Supporting Information

Tetrazole Amides as Hydrogen-Bonding Donor Catalysts in the Chemoselective Oxidation of Sulphides and Disulphides

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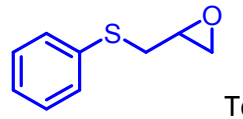
1. Synthesis

1.1 General methods

^{1}H NMR spectra were recorded on 400 and 500 MHz Varian spectrometers at 27°C using $CDCl_3$, DMF-d_7 or DMSO-d_6 as solvent. ^{13}C NMR were recorded at 100 and 125 MHz at 27°C using $CDCl_3$, DMF-d_7 or DMSO-d_6 as solvent. Chemical shifts (δ) are given in ppm. Coupling constants (J) are reported in Hz. Infrared spectra were recorded on a FT-IR Bruker spectrophotometer and are reported in wavenumbers. Low Mass spectra analysis were recorded on an Agilent-HP GC-MS (E.I. 70eV).
Analytical thin layer chromatography was performed using 0.25 mm silica gel 60-F plates. Flash chromatography was performed using 70-200 mesh silica gel. Yields refer to chromatography and spectroscopically pure materials. Analytical standards of tetrazoles **2a**, **2d**, **2e** were purchased from Sigma Aldrich and used to value the purity of the corresponding synthetized tetrazoles. Sulphides **5a-f**, **5h**, **5j**, **5k**, **5m**, **5o**, **5p**, **5q**, **5r** were purchased from Sigma Aldrich. Sulphides **5g, 5i, 5l, 5n, 5s,** were synthetized as described below.

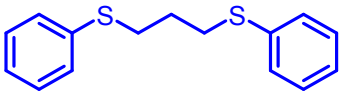
1.2 Synthesis of sulphides 5g, 5i, 5l, 5n, 5s

Synthesis of sulphide 5g.



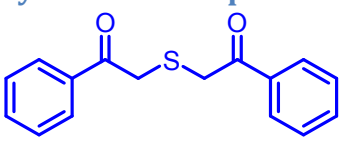
To a stirring suspension of NaH (1.45g, ~60%, 0.036 mol) in dry THF, (50 mL), cooled at 0°C, thiophenol (4g, 0.036) was slowly added in (15 mL of THF). After 1h, 2-(chloromethyl)oxirane (3.32g, 0.036 mol) was added dropwise in 15 mL of dry THF and the reaction was stirred at the same temperature for 6h. The resulting reaction mixture was warmed up to room temperature and filtered. The organic phase was washed with $NaHCO_3$ and brine. Once dried on Na_2SO_4, the solution was concentrated under reduced pressure to afford a yellow oil. Pure sulphide **5g** was obtained by flash column chromatography (silica gel, 80:20 hexane/ether) in 71% yield (4.2 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40 (d, 2 H, *J* = 7.6 Hz), 7.27 (t, 2 H, *J* = 7.6 Hz), 7.19 (t, 1 H, *J* = 7.6 Hz), 3.14-3.10 (m, 2H), 2.91 (dd, 1H, *J* = 7.2 Hz, *J* = 15.2 Hz), 2.73 (t, 1H, *J* = 3.6 Hz), 2.48 (t, 1H, *J* = Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.1, 130.0, 128.8, 126.5, 50.8, 47.1, 36.4. Spectroscopic data are in accordance with those previously reported.[1]

Synthesis of sulphide 5i.



Sodium (0) (1.45g, 0.063 mol) was added (small chunks) in 100 ml of dry MeOH stirred at 0°C under Argon. The mixture was stirred until all the metal disappeared. Thiophenol (7g, 0.063 mol), (dissolved in 20 mL of dry MeOH) was added dropwise and the reaction mixture was stirred at 0°C for 1h. 1,3-dibromopropane (6.2g, 0.031 mol) was added dropwise (in 20 mL of MeOH). The cooling bath was removed and the reaction was stirred overnight at 50°C. The reaction mixture was diluted with Et_2O (100 mL) and filtered. The resulting clear solution was washed with NaOH 2M (50 mL) and brine. The organic layer was dried on Na_2SO_4 and filtered. The clear organic phase was concentrated under reduced pressure and the obtained oil was distilled at low pressure. Pure 1,3-bisdiphenylthiopropane **7i** was afforded as colourless oil in 85% yield (6.8g). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39-7.33 (m, 4H), 7.28 (t, 4H, *J* = 7.2 Hz), 7.19 (t, 2H. *J* = 7.2 Hz), 3.06 (t, 4H, *J* = 7.2 Hz), 1.98 (t, 2H, *J* = 7.2 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.0, 129.3, 128.9, 126.0, 32.4, 28.3 ppm. Spectroscopic data are in accordance with those previously reported.[2]

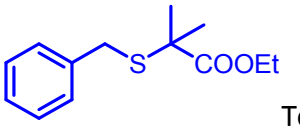
Synthesis of sulphide 5l.



To a solution of α-bromoacetophenone (5g, 0.025g), in dry THF (70 mL), Na_2S was added and the suspension was stirred at reflux overnight. The reaction mixture was cooled to room temperature and filtered. The solid was diluted

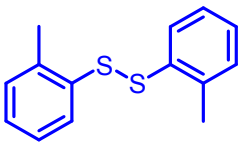
with CH_2Cl_2 (100 mL) and washed with brine. The organic phase was dried with Na2SO4 and concentrated under reduced pressure to afford a yellow solid that was recrystallized by MeOH/hexane to afford sulphide **5l** in 60% yield (4.0g). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (d, 4 H, *J* = 7.5 Hz), 7.57 (t, 2 H, *J* = 7.5 Hz), 7.46 (t, 4 H, *J* = 7.5 Hz), 3.98 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 194.1, 135.4, 133.5, 128.7, 128.6, 37.6 ppm. Spectroscopic data are in accordance with those previously reported.[3]

Synthesis of sulphide 5n.



To a stirring solution of phenylmethanethiol (4g, 0.032 mol) in THF, (60 mL), K_2CO_3 (8.83g, 0.064 mol) was added. After 30 min. ethyl 2-Chloro-2-methylpropanoate (7.2g, 0.048 mol) was added dropwise in 20 mL of dry THF and the reaction was warmed up to reflux for 14h. The resulting reaction mixture was cooled to room temperature and filtered. The organic phase was washed with brine. Once dried on Na_2SO_4, the solution was concentrated under reduced pressure to afford a yellow oil. Pure sulphide **5n** was obtained by flash column chromatography (silica gel, 80:20 hexane/ether) in 58% yield (4.4 g). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.30-7.29 (m, 5 H), 4.21-4.08 (m, 2 H), 3.86 (dd, 1 H, *J* = 1.2 Hz, *J* = 12.8 Hz), 3.67 (dd, 1H, *J* = 1.2 Hz, *J* = 12.8 Hz), 1.55 (d, 3H, *J* = 1.6 Hz), 1.53 (d, 3H, *J* = 1.6 Hz), 1.26 (dt, 3H, *J* = 1.6, 6.8 Hz) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.1, 131.0, 130.3, 129.9, 128.7, 128.1, 61.7, 55.1, 21.5, 15.7, 14.0 ppm. Spectroscopic data are in accordance with those previously reported.[4]

Synthesis of sulphide 5s.

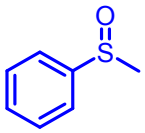


To a stirring solution of 2-Methyl-benzenethiol (5g, 0.040 mol) in MeOH, (50 mL), air was doubled for 4 days at room temperature. The resulting reaction mixture was concentrated under reduced pressure. Pure sulphide **5s** was obtained by flash column chromatography (silica gel, 95:5-90:10 hexane/ether) in 42% yield (2.08 g). FTIR (KBr) cm^{-1} ν: 3007, 2989, 2884, 1102, 1023. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.50 (t, 2 H, *J* = 6.0 Hz), 7.14-7.10 (m, 6 H), 2.41 (s, 6 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 137.4, 135.4, 130.4, 128.7, 127.3, 126.6, 19.9 ppm. Ms *e/z*:(M^+246, (68%), 211 (10%), 123 (100%), 77 (33%), 45 (80%).

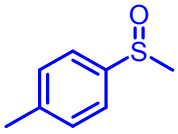
1.3 Synthesis of sulfoxides 6a-6t.

General procedure for the synthesis of sulfoxides 6a-6t

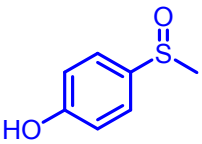
To a 0.3 M solution of sulphide **5a** and tetrazole **2a** (5 mol. %) in CH_2Cl_2 (3.0 mL), *t*BuOOH (5.5 M in decane 1.1 eq.) was added in one injection and the resulting mixture was stirred at room temperature and followed by Gc-Ms until completion (6/7 ratio >99: <1). The reaction mixture was filtered and the filtrate was washed two times with 5 mL of CH_2Cl_2. The organic phase was concentrated under reduced pressure. Pure sulfoxide **6a** was obtained by flash column chromatography (silica gel, 90:10 hexane/ether) in 92% yield.



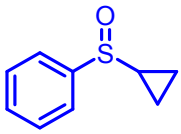
Sulfoxide 6a Colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.62-7.60 (m, 2 H), 7.48-7.46 (m, 3 H), 2.68 (s, 3 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 145.6, 130.8, 129.2, 123.3, 43.8 ppm. Ms *e/z*:(M^+140, (100%), 125 (98%), 97 (60%), 77 (50%), 51 (35%). Spectroscopic data are in accordance with those previously reported.[5]



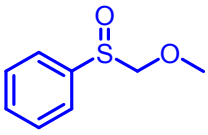
Sulfoxide 6b. Colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.36 (d, 2 H, *J* = 8.5 Hz), 7.14 (d, 2 H *J* = 8.5 Hz), 2.51 (s, 3 H), 2.22 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 142.1, 140.0, 129.4, 122.9, 43.4, 20.8 ppm. Ms *e/z*: (M^+154, (64%), 139 (100%), 111 (8%), 91 (30%), 30 (24%), 63 (15%). Spectroscopic data are in accordance with those previously reported.[6]



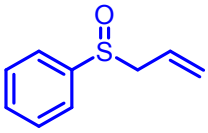
Sulfoxide 6c. White solid. FTIR (KBr) cm^{-1} ν: 3415, 3060, 2905, 2331, 1574, 1555, 1471, 1444, 1306, 1021, 790. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.50 (d, 2 H, *J* = 8.5 Hz),7.97 (d, 2 H, *J* = 8.5 Hz), 2.75 (s, 3 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 160.6, 133.1, 126.0, 116.8, 42.9 ppm. Ms *e/z*:(M^+156, (31%), 141 (100%), 125 (10%), 109 (10%), 85 (9%), 65 (11%). Spectroscopic data are in accordance with those previously reported.[6]



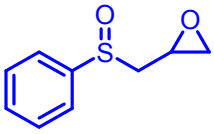
Sulfoxide 6d. Colourless oil. FTIR (KBr) cm^{-1} ν: 3056, 3007, 2872, 1478, 1045, 1022, 790, 750. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.64 (t, 2 H, *J* = 7.5 Hz), 7.50-7.46 (m, 3 H), 2.23 (ddd, 1 H, *J* = 5 Hz, *J* = 8 Hz, 13 Hz), 1.20 (dt, 1H, *J* = 5 Hz, *J* = 15 Hz), 1.03-0.99 (m, 1H), 0.98-0.93 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 144.7, 130.6, 128.9, 123.7, 33.5, 3.1, 2.4 ppm. Ms *e/z*:(M^+166, (10%), 150 (22%), 135 (28%), 125 (100%), 117 (53%), 109 (35%), 77 (41%), 65 (33%), 62 (65%). Spectroscopic data are in accordance with those previously reported.[7]



Sulfoxide 6e. White solid. FTIR (KBr) cm^{-1} ν: 3057, 2943, 2892, 2830, 1444, 1189, 1110, 1040, 752. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.65-7.62 (m, 2 H), 7.54-7.51 (m, 3 H), 4.39 (AB q, 2H, *J* = 10 Hz), 3.65 (s, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.6, 131.0, 128.9, 124.0, 93.9, 60.57 ppm. Ms *e/z*:(M^+) 170, (18%), 155 (30%), 138 (61%), 125 (100%), 109 (43%), 77 (47%), 65 (39%), 62 (65%). Spectroscopic data are in accordance with those previously reported.[8]

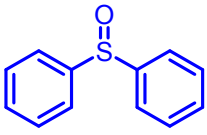


Sulfoxide 6f. Colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.59-7.57 (m, 2 H), 7.51-7.47 (m, 3 H), 5.63 (ddt, 1 H, *J* = 7.5 Hz, *J* = 10 Hz, 17.5 Hz), 5.30 (d, 1H, *J* = 10 Hz), 5.17 (dd, 1H, *J* = 1 Hz, *J* = 17.5 Hz), 3.55 (dd, 1H, *J* = 7.5 Hz, *J* = 13 Hz), 3.48 (dd, 1H, *J* = 7.5 Hz, 13 Hz) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 142.9, 131.0, 128.9, 125.2, 124.2123.7, 60.8 ppm. Ms *e/z*: (M^+) 166, (50%), 149 (10%), 125 (100%), 118 (41%), 97 (40%), 77 (45%), 77 (41%), 41 (58%). Spectroscopic data are in accordance with those previously reported .[9]

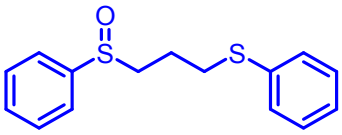


Sulfoxide 6g. Colourless oil (1:1 mixture of diastereoisomers). FTIR (KBr) cm^{-1} ν: 3057, 2999, 2908, 2335, 1477, 1444, 1088, 1037, 848, 749. ^{1}H NMR *syn* (500 MHz, $CDCl_3$) δ: 7.64-7.60 (m, 2 H),7.50-7.47 (m, 3 H), 2.93 (dd, 1 H, *J* = 5 Hz, *J* = 15 Hz), 2.81 (t, 1H. *J* = 4.5 Hz), 2.78 (t, 1H, *J* = 5 Hz), 2.63 (dd, 1H, *J* = 2 Hz, *J* = 5 Hz), 2.50 (dd, 1H, *J* = 2.5 Hz, *J* = 4.5 Hz) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 142.6, 131.2, 129.2, 123.7, 58.7, 46.2, 45.3 ppm. Ms *e/z*:(M^+182, (10%), 164 (61%), 166 (18%), 125 (100%), 109 (50%), 77 (46%), 57 (21%).

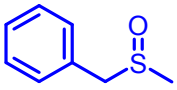
^{1}H NMR *anti* (500 MHz, $CDCl_3$) δ: 7.64-7.60 (m, 2 H),7.50-7.47 (m, 3 H), 3.32 (ddt, 1 H, *J* = 2.5 Hz, *J* = 4 Hz, *J* = 7 Hz), 3.07-3.02 (m, 2H), 2.86 (dd, 1H, *J* = 7 Hz, *J* = 13.5 Hz), 2.96 (dd, 1H, *J* = 7 Hz, *J* = 18.5 Hz) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 143.4, 131.2, 129.2, 123.9, 60.8, 46.9, 46.0 ppm. Ms *e/z*:(M^+182, (12%), 164 (58%), 165 (24%), 125 (100%), 109 (57%), 77 (40%), 57 (27%). Spectroscopic data are in accordance with those previously reported.[10]



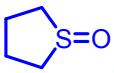
Sulfoxide 6h. White solid. FTIR (KBr) cm^{-1} ν: 3057, 1475, 1091, 1048, 910. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.64 (dd, 4H, *J* = 1.5 Hz, *J* = 8 Hz), 7.44-7.40 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 145.4, 130.8, 129.1, 124.5 ppm. Ms *e/z*: (M^+202, (100%), 185 (21%), 173 (32%), 154 (70%), 125 (13%), 109 (60%), 77 (35%), 51 (33%).



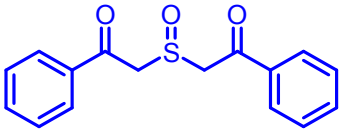
Sulfoxide 6i. Colourless oil. FTIR (KBr) cm^{-1} ν: 3056, 2938, 2866, 1582, 1479, 1441, 1303, 1255, 1086, 1044, 997. ^1H NMR (500 MHz, $CDCl_3$) δ: 7.49 (d, 1H, *J* = 2.5 Hz); 7.47 (d, 1H, *J* = 2.0 Hz), 7.42-7.38 (m, 3H), 7.20-7.17 (m, 2H), 7.16-7.15 (m, 2H), 7.10-7.07 (m, 1H), 2.93-2.87 (m, 1H), 2.91 (t, 2H, *J* = 7 Hz), 2.77 (ddd, 1H, *J* = 5 Hz, *J* = 9 Hz, *J* = 18.5Hz), 2.01 8m, 1H), 1.82 (m, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 143.4, 135.1, 130.8, 129.8, 129.1, 128.8, 126.3, 123.8, 55.2, 32.8, 21.5 ppm. Ms *e/z*: (M^+) 276 (38%), 170 (60%), 167 (51%), 109 (100%), 77 (70%). Spectroscopic data are in accordance with those previously reported.[5]



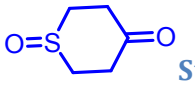
Sulfoxide 6j. Colourless oil. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.35−7.23 (m, 5H), 4.00 (d, 1H, *J* = 12.8 Hz), 3.88 (d, 1H, *J* = 12.8 Hz), 2.41 (s, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 130.1, 129.7, 128.9, 128.5, 60.3, 37.3 ppm. Ms *e/z*:(M^+154, (6%), 138 (6%), 121 (8%), 91 (100%), 65 (23%), 51 (15%). Spectroscopic data are in accordance with those previously reported.[11]



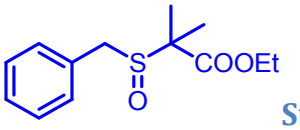
Sulfoxide 6k. Colourless oil. ^1H NMR (400 MHz, $CDCl_3$) δ: 2.93-2.84 (m, 4H), 2.61-2.40 (m, 2H), 2.23-2.02 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 53.7, 24.6 ppm. Ms *e/z*:(M^+104, (100%), 88 (22%), 76 (57%), 62 (41%).



Sulfoxide 6l. White solid. ^1H NMR (500 MHz, $CDCl_3$) δ: 7.97 (t, 4H, *J* = 8 Hz), 7.62 (t, 2H, *J* = 7.5 Hz), 7.5 (m, 4H), 4.76 (d, 2H, *J* = 15 Hz), 4.43 (d, 2H, *J* = 15 Hz) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 192.3, 136.1, 134.3, 128.8, 59.3 ppm. Ms *e/z*: (M^+) 286 (51%), 181 (64%), 119 (43%), 105 (100%), 77 (65%). Spectroscopic data are in accordance with those previously reported.[12]

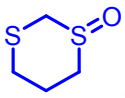


Sulfoxide 6m. White solid. FTIR (KBr) cm^{-1} ν: 2981, 2683, 1725, 1658, 1462, 1325, 1217, 1067, 928. ^1H NMR (500 MHz, $CDCl_3$) δ: 3.34-3.25 (m, 4H), 2.87 (dt, 2H, *J* = 6 Hz, *J* = 13 Hz), 2.53-2.48 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 114.6, 47.2, 32.1 ppm. Ms *e/z*:(M^+132, (5%), 104 (60%), 76 (8%), 55 (100%). Spectroscopic data are in accordance with those previously reported.[13]

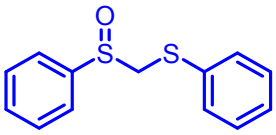


Sulfoxide 6n. Yellow oil. FTIR (KBr) cm^{-1} ν: 3031, 2981, 2936, 1732, 1556, 1446, 1271, 1050, 1039. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.34-7.30 (m, 5H), 4.17 (ddq, 2H, *J* = 3.6 Hz, *J* = 7.2 Hz, *J* = 22.4 Hz), 3.80 (ABq, 2H, *J* = 12.8 Hz), 1.58 (s, 3H), 1.56 (s, 3H), 1.29 (t, 3H, *J* = 7.2 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.1, 131.0, 129.9, 128.7, 128.1, 62.6, 61.7, 55.1, 21.5, 15.7, 14.0 ppm. Ms *e/z*: (M^+) 254 (23%), 239 (10%), 225 (68%), 209 (43%), 181 (84%), 162 (52%), 123

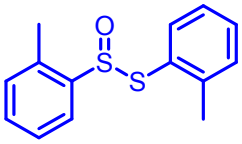
(30%), 91 (100%), 77 (48%). Anal. Calcd for $C_{13}H_{18}O_3S$: C, 61.39; H, 7.13; S, 12.61. Found: C, 61.14; H, 7.11; S, 12.57.



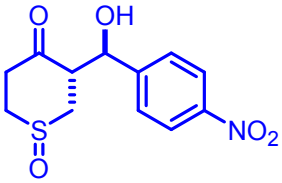
Sulfoxide 6o. White solid. FTIR (KBr) cm^{-1} ν: 2954, 2901, 2837, 2216, 1642, 1427, 1275, 1017, 919. ^1H NMR (500 MHz, $CDCl_3$) δ: 3.98 (dd, 1H, *J* = 1.5 Hz, *J* = 12.5 Hz), 3.63 (d, 1H, *J* = 12.5 Hz), 3.30 (ddd, 1H, *J* = 3 Hz, *J* = 6 Hz, 13 Hz), 2.60 (ddt, 2H, *J* = 2.5 Hz, *J* = 18.5 Hz, *J* = 25.5 Hz), 2.54-2.46 (m, 2H), 2.21-2.13 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ: 52.9, 50.4, 28.2, 27.0 ppm. Ms *e/z*:(M^+136, (100%), 119 (12%), 106 (51%), 90 (64%), 73 (43%), 60 (37%), 45 (96%), 41 (80%). Spectroscopic data are in accordance with those previously reported.[14]



Sulfoxide 6p. Colourless liquid. FTIR (KBr) cm^{-1} ν: 3055, 2974, 2934, 2387, 1581, 1548, 1479, 1178, 1084, 1046, 743. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.70-7.68 (m, 2H), 7.49-7.48 (m, 3H), 7.44-7.43 (m, 2H), 7.30-7.25 (m, 3H), 4.13 (ABq, 2H, *J* = 13.6 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.6, 133.4, 131.5, 130.8, 129.1, 129.0, 127.6, 124.7, 60.8 ppm. Ms *e/z*: (M^+) 246 (70%), 155 (38%), 137 (32%), 124 (100%), 109 (90%), 77 (53%). Spectroscopic data are in accordance with those previously reported.[14]



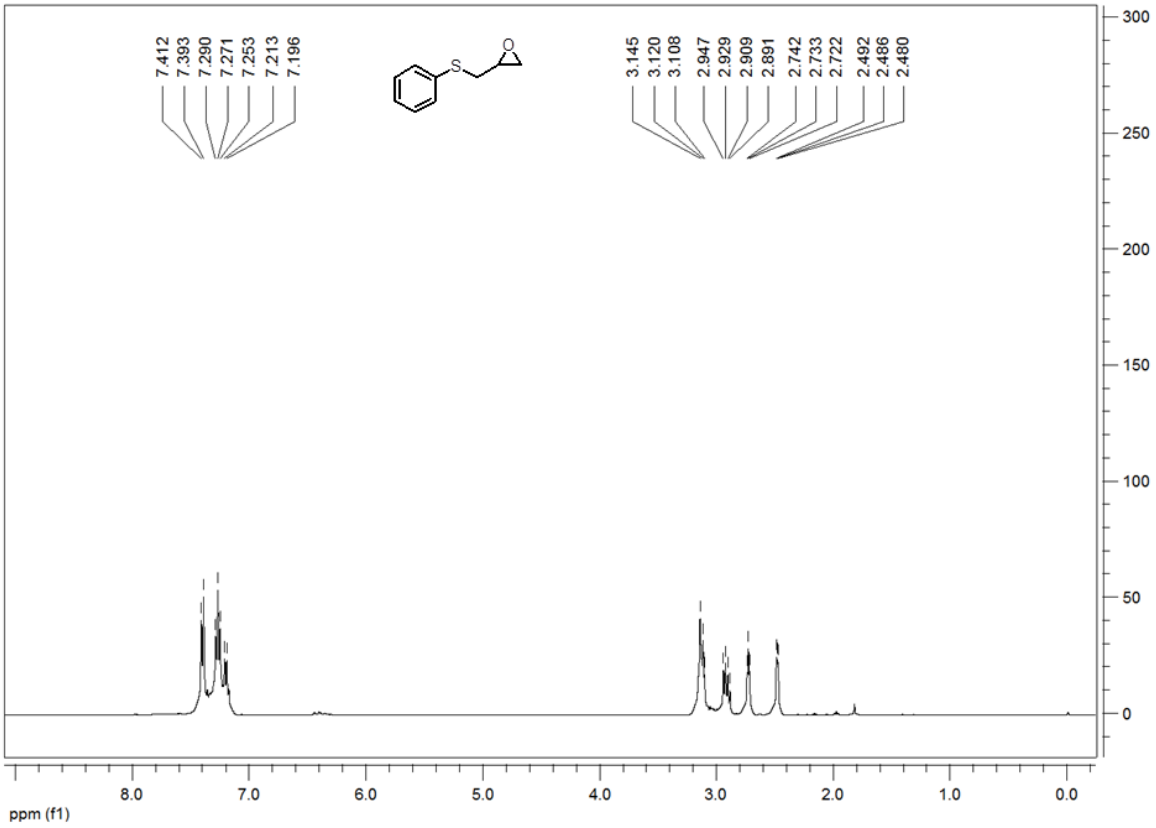
Sulfoxide 6s. deliquescent yellow solid. FTIR (KBr) cm^{-1} ν: 3008, 2975, 2865, 1459, 1184, 1069, 911. ^1H NMR (500 MHz, $CDCl_3$) δ: 7.74 (dd, 1H, *J* = 1.5 Hz, *J* = 8 Hz), 7.56 (dd, 1H, *J* = 1.0 Hz, *J* = 8.0 Hz), 7.38 (dd, 1H, 1.5 Hz, *J* = 7.5 Hz), 7.34 (d, 1H, *J* = 1.0 Hz), 7.33-7.32 (m, 1H), 7.32-7.31 (m, 1H), 7.30-7.20 (m, 2H), 2.51 (s, 3H), 2.37 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 143.0, 138.3, 137.0, 134.1, 132.8, 131.4, 130.6, 130.2, 128.7, 126.7, 125.8, 124.2, 21.1, 18.2 ppm. Ms *e/z*:(M^+) 262, (18%), 139 (100%), 123 (31%), 91 (40%), 65 (13%). Anal. Calcd for $C_{14}H_{14}OS_2$: C, 64.08; H, 5.38; S, 24.44. Found: C, 63.99; H, 5.37; S, 24.46.

