General Method for the Asymmetric Synthesis of N-H Sulfoximines via C-S Bond Formation

Supporting Information

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Contents

Experimental Methods **1**

General Procedures **2**

Synthesis and Characterisation **6**

Synthesis and Characterisation of the Cyclic Sulfonimidates 7a-9a and 7b-9b 6
Synthesis and Characterisation of Sulfoximines derived from 8a and 8b 15
Synthesis and Characterisation of Sulfoximines derived from 7a and 7b 21
Screening of Conditions for Removal of the Chiral Auxiliary 39
Synthesis of N-H Sulfoximines 40

Single Crystal X-ray Diffraction **73**

References **75**

NMR Spectra **77**

Experimental Methods

Unless otherwise stated, all reagents were purchased from commercial sources and used without additional purification. THF was freshly distilled under argon from the sodium anion of benzophenone. All other anhydrous solvents were purchased or obtained from in house solvent purification towers. Petroleum ether means the petroleum fraction b.p. 40-60 °C. Water was deionised prior to use. All air or moisture-sensitive reactions were conducted in flame-dried glassware under an atmosphere of argon. Brine is a saturated aqueous solution of sodium chloride. For reactions that required heating, a heating block was used as the heat source. Thin Layer Chromatography was performed on Merck silica gel 60 F254 and visualised by UV lamp, aqueous alkaline potassium permanganate, phosphomolybdic acid and cerium molybdate. Column chromatography was performed on silica gel Fluka 60. ^{1}H, ^{13}C and ^{19}F NMR spectral data were recorded using a Bruker DPX300, Bruker DPX400, Bruker AV400 and Bruker AV(III)400 spectrometers. Chemical shifts are quoted in ppm. Coupling constant values J are given in Hertz. Infrared spectral data were recorded using a Perkin-Elmer 1600 FTIR spectrometer. HRMS analyses were performed on a Bruker microTOFII mass spectrometer (TOF mass analyser, Bruker Daltonik, Bremen, Germany), interfaced to an Agilent 1200 HPLC (Agilent Technologies, Santa Clara, USA). Samples were presented in solution for analysis by Flow Injection, 1 μL of solution being injected into the ion source of the instrument along with a flow of 0.2 mL min^{-1} of 70% methanol/water eluent. The mass spectrometer was operated in electrospray ionisation (ESI) mode at a typical resolving power of 8000. The machine interface was provided by Bruker's Compass Open Access QC (v1.4; Bruker Daltonik, Bremen, Germany) and acquired and processed using Bruker Compass (v1.7; Bruker Daltonik, Bremen, Germany). Melting points are uncorrected and were recorded using Stuart Scientific SMP3.

General Procedures

Preparation of Sulfinyl Chlorides (GP1)

The corresponding disulfide (1 equiv., 23-100 mmol) and acetic acid (2 equiv., 46-200 mmol) were mixed and cooled to -20 °C. Sulfuryl chloride (3.1 equiv., 71-310 mmol) was added dropwise with stirring over a period of 30 min. The reaction mixture was then stirred for 3 h at -20 °C and then allowed to warm to room temperature over a period of about 2 h. Evolution of SO_2 and HCl was observed during this time. The mixture was warmed to 35 °C for 1 h. The resulting acetyl chloride was evaporated under reduced pressure, providing the desired product as a liquid which was used without further purification.

Preparation of Sulfinamides (GP2)

A mixture of Et_3N (3.0 equiv., 70.3-120 mmol) and amino alcohol (1.0 equiv., 23.4-40.1 mmol) in CH_2Cl_2 (0.5 M) was added dropwise over 5 min to a stirred mixture of sulfinyl chloride (2.2 equiv., 51.5-88.2 mmol) in CH_2Cl_2 (0.5 M) at 0 °C. The mixture was stirred at 0 °C for 1 h and then brought to rt for a further 3-4 h (reaction completion was monitored by TLC, 1:1 petroleum ether/ethyl acetate). The mixture was quenched with sat. aq. $NaHCO_3$ (5 mL) and extracted with CH_2Cl_2 (3 $\times$ 30 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure. The residue was dissolved in MeOH (0.1 M) and cooled to 0 °C. A 1 M solution of NaOH in MeOH (1.05 equiv. of base) was added dropwise over 5 min, and the reaction was stirred for a further 5 min (reaction completion was monitored by TLC, 1:1 petroleum ether/ethyl acetate for disappearance of the *bis*-protected substrate). After completion, the solvent was removed under reduced pressure. Addition of sat. aq. $NaHCO_3$ solution (5 mL), followed by extraction of the product using CH_2Cl_2 (3 x 30 mL). The combined organic phase was dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography.

Preparation of Cyclic Sulfonimidates (GP3)

To the solution of sulfinamide (1.0 equiv., 0.20-13.9 mmol) in THF (0.2 M) at -78 °C was added oxidant *t*BuOCl (1.1 equiv., 0.22-15.3 mmol) or (*N*-chlorosuccinimide (2.0 equiv.). After stirring at this temperature for 30 min, 1,8-diazabicyclo(5.4.0)undec-7-ene (2 equiv., 0.40-27.9 mmol) was added and the mixture was stirred for another 15 min. The reaction was quenched with sat. aq. NH_4Cl, the aqueous layer was extracted with Et_2O (3×5 mL) and the combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography.

Preparation of Sulfoximines (GP4)

To a solution of sulfonimidate (1.0 equiv., 0.233-1.20 mmol) in dry THF at -78 °C, Grignard reagent (2 equiv., 0.465-2.40 mmol) were added. After 5 min, the reaction mixture was allowed to reach 0 °C and then rt and the reaction was stirred for another 45 min at this temperature. The reaction was quenched with saturated NH_4Cl solution (2 mL) and the aqueous layer was extracted with Et_2O (3×5 mL) and the combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography.

Cleavage of Phenyl Ethanol Group (GP5)

Freshly ground NaOH (10 equiv., 0.891-6.48 mmol) was added to a solution of sulfoximine (1 equiv., 0.0891-0.648 mmol) in MTBE. The round bottomed flask was equipped with two balloons containing O_2 and the mixture was warmed at 40 °C for 16 h. The reaction was monitored by TLC and after completion, H_2O (5 mL) was added and the aqueous phase was extracted with CH_2Cl_2 (3×10 mL). The combined organic phases were dried with $MgSO_4$ and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography.

Preparation of Racemic Sulfoximines (GP6)

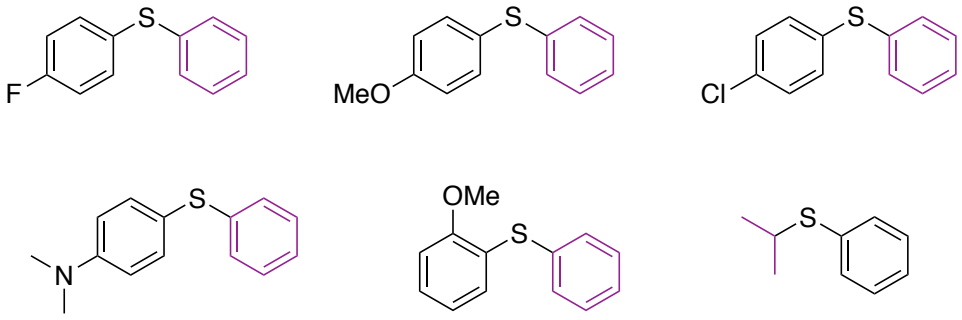
The sulfide (1 equiv., 0.344-3.83 mmol), (diacetoxyiodo)benzene (2.5 equiv., 0.859-9.58 mmol) and ammonium carbamate (2.0 equiv., 0.688-7.66 mmol) were added to a round bottom flask containing a stirrer bar. MeOH (0.5 M) was added and the reaction was stirred at 25 °C for 3 h. The solvent was removed under reduced pressure. The resulting residue was purified by flash column chromatography.

Preparation of Sulfides I (GP7)

For a solid disulfide: A schlenk tube with a magnetic stirring bar was charged with aniline (1 equiv.) and disulfide (1 equiv.). The tube was evacuated and backfilled three times with dry nitrogen. Acetonitrile was added by syringe, followed by L-ascorbic acid (0.5 equiv.) dissolved in DMSO (0.1 mL).

For liquid disulfide: A 10-mL schlenk tube with a magnetic stirring bar was charged with aniline (0.2 mmol). The tube was evacuated and backfilled with dry nitrogen (this operation was repeated three times). Acetonitrile (1 mL) was added by syringe, followed by disulfide (0.2 mmol or 0.4 mmol) and L-ascorbic acid (0.5 equiv.) dissolved in DMSO (0.1 mL).

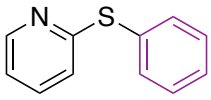
The mixture was then stirred vigorously for 1 minute before *t*-BuONO (0.3 mmol), was added *via* syringe. After the resulting mixture was stirred at 20 °C for 4 hours, the solvent was removed under reduced pressure. The resulting residue was purified by flash column chromatography.



Note: Disulfide fragment is shown above in purple. All compounds above are known in the literature.[1],[2],[3],[4]

Preparation of Sulfides II (GP8)

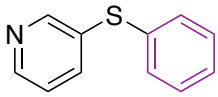
A suspension of a heteroaryl halide (1 equiv.) and thiol (1.2 equiv.) in H_2O (0.2 M) was added to a round bottom flask and stirred at 100 °C for 8 h. After completion of the reaction (as indicated by TLC), the product was extracted with EtOAc (3x), and the combined organic extracts were dried (Na_2SO_4). The solvent was removed under reduced pressure. The resulting residue was purified by flash column chromatography.



Note: Thiol fragment is shown above in purple. The compound above is known in the literature.[5]

Preparation of Sulfides III (GP9)

A mixture of thiol (1 equiv.), aryl halide (1.2 equiv.), CuI (5 mol%), DABCO (10 mol%), K_2CO_3 (2 equiv.) and DME (0.2 M) were added to an oven dried sealed tube equipped with a stirring bar under nitrogen. The reaction was heated for 12 h at 120 °C. After being cooled to rt, the mixture was diluted with EtOAc and washed with sat. aqueous NaCl solution (3 ×). The organic phase was dried with anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure. The resulting residue was purified by flash column chromatography.

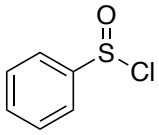


Note: Thiol fragment is shown above in purple. The compound above is known in the literature.[6]

Synthesis and Characterisation

Synthesis and Characterisation of the Cyclic Sulfonimidates 7a-9a and 7b-9b

(±)-Benzenesulfinic chloride (S1)[7]

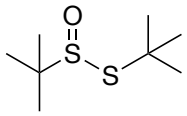


Following GP1, benzenesulfinic chloride (**S1**) was prepared from diphenyl disulfide (5.00 g, 23.0 mmol), sulfuryl chloride (9.58 g, 71.0 mmol) and acetic acid (2.75 g, 46.0 mmol), affording the desired compound as a pale yellow liquid (6.22 g, 85%); IR ν_{max} (cm^{-1}): 3066, 3005, 2927, 2854, 1476, 1327, 1147, 1092, 1035; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.89 (2H, m), 7.68-7.56 (3H, m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.7, 133.8, 129.6, 123.8; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_7H_9O_2S$ (compound was treated with MeOH and analysed as the corresponding methyl ester) 157.0318, found 157.0323.

(±)-Methanesulfinic chloride (S2)[7]

Following GP1, methanesulfinic chloride (**S2**) was prepared from dimethyl disulfide (9.42 g, 100 mmol), sulfuryl chloride (41.8 g, 310 mmol) and acetic acid (12.0 g, 200 mmol), affording the desired compound as a pale yellow liquid (19.1 g, 97%); IR ν_{max} (cm^{-1}): 2924, 2533, 1651, 1404, 1304, 1214, 1046, 953, 813, 747, 703; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.38 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 52.5.

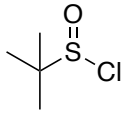
(±)-*S*-(*tert*-butyl)-2-Methylpropane-2-sulfinothioate (S3)[8]



Hydrogen peroxide (10.0 mL, 97.0 mmol, 30% aqueous solution) was added slowly to a solution of di-*tert*-butyl disulfide (17.0 mL, 88.0 mmol) in glacial acetic acid (88.0 mL) at 0 °C.

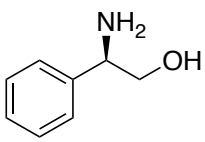
After addition, the reaction was warmed slowly to room temperature and stirred for 16 h. The reaction was quenched by adding ice/water (100 mL), and the mixture was extracted with CH_2Cl_2 (2 × 20 mL). The organic layer was washed with saturated aq. $NaHCO_3$ solution (20 mL), water (20 mL), dried ($MgSO_4$), filtered and concentrated under reduced pressure. The product was afforded as a colourless oil (14.1 g, 83%); IR ν_{max} (cm^{-1}): 2959, 2925, 1467, 1363, 1160, 1069, 1034, 565, 511, 463; ^1H NMR (400 MHz, $CDCl_3$) δ 1.56 (9H, s), 1.38 (9H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 59.6, 48.8, 32.5, 24.4; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_8H_{19}OS_2$ 195.0872, found 195.0873; / m/z: $[M + Na]^+$ calcd for $C_8H_{18}OS_2Na$ 217.0691, found 217.0692.

(±)-2-Methylpropane-2-sulfinic chloride (S4)[8]



S-(*tert*-butyl)-2-Methylpropane-2-sulfinothioate (**S3**) (14.1 g, 72.7 mmol) was dissolved in CH_2Cl_2 (100 mL), and the solution was cooled to 0 °C. A solution of sulfuryl chloride (9.81 g, 72.7 mmol) in CH_2Cl_2 (100 mL) was added dropwise. After the addition was complete, the reaction mixture was stirred for 1 h, during which time the temperature was allowed to rise slowly to room temperature. The volatiles were removed under reduced pressure without heating to give the title compound as a yellow liquid and in good purity, with no further purification necessary (15.9 g, 78%); IR ν_{max} (cm^{-1}): 2965, 2924, 2853, 1456, 1365, 1310, 1214, 1181, 1160, 1110, 1059, 1017, 752, 667, 634, 565, 485; ^1H NMR (400 MHz, $CDCl_3$) δ 1.41 (9H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 64.5, 22.6; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_5H_{13}O_2S_1$ (compound was dissolved in MeOH and analysed as the corresponding methyl ester) 137.0631, found 137.0632.

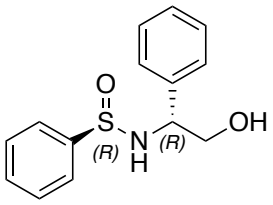
(*R*)-2-Amino-2-phenylethan-1-ol (S5)[9]



Lithium aluminium hydride (4.90 g, 129 mmol, 1.95 eq.) was suspended in dry THF (200 mL) under argon at 0 °C. Solid (*R*)-2-phenylglycine (10.0 g, 66.15 mmol) was added in small

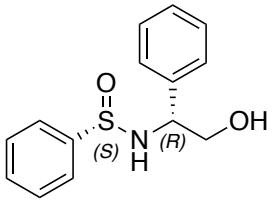
portions. The mixture was stirred at 0 °C for 1 h, then slowly heated to reflux at 80 °C for 16 h. The reaction was cooled to 0 °C and then a saturated potassium carbonate solution (75 mL) was added very slowly to the mixture. The mixture was filtered, and the solvents were removed from the filtrate under reduced pressure. The crude yellow solid was recrystallised from hot toluene to yield a white crystalline solid (7.62 g, 84%); m.p. 77-79 °C, lit.[9] 76-78 °C; IR ν_{max} (cm^{-1}): 3327, 3115, 3028, 2893, 2833, 1597, 1495, 1450, 1392, 1357, 1317, 1298, 1209, 1063, 1044, 1027, 979, 933, 866, 794, 765, 751, 703, 618, 586, 554, 491, 425; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.26 (5H, m), 4.05 (1H, dd, *J* = 8.5, 4.5 Hz), 3.74 (1H, dd, *J* = 10.5, 4.5 Hz), 3.55 (1H, dd, *J* = 10.5, 8.5 Hz), 1.92 (2H, s), (OH not observed); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 128.8, 127.7, 126.6, 68.2, 57.5; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_8H_{12}NO$ 138.0913, found 138.0923 / m/z: $[M + Na]^+$ calcd for $C_8H_{11}NONa$ 160.0733, found 160.0732.

(*R*)-*N*-((*R*)-2-Hydroxy-1-phenylethyl)benzenesulfinamide (4a)



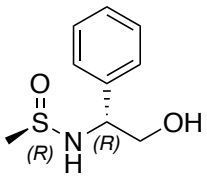
Following GP2, the title compound was prepared from (*R*)-phenylglycinol **S5** (5.5 g, 40.1 mmol), benzenesulfinic chloride **S1** (14.2 g, 88.2 mmol) and Et_3N (12.2 g, 120.3 mmol). The crude mixture was purified by flash chromatography (1:1 petroleum ether/ethyl acetate to 9.5:0.5 dichloromethane/methanol) to afford the title compound as a colourless oil (combined yield for both diastereomers, 9.42 g, 90%); $[\alpha]_D^{28}$ –136.41 (c 0.660 $CHCl_3$); IR ν_{max} (cm^{-1}): 3272, 3060, 3029, 2919, 2871, 1652, 1603, 1582, 1493, 1475, 1453, 1342, 1085, 1044, 998, 923, 749, 698, 561, 504, 449; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.65 (2H, m), 7.47 (3H, dd, *J* = 5.5, 2.0 Hz), 7.43-7.36 (4H, m), 7.35-7.30 (1H, m), 5.05 (1H, d, *J* = 5.5 Hz), 4.68 (1H, ddd, *J* = 9.0, 5.5, 4.0 Hz), 3.90 (1H, dt, *J* = 11.5, 4.0 Hz), 3.80 (1H, s), 3.72-3.63 (1H, m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 138.8, 131.3, 129.1, 128.9, 128.3, 127.6, 125.7, 67.3, 61.7; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{16}NO_2S$ 262.0896, found 262.0904 / m/z: $[M + Na]^+$ calcd for $C_{14}H_{15}NO_2SNa$ 284.0716, found 284.0723.

(*S*)-*N*-((*R*)-2-Hydroxy-1-phenylethyl)benzenesulfinamide (4b)



Following GP2, the title compound was prepared from (*R*)-phenylglycinol **S5** (5.5 g, 40.1 mmol), benzenesulfinic chloride **S1** (14.2 g, 88.2 mmol) and Et_3N (12.2 g, 120.3 mmol). The crude mixture was purified by flash chromatography (1:1 petroleum ether/ethyl acetate to 9.5:0.5 dichloromethane/methanol) to afford the title compound as a colourless oil (combined yield for both diastereomers, 9.42 g, 90%); $[\alpha]_D^{28}$ –215.02 (c 0.620 $CHCl_3$); IR ν_{max} (cm^{-1}): 3277, 3180, 3058, 3029, 2912, 2886, 1600, 1584, 1494, 1475, 1444, 1334, 1306, 1236, 1195, 1186, 1154, 1083, 1071, 1039, 1021, 996, 989, 924, 914, 875, 750, 694; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.66 (2H, m), 7.52-7.46 (3H, m), 7.31-7.26 (3H, m), 7.10-7.04 (2H, m), 5.04 (1H, d, *J* = 8.5 Hz), 4.18 (1H, td, *J* = 8.5, 3.5 Hz), 3.82-3.68 (2H, m), 1.73 (1H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 138.9, 131.4, 129.1, 128.9, 128.0, 126.68, 126.65, 66.4, 59.8; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{16}NO_2S$ 262.0896, found 262.0902 / m/z: $[M + Na]^+$ calcd for $C_{14}H_{15}NO_2SNa$ 284.0716, found 284.0723.

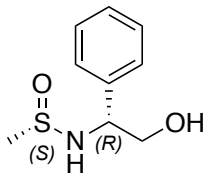
(*R*)-*N*-((*R*)-2-Hydroxy-1-phenylethyl)methanesulfinamide (5a)



Following GP2, the title compound was prepared from (*R*)-phenylglycinol **S5** (3.23 g, 23.6 mmol), methanesulfinic chloride **S2** (5.11 g, 51.9 mmol) and Et_3N (7.16 g, 70.7 mmol). The crude mixture was purified by flash chromatography (1:1 petroleum ether/ethyl acetate to 9.5:0.5 dichloromethane/methanol) to afford the title compound as a colourless oil (combined yield for both diastereoisomers, 3.77 g, 80%); $[\alpha]_D^{25}$ –49.38 (c 0.955 $CHCl_3$); IR ν_{max} (cm^{-1}): 3230, 2920, 2899, 2871, 2088, 1651, 1602, 1493, 1453, 1023, 960, 757, 699; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.31 (5H, m), 5.24 (1H, t, *J* = 4.5 Hz), 4.54 (1H, ddd, *J* = 8.5, 4.5, 3.5 Hz), 3.87 (1H, dd, *J* = 12.0, 3.5 Hz), 3.69-3.60 (1H, m), 2.73 (3H, s), (OH not observed); ^{13}C NMR

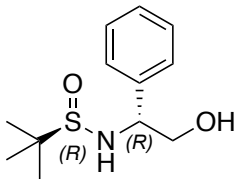
(101 MHz, $CDCl_3$) δ 138.7, 128.9, 128.3, 127.4, 67.3, 61.9, 42.9; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_9H_{14}NO_2S$ 200.0740, found 200.0749 / m/z: $[M + Na]^+$ calcd for $C_9H_{13}NO_2SNa$ 222.0559, found 222.0571.

(*S*)-*N*-((*R*)-2-Hydroxy-1-phenylethyl)methanesulfinamide (5b)



Following GP2, the title compound was prepared from (*R*)-phenylglycinol **S5** (3.23 g, 23.6 mmol), methanesulfinic chloride **S2** (5.11 g, 51.9 mmol) and Et_3N (7.16 g, 70.7 mmol). The crude mixture was purified by flash chromatography (1:1 petroleum ether/ethyl acetate to 9.5:0.5 dichloromethane/methanol) to afford the title compound as a colourless oil (combined yield for both diastereoisomers, 3.77 g, 80%); $[\alpha]_D^{20}$ –84.11 (c 2.13 $CHCl_3$); IR ν_{max} (cm^{-1}): 3247, 3202, 2919, 2868, 2353, 1651, 1494, 1453, 1041, 1024, 785, 700; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38-7.27 (5H, m), 5.04 (1H, d, *J* = 5.5 Hz), 4.76 (1H, ddd, *J* = 8.5, 5.5, 4.0 Hz), 3.86 (1H, dd, *J* = 12.0, 4.0 Hz), 3.66 (1H, dd, *J* = 12.0, 8.5 Hz), 2.51 (3H, s), (OH not observed); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.8, 129.0, 128.2, 127.1, 66.8, 56.5, 40.7; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_9H_{14}NO_2S$ 200.0740, found 200.0736 / m/z: $[M + Na]^+$ calcd for $C_9H_{13}NO_2SNa$ 222.0559, found 222.0563.

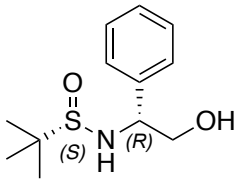
(*R*)-*N*-((*R*)-2-Hydroxy-1-phenylethyl)-2-methylpropane-2-sulfinamide (6a)[10]



Following GP2, the title compound was prepared from (*R*)-phenylglycinol **S5** (3.21 g, 23.4 mmol), *tert*-butylsulfinyl chloride **S4** (7.25 g, 51.5 mmol) and Et_3N (7.11 g, 70.3 mmol). The crude mixture was purified by flash chromatography (1:1 pentane/diethyl ether to 9.5:0.5

dichloromethane/methanol) to afford the title compound as a colourless oil (combined yield for both diastereomers 5.09 g, 90%); $[\alpha]_D^{19}$ +22.18 (c 0.755 $CHCl_3$); IR ν_{max} (cm^{-1}): 3241, 2954, 2925, 2867, 1453, 1390, 1363, 1181, 1027, 931, 757, 699, 637, 596, 532; ^1H NMR (400 MHz, $CDCl_3$) δ 7.39-7.29 (5H, m), 4.51 (1H, dt, *J* = 7.0, 5.5 Hz), 4.26 (1H, d, *J* = 5.5 Hz), 3.93-3.81 (2H, m), 3.40 (1H, s), 1.22 (9H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.4, 128.8, 128.0, 127.5, 66.3, 60.2, 56.5, 22.8; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{12}H_{20}NO_2S$ 242.1209, found 242.1216 / m/z: $[M + Na]^+$ calcd for $C_{12}H_{19}NO_2SNa$ 264.1029, found 264.1034.

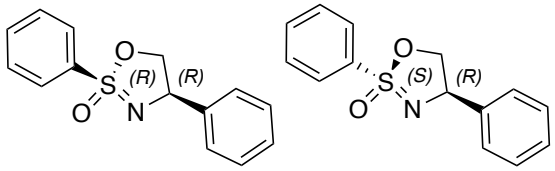
(*S*)-*N*-((*R*)-2-Hydroxy-1-phenylethyl)-2-methylpropane-2-sulfinamide (6b)



Following GP2, the title compound was prepared from (*R*)-phenylglycinol **S5** (3.21 g, 23.4 mmol), *tert*-butylsulfinyl chloride **S4** (7.25 g, 51.5 mmol) and Et_3N (7.11 g, 70.3 mmol). The crude mixture was purified by flash chromatography (1:1 pentane/diethyl ether to 9.5:0.5 dichloromethane/methanol) to afford the title compound as a colourless oil (combined yield for both diastereomers 5.09 g, 90%); IR ν_{max} (cm^{-1}): 3274, 2952, 2924, 2867, 2106, 1659, 1602, 1493, 1453, 1363, 1180, 1027, 931, 757, 699, 679, 636, 598, 531; $[\alpha]_D^{21}$ +85.25 (c 0.290 $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.41-7.30 (5H, m), 4.56 (1H, dt, *J* = 7.0, 5.5 Hz), 4.02 (1H, d, *J* = 5.5 Hz), 3.93 (2H, t, *J* = 6.0 Hz), 2.79 (1H, s), 1.25 (9H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.3, 128.9, 128.2, 127.5, 66.3, 60.2, 56.5, 22.8; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{12}H_{20}NO_2S$ 242.1209, found 242.1212 / m/z: $[M + Na]^+$ calcd for $C_{12}H_{19}NO_2SNa$ 264.1029, found 264.1033.

(2*R*,4*R*)-2,4-Diphenyl-4,5-dihydro-1,2,3-oxathiazole 2-oxide (7a) and

(2*S*,4*R*)-2,4-Diphenyl-4,5-dihydro-1,2,3-oxathiazole 2-oxide (7b)



Following GP3, the title compounds were prepared from the sulfinamides **4a**/**4b** (1:1) (52 mg, 0.2 mmol), *t*BuOCl (24 mg, 0.22 mmol) and DBU (61 mg, 0.40 mmol). The crude mixture was purified by flash chromatography (9:1 petroleum ether/ethyl acetate) to afford the title compounds **7a** (first to elute) and **7b** as colourless oils (combined yield for both diastereoisomers, 47 mg, 92%).

Following GP3, the title compounds were prepared from the sulfinamides **4a**/**4b** (1:1) (3.01 g, 11.5 mmol), *t*BuOCl (1.37 g, 12.7 mmol) and DBU (3.50 g, 23.0 mmol). The crude mixture was purified by flash chromatography (9:1 petroleum ether/ethyl acetate) to afford the title compounds **7a** (first to elute) and **7b** as colourless oils (combined yield for both diastereoisomers, 2.25 g, 76%).

7a(R_s)

$[\alpha]_D^{28}$ +93.0 (c 0.35 $CHCl_3$); IR ν_{max} (cm^{-1}): 3061, 2884, 1493, 1447, 1291, 1261, 1118, 1070, 1024, 980, 949, 906, 836, 742, 723, 699, 684, 634, 618, 591, 530, 519, 487; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08-8.01 (2H, m), 7.70-7.63 (1H, m), 7.59-7.52 (2H, m), 7.51-7.46 (2H, m), 7.41 (2H, ddd, *J* = 7.5, 7.0, 1.5 Hz), 7.37-7.31 (1H, m), 5.51 (1H, dd, *J* = 9.0, 6.5 Hz), 4.98 (1H, dd, *J* = 8.0, 6.5 Hz), 3.99 (1H, dd, *J* = 9.0, 8.0 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.2, 138.0, 134.2, 129.4, 129.3, 129.0, 128.2, 126.3, 78.1, 67.2; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{14}NO_2S$ 260.0740, found 260.0758 / m/z: $[M + Na]^+$ calcd for $C_{14}H_{13}NO_2SNa$ 282.0559, found 282.0565.

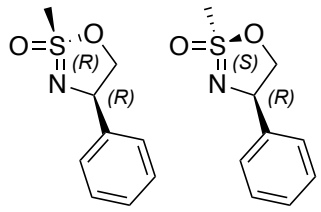
7b(S_s)

$[\alpha]_D^{29}$ +106.00 (c 0.490 $CHCl_3$); IR ν_{max} (cm^{-1}): 3062, 2912, 1602, 1582, 1492, 1474, 1446, 1329, 1272, 1215, 1130, 1094, 1072, 1031, 978, 937, 901, 834, 810, 741, 719, 699, 685, 638, 616, 590, 535, 490; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-7.94 (2H, m), 7.64 (1H, ddt, *J* = 8.5, 7.0, 1.5 Hz), 7.59-7.51 (4H, m), 7.43-7.37 (2H, m), 7.36-7.30 (1H, m), 5.29 (1H, dd, *J* = 7.5, 7.0 Hz), 4.66

(1H, dd, *J* = 7.5, 7.0 Hz), 4.18 (1H, dd, *J* = 7.5, 7.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0, 139.4, 133.6, 129.4, 128.8, 128.2, 127.8, 126.5, 76.5, 69.5; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{14}NO_2S$ 260.0740, found 260.0763 / m/z: $[M + Na]^+$ calcd for $C_{14}H_{13}NO_2SNa$ 282.0559, found 282.0570.

(2*R*,4*R*)-2-Methyl-4-phenyl-4,5-dihydro-1,2λ^6,3-oxathiazole 2-oxide (8a) and

(2*S*,4*R*)-2-Methyl-4-phenyl-4,5-dihydro-1,2λ^6,3-oxathiazole 2-oxide (8b)



Following GP3, the title compounds were prepared from sulfinamide **5a**/**5b** (1:1) (100 mg, 0.5 mmol), *t*BuOCl (60 mg, 0.55 mmol) and DBU (153 mg, 1.0 mmol). The crude mixture was purified by flash chromatography (7:3 petroleum ether/ethyl acetate) to afford the title compounds as colourless oils **8a** (first to elute) and **8b** (combined yield for both diastereoisomers, 93 mg, 94%).

Following GP3, the title compounds were prepared from sulfinamide **5a**/**5b** (1:1) (2.78 g, 13.9 mmol), *t*BuOCl (1.67 g, 15.3 mmol) and DBU (4.25 g, 27.9 mmol). The crude mixture was purified by flash chromatography (7:3 petroleum ether/ethyl acetate) to afford the title compounds **8a** (first to elute) and **8b** as a colourless oils (combined yield for both diastereoisomers, 2.06 g, 75%).

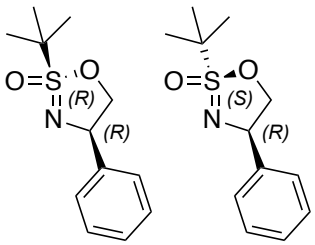
8a(R_s)

$[\alpha]_D^{20}$ +17.66 (c 3.255 $CHCl_3$); IR ν_{max} (cm^{-1}): 3285, 3028, 2935, 1454, 1322, 1147, 963, 772, 701, 587, 515; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.29 (5H, m), 5.34 (1H, dd, *J* = 6.0, 6.0 Hz), 4.84 (1H, dd, *J* = 7.0, 6.0 Hz), 4.26 (1H, dd, *J* = 7.0, 6.0 Hz), 3.25 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.9, 128.9, 128.1, 126.0, 77.5, 67.4, 42.4; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_9H_{12}NO_2S$ 198.0583, found 198.0595.

8b(S_s)

$[\alpha]_D^{25}$ –62.74 (c 0.755 $CHCl_3$); IR ν_{max} (cm^{-1}): 3289, 3063, 2927, 1706, 1454, 1319, 1277, 1147, 1074, 977, 927, 785, 700, 517; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.44 (2H, m), 7.39-7.29 (3H, m), 4.99 (1H, dd, *J* = 9.0, 6.5 Hz), 4.59 (1H, dd, *J* = 7.5, 6.5 Hz), 3.96 (1H, dd, *J* = 9.0, 7.5 Hz), 3.22 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 128.9, 128.4, 126.6, 76.0, 68.1, 40.6; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_9H_{12}NO_2S$ 198.0583, found 198.0586 / m/z: $[M + Na]^+$ calcd for $C_9H_{11}NO_2SNa$ 220.0403, found 220.0399.

(2*R*,4*R*)-2-(*tert*-Butyl)-4-phenyl-4,5-dihydro-1,2λ^6,3-oxathiazole 2-oxide (9a) and (2*S*,4*R*)-2-(*tert*-Butyl)-4-phenyl-4,5-dihydro-1,2λ^6,3-oxathiazole 2-oxide (9b)



Following GP3, the title compounds were prepared from the sulfinamides **6a**/**6b** (1:1) (100 mg, 0.41 mmol), *t*BuOCl (49 mg, 0.45 mmol) and DBU (125 mg, 0.82 mmol). The crude mixture was purified by flash chromatography (8:2 pentane/diethyl ether) to afford the title compounds **9a** (first to elute) and **9b** as a colourless oils (combined yield for both diastereoisomers, 78 mg, 80%).

Following GP3, the title compounds were prepared from the sulfinamides **6a**/**6b** (1:1) (2.51 g, 10.4 mmol), *t*BuOCl (1.24 g, 11.4 mmol) and DBU (3.16 g, 20.8 mmol). The crude mixture was purified by flash chromatography (8:2 pentane/diethyl ether) to afford the title compounds **9a** (first to elute) and **9b** as a colourless oils (combined yield for both diastereoisomers, 1.85 g, 75%).

9a(R_s)

$[\alpha]_D^{19}$ –32.60 (c 1.198 $CHCl_3$); IR ν_{max} (cm^{-1}): 2981, 2936, 2868, 1477, 1455, 1365, 1256, 1057, 1032, 747, 700, 670; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.29 (5H, m), 5.43-5.35 (1H, m), 4.93 (1H, dd, *J* = 7.0, 7.0 Hz), 3.77 (1H, dd, *J* = 9.0, 7.0 Hz), 1.59 (9H, s); ^{13}C NMR (101 MHz, $CDCl_3$)

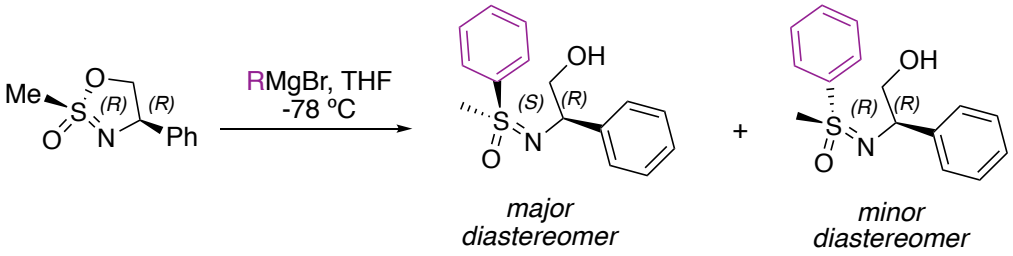
δ 140.3, 128.8, 128.1, 126.3, 79.6, 66.8, 62.3, 25.5; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{12}H_{18}NO_2S$ 240.1053, found 240.1051 / m/z: $[M + Na]^+$ calcd for $C_{12}H_{17}NO_2SNa$ 262.0872, found 262.0870.

9b(S_s)

$[\alpha]_D^{20}$ –61.31 (c 0.244 $CHCl_3$); IR ν_{max} (cm^{-1}): 3063, 3029, 2971, 2923, 1731, 1478, 1304, 1265, 1126, 1031, 757, 700; ^1H NMR (400 MHz, $CDCl_3$) δ 7.50-7.44 (2H, m), 7.40-7.30 (3H, m), 5.06 (1H, dd, *J* = 7.5, 7.5 Hz), 4.58 (1H, dd, *J* = 7.5, 7.5 Hz), 4.04 (1H, dd, *J* = 9.5, 7.5 Hz), 1.57 (9H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.2, 128.8, 128.2, 126.6, 76.5, 70.2, 63.7, 25.0; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{12}H_{18}NO_2S$ 240.1053, found 240.1053 / m/z: $[M + Na]^+$ calcd for $C_{12}H_{17}NO_2SNa$ 262.0872, found 262.0870.

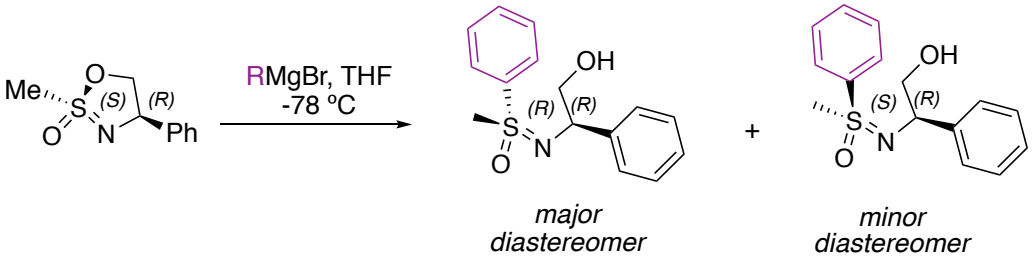
Synthesis and Characterisation of Sulfoximines derived from 8a and 8b

(*S*)-(((*R*)-2-Hydroxy-1-phenylethyl)imino)(methyl)(phenyl)-λ⁶-sulfanone (12a)



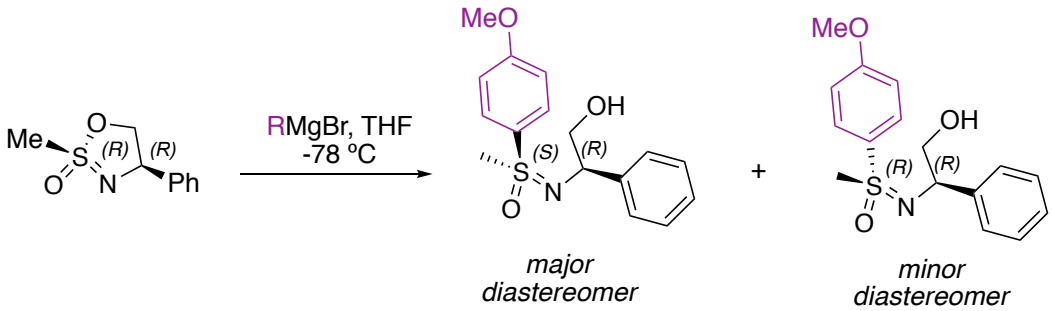
Following GP4, the title compound was prepared from the cyclic sulfonimidate **8a** (221 mg, 1.12 mmol) dissolved in THF (5 mL) and phenylmagnesium bromide (2.24 mL, 2.24 mmol, 1M). The crude mixture (dr = 2:1) was purified by flash chromatography (4:6 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (dr = 2:1, 264 mg, 86%) and an analytical sample of of the major diastereomer **12a** (reported); IR ν_{max} (cm^{-1}): 3387, 3060, 3026, 2926, 2866, 1445, 1403, 1224, 1127, 1066, 1028, 910, 785, 742, 700, 689, 633, 528; ^1H NMR (400 MHz, $CDCl_3$) δ 7.77-7.73 (2H, m), 7.60-7.54 (1H, m), 7.49-7.42 (2H, m), 7.31-7.28 (4H, m), 7.27-7.22 (1H, m), 4.14 (1H, dd, *J* = 7.0, 5.5 Hz), 3.65-3.61 (2H, m), 3.23 (3H, s), (OH, not observed); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 138.7, 133.2, 129.5, 128.9, 128.4, 127.2, 127.1, 69.1, 61.9, 46.0; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{18}NO_2S$ 276.1053, found 276.1055 / m/z: $[M + Na]^+$ calcd for $C_{15}H_{17}NO_2SNa$ 298.0872, found 298.0872.

(*R*)-(((*R*)-2-Hydroxy-1-phenylethyl)imino)(methyl)(phenyl)-λ^6-sulfanone (12b)



Following GP4, the title compound was prepared the cyclic sulfonimidate **8b** (173 mg, 0.877 mmol) dissolved in THF (5 mL) and phenylmagnesium bromide (1.75 mL, 1.75 mmol, 1M). The crude mixture (dr = 5:1) was purified by flash chromatography (4:6 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (dr = 5:1, 85 mg, 35%) and an analytical sample of of the major diastereomer **12b** (reported); IR ν_{max} (cm^{-1}): 3434, 3060, 3025, 2927, 2866, 1491, 1445, 1403, 1353, 1310, 1223, 1127, 1085, 1066, 1028, 977, 854, 784, 743, 700, 688, 633, 527, 516; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-8.01 (2H, m), 7.70-7.64 (1H, m), 7.63-7.58 (2H, m), 7.48-7.43 (2H, m), 7.39-7.32 (2H, m), 7.31-7.25 (1H, m), 4.41 (1H, dd, *J* = 8.0, 4.5 Hz), 3.70 (1H, ddd, *J* = 10.5, 8.5, 4.5 Hz), 3.65-3.57 (1H, m), 3.05 (3H, s), 2.72 (1H, dd, *J* = 10.5, 4.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 139.8, 133.3, 129.5, 128.5, 128.4, 127.4, 127.1, 69.1, 60.9, 44.5; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{18}NO_2S$ 276.1053, found 276.1067 / m/z: $[M + Na]^+$ calcd for $C_{15}H_{17}NO_2SNa$ 298.0872, found 298.0887.

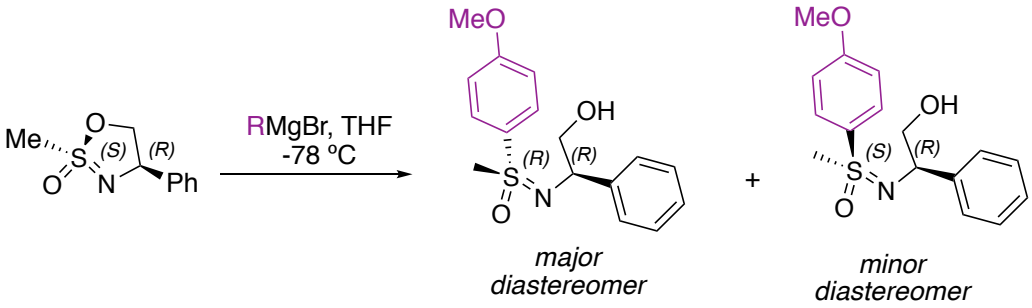
(*S*)-(((*R*)-2-Hydroxy-1-phenylethyl)imino)(4-methoxyphenyl)(methyl)-λ^6-sulfanone (13a)



Following GP4, the title compound was prepared from the cyclic sulfonimidate **8a** (237 mg, 1.20 mmol) dissolved in THF (5 mL) and 4-methoxyphenylmagnesium bromide (4.81 mL, 2.40 mmol, 0.5M). The crude mixture (dr = 3:1) was purified by flash chromatography (4:6 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (dr = 3:1, 221 mg, 60%) and an analytical sample of of the major diastereomer **13a** (reported); IR ν_{max}

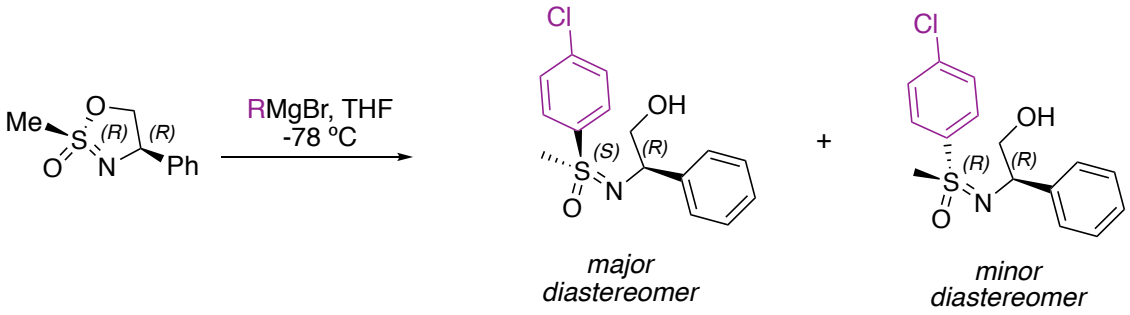
(cm^{-1}): 3382, 3024, 2927, 2841, 1592, 1577, 1493, 1452, 1408, 1355, 1255, 1223, 1124, 1087, 1023, 980, 910, 834, 803, 759, 730, 701, 631, 535; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.63 (2H, m), 7.33-7.23 (5H, m), 6.94-6.88 (2H, m), 4.14 (1H, dd, *J* = 7.5, 4.5 Hz), 3.86 (3H, s), 3.65-3.58 (2H, m), 3.20 (3H, s), 3.14 (1H, dd, *J* = 9.0, 4.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5, 142.0, 131.1, 129.7, 128.4, 127.2, 127.1, 114.7, 69.1, 61.9, 55.8, 46.3; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{20}NO_3S$ 306.1158, found 306.1167 / m/z: $[M + Na]^+$ calcd for $C_{16}H_{19}NO_3SNa$ 328.0978, found 328.0972.

(*R*)-(((*R*)-2-Hydroxy-1-phenylethyl)imino)(4-methoxyphenyl)(methyl)-λ^6-sulfanone (13b)



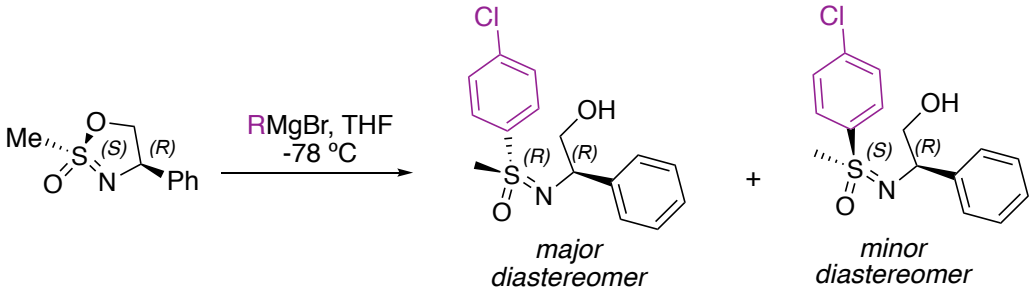
Following GP4, the title compound was prepared from the cyclic sulfonimidate **8b** (45.9 mg, 0.233 mmol) dissolved in THF (5 mL) and 4-methoxyphenylmagnesium bromide (0.931 mL, 0.465 mmol, 0.5M). The crude mixture (dr = 6:1) was purified by flash chromatography (4:6 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (dr = 6:1, 21.6 mg, 30%) and an analytical sample of of the major diastereomer **13b** (reported); IR ν_{max} (cm^{-1}): 3424, 3060, 3024, 2927, 2841, 1592, 1577, 1494, 1452, 1408, 1308, 1254, 1223, 1176, 1124, 1087, 1065, 1022, 959, 833, 802, 757, 733, 700, 638, 532, 471; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.92 (2H, m), 7.46-7.41 (2H, m), 7.37-7.31 (2H, m), 7.29-7.24 (1H, m), 7.09-7.02 (2H, m), 4.38 (1H, dd, *J* = 8.5, 4.5 Hz), 3.90 (3H, s), 3.71-3.60 (2H, m), 3.04 (3H, s), (OH not observed); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5, 142.6, 130.8, 130.6, 128.4, 127.3, 127.1, 114.7, 69.0, 60.8, 55.8, 44.7; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{20}NO_3S$ 306.1158, found 306.1179 / m/z: $[M + Na]^+$ calcd for $C_{16}H_{19}NO_3SNa$ 328.0978, found 328.0982.

(*S*)-(4-Chlorophenyl)(((*R*)-2-hydroxy-1-phenylethyl)imino)(methyl)-λ^6-sulfanone (14a)



Following GP4, the title compound was prepared from the cyclic sulfonimidate **8a** (235 mg, 1.19 mmol) dissolved in THF (5 mL) and 4-chlorophenylmagnesium bromide (2.38 mL, 2.38 mmol, 1M). The crude mixture (dr = 3:1) was purified by flash chromatography (4:6 petroleum ether/ethyl acetate) to afford the title compounds as a colourless oil (dr = 3:1, 271 mg, 74%) and an analytical sample of of the major diastereomer **14a** (reported); IR ν_{max} (cm^{-1}): 3362, 3084, 3062, 3025, 3006, 2927, 2867, 1573, 1492, 1472, 1452, 1433, 1392, 1357, 1318, 1230, 1133, 1084, 1009, 971, 829, 779, 759, 735, 701, 635, 559, 522, 463; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.63 (2H, m), 7.43-7.38 (2H, m), 7.31-7.27 (5H, m), 4.13 (1H, dd, *J* = 7.0, 5.5 Hz), 3.65-3.60 (2H, m), 3.21 (3H, s), 2.97 (1H, dd, *J* = 7.5, 6.0 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 139.8, 137.3, 130.3, 129.6, 128.3, 127.2, 127.0, 68.8, 61.7, 45.9; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{17}{}^{35}ClNO_2S$ 310.0663, found 310.0662 / m/z: $[M + Na]^+$ calcd for $C_{15}H_{16}{}^{35}ClNO_2SNa$ 332.0482, found 332.0483.

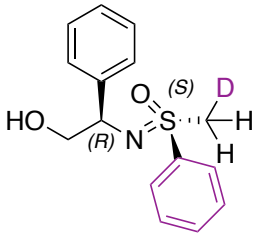
(*R*)-(4-Chlorophenyl)(((*R*)-2-hydroxy-1-phenylethyl)imino)(methyl)-λ^6-sulfanone (14b)



Following GP4, the title compound was prepared from the cyclic sulfonimidate **8b** (163 mg, 0.828 mmol) dissolved in THF (5 mL) and 4-chlorophenylmagnesium bromide (1.66 mL, 1.66 mmol, 1M). The crude mixture (dr = 8:1) was purified by flash chromatography (4:6 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (dr = 8:1, 71.3

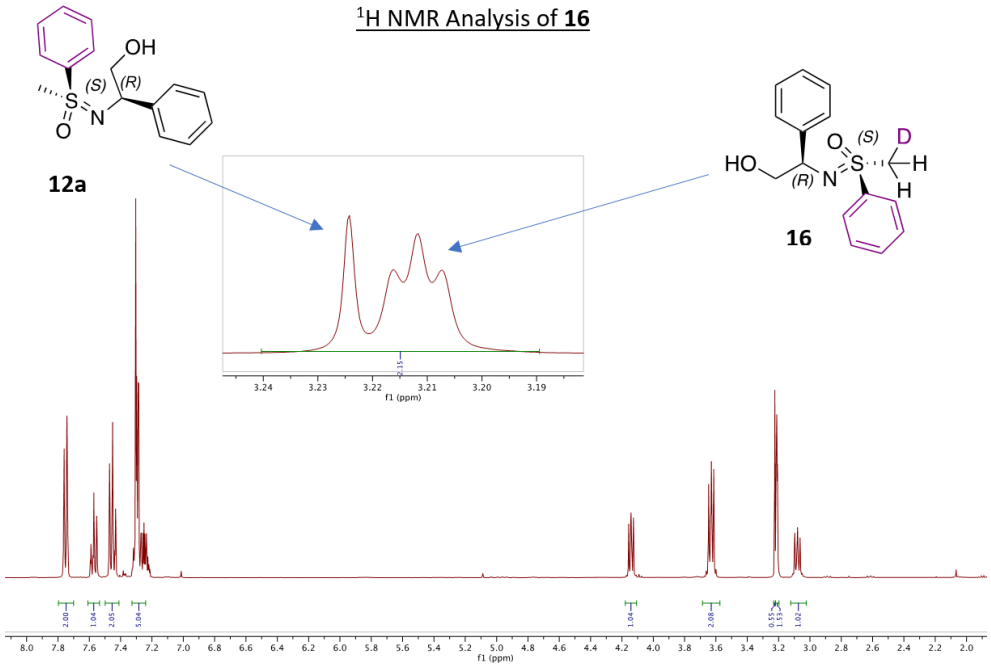
mg, 28%) and an analytical sample of of the major diastereomer **14b** (reported); IR ν_{max} (cm^{-1}): 3370, 3085, 3061, 3025, 2926, 2866, 1574, 1491, 1472, 1452, 1392, 1228, 1131, 1082, 1031, 1008, 966, 851, 828, 778, 758, 735, 700, 634, 558, 521, 461; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99-7.93 (2H, m), 7.60-7.55 (2H, m), 7.45-7.40 (2H, m), 7.38-7.33 (2H, m), 7.30-7.27 (1H, m), 4.37 (1H, dd, *J* = 8.5, 4.5 Hz), 3.74-3.65 (2H, m), 3.05 (3H, s), 2.63 (1H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.2, 140.0, 138.3, 130.0, 129.8, 128.6, 127.5, 127.1, 69.1, 61.0, 44.7; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{17}{}^{35}ClNO_2S$ 310.0663, found 310.0674 / m/z: $[M + Na]^+$ calcd for $C_{15}H_{16}{}^{35}ClNO_2SNa$ 332.0482, found 332.0483.

(*S*)-(((*R*)-2-Hydroxy-1-phenylethyl)imino)(methyl-*d*)(phenyl)-λ^6-sulfanone (16)

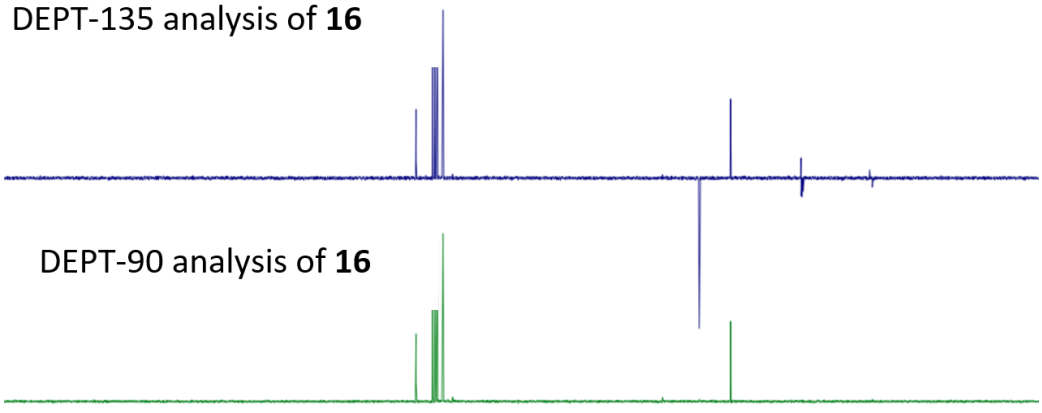


Following GP4, the title compound was prepared from the cyclic sulfonimidate **8a** (61.9 mg, 0.314 mmol) dissolved in THF (3 mL) and phenylmagnesium bromide (0.628 mL, 0.628 mmol, 1M). After completion, the reaction was quenched with CD_3OD. The crude mixture was purified by flash chromatography (4:6 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil; 3:1 ratio of **16**(deteurated):**12a**(non-deuterated); IR ν_{max} (cm^{-1}): 3392, 3060, 3025, 2925, 2865, 1492, 1476, 1446, 1392, 1357, 1222, 1128, 1084, 1068, 1028, 997, 746, 730, 701, 689, 633, 527, 516; ^{1}H NMR (400 MHz, $CDCl_3$) data match those found for **12a** except; δ 3.21 (2H, t, *J* = 2.0 Hz, CH_2D); ^{13}C NMR (101 MHz, $CDCl_3$) data match those found for **12a** except; 45.6 (CH_2D) (t, *J* = 21.0 Hz); HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{17}DNO_2S$ 277.1116, found 277.1131 / m/z: $[M + Na]^+$ calcd for $C_{15}H_{16}DNO_2SNa$ 299.0935, found 299.0931.

^{1}H NMR Analysis of **16**

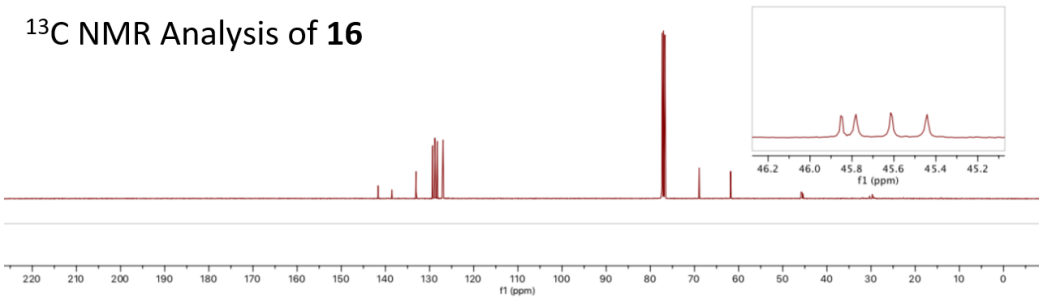


DEPT-135 analysis of **16**



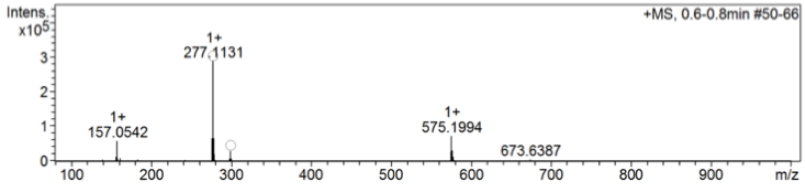
DEPT-90 analysis of **16**

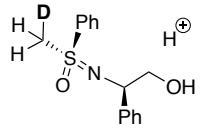
^{13}C NMR Analysis of **16**



Sample-ID	p_men_PM-R575	Lab	C13
Submitter	Priscilla Mendonca Matos	Supervisor	Robert Stockman
Analysis Name	p_men_PM-R575_582488_31_01_73608.d	Acquisition Date	3/13/2019 12:13:05 PM
Ionisation Mode	ESI Positive	Instrument	Bruker MicroTOF

+MS, 0.6-0.8min #50-66

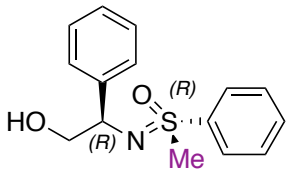




Chemical Formula: $C_{15}H_{17}DNO_2S^+$
Exact Mass: 277.1116

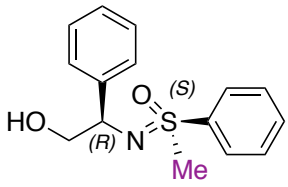
Synthesis and Characterisation of Sulfoximines derived from 7a and 7b

(*R*)-(((*R*)-2-Hydroxy-1-phenylethyl)imino)(methyl)(phenyl)-λ^6-sulfanone (12b)



Following GP4, the title compound was prepared from the cyclic sulfonimidate **7a** (146 mg, 0.563 mmol) dissolved in THF (5 mL) and methylmagnesium bromide (0.376 mL, 1.13 mmol, 3M). The crude mixture was purified by flash chromatography (4:6 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (147 mg, 95%); IR ν_{max} (cm^{-1}): 3411, 3059, 3024, 2925, 2865, 1600, 1581, 1445, 1404, 1349, 1309, 1230, 1132, 1086, 1067, 1032, 1012, 997, 854, 785, 745, 700, 690, 636, 562, 525; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-8.01 (2H, m), 7.70-7.64 (1H, m), 7.63-7.58 (2H, m), 7.48-7.43 (2H, m), 7.39-7.32 (2H, m), 7.31-7.25 (1H, m), 4.41 (1H, dd, *J* = 8.0, 4.5 Hz), 3.70 (1H, ddd, *J* = 10.5, 8.5, 4.5 Hz), 3.65-3.57 (1H, m), 3.05 (3H, s), 2.72 (1H, dd, *J* = 10.5, 4.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 139.8, 133.3, 129.5, 128.5, 128.4, 127.4, 127.1, 69.1, 60.9, 44.5; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{18}NO_2S$ 276.1053, found 276.1068 / m/z: $[M + Na]^+$ calcd for $C_{15}H_{17}NO_2SNa$ 298.0872, found 298.0872.

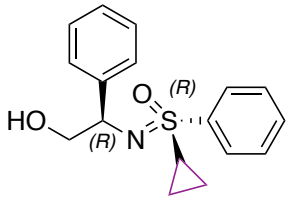
(*S*)-(((*R*)-2-Hydroxy-1-phenylethyl)imino)(methyl)(phenyl)-λ^6-sulfanone (12a)



Following GP4, the title compound was prepared from the cyclic sulfonimidate **7b** (66.5 mg, 0.256 mmol) dissolved in THF (5 mL) and methylmagnesium bromide (0.171 mL, 0.513 mmol, 3M). The crude mixture was purified by flash chromatography (4:6 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (68.6 mg, 97%); IR ν_{max} (cm^{-1}): 3400, 3060, 3025, 3008, 2927, 2865, 1492, 1476, 1446, 1403, 1356, 1310, 1228, 1129, 1085, 1068, 1030, 978, 854, 785, 744, 701, 689, 530, 515; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.73 (2H, m), 7.60-7.54 (1H, m), 7.49-7.42 (2H, m), 7.31-7.28 (4H, m), 7.27-7.22 (1H, m), 4.14 (1H, dd, *J* =

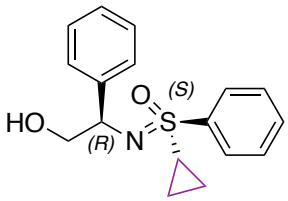
7.0, 5.5 Hz), 3.65-3.61 (2H, m), 3.22 (3H, s), 3.08 (1H, t, *J* = 7.0 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 138.7, 133.2, 129.5, 128.9, 128.4, 127.2, 127.1, 69.1, 61.9, 46.0; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{15}H_{18}NO_2S$ 276.1053, found 276.1074 / m/z: [M + Na]$^+$ calcd for $C_{15}H_{17}NO_2SNa$ 298.0872, found 298.0881.

(*R*)-Cyclopropyl(((*R*)-2-hydroxy-1-phenylethyl)imino)(phenyl)-λ^6-sulfanone (18a)



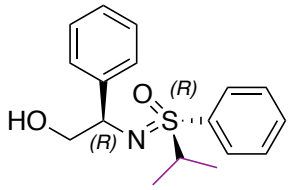
Following GP4 the title compound was prepared from the cyclic sulfonimidate **7a** (172 mg, 0.663 mmol) dissolved in THF (5 mL) and cyclopropylmagnesium bromide (1.33 mL, 1.33 mmol, 1M). The crude mixture was purified by flash chromatography (1:1 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (174 mg, 87%); IR ν_{max} (cm^{-1}): 3241, 3060, 2867, 2245, 1491, 1477, 1445, 1349, 1234, 1185, 1130, 1086, 1064, 1036, 997, 907, 884, 856, 825, 755, 726, 699, 665, 645, 635, 556, 532; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-7.94 (2H, m), 7.66-7.61 (1H, m), 7.60-7.54 (2H, m), 7.50-7.45 (2H, m), 7.38-7.32 (2H, m), 7.30-7.23 (1H, m), 4.55 (1H, dd, *J* = 8.5, 4.5 Hz), 3.68 (1H, dd, *J* = 10.5, 4.5 Hz), 3.60 (1H, dd, *J* = 10.5, 8.5 Hz), 2.92 (1H, s), 2.28-2.20 (1H, m), 1.55 (1H, dtt, *J* = 8.5, 4.0, 1.5 Hz), 1.04-0.94 (2H, m), 0.81-0.70 (1H, m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 139.8, 132.9, 129.3, 128.4, 128.3, 127.2, 127.1, 69.1, 60.5, 32.2, 6.56, 5.56; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{17}H_{20}NO_2S$ 302.1209, found 302.1211 / m/z: [M + Na]$^+$ calcd for $C_{17}H_{19}NO_2SNa$ 324.1029, found 324.1040.

(*S*)-Cyclopropyl(((*R*)-2-hydroxy-1-phenylethyl)imino)(phenyl)-λ^6-sulfanone (18b)



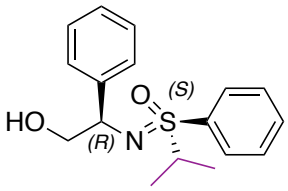
Following GP4, the title compound was prepared from the cyclic sulfonimidate **7b** (133 mg, 0.511 mmol) dissolved in THF (5 mL) and cyclopropylmagnesium bromide (1.02 mL, 1.02 mmol, 1M). The crude mixture was purified by flash chromatography (1:1 pentane/diethyl ether) to afford the title compound as a colourless oil (63.7 mg, 41%); IR ν_{max} (cm^{-1}): 3468, 3059, 3024, 2921, 2866, 1445, 1396, 1352, 1235, 1186, 1129, 1085, 1065, 1033, 885, 827, 756, 722, 700, 632, 566, 546; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73-7.67 (2H, m), 7.57-7.52 (1H, m), 7.43 (2H, dd, *J* = 8.5, 7.0 Hz), 7.35-7.27 (4H, m), 7.26-7.21 (1H, m), 4.19 (1H, dd, *J* = 8.5, 4.0 Hz), 3.67-3.52 (2H, m), 3.07 (1H, dd, *J* = 10.0, 3.5 Hz), 2.64 (1H, tt, *J* = 8.0, 5.0 Hz), 1.51 (1H, ddt, *J* = 10.0, 7.0, 5.0 Hz), 1.27 (1H, ddt, *J* = 10.0, 7.0, 5.0 Hz), 1.15 (1H, dtd, *J* = 9.0, 7.5, 5.0 Hz), 0.92 (1H, dtd, *J* = 9.0, 7.5, 5.0 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0, 139.0, 132.9, 129.3, 129.0, 128.3, 127.1, 127.0, 69.1, 61.6, 33.6, 6.94, 5.18; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{20}NO_2S$ 302.1209, found 302.1210 / m/z: $[M + Na]^+$ calcd for $C_{17}H_{19}NO_2SNa$ 324.1029, found 324.1029.

(*R*)-(((*R*)-2-Hydroxy-1-phenylethyl)imino)(isopropyl)(phenyl)-λ^6-sulfanone (19a)

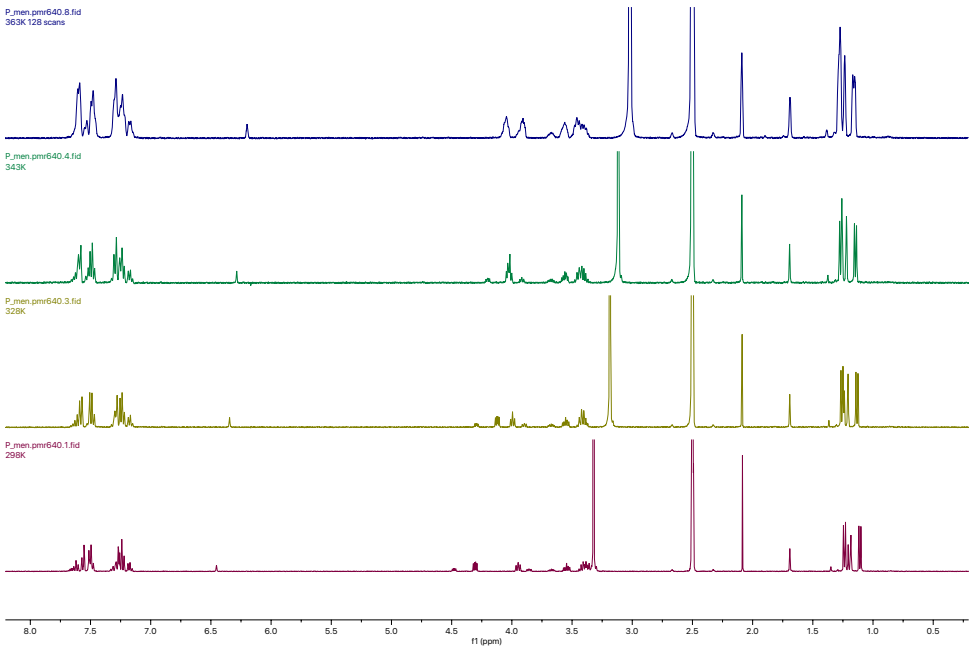


Following GP4, the title compound was prepared from the cyclic sulfonimidate **7a** (95.5 mg, 0.368 mmol) dissolved in THF (5 mL) and isopropylmagnesium chloride (0.737 mL, 0.737 mmol, 1M). The crude mixture was purified by flash chromatography (1:1 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (99.7 mg, 89%); IR ν_{max} (cm^{-1}): 3447, 3059, 2924, 2867, 1467, 1445, 1385, 1364, 1349, 1224, 1129, 1066, 815, 755, 717, 672, 564; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.88 (2H, m), 7.66-7.61 (1H, m), 7.57 (2H, ddt, *J* = 8.5, 6.5, 1.5 Hz), 7.42-7.37 (2H, m), 7.33-7.27 (2H, m), 7.25-7.19 (1H, m), 4.34 (1H, dd, *J* = 8.0, 4.5 Hz), 3.65 (1H, ddd, *J* = 10.5, 8.5, 4.5 Hz), 3.57 (1H, ddd, *J* = 10.5, 8.0, 4.0 Hz), 3.40 (1H, hept, *J* = 7.0 Hz), 2.70 (1H, dd, *J* = 9.0, 4.0 Hz), 1.36 (3H, d, *J* = 7.0 Hz), 1.13 (3H, d, *J* = 7.0 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 135.9, 133.1, 130.3, 129.2, 128.3, 127.2, 127.1, 69.3, 60.3, 55.9, 16.7, 16.3; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{22}NO_2S$ 304.1366, found 304.1379 / m/z: $[M + Na]^+$ calcd for $C_{17}H_{21}NO_2SNa$ 326.1185, found 326.1179.

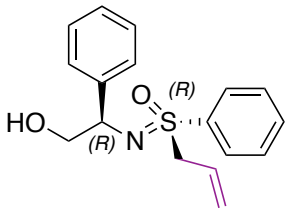
(*S*)-(((*R*)-2-Hydroxy-1-phenylethyl)imino)(isopropyl)(phenyl)-λ^6-sulfanone (19b)



Following GP4, the title compound was prepared from the cyclic sulfonimidate **7b** (97 mg, 0.374 mmol) dissolved in THF (5 mL) and isopropylmagnesium chloride (0.748 mL, 0.748 mmol, 1M). The crude mixture was purified by flash chromatography (4:6 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (104 mg, 92%); Note: This compound is observed as a mixture of rotameric isomers by ^{1}H and ^{13}C NMR spectroscopy. This was confirmed by a variable temperature NMR study in DMSO-d_6 (below). The signals from the major component are reported; IR ν_{max} (cm^{-1}): 3467, 3060, 2980, 2935, 2867, 1444, 1395, 1221, 1124, 1105, 1066, 991, 959, 934, 856, 821, 756, 717, 693, 671, 649, 630, 566, 545; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.63 (2H, m), 7.59-7.54 (1H, m), 7.47-7.41 (2H, m), 7.40-7.35 (2H, m), 7.34-7.30 (2H, m), 7.29-7.25 (1H, m), 4.19 (1H, dd, *J* = 8.5, 3.5 Hz), 3.63-3.52 (2H, m), 3.37 (1H, hept, *J* = 6.5 Hz), 3.29 (1H, dd, *J* = 10.5, 3.0 Hz), 1.41 (3H, d, *J* = 6.5 Hz), 1.33 (3H, d, *J* = 6.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.2, 135.1, 133.1, 130.5, 129.1, 128.7, 128.2, 126.9, 69.4, 61.6, 56.7, 16.6, 15.8; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{22}NO_2S$ 304.1366, found 304.1374.

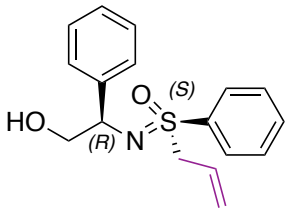


(*R*)-Allyl(((*R*)-2-hydroxy-1-phenylethyl)imino)(phenyl)-λ^6-sulfanone (21a)



Following GP4, the title compound was prepared from the cyclic sulfonimidate **7a** (135 mg, 0.519 mmol) dissolved in THF (5 mL) and allylmagnesium bromide (1.04 mL, 1.04 mmol, 1M). The crude mixture was purified by flash chromatography (1:1 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (26.1 mg, 17%); IR ν_{max} (cm^{-1}): 3438, 3060, 3026, 2920, 2863, 1445, 1421, 1392, 1349, 1240, 1130, 1067, 1032, 997, 932, 872, 854, 816, 791, 750, 689, 636, 608, 523; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-7.95 (2H, m), 7.70-7.64 (1H, m), 7.63-7.56 (2H, m), 7.49-7.43 (2H, m), 7.40-7.33 (2H, m), 7.30 (1H, t, *J* = 1.5 Hz), 5.62 (1H, ddt, *J* = 17.0, 10.0, 7.5 Hz), 5.19 (1H, dd, *J* = 10.0, 1.0 Hz), 4.95 (1H, dd, *J* = 17.0, 1.5 Hz), 4.51 (1H, dd, *J* = 8.5, 4.5 Hz), 4.02-3.83 (2H, m), 3.75-3.61 (2H, m), (OH not observed); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.3, 136.8, 133.5, 129.5, 129.2, 128.5, 127.5, 127.1, 125.6, 124.3, 69.1, 60.8, 60.4; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{20}NO_2S$ 302.1209, found 302.1216 / m/z: $[M + Na]^+$ calcd for $C_{17}H_{19}NO_2SNa$ 324.1029, found 324.1034.

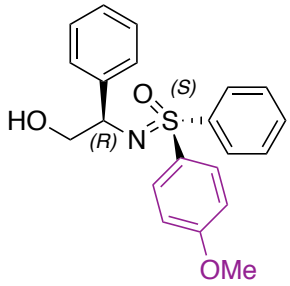
(*S*)-Allyl(((*R*)-2-hydroxy-1-phenylethyl)imino)(phenyl)-λ^6-sulfanone (21b)



Following GP4, the title compound was prepared from the cyclic sulfonimidate **7b** (189 mg, 0.729 mmol) dissolved in THF (5 mL) and allyl magnesium bromide (1.46 mL, 1.46 mmol, 1M). The crude mixture was purified by flash chromatography (4:6 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (41.3 mg, 19%); IR ν_{max} (cm^{-1}): 3498, 3083, 3061, 3027, 2920, 2867, 1638, 1615, 1601, 1582, 1492, 1476, 1445, 1421, 1394, 1355, 1227, 1124, 1066, 990, 931, 910, 819, 785, 749, 730, 688, 642, 618, 539, 510; ^{1}H NMR (400 MHz,

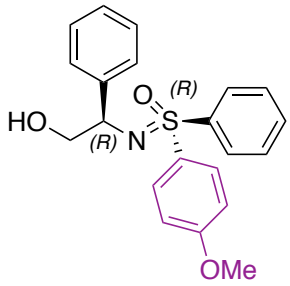
$CDCl_3$) δ 7.69-7.64 (2H, m), 7.59-7.53 (1H, m), 7.46-7.40 (2H, m), 7.38-7.25 (5H, m), 5.87 (1H, ddt, *J* = 17.5, 10.0, 7.5 Hz), 5.31 (1H, dd, *J* = 10.0, 1.0 Hz), 5.11 (1H, dd, *J* = 17.0, 1.0 Hz), 4.21 (1H, dd, *J* = 8.0, 4.0 Hz), 4.05-3.92 (2H, m), 3.68-3.56 (2H, m), 3.12 (1H, dd, *J* = 10.0, 4.0 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0, 136.5, 133.3, 130.0, 129.2, 128.4, 127.2, 127.1, 125.5, 124.4, 69.2, 62.0, 61.8; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{20}NO_2S$ 302.1209, found 302.1211 / m/z: $[M + Na]^+$ calcd for $C_{17}H_{19}NO_2SNa$] 324.1029, found 324.1033.

