Supporting Information for

5-(Diarylimino)- and 5-(Sulfoximido)dibenzothiophenium Triflates: Synthesis and Application as Electrophilic Aminating Reagents.

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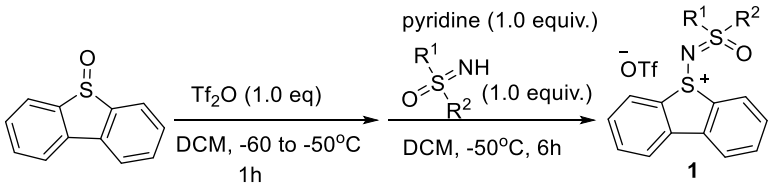
1 General information

Unless otherwise noted, all experiments were carried out in dried glassware under an atmosphere of nitrogen using standard Schlenk techniques. All dry solvents were obtained from a solvent purification system MBSPS7 from M. Braun. All NMR spectra were recorded on Bruker AV600, and AV400; ^{1}H and ^{13}C chemical shifts (δ) are given in ppm relative to TMS, using the solvent signals as references and converting the chemical shifts to the TMS scale. Coupling constants (*J*) are given in Hz. All high-resolution mass spectra were obtained on Finnigan MAT 95 (70 eV, EI), Finnigan LCQ (ESI) and APEX IV 7T FTICR, Bruker Daltonic (HRMS). IR spectra were recorded on a JASCO FT/IR-4100 spectrometer at room temperature; the stretching frequencies are reported in wavenumbers (cm^{-1}). Column chromatography was performed on Merck 60 (40-63 μm) silica gel. Thin-layer chromatographic analysis (TLC) analysis was performed using POLYGRAM® SIL G/UV254 TLC plates from Macherey-Nagel and compounds were visualized with a UV light at 254 nm. All commercially available compounds (Acros, ABCR, Alfa Aesar, Aldrich, Fluorochem, TCI) were used as received unless stated otherwise. All commercially available compounds (Acros, ABCR, Alfa Aesar, Aldrich, Fluorochem, TCI) were used as received unless otherwise stated.

2 Synthetic Procedure

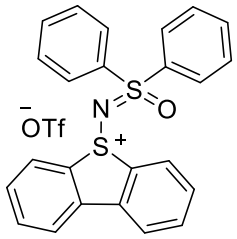
2.1 General Procedure (GP1) for the synthesis of salts 1a, 1b and 1c



Triflic anhydride (1.0 equiv.) was added dropwise to a stirred solution of dibenzothiophene-S-oxide in dry DCM (0.1 M) at a temperature between -60 °C and -50 °C. After stirring the resulting mixture for an additional 1 hour, pyridine (1.0 equiv.) and the respective sulfonimines [1] (1.0 equiv.) were consequently added dropwise, and the reaction mixture was further stirred at –50 °C for an additional 6 h. Then, the cooling system was removed, and the formed solution was allowed reaching room temperature. The aqueous K_2CO_3 solution was added, and the organic phase was separated and dried with anhydrous $MgSO_4$. The solvent was filtered and evaporated in vacuo, the residue was washed three times with dry Et_2O and finally dried under vacuum.

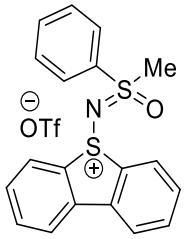
2.2 Characterization of products 1a, 1b and 1c

5-[(Oxodiphenyl-λ⁶-sulfaneylidene)amino]-5*H*-dibenzo[*b*,*d*]thiophen-5-ium Trifluoromethanesulfonate (1a):



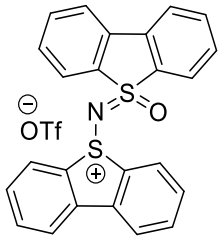
Sulfonium salt **1a** was obtained as a beige solid in 83% yield. **^{1}H NMR** (400 MHz, CD_3CN) δ = 8.15 – 8.06 (m, 2H), 8.04 – 7.95 (m, 6H), 7.89 – 7.77 (m, 4H), 7.74 – 7.55 (m, 6H) ppm. **^{13}C NMR** (101 MHz, CD_3CN) δ = 138.6, 136.6, 135.8, 135.2, 133.6, 131.2, 130.6, 128.7, 128.0, 124.0, 121.2 (d, *J* = 321.0 Hz) ppm. **IR** (neat): 3566, 3088, 1709, 1577, 1448, 1362, 1258, 1224, 1152, 1088, 1029, 1005, 969, 758, 738, 707, 685, 637, 613, 589, 573, 541, 518, 422 cm^{-1}. **HRMS** calculated *m*/*z* for $C_{24}H_{18}NOS_2^+$ $[M–OTf]^+$: 400.0824, found (ESI) 400.0831.

5-{[Methyl(oxo)(phenyl)-λ⁶-sulfaneylidene]amino}-5*H*-dibenzo[*b*,*d*]thiophen-5-ium Trifluoromethanesulfonate (1b):



Sulfonium salt **1b** was obtained as a beige solid in 86% yield. **^{1}H NMR** (400 MHz, CD_3CN) δ = 8.11 (dd, *J* = 7.7, 15.5Hz, 2H), 8.02 – 7.84 (m, 6H), 7.84 – 7.66 (m, 4H), 7.56 (t, *J* = 7.8 Hz, 1H), 3.68 (s, 3H) ppm. **^{13}C NMR** (101 MHz, CD_3CN) δ = 138.4, 138.3, 136.0, 135.6, 135.1, 135.0, 134.2, 133.4, 131.1, 131.0, 130.5, 128.5, 128.4, 128.0, 124.0, 123.9, 121.2 (d, *J* = 321.0 Hz), 45.0 ppm. **IR** (neat): 3566, 3009, 2919, 1707, 1448, 1258, 1225, 1154, 1089, 1029, 1004, 984, 757, 707, 685, 637, 573, 517, 416 cm^{-1}. **HRMS** calculated *m*/*z* for $C_{19}H_{16}NOS_2^+$ $[M–OTf]^+$: 338.0668, found (ESI) 338.0669.

5-{(5-Oxido-5λ⁴-dibenzo[*b*,*d*]thiophen-5-ylidene)amino}-5*H*-dibenzo[*b*,*d*]thiophen-5-ium Trifluoromethanesulfonate (1c):



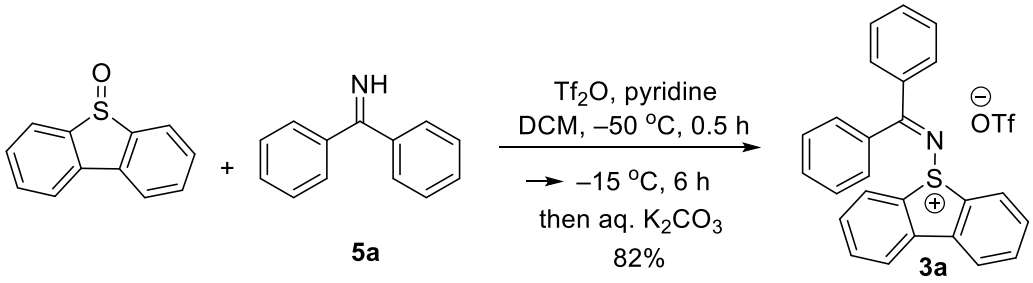
Sulfonium salt **1c** was obtained as a beige solid in 81% yield. **^{1}H NMR** (400 MHz, CD_3CN) δ = 7.90 – 7.69 (m, 12H), 7.59 – 7.43 (m, 4H) ppm. **^{13}C NMR** (101 MHz, CD_3CN) δ = 138.3, 137.1, 135.2, 133.4, 132.8, 131.8, 131.3, 131.2, 128.4, 124.3, 123.8, 123.4, 121.2 (d, *J* = 320.9 Hz) ppm. **IR** (neat): 3566, 3087, 1577, 1482, 1449, 1258, 1225, 1155, 1064, 1030, 983, 759, 707, 637, 573, 554, 518, 479, 418 cm^{-1}. **HRMS** calculated *m*/*z* for $C_{24}H_{16}NOS_2^+$ $[M–OTf]^+$: 398.0668, found (ESI) 398.0668.

2.3 General Procedure (GP2) for the synthesis of sulfonium salts 3a-3f

Triflic acid anhydride (370 µL, 621 mg, 2.2 mmol, 1.1 equiv.) was slowly added at –50 °C to a stirred suspension of respective dibenzothiophene-*S*-oxide (2.0 mmol, 1.0 equiv.) in dry dichloromethane (8 mL/mmol). The reaction mixture was stirred for 30 min at the indicated temperature, then pyridine (177 µL, 174 mg, 2.2 mmol, 1.1 equiv.) and respective benzophenone imine (2.2 mmol, 1.1 equiv.) were added as a solution in dichloromethane (1 mL/mmol). After this, the reaction mixture was slowly warmed to –15 °C and stirred for another 6 h at this temperature. Then the reaction mixture was washed with aq. K_2CO_3 and extracted with dichloromethane. The

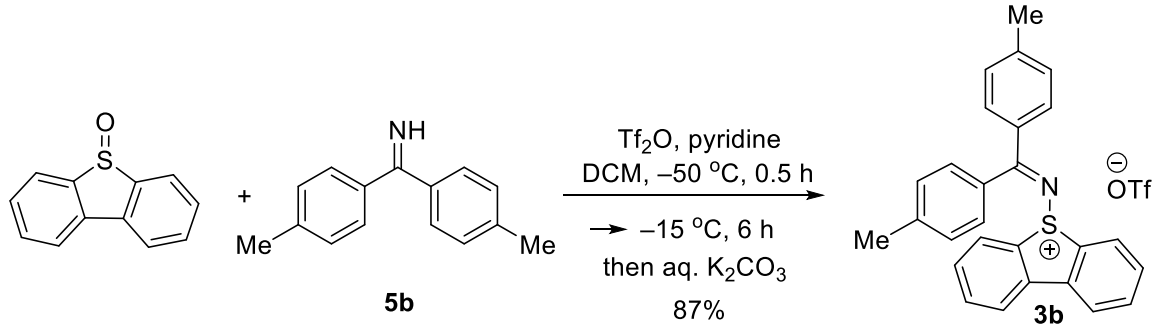
solvent was evaporated *in vacuo*, the residue was washed with dry Et_2O (2 × 10 mL) and dried *in vacuo* affording the desired product.

5-[(Diphenylmethylene)amino]-5*H*-dibenzo[*b*,*d*]thiophen-5-ium Trifluoromethanesulfonate (3a):



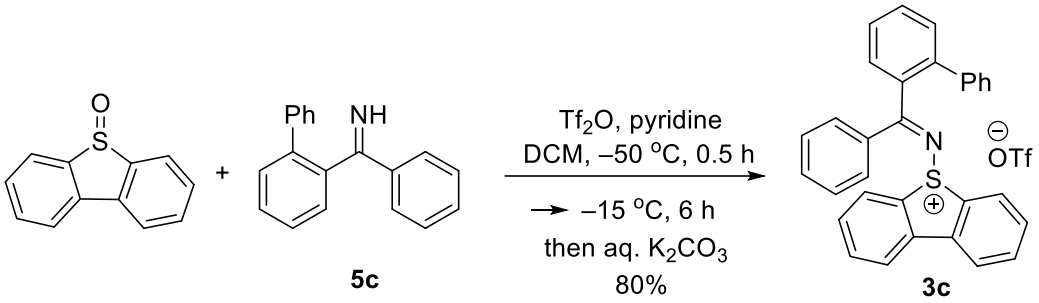
Compound **3a** was obtained from dibenzothiophene-*S*-oxide (0.40 g, 2.0 mmol, 1.0 equiv.) and benzophenone imine (369 µL, 399 mg, 2.2 mmol, 1.1 equiv.) according to GP2 (0.84 g, 82%) as a pale-yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.03 (d, *J* = 7.8 Hz, 2H), 7.88 (d, *J* = 7.3 Hz, 2H), 7.84 – 7.75 (m, 5H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.57 – 7.53 (m, 5H), 7.35 (t, *J* = 7.8 Hz, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 190.7, 139.5, 135.9, 135.5, 135.3, 134.6, 132.9, 132.5, 131.6, 131.3, 130.4, 129.7, 129.0, 128.9, 124.1, 121.0 (q, *J* = 322.2 Hz) ppm; **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -78.11 ppm; **IR** (ATR): 3061, 1710, 1657, 1582, 1526, 1482, 1446, 1259, 1223, 1155, 1029, 999, 955, 761, 707, 637, 572, 517 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{25}H_{18}NS^+$ $[M–OTf]^+$: 364.1155, found 364.1156; **Mp**: 122–123 °C.

5-[(Di-*p*-tolylmethylene)amino]-5*H*-dibenzo[*b*,*d*]thiophen-5-ium Trifluoromethanesulfonate (3b):



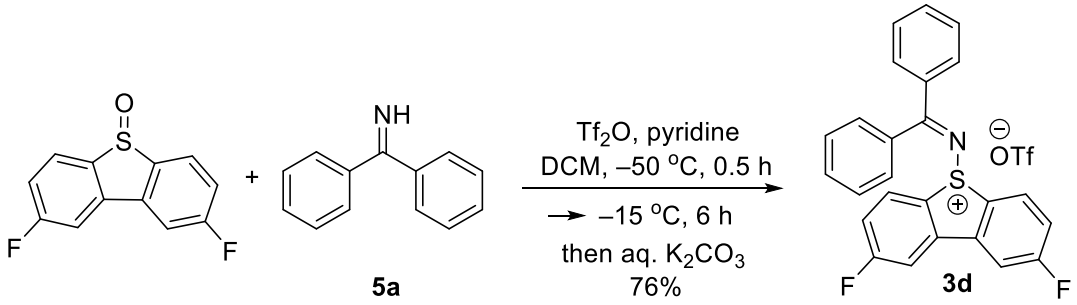
Compound **3b** was obtained from dibenzothiophene-*S*-oxide (0.20 g, 1.0 mmol, 1.0 equiv.) and imine **5b** (0.23 g, 1.1 mmol, 1.1 equiv.) using Tf_2O (0.31 g, 1.1 mmol, 1.1 equiv.) and pyridine (89 µL, 87 mg, 1.1 mmol, 1.1 equiv.) according to GP2 (0.47 g, 87%) as a white solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.04 (dd, *J* = 7.8, 1.1 Hz, 2H), 7.86 – 7.70 (m, 6H), 7.64 – 7.53 (m, 4H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 2.56 (s, 3H), 2.38 (s, 3H) ppm; **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 191.0, 147.0, 143.8, 139.5, 135.4, 132.8, 131.6, 131.5, 130.9, 130.3, 129.7, 129.5, 129.1, 129.0, 124.0, 121.0 (q, *J* = 322.2 Hz), 22.02, 21.89 ppm; **^{19}F NMR** (565 MHz, $CDCl_3$) δ = -78.14 ppm; **IR** (ATR): 3087, 1607, 1572, 1522, 1496, 1259, 1223, 1155, 1029, 827, 762, 737, 706, 637, 573 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{27}H_{22}NS^+$ $[M–OTf]^+$: 392.1468, found 392.1471; **Mp**: 128–129 °C.

(*E*/*Z*)-5-({[1,1'-Biphenyl]-2-yl(phenyl)methylene}amino)-5*H*-dibenzo[*b*,*d*]thiophen-5-ium Trifluoromethanesulfonate (**3c**):



Compound **3c** was obtained from dibenzothiophene-*S*-oxide (0.20 g, 1.0 mmol, 1.0 equiv.) and imine **5c** (283 mg, 1.1 mmol, 1.1 equiv.) using Tf_2O (0.31 g, 1.1 mmol, 1.1 equiv.) and pyridine (89 µL, 87 mg, 1.1 mmol, 1.1 equiv.) according to GP2 (0.47 g, 80%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.08 (d, *J* = 7.7 Hz, 2H), 7.94 – 7.83 (m, 2H), 7.81 (dt, *J* = 7.3, 3.7 Hz, 5H), 7.73 – 7.63 (m, 3H), 7.59 (t, *J* = 7.6 Hz, 2H), 7.49 (ddd, *J* = 12.1, 9.4, 5.9 Hz, 6H), 7.38 (t, *J* = 7.7 Hz, 1H), 6.00 (d, *J* = 7.9 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 192.3, 140.2, 140.0, 139.8, 138.8, 136.3, 136.0, 135.6, 133.2, 132.9, 132.4, 132.0, 131.5, 131.4, 131.3, 131.1, 130.0, 129.6, 129.5, 129.4, 129.3, 128.8, 128.1, 124.6, 124.5, 121.0 (q, *J* = 322.2 Hz) ppm; **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -78.13 ppm; **IR** (ATR): 3060, 1706, 1520, 1475, 1445, 1361, 1256, 1221, 1148, 1076, 1027, 778, 755, 698, 634, 571, 515 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{31}H_{22}NS^+$ $[M–OTf]^+$: 440.1468, found 440.1470; **Mp**: 137–138 °C.

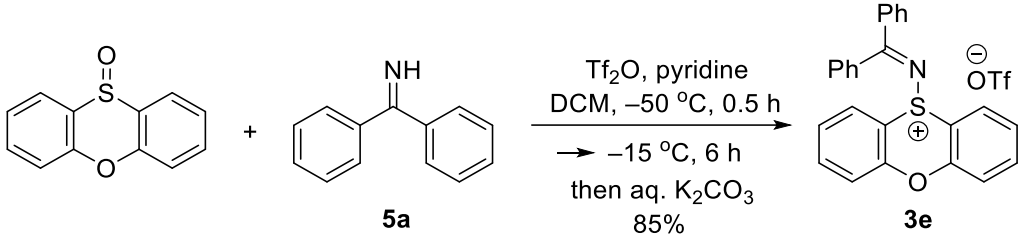
5-[(Diphenylmethylene)amino]-2,8-difluoro-5*H*-dibenzo[*b*,*d*]thiophen-5-ium Trifluoromethanesulfonate (**3d**):



Compound **3d** was obtained from 2,8-difluorodibenzothiophene-*S*-oxide (0.47 g, 2.0 mmol, 1.0 equiv.) and benzophenone imine (369 µL, 399 mg, 2.2 mmol, 1.1 equiv.) according to GP2 (0.83 g, 76%) as an off white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.91 (d, *J* = 6.9 Hz, 2H), 7.86 – 7.76 (m, 3H), 7.76 – 7.64 (m, 4H), 7.62 – 7.57 (m, 3H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.34 – 7.25 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 190.4, 167.2 (d, *J* = 260.5 Hz), 141.5 (dd, *J* = 10.4, 2.5 Hz), 135.9, 135.4, 134.4, 133.1, 132.4 (d, *J* = 10.4 Hz), 131.3, 130.5, 130.2, 129.2 (d, *J* = 3.1 Hz), 129.0 (d, *J* = 5.6 Hz), 121.0 (q, *J* = 322.2 Hz), 119.6 (d, *J* = 24.1 Hz), 111.9 (d, *J* = 25.3 Hz); **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -78.26 (s, 3F), -99.65 (tt, q, *J* = 8.5, 5.0 Hz, 2F) ppm; **IR** (ATR):

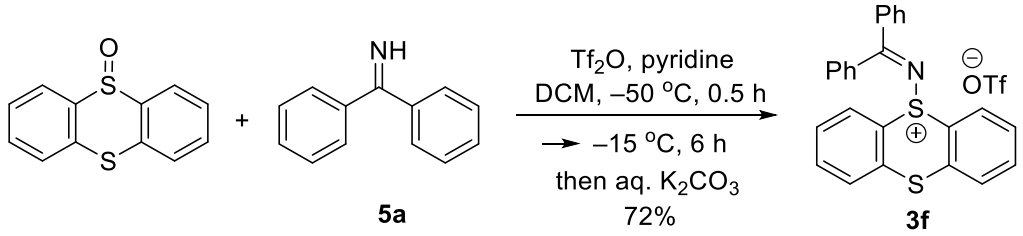
3093, 1584, 1526, 1480, 1438, 1257, 1220, 1159, 1029, 943, 830, 776, 703, 638, 572, 516, 498, 465 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{25}H_{16}F_2NS^+$ $[M–OTf]^+$: 400.0966, found 400.0966. **Mp**: 124–125 °C.

10-[(Diphenylmethylene)amino]-10*H*-phenoxathiin-10-ium Trifluoromethanesulfonate (**3e**):



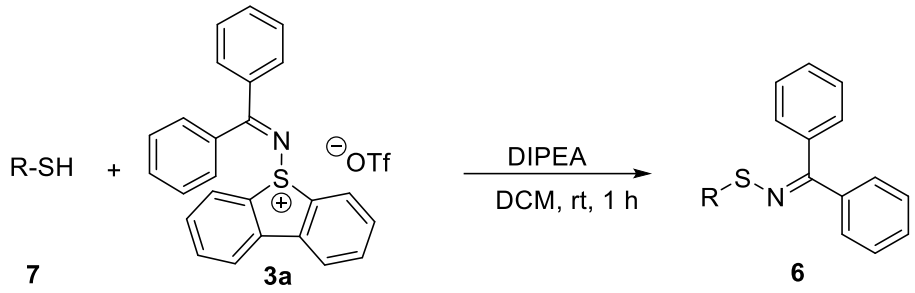
Compound **3e** was obtained from phenoxathiine-10-oxide (0.43 g, 2.0 mmol, 1.0 equiv.) and benzophenone imine (369 µL, 399 mg, 2.2 mmol, 1.1 equiv.) according to GP2 (0.90 g, 85%) as a pale-yellow solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.93 – 7.73 (m, 5H), 7.65 – 7.61 (m, 4H), 7.58 – 7.44 (m, 5H), 7.44 – 7.28 (m, 4H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 186.9, 152.6, 136.9, 135.7, 135.2, 133.8, 132.7, 132.1, 131.1, 130.4, 128.9, 128.5, 126.6, 120.1, 121.0 (q, *J* = 322.2 Hz), 110.1 ppm; **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -78.14 ppm; **IR** (ATR): 3063, 1737, 1583, 1528, 1460, 1442, 1271, 1224, 1156, 1072, 1029, 886, 765, 708, 637, 572, 518, 491 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{25}H_{18}NOS^+$ $[M–OTf]^+$: 380.1104, found 380.1108. **Mp**: 148–149 °C.

5-[(Diphenylmethylene)amino]-5*H*-thianthren-5-ium Trifluoromethanesulfonate (**3f**):



Compound **3f** was obtained from thianthrene-5-oxide (0.46 g, 2.0 mmol, 1.0 equiv.) and benzophenone imine (369 µL, 399 mg, 2.2 mmol, 1.1 equiv.) according to GP2 (0.78 g, 72%) as a pale-yellow solid. Compound **5f** was decomposed in $CDCl_3$. **^{1}H NMR** (600 MHz, CD_3CN) δ = 8.00 (dd, *J* = 7.9, 1.2 Hz, 2H), 7.76 (qd, *J* = 7.7, 1.4 Hz, 3H), 7.63 (tt, *J* = 8.0, 2.2 Hz, 5H), 7.55 – 7.48 (m, 4H), 7.41 (dd, *J* = 8.5, 7.4 Hz, 2H), 7.34 – 7.23 (m, 2H) ppm; **^{13}C NMR** (151 MHz, CD_3CN) δ = 189.4, 137.2, 137.2, 135.9, 135.5, 134.7, 133.3, 131.5, 131.2, 130.8, 129.9, 129.8, 129.0, 128.3, 123.5 ppm; **^{19}F NMR** (565 MHz, CD_3CN) δ = -79.28 ppm; **IR** (ATR): 3067, 1534, 1487, 1446, 1260, 1223, 1153, 1029, 760, 705, 636, 572, 544, 516, 462 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{25}H_{18}NS_2^+$ $[M–OTf]^+$: 396.0875, found 396.0877; **Mp**: 166–167 °C.

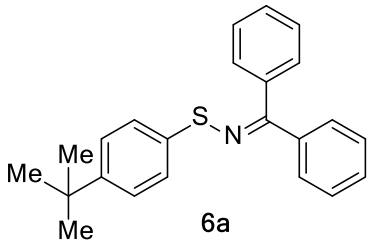
2.4 General Procedure (GP3) for the transfer-reaction with thiols



7 3a 6

Dry DCM (0.1 M) was added to the mixture of selected nucleophile (1.00 equiv.), DIPEA (1.10 equiv.) and dibenzothiophenium salt **3** (1.50 equiv.) at room temperature. The reaction mixture was stirred for 1 h at the same temperature. After quenching the reaction with water (8 mL), the mixture was extracted with DCM (3 × 10 mL), the combined organic layers were dried over $MgSO_4$ and the solvents were removed *in vacuo*. The crude products were purified by column chromatography.

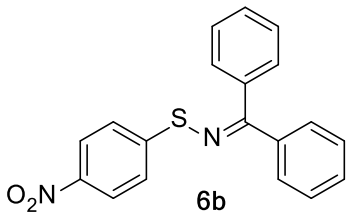
***S*-[4-(*tert*-Butyl)phenyl]-*N*-(diphenylmethylene)thiohydroxylamine** (**6a**):



6a

Using the GP3, compound **6a** was prepared from 4-(*tert*-butyl)benzenethiol (**7a**) (34.4 µL, 33.2 mg, 0.2 mmol, 1.00 equiv.), DIPEA (38.3 µL, 28.4 mg, 0.22 mmol, 1.10 equiv.) and the salt **3a** (154 mg, 0.3 mmol, 1.50 equiv.) in dry DCM. The reaction was carried out at RT for 1 h. After flash chromatography (hexane/EtOAc: 95/5) compound **6a** was obtained as a colorless oil (42.1 mg, 61%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.65 (d, *J* = 8.2 Hz, 2H), 7.58 – 7.47 (m, 5H), 7.42 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.37 (ddd, *J* = 9.1, 6.9, 3.8 Hz, 5H), 1.34 (s, 9H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 163.8, 149.4, 139.0, 138.0, 136.5, 129.7, 129.4, 129.0, 128.3, 127.9, 127.6, 126.0, 125.2, 34.7, 31.5 ppm; **IR** (ATR): 3058, 2961, 1660, 1596, 1490, 1443, 1397, 1362, 1314, 1268, 1167, 1117, 1012, 950, 823, 775, 695, 637, 545, 484 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{23}H_{24}NS^+$ $[M+H]^+$: 346.1624, found 346.1615.

***N*-(Diphenylmethylene)-*S*-(4-nitrophenyl)thiohydroxylamine** (**6b**):

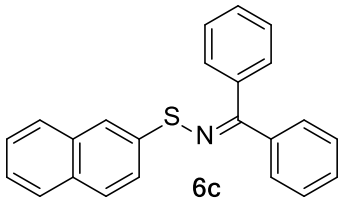


6b

Using the GP3, compound **6b** was prepared from 4-nitrobenzenethiol (**7b**) (31.0 mg, 0.2 mmol, 1.00 equiv.), DIPEA (38.3 µL, 28.4 mg, 0.22 mmol, 1.10 equiv.) and **3a** (154 mg, 0.3 mmol, 1.50 equiv.) in dry DCM. The reaction was carried out at RT for 1 h. After flash chromatography (hexane/EtOAc: 95/5) compound **6b** was obtained as a yellow solid (46.1 mg, 69%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.24 (d, *J* = 8.8 Hz, 2H), 7.74 (d, *J* = 8.7 Hz, 2H), 7.71 – 7.65 (m, 2H), 7.56 (m, 3H), 7.48 – 7.33 (m, 5H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 166.7, 149.3, 145.5, 138.4, 137.6, 130.6, 129.9, 129.2, 128.6, 128.3, 127.4, 124.2,

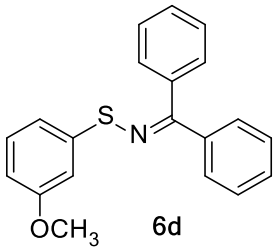
123.6 ppm; **IR** (ATR): 3058, 1658, 1577, 1509, 1475, 1443, 1336, 1108, 1090, 951, 851, 741, 695, 637, 465, 433 cm^{-1}; **HRMS** calculated m/z for $C_{19}H_{15}N_2O_2S^+$ $[M+H]^+$: 335.0848, found 335.0851; **Mp**: 120–121 °C.

***N*-(Diphenylmethylene)-*S*-(naphthalen-2-yl)thiohydroxylamine** (**6c**):



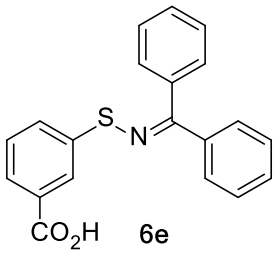
Using the GP3, compound **6c** was prepared from naphthalene-2-thiol (**7c**) (32.0 mg, 0.2 mmol, 1.00 equiv.), DIPEA (38.3 µL, 28.4 mg, 0.22 mmol, 1.10 equiv.) and **3a** (154 mg, 0.3 mmol, 1.50 equiv.) in dry DCM. The reaction was carried out at RT for 1 h. After flash chromatography (hexane/EtOAc: 95/5) compound **6c** was obtained as a white solid (36.5 mg, 54%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.07 (s, 1H), 7.88-7.82 (m, 3H), 7.74-7.71 (m, 3H), 7.65 – 7.52 (m, 3H), 7.52 – 7.36 (m, 7H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 164.5, 138.9, 137.9, 137.4, 133.8, 132.1, 129.9, 129.5, 129.0, 128.6, 128.4, 128.0, 127.9, 127.6, 127.5, 126.6, 125.6, 123.5, 122.7 ppm; **IR** (ATR): 3053, 2924, 1624, 1588, 1500, 1442, 1314, 1294, 1132, 1073, 1028, 943, 851, 811, 775, 744, 694, 630, 472 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{23}H_{18}NS^+$ $[M+H]^+$: 340.1155, found 340.1156; **Mp**: 118–119 °C.

***N*-(Diphenylmethylene)-*S*-(3-methoxyphenyl)thiohydroxylamine** (**6d**):



Using the GP3, compound **6d** was prepared from 3-methoxybenzenethiol (**7d**) (24.8 µL, 28.04 mg, 0.2 mmol, 1.00 equiv.), DIPEA (38.3 µL, 28.4 mg, 0.22 mmol, 1.10 equiv.) and **3a** (154 mg, 0.3 mmol, 1.50 equiv.) in dry DCM. The reaction was carried out at RT for 1 h. After flash chromatography (hexane/EtOAc: 95/5) compound **6d** was obtained as a white solid (36.3 mg, 57%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.70 – 7.60 (m, 2H), 7.59 – 7.44 (m, 3H), 7.41 – 7.34 (m, 5H), 7.33 – 7.23 (m, 2H), 7.19 – 7.09 (m, 1H), 6.75 (ddd, *J* = 8.2, 2.6, 1.2 Hz, 1H), 3.85 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 164.1, 160.2, 141.3, 138.9, 137.9, 129.9, 129.8, 129.5, 129.0, 128.4, 127.9, 127.5, 116.9, 111.9, 109.9, 55.5 ppm; **IR** (ATR): 3057, 2935, 2832, 1659, 1589, 1475, 1442, 1315, 1280, 1246, 1230, 1072, 1043, 951, 863, 773, 693, 634 cm^{-1}; **HRMS** calculated *m*/z for $C_{20}H_{18}NOS^+$ $[M+H]^+$: 320.1104, found 320.1098. **Mp**: 79–80 °C.

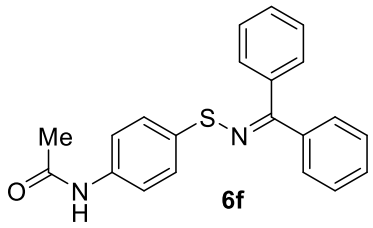
3-{[(Diphenylmethylene)amino]thio}benzoic Acid (**6e**):



Using the GP3, compound **6e** was prepared from 3-mercaptobenzoic acid (**7e**) (30.83 mg, 0.2 mmol, 1.00 equiv.), DIPEA (38.3 µL, 28.4 mg, 0.22 mmol, 1.10 equiv.) and **3a** (154 mg, 0.3 mmol, 1.50 equiv.) in dry DCM. The reaction was carried out at RT for 1 h. After flash chromatography (hexane/EtOAc: 9/1) compound **6e** was obtained as a white solid (38.6 mg,

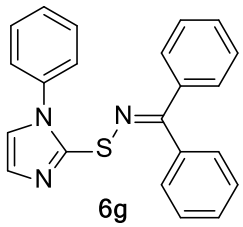
58%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.36 – 8.32 (m, 1H), 7.94 (ddd, *J* = 7.8, 1.7, 1.2 Hz, 1H), 7.89 (ddd, *J* = 8.0, 1.9, 1.1 Hz, 1H), 7.71 – 7.65 (m, 2H), 7.61 – 7.46 (m, 4H), 7.44 – 7.35 (m, 5H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 165.1, 141.0, 138.7, 137.9, 130.1, 130.0, 129.8, 129.6, 129.1, 128.5, 128.1, 127.7, 127.5, 126.4 ppm; **IR** (ATR): 3061, 2925, 2854, 1710, 1659, 1598, 1577, 1446, 1358, 1318, 1277, 1221, 942, 763, 701, 639, 530 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{20}H_{16}NO_2S^+$ $[M+H]^+$: 334.0896, found 334.0898; **Mp**: 159–160 °C.

***N*-(4-{[(Diphenylmethylene)amino]thio}phenyl)acetamide** (**6f**):



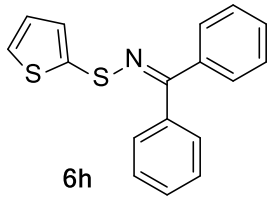
Using the GP3, compound **6f** was prepared from *N*-(4-mercaptophenyl)acetamide (**7f**) (33.4 mg, 0.2 mmol, 1.00 equiv.), DIPEA (38.3 µL, 28.4 mg, 0.22 mmol, 1.10 equiv.) and **3a** (154 mg, 0.3 mmol, 1.50 equiv.) in dry DCM. The reaction was carried out at RT for 1 h. After flash chromatography (hexane/EtOAc: 6/4) compound **6f** was obtained as a white solid (49.1 mg, 71%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.63 (d, *J* = 8.1 Hz, 2H), 7.58 – 7.47 (m, 7H), 7.39 – 7.35 (m, 5H), 2.19 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 168.3, 164.12, 138.9, 137.9, 136.3, 135.2, 129.8, 129.5, 129.0, 128.4, 127.9, 127.5, 126.1, 120.4, 24.8 ppm; **IR** (ATR): 3296, 3055, 1662, 1594, 1529, 1491, 1443, 1396, 1314, 1258, 1157, 1014, 825, 756, 695, 508, 480 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{21}H_{19}N_2OS^+$ $[M+H]^+$: 347.1213, found 347.1207; **Mp**: 169–170 °C.

***N*-(Diphenylmethylene)-*S*-(1-phenyl-1*H*-imidazol-2-yl)thiohydroxylamine** (**6g**):



Using the GP3, compound **6g** was prepared from 1-phenyl-1*H*-imidazole-2-thiol (**7g**) (35.2 mg, 0.2 mmol, 1.00 equiv.), DIPEA (38.3 µL, 28.4 mg, 0.22 mmol, 1.10 equiv.) and **3a** (154 mg, 0.3 mmol, 1.50 equiv.) in dry DCM. The reaction was carried out at RT for 1 h. After flash chromatography (hexane/EtOAc: 9/1) compound **6g** was obtained as a light yellow solid (37.6 mg, 53%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.51 – 7.41 (m, 6H), 7.44 – 7.38 (m, 2H), 7.35-7.31 (m, 5H), 7.28 – 7.24 (m, 2H), 7.23 – 7.18 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 165.7, 142.1, 138.5, 138.1, 136.9, 130.4, 129.9, 129.5, 129.1, 128.9, 128.4, 128.1, 127.9, 127.5, 126.3, 124.3 ppm; **IR** (ATR): 3057, 1657, 1596, 1499, 1428, 1303, 1277, 1121, 1074, 951, 917, 761, 695, 638, 508, 475 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{22}H_{18}N_3S^+$ $[M+H]^+$: 356.1216, found (ESI) 356.1226; **Mp**: 146–147 °C.

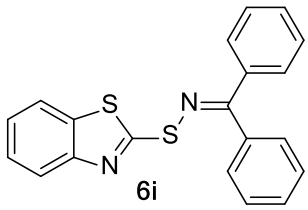
***N*-(Diphenylmethylene)-*S*-(thiophen-2-yl)thiohydroxylamine** (**6h**):



Using the GP3, compound **6h** was prepared from thiophene-2-thiol (**7h**) (18.23 µL, 23.2 mg, 0.2 mmol, 1.00 equiv.), DIPEA (38.3 µL, 28.4 mg, 0.22 mmol, 1.10 equiv.) and **3a** (154 mg, 0.3 mmol, 1.50 equiv.) in dry DCM. The reaction was carried out at RT for 1 h. After flash chromatography

(hexane/EtOAc: 9/1) compound **6h** was obtained as a white solid (35.4 mg, 60%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.62 – 7.49 (m, 5H), 7.47 (dd, *J* = 5.3, 1.3 Hz, 1H), 7.41 – 7.30 (m, 5H), 7.14 (dd, *J* = 3.6, 1.1 Hz, 1H), 7.03 (dd, *J* = 5.2, 3.6 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 164.4, 139.1, 138.6, 137.4, 129.9, 129.6, 129.2, 129.0, 128.7, 128.3, 128.0, 127.6, 127.5 ppm; **IR** (ATR): 3058, 1656, 1597, 1548, 1489, 1444, 1403, 1317, 1277, 1162, 1026, 942, 848, 777, 695, 638, 593, 530, 458 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{17}H_{14}NS_2^+$ $[M+H]^+$: 296.0562, found 296.0560. **Mp**: 101–102 °C.

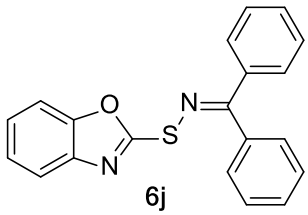
***S*-(Benzo[*d*]thiazol-2-yl)-*N*-(diphenylmethylene)thiohydroxylamine** (**6i**):



6i

Using the GP3, compound **6i** was prepared from 2-mercaptobenzothiazole (**7i**) (33.4 mg, 0.2 mmol, 1.00 equiv.), DIPEA (38.3 μL, 28.4 mg, 0.22 mmol, 1.10 equiv.) and **3a** (154 mg, 0.3 mmol, 1.50 equiv.) in dry DCM. The reaction was carried out at RT for 1 h. After flash chromatography (hexane/EtOAc: 9/1) compound **6i** was obtained as a white solid (40.8 mg, 59%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.91 – 7.83 (m, 2H), 7.74 (dd, *J* = 8.1, 1.7 Hz, 2H), 7.56 (dd, *J* = 5.2, 1.9 Hz, 3H), 7.42 (m, 6H), 7.35 – 7.28 (m, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 174.0, 167.5, 154.4, 138.1, 136.9, 135.1, 130.8, 130.2, 129.2, 128.6, 128.5, 127.4, 126.1, 123.9, 122.0, 121.1 ppm; **IR** (ATR): 3056, 1657, 1550, 1444, 1378, 1316, 1297, 1195, 1176, 1073, 950, 773, 696, 636, 495 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{20}H_{14}N_2S_2^+$ $[M]^+$: 346.0598, found (EI) 346.0600; **Mp**: 161–162 °C.

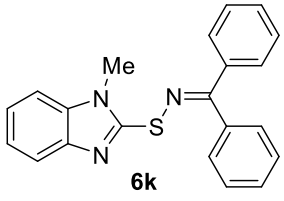
***S*-(Benzo[*d*]oxazol-2-yl)-*N*-(diphenylmethylene)thiohydroxylamine** (**6j**):



6j

Using the GP3, compound **6j** was prepared from 2-mercaptobenzoxazole (**7j**) (30.2 mg, 0.2 mmol, 1.00 equiv.), DIPEA (38.3 μL, 28.4 mg, 0.22 mmol, 1.10 equiv.) and **3a** (154 mg, 0.3 mmol, 1.50 equiv.) in dry DCM. The reaction was carried out at RT for 1 h. After flash chromatography (hexane/EtOAc: 9/1) compound **6j** was obtained as a white solid (40.3 mg, 61%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.74 – 7.67 (m, 3H), 7.60 – 7.51 (m, 4H), 7.50 – 7.36 (m, 5H), 7.35 – 7.28 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 169.1, 164.1, 151.9, 142.1, 138.2, 136.8, 130.8, 130.2, 129.3, 128.5, 128.5, 127.3, 124.6, 124.5, 119.5, 110.5 ppm; **IR** (ATR): 3058, 1657, 1496, 1450, 1317, 1277, 1239, 1131, 1095, 1000, 920, 805, 744, 697, 638, 428 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{20}H_{15}N_2OS^+$ $[M+H]^+$: 331.0900, found (ESI) 331.0904; **Mp**: 106–107 °C.

***N*-(Diphenylmethylene)-*S*-(1-methyl-1*H*-benzo[*d*]imidazol-2-yl)thiohydroxylamine** (**6k**):

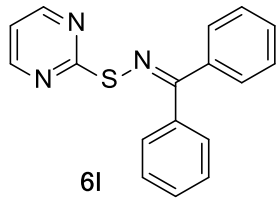


6k

Using the GP3, compound **6k** was prepared from 1-methyl-1*H*-benzimidazole-2-thiol (**7k**) (32.8 mg, 0.2 mmol, 1.00 equiv.), DIPEA (38.3 μL, 28.4 mg, 0.22 mmol, 1.10 equiv.) and **3a** (154 mg, 0.3 mmol, 1.50 equiv.) in dry DCM. The reaction was carried out at RT for 1 h. After flash

chromatography (hexane/EtOAc: 9/1) compound **6k** was obtained as a white solid (39.1 mg, 57%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.80 (d, *J* = 7.2 Hz, 1H), 7.61 – 7.52 (m, 5H), 7.45 – 7.37 (m, 4H), 7.35 – 7.28 (m, 4H), 3.96 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 167.2, 150.1, 143.1, 138.3, 136.9, 136.9, 130.3, 129.9, 129.2, 128.4, 128.0, 127.4, 123.5, 122.6, 120.3, 109.6, 31.5 ppm; **IR** (ATR): 3058, 1551, 1444, 1414, 1328, 1278, 1153, 952, 816, 744, 696, 634, 503, 474 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{21}H_{18}N_3S^+$ $[M+H]^+$: 344.1216, found (ESI) 344.1219; **Mp**: 129–130 °C.

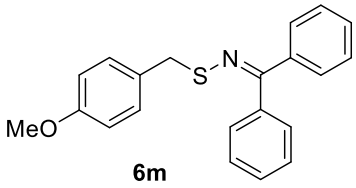
***N*-(Diphenylmethylene)-*S*-(pyrimidin-2-yl)thiohydroxylamine** (**6l**):



6l

Using the GP3, compound **6l** was prepared from pyrimidine-2-thiol (**7l**) (22.4 mg, 0.2 mmol, 1.00 equiv.), DIPEA (38.3 µL, 28.4 mg, 0.22 mmol, 1.10 equiv.) and **3a** (154 mg, 0.3 mmol, 1.50 equiv.) in dry DCM. The reaction was carried out at RT for 1 h. After flash chromatography (hexane/EtOAc: 9/1) compound **6l** was obtained as a light yellow solid (34.3 mg, 59%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.67 (d, *J* = 4.8 Hz, 2H), 7.76 – 7.68 (m, 2H), 7.54– 7.50 (m, 3H), 7.43 – 7.31 (m, 5H), 7.05 (t, *J* = 4.8 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 172.6, 167.1, 157.9, 138.8, 137.6, 130.4, 129.7, 129.1, 128.5, 128.4, 127.5, 117.4 ppm; **IR** (ATR): 3056, 1657, 1549, 1443, 1378, 1315, 1195, 1176, 950, 773, 696, 636, 496, 441 cm^{-1}; H**RMS** calculated *m*/*z* for $C_{17}H_{14}N_3S^+$ $[M+H]^+$: 292.0903, found (ESI) 292.0904; **Mp**: 161–162 °C.

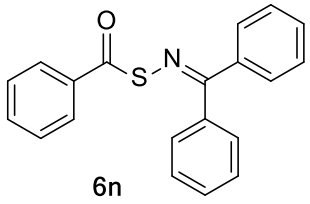
***N*-(Diphenylmethylene)-*S*-(4-methoxybenzyl)thiohydroxylamine** (**6m**):



6m

Using the GP3, compound **6m** was prepared from (4-methoxyphenyl)methanethiol (**7m**) (27.8 µL, 30.8 mg, 0.2 mmol, 1.00 equiv.), DIPEA (38.3 µL, 28.4 mg, 0.22 mmol, 1.10 equiv.) and **3a** (154 mg, 0.3 mmol, 1.50 equiv.) in dry DCM. The reaction was carried out at RT for 1 h. After flash chromatography (hexane/EtOAc: 9/1) compound **6m** was obtained as a white solid (38.0 mg, 57%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.53 (d, *J* = 2.1 Hz, 2H), 7.49 – 7.39 (m, 3H), 7.37 – 7.27 (m, 7H), 6.86 (d, *J* = 8.7 Hz, 2H), 4.33 (s, 2H), 3.79 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 163.2, 158.9, 139.1, 137.8, 130.6, 129.7, 129.4, 129.1, 128.8, 128.2, 127.7, 127.6, 114.0, 55.4, 43.9 ppm; **IR** (ATR): 2926, 1610, 1510, 1442, 1299, 1248, 1176, 1033, 951, 833, 757, 695, 631, 551, 491 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{21}H_{20}NOS^+$ $[M+H]^+$: 334.1260, found 334.1266; **Mp**: 122-123 °C.

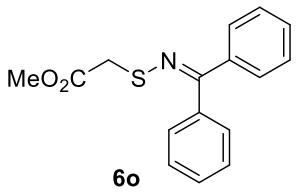
***S*-Benzoyl-*N*-(diphenylmethylene)thiohydroxylamine** (**6n**):



6n

Using the GP3, compound **6n** was prepared from thiobenzoic acid (**7n**) (23.4 µL, 27.6 mg, 0.2 mmol, 1.00 equiv.), DIPEA (38.3 µL, 28.4 mg, 0.22 mmol, 1.10 equiv.) and **3a** (154 mg, 0.3 mmol, 1.50 equiv.) in dry DCM. The reaction was carried out at RT for 1 h. After flash chromatography (hexane/EtOAc: 9/1) compound **6n** was obtained as a white solid (27.2 mg, 43%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.88 (d, *J* = 8.7 Hz, 2H), 7.77 (d, *J* = 7.0 Hz, 2H), 7.58 – 7.51 (m, 4H), 7.47 – 7.35 (m, 5H), 7.35 – 7.28 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 188.9, 169.6, 138.5, 138.1, 136.2, 133.7, 130.9, 129.8, 129.0, 128.9, 128.9, 128.4, 127.3, 127.2 ppm; **IR** (ATR): 3059, 1685, 1555, 1445, 1293, 1206, 1176, 898, 773, 688, 646, 457, 441 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{20}H_{16}NOS^+$ $[M+H]^+$: 318.0947, found 318.0953.

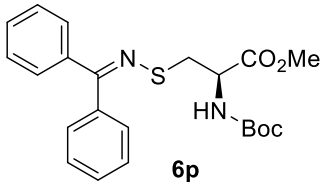
Methyl 2-{[(Diphenylmethylene)amino]thio}acetate (**6o**):



6o

Using the GP3, compound **6o** was prepared from methyl 2-mercaptoacetate (**7o**) (18.2 µL, 21.2 mg, 0.2 mmol, 1.00 equiv.), DIPEA (38.3 µL, 28.4 mg, 0.22 mmol, 1.10 equiv.) and **3a** (154 mg, 0.3 mmol, 1.50 equiv.) in dry DCM. The reaction was carried out at RT for 1 h. After flash chromatography ((hexane/EtOAc: 9/1) compound **6o** was obtained as a colorless oil (8.5 mg, 15%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.60 – 7.41 (m, 5H), 7.37 – 7.29 (m, 5H), 3.91 (s, 2H), 3.79 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 170.3, 164.6, 138.7, 137.4, 129.7, 129.4, 128.9, 128.3, 127.8, 127.6, 52.7, 41.9 ppm; **IR** (ATR): 3053, 1658, 1446, 1277, 1155, 700, 757, 639, 477, 428 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{16}H_{16}NO_2S^+$ $[M+H]^+$: 286.0896, found 286.0894.

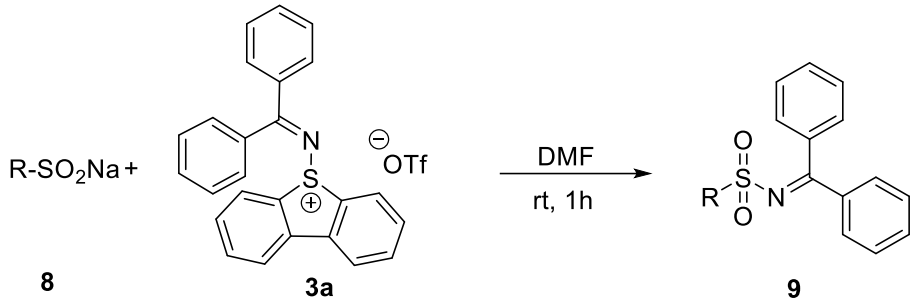
Methyl *N*-(*tert*-Butoxycarbonyl)-*S*-[(diphenylmethylene)amino]-*L*-cysteinate (**6p**):



6p

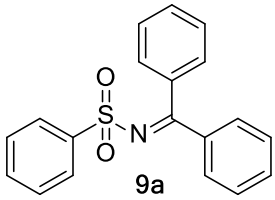
Using the GP3, compound **6p** was prepared from methyl (*tert*-butoxycarbonyl)-*L*-cysteinate (**7p**) (47.0 mg, 0.2 mmol, 1.00 equiv.), DIPEA (38.3 µL, 28.4 mg, 0.22 mmol, 1.10 equiv.) and **3a** (154 mg, 0.3 mmol, 1.50 equiv.) in dry DCM. The reaction was carried out at RT for 1 h. After flash chromatography (hexane/EtOAc: 9/1) compound **6p** was obtained as a colorless dense oil (43.1 mg, 52%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.56 – 7.42 (m, 5H), 7.40 – 7.27 (m, 5H), 6.06 (d, *J* = 8.2 Hz, 1H), 4.79 (dt, *J* = 8.9, 4.8 Hz, 1H), 3.73 (s, 3H), 3.55 – 3.38 (m, 2H), 1.46 (s, 9H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 171.5, 165.3, 155.5, 138.7, 137.4, 129.8, 129.4, 128.9, 128.3, 127.8, 127.5, 79.9, 54.5, 52.6, 40.6, 28.5 ppm; **IR** (ATR): 3363, 2977, 1747, 1714, 1658, 1598, 1505, 1447, 1318, 1277, 1164, 942, 919, 810, 764, 701, 639, 508, 456 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{22}H_{27}N_2O_4S^+$ $[M+H]^+$: 415.1686, found 415.1677.

2.5 General Procedure (GP4) for the transfer-reaction with sodium sulfinate salts.



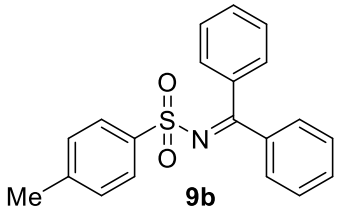
Dry DMF (0.1 M) was added to the mixture of dibenzothiophenium salt **3a** (1.0 equiv) and respective sodium sulfinate salt (1.50 equiv.) at room temperature. The reaction was stirred for 1 h at the same temperature. After quenching reaction with water (8 mL), the reaction mixture was extracted with ethyl acetate (3 × 10 mL), the combined organic layers were dried over $MgSO_4$ and the solvents were removed *in vacuo*. The crude products were purified by column chromatography.

***N*-(Diphenylmethylene)benzenesulfonamide** (**9a**):



Using the GP4, compound **9a** was prepared from sodium benzenesulfinate (**8a**) (49.2 mg, 0.3 mmol, 1.5 equiv.) and **3a** (102.7 mg, 0.2 mmol, 1.00 equiv.) in dry DMF. After flash chromatography (hexane/EtOAc: 9/1) compound **9a** was obtained as a colorless oil (39.7 mg, 62%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.99 – 7.91 (m, 2H), 7.64 – 7.34 (m, 13H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 179.3, 141.6, 132.7, 132.5, 130.2, 128.9, 128.4, 128.3, 127.4 ppm; four signals more at ca. 130 ppm are close to their coalescence temperature and broadened;[7b] **IR** (ATR): 3343, 3253, 1656, 1597, 1446, 1317, 1276, 1159, 1090, 941, 755, 698, 638, 593, 537 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{19}H_{16}NO_2S^+$ $[M+H]^+$: 322.0896, found 322.0895.

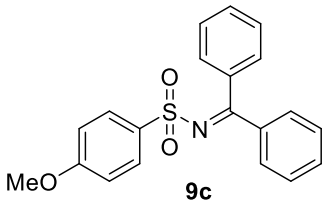
***N*-(Diphenylmethylene)-4-methylbenzenesulfonamide** (**9b**):



Using the GP4, compound **9b** was prepared from sodium 4-methylbenzenesulfinate (**8b**) (53.4 mg, 0.3 mmol, 1.5 equiv.) and **3a** (102.7 mg, 0.2 mmol, 1.00 equiv.) in dry DMF. After flash chromatography (hexane/EtOAc: 9/1) compound **9b** was obtained as a white solid (44.7 mg, 67%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.83 (d, *J* = 8.4 Hz, 2H), 7.62 – 7.36 (m, 10H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 178.9, 143.5, 138.7, 132.5, 130.2, 129.5, 128.4, 128.3, 127.5, 21.7 ppm; four signals more at ca. 130 ppm are close to their

coalescence temperature and broadened;[7b] **IR** (ATR): 3356, 3261, 1657, 1597, 1557, 1446, 1304, 1277, 1158, 1092, 918, 814, 764, 700, 638, 576, 555, 537, 411 cm^{-1}; **HRMS** calculated *m/z* for $C_{20}H_{18}NO_2S^+$ $[M+H]^+$: 336.1053, found 336.1052; **Mp**: 105–106 °C. The spectroscopic data are in agreement with those previously reported.[2]

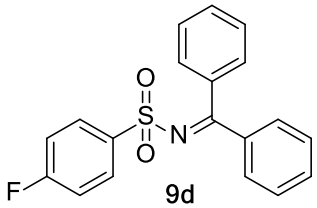
***N*-(Diphenylmethylene)-4-methoxybenzenesulfonamide** (**9c**):



9c

Using the GP4, compound **9c** was prepared from sodium 4-methoxybenzenesulfinate (**8c**) (58.2 mg, 0.3 mmol, 1.5 equiv.) and **3a** (102.7 mg, 0.2 mmol, 1.00 equiv.) in dry DMF. After flash chromatography (hexane/EtOAc: 9/1) compound **9c** was obtained as a white solid (49.7 mg, 71%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.86 (d, *J* = 9.0 Hz, 2H), 7.53 (m, 5H), 7.43 (m, 5H), 6.95 (d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 178.5, 162.9, 138.5, 133.2, 130.0, 129.6, 128.4, 128.2, 114.1, 55.7 ppm; four signals more at ca. 130 ppm are close to their coalescence temperature and broadened;[7b] **IR** (ATR): 3264, 3061, 2840, 1656, 1593, 1556, 1497, 1445, 1318, 1258, 1148, 1090, 1025, 946, 816, 699, 639, 577, 561, 449 cm^{-1}; **HRMS** calculated *m/z* for $C_{20}H_{18}NO_3S^+$ $[M+H]^+$: 352.1002, found 352.0990. **Mp**: 109–110 °C.

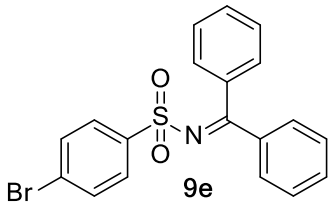
***N*-(Diphenylmethylene)-4-fluorobenzenesulfonam** (**9d**):



9d

Using the GP4, compound **9d** was prepared from sodium 4-fluorobenzenesulfinate (**8d**) (54.6 mg, 0.3 mmol, 1.5 equiv.) and **3a** (102.7 mg, 0.2 mmol, 1.00 equiv.) in dry DMF. After flash chromatography (hexane/EtOAc: 9/1) compound **9d** was obtained as a white solid (37.9 mg, 56%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.99 – 7.90 (m, 2H), 7.60 – 7.38 (m, 10H), 7.20 – 7.13 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 179.5, 165.2 (d, *J* = 254.6 Hz), 137.6 (d, *J* = 3.2 Hz), 132.6, 130.2 (d, *J* = 9.3 Hz), 130.1, 128.4, 128.3, 116.11 (d, *J* = 22.5 Hz) ppm; three signals more at ca. 130 ppm are close to their coalescence temperature and broadened;[7b] **^{19}F NMR** (377 MHz, $CDCl_3$) δ = -105.53 (ddd, *J* = 13.5, 8.7, 5.1 Hz) ppm; **IR** (ATR): 3261, 3059, 1655, 1591, 1556, 1494, 1447, 1320, 1291, 1237, 1154, 1091, 919, 836, 702, 554, 426 cm^{-1}; **HRMS** calculated *m/z* for $C_{19}H_{15}FNO_2S^+$ $[M+H]^+$: 340.0802, found 340.0799. **Mp**: 112–113 °C.

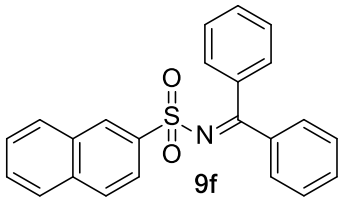
4-Bromo-*N*-(diphenylmethylene)benzenesulfonamide (**9e**):



9e

Using the GP4, compound **9e** was prepared from sodium 4-bromobenzenesulfinate (**8e**) (72.9 mg, 0.3 mmol, 1.5 equiv.) and **3a** (102.7 mg, 0.2 mmol, 1.00 equiv.) in dry DMF. The reaction was carried out at RT for 1 h. After flash chromatography (hexane/EtOAc: 9/1) compound **9e** was obtained as a white solid (43.1 mg, 54%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.83 – 7.79 (m, 2H), 7.66 – 7.61 (m, 2H), 7.60 – 7.39 (m, 10H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 179.7, 140.6, 132.5, 132.2, 130.2, 129.0, 128.4, 128.4, 127.7 ppm; four signals more at ca. 130 ppm are close to their coalescence temperature and broadened;[7b] **IR** (ATR): 3263, 3061, 1656, 1554, 1446, 1388, 1319, 1277, 1154, 1087, 1067, 1010, 817, 739, 700, 660, 593, 572 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{19}H_{15}BrNO_2S^+$ $[M+H]^+$: 400.0001, found 399.9992. **Mp**: 117–118 °C.

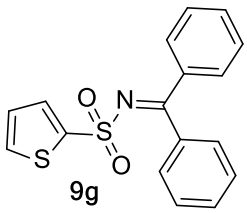
***N*-(Diphenylmethylene)naphthalene-2-sulfonamide** (**9f**):



9f

Using the GP4, compound **9f** was prepared from sodium naphthalene-2-sulfinate (**8f**) (64.2 mg, 0.3 mmol, 1.5 equiv.) and **3a** (102.7 mg, 0.2 mmol, 1.00 equiv.) in dry DMF. After flash chromatography (hexane/EtOAc: 9/1) compound **9f** was obtained as a white solid (49.7 mg, 71%). (51.1 mg, 69%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.43 (s, 1H), 8.02 – 7.95 (m, 2H), 7.95 – 7.88 (m, 2H), 7.67 – 7.49 (m, 8H), 7.43 – 7.39 (m, 4H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 179.2, 138.3, 134.9, 132.5, 132.2, 130.2, 129.5, 129.2, 128.9, 128.6, 128.4, 128.3, 127.9, 127.4, 123.1 ppm; two signals more at ca. 130 ppm are close to their coalescence temperature and broadened;[7b] **IR** (ATR): 3341, 3248, 3059, 1657, 1587, 1555, 1446, 1318, 1277, 1153, 1130, 1075, 946, 861, 810, 751, 701, 638, 551, 485 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{23}H_{17}NNaO_2S^+$ $[M+Na]^+$: 394.0872, found 394.0875; **Mp**: 114–115 °C.

***N*-(Diphenylmethylene)thiophene-2-sulfonamide** (**9g**):



9g

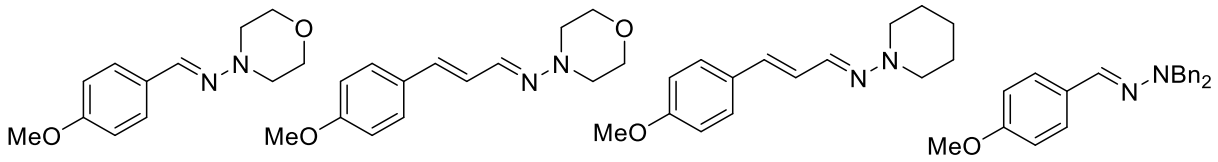
Using the GP4, compound **9g** was prepared from sodium thiophene-2-sulfinate (**8g**) (51.0 mg, 0.3 mmol, 1.5 equiv.) and **3a** (102.7 mg, 0.2 mmol, 1.00 equiv.) in dry DMF. After flash chromatography (hexane/EtOAc: 9/1) compound **9g** was obtained as a white solid (42.4 mg, 65%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.69 – 7.51 (m, 8H), 7.47 – 7.43 (m, 4H), 7.05 (dd, *J* = 5.0, 3.8 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 179.1, 142.5, 132.5, 128.4, 127.1 ppm; **IR** (ATR): 3269, 3100, 1655, 1586, 1555, 1446, 1404, 1318, 1278, 1149, 1090, 1017, 855, 814, 703,

579, 531, 476 cm^{-1}; **HRMS** calculated *m/z* for $C_{17}H_{14}NO_2S_2^+$ $[M+H]^+$: 328.0461, found 328.0447; **Mp**: 157–158 °C.

2.6 General Procedures (GP5) for the synthesis of hydrazones 12 from aldehydes

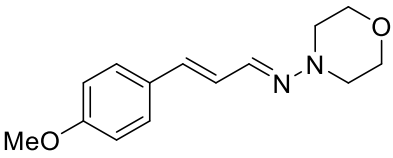
12a-d

A mixture of respective hydrazine (2.4 mmol), aldehyde (2.0 mmol) and anhydrous $MgSO_4$ (0.5 g) in CH_2Cl_2 (10 mL) was stirred overnight at room temperature. After filtration from $MgSO_4$, CH_2Cl_2 was removed under reduced pressure, and the residue was purified by column chromatography to give the desired product in almost quantitative yields.[3]



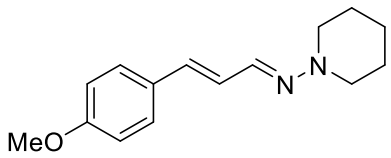
12a **12b** **12c** **12d**

(1*E*,2*E*)-3-(4-methoxyphenyl)-*N*-morpholinoprop-2-en-1-imine (12b). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.7 Hz, 1H), 7.37 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.81 (dd, *J* = 15.9, 8.7 Hz, 1H), 6.66 (d, *J* = 16.0 Hz, 1H), 3.89 – 3.83 (m, 4H), 3.81 (s, 3H), 3.13 – 3.06 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.7, 139.6, 134.7, 129.7, 127.9, 124.9, 114.3, 66.5, 55.4, 52.1. **IR** (ATR): 2970, 2832, 1603, 1576, 1508, 1457, 1439, 1367, 1354, 1323, 1299, 1272, 1254, 1173, 1158, 1132, 1093, 1065, 1021, 995, 932, 907, 868, 857, 849, 784, 763, 673, 592, 543, 526, 499, 434 cm^{-1}; **HRMS** calculated *m/z* for $C_{14}H_{19}N_2O_2^+$ $[M+H]^+$: 247.1441, found 247.1444.



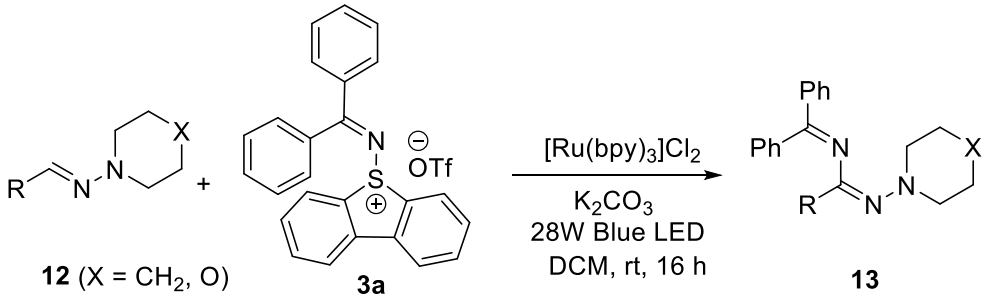
12b

(1*E*,2*E*)-3-(4-methoxyphenyl)-*N*-(piperidin-1-yl)prop-2-en-1-imine (12c). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.8 Hz, 1H), 7.35 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 6.7 Hz, 2H), 6.82 (dd, *J* = 14.9, 7.7 Hz, 1H), 6.60 (d, *J* = 15.9 Hz, 1H), 3.81 (s, 3H), 3.17 – 3.01 (m, 4H), 1.80 – 1.66 (m, 4H), 1.60 – 1.46 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.5, 138.1, 133.1, 130.1, 127.8, 125.7, 114.3, 55.4, 52.3, 25.2, 24.2. **IR** (ATR): 2943, 2851, 2840, 2790, 1603, 1574, 1561, 1456, 1441, 1422, 1372, 1351, 1304, 1265, 1198, 1174, 1153, 1123, 1109, 989, 917, 900, 850, 826, 777, 756, 632, 581, 497, 433 cm^{-1}; **HRMS** calculated *m/z* for $C_{15}H_{21}N_2O^+$ $[M+H]^+$: 245.1648, found 245.1655.



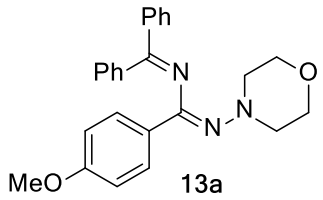
12c

2.7 General Procedure (GP6) for the imination of aldehyde hydrazones 12

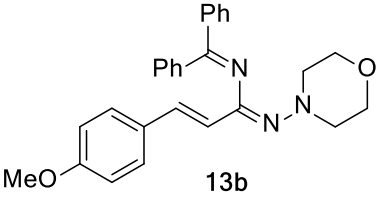


A 10-mL Schlenk tube was equipped with a magnetic stir bar and charged with hydrazone **12** (0.1 mmol, 1.0 equiv.), **3a** (0.2 mmol, 2.0 equiv.), photocatalyst (2–5 mol%) and base (2.0 equiv, 0.2 mmol). The flask was evacuated and backfilled with N_2 for 3 times. Dry DCM (2.0 mL) was added with syringe under N_2. The tube was then irradiated by a 28W blue LED with TLC monitoring. After the reaction was complete, the reaction mixture was concentrated under vacuum to remove DCM. The residue was then purified by chromatography on silica gel (EtOAc : hexane = 3:7) to afford **13**.

(*Z*)-*N*-(Diphenylmethylene)-4-methoxy-*N*'-morpholinobenzimidamide (**13a**) was prepared according to the GP6 from **12a** (22.0 mg, 0.1 mmol, 1 equiv.) and **3a** (102.7 mg, 0.2 mmol, 2 equiv.) using $[Ru(bpy)_3]Cl_2$ (3.2 mg, 5 μmol, 5 mol%) and K_2CO_3 (27.6 mg, 0.2 mmol, 2 equiv.) (RT/16 h). After flash chromatography (hexane/EtOAc: 7/3) compound **13a** was obtained as a yellow solid (25.5 mg, 64%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.66 (d, *J* = 8.9 Hz, 2H), 7.57 – 7.40 (m, 6H), 7.34 (t, *J* = 7.0 Hz, 4H), 6.82 (d, *J* = 8.9 Hz, 2H), 3.80 (s, 3H), 3.67 (t, *J* = 4.7 Hz, 4H), 2.73 (br, 4H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 167.5, 161.0, 159.9, 137.5, 130.4, 128.8, 128.4, 128.0, 127.9, 113.7, 66.8, 55.4, 53.9 ppm; **IR** (ATR): 2958, 2833, 1712, 1607, 1509, 1446, 1360, 1313, 1253, 1171, 1111, 1029, 978, 840, 698, 648, 620 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{25}H_{26}N_3O_2^+$ $[M+H]^+$: 400.2020, found 400.2020; **Mp**: 144–145 °C.

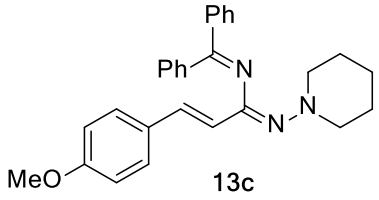


(1*Z*,2*E*)-*N*-(Diphenylmethylene)-3-(4-methoxyphenyl)-*N*'-morpholinoacrylimidamide (**13b**) was prepared according to the GP6 from **12b** (24.6 mg, 0.1 mmol, 1 equiv.) and **3a** (102.7 mg, 0.2 mmol, 2 equiv.) using $[Ru(bpy)_3]Cl_2$ (3.2 mg, 5 μmol, 5 mol%) and K_2CO_3 (27.6 mg, 0.2 mmol, 2 equiv.) (RT/16 h). After flash chromatography (hexane/EtOAc: 6/4) compound **13b** was obtained as a yellow solid (26.1 mg, 61%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.66 – 7.31 (m, 12H), 6.88 – 6.78 (m, 3H), 6.53 (d, *J* = 16.2 Hz, 1H), 3.80 (s, 3H), 3.67 (t, *J* = 4.7 Hz, 4H), 2.77 (br, 4H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.1, 161.2, 160.2, 137.4, 135.5, 130.4, 129.1, 128.6, 128.1, 127.9, 122.6, 114.3, 66.7, 55.5, 53.9 ppm; **IR** (ATR): 2957, 2832, 1738, 1604, 1574, 1509, 1445, 1246, 1174, 1111, 1029,



991, 960, 865, 824, 744, 697, 616 cm^{-1}; **HRMS** calculated *m/z* for $C_{27}H_{28}N_3O_2^+$ $[M+H]^+$: 426.2176, found 426.2177; **Mp**: 175–176 °C.

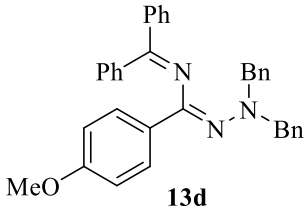
(1*Z*,2*E*)-*N*-(Diphenylmethylene)-3-(4-methoxyphenyl)-*N*'-(piperidin-1-yl)acrylimidamide



13c

(**13c**) was prepared according to the GP6 from **12c** (24.4 mg, 0.1 mmol, 1 equiv.) and **3a** (102.7 mg, 0.2 mmol, 2 equiv.) using $Ir(ppy)_3$ (1.31 mg, 2 μmol, 2 mol%) and K_2CO_3 (27.6 mg, 0.2 mmol, 2 equiv.) (RT/16 h). After flash chromatography (hexane/EtOAc: 6/4) compound **13c** was obtained as a yellow solid (28.9 mg, 68%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.35 (m, 12H), 6.86 – 6.82 (m, 3H), 6.54 (d, *J* = 16.2 Hz, 1H), 3.80 (s, 3H), 2.65 (br, 4H), 1.55 – 1.549 (m, 4H), 1.39 – 1.33 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.1, 160.6, 160.1, 134.9, 132.5, 130.2, 129.3, 128.5, 128.4, 128.0, 123.2, 114.2, 55.5, 54.6, 25.7, 24.2 ppm; **IR** (ATR): 2932, 2804, 1604, 1509, 1445, 1246, 1173, 1106, 1032, 959, 823, 780, 743, 696, 620, 596 cm^{-1}; **HRMS** calculated *m/z* for $C_{28}H_{30}N_3O^+$ $[M+H]^+$: 424.2383, found 424.2385. **Mp**: 139–140 °C.

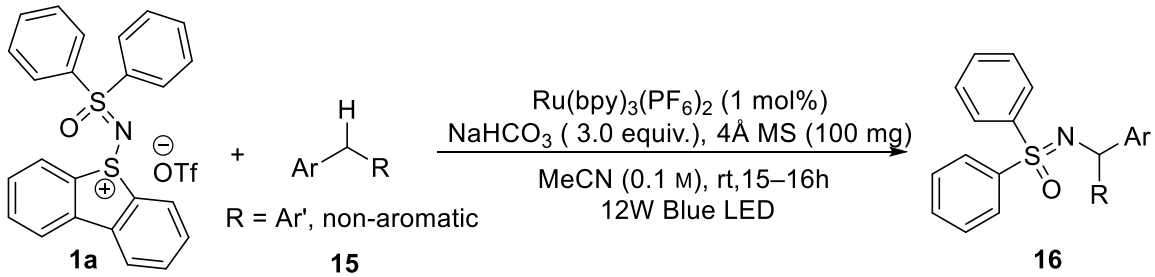
(*Z*)-*N*-(Diphenylmethylene)-4-methoxy-*N*',*N*'(dibenzyl)benzimidamide (13d): A mixture of



13d

$Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $KHCO_3$ (60.1 mg, 0.6 mmol, 3.0 equiv.), **3a** (154.1 mg, 0.3 mmol, 1.5 equiv.) and **13d** (66.1 mg, 0.2 mmol, 1.0 equiv.) in PhCl (4 mL) was stirred at room temperature under blue light irradiation for 3 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 10:1) afforded **14d** in 63% yield (64.2 mg) as a yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.49 – 7.10 (m, 22H), 6.71 – 6.68 (m, 2H), 4.11 (bs, 4H), 3.72 (s, 3H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ 166.4, 160.4, 157.1, 139.4, 137.0(br), 130.3(br), 129.9, 129.0(br), 128.1, 128.0, 127.9, 126.8, 113.5, 59.4, 55.3 ppm; **IR** (ATR): 3027, 2835, 1605, 1589, 1509, 1494, 1445, 1313, 1248, 1166, 1062, 1026, 950, 914, 836, 768, 736, 694, 639, 624, 563, 507 cm^{-1}; **HRMS** calculated m/z for $C_{35}H_{32}N_3O^+$ $[M+H]^+$: 510.2540, found 510.2542.

2.9 General Procedure (GP7) for the benzylic C–H sulfoximination



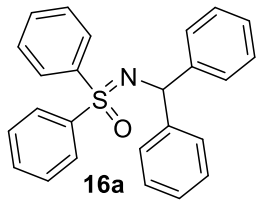
Under a nitrogen atmosphere, a dry Schlenk tube was charged with sulfonium salt **1a** (0.2 mmol, 110 mg, 1 equiv.), $Ru(bpy)_3(PF_6)_2$ (1.72 mg, 2 μmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3

equiv.), 4Å MS (100 mg), benzylic compound **15** (1 mmol, 5 equiv.), and degassed MeCN (2 mL). The resulting orange suspension was irradiated by blue LED strips (12 W) and magnetically stirred (a rotary fan was positioned adjacent to the reaction tube, keeping that the reaction mixture setup at room temperature). After 15–16 hours, the reaction solution was concentrated, and the product was purified by column chromatography (SiO_2, EtOAc and pentane as eluent).

2.10 Preparation of substrates 15

The diarylmethanes **15b-k** were synthesized from corresponding diarylmethanone according to the reported method.[4] The substrates **15v** and **15w**,[5] **15ae**,[6] **15ab** and **15ac**[7] were prepared according to the reported procedures. The propargylic arenes **15ah-aj**[8a] were obtained following the reported protocols. Other substrates were commercially available.

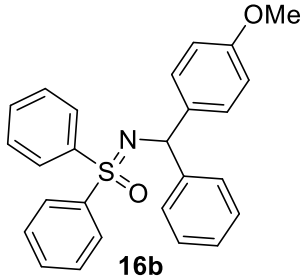
2.11 Characterization of products 16



16a

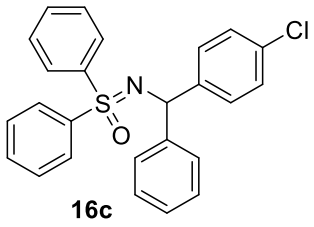
(Benzhydrylimino)diphenyl-λ⁶-sulfanone (**16a**) was prepared from **1a** and diphenylmethane (**15a**) as a white solid (67% yield). R_f = 0.3 (pentane/EtOAc, 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.98 – 7.85 (m, 4H), 7.51 – 7.35 (m, 10H), 7.29 – 7.23 (m, 4H), 7.20 – 7.11 (m, 2H), 5.42 (s, 1H);. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 145.7, 140.90, 132.3, 128.9, 128.6, 128.1, 127.4, 126.4, 61.7 ppm; **IR** (neat): 3060, 2849, 1709, 1598, 1491, 1474, 1445, 1239, 1134, 1092, 1068, 1024, 999, 932, 840, 758, 739, 725, 690, 648, 608, 587, 553, 466 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{25}H_{22}NOS^+$ $[M+H]^+$: 384.1417, found (ESI) 384.1418.

{[(4-Methoxyphenyl)(phenyl)methyl]imino}diphenyl-λ⁶-sulfanone (**16b**) was prepared from **1a** and 1-benzyl-4-methoxybenzene (**15b**) as a pale-yellow oil (78% yield).



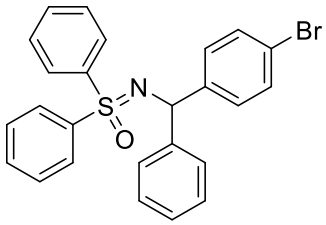
16b

R_f = 0.2 (pentane/EtOAc, 6:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.96 – 7.88 (m, 4H), 7.50 – 7.42 (m, 2H), 7.42 – 7.36 (m, 6H), 7.32 – 7.22 (m, 4H), 7.19 – 7.12 (m, 1H), 6.84 – 6.63 (m, 2H), 5.38 (s, 1H), 3.75 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.1, 146.0, 141.02, 140.95, 138.1, 132.2, 128.90, 128.88, 128.7, 128.4, 128.0, 127.3, 126.3, 113.4, 61.1, 55.1 ppm; **IR** (neat): 1608, 1508, 1445, 1360, 1240, 1171, 1136, 1092, 1068, 1030, 999, 908,808, 784, 759, 725, 692, 629, 594, 574, 553, 529 cm^{-1};**HRMS** calculated *m*/*z* for $C_{26}H_{24}NO_2S^+$ $[M+H]^+$: 414.1522, found (ESI) 414.1526.

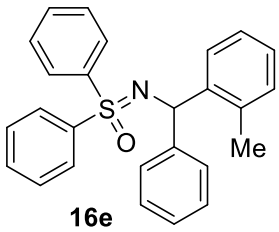


16c

{[(4-Chlorophenyl)(phenyl)methyl]imino}diphenyl-λ^6-sulfanone (**16c**) was prepared from **1a** and 1-benzyl-4-chlorobenzene (**15c**) as a white solid (65% yield). R_f = 0.2 (pentane/EtOAc, 8:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.94 – 7.85 (m, 4H), 7.50 – 7.44 (m, 2H), 7.43 – 7.37 (m, 4H), 7.36 – 7.33 (m, 2H), 7.33 – 7.29 (m, 2H), 7.27 – 7.23 (m, 2H), 7.21 – 7.13 (m, 3H), 5.37 (s, 1H) ppm; **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 145.3, 144.4, 140.8, 140.7, 132.4, 132.1, 129.00, 128.99, 128.8, 128.7, 128.6, 128.20, 128.18, 127.3, 126.6, 61.0 ppm. **IR** (neat): 3059, 1901, 1487, 1445, 1360, 1239, 1135,1089, 1068, 1013,998, 929, 800, 757, 727, 686, 624, 591, 554, 528 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{25}H_{21}ClNOS^+$ $[M+H]^+$: 418.1027, found (ESI) 418.1030.

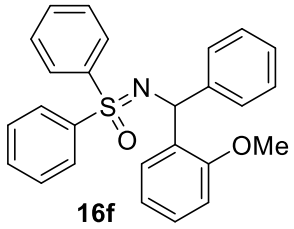


{[(4-Bromophenyl)(phenyl)methyl]imino}diphenyl-λ^6-sulfanone (**16d**) was prepared from **1a** and 1-benzyl-4-chlorobenzene (**15d**) as a white solid (66% yield). R_f = 0.2 (pentane/EtOAc, 8:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.00 – 7.86 (m, 4H), 7.56 – 7.34 (m, 10H), 7.33 – 7.26 (m, 4H), 7.25 – 7.17 (m, 1H), 5.39 (s, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 145.3, 145.0, 140.9, 140.7, 132.4, 131.2, 129.2, 129.0, 128.7, 128.6, 128.3, 127.3, 126.7, 120.3, 61.2 ppm; **IR** (neat): 3060, 1906,1710,1483, 1445, 1239, 1135, 1092, 1068, 1024, 1010, 928, 796, 756, 726, 687, 621, 590, 553, 480 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{25}H_{21}BrNOS^+$ $[M+H]^+$: 462.0522, found (ESI) 462.0527.



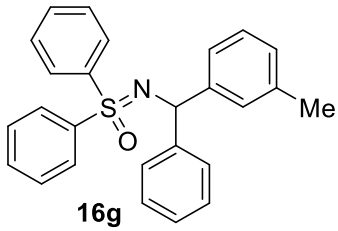
16e

Diphenyl{[phenyl(*o*-tolyl)methyl]imino}-λ^6-sulfanone (**16e**) was prepared from **1a** and 1-benzyl-2-methylbenzene (**15e**) as a white solid (58% yield). R_f = 0.3 (pentane/EtOAc, 8:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.02 – 7.96 (m, 2H), 7.85 – 7.80 (m, 2H), 7.77 (dd, *J* = 1.4, 7.8Hz, 1H), 7.51 – 7.37 (m, 4H), 7.36 – 7.30 (m, 4H), 7.23 – 7.17 (m, 3H), 7.14 – 7.08 (m, 2H), 7.02 – 6.95 (m, 1H), 5.59 (s, 1H), 1.98 (s, 3H) ppm; **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 144.8, 143.4, 141.08, 141.05, 134.9, 132.3, 132.2, 130.1, 128.93, 128.87, 128.7, 128.5, 128.3, 128.0, 127.6, 126.5, 126.2, 125.9, 58.3, 19.5 ppm; **IR** (neat): 3060, 1812, 1600, 1490, 1445, 1359, 1238, 1134,1092, 1068, 1024, 998, 928, 839, 756,724, 687, 645, 611, 592, 559, 499 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{26}H_{24}NOS^+$ $[M+H]^+$: 398.1573, found (ESI) 398.1577.



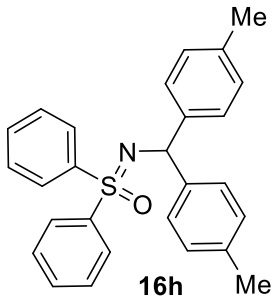
16f

{[(2-Methoxyphenyl)(phenyl)methyl]imino}diphenyl-λ^6-sulfanone (**16f**) was prepared from **1a** and 1-benzyl-2-methoxybenzene (**15f**) as a white solid (64% yield). R_f = 0.2 (pentane/EtOAc, 8:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.02 – 7.95 (m, 2H), 7.95 – 7.82 (m, 3H), 7.53 – 7.35 (m, 8H), 7.30 – 7.12 (m, 4H), 7.06 – 6.97 (m, 1H), 6.74 (dd, *J* = 1.1, 8.2Hz, 1H), 5.96 (s, 1H), 3.58 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 155.7, 145.9, 141.4, 141.2, 134.6, 132.2, 132.0, 128.9, 128.77, 128.75, 128.7, 127.8, 127.5, 127.4, 126.0, 120.8, 110.3, 55.2, 54.2 ppm; **IR** (neat): 3198, 1711, 1599, 1488, 1445, 1237, 1137, 1105, 1068, 1048, 1026, 929, 787, 754, 725, 694, 592, 561, 540, 407 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{26}H_{24}NO_2S^+$ $[M+H]^+$: 414.1522, found (ESI) 414.1523.



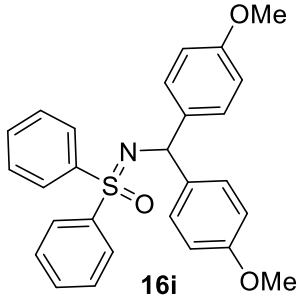
16g

Diphenyl[(phenyl(*m*-tolyl)methyl)imino]-λ^6-sulfanone (**16g**) was prepared from **1a** and 1-benzyl-3-methylbenzene (**15g**) as a pale-yellow solid (61% yield). R_f = 0.3 (pentane/EtOAc, 8:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.94 – 7.88 (m, 4H), 7.48 – 7.44 (m, 2H), 7.42 – 7.36 (m, 6H), 7.28 – 7.22 (m, 2H), 7.20 – 7.11 (m, 4H), 7.00 – 6.91 (m, 1H), 5.38 (s, 1H), 2.27 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 145.9, 145.6, 1401.0, 137.6, 132.32, 132.31, 129.0, 128.9, 128.8, 128.7, 128.2, 128.1, 128.0, 127.4, 127.2, 126.4, 124.5, 61.8, 21. ppm 5; **IR** (neat): 3060, 2921, 1811, 1604, 1490, 1445, 1240, 1133, 1092, 1068, 1024, 998, 928, 842, 757, 724, 687,623, 590, 564, 540, 503, 441 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{26}H_{24}NOS^+$ $[M+H]^+$: 398.1573, found (ESI) 398.1576.



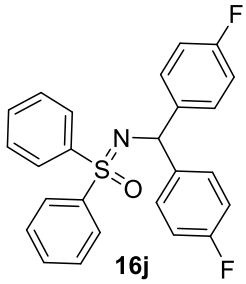
16h

[(Di-*p*-tolylmethyl)imino]diphenyl-λ^6-sulfanone (**16h**) was prepared from **1a** and di-*p*-tolylmethane (**15h**) as a white solid (68% yield). R_f = 0.4 (pentane/EtOAc, 6:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.97 – 7.89 (m, 4H), 7.51 – 7.43 (m, 2H), 7.43 – 7.36 (m, 4H), 7.31 – 7.26 (m, 4H), 7.10 – 7.03 (m, 4H), 5.35 (s, 1H), 2.30 (s, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 143.1, 141.0, 135.7, 132.2, 128.9, 128.8, 128.7, 127.2, 61.3, 21.0 ppm; **IR** (neat): 2920, 1508, 1445, 1243, 1137, 1092, 1068, 1021, 922, 806, 774, 726, 691, 594, 563, 482 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{27}H_{26}NOS^+$ $[M+H]^+$: 412.1730, found (ESI) 412.1731.



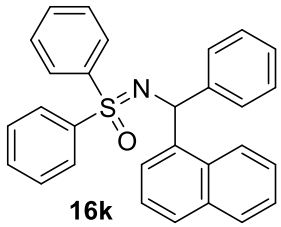
16i

{[Bis(4-methoxyphenyl)methyl]imino}diphenyl-λ⁶-sulfanone (**16i**) was prepared from **1a** and bis(4-methoxyphenyl)methane (**15i**) as a pale-yellow solid (74% yield). R_f = 0.25 (pentane/EtOAc, 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.96 (dt, *J* = 1.0, 7.6 Hz, 4H), 7.59 – 7.39 (m, 6H), 7.40 – 7.29 (m, 4H), 6.84 (d, *J* = 8.7 Hz, 4H), 5.39 (s, 1H), 3.80 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.1, 141.1, 138.5, 132.3, 129.0, 128.8, 128.4, 113.5, 60.6, 55.2 ppm; **IR** (neat): 2835, 1607,1508,1446, 1360, 1301, 1243, 1173, 1138, 1092, 1033, 812, 758, 728, 691,595, 555, 506 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{27}H_{25}NNaO_3S^+$ $[M+Na]^+$: 466.1447, found (ESI) 466.1447.



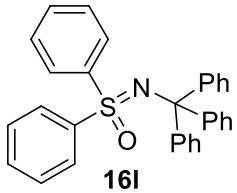
16j

{[Bis(4-fluorophenyl)methyl]imino}diphenyl-λ⁶-sulfanone (**16j**) was prepared from **1a** and bis(4-fluorophenyl)methane (**15j**) as a white solid (73% yield). R_f = 0.2 (pentane/EtOAc, 8:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.96 – 7.79 (m, 4H), 7.56 – 7.25 (m, 10H), 7.01 – 6.82 (m, 4H), 5.38 (s, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 161.5 (d, *J* = 245.4 Hz), 141.4 (d, *J* = 3.2 Hz), 140.7, 132.4, 129.0, 128.8, 128.7, 128.5, 115.0, 114.7, 60.2 ppm; **IR** (neat): 3060, 2835, 1711, 1606, 1505, 1445, 1409, 1362, 1228, 1172, 1130, 1085, 1069, 1030, 980, 821, 781, 727, 688, 626, 593, 552, 531, 514 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{25}H_{20}F_2NOS^+$ $[M+H]^+$: 420.1228, found (ESI) 420.1231.



16k

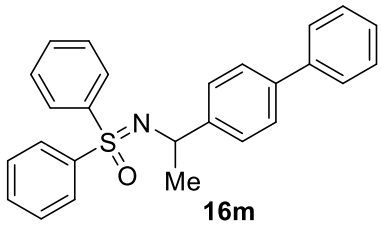
{[Naphthalen-1-yl(phenyl)methyl]imino}diphenyl-λ⁶-sulfanone (**16k**) was prepared from **1a** and 1-benzylnaphthalene (**15k**) as a yellow oil (72% yield). R_f = 0.23 (pentane/EtOAc, 8:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.06 – 7.92 (m, 4H), 7.89 – 7.74 (m, 4H), 7.62 – 7.55 (m, 1H), 7.55 – 7.43 (m, 8H), 7.43 – 7.37 (m, 2H), 7.35 – 7.27 (m, 2H), 7.27 – 7.19 (m, 1H), 5.65 (s, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 145.6, 143.2, 141.03, 140.95, 133.4, 132.5, 132.41, 132.36, 129.04, 128.99, 128.77, 128.75, 128.2, 128.05, 127.98, 127.60, 127.57, 126.6, 126.3, 125.8, 125.6, 125.4, 61.9 ppm; **IR** (neat): 3059, 1709, 1446, 1360, 1220, 1136, 1092, 1068, 1023, 999, 918,815, 724, 692, 619, 593, 553,528, 477 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{29}H_{24}NOS^+$ $[M+H]^+$: 434.1573, found (ESI) 434.1576.



16l

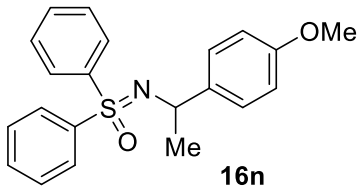
Diphenyl(tritylimino)-λ⁶-sulfanone (**16l**) was prepared from **1a** and triphenylmethane (**15l**) as a white solid (80% yield). R_f = 0.3 (pentane/EtOAc, 8:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.82 (dd, *J* = 1.9, 7.3Hz, 4H), 7.66 – 7.55 (m, 6H), 7.41 – 7.26 (m, 6H), 7.22 – 7.07 (m, 9H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 147.5, 144.5, 131.1, 129.3, 128.6, 127.7, 127.3, 126.2, 72.2 ppm; **IR** (neat): 3057,1710,1489, 1445, 1360, 1255, 1220, 1142, 1089, 1023, 999, 910, 750,722,

686, 634, 601, 558 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{31}H_{25}NNaOS^+$ $[M+Na]^+$: 482.1549, found (ESI) 482.1535.



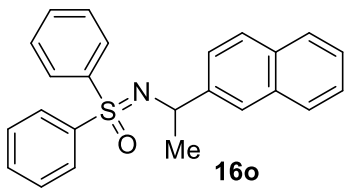
16m

{[1-([1,1'-Biphenyl]-4-yl)ethyl]imino}diphenyl-λ⁶-sulfanone (**16m**) was prepared from **1a** and 4-ethyl-1,1'-biphenyl (**15m**) as a white oil (25% yield). R_f = 0.3 (pentane/EtOAc, 8:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.10 – 8.00 (m, 2H), 7.88 – 7.76 (m, 2H), 7.63 – 7.56 (m, 2H), 7.54 – 7.27 (m, 13H), 4.43 (q, *J* = 6.6 Hz, 1H), 1.58 (d, *J* = 6.6 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 146.6, 141.5, 141.2, 140.8, 139.2, 132.4, 132.2, 129.0, 128.9, 128.7, 128.4, 127.03, 126.96, 126.9, 126.6, 53.9, 28.1 ppm; **IR** (neat): 3060, 3027, 2969, 2923, 2861, 1712, 1599, 1486, 1445, 1402, 1364, 1243, 1138, 1093, 1023, 1008, 998, 842, 792, 764, 729, 692, 617, 583, 569, 557, 548, 518 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{26}H_{24}NOS^+$ $[M+H]^+$: 398.1573, found (ESI) 398.1574.



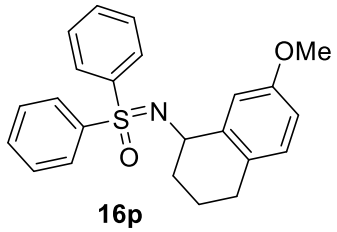
16n

{[1-(4-Methoxyphenyl)ethyl]imino}diphenyl-λ⁶-sulfanone (**16n**) was prepared from **1a** and 1-ethyl-4-methoxybenzene (**15n**) as a pale-yellow oil (69% yield). R_f = 0.4 (pentane/EtOAc, 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.08 – 7.96 (m, 2H), 7.84 – 7.75 (m, 2H), 7.51 – 7.40 (m, 4H), 7.39 – 7.27 (m, 4H), 6.87 – 6.79 (m, 2H), 4.35 (q, *J* = 6.6 Hz, 1H), 3.78 (s, 3H), 1.52 (d, *J* = 6.6 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.0, 141.4, 140.8, 139.7, 132.24, 132.13, 128.9, 128.8, 128.4, 127.1, 113.4, 55.2, 53.6, 28.1 ppm; **IR** (neat): 2964, 2360, 1609, 1508, 1444, 1236, 1172, 1133, 1082, 1032, 998, 829, 805, 756, 725, 687, 637, 593, 555 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{21}H_{22}NOS^+$ $[M+H]^+$: 352.1366, found (ESI) 352.1365.



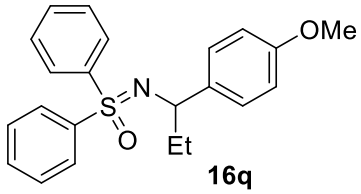
16o

{[1-(Naphthalen-2-yl)ethyl]imino]diphenyl-λ⁶-sulfanone (**16o**) was prepared from **1a** and 2-ethylnaphthalene (**15o**) as a white oil (35% yield). R_f = 0.3 (pentane/EtOAc, 8:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.09 – 8.00 (m, 2H), 7.85 – 7.73 (m, 6H), 7.60 (dd, *J* = 1.8, 8.5 Hz, 1H), 7.53 – 7.38 (m, 6H), 7.36 – 7.28 (m, 2H), 4.54 (q, *J* = 6.6 Hz, 1H), 1.62 (d, *J* = 6.6 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 144.9, 141.5, 140.7, 133.4, 132.5, 132.4, 132.2, 129.04, 129.01, 128.9, 128.4, 127.9, 127.8, 127.6, 125.7, 125.23, 125.18, 124.2, 54.4, 28.1 ppm; **IR (neat):** 3058, 2969, 1713, 1600, 1507, 1474, 1445, 1365, 1243, 1138, 1093, 1023, 998, 950, 887, 858, 820, 749, 731, 691, 624, 591, 579, 565, 479 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{24}H_{22}NOS^+$ $[M+H]^+$: 372.1417, found (ESI) 372.1421.



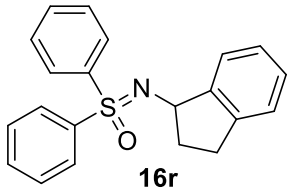
16p

[(7-Methoxy-1,2,3,4-tetrahydronaphthalen-1-yl)imino)diphenyl-λ^6-sulfanone (**16p**,) was prepared from **1a** and 6-methoxy-1,2,3,4-tetrahydronaphthalene (**15p**) as a yellow solid (57% yield). R_f = 0.25 (pentane/EtOAc, 8:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.10 – 7.92 (m, 4H), 7.55 – 7.38 (m, 7H), 6.81 – 6.67 (m, 1H), 6.58 – 6.48 (m, 1H), 4.28 (dd, *J* = 4.7, 7.8Hz, 1H), 3.75 (s, 3H), 2.92 – 2.73 (m, 1H), 2.71 – 2.58 (m, 1H), 2.09 – 1.96 (m, 2H), 1.97 – 1.85 (m, 1H), 1.72 – 1.62 (m, 1H) ppm; **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 158.0, 141.8, 141.0, 138.2, 132.9, 132.21, 132.17, 130.0, 129.0, 128.9, 128.7, 128.6, 113.1, 112.0, 55.2, 52.5, 34.1, 29.7, 20.5 ppm; **IR** (neat): 2932, 1607, 1498, 1445, 1233, 1131, 1092, 1068, 1038, 998, 853, 755, 727, 690, 600, 557 cm^{-1}. **HRMS** calculated *m*/*z* for $C_{23}H_{24}NO_2S^+$ $[M+H]^+$: 378.1522, found (ESI) 358.1519.



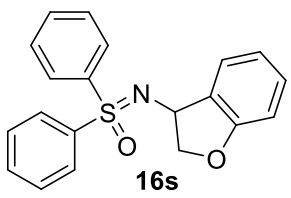
16q

{[1-(4-Methoxyphenyl)propyl]imino}diphenyl-λ^6-sulfanone (**16q**) was prepared from **1a** and 1-methoxy-4-propylbenzene (**15q**) as a yellow oil (62% yield). R_f = 0.25 (pentane/EtOAc, 8:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.03 – 7.92 (m, 2H), 7.79 – 7.69 (m, 2H), 7.50 – 7.37 (m, 4H), 7.36 – 7.28 (m, 2H), 7.23 – 7.15 (m, 2H), 6.82 – 6.74 (m, 2H), 4.01 (t, *J* = 6.7 Hz, 1H), 3.78 (s, 3H), 2.04 – 1.60 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.0, 141.3, 141.0, 138.4, 132.2, 132.0, 128.93, 128.90, 128.8, 128.4, 127.8, 113.3, 59.9, 55.2, 34.3, 11.0 ppm; **IR** (neat): 2958, 1609, 1508, 1445, 1238, 1172, 1134, 1092, 1067, 1034, 884, 826, 757, 726, 689, 592, 553 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{22}H_{24}NO_2S^+$ $[M+H]^+$: 366.1522, found (ESI) 366.1515.

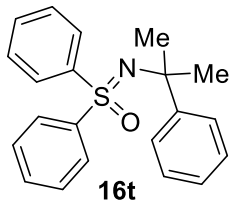


16r

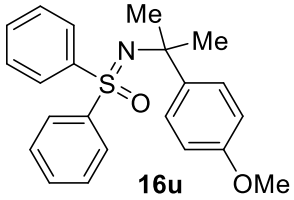
[(2,3-Dihydro-1*H*-inden-1-yl)imino]diphenyl-λ^6-sulfanone (**16r**) was prepared from **1a** and 2,3-dihydro-1*H*-indene (**15r**) as a white solid (32% yield). R_f = 0.3 (pentane/EtOAc, 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.29 – 7.97 (m, 4H), 7.66 – 7.44 (m, 7H), 7.39 – 6.92 (m, 3H), 4.68 (t, *J* = 7.8 Hz, 1H), 3.15 – 2.93 (m, 1H), 2.86 – 2.69 (m, 1H), 2.54 – 2.34 (m, 1H), 2.29 – 2.03 (m, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 146.6, 142.6, 141.3, 140.8, 132.42, 132.38, 129.1, 128.8, 128.7, 126.9, 126.4, 124.6, 124.3, 59.3, 37.3, 30.5 ppm; **IR (neat):** 3064, 2940, 1738, 1474, 1446, 1341, 1241, 1138, 1091, 1069, 1023, 997, 927, 828, 742, 727, 691, 633, 582, 555, 438 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{21}H_{20}NOS^+$ $[M+H]^+$: 334.1260, found (ESI) 334.1256.



