Rhodium(I)-Catalyzed Addition of Arylboronic Acids to (Benzyl-/Arylsulfonyl)acetonitriles: Efficient Synthesis of (*Z*)-*β*-Sulfonylvinylamines and *β*-Keto Sulfones

Gavin Chit Tsui, Quentin Glenadel, Chan Lau, and Mark Lautens*

Supporting Information

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General Experimental. Unless otherwise noted, reactions were carried out under argon atmosphere, in flame-dried, single-neck, round bottom flasks fitted with a rubber septum, with magnetic stirring. Air- or water-sensitive liquids and solutions were transferred via syringe or stainless steel canula. Organic solutions were concentrated by rotary evaporation at 23–40 °C under 40 Torr (house vacuum). Analytical thin layer chromatography (TLC) was performed with Silicycle™ normal phase glass plates (0.25 mm, 60-A pore size, 230-400 mesh). Visualization was done under a 254 nm UV light source and generally by immersion in potassium permanganate ($KMnO_4$), followed by heating using a heat gun. Purification of reaction products was generally done by flash chromatography with Silicycle™ Ultra-Pure 230-400 mesh silica gel, as described by Still *et al*.[1]

Materials. $[Rh(COD)OH]_2$, $[Rh(COD)Cl]_2$, BINAP, BIPHEP, DPPP, DPPF and DPPB were purchased from Strem Chemicals Inc. and used as received. Arylboronic acids were purchased from Combi-Blocks, Inc. and Sigma-Aldrich, Inc., and used without further purification. Tetrahydrofuran, 1,4-dioxane and toluene were purified by distillation under N_2 from Na/benzophenone immediately prior to use. Ether and dichloromethane were purified by the method of Pangborn *et al*.[2] Hexanes used for chromatography was purified by simple distillation before use. Chloroacetonitrile, (phenylsulfonyl)acetonitrile **1a** and

[1] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
[2] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

benzoylacetonitrile **10** were purchased from Sigma-Aldrich, Inc., and used without further purification. Substrates **4**[3], **8**[4], **9**[5] and **11**[6] were prepared according to literature procedures.

Instrumentation. Proton nuclear magnetic resonance spectra (^{1}H NMR) spectra and carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded at 23 °C with a Varian Mercury 400 (400 MHz/100 MHz) NMR spectrometer equipped with a Nalorac4N-400 probe, or a Varian 400 (400 MHz/100 MHz) NMR spectrometer equipped with ATB8123-400 probe. Recorded shifts for protons are reported in parts per million (δ scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvents ($CHCl_3$: δ 7.26, $CHDCl_2$: δ 5.29, C_6HD_5: δ 7.15, CD_2HOD: δ 3.30). Chemical shifts for carbon resonances are reported in parts per million (δ scale) downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$: δ 77.0, CH_2Cl_2: δ 53.8, C_6D_6: δ 128.0, CD_3OD: δ 49.2). Data are represented as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet,, qn = quintuplet, sx = sextet, sp = septuplet, m = multiplet, br = broad), and coupling constant (*J*, Hz). Infrared (IR) spectra were obtained using a Perkin-Elmer Spectrum 1000 FT-IR spectrometer as a neat film on a NaCl plate. Data is presented as frequency of absorption (cm^{-1}). High resolution mass spectra were obtained from a SI2 Micromass 70S-250 mass spectrometer (EI) or an ABI/Sciex Qstar mass spectrometer (ESI). Melting points were taken on a Fisher-Johns melting point apparatus and are uncorrected.

Experimental Procedures. **General procedure (A) for the synthesis of (*Z*)-*β*-sulfonylvinylamines via Rh(I)-catalyzed addition of arylboronic acids to (phenylsulfonyl)acetonitrile (Equation 1)**: To a 2-dram vial equipped with a magnetic stir bar was added $[Rh(COD)OH]_2$ (3.0 mg, 0.0066 mmol, 2 mol%), BINAP (12.0 mg, 0.019 mmol, 6 mol%) and Cs_2CO_3 (105 mg, 0.32 mmol). The vial was capped with a septum and flushed with argon. Dioxane (1.0 mL) was added and the solution was stirred for 10 min in a 50 ^oC oil bath (slowly turned orange/reddish) then cooled to room temperature. (Phenylsulfonyl)acetonitrile **1a** (0.32 mmol, 1.0 eq.) and arylboronic acid (0.80 mmol, 2.5 eq.) were added as a solution in dioxane/H_2O (1.5 mL/0.25 mL). The vial was sealed and heated in a 75 ^oC oil bath for 14 hrs. The solvent was removed *in vacuo* and the crude was purified by flash column chromatography (EtOAc/hexanes/1% Et_3N) on silica gel.

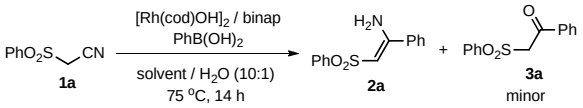
General procedure (B) for the synthesis of *β*-keto sulfones via Rh(I)-catalyzed addition of arylboronic acids to (benzyl-/arylsulfonyl)acetonitriles followed by hydrolysis (Table 2): To a 2-dram vial equipped with a magnetic stir bar was added $[Rh(COD)OH]_2$ (3.0 mg, 0.0066 mmol, 2 mol%) and BINAP (12.0 mg, 0.019 mmol, 6 mol%). The vial was capped with a septum and flushed with argon. Dioxane (1.0 mL) was

[3] Sakamoto, T.; Katoh, E.; Kondo, Y.; Yamanaka, H. *Chem. Pharm. Bull.* **1990**, *38*, 1513.
[4] Ono, T.; Tamaoka, T.; Yuasa, Y.; Matsuda, T.; Nokami, J.; Wakabayashi, S. *J. Am. Chem. Soc.* **1984**, *106*, 7890.
[5] Numata, T.; Itoh, O.; Yoshimura, T.; Oae, S. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 257.
[6] Murakami, T.; Furusawa, K. *Synthesis* **2002**, 479.

added and the solution was stirred for 10 min in a 50 ^{o}C oil bath (slowly turned orange/reddish) then cooled to room temperature. (Benzyl-/arylsulfonyl)acetonitrile **1** (0.32 mmol, 1.0 eq.) and arylboronic acid (0.80 mmol, 2.5 eq.) were added as a solution in dioxane/H_2O (1.5 mL/0.25 mL). The vial was sealed and heated in a 75 ^{o}C oil bath for 14 or 2.5 hrs. Upon completion of the catalytic reaction, 1M aqueous HCl (1 mL) was added (turned yellow) and the mixture was heated at 75 ^{o}C for 3 hrs. The reaction crude was concentrated *in vacuo* and purified by flash column chromatography (EtOAc/hexanes) on silica gel.

General procedure (C) for the synthesis of (benzyl-/arylsulfonyl)acetonitriles 1b-h (Table 2). *Sulfide synthesis*. To a 50-mL flask were added the thiol (3.6 mmol), Na_2CO_3 (0.59g, 5.6 mmol), acetone (20 mL) and chloroacetonitrile (0.23 mL, 3.6 mmol). The mixture was heated at 50 ^{o}C for 5 to 12 hrs until all starting materials were consumed. The mixture was then filtered through a funnel to remove insolubles and the filtrate was concentrated *in vacuo*. The corresponding crude sulfide product was obtained in quantitative yield and used in the next step without further purification. *Oxidation of sulfide to sulfone*. To a 100-mL flask was dissolved the sulfide (3.2 mmol) in dichloromethane (40 mL), added MCPBA (77%) (1.6 g, 7.1 mmol) as a solid portion-wise at 0 ^{o}C. The mixture was stirred at r.t. for 12 hrs then quenched with aq. sat. $Na_2S_2O_3$ solution (20 mL). The aqueous layer was extracted with dichloromethane (20 mL x 3). The combined organic layer was washed with aq. sat. $NaHCO_3$ solution, water then brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude was purified by flash column chromatography on silica gel (EtOAc/hexanes).

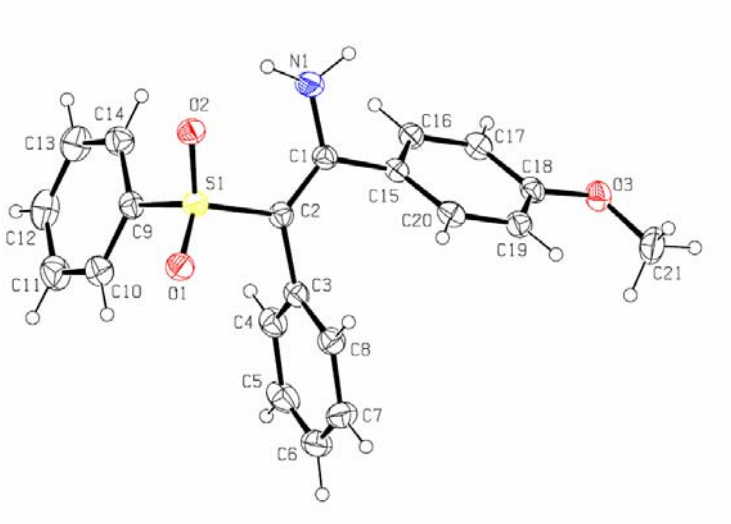
Solvent Screen. Solvent effects on the addition of phenylboronic acid to (phenylsulfonyl)acetonitrile **1a**[a]

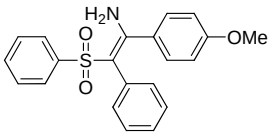


entry	solvent	conversion (%)[b]	2a:3a[b]
1	dioxane	>99 (90)[c]	7:1
2	DME	>99	7:1
3	DCE	>99	5:1
4	toluene	>99	5:1
5	THF	63	10:1
6	MeOH	33	7:1
7	MeCN	0	-

[a] All reactions were carried out using nitrile **1a** (0.2 mmol), boronic acid (0.5 mmol), $[Rh(cod)OH]_2$ (2 mol %), binap (6 mol %), solvent (2 mL), and H_2O (0.2 mL) at 75 °C for 14 h under argon. [b] Measured by ^1H NMR (400 MHz) of the crude material, using mesitylene as an internal standard. [c] Isolated yield of **2a**+**3a** (7:1) by flash column chromatography on silica gel using hexanes, ethyl acetate and 1% Et_3N as the eluent solvent. The isolated ratio did not change from the crude ratio.

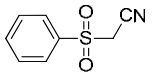
X-ray Crystal Structure of 5b. Molecular structure of **5b** showing 30% displacement ellipsoids.



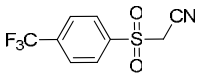


5b (*Z*-alkene)

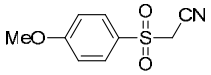
Characterization Data.



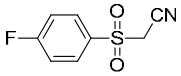
(1a): (phenylsulfonyl)acetonitrile. Purchased from Sigma-Aldrich, Inc. and used without further purification. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.07-8.03 (2H, m), 7.82-7.77 (1H, m), 7.70-7.65 (2H, m), 4.07 (2H, m) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 136.6, 135.4, 129.8, 128.8, 110.4, 45.7 ppm.



(1b): 2-((4-(trifluoromethyl)phenyl)sulfonyl)acetonitrile. Oxidation of the sulfide with MCPBA (general procedure C) gave 26% yield of the sulfoxide product (white solid, 218 mg) and no desired sulfone product. The sulfoxide (103 mg, 0.44 mmol) was dissolved in EtOH (4.3 mL), followed by the addition of ammonium molybdate tetrahydrate (114 mg, 0.092 mmol) and 30% aq. H_2O_2 (0.26 mL, 2.55 mmol) at r.t. The mixture was stirred at r.t. for 18 hrs then concentrated *in vacuo*. The crude was purified by flash column chromatography on silica gel (EtOAc/hexanes) to afford the sulfone product **1b** in quantitative yield as a white solid (110 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.20 (2H, d, J = 8.7 Hz), 7.95 (2H, d, J = 8.5 Hz), 4.11 (2H, s) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 139.9, 137.3, 136.9, 129.7, 127.0 (q, J = 3.6 Hz), 124.1, 121.4, 109.9, 45.7 ppm. **IR** (NaCl, neat film): 2986, 2932, 2261, 1404, 1381, 1335, 1319, 1296, 1157, 1142, 1107, 1084, 1065, 1015, 845 cm^{-1}. **HRMS** *m/z* (ESI): calcd. for $C_9H_7NO_2F_3S$ [MH$^+$]: 250.0144; found: 250.0137. **M.p.** 138-140 ^{o}C.

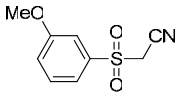


(1c): 2-((4-methoxyphenyl)sulfonyl)acetonitrile. Prepared according to general procedure C. The product was obtained as a white solid in 96% yield (475 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.96 (2H, d, J = 9.0 Hz), 7.09 (2H, d, J = 9.0 Hz), 4.04 (2H, s), 3.92 (3H, s) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.1, 131.3, 128.0, 115.0, 110.7, 55.9, 46.1 ppm. **IR** (NaCl, neat film): 2986, 2932, 2843, 2257, 1902, 1597, 1578, 1497, 1312, 1296, 1273, 1177, 1150, 1022, 833 cm^{-1}. **HRMS** *m/z* (ESI): calcd. for $C_9H_{10}NO_3S$ [MH$^+$]: 212.0375; found: 212.0381. **M.p.** 110-112 ^{o}C.

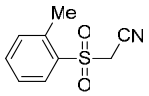


(1d): 2-((4-fluorophenyl)sulfonyl)acetonitrile. Prepared according to general procedure C. The product was obtained as a white solid in 22% yield (215 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.10-8.05 (2H, m), 7.37-7.32 (2H, m), 4.09 (2H, s) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 168.2, 165.6, 132.7, 132.6, 132.2, 132.1, 117.5, 117.3, 110.4, 45.9 ppm. **IR** (NaCl, neat film): 2990, 2936, 2257, 1593, 1586, 1493, 1319,

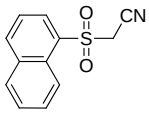
1300, 1288, 1238, 1165, 1150, 1084, 841, 745 cm^{-1}. **HRMS** *m/z* (EI): calcd. for $C_8H_6NO_2SF$ [M^+]: 199.0103; found: 199.0106. **M.p.** 82-83 °C.



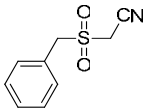
(1e): 2-((3-methoxyphenyl)sulfonyl)acetonitrile. Prepared according to general procedure C. The product was obtained as a white solid in 92% yield (696 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.63-7.53 (2H, m), 7.51-7.49 (1H, m), 7.31-7.27 (1H, m), 4.08 (2H, s), 3.90 (3H, s) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 160.3, 137.7, 130.9, 122.1, 120.8, 113.0, 110.4, 55.9, 45.7 ppm. **IR** (NaCl, neat film): 3078, 2978, 2924, 2839, 2261, 1597, 1481, 1435, 1323, 1288, 1254, 1173, 1142, 1034, 883, 752 cm^{-1}. **HRMS** *m/z* (ESI): calcd. for $C_9H_{10}NO_3S$ [MH^+]: 212.0375; found: 212.0377. **M.p.** 63-64 °C.



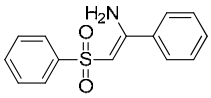
(1f): 2-(o-tolylsulfonyl)acetonitrile. Prepared according to general procedure C. The product was obtained as a white solid in 84% yield (178 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.09 (1H, dd, J = 1.4, 8.0 Hz), 7.63 (1H, dt, J = 1.4, 7.6 Hz), 7.49-7.40 (2H, m), 4.10 (2H, s), 2.75 (3H, s) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 139.1, 135.6, 135.2, 133.6, 131.6, 127.5, 110.4, 45.4, 20.9 ppm. **IR** (NaCl, neat film): 2982, 2928, 2261, 1593, 1566, 1474, 1458, 1389, 1331, 1246, 1161, 1150, 1130, 1061, 872, 752 cm^{-1}. **HRMS** *m/z* (ESI): calcd. for $C_9H_{10}NO_2S$ [MH^+]: 196.0426; found: 196.0424. **M.p.** 49-50 °C.



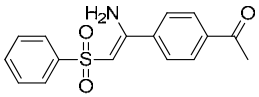
(1g): 2-(naphthalen-1-ylsulfonyl)acetonitrile. Prepared according to general procedure C. The product was obtained as a pale yellow solid in 72% yield (527 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.70 (1H, d, J = 8.6 Hz), 8.45 (1H, dd, J = 1.0, 7.4 Hz), 8.25 (1H, d, J = 8.2 Hz), 8.04 (1H, d, J = 8.1 Hz), 7.80-7.75 (1H, m), 7.71-7.66 (2H, m), 4.27 (2H, s) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 137.0, 134.3, 132.7, 131.4, 129.7 (2), 128.5, 127.6, 124.5, 123.1, 110.1, 45.2 ppm. **IR** (NaCl, neat film): 2978, 2924, 2257, 1508, 1331, 1173, 1126, 976, 806, 768 cm^{-1}. **HRMS** *m/z* (EI): calcd. for $C_{12}H_9NO_2S$ [M^+]: 231.0354; found: 231.0350.
M.p. 104-106 °C.



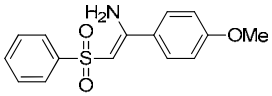
(1h): 2-(benzylsulfonyl)acetonitrile. Prepared according to general procedure C. The product was obtained as a white solid in 47% yield (332 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.56-7.52 (2H, m), 7.49-7.45 (3H, m), 4.75 (2H, s), 4.56 (2H, s) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 133.1, 131.0, 130.7, 129.1, 113.0, 61.1, 42.8 ppm. The characterization data are fully concordant with the literature report.[7]



(2a): (*Z*)-1-phenyl-2-(phenylsulfonyl)ethenamine. Prepared according to general procedure A. The product was obtained as a viscous yellow oil in 91% yield (76 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.97-7.93 (2H, m), 7.57-7.36 (8H, m), 5.99 (2H, br. s), 5.09 (s, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.5, 144.4, 136.8, 132.3, 130.8, 128.9 (2), 126.3, 125.9, 91.7 ppm. **IR** (NaCl, neat film): 3457, 3356, 3237, 3063, 3028, 1628, 1620, 1559, 1550, 1447, 1296, 1285, 1134, 1084, 833, 721 cm^{-1}. **HRMS** *m/z* (EI): calcd. for $C_{14}H_{13}NO_2S$ [M$^+$]: 259.0667; found: 259.0668.



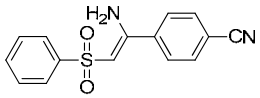
(2b): (*Z*)-1-(4-(1-amino-2-(phenylsulfonyl)vinyl)phenyl)ethanone. Prepared according to general procedure A. The product was obtained as an off-white solid in 96% yield (92 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.96-7.92 (4H, m), 7.58-7.49 (5H, m), 6.11 (2H, br. s), 5.11 (1H, s), 2.59 (3H, s) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.1, 155.0, 144.0, 141.0, 138.7, 132.5, 129.0, 128.8, 126.7, 126.0, 93.1, 26.7 ppm. **IR** (NaCl, neat film): 3449, 3349, 3237, 3071, 3005, 1686, 1620, 1578, 1551, 1447, 1358, 1300, 1285, 1269, 1134, 1080, 856, 826, 687 cm^{-1}. **HRMS** *m/z* (ESI): calcd. for $C_{16}H_{16}NO_3S$ [MH$^+$]: 302.0845; found: 302.0855. **M.p.** 134-136 ^{o}C.



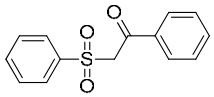
(2c): (*Z*)-1-(4-methoxyphenyl)-2-(phenylsulfonyl)ethenamine. Prepared according to general procedure A. The product was obtained as a viscous yellow oil in 97% yield (89 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.96-7.93 (2H, m), 7.57-7.47 (3H, m), 7.44-7.39 (2H, m), 6.91-6.87 (2H, m), 5.97 (2H, br. s), 5.06 (1H, s), 3.81 (3H, s) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.7, 156.2, 144.6, 132.2, 128.9 (2), 127.7, 125.9,

[7] Bostick, T. M.; Christie, S. D.; Connolly, T. J.; Copp, S.; Langler, R. F.; Reid, D. L.; Zaworotko, M. *Aust. J. Chem.* **1996**, *49*, 243.

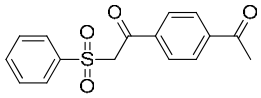
114.2, 90.7, 55.4 ppm. **IR** (NaCl, neat film): 3457, 3356, 3237, 3067, 3013, 2963, 2936, 2839, 1609, 1543, 1512, 1447, 1424, 1285, 1258, 1180, 1130, 1084, 1026, 849, 752 cm^{-1}. **HRMS** *m/z* (ESI): calcd. for $C_{15}H_{16}NO_3S$ [MH^+]: 290.0845; found: 290.0833.



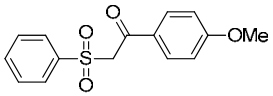
(2d): **(*Z*)-4-(1-amino-2-(phenylsulfonyl)vinyl)benzonitrile.** Prepared according to general procedure A. The product was obtained as a viscous yellow oil in 56% yield (51 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.95-7.92 (2H, m), 7.69-7.65 (2H, m), 7.61-7.57 (3H, m), 7.55-7.50 (2H, m), 6.07 (2H, br. s), 5.10 (1H, s) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 154.2, 143.7, 141.1, 132.7 (2), 129.1, 127.2, 126.0, 117.8, 114.3, 93.8 ppm. **IR** (NaCl, neat film): 3449, 3352, 3237, 3075, 3021, 2230, 1620, 1578, 1551, 1447, 1331, 1288, 1134, 1084, 856, 826, 741 cm^{-1}. **HRMS** *m/z* (EI): calcd. for $C_{15}H_{12}N_2O_2S$ [M^+]: 284.0619; found: 284.0613.



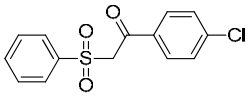
(3a): 1-phenyl-2-(phenylsulfonyl)ethanone. Prepared according to general procedure B. The product was obtained as a white solid in 97% yield (81 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.95-7.88 (4H, m), 7.68-7.59 (2H, m), 7.57-7.52 (2H, m), 7.50-7.45 (2H, m), 4.75 (2H, s) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 187.9, 138.7, 135.7, 134.3, 134.2, 129.2 (2), 128.8, 128.5, 63.4 ppm. **IR** (NaCl, neat film): 3063, 3001, 2940, 1682, 1597, 1582, 1451, 1404, 1319, 1273, 1227, 1211, 1157, 1088 cm^{-1}. **HRMS** *m/z* (EI): calcd. for $C_{14}H_{12}O_3S$ [M^+]: 260.0507; found: 260.0504. **M.p.** 93-95 ^oC.