(*S*)-(((*R*)-2-Hydroxy-1-phenylethyl)imino)(4-methoxyphenyl)(phenyl)-λ^6-sulfanone (22a)



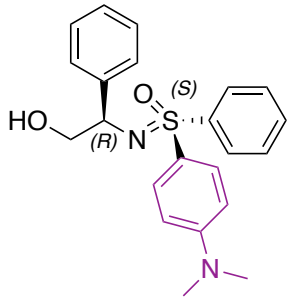
Following GP4, the title compound was prepared from the cyclic sulfonimidate **7a** (125 mg, 0.481 mmol) dissolved in THF (5 mL) and 4-methoxyphenylmagnesium bromide (1.92 mL, 0.962 mmol, 0.5M). The crude mixture was purified by flash chromatography (1:1 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (168 mg, 95%); IR ν_{max} (cm^{-1}): 3488, 3061, 2941, 2867, 1591, 1577, 1493, 1445, 1409, 1351, 1307, 1255, 1238, 1132, 1094, 1063, 1023, 909, 832, 801, 729, 701, 686, 647, 579, 548; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13-8.08 (2H, m), 7.73-7.68 (2H, m), 7.55-7.45 (5H, m), 7.40-7.34 (2H, m), 7.32-7.27 (1H, m), 6.89-6.84 (2H, m), 4.34 (1H, dd, *J* = 8.0, 4.5 Hz), 3.81 (3H, s), 3.73-3.64 (2H, m) 3.15 (1H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1, 142.3, 141.5, 132.6, 131.2, 130.7, 129.2, 128.4, 128.2, 127.2, 127.1, 114.6, 69.3, 61.9, 55.7; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{22}NO_3S$ 368.1315, found 368.1341 / m/z: $[M + Na]^+$ calcd for $C_{21}H_{21}NO_3SNa$ 390.1134, found 390.1118.

(*R*)-(((*R*)-2-Hydroxy-1-phenylethyl)imino)(4-methoxyphenyl)(phenyl)-λ^6-sulfanone (22b)



Following GP4, the title compound was prepared from the cyclic sulfonimidate **7b** (88.8 mg, 0.342 mmol) dissolved in THF (5 mL) and 4-methoxyphenylmagnesium bromide (1.37 mL, 0.685 mmol, 0.5 M). The crude mixture was purified by flash chromatography (1:1 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (123 mg, 98%); IR ν_{max} (cm^{-1}): 3488, 3061, 3026, 2941, 2868, 2840, 2245, 1591, 1493, 1444, 1411, 1393, 1352, 1308, 1255, 1238, 1131, 1108, 1063, 1024, 908, 832, 802, 753, 730, 701, 688, 666, 645, 627, 570, 551; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-8.02 (2H, m), 7.78-7.74 (2H, m), 7.44 (3H, dd, *J* = 8.0, 1.5 Hz), 7.39-7.32 (4H, m), 7.30-7.25 (1H, m), 7.00-6.95 (2H, m), 4.30 (1H, dd, *J* = 7.5, 5.0 Hz), 3.83 (3H, s), 3.72-3.66 (2H, m), 3.21 (1H, dd, *J* = 8.5, 5.0 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2, 142.2, 140.2, 132.4, 132.0, 130.6, 129.2, 128.7, 128.3, 127.1, 127.0, 114.4, 69.2, 61.9, 55.6; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{22}NO_3S$ 368.1315, found 368.1327 / m/z: $[M + Na]^+$ calcd for $C_{21}H_{21}NO_3SNa$ 390.1134, found 390.1136.

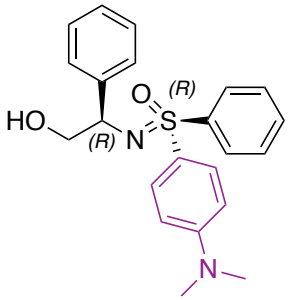
(*S*)-(4-(Dimethylamino)phenyl)(((*R*)-2-hydroxy-1-phenylethyl)imino)(phenyl)-λ^6-sulfanone (23a)



Following GP4 the title compound was prepared from the cyclic sulfonimidate **7a** (166 mg, 0.640 mmol) dissolved in THF (5 mL) and 4-(*N*,*N*-dimethyl)aniline magnesium bromide solution (1.28 mL, 1.28 mmol, 1M). The crude mixture was purified by flash chromatography

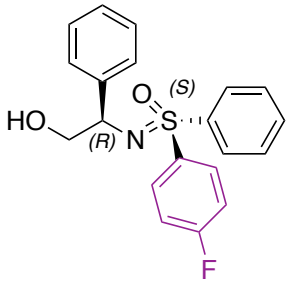
(6:4 petroleum ether/ethyl acetate) to afford the title compound as a pale yellow oil (217 mg, 89%); IR ν_{max} (cm^{-1}): 3482, 3060, 2913, 2864, 2246, 1591, 1491, 1444, 1368, 1230, 1200, 1126, 1092, 1064, 1026, 998, 943, 908, 815, 727, 687, 627, 577, 543; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (2H, d, *J* = 8.0 Hz), 7.62-7.56 (2H, m), 7.54-7.50 (2H, m), 7.49-7.45 (3H, m), 7.42-7.35 (2H, m), 7.33-7.27 (1H, m), 6.57 (2H, d, *J* = 7.5 Hz), 4.42-4.35 (1H, m), 3.76-3.60 (2H, m), 3.32 (1H, s), 2.98 (6H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.9, 142.6, 142.4, 132.0, 130.8, 129.0, 128.3, 127.8, 127.1, 127.0, 123.4, 111.3, 69.4, 61.7, 40.0; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{25}N_2O_2S$ 381.1631, found 381.1649 / m/z: $[M + Na]^+$ calcd for $C_{22}H_{24}N_2O_2SNa$ 403.1451, found 403.1454.

(*R*)-(4-(Dimethylamino)phenyl)(((*R*)-2-hydroxy-1-phenylethyl)imino)(phenyl)-λ6-sulfanone (23b)



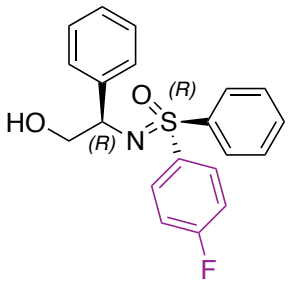
Following GP4, the title compound was prepared from the cyclic sulfonimidate **7b** (174 mg, 0.669 mmol) dissolved in THF (5 mL) and 4-(*N*,*N*-dimethyl)aniline magnesium bromide (1.34 mL, 1.34 mmol, 1M). The crude mixture was purified by flash chromatography (1:1 petroleum ether/ethyl acetate) to afford the title compound as a pale yellow oil (213 mg, 84%); IR ν_{max} (cm^{-1}): 3481, 3059, 3026, 2912, 2863, 2245, 1591, 1513, 1444, 1368, 1228, 1121, 1096, 1064, 1035, 998, 943, 908, 858, 813, 752, 728, 701, 689, 656, 626, 562, 547; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.90 (2H, m), 7.77-7.71 (2H, m), 7.48-7.44 (2H, m), 7.43-7.40 (1H, m), 7.38-7.32 (4H, m), 7.31-7.25 (1H, m), 6.72-6.67 (2H, m), 4.28 (1H, dd, *J* = 8.0, 4.0 Hz), 3.74-3.62 (2H, m), 3.28 (1H, dd, *J* = 9.5, 3.5 Hz), 3.03 (6H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0, 142.5, 141.0, 132.0, 130.3, 129.1, 128.5, 128.3, 127.1, 127.0, 125.3, 111.3, 69.4, 61.9, 40.2; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{25}N_2O_2S$ 381.1631, found 381.1652 / m/z: $[M + Na]^+$ calcd for $C_{22}H_{24}N_2O_2SNa$ 403.1451, found 403.1455.

(*S*)-(4-Fluorophenyl)(((*R*)-2-hydroxy-1-phenylethyl)imino)(phenyl)-λ^6-sulfanone (24a)



Following GP4, the title compound was prepared from the cyclic sulfonimidate **7a** (114 mg, 0.439 mmol) dissolved in THF (5 mL) and 4-fluorophenylmagnesium bromide (0.878 mL, 0.878 mmol, 1M). The crude mixture was purified by flash chromatography (1:1 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (137 mg, 88%); IR ν_{max} (cm^{-1}): 3478, 3063, 2918, 2868, 1586, 1489, 1446, 1400, 1349, 1234, 1135, 1093, 1062, 1025, 997, 909, 836, 818, 753, 730, 700, 686, 644, 578, 556, 541; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (2H, d, *J* = 7.5 Hz), 7.81-7.73 (2H, m), 7.59-7.49 (3H, m), 7.44 (2H, d, *J* = 7.5 Hz), 7.36 (2H, t, *J* = 7.5 Hz), 7.30 (1H, dd, *J* = 7.5, 5.5 Hz), 7.09-7.01 (2H, m), 4.35-4.29 (1H, m), 3.70 (2H, d, *J* = 6.5 Hz), 3.02 (1H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3 (d, *J* = 255 Hz), 142.0, 140.7, 135.7 (d, *J* = 3.0 Hz), 133.0, 131.8 (d, *J* = 9.5 Hz), 129.4, 128.5, 128.4, 127.4, 127.1, 116.6 (d, *J* = 22.5 Hz), 69.2, 61.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.5; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{19}FNO_2S$ 356.1115, found 356.1133 / m/z: $[M + Na]^+$ calcd for $C_{20}H_{18}FNO_2SNa$ 378.0934, found 378.0936.

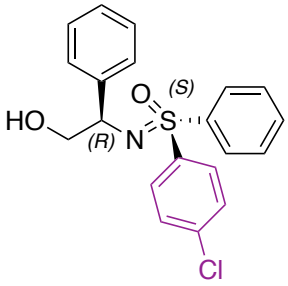
(*R*)-(4-Fluorophenyl)(((*R*)-2-hydroxy-1-phenylethyl)imino)(phenyl)-λ6-sulfanone (24b)



Following GP4, the title compound was prepared from the cyclic sulfonimidate **7b** (129 mg, 0.496 mmol) dissolved in THF (5 mL) and 4-fluorophenylmagnesium bromide (0.993 mL, 0.993 mmol, 1M). The crude mixture was purified by flash chromatography (1:1 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (157 mg, 89%); IR ν_{max}

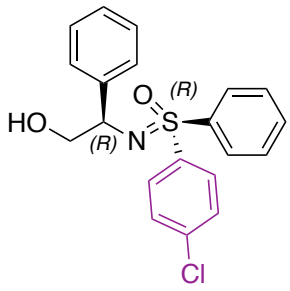
(cm^{-1}): 3483, 3063, 2925, 2869, 1587, 1489, 1446, 1401, 1351, 1306, 1289, 1234, 1137, 1094, 1064, 837, 819, 754, 732, 717, 701, 688, 666, 633, 582, 564, 542; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16-8.10 (2H, m), 7.79-7.74 (2H, m), 7.53-7.48 (1H, m), 7.45-7.40 (4H, m), 7.38-7.34 (2H, m), 7.32-7.28 (1H, m), 7.21-7.16 (2H, m), 4.34-4.28 (1H, m), 3.69 (2H, d, *J* = 7.0 Hz), 3.04 (1H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4 (d, *J* = 255 Hz), 142.0, 139.6, 136.8 (d, *J* = 3.0 Hz), 132.9, 131.3 (d, *J* = 9.5 Hz), 129.4, 129.0, 128.5, 127.3, 127.1, 116.5 (d, *J* = 23.0 Hz), 69.3, 62.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.4; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{19}FNO_2S$ 356.1115, found 356.1139 / m/z: $[M + Na]^+$ calcd for $C_{20}H_{18}FNO_2SNa$ 378.0934, found 378.0936.

(*S*)-(4-Chlorophenyl)(((*R*)-2-hydroxy-1-phenylethyl)imino)(phenyl)-λ⁶-sulfanone (25a)



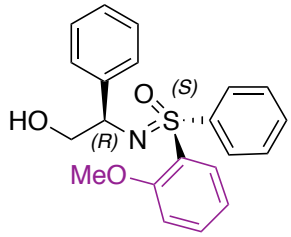
Following GP4, the title compound was prepared from the cyclic sulfonimidate **7a** (117 mg, 0.452 mmol) dissolved in THF (5 mL) and 4-chlorophenylmagnesium bromide (0.904 mL, 0.904 mmol, 1M). The crude mixture was purified by flash chromatography (1:1 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (158 mg, 94%); IR ν_{max} (cm^{-1}): 3514, 3257, 3062, 2924, 2868, 1573, 1491, 1473, 1446, 1391, 1330, 1307, 1241, 1137, 1307, 1241, 1137, 1085, 1067, 1012, 908, 825, 746, 723, 699, 686, 601, 589, 558, 539, 493, 459; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13-8.09 (2H, m), 7.71-7.67 (2H, m), 7.61-7.56 (1H, m), 7.55-7.51 (2H, m), 7.46-7.42 (2H, m), 7.39-7.33 (4H, m), 7.32-7.27 (1H, m), 4.32 (1H, dd, *J* = 7.5, 5.0 Hz), 3.70 (2H, d, *J* = 7.5 Hz), (OH not observed); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9, 140.5, 139.4, 138.4, 133.1, 130.5, 129.6, 129.4, 128.51, 128.46, 127.4, 127.1, 69.3, 61.9; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{19}{}^{35}ClNO_2S$ 372.0820, found 372.0830 / m/z: $[M + Na]^+$ calcd for $C_{20}H_{18}{}^{35}ClNO_2SNa$ 394.0639, found 394.0638.

(*R*)-(4-Chlorophenyl)(((*R*)-2-hydroxy-1-phenylethyl)imino)(phenyl)-λ^6-sulfanone (25b)



Following GP4, the title compound was prepared from the cyclic sulfonimidate **7b** (85.8 mg, 0.331 mmol) dissolved in THF (5 mL) and 4-chlorophenylmagnesium bromide (0.662 mL, 0.662 mmol, 1M). The crude mixture was purified by flash chromatography (1:1 petroleum ether/ethyl acetate) to afford the title compound as a pale yellow oil (114 mg, 92%); IR ν_{max} (cm^{-1}): 3449, 3062, 3027, 2918, 2869, 2246, 1600, 1574, 1491, 1472, 1445, 1392, 1241, 1137, 1086, 1065, 1027, 1012, 908, 819, 762, 746, 730, 687, 641, 612, 578, 554, 495; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (2H, d, *J* = 7.0 Hz), 7.77 (2H, d, *J* = 8.0 Hz), 7.53-7.46 (3H, m), 7.45-7.39 (4H, m), 7.38-7.33 (2H, m), 7.29 (1H, td, *J* = 7.0, 2.5 Hz), 4.32 (1H, t, *J* = 6.5 Hz), 3.70 (2H, d, *J* = 6.5 Hz), 3.04 (1H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0, 139.5, 139.42, 139.36, 132.9, 130.0, 129.5, 129.4, 129.0, 128.4, 127.3, 127.0, 69.2, 62.0; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{19}{}^{35}ClNO_2S$ 372.0820, found 372.0833 / m/z: $[M + Na]^+$ calcd for $C_{20}H_{18}{}^{35}ClNO_2SNa$ 394.0639, found 394.0633.

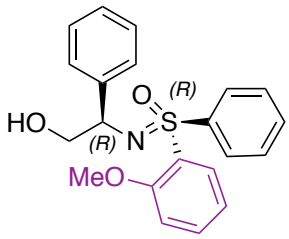
(*S*)-(((*R*)-2-Hydroxy-1-phenylethyl)imino)(2-methoxyphenyl)(phenyl)-λ^6-sulfanone (26a)



Following GP4, the title compound was prepared from the cyclic sulfonimidate **7a** (205 mg, 0.791 mmol) dissolved in THF (5 mL) and 2-methoxyphenylmagnesium bromide (1.58 mL, 1.58 mmol, 1M). The crude mixture was purified by flash chromatography (1:1 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (238 mg, 82%); IR ν_{max} (cm^{-1}): 3488, 3060, 3025, 2937, 2918, 2865, 2840, 1588, 1476, 1464, 1446, 1433, 1391, 1353,

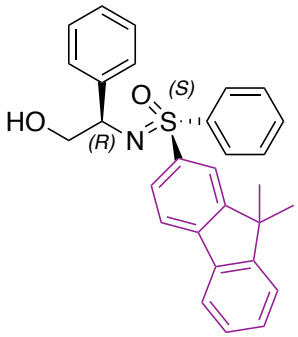
1278, 1250, 1131, 1057, 1020, 909, 858, 821, 800, 754, 735, 700, 686, 647, 591, 556, 539; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23-8.15 (3H, m), 7.59-7.53 (1H, m), 7.52-7.48 (2H, m), 7.47-7.44 (1H, m), 7.40-7.36 (2H, m), 7.33-7.28 (2H, m), 7.25-7.20 (1H, m), 7.09 (1H, td, *J* = 8.0, 1.0 Hz), 6.68 (1H, dd, *J* = 8.0, 1.0 Hz), 4.24 (1H, dd, *J* = 9.0, 4.0 Hz), 3.72-3.57 (2H, m), 3.22 (3H, s), 3.18 (1H, dd, *J* = 10.5, 3.0 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8, 142.3, 140.3, 135.1, 132.62, 132.55, 129.6, 128.5, 128.0, 127.0, 126.8, 126.0, 120.7, 111.8, 69.0, 62.2, 54.8; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{22}NO_3S$ 368.1315, found 368.1324 / m/z: $[M + Na]^+$ calcd for $C_{21}H_{21}NO_3SNa$ 390.1134, found 390.1136.

(*R*)-(((*R*)-2-Hydroxy-1-phenylethyl)imino)(2-methoxyphenyl)(phenyl)-λ6-sulfanone (26b)



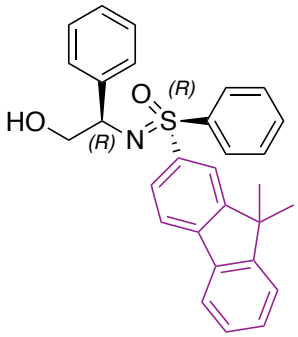
Following GP4, the title compound was prepared from the cyclic sulfonimidate **7b** (193 mg, 0.742 mmol) dissolved in THF (5 mL) and 2-methoxyphenylmagnesium bromide (1.48 mL, 1.48 mmol, 1M). The crude mixture was purified by flash chromatography (1:1 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (217 mg, 80%); IR ν_{max} (cm^{-1}): 3499, 3061, 3024, 2941, 2857, 1587, 1475, 1446, 1276, 1246, 1134, 1083, 1058, 1040, 1016, 909, 857, 802, 754, 732, 700, 688, 646, 600, 560, 541; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (1H, dd, *J* = 8.0, 2.0 Hz), 8.01-7.95 (2H, m), 7.56-7.48 (2H, m), 7.46-7.37 (4H, m), 7.32-7.27 (2H, m), 7.25-7.19 (1H, m), 7.12 (1H, ddd, *J* = 8.5, 7.5, 1.0 Hz), 6.91 (1H, dd, *J* = 8.5, 1.0 Hz), 4.23 (1H, t, *J* = 6.5 Hz), 3.70 (3H, s), 3.67-3.60 (2H, m), 3.31 (1H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 142.4, 140.1, 135.1, 132.5, 131.9, 129.3, 128.4, 128.2, 127.4, 127.00, 126.97, 120.8, 112.7, 69.1, 61.4, 55.7; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{22}NO_3S$ 368.1315, found 368.1326 / m/z: $[M + Na]^+$ calcd for $C_{21}H_{21}NO_3SNa$ 390.1134, found 390.1135.

(*S*)-(9,9-Dimethyl-9*H*-fluoren-2-yl)(((*R*)-2-hydroxy-1-phenylethyl)imino)(phenyl)-λ^6-sulfanone (27a)



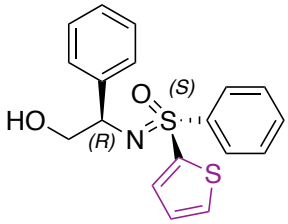
Following GP4, the title compound was prepared from the cyclic sulfonimidate **7a** (134 mg, 0.518 mmol) dissolved in THF (5 mL) and (9,9-dimethyl-9*H*-fluoren-2-yl)magnesium bromide (1.04 mL, 1.04 mmol, 1M). The crude mixture was purified by flash chromatography (7:3 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (54.8 mg, 23%) IR ν_{max} (cm^{-1}): 3490, 3061, 3027, 2961, 2923, 2866, 1600, 1471, 1445, 1405, 1361, 1305, 1289, 1237, 1136, 1097, 1062, 1026, 999, 933, 908, 840, 756, 736, 726, 701, 686, 659, 637, 618, 580, 567, 543, 479, 447, 411; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21-8.16 (2H, m), 7.82-7.67 (4H, m), 7.59-7.51 (3H, m), 7.50-7.47 (2H, m), 7.45-7.35 (5H, m), 7.33-7.28 (1H, m), 4.40 (1H, dd, *J* = 7.5, 4.5 Hz), 3.77-3.67 (2H, m), 3.13-2.94 (1H, m), 1.40 (3H, s), 1.29 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7, 154.6, 144.0, 142.4, 141.4, 137.8, 137.3, 132.7, 129.3, 129.0, 128.7, 128.5, 128.3, 127.4, 127.3, 127.1, 123.5, 122.9, 121.1, 120.6, 69.4, 61.8, 47.2, 26.9, 26.7; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{29}H_{28}NO_2S$ 454.1835, found 454.1856 / m/z: $[M + Na]^+$ calcd for $C_{29}H_{27}NO_2SNa$ 476.1655, found 476.1651.

(*R*)-(9,9-Dimethyl-9*H*-fluoren-2-yl)(((*R*)-2-hydroxy-1-phenylethyl)imino)(phenyl)-λ6-sulfanone (27b)



Following GP4, the title compound was prepared from the cyclic sulfonimidate **7b** (102 mg, 0.393 mmol) dissolved in THF (5 mL) and (9,9-dimethyl-9*H*-fluoren-2-yl)magnesium bromide (0.786 mL, 0.786 mmol, 1M). The crude mixture was purified by flash chromatography (7:3 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (56 mg, 31%); IR ν_{max} (cm^{-1}): 3497, 3061, 3027, 2960, 2923, 2865, 1601, 1585, 1444, 1406, 1359, 1346, 1305, 1237, 1136, 1098, 1065, 1032, 1004, 908, 837, 781, 756, 735, 701, 688, 615, 588, 568, 542; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (1H, d, *J* = 2.0 Hz), 8.12 (1H, dd, *J* = 8.0, 2.0 Hz), 7.87-7.81 (3H, m), 7.79-7.76 (1H, m), 7.52-7.47 (4H, m), 7.43 (1H, d, *J* = 2.0 Hz), 7.42-7.37 (5H, m), 7.34-7.29 (1H, m), 4.36 (1H, dd, *J* = 7.0, 5.0 Hz), 3.73 (2H, d, *J* = 7.0 Hz), 3.17 (1H, s), 1.52 (6H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7, 154.5, 144.1, 142.3, 140.1, 138.9, 137.3, 132.6, 129.3, 129.03, 129.00, 128.4, 128.2, 127.5, 127.3, 127.1, 122.9, 122.8, 121.2, 120.5, 69.4, 62.1, 47.4, 27.1, 26.9; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{29}H_{28}NO_2S$ 454.1835, found 454.1852 / m/z: $[M + Na]^+$ calcd for $C_{29}H_{27}NO_2SNa$ 476.1655, found 476.1654.

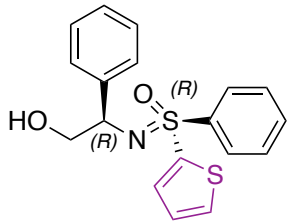
(*S*)-(((*R*)-2-Hydroxy-1-phenylethyl)imino)(phenyl)(thiophen-2-yl)-λ^6-sulfanone (28a)



Following GP4, the title compound was prepared from the cyclic sulfonimidate **7a** (68.7 mg, 0.265 mmol) dissolved in THF (3 mL) and 2-thienylmagnesium bromide (0.530 mL, 0.530 mmol, 1M). The crude mixture was purified by flash chromatography (7:3 petroleum

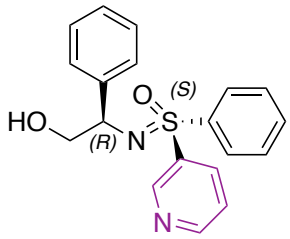
ether/ethyl acetate) to afford the title compound as a colourless oil (89.2 mg, 98%); IR ν_{max} (cm^{-1}): 3507, 3085, 3063, 2921, 2869, 1492, 1475, 1446, 1399, 1341, 1306, 1250, 1224, 1137, 1095, 1063, 1032, 1010, 855, 817, 752, 726, 701, 686, 654, 593, 566, 548, 535; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19-8.14 (2H, m), 7.60-7.52 (4H, m), 7.50-7.46 (2H, m), 7.41-7.36 (2H, m), 7.35 (1H, dd, *J* = 4.0, 1.5 Hz), 7.33-7.29 (1H, m), 6.98 (1H, dd, *J* = 5.0, 4.0 Hz), 4.55 (1H, dd, *J* = 8.5, 4.0 Hz), 3.79-3.65 (2H, m), 3.00 (1H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 141.7, 141.6, 134.3, 134.0, 133.0, 129.3, 128.5, 128.2, 128.1, 127.3, 127.1, 69.3, 62.1; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{18}NO_2S_2$ 344.0773, found 344.0782 / m/z: $[M + Na]^+$ calcd for $C_{18}H_{17}NO_2S_2Na$ 366.0593, found 366.0594.

(*R*)-(((*R*)-2-Hydroxy-1-phenylethyl)imino)(phenyl)(thiophen-2-yl)-λ6-sulfanone (28b)



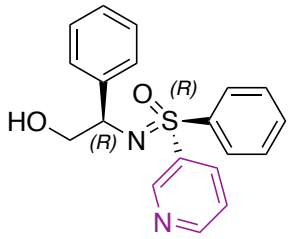
Following GP4, the title compound was prepared from the cyclic sulfonimidate **7b** (110 mg, 0.424 mmol) dissolved in THF (5 mL) and 2-thienylmagnesium bromide (0.848 mL, 0.848 mmol, 1M). The crude mixture was purified by flash chromatography (7:3 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (88.9 mg, 61%); IR ν_{max} (cm^{-1}): 3493, 3085, 3062, 3026, 2917, 2867, 1492, 1474, 1446, 1401, 1344, 1306, 1251, 1224, 1140, 1096, 1065, 1017, 929, 854, 818, 753, 727, 701, 687, 594, 566, 544; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.85 (2H, m), 7.69-7.62 (2H, m), 7.55-7.48 (1H, m), 7.46-7.39 (4H, m), 7.38-7.32 (2H, m), 7.31-7.25 (1H, m), 7.09 (1H, dd, *J* = 5.0, 4.0 Hz), 4.34 (1H, dd, *J* = 8.0, 4.5 Hz), 3.76-3.63 (2H, m), 2.88 (1H, dd, *J* = 9.0, 4.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 141.8, 140.2, 134.3, 133.8, 132.9, 129.4, 128.7, 128.4, 128.2, 127.3, 127.1, 69.2, 62.0; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{18}NO_2S_2$ 344.0773, found 344.0783 / m/z: $[M + Na]^+$ calcd for $C_{18}H_{17}NO_2S_2Na$ 366.0593, found 366.0583.

(*S*)-(((*R*)-2-Hydroxy-1-phenylethyl)imino)(phenyl)(pyridin-3-yl)-λ^6-sulfanone (29a)



Following GP4, the title compound was prepared from the cyclic sulfonimidate **7a** (101 mg, 0.388 mmol) dissolved in THF (5 mL) and 3-pyridylmagnesium bromide (0.776 mL, 0.776 mmol, 1M). The crude mixture was purified by flash chromatography (1:1 to 1:9 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (77.7 mg, 59%); IR ν_{max} (cm^{-1}): 3366, 3060, 2918, 2868, 1571, 1463, 1446, 1413, 1246, 1193, 1141, 1119, 1065, 1022, 997, 909, 856, 805, 734, 687, 620, 593, 557, 535; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (1H, d, *J* = 2.5 Hz), 8.66 (1H, dd, *J* = 5.0, 1.5 Hz), 8.16-8.09 (2H, m), 8.00 (1H, dt, *J* = 8.0, 2.0 Hz), 7.62-7.57 (1H, m), 7.54 (2H, dd, *J* = 8.5, 6.5 Hz), 7.43-7.39 (2H, m), 7.36-7.31 (2H, m), 7.29 (1H, dd, *J* = 4.5, 3.0 Hz), 7.26 (1H, d, *J* = 7.5 Hz), 4.35 (1H, t, *J* = 6.0 Hz), 3.77-3.66 (2H, m), 2.98 (1H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0, 149.9, 141.6, 140.1, 136.8, 136.7, 133.3, 129.5, 128.53, 128.52, 127.5, 127.0, 123.8, 69.1, 61.7; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{19}N_2O_2S$ 339.1162, found 339.1176 / m/z: $[M + Na]^+$ calcd for $C_{19}H_{18}N_2O_2SNa$ 361.0981, found 361.0980.

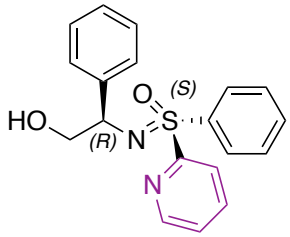
(*R*)-(((*R*)-2-Hydroxy-1-phenylethyl)imino)(phenyl)(pyridin-3-yl)-λ6-sulfanone (29b)



Following GP4, the title compound was prepared from the cyclic sulfonimidate **7b** (153 mg, 0.591 mmol) dissolved in THF (5 mL) and 3-pyridylmagnesium bromide (1.18 mL, 1.18 mmol, 1M). The crude mixture was purified by flash chromatography (1:1 to 1:9 petroleum ether/ethyl acetate) to afford the title compound as a yellow oil (58.5 mg, 29%); IR ν_{max} (cm^{-1}): 3422, 3059, 2919, 2867, 1571, 1491, 1446, 1414, 1248, 1193, 1142, 1066, 1021, 909, 856,

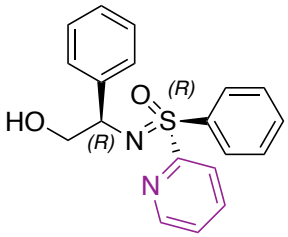
807, 738, 699, 688, 619, 594, 558, 536; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.32 (1H, dd, *J* = 2.5, 1.0 Hz), 8.77 (1H, dd, *J* = 5.0, 1.5 Hz), 8.36 (1H, dt, *J* = 8.0, 2.0 Hz), 7.79 (2H, dd, *J* = 8.5, 1.5 Hz), 7.55-7.50 (1H, m), 7.48-7.40 (5H, m), 7.38-7.33 (2H, m), 7.32-7.27 (1H, m), 4.33 (1H, t, *J* = 6.0 Hz), 3.70 (2H, d, *J* = 6.5 Hz), 2.97 (1H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.2, 149.7, 141.8, 139.0, 137.7, 136.2, 133.3, 129.6, 129.2, 128.5, 127.4, 127.0, 123.7, 69.2, 62.1; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{19}N_2O_2S$ 339.1162, found 339.1172 / m/z: $[M + Na]^+$ calcd for $C_{19}H_{18}N_2O_2SNa$ 361.0981, found 361.0975.

(*S*)-(((*R*)-2-Hydroxy-1-phenylethyl)imino)(phenyl)(pyridin-2-yl)-λ^6-sulfanone (30a)



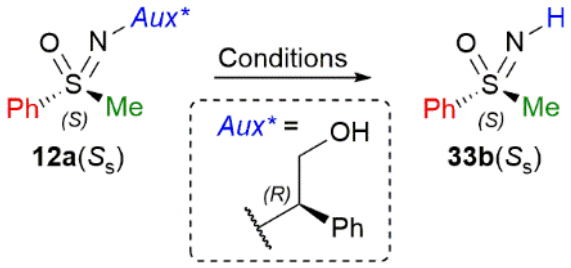
Following GP4, the title compound was prepared from the cyclic sulfonimidate **7a** (152 mg, 0.586 mmol) dissolved in THF (5 mL) and 2-pyridylmagnesium bromide (1.17 mL, 1.17 mmol, 1M). The crude mixture was purified by flash chromatography (1:1 to 1:9 petroleum ether/ethyl acetate) to afford the title compound as a yellow oil (67.3 mg, 34%); IR ν_{max} (cm^{-1}): 3424, 3059, 3027, 2922, 2856, 1732, 1600, 1575, 1562, 1491, 1475, 1447, 1423, 1240, 1143, 1115, 1064, 1040, 990, 932, 857, 818, 756, 739, 700, 686, 589, 555; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (1H, d, *J* = 5.0 Hz), 8.24-8.19 (2H, m), 8.15 (1H, d, *J* = 8.0 Hz), 7.82 (1H, td, *J* = 8.0, 4.0 Hz), 7.64-7.58 (1H, m), 7.55 (2H, td, *J* = 7.5, 2.0 Hz), 7.38 (2H, d, *J* = 8.0 Hz), 7.36-7.32 (1H, m), 7.30-7.26 (2H, m), 7.25-7.19 (1H, m), 4.38 (1H, dd, *J* = 8.5, 4.5 Hz), 3.79-3.66 (2H, m), 3.21 (1H, dd, *J* = 9.5, 4.0 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 150.4, 141.7, 138.2, 137.8, 133.3, 129.8, 129.1, 128.3, 127.2, 127.1, 126.2, 124.2, 69.2, 61.8; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{19}N_2O_2S$ 339.1162, found 339.1180 / m/z: $[M + Na]^+$ calcd for $C_{19}H_{18}N_2O_2SNa$ 361.0981, found 361.0965.

(*R*)-(((*R*)-2-Hydroxy-1-phenylethyl)imino)(phenyl)(pyridin-2-yl)-λ6-sulfanone (30b)



Following GP4, the title compound was prepared from the cyclic sulfonimidate **7b** (102 mg, 0.394 mmol) dissolved in THF (5 mL) and 2-pyridylmagnesium bromide (0.788 mL, 0.788 mmol, 1M). The crude mixture was purified by flash chromatography (1:1 to 1:9 petroleum ether/ethyl acetate) to afford the title compound as a yellow oil (89.6 mg, 67%); IR ν_{max} (cm^{-1}): 3397, 3059, 3027, 2921, 2865, 2244, 1601, 1576, 1562, 1446, 1424, 1352, 1243, 1145, 1114, 1081, 1066, 1032, 992, 909, 857, 818, 729, 700, 686, 645, 618, 595, 534; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (1H, ddd, *J* = 4.5, 2.0, 1.0 Hz), 8.35 (1H, dt, *J* = 8.0, 1.0 Hz), 8.09-8.03 (2H, m), 7.92 (1H, td, *J* = 8.0, 2.0 Hz), 7.57-7.51 (1H, m), 7.49-7.41 (5H, m), 7.34-7.27 (2H, m), 7.25-7.20 (1H, m), 4.38 (1H, dd, *J* = 8.5, 4.0 Hz), 3.81-3.75 (1H, m), 3.75-3.64 (2H, m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 150.3, 142.1, 138.5, 138.4, 133.2, 129.6, 129.2, 128.4, 127.2, 127.0, 126.7, 124.8, 69.6, 61.3; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{19}N_2O_2S$ 339.1162, found 339.1174 / m/z: $[M + Na]^+$ calcd for $C_{19}H_{18}N_2O_2SNa$ 361.0981, found 361.0988.

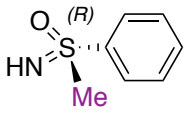
Screening of Conditions for Removal of the Chiral Auxiliary



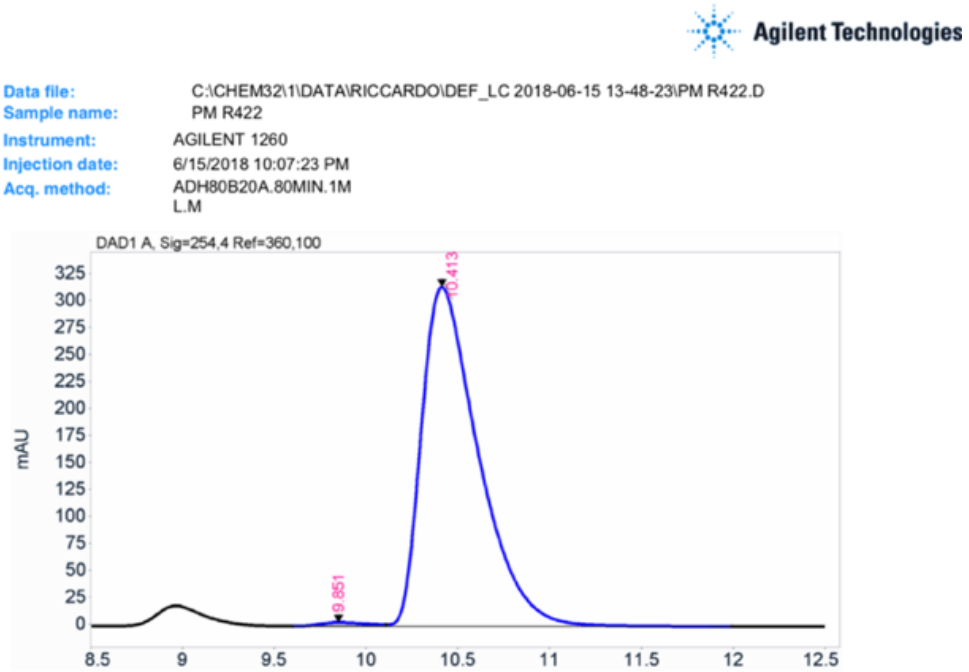
Entry	Reagents	Solvents	Temp (ºC)	Time (h)	Yield (%)
1	Anhydrous HCl (1.25 M)	MeOH	25	24	0
2	H_2 (1 bar)/ Pd/C (10 mol%)	Ethyl Acetate	25	24	0
3	H_2 (1 bar) / Pd/C (10 mol%)	Ethanol	25	72	0
4	H_2 (1 bar) /$Pd(OH)_2$	MeOH	25	24	0
5	H_2 (40 bar) /$Pd(OH)_2$	MeOH	25	20	0
7	NaOH (10 eq.), O_2 (1 atm.)	MTBE	40	16	**80**
8	NaOH (10 eq.), N_2 (1 atm.)	MTBE	40	24	trace

Synthesis of N-H Sulfoximines

(*R*)-Imino(methyl)(phenyl)-λ^6-sulfanone (33a)[11]



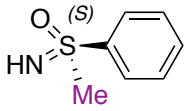
Following GP5, the title compound was prepared from the sulfoximine **12b** (147 mg, 0.534 mmol), NaOH (214 mg, 5.34 mmol) dissolved in MTBE (5 mL). The crude mixture was purified by flash chromatography (1:1 petroleum ether/ethyl acetate to 9.5:0.5 DCM/MeOH) to afford the title compound as a colourless oil (62.9 mg, 76%); $[\alpha]_D^{29}$ –23.46 (c 0.31 $CHCl_3$); HPLC: Chiracel ADH, mobile phase: 80:20 isohexane/isopropanol, flow rate: 1.0 mL/min, λ = 254 nm, retention time: major enantiomer = 10.4 min (99.1%), minor enantiomer = 9.9 min (0.9%), ee = 98%; IR ν_{max} (cm^{-1}): 3263, 2924, 1476, 1445, 1409, 1320, 1215, 1096, 1028, 1009, 992, 767, 741, 688, 522, 506; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03-7.99 (2H, m), 7.65-7.59 (1H, m), 7.58-7.52 (2H, m), 3.11 (3H, s), 2.67 (1H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 133.2, 129.4, 127.8, 46.3; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_7H_{10}NOS$ 156.0478, found 156.0479 / m/z: $[M + Na]^+$ calcd for C_7H_9NOSNa 178.0297, found 178.0296.



Signal: DAD1 A, Sig=254,4 Ref=360,100

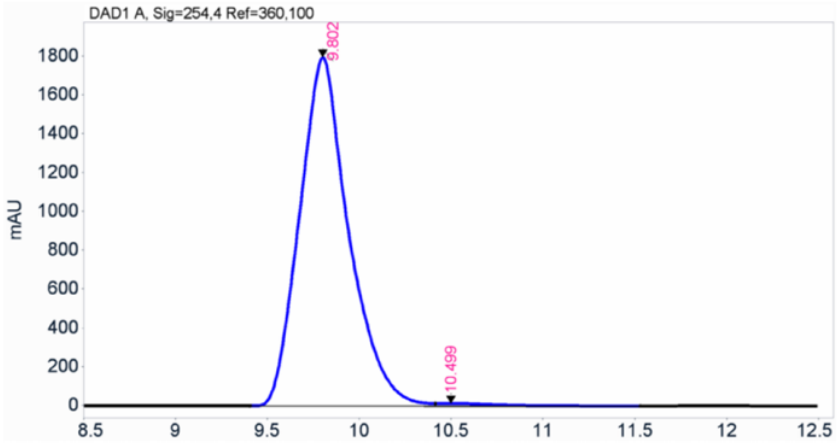
RT [min]	Type	Width [min]	Area	Height	Area%
9.851	BV	0.2740	61.271	3.4042	0.90
10.413	VB	0.3226	6750.213	314.2317	99.10

(*S*)-Imino(methyl)(phenyl)-λ^6-sulfanone (33b)[11]



Following GP5, the title compound was prepared from the sulfoximine **12a** (63.7 mg, 0.231 mmol), NaOH (92.5 mg, 2.31 mmol) dissolved in MTBE (5 mL). The crude mixture was purified by flash chromatography (1:1 petroleum ether/ethyl acetate to 9.5:0.5 DCM/MeOH) to afford the title compound as colourless oil (28.8 mg, 80%); $[\alpha]_D^{23}$ +31.39 (c 0.075 $CHCl_3$); HPLC: Chiracel ADH, mobile phase: 80:20 isohexane/isopropanol, flow rate: 1.0 mL/min, λ= 254 nm, retention time: major enantiomer = 9.8 min (99.1%), minor enantiomer = 10.5 min (0.9%), ee = 98%; All other spectral data were identical to **33a**.

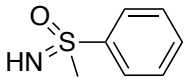
Data file: C:\CHEM32\1\DATA\RICCARDO\DEF_LC 2018-06-15 13-48-23\PM R417.D
Sample name: PM R417
Instrument: AGILENT 1260
Injection date: 6/15/2018 7:24:28 PM
Acq. method: ADH80B20A.80MIN.1M L.M



Signal: DAD1 A, Sig=254,4 Ref=360,100

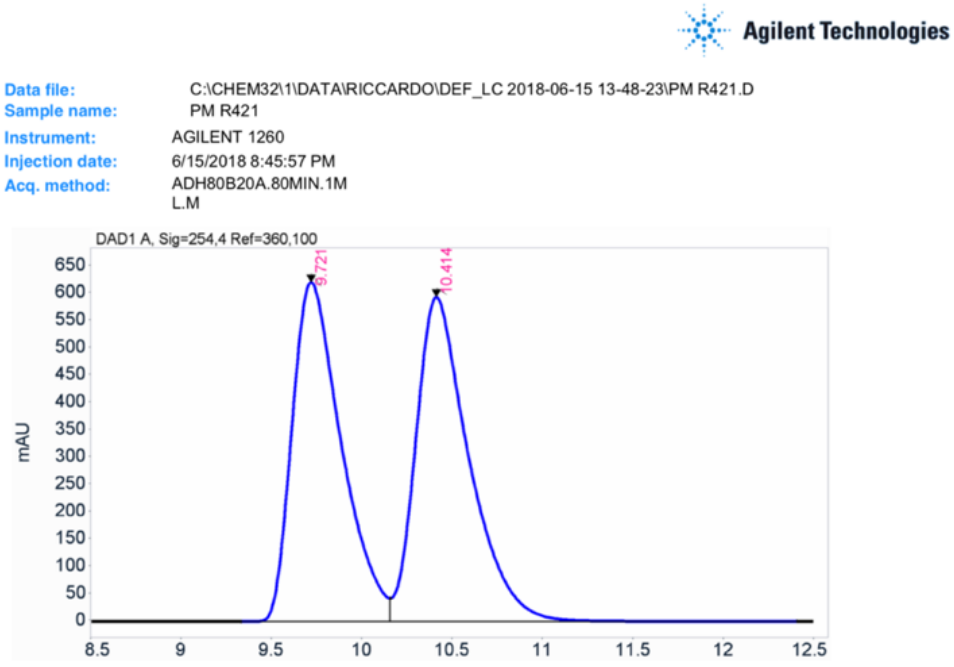
RT [min]	Type	Width [min]	Area	Height	Area%
9.802	BV	0.2727	33353.059	1795.9058	99.13
10.499	VB	0.3104	293.729	13.7960	0.87

(±)-Imino(methyl)(phenyl)-λ^6-sulfanone (*rac*-33)[12]

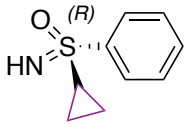


5

Following GP6, the title compound was prepared from methyl(phenyl)sulfane (42.7 mg, 0.344 mmol), (diacetoxyiodo)benzene (277 mg, 0.859 mmol) and ammonium carbamate (53.7 mg, 0.688 mmol) in methanol (0.7 mL). The crude mixture was purified by flash chromatography (1:1 petroleum ether/ethyl acetate to 9.5:0.5 DCM/MeOH) to afford the title compound as a colourless oil (49.3 mg, 92%); HPLC: Chiracel ADH, mobile phase: 80:20 isohexane/isopropanol, flow rate: 1.0 mL/min, λ = 254 nm, retention time: 9.7 and 10.4 min, (49:51%); All other spectral data were identical to **33a**.



(*R*)-Cyclopropyl(imino)(phenyl)-λ^6-sulfanone (34a)[13]



Following GP5, the title compound was prepared from the sulfoximine **18a** (174 mg, 0.577 mmol), NaOH (231 mg, 5.77 mmol), dissolved in MTBE (5 mL). The crude mixture was purified by flash chromatography (1:1 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (93 mg, 89%); $[\alpha]_D^{22}$ +6.34 (c 2.24 $CHCl_3$); HPLC: Chiracel ADH, mobile phase: 80:20 isohexane/isopropanol, flow rate: 0.8 mL/min, λ = 254 nm, retention time: major enantiomer = 16.0 min (99.2%), minor enantiomer = 13.3 min (0.8%), ee = 98%; IR ν_{max} (cm^{-1}): 3265, 3060, 3013, 1476, 1444, 1417, 1220, 1187, 1127, 1093, 1066, 1034, 976, 883, 826, 757, 716, 689, 669, 560, 524; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99-7.92 (2H, m), 7.62-7.57 (1H, m), 7.56-7.50 (2H, m), 2.69 (1H, s), 2.59-2.49 (1H, m), 1.39 (1H, ddtd, *J* = 10.0, 6.5, 5.0, 1.5 Hz), 1.18 (1H, ddtd, *J* = 10.0, 6.5, 5.0, 1.5 Hz), 1.04 (1H, ddddd, *J* = 9.5, 8.0, 6.5, 5.0, 1.5 Hz), 0.95-0.85 (1H, m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 132.9, 129.2, 128.0, 34.3, 6.09, 5.72; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_9H_{12}NOS$ 182.0634, found 182.0642 / m/z: $[M + Na]^+$ calcd for $C_9H_{11}NOSNa$ 204.0454, found 204.0455.

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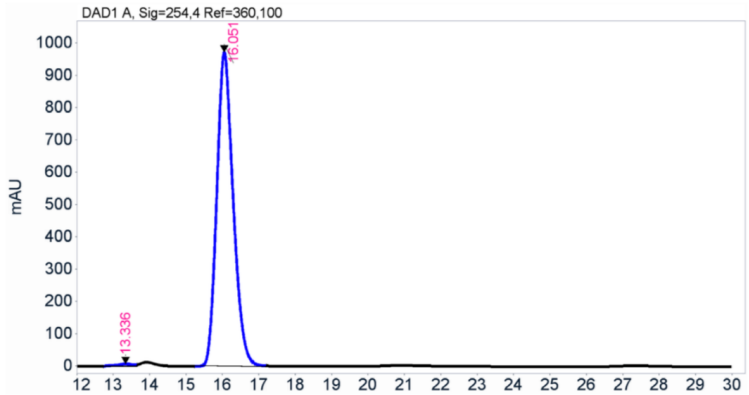
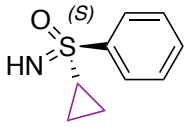
Data file: C:\CHEM32\1\DATA\HARLEY\HG 2019-01-22 10-08-53\PM-R515.D
Sample name: PM-R515
Instrument: AGILENT 1260
Injection date: 1/22/2019 5:11:32 PM
Acq. method: ADH80B20A.45MIN.0.8 ML.M



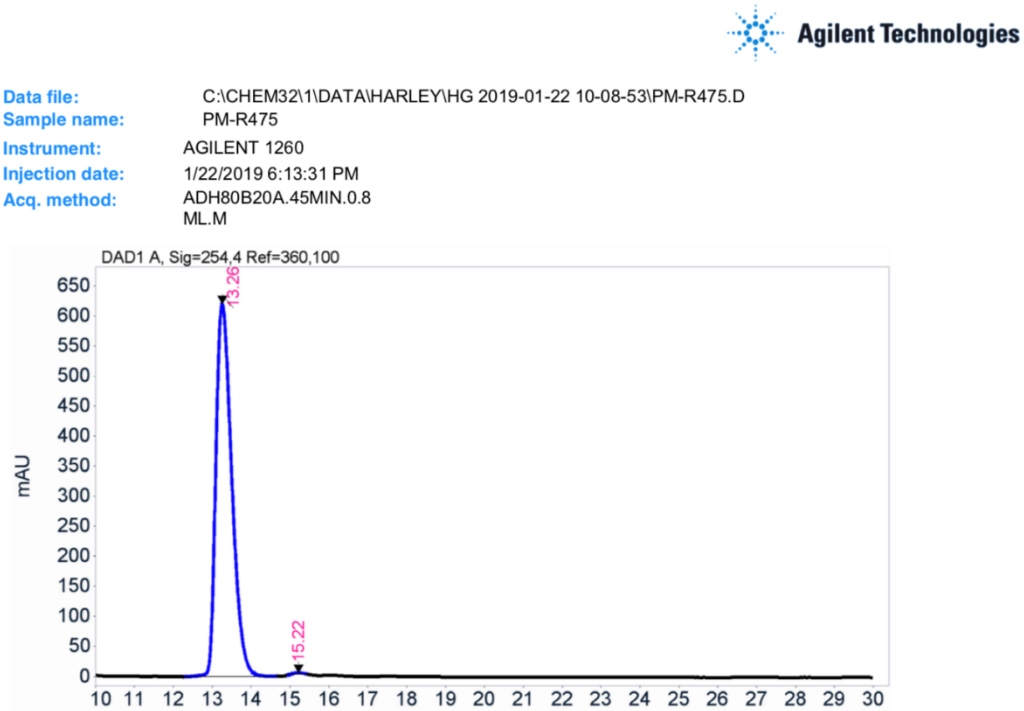
Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
13.336	MF	0.5389	246.473	7.6234	0.81
16.051	MM	0.5203	30336.021	971.7640	99.19

(*S*)-Cyclopropyl(imino)(phenyl)-λ^6-sulfanone (34b)[13]



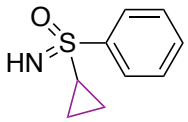
Following GP5, the title compound was prepared from the sulfoximine **18b** (63.7 mg, 0.211 mmol), NaOH (84.5 mg, 2.11 mmol) dissolved in MTBE (5 mL). The crude mixture was purified by flash chromatography (1:1 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (33.1 mg, 86%); $[\alpha]_D^{22}$ +18.15 (c 0.935 $CHCl_3$); HPLC: Chiracel ADH, mobile phase: 80:20 isohexane/isopropanol, flow rate: 0.8 mL/min, λ = 254 nm, retention time: major enantiomer = 13.3 min (99.8%), minor enantiomer = 15.2 min (0.2%), ee = 99%; All other spectral data were identical to **34a**.



Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
13.260	BB	0.4452	17594.568	619.7029	99.76
15.220	MM	0.2895	42.332	2.4370	0.24

(±)-Cyclopropyl(imino)(phenyl)-λ^6-sulfanone (*rac*-34)[14]



Following GP6, the title compound was prepared from cyclopropyl(phenyl)sulfane (500 mg, 3.33 mmol), (diacetoxyiodo)benzene (2.68 g, 8.32 mmol) and ammonium carbamate (520 mg, 6.66 mmol) in methanol (7 mL). The crude mixture was purified by flash chromatography (1:1 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (539 mg, 89%); HPLC: Chiracel ADH, mobile phase: 80:20 isohexane/isopropanol, flow rate: 0.8 mL/min, λ = 254 nm, retention time: 13.3 and 16.0 min (50:50); All other spectral data were identical to **34a**.

Agilent Technologies

Data file: C:\CHEM32\1\DATA\HARLEY\HG 2019-01-21 12-02-31\PM-R482.D
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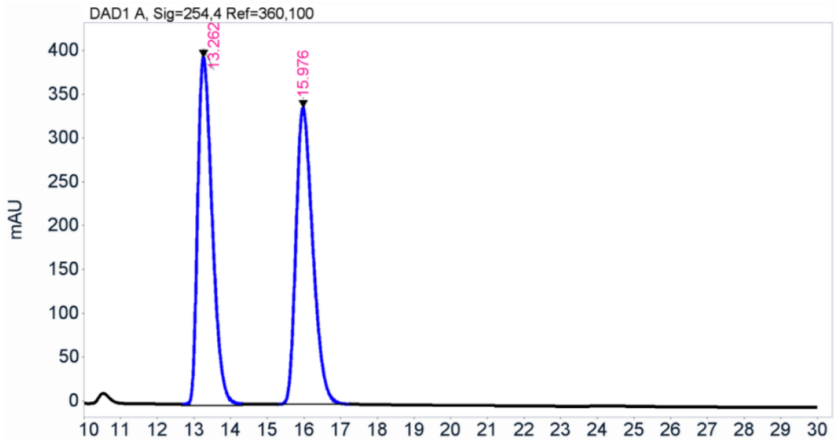
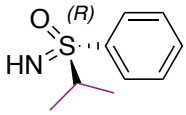
Instrument: AGILENT 1260
Injection date: 1/21/2019 2:14:19 PM
Acq. method: ADH80B20A.45MIN.0.8 ML.M



Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
13.262	MM	0.4600	10952.464	396.8429	50.40
15.976	MM	0.5316	10777.328	337.8811	49.60

(*R*)-Imino(isopropyl)(phenyl)-λ^6-sulfanone (35a)



Following GP5, the title compound was prepared from the sulfoximine **19a** (99.7 mg, 0.329 mmol), NaOH (131 mg, 3.29 mmol) dissolved in MTBE (5 mL). The crude mixture was purified by flash chromatography (4:6 petroleum ether/ethyl acetate) to afford the title compound as colourless oil (52.5 mg, 87%); $[\alpha]_D^{22}$ –30.0 (c 0.60 $CHCl_3$); HPLC: Chiracel OJH, mobile phase: 85:15 isohexane/isopropanol, flow rate: 1.0 mL/min, λ= 254 nm, retention time: major enantiomer = 10.9 min (98.4%), minor enantiomer = 9.62 min (1.6%), ee = 97%; IR ν_{max} (cm^{-1}): 3263, 3060, 2974, 2933, 1466, 1444, 1384, 1365, 1209, 1125, 1103, 1070, 1049, 970, 878, 758, 714, 691, 648, 563, 547, 524, 449; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.90 (2H, m), 7.65-7.58 (1H, m), 7.57-7.50 (2H, m), 3.24 (1H, hept, *J* = 7.0 Hz), 2.61 (1H, s), 1.31 (3H, d, *J* = 7.0 Hz), 1.27 (3H, d, *J* = 7.0 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.9, 133.1, 129.5, 129.1, 56.6, 16.5, 16.1; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_9H_{14}NOS$ 184.0791, found 184.0802 / m/z: $[M + Na]^+$ calcd for $C_9H_{13}NOSNa$ 206.0610, found 206.0605.

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Injection Date  : 18/03/2019 08:48:11 PM
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Acq. Operator   : MJP
Acq. Method     : C:\HPCHEM\2\METHODS\MJP-NP-C.M
Last changed    : 12/03/2019 11:26:42 PM by MJP
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\MJP-NP-C.M
Last changed    : 25/03/2019 14:04:27 PM by MJP
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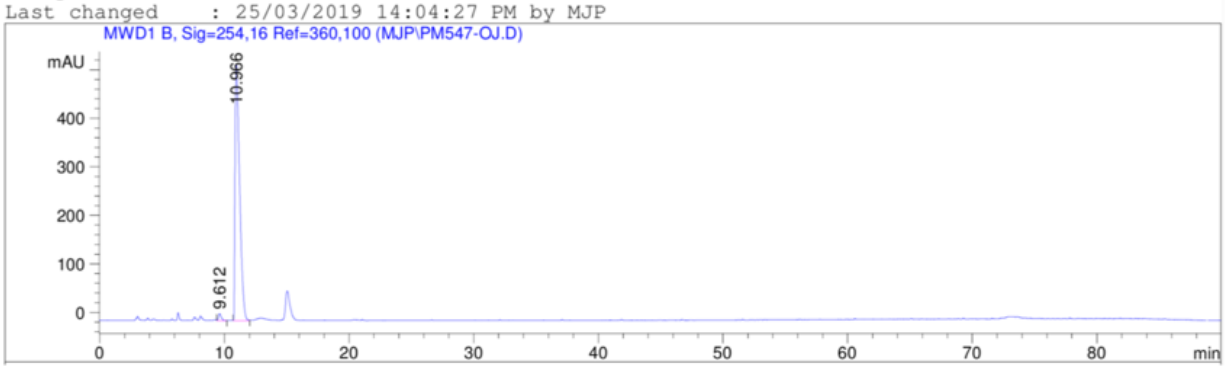
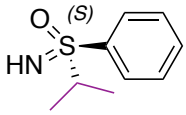


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.612	VB	0.2139	213.77594	14.34361	1.5707
2	10.966	VV	0.3841	1.33966e4	527.84338	98.4293
Totals :				1.36104e4	542.18700	

(*S*)-Imino(isopropyl)(phenyl)-λ^6-sulfanone (35b)



Following GP5, the title compound was prepared from the sulfoximine **19b** (104 mg, 0.343 mmol), NaOH (137 mg, 3.43 mmol) dissolved in MTBE (5 mL). The crude mixture was purified by flash chromatography (4:6 petroleum ether/ethyl acetate) to afford the title compound as colourless oil (56.3 mg, 90%); $[\alpha]_D^{21}$ +17.7 (c 0.36 $CHCl_3$); HPLC: Chiracel OJH, Mobile phase: 85:15 isohexane/isopropanol, flow rate: 1.0 mL/min, λ= 254 nm, retention time: major enantiomer = 9.62 min (99.4%), minor enantiomer = 11.4 min (0.6%), ee = 99%; All other spectral data were identical to **35a**.

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Injection Date  : 18/03/2019 07:16:02 PM
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Acq. Method     : C:\HPCHEM\2\METHODS\MJP-NP-C.M
Last changed    : 12/03/2019 11:26:42 PM by MJP
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\MJP-NP-C.M
Last changed    : 25/03/2019 14:04:27 PM by MJP
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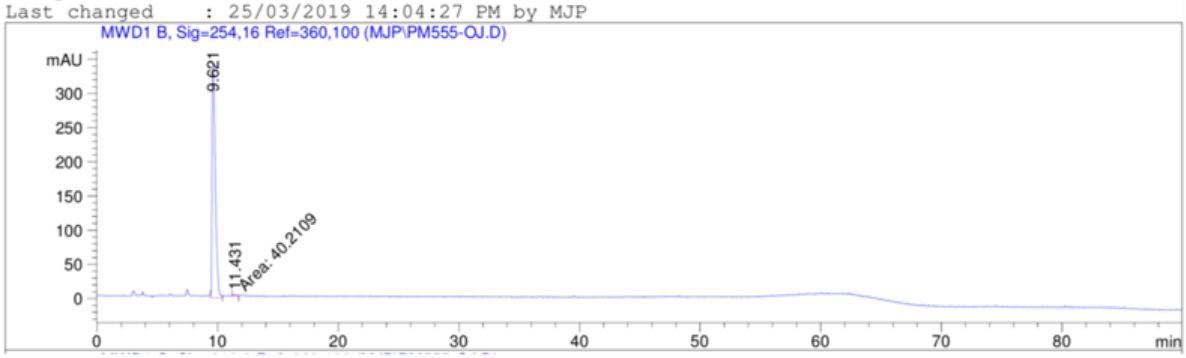
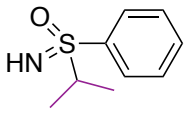


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.621	VV	0.2902	6495.23779	344.18237	99.3847
2	11.431	MM	0.2737	40.21089	2.44902	0.6153
Totals :				6535.44868	346.63139	

(±)-Imino(isopropyl)(phenyl)-λ^6-sulfanone (*rac*-35)[15]



Following GP6, the title compound was prepared from isopropyl(phenyl)sulfane (477 mg, 3.13 mmol), (diacetoxyiodo)benzene (2.52 g, 7.83 mmol) and ammonium carbamate (489 mg, 6.26 mmol) in methanol (6.5 mL). The crude mixture was purified by flash chromatography (4:6 petroelum ether/ether) to afford the title compound as a colourless oil (528 mg, 92%); HPLC: Chiracel OJH, mobile phase: 85:15 isohexane/isopropanol, flow rate: 1.0 mL/min, λ= 210 nm, retention time: 9.28 and 10.9 min (49:51); All other spectral data were identical to **35a**.

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Acq. Operator   : MJP
Acq. Method     : C:\HPCHEM\2\METHODS\MJP-NP-C.M
Last changed    : 27/03/2019 10:27:32 PM by MJP
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\MJP-NP-C.M
Last changed    : 25/03/2019 14:04:27 PM by MJP
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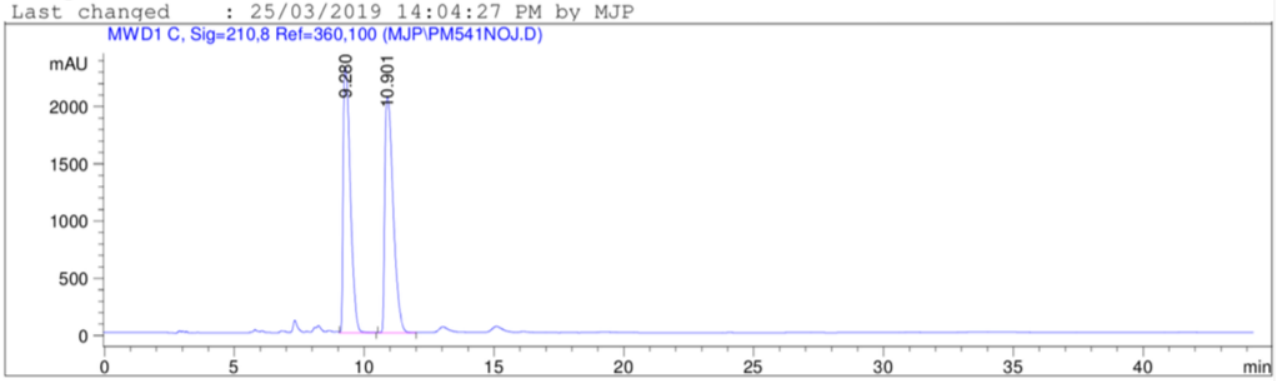
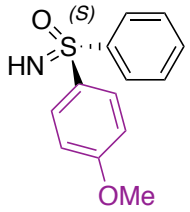
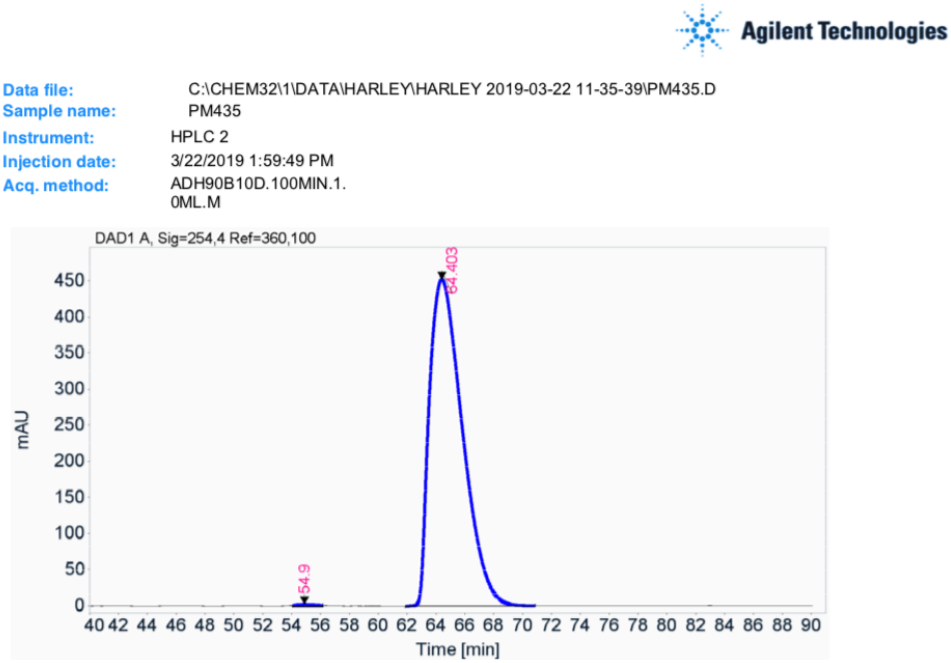


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.280	VB	0.3005	4.47488e4	2325.77490	48.8996
2	10.901	BV	0.3536	4.67628e4	2069.89478	51.1004
Totals :				9.15116e4	4395.66968	

(*S*)-Imino(4-methoxyphenyl)(phenyl)-λ^6-sulfanone (37a)



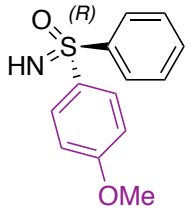
Following GP5, the title compound was prepared from the sulfoximine **22a** (168 mg, 0.457 mmol), NaOH (183 mg, 4.57 mmol), dissolved in MTBE (5 mL). The crude mixture was purified by flash chromatography (1:1 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (106 mg, 94%); $[\alpha]_D^{21}$ –11.23 (c 0.635 $CHCl_3$); HPLC: Chiracel ADH, mobile phase: 90:10 isohexane/ethanol, flow rate: 1.0 mL/min, λ = 254 nm, retention time: major enantiomer = 64.4 min (99.5%), minor enantiomer = 54.9 min (0.5%), ee = 99%; IR ν_{max} (cm^{-1}): 3272, 3062, 2839, 1592, 1577, 1493, 1444, 1410, 1308, 1256, 1225, 1174, 1127, 1094, 1022, 979, 833, 800, 756, 720, 706, 688, 665, 648, 626, 561, 542; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03-7.99 (2H, m), 7.98-7.95 (2H, m), 7.53-7.42 (3H, m), 6.96-6.91 (2H, m), 3.82 (3H, s), 2.98 (1H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1, 144.3, 134.9, 132.4, 130.3, 129.2, 127.7, 114.5, 55.7; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{14}NO_2S$ 248.0740, found 248.0749 / m/z: $[M + Na]^+$ calcd for $C_{13}H_{13}NO_2SNa$ 270.0559, found 270.0558.



Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
54.900	MM	1.7310	381.625	3.6745	0.53
64.403	BB	2.3818	71687.117	452.1283	99.47

(*R*)-Imino(4-methoxyphenyl)(phenyl)-λ^6-sulfanone (37b)



Following GP5, the title compound was prepared from the sulfoximine **22b** (123 mg, 0.335 mmol), NaOH (134 mg, 3.35 mmol), dissolved in MTBE (5 mL). The crude mixture was purified by flash chromatography (1:1 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (78.3 mg, 95%); $[\alpha]_D^{21}$ +24.27 (c 0.1165 $CHCl_3$); HPLC: Chiracel ADH, mobile phase: 90:10 isohexane/ethanol, flow rate: 1.0 mL/min, λ= 254 nm, retention time: major enantiomer = 54.7 min (99.5%), minor enantiomer = 65.5 min (0.5%), ee = 99%; All other spectral data were identical to **37a**.

Agilent Technologies

Data file:	C:\CHEM32\1\DATA\HARLEY\HARLEY 2019-03-22 11-35-39\PM423.D
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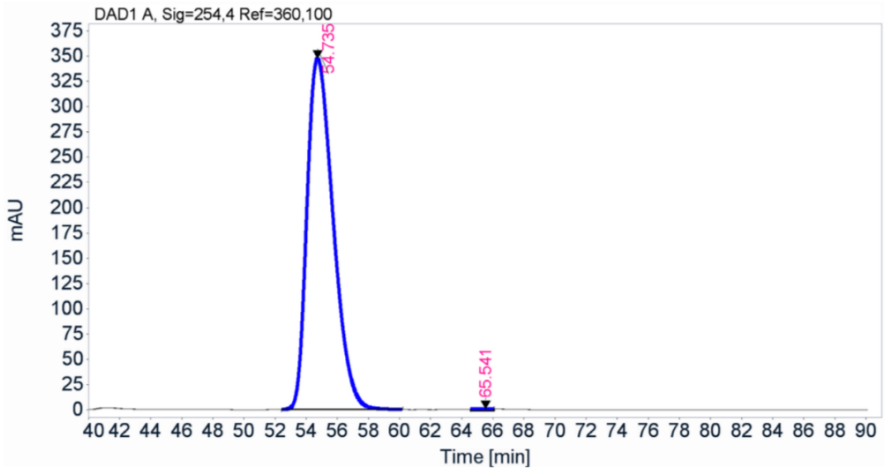
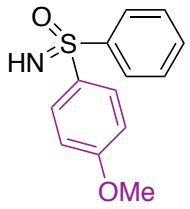
Instrument:	HPLC 2
Injection date:	3/22/2019 4:11:16 PM
Acq. method:	ADH90B10D.100MIN.1.0ML.M



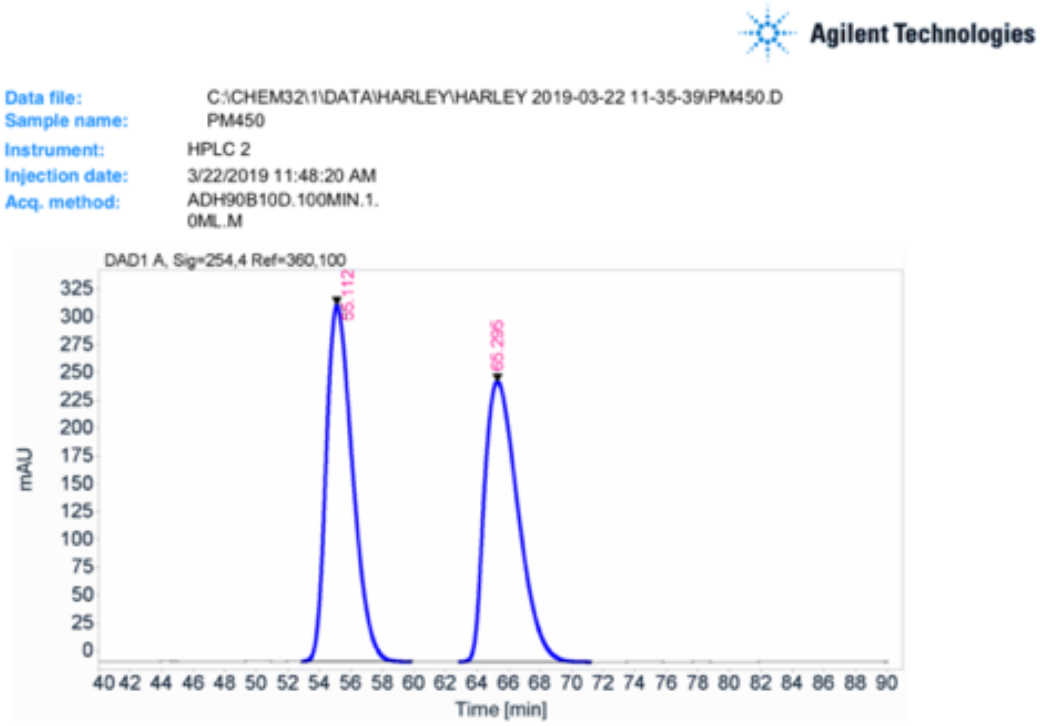
Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
54.735	BB	1.8037	40541.578	347.3546	99.51
65.541	MM	1.4192	198.234	2.3279	0.49

(±)-Imino(4-methoxyphenyl)(phenyl)-λ^6-sulfanone (*rac*-37)[16]



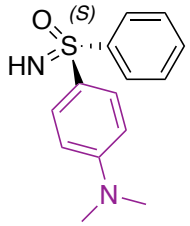
Following GP6, the title compound was prepared from (4-methoxyphenyl)(phenyl)sulfane (829 mg, 3.83 mmol), (diacetoxyiodo)benzene (3.08 g, 9.58 mmol) and ammonium carbamate (598 mg, 7.66 mmol) in methanol (8 mL). The crude mixture was purified by flash chromatography (1:1 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (903 mg, 95%); HPLC: Chiracel ADH, mobile phase: 90:10 isohexane/ethanol, flow rate: 1.0 mL/min, λ = 254 nm, retention time: 55.1 and 65.3 min (50:50); All other spectral data were identical to **37a**.



Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
55.112	BB	1.8025	36976.484	319.9135	49.92
65.295	BB	2.2698	37087.754	251.5999	50.08

(*S*)-(4-(Dimethylamino)phenyl)(imino)(phenyl)-λ^6-sulfanone (38a)



Following GP5, the title compound was prepared from the sulfoximine **23a** (217 mg, 0.571 mmol), NaOH (228 mg, 5.71 mmol) dissolved in MTBE (5 mL).The crude mixture was purified by flash chromatography (1:1 petroleum ether/ethyl acetate) to afford the title compound as a pale yellow oil (88.1 mg, 59%); $[\alpha]_D^{23}$ −14.93 (c 1.345 $CHCl_3$); HPLC: Chiracel OJH, mobile phase: gradient 0-20 min, 80:20 – 20-60 min, 60:40 isohexane/isopropanol, flow rate: 1.0 mL/min, λ = 254 nm, retention time: major enantiomer = 44.6 min (97.7%), minor enantiomer = 55.6 min (2.3%), ee = 95%; IR ν_{max} (cm^{-1}): 3332, 3252, 3061, 2912, 2817, 1589, 1552, 1514, 1476, 1444, 1369, 1222, 1121, 1092, 1068, 1002, 969, 818, 755, 688, 628, 549, 537; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-7.96 (2H, m), 7.86-7.81 (2H, m), 7.45-7.38 (3H, m), 6.66-6.61 (2H, m), 2.99 (6H, s), 2.70 (1H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.9, 145.0, 131.9, 129.8, 129.0, 128.1, 127.3, 111.2, 40.1; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{17}N_2OS$ 261.1056, found 261.1063 / m/z: $[M + Na]^+$ calcd for $C_{14}H_{16}N_2OSNa$ 283.0876, found 283.0873.

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Last changed    : 19/03/2019 15:03:43 PM by MJP
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\MJP-NP-C.M
Last changed    : 25/03/2019 14:11:05 PM by MJP
                  (modified after loading)
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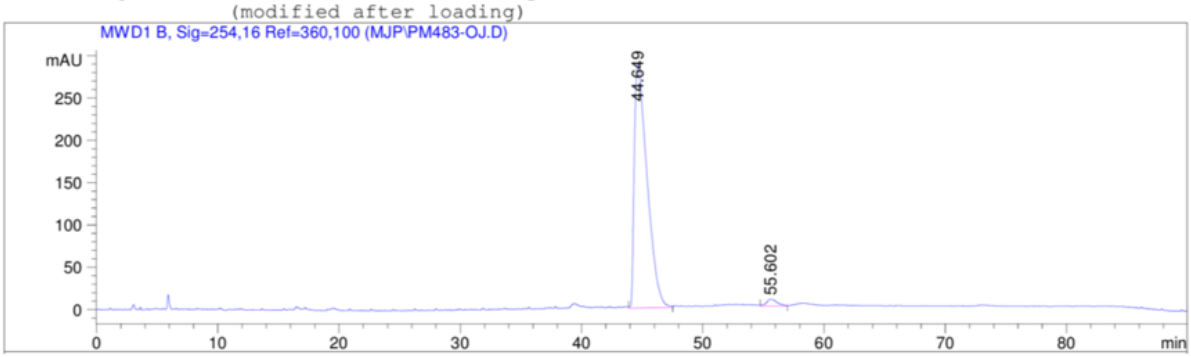
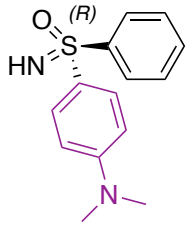


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	44.649	VV	1.0594	2.11257e4	289.48007	97.6629
2	55.602	BV	0.7755	505.53970	8.01905	2.3371
Totals :				2.16313e4	297.49912	

(*R*)-(4-(Dimethylamino)phenyl)(imino)(phenyl)-λ^6-sulfanone (38b)



Following GP5, the title compound was prepared from the sulfoximine **23b** (213 mg, 0.560 mmol), NaOH (224 mg, 5.60 mmol) dissolved in MTBE (5 mL). The crude mixture was purified by flash chromatography (1:1 petroleum ether/ethyl acetate) to afford the title compound as a pale yellow oil (73 mg, 50%); $[\alpha]_D^{23}$ +14.98 (c 1.045 $CHCl_3$); HPLC: Chiracel OJH, mobile phase: gradient 0-20 min, 80:20 – 20-60 min, 60:40 isohexane/isopropanol, flow rate: 1.0 mL/min, λ = 254 nm, retention time: major enantiomer = 55.8 min (99.1%), minor enantiomer = 47.4 min (0.9%), ee = 98%; All other spectral data were identical to **38a**.

