SUPPORTING INFORMATION

Oxidized Multiwalled Nanotubes as efficient carbocatalyst for the general synthesis of Azines.

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Summary

1. EXTENDED SYNTHESIS AND CHARACTERIZATION OF ORGANIC COMPOUNDS

1.1 General silane protection procedure (GSP) [1]

In a round-bottom flask, 2.5 mmol of OH-containing aldehyde was dissolved, at 0 °C using an ice bath, in 25 mL of dichloromethane with the help of magnetic stirring. To this solution, 1 equivalent of imidazole was added, and then, in a slow addition, 3.1 mmol of the corresponding silyl chloride (triisopropylsilyl chloride or *tert*-butyldiphenylsilyl chloride). Then, the ice bath was removed allowing the reaction to reach room temperature, and it was sustained at these conditions for 16 h. After this time, solvent was removed under reduced pressure and the organic residue was then purified by flash column chromatography.

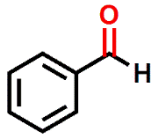
1.2 General silane deprotection procedure (GSD) [2]

In a 19 mL glass vial, 0.125 mmol of protected silane azine was dissolved in 4 mL of tetrahydrofuran (THF) with the help of magnetic stirring at room temperature. Then, 0.275 mL (2.2 equivalents) of 1M solution of tetrabutylammonium fluoride in THF was added. Reaction was sustained at room temperature for 1.5 h. After this time (completion of reaction was monitored by TLC), the reaction mixture was quenched with saturated $NaHCO_3$ solution and extracted 3 times with Et_2O. Drying with $MgSO_4$ and removal of the solvent under vacuum yielded the alcohol.

1.3 Characterization of compounds

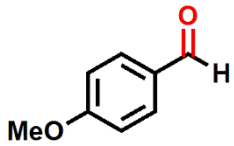
All the experimental data of known compounds have been checked with commercial references or are in agreement with reported spectroscopic data. [3],[4]

Benzaldehyde (1a): Prepared according to the catalytic benzyl alcohol oxidation procedure in 82% conversion (not isolated).



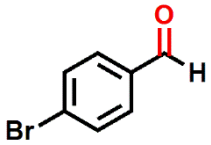
^{1}H-NMR (300 MHz, $CDCl_3$): δ 9.99 (s, 1H), 7.88 (d, *J* = 7.9 Hz, 2H), 7.68-7-60 (m, 1H), 7.55-7.50 (m, 2H). [3a]

***p*-anisaldehyde (1e)**: Prepared according to the catalytic benzyl alcohol oxidation in 86% conversion (not isolated).



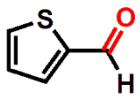
^{1}H-NMR (300 MHz, $CDCl_3$): δ 9.88 (s, 1H), 7.83 (d, *J* = 7.8 Hz, 2H), 7.00 (d, *J* = 7.9 Hz, 2H) 3.89 (s, 3H). [3a]

4-bromobenzaldehyde (1h): Prepared according to the catalytic benzyl alcohol oxidation procedure in 84% conversion (not isolated).



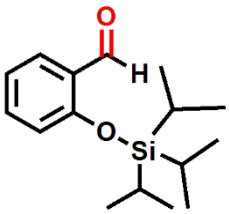
^{1}H-NMR (300 MHz, $CDCl_3$): δ 9.96 (s, 1H), 7.80-7.73 (m, 4H). [3b]

Thiophene-2-carbaldehyde (1k): Prepared according to the catalytic benzyl alcohol oxidation in 77% conversion (not isolated).



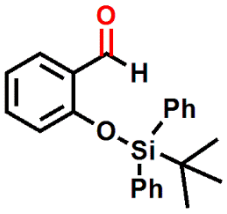
^{1}H-NMR (300 MHz, $CDCl_3$): δ 9.94 (s, 1H), 7.75-7.72 (m, 2H), 7.20-7.16 (m, 1H). [3c]

2-((triisopropylsilyl)oxy)benzaldehyde (1n): Prepared according to the **GSP** procedure. After purification by flash column chromatography (Cyclohexane (Cy) : Ethyl acetate (EtOAc) = 95 : 5), a colourless oil was yielded (quantitative yield).



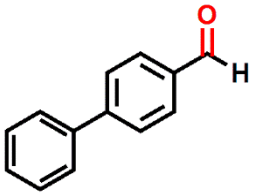
^{1}H-NMR (300 MHz, $CDCl_3$): δ 10.54 (s, 1H), 7.86 – 7.72 (m, 1H), 7.39 (ddt, *J* = 7.2 Hz, 5.2 Hz, 2.6 Hz, 1H), 6.96 (dd, *J* = 9.6 Hz, 5.5 Hz Hz, 1H), 6.87 (dt, *J* = 13.7 Hz, 4.3 Hz, 1H), 1.36 (m, 3H), 1.10 (d, *J* = 7.1 Hz, 18H). [3b]

2-((tert-butyldiphenylsilyl)oxy)benzaldehyde (1o): Prepared according to the **GSP** procedure. After purification by flash column chromatography (Cy : EtOAc = 95 : 5), a white solid was yielded (quantitative yield).



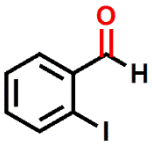
^{1}H-NMR (300 MHz, $CDCl_3$): δ 10.85 (s, 1H), 7.87 (dd, *J* = 7.8 Hz, 1.9 Hz, 1H), 7.81 – 7.74 (m, 4H), 7.52 – 7.37 (m, 6H), 7.14 (ddd, *J* = 8.3 Hz, 7.3 Hz, 1.9 Hz, 1H), 6.94 (t, *J* = 10.9 Hz, 1H), 6.55 (d, *J* = 8.4 Hz, 1H), 1.16 (s, 9H). [3b]

[1,1'-biphenyl]-4-carbaldehyde (1q): Prepared according to the catalytic benzyl alcohol oxidation procedure in 66% conversion (not isolated).



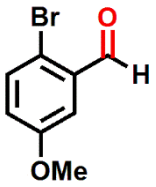
^{1}H-NMR (300 MHz, $CDCl_3$): δ 10.04 (s, 1H), 7.94 (d, *J* = 8.1 Hz, 2H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.66-7.63 (m, 2H), 7.54-7.50 (m, 2H), 7.45-7.42 (m, 1H). [3a]

2-iodobenzaldehyde (1r): Prepared according to the catalytic benzyl alcohol oxidation procedure in 79% conversion (not isolated).



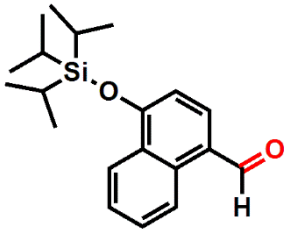
^{1}H-NMR (300 MHz, $CDCl_3$): δ 10.06 (s, 1H), 7.96 (d, *J* = 7.9 Hz, 1H), 7.87 (dd, *J* = 7.8 Hz, 1.7 Hz, 1H), 7.28-7.25 (m, 2H). [3b]

2-bromo-5-methoxy-benzaldehyde (1s): Prepared according to the catalytic benzyl alcohol oxidation procedure in 66% conversion (not isolated).



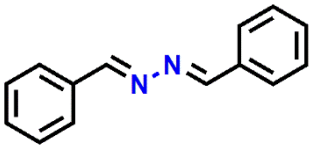
^{1}H-NMR (300 MHz, $CDCl_3$): δ 10.31 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 3.0 Hz, 1H), 7.03 (dd, *J* = 8.0, 3.0 Hz, 1H), 3.85 (s, 3H). [3d]

4-((triisopropylsilyl)oxy)-1-naphthaldehyde (1t): Prepared according to the **GSP** procedure. After purification by flash column chromatography (Cy : EtOAc = 90 : 10), a green solid was yielded (quantitative yield).



^{1}H-NMR (300 MHz, $CDCl_3$): δ 10.19 (s 1H), 9.31 (d, *J* = 8.5 Hz, 1H), 8.35 (d, *J* = 7.6 Hz, 1H), 7.84 (t, *J* = 11.5 Hz, 1H), 7.70 (ddd, *J* = 8.4 Hz, 6.9 Hz, 1.4 Hz, 1H), 7.58 (ddd, *J* = 8.2 Hz, 6.9 Hz, 1.2 Hz, 1H), 6.95 (t, *J* = 9.0 Hz, 1H), 1.61 – 1.30 (m, 3H), 1.10 (d, *J* = 7.2 Hz, 18H). [3b]

(1*E*,2*E*)-1,2-dibenzylidenehydrazine (3a): Prepared according to the general symmetric azine synthesis procedure (or the general one-pot synthesis). **3a** was obtained (48.4 mg, 93% yield) as a pale-yellow solid.

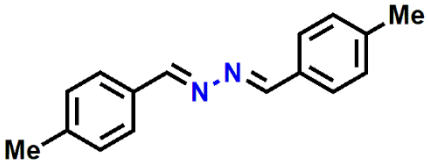


^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.68 (s, 2H), 7.90-7.82 (m, 4H), 7.53-7.46 (m, 6H). [4a]

^{13}C-NMR (75 MHz, $CDCl_3$): δ 162.1, 134.6, 132.1, 129.2, 128.6. [4a]

MS (ESI): (m/z): 209.2 ($M+H^+$).

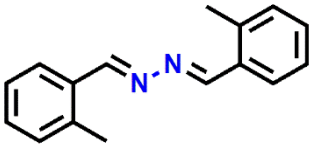
(1*E*,2*E*)-1,2-bis(4-methylbenzylidene)hydrazine (3b): Prepared according to the general symmetric azine synthesis procedure. **3b** was obtained (52.5 mg, 89% yield) as a yellow-green solid.



^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.62 (s, 2H), 7.71 (d, *J* = 8.2 Hz, 4H), 7.29-7.19 (m, 4H), 2.39 (s, 6H). [4a]

MS (ESI): (m/z): 237.2 ($M+H^+$).

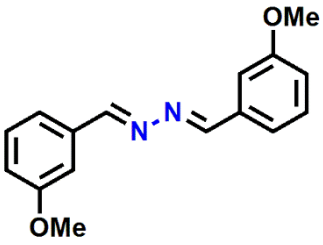
(1*E*,2*E*)-1,2-bis(2-methylbenzylidene)hydrazine (3c): Prepared according to the general symmetric azine synthesis procedure. After purification by flash column chromatography (Cy : EtOAc = 90 : 10), **3c** was obtained (52.4 mg, 89% yield) as a white-yellow solid.



^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.62 (s, 2H), 7.71 (d, *J* = 7.9 Hz, 2H), 7.33-7.27 (m, 6H), 2.49 (s, 6H).[4b]

MS (ESI): (m/z): 237.2 ($M+H^+$).

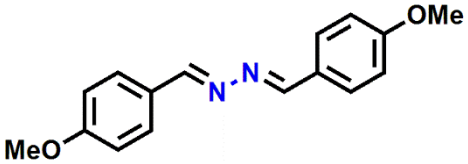
(1*E*,2*E*)-1,2-bis(3-methoxybenzylidene)hydrazine (3d): Prepared according to the general symmetric azine synthesis procedure. After purification by flash column chromatography (Cy : EtOAc = 90 : 10), **3d** was obtained (41 mg, 61% yield) as a yellow solid.



H-NMR (300 MHz, $CDCl_3$): δ 8.59 (s, 2H), 7.45-7.39 (m, 2H), 7.32-7.30 (m, 4H), 7.03-6.97 (m, 2H), 3.84 (s, 6H) [4a].

MS (ESI): (m/z): 269.2 ($M+H^+$).

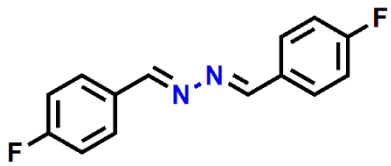
(1*E*,2*E*)-1,2-bis(4-methoxybenzylidene)hydrazine (3e): Prepared according to the general symmetric azine synthesis procedure (or the general one-pot synthesis). **3e** was obtained (61.7 mg, 92% yield) as a yellow-green solid.



^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.56 (s, 2H), 7.74 (d, *J* = 8.1 Hz, 4H), 6.91 (d, *J* = 8.0 Hz, 4H), 3.82 (s, 6H) [4a].

MS (ESI): (m/z): 269.2 ($M+H^+$)

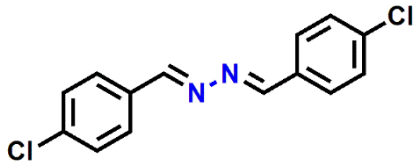
(1*E*,2*E*)-1,2-bis(4-fluorobenzylidene)hydrazine (3f): Prepared according to the general symmetric azine synthesis procedure. **3f** (57.4 mg, 94% yield) was obtained as a yellow solid.



^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.60 (s, 2H), 7.82 (d, *J* = 7.9 Hz, 4H), 7.13 (d, *J* = 8.0 Hz, 4H). [4c]

MS (ESI): (m/z): 245.3 ($M+H^+$).

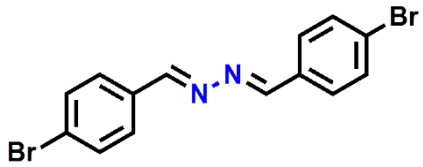
(1*E*,2*E*)-1,2-bis(4-chlorobenzylidene)hydrazine (3g): Prepared according to the general symmetric azine synthesis procedure. **3g** (65.8 mg, 95% yield) was obtained as a yellow solid.



^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.59 (s, 2H), 7.77 (d, *J* = 7.9 Hz, 4H), 7.41 (d, *J* = 8.1 Hz, 4H) [4a].

MS (ESI): (m/z): 278.0 ($M+H^+$).

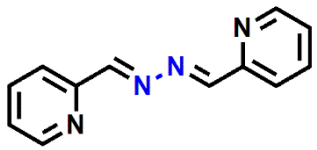
(1*E*,2*E*)-1,2-bis(4-bromobenzylidene)hydrazine (3h): Prepared according to the general symmetric azine synthesis procedure (or the general one-pot synthesis). **3h** was obtained (84 mg, 91% yield) as a yellow solid in 91 % yield.



^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.58 (s, 2H), 7.69 (d, *J* = 7.8 Hz, 4H), 7.57 (d, *J* = 7.9 Hz, 4H) [4a].

MS (ESI): (m/z): 367.1 ($M+H^+$).

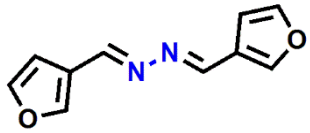
(1*E*,2*E*)-1,2-bis(pyridin-2-ylmethylene)hydrazine (3i): Prepared according to the general symmetric azine synthesis procedure. **3i** was obtained (48.4 mg, 92% yield) as a yellow solid.



^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.69 (d, *J* = 4.7 Hz, 2H), 8.65 (s, 2H), 8.10 (d, *J* = 7.9 Hz, 2H), 7.77 (dd, *J* = 14.5, 5.1 Hz, 4H), 7.38 – 7.30 (m, 2H) [4a].

MS (ESI): (m/z): 211.3 ($M+H^+$).

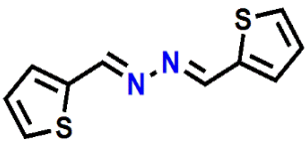
(1*E*,2*E*)-1,2-bis(furan-3-ylmethylene)hydrazine (3j): Prepared according to the general symmetric azine synthesis procedure. **3j** was obtained (41 mg, 87% yield) as a white-yellow solid.



^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.54 (s, 2H), 7.79 (s, 2H), 7.46 (s, 2H), 6.84 (s, 2H). [4d]

MS (ESI): (m/z): 189.2 ($M+H^+$).

(1*E*,2*E*)-1,2-bis(thiophen-2-ylmethylene)hydrazine (3k): Prepared according to the general symmetric azine synthesis procedure (or to the general one-pot procedure). **3k** was obtained (53 mg, 96% yield) as a yellow-brown solid.

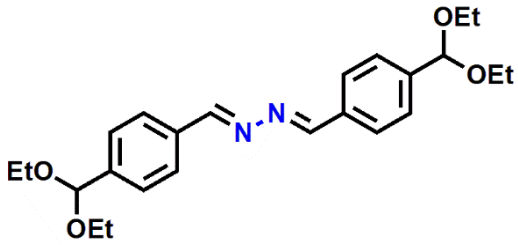


^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.78 (s, 2H), 7.48 (d, *J* = 4.9 Hz, 2H), 7.42 (d, *J* = 2.7 Hz, 2H), 7.12 (dd, *J* = 5.0, 3.7 Hz, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$): 155.9, 149.2, 132.6, 130.2, 127.9.

MS (ESI): (m/z): 221.2 ($M+H^+$).

(1*E*,2*E*)-1,2-bis(4-(diethoxymethyl)benzylidene)hydrazine (3m): Prepared according to the general symmetric azine synthesis procedure. After purification by flash column chromatography (Cy : EtOAc = 90 : 10), **3m** was obtained (72.2 mg, 70% yield) as a yellow solid.

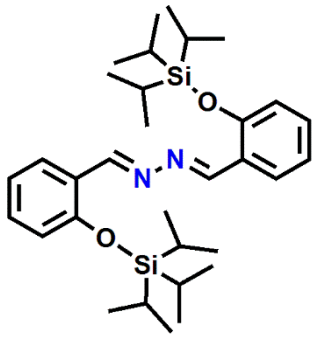


^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.68 (s, 2H), 7.84 (d, *J* = 8.2 Hz, 4H), 7.57 (d, *J* = 8.1 Hz, 4H), 5.55 (s, 2H), 3.59 (m, 8H), 1.25 (dd, *J* = 8.9, 5.2 Hz, 12H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ 161.9, 142.3, 134.1, 128.5, 127.2, 101.1, 61.1, 15.2.

