Umpolung Synthesis of Vicinal Diamines: Diastereoselective Addition of 2-Azaallyl Anions to Davis-Ellman's Imines.

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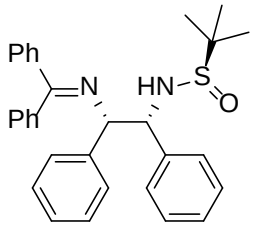
General Information.

All the reactions were performed under nitrogen gas in glasswares that was flame-dried and equipped with a magnetic stirring bar. Thin-layer chromatography (TLC) was performed using silica gel 60 F254 pre-coated plates (0.25 mm). All the reactions monitored by the TLC analysis (single spot/ two solvent systems) using a UV lamp or PMA for detection purposes. Flash chromatography was performed using silica gel (40 µm particle size). ^{1}H and ^{13}C NMR spectra were recorded on a FT-NMR spectrometer at 400 and 100 MHz, respectively. Low-resolution mass spectroscopy (LRMS) was carried out in electro spray mode. The diastereoselectivity was determined by ^{1}H NMR analysis of the crude product. The ">95:5" dr denotes that signal for only one diastereomer were observed. Mass spectra (HRMS) were obtained using an electrospray ionization (ESI-TOF) mass spectrometer. The aldehydes and *N-tert*-Butanesulfamide were purchased from Aldrich. All solvents were purchased from Aldrich and used without further purification. Unless indicated otherwise, the reaction temperatures refer to external reaction temperatures. All the Ellman's Imines (**4a-f**) were synthesized using known procedures.

General Procedure:

To a solution of Ketimine **1** (2.0 mmol) in anhydrous THF (20 V) was added LiHMDS (1*M* in THF, 1.8 mmol) at -78 ^{o}C under a N_2 atmosphere. After 15 min stirring, solution of sulfinamide **4** (1.0 mmol) in dry THF (10 V) was added dropwise over a period of 15 min. The reaction mixture was stirred for 3 h at -78 ^{o}C. Reaction was monitored by TLC then quenched with water slowly at -78 ^{o}C and warmed the reaction mixture to room temperature. Reaction mixture was extracted with EtOAc. The combined organic extract was dried over sodium sulphate and the solvent concentrated *in vacuo.* The crude product was purified by column chromatography (1 : 3, EtOAc/hexane) to obtain the final product.

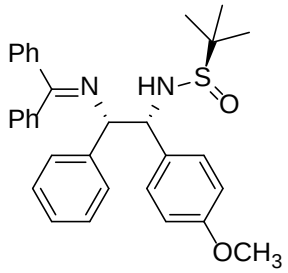
(*R*)-N-((1*R*,2*S*)-2-((diphenylmethylene)amino)-1,2-diphenylethyl)-2-methylpropane-2-sulfinamide (5a):



Obtained **5a** as a white solid (428 mg, 93%) according to the general procedure using *N-tert*-butanesulfinyl aldimine (R_S) **4a** (200 mg, 0.95 mmol), Ketimine **1a** (1.91 mmol) and *LiHMDS* (1 *M* in THF, 1.72 mmol). mp 120-122 ^{o}C, $[\alpha]_D^{25}$ = 108.57 (c. 0.25, $CHCl_3$), IR: 3329, 3024, 1629, 1598, 1074, 700. ^{1}H-NMR: (400 MHz, DMSO-d_6) δ ppm 7.62 (d, *J*=7.2 Hz, 2H), 7.47-7.17 (m, 16H), 6.35 (d,

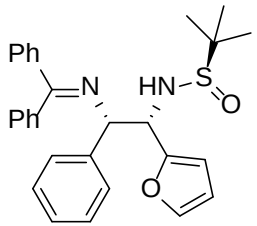
J=7.2 Hz, 2H), 5.34 (d, *J*=10.0 Hz, 1H), 4.76 (dd, *J*=9.6, 4.0 Hz, 1H), 4.57 (d, *J*=4.0 Hz, 1H), 0.90 (s. 9H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm: 168.6, 142.3, 139.2, 136.0, 130.8, 128.8, 128.6, 128.4, 128.2, 128.0, 127.6, 127.3, 127.2, 127.0, 71.3, 66.9, 56.2, 22.5. HRMS (ESI) calcd for $C_{31}H_{33}N_2OS$ $[M+H]^+$, 481.2308; found 481.2298.

(*R*)-N-((1*R*,2*S*)-2-((diphenylmethylene)amino)-1-(4-methoxyphenyl)-2-phenylethyl)-2-methylpropane-2-sulfinamide (5b):



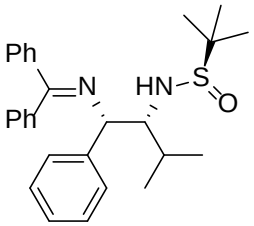
Obtained **23** as an off-white solid (366 mg, 86%) according to the general experimental procedure as described above using *N-tert*-butanesulfinyl aldimine (R_S) **4b** (200 mg, 0.83 mmol), Ketimine **1a** (1.67 mmol) and *LiHMDS* (1 *M* in THF, 1.5 mmol). mp 56-58 ^{o}C, $[\alpha]_D^{25}$ = 59.53 (c. 0.25, $CHCl_3$), IR: 3334, 3059, 2954, 1612, 1512, 1072, 700. ^{1}H-NMR: (400 MHz, DMSO-d_6) δ ppm 7.61 (d, *J*=6.8, 2H), 7.46-7.29 (m, 6H), 7.21-7.15 (m, 7H), 6.77 (d, *J*=8.4 Hz, 2H), 6.45 (d, *J*= 7.2 Hz, 2H), 5.23 (d, *J*= 9.6 Hz, 1H), 4.70 (dd, *J*= 9.2, 4.4 Hz, 1H), 4.54 (d, *J*= 4.4 Hz, 1H), 3.70 (s, 3H), 0.9 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm: 168.4, 158.6, 142.4, 139.3, 136.1, 134.3, 130.8, 130.1, 129.3, 128.9, 128.7, 128.6, 128.3, 127.7, 127.1, 113.4, 71.4, 66.4, 56.1, 55.5, 22.5. HRMS (ESI) calcd for $C_{32}H_{35}N_2O_2S$ $[M+H]^+$, 511.2414; found 511.2404.

(*R*)-N-((1*S*,2*S*)-2-((diphenylmethylene)amino)-1-(furan-2-yl)-2-phenylethyl)-2-methylpropane-2-sulfinamide (5c):



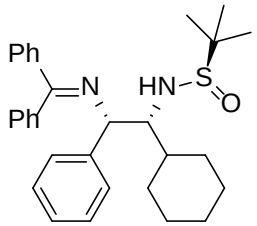
Obtained **5c** as an off-white solid (417 mg, 89%) according to the general experimental procedure as described above using *N-tert*-butanesulfinyl aldimine (R_S) **4c** (200 mg, 0.99 mmol), Ketimine **1a** (1.98 mmol) and *LiHMDS* (1 *M* in THF, 1.78 mmol). mp 136-138 ^{o}C, $[\alpha]_D^{25}$ = 42.72 (c. 0.25, $CHCl_3$), IR: 3338, 3118, 2872, 1568, 1072, 738. ^{1}H-NMR: (400 MHz, DMSO-d_6) δ ppm 7.63 (d, *J*= 7.2 Hz, 2H), 7.48-7.40 (m, 8H), 7.28-7.18 (m, 5H), 6.77 (d, *J*= 6.0 Hz, 2H), 6.26 (s, 1H), 5.06 (d, *J*= 10.0 Hz, 1H), 4.72-4.69 (m, 1H), 4.58 (d, J= 5.2 Hz, 1H), 0.92 (s, 9 H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm: 168.2, 143.0, 142.3, 140.6, 139.4, 136.1, 130.8, 129.0, 128.8, 128.6, 128.4, 127.8, 127.4, 127.3, 126.9, 110.8, 70.7, 59.8, 56.0, 22.6. HRMS (ESI) calcd for $C_{29}H_{31}N_2O_2S$ $[M+H]^+$, 471.2101; found, 471.2090.

(*R*)-N-((1*S*,2*R*)-1-((diphenylmethylene)amino)-3-methyl-1-phenylbutan-2-yl)-2-methylpropane-2-sulfinamide (5d)



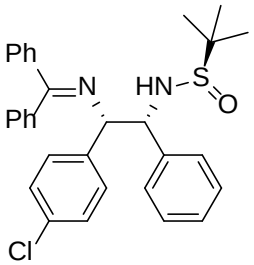
Obtained **5d** as a white solid (460 mg, 92%) according to the general experimental procedure as described above using *N-tert*-butanesulfinyl aldimine (R_S) **4e** (200 mg, 1.14 mmol), Ketimine **1a** (2.28 mmol) and *LiHMDS* (1 *M* in THF, 2.05 mmol). mp 150-152 ^{o}C, $[\alpha]_D^{25}$ = 14.56 (c. 0.25, $CHCl_3$), IR: 3346, 2960, 1571, 1064, 761. ^{1}H-NMR: (400 MHz, DMSO-d_6) δ ppm 7.63 (d, *J*= 6.8 Hz, 2H), 7.47-7.40 (m, 6H), 7.30-7.26 (m, 2H), 7.22-7.18 (m, 1H), 7.14 (d, *J*=7.2 Hz, 2H), 6.93 (d, *J*= 5.6 Hz, 2H), 4.53-4.50 (m, , 1H), 3.46-3.41 (m, 1H), 1.68-1.63 (m, 1H), 0.91 (s, 9H), 0.84 (t, *J*= 7.6 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm: 167.7, 143.7, 139.5, 136.2, 130.1, 130.0, 129.2, 128.8, 128.7, 128.6, 128.6, 127.5, 127.1, 68.9, 67.8, 55.9, 31.1, 22.8, 20.3, 18.5. HRMS (ESI) calcd for $C_{28}H_{35}N_2OS$ $[M+H]^+$,447.2465; found, 447.2453.

(*R*)-N-((1*R*,2*S*)-1-cyclohexyl-2-((diphenylmethylene)amino)-2-phenylethyl)-2-methylpropane-2-sulfinamide (5e):



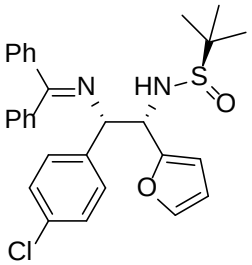
Obtained **5e** as pale yellow viscous liquid (389 mg, 88%) according to the general experimental procedure as described above using *N-tert*-butanesulfinyl aldimine (R_S) **4f** (200 mg, 0.93 mmol), Ketimine **1a** (1.86 mmol) and *LiHMDS* (1 *M* in THF, 1.67 mmol). $[\alpha]_D^{25}$ = 11.36 (c. 0.25, $CHCl_3$), IR: 3273, 3059, 2924, 1622, 1446, 1070, 700. ^{1}H-NMR: (400 MHz, DMSO-d_6) δ ppm 7.64 (d, *J*= 6.8 Hz, 2H), 7.51-7.39 (m, 6H), 7.32-7.24 (m, 2H), 7.24-7.16 (m, 1H), 7.14 (d, *J*= 7.2 Hz, 2H), 6.92 (d, *J*= 5.6 Hz, 2H), 4.60-4.54 (m, 2H), 3.44-3.35 (m, 1H), 1.78-1.74 (m, 1H), 1.73-1.44 (m, 4H), 1.34-1.24 (m, 2H), 1.23-1.03 (m, 4H), 0.89 (s, 9 H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm: 168.5, 143.8, 139.6, 136.3, 130.8, 129.2, 129.0, 128.8, 128.7, 128.6, 127.5, 127.4, 127.1, 68.5, 67.3, 55.9, 41.6, 30.0, 28.9, 26.5, 26.4, 22.8. HRMS (ESI) calcd for $C_{31}H_{39}N_2OS$ $[M+H]^+$, 487.2778; found 487.2767.

(*R*)-N-((1*R*,2*S*)-2-(4-chlorophenyl)-2-((diphenylmethylene)amino)-1-phenylethyl)-2-methylpropane-2-sulfinamide (5f):



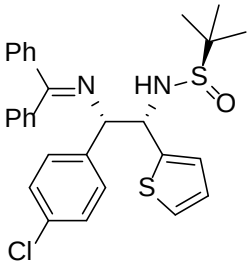
Obtained **5f** as an off-white solid (459 mg, 93%) according to the general experimental procedure as described above using *N-tert*-butanesulfinyl aldimine (R_S) **4a** (200 mg, 0.95 mmol), Ketimine **1b** (1.91 mmol) and *LiHMDS* (1 *M* in THF, 1.72 mmol). mp 158-160 ^{o}C,$[\alpha]_D^{25}$ = 105.77 (c. 0.25, $CHCl_3$), IR: 3340, 3059, 1624, 1390, 1074, 704. ^{1}H-NMR: (400 MHz, DMSO-d_6) δ ppm 7.63 (d, *J*= 7.2 Hz, 2H), 7.49-7.2 (m, 15H), 6.34 (d, *J*= 7.2 Hz, 2H), 5.45 (d, *J*= 10.0 Hz, 1H), 4.77-4.73 (m, 1H), 4.54 (s, 1H), 0.91 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm: 169.0, 142.2, 141.3, 139.1, 135.9, 131.7, 131.0, 129.6, 128.9, 128.7, 128.7, 128.3, 128.2, 128.1, 127.3, 127.0, 70.7, 66.3, 56.2, 22.6. HRMS (ESI) calcd for $C_{31}H_{32}ClN_2OS$ $[M+H]^+$, 516.1918; found, 516.1908.

(*R*)-N-((1*S*,2*S*)-2-(4-chlorophenyl)-2-((diphenylmethylene)amino)-1-(furan-2-yl)ethyl)-2-methylpropane-2-sulfinamide (5g):



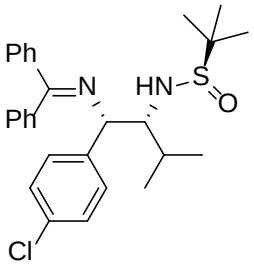
Obtained **5g** as an off-white solid (470 mg, 94%) according to the general experimental procedure as described above using *N-tert*-butanesulfinyl aldimine (R_S) **4c** (200 mg, 0.99 mmol), Ketimine **1b** (1.98 mmol) and *LiHMDS* (1*M* in THF, 1.78 mmol). mp 110-112 ^{o}C, $[\alpha]_D^{25}$ = 66.49 (c. 0.25, $CHCl_3$), IR: 3331, 2953, 1446, 1074, 702. ^{1}H-NMR: (400 MHz, DMSO-d_6) δ ppm 7.64 (d, *J*= 7.2 Hz, 2H), 7.52-7.38 (m, 8H), 7.33 (d, *J*= 8.4 Hz, 2H), 7.22 (d, J= 8.4 Hz, 2H), 6.76-7.73 (m, 2H), 6.31 (s, 1H), 5.12 (d, *J*= 9.6 Hz, 1H), 4.72-4.67 (m, 1H), 4.58 (d, *J*= 5.2 Hz, 1H), 0.93 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm: 168.7, 143.0, 141.3, 140.7, 139.3, 136.0, 131.7, 130.9, 129.7, 129.1, 128.9, 128.7, 128.7, 128.4, 127.3, 126.8, 110.7, 70.1, 59.5, 56.1, 22.6. HRMS (ESI) calcd for $C_{29}H_{30}ClN_2O_2S$ $[M+H]^+$, 506.1711; found, 506.1700.