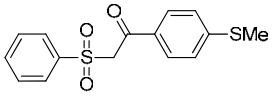
(3b): 1-(4-acetylphenyl)-2-(phenylsulfonyl)ethanone. Prepared according to general procedure B. The product was obtained as a yellow solid in 97% yield (97 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.03 (4H, br. s), 7.90-7.87 (2H, m), 7.71-7.66 (1H, m), 7.59-7.54 (2H, m), 4.77 (2H, s), 2.65 (3H, s) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.1, 187.6, 140.9, 138.6, 138.5, 134.4, 129.5, 129.3, 128.5 (2), 63.7, 26.9 ppm. **IR** (NaCl, neat film): 3063, 3001, 2940, 2924, 1682, 1504, 1451, 1404, 1312, 1265, 1157, 1088 cm^{-1}. **HRMS** *m/z* (EI): calcd. for $C_{16}H_{14}O_4S$ [M^+]: 302.0613; found: 302.0609. **M.p.** 132-134 ^oC.



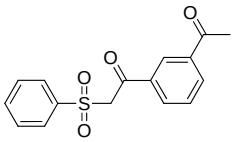
(3c): 1-(4-methoxyphenyl)-2-(phenylsulfonyl)ethanone. Prepared according to general procedure B. The product was obtained as a yellow solid in 95% yield (88 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* 7.95-7.87 (4H, m), 7.68-7.63 (1H, m), 7.56-7.52 (2H, m), 6.96-6.92 (2H, m), 4.68 (2H, s), 3.88 (3H, s) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): *δ* 186.1, 164.5, 138.7, 134.1, 131.8, 129.1, 128.8, 128.5, 114.1, 63.4, 55.6 ppm. **IR** (NaCl, neat film): 3063, 2940, 2847, 1667, 1597, 1574, 1512, 1451, 1427, 1319, 1265, 1180, 1157, 1088 cm^{-1}. **HRMS** *m/z* (EI): calcd. for $C_{15}H_{14}O_4S$ [M$^+$]: 290.0613; found: 290.0608. **M.p.** 116-118 ^{o}C.



(3d): 2-benzenesulfonyl-1-(4-chloro-phenyl)-ethanone. Prepared according to general procedure B. The product was obtained as an off-white solid in 92% yield (90 mg). **^{1}H NMR** (400MHz, $CDCl_3$): δ 7.91-7.85 (4H, m), 7.71-7.64 (1H, m), 7.59-7.52 (2H, m), 7.48-7.43 (2H, m), 4.70 (2H, s) ppm. **^{13}C NMR** (100MHz, $CDCl_3$): δ 186.9, 141.2, 138.6, 134.4, 134.1, 130.8, 129.3, 129.3, 128.6, 63.6 ppm. **IR** (NaCl, neat film): 3001, 2951, 2905, 1694, 1674, 1589, 1447, 1412, 1308, 1277, 1157, 1084, 1003, 799, 756, 687 cm^{-1}. **MS** *m/z* (ESI): calcd. for $C_{14}H_{12}O_3SCl$ [MH$^+$]: 295.0190 ; found: 295.0191. **M.p.** 126-127 °C.

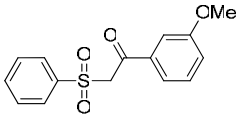


(3e): 2-benzenesulfonyl-1-(4-methylsulfanyl-phenyl)-ethanone. Prepared according to general procedure B. The product was obtained as a white solid in 86% yield (84 mg). **^{1}H NMR** (400MHz, $CDCl_3$): δ 7.83-7.76 (4H, m), 7.62-7.57 (1H, m), 7.51-7.45 (2H, m), 7.21-7.18 (2H, m), 4.62 (2H, s), 2.46 (3H, s) ppm. **^{13}C NMR** (100MHz, $CDCl_3$): δ 186.7, 148.3, 138.7, 134.3, 131.9, 129.7, 129.2, 128.6, 124.9, 63.5, 14.6 ppm. **IR** (NaCl, neat film): 3063, 2924, 1670, 1589, 1447, 1408, 1323, 1312, 1285, 1192, 1153, 1084, 999, 791, 756, 737, 687 cm^{-1}. **MS** *m/z* (ESI): calcd. for $C_{15}H_{15}O_3S_2$ [MH$^+$]: 307.0457 ; found: 307.0464. **M.p.** 119-120 °C.

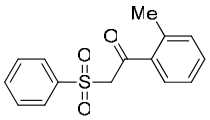


(3f): 1-(3-acetyl-phenyl)-2-benzenesulfonyl-ethanone. Prepared according to general procedure B. The product was obtained as a yellow solid in 92% yield (89 mg). **^{1}H NMR** (400MHz, $CDCl_3$): δ 8.49-8.48 (1H, m), 8.23-8.14 (2H, m), 7.92-7.88 (2H, m), 7.71-7.66 (1H, m), 7.62 (1H, t, *J* = 7.8 Hz), 7.59-7.54 (2H, m),

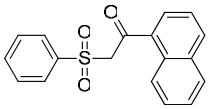
4.79 (2H, s), 2,66 (3H, s) ppm. **^{13}C NMR** (100MHz, $CDCl_3$): δ 196.8, 187.5, 138.7, 137.6, 136.1, 134.4, 133.6, 133.5, 129.4 (2), 129.0, 128.6, 63.6, 26.7 ppm. **IR** (NaCl, neat film): 3067, 2924, 2851, 1686, 1597, 1447, 1362, 1323, 1308, 1238, 1153, 1084, 1015, 791, 760, 687 cm^{-1}. **MS** *m/z* (ESI): calcd. for $C_{16}H_{15}O_4S$ [MH^+]: 303.0685 ; found: 303.0693. **M.p.** 133-134 °C.



(3g): 2-benzenesulfonyl-1-(3-methoxy-phenyl)-ethanone. Prepared according to general procedure B. The product was obtained as an off-white solid in 98% yield (91 mg). **^{1}H NMR** (400MHz, $CDCl_3$): δ 7.86-7.82 (2H, m), 7.62-7.57 (1H, m), 7.51-7.42 (3H, m), 7.38-7.36 (1H, m), 7.31 (1H, t, *J* = 8.0 Hz), 7.11-7.07 (1H, m), 4.65 (2H, s), 3.77 (3H, s) ppm. **^{13}C NMR** (100MHz, $CDCl_3$): δ 187.8, 160.0, 138.8, 137.1, 134.3, 129.9, 129.2, 128.6, 122.2, 121.2, 113.0, 63.6, 55.5 ppm. **IR** (NaCl, neat film): 3067, 3005, 2947, 2839, 1686, 1678, 1670, 1597, 1582, 1489, 1466, 1447, 1435, 1281, 1258, 1231, 1153, 1138, 1084, 1045, 1015, 864, 814, 760, 741, 687, 667 cm^{-1}. **MS** *m/z* (ESI): calcd. for $C_{15}H_{15}O_4S$ [MH^+]: 291.0685 ; found: 291.0683. **M.p.** 90-91 °C.

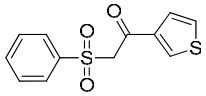


(3h): 2-benzenesulfonyl-1-*o*-tolyl-ethanone. Prepared according to general procedure B. The product was obtained as an off-white solid in 89% yield (78 mg). **^{1}H NMR** (400MHz, $CDCl_3$): δ 7.83-7.79 (2H, m), 7.65-7.56 (2H, m), 7.50-7.44 (2H, m), 7.37-7.33 (1H, m), 7.22-7.16 (2H, m), 4.34 (2H, s), 2.36 (3H, s) ppm. **^{13}C NMR** (100MHz, $CDCl_3$): δ 190.4, 140.1, 139.0, 135.7, 134.2, 132.8, 132.3, 130.4, 129.2, 128.5, 126.0, 65.5, 21.5 ppm. **IR** (NaCl, neat film): 3063, 2967, 2928, 1686, 1678, 1447, 1323, 1312, 1261, 1215, 1084, 988, 748, 687 cm^{-1}. **MS** *m/z* (ESI): calcd. for $C_{15}H_{15}O_3S$ [MH^+]: 275.0736 ; found: 275.0738. **M.p.** 48-50 °C.

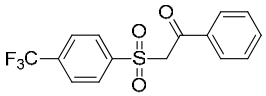


(3i): 2-benzenesulfonyl-1-naphthalen-1-yl-ethanone. Prepared according to general procedure B. The product was obtained as a pale yellow solid in 94% yield (93 mg). **^{1}H NMR** (400MHz, $CDCl_3$): δ 8.58-8.54 (1H, m), 8.04 (1H, d, *J* = 8.2 Hz), 8.01-7.98 (1H, m), 7.89-7.85 (3H, m), 7.65-7.46 (6H, m), 4.86 (2H, s) ppm. **^{13}C NMR** (100MHz, $CDCl_3$): δ 190.4, 138.8, 134.7, 134.2, 134.0, 133.4, 130.8, 130.4, 129.2, 128.9, 128.6, 128.6, 126.9, 125.6, 124.3, 66.2 ppm. **IR** (NaCl, neat film): 3059, 3005, 1678, 1508, 1447, 1323,

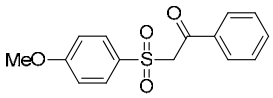
1312, 1285, 1246, 1153, 1080, 953, 799, 791, 772, 737, 687 cm^{-1}. **MS** *m/z* (ESI): calcd. for $C_{18}H_{15}O_3S$ [MH^+]: 311.0736 ; found: 311.0726. **M.p.** 135-137 °C.



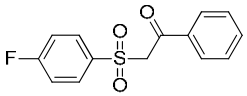
(3j): 2-(phenylsulfonyl)-1-(thiophen-3-yl)ethanone. Prepared according to general procedure B. The product was inseparable from a small amount of unreacted starting material **1a** (6.7:1 ratio), and was obtained as an off-white solid in 83% yield (70 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.20-8.18 (1H, m), 7.91-7.87 (2H, m), 7.69-7.64 (1H, m), 7.58-7.50 (3H, m), 7.34-7.31 (1H, m), 4.62 (2H, s) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 181.5, 141.1, 138.5, 135.5, 134.2, 129.2, 128.5, 127.2, 126.9, 65.1 ppm. **IR** (NaCl, neat film): 3106, 2951, 2905, 1670, 1508, 1447, 1416, 1319, 1265, 1153, 1084, 1022, 999, 876 cm^{-1}. **HRMS** *m/z* (ESI): calcd. for $C_{12}H_{11}O_3S_2$ [MH^+]: 267.0144; found: 267.0153. **M.p.** 110-112 °C.



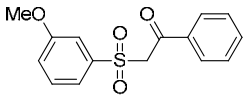
(3k): 1-phenyl-2-((4-(trifluoromethyl)phenyl)sulfonyl)ethanone. Prepared according to general procedure B. The product was obtained as a white solid in 91% yield (51 mg, 0.17 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.05 (2H, d, J = 8.2 Hz), 7.94-7.91 (2H, m), 7.82 (2H, d, J = 8.3 Hz), 7.67-7.62 (1H, m), 7.52-7.47 (2H, m), 4.79 (2H, s) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 187.7, 142.1 (2), 136.0, 135.6, 135.5, 134.6, 129.4, 129.2, 129.0, 126.3 (q, J = 3.7 Hz), 124.4, 121.7, 63.0 ppm. **IR** (NaCl, neat film): 3102, 3067, 3005, 2920, 1678, 1404, 1323, 1169, 1153, 1126, 1088, 849, 748 cm^{-1}. **HRMS** *m/z* (EI): calcd. for $C_{15}H_{11}O_3SF_3$ [M^+]: 328.0381; found: 328.0385. **M.p.** 104-106 °C.



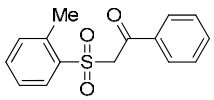
(3l): 2-((4-methoxyphenyl)sulfonyl)-1-phenylethanone. Prepared according to general procedure B. The product was obtained as a yellow solid in 99% yield (58 mg, 0.20 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.95 (2H, d, J = 7.4 Hz), 7.80 (2H, d, J = 8.7 Hz), 7.64-7.59 (1H, m), 7.51-7.46 (2H, m), 6.99 (2H, d, J = 8.8 Hz), 4.72 (2H, s), 3.87 (3H, s) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 188.3, 164.1, 135.8, 134.3, 130.8, 130.2, 129.3, 128.8, 114.3, 63.7, 55.7 ppm. **IR** (NaCl, neat film): 3063, 3005, 2947, 2843, 1678, 1597, 1578, 1497, 1447, 1323, 1300, 1261, 1150, 1088, 1022, 1003, 837, 752 cm^{-1}. **HRMS** *m/z* (EI): calcd. for $C_{15}H_{14}O_4S$ [M^+]: 290.0613; found: 290.0612. **M.p.** 103-105 °C.



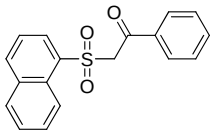
(3m): 2-((4-fluorophenyl)sulfonyl)-1-phenylethanone. Prepared according to general procedure B. The product was obtained as a white solid in 96% yield (51 mg, 0.19 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.95-7.90 (4H, m), 7.66-7.61 (1H, m), 7.52-7.47 (2H, m), 7.25-7.19 (2H, m), 4.75 (2H, s) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 188.0, 167.4, 164.8, 135.6, 134.7, 134.6, 134.5, 131.7, 131.6, 129.2, 128.9, 116.6, 116.4, 63.4 ppm. **IR** (NaCl, neat film): 3106, 3067, 2951, 1678, 1589, 1493, 1451, 1404, 1327, 1292, 1277, 1238, 1150, 1084, 995, 837, 752 cm^{-1}. **HRMS** *m/z* (EI): calcd. for $C_{14}H_{11}O_3SF$ [M$^+$]: 278.0413; found: 278.0412. **M.p.** 146-148 ^{o}C.



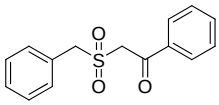
(3n): 2-((3-methoxyphenyl)sulfonyl)-1-phenylethanone. Prepared according to general procedure B. The product was obtained as an off-white solid in 93% yield (54 mg, 0.20 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.95-7.91 (2H, m), 7.64-7.59 (1H, m), 7.51-7.41 (4H, m), 7.37-7.35 (1H, m), 7.19-7.15 (1H, m), 4.74 (2H, s), 3.82 (3H, s) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 187.8, 159.9, 139.8, 135.7, 134.3, 130.3, 129.3, 128.8, 120.9, 120.6, 112.8, 63.5, 55.7 ppm. **IR** (NaCl, neat film): 3067, 3005, 2943, 2839, 1678, 1597, 1481, 1451, 1316, 1288, 1277, 1250, 1150, 1034, 1003, 752 cm^{-1}. **HRMS** *m/z* (EI): calcd. for $C_{15}H_{14}O_4S$ [M$^+$]: 290.0613; found: 290.0608. **M.p.** 80-82 ^{o}C.



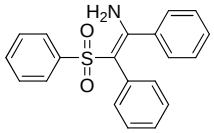
(3o): 1-phenyl-2-(o-tolylsulfonyl)ethanone. Prepared according to general procedure B. The product was obtained as a yellow solid in 97% yield (53 mg, 0.20 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.95 (2H, d, J = 8.0 Hz), 7.89 (1H, d, J = 7.9 Hz), 7.65-7.59 (1H, m), 7.55-7.45 (3H, m), 7.37-7.29 (2H, m), 4.76 (2H, s), 2.73 (3H, s) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 187.9, 138.3, 136.9, 135.8, 134.3, 134.2, 132.7, 130.5, 129.3, 128.8, 126.6, 62.9, 20.5 ppm. **IR** (NaCl, neat film): 3063, 3005, 2947, 1678, 1593, 1451, 1319, 1277, 1211, 1157, 1126, 1061, 995, 748 cm^{-1}. **HRMS** *m/z* (EI): calcd. for $C_{15}H_{14}O_3S$ [M$^+$]: 274.0664; found: 274.0672. **M.p.** 58-60 ^{o}C.



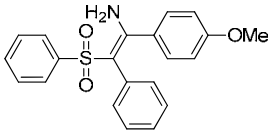
(3p): 2-(naphthalen-1-ylsulfonyl)-1-phenylethanone. Prepared according to general procedure B. The product was obtained as a viscous, colourless oil in 98% yield (61 mg, 0.20 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.79 (1H, d, J = 8.1 Hz), 8.22 (1H, dd, J = 7.4, 1.2 Hz), 8.13 (1H, d, J = 8.2 Hz), 7.98 (1H, d, J = 8.2 Hz), 7.88-7.85 (2H, m), 7.77-7.72 (1H, m), 7.67-7.62 (1H, m), 7.59-7.51 (2H, m), 7.43-7.38 (2H, m), 4.90 (2H, s) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 187.8, 135.8, 134.2, 134.1, 133.8 (2), 131.3, 129.4, 129.1, 129.0, 128.7, 127.1, 124.2, 123.6, 62.8 ppm. **IR** (NaCl, neat film): 3063, 3028, 3013, 2947, 1678, 1597, 1508, 1447, 1319, 1273, 1157, 1123, 995, 806, 772, 752 cm^{-1}. **HRMS** *m/z* (EI): calcd. for $C_{18}H_{14}O_3S$ [M$^+$]: 310.0664; found: 310.0668.



(3q): 2-(benzylsulfonyl)-1-phenylethanone. Prepared according to general procedure B. The product was obtained as a white solid in 98% yield (51 mg, 0.19 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.97-7.94 (2H, m), 7.67-7.62 (1H, m), 7.55-7.48 (4H, m), 7.42-7.38 (3H, m), 4.55 (2H, s), 4.39 (2H, s) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 189.5, 135.8, 134.6, 131.0, 129.2, 129.1, 129.0, 127.8, 59.8, 56.7 ppm. **IR** (NaCl, neat film): 3051, 2970, 2924, 1690, 1451, 1319, 1304, 1138, 999, 756, 748 cm^{-1}. **HRMS** *m/z* (ESI): calcd. for $C_{15}H_{15}O_3S$ [MH$^+$]: 275.0736; found: 275.0737. **M.p.** 106-108 ^{o}C.



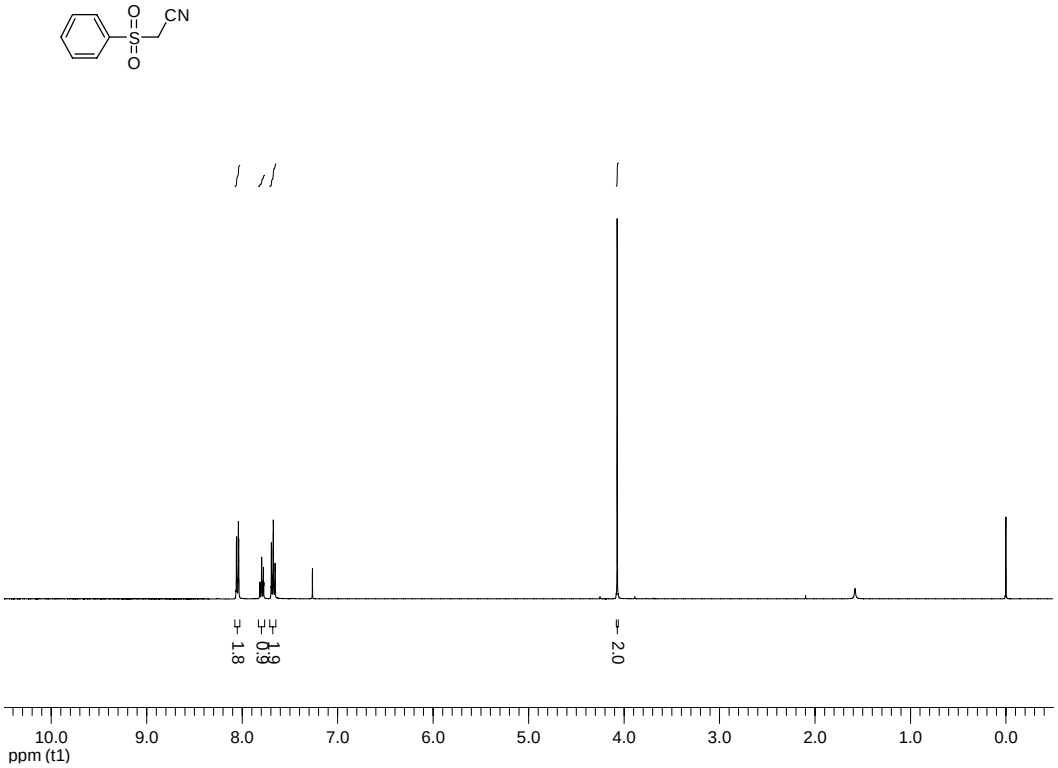
(5a): (*Z*)-1,2-diphenyl-2-(phenylsulfonyl)ethenamine. Prepared according to general procedure A without Cs_2CO_3. The reaction was run for 6 hrs. The product was obtained as a yellow solid in 91% yield (61 mg, 0.20 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.68-7.65 (2H, m), 7.50-7.45 (1H, m), 7.41-7.34 (3H, m), 7.16-7.07 (6H, m), 7.02-6.92 (3H, m), 6.90-6.86 (2H, m) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 155.3, 142.4, 137.8, 133.9, 133.5, 132.3, 128.9, 128.4, 128.3, 128.0, 127.4, 127.0, 126.8, 105.4 ppm. **IR** (NaCl, neat film): 3453, 3349, 3059, 3024, 2924, 1613, 1543, 1493, 1447, 1385, 1281, 1150, 1126, 1076, 934, 725 cm^{-1}. **HRMS** *m/z* (ESI): calcd. for $C_{20}H_{18}NO_2S$ [MH$^+$]: 336.1052; found: 336.1063. **M.p.** 108-110 ^{o}C.



(5b): (*Z*)-1-(4-methoxyphenyl)-2-phenyl-2-(phenylsulfonyl)ethenamine. Prepared according to general procedure A without Cs_2CO_3. The reaction was run for 6 hrs. The product was obtained as a yellow solid in 80% yield (93.4 mg, 0.32 mmol scale). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.69-7.65 (2H, m), 7.49-7.45 (1H, m), 7.39-7.34 (2H, m), 7.11-7.06 (2H, m), 7.03-6.96 (3H, m), 6.92-6.88 (2H, m), 6.64-6.59 (2H, m), 3.68 (3H, s) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.9, 155.1, 142.5, 133.9 (2), 132.2, 130.1, 129.8, 128.4, 127.5, 126.9 (2), 113.4, 105.1, 55.1 ppm. **IR** (NaCl, neat film): 3457, 3349, 1609, 1547, 1508, 1443, 1385, 1281, 1250, 1126, 1076, 837 cm^{-1}. **HRMS** *m/z* (EI): calcd. for $C_{21}H_{19}NO_3S$ [M^+]: 365.1086; found: 365.1084. **M.p.** 152-155 ^{o}C.

