 0 | 5.65375 | 2.59325 | -1.19047 |
| 1 | 0 | 0.95171 | -2.09675 | 0.41351 |
| 1 | 0 | 4.94057 | -3.40118 | -0.33299 |
| 1 | 0 | 4.28898 | -4.02939 | 1.21565 |
| 1 | 0 | 3.73012 | -4.71457 | -0.31127 |

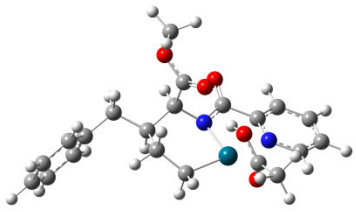
| | | | | |
|---|---|---|---|---|
| 1 | 0 | -2.88404 | -2.40095 | -0.52138 |
| 1 | 0 | -2.96473 | -1.55917 | 1.01769 |
| 6 | 0 | -3.98168 | -0.56811 | -0.60708 |
| 6 | 0 | -2.35647 | 0.0767 | 3.98103 |
| 1 | 0 | 4.41914 | 4.70438 | -0.62613 |
| 6 | 0 | -4.35359 | -0.68852 | -1.95385 |
| 6 | 0 | -4.65487 | 0.36709 | 0.19063 |
| 1 | 0 | -2.08441 | -0.96722 | 4.16115 |
| 1 | 0 | -3.38422 | 0.26752 | 4.2912 |
| 1 | 0 | -1.662 | 0.72304 | 4.52422 |
| 6 | 0 | -5.36977 | 0.10159 | -2.49174 |
| 1 | 0 | -3.84062 | -1.41227 | -2.58464 |
| 6 | 0 | -5.67287 | 1.15971 | -0.34443 |
| 1 | 0 | -4.36563 | 0.48082 | 1.23088 |
| 6 | 0 | -6.03444 | 1.02999 | -1.68657 |
| 1 | 0 | -5.64499 | -0.00939 | -3.53755 |
| 1 | 0 | -6.18248 | 1.8807 | 0.28971 |
| 1 | 0 | -6.82686 | 1.64648 | -2.10264 |
| 6 | 0 | -0.27307 | -2.79185 | -1.41997 |
| 1 | 0 | -1.2424 | -3.27855 | -1.59184 |
| 1 | 0 | -0.0125 | -2.24333 | -2.33177 |
| 1 | 0 | 0.46793 | -3.58305 | -1.27465 |
| 1 | 0 | -0.57613 | -2.44125 | 0.68945 |
| 6 | 0 | 0.50498 | 2.24378 | 0.19329 |
| 8 | 0 | -0.16412 | 3.18783 | 0.6186 |



**TS2-F-12a**

E(B3LYP/BS1) = -1427.169746
H(correction) = 0.45009785
G(correction) = 0.3621278
E(M06/BS2) = -1427.783464
Imaginary frequencies: -1217.09

| | | | | |
|---|---|---|---|---|
| 46 | 0 | 0.82896 | 0.56579 | -0.11633 |
| 7 | 0 | 0.10687 | -1.3335 | -0.10514 |
| 7 | 0 | 2.60821 | -0.47826 | -0.38281 |
| 6 | 0 | -1.28016 | -1.75535 | -0.06908 |
| 6 | 0 | 2.43666 | -1.81271 | -0.38631 |
| 6 | 0 | 3.83292 | 0.04927 | -0.52801 |
| 6 | 0 | -1.97017 | -1.53728 | 1.30601 |
| 1 | 0 | -1.28259 | -2.84137 | -0.2343 |
| 6 | 0 | -2.04012 | -1.21035 | -1.28053 |
| 6 | 0 | 3.51242 | -2.68313 | -0.53627 |
| 1 | 0 | 3.88484 | 1.13252 | -0.51269 |
| 6 | 0 | 4.95427 | -0.76146 | -0.68575 |
| 6 | 0 | -1.87753 | -0.07644 | 1.82264 |
| 6 | 0 | -1.38847 | -2.52316 | 2.33691 |
| 1 | 0 | -3.03019 | -1.77588 | 1.15693 |
| 8 | 0 | -1.55707 | -0.63001 | -2.22591 |
| 8 | 0 | -3.35069 | -1.55533 | -1.21427 |
| 6 | 0 | 4.79029 | -2.14923 | -0.68859 |
| 1 | 0 | 3.30697 | -3.7476 | -0.5325 |
| 1 | 0 | 5.93295 | -0.30798 | -0.80373 |
| 1 | 0 | -0.87652 | 0.08822 | 2.23801 |
| 1 | 0 | -2.596 | 0.04738 | 2.64093 |
| 6 | 0 | -2.14183 | 0.93968 | 0.74434 |
| 1 | 0 | -0.31593 | -2.31785 | 2.45175 |
| 1 | 0 | -1.45839 | -3.53845 | 1.92672 |
| 6 | 0 | -4.14102 | -1.142 | -2.33762 |
| 1 | 0 | 5.64904 | -2.80338 | -0.80958 |
| 6 | 0 | -3.4549 | 1.24072 | 0.36327 |
| 6 | 0 | -1.05906 | 1.55303 | 0.06696 |
| 1 | 0 | -4.11959 | -0.05305 | -2.43468 |
| 1 | 0 | -5.15367 | -1.49106 | -2.12953 |
| 1 | 0 | -3.762 | -1.5889 | -3.26134 |
| 1 | 0 | -4.28444 | 0.777 | 0.89203 |
| 6 | 0 | -3.70745 | 2.10305 | -0.70385 |
| 6 | 0 | -1.34333 | 2.42258 | -1.01242 |
| 6 | 0 | -2.64898 | 2.69166 | -1.40552 |
| 1 | 0 | -4.73441 | 2.32105 | -0.9877 |
| 1 | 0 | -0.5162 | 2.90579 | -1.52698 |
| 1 | 0 | -2.84894 | 3.35911 | -2.2393 |
| 6 | 0 | -2.07668 | -2.48254 | 3.70575 |
| 1 | 0 | -1.688 | -3.27214 | 4.35882 |
| 1 | 0 | -1.91855 | -1.52716 | 4.21857 |
| 1 | 0 | -3.15962 | -2.6339 | 3.60858 |
| 6 | 0 | 1.52889 | 3.2256 | 0.83499 |
| 8 | 0 | 1.87137 | 2.39053 | -0.05951 |
| 6 | 0 | 2.41753 | 4.42472 | 1.07578 |
| 1 | 0 | 1.88737 | 5.32864 | 0.75706 |
| 1 | 0 | 2.61505 | 4.52189 | 2.14727 |
| 1 | 0 | 3.35367 | 4.33452 | 0.52286 |
| 8 | 0 | 0.46888 | 3.12867 | 1.52976 |
| 1 | 0 | -0.24584 | 2.21364 | 0.9267 |
| 6 | 0 | 1.02557 | -2.31999 | -0.24207 |
| 8 | 0 | 0.81876 | -3.54075 | -0.26641 |

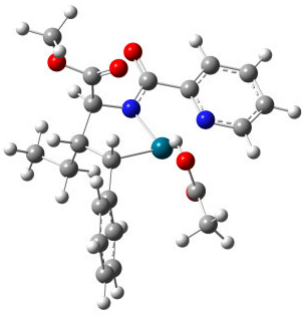


**IM3-A-12a**

E(B3LYP/BS1) = -1427.179146
H(correction) = 0.45558472
G(correction) = 0.36436072
E(M06/BS2) = -1427.799980
Imaginary frequencies: 0

| | | | | |
|---|---|---|---|---|
| 6 | 0 | 1.74814 | 0.98682 | -0.09602 |
| 1 | 0 | 2.68268 | 1.42201 | -0.47995 |
| 1 | 0 | 1.6518 | 1.34379 | 0.93803 |
| 6 | 0 | 1.90963 | -0.54193 | -0.09234 |
| 1 | 0 | 1.90358 | -0.89012 | -1.13457 |
| 6 | 0 | 0.71571 | -1.27516 | 0.57681 |
| 1 | 0 | 0.9704 | -2.33404 | 0.67898 |
| 6 | 0 | 0.5921 | 1.50083 | -0.94014 |
| 1 | 0 | 0.46012 | 2.58174 | -0.8021 |
| 1 | 0 | 0.78582 | 1.31653 | -2.0072 |
| 7 | 0 | -0.50718 | -1.16047 | -0.19238 |
| 46 | 0 | -1.2448 | 0.65099 | -0.71049 |
| 6 | 0 | 0.48199 | -0.73535 | 1.99513 |
| 8 | 0 | -0.23392 | 0.20525 | 2.30105 |
| 8 | 0 | 1.20969 | -1.40629 | 2.90332 |
| 6 | 0 | 3.25351 | -0.973 | 0.54793 |
| 1 | 0 | 3.2637 | -2.06657 | 0.64132 |
| 1 | 0 | 3.31344 | -0.57888 | 1.56933 |
| 6 | 0 | 4.46034 | -0.5261 | -0.24781 |
| 6 | 0 | 5.2772 | 0.52417 | 0.19011 |
| 6 | 0 | 4.77247 | -1.14677 | -1.46633 |
| 6 | 0 | 6.37348 | 0.94644 | -0.56583 |
| 1 | 0 | 5.04976 | 1.01636 | 1.13322 |

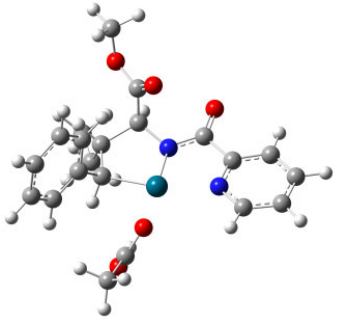
| | | | | |
|---|---|---|---|---|
| 6 | 0 | 5.86552 | -0.72969 | -2.22569 |
| 1 | 0 | 4.15108 | -1.96734 | -1.81919 |
| 6 | 0 | 6.67105 | 0.32079 | -1.77742 |
| 1 | 0 | 6.99427 | 1.76345 | -0.20675 |
| 1 | 0 | 6.09126 | -1.2261 | -3.16607 |
| 1 | 0 | 7.52393 | 0.64645 | -2.36704 |
| 6 | 0 | -2.80247 | -1.8423 | -0.50517 |
| 6 | 0 | -3.76289 | -2.84809 | -0.6058 |
| 7 | 0 | -3.0927 | -0.55379 | -0.77024 |
| 6 | 0 | -5.0506 | -2.50872 | -1.01376 |
| 1 | 0 | -3.47038 | -3.86058 | -0.35168 |
| 6 | 0 | -4.33387 | -0.22277 | -1.15283 |
| 6 | 0 | -5.34495 | -1.17118 | -1.2917 |
| 1 | 0 | -5.81753 | -3.27232 | -1.10947 |
| 1 | 0 | -4.5041 | 0.8325 | -1.3472 |
| 1 | 0 | -6.33739 | -0.86407 | -1.6059 |
| 6 | 0 | -2.066 | 3.21544 | 0.45128 |
| 8 | 0 | -2.13667 | 2.65423 | -0.6499 |
| 8 | 0 | -1.50731 | 2.70252 | 1.53163 |
| 1 | 0 | -1.14031 | 1.78724 | 1.37635 |
| 6 | 0 | -2.6272 | 4.59243 | 0.67658 |
| 1 | 0 | -3.34556 | 4.56802 | 1.50213 |
| 1 | 0 | -1.81787 | 5.27036 | 0.96739 |
| 1 | 0 | -3.10657 | 4.95282 | -0.23361 |
| 6 | 0 | 1.09837 | -0.94347 | 4.26123 |
| 1 | 0 | 1.75867 | -1.58657 | 4.84342 |
| 1 | 0 | 1.40979 | 0.10235 | 4.33641 |
| 1 | 0 | 0.06581 | -1.03309 | 4.60911 |
| 6 | 0 | -1.40959 | -2.15479 | -0.00296 |
| 8 | 0 | -1.20782 | -3.24012 | 0.55942 |