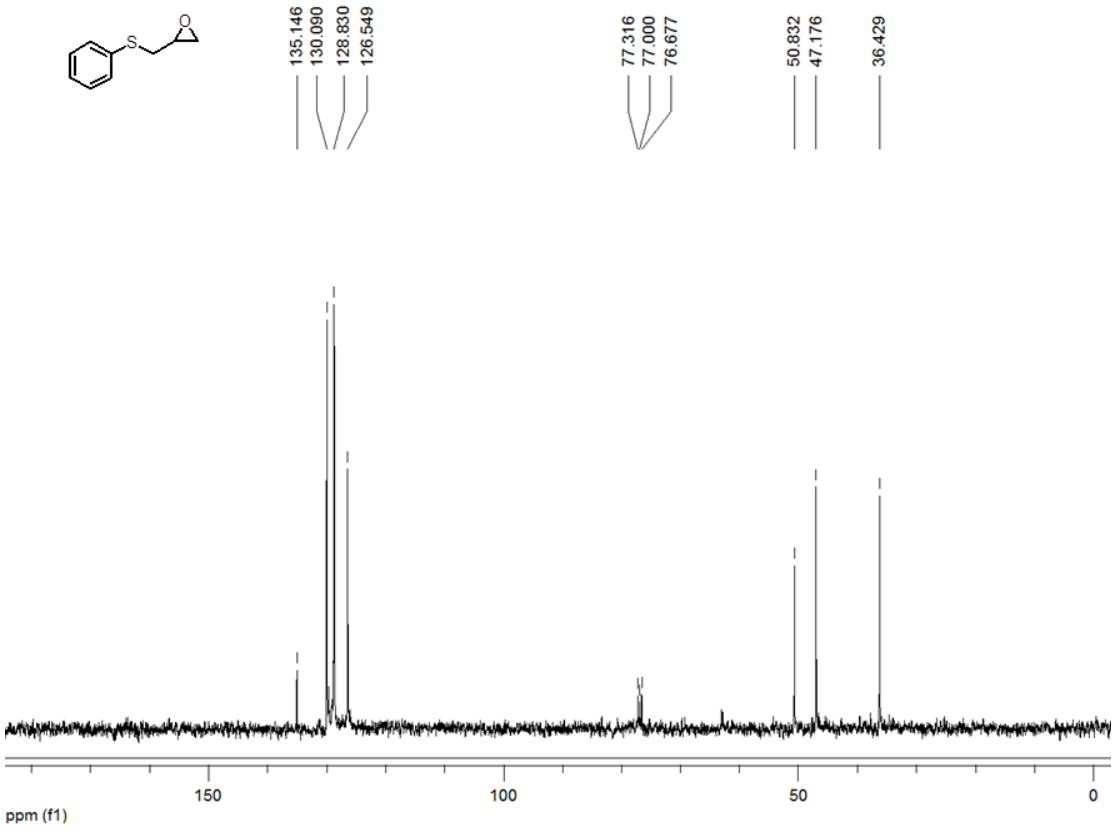


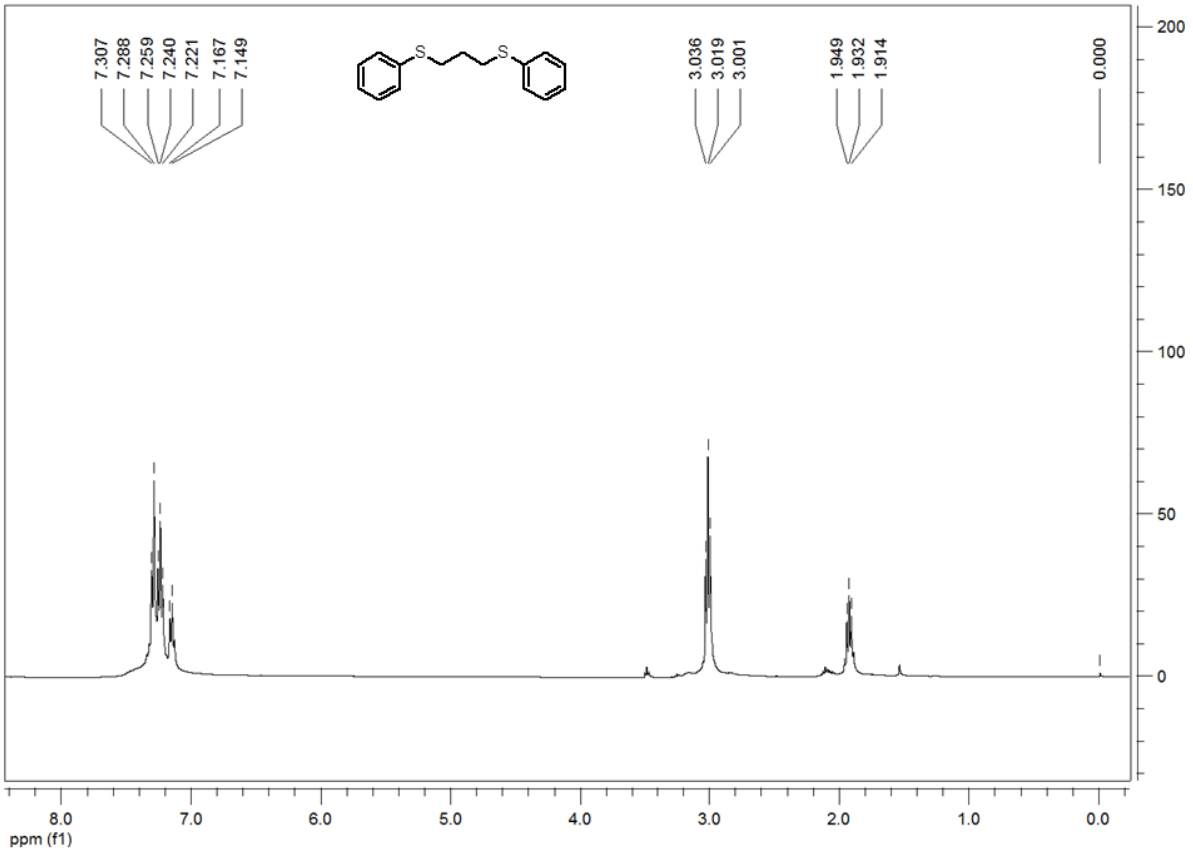
Sulfoxide 6t. pale yellow solid. M.p. 81 °C; $[a]^{27.2°C}_D$ = +24 (*conc.* 0.034 in MeOH); FTIR (KBr) cm^{-1} ν: 3507, 1774, 1196, 1067. ^1H NMR (500 MHz, DMSO-d_6) δ: 8.19 (d, 2H, *J* = 8.5 Hz), 8.63 (d, 2H, *J* = 8.5 Hz), 5.88 (d, 1H, 4.5 Hz), 5.34 (t, 1H, *J* = 3.5 Hz), 3.68 (t, 1H, *J* = 13.5 Hz), 3.44-3.40 (m, 1H), 3.24 (m, 2H), 2.96 (t, 1H, J = 5.0 Hz), 2.94-2.85 (m, 1H), 2.72 (t, 1H, *J* = 5.0 Hz), 2.69 (t, 1H, J = 5.5 Hz) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ: 202.5, 151.0, 146.8, 127.5, 123.4, 67.9, 53.3, 48.8, 48.4, 37.8 ppm.

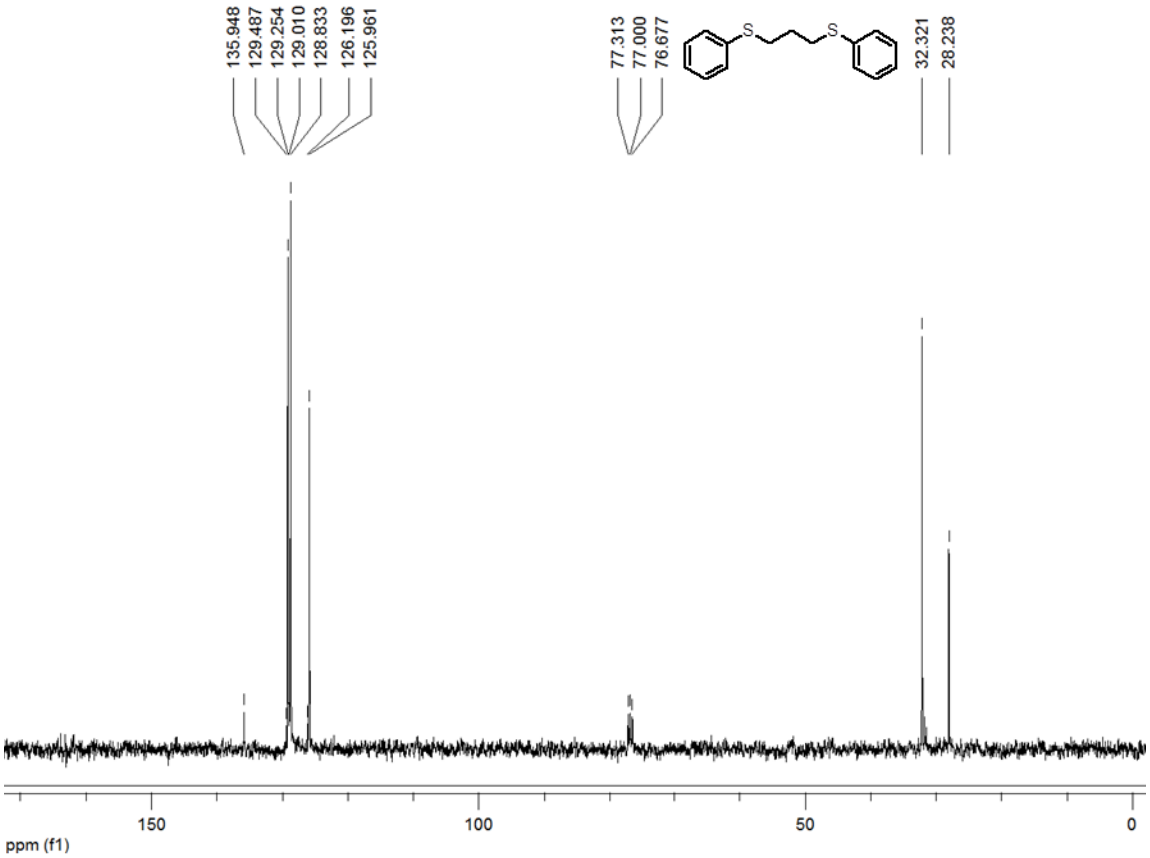
2. Spectroscopic NMR data

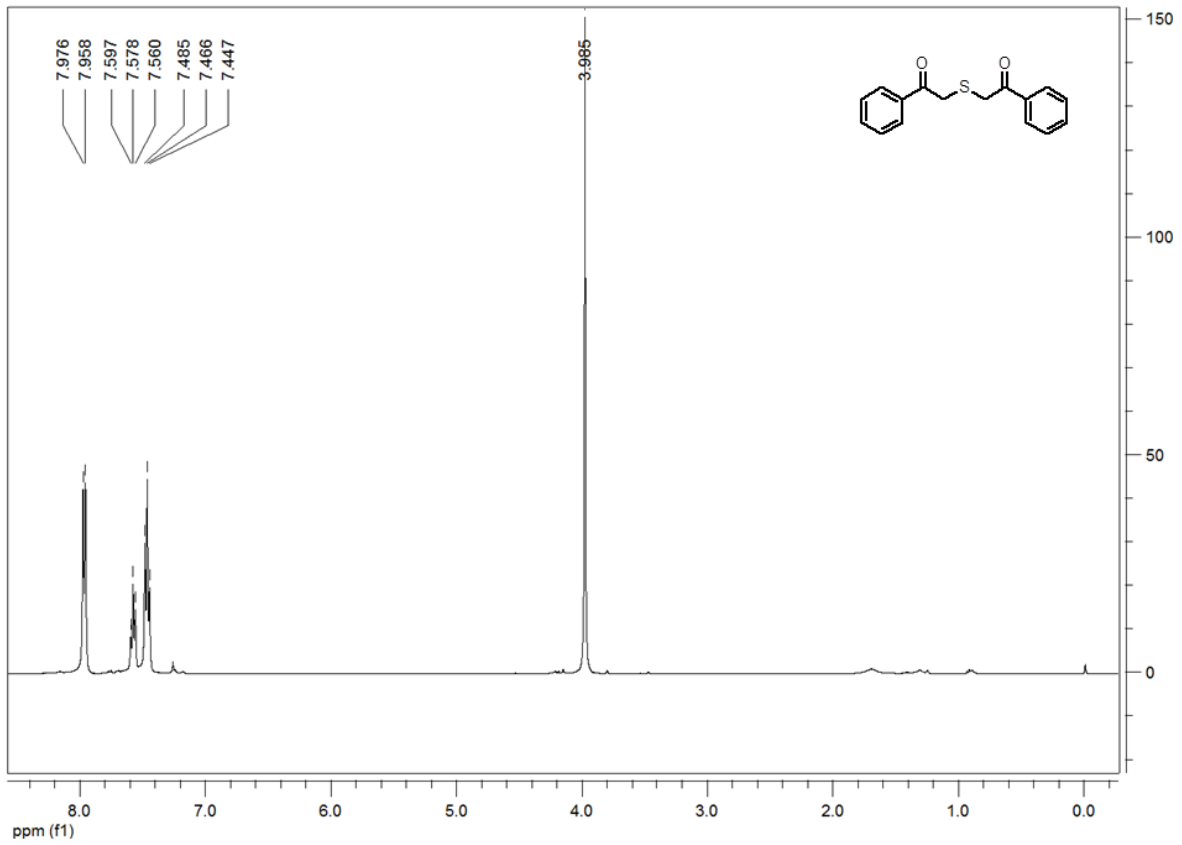
2.1 ^{1}H and ^{13}C NMR spectra data of compound 5g, 5i, 5l, 5n, 5s

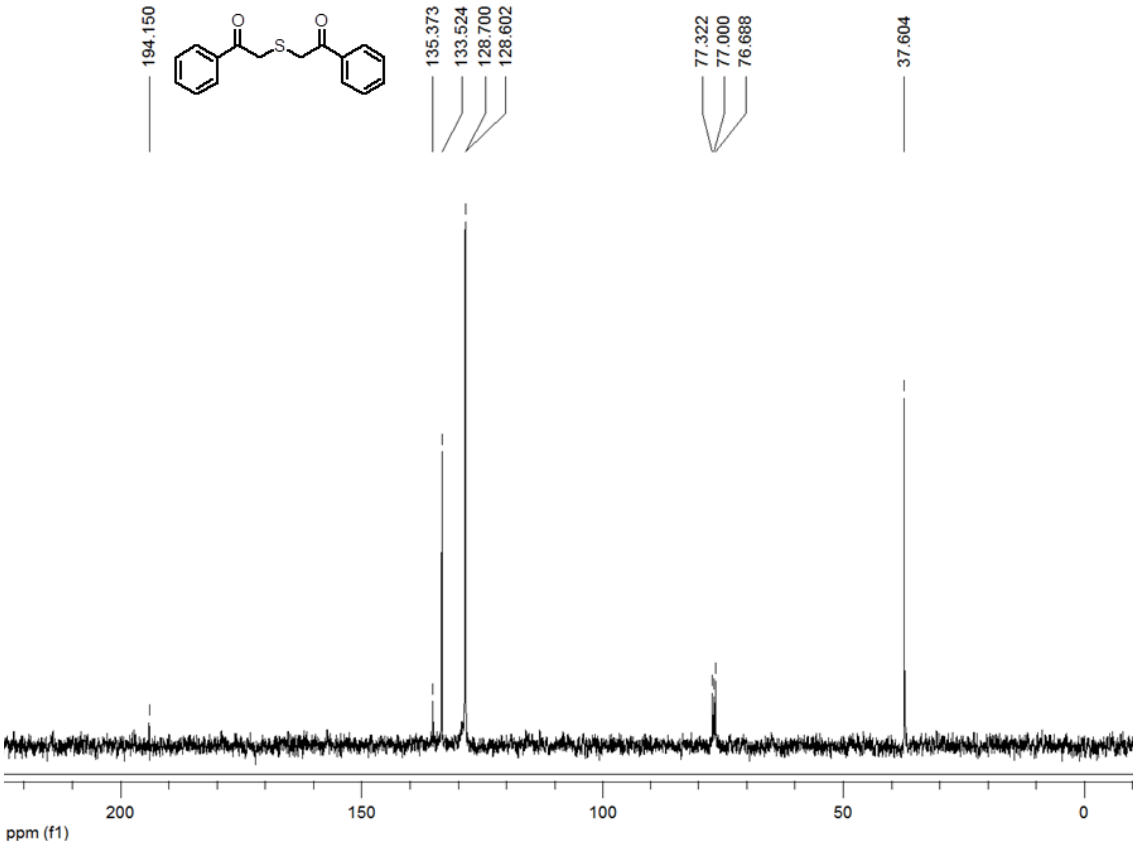


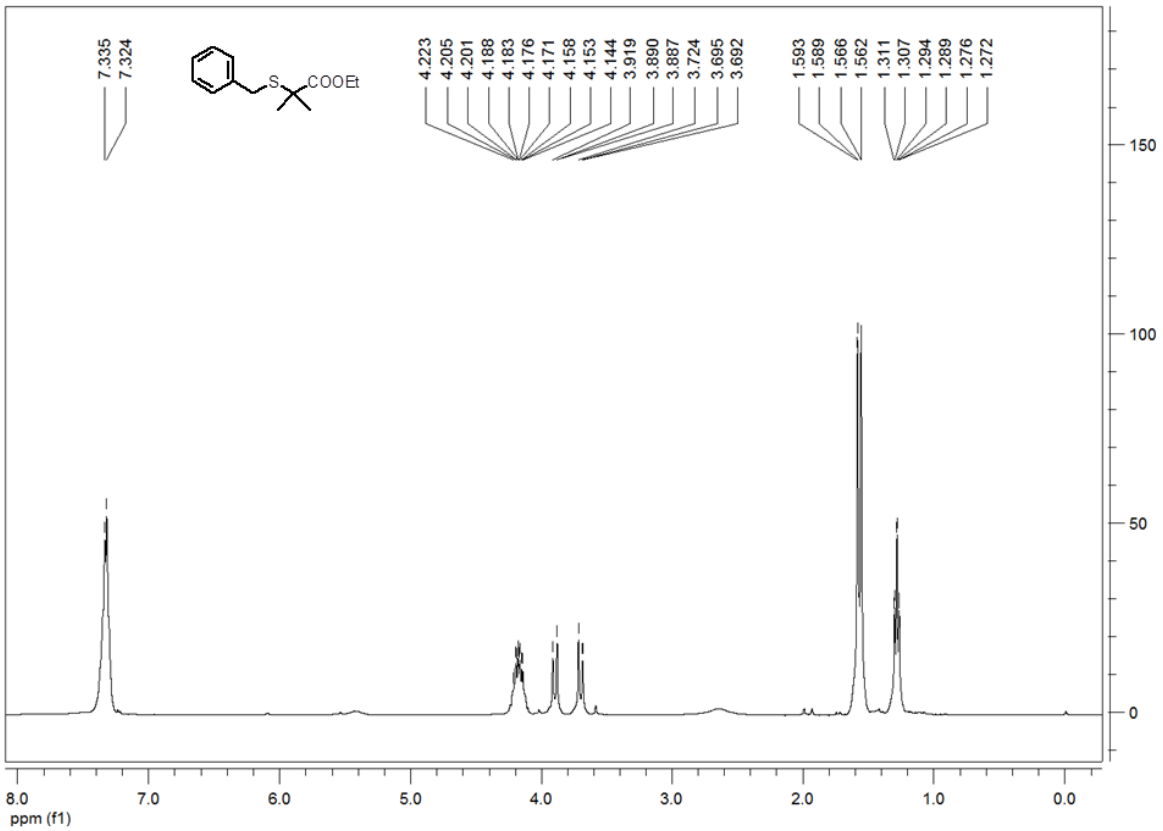


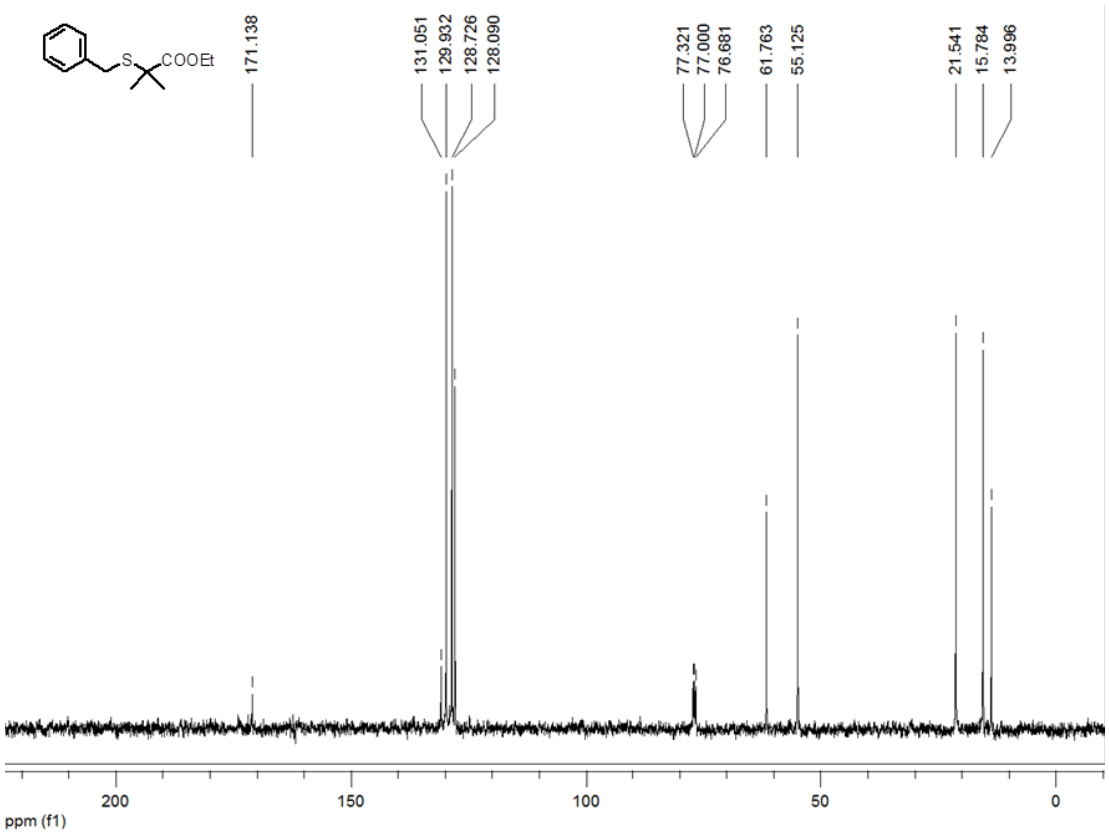

7.307
7.288
7.259
7.240
7.221
7.167
7.149
3.036
3.019
3.001
1.949
1.932
1.914
0.000
200
150
100
50
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

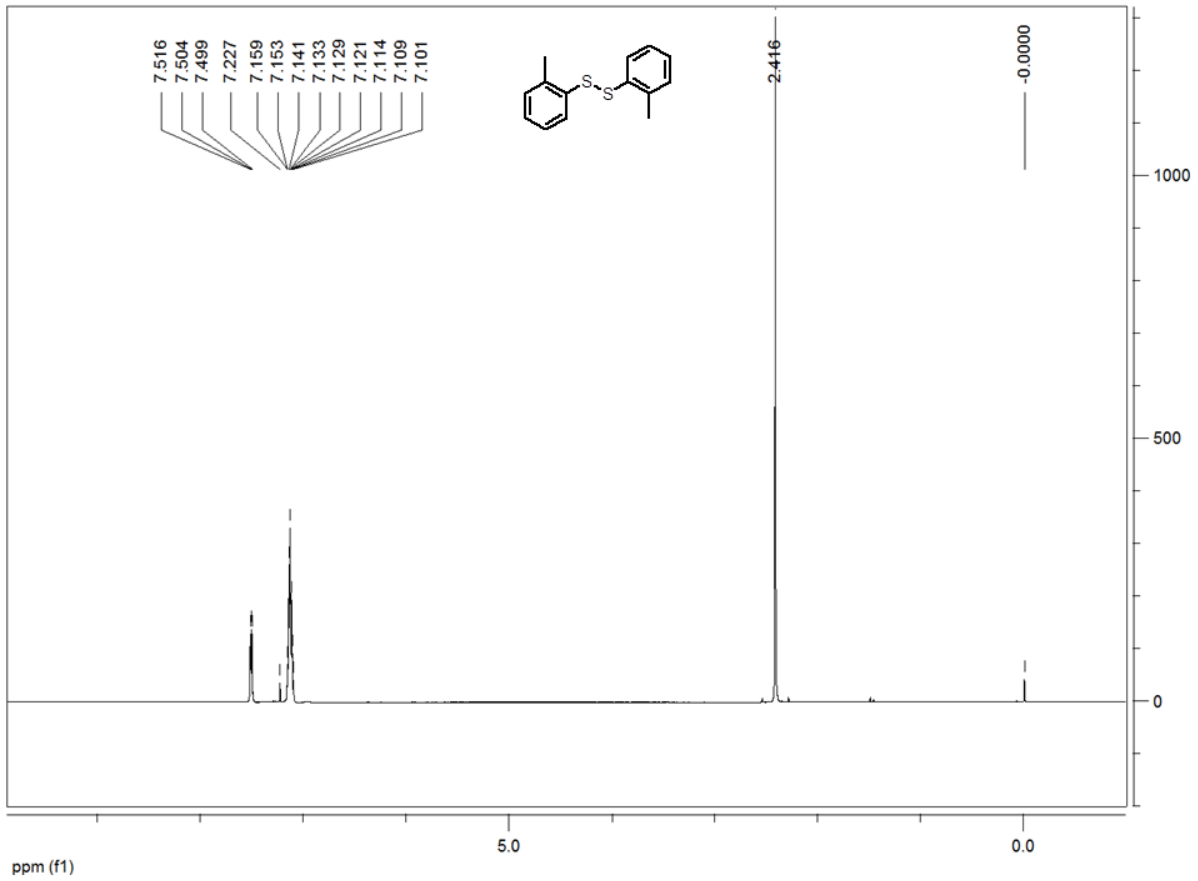

135.948
129.487
129.254
129.010
128.833
126.196
125.961
77.313
77.000
76.677
32.321
28.238
150
100
50
0
ppm (f1)

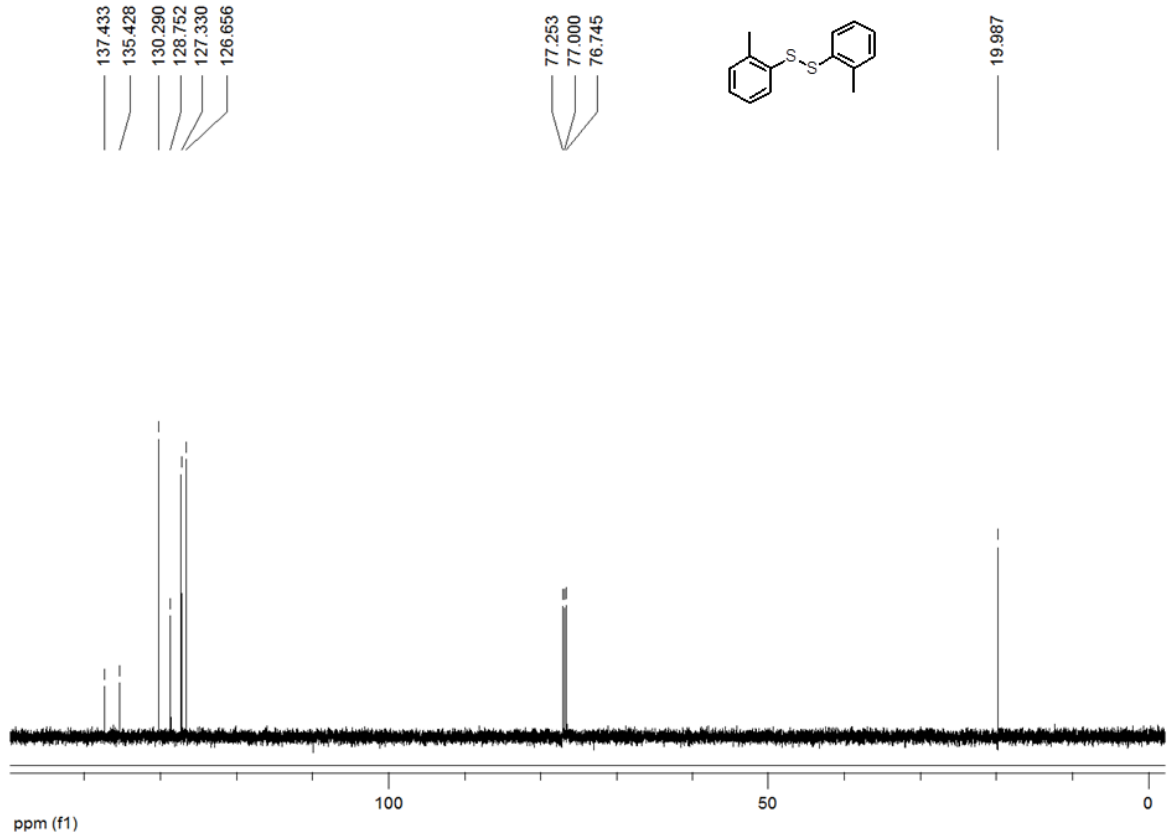

7.976
7.958
7.597
7.578
7.560
7.485
7.466
7.447
3.985
O
S
O
150
100
50
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