(*R*)-N-((1*S*,2*S*)-2-(4-chlorophenyl)-2-((diphenylmethylene)amino)-1-(thiophen-2-yl)ethyl)-2-methylpropane-2-sulfinamide (5h):



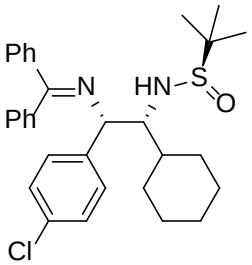
Obtained **5h** as an off-white solid (426 mg, 89%) according to the general experimental procedure as described above using *N*-*tert*-butanesulfinyl aldimine (R_S) **4d** (200 mg, 0.92 mmol), Ketimine **1b** (1.84 mmol) and *LiHMDS* (1 *M* in THF, 1.65 mmol). mp 117-119 ^{o}C, $[\alpha]_D^{25}$ = 130.89 (c. 0.25, $CHCl_3$), IR: 3323, 3026, 1624, 1487, 1076, 700. ^{1}H-NMR: (400 MHz, DMSO-d_6) δ ppm 7.67 (d, *J*= 7.2 Hz, 2H), 7.50-7.37 (m, 7H), 7.32 (d, *J*= 8.4 Hz, 2H), 7.26 (d, *J*= 8.0 Hz, 2H), 7.02 (d, *J*= 8 Hz, 1H), 6.95-6.88 (m, 1H), 6.63 (d, *J*= 6.8 Hz, 2H), 5.34 (d, *J*= 9.6 Hz, 1H), 5.2-4.97 (m, 1H), 4.62 (d, *J*= 4.4 Hz, 1H), 0.92 (s, 9 H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm: 169.5, 145.6, 141.0, 139.2, 136.0, 131.9, 131.1, 129.7, 129.1, 128.9, 128.8, 128.7, 128.4, 127.2, 126.6, 126.4, 125.8, 70.8, 61.9, 56.3, 22.5. HRMS (ESI) calcd for $C_{29}H_{30}ClN_2OS_2$ $[M+H]^+$, 522.1483; found, 522.1471.

(*R*)-N-((1*S*,2*R*)-1-(4-chlorophenyl)-1-((diphenylmethylene)amino)-3-methylbutan-2-yl)-2-methylpropane-2-sulfinamide (5i):



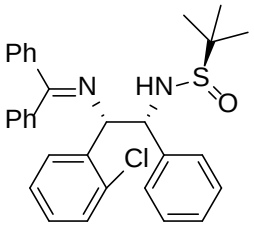
Obtained **5i** as an off-white solid (477 mg, 87%) according to the general experimental procedure as described above using *N-tert*-butanesulfinyl aldimine (R_S) **4e** (200 mg, 1.14 mmol), Ketimine **1b** (2.28 mmol) and *LiHMDS* (1*M* in THF, 2.05 mmol). mp 102-104 ^{o}C, $[\alpha]_D^{25}$ = 60.33 (c. 0.25, $CHCl_3$), IR: 3344, 2953, 1595, 1064, 702. ^{1}H-NMR: (400 MHz, DMSO-d_6) δ ppm 6.64 (d, *J*= 6.8 Hz, 2H), 7.51-7.39 (m, 6H), 7.34 (d, *J*= 8.4 Hz, 2H), 7.16 (d, *J*= 8.4 Hz, 2H), 6.93 (d, *J*= 4.0 Hz, 2H), 4.57 (d, *J*= 9.6 Hz, 1H), 4.50 (d, *J*= 4.0 Hz, 1H), 3.40-3.35 (m, 1H), 1.70-1.63 (m, 1H), 0.91 (s, 9H), 0.85 (d, *J*= 6.8 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm: 168.3, 142.7, 139.4, 136.1, 131.5, 130.9, 129.4, 129.2, 128.9, 128.8, 128.7, 128.5, 127.4, 68.8, 67.2, 55.9, 31.3, 22.8, 20.2, 18.8. HRMS (ESI) calcd for $C_{28}H_{34}ClN_2OS$ $[M+H]^+$, 482.2075; found, 482.2063.

(*R*)-N-((1*R*,2*S*)-2-(4-chlorophenyl)-1-cyclohexyl-2-((diphenylmethylene)amino)ethyl)-2-methylpropane-2-sulfinamide (5j):



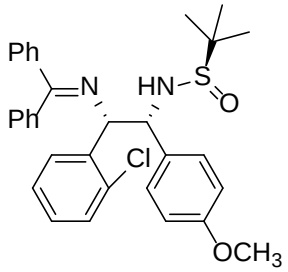
Obtained **5j** as a colourless viscous liquid(408 mg, 85%) according to the general experimental procedure as described above using *N-tert*-butanesulfinyl aldimine (R_S) **4f** (200 mg, 0.93 mmol), Ketimine **1b** (1.86 mmol) and *LiHMDS* (1*M* in THF, 1.67 mmol). $[\alpha]_D^{25}$ = 33.52 (c. 0.25, $CHCl_3$), IR: 3273, 3059, 1728, 1489, 1072, 742. ^{1}H-NMR: (400 MHz, DMSO-d_6) δ ppm 7.65 (d, *J*= 7.2 Hz, 2H), 7.51-7.39 (m, 6H), 7.34 (d, *J*= 8.4 Hz, 2H), 7.17 (d, *J*= 8.4 Hz, 2H), 6.92 (d, *J*= 3.6 Hz, 2H), 4.61 (d, *J*= 8.6 Hz, 1H), 4.55 (d, *J*= 3.6 Hz, 1H), 1.88-1.75 (m, 1H), 1.68-1.52 (m, 3H), 1.50-1.41 (m, 1H), 1.40-1.22 (m, 3H), 1.20-0.98 (m, 4H), 0.90 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm: 168.4, 142.8, 139.5, 136.2, 131.5, 130.9, 130.0, 129.4, 129.3, 129.0, 128.9, 128.8, 128.7, 128.5, 127.4, 68.4, 66.7, 56.0, 41.6, 29.9, 29.1, 26.5, 26.4, 26.4, 22.8. HRMS (ESI) calcd for $C_{31}H_{38}ClN_2OS$ $[M+H]^+$, 522.2388; found, 521.2374.

(*R*)-N-((1*R*,2*S*)-2-(2-chlorophenyl)-2-((diphenylmethylene)amino)-1-phenylethyl)-2-methylpropane-2-sulfinamide (5k):



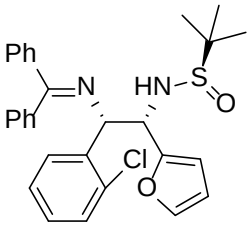
Obtained **5k** as an off-white solid (424 mg, 86%) according to the general experimental procedure as described above using *N-tert*-butanesulfinyl aldimine (R_S) **4a** (200 mg, 0.95 mmol), Ketimine **1c** (1.91 mmol) and *LiHMDS* (1*M* in THF, 1.72 mmol). mp 110-112 ^{o}C, $[\alpha]_D^{25}$ = 23.12 (c. 0.25, $CHCl_3$), IR: 3342, 3059, 1635, 1388, 1072, 696. ^{1}H-NMR: (400 MHz, DMSO-d_6) δ ppm 7.75 (d, *J*= 7.2 Hz, 1H), 7.68 (d, *J*= 7.2 Hz, 2H), 7.51-7.39 (m, 3H), 7.38-7.32 (m, 3H), 7.32-7.21 (m, 8H), 6.20 (d, *J*=6.8 Hz, 2H), 5.72 (d, *J*= 10 Hz, 1H), 4.92 (d, *J*= 2.4 Hz, 1H), 4.77-4.71 (m, 1H), 0.9 (s, 9 H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm: 169.7, 142.4, 139.5, 138.9, 136.1, 131.5, 131.1, 130.9, 129.5, 128.9, 128.7, 128.2, 127.7, 127.4, 127.2, 126.7, 68.0, 63.0, 56.3, 22.5. HRMS (ESI) calcd for $C_{31}H_{32}ClN_2OS$ $[M+H]^+$, 516.1918; found, 516.1909.

(*R*)-N-((1*R*,2*S*)-2-(2-chlorophenyl)-2-((diphenylmethylene)amino)-1-(4-methoxyphenyl)ethyl)-2-methylpropane-2-sulfinamide (5l):



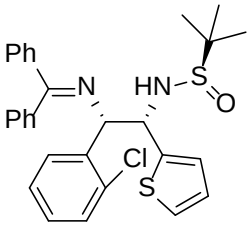
Obtained **5l** as a pale yellow solid (401 mg, 88%) according to the general experimental procedure as described above using *N*-*tert*-butanesulfinyl aldimine (R_S) **4b** (200 mg, 0.83 mmol), Ketimine **1c** (1.67 mmol) and *LiHMDS* (1 *M* in THF, 1.5 mmol). mp 52-54 ^{o}C, $[\alpha]_D^{25}$ = 7.68 (c. 0.25, $CHCl_3$), IR: 3327, 3059, 2927, 1612, 1512, 1074, 698. ^{1}H-NMR: (400 MHz, DMSO-d_6) δ ppm 7.73 (d, *J*= 7.2 Hz, 1H), 7.68 (d, *J*= 7.6 Hz, 2H), 7.51-7.20 (m, 9H), 7.16 (d, *J*= 8.8 Hz, 2H), 6.81 (d, *J*= 8.4 Hz, 2H), 6.30 (d, *J*= 7.2 Hz, 2H), 5.59 (d, *J*= 10.0 Hz, 1H), 4.91 (d, *J*= 3.2 Hz, 1H), 4.71-4.64 (m, 1H), 3.73 (s, 3H), 0.90 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm: 169.6, 158.7, 139.7, 139.1, 136.1, 134.4, 131.5, 131.1, 130.0, 129.5, 128.9, 128.9, 128.7, 128.6, 128.5, 127.6, 127.2, 126.8, 113.6, 68.0, 62.8, 56.3, 55.7, 55.5, 22.5. HRMS (ESI) calcd for $C_{32}H_{34}ClN_2O_2S$ $[M+H]^+$, 546.2024; found, 546.2010.

(*R*)-N-((1*S*,2*S*)-2-(2-chlorophenyl)-2-((diphenylmethylene)amino)-1-(furan-2-yl)ethyl)-2-methylpropane-2-sulfinamide (5m):



Obtained **5m** as an off-white solid (465 mg, 92%) according to the general experimental procedure as described above using *N*-*tert*-butanesulfinyl aldimine (R_S) **4c** (200 mg, 0.99 mmol), Ketimine **1c** (1.98 mmol) and *LiHMDS* (1 *M* in THF, 1.78 mmol). mp 126-128 ^{o}C, $[\alpha]_D^{25}$ = -65.13 (c. 0.25, $CHCl_3$), IR: 3336, 3057, 1568, 1028, 754. ^{1}H-NMR: (400 MHz, DMSO-d_6) δ ppm 7.71-7.62 (m, 3H), 7.54-7.29 (m, 10H), 7.28-7.22 (m, 1H), 6.65 (d, *J*= 6.8 Hz, 2H), 6.24 (s, 1H), 5.31 (d, *J*= 10.0 Hz, 1H), 4.97 (d, *J*= 4.0 Hz, 1H), 4.67-4.60 (m, 1H), 0.94 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm: 169.6, 143.3, 140.5, 139.6, 139.2, 136.2, 131.6, 131.1, 129.4, 129.1, 128.9, 128.9, 128.7, 127.3, 127.1, 127.0, 110.4, 67.0, 57.4, 56.2, 22.6. HRMS (ESI) calcd for $C_{29}H_{30}ClN_2O_2S$ $[M+H]^+$, 506.1711; found 506.1703.

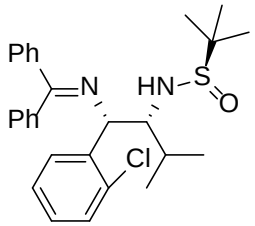
(*R*)-N-((1*S*,2*S*)-2-(2-chlorophenyl)-2-((diphenylmethylene)amino)-1-(thiophen-2-yl)ethyl)-2-methylpropane-2-sulfinamide (5n):



Obtained **5n** as an off-white solid (435 mg, 90%) according to the general experimental procedure as described above using *N-tert*-butanesulfinyl aldimine (R_S) **4d** (200 mg, 0.92 mmol), Ketimine **1c** (1.84 mmol) and *LiHMDS* (1.0 M in THF, 1.65 mmol).

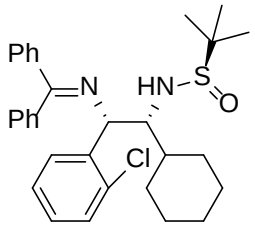
mp 140-142 ^{o}C, $[\alpha]_D^{25}$ = 30.64 (c. 0.25, $CHCl_3$), IR: 3321, 3057, 1635, 1571, 1311, 1029, 723. ^{1}H-NMR: (400 MHz, DMSO-d_6) δ ppm 7.74-7.63 (m, 3H), 7.54-7.25 (m, 11H), 7.01 (d, *J*= 3.2 Hz, 1H), 6.98-6.92 (m, 1H), 6.49 (d, *J*= 6.8 Hz, 1H), 5.58 (d, *J*= 9.6 Hz, 1H), 4.50-4.90 (m, 2H), 0.91 (s, 9 H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm: 170.5, 146.1, 139.4, 139.1, 136.1, 131.6, 131.2, 130.9, 129.5, 129.1, 128.8, 128.7, 127.3, 126.9, 126.8, 125.8, 125.8, 68.1, 58.9, 56.4, 22.5. HRMS (ESI) calcd for $C_{29}H_{30}ClN_2OS_2$ $[M+H]^+$, 522.1483; found 522.1472.

(R)-N-((1S,2R)-1-(2-chlorophenyl)-1-((diphenylmethylene)amino)-3-methylbutan-2-yl)-2-methylpropane-2-sulfinamide (5o):



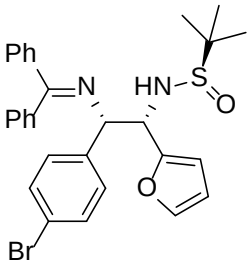
Obtained **5o** as an off-white solid (513 mg, 93%) according to the general experimental procedure as described above using *N-tert*-butanesulfinyl aldimine (R_S) **4e** (200 mg, 1.14 mmol), Ketimine **1c** (2.28 mmol) and *LiHMDS* (1 *M* in THF, 2.05 mmol). mp 132-134 ^{o}C, $[\alpha]_D^{25}$ = -94.65 (c. 0.25, $CHCl_3$), IR: 3348, 2956, 1606, 1593, 1066, 702. ^{1}H-NMR: (400 MHz, DMSO-d_6) δ ppm 7.68 (d, *J*= 7.2 Hz, 2H), 7.53-7.39 (m, 7H), 7.37-7.22 (m, 3H), 6.83 (d, *J*= 6.4 Hz, 2H), 4.90 (d, *J*= 2.8 Hz, 1H), 4.77 (d, *J*= 9.6 Hz, 1H), 1.88-1.79 (m, 1H), 0.95-0.87 (m, 15H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm: 169.0, 141.4, 139.3, 136.4, 131.3, 131.2, 131.1, 129.5, 129.3, 128.9, 128.8, 128.8, 128.7, 127.3, 127.2, 66.1, 63.5, 56.1, 32.6, 22.8, 19.8, 19.5. HRMS (ESI) calcd for $C_{28}H_{34}ClN_2OS$ $[M+H]^+$, 482.2075; found 481.2063.