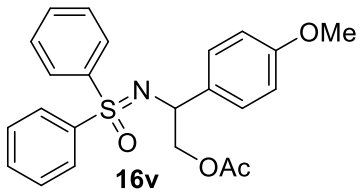
[(2,3-Dihydrobenzofuran-3-yl)imino]diphenyl-λ⁶-sulfanone (**16s**) was prepared from **1a** and 2,3-dihydrobenzofuran (**15s**) as a white oil (28% yield). R_f = 0.25 (pentane/EtOAc, 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.09 – 7.84 (m, 4H), 7.57 – 7.43 (m, 6H), 7.38 (dt, *J* = 7.5, 1.3 Hz, 1H), 7.12 (td, *J* = 7.7, 1.4 Hz, 1H), 6.87 (td, *J* = 7.4, 1.0 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 5.08 – 4.90 (m, 1H), 4.70 – 4.52 (m, 1H), 4.47 (dd, *J* = 9.1, 6.2 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 159.7, 140.6, 140.5, 132.6, 129.8, 129.3, 129.2, 129.0, 128.62, 128.56, 125.6, 120.7, 109.9, 79.0, 55.8 ppm; **IR (neat):** 3062, 1738, 1600, 1478, 1446, 1363, 1322, 1229, 1165, 1135, 1092, 1014, 995, 838, 752, 730, 690, 619, 585, 555 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{20}H_{18}NO_2S^+$ $[M+H]^+$: 336.1053, found (ESI) 336.1055.



Diphenyl[(2-phenylpropan-2-yl)imino]-λ⁶-sulfanone (**16t**) was prepared from **1a** and cumene (**15t**) as a pale-yellow oil (33% yield). R_f = 0.3 (pentane/EtOAc, 8:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.96 – 7.85 (m, 4H), 7.66 – 7.58 (m, 2H), 7.44 – 7.32 (m, 6H), 7.30 – 7.22 (m, 2H), 7.19 – 7.13 (m, 1H), 1.62 (s, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 150.6, 144.7, 131.5, 128.7, 127.9, 127.8, 125.8, 125.4, 59.4, 33.1 ppm; **IR** (neat): 3057, 2973, 1810, 1492, 1474, 1444, 1244, 1169, 1126, 1089, 1065, 1024, 998, 756, 723, 687, 609, 568, 537 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{21}H_{21}NNaOS^+$ $[M+Na]^+$: 358.1236, found (ESI) 358.1237.

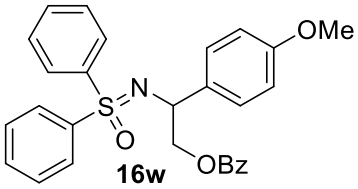


{[2-(4-methoxyphenyl)propan-2-yl]imino}diphenyl-λ⁶-sulfanone (**16u**) was prepared from **1a** and 1-isopropyl-4-methoxybenzene (**15u**) as a pale-yellow oil (56% yield). R_f = 0.2 (pentane/EtOAc, 8:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.98 – 7.90 (m, 4H), 7.60 – 7.50 (m, 2H), 7.47 – 7.32 (m, 6H), 6.90 – 6.71 (m, 2H), 3.82 (s, 3H), 1.65 (s, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 157.7, 144.7, 142.9, 131.5, 128.7, 128.0, 126.5, 113.1, 59.0, 55.2, 33.2 ppm; **IR** (neat): 2967, 1608, 1508,1444,1360, 1238, 1167, 1125, 1088,1065, 1032, 998, 917, 829, 778, 754, 722, 687, 600, 566, 533 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{22}H_{23}NNaO_2S^+$ $[M+Na]^+$: 388.1342, found (ESI) 388.1342.



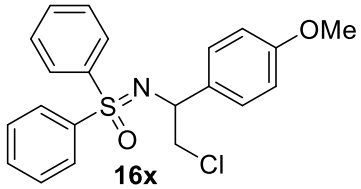
2-(4-Methoxyphenyl)-2-[(oxodiphenyl-λ⁶-sulfaneylidene)amino]ethyl acetate (**16v**) was prepared from **1a** and 4-methoxyphenethyl acetate (**15v**) as a pale-yellow oil (43% yield). R_f = 0.2 (pentane/EtOAc, 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.09 – 7.97 (m, 2H), 7.85 – 7.76 (m, 2H), 7.57 – 7.44 (m, 4H), 7.44 – 7.31 (m, 4H), 6.93 – 6.79 (m, 2H), 4.43 (t, *J* = 6.7 Hz, 1H), 4.27 (d, *J* = 6.6 Hz, 2H), 3.83 (s, 3H), 2.08 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 171.0, 158.7, 141.0, 140.6, 134.3, 132.5, 132.4, 129.0, 128.84, 128.82,

128.6, 128.2, 113.6, 70.0, 56.8, 55.2, 21.1 ppm; **IR** (neat): 2947, 1610, 1509, 1445, 1378, 1238, 1140, 1092, 1033, 829, 758, 727, 690, 593, 553 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{23}H_{24}NO_4S^+$ $[M+H]^+$: 410.1421, found (ESI) 410.1428.



16w

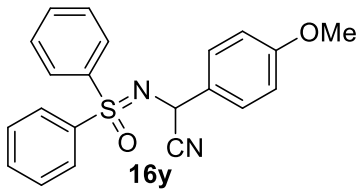
2-(4-Methoxyphenyl)-2-[(oxodiphenyl-λ^6-sulfaneylidene)amino]-ethyl benzoate (**16w**) was prepared from **1a** and 4-methoxyphenethyl benzoate (**15w**) as a pale-yellow oil (53% yield). R_f = 0.25 (pentane/EtOAc, 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.13 – 8.03 (m, 2H), 8.03 – 7.97 (m, 2H), 7.90 – 7.74 (m, 2H), 7.63 – 7.34 (m, 11H), 6.95 – 6.79 (m, 2H), 4.60 – 4.38 (m, 3H), 3.83 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 166.4, 158.8, 140.8, 140.7, 134.5, 132.8, 132.42, 132.39, 130.5, 129.7, 129.04, 129.00, 128.8, 128.6, 128.3, 113.7, 70.6, 57.0, 55.2 ppm; **IR** (neat): 3062, 1609, 1583, 1509, 1446, 1240, 1173, 1141, 1109, 1068, 1026, 998, 828, 757, 711, 687, 637, 557 cm^{-1}. **HRMS** calculated *m*/*z* for $C_{28}H_{26}NO_4S^+$ $[M+H]^+$: 472.1577, found (ESI) 472.1578.



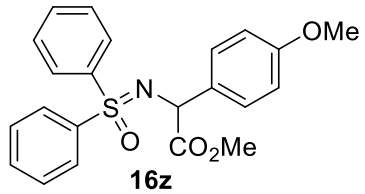
16x

{[2-Chloro-1-(4-methoxyphenyl)ethyl]imino}diphenyl-λ^6-sulfan-one (**16x**) was prepared from **1a** and 1-(2-chloroethyl)-4-methoxybenzene (**15x**) as a yellow oil (60% yield). R_f = 0.4 (pentane/EtOAc, 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.06 – 7.94 (m, 2H), 7.91 – 7.76 (m, 2H), 7.58 – 7.43 (m, 4H), 7.42 – 7.34 (m, 2H), 7.30 – 7.14 (m, 2H), 6.91 – 6.70 (m, 2H), 4.29 (t, *J* = 6.9 Hz, 1H), 3.85 (dd, *J* = 7.0, 10.6Hz, 1H), 3.78 (s, 3H), 3.68 (dd, *J* = 7.0, 10.6Hz, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.8, 140.5, 140.2, 134.7, 132.5, 129.04, 129.00, 128.8, 128.6, 128.2, 113.6, 59.7, 55.1, 51.3 ppm; **IR** (neat): 3060, 2835, 2360, 2341, 1609, 1509, 1445, 1239, 1173, 1137, 1092, 1032, 829, 757, 727, 689, 599, 554 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{21}H_{21}ClNO_2S^+$ $[M+H]^+$: 386.0976, found (ESI) 386.0978.

2-(4-Methoxyphenyl)-2-[(oxodiphenyl-λ^6-sulfaneylidene)amino]acetonitrile (**16y**) was prepared from **1a** and 2-(4-methoxyphenyl)acetonitrile (**15y**) as a yellow oil (73% yield). R_f = 0.2 (pentane/EtOAc, 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.04 – 8.00 (m, 2H), 7.99 – 7.95 (m, 2H), 7.59 – 7.49 (m, 4H), 7.49 – 7.39 (m, 4H), 6.90 – 6.83 (m, 2H), 5.19 (s, 1H), 3.78 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 159.6, 139.6, 139.5, 133.2, 133.1, 129.5, 129.3, 128.6, 128.24, 128.21, 120.0, 114.1, 55.3, 47.6 ppm; **IR** (neat): 2838, 1609, 1509, 1446, 1361, 1305, 1236, 1174, 1132, 1092, 1026, 998, 902, 819,779,757, 727, 685, 593, 569, 529 cm^{-1}. **HRMS** calculated *m*/*z* for $C_{21}H_{19}N_2O_2S^+$ $[M+H]^+$: 363.1162, found (ESI) 363.1165.

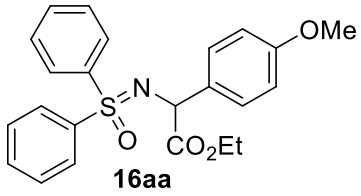


16y



16z

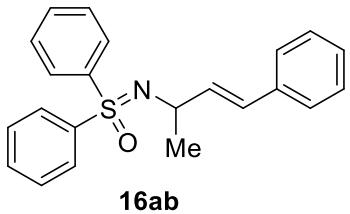
Methyl 2-(4-methoxyphenyl)-2-[(oxodiphenyl-λ^6-sulfaneylidene)amino]acetate (**16z**) was prepared from **1a** and methyl 2-(4-methoxyphenyl)acetate (**15z**) as a pale-yellow oil (63% yield). R_f = 0.1 (pentane/EtOAc, 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 – 7.97 (m, 2H), 7.98 – 7.79 (m, 2H), 7.64 – 7.38 (m, 8H), 6.96 – 6.68 (m, 2H), 4.91 (s, 1H), 3.81 (s, 3H), 3.66 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 173.2, 159.1, 140.5, 140.2, 132.7, 132.6, 132.1, 129.2, 129.1, 128.7, 128.6, 128.4, 113.8, 60.2, 55.2, 52.3; **IR** (neat): 2951, 1747, 1609, 1508, 1445, 1239, 1142, 1092, 1025, 929, 827, 795, 759, 727, 687, 634, 595, 576, 545 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{22}H_{22}NO_4S^+$ $[M+H]^+$: 396.1264, found (ESI) 396.1264.



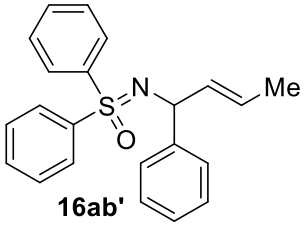
16aa

Ethyl 2-(4-methoxyphenyl)-2-((oxodiphenyl-λ^6-sulfaneylidene)amino)acetate (**16aa**) was prepared from **1a** and ethyl 2-(4-methoxyphenyl)acetate (**15aa**) as a pale-yellow oil (60% yield). R_f = 0.1 (pentane/EtOAc, 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.08 – 7.98 (m, 2H), 7.97 – 7.90 (m, 2H), 7.57 – 7.35 (m, 8H), 6.91 – 6.73 (m, 2H), 4.89 (s, 1H), 4.13 (qd, *J* = 0.9, 7.1Hz, 2H), 3.81 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 172.7, 159.0, 140.6, 140.4, 132.60, 132.56, 132.2, 129.12, 129.09, 128.73, 128.66, 128.4, 113.7, 61.0, 60.2, 55.2, 14.1 ppm; **IR** (neat): 2979, 1741, 1723, 1609, 1583, 1508, 1445, 1301, 1239, 1141, 1092, 1025, 999, 930, 831, 795, 758, 727, 687, 634, 595 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{23}H_{24}NO_4S^+$ $[M+H]^+$: 410.1421, found (ESI) 410.1423.

(*E*)-diphenyl[(4-phenylbut-3-en-2-yl)imino]-λ^6-sulfanone (**16ab**) and **(*E*)-diphenyl((1-phenylbut-2-en-1-yl)imino)-λ^6-sulfanone** (**16ab'**) were prepared from **1a** and (*E*)-but-1-en-1-ylbenzene (**15ab**) as white solids in 30 and 15% yield, respectively.



16ab

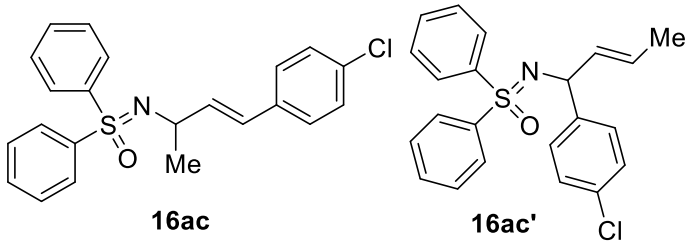


16ab'

Compound 16ab: R_f = 0.28 (pentane/EtOAc, 8:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.07 – 8.00 (m, 2H), 7.99 – 7.89 (m, 2H), 7.50 – 7.39 (m, 6H), 7.36 – 7.31 (m, 2H), 7.30 – 7.25 (m, 2H), 7.21 – 7.13 (m, 1H), 6.45 (dd, *J* = 1.2, 15.8Hz, 1H), 6.30 (dd, *J* = 6.2, 15.8Hz, 1H), 4.11 – 3.92 (m, 1H), 1.42 (d, *J* = 6.6 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 141.4, 141.0, 137.5, 135.6, 132.33, 132.32, 129.1, 129.0, 128.9, 128.38, 128.37, 127.7, 127.0, 126.3, 52.5, 25.5 ppm; **IR (neat):** 2965,

2359, 1494, 1474, 1445, 1242, 1130, 1092, 1068, 1024, 965, 803, 749, 727, 691, 590, 562 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{22}H_{22}NOS^+$ $[M+H]^+$: 348.1417, found (ESI) 348.1421.

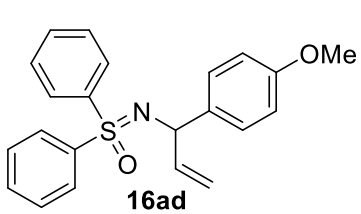
Compound 16ab': R_f = 0.28 (pentane/EtOAc, 8:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.05 – 7.96 (m, 2H), 7.91 – 7.78 (m, 2H), 7.54 – 7.34 (m, 8H), 7.32 – 7.23 (m, 2H), 7.22 – 7.14 (m, 1H), 5.72 – 5.61 (m, 1H), 5.56 – 5.40 (m, 1H), 4.77 (d, *J* = 6.6 Hz, 1H), 1.60 (d, *J* = 6.5 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.0, 141.4, 141.1, 135.6, 132.3, 132.2, 129.0, 128.9, 128.70, 128.68, 128.1, 127.0, 126.4, 124.6, 60.3, 17.6 ppm; **IR (neat):** 3728, 3061, 2360, 1490, 1446, 1246, 1139, 1093, 1069, 1024, 964, 914, 750, 727, 693, 594, 561, 499, 445, 422 cm^{-1}. **HRMS** calculated *m*/*z* for $C_{22}H_{22}NOS^+$ $[M+H]^+$: 348.1417, found (ESI) 348.1414.



(*E*)-{[4-(4-chlorophenyl)but-3-en-2-yl]imino}diphenyl-λ^6-sulfanone (**16ac**) and **(*E*)-{[1-(4-chlorophenyl)but-2-en-1-yl]imino)diphenyl-λ^6-sulfanone** (**16ac'**) were prepared from **1a** and (*E*)-1-(but-1-en-1-yl)-4-chlorobenzene (**15ac**) as white oils in 24 and 12% yield, respectively.

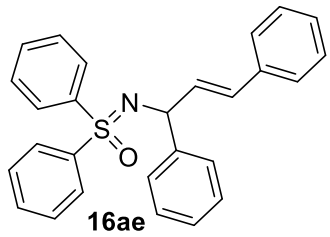
Compound 16ac: R_f = 0.18 (pentane/EtOAc, 8:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.10 – 7.84 (m, 4H), 7.60 – 7.37 (m, 6H), 7.29 – 7.07 (m, 4H), 6.41 (dd, *J* = 1.3, 15.8Hz, 1H), 6.27 (dd, *J* = 6.1, 15.7 Hz, 1H), 4.04 – 3.84 (m, 1H), 1.41 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 141.3, 141.0, 136.3, 136.0, 132.5, 132.38, 132.36, 129.1, 128.8, 128.5, 128.4, 127.6, 126.5, 52.3, 25.3 ppm; **IR (neat):** 2970, 1738, 1490, 1446, 1365, 1238, 1130, 1092, 1012, 998, 967, 813, 757, 727, 690, 598, 563, 440 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{22}H_{21}ClNOS^+$ $[M+H]^+$: 382.1027, found (ESI) 382.1018.

Compound 16ac': R_f = 0.19 (pentane/EtOAc, 8:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.01 – 7.95 (m, 2H), 7.89 – 7.81 (m, 2H), 7.53 – 7.42 (m, 4H), 7.41 – 7.36 (m, 2H), 7.35 – 7.30 (m, 2H), 7.25 – 7.19 (m, 2H), 5.68 – 5.57 (m, 1H), 5.53 – 5.44 (m, 1H), 4.72 (d, *J* = 6.6 Hz, 1H), 1.63 – 1.54 (m, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 143.6, 141.2, 141.0, 135.1, 132.4, 132.3, 132.1, 129.03, 128.99, 128.7, 128.6, 128.4, 128.2, 125.0, 59.6, 17.6 ppm; **IR (neat):** 3063, 1738, 1588, 1487, 1446, 1376, 1238, 1138, 1092, 1014, 999, 964, 815, 757, 728, 688, 596, 559, 543, 422 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{22}H_{21}ClNOS^+$ $[M+H]^+$: 382.1027, found (ESI) 382.1023.



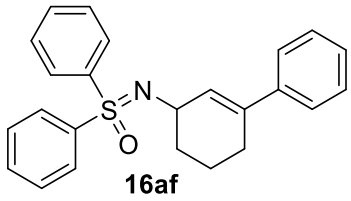
16ad

{[1-(4-Methoxyphenyl)allyl]imino}diphenyl-λ^6-sulfanone (**16ad**) was prepared from **1a** and 1-allyl-4-methoxybenzene (**15ad**) as a white oil (36% yield). R_f = 0.25 (pentane/EtOAc, 8:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.04 – 7.97 (m, 2H), 7.91 – 7.83 (m, 2H), 7.53 – 7.35 (m, 6H), 7.33 – 7.28 (m, 2H), 6.90 – 6.69 (m, 2H), 6.16 – 5.94 (m, 1H), 5.19 (dt, *J* = 1.6, 16.9Hz, 1H), 5.08 – 4.96 (m, 1H), 4.77 – 4.69 (m, 1H), 3.77 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.3, 142.6, 141.2, 141.0, 136.5, 132.4, 132.3, 128.99, 128.97, 128.7, 128.6, 128.1, 113.6, 113.1, 60.3, 55.2 ppm; **IR (neat):** 2835, 1739, 1608, 1508, 1445, 1238, 1172, 1139, 1092, 1068, 1034, 998, 915, 826, 758, 727, 693, 593, 435 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{22}H_{22}NO_2S^+$ $[M+H]^+$: 364.1366, found (ESI) 364.1360.



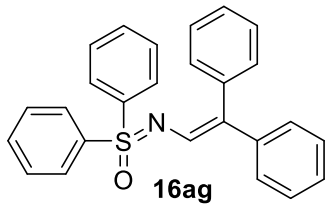
16ae

(*E*)-[(1,3-diphenylallyl)imino]diphenyl-λ^6-sulfanone (**16ae**) was prepared from **1a** and (*E*)-prop-1-ene-1,3-diyldibenzene (**15ae**) as a white solid (59% yield). R_f = 0.4 (pentane/EtOAc, 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.14 – 8.03 (m, 2H), 8.01 – 7.87 (m, 2H), 7.57 – 7.39 (m, 8H), 7.40 – 7.18 (m, 8H), 6.61 – 6.28 (m, 2H), 5.04 (d, *J* = 6.4 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 144.4, 141.3, 141.0, 137.3, 134.1, 132.41, 132.38, 129.1, 128.77, 128.75, 128.7, 128.4, 128.3, 127.2, 127.1, 126.7, 126.5, 60.5 ppm; **IR** (neat): 3058, 1599, 1491,1445, 1239, 1134, 1091, 1067, 1023, 998, 963, 927, 743, 725, 688, 585, 556 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{27}H_{24}NOS^+$ $[M+H]^+$: 410.1573, found (ESI) 410.1575.

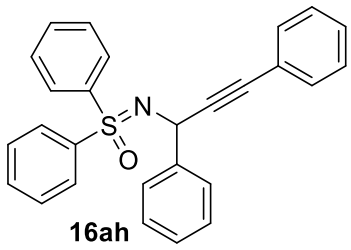


16af

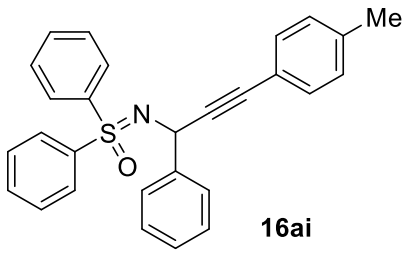
Diphenyl{(3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-yl)imino}-λ^6-sulfanone (**16af**) was prepared from **1a** and 2,3,4,5-tetrahydro-1,1'-biphenyl (**15af**) as a white oil (44% yield). R_f = 0.25 (pentane/EtOAc, 8:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.06 – 7.95 (m, 4H), 7.56 – 7.42 (m, 6H), 7.40 – 7.34 (m, 2H), 7.30 – 7.25 (m, 2H), 7.22 – 7.14 (m, 1H), 6.33 – 5.85 (m, 1H), 3.99 – 3.80 (m, 1H), 2.49 – 2.39 (m, 1H), 2.35 – 2.26 (m, 1H), 2.03 – 1.94 (m, 2H), 1.86 – 1.78 (m, 1H), 1.70 – 1.60 (m, 1H) ppm; **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 142.0, 141.33, 141.28, 137.5, 132.3, 129.6, 129.1, 129.0, 128.64, 128.57, 128.0, 126.8, 125.4, 51.2, 33.0, 27.1, 21.0 ppm; **IR (neat):** 3058, 2928, 2857, 1712, 1597, 1494, 1474, 1444, 1354, 1306, 1231, 1128, 1092, 1068, 1023, 997, 942, 903, 815, 754, 725, 687, 599, 572, 556 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{24}H_{24}NOS^+$ $[M+H]^+$: 374.1573, found (ESI) 374.1573.



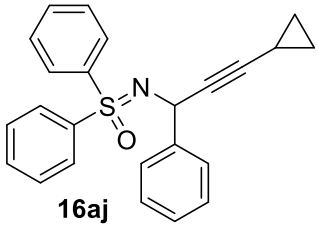
[(2,2-Diphenylvinyl)imino]diphenyl-λ^6-sulfanone (**16ag**) was prepared from **1a** and 1,1-diphenylethene (**15ag**) as a yellow solid (55% yield). R_f = 0.3 (pentane/EtOAc, 8:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.02 – 7.93 (m, 4H), 7.71 – 7.64 (m, 2H), 7.60 – 7.41 (m, 8H), 7.36 – 7.13 (m, 6H), 6.91 (s, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 142.6, 140.6, 139.6, 132.9, 130.71, 129.5, 129.4, 128.5, 128.0, 127.9, 127.7, 127,0, 126.3, 126.0 ppm; **IR** (neat): 3057, 1595, 1495, 1475 ,1444, 1242, 1194, 1134, 1086, 1027, 984, 917, 885, 756, 738, 723, 696, 603, 547 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{26}H_{21}NNaOS^+$ $[M+Na]^+$: 418.1236, found (ESI) 418.1234.



[(1,3-Diphenylprop-2-yn-1-yl)imino]diphenyl-λ^6-sulfanone (**16ah**) was prepared from **1a** and prop-1-yne-1,3-diyldibenzene (**15ah**) as a pale-yellow oil (32% yield). R_f = 0.2 (pentane/EtOAc, 8:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.12 – 8.06 (m, 2H), 8.03 – 7.96 (m, 2H), 7.71 – 7.62 (m, 2H), 7.52 – 7.40 (m, 6H), 7.37 – 7.29 (m, 4H), 7.27 – 7.19 (m, 4H), 5.43 (s, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 142.18, 140.97, 140.86, 132.52, 132.50, 131.65, 129.07, 129.06, 128.35, 128.32, 128.01, 127.88, 127.20, 127.19, 123.35, 90.75, 84.39, 49.21 ppm; **IR** (neat): 3061, 1490, 1446, 1234, 1132, 1093, 1069, 1025, 757, 726, 691, 593, 561 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{27}H_{22}NOS^+$ $[M+H]^+$: 408.1417, found (ESI) 408.1417.

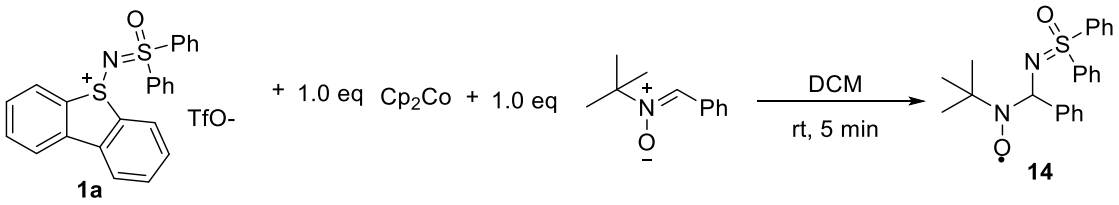


Diphenyl{[1-phenyl-3-(p-tolyl)prop-2-yn-1-yl]imino}-λ^6-sulfanone (**16ai**) was prepared from **1a** and 1-methyl-4-(3-phenylprop-1-yn-1-yl)benzene (**15ai**) as a pale-yellow oil (60% yield). R_f = 0.19 (pentane/EtOAc, 8:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.20 – 7.99 (m, 4H), 7.77 – 7.69 (m, 2H), 7.57 – 7.44 (m, 6H), 7.43 – 7.35 (m, 2H), 7.33 – 7.20 (m, 3H), 7.14 – 7.02 (m, 2H), 5.50 (s, 1H), 2.36 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 142.4, 141.1, 141.0, 137.9, 132.6, 132.5, 131.6, 129.12, 129.10, 128.8, 128.4, 128.3, 127.3, 127.2, 120.3, 90.1, 84.6, 49.3, 21.5 ppm; **IR** (neat): 3060, 1637, 1509, 1492, 1446, 1310, 1270, 1232, 1132, 1093, 1068, 1023, 999, 818, 762, 757, 755, 747, 727, 688, 592, 564 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{28}H_{23}NNaOS^+$ $[M+Na]^+$: 444.1393, found (ESI) 444.1387.

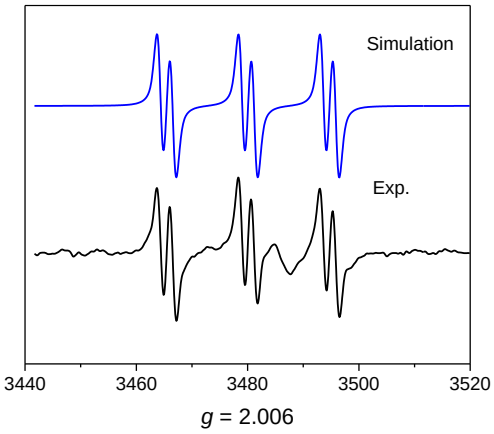


[(3-Cyclopropyl-1-phenylprop-2-yn-1-yl)imino]diphenyl-λ⁶-sulfanone (**16aj**) was prepared from **1a** and (3-cyclopropylprop-2-yn-1-yl)benzene (**15aj**) as a pale-yellow oil (59% yield). R_f = 0.17 (pentane/EtOAc, 8:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 – 8.05 (m, 2H), 8.03 – 7.94 (m, 2H), 7.61 (dd, *J* = 1.8, 7.4Hz, 2H), 7.58 – 7.40 (m, 6H), 7.38 – 7.31 (m, 2H), 7.30 – 7.22 (m, 1H), 5.21 (d, *J* = 1.7 Hz, 1H), 1.29 – 1.09 (m, 1H), 0.75 – 0.64 (m, 2H), 0.62 – 0.49 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 142.8, 141.3, 141.0, 132.43, 132.39, 129.02, 128.97, 128.4, 128.2, 127.1, 127.0, 87.8, 76.6, 48.9, 8.05, 8.03, –0.3 ppm; **IR** (neat): 3060, 2246, 1635, 1491, 1474, 1445, 1356, 1309, 1270, 1229, 1127, 1092, 1067, 1023, 998, 887, 836, 762, 757, 746, 724, 686, 634, 590, 560 cm^{-1}; **HRMS** calculated *m*/*z* for $C_{24}H_{21}NNaOS^+$ $[M+Na]^+$: 394.1236, found (ESI) 394.1227.

2.12 EPR studies



In a dried Schlenk tube, **1a** (27.5 mg, 0.05 mmol, 1.0 equiv.) and Cp_2Co (9.5 mg, 0.05 mmol, 1.0 equiv.) were dissolved in DCM (2.0 mL) under N_2 atmosphere, and the mixture was stirred for 5 minutes. Then (*Z*)-*N*-tert-butyl-1-phenylmethanimine oxide (8.9 mg, 0.05 mmol, 1.0 equiv.) was added. The reaction mixture was analyzed by electron paramagnetic resonance (EPR). EPR spectra were recorded at room temperature on a Bruker E500-10/12.



3 Stern-Volmer Fluorescence Quenching Studies.

3.1 Stern-Volmer Quenching Studies with 3a

The measurements were carried out mixing a $1 \cdot 10^{-4}$ M solution of $Ru(bpy)_3(PF_6)_2$ in MeCN (1 mL) with the appropriate amount of quencher in a quartz cuvette equipped with a septum under nitrogen atmosphere. The samples were previously degassed with nitrogen for 10 minutes. All solutions

were irradiated at λ = 452 nm (absorption maximum of $Ru(bpy)_3(PF_6)_2$). Plots were constructed according to the SternVolmer equation and K_{sv} were calculated.[9]

Stern-Volmer equation $I_0/I = 1 + K_{SV}[Q]$

The emission of $Ru(bpy)_3(PF_6)_2$ was measured with varying amounts of **3a** (0.00, 0.05, 0.10, 0.15 M solutions in MeCN). As shown in Figure 1, the emission intensity decreased with increasing amounts of **3a**, providing evidence for the direct substrate reduction by photoexcited $Ru(bpy)_3(PF_6)_2$*.

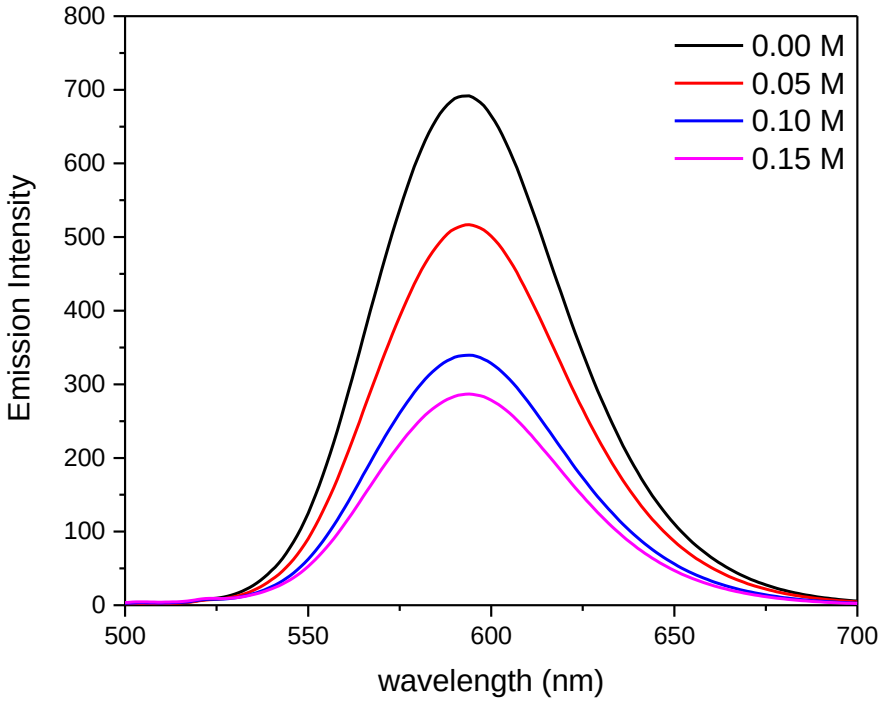


Figure 1. Emission spectrum of $Ru(bpy)_3(PF_6)_2$* varying concentration of **3a**.

The Stern-Volmer plot reported in Figure 2 shows a linear correlation between the amounts of **3a** and the ratio I_0/I with a constant K_{sv} of 9.872 M^{-1}.

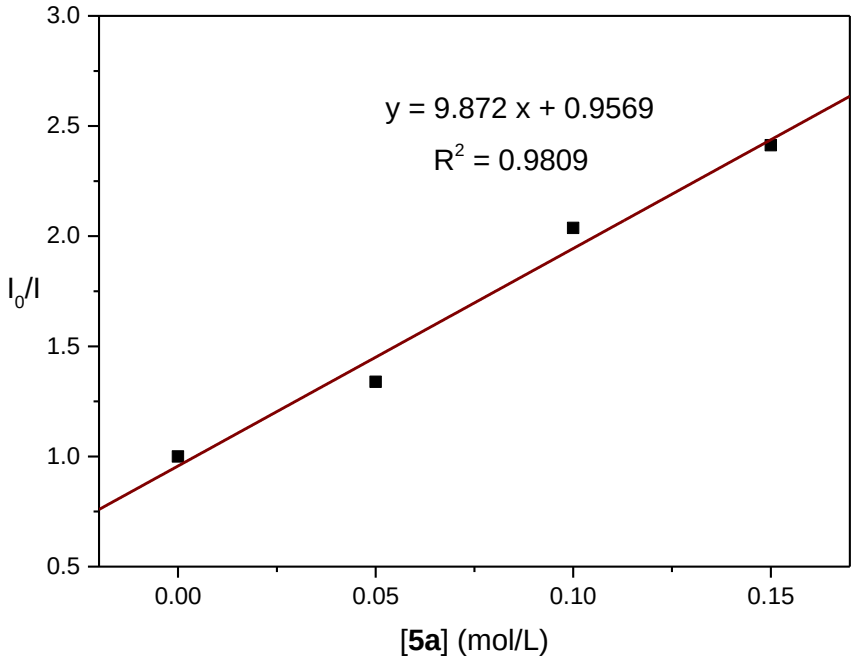


Figure 2. Stern-Volmer plot of $Ru(bpy)_3(PF_6)_2$ quenching with varying concentration of **3a**.

3.2 Stern-Volmer Quenching Studies with 1a

Fluorescence quenching experiments were performed on Fluorescence Spectrophotometer. The measurements were carried out mixing a $2 \cdot 10^{-4}$ M solution of $Ru(bpy)_3(PF_6)_2$ in MeCN (1 mL) with the appropriate amount of quencher in a quartz cuvette equipped with a septum under nitrogen atmosphere. The samples were previously degassed with nitrogen for 10 minutes. All solutions were irradiated at $\lambda = 452$ nm (absorption maximum of $Ru(bpy)_3(PF_6)_2$) and the emission intensity at 593 nm was observed (emission maximum). Plots were constructed according to the Stern-Volmer equation and KSV were calculated.

Stern-Volmer equation $I_0/I = 1 + K_{SV}[Q]$

The emission of $Ru(bpy)_3(PF_6)_2$ was measured with varying amounts of dibenzothiophenium salt, **1a** (0.00, 0.01, 0.02 & 0.04 M solutions in MeCN). As shown in Figure S3, the emission intensity decreased with increasing amounts of **1a**, providing evidence for the direct substrate reduction by photoexcited $[Ru(bpy)_3^{2+}]^*$.

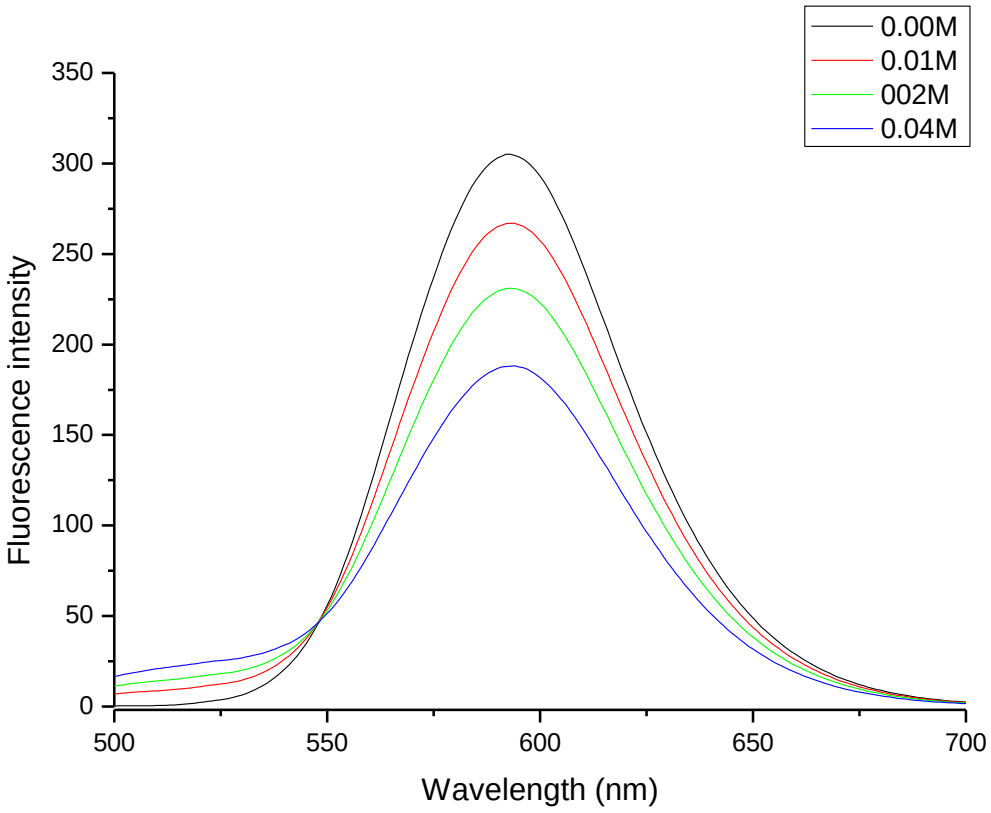


Figure S3. Emission spectrum of $[Ru(bpy)_3^{2+}]$*varying concentration of **1a**.

The Stern-Volmer plot reported in Figure S4 shows a linear correlation between the amounts of **1a** and the ratio I_0/I with a constant K_{SV} of 15.69576 M^{-1}.

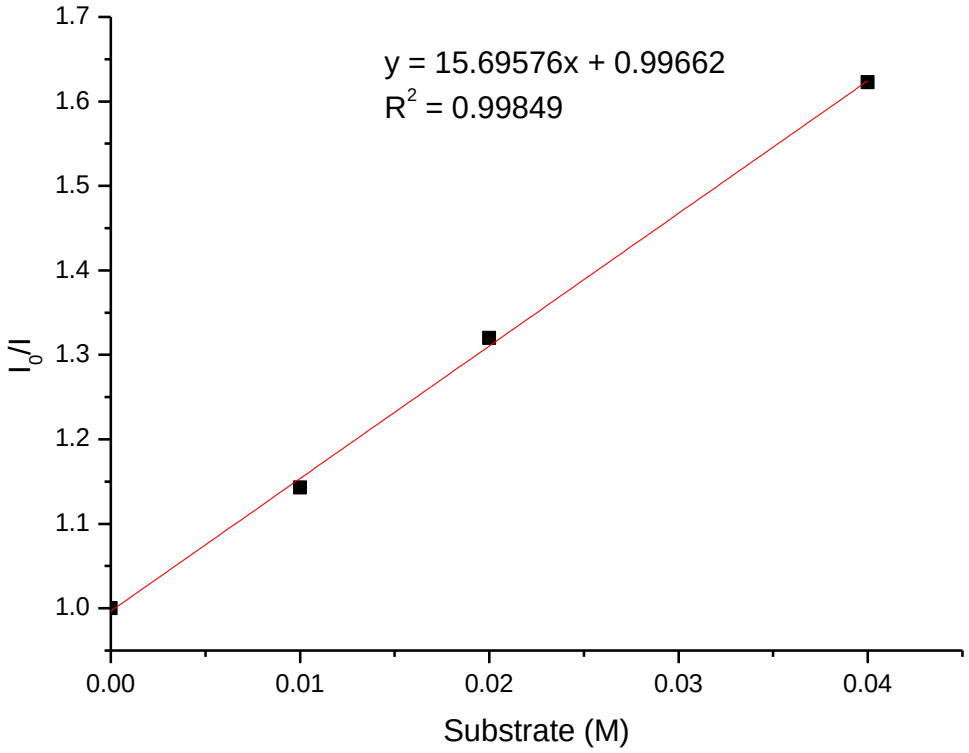


Figure S4. Stern-Volmer plot of $Ru(bpy)_3(PF_6)_2$ quenching with varying concentration of **1a**.

4 Cyclic voltammetry measurements.

4.1 Measurements of 3a, 3d-f

Cyclic voltammetry was conducted on an EmStat (PalmSens) potentiostat using a 3-electrode cell configuration. A glassy carbon working electrode was employed alongside a platinum wire counter electrode and a Ag/AgCl reference electrode. All the solutions were degassed by bubbling N_2 prior to measurements. 0.15 M of tetrabutylammonium hexafluorophosphate in dry DMSO as supporting electrolyte and were examined at a scan rate of 0.3 V s^{-1}. Ferrocene ($E_{1/2}$ = +0.435 V vs SCE)[10] was added at the end of the measurements as an internal standard to determine the precise potential scale. Potential values are given versus the saturated calomel electrode (SCE). Irreversible reduction waves were obtained in all cases; therefore, the reduction potentials were obtained from the maximum, $E_p$max.

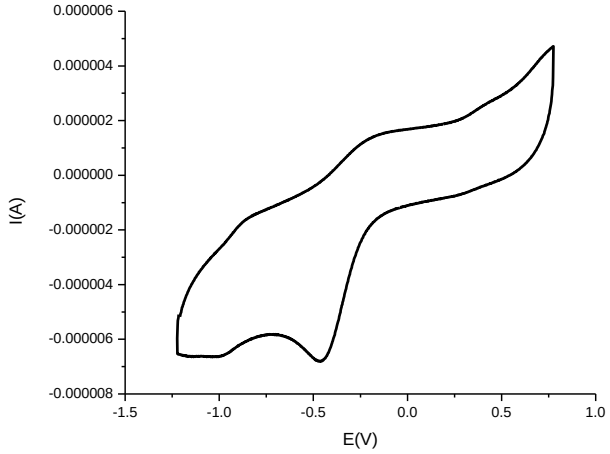


Figure 5. Cyclic voltammogram of **3a**

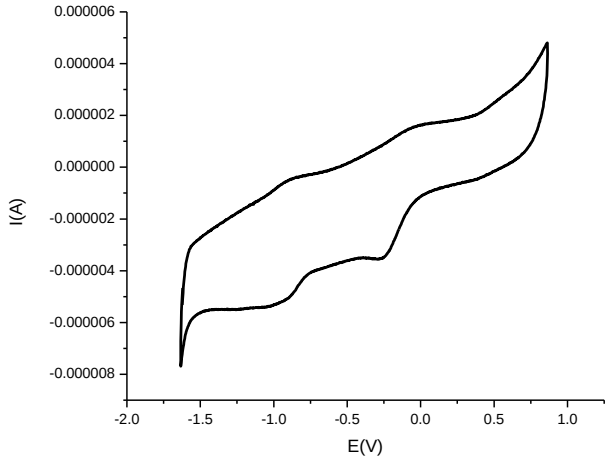


Figure 6. Cyclic voltammogram of **3d**

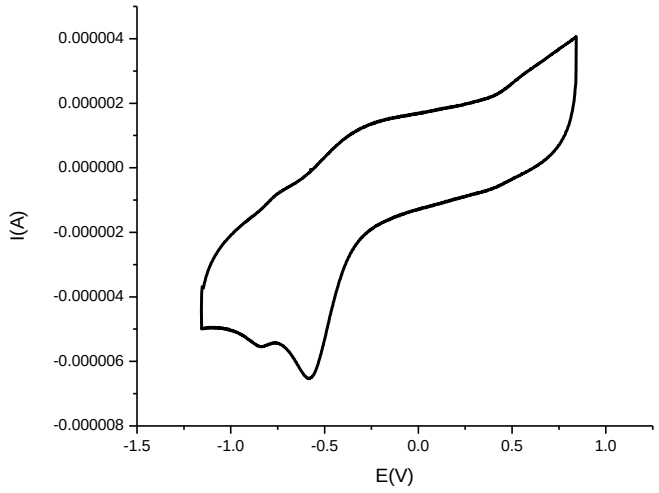


Figure S7. Cyclic voltammogram of **3e**

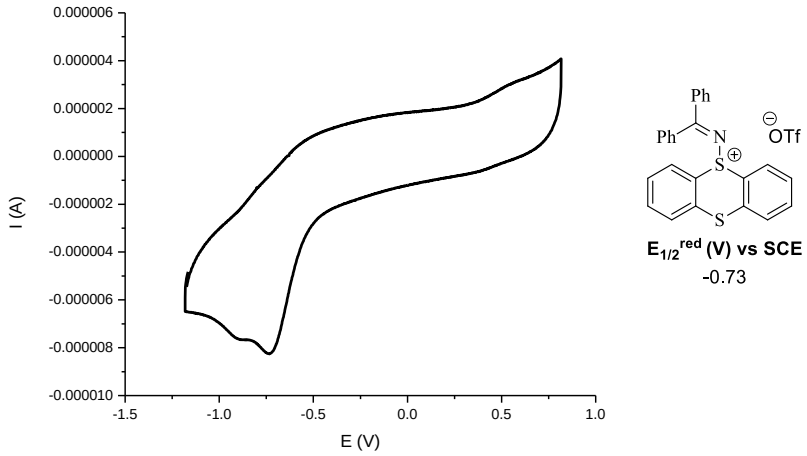


Figure S8. Cyclic voltammogram of **3f**

4.2 Measurements of 1a, 1b, 1c

Cyclic voltammetry was conducted on a potentiostat using a 3-electrode cell configuration. A carbon working electrode, a platinum counter electrode and an Au reference electrode. All the solutions were degassed by bubbling N_2 prior to measurements. A 0.2 M of tetrabutylammonium hexafluorophosphate in MeCN as supporting electrolyte and were examined at a scan rate of 0.2V/s. Ferrocene ($E_{(Fc/Fc+)}^{0}$ =0.424 V vs SCE) [11,12] was added at the end of the measurements as an internal standard to determine the precise potential scale. The reduction potential values are given versus the Ferrocene.

Irreversible reduction waves were obtained in all cases. The excited state of $[Ru(bpy)_3]^{2+}$ with $E_{½}^{red*} = -0.81$ V versus saturated calomel electrode (SCE) [13,14].

Figure S9. Cyclic voltammogram of **1a** ($E_{½} = -0.462$ V vs. SCE)

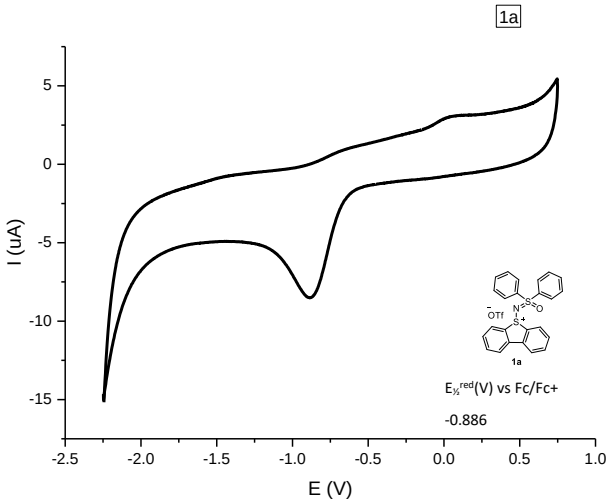


Figure S10. Cyclic voltammogram of **1b** ($E_{½}$ = − 0.606 V vs. SCE)

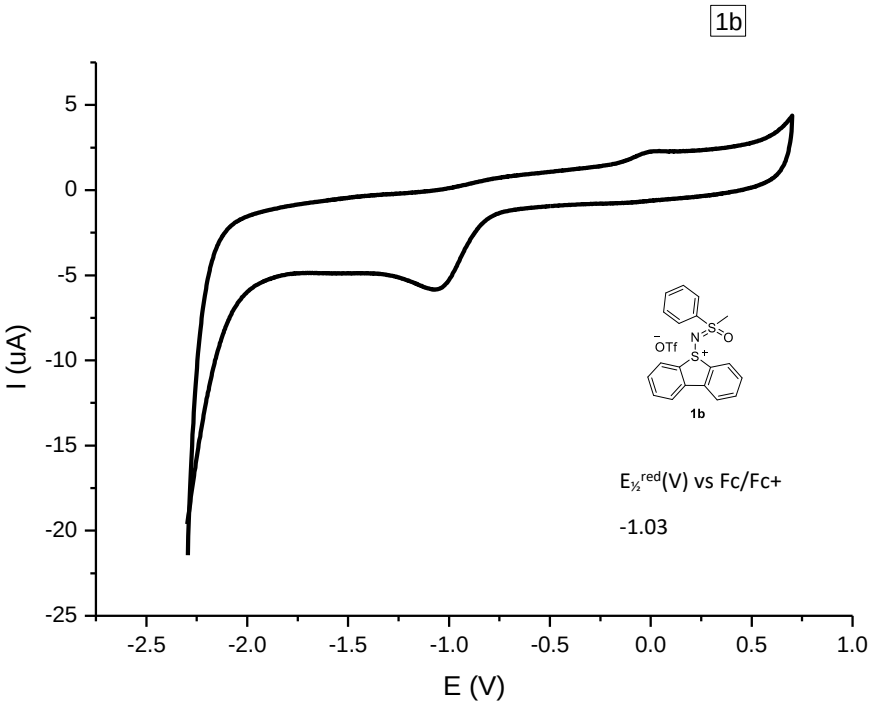
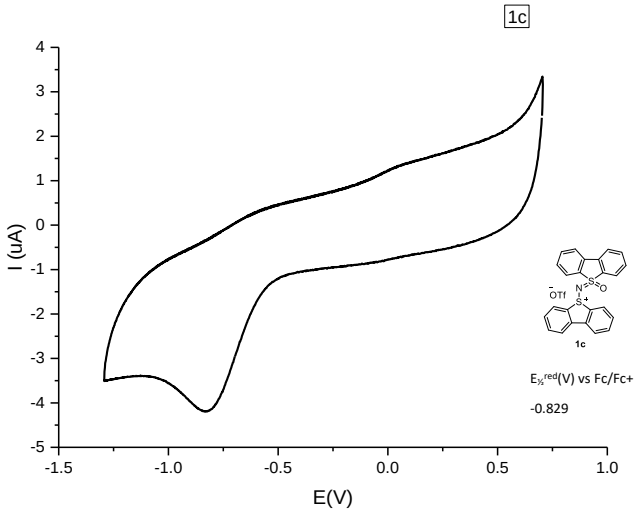
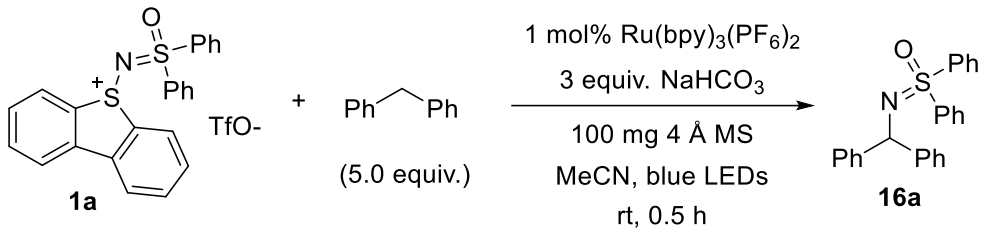


Figure S11. Cyclic voltammogram of **1c** ($E_{½}$ = − 0.405 V vs. SCE)



5 Determination of the quantum yield of the transformation



To a 10 mL oven-dried Schlenk tube equipped with a stirring bar was added $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv), 4 Å molecular sieve (100 mg), **1a** (110 mg, 0.2 mmol, 1.0 equiv) and diphenylmethane (167 μL, 1.0 mmol, 5.0 equiv). The Schlenk tube was then evacuated and backfilled with N_2 three times; CH_2Br_2 (0.2 mmol, 14.0 μL, 1.0 equiv) and acetonitrile (4 mL) were added under N_2. The tube was positioned 5 cm from a single PR160L-440 nm Kessil LED lamp (λ_{max} = 440 nm, 25% of the maximum intensity). The reaction was stirred at 500 rpm and approximate 0.1 mL reaction mixture was taken by a syringe after 30 minutes, which was diluted with $CDCl_3$, and comparison of the integration of the internal standard CH_2Br_2 (4.97 ppm, s, 2H) with that of the formed product (5.41 ppm, s, 1H) revealed yields of **16a** in 24%.

The quantum yield (Φ) was then calculated using:

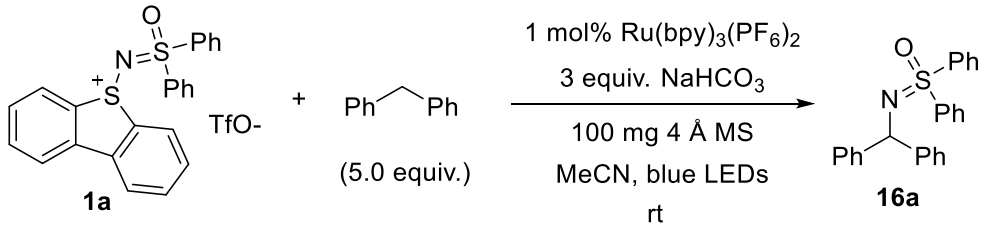
$$\Phi = \frac{moles\ of\ product}{photon\ flux \cdot t \cdot f}$$

where flux is the photon flux determined by ferrioxalate actinometry (6.07×10^{-7} Einstein/s),[14] *t* is the time, and *f* is the fraction of light absorbed by $Ru(bpy)_3(PF_6)_2$ at 440 nm.
A 1.0×10^{-4} M solution of $Ru(bpy)_3(PF_6)_2$ in acetonitrile was prepared, and the absorbance of the solution at 440 nm was 2.168. The fraction of light absorbed at 440 nm was calculated:

$$f = 1 - 10^{-A} = 0.9932$$

The quantum yield Φ is 0.044.

6 Light on/off experiment



To a 10 mL oven-dried Schlenk tube equipped with a stirring bar was added $Ru(bpy)_3(PF_6)_2$ (1.7 mg, 0.002 mmol, 1 mol%), $NaHCO_3$ (50.4 mg, 0.6 mmol, 3.0 equiv), 4 Å molecular sieve (100 mg), **1a** (110 mg, 0.2 mmol, 1.0 equiv) and diphenylmethane (167 μL, 1.0 mmol, 5.0 equiv). The Schlenk tube was then evacuated and backfilled with N_2 three times after which CH_2Br_2 (0.2 mmol, 14.0 μL, 1.0 equiv) and CD_3CN (4 mL) were added under N_2. Then, the reaction tube was placed in a photoreactor equipped with blue LED strips (wavelength range: 430-435 nm, 12 W). A mini-

fan was kept on top to maintain room temperature. The reaction mixture was stirred at room temperature, and the light was turned on and off every 15 minutes. During each on/off shift, approximate 0.4 mL reaction mixture was taken by a syringe, which was directly transferred into an NMR tube over a syringe filter (additional CD_3CN was added if it is necessary). Comparison of the integration of the internal standard CH_2Br_2 (5.09 ppm, s, 2H) with that of the formed product (5.41 ppm, s, 1H) revealed yields of **16a** (Figure S12).

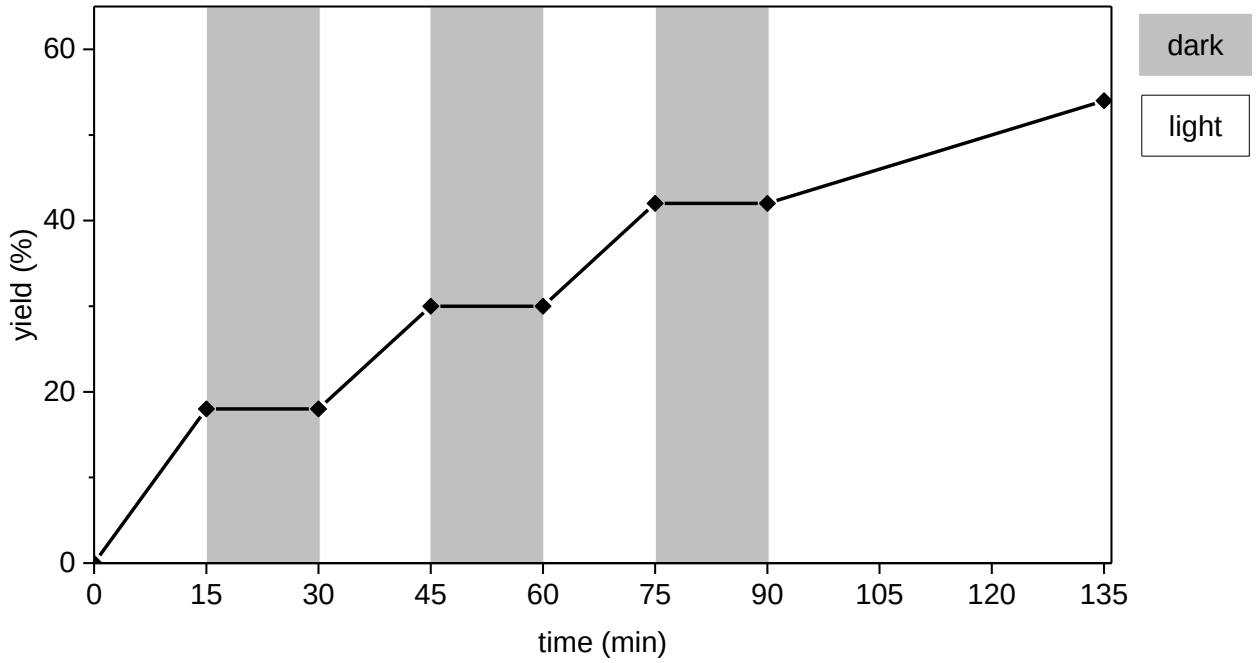
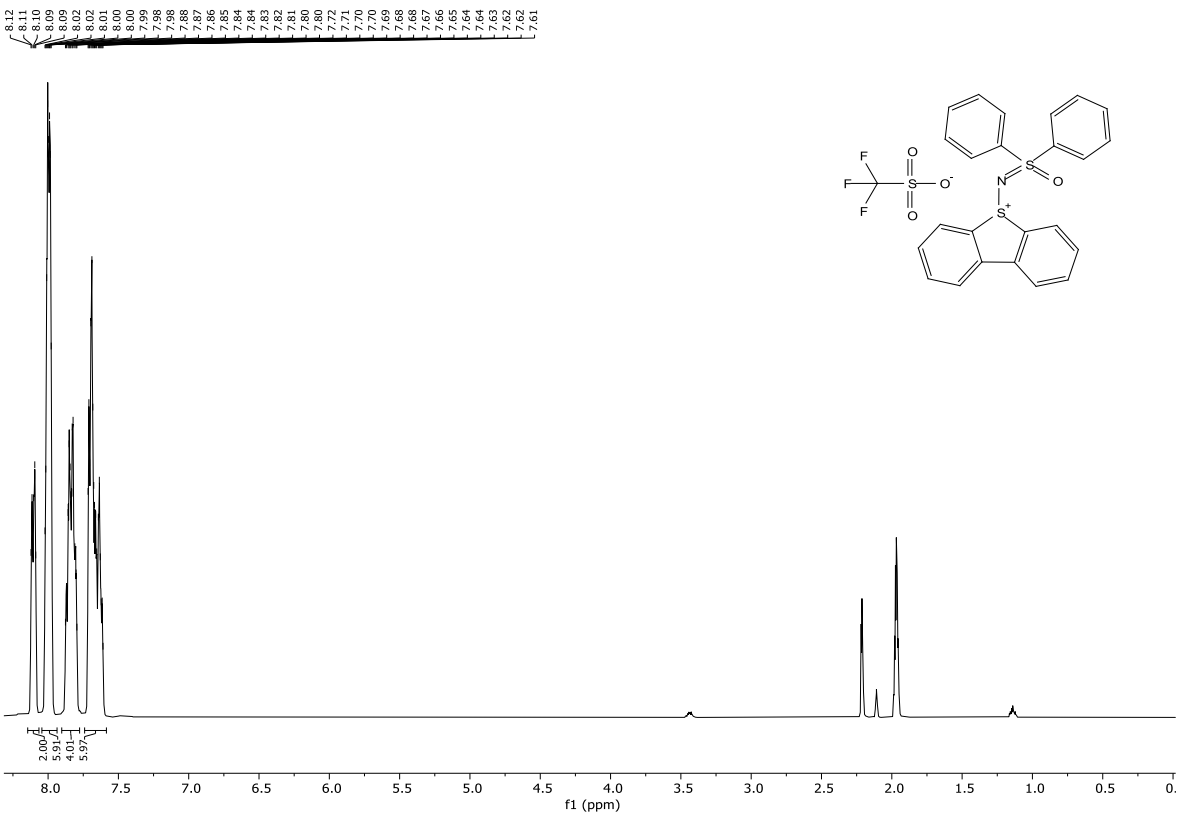


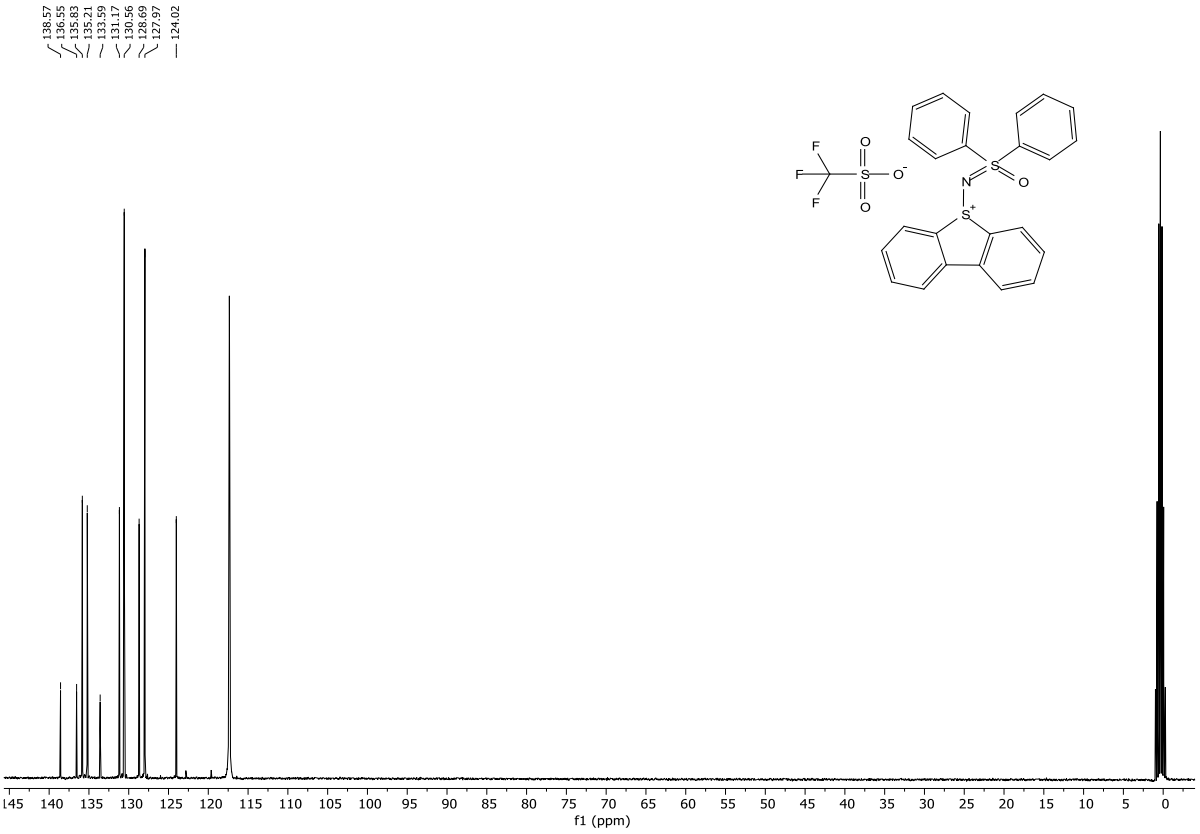
Figure S12. Time profile of the reaction with and without light

7 NMR spectra

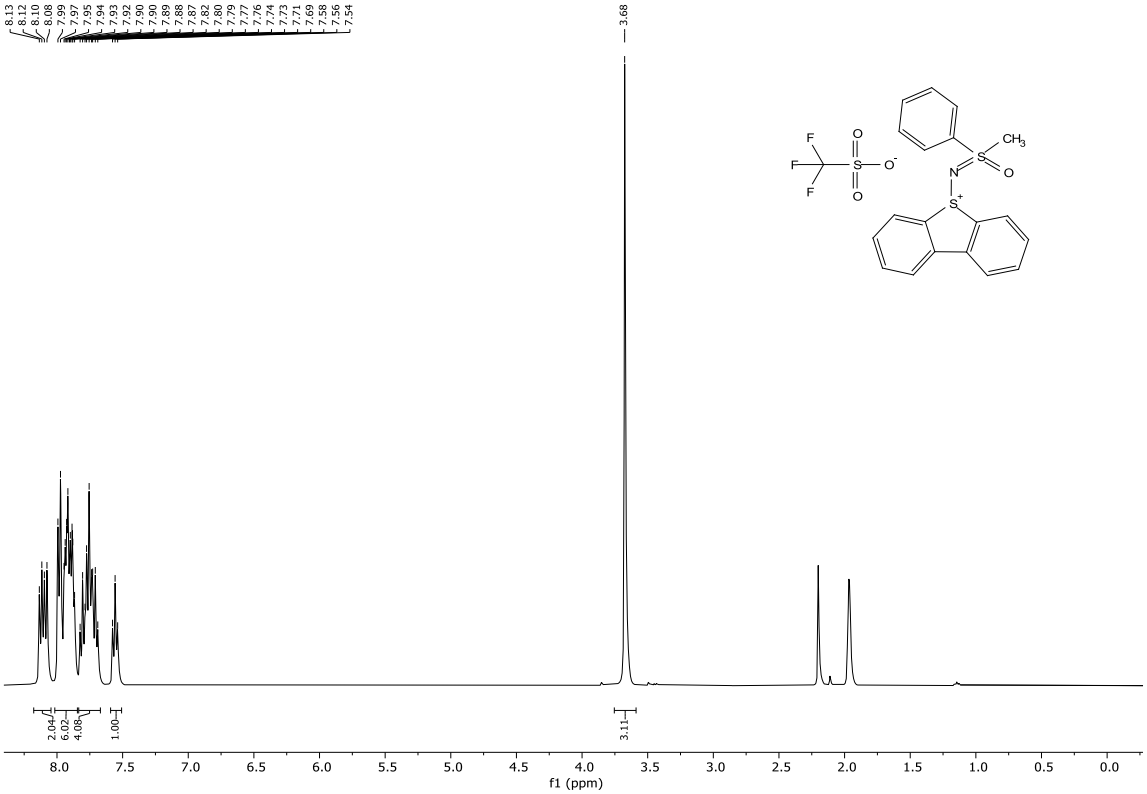
^{1}H NMR (400 MHz, CD_3CN) of **1a**



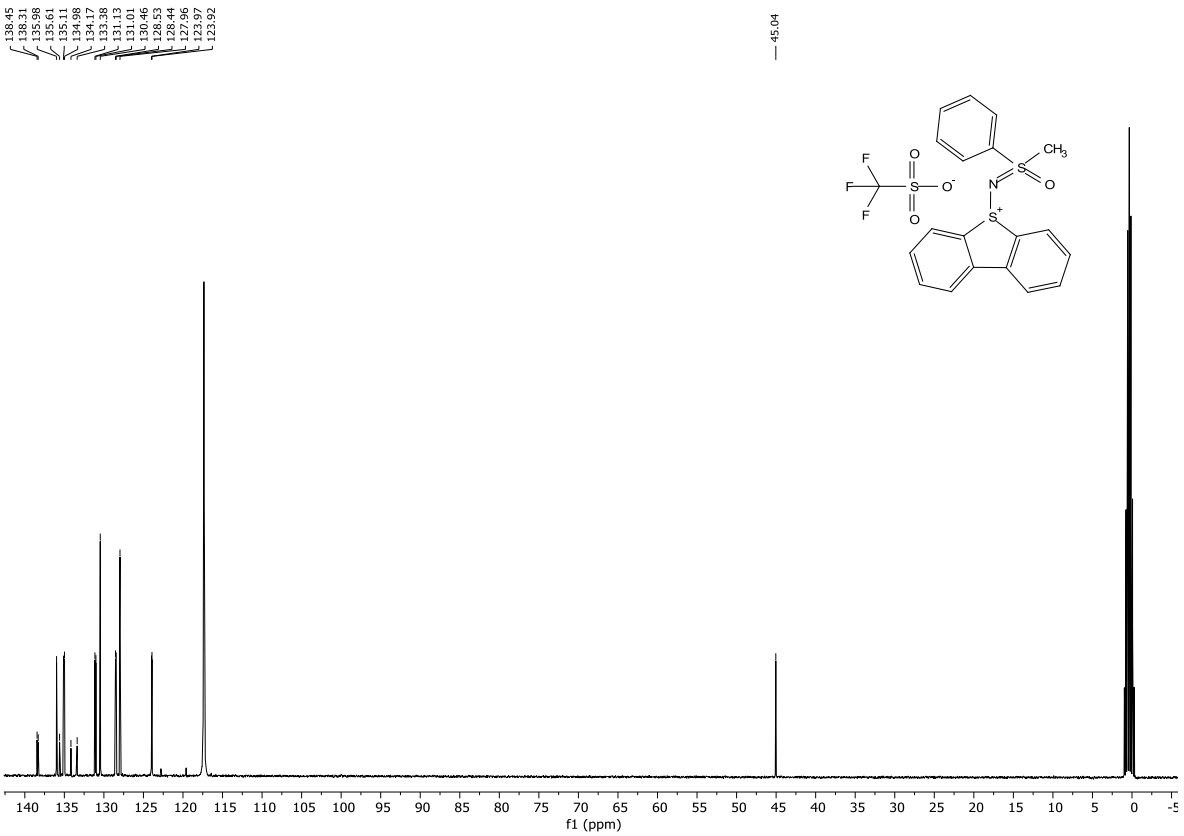
^{13}C NMR (100 MHz, CD_3CN) of **1a**



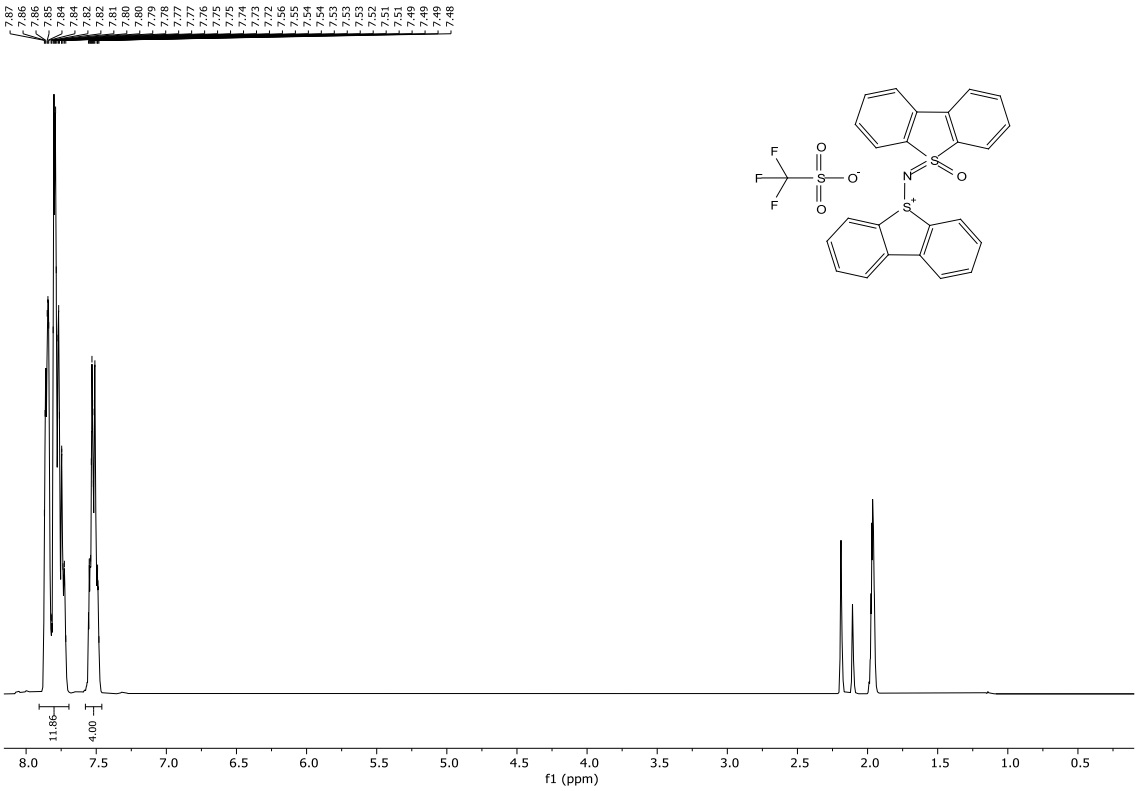
^{1}H NMR (400 MHz, CD_3CN) of **1b**



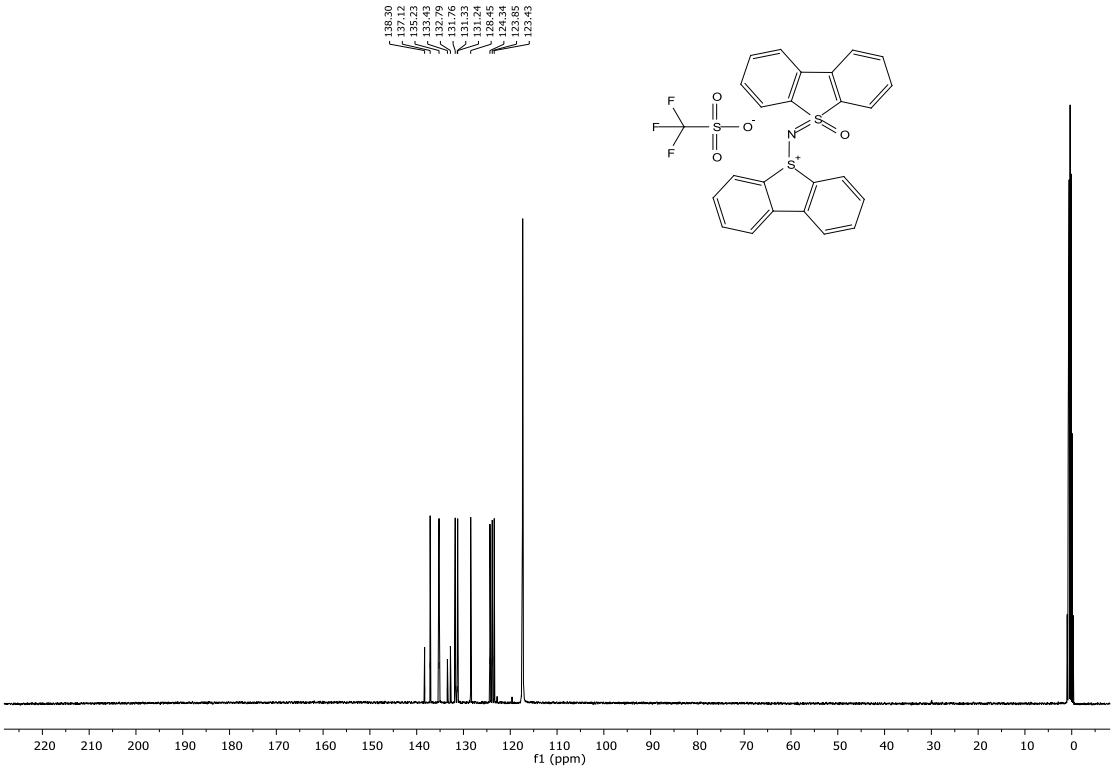
^{13}C NMR (100 MHz, CD_3CN) of **1b**



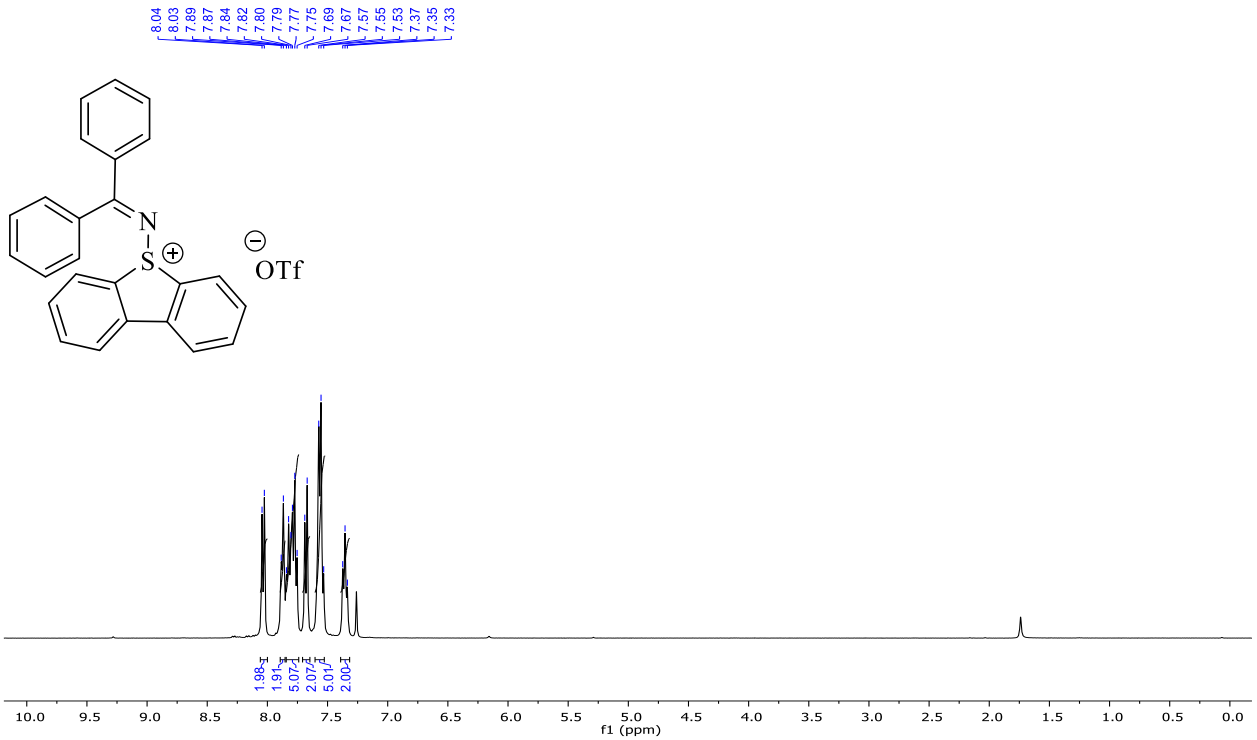
^{1}H NMR (400 MHz, CD_3CN) of **1c**



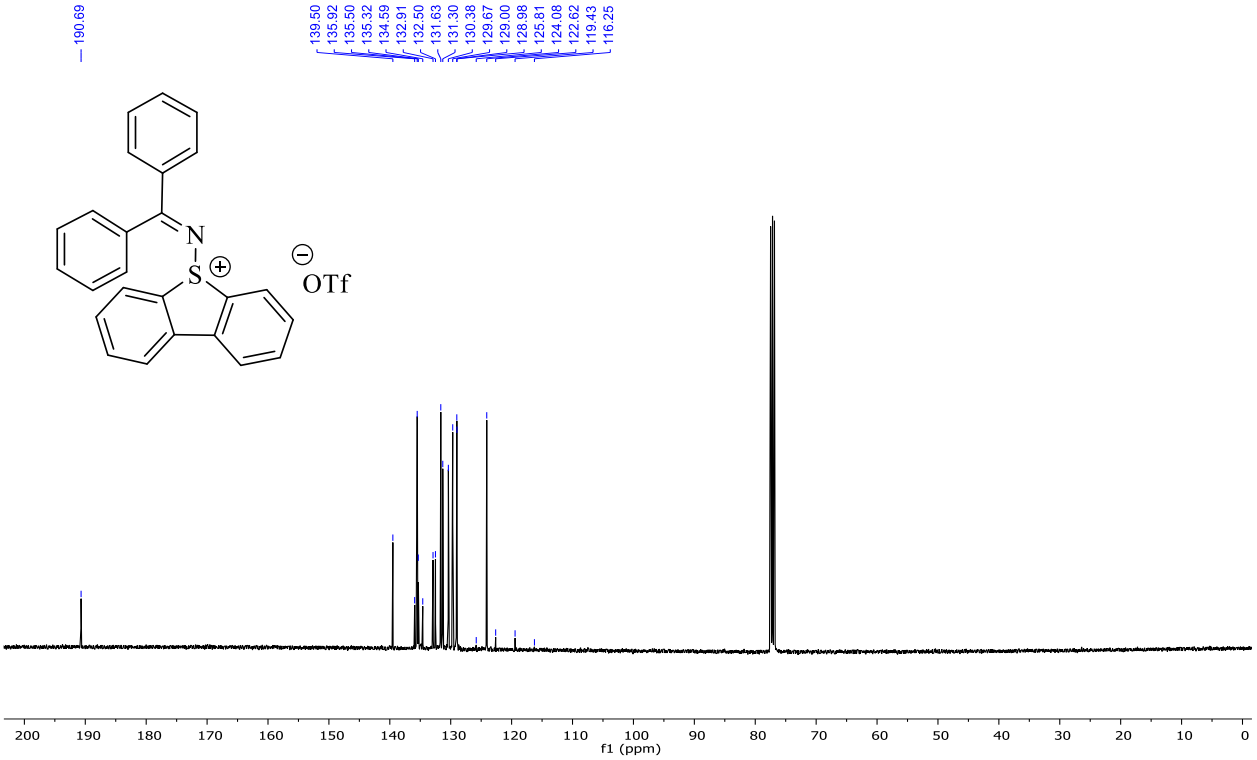
^{13}C NMR (400 MHz, CD_3CN) of **1c**



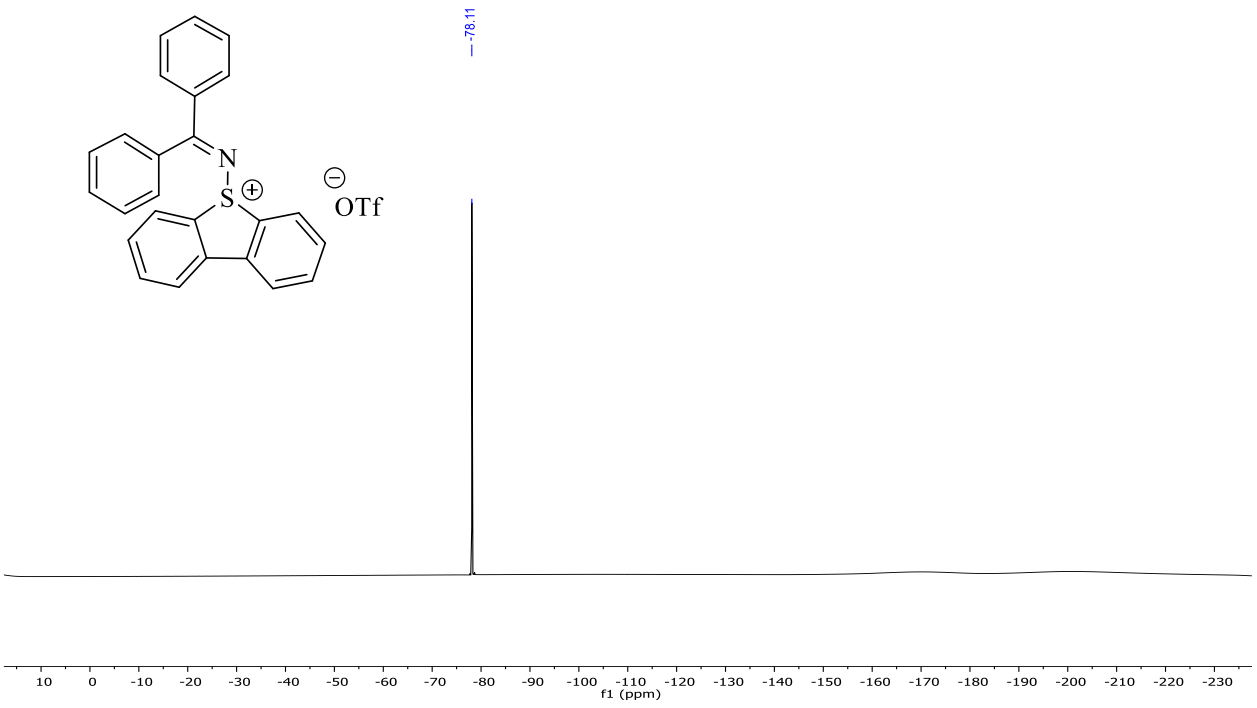
^{1}H NMR (400 MHz, $CDCl_3$) of **3a**



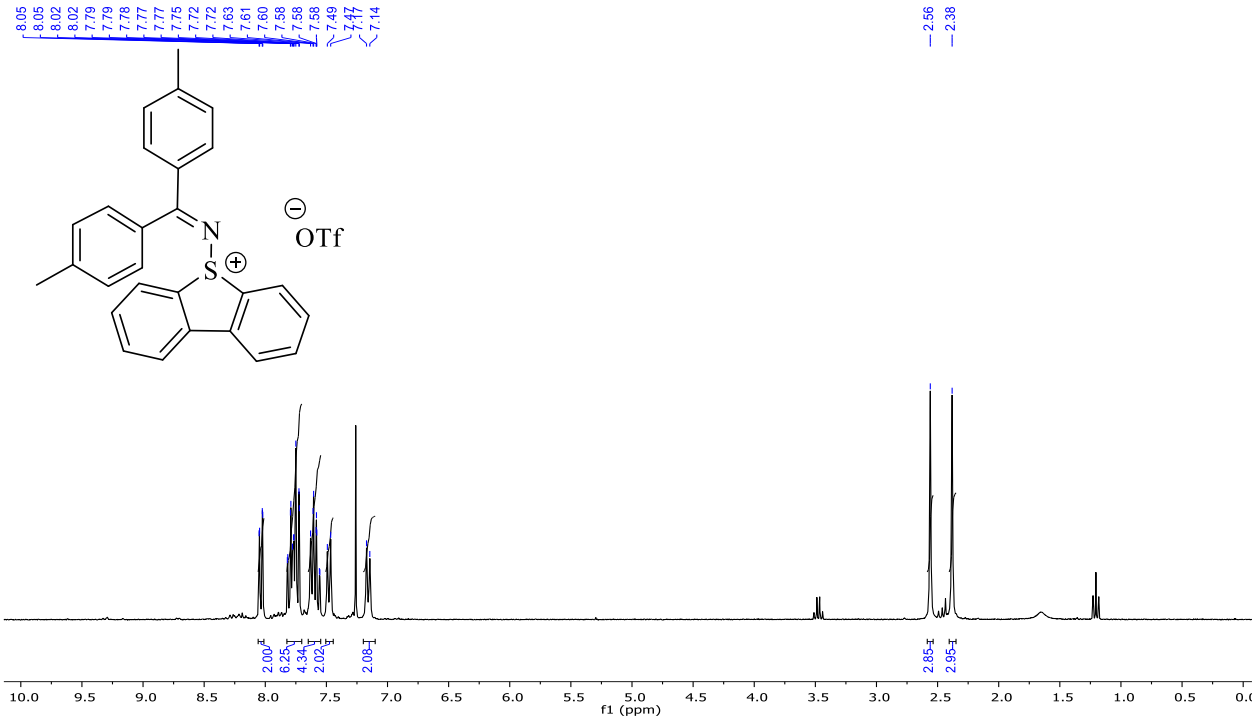
^{13}C NMR (101 MHz, $CDCl_3$) of **3a**



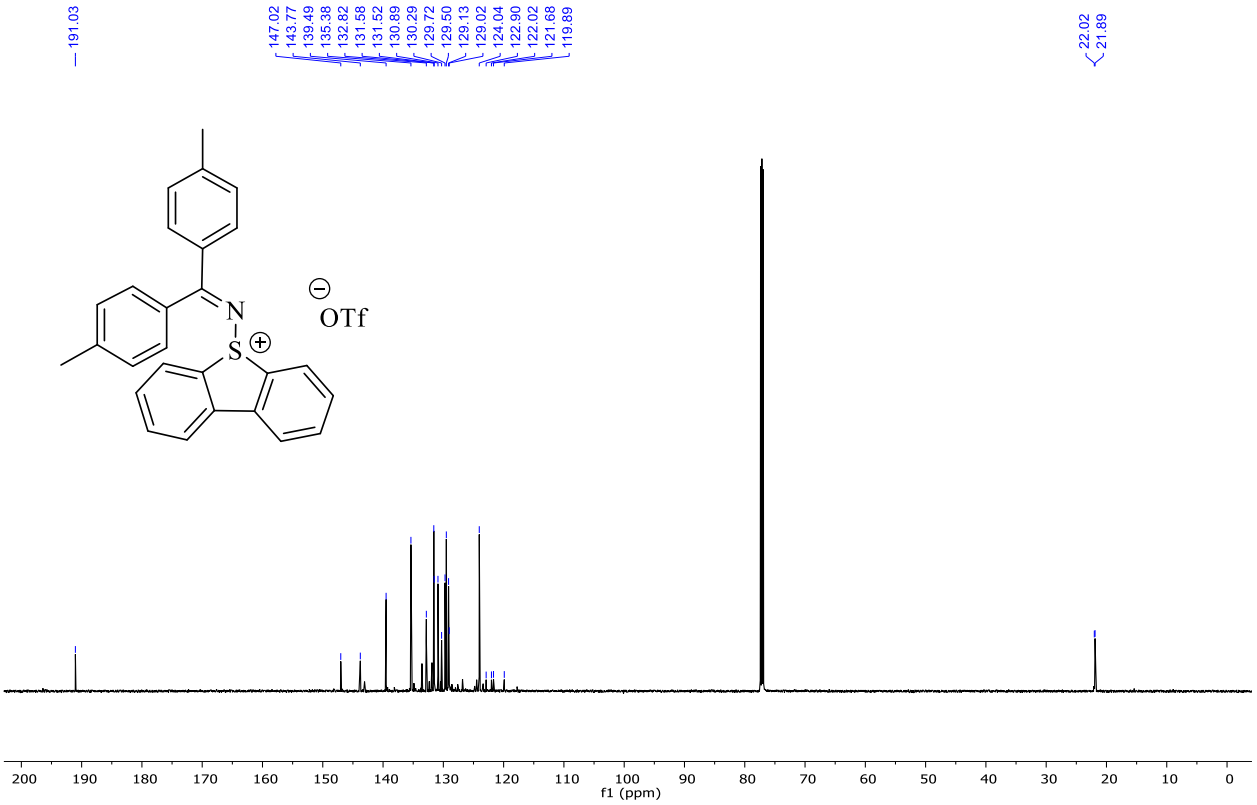
^{19}F NMR (377 MHz, $CDCl_3$) of **3a**



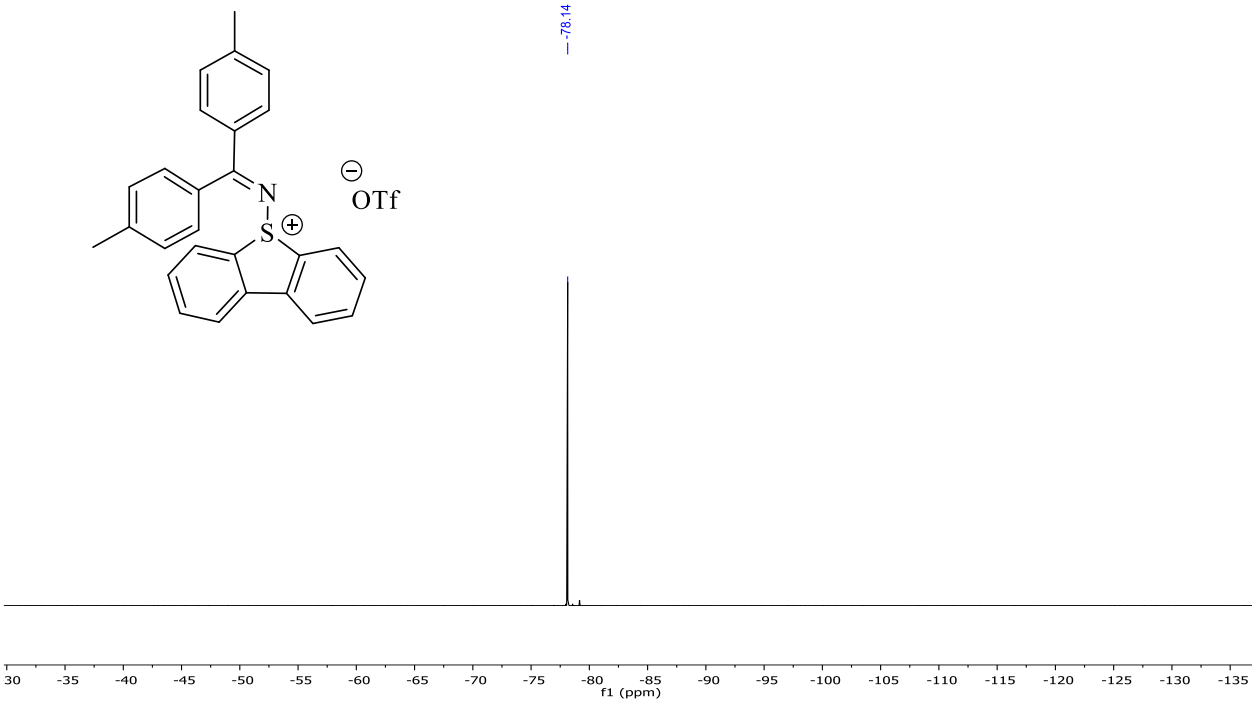
^{1}H NMR (300 MHz, $CDCl_3$) of **3b**



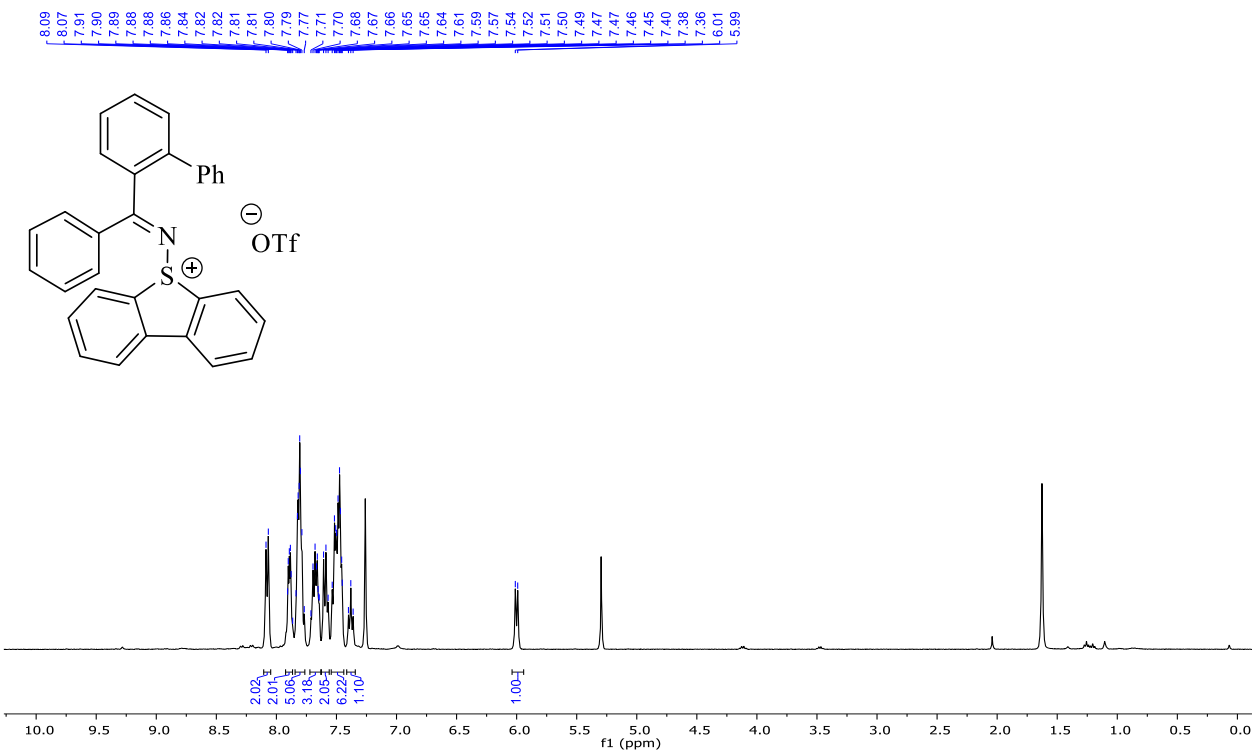
^{13}C NMR (151 MHz, $CDCl_3$) of **3b**



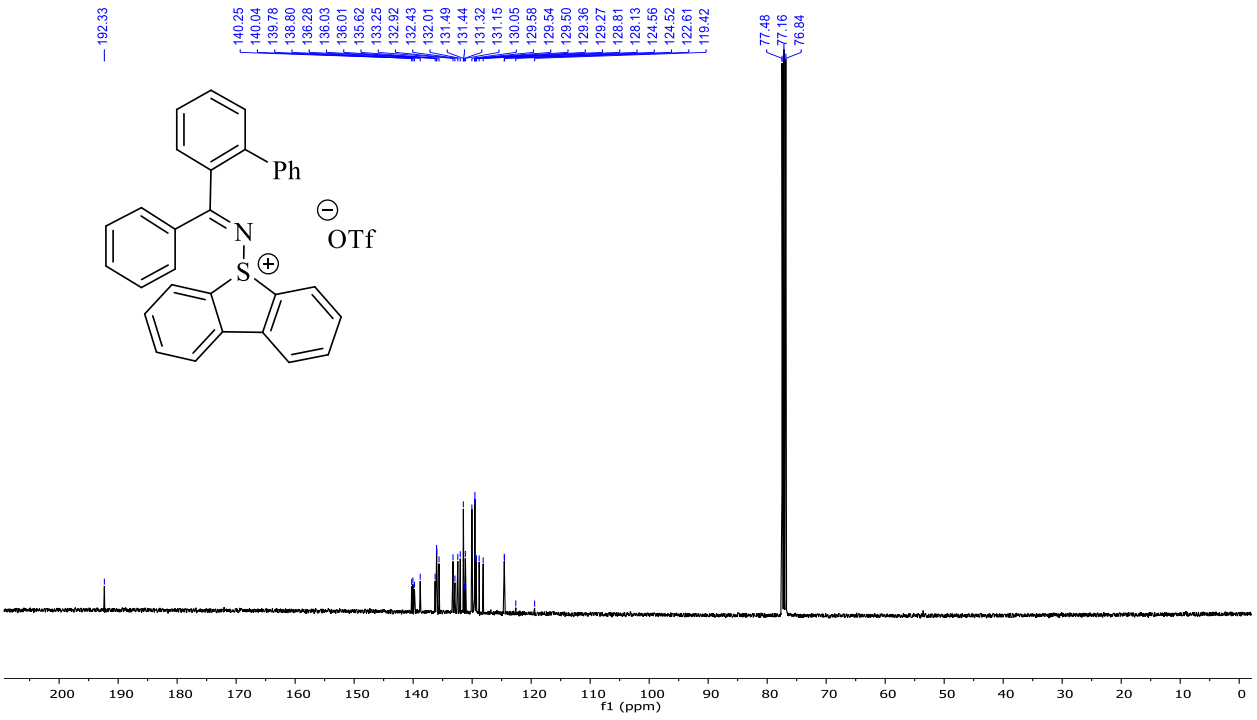
^{19}F NMR (565 MHz, $CDCl_3$) of **3b**



