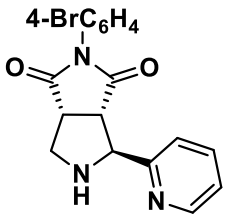
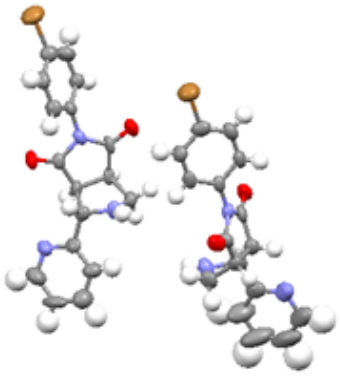
Anexo III:
X-Ray difraction

Capítulo 2: Catalytic asymmetric 1,3 dipolar cycloaddition of α-heteroarylsilylimines and activated olefins



trans-**32**



Computing details

Data collection: Bruker Instrument Service v2010.9.0.0; cell refinement: *SAINT* V7.68A (Bruker AXS, 2009); data reduction: *SAINT* V7.68A (Bruker AXS, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008).

Crystal data

$C_{17}H_{14}BrN_3O_2$	$F(000) = 752$
$M_r = 372.22$	$D_x = 1.546$ Mg m^{-3}
Monoclinic, $P2_1$	Cell parameters from 2401 reflections
$a = 6.0087$ (4) Å	$\theta = 2.9–18.7°$
$b = 17.4567$ (9) Å	$\mu = 2.58$ mm^{-1}
$c = 15.2518$ (12) Å	$T = 296$ K
$\beta = 91.114$ (2)°	Plate, clear colourless
$V = 1599.49$ (18) Å^3	0.45 × 0.20 × 0.04 mm
$Z = 4$	

Data collection

Detector resolution: 8.3333 pixels mm^{-1}	$R_{int} = 0.053$
Absorption correction: multi-scan *SADABS*	$\theta_{max} = 25.4°$, $\theta_{min} = 1.3°$
$T_{min} = 0.73$, $T_{max} = 0.90$	$h = -7\rightarrow7$
14467 measured reflections	$k = -20\rightarrow20$
5540 independent reflections	$l = -18\rightarrow18$
3015 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites

$R[F^2 > 2\sigma(F^2)] = 0.054$	Only H-atom coordinates refined
$wR(F^2) = 0.183$	$w = 1/[\sigma^2(F_o^2) + (0.0839P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{max} < 0.001$
5540 reflections	$\Delta\rho_{max} = 0.57$ e Å^{-3}
415 parameters	$\Delta\rho_{min} = -0.33$ e Å^{-3}
13 restraints	Absolute structure: Flack H D (1983), Acta Cryst. A39, 876-881
Primary atom site location: structure-invariant direct methods	Absolute structure parameter: 0.016 (14)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F*set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.0069 (3)	0.90386 (7)	0.10343 (8)	0.1044 (5)
Br2	0.5209 (2)	0.09031 (7)	0.10486 (8)	0.0980 (5)
C1	−0.0332 (18)	0.8914 (6)	0.2265 (7)	0.057 (3)
C2	−0.2286 (17)	0.9157 (6)	0.2628 (7)	0.067 (3)
H2	−0.3402	0.9365	0.227	0.08*
C3	−0.2598 (14)	0.9097 (5)	0.3504 (6)	0.049 (2)
H3	−0.3926	0.9254	0.375	0.058*
C4	−0.0904 (14)	0.8796 (5)	0.4023 (6)	0.042 (2)
C5	0.1091 (15)	0.8555 (5)	0.3669 (8)	0.056 (3)
H5	0.2221	0.835	0.4023	0.067*
C6	0.1348 (16)	0.8629 (6)	0.2765 (8)	0.061 (3)
H6	0.2674	0.8482	0.2509	0.073*
C7	−0.2875 (13)	0.8466 (5)	0.5404 (7)	0.044 (2)
C8	−0.2581 (12)	0.8633 (4)	0.6366 (6)	0.038 (2)
H8	−0.3711	0.8994	0.6566	0.046*
C9	−0.0238 (13)	0.8980 (5)	0.6447 (7)	0.046 (2)
H9	−0.0192	0.9442	0.6814	0.055*

C10	0.0433 (13)	0.9132 (5)	0.5526 (6)	0.041 (2)
C11	0.1215 (13)	0.8283 (5)	0.6861 (6)	0.047 (2)
H11	0.2454	0.8179	0.6469	0.057*
C12	−0.2509 (13)	0.7913 (5)	0.6940 (6)	0.045 (2)
H12A	−0.2809	0.8039	0.7546	0.053*
H12B	−0.3597	0.754	0.6735	0.053*
C13	0.2171 (11)	0.8494 (5)	0.7751 (5)	0.0471 (19)
C14	0.2006 (15)	0.8004 (5)	0.8459 (6)	0.064 (2)
H14	0.121	0.7549	0.8405	0.077*
C15	0.3004 (19)	0.8190 (6)	0.9228 (8)	0.087 (3)
H15	0.2899	0.787	0.9713	0.105*
C16	0.4127 (18)	0.8832 (8)	0.9277 (7)	0.089 (4)
H16	0.4841	0.8969	0.98	0.107*
C17	0.4257 (19)	0.9312 (7)	0.8549 (8)	0.090 (4)
H17	0.5069	0.9764	0.8603	0.109*
C18	0.4737 (16)	0.0956 (7)	0.2263 (6)	0.061 (3)
C19	0.2751 (15)	0.0706 (5)	0.2607 (7)	0.058 (3)
H19	0.161	0.0534	0.2237	0.069*
C20	0.2470 (14)	0.0715 (5)	0.3517 (7)	0.053 (3)
H20	0.115	0.0537	0.3752	0.063*
C21	0.4156 (12)	0.0988 (5)	0.4068 (6)	0.042 (2)
C22	0.6136 (13)	0.1233 (4)	0.3684 (8)	0.048 (3)
H22	0.7278	0.1411	0.4051	0.058*
C23	0.6470 (15)	0.1226 (6)	0.2818 (8)	0.056 (3)
H23	0.7808	0.1393	0.2589	0.067*
C25	0.5368 (15)	0.0639 (5)	0.5566 (6)	0.048 (2)
C26	0.4603 (12)	0.0837 (5)	0.6451 (6)	0.045 (2)
H26	0.4648	0.0383	0.6829	0.054*
C27	0.2246 (13)	0.1126 (5)	0.6356 (7)	0.051 (2)
H27	0.1153	0.0738	0.6522	0.061*
C28	0.2038 (15)	0.1339 (5)	0.5395 (7)	0.050 (3)
C29	0.2200 (14)	0.1815 (6)	0.6950 (7)	0.060 (3)
H29	0.1094	0.2177	0.6715	0.072*
C30	0.5891 (14)	0.1486 (5)	0.6881 (7)	0.062 (3)
H30A	0.6326	0.1348	0.7477	0.074*
H30B	0.7224	0.1596	0.6556	0.074*
C31	0.1646 (14)	0.1645 (6)	0.7895 (7)	0.070 (2)
C32	0.238 (3)	0.2115 (8)	0.8574 (8)	0.126 (5)
H32	0.3281	0.2536	0.846	0.151*
C33	0.178 (4)	0.1952 (10)	0.9402 (10)	0.155 (7)
H33	0.2223	0.2263	0.9868	0.186*
C34	0.055 (3)	0.1335 (11)	0.9528 (10)	0.145 (6)
H34	0.0086	0.123	1.0094	0.174*

C35	−0.0098 (19)	0.0827 (12)	0.8848 (10)	0.133 (6)
H35	−0.0884	0.038	0.8961	0.159*
N1	−0.1102 (11)	0.8776 (4)	0.4956 (5)	0.0398 (18)
N2	−0.0245 (10)	0.7616 (4)	0.6855 (5)	0.050 (2)
H2A	0.0145	0.7143	0.6812	0.061*
N3	0.3282 (11)	0.9155 (4)	0.7786 (4)	0.0608 (18)
N4	0.3881 (10)	0.1007 (4)	0.4972 (5)	0.0393 (16)
N5	0.4405 (12)	0.2163 (4)	0.6884 (6)	0.067 (2)
H5A	0.475	0.264	0.6853	0.08*
N6	0.0486 (13)	0.1024 (7)	0.8013 (6)	0.112 (3)
O1	−0.4356 (9)	0.8097 (3)	0.5035 (5)	0.0536 (17)
O2	0.2059 (10)	0.9480 (3)	0.5302 (5)	0.0558 (18)
O3	0.0594 (8)	0.1701 (3)	0.5026 (5)	0.0511 (16)
O4	0.6979 (10)	0.0303 (3)	0.5342 (5)	0.0542 (17)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.1473 (13)	0.1117 (11)	0.0548 (9)	−0.0157 (9)	0.0126 (8)	0.0019 (8)
Br2	0.1167 (10)	0.1174 (11)	0.0601 (9)	−0.0122 (8)	0.0041 (7)	0.0002 (8)
C1	0.066 (7)	0.050 (6)	0.056 (8)	0.005 (5)	0.002 (6)	−0.004 (5)
C2	0.070 (7)	0.069 (7)	0.060 (8)	0.008 (6)	−0.019 (6)	0.005 (7)
C3	0.040 (5)	0.049 (5)	0.056 (6)	0.003 (4)	0.004 (5)	0.003 (6)
C4	0.042 (5)	0.036 (5)	0.047 (6)	−0.010 (4)	−0.005 (4)	−0.004 (4)
C5	0.044 (6)	0.054 (6)	0.070 (8)	0.008 (4)	0.006 (5)	−0.002 (6)
C6	0.054 (7)	0.068 (7)	0.061 (8)	−0.011 (5)	0.009 (6)	−0.007 (6)
C7	0.021 (4)	0.036 (5)	0.074 (7)	−0.004 (4)	0.004 (4)	−0.009 (5)
C8	0.029 (4)	0.024 (4)	0.062 (6)	0.002 (3)	0.012 (4)	−0.004 (4)
C9	0.039 (5)	0.044 (6)	0.055 (6)	−0.011 (4)	0.005 (4)	0.006 (5)
C10	0.035 (5)	0.029 (4)	0.058 (6)	0.002 (4)	0.006 (4)	−0.005 (5)
C11	0.038 (4)	0.055 (6)	0.050 (6)	0.009 (4)	0.003 (4)	0.005 (4)
C12	0.042 (5)	0.042 (5)	0.050 (6)	−0.010 (4)	0.003 (4)	−0.002 (4)
C13	0.037 (4)	0.064 (5)	0.042 (5)	0.007 (4)	0.013 (3)	−0.003 (4)
C14	0.082 (6)	0.064 (5)	0.045 (6)	0.007 (5)	−0.002 (5)	−0.001 (5)
C15	0.112 (9)	0.077 (7)	0.073 (8)	−0.007 (7)	−0.003 (7)	−0.003 (6)
C16	0.072 (7)	0.158 (12)	0.036 (6)	0.022 (7)	−0.011 (5)	0.005 (7)
C17	0.086 (8)	0.112 (9)	0.072 (8)	−0.018 (6)	−0.018 (6)	−0.013 (7)
C18	0.066 (7)	0.061 (6)	0.055 (7)	0.023 (6)	0.001 (5)	0.007 (6)
C19	0.045 (6)	0.051 (6)	0.076 (9)	−0.004 (4)	−0.012 (5)	−0.002 (6)
C20	0.043 (5)	0.039 (5)	0.075 (8)	−0.008 (4)	−0.008 (5)	0.007 (5)
C21	0.035 (5)	0.028 (4)	0.062 (7)	0.000 (4)	0.001 (4)	0.000 (5)
C22	0.031 (5)	0.035 (5)	0.078 (8)	0.008 (3)	−0.002 (5)	0.006 (5)
C23	0.046 (6)	0.062 (7)	0.060 (8)	−0.005 (4)	0.007 (5)	0.003 (5)
C25	0.041 (5)	0.049 (6)	0.055 (7)	0.003 (4)	−0.011 (5)	−0.001 (5)

C26	0.038 (5)	0.044 (5)	0.054 (6)	0.007 (4)	−0.006 (4)	0.012 (5)
C27	0.044 (5)	0.046 (6)	0.061 (7)	0.006 (4)	−0.004 (4)	0.007 (5)
C28	0.039 (6)	0.048 (5)	0.065 (7)	−0.018 (4)	0.001 (5)	−0.007 (5)
C29	0.038 (5)	0.062 (6)	0.081 (8)	0.011 (4)	−0.009 (5)	0.001 (5)
C30	0.035 (5)	0.073 (7)	0.077 (8)	0.013 (5)	−0.008 (5)	0.003 (6)
C31	0.051 (5)	0.092 (7)	0.067 (6)	0.021 (4)	−0.002 (4)	0.014 (5)
C32	0.210 (15)	0.100 (9)	0.068 (7)	0.017 (7)	0.005 (8)	−0.008 (6)
C33	0.26 (2)	0.141 (12)	0.065 (7)	0.054 (11)	0.009 (10)	0.017 (8)
C34	0.115 (12)	0.243 (19)	0.078 (8)	0.052 (11)	0.006 (8)	0.059 (9)
C35	0.068 (7)	0.230 (17)	0.101 (9)	−0.001 (9)	0.011 (8)	0.069 (10)
N1	0.034 (4)	0.031 (4)	0.054 (5)	0.000 (3)	−0.008 (4)	−0.006 (3)
N2	0.043 (4)	0.031 (4)	0.077 (6)	0.007 (3)	−0.001 (4)	0.004 (4)
N3	0.055 (4)	0.078 (5)	0.049 (4)	−0.019 (4)	−0.002 (3)	−0.004 (4)
N4	0.032 (4)	0.036 (4)	0.050 (5)	0.002 (3)	0.009 (3)	0.001 (4)
N5	0.056 (5)	0.051 (5)	0.093 (7)	−0.007 (4)	−0.006 (4)	−0.015 (4)
N6	0.061 (5)	0.181 (9)	0.093 (6)	−0.031 (6)	−0.006 (4)	0.046 (6)
O1	0.039 (4)	0.047 (3)	0.074 (5)	−0.006 (3)	−0.011 (3)	0.000 (3)
O2	0.047 (4)	0.056 (4)	0.065 (5)	−0.022 (3)	0.010 (3)	−0.010 (3)
O3	0.028 (3)	0.061 (4)	0.064 (4)	0.007 (3)	−0.003 (3)	0.004 (3)
O4	0.040 (3)	0.054 (4)	0.068 (5)	0.020 (3)	−0.001 (3)	−0.003 (3)