(*R*)-N-((1*R*,2*S*)-2-(2-chlorophenyl)-1-cyclohexyl-2-((diphenylmethylene)amino)ethyl)-2-methylpropane-2-sulfinamide (5p):



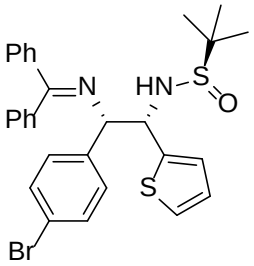
Obtained **5p** as pale yellow solid (452 mg, 93%) according to the general experimental procedure as described above using *N-tert*-butanesulfinyl aldimine (R_S) **4f** (200 mg, 0.93 mmol), Ketimine **1c** (1.86 mmol) and *LiHMDS* (1 *M* in THF, 1.67 mmol). mp 142-144 ^{o}C, $[\alpha]_D^{25}$ = -84.41 (c. 0.25, $CHCl_3$), IR: 3344, 3059, 2850, 1730, 1446, 1029, 700. ^{1}H-NMR: (400 MHz, DMSO-d_6) δ ppm 7.68 (d, *J*= 7.2 Hz, 2H), 7.54-7.39 (m, 7H), 7.37-7.32 (m, 1H), 7.32-7.20 (m, 2H), 6.82 (d, *J*= 6.4 Hz, 2H), 4.93 (d, *J*= 2.0 Hz, 1H), 4.80 (d, *J*= 10.0 Hz, 1H), 3.35-3.30 (m, 1H), 1.91-1.86 (m, 1H), 1.71-1.48 (m, 5H), 1.48-1.00 (m, 5H), 0.95 (s, 9 H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm: 168.9, 141.4, 139.3, 136.4, 131.3, 131.4, 131.0, 129.5, 129.3, 128.9, 128.8, 128.7, 127.2, 127.1, 65.5, 63.3, 56.1, 42.6, 29.9, 29.3, 26.5, 26.4, 22.8. HRMS (ESI) calcd for $C_{31}H_{38}ClN_2OS$ $[M+H]^+$, 522.2388; found 522.2375.

(*R*)-N-((1*S*,2*S*)-2-(4-bromophenyl)-2-((diphenylmethylene)amino)-1-(furan-2-yl)ethyl)-2-methylpropane-2-sulfinamide (5q):



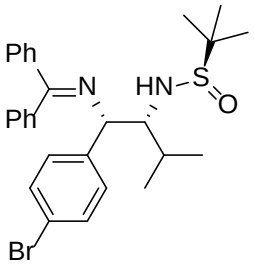
Obtained **5q** as an off-white solid (490 mg, 90%) according to the general experimental procedure as described above using *N-tert*-butanesulfinyl aldimine (R_S) **4c** (200 mg, 0.99 mmol), Ketimine **1d** (1.98 mmol) and *LiHMDS* (1 *M* in THF, 1.78 mmol). mp 112-114 ^{o}C, $[\alpha]_D^{25}$ = 68.81 (c. 0.25, $CHCl_3$), IR: 3329, 3132, 2972, 1608, 1489, 1066, 702. ^{1}H-NMR: (400 MHz, DMSO-d_6) δ ppm 7.63 (d, *J*= 7.2 Hz, 2H), 7.52-7.39 (m, 10H), 7.15 (d, *J*= 8.4 Hz, 2H), 6.75 (d, *J*= 6.0 Hz, 2H), 6.31 (s, 1H), 5.11 (d, *J*= 9.6 Hz, 1H), 4.72-4.64 (m, 1H), 4.56 (d, *J*= 5.2 Hz, 1H), 0.93 (s, 9 H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm: 168.8, 143.1, 141.8, 140.7, 139.3, 136.1, 131.3, 131.0, 130.1, 129.1, 128.9, 128.8, 128.7, 127.4, 126.8, 120.3, 110.8, 70.2, 59.4, 56.1, 22.7. HRMS (ESI) calcd for $C_{29}H_{30}BrN_2O_2S$ $[M+H]^+$, 550.1206; found, 550.1194.

(*R*)-N-((1*S*,2*S*)-2-(4-bromophenyl)-2-((diphenylmethylene)amino)-1-(thiophen-2-yl)ethyl)-2-methylpropane-2-sulfinamide (5r):



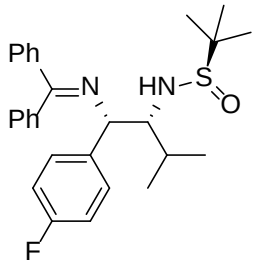
Obtained **5r** as an off-white solid (472 mg, 91%) according to the general experimental procedure as described above using *N-tert*-butanesulfinyl aldimine (R_S) **4d** (200 mg, 0.92 mmol), Ketimine **1d** (1.84 mmol) and *LiHMDS* (1 *M* in THF, 1.65 mmol). mp 122-124 ^{o}C, $[\alpha]_D^{25}$ = 108.57 (c. 0.25, $CHCl_3$), IR: 3323, 3055, 2924, 1622, 1483, 1074, 704. ^{1}H-NMR: (400 MHz, DMSO-d_6) δ ppm 7.67 (d, *J*= 7.2 Hz, 2H), 7.52-7.34 (m, 9H), 7.19 (d, *J*= 8.0 Hz, 2H), 7.02 (d, *J*= 2.8 Hz, 1H), 6.95-6.88 (m, 1H), 6.64 (d, *J*= 6.8 Hz, 2H), 5.34 (d, *J*= 9.6 Hz, 1H), 5.04-4.96 (m, 1H), 4.60 (d, *J*= 4.4 Hz, 1H), 0.92 (s, 9 H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm: 169.6, 145.6, 141.4, 139.2, 136.0, 131.3, 131.1, 130.1, 129.1, 128.9, 128.8, 128.7, 127.2, 126.7, 126.4, 125.8, 120.4, 70.9, 61.8, 56.3, 22.5. HRMS (ESI) calcd for $C_{29}H_{30}BrN_2OS_2$ $[M+H]^+$, 566.0977; found, 566.0969.

(*R*)-N-((1*S*,2*R*)-1-(4-bromophenyl)-1-((diphenylmethylene)amino)-3-methylbutan-2-yl)-2-methylpropane-2-sulfinamide (5s):



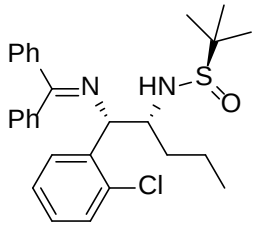
Obtained **5s** as an off-white solid (506 mg, 84%) according to the general experimental procedure as described above using *N-tert*-butanesulfinyl aldimine (R_S) **4e** (200 mg, 1.14 mmol), Ketimine **1d** (2.28 mmol) and *LiHMDS* (1 *M* in THF, 2.05 mmol). mp 100-102 ^{o}C, $[\alpha]_D^{25}$ = 67.93 (c. 0.25, $CHCl_3$), IR: 3344, 3039, 224, 1568, 1064, 700. ^{1}H-NMR: (400 MHz, DMSO-d_6) δ ppm 7.64 (d, *J*= 6.8 Hz, 2H), 7.52-7.39 (m, 8H), 7.11 (d, *J*= 8.4 Hz, 2H), 6.96-6.91 (m, 2H), 4.57 (d, *J*= 9.2 Hz, 1H), 4.49 (d, *J*=4.0 Hz, 1H), 3.43-3.35 (m, 1H), 1.70-1.61 (m, 1H), 0.91 (s, 9H), 0.85 (d, *J*=6.8 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm: 168.3, 143.2, 139.4, 136.1, 131.5, 130.9, 129.8, 129.3, 128.9, 128.7, 128.7, 127.5, 120.1, 68.8, 67.3, 56.0, 31.3, 22.8, 20.3, 18.8. HRMS (ESI) calcd for $C_{28}H_{34}BrN_2OS$ $[M+H]^+$, 526.1570; found, 526.1559.

(*R*)-N-((1*S*,2R)-1-((diphenylmethylene)amino)-1-(4-fluorophenyl)-3-methylbutan-2-yl)-2-methylpropane-2-sulfinamide (5t):



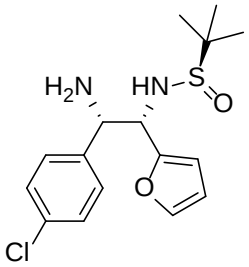
Obtained **5t** as an off-white solid (454 mg, 85%) according to the general experimental procedure as described above using *N-tert*-butanesulfinyl aldimine (R_S) **4e** (200 mg, 1.14 mmol), Ketimine **1e** (2.28 mmol) and *LiHMDS* (1 *M* in THF, 2.05 mmol). mp 118-120 ^{o}C, $[\alpha]_D^{25}$ = 5.36 (c. 0.25, $CHCl_3$), IR: 3344, 3043, 2958, 1508, 1068, 696. ^{1}H-NMR: (400 MHz, DMSO-d_6) δ ppm 7.63 (d, *J*= 7.2 Hz, 2H), 7.50-7.39 (m, 6H), 7.20-7.06 (m, 4H), 6.93 (d, *J*= 4.8 Hz, 2H), 4.57-4.49 (m, 2H), 3.40-3.38 (m, 1H), 1.68-1.63 (m, 1H), 0.93 (s, 9H), 0.82 (m, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm: 168.1, 162.6, 160.2, 140.0, 139.9, 139.5, 136.2, 130.9, 129.4, 129.3, 129.2, 128.9, 128.7, 127.5, 115.4, 115.2, 68.8, 67.1, 55.9, 31.3, 22.8, 20.3, 18.7. HRMS (ESI) calcd for $C_{28}H_{34}FN_2OS$ $[M+H]^+$, 465.2370; found, 465.2360.

(*R*)-N-((1*S*,2*R*)-1-(2-chlorophenyl)-1-((diphenylmethylene)amino)pentan-2-yl)-2-methylpropane-2-sulfinamide (5u):



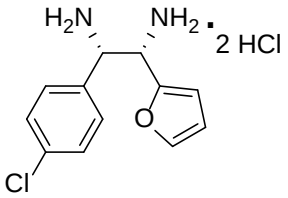
Obtained **5u** as a pale yellow oil (400 mg, 72%) according to the general experimental procedure as described above using *N-tert*-butanesulfinyl aldimine (R_S) **4e** (200 mg, 1.14 mmol), Ketimine **1e** (2.28 mmol) and *LiHMDS* (1 *M* in THF, 2.05 mmol). $[\alpha]_D^{25} = -91.6$ (c. 0.1, $CHCl_3$), ^{1}H-NMR: (400 MHz, $CDCl_3$) δ ppm 7.63 (d, *J*= 7.6 Hz, 2H), 7.56-7.33 (m, 7H), 7.26 (d, *J*= 1.6 Hz, 1H), 7.20-7.12 (m, 2H), 6.88 (d, *J*= 6.8 Hz, 2H), 4.91 (d, *J*= 2.0 Hz, 1H), 4.27 (d, *J*= 10.0 Hz, 1H), 3.58-3.55 (m, 1H), 1.88-181 (m, 1H), 1.49-1.47 (m, 1H), 1.42-1.1.37 (m, 2H), 1.15 (s, 9H), 0.87 (t, *J*= 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 170.466, 140.8, 139.2, 136.3, 131.6, 130.8, 130.5, 129.1, 128.7, 128.3, 128.2, 127.8, 127.2, 126.2, 63.8, 61.0, 56.2, 38.1, 24.2, 22.4, 18.9, 14.0. HRMS (ESI) calcd for $C_{28}H_{33}ClN_2OS$ $[M+H]^+$, 481.2075; found, 481.2084.

(*R*)-N-((1*S*,2*S*)-2-amino-2-(4-chlorophenyl)-1-(furan-2-yl)ethyl)-2-methylpropane-2-sulfinamide (6):



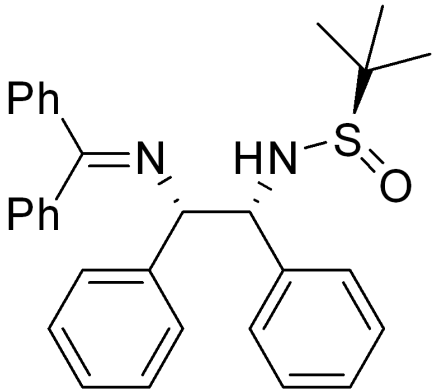
Compound **5g** (200 mg, 0.39 mmol) was taken in 1,4-dioxane (10 V) to it was added aq. H_2SO_4 (1*N*, 10 V) at room temperature and stirred for 6 h. Upon completion of reaction, diluted with water (5 V) and basified till pH 10 using aq. NaOH solution (2*N*) and aq. Layer extracted with ethyl acetate. Organic solvent was dried on Na_2SO_4 and removed completely under reduced pressure to obtain the title compound **6** as an off-white solid (124 mg, 92%). mp 114-116 ^{o}C, $[\alpha]_D^{25}$ = 11.20 (c. 0.25, $CHCl_3$), IR: 3340, 2893, 1587, 1492, 1016, 794 ^{1}H-NMR: (400 MHz, DMSO-d_6) δ ppm 7.53 (s, 1H), 7.46 (s, 1H), 7.38-7.28 (m, 4H), 6.50 (s, 1H), 5.33 (d, *J*= 9.2 Hz, 1H), 4.31-4.23 (m, 1H), 4.19 (d, *J*= 6.4 Hz, 1H), 1.00 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm: 143.3, 142.8, 141.1, 131.5, 129.8, 128.1, 126.6, 110.8, 59.9, 59.3, 56.2, 22.9. HRMS (ESI) calcd for $C_{16}H_{21}ClN_2O_2S$ $[M+H]^+$, 341.1085; found 341.1078.

(1*S*,2*S*)-1-(4-chlorophenyl)-2-(furan-2-yl)ethane-1,2-diamine (7):



Compound **5g** (500 mg, 0.99 mmol) was taken in 1,4-dioxane (3 V) and to it was added HCl in 1,4-dioxane.HCl (4*M*, 10 V) and stirred at room temperature for 16 h. Upon completion of the reaction, solvent was removed completely under reduced pressure and residue was washed with ethyl acetate (5 V), dried under *vacuo* to obtain the title compound **7** as a white solid (300 mg, 96%). mp >250 ^{o}C. $[\alpha]_D^{25}$ = 10.40 (c. 0.25, H_2O), IR: 2949, 2887, 1589, 1521, 1016, 700, ^{1}H-NMR: (400 MHz, D_2O) δ ppm 7.51 (s, 1H), 7.42 (s, 1H), 7.39 (d, *J*= 8.4 Hz, 2H), 7.18 (d, *J*= 8.4 Hz, 2H), 6.14 (s, 1H), 4.98 (d, *J*= 7.2 Hz, 1H), 4.86 (d, *J*= 6.8 Hz, 1H). ^{13}C NMR (100 MHz, D_2O) δ ppm: 145.0, 143.3, 136.0, 129.7, 129.4, 128.7, 114.9, 108.5, 55.2, 48.8. HRMS (ESI) calcd for $C_{12}H_{14}ClN_2O$ $[M+H]^+$, 237.0789; found 237.0784.