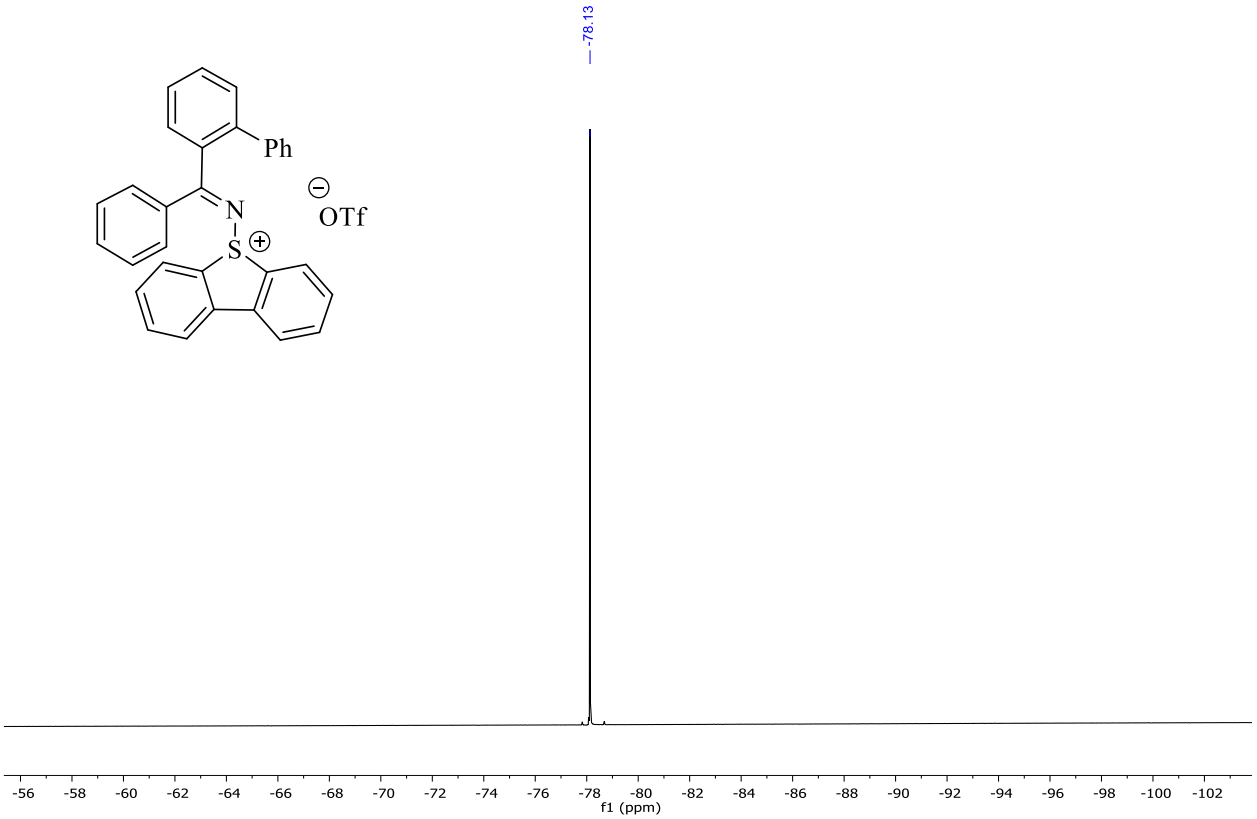
^{1}H NMR (400 MHz, $CDCl_3$) of **3c**



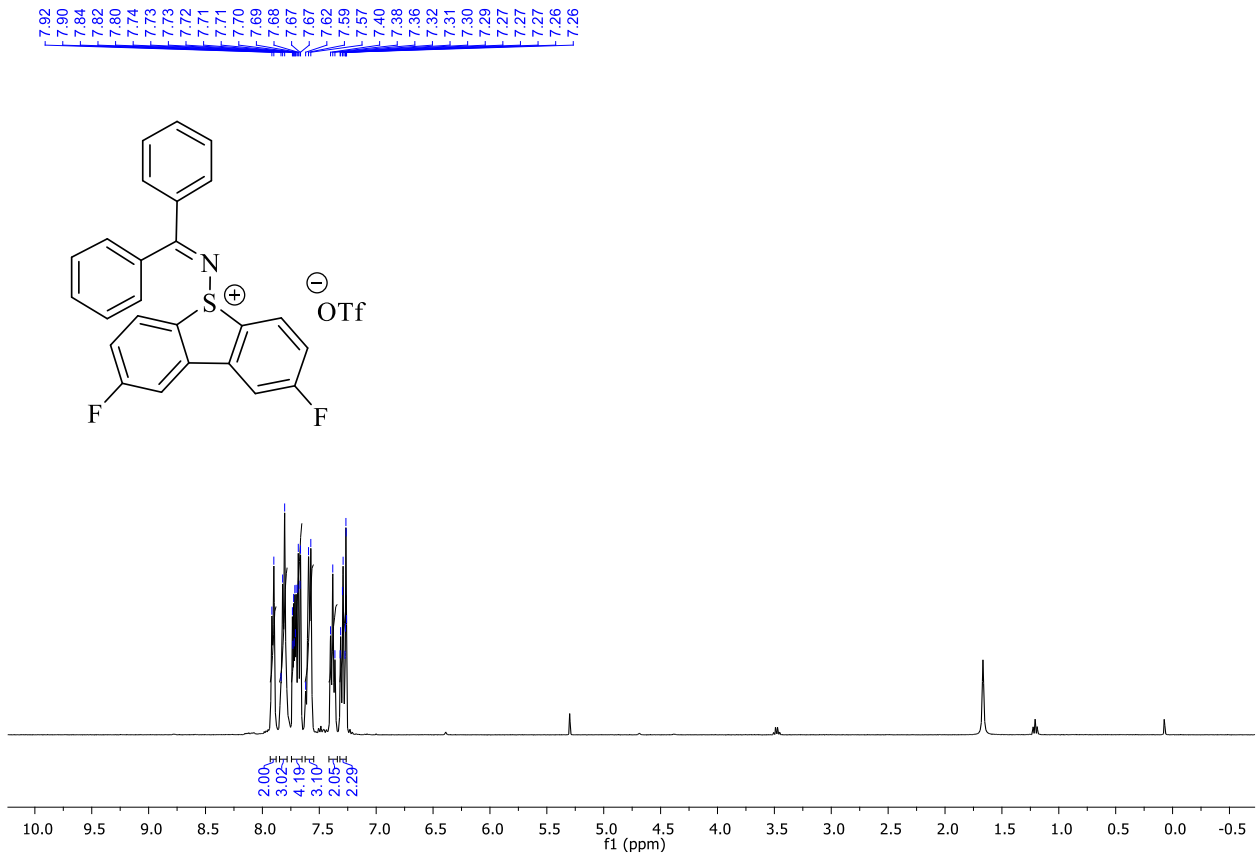
^{13}C NMR (101 MHz, $CDCl_3$) of **3c**



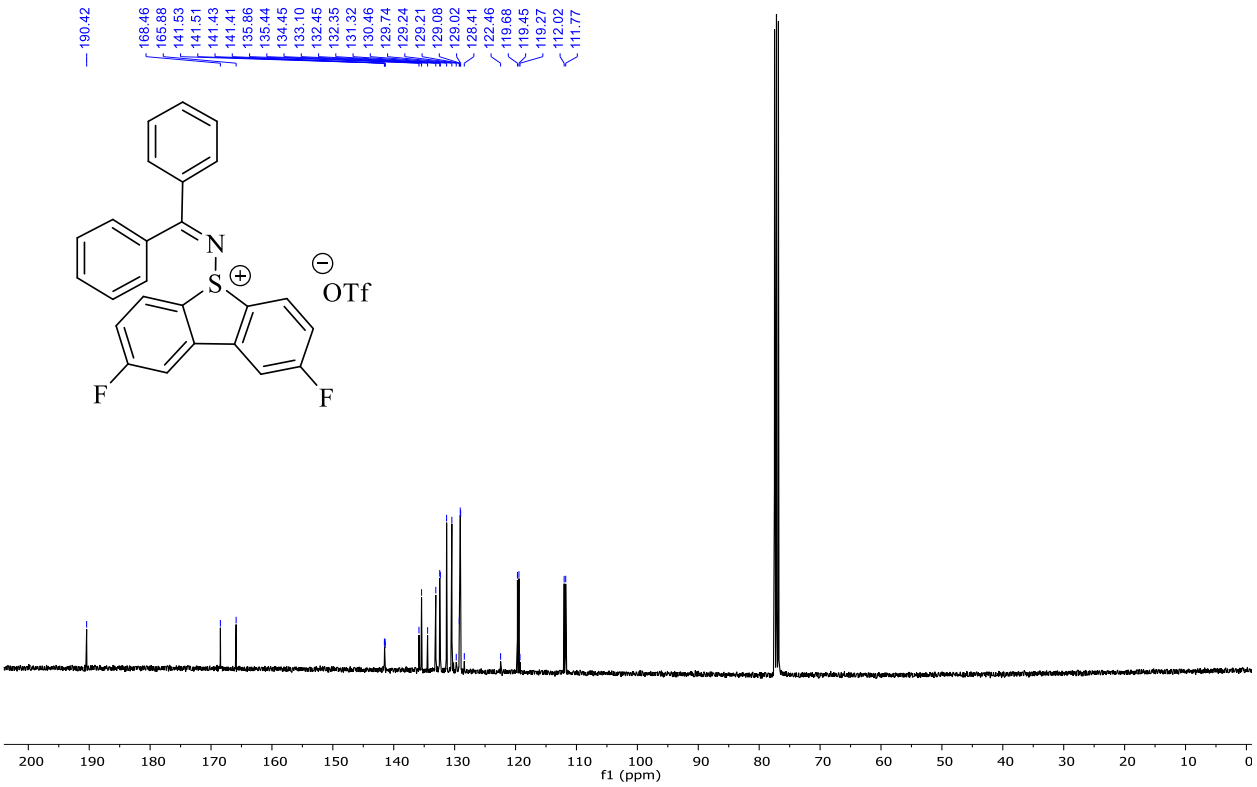
^{19}F NMR (377 MHz, $CDCl_3$) of **3c**



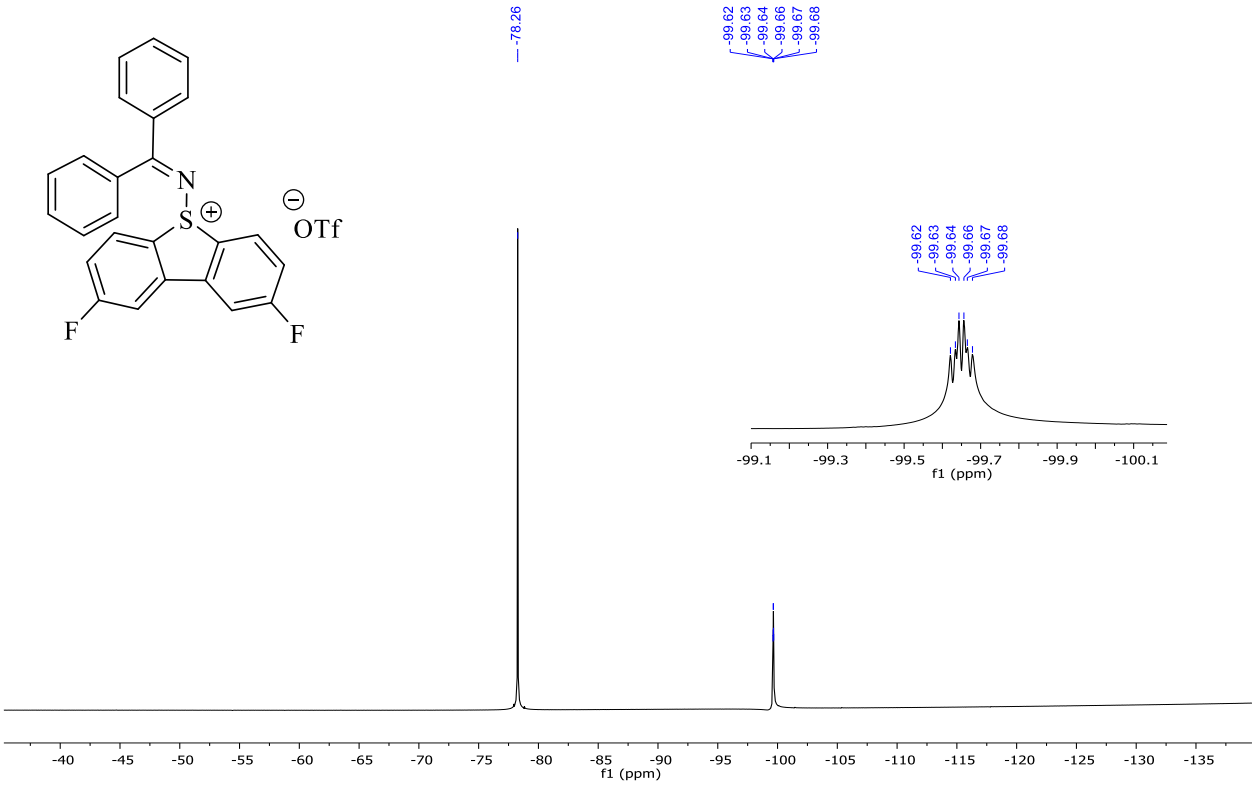
^{1}H NMR (400 MHz, $CDCl_3$) of **3d**



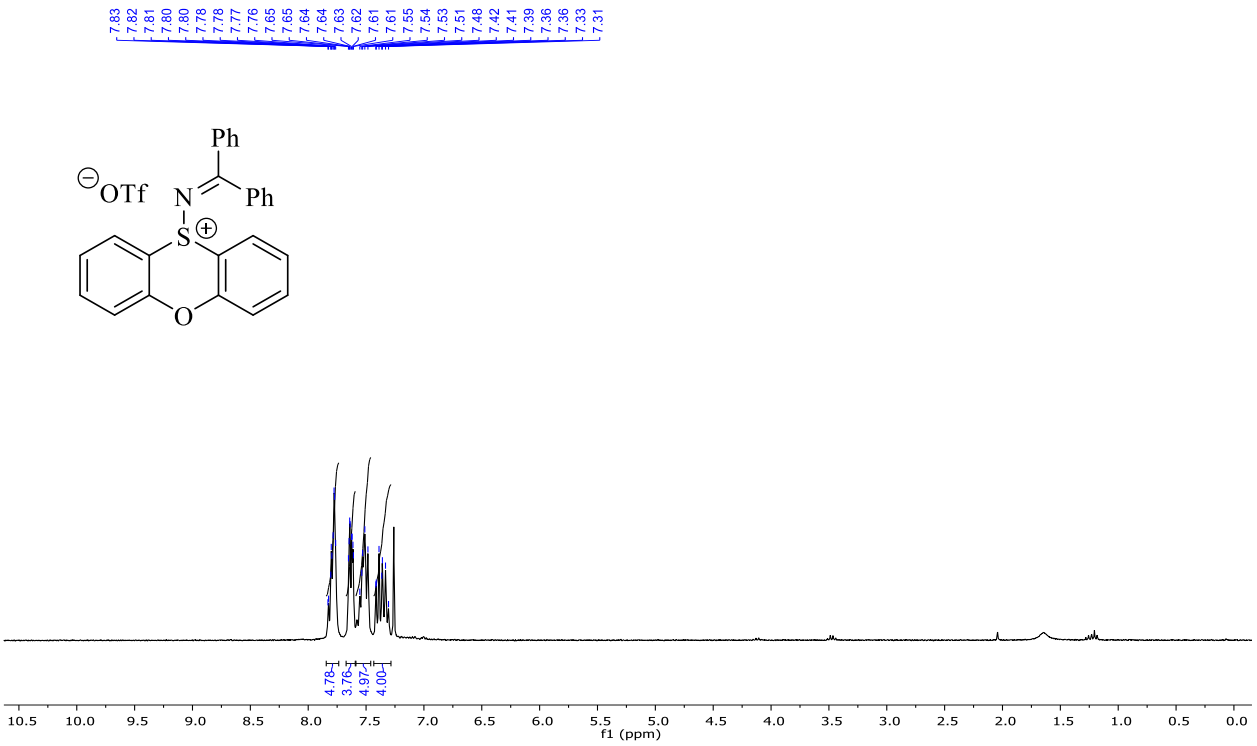
^{13}C NMR (101 MHz, $CDCl_3$) of **3d**



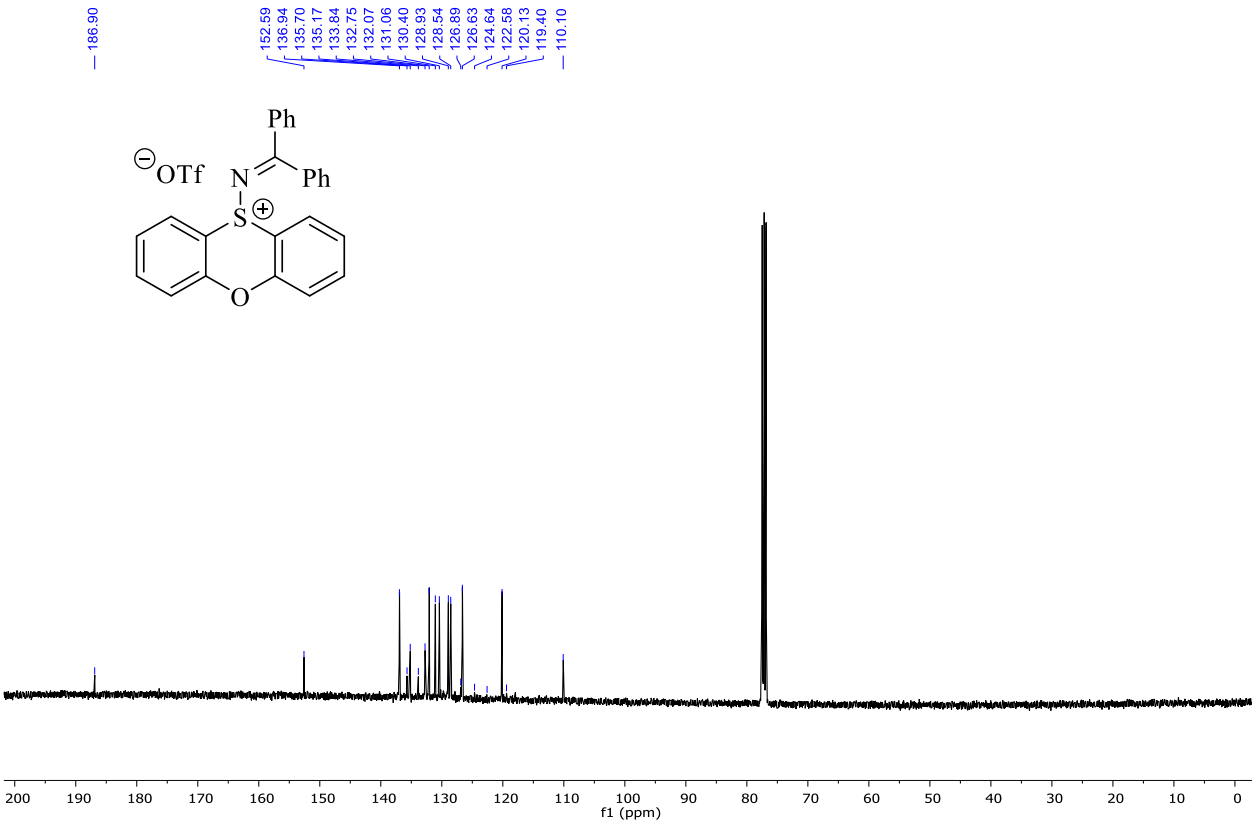
^{19}F NMR (377 MHz, $CDCl_3$) of **3d**



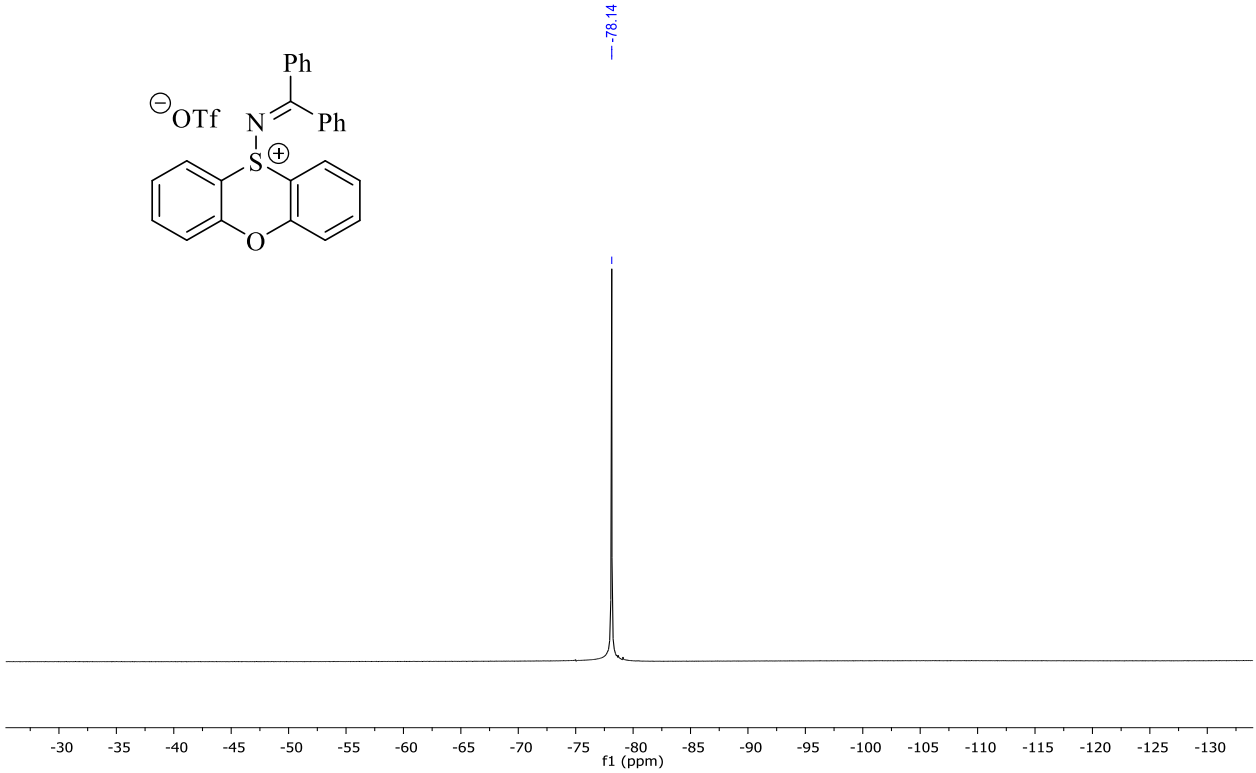
^{1}H NMR (300 MHz, $CDCl_3$) of **3e**



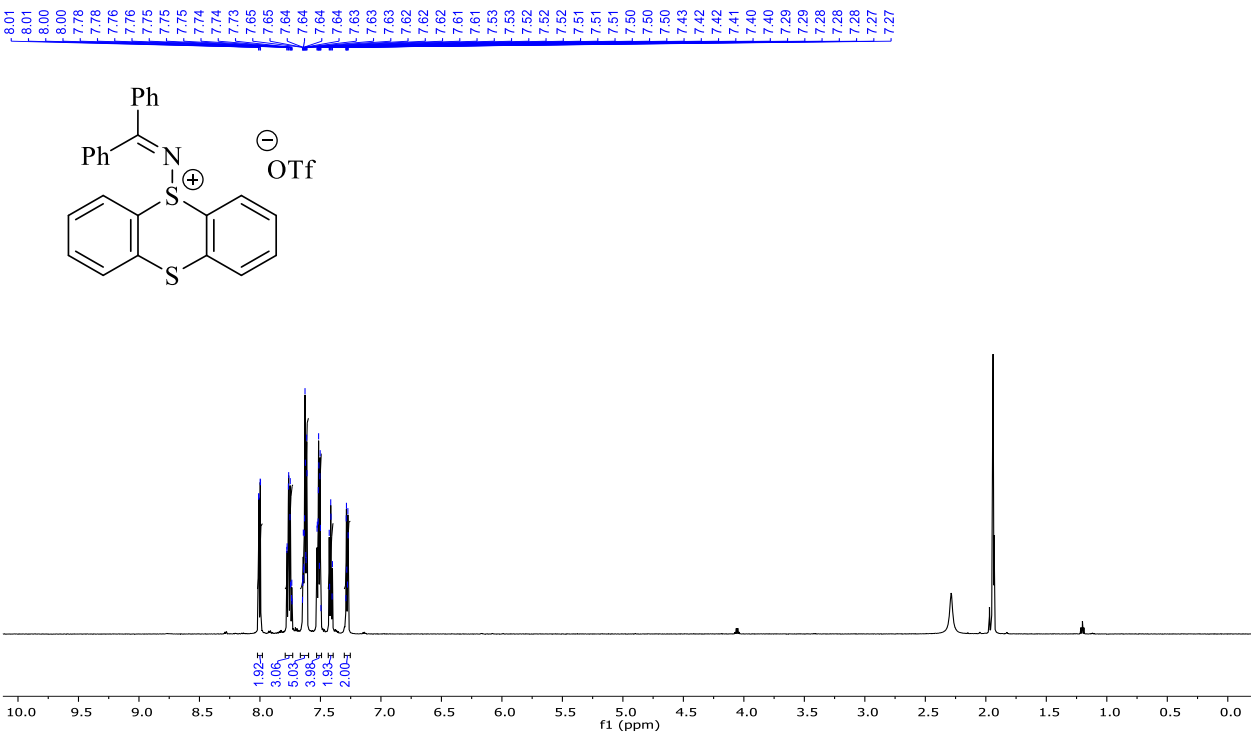
^{13}C NMR (101 MHz, $CDCl_3$) of **3e**



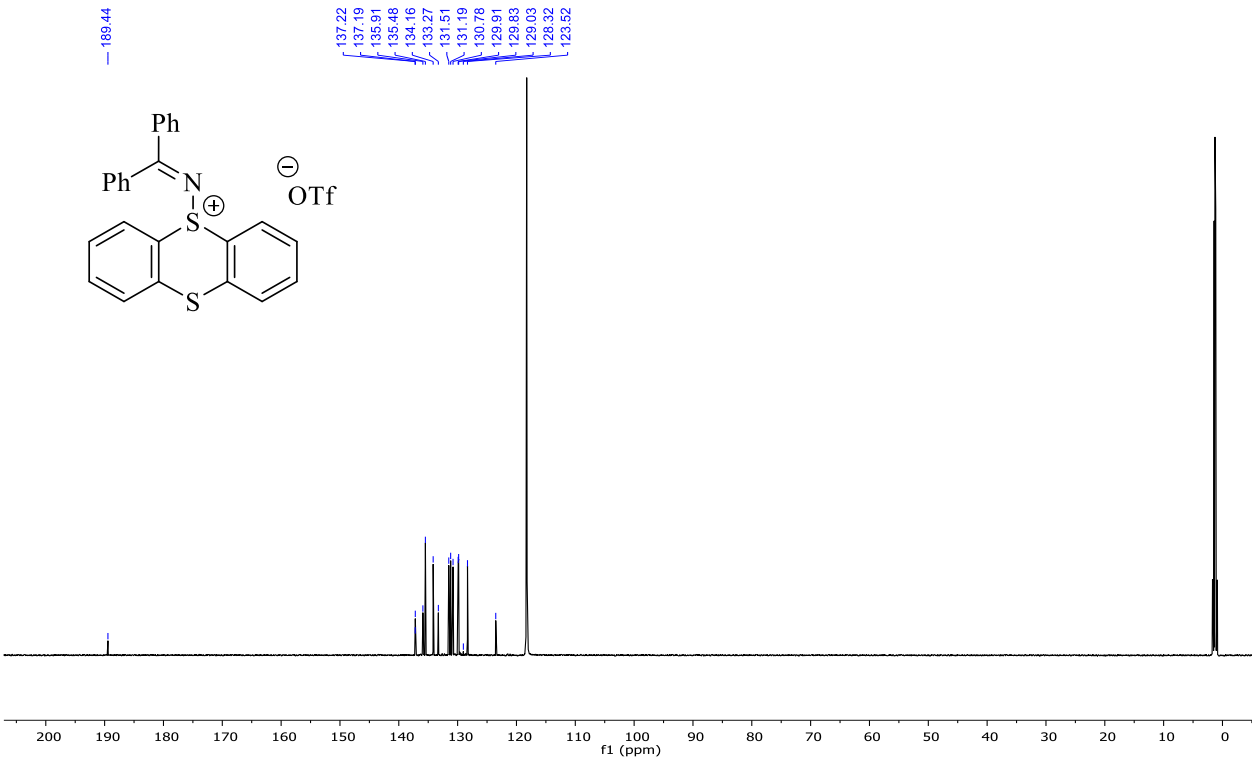
^{19}F NMR (377 MHz, $CDCl_3$) of **3e**



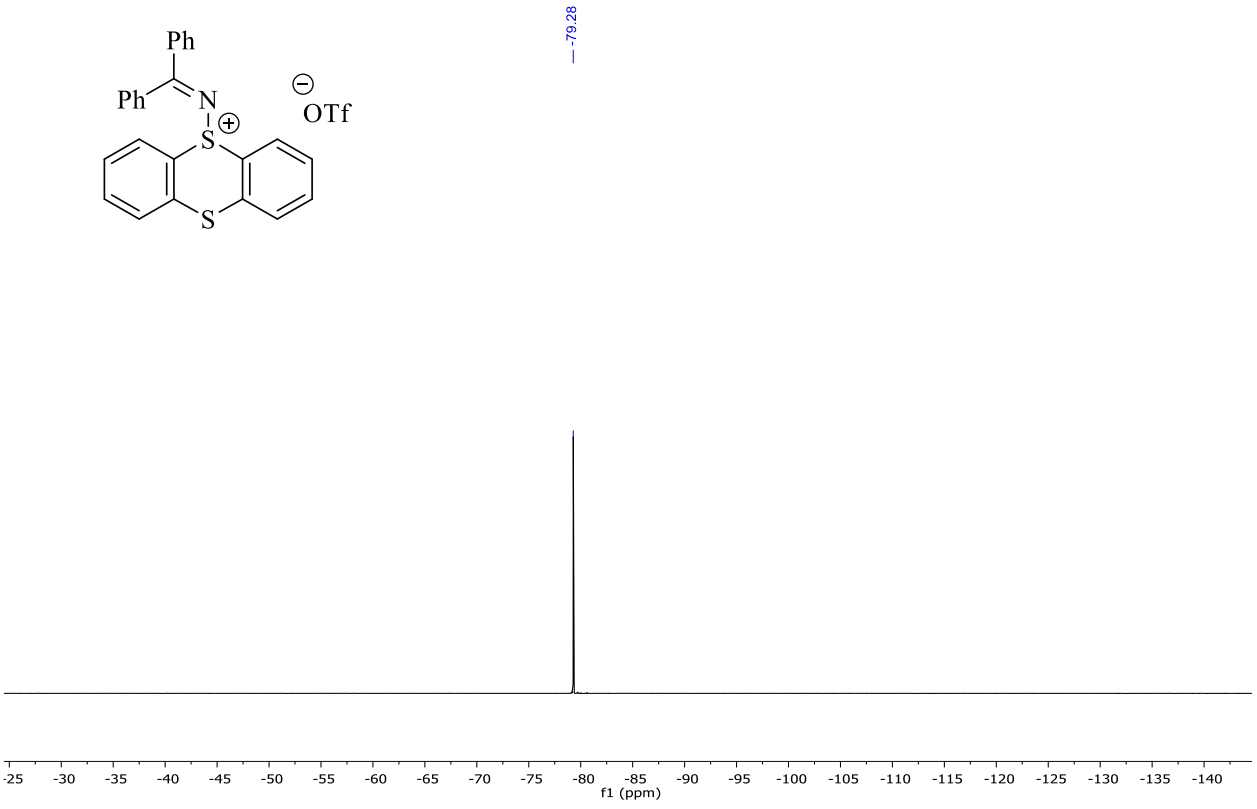
^{1}H NMR (600 MHz, CD_3CN) of **3f**



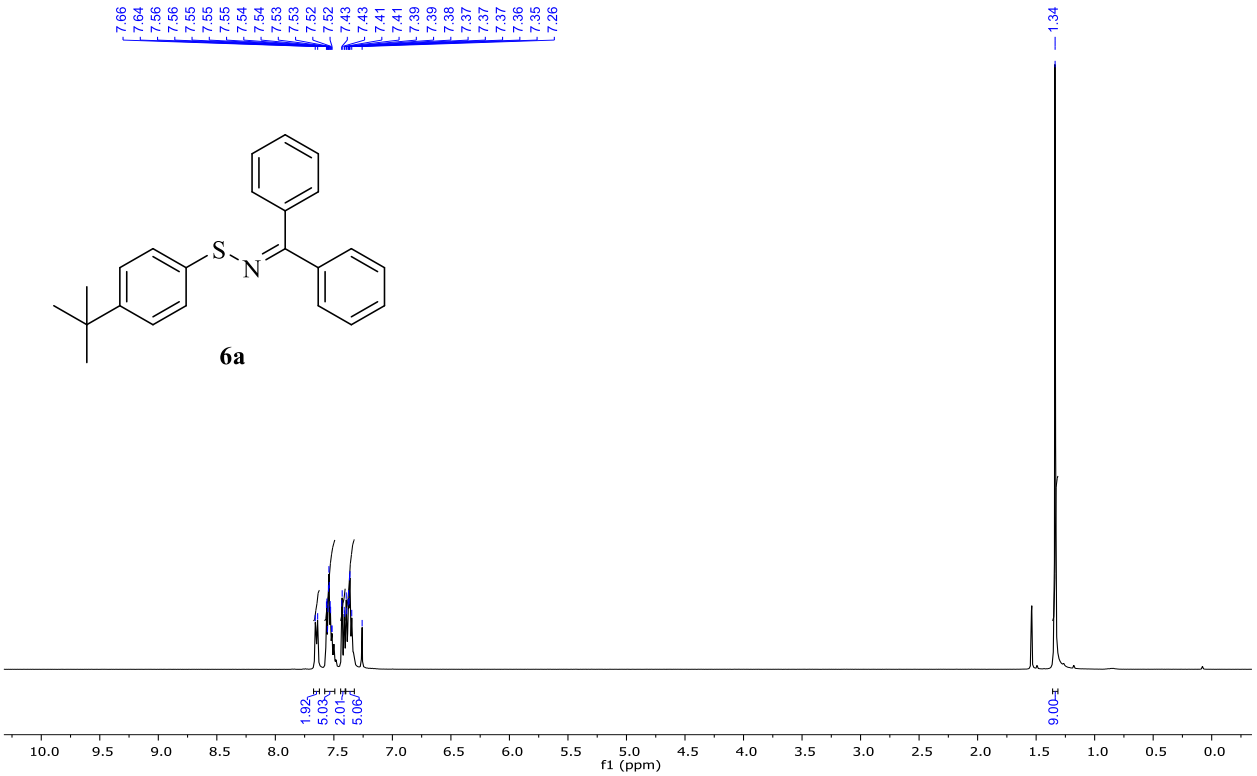
^{13}C NMR (151 MHz, CD3CN) of **3f**



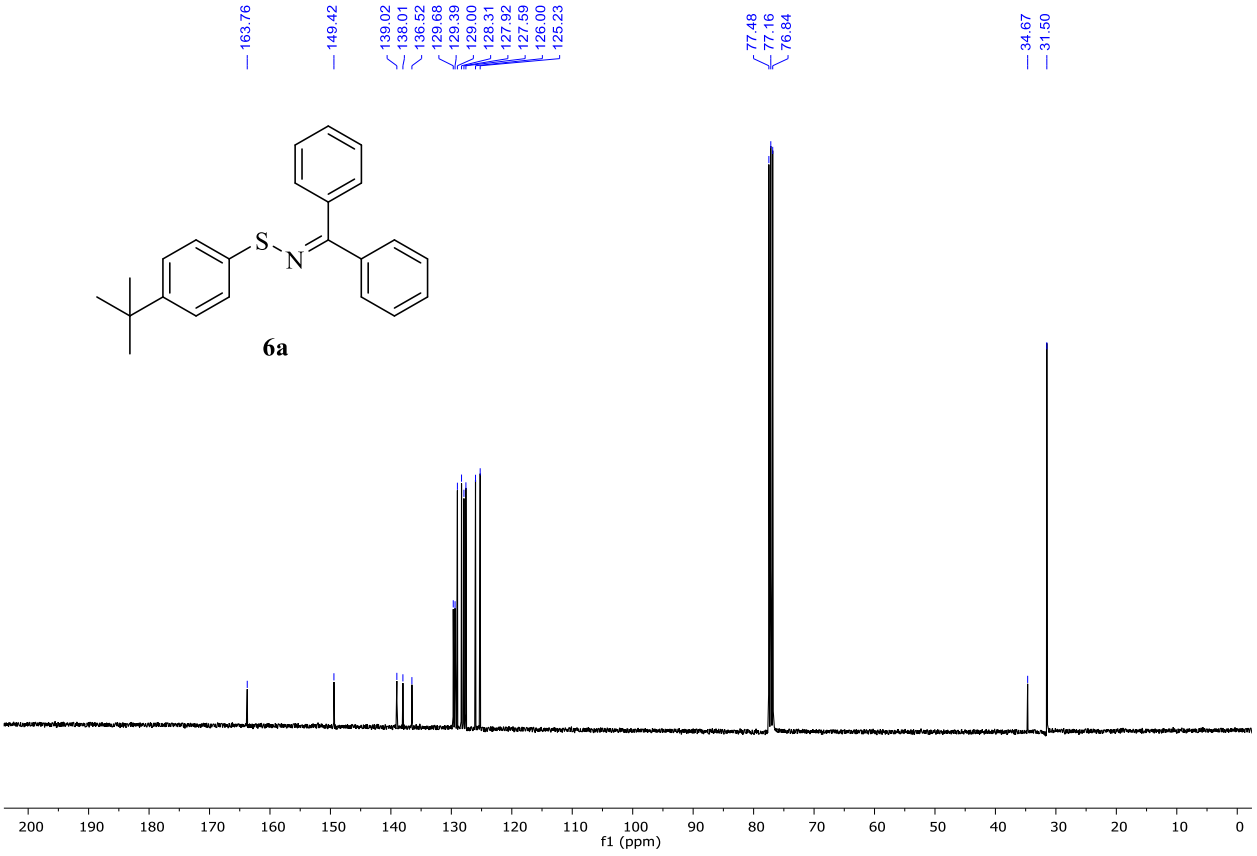
^{19}F NMR (3565 MHz, CD_3CN) of **3f**



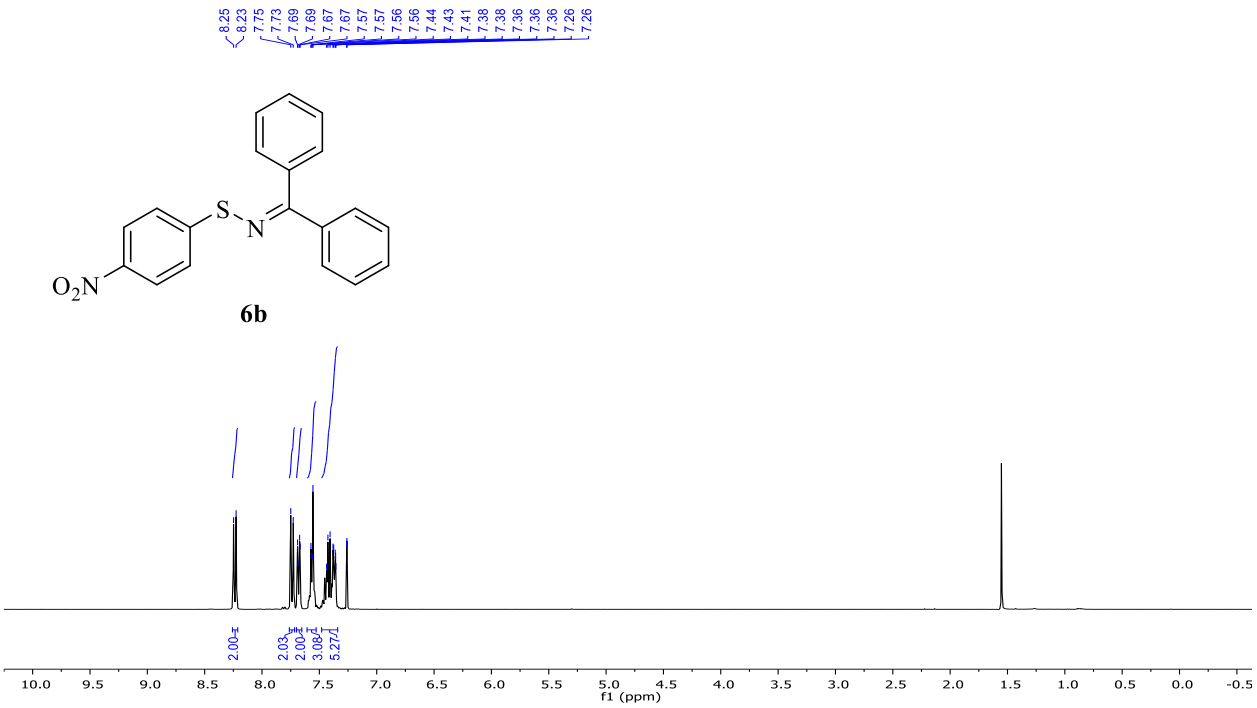
^{1}H NMR (400 MHz, $CDCl_3$) of **6a**



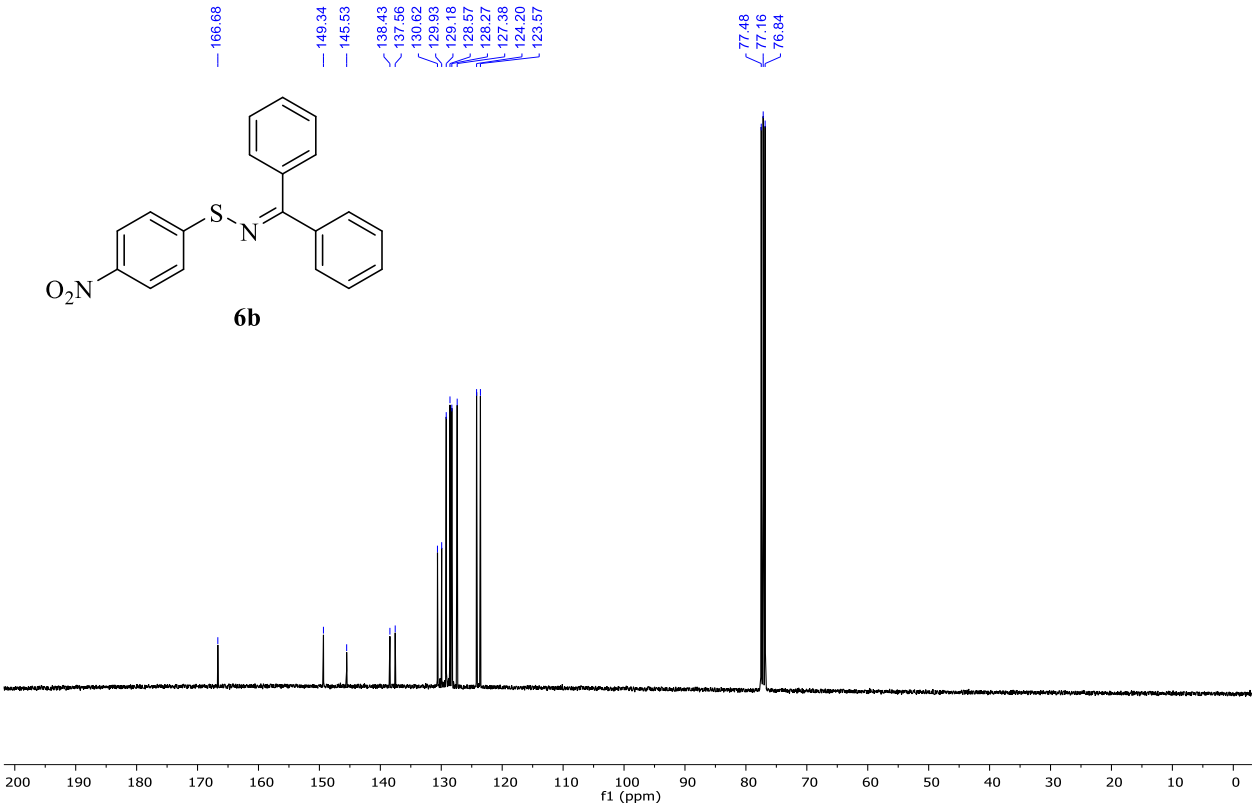
^{13}C NMR (101 MHz, $CDCl_3$) of **6a**



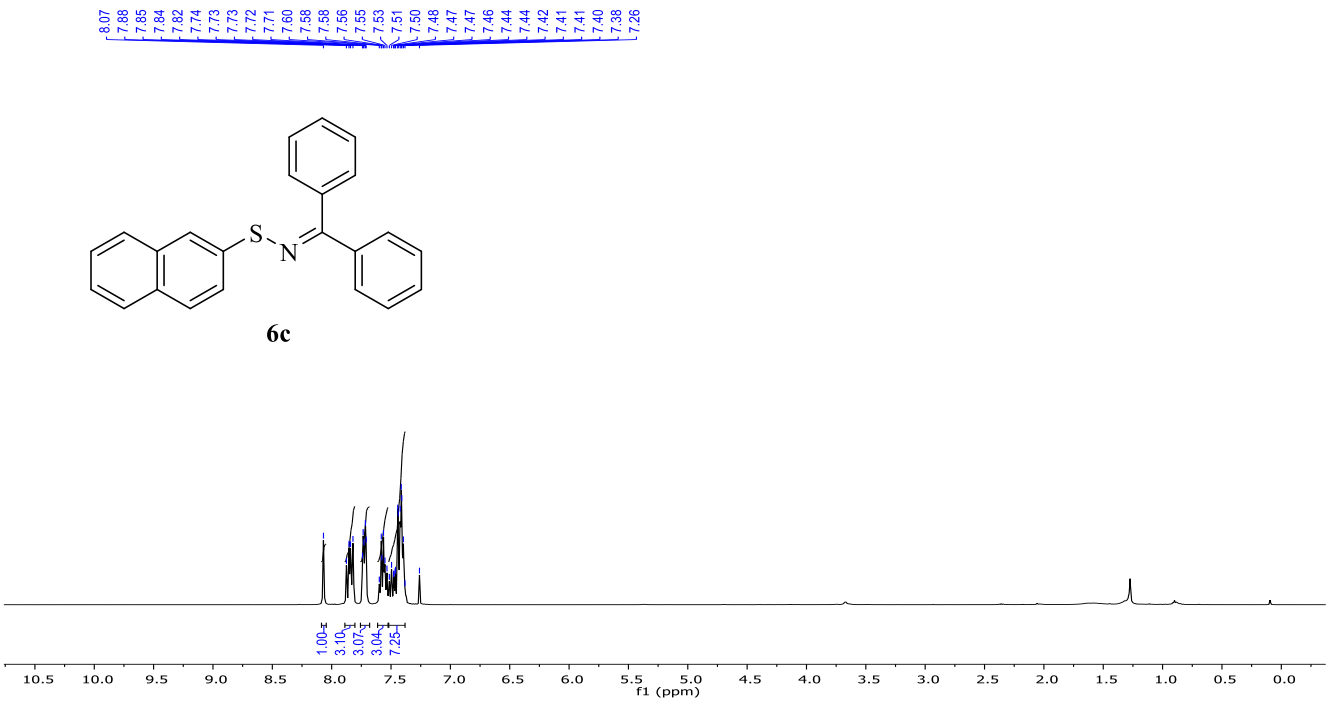
^{1}H NMR (400 MHz, $CDCl_3$) of **6b**



^{13}C NMR (101 MHz, $CDCl_3$) of **6b**

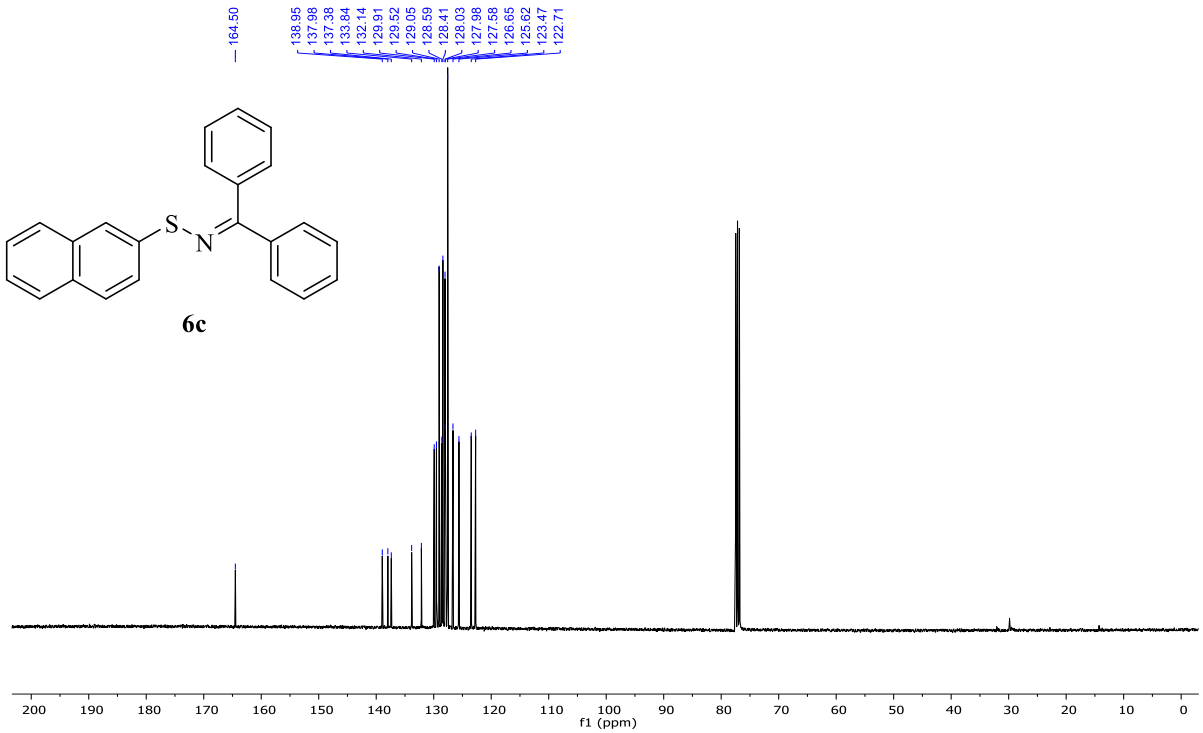


^{1}H NMR (400 MHz, $CDCl_3$) of **6c**



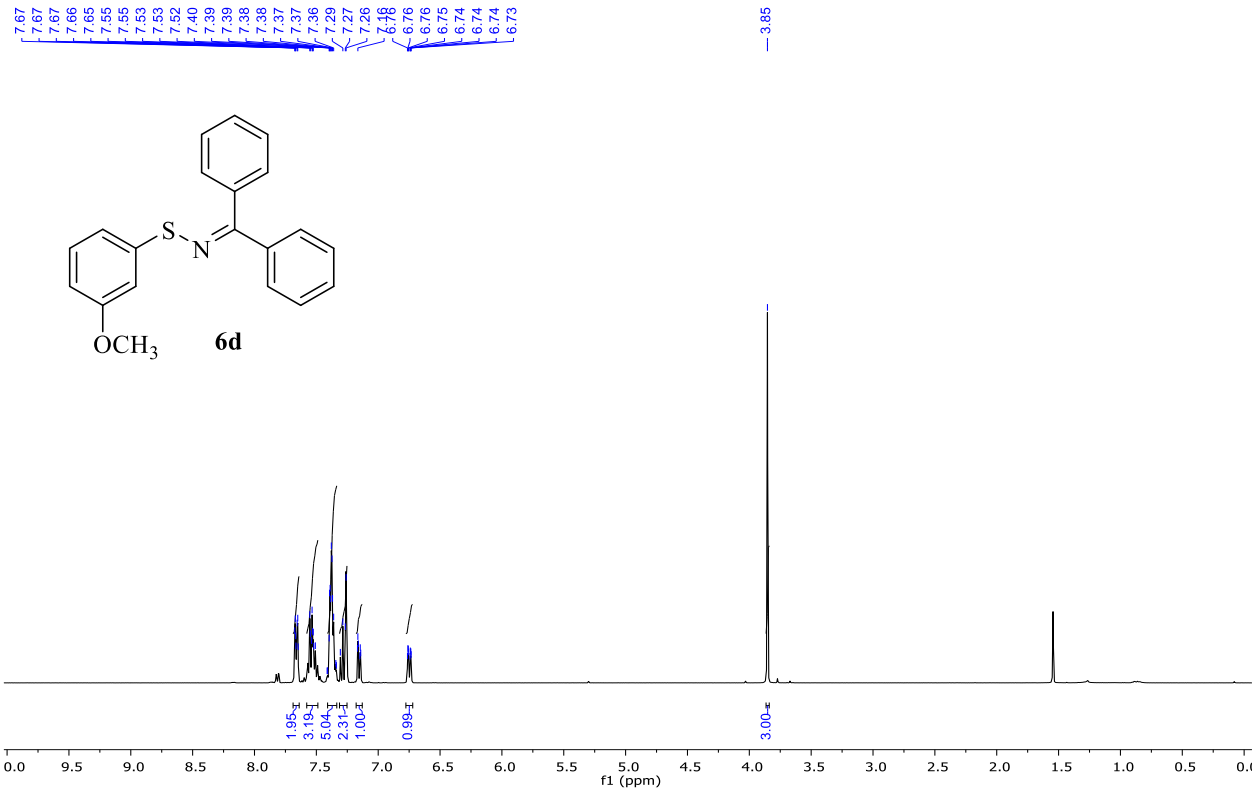
6c

^{13}C NMR (101 MHz, $CDCl_3$) of **6c**

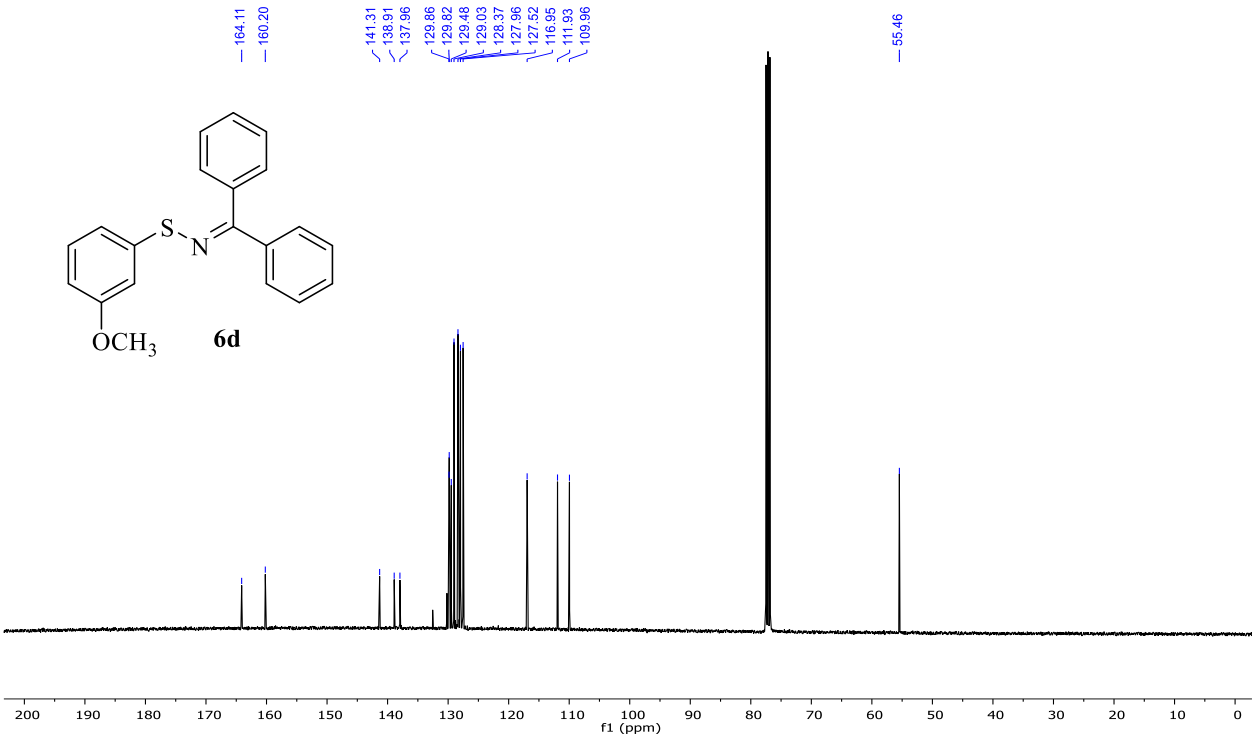


6c

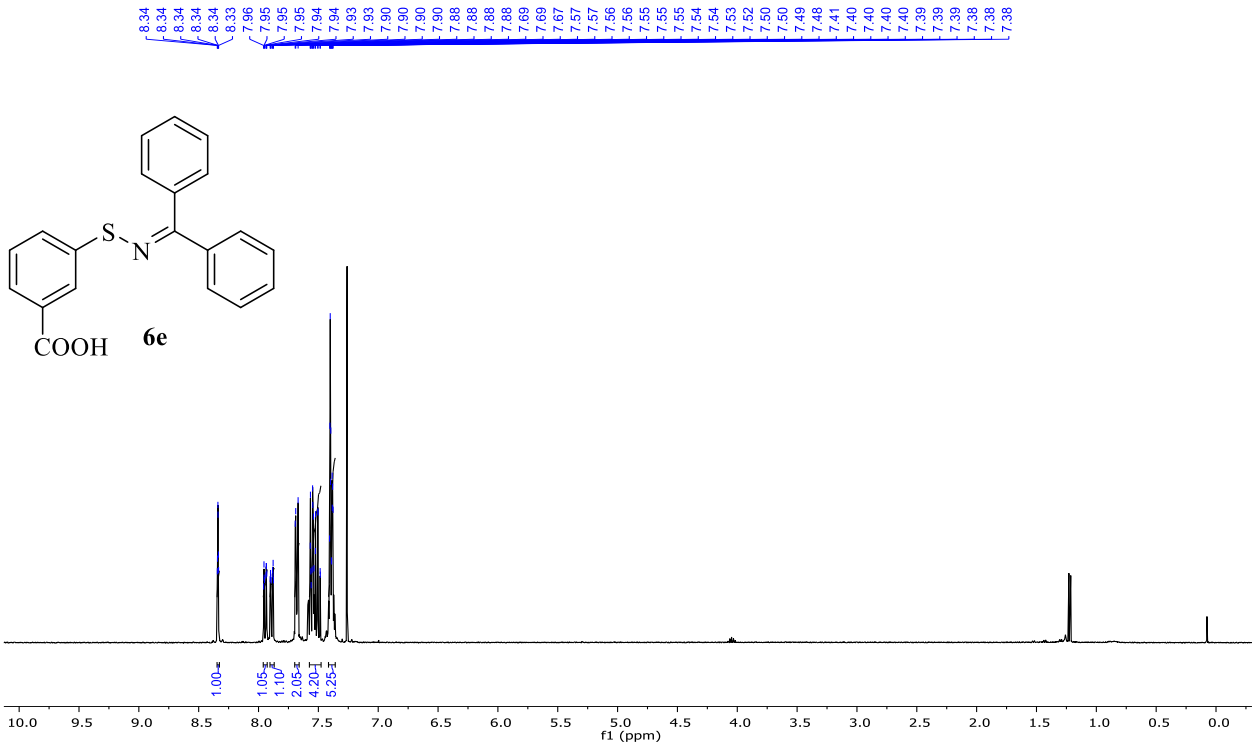
^{1}H NMR (400 MHz, $CDCl_3$) of **6d**



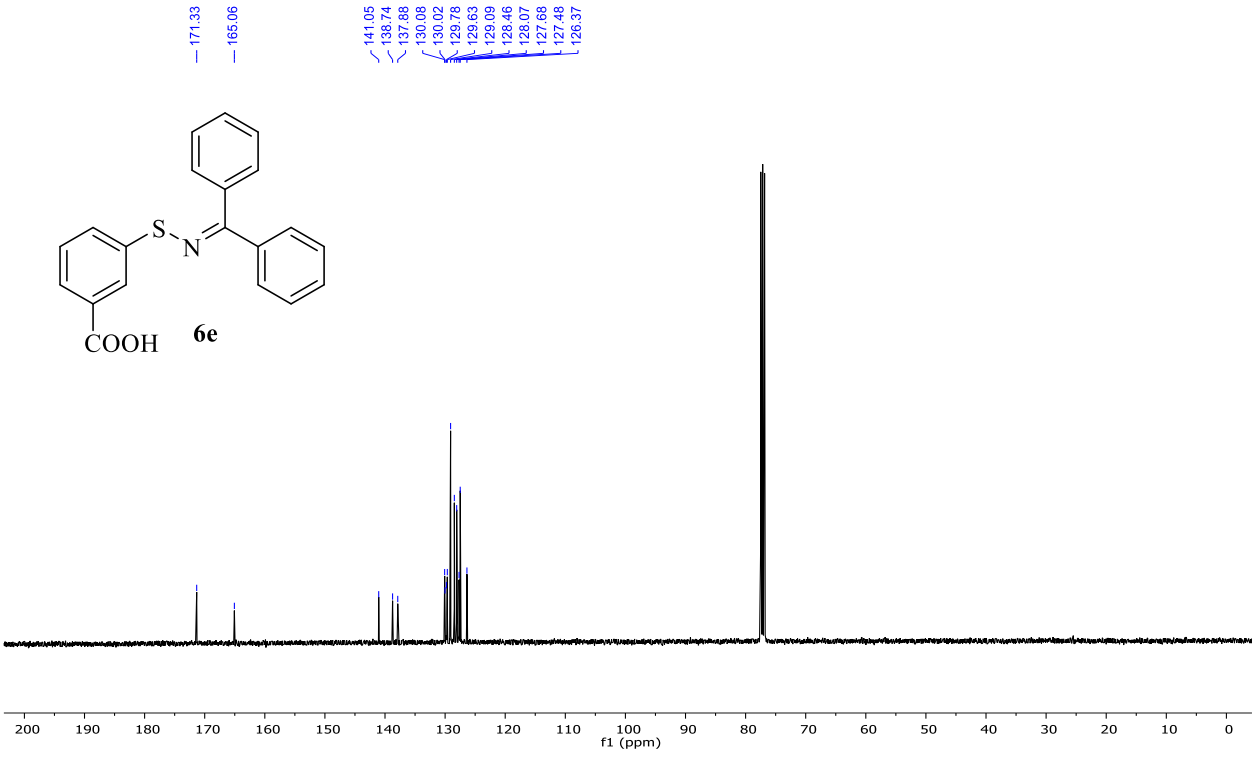
^{13}C NMR (101 MHz, $CDCl_3$) of **6d**



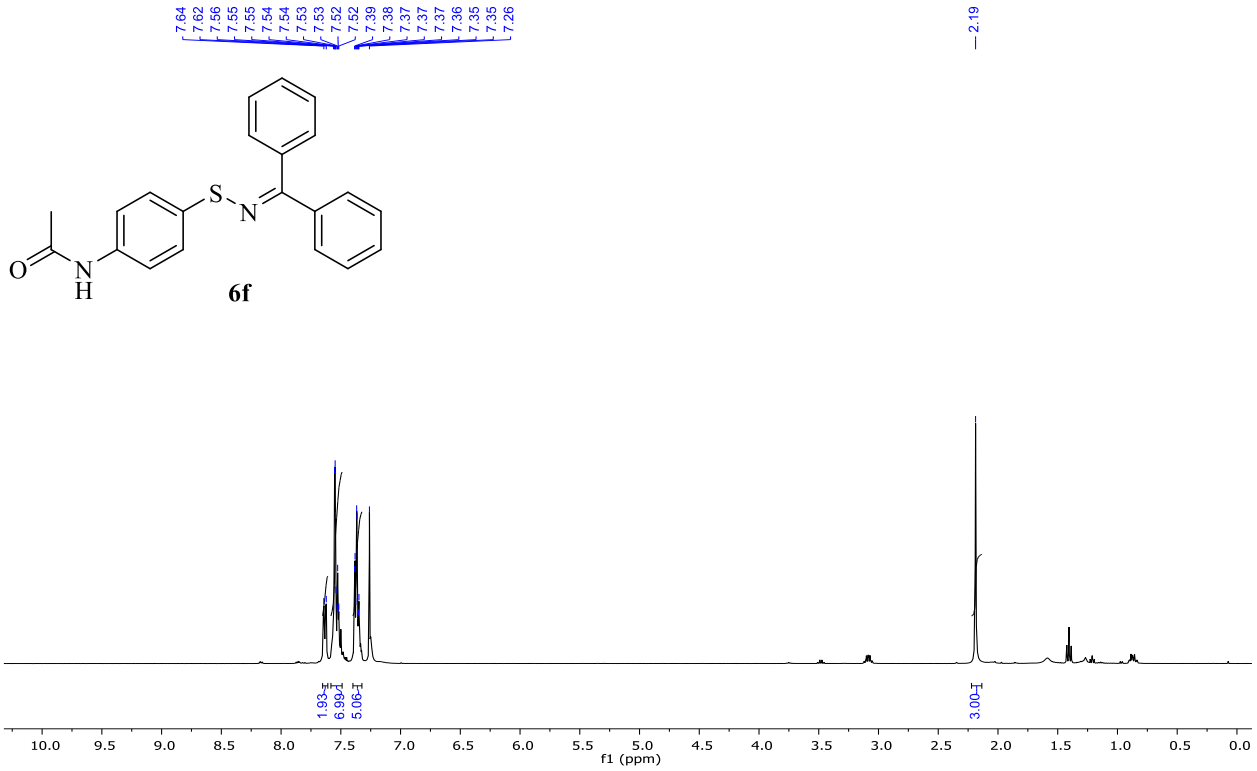
^{1}H NMR (400 MHz, Chloroform-*d*) of 6e



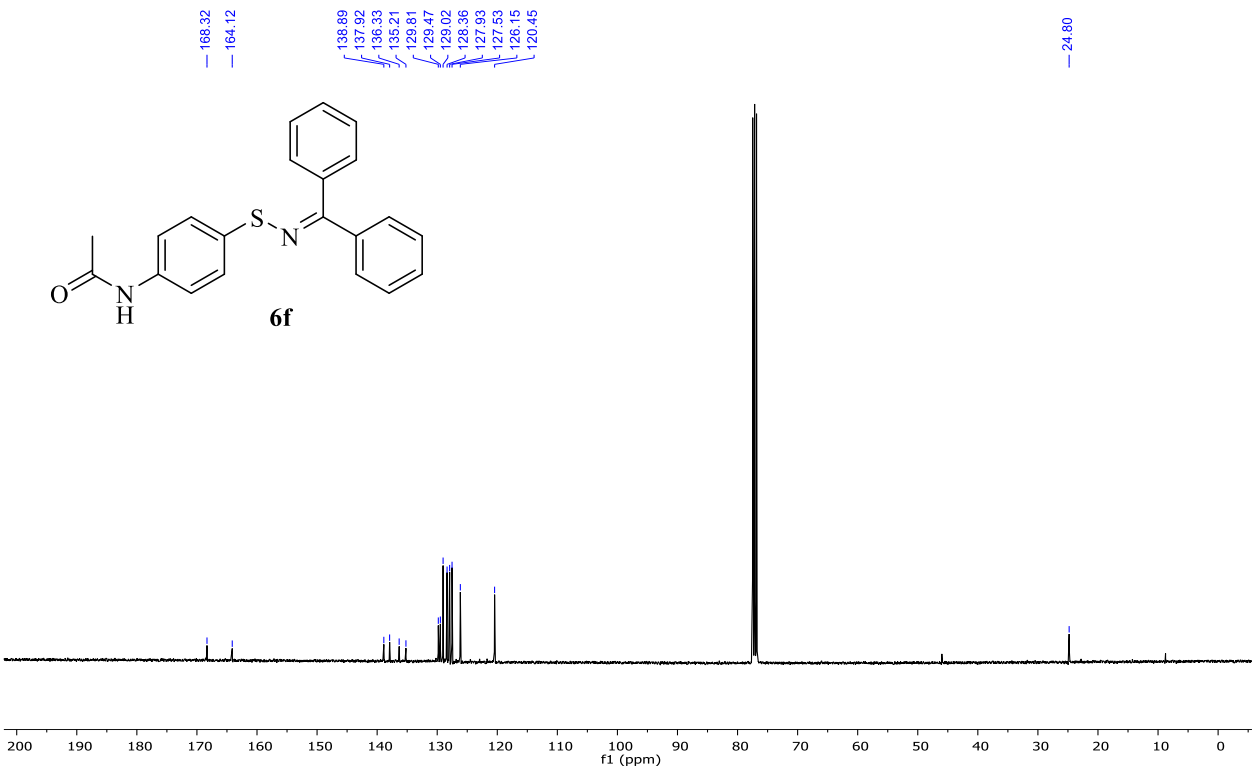
^{13}C NMR (101 MHz, $CDCl_3$) of **6e**