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Sample Name     : PM479-OJ                          Location : Vial 1
Acq. Operator   : MJP
Acq. Method     : C:\HPCHEM\2\METHODS\MJP-NP-C.M
Last changed    : 19/03/2019 15:03:43 PM by MJP
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\MJP-NP-C.M
Last changed    : 25/03/2019 14:11:05 PM by MJP
                  (modified after loading)
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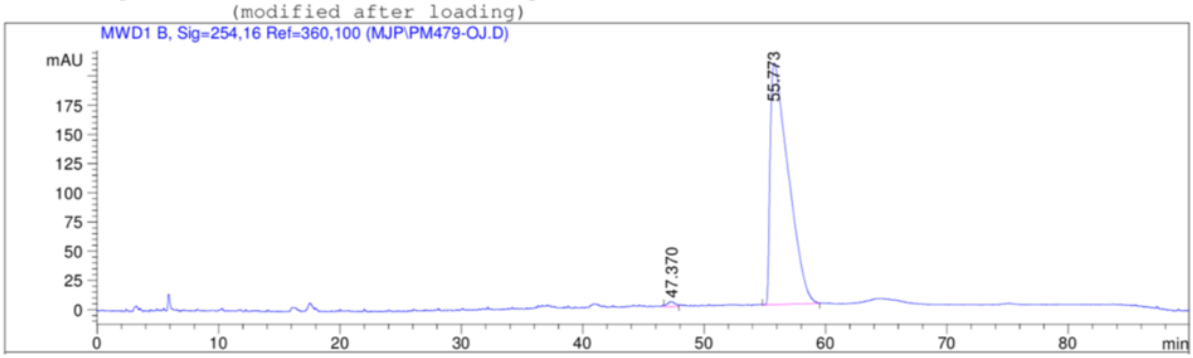
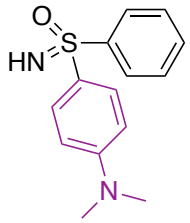


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	47.370	VV	0.5624	194.57408	4.16965	0.9035
2	55.773	VB	1.3962	2.13400e4	206.75011	99.0965
Totals :				2.15346e4	210.91975	

(±)-(4-(Dimethylamino)phenyl)(imino)(phenyl)-λ^6-sulfanone (*rac*-38)



Following GP6, the title compound was prepared from *N*,*N*-dimethyl-4-(phenylthio)aniline (396 mg, 1.73 mmol), (diacetoxyiodo)benzene (1.39 g, 4.31 mmol) and ammonium carbamate (269 mg, 3.45 mmol) in methanol (3.5 mL). The crude mixture was purified by flash chromatography (1:1 petroleum ether/ ethyl acetate) to afford the title compound as a yellow oil (271 mg, 60%); HPLC: Chiracel OJH, mobile phase: gradient 0-20 min, 80:20 – 20-60 min, 60:40 isohexane/isopropanol, flow rate: 1.0 mL/min, λ= 254 nm, retention time: 46.3 and 56.4 min (53:47); All other spectral data were identical to **38a**.

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Injection Date  : 19/03/2019 15:05:17 PM
Sample Name     : PM462aOJ                          Location : Vial 1
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Acq. Method     : C:\HPCHEM\2\METHODS\MJP-NP-C.M
Last changed    : 19/03/2019 15:03:43 PM by MJP
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\MJP-NP-C.M
Last changed    : 25/03/2019 14:11:05 PM by MJP
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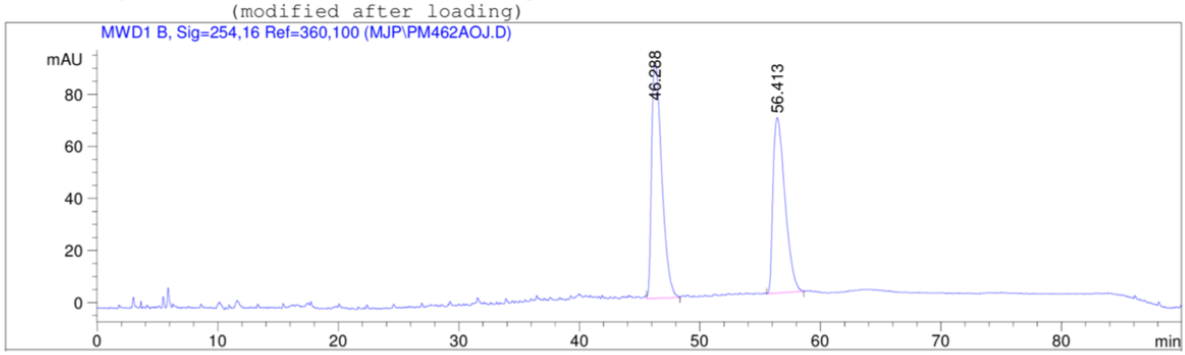
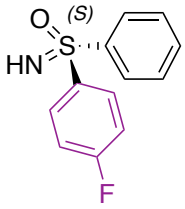
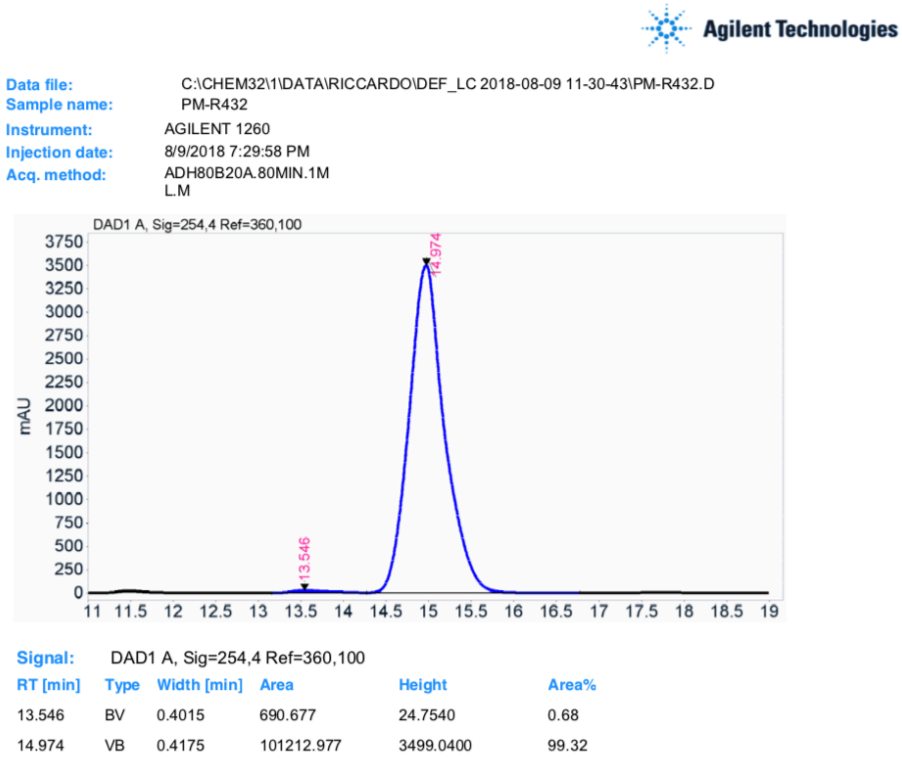


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	46.288	VV	0.8397	5333.28955	90.73553	53.4688
2	56.413	VV	0.9956	4641.29346	67.38133	46.5312
Totals :				9974.58301	158.11687	

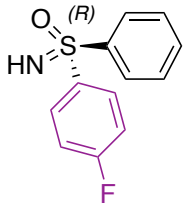
(*S*)-(4-Fluorophenyl)(imino)(phenyl)-λ^6-sulfanone (39a)



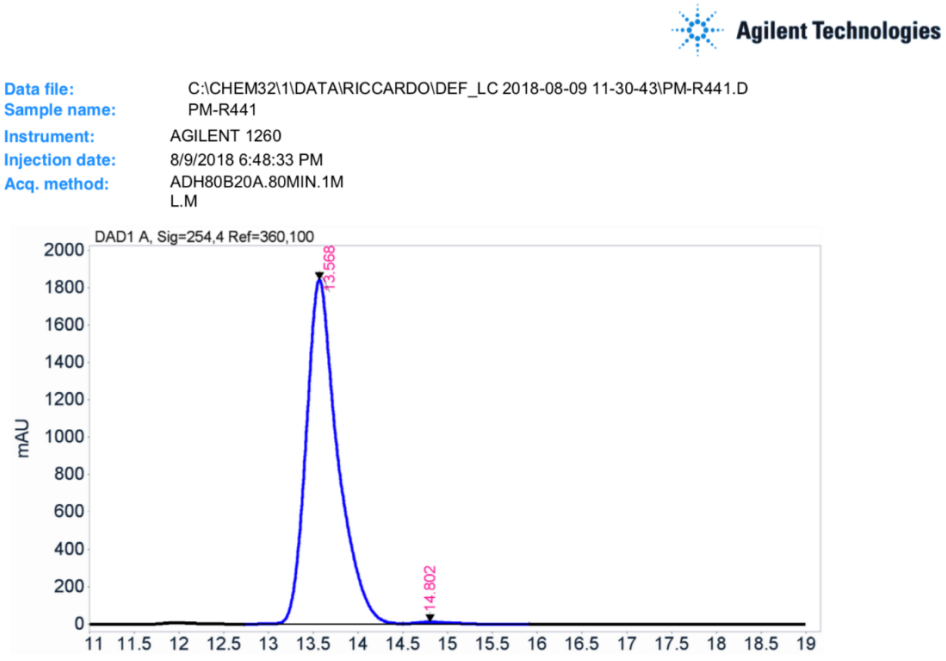
Following GP5, the title compound was prepared from the sulfoximine **24a** (137 mg, 0.387 mmol), NaOH (155 mg, 3.87 mmol) dissolved in MTBE (5 mL). The crude mixture was purified by flash chromatography (1:1 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (74.7 mg, 82%); $[\alpha]_D^{21}$ +7.36 (c 0.32 $CHCl_3$); HPLC: Chiracel ADH, mobile phase: 80:20 isohexane/isopropanol, flow rate: 1.0 mL/min, λ = 254 nm, retention time: major enantiomer = 14.9 min (99.3%) minor enantiomer = 13.5 min (0.7%), ee = 98%; IR ν_{max} (cm^{-1}): 3264, 3098, 3064, 1587, 1488, 1445, 1401, 1306, 1227, 1154, 1130, 1093, 1067, 977, 837, 817, 755, 717, 702, 687, 643, 643, 558, 534; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08-8.04 (2H, m), 8.03-8.00 (2H, m), 7.55-7.46 (3H, m), 7.18-7.11 (2H, m), 3.05 (1H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3 (d, *J* = 255 Hz), 143.5, 139.5 (d, *J* = 3.0 Hz), 132.8, 130.9 (d, *J* = 9.0 Hz), 129.4, 127.9, 116.5 (d, *J* = 23.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.8; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{12}H_{11}FNOS$ 236.0540, found 236.0540 / m/z: $[M + Na]^+$ calcd for $C_{12}H_{10}FNOSNa$ 258.0359, found 258.0356.



(*R*)-(4-Fluorophenyl)(imino)(phenyl)-λ^6-sulfanone (39b)



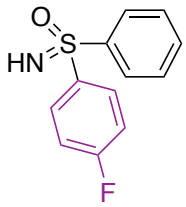
Following GP5, the title compound was prepared from the sulfoximine **24b** (157 mg, 0.442 mmol), NaOH (177 mg, 4.42 mmol), dissolved in MTBE (5 mL). The crude mixture was purified by flash chromatography (1:1 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (92.7 mg, 89%); $[\alpha]_D^{21}$ +17.81 (c 0.14 $CHCl_3$); HPLC: Chiracel ADH, mobile phase: 80:20 isohexane/isopropanol, flow rate: 1.0 mL/min, λ= 254 nm, retention time: major enantiomer = 13.5 min (99.3%), minor enantiomer = 14.8 min (0.7%), ee = 98%; All other spectral data were identical to **39a**.



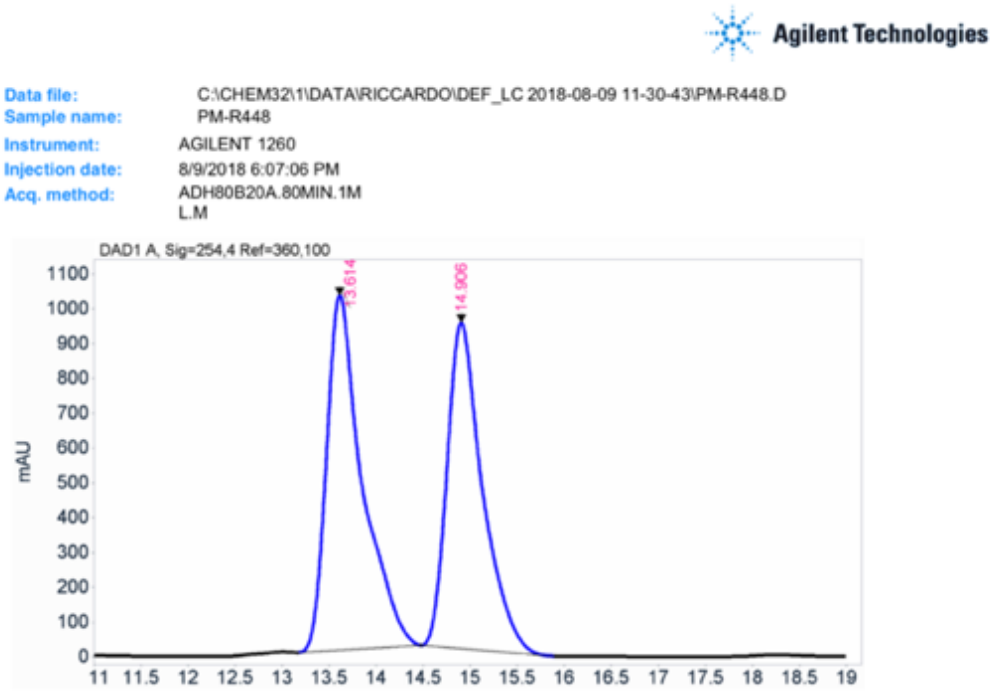
Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
13.568	BV	0.3557	45104.664	1842.0343	99.30
14.802	VB	0.3940	316.588	11.7622	0.70

(±)-(4-Fluorophenyl)(imino)(phenyl)-λ^6-sulfanone (*rac*-39)



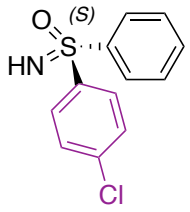
Folowing GP6, the title compound was prepared from (4-fluorophenyl)(phenyl)sulfane (579 mg, 2.83 mmol), (diacetoxyiodo)benzene (2.28 g, 7.09 mmol) and ammonium carbamate (443 mg, 5.67 mmol) in methanol (6 mL). The crude mixture was purified by flash chromatography (1:1 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (504 mg, 76%); HPLC: Chiracel ADH, mobile phase: 80:20 isohexane/isopropanol, flow rate: 1.0 mL/min, λ = 254 nm, retention time: 13.6 and 14.9 min (52:48); All other spectral data were identical to **39a**.



Signal: DAD1 A, Sig=254,4 Ref=360,100

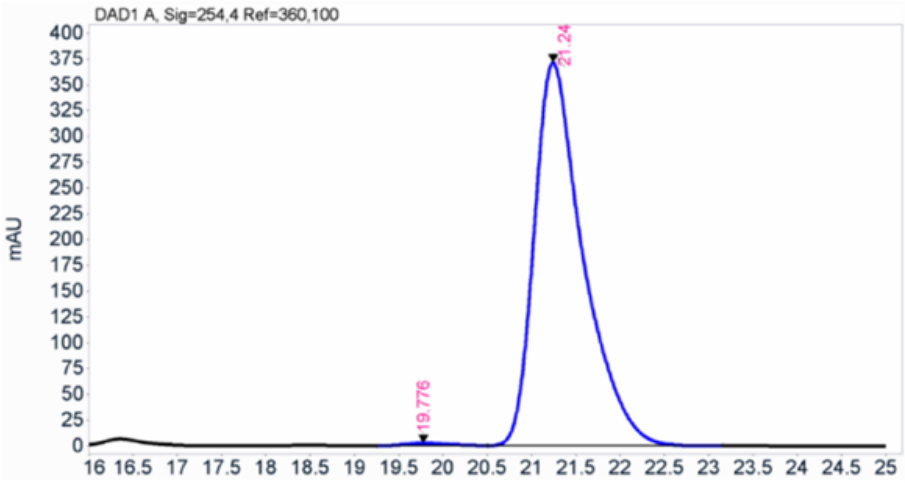
RT [min]	Type	Width [min]	Area	Height	Area%
13.614	MM T	0.4389	26842.396	1019.3428	52.32
14.906	MM T	0.4352	24457.213	936.5317	47.68

(*S*)-(4-Chlorophenyl)(imino)(phenyl)-λ^6-sulfanone (40a)



Following GP5, the title compound was prepared the sulfoximine **25a** (158 mg, 0.424 mmol), NaOH (169 mg, 4.24 mmol) dissolved in MTBE (5 mL). The crude mixture was purified by flash chromatography (1:1 petroleum ether/ethyl acetate) to afford the title compound as a pale yellow oil (98.8 mg, 93%); $[\alpha]_D^{21}$ +11.02 (c 0.49 $CHCl_3$); HPLC: Chiracel ADH, mobile phase: 85:15 isohexane/isopropanol, flow rate: 1.0 mL/min, λ = 254 nm, retention time: major enantiomer = 21.2 min (99.5%), minor enantiomer = 19.8 min (0.5%), ee = 99%; IR ν_{max} (cm^{-1}): 3270, 1576, 1473, 1456, 1445, 1392, 1232, 1130, 1093, 975, 827, 746, 712, 697, 686, 594, 547, 493, 466; ^{1}H NMR δ 8.04-7.95 (4H, m), 7.56-7.42 (5H, m), 3.07 (1H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 142.1, 139.4, 132.9, 129.6, 129.5, 129.4, 128.0; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{12}H_{11}{}^{35}ClNOS$ 252.0244, found 252.0244 / m/z: $[M + Na]^+$ calcd for $C_{12}H_{10}{}^{35}ClNOSNa$ 274.0064, found 274.0063.

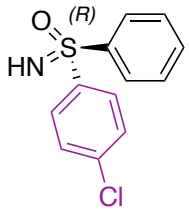
Sample name: PM-R442
Instrument: AGILENT 1260
Injection date: 8/10/2018 7:54:23 AM
Acq. method: ADH85B15A.50MIN.1.0 ML.M



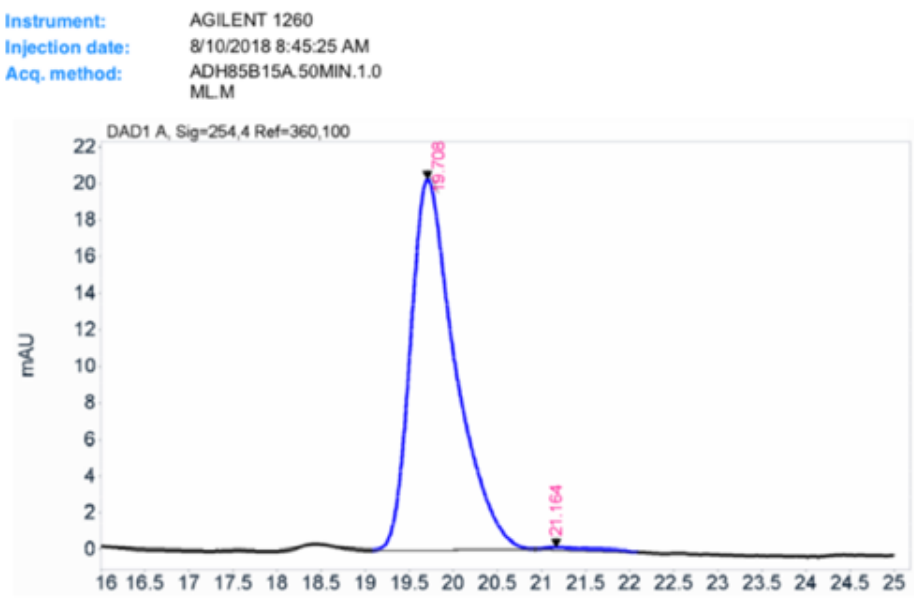
Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
19.776	BB	0.4169	75.717	2.3944	0.53
21.240	BB	0.5656	14245.813	371.3048	99.47

(*R*)-(4-Chlorophenyl)(imino)(phenyl)-λ^6-sulfanone (40b)



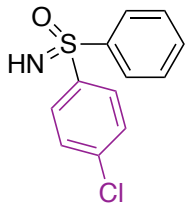
Following GP5, the title compound was prepared from the sulfoximine **25b** (114 mg, 0.307 mmol), NaOH (123 mg, 3.07 mmol) dissolved in MTBE (5 mL). The crude mixture was purified by flash chromatography (1:1 petroleum ether/ethyl acetate) to afford the title compound as a pale yellow oil (70.5 mg, 91%); $[\alpha]_D^{21}$ –11.77 (c 0.49 $CHCl_3$); HPLC: Chiracel ADH, mobile phase: 85:15 /isohexane/isopropanol, flow rate: 1.0 mL/min, λ= 254 nm, retention time: major enantiomer = 19.7 min (99.2%), minor enantiomer = 21.2 min (0.8%), ee = 98%; All other spectral data were identical to **40a**.



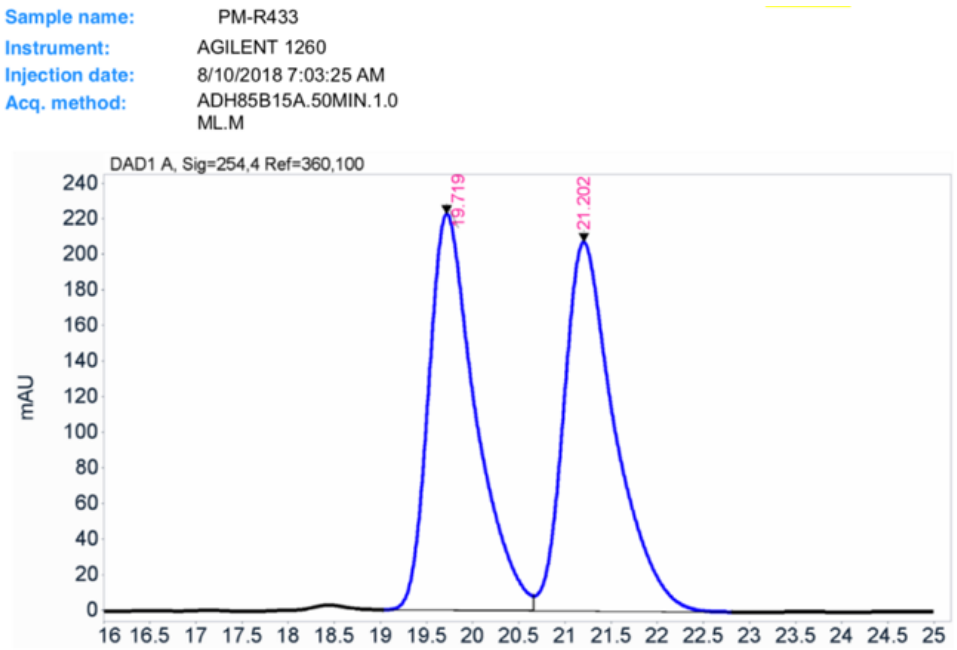
Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
19.708	BB	0.5205	715.670	20.2425	99.18
21.164	MM T	0.7231	5.923	0.1365	0.82

(±)-(4-Chlorophenyl)(imino)(phenyl)-λ^6-sulfanone (*rac*-40)[17]



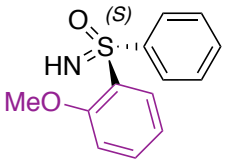
Following GP6, the title compound was prepared from (4-chlorophenyl)(phenyl)sulfane (735 mg, 3.33 mmol), (diacetoxyiodo)benzene (2.68 g, 8.33 mmol) and ammonium carbamate (520 mg, 6.66 mmol) in methanol (7 mL). The crude mixture was purified by flash chromatography (1:1 petroleum ether/ethyl acetate) to afford the title compound as yellow oil (687 mg, 82%); HPLC: Chiracel ADH, mobile phase: 85:15 isohexane/isopropanol, flow rate: 1.0 mL/min, λ = 254 nm, retention time: 19.7 and 21.2 min (50:50); All other spectral data were identical to **40a**.



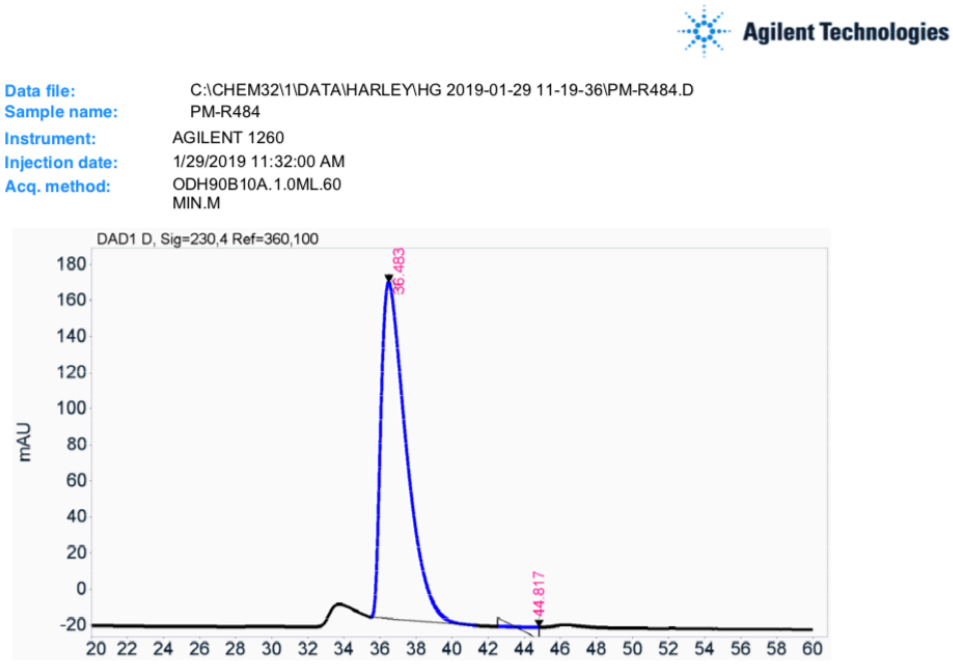
Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
19.719	BV	0.5204	7874.095	222.7290	49.69
21.202	VB	0.5664	7973.799	207.4429	50.31

(*S*)-Imino(2-methoxyphenyl)(phenyl)-λ^6-sulfanone (41a)[18]

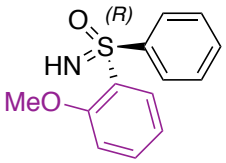


Following GP5, the title compound was prepared from the sulfoximine **26a** (238 mg, 0.648 mmol), NaOH (259 mg, 6.48 mmol) dissolved in MTBE (5 mL). The crude mixture was purified by flash chromatography (1:1 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (137 mg, 85%); $[\alpha]_D^{22}$ +22.95 (c 0.335 $CHCl_3$); HPLC: Chiracel ODH, mobile phase: 90:10 isohexane/isopropanol, flow rate: 1.0 mL/min, λ = 230 nm, retention time: major enantiomer = 36.5 min (98.7%), minor enantiomer = 44.8 min (1.3%), ee = 97%; IR ν_{max} (cm^{-1}): 3265, 3064, 2938, 2839, 1588, 1477, 1445, 1433, 1279, 1248, 1224, 1134, 1085, 1069, 1043, 1017, 974, 800, 756, 729, 712, 688, 569, 551, 530; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (1H, dd, *J* = 8.0, 1.5 Hz), 8.05-8.01 (2H, m), 7.55-7.50 (1H, m), 7.49-7.42 (3H, m), 7.04 (1H, ddd, *J* = 8.0, 7.5, 1.0 Hz), 6.88 (1H, dd, *J* = 8.0, 1.0 Hz), 3.72 (3H, s), 3.01 (1H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8, 142.6, 134.7, 132.5, 131.2, 129.4, 128.7, 128.5, 120.5, 112.7, 55.9; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{14}NO_2S$ 248.0740, found 248.0742.



Signal:	DAD1 D, Sig=230,4 Ref=360,100				
RT [min]	Type	Width [min]	Area	Height	Area%
36.483	BB	1.4446	18082.627	186.2704	98.65
44.817	MM	0.6361	247.971	6.4971	1.35

(*R*)-Imino(2-methoxyphenyl)(phenyl)-λ^6-sulfanone (41b)



Following GP5, the title compound was prepared from the sulfoximine **26b** (217 mg, 0.591 mmol), NaOH (236 mg, 5.91 mmol) dissolved in MTBE (5 mL). The crude mixture was purified by flash chromatography (1:1 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (109 mg, 75%); $[\alpha]_D^{23}$ +59.5 (c 0.10 $CHCl_3$); HPLC: Chiracel ODH, mobile phase: 90:10 isohexane/isopropanol, flow rate: 1.0 mL/min, λ= 230 nm, retention time: major enantiomer = 45.1 min (99.5%), minor enantiomer = 37.5 min (0.5%), ee = 99%; All other spectral data were identical to **41a**.

Agilent Technologies

Data file:	C:\CHEM32\1\DATA\HARLEY\HG 2019-01-29 11-19-36\PM-R506.D
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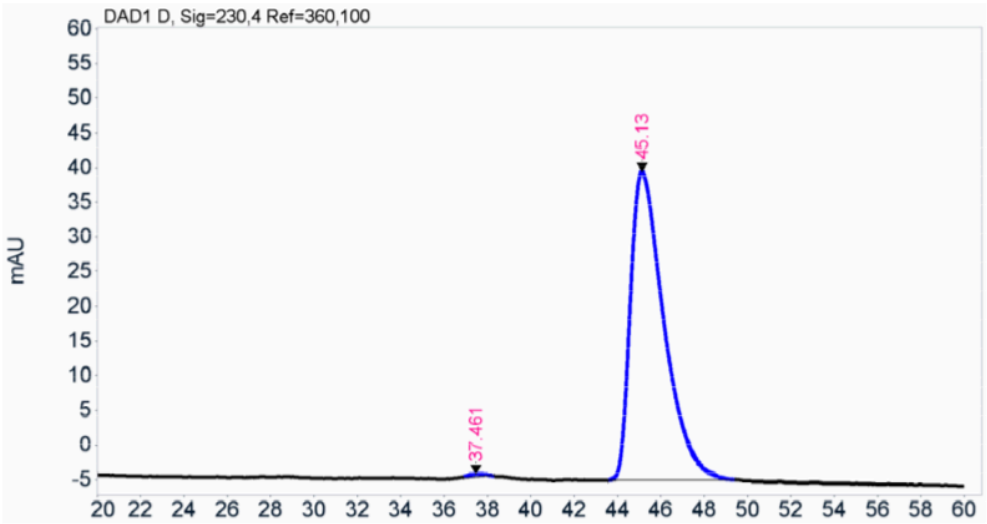
Injection date:	1/29/2019 12:43:28 PM
Acq. method:	ODH90B10A.1.0ML.60 MIN.M



Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
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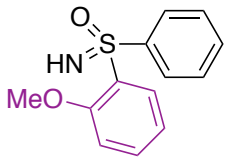
45.130	BB	1.5688	4786.744	44.5060	99.52

(±)-Imino(2-methoxyphenyl)(phenyl)-λ^6-sulfanone (*rac*-41)[17]



Following GP6, the title compound was prepared from (2-methoxyphenyl)(phenyl)sulfane (746 mg, 3.45 mmol), (diacetoxyiodo)benzene (2.78 g, 8.62 mmol) and ammonium carbamate (539 mg, 6.90 mmol) in methanol (7 mL). The crude mixture was purified by flash chromatography (1:1 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (797 mg, 93%); HPLC: Chiracel ODH, mobile phase: 90:10 isohexane/isopropanol, flow rate: 1.0 mL/min, λ = 230 nm, retention time: 36.5 and 44.8 min (49:51); All other spectral data were identical to **41a**.

Agilent Technologies

Data file:	C:\CHEM32\1\DATA\HARLEY\HG 2019-01-25 10-11-38\PM-R510-ODH.D
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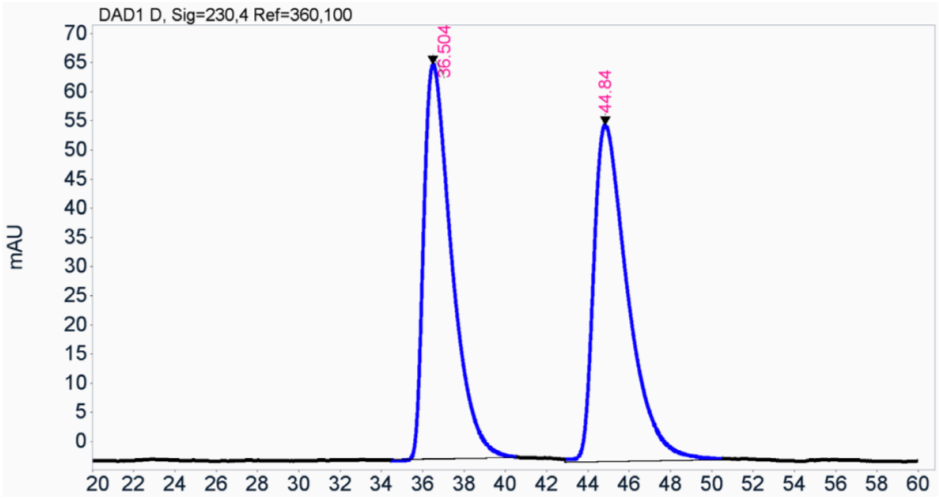
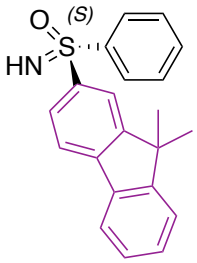
Acq. method:	ODH90B10A.1.0ML.60 MIN.M



Signal: DAD1 D, Sig=230,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
36.504	MM	1.5650	6354.926	67.6759	48.95
44.840	MM	1.9158	6628.841	57.6688	51.05

(*S*)-(9,9-Dimethyl-9*H*-fluoren-2-yl)(imino)(phenyl)-λ^6-sulfanone (42a)



Following GP5, the title compound was prepared from the sulfoximine **27a** (54.8 mg, 0.121 mmol), NaOH (48.3 mg, 1.21 mmol) dissolved in MTBE (5 mL). The crude mixture was purified by flash chromatography (7:3 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (26.3 mg, 65%); $[\alpha]_D^{22}$ +3.89 (c 0.285 $CHCl_3$); HPLC: Chiracel OJH, mobile phase: 90:10 isohexane/isopropanol, flow rate: 1.0 mL/min, λ = 254 nm, retention time: major enantiomer = 18.3 min (98.4%), minor enantiomer = 22.2 min (1.6%), ee = 97%; IR ν_{max} (cm^{-1}): 3312, 3270, 3060, 2960, 2940, 1600, 1470, 1444, 1407, 1227, 1157, 1127, 1097, 1067, 1001, 908, 834, 782, 757, 736, 710, 687, 660, 616, 575, 560, 520; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14-8.12 (1H, m), 8.10-8.06 (2H, m), 8.00 (1H, dd, *J* = 8.0, 2.0 Hz), 7.80-7.76 (1H, m), 7.75-7.72 (1H, m), 7.53-7.43 (4H, m), 7.41-7.33 (2H, m), 3.07 (1H, s), 1.49 (6H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7, 154.6, 144.0, 143.9, 141.7, 137.4, 132.6, 129.3, 129.0, 127.9, 127.7, 127.5, 123.0, 122.4, 121.1, 120.5, 47.4, 27.02, 26.98; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{20}NOS$ 334.1260, found 334.1279 / m/z: $[M + Na]^+$ calcd for $C_{21}H_{19}NOSNa$ 356.1080, found 356.1077.

```
Injection Date  : 18/03/2019 13:14:06 PM
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Acq. Operator   : MJP
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Last changed    : 18/03/2019 12:03:47 PM by MJP
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\MJP-NP-C.M
Last changed    : 25/03/2019 14:11:05 PM by MJP
                  (modified after loading)
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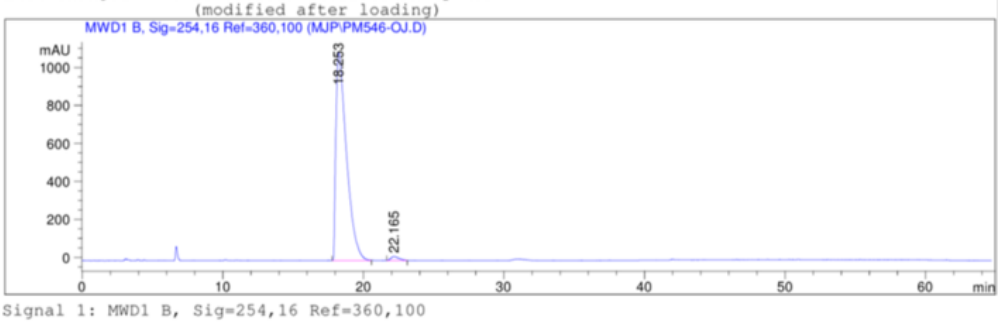
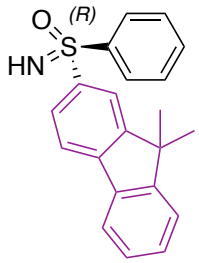



```
Signal 1: MWD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  18.253 VV    0.7948 5.73523e4  1095.51123  98.4365
   2  22.165 VV    0.6030  910.92108   20.96251   1.5635

Totals :                 5.82632e4  1116.47374
```

(*R*)-(9,9-Dimethyl-9*H*-fluoren-2-yl)(imino)(phenyl)-λ^6-sulfanone (42b)



Following GP5, the title compound was prepared from the sulfoximine **27b** (40.4 mg, 0.0891 mmol), NaOH (35.6 mg, 0.891 mmol) dissolved in MTBE (5 mL). The crude mixture was purified by flash chromatography (7:3 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (21.5 mg, 72%); $[\alpha]_D^{22}$ +26.6 (c 0.196 $CHCl_3$); HPLC: Chiracel OJH, mobile phase: 90:10 isohexane/isopropanol, flow rate: 1.0 mL/min, λ= 254 nm, retention time: major enantiomer = 22.1 min (98.2%), minor enantiomer = 19.7 min (1.8%), ee = 96%; All other spectral data were identical to **42a**.

```
Injection Date  : 18/03/2019 15:05:16 PM
Sample Name     : PM545-OJ                          Location : Vial 1
Acq. Operator   : MJP
Acq. Method     : C:\HPCHEM\2\METHODS\MJP-NP-C.M
Last changed    : 18/03/2019 12:03:47 PM by MJP
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Analysis Method : C:\HPCHEM\2\METHODS\MJP-NP-C.M
Last changed    : 25/03/2019 14:11:05 PM by MJP
                  (modified after loading)
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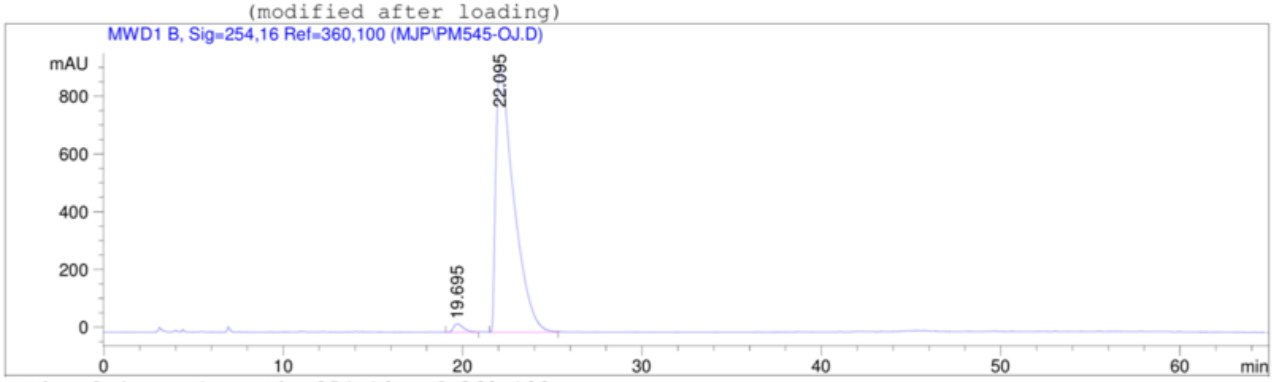
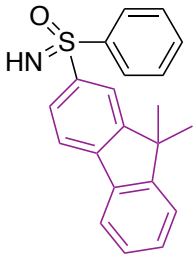



```
Signal 1: MWD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  19.695 VB    0.5942 1162.95508   29.22615   1.7901
   2  22.095 VV    0.9747 6.38037e4   920.41510  98.2099

Totals :                  6.49666e4   949.64125
```

(±)-(9,9-Dimethyl-9*H*-fluoren-2-yl)(imino)(phenyl)-λ^6-sulfanone (*rac*-42)



A mixture of the enantiomers **42a** and **42b** was used as a racemic sample for HPLC analysis. HPLC: Chiracel OJH, mobile phase: 90:10 isohexane/isopropanol, flow rate: 1.0 mL/min, λ= 210 nm, retention time: 18.7 and 21.6 min (36:64).

```
Injection Date  : 18/03/2019 12:07:04 PM
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Acq. Operator   : MJP
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Last changed    : 18/03/2019 12:03:47 PM by MJP
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Analysis Method : C:\HPCHEM\2\METHODS\MJP-NP-C.M
Last changed    : 25/03/2019 14:11:05 PM by MJP
                  (modified after loading)
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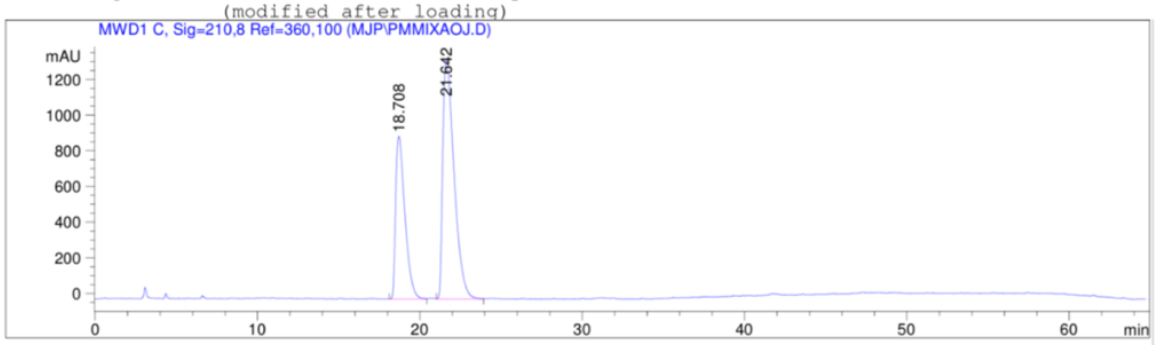
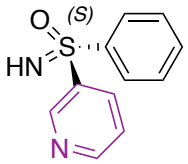


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.708	BV	0.6112	3.61868e4	911.48102	35.7198
2	21.642	VB	0.7404	6.51207e4	1346.19788	64.2802
Totals :				1.01308e5	2257.67889	

(*S*)-Imino(phenyl)(pyridin-3-yl)-λ^6-sulfanone (44a)



Following GP5, the title compound was prepared from the sulfoximine **29a** (77.7 mg, 0.230 mmol), NaOH (91.8 mg, 2.30 mmol) dissolved in MTBE (5 mL). The crude mixture was purified by flash chromatography (4:6 petroleum ether/ethyl acetate to 100% ethyl acetate) to afford the title compound as a colourless oil (31.9 mg, 64%); $[\alpha]_D^{22}$ +7.88 (c 0.91 $CHCl_3$); HPLC: Chiracel OJH, mobile phase: gradient 0-50 min, 85:15 – 50-70 min 75:25 isohexane/isopropanol, flow rate: 1.0 mL/min, λ = 254 nm, retention time: major enantiomer = 54.4 min (96.3%), minor enantiomer = 47.4 min (3.7%), ee = 93%; IR ν_{max} (cm^{-1}): 3262, 3061, 2923, 1571, 1464, 1445, 1413, 1235, 1192, 1136, 1100, 982, 807, 759, 736, 702, 687, 618, 573, 545; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (1H, dd, *J* = 2.5, 1.0 Hz), 8.67 (1H, dd, *J* = 5.0, 1.5 Hz), 8.26 (1H, ddd, *J* = 8.0, 2.5, 1.5 Hz), 8.04-7.97 (2H, m), 7.54-7.42 (3H, m), 7.36 (1H, ddd, *J* = 8.0, 5.0, 1.0 Hz), 3.38 (1H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.9, 148.9, 142.6, 139.9, 135.5, 133.0, 129.3, 127.9, 123.6; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{11}H_{11}N_2OS$ 219.0587, found 219.0600 / m/z: $[M + Na]^+$ calcd for $C_{11}H_{10}N_2OSNa$ 241.0406, found 241.0415.

```
Injection Date  : 15/03/2019 09:56:51 PM
Sample Name     : PM551-OJ                          Location : Vial 1
Acq. Operator   : MJP
Acq. Method     : C:\HPCHEM\2\METHODS\MJP-NP-C.M
Last changed    : 12/03/2019 11:26:42 PM by MJP
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Analysis Method : C:\HPCHEM\2\METHODS\MJP-NP-C.M
Last changed    : 25/03/2019 14:11:05 PM by MJP
                  (modified after loading)
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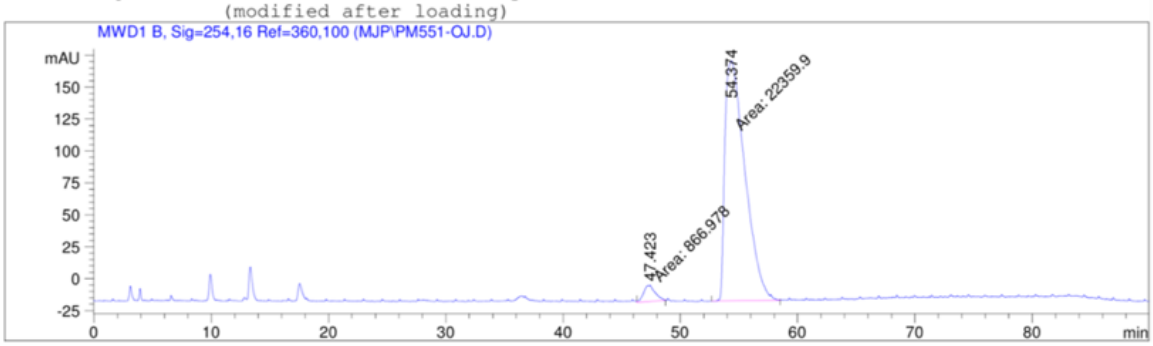
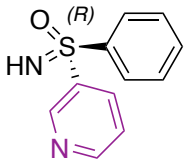


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	47.423	MM	1.1282	866.97754	12.80794	3.7327
2	54.374	MM	1.9845	2.23599e4	187.79199	96.2673
Totals :				2.32268e4	200.59993	

(*R*)-Imino(phenyl)(pyridin-3-yl)-λ6-sulfanone (44b)



Following GP5, the title compound was prepared from the sulfoximine **29b** (58.5 mg, 0.173 mmol), NaOH (69.1 mg, 1.73 mmol) dissolved in MTBE (5 mL). The crude mixture was purified by flash chromatography (4:6 petroleum ether/ethyl acetate to 100% ethyl acetate) to afford the title compound as a colourless oil (25.1 mg, 67%); $[\alpha]_D^{21}$ +38.3 (c 0.215 $CHCl_3$); HPLC: Chiracel OJH, mobile phase: gradient 0-50 min, 85:15 – 50-70 min 75:25 isohexane/isopropanol, flow rate: 1.0 mL/min, λ = 254 nm, retention time: major enantiomer = 47.1 min (96.5%), minor enantiomer = 55.6 min (3.5%), ee = 93%; All other spectral data were identical to **44a**.

```
Injection Date  : 15/03/2019 08:24:37 PM
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Acq. Method     : C:\HPCHEM\2\METHODS\MJP-NP-C.M
Last changed    : 12/03/2019 11:26:42 PM by MJP
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\MJP-NP-C.M
Last changed    : 25/03/2019 14:11:05 PM by MJP
                  (modified after loading)
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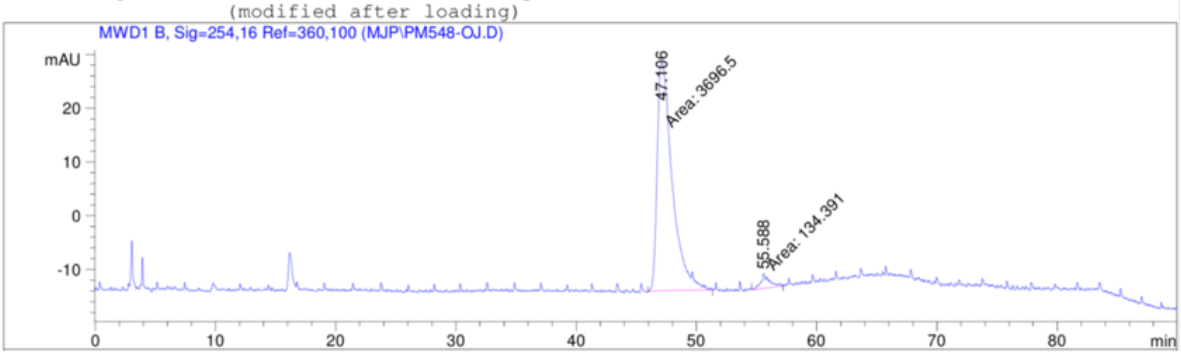
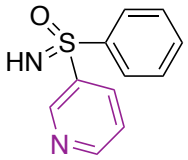


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	47.106	MM	1.4528	3696.50000	42.40797	96.4919
2	55.588	MM	0.8122	134.39131	2.75763	3.5081
Totals :				3830.89131	45.16560	

(±)-Imino(phenyl)(pyridin-3-yl)-λ^6-sulfanone (*rac*-44)



Following GP6, the title compound was prepared from 3-(phenylthio)pyridine (285 mg, 1.52 mmol), (diacetoxyiodo)benzene (1.22 g, 3.80 mmol) and ammonium carbamate (237 mg, 3.04 mmol) in methanol (3 mL). The crude mixture was purified by flash chromatography (4:6 petroelum ether/diethyl ether to 9.5:0.5 dichloromethane/methanol) to afford the title compound as a colourless oil (205 mg, 62%); HPLC: Chiracel OJH, mobile phase: gradient 0-50 min, 85:15 – 50-70 min 75:25 isohexane/isopropanol, flow rate: 1.0 mL/min, λ = 254 nm, retention time: 48.4 and 57.2 min (50:50); All other spectral data were identical to **44a**.

```
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Acq. Operator   : MJP
Acq. Method     : C:\HPCHEM\2\METHODS\MJP-NP-C.M
Last changed    : 12/03/2019 11:26:42 PM by MJP
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\MJP-NP-C.M
Last changed    : 25/03/2019 14:11:05 PM by MJP
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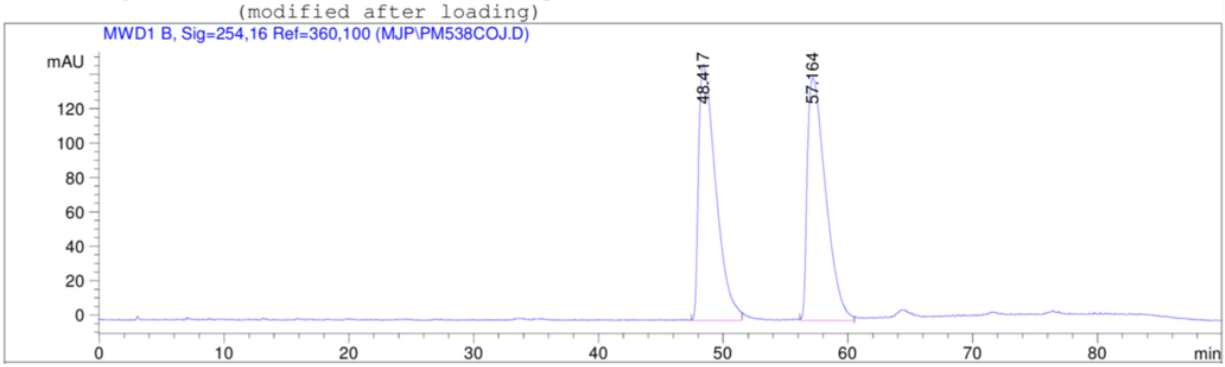
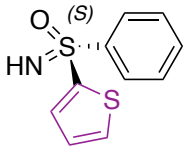
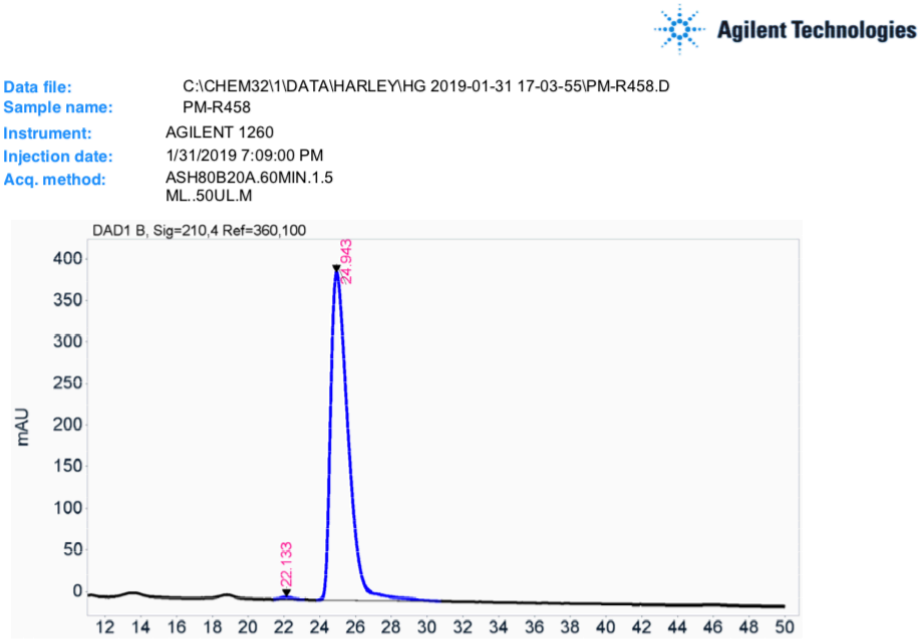


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	48.417	VV	1.2830	1.43193e4	148.76273	49.8357
2	57.164	VV	1.3471	1.44137e4	140.93759	50.1643
Totals :				2.87329e4	289.70032	

(*S*)-Imino(phenyl)(thiophen-2-yl)-λ^6-sulfanone (45a)



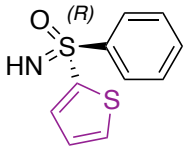
Following GP5, the title compound was prepared from the sulfoximine **28a** (89.2 mg, 0.260 mmol), NaOH (104 mg, 2.60 mmol) dissolved in MTBE (5 mL). The crude mixture was purified by flash chromatography (6:4 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (31.8 mg, 55%); $[\alpha]_D^{25}$ +140.35 (c 0.075 $CHCl_3$); HPLC: Chiracel ASH, mobile phase: 80:20 isohexane/isopropanol, flow rate: 1.5 mL/min, λ = 210 nm, retention time: major enantiomer = 24.9 min (99.5%), minor enantiomer = 22.1 min (0.5%), ee = 99%; IR ν_{max} (cm^{-1}): 3263, 3088, 2922, 1445, 1401, 1342, 1236, 1127, 1094, 1060, 1014, 977, 853, 754, 715, 686, 654, 577, 563, 534; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12-8.06 (2H, m), 7.63 (1H, dd, *J* = 4.0, 1.5 Hz), 7.57 (1H, dd, *J* = 5.0, 1.5 Hz), 7.55-7.44 (3H, m), 7.02 (1H, dd, *J* = 5.0, 4.0 Hz), 3.37 (1H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.1, 143.4, 133.9, 133.3, 132.8, 129.2, 128.0, 127.7; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{10}H_{10}NOS_2$ 224.0198, found 224.0205 / m/z: $[M + Na]^+$ calcd for $C_{10}H_9NOS_2Na$ $[M + Na]^+$ 246.0018, found 246.0011.



Signal: DAD1 B, Sig=210,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
22.133	BB	0.5456	137.148	3.0795	0.51
24.943	BB	1.0230	26775.004	393.9163	99.49

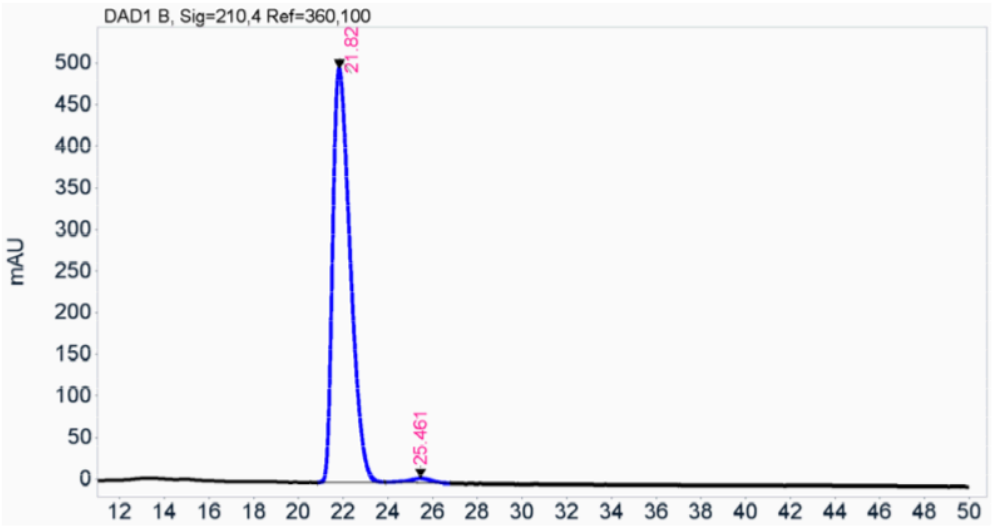
(*R*)-Imino(phenyl)(thiophen-2-yl)-λ^6-sulfanone (45b)



Following GP5, the title compound was prepared from the sulfoximine **28b** (88.9 mg, 0.259 mmol), NaOH (104 mg, 2.59 mmol) dissolved in MTBE (5 mL). The crude mixture was purified by flash chromatography (6:4 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (28.7 mg, 50%); $[\alpha]_D^{22}$ +70.93 (c 0.165 $CHCl_3$); HPLC: Chiracel ASH, mobile phase: 80:20 isohexane/isopropanol, flow rate: 1.5 mL/min, λ = 210 nm, retention time: major enantiomer = 21.8 min (98.6%), minor enantiomer = 25.5 min (1.4%), ee = 97%; All other spectral data were identical to **45a**.

Agilent Technologies

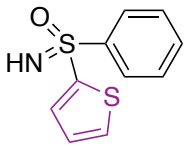
Data file:	C:\CHEM32\1\DATA\HARLEY\HG 2019-01-31 17-03-55\PM-R459.D
Sample name:	PM-R459
Instrument:	AGILENT 1260
Injection date:	1/31/2019 8:20:54 PM
Acq. method:	ASH80B20A.60MIN.1.5 ML..50UL.M



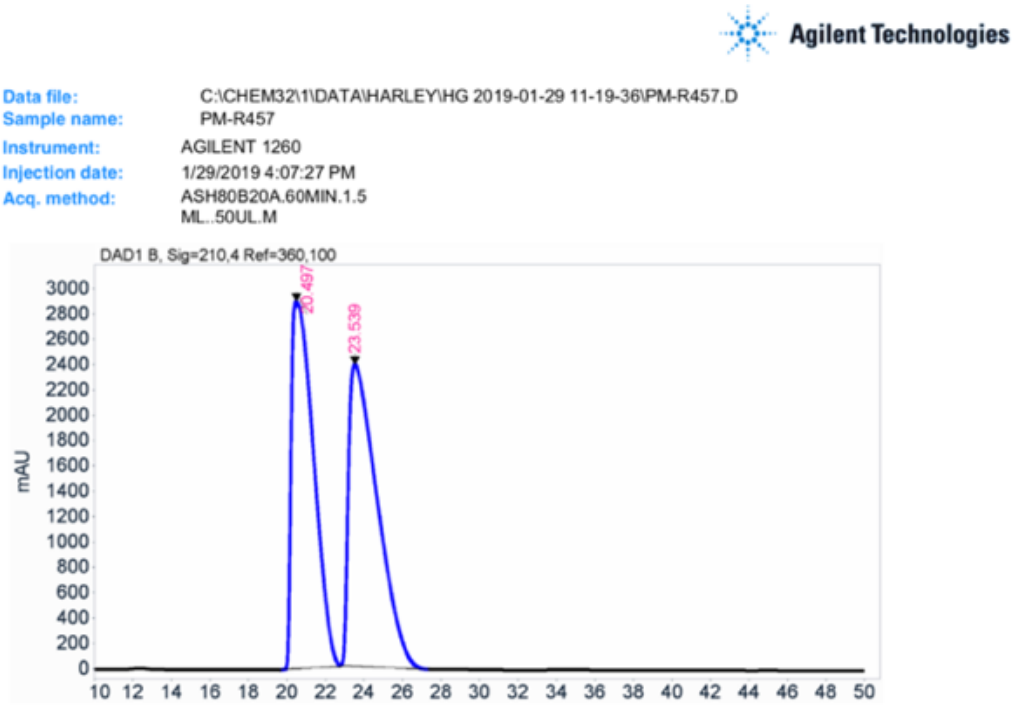
Signal: DAD1 B, Sig=210,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
21.820	BB	0.8578	27117.668	497.6255	98.61
25.461	BB	0.7961	383.378	5.7042	1.39

(±)-Imino(phenyl)(thiophen-2-yl)-λ^6-sulfanone (*rac*-45)



Following GP6, the title compound was prepared from 2-(phenylthio)thiophene (250 mg, 1.30 mmol), (diacetoxyiodo)benzene (1.05 g, 3.25 mmol) and ammonium carbamate (203 mg, 2.60 mmol) in methanol (3 mL). The crude mixture was purified by flash chromatography (7:3 petroleum ether/ethyl acetate) to afford the title compound as a colourless oil (276 mg, 95%); HPLC: Chiracel ASH, mobile phase: 80:20 isohexane/isopropanol, flow rate: 1.5 mL/min, λ = 210 nm, retention time: 20.5 and 23.5 min (49:51); All other spectral data were identical to **45a**.



Signal: DAD1 B, Sig=210,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
20.497	MM	1.3389	232770.953	2897.5310	48.53
23.539	BB	1.2265	246914.141	2379.7964	51.47

Single Crystal X-ray Diffraction

Experimental Procedures

All crystals were obtained by slow evaporation from a solution in EtOAc. Single crystals were selected and mounted using Fomblin® (YR-1800 perfluoropolyether oil) on a polymer-tipped MiTeGen MicroMountTM and cooled rapidly to 120 K in a stream of cold N_2 using an Oxford Cryosystems open flow cryostat.[19] Single crystal X-ray diffraction data were collected on an Oxford Diffraction SuperNova Duo diffractometer (Atlas CCD area detector, mirror-monochromated Cu-Kα radiation source; λ = 1.54184 Å; ω scans; **4b**, **7a**, **9b**, **12a**, **12b**), an Oxford Diffraction GV1000 (TitanS2 CCD area detector, mirror-monochromated Cu-Kα radiation source; λ = 1.54184 Å, ω scans; **6b**, **8a**, **9a**) an Oxford Diffraction GV1000 (AtlasS2 CCD area detector, mirror-monochromated Cu-Kα radiation source; λ = 1.54184 Å, ω scans; **7b**) or an XtaLAB PRO MM007 (PILATUS3 R 200K Hybrid Pixel Array detector, mirror-monochromated Cu-Kα radiation source; λ = 1.54184 Å, ω scans; **5b**). Cell parameters were refined from the observed positions of all strong reflections and absorption corrections were applied using a Gaussian numerical method with beam profile correction (CrysAlisPro).[20] Structures were solved within Olex2[21] by dual space iterative methods (SHELXT)[22] and all non-hydrogen atoms refined by full-matrix least-squares on all unique F2 values with anisotropic displacement parameters (SHELXL).[23] All hydrogen atoms, unless otherwise stated, were geometrically placed and refined with a riding model and isotropic displacement parameter linked to that of their parent atom. Structures were checked with checkCIF.[24] CCDC- 1965332-1965341 contains the supplementary data for these compounds. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Refinement Details

6b

The hydroxy and amine hydrogen atoms were observed in the electron density map and refined. Geometric restraints were applied to the O-H and N-H bond lengths (DFIX). The isotropic displacement parameters of the hydroxy and amine hydrogen atoms were fixed at 1.5 times that of their parent atoms.

	4b_PMMRSZ	**5b_PMMRSH**	**6b_PMMRTG**	**7a_PMMRTD**	**7b_PMMRTE**	**8a_PMMRTH**	**9a_PMMRSS**	**9b_PMMRSR**	**12b_PMMRTC**	**12a_PMMRTB**
Chemical formula	$C_{14}H_{15}NO_2S$	$C_9H_{13}NO_2S$	$C_{12}H_{19}NO_2S$	$C_{14}H_{13}NO_2S$	$C_{14}H_{13}NO_2S$	$C_9H_{11}NO_2S$	$C_{12}H_{17}NO_2S$	$C_{12}H_{17}NO_2S$	$C_{15}H_{17}NO_2S{\cdot}H_2O$	$C_{15}H_{17}NO_2S$
M_r	261.33	199.26	241.34	259.31	259.31	197.25	239.32	239.32	293.37	275.35
Crystal system, space group	Orthorhombic, $P2_12_12_1$	Monoclinic, $P2_1$	Orthorhombic, $P2_12_12_1$	Trigonal, $P3_2$	Monoclinic, $P2_1$	Monoclinic, $I2$	Monoclinic, $P2_1$	Monoclinic, $P2_1$	Trigonal, $P3_1$	Monoclinic, $P2_1$
a, b, c (Å)	5.1446 (4), 13.9660 (12), 18.3542 (16)	11.6171 (5), 7.3962 (3), 11.7096 (6)	6.2244 (1), 11.1272 (2), 19.2804 (4)	13.3192 (4), 13.3192 (4), 6.0701 (3)	5.8528 (3), 7.5096 (4), 14.0649 (6)	9.4562 (3), 5.3529 (2), 19.3334 (6)	11.0954 (7), 5.8622 (4), 18.8002 (13)	6.02621 (19), 23.1524 (8), 8.7719 (3)	14.5653 (6), 14.5653 (6), 6.3425 (3)	10.0075 (5), 10.2709 (5), 13.7357 (7)
α, β, γ (°)	90, 90, 90	90, 94.740 (4), 90	90, 90, 90	90, 90, 120	90, 91.222 (4), 90	90, 100.579 (3), 90	90, 98.417 (6), 90	90, 94.755 (3), 90	90, 90, 120	90, 96.642 (5), 90
V (Å^3)	1318.8(2)	1002.67(8)	1335.36(4)	932.57(8)	618.05(5)	961.99(6)	1209.66(14)	1219.65(7)	1165.28(11)	1402.36(12)
Z	4	4	4	3	2	4	4	4	3	4
Temperature (K)	120	120	120	120	120	120	120	120	120	120
Radiation	Cu $K\alpha$	Cu $K\alpha$	Cu $K\alpha$	Cu $K\alpha$	Cu $K\alpha$	Cu $K\alpha$	Cu $K\alpha$	Cu $K\alpha$	Cu $K\alpha$	Cu $K\alpha$
μ (mm^{-1})	2.13	2.62	2.05	2.26	2.27	2.73	2.26	2.24	1.91	2.03
Crystal size (mm)	0.16×0.0 ×0.03	0.10×0.07×0.04	0.22×0.18×0.09	0.78×0.04×0.03	0.10×0.06×0.02	0.39×0.14× 0.10	0.42×0.37×0.10	0.25×0.11×0.03	0.37×0.04×0.02	0.17×0.12×0.09
Diffractometer	SuperNova, Atlas	XtalLAB PRO PILATUS3 R	SuperNova, Titan S2	SuperNova, Atlas	SuperNova, Atlas S2	SuperNova, Titan S2	SuperNova, Titan S2	SuperNova, Atlas	SuperNova, Atlas	SuperNova, Atlas
T_{min}, T_{max}	0.783, 1.000	0.846, 0.917	0.629, 1.000	0.390, 1.000	0.881, 0.988	0.463, 1.000	0.468, 0.807	0.693, 0.930	0.612, 1.000	0.781, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4737, 2598, 2357	11232, 4090, 3451	9196, 2659, 2594	10617, 2443, 2346	6269, 2409, 2297	4066, 1850, 1819	9566, 4743, 4645	15402, 4856, 4741	6123, 3066, 2952	10434, 5580, 5393
R_{int}	0.033	0.060	0.027	0.038	0.031	0.022	0.035	0.031	0.025	0.031
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.624	0.633	0.623	0.624	0.624	0.622	0.624	0.623	0.624	0.627
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.036, 0.094, 1.07	0.053, 0.136, 1.09	0.025, 0.063, 1.03	0.038, 0.102, 1.07	0.034, 0.090, 1.06	0.045, 0.117, 1.06	0.052, 0.139, 1.06	0.033, 0.085, 1.06	0.030, 0.077, 1.06	0.031, 0.077, 1.05
No. of reflections	2598	4090	2659	2443	2409	1850	4743	4856	3066	5580
No. of parameters	169	249	154	163	163	119	295	295	191	351
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.23, -0.26	0.32, -0.39	0.28, -0.18	0.22, -0.28	0.14, -0.36	0.44, -0.33	0.58, -0.52	0.15, -0.47	0.15, -0.24	0.26, -0.25
Absolute structure parameter	0.00(2)	0.01(2)	-0.006(8)	0.01(3)	-0.004(18)	-0.04(3)	0.00(2)	-0.014(12)	-0.015(15)	-0.005(10)
CCDC Number	1965332	1965333	1965334	1965335	1965336	1965337	1965338	1965339	1965340	1965341

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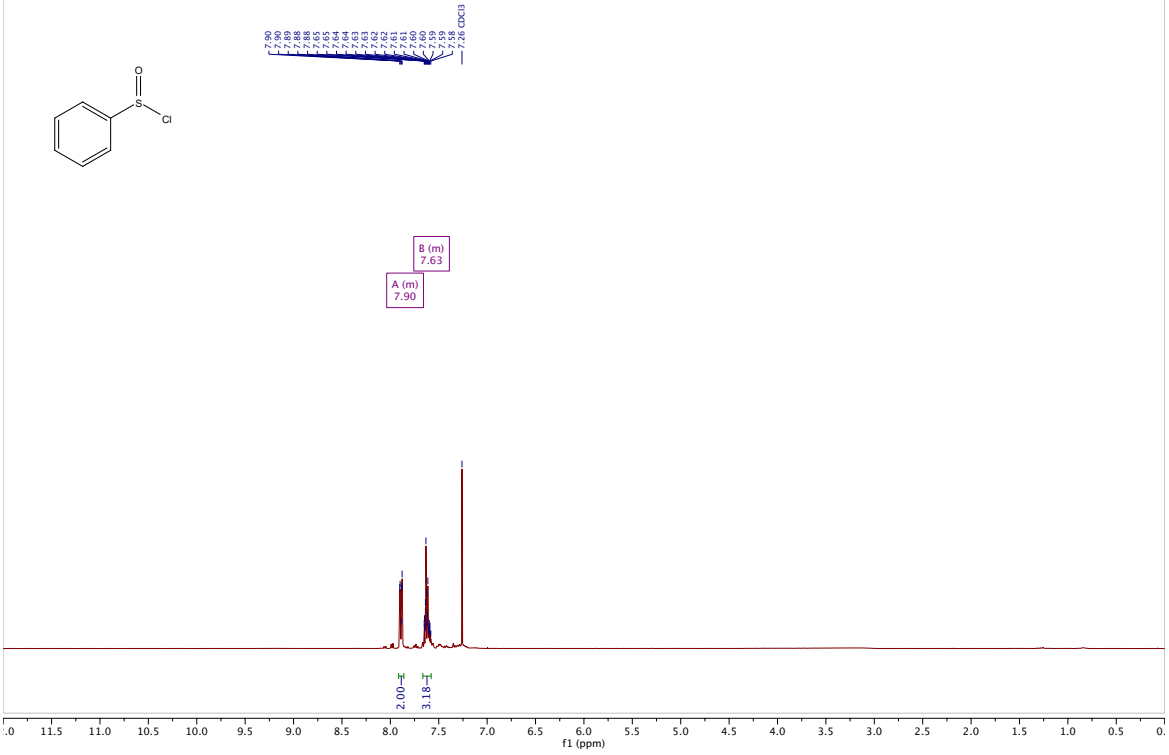
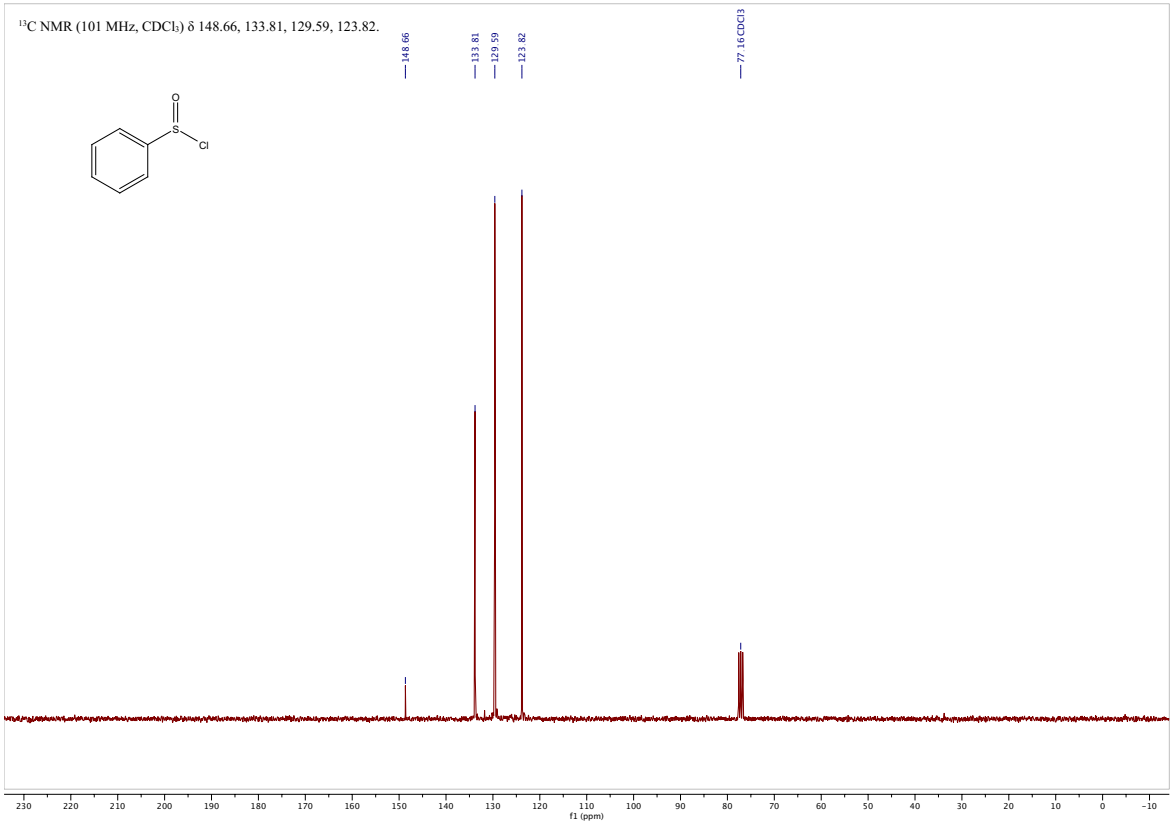
NMR Spectra

(±)-Benzenesulfinic chloride (S1)

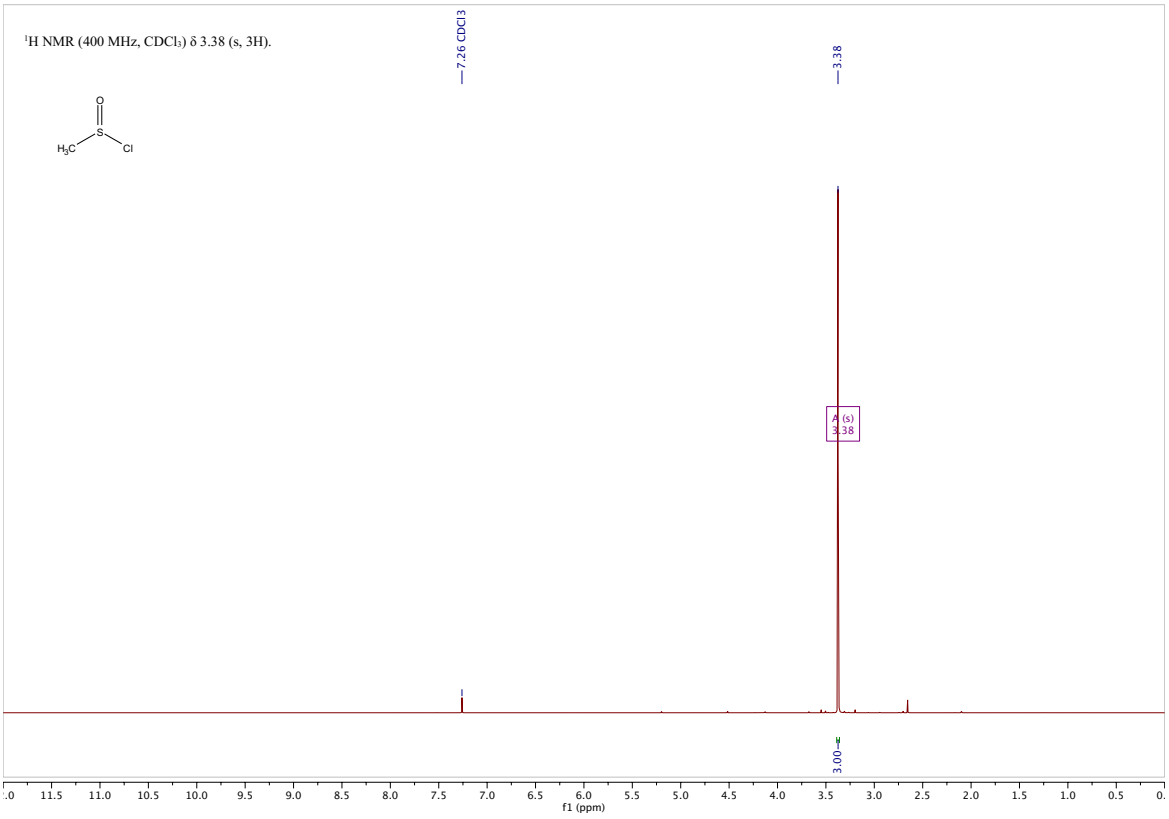
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.89 (m, 2H), 7.68 – 7.56 (m, 3H).