Spectra.

1a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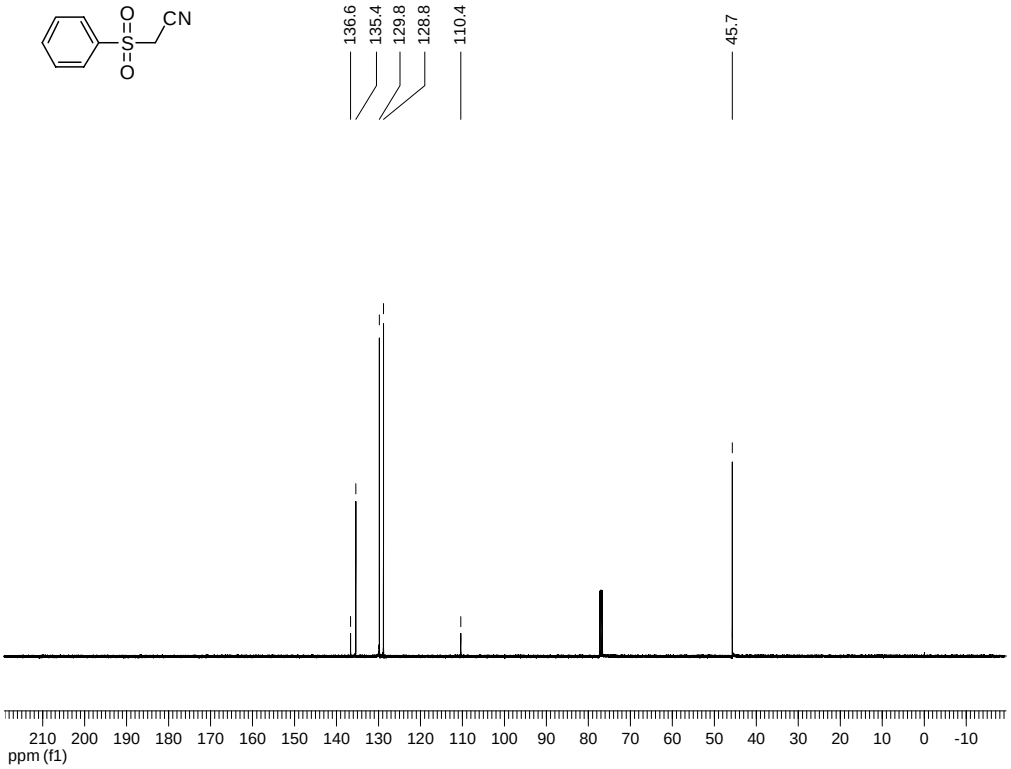
ppm (t1)


CN
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S
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136.6
135.4
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110.4
45.7
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200
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20
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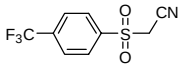
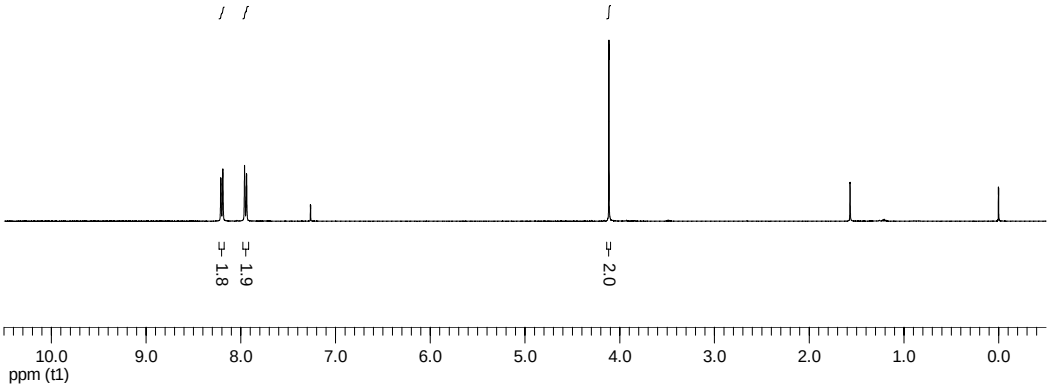
ppm (f1)

1b


F3C
O
S
O
CN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4.0
3.0
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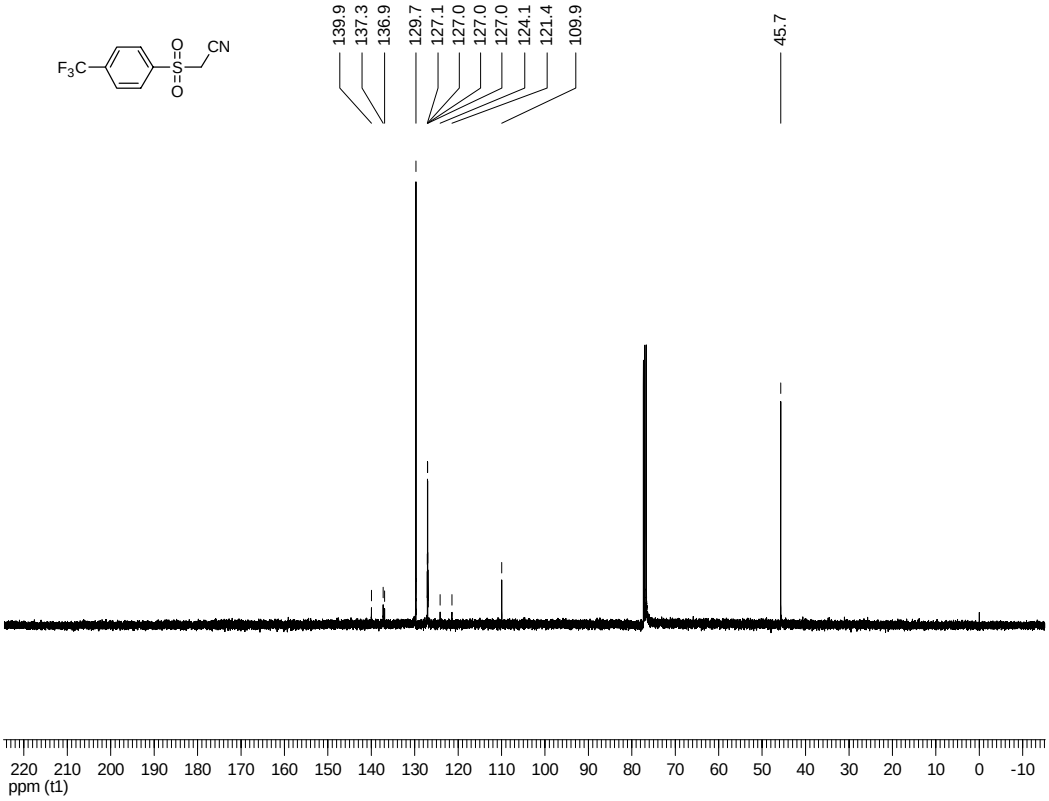
1.0
0.0
ppm (t1)

F3C
O
S
O
CN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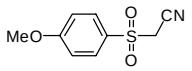
136.9
129.7
127.1
127.0
127.0
127.0
124.1
121.4
109.9
45.7
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm (t1)

1c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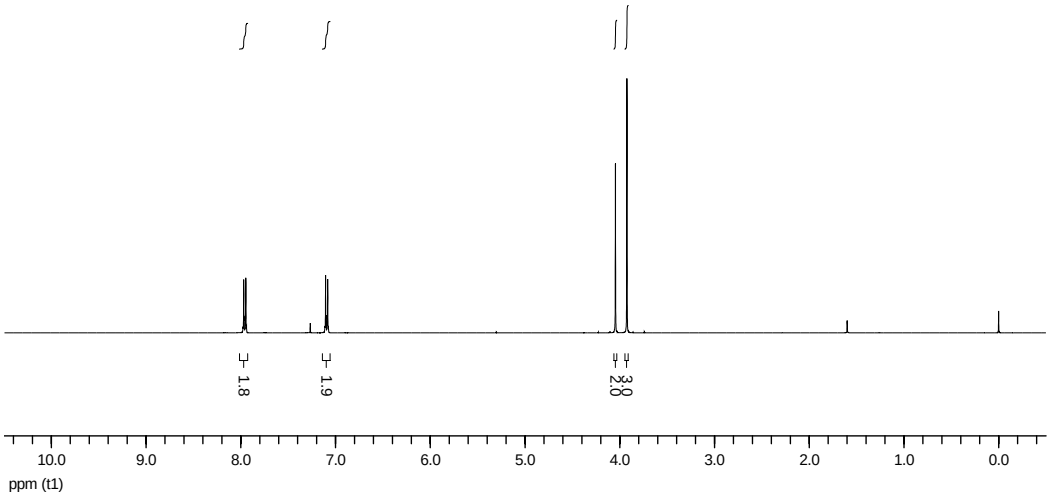
S
O
CN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ppm (t1)

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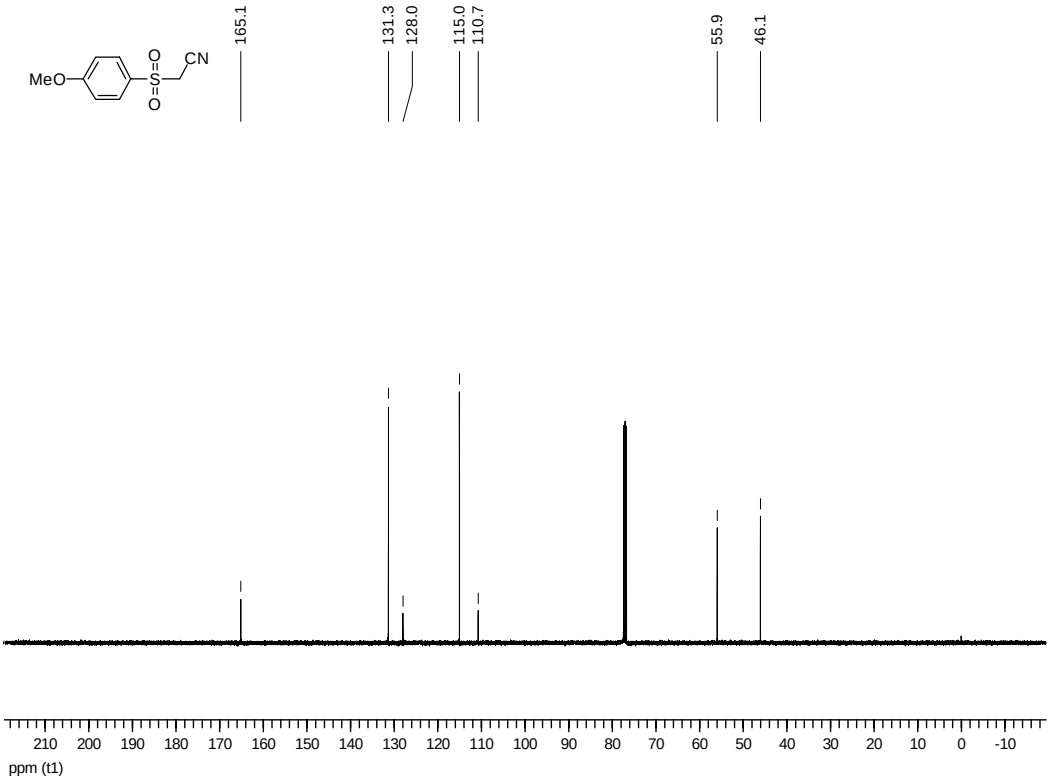
S
O
CN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20
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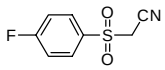
ppm (t1)

1d


F
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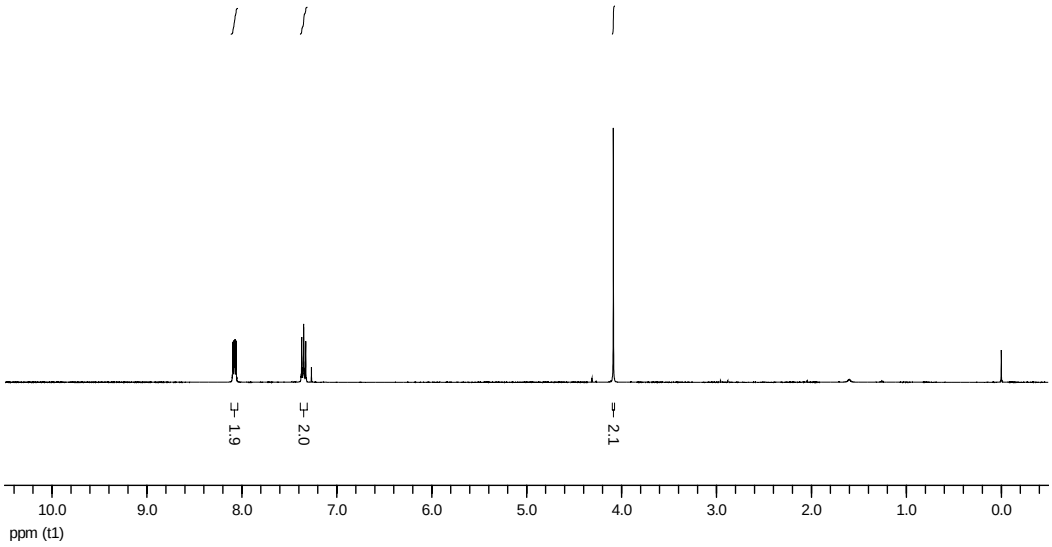
S
O
CN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4.0
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2.0
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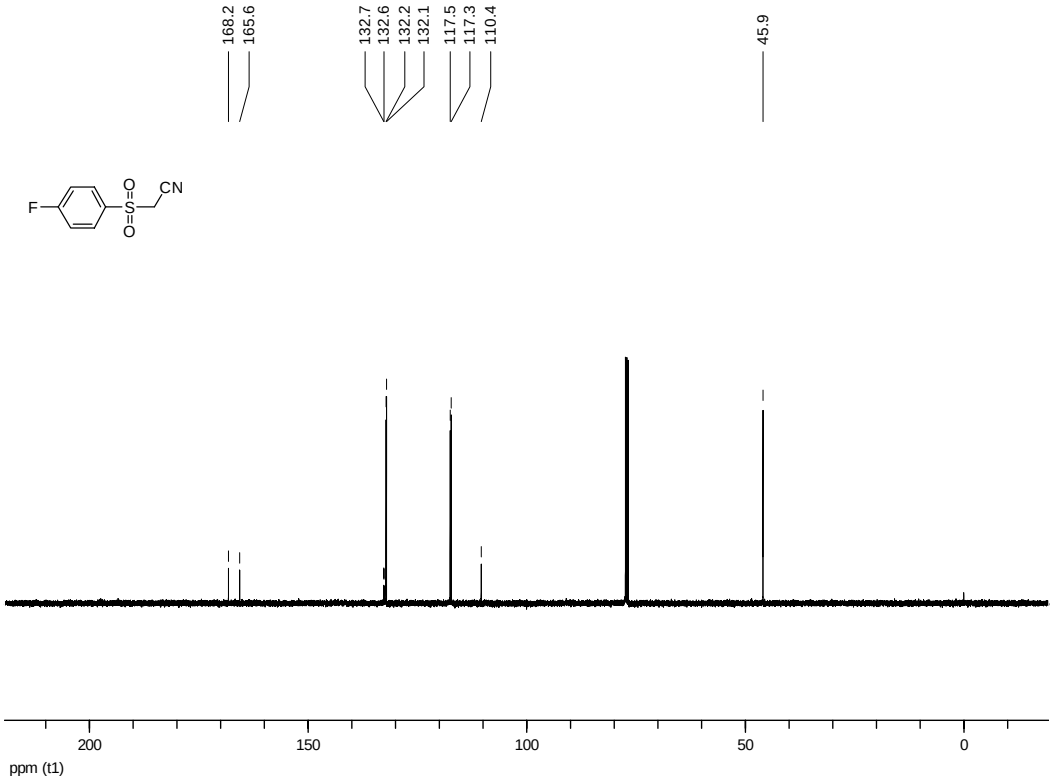
0.0
ppm (t1)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165.6
132.7
132.6
132.2
132.1
117.5
117.3
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45.9
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S
O
CN
200
150
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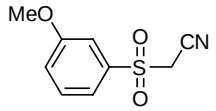
50
0
ppm (t1)

1e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S
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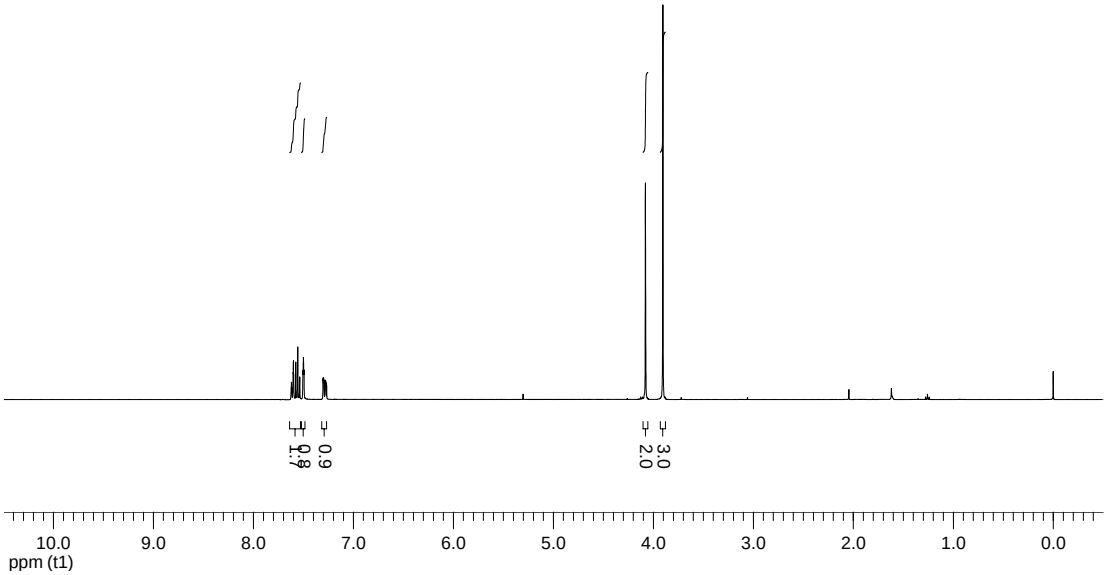
CN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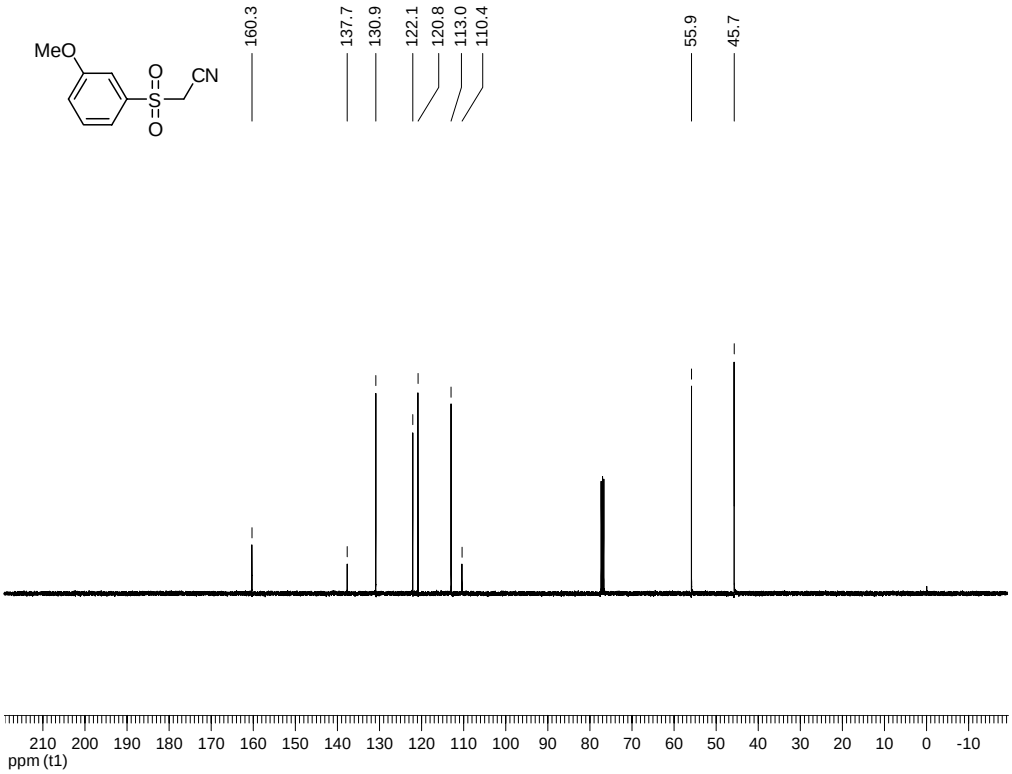
ppm (t1)

MeO
O
S
O
CN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45.7
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ppm (t1)