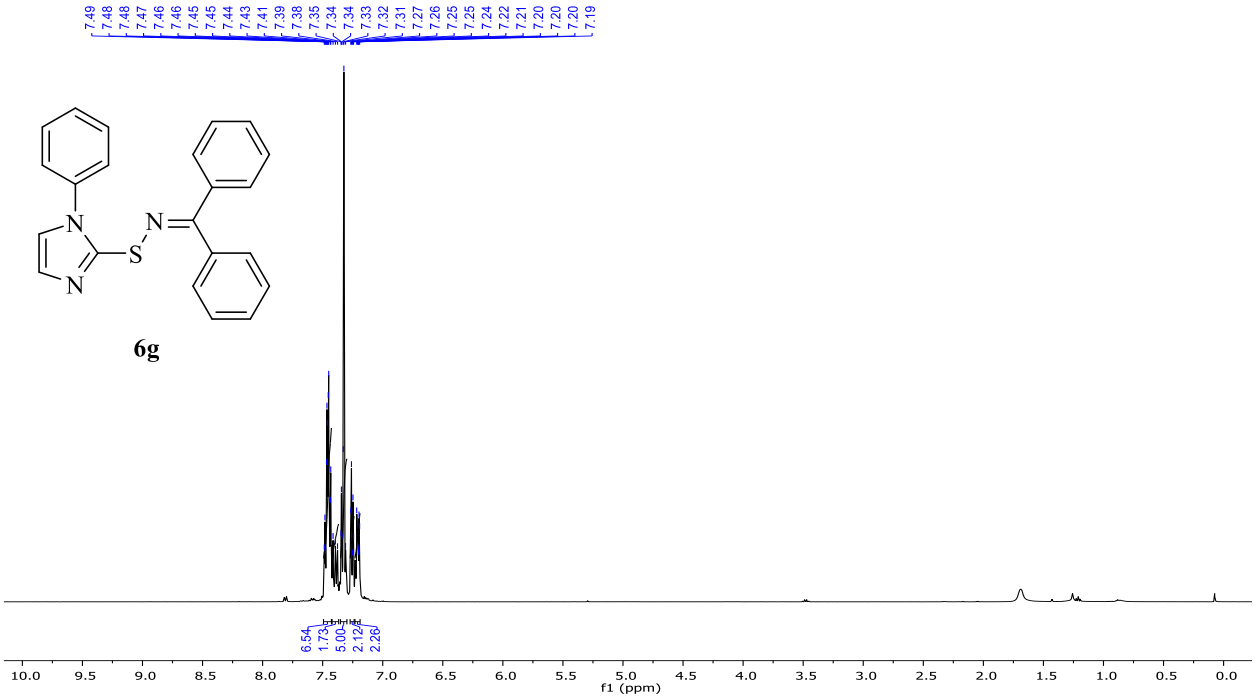
^{1}H NMR (400 MHz, $CDCl_3$) of **6f**



^{13}C NMR (101 MHz, $CDCl_3$) of **6f**

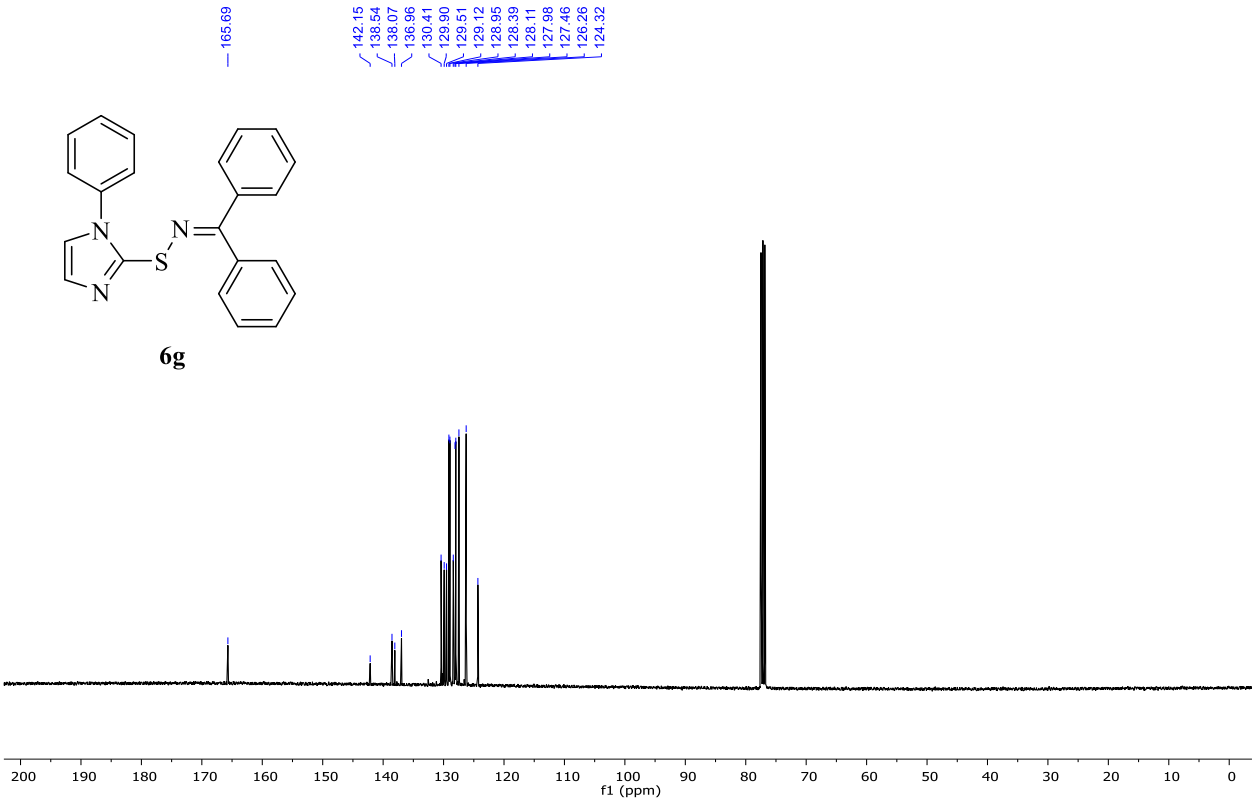


^{1}H NMR (400 MHz, $CDCl_3$) of **6g**



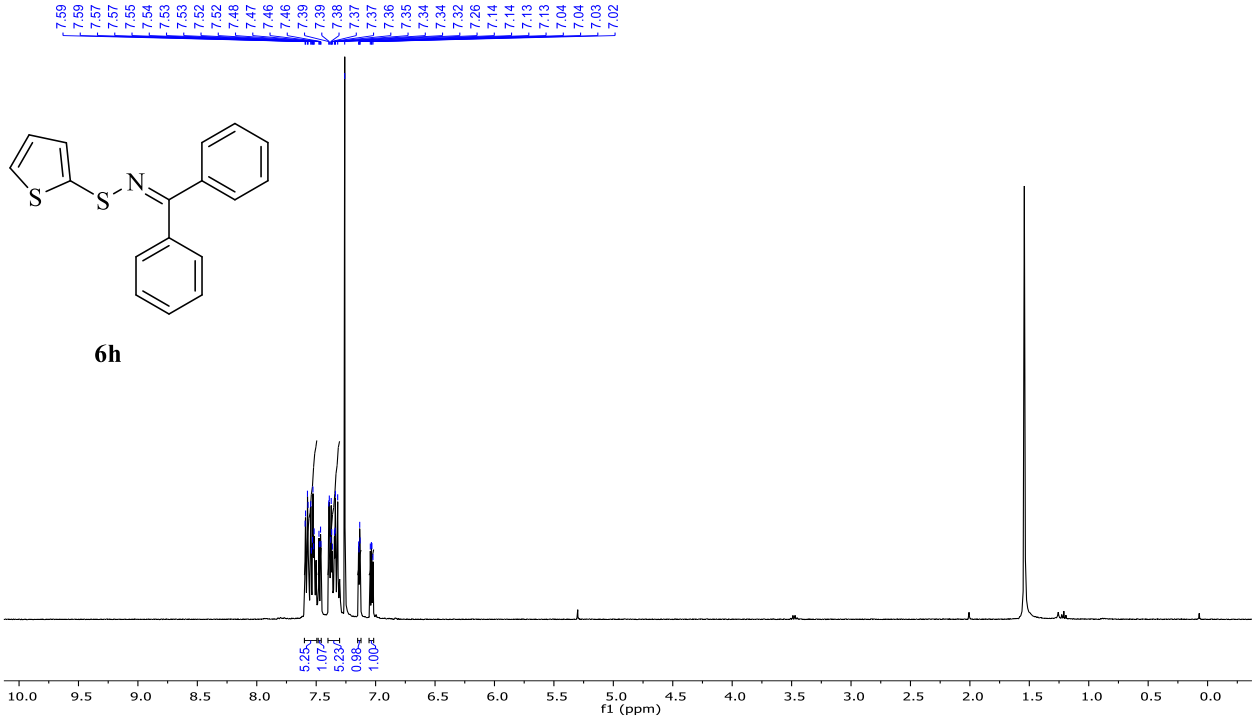
6g

^{13}C NMR (101 MHz, $CDCl_3$) of **6g**

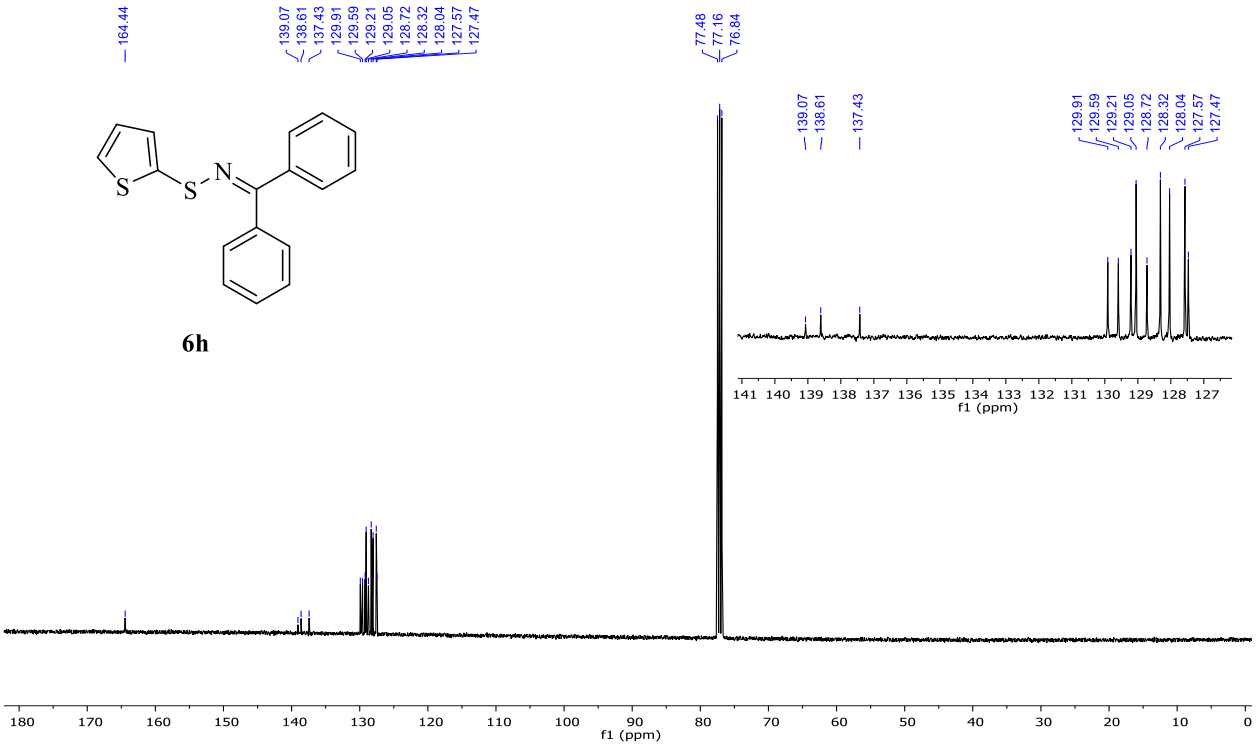


6g

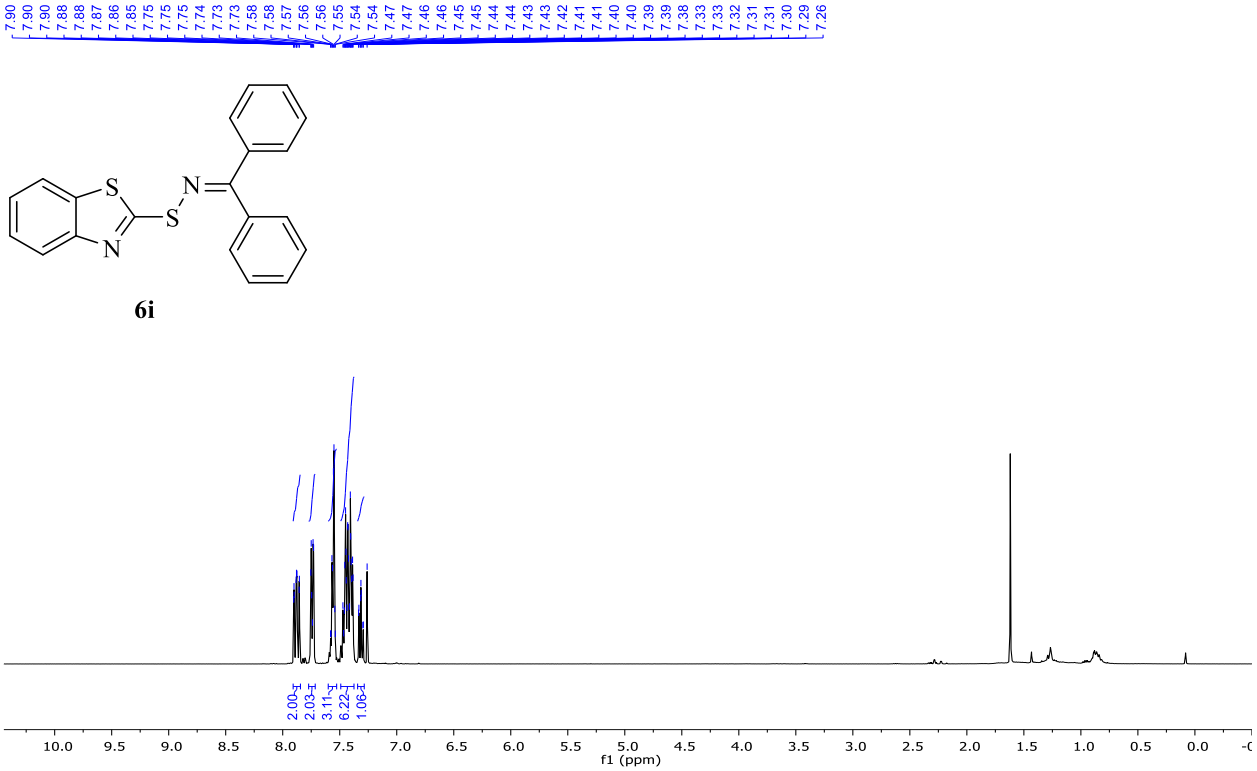
^{1}H NMR (400 MHz, $CDCl_3$) of **6h**



^{13}C NMR (101 MHz, $CDCl_3$) of **6h**

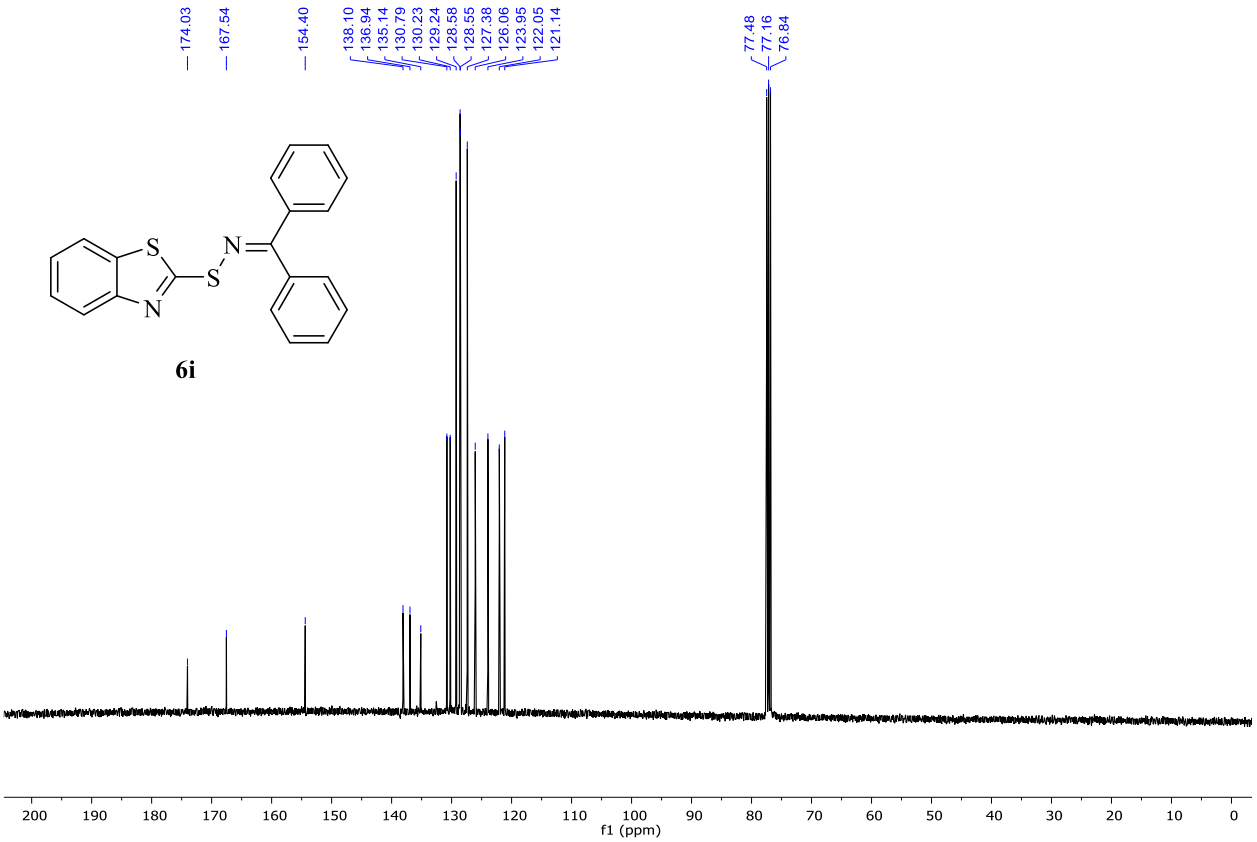


^{1}H NMR (400 MHz, $CDCl_3$) of **6i**



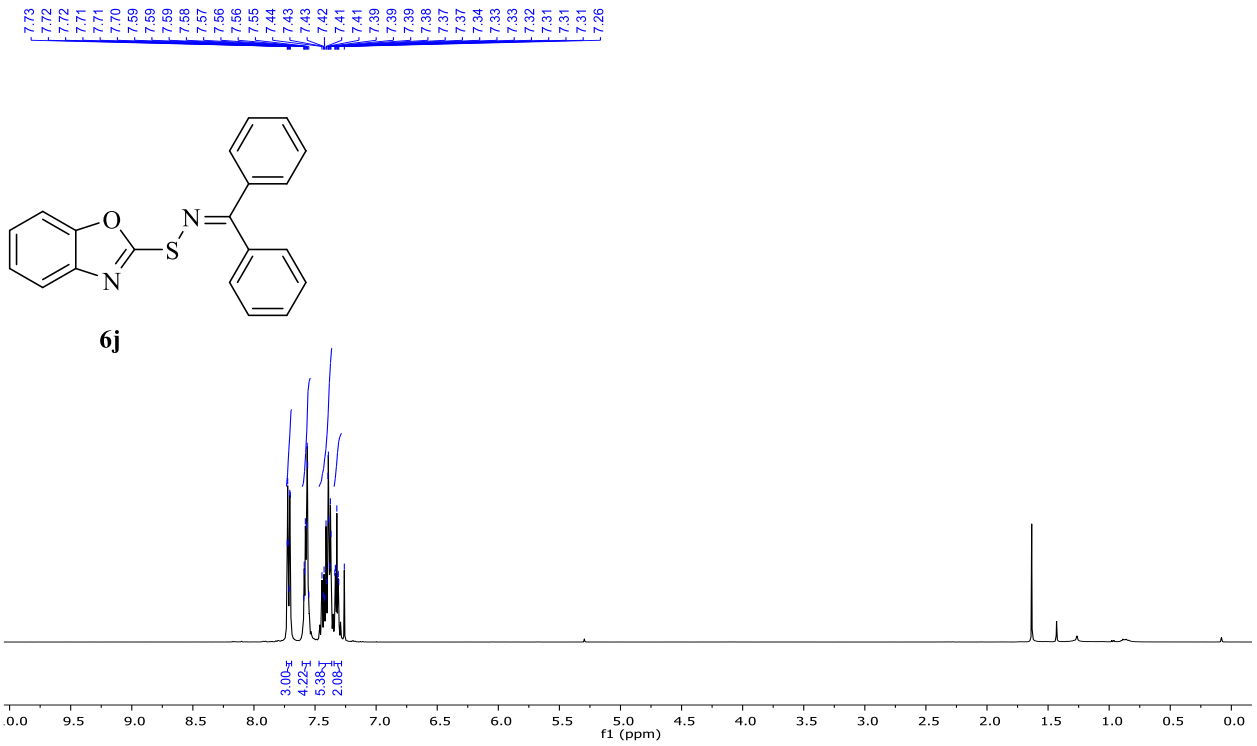
6i

^{13}C NMR (101 MHz, $CDCl_3$) of **6i**

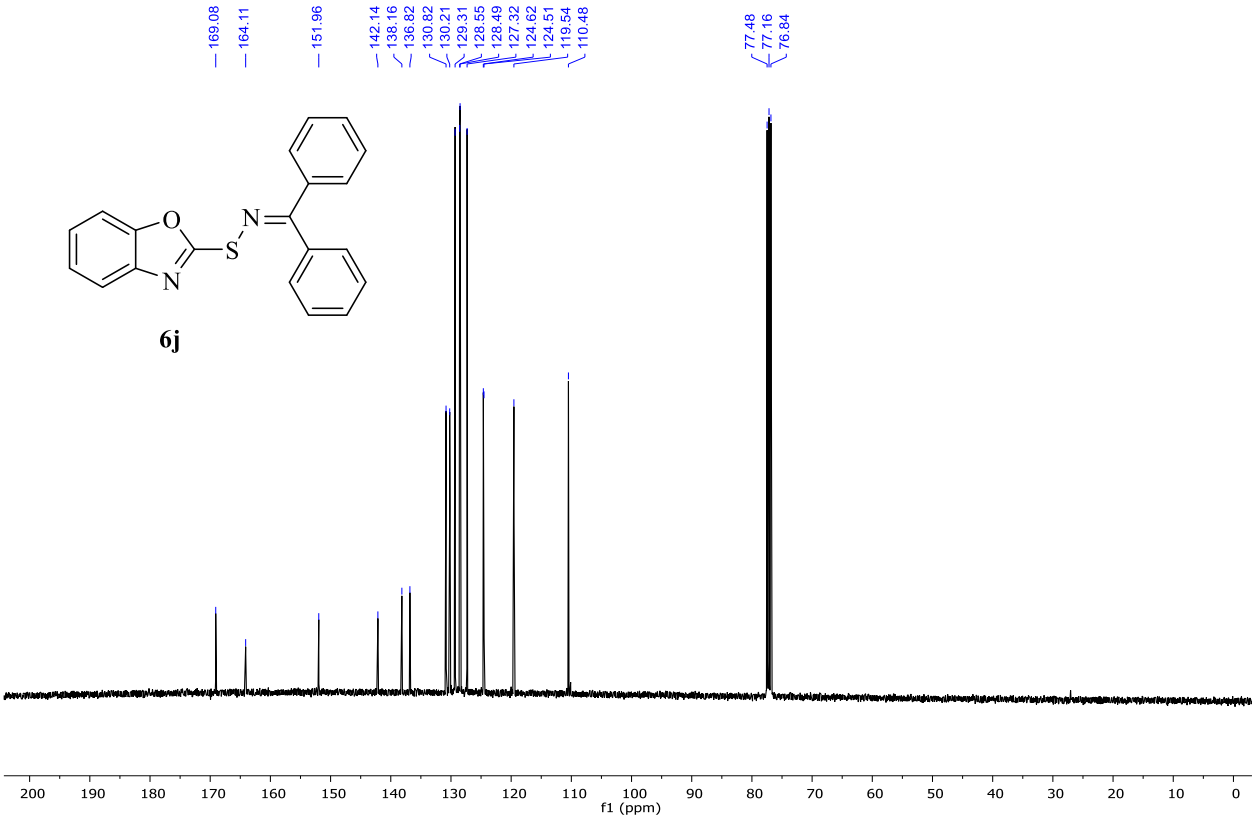


6i

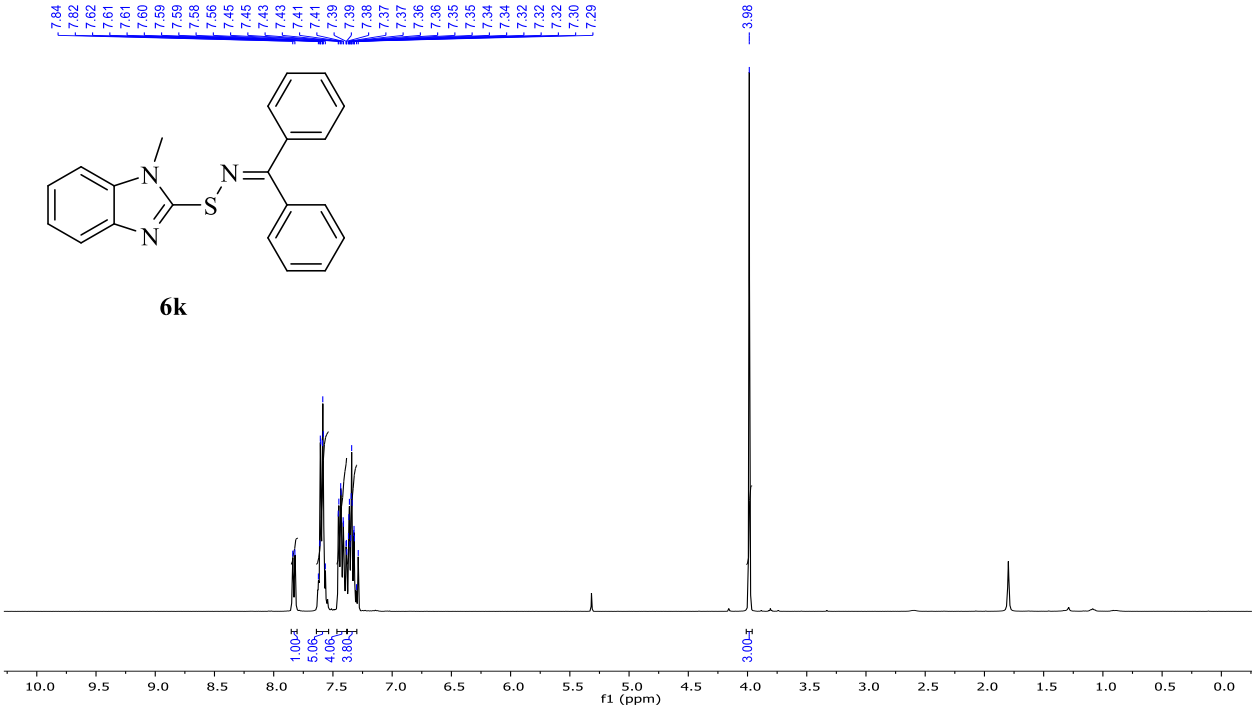
^{1}H NMR (400 MHz, $CDCl_3$) of **6j**



^{13}C NMR (101 MHz, $CDCl_3$) of **6j**

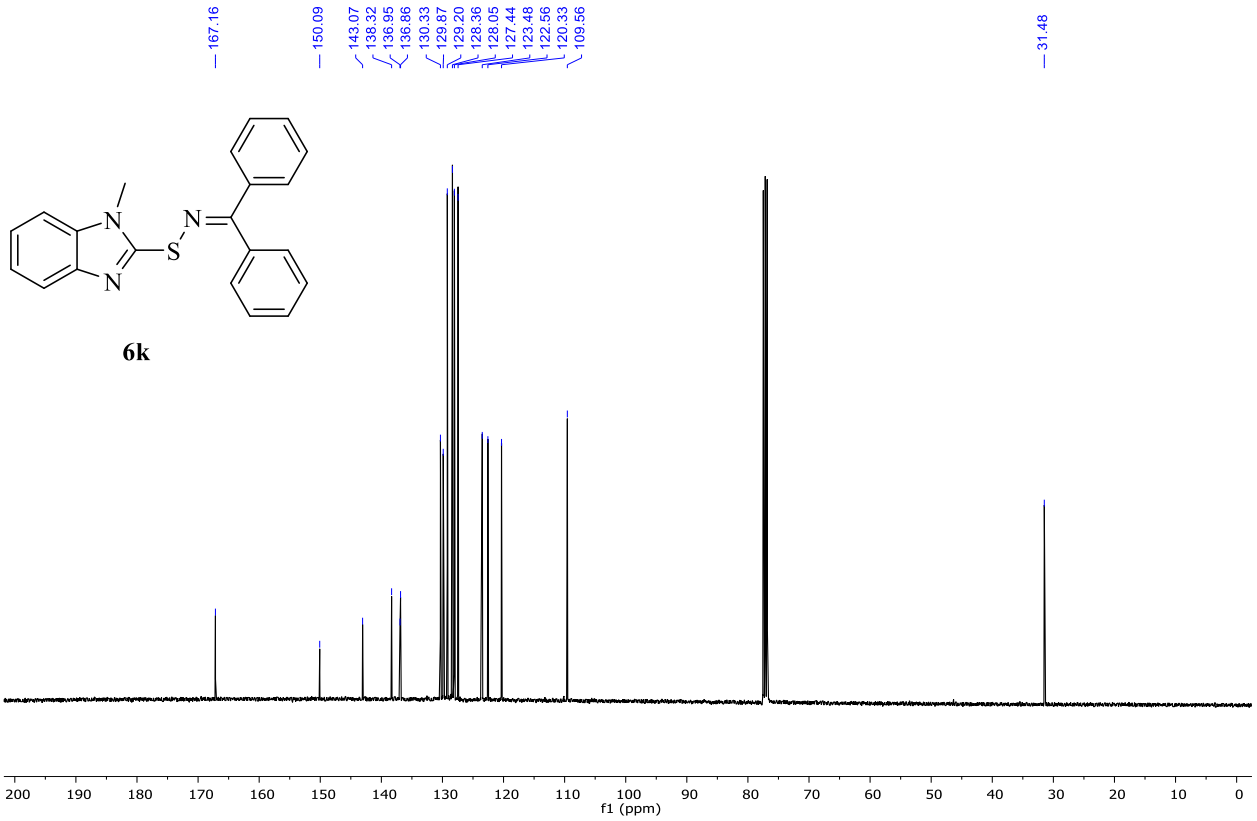


^{1}H NMR (400 MHz, $CDCl_3$) of **6k**



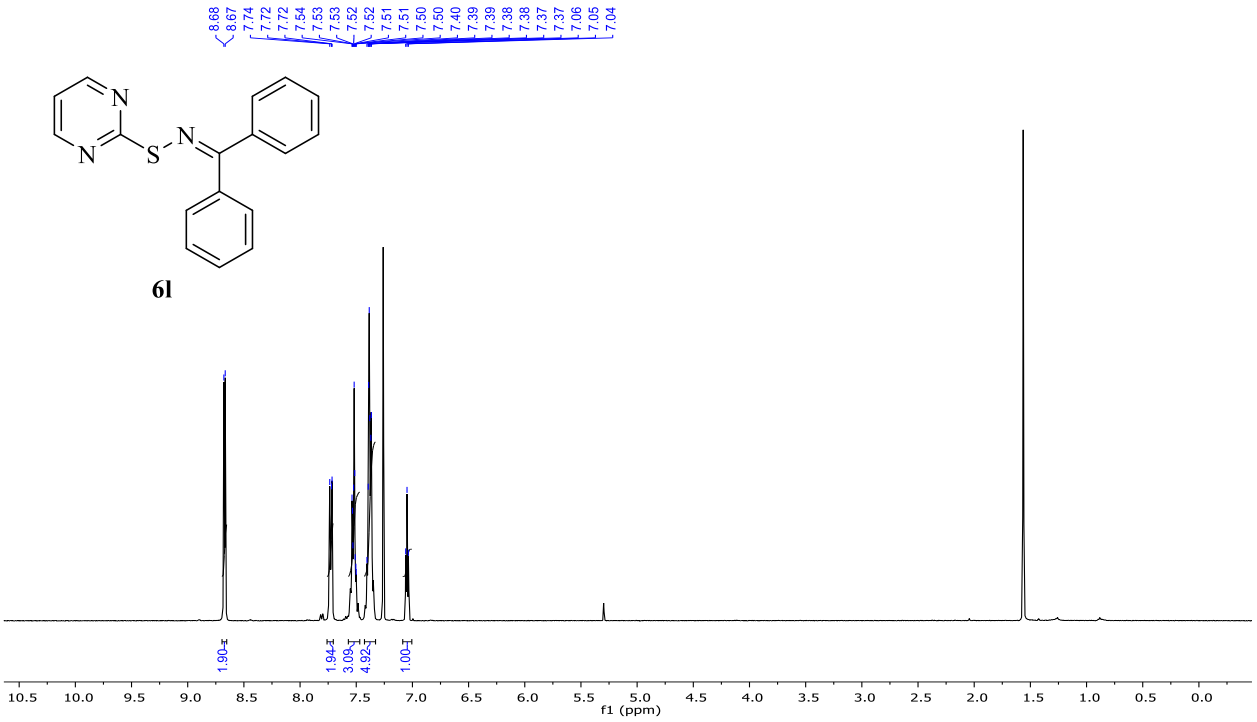
6k

^{13}C NMR (101 MHz, $CDCl_3$) of **6k**

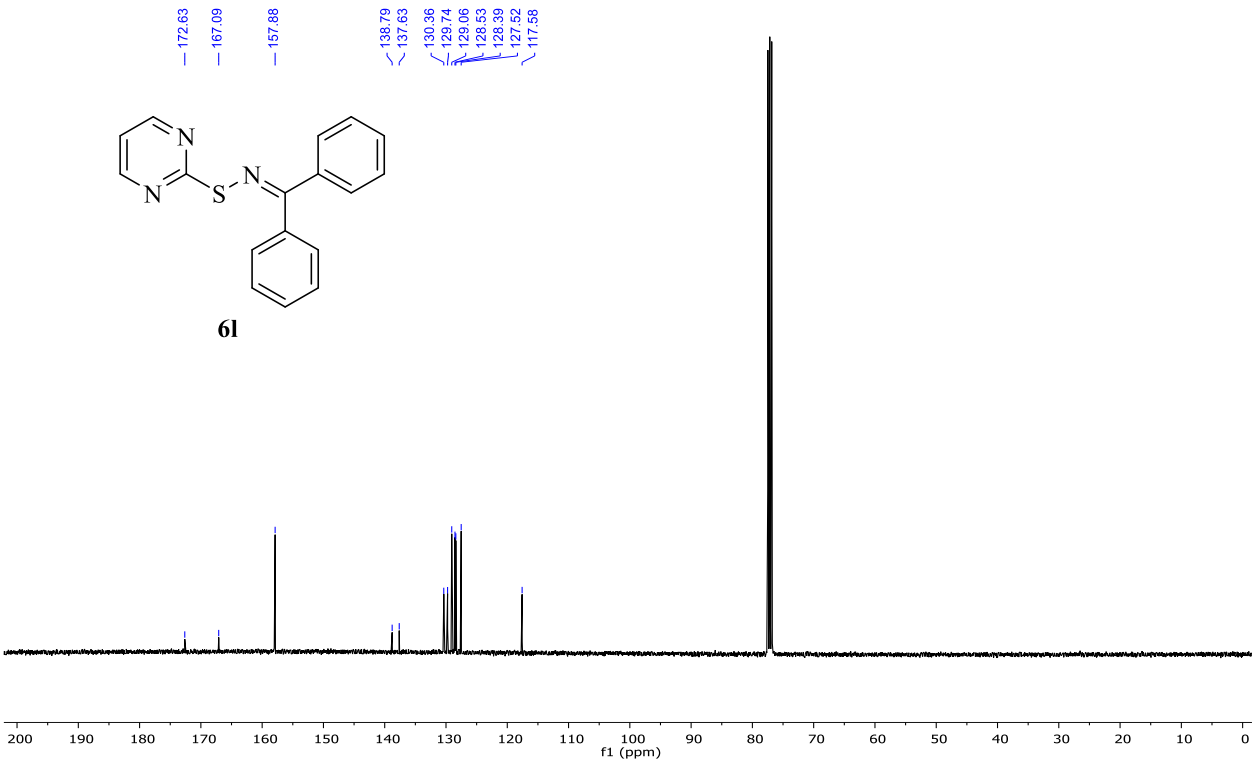


6k

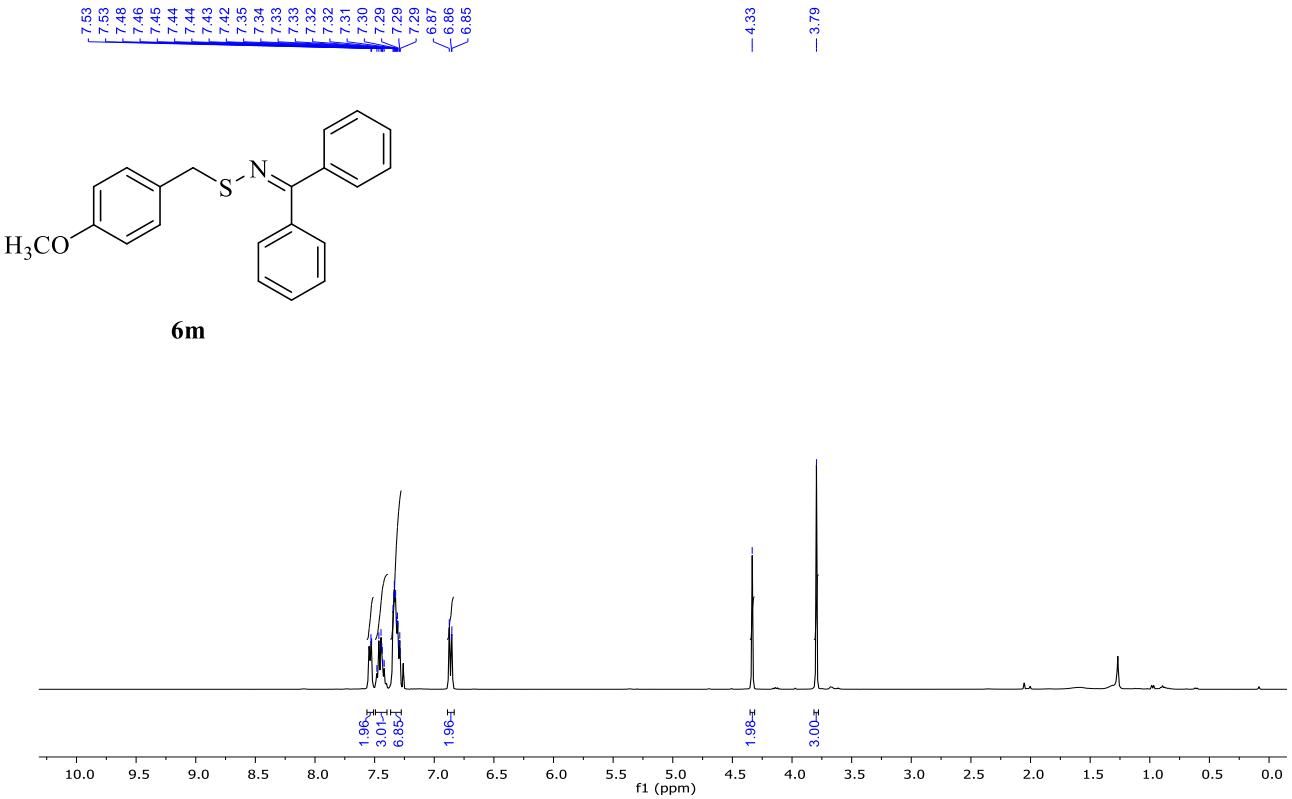
^{1}H NMR (400 MHz, $CDCl_3$) of **6l**



^{13}C NMR (101 MHz, $CDCl_3$) of **6l**

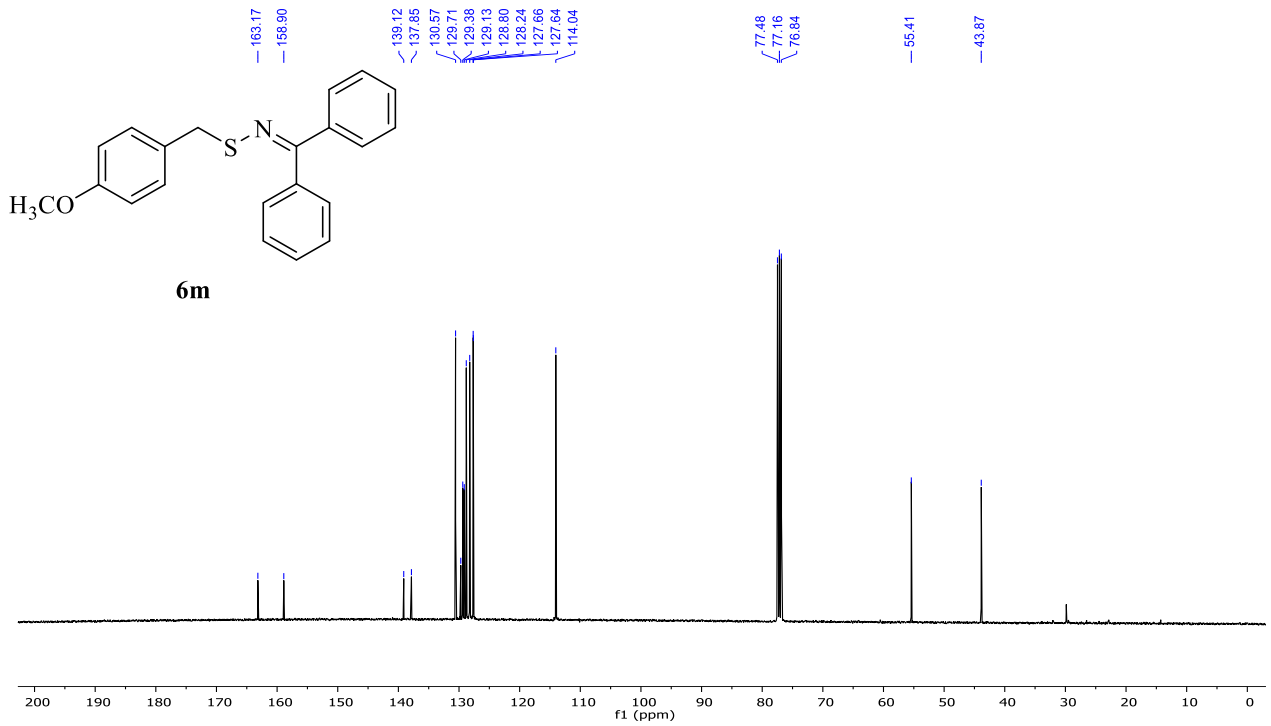


^{1}H NMR (400 MHz, $CDCl_3$) of **6m**



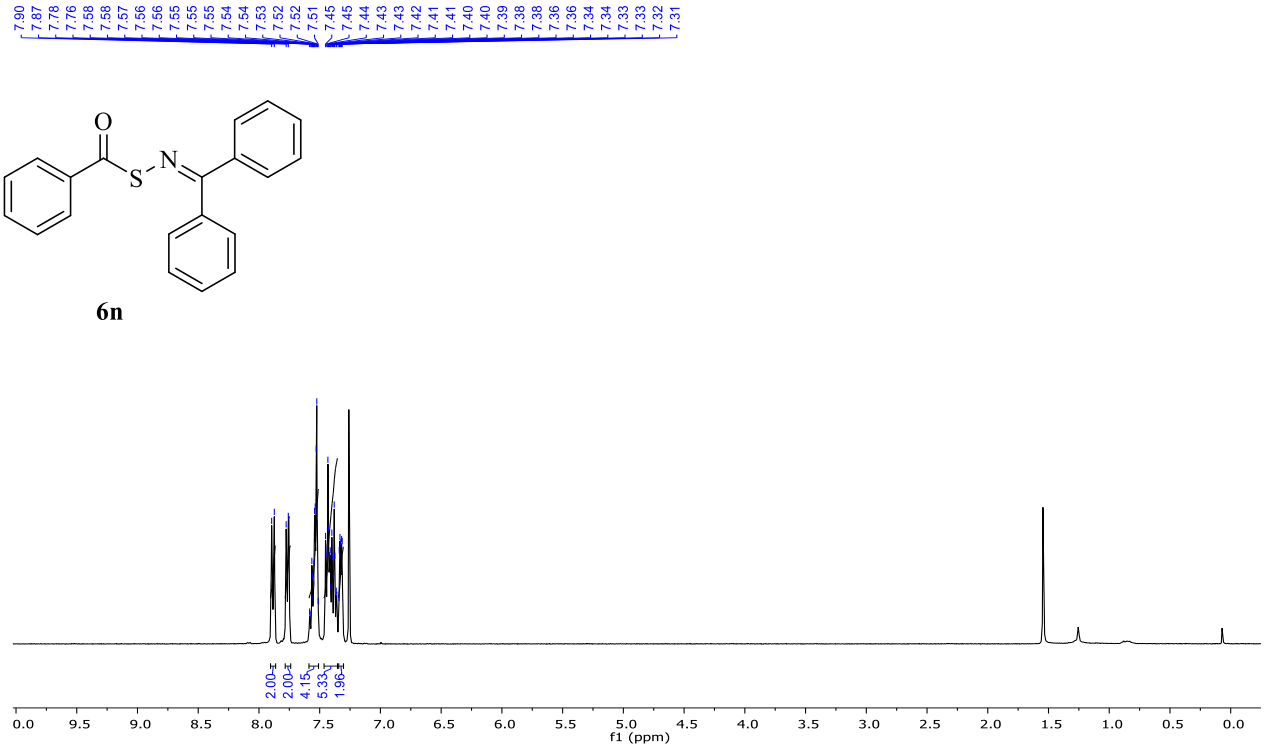
6m

^{13}C NMR (101 MHz, $CDCl_3$) of **6m**

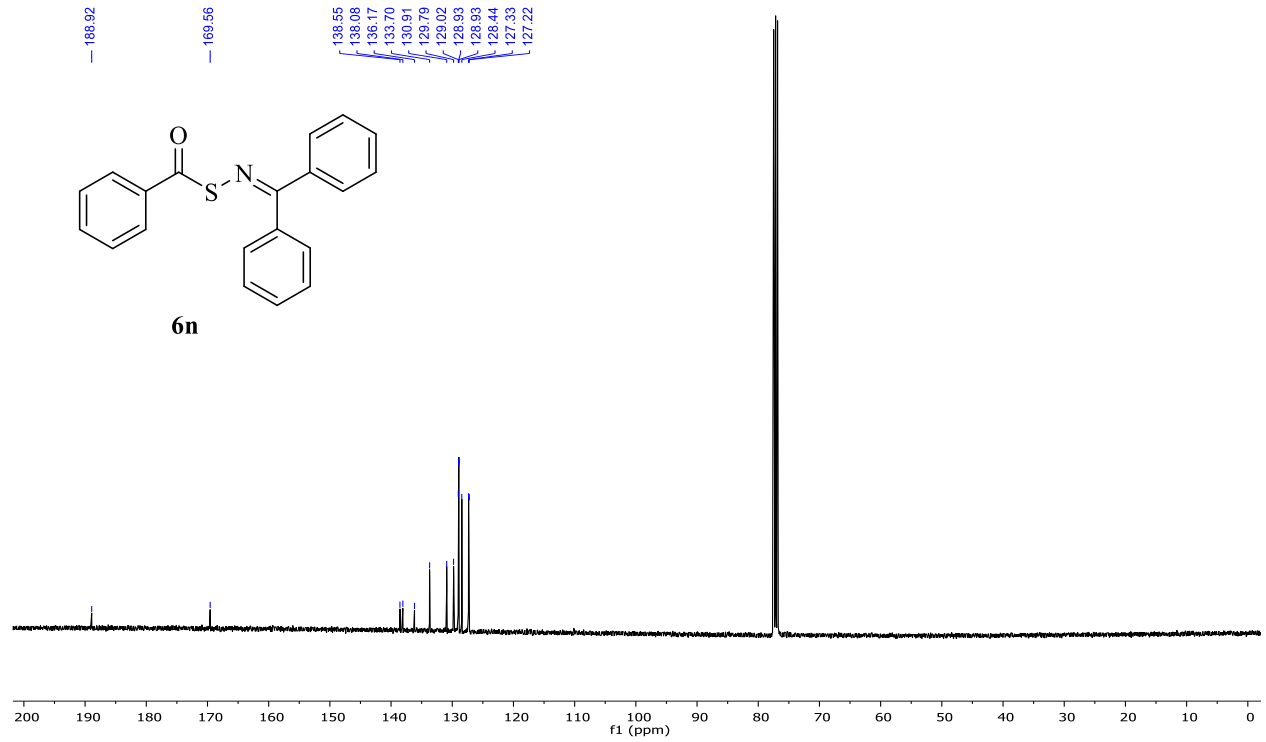


6m

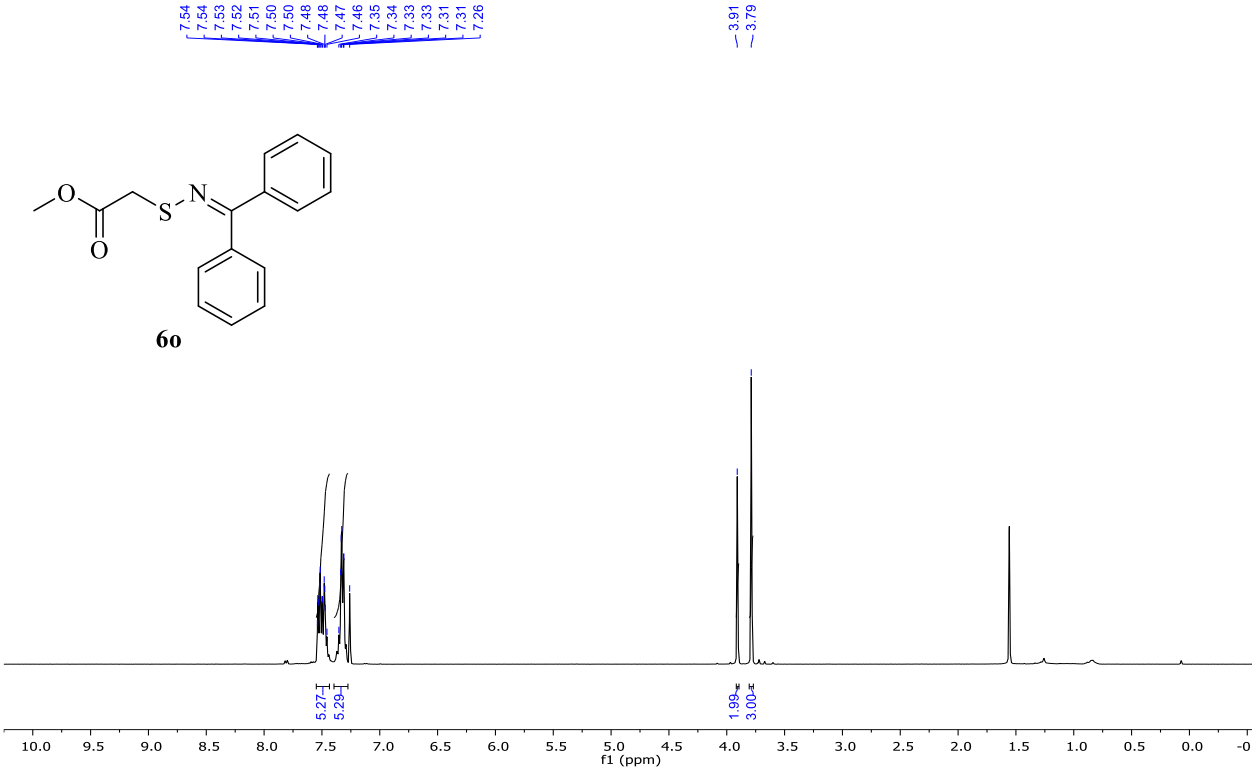
^{1}H NMR (400 MHz $CDCl_3$) of **6n**



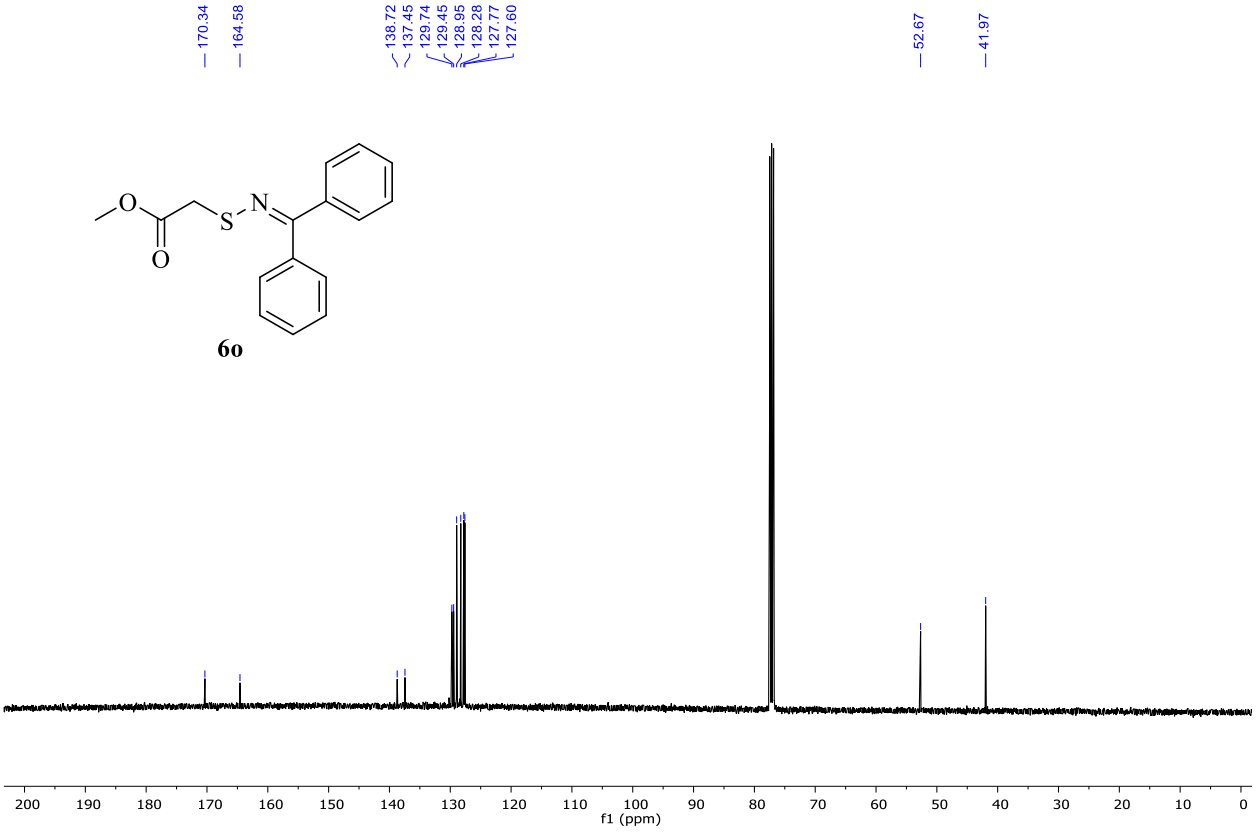
^{13}C NMR (101 MHz, $CDCl_3$) of **6n**



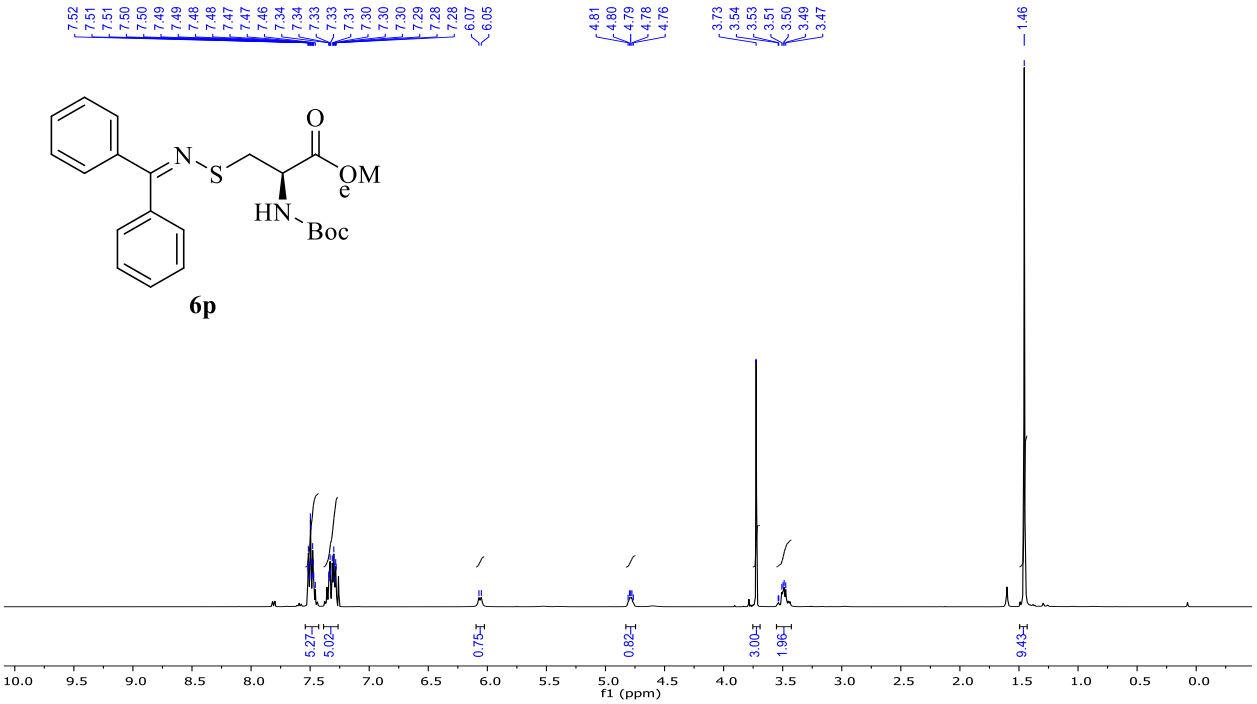
^{1}H NMR (400 MHz, $CDCl_3$) of **6o**



^{13}C NMR (101 MHz, $CDCl_3$) of **6o**

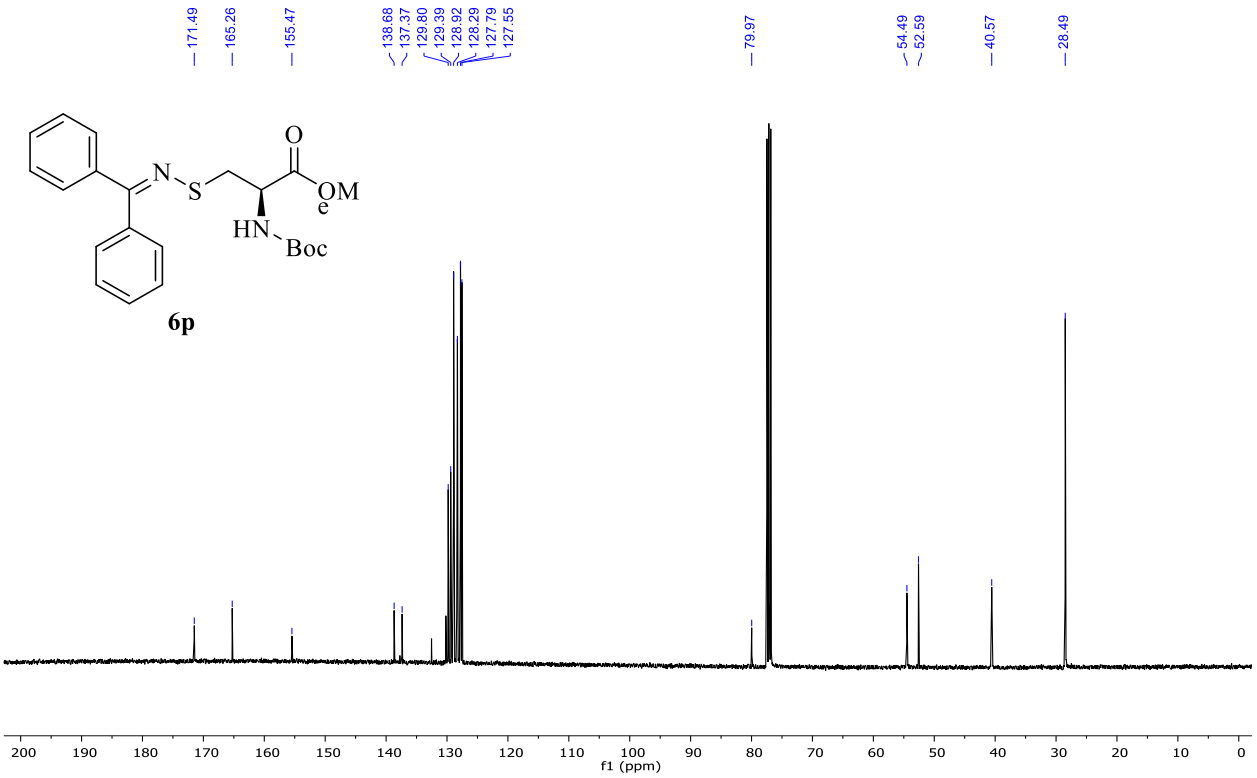


^{1}H NMR (400 MHz, $CDCl_3$) **of 6p**



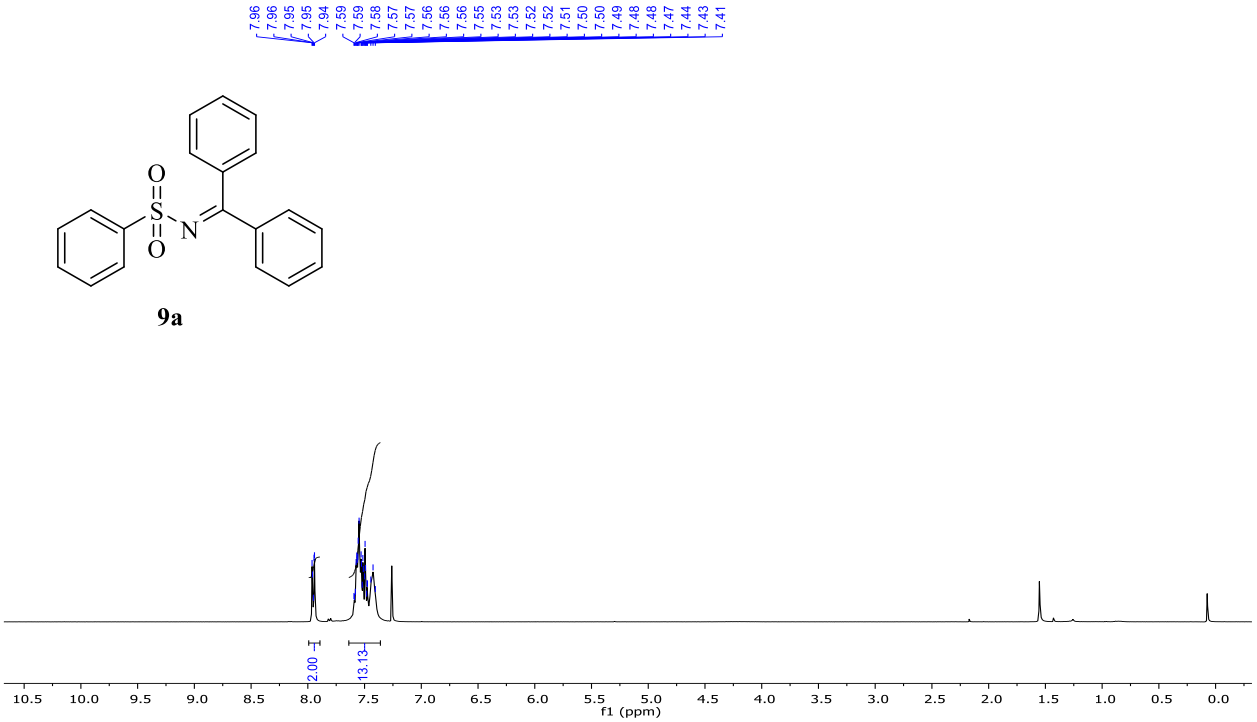
6p

^{13}C NMR (101 MHz, $CDCl_3$) of **6p**

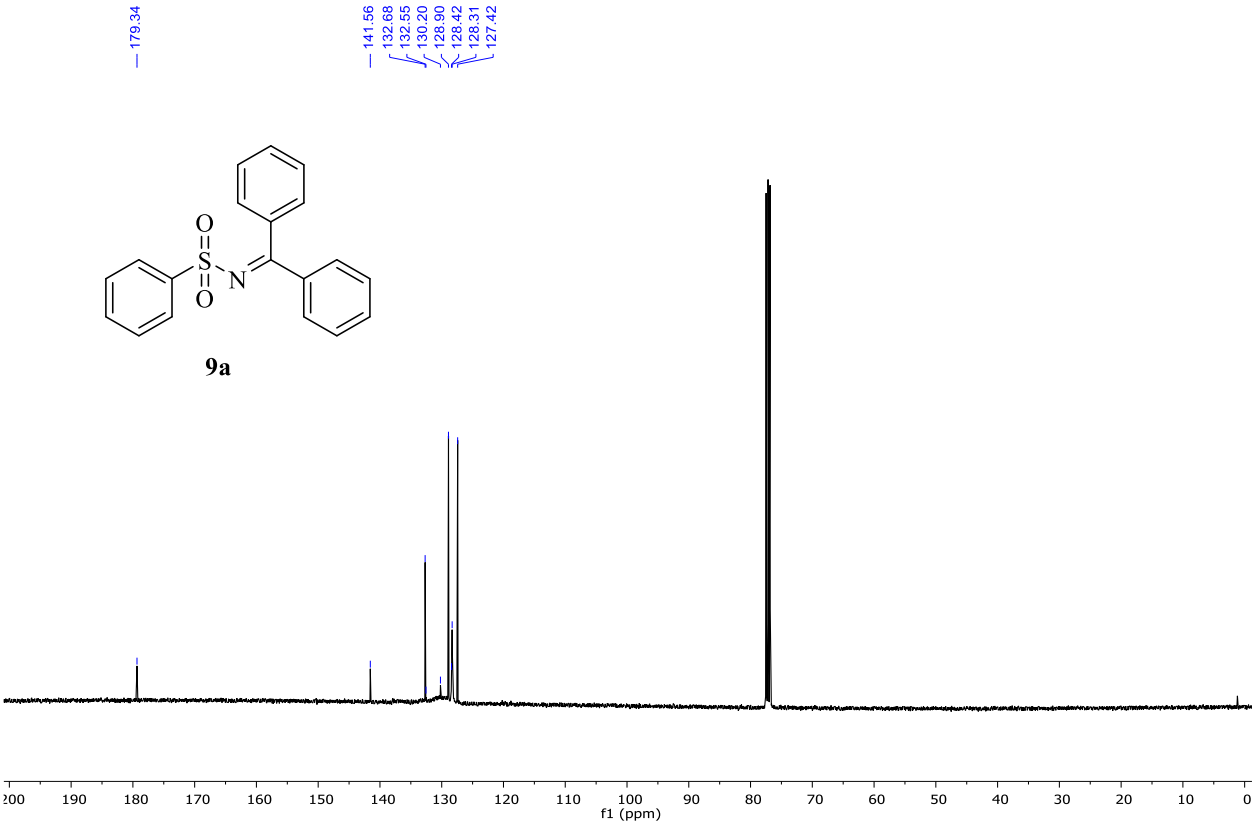


6p

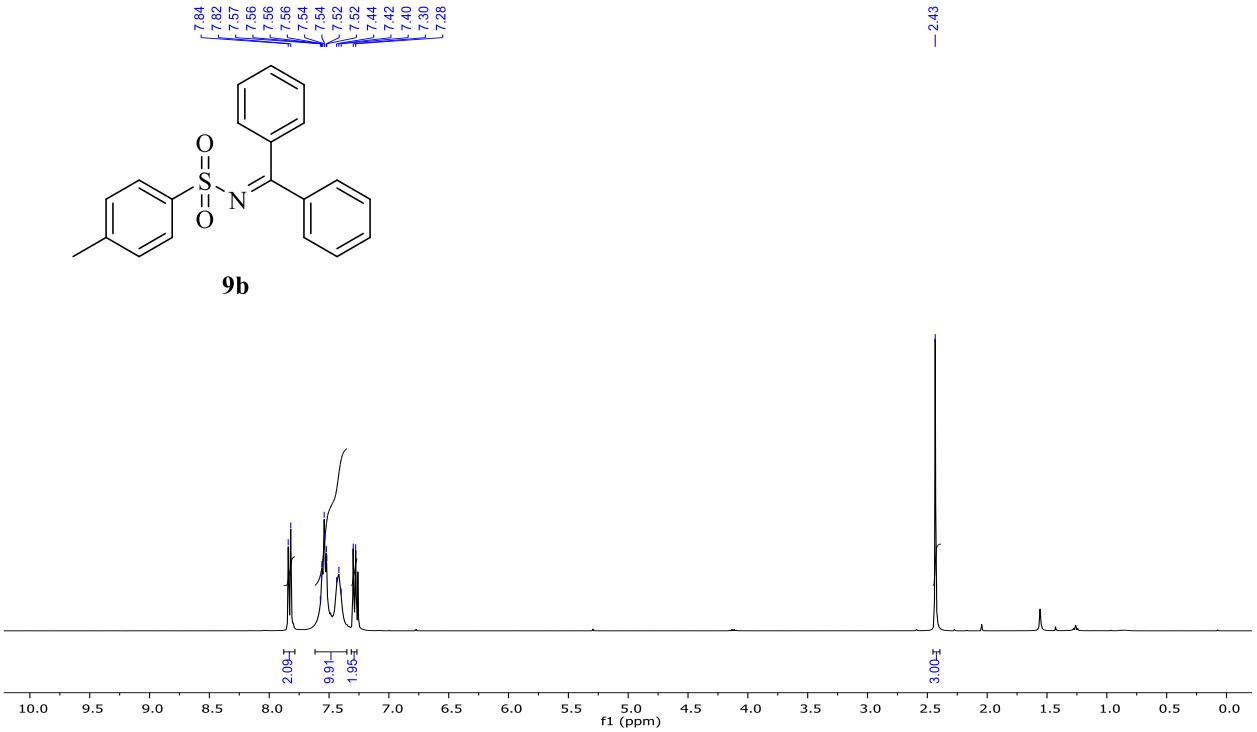
^{1}H NMR (400 MHz, $CDCl_3$) of **9a**



^{13}C NMR (101 MHz, $CDCl_3$) of **9a**

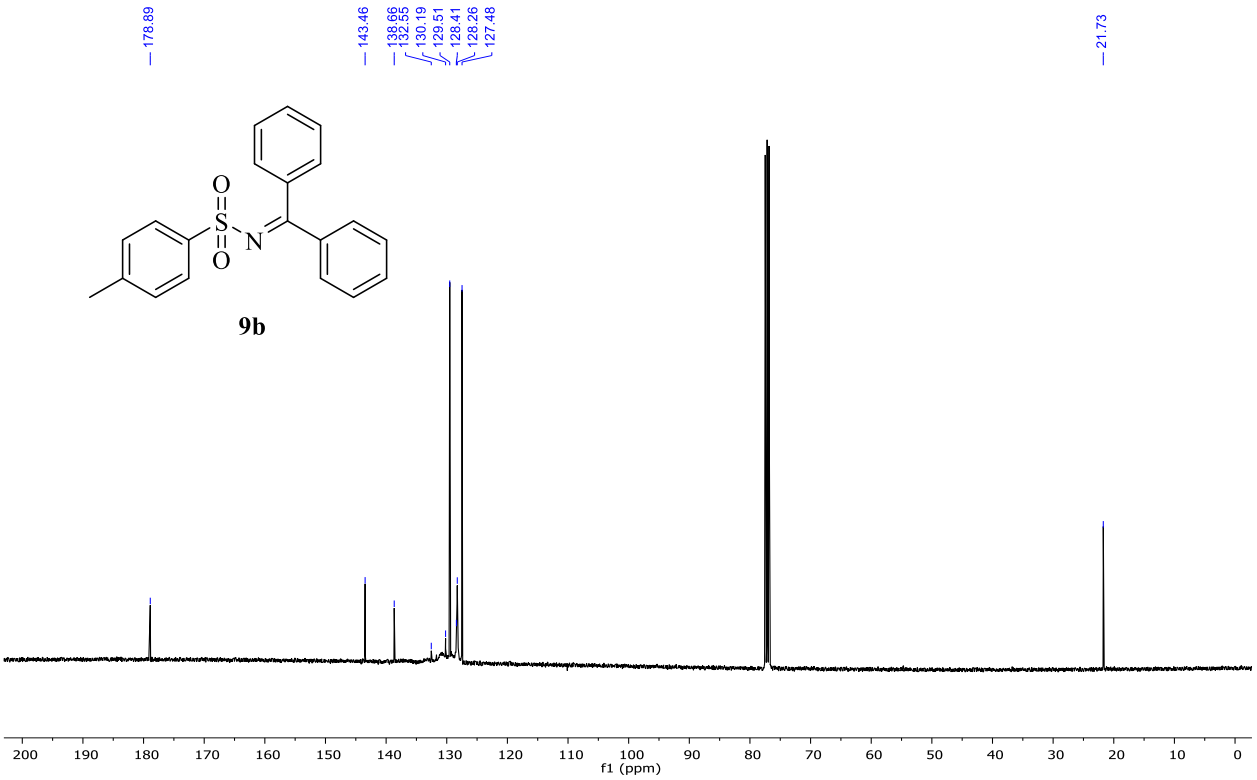


^{1}H NMR (400 MHz, $CDCl_3$) of **9b**



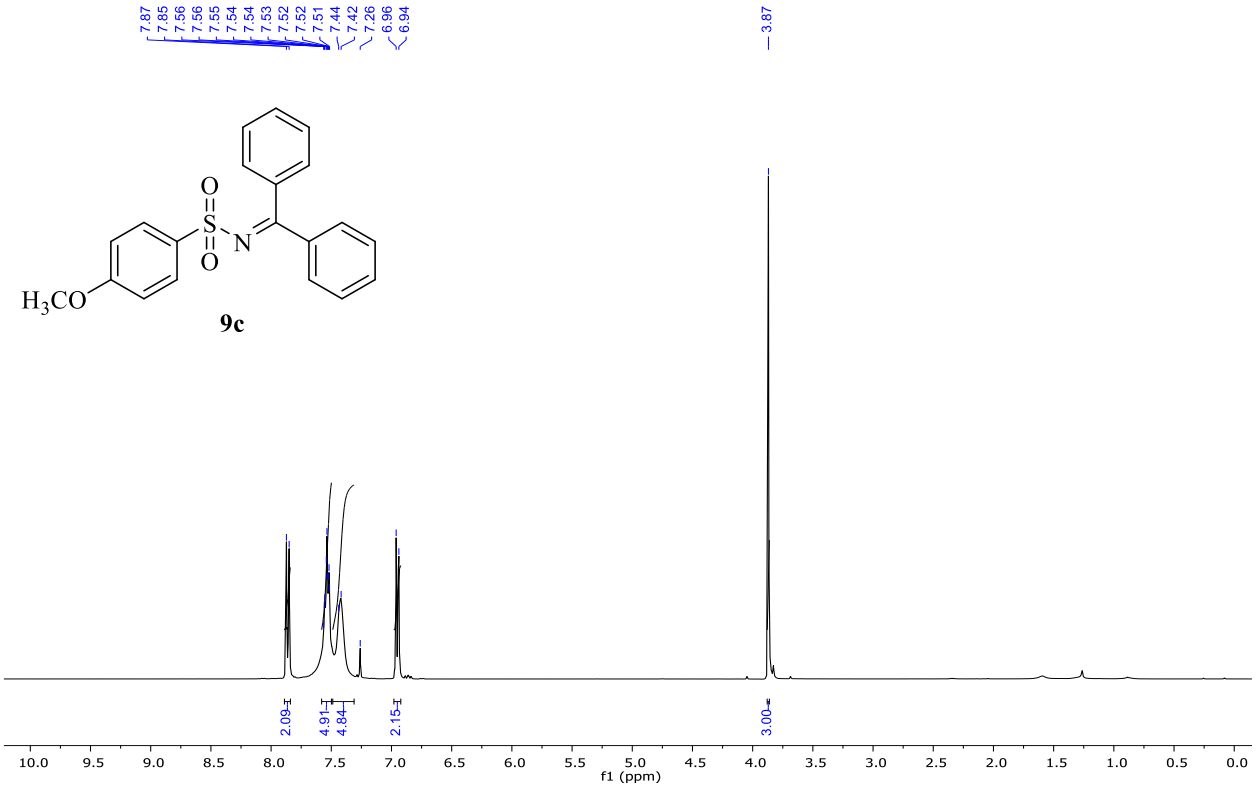
9b

^{13}C NMR (101 MHz, $CDCl_3$) of **9b**

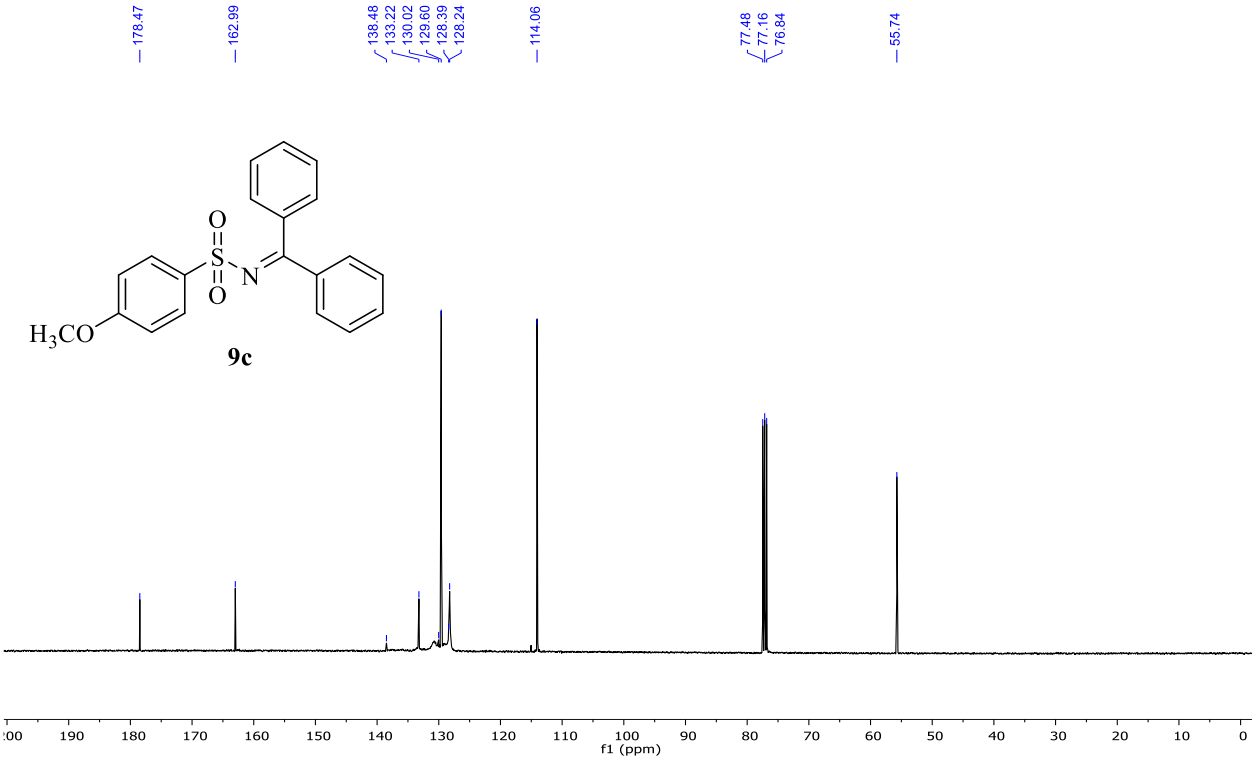


9b

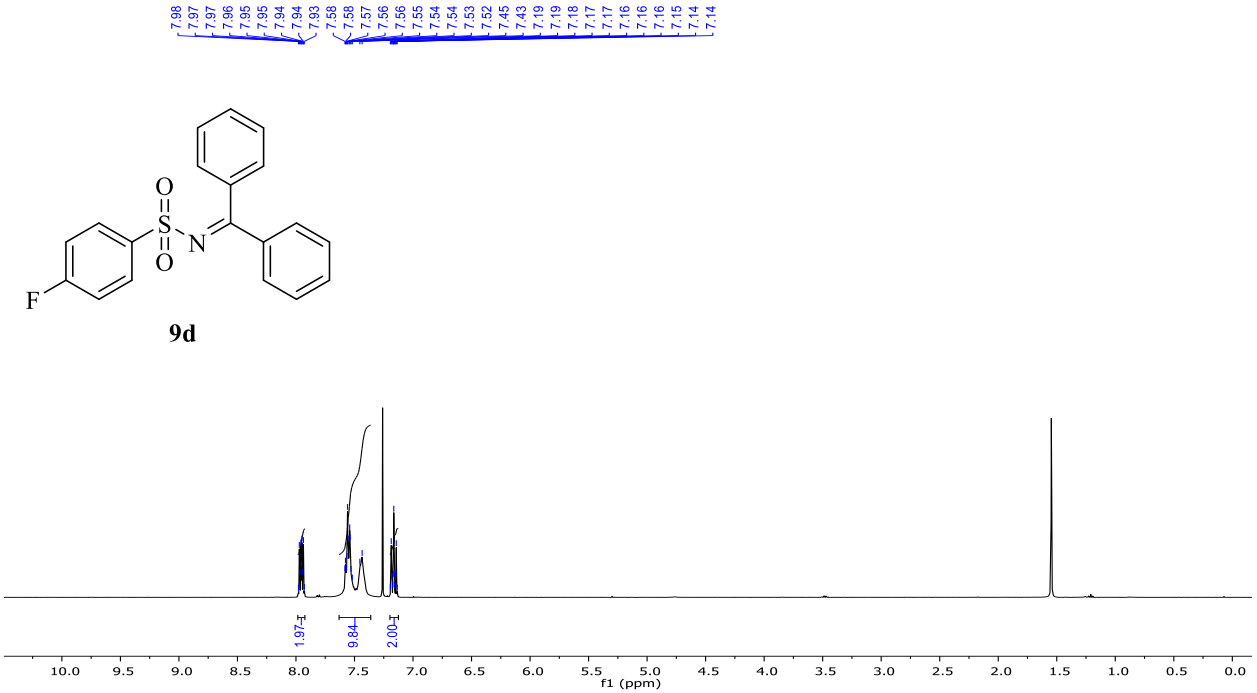
^{1}H NMR (400 MHz, $CDCl_3$) of **9c**



^{13}C NMR (101 MHz, $CDCl_3$) of **9c**

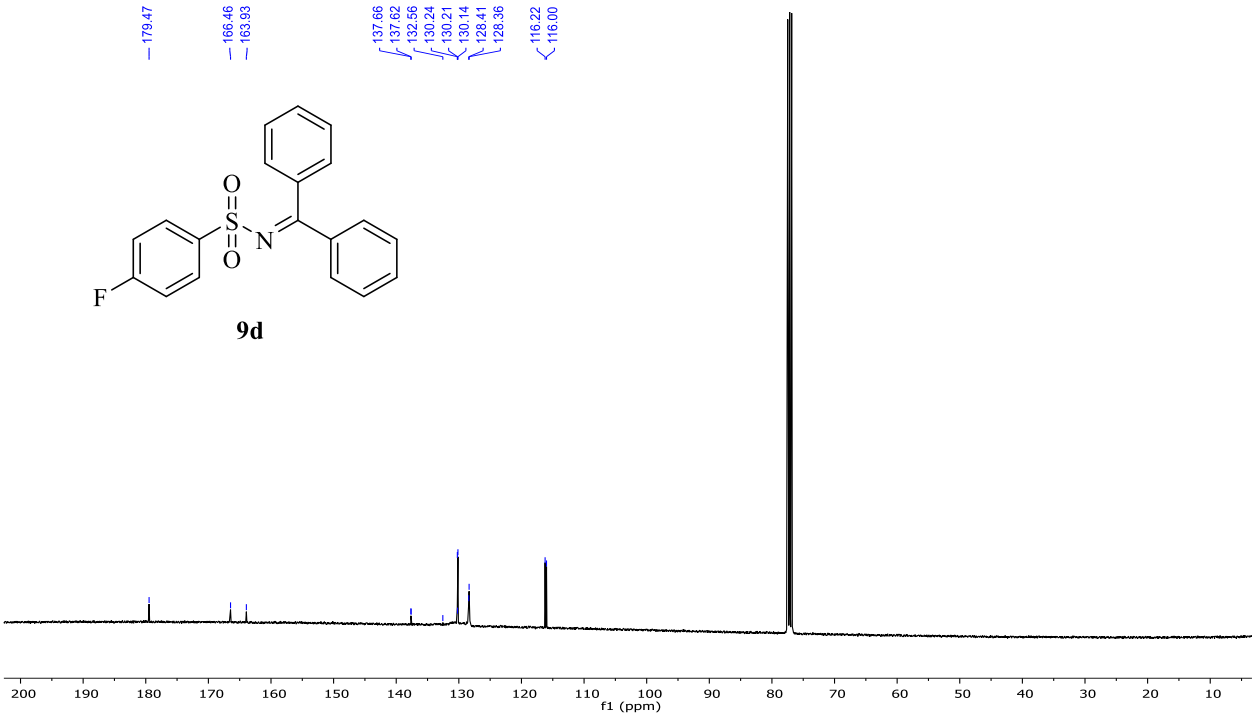


^{1}H NMR (400 MHz, $CDCl_3$) of **9d**



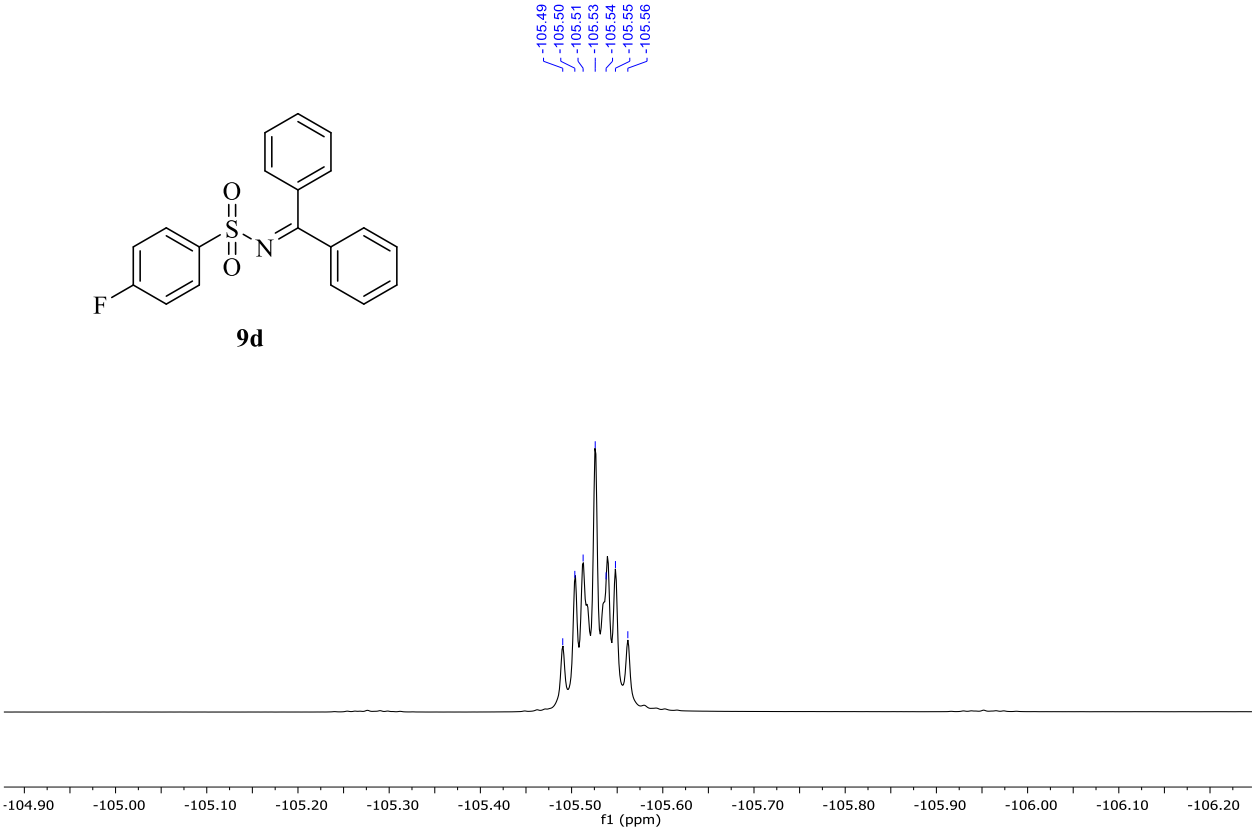
9d

^{13}C NMR (101 MHz, $CDCl_3$) of **9d**



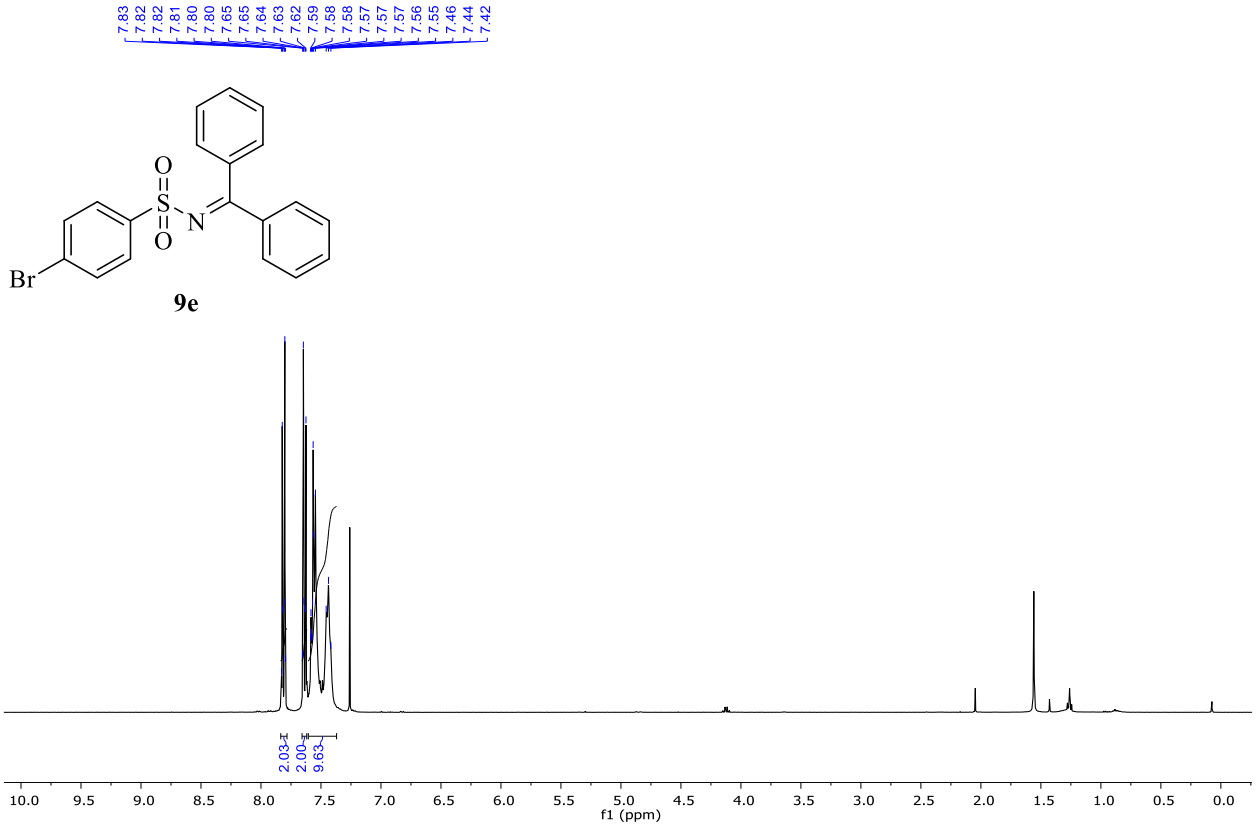
9d

^{19}F NMR (377 MHz, $CDCl_3$) of **9d**



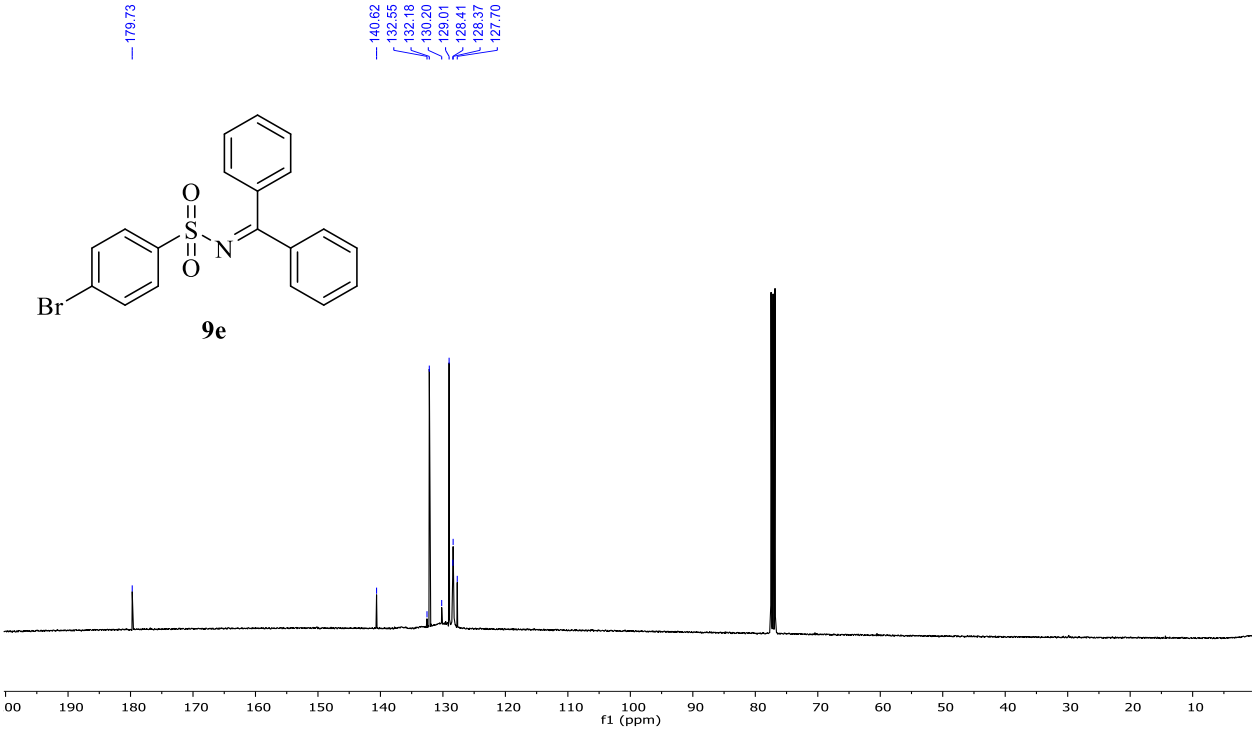
9d

^{1}H NMR (400 MHz, $CDCl_3$) of **9e**

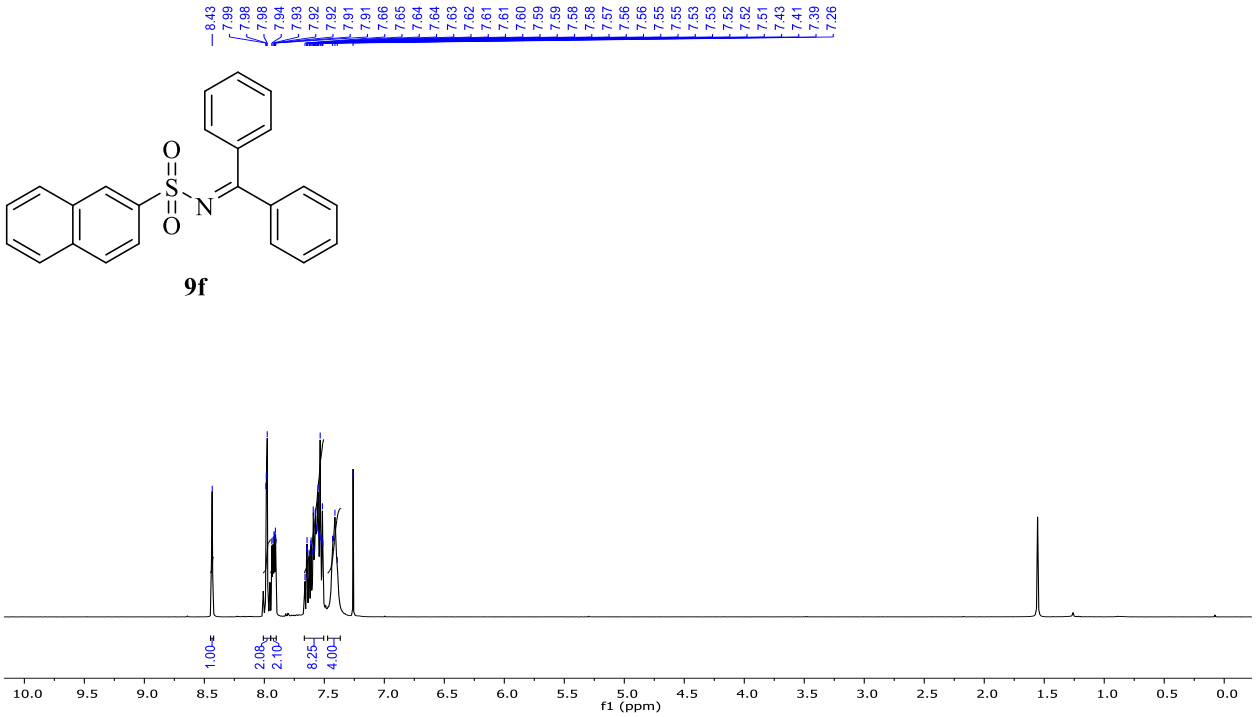


9e

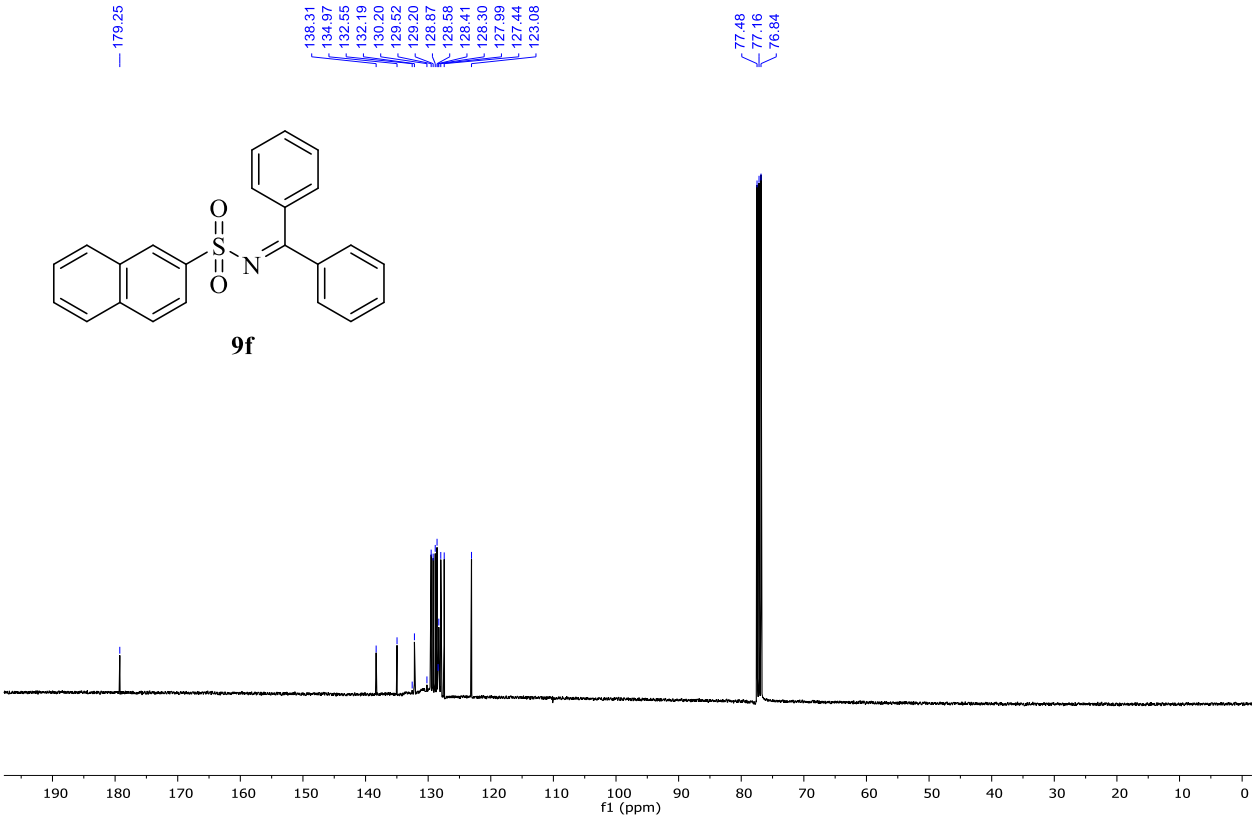
^{13}C NMR (101 MHz, $CDCl_3$) of **9e**



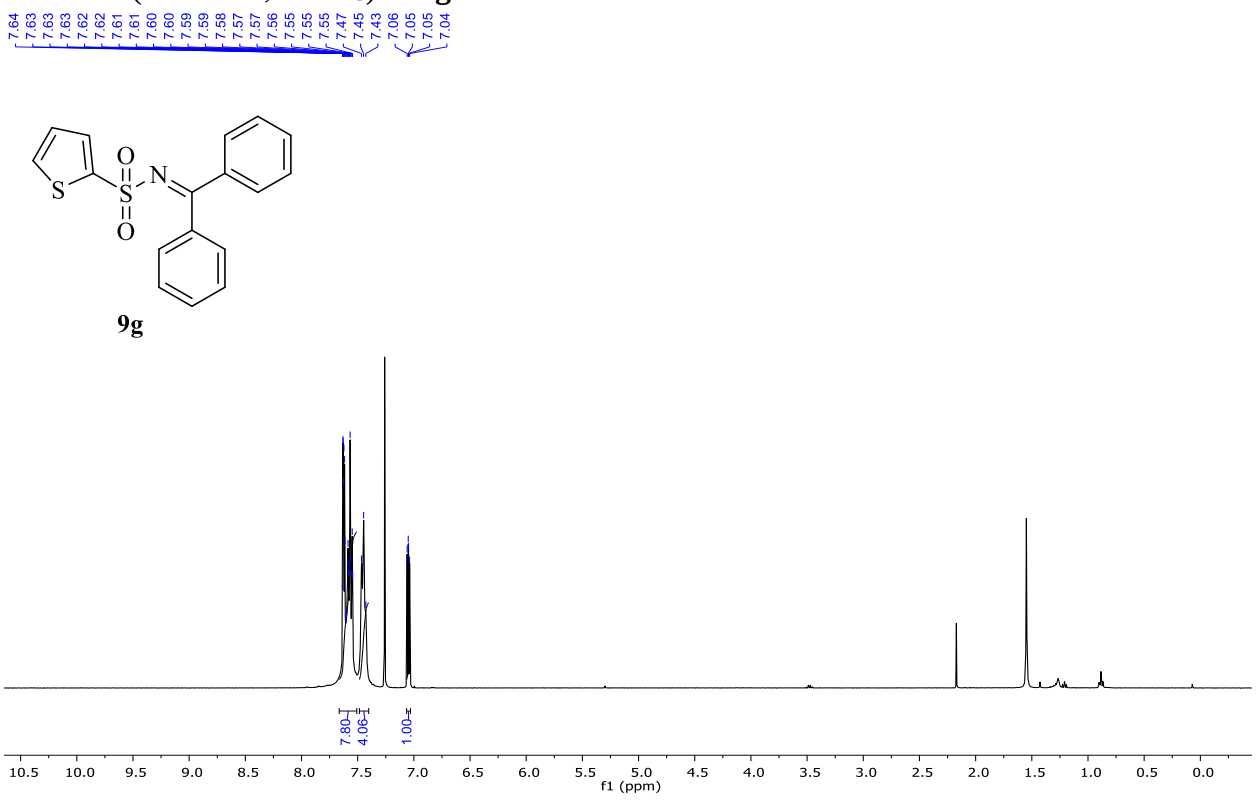
^{1}H NMR (400 MHz, $CDCl_3$) of **9f**



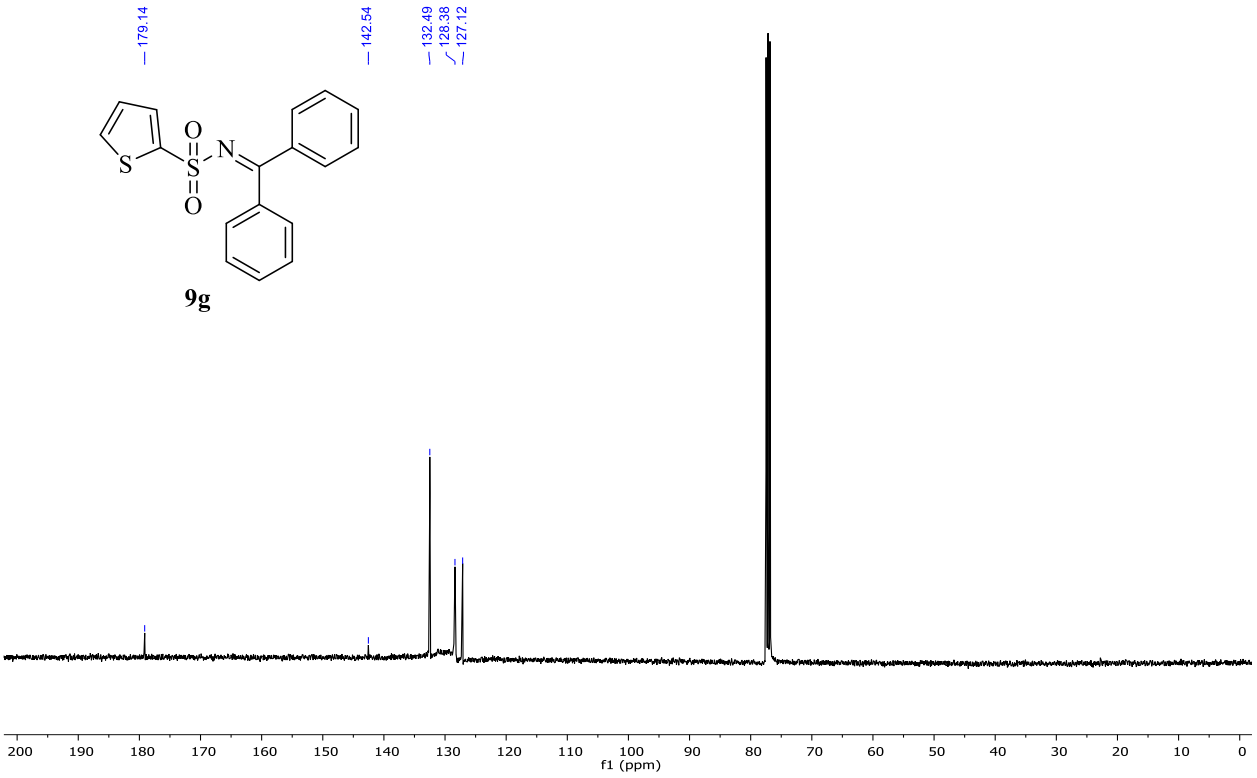
^{13}C NMR (101 MHz, $CDCl_3$) of **9f**



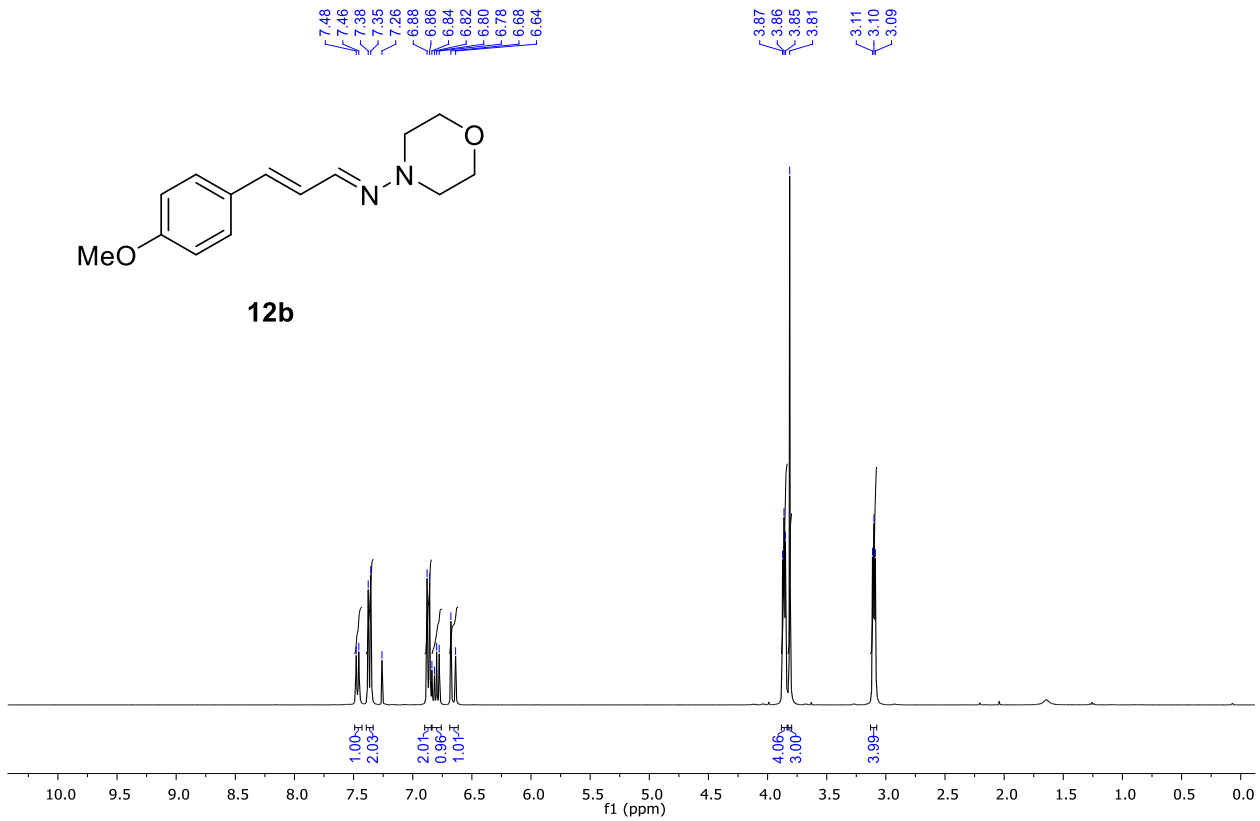
^{1}H NMR (400 MHz, $CDCl_3$) of **9g**



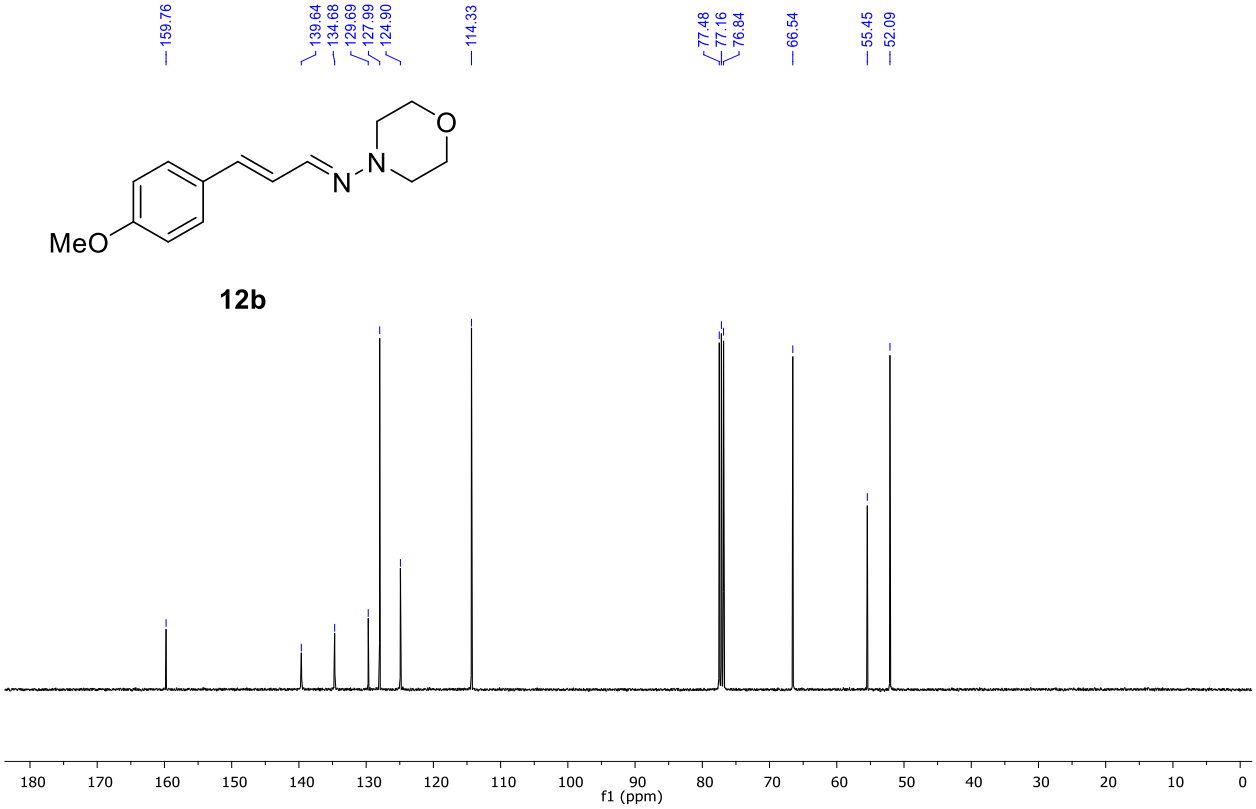
^{13}C NMR (101 MHz, $CDCl_3$) of **9g**



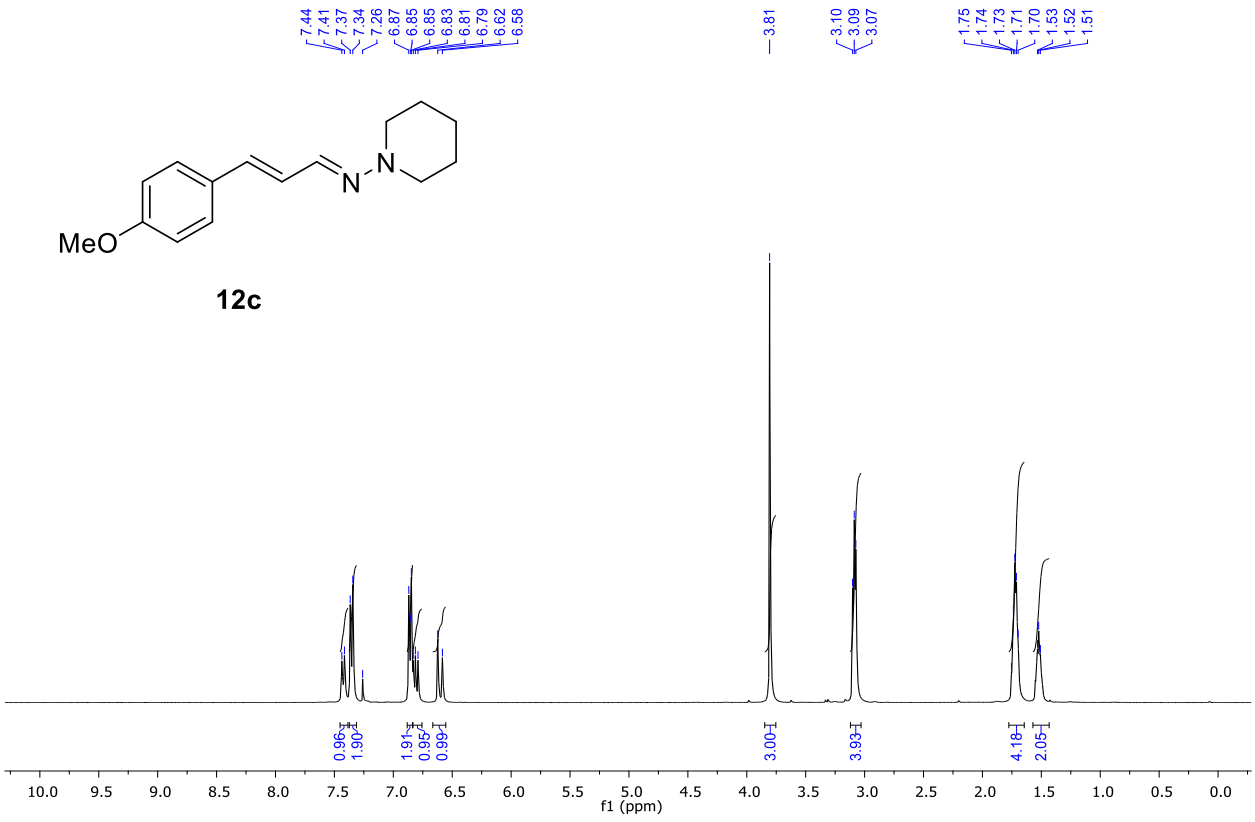
^{1}H NMR (400 MHz, $CDCl_3$) of **12b**



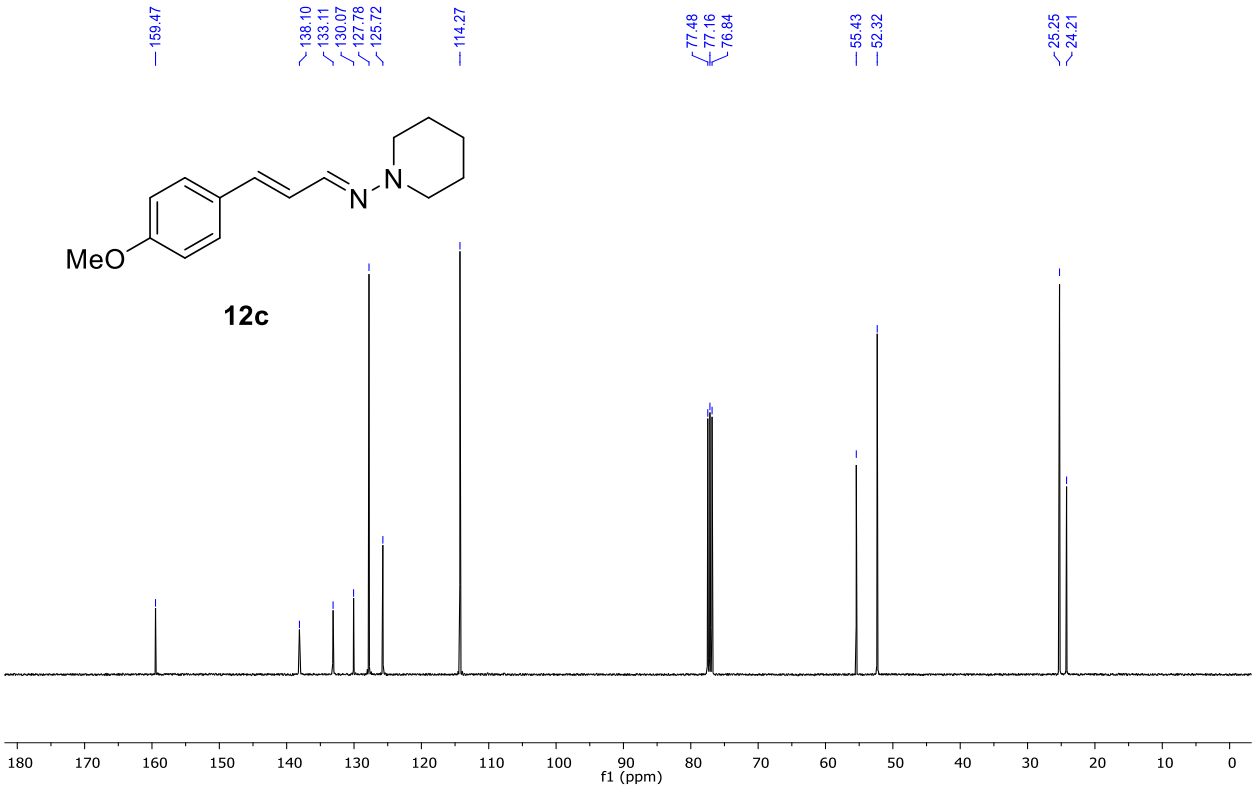
^{13}C NMR (101 MHz, $CDCl_3$) of **12b**



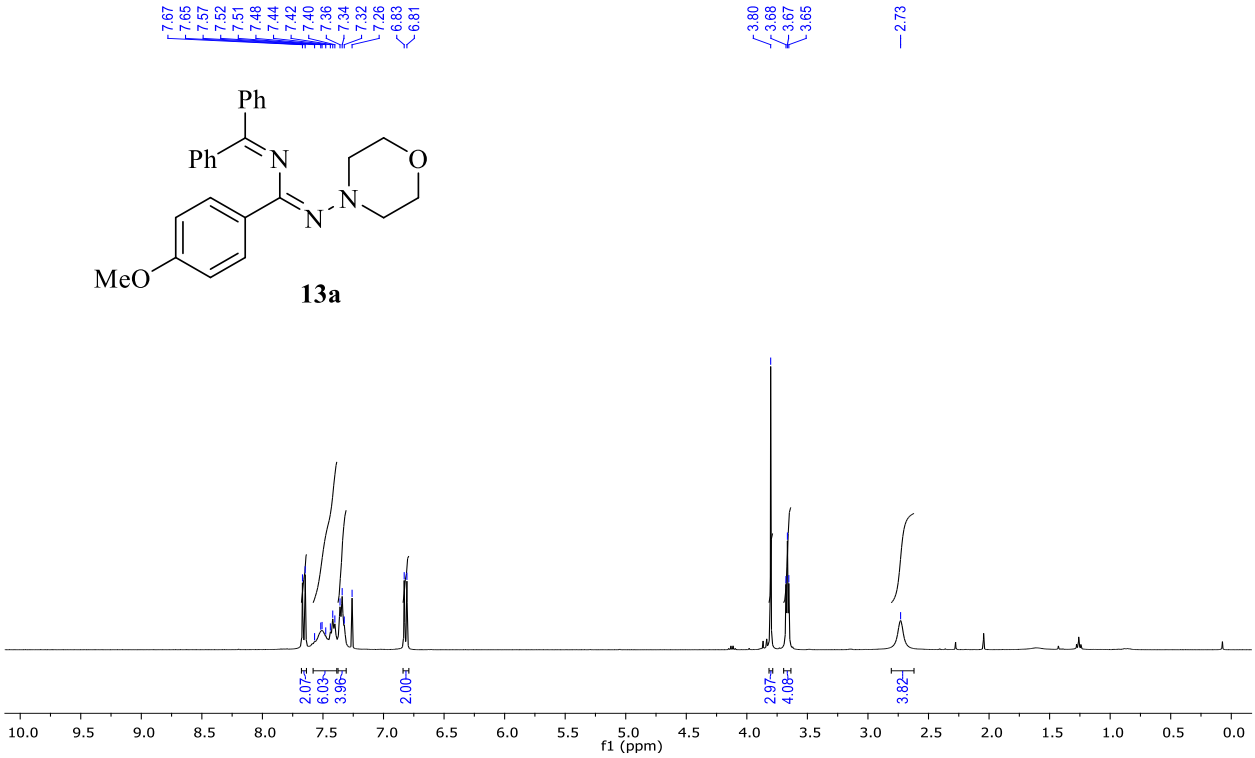
^{1}H NMR (400 MHz, $CDCl_3$) of **12c**



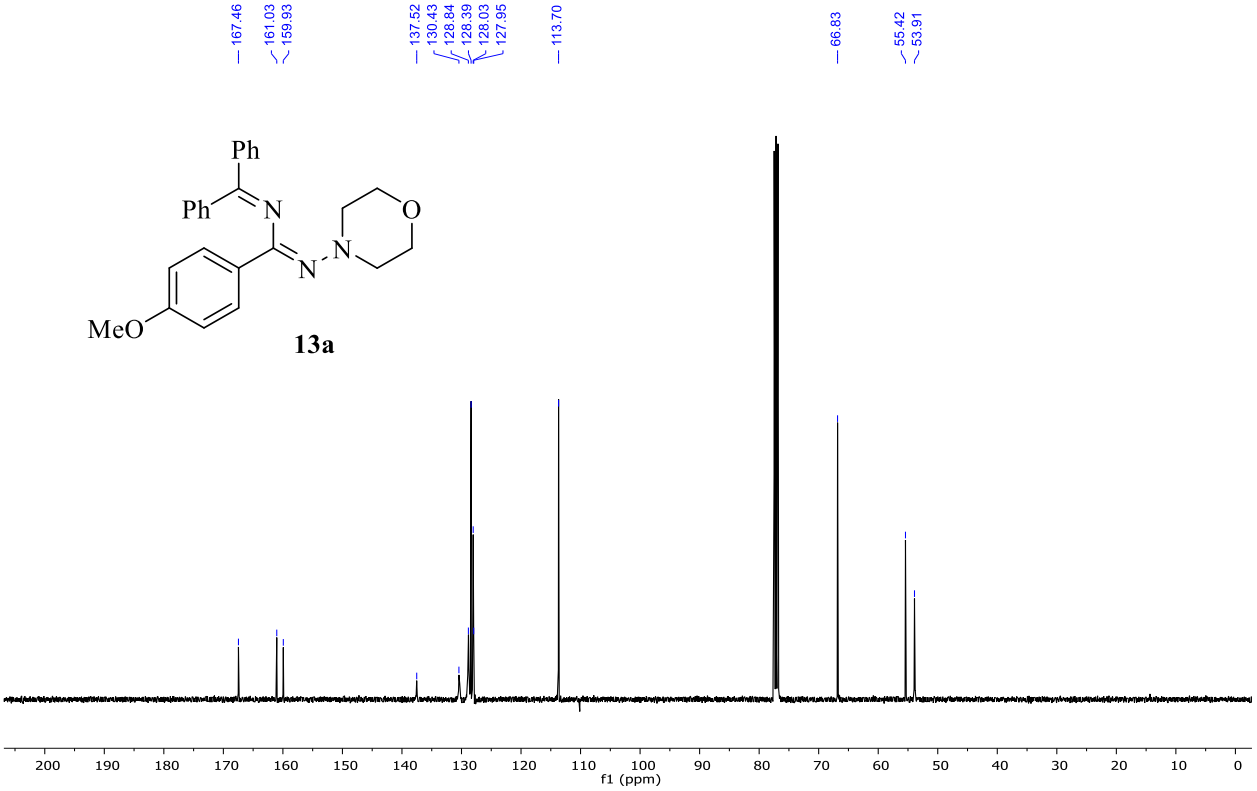
^{13}C NMR (101 MHz, $CDCl_3$) of **12c**



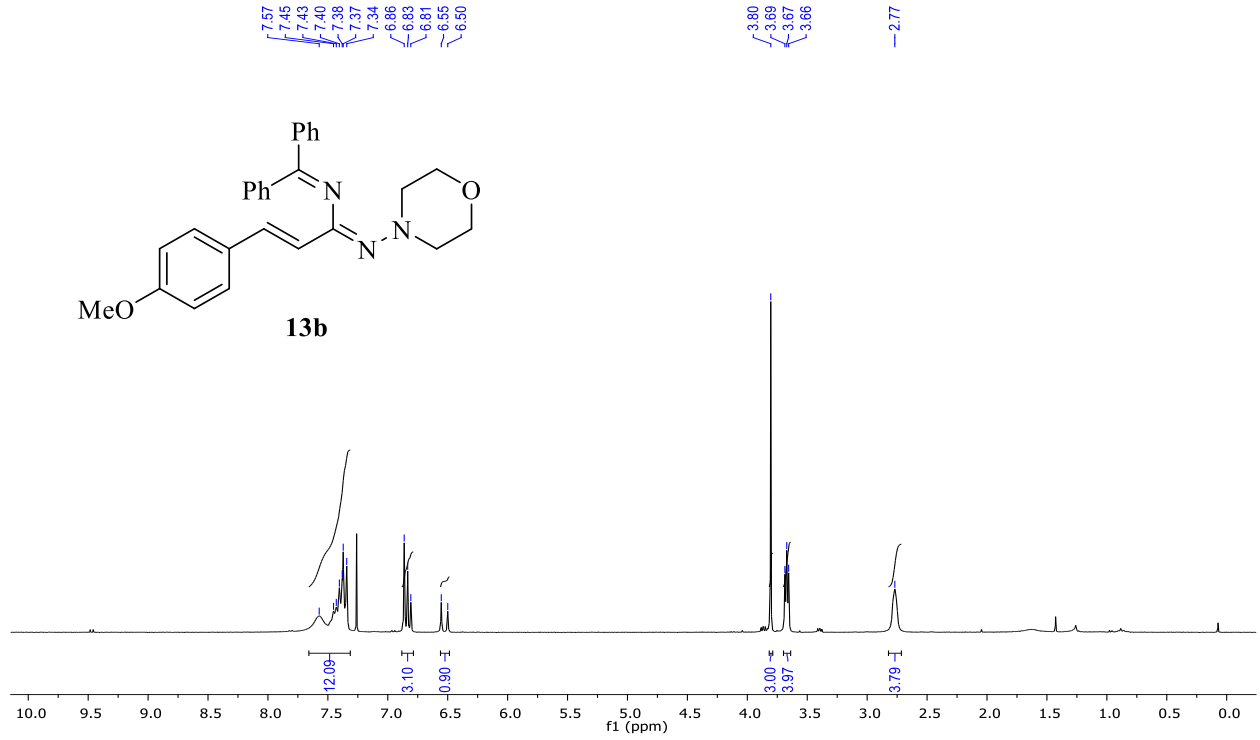
^{1}H NMR (400 MHz, $CDCl_3$) of **13a**