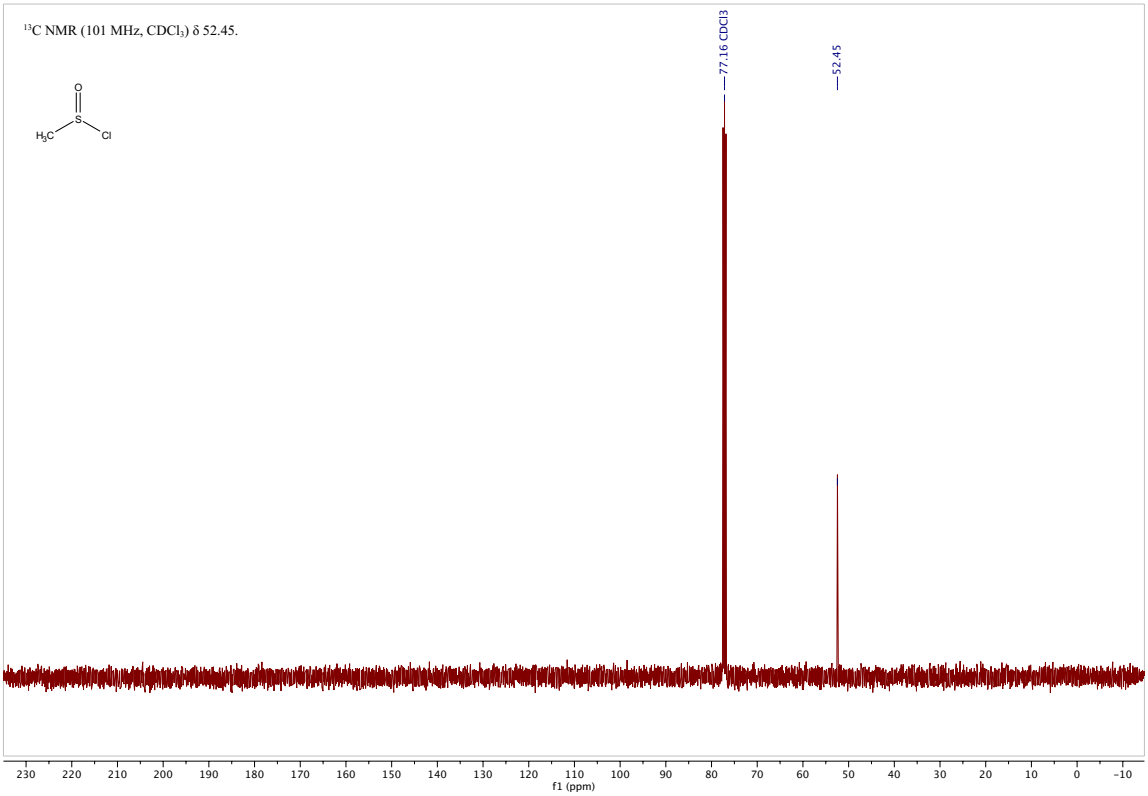


^{13}C NMR (101 MHz, $CDCl_3$) δ 148.66, 133.81, 129.59, 123.82.



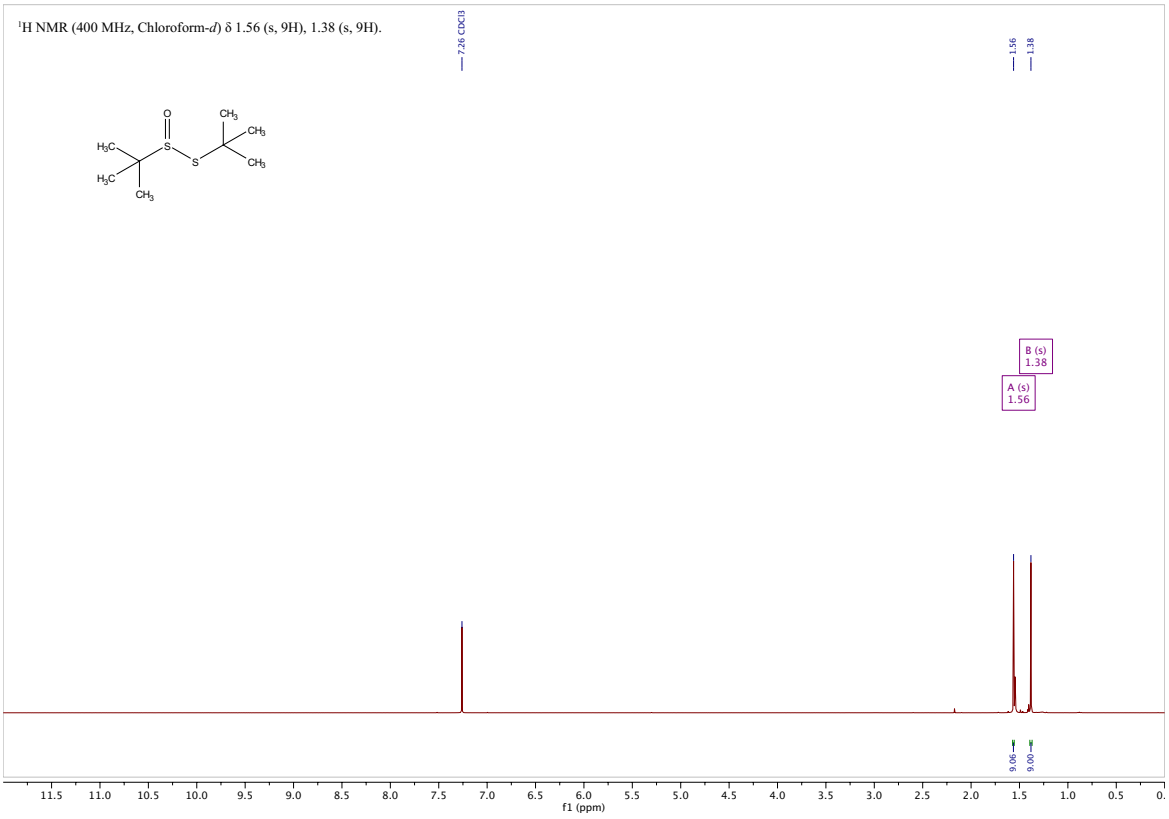
(±)-Methanesulfinic chloride (S2)



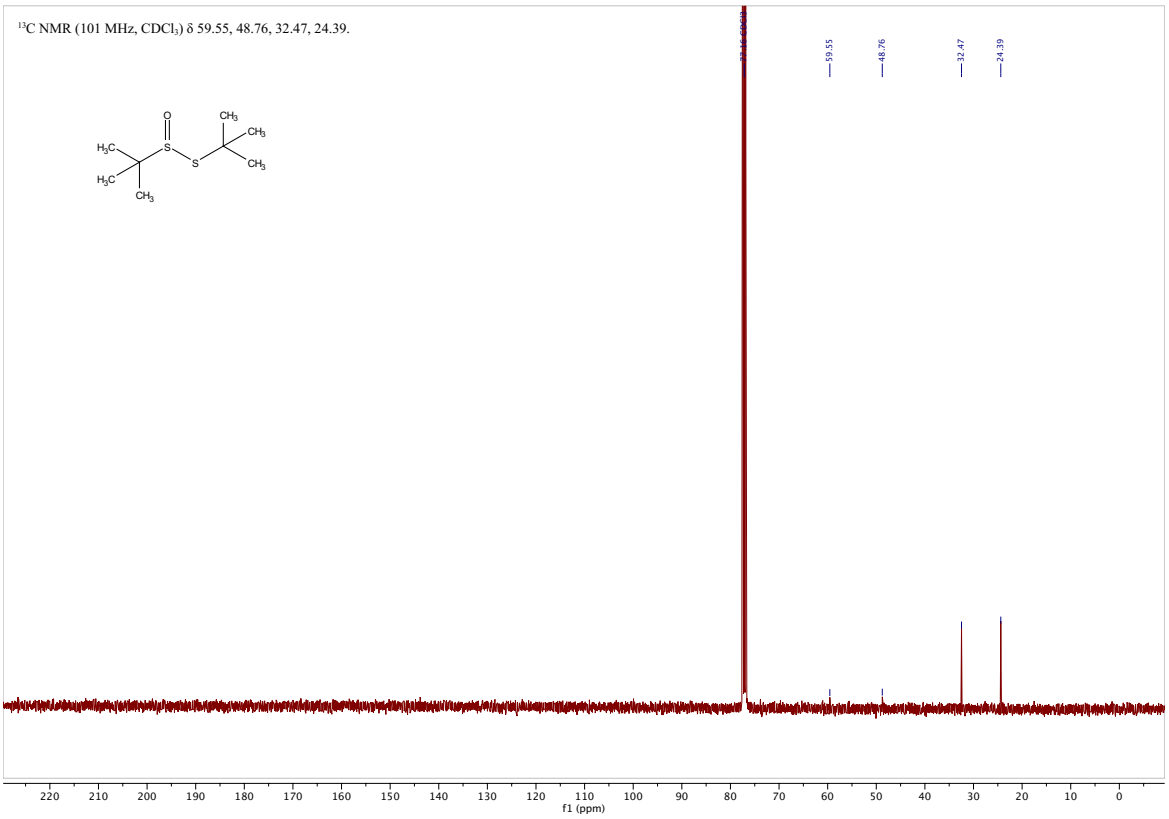


(±)-*S*-(*tert*-butyl)-2-Methylpropane-2-sulfinothioate (S3)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.56 (s, 9H), 1.38 (s, 9H).

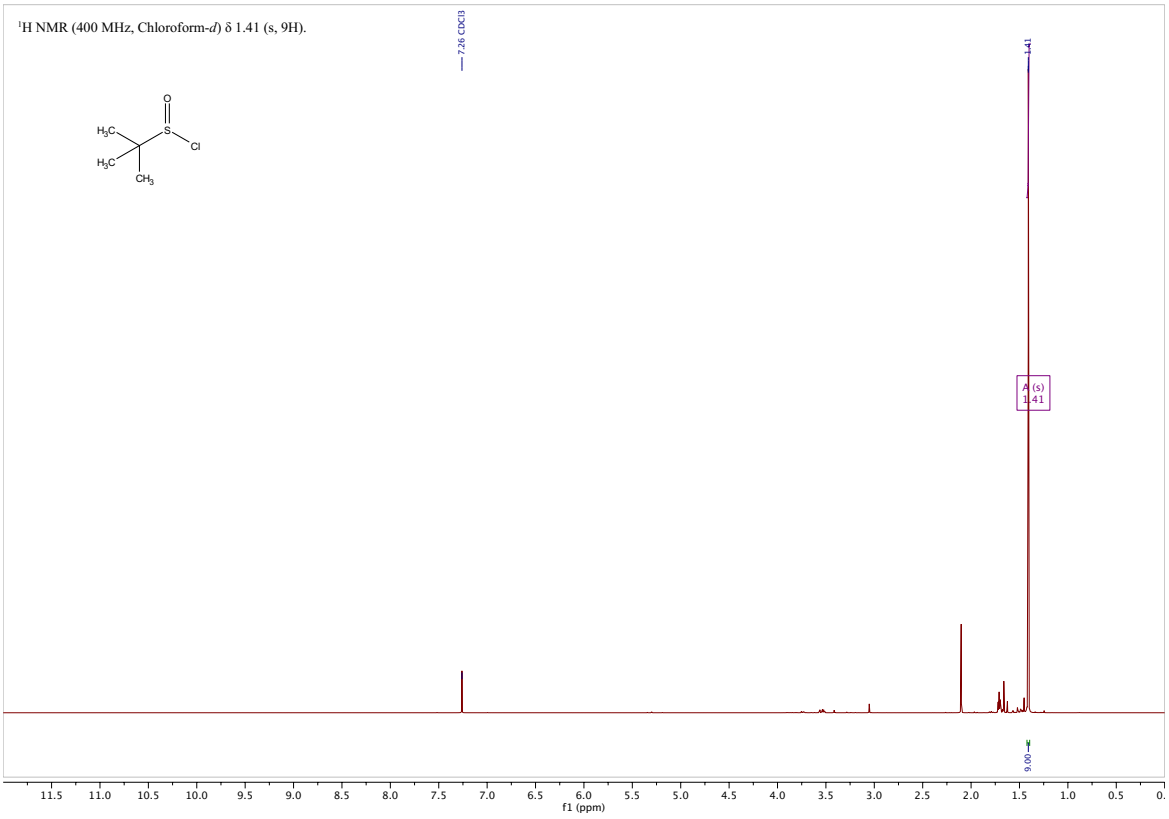


^{13}C NMR (101 MHz, $CDCl_3$) δ 59.55, 48.76, 32.47, 24.39.

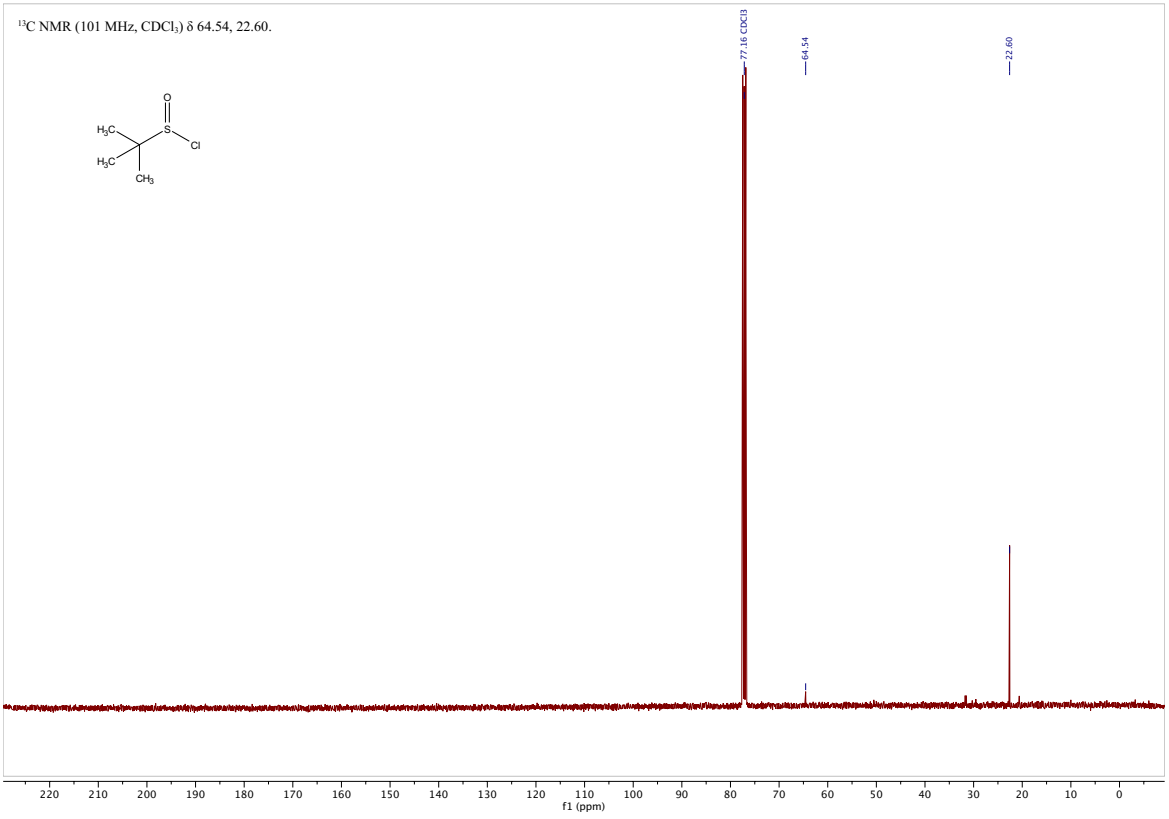


(±)-2-Methylpropane-2-sulfinic chloride (S4)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.41 (s, 9H).

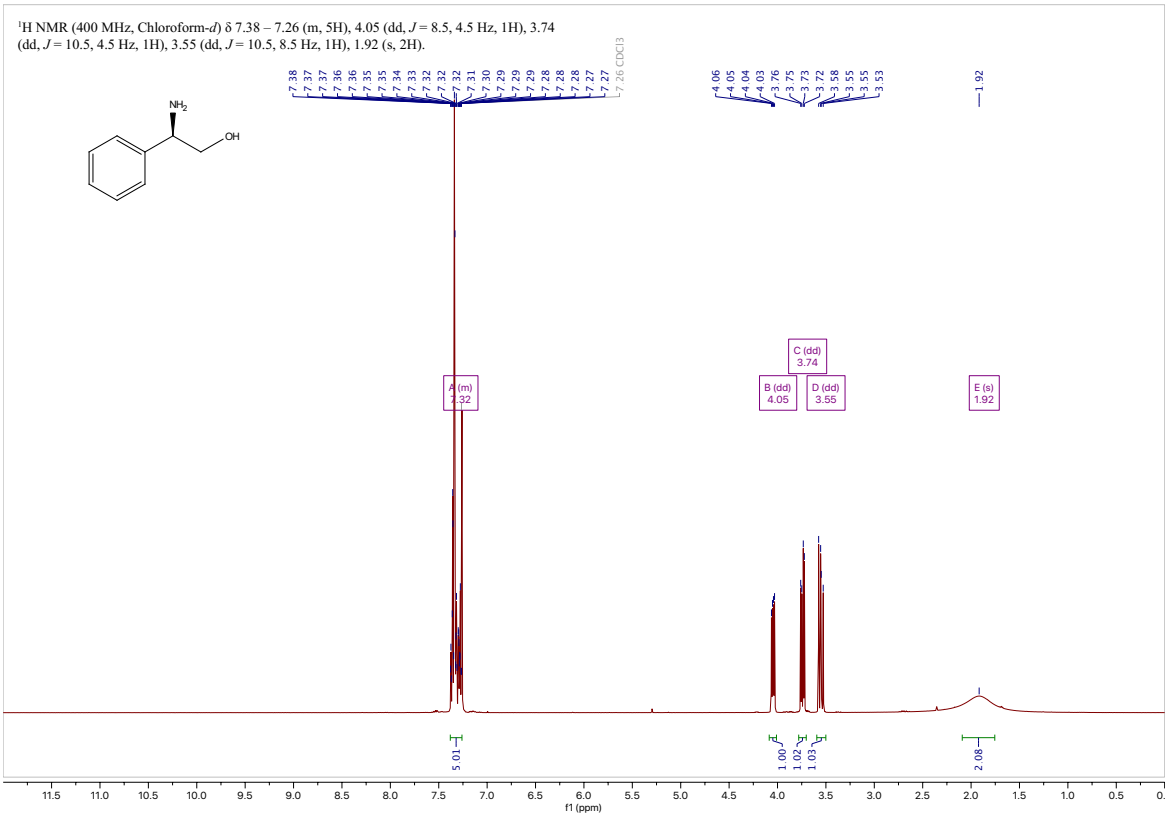


^{13}C NMR (101 MHz, $CDCl_3$) δ 64.54, 22.60.

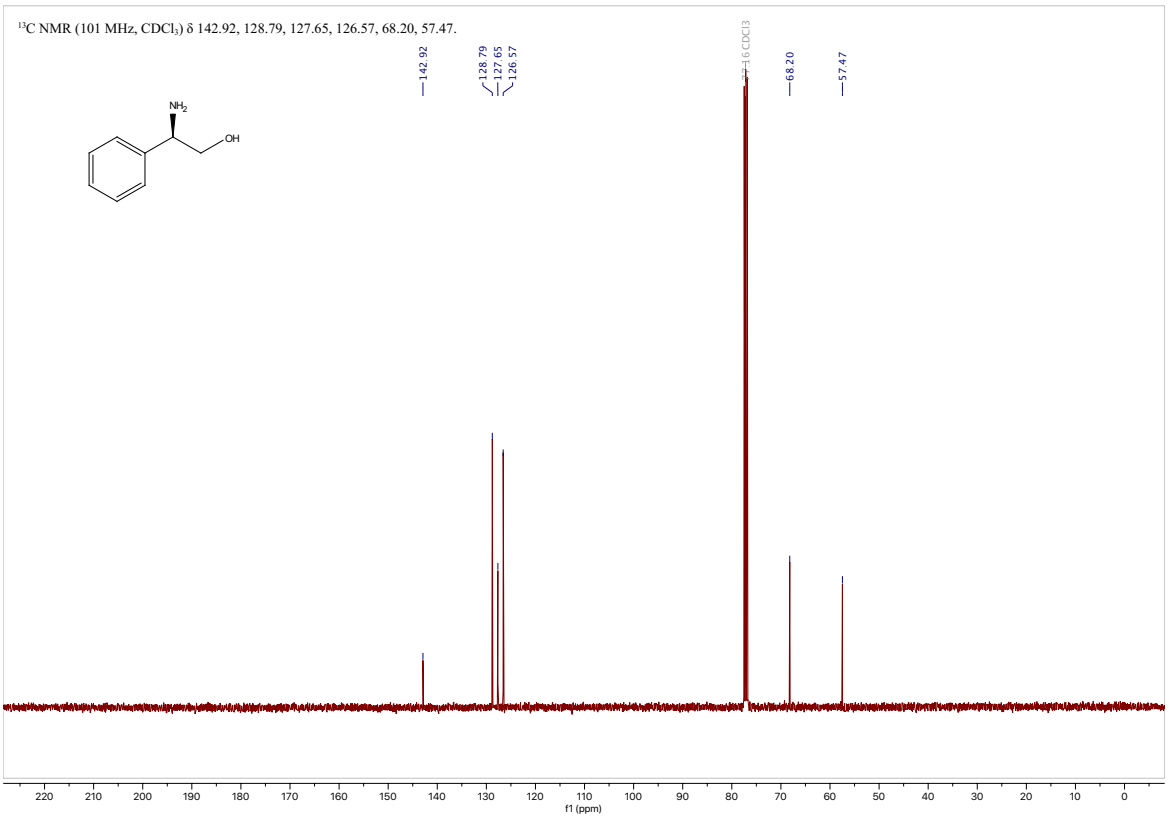


(*R*)-2-Amino-2-phenylethan-1-ol (S5)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.26 (m, 5H), 4.05 (dd, *J* = 8.5, 4.5 Hz, 1H), 3.74 (dd, *J* = 10.5, 4.5 Hz, 1H), 3.55 (dd, *J* = 10.5, 8.5 Hz, 1H), 1.92 (s, 2H).

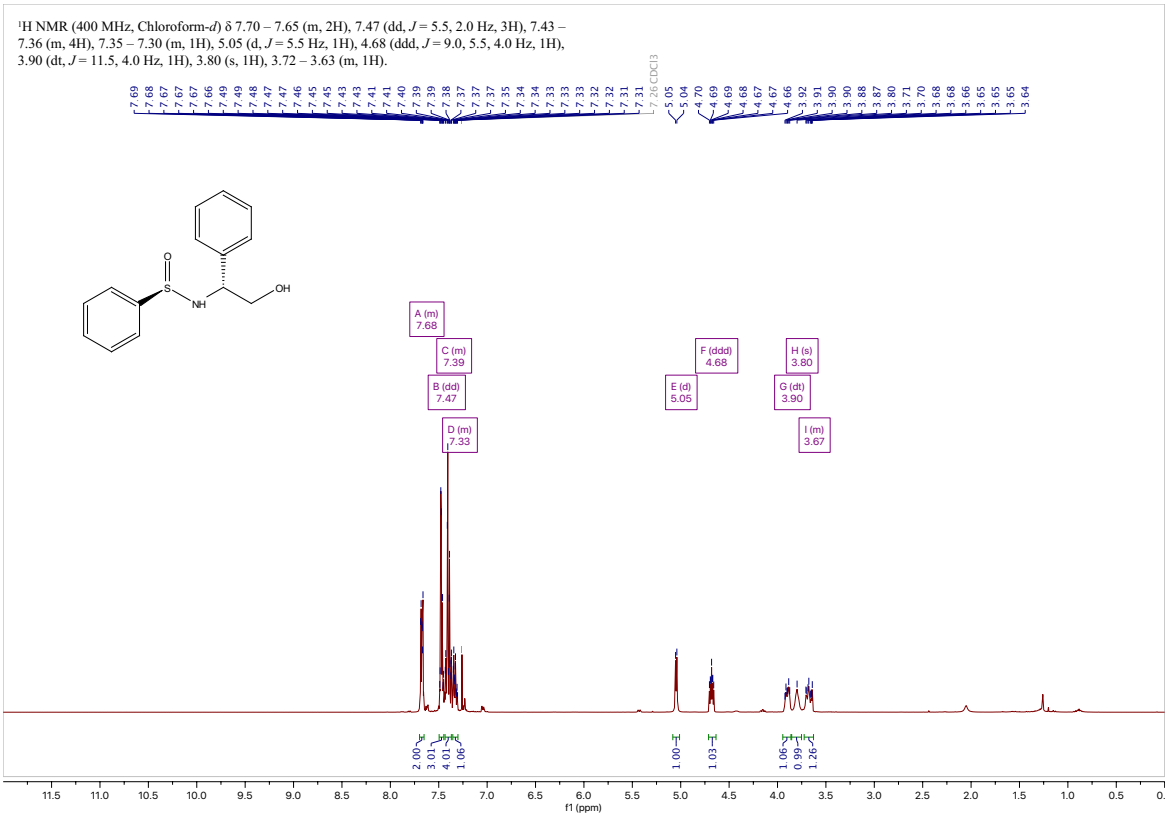


^{13}C NMR (101 MHz, $CDCl_3$) δ 142.92, 128.79, 127.65, 126.57, 68.20, 57.47.

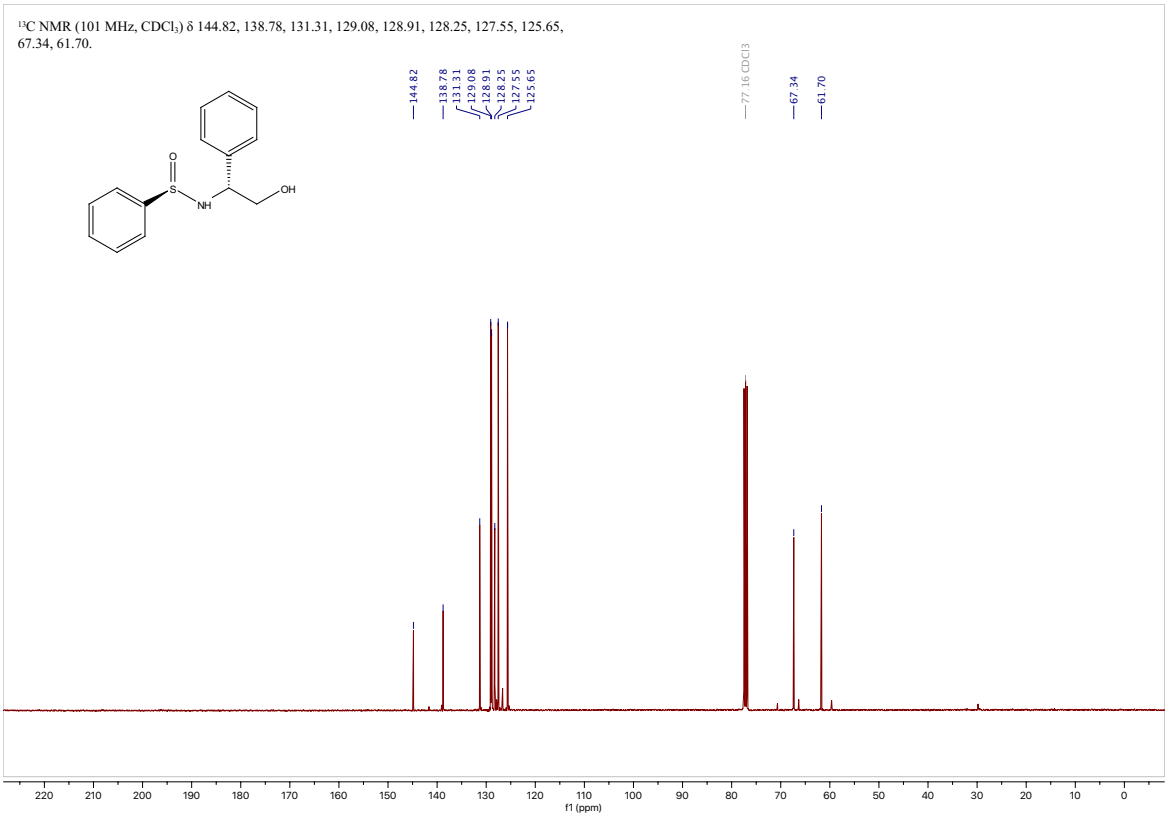


(*R*)-*N*-((*R*)-2-Hydroxy-1-phenylethyl)benzenesulfinamide (4a)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.65 (m, 2H), 7.47 (dd, *J* = 5.5, 2.0 Hz, 3H), 7.43 – 7.36 (m, 4H), 7.35 – 7.30 (m, 1H), 5.05 (d, *J* = 5.5 Hz, 1H), 4.68 (ddd, *J* = 9.0, 5.5, 4.0 Hz, 1H), 3.90 (dt, *J* = 11.5, 4.0 Hz, 1H), 3.80 (s, 1H), 3.72 – 3.63 (m, 1H).

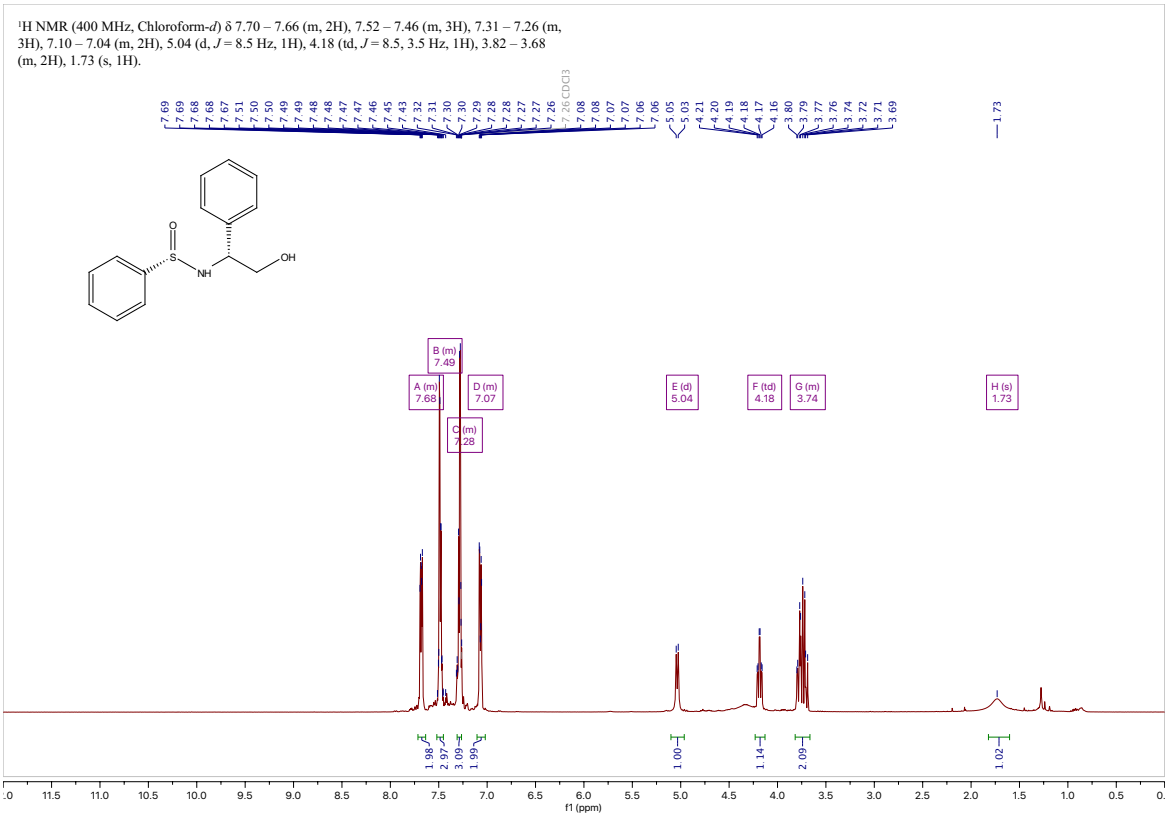


^{13}C NMR (101 MHz, $CDCl_3$) δ 144.82, 138.78, 131.31, 129.08, 128.91, 128.25, 127.55, 125.65, 67.34, 61.70.

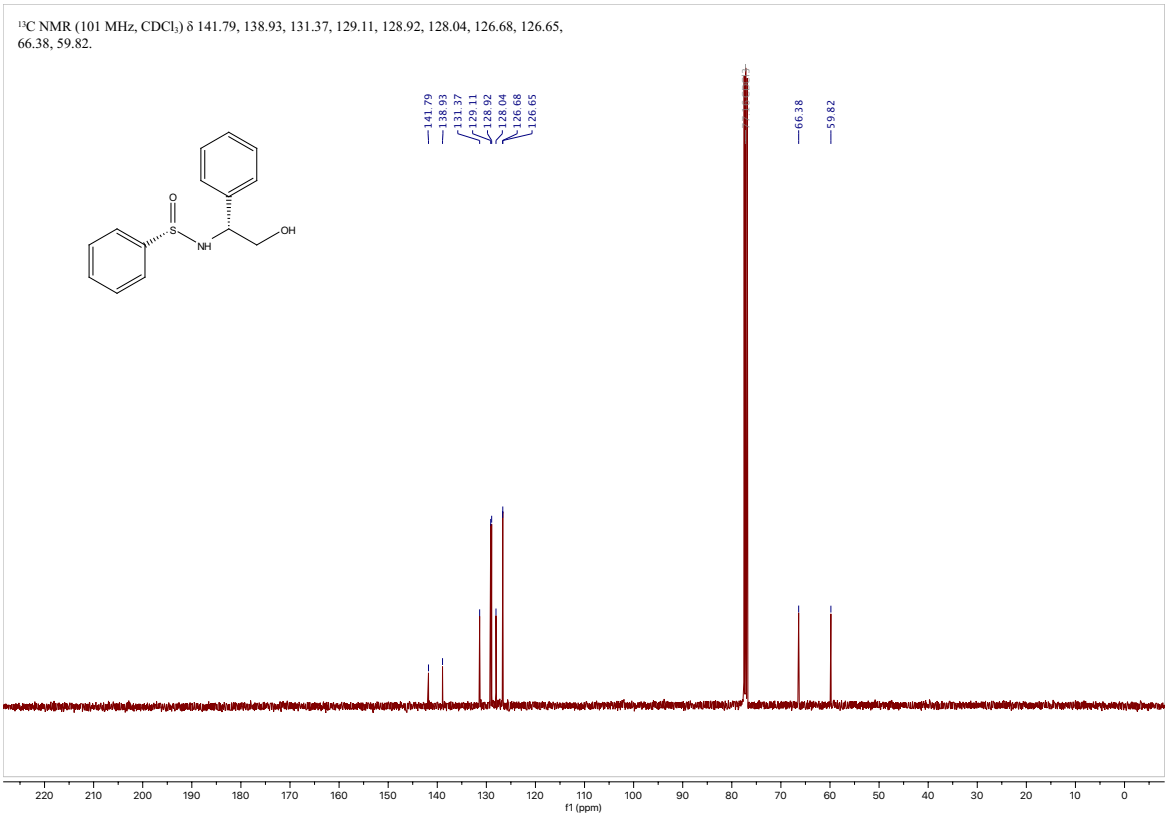


(*S*)-*N*-((*R*)-2-Hydroxy-1-phenylethyl)benzenesulfinamide (4b)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.66 (m, 2H), 7.52 – 7.46 (m, 3H), 7.31 – 7.26 (m, 3H), 7.10 – 7.04 (m, 2H), 5.04 (d, *J* = 8.5 Hz, 1H), 4.18 (td, *J* = 8.5, 3.5 Hz, 1H), 3.82 – 3.68 (m, 2H), 1.73 (s, 1H).

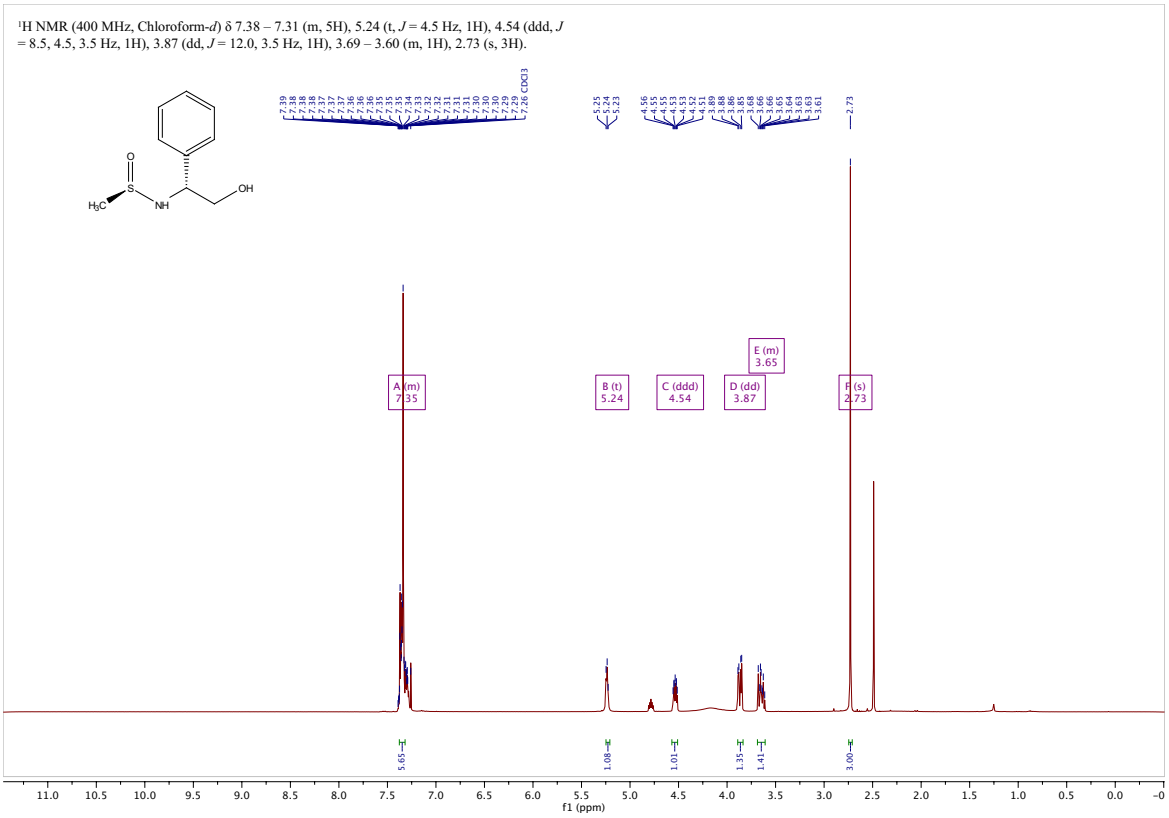


^{13}C NMR (101 MHz, $CDCl_3$) δ 141.79, 138.93, 131.37, 129.11, 128.92, 128.04, 126.68, 126.65, 66.38, 59.82.

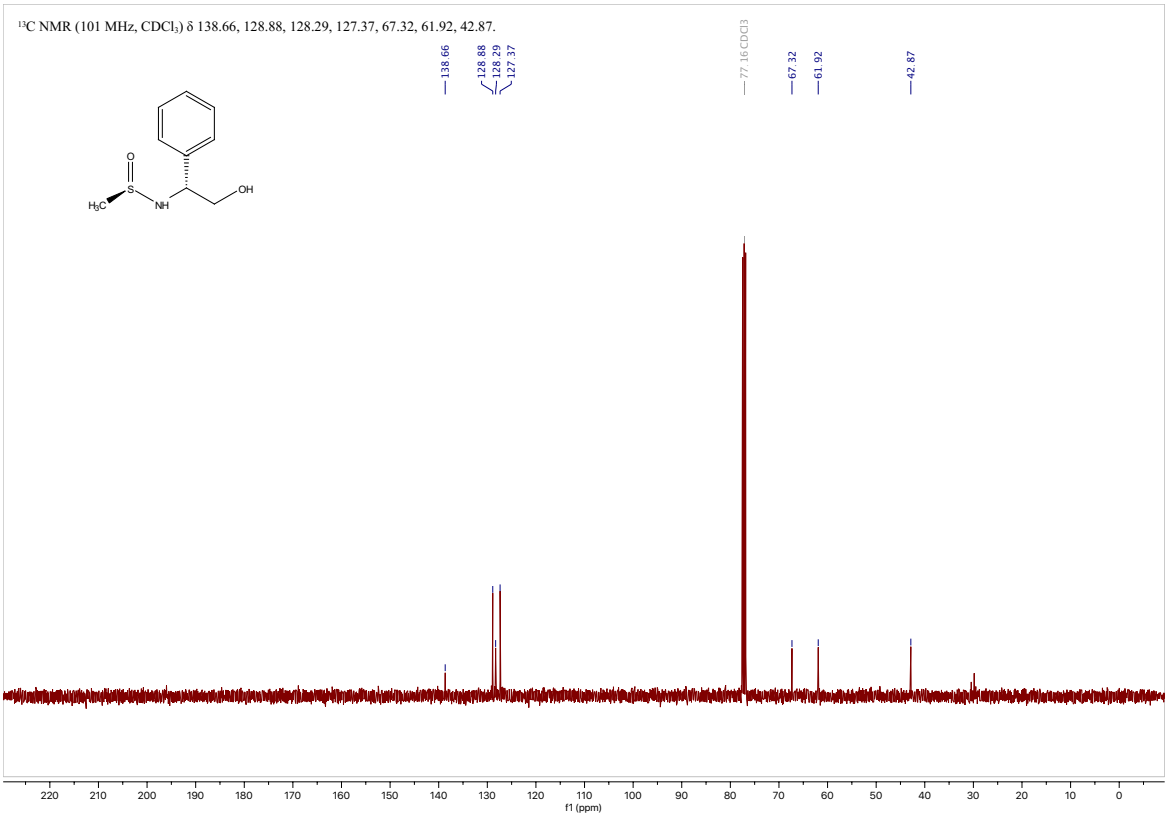


(*R*)-*N*-((*R*)-2-Hydroxy-1-phenylethyl)methanesulfinamide (5a)

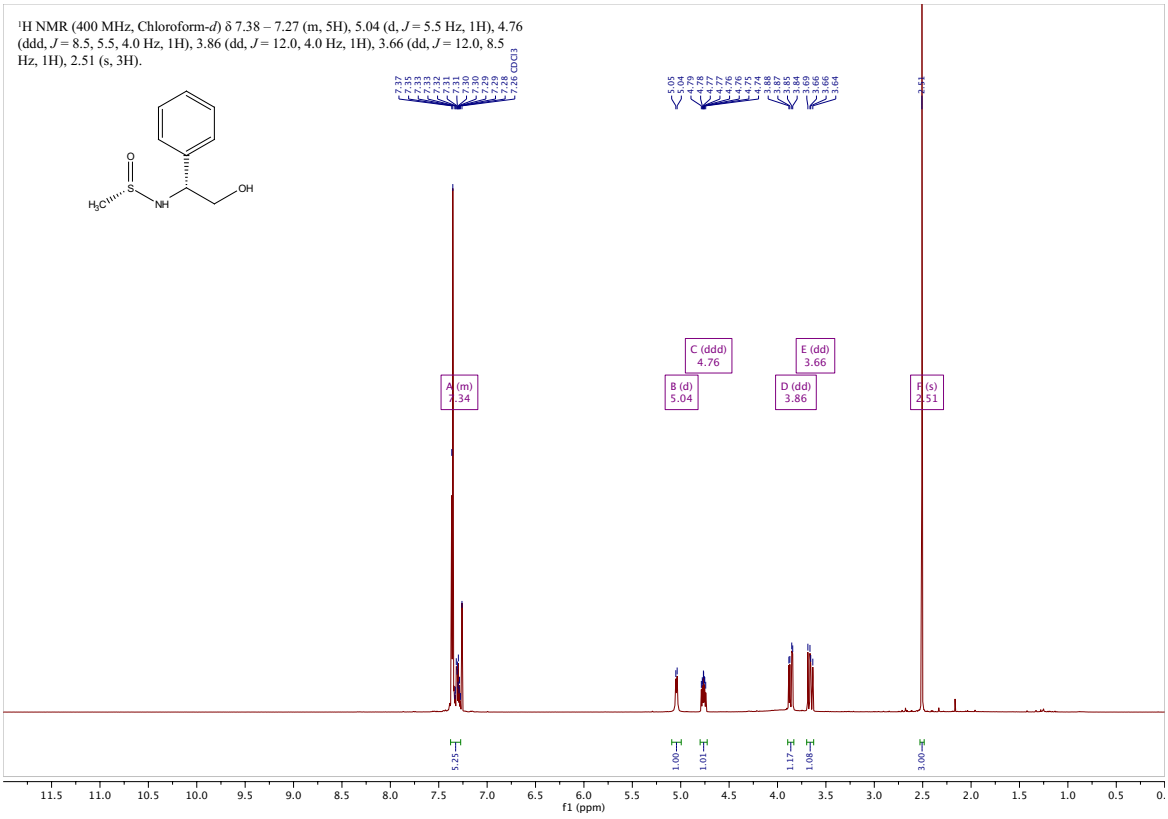
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.31 (m, 5H), 5.24 (t, *J* = 4.5 Hz, 1H), 4.54 (ddd, *J* = 8.5, 4.5, 3.5 Hz, 1H), 3.87 (dd, *J* = 12.0, 3.5 Hz, 1H), 3.69 – 3.60 (m, 1H), 2.73 (s, 3H).

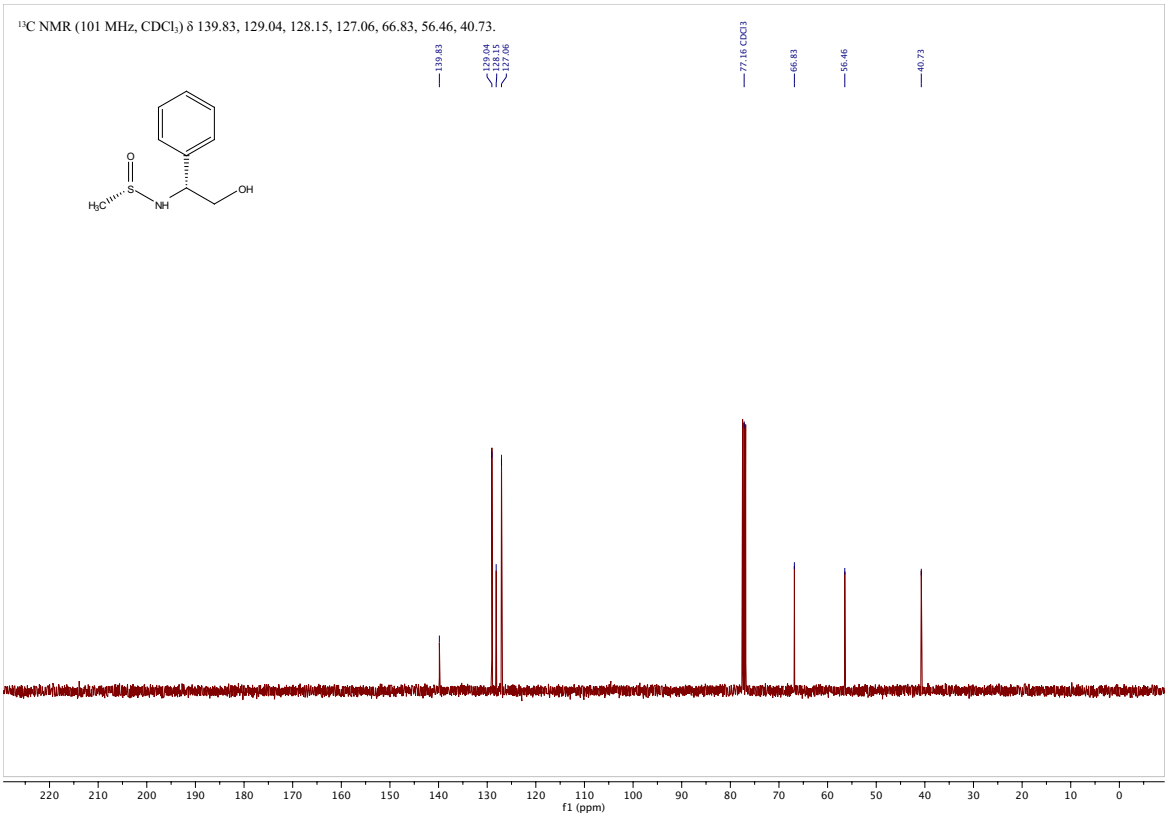


^{13}C NMR (101 MHz, $CDCl_3$) δ 138.66, 128.88, 128.29, 127.37, 67.32, 61.92, 42.87.



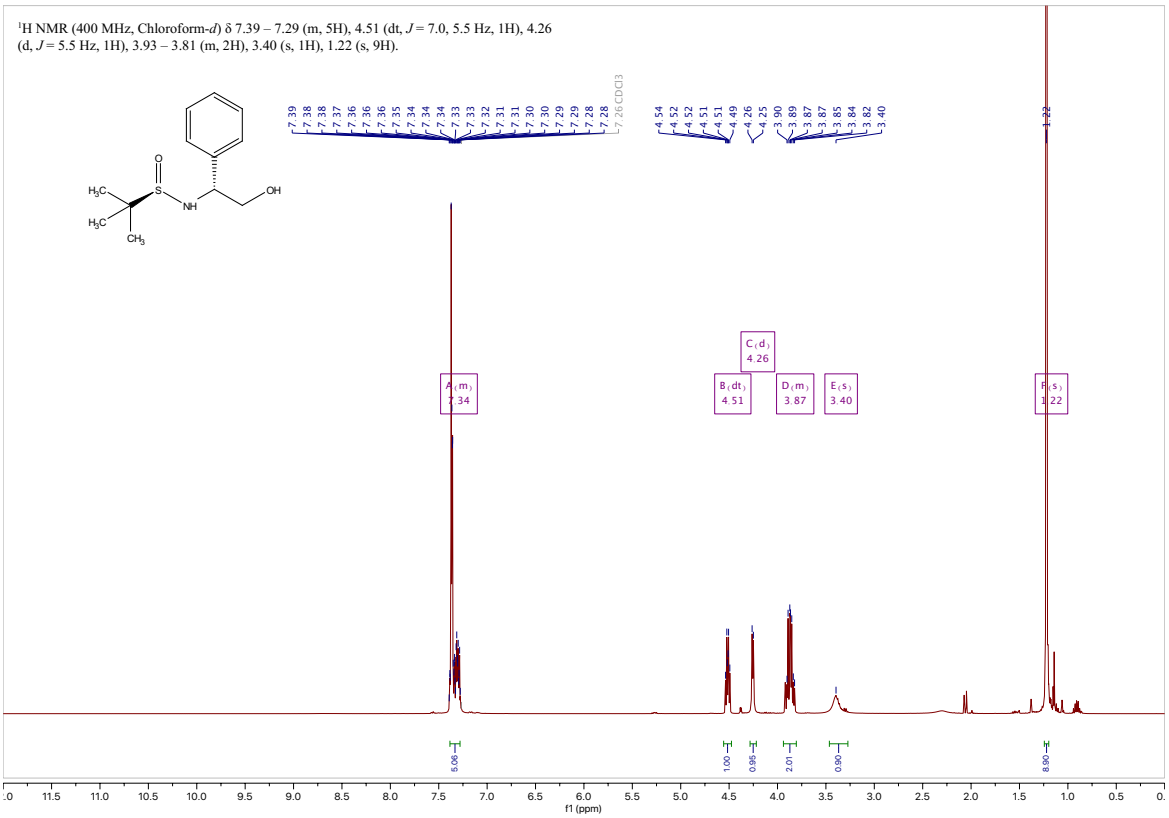
(*S*)-*N*-((*R*)-2-Hydroxy-1-phenylethyl)methanesulfinamide (5b)



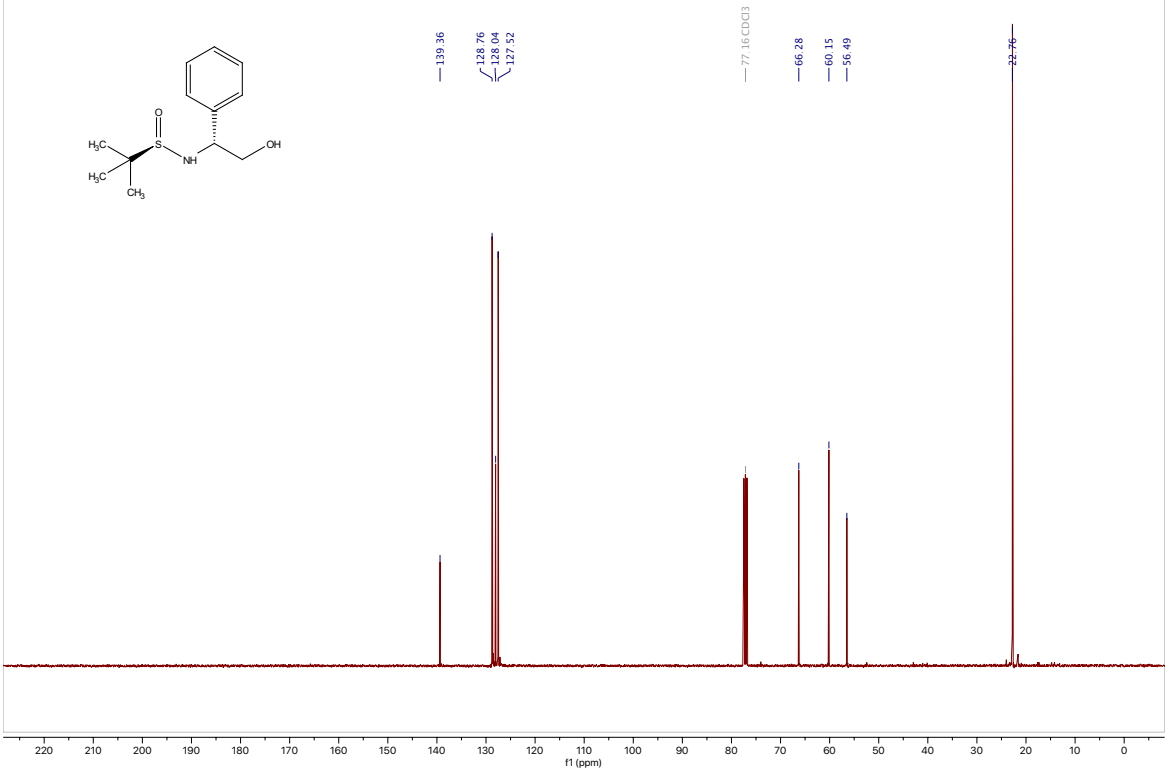


(*R*)-*N*-((*R*)-2-Hydroxy-1-phenylethyl)-2-methylpropane-2-sulfinamide (6a)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.29 (m, 5H), 4.51 (dt, *J* = 7.0, 5.5 Hz, 1H), 4.26 (d, *J* = 5.5 Hz, 1H), 3.93 – 3.81 (m, 2H), 3.40 (s, 1H), 1.22 (s, 9H).

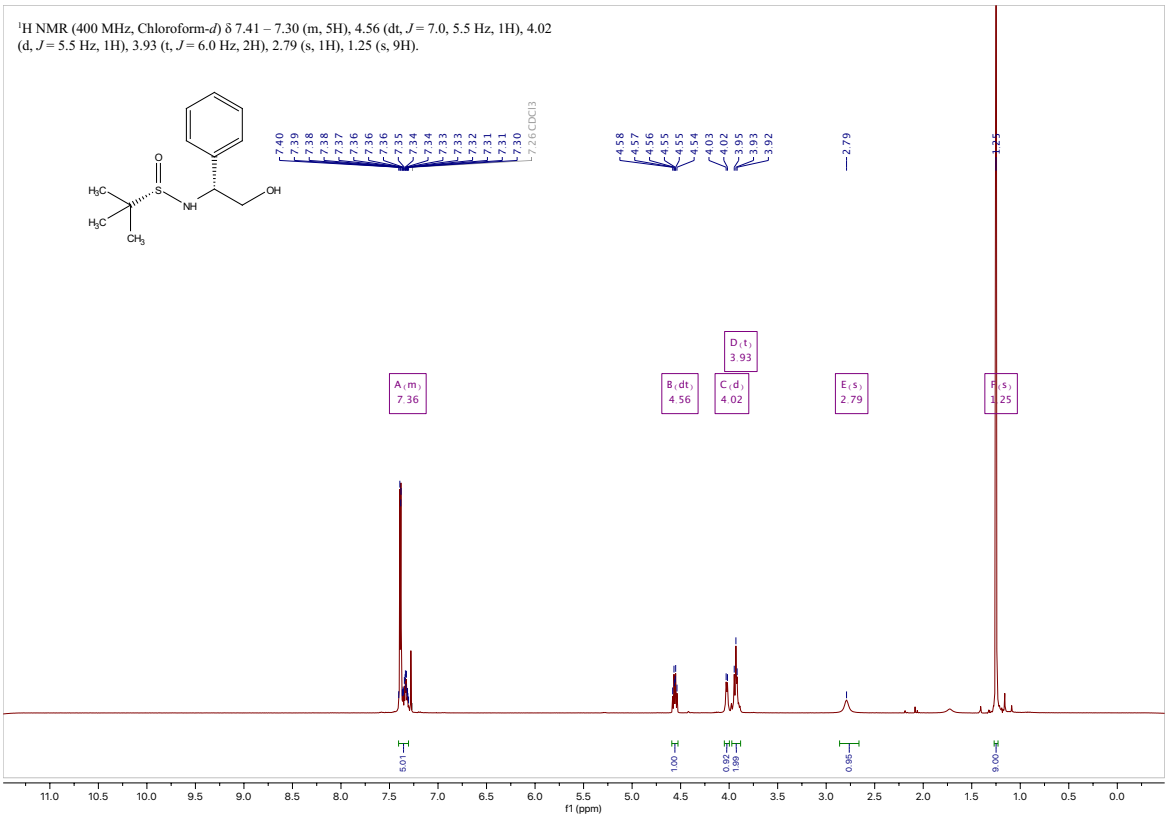


^{13}C NMR (101 MHz, $CDCl_3$) δ 139.36, 128.76, 128.04, 127.52, 66.28, 60.15, 56.49, 22.76.

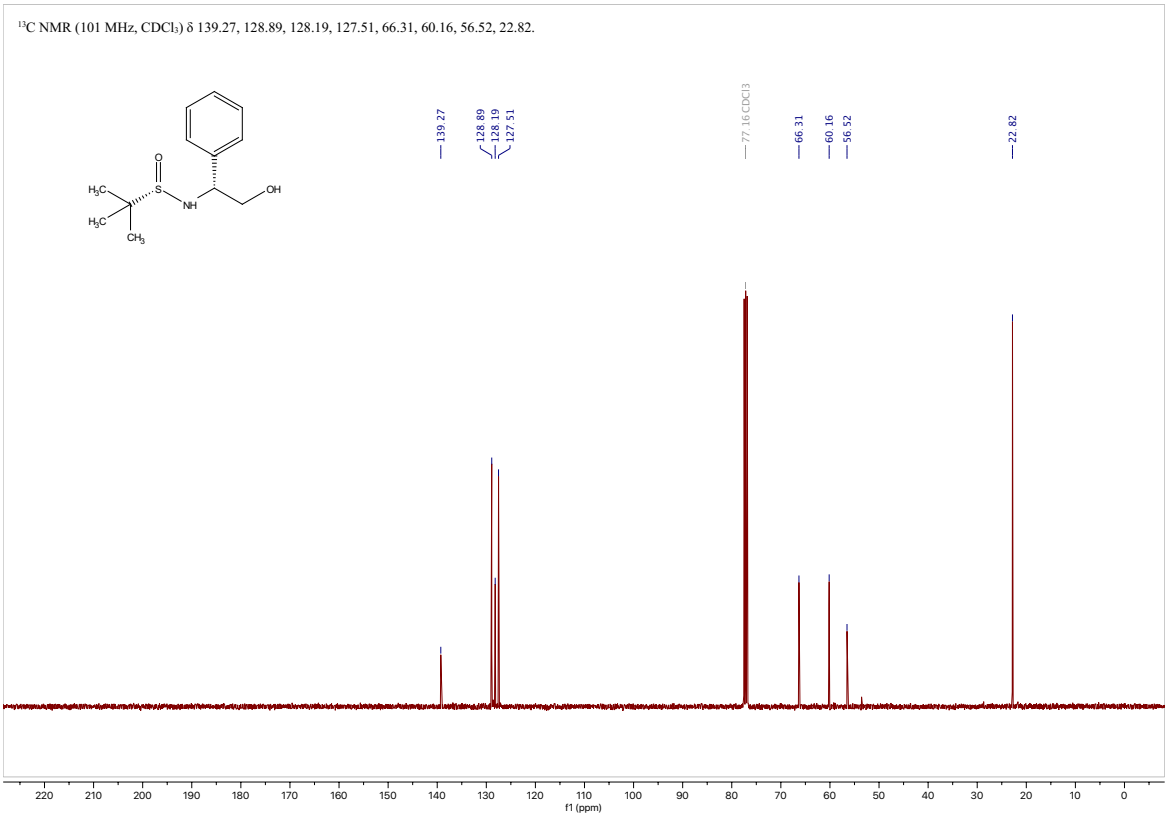


(*S*)-*N*-((*R*)-2-Hydroxy-1-phenylethyl)-2-methylpropane-2-sulfinamide (6b)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.30 (m, 5H), 4.56 (dt, *J* = 7.0, 5.5 Hz, 1H), 4.02 (d, *J* = 5.5 Hz, 1H), 3.93 (t, *J* = 6.0 Hz, 2H), 2.79 (s, 1H), 1.25 (s, 9H).

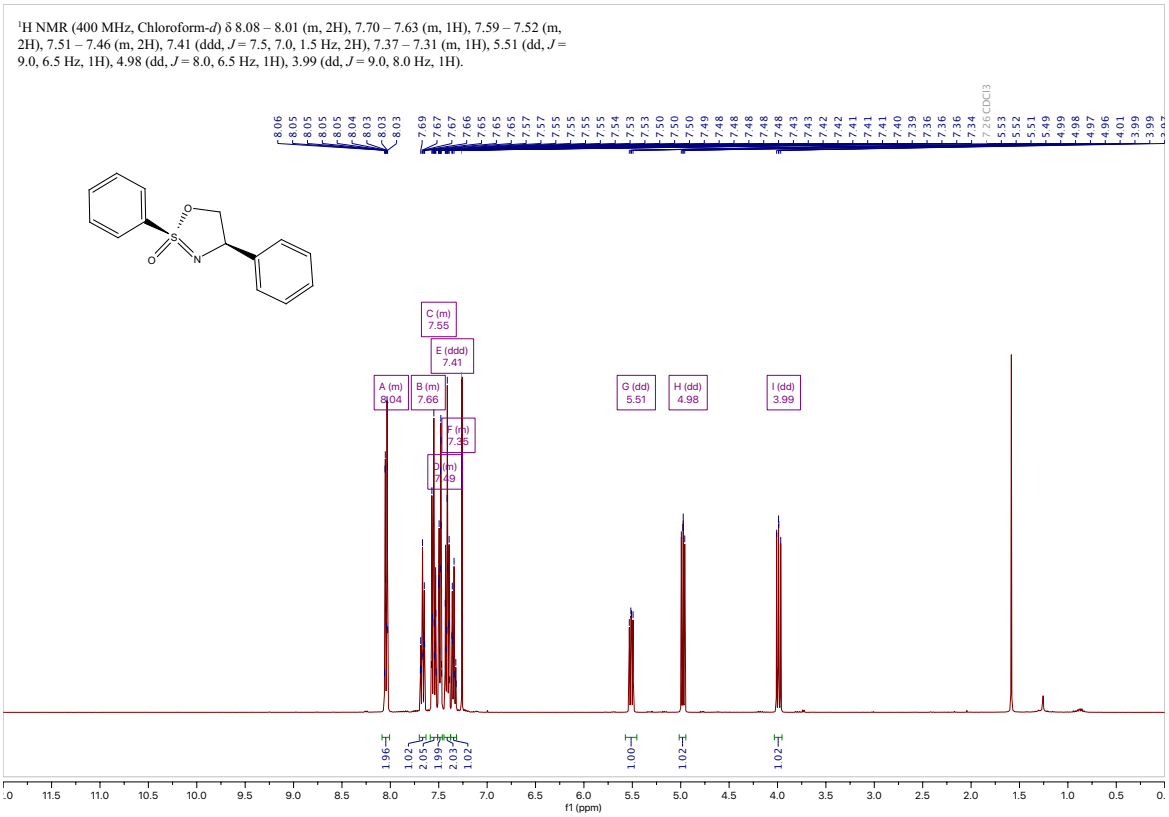


^{13}C NMR (101 MHz, $CDCl_3$) δ 139.27, 128.89, 128.19, 127.51, 66.31, 60.16, 56.52, 22.82.

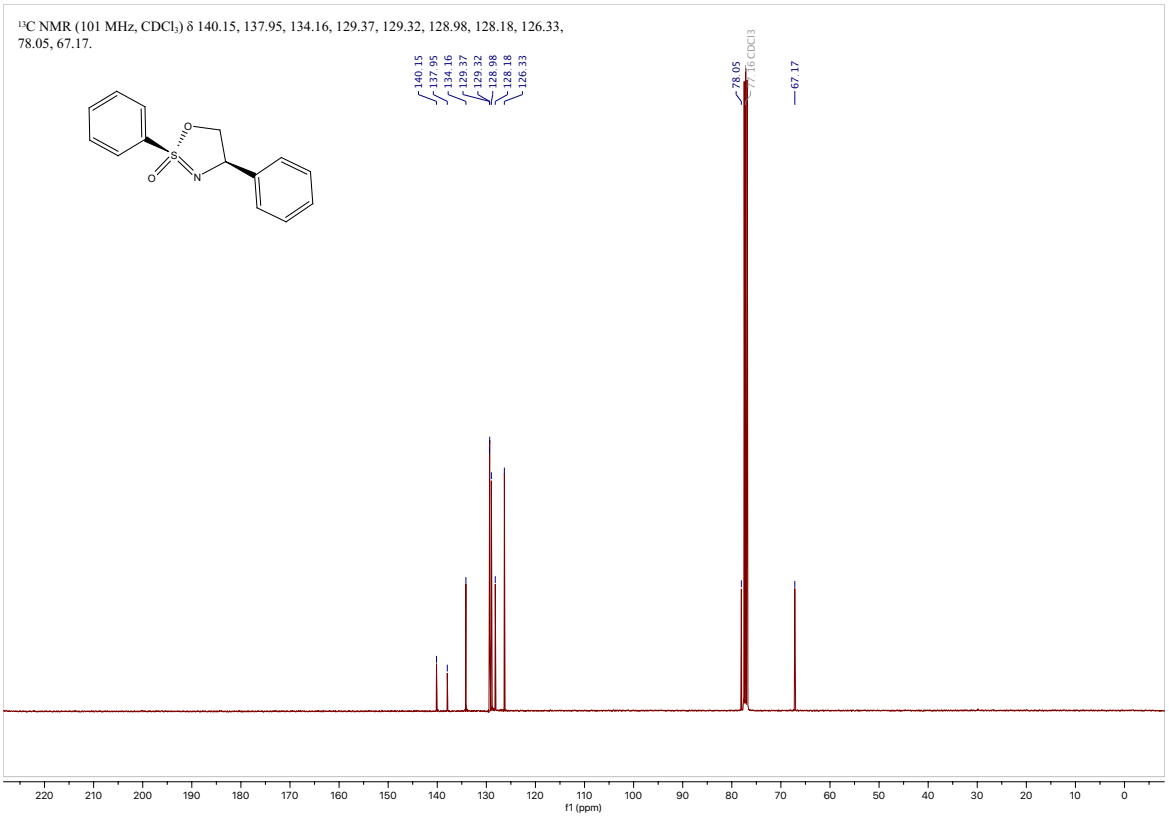


(2*R*,4*R*)-2,4-Diphenyl-4,5-dihydro-1,2,3-oxathiazole 2-oxide (7a)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 – 8.01 (m, 2H), 7.70 – 7.63 (m, 1H), 7.59 – 7.52 (m, 2H), 7.51 – 7.46 (m, 2H), 7.41 (ddd, *J* = 7.5, 7.0, 1.5 Hz, 2H), 7.37 – 7.31 (m, 1H), 5.51 (dd, *J* = 9.0, 6.5 Hz, 1H), 4.98 (dd, *J* = 8.0, 6.5 Hz, 1H), 3.99 (dd, *J* = 9.0, 8.0 Hz, 1H).

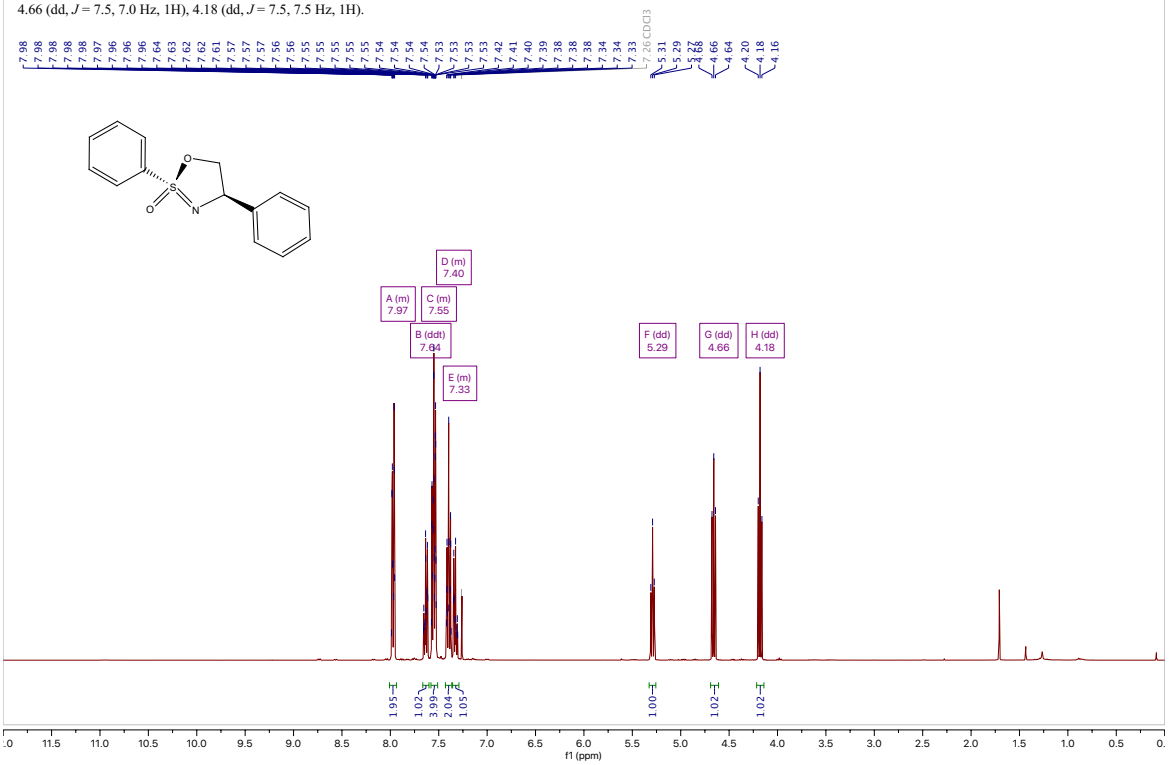


^{13}C NMR (101 MHz, $CDCl_3$) δ 140.15, 137.95, 134.16, 129.37, 129.32, 128.98, 128.18, 126.33, 78.05, 67.17.

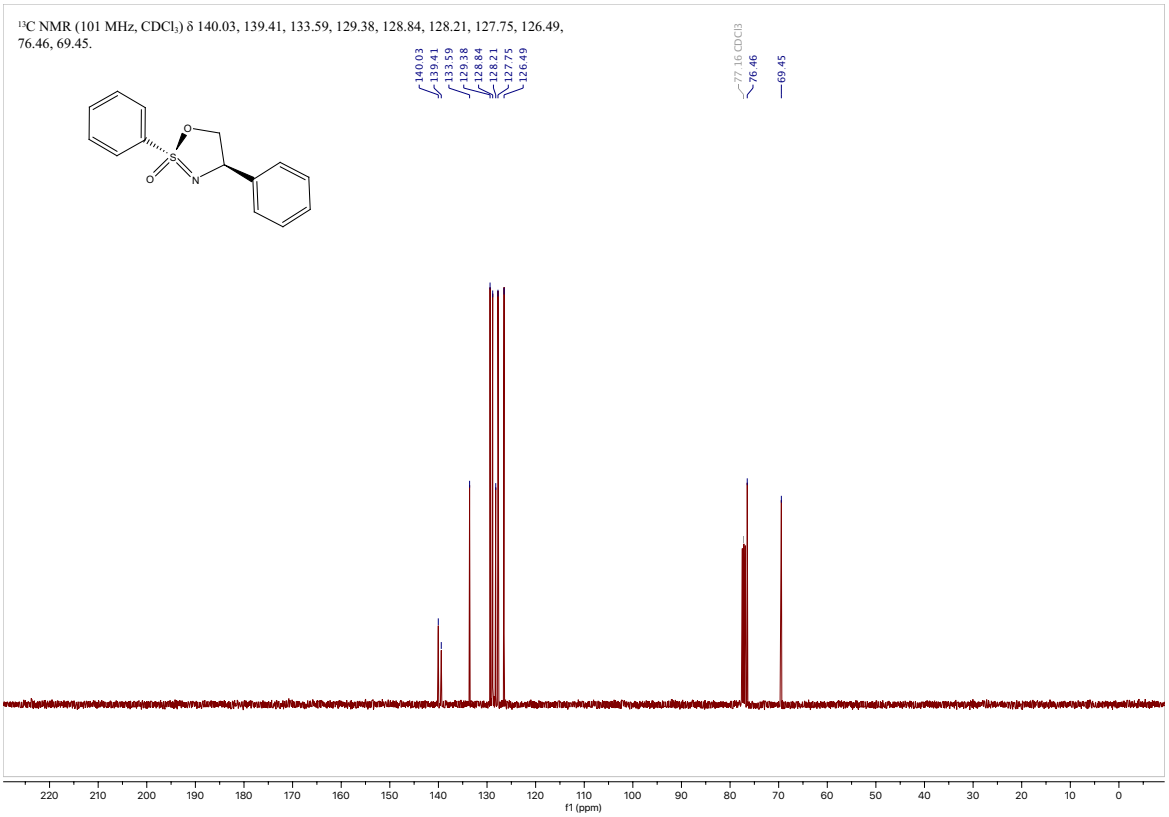


(2*S*,4*R*)-2,4-Diphenyl-4,5-dihydro-1,2,3-oxathiazole 2-oxide (7b)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.94 (m, 2H), 7.64 (ddt, *J* = 8.5, 7.0, 1.5 Hz, 1H), 7.59 – 7.51 (m, 4H), 7.43 – 7.37 (m, 2H), 7.36 – 7.30 (m, 1H), 5.29 (dd, *J* = 7.5, 7.0 Hz, 1H), 4.66 (dd, *J* = 7.5, 7.0 Hz, 1H), 4.18 (dd, *J* = 7.5, 7.5 Hz, 1H).