MS (ESI): (m/z): 413.4 ($M+H^+$).

(1*E*,2*E*)-1,2-bis(2-((triisopropylsilyl)oxy)benzylidene)hydrazine (3n): Prepared according to the general symmetric azine synthesis procedure. **3n** was obtained (129 mg, 94% yield) as a yellow solid.

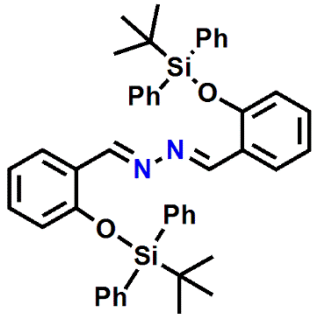


^{1}H-NMR (300 MHz, $CDCl_3$): δ 9.04 (s, 2H), 8.08 (d, *J* = 7.8 Hz, 2H), 6.96 (t, *J* = 7.4 Hz, 2H), 6.83 (d, *J* = 8.2 Hz, 2H), 1.32 (sx, *J* = 7.4 Hz, 6H), 1.10 (d, *J* = 7.3 Hz, 36H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 157.8, 156.3, 132.1, 127.8, 125.1, 121.3, 119.3, 18.2, 13.2.

MS (ESI): (m/z): 553.8 ($M+H^+$).

(1*E*,2*E*)-1,2-bis(2-((tert-butyldiphenylsilyl)oxy)benzylidene)hydrazine (3o): Prepared according to the general symmetric azine synthesis procedure. **3o** was obtained (165 mg, 91% yield) as an orange solid.

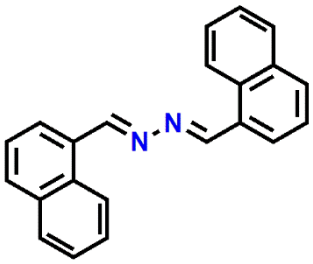


^{1}H-NMR (300 MHz, $CDCl_3$): δ 9.34 (s, 2H), 8-23-8.16 (m, 2H), 7.77-7.70 (m, 8H), 7.42-7.32 (m, 12H), 6.98-6.93 (m, 4H), 6.49-6.44 (m, 2H), 1.13 (s, 18H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 161.9, 159.8, 139.7, 136.5, 135.9, 134.3, 132.1, 131.8, 128.9, 125.5, 123.9, 30.8, 23.9.

MS (ESI): (m/z): 718.1 ($M+H^+$).

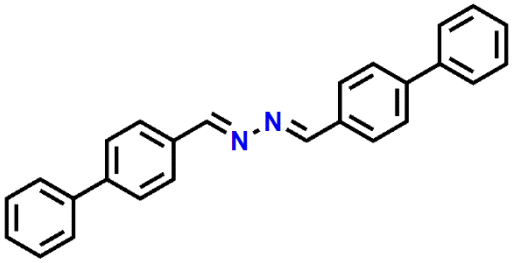
(1*E*,2*E*)-1,2-Bis(naphthalen-1-ylmethylene)hydrazine (3p): Prepared according to the general symmetric azine synthesis procedure. **3p** was obtained (64.6 mg, 84% yield) as a yellow solid.



^{1}H-NMR (300 MHz, $CDCl_3$): δ 9.30 (s, 2H), 9.03-8.97 (m, 2H), 8.20-8.14 (m, 2H), 8.05-7.96(m, 4H), 7.78-7.60 (m, 6H). [4e]

MS (ESI): (m/z): 309.4 ($M+H^+$).

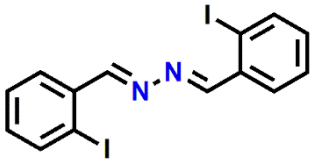
(1*E*,2*E*)-bis([1,1'-biphenyl]-4-ylmethylene)hydrazine (3q): Prepared according to the general symmetric azine synthesis procedure. **3q** was obtained (75.6 mg, 84% yield) as a white-yellow solid.



^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.72 (s, 2H), 7.92 (d, J = 7.9 Hz, 4H), 7.76-7.55 (m, 10 H), 7.50-7.33 (m, 8H).[4f]

MS (ESI): (m/z): 361.5 ($M+H^+$).

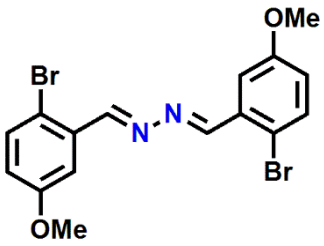
(1*E*,2*E*)-1,2-bis(2-iodobenzylidene)hydrazine (3r): Prepared according to the general one-pot azine synthesis procedure. After purification by flash column chromatography (Cy : EtOAc = 90 : 10), **3r** was obtained (87.4 mg, 76% yield) as a white-yellow solid.



^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.83 (s, 2H), 8.15 (d, *J* = 7.9 Hz, 2H), 7.95-9.77 (m, 6H). [4g]

MS (ESI): (m/z): 461.0 ($M+H^+$).

(1*E*,2*E*)-1,2-bis(2-bromo-5-methoxybenzylidene)hydrazine (3s): Prepared according to the general one-pot azine synthesis procedure. After purification by flash column chromatography (Cy : EtOAc = 95 : 5), **3s** was obtained (50 mg, 47% yield) as an orange solid.

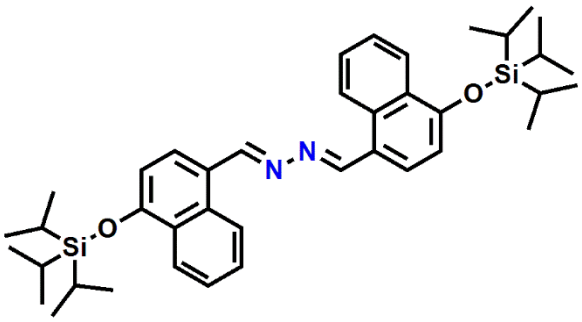


^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.99 (s, 1H), 7.74 (d, *J* = 3.2 Hz, 1H), 7.50 (d, *J* = 8.8 Hz, 1H), 6.92 (dd, *J* = 8.8, 3.2 Hz, 1H), 3.89 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 161.4, 159.0, 133.9, 133.4, 120.4, 116.7, 111.9, 55.7.

MS (ESI): (m/z): 427.0 ($M+H^+$).

(1*E*,2*E*)-1,2-bis((4-((triisopropylsilyl)oxy)naphthalen-1-yl)methylene)hydrazine (3t): Prepared according the general symmetric azine synthesis procedure. **3t** was obtained (142 mg, 97% yield) as a brown solid.

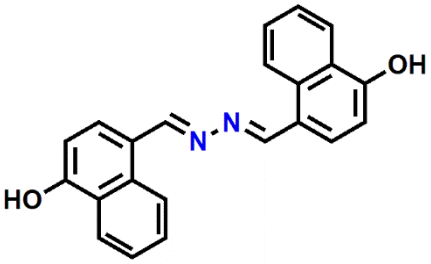


^{1}H NMR (300 MHz, $CDCl_3$) δ 9.37 (s, 2H), 9.01 (t, *J* = 8.0 Hz, 2H), 8.34 (t, *J* = 8.2 Hz, 2H), 7.99 (t, *J* = 8.0 Hz, 2H), 7.63 (dt, *J* = 14.8, J = 7.1 Hz, 4H), 6.99 (d, *J* = 8.0 Hz, 2H), 1.48 (sx, *J* = 7.4 Hz, 6H), 1.20 (d, *J* = 7.3 Hz, 36H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 161.5, 155.3, 133.1, 130.6, 127.9, 127.8, 125.6, 124.7, 123.4, 122.9, 111.9, 18.2, 13.2.

MS (ESI): (m/z): 653.9 ($M+H^+$).

4,4'-((1*E*,1'*E*)-hydrazine-1,2-diylidenebis(methanylylidene))bis(naphthalen-1-ol) (3u):

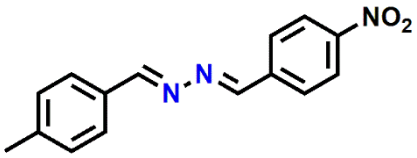


Prepared according the **GSD** procedure to yield a brown solid in quantitative yield.

^{1}H-NMR (300 MHz, DMSO-d_6) δ 10.95 (s, 2H), 9.26 (d, *J* = 8.6 Hz, 2H), 9.20 (s, 2H), 8.23 (d, *J* = 8.1 Hz, 2H), 7.92 (d, *J* = 8.1 Hz, 2H), 7.65 (t, *J* = 7.1 Hz, 2H), 7.59 – 7.49 (m, 2H), 6.97 (d, *J* = 8.0 Hz, 2H). [4k]

MS (ESI): (m/z): 341.4. ($M+H^+$).

(1*E*,2*E*)-1-(4-methylbenzylidene)-2-(4-nitrobenzylidene)hydrazine (5a): Prepared according to the general asymmetric azine synthetic procedure. After purification by flash column chromatography (Cy : EtOAc = 98 : 2), **5a** (58.8 mg, 88% yield) was obtained as a green-yellow solid.

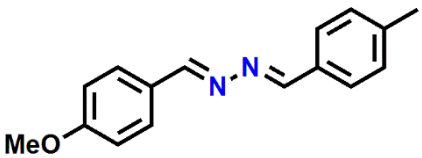


^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.69 (s, 1H), 8.66 (s, 1H), 8.29 (d, *J* = 8.8 Hz, 2H), 8.00 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 2.42 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 163.9, 159.0, 142.5, 140.1, 130.9, 129.7, 129.6, 129.1, 128.9, 128.6 124.0, 21.7.

MS (ESI): (m/z): 268.1 ($M+H^+$).

(1*E*,2*E*)-1-(4-methoxybenzylidene)-2-(4-methylbenzylidene)hydrazine (5b): Prepared according to the general asymmetric azine synthetic procedure. **5b** was obtained (57.4 mg, 91% yield) as a pale-yellow solid.

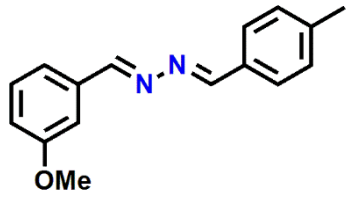


^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.61 (s, 1H), 8.60 (s, 1H), 7.77 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 7.9 Hz, 2H), 7.35-7.36 (m, 2H) 6.93 (d, J = 8.1 Hz, 2H), 3.85 (s, 3H), 2.39 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 162.2, 161.6, 141.7, 141.5, 130.3, 129.6, 128.6, 114.4, 55.5, 21.7.

MS (ESI): (m/z): 253.2 ($M+H^+$).

(1*E*,2*E*)-1-(3-methoxybenzylidene)-2-(4-methylbenzylidene)hydrazine (5c): Prepared according to the general asymmetric azine synthetic procedure. **5c** was obtained (56.7 mg, 90% yield) as a yellow solid.

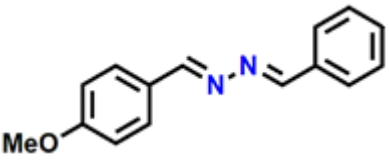


^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.66 (s, 1H), 8.64 (s, 1H), 7.75 (d, J = 8.1 Hz, 2H), 7.46 (dd, J = 4.1, 1.9 Hz, 2H), 7.38 – 7.33 (m, 2H), 7.29 – 7.23 (m, 2H), 7.08 – 6.96 (m, 1H), 3.87 (s, 3H), 2.42 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 162.3, 161.7, 159.9, 141.8, 135.6, 131.4, 129.8, 129.6, 128.6, 121.9, 117.9, 111.9, 55.4, 21.7.

MS (ESI): (m/z): 253.2. ($M+H^+$).

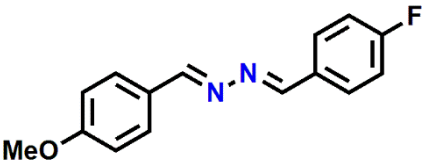
(1*E*,2*E*)-1-benzylidene-2-(4-methoxybenzylidene)hydrazine (5d): Prepared according to the general asymmetric azine synthetic procedure. **5d** was obtained (23.8 mg, 40% yield) as an orange solid.



^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.69 (s, 1H), 8.64 (s, 1H), 7.88 – 7.79 (m, 4H), 7.46 (dt, *J* = 4.1, 2.3 Hz, 3H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H). [4h]

MS (ESI): (m/z): 239.2 ($M+H^+$).

(*1*E,2*E*)-1-(4-fluorobenzylidene)-2-(4-methoxybenzylidene)hydrazine (5e): Prepared according to the general asymmetric azine synthetic procedure. **5e** was obtained (56.3 mg, 88% yield) as a yellow-brown solid.



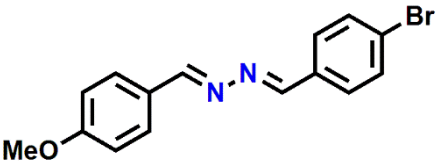
^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.62 (s, 1H), 8.61 (s 1H), 7.89 – 7.69 (m, 4H), 7.17 – 7.05 (m, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 3.84 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 162.21, 162.01, 161.0 (d, *J* = 17.3 Hz), 160.10, 130.62, 130.50, 130.46, 130.34, 130.19, 126.96, 126.72, 116.15 (d, *J* = 4.9 Hz), 115,9 (d, *J* = 4.8 Hz), 114.31, 114.27, 55.41.

^{19}F-NMR (471 MHz, $CDCl_3$) δ -108.55 (s).

MS (ESI): (m/z): 257.1 ($M+H^+$).

(1*E*,2*E*)-1-(4-bromobenzylidene)-2-(4-methoxybenzylidene)hydrazine (5f): Prepared according to the general asymmetric azine synthetic procedure. **5f** was obtained (74.2 mg, 94% yield) as a yellow solid.

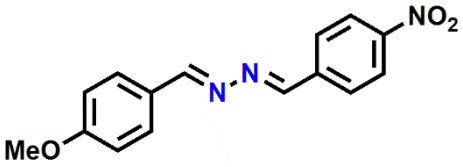


^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.60 (s, 1H), 8.58 (s, 1H), 7.77 (d, *J* = 7.9 Hz, 2H), 7.67 (d, *J* = 7.9 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H) 6.95 (d, *J* = 8.2 Hz, 2H), 3.85 (s, 3H).

^{13}C-NMR (75 MHz,) δ 162.3, 161.2, 160.2, 133.3, 132.1, 130.5, 129.9, 126.7, 125.5, 114.4, 55.5.

MS (ESI): (m/z): 317.1 ($M+H^+$).

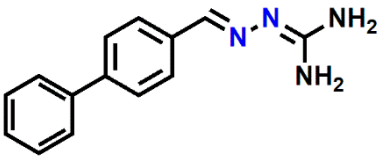
(1*E*,2*E*)-1-(4-methoxybenzylidene)-2-(4-nitrobenzylidene)hydrazine (5g): Prepared according to the general asymmetric azine synthetic procedure. **5g** was obtained (65.1 mg, 92% yield) as a yellow-green solid.



^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.68 (s, 1H), 8.64 (s, 1H), 8.28 (d, *J* = 7.8 Hz, 2H), 7.98 (d, *J* = 7.9 Hz, 2H), 7.80 (d, *J* = 8.1 Hz, 2H) 6.97 (d, *J* = 8.1 Hz, 2H), 3.87 (s, 3H). [4i]

MS (ESI): (m/z): 284.3 ($M+H^+$).

(*E*)-4-([1,1'-Biphenyl]-4-yl)-1,1-diamino-2,3-diazabuta-1,3-diene (5q): Prepared according to the general one-pot azine synthetic procedure, but once the aldehyde was synthetized, amino guanidine was added in the form of 0.5 mL of 1M aqueous NaOH solution. After purification by flash column chromatography (EtOAc : Methanol (MeOH) = 90 : 10), **5q** (54.2 mg, 78% yield) was obtained as a pale-white solid.



^{1}H-NMR (300 MHz, DMSO-d_6): δ 8.64 (s, 1H), 7.99 (s, 1H), 7.72 (d, *J* = 7.9 Hz, 2H), 7.70-7.58 (m, 3H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.37-7.30 (m, 1H), 5.98 (bs, 2H), 5.56 (bs, 2H). [4j]

MS (ESI): (m/z): 239.1 ($M+H^+$).