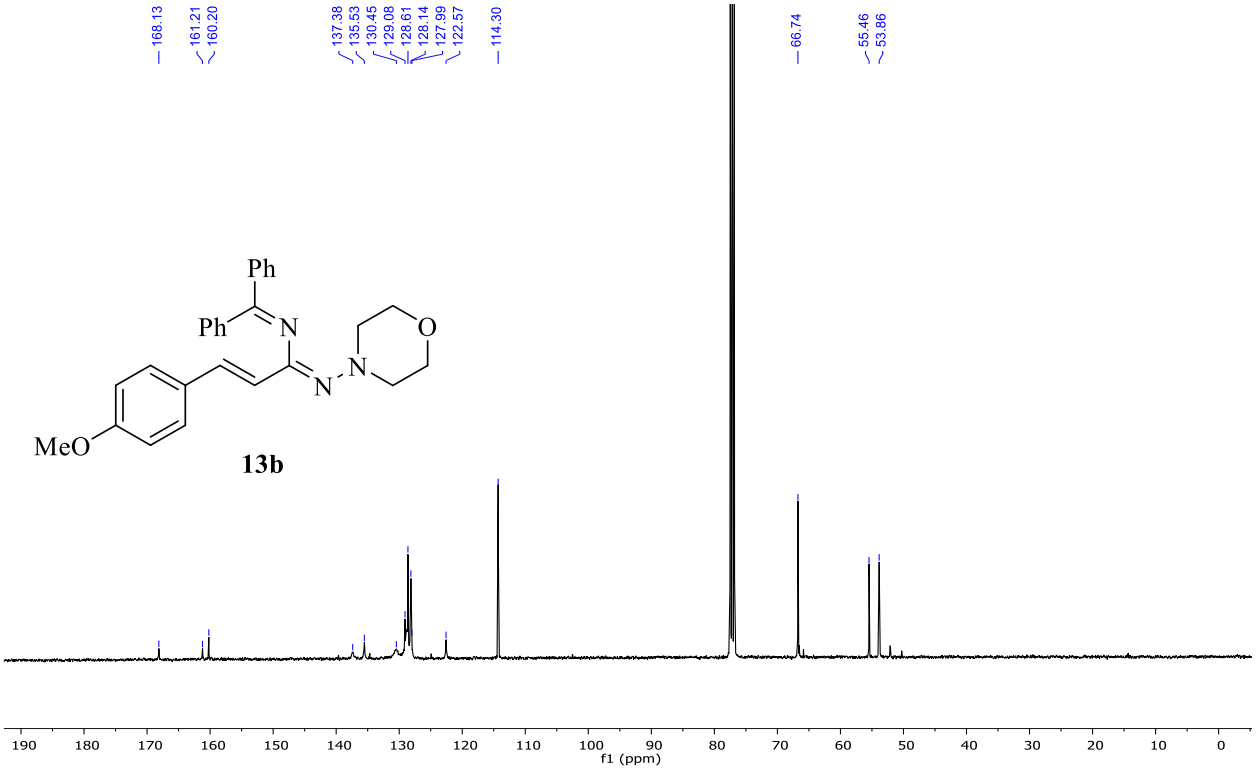
^{13}C NMR (101 MHz, $CDCl_3$) of **13a**



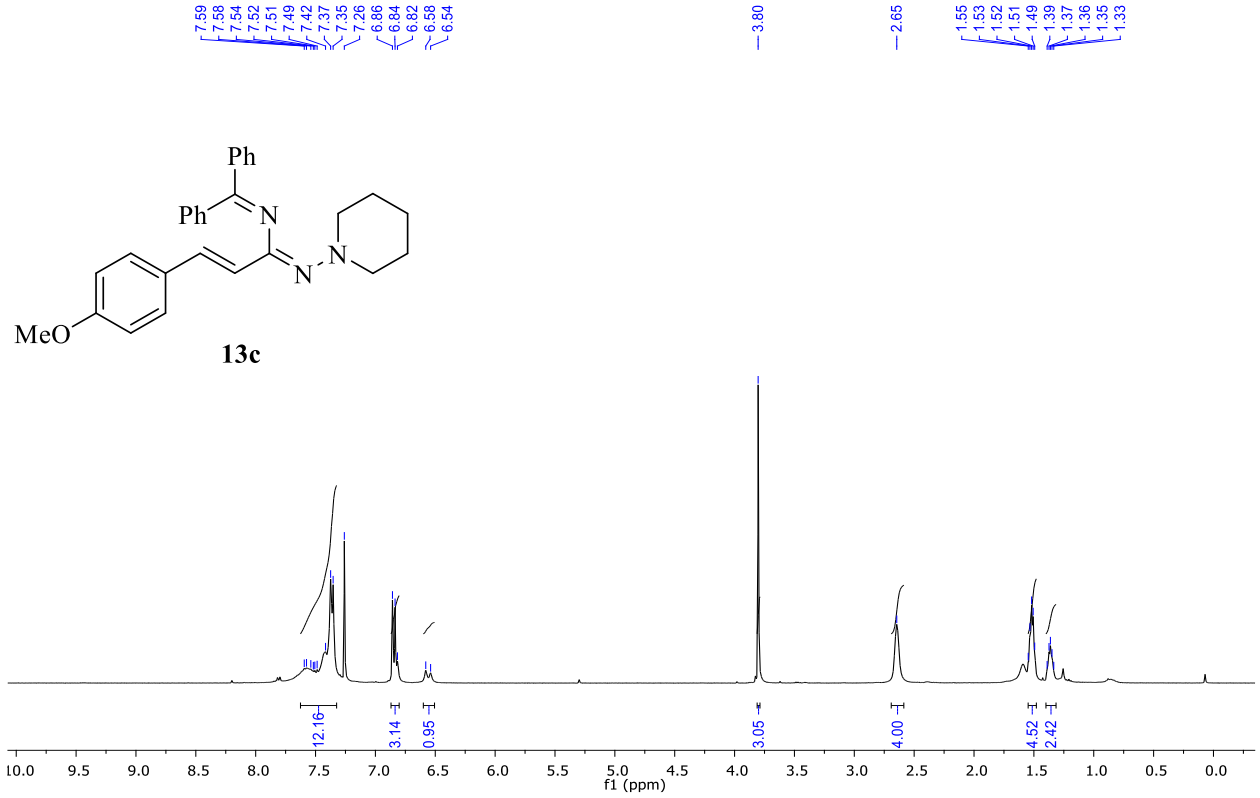
^{1}H NMR (400 MHz, $CDCl_3$) of **13b**



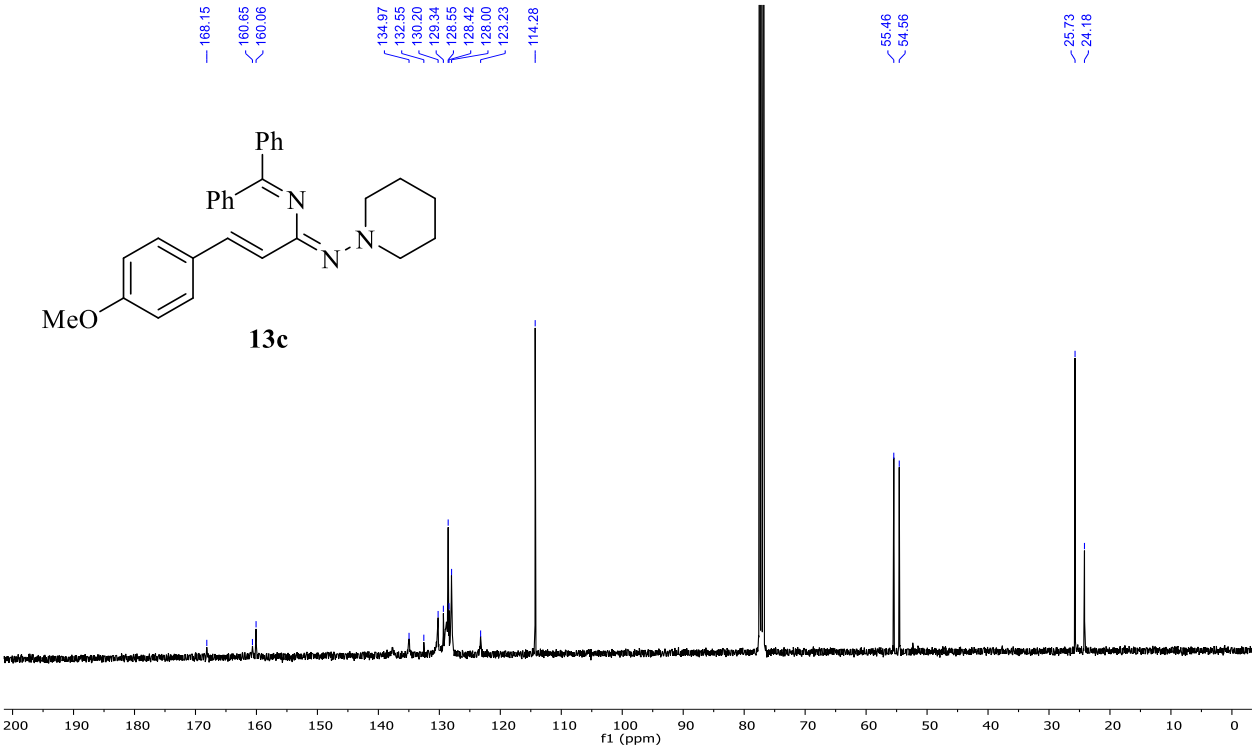
^{13}C NMR (101 MHz, $CDCl_3$) of **13b**



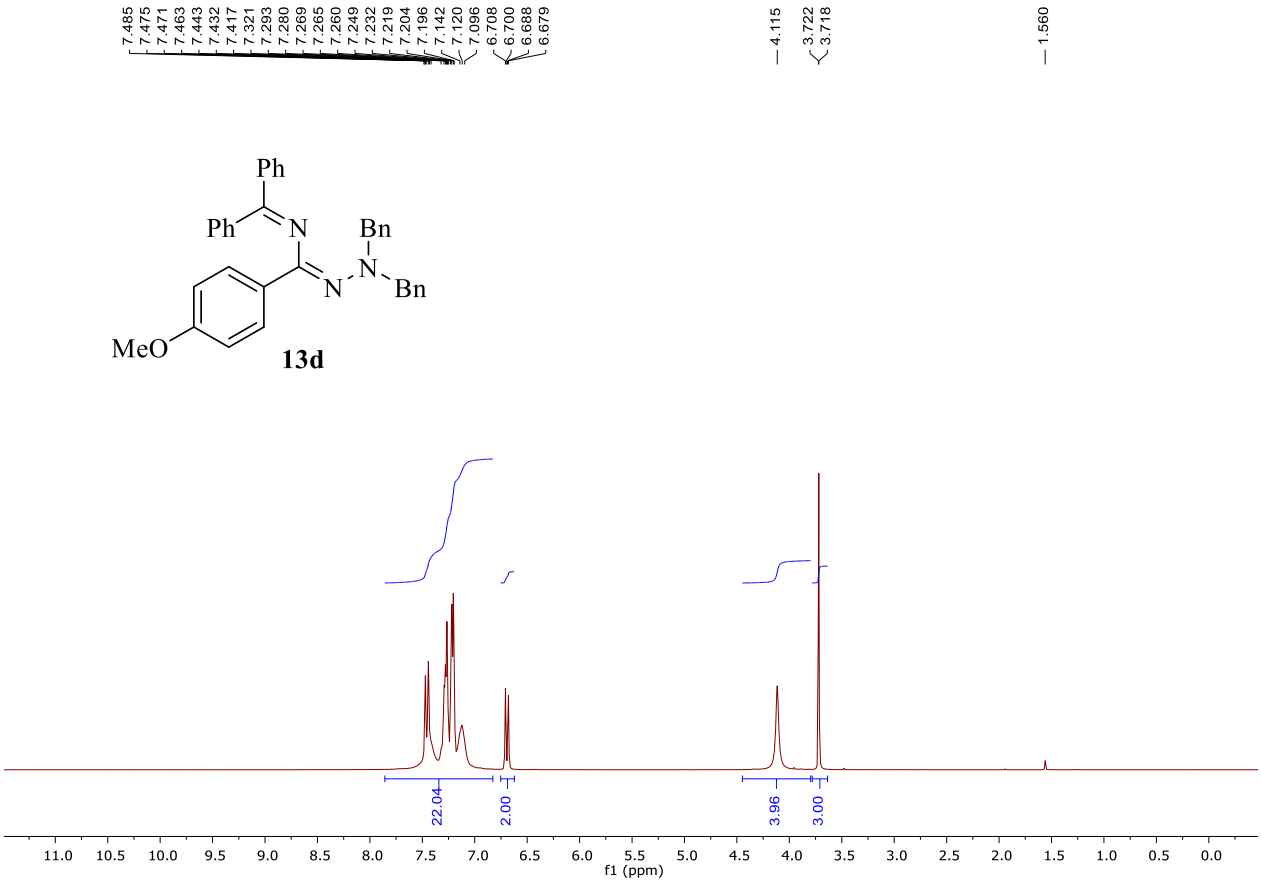
^{1}H NMR (400 MHz, $CDCl_3$) of **13c**



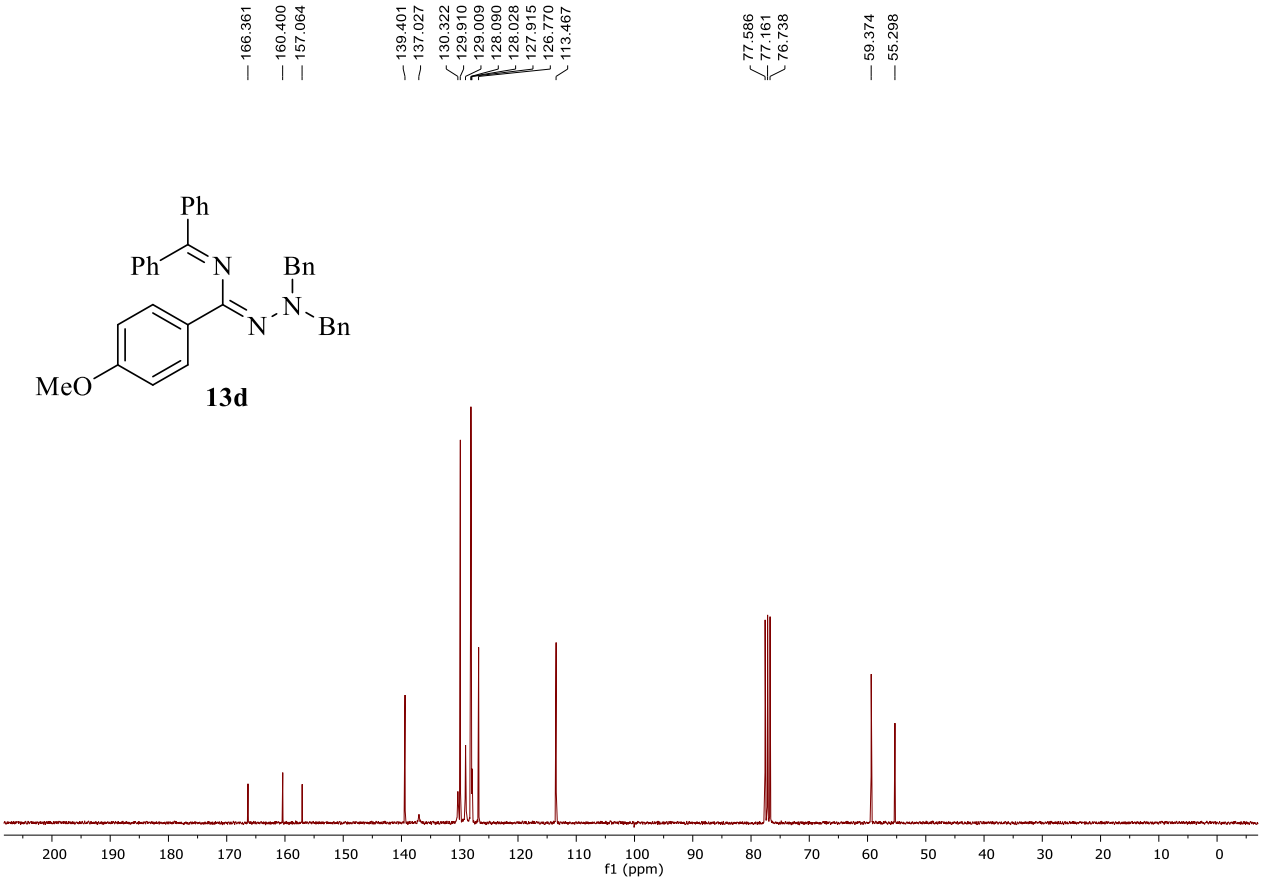
^{13}C NMR (101 MHz, $CDCl_3$) of **13c**



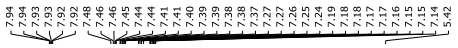
^{1}H NMR (300 MHz, $CDCl_3$) of **13d**

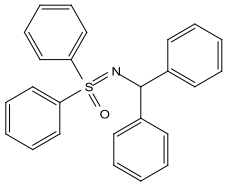


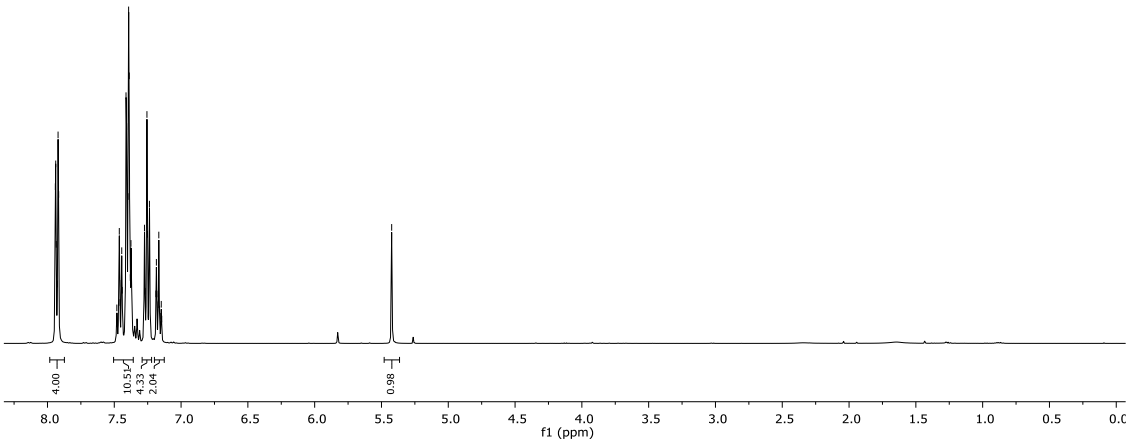
^{13}C NMR (75 MHz, $CDCl_3$) of **13d**



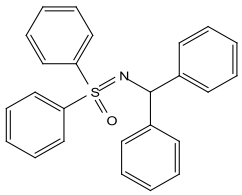
^{1}H NMR (400 MHz, $CDCl_3$) of **16a**

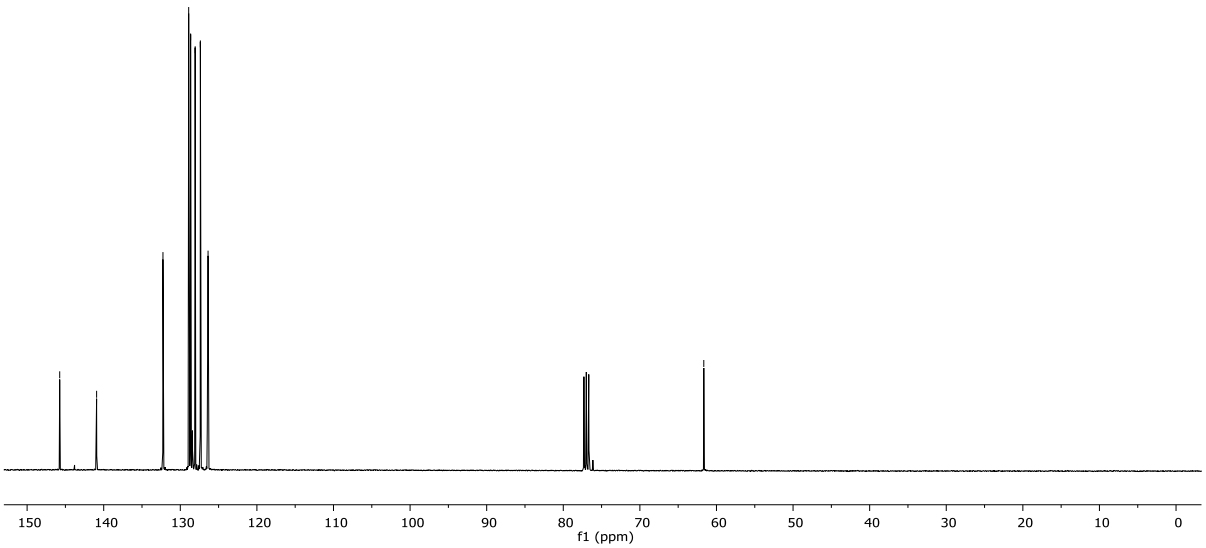




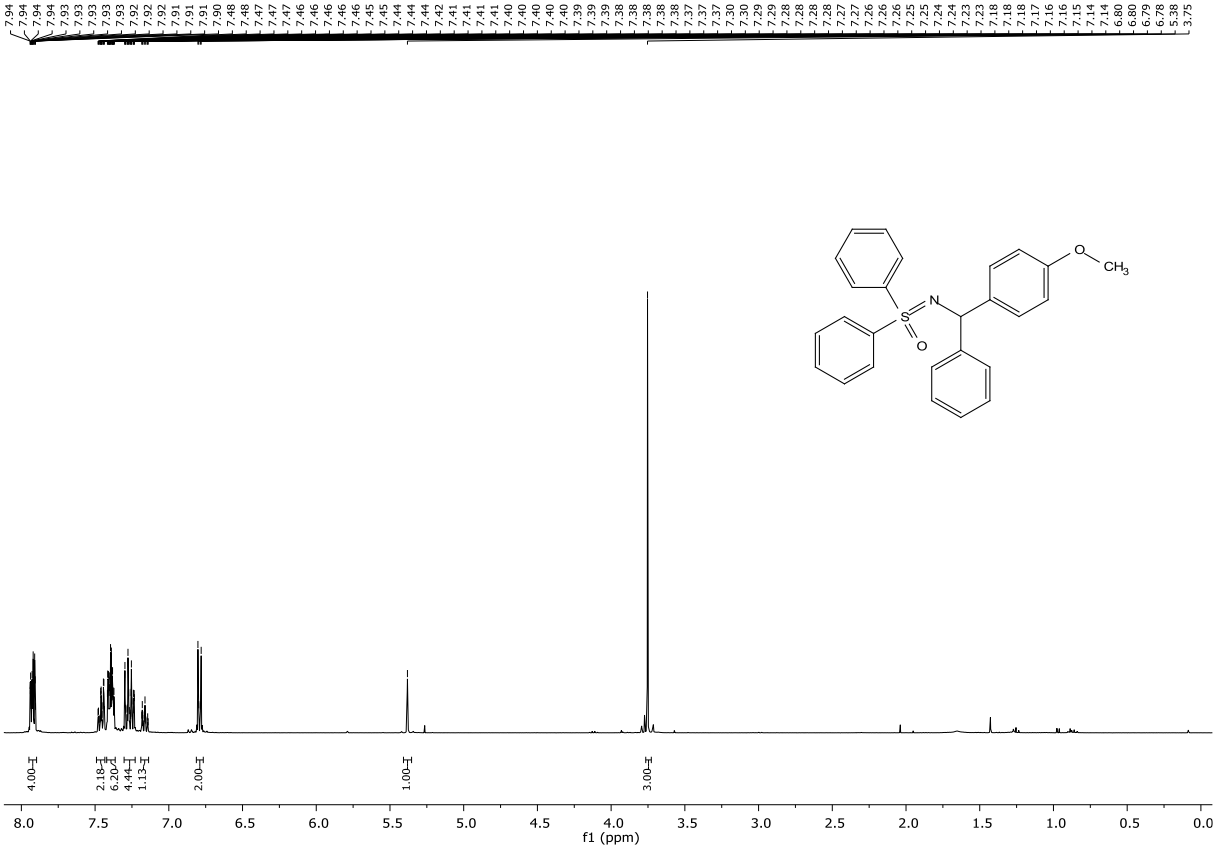


^{13}C NMR (100 MHz, $CDCl_3$) of **16a**

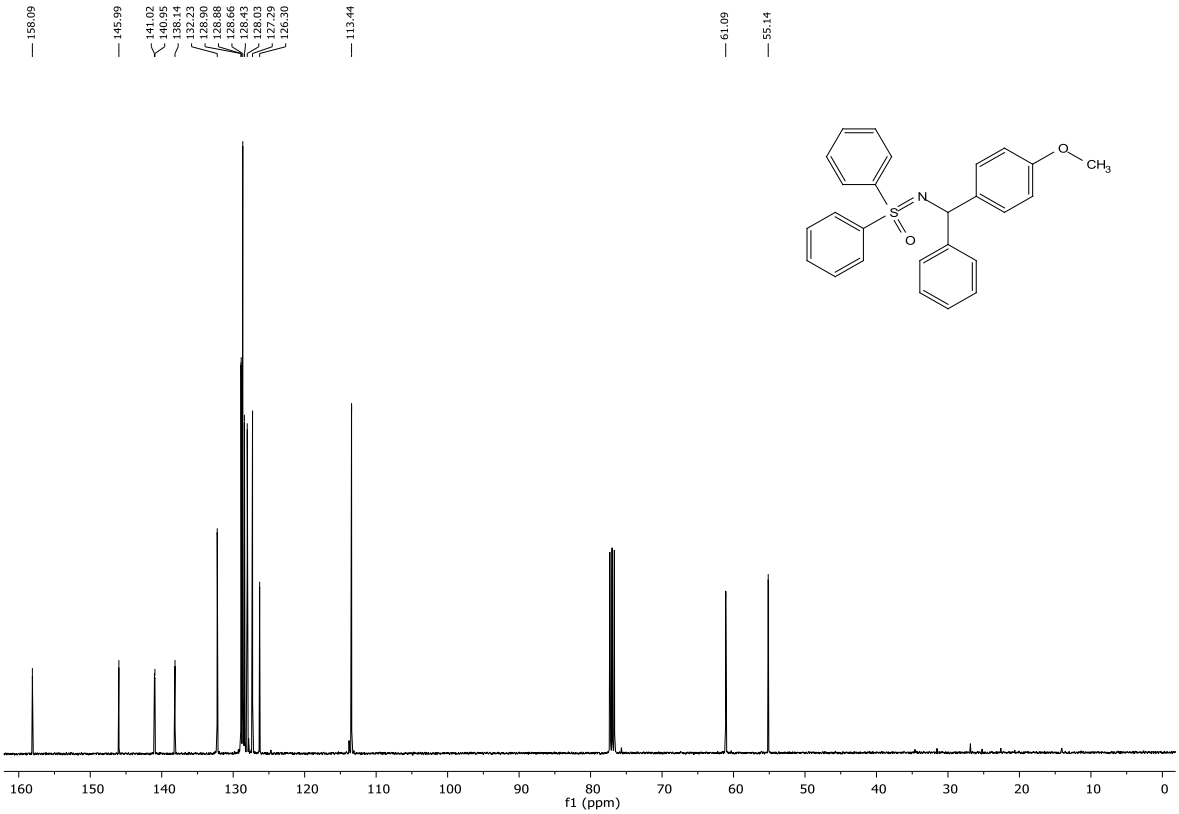




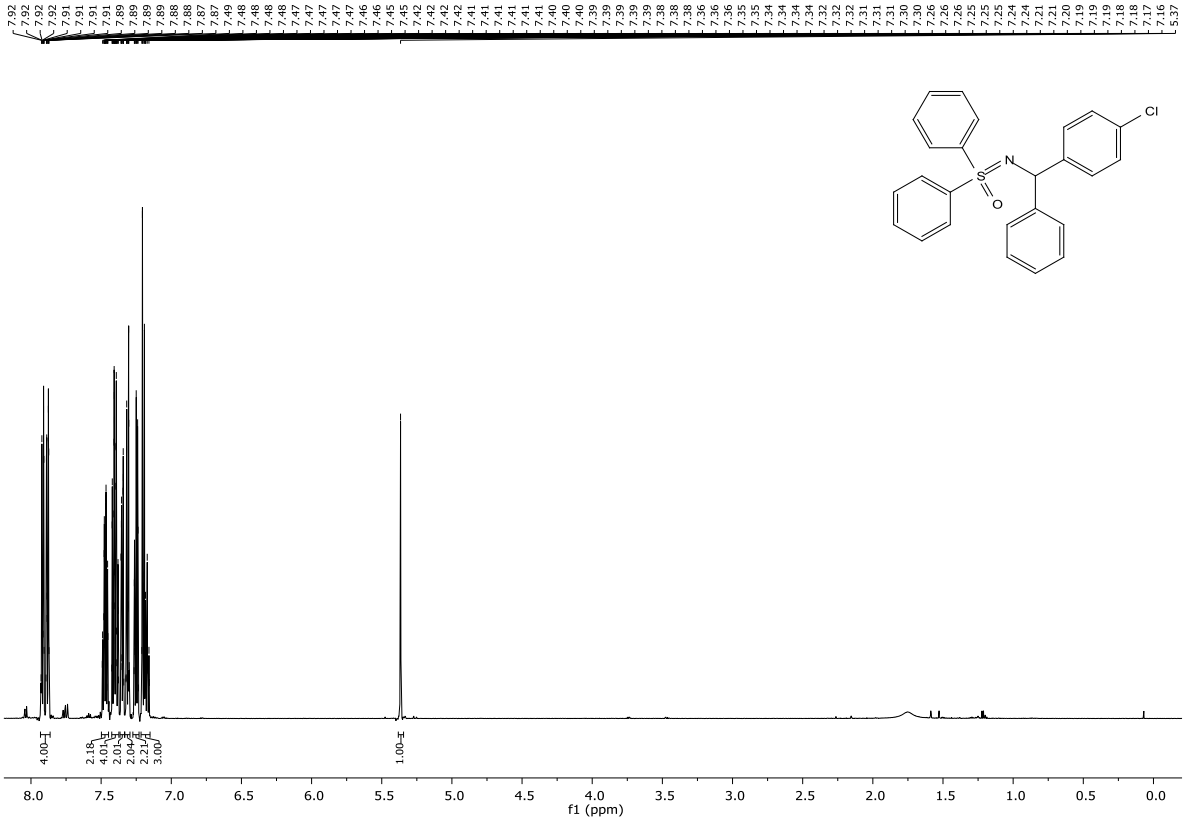
^{1}H NMR (400 MHz, $CDCl_3$) of **16b**



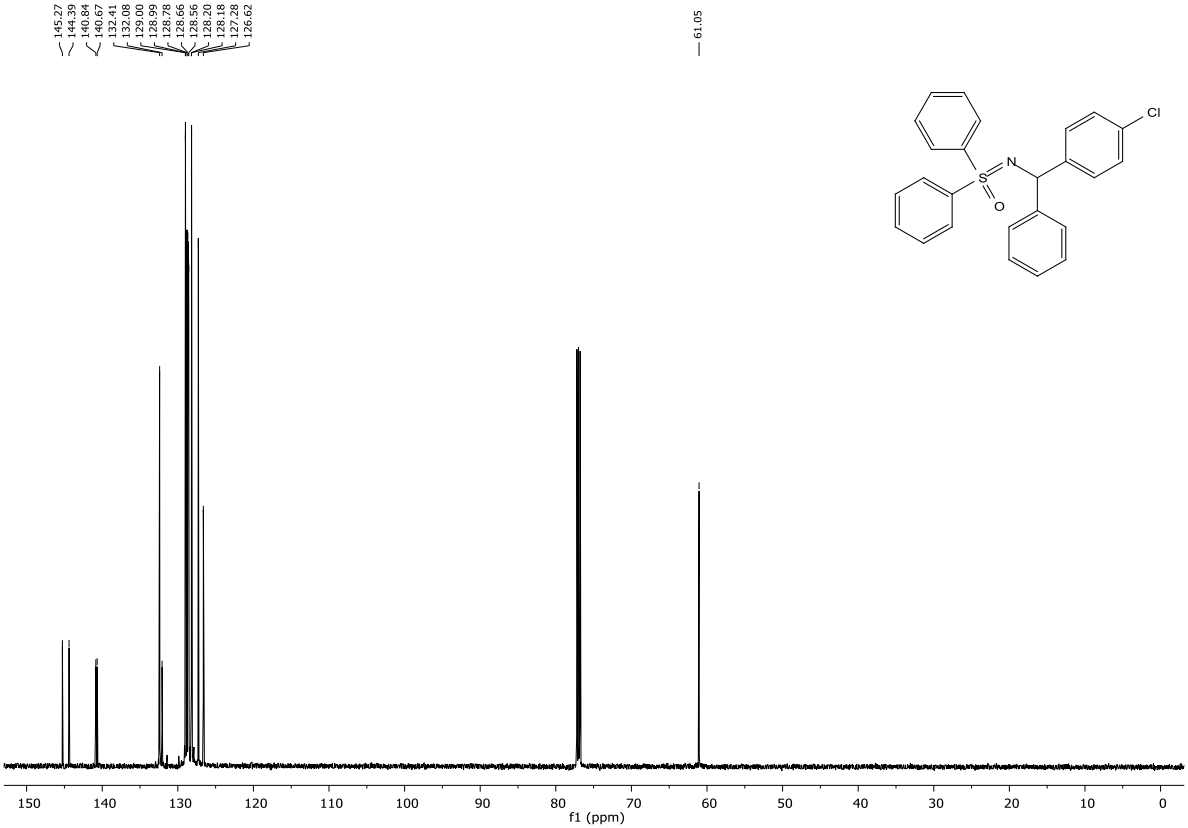
^{13}C NMR (400 MHz, $CDCl_3$) of **16b**



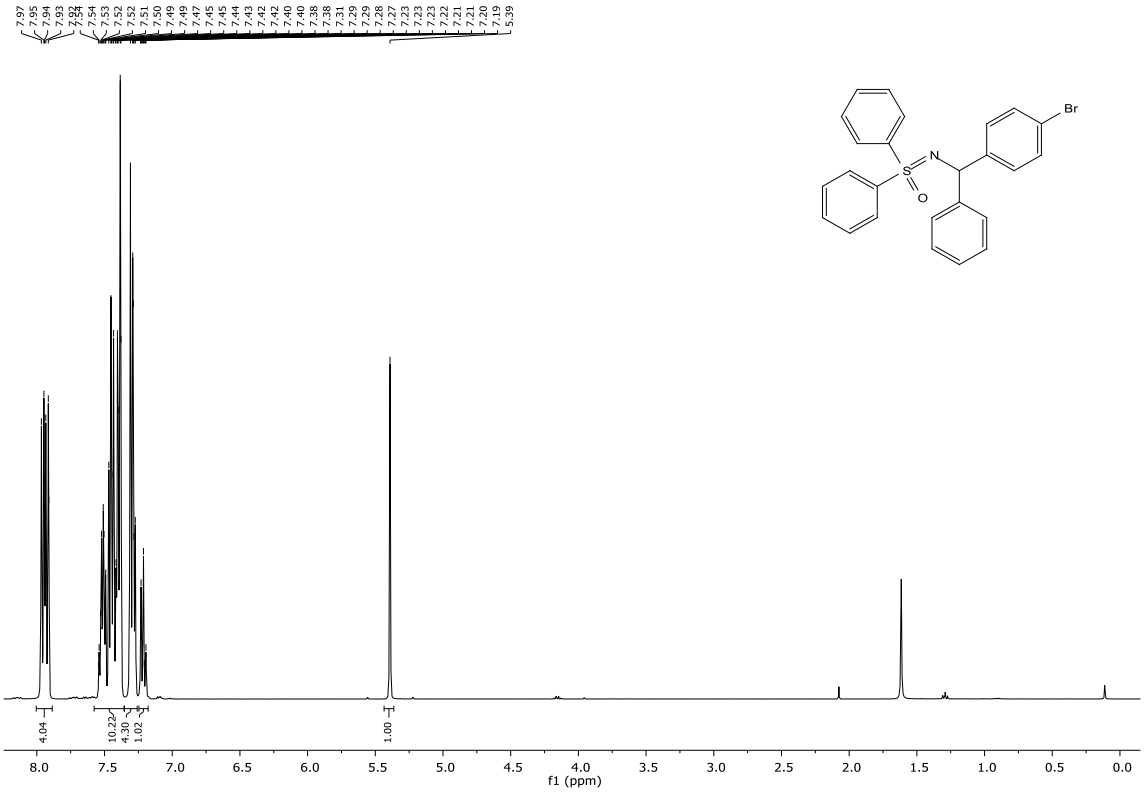
^{1}H NMR (600 MHz, $CDCl_3$) of **16c**



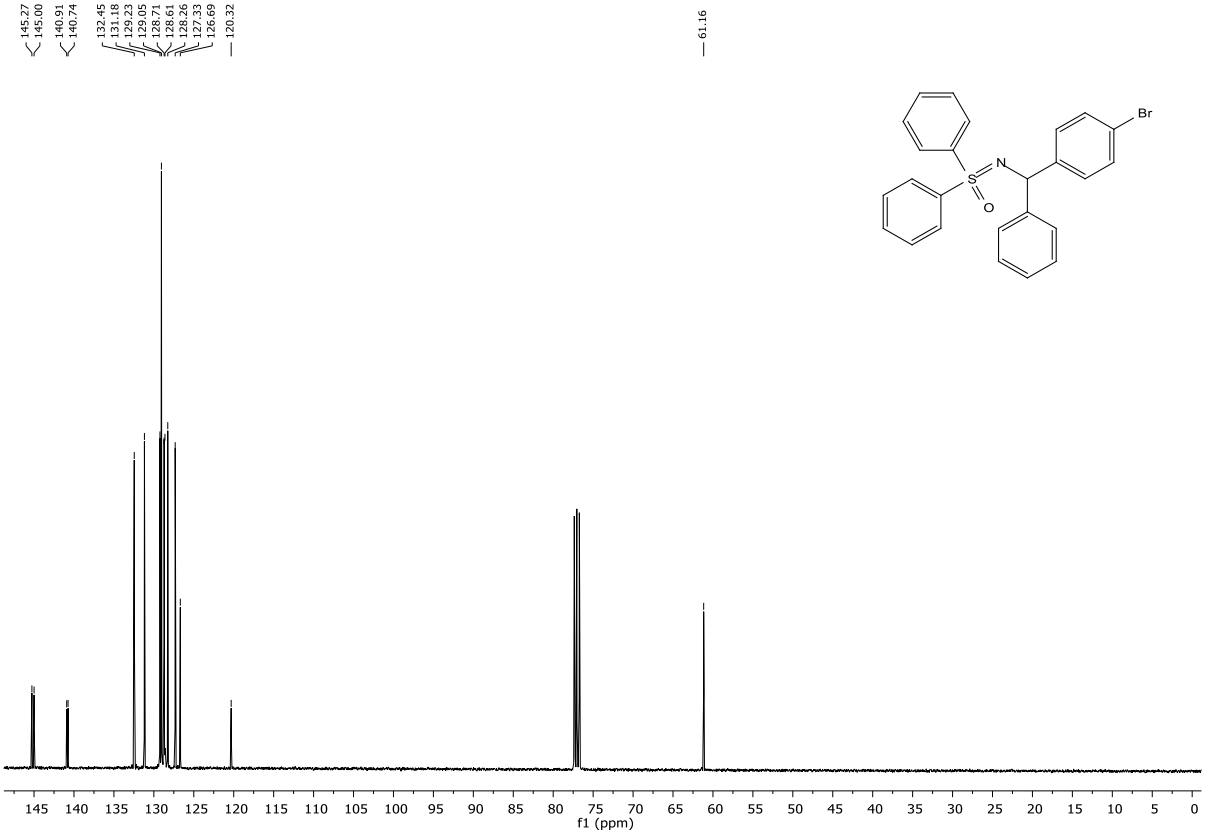
^{13}C NMR (150 MHz, $CDCl_3$) of **16c**



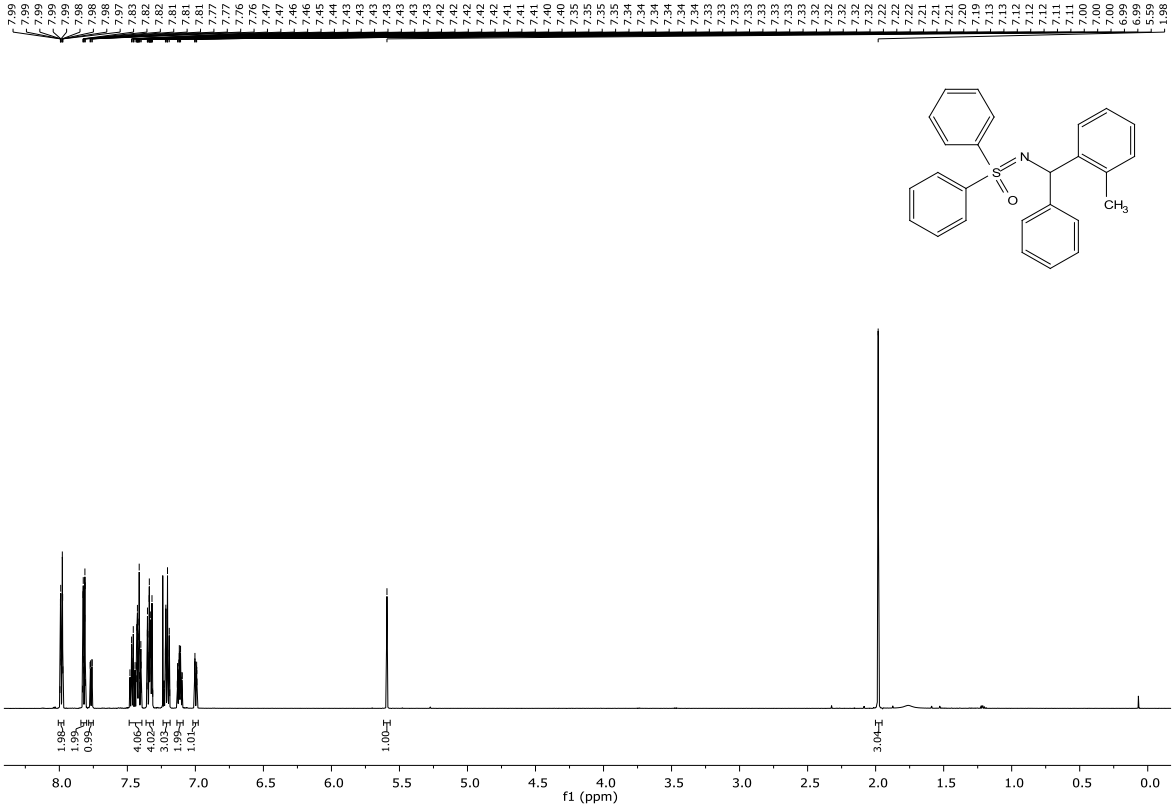
^{1}H NMR (400 MHz, $CDCl_3$) of **16d**



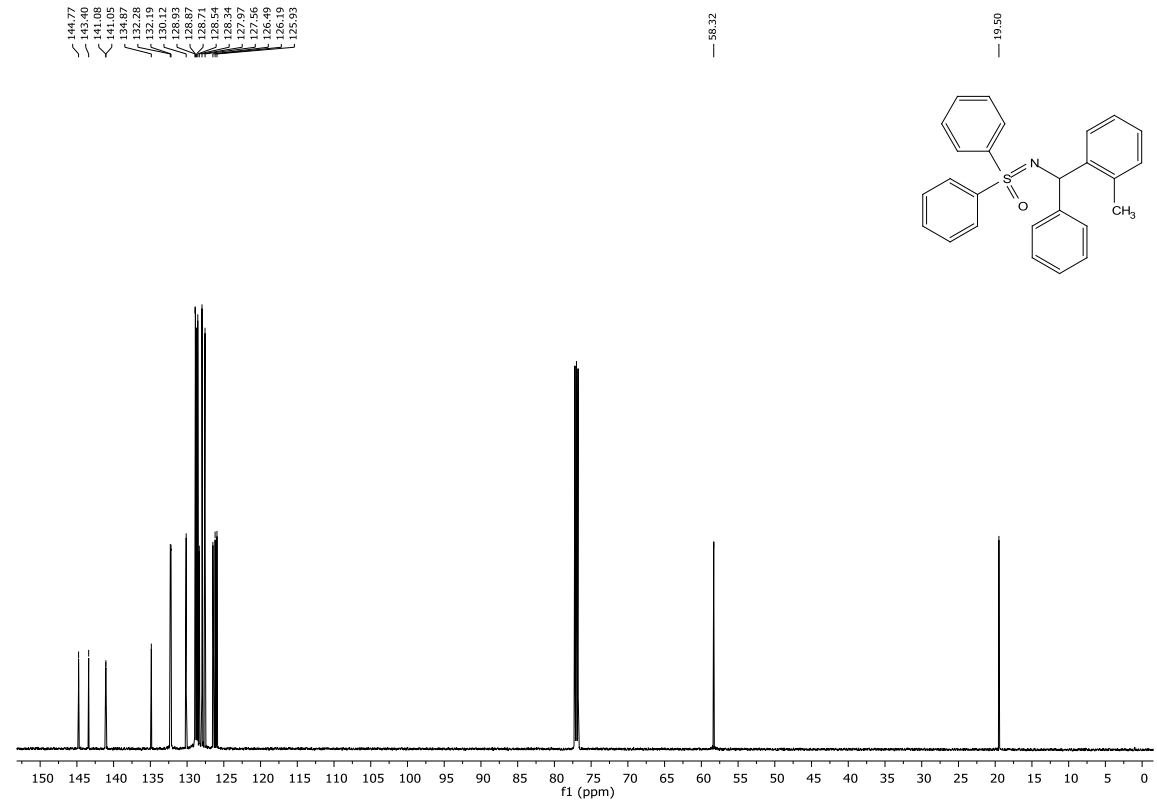
^{13}C NMR (400 MHz, $CDCl_3$) of **16d**



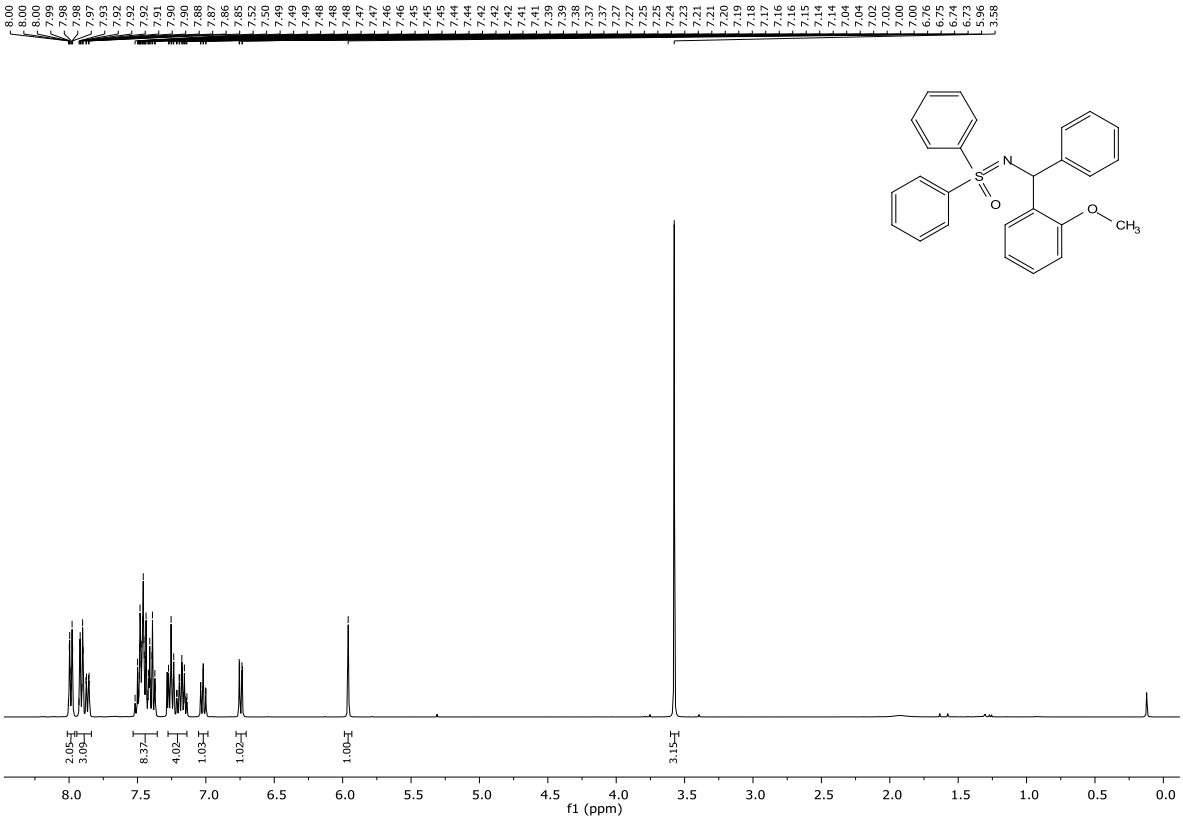
^{1}H NMR (600 MHz, $CDCl_3$) of **16e**



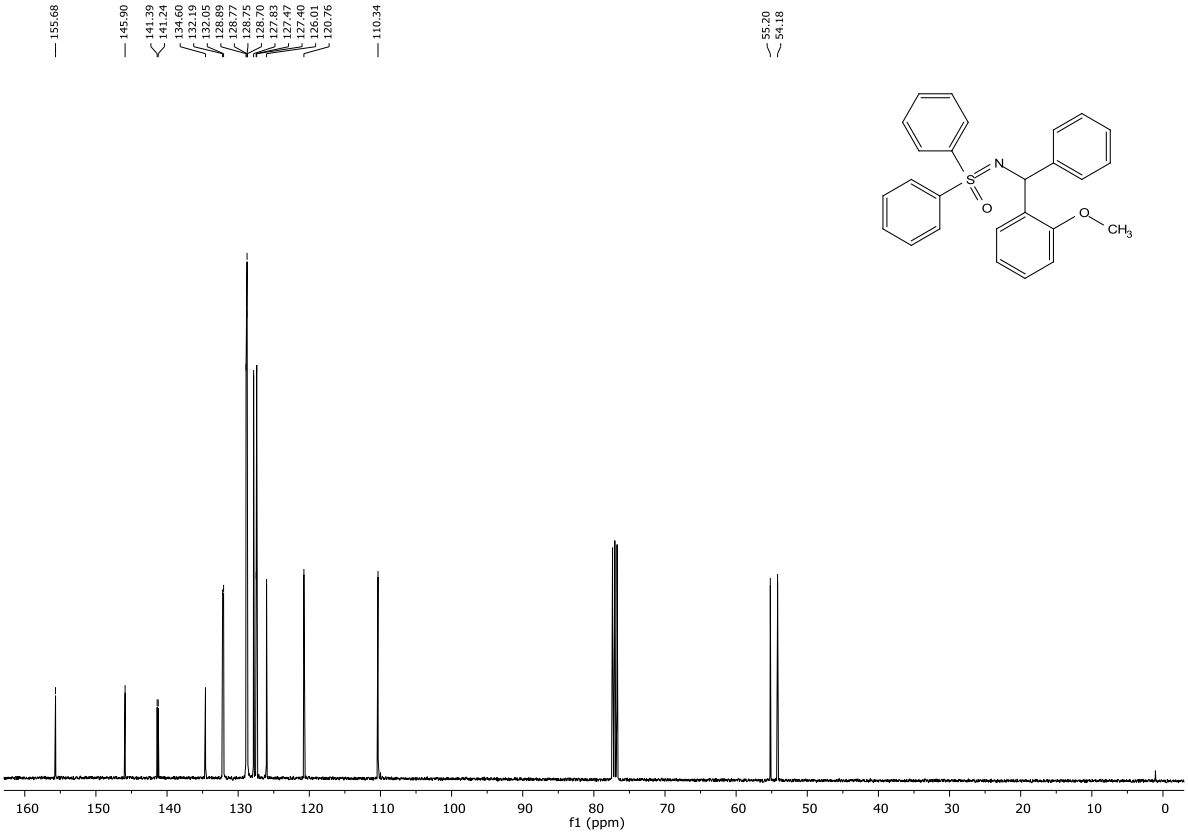
^{13}C NMR (150 MHz, $CDCl_3$) of **16e**



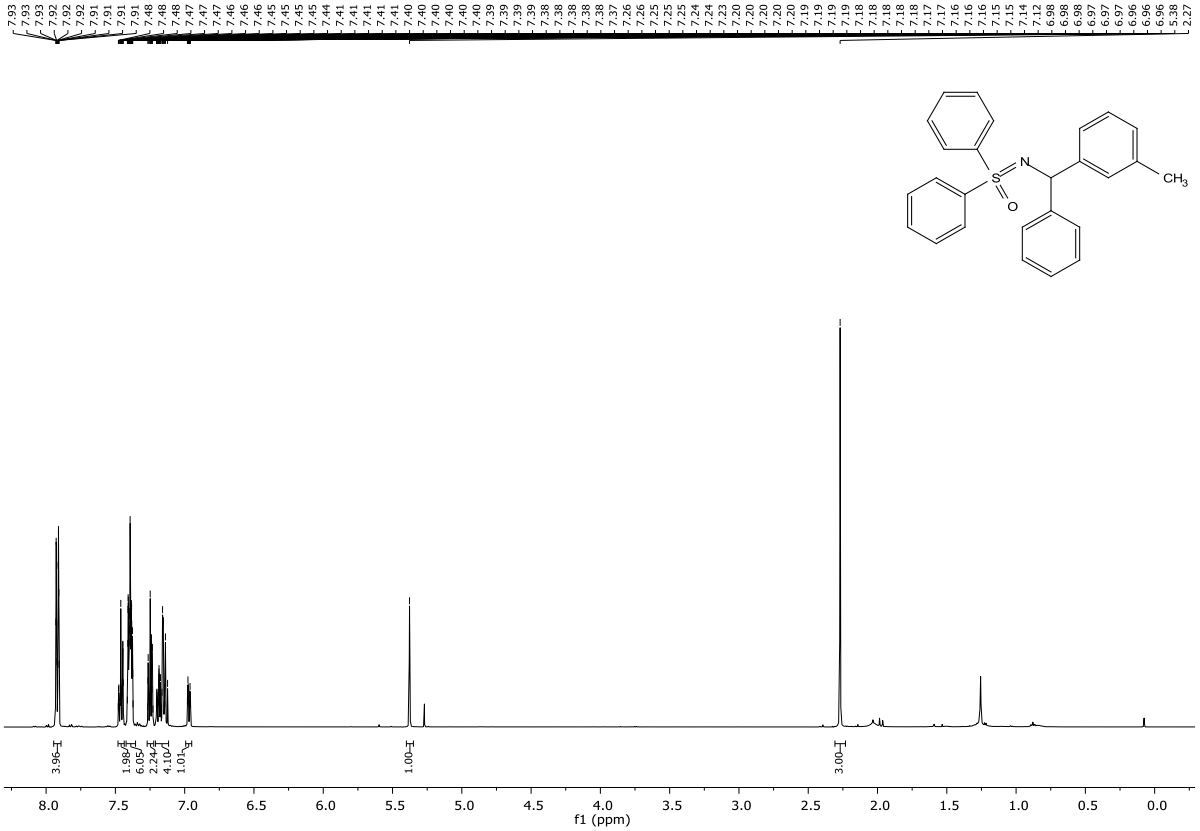
^{1}H NMR (400 MHz, $CDCl_3$) of **16f**



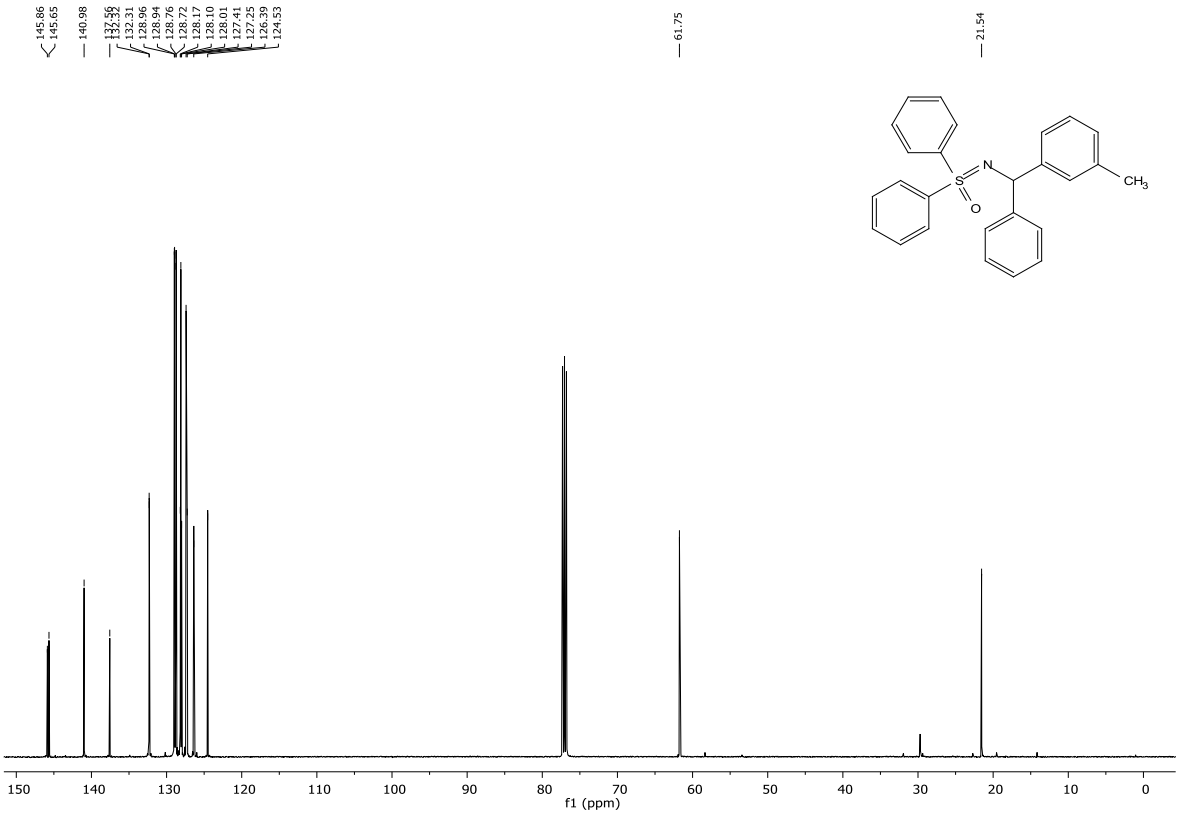
^{13}C NMR (100 MHz, $CDCl_3$) of **16f**



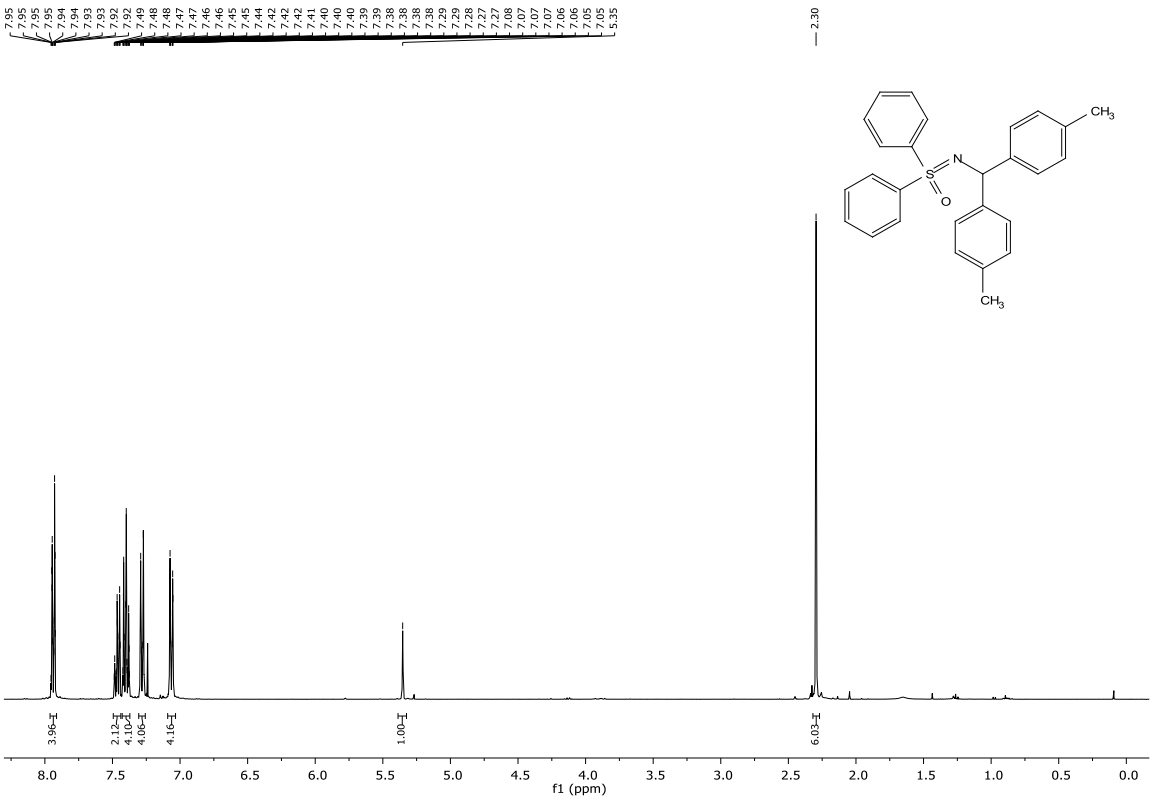
^{1}H NMR (500 MHz, $CDCl_3$) of **16g**



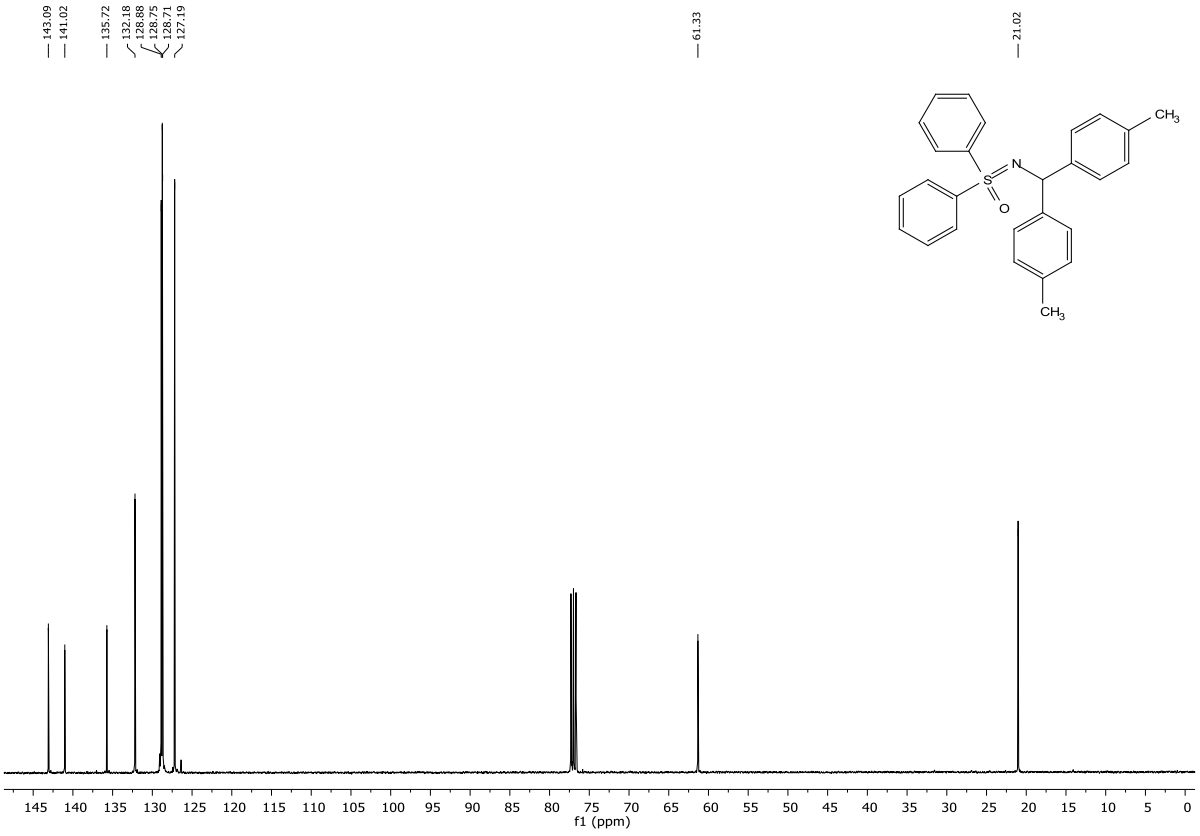
^{13}C NMR (125 MHz, $CDCl_3$) of **16g**



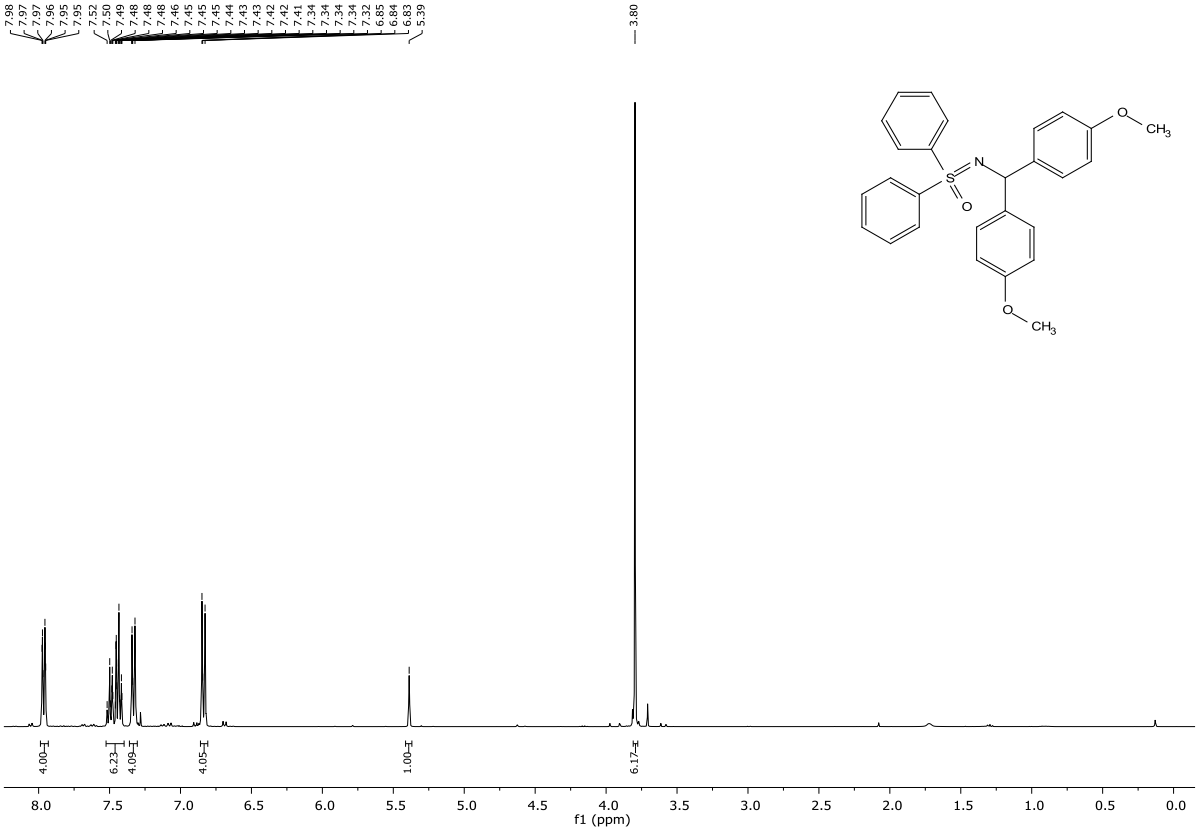
^{1}H NMR (500 MHz, $CDCl_3$) of **16h**



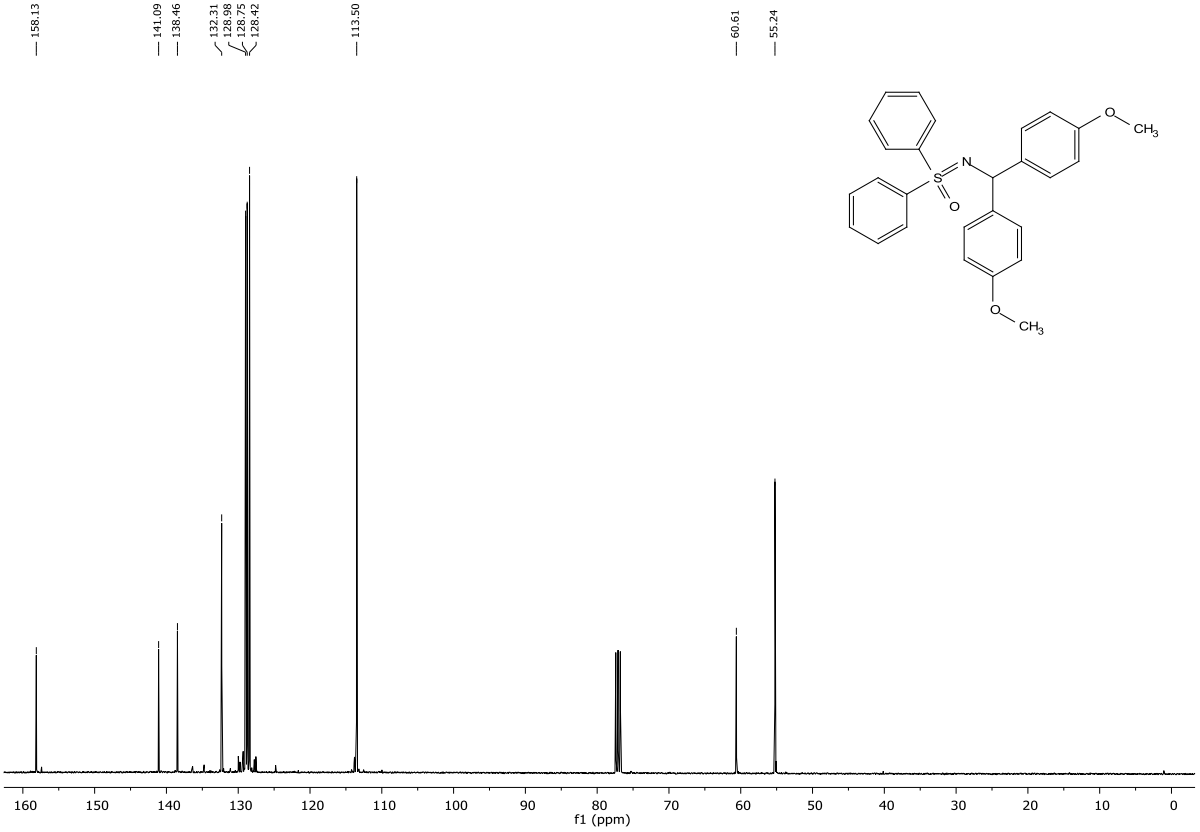
^{13}C NMR (100 MHz, $CDCl_3$) of **16h**



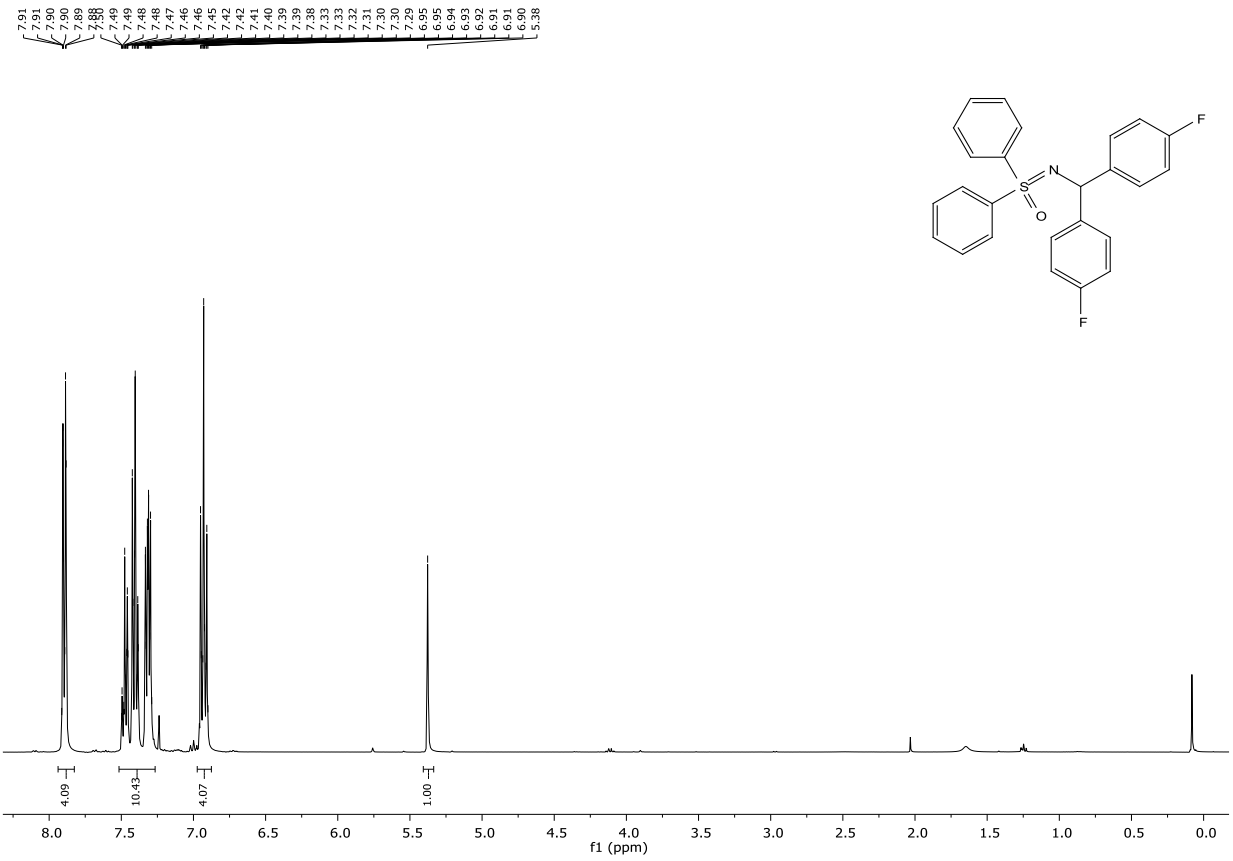
^{1}H NMR (400 MHz, $CDCl_3$) of **16i**



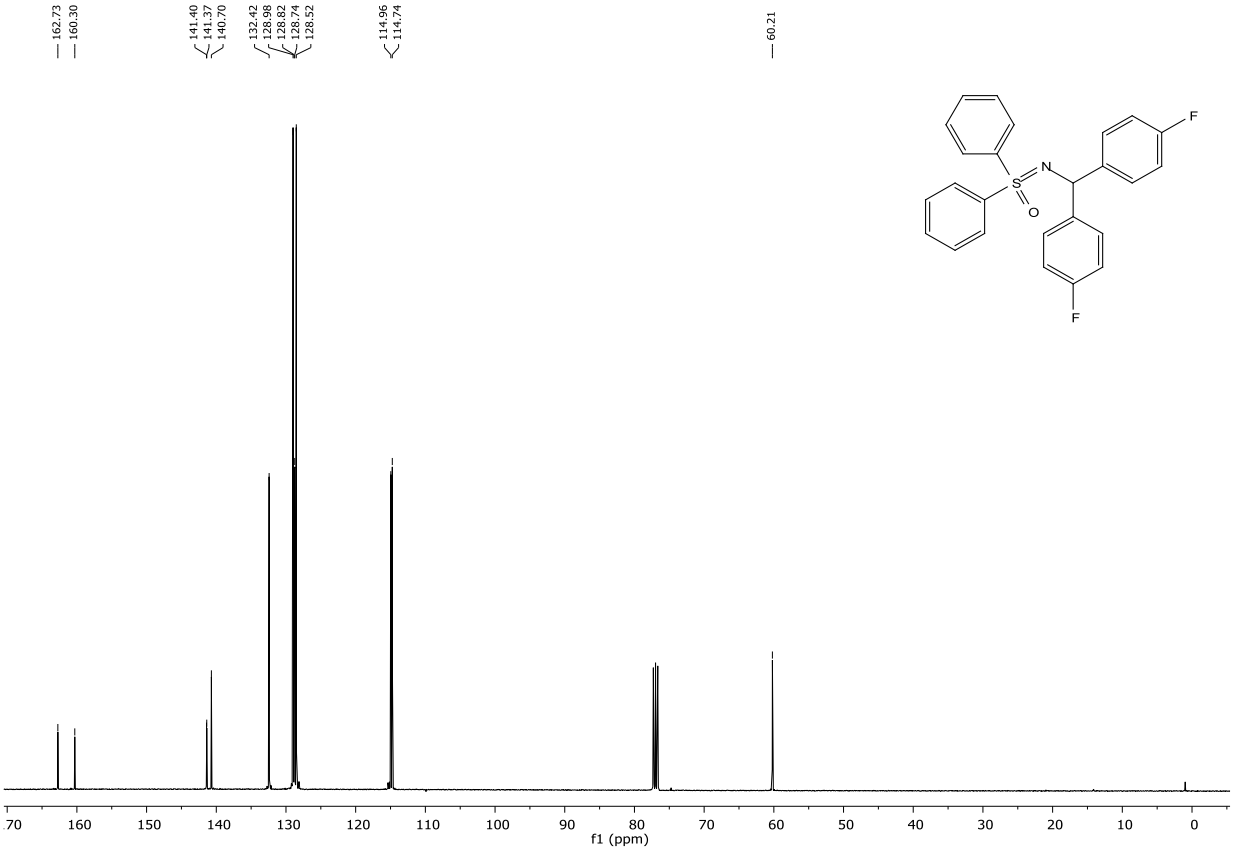
^{13}C NMR (100 MHz, $CDCl_3$) of **16i**



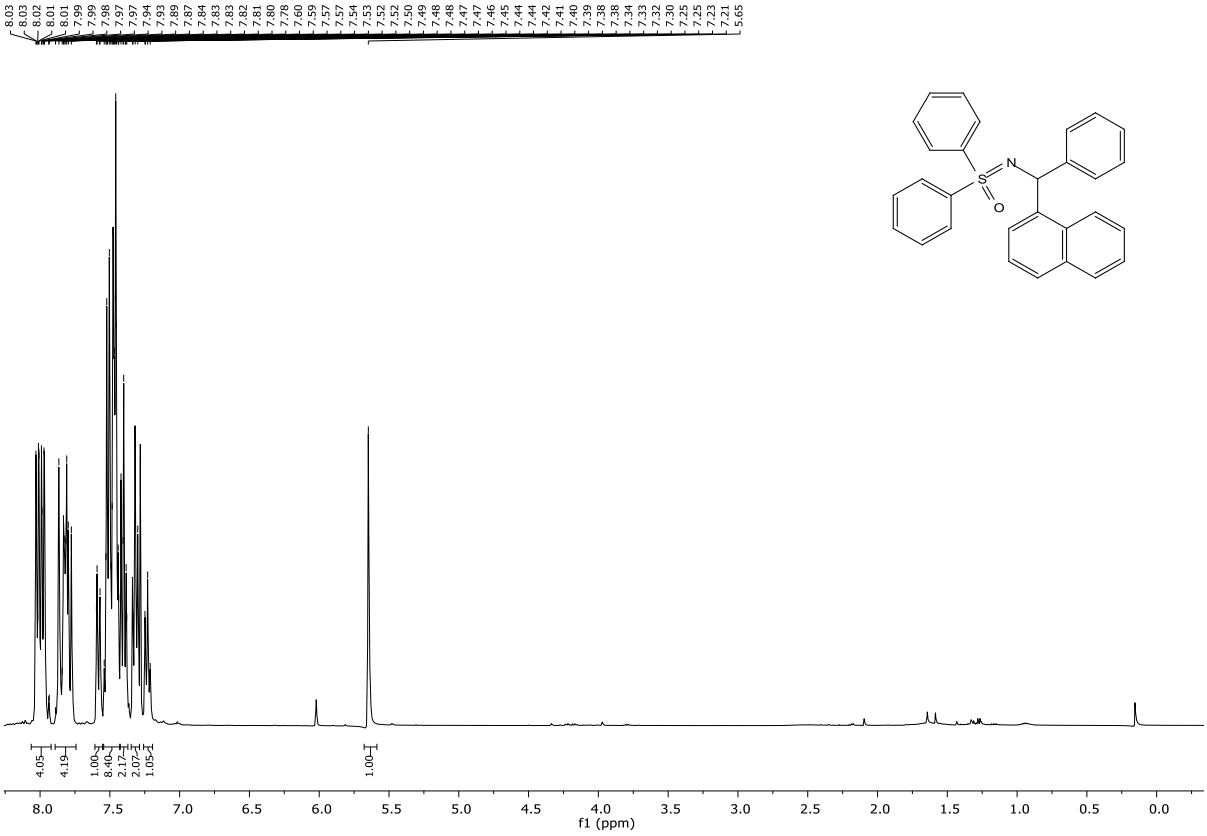
^{1}H NMR (400 MHz, $CDCl_3$) of **16j**



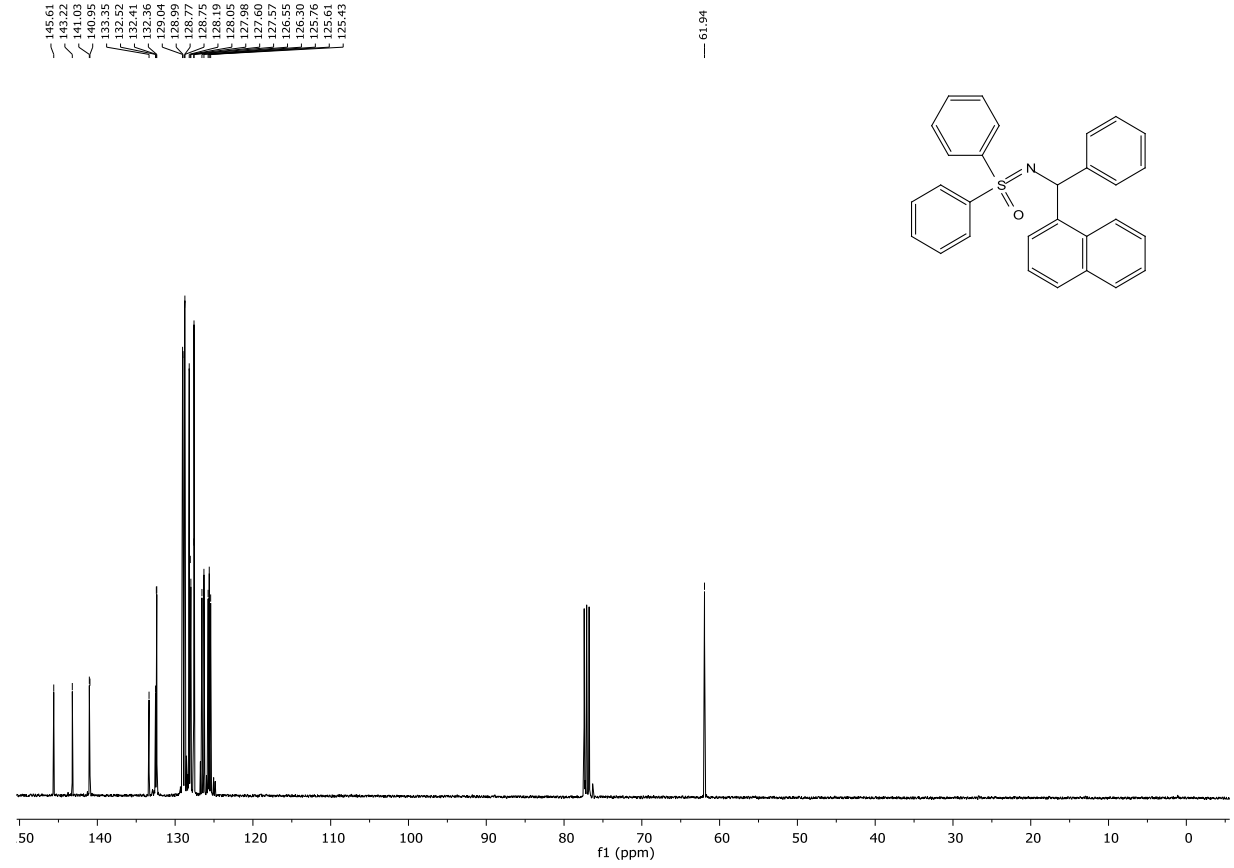
^{13}C NMR (100 MHz, $CDCl_3$) of **16j**



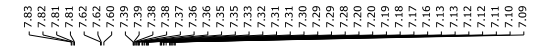
^{1}H NMR (400 MHz, $CDCl_3$) of **16k**

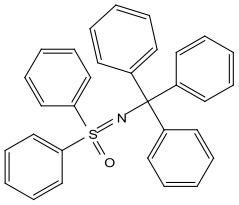


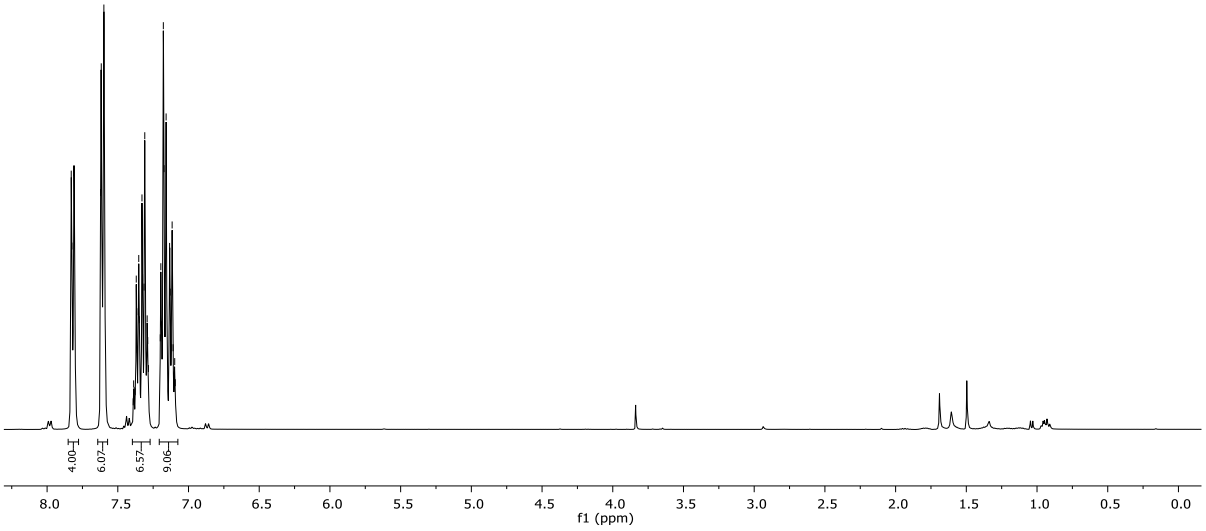
^{13}C NMR (100 MHz, $CDCl_3$) of **16k**



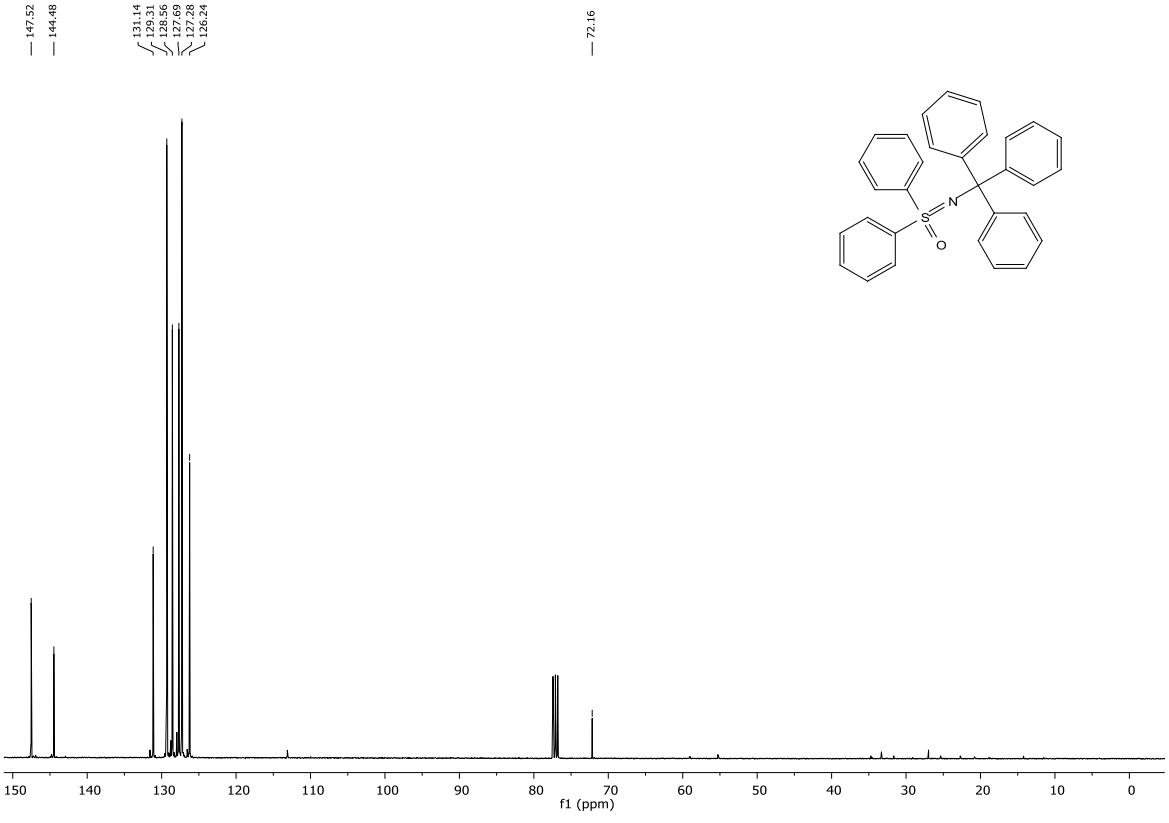
^{1}H NMR (400 MHz, $CDCl_3$) of **16l**



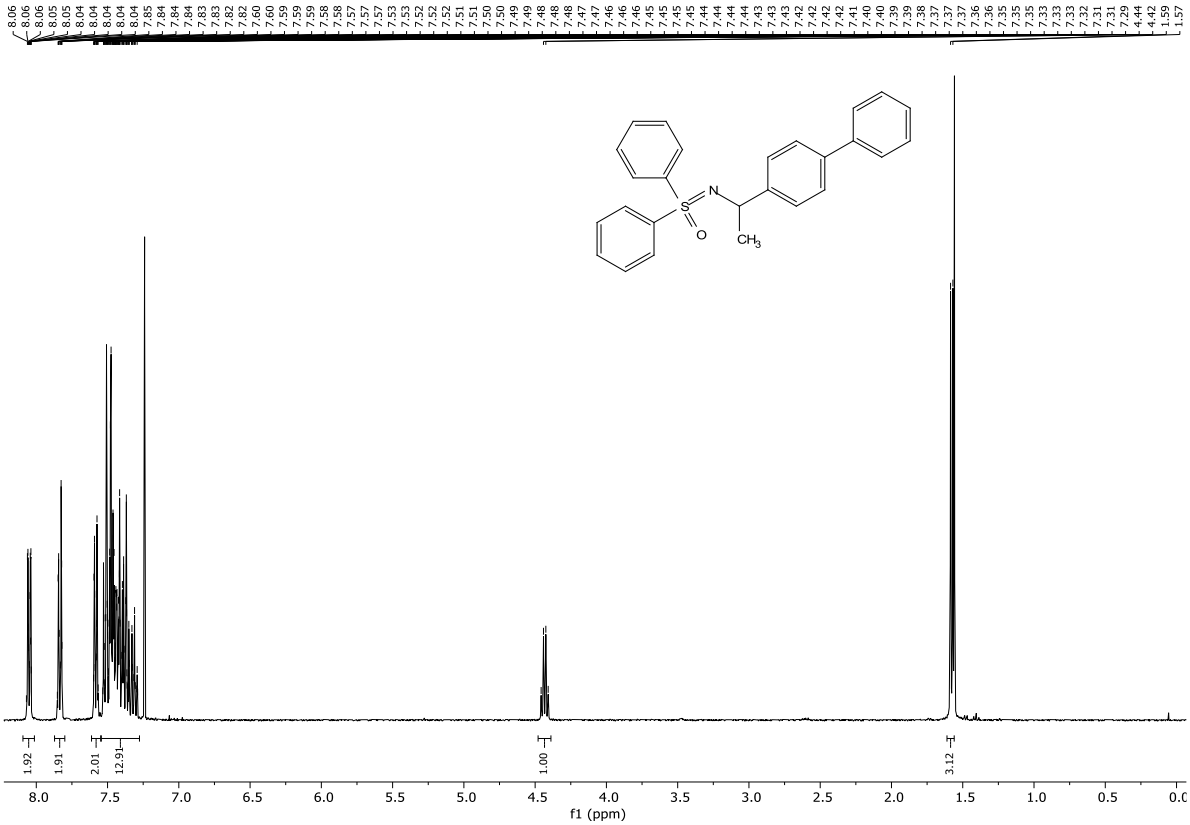




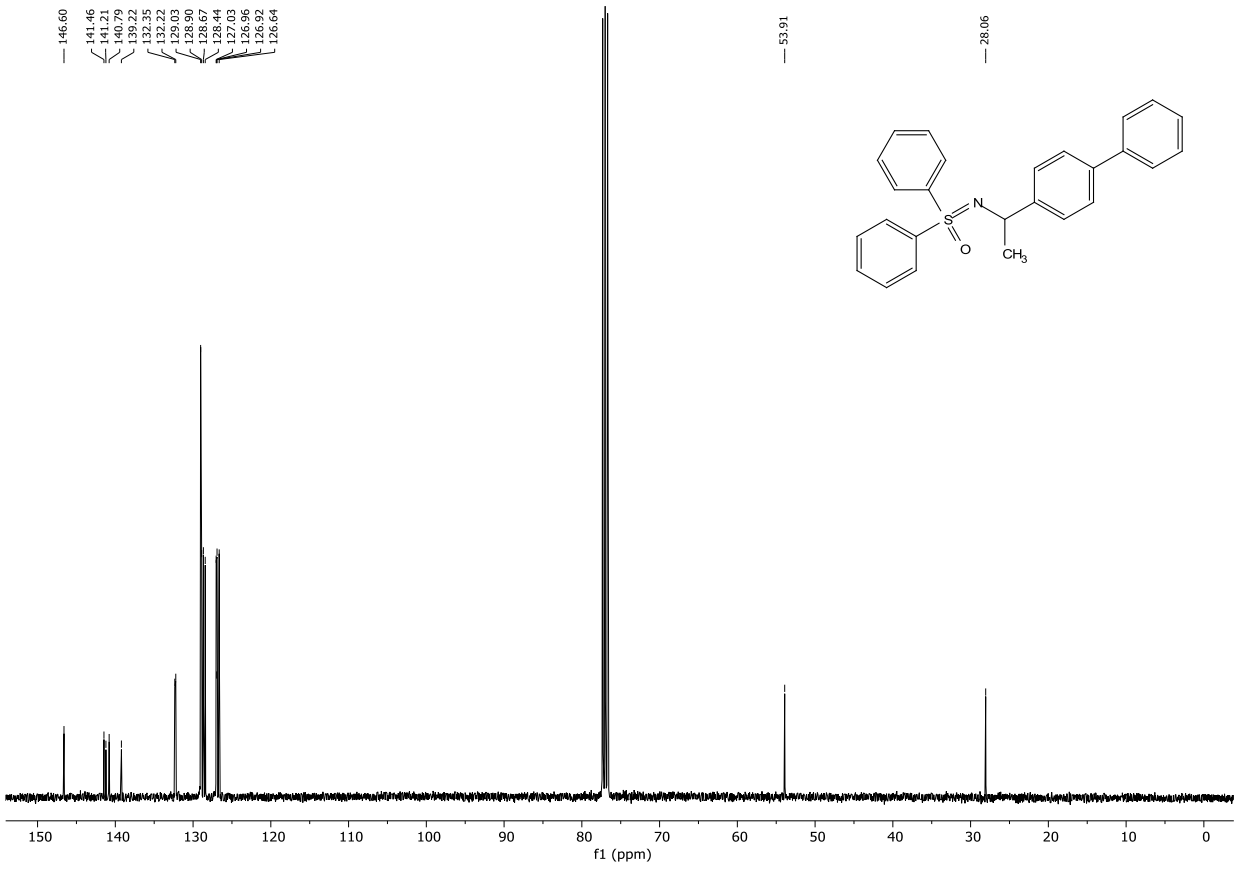
^{13}C NMR (100 MHz, $CDCl_3$) of **16l**



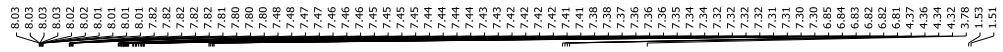
^{1}H NMR (400 MHz, $CDCl_3$) of **16m**