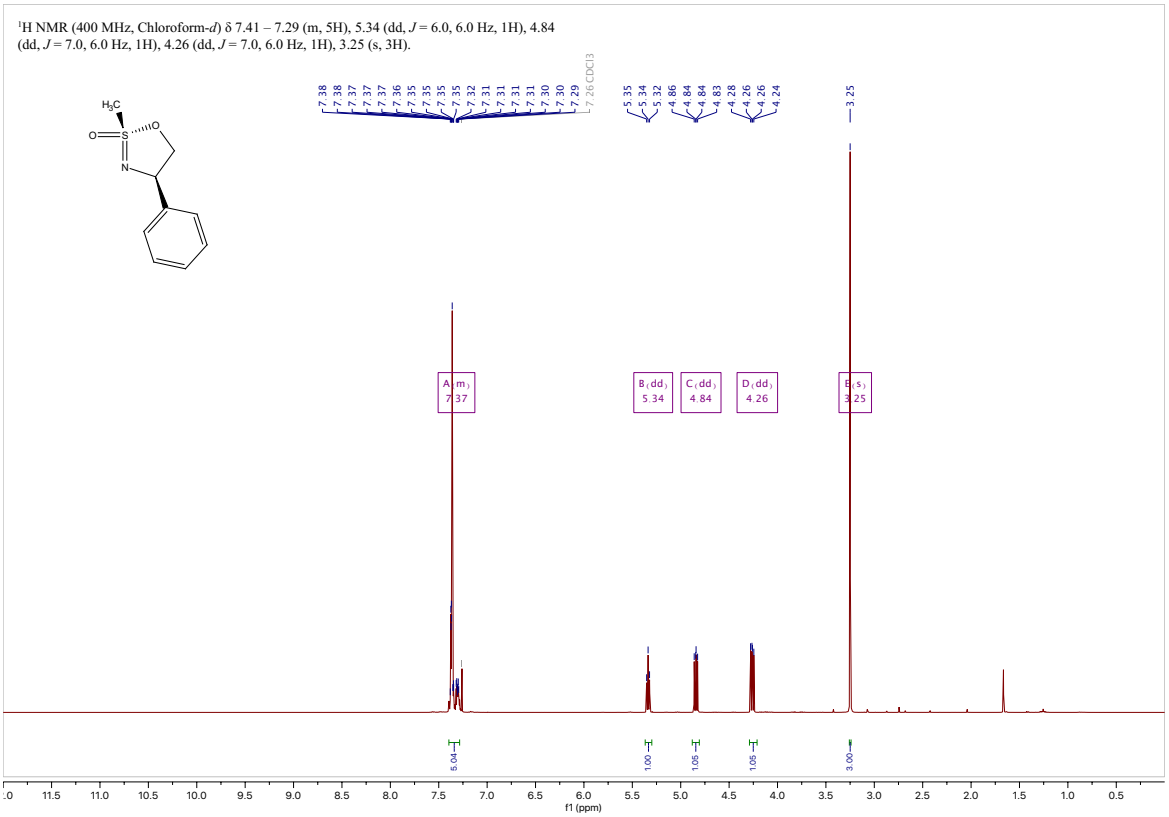


^{13}C NMR (101 MHz, $CDCl_3$) δ 140.03, 139.41, 133.59, 129.38, 128.84, 128.21, 127.75, 126.49, 76.46, 69.45.

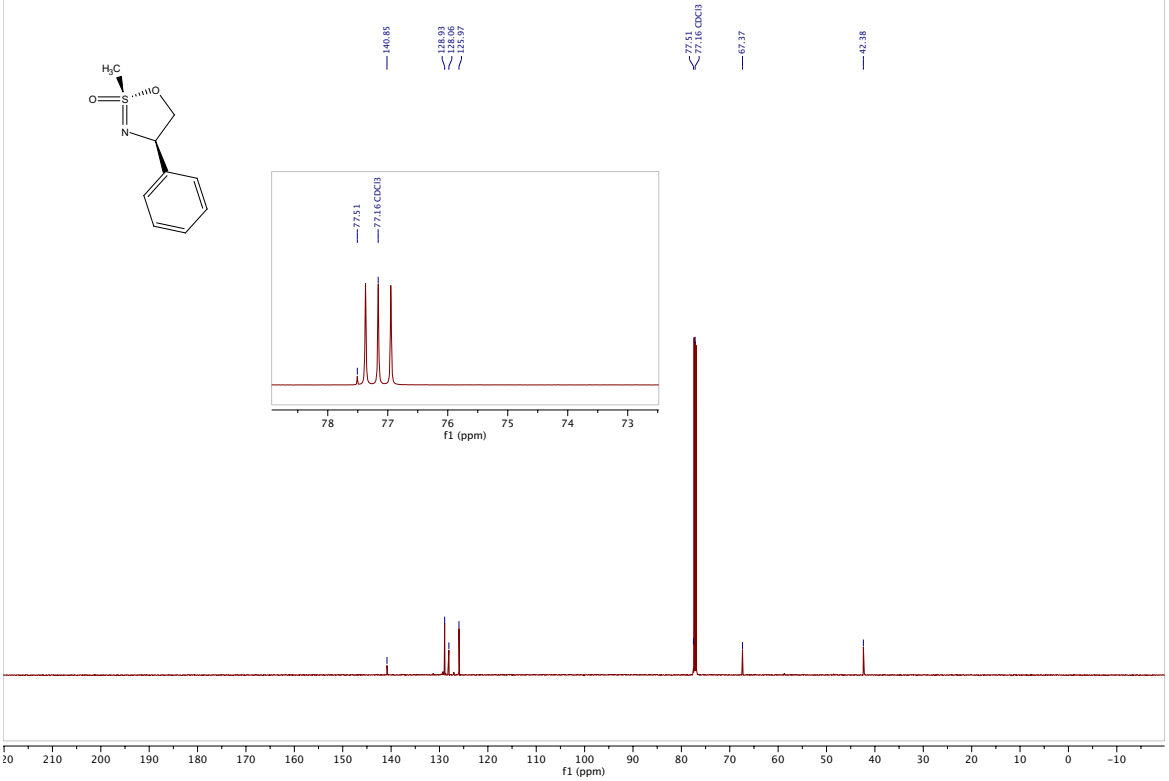


(2*R*,4*R*)-2-Methyl-4-phenyl-4,5-dihydro-1,2λ^6,3-oxathiazole 2-oxide (8a)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.29 (m, 5H), 5.34 (dd, *J* = 6.0, 6.0 Hz, 1H), 4.84 (dd, *J* = 7.0, 6.0 Hz, 1H), 4.26 (dd, *J* = 7.0, 6.0 Hz, 1H), 3.25 (s, 3H).

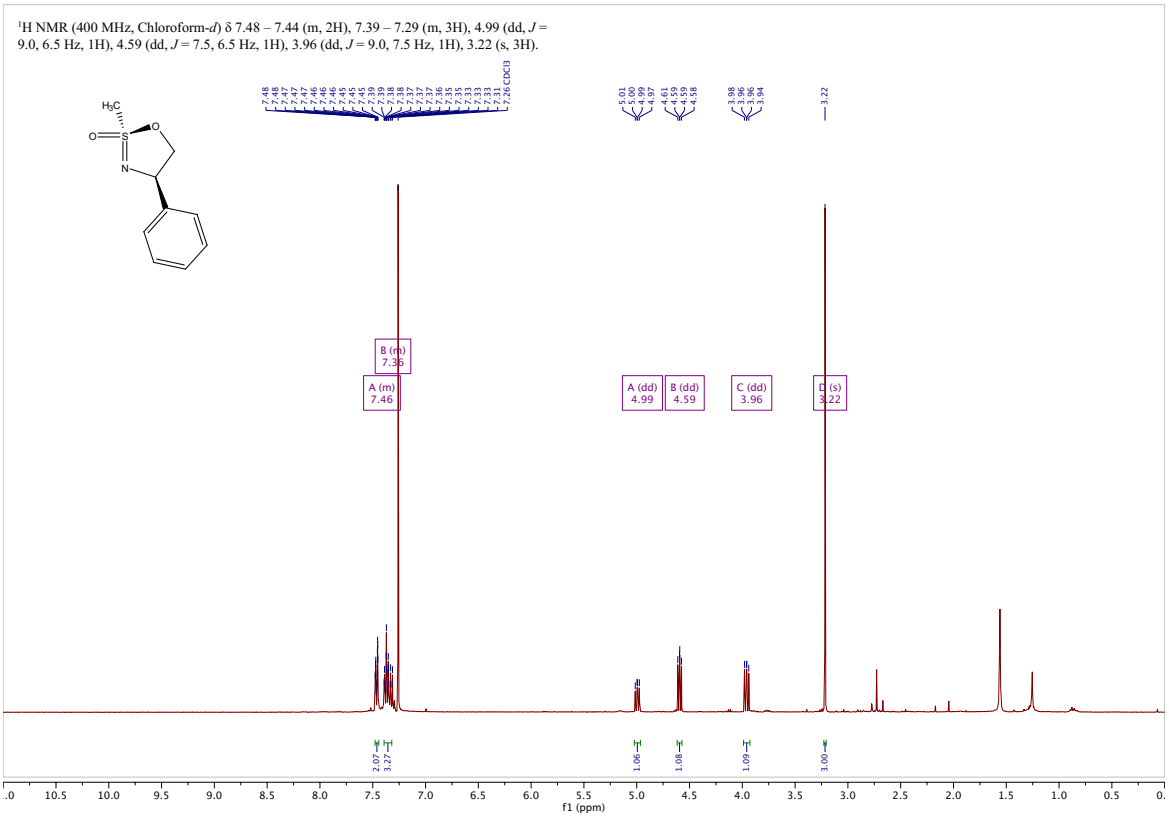


^{13}C NMR (151 MHz, $CDCl_3$) δ 140.85, 128.93, 128.06, 125.97, 77.51, 67.37, 42.38.

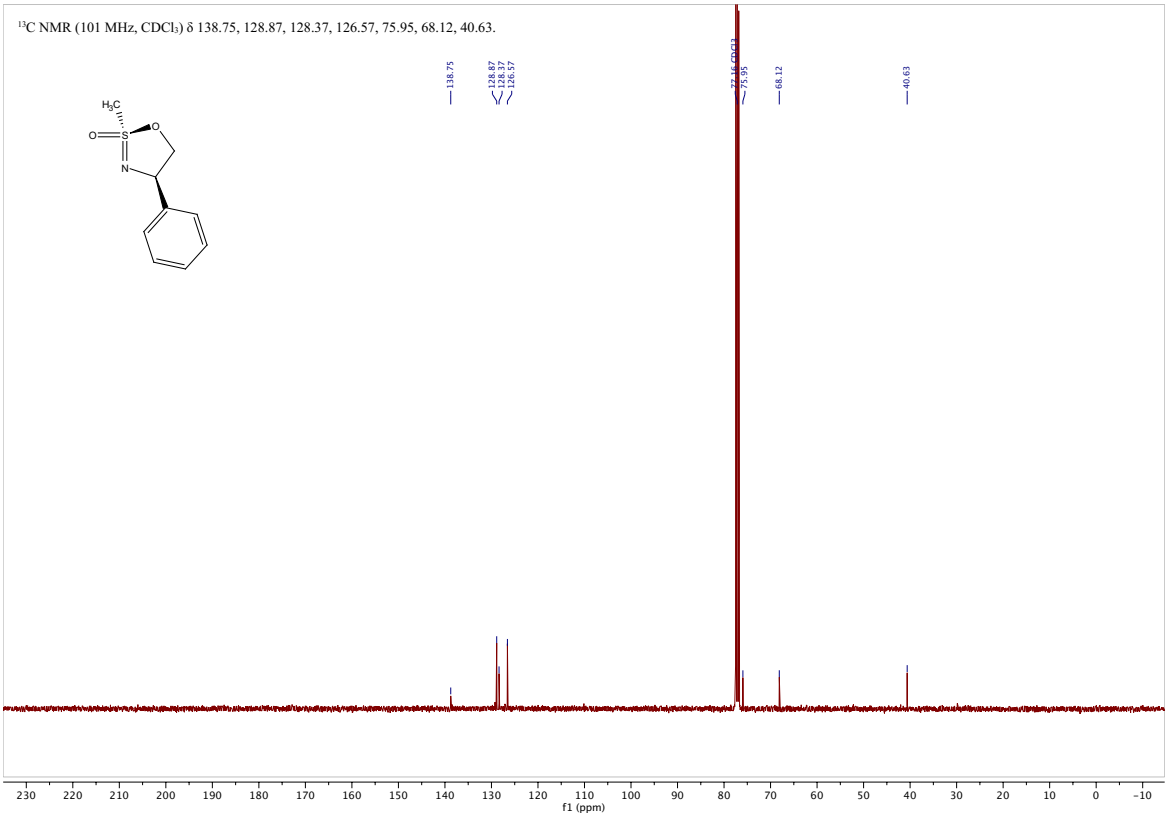


(2*S*,4*R*)-2-Methyl-4-phenyl-4,5-dihydro-1,2λ^6,3-oxathiazole 2-oxide (8b)

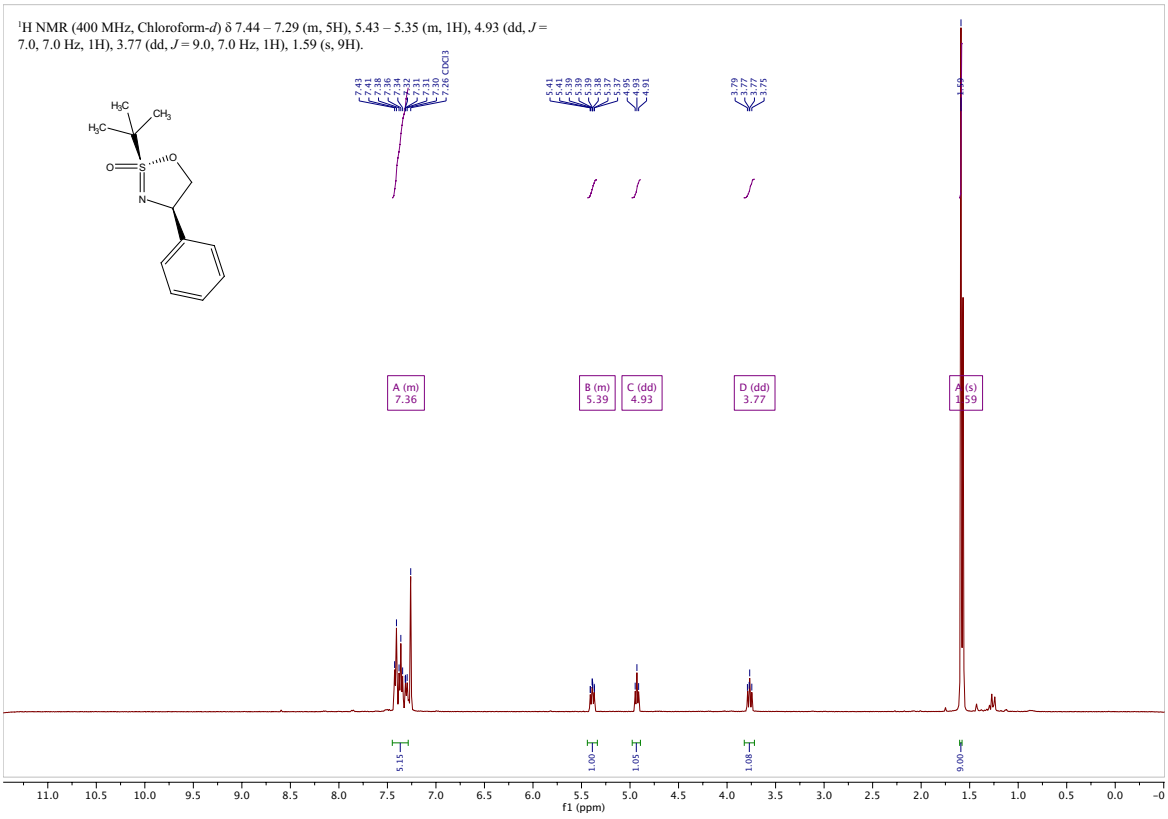
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.44 (m, 2H), 7.39 – 7.29 (m, 3H), 4.99 (dd, *J* = 9.0, 6.5 Hz, 1H), 4.59 (dd, *J* = 7.5, 6.5 Hz, 1H), 3.96 (dd, *J* = 9.0, 7.5 Hz, 1H), 3.22 (s, 3H).

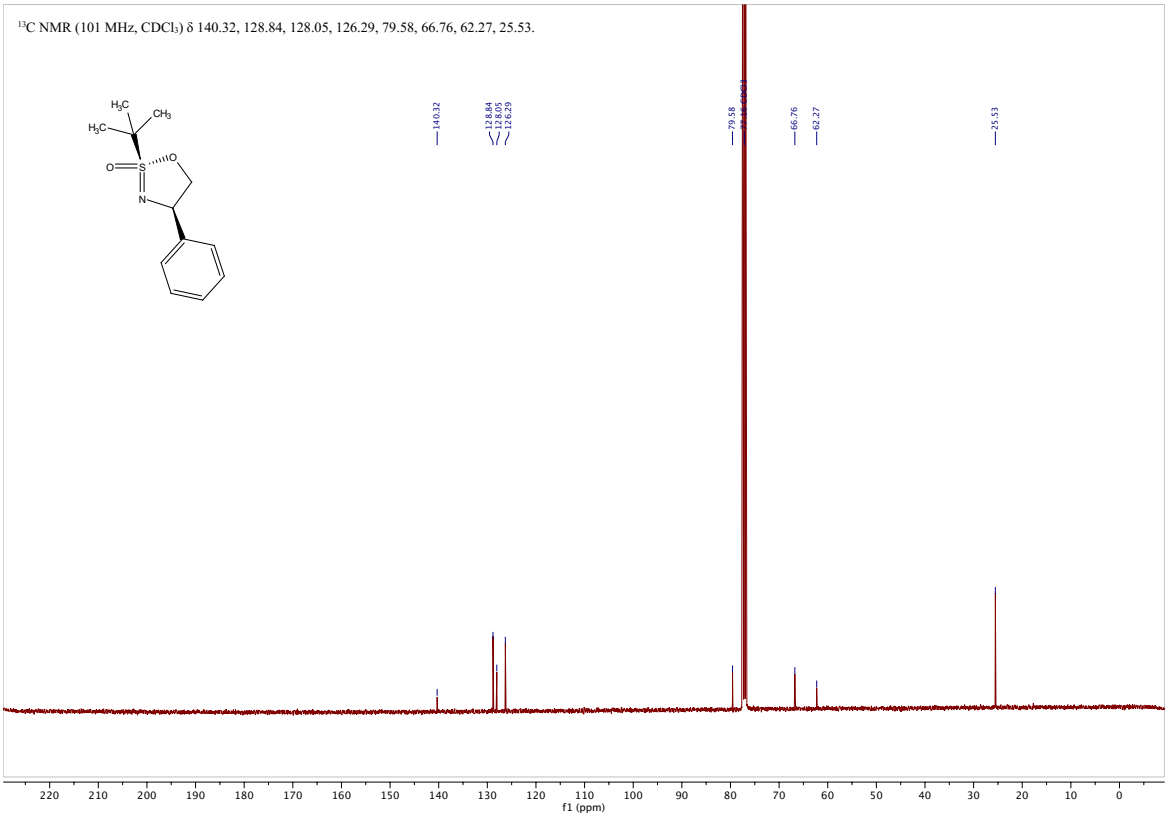


^{13}C NMR (101 MHz, $CDCl_3$) δ 138.75, 128.87, 128.37, 126.57, 75.95, 68.12, 40.63.



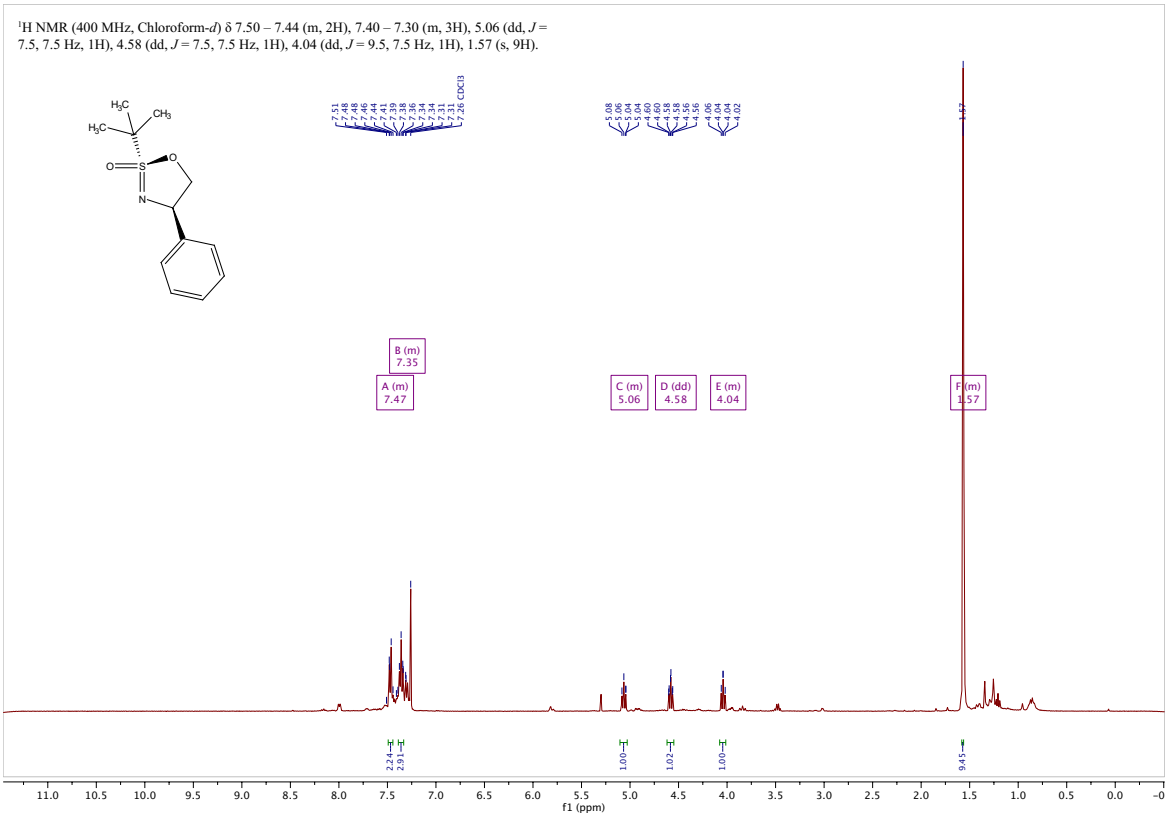
(2*R*,4*R*)-2-(*tert*-Butyl)-4-phenyl-4,5-dihydro-1,2λ^6,3-oxathiazole 2-oxide (9a)



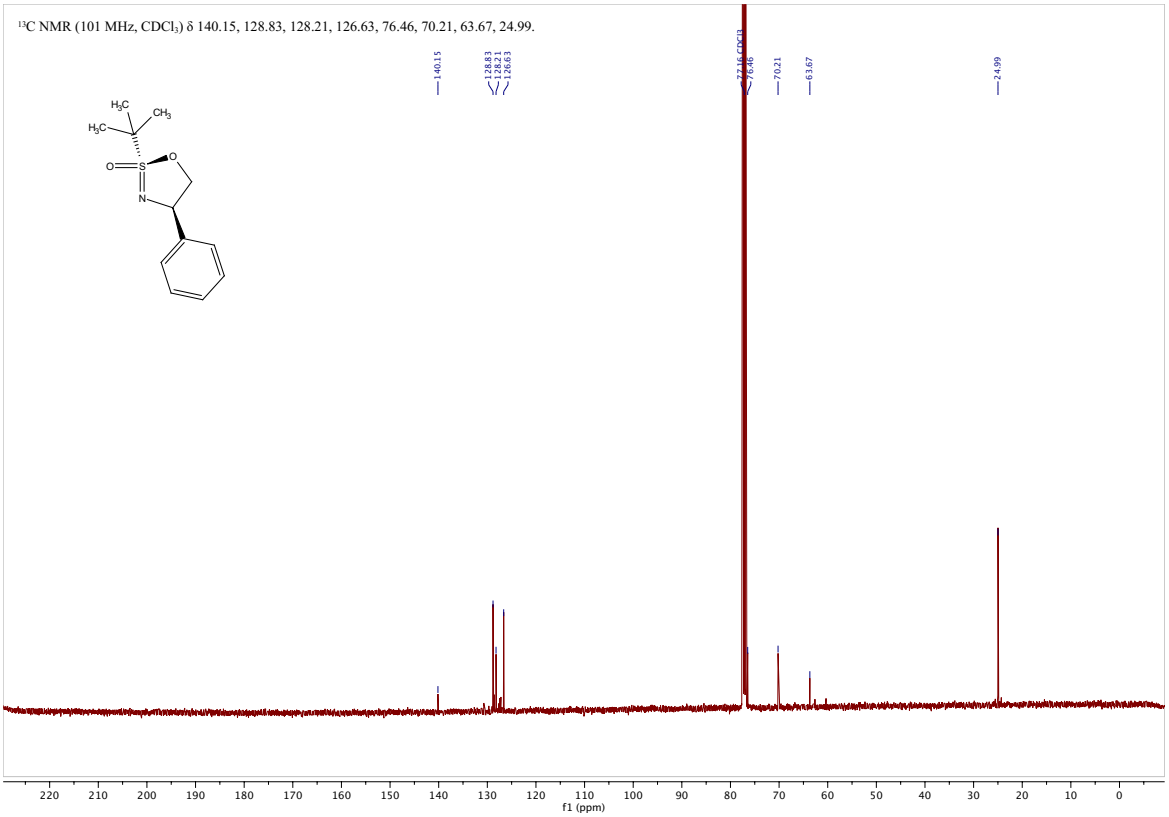


(2*S*,4*R*)-2-(*tert*-Butyl)-4-phenyl-4,5-dihydro-1,2λ^6,3-oxathiazole 2-oxide (9b)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 – 7.44 (m, 2H), 7.40 – 7.30 (m, 3H), 5.06 (dd, *J* = 7.5, 7.5 Hz, 1H), 4.58 (dd, *J* = 7.5, 7.5 Hz, 1H), 4.04 (dd, *J* = 9.5, 7.5 Hz, 1H), 1.57 (s, 9H).

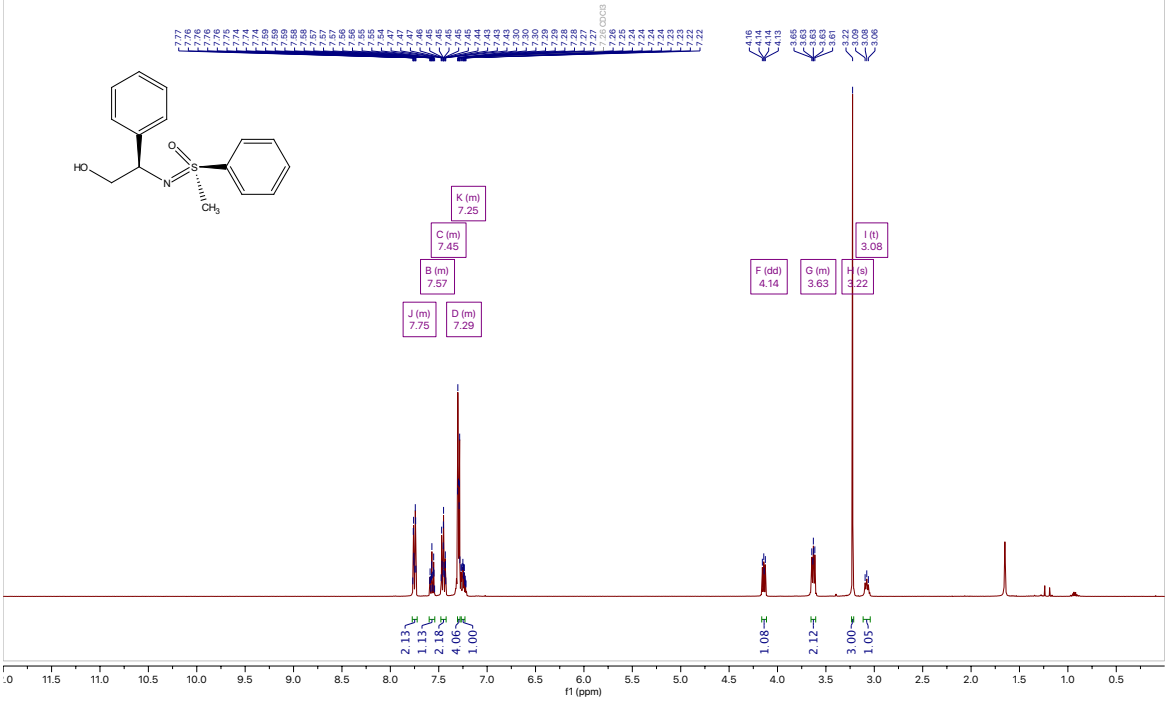


^{13}C NMR (101 MHz, $CDCl_3$) δ 140.15, 128.83, 128.21, 126.63, 76.46, 70.21, 63.67, 24.99.

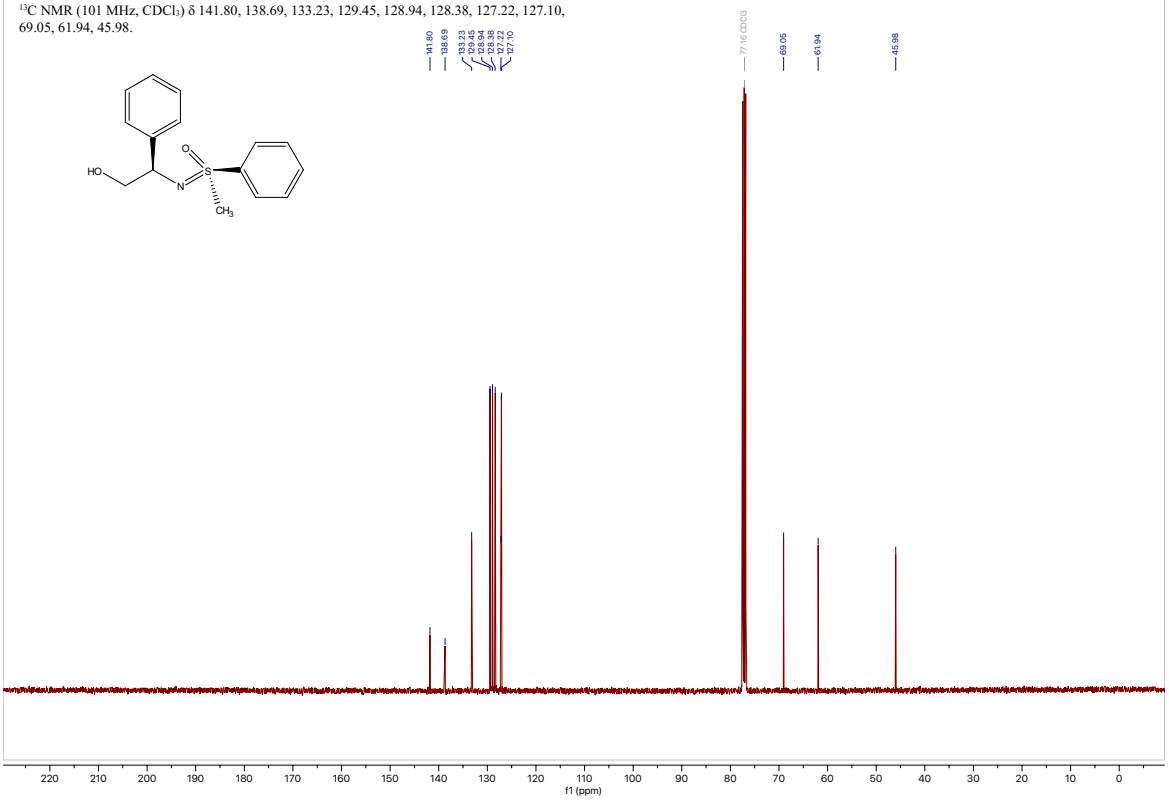


(*S*)-(((*R*)-2-Hydroxy-1-phenylethyl)imino)(methyl)(phenyl)-λ^6-sulfanone (12a)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 – 7.73 (m, 2H), 7.60 – 7.54 (m, 1H), 7.49 – 7.42 (m, 2H), 7.31 – 7.28 (m, 4H), 7.27 – 7.22 (m, 1H), 4.14 (dd, *J* = 7.0, 5.5 Hz, 1H), 3.65 – 3.61 (m, 2H), 3.22 (s, 3H), 3.08 (t, *J* = 7.0 Hz, 1H).

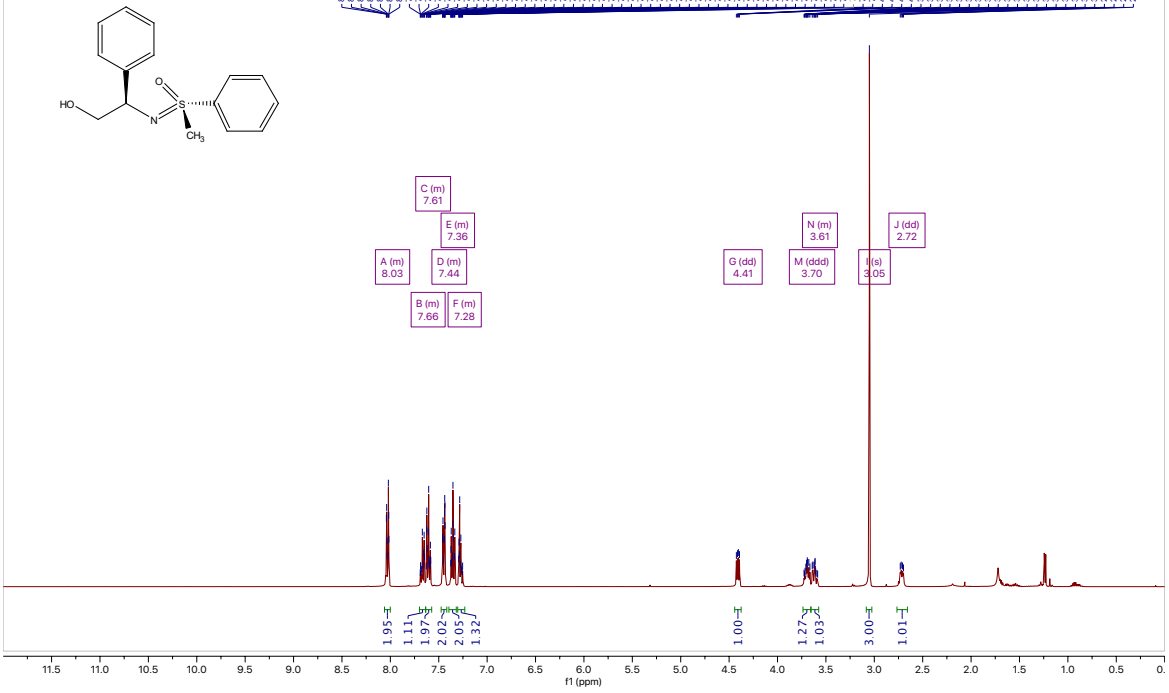


^{13}C NMR (101 MHz, $CDCl_3$) δ 141.80, 138.69, 133.23, 129.45, 128.94, 128.38, 127.22, 127.10, 69.05, 61.94, 45.98.

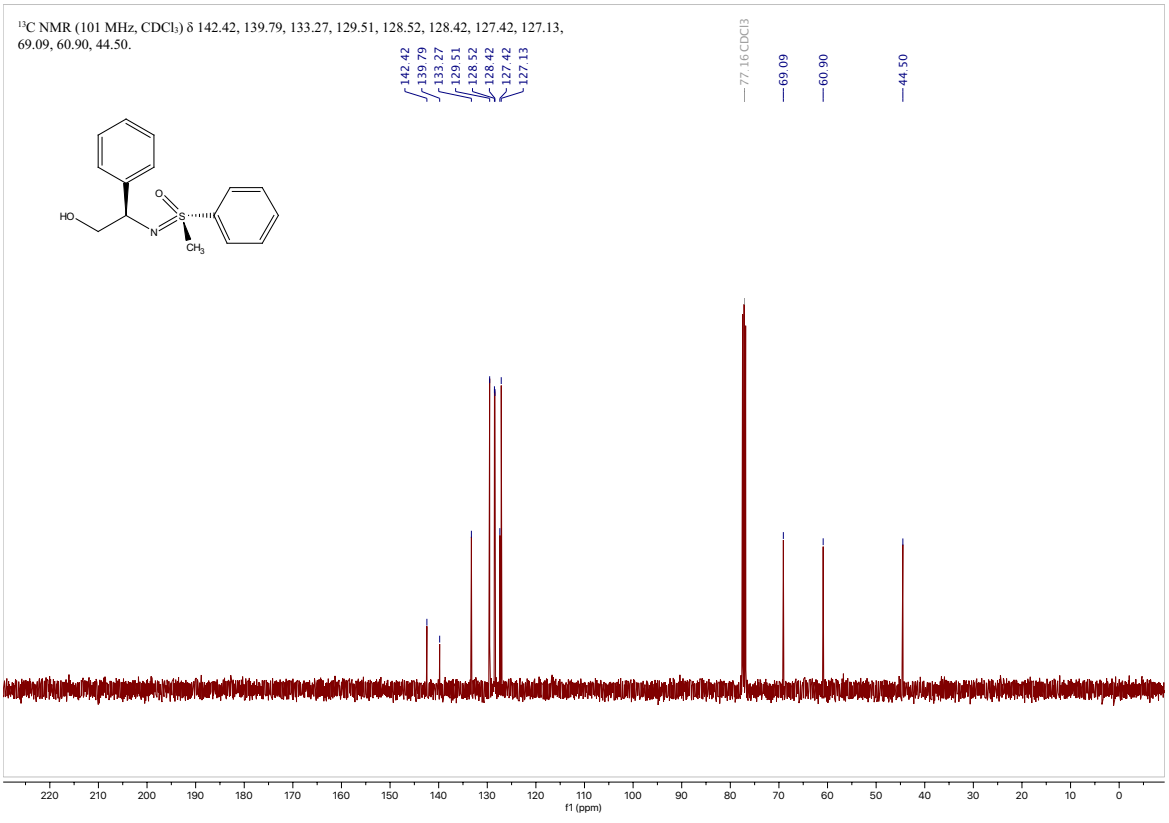


(*R*)-(((*R*)-2-Hydroxy-1-phenylethyl)imino)(methyl)(phenyl)-λ^6-sulfanone (12b)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 – 8.01 (m, 2H), 7.70 – 7.64 (m, 1H), 7.63 – 7.58 (m, 2H), 7.48 – 7.43 (m, 2H), 7.39 – 7.32 (m, 2H), 7.31 – 7.25 (m, 1H), 4.41 (dd, *J* = 8.0, 4.5 Hz, 1H), 3.70 (ddd, *J* = 10.5, 8.5, 4.5 Hz, 1H), 3.65 – 3.57 (m, 1H), 3.05 (s, 3H), 2.72 (dd, *J* = 10.5, 4.5 Hz, 1H).

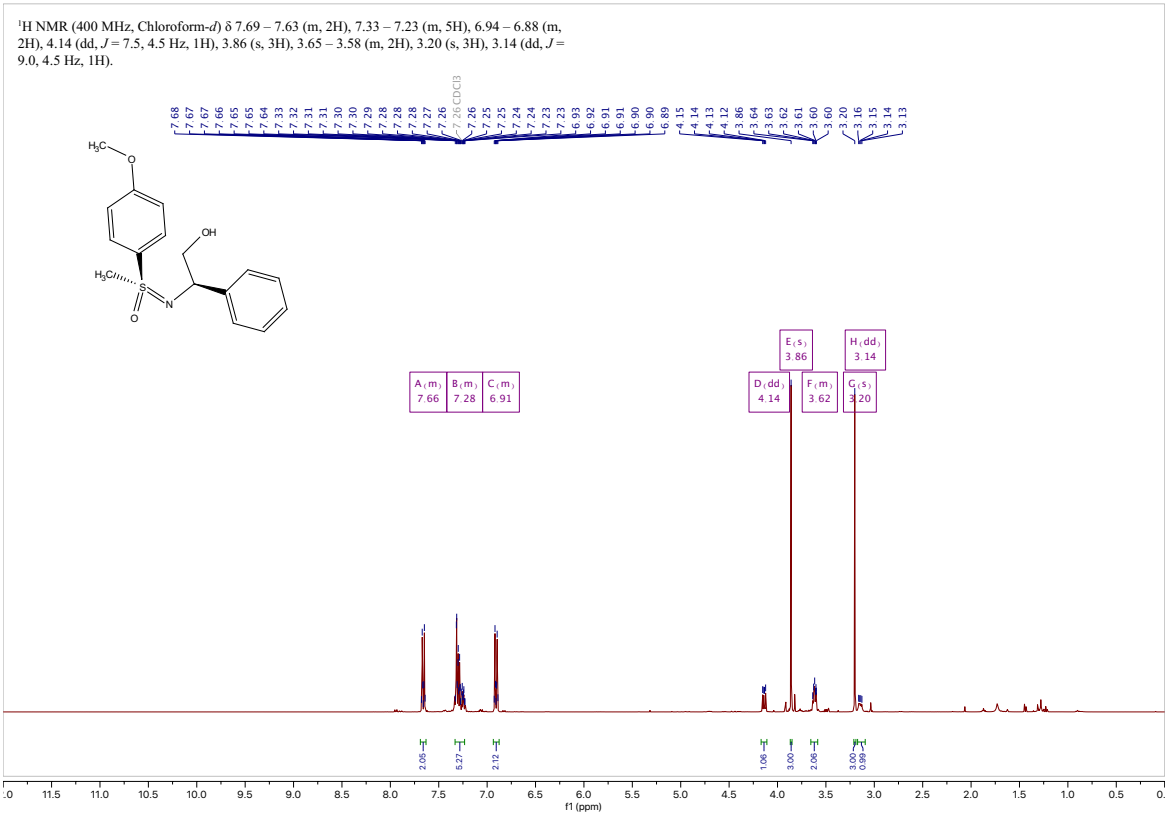


^{13}C NMR (101 MHz, $CDCl_3$) δ 142.42, 139.79, 133.27, 129.51, 128.52, 128.42, 127.42, 127.13, 69.09, 60.90, 44.50.

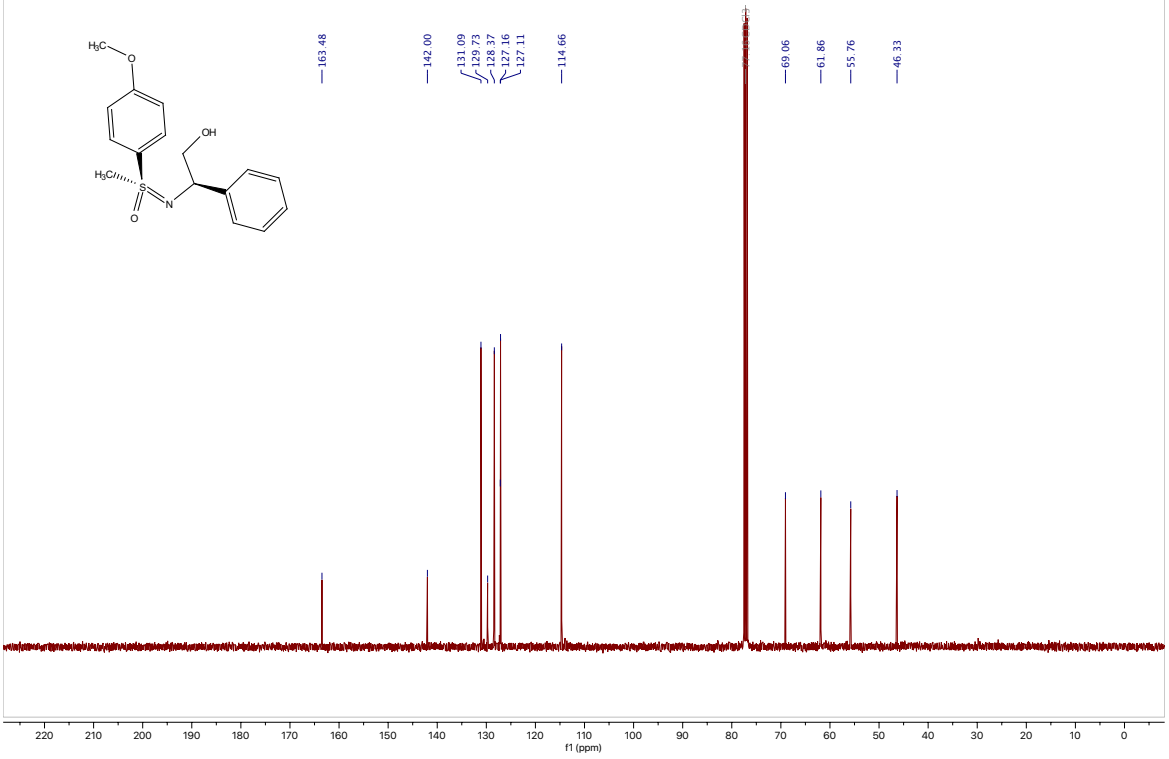


(*S*)-(((*R*)-2-Hydroxy-1-phenylethyl)imino)(4-methoxyphenyl)(methyl)-λ^6-sulfanone (13a)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 – 7.63 (m, 2H), 7.33 – 7.23 (m, 5H), 6.94 – 6.88 (m, 2H), 4.14 (dd, *J* = 7.5, 4.5 Hz, 1H), 3.86 (s, 3H), 3.65 – 3.58 (m, 2H), 3.20 (s, 3H), 3.14 (dd, *J* = 9.0, 4.5 Hz, 1H).

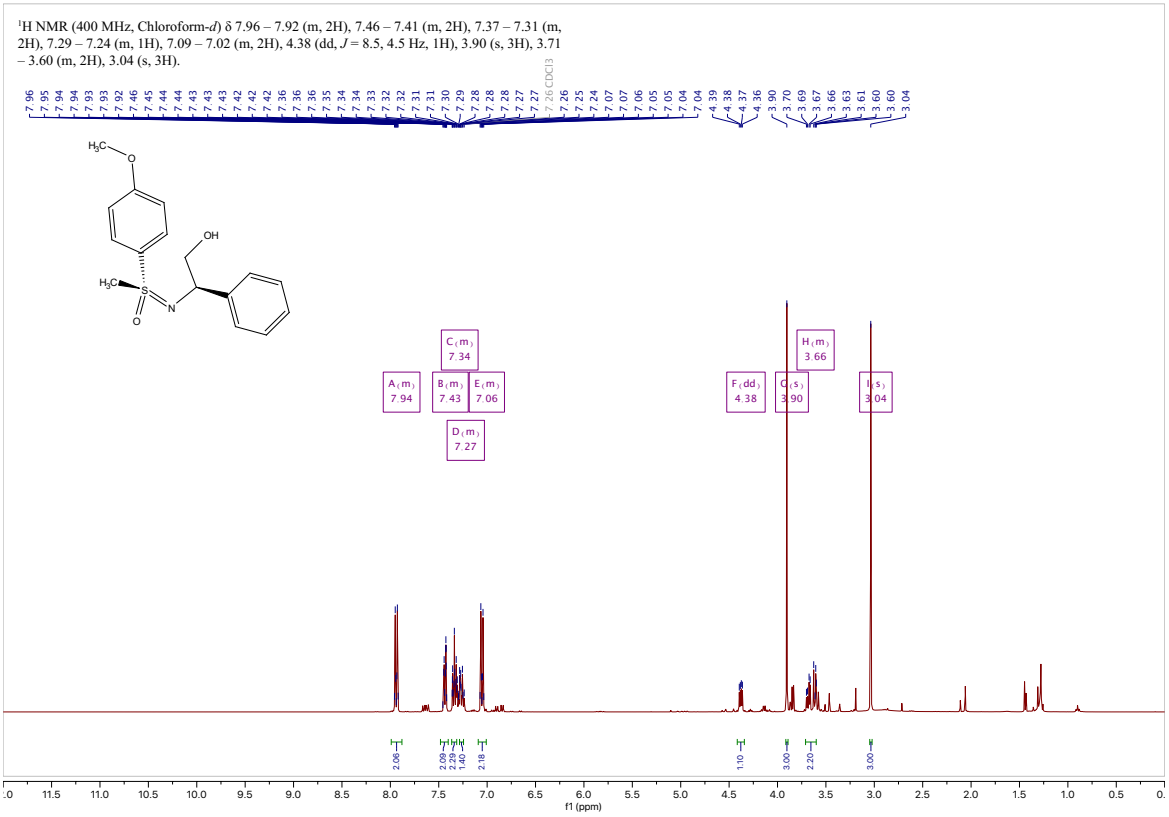


^{13}C NMR (101 MHz, $CDCl_3$) δ 163.48, 142.00, 131.09, 129.73, 128.37, 127.16, 127.11, 114.66, 69.06, 61.86, 55.76, 46.33.

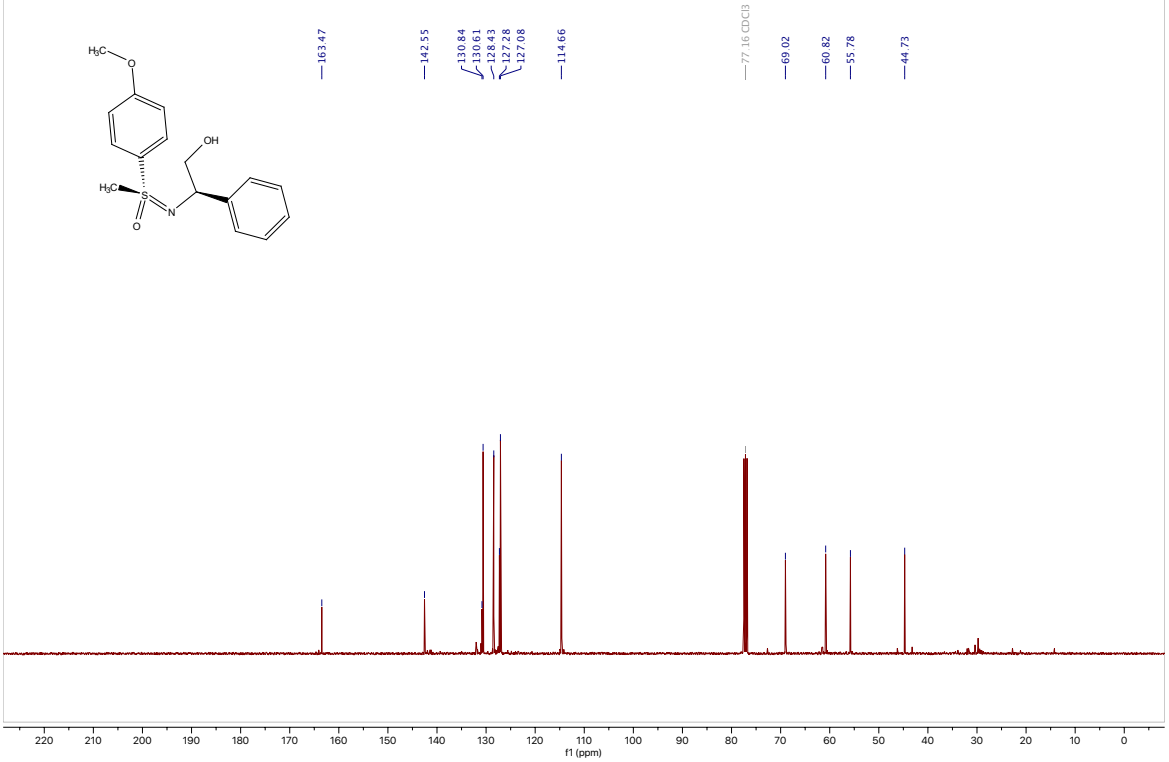


(*R*)-(((*R*)-2-Hydroxy-1-phenylethyl)imino)(4-methoxyphenyl)(methyl)-λ^6-sulfanone (13b)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 – 7.92 (m, 2H), 7.46 – 7.41 (m, 2H), 7.37 – 7.31 (m, 2H), 7.29 – 7.24 (m, 1H), 7.09 – 7.02 (m, 2H), 4.38 (dd, *J* = 8.5, 4.5 Hz, 1H), 3.90 (s, 3H), 3.71 – 3.60 (m, 2H), 3.04 (s, 3H).

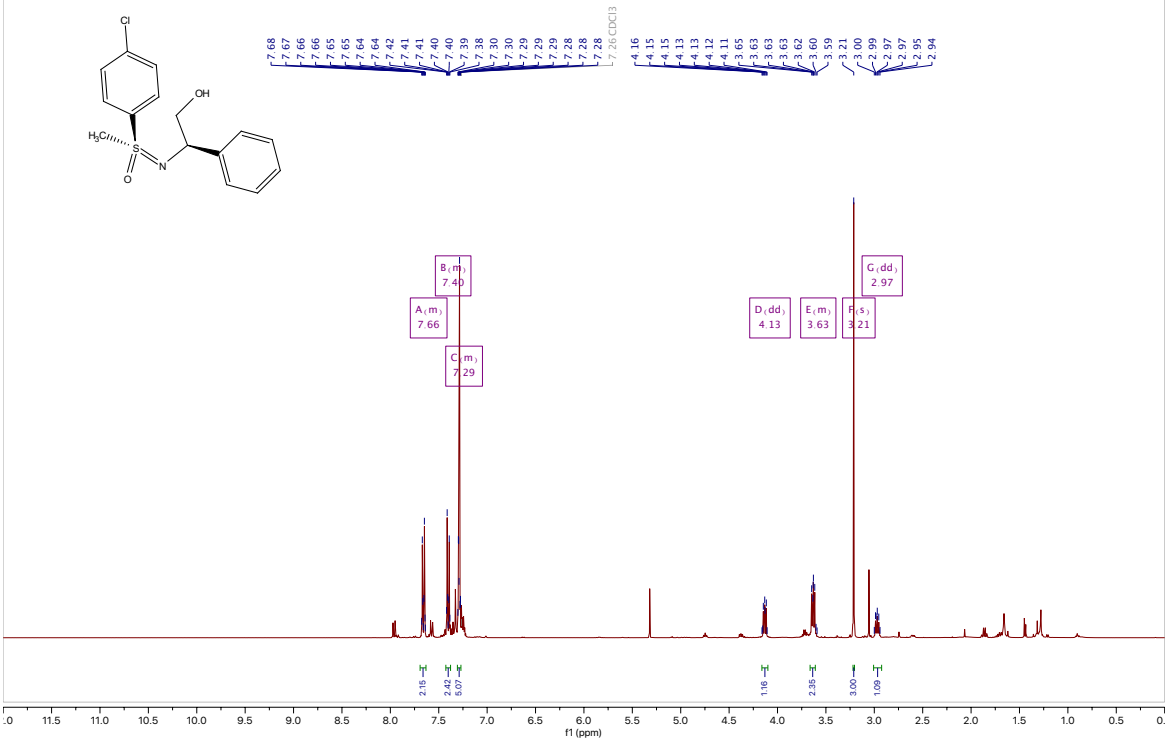


^{13}C NMR (101 MHz, $CDCl_3$) δ 163.47, 142.55, 130.84, 130.61, 128.43, 127.28, 127.08, 114.66, 69.02, 60.82, 55.78, 44.73.

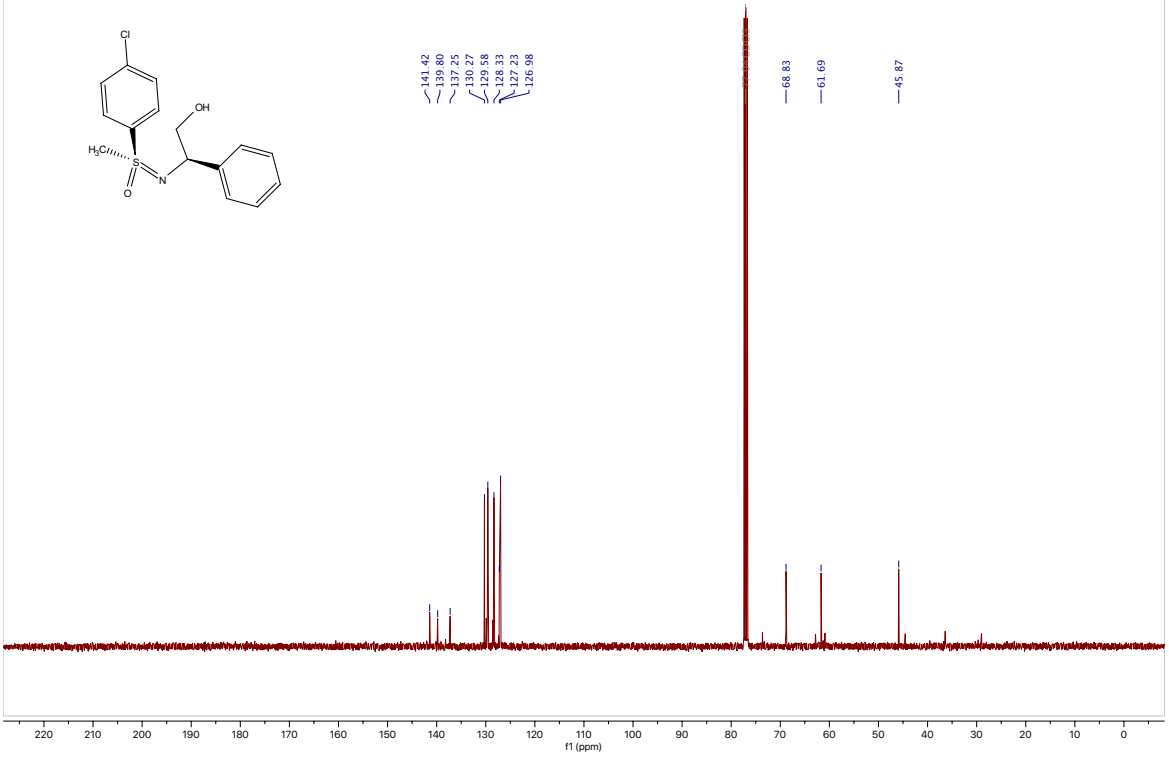


(*S*)-(4-Chlorophenyl)(((*R*)-2-hydroxy-1-phenylethyl)imino)(methyl)-λ^6-sulfanone (14a)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 – 7.63 (m, 2H), 7.43 – 7.38 (m, 2H), 7.31 – 7.27 (m, 5H), 4.13 (dd, *J* = 7.0, 5.5 Hz, 1H), 3.65 – 3.60 (m, 2H), 3.21 (s, 3H), 2.97 (dd, *J* = 7.5, 6.0 Hz, 1H).

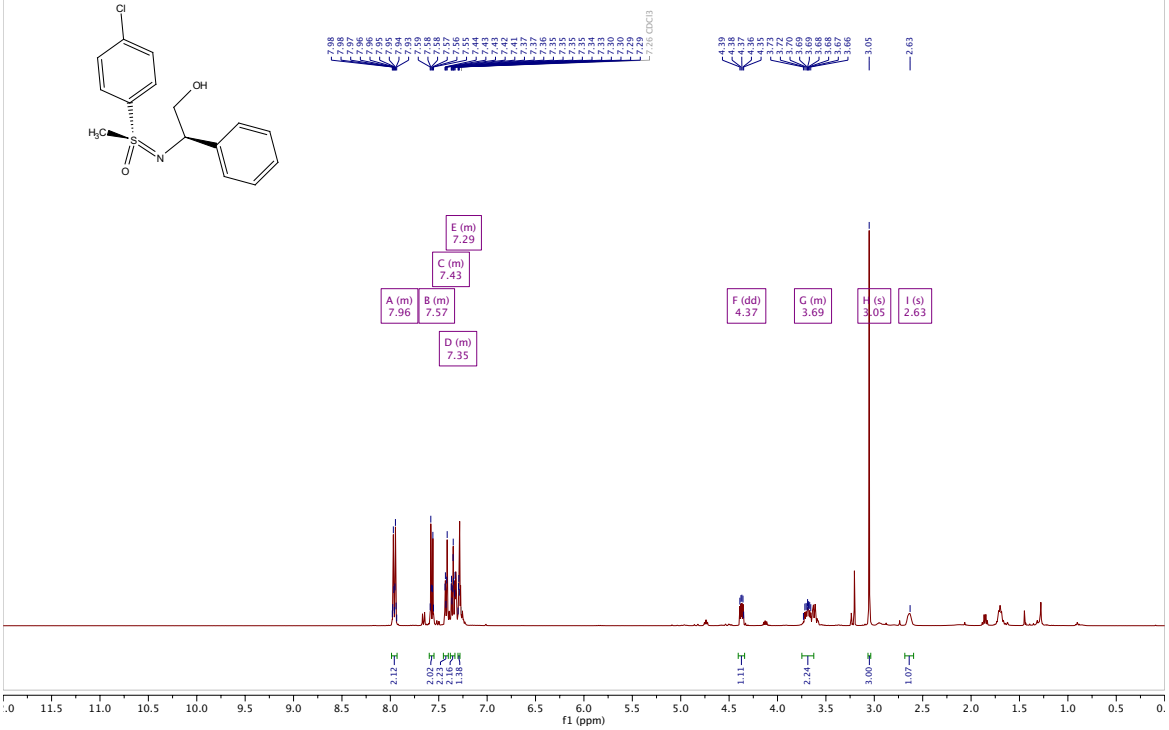


^{13}C NMR (101 MHz, $CDCl_3$) δ 141.42, 139.80, 137.25, 130.27, 129.58, 128.33, 127.23, 126.98, 68.83, 61.69, 45.87.

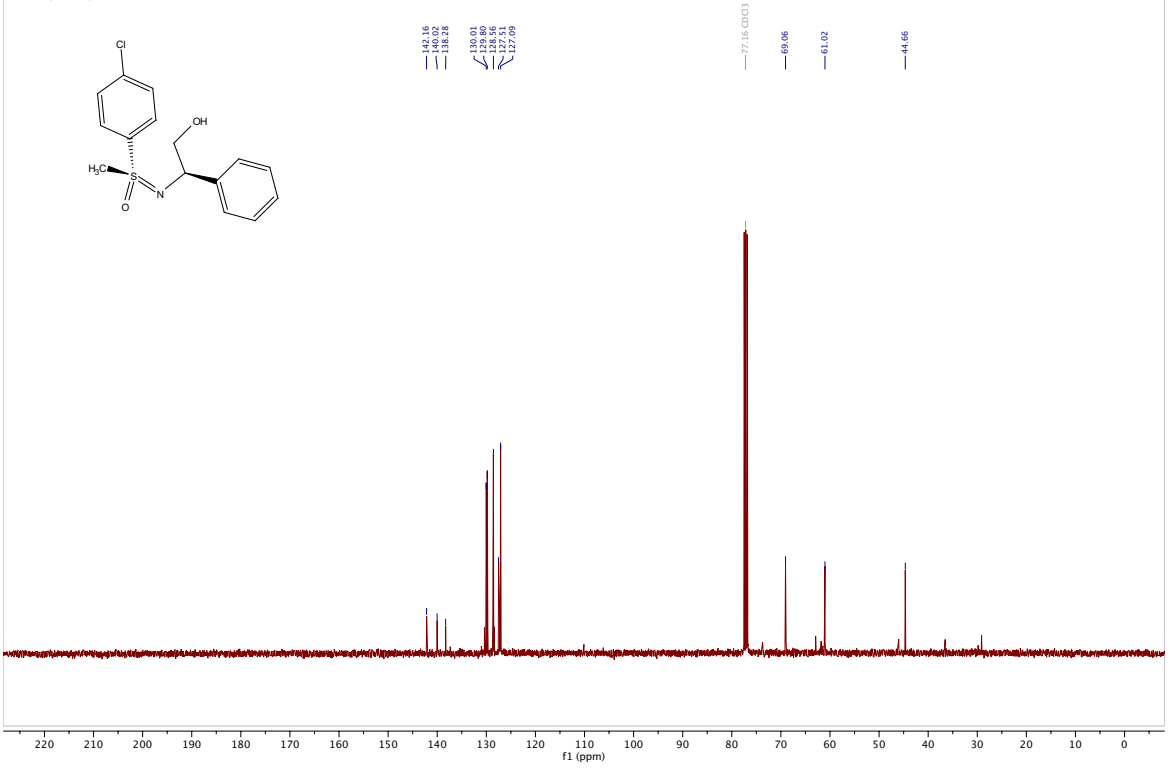


(*R*)-(4-Chlorophenyl)(((*R*)-2-hydroxy-1-phenylethyl)imino)(methyl)-λ^6-sulfanone (14b)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 – 7.93 (m, 2H), 7.60 – 7.55 (m, 2H), 7.45 – 7.40 (m, 2H), 7.38 – 7.33 (m, 2H), 7.30 – 7.27 (m, 1H), 4.37 (dd, *J* = 8.5, 4.5 Hz, 1H), 3.74 – 3.65 (m, 2H), 3.05 (s, 3H), 2.63 (s, 1H).

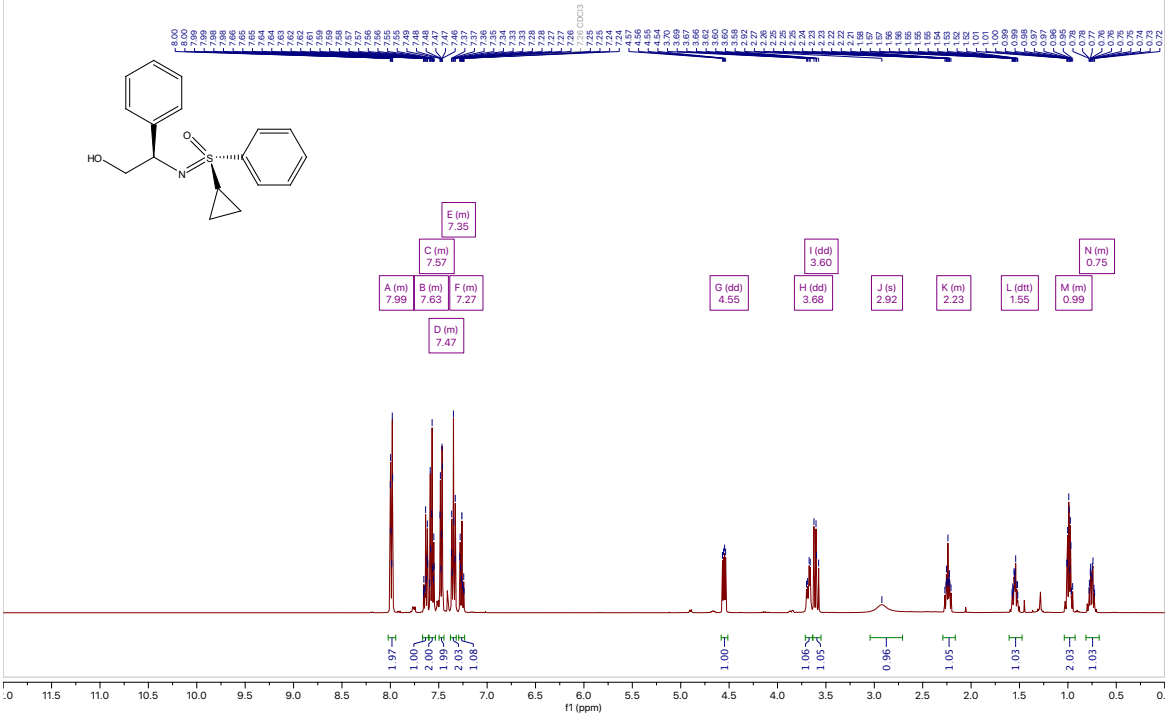


^{13}C NMR (101 MHz, $CDCl_3$) δ 142.16, 140.02, 138.28, 130.01, 129.80, 128.56, 127.51, 127.09, 69.06, 61.02, 44.66.

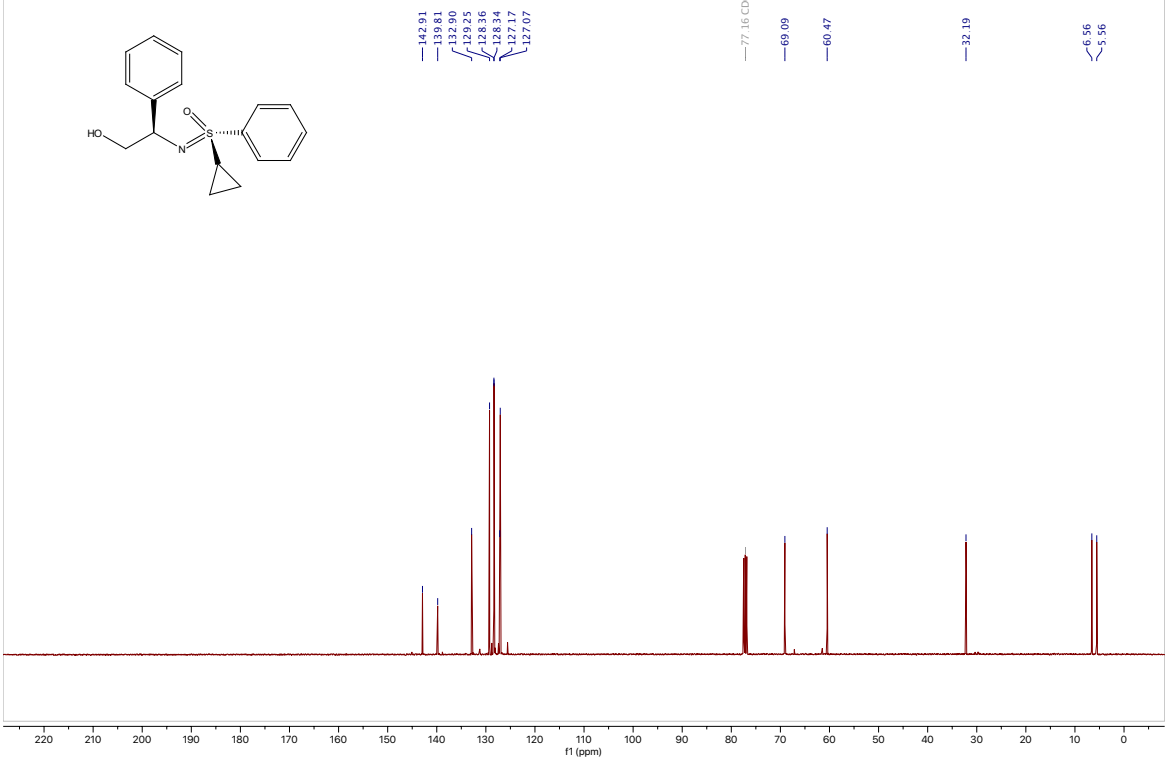


(*R*)-Cyclopropyl(((*R*)-2-hydroxy-1-phenylethyl)imino)(phenyl)-λ^6-sulfanone (18a)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.94 (m, 2H), 7.66 – 7.61 (m, 1H), 7.60 – 7.54 (m, 2H), 7.50 – 7.45 (m, 2H), 7.38 – 7.32 (m, 2H), 7.30 – 7.23 (m, 1H), 4.55 (dd, *J* = 8.5, 4.5 Hz, 1H), 3.68 (dd, *J* = 10.5, 4.5 Hz, 1H), 3.60 (dd, *J* = 10.5, 8.5 Hz, 1H), 2.92 (s, 1H), 2.28 – 2.20 (m, 1H), 1.55 (dtt, *J* = 8.5, 4.0, 1.5 Hz, 1H), 1.04 – 0.94 (m, 2H), 0.81 – 0.70 (m, 1H).

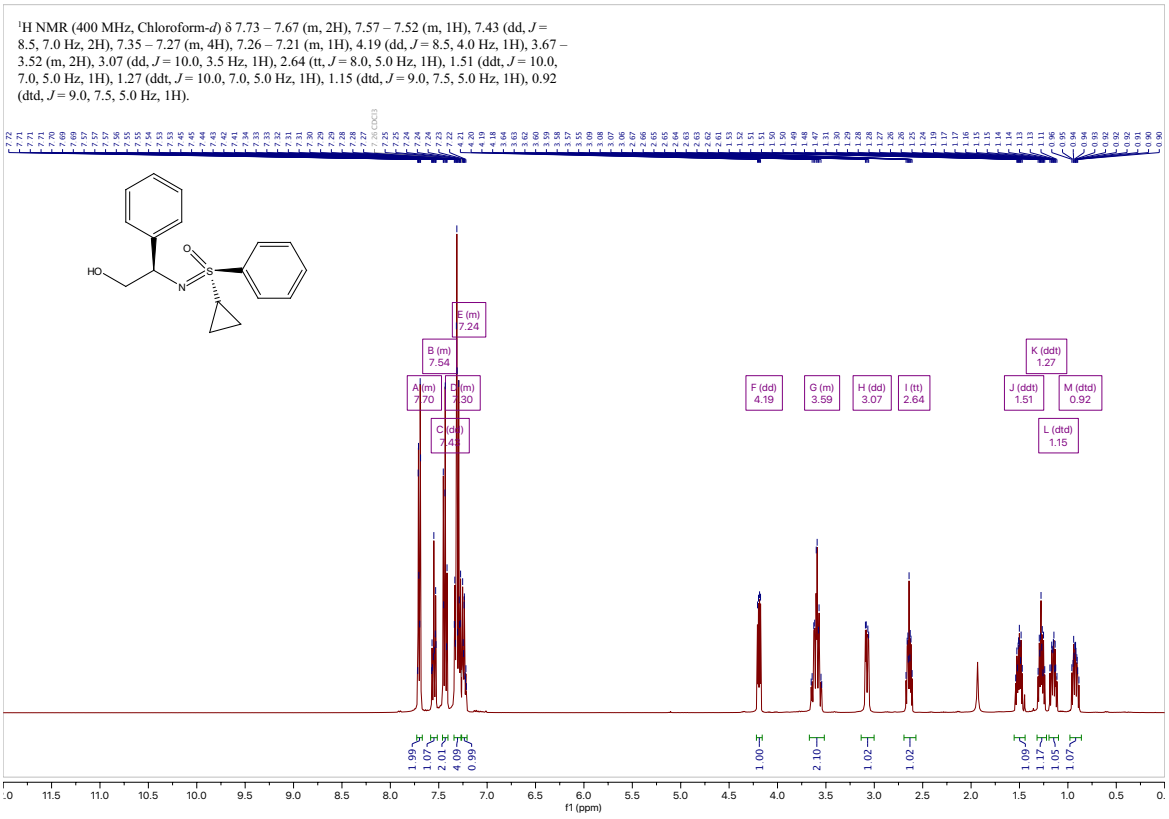


^{13}C NMR (101 MHz, $CDCl_3$) δ 142.91, 139.81, 132.90, 129.25, 128.36, 128.34, 127.17, 127.07, 69.09, 60.47, 32.19, 6.56, 5.56.