1.4 NMR spectra section

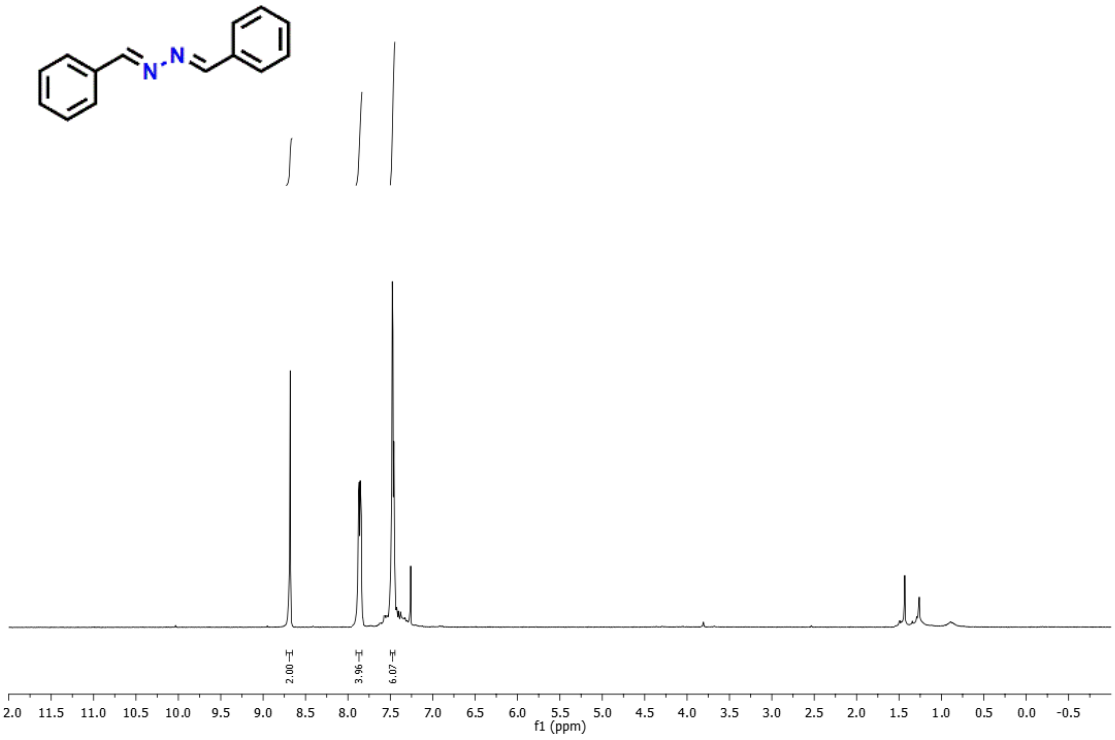


Figure S1. ^{1}H-NMR spectrum (300 MHz, 298K, $CDCl_3$) of **3a**.

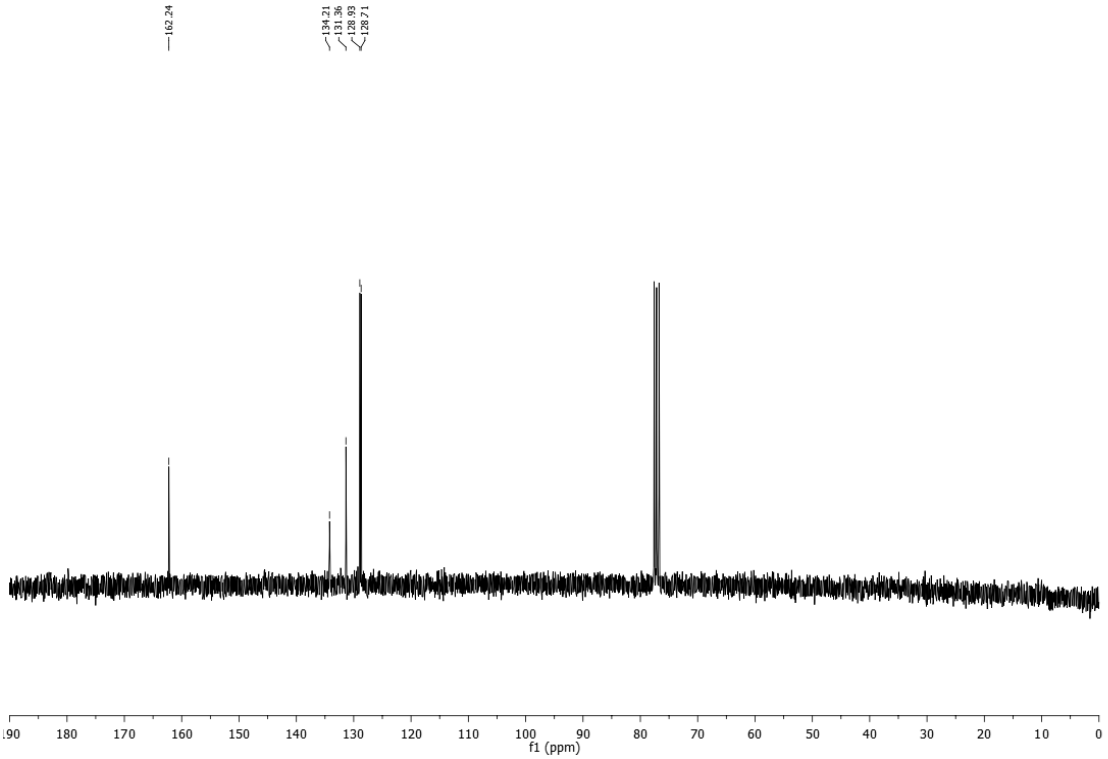


Figure S2. ^{13}C-NMR spectrum (75 MHz, 298K, $CDCl_3$) of **3a**.

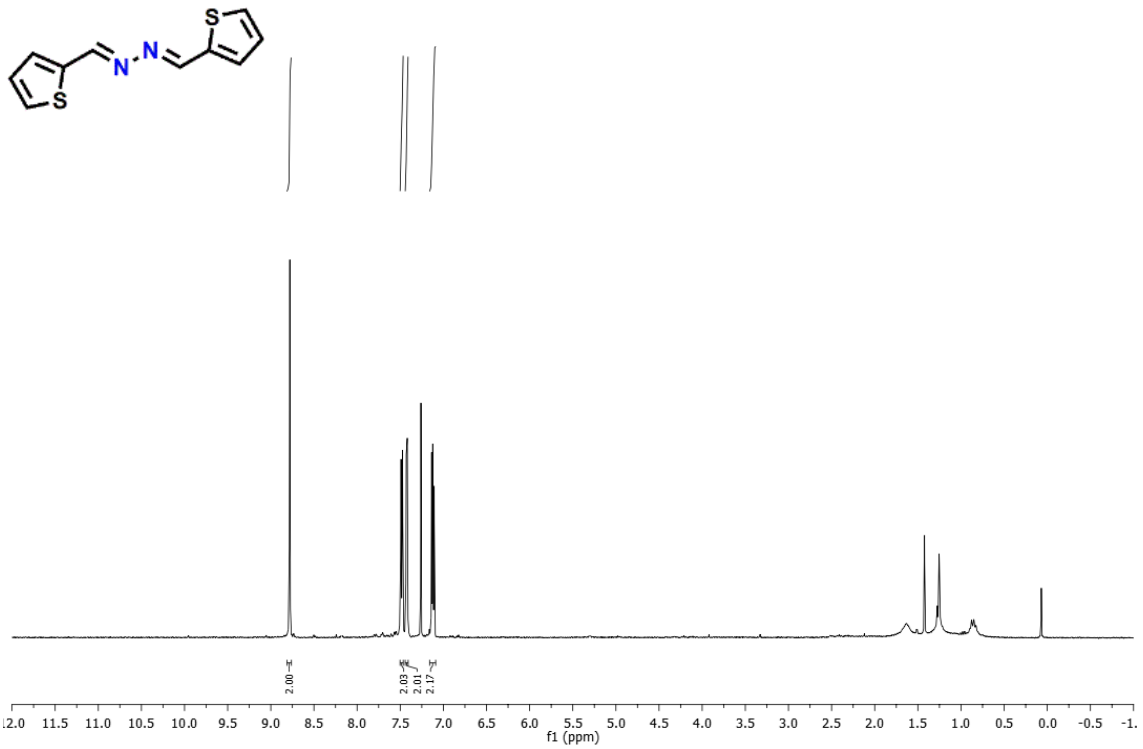


Figure S3. ^{1}H-NMR spectrum (300 MHz, 298K, $CDCl_3$) of **3k**.

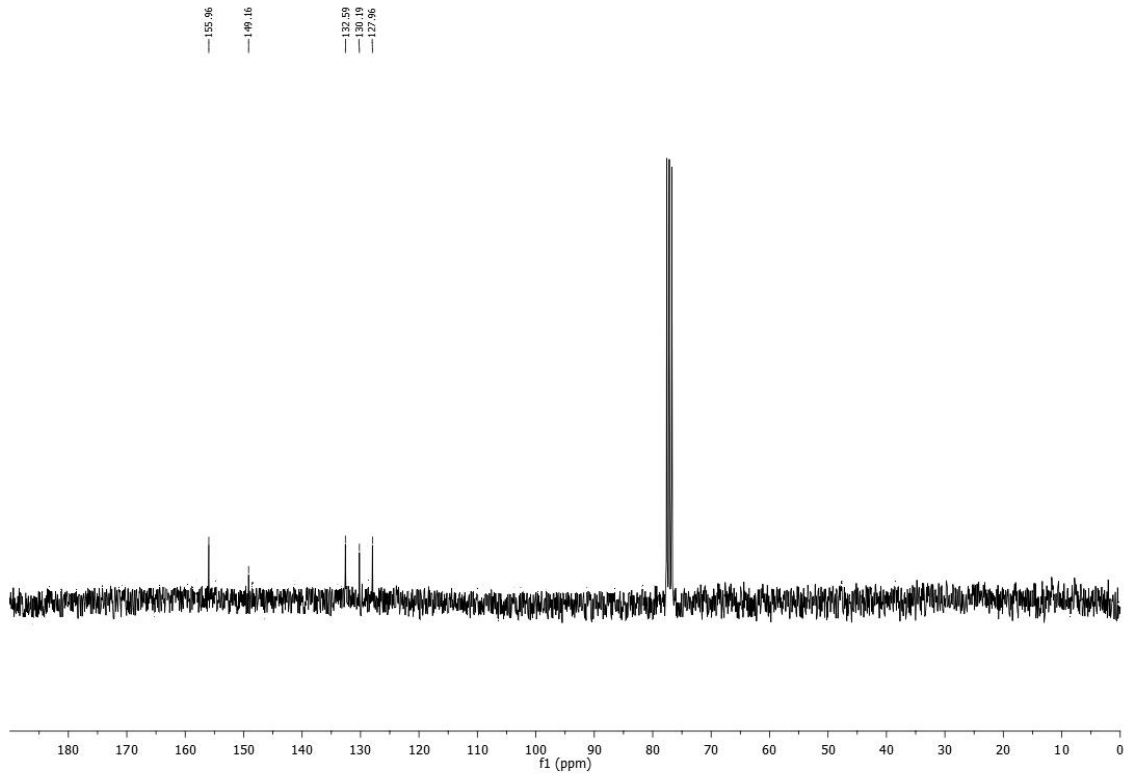


Figure S4. ^{13}C-NMR spectrum (75 MHz, 298K, $CDCl_3$) of **3k**.

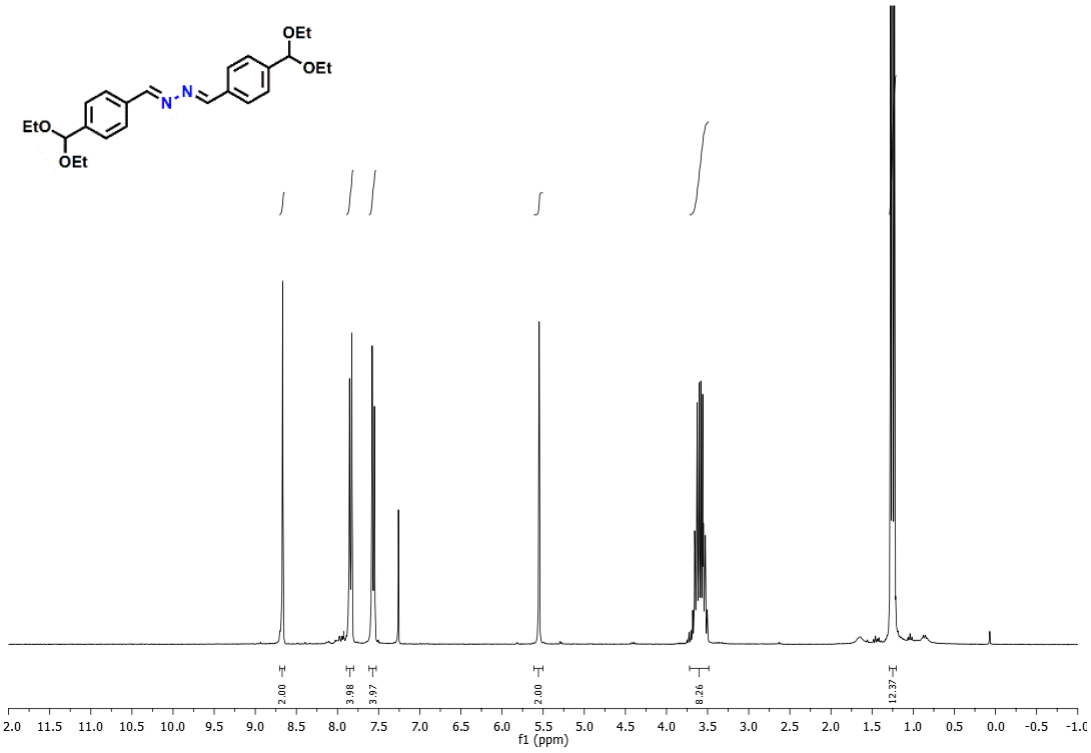


Figure S5. ^{1}H-NMR spectrum (300 MHz, 298K, $CDCl_3$) of **3m.**

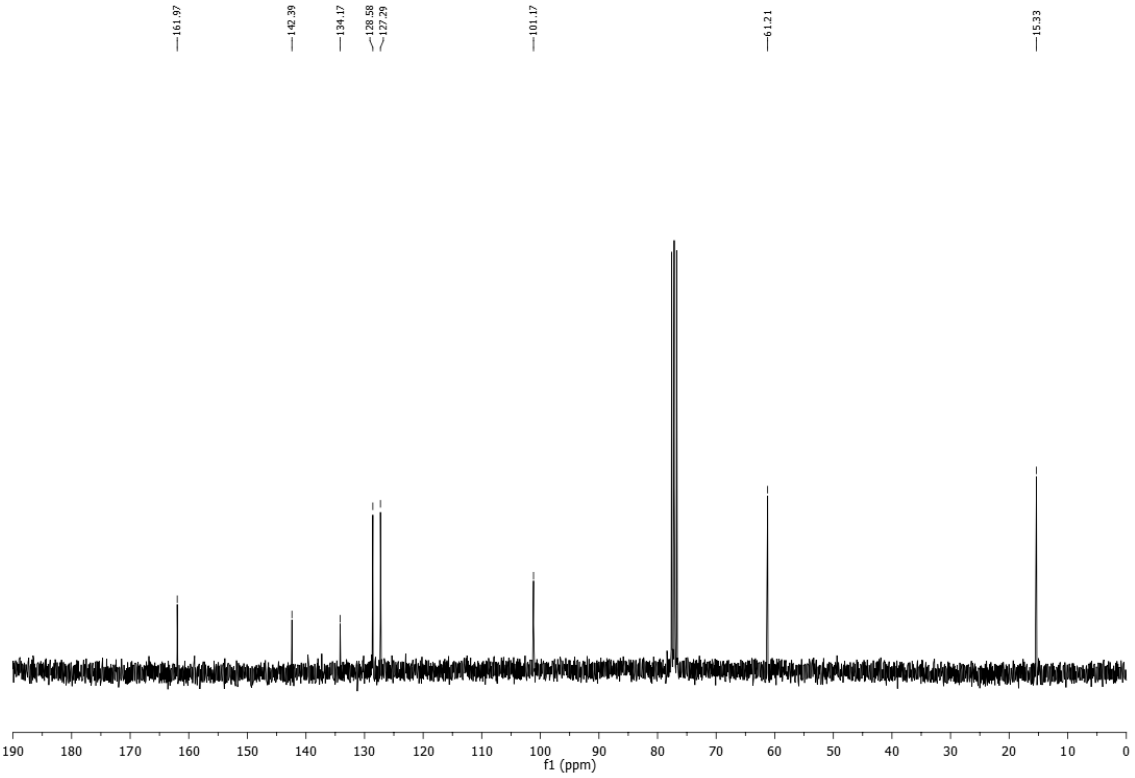


Figure S6. ^{13}C-NMR spectrum (75 MHz, 298K, $CDCl_3$) of **3m.**

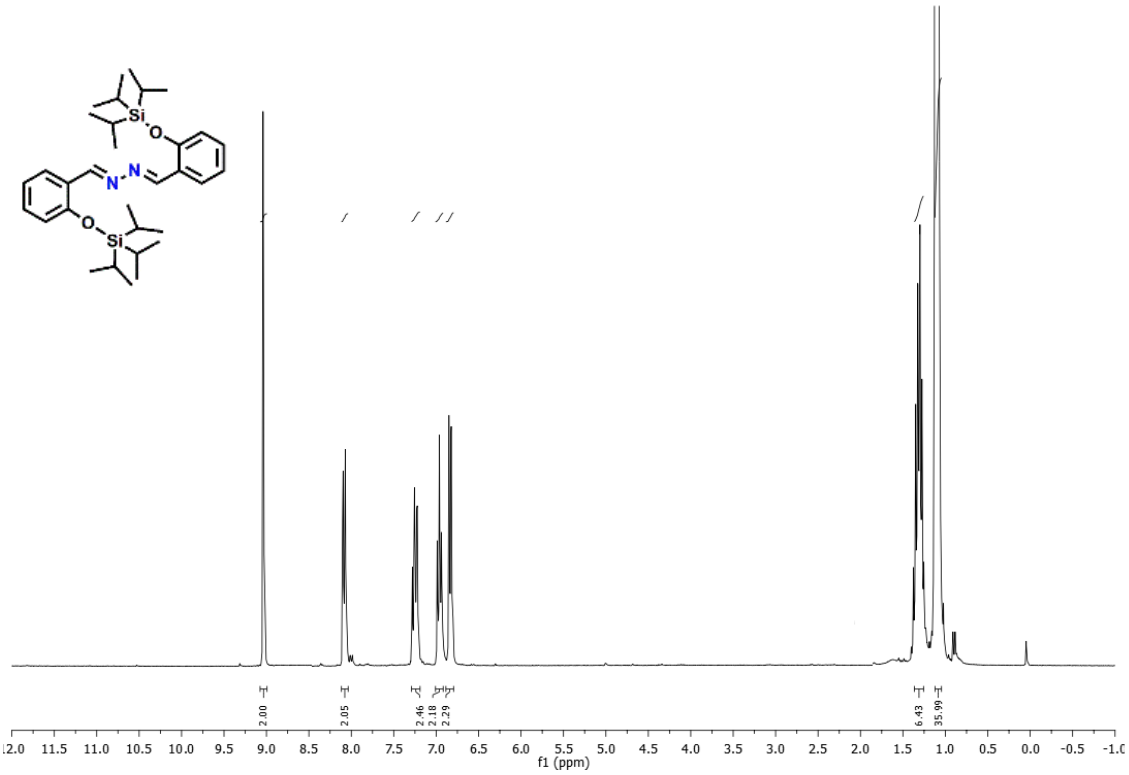


Figure S7. ^{1}H-NMR spectrum (300 MHz, 298K, $CDCl_3$) of **3n**.