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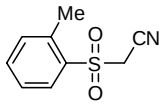
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S
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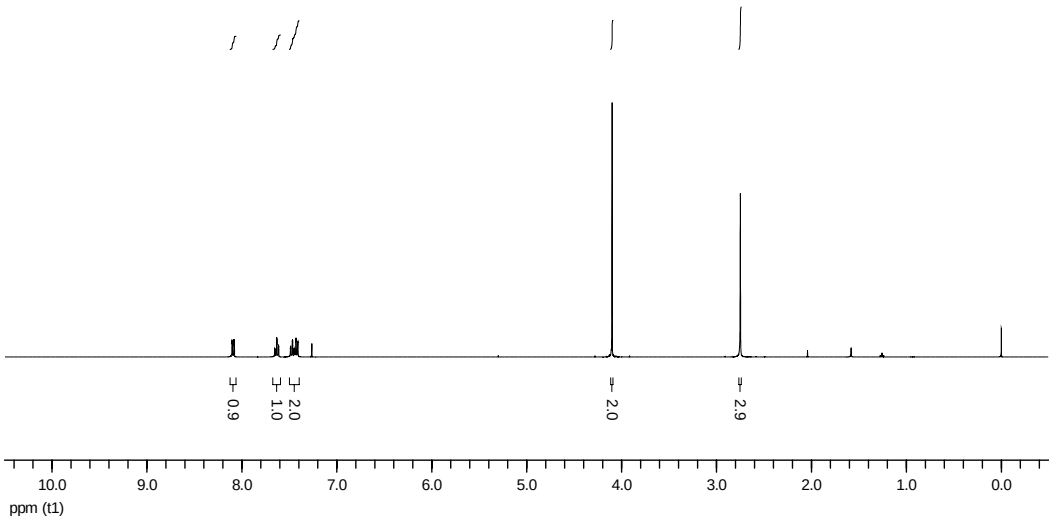
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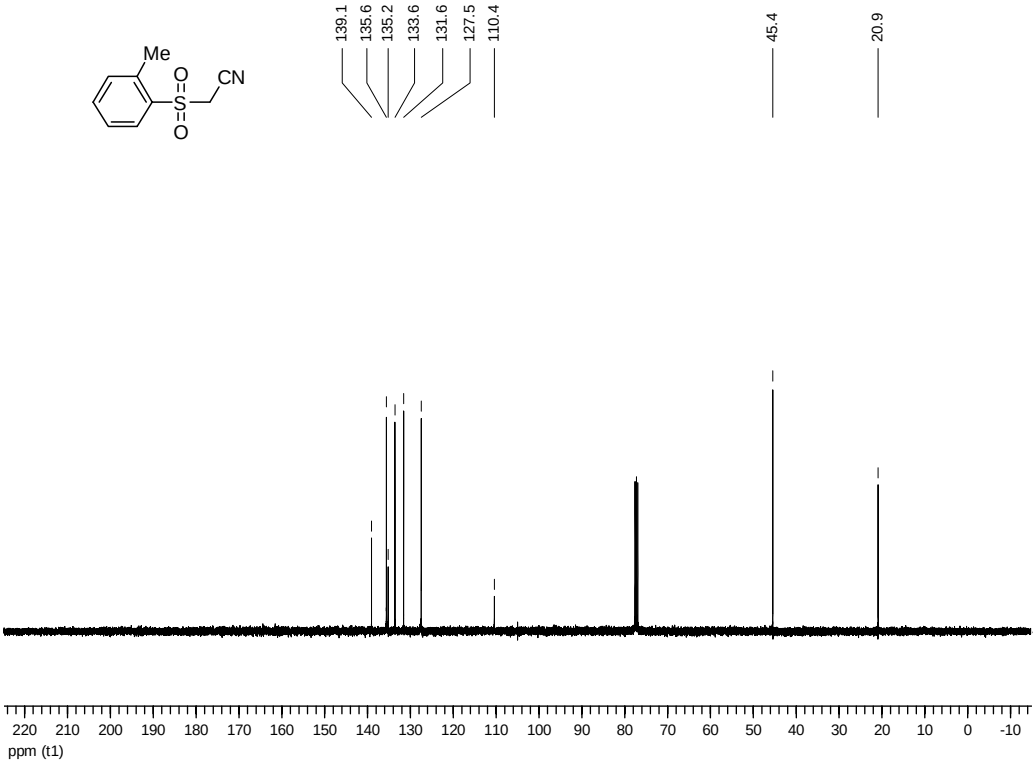
1.0
0.0
ppm (t1)

Me
O
S
O
CN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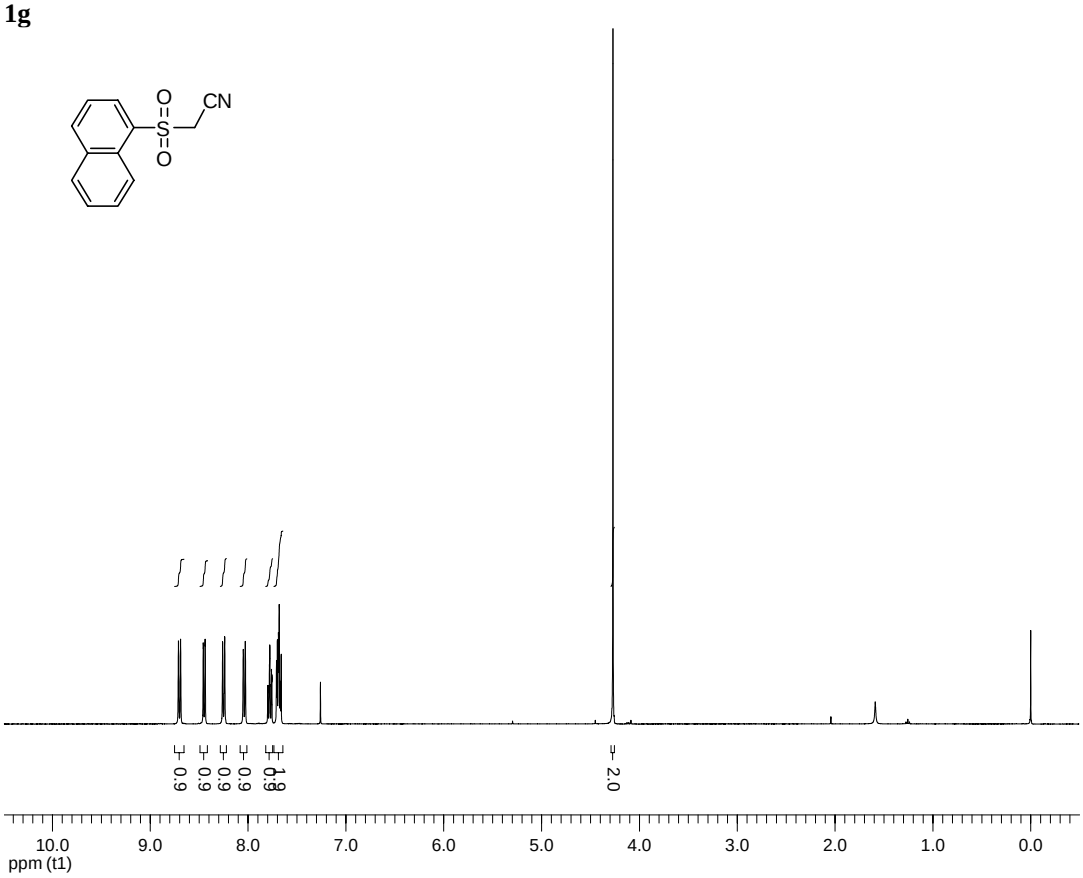
-10
ppm (t1)

1g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S
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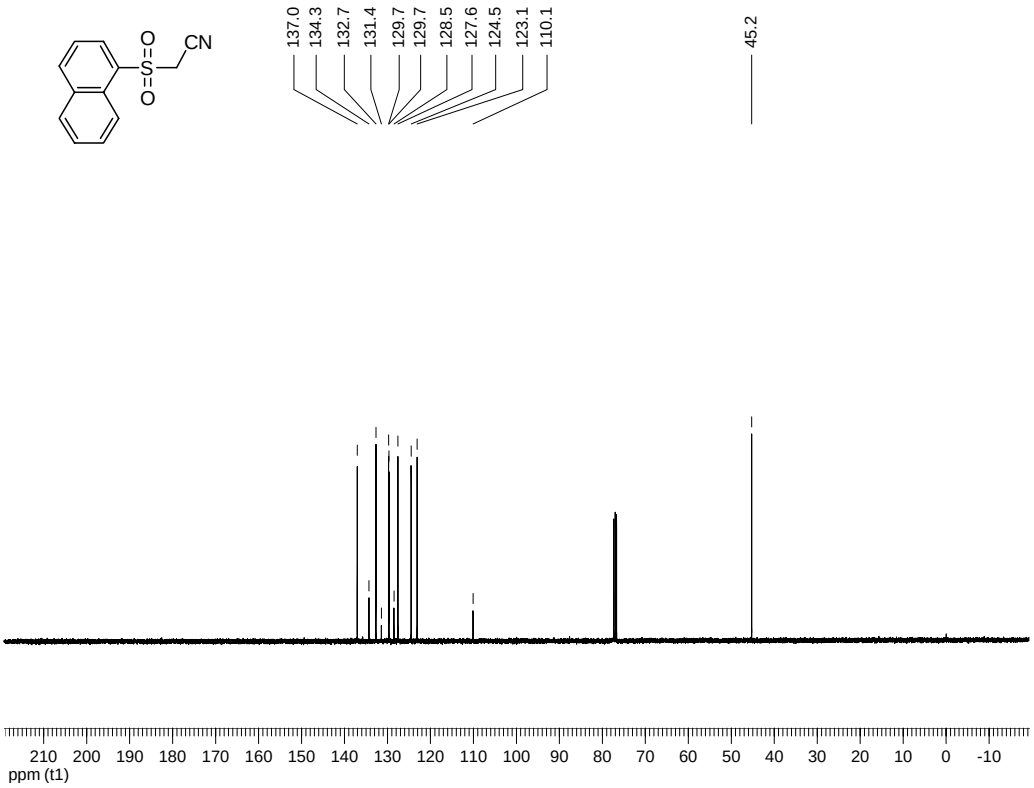
ppm (t1)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CN
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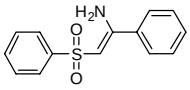
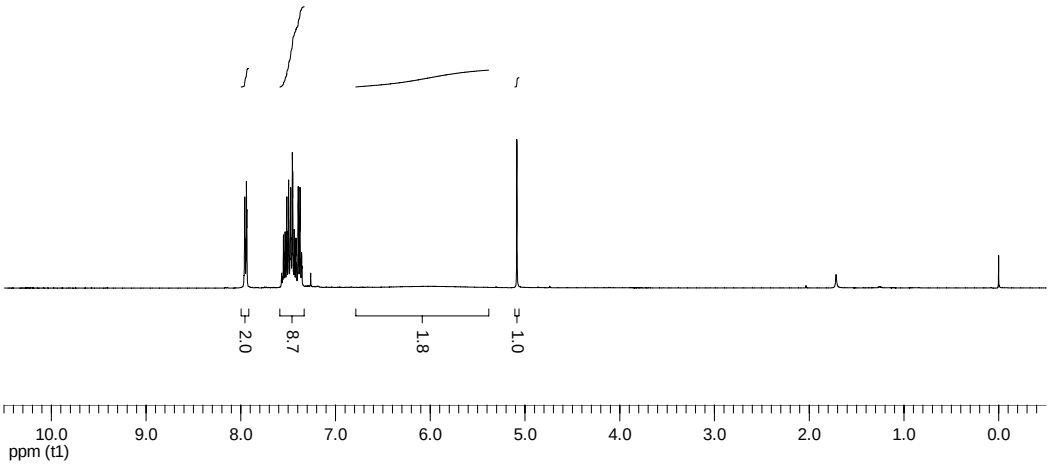
ppm (t1)

2a


H2N
O
S
O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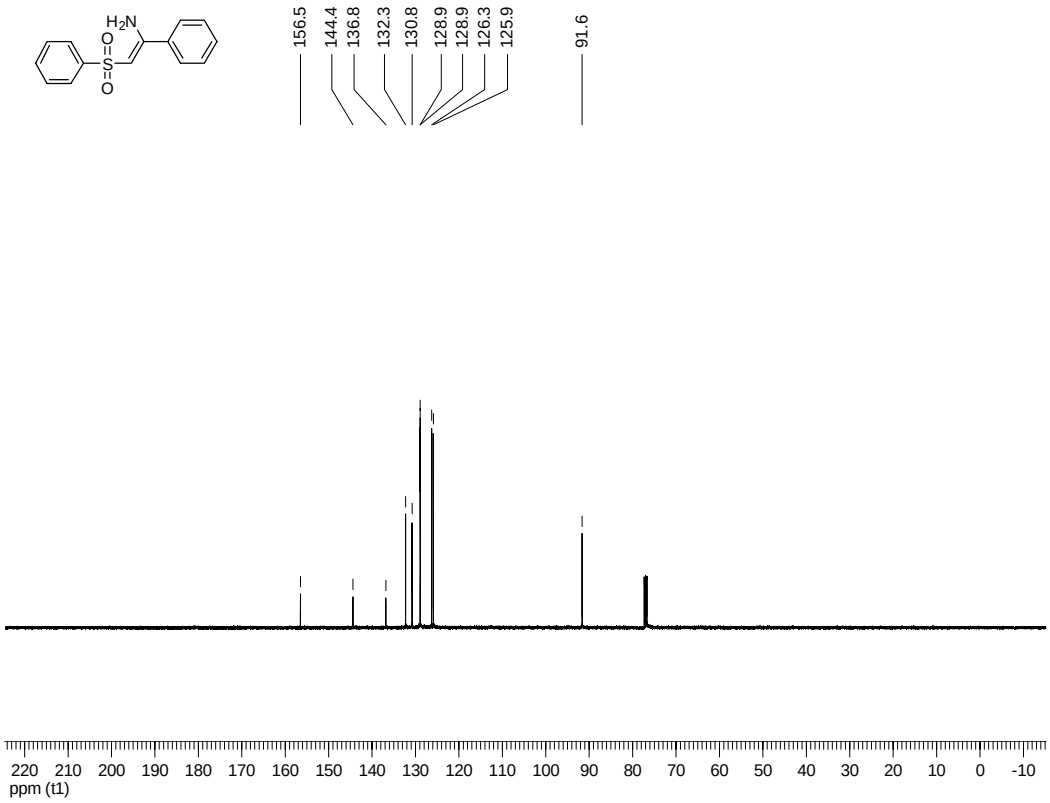
0.0
ppm (t1)

H2N
O
S
O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170
160
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90
80
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40
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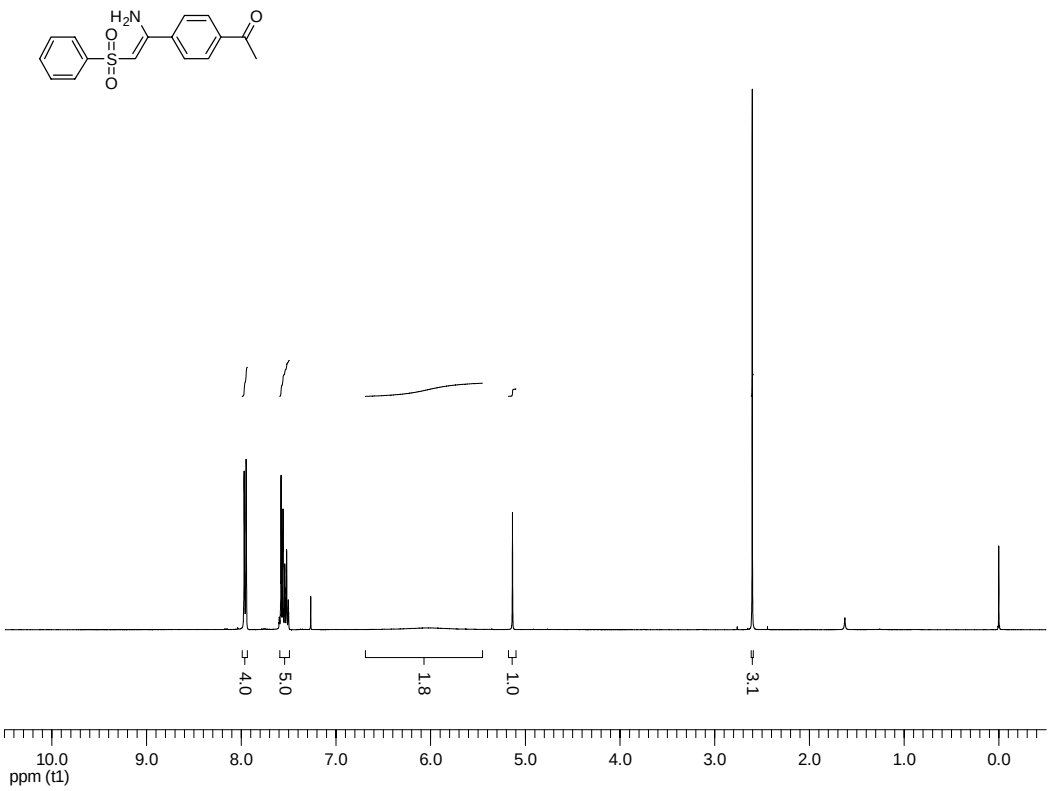
20
10
0
-10
ppm (t1)

2b


H2N
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S
O
O
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4.0
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2.0
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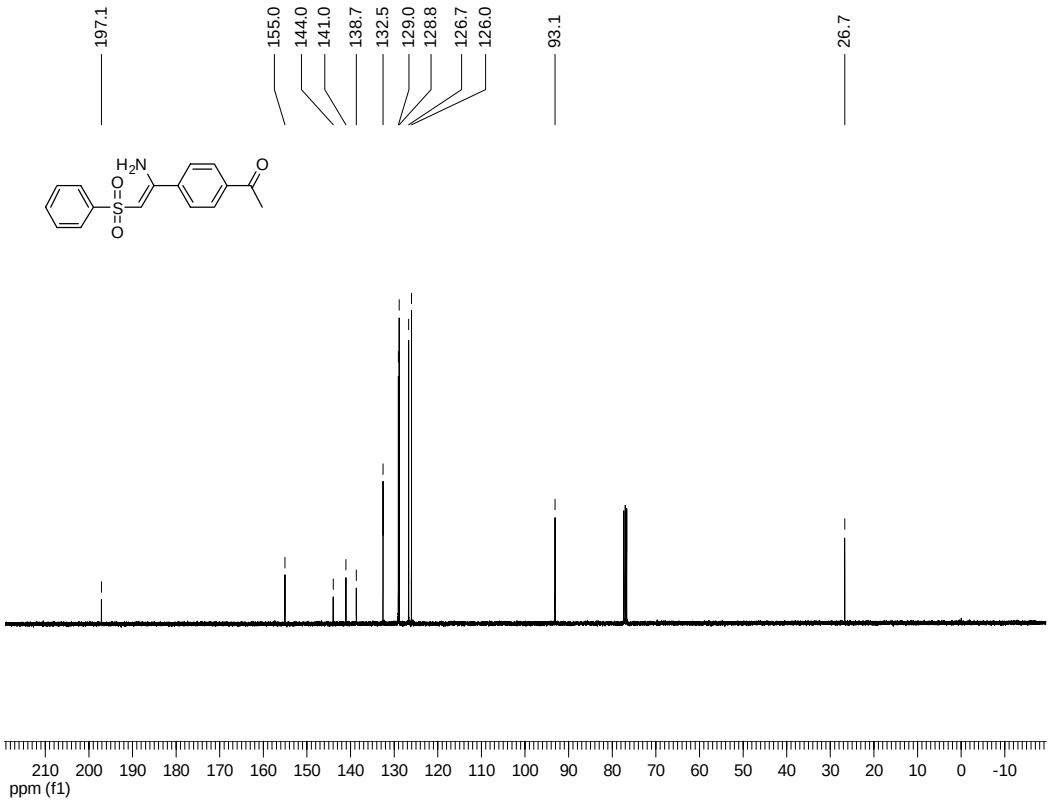
ppm (t1)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O
S
O
O
210
200
190
180
170
160
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60
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20
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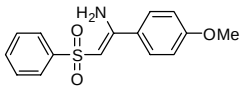
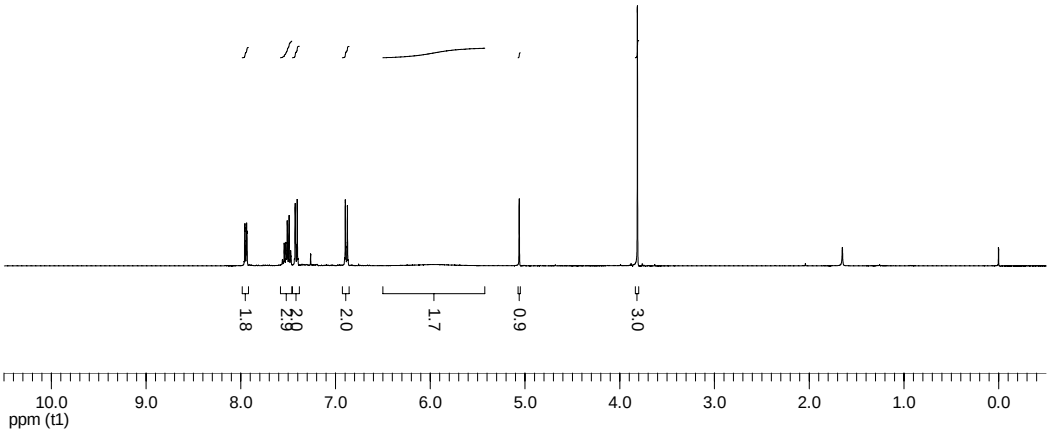
0
-10
ppm (f1)

2c


H2N
O
S
O
OMe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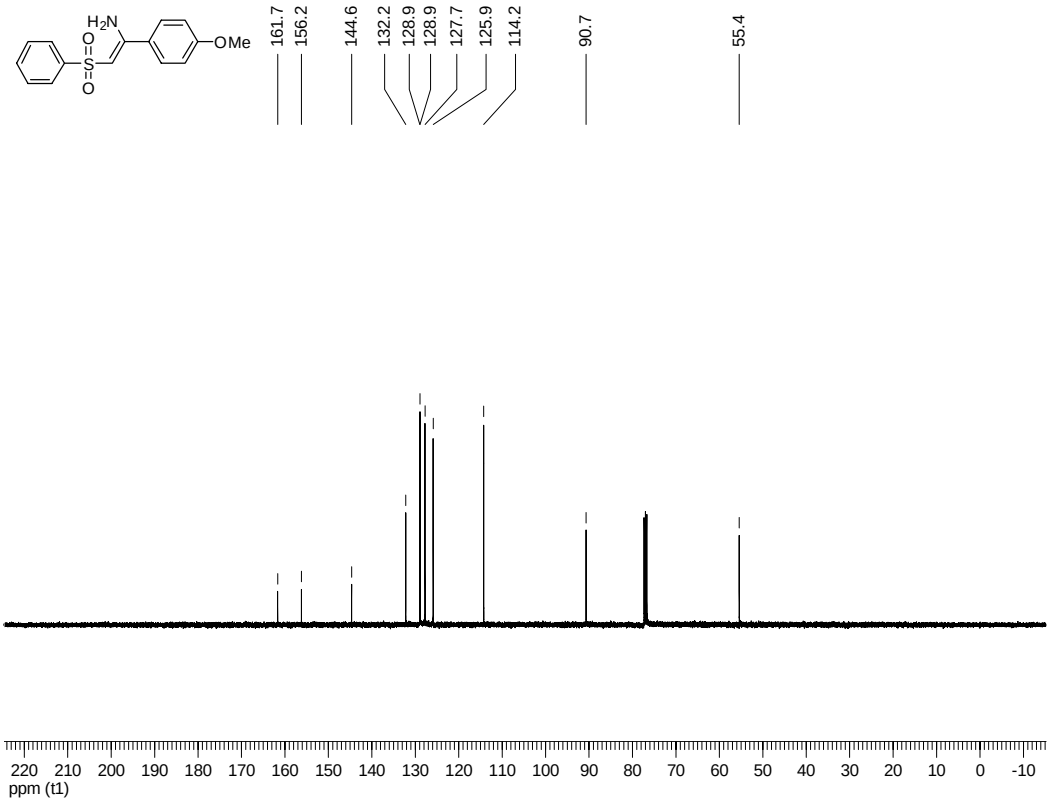
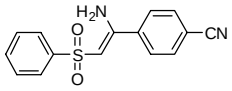
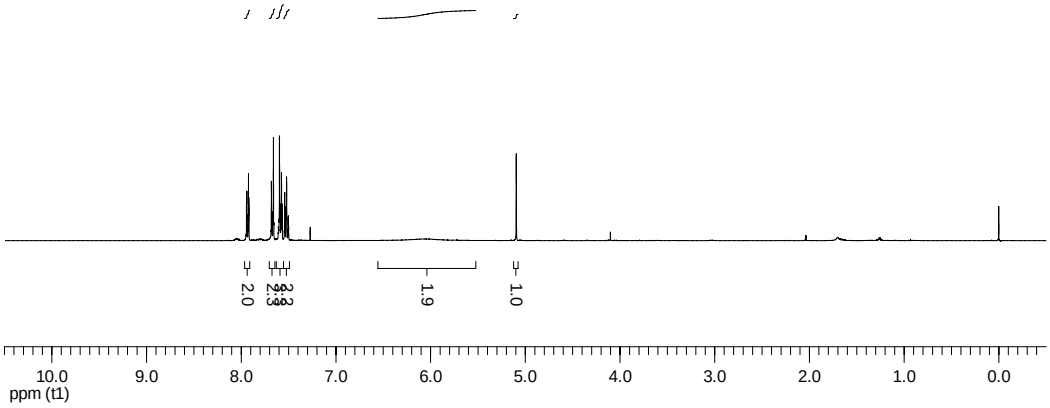
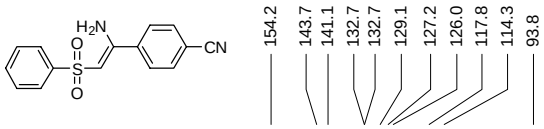
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