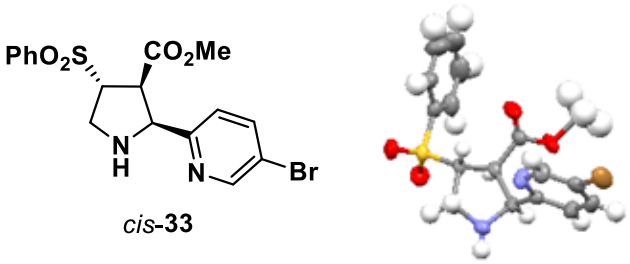
Geometric parameters (Å, º)

Br1—C1	1.910 (10)	C18—C19	1.384 (13)
Br2—C18	1.881 (9)	C18—C23	1.410 (14)
C1—C6	1.349 (14)	C19—C20	1.401 (13)
C1—C2	1.375 (13)	C19—H19	0.93
C2—C3	1.357 (13)	C20—C21	1.389 (12)
C2—H2	0.93	C20—H20	0.93
C3—C4	1.381 (11)	C21—N4	1.393 (10)
C3—H3	0.93	C21—C22	1.402 (12)
C4—C5	1.390 (13)	C22—C23	1.340 (14)
C4—N1	1.430 (12)	C22—H22	0.93
C5—C6	1.395 (14)	C23—H23	0.93
C5—H5	0.93	C25—O4	1.187 (10)
C6—H6	0.93	C25—N4	1.415 (11)
C7—O1	1.226 (9)	C25—C26	1.476 (13)
C7—N1	1.387 (11)	C26—C27	1.508 (11)
C7—C8	1.502 (12)	C26—C30	1.514 (12)
C8—C12	1.532 (12)	C26—H26	0.98
C8—C9	1.536 (11)	C27—C29	1.506 (14)
C8—H8	0.98	C27—C28	1.515 (13)
C9—C10	1.493 (13)	C27—H27	0.98
C9—C11	1.618 (12)	C28—O3	1.205 (11)

C9—H9	0.98	C28—N4	1.416 (12)
C10—O2	1.205 (9)	C29—N5	1.463 (11)
C10—N1	1.400 (10)	C29—C31	1.514 (13)
C11—N2	1.459 (10)	C29—H29	0.98
C11—C13	1.510 (11)	C30—N5	1.482 (11)
C11—H11	0.98	C30—H30A	0.97
C12—N2	1.464 (10)	C30—H30B	0.97
C12—H12A	0.97	C31—N6	1.302 (13)
C12—H12B	0.97	C31—C32	1.387 (15)
C13—N3	1.333 (10)	C32—C33	1.350 (17)
C13—C14	1.383 (11)	C32—H32	0.93
C14—C15	1.346 (13)	C33—C34	1.32 (2)
C14—H14	0.93	C33—H33	0.93
C15—C16	1.309 (15)	C34—C35	1.41 (2)
C15—H15	0.93	C34—H34	0.93
C16—C17	1.394 (16)	C35—N6	1.371 (15)
C16—H16	0.93	C35—H35	0.93
C17—N3	1.322 (13)	N2—H2A	0.86
C17—H17	0.93	N5—H5A	0.86
C6—C1—C2	121.5 (10)	C21—C20—H20	119.9
C6—C1—Br1	119.4 (8)	C19—C20—H20	119.9
C2—C1—Br1	119.0 (8)	C20—C21—N4	120.6 (8)
C3—C2—C1	120.5 (9)	C20—C21—C22	117.9 (10)
C3—C2—H2	119.7	N4—C21—C22	121.6 (8)
C1—C2—H2	119.7	C23—C22—C21	123.5 (9)
C2—C3—C4	118.7 (9)	C23—C22—H22	118.2
C2—C3—H3	120.7	C21—C22—H22	118.2
C4—C3—H3	120.7	C22—C23—C18	118.2 (9)
C3—C4—C5	121.6 (9)	C22—C23—H23	120.9
C3—C4—N1	120.3 (8)	C18—C23—H23	120.9
C5—C4—N1	118.0 (8)	O4—C25—N4	123.3 (9)
C4—C5—C6	118.0 (9)	O4—C25—C26	130.4 (8)
C4—C5—H5	121.0	N4—C25—C26	106.0 (8)
C6—C5—H5	121.0	C25—C26—C27	107.4 (8)
C1—C6—C5	119.8 (10)	C25—C26—C30	114.0 (8)
C1—C6—H6	120.1	C27—C26—C30	105.2 (7)
C5—C6—H6	120.1	C25—C26—H26	110.0
O1—C7—N1	122.5 (9)	C27—C26—H26	110.0
O1—C7—C8	128.3 (8)	C30—C26—H26	110.0
N1—C7—C8	109.2 (7)	C29—C27—C26	103.7 (7)
C7—C8—C12	113.6 (7)	C29—C27—C28	112.6 (8)
C7—C8—C9	104.2 (7)	C26—C27—C28	103.6 (7)

C12—C8—C9	105.2 (6)	C29—C27—H27	112.1
C7—C8—H8	111.1	C26—C27—H27	112.1
C12—C8—H8	111.1	C28—C27—H27	112.1
C9—C8—H8	111.1	O3—C28—N4	124.3 (10)
C10—C9—C8	104.9 (8)	O3—C28—C27	128.8 (9)
C10—C9—C11	110.2 (7)	N4—C28—C27	106.9 (8)
C8—C9—C11	102.8 (6)	N5—C29—C27	105.2 (8)
C10—C9—H9	112.7	N5—C29—C31	111.3 (8)
C8—C9—H9	112.7	C27—C29—C31	115.0 (9)
C11—C9—H9	112.7	N5—C29—H29	108.3
O2—C10—N1	125.1 (9)	C27—C29—H29	108.3
O2—C10—C9	126.2 (8)	C31—C29—H29	108.3
N1—C10—C9	108.6 (7)	N5—C30—C26	107.2 (6)
N2—C11—C13	114.7 (7)	N5—C30—H30A	110.3
N2—C11—C9	106.2 (6)	C26—C30—H30A	110.3
C13—C11—C9	111.1 (7)	N5—C30—H30B	110.3
N2—C11—H11	108.2	C26—C30—H30B	110.3
C13—C11—H11	108.2	H30A—C30—H30B	108.5
C9—C11—H11	108.2	N6—C31—C32	123.6 (11)
N2—C12—C8	104.8 (6)	N6—C31—C29	115.0 (9)
N2—C12—H12A	110.8	C32—C31—C29	121.4 (10)
C8—C12—H12A	110.8	C33—C32—C31	119.0 (15)
N2—C12—H12B	110.8	C33—C32—H32	120.5
C8—C12—H12B	110.8	C31—C32—H32	120.5
H12A—C12—H12B	108.9	C34—C33—C32	118.0 (18)
N3—C13—C14	123.2 (8)	C34—C33—H33	121.0
N3—C13—C11	115.3 (7)	C32—C33—H33	121.0
C14—C13—C11	121.3 (8)	C33—C34—C35	123.3 (16)
C15—C14—C13	119.5 (9)	C33—C34—H34	118.3
C15—C14—H14	120.2	C35—C34—H34	118.3
C13—C14—H14	120.2	N6—C35—C34	116.9 (17)
C16—C15—C14	118.5 (11)	N6—C35—H35	121.5
C16—C15—H15	120.8	C34—C35—H35	121.5
C14—C15—H15	120.8	C7—N1—C10	111.7 (8)
C15—C16—C17	120.4 (11)	C7—N1—C4	125.4 (7)
C15—C16—H16	119.8	C10—N1—C4	122.7 (7)
C17—C16—H16	119.8	C11—N2—C12	106.0 (6)
N3—C17—C16	123.1 (11)	C11—N2—H2A	127.0
N3—C17—H17	118.5	C12—N2—H2A	127.0
C16—C17—H17	118.5	C17—N3—C13	115.3 (8)
C19—C18—C23	120.7 (9)	C21—N4—C25	122.5 (7)
C19—C18—Br2	120.4 (8)	C21—N4—C28	124.7 (7)
C23—C18—Br2	118.9 (8)	C25—N4—C28	112.6 (8)

C18—C19—C20	119.6 (8)	C29—N5—C30	102.4 (7)
C18—C19—H19	120.2	C29—N5—H5A	128.8
C20—C19—H19	120.2	C30—N5—H5A	128.8
C21—C20—C19	120.2 (9)	C31—N6—C35	118.9 (13)



cis-**33**

Computing details
Data collection: Bruker Instrument Service v2010.9.0.0; cell refinement: *SAINT* V7.68A (Bruker AXS, 2009); data reduction: *SAINT* V7.68A (Bruker AXS, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008).

Crystal data

$C_{17}H_{17}BrN_2O_4S$	$F(000)$ = 432
M_r = 425.30	D_x = 1.570 Mg m^{-3}
Monoclinic, $P2_1$	Cell parameters from 7255 reflections
a = 12.6698 (6) Å	θ = 3.2–25.2°
b = 5.9884 (4) Å	μ = 2.42 mm^{-1}
c = 12.7916 (8) Å	T = 296 K
β = 112.067 (2)°	Needle, clear colourless
V = 899.43 (9) Å^3	0.30 × 0.08 × 0.07 mm
Z = 2	

Data collection

Detector resolution: 8.3333 pixels mm^{-1}	R_{int} = 0.028
Absorption correction: multi-scan *SADABS*	θ_{max} = 25.4°, θ_{min} = 1.7°
T_{min} = 0.68, T_{max} = 0.85	h = −13→14
14235 measured reflections	k = −7→7
3208 independent reflections	l = −15→15
2961 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites

$R[F^2 > 2\sigma(F^2)] = 0.028$	Only H-atom coordinates refined
$wR(F^2) = 0.100$	$w = 1/[\sigma^2(F_o^2) + (0.0598P)^2 + 0.1474P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.18$	$(\Delta/\sigma)_{max} = 0.004$
3208 reflections	$\Delta\rho_{max} = 0.37$ e Å^{-3}
227 parameters	$\Delta\rho_{min} = -0.43$ e Å^{-3}
1 restraint	Absolute structure: Flack H D (1983), Acta Cryst. A39, 876-881
Primary atom site location: structure-invariant direct methods	Absolute structure parameter: −0.012 (9)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F*set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	−0.28385 (3)	0.58697 (9)	0.29556 (4)	0.06607 (18)
C1	−0.0575 (4)	0.5051 (7)	0.3108 (4)	0.0524 (10)
H1	−0.0876	0.369	0.2782	0.063*
C2	−0.1294 (3)	0.6603 (7)	0.3288 (3)	0.0445 (9)
C3	−0.0881 (4)	0.8624 (7)	0.3743 (3)	0.0508 (10)
H3	−0.1354	0.9696	0.3864	0.061*
C4	0.0272 (3)	0.9031 (7)	0.4021 (3)	0.0449 (8)
H4	0.0583	1.0403	0.4321	0.054*
C5	0.0954 (3)	0.7383 (6)	0.3850 (3)	0.0366 (8)
C6	0.2217 (3)	0.7723 (6)	0.4179 (3)	0.0357 (7)
H6	0.2416	0.9263	0.4437	0.043*
C7	0.2617 (3)	0.7221 (5)	0.3185 (3)	0.0318 (7)
H7	0.3314	0.8074	0.3309	0.038*
C8	0.1742 (3)	0.7856 (6)	0.2051 (3)	0.0375 (8)
C9	0.0568 (4)	1.0823 (8)	0.1045 (4)	0.0731 (14)
H9A	0.0784	1.0644	0.0406	0.11*

H9B	0.0434	1.2375	0.1138	0.11*
H9C	−0.0115	0.9989	0.0925	0.11*
C10	0.2918 (3)	0.4743 (5)	0.3318 (3)	0.0327 (7)
H10	0.2279	0.3882	0.2795	0.039*
C11	0.3064 (3)	0.4165 (7)	0.4548 (3)	0.0454 (8)
H11A	0.252	0.3026	0.455	0.055*
H11B	0.3825	0.3602	0.4961	0.055*
C12	0.3863 (3)	0.4815 (6)	0.1656 (3)	0.0457 (9)
C13	0.4192 (4)	0.6866 (7)	0.1391 (4)	0.0575 (11)
H13	0.4584	0.7885	0.1951	0.069*
C14	0.3912 (5)	0.7357 (10)	0.0244 (5)	0.0822 (18)
H14	0.4129	0.8715	0.0034	0.099*
C15	0.3321 (6)	0.5846 (14)	−0.0564 (5)	0.0920 (18)
H15	0.3128	0.6197	−0.1322	0.11*
C16	0.3016 (6)	0.3864 (13)	−0.0279 (5)	0.0893 (18)
H16	0.2615	0.2857	−0.0841	0.107*
C17	0.3289 (4)	0.3303 (8)	0.0834 (4)	0.0634 (13)
H17	0.3086	0.1915	0.1027	0.076*
N1	0.0532 (3)	0.5422 (5)	0.3383 (3)	0.0495 (8)
N2	0.2873 (3)	0.6180 (5)	0.5071 (2)	0.0421 (7)
H2	0.3105	0.643	0.5784	0.051*
O1	0.1474 (2)	1.0011 (4)	0.2050 (2)	0.0521 (7)
O2	0.1318 (3)	0.6649 (5)	0.1263 (2)	0.0630 (9)
O3	0.5099 (2)	0.5454 (5)	0.3787 (2)	0.0558 (7)
O4	0.4336 (3)	0.1692 (4)	0.3186 (3)	0.0530 (7)
S1	0.41752 (7)	0.40721 (15)	0.30826 (7)	0.0381 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0361 (2)	0.0982 (4)	0.0681 (3)	−0.0022 (2)	0.02437 (18)	0.0135 (3)
C1	0.043 (2)	0.045 (2)	0.067 (3)	−0.0085 (17)	0.0168 (19)	−0.0073 (18)
C2	0.033 (2)	0.065 (2)	0.0369 (18)	0.0009 (16)	0.0146 (15)	0.0102 (16)
C3	0.054 (3)	0.053 (2)	0.051 (2)	0.0148 (19)	0.0269 (19)	0.0017 (18)
C4	0.043 (2)	0.0393 (17)	0.052 (2)	0.0007 (18)	0.0180 (16)	−0.0074 (17)
C5	0.039 (2)	0.0352 (18)	0.0349 (17)	0.0021 (15)	0.0124 (14)	0.0001 (14)
C6	0.036 (2)	0.0276 (15)	0.0385 (17)	−0.0034 (14)	0.0088 (14)	−0.0060 (14)
C7	0.0208 (17)	0.0296 (16)	0.0405 (18)	−0.0043 (13)	0.0065 (13)	−0.0011 (13)
C8	0.036 (2)	0.0323 (18)	0.0399 (18)	0.0024 (15)	0.0088 (15)	0.0043 (15)
C9	0.068 (3)	0.047 (2)	0.068 (3)	0.007 (2)	−0.016 (2)	0.017 (2)
C10	0.0193 (16)	0.0312 (16)	0.0440 (19)	−0.0005 (12)	0.0077 (13)	0.0004 (13)
C11	0.039 (2)	0.0425 (19)	0.055 (2)	0.0077 (17)	0.0176 (16)	0.0128 (18)
C12	0.046 (2)	0.0453 (19)	0.050 (2)	0.0090 (16)	0.0222 (18)	−0.0001 (16)
C13	0.052 (3)	0.051 (2)	0.074 (3)	0.0046 (19)	0.028 (2)	0.009 (2)