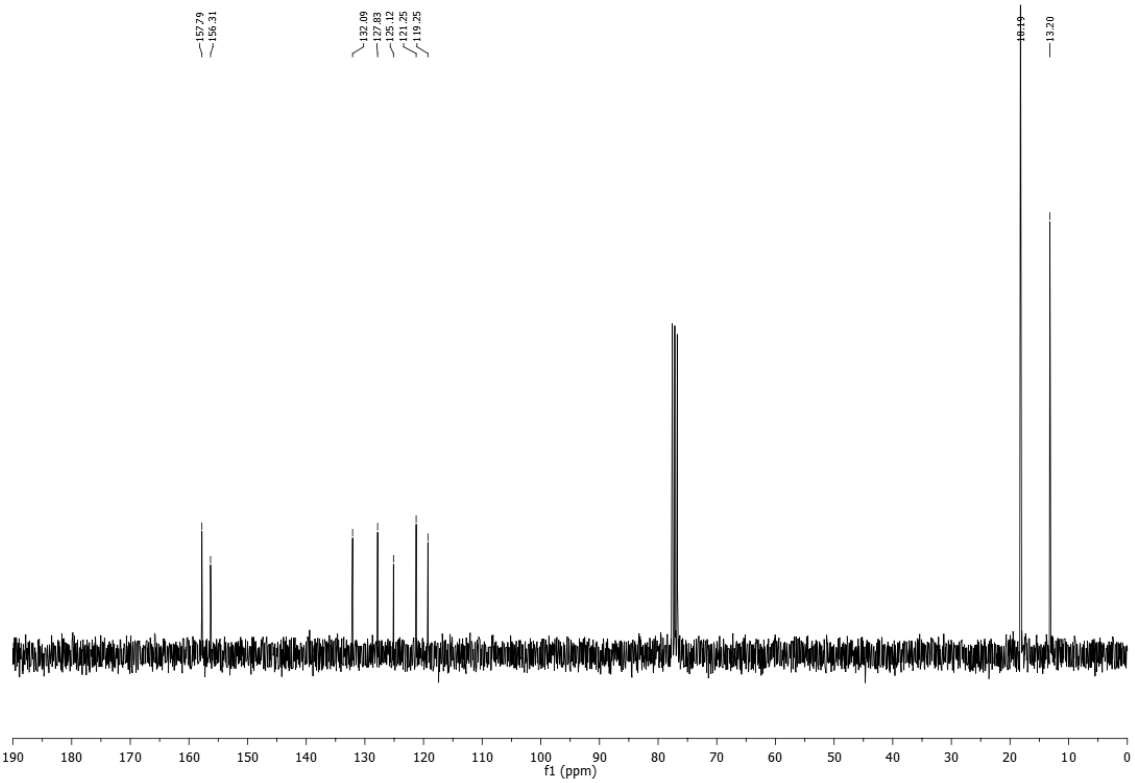


Figure S8. ^{13}C-NMR spectrum (75 MHz, 298K, $CDCl_3$) of **3n**.

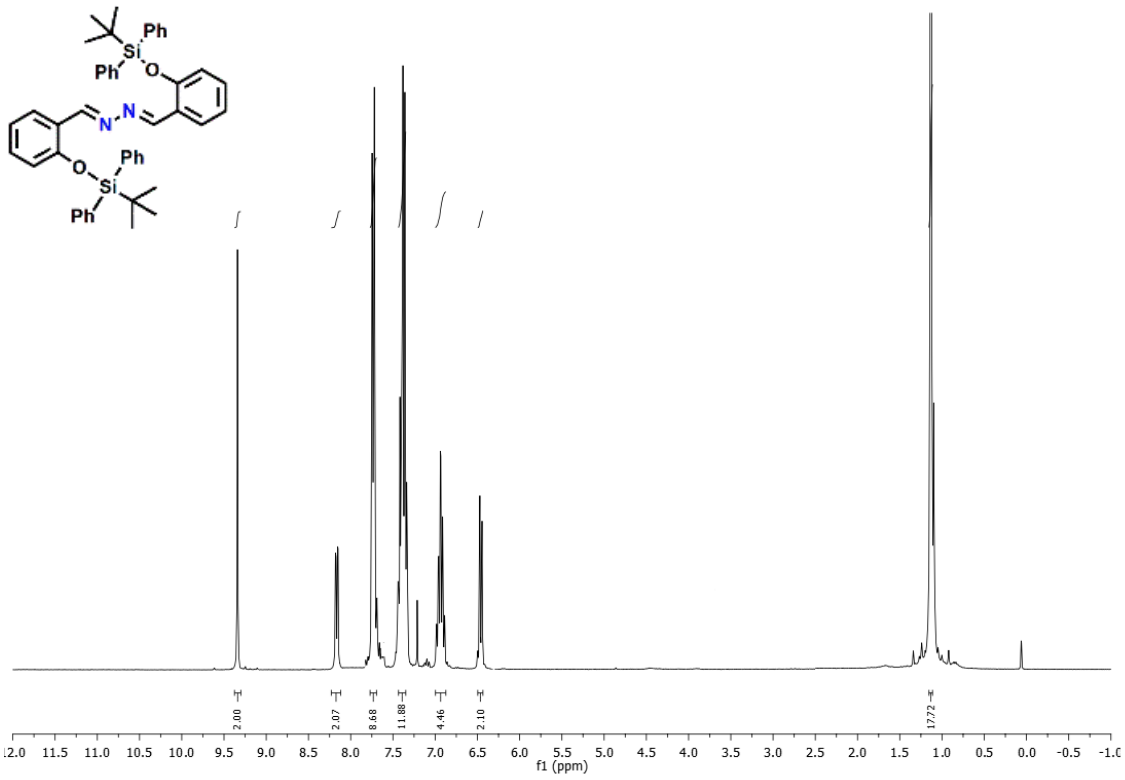


Figure S9. ^{1}H-NMR spectrum (300 MHz, 298K, $CDCl_3$) of **3o.**

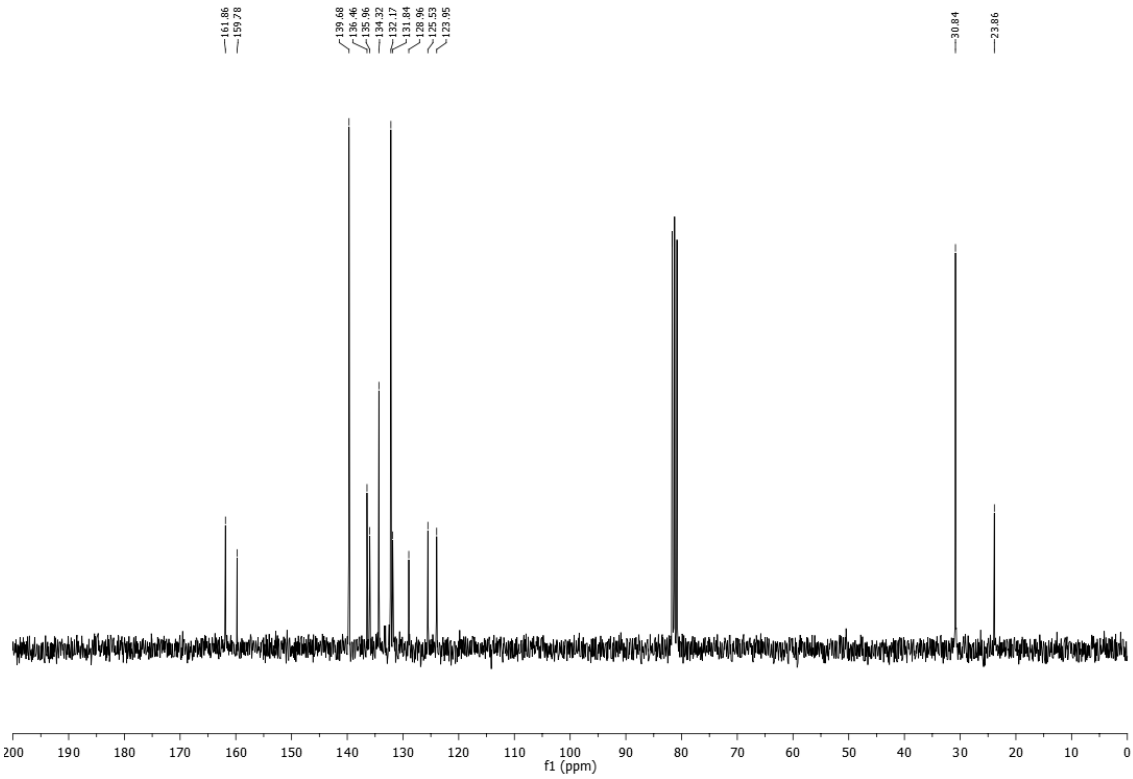


Figure S10. ^{13}C-NMR spectrum (75 MHz, 298K, $CDCl_3$) of **3o.**

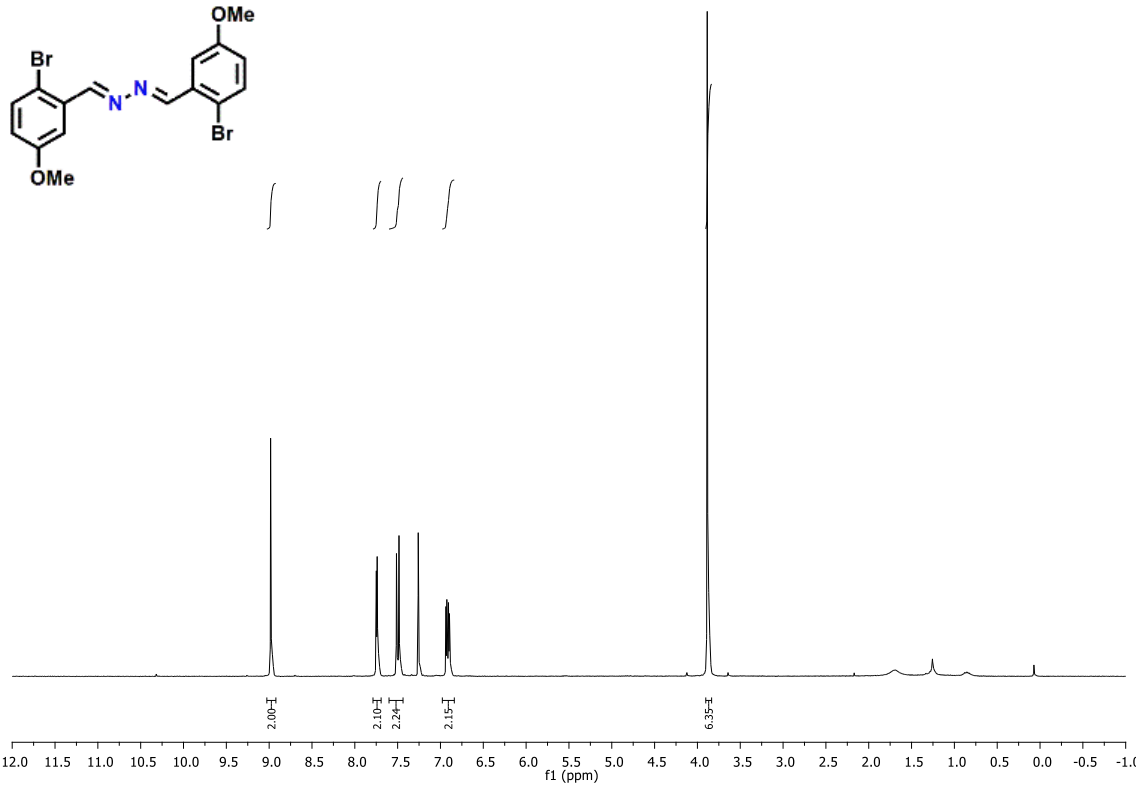


Figure S11. ^{1}H-NMR spectrum (300 MHz, 298K, $CDCl_3$) of **3s.**

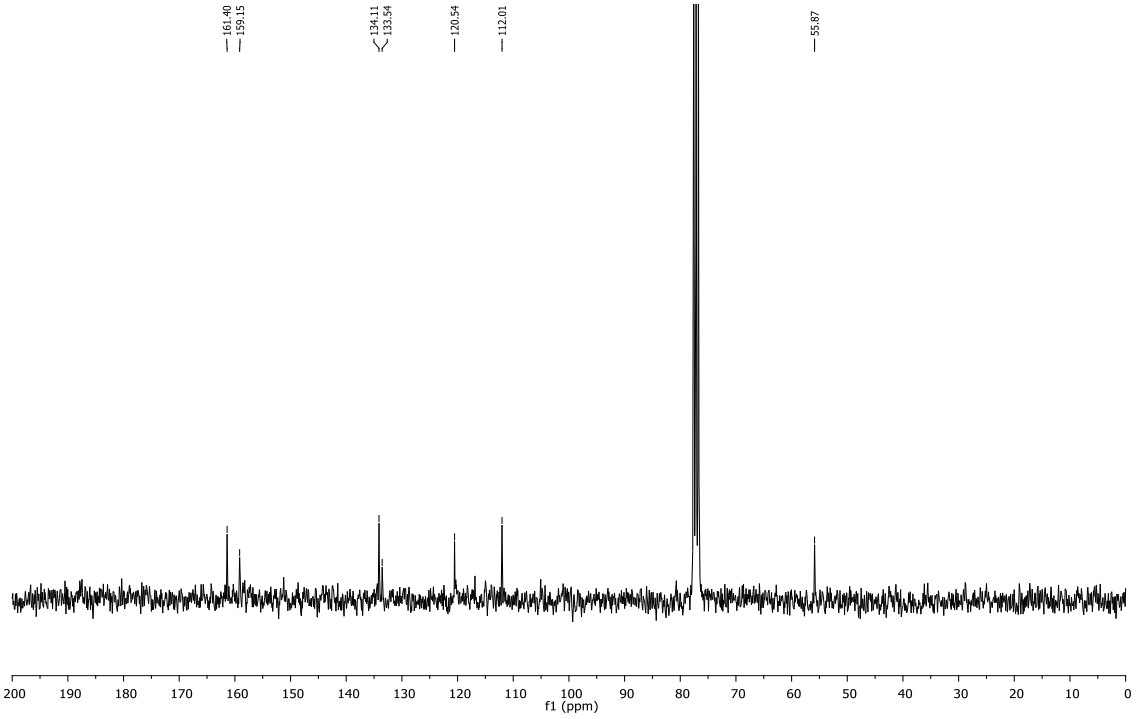


Figure S12. ^{13}C-NMR spectrum (75 MHz, 298K, $CDCl_3$) of **3s**.

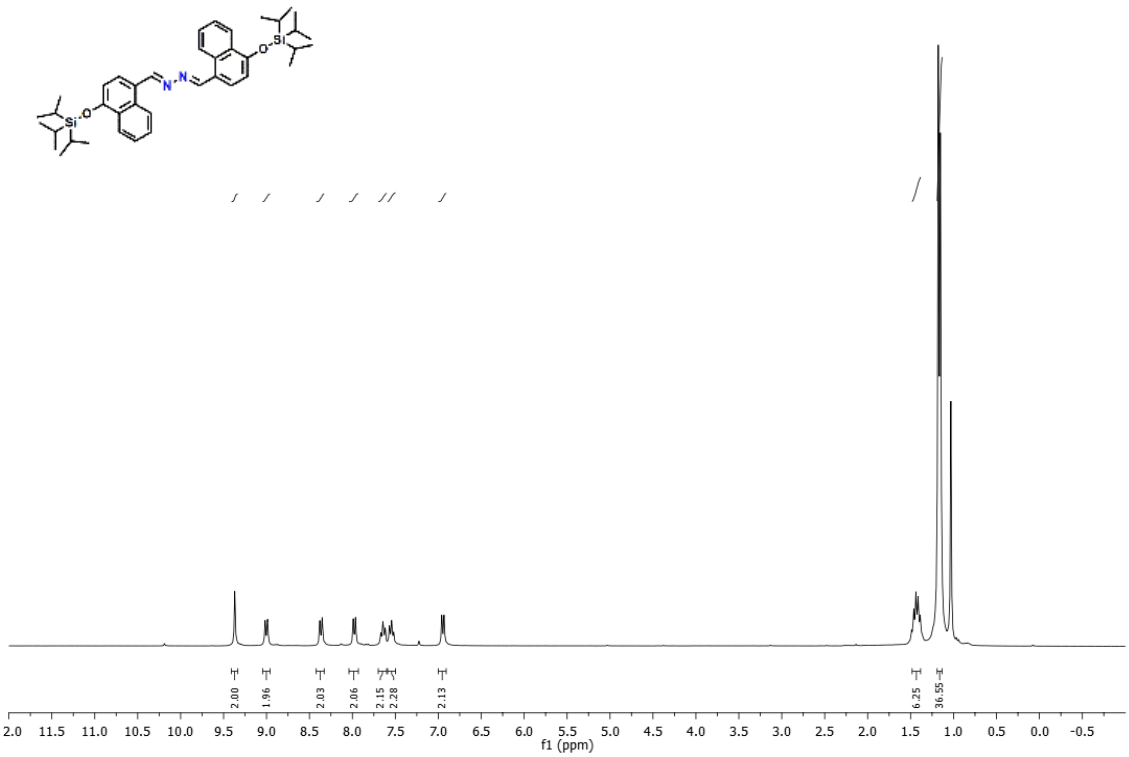


Figure S13. ^{1}H-NMR spectrum (300 MHz, 298K, $CDCl_3$) of **3t**.