**IM3-B-12a**

E(B3LYP/BS1) = -1427.182161
H(correction) = 0.4555542
G(correction) = 0.3633852
E(M06/BS2) = -1427.803154
Imaginary frequencies: 0

| | | | | |
|---|---|---|---|---|
| 46 | 0 | -0.23275 | -0.71905 | 0.10337 |
| 7 | 0 | -1.43604 | 0.81307 | 0.42256 |
| 7 | 0 | -2.21459 | -1.74749 | 0.22606 |
| 8 | 0 | 1.15255 | -2.38101 | -0.29158 |
| 6 | 0 | -0.85092 | 2.13174 | 0.30187 |
| 6 | 0 | -3.1854 | -0.81261 | 0.3273 |
| 6 | 0 | -2.55414 | -3.04247 | 0.18134 |
| 6 | 0 | 1.82033 | -2.33936 | -1.32897 |
| 6 | 0 | 0.62167 | 1.99508 | 0.77442 |
| 1 | 0 | -1.40586 | 2.86024 | 0.89969 |
| 6 | 0 | -0.89762 | 2.62292 | -1.14755 |
| 6 | 0 | -4.53411 | -1.15765 | 0.37977 |
| 1 | 0 | -1.7309 | -3.74648 | 0.09863 |
| 6 | 0 | -3.88082 | -3.46737 | 0.2375 |
| 8 | 0 | 1.54935 | -1.51579 | -2.33338 |
| 6 | 0 | 3.0468 | -3.1735 | -1.53322 |
| 6 | 0 | 1.20937 | 0.77414 | -0.00079 |
| 8 | 0 | -0.98721 | 1.92745 | -2.13749 |
| 8 | 0 | -0.76397 | 3.96656 | -1.19117 |
| 6 | 0 | -4.88751 | -2.50481 | 0.33738 |
| 1 | 0 | -5.26082 | -0.3557 | 0.44801 |
| 1 | 0 | -4.11238 | -4.52708 | 0.20141 |
| 1 | 0 | 0.78619 | -0.94523 | -2.0627 |
| 1 | 0 | 2.98068 | -4.08293 | -0.93454 |
| 1 | 0 | 3.19973 | -3.40463 | -2.5893 |
| 1 | 0 | 3.8973 | -2.57855 | -1.17647 |
| 6 | 0 | -0.74122 | 4.53816 | -2.50854 |
| 1 | 0 | -5.93157 | -2.8024 | 0.3799 |
| 1 | 0 | 0.09731 | 4.13915 | -3.08752 |
| 1 | 0 | -0.62946 | 5.61313 | -2.36172 |
| 1 | 0 | -1.67219 | 4.3161 | -3.03785 |
| 6 | 0 | 0.71127 | 1.89912 | 2.30744 |
| 1 | 0 | 0.14085 | 1.02496 | 2.64627 |
| 1 | 0 | 1.75781 | 1.71665 | 2.57512 |
| 6 | 0 | 0.23214 | 3.1561 | 3.04318 |
| 1 | 0 | -0.84242 | 3.32601 | 2.91667 |
| 1 | 0 | 0.42304 | 3.06867 | 4.11891 |
| 1 | 0 | 0.75569 | 4.05034 | 2.68215 |
| 1 | 0 | 1.1762 | 2.89741 | 0.47012 |
| 6 | 0 | 2.5972 | 0.31323 | 0.33054 |
| 6 | 0 | 2.90739 | -0.39156 | 1.51001 |
| 6 | 0 | 3.63575 | 0.51245 | -0.59682 |
| 6 | 0 | 4.19683 | -0.85995 | 1.75532 |
| 1 | 0 | 2.11483 | -0.60116 | 2.22154 |
| 6 | 0 | 4.92973 | 0.04368 | -0.35723 |
| 1 | 0 | 3.42027 | 1.03811 | -1.52427 |
| 6 | 0 | 5.21725 | -0.64541 | 0.82293 |
| 1 | 0 | 4.40435 | -1.40539 | 2.67246 |
| 1 | 0 | 5.71102 | 0.21709 | -1.09331 |
| 1 | 0 | 6.22172 | -1.01393 | 1.0138 |
| 1 | 0 | 1.1908 | 1.05196 | -1.06246 |
| 6 | 0 | -2.77107 | 0.64692 | 0.35977 |
| 8 | 0 | -3.62179 | 1.54378 | 0.34313 |

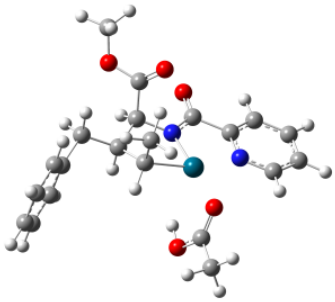


**IM3-C-12a**

E(B3LYP/BS1) = -1427.176783
H(correction) = 0.45539036
G(correction) = 0.36160336
E(M06/BS2) = -1427.798507
Imaginary frequencies: 0

| | | | | |
|---|---|---|---|---|
| 46 | 0 | 0.33424 | 0.78256 | 0.19329 |
| 7 | 0 | 1.25643 | -0.91688 | 0.56633 |
| 7 | 0 | 2.43014 | 1.34209 | -0.30851 |
| 8 | 0 | -0.71632 | 2.65434 | -0.30364 |
| 6 | 0 | 0.43437 | -2.1086 | 0.62918 |
| 6 | 0 | 3.22389 | 0.26369 | -0.13085 |
| 6 | 0 | 2.97612 | 2.50245 | -0.69472 |
| 6 | 0 | -1.3702 | 3.24405 | 0.55746 |
| 6 | 0 | -0.94857 | -1.71508 | 1.21585 |
| 1 | 0 | 0.92291 | -2.87028 | 1.24605 |
| 6 | 0 | 0.28301 | -2.73822 | -0.75744 |

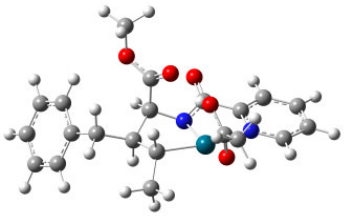
| | | | | |
|---|---|---|---|---|
| 6 | 0 | 4.59968 | 0.32229 | -0.34168 |
| 1 | 0 | 2.28545 | 3.32982 | -0.83098 |
| 6 | 0 | 4.34529 | 2.64364 | -0.91552 |
| 8 | 0 | -1.29468 | 2.94207 | 1.85002 |
| 6 | 0 | -2.35548 | 4.3238 | 0.22976 |
| 6 | 0 | -1.34263 | -0.2369 | 0.85574 |
| 8 | 0 | 0.52572 | -2.2076 | -1.82017 |
| 8 | 0 | -0.21972 | -3.98772 | -0.64604 |
| 6 | 0 | 5.1702 | 1.53131 | -0.73415 |
| 1 | 0 | 5.17457 | -0.58609 | -0.19959 |
| 1 | 0 | 4.74799 | 3.60207 | -1.22721 |
| 1 | 0 | -0.67134 | 2.17764 | 1.93284 |
| 1 | 0 | -2.03916 | 4.84756 | -0.67364 |
| 1 | 0 | -3.3137 | 3.8314 | 0.02349 |
| 1 | 0 | -2.48363 | 5.01581 | 1.06419 |
| 1 | 0 | -1.62969 | 0.25203 | 1.79513 |
| 6 | 0 | -0.46549 | -4.66253 | -1.88978 |
| 1 | 0 | 6.24091 | 1.6067 | -0.90224 |
| 1 | 0 | -1.2064 | -4.1171 | -2.48252 |
| 1 | 0 | -0.8431 | -5.64955 | -1.61997 |
| 1 | 0 | 0.45809 | -4.74689 | -2.46921 |
| 6 | 0 | -2.46164 | -0.02944 | -0.11585 |
| 6 | 0 | -2.4615 | -0.58701 | -1.40872 |
| 6 | 0 | -3.5528 | 0.78448 | 0.24424 |
| 6 | 0 | -3.50713 | -0.33828 | -2.29634 |
| 1 | 0 | -1.6162 | -1.18495 | -1.73105 |
| 6 | 0 | -4.5979 | 1.03851 | -0.64564 |
| 1 | 0 | -3.58002 | 1.21899 | 1.24199 |
| 6 | 0 | -4.58046 | 0.47661 | -1.92387 |
| 1 | 0 | -3.47834 | -0.77604 | -3.29116 |
| 1 | 0 | -5.43234 | 1.66361 | -0.33499 |
| 1 | 0 | -5.39228 | 0.66898 | -2.62025 |
| 6 | 0 | -0.95752 | -1.88962 | 2.74868 |
| 1 | 0 | -0.14152 | -1.28667 | 3.17212 |
| 1 | 0 | -1.89418 | -1.46409 | 3.13376 |
| 6 | 0 | -0.84863 | -3.3411 | 3.22797 |
| 1 | 0 | 0.09845 | -3.80471 | 2.93155 |
| 1 | 0 | -0.91283 | -3.39582 | 4.32086 |
| 1 | 0 | -1.6587 | -3.95204 | 2.81101 |
| 1 | 0 | -1.707 | -2.3925 | 0.80256 |
| 6 | 0 | 2.56277 | -1.04559 | 0.25129 |
| 8 | 0 | 3.20733 | -2.10017 | 0.24206 |



**IM3-D-12a**

E(B3LYP/BS1) = -1427.172037
H(correction) = 0.45530555
G(correction) = 0.36242355
E(M06/BS2) = -1427.796544
Imaginary frequencies: 0

| | | | | |
|---|---|---|---|---|
| 46 | 0 | 0.92968 | -0.77337 | 0.26569 |
| 7 | 0 | 1.0361 | 1.01099 | -0.57541 |
| 7 | 0 | 3.14389 | -0.60494 | -0.13453 |
| 8 | 0 | 0.707 | -2.78765 | 1.1202 |
| 6 | 0 | -0.16215 | 1.82762 | -0.59665 |
| 6 | 0 | 3.39724 | 0.62305 | -0.63842 |
| 6 | 0 | 4.1634 | -1.44757 | 0.07563 |
| 6 | 0 | 0.14146 | -3.63435 | 0.42228 |
| 6 | 0 | -1.34898 | 0.83168 | -0.51938 |
| 1 | 0 | -0.22141 | 2.40381 | -1.52798 |
| 6 | 0 | -0.13083 | 2.86414 | 0.53305 |
| 6 | 0 | 4.69153 | 1.03802 | -0.94639 |
| 1 | 0 | 3.90065 | -2.41664 | 0.49108 |
| 6 | 0 | 5.48486 | -1.10963 | -0.21265 |
| 8 | 0 | -0.2691 | -3.39276 | -0.81549 |
| 6 | 0 | -0.15318 | -5.0253 | 0.90093 |
| 6 | 0 | -1.06022 | -0.31539 | 0.48927 |
| 6 | 0 | -2.72843 | 1.50853 | -0.3371 |
| 1 | 0 | -1.35296 | 0.36129 | -1.51161 |
| 8 | 0 | 0.48409 | 2.77751 | 1.57287 |
| 8 | 0 | -0.91838 | 3.91915 | 0.22228 |
| 6 | 0 | 5.75079 | 0.15835 | -0.7337 |
| 1 | 0 | 4.82306 | 2.04082 | -1.33736 |
| 1 | 0 | 6.28048 | -1.8242 | -0.02734 |
| 1 | 0 | -0.0548 | -2.43922 | -1.01073 |
| 1 | 0 | 0.29601 | -5.18298 | 1.88142 |
| 1 | 0 | -1.23868 | -5.15911 | 0.96337 |
| 1 | 0 | 0.22696 | -5.75661 | 0.18121 |
| 1 | 0 | -1.67335 | -1.18097 | 0.20353 |
| 1 | 0 | -2.78409 | 1.98933 | 0.64502 |
| 1 | 0 | -2.8163 | 2.31781 | -1.07338 |
| 6 | 0 | -3.87852 | 0.53616 | -0.5004 |
| 6 | 0 | -0.98233 | 4.94777 | 1.22244 |
| 1 | 0 | 6.76956 | 0.45576 | -0.96634 |
| 6 | 0 | -4.73549 | 0.2335 | 0.56502 |
| 6 | 0 | -4.10594 | -0.09701 | -1.7321 |
| 1 | 0 | -1.37873 | 4.54857 | 2.1611 |
| 1 | 0 | -1.64781 | 5.71143 | 0.81792 |
| 1 | 0 | 0.013 | 5.36105 | 1.40762 |
| 6 | 0 | -5.77964 | -0.68223 | 0.41353 |
| 1 | 0 | -4.58602 | 0.72402 | 1.5239 |
| 6 | 0 | -5.14601 | -1.0127 | -1.88995 |
| 1 | 0 | -3.46207 | 0.135 | -2.57782 |
| 6 | 0 | -5.98672 | -1.31216 | -0.81426 |
| 1 | 0 | -6.43144 | -0.90062 | 1.25573 |
| 1 | 0 | -5.3041 | -1.48937 | -2.85416 |
| 1 | 0 | -6.79849 | -2.0246 | -0.93529 |
| 6 | 0 | -1.30368 | -0.01545 | 1.96944 |
| 1 | 0 | -2.36904 | 0.18143 | 2.15954 |
| 1 | 0 | -1.0274 | -0.8812 | 2.58319 |
| 1 | 0 | -0.73018 | 0.84548 | 2.32012 |
| 6 | 0 | 2.23008 | 1.57091 | -0.84199 |
| 8 | 0 | 2.4212 | 2.73186 | -1.22444 |