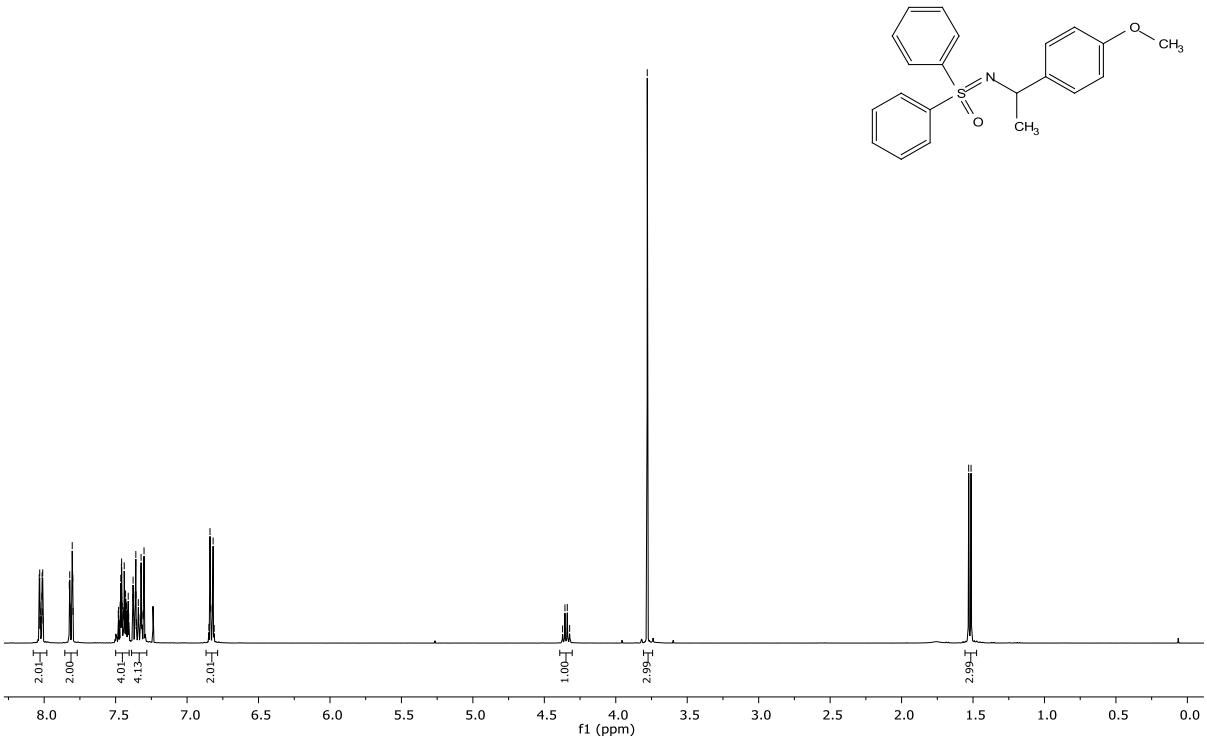


^{13}C NMR (100 MHz, $CDCl_3$) of **16m**

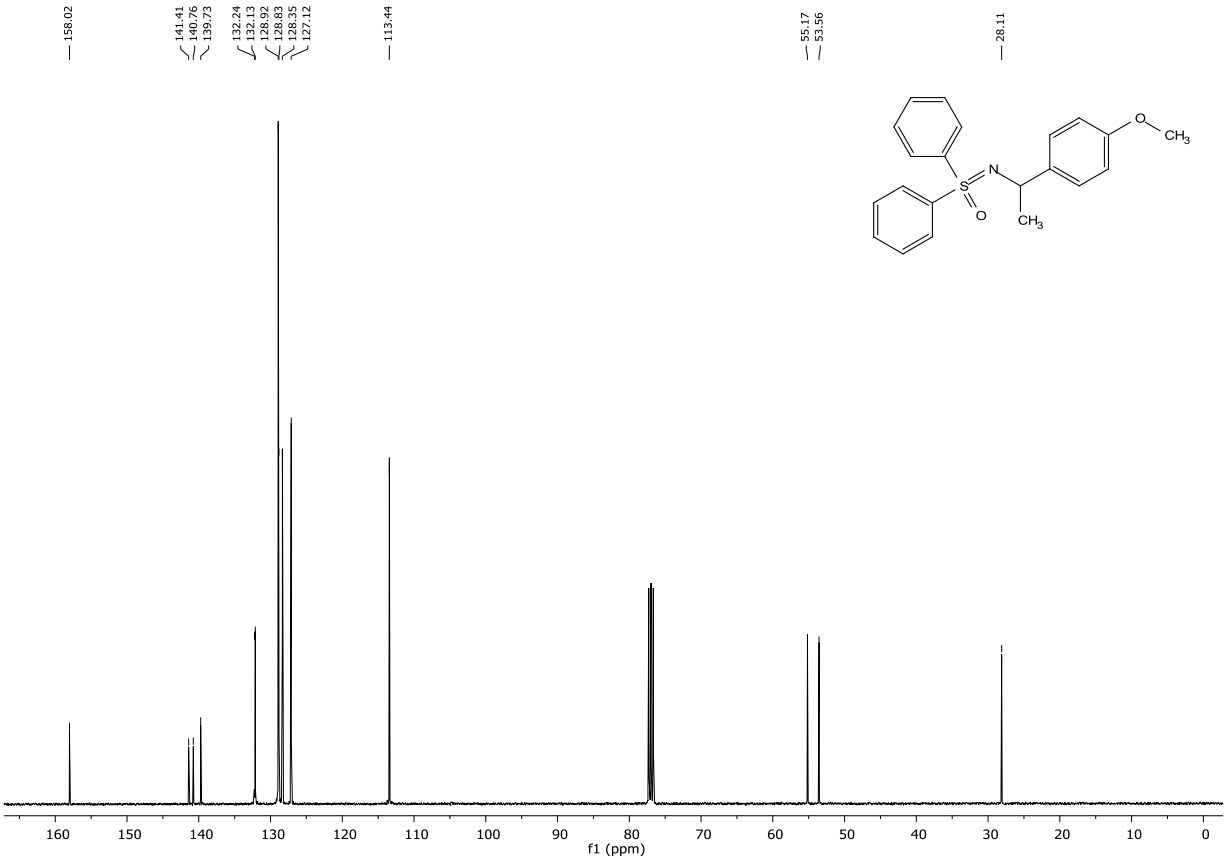


^{1}H NMR (400 MHz, $CDCl_3$) of **16n**

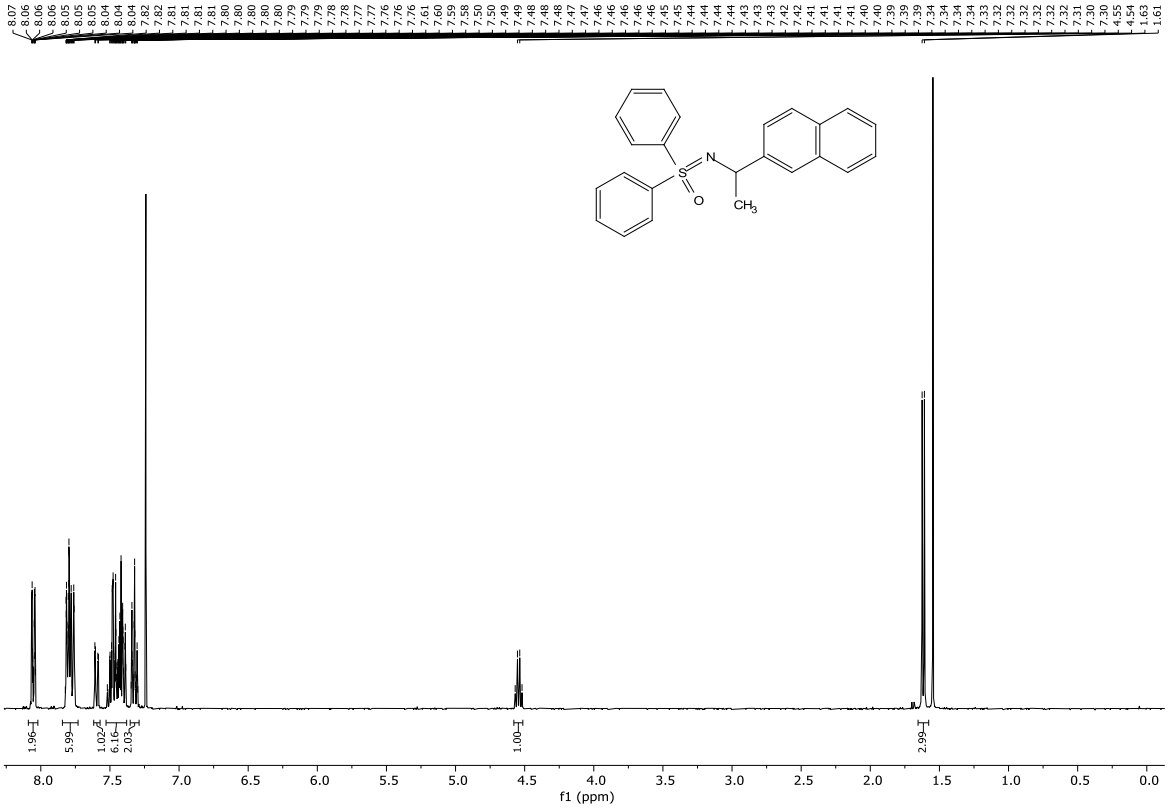




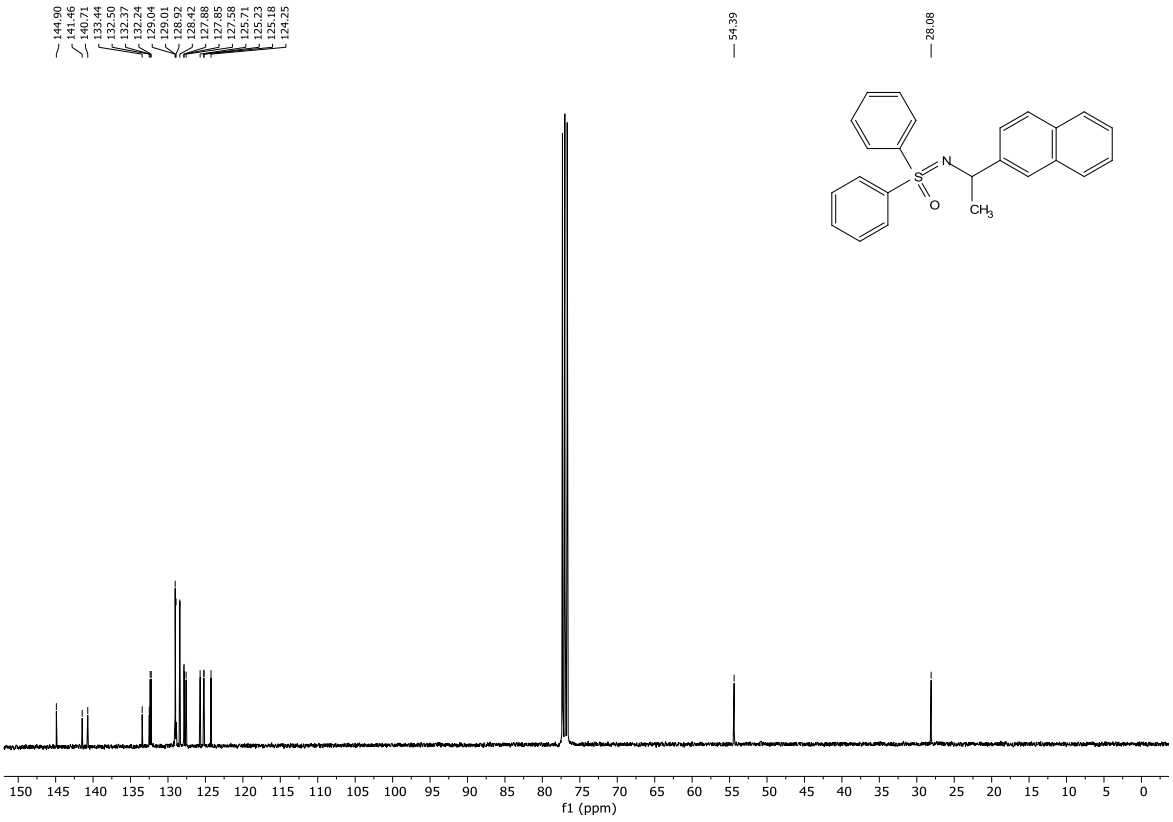
^{13}C NMR (100 MHz, $CDCl_3$) of **16n**



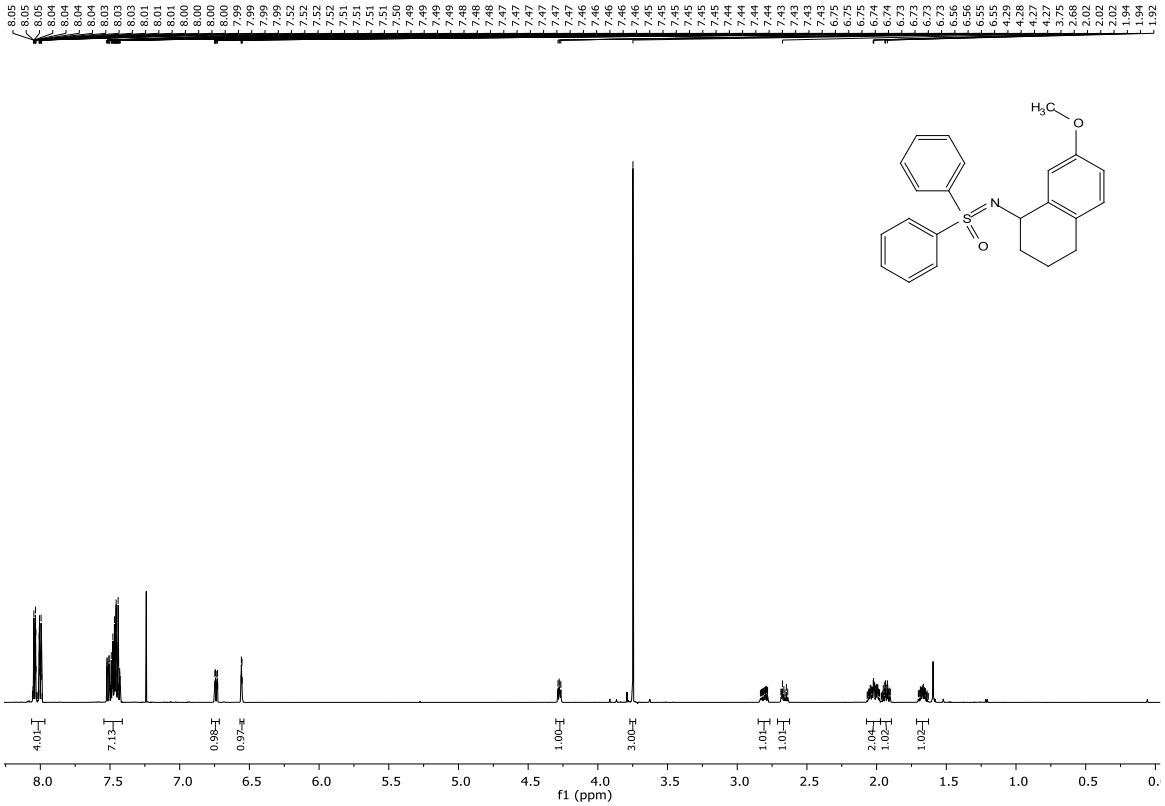
^{1}H NMR (400 MHz, $CDCl_3$) of **16o**



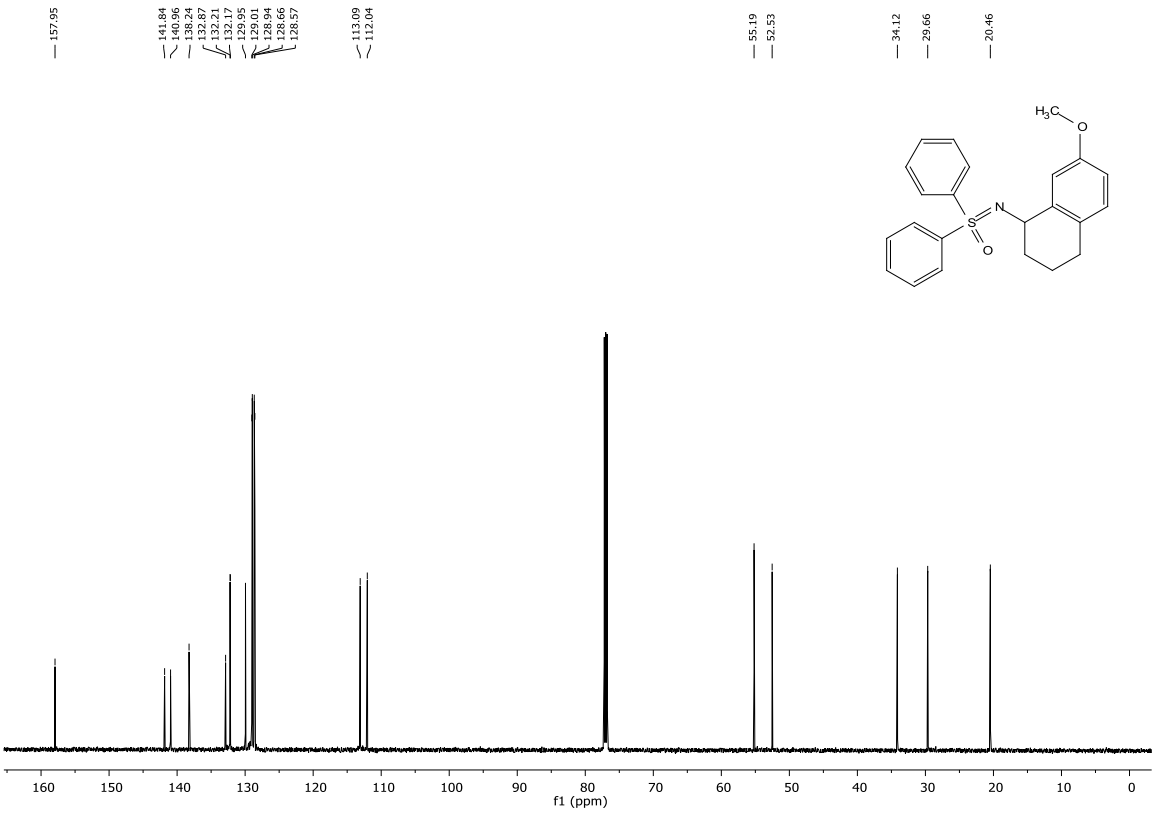
^{13}C NMR (100 MHz, $CDCl_3$) of **16o**



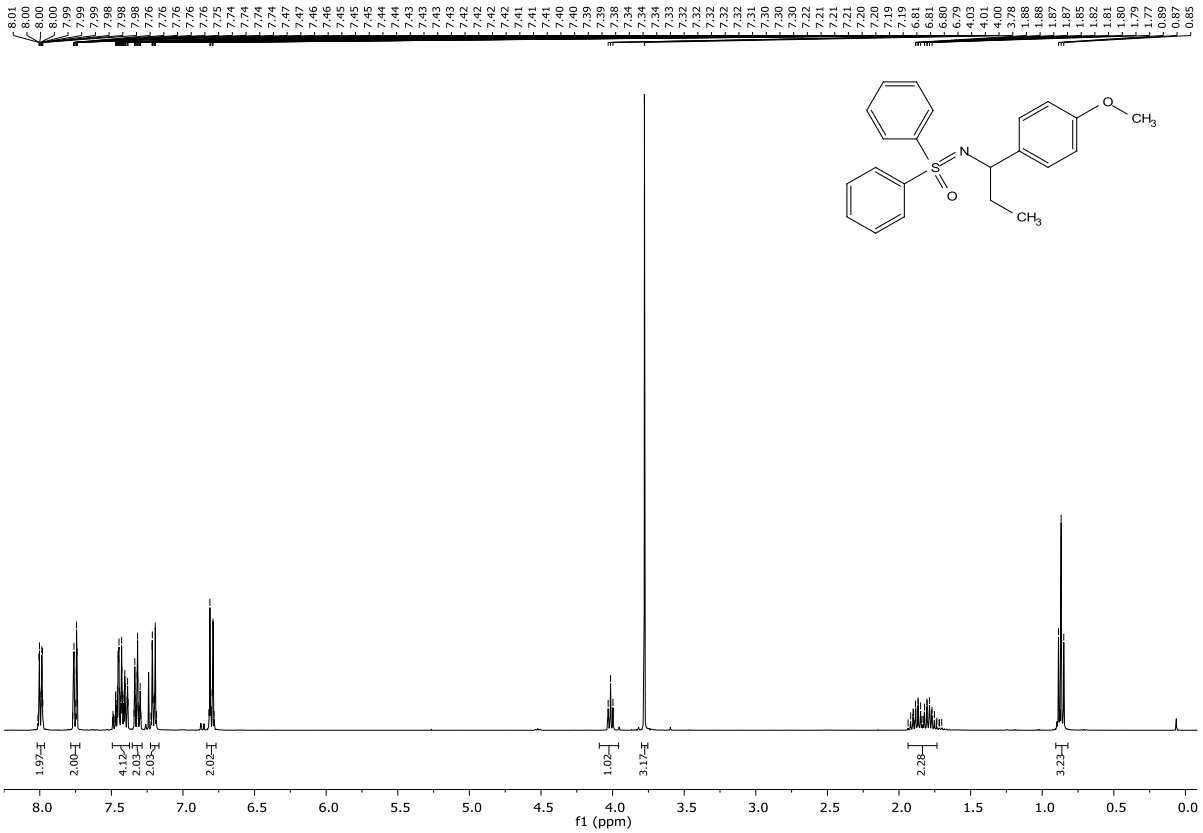
^{1}H NMR (600 MHz, $CDCl_3$) of **16p**



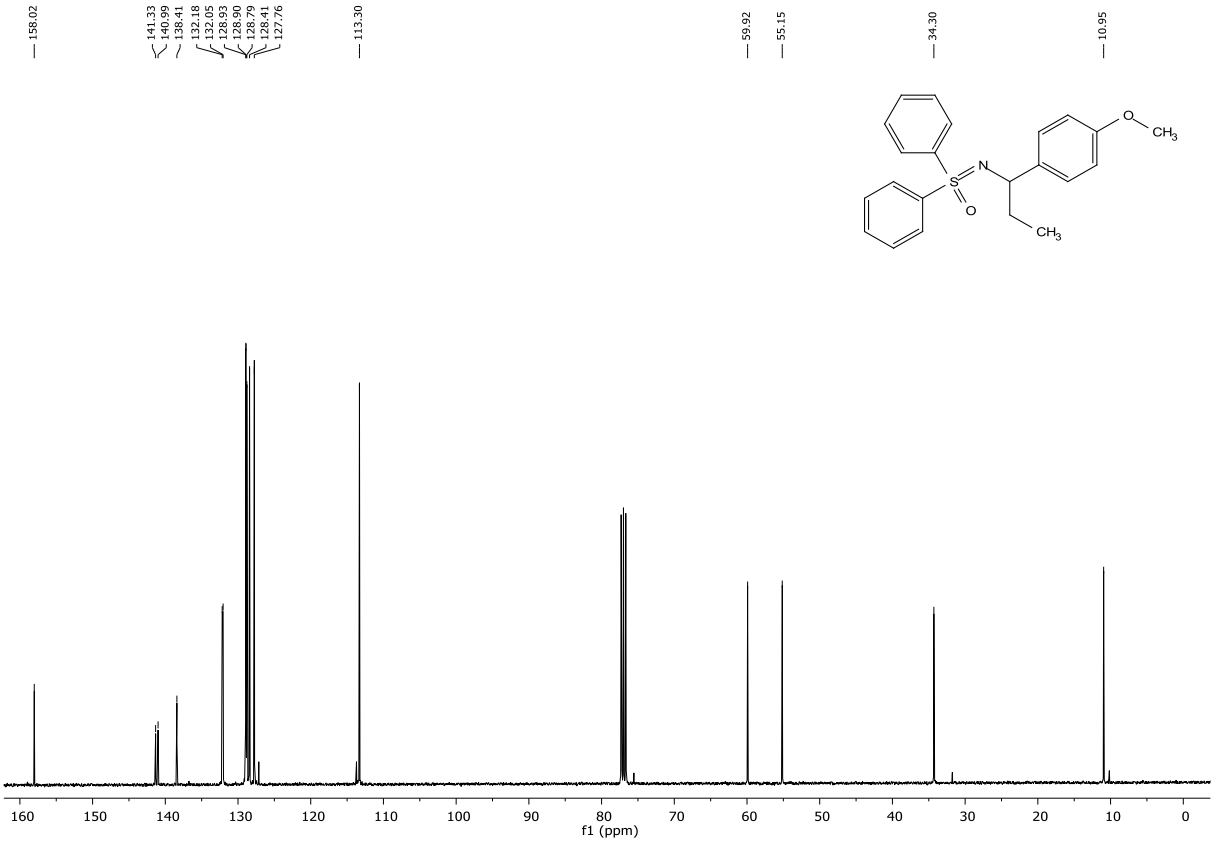
^{1}H NMR (150 MHz, $CDCl_3$) of **16p**



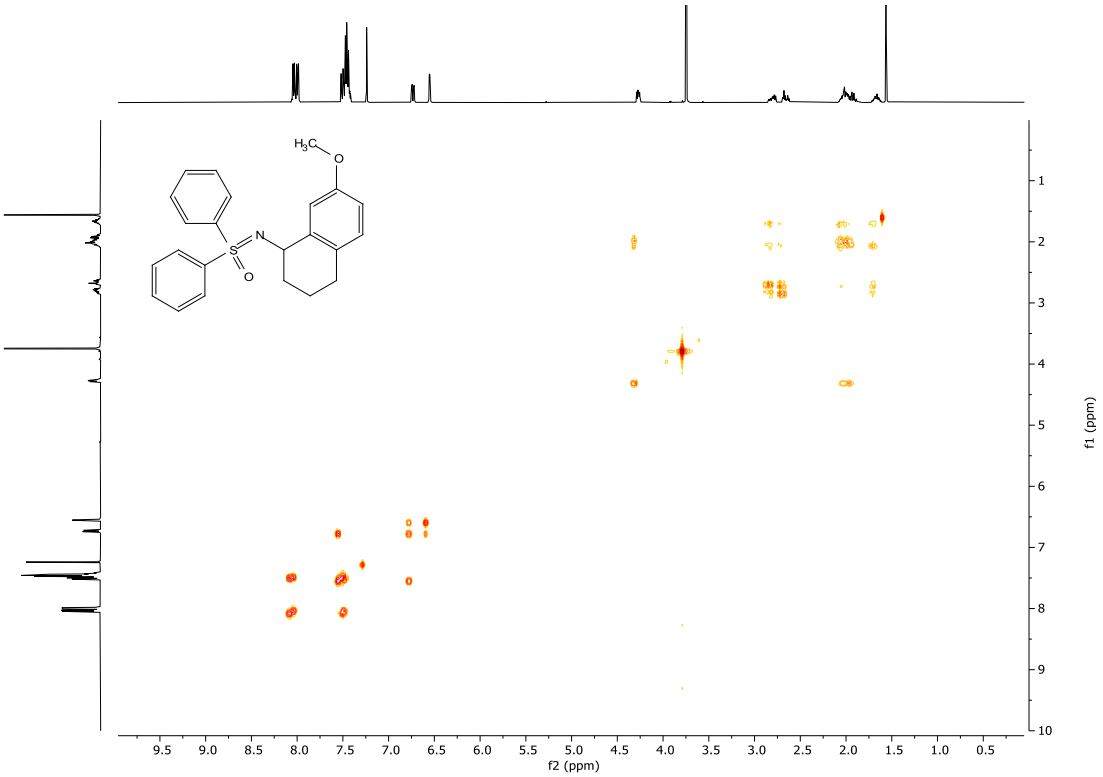
^{1}H NMR (400 MHz, $CDCl_3$) of **16q**

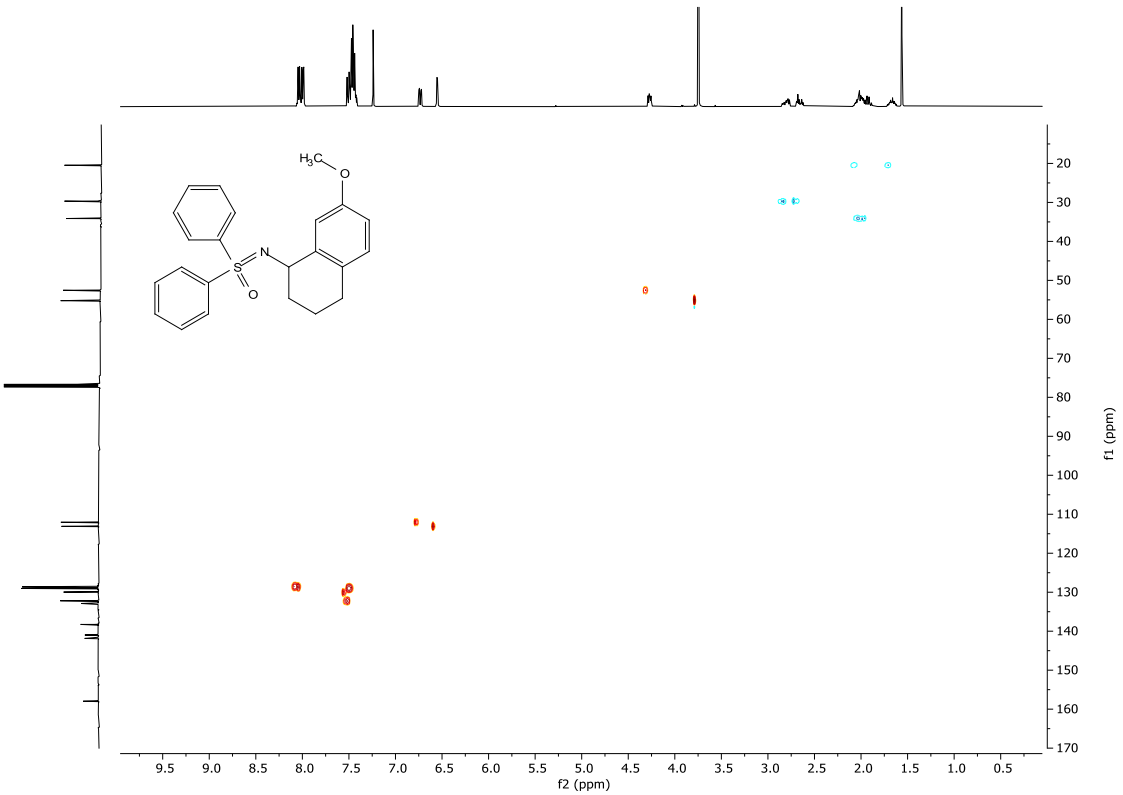


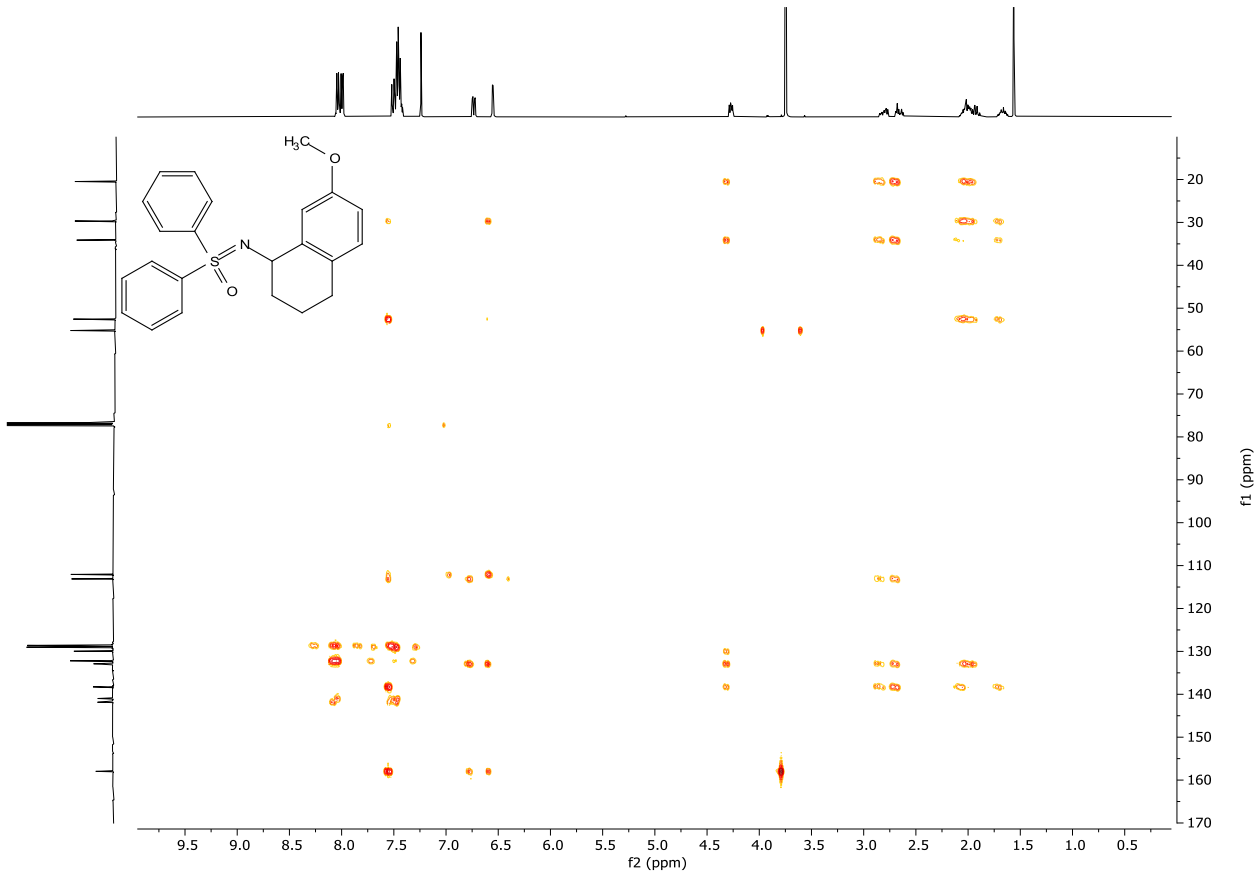
^{13}C NMR (100 MHz, $CDCl_3$) of **16q**



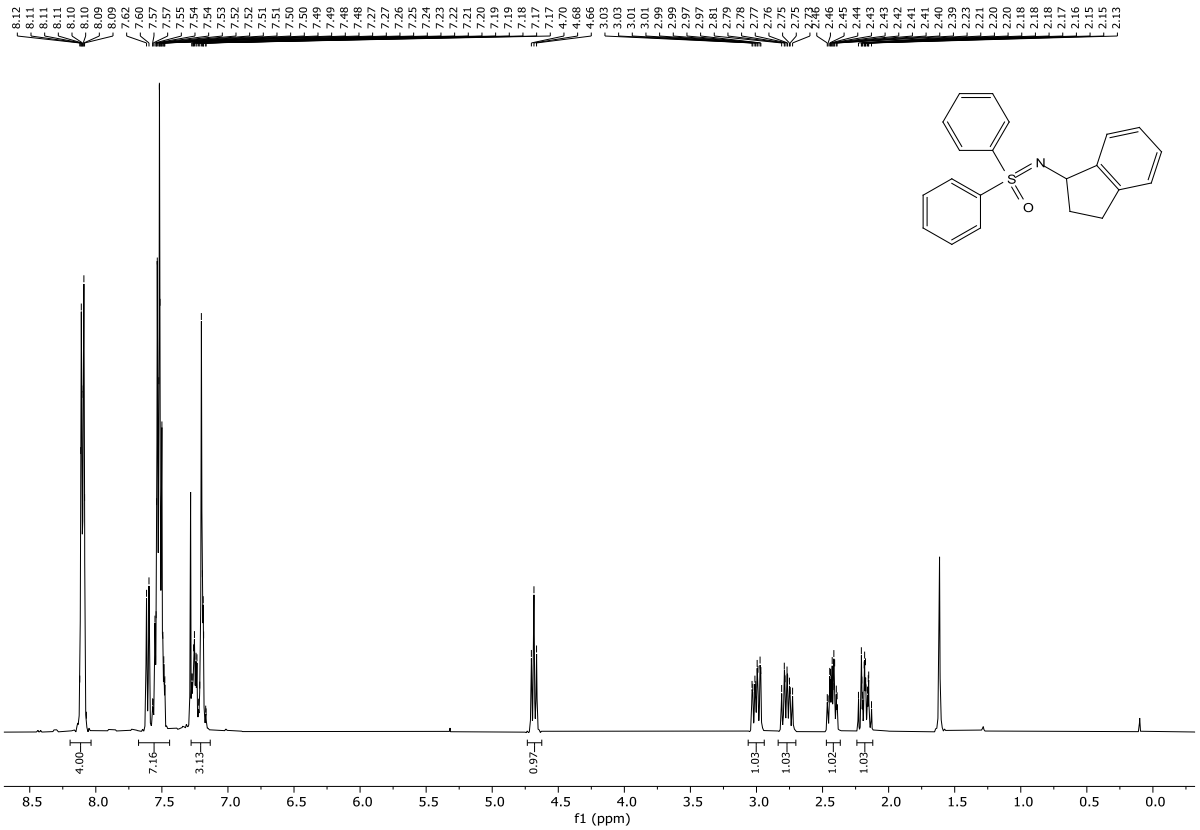
2D NMR (cosy, HSQC, HMBC)



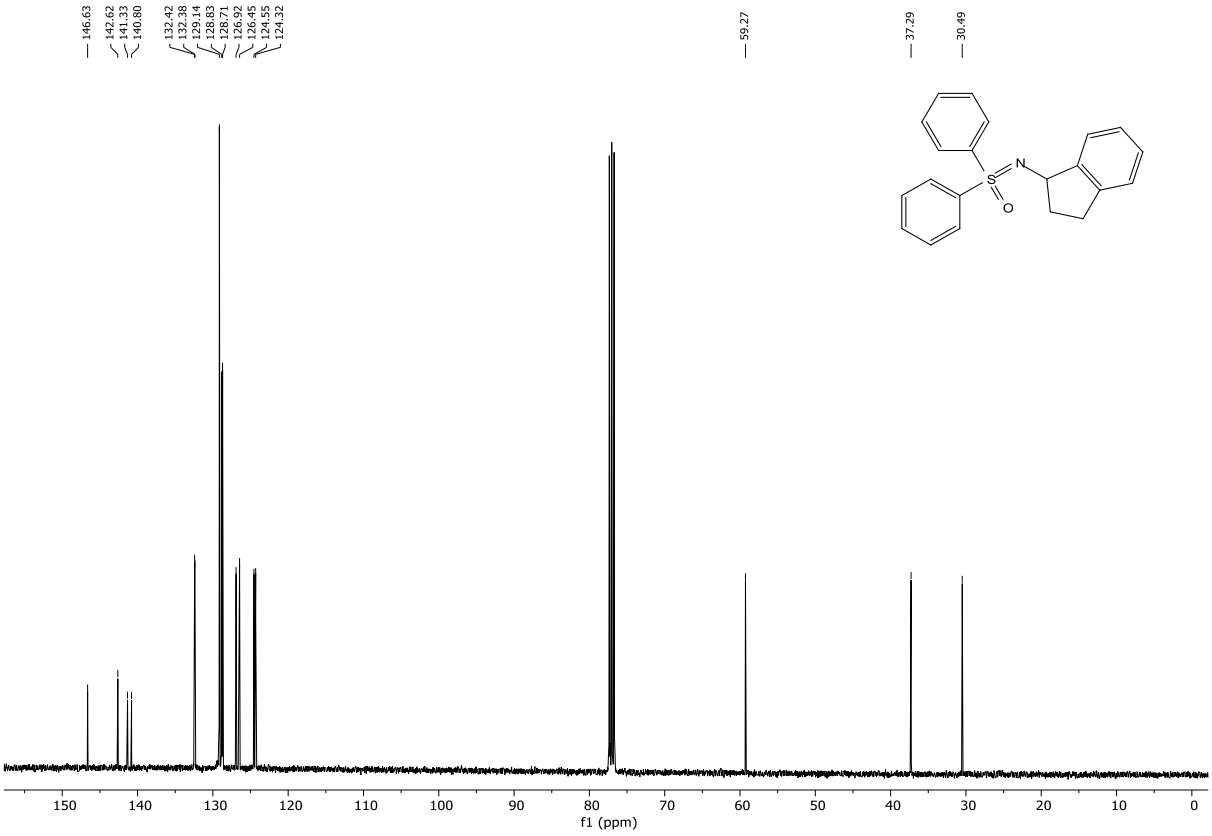



H3C
O
N
S
O
f2 (ppm)
f1 (ppm)

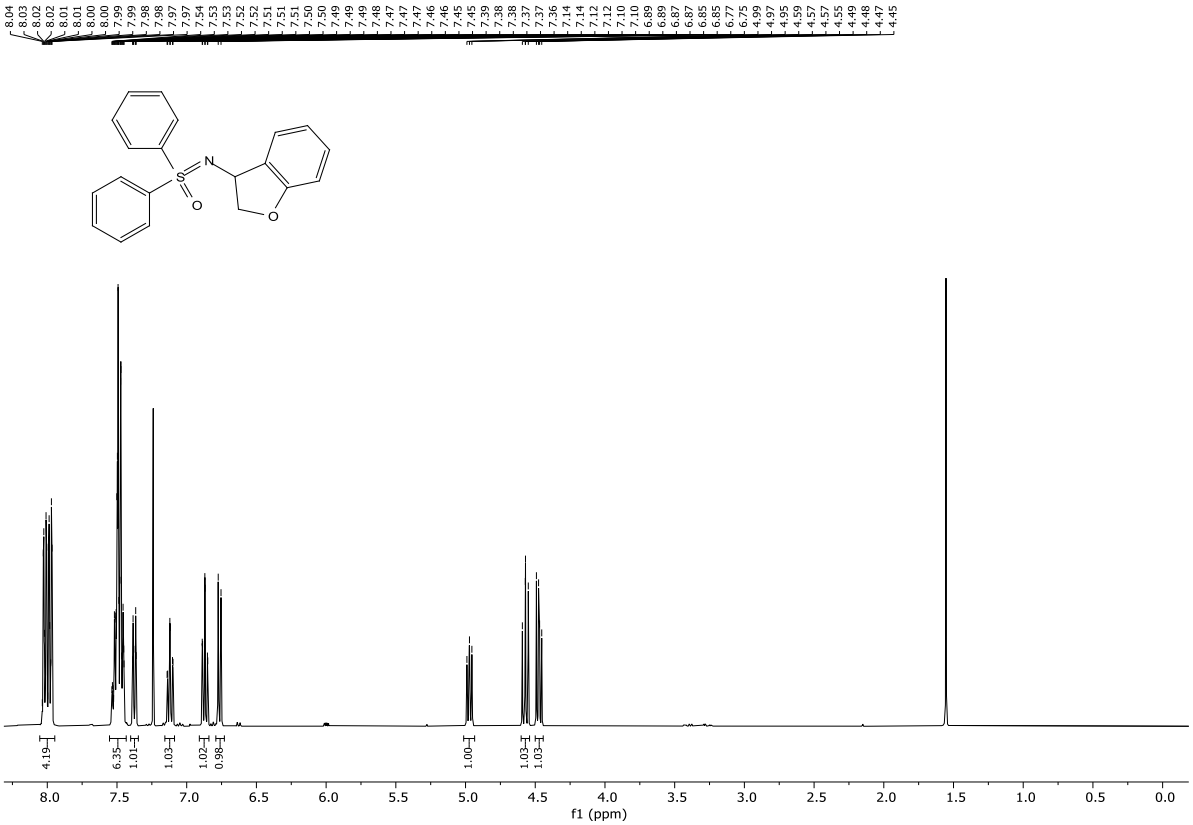
^{1}H NMR (400 MHz, $CDCl_3$) of **16r**



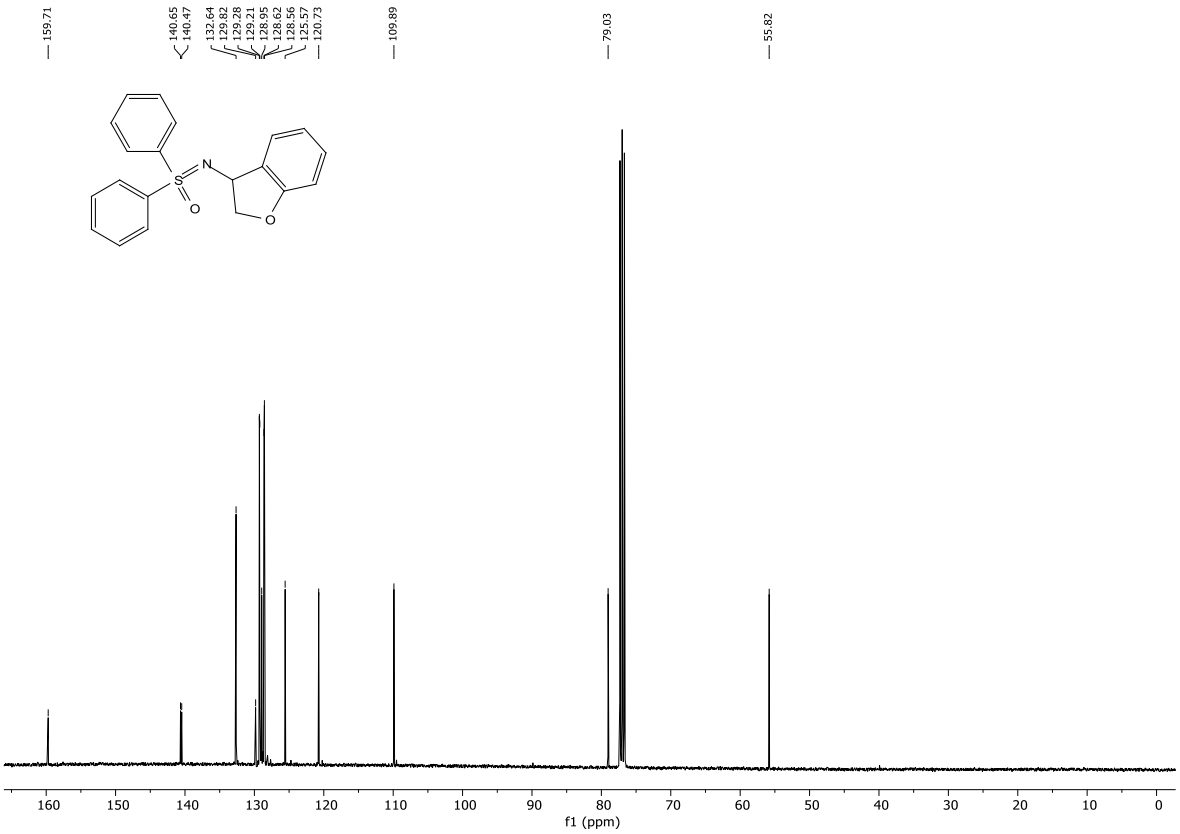
^{13}C NMR (100 MHz, $CDCl_3$) of **16r**



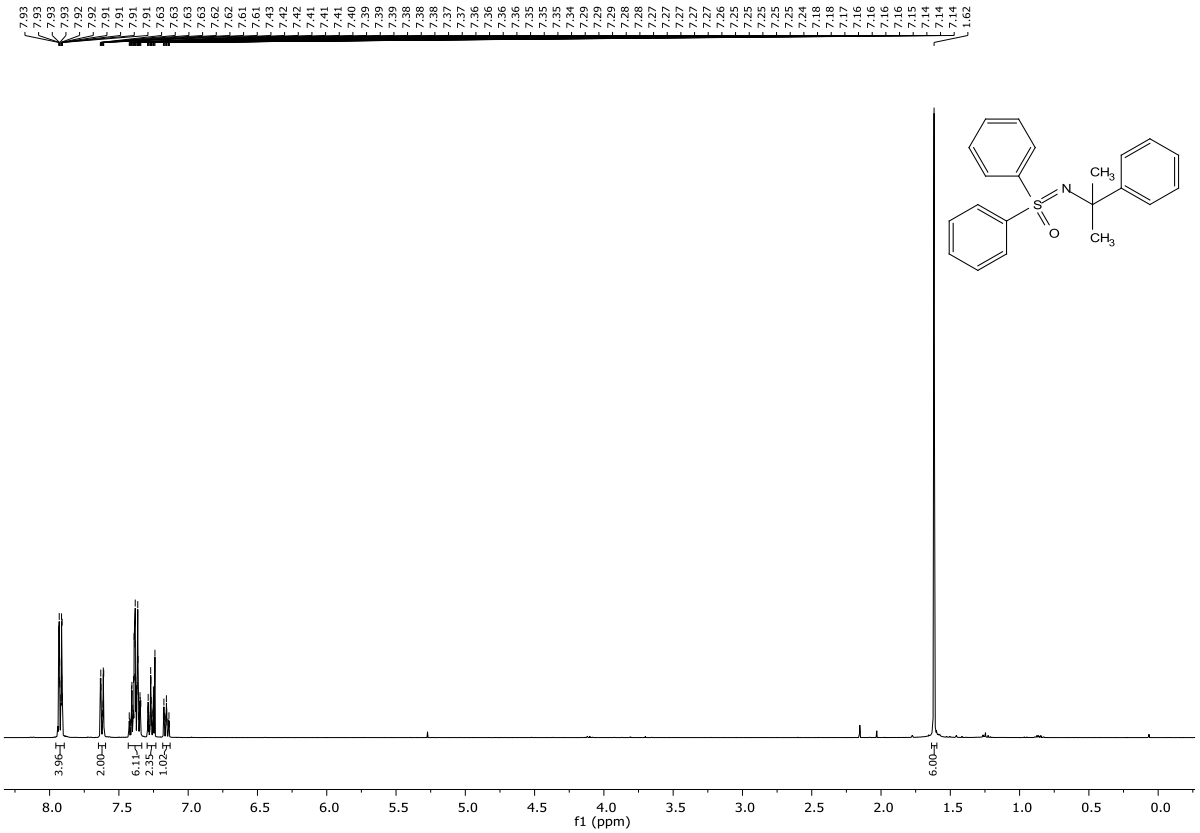
^{1}H NMR (400 MHz, $CDCl_3$) of **16s**



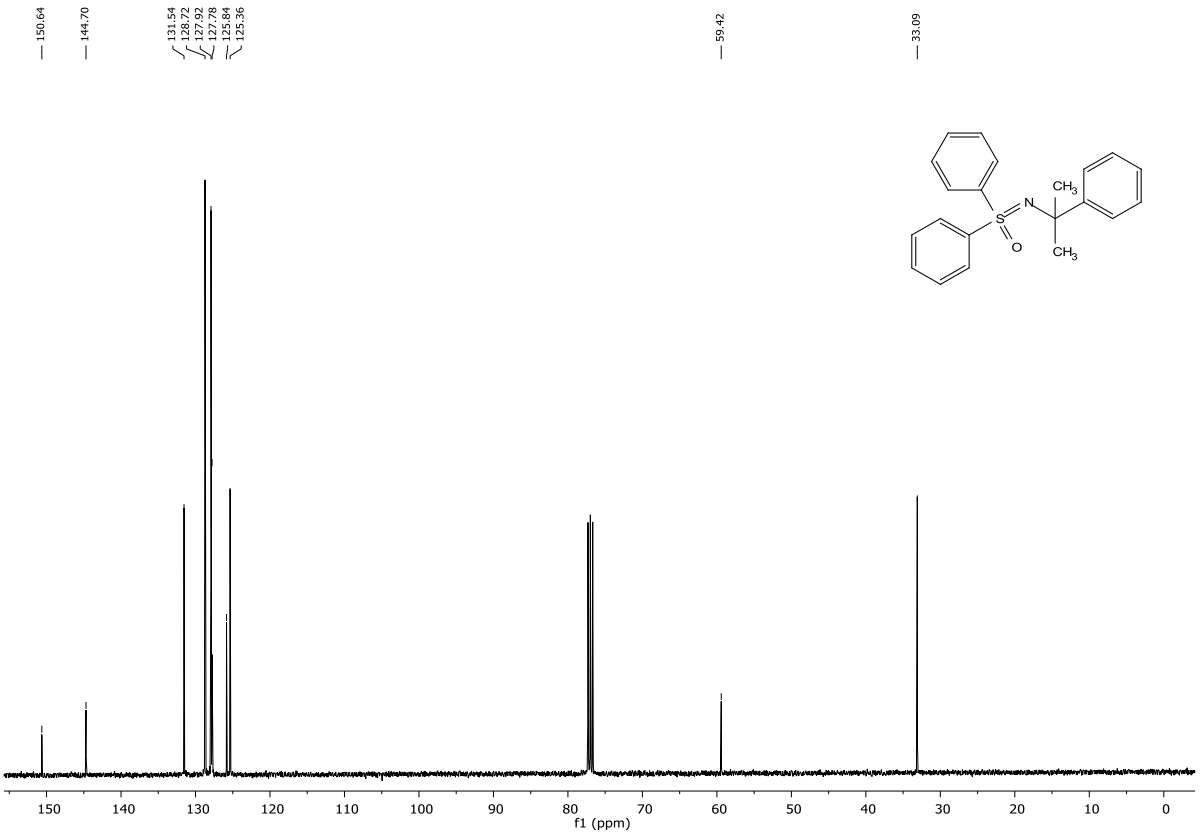
^{13}C NMR (100 MHz, $CDCl_3$) of **16s**



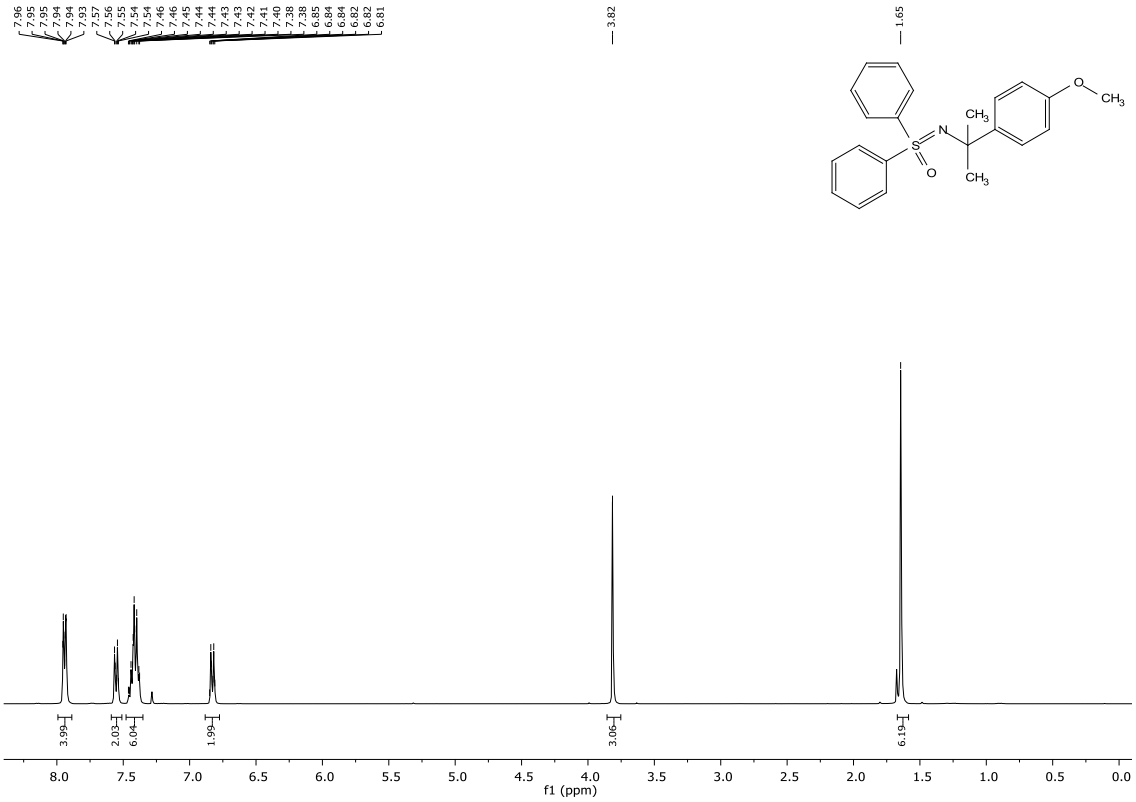
^{1}H NMR (400 MHz, $CDCl_3$) of **16t**



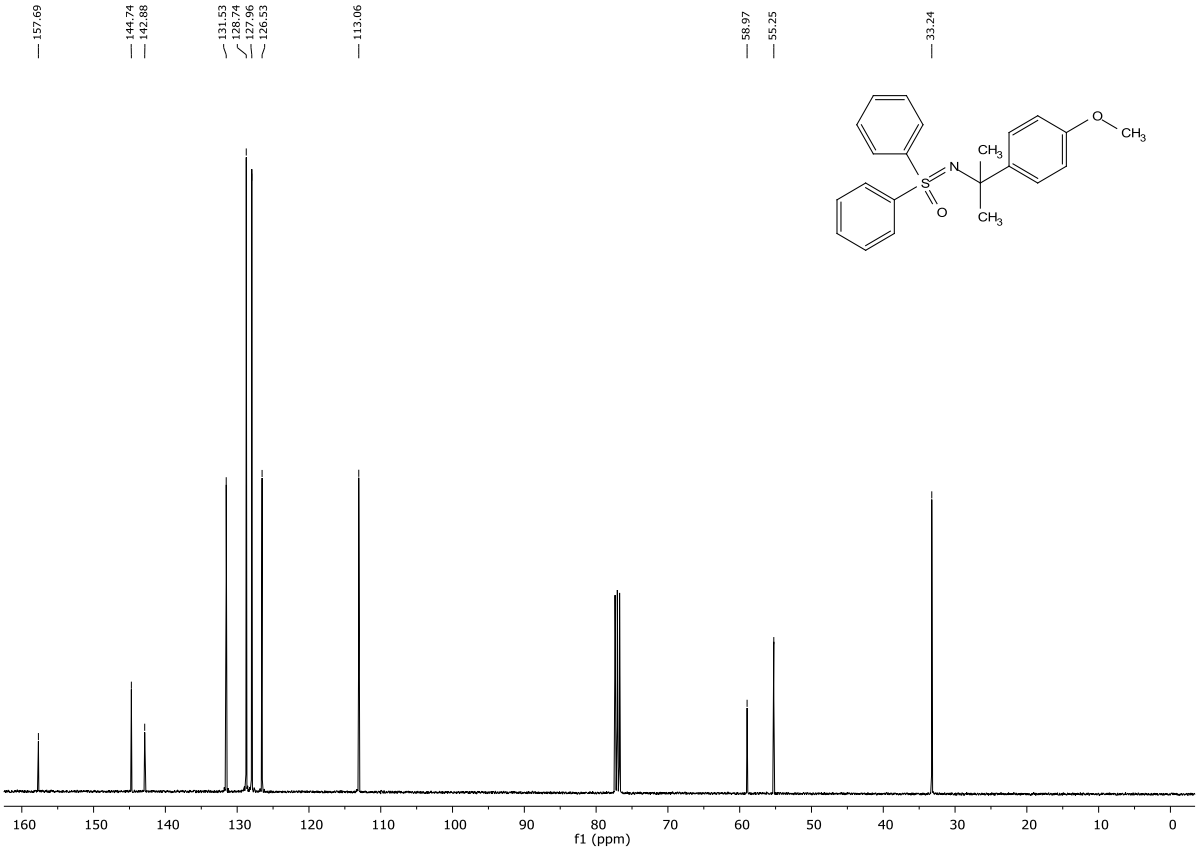
^{13}C NMR (100 MHz, $CDCl_3$) of **16t**



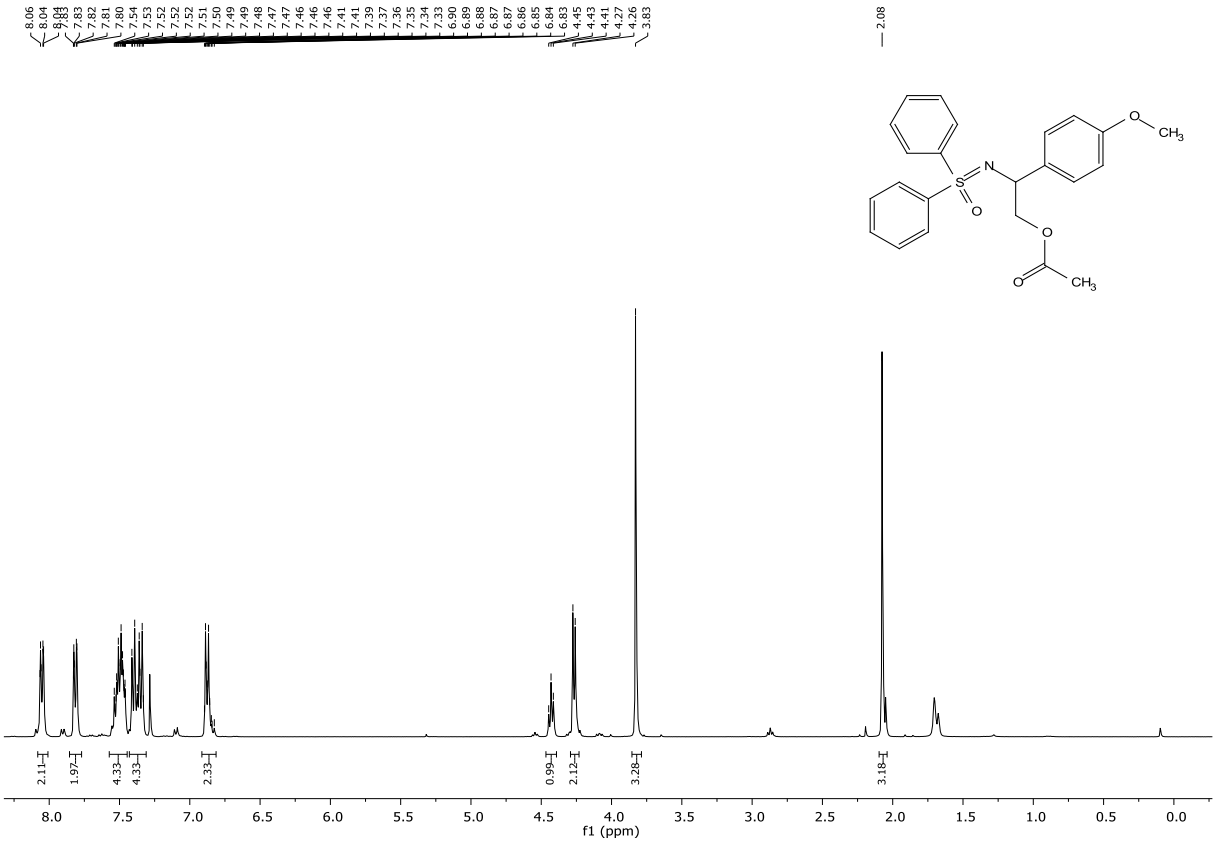
^{1}H NMR (400 MHz, $CDCl_3$) of **16u**



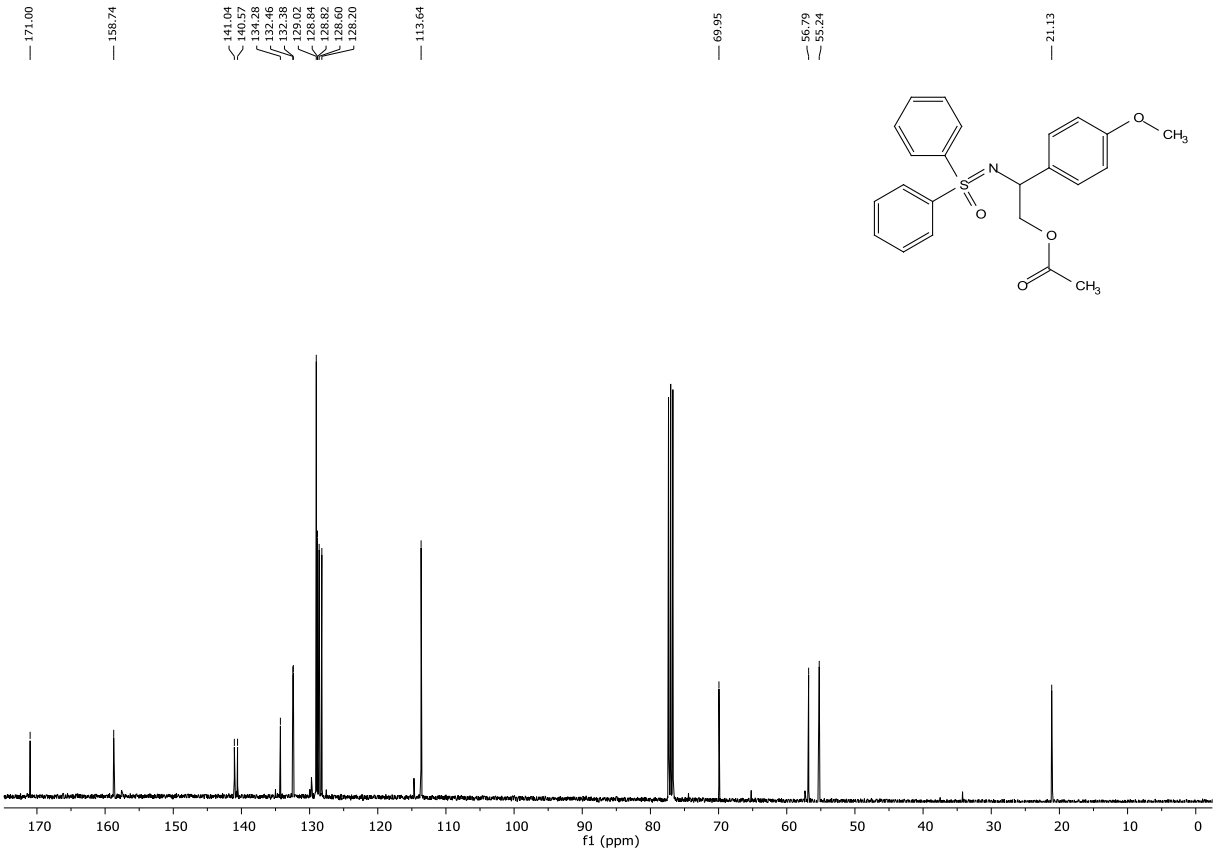
^{13}C NMR (100 MHz, $CDCl_3$) of **16u**



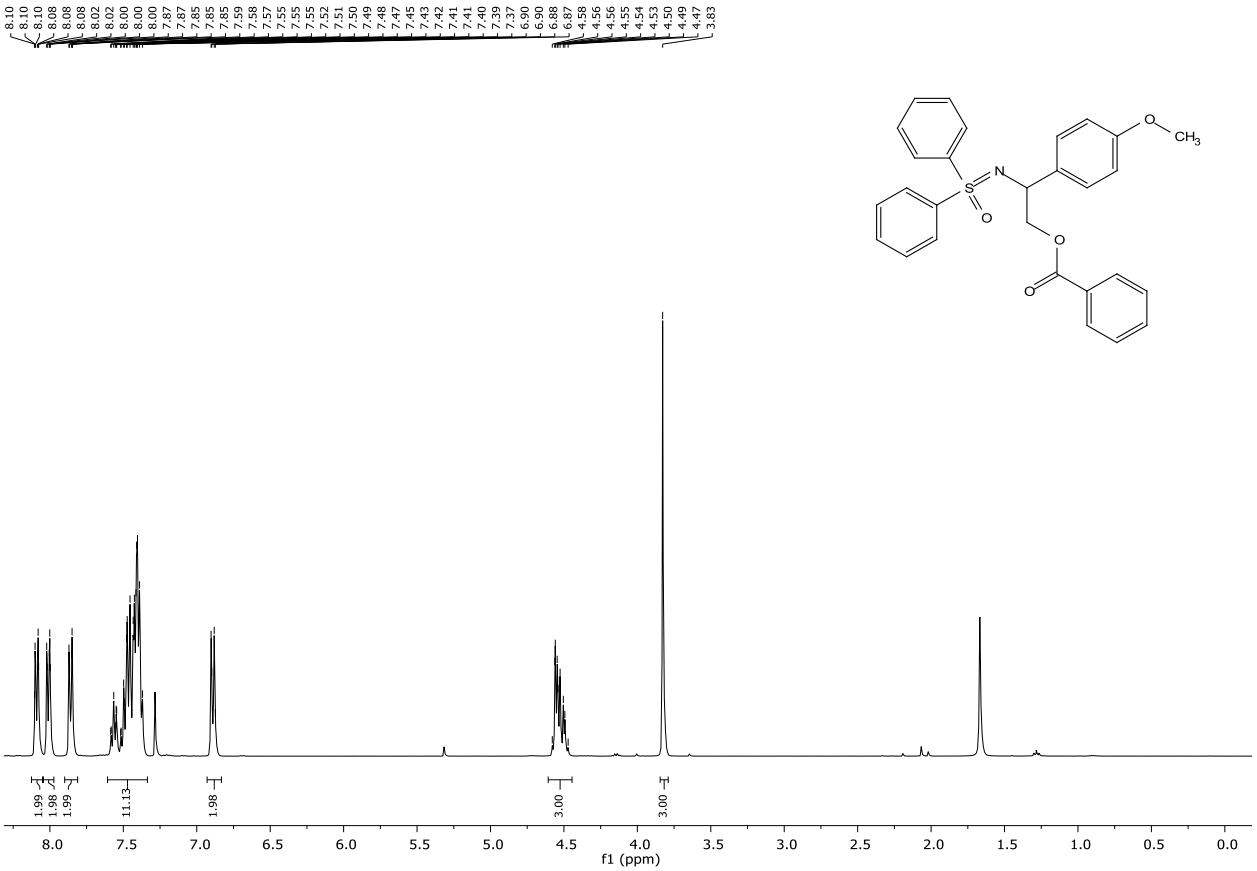
^{1}H NMR (400 MHz, $CDCl_3$) of **16v**



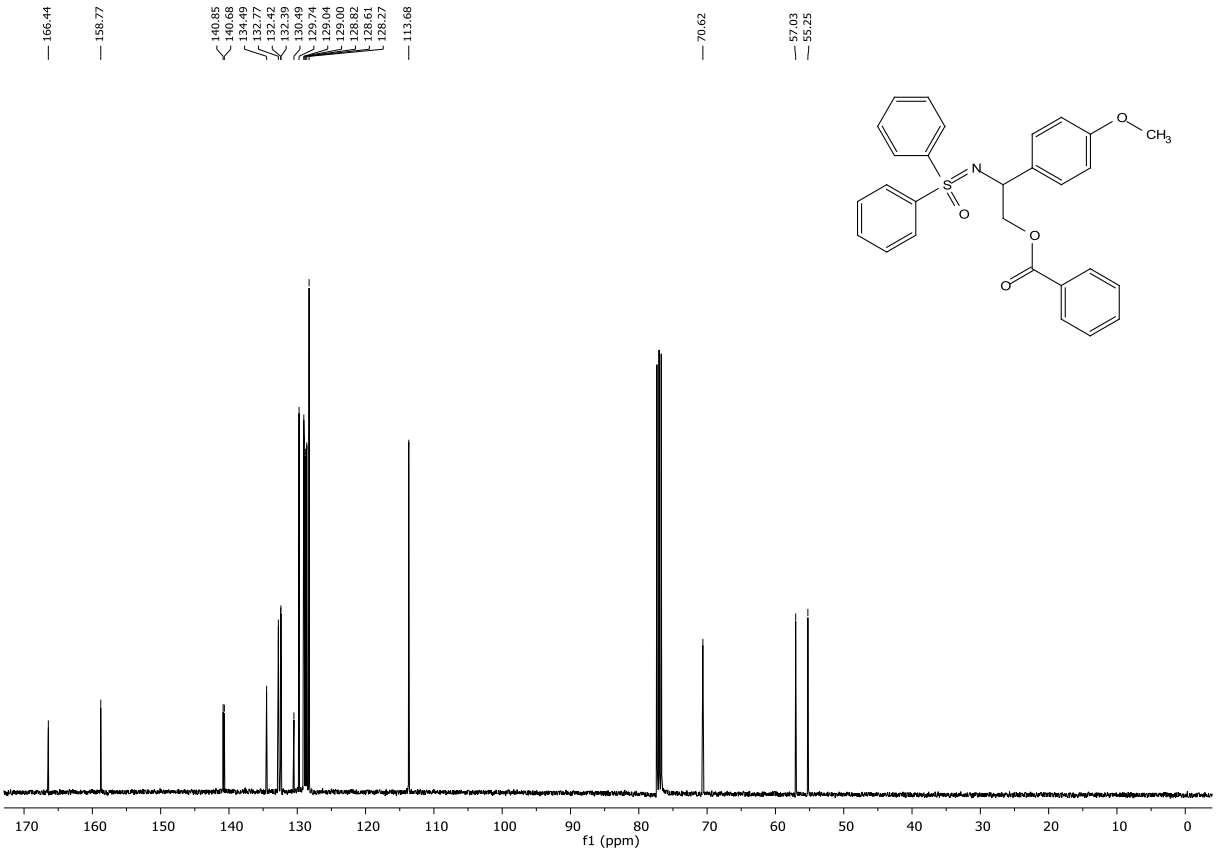
^{13}C NMR (100 MHz, $CDCl_3$) of **16v**



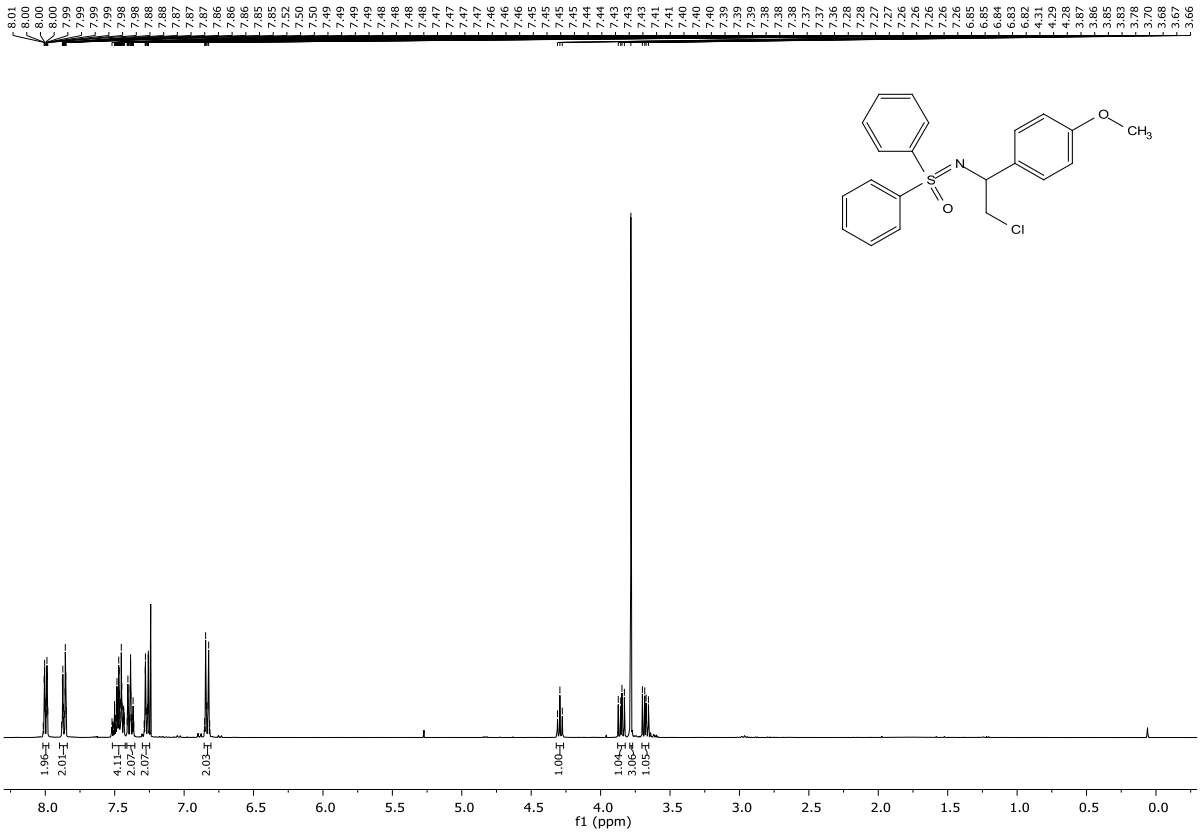
^{1}H NMR (400 MHz, $CDCl_3$) of **16w**



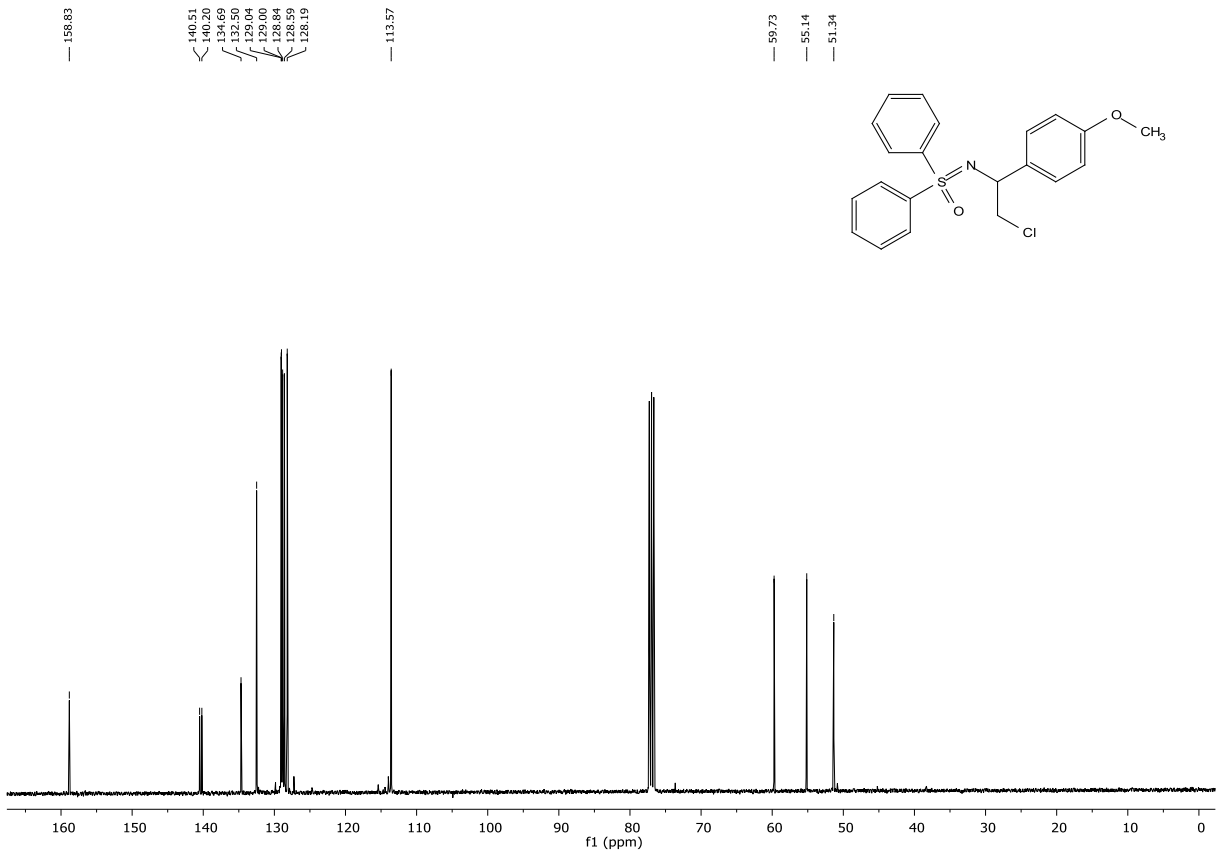
^{13}C NMR (100 MHz, $CDCl_3$) of **16w**



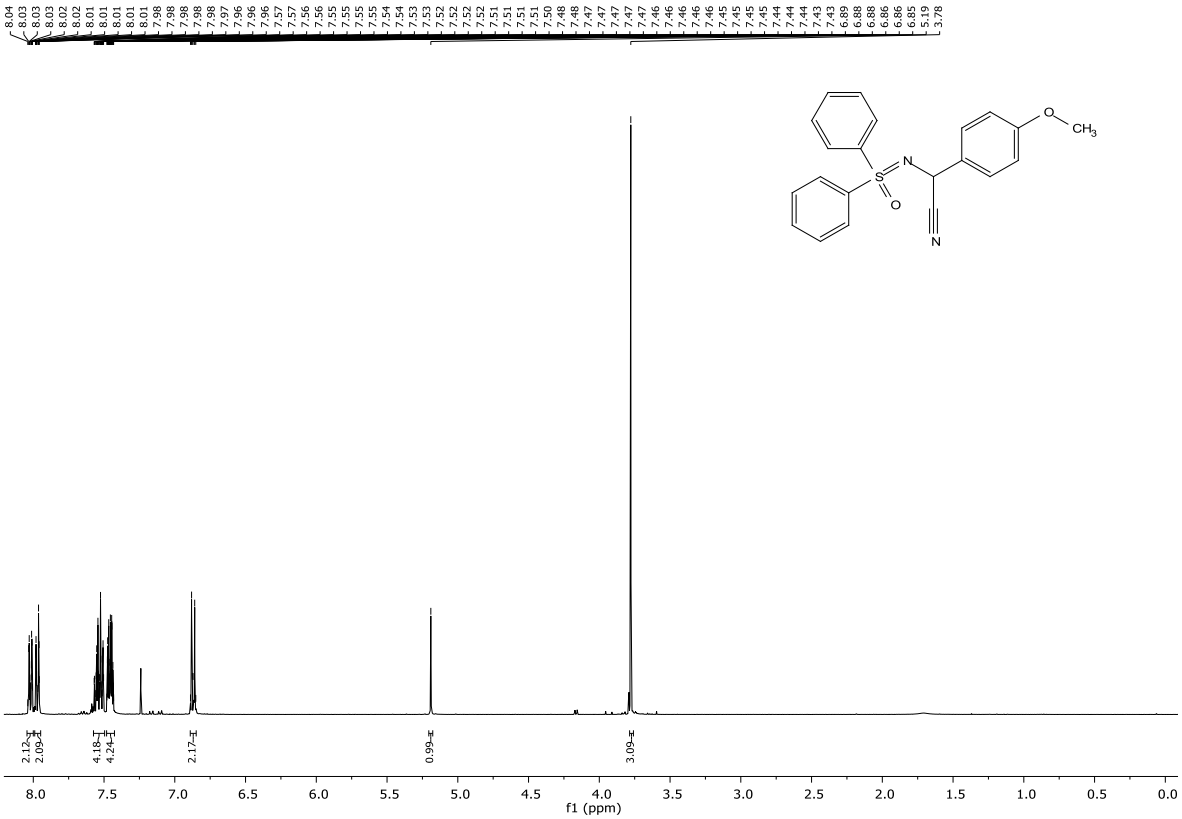
^{1}H NMR (400 MHz, $CDCl_3$) of **16x**



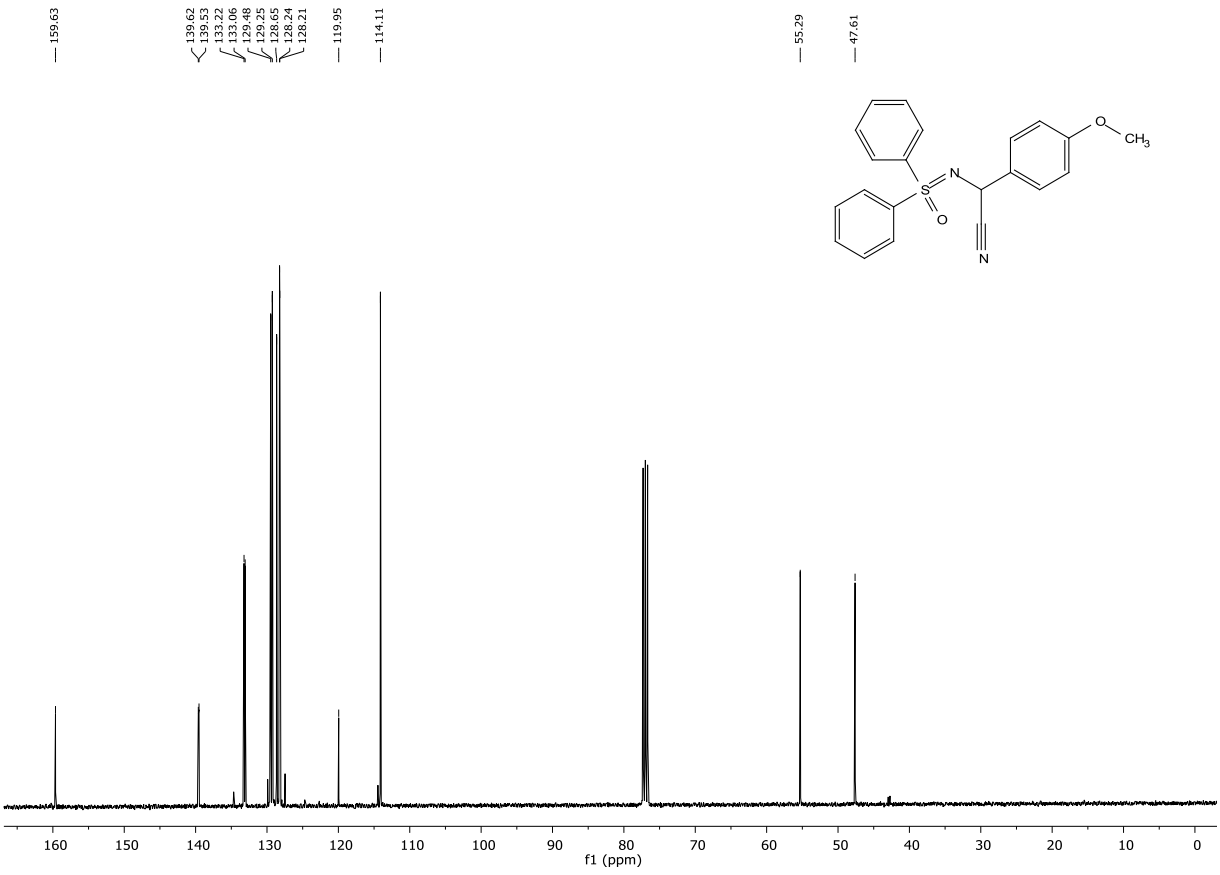
^{1}H NMR (400 MHz, $CDCl_3$) of **16x**



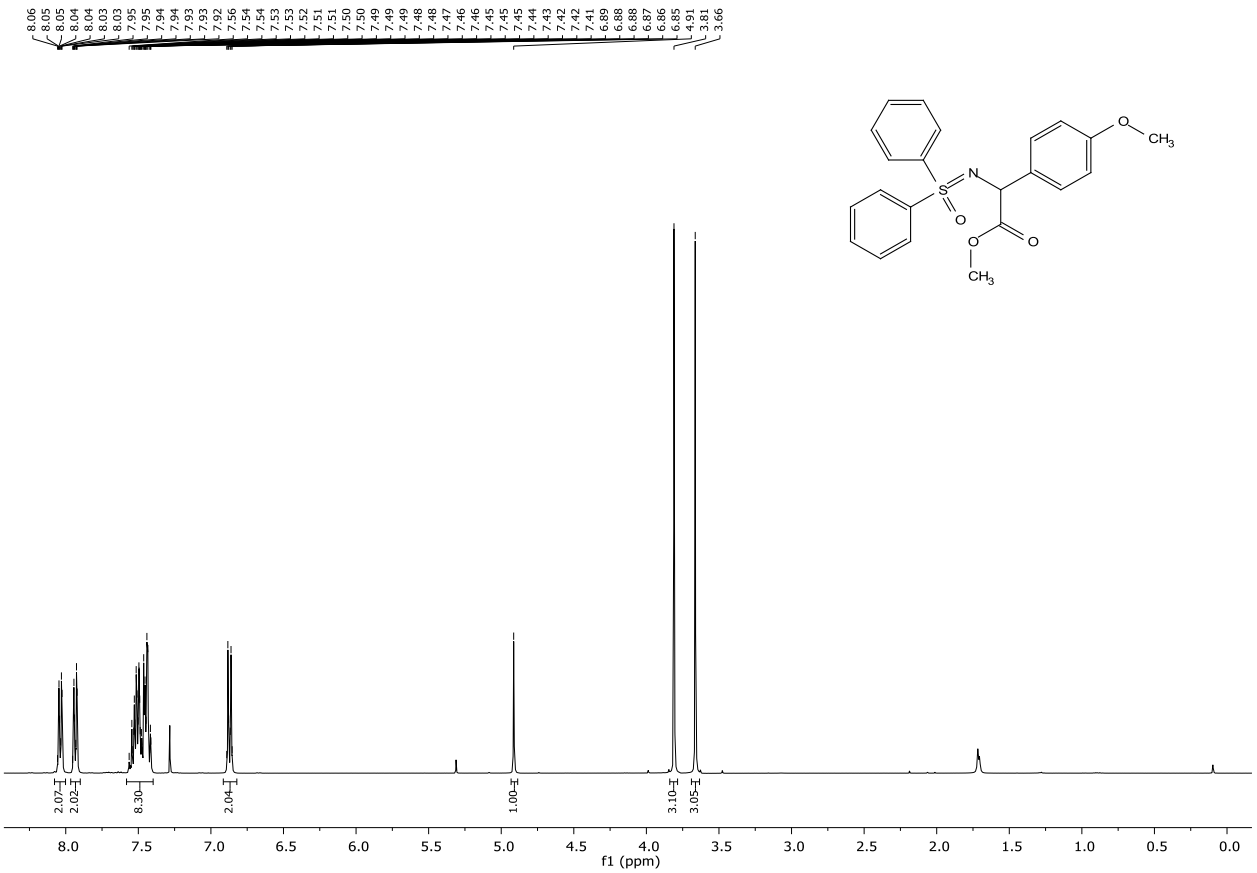
^{1}H NMR (400 MHz, $CDCl_3$) of **16y**



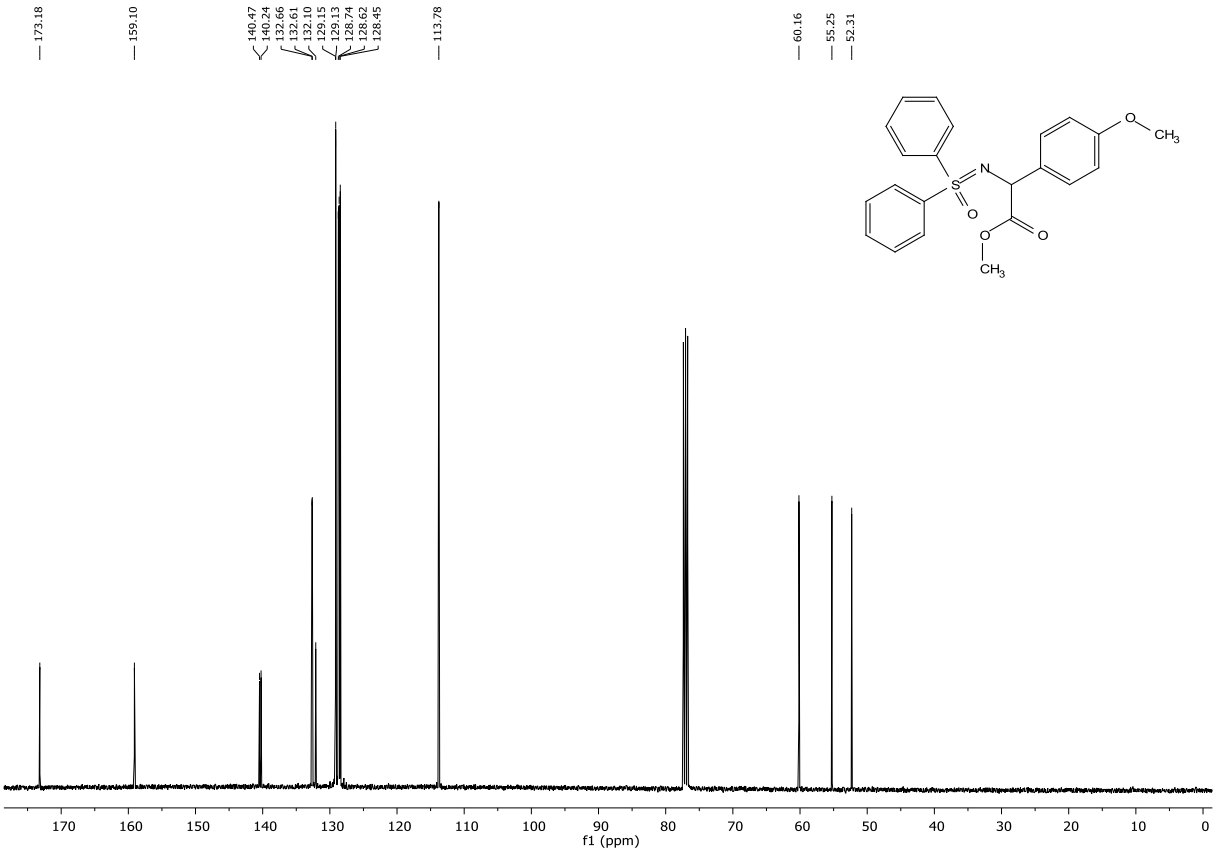
^{13}C NMR (100 MHz, $CDCl_3$) of **16y**



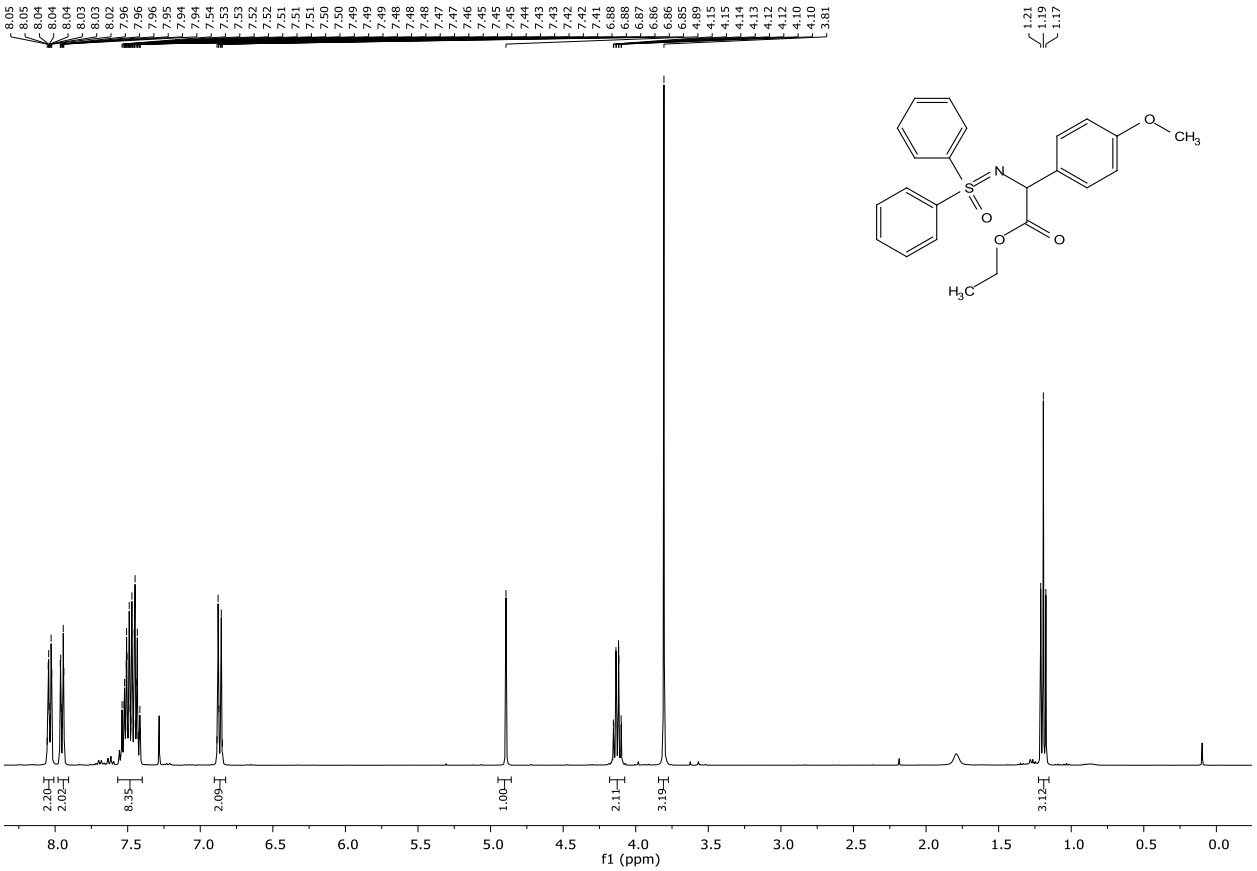
^{1}H NMR (400 MHz, $CDCl_3$) of **16z**



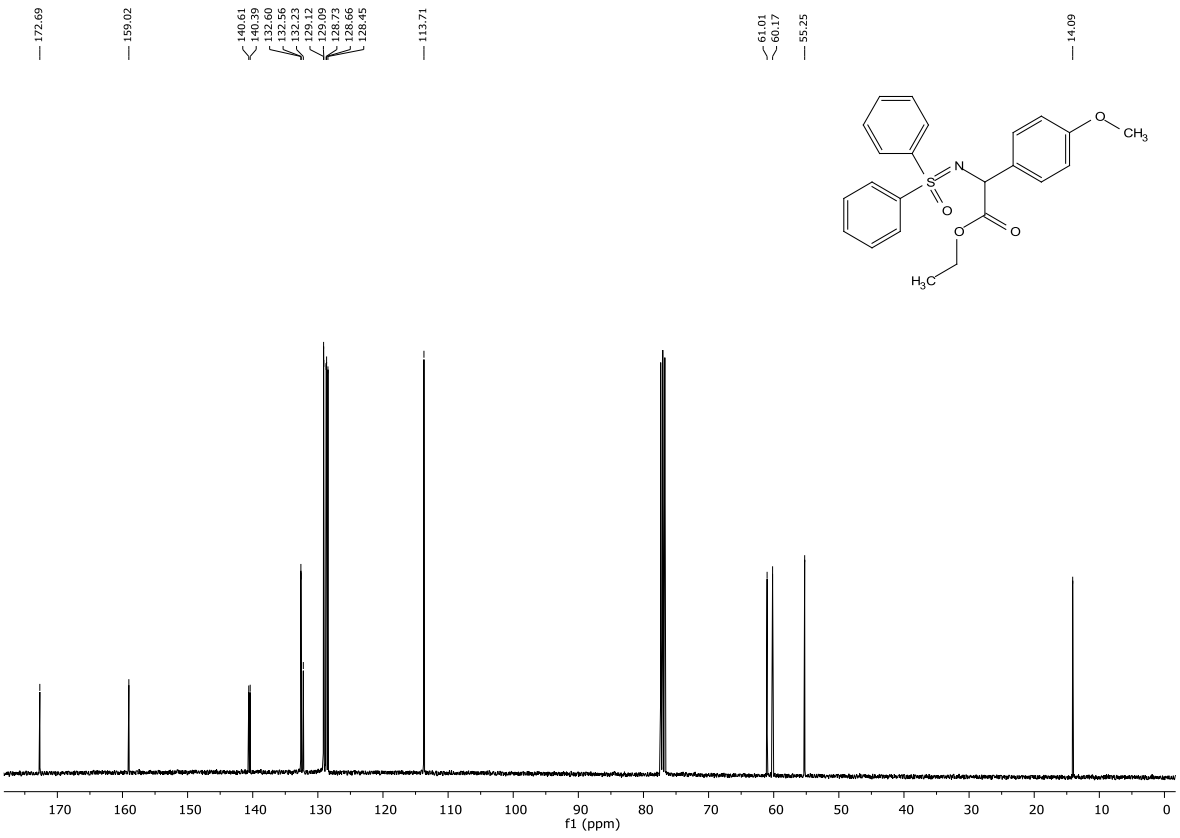
^{13}C NMR (100 MHz, $CDCl_3$) of **16z**



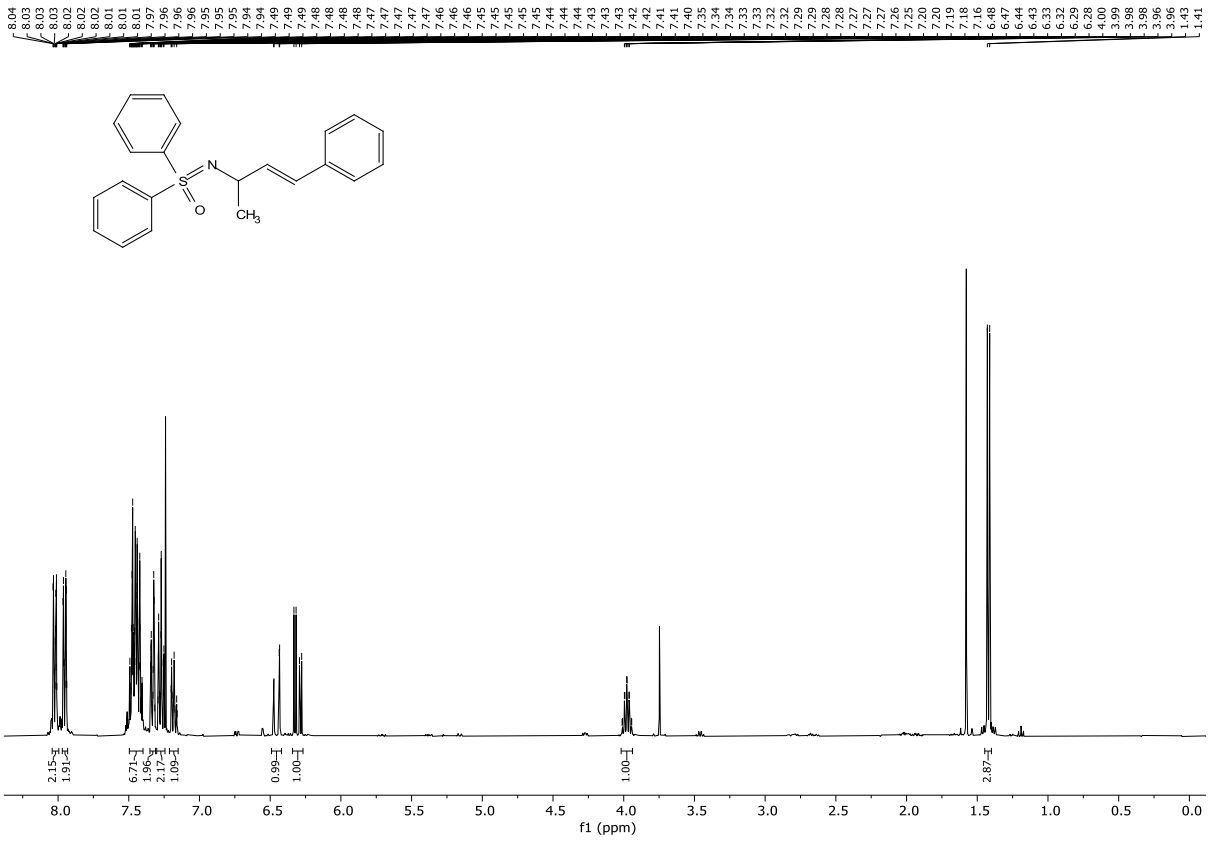
^{1}H NMR (400 MHz, $CDCl_3$) of **16aa**