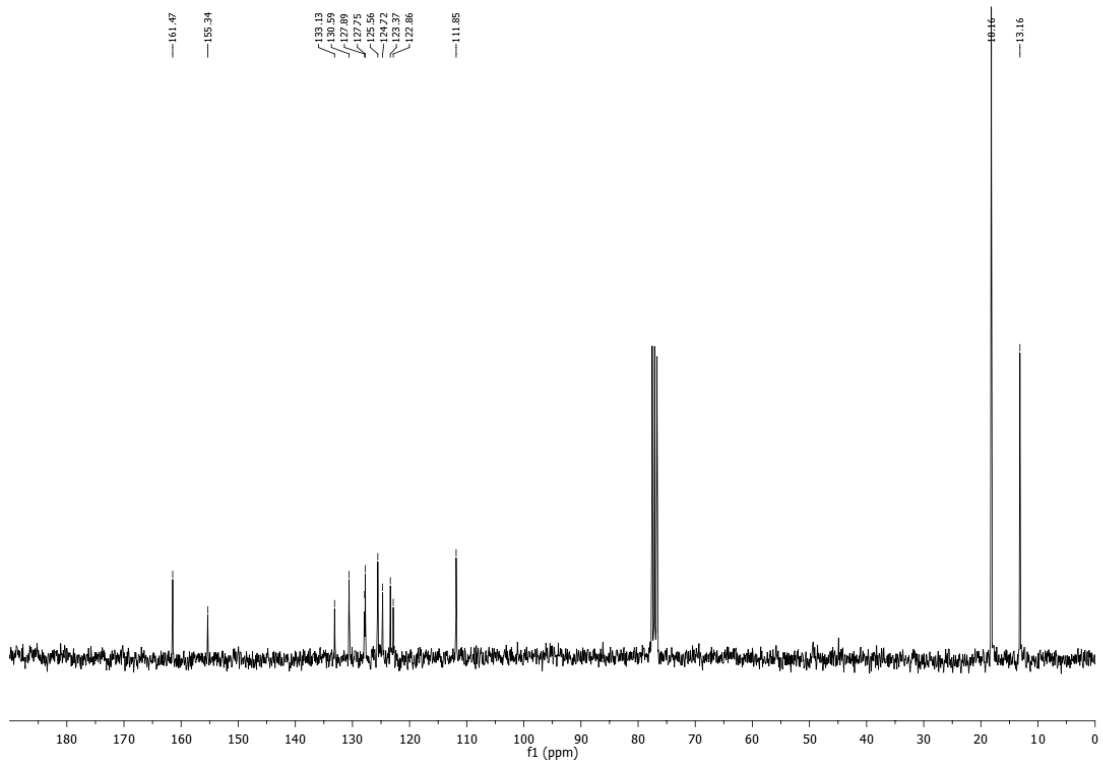


Figure S14. ^{13}C-NMR spectrum (75 MHz, 298K, $CDCl_3$) of **3t**.

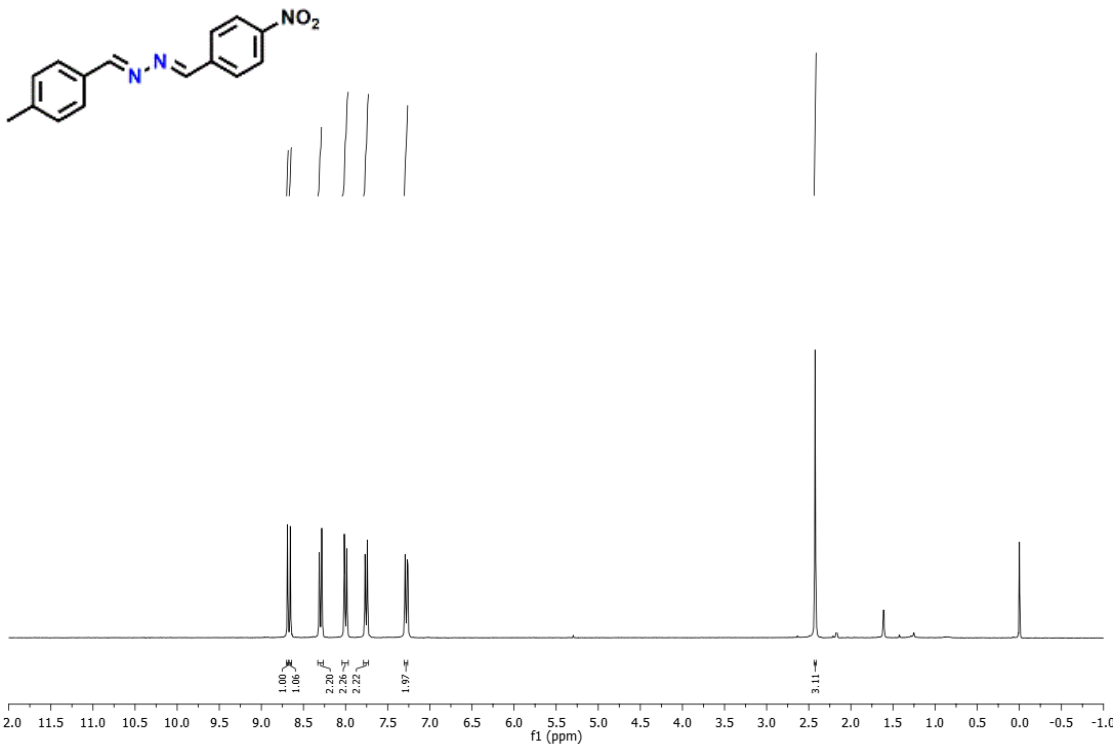


Figure S15. ^{1}H-NMR spectrum (300 MHz, 298K, $CDCl_3$) of **5a**.

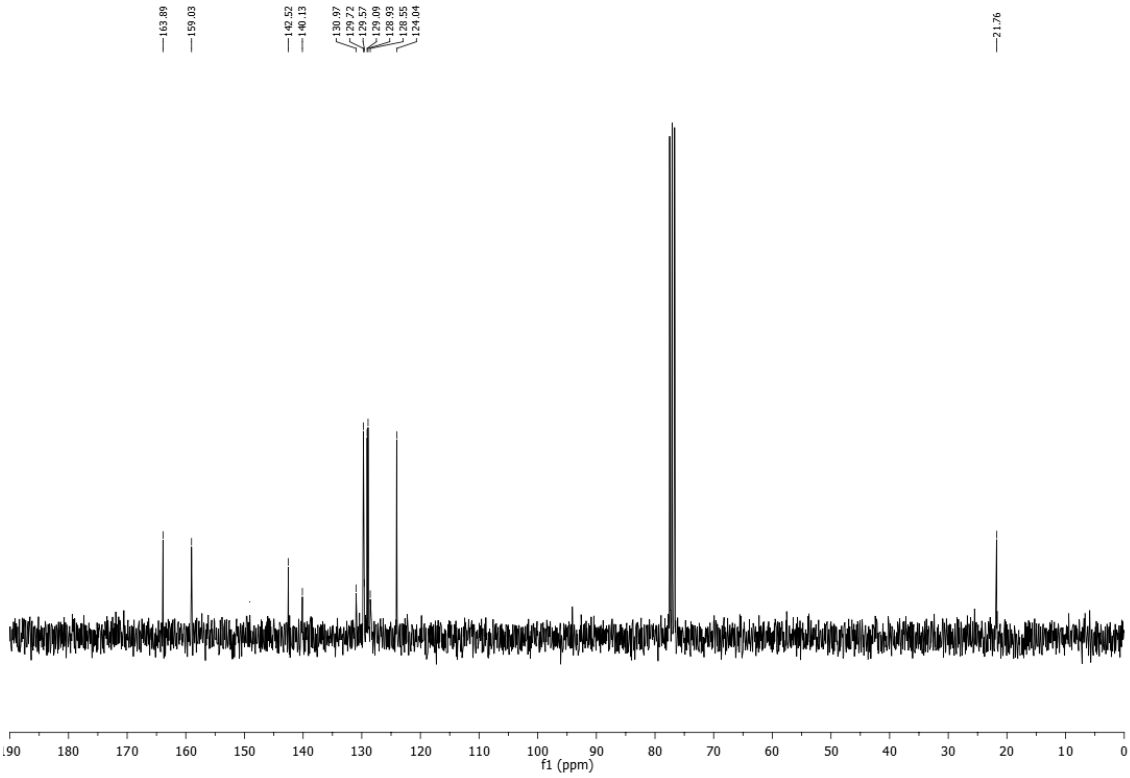


Figure S16. ^{13}C -NMR spectrum (75 MHz, 298K, $CDCl_3$) of **5a.**

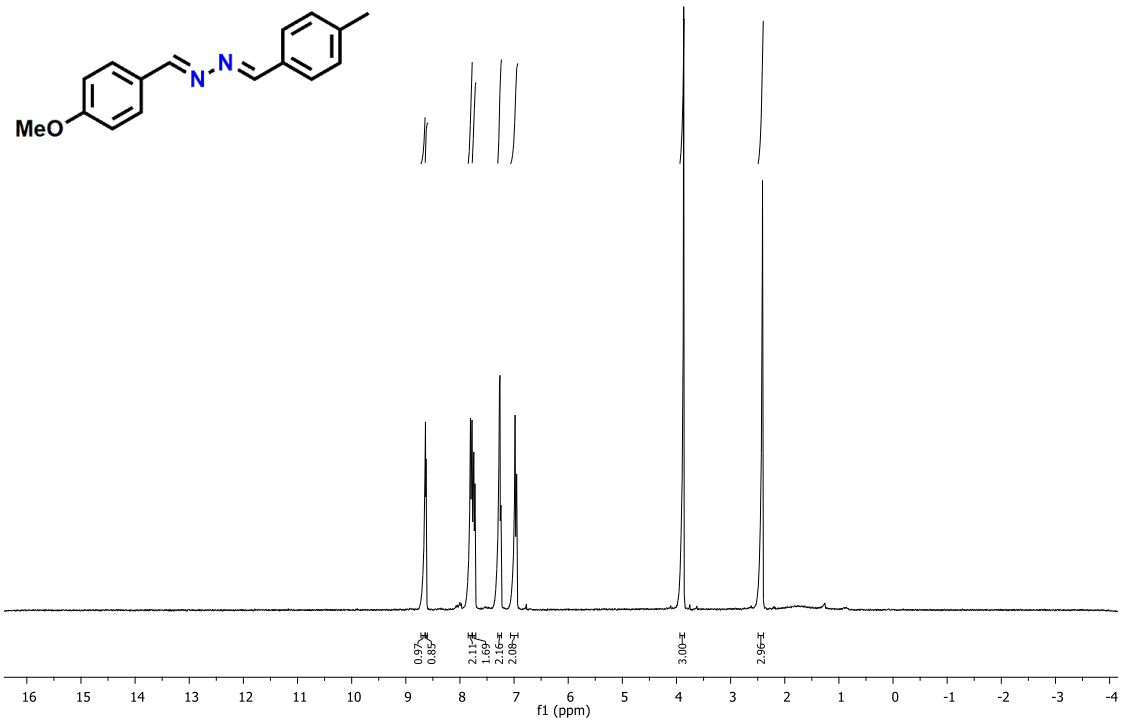


Figure S17. ^{1}H-NMR spectrum (300 MHz, 298K, $CDCl_3$) of **5b**.

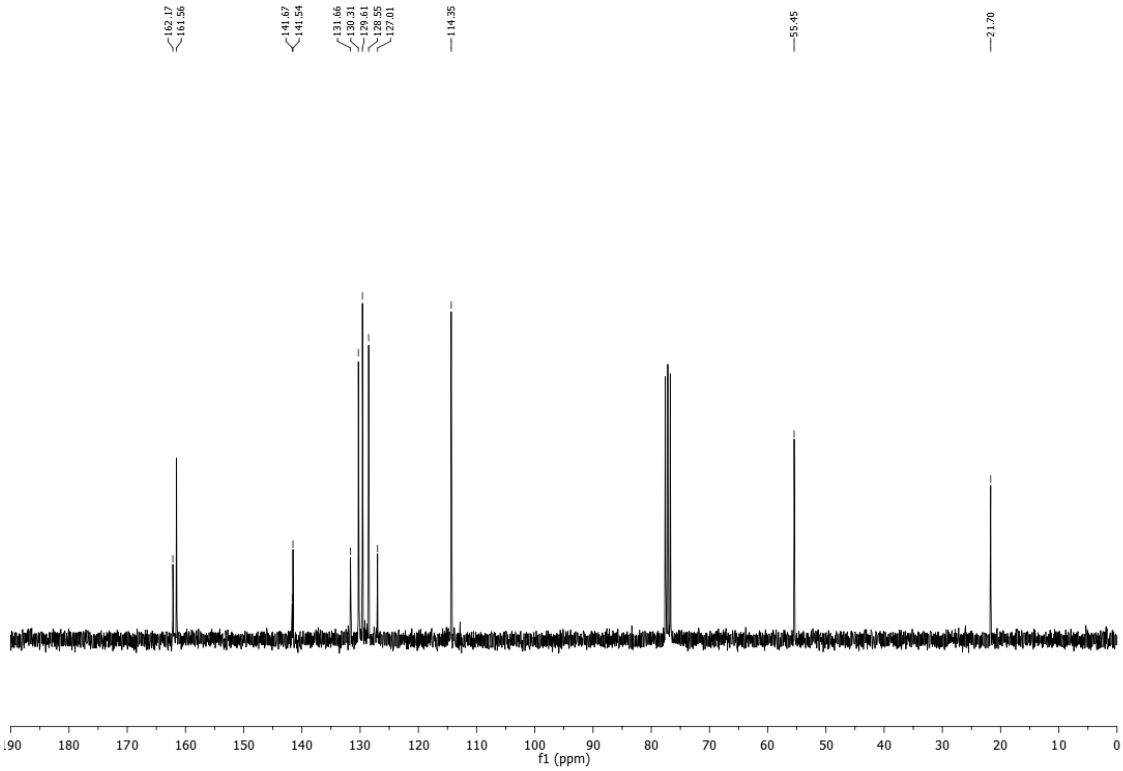


Figure S18. ^{13}C-NMR spectrum (75 MHz, 298K, $CDCl_3$) of **5b**.