194.150
O
S
O
135.373
133.524
128.700
128.602
77.322
77.000
76.688
37.604
200
150
100
50
0
ppm (f1)

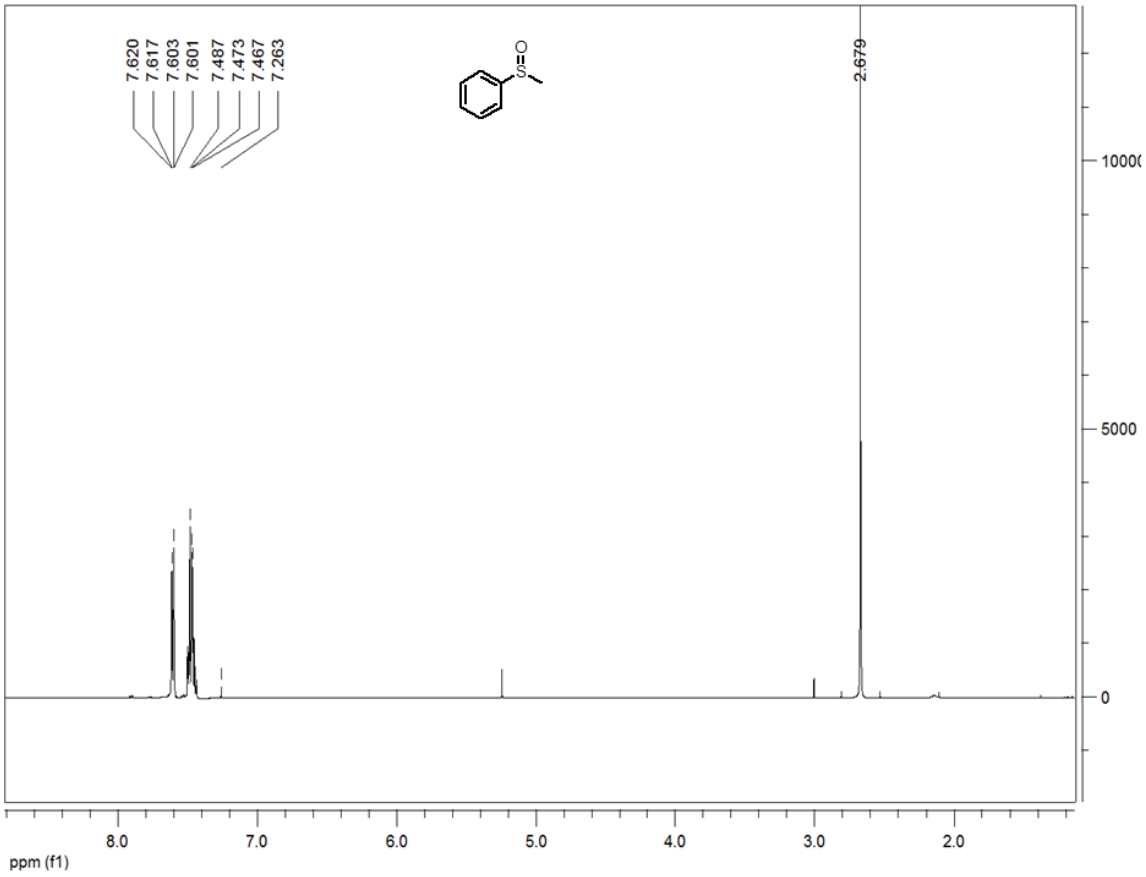

7.335
7.324
S
COOEt
4.223
4.205
4.201
4.188
4.183
4.176
4.171
4.158
4.153
4.144
3.919
3.890
3.887
3.724
3.695
3.692
1.593
1.589
1.566
1.562
1.311
1.307
1.294
1.289
1.276
1.272
150
100
50
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

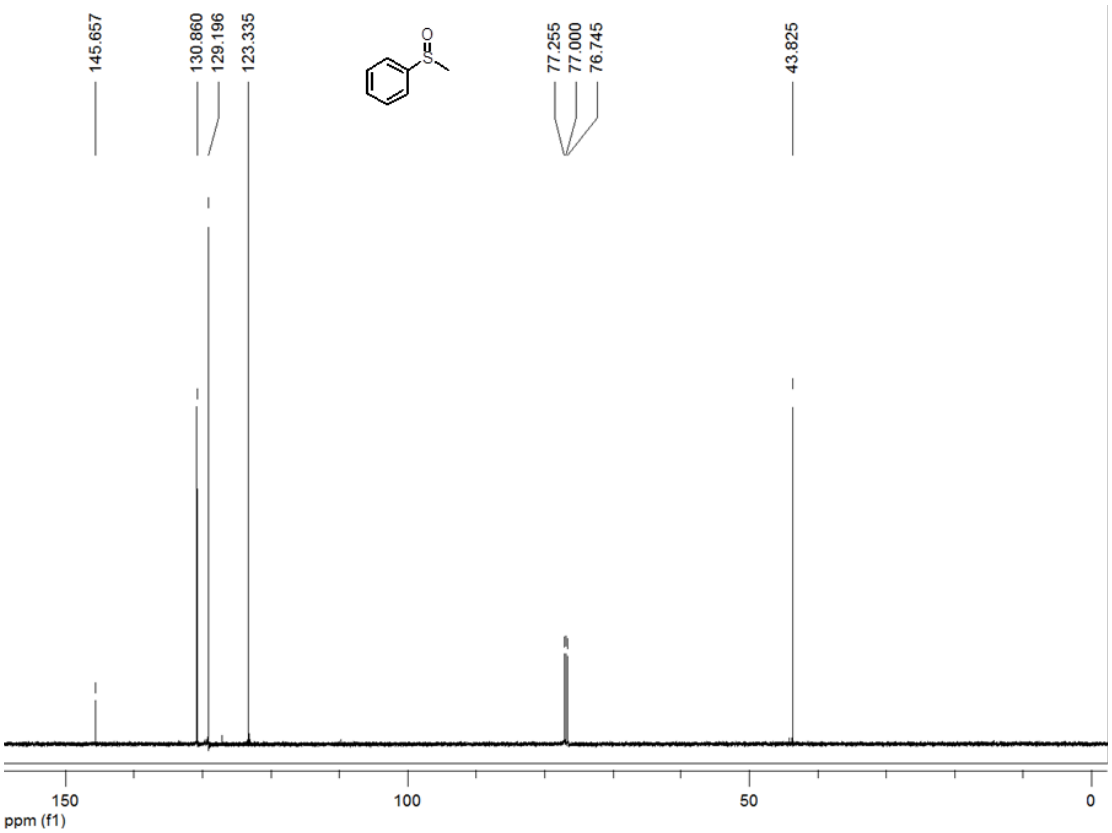

S
COOEt
171.138
131.051
129.932
128.726
128.090
77.321
77.000
76.681
61.763
55.125
21.541
15.784
13.996
200
150
100
50
0
ppm (f1)

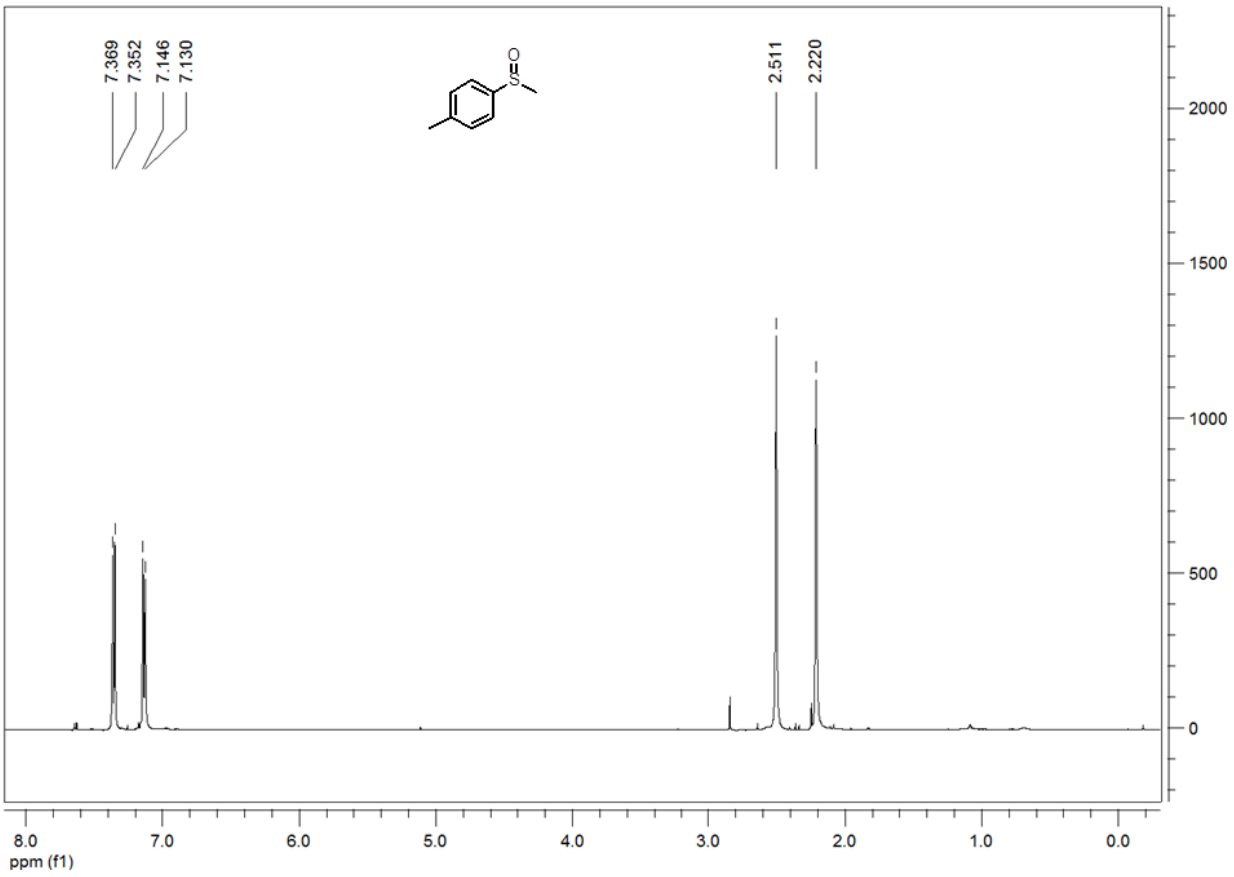

7.516
7.504
7.499
7.227
7.159
7.153
7.141
7.133
7.129
7.121
7.114
7.109
7.101
2.416
-0.0000
1000
500
0
5.0
0.0
ppm (f1)

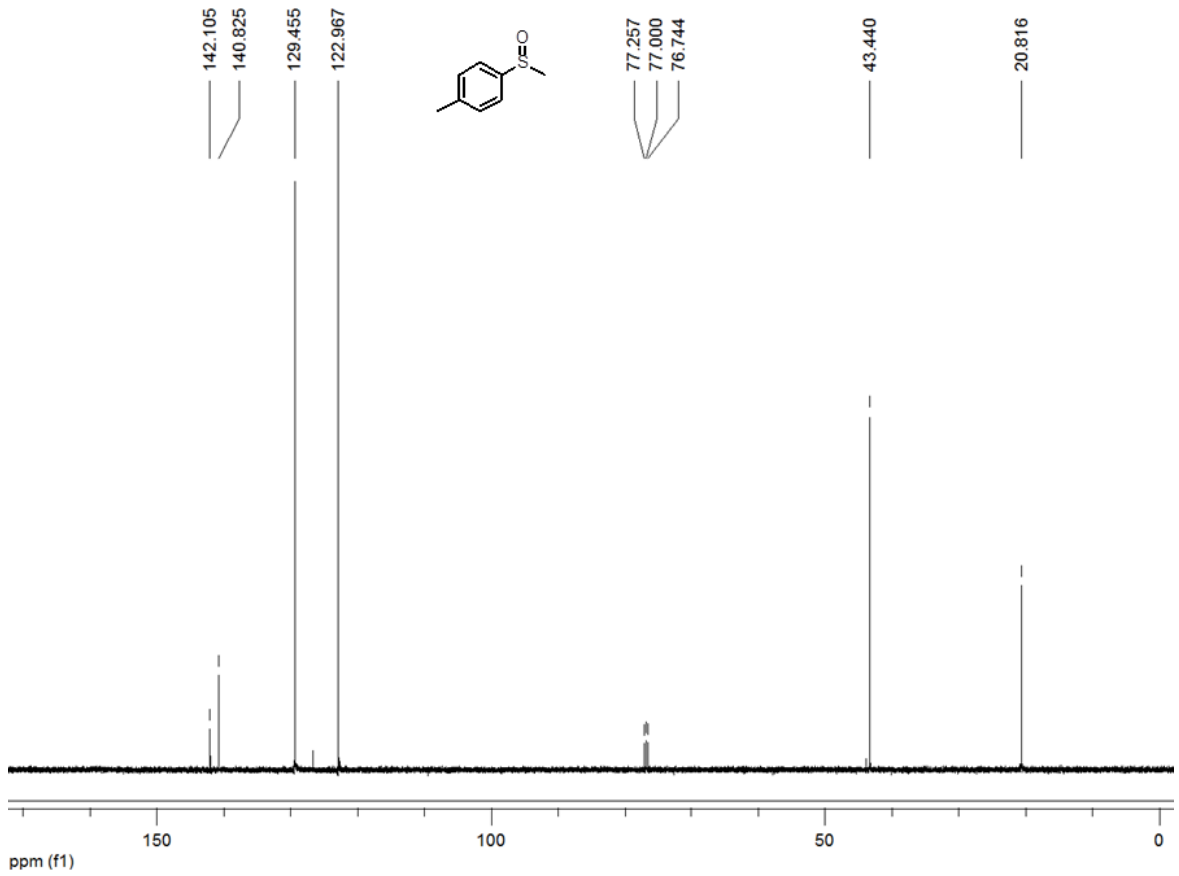

137.433
135.428
130.290
128.752
127.330
126.656
77.253
77.000
76.745
19.987
100
50
0
ppm (f1)

2.2 ^{1}H and ^{13}C NMR spectra data of compound 6a–6p, 6s, 6t






7.369
7.352
7.146
7.130
2.511
2.220
2000
1500
1000
500
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


142.105
140.825
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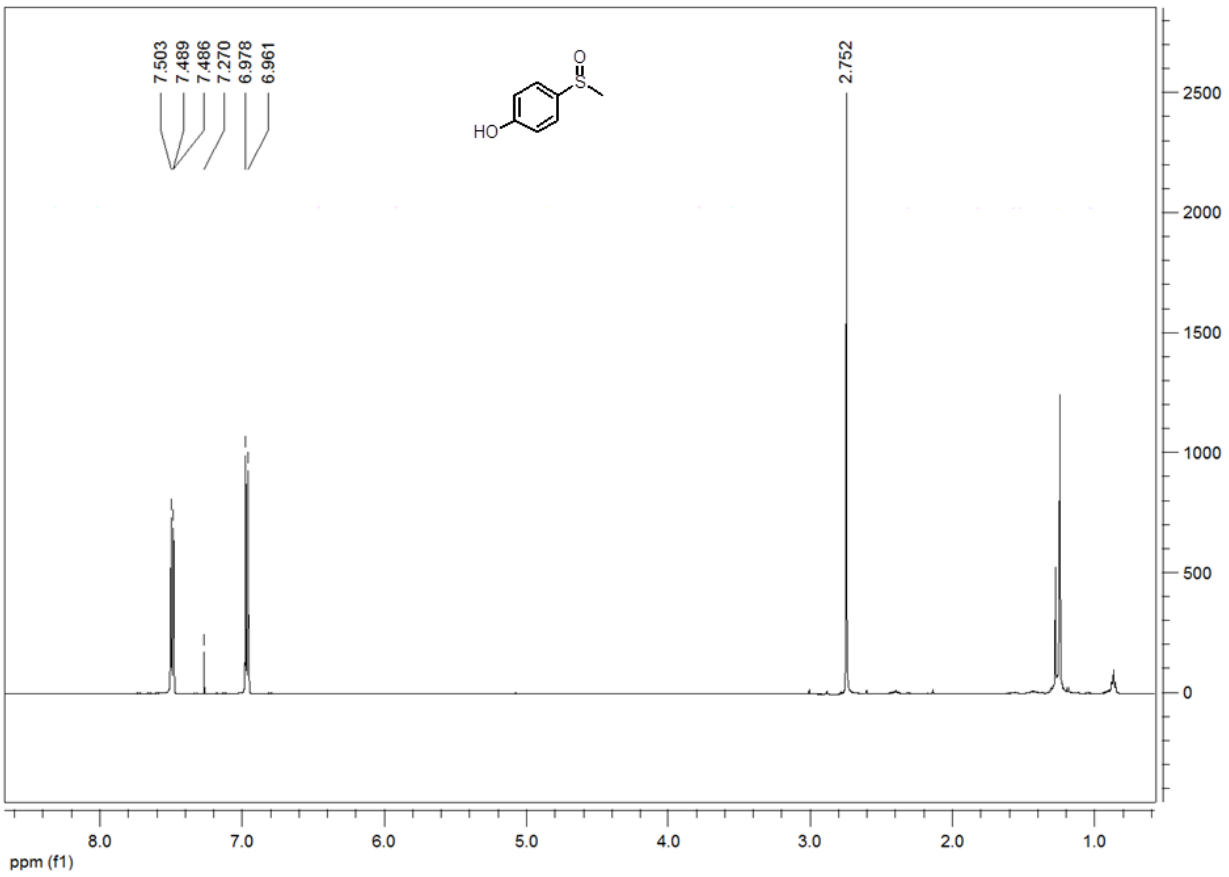
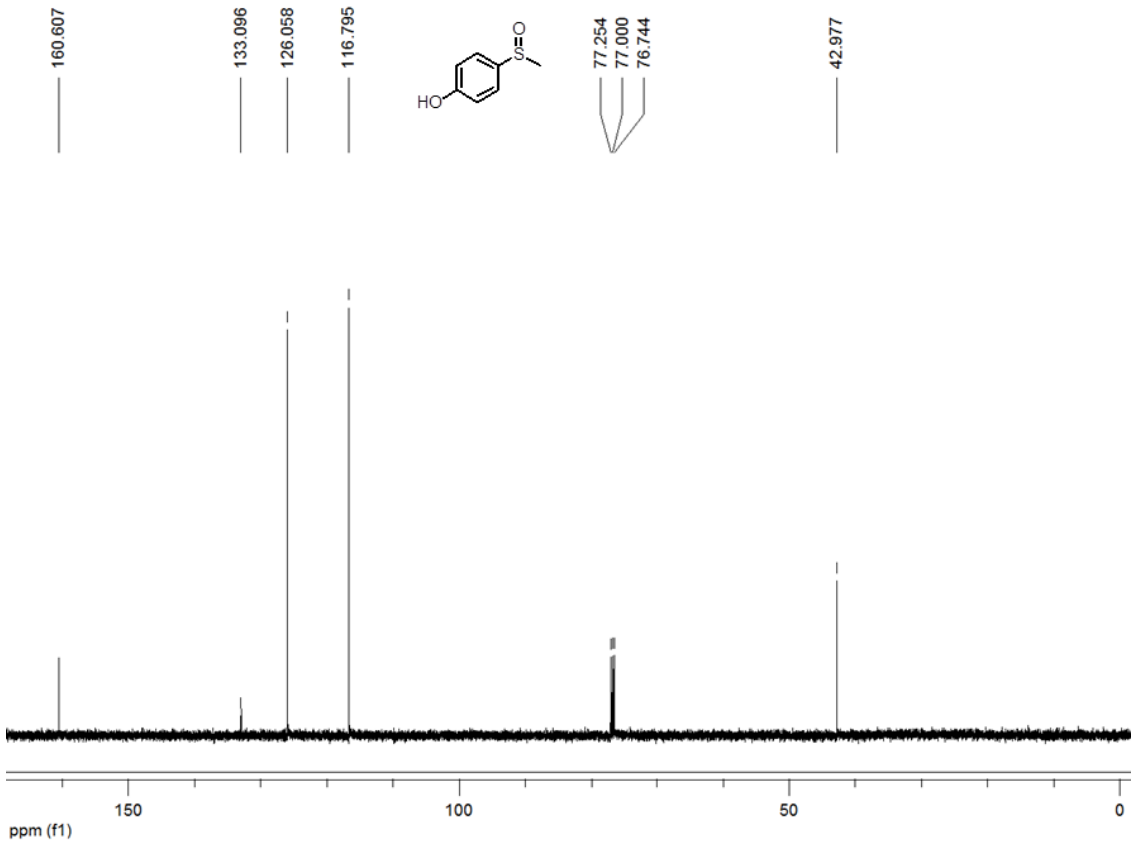
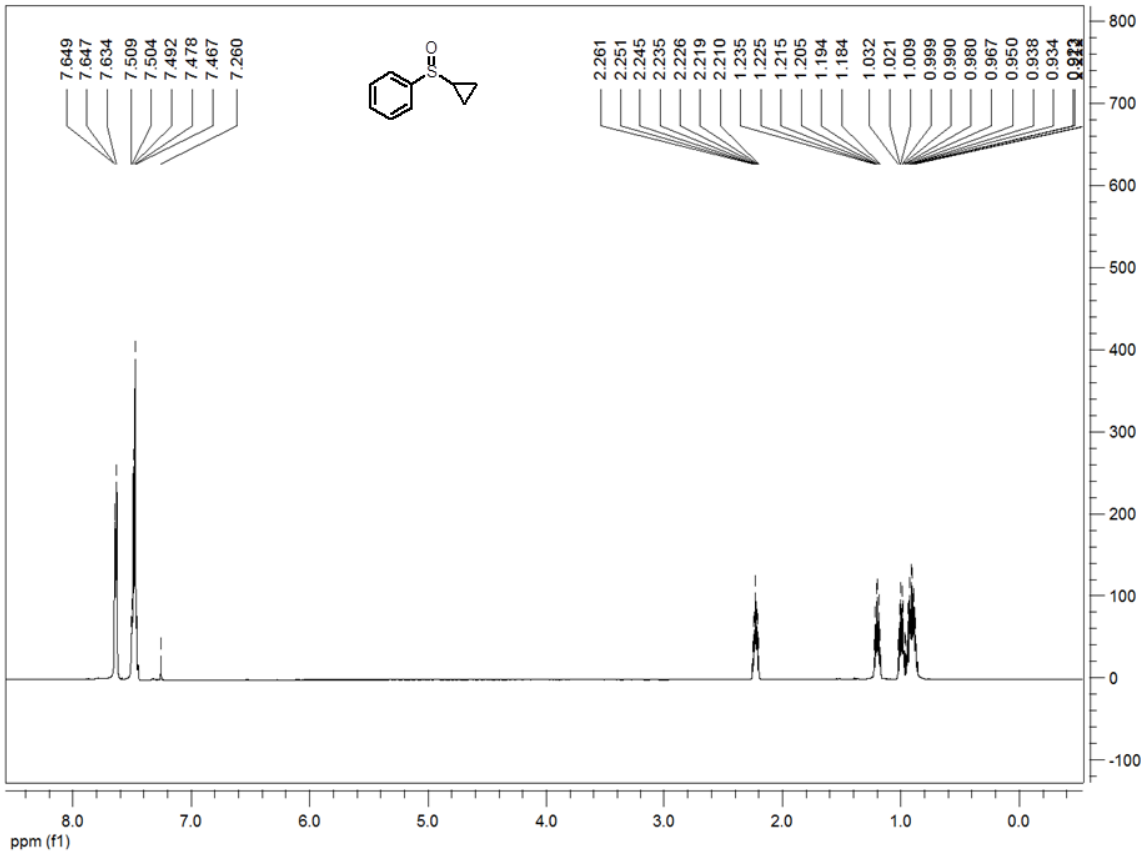
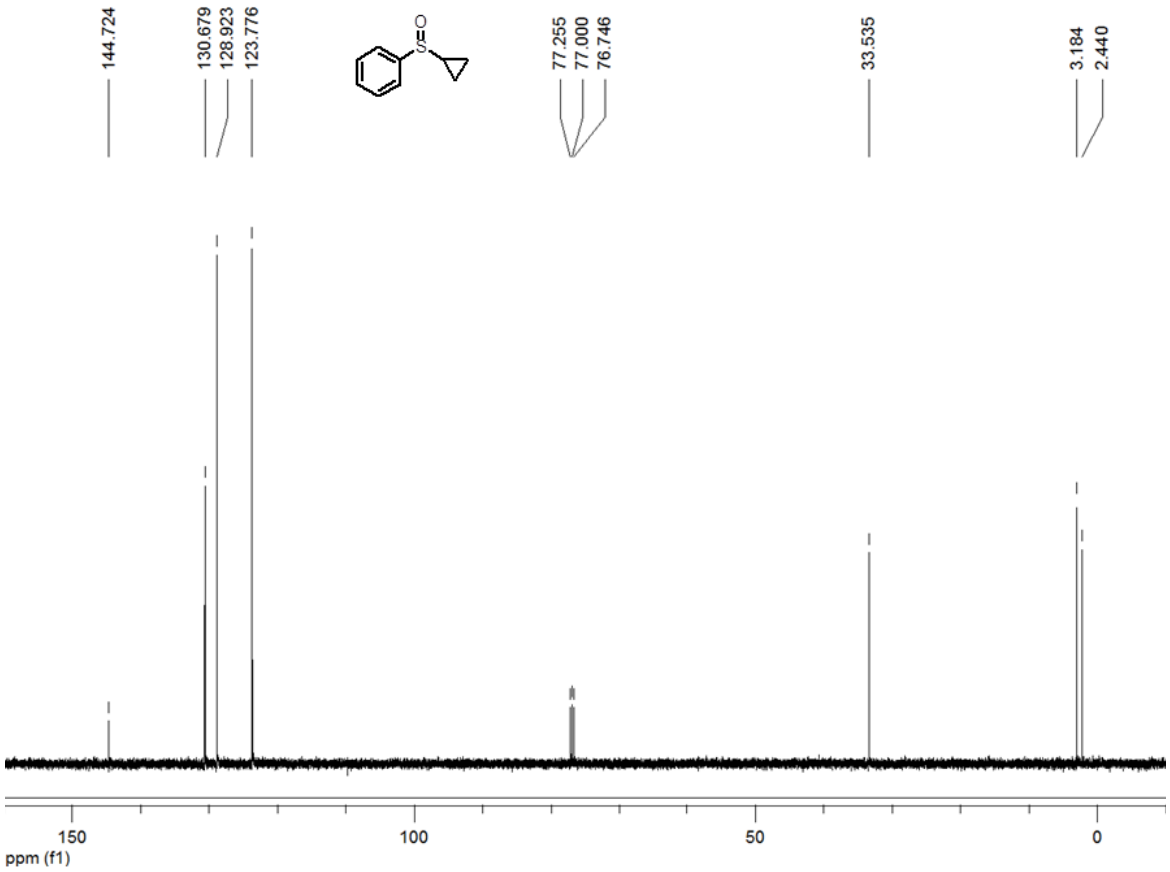
122.967
77.257
77.000
76.744
43.440
20.816
150
100
50
0
ppm (f1)


7.503
7.489
7.486
7.270
6.978
6.961
2.752
HO
O
S
2500
2000
1500
1000
500
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)


160.607
133.096
126.058
116.795
77.254
77.000
76.744
42.977
HO
O
S
150
100
50
0
ppm (f1)