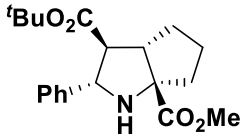
C14	0.093 (4)	0.073 (3)	0.102 (5)	0.020 (3)	0.060 (4)	0.034 (3)
C15	0.121 (5)	0.102 (4)	0.066 (3)	0.027 (5)	0.050 (3)	0.016 (4)
C16	0.105 (5)	0.105 (5)	0.060 (3)	0.006 (4)	0.033 (3)	−0.018 (3)
C17	0.072 (3)	0.063 (3)	0.057 (3)	0.000 (2)	0.025 (2)	−0.012 (2)
N1	0.0358 (17)	0.0388 (19)	0.073 (2)	−0.0057 (13)	0.0190 (15)	−0.0138 (15)
N2	0.0418 (17)	0.0434 (17)	0.0347 (14)	−0.0008 (14)	0.0070 (12)	0.0003 (14)
O1	0.0541 (17)	0.0287 (12)	0.0503 (15)	0.0043 (11)	−0.0069 (12)	0.0064 (11)
O2	0.065 (2)	0.0505 (17)	0.0466 (15)	0.0078 (14)	−0.0097 (14)	−0.0087 (13)
O3	0.0259 (13)	0.067 (2)	0.0667 (17)	−0.0091 (13)	0.0085 (11)	−0.0150 (15)
O4	0.0532 (18)	0.0393 (14)	0.0661 (18)	0.0144 (12)	0.0219 (14)	0.0056 (12)
S1	0.0280 (4)	0.0352 (4)	0.0472 (5)	0.0031 (4)	0.0098 (3)	−0.0015 (4)

Geometric parameters (Å, º)

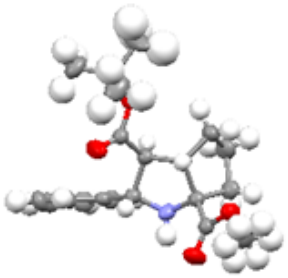
Br1—C2	1.891 (4)	C9—H9C	0.96
C1—N1	1.331 (5)	C10—C11	1.553 (5)
C1—C2	1.380 (6)	C10—S1	1.775 (4)
C1—H1	0.93	C10—H10	0.98
C2—C3	1.359 (6)	C11—N2	1.443 (5)
C3—C4	1.389 (6)	C11—H11A	0.97
C3—H3	0.93	C11—H11B	0.97
C4—C5	1.382 (5)	C12—C17	1.371 (6)
C4—H4	0.93	C12—C13	1.379 (6)
C5—N1	1.334 (5)	C12—S1	1.773 (4)
C5—C6	1.508 (5)	C13—C14	1.405 (7)
C6—N2	1.461 (5)	C13—H13	0.93
C6—C7	1.564 (5)	C14—C15	1.366 (10)
C6—H6	0.98	C14—H14	0.93
C7—C8	1.506 (5)	C15—C16	1.340 (11)
C7—C10	1.526 (4)	C15—H15	0.93
C7—H7	0.98	C16—C17	1.374 (8)
C8—O2	1.192 (5)	C16—H16	0.93
C8—O1	1.334 (4)	C17—H17	0.93
C9—O1	1.448 (4)	N2—H2	0.86
C9—H9A	0.96	O3—S1	1.440 (3)
C9—H9B	0.96	O4—S1	1.439 (3)
N1—C1—C2	122.7 (4)	C7—C10—H10	109.2
N1—C1—H1	118.7	C11—C10—H10	109.2
C2—C1—H1	118.7	S1—C10—H10	109.2
C3—C2—C1	119.9 (4)	N2—C11—C10	107.8 (3)
C3—C2—Br1	120.2 (3)	N2—C11—H11A	110.1
C1—C2—Br1	119.9 (3)	C10—C11—H11A	110.1
C2—C3—C4	117.7 (4)	N2—C11—H11B	110.1

C2—C3—H3	121.1	C10—C11—H11B	110.1
C4—C3—H3	121.1	H11A—C11—H11B	108.5
C3—C4—C5	119.6 (4)	C17—C12—C13	121.5 (4)
C3—C4—H4	120.2	C17—C12—S1	118.2 (3)
C5—C4—H4	120.2	C13—C12—S1	120.3 (3)
N1—C5—C4	122.0 (3)	C12—C13—C14	117.5 (5)
N1—C5—C6	116.6 (3)	C12—C13—H13	121.3
C4—C5—C6	121.4 (3)	C14—C13—H13	121.3
N2—C6—C5	111.4 (3)	C15—C14—C13	120.2 (5)
N2—C6—C7	104.5 (3)	C15—C14—H14	119.9
C5—C6—C7	112.4 (3)	C13—C14—H14	119.9
N2—C6—H6	109.5	C16—C15—C14	120.8 (5)
C5—C6—H6	109.5	C16—C15—H15	119.6
C7—C6—H6	109.5	C14—C15—H15	119.6
C8—C7—C10	114.6 (3)	C15—C16—C17	120.8 (6)
C8—C7—C6	112.9 (3)	C15—C16—H16	119.6
C10—C7—C6	103.9 (3)	C17—C16—H16	119.6
C8—C7—H7	108.4	C16—C17—C12	119.1 (5)
C10—C7—H7	108.4	C16—C17—H17	120.4
C6—C7—H7	108.4	C12—C17—H17	120.4
O2—C8—O1	123.5 (3)	C1—N1—C5	118.0 (3)
O2—C8—C7	126.6 (3)	C11—N2—C6	108.2 (3)
O1—C8—C7	109.9 (3)	C11—N2—H2	125.9
O1—C9—H9A	109.5	C6—N2—H2	125.9
O1—C9—H9B	109.5	C8—O1—C9	116.3 (3)
H9A—C9—H9B	109.5	O3—S1—O4	117.27 (19)
O1—C9—H9C	109.5	O3—S1—C12	108.34 (19)
H9A—C9—H9C	109.5	O4—S1—C12	108.20 (18)
H9B—C9—H9C	109.5	O3—S1—C10	109.50 (17)
C7—C10—C11	105.0 (3)	O4—S1—C10	108.28 (17)
C7—C10—S1	113.8 (3)	C12—S1—C10	104.51 (17)
C11—C10—S1	110.4 (2)		

Capítulo 3: Catalytic asymmetric synthesis of azabicycles by 1,3-dipolar cycloaddition/intramolecular alkylation



(±)-*exo*-**54a**



Computing details

Data collection: Bruker Instrument Service v2010.9.0.0; cell refinement: *SAINT* V7.68A (Bruker AXS, 2009); data reduction: *SAINT* V7.68A (Bruker AXS, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008).

Crystal data

$C_{20}H_{27}NO_4$	$F(000)$ = 1488
M_r = 345.43	D_x = 1.211 Mg m^{-3}
Monoclinic, $C2/c$	Cell parameters from 7850 reflections
a = 30.1898 (4) Å	θ = 2.8–25.6°
b = 6.3221 (1) Å	μ = 0.08 mm^{-1}
c = 21.9555 (3) Å	T = 296 K
β = 115.323 (1)°	Prismatic, clear colourless
V = 3787.83 (9) Å^3	0.40 × 0.16 × 0.12 mm
Z = 8	

Data collection

Bruker Kappa Apex II diffractometer	2656 reflections with $I > 2\sigma(I)$
Detector resolution: 8.3333 pixels mm^{-1}	R_{int} = 0.033
Absorption correction: multi-scan *SADABS*	θ_{max} = 25.4°, θ_{min} = 2.0°
T_{min} = 0.88, T_{max} = 0.99	$h = -36 \rightarrow 36$
24629 measured reflections	$k = -7 \rightarrow 7$
3473 independent reflections	$l = -26 \rightarrow 26$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.043	Hydrogen site location: inferred from neighbouring sites

$wR(F^2)$ = 0.146	Only H-atom coordinates refined
S = 1.07	$w = 1/[\sigma^2(F_o^2) + (0.0788P)^2 + 1.7115P]$ where $P = (F_o^2 + 2F_c^2)/3$
3473 reflections	$(\Delta/\sigma)_{max} < 0.001$
233 parameters	$\Delta\rho_{max}$ = 0.25 e Å^{-3}
0 restraints	$\Delta\rho_{min}$ = −0.25 e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F*set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
C1	0.02622 (6)	0.1733 (3)	0.11965 (8)	0.0391 (4)	
C2	0.00669 (7)	−0.0433 (3)	0.12971 (10)	0.0516 (5)	
H2A	−0.0198	−0.0258	0.1432	0.062*	
H2B	−0.005	−0.1264	0.0887	0.062*	
C3	0.05082 (8)	−0.1476 (3)	0.18536 (11)	0.0629 (6)	
H3A	0.0407	−0.258	0.2074	0.075*	
H3B	0.0725	−0.2077	0.1678	0.075*	
C4	0.07541 (7)	0.0332 (3)	0.23345 (9)	0.0550 (5)	
H4A	0.1092	−0.001	0.263	0.066*	
H4B	0.0581	0.0663	0.2606	0.066*	
C5	0.07261 (6)	0.2168 (3)	0.18679 (8)	0.0382 (4)	
H5	0.0694	0.3517	0.2065	0.046*	
C6	0.11476 (6)	0.2267 (3)	0.16500 (8)	0.0378 (4)	
H6	0.1292	0.0854	0.1693	0.045*	
C7	0.08968 (6)	0.2868 (3)	0.09018 (8)	0.0404 (4)	
H7	0.0819	0.4381	0.0855	0.048*	
C8	0.11873 (6)	0.2309 (3)	0.05095 (8)	0.0418 (4)	
C9	0.15034 (7)	0.3781 (3)	0.04397 (9)	0.0529 (5)	
H9	0.1532	0.5119	0.0629	0.063*	
C10	0.17773 (8)	0.3271 (4)	0.00902 (11)	0.0628 (6)	

H10	0.1989	0.4266	0.0048	0.075*	
C11	0.17382 (8)	0.1311 (4)	−0.01925 (10)	0.0641 (6)	
H11	0.1921	0.0978	−0.043	0.077*	
C12	0.14280 (8)	−0.0161 (4)	−0.01244 (10)	0.0617 (6)	
H12	0.1401	−0.1494	−0.0316	0.074*	
C13	0.11562 (7)	0.0328 (3)	0.02278 (9)	0.0516 (5)	
H13	0.095	−0.0686	0.0276	0.062*	
C14	−0.01306 (6)	0.3412 (3)	0.10366 (8)	0.0410 (4)	
C15	−0.06584 (8)	0.5072 (4)	0.14378 (12)	0.0655 (6)	
H15A	−0.0714	0.513	0.1837	0.098*	0.5
H15B	−0.0948	0.4557	0.1068	0.098*	0.5
H15C	−0.0583	0.6462	0.1334	0.098*	0.5
H15D	−0.0783	0.5636	0.0989	0.098*	0.5
H15E	−0.0548	0.6209	0.1758	0.098*	0.5
H15F	−0.0913	0.4303	0.1492	0.098*	0.5
C16	0.15403 (6)	0.3789 (3)	0.20845 (8)	0.0418 (4)	
C17	0.21503 (7)	0.4205 (3)	0.32628 (9)	0.0514 (5)	
C18	0.22538 (13)	0.2761 (5)	0.38504 (12)	0.1197 (14)	
H18A	0.1953	0.245	0.3883	0.18*	
H18B	0.2478	0.344	0.4257	0.18*	
H18C	0.2397	0.1471	0.3787	0.18*	
C19	0.19364 (9)	0.6268 (5)	0.33589 (13)	0.0865 (8)	
H19A	0.1881	0.719	0.2986	0.13*	
H19B	0.2161	0.6925	0.3769	0.13*	
H19C	0.1631	0.6	0.3383	0.13*	
C20	0.25956 (7)	0.4581 (4)	0.31386 (12)	0.0715 (7)	
H20A	0.2736	0.3248	0.3105	0.107*	
H20B	0.2832	0.5381	0.3505	0.107*	
H20C	0.2504	0.5356	0.2726	0.107*	
N1	0.04433 (5)	0.1626 (3)	0.06805 (8)	0.0476 (4)	
O1	−0.02556 (5)	0.3674 (2)	0.15488 (7)	0.0570 (4)	
O2	−0.03156 (6)	0.4361 (3)	0.05240 (7)	0.0694 (5)	
O3	0.17778 (4)	0.2987 (2)	0.27001 (6)	0.0529 (4)	
O4	0.16153 (6)	0.5490 (2)	0.19109 (7)	0.0714 (5)	
H1	0.0223 (9)	0.212 (4)	0.0309 (12)	0.067 (7)*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0367 (8)	0.0436 (10)	0.0345 (8)	0.0000 (7)	0.0128 (7)	−0.0027 (7)
C2	0.0516 (10)	0.0442 (11)	0.0554 (11)	−0.0065 (8)	0.0195 (9)	−0.0064 (9)
C3	0.0657 (13)	0.0455 (12)	0.0743 (14)	0.0006 (9)	0.0271 (11)	0.0113 (10)
C4	0.0509 (10)	0.0660 (13)	0.0442 (10)	−0.0023 (9)	0.0166 (9)	0.0124 (9)
C5	0.0388 (8)	0.0408 (9)	0.0328 (8)	−0.0005 (7)	0.0133 (7)	−0.0024 (7)