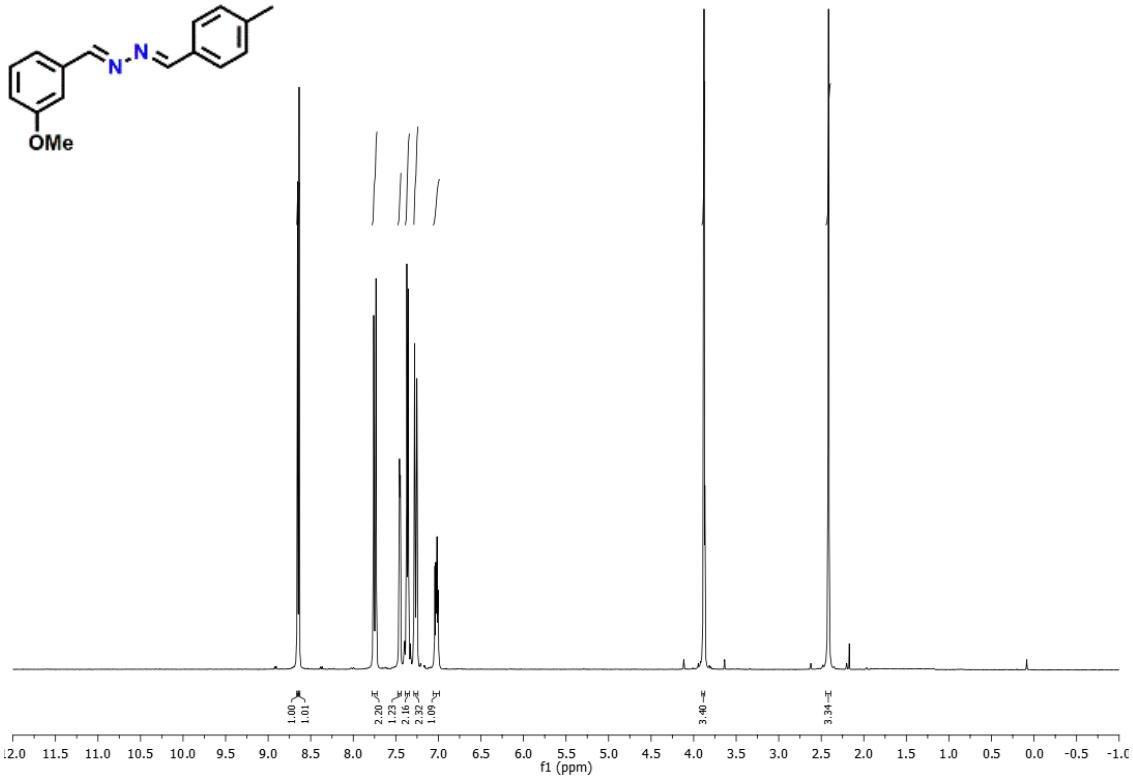


Figure S19. ^{1}H-NMR spectrum (300 MHz, 298K, $CDCl_3$) of **5c.**

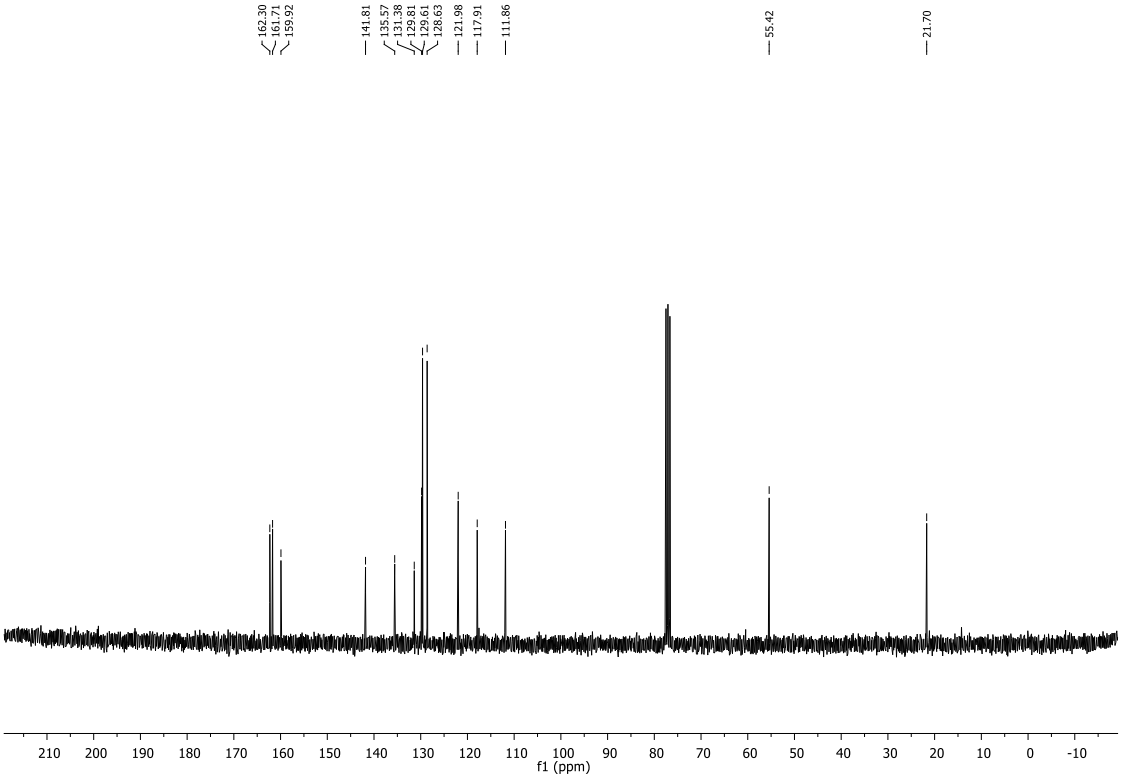


Figure S20. ^{13}C-NMR spectrum (75 MHz, 298K, $CDCl_3$) of **5c.**

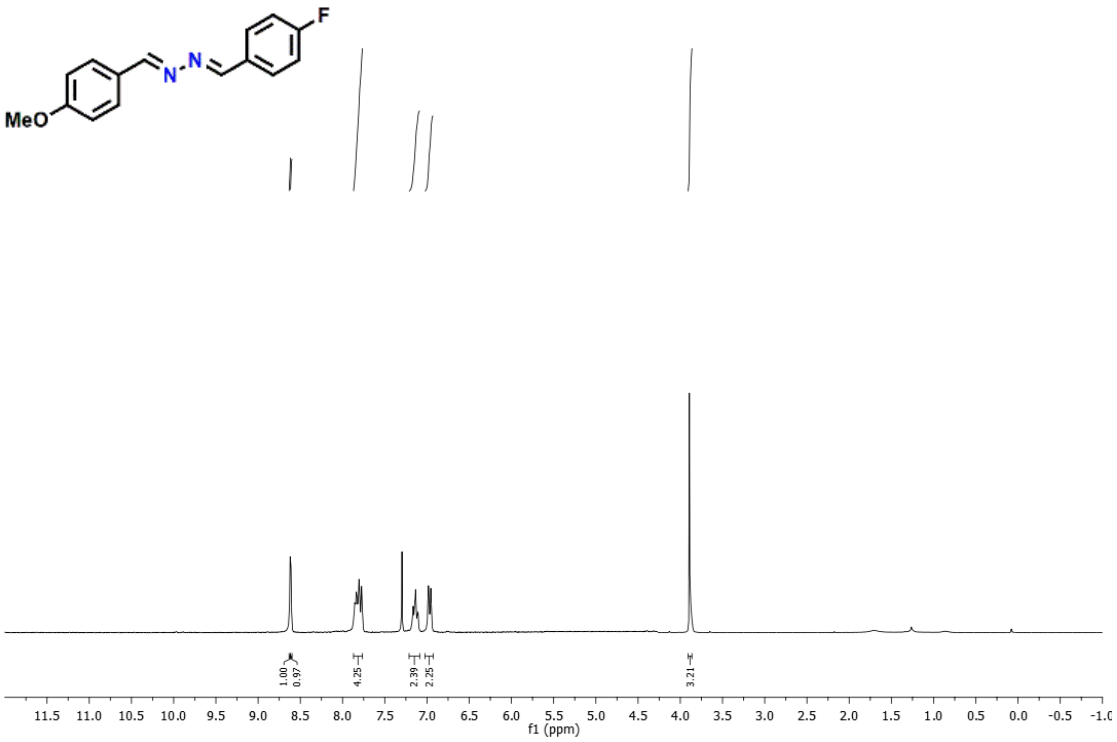


Figure S21. ^{1}H-NMR spectrum (300 MHz, 298K, $CDCl_3$) of **5e**.

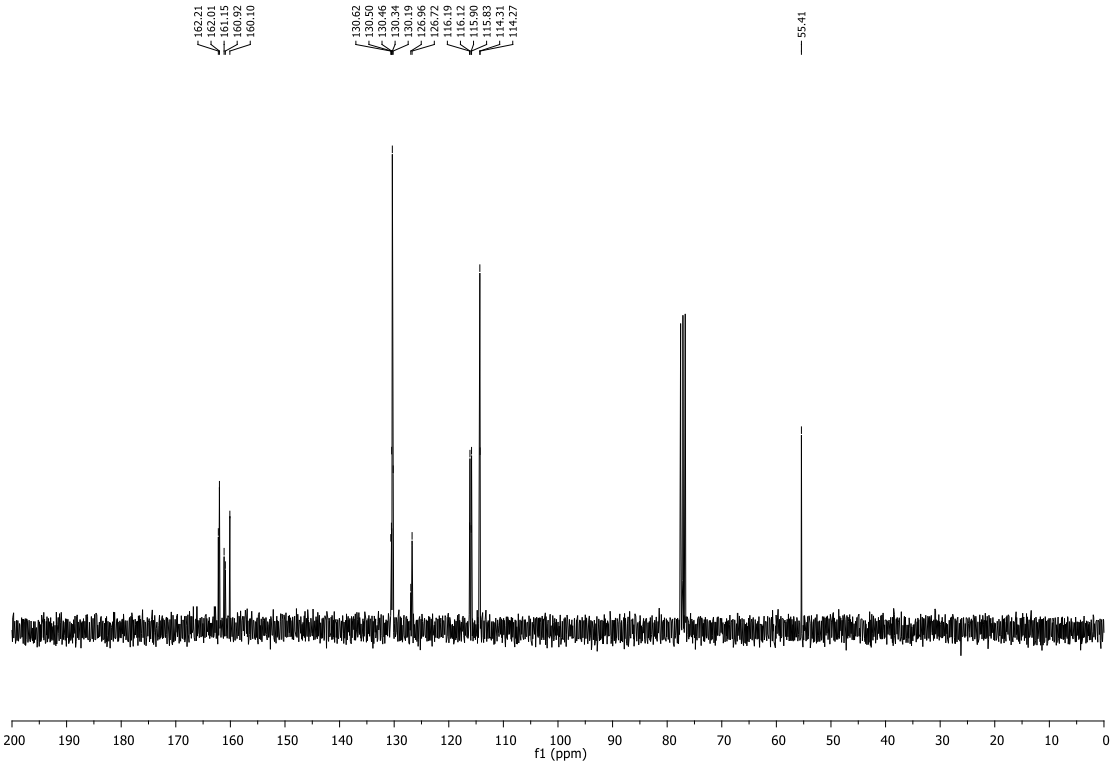


Figure S22. ^{13}C-NMR spectrum (75 MHz, 298K, $CDCl_3$) of **5e.**

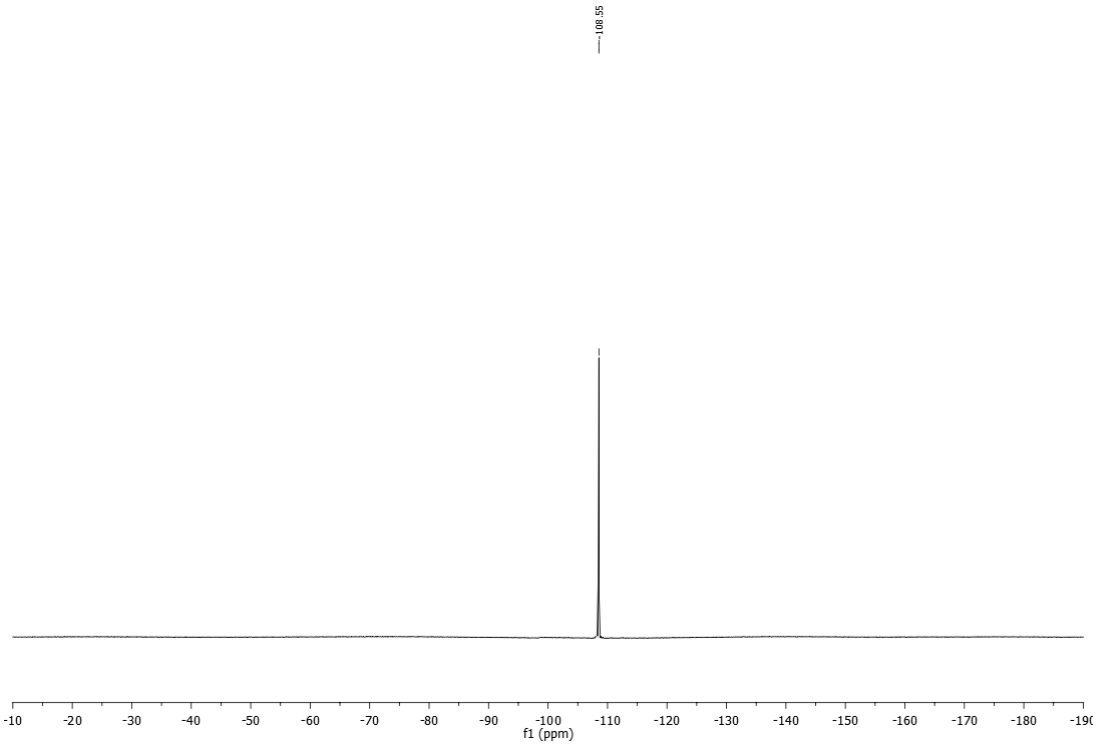


Figure S23. ^{19}F-NMR spectrum (471 MHz, $CDCl_3$) of **5e.**

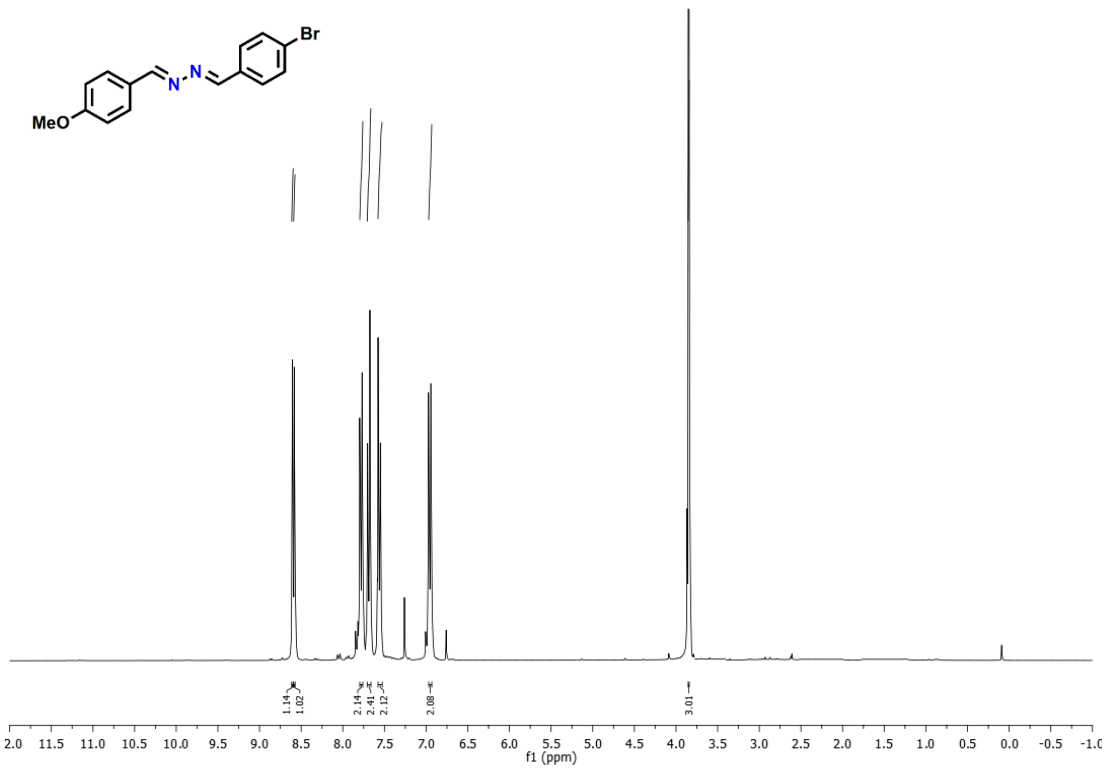


Figure S24. ^{1}H-NMR spectrum (300 MHz, 298K, $CDCl_3$) of **5f**.

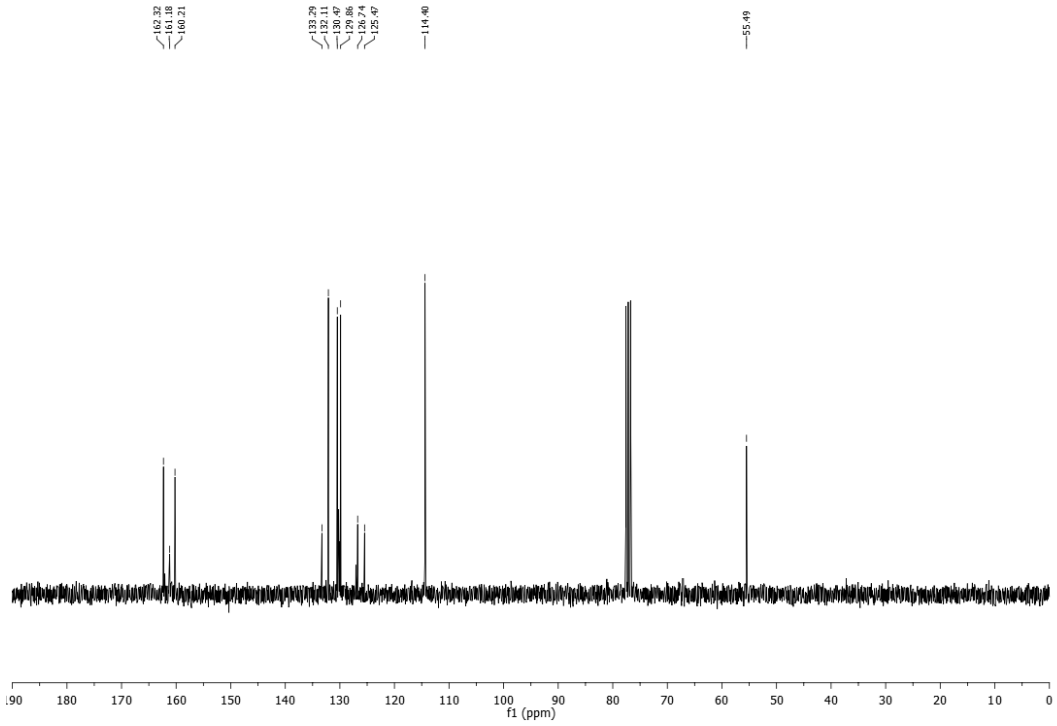


Figure S25. ^{13}C-NMR spectrum (75 MHz, 298K, $CDCl_3$) of **5f.**

2. EXTENDED CHARACTERIZATION OF MATERIALS

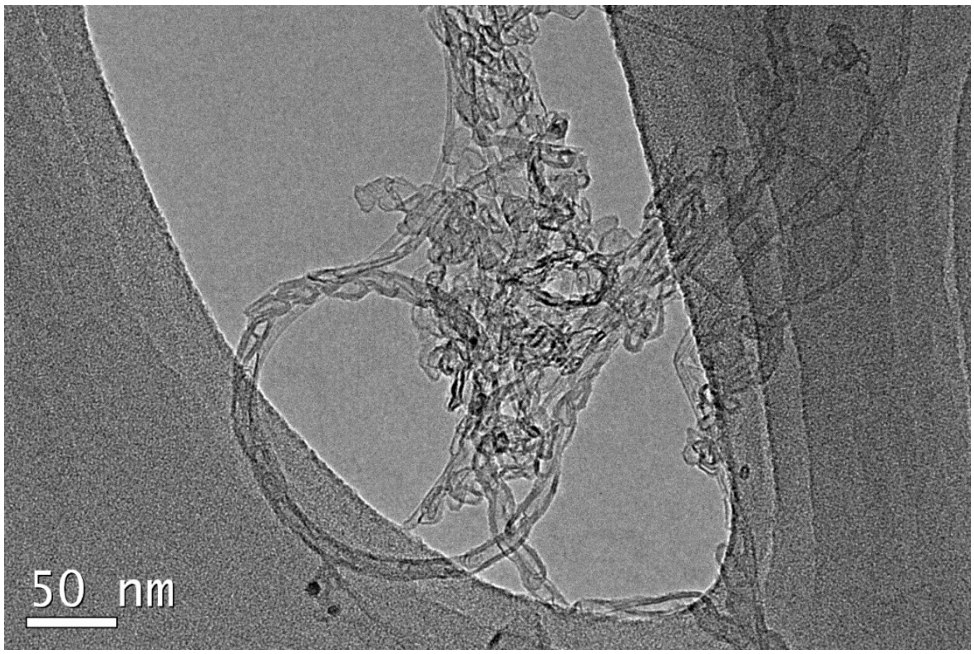


Figure S26. Low-magnification HRTEM image of pristine HCl - treated MWNT.