7.649
7.647
7.634
7.509
7.504
7.492
7.478
7.467
7.260
2.261
2.251
2.245
2.235
2.226
2.219
2.210
1.235
1.225
1.215
1.205
1.194
1.184
1.032
1.021
1.009
0.999
0.990
0.980
0.967
0.950
0.938
0.934
800
700
600
500
400
300
200
100
0
-100
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)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50
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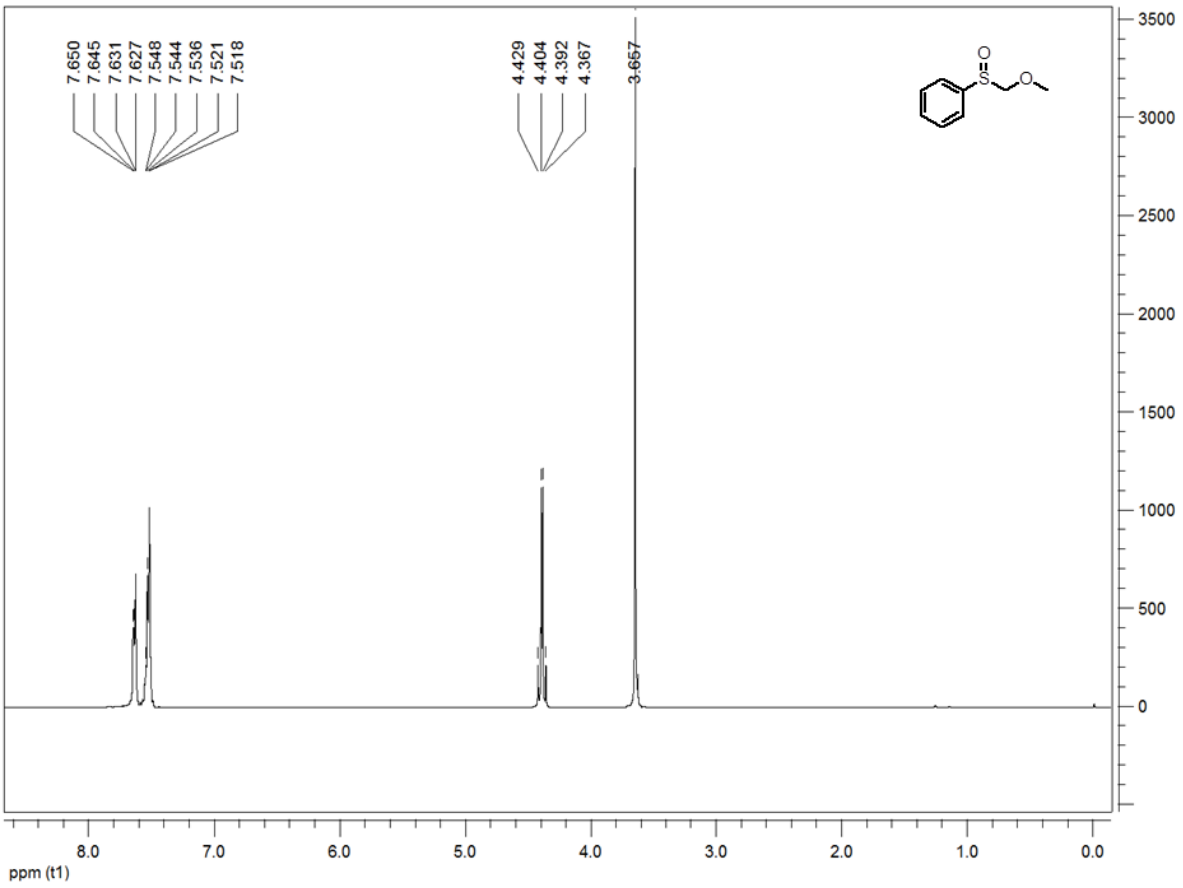
ppm (f1)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7.548
7.544
7.536
7.521
7.518
4.429
4.404
4.392
4.367
3.657
3500
3000
2500
2000
1500
1000
500
0
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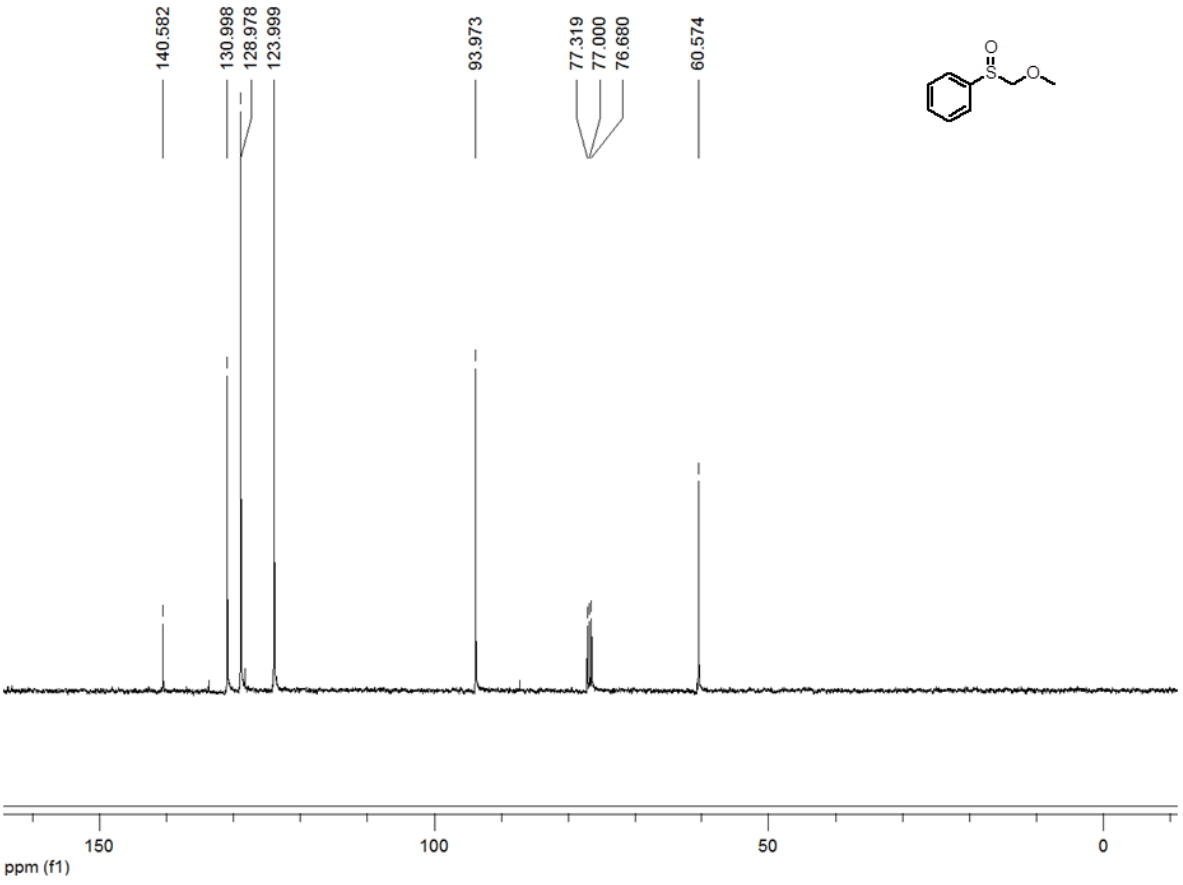
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


140.582
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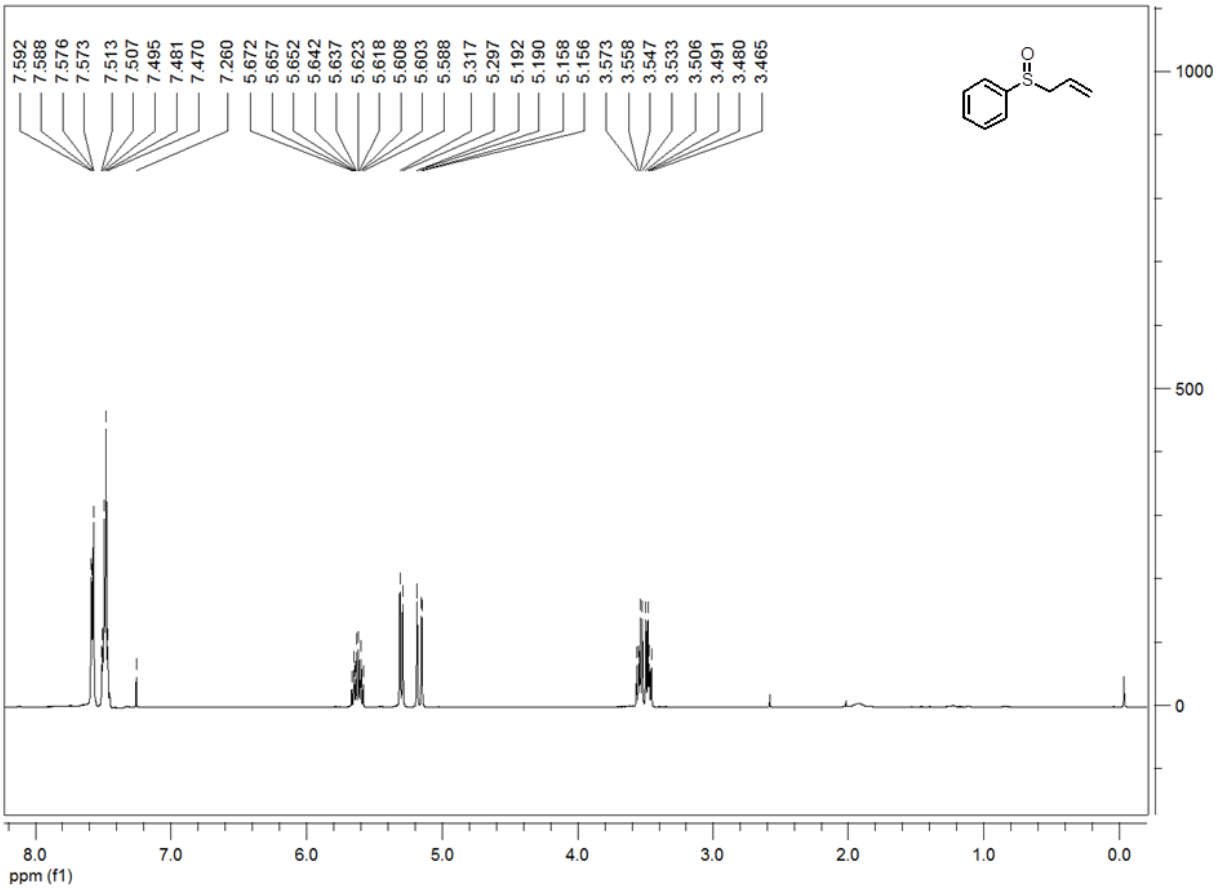
128.978
123.999
93.973
77.319
77.000
76.680
60.574
150
100
50
0
ppm (f1)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7.588
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7.507
7.495
7.481
7.470
7.260
5.672
5.657
5.652
5.642
5.637
5.623
5.618
5.608
5.603
5.588
5.317
5.297
5.192
5.190
5.158
5.156
3.573
3.558
3.547
3.533
3.506
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3.480
3.465
1000
500
0
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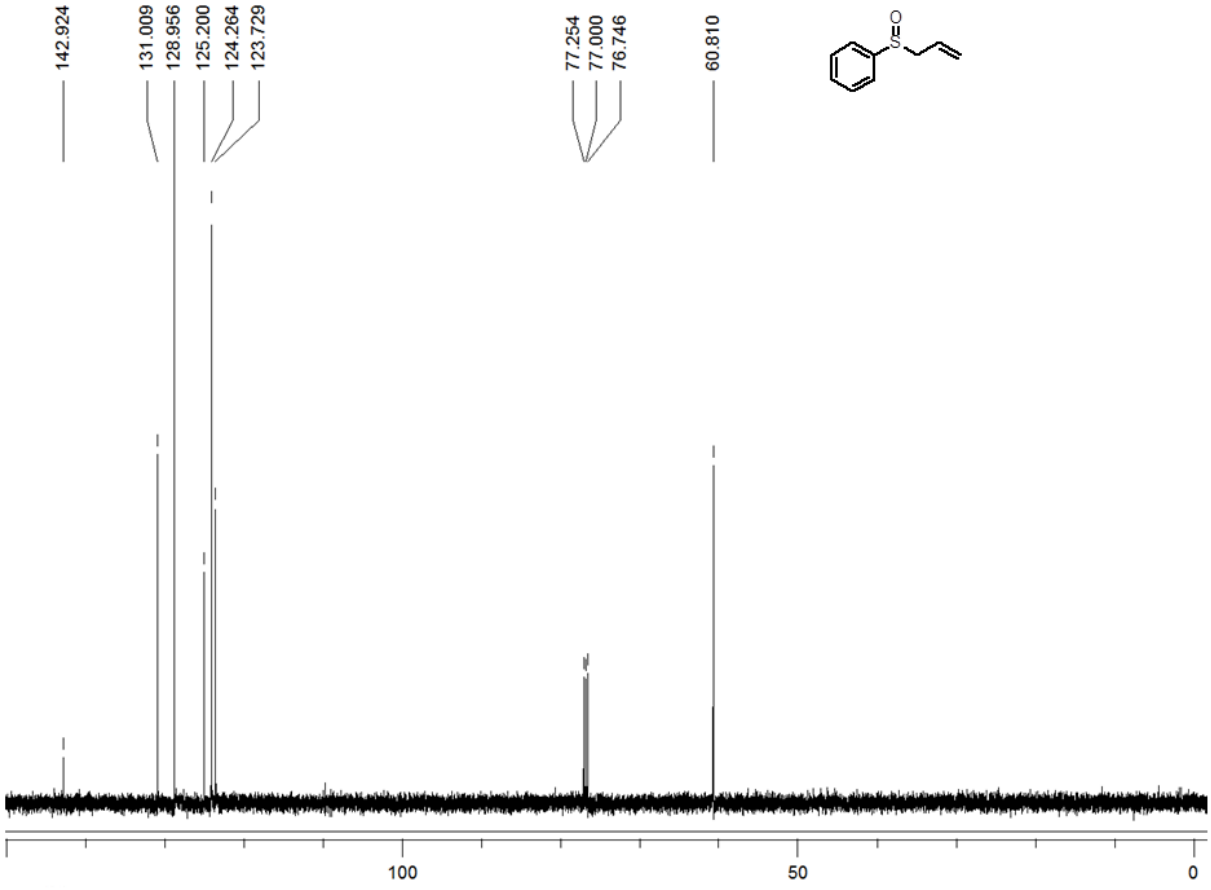
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)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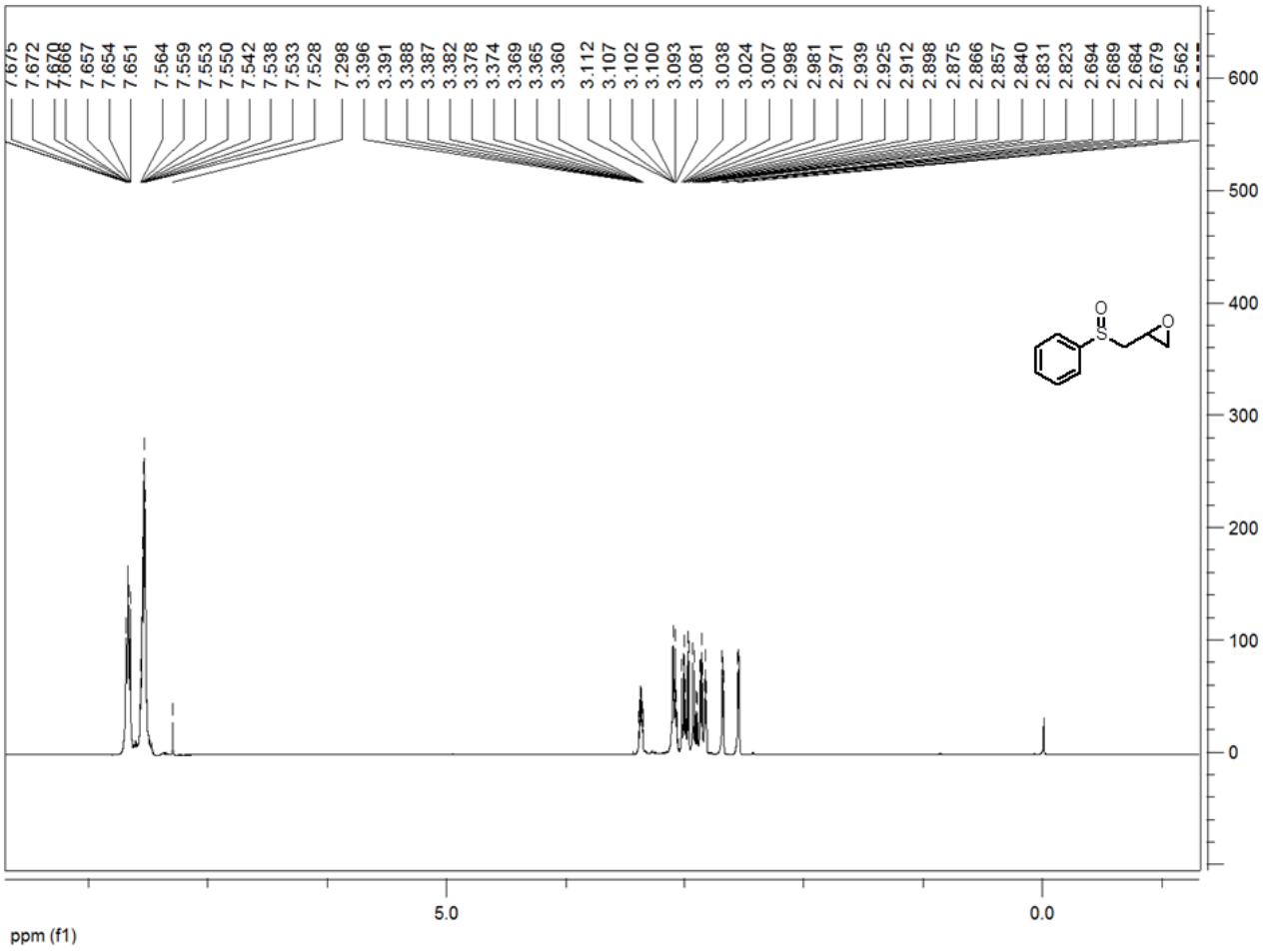
60.810
100
50
0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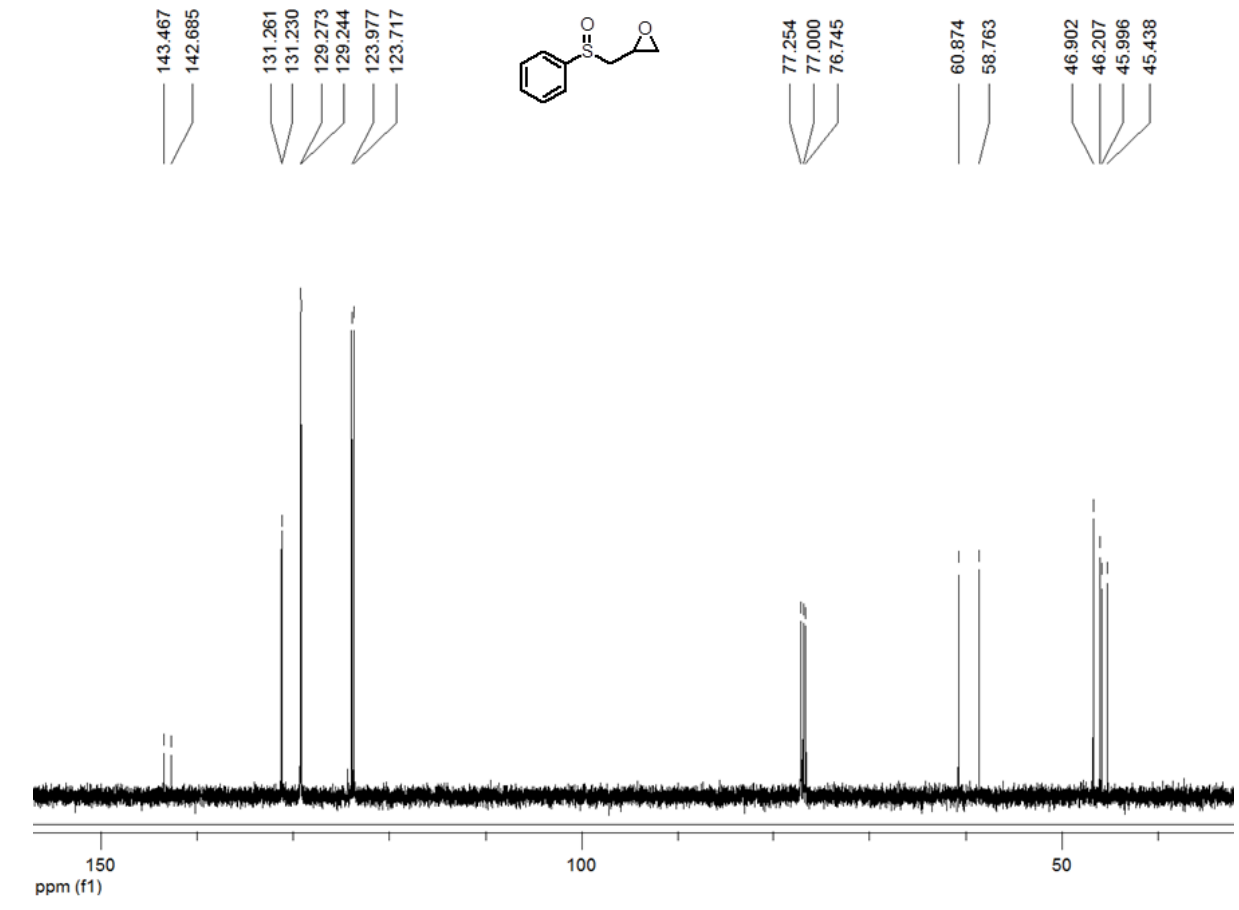
7.542
7.538
7.533
7.528
7.298
3.396
3.391
3.388
3.387
3.382
3.378
3.374
3.369
3.365
3.360
3.112
3.107
3.102
3.100
3.093
3.081
3.038
3.024
3.007
2.998
2.981
2.971
2.939
2.925
2.912
2.898
2.875
2.866
2.857
2.840
2.831
2.823
2.694
2.689
2.684
2.679
2.562
600
500
400
300
200
100
0
5.0
0.0
ppm (f1)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131.230
129.273
129.244
123.977
123.717
77.254
77.000
76.745
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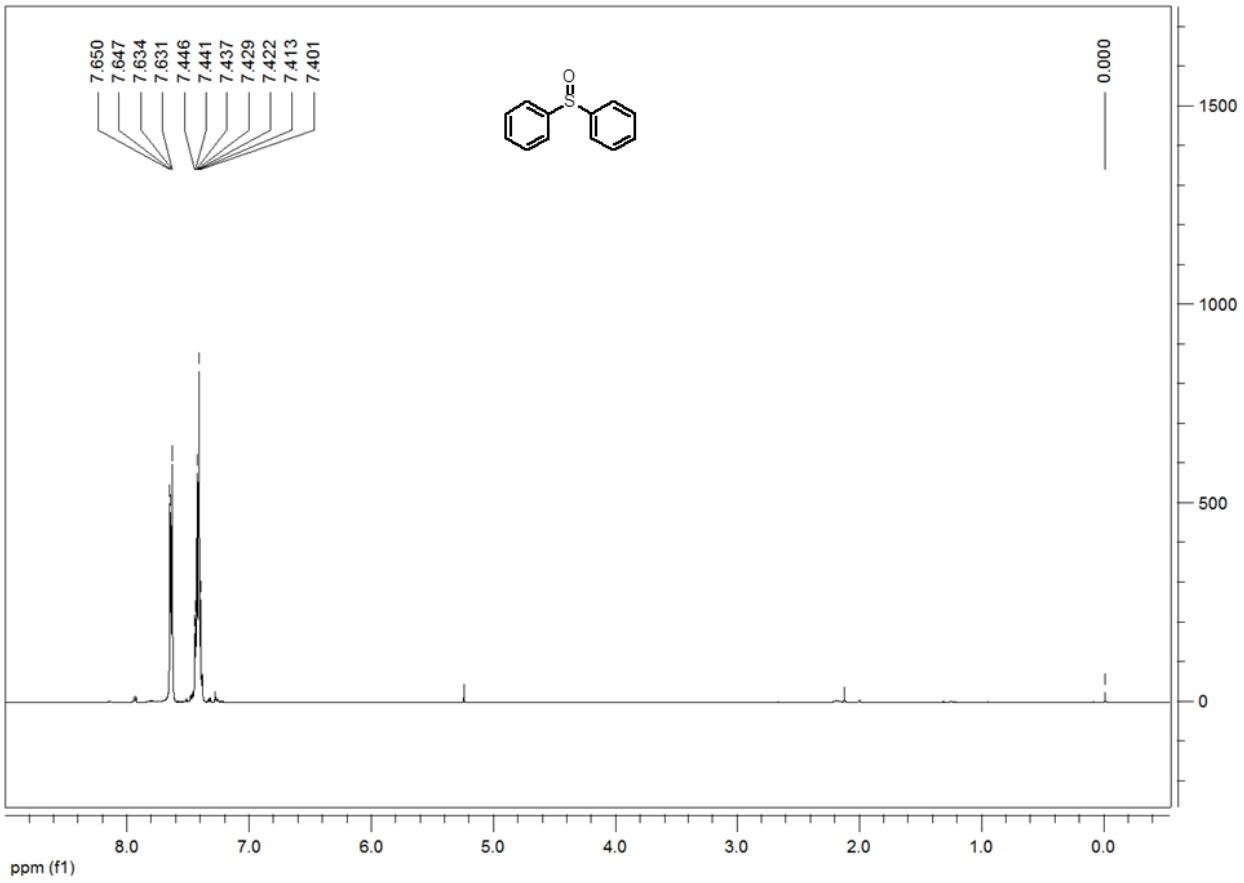
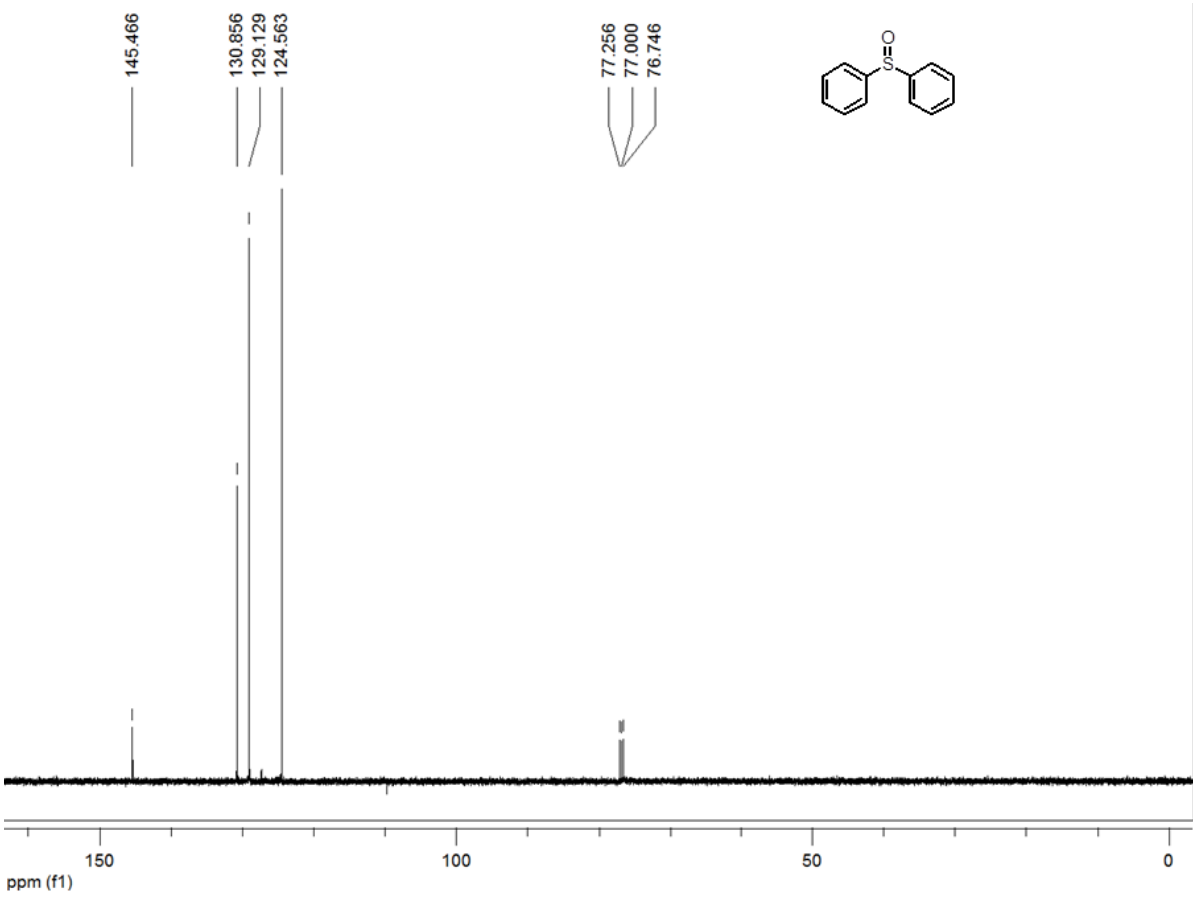
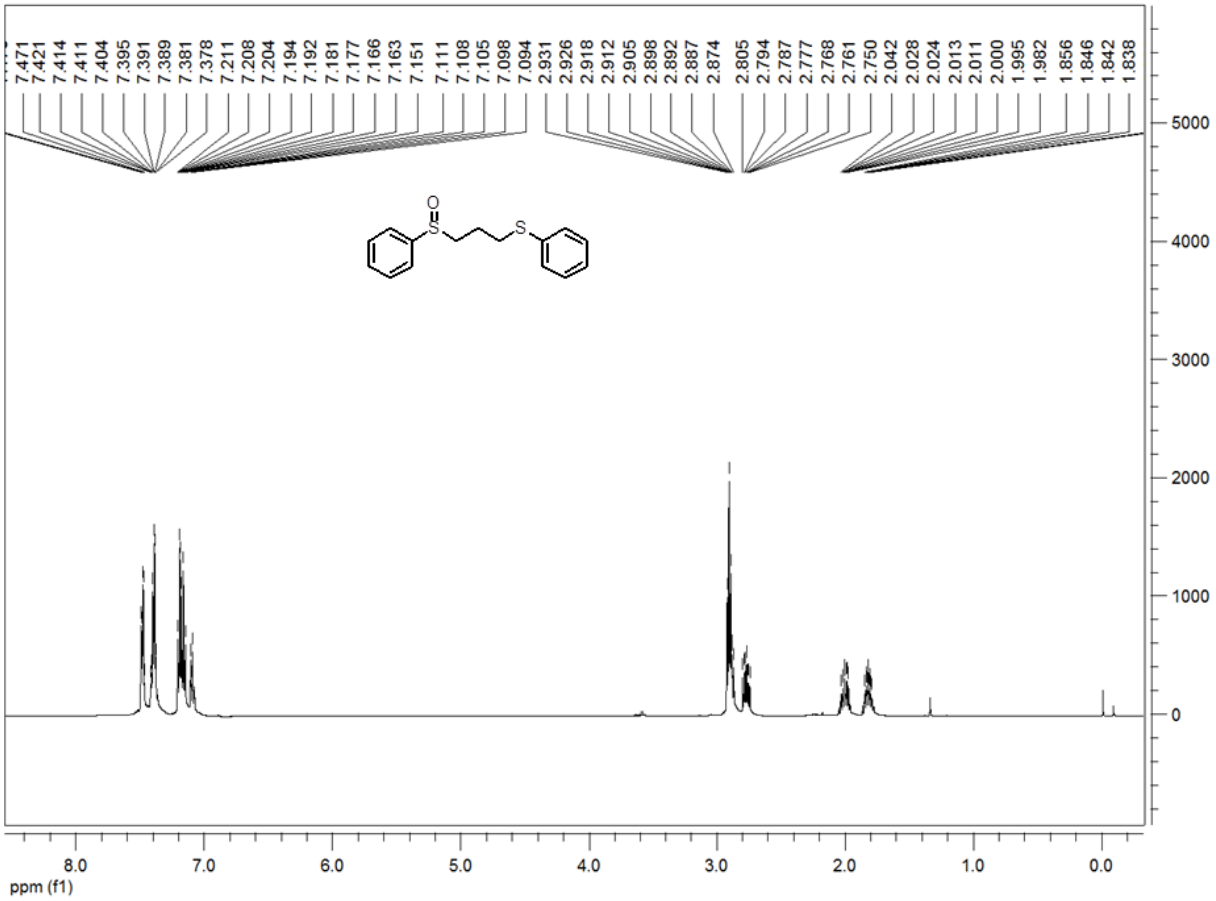
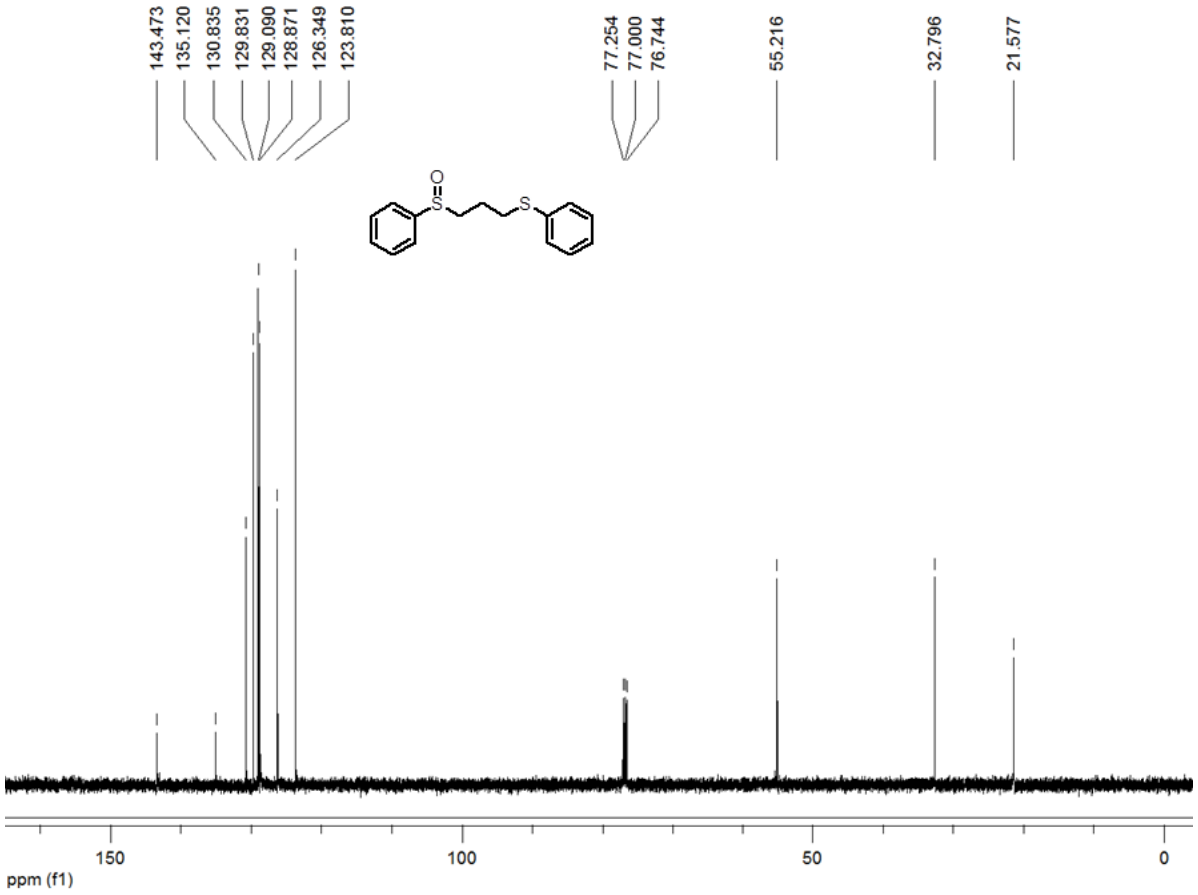
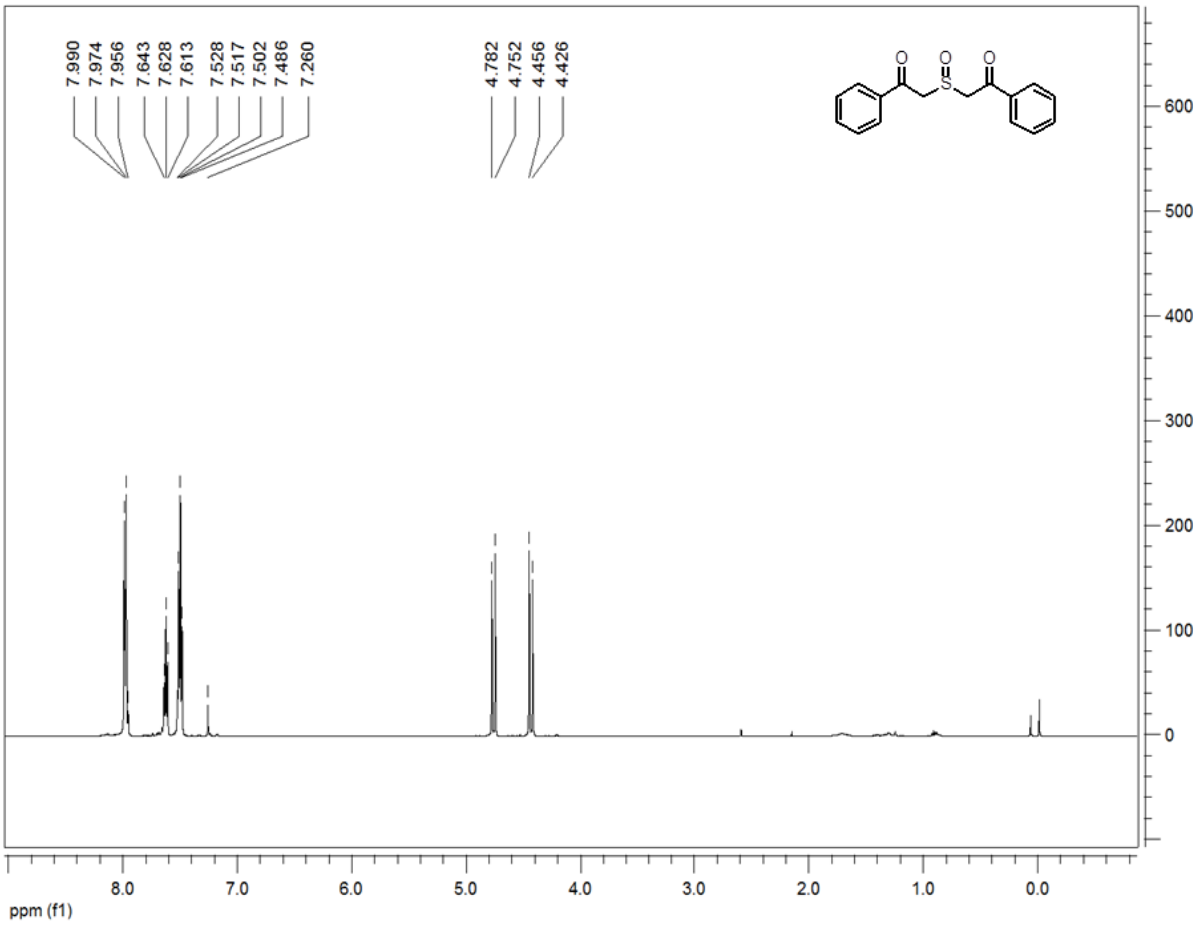
58.763
46.902
46.207
45.996
45.438
150
100
50
ppm (f1)