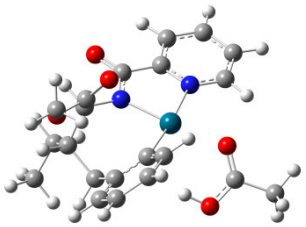


**IM3-E-12a**

E(B3LYP/BS1) = -1427.179631
H(correction) = 0.45526952
G(correction) = 0.36403852
E(M06/BS2) = -1427.798822
Imaginary frequencies: 0

| | | | | |
|---|---|---|---|---|
| 46 | 0 | 1.35386 | -0.50889 | -0.70526 |
| 7 | 0 | 0.1467 | 1.01769 | -0.2766 |
| 7 | 0 | 2.81345 | 1.20838 | -0.64743 |

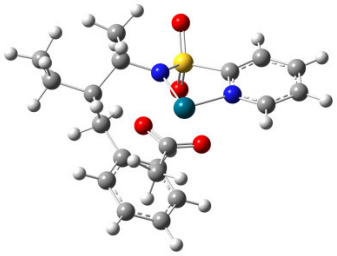
| | | | | |
|---|---|---|---|---|
| 8 | 0 | 2.63449 | -2.29618 | -0.56831 |
| 6 | 0 | -1.12088 | 0.57982 | 0.28822 |
| 6 | 0 | 2.16163 | 2.30999 | -0.21465 |
| 6 | 0 | 4.11205 | 1.30118 | -0.96334 |
| 6 | 0 | 2.70967 | -2.81462 | 0.55213 |
| 6 | 0 | -1.54735 | -0.63272 | -0.57255 |
| 1 | 0 | -1.86967 | 1.37662 | 0.26862 |
| 6 | 0 | -0.91697 | 0.16828 | 1.75395 |
| 6 | 0 | 2.80459 | 3.53849 | -0.07357 |
| 1 | 0 | 4.58569 | 0.38292 | -1.29931 |
| 6 | 0 | 4.82081 | 2.49784 | -0.86806 |
| 8 | 0 | 2.08494 | -2.38659 | 1.63475 |
| 6 | 0 | 3.54891 | -4.03691 | 0.80591 |
| 6 | 0 | -0.36894 | -1.63316 | -0.6683 |
| 6 | 0 | -2.87478 | -1.29256 | -0.11709 |
| 1 | 0 | -1.7091 | -0.21421 | -1.57512 |
| 8 | 0 | 0.04358 | -0.43954 | 2.20104 |
| 8 | 0 | -1.9563 | 0.52197 | 2.52653 |
| 6 | 0 | 4.15212 | 3.63655 | -0.41347 |
| 1 | 0 | 2.22842 | 4.37511 | 0.30574 |
| 1 | 0 | 5.87107 | 2.52904 | -1.1401 |
| 1 | 0 | 1.50404 | -1.59471 | 1.46282 |
| 1 | 0 | 4.08439 | -4.31614 | -0.10152 |
| 1 | 0 | 4.25359 | -3.83925 | 1.61973 |
| 1 | 0 | 2.90176 | -4.86005 | 1.12699 |
| 1 | 0 | -2.9668 | -2.25934 | -0.62493 |
| 1 | 0 | -2.82841 | -1.5125 | 0.95686 |
| 6 | 0 | -4.09527 | -0.45259 | -0.43188 |
| 6 | 0 | -1.85969 | 0.15564 | 3.91546 |
| 1 | 0 | 4.6765 | 4.58373 | -0.32231 |
| 6 | 0 | -4.70036 | -0.54445 | -1.69358 |
| 6 | 0 | -4.62043 | 0.45911 | 0.49432 |
| 1 | 0 | -1.76575 | -0.92888 | 4.01998 |
| 1 | 0 | -2.78263 | 0.51046 | 4.37429 |
| 1 | 0 | -0.99045 | 0.63599 | 4.37182 |
| 6 | 0 | -5.7987 | 0.25004 | -2.02411 |
| 1 | 0 | -4.3041 | -1.24869 | -2.42273 |
| 6 | 0 | -5.71942 | 1.25625 | 0.16712 |
| 1 | 0 | -4.1538 | 0.55228 | 1.47016 |
| 6 | 0 | -6.31316 | 1.15486 | -1.09241 |
| 1 | 0 | -6.25448 | 0.16067 | -3.00705 |
| 1 | 0 | -6.11109 | 1.95856 | 0.89874 |
| 1 | 0 | -7.16898 | 1.77481 | -1.34631 |
| 6 | 0 | -0.44138 | -2.55562 | -1.88111 |
| 1 | 0 | -1.33762 | -3.19622 | -1.85796 |
| 1 | 0 | -0.47299 | -1.98339 | -2.81602 |
| 1 | 0 | 0.42998 | -3.21898 | -1.92201 |
| 1 | 0 | -0.32294 | -2.23289 | 0.2518 |
| 6 | 0 | 0.70531 | 2.15754 | 0.18281 |
| 8 | 0 | 0.15305 | 3.02204 | 0.8739 |



**IM3-F-12a**

E(B3LYP/BS1) = -1427.186343
H(correction) = 0.45555565
G(correction) = 0.36408665
E(M06/BS2) = -1427.805044
Imaginary frequencies: 0

| | | | | |
|---|---|---|---|---|
| 46 | 0 | -0.64643 | 0.45545 | -0.60838 |
| 7 | 0 | -0.1728 | -1.27169 | 0.34879 |
| 7 | 0 | -2.62064 | -0.41498 | -0.34818 |
| 6 | 0 | 1.12235 | -1.50581 | 0.95479 |
| 6 | 0 | -2.54433 | -1.63157 | 0.2246 |
| 6 | 0 | -3.80847 | 0.05516 | -0.7549 |
| 6 | 0 | 2.14043 | -2.08546 | -0.06485 |
| 1 | 0 | 0.98756 | -2.25801 | 1.74616 |
| 6 | 0 | 1.5718 | -0.24638 | 1.70926 |
| 6 | 0 | -3.67454 | -2.42438 | 0.41391 |
| 1 | 0 | -3.79701 | 1.04416 | -1.20334 |
| 6 | 0 | -4.98215 | -0.68021 | -0.60506 |
| 6 | 0 | 2.10407 | -1.31063 | -1.40169 |
| 6 | 0 | 1.85152 | -3.58594 | -0.27341 |
| 1 | 0 | 3.14284 | -1.98346 | 0.36771 |
| 8 | 0 | 0.83805 | 0.64427 | 2.10891 |
| 8 | 0 | 2.88799 | -0.25585 | 1.96089 |
| 6 | 0 | -4.91093 | -1.94294 | -0.01058 |
| 1 | 0 | -3.54542 | -3.38797 | 0.89369 |
| 1 | 0 | -5.92652 | -0.26829 | -0.94591 |
| 1 | 0 | 1.1479 | -1.5141 | -1.89533 |
| 1 | 0 | 2.8891 | -1.70794 | -2.0535 |
| 6 | 0 | 2.30834 | 0.18114 | -1.24666 |
| 1 | 0 | 0.82997 | -3.70437 | -0.65624 |
| 1 | 0 | 1.85988 | -4.08011 | 0.70681 |
| 6 | 0 | 3.41256 | 0.93623 | 2.57323 |
| 1 | 0 | -5.8089 | -2.54004 | 0.12109 |
| 6 | 0 | 3.60981 | 0.68577 | -1.40487 |
| 6 | 0 | 1.26047 | 1.06627 | -0.90855 |
| 1 | 0 | 3.24636 | 1.78947 | 1.91034 |
| 1 | 0 | 4.47942 | 0.75078 | 2.70038 |
| 1 | 0 | 2.93182 | 1.11912 | 3.53782 |
| 1 | 0 | 4.40928 | -0.00699 | -1.6619 |
| 6 | 0 | 3.90112 | 2.03764 | -1.23909 |
| 6 | 0 | 1.56825 | 2.42965 | -0.75703 |
| 6 | 0 | 2.86789 | 2.91721 | -0.91852 |
| 1 | 0 | 4.9183 | 2.39934 | -1.36671 |
| 1 | 0 | 0.79185 | 3.14434 | -0.5116 |
| 1 | 0 | 3.06532 | 3.97972 | -0.79435 |
| 6 | 0 | 2.84425 | -4.29725 | -1.19996 |
| 1 | 0 | 2.65813 | -5.37729 | -1.2109 |
| 1 | 0 | 2.77085 | -3.94277 | -2.23389 |
| 1 | 0 | 3.87851 | -4.14036 | -0.86682 |
| 6 | 0 | -1.63011 | 3.08963 | 0.31501 |
| 8 | 0 | -1.55901 | 2.4926 | -0.7679 |
| 6 | 0 | -2.40732 | 4.36885 | 0.4639 |
| 1 | 0 | -3.13906 | 4.26453 | 1.27127 |
| 1 | 0 | -1.72363 | 5.17665 | 0.74552 |
| 1 | 0 | -2.90652 | 4.61333 | -0.47372 |
| 8 | 0 | -1.04508 | 2.71386 | 1.43647 |
| 1 | 0 | -0.50994 | 1.8762 | 1.35465 |
| 6 | 0 | -1.1877 | -2.08899 | 0.70821 |
| 8 | 0 | -1.10497 | -3.11965 | 1.39083 |

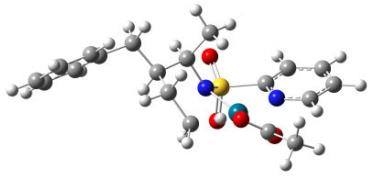


**IM2-14$_{Ph}$**

E(B3LYP/BS1) = -1673.846038
H(correction) = 0.44010549
G(correction) = 0.35354849