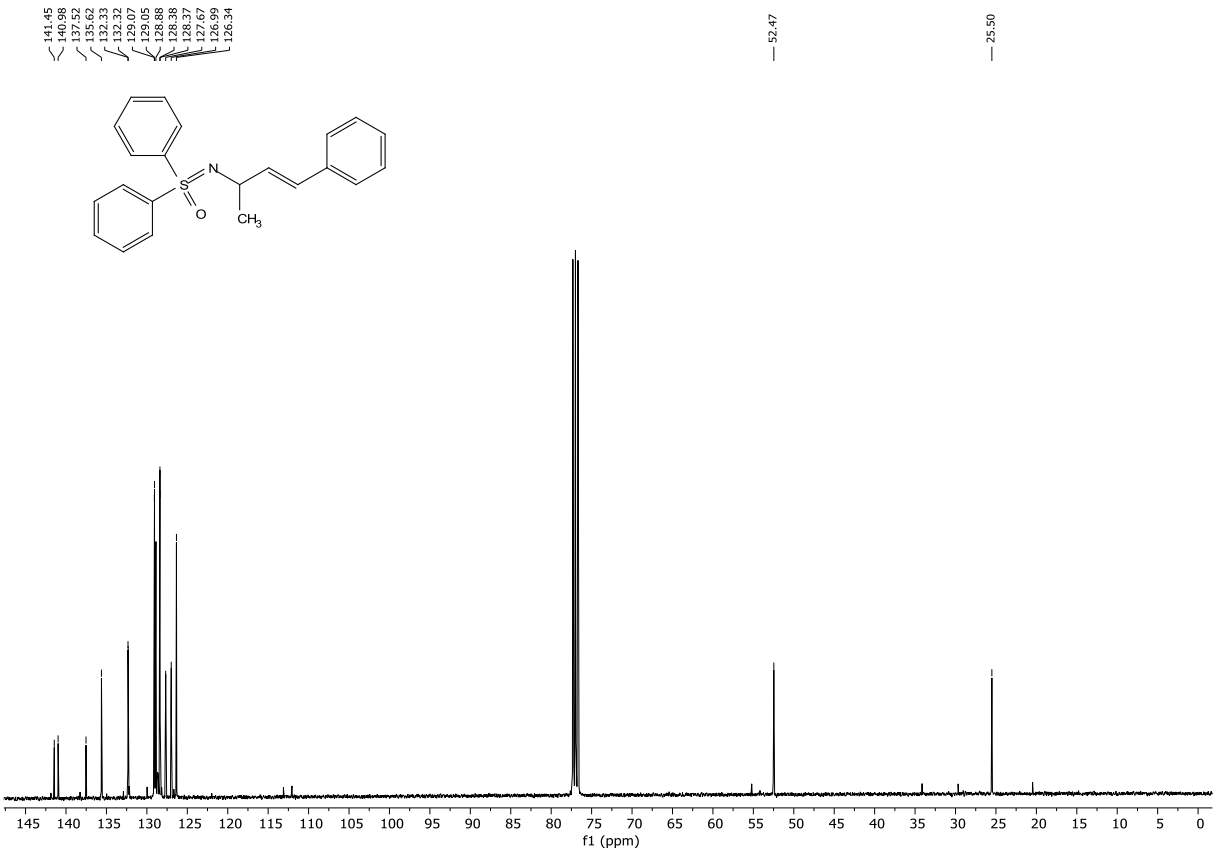
^{13}C NMR (100 MHz, $CDCl_3$) of **16aa**



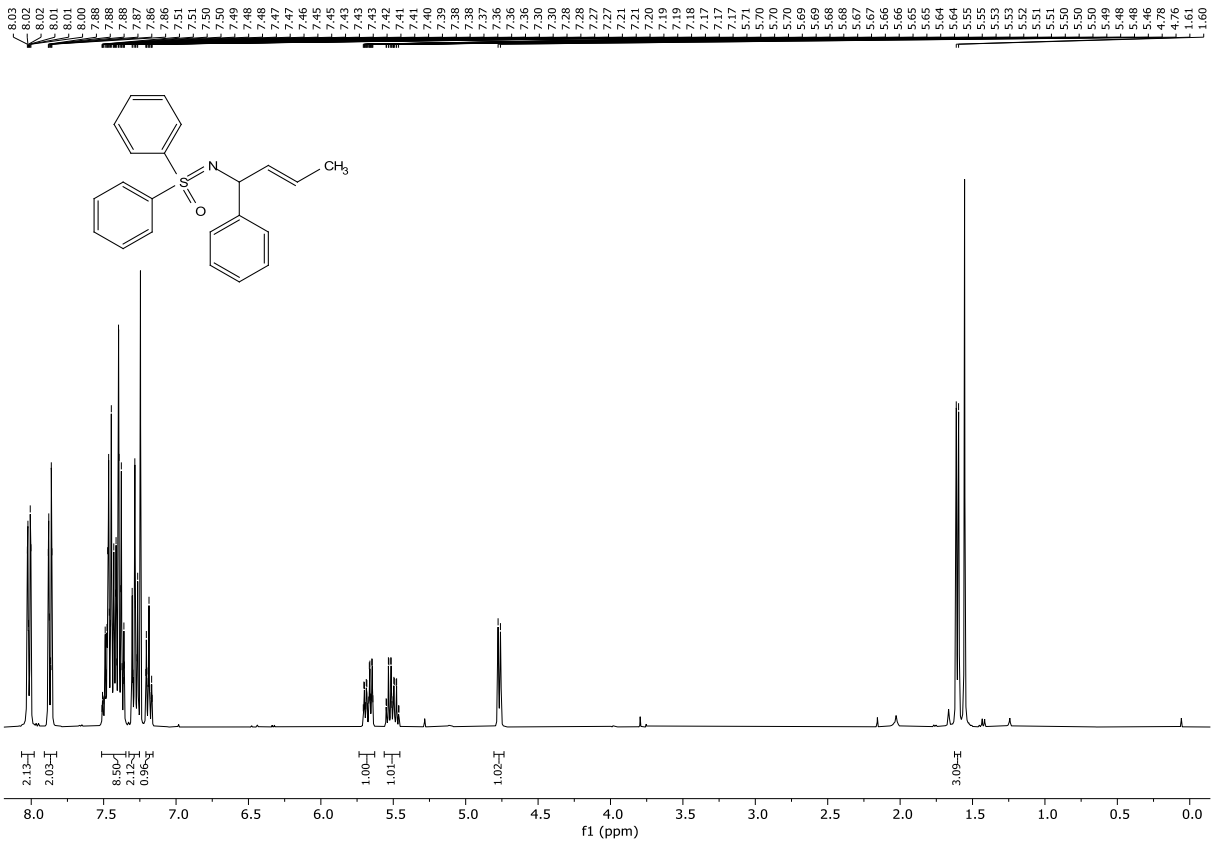
^{1}H NMR (400 MHz, $CDCl_3$) of **16ab**



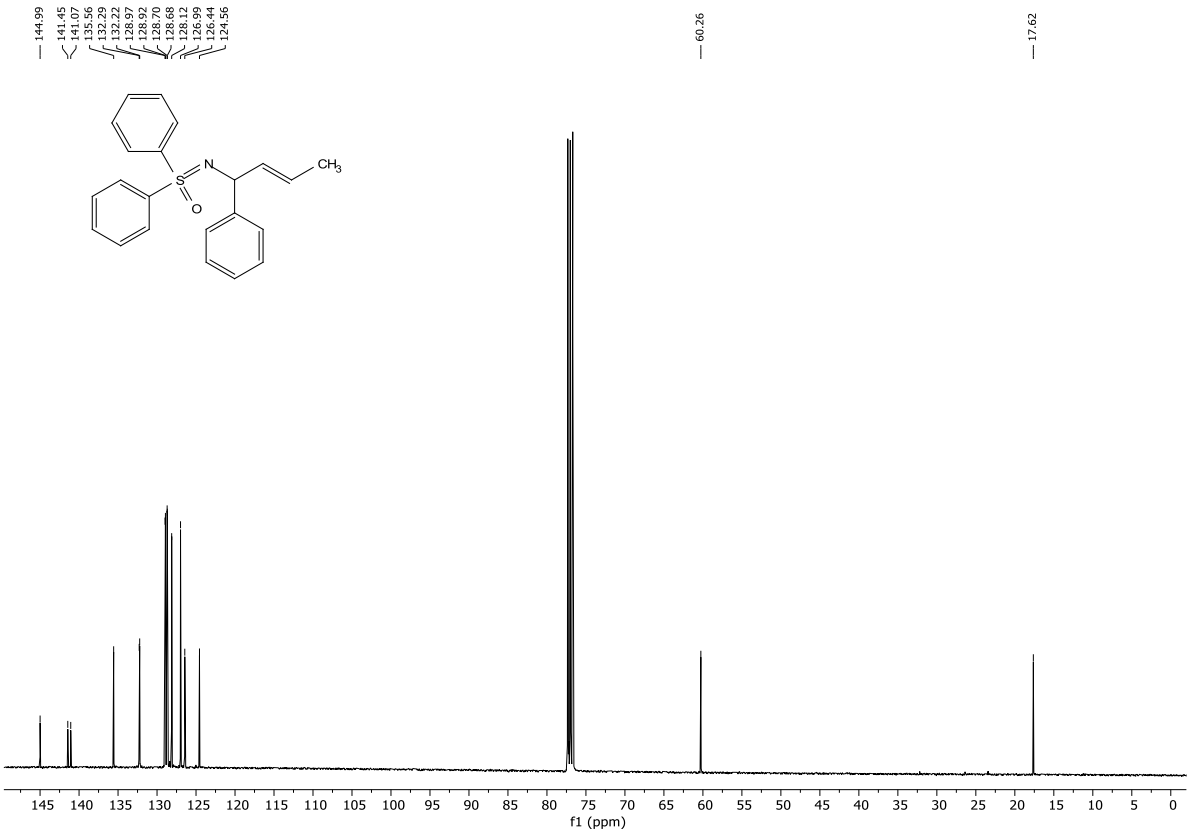
^{13}C NMR (100 MHz, $CDCl_3$) of **16ab**



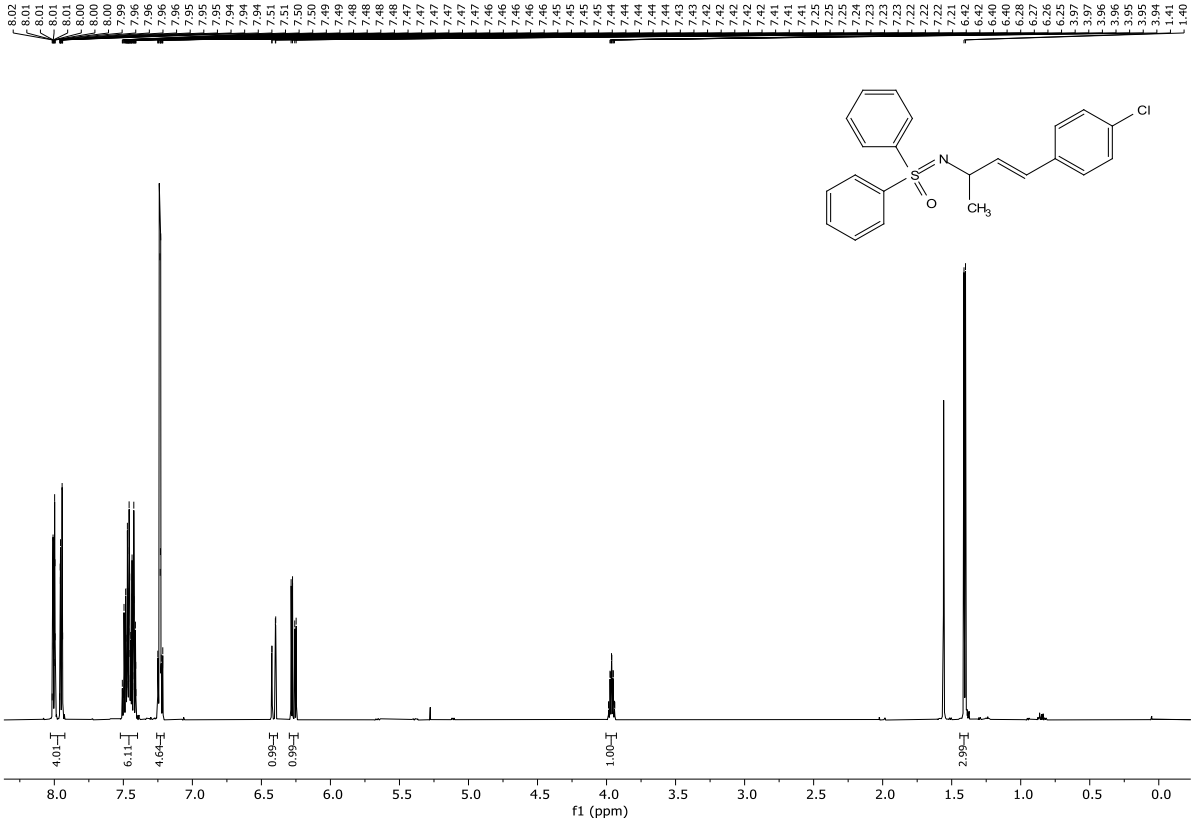
^{1}H NMR (400 MHz, $CDCl_3$) of **16ab'**



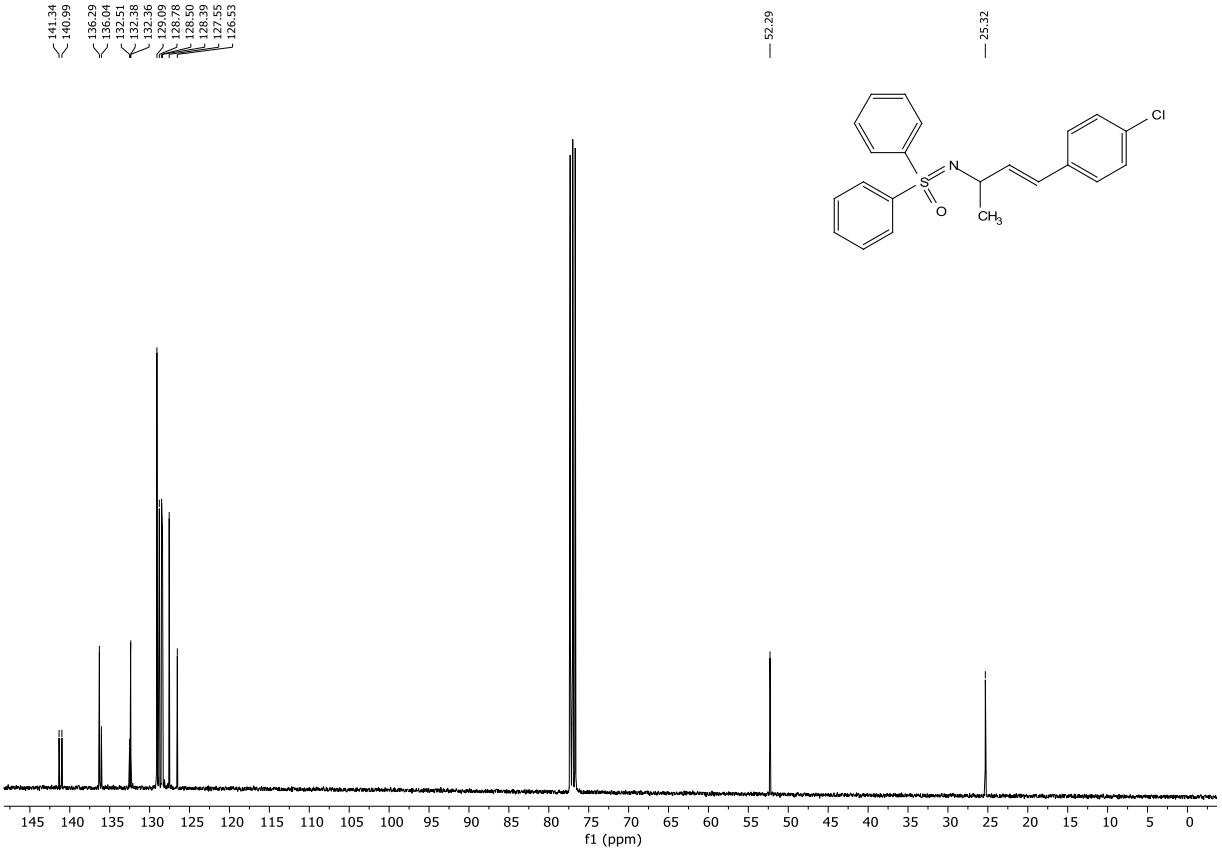
^{13}C NMR (100 MHz, $CDCl_3$) of **16ab'**



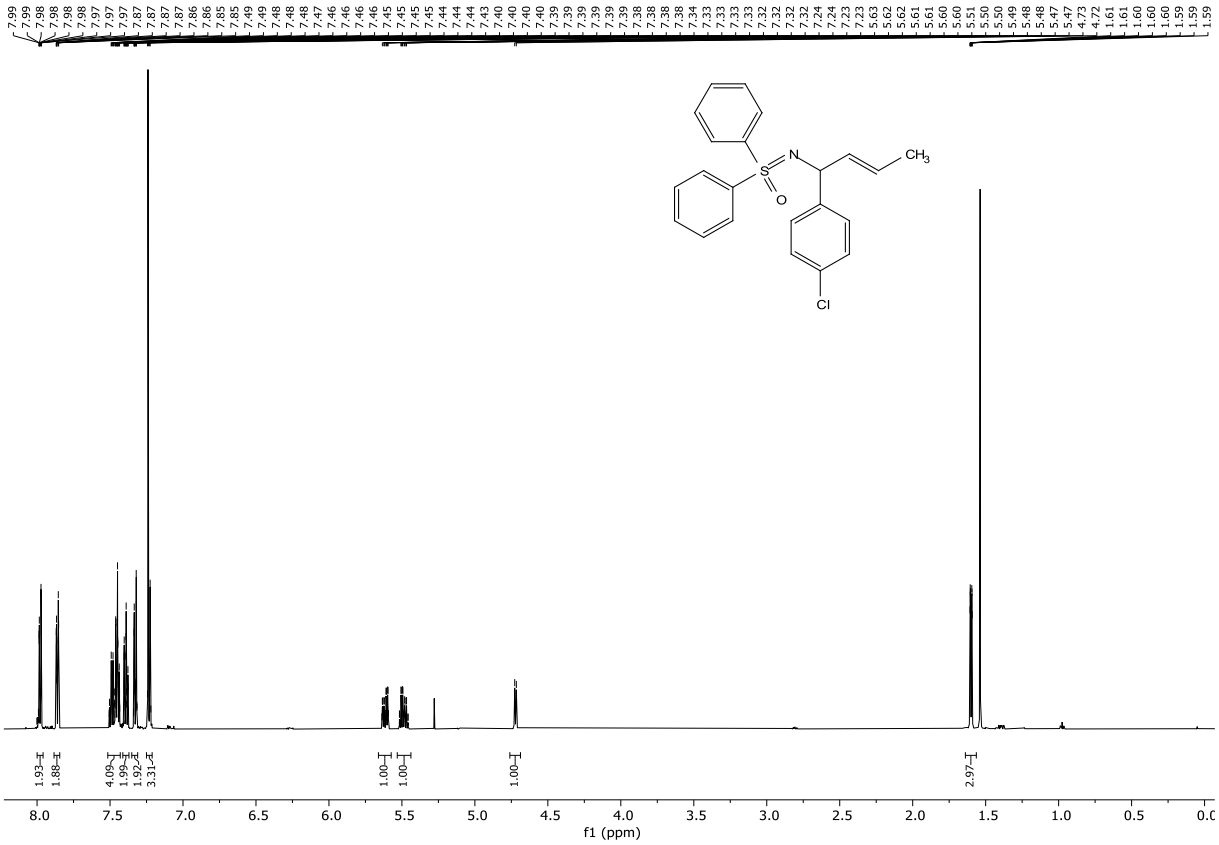
^{1}H NMR (400 MHz, $CDCl_3$) of **16ac**



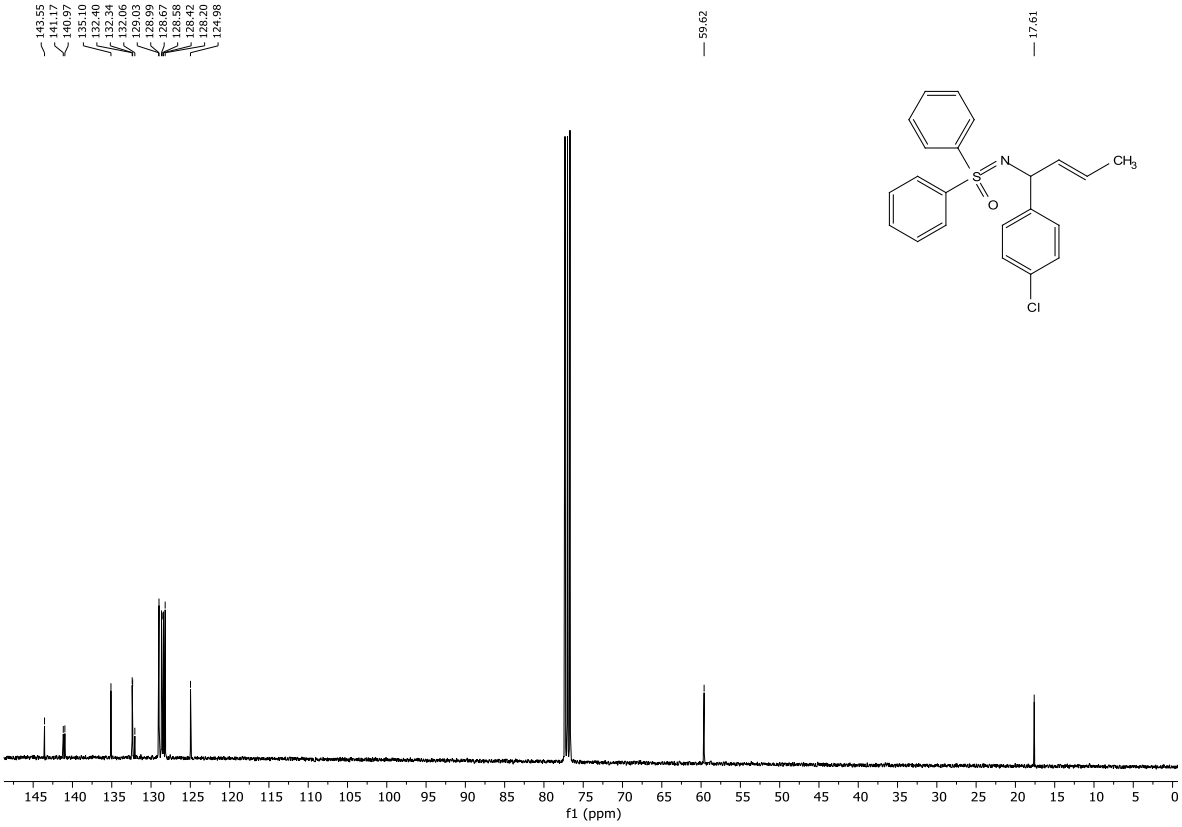
^{13}C NMR (100 MHz, $CDCl_3$) of **16ac**



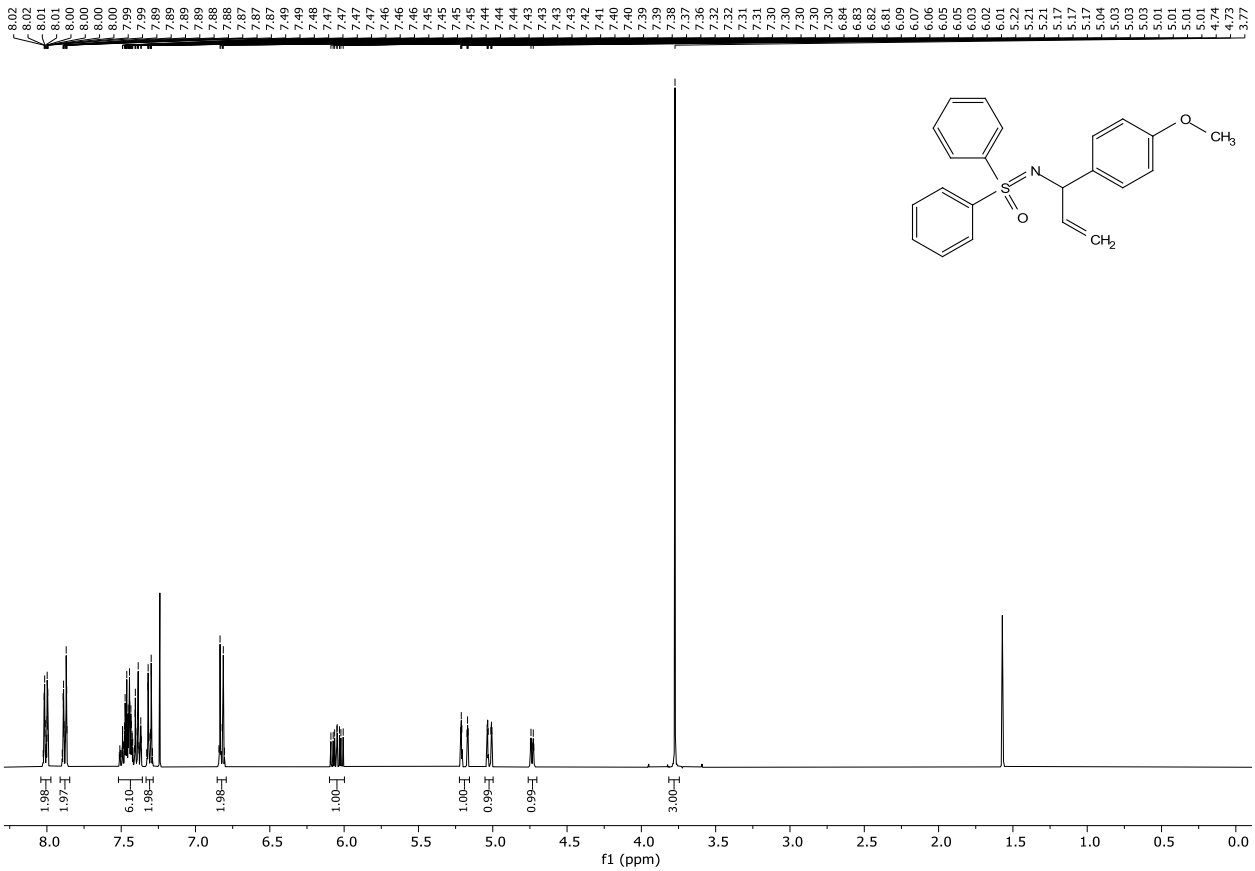
^{1}H NMR (600 MHz, $CDCl_3$) of **16ac'**



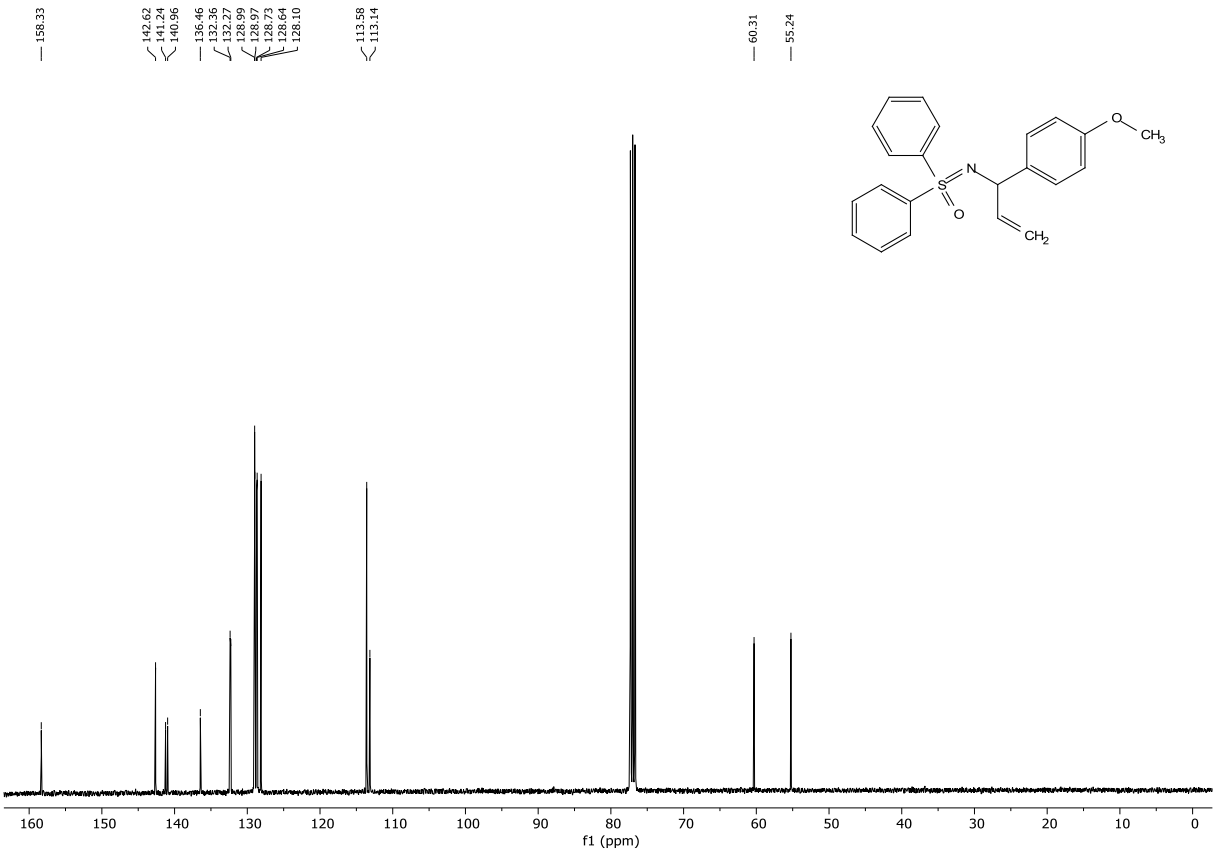
^{13}C NMR (150 MHz, $CDCl_3$) of **16ac'**



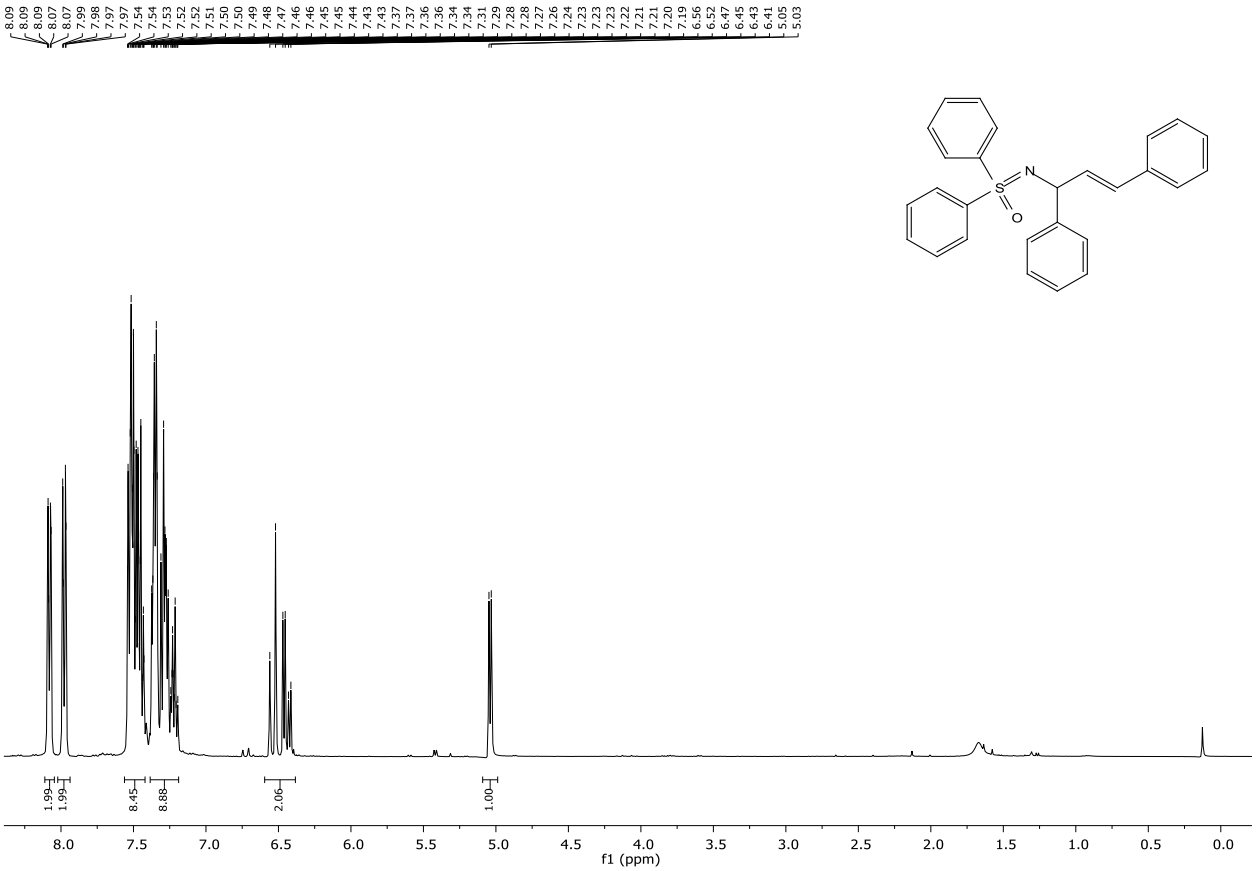
^{1}H NMR (400 MHz, $CDCl_3$) of **16ad**



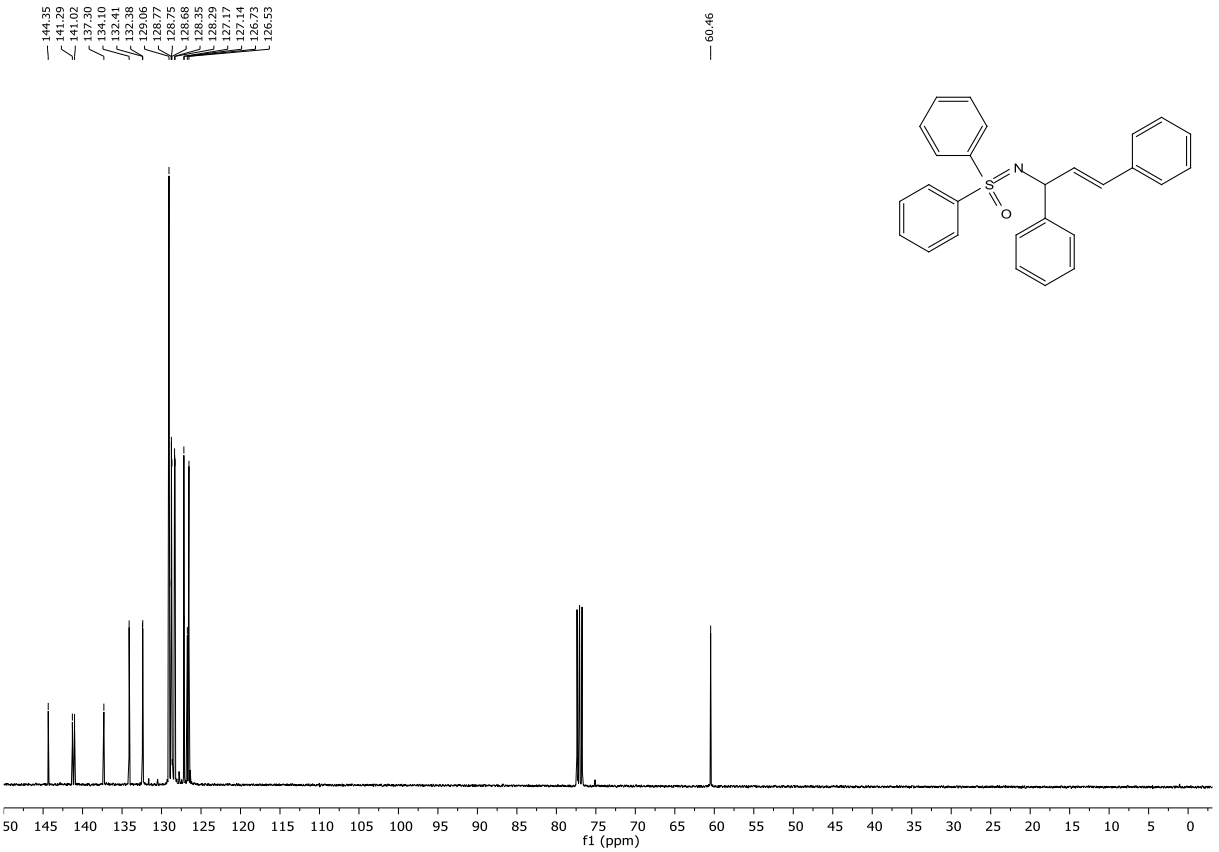
^{13}C NMR (100 MHz, $CDCl_3$) of **16ad**



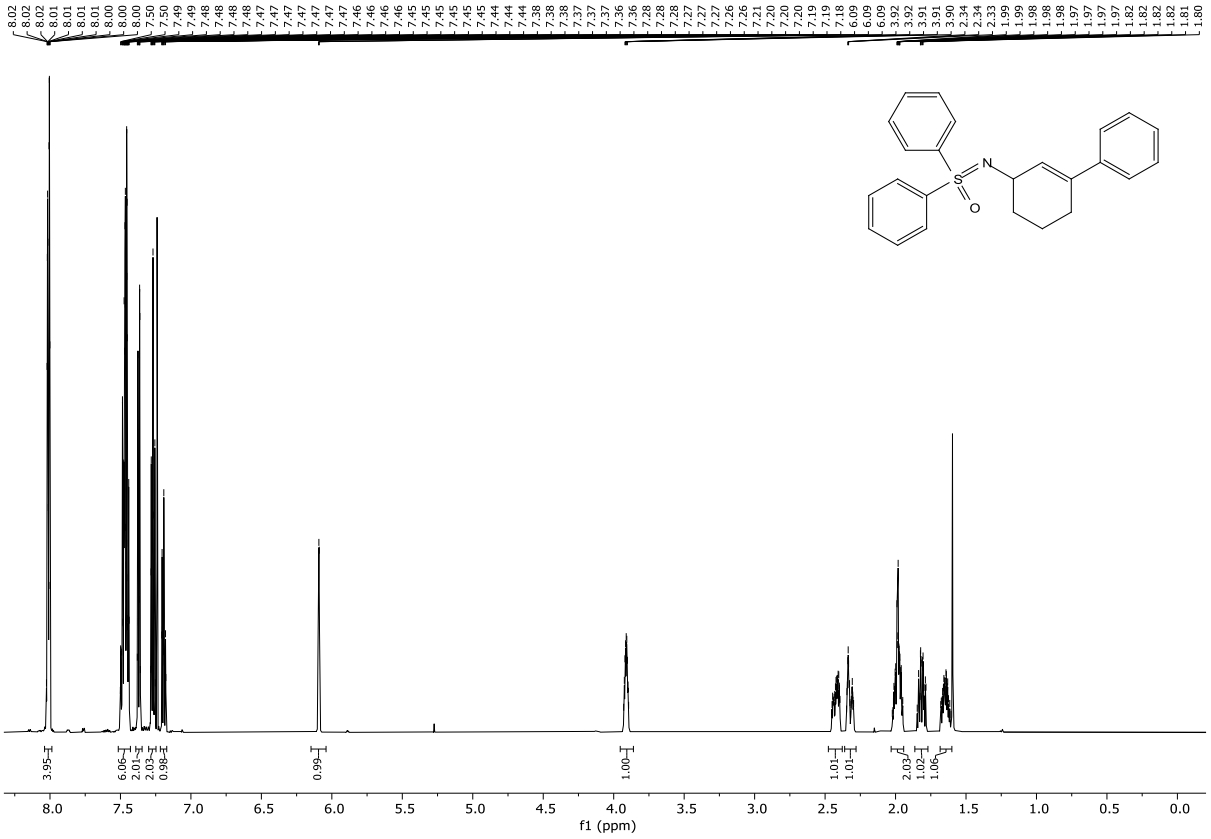
^{1}H NMR (400 MHz, $CDCl_3$) of **16ae**



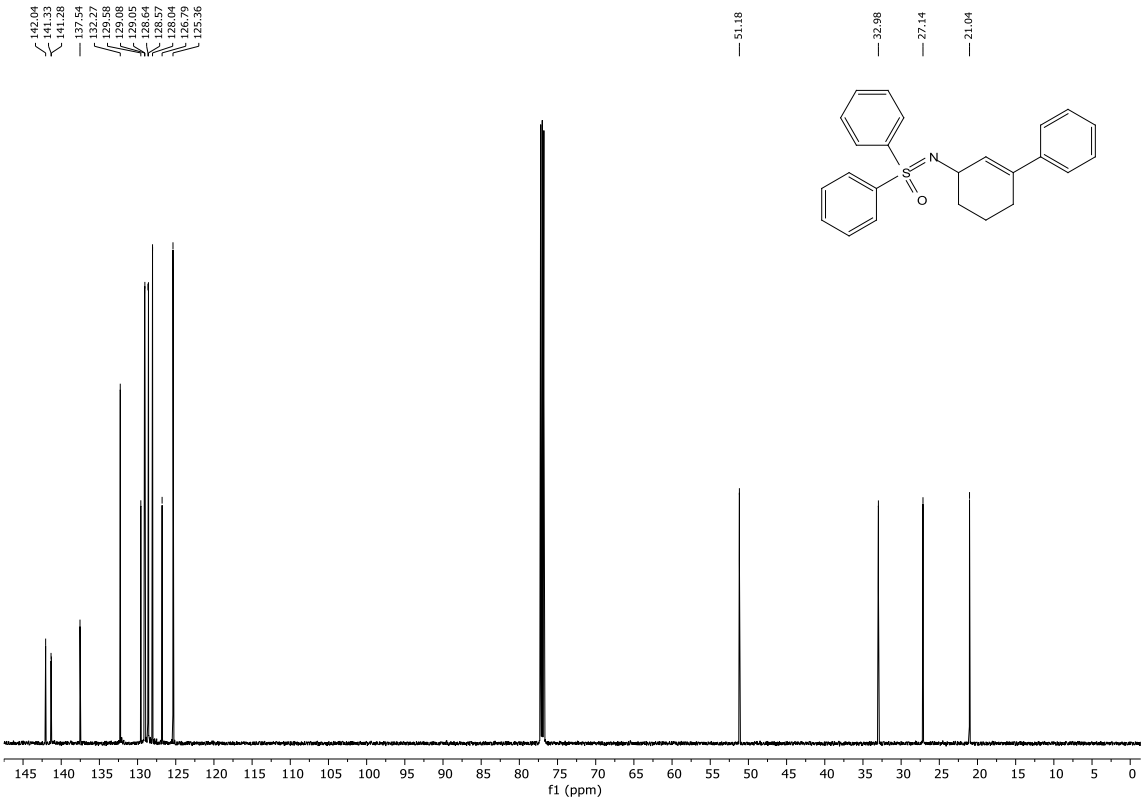
^{13}C NMR (100 MHz, $CDCl_3$) of **16ae**



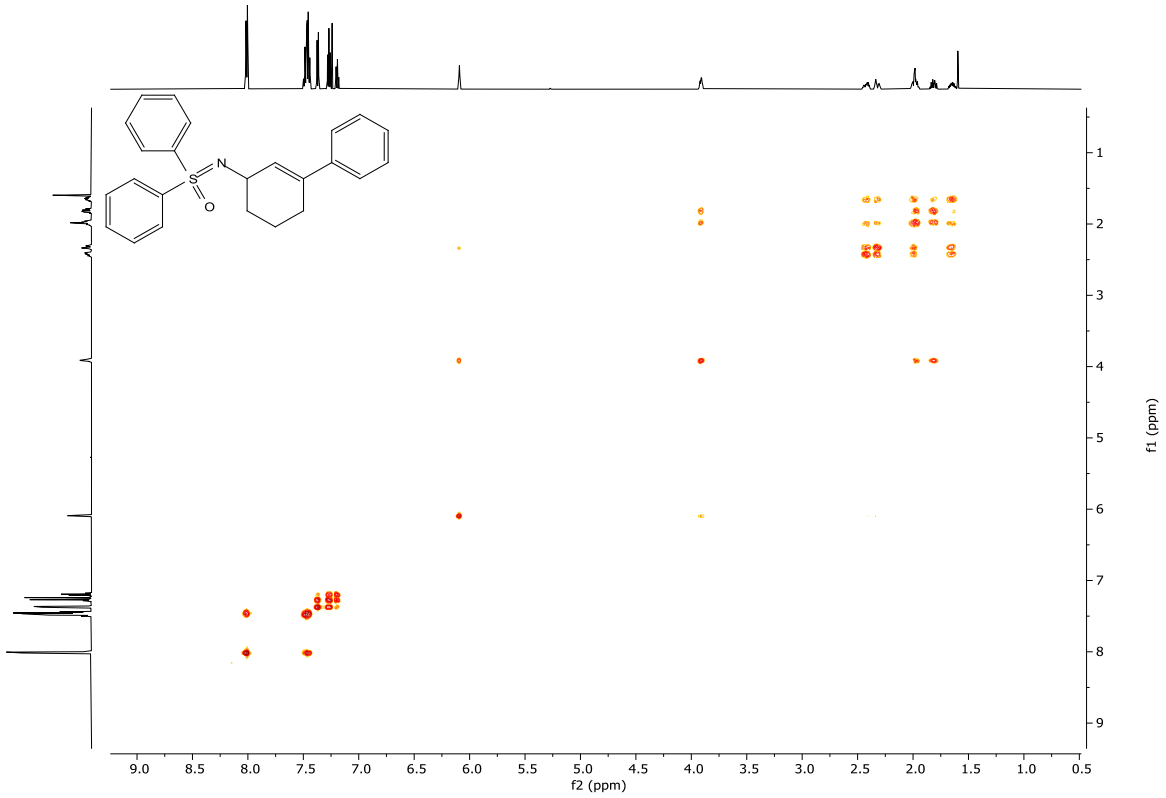
^{1}H NMR (600 MHz, $CDCl_3$) of **16af**

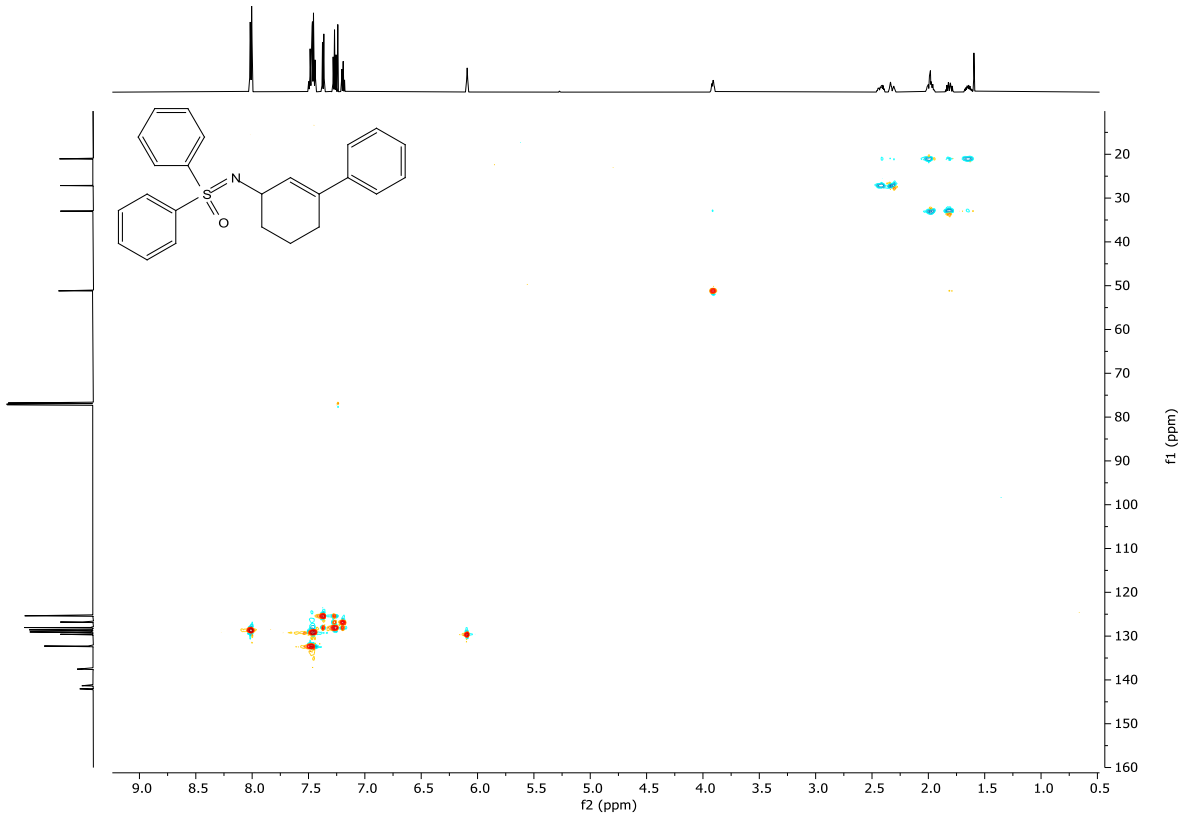


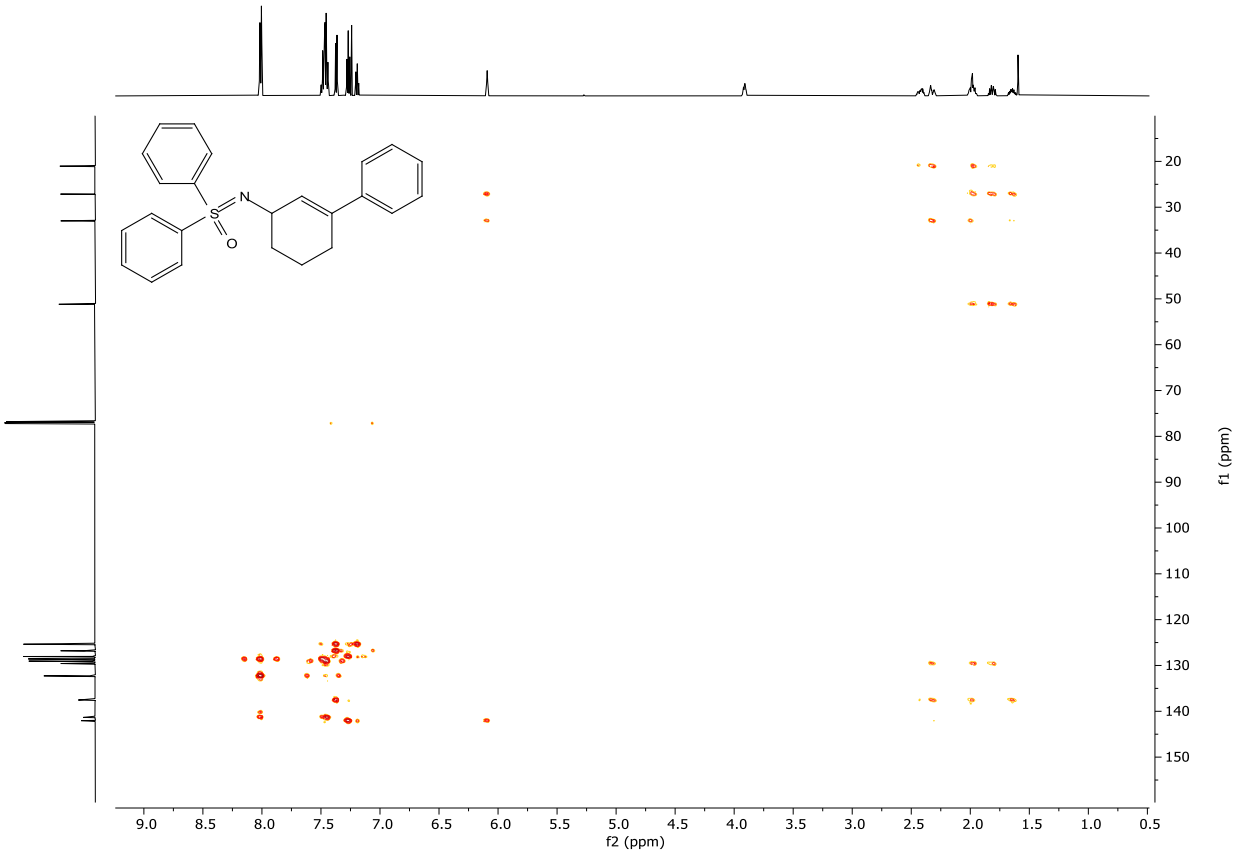
^{13}C NMR (150 MHz, $CDCl_3$) of **16af**



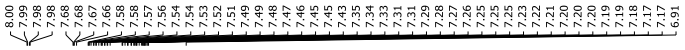
2D NMR (cosy, HSQC, HMBC)

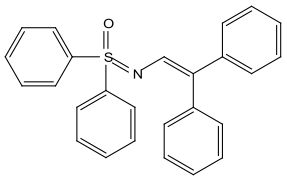




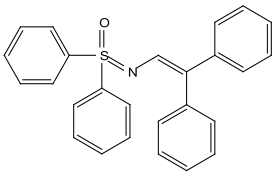

S
N
O
f2 (ppm)
f1 (ppm)

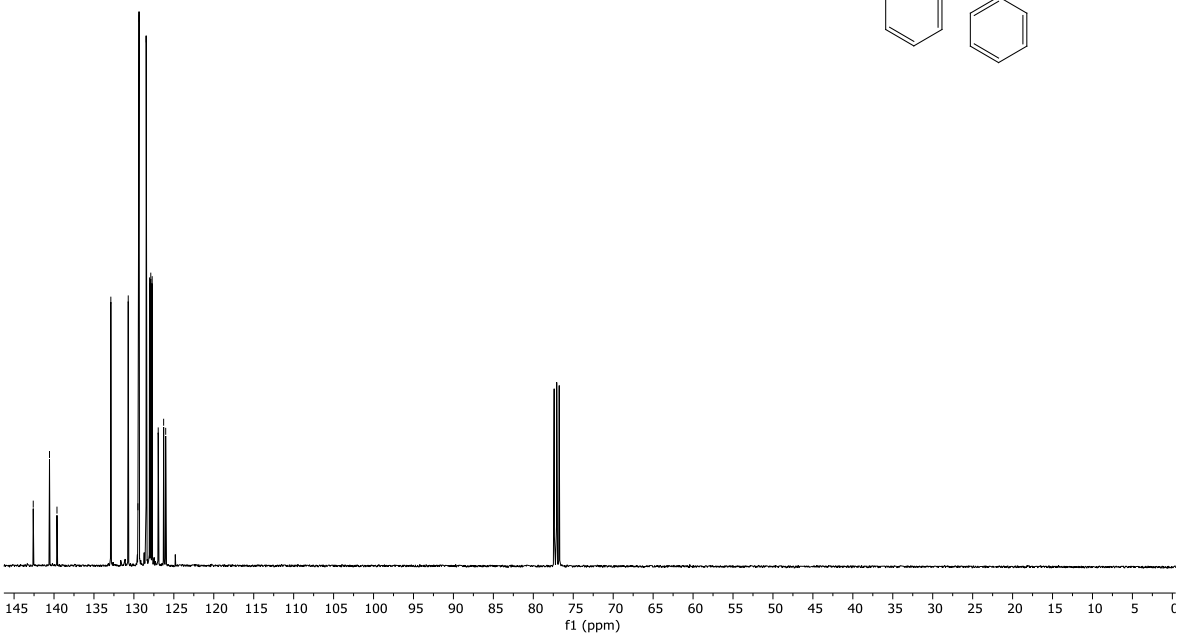
^{1}H NMR (400 MHz, $CDCl_3$) of **16ag**





^{13}C NMR (400 MHz, $CDCl_3$) of **16ag**

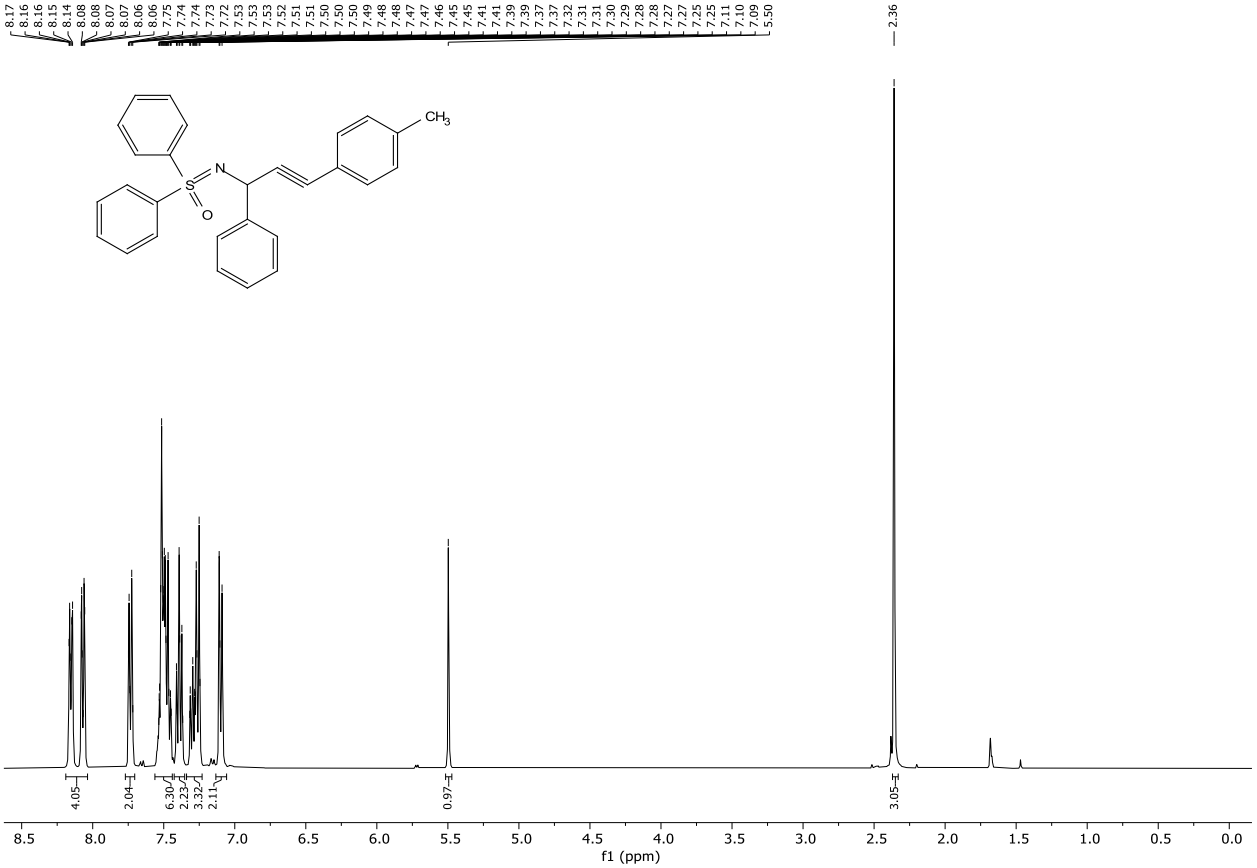




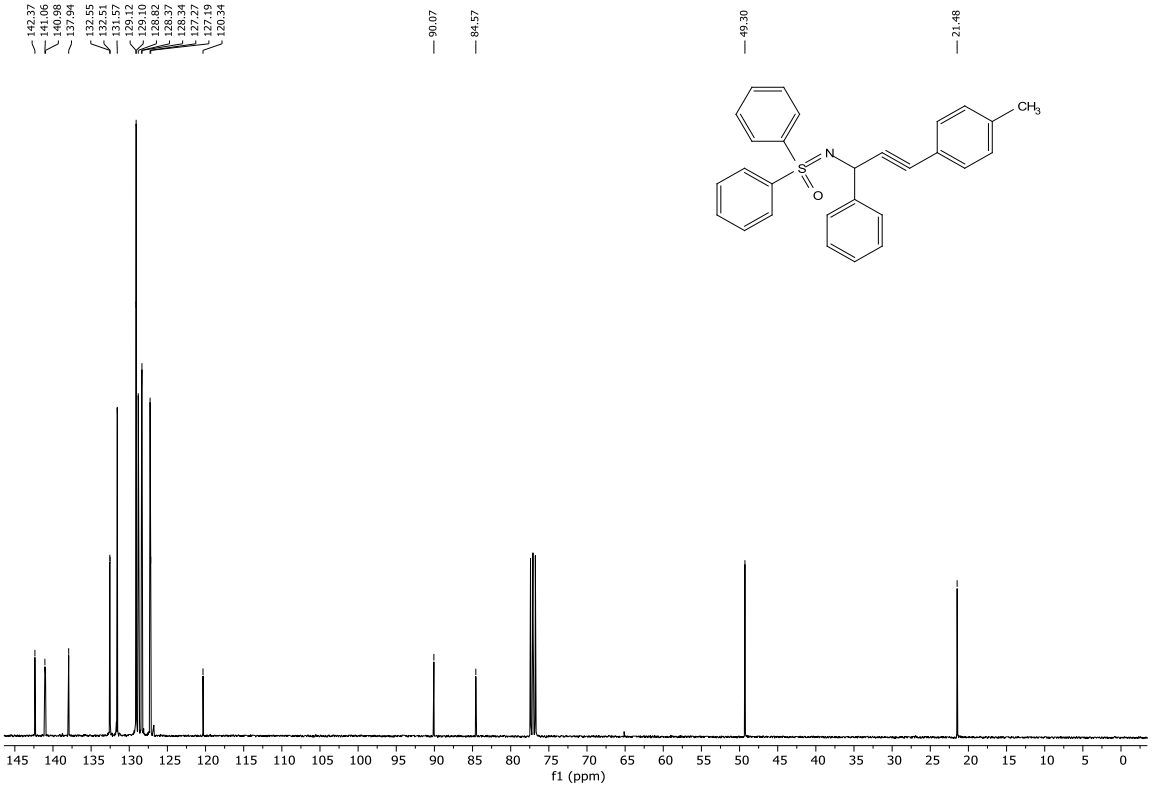
^{1}H NMR (500 MHz, $CDCl_3$) of **16ah**

^{13}C NMR (125 MHz, $CDCl_3$) of **16ah**

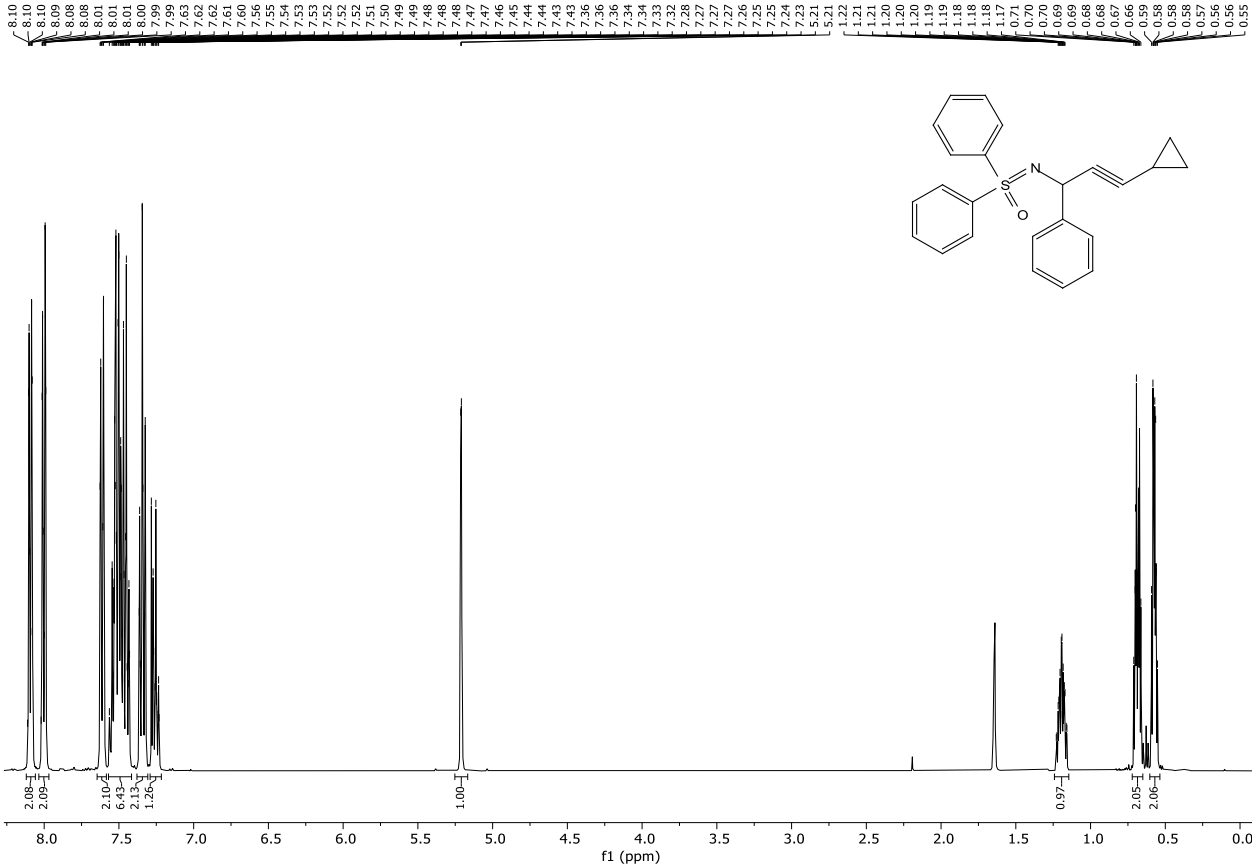
^{1}H NMR (400 MHz, $CDCl_3$) of **16ai**



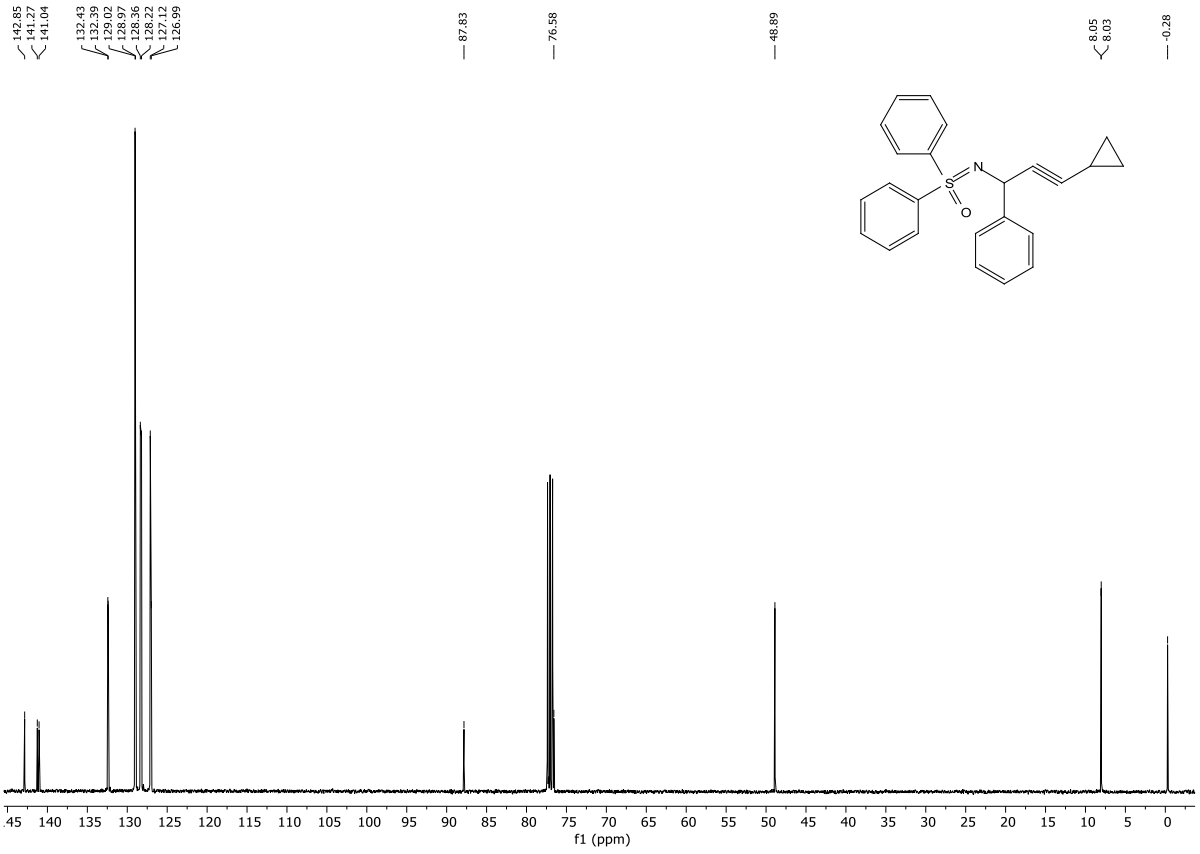
^{13}C NMR (100 MHz, $CDCl_3$) of **16ai**



^{1}H NMR (400 MHz, $CDCl_3$) of **16aj**



^{13}C NMR (100 MHz, $CDCl_3$) of **16aj**



8 Differential scanning calorimetry (DSC)

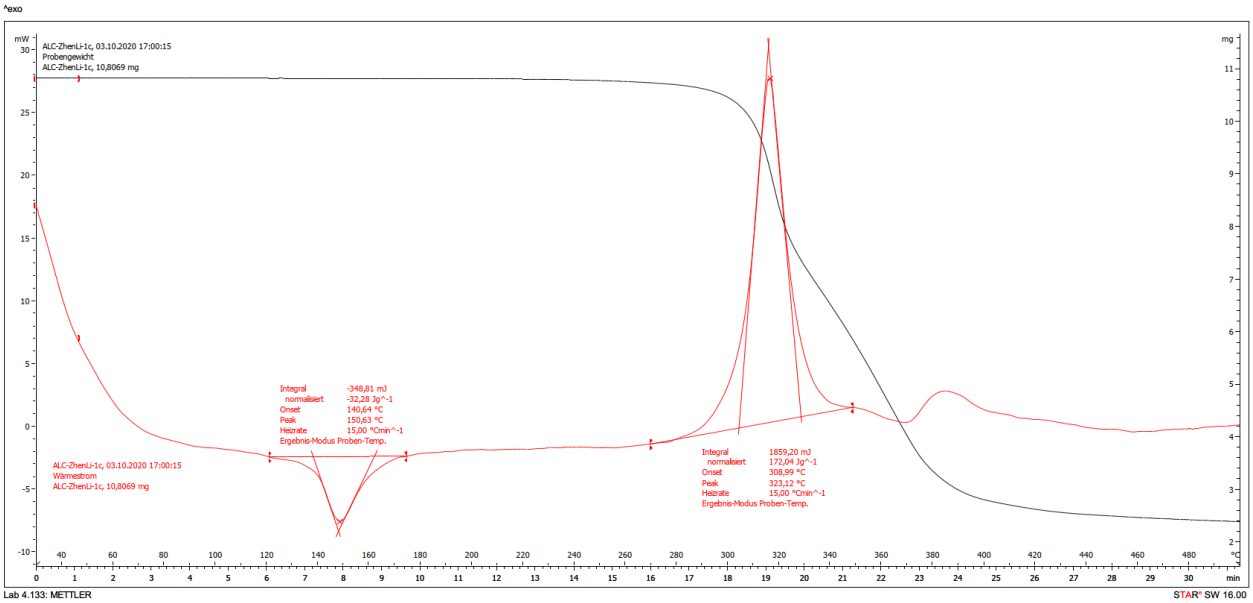


Figure S13. DSC for **1a** shows rapid decomposition with exotherm (221 J/g) initiating at 280°C. Also note endothermic melting at 130°C.

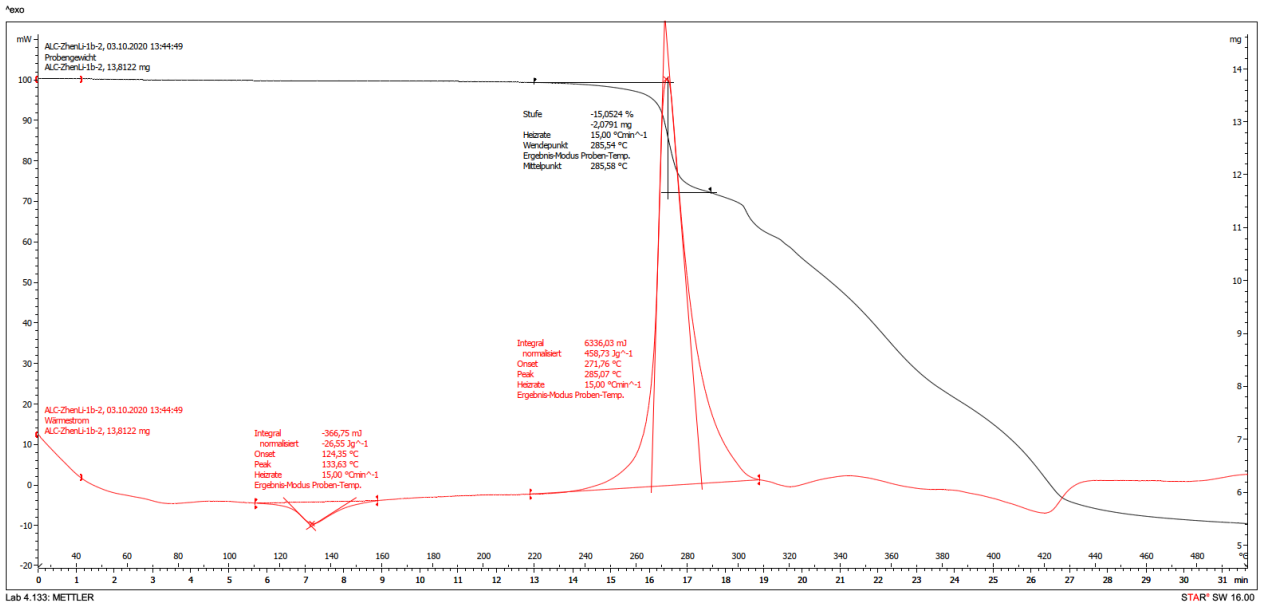


Figure S14. DSC for **1b** shows rapid decomposition with exotherm (753 J/g) initiating at 240°C. Also note endothermic melting at 120°C.

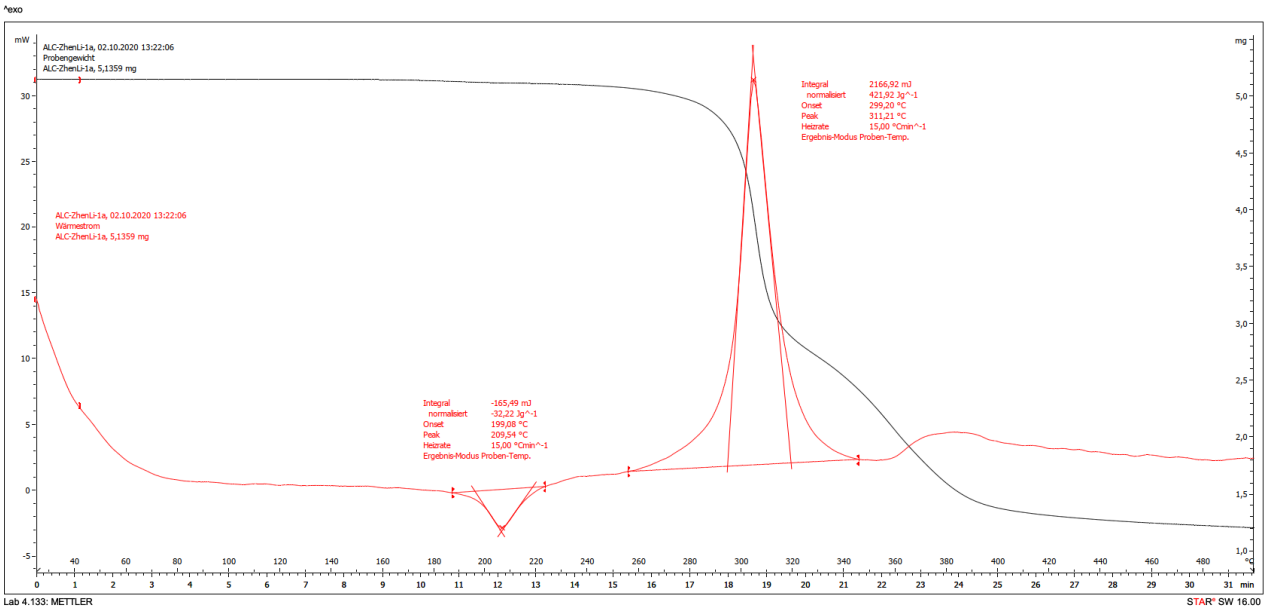
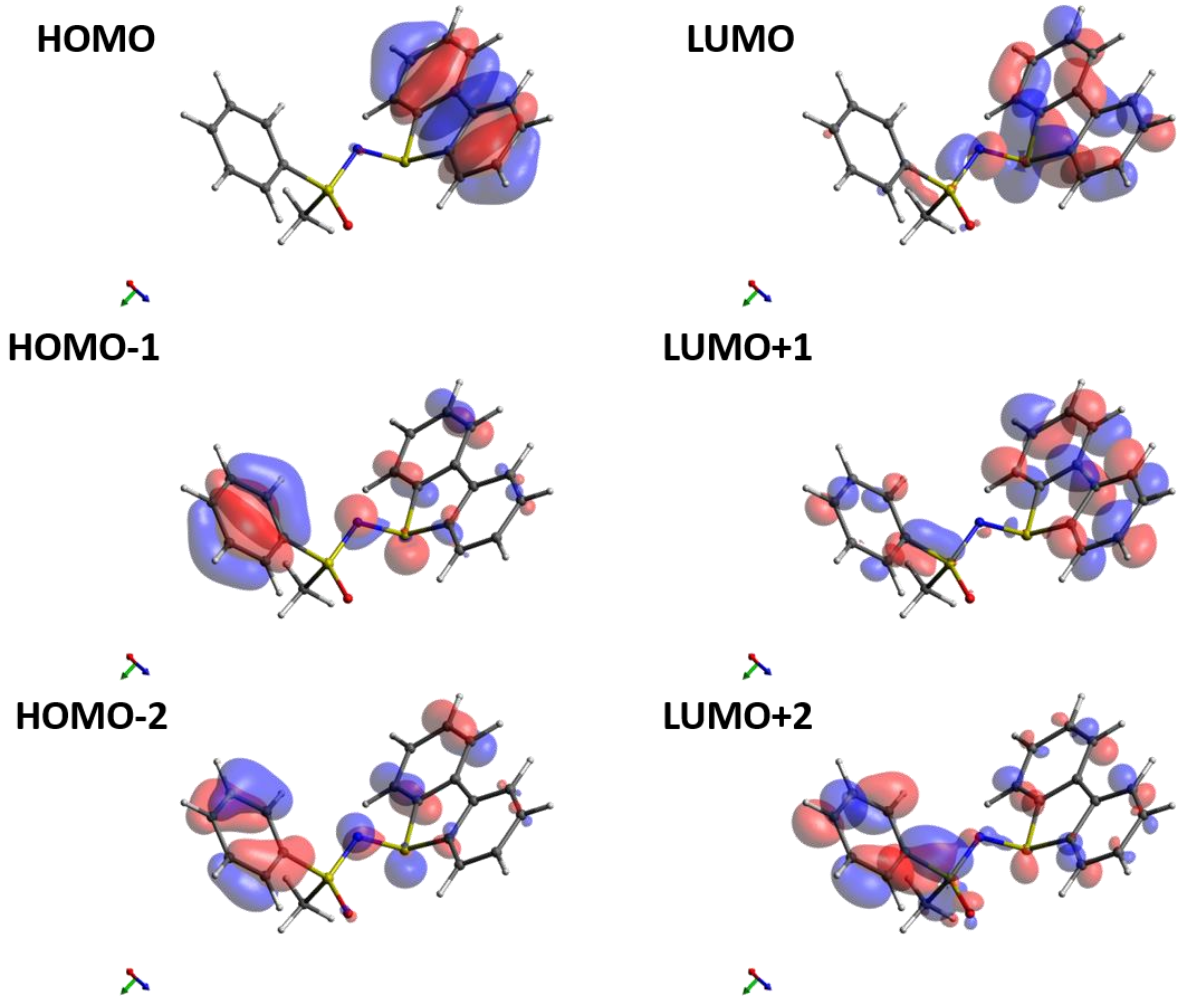


Figure S15. DSC for **1c** shows rapid decomposition with exotherm (550 J/g) initiating at 260°C. Also note endothermic melting at 190°C.

9 DFT calculation supplement

General Information

Geometry optimization and frequency calculations were done with Gaussian16, Revision A.03[16]. Input file creation and analysis was done with GaussView 6.0, visualization of molecular orbitals with Avogadro 1.2.0 [17]. The input geometry of each molecule's geometry optimization is based on the coordinates found in the single crystal. Calculation and visualization of IBOs with IboView v20150427 [18]. Input for IBOView are the previously optimized geometries from Gaussian which are given below each molecular orbital figure.



FigureS16: Molecular orbitals of **1b**. Level of theory B3LYP/def2TZVP. Isosurface level drawn at 0.04.

SCF Energy: -1041724.4594880

S	3.57921	17.36819	1.47810
S	2.08059	15.08767	1.74172
O	3.51328	17.76905	2.86631
N	3.43286	15.82919	1.13043
C	2.36428	18.33427	0.57869
H	1.38332	18.06798	0.97212

H	2.43863	18.11156	-0.48327
H	2.57070	19.38471	0.77526
C	5.13821	17.76956	0.75013
C	5.91180	18.71067	1.42434
H	5.57282	19.12742	2.36267
C	7.13247	19.08235	0.87503
H	7.75001	19.80713	1.38814
C	7.55851	18.52063	-0.32304
H	8.51099	18.81355	-0.74492
C	6.77295	17.57769	-0.98137
H	7.11540	17.13630	-1.90767
C	5.55197	17.19156	-0.44867
H	4.94662	16.44305	-0.93920
C	1.81369	13.70881	0.65287
C	2.04674	12.49193	1.30442
C	2.50305	12.66409	2.68716
C	2.60544	14.00943	3.05822
C	3.01274	14.42901	4.31121
H	3.08188	15.47962	4.56075
C	3.34921	13.44388	5.23566
H	3.68190	13.72998	6.22412
C	3.25262	12.09601	4.89625
H	3.51023	11.34369	5.63000
C	2.82907	11.69718	3.63166
H	2.75646	10.64482	3.39134
C	1.82461	11.31629	0.59475
H	1.98650	10.35407	1.06195
C	1.39155	11.38551	-0.72557
H	1.22219	10.47001	-1.27681
C	1.16755	12.61123	-1.34919
H	0.82786	12.64243	-2.37543
C	1.36922	13.79930	-0.65340
H	1.18736	14.75514	-1.12610

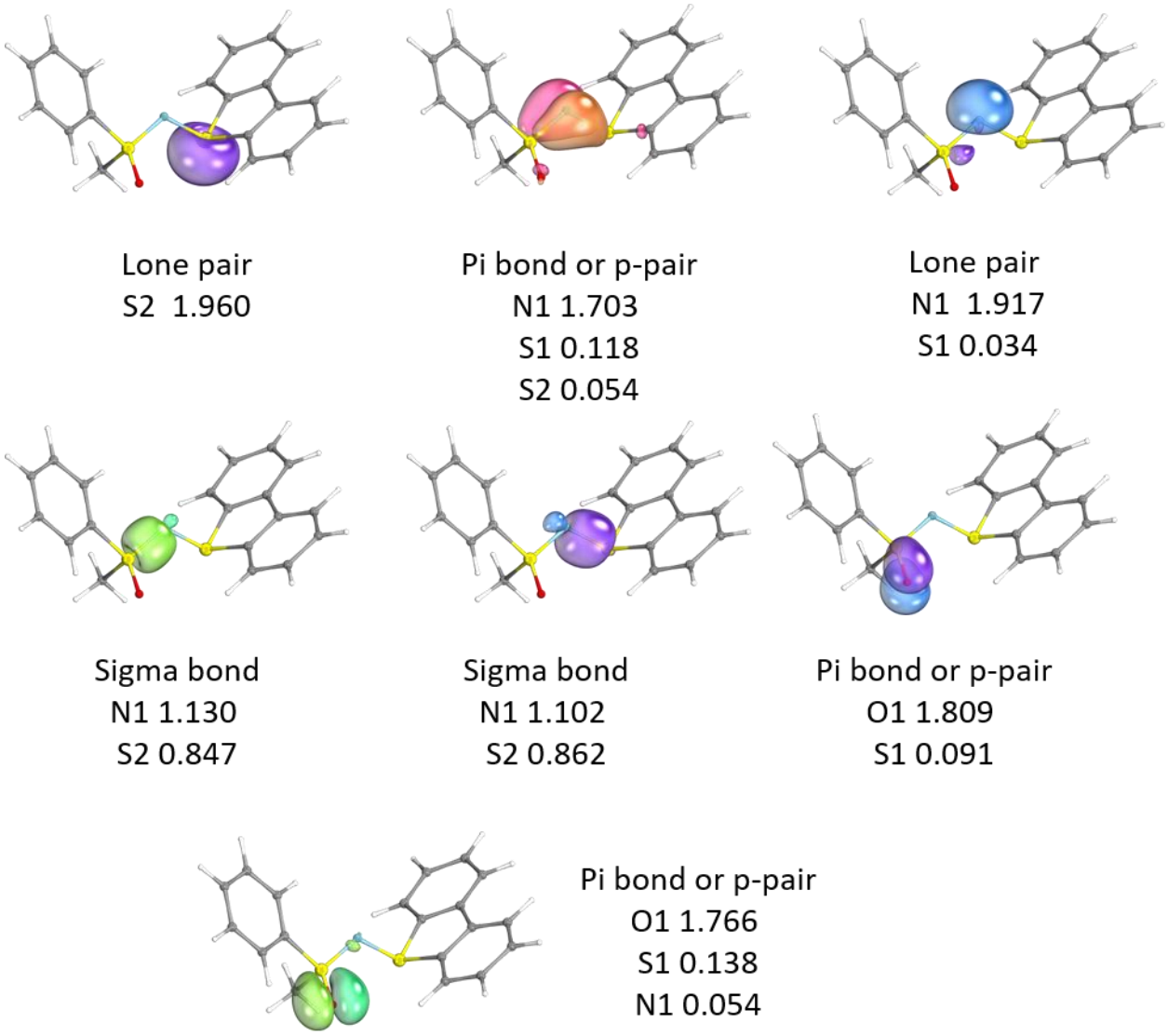


Figure S17: IBOs of **1b** drawn at Isosurface level 80. Level of theory for generation of IBOs PBE/def2TZVP/univ-JFIT.

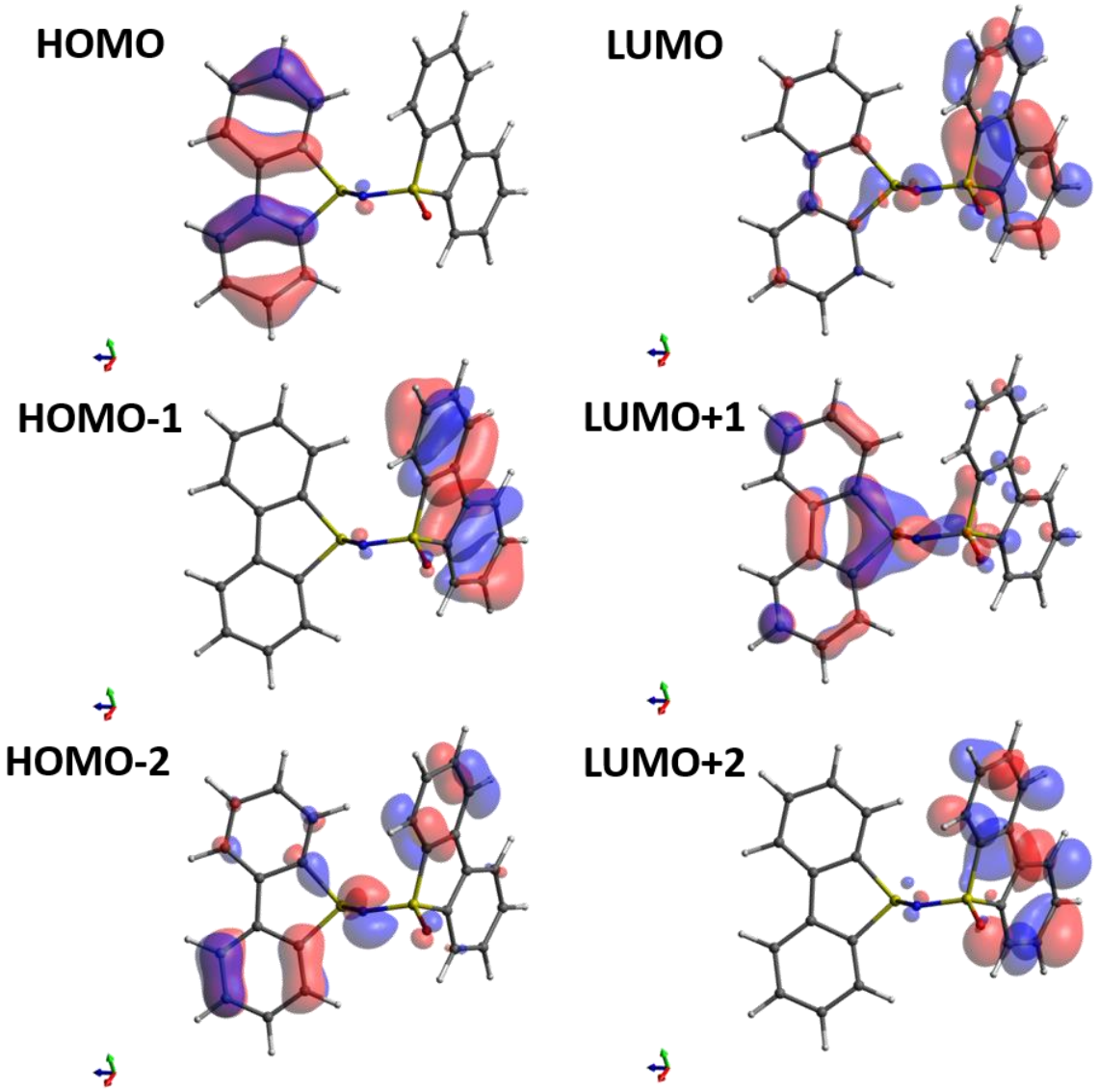


Figure S18: Molecular orbitals of **1c**. Level of theory B3LYP/def2TZVP. Isosurface level drawn at 0.04.

SCF Energy: -266.975654616926

S	3.90839	6.23673	8.26256
S	3.54041	5.84960	11.02940
O	5.01304	6.06817	7.36009
N	4.44842	6.32315	9.75042
C	2.57813	5.08370	8.04143
C	1.40179	5.75693	7.69421
C	1.57772	7.21833	7.60024
C	2.88719	7.62988	7.86748
C	3.30029	8.94769	7.80360
H	4.32702	9.22551	8.00150
C	2.34659	9.90297	7.46095
H	2.63215	10.94380	7.39054

C	1.03202	9.52236	7.19948
H	0.30358	10.27617	6.93104
C	0.63875	8.18759	7.26605
H	-0.38516	7.91417	7.04843
C	0.26013	5.00189	7.45290
H	-0.67022	5.47985	7.17652
C	0.32527	3.61423	7.55477
H	-0.56276	3.02706	7.36117
C	1.51351	2.96757	7.88690
H	1.54420	1.88804	7.94394
C	2.66701	3.70648	8.13492
H	3.60265	3.21625	8.36998
C	4.73157	5.17310	12.16773
C	4.84128	5.95211	13.32396
C	3.99826	7.15073	13.28257
C	3.26703	7.25636	12.09392
C	2.39331	8.29654	11.83296
H	1.83101	8.34713	10.91014
C	2.26560	9.29060	12.79882
H	1.59997	10.12501	12.62456
C	2.98304	9.20932	13.99030
H	2.86644	9.98521	14.73536
C	3.84324	8.14518	14.24247
H	4.38415	8.09601	15.17812
C	5.70404	5.52192	14.32663
H	5.81505	6.09231	15.23918
C	6.43241	4.35065	14.14419
H	7.10794	4.01940	14.92174
C	6.30990	3.59865	12.97772
H	6.88990	2.69441	12.85337
C	5.44088	4.00355	11.96905
H	5.34131	3.42708	11.05943

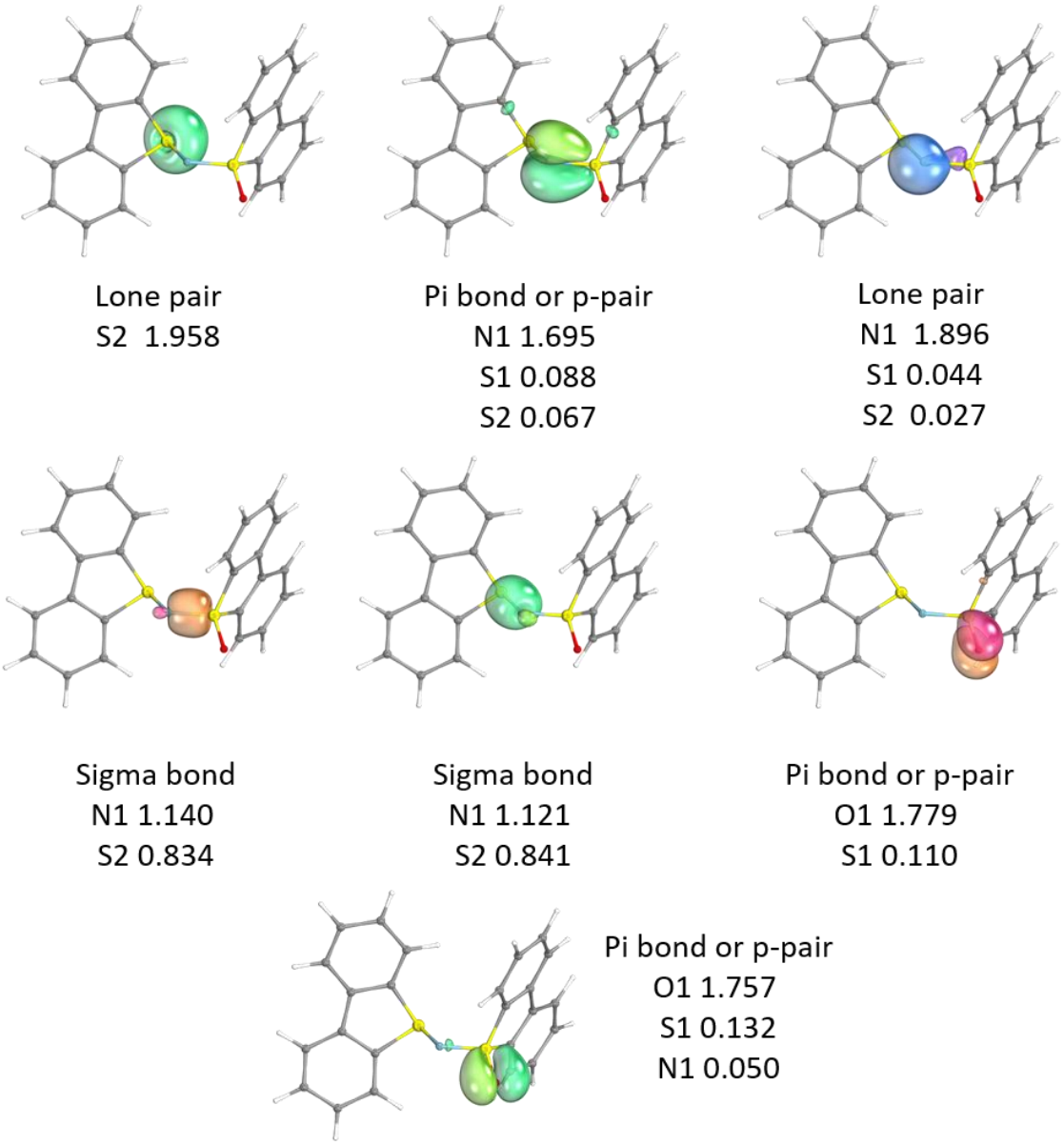


Figure S19: IBOs of **1c** drawn at Isosurface level 80. Level of theory for generation of IBOs PBE/def2TZVP/univ-JFIT.

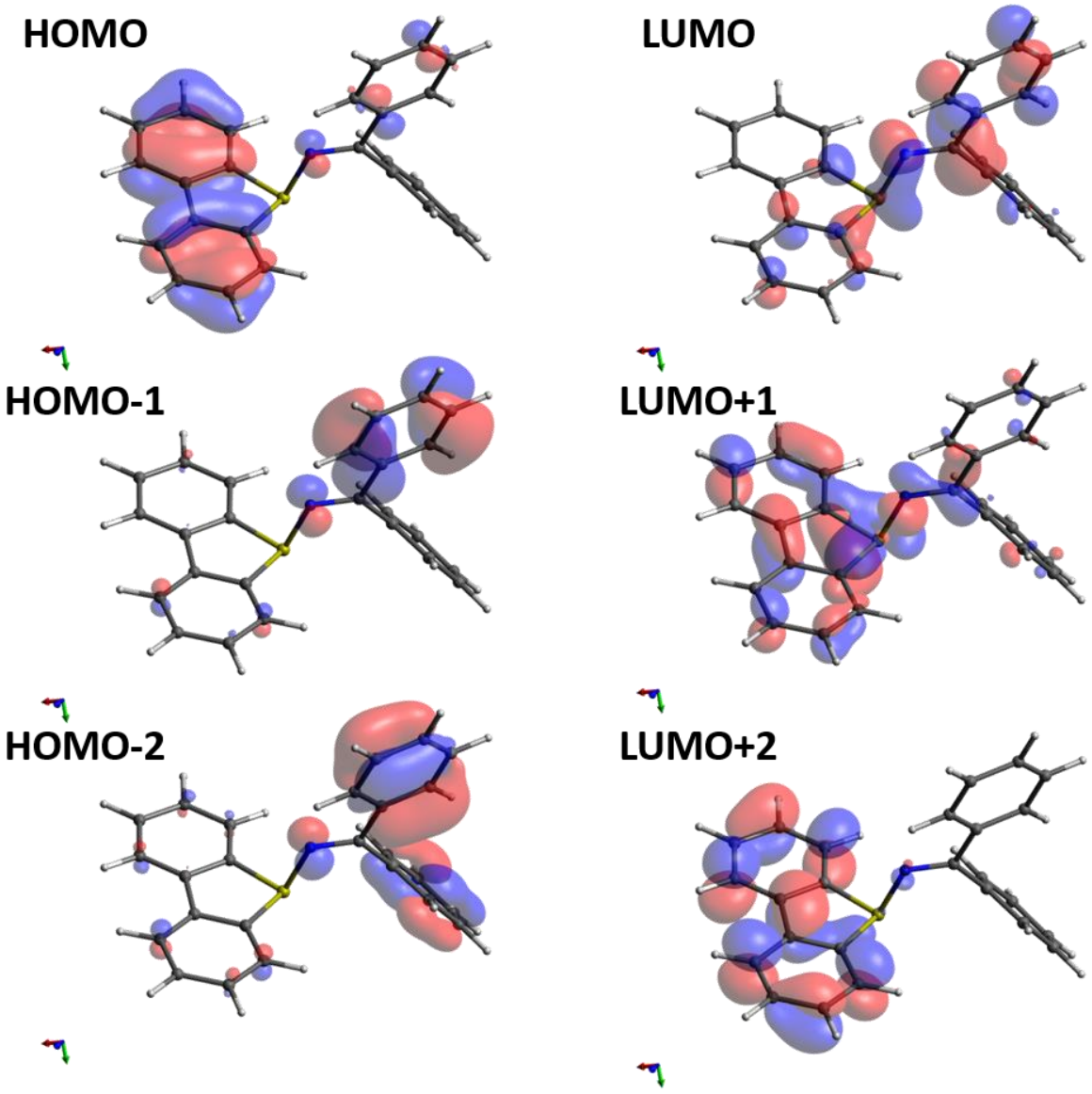


Figure S20: Molecular orbitals of **3a**. Level of theory B3LYP/def2TZVP. Isosurface level drawn at 0.04.