C6	0.0362 (8)	0.0408 (9)	0.0336 (8)	0.0018 (7)	0.0122 (7)	−0.0014 (7)
C7	0.0393 (9)	0.0466 (10)	0.0343 (8)	0.0047 (7)	0.0148 (7)	0.0002 (7)
C8	0.0391 (9)	0.0524 (11)	0.0309 (8)	0.0082 (8)	0.0121 (7)	0.0047 (8)
C9	0.0593 (11)	0.0555 (12)	0.0476 (10)	0.0054 (9)	0.0264 (9)	0.0063 (9)
C10	0.0626 (12)	0.0778 (16)	0.0599 (12)	0.0043 (11)	0.0375 (11)	0.0163 (12)
C11	0.0658 (13)	0.0840 (17)	0.0548 (12)	0.0209 (12)	0.0375 (11)	0.0107 (12)
C12	0.0673 (13)	0.0671 (14)	0.0561 (12)	0.0120 (11)	0.0315 (11)	−0.0085 (10)
C13	0.0500 (10)	0.0594 (13)	0.0475 (10)	0.0031 (9)	0.0228 (9)	−0.0045 (9)
C14	0.0371 (8)	0.0459 (10)	0.0397 (9)	−0.0016 (7)	0.0162 (7)	−0.0008 (8)
C15	0.0547 (12)	0.0707 (14)	0.0807 (15)	0.0118 (10)	0.0381 (11)	−0.0063 (12)
C16	0.0390 (8)	0.0477 (11)	0.0375 (9)	−0.0015 (8)	0.0152 (7)	−0.0012 (8)
C17	0.0480 (10)	0.0618 (12)	0.0362 (9)	−0.0144 (9)	0.0101 (8)	−0.0073 (9)
C18	0.133 (3)	0.125 (3)	0.0462 (13)	−0.062 (2)	−0.0147 (15)	0.0195 (15)
C19	0.0689 (14)	0.108 (2)	0.0838 (17)	−0.0066 (14)	0.0336 (13)	−0.0483 (16)
C20	0.0425 (10)	0.0940 (18)	0.0703 (14)	−0.0076 (11)	0.0167 (10)	−0.0219 (13)
N1	0.0353 (8)	0.0693 (11)	0.0341 (8)	0.0004 (7)	0.0109 (6)	−0.0096 (7)
O1	0.0554 (8)	0.0705 (9)	0.0529 (8)	0.0163 (7)	0.0307 (6)	0.0058 (7)
O2	0.0699 (9)	0.0875 (12)	0.0537 (8)	0.0336 (8)	0.0292 (7)	0.0251 (8)
O3	0.0516 (7)	0.0552 (8)	0.0364 (7)	−0.0138 (6)	0.0041 (6)	0.0011 (6)
O4	0.0755 (10)	0.0646 (10)	0.0551 (9)	−0.0261 (8)	0.0099 (7)	0.0087 (7)

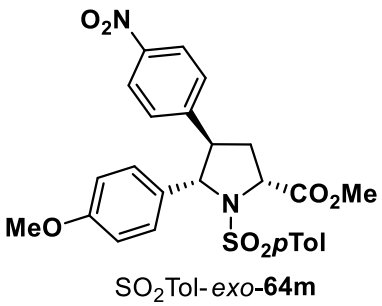
Geometric parameters (Å, º)

C1—N1	1.455 (2)	C12—C13	1.382 (3)
C1—C14	1.517 (2)	C12—H12	0.93
C1—C2	1.543 (2)	C13—H13	0.93
C1—C5	1.563 (2)	C14—O2	1.183 (2)
C2—C3	1.520 (3)	C14—O1	1.341 (2)
C2—H2A	0.97	C15—O1	1.437 (2)
C2—H2B	0.97	C15—H15A	0.96
C3—C4	1.517 (3)	C15—H15B	0.96
C3—H3A	0.97	C15—H15C	0.96
C3—H3B	0.97	C15—H15D	0.96
C4—C5	1.527 (3)	C15—H15E	0.96
C4—H4A	0.97	C15—H15F	0.96
C4—H4B	0.97	C16—O4	1.195 (2)
C5—C6	1.541 (2)	C16—O3	1.330 (2)
C5—H5	0.98	C17—O3	1.481 (2)
C6—C16	1.508 (2)	C17—C18	1.500 (3)
C6—C7	1.534 (2)	C17—C20	1.501 (3)
C6—H6	0.98	C17—C19	1.510 (3)
C7—N1	1.469 (2)	C18—H18A	0.96
C7—C8	1.511 (2)	C18—H18B	0.96
C7—H7	0.98	C18—H18C	0.96

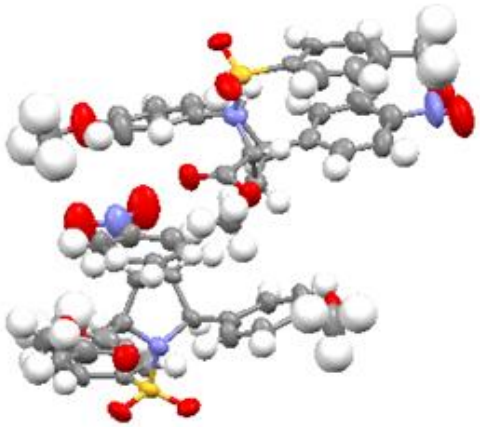
C8—C13	1.382 (3)	C19—H19A	0.96
C8—C9	1.388 (3)	C19—H19B	0.96
C9—C10	1.385 (3)	C19—H19C	0.96
C9—H9	0.93	C20—H20A	0.96
C10—C11	1.368 (3)	C20—H20B	0.96
C10—H10	0.93	C20—H20C	0.96
C11—C12	1.373 (3)	N1—H1	0.86 (2)
C11—H11	0.93		
N1—C1—C14	111.67 (14)	C12—C13—H13	119.6
N1—C1—C2	111.33 (14)	C8—C13—H13	119.6
C14—C1—C2	110.21 (14)	O2—C14—O1	123.20 (16)
N1—C1—C5	105.01 (13)	O2—C14—C1	125.39 (16)
C14—C1—C5	113.04 (14)	O1—C14—C1	111.40 (14)
C2—C1—C5	105.32 (13)	O1—C15—H15A	109.5
C3—C2—C1	104.05 (15)	O1—C15—H15B	109.5
C3—C2—H2A	110.9	H15A—C15—H15B	109.5
C1—C2—H2A	110.9	O1—C15—H15C	109.5
C3—C2—H2B	110.9	H15A—C15—H15C	109.5
C1—C2—H2B	110.9	H15B—C15—H15C	109.5
H2A—C2—H2B	109.0	O1—C15—H15D	109.5
C4—C3—C2	103.44 (16)	H15A—C15—H15D	141.1
C4—C3—H3A	111.1	H15B—C15—H15D	56.3
C2—C3—H3A	111.1	H15C—C15—H15D	56.3
C4—C3—H3B	111.1	O1—C15—H15E	109.5
C2—C3—H3B	111.1	H15A—C15—H15E	56.3
H3A—C3—H3B	109.0	H15B—C15—H15E	141.1
C3—C4—C5	103.64 (15)	H15C—C15—H15E	56.3
C3—C4—H4A	111.0	H15D—C15—H15E	109.5
C5—C4—H4A	111.0	O1—C15—H15F	109.5
C3—C4—H4B	111.0	H15A—C15—H15F	56.3
C5—C4—H4B	111.0	H15B—C15—H15F	56.3
H4A—C4—H4B	109.0	H15C—C15—H15F	141.1
C4—C5—C6	115.03 (15)	H15D—C15—H15F	109.5
C4—C5—C1	105.60 (14)	H15E—C15—H15F	109.5
C6—C5—C1	103.90 (12)	O4—C16—O3	125.02 (16)
C4—C5—H5	110.7	O4—C16—C6	125.28 (16)
C6—C5—H5	110.7	O3—C16—C6	109.64 (15)
C1—C5—H5	110.7	O3—C17—C18	101.88 (16)
C16—C6—C7	114.45 (15)	O3—C17—C20	110.51 (15)
C16—C6—C5	111.07 (13)	C18—C17—C20	112.3 (2)
C7—C6—C5	104.33 (12)	O3—C17—C19	110.36 (16)
C16—C6—H6	108.9	C18—C17—C19	110.5 (2)

C7—C6—H6	108.9	C20—C17—C19	111.00 (19)
C5—C6—H6	108.9	C17—C18—H18A	109.5
N1—C7—C8	111.87 (14)	C17—C18—H18B	109.5
N1—C7—C6	100.67 (14)	H18A—C18—H18B	109.5
C8—C7—C6	114.31 (13)	C17—C18—H18C	109.5
N1—C7—H7	109.9	H18A—C18—H18C	109.5
C8—C7—H7	109.9	H18B—C18—H18C	109.5
C6—C7—H7	109.9	C17—C19—H19A	109.5
C13—C8—C9	118.46 (17)	C17—C19—H19B	109.5
C13—C8—C7	121.50 (17)	H19A—C19—H19B	109.5
C9—C8—C7	120.02 (17)	C17—C19—H19C	109.5
C10—C9—C8	120.4 (2)	H19A—C19—H19C	109.5
C10—C9—H9	119.8	H19B—C19—H19C	109.5
C8—C9—H9	119.8	C17—C20—H20A	109.5
C11—C10—C9	120.4 (2)	C17—C20—H20B	109.5
C11—C10—H10	119.8	H20A—C20—H20B	109.5
C9—C10—H10	119.8	C17—C20—H20C	109.5
C10—C11—C12	119.67 (19)	H20A—C20—H20C	109.5
C10—C11—H11	120.2	H20B—C20—H20C	109.5
C12—C11—H11	120.2	C1—N1—C7	108.96 (13)
C11—C12—C13	120.3 (2)	C1—N1—H1	109.0 (15)
C11—C12—H12	119.8	C7—N1—H1	110.6 (15)
C13—C12—H12	119.8	C14—O1—C15	117.06 (15)
C12—C13—C8	120.7 (2)	C16—O3—C17	122.46 (14)

Capítulo 4: Alkenylarenes as dipolarophiles in catalytic asymmetric 1,3-dipolar cycloadditions of azomethine ylides



SO_2Tol-*exo*-**64m**



Computing details

Data collection: Bruker *APEX2*; cell refinement: Bruker *SAINT*; data reduction: Bruker *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick 2014); molecular graphics: Bruker *SHELXTL*; software used to prepare material for publication: Bruker *SHELXTL*.

Crystal data

$C_{52}H_{52}N_4O_{14}S_2$	$F(000)$ = 1072
M_r = 1021.09	D_x = 1.348 Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation, λ = 0.71073 Å
a = 12.3708 (4) Å	Cell parameters from 3881 reflections
b = 14.1449 (5) Å	θ = 2.6–21.4°
c = 14.3729 (5) Å	μ = 0.18 mm^{-1}
β = 90.302 (1)°	T = 296 K
V = 2514.99 (15) Å^3	Prismatic, clear colourless
Z = 2	0.20 × 0.14 × 0.12 mm

Data collection

Bruker Kappa Apex II diffractometer	5322 reflections with $I > 2\sigma(I)$
Detector resolution: 8.3333 pixels mm^{-1}	R_{int} = 0.039
φ and ω scans	θ_{max} = 25.4°, θ_{min} = 1.4°
Absorption correction: multi-scan *SADABS*	h = −14→14
T_{min} = 0.88, T_{max} = 0.98	k = −17→15
19872 measured reflections	l = −12→17
8336 independent reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.082$	$w = 1/[\sigma^2(F_o^2) + (0.1635P)^2 + 2.3388P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.285$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.05$	$\Delta\rho_{max} = 0.39$ e Å^{-3}
8336 reflections	$\Delta\rho_{min} = -0.59$ e Å^{-3}
655 parameters	Absolute structure: Flack x determined using 1769 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
1 restraint	Absolute structure parameter: 0.08 (4)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.2997 (8)	0.3089 (8)	0.4134 (7)	0.045 (2)
C2	0.1995 (9)	0.2636 (9)	0.4238 (8)	0.059 (3)
H2	0.1949	0.1987	0.4338	0.071*
C3	0.1062 (10)	0.3204 (11)	0.4186 (9)	0.070 (4)
H3	0.039	0.2923	0.4267	0.084*
C4	0.1111 (12)	0.4154 (12)	0.4020 (11)	0.087 (4)
C5	0.2128 (11)	0.4556 (9)	0.3918 (10)	0.071 (4)
H5	0.2175	0.5203	0.3814	0.085*
C6	0.3049 (9)	0.4049 (8)	0.3963 (8)	0.055 (3)
H6	0.3714	0.4343	0.3881	0.066*
C7	0.0074 (14)	0.4746 (15)	0.3994 (17)	0.130 (7)
H7A	0.018	0.5315	0.4347	0.195*
H7B	−0.0509	0.4389	0.4257	0.195*
H7C	−0.0098	0.4905	0.3361	0.195*
C8	0.3864 (9)	0.2036 (7)	0.6034 (7)	0.045 (2)

H8	0.3103	0.2157	0.5884	0.054*
C9	0.4165 (10)	0.2558 (8)	0.6920 (7)	0.056 (3)
H9A	0.4783	0.2265	0.7221	0.067*
H9B	0.3565	0.2566	0.7351	0.067*
C10	0.4445 (8)	0.3581 (7)	0.6585 (6)	0.045 (2)
H10	0.4962	0.3851	0.703	0.054*
C11	0.5058 (8)	0.3377 (7)	0.5670 (7)	0.044 (2)
H11	0.4914	0.3888	0.5226	0.053*
C12	0.4033 (11)	0.1011 (8)	0.6140 (7)	0.060 (3)
C13	0.3216 (12)	−0.0412 (9)	0.6678 (10)	0.076 (4)
H13A	0.312	−0.0766	0.6114	0.114*
H13B	0.2647	−0.0565	0.7104	0.114*
H13C	0.3901	−0.0568	0.6954	0.114*
C14	0.6272 (9)	0.3284 (8)	0.5814 (7)	0.048 (3)
C15	0.6778 (9)	0.2448 (9)	0.5894 (9)	0.062 (3)
H15	0.6377	0.19	0.58	0.075*
C16	0.7900 (10)	0.2358 (9)	0.6117 (10)	0.073 (4)
H16	0.823	0.1769	0.6159	0.088*
C17	0.8483 (10)	0.3196 (9)	0.6269 (10)	0.069 (3)
C18	0.7987 (9)	0.4043 (9)	0.6216 (9)	0.064 (3)
H18	0.8367	0.4595	0.6348	0.077*
C19	0.6909 (9)	0.4083 (8)	0.5963 (7)	0.051 (3)
H19	0.6592	0.4675	0.5889	0.061*
C20	1.0090 (11)	0.2314 (13)	0.6637 (15)	0.113 (6)
H20A	0.9667	0.1905	0.7023	0.17*
H20B	1.0782	0.2421	0.6924	0.17*
H20C	1.019	0.2025	0.6039	0.17*
C21	0.3550 (10)	0.4261 (8)	0.6469 (7)	0.053 (3)
C22	0.3790 (9)	0.5208 (8)	0.6311 (7)	0.052 (3)
H22	0.4512	0.5383	0.6259	0.063*
C23	0.2990 (10)	0.5918 (9)	0.6225 (8)	0.063 (3)
H23	0.3162	0.6547	0.6109	0.076*
C24	0.1931 (9)	0.5612 (9)	0.6324 (9)	0.062 (3)
C25	0.1662 (11)	0.4703 (10)	0.6472 (12)	0.086 (4)
H25	0.094	0.4528	0.6523	0.103*
C26	0.2449 (9)	0.4046 (9)	0.6547 (9)	0.062 (3)
H26	0.2251	0.3421	0.6655	0.075*
C27	0.6991 (9)	0.6367 (8)	1.0856 (6)	0.046 (3)
C28	0.6941 (9)	0.7332 (8)	1.0851 (7)	0.053 (3)
H28	0.6276	0.7639	1.0868	0.064*
C29	0.7916 (10)	0.7861 (9)	1.0821 (8)	0.062 (3)
H29	0.7894	0.8517	1.0785	0.075*
C30	0.8871 (13)	0.7409 (11)	1.0845 (10)	0.087 (5)