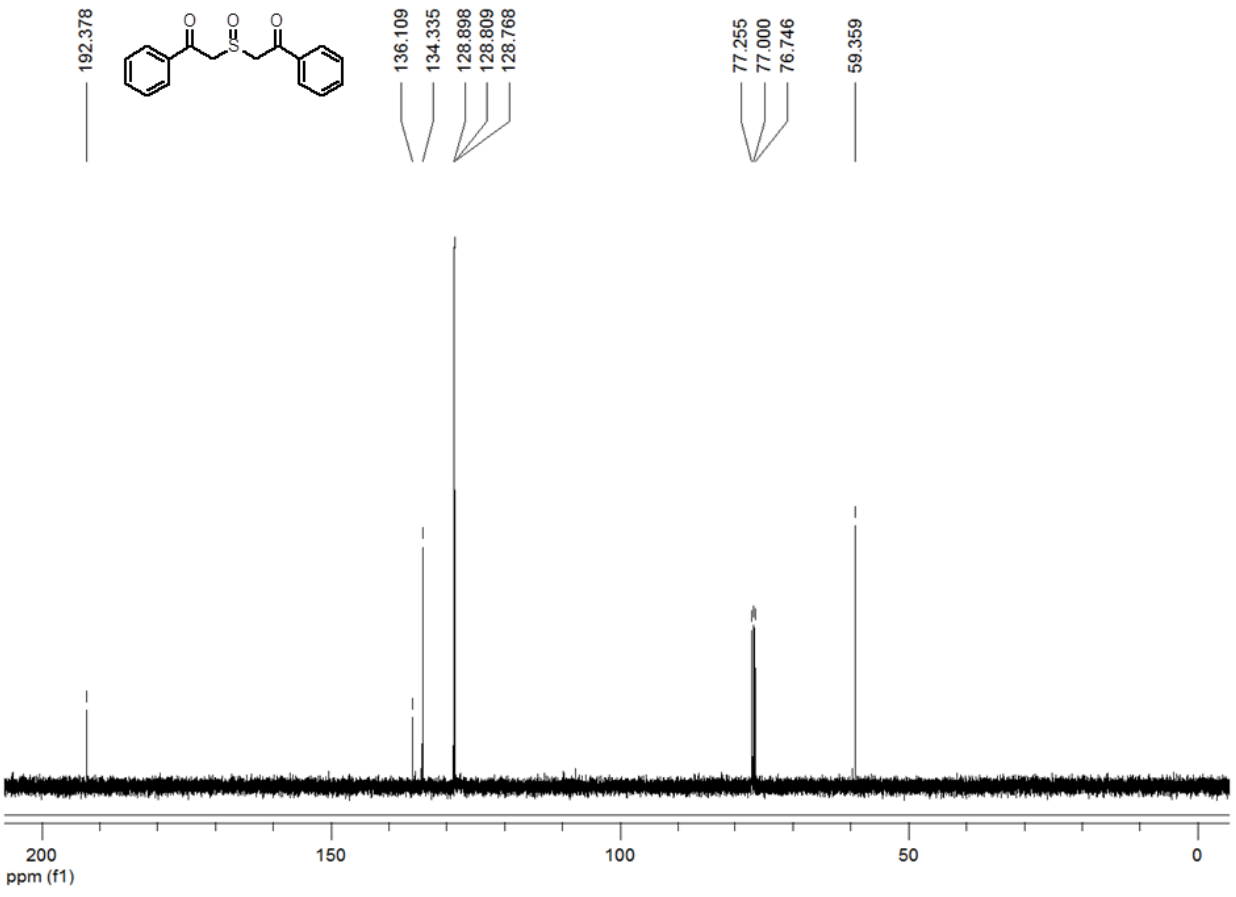

7.650
7.647
7.634
7.631
7.446
7.441
7.437
7.429
7.422
7.413
7.401
0.000
1500
1000
500
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

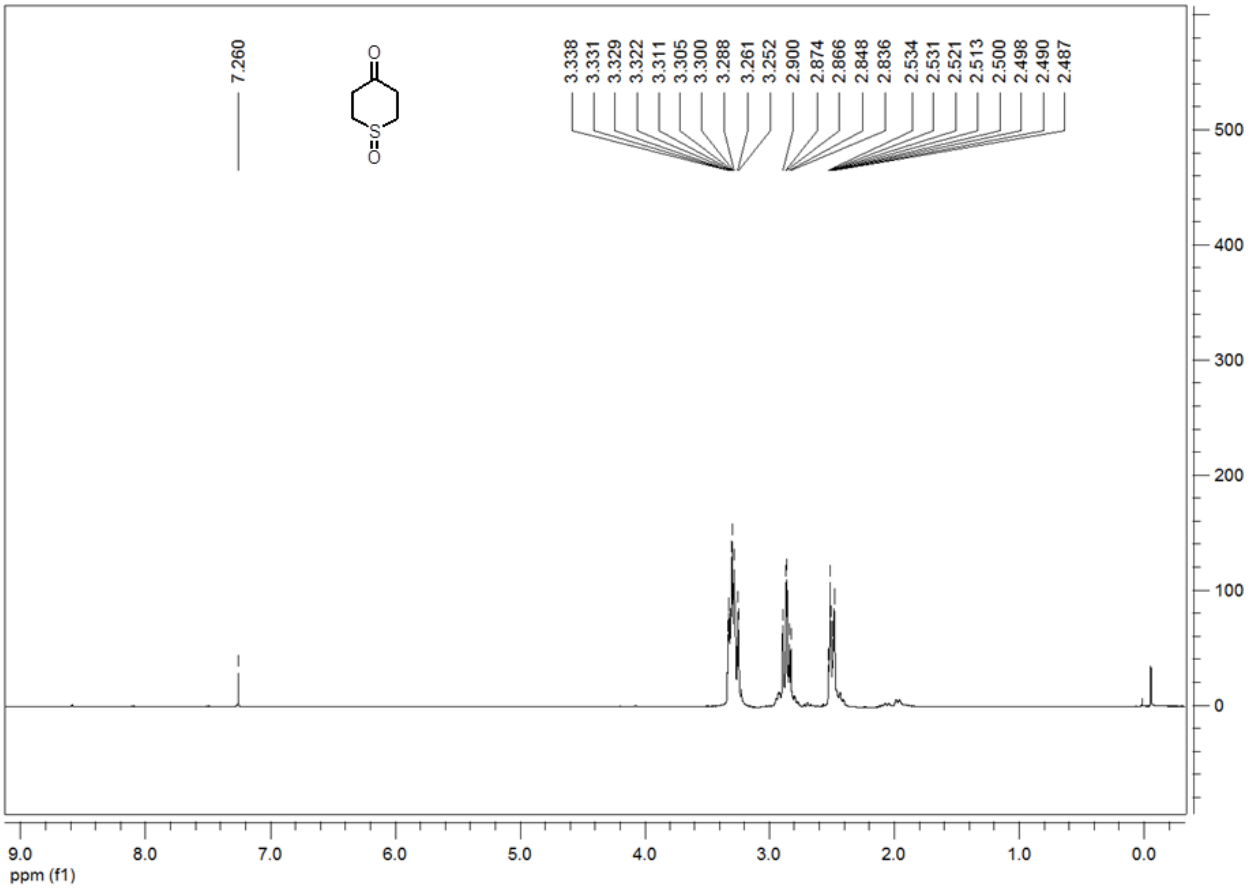

145.466
130.856
129.129
124.563
77.256
77.000
76.746
150
100
50
0
ppm (f1)

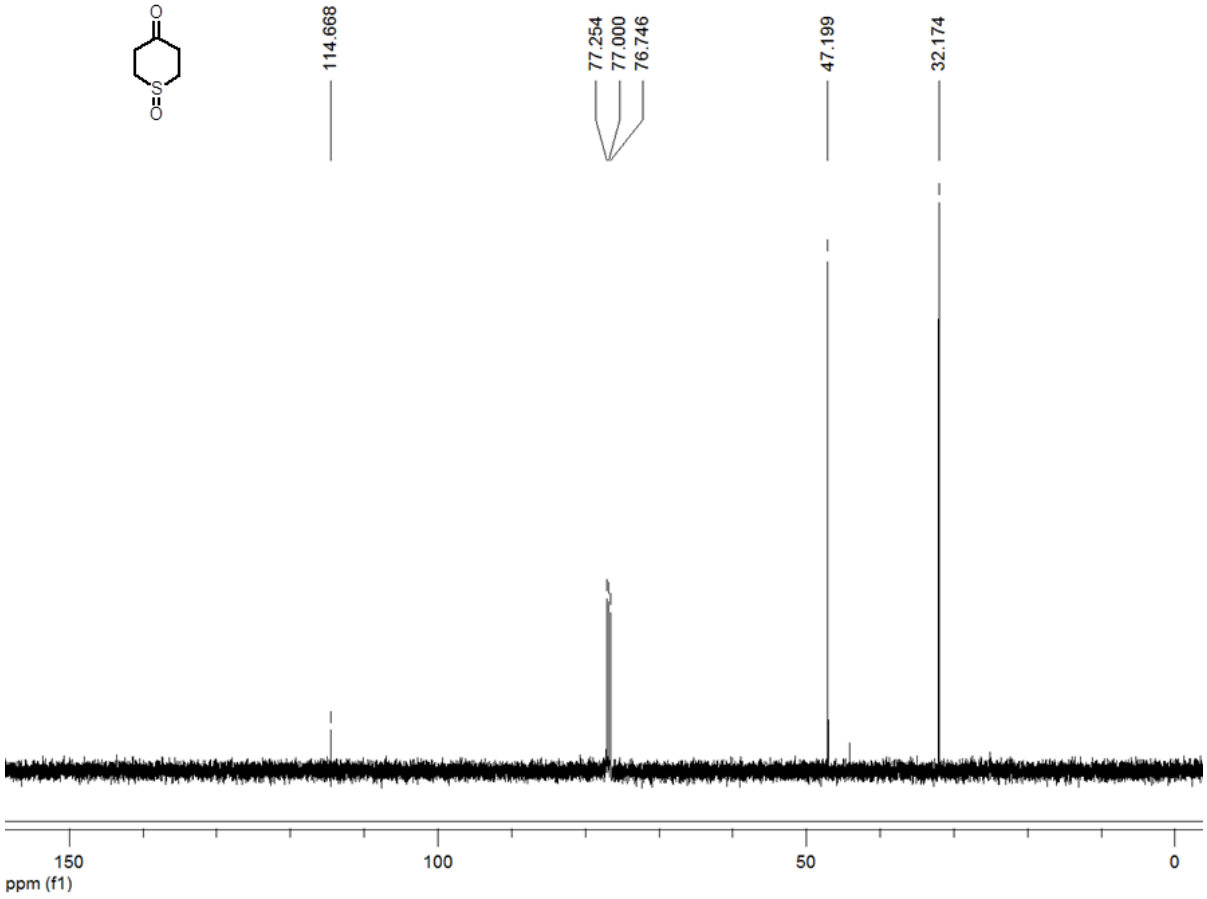

7.471
7.421
7.414
7.411
7.404
7.395
7.391
7.389
7.381
7.378
7.211
7.208
7.204
7.194
7.192
7.181
7.177
7.166
7.163
7.151
7.111
7.108
7.105
7.098
7.094
2.931
2.926
2.918
2.912
2.905
2.898
2.892
2.887
2.874
2.805
2.794
2.787
2.777
2.768
2.761
2.750
2.042
2.028
2.024
2.013
2.011
2.000
1.995
1.982
1.856
1.846
1.842
1.838
O
S
S
5000
4000
3000
2000
1000
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

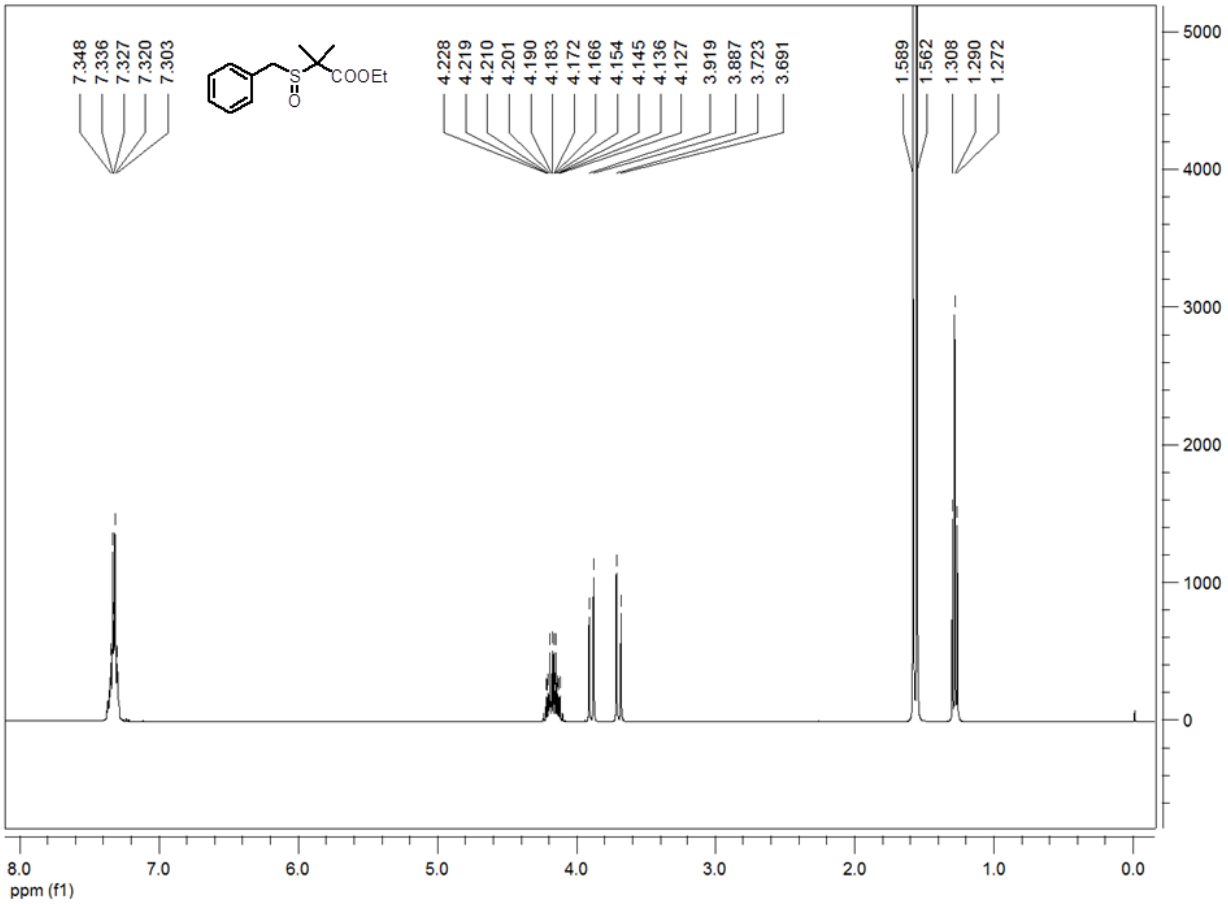

143.473
135.120
130.835
129.831
129.090
128.871
126.349
123.810
77.254
77.000
76.744
55.216
32.796
21.577
O
S
S
150
100
50
0
ppm (f1)

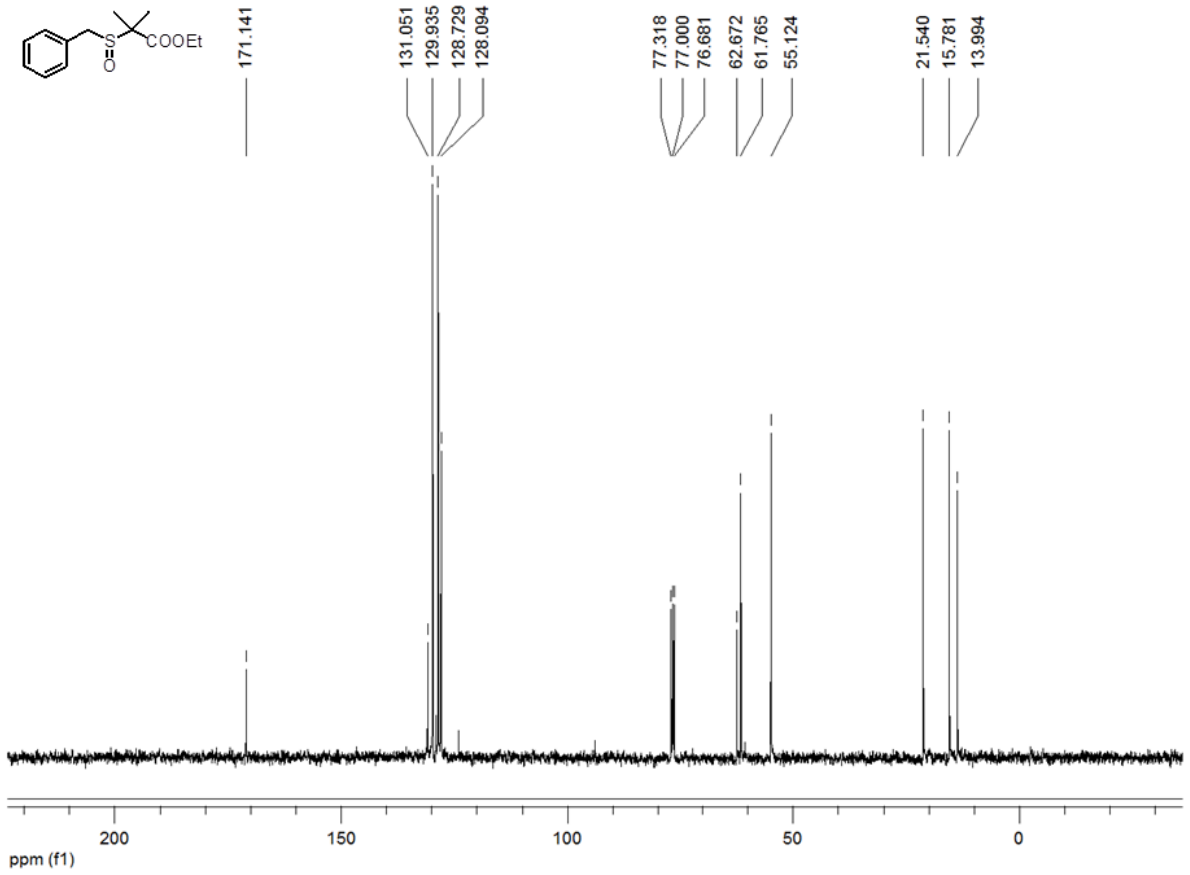

7.990
7.974
7.956
7.643
7.628
7.613
7.528
7.517
7.502
7.486
7.260
4.782
4.752
4.456
4.426
O
O
S
O
600
500
400
300
200
100
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