1H NMR of 5a — AAA_PROTON DMSO {D:\2018\03 MAR 18} O2B 18 —



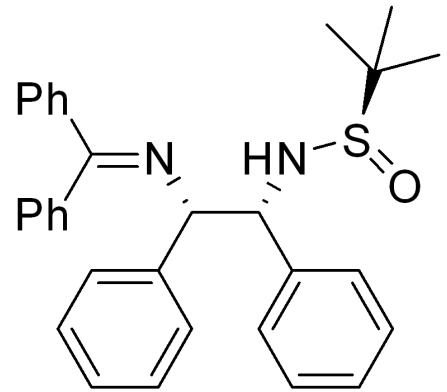
7.61 7.60 7.59 7.47 7.46 7.45 7.44 7.42 7.41 7.39 7.38 7.36 7.34 7.29 7.27 7.26 7.25 7.24 7.23 7.21 7.19 7.18 7.16 7.15 7.15 6.99 6.74 6.34 6.33 5.33 5.31 4.77 4.76 4.74 4.73 4.56 4.55 3.33 HDO 2.60 2.51 DMSO 2.50 DMSO 2.50 DMSO 2.50 DMSO 2.49 DMSO 1.23 1.04 0.99 0.89 0.73 0.67

1.93 3.85 10.86 1.85 1.06 1.07 1.00 8.81

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0

f1 (ppm)

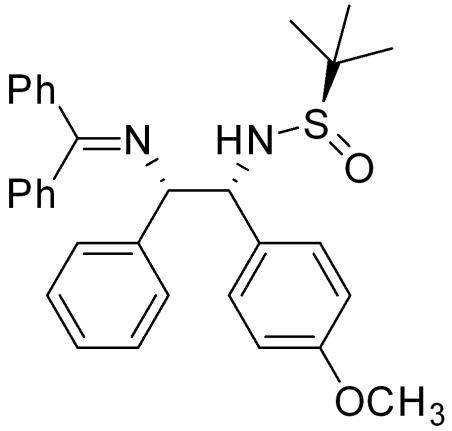
13C NMR of 5a — C13CPD DMSO {E:\2018\03 MAR 18} O2B 1 —



168.62
142.36
139.25
136.03
130.88
128.89
128.71
128.67
128.41
128.23
128.06
127.67
127.29
127.22
127.08
71.37
66.94
56.20
40.61 DMSO
40.40 DMSO
40.19 DMSO
39.98 DMSO
39.77 DMSO
39.56 DMSO
39.36 DMSO
22.53

f1 (ppm)

1H NMR of 5b — Proton DMSO{Y:\2018\02 FEB 18} O2B 1 —

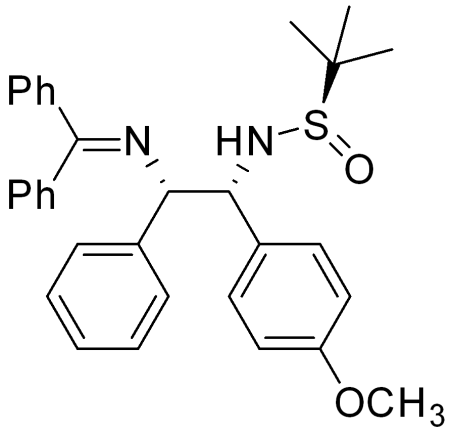


7.62 7.60 7.47 7.45 7.44 7.42 7.41 7.39 7.37 7.36 7.33 7.31 7.29 7.24 7.22 7.21 7.19 7.16 7.14 6.96 6.77 6.75 6.45 6.43 5.22 5.20 4.71 4.70 4.69 4.68 4.55 4.53 3.70 3.66 3.34 HDO 2.50 DMSO 1.99 1.26 1.23 1.16 1.08 1.04 0.94 0.89

2.11 6.01 6.81 2.11 1.89 1.00 1.06 1.08 3.06 9.31

f1 (ppm)

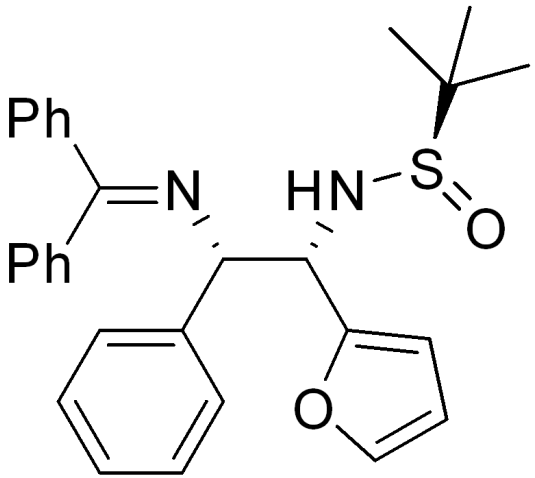
13C NMR of 5b — C13CPD DMSO {E:\2018\03 MAR 18} O2B 1 —



168.41
158.62
142.45
139.33
136.09
134.31
130.85
129.34
128.90
128.72
128.65
128.39
127.71
127.18
113.45
71.49
66.50
56.13
55.50
40.59 DMSO
40.38 DMSO
40.17 DMSO
39.96 DMSO
39.75 DMSO
39.55 DMSO
39.34 DMSO
22.56

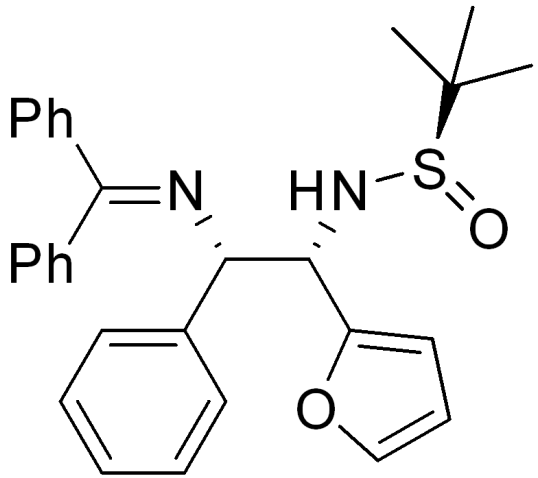
f1 (ppm)

1H NMR of 5c — AAA_PROTON DMSO {D:\2018\03 MAR 18} O2B 45 —



f1 (ppm)

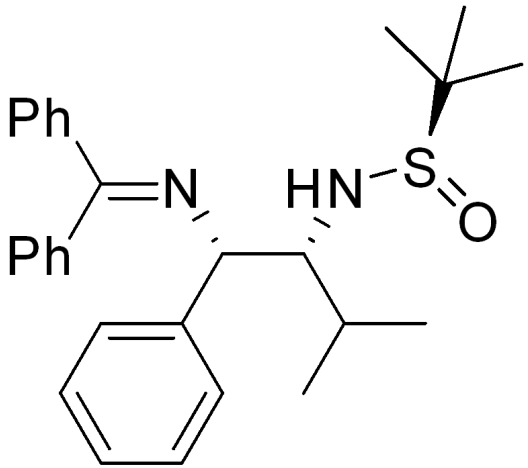
13C NMR of 5c — C13CPD DMSO {E:\2018\03 MAR 18} O2B 1 —



168.28
143.01
142.38
140.68
139.49
136.18
130.83
129.05
128.85
128.69
128.46
127.84
127.47
127.30
126.99
110.80
70.76
59.81
56.03
40.59 DMSO
40.38 DMSO
40.17 DMSO
39.97 DMSO
39.76 DMSO
39.55 DMSO
39.34 DMSO
22.68

f1 (ppm)

1H NMR of 5d — AAA_PROTON DMSO {D:\2018\03 MAR 18} O2B 15 —



7.62 7.60 7.60 7.47 7.46 7.44 7.44 7.43 7.41 7.41 7.39 7.39 7.29 7.27 7.25 7.21 7.19 7.17 7.12 7.11 6.92 6.91 6.90 6.61

4.52 4.51 4.49

3.45 3.44 3.42 3.41 3.40 3.33 HDO

2.52 DMSO 2.51 DMSO 2.50 DMSO 2.50 DMSO 2.50 DMSO 2.49 DMSO

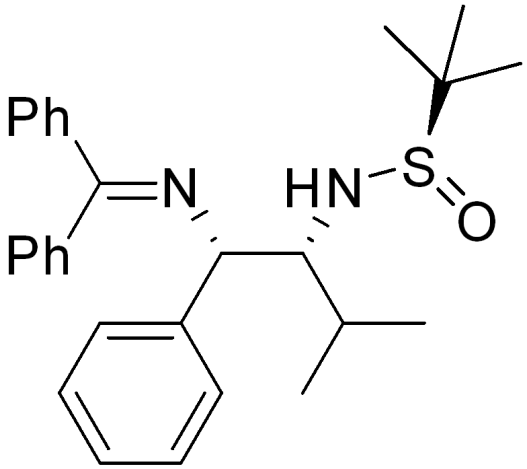
1.66 1.65 1.63 1.62 1.27 1.23 1.10 1.07 1.01 0.90 0.85 0.84 0.83 0.81

2.00 5.90 2.10 1.14 2.04 2.00 2.05 1.21 1.10 9.03 6.07

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0

f1 (ppm)

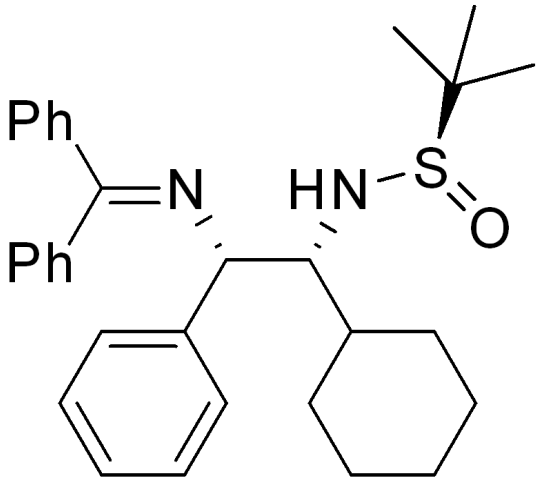
13C NMR of 5d — C13CPD DMSO {E:\2018\03 MAR 18} O2B 1 —



167.76
143.74
139.59
136.27
130.79
130.08
129.21
128.87
128.70
128.67
128.63
127.54
127.12
68.90
67.88
55.95
40.60 DMSO
40.39 DMSO
40.18 DMSO
39.98 DMSO
39.77 DMSO
39.56 DMSO
39.35 DMSO
31.20
24.44
22.85
20.34
18.59

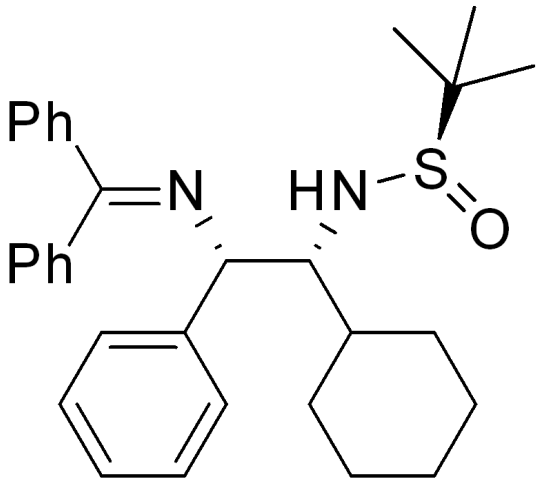
f1 (ppm)

1H NMR of 5e — AAA_PROTON DMSO {D:\2018\03 MAR 18} O2B 26 —



f1 (ppm)

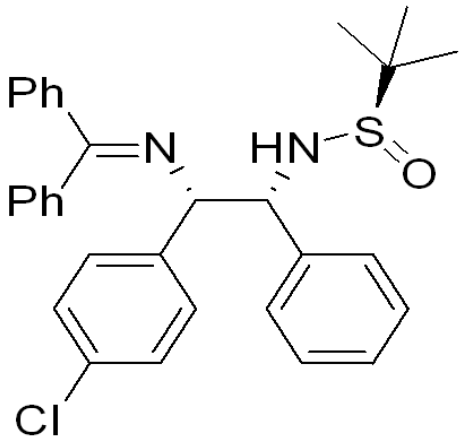
13C NMR of 5e — C13CPD DMSO {D:\2018\03 MAR 18} O2B 40 —



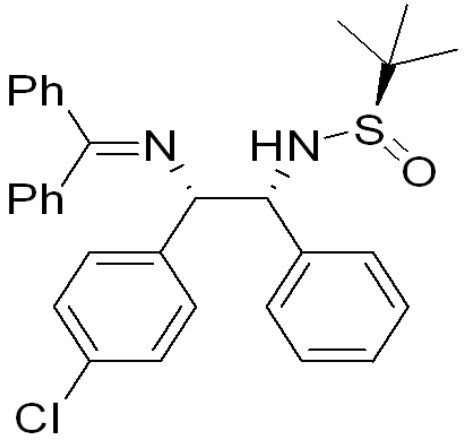
167.91
143.85
139.61
136.33
130.84
130.07
129.26
129.05
128.88
128.76
128.70
128.60
127.51
127.46
127.08
116.82
68.54
67.31
55.96
41.63
40.64 DMSO
40.43 DMSO
40.23 DMSO
40.02 DMSO
39.81 DMSO
39.60 DMSO
39.39 DMSO
36.70
30.02
28.99
26.58
26.46
26.43
24.77
22.84

f1 (ppm)

1H NMR of 5f — AAA_PROTON DMSO {D:\2018\03 MAR 18} O2B 39 —

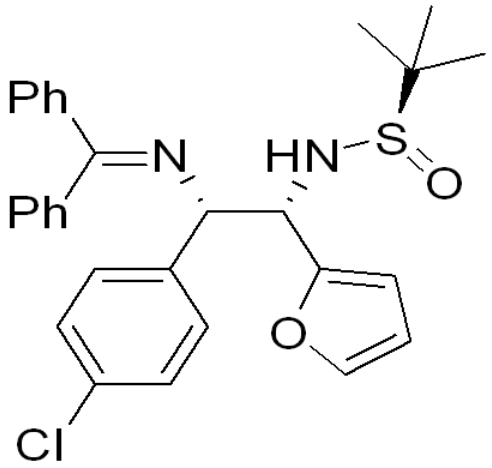


13C NMR of 5f — C13CPD DMSO {D:\2018\03 MAR 18} O2B 36 —



169.04
142.23
141.37
139.15
135.96
131.71
130.99
129.62
128.96
128.78
128.75
128.72
128.37
128.26
128.11
127.36
127.04
70.78
66.32
56.27
40.63 DMSO
40.42 DMSO
40.21 DMSO
40.00 DMSO
39.79 DMSO
39.58 DMSO
39.37 DMSO
22.60

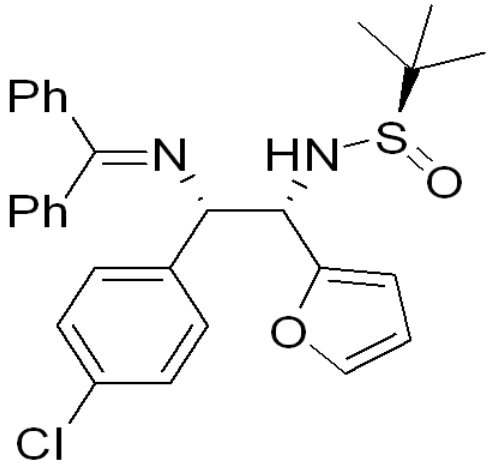
1H NMR of 5g — AAA_PROTON DMSO {D:\2018\03 MAR 18} O2B 44 —



f1 (ppm)