Table S1. TXRF analysis of HCl – treated MWNT.

Element	Line	Conc./ mg/l	Sigma/ mg/l	RSD/ %	LLD/ mg/l	Net area	Backgr.	Chi
Si	K12	100.90	0.78	0.8	0.30	23108	534	2.85
P	K12	0.183	0.075	41.2	0.154	85	568	1.31
S	K12	1.957	0.072	3.7	0.107	1645	897	1.42
Cl	K12	0.115	0.025	21.3	0.048	160	491	1.93
K	K12	0.038	0.010	26.3	0.020	116	401	1.45
Ca	K12	0.693	0.016	2.4	0.016	2540	373	0.91
Ti	K12	0.013	0.004	32.7	0.009	93	416	1.46
V (IS)	K12	5.000	0.029	0.6	0.010	44093	793	0.98
Cr	K12	0.034	0.003	9.2	0.005	372	391	1.39
Mn	K12	Not det.			0.004	27	371	1.99
Fe	K12	0.205	0.004	2.0	0.003	3477	356	0.99
Co	K12	1.719	0.011	0.6	0.003	34703	308	1.47
Ni	K12	0.005	0.001	21.5	0.002	123	282	0.83
Cu	K12	0.034	0.001	4.1	0.002	978	259	0.86
Zn	K12	0.051	0.002	2.9	0.001	1721	265	1.20
As	K12	0.024	0.001	3.7	0.001	1069	188	1.12
Br	K12	0.027	0.001	3.1	0.001	1428	191	0.96
Sr	K12	0.001	0.001	39.2	0.001	83	481	1.10
Mo	L1	5.42	0.13	2.4	0.16	3099	890	1.44
Ru	L1	0.079	0.037	46.0	0.075	71	490	1.22
Sn	L1	Not det.			0.024	3	381	1.25
Pb	L1	Not det.			0.001	29	174	1.17

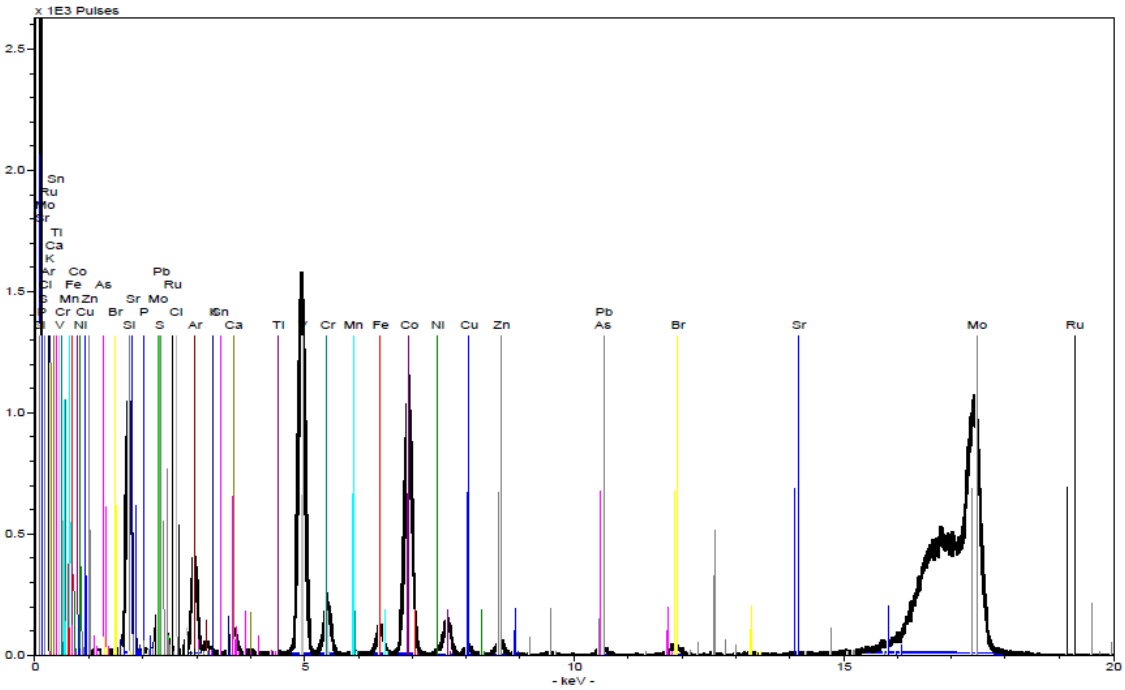


Figure S27. TXRF spectrum of sample HCl-treated MWNT

Table S2. Elemental analysis of samples under study.

Sample	C	H	N	S	O[a]
MWNT	81.1	1.9	0.5	0.1	16.4
oxMWNT	72.4	2.0	0.6	0.1	24.9
oxMWNT*	65.3	2.9	0.7	0.2	30.9
oxMWNT-TR450	91.5	0.7	0.1	0	7.7
oxMWNT-AC	73.4	1.9	0.7	0.1	23.9
Values stand for % wt. AC denotes recovered after catalysis. a) Determined by difference					

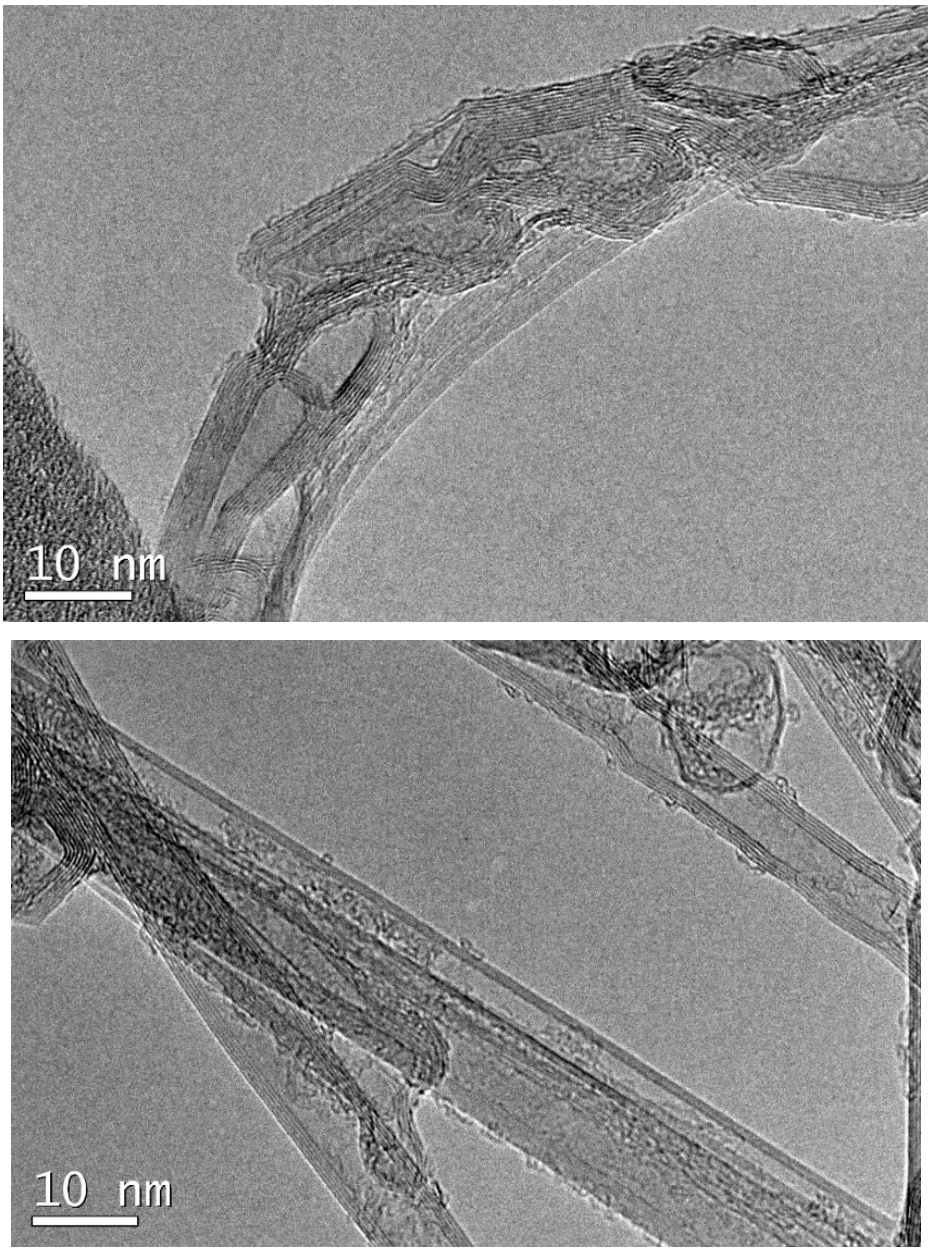


Figure S28. Additional HRTEM images of sample **oxMWNT**.

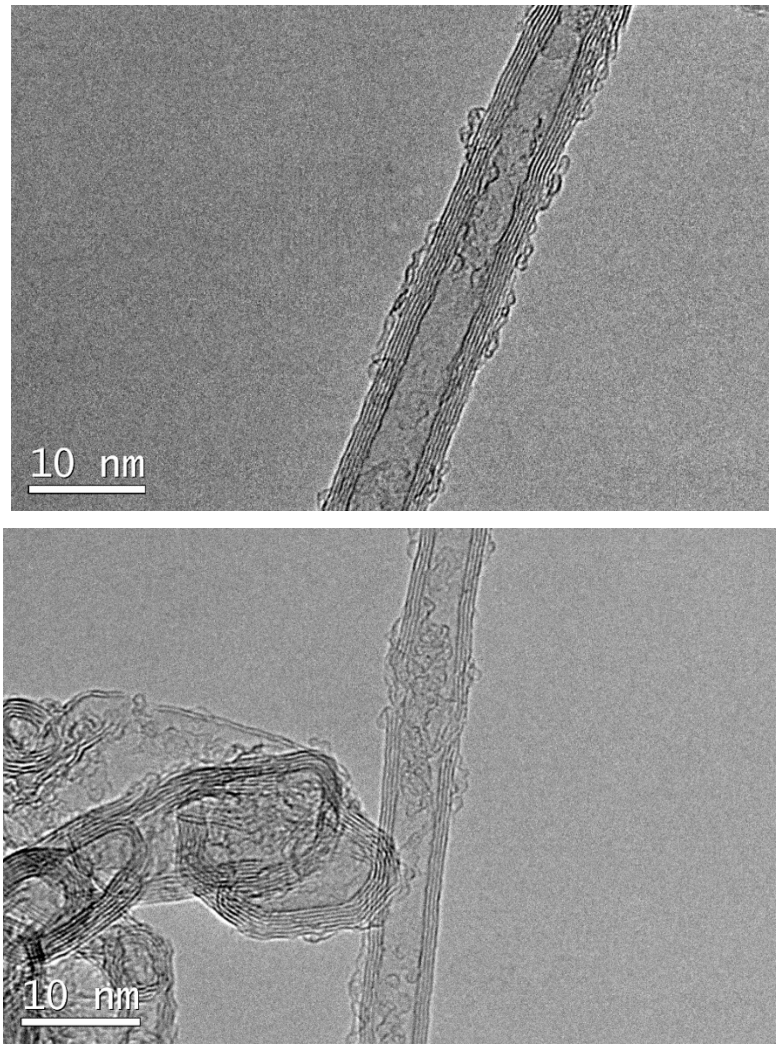


Figure S29. HRTEM images of **oxMWNT** recovered after the catalytic study.

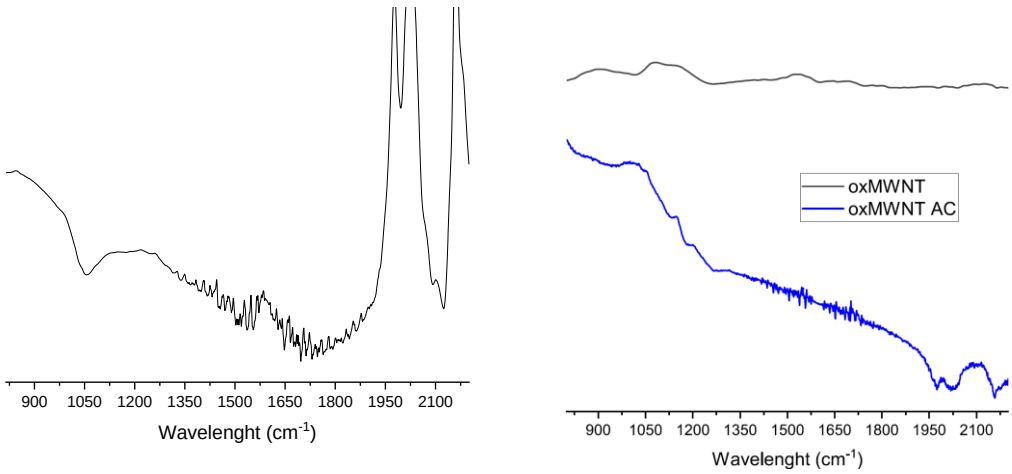


Figure S30. FTIR spectrum of samples: left) **MWNT** and right) **oxMWNT-AC** (blue) recovered after the catalytic study compared with fresh **oxMWNT** (grey).

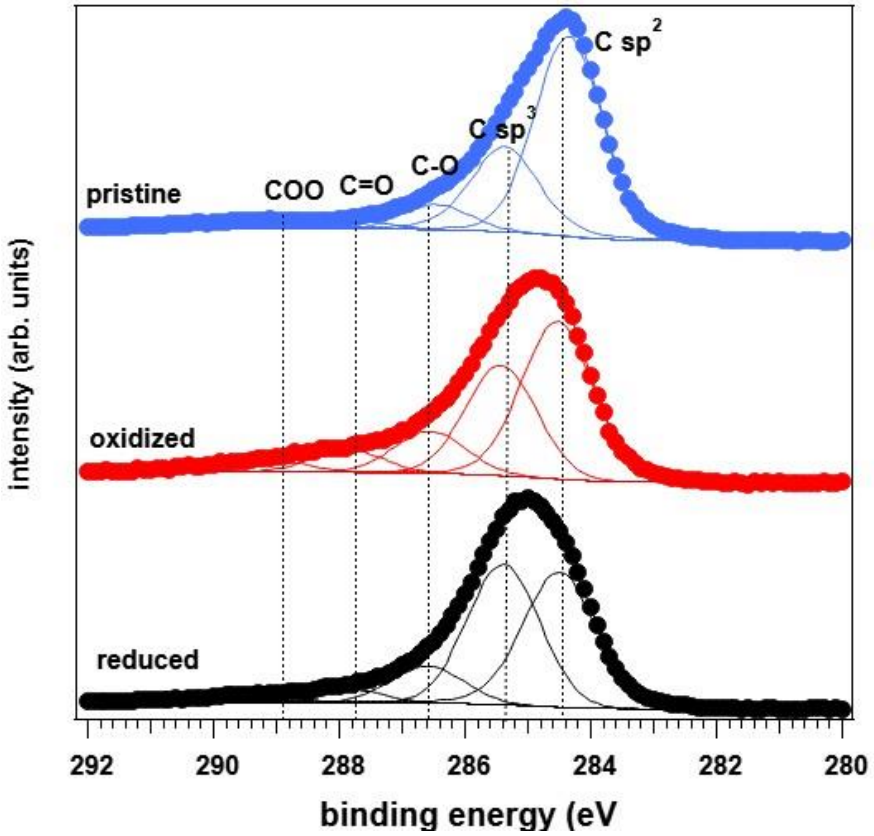
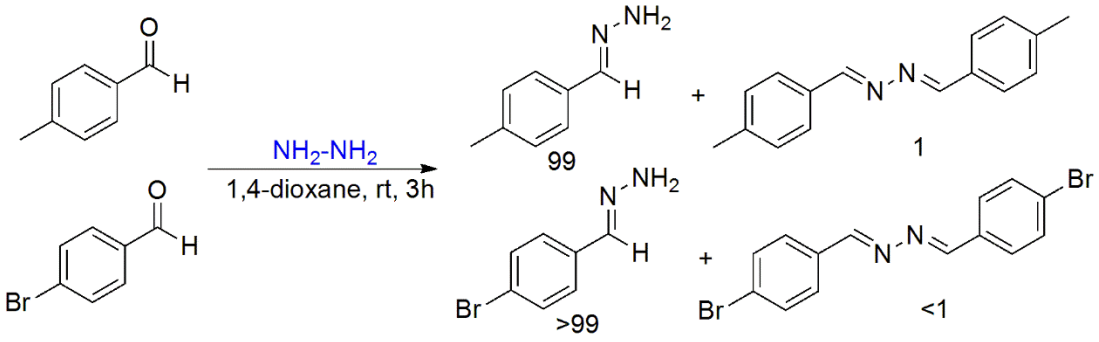


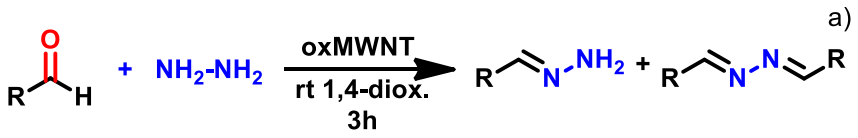
Figure S31. C 1s XPS core level region of the nanotube carbocatalysts with the corresponding fitting into individual components.