E(M06/BS2) = -1674.492436
Imaginary frequencies: 0

| | | | | |
|---|---|---|---|---|
| 6 | 0 | -3.36392 | -2.61989 | -0.57606 |
| 1 | 0 | -3.53208 | -2.6638 | -1.65888 |
| 1 | 0 | -4.28329 | -2.19427 | -0.15096 |
| 6 | 0 | -2.2106 | -1.63534 | -0.26383 |
| 1 | 0 | -2.4643 | -0.69058 | -0.7559 |
| 6 | 0 | -0.86713 | -2.10952 | -0.88277 |
| 1 | 0 | -0.65314 | -3.11551 | -0.50188 |
| 6 | 0 | -3.17537 | -4.04329 | -0.03425 |
| 1 | 0 | -4.07587 | -4.64481 | -0.20246 |
| 1 | 0 | -2.34201 | -4.55958 | -0.52412 |
| 7 | 0 | 0.27307 | -1.25328 | -0.48523 |
| 46 | 0 | 0.33028 | 0.75575 | -0.71811 |
| 6 | 0 | -2.10625 | -1.36766 | 1.27034 |
| 1 | 0 | -1.28107 | -1.93949 | 1.70322 |
| 1 | 0 | -3.02266 | -1.74007 | 1.74784 |
| 6 | 0 | -1.95783 | 0.09651 | 1.64058 |
| 6 | 0 | -2.96385 | 1.0136 | 1.30153 |
| 6 | 0 | -0.83139 | 0.57388 | 2.32677 |
| 6 | 0 | -2.84408 | 2.36673 | 1.61782 |
| 1 | 0 | -3.84762 | 0.66276 | 0.7734 |
| 6 | 0 | -0.70485 | 1.9306 | 2.64033 |
| 1 | 0 | -0.04609 | -0.12432 | 2.59718 |
| 6 | 0 | -1.70656 | 2.83448 | 2.28269 |
| 1 | 0 | -3.64295 | 3.05582 | 1.35241 |
| 1 | 0 | 0.1802 | 2.27921 | 3.16728 |
| 1 | 0 | -1.6092 | 3.88887 | 2.52833 |
| 16 | 0 | 1.43465 | -1.93597 | 0.42242 |
| 8 | 0 | 1.19152 | -1.96653 | 1.88156 |
| 8 | 0 | 1.93444 | -3.18942 | -0.16821 |
| 6 | 0 | 2.7022 | -0.65884 | 0.21483 |
| 6 | 0 | 4.0374 | -0.92703 | 0.48998 |
| 7 | 0 | 2.26949 | 0.55751 | -0.13626 |
| 6 | 0 | 4.94635 | 0.12582 | 0.40717 |
| 1 | 0 | 4.33325 | -1.93734 | 0.75101 |
| 6 | 0 | 3.13808 | 1.583 | -0.21524 |
| 6 | 0 | 4.48893 | 1.40025 | 0.05762 |
| 1 | 0 | 5.99931 | -0.04277 | 0.61172 |
| 1 | 0 | 2.71674 | 2.53927 | -0.50753 |
| 1 | 0 | 5.16728 | 2.24353 | -0.01277 |
| 6 | 0 | -1.10783 | 2.59898 | -1.46377 |
| 8 | 0 | -1.51816 | 1.39121 | -1.50507 |
| 8 | 0 | 0.10388 | 2.80475 | -1.10194 |
| 6 | 0 | -2.02854 | 3.73664 | -1.77973 |
| 1 | 0 | -2.57505 | 3.9919 | -0.86465 |
| 1 | 0 | -1.4595 | 4.60971 | -2.1068 |
| 1 | 0 | -2.75223 | 3.43575 | -2.54114 |
| 6 | 0 | -0.90419 | -2.17855 | -2.41454 |
| 1 | 0 | -1.65788 | -2.88794 | -2.77165 |
| 1 | 0 | -1.13382 | -1.19103 | -2.83238 |
| 1 | 0 | 0.0738 | -2.4959 | -2.78747 |
| 1 | 0 | -2.97373 | -4.04017 | 1.04326 |

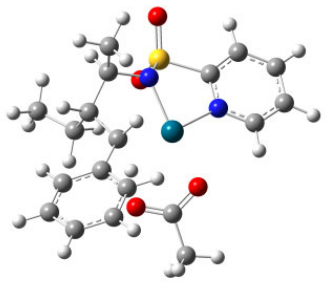


**TS2-A-14$_{Ph}$**

E(B3LYP/BS1) = -1673.798926
H(correction) = 0.43378951
G(correction) = 0.34799151
E(M06/BS2) = -1674.460574

Imaginary frequencies: -1324.48

| | | | | |
|---|---|---|---|---|
| 6 | 0 | 1.95554 | 1.00906 | 0.07293 |
| 1 | 0 | 2.93208 | 1.36126 | -0.28371 |
| 1 | 0 | 1.79932 | 1.50447 | 1.0415 |
| 6 | 0 | 2.07465 | -0.51156 | 0.28217 |
| 1 | 0 | 2.29141 | -0.95973 | -0.6972 |
| 6 | 0 | 0.78161 | -1.21006 | 0.76996 |
| 1 | 0 | 1.01143 | -2.27955 | 0.83569 |
| 6 | 0 | 0.88261 | 1.46293 | -0.92946 |
| 1 | 0 | 1.15738 | 2.4231 | -1.39026 |
| 1 | 0 | 0.81088 | 0.77731 | -1.78035 |
| 7 | 0 | -0.2388 | -1.05903 | -0.2824 |
| 46 | 0 | -1.1804 | 0.73407 | -0.47078 |
| 6 | 0 | 3.26239 | -0.84218 | 1.2221 |
| 1 | 0 | 3.22536 | -1.91249 | 1.46758 |
| 1 | 0 | 3.14352 | -0.30016 | 2.16845 |
| 6 | 0 | 4.61136 | -0.5162 | 0.61804 |
| 6 | 0 | 5.34943 | 0.59863 | 1.03559 |
| 6 | 0 | 5.13891 | -1.3192 | -0.40393 |
| 6 | 0 | 6.57944 | 0.90684 | 0.44911 |
| 1 | 0 | 4.95561 | 1.23074 | 1.82861 |
| 6 | 0 | 6.36648 | -1.01674 | -0.99262 |
| 1 | 0 | 4.57894 | -2.19031 | -0.73786 |
| 6 | 0 | 7.09205 | 0.09969 | -0.56758 |
| 1 | 0 | 7.13636 | 1.77646 | 0.78865 |
| 1 | 0 | 6.75896 | -1.65364 | -1.7812 |
| 1 | 0 | 8.04953 | 0.33599 | -1.02411 |
| 16 | 0 | -1.26008 | -2.28445 | -0.61353 |
| 8 | 0 | -1.51464 | -2.36229 | -2.05649 |
| 8 | 0 | -0.93567 | -3.50672 | 0.13859 |
| 6 | 0 | -2.83179 | -1.65126 | 0.04794 |
| 6 | 0 | -3.84626 | -2.48092 | 0.50748 |
| 7 | 0 | -2.9495 | -0.31631 | -0.0036 |
| 6 | 0 | -5.04203 | -1.88781 | 0.91135 |
| 1 | 0 | -3.67975 | -3.55194 | 0.54435 |
| 6 | 0 | -4.1011 | 0.26113 | 0.37913 |
| 6 | 0 | -5.17396 | -0.49863 | 0.83714 |
| 1 | 0 | -5.86144 | -2.49928 | 1.27789 |
| 1 | 0 | -4.1302 | 1.34255 | 0.30782 |
| 1 | 0 | -6.09109 | -0.00339 | 1.13773 |
| 6 | 0 | -1.6182 | 3.52319 | -0.03089 |
| 8 | 0 | -2.25358 | 2.53651 | -0.52084 |
| 8 | 0 | -0.39156 | 3.46621 | 0.2936 |
| 1 | 0 | 0.0385 | 2.32541 | -0.22 |
| 6 | 0 | -2.34735 | 4.83184 | 0.15551 |
| 1 | 0 | -2.16233 | 5.21354 | 1.1636 |
| 1 | 0 | -1.94367 | 5.56414 | -0.55202 |
| 1 | 0 | -3.4177 | 4.71119 | -0.01713 |
| 6 | 0 | 0.28174 | -0.75071 | 2.14759 |
| 1 | 0 | 1.02834 | -0.93907 | 2.92686 |
| 1 | 0 | 0.0436 | 0.31925 | 2.15029 |
| 1 | 0 | -0.62715 | -1.30211 | 2.41082 |

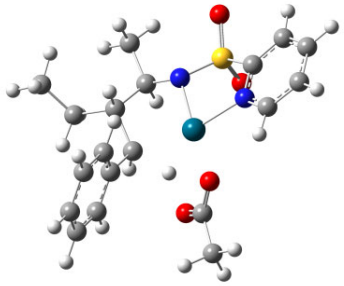


**TS2-B-14$_{Ph}$**

E(B3LYP/BS1) = -1673.799643
H(correction) = 0.43329476

G(correction) = 0.34772276
E(M06/BS2) = -1674.456878
Imaginary frequencies: -1363.47

| | | | | |
|---|---|---|---|---|
| 46 | 0 | 0.34501 | 0.58376 | -0.20915 |
| 7 | 0 | 1.12464 | -1.23788 | -0.62064 |
| 7 | 0 | 2.34352 | 1.19309 | -0.18593 |
| 8 | 0 | -0.39455 | 2.49511 | 0.23157 |
| 6 | 0 | 0.18709 | -2.39443 | -0.6355 |
| 16 | 0 | 2.5312 | -1.45695 | 0.19765 |
| 6 | 0 | 3.22905 | 0.18832 | -0.13498 |
| 6 | 0 | 2.77794 | 2.45616 | -0.32243 |
| 6 | 0 | -1.3509 | 2.42827 | 1.07102 |
| 6 | 0 | -1.14736 | -1.97794 | 0.03743 |
| 8 | 0 | 3.38844 | -2.46017 | -0.45336 |
| 8 | 0 | 2.39401 | -1.54 | 1.66574 |
| 6 | 0 | 4.59855 | 0.38381 | -0.24203 |
| 1 | 0 | 2.00689 | 3.2189 | -0.34641 |
| 6 | 0 | 4.13716 | 2.7433 | -0.42222 |
| 8 | 0 | -1.87793 | 1.3345 | 1.44155 |
| 6 | 0 | -1.91798 | 3.71189 | 1.6245 |
| 6 | 0 | -1.5632 | -0.59021 | -0.49694 |
| 6 | 0 | 5.05815 | 1.6933 | -0.38899 |
| 1 | 0 | 5.26186 | -0.47387 | -0.21582 |
| 1 | 0 | 4.46108 | 3.7728 | -0.53107 |
| 1 | 0 | -1.46972 | 0.41401 | 0.56567 |
| 1 | 0 | -2.89624 | 3.88203 | 1.16073 |
| 1 | 0 | -2.07633 | 3.61118 | 2.70136 |
| 1 | 0 | -1.26199 | 4.55673 | 1.40955 |
| 1 | 0 | 6.12199 | 1.89283 | -0.47686 |
| 6 | 0 | -3.03893 | -0.25836 | -0.56942 |
| 6 | 0 | -4.02129 | -0.98073 | 0.11998 |
| 6 | 0 | -3.4422 | 0.83883 | -1.34959 |
| 6 | 0 | -5.36894 | -0.62667 | 0.01646 |
| 1 | 0 | -3.74286 | -1.82621 | 0.73959 |
| 6 | 0 | -4.78372 | 1.19746 | -1.4472 |
| 1 | 0 | -2.68499 | 1.41718 | -1.87624 |
| 6 | 0 | -5.7574 | 0.46278 | -0.76269 |
| 1 | 0 | -6.11576 | -1.20592 | 0.55339 |
| 1 | 0 | -5.07206 | 2.04722 | -2.06091 |
| 1 | 0 | -6.80587 | 0.73786 | -0.83792 |
| 1 | 0 | -1.21372 | -0.46706 | -1.52928 |
| 1 | 0 | 0.61493 | -3.22028 | -0.05557 |
| 1 | 0 | -1.90903 | -2.71071 | -0.27148 |
| 6 | 0 | 0.02332 | -2.87386 | -2.08098 |
| 1 | 0 | 1.00047 | -3.1515 | -2.48623 |
| 1 | 0 | -0.64162 | -3.74449 | -2.12985 |
| 1 | 0 | -0.393 | -2.08481 | -2.71722 |
| 6 | 0 | -1.04444 | -2.01203 | 1.57881 |
| 1 | 0 | -1.8791 | -1.44433 | 2.00707 |
| 1 | 0 | -0.13068 | -1.48726 | 1.88258 |
| 6 | 0 | -1.03955 | -3.42657 | 2.16589 |
| 1 | 0 | -1.94991 | -3.97609 | 1.8922 |
| 1 | 0 | -0.17968 | -4.00969 | 1.81732 |
| 1 | 0 | -0.98341 | -3.39189 | 3.25926 |