C31	0.8881 (11)	0.6421 (13)	1.0893 (11)	0.090 (5)
H31	0.9542	0.6109	1.0908	0.108*
C32	0.7951 (11)	0.5900 (11)	1.0920 (10)	0.079 (4)
H32	0.7974	0.5245	1.0979	0.095*
C33	0.9953 (13)	0.7974 (16)	1.0741 (16)	0.128 (7)
H33A	0.9932	0.8336	1.0176	0.193*
H33B	1.0549	0.754	1.0722	0.193*
H33C	1.004	0.8392	1.1262	0.193*
C34	0.6147 (9)	0.5306 (7)	0.9000 (6)	0.045 (2)
H34	0.69	0.5456	0.9154	0.054*
C35	0.5840 (9)	0.5758 (8)	0.8057 (7)	0.055 (3)
H35A	0.5243	0.5424	0.7765	0.066*
H35B	0.6451	0.5762	0.7636	0.066*
C36	0.5511 (9)	0.6767 (8)	0.8328 (6)	0.050 (3)
H36	0.4988	0.6993	0.7865	0.06*
C37	0.4902 (8)	0.6629 (7)	0.9259 (6)	0.045 (2)
H37	0.5044	0.7172	0.9665	0.054*
C38	0.6005 (10)	0.4260 (8)	0.8957 (7)	0.052 (3)
C39	0.6962 (11)	0.2834 (8)	0.8592 (10)	0.067 (3)
H39A	0.7346	0.2512	0.908	0.1*
H39B	0.7315	0.2722	0.8009	0.1*
H39C	0.6233	0.2602	0.856	0.1*
C40	0.3707 (9)	0.6526 (7)	0.9122 (7)	0.047 (3)
C41	0.3167 (9)	0.5698 (10)	0.9166 (9)	0.068 (3)
H41	0.3559	0.5158	0.9319	0.081*
C42	0.2094 (10)	0.5600 (10)	0.9003 (11)	0.081 (4)
H42	0.1763	0.5013	0.9065	0.097*
C43	0.1488 (12)	0.6398 (10)	0.8739 (13)	0.088 (5)
C44	0.2024 (11)	0.7272 (10)	0.8671 (11)	0.079 (4)
H44	0.1648	0.7811	0.849	0.095*
C45	0.3094 (10)	0.7321 (9)	0.8871 (9)	0.069 (3)
H45	0.3435	0.7906	0.884	0.082*
C46	−0.0114 (13)	0.5550 (16)	0.8591 (17)	0.138 (8)
H46A	0.0319	0.5087	0.8278	0.207*
H46B	−0.0811	0.5588	0.8296	0.207*
H46C	−0.02	0.5371	0.923	0.207*
C47	0.6397 (9)	0.7492 (9)	0.8403 (7)	0.056 (3)
C48	0.7484 (11)	0.7296 (9)	0.8300 (9)	0.069 (3)
H48	0.7686	0.6669	0.8216	0.083*
C49	0.8295 (11)	0.7973 (10)	0.8314 (10)	0.075 (4)
H49	0.9014	0.7814	0.8215	0.091*
C50	0.7993 (12)	0.8866 (10)	0.8478 (10)	0.073 (4)
C51	0.6926 (13)	0.9141 (10)	0.8583 (9)	0.078 (4)

H51	0.6738	0.9773	0.866	0.093*
C52	0.6147 (11)	0.8433 (9)	0.8569 (8)	0.060 (3)
H52	0.5429	0.8596	0.8674	0.073*
N1	0.4558 (6)	0.2496 (6)	0.5324 (5)	0.047 (2)
N2	0.1115 (11)	0.6331 (12)	0.6233 (12)	0.103 (4)
N3	0.5423 (7)	0.5785 (6)	0.9655 (5)	0.052 (2)
N4	0.8833 (15)	0.9593 (13)	0.8465 (11)	0.116 (5)
O1	0.3875 (7)	0.1453 (5)	0.4094 (5)	0.059 (2)
O2	0.5023 (6)	0.2827 (6)	0.3702 (5)	0.060 (2)
O3	0.3185 (7)	0.0594 (6)	0.6470 (6)	0.066 (2)
O4	0.4878 (7)	0.0580 (6)	0.5955 (6)	0.072 (2)
O5	0.9545 (7)	0.3190 (8)	0.6524 (8)	0.092 (3)
O6	0.0150 (10)	0.6053 (11)	0.6190 (13)	0.148 (6)
O7	0.1361 (11)	0.7170 (10)	0.6232 (12)	0.137 (5)
O8	0.4959 (7)	0.6195 (6)	1.1264 (5)	0.063 (2)
O9	0.6047 (7)	0.4764 (6)	1.0930 (6)	0.072 (3)
O10	0.6949 (6)	0.3846 (5)	0.8784 (6)	0.064 (2)
O11	0.5172 (7)	0.3847 (6)	0.9002 (6)	0.069 (2)
O12	0.0387 (9)	0.6417 (9)	0.8545 (11)	0.128 (5)
O13	0.8528 (12)	1.0443 (10)	0.8415 (10)	0.133 (5)
O14	0.9776 (12)	0.9374 (10)	0.8497 (12)	0.139 (5)
S1	0.4185 (2)	0.24172 (17)	0.42358 (16)	0.0450 (7)
S2	0.5777 (2)	0.57256 (18)	1.07532 (16)	0.0484 (8)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.041 (6)	0.047 (7)	0.046 (5)	−0.001 (4)	−0.003 (4)	−0.003 (5)
C2	0.052 (7)	0.053 (8)	0.071 (7)	−0.015 (5)	−0.008 (5)	−0.011 (6)
C3	0.049 (7)	0.079 (11)	0.083 (9)	−0.005 (6)	0.009 (6)	−0.005 (7)
C4	0.084 (10)	0.080 (12)	0.097 (10)	0.023 (9)	−0.012 (8)	−0.025 (9)
C5	0.073 (9)	0.036 (7)	0.105 (10)	0.007 (6)	−0.014 (7)	0.001 (7)
C6	0.060 (7)	0.040 (7)	0.064 (6)	−0.010 (5)	0.000 (5)	0.015 (5)
C7	0.082 (12)	0.110 (16)	0.20 (2)	0.031 (11)	−0.026 (12)	0.005 (14)
C8	0.055 (6)	0.035 (6)	0.046 (5)	0.004 (5)	0.004 (5)	0.003 (4)
C9	0.072 (7)	0.049 (7)	0.047 (6)	−0.003 (6)	0.011 (5)	−0.011 (5)
C10	0.063 (7)	0.040 (6)	0.033 (5)	0.000 (5)	−0.009 (4)	−0.005 (4)
C11	0.053 (6)	0.031 (6)	0.048 (5)	−0.005 (4)	−0.008 (4)	−0.008 (4)
C12	0.086 (9)	0.045 (7)	0.048 (6)	0.015 (7)	−0.018 (6)	0.005 (5)
C13	0.102 (11)	0.040 (7)	0.086 (9)	−0.010 (7)	0.034 (8)	0.004 (6)
C14	0.054 (7)	0.042 (7)	0.048 (6)	0.005 (5)	−0.008 (5)	−0.012 (5)
C15	0.049 (7)	0.045 (7)	0.093 (9)	0.000 (6)	−0.003 (6)	−0.003 (7)
C16	0.058 (7)	0.043 (8)	0.119 (11)	0.006 (6)	−0.017 (7)	0.005 (7)
C17	0.059 (8)	0.056 (9)	0.092 (9)	−0.015 (6)	−0.007 (6)	0.001 (7)

C18	0.059 (7)	0.039 (7)	0.095 (9)	−0.016 (6)	−0.004 (6)	0.007 (6)
C19	0.062 (7)	0.030 (6)	0.061 (6)	−0.008 (5)	0.006 (5)	−0.002 (5)
C20	0.055 (9)	0.102 (14)	0.183 (19)	−0.006 (9)	−0.015 (10)	0.017 (13)
C21	0.062 (7)	0.046 (7)	0.051 (6)	0.001 (5)	−0.005 (5)	−0.011 (5)
C22	0.046 (6)	0.053 (8)	0.058 (6)	−0.001 (5)	−0.009 (5)	0.000 (5)
C23	0.072 (8)	0.049 (8)	0.069 (7)	0.002 (6)	−0.004 (6)	0.004 (6)
C24	0.049 (7)	0.053 (8)	0.083 (8)	0.007 (6)	0.012 (5)	−0.006 (6)
C25	0.052 (8)	0.068 (10)	0.138 (13)	−0.002 (7)	0.018 (8)	−0.030 (9)
C26	0.057 (7)	0.037 (7)	0.093 (9)	−0.003 (6)	0.012 (6)	0.004 (6)
C27	0.059 (7)	0.046 (7)	0.034 (5)	0.006 (5)	−0.014 (4)	−0.005 (4)
C28	0.066 (7)	0.037 (7)	0.055 (6)	0.004 (5)	−0.001 (5)	−0.017 (5)
C29	0.072 (8)	0.048 (7)	0.068 (7)	−0.007 (6)	−0.005 (6)	−0.005 (6)
C30	0.094 (11)	0.067 (10)	0.101 (11)	−0.025 (9)	−0.029 (8)	0.019 (8)
C31	0.058 (9)	0.108 (14)	0.102 (11)	0.016 (8)	−0.032 (7)	−0.009 (9)
C32	0.074 (9)	0.059 (9)	0.105 (10)	0.006 (7)	−0.028 (8)	0.000 (8)
C33	0.067 (10)	0.145 (18)	0.172 (19)	−0.010 (10)	−0.031 (11)	−0.001 (15)
C34	0.064 (7)	0.034 (6)	0.038 (5)	0.000 (5)	0.004 (4)	−0.002 (4)
C35	0.063 (7)	0.054 (7)	0.049 (6)	−0.008 (6)	−0.003 (5)	0.001 (5)
C36	0.059 (7)	0.056 (7)	0.036 (5)	0.001 (5)	−0.008 (5)	0.011 (5)
C37	0.059 (7)	0.041 (6)	0.036 (5)	0.007 (5)	−0.005 (4)	0.000 (4)
C38	0.069 (8)	0.044 (7)	0.042 (5)	−0.008 (6)	−0.007 (5)	0.003 (5)
C39	0.070 (8)	0.041 (7)	0.090 (9)	0.000 (6)	0.000 (6)	−0.003 (6)
C40	0.056 (7)	0.036 (6)	0.050 (6)	0.000 (5)	−0.002 (5)	−0.001 (4)
C41	0.049 (7)	0.051 (8)	0.102 (9)	0.001 (6)	−0.003 (6)	−0.003 (7)
C42	0.059 (8)	0.057 (9)	0.127 (12)	−0.005 (6)	−0.024 (7)	0.009 (8)
C43	0.062 (9)	0.059 (10)	0.144 (14)	0.009 (7)	−0.016 (8)	0.005 (9)
C44	0.065 (8)	0.052 (9)	0.120 (11)	0.010 (7)	−0.002 (7)	−0.001 (8)
C45	0.061 (8)	0.042 (7)	0.102 (10)	0.008 (6)	−0.006 (6)	0.002 (7)
C46	0.060 (10)	0.133 (19)	0.22 (2)	−0.013 (11)	−0.034 (12)	0.030 (16)
C47	0.060 (7)	0.065 (8)	0.042 (5)	0.000 (6)	0.006 (5)	0.014 (5)
C48	0.083 (10)	0.048 (8)	0.077 (8)	0.008 (7)	0.011 (7)	0.020 (6)
C49	0.063 (8)	0.072 (10)	0.091 (9)	−0.011 (7)	0.005 (7)	0.021 (7)
C50	0.078 (10)	0.051 (9)	0.091 (9)	−0.006 (7)	0.001 (7)	0.006 (7)
C51	0.111 (12)	0.048 (8)	0.075 (8)	−0.010 (8)	−0.007 (7)	−0.008 (6)
C52	0.075 (8)	0.044 (8)	0.063 (7)	−0.003 (6)	0.012 (6)	0.006 (6)
N1	0.054 (5)	0.041 (5)	0.047 (4)	−0.003 (4)	−0.003 (4)	−0.006 (4)
N2	0.070 (9)	0.087 (11)	0.151 (13)	0.009 (8)	−0.015 (8)	−0.004 (9)
N3	0.075 (6)	0.035 (5)	0.046 (4)	0.005 (4)	−0.007 (4)	0.003 (4)
N4	0.098 (11)	0.103 (13)	0.147 (13)	−0.060 (10)	−0.003 (9)	0.009 (10)
O1	0.075 (5)	0.042 (5)	0.061 (4)	−0.005 (4)	−0.011 (4)	−0.016 (3)
O2	0.060 (5)	0.080 (6)	0.039 (4)	0.001 (4)	0.006 (3)	−0.004 (4)
O3	0.059 (5)	0.045 (5)	0.095 (6)	−0.008 (4)	0.008 (4)	0.000 (4)
O4	0.069 (5)	0.051 (6)	0.095 (6)	0.017 (4)	0.006 (4)	0.008 (5)