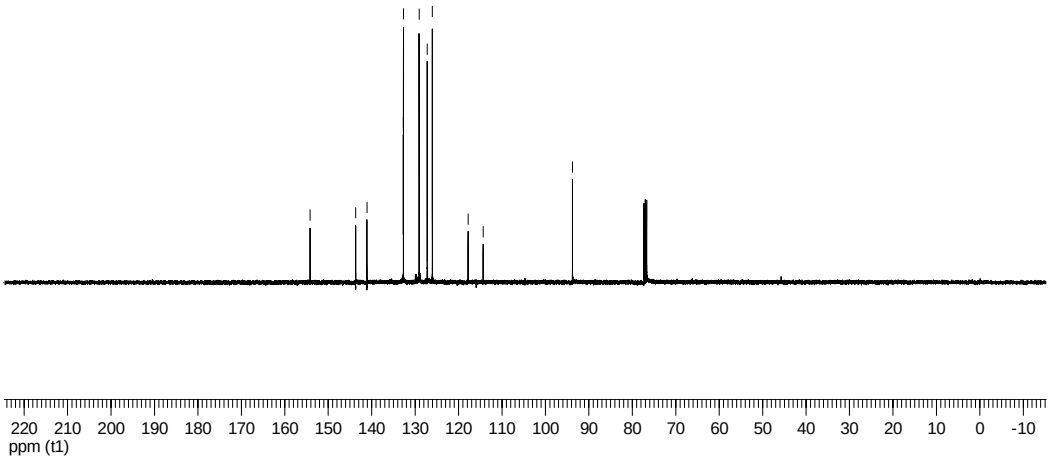

H2N
O
S
O
OMe
161.7
156.2
144.6
132.2
128.9
128.9
127.7
125.9
114.2
90.7
55.4
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm (t1)

2d

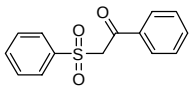

H2N
O
S
O
CN

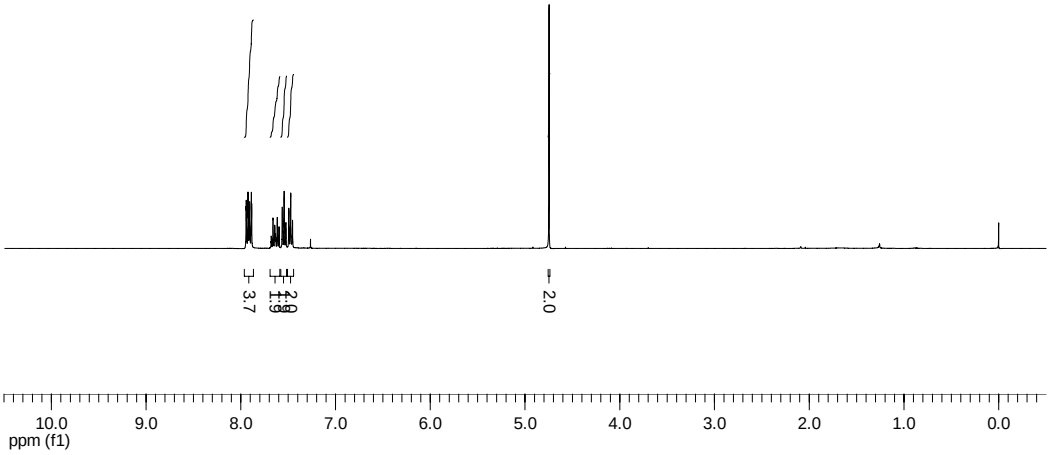

2.0
1.9
1.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

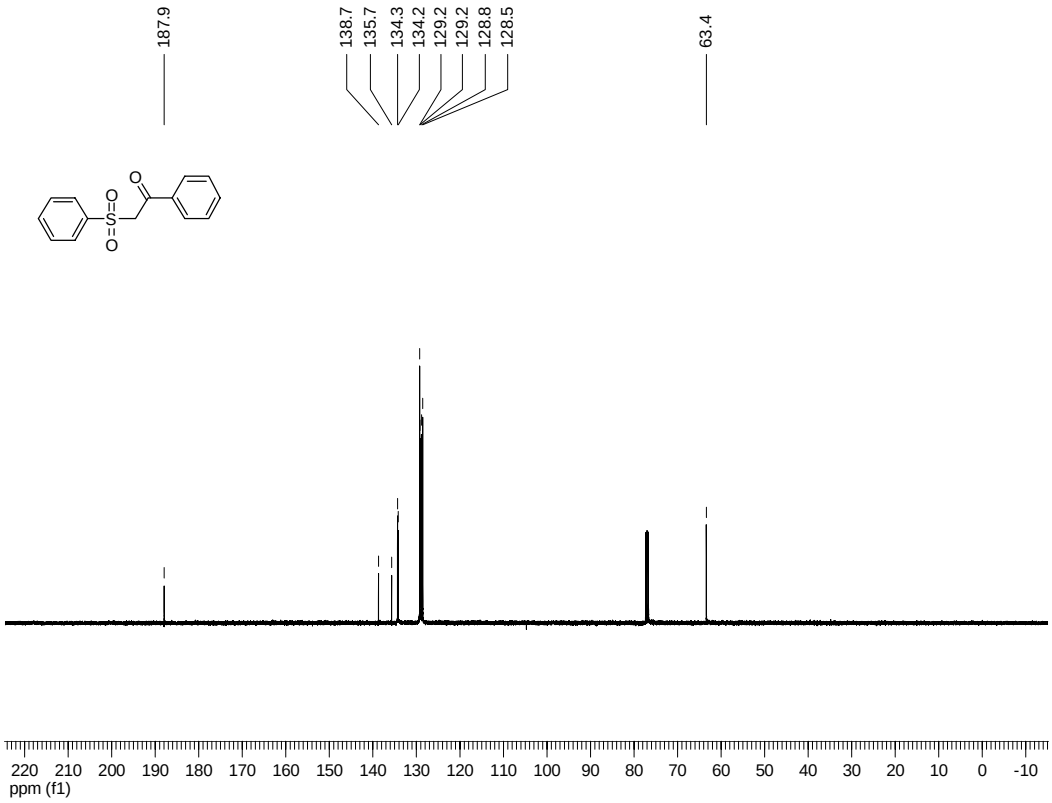

H2N
O
S
O
CN
154.2
143.7
141.1
132.7
132.7
129.1
127.2
126.0
117.8
114.3
93.8


220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm (t1)

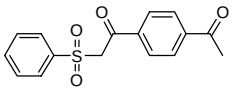
3a

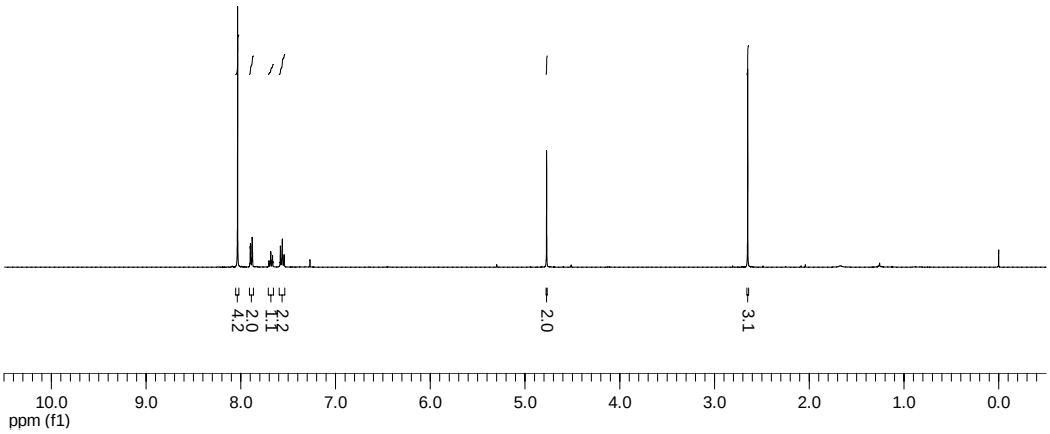


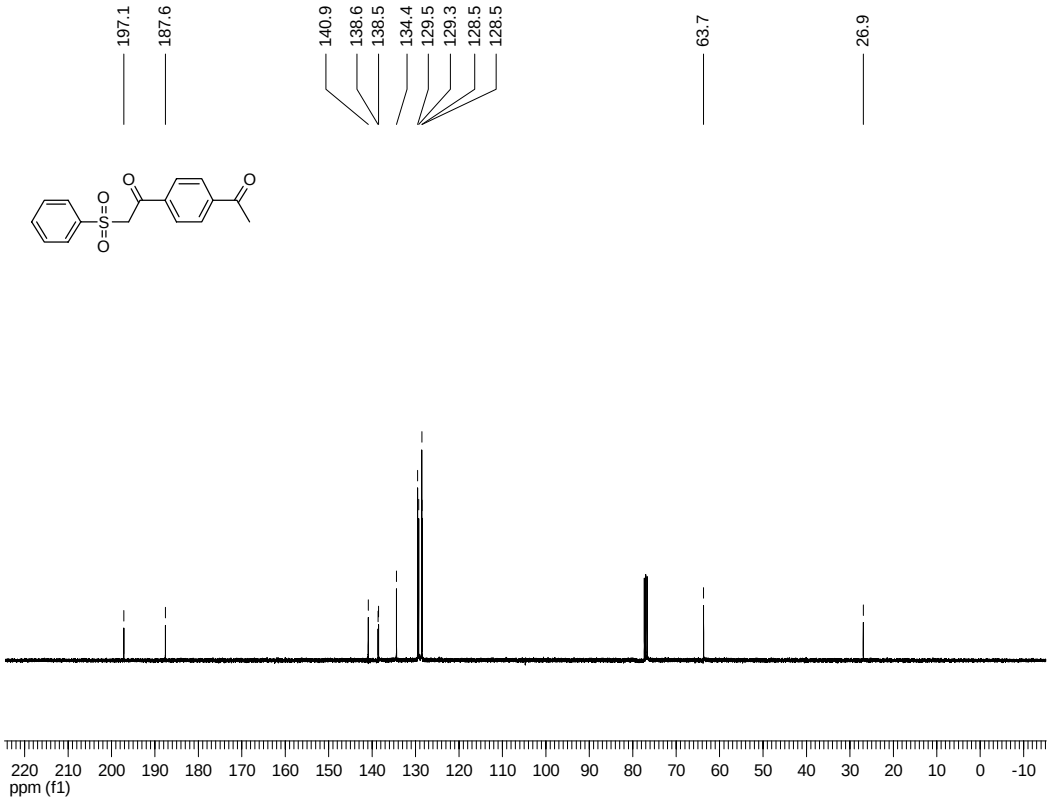

3.7
2.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


187.9
138.7
135.7
134.3
134.2
129.2
129.2
128.8
128.5
63.4
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm (f1)

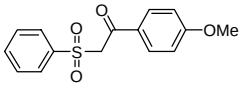
3b

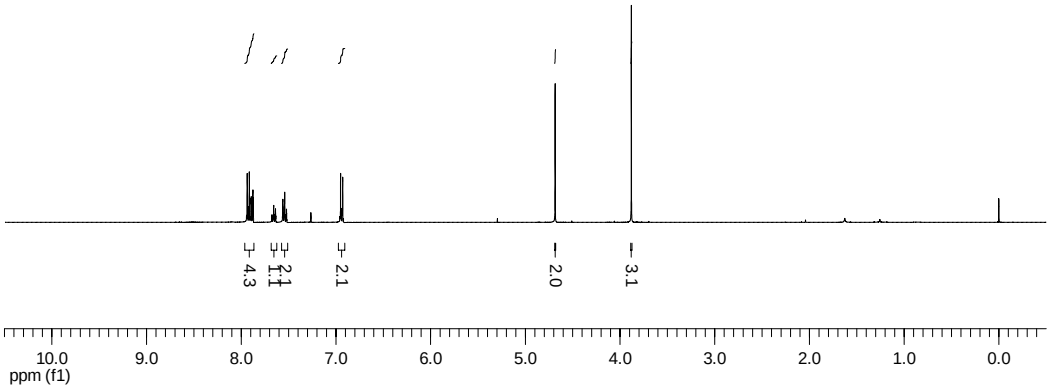



4.2
2.0
2.2
1.1
1.1
2.0
3.1
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

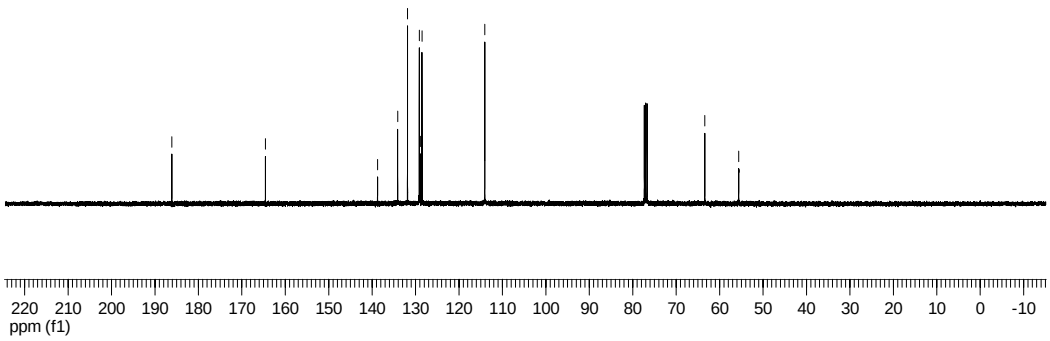

197.1
187.6
140.9
138.6
138.5
134.4
129.5
129.3
128.5
128.5
63.7
26.9
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm (f1)

3c

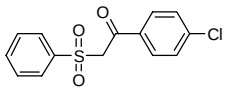

O
O
S
O
OMe

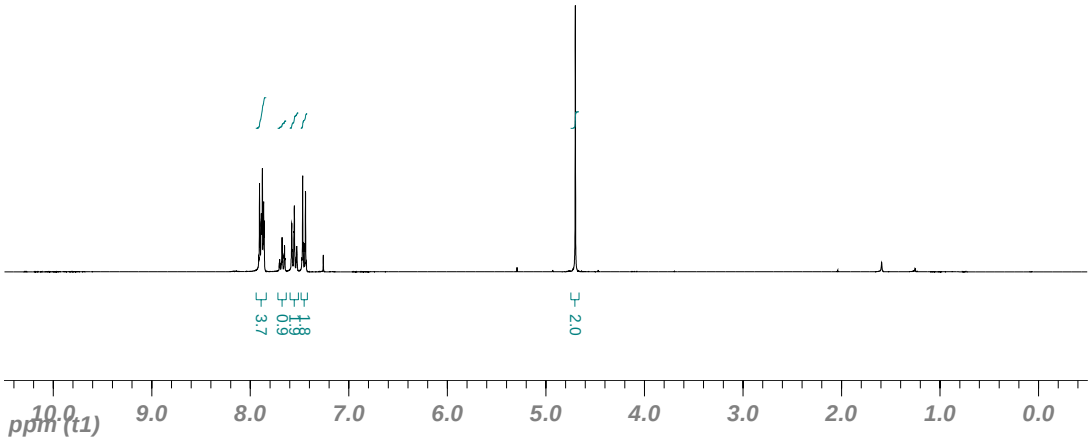

4.3
2.1
1.1
1.1
2.1
2.0
3.1
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

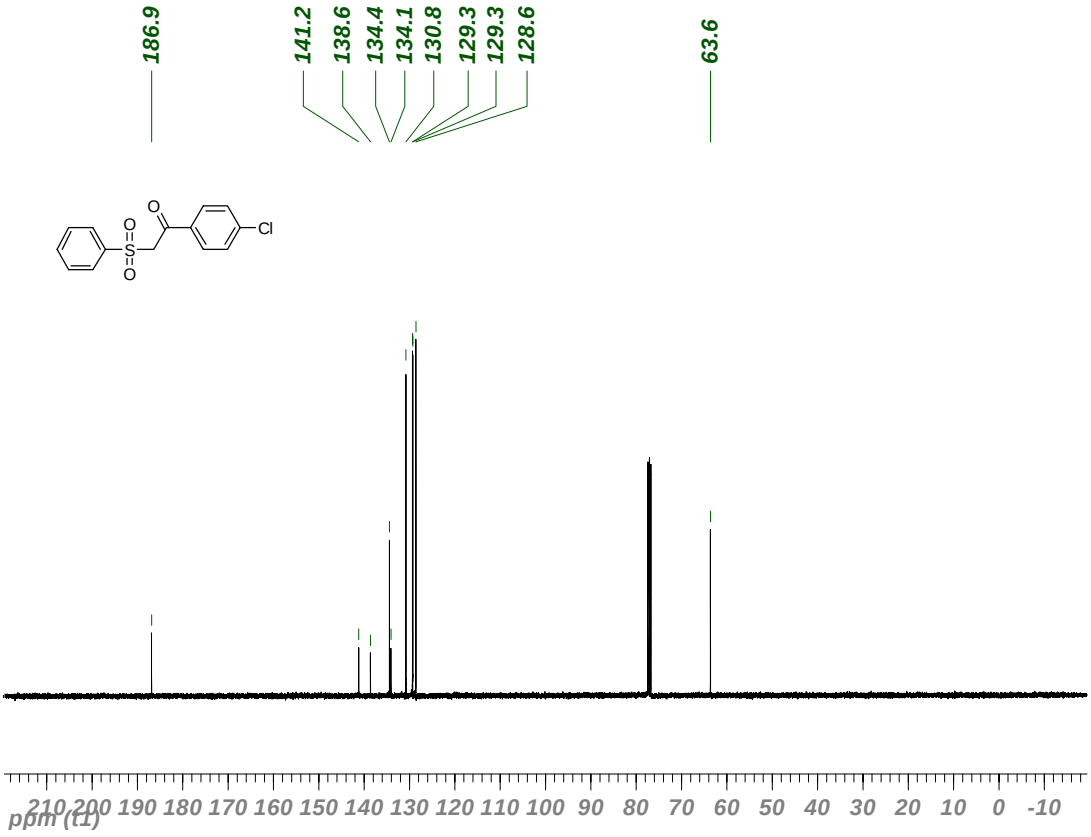
186.1
164.5
138.7
134.1
131.8
129.1
128.8
128.5
114.1
63.4
55.6
O
O
S
O
OMe


220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm (f1)

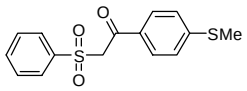
3d

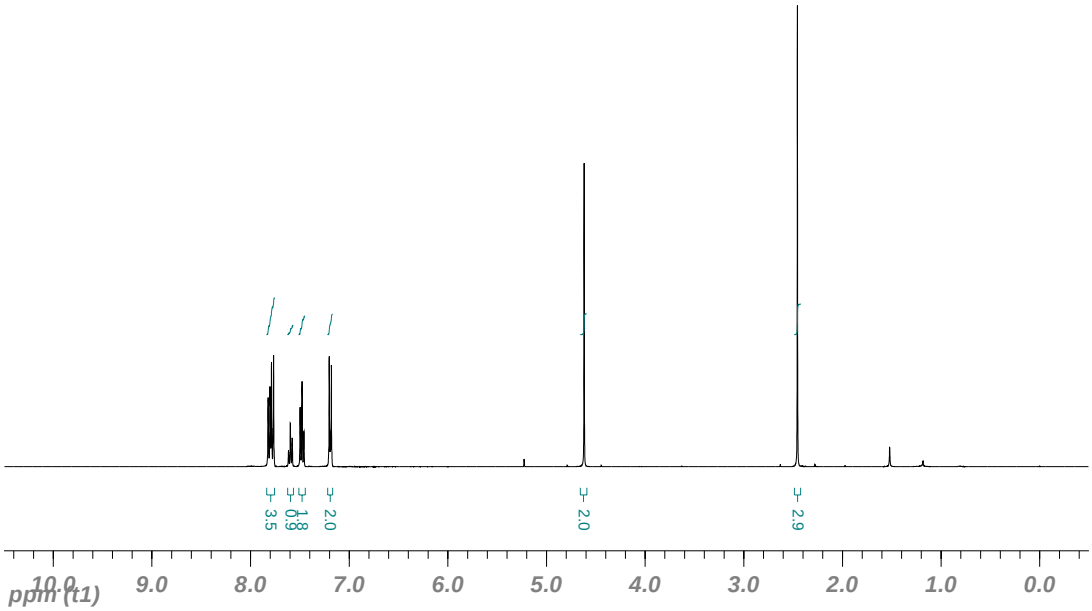

O
O
S
O
Cl

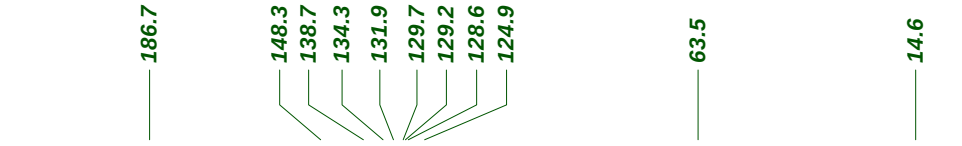

3.7
1.8
1.9
0.9
2.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

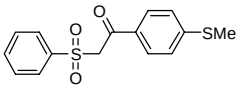

186.9
141.2
138.6
134.4
134.1
130.8
129.3
129.3
128.6
63.6
O
O
S
O
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm (t1)