SCF Energy: -888923.5379629

S	18.88047	5.47623	8.88528
N	17.72931	4.27352	9.23828
C	20.36642	4.53347	8.61808
C	21.23923	4.62948	9.70930
C	20.69902	5.44815	10.79647
C	19.42648	5.95527	10.50829
C	18.71843	6.77044	11.37270
H	17.74143	7.15757	11.11615
C	19.30811	7.07634	12.59563
H	18.78249	7.70582	13.30062
C	20.57334	6.58406	12.90916
H	21.02127	6.83777	13.86082

C	21.27518	5.77735	12.01880
H	22.26004	5.41282	12.27882
C	22.46363	3.97442	9.63108
H	23.16867	4.02855	10.44987
C	22.77754	3.24569	8.48841
H	23.72901	2.73392	8.43003
C	21.89106	3.16722	7.41671
H	22.15534	2.59787	6.53609
C	20.66593	3.82521	7.46856
H	19.97830	3.77468	6.63567
C	16.56622	4.34912	8.65162
C	16.21465	5.33266	7.59021
C	15.24115	6.30523	7.83426
H	14.72842	6.32944	8.78747
C	14.93631	7.24469	6.85803
H	14.19252	8.00435	7.05944
C	15.57372	7.20214	5.62240
H	15.32381	7.92712	4.85905
C	16.52350	6.22037	5.36463
H	17.00742	6.17237	4.39801
C	16.85047	5.29376	6.34639
H	17.57279	4.51570	6.13227
C	15.55400	3.37784	9.08948
C	15.72417	2.66022	10.28618
H	16.59743	2.84584	10.89474
C	14.77778	1.73429	10.68411
H	14.91049	1.19281	11.61139
C	13.65284	1.49963	9.89457
H	12.91517	0.77250	10.20877
C	13.47551	2.19863	8.70600
H	12.60534	2.01304	8.09061
C	14.41522	3.13605	8.30535
H	14.27386	3.66953	7.37628

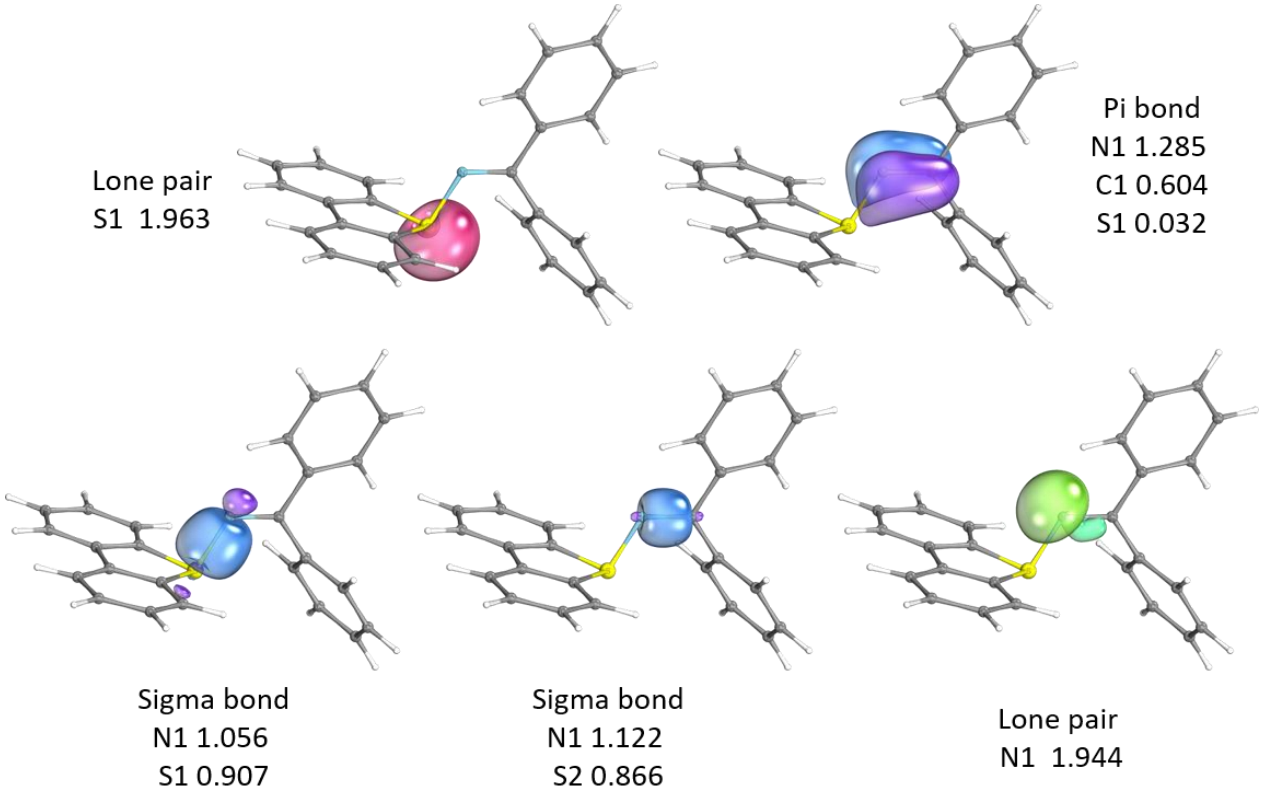


Figure S21: IBOs of **3a** drawn at isosurface level 80. Level of theory for generation of IBOs PBE/def2TZVP/univ-JFIT.

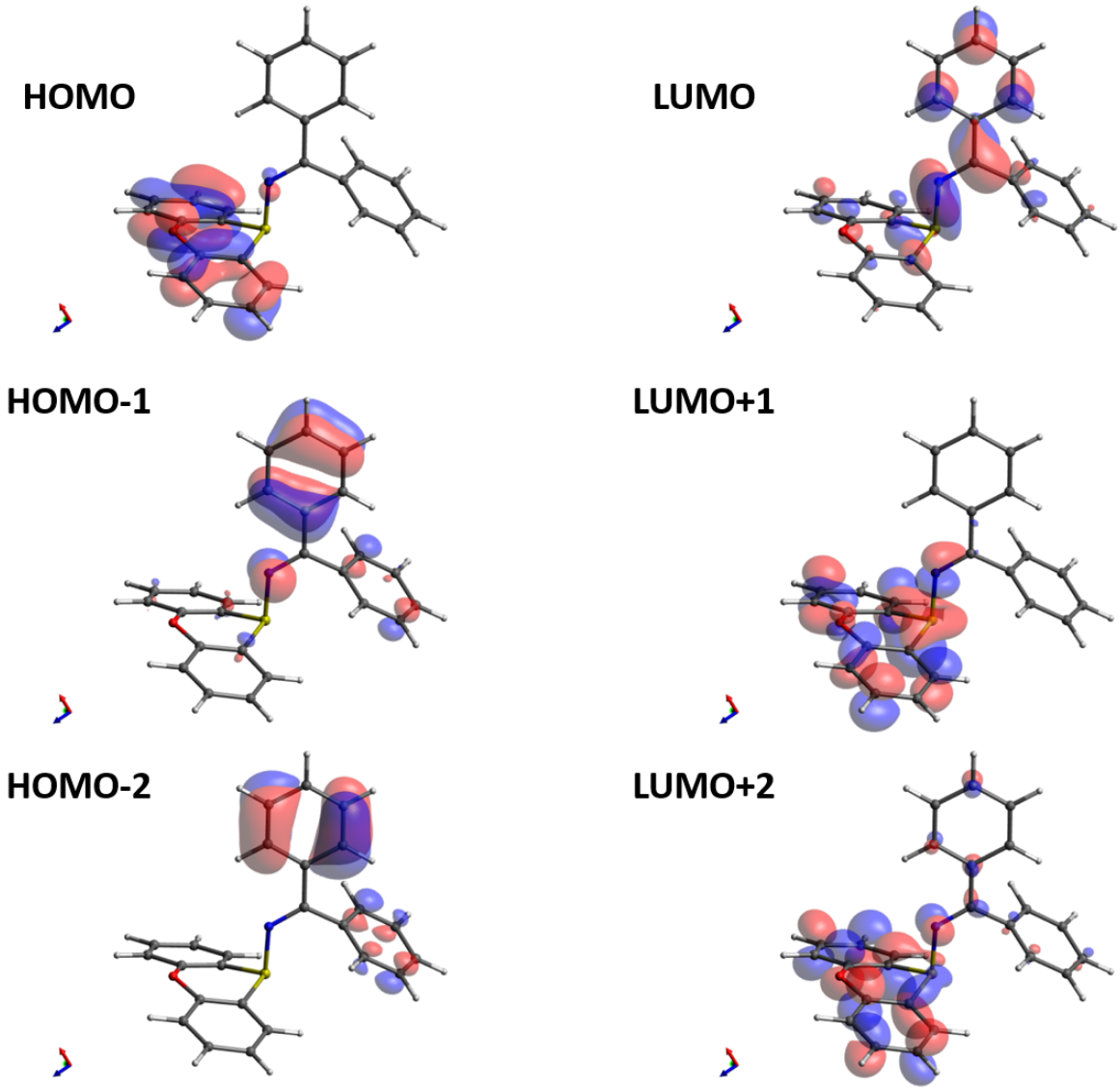


Figure S22: Molecular orbitals of **3e**. Level of theory B3LYP/def2TZVP. Isosurface level drawn at 0.04.

SCF Energy: -1041724.4594880

S	3.57921	17.36819	1.47810
S	2.08059	15.08767	1.74172
O	3.51328	17.76905	2.86631
N	3.43286	15.82919	1.13043
C	2.36428	18.33427	0.57869
H	1.38332	18.06798	0.97212
H	2.43863	18.11156	-0.48327
H	2.57070	19.38471	0.77526
C	5.13821	17.76956	0.75013
C	5.91180	18.71067	1.42434
H	5.57282	19.12742	2.36267
C	7.13247	19.08235	0.87503
H	7.75001	19.80713	1.38814

C	7.55851	18.52063	-0.32304
H	8.51099	18.81355	-0.74492
C	6.77295	17.57769	-0.98137
H	7.11540	17.13630	-1.90767
C	5.55197	17.19156	-0.44867
H	4.94662	16.44305	-0.93920
C	1.81369	13.70881	0.65287
C	2.04674	12.49193	1.30442
C	2.50305	12.66409	2.68716
C	2.60544	14.00943	3.05822
C	3.01274	14.42901	4.31121
H	3.08188	15.47962	4.56075
C	3.34921	13.44388	5.23566
H	3.68190	13.72998	6.22412
C	3.25262	12.09601	4.89625
H	3.51023	11.34369	5.63000
C	2.82907	11.69718	3.63166
H	2.75646	10.64482	3.39134
C	1.82461	11.31629	0.59475
H	1.98650	10.35407	1.06195
C	1.39155	11.38551	-0.72557
H	1.22219	10.47001	-1.27681
C	1.16755	12.61123	-1.34919
H	0.82786	12.64243	-2.37543
C	1.36922	13.79930	-0.65340
H	1.18736	14.75514	-1.12610

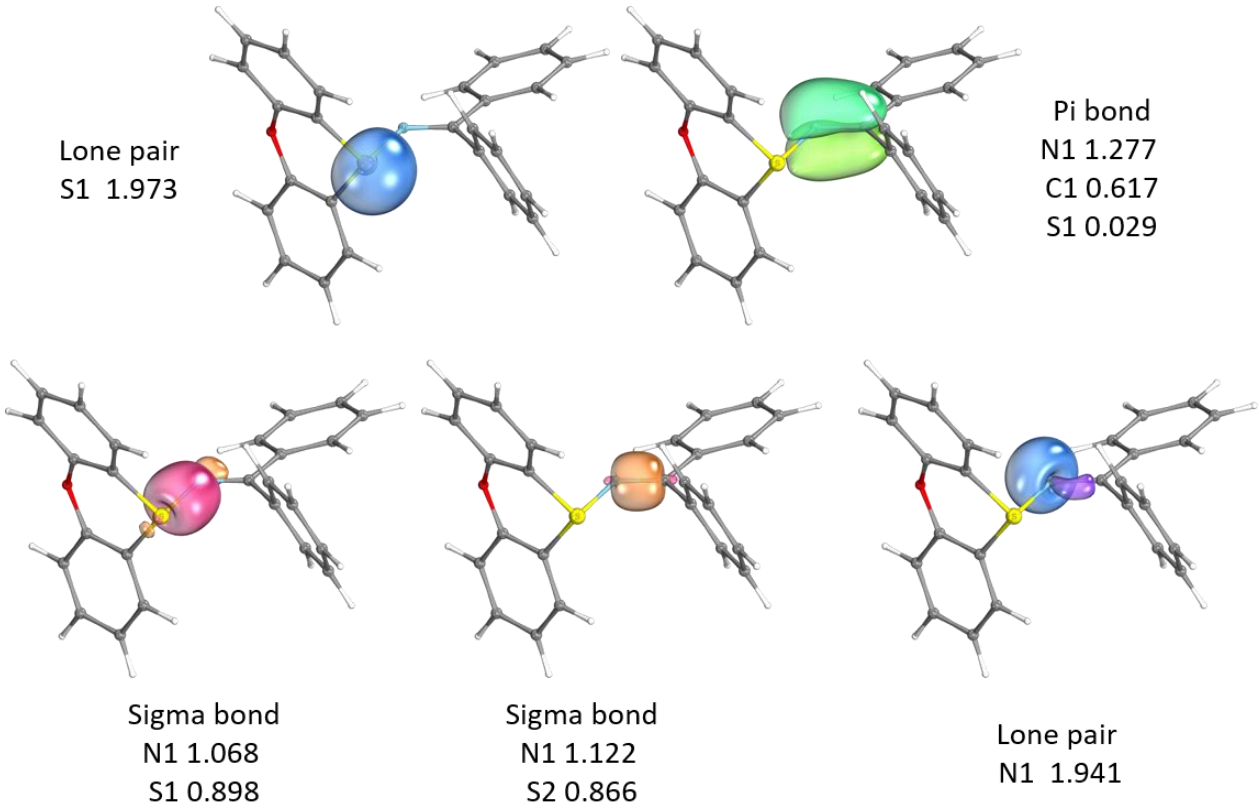


Figure S23: IBOs of **3e** drawn at isosurface level 80. Level of theory for generation of IBOs PBE/def2TZVP/univ-JFIT.

10 Single crystal X-ray diffraction analysis supplement

General Information

Data collection was done on two dual source equipped *Bruker D8 Venture* four-circle-diffractometer from *Bruker AXS GmbH*; used X-ray sources: microfocus *IμS 2.0* Cu/Mo and microfocus *IμS 3.0* Ag/Mo from *Incoatec GmbH* with mirror optics *HELIOS* and single-hole collimator from *Bruker AXS GmbH;* used detector: *Photon III CE14* (Cu/Mo) and Photon III HE (Ag/Mo) from *Bruker AXS GmbH*.

Used programs: *APEX3 Suite* (v2018.7-2) for data collection and therein integrated programs *SAINT* V8.38A (Integration) und *SADABS* 2016/2 (Absorption correction) from *Bruker AXS GmbH*; structure solution was done with *SHELXT*, refinement with *SHELXL*-2018/3 [18]; OLEX^2 was used for data finalization [20].

Special Utilities: *SMZ1270* stereomicroscope from *Nikon Metrology GmbH* was used for sample preparation; crystals were mounted on *MicroMounts* or *MicroLoops* from *MiTeGen* in NVH oil.

All compounds were crystalized by diffusion of diethylether into dichloromethane solutions of the title compounds.

Compound **1a**

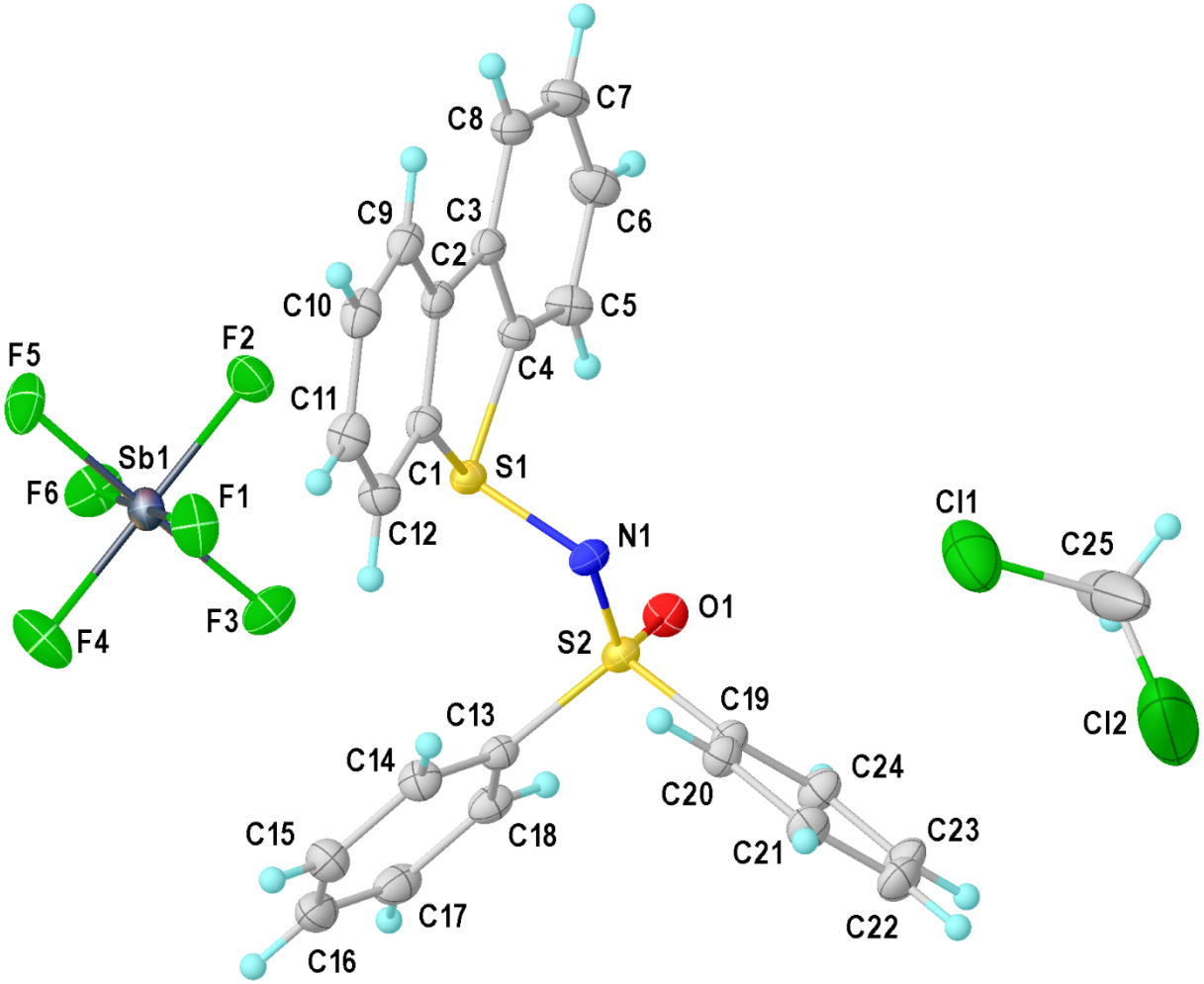


Figure S24: Molecular structure of full asymmetric unit and numbering scheme of compound **1a**. Ellipsoids drawn at 50% probability level.

Crystal data and structure refinement for **1a**.

CCDC	2062172
Empirical formula	$C_{49}H_{38}Cl_2F_{12}N_2O_2S_4Sb_2$
Formula weight	1357.45
Temperature/K	100
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	8.2412(3)
b/Å	17.5619(6)
c/Å	18.4820(5)
α/°	90
β/°	99.5660(10)
γ/°	90
Volume/Å^3	2637.73(15)

Z	2
ρ_{calc}g/cm^3	1.709
μ/mm^{-1}	1.367
F(000)	1340.0
Crystal size/mm^3	0.335 × 0.25 × 0.198
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.036 to 61.076
Index ranges	-11 ≤ h ≤ 11, -25 ≤ k ≤ 25, -26 ≤ l ≤ 26
Reflections collected	161835
Independent reflections	8064 [R_{int} = 0.0209, R_{sigma} = 0.0065]
Data/restraints/parameters	8064/22/343
Goodness-of-fit on F^2	1.071
Final R indexes [I>=2σ (I)]	R_1 = 0.0279, wR_2 = 0.0842
Final R indexes [all data]	R_1 = 0.0286, wR_2 = 0.0850
Largest diff. peak/hole / e Å^{-3}	2.64/-1.03

Compound **1b**

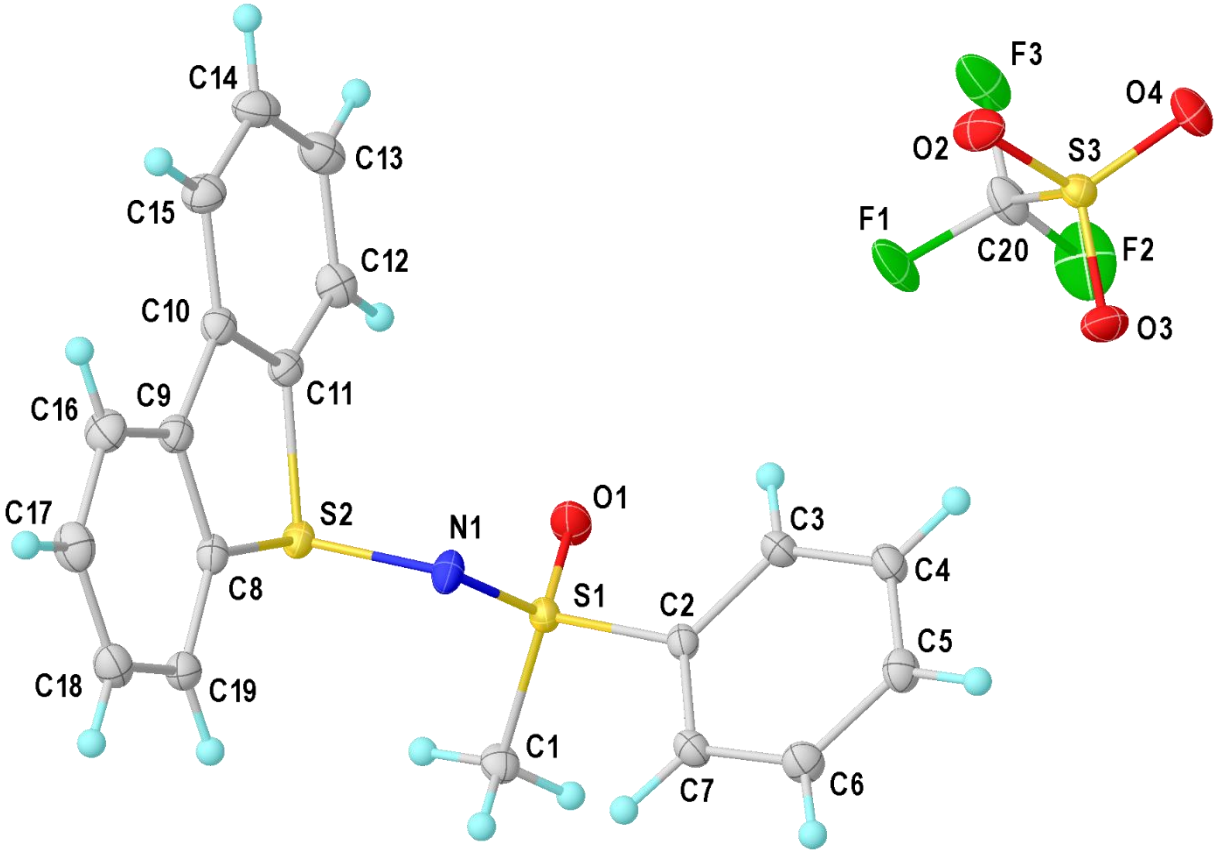


Figure S15: Molecular structure of full asymmetric unit and numbering scheme of compound **1b**. Ellipsoids drawn at 50% probability level.

Crystal data and structure refinement for **1b**.

CCDC	2062173
Empirical formula	$C_{20}H_{16}F_3NO_4S_3$
Formula weight	487.52
Temperature/K	100
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	10.8928(10)
b/Å	26.053(2)
c/Å	7.3295(5)
α/°	90
β/°	103.374(3)
γ/°	90
Volume/Å^3	2023.7(3)
Z	4
ρ_{calc}g/cm^3	1.600
μ/mm^{-1}	0.423

F(000)	1000.0
Crystal size/mm^3	0.321 × 0.189 × 0.172
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.956 to 59.252
Index ranges	$-15 \leq h \leq 15$, $-36 \leq k \leq 36$, $-10 \leq l \leq 10$
Reflections collected	61810
Independent reflections	5697 [R_{int} = 0.0286, R_{sigma} = 0.0138]
Data/restraints/parameters	5697/0/281
Goodness-of-fit on F^2	1.067
Final R indexes [I>=2σ (I)]	R_1 = 0.0288, wR_2 = 0.0724
Final R indexes [all data]	R_1 = 0.0313, wR_2 = 0.0743
Largest diff. peak/hole / e $Å^{-3}$	0.43/-0.42

Compound **1c**

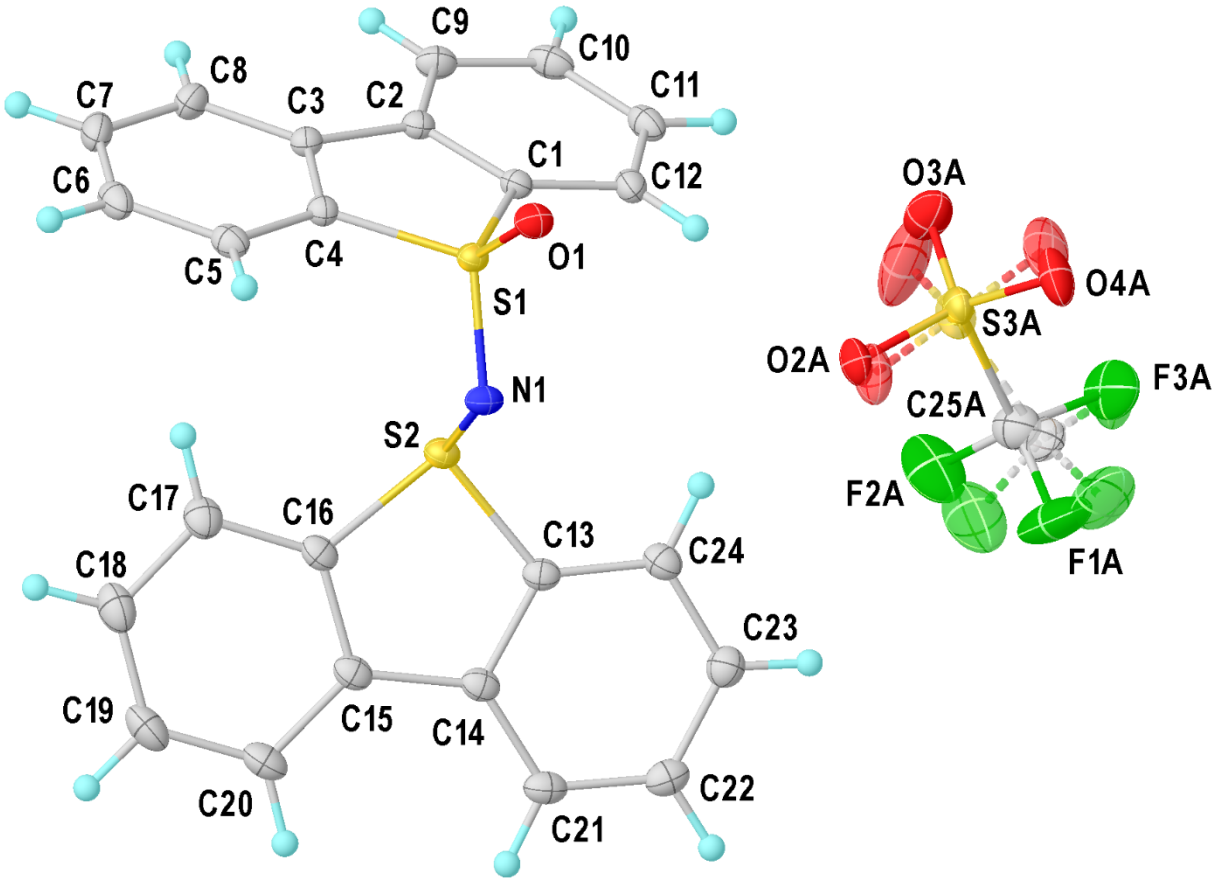


Figure S26: Molecular structure of full asymmetric unit and numbering scheme of compound **1c**. Ellipsoids drawn at 50% probability level. Minor disorder drawn with translucent ellipsoids and stippled bonds. The refined occupancy of the major disorder part is 0.865(8).

Crystal data and structure refinement for **1c**.

CCDC	2062174
Empirical formula	$C_{25}H_{16}F_3NO_4S_3$
Formula weight	547.57
Temperature/K	100
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	7.7343(9)
b/Å	11.6345(13)
c/Å	25.586(2)
α/°	90
β/°	95.771(3)
γ/°	90
Volume/Å^3	2290.7(4)
Z	4

ρ_{calc}g/cm^3	1.588
μ/mm^{-1}	0.384
F(000)	1120.0
Crystal size/mm^3	0.203 × 0.182 × 0.066
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.744 to 59.302
Index ranges	$-10 \leq h \leq 10$, $-16 \leq k \leq 16$, $-35 \leq l \leq 35$
Reflections collected	114032
Independent reflections	6453 [R_{int} = 0.0278, R_{sigma} = 0.0110]
Data/restraints/parameters	6453/78/398
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0294, wR_2 = 0.0802
Final R indexes [all data]	R_1 = 0.0305, wR_2 = 0.0811
Largest diff. peak/hole / e Å^{-3}	0.48/-0.38

Compound **3a**

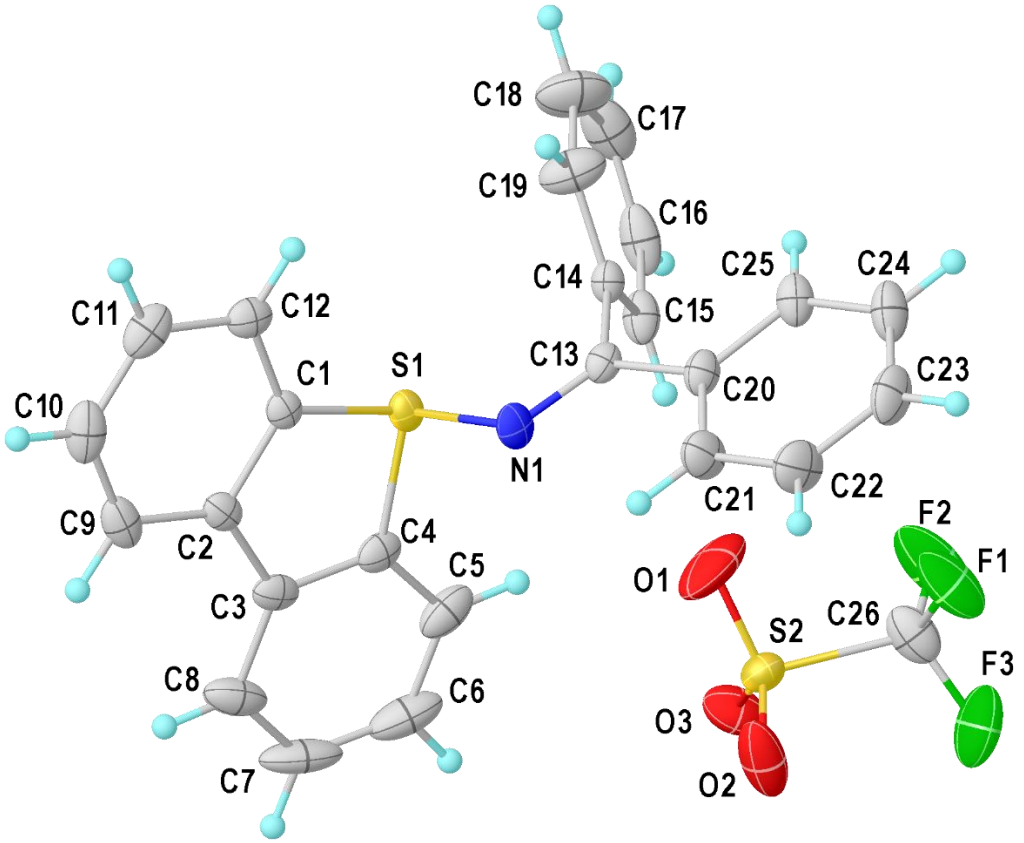


Figure S27: Molecular structure of full asymmetric unit and numbering scheme of compound **3a**. Ellipsoids drawn at 50% probability level.

Crystal data and structure refinement for **3a**.

CCDC	2062175
Empirical formula	$C_{26}H_{18}F_3NO_3S_2$
Formula weight	513.53
Temperature/K	100
Crystal system	Monoclinic
Space group	C2/c
a/Å	32.2922(19)
b/Å	8.2812(5)
c/Å	18.3803(9)
α/°	90
β/°	111.542(2)
γ/°	90
Volume/Å^3	4571.9(4)
Z	8
ρ_{calc}g/cm^3	1.492
μ/mm^{-1}	0.288
F(000)	2112.0

Crystal size/mm^3	0.36 × 0.249 × 0.098
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.536 to 55.854
Index ranges	$-42 \leq h \leq 42$, $-10 \leq k \leq 10$, $-24 \leq l \leq 24$
Reflections collected	24330
Independent reflections	5458 [R_{int} = 0.0204, R_{sigma} = 0.0167]
Data/restraints/parameters	5458/0/316
Goodness-of-fit on F^2	1.058
Final R indexes [I>=2σ (I)]	R_1 = 0.0387, wR_2 = 0.0956
Final R indexes [all data]	R_1 = 0.0437, wR_2 = 0.1003
Largest diff. peak/hole / e $Å^{-3}$	0.58/-0.66

Compound **3b**

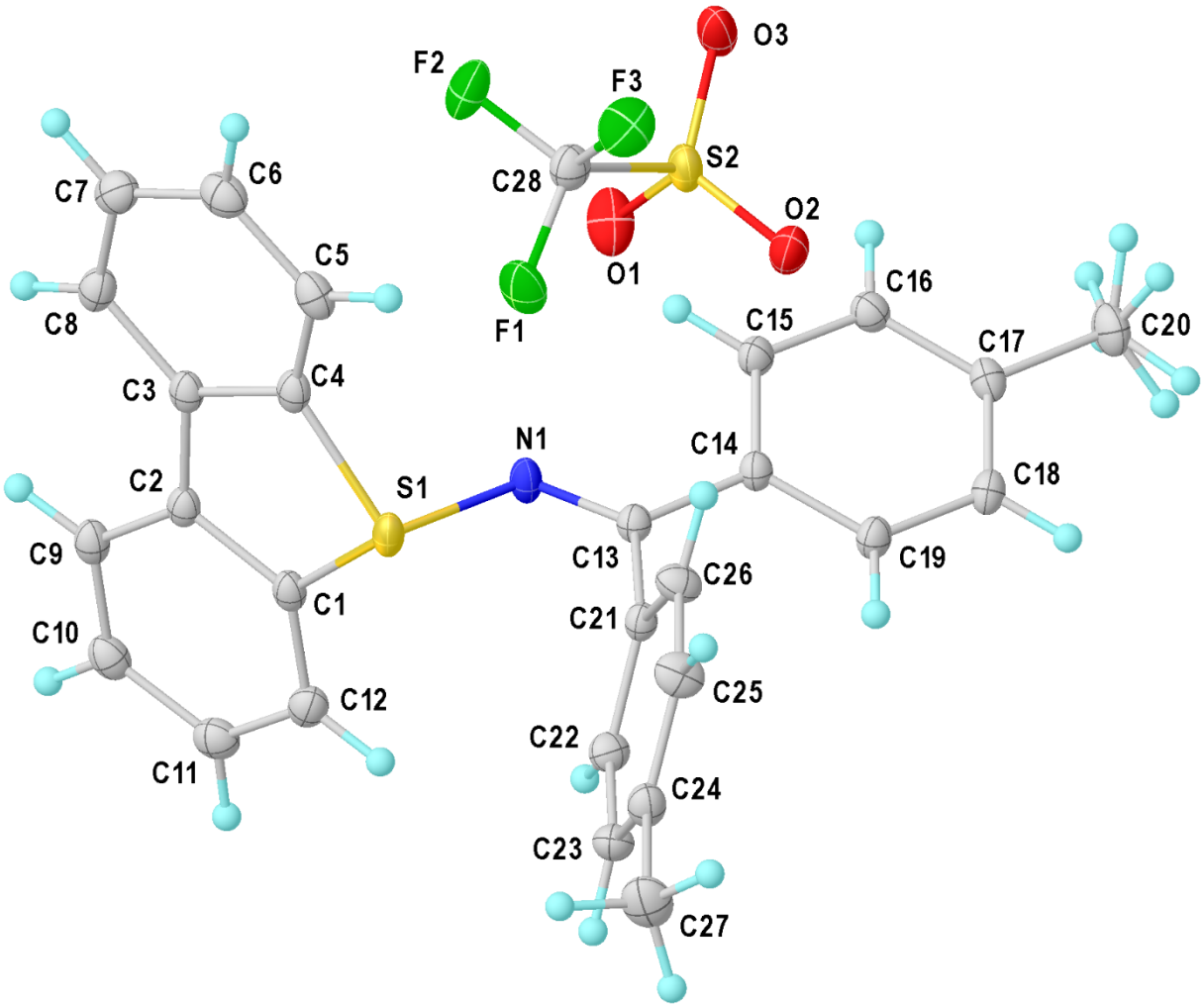


Figure S28: Molecular structure of full asymmetric unit and numbering scheme of compound **3b**. Ellipsoids drawn at 50% probability level. The methyl group C20 features rotational disorder.

Crystal data and structure refinement for **3b**.

CCDC	2062176
Empirical formula	$C_{28}H_{22}F_3NO_3S_2$
Formula weight	541.58
Temperature/K	100
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	8.0241(6)
b/Å	20.8105(12)
c/Å	15.2442(8)
α/°	90
β/°	105.143(2)
γ/°	90
Volume/Å^3	2457.2(3)

Z	4
ρ_{calc}g/cm^3	1.464
μ/mm^{-1}	0.272
F(000)	1120.0
Crystal size/mm^3	0.336 × 0.249 × 0.038
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.794 to 61.056
Index ranges	$-11 \leq h \leq 10$, $-29 \leq k \leq 29$, $-21 \leq l \leq 21$
Reflections collected	47717
Independent reflections	7440 [R_{int} = 0.0273, R_{sigma} = 0.0178]
Data/restraints/parameters	7440/3/337
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0336, wR_2 = 0.0865
Final R indexes [all data]	R_1 = 0.0396, wR_2 = 0.0910
Largest diff. peak/hole / e Å^{-3}	0.44/-0.41

Compound **3c**

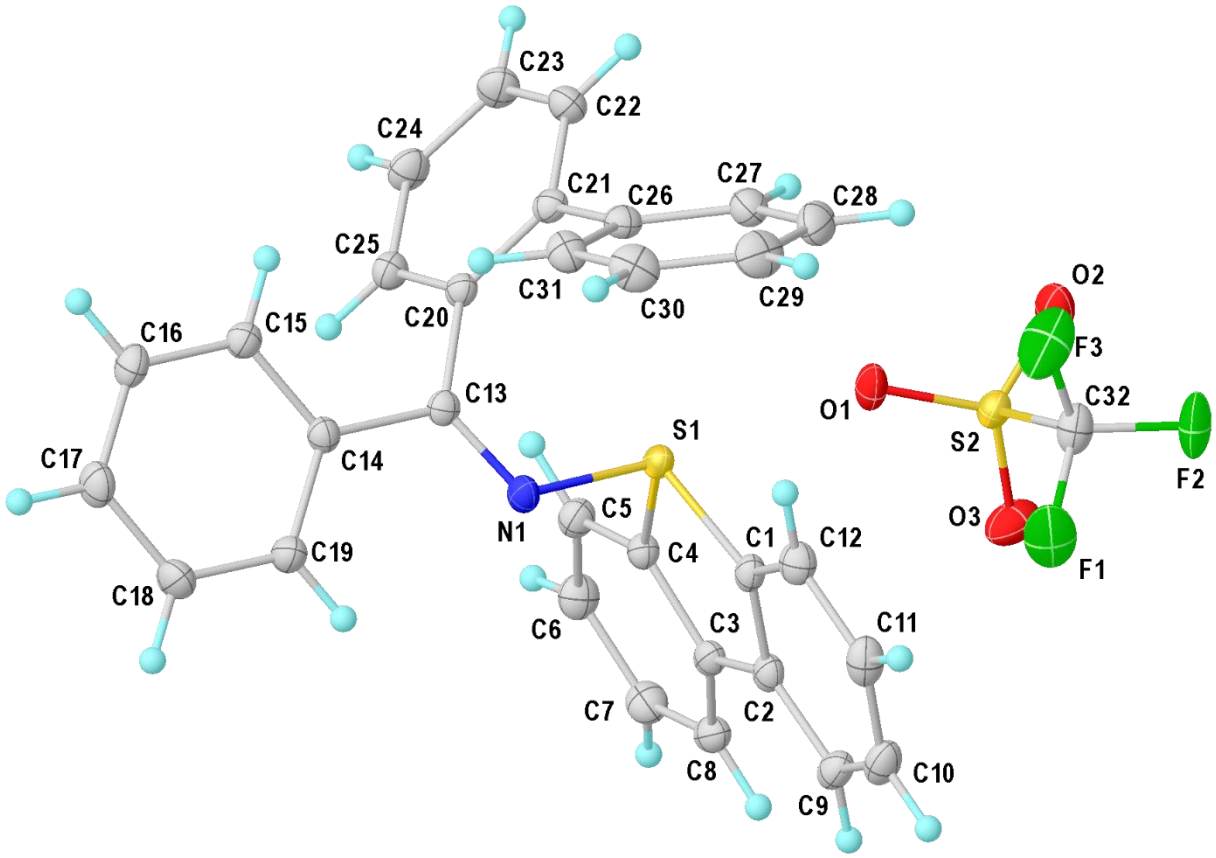


Figure S29: Molecular structure of full asymmetric unit and numbering scheme of compound **3c**. Ellipsoids drawn at 50% probability level.

Crystal data and structure refinement for **3c**.

CCDC	2062177
Empirical formula	$C_{32}H_{22}F_3NO_3S_2$
Formula weight	589.62
Temperature/K	100
Crystal system	Triclinic
Space group	P-1
a/Å	10.266(2)
b/Å	10.436(2)
c/Å	13.703(3)
α/°	77.481(7)
β/°	74.186(7)
γ/°	87.828(8)
Volume/Å^3	1378.5(6)
Z	2
ρ_{calc}g/cm^3	1.421
μ/mm^{-1}	0.249

F(000)	608.0
Crystal size/mm^3	0.351 × 0.23 × 0.092
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4 to 56.622
Index ranges	$-13 \leq h \leq 13$, $-13 \leq k \leq 13$, $-18 \leq l \leq 18$
Reflections collected	75438
Independent reflections	6830 [R_{int} = 0.0448, R_{sigma} = 0.0223]
Data/restraints/parameters	6830/0/371
Goodness-of-fit on F^2	1.073
Final R indexes [I>=2σ (I)]	R_1 = 0.0437, wR_2 = 0.1036
Final R indexes [all data]	R_1 = 0.0541, wR_2 = 0.1126
Largest diff. peak/hole / e $Å^{-3}$	0.78/-0.56

Compound **3d**

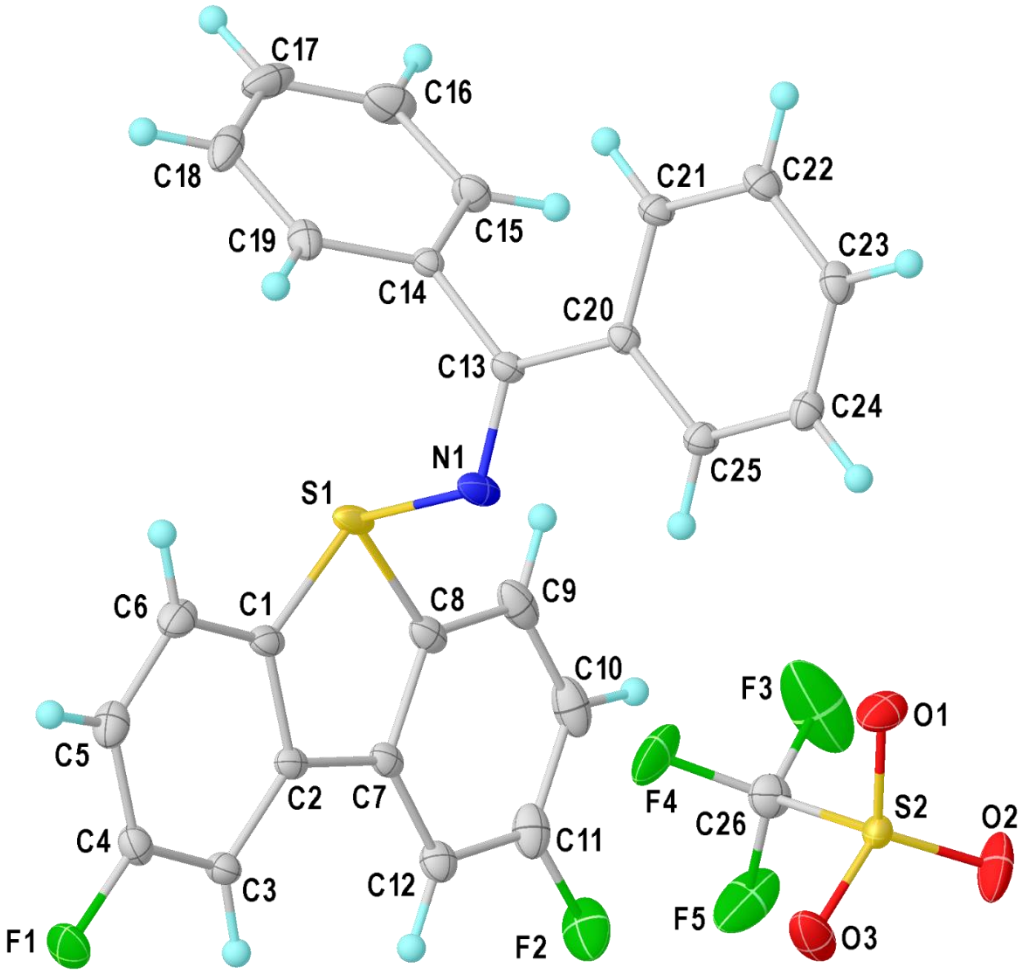


Figure S30: Molecular structure of full asymmetric unit and numbering scheme of compound **3d**. Ellipsoids drawn at 50% probability level.

Crystal data and structure refinement for **3d**.

CCDC	2062178
Empirical formula	$C_{26}H_{16}F_5NO_3S_2$
Formula weight	549.52
Temperature/K	100
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	10.9164(9)
b/Å	15.2555(15)
c/Å	14.1703(13)
α/°	90
β/°	99.893(4)
γ/°	90
Volume/Å^3	2324.8(4)

Z	4
ρ_{calc}g/cm^3	1.570
μ/mm^{-1}	0.301
F(000)	1120.0
Crystal size/mm^3	0.481 × 0.4 × 0.248
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.366 to 61.074
Index ranges	$-15 \leq h \leq 15$, $-21 \leq k \leq 21$, $-20 \leq l \leq 20$
Reflections collected	75701
Independent reflections	7099 [R_{int} = 0.0279, R_{sigma} = 0.0161]
Data/restraints/parameters	7099/0/334
Goodness-of-fit on F^2	1.094
Final R indexes [I>=2σ (I)]	R_1 = 0.0424, wR_2 = 0.1041
Final R indexes [all data]	R_1 = 0.0456, wR_2 = 0.1066
Largest diff. peak/hole / e Å^{-3}	0.63/-0.54

Compound **3e**

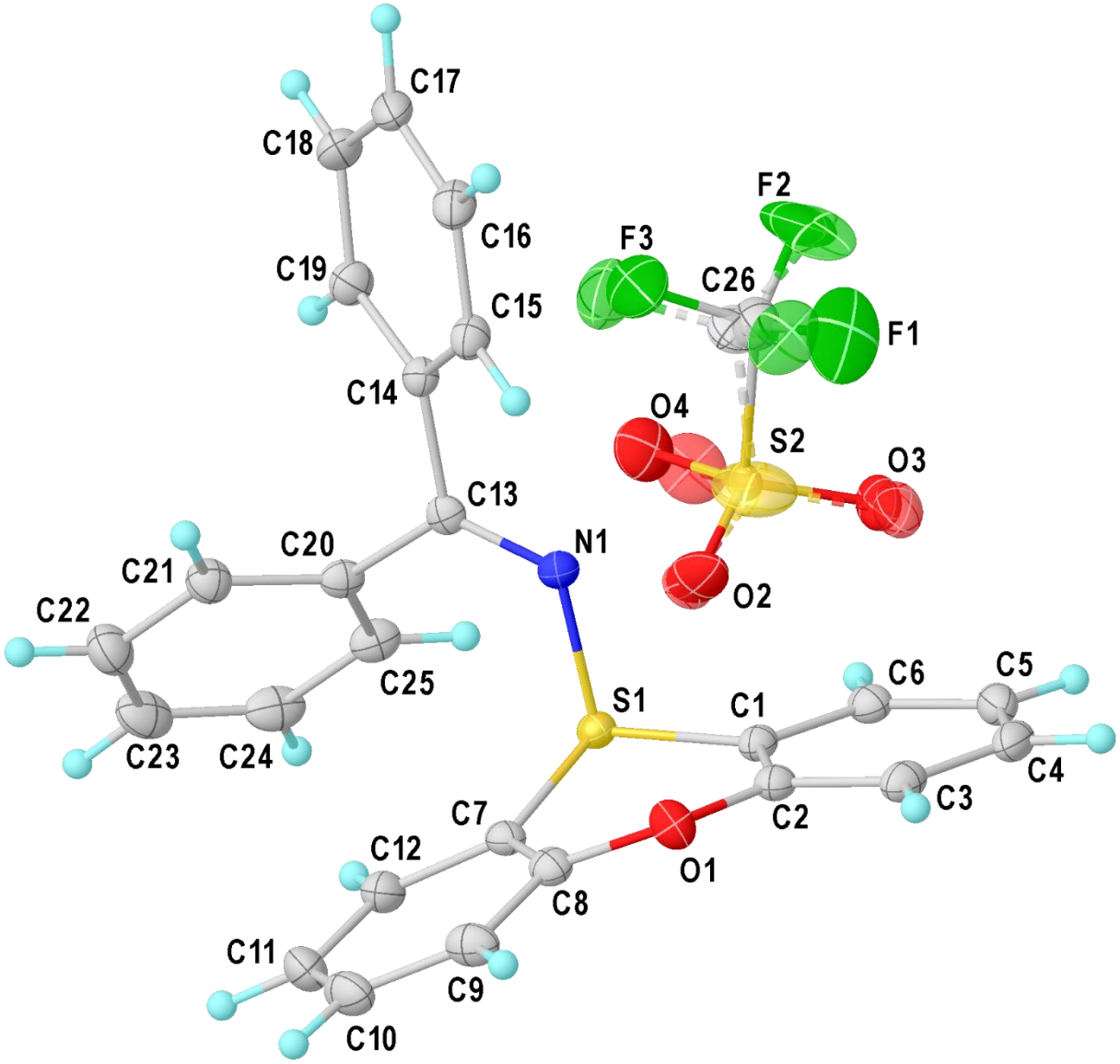


Figure S31: Molecular structure of full asymmetric unit and numbering scheme of compound **3e**. Ellipsoids drawn at 50% probability level. Minor disorder drawn with translucent ellipsoids and stippled bonds. The refined occupancy of the major disorder part is 0.88(1).

Crystal data and structure refinement for **3e**.

CCDC	2062179
Empirical formula	$C_{26}H_{18}F_3NO_4S_2$
Formula weight	529.53
Temperature/K	100
Crystal system	Orthorhombic
Space group	Pbca
a/Å	9.8155(6)
b/Å	16.0505(14)
c/Å	29.742(2)

α/°	90
β/°	90
γ/°	90
Volume/Å^3	4685.7(6)
Z	8
ρ_{calc}g/cm^3	1.501
μ/mm^{-1}	0.287
F(000)	2176.0
Crystal size/mm^3	0.249 × 0.194 × 0.046
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.972 to 57.392
Index ranges	-13 ≤ h ≤ 13, -21 ≤ k ≤ 21, -40 ≤ l ≤ 40
Reflections collected	89715
Independent reflections	6055 [R_{int} = 0.0432, R_{sigma} = 0.0178]
Data/restraints/parameters	6055/74/398
Goodness-of-fit on F^2	1.105
Final R indexes [I>=2σ (I)]	R_1 = 0.0393, wR_2 = 0.0796
Final R indexes [all data]	R_1 = 0.0449, wR_2 = 0.0830
Largest diff. peak/hole / e Å^{-3}	0.33/-0.39

Compound **3f** ◦ thianthrene S-oxide

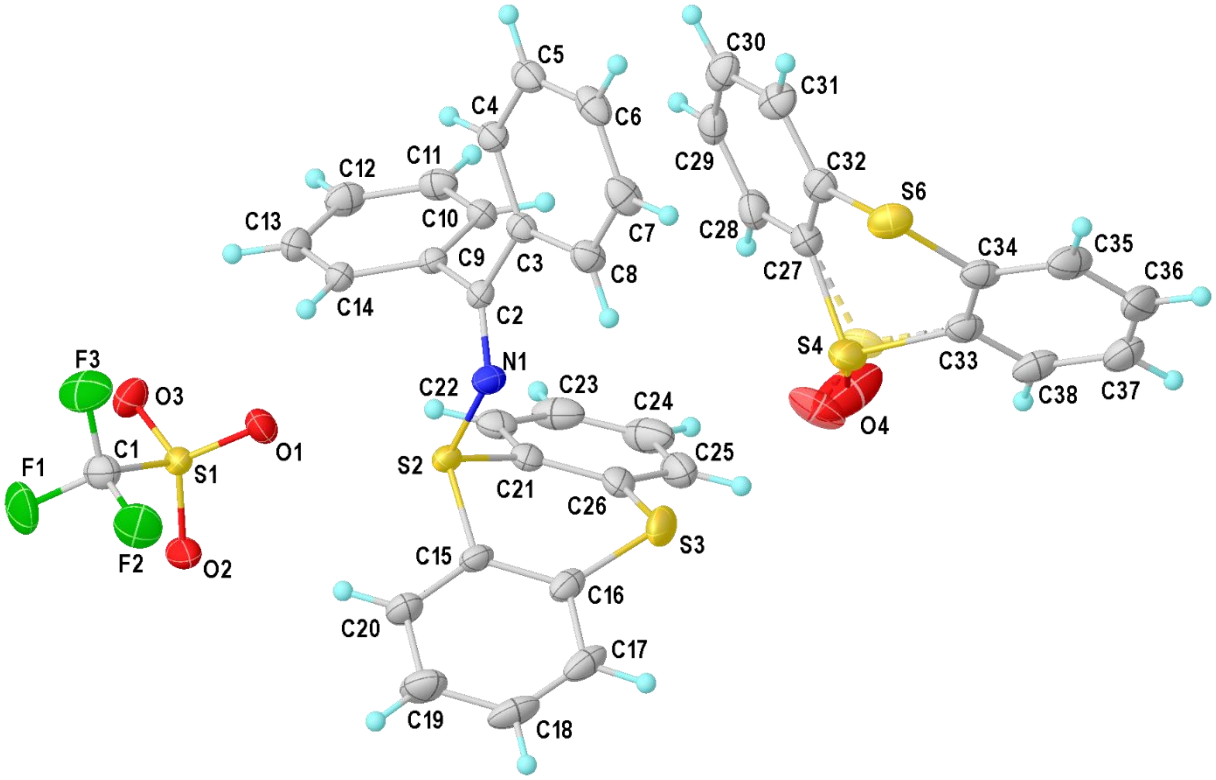


Figure S32: Molecular structure of full asymmetric unit and numbering scheme of compound **3f**. Ellipsoids drawn at 50% probability level. Minor disorder drawn with translucent ellipsoids and stippled bonds. The refined occupancy of the major disorder part is 0.751(5). **3f** tends to co-crystalize with one equivalent of thianthrene S-oxide, if remaining from the synthesis. Noteworthy chalcogenic interaction can be found between O1 and S2, which is rather typical for these compounds; and for O4 and S3, which is explaining the favored co-crystallization.

Crystal data and structure refinement for **3f** ○ thianthrene S-oxide.

CCDC	2062180
Empirical formula	$C_{38}H_{26}F_3NO_4S_5$
Formula weight	777.90
Temperature/K	100
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	11.0127(8)
b/Å	18.919(2)
c/Å	17.186(2)
α/°	90
β/°	106.981(3)
γ/°	90
Volume/Å^3	3424.5(6)
Z	4

ρ_{calc}g/cm^3	1.509
μ/mm^{-1}	0.399
F(000)	1600.0
Crystal size/mm^3	0.264 × 0.242 × 0.187
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.306 to 60.992
Index ranges	$-15 \leq h \leq 14$, $-25 \leq k \leq 27$, $-24 \leq l \leq 24$
Reflections collected	69718
Independent reflections	10273 [R_{int} = 0.0283, R_{sigma} = 0.0211]
Data/restraints/parameters	10273/11/479
Goodness-of-fit on F^2	1.057
Final R indexes [I>=2σ (I)]	R_1 = 0.0465, wR_2 = 0.1043
Final R indexes [all data]	R_1 = 0.0578, wR_2 = 0.1111
Largest diff. peak/hole / e Å^{-3}	0.90/-1.14

Compound **3f**

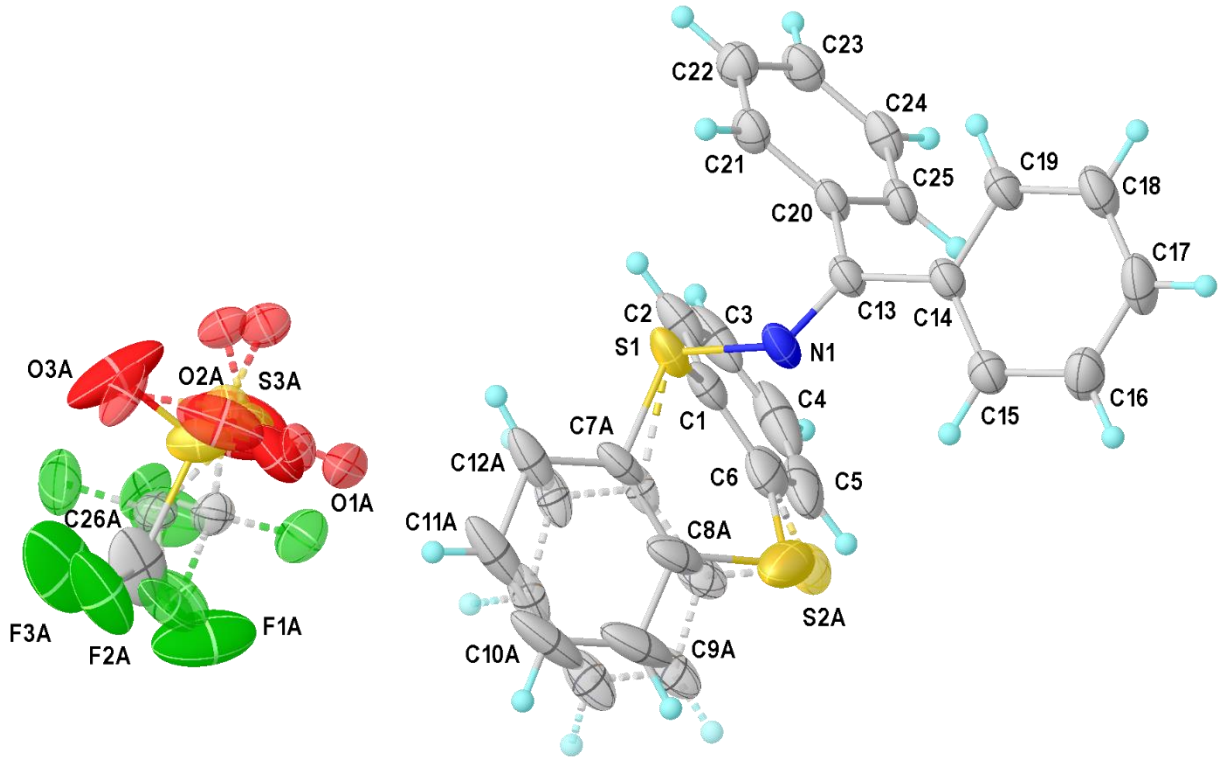


Figure S33: Molecular structure of full asymmetric unit and numbering scheme of compound **3f**. Ellipsoids drawn at 50% probability level. Minor disorder drawn with translucent ellipsoids and stippled bonds. The thianthrene and triflate disorder were modelled separately: The thianthrene was partly splited in two positions with the major part occupancy factor refined to 0.66(2). The triflate anion was split in three positions with each position's occupancy factor refined separately and the sum of occupancies restrained to 1. The final occupancy factors were refined to 0.395(3), 0.376(3) and 0.229(3).

Crystal data and structure refinement for **3f**.

CCDC	2062181
Empirical formula	$C_{26}H_{18}F_3NO_3S_3$
Formula weight	545.59
Temperature/K	100
Crystal system	Tetragonal
Space group	$P4_12_12$
a/Å	13.0989(6)
b/Å	13.0989(6)
c/Å	27.9396(10)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4793.9(5)
Z	8

ρ_{calc}g/cm^3	1.512
μ/mm^{-1}	0.363
F(000)	2240.0
Crystal size/mm^3	0.15 × 0.133 × 0.127
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.262 to 61.028
Index ranges	-18 ≤ h ≤ 18, -18 ≤ k ≤ 18, -39 ≤ l ≤ 39
Reflections collected	265858
Independent reflections	7323 [R_{int} = 0.0299, R_{sigma} = 0.0092]
Data/restraints/parameters	7323/183/483
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0491, wR_2 = 0.1256
Final R indexes [all data]	R_1 = 0.0559, wR_2 = 0.1332
Largest diff. peak/hole / e Å^{-3}	0.55/-0.79
Flack parameter	0.47(11)*

* refined as Inversion twin.

Compound 6j

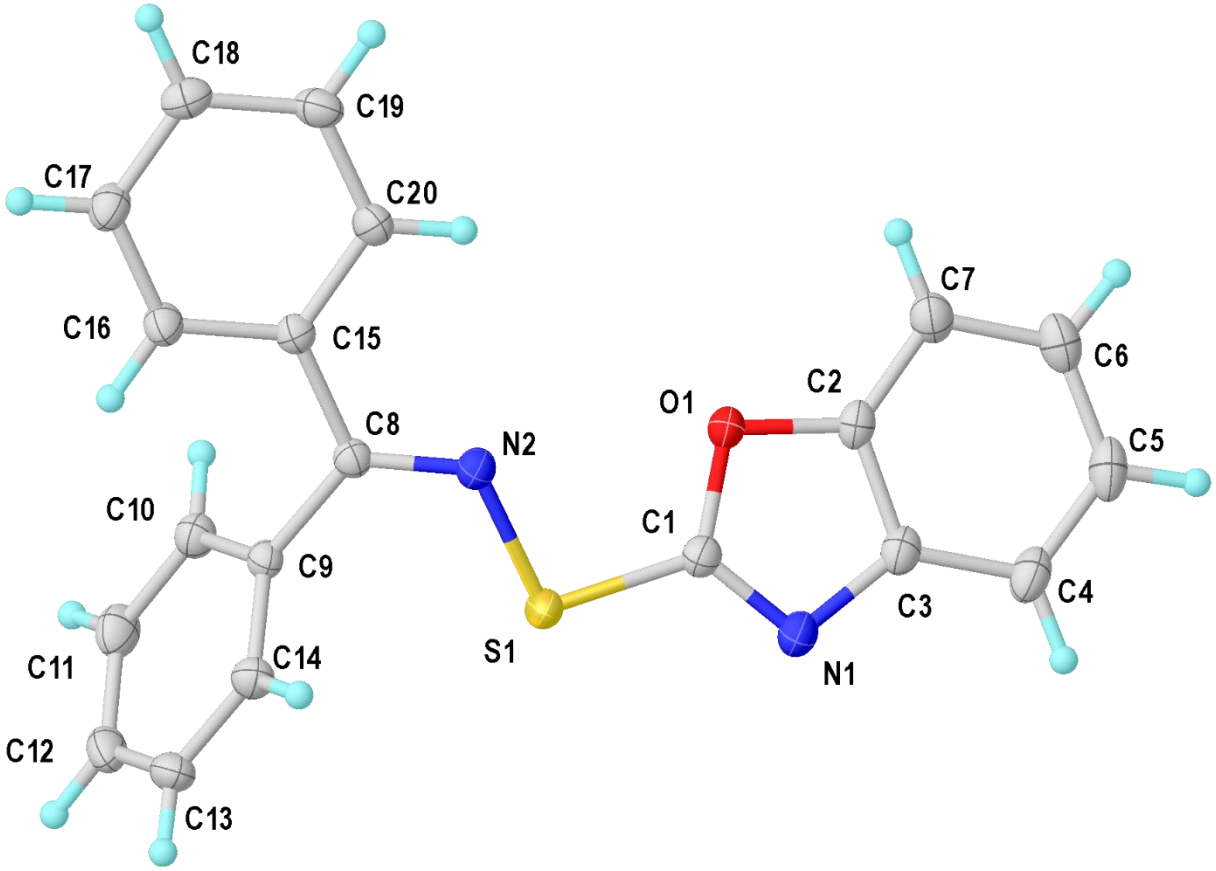


Figure 34: Molecular structure of full asymmetric unit and numbering scheme of compound **6j**. Ellipsoids drawn at 50% probability level.

Crystal data and structure refinement for **6j**.

CCDC	2063032
Empirical formula	$C_{20}H_{14}N_2OS$
Formula weight	330.39
Temperature/K	150
Crystal system	Triclinic
Space group	P-1
a/Å	8.5809(8)
b/Å	9.1772(7)
c/Å	10.4716(9)
α/°	103.021(4)
β/°	93.915(4)
γ/°	96.530(3)
Volume/Å^3	794.44(12)
Z	2
ρ_{calc}g/cm^3	1.381
μ/mm^{-1}	0.212

F(000)	344.0
Crystal size/mm^3	0.35 × 0.3 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.596 to 59.268
Index ranges	-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -14 ≤ l ≤ 14
Reflections collected	26461
Independent reflections	4469 [R_{int} = 0.0265, R_{sigma} = 0.0183]
Data/restraints/parameters	4469/0/217
Goodness-of-fit on F^2	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.0337, wR_2 = 0.0836
Final R indexes [all data]	R_1 = 0.0382, wR_2 = 0.0876
Largest diff. peak/hole / e $Å^{-3}$	0.33/-0.33

Compound 13b

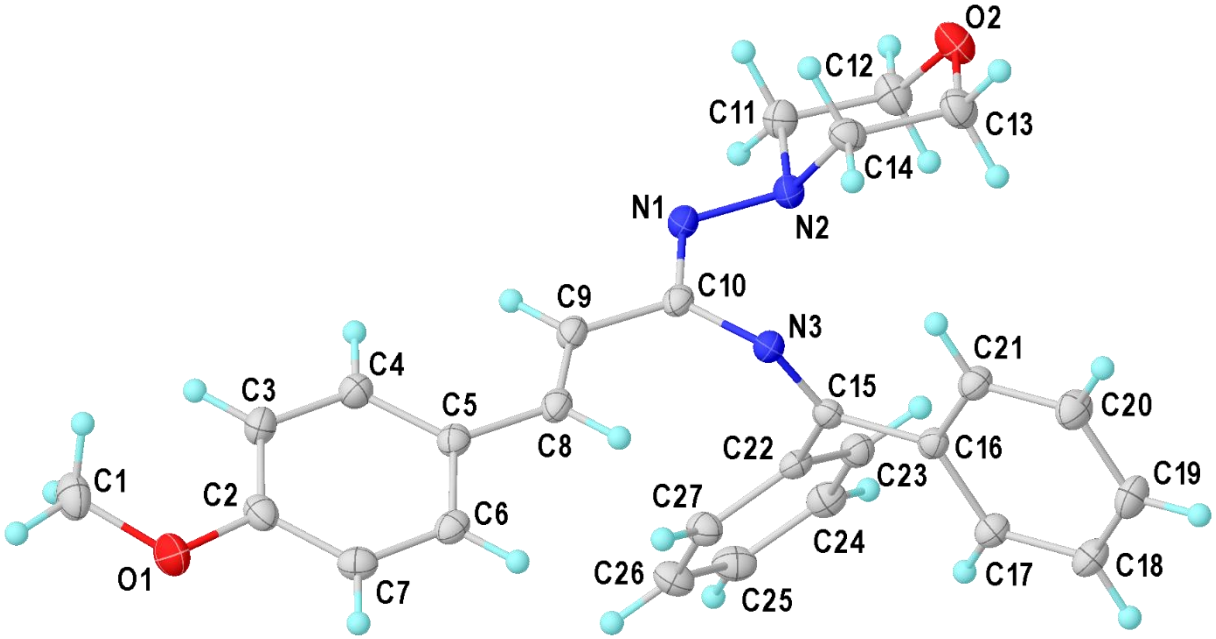


Figure 35: Molecular structure of full asymmetric unit and numbering scheme of compound **13b**. Ellipsoids drawn at 50% probability level.

Crystal data and structure refinement for **13b**.

CCDC	2063033
Empirical formula	$C_{27}H_{27}N_3O_2$
Formula weight	425.51
Temperature/K	100
Crystal system	Triclinic
Space group	P-1
a/Å	10.1835(13)
b/Å	10.1873(12)
c/Å	12.0324(13)
α/°	73.061(4)
β/°	85.268(5)
γ/°	71.102(4)
Volume/Å^3	1129.7(2)
Z	2
ρ_{calc}g/cm^3	1.251
μ/mm^{-1}	0.080
F(000)	452.0
Crystal size/mm^3	0.194 × 0.159 × 0.155
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.228 to 56.702
Index ranges	-13 ≤ h ≤ 13, -13 ≤ k ≤ 13, -16 ≤ l ≤ 15

Reflections collected	53011
Independent reflections	5631 [R_{int} = 0.0334, R_{sigma} = 0.0172]
Data/restraints/parameters	5631/0/291
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0383, wR_2 = 0.0961
Final R indexes [all data]	R_1 = 0.0432, wR_2 = 0.1001
Largest diff. peak/hole / e $Å^{-3}$	0.32/-0.17

Compound 16b

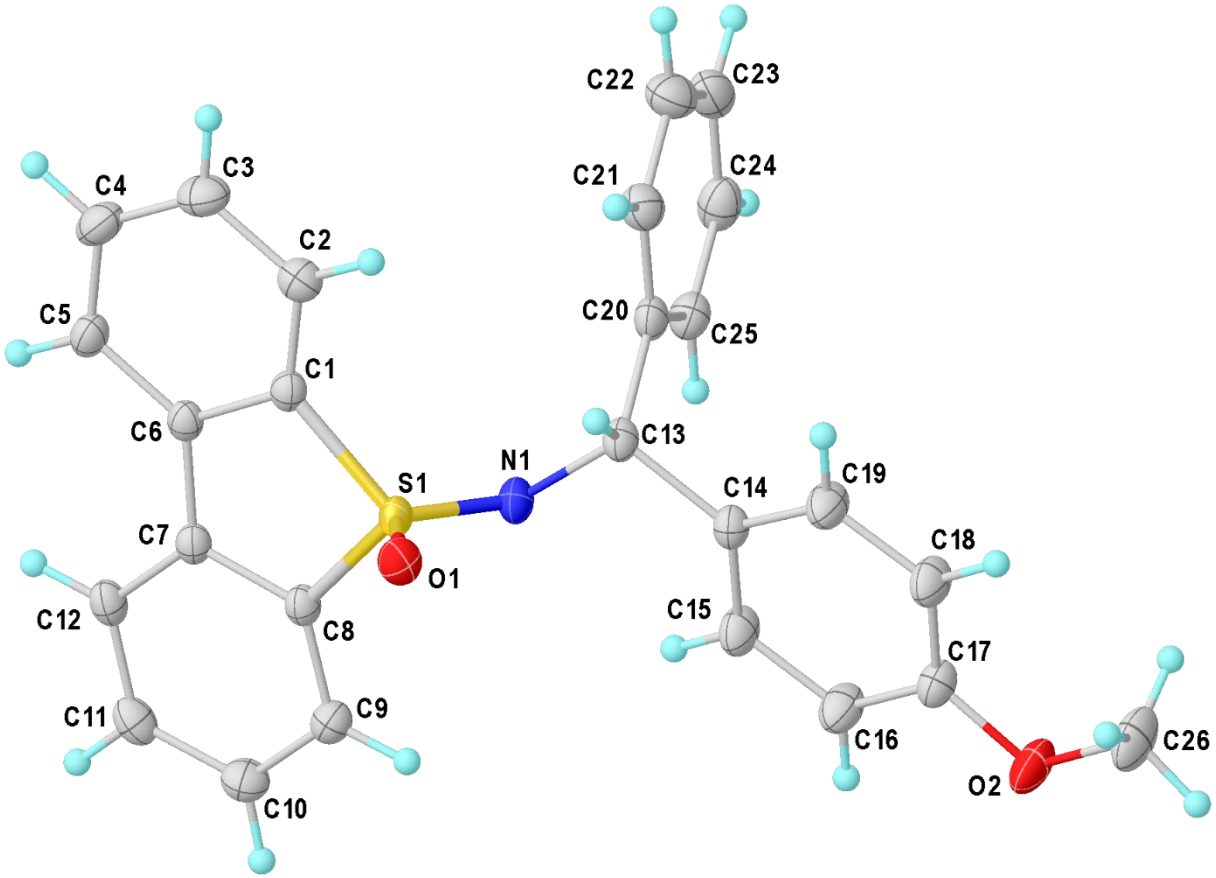


Figure 36: Molecular structure of full asymmetric unit and numbering scheme of compound **16b**. Ellipsoids drawn at 50% probability level.

Crystal data and structure refinement for **16b**.

CCDC	2063034
Empirical formula	$C_{26}H_{21}NO_2S$
Formula weight	411.50
Temperature/K	100
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	12.890(3)
b/Å	17.696(4)
c/Å	9.0179(16)
α/°	90
β/°	99.136(6)
γ/°	90
Volume/Å^3	2031.0(8)
Z	4
ρ_{calc}g/cm^3	1.346

μ/mm^{-1}	0.183
F(000)	864.0
Crystal size/mm^3	0.204 × 0.117 × 0.107
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.604 to 65.982
Index ranges	-19 ≤ h ≤ 19, -26 ≤ k ≤ 26, -13 ≤ l ≤ 13
Reflections collected	52320
Independent reflections	6915 [R_{int} = 0.0448, R_{sigma} = 0.0341]
Data/restraints/parameters	6915/0/272
Goodness-of-fit on F^2	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.0517, wR_2 = 0.1213
Final R indexes [all data]	R_1 = 0.0676, wR_2 = 0.1291
Largest diff. peak/hole / e $Å^{-3}$	0.48/-0.52

Compound 16h

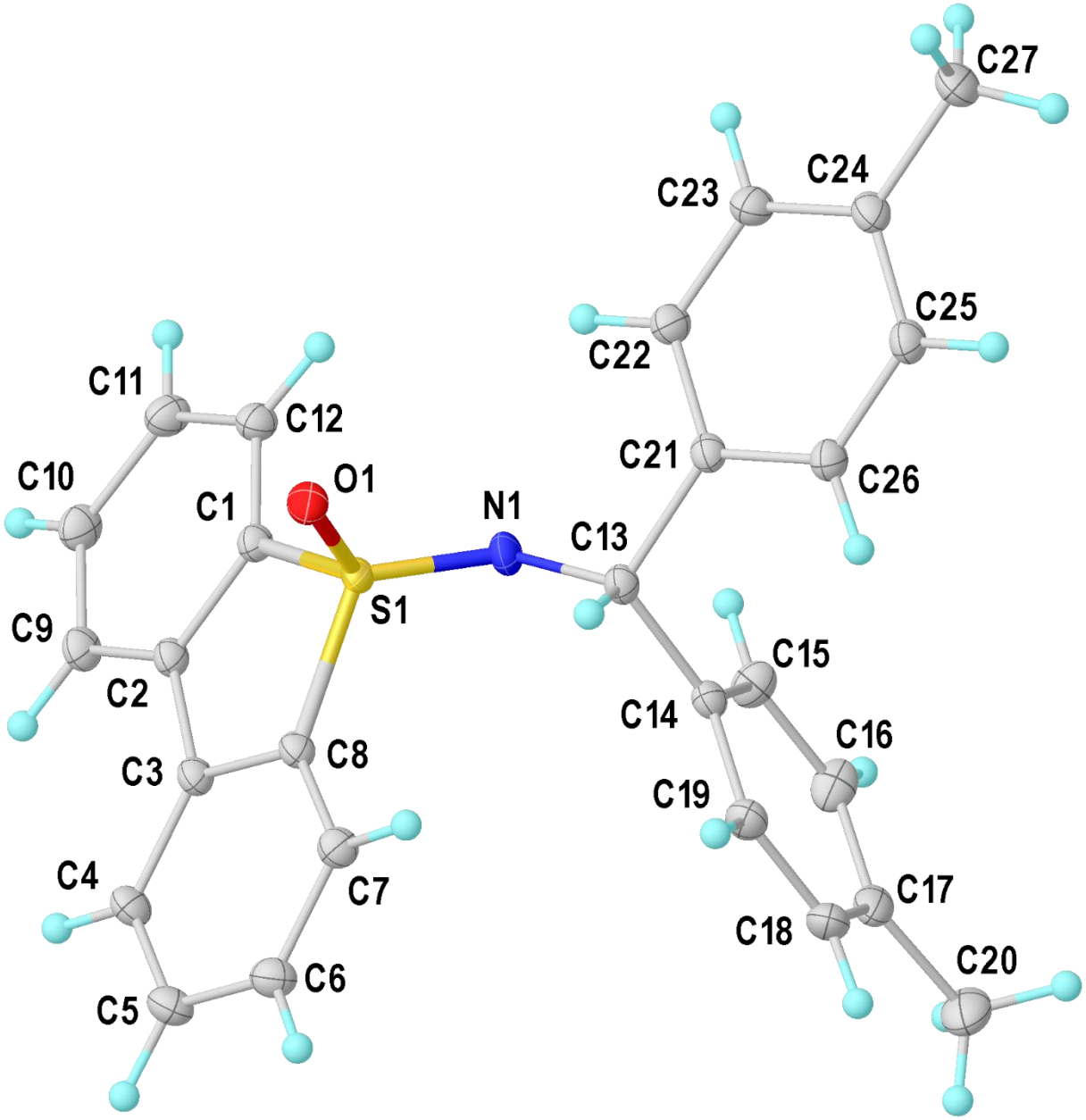


Figure 37: Molecular structure of full asymmetric unit and numbering scheme of compound **16h**. Ellipsoids drawn at 50% probability level.

Crystal data and structure refinement for **16h**.

CCDC	2063035
Empirical formula	$C_{27}H_{23}NOS$
Formula weight	409.52
Temperature/K	100
Crystal system	Triclinic
Space group	P-1

a/Å	9.6947(3)
b/Å	10.8404(3)
c/Å	12.1920(4)
α/°	99.1640(10)
β/°	113.4380(10)
γ/°	109.7450(10)
Volume/Å^3	1040.54(6)
Z	2
ρ_{calc}g/cm^3	1.307
μ/mm^{-1}	0.175
F(000)	432.0
Crystal size/mm^3	0.426 × 0.272 × 0.142
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.672 to 68.762
Index ranges	-14 ≤ h ≤ 15, -17 ≤ k ≤ 17, -19 ≤ l ≤ 19
Reflections collected	78916
Independent reflections	7926 [R_{int} = 0.0265, R_{sigma} = 0.0168]
Data/restraints/parameters	7926/0/340
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0338, wR_2 = 0.0919
Final R indexes [all data]	R_1 = 0.0370, wR_2 = 0.0976
Largest diff. peak/hole / e Å^{-3}	0.47/-0.43

Compound 16i

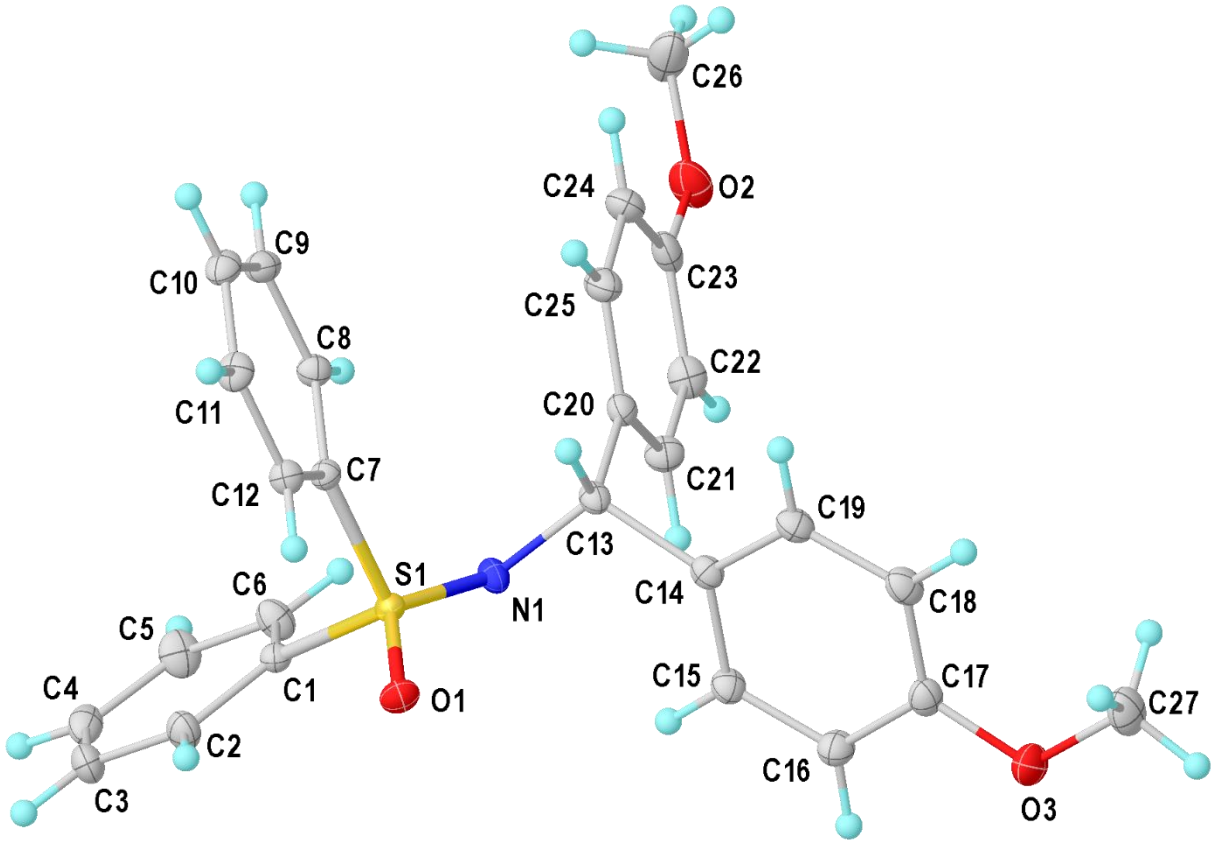


Figure 38: Molecular structure of full asymmetric unit and numbering scheme of compound **16i**. Ellipsoids drawn at 50% probability level.

Crystal data and structure refinement for **16i**.

CCDC	2063036
Empirical formula	$C_{27}H_{25}NO_3S$
Formula weight	443.54
Temperature/K	100
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	12.3013(16)
b/Å	11.0116(11)
c/Å	16.542(2)
α/°	90
β/°	100.472(4)
γ/°	90
Volume/Å^3	2203.4(5)
Z	4
ρ_{calc}g/cm^3	1.337
μ/mm^{-1}	0.177

F(000)	936.0
Crystal size/mm^3	0.291 × 0.278 × 0.112
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.466 to 59.338
Index ranges	-16 ≤ h ≤ 17, -14 ≤ k ≤ 15, -23 ≤ l ≤ 23
Reflections collected	81796
Independent reflections	6220 [R_{int} = 0.0277, R_{sigma} = 0.0130]
Data/restraints/parameters	6220/0/291
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0324, wR_2 = 0.0869
Final R indexes [all data]	R_1 = 0.0346, wR_2 = 0.0890
Largest diff. peak/hole / e $Å^{-3}$	0.40/-0.42

Compound 16l

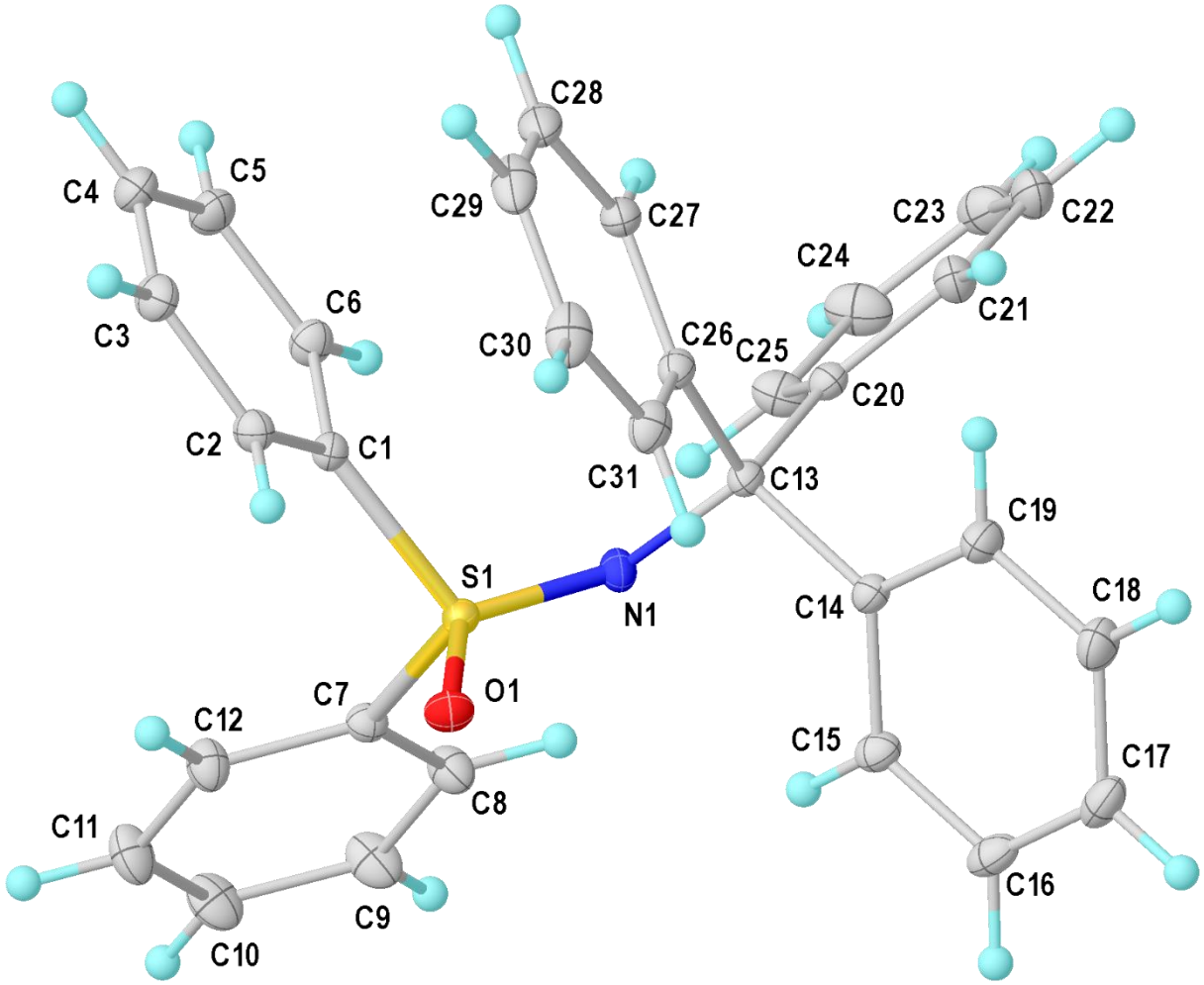


Figure 39: Molecular structure of full asymmetric unit and numbering scheme of compound **16l**. Ellipsoids drawn at 50% probability level.

Crystal data and structure refinement for **16l**.

CCDC	2063037
Empirical formula	$C_{31}H_{25}NOS$
Formula weight	459.58
Temperature/K	100
Crystal system	Monoclinic
Space group	C2/c
a/Å	24.1618(13)
b/Å	8.1430(5)
c/Å	24.1637(15)
α/°	90
β/°	99.543(2)
γ/°	90
Volume/Å^3	4688.4(5)

Z	8
ρ_{calc}g/cm^3	1.302
μ/mm^{-1}	0.163
F(000)	1936.0
Crystal size/mm^3	0.475 × 0.332 × 0.3
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.286 to 61.198
Index ranges	-34 ≤ h ≤ 34, -11 ≤ k ≤ 11, -34 ≤ l ≤ 34
Reflections collected	62839
Independent reflections	7196 [R_{int} = 0.0271, R_{sigma} = 0.0160]
Data/restraints/parameters	7196/0/307
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0330, wR_2 = 0.0890
Final R indexes [all data]	R_1 = 0.0344, wR_2 = 0.0903
Largest diff. peak/hole / e Å^{-3}	0.41/-0.44

Compound 16ae

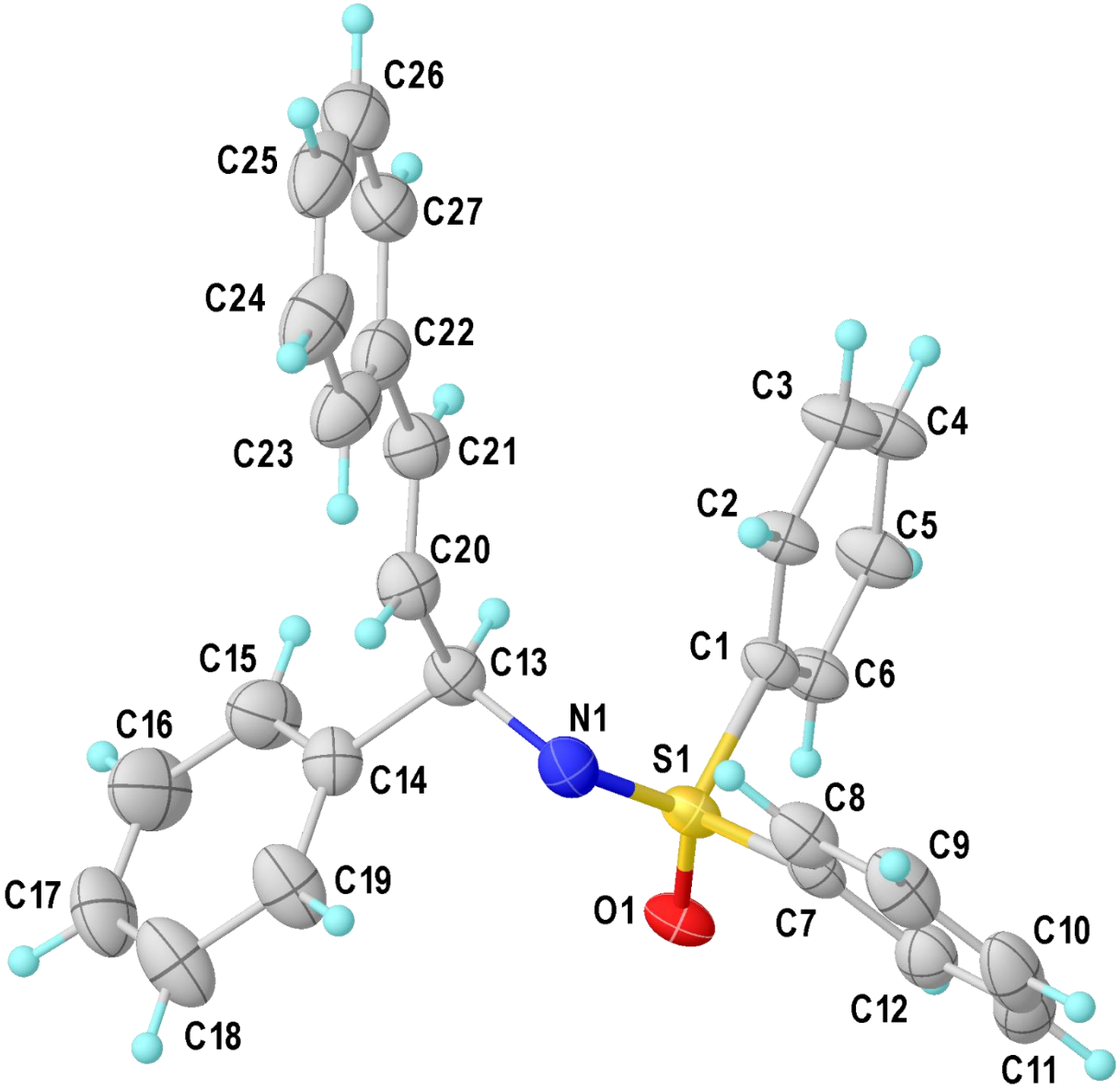


Figure 40: Molecular structure of full asymmetric unit and numbering scheme of compound **16ae**. Ellipsoids drawn at 50% probability level.

Crystal data and structure refinement for **16ae**.

CCDC	2063038
Empirical formula	$C_{27}H_{23}NOS$
Formula weight	409.52
Temperature/K	100
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	12.066(5)
b/Å	11.422(5)

c/Å	16.283(7)
α/°	90
β/°	103.093(11)
γ/°	90
Volume/Å^3	2185.8(16)
Z	4
ρ_{calc}g/cm^3	1.244
μ/mm^{-1}	0.166
F(000)	864.0
Crystal size/mm^3	0.285 × 0.25 × 0.018
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.394 to 57.482
Index ranges	-16 ≤ h ≤ 16, -15 ≤ k ≤ 15, -20 ≤ l ≤ 21
Reflections collected	62399
Independent reflections	5646 [R_{int} = 0.0556, R_{sigma} = 0.0336]
Data/restraints/parameters	5646/0/272
Goodness-of-fit on F^2	1.092
Final R indexes [I>=2σ (I)]	R_1 = 0.0679, wR_2 = 0.1777
Final R indexes [all data]	R_1 = 0.0961, wR_2 = 0.2025
Largest diff. peak/hole / e Å^{-3}	0.60/-0.64

Compound 16ag

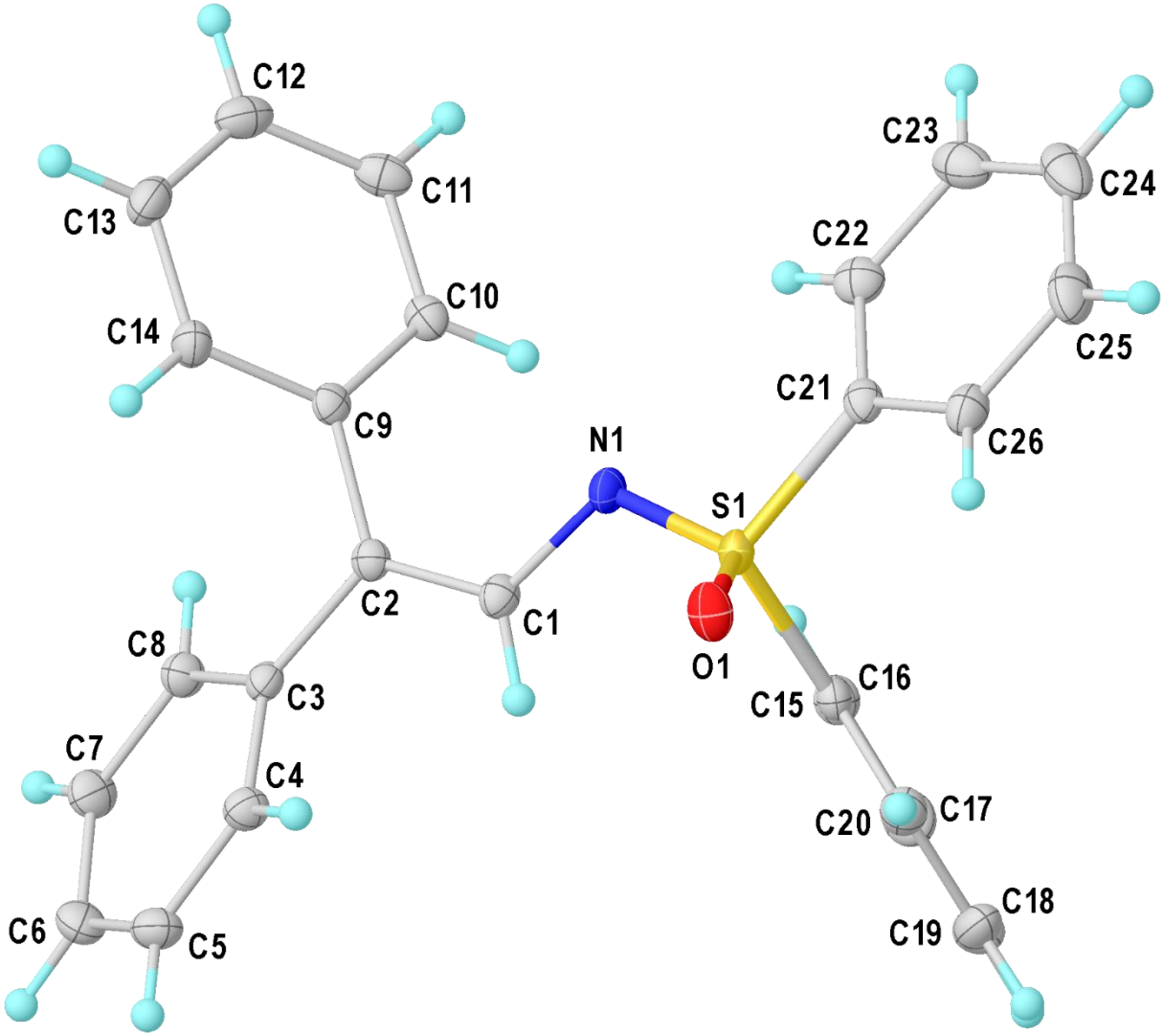


Figure 41: Molecular structure of full asymmetric unit and numbering scheme of compound **16ag**. Ellipsoids drawn at 50% probability level.

Crystal data and structure refinement for **16ag**.

CCDC	2063039
Empirical formula	$C_{26}H_{21}NOS$
Formula weight	395.50
Temperature/K	100
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å	6.149(2)
b/Å	16.882(5)
c/Å	19.240(6)
α/°	90
β/°	90

γ/°	90
Volume/Å^3	1997.4(11)
Z	4
ρ_{calc}g/cm^3	1.315
μ/mm^{-1}	0.179
F(000)	832.0
Crystal size/mm^3	0.77 × 0.083 × 0.073
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.234 to 61.26
Index ranges	-8 ≤ h ≤ 8, -24 ≤ k ≤ 23, -27 ≤ l ≤ 27
Reflections collected	46833
Independent reflections	6128 [R_{int} = 0.0479, R_{sigma} = 0.0298]
Data/restraints/parameters	6128/0/262
Goodness-of-fit on F^2	1.058
Final R indexes [I>=2σ (I)]	R_1 = 0.0345, wR_2 = 0.0804
Final R indexes [all data]	R_1 = 0.0386, wR_2 = 0.0841
Largest diff. peak/hole / e Å^{-3}	0.29/-0.38
Flack parameter	0.097(19)

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