Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

[2.2]Paracyclophane-based coumarins: effective organo-photocatalysts for light-induced desulfonylation processes

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Supporting information

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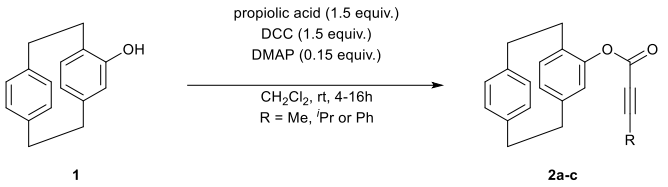
General Remarks

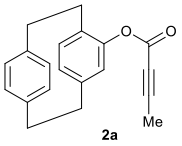
All reactions were carried out under inert atmosphere (in oven-dried glassware, using dry solvents), unless otherwise specified. All commercially available compounds, including anilines 1a-f and isothiocyanates 2a-c, were purchased from Merck, Fisher Scientific or TCI chemicals and used as received. Analytical thin layer chromatography (TLC) was performed on silica gel plates (Merck 60F254) visualized with a UV lamp (254 nm). Flash chromatography was performed on silica gel (60-230 mesh) unless otherwise specified. Organic extracts were dried over anhydrous $MgSO_4$. NMR spectra (^1H and $^{13}C\{^1H\}$) were recorded on Bruker Avancell 500 spectrometer, at 500 MHz (H value) in $CDCl_3$ or DMSO-d_6. Spectra were referenced to residual chloroform (7.26 ppm, ^1H; 77.0 ppm, $^{13}C\{^1H\}$) or dimethyl sulfoxide (2.50 ppm, ^1H; 39.52 ppm, $^{13}C\{^1H\}$). Chemical shifts are reported in ppm, multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), and m (multiplet or overlap of nonequivalent resonances), dd (doublet of doublet), td (triplet of doublet), and br (broad signal). Coupling constants, *J*, are reported in hertz (Hz). All NMR spectra were obtained at 300K unless otherwise specified. IR spectra were obtained using a spectrum one FT-IR spectrometer (Perkin Elmer). High Resolution mass spectra were recorded on a ThermoFischer Exactive Orbitrap spectrometer. HPLC analyses were performed on a Shimadzu chromatograph equipped with a diode array UV/VIS detector. Optical rotations (α_D) were measured on a Perkin Elmer polarimeter (model 341) at 20 °C. All photochemical transformations have been performed in a Rayonet RPR-200 photochemical reactor (Manufacturer: The Southern New England Ultraviolet Co) equipped with eight 300 nm lamps (12'' in length, 14 w. Manufacturer: The Southern New England Ultraviolet Co Reference: RPR-3500A). Borosilicate glass vials (sealed tubes) placed in the middle of the reactor chamber were employed to run the reactions (distance from the light source to the irradiation vessel ~ 12 cm). For more information about the photochemical apparatus see the supporting information.

Synthesis and characterization of photocatalysts 3a-c

General procedure for the esterification reactions (GP1)