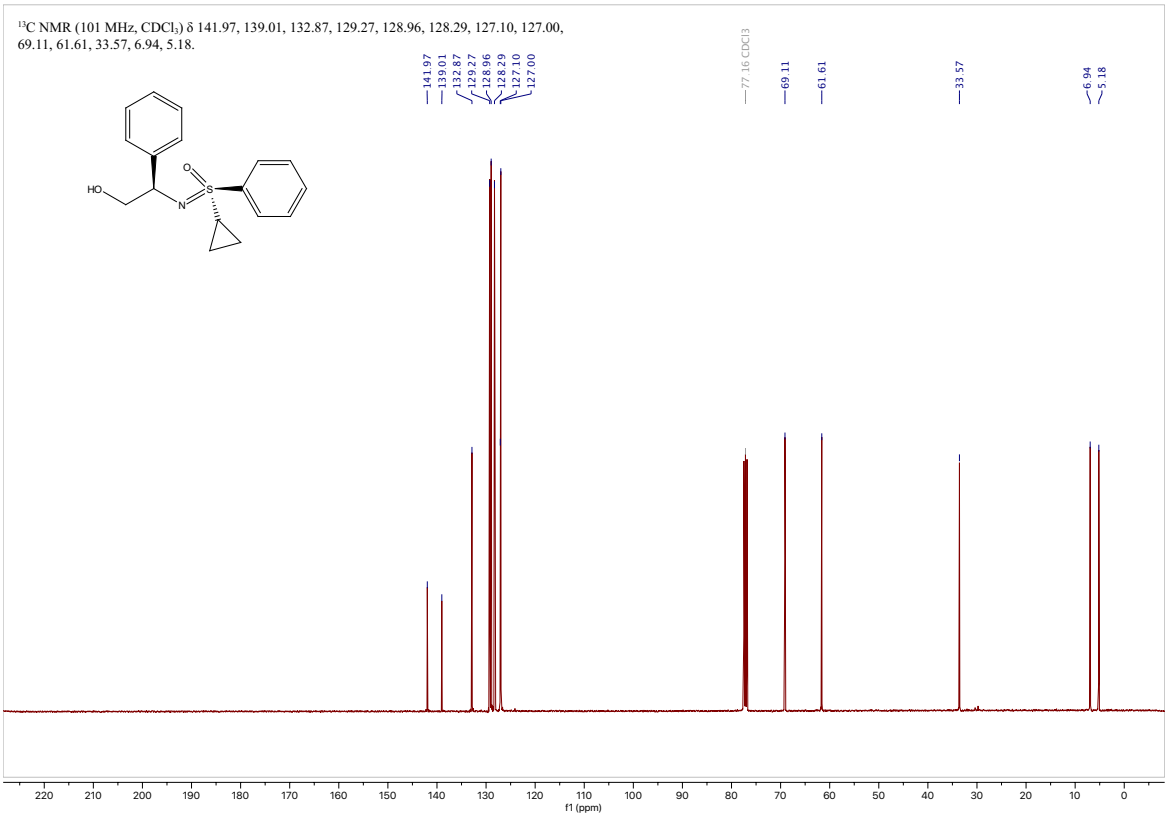


(*S*)-Cyclopropyl(((*R*)-2-hydroxy-1-phenylethyl)imino)(phenyl)-λ^6-sulfanone (18b)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 – 7.67 (m, 2H), 7.57 – 7.52 (m, 1H), 7.43 (dd, *J* = 8.5, 7.0 Hz, 2H), 7.35 – 7.27 (m, 4H), 7.26 – 7.21 (m, 1H), 4.19 (dd, *J* = 8.5, 4.0 Hz, 1H), 3.67 – 3.52 (m, 2H), 3.07 (dd, *J* = 10.0, 3.5 Hz, 1H), 2.64 (tt, *J* = 8.0, 5.0 Hz, 1H), 1.51 (ddt, *J* = 10.0, 7.0, 5.0 Hz, 1H), 1.27 (ddt, *J* = 10.0, 7.0, 5.0 Hz, 1H), 1.15 (dtd, *J* = 9.0, 7.5, 5.0 Hz, 1H), 0.92 (dtd, *J* = 9.0, 7.5, 5.0 Hz, 1H).

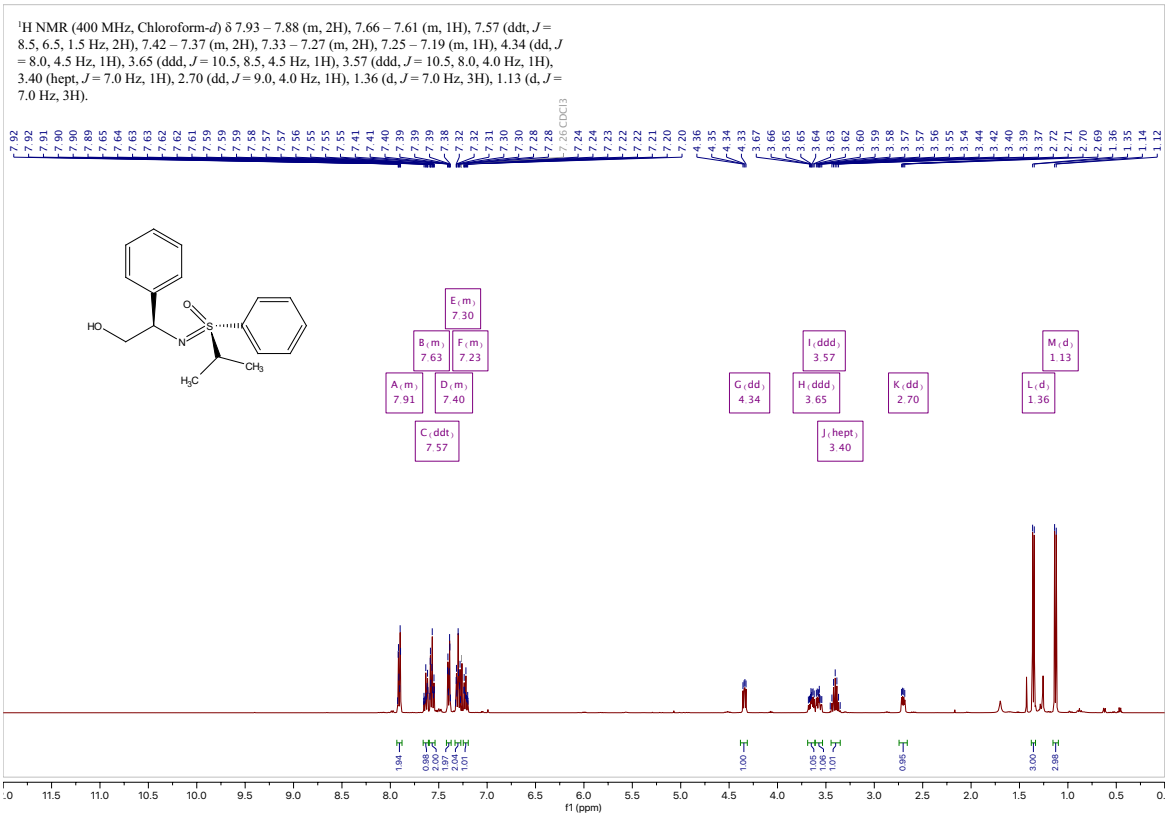


^{13}C NMR (101 MHz, $CDCl_3$) δ 141.97, 139.01, 132.87, 129.27, 128.96, 128.29, 127.10, 127.00, 69.11, 61.61, 33.57, 6.94, 5.18.

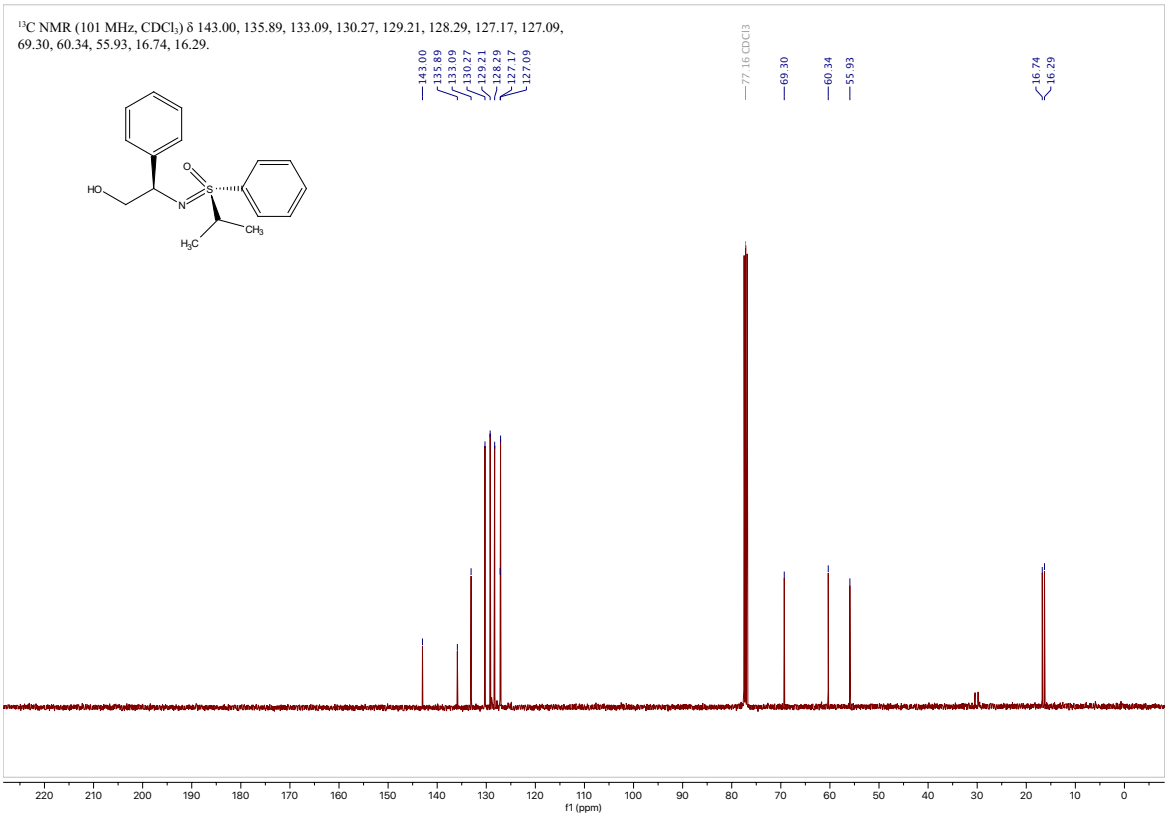


(*R*)-(((*R*)-2-Hydroxy-1-phenylethyl)imino)(isopropyl)(phenyl)-λ^6-sulfanone (19a)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.88 (m, 2H), 7.66 – 7.61 (m, 1H), 7.57 (ddt, *J* = 8.5, 6.5, 1.5 Hz, 2H), 7.42 – 7.37 (m, 2H), 7.33 – 7.27 (m, 2H), 7.25 – 7.19 (m, 1H), 4.34 (dd, *J* = 8.0, 4.5 Hz, 1H), 3.65 (ddd, *J* = 10.5, 8.5, 4.5 Hz, 1H), 3.57 (ddd, *J* = 10.5, 8.0, 4.0 Hz, 1H), 3.40 (hept, *J* = 7.0 Hz, 1H), 2.70 (dd, *J* = 9.0, 4.0 Hz, 1H), 1.36 (d, *J* = 7.0 Hz, 3H), 1.13 (d, *J* = 7.0 Hz, 3H).

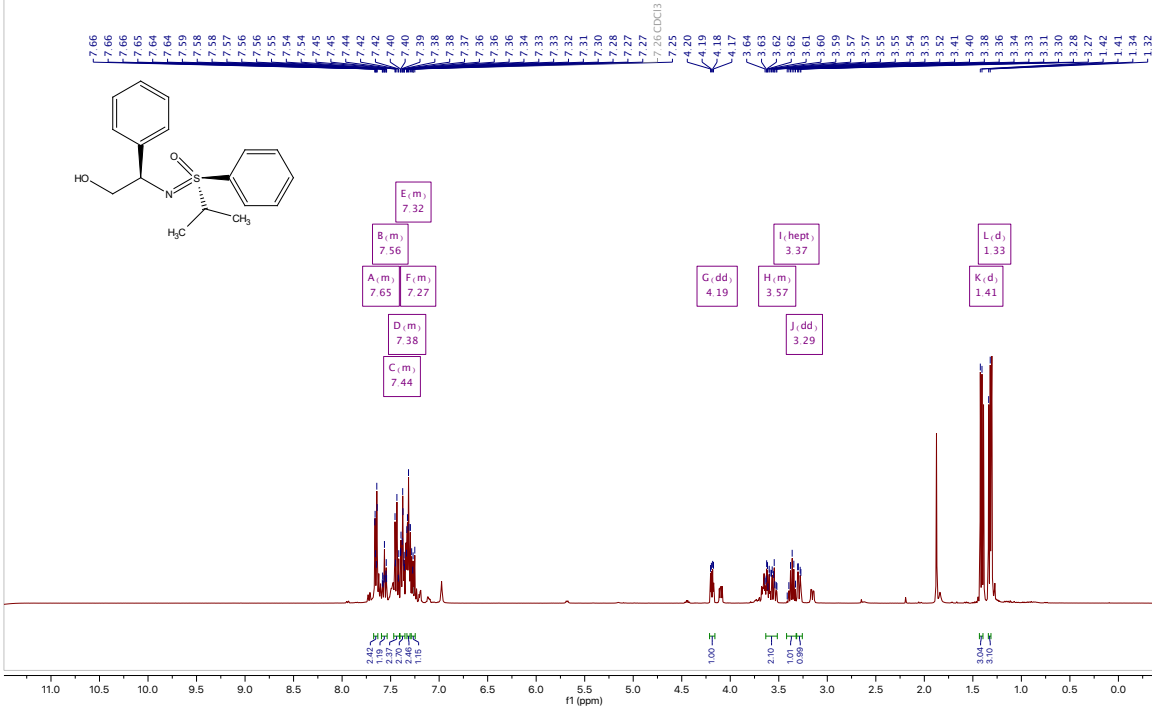


^{13}C NMR (101 MHz, $CDCl_3$) δ 143.00, 135.89, 133.09, 130.27, 129.21, 128.29, 127.17, 127.09, 69.30, 60.34, 55.93, 16.74, 16.29.

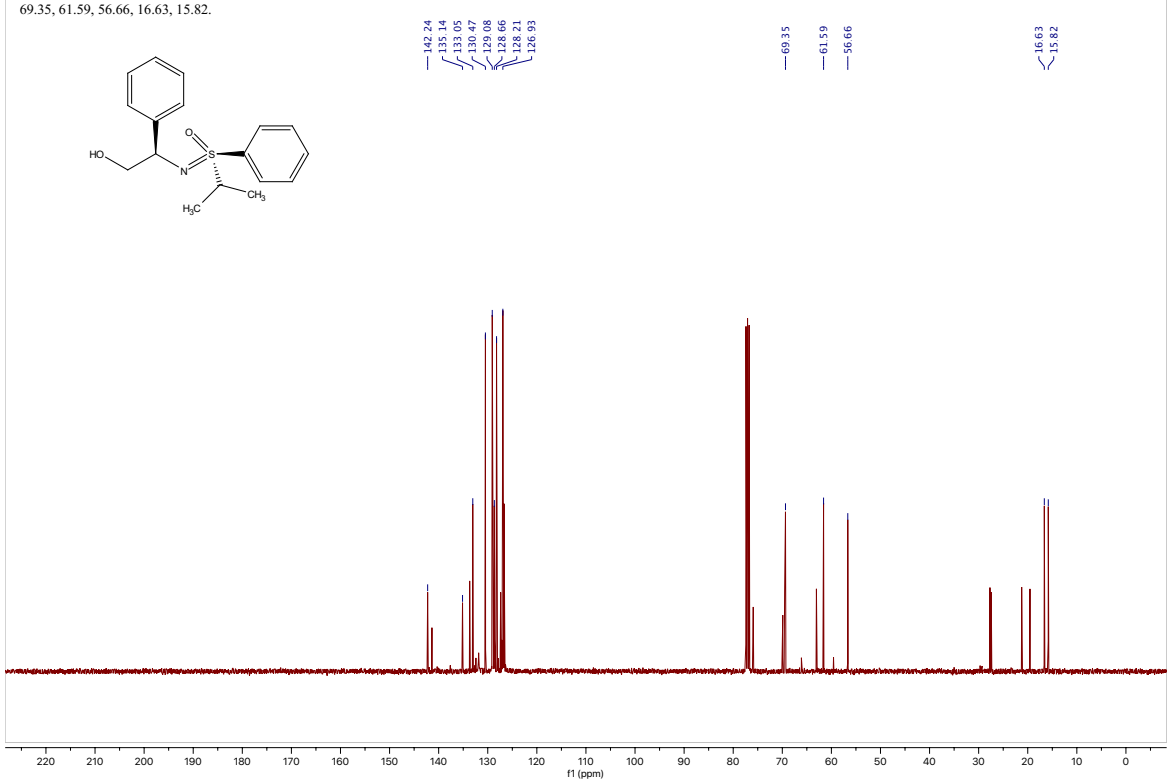


(*S*)-(((*R*)-2-Hydroxy-1-phenylethyl)imino)(isopropyl)(phenyl)-λ^6-sulfanone (19b)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.63 (m, 2H), 7.59 – 7.54 (m, 1H), 7.47 – 7.41 (m, 2H), 7.40 – 7.35 (m, 2H), 7.34 – 7.30 (m, 2H), 7.29 – 7.25 (m, 1H), 4.19 (dd, *J* = 8.5, 3.5 Hz, 1H), 3.63 – 3.52 (m, 2H), 3.37 (hept, *J* = 6.5 Hz, 1H), 3.29 (dd, *J* = 10.5, 3.0 Hz, 1H), 1.41 (d, *J* = 6.5 Hz, 3H), 1.33 (d, *J* = 6.5 Hz, 3H).

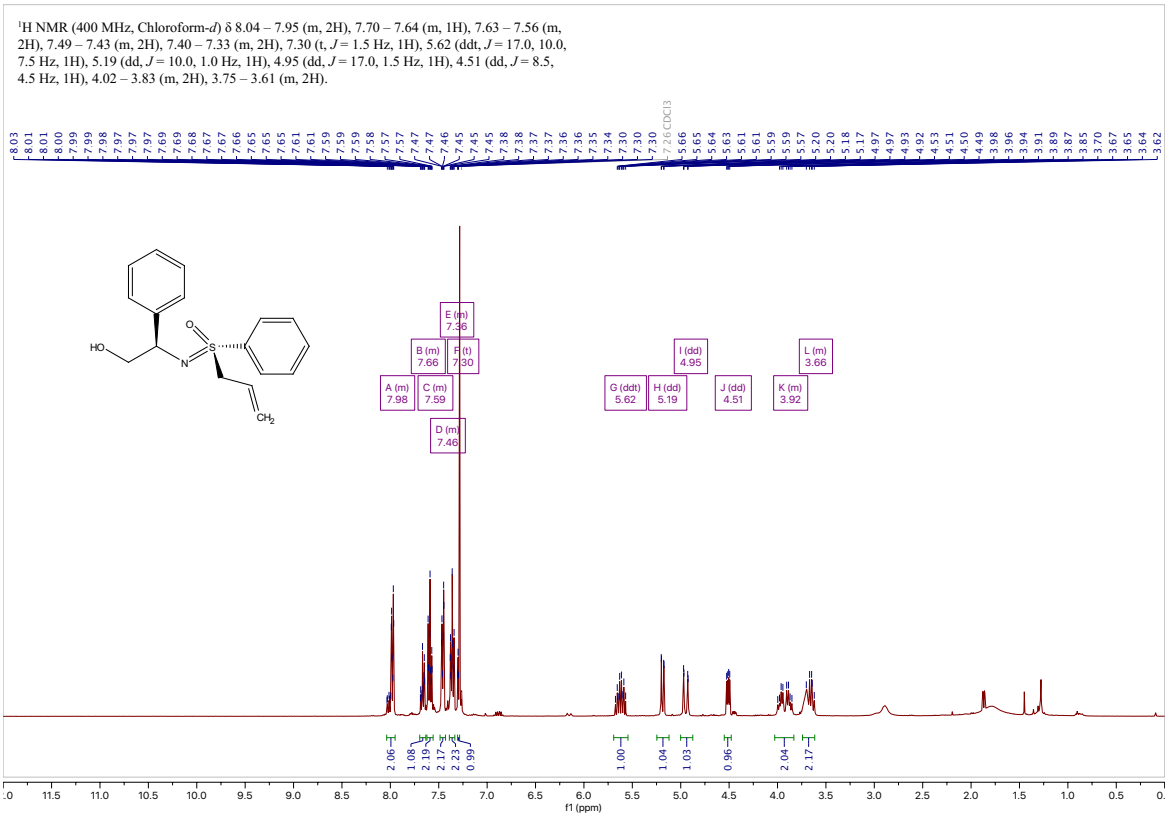


^{13}C NMR (101 MHz, $CDCl_3$) δ 142.24, 135.14, 133.05, 130.47, 129.08, 128.66, 128.21, 126.93, 69.35, 61.59, 56.66, 16.63, 15.82.

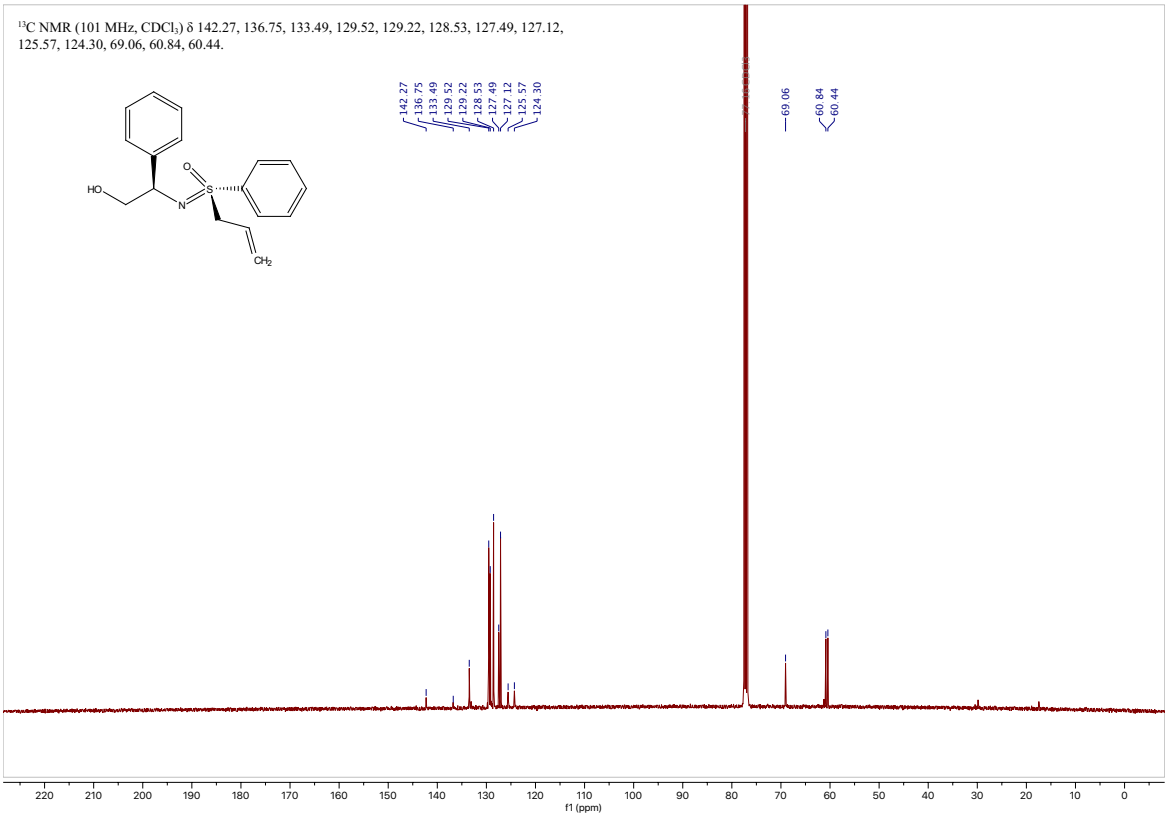


(*R*)-Allyl(((*R*)-2-hydroxy-1-phenylethyl)imino)(phenyl)-λ^6-sulfanone (21a)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 – 7.95 (m, 2H), 7.70 – 7.64 (m, 1H), 7.63 – 7.56 (m, 2H), 7.49 – 7.43 (m, 2H), 7.40 – 7.33 (m, 2H), 7.30 (t, *J* = 1.5 Hz, 1H), 5.62 (ddt, *J* = 17.0, 10.0, 7.5 Hz, 1H), 5.19 (dd, *J* = 10.0, 1.0 Hz, 1H), 4.95 (dd, *J* = 17.0, 1.5 Hz, 1H), 4.51 (dd, *J* = 8.5, 4.5 Hz, 1H), 4.02 – 3.83 (m, 2H), 3.75 – 3.61 (m, 2H).

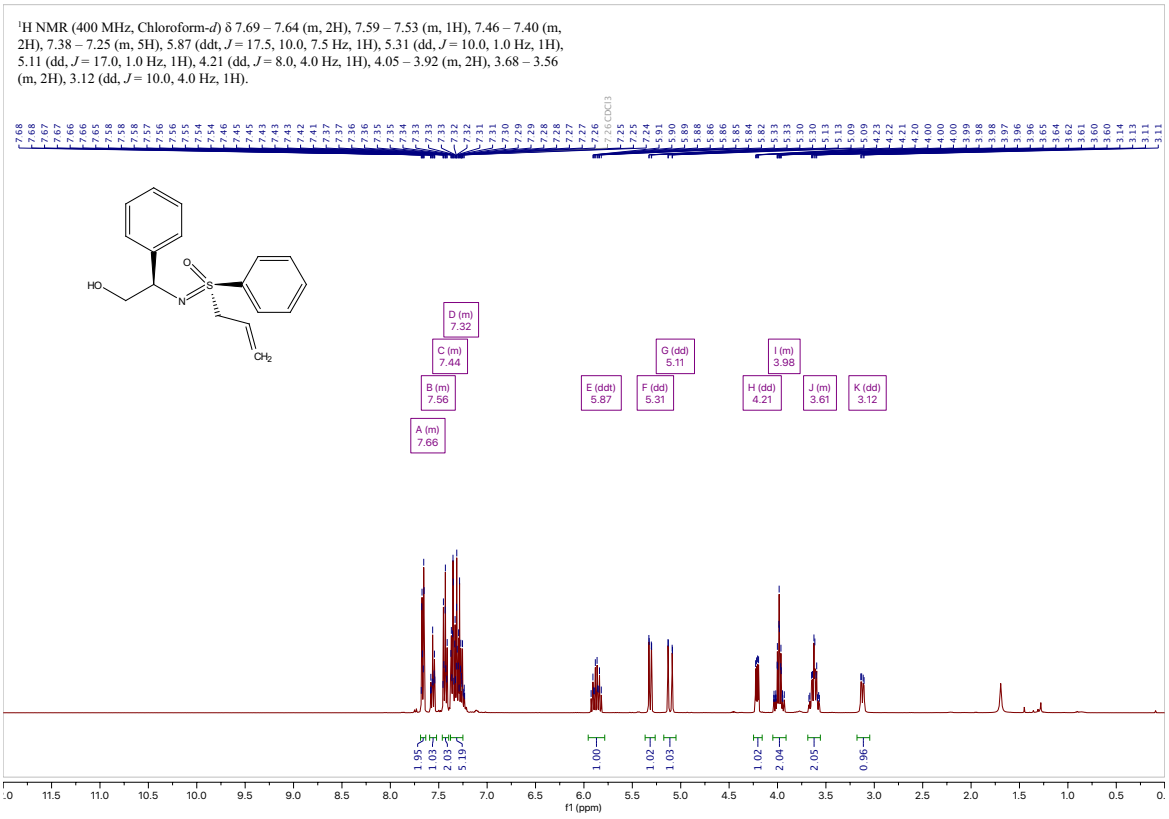


^{13}C NMR (101 MHz, $CDCl_3$) δ 142.27, 136.75, 133.49, 129.52, 129.22, 128.53, 127.49, 127.12, 125.57, 124.30, 69.06, 60.84, 60.44.

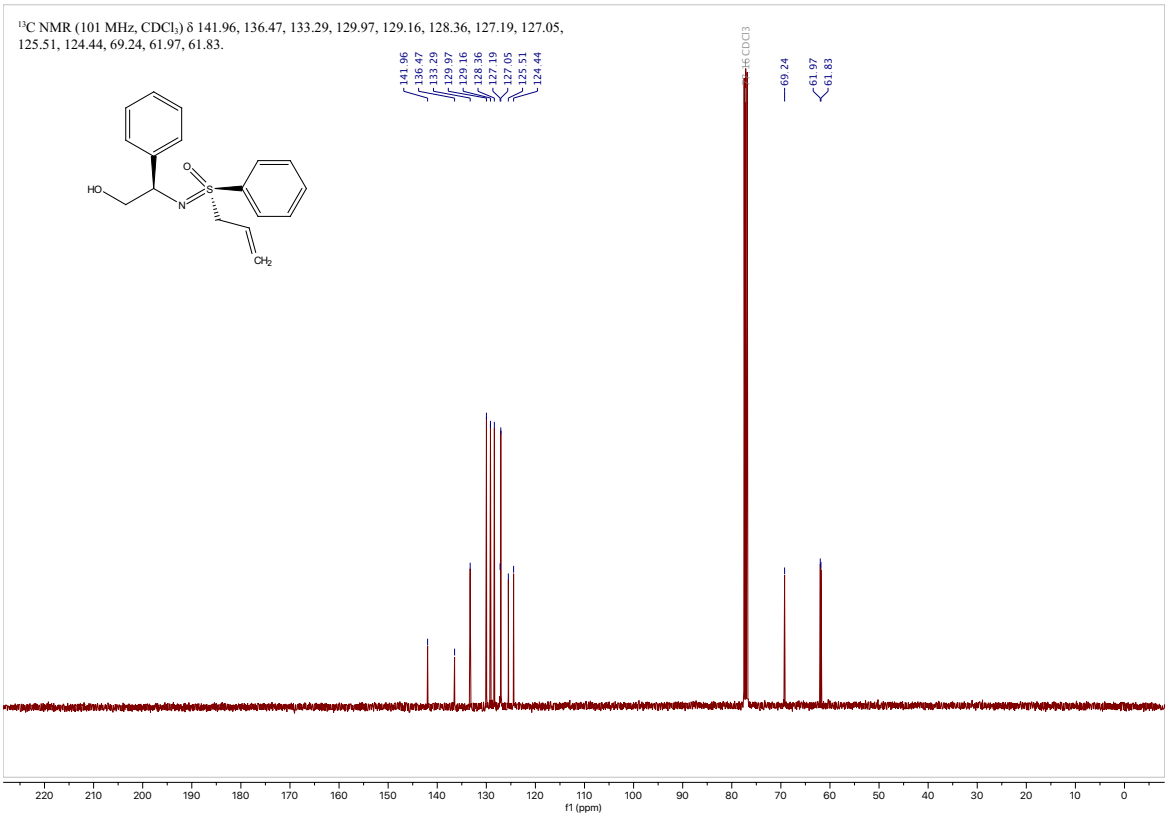


(*S*)-Allyl(((*R*)-2-hydroxy-1-phenylethyl)imino)(phenyl)-λ^6-sulfanone (21b)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 – 7.64 (m, 2H), 7.59 – 7.53 (m, 1H), 7.46 – 7.40 (m, 2H), 7.38 – 7.25 (m, 5H), 5.87 (ddt, *J* = 17.5, 10.0, 7.5 Hz, 1H), 5.31 (dd, *J* = 10.0, 1.0 Hz, 1H), 5.11 (dd, *J* = 17.0, 1.0 Hz, 1H), 4.21 (dd, *J* = 8.0, 4.0 Hz, 1H), 4.05 – 3.92 (m, 2H), 3.68 – 3.56 (m, 2H), 3.12 (dd, *J* = 10.0, 4.0 Hz, 1H).

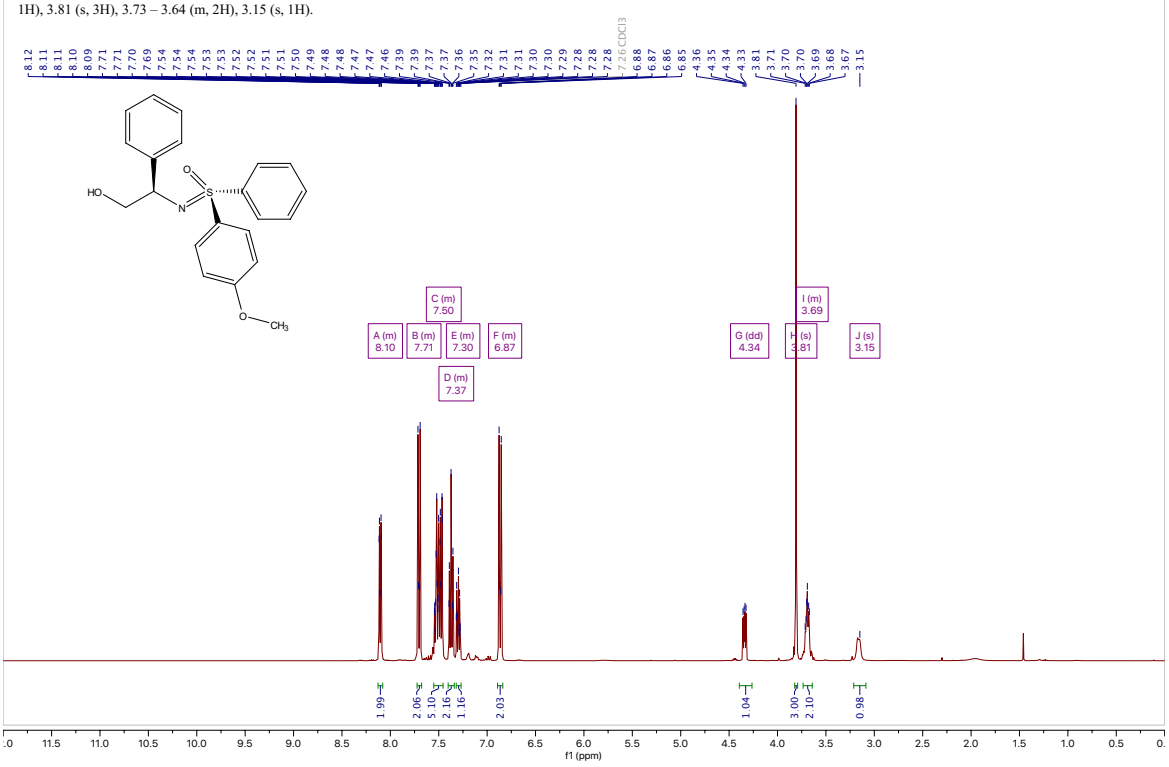


^{13}C NMR (101 MHz, $CDCl_3$) δ 141.96, 136.47, 133.29, 129.97, 129.16, 128.36, 127.19, 127.05, 125.51, 124.44, 69.24, 61.97, 61.83.

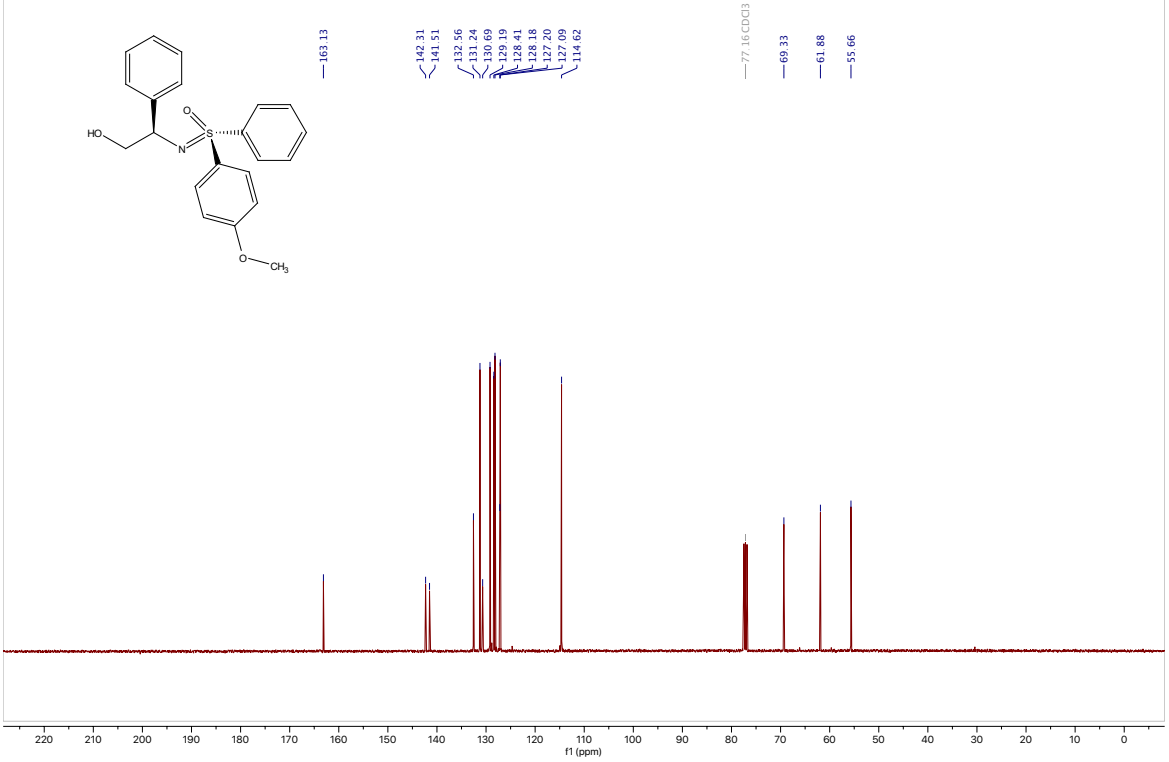


(*S*)-(((*R*)-2-Hydroxy-1-phenylethyl)imino)(4-methoxyphenyl)(phenyl)-λ^6-sulfanone (22a)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 – 8.08 (m, 2H), 7.73 – 7.68 (m, 2H), 7.55 – 7.45 (m, 5H), 7.40 – 7.34 (m, 2H), 7.32 – 7.27 (m, 1H), 6.89 – 6.84 (m, 2H), 4.34 (dd, *J* = 8.0, 4.5 Hz, 1H), 3.81 (s, 3H), 3.73 – 3.64 (m, 2H), 3.15 (s, 1H).

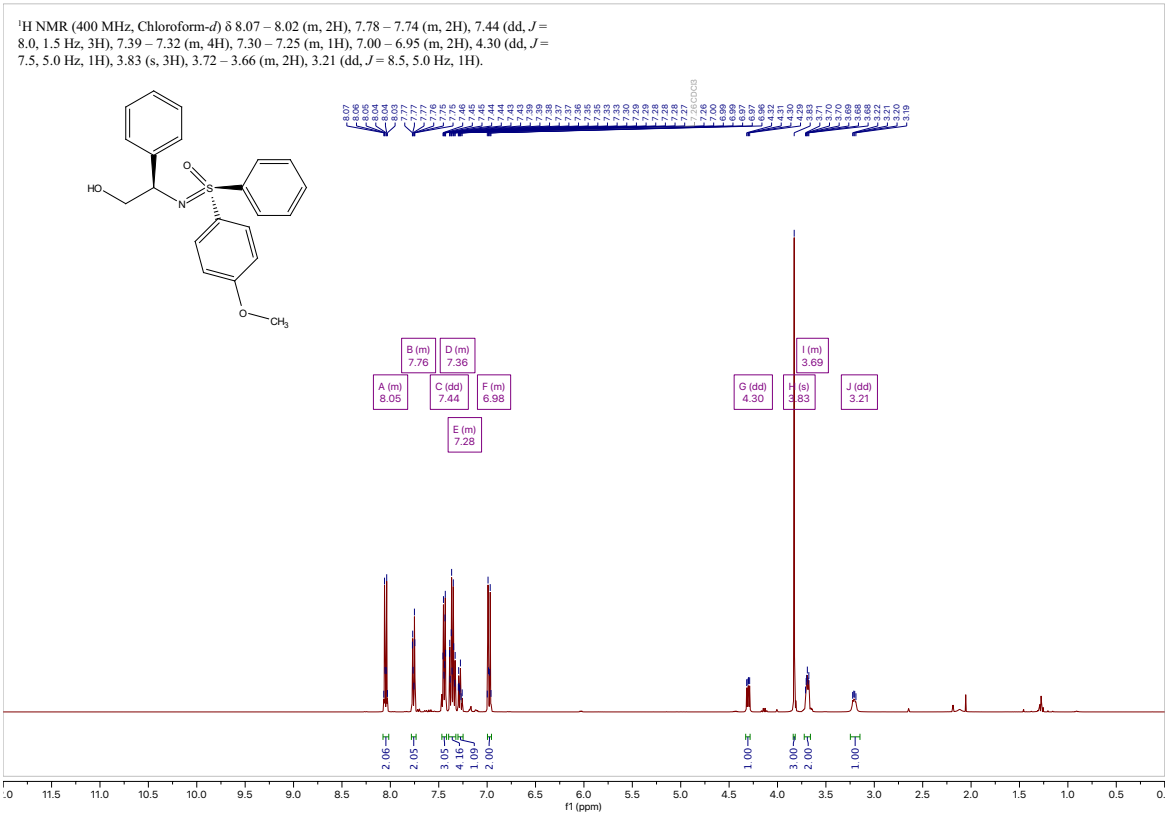


^{13}C NMR (101 MHz, $CDCl_3$) δ 163.13, 142.31, 141.51, 132.56, 131.24, 130.69, 129.19, 128.41, 128.18, 127.20, 127.09, 114.62, 69.33, 61.88, 55.66.

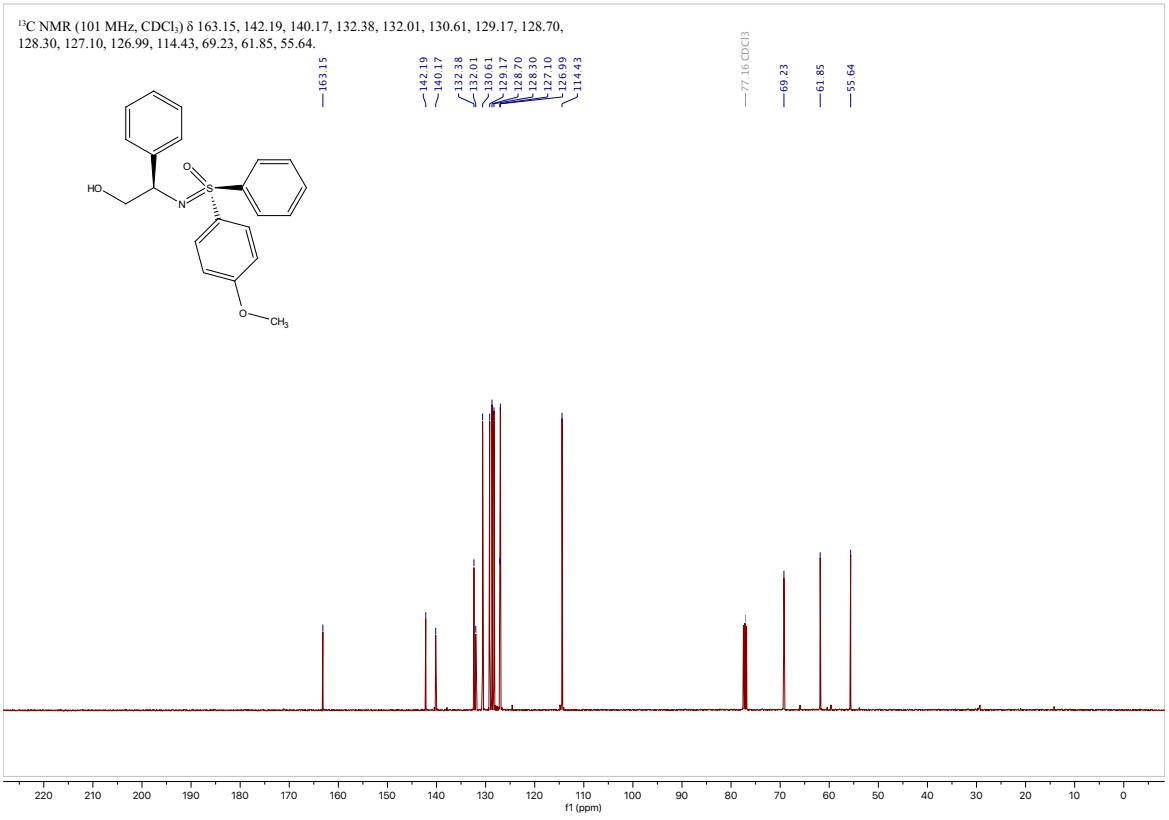


(*R*)-(((*R*)-2-Hydroxy-1-phenylethyl)imino)(4-methoxyphenyl)(phenyl)-λ^6-sulfanone (22b)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 – 8.02 (m, 2H), 7.78 – 7.74 (m, 2H), 7.44 (dd, *J* = 8.0, 1.5 Hz, 3H), 7.39 – 7.32 (m, 4H), 7.30 – 7.25 (m, 1H), 7.00 – 6.95 (m, 2H), 4.30 (dd, *J* = 7.5, 5.0 Hz, 1H), 3.83 (s, 3H), 3.72 – 3.66 (m, 2H), 3.21 (dd, *J* = 8.5, 5.0 Hz, 1H).

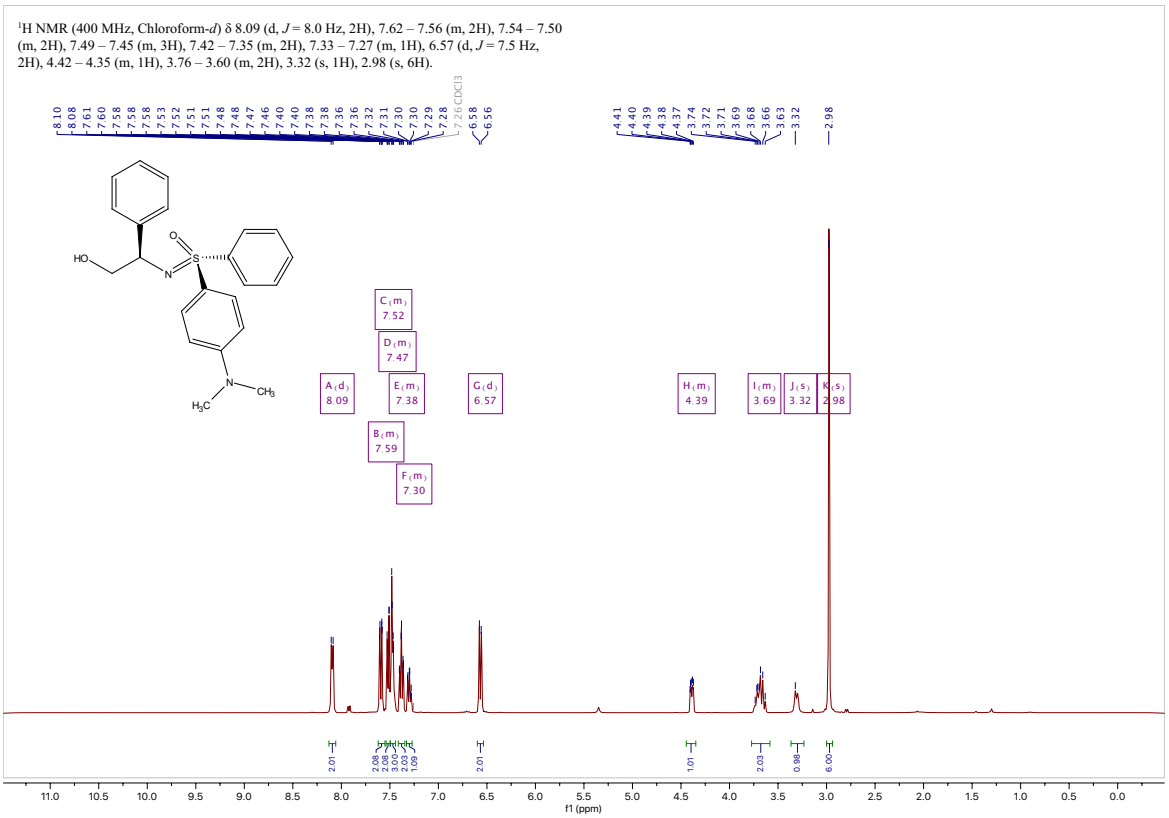


^{13}C NMR (101 MHz, $CDCl_3$) δ 163.15, 142.19, 140.17, 132.38, 132.01, 130.61, 129.17, 128.70, 128.30, 127.10, 126.99, 114.43, 69.23, 61.85, 55.64.

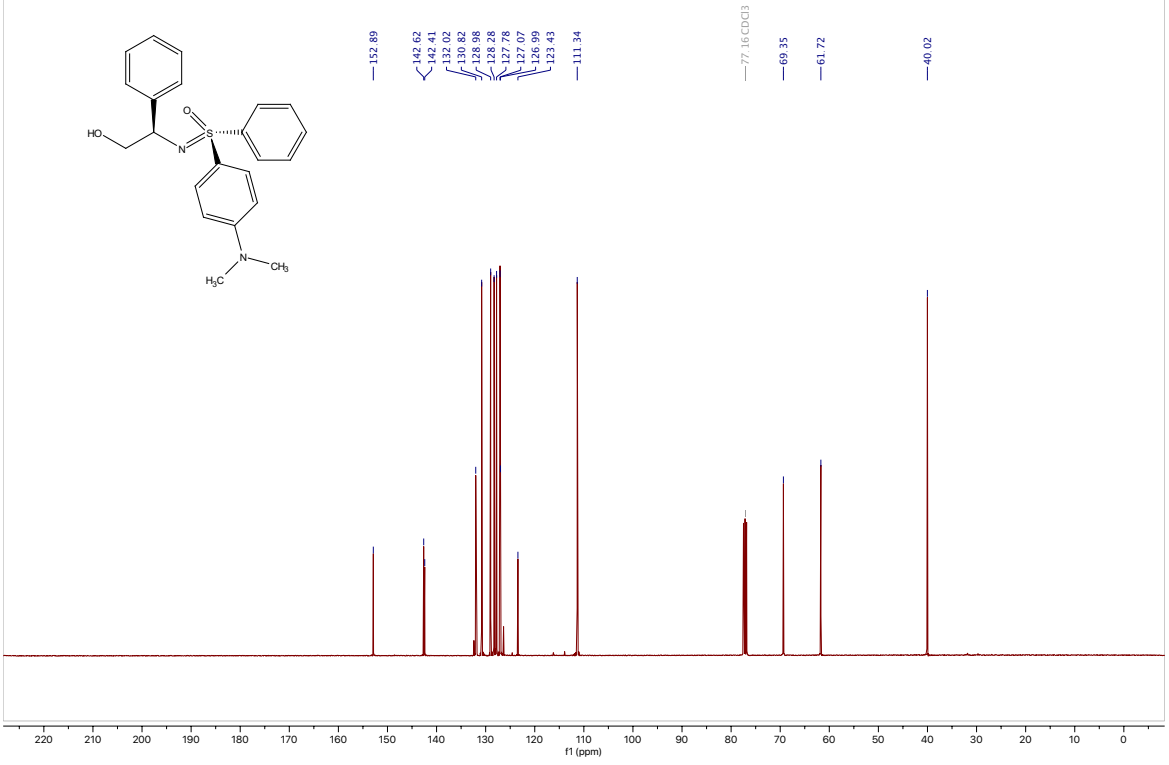


(*S*)-(4-(Dimethylamino)phenyl)(((*R*)-2-hydroxy-1-phenylethyl)imino)(phenyl)-λ^6-sulfanone (23a)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 8.0 Hz, 2H), 7.62 – 7.56 (m, 2H), 7.54 – 7.50 (m, 2H), 7.49 – 7.45 (m, 3H), 7.42 – 7.35 (m, 2H), 7.33 – 7.27 (m, 1H), 6.57 (d, *J* = 7.5 Hz, 2H), 4.42 – 4.35 (m, 1H), 3.76 – 3.60 (m, 2H), 3.32 (s, 1H), 2.98 (s, 6H).

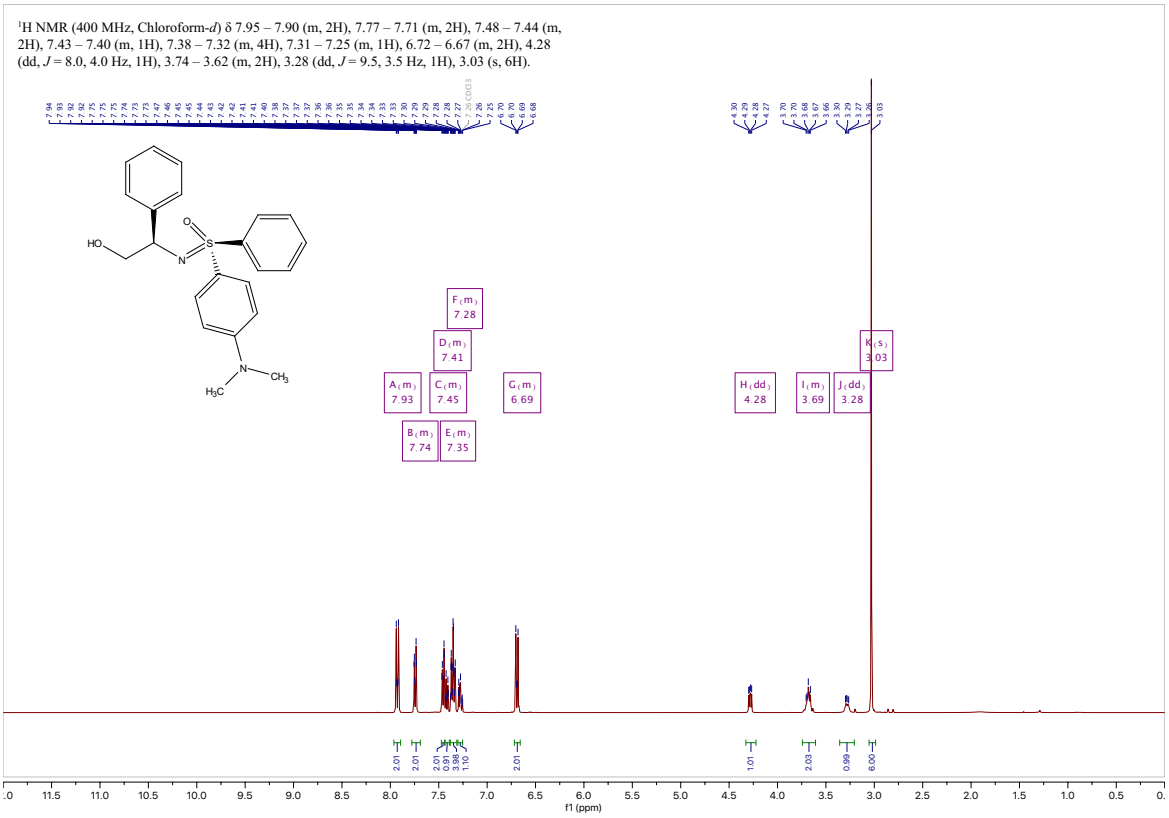


^{13}C NMR (101 MHz, $CDCl_3$) δ 152.89, 142.62, 142.41, 132.02, 130.82, 128.98, 128.28, 127.78, 127.07, 126.99, 123.43, 111.34, 69.35, 61.72, 40.02.

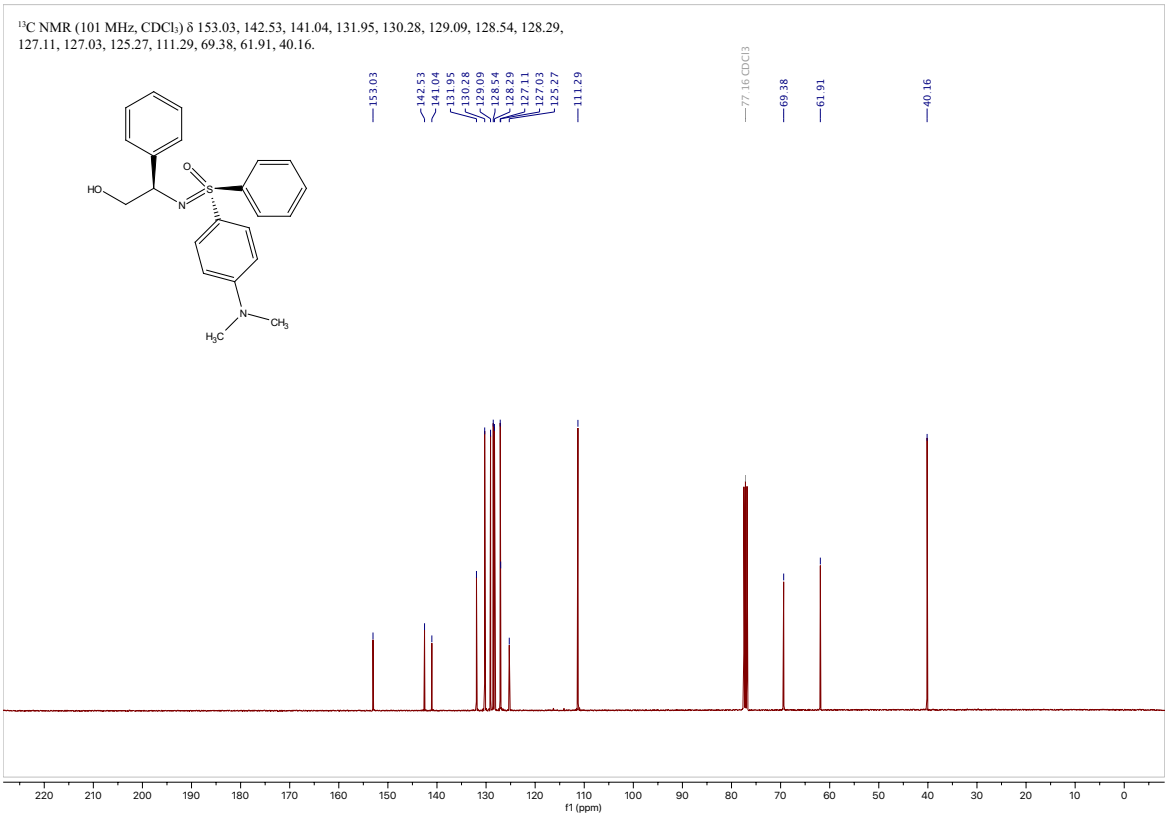


(*R*)-(4-(Dimethylamino)phenyl)(((*R*)-2-hydroxy-1-phenylethyl)imino)(phenyl)-λ6-sulfanone (23b)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.90 (m, 2H), 7.77 – 7.71 (m, 2H), 7.48 – 7.44 (m, 2H), 7.43 – 7.40 (m, 1H), 7.38 – 7.32 (m, 4H), 7.31 – 7.25 (m, 1H), 6.72 – 6.67 (m, 2H), 4.28 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.74 – 3.62 (m, 2H), 3.28 (dd, *J* = 9.5, 3.5 Hz, 1H), 3.03 (s, 6H).

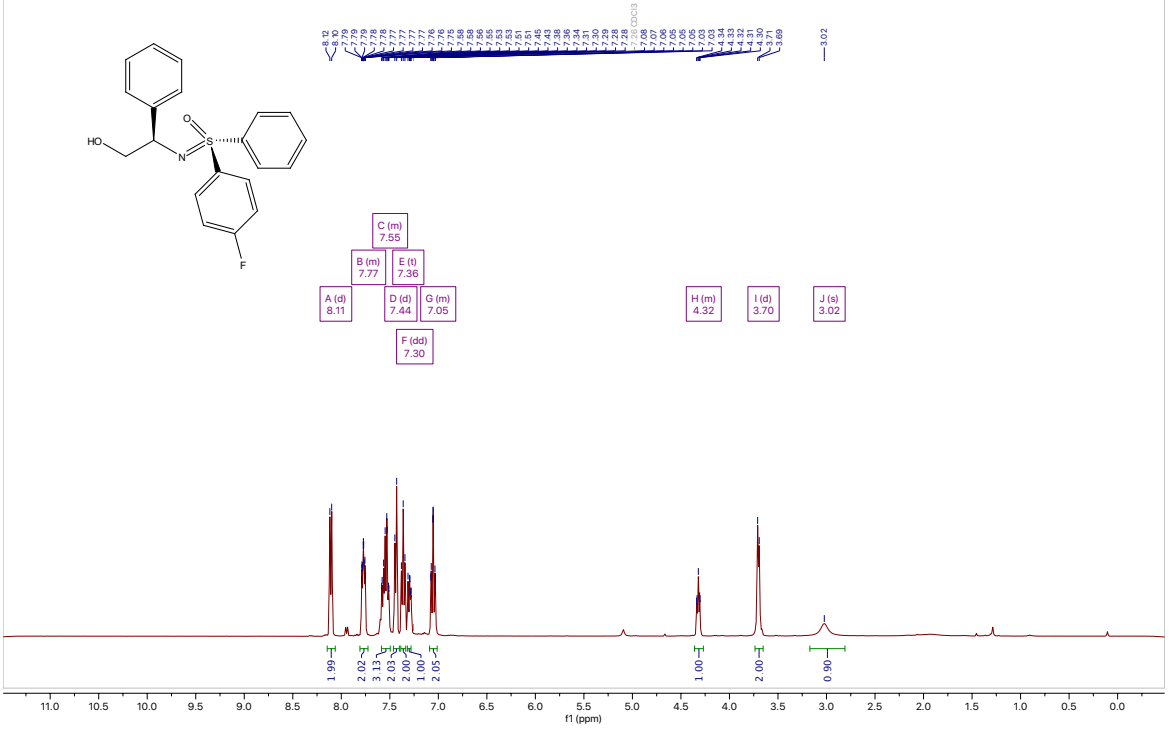


^{13}C NMR (101 MHz, $CDCl_3$) δ 153.03, 142.53, 141.04, 131.95, 130.28, 129.09, 128.54, 128.29, 127.11, 127.03, 125.27, 111.29, 69.38, 61.91, 40.16.

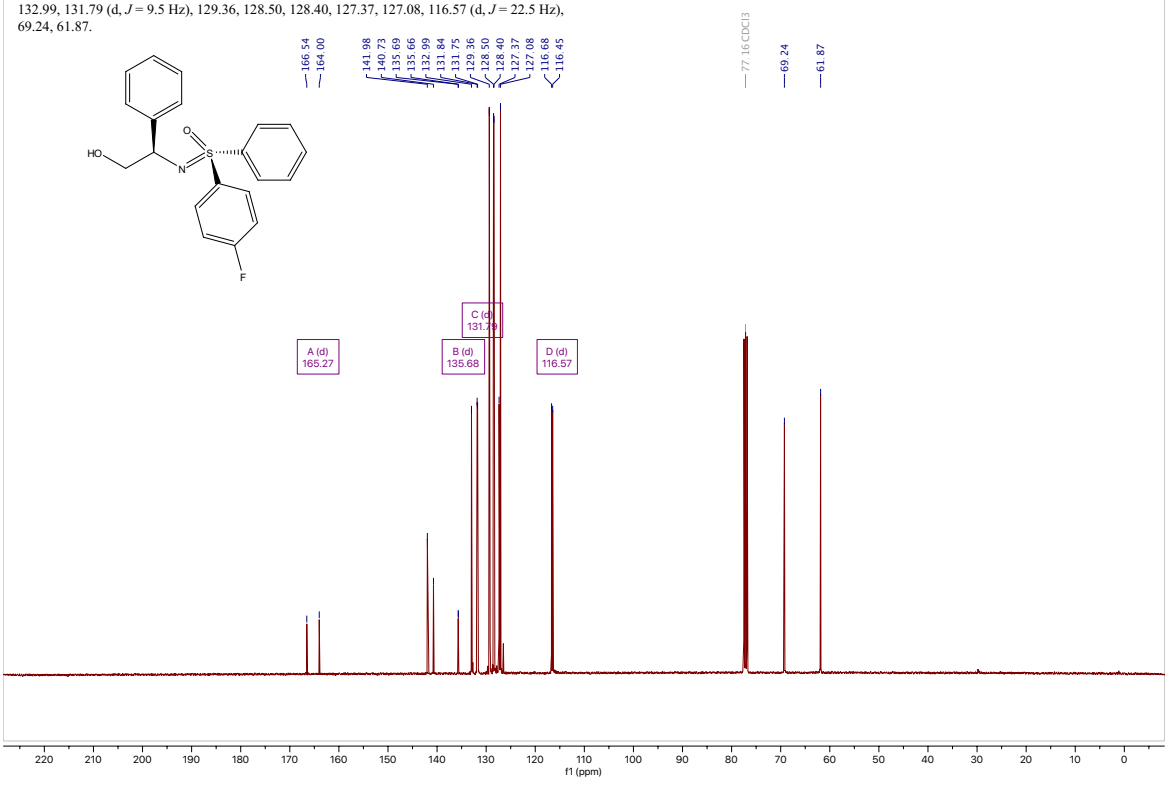


(*S*)-(4-Fluorophenyl)(((*R*)-2-hydroxy-1-phenylethyl)imino)(phenyl)-λ^6-sulfanone (24a)

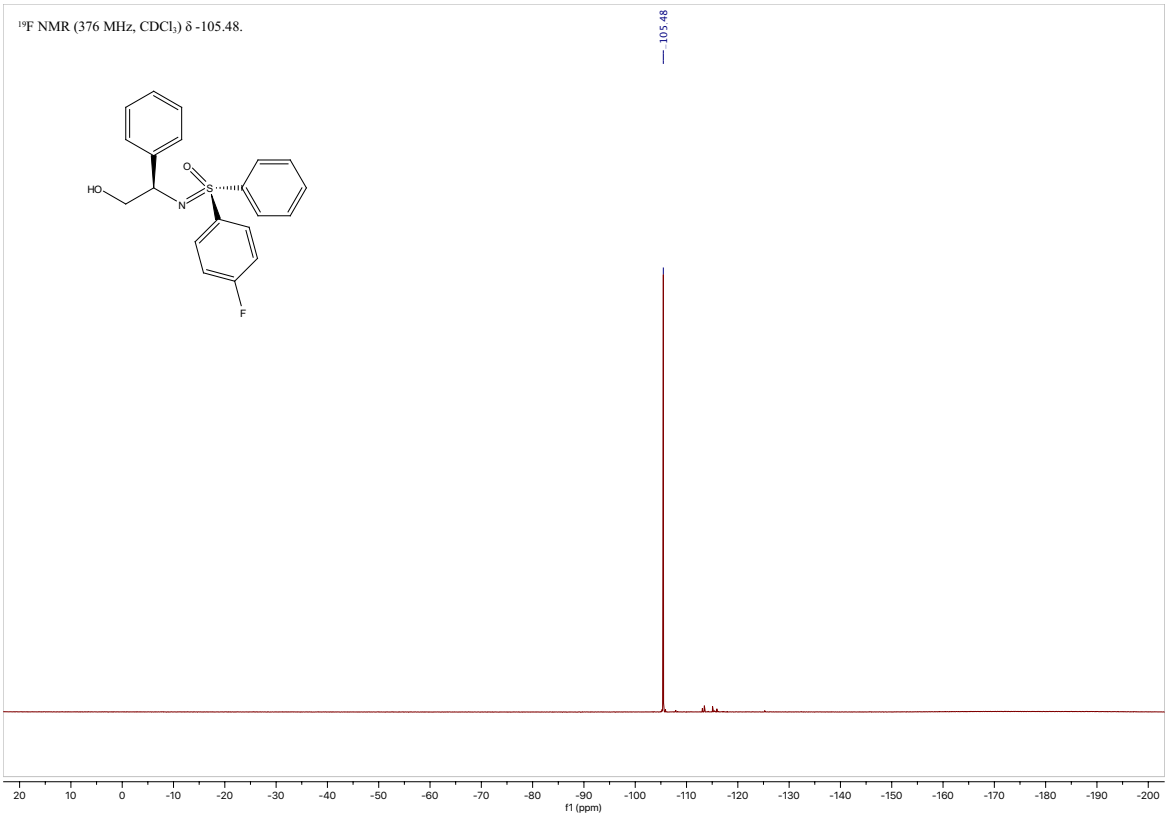
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 7.5 Hz, 2H), 7.81 – 7.73 (m, 2H), 7.59 – 7.49 (m, 3H), 7.44 (d, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.30 (dd, *J* = 7.5, 5.5 Hz, 1H), 7.09 – 7.01 (m, 2H), 4.35 – 4.29 (m, 1H), 3.70 (d, *J* = 6.5 Hz, 2H), 3.02 (s, 1H).



^{13}C NMR (101 MHz, $CDCl_3$) δ 165.27 (d, *J* = 255.0 Hz), 141.98, 140.73, 135.68 (d, *J* = 3.0 Hz), 132.99, 131.79 (d, *J* = 9.5 Hz), 129.36, 128.50, 128.40, 127.37, 127.08, 116.57 (d, *J* = 22.5 Hz), 69.24, 61.87.

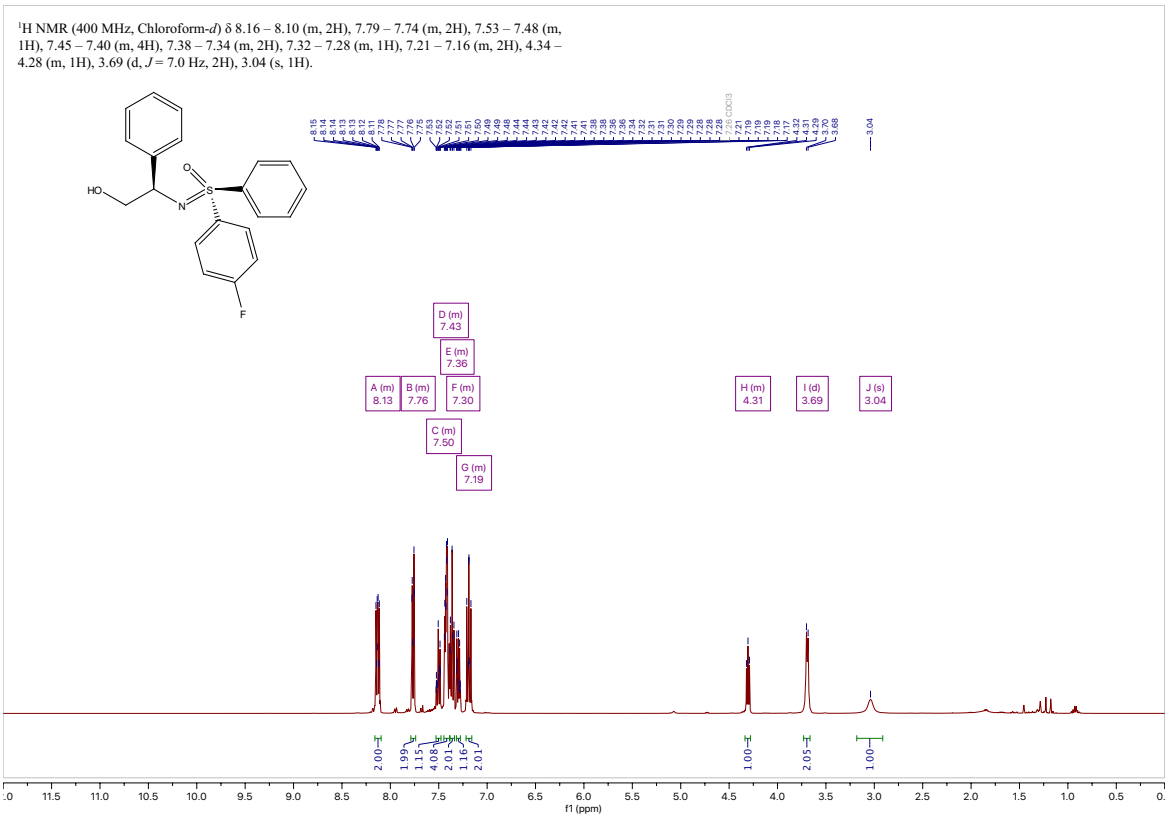


^{19}F NMR (376 MHz, $CDCl_3$) δ -105.48.

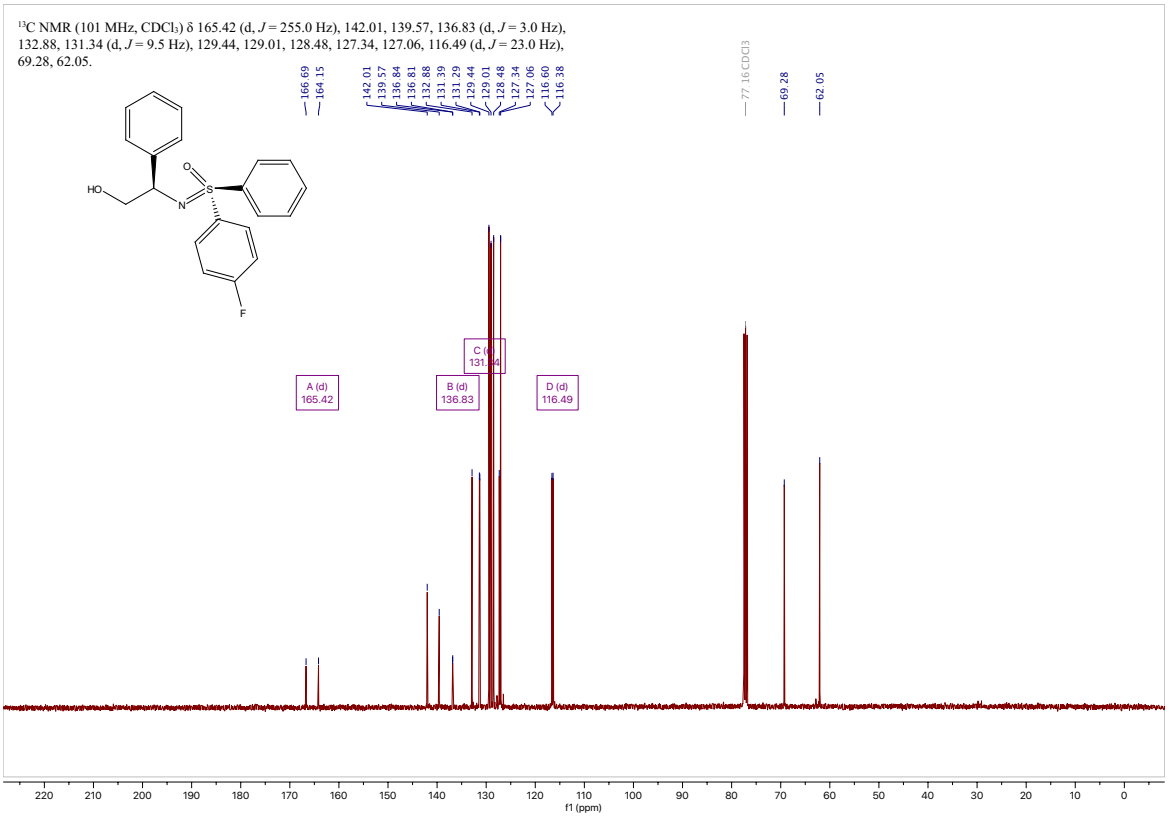


(*R*)-(4-Fluorophenyl)(((*R*)-2-hydroxy-1-phenylethyl)imino)(phenyl)-λ6-sulfanone (24b)

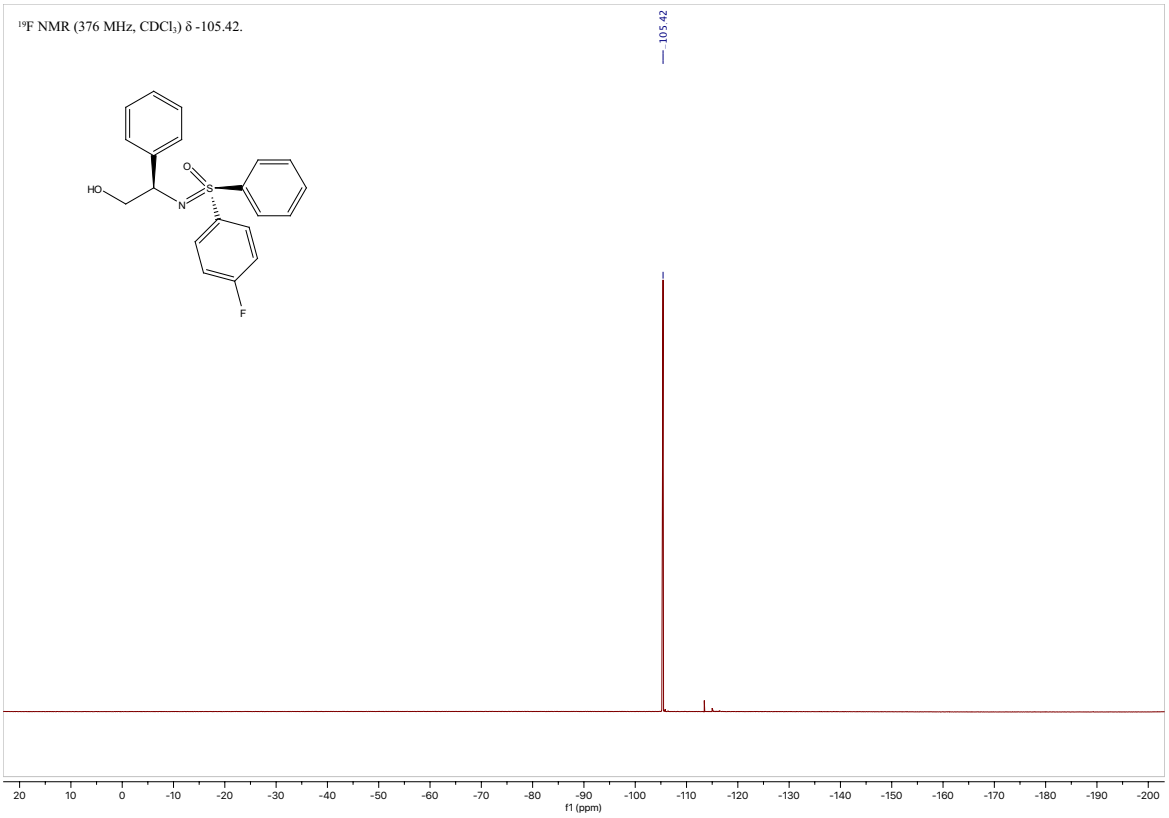
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 – 8.10 (m, 2H), 7.79 – 7.74 (m, 2H), 7.53 – 7.48 (m, 1H), 7.45 – 7.40 (m, 4H), 7.38 – 7.34 (m, 2H), 7.32 – 7.28 (m, 1H), 7.21 – 7.16 (m, 2H), 4.34 – 4.28 (m, 1H), 3.69 (d, *J* = 7.0 Hz, 2H), 3.04 (s, 1H).