O5	0.054 (6)	0.079 (7)	0.143 (9)	−0.024 (5)	−0.013 (5)	−0.002 (6)
O6	0.077 (8)	0.117 (11)	0.252 (19)	0.027 (8)	−0.023 (9)	−0.005 (11)
O7	0.104 (9)	0.076 (9)	0.233 (16)	0.026 (7)	−0.015 (9)	0.035 (9)
O8	0.075 (5)	0.070 (6)	0.044 (4)	−0.002 (4)	0.013 (4)	−0.011 (4)
O9	0.101 (7)	0.043 (5)	0.072 (5)	−0.010 (4)	−0.020 (5)	0.025 (4)
O10	0.060 (5)	0.042 (5)	0.092 (6)	0.000 (4)	0.010 (4)	−0.009 (4)
O11	0.057 (5)	0.050 (6)	0.100 (6)	−0.006 (4)	0.000 (4)	−0.011 (5)
O12	0.066 (7)	0.094 (10)	0.224 (16)	0.004 (6)	−0.033 (8)	0.029 (9)
O13	0.155 (12)	0.072 (9)	0.174 (13)	−0.056 (8)	0.006 (9)	−0.010 (9)
O14	0.097 (10)	0.113 (11)	0.208 (15)	−0.034 (8)	−0.020 (10)	0.004 (10)
S1	0.0532 (16)	0.0401 (18)	0.0417 (13)	0.0009 (12)	−0.0028 (12)	−0.0109 (11)
S2	0.0635 (19)	0.0406 (19)	0.0411 (14)	−0.0019 (13)	−0.0022 (13)	0.0031 (12)

Geometric parameters (Å, º)

C1—C6	1.383 (15)	C29—C30	1.34 (2)
C1—C2	1.403 (15)	C29—H29	0.93
C1—S1	1.756 (11)	C30—C31	1.40 (2)
C2—C3	1.408 (18)	C30—C33	1.57 (2)
C2—H2	0.93	C31—C32	1.37 (2)
C3—C4	1.37 (2)	C31—H31	0.93
C3—H3	0.93	C32—H32	0.93
C4—C5	1.39 (2)	C33—H33A	0.96
C4—C7	1.53 (2)	C33—H33B	0.96
C5—C6	1.347 (17)	C33—H33C	0.96
C5—H5	0.93	C34—N3	1.469 (13)
C6—H6	0.93	C34—C38	1.491 (15)
C7—H7A	0.96	C34—C35	1.545 (14)
C7—H7B	0.96	C34—H34	0.98
C7—H7C	0.96	C35—C36	1.535 (16)
C8—C12	1.473 (15)	C35—H35A	0.97
C8—N1	1.486 (13)	C35—H35B	0.97
C8—C9	1.516 (14)	C36—C47	1.504 (16)
C8—H8	0.98	C36—C37	1.551 (14)
C9—C10	1.563 (15)	C36—H36	0.98
C9—H9A	0.97	C37—N3	1.470 (13)
C9—H9B	0.97	C37—C40	1.498 (15)
C10—C21	1.476 (15)	C37—H37	0.98
C10—C11	1.548 (14)	C38—O11	1.186 (13)
C10—H10	0.98	C38—O10	1.330 (14)
C11—N1	1.476 (12)	C39—O10	1.458 (14)
C11—C14	1.521 (14)	C39—H39A	0.96
C11—H11	0.98	C39—H39B	0.96
C12—O4	1.240 (14)	C39—H39C	0.96

C12—O3	1.296 (15)	C40—C41	1.350 (16)
C13—O3	1.455 (14)	C40—C45	1.403 (15)
C13—H13A	0.96	C41—C42	1.353 (17)
C13—H13B	0.96	C41—H41	0.93
C13—H13C	0.96	C42—C43	1.407 (19)
C14—C15	1.342 (16)	C42—H42	0.93
C14—C19	1.395 (14)	C43—O12	1.388 (17)
C15—C16	1.429 (16)	C43—C44	1.41 (2)
C15—H15	0.93	C44—C45	1.354 (17)
C16—C17	1.404 (17)	C44—H44	0.93
C16—H16	0.93	C45—H45	0.93
C17—C18	1.348 (17)	C46—O12	1.38 (2)
C17—O5	1.362 (15)	C46—H46A	0.96
C18—C19	1.381 (16)	C46—H46B	0.96
C18—H18	0.93	C46—H46C	0.96
C19—H19	0.93	C47—C48	1.382 (17)
C20—O5	1.420 (19)	C47—C52	1.387 (17)
C20—H20A	0.96	C48—C49	1.386 (18)
C20—H20B	0.96	C48—H48	0.93
C20—H20C	0.96	C49—C50	1.339 (19)
C21—C22	1.391 (16)	C49—H49	0.93
C21—C26	1.401 (16)	C50—C51	1.39 (2)
C22—C23	1.415 (16)	C50—N4	1.462 (19)
C22—H22	0.93	C51—C52	1.391 (18)
C23—C24	1.388 (17)	C51—H51	0.93
C23—H23	0.93	C52—H52	0.93
C24—C25	1.345 (19)	N1—S1	1.633 (8)
C24—N2	1.439 (17)	N2—O7	1.225 (17)
C25—C26	1.350 (18)	N2—O6	1.258 (17)
C25—H25	0.93	N3—S2	1.637 (8)
C26—H26	0.93	N4—O14	1.21 (2)
C27—C32	1.362 (17)	N4—O13	1.26 (2)
C27—C28	1.367 (14)	O1—S1	1.432 (8)
C27—S2	1.760 (11)	O2—S1	1.417 (8)
C28—C29	1.421 (16)	O8—S2	1.419 (8)
C28—H28	0.93	O9—S2	1.422 (8)
C6—C1—C2	120.6 (10)	C30—C31—H31	118.9
C6—C1—S1	120.4 (8)	C27—C32—C31	118.0 (13)
C2—C1—S1	118.9 (9)	C27—C32—H32	121.0
C1—C2—C3	117.2 (12)	C31—C32—H32	121.0
C1—C2—H2	121.4	C30—C33—H33A	109.5
C3—C2—H2	121.4	C30—C33—H33B	109.5

C4—C3—C2	122.3 (13)	H33A—C33—H33B	109.5
C4—C3—H3	118.9	C30—C33—H33C	109.5
C2—C3—H3	118.9	H33A—C33—H33C	109.5
C3—C4—C5	117.5 (13)	H33B—C33—H33C	109.5
C3—C4—C7	120.3 (16)	N3—C34—C38	114.4 (9)
C5—C4—C7	122.2 (16)	N3—C34—C35	102.9 (8)
C6—C5—C4	122.9 (12)	C38—C34—C35	110.2 (8)
C6—C5—H5	118.5	N3—C34—H34	109.7
C4—C5—H5	118.5	C38—C34—H34	109.7
C5—C6—C1	119.4 (11)	C35—C34—H34	109.7
C5—C6—H6	120.3	C34—C35—C36	103.1 (8)
C1—C6—H6	120.3	C34—C35—H35A	111.1
C4—C7—H7A	109.5	C36—C35—H35A	111.1
C4—C7—H7B	109.5	C34—C35—H35B	111.1
H7A—C7—H7B	109.5	C36—C35—H35B	111.1
C4—C7—H7C	109.5	H35A—C35—H35B	109.1
H7A—C7—H7C	109.5	C47—C36—C35	117.2 (9)
H7B—C7—H7C	109.5	C47—C36—C37	112.4 (8)
C12—C8—N1	114.8 (9)	C35—C36—C37	103.4 (8)
C12—C8—C9	111.0 (9)	C47—C36—H36	107.8
N1—C8—C9	102.9 (8)	C35—C36—H36	107.8
C12—C8—H8	109.3	C37—C36—H36	107.8
N1—C8—H8	109.3	N3—C37—C40	113.7 (9)
C9—C8—H8	109.3	N3—C37—C36	102.9 (8)
C8—C9—C10	104.2 (8)	C40—C37—C36	112.5 (8)
C8—C9—H9A	110.9	N3—C37—H37	109.2
C10—C9—H9A	110.9	C40—C37—H37	109.2
C8—C9—H9B	110.9	C36—C37—H37	109.2
C10—C9—H9B	110.9	O11—C38—O10	123.9 (11)
H9A—C9—H9B	108.9	O11—C38—C34	126.0 (12)
C21—C10—C11	113.3 (8)	O10—C38—C34	109.9 (10)
C21—C10—C9	118.1 (9)	O10—C39—H39A	109.5
C11—C10—C9	101.5 (8)	O10—C39—H39B	109.5
C21—C10—H10	107.8	H39A—C39—H39B	109.5
C11—C10—H10	107.8	O10—C39—H39C	109.5
C9—C10—H10	107.8	H39A—C39—H39C	109.5
N1—C11—C14	112.6 (8)	H39B—C39—H39C	109.5
N1—C11—C10	103.7 (8)	C41—C40—C45	116.2 (11)
C14—C11—C10	112.8 (8)	C41—C40—C37	124.5 (10)
N1—C11—H11	109.2	C45—C40—C37	119.2 (10)
C14—C11—H11	109.2	C40—C41—C42	124.4 (13)
C10—C11—H11	109.2	C40—C41—H41	117.8
O4—C12—O3	122.7 (11)	C42—C41—H41	117.8

O4—C12—C8	125.6 (13)	C41—C42—C43	119.0 (13)
O3—C12—C8	111.7 (11)	C41—C42—H42	120.5
O3—C13—H13A	109.5	C43—C42—H42	120.5
O3—C13—H13B	109.5	O12—C43—C44	115.6 (12)
H13A—C13—H13B	109.5	O12—C43—C42	126.2 (13)
O3—C13—H13C	109.5	C44—C43—C42	118.2 (12)
H13A—C13—H13C	109.5	C45—C44—C43	119.5 (12)
H13B—C13—H13C	109.5	C45—C44—H44	120.3
C15—C14—C19	116.0 (10)	C43—C44—H44	120.3
C15—C14—C11	123.2 (10)	C44—C45—C40	122.6 (12)
C19—C14—C11	120.5 (9)	C44—C45—H45	118.7
C14—C15—C16	123.4 (12)	C40—C45—H45	118.7
C14—C15—H15	118.3	O12—C46—H46A	109.5
C16—C15—H15	118.3	O12—C46—H46B	109.5
C17—C16—C15	117.2 (12)	H46A—C46—H46B	109.5
C17—C16—H16	121.4	O12—C46—H46C	109.5
C15—C16—H16	121.4	H46A—C46—H46C	109.5
C18—C17—O5	117.3 (11)	H46B—C46—H46C	109.5
C18—C17—C16	120.5 (11)	C48—C47—C52	115.4 (12)
O5—C17—C16	122.1 (12)	C48—C47—C36	124.5 (12)
C17—C18—C19	119.4 (11)	C52—C47—C36	120.1 (11)
C17—C18—H18	120.3	C47—C48—C49	124.4 (13)
C19—C18—H18	120.3	C47—C48—H48	117.8
C18—C19—C14	123.4 (11)	C49—C48—H48	117.8
C18—C19—H19	118.3	C50—C49—C48	116.9 (13)
C14—C19—H19	118.3	C50—C49—H49	121.6
O5—C20—H20A	109.5	C48—C49—H49	121.6
O5—C20—H20B	109.5	C49—C50—C51	123.4 (13)
H20A—C20—H20B	109.5	C49—C50—N4	117.6 (15)
O5—C20—H20C	109.5	C51—C50—N4	118.8 (15)
H20A—C20—H20C	109.5	C50—C51—C52	117.2 (13)
H20B—C20—H20C	109.5	C50—C51—H51	121.4
C22—C21—C26	115.5 (10)	C52—C51—H51	121.4
C22—C21—C10	119.0 (10)	C47—C52—C51	122.6 (13)
C26—C21—C10	125.4 (11)	C47—C52—H52	118.7
C21—C22—C23	123.2 (11)	C51—C52—H52	118.7
C21—C22—H22	118.4	C11—N1—C8	112.4 (8)
C23—C22—H22	118.4	C11—N1—S1	119.8 (7)
C24—C23—C22	115.5 (11)	C8—N1—S1	117.8 (6)
C24—C23—H23	122.3	O7—N2—O6	122.6 (15)
C22—C23—H23	122.3	O7—N2—C24	120.7 (13)
C25—C24—C23	123.3 (12)	O6—N2—C24	116.7 (15)
C25—C24—N2	121.0 (12)	C34—N3—C37	113.2 (8)

C23—C24—N2	115.6 (12)	C34—N3—S2	115.7 (7)
C24—C25—C26	119.4 (12)	C37—N3—S2	122.0 (7)
C24—C25—H25	120.3	O14—N4—O13	122.3 (14)
C26—C25—H25	120.3	O14—N4—C50	120.4 (18)
C25—C26—C21	123.1 (12)	O13—N4—C50	117.3 (17)
C25—C26—H26	118.5	C12—O3—C13	119.9 (10)
C21—C26—H26	118.5	C17—O5—C20	119.5 (11)
C32—C27—C28	121.6 (11)	C38—O10—C39	118.5 (9)
C32—C27—S2	120.0 (9)	C46—O12—C43	114.5 (12)
C28—C27—S2	118.4 (8)	O2—S1—O1	120.6 (5)
C27—C28—C29	119.2 (11)	O2—S1—N1	106.7 (4)
C27—C28—H28	120.4	O1—S1—N1	106.0 (5)
C29—C28—H28	120.4	O2—S1—C1	110.4 (5)
C30—C29—C28	119.7 (12)	O1—S1—C1	106.3 (5)
C30—C29—H29	120.1	N1—S1—C1	106.0 (4)
C28—C29—H29	120.1	O8—S2—O9	121.5 (5)
C29—C30—C31	118.9 (13)	O8—S2—N3	106.7 (5)
C29—C30—C33	120.4 (15)	O9—S2—N3	106.4 (5)
C31—C30—C33	120.5 (16)	O8—S2—C27	109.0 (5)
C32—C31—C30	122.2 (14)	O9—S2—C27	106.2 (5)
C32—C31—H31	118.9	N3—S2—C27	106.2 (5)
C6—C1—C2—C3	−1.6 (15)	C40—C41—C42—C43	2 (2)
S1—C1—C2—C3	177.7 (9)	C41—C42—C43—O12	179.8 (16)
C1—C2—C3—C4	1.4 (18)	C41—C42—C43—C44	−1 (2)
C2—C3—C4—C5	−1 (2)	O12—C43—C44—C45	178.4 (15)
C2—C3—C4—C7	−178.4 (14)	C42—C43—C44—C45	−1 (2)
C3—C4—C5—C6	1 (2)	C43—C44—C45—C40	2 (2)
C7—C4—C5—C6	178.2 (15)	C41—C40—C45—C44	−0.8 (19)
C4—C5—C6—C1	−1 (2)	C37—C40—C45—C44	175.2 (12)
C2—C1—C6—C5	1.5 (16)	C35—C36—C47—C48	−4.1 (15)
S1—C1—C6—C5	−177.8 (9)	C37—C36—C47—C48	115.6 (11)
C12—C8—C9—C10	155.4 (10)	C35—C36—C47—C52	174.6 (9)
N1—C8—C9—C10	32.1 (10)	C37—C36—C47—C52	−65.8 (13)
C8—C9—C10—C21	85.0 (10)	C52—C47—C48—C49	−2.8 (17)
C8—C9—C10—C11	−39.5 (10)	C36—C47—C48—C49	175.9 (11)
C21—C10—C11—N1	−96.8 (10)	C47—C48—C49—C50	3 (2)
C9—C10—C11—N1	30.8 (9)	C48—C49—C50—C51	−3 (2)
C21—C10—C11—C14	141.1 (9)	C48—C49—C50—N4	−178.1 (13)
C9—C10—C11—C14	−91.3 (10)	C49—C50—C51—C52	4 (2)
N1—C8—C12—O4	25.6 (15)	N4—C50—C51—C52	178.4 (12)
C9—C8—C12—O4	−90.6 (13)	C48—C47—C52—C51	3.2 (16)
N1—C8—C12—O3	−155.4 (9)	C36—C47—C52—C51	−175.6 (11)