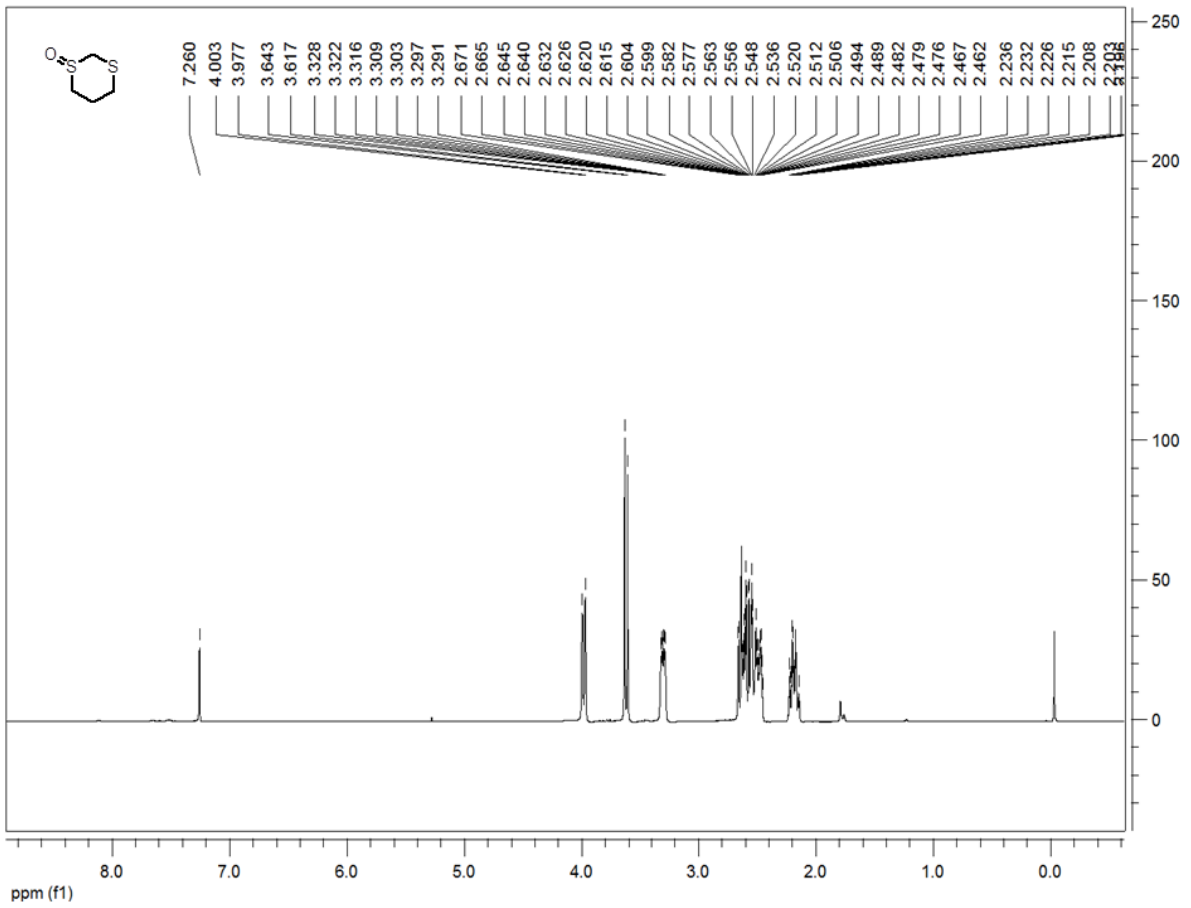

192.378
O
O
S
O
136.109
134.335
128.898
128.809
128.768
77.255
77.000
76.746
59.359
200
150
100
50
0
ppm (f1)

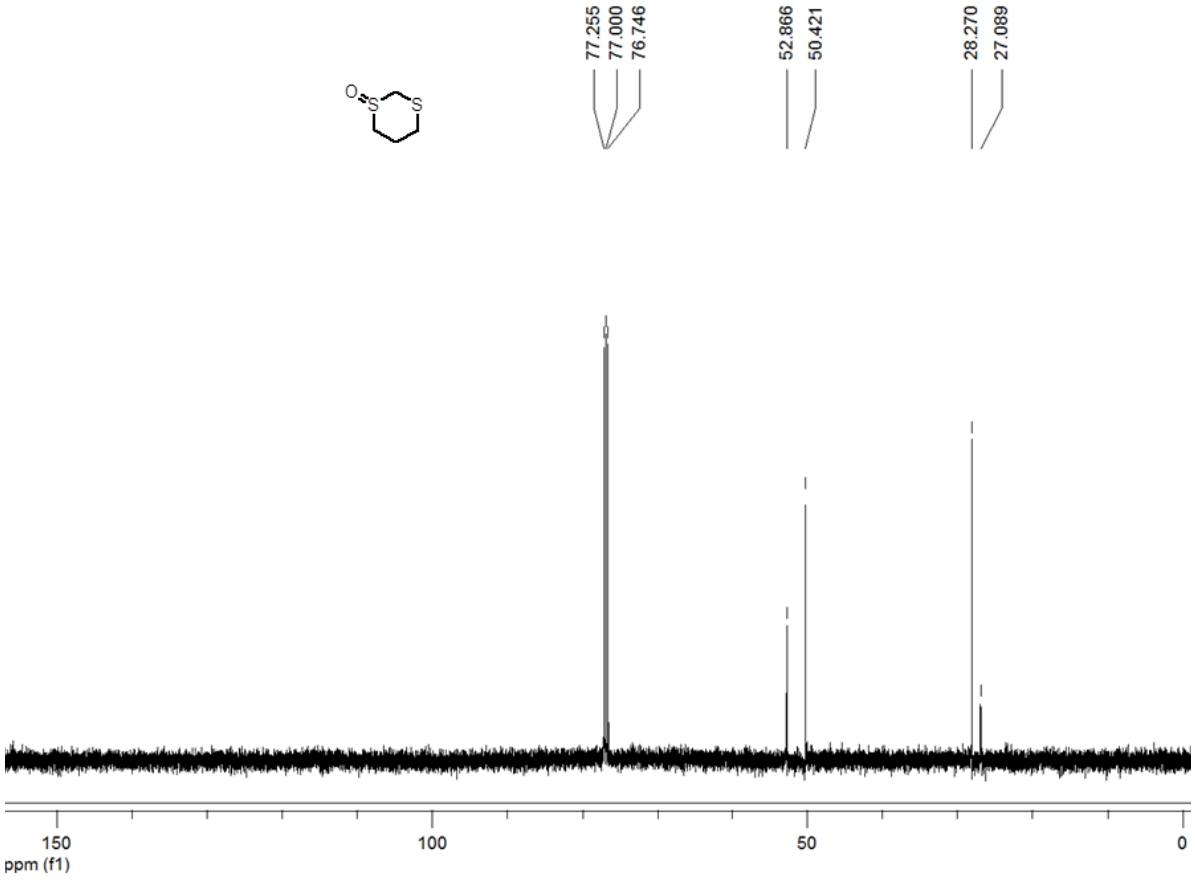

7.260
3.338
3.331
3.329
3.322
3.311
3.305
3.300
3.288
3.261
3.252
2.900
2.874
2.866
2.848
2.836
2.534
2.531
2.521
2.513
2.500
2.498
2.490
2.487
500
400
300
200
100
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

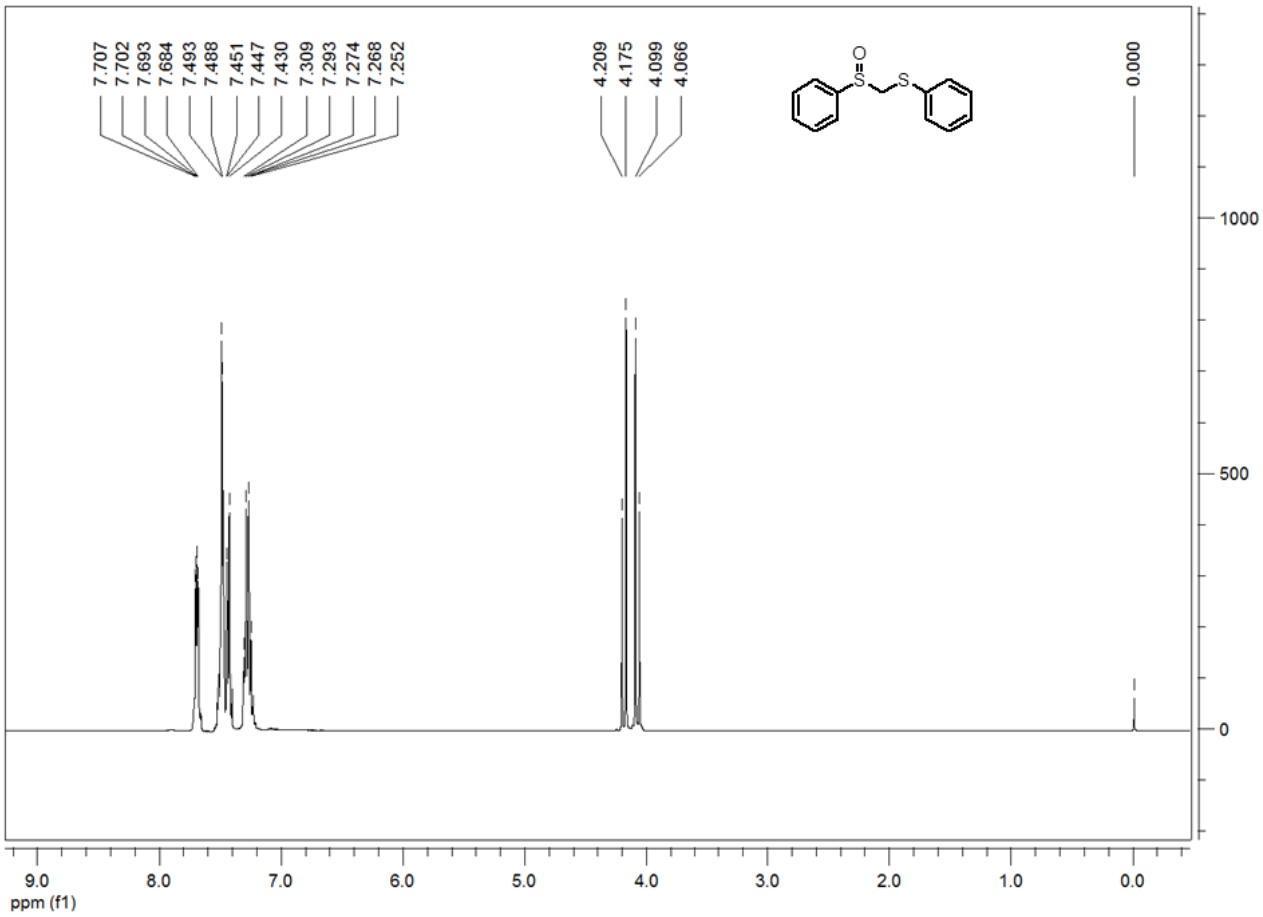

114.668
77.254
77.000
76.746
47.199
32.174
150
100
50
0
ppm (f1)

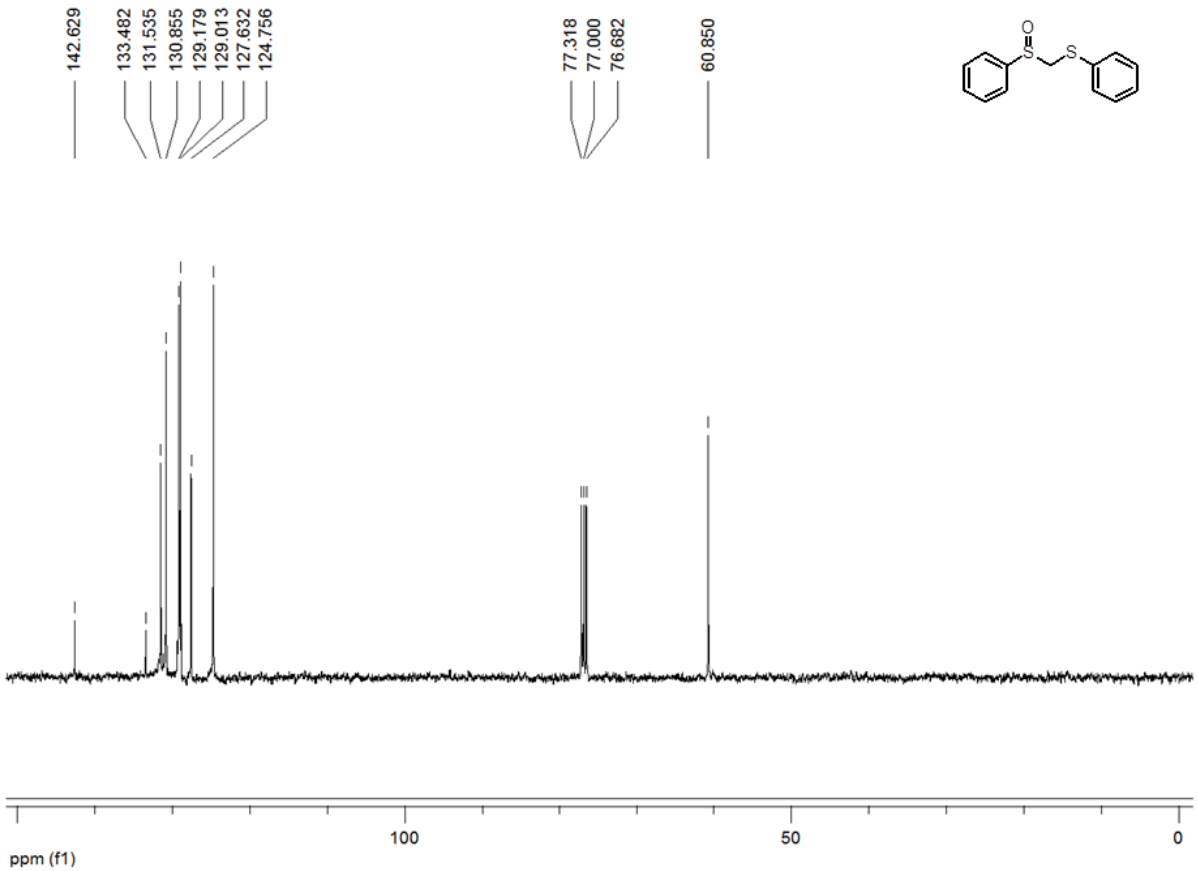

7.348
7.336
7.327
7.320
7.303
4.228
4.219
4.210
4.201
4.190
4.183
4.172
4.166
4.154
4.145
4.136
4.127
3.919
3.887
3.723
3.691
1.589
1.562
1.308
1.290
1.272
COOEt
5000
4000
3000
2000
1000
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

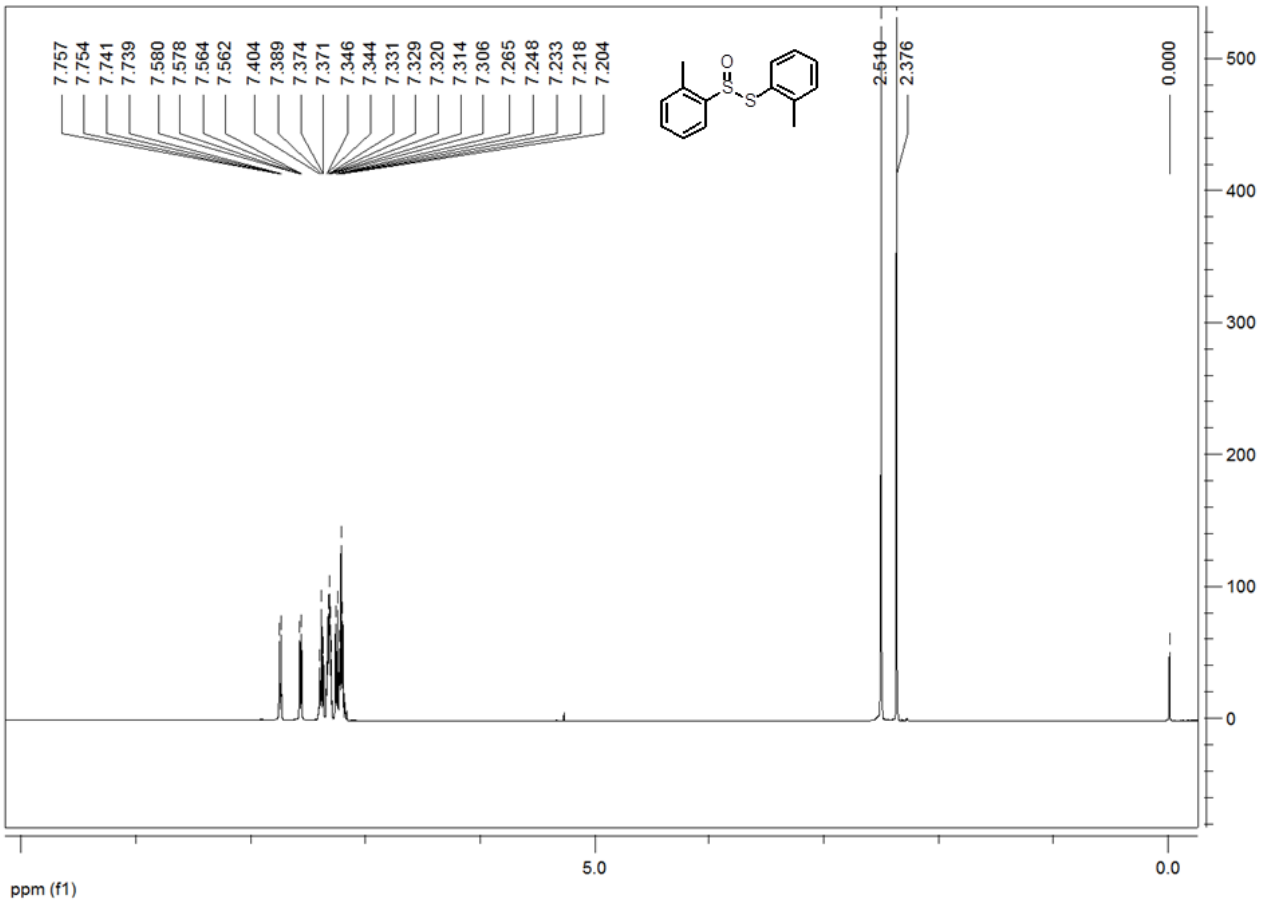

171.141
131.051
129.935
128.729
128.094
77.318
77.000
76.681
62.672
61.765
55.124
21.540
15.781
13.994
COOEt
200
150
100
50
0
ppm (f1)

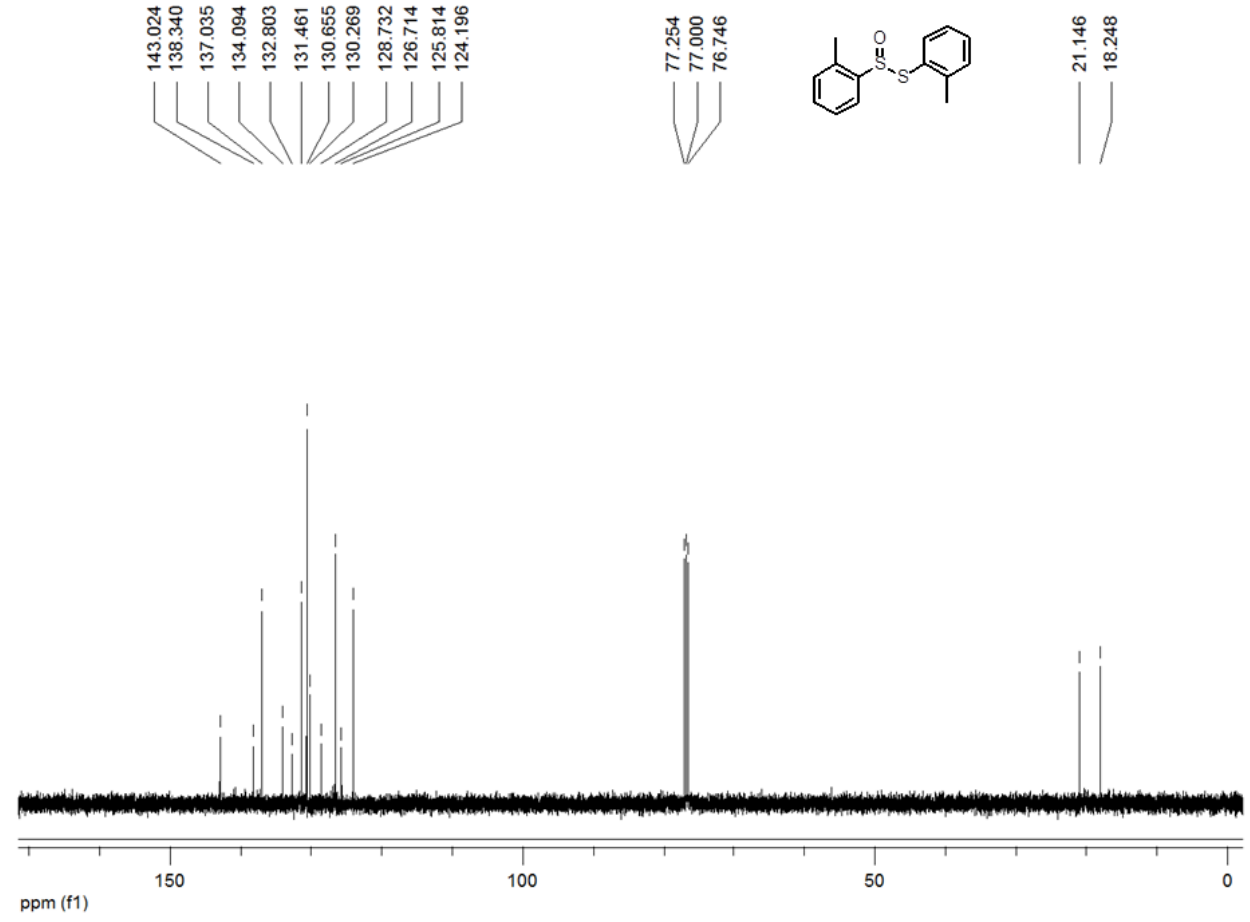

7.260
4.003
3.977
3.643
3.617
3.328
3.322
3.316
3.309
3.303
3.297
3.291
2.671
2.665
2.645
2.640
2.632
2.626
2.620
2.615
2.604
2.599
2.582
2.577
2.563
2.556
2.548
2.536
2.520
2.512
2.506
2.494
2.489
2.482
2.479
2.476
2.467
2.462
2.236
2.232
2.226
2.215
2.208
250
200
150
100
50
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

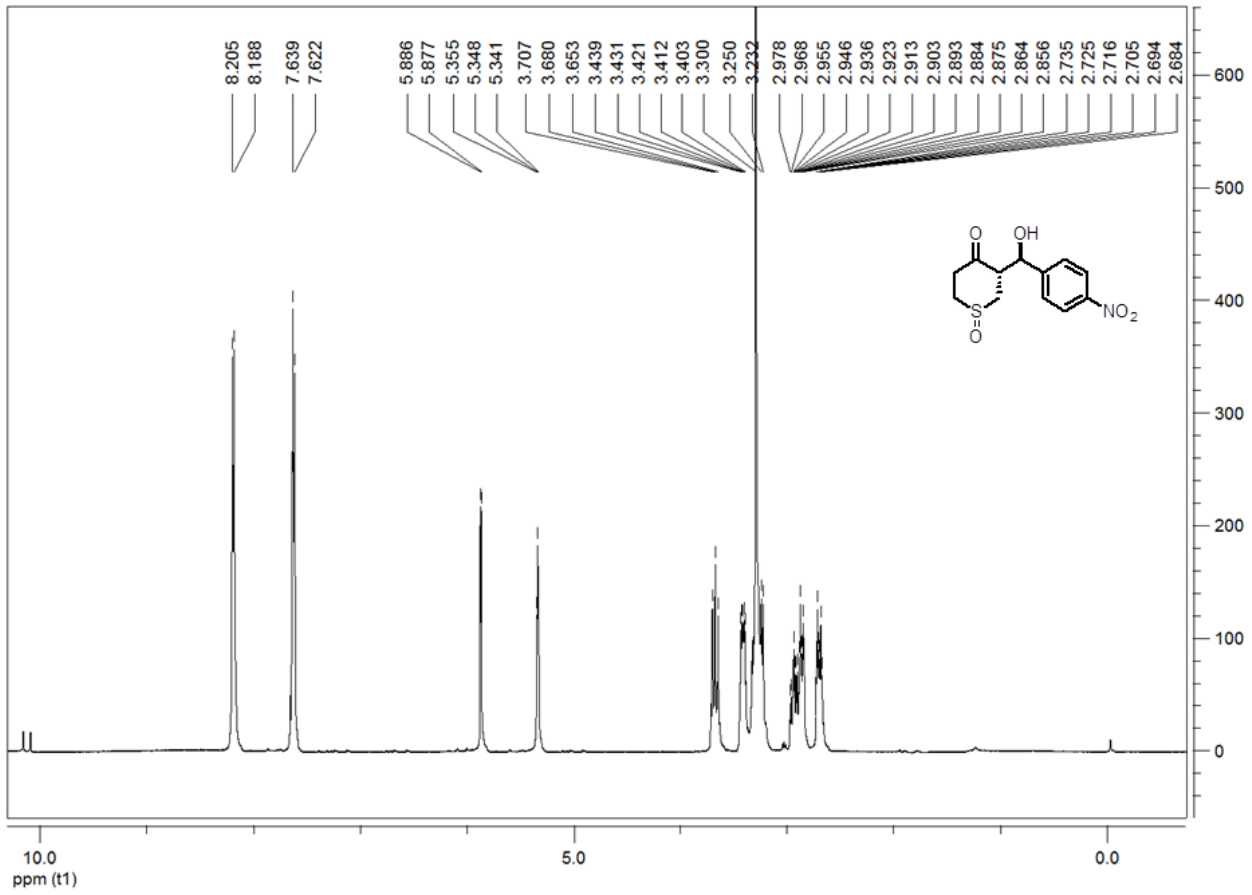

77.255
77.000
76.746
52.866
50.421
28.270
27.089
150
100
50
0
ppm (f1)

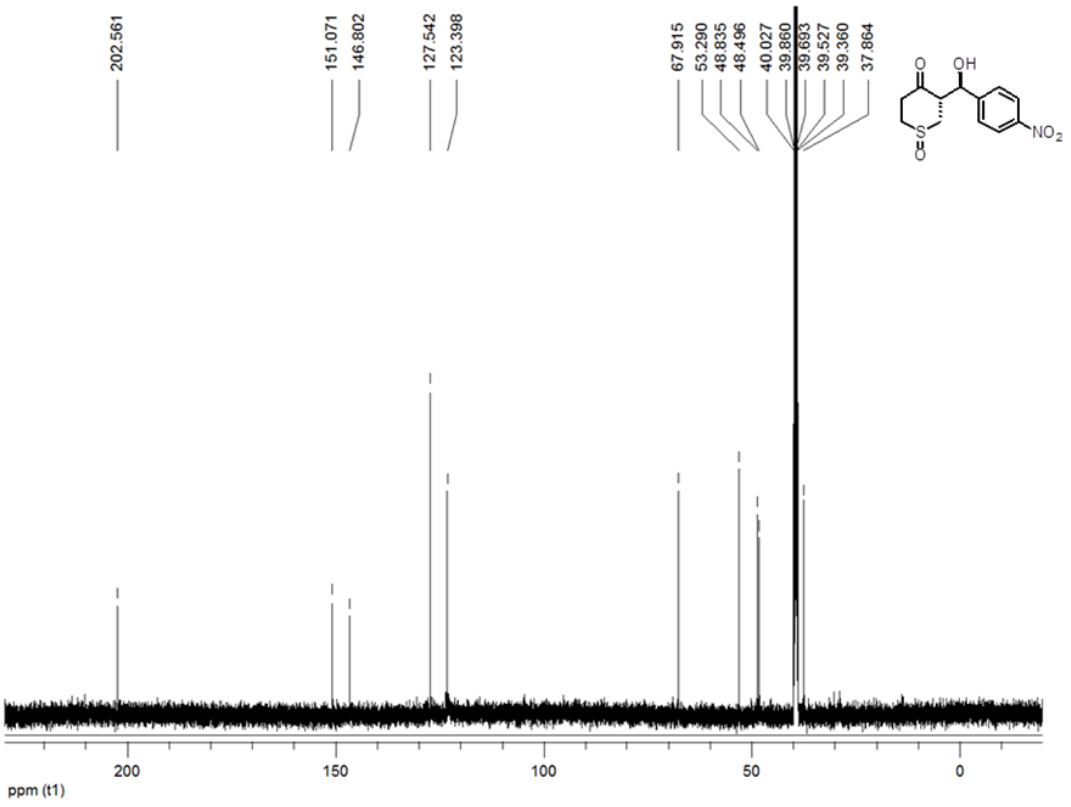

7.707
7.702
7.693
7.684
7.493
7.488
7.451
7.447
7.430
7.309
7.293
7.274
7.268
7.252
4.209
4.175
4.099
4.066
0.000
1000
500
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


142.629
133.482
131.535
130.855
129.179
129.013
127.632
124.756
77.318
77.000
76.682
60.850
100
50
0
ppm (f1)

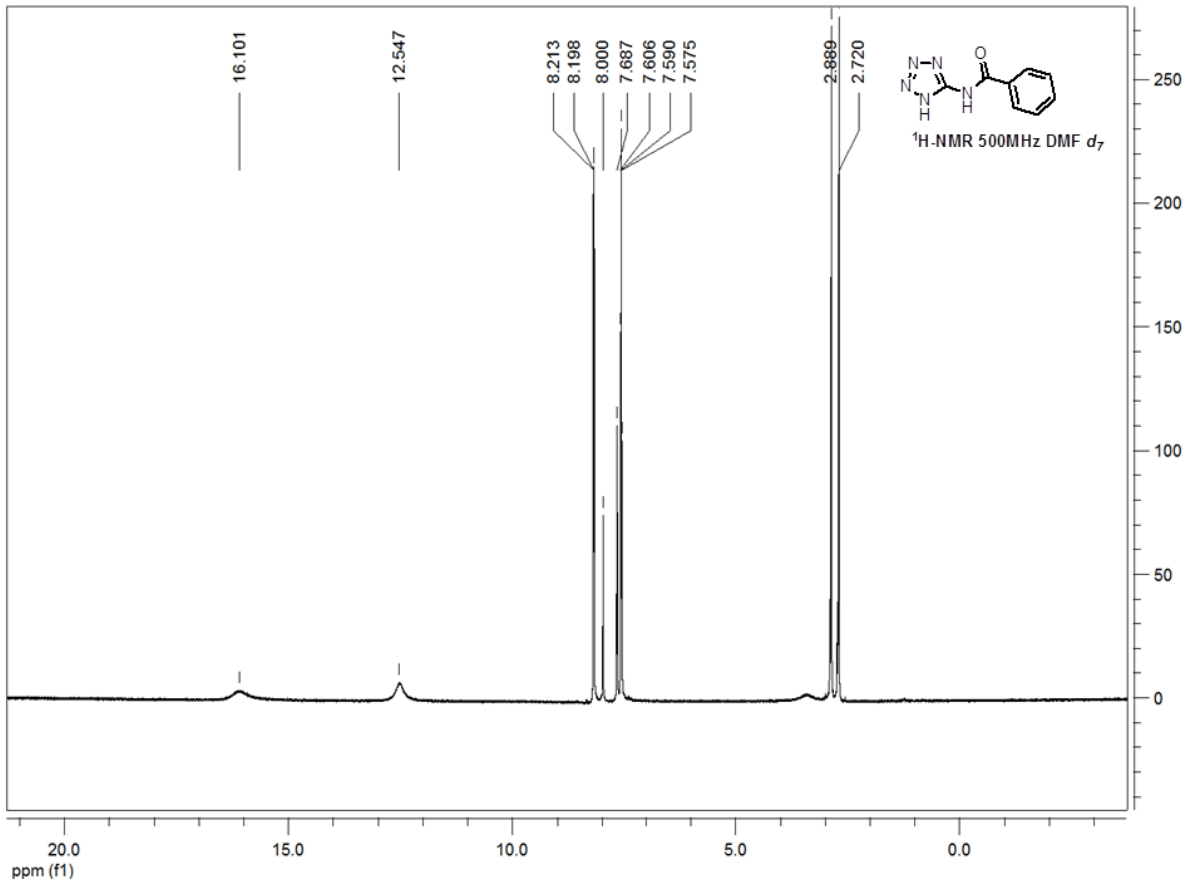

7.757
7.754
7.741
7.739
7.580
7.578
7.564
7.562
7.404
7.389
7.374
7.371
7.346
7.344
7.331
7.329
7.320
7.314
7.306
7.265
7.248
7.233
7.218
7.204
2.610
2.376
0.000
500
400
300
200
100
0
5.0
0.0
ppm (f1)