3. EXTENDED CATALYTIC DATA



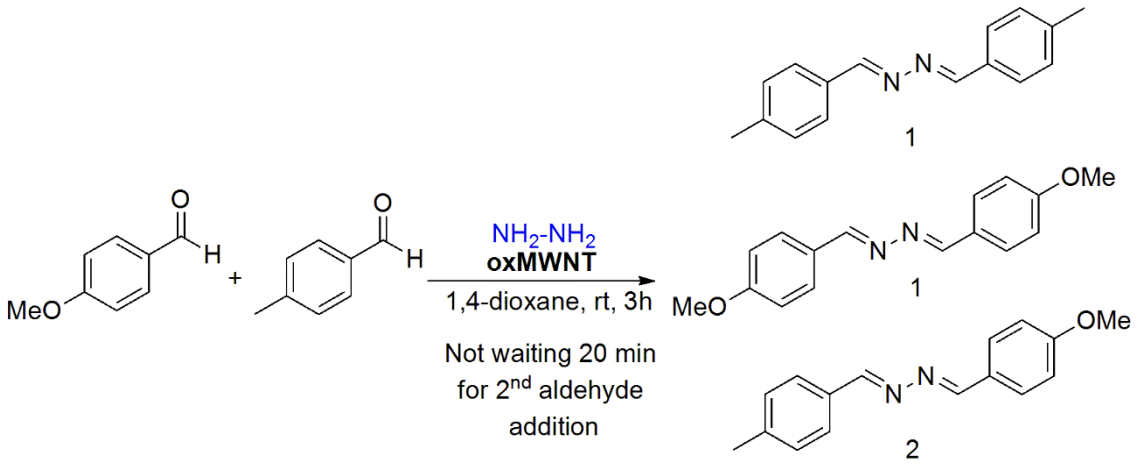
Scheme S1. Reactions of aldehydes without the presence of **oxMWNT**.

Table S3. Aliphatic aldehydes reacted with hydrazine in the presence of **oxMWNT**.



R	% Hydrazone[b]	% Azine[b]
Propyl	>99	<1
Butyl	98	2
Pentyl	>99	<1
Tert-butyl	>99	<1

a) Reaction conditions: 0.25 mmol of the aldehyde, 0.5 mL of 1,4-diozane with 5 %wt. loading of oxMWNT as catalyst at room temperature for 3h. b) Determined by ^{1}H-NMR



Scheme S2. Asymmetric azine formation attempt without waiting 20 min for the second aldehyde addition.

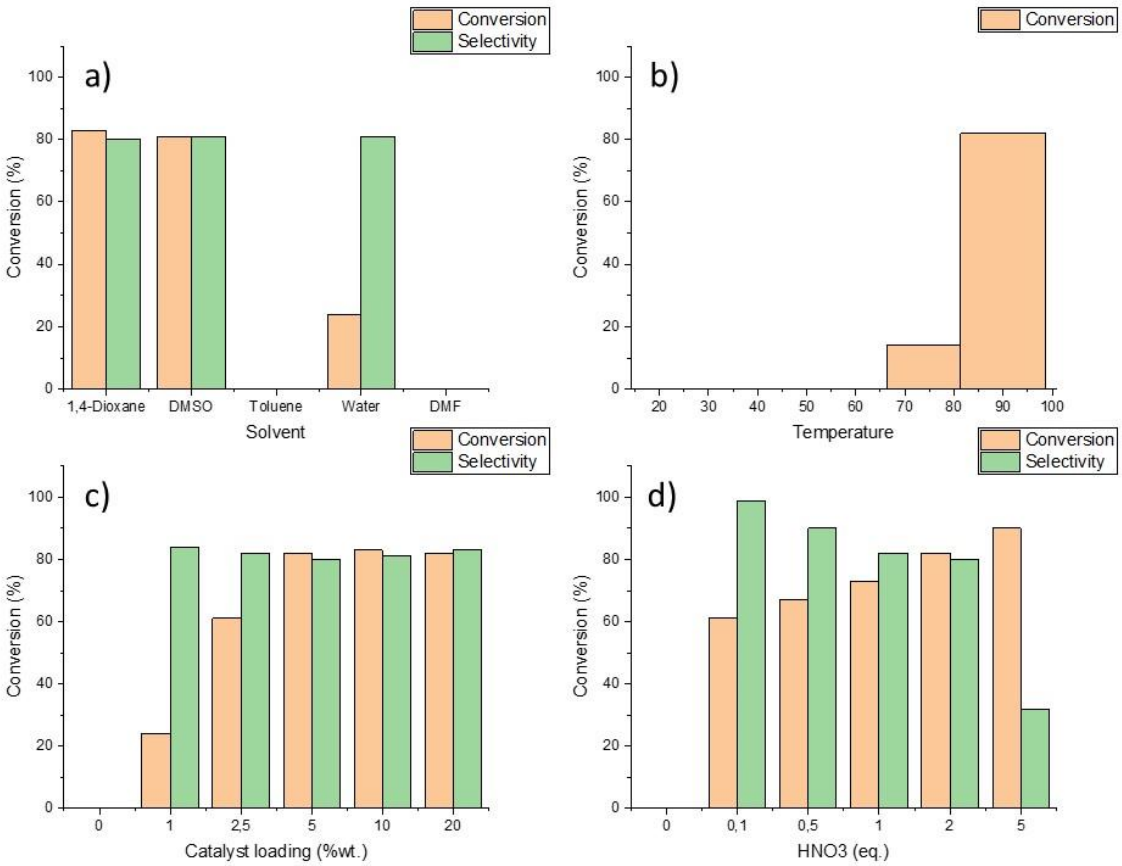
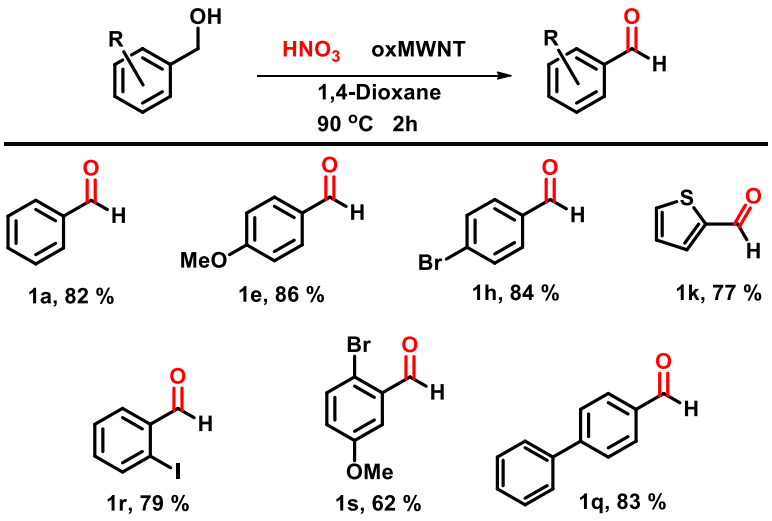


Figure S32. Optimization of the benzyl alcohol oxidation to benzaldehyde (or benzoic acid) in terms of a) solvent, b) temperature, c) catalysts loading and d) equivalents of HNO_3.

Table S4. Alcohol oxidation to aldehyde catalysed by **oxMWNT.**



Reaction conditions: 0.25 mmol of alcohol, 0.5 mmol of HNO_3, 0.5 M 1,4-dioxane, 5 %wt. oxMWNT, for 2h at 90 °C. Values stand for conversion (determined by ^{1}H-NMR)

Table S5. Activity comparison with other state-of-the-art catalysts for oxidation of alcohols

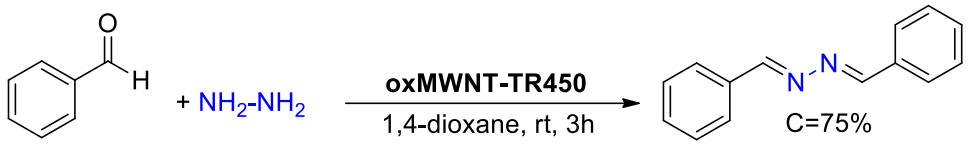
Catalyst	Reac[a]	Conv[b]	Select.[c]	Time	Activity[d]	Conditions	Ref
oxMWNT	BA	80	85	120 min	104	2 mmol HNO_3 90 °C 1,4-dioxane (5 %.wt loading) towards benzaldehyde	This work
GA	BA	95	70	75 min	152	2 mmol HNO_3 90 °C 1,4-dioxane (5 %.wt loading) towards benzaldehyde	[5]
GO	BA	100	94	3h	66	2.0 mmol HNO_3 autoclave (5 %.wt loading) towards benzaldehyde	[6]
ox. CNT	BA	96	88	5h	3.8	Catalyst (100 mg), benzyl alcohol (2 mmol), 1,4-dioxane, 65–68% HNO_3 (2 mmol), reaction temperature (90 °C), reaction time (5 h), O_2 (balloon pressure)	[7]
mp C_3N_4	BA	57	100	3h	3.8	50 mg, hv O_2 (8 bar) trifluorotoluene	[8]
mp C_3N_4	BA	61	100	9h	1.4	hv O_2	[9]
Pd/CNT	BA	98	95	6h	12	300 mg of catalyst; 2.4 g of benzyl alcohol in 50 mL of xylene; air flow rate of 100 mL min^{-1} ; 90 °C	[10]
Pd/carbon	BA	65	91	1h	75	20 mg; benzyl alcohol 2.5 g, O_2, 30 ml/min; temperature, 160 °C	[11]
Rh/carbon	BA	47	93	1h	60	20 mg; benzyl alcohol 2.5 g, O_2, 30 ml/min; temperature, 160 °C	[11]
Activated carbon	BA	>95	?	2h	10	40 mmol BA, TEMPO (0.2 mol%), HNO_3 (4 mol%), O_2 (1 atm), AC (200 mg), 90 °C towards benzaldehyde	[12]
Ox. Zeolite	BA	99	99	4h	0.5	0.5g cat, 90 °C H_2O_2 towards benzaldehyde	[13]
MCM-41	BA	51	66	5h	2	catalyst 100 mg, BA 2 mmol, 1,4-dioxane, 65–68% HNO_3(2 mmol), 90 °C, 5 h, O_2 (balloon pressure)	[7]
Al_2O_3	BA	50	64	5h	2	catalyst 100 mg, BA 2 mmol, 1,4-dioxane, 65–68% HNO_3(2 mmol), 90 °C, 5 h, O_2 (balloon pressure) towards benzaldehyde	[7]
[Cu]	BA	76	?	6h	59	acetonitrile (5 ml) with H_2O_2 (1 ml, 30 vol%) with substrates (5 mmol) and tris(3,5-dimethylpyrazole)copper(II) nitrate	[14]
$CuBr_2$/bmimbf4	BA	81	?	4h	-	60 °C	[15]
-	Lignine	100	100	24h	-	TEMPO HNO_3 HCl	[16]
-	BA	91	?	4h	-	HNO_3 $NaNO_2$ neat	[17]
Amberlist	BA	80	?	6-8h	0.83	80 °C O_2	[18]

a) Reactant (BA stands for benzyl alcohol, AP stands for acetophenone); [b] Conversion (%); [c] Selectivity (%): [d] mmol converted g^{-1} h^{-1}.

Table S6. Activity comparison with other state-of-the-art catalysts for azine formation

Catalyst	Reac[a]	Conv[b]	Select.[c]	Time	Activity[d]	Conditions	Ref
oxMWNT	BA	80	80	240 min	40	One-pot azine synthesis	This work
oxMWNT	BAY	100	100	180 min	60	Symmetric and asymmetric synthesis of azines	This work
GO	BA	91	100	24 h	1.26	Toluene KOH 110 ^{o}C 30 mg of catalyst for the synthesis of triazines	[19]
[Ru]	BA	88	82	67 h	6.1	One pot azine synthesis. Toluene, KO^{t}Bu, reflux, 1g molecular sieves.	[20]
[Ru]	AP	99	92	12 h	30.2	One pot azine synthesis. Toluene, base, reflux, molecular sieves	[21]
[Ni]	BA	68	63	24 h	9.4	One pot azine synthesis. THF, $NaBH_4$, reflux, base	[22]

a) Reactant (BA stands for benzyl alcohol, AP stands for acetophenone, BAY stands for benzaldehyde); [b] Conversion (%); [c] Selectivity (%): [d] mmol converted g^{-1} h^{-1}.



Scheme S3. Catalytic attempt in the general azine formation reaction using **oxMWNT-TR450** as catalyst

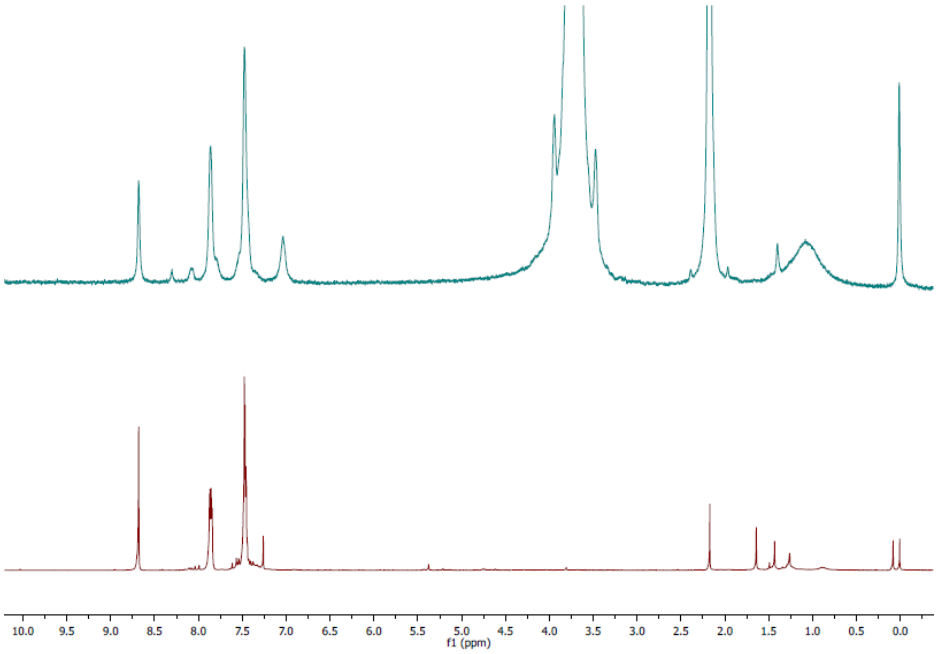


Figure S33. ^{1}H-NMR (300 MHz, 298 K, $CDCl_3$) spectrum of the reaction crude for the synthesis of 1,2-dibenzylidenehydrazine catalysed by **oxMWNT** in the presence of 3.6 equivalents of TEMPO (blue) compared with the pure 1,2-dibenzylidenehydrazine synthetized without the radical scavenger (red).

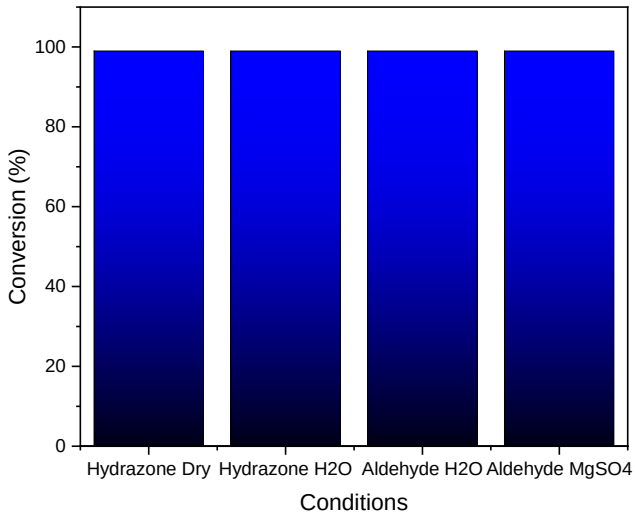


Figure S34. Water influence in the azine condensation reaction catalysed by **oxMWNT.**

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