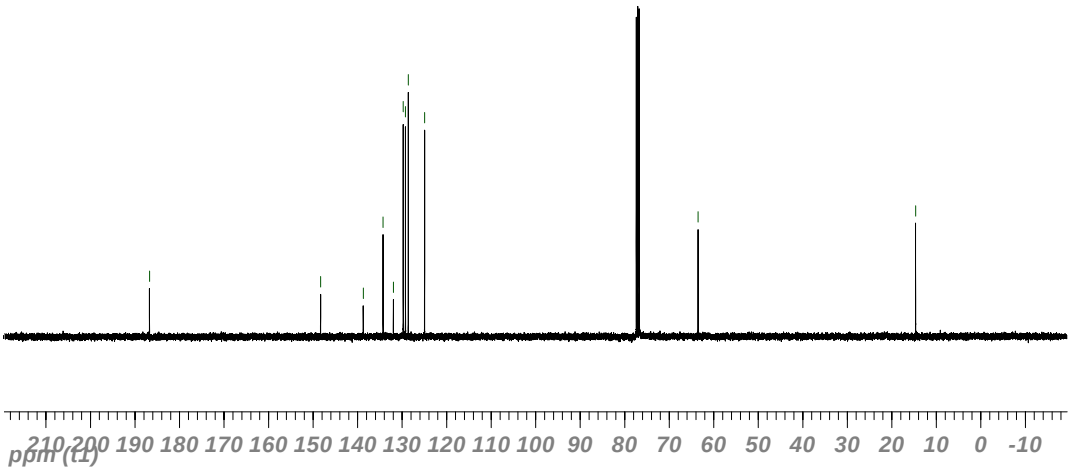
3e


O
O
S
O
SMe

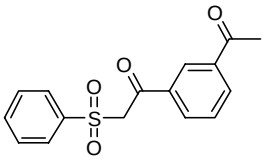

3.5
1.8
1.6
2.0
2.0
2.9
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

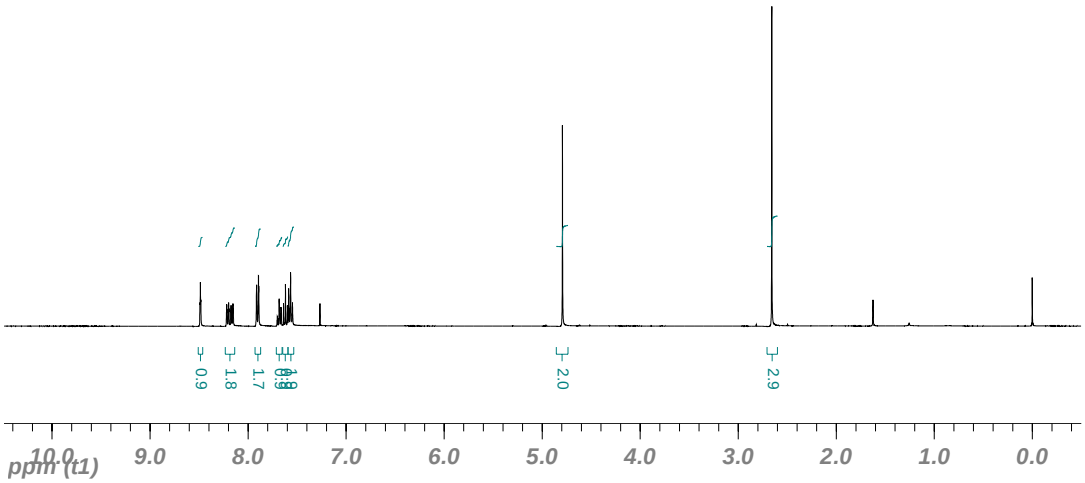

186.7
148.3
138.7
134.3
131.9
129.7
129.2
128.6
124.9
63.5
14.6

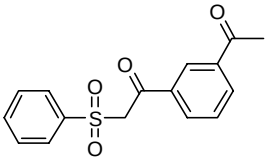

O
O
S
O
SMe

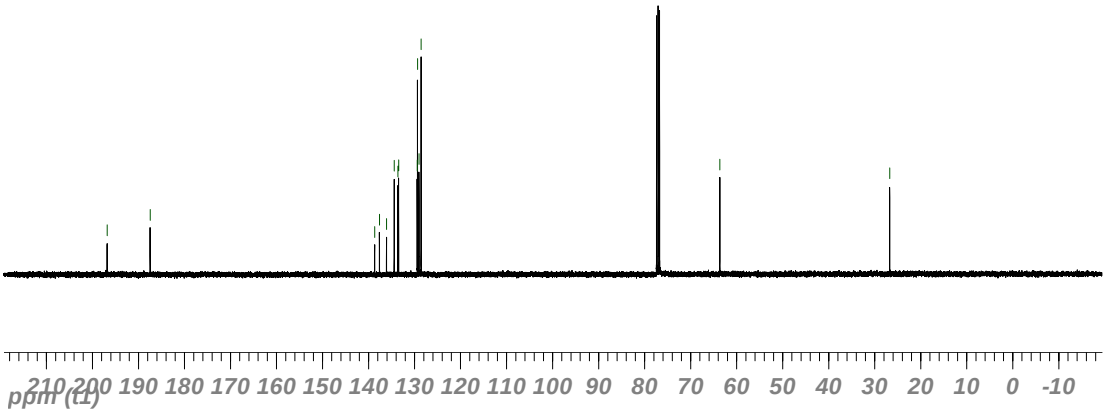

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm (t1)

3f

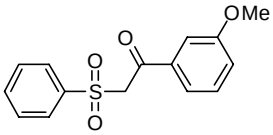


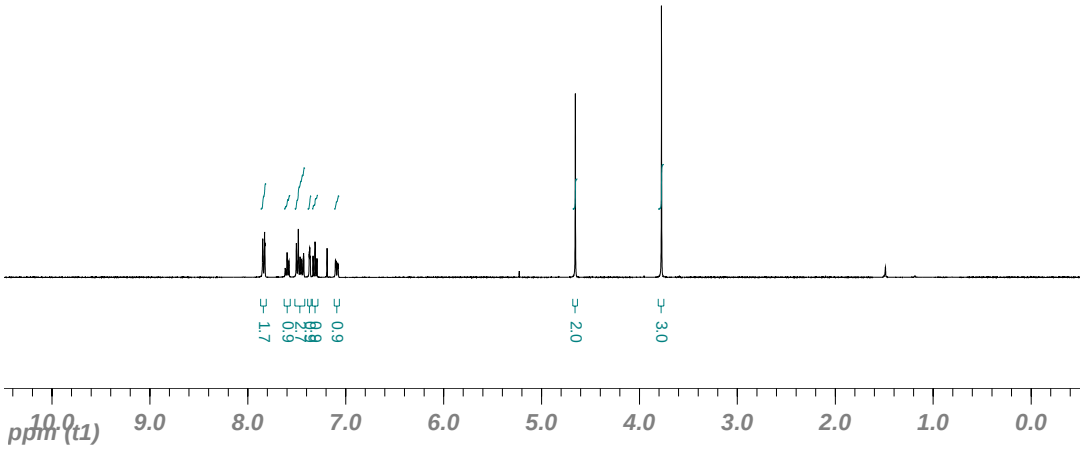

0.9
1.8
1.7
2.0
2.9
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
ppm (t1)

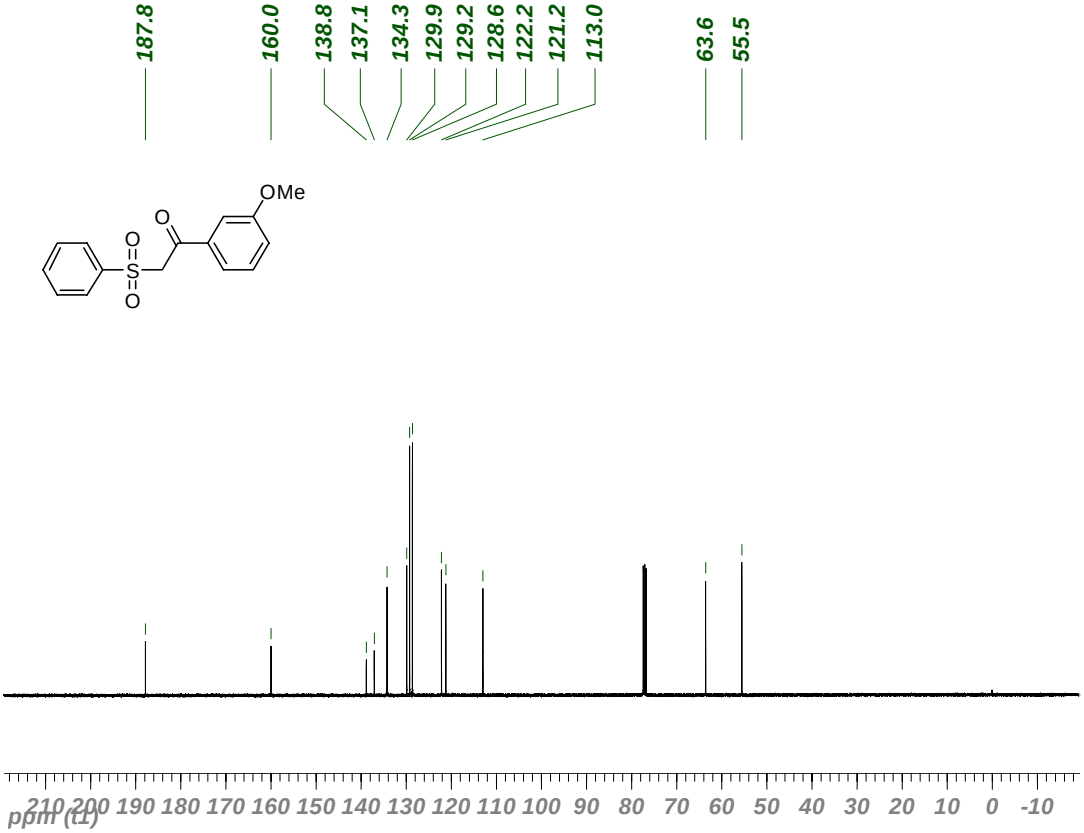



196.8
187.5
138.7
137.6
136.1
134.4
133.6
133.5
129.4
129.4
129.0
128.6
63.6
26.7
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm (t1)

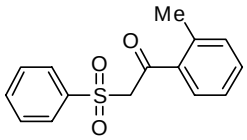
3g

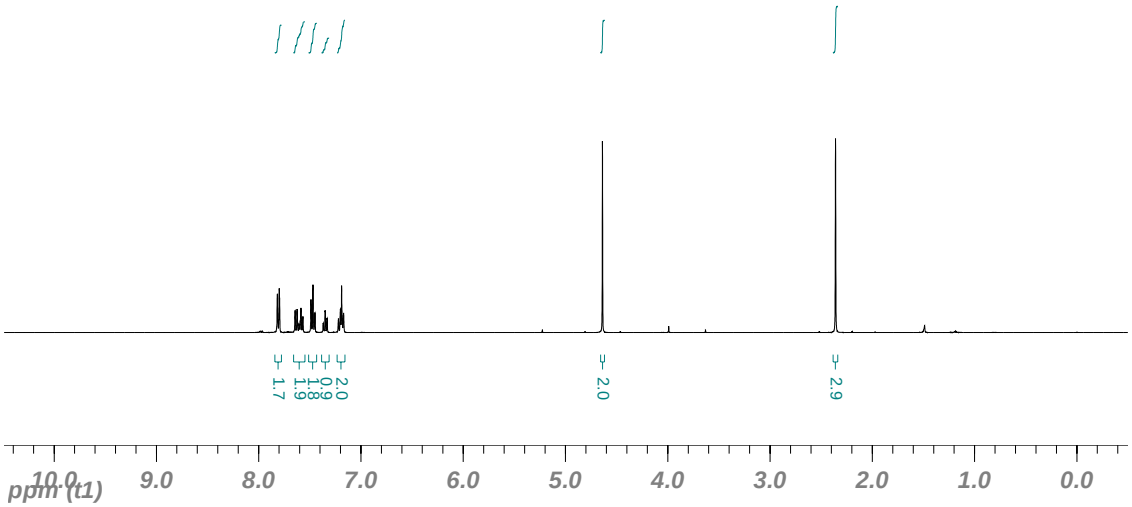

OMe
O
O
S
O

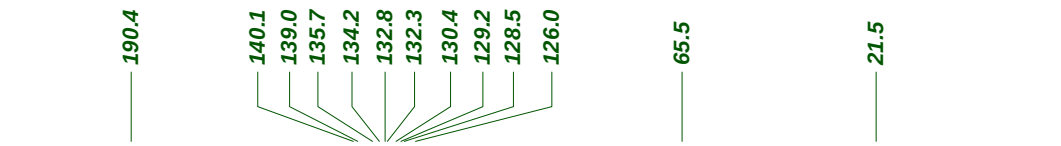

1.7
0.9
2.0
3.0
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
ppm (t1)

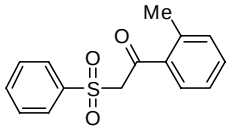

187.8
160.0
138.8
137.1
134.3
129.9
129.2
128.6
122.2
121.2
113.0
63.6
55.5
OMe
O
O
S
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm (t1)

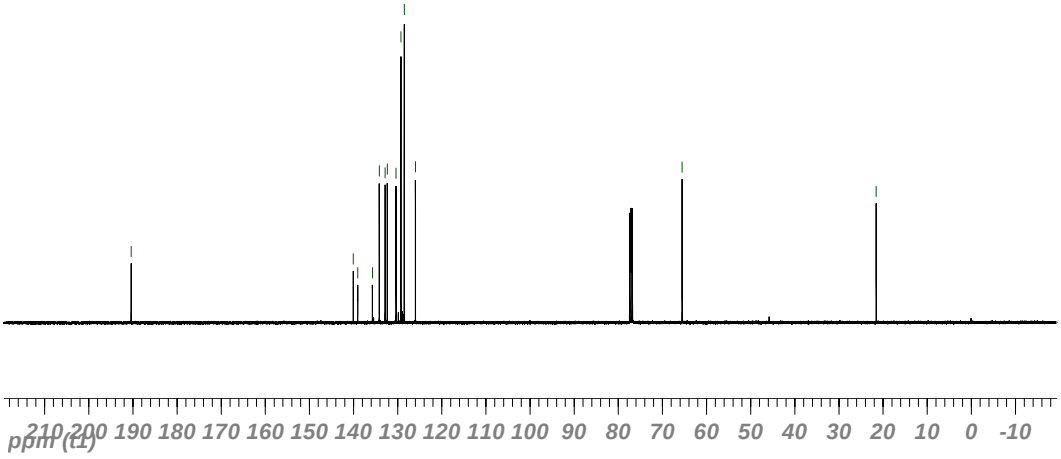
3h


Me
O
O
S
O

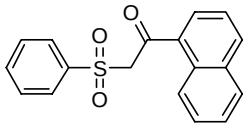

1.7
2.0
0.9
1.8
1.9
2.0
2.9
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
ppm (t1)

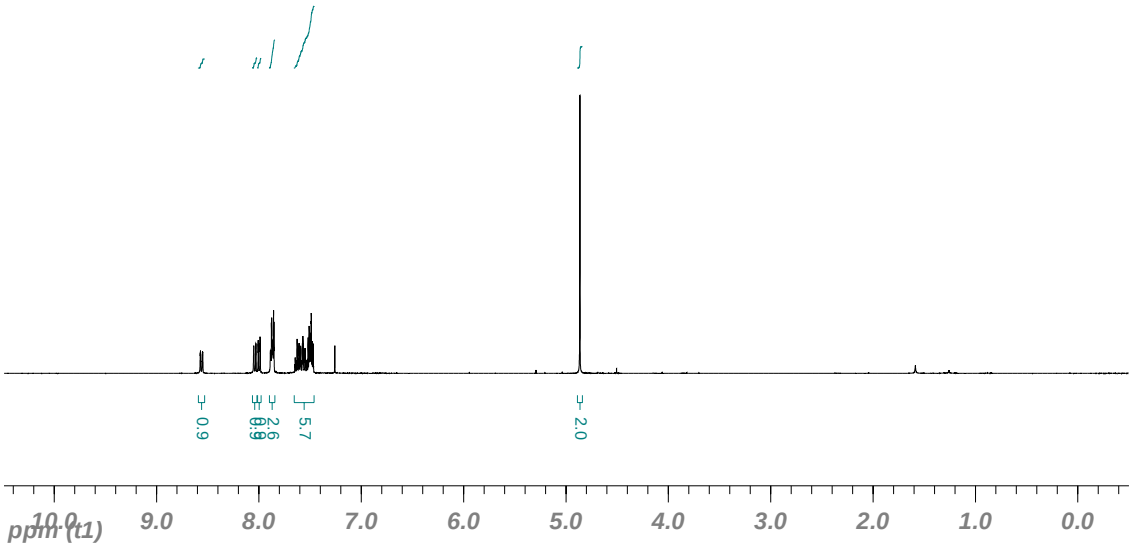

190.4
140.1
139.0
135.7
134.2
132.8
132.3
130.4
129.2
128.5
126.0
65.5
21.5

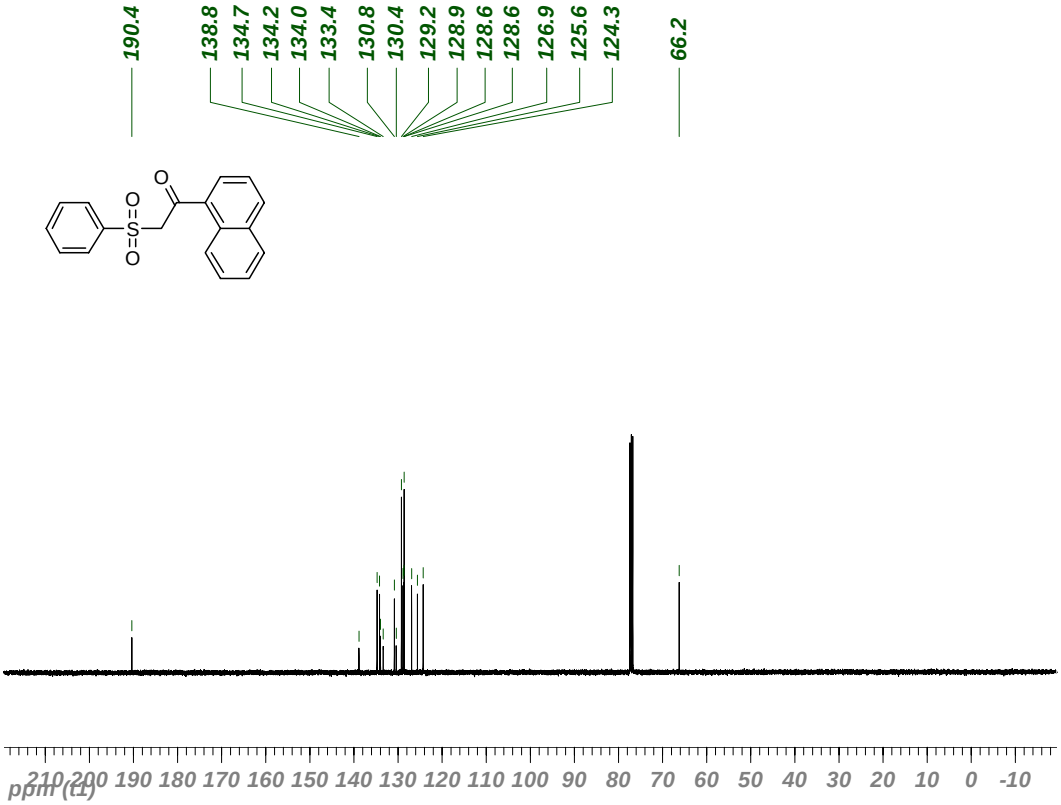

Me
O
O
S
O


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm (t1)