143.024
138.340
137.035
134.094
132.803
131.461
130.655
130.269
128.732
126.714
125.814
124.196
77.254
77.000
76.746
21.146
18.248
150
100
50
0
ppm (f1)

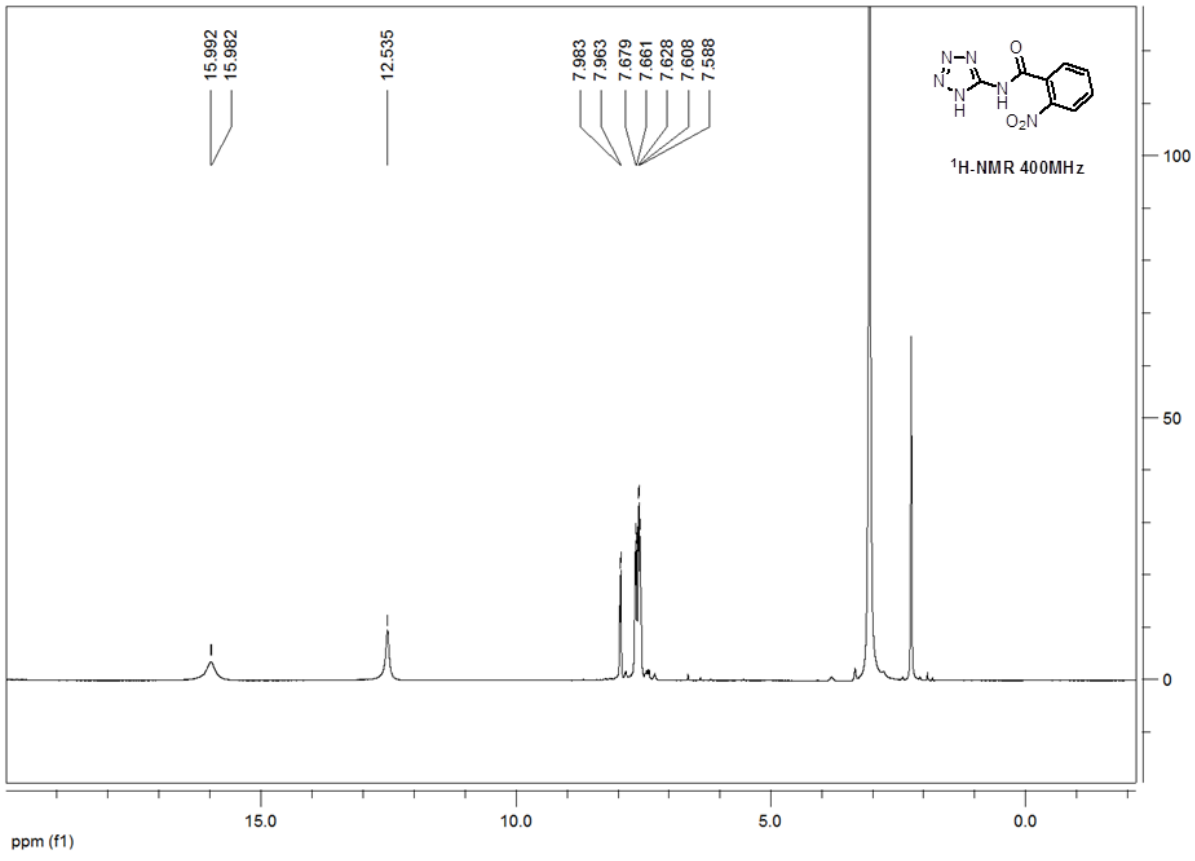

8.205
8.188
7.639
7.622
5.886
5.877
5.355
5.348
5.341
3.707
3.680
3.653
3.439
3.431
3.421
3.412
3.403
3.300
3.250
3.232
2.978
2.968
2.955
2.946
2.936
2.923
2.913
2.903
2.893
2.884
2.875
2.864
2.856
2.735
2.725
2.716
2.705
2.694
2.684
O
OH
S
O
NO2
600
500
400
300
200
100
0
10.0
5.0
0.0
ppm (t1)

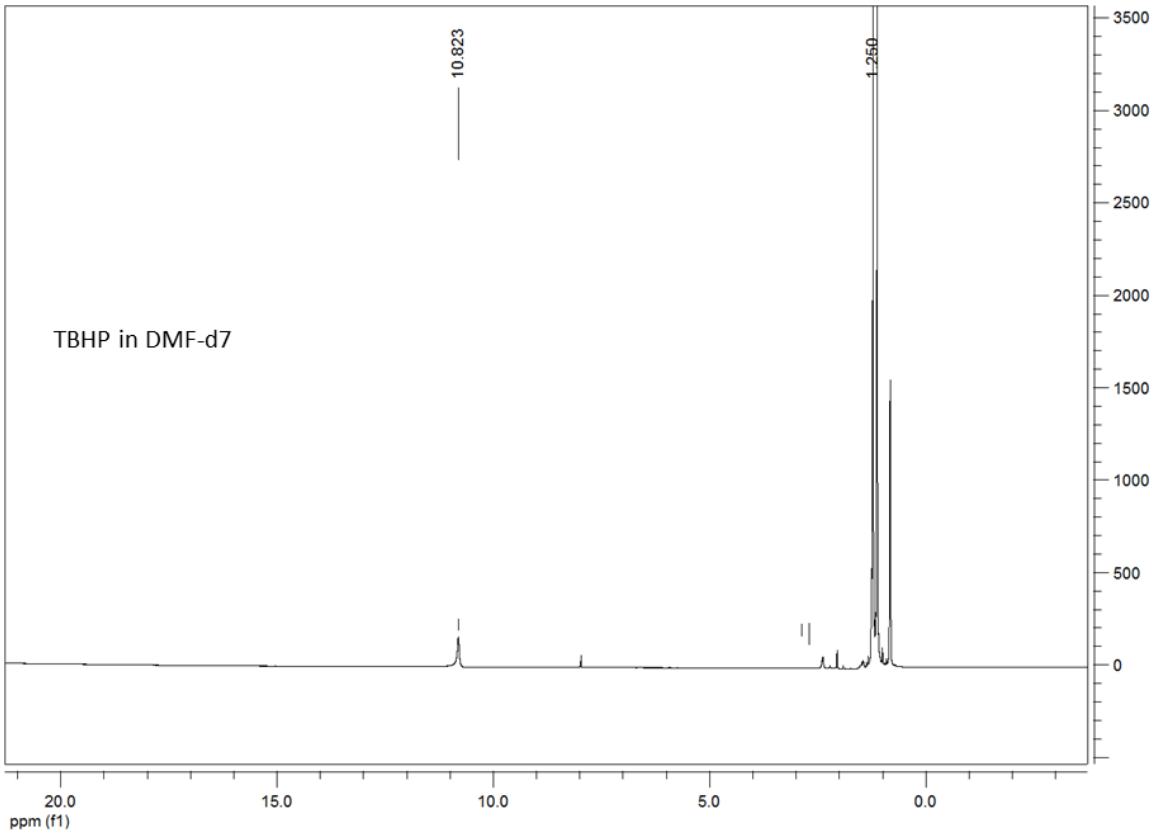

202.561
151.071
146.802
127.542
123.398
67.915
53.290
48.835
48.496
40.027
39.860
39.693
39.527
39.360
37.864
O
OH
S
O
NO2
200
150
100
50
0
ppm (t1)

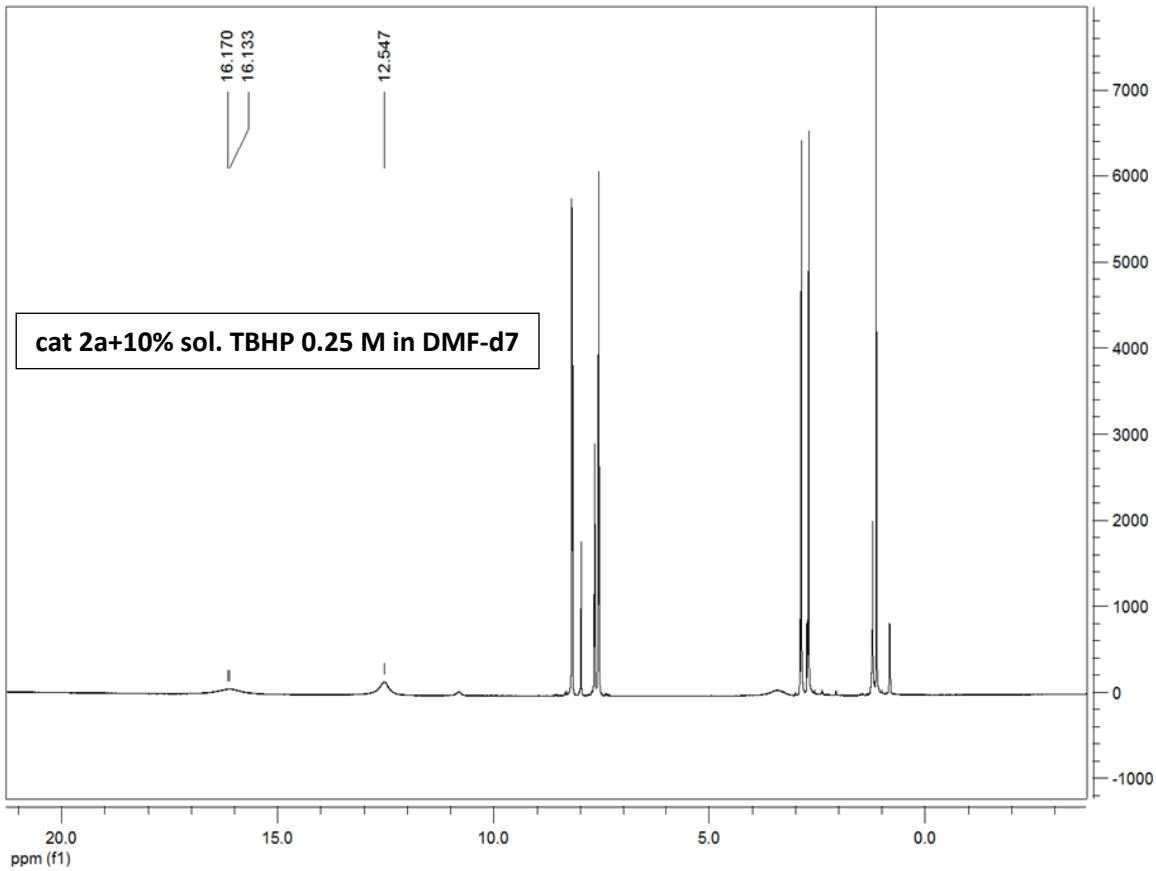
2.3. ^{1}H NMR spectra and titration of compound 2a with TBHP

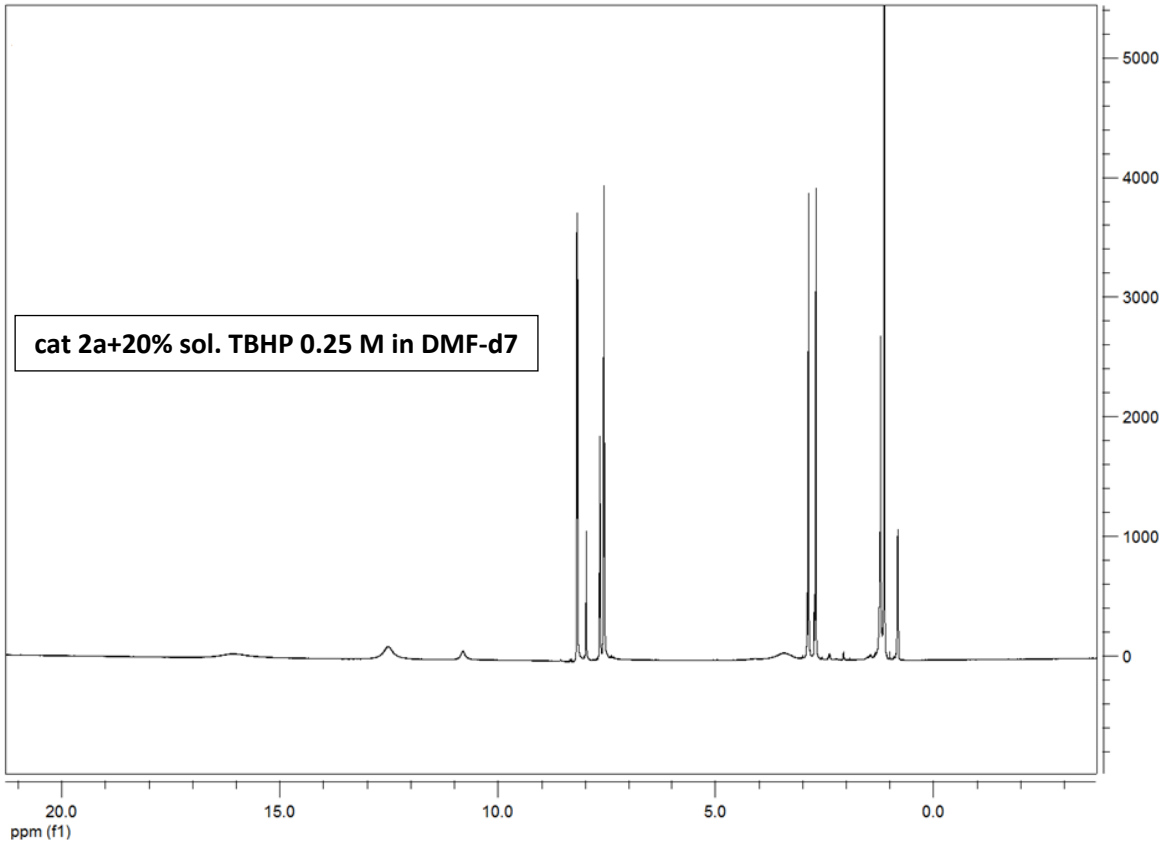


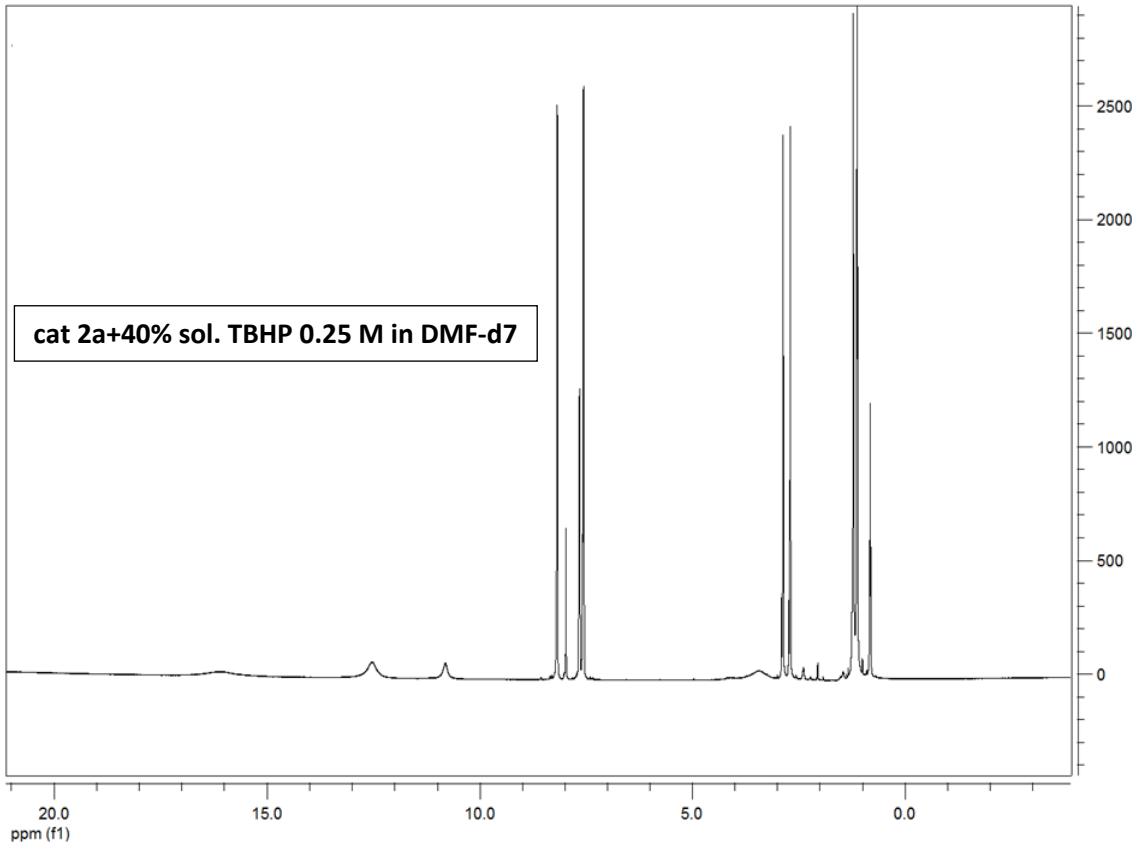
^{1}H NMR spectra and titration of compound 2b with TBHP

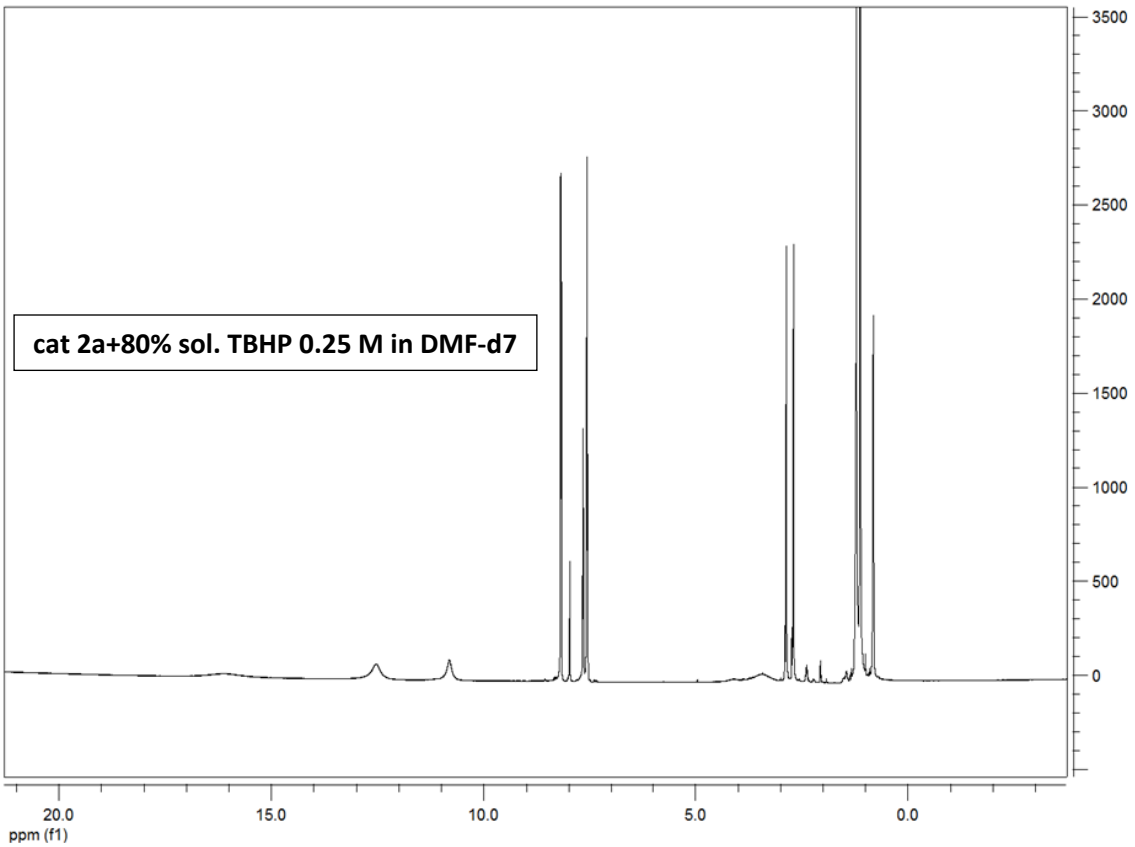


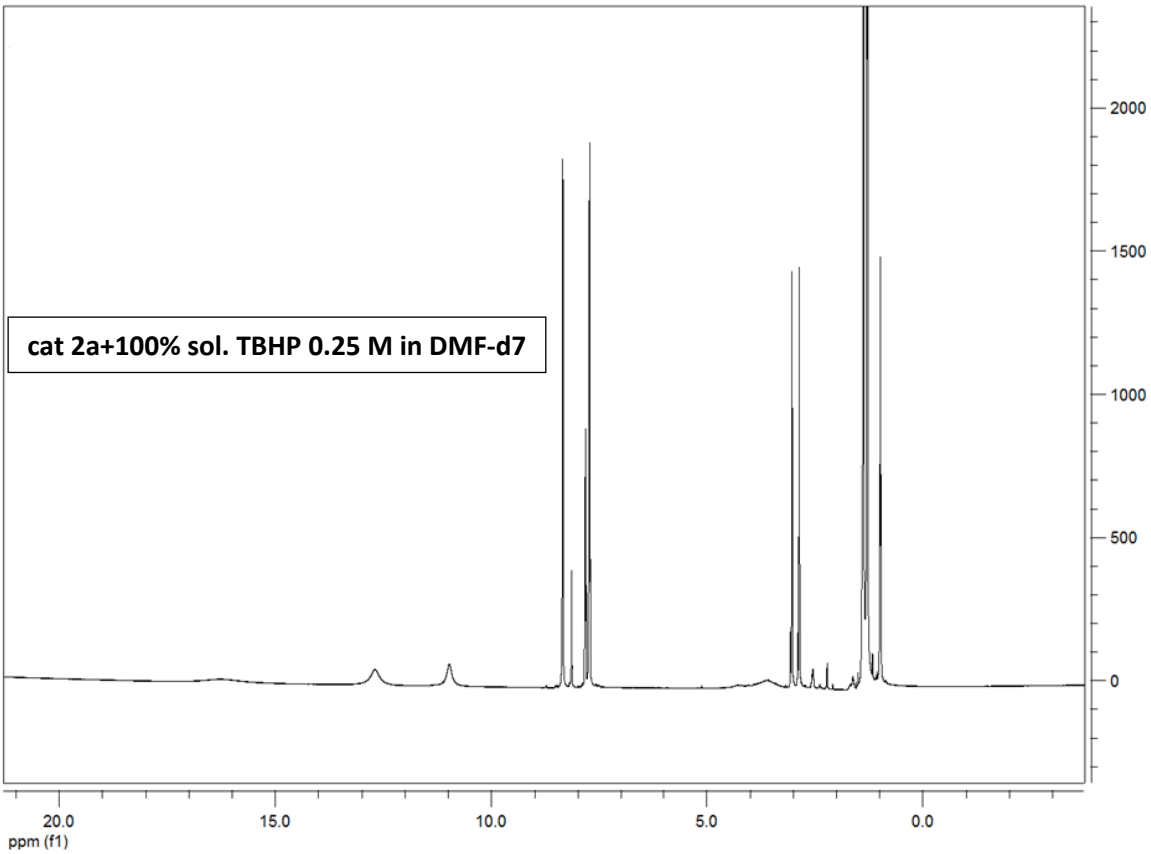

10.823
1.250
TBHP in DMF-d7
3500
3000
2500
2000
1500
1000
500
0
20.0
15.0
10.0
5.0
0.0
ppm (f1)

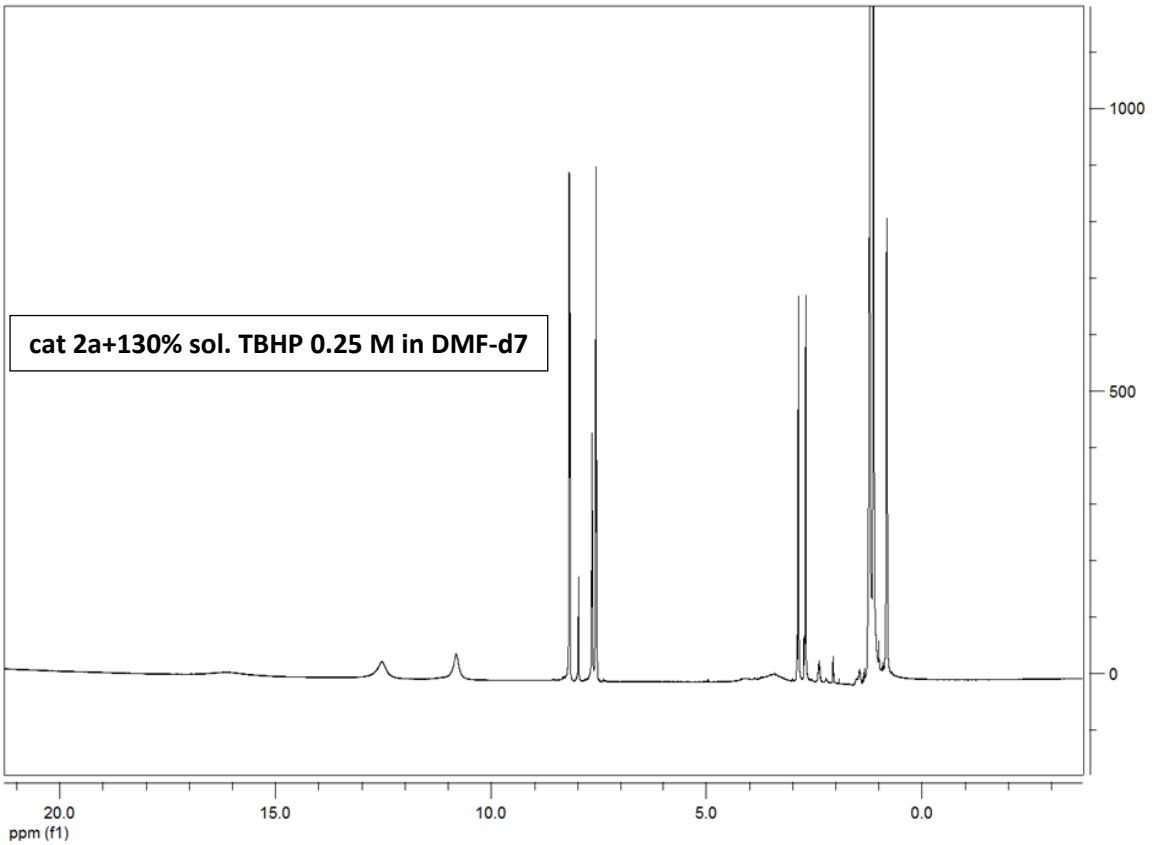

16.170
16.133
12.547
cat 2a+10% sol. TBHP 0.25 M in DMF-d7
7000
6000
5000
4000
3000
2000
1000
0
-1000
20.0
15.0
10.0
5.0
0.0
ppm (f1)