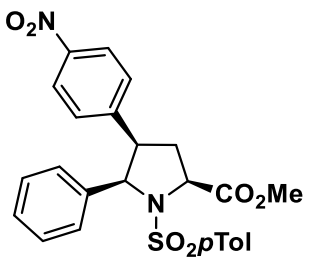
C9—C8—C12—O3	88.5 (11)	C50—C51—C52—C47	−3.7 (19)
N1—C11—C14—C15	−18.9 (15)	C14—C11—N1—C8	110.3 (9)
C10—C11—C14—C15	98.1 (12)	C10—C11—N1—C8	−12.0 (10)
N1—C11—C14—C19	167.5 (9)	C14—C11—N1—S1	−105.0 (9)
C10—C11—C14—C19	−75.5 (12)	C10—C11—N1—S1	132.7 (7)
C19—C14—C15—C16	0.0 (18)	C12—C8—N1—C11	−133.5 (9)
C11—C14—C15—C16	−173.9 (11)	C9—C8—N1—C11	−12.8 (11)
C14—C15—C16—C17	1 (2)	C12—C8—N1—S1	81.0 (10)
C15—C16—C17—C18	1 (2)	C9—C8—N1—S1	−158.3 (7)
C15—C16—C17—O5	177.2 (13)	C25—C24—N2—O7	169.5 (17)
O5—C17—C18—C19	−179.8 (12)	C23—C24—N2—O7	−12 (2)
C16—C17—C18—C19	−3 (2)	C25—C24—N2—O6	−8 (2)
C17—C18—C19—C14	4.3 (19)	C23—C24—N2—O6	170.3 (15)
C15—C14—C19—C18	−2.6 (16)	C38—C34—N3—C37	−133.4 (9)
C11—C14—C19—C18	171.5 (10)	C35—C34—N3—C37	−13.9 (11)
C11—C10—C21—C22	−71.3 (12)	C38—C34—N3—S2	78.9 (10)
C9—C10—C21—C22	170.3 (9)	C35—C34—N3—S2	−161.5 (7)
C11—C10—C21—C26	111.9 (12)	C40—C37—N3—C34	112.2 (10)
C9—C10—C21—C26	−6.5 (15)	C36—C37—N3—C34	−9.8 (11)
C26—C21—C22—C23	−0.4 (16)	C40—C37—N3—S2	−102.5 (9)
C10—C21—C22—C23	−177.6 (10)	C36—C37—N3—S2	135.6 (8)
C21—C22—C23—C24	1.0 (17)	C49—C50—N4—O14	−15 (2)
C22—C23—C24—C25	−1.5 (19)	C51—C50—N4—O14	170.2 (16)
C22—C23—C24—N2	−179.7 (11)	C49—C50—N4—O13	164.9 (16)
C23—C24—C25—C26	1 (2)	C51—C50—N4—O13	−10 (2)
N2—C24—C25—C26	179.5 (14)	O4—C12—O3—C13	2.8 (17)
C24—C25—C26—C21	−1 (2)	C8—C12—O3—C13	−176.2 (10)
C22—C21—C26—C25	0.2 (18)	C18—C17—O5—C20	176.8 (15)
C10—C21—C26—C25	177.2 (12)	C16—C17—O5—C20	0 (2)
C32—C27—C28—C29	6.2 (16)	O11—C38—O10—C39	3.2 (16)
S2—C27—C28—C29	−172.5 (8)	C34—C38—O10—C39	−172.0 (9)
C27—C28—C29—C30	−3.4 (17)	C44—C43—O12—C46	178.3 (18)
C28—C29—C30—C31	0 (2)	C42—C43—O12—C46	−3 (3)
C28—C29—C30—C33	175.7 (13)	C11—N1—S1—O2	42.6 (8)
C29—C30—C31—C32	0 (2)	C8—N1—S1—O2	−174.5 (7)
C33—C30—C31—C32	−175.4 (15)	C11—N1—S1—O1	172.3 (7)
C28—C27—C32—C31	−5.9 (19)	C8—N1—S1—O1	−44.8 (8)
S2—C27—C32—C31	172.8 (10)	C11—N1—S1—C1	−75.0 (8)
C30—C31—C32—C27	3 (2)	C8—N1—S1—C1	67.9 (8)
N3—C34—C35—C36	31.9 (10)	C6—C1—S1—O2	−28.6 (10)
C38—C34—C35—C36	154.3 (10)	C2—C1—S1—O2	152.1 (8)
C34—C35—C36—C47	86.0 (10)	C6—C1—S1—O1	−161.0 (8)
C34—C35—C36—C37	−38.3 (10)	C2—C1—S1—O1	19.7 (9)

C47—C36—C37—N3	−97.8 (10)	C6—C1—S1—N1	86.5 (9)
C35—C36—C37—N3	29.6 (10)	C2—C1—S1—N1	−92.8 (9)
C47—C36—C37—C40	139.4 (9)	C34—N3—S2—O8	−177.8 (7)
C35—C36—C37—C40	−93.2 (10)	C37—N3—S2—O8	37.6 (9)
N3—C34—C38—O11	37.6 (14)	C34—N3—S2—O9	−46.8 (9)
C35—C34—C38—O11	−77.8 (13)	C37—N3—S2—O9	168.6 (8)
N3—C34—C38—O10	−147.3 (9)	C34—N3—S2—C27	66.0 (8)
C35—C34—C38—O10	97.3 (10)	C37—N3—S2—C27	−78.6 (9)
N3—C37—C40—C41	−13.1 (15)	C32—C27—S2—O8	143.0 (10)
C36—C37—C40—C41	103.4 (13)	C28—C27—S2—O8	−38.3 (9)
N3—C37—C40—C45	171.2 (9)	C32—C27—S2—O9	10.5 (11)
C36—C37—C40—C45	−72.3 (13)	C28—C27—S2—O9	−170.8 (8)
C45—C40—C41—C42	−1 (2)	C32—C27—S2—N3	−102.4 (10)
C37—C40—C41—C42	−177.1 (12)	C28—C27—S2—N3	76.3 (9)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6—H6···O4^{i}	0.93	2.48	3.357 (14)	158
C25—H25···O5^{ii}	0.93	2.56	3.382 (17)	148
C28—H28···O11^{iii}	0.93	2.48	3.388 (14)	164
C36—H36···O2^{i}	0.98	2.54	3.344 (11)	139
C39—H39*C*···O8^{iv}	0.96	2.49	3.327 (15)	146
C49—H49···O12^{v}	0.93	2.65	3.412 (19)	140

Symmetry codes: (i) −*x*+1, *y*+1/2, −*z*+1; (ii) *x*−1, *y*, *z*; (iii) −*x*+1, *y*+1/2, −*z*+2; (iv) −*x*+1, *y*−1/2, −*z*+2; (v) *x*+1, *y*, *z*.



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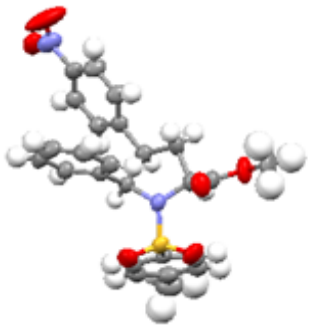

Computing details

Cell refinement: *SAINT* V8.34A (Bruker AXS Inc., 2013); data reduction: *SAINT* V8.34A (Bruker AXS Inc., 2013); program(s) used to refine structure: *SHELXL2014*/7 (Sheldrick, 2014).

Crystal data

$C_{25}H_{24}N_2O_6S$	D_x = 1.349 Mg m^{-3}
M_r = 480.52	Mo $K\alpha$ radiation, λ = 0.71073 Å
Orthorhombic, $P2_12_12_1$	Cell parameters from 8759 reflections
a = 10.2289 (2) Å	θ = 2.4–21.1°
b = 15.1538 (2) Å	μ = 0.18 mm^{-1}
c = 15.2606 (2) Å	T = 293 K
V = 2365.50 (6) Å^3	Prismatic, clear colourless
Z = 4	0.25 × 0.14 × 0.12 mm
F(000) = 1008	

Data collection

Bruker Kappa ApexII diffractometer	3512 reflections with $I > 2\sigma(I)$
Detector resolution: 8.3333 pixels mm^{-1}	R_{int} = 0.048
Absorption correction: multi-scan *SADABS*	θ_{max} = 25.4°, θ_{min} = 1.9°
T_{min} = 0.93, T_{max} = 0.98	h = −12→12
39541 measured reflections	k = −18→18
4326 independent reflections	l = −18→18

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.037	$w = 1/[\sigma^2(F_o^2) + (0.0752P)^2 + 0.0514P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.116	$(\Delta/\sigma)_{max} < 0.001$
S = 1.05	$\Delta\rho_{max}$ = 0.27 e Å^{-3}
4326 reflections	$\Delta\rho_{min}$ = −0.22 e Å^{-3}
309 parameters	Absolute structure: Flack x determined using 1314 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
0 restraints	Absolute structure parameter: −0.02 (3)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles;

correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.6376 (4)	0.5604 (2)	0.4164 (2)	0.0477 (8)
C2	0.6524 (5)	0.6243 (2)	0.3517 (3)	0.0588 (10)
H2	0.5908	0.6295	0.3071	0.071*
C3	0.7593 (5)	0.6799 (3)	0.3542 (3)	0.0684 (12)
H3	0.7688	0.7225	0.3107	0.082*
C4	0.8525 (5)	0.6741 (3)	0.4193 (3)	0.0654 (11)
C5	0.8363 (5)	0.6098 (3)	0.4823 (3)	0.0666 (12)
H5	0.8988	0.604	0.5262	0.08*
C6	0.7299 (4)	0.5538 (3)	0.4821 (2)	0.0581 (10)
H6	0.7204	0.5118	0.5261	0.07*
C7	0.9687 (5)	0.7345 (3)	0.4224 (4)	0.0967 (16)
H7A	1.0474	0.7	0.4226	0.145*
H7B	0.9649	0.7697	0.4746	0.145*
H7C	0.968	0.7723	0.3719	0.145*
C8	0.5340 (3)	0.4132 (2)	0.2572 (2)	0.0488 (8)
H8	0.571	0.47	0.2391	0.059*
C9	0.6201 (4)	0.3374 (3)	0.2249 (2)	0.0556 (10)
H9A	0.5706	0.283	0.2207	0.067*
H9B	0.6576	0.3508	0.1681	0.067*
C10	0.7259 (3)	0.3306 (2)	0.2948 (2)	0.0453 (8)
H10	0.7828	0.3822	0.2881	0.054*
C11	0.6478 (3)	0.3435 (2)	0.3812 (2)	0.0402 (7)
H11	0.7032	0.3739	0.424	0.048*
C12	0.3967 (4)	0.4038 (2)	0.2229 (2)	0.0517 (9)
C13	0.2686 (5)	0.4278 (4)	0.0954 (3)	0.0926 (17)
H13A	0.1995	0.4553	0.128	0.139*
H13B	0.2494	0.3663	0.0878	0.139*
H13C	0.2762	0.4555	0.039	0.139*
C14	0.5982 (3)	0.2584 (2)	0.4209 (2)	0.0395 (7)
C15	0.6779 (4)	0.2148 (2)	0.4806 (2)	0.0487 (8)
H15	0.7572	0.2399	0.4969	0.058*
C16	0.6409 (4)	0.1348 (2)	0.5163 (3)	0.0596 (10)
H16	0.6947	0.1069	0.5568	0.072*
C17	0.5253 (5)	0.0965 (2)	0.4919 (3)	0.0668 (11)
H17	0.5001	0.0428	0.516	0.08*
C18	0.4469 (4)	0.1381 (3)	0.4319 (3)	0.0624 (11)