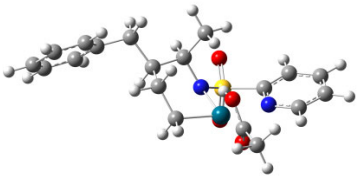


**TS2-C-14$_{Ph}$**

E(B3LYP/BS1) = -1673.797056
H(correction) = 0.43349358
G(correction) = 0.34798658
E(M06/BS2) = -1674.453642
Imaginary frequencies: -1274.10

| | | | | |
|---|---|---|---|---|
| 46 | 0 | 0.25873 | -0.48478 | -0.14806 |
| 7 | 0 | 1.149 | 1.31975 | 0.07088 |
| 7 | 0 | 2.10592 | -1.24573 | 0.44804 |
| 8 | 0 | -0.59301 | -2.39155 | -0.29611 |
| 6 | 0 | 0.32226 | 2.41676 | -0.49725 |
| 16 | 0 | 2.7158 | 1.20619 | -0.46761 |
| 6 | 0 | 3.11103 | -0.36518 | 0.36329 |
| 6 | 0 | 2.32848 | -2.46658 | 0.95973 |
| 6 | 0 | -1.34998 | -2.48031 | -1.32141 |
| 6 | 0 | -1.10037 | 2.09615 | 0.00089 |
| 8 | 0 | 3.60051 | 2.22226 | 0.12517 |
| 8 | 0 | 2.83121 | 0.96047 | -1.9173 |
| 6 | 0 | 4.39656 | -0.64327 | 0.8048 |
| 1 | 0 | 1.46954 | -3.12846 | 0.98687 |
| 6 | 0 | 3.59292 | -2.83409 | 1.41412 |
| 8 | 0 | -1.59335 | -1.50585 | -2.08969 |
| 6 | 0 | -2.03167 | -3.80088 | -1.58611 |
| 6 | 0 | -1.60588 | 0.73622 | -0.57627 |
| 6 | 0 | 4.63748 | -1.90924 | 1.34123 |
| 1 | 0 | 5.16169 | 0.12158 | 0.7303 |
| 1 | 0 | 3.74809 | -3.82673 | 1.82307 |
| 1 | 0 | -1.15458 | -0.36301 | -1.33547 |
| 1 | 0 | -1.52246 | -4.61788 | -1.07208 |
| 1 | 0 | -3.05832 | -3.72691 | -1.20822 |
| 1 | 0 | -2.08059 | -3.98972 | -2.66107 |
| 1 | 0 | -1.94454 | 0.98025 | -1.59662 |
| 1 | 0 | 5.6285 | -2.17112 | 1.6999 |
| 6 | 0 | -2.76778 | 0.14176 | 0.18465 |
| 6 | 0 | -3.9289 | -0.25936 | -0.49327 |
| 6 | 0 | -2.71082 | -0.05412 | 1.57419 |
| 6 | 0 | -5.00044 | -0.83419 | 0.19197 |
| 1 | 0 | -3.98138 | -0.13517 | -1.57135 |
| 6 | 0 | -3.78047 | -0.6249 | 2.26258 |
| 1 | 0 | -1.81358 | 0.22868 | 2.11826 |
| 6 | 0 | -4.93129 | -1.01801 | 1.57436 |
| 1 | 0 | -5.8902 | -1.13506 | -0.3552 |
| 1 | 0 | -3.71313 | -0.76752 | 3.33797 |
| 1 | 0 | -5.76452 | -1.4641 | 2.11068 |
| 1 | 0 | -1.02126 | 2.00418 | 1.09044 |
| 6 | 0 | -2.14828 | 3.19454 | -0.32051 |
| 1 | 0 | -3.10597 | 2.7105 | -0.54638 |
| 1 | 0 | -1.85405 | 3.72208 | -1.23871 |
| 6 | 0 | -2.38686 | 4.19167 | 0.82007 |
| 1 | 0 | -1.4762 | 4.72764 | 1.10333 |
| 1 | 0 | -3.13999 | 4.93614 | 0.53691 |
| 1 | 0 | -2.75397 | 3.66674 | 1.71037 |
| 1 | 0 | 0.32616 | 2.37054 | -1.59884 |
| 6 | 0 | 0.84086 | 3.78943 | -0.05552 |
| 1 | 0 | 1.863 | 3.95396 | -0.40276 |

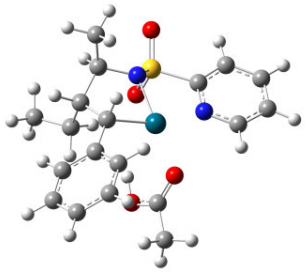
| | | | | |
|---|---|---|---|---|
| 1 | 0 | 0.2115 | 4.58572 | -0.46457 |
| 1 | 0 | 0.84337 | 3.85931 | 1.03726 |



**IM3-A-14$_{Ph}$**

E(B3LYP/BS1) = -1673.827476
H(correction) = 0.43904043
G(correction) = 0.35108843
E(M06/BS2) = -1674.491609
Imaginary frequencies: 0

| | | | | |
|---|---|---|---|---|
| 6 | 0 | 1.88302 | 0.9041 | 0.0749 |
| 1 | 0 | 2.86835 | 1.30775 | -0.20428 |
| 1 | 0 | 1.64603 | 1.36823 | 1.0446 |
| 6 | 0 | 2.04395 | -0.61596 | 0.25711 |
| 1 | 0 | 2.28257 | -1.03512 | -0.73001 |
| 6 | 0 | 0.75409 | -1.34534 | 0.70881 |
| 1 | 0 | 0.99139 | -2.41535 | 0.72183 |
| 6 | 0 | 0.87864 | 1.32938 | -0.99247 |
| 1 | 0 | 0.84905 | 2.42168 | -1.1018 |
| 1 | 0 | 1.12596 | 0.88529 | -1.96339 |
| 7 | 0 | -0.26147 | -1.13887 | -0.33466 |
| 46 | 0 | -1.03203 | 0.72436 | -0.63959 |
| 6 | 0 | 3.22593 | -0.94084 | 1.20525 |
| 1 | 0 | 3.21154 | -2.01697 | 1.42578 |
| 1 | 0 | 3.08176 | -0.42434 | 2.1625 |
| 6 | 0 | 4.57432 | -0.56695 | 0.62833 |
| 6 | 0 | 5.28529 | 0.54633 | 1.09439 |
| 6 | 0 | 5.12931 | -1.32071 | -0.41646 |
| 6 | 0 | 6.51475 | 0.90128 | 0.53367 |
| 1 | 0 | 4.87017 | 1.14017 | 1.90601 |
| 6 | 0 | 6.35634 | -0.97153 | -0.9799 |
| 1 | 0 | 4.59059 | -2.18961 | -0.7886 |
| 6 | 0 | 7.05438 | 0.143 | -0.50628 |
| 1 | 0 | 7.05003 | 1.76893 | 0.91115 |
| 1 | 0 | 6.76986 | -1.57037 | -1.78733 |
| 1 | 0 | 8.0112 | 0.41559 | -0.94362 |
| 16 | 0 | -1.38507 | -2.28596 | -0.60053 |
| 8 | 0 | -1.6804 | -2.38673 | -2.03574 |
| 8 | 0 | -1.12488 | -3.50899 | 0.18 |
| 6 | 0 | -2.91525 | -1.55622 | 0.07866 |
| 6 | 0 | -3.90194 | -2.34395 | 0.6619 |
| 7 | 0 | -3.02884 | -0.23181 | -0.08242 |
| 6 | 0 | -5.07346 | -1.71484 | 1.08242 |
| 1 | 0 | -3.73313 | -3.40879 | 0.77815 |
| 6 | 0 | -4.15846 | 0.36962 | 0.31764 |
| 6 | 0 | -5.20901 | -0.33607 | 0.90091 |
| 1 | 0 | -5.87065 | -2.29027 | 1.54453 |
| 1 | 0 | -4.2027 | 1.44361 | 0.16094 |
| 1 | 0 | -6.10706 | 0.1877 | 1.21169 |
| 6 | 0 | -1.535 | 3.57273 | 0.0738 |
| 8 | 0 | -1.82305 | 2.76684 | -0.81616 |
| 8 | 0 | -0.79469 | 3.25088 | 1.12685 |
| 1 | 0 | -0.53791 | 2.29665 | 1.02161 |
| 6 | 0 | -1.98385 | 5.00383 | 0.05902 |
| 1 | 0 | -2.47458 | 5.25099 | 1.00538 |
| 1 | 0 | -1.10692 | 5.65348 | -0.03559 |
| 1 | 0 | -2.66004 | 5.17128 | -0.77923 |
| 6 | 0 | 0.2522 | -0.96705 | 2.11088 |
| 1 | 0 | 1.00451 | -1.16959 | 2.88125 |
| 1 | 0 | -0.02107 | 0.09378 | 2.16416 |
| 1 | 0 | -0.63984 | -1.55572 | 2.34824 |