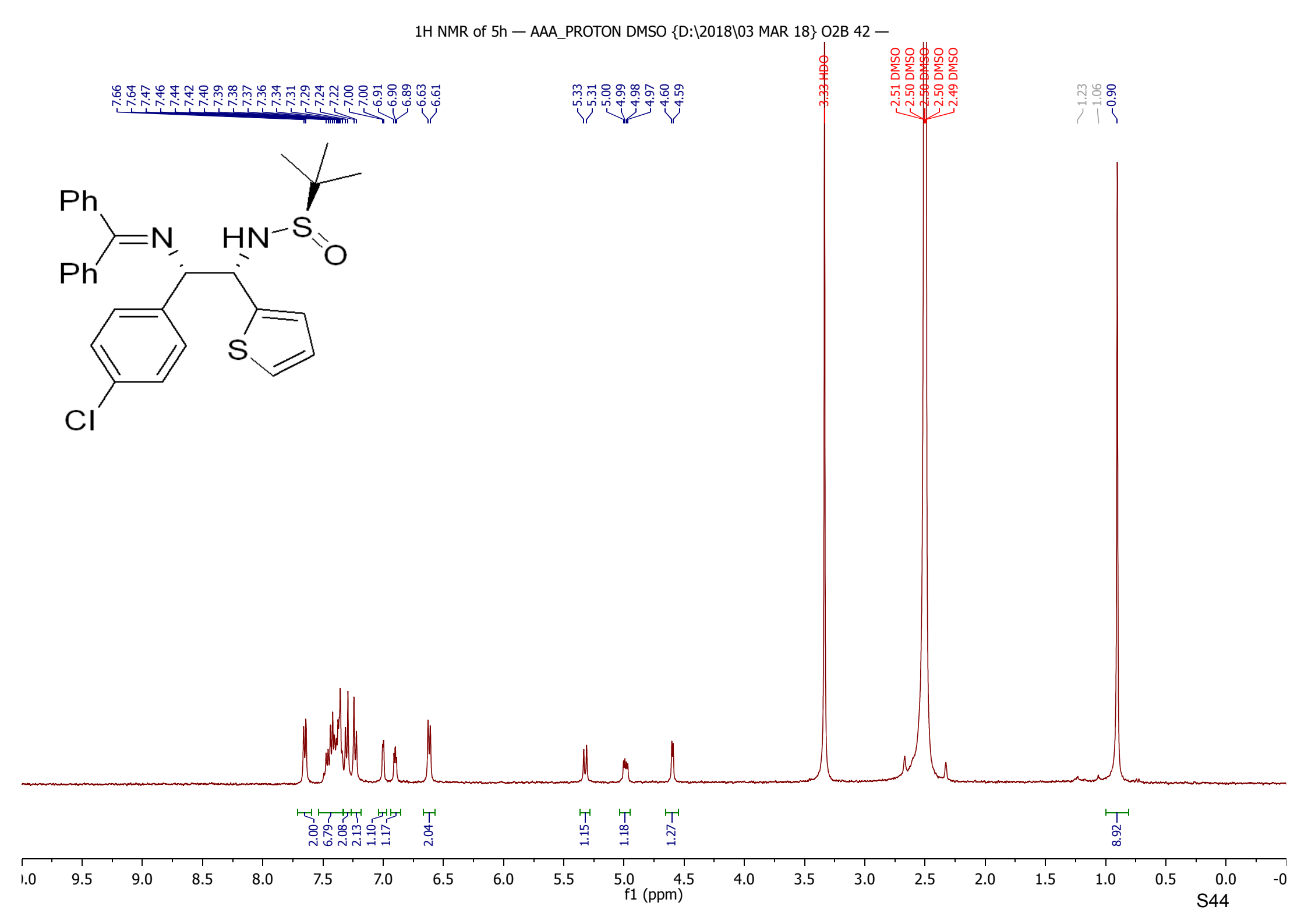
S42

13C NMR of 5g — C13CPD DMSO {E:\2018\03 MAR 18} O2B 1 —

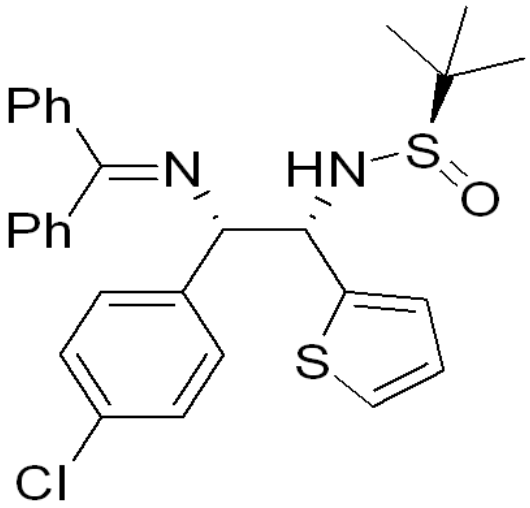


168.79
143.09
141.35
140.71
139.35
136.09
131.75
130.94
129.71
129.10
128.91
128.76
128.69
128.41
127.38
126.83
110.79
70.13
59.51
56.07
40.59 DMSO
40.38 DMSO
40.17 DMSO
39.97 DMSO
39.76 DMSO
39.55 DMSO
39.34 DMSO
22.69

f1 (ppm)

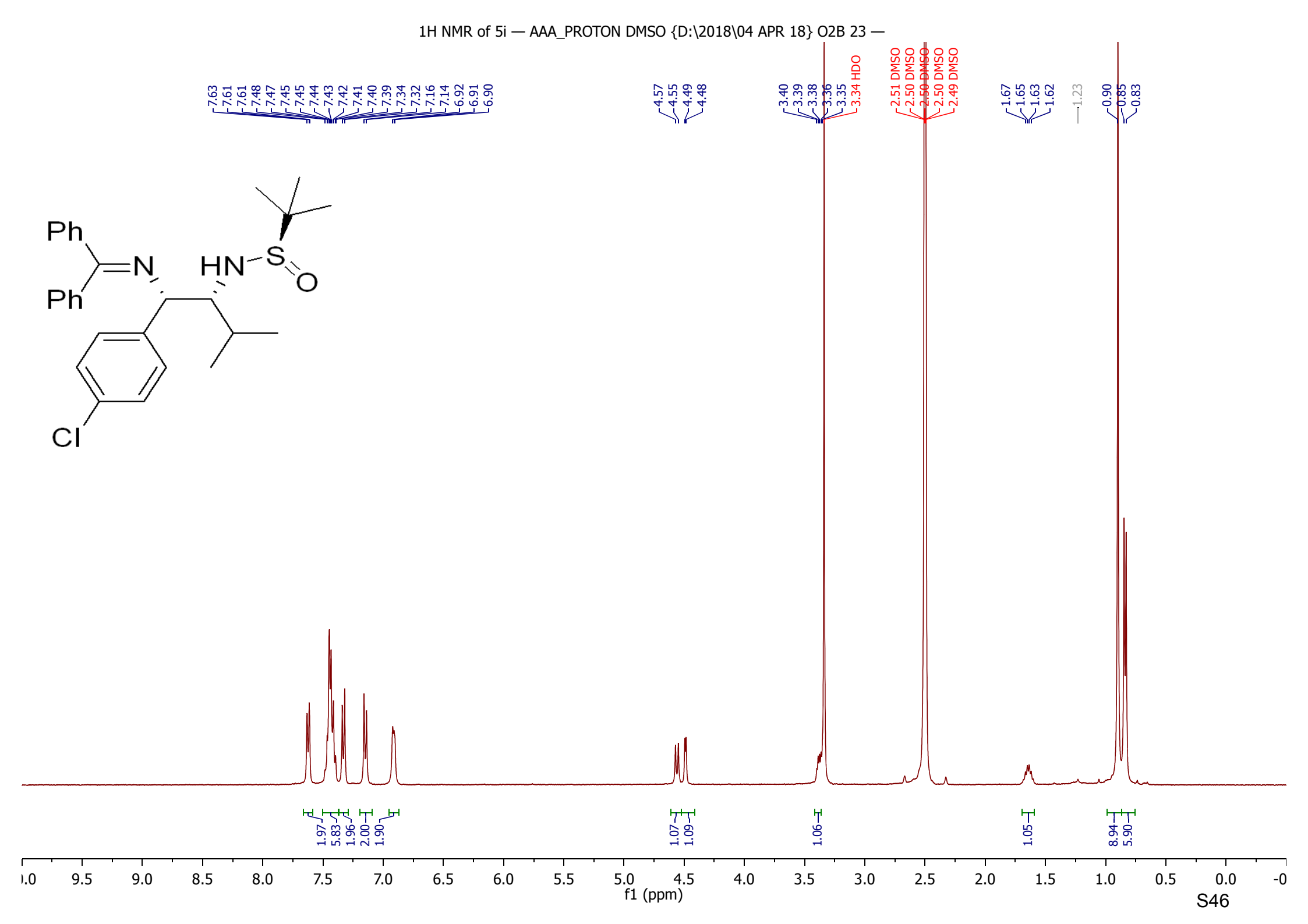

1H NMR of 5h — AAA_PROTON DMSO {D:\2018\03 MAR 18} O2B 42 —
7.66
7.64
7.47
7.46
7.44
7.42
7.40
7.39
7.38
7.37
7.36
7.34
7.31
7.29
7.24
7.22
7.00
7.00
6.91
6.90
6.89
6.63
6.61
5.33
5.31
5.00
4.99
4.98
4.97
4.60
4.59
3.33 HDO
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.50 DMSO
2.49 DMSO
1.23
1.06
0.90
Ph
N
HN
S
O
Ph
S
Cl
2.00
6.79
2.08
2.13
1.10
1.17
2.04
1.15
1.18
1.27
8.92
f1 (ppm)
S44

13C NMR of 5h — C13CPD DMSO {D:\2018\03 MAR 18} O2B 31 —

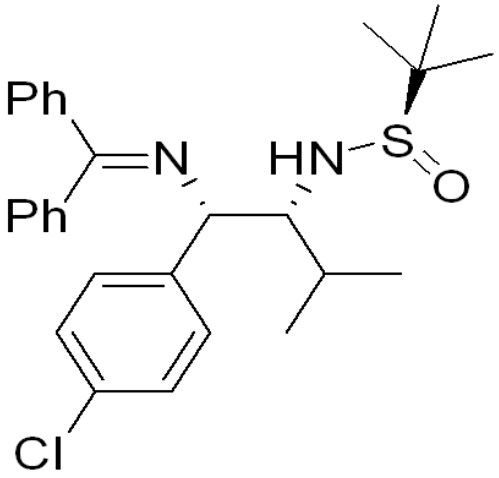


169.58
145.63
141.07
139.26
136.00
131.89
131.09
129.73
129.13
128.93
128.85
128.74
128.44
127.25
126.68
126.40
125.86
70.87
61.95
56.32
40.63 DMSO
40.42 DMSO
40.21 DMSO
40.00 DMSO
39.79 DMSO
39.58 DMSO
39.37 DMSO
22.59

f1 (ppm)


1H NMR of 5i — AAA_PROTON DMSO {D:\2018\04 APR 18} O2B 23 —
7.63 7.61 7.61 7.48 7.47 7.45 7.45 7.44 7.43 7.42 7.41 7.40 7.39 7.34 7.32 7.16 7.14 6.92 6.91 6.90
4.57 4.55 4.49 4.48
3.40 3.39 3.38 3.36 3.35 3.34 HDO
2.51 DMSO 2.50 DMSO 2.50 DMSO 2.50 DMSO 2.49 DMSO
1.67 1.65 1.63 1.62
1.23
0.90 0.85 0.83
Ph
N
HN
S
O
Ph
Cl
1.97 5.83 1.96 2.00 1.90
1.07 1.09
1.06
1.05
8.94 5.90
f1 (ppm)
S46

13C NMR OF 5i — C13CPD DMSO {E:\2018\03 MAR 18} O2B 2 —

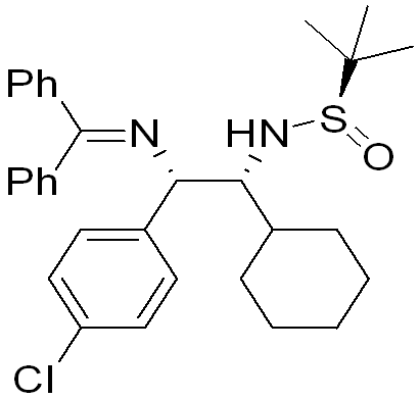


168.34
142.75
139.46
136.15
131.56
130.91
129.42
129.29
128.94
128.75
128.72
128.56
127.47
68.83
67.23
56.66
55.99
40.60 DMSO
40.40 DMSO
40.19 DMSO
39.98 DMSO
39.77 DMSO
39.56 DMSO
39.35 DMSO
31.35
22.84
20.30
18.85

)0 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

f1 (ppm)

1H NMR of 5j — AAA_PROTON DMSO {D:\2018\03 MAR 18} O2B 24 —



7.75 7.73 7.70 7.69 7.64 7.62 7.62 7.59 7.57 7.47 7.46 7.45 7.45 7.44 7.44 7.43 7.42 7.40 7.40 7.34 7.33 7.32 7.16 7.14 6.91 6.90 6.89 6.75 6.73

4.61 4.58 4.54 4.53 4.34 4.29 4.13

3.36 3.34 HDO

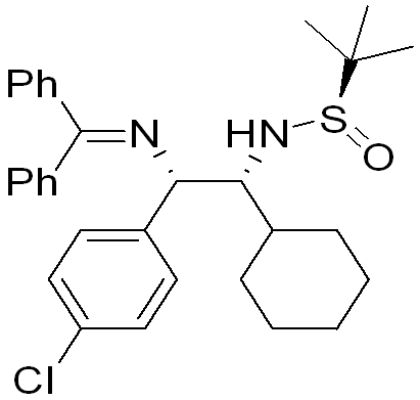
2.52 DMSO 2.51 DMSO 2.50 DMSO 2.50 DMSO 2.50 DMSO 2.49 DMSO

1.76 1.63 1.59 1.54 1.45 1.42 1.28 1.26 1.23 1.12 1.10 1.09 1.04 1.03 0.88 0.86 0.85 0.84 0.84 0.80

1.66 4.49 1.65 1.49 1.51 0.76 0.81 1.00 3.13 1.14 2.23 3.12 9.09

f1 (ppm)

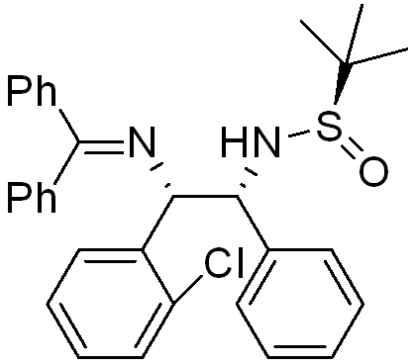
13C NMR OF 5j — C13CPD DMSO {D:\2018\03 MAR 18} O2B 38 —



168.44
142.85
139.48
136.20
133.17
132.05
131.53
130.96
130.08
129.82
129.41
129.34
129.14
129.05
128.95
128.80
128.78
128.54
127.40
68.43
66.71
55.99
41.60
40.65 DMSO
40.44 DMSO
40.23 DMSO
40.02 DMSO
39.81 DMSO
39.60 DMSO
39.39 DMSO
38.57
36.70
30.29
29.99
29.14
28.85
26.55
26.45
26.41
23.73
22.85
14.38
11.28

f1 (ppm)

1H NMR of 5k — AAA_PROTON DMSO {D:\2018\03 MAR 18} O2B 53 —

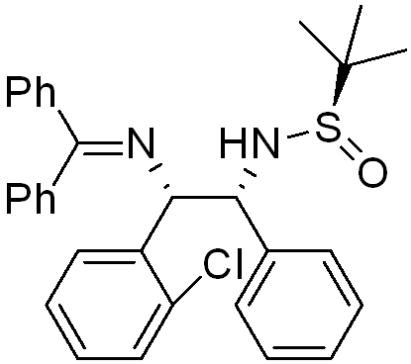


7.74 7.73 7.67 7.65 7.49 7.47 7.45 7.43 7.41 7.39 7.36 7.34 7.32 7.31 7.25 7.24 7.23 7.22 6.19 6.17 5.71 5.69 4.90 4.90 4.74 4.73 4.71 4.71 3.34 HDO 2.50 DMSO 1.26 0.89 0.78

1.03 1.92 3.16 2.97 7.28 1.91 1.01 1.00 1.06 8.72

f1 (ppm)

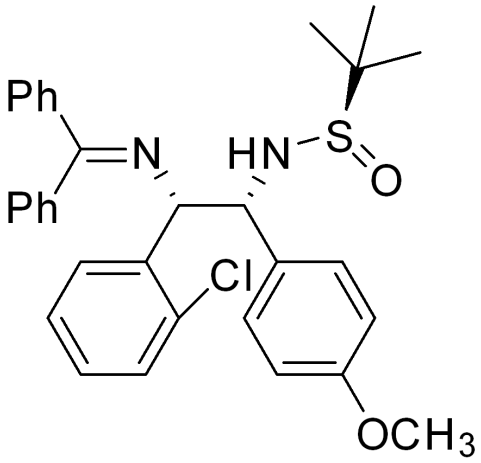
13C NMR OF 5k — C13CPD DMSO {E:\2018\03 MAR 18} O2B 1 —