H18	0.3696	0.1113	0.414	0.075*
C19	0.4815 (4)	0.2193 (2)	0.3975 (2)	0.0504 (9)
H19	0.4258	0.2476	0.3584	0.061*
C20	0.8125 (3)	0.2500 (2)	0.2912 (2)	0.0446 (8)
C21	0.9361 (4)	0.2550 (3)	0.3267 (2)	0.0532 (9)
H21	0.9644	0.3081	0.3507	0.064*
C22	1.0186 (4)	0.1837 (2)	0.3274 (2)	0.0566 (10)
H22	1.101	0.1878	0.3528	0.068*
C23	0.9775 (4)	0.1068 (2)	0.2903 (2)	0.0512 (9)
C24	0.8559 (4)	0.0992 (3)	0.2536 (3)	0.0635 (11)
H24	0.8293	0.0464	0.2282	0.076*
C25	0.7739 (4)	0.1709 (2)	0.2551 (3)	0.0573 (10)
H25	0.6906	0.166	0.2312	0.069*
N1	0.5406 (3)	0.40410 (18)	0.35338 (18)	0.0456 (7)
N2	1.0645 (4)	0.0304 (3)	0.2901 (3)	0.0740 (11)
O1	0.4874 (3)	0.45480 (18)	0.50189 (16)	0.0656 (7)
O2	0.3985 (3)	0.53186 (19)	0.3713 (2)	0.0713 (8)
O3	0.3909 (3)	0.4374 (2)	0.14279 (19)	0.0743 (9)
O4	0.3080 (3)	0.3673 (2)	0.25853 (19)	0.0713 (8)
O5	1.0229 (4)	−0.0392 (3)	0.2652 (5)	0.155 (2)
O6	1.1765 (3)	0.0390 (2)	0.3158 (2)	0.0739 (8)
S001	0.50272 (9)	0.48802 (6)	0.41514 (6)	0.0518 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.053 (2)	0.0400 (17)	0.0507 (19)	0.0133 (15)	0.0014 (18)	−0.0030 (15)
C2	0.067 (3)	0.050 (2)	0.059 (2)	0.0078 (19)	−0.006 (2)	0.0042 (17)
C3	0.087 (3)	0.054 (2)	0.064 (2)	0.005 (2)	0.009 (2)	0.0024 (19)
C4	0.070 (3)	0.055 (2)	0.072 (3)	0.002 (2)	0.010 (2)	−0.015 (2)
C5	0.066 (3)	0.075 (3)	0.058 (2)	0.009 (2)	−0.007 (2)	−0.018 (2)
C6	0.062 (3)	0.061 (2)	0.051 (2)	0.011 (2)	−0.001 (2)	0.0004 (18)
C7	0.086 (4)	0.088 (3)	0.116 (4)	−0.018 (3)	0.010 (3)	−0.021 (3)
C8	0.040 (2)	0.0522 (18)	0.0545 (19)	0.0048 (16)	−0.0022 (16)	0.0082 (16)
C9	0.051 (2)	0.071 (2)	0.0447 (19)	0.013 (2)	0.0025 (17)	0.0070 (16)
C10	0.0361 (18)	0.0479 (18)	0.052 (2)	0.0005 (16)	0.0044 (16)	0.0062 (15)
C11	0.0319 (18)	0.0443 (17)	0.0444 (17)	0.0047 (14)	−0.0035 (14)	0.0011 (13)
C12	0.049 (2)	0.053 (2)	0.054 (2)	0.0077 (18)	−0.0047 (18)	0.0056 (17)
C13	0.076 (3)	0.112 (4)	0.089 (3)	−0.009 (3)	−0.043 (3)	0.033 (3)

C14	0.0352 (17)	0.0433 (16)	0.0399 (16)	0.0010 (13)	0.0053 (15)	−0.0020 (14)
C15	0.043 (2)	0.0492 (19)	0.054 (2)	0.0019 (16)	−0.0014 (17)	0.0010 (16)
C16	0.062 (3)	0.052 (2)	0.065 (2)	0.013 (2)	0.008 (2)	0.0127 (18)
C17	0.072 (3)	0.044 (2)	0.084 (3)	−0.001 (2)	0.019 (3)	0.0045 (19)
C18	0.050 (2)	0.054 (2)	0.083 (3)	−0.0135 (18)	0.008 (2)	−0.008 (2)
C19	0.037 (2)	0.0571 (19)	0.057 (2)	0.0001 (17)	0.0023 (17)	−0.0009 (16)
C20	0.0352 (19)	0.0517 (19)	0.0467 (19)	−0.0002 (16)	0.0076 (15)	0.0027 (15)
C21	0.042 (2)	0.059 (2)	0.058 (2)	0.0043 (18)	−0.0095 (18)	−0.0102 (17)
C22	0.042 (2)	0.070 (2)	0.057 (2)	0.0073 (19)	−0.0105 (18)	−0.0073 (18)
C23	0.038 (2)	0.055 (2)	0.061 (2)	0.0075 (17)	0.0070 (17)	−0.0021 (17)
C24	0.048 (2)	0.056 (2)	0.087 (3)	−0.0031 (19)	−0.003 (2)	−0.013 (2)
C25	0.0303 (18)	0.059 (2)	0.082 (3)	−0.0003 (17)	−0.0032 (18)	−0.008 (2)
N1	0.0421 (17)	0.0469 (15)	0.0479 (15)	0.0084 (13)	−0.0036 (13)	0.0060 (12)
N2	0.050 (2)	0.070 (2)	0.103 (3)	0.0144 (18)	0.011 (2)	−0.008 (2)
O1	0.0669 (18)	0.0744 (16)	0.0555 (14)	0.0090 (15)	0.0179 (14)	0.0043 (12)
O2	0.0508 (17)	0.0682 (17)	0.095 (2)	0.0248 (14)	−0.0060 (15)	0.0036 (15)
O3	0.0566 (18)	0.095 (2)	0.0708 (17)	−0.0072 (17)	−0.0240 (15)	0.0324 (16)
O4	0.0471 (18)	0.098 (2)	0.0689 (18)	−0.0086 (16)	−0.0079 (15)	0.0115 (16)
O5	0.074 (3)	0.077 (2)	0.315 (7)	0.023 (2)	−0.018 (4)	−0.075 (3)
O6	0.0534 (19)	0.090 (2)	0.0786 (19)	0.0242 (16)	0.0008 (15)	0.0055 (16)
S001	0.0435 (5)	0.0535 (5)	0.0585 (5)	0.0138 (4)	0.0034 (4)	0.0020 (4)

Geometric parameters (Å, º)

C1—C6	1.382 (5)	C13—H13A	0.96
C1—C2	1.391 (5)	C13—H13B	0.96
C1—S001	1.763 (4)	C13—H13C	0.96
C2—C3	1.382 (6)	C14—C19	1.380 (5)
C2—H2	0.93	C14—C15	1.390 (5)
C3—C4	1.380 (7)	C15—C16	1.382 (5)

C3—H3	0.93	C15—H15	0.93
C4—C5	1.379 (6)	C16—C17	1.368 (6)
C4—C7	1.500 (7)	C16—H16	0.93
C5—C6	1.380 (6)	C17—C18	1.371 (6)
C5—H5	0.93	C17—H17	0.93
C6—H6	0.93	C18—C19	1.384 (5)
C7—H7A	0.96	C18—H18	0.93
C7—H7B	0.96	C19—H19	0.93
C7—H7C	0.96	C20—C21	1.378 (5)
C8—N1	1.475 (4)	C20—C25	1.377 (5)
C8—C12	1.506 (5)	C21—C22	1.370 (5)
C8—C9	1.530 (5)	C21—H21	0.93
C8—H8	0.98	C22—C23	1.362 (5)
C9—C10	1.524 (5)	C22—H22	0.93
C9—H9A	0.97	C23—C24	1.369 (6)
C9—H9B	0.97	C23—N2	1.460 (5)
C10—C20	1.509 (5)	C24—C25	1.374 (6)
C10—C11	1.554 (5)	C24—H24	0.93
C10—H10	0.98	C25—H25	0.93
C11—N1	1.491 (4)	N1—S001	1.629 (3)
C11—C14	1.513 (4)	N2—O5	1.200 (5)
C11—H11	0.98	N2—O6	1.217 (5)
C12—O4	1.193 (5)	O1—S001	1.425 (3)
C12—O3	1.325 (5)	O2—S001	1.423 (3)
C13—O3	1.452 (5)		
C6—C1—C2	119.4 (4)	H13A—C13—H13B	109.5
C6—C1—S001	119.8 (3)	O3—C13—H13C	109.5
C2—C1—S001	120.7 (3)	H13A—C13—H13C	109.5
C3—C2—C1	119.5 (4)	H13B—C13—H13C	109.5
C3—C2—H2	120.3	C19—C14—C15	118.2 (3)
C1—C2—H2	120.3	C19—C14—C11	123.5 (3)
C4—C3—C2	121.8 (4)	C15—C14—C11	118.1 (3)
C4—C3—H3	119.1	C16—C15—C14	121.0 (4)
C2—C3—H3	119.1	C16—C15—H15	119.5
C3—C4—C5	117.7 (4)	C14—C15—H15	119.5
C3—C4—C7	122.0 (4)	C17—C16—C15	120.1 (4)
C5—C4—C7	120.3 (5)	C17—C16—H16	120.0
C6—C5—C4	121.8 (4)	C15—C16—H16	120.0
C6—C5—H5	119.1	C16—C17—C18	119.5 (4)
C4—C5—H5	119.1	C16—C17—H17	120.2
C5—C6—C1	119.7 (4)	C18—C17—H17	120.2
C5—C6—H6	120.1	C17—C18—C19	120.8 (4)

C1—C6—H6	120.1	C17—C18—H18	119.6
C4—C7—H7A	109.5	C19—C18—H18	119.6
C4—C7—H7B	109.5	C14—C19—C18	120.3 (4)
H7A—C7—H7B	109.5	C14—C19—H19	119.8
C4—C7—H7C	109.5	C18—C19—H19	119.8
H7A—C7—H7C	109.5	C21—C20—C25	117.9 (3)
H7B—C7—H7C	109.5	C21—C20—C10	118.7 (3)
N1—C8—C12	112.3 (3)	C25—C20—C10	123.4 (3)
N1—C8—C9	103.0 (3)	C22—C21—C20	121.7 (3)
C12—C8—C9	110.7 (3)	C22—C21—H21	119.2
N1—C8—H8	110.2	C20—C21—H21	119.2
C12—C8—H8	110.2	C23—C22—C21	118.8 (3)
C9—C8—H8	110.2	C23—C22—H22	120.6
C10—C9—C8	103.5 (3)	C21—C22—H22	120.6
C10—C9—H9A	111.1	C22—C23—C24	121.5 (3)
C8—C9—H9A	111.1	C22—C23—N2	119.4 (3)
C10—C9—H9B	111.1	C24—C23—N2	119.1 (3)
C8—C9—H9B	111.1	C23—C24—C25	118.8 (4)
H9A—C9—H9B	109.0	C23—C24—H24	120.6
C20—C10—C9	116.5 (3)	C25—C24—H24	120.6
C20—C10—C11	115.8 (3)	C24—C25—C20	121.4 (4)
C9—C10—C11	102.7 (3)	C24—C25—H25	119.3
C20—C10—H10	107.1	C20—C25—H25	119.3
C9—C10—H10	107.1	C8—N1—C11	112.0 (3)
C11—C10—H10	107.1	C8—N1—S001	119.4 (2)
N1—C11—C14	113.1 (3)	C11—N1—S001	119.4 (2)
N1—C11—C10	102.4 (2)	O5—N2—O6	122.0 (4)
C14—C11—C10	113.9 (3)	O5—N2—C23	118.8 (4)
N1—C11—H11	109.1	O6—N2—C23	119.3 (4)
C14—C11—H11	109.1	C12—O3—C13	117.3 (4)
C10—C11—H11	109.1	O2—S001—O1	121.25 (18)
O4—C12—O3	124.4 (4)	O2—S001—N1	105.70 (17)
O4—C12—C8	126.5 (3)	O1—S001—N1	106.73 (15)
O3—C12—C8	109.0 (3)	O2—S001—C1	107.50 (17)
O3—C13—H13A	109.5	O1—S001—C1	107.24 (17)
O3—C13—H13B	109.5	N1—S001—C1	107.80 (16)
C6—C1—C2—C3	0.2 (5)	C11—C10—C20—C25	94.8 (4)
S001—C1—C2—C3	−179.8 (3)	C25—C20—C21—C22	−0.8 (6)
C1—C2—C3—C4	−0.1 (6)	C10—C20—C21—C22	178.5 (3)
C2—C3—C4—C5	0.6 (6)	C20—C21—C22—C23	1.5 (6)
C2—C3—C4—C7	−179.9 (4)	C21—C22—C23—C24	−0.8 (6)
C3—C4—C5—C6	−1.2 (6)	C21—C22—C23—N2	179.6 (3)

C7—C4—C5—C6	179.3 (4)	C22—C23—C24—C25	−0.4 (6)
C4—C5—C6—C1	1.4 (5)	N2—C23—C24—C25	179.2 (4)
C2—C1—C6—C5	−0.8 (5)	C23—C24—C25—C20	1.1 (6)
S001—C1—C6—C5	179.2 (3)	C21—C20—C25—C24	−0.5 (6)
N1—C8—C9—C10	−33.7 (4)	C10—C20—C25—C24	−179.7 (3)
C12—C8—C9—C10	−154.0 (3)	C12—C8—N1—C11	132.9 (3)
C8—C9—C10—C20	168.6 (3)	C9—C8—N1—C11	13.8 (4)
C8—C9—C10—C11	40.9 (3)	C12—C8—N1—S001	−80.6 (4)
C20—C10—C11—N1	−159.8 (3)	C9—C8—N1—S001	160.4 (3)
C9—C10—C11—N1	−31.7 (3)	C14—C11—N1—C8	−111.8 (3)
C20—C10—C11—C14	−37.3 (4)	C10—C11—N1—C8	11.2 (3)
C9—C10—C11—C14	90.7 (3)	C14—C11—N1—S001	101.6 (3)
N1—C8—C12—O4	−22.3 (6)	C10—C11—N1—S001	−135.4 (2)
C9—C8—C12—O4	92.1 (4)	C22—C23—N2—O5	172.7 (5)
N1—C8—C12—O3	161.9 (3)	C24—C23—N2—O5	−6.9 (7)
C9—C8—C12—O3	−83.6 (4)	C22—C23—N2—O6	−6.6 (6)
N1—C11—C14—C19	30.3 (4)	C24—C23—N2—O6	173.8 (4)
C10—C11—C14—C19	−86.1 (4)	O4—C12—O3—C13	−0.9 (6)
N1—C11—C14—C15	−153.4 (3)	C8—C12—O3—C13	175.0 (4)
C10—C11—C14—C15	90.3 (4)	C8—N1—S001—O2	36.0 (3)
C19—C14—C15—C16	−0.5 (5)	C11—N1—S001—O2	−179.9 (2)
C11—C14—C15—C16	−177.1 (3)	C8—N1—S001—O1	166.4 (3)
C14—C15—C16—C17	1.0 (6)	C11—N1—S001—O1	−49.5 (3)
C15—C16—C17—C18	0.2 (6)	C8—N1—S001—C1	−78.7 (3)
C16—C17—C18—C19	−1.9 (6)	C11—N1—S001—C1	65.4 (3)
C15—C14—C19—C18	−1.1 (5)	C6—C1—S001—O2	153.1 (3)
C11—C14—C19—C18	175.2 (3)	C2—C1—S001—O2	−27.0 (3)
C17—C18—C19—C14	2.3 (6)	C6—C1—S001—O1	21.2 (3)
C9—C10—C20—C21	154.6 (3)	C2—C1—S001—O1	−158.9 (3)
C11—C10—C20—C21	−84.5 (4)	C6—C1—S001—N1	−93.4 (3)
C9—C10—C20—C25	−26.1 (5)	C2—C1—S001—N1	86.5 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6—H6···O6^{i}	0.93	2.57	3.432 (5)	154
C10—H10···O5^{ii}	0.98	2.46	3.367 (5)	154

Symmetry codes: (i) *x*−1/2, −*y*+1/2, −*z*+1; (ii) −*x*+2, *y*+1/2, −*z*+1/2.