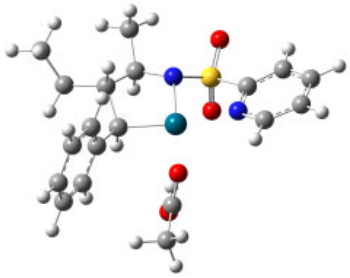


**IM3-B-14$_{Ph}$**

E(B3LYP/BS1) = -1673.833820
H(correction) = 0.43891703
G(correction) = 0.35239103
E(M06/BS2) = -1674.492211
Imaginary frequencies: 0

| | | | | |
|---|---|---|---|---|
| 46 | 0 | 0.17448 | 0.4488 | -0.34459 |
| 7 | 0 | 1.29501 | -1.21771 | -0.62685 |
| 7 | 0 | 2.14903 | 1.42898 | -0.0496 |
| 8 | 0 | -1.03235 | 2.22409 | -0.0061 |
| 6 | 0 | 0.54527 | -2.50898 | -0.67502 |
| 16 | 0 | 2.63603 | -1.19929 | 0.31465 |
| 6 | 0 | 3.13531 | 0.52573 | 0.01975 |
| 6 | 0 | 2.47105 | 2.7245 | -0.18047 |
| 6 | 0 | -1.75663 | 2.23789 | 0.99731 |
| 6 | 0 | -0.88753 | -2.2123 | -0.16292 |
| 8 | 0 | 3.69328 | -2.07181 | -0.22703 |
| 8 | 0 | 2.38187 | -1.29405 | 1.76996 |
| 6 | 0 | 4.48347 | 0.85496 | -0.04822 |
| 1 | 0 | 1.63441 | 3.41392 | -0.24256 |
| 6 | 0 | 3.79531 | 3.15488 | -0.23886 |
| 8 | 0 | -1.7293 | 1.29296 | 1.92166 |
| 6 | 0 | -2.78074 | 3.3028 | 1.23895 |
| 6 | 0 | -1.33505 | -0.89413 | -0.82342 |
| 6 | 0 | 4.81614 | 2.20377 | -0.17645 |
| 1 | 0 | 5.2266 | 0.06614 | -0.0099 |
| 1 | 0 | 4.016 | 4.21242 | -0.33985 |
| 1 | 0 | -1.09296 | 0.59197 | 1.62265 |
| 1 | 0 | -3.73692 | 2.9177 | 0.86358 |
| 1 | 0 | -2.88584 | 3.51304 | 2.30548 |
| 1 | 0 | -2.51974 | 4.20406 | 0.68298 |
| 1 | 0 | 5.85715 | 2.50868 | -0.23136 |
| 6 | 0 | -2.75022 | -0.43183 | -0.68092 |
| 6 | 0 | -3.70705 | -1.05166 | 0.14333 |
| 6 | 0 | -3.17775 | 0.67759 | -1.44183 |
| 6 | 0 | -5.01206 | -0.56133 | 0.23521 |
| 1 | 0 | -3.44481 | -1.93885 | 0.70778 |
| 6 | 0 | -4.47655 | 1.17059 | -1.35066 |
| 1 | 0 | -2.46251 | 1.16409 | -2.10012 |
| 6 | 0 | -5.40353 | 0.55813 | -0.49907 |
| 1 | 0 | -5.7261 | -1.06438 | 0.88239 |
| 1 | 0 | -4.77014 | 2.02792 | -1.95177 |
| 1 | 0 | -6.41896 | 0.93818 | -0.42566 |
| 1 | 0 | -1.10957 | -0.9308 | -1.89655 |
| 1 | 0 | 1.01066 | -3.23927 | -0.0012 |
| 1 | 0 | -1.56283 | -3.02069 | -0.49353 |
| 6 | 0 | 0.61402 | -3.07658 | -2.0947 |
| 1 | 0 | 1.65929 | -3.25007 | -2.36646 |
| 1 | 0 | 0.06841 | -4.02591 | -2.16095 |
| 1 | 0 | 0.18893 | -2.37884 | -2.82399 |
| 6 | 0 | -0.88857 | -2.19369 | 1.38754 |
| 1 | 0 | -1.71044 | -1.57368 | 1.76229 |
| 1 | 0 | 0.03957 | -1.72799 | 1.73729 |
| 6 | 0 | -1.01095 | -3.59384 | 1.99901 |
| 1 | 0 | -1.96402 | -4.06588 | 1.72659 |

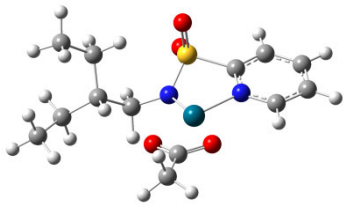
| | | | | |
|---|---|---|---|---|
| 1 | 0 | -0.20518 | -4.25208 | 1.65315 |
| 1 | 0 | -0.95342 | -3.5531 | 3.09224 |



**IM3-C-14$_{Ph}$**

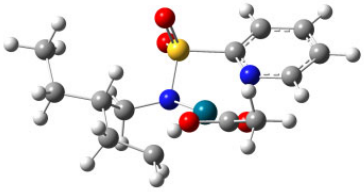
E(B3LYP/BS1) = -1673.837698
H(correction) = 0.43889518
G(correction) = 0.35130518
E(M06/BS2) = -1674.496727
Imaginary frequencies: 0

| | | | | |
|---|---|---|---|---|
| 46 | 0 | 0.18507 | -0.40522 | 0.07275 |
| 7 | 0 | 1.20702 | 1.34725 | 0.11313 |
| 7 | 0 | 2.18268 | -1.29755 | 0.48118 |
| 8 | 0 | -0.9231 | -2.28582 | 0.14027 |
| 6 | 0 | 0.40713 | 2.51727 | -0.34664 |
| 16 | 0 | 2.64693 | 1.10512 | -0.66394 |
| 6 | 0 | 3.1503 | -0.41143 | 0.21637 |
| 6 | 0 | 2.51323 | -2.45622 | 1.06932 |
| 6 | 0 | -1.40374 | -2.71409 | -0.91291 |
| 6 | 0 | -1.02988 | 2.21374 | 0.11732 |
| 8 | 0 | 3.65574 | 2.12863 | -0.33329 |
| 8 | 0 | 2.50438 | 0.73608 | -2.0887 |
| 6 | 0 | 4.48861 | -0.62176 | 0.52468 |
| 1 | 0 | 1.6895 | -3.13394 | 1.27248 |
| 6 | 0 | 3.83076 | -2.76564 | 1.4032 |
| 8 | 0 | -1.14688 | -2.171 | -2.09516 |
| 6 | 0 | -2.3677 | -3.85962 | -0.95487 |
| 6 | 0 | -1.40255 | 0.81078 | -0.40792 |
| 6 | 0 | 4.83219 | -1.83191 | 1.12856 |
| 1 | 0 | 5.21427 | 0.15243 | 0.30181 |
| 1 | 0 | 4.06012 | -3.71497 | 1.87601 |
| 1 | 0 | -0.55077 | -1.39196 | -1.94216 |
| 1 | 0 | -2.19776 | -4.51628 | -0.10042 |
| 1 | 0 | -3.37492 | -3.43382 | -0.87231 |
| 1 | 0 | -2.29208 | -4.40778 | -1.89602 |
| 1 | 0 | -1.40235 | 0.84619 | -1.50779 |
| 1 | 0 | 5.86617 | -2.04119 | 1.38703 |
| 6 | 0 | -2.68852 | 0.23074 | 0.07806 |
| 6 | 0 | -3.60837 | -0.32741 | -0.82815 |
| 6 | 0 | -3.00862 | 0.1821 | 1.44814 |
| 6 | 0 | -4.79285 | -0.92138 | -0.38714 |
| 1 | 0 | -3.38677 | -0.29526 | -1.89253 |
| 6 | 0 | -4.19064 | -0.40729 | 1.89131 |
| 1 | 0 | -2.3093 | 0.59442 | 2.16989 |
| 6 | 0 | -5.08917 | -0.96668 | 0.97715 |
| 1 | 0 | -5.49018 | -1.33619 | -1.1115 |
| 1 | 0 | -4.4117 | -0.43444 | 2.95533 |
| 1 | 0 | -6.01105 | -1.42528 | 1.32444 |
| 1 | 0 | -1.00367 | 2.18628 | 1.2155 |
| 6 | 0 | -2.06126 | 3.28647 | -0.32504 |
| 1 | 0 | -2.97978 | 2.78463 | -0.65314 |
| 1 | 0 | -1.6779 | 3.81856 | -1.2066 |
| 6 | 0 | -2.42477 | 4.28745 | 0.77805 |
| 1 | 0 | -1.5424 | 4.81596 | 1.15392 |
| 1 | 0 | -3.13848 | 5.03718 | 0.41663 |
| 1 | 0 | -2.88588 | 3.76778 | 1.62704 |
| 1 | 0 | 0.39725 | 2.56052 | -1.44879 |
| 6 | 0 | 0.97381 | 3.82938 | 0.20275 |
| 1 | 0 | 2.01026 | 3.96645 | -0.11282 |
| 1 | 0 | 0.38673 | 4.68206 | -0.156 |
| 1 | 0 | 0.94966 | 3.81888 | 1.29816 |



**IM2-XVI**

E(B3LYP/BS1) = -1442.777273
H(correction) = 0.35410173
G(correction) = 0.27481373
E(M06/BS2) = -1443.558260
Imaginary frequencies: 0

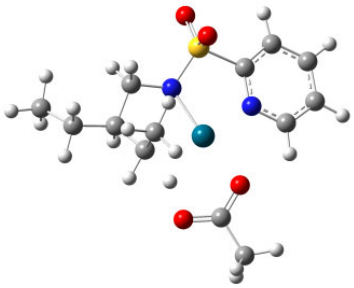


**TS2-A-XVI**

E(B3LYP/BS1) = -1442.739298
H(correction) = 0.34796226
G(correction) = 0.2730703
E(M06/BS2) = -1443.529054
Imaginary frequencies: -1348.21

| | | | | |
|---|---|---|---|---|
| 6 | 0 | 2.65232 | 1.80583 | -0.51977 |
| 1 | 0 | 3.39937 | 2.00136 | -1.30546 |
| 1 | 0 | 2.85688 | 2.52058 | 0.2876 |
| 6 | 0 | 2.87118 | 0.37581 | 0.0107 |
| 6 | 0 | 2.28988 | -0.65893 | -0.97841 |
| 6 | 0 | 1.25708 | 2.07396 | -1.09857 |
| 1 | 0 | 1.15047 | 3.12676 | -1.39669 |
| 1 | 0 | 1.11219 | 1.53652 | -2.04441 |
| 7 | 0 | 0.83529 | -0.86928 | -0.83981 |
| 46 | 0 | -0.40469 | 0.71688 | -0.46892 |
| 16 | 0 | 0.48354 | -2.06707 | 0.2507 |
| 8 | 0 | 0.94532 | -3.38128 | -0.2236 |
| 8 | 0 | 0.75312 | -1.72191 | 1.66111 |
| 6 | 0 | -1.31806 | -2.00981 | 0.06683 |
| 6 | 0 | -2.10191 | -3.14819 | 0.18651 |
| 7 | 0 | -1.82608 | -0.78482 | -0.10751 |
| 6 | 0 | -3.48718 | -2.98674 | 0.13553 |
| 1 | 0 | -1.6237 | -4.11411 | 0.30597 |
| 6 | 0 | -3.15783 | -0.62035 | -0.15224 |
| 6 | 0 | -4.02141 | -1.7065 | -0.02917 |
| 1 | 0 | -4.14219 | -3.84854 | 0.22252 |
| 1 | 0 | -3.50262 | 0.39922 | -0.28457 |
| 1 | 0 | -5.09341 | -1.54558 | -0.06969 |
| 6 | 0 | -1.36687 | 3.18766 | 0.58739 |
| 8 | 0 | -1.83523 | 2.19939 | -0.06063 |
| 8 | 0 | -0.12296 | 3.36979 | 0.77873 |
| 1 | 0 | 0.46252 | 2.5054 | -0.01251 |
| 6 | 0 | -2.32881 | 4.20077 | 1.15949 |
| 1 | 0 | -2.21445 | 4.2243 | 2.24809 |
| 1 | 0 | -2.07285 | 5.19567 | 0.78251 |
| 1 | 0 | -3.35864 | 3.95283 | 0.89926 |
| 1 | 0 | 2.78678 | -1.62932 | -0.87049 |
| 1 | 0 | 2.47524 | -0.33833 | -2.01128 |

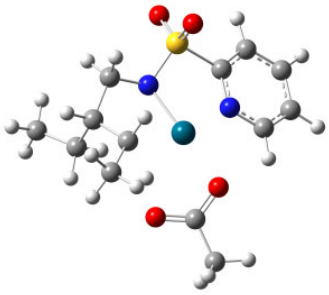
| | | | | |
|---|---|---|---|---|
| 1 | 0 | 2.31629 | 0.26574 | 0.95161 |
| 6 | 0 | 4.36073 | 0.11919 | 0.30227 |
| 1 | 0 | 4.9099 | 0.04921 | -0.64907 |
| 1 | 0 | 4.77005 | 0.99653 | 0.82209 |
| 6 | 0 | 4.61891 | -1.13084 | 1.15296 |
| 1 | 0 | 4.08513 | -1.06783 | 2.10819 |
| 1 | 0 | 4.27951 | -2.04624 | 0.65539 |
| 1 | 0 | 5.6878 | -1.24787 | 1.36534 |