^{13}C NMR (101 MHz, $CDCl_3$) δ 165.42 (d, *J* = 255.0 Hz), 142.01, 139.57, 136.83 (d, *J* = 3.0 Hz), 132.88, 131.34 (d, *J* = 9.5 Hz), 129.44, 129.01, 128.48, 127.34, 127.06, 116.49 (d, *J* = 23.0 Hz), 69.28, 62.05.

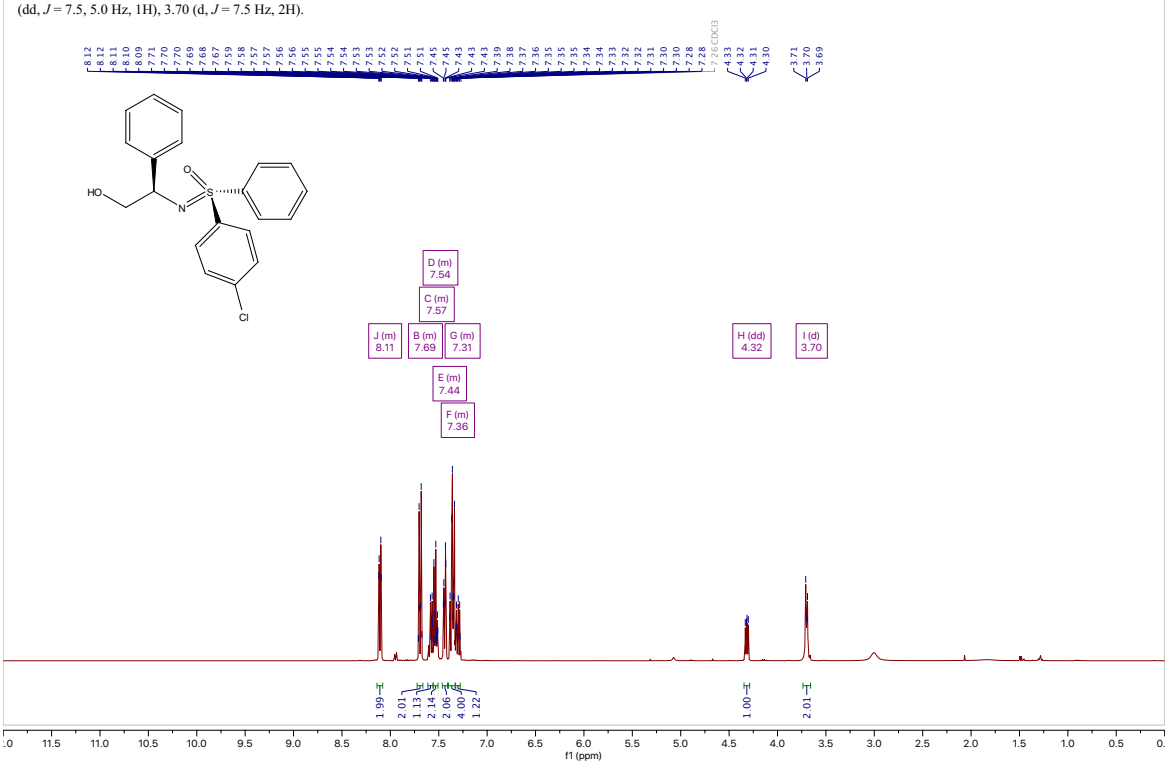


^{19}F NMR (376 MHz, $CDCl_3$) δ -105.42.

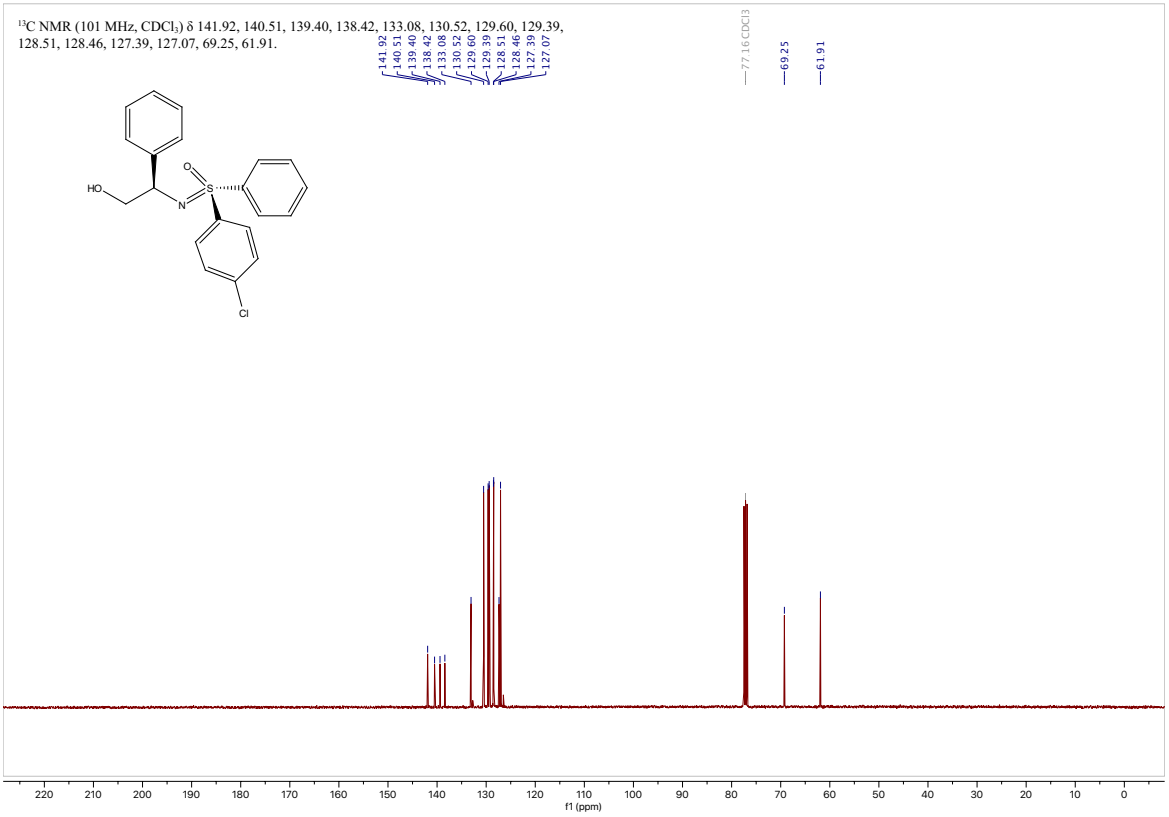


(*S*)-(4-Chlorophenyl)(((*R*)-2-hydroxy-1-phenylethyl)imino)(phenyl)-λ^6-sulfanone (25a)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 – 8.09 (m, 2H), 7.71 – 7.67 (m, 2H), 7.61 – 7.56 (m, 1H), 7.55 – 7.51 (m, 2H), 7.46 – 7.42 (m, 2H), 7.39 – 7.33 (m, 4H), 7.32 – 7.27 (m, 1H), 4.32 (dd, *J* = 7.5, 5.0 Hz, 1H), 3.70 (d, *J* = 7.5 Hz, 2H).

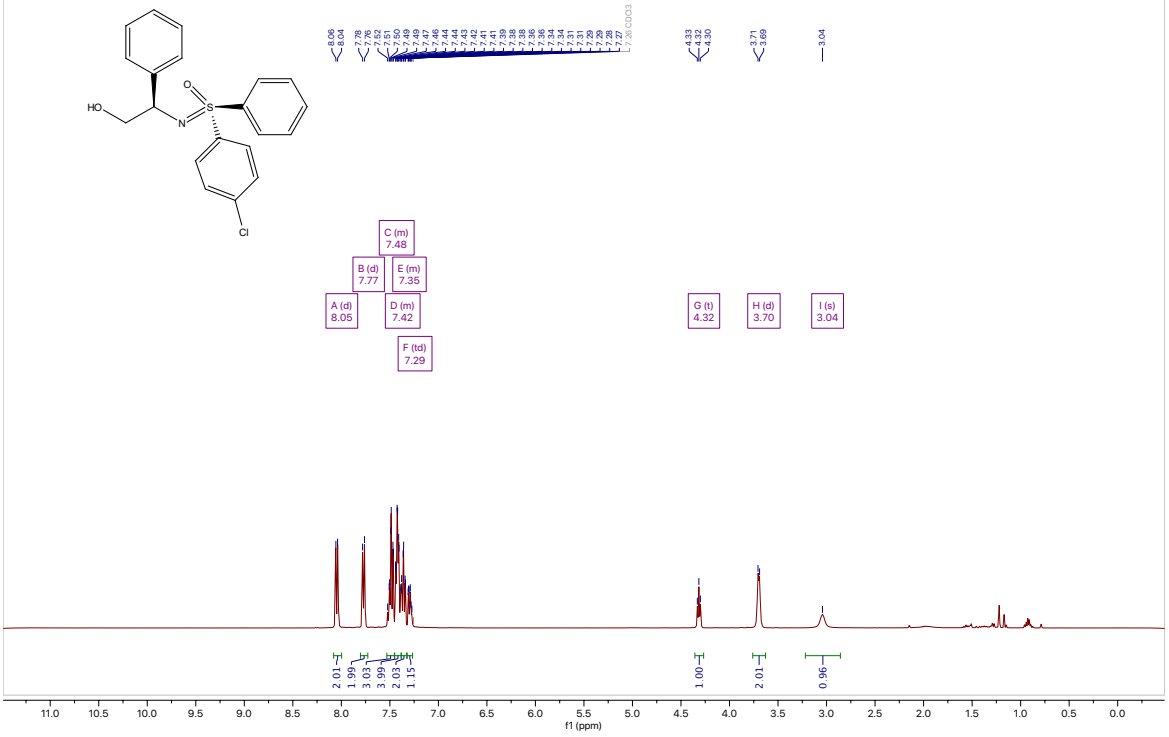


^{13}C NMR (101 MHz, $CDCl_3$) δ 141.92, 140.51, 139.40, 138.42, 133.08, 130.52, 129.60, 129.39, 128.51, 128.46, 127.39, 127.07, 69.25, 61.91.

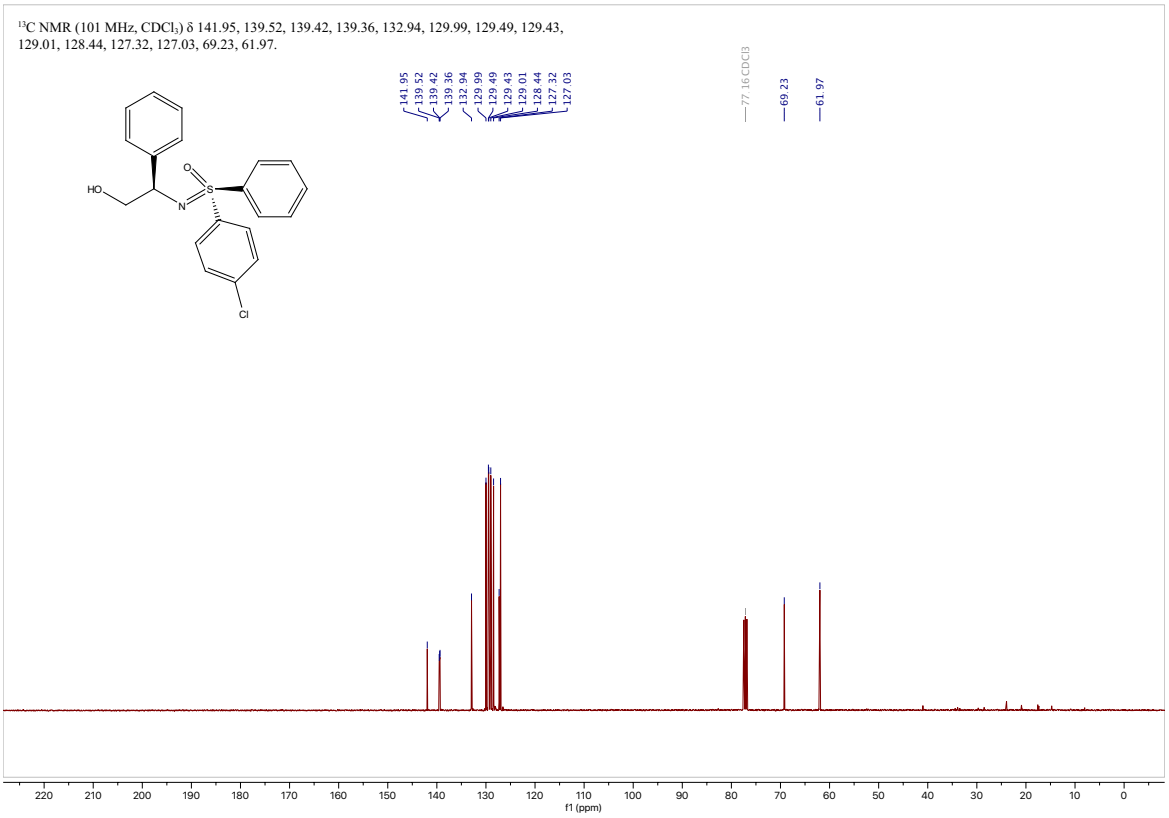


(*R*)-(4-Chlorophenyl)(((*R*)-2-hydroxy-1-phenylethyl)imino)(phenyl)-λ^6-sulfanone (25b)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 7.0 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.53 – 7.46 (m, 3H), 7.45 – 7.39 (m, 4H), 7.38 – 7.33 (m, 2H), 7.29 (td, *J* = 7.0, 2.5 Hz, 1H), 4.32 (t, *J* = 6.5 Hz, 1H), 3.70 (d, *J* = 6.5 Hz, 2H), 3.04 (s, 1H).

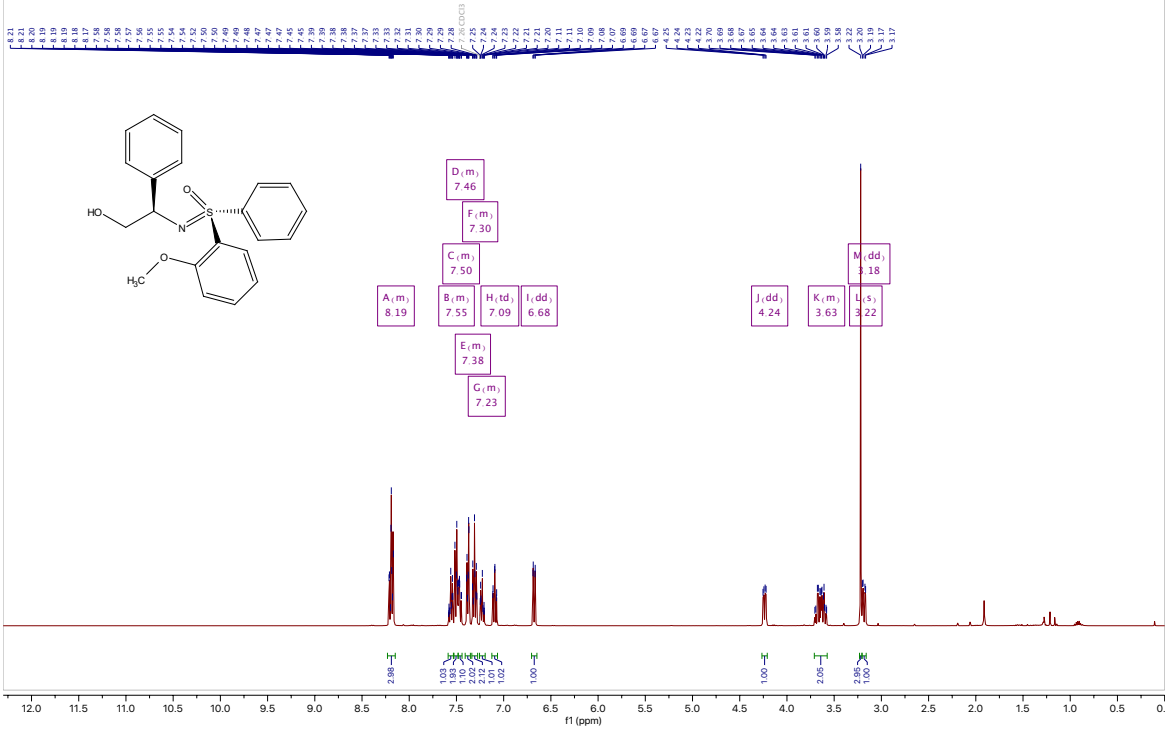


^{13}C NMR (101 MHz, $CDCl_3$) δ 141.95, 139.52, 139.42, 139.36, 132.94, 129.99, 129.49, 129.43, 129.01, 128.44, 127.32, 127.03, 69.23, 61.97.

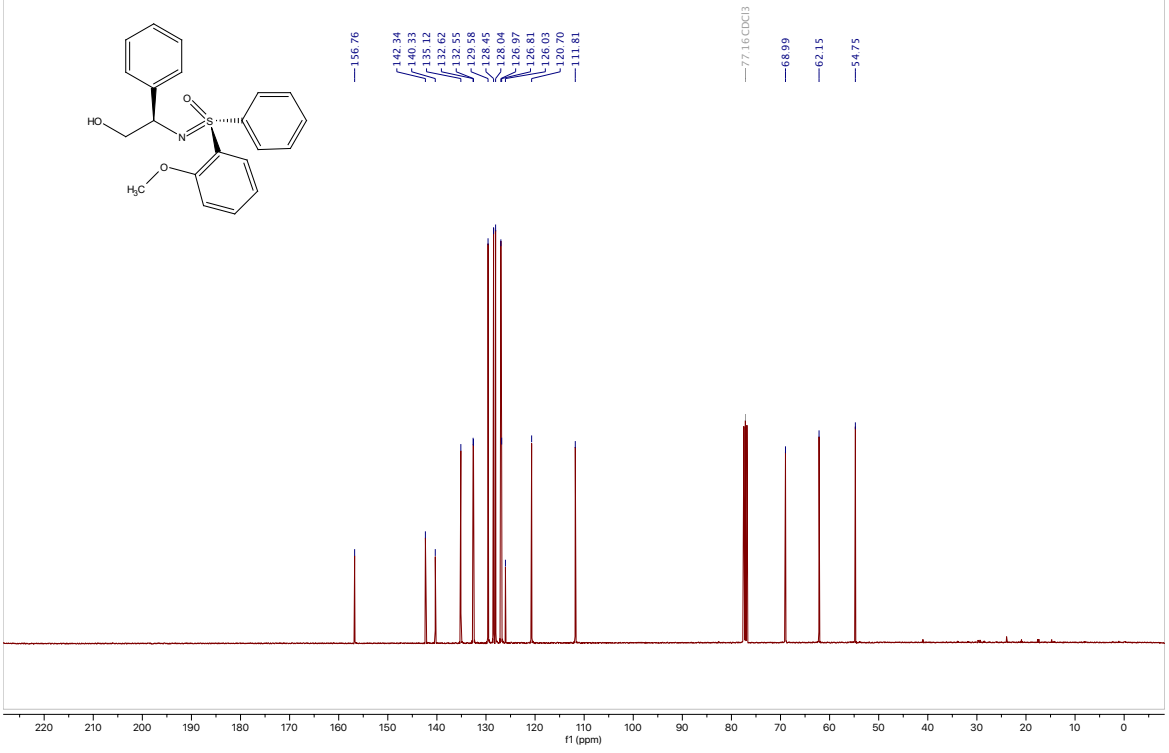


(*S*)-(((*R*)-2-Hydroxy-1-phenylethyl)imino)(2-methoxyphenyl)(phenyl)-λ^6-sulfanone (26a)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.23 – 8.15 (m, 3H), 7.59 – 7.53 (m, 1H), 7.52 – 7.48 (m, 2H), 7.47 – 7.44 (m, 1H), 7.40 – 7.36 (m, 2H), 7.33 – 7.28 (m, 2H), 7.25 – 7.20 (m, 1H), 7.09 (td, *J* = 8.0, 1.0 Hz, 1H), 6.68 (dd, *J* = 8.0, 1.0 Hz, 1H), 4.24 (dd, *J* = 9.0, 4.0 Hz, 1H), 3.72 – 3.57 (m, 2H), 3.22 (s, 3H), 3.18 (dd, *J* = 10.5, 3.0 Hz, 1H).

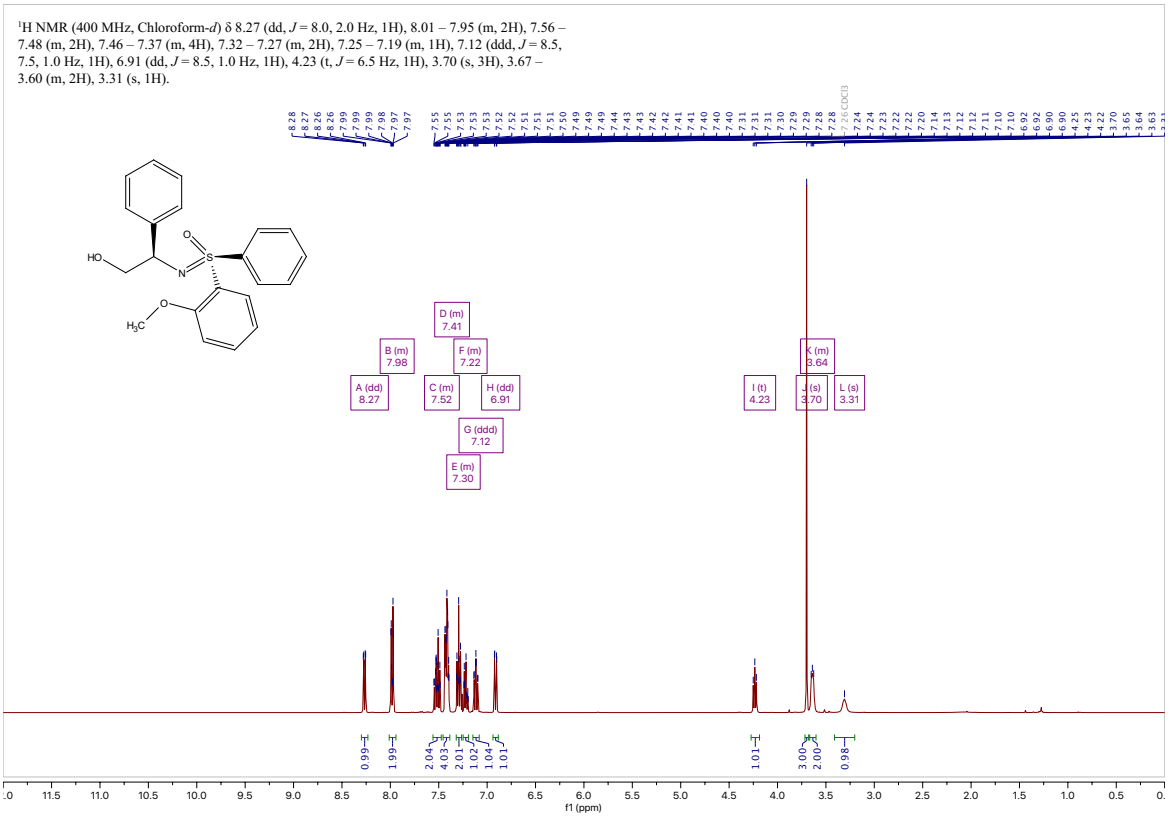


^{13}C NMR (101 MHz, $CDCl_3$) δ 156.76, 142.34, 140.33, 135.12, 132.62, 132.55, 129.58, 128.45, 128.04, 126.97, 126.81, 126.03, 120.70, 111.81, 68.99, 62.15, 54.75.

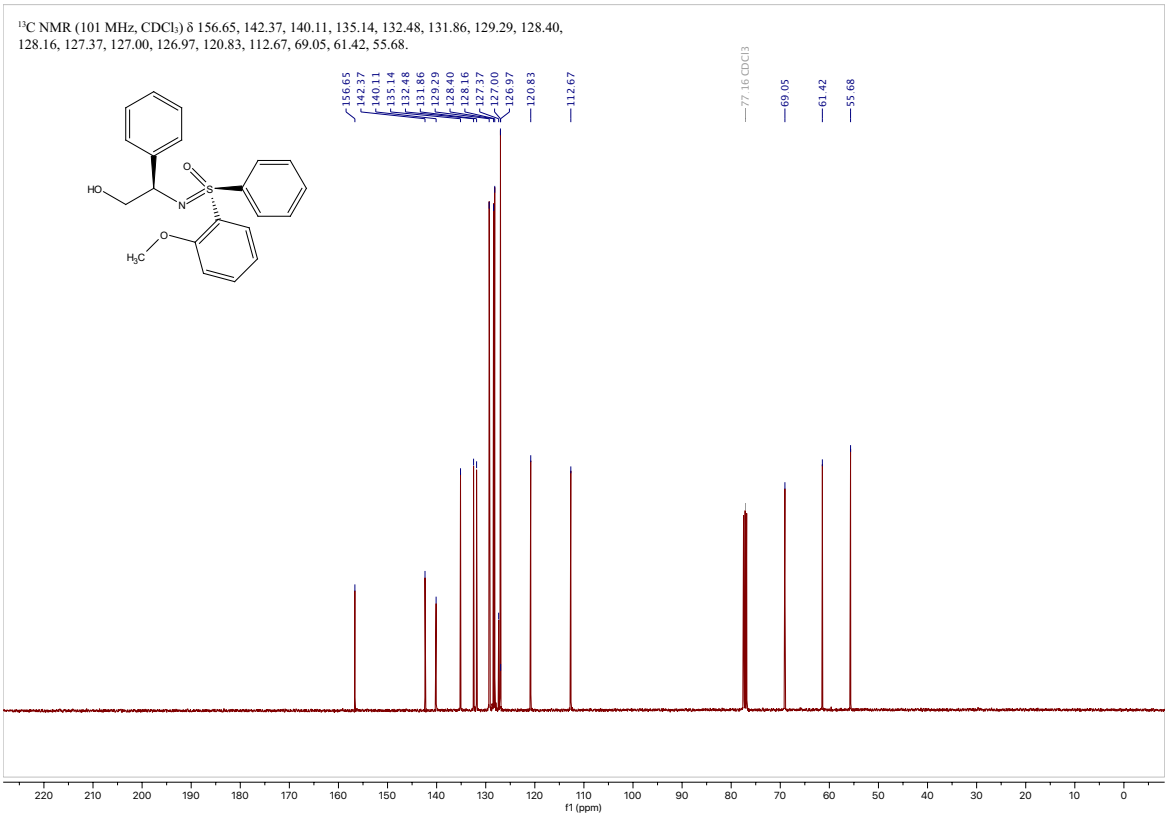


(*R*)-(((*R*)-2-Hydroxy-1-phenylethyl)imino)(2-methoxyphenyl)(phenyl)-λ6-sulfanone (26b)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.27 (dd, *J* = 8.0, 2.0 Hz, 1H), 8.01 – 7.95 (m, 2H), 7.56 – 7.48 (m, 2H), 7.46 – 7.37 (m, 4H), 7.32 – 7.27 (m, 2H), 7.25 – 7.19 (m, 1H), 7.12 (ddd, *J* = 8.5, 7.5, 1.0 Hz, 1H), 6.91 (dd, *J* = 8.5, 1.0 Hz, 1H), 4.23 (t, *J* = 6.5 Hz, 1H), 3.70 (s, 3H), 3.67 – 3.60 (m, 2H), 3.31 (s, 1H).

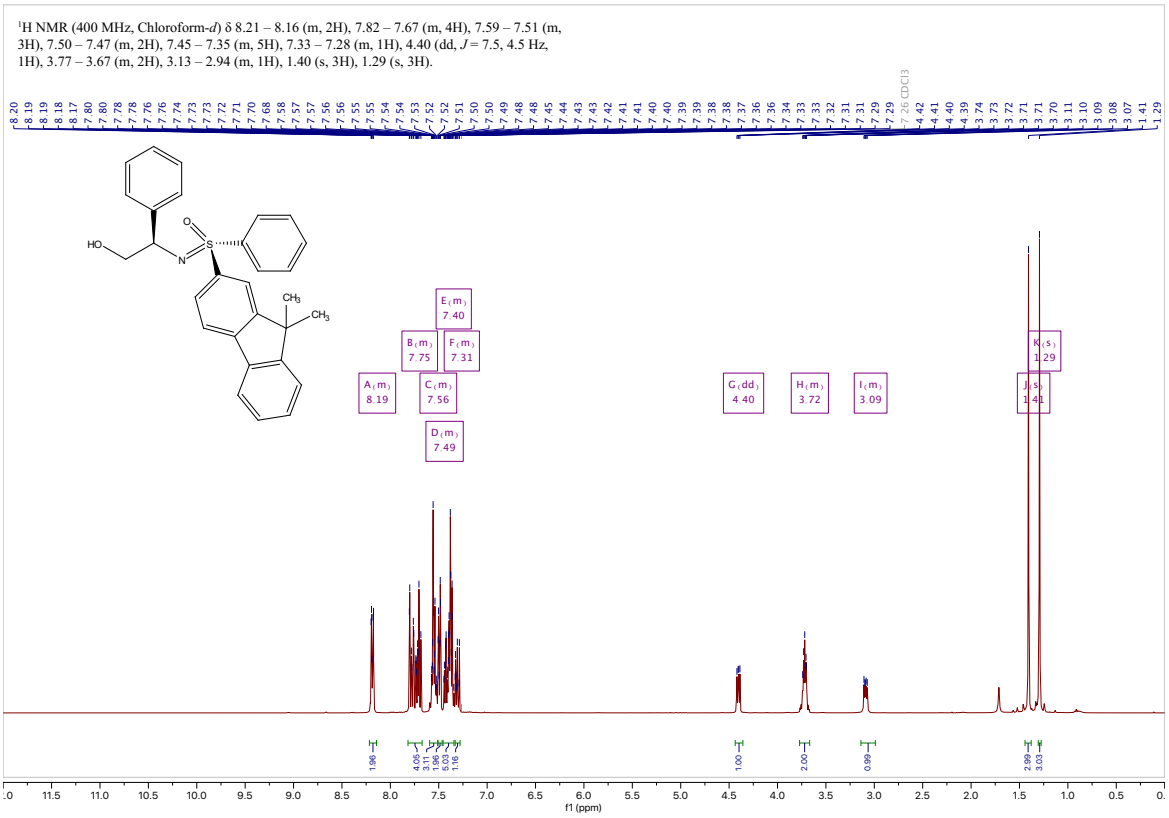


^{13}C NMR (101 MHz, $CDCl_3$) δ 156.65, 142.37, 140.11, 135.14, 132.48, 131.86, 129.29, 128.40, 128.16, 127.37, 127.00, 126.97, 120.83, 112.67, 69.05, 61.42, 55.68.

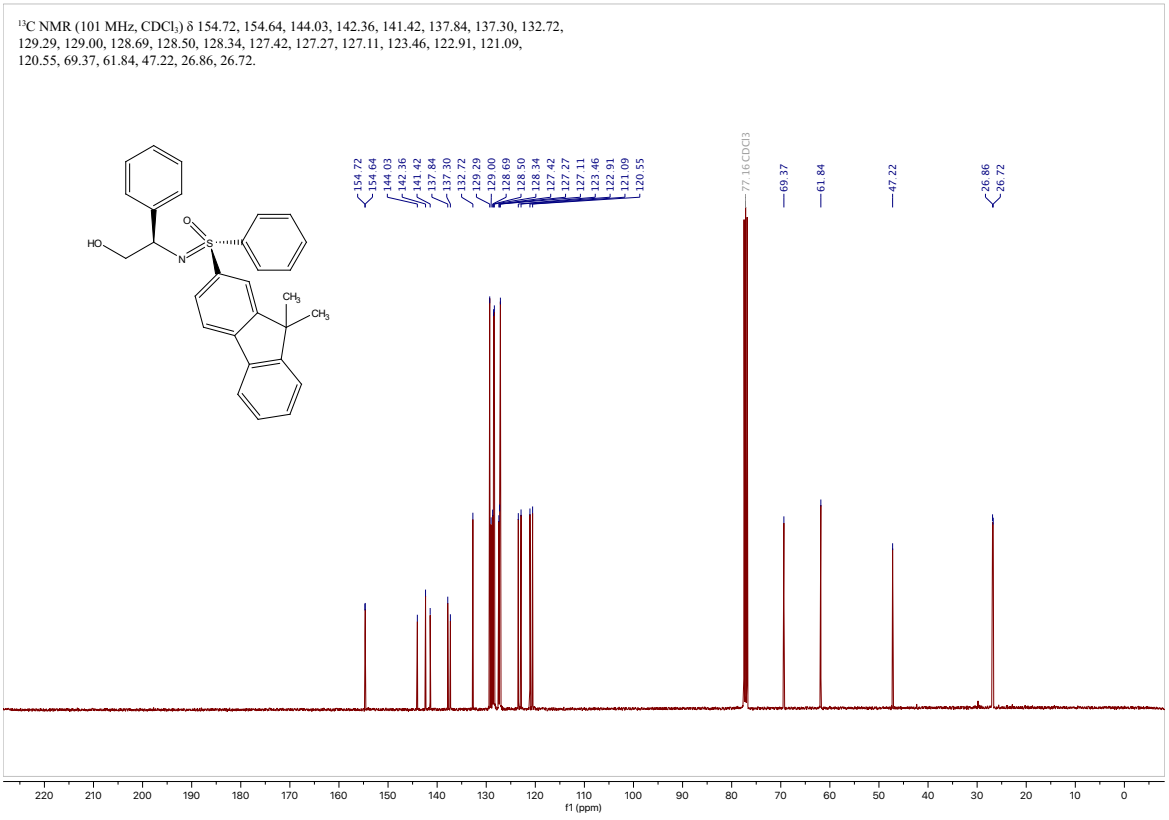


(*S*)-(9,9-Dimethyl-9*H*-fluoren-2-yl)(((*R*)-2-hydroxy-1-phenylethyl)imino)(phenyl)-λ^6-sulfanone (27a)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 – 8.16 (m, 2H), 7.82 – 7.67 (m, 4H), 7.59 – 7.51 (m, 3H), 7.50 – 7.47 (m, 2H), 7.45 – 7.35 (m, 5H), 7.33 – 7.28 (m, 1H), 4.40 (dd, *J* = 7.5, 4.5 Hz, 1H), 3.77 – 3.67 (m, 2H), 3.13 – 2.94 (m, 1H), 1.40 (s, 3H), 1.29 (s, 3H).

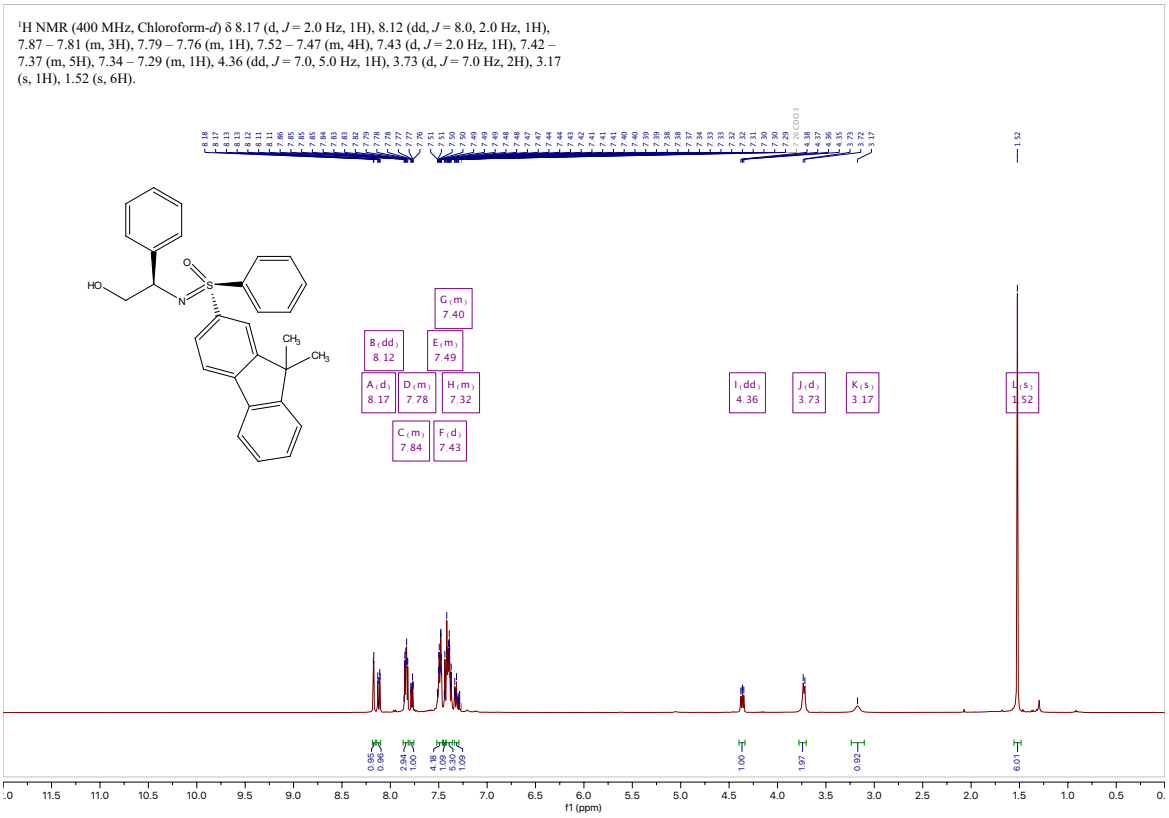


^{13}C NMR (101 MHz, $CDCl_3$) δ 154.72, 154.64, 144.03, 142.36, 141.42, 137.84, 137.30, 132.72, 129.29, 129.00, 128.69, 128.50, 128.34, 127.42, 127.27, 127.11, 123.46, 122.91, 121.09, 120.55, 69.37, 61.84, 47.22, 26.86, 26.72.

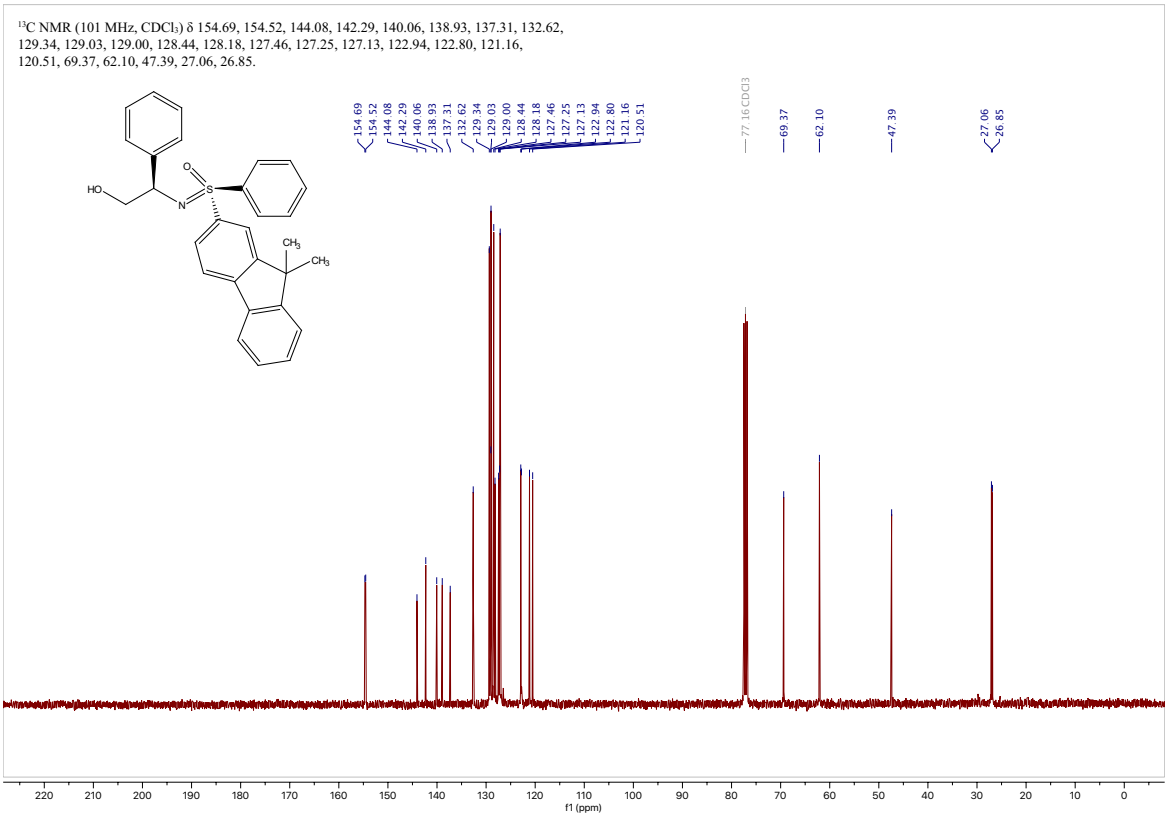


(*R*)-(9,9-Dimethyl-9*H*-fluoren-2-yl)(((*R*)-2-hydroxy-1-phenylethyl)imino)(phenyl)-λ6-sulfanone (27b)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 (d, *J* = 2.0 Hz, 1H), 8.12 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.87 – 7.81 (m, 3H), 7.79 – 7.76 (m, 1H), 7.52 – 7.47 (m, 4H), 7.43 (d, *J* = 2.0 Hz, 1H), 7.42 – 7.37 (m, 5H), 7.34 – 7.29 (m, 1H), 4.36 (dd, *J* = 7.0, 5.0 Hz, 1H), 3.73 (d, *J* = 7.0 Hz, 2H), 3.17 (s, 1H), 1.52 (s, 6H).

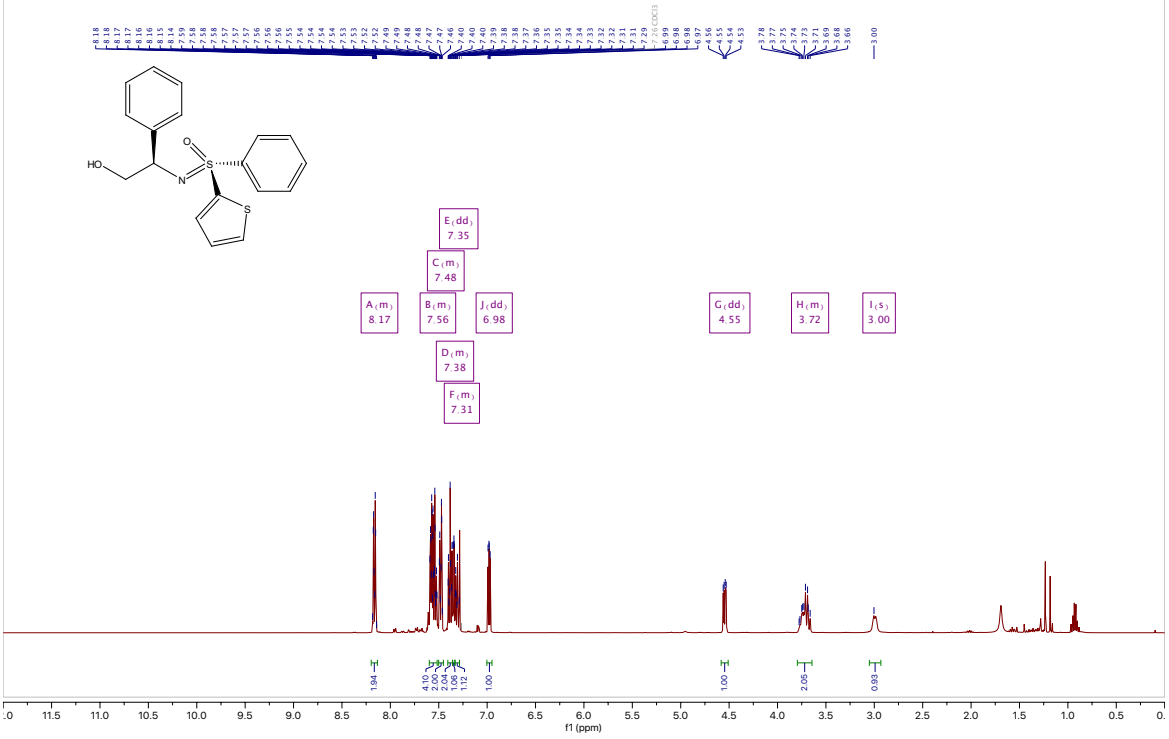


^{13}C NMR (101 MHz, $CDCl_3$) δ 154.69, 154.52, 144.08, 142.29, 140.06, 138.93, 137.31, 132.62, 129.34, 129.03, 129.00, 128.44, 128.18, 127.46, 127.25, 127.13, 122.94, 122.80, 121.16, 120.51, 69.37, 62.10, 47.39, 27.06, 26.85.

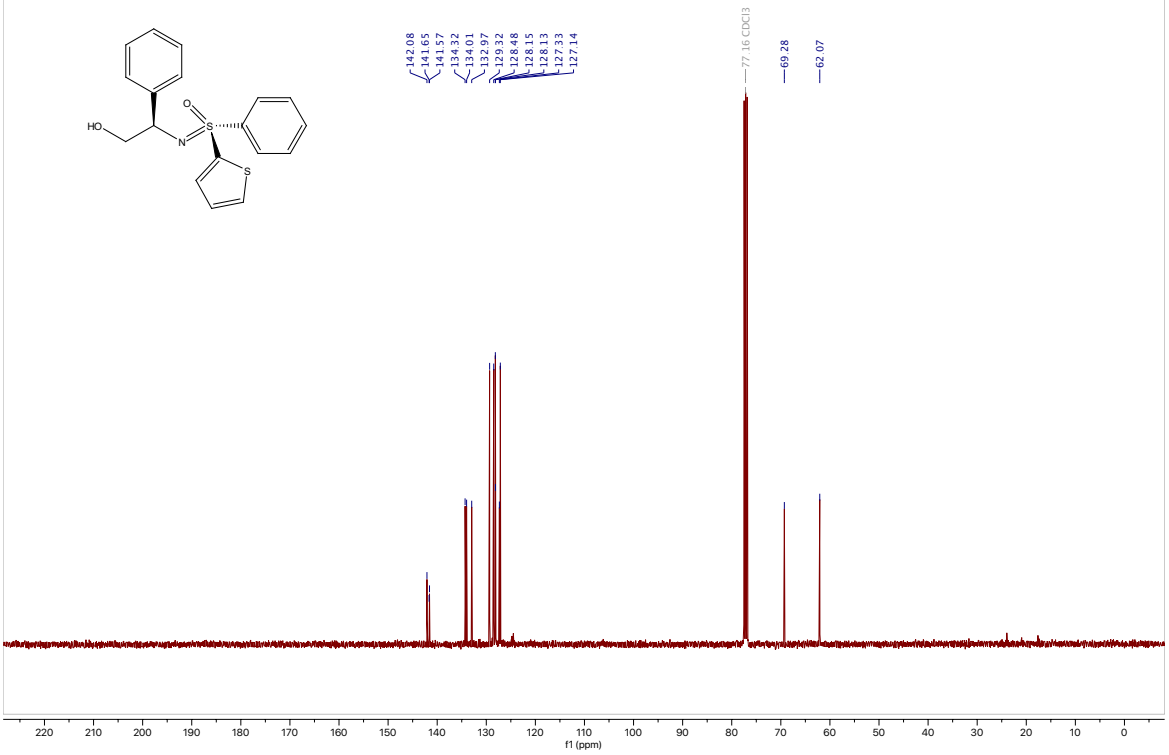


(*S*)-(((*R*)-2-Hydroxy-1-phenylethyl)imino)(phenyl)(thiophen-2-yl)-λ^6-sulfanone (28a)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19 – 8.14 (m, 2H), 7.60 – 7.52 (m, 4H), 7.50 – 7.46 (m, 2H), 7.41 – 7.36 (m, 2H), 7.35 (dd, *J* = 4.0, 1.5 Hz, 1H), 7.33 – 7.29 (m, 1H), 6.98 (dd, *J* = 5.0, 4.0 Hz, 1H), 4.55 (dd, *J* = 8.5, 4.0 Hz, 1H), 3.79 – 3.65 (m, 2H), 3.00 (s, 1H).

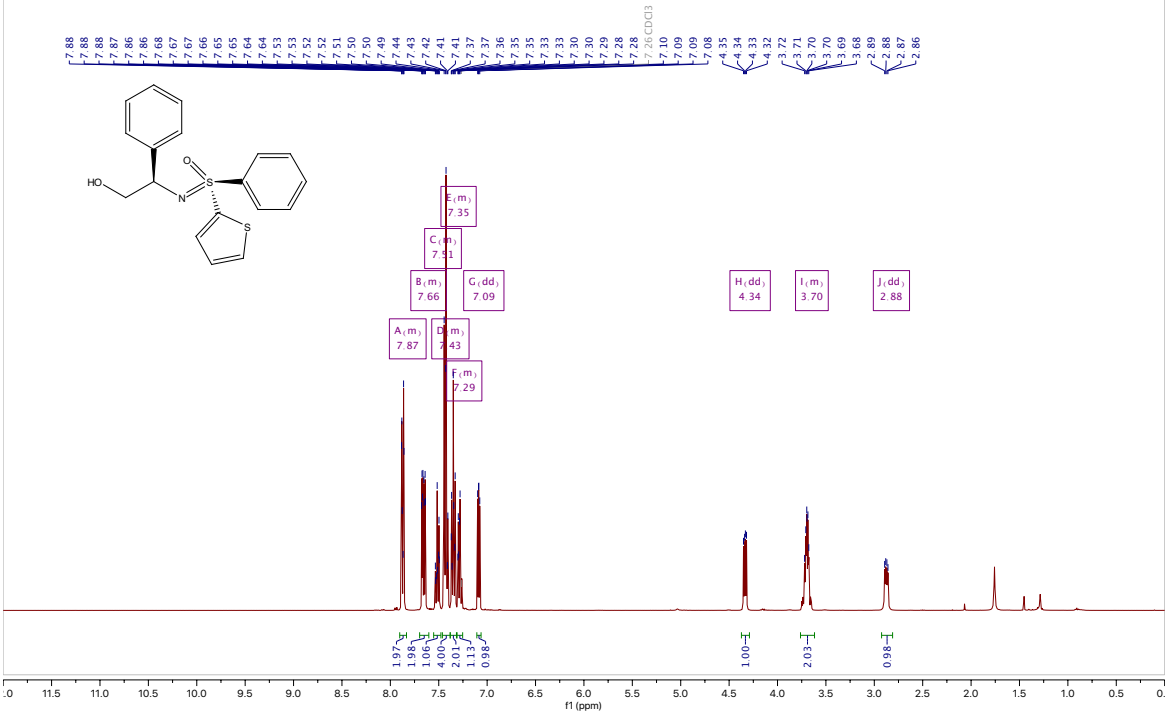


^{13}C NMR (101 MHz, $CDCl_3$) δ 142.08, 141.65, 141.57, 134.32, 134.01, 132.97, 129.32, 128.48, 128.15, 128.13, 127.33, 127.14, 69.28, 62.07.

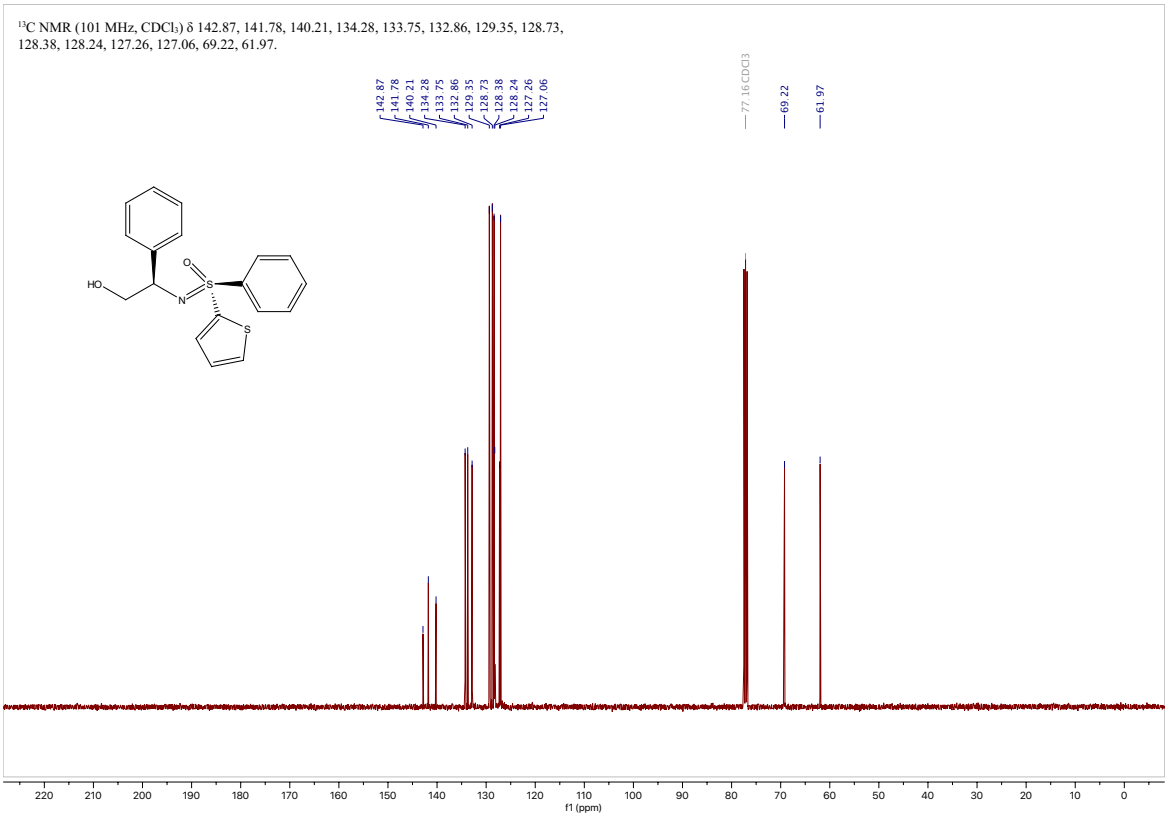


(*R*)-(((*R*)-2-Hydroxy-1-phenylethyl)imino)(phenyl)(thiophen-2-yl)-λ6-sulfanone (28b)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.85 (m, 2H), 7.69 – 7.62 (m, 2H), 7.55 – 7.48 (m, 1H), 7.46 – 7.39 (m, 4H), 7.38 – 7.32 (m, 2H), 7.31 – 7.25 (m, 1H), 7.09 (dd, *J* = 5.0, 4.0 Hz, 1H), 4.34 (dd, *J* = 8.0, 4.5 Hz, 1H), 3.76 – 3.63 (m, 2H), 2.88 (dd, *J* = 9.0, 4.5 Hz, 1H).

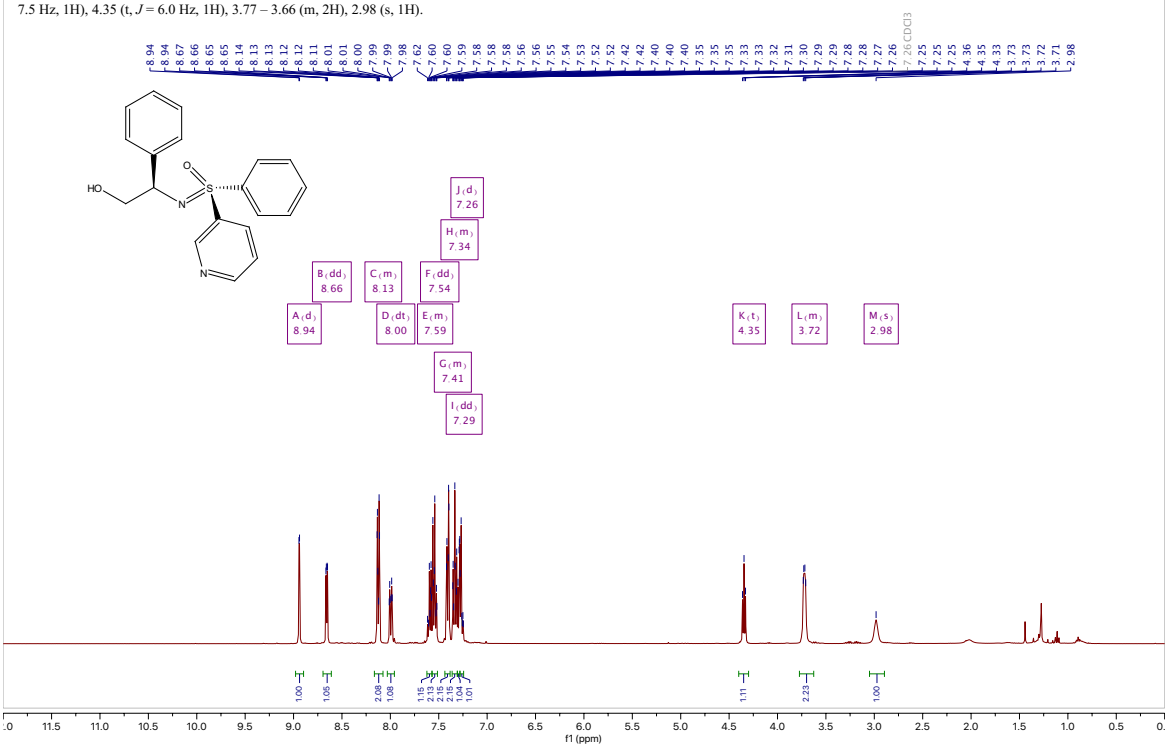


^{13}C NMR (101 MHz, $CDCl_3$) δ 142.87, 141.78, 140.21, 134.28, 133.75, 132.86, 129.35, 128.73, 128.38, 128.24, 127.26, 127.06, 69.22, 61.97.

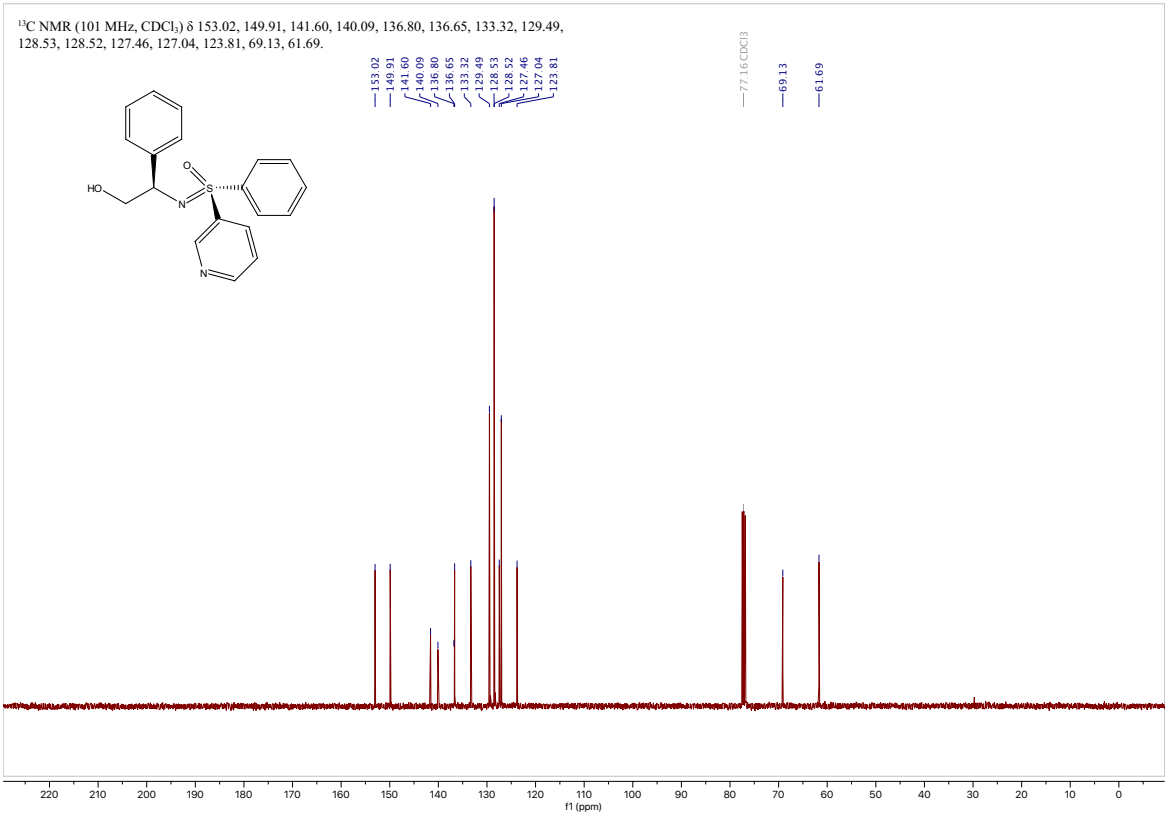


(*S*)-(((*R*)-2-Hydroxy-1-phenylethyl)imino)(phenyl)(pyridin-3-yl)-λ^6-sulfanone (29a)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.94 (d, *J* = 2.5 Hz, 1H), 8.66 (dd, *J* = 5.0, 1.5 Hz, 1H), 8.16 – 8.09 (m, 2H), 8.00 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.62 – 7.57 (m, 1H), 7.54 (dd, *J* = 8.5, 6.5 Hz, 2H), 7.43 – 7.39 (m, 2H), 7.36 – 7.31 (m, 2H), 7.29 (dd, *J* = 4.5, 3.0 Hz, 1H), 7.26 (d, *J* = 7.5 Hz, 1H), 4.35 (t, *J* = 6.0 Hz, 1H), 3.77 – 3.66 (m, 2H), 2.98 (s, 1H).

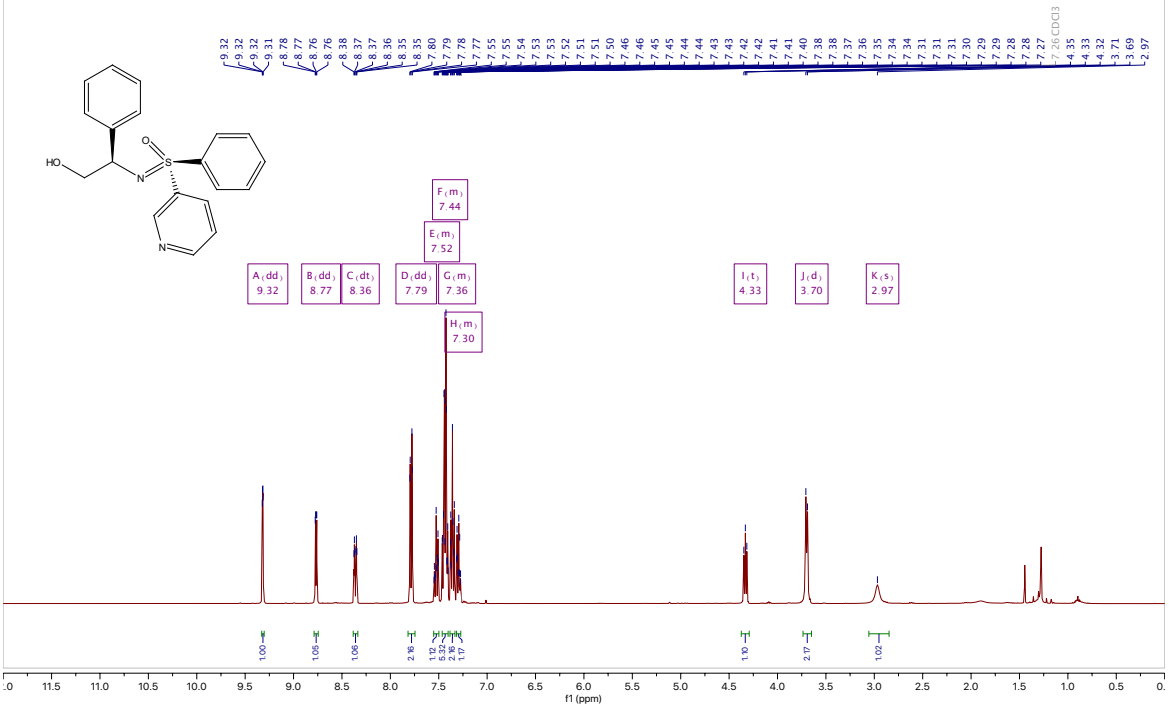


^{13}C NMR (101 MHz, $CDCl_3$) δ 153.02, 149.91, 141.60, 140.09, 136.80, 136.65, 133.32, 129.49, 128.53, 128.52, 127.46, 127.04, 123.81, 69.13, 61.69.

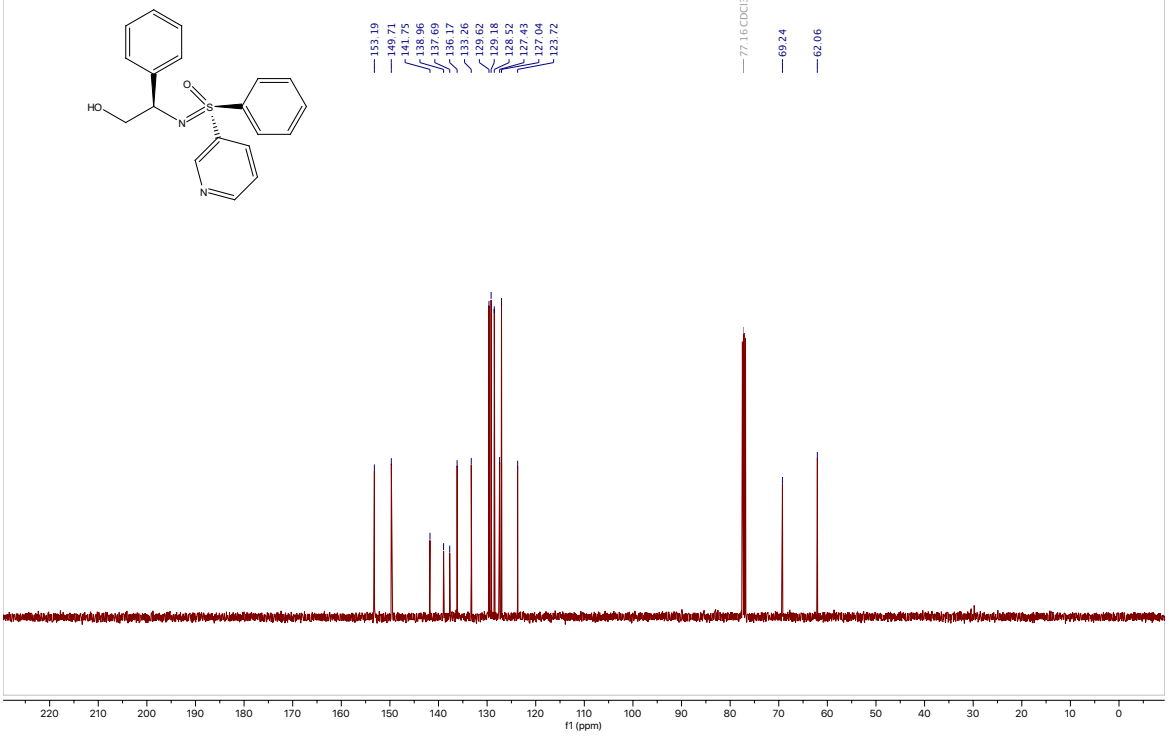


(*R*)-(((*R*)-2-Hydroxy-1-phenylethyl)imino)(phenyl)(pyridin-3-yl)-λ6-sulfanone (29b)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.32 (dd, *J* = 2.5, 1.0 Hz, 1H), 8.77 (dd, *J* = 5.0, 1.5 Hz, 1H), 8.36 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.79 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.55 – 7.50 (m, 1H), 7.48 – 7.40 (m, 5H), 7.38 – 7.33 (m, 2H), 7.32 – 7.27 (m, 1H), 4.33 (t, *J* = 6.0 Hz, 1H), 3.70 (d, *J* = 6.5 Hz, 2H), 2.97 (s, 1H).

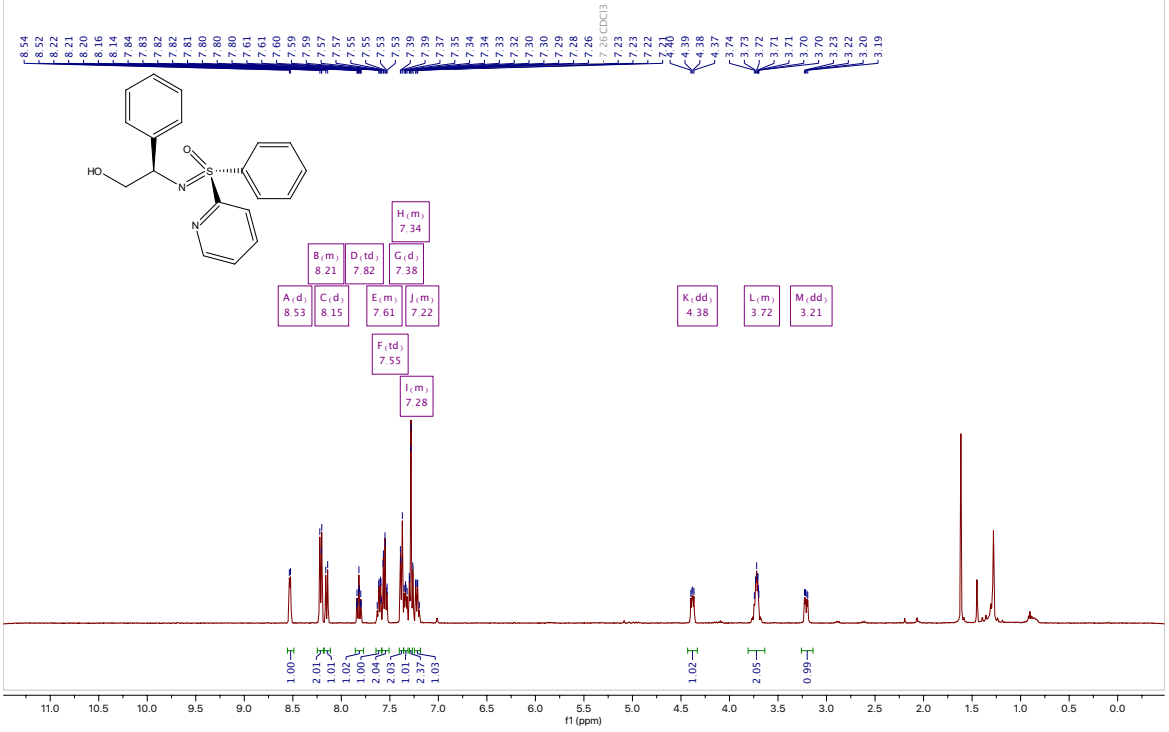


^{13}C NMR (101 MHz, $CDCl_3$) δ 153.19, 149.71, 141.75, 138.96, 137.69, 136.17, 133.26, 129.62, 129.18, 128.52, 127.43, 127.04, 123.72, 69.24, 62.06.

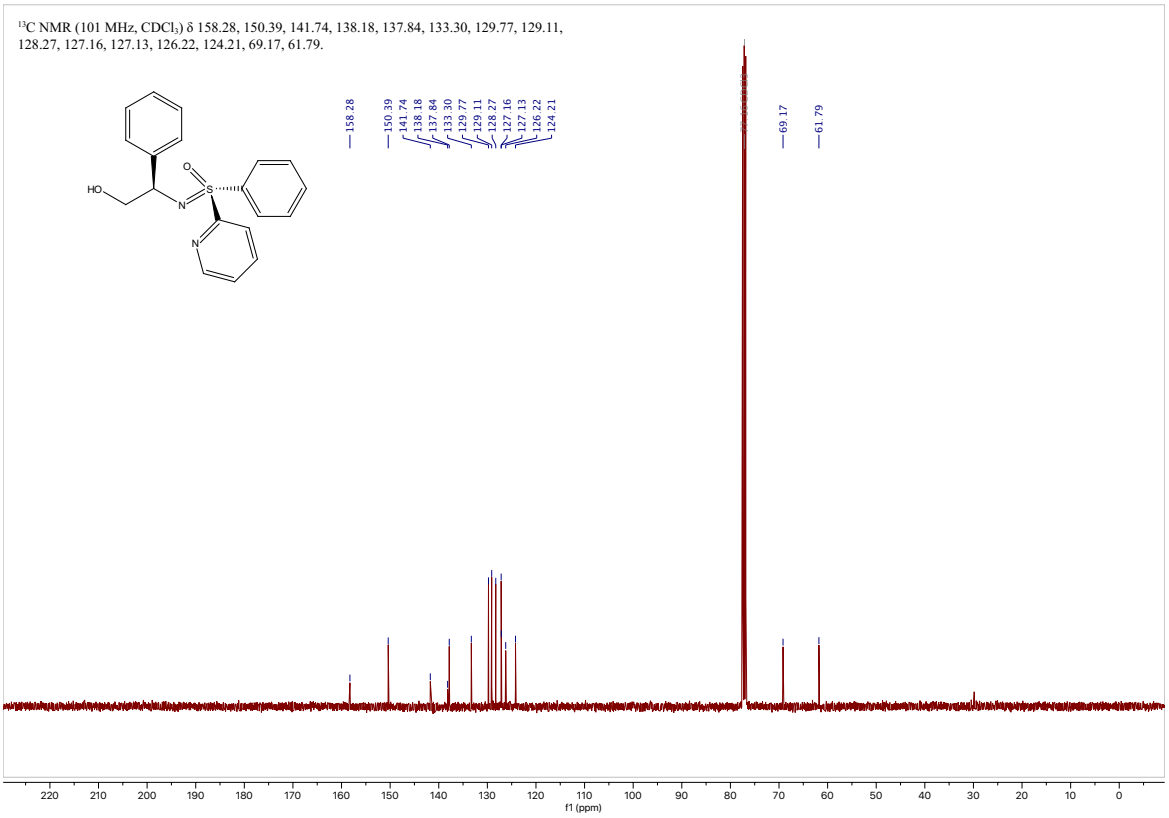


(*S*)-(((*R*)-2-Hydroxy-1-phenylethyl)imino)(phenyl)(pyridin-2-yl)-λ^6-sulfanone (30a)

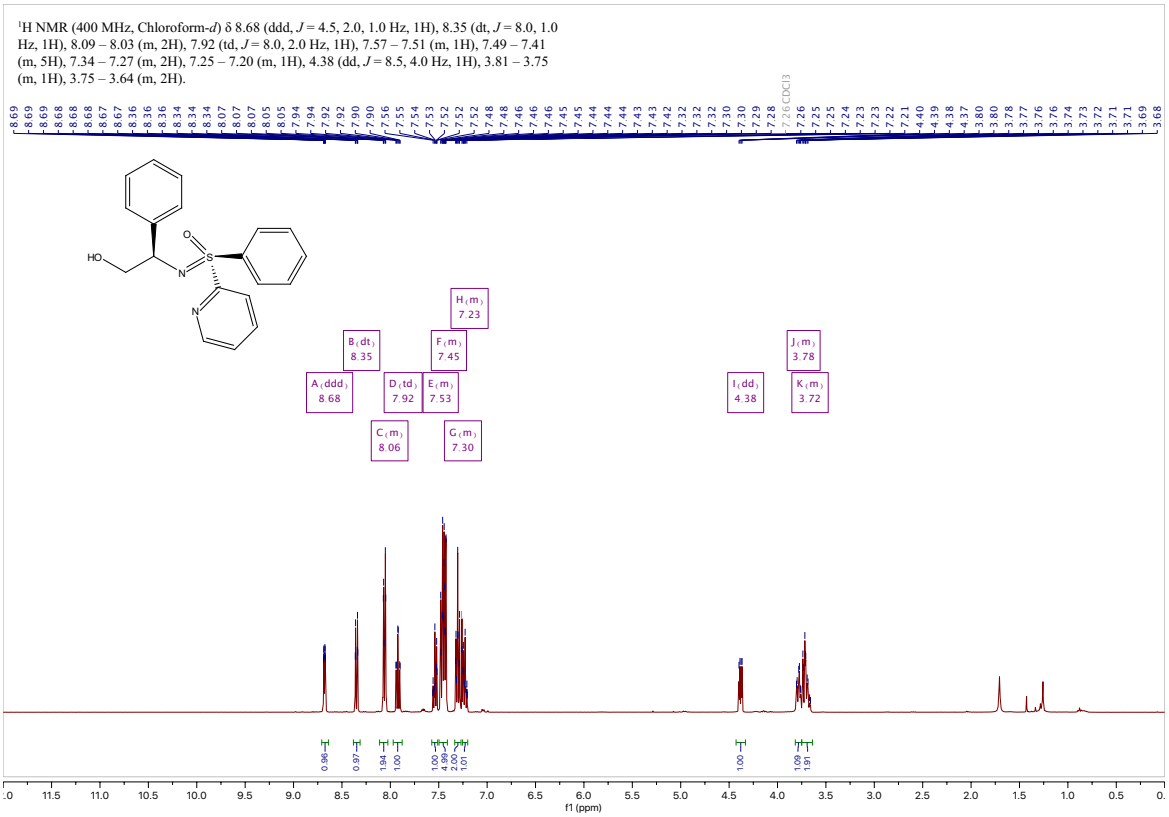
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.53 (d, *J* = 5.0 Hz, 1H), 8.24 – 8.19 (m, 2H), 8.15 (d, *J* = 8.0 Hz, 1H), 7.82 (td, *J* = 8.0, 4.0 Hz, 1H), 7.64 – 7.58 (m, 1H), 7.55 (td, *J* = 7.5, 2.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.36 – 7.32 (m, 1H), 7.30 – 7.26 (m, 2H), 7.25 – 7.19 (m, 1H), 4.38 (dd, *J* = 8.5, 4.5 Hz, 1H), 3.79 – 3.66 (m, 2H), 3.21 (dd, *J* = 9.5, 4.0 Hz, 1H).