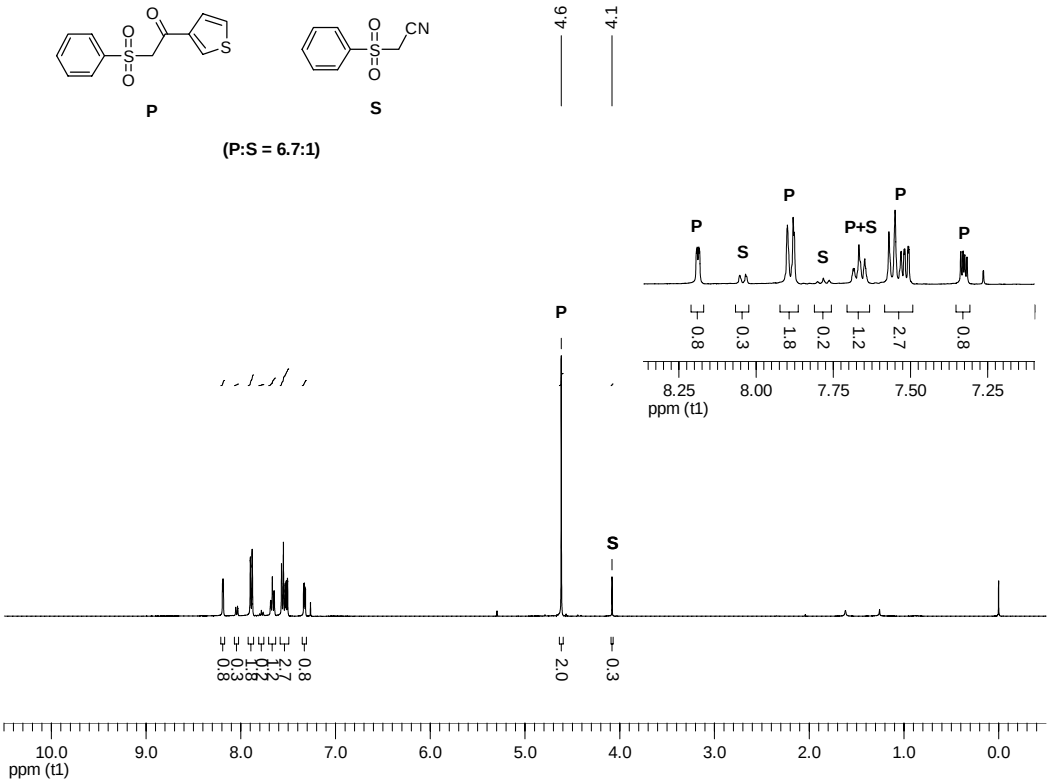
3i

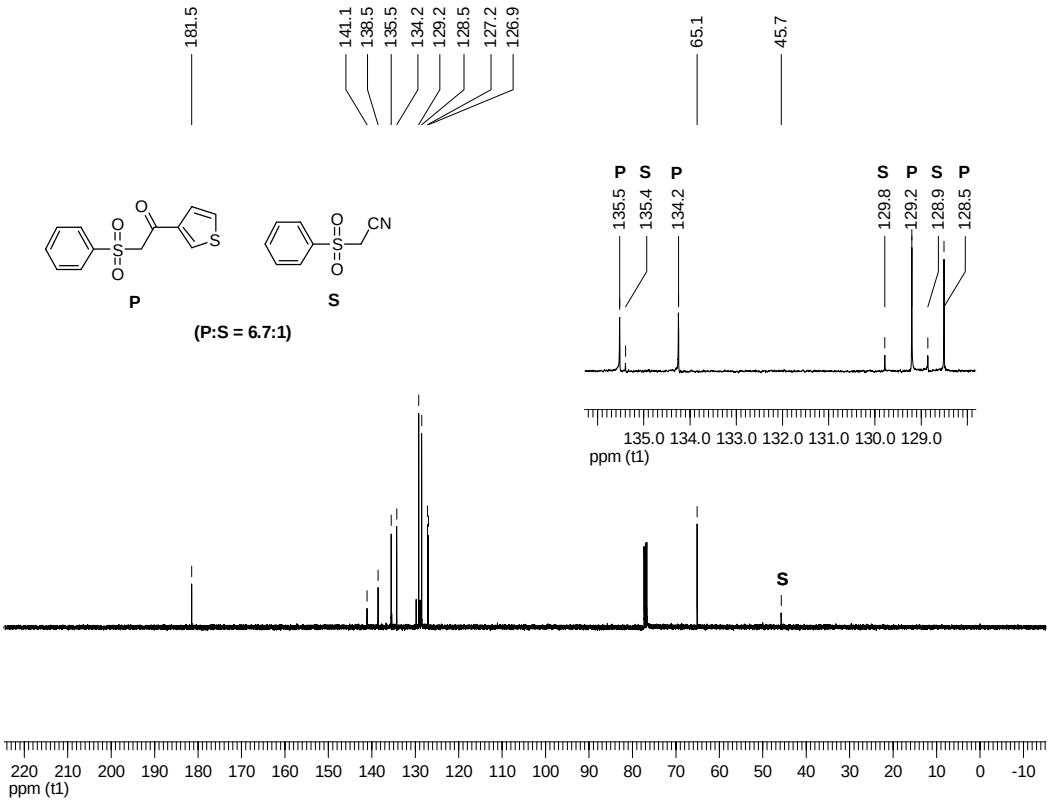



0.9
2.6
0.9
5.7
2.0
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
ppm (t1)

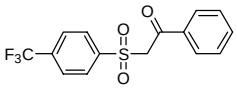

190.4
138.8
134.7
134.2
134.0
133.4
130.8
130.4
129.2
128.9
128.6
128.6
126.9
125.6
124.3
66.2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm (t1)

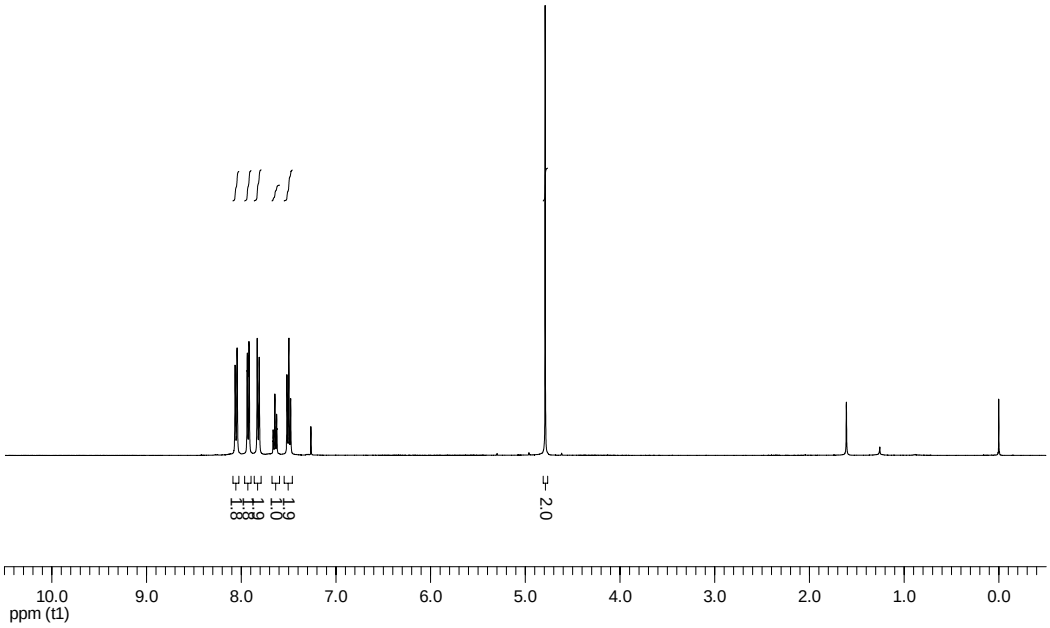
3j


P
S
(P:S = 6.7:1)
4.6
4.1
P+S
0.8
0.3
1.8
0.2
1.2
2.7
2.0
ppm (t1)


181.5
141.1
138.5
135.5
134.2
129.2
128.5
127.2
126.9
65.1
45.7
P
S
(P:S = 6.7:1)
135.5
135.4
134.2
129.8
129.2
128.9
128.5
ppm (t1)

3k




8.08
8.06
7.49
7.47
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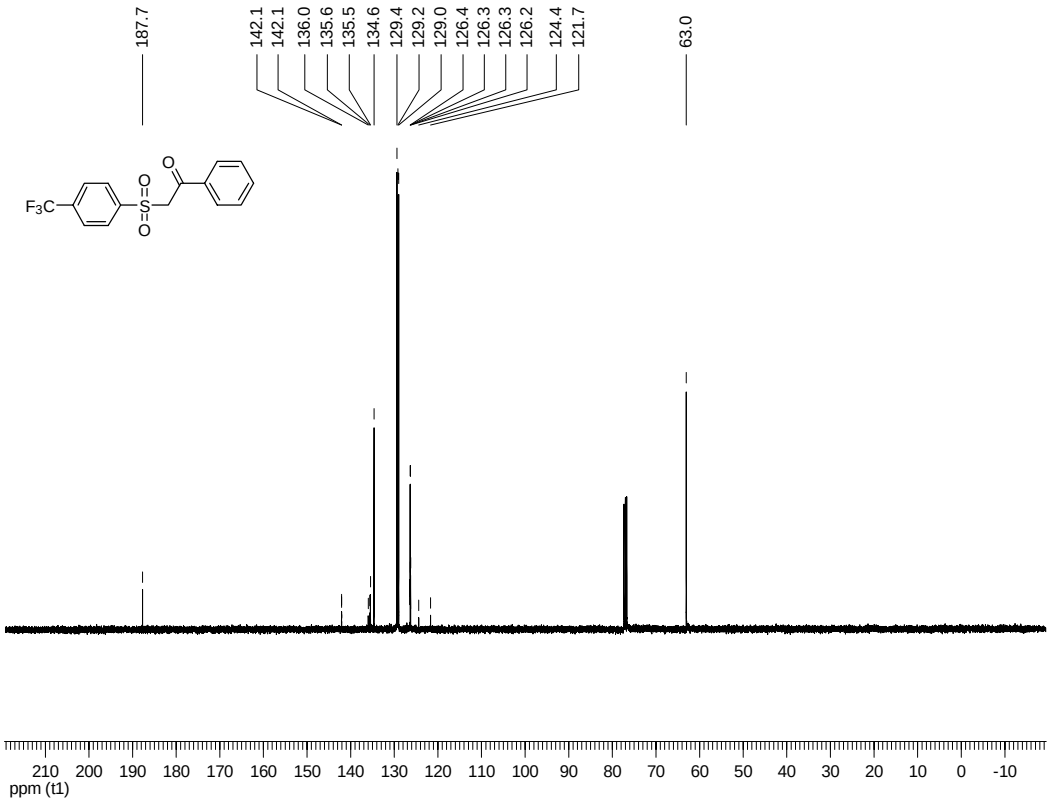
7.45
7.44
7.43
7.42
7.41
7.40
7.39
7.38
7.37
7.36
7.35
7.34
7.33
7.32
7.31
7.30
7.29
7.28
7.27
7.26
7.25
7.24
7.23
7.22
7.21
7.20
7.19
7.18
5.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


187.7
142.1
142.1
136.0
135.6
135.5
134.6
129.4
129.2
129.0
126.4
126.3
126.3
126.2
124.4
121.7
63.0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
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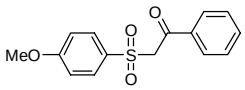
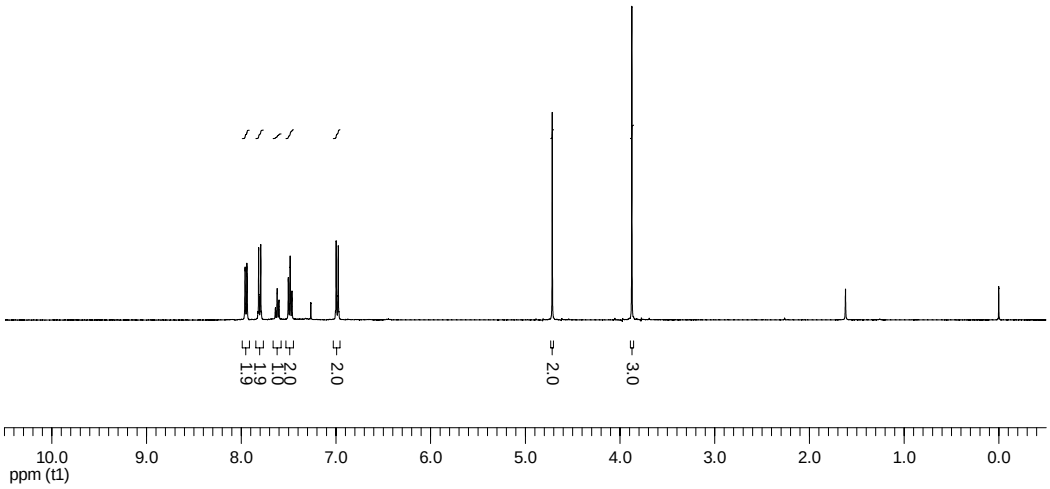
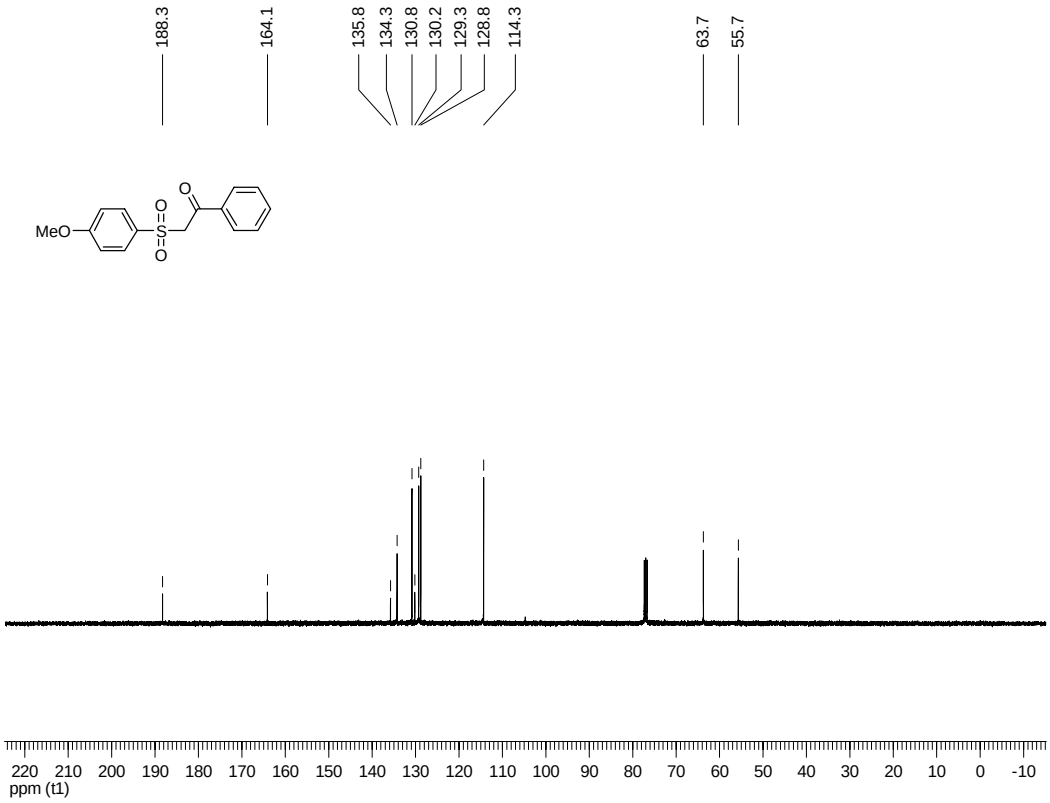
0
-10
ppm (t1)

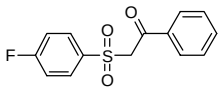
3l

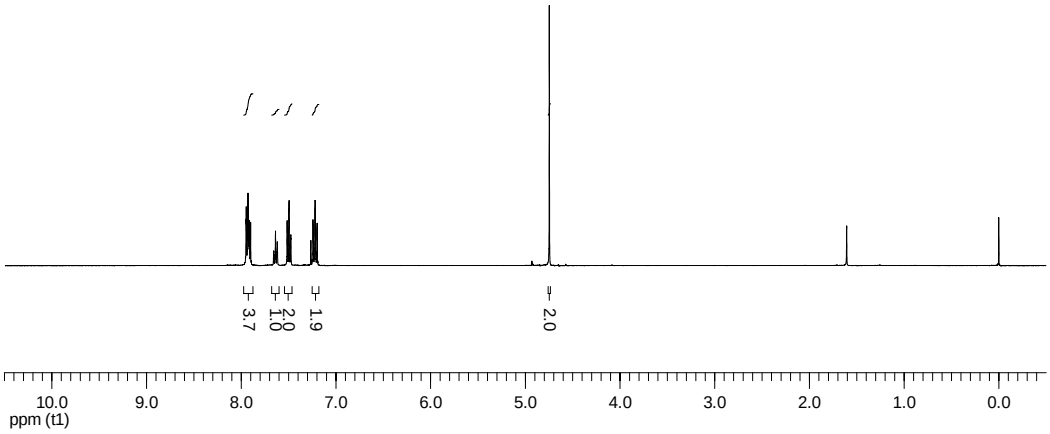

MeO
O
O
S
O

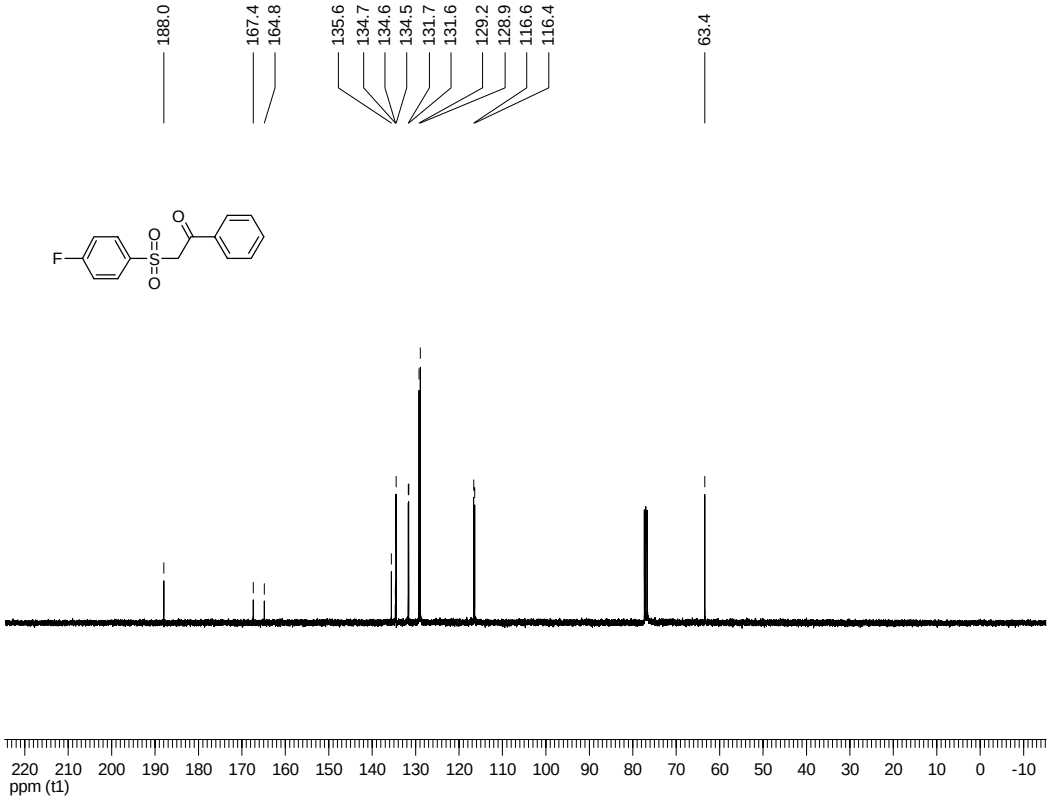

1.9
1.6
1.0
2.0
2.0
2.0
3.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


188.3
164.1
135.8
134.3
130.8
130.2
129.3
128.8
114.3
63.7
55.7
MeO
O
O
S
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm (t1)

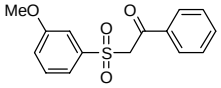
3m

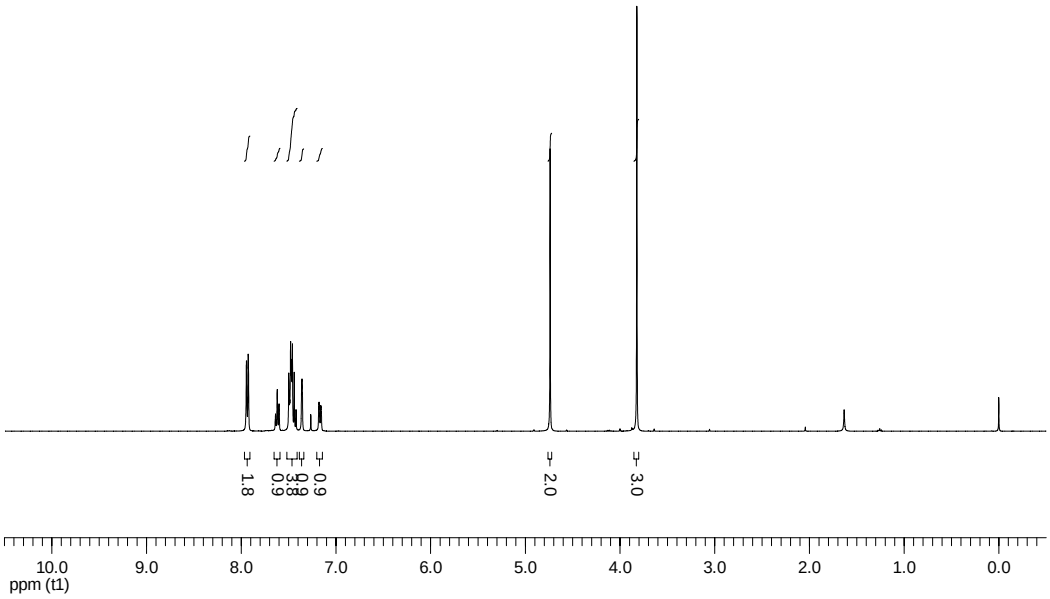


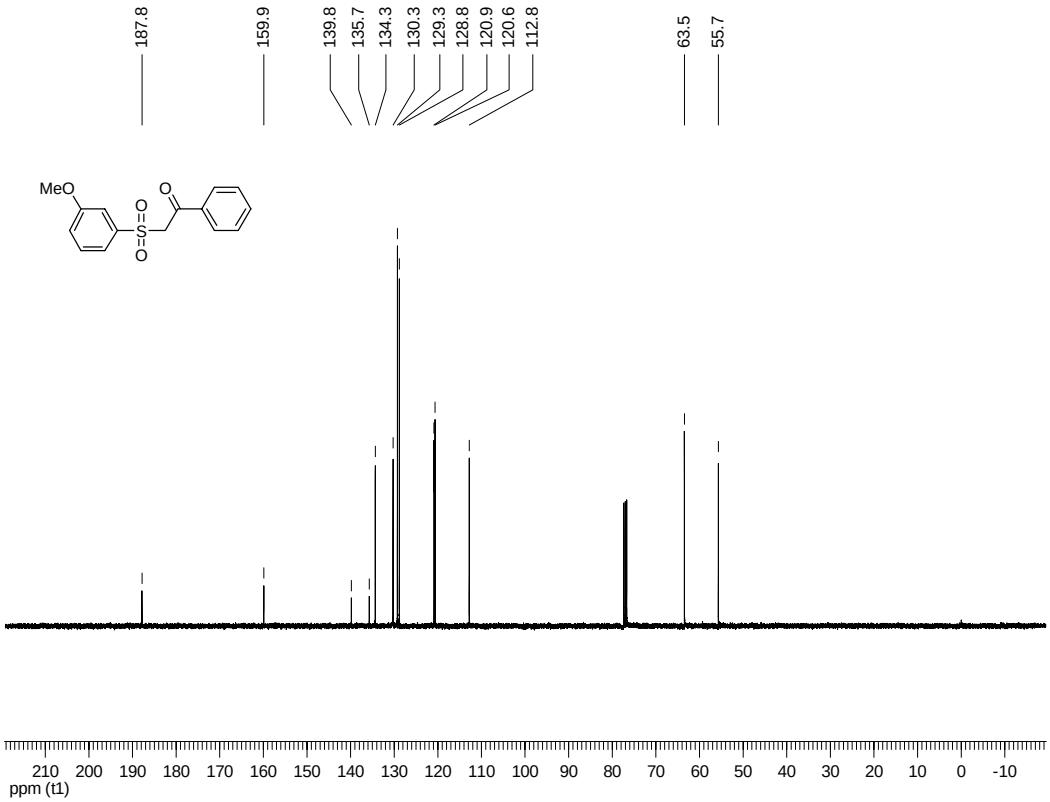

3.7
1.0
2.0
1.9
2.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


188.0
167.4
164.8
135.6
134.7
134.6
134.5
131.7
131.6
129.2
128.9
116.6
116.4
63.4
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm (t1)