**TS2-D-XVI**

E(B3LYP/BS1) = -1442.737533
H(correction) = 0.34787516
G(correction) = 0.27211216
E(M06/BS2) = -1443.527976
Imaginary frequencies: -1342.99

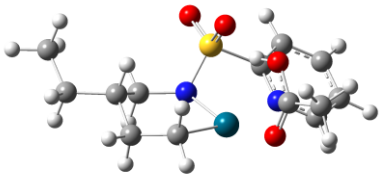
| | | | | |
|---|---|---|---|---|
| 46 | 0 | 0.09124 | 0.63965 | 0.00194 |
| 7 | 0 | 0.21621 | -1.34163 | -0.40809 |
| 7 | 0 | -1.97994 | 0.29895 | -0.11707 |
| 8 | 0 | -0.25474 | 2.69952 | 0.22159 |
| 6 | 0 | 1.53876 | -1.9598 | -0.19967 |
| 16 | 0 | -1.01078 | -2.15348 | 0.34572 |
| 6 | 0 | -2.33791 | -0.99095 | -0.07681 |
| 6 | 0 | -2.91588 | 1.2376 | -0.33159 |
| 6 | 0 | 0.73996 | 3.42562 | -0.08917 |
| 6 | 0 | 2.58594 | -0.88889 | -0.49858 |
| 8 | 0 | -0.91152 | -2.14619 | 1.81893 |
| 8 | 0 | -1.31239 | -3.43412 | -0.31119 |
| 6 | 0 | -3.64236 | -1.42322 | -0.26727 |
| 1 | 0 | -2.55854 | 2.26111 | -0.34801 |
| 6 | 0 | -4.25308 | 0.89393 | -0.51726 |
| 8 | 0 | 1.8732 | 2.94811 | -0.40161 |
| 6 | 0 | 0.57287 | 4.92633 | -0.08558 |
| 6 | 0 | 2.31766 | 0.38699 | 0.3426 |
| 6 | 0 | -4.62033 | -0.45333 | -0.49123 |
| 1 | 0 | -3.85883 | -2.48569 | -0.24619 |
| 1 | 0 | -4.98763 | 1.6739 | -0.6871 |
| 1 | 0 | 1.80141 | 1.62699 | -0.18455 |
| 1 | 0 | 0.79522 | 5.3148 | -1.0846 |
| 1 | 0 | -0.43938 | 5.20722 | 0.20806 |
| 1 | 0 | 1.29888 | 5.367 | 0.60481 |
| 1 | 0 | -5.65495 | -0.74469 | -0.64605 |
| 1 | 0 | 1.66956 | -2.32013 | 0.83165 |
| 1 | 0 | 1.63901 | -2.82016 | -0.86987 |
| 1 | 0 | 3.17712 | 1.044 | 0.12962 |
| 6 | 0 | 2.30133 | 0.21559 | 1.8714 |
| 1 | 0 | 3.27086 | -0.15421 | 2.2327 |
| 1 | 0 | 2.12132 | 1.18176 | 2.35599 |
| 1 | 0 | 1.5293 | -0.47843 | 2.21783 |
| 1 | 0 | 2.47989 | -0.61098 | -1.557 |
| 6 | 0 | 4.02259 | -1.41288 | -0.29094 |
| 1 | 0 | 4.71692 | -0.56972 | -0.41316 |
| 1 | 0 | 4.14074 | -1.7605 | 0.74403 |
| 6 | 0 | 4.42711 | -2.53511 | -1.25537 |
| 1 | 0 | 5.48307 | -2.79892 | -1.12733 |
| 1 | 0 | 3.83898 | -3.44474 | -1.09211 |
| 1 | 0 | 4.28255 | -2.22785 | -2.29859 |



**TS2-E-XVI**

E(B3LYP/BS1) = -1442.738114
H(correction) = 0.34770918
G(correction) = 0.27260818
E(M06/BS2) = -1443.527747
Imaginary frequencies: -1321.82

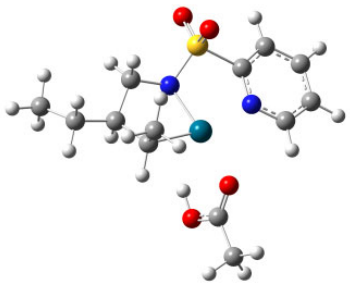
| | | | | |
|---|---|---|---|---|
| 46 | 0 | -0.32195 | 0.44676 | -0.30283 |
| 7 | 0 | 0.36828 | -1.41629 | 0.10183 |
| 7 | 0 | 1.65335 | 1.02986 | 0.06283 |
| 8 | 0 | -1.00283 | 2.43643 | -0.36754 |
| 6 | 0 | -0.53571 | -2.51163 | -0.29838 |
| 16 | 0 | 1.92411 | -1.59627 | -0.42981 |
| 6 | 0 | 2.53664 | 0.02381 | 0.11866 |
| 6 | 0 | 2.05122 | 2.27772 | 0.3609 |
| 6 | 0 | -2.16182 | 2.54176 | 0.14542 |
| 6 | 0 | -1.97626 | -2.03153 | -0.07442 |
| 8 | 0 | 2.05867 | -1.60774 | -1.89858 |
| 8 | 0 | 2.64895 | -2.62452 | 0.3316 |
| 6 | 0 | 3.86151 | 0.20025 | 0.49177 |
| 1 | 0 | 1.28419 | 3.04206 | 0.29862 |
| 6 | 0 | 3.36746 | 2.5468 | 0.72783 |
| 8 | 0 | -2.87824 | 1.54199 | 0.4648 |
| 6 | 0 | -2.72981 | 3.92258 | 0.37179 |
| 6 | 0 | -2.17744 | -0.7293 | -0.88117 |
| 6 | 0 | 4.28274 | 1.49414 | 0.80059 |
| 1 | 0 | 4.51883 | -0.66095 | 0.5413 |
| 1 | 0 | 3.66122 | 3.56484 | 0.96033 |
| 1 | 0 | -2.28684 | 0.47235 | -0.05543 |
| 1 | 0 | -3.58746 | 4.06572 | -0.29423 |
| 1 | 0 | -3.09705 | 4.00167 | 1.39914 |
| 1 | 0 | -1.9813 | 4.69135 | 0.17494 |
| 1 | 0 | 5.31089 | 1.67885 | 1.09736 |
| 1 | 0 | -1.61941 | -0.79148 | -1.82579 |
| 1 | 0 | -0.30566 | -3.40273 | 0.29705 |
| 1 | 0 | -2.64239 | -2.8013 | -0.49916 |
| 6 | 0 | -2.34052 | -1.86969 | 1.41481 |
| 1 | 0 | -3.30793 | -1.35547 | 1.48222 |
| 1 | 0 | -1.60633 | -1.20736 | 1.88918 |
| 6 | 0 | -2.41801 | -3.19282 | 2.18371 |
| 1 | 0 | -3.14402 | -3.87669 | 1.72571 |
| 1 | 0 | -1.44909 | -3.70403 | 2.21064 |
| 1 | 0 | -2.72719 | -3.02378 | 3.22134 |
| 1 | 0 | -0.40932 | -2.77244 | -1.35994 |
| 6 | 0 | -3.64474 | -0.48729 | -1.29717 |
| 1 | 0 | -3.97423 | -1.31876 | -1.93442 |
| 1 | 0 | -4.31733 | -0.42652 | -0.43647 |
| 1 | 0 | -3.75114 | 0.44133 | -1.8662 |



**IM3-A-XVI**

E(B3LYP/BS1) = -1442.771170
H(correction) = 0.35291527
G(correction) = 0.27647427
E(M06/BS2) = -1443.5612
Imaginary frequencies: 0

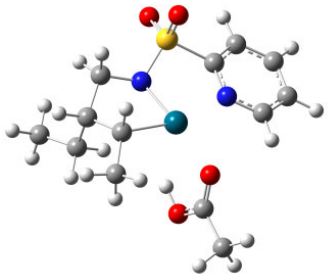
| | | | | |
|---|---|---|---|---|
| 6 | 0 | 2.76829 | 1.53111 | -0.90413 |
| 1 | 0 | 2.84599 | 1.31148 | -1.97902 |
| 1 | 0 | 3.50196 | 2.33003 | -0.70494 |
| 6 | 0 | 3.19068 | 0.28089 | -0.10706 |
| 6 | 0 | 2.41579 | -0.95589 | -0.59824 |
| 6 | 0 | 1.39049 | 2.08753 | -0.57977 |
| 1 | 0 | 1.34513 | 2.43318 | 0.46262 |
| 1 | 0 | 1.12254 | 2.92134 | -1.24266 |
| 7 | 0 | 0.96199 | -0.85566 | -0.47071 |
| 46 | 0 | -0.18572 | 0.83233 | -0.74891 |
| 16 | 0 | 0.25694 | -1.52831 | 0.83586 |
| 8 | 0 | 0.84951 | -2.81805 | 1.22451 |
| 8 | 0 | -0.04548 | -0.57281 | 1.94942 |
| 6 | 0 | -1.36896 | -1.83741 | 0.08984 |
| 6 | 0 | -2.04247 | -3.03565 | 0.28686 |
| 7 | 0 | -1.85548 | -0.81069 | -0.61741 |
| 6 | 0 | -3.30739 | -3.16293 | -0.29016 |
| 1 | 0 | -1.57532 | -3.82499 | 0.86496 |
| 6 | 0 | -3.0693 | -0.93804 | -1.16807 |
| 6 | 0 | -3.83108 | -2.09882 | -1.02703 |
| 1 | 0 | -3.87571 | -4.08049 | -0.16782 |
| 1 | 0 | -3.42525 | -0.08394 | -1.73683 |
| 1 | 0 | -4.80933 | -2.16371 | -1.49198 |
| 6 | 0 | -1.87885 | 2.64266 | 0.8692 |
| 8 | 0 | -1.54634 | 2.51067 | -0.31595 |
| 8 | 0 | -1.52707 | 1.85355 | 1.8656 |
| 1 | 0 | -0.9454 | 1.08176 | 1.61163 |
| 6 | 0 | -2.76193 | 3.77758 | 1.31472 |
| 1 | 0 | -3.64967 | 3.3791 | 1.81604 |
| 1 | 0 | -2.22315 | 4.39055 | 2.04482 |
| 1 | 0 | -3.05078 | 4.38486 | 0.45687 |
| 1 | 0 | 2.75038 | -1.85585 | -0.07228 |
| 1 | 0 | 2.63418 | -1.10518 | -1.66464 |
| 1 | 0 | 2.93637 | 0.43993 | 0.95241 |
| 6 | 0 | 4.71157 | 0.05119 | -0.21319 |
| 1 | 0 | 4.96971 | -0.16249 | -1.26155 |
| 1 | 0 | 5.22076 | 0.99172 | 0.03681 |
| 6 | 0 | 5.25913 | -1.06025 | 0.69203 |
| 1 | 0 | 4.97648 | -0.88679 | 1.7377 |
| 1 | 0 | 4.88336 | -2.04938 | 0.4096 |
| 1 | 0 | 6.35343 | -1.09957 | 0.64262 |