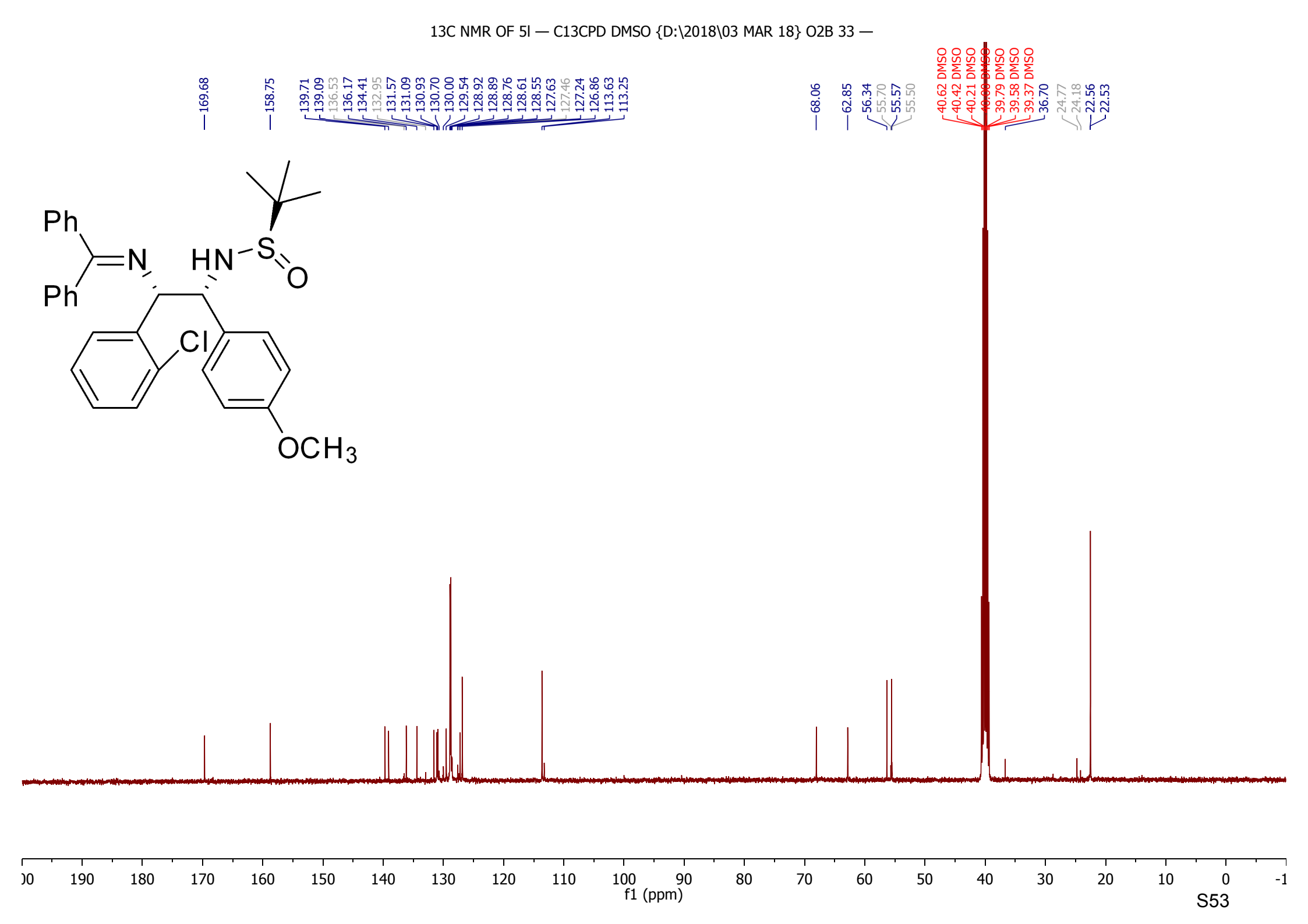


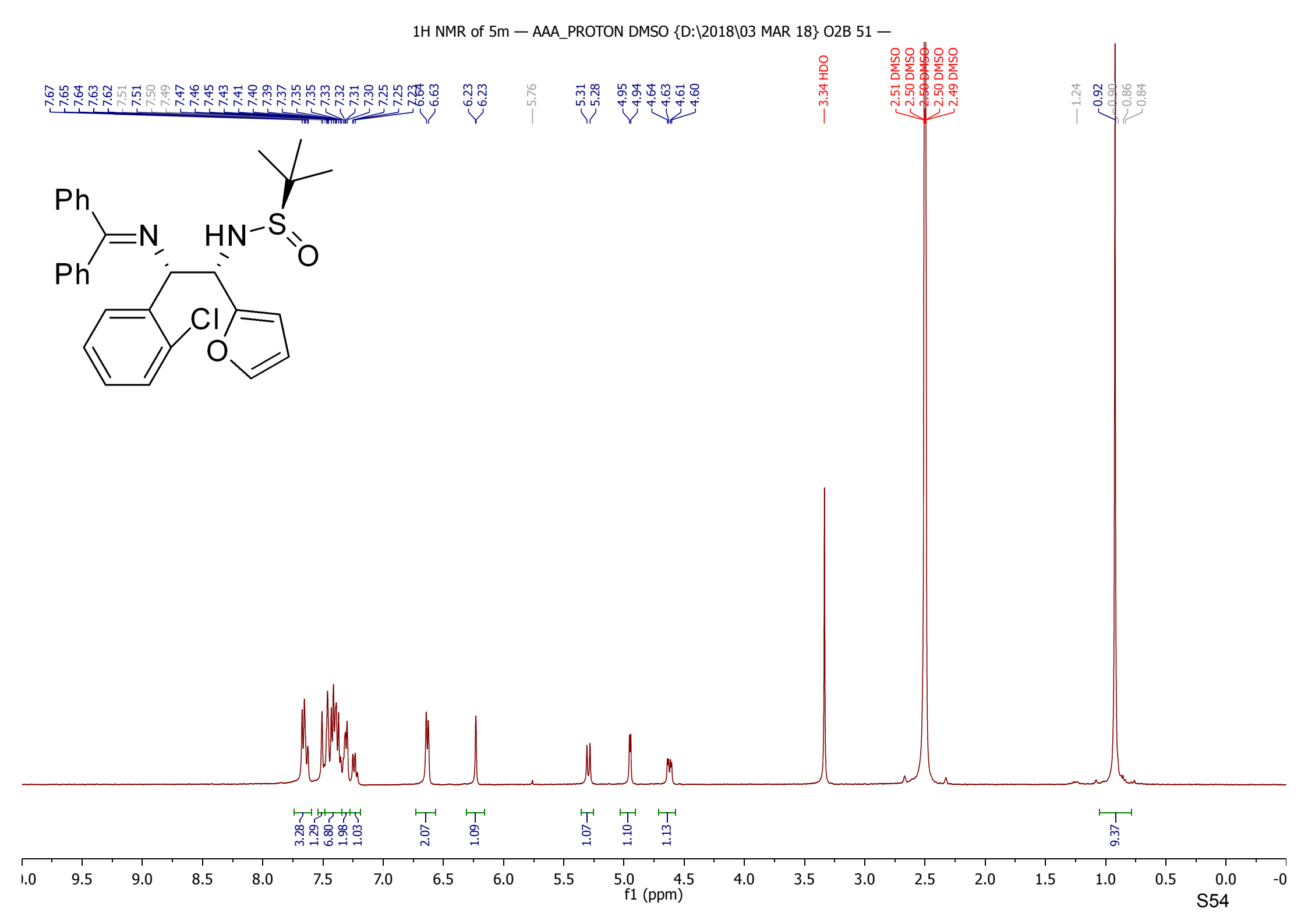
169.77
142.41
139.55
138.99
136.09
131.53
131.09
130.95
129.55
128.93
128.72
128.23
127.76
127.40
127.24
126.76
68.05
63.03
56.39
40.60 DMSO
40.39 DMSO
40.18 DMSO
39.98 DMSO
39.77 DMSO
39.56 DMSO
39.35 DMSO
22.49

f1 (ppm)

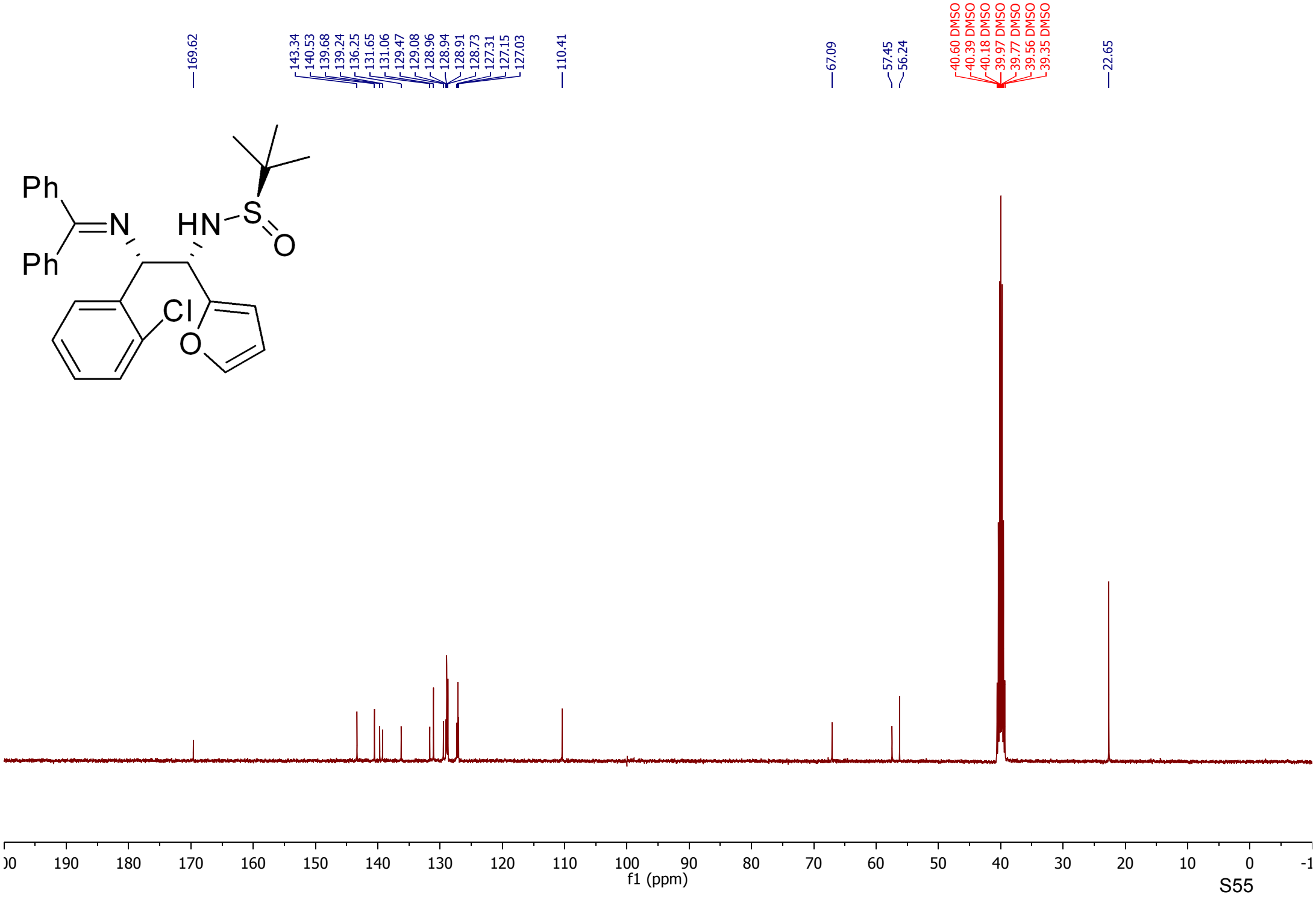
1H NMR of 5l — AAA_PROTON DMSO {D:\2018\03 MAR 18} O2B 25 —



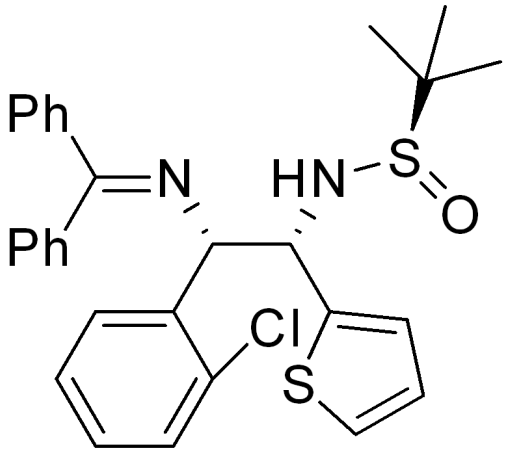

13C NMR OF 5l — C13CPD DMSO {D:\2018\03 MAR 18} O2B 33 —
169.68
158.75
139.71
139.09
136.53
136.17
134.41
132.95
131.57
131.09
130.93
130.70
130.00
129.54
128.92
128.89
128.76
128.61
128.55
127.63
127.46
127.24
126.86
113.63
113.25
68.06
62.85
56.34
55.70
55.57
55.50
40.62 DMSO
40.42 DMSO
40.21 DMSO
40.00 DMSO
39.79 DMSO
39.58 DMSO
39.37 DMSO
36.70
24.77
24.18
22.56
22.53
Ph
N
HN
S
O
Ph
Cl
OCH3
f1 (ppm)
S53


1H NMR of 5m — AAA_PROTON DMSO {D:\2018\03 MAR 18} O2B 51 —
7.67
7.65
7.64
7.63
7.62
7.51
7.51
7.50
7.49
7.47
7.46
7.45
7.43
7.41
7.40
7.39
7.37
7.35
7.35
7.33
7.32
7.31
7.30
7.25
7.25
7.23
6.64
6.63
6.23
6.23
5.76
5.31
5.28
4.95
4.94
4.64
4.63
4.61
4.60
3.34 HDO
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.50 DMSO
2.49 DMSO
1.24
0.92
0.90
0.86
0.84
Ph
N
HN
S
O
Ph
Cl
O
3.28
1.29
6.80
1.98
1.03
2.07
1.09
1.07
1.10
1.13
9.37
f1 (ppm)
S54

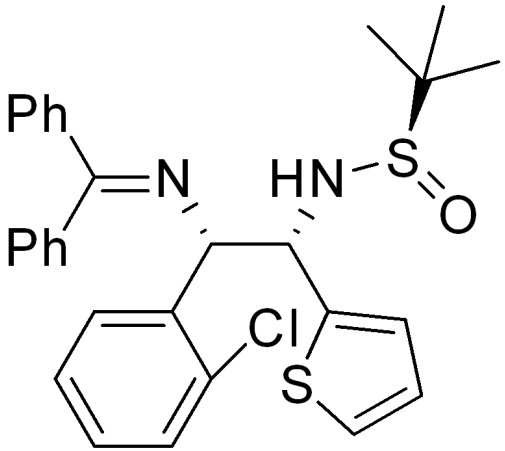
13C NMR OF 5m — C13CPD DMSO {E:\2018\03 MAR 18} O2B 1 —



1H NMR of 5n — AAA_PROTON DMSO {D:\2018\03 MAR 18} O2B 2 —



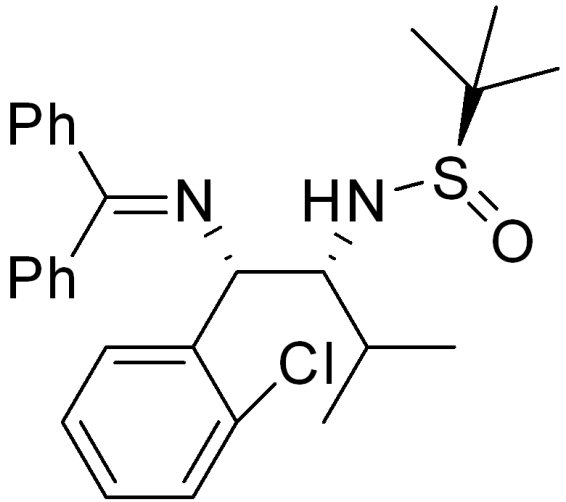
13C NMR OF 5n — C13CPD DMSO {D:\2018\03 MAR 18} O2B 37 —