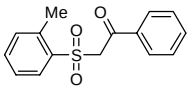
3n

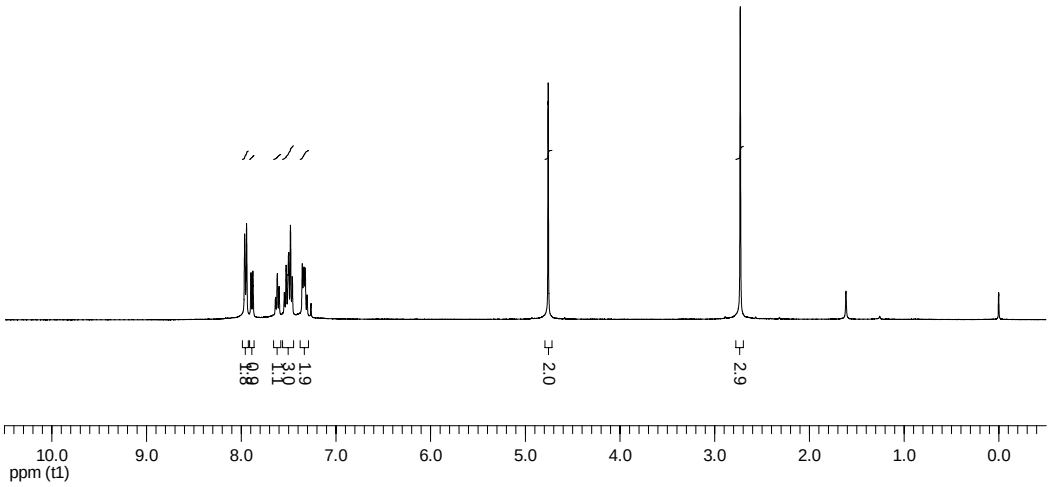

MeO
O
O
S
O

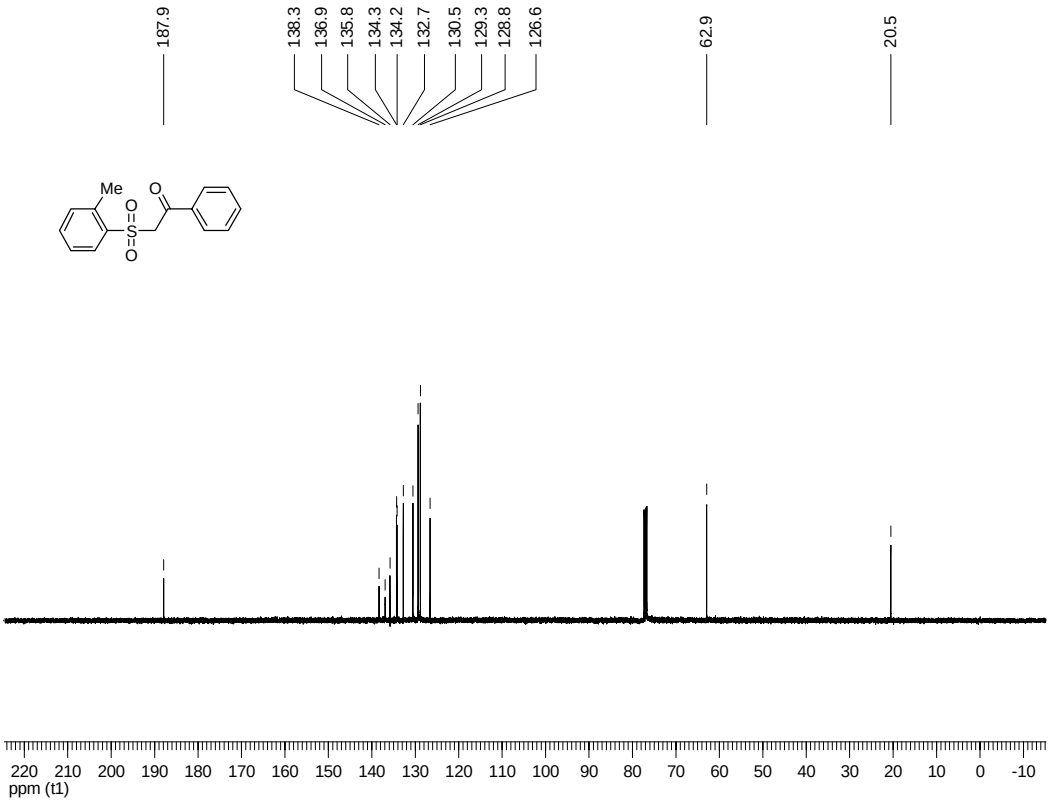

1.8
0.9
0.8
0.8
0.9
2.0
3.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


187.8
159.9
139.8
135.7
134.3
130.3
129.3
128.8
120.9
120.6
112.8
63.5
55.7
MeO
O
O
S
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm (t1)

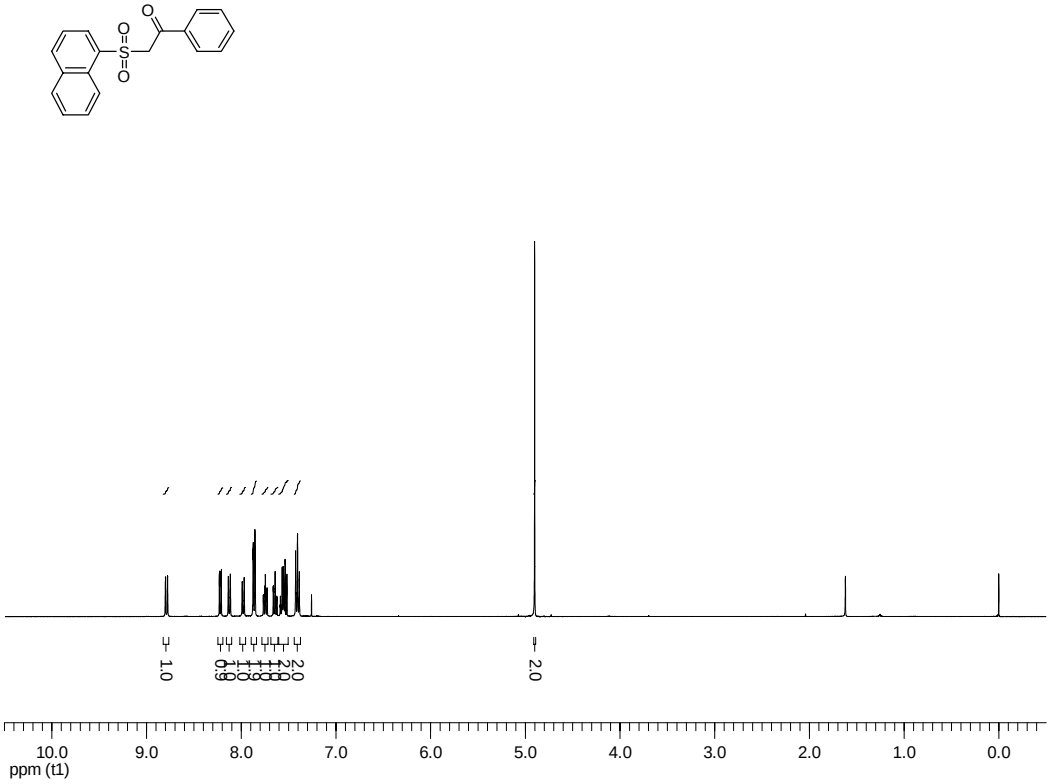
3o

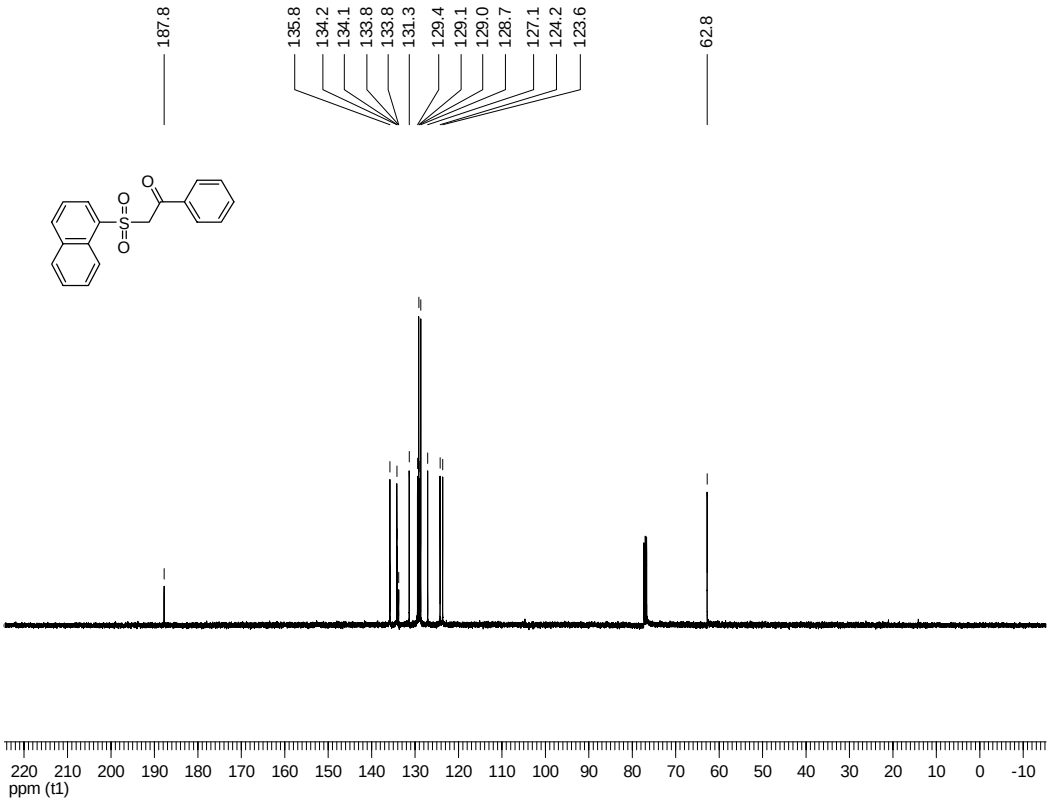

Me
O
O
S
O


8.0
7.5
7.4
2.0
2.9
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

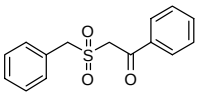

187.9
138.3
136.9
135.8
134.3
134.2
132.7
130.5
129.3
128.8
126.6
62.9
20.5
Me
O
O
S
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm (t1)

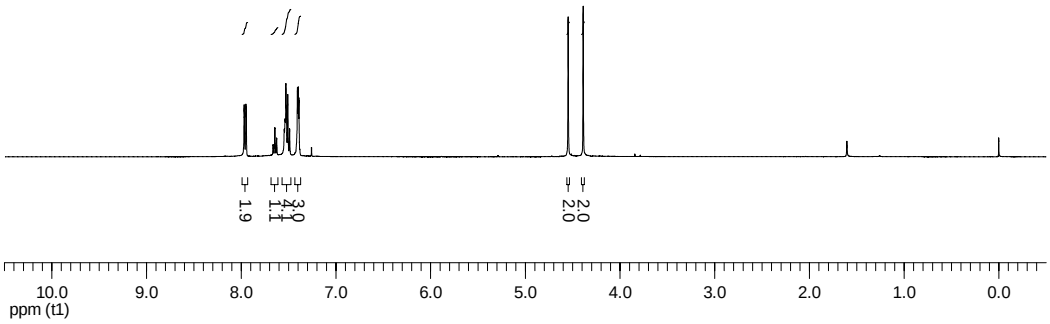
3p

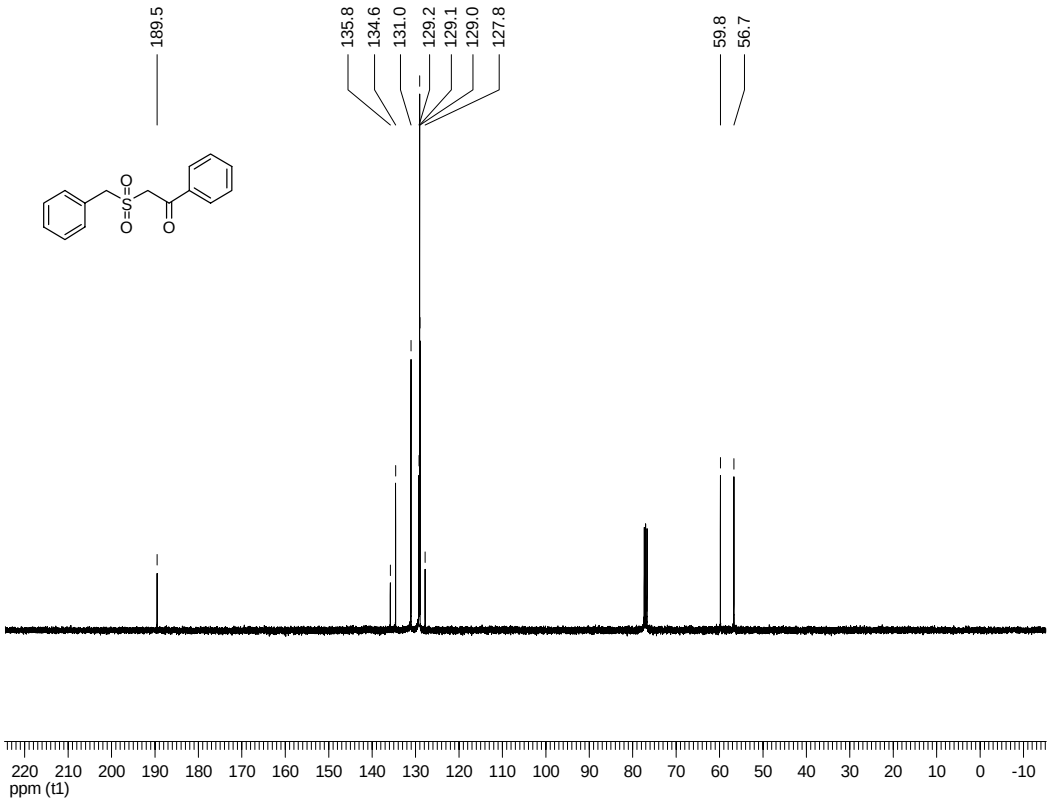

1.0
2.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


187.8
135.8
134.2
134.1
133.8
133.8
131.3
129.4
129.1
129.0
128.7
127.1
124.2
123.6
62.8
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm (t1)

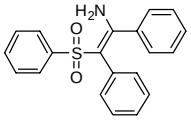
3q

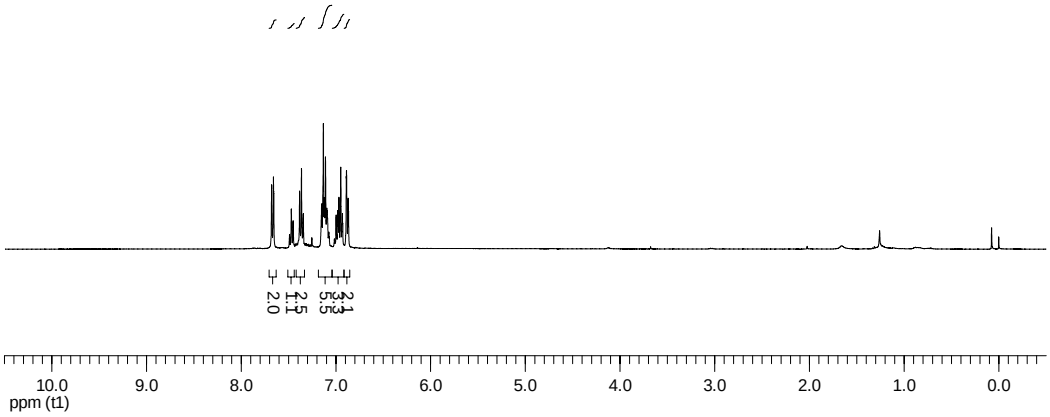


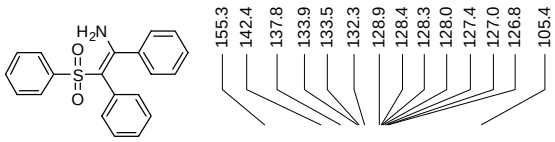

1.9
1.1
1.1
3.0
2.0
2.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

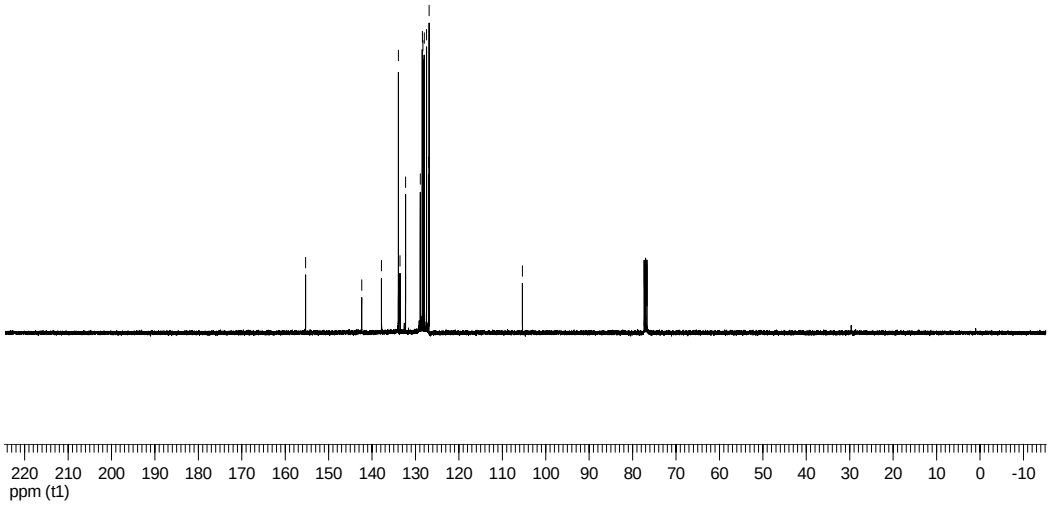

189.5
135.8
134.6
131.0
129.2
129.1
129.0
127.8
59.8
56.7
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm (t1)

5a

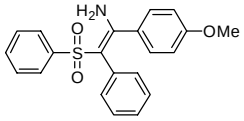

H2N
O
S
O

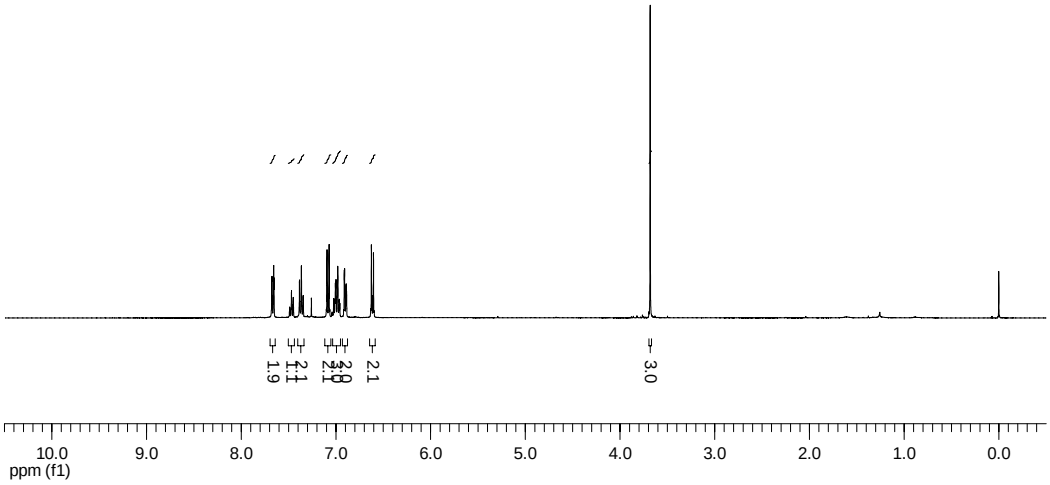

2.0
1.1
2.5
1.1
5.5
2.3
2.3
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

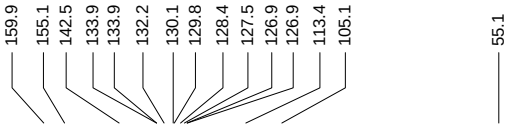

H2N
O
S
O
155.3
142.4
137.8
133.9
133.5
132.3
128.9
128.4
128.3
128.0
127.4
127.0
126.8
105.4

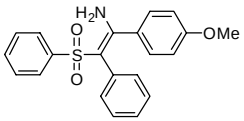

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm (t1)

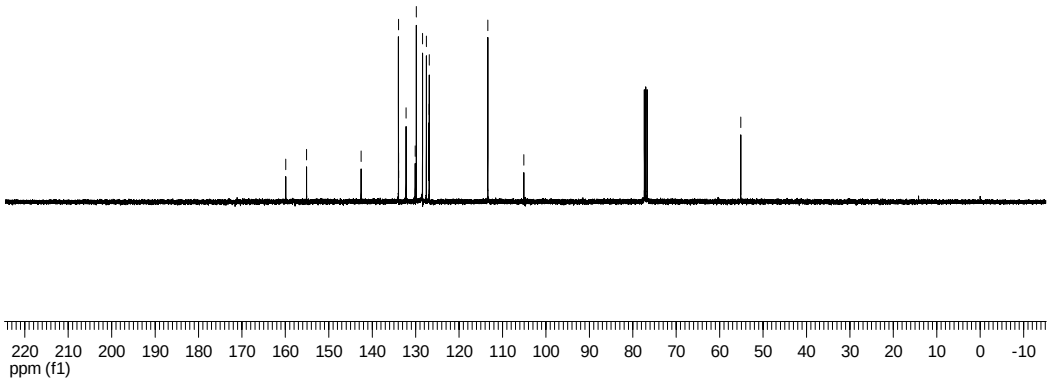
5b


H2N
O
S
O
OMe


1.9
1.1
2.1
2.0
2.1
3.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


159.9
155.1
142.5
133.9
133.9
132.2
130.1
129.8
128.4
127.5
126.9
126.9
113.4
105.1
55.1


H2N
O
S
O
OMe


220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm (f1)