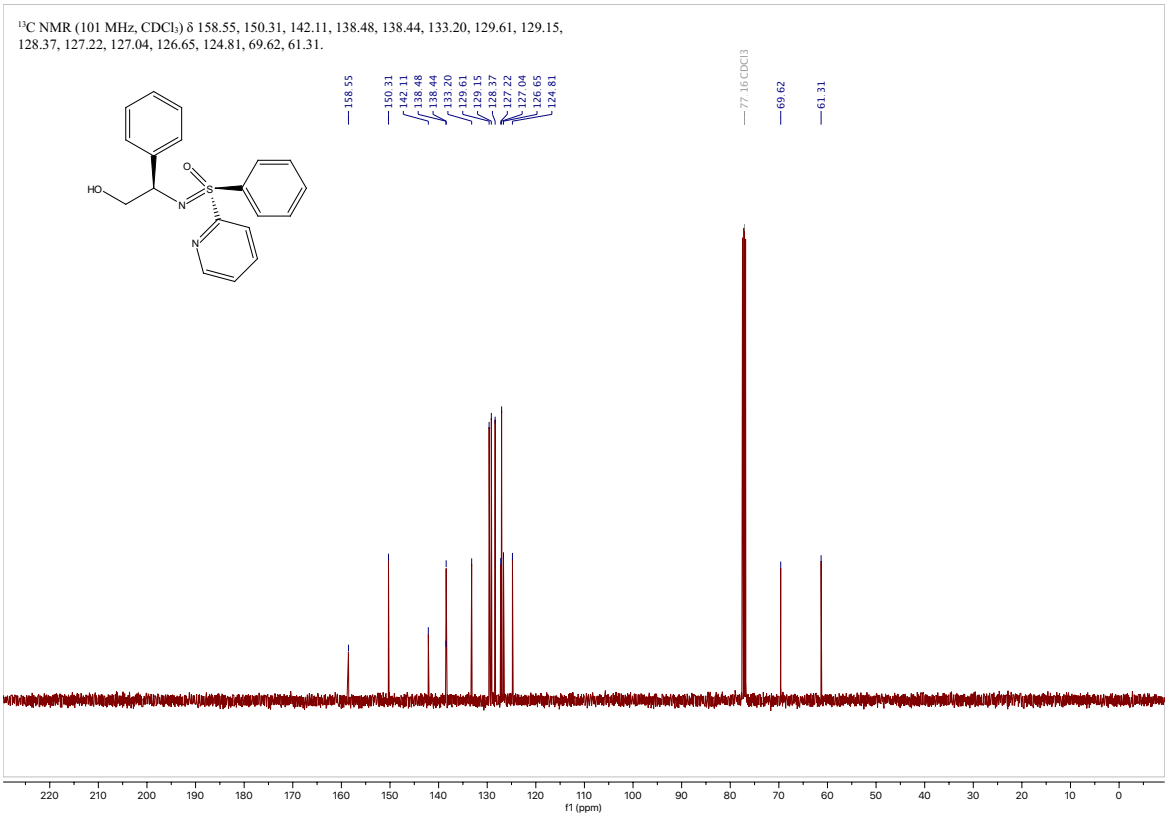


^{13}C NMR (101 MHz, $CDCl_3$) δ 158.28, 150.39, 141.74, 138.18, 137.84, 133.30, 129.77, 129.11, 128.27, 127.16, 127.13, 126.22, 124.21, 69.17, 61.79.



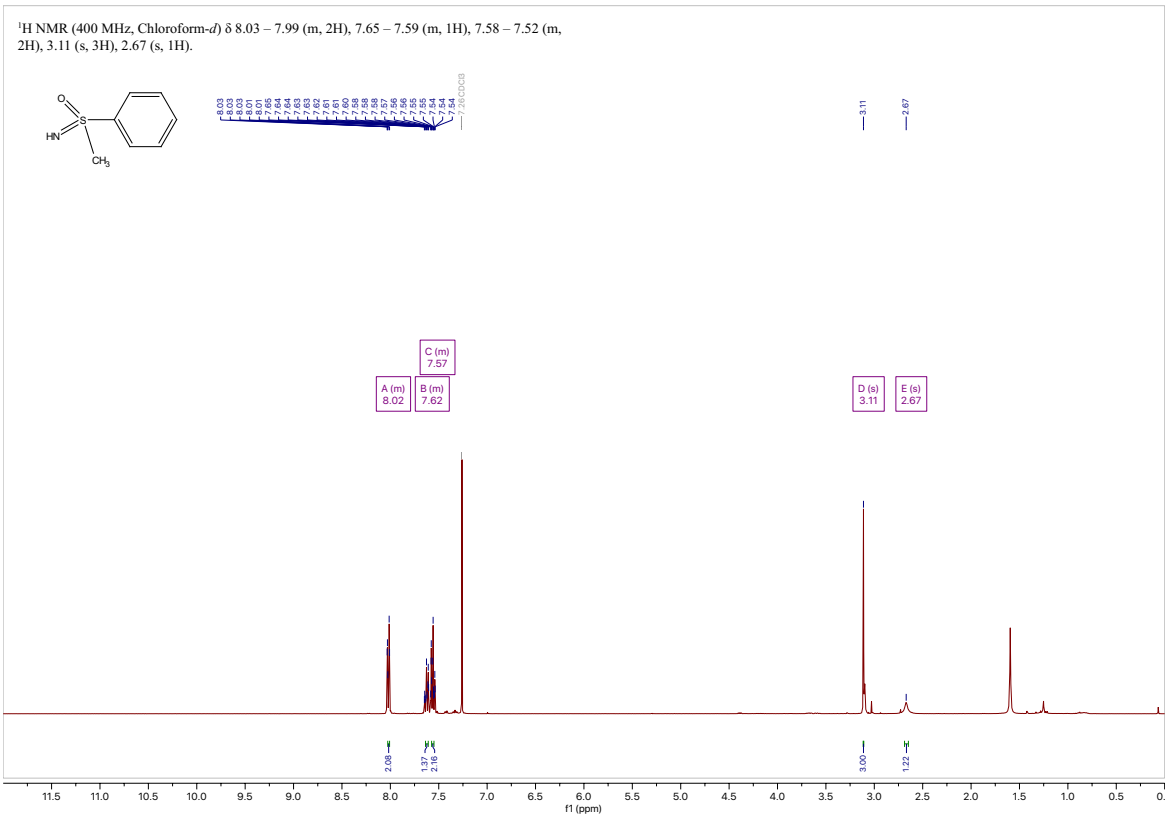
(*R*)-(((*R*)-2-Hydroxy-1-phenylethyl)imino)(phenyl)(pyridin-2-yl)-λ6-sulfanone (30b)



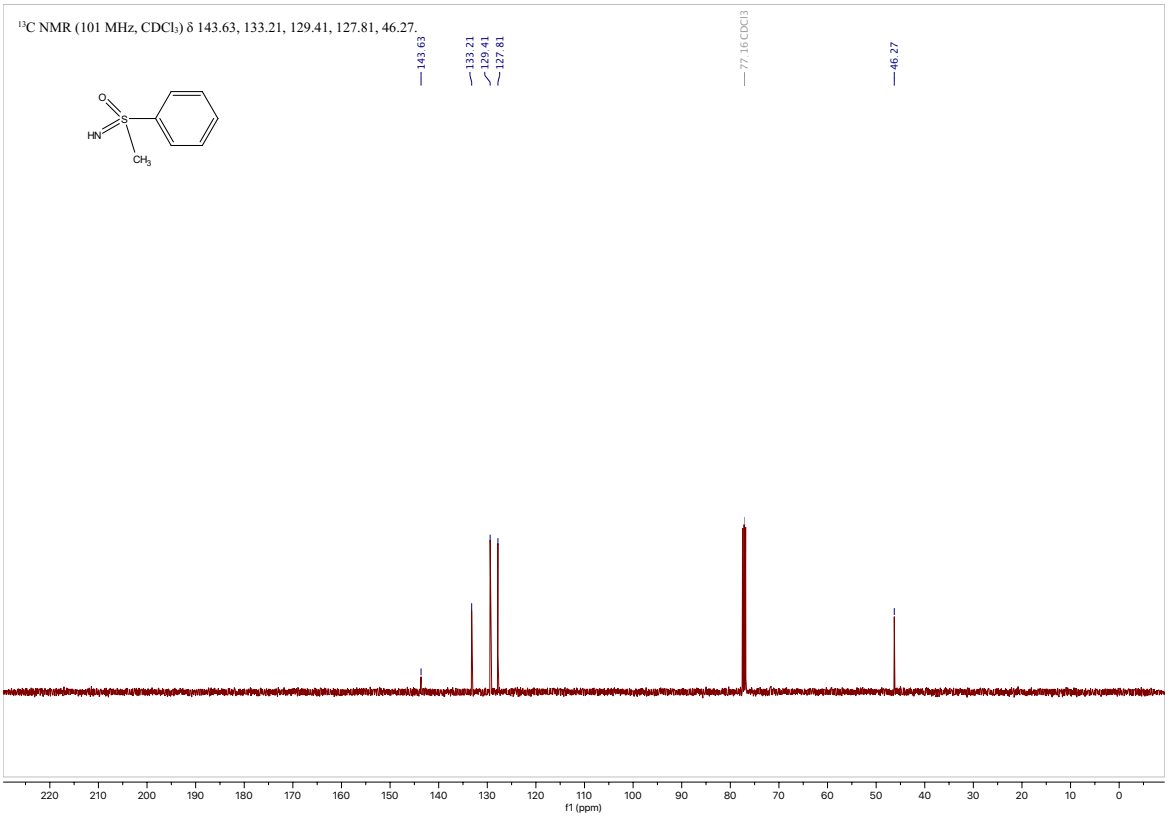


Imino(methyl)(phenyl)-λ^6-sulfanone (33)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 – 7.99 (m, 2H), 7.65 – 7.59 (m, 1H), 7.58 – 7.52 (m, 2H), 3.11 (s, 3H), 2.67 (s, 1H).

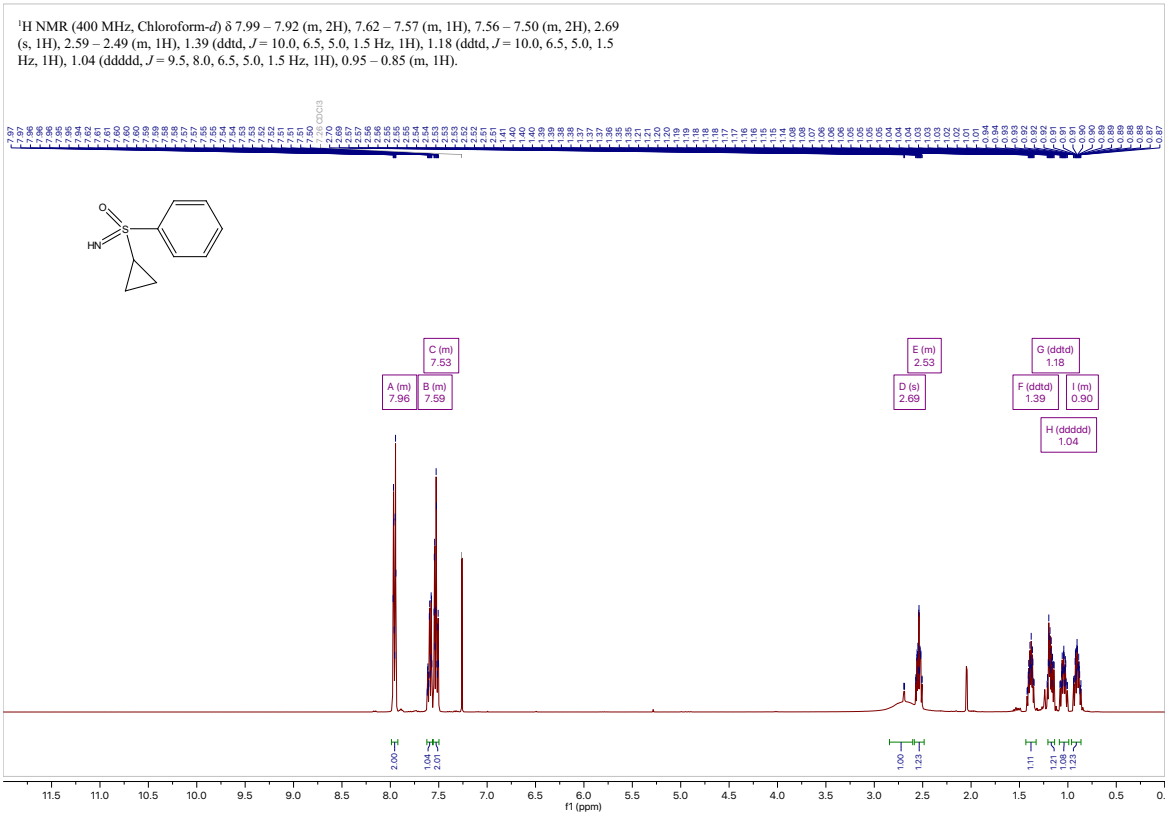


^{13}C NMR (101 MHz, $CDCl_3$) δ 143.63, 133.21, 129.41, 127.81, 46.27.

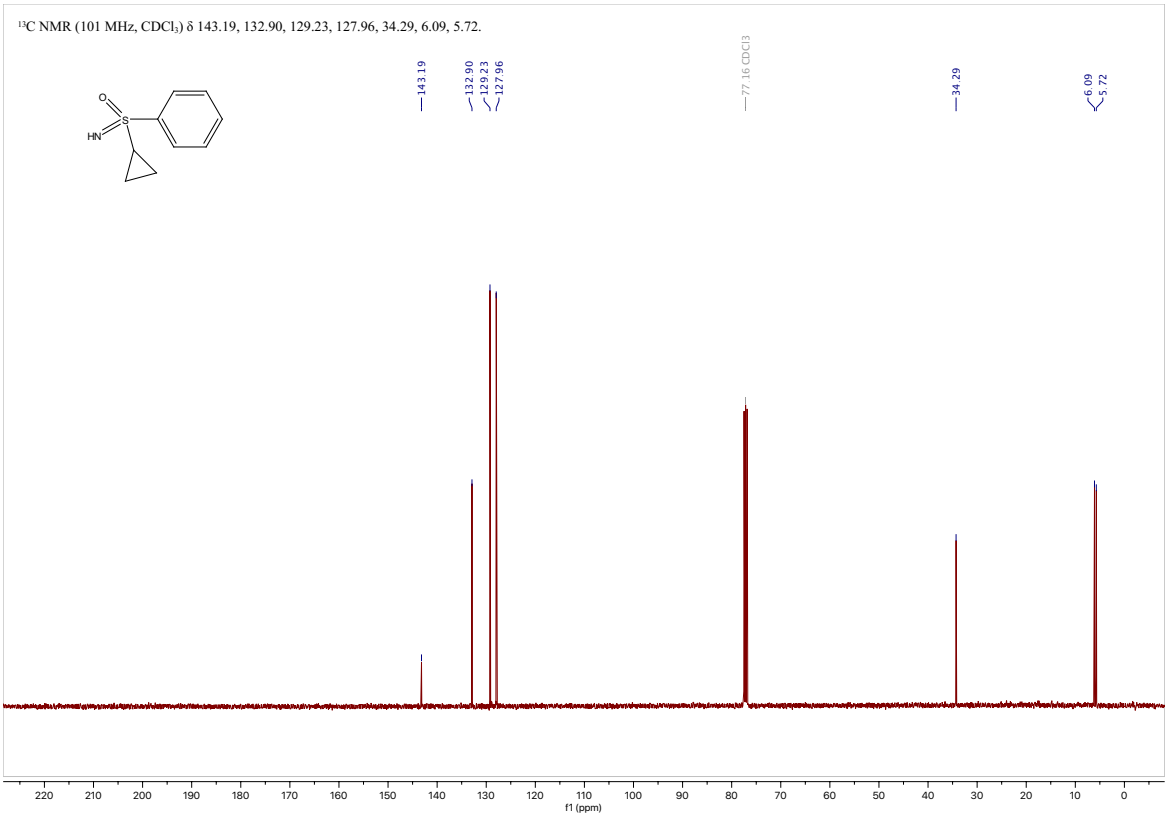


Cyclopropyl(imino)(phenyl)-λ^6-sulfanone (34)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 – 7.92 (m, 2H), 7.62 – 7.57 (m, 1H), 7.56 – 7.50 (m, 2H), 2.69 (s, 1H), 2.59 – 2.49 (m, 1H), 1.39 (ddtd, *J* = 10.0, 6.5, 5.0, 1.5 Hz, 1H), 1.18 (ddtd, *J* = 10.0, 6.5, 5.0, 1.5 Hz, 1H), 1.04 (ddddd, *J* = 9.5, 8.0, 6.5, 5.0, 1.5 Hz, 1H), 0.95 – 0.85 (m, 1H).

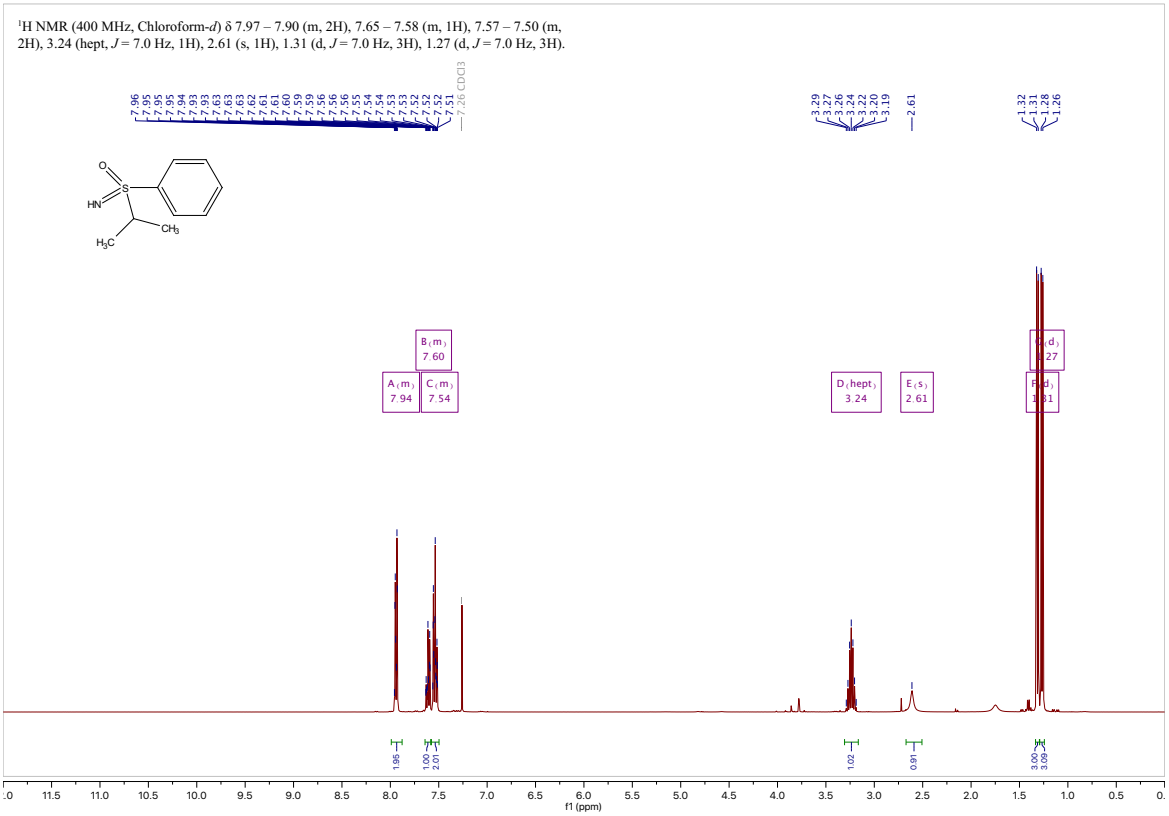


^{13}C NMR (101 MHz, $CDCl_3$) δ 143.19, 132.90, 129.23, 127.96, 34.29, 6.09, 5.72.

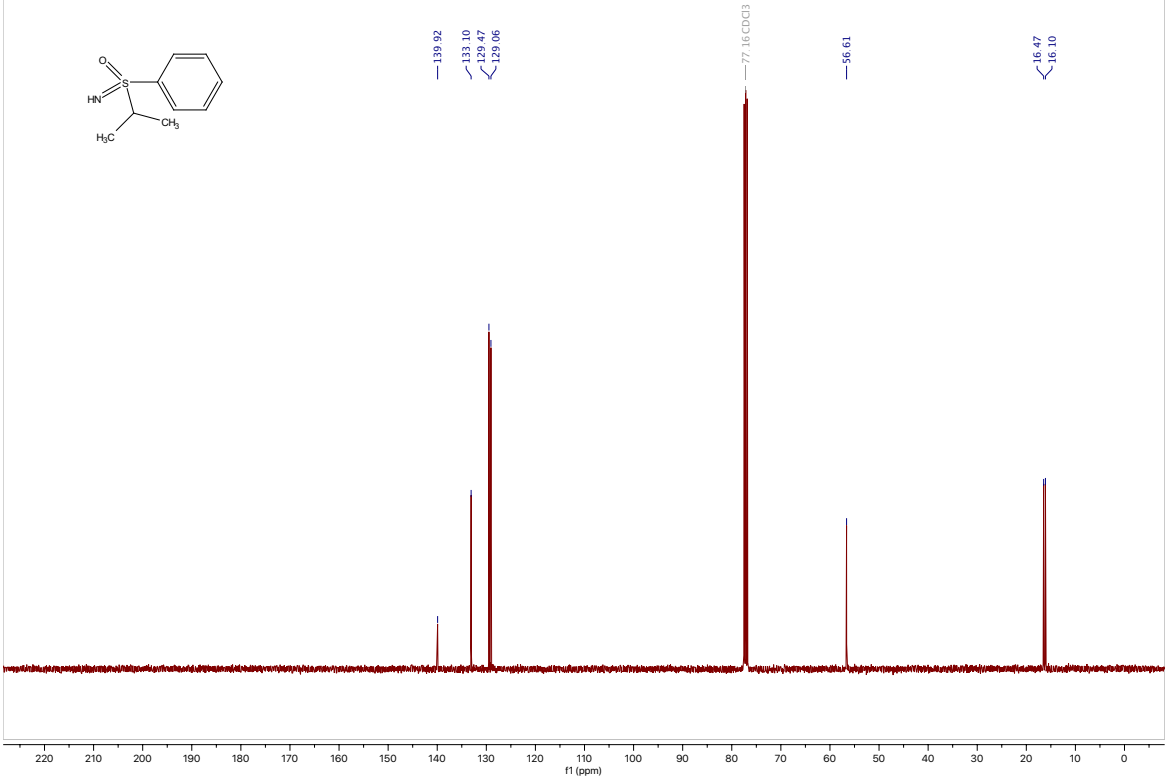


Imino(isopropyl)(phenyl)-λ^6-sulfanone (35)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.90 (m, 2H), 7.65 – 7.58 (m, 1H), 7.57 – 7.50 (m, 2H), 3.24 (hept, *J* = 7.0 Hz, 1H), 2.61 (s, 1H), 1.31 (d, *J* = 7.0 Hz, 3H), 1.27 (d, *J* = 7.0 Hz, 3H).

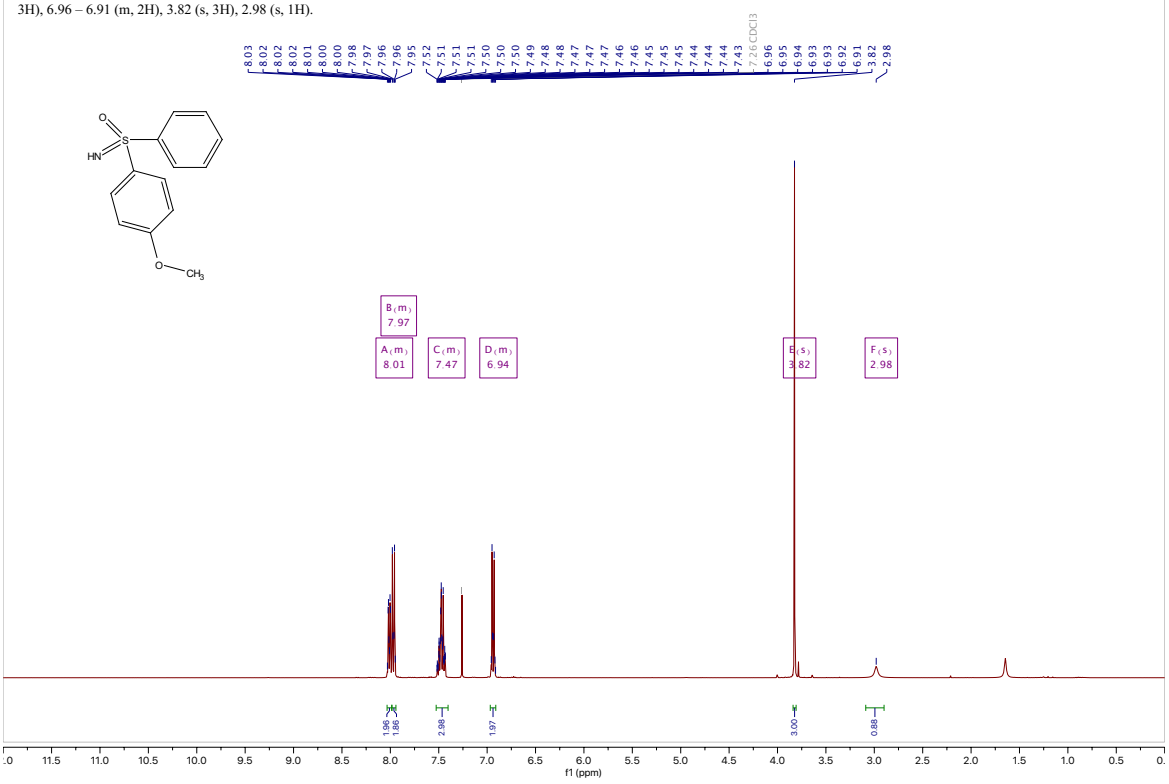


^{13}C NMR (101 MHz, $CDCl_3$) δ 139.92, 133.10, 129.47, 129.06, 56.61, 16.47, 16.10.

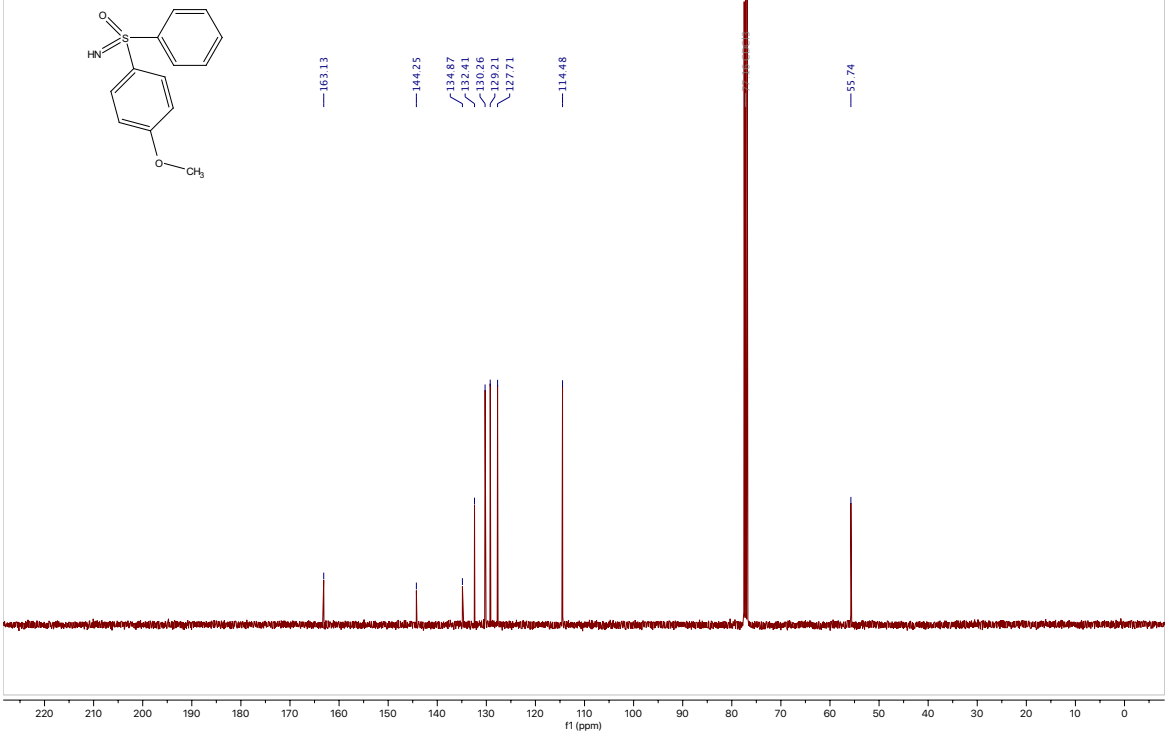


Imino(4-methoxyphenyl)(phenyl)-λ^6-sulfanone (37)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 – 7.99 (m, 2H), 7.98 – 7.95 (m, 2H), 7.53 – 7.42 (m, 3H), 6.96 – 6.91 (m, 2H), 3.82 (s, 3H), 2.98 (s, 1H).

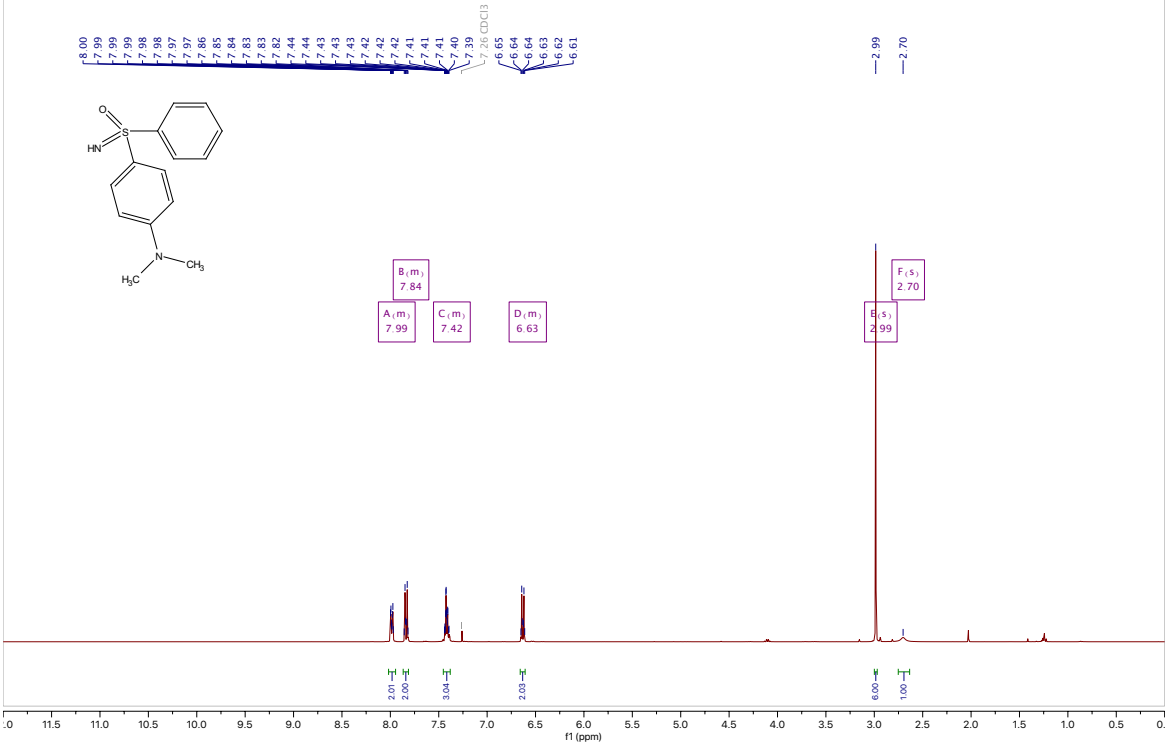


^{13}C NMR (101 MHz, $CDCl_3$) δ 163.13, 144.25, 134.87, 132.41, 130.26, 129.21, 127.71, 114.48, 55.74.

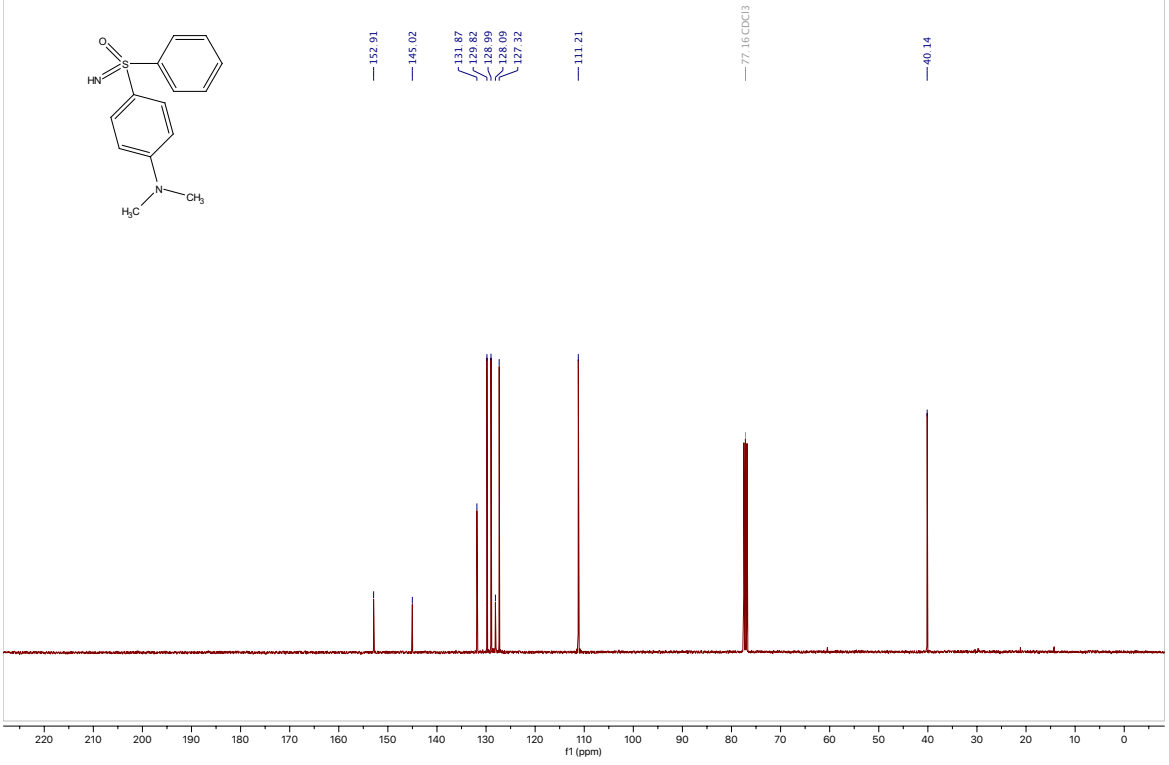


(4-(Dimethylamino)phenyl)(imino)(phenyl)-λ⁶-sulfanone (38)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.96 (m, 2H), 7.86 – 7.81 (m, 2H), 7.45 – 7.38 (m, 3H), 6.66 – 6.61 (m, 2H), 2.99 (s, 6H), 2.70 (s, 1H).

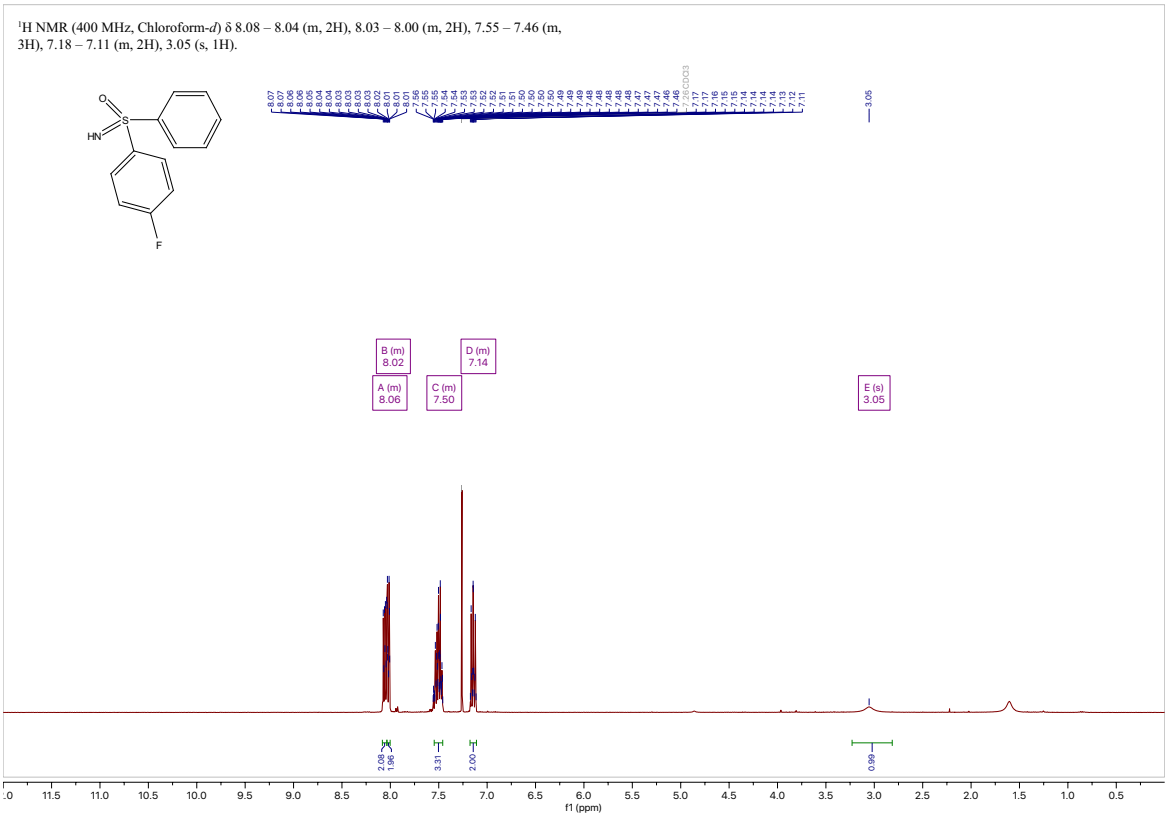


^{13}C NMR (101 MHz, $CDCl_3$) δ 152.91, 145.02, 131.87, 129.82, 128.99, 128.09, 127.32, 111.21, 40.14.

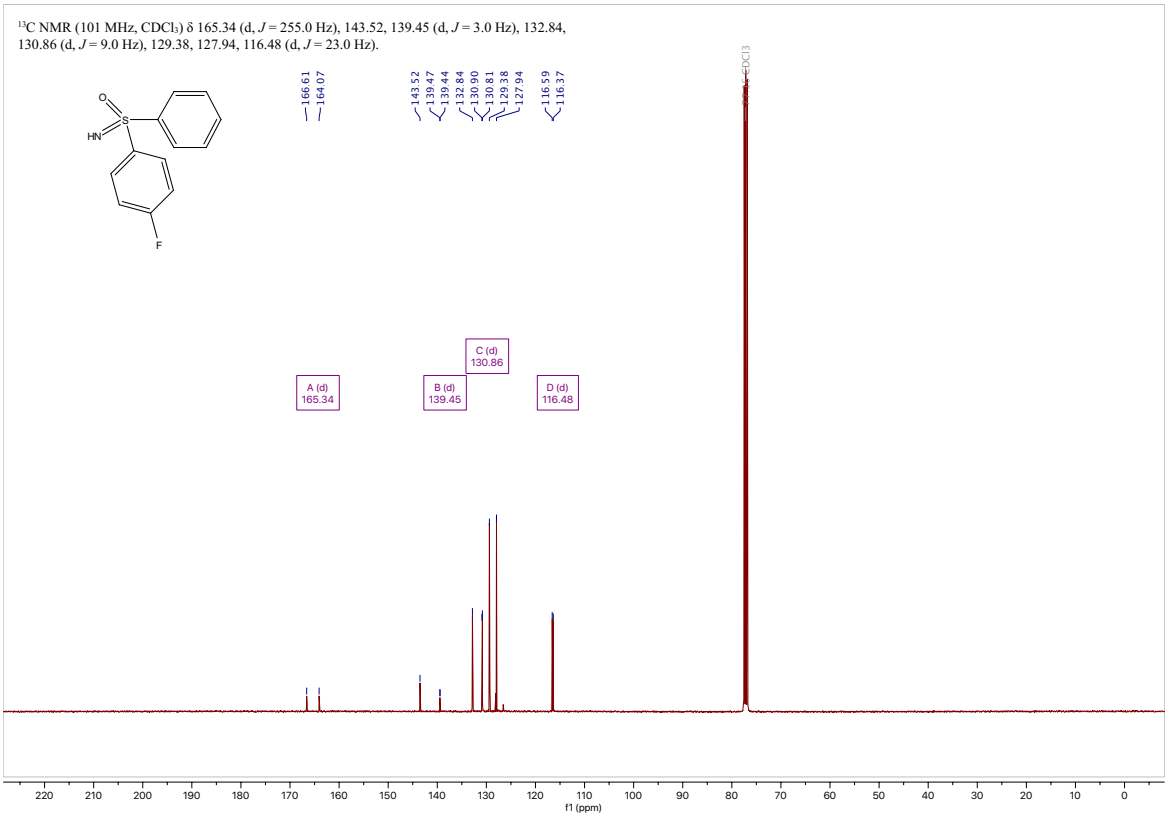


(4-Fluorophenyl)(imino)(phenyl)-λ⁶-sulfanone (39)

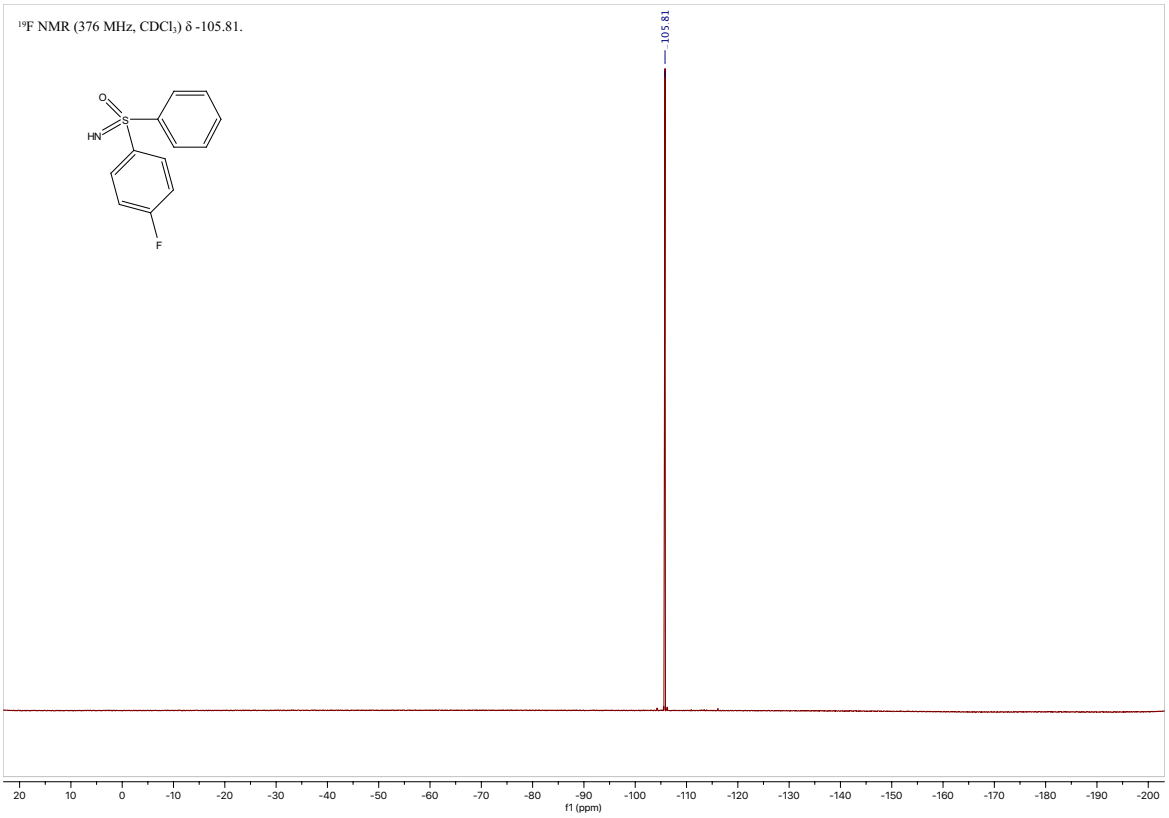
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 – 8.04 (m, 2H), 8.03 – 8.00 (m, 2H), 7.55 – 7.46 (m, 3H), 7.18 – 7.11 (m, 2H), 3.05 (s, 1H).



^{13}C NMR (101 MHz, $CDCl_3$) δ 165.34 (d, *J* = 255.0 Hz), 143.52, 139.45 (d, *J* = 3.0 Hz), 132.84, 130.86 (d, *J* = 9.0 Hz), 129.38, 127.94, 116.48 (d, *J* = 23.0 Hz).

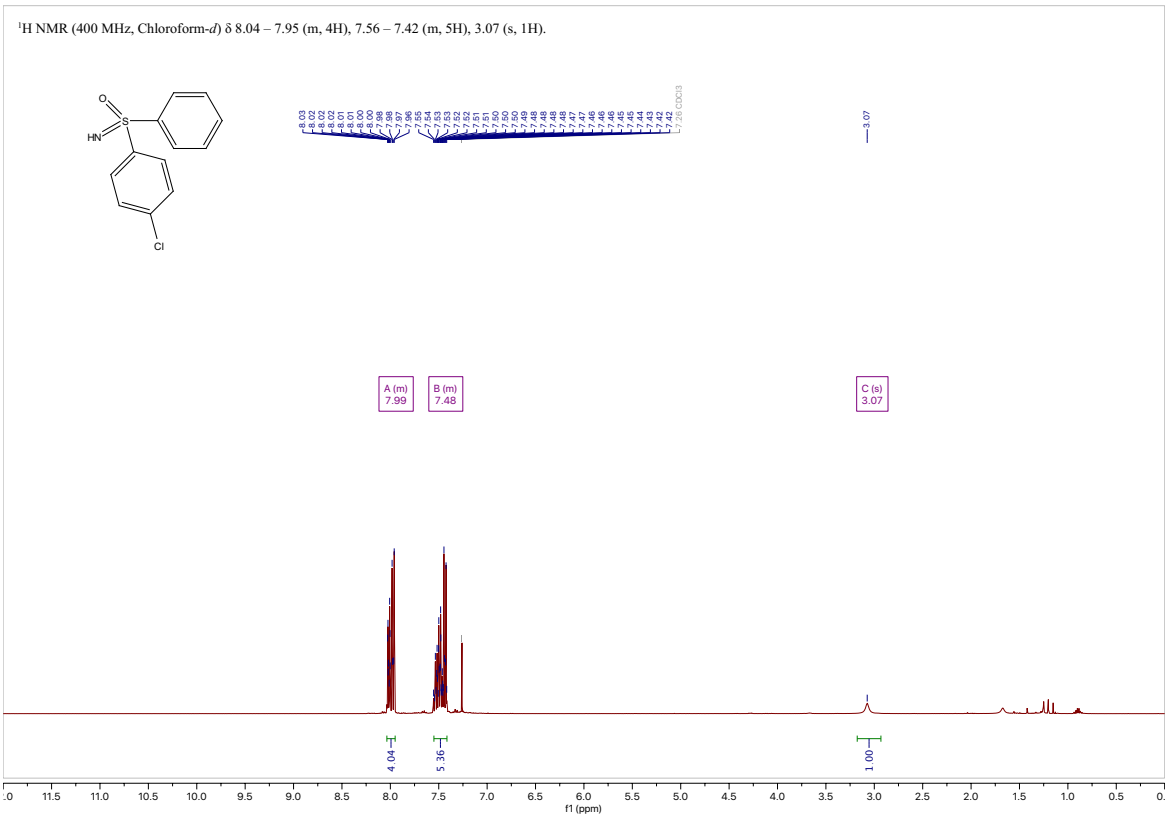


^{19}F NMR (376 MHz, $CDCl_3$) δ -105.81.

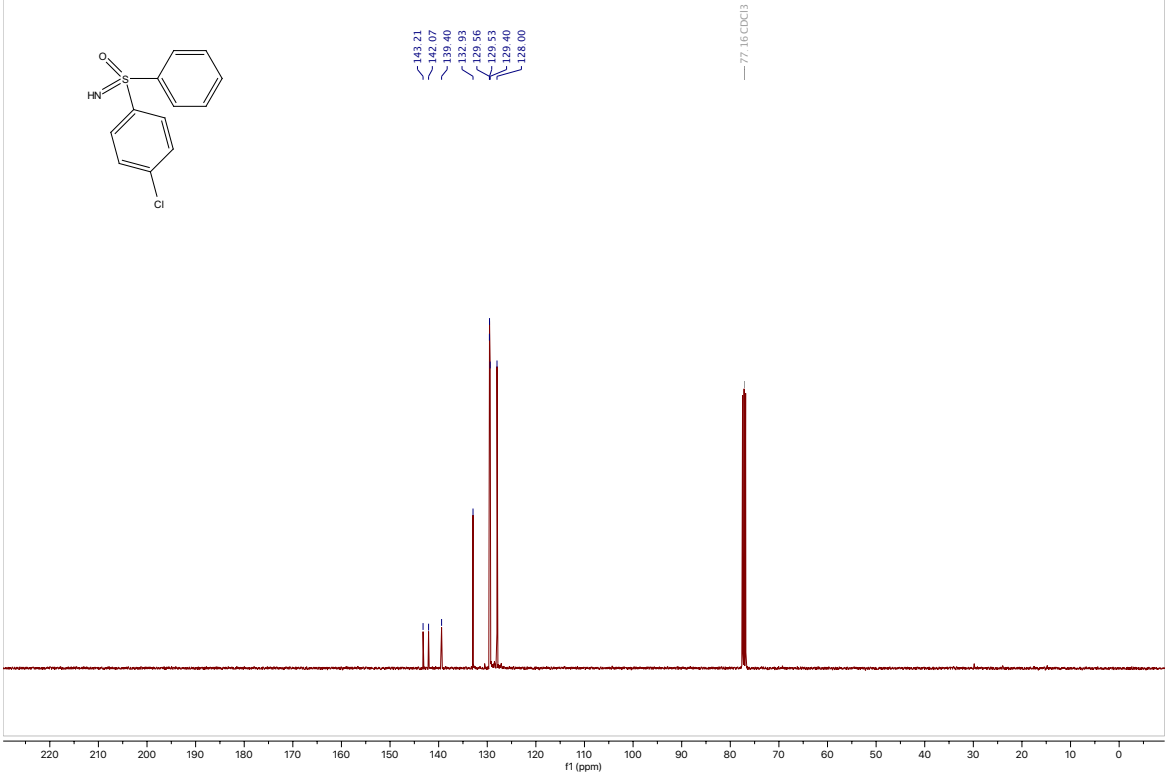


(4-Chlorophenyl)(imino)(phenyl)-λ^6-sulfanone (40)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 – 7.95 (m, 4H), 7.56 – 7.42 (m, 5H), 3.07 (s, 1H).

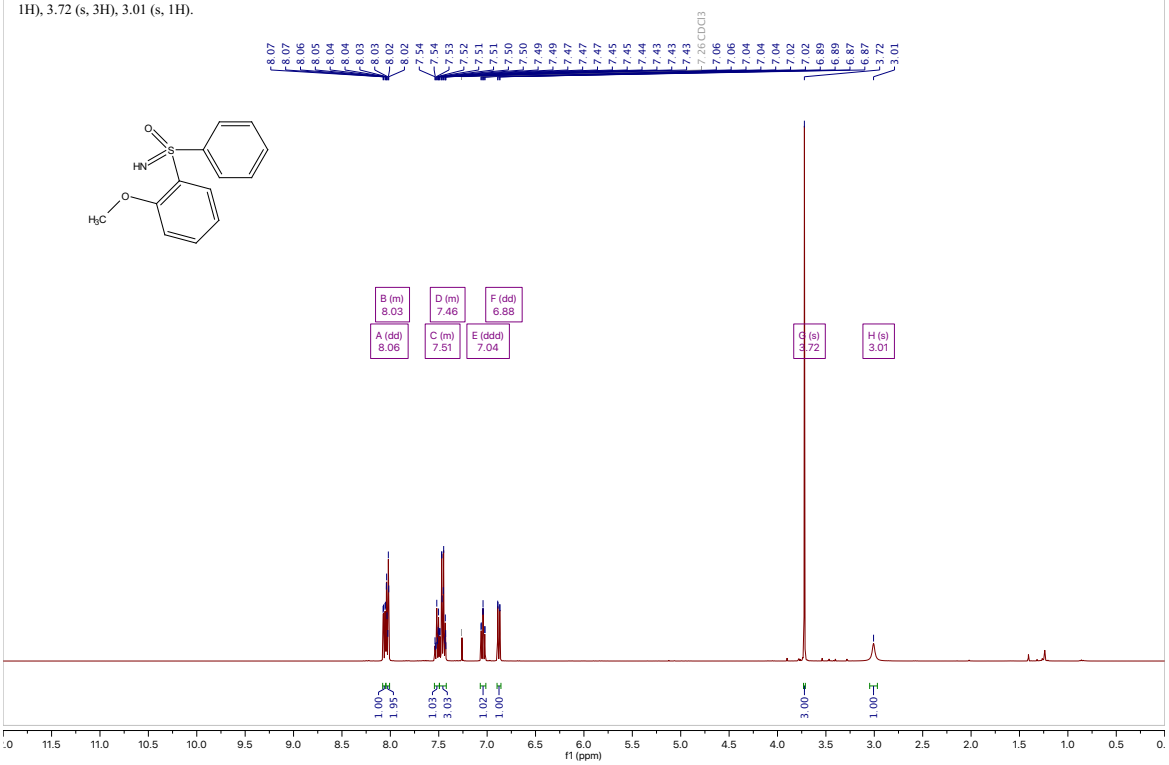


^{13}C NMR (101 MHz, $CDCl_3$) δ 143.21, 142.07, 139.40, 132.93, 129.56, 129.53, 129.40, 128.00.

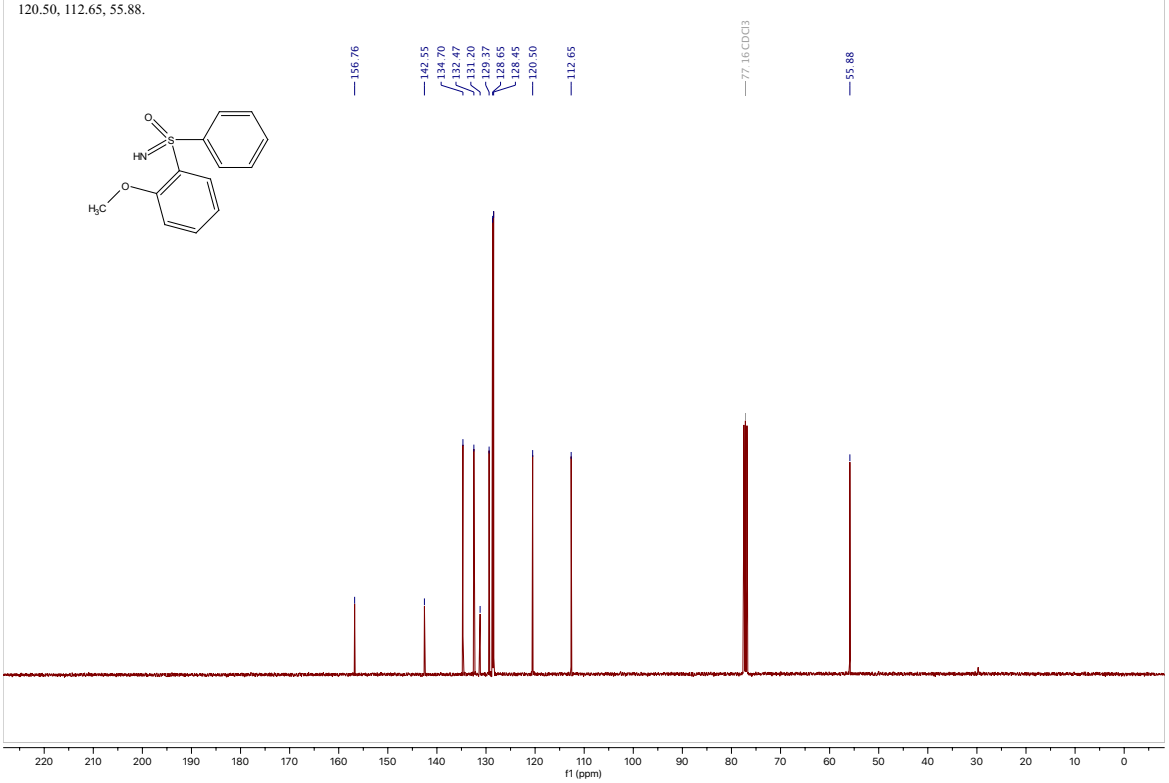


Imino(2-methoxyphenyl)(phenyl)-λ^6-sulfanone (41)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (dd, *J* = 8.0, 1.5 Hz, 1H), 8.05 – 8.01 (m, 2H), 7.55 – 7.50 (m, 1H), 7.49 – 7.42 (m, 3H), 7.04 (ddd, *J* = 8.0, 7.5, 1.0 Hz, 1H), 6.88 (dd, *J* = 8.0, 1.0 Hz, 1H), 3.72 (s, 3H), 3.01 (s, 1H).

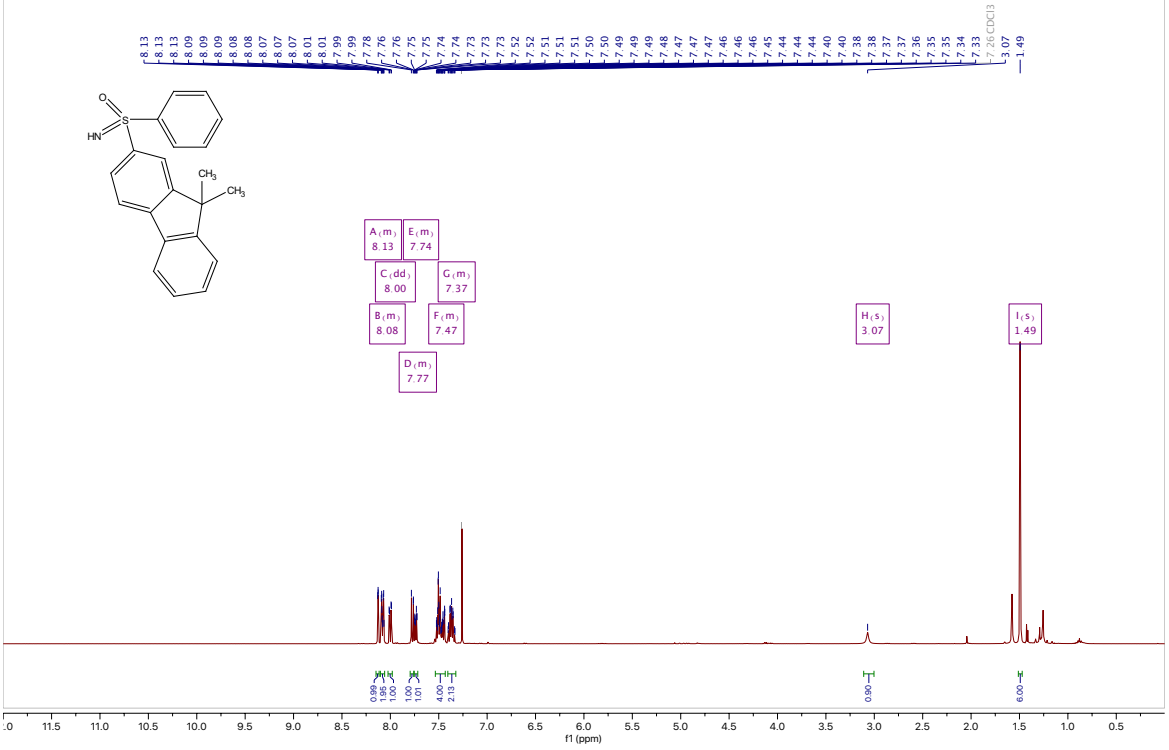


^{13}C NMR (101 MHz, $CDCl_3$) δ 156.76, 142.55, 134.70, 132.47, 131.20, 129.37, 128.65, 128.45, 120.50, 112.65, 55.88.

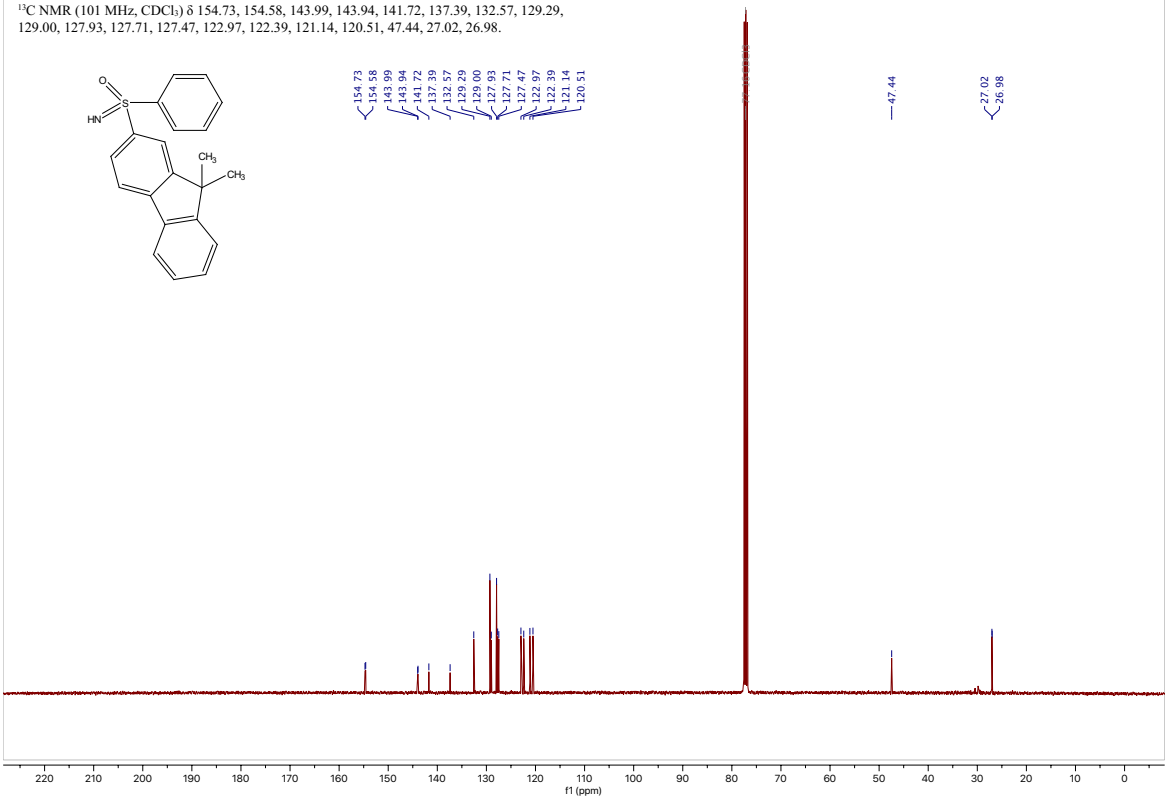


(9,9-Dimethyl-9*H*-fluoren-2-yl)(imino)(phenyl)-λ^6-sulfanone (42)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 – 8.12 (m, 1H), 8.10 – 8.06 (m, 2H), 8.00 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.80 – 7.76 (m, 1H), 7.75 – 7.72 (m, 1H), 7.53 – 7.43 (m, 4H), 7.41 – 7.33 (m, 2H), 3.07 (s, 1H), 1.49 (s, 6H).

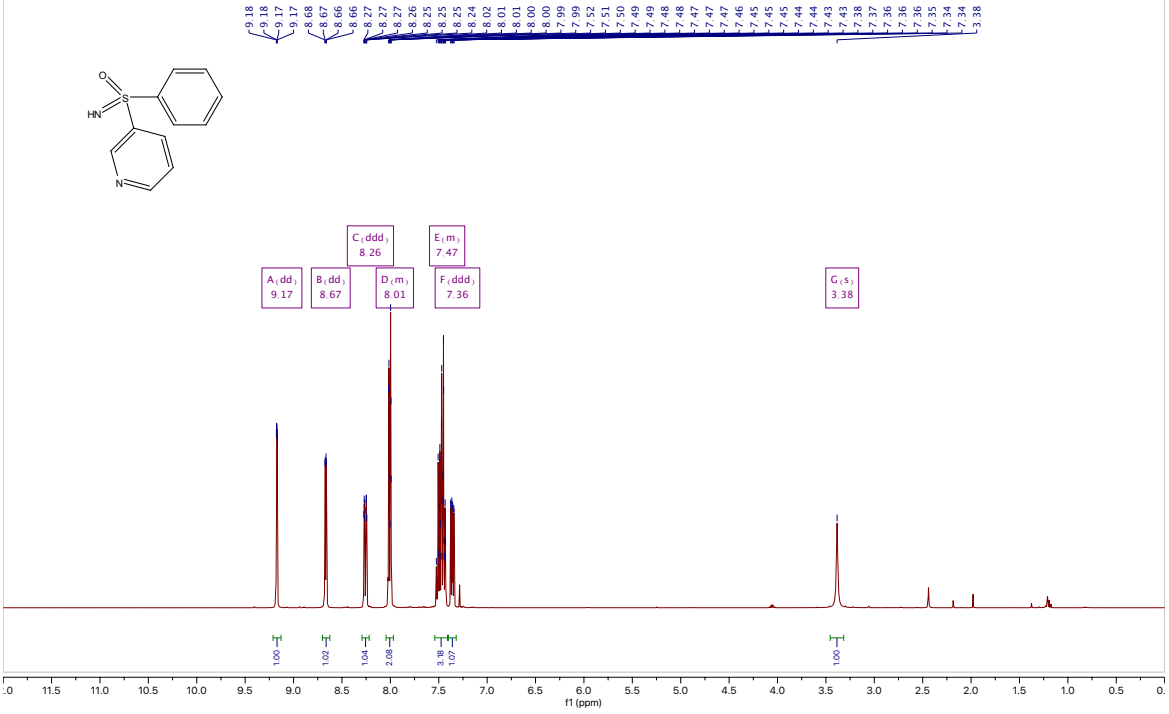


^{13}C NMR (101 MHz, $CDCl_3$) δ 154.73, 154.58, 143.99, 143.94, 141.72, 137.39, 132.57, 129.29, 129.00, 127.93, 127.71, 127.47, 122.97, 122.39, 121.14, 120.51, 47.44, 27.02, 26.98.

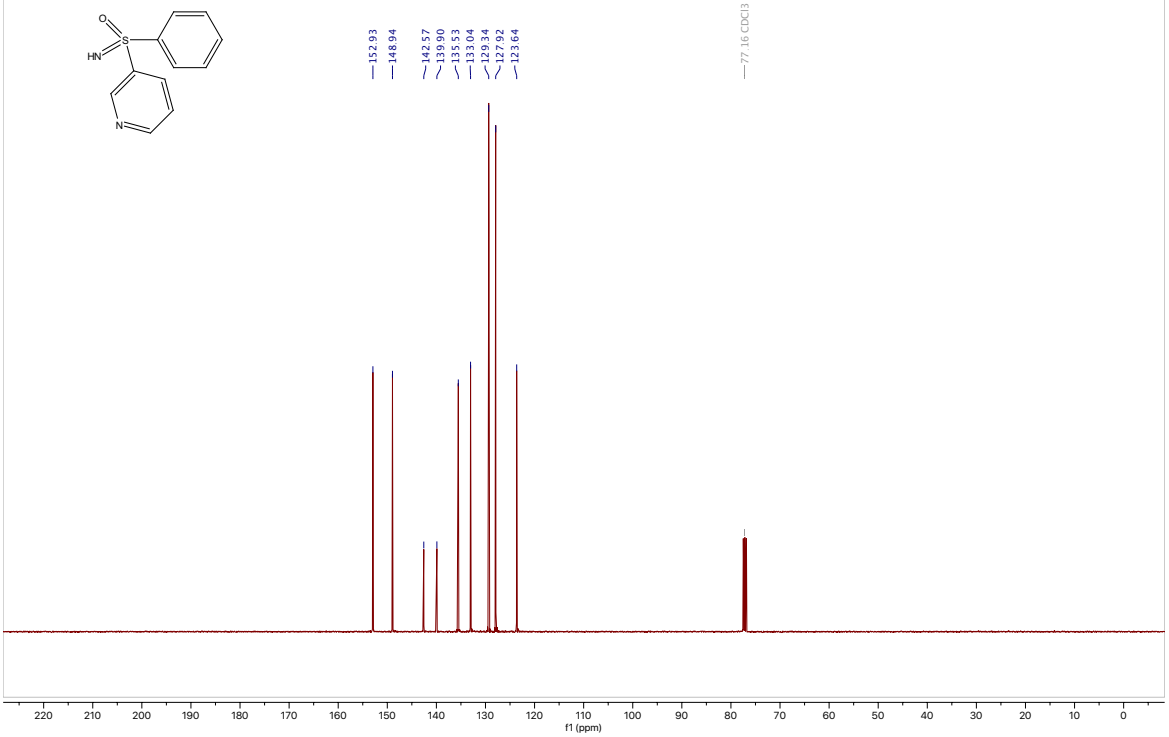


Imino(phenyl)(pyridin-3-yl)-λ^6-sulfanone (44)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.17 (dd, *J* = 2.5, 1.0 Hz, 1H), 8.67 (dd, *J* = 5.0, 1.5 Hz, 1H), 8.26 (ddd, *J* = 8.0, 2.5, 1.5 Hz, 1H), 8.04 – 7.97 (m, 2H), 7.54 – 7.42 (m, 3H), 7.36 (ddd, *J* = 8.0, 5.0, 1.0 Hz, 1H), 3.38 (s, 1H).

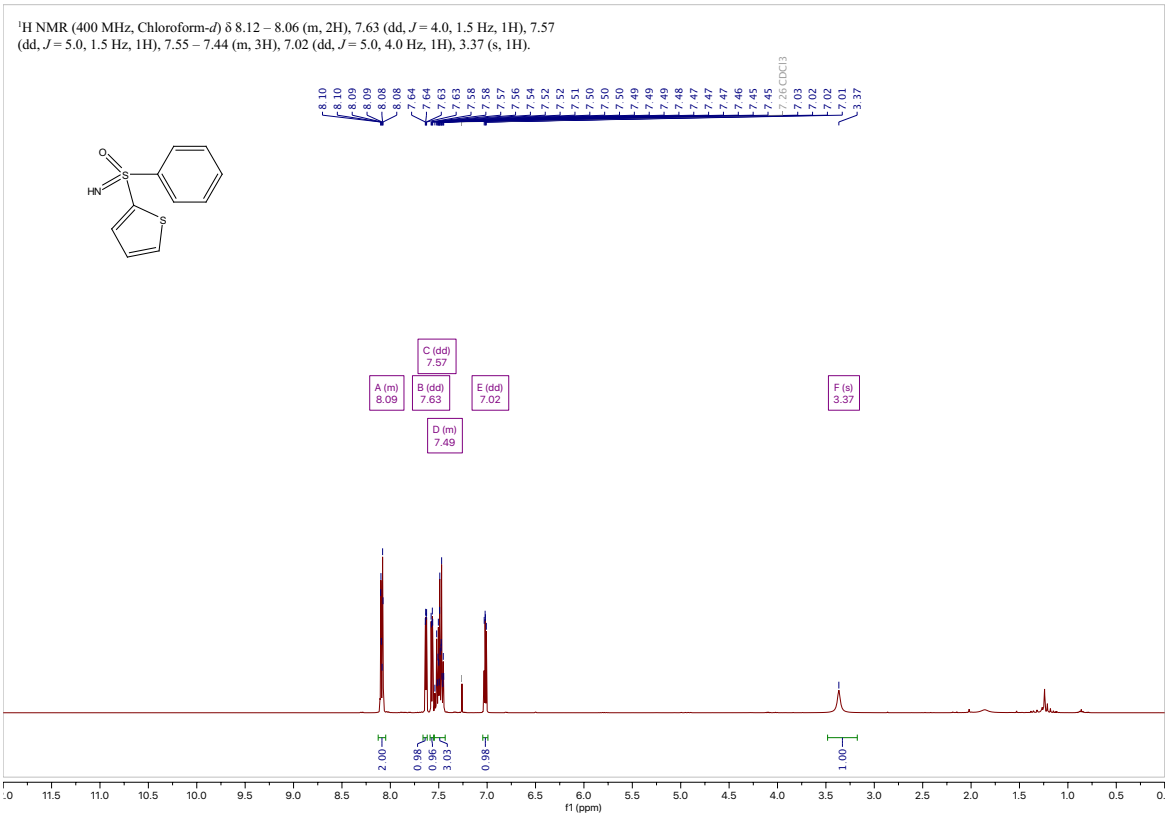


^{13}C NMR (101 MHz, $CDCl_3$) δ 152.93, 148.94, 142.57, 139.90, 135.53, 133.04, 129.34, 127.92, 123.64.



Imino(phenyl)(thiophen-2-yl)-λ^6-sulfanone (45)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 – 8.06 (m, 2H), 7.63 (dd, *J* = 4.0, 1.5 Hz, 1H), 7.57 (dd, *J* = 5.0, 1.5 Hz, 1H), 7.55 – 7.44 (m, 3H), 7.02 (dd, *J* = 5.0, 4.0 Hz, 1H), 3.37 (s, 1H).



^{13}C NMR (101 MHz, $CDCl_3$) δ 146.13, 143.36, 133.87, 133.28, 132.79, 129.23, 128.02, 127.68.