**IM3-D-XVI**

E(B3LYP/BS1) = -1442.764336
H(correction) = 0.35291029
G(correction) = 0.27501329
E(M06/BS2) = -1443.558867
Imaginary frequencies: 0

| | | | | |
|---|---|---|---|---|
| 46 | 0 | 0.21715 | 0.57522 | 0.21952 |
| 7 | 0 | 0.10649 | -1.35283 | -0.39852 |
| 7 | 0 | -2.02466 | 0.4852 | 0.04908 |
| 8 | 0 | 0.47403 | 2.69469 | 0.6524 |
| 6 | 0 | 1.37392 | -2.09382 | -0.20058 |
| 16 | 0 | -1.21875 | -2.09012 | 0.24551 |
| 6 | 0 | -2.4372 | -0.78019 | -0.10251 |
| 6 | 0 | -2.91953 | 1.47157 | -0.10886 |
| 6 | 0 | 0.95613 | 3.39315 | -0.24492 |
| 6 | 0 | 2.48755 | -1.08281 | -0.48052 |
| 8 | 0 | -1.17457 | -2.2287 | 1.71594 |
| 8 | 0 | -1.62675 | -3.27363 | -0.53171 |
| 6 | 0 | -3.74191 | -1.12889 | -0.43189 |
| 1 | 0 | -2.5395 | 2.48053 | 0.02261 |
| 6 | 0 | -4.25431 | 1.22259 | -0.42245 |
| 8 | 0 | 1.26446 | 2.91542 | -1.44279 |
| 6 | 0 | 1.25413 | 4.85315 | -0.07273 |
| 6 | 0 | 2.22231 | 0.18414 | 0.37212 |
| 6 | 0 | -4.66979 | -0.09984 | -0.59167 |
| 1 | 0 | -3.99486 | -2.17511 | -0.56327 |
| 1 | 0 | -4.9468 | 2.05012 | -0.53688 |
| 1 | 0 | 1.05442 | 1.9402 | -1.42885 |
| 1 | 0 | 0.80054 | 5.42626 | -0.88701 |
| 1 | 0 | 0.88121 | 5.19614 | 0.89232 |
| 1 | 0 | 2.33752 | 5.00613 | -0.12754 |
| 1 | 0 | -5.70096 | -0.32546 | -0.84764 |
| 1 | 0 | 1.47009 | -2.47374 | 0.82794 |
| 1 | 0 | 1.40723 | -2.95307 | -0.88041 |
| 1 | 0 | 2.79749 | 1.02891 | -0.03575 |
| 6 | 0 | 2.52114 | 0.05496 | 1.86716 |
| 1 | 0 | 3.59266 | -0.12491 | 2.04274 |
| 1 | 0 | 2.25831 | 0.97683 | 2.39875 |
| 1 | 0 | 1.96693 | -0.76782 | 2.33202 |
| 1 | 0 | 2.39139 | -0.78905 | -1.53662 |
| 6 | 0 | 3.90258 | -1.65963 | -0.28213 |
| 1 | 0 | 4.62415 | -0.83172 | -0.33562 |
| 1 | 0 | 3.98962 | -2.07631 | 0.73001 |
| 6 | 0 | 4.28673 | -2.7304 | -1.31118 |
| 1 | 0 | 5.32153 | -3.06264 | -1.16806 |
| 1 | 0 | 3.64227 | -3.61308 | -1.23461 |
| 1 | 0 | 4.19754 | -2.34294 | -2.33383 |

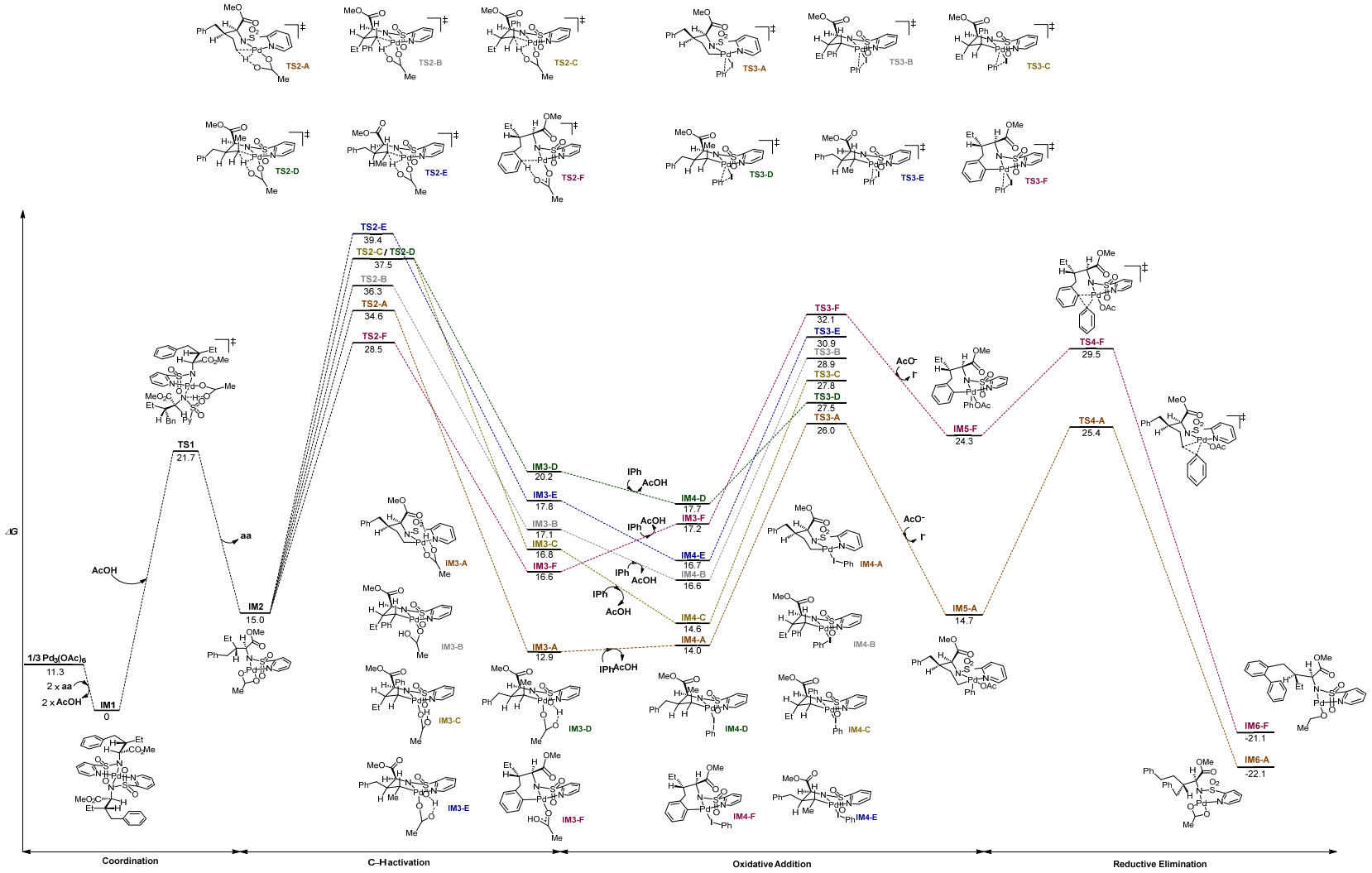


**IM3-E-XVI**

E(B3LYP/BS1) = -1442.766024
H(correction) = 0.35285249
G(correction) = 0.27584949
E(M06/BS2) = -1443.558796
Imaginary frequencies: 0

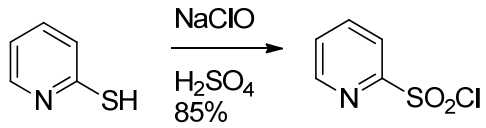
| | | | | |
|---|---|---|---|---|
| 46 | 0 | -0.47805 | 0.27976 | -0.51148 |
| 7 | 0 | 0.511 | -1.40633 | 0.04147 |
| 7 | 0 | 1.53072 | 1.25534 | -0.02853 |
| 8 | 0 | -1.6763 | 2.13442 | -0.75224 |
| 6 | 0 | -0.21062 | -2.64423 | -0.32689 |
| 16 | 0 | 2.09512 | -1.36469 | -0.41244 |
| 6 | 0 | 2.47859 | 0.32613 | 0.15041 |
| 6 | 0 | 1.81495 | 2.5268 | 0.28906 |
| 6 | 0 | -2.37066 | 2.45951 | 0.21502 |
| 6 | 0 | -1.69544 | -2.32934 | -0.10616 |
| 8 | 0 | 2.30999 | -1.36794 | -1.87316 |
| 8 | 0 | 2.91441 | -2.2852 | 0.39528 |
| 6 | 0 | 3.74033 | 0.60472 | 0.66392 |
| 1 | 0 | 1.0151 | 3.2437 | 0.12747 |
| 6 | 0 | 3.05612 | 2.90863 | 0.79495 |
| 8 | 0 | -2.39759 | 1.77359 | 1.35089 |
| 6 | 0 | -3.28163 | 3.65124 | 0.20428 |
| 6 | 0 | -1.98136 | -1.05857 | -0.93846 |
| 6 | 0 | 4.03205 | 1.92907 | 0.99018 |
| 1 | 0 | 4.44809 | -0.20481 | 0.80394 |
| 1 | 0 | 3.24613 | 3.9496 | 1.03527 |
| 1 | 0 | -1.80236 | 0.98241 | 1.23187 |
| 1 | 0 | -4.31869 | 3.29864 | 0.165 |
| 1 | 0 | -3.16389 | 4.22823 | 1.12574 |
| 1 | 0 | -3.07423 | 4.26879 | -0.66969 |
| 1 | 0 | 5.00529 | 2.19307 | 1.39375 |
| 1 | 0 | -1.71582 | -1.27036 | -1.98575 |
| 1 | 0 | 0.14815 | -3.48112 | 0.28325 |
| 1 | 0 | -2.29673 | -3.15815 | -0.52091 |
| 6 | 0 | -2.06552 | -2.19923 | 1.38488 |
| 1 | 0 | -3.10481 | -1.85548 | 1.46212 |
| 1 | 0 | -1.43874 | -1.42246 | 1.84249 |
| 6 | 0 | -1.92192 | -3.50245 | 2.17945 |
| 1 | 0 | -2.51448 | -4.30851 | 1.7283 |
| 1 | 0 | -0.88057 | -3.83817 | 2.22409 |
| 1 | 0 | -2.26834 | -3.37098 | 3.21102 |
| 1 | 0 | -0.05283 | -2.9063 | -1.38414 |
| 6 | 0 | -3.40999 | -0.53136 | -0.89065 |
| 1 | 0 | -4.11906 | -1.32509 | -1.17457 |
| 1 | 0 | -3.70482 | -0.18199 | 0.1046 |
| 1 | 0 | -3.54477 | 0.29752 | -1.59373 |

## 7.4. Energy profile for the activation of ε-C($sp^2$), δ-$CH_3$ and γ-$CH_2$ positions in substrate 12b.



## 8. References


(1) The N-(2-pyridyl)sulfonyl group was prepared in situ by oxidation of the commercial 2-mercaptopyridine with sodium hypochlorite (commercial bleach, see scheme below), following the protocol described by Walsh. See, for instance: Diltz, S.; Aguirre, G.; Ortega, F.; Walsh, P. J. Synthesis of chiral heteroaromatic tetradentate sulfonamide based ligands. *Tetrahedron: Asymmetry* **1997**, *8*, 3559-3562.




(2) Rodríguez, N.; Romero-Revilla, J. A.; Fernández-Ibáñez, M. Á; Carretero, J. C. Palladium-catalyzed *N*-(2-pyridyl)sulfonyl-directed C($sp^3$)–H γ-arylation of amino acid derivatives. *Chem. Sci.* **2013**, *4*, 175-179.

(3) Guin, S.; Dolui, P.; Zhang, X.; Paul, S.; Singh, V. K.; Pradhan, S.; Chandrashekar, H. B.; Anjana, S. S.; Paton, R. S.; Maiti, D. Iterative Arylation of Amino Acids and Aliphatic Amines via δ-C($sp^3$)–H Activation: Experimental and Computational Exploration. *Angew. Chem. Int. Ed.* **2019**, *58*, 5633-5638.

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