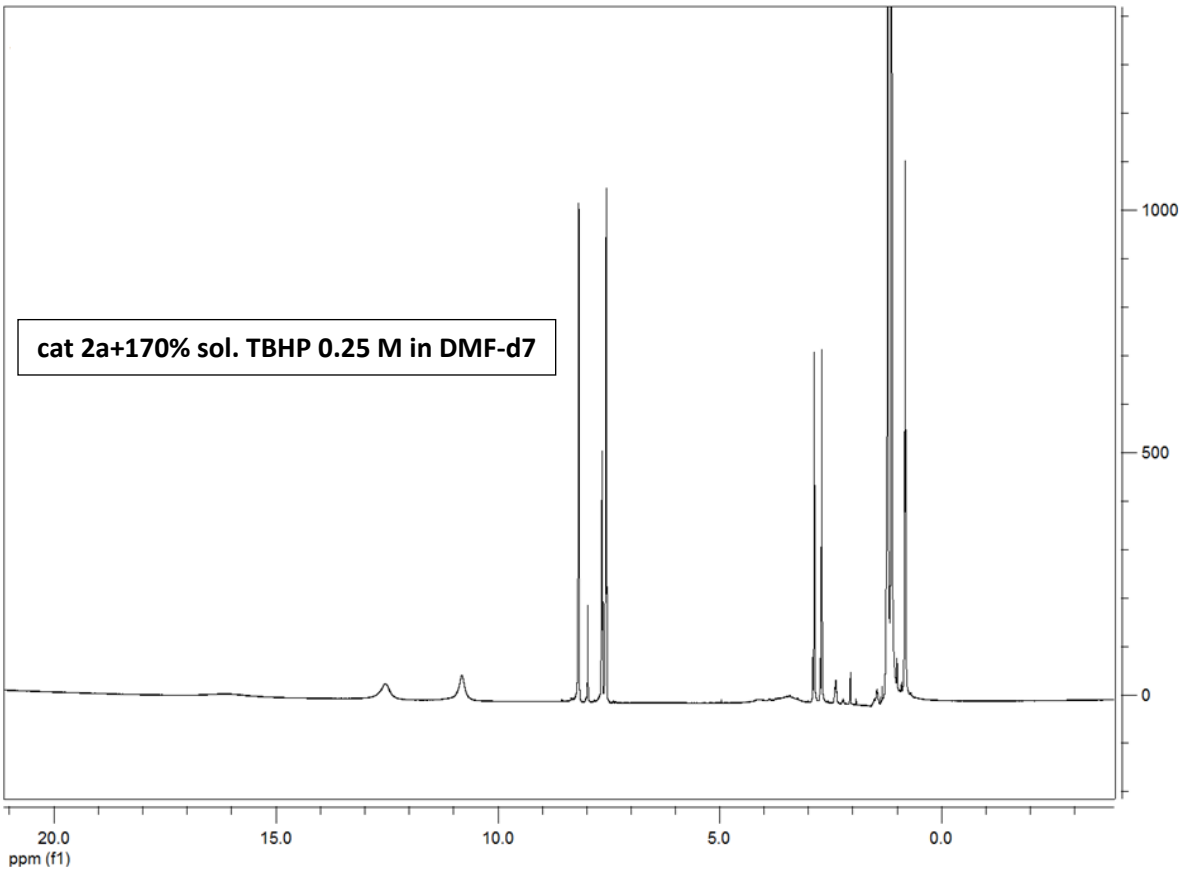

cat 2a+20% sol. TBHP 0.25 M in DMF-d7
5000
4000
3000
2000
1000
0
20.0
15.0
10.0
5.0
0.0
ppm (f1)

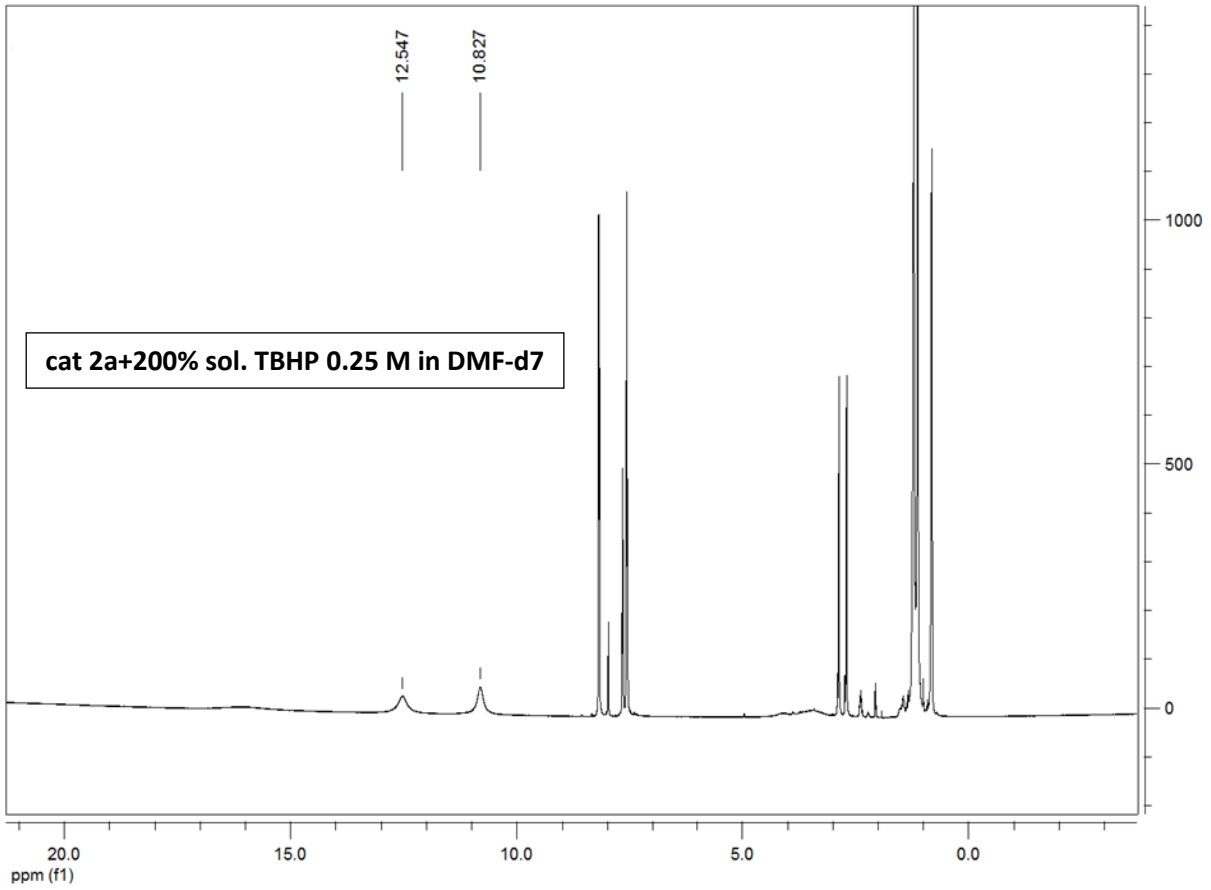

cat 2a+40% sol. TBHP 0.25 M in DMF-d7
2500
2000
1500
1000
500
0
20.0
15.0
10.0
5.0
0.0
ppm (f1)

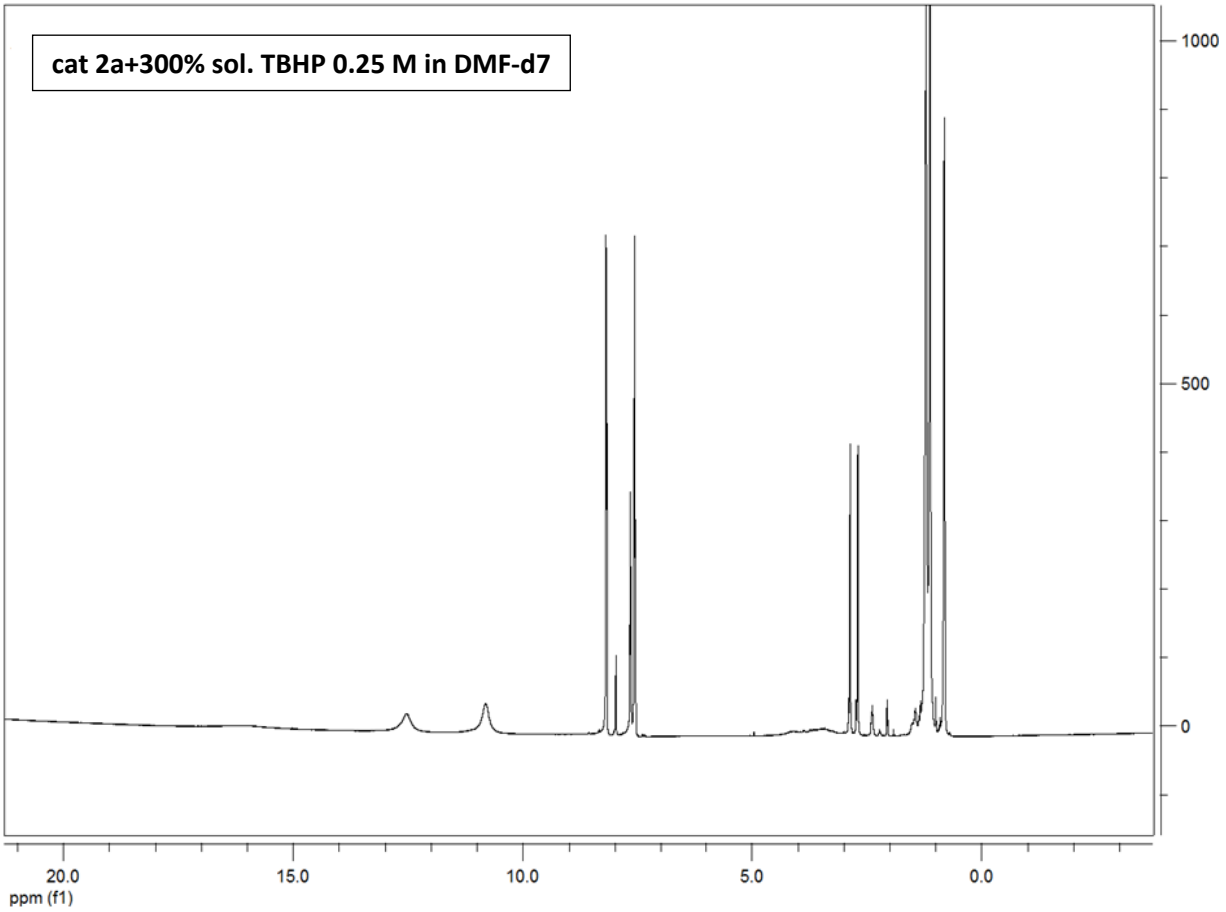

cat 2a+80% sol. TBHP 0.25 M in DMF-d7
3500
3000
2500
2000
1500
1000
500
0
20.0
15.0
10.0
5.0
0.0
ppm (f1)

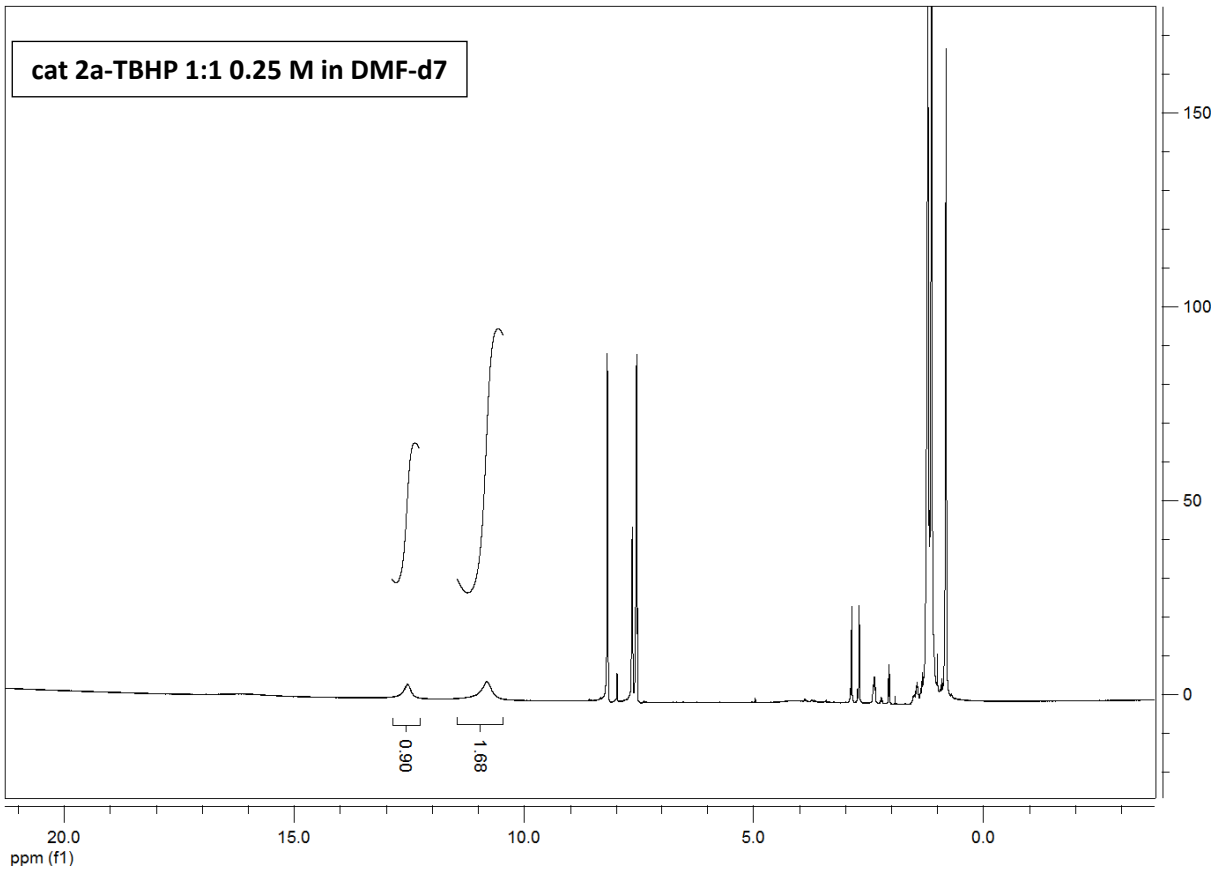

cat 2a+100% sol. TBHP 0.25 M in DMF-d7
2000
1500
1000
500
0
20.0
15.0
10.0
5.0
0.0
ppm (f1)

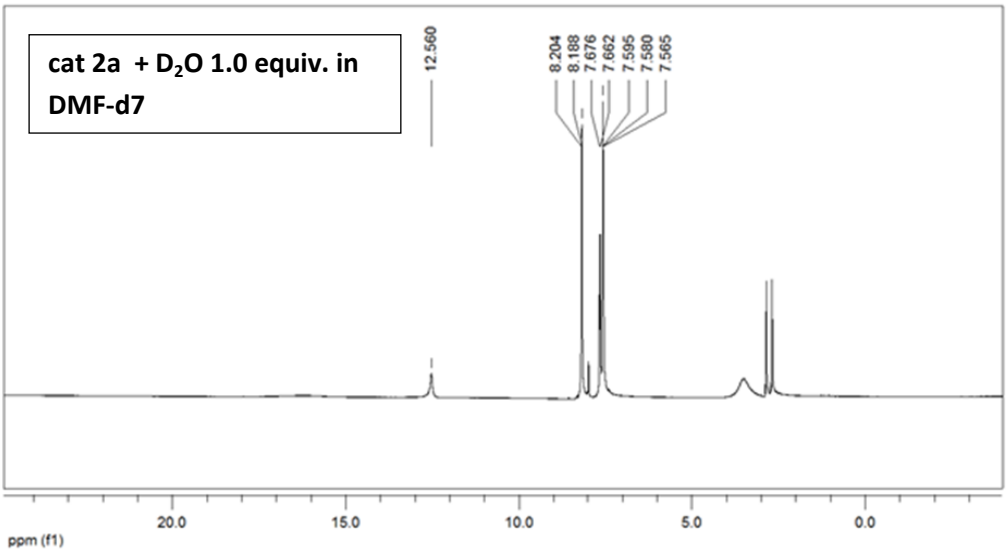

cat 2a+130% sol. TBHP 0.25 M in DMF-d7
1000
500
0
20.0
15.0
10.0
5.0
0.0
ppm (f1)

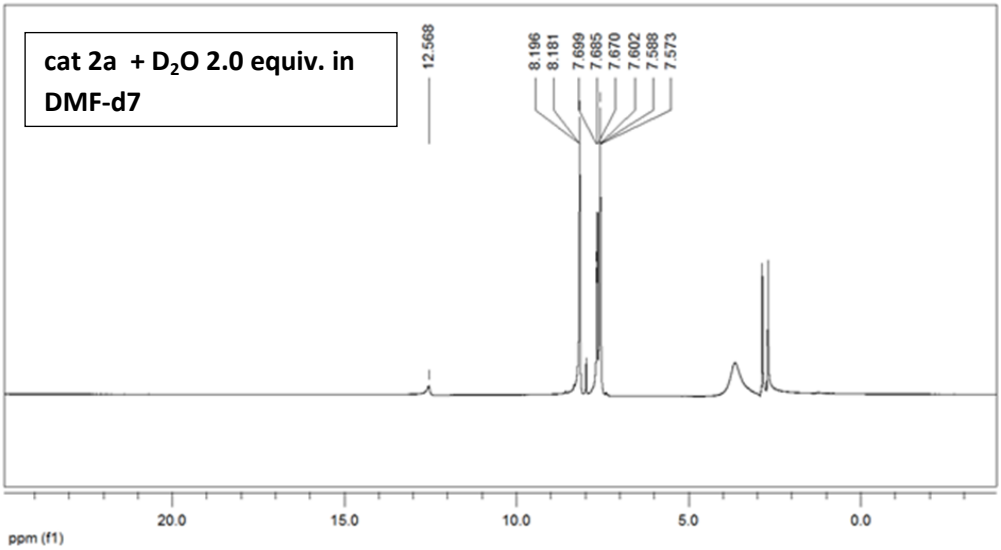

cat 2a+170% sol. TBHP 0.25 M in DMF-d7
1000
500
0
20.0
15.0
10.0
5.0
0.0
ppm (f1)


12.547
10.827
cat 2a+200% sol. TBHP 0.25 M in DMF-d7
1000
500
0
20.0
15.0
10.0
5.0
0.0
ppm (f1)


cat 2a+300% sol. TBHP 0.25 M in DMF-d7
1000
500
0
20.0
15.0
10.0
5.0
0.0
ppm (f1)


cat 2a-TBHP 1:1 0.25 M in DMF-d7
150
100
50
0
0.90
1.68
20.0
15.0
10.0
5.0
0.0
ppm (f1)


cat 2a + D2O 1.0 equiv. in DMF-d7
12.560
8.204
8.188
7.676
7.662
7.595
7.580
7.565
20.0
15.0
10.0
5.0
0.0
ppm (f1)


cat 2a + D2O 2.0 equiv. in DMF-d7
12.568
8.196
8.181
7.699
7.685
7.670
7.602
7.588
7.573
20.0
15.0
10.0
5.0
0.0
ppm (f1)

3. DFT-Optimized metric parameters

Table 3.1 DFT-optimized geometry for TBHP in orthogonal Cartesian coordinate format.

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.054168	0.000000	-0.026033
2	8	-0.008903	0.000000	1.398482
3	8	1.334236	0.000000	1.902590
4	1	1.135446	0.000000	2.846543
5	6	-1.420626	0.000000	-0.412339
6	6	0.752808	1.262920	-0.523533
7	6	0.752808	-1.262920	-0.523533
8	1	-1.523810	0.000000	-1.505824
9	1	-1.924593	-0.891056	-0.013706
10	1	-1.924593	0.891056	-0.013706
11	1	0.750337	-1.299216	-1.621937
12	1	1.793200	-1.291593	-0.176548
13	1	0.238350	-2.156719	-0.143653
14	1	0.750337	1.299216	-1.621937
15	1	0.238350	2.156719	-0.143653
16	1	1.793200	1.291593	-0.176548

Table 3.2. DFT-optimized geometry for **2a** in orthogonal Cartesian coordinate format.

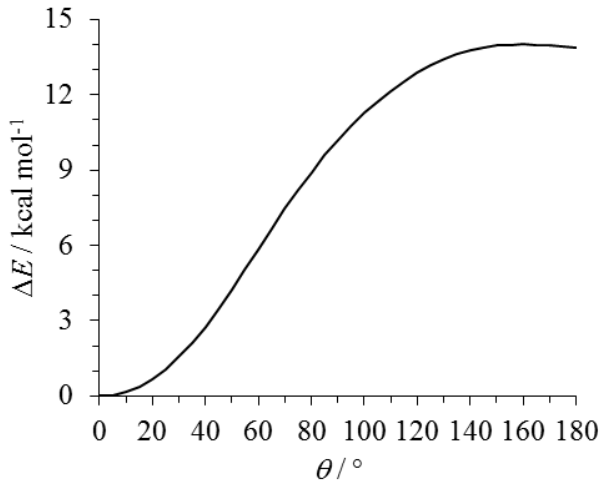
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	0.039523	0.147031	-0.003513
2	6	0.030625	0.166088	1.321863
3	7	1.244213	0.036604	1.859853
4	7	2.042801	-0.070705	0.801622
5	7	1.334787	-0.006860	-0.295386
6	7	-1.058616	0.326153	2.187958
7	6	-2.391990	0.333819	1.952867
8	8	-2.934459	0.170419	0.875642
9	6	-3.233856	0.555760	3.194339
10	6	-4.574778	0.162004	3.122180
11	6	-5.427555	0.332933	4.207874
12	6	-4.956266	0.919659	5.383319
13	6	-3.628586	1.337310	5.458792
14	6	-2.773988	1.157688	4.371816
15	1	-6.468961	0.010796	4.137935
16	1	-4.916429	-0.273433	2.181916
17	1	-1.745695	1.518792	4.440666
18	1	-3.255034	1.814693	6.367241
19	1	-5.624665	1.059121	6.235748
20	1	-0.750466	0.344560	3.150527

Table 3.3. DFT-optimized geometry for the complex **2a**-TBHP in orthogonal Cartesian coordinate format.

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.086930	0.028138	-0.079202
2	6	0.007469	0.035760	1.318983
3	6	1.174135	-0.138913	2.071344
4	6	2.394977	-0.347329	1.438938
5	6	2.466338	-0.366135	0.045694
6	6	1.312664	-0.171143	-0.711691
7	6	-1.264138	0.263554	2.085655
8	8	-1.267085	0.626830	3.234351
9	7	-2.417006	-0.007074	1.362892
10	6	-3.709982	0.159815	1.798926
11	7	-4.741110	-0.447205	1.179122
12	7	-5.871761	-0.070047	1.786123
13	7	-5.525743	0.717810	2.731766
14	7	-4.193328	0.892808	2.776438
15	1	3.298065	-0.490646	2.034548
16	1	1.094272	-0.102679	3.158533
17	1	-0.800510	0.209738	-0.689040
18	1	1.368827	-0.161315	-1.801659
19	1	3.425400	-0.523062	-0.451201
20	1	-2.325730	-0.486304	0.471143
21	1	-4.732551	-1.082148	0.375455
22	8	-2.847037	-1.553607	-1.258808
23	8	-4.195118	-1.993244	-1.166271
24	1	-2.367371	-2.394123	-1.308207
25	6	-4.911802	-1.730603	-2.403578
26	6	-6.306705	-2.236718	-2.059867
27	6	-4.908976	-0.237185	-2.697317
28	6	-4.279904	-2.537856	-3.528192
29	1	-6.968539	-2.106457	-2.926231
30	1	-6.283328	-3.303173	-1.798240
31	1	-6.735601	-1.677686	-1.216549
32	1	-5.496562	-0.030775	-3.602075
33	1	-5.353656	0.327118	-1.866153
34	1	-3.887602	0.128462	-2.863709
35	1	-4.857748	-2.415321	-4.454033
36	1	-3.254656	-2.198873	-3.728922
37	1	-4.261764	-3.607872	-3.276616

3.2 Energy Surface Investigation for 2a

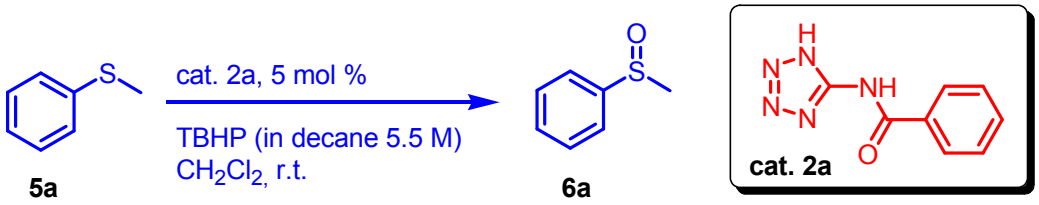
Figure S1. Potential energy surface obtained on varying the torsion angle θ of the tetrazole ring with respect to the benzene plane (dihedral N2–C1–N1–C2 in Figure 5).



4 Catalyst recovery and scaling-up experiments

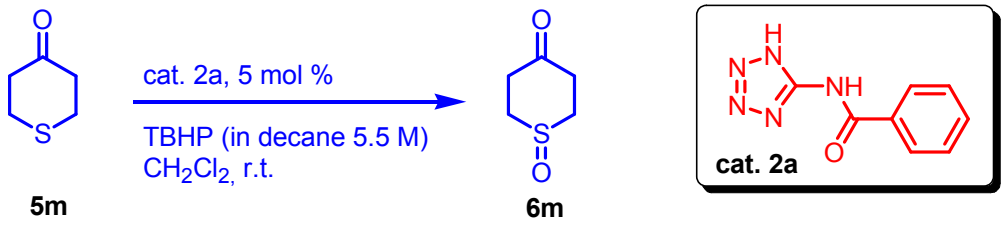
4.1 Scaling-up

Oxidation of sulphide 5a



To a solution of sulphide **5a** (10 g, 0.080 mol) and tetrazole **2a** (750 mg, 0.0040 mol) in CH_2Cl_2 (250 mL), *t*BuOOH (16 mL, 5.5 M in decane 1.1 eq.) was added dropwise over 10 min. The resulting mixture was stirred at room temperature and followed by Gc-Ms until completion. after 50h, the reaction mixture was filtered and the white solid was washed with CH_2Cl_2 3X70 mL. The organic phase was concentrated under reduced pressure and the resulting yellow oil was purified by flash chromatography (silica gel, 80:20 hexane/ether). 92 % yield. Conversion >99%, ratio **6a**/**7a** = 99:1.

Oxidation of sulphide 5m



To a solution of sulphide **5m** (10 g, 0.086 mol) and tetrazole **2a** (814 mg, 0.0043 mol) in CH_2Cl_2 (250 mL), *t*BuOOH (16 mL, 5.5 M in decane 1.1 eq.) was added dropwise over 10 min. The resulting mixture was stirred at room temperature and followed by Gc-Ms until completion. after 90h, the reaction mixture was filtered and the white solid was washed with CH_2Cl_2 3X70 mL. The organic phase was concentrated under reduced pressure and the resulting yellow oil was purified by flash chromatography (silica gel, 80:20 hexane/ether). 90 % yield. Conversion >95%, ratio **6a**/**7a** = 99:1.

4.3 Catalyst recovery. Oxidation of sulphide 5a

To value the catalyst recovery, we carried out a set of experiments as reported in table 4.1.

1) 150 mg of cat. **2a** were loaded for the oxidation of 2 g of sulphide **5a**. At completion, the reaction mixture was filtered and washed with CH_2Cl_2 (2 x 20 mL). Cat. **2a** was collected and dried under reduced pressure for 12h at room temperature. The catalyst recovery % was determined by weighting of the dried white solid. (126 mg of catalyst, 84% recovered).

2) 120 mg of cat. **2a** were loaded for the oxidation of 1.60 g of sulphide **5a**. After filtration and drying, the catalyst recovery % was determined by weighting of the dried white solid. (100 mg of catalyst, 83% recovered).
3) 100 mg of cat. **2a** were loaded for the oxidation of 1.33 g of sulphide **5a**. After filtration and drying, the catalyst recovery % was determined by weighting of the dried white solid. (86 mg of catalyst, 84% recovered).
4) 82.5 mg of cat. **2a** were loaded for the oxidation of 1.10 g of sulphide **5a**. After filtration and drying, the catalyst recovery % was determined by weighting of the dried white solid. (60 mg of catalyst, 80% recovered).
5) 60 mg of cat. **2a** were loaded for the oxidation of 0.80 g of sulphide **5a**. After filtration and drying, the catalyst recovery % was determined by weighting of the dried white solid. (43 mg of catalyst, 72% recovered).
6) 37.5 mg of cat. **2a** were loaded for the oxidation of 0.50 g of sulphide **5a**. After filtration and drying, the catalyst recovery % was determined by weighting of the dried white solid. (21 mg of catalyst, 56% recovered).

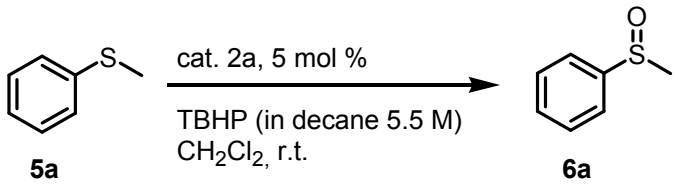


Table 4.1. Catalyst recovery.

Reaction number	Reaction scale/g	cat. 2a 5 mol % (mg)	cat. 2a recovery g/(%)	5a yield %	Time/h	6a/7a ratio
1	2.0 g	150.0 mg	126 mg (84%)	90 %	60h	99:1
2	1.60 g	120.0 mg	100 mg (83%)	87 %	60h	99:1
3	1.33 g	100.0 mg	84 mg (84%)	88 %	74h	99:1
4	1.10 g	82.5 mg	75 mg (90%)	86 %	70h	99:1
5	1.00 g	75.0 mg	60 mg (80%)	89 %	80h	98:2
6	0.80 g	60.0 mg	43 mg (72%)	78 %	80h	98:2
7	0.50 g	37.5 mg	21 mg (56%)	85%	70h	99:1

TBHP (1.1 equiv. in decane), **2a** 5 mol %, in CH_2Cl_2 (3 M), r.t. a) Yields calculated after flash chromatography. The reaction were followed by GC-Ms until completion.

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