170.57
146.12
139.43
139.13
136.16
131.65
131.23
130.98
129.54
129.12
129.09
128.84
128.78
127.35
126.92
126.86
125.85
125.80
68.10
58.99
56.49
40.64 DMSO
40.43 DMSO
40.23 DMSO
40.02 DMSO
39.81 DMSO
39.60 DMSO
39.39 DMSO
22.50

f1 (ppm)

1H NMR of 5o — AAA_PROTON DMSO {D:\2018\03 MAR 18} O2B 37 —



7.67 7.65 7.65 7.49 7.47 7.47 7.46 7.45 7.45 7.43 7.42 7.41 7.40 7.39 7.34 7.34 7.32 7.32 7.28 7.28 7.26 7.25 7.25 7.23 7.23 6.82 6.81

5.76

4.89 4.89 4.77 4.75

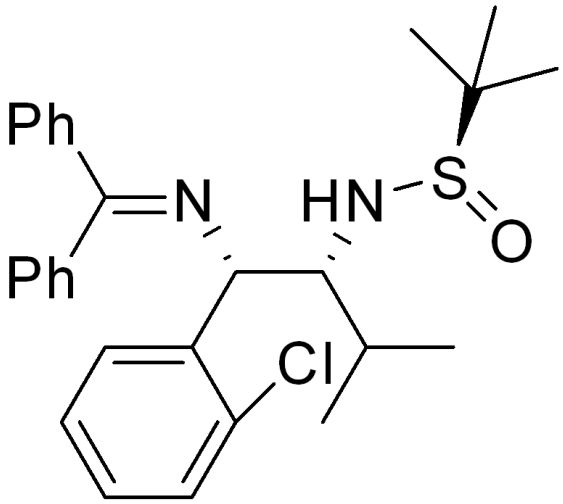
3.33 HDO 3.31 3.30 3.30 3.29 2.61 2.52 DMSO 2.51 DMSO 2.51 DMSO 2.50 DMSO 2.50 DMSO 2.49 DMSO 1.84 1.82 1.80 1.79 1.77 1.33 1.31 1.23 1.12 0.94 0.92 0.85 0.84

1.96 6.70 2.99 1.94 1.12 1.09 1.00 9.12 3.23

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0

f1 (ppm)

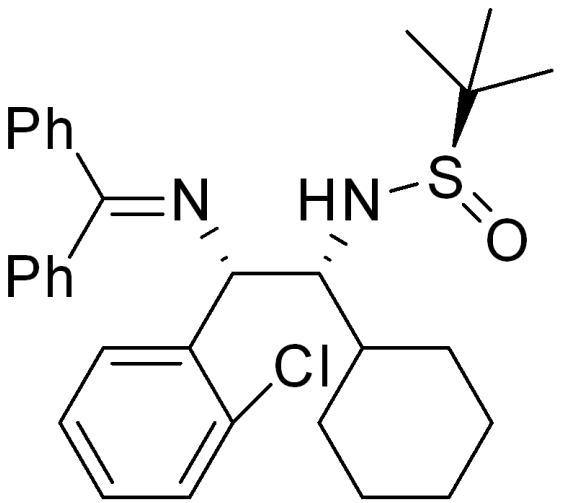
13C NMR OF 5o — C13CPD DMSO {D:\2018\03 MAR 18} O2B 34 —



169.02
141.41
139.37
136.44
131.33
131.16
131.07
130.09
129.53
129.30
129.06
128.97
128.84
128.82
128.78
127.31
127.20
66.07
63.57
56.16
40.63 DMSO
40.42 DMSO
40.21 DMSO
40.00 DMSO
39.79 DMSO
39.58 DMSO
39.38 DMSO
32.60
22.85
22.74
19.81
19.52

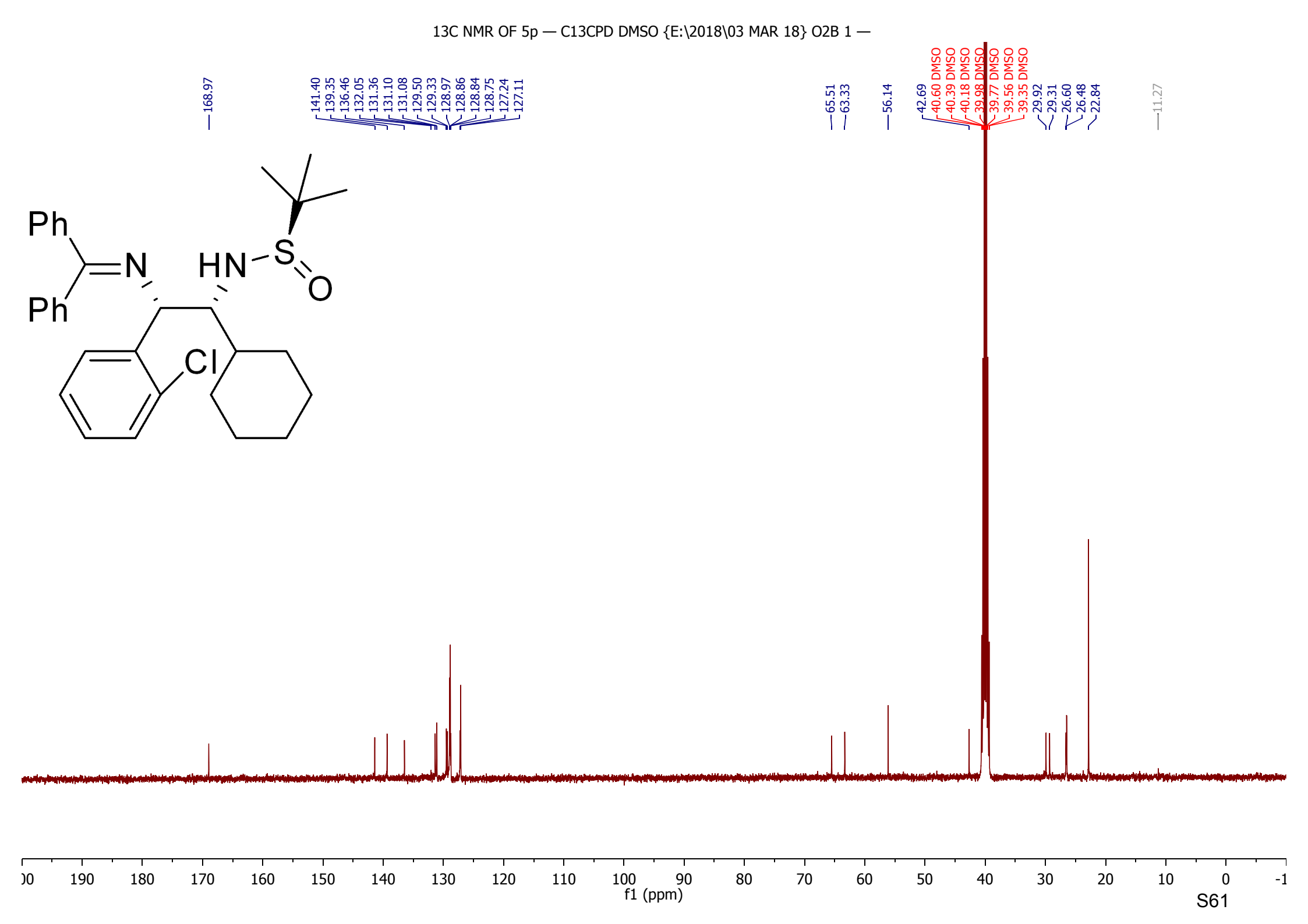
f1 (ppm)

1H NMR of 5p — AAA_PROTON DMSO {D:\2018\03 MAR 18} O2B 50 —

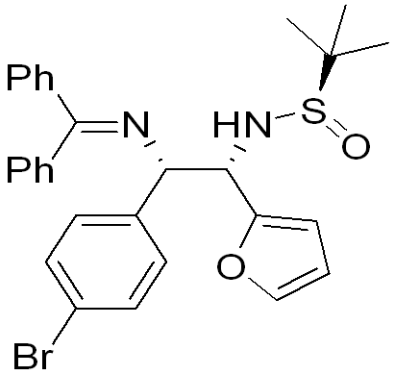


f1 (ppm)

S60


13C NMR OF 5p — C13CPD DMSO {E:\2018\03 MAR 18} O2B 1 —
168.97
141.40
139.35
136.46
132.05
131.36
131.10
131.08
129.50
129.33
128.97
128.86
128.84
128.75
127.24
127.11
65.51
63.33
56.14
42.69
40.60 DMSO
40.39 DMSO
40.18 DMSO
39.98 DMSO
39.77 DMSO
39.56 DMSO
39.35 DMSO
29.92
29.31
26.60
26.48
22.84
11.27
Ph
N
HN
S
O
Ph
Cl
f1 (ppm)
S61

1H NMR of 5q — AAA_PROTON DMSO {D:\2018\03 MAR 18} O2B 49 —



7.62 7.61 7.60 7.49 7.48 7.48 7.46 7.45 7.44 7.43 7.42 7.41 7.40 7.38 7.15 7.13 6.75 6.74 6.73 6.72 6.29 6.29

5.10 5.08 4.69 4.67 4.66 4.65 4.55 4.54

3.33 HDO

2.51 DMSO 2.51 DMSO 2.50 DMSO 2.50 DMSO 2.49 DMSO

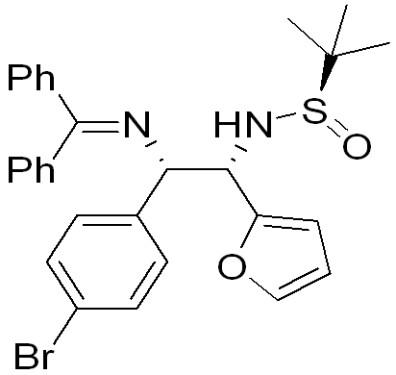
1.23

0.92

2.16 9.78 1.96 2.00 1.00 1.00 1.08 1.03 8.90

f1 (ppm)

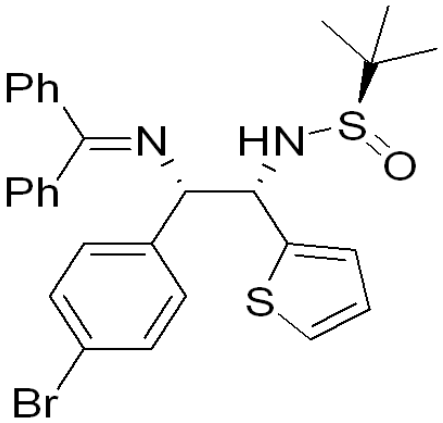
13C NMR OF 5q — C13CPD DMSO {D:\2018\03 MAR 18} O2B 35 —



168.83
143.11
141.78
140.74
139.38
136.10
131.34
130.96
130.10
129.13
128.93
128.78
128.71
127.41
126.83
120.34
110.81
70.22
59.47
56.10
40.63 DMSO
40.42 DMSO
40.21 DMSO
40.00 DMSO
39.79 DMSO
39.58 DMSO
39.38 DMSO
22.71

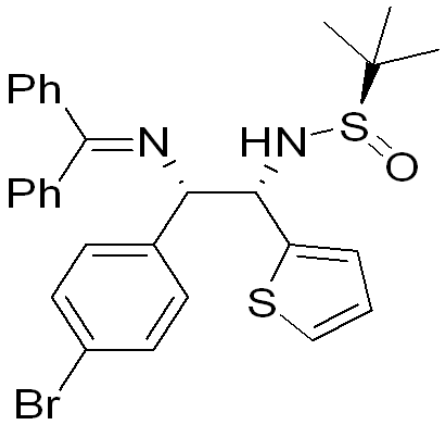
f1 (ppm)

1H NMR of 5r — AAA_PROTON DMSO {D:\2018\03 MAR 18} O2B 27 —



f1 (ppm)

13C NMR OF 5r — C13CPD DMSO {D:\2018\03 MAR 18} O2B 41 —

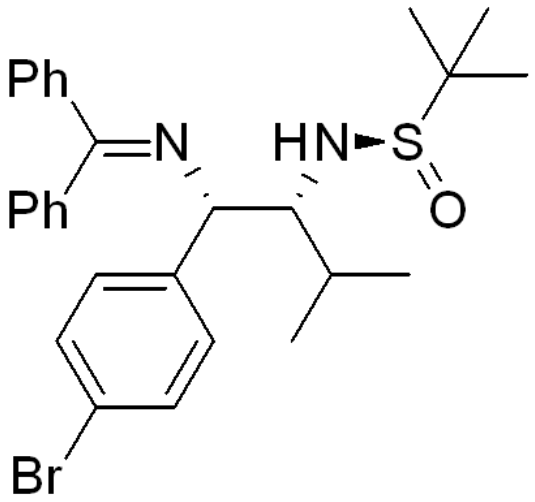


169.62
145.59
141.46
139.27
136.00
131.34
131.07
130.10
129.12
128.91
128.84
128.73
127.25
126.68
126.39
125.84
120.47
70.95
61.87
56.33
40.66 DMSO
40.45 DMSO
40.25 DMSO
40.04 DMSO
39.83 DMSO
39.62 DMSO
39.41 DMSO
36.72
24.19
22.60

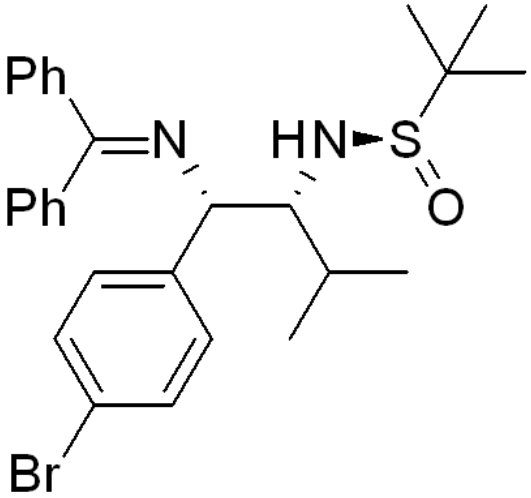
)0 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2

f1 (ppm)

1H NMR of 5s — AAA_PROTON DMSO {D:\2018\03 MAR 18} O2B 48 —



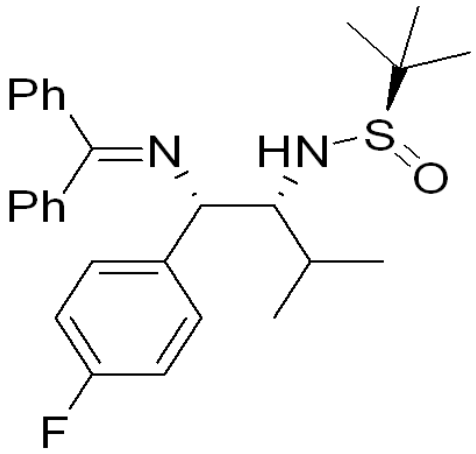
13C NMR OF 5s — C13CPD DMSO {D:\2018\03 MAR 18} O2B 28 —



168.36
143.19
139.47
136.15
131.50
130.94
129.83
129.32
128.97
128.78
128.74
127.50
120.10
68.83
67.32
56.01
40.62 DMSO
40.41 DMSO
40.20 DMSO
39.99 DMSO
39.78 DMSO
39.57 DMSO
39.37 DMSO
31.34
22.87
20.33
18.86

)0 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

1H NMR of 5t — AAA_PROTON DMSO {D:\2018\03 MAR 18} O2B 27 —



7.63 7.61 7.61 7.48 7.46 7.45 7.44 7.43 7.42 7.41 7.39 7.39 7.17 7.15 7.15 7.13 7.11 7.09 7.07 6.92 6.91 6.90

4.54 4.52 4.50 4.49

3.40 3.39 3.38 3.36 3.35 3.33 HDO 3.28 2.60 2.51 DMSO 2.50 DMSO 2.50 DMSO 2.50 DMSO 2.49 DMSO

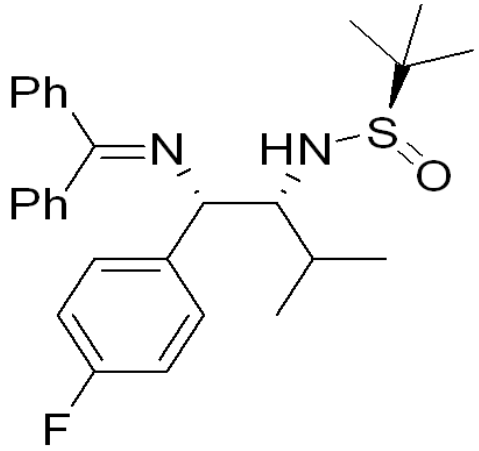
1.67 1.65 1.64 1.62 1.27 1.23 0.91 0.85 0.84 0.84 0.82

1.93 5.66 3.76 1.86 1.98 1.19 1.08 8.76 6.00

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0

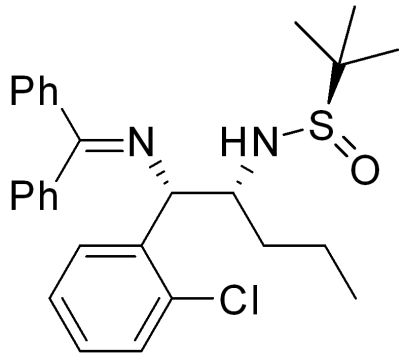
f1 (ppm)

13C NMR OF 5t — C13CPD DMSO {D:\2018\03 MAR 18} O2B 32 —



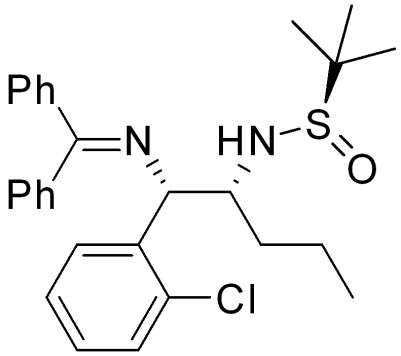
168.10
162.57
160.17
139.94
139.91
139.52
136.22
130.88
129.42
129.34
129.26
128.93
128.73
127.49
115.45
115.24
68.89
67.17
55.97
40.63 DMSO
40.42 DMSO
40.21 DMSO
40.00 DMSO
39.79 DMSO
39.58 DMSO
39.37 DMSO
31.30
22.86
20.34
18.76

1H NMR OF 5u — PROTON CDCl3 {E:\2018\08 AUG 18} O2B 2 —



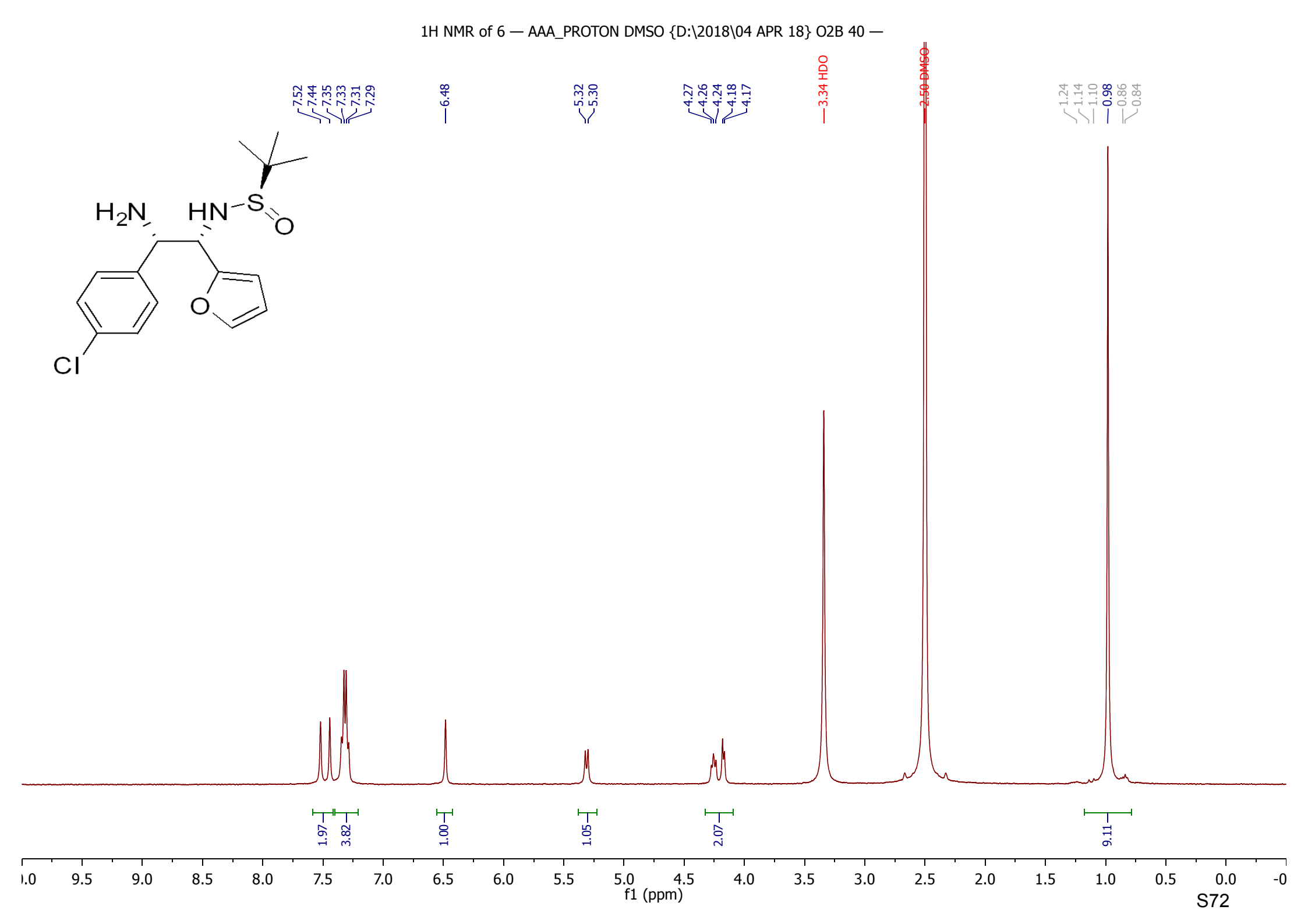
f1 (ppm)

13C NMR OF 5u — C13CPD CDCl3 {E:\2018\08 AUG 18} O2B 2 —

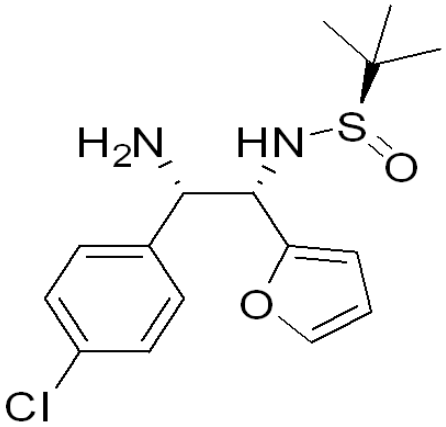


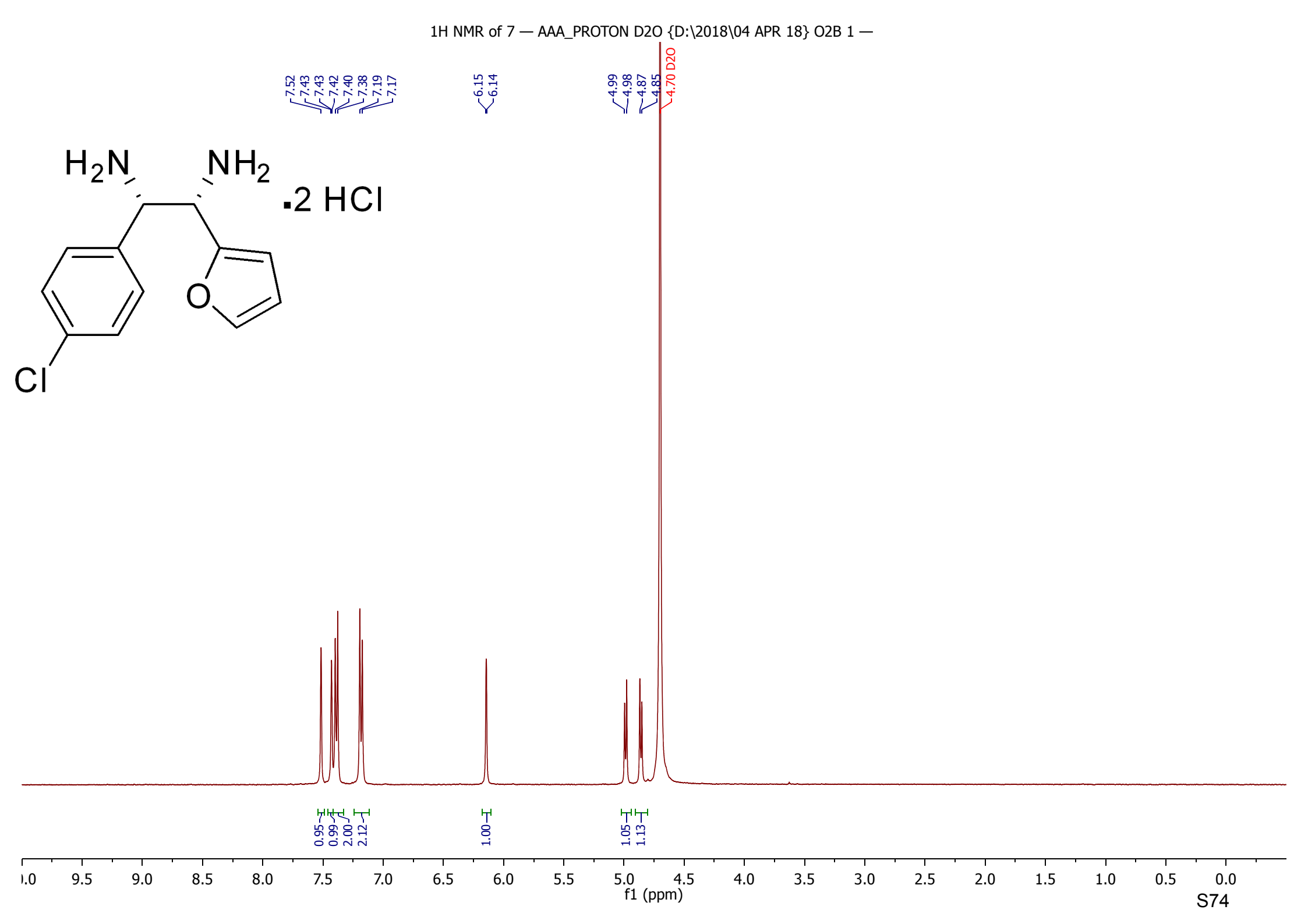
170.45
140.88
139.22
136.31
131.60
130.85
130.59
129.18
128.73
128.70
128.36
128.21
127.80
127.25
126.21
77.37 CDCl3
77.25
77.05 CDCl3
76.73 CDCl3
63.80
61.04
58.99
56.25
38.18
29.72
24.22
22.45
22.27
18.98
14.03

f1 (ppm)


1H NMR of 6 — AAA_PROTON DMSO {D:\2018\04 APR 18} O2B 40 —
7.52
7.44
7.35
7.33
7.31
7.29
6.48
5.32
5.30
4.27
4.26
4.24
4.18
4.17
3.34 HDO
2.50 DMSO
1.24
1.14
1.10
0.98
0.86
0.84
H2N
HN
S
O
O
Cl
1.97
3.82
1.00
1.05
2.07
9.11
f1 (ppm)
S72

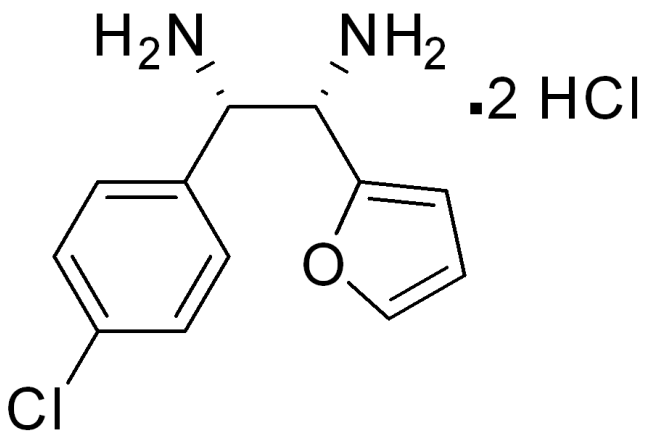
13C NMR OF 6 — C13CPD DMSO {D:\2018\04 APR 18} O2B 35 —

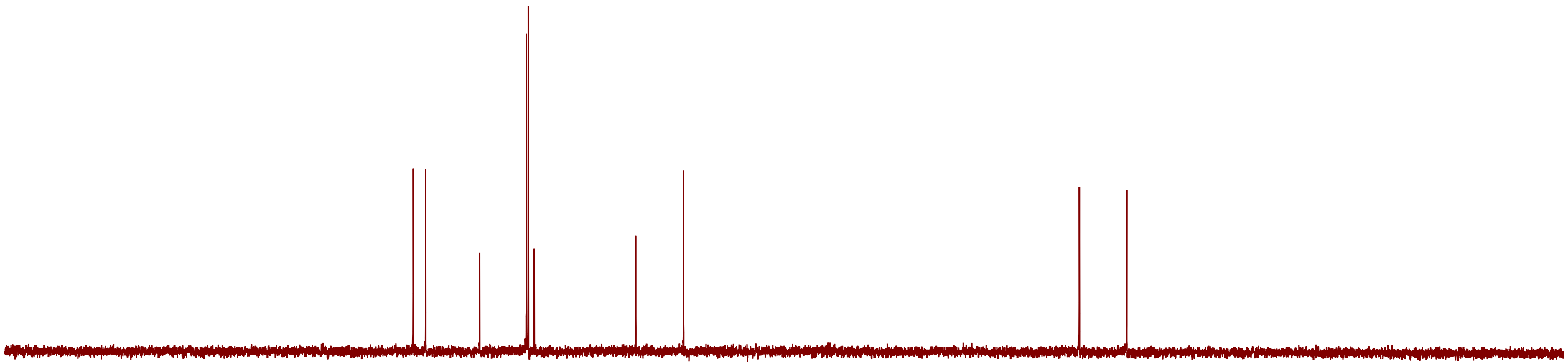



1H NMR of 7 — AAA_PROTON D2O {D:\2018\04 APR 18} O2B 1 —
7.52
7.43
7.43
7.42
7.40
7.38
7.19
7.17
6.15
6.14
4.99
4.98
4.87
4.85
4.70 D2O
H2N
NH2
.2 HCl
O
Cl
0.95
0.99
2.00
2.12
1.00
1.05
1.13
f1 (ppm)

13C NMR OF 7 — C13CPD D2O {E:\2018\04 APR 18} O2B 2 —

144.99
143.28
136.02
129.73
129.46
128.68
114.98
108.55
55.23
48.83





f1 (ppm)

Preparation of the Single crystal: Compound **5g** was taken in MTBE (1 mL) and the solution was kept for 3 days at room temperature. The solvent was slowly evaporated and nice crystal was formed.

X-Ray Crystal structure of **5g (**Wireframe ORTEP), Thermal ellipsoids are shown at the at Probability Level 30% (CCDC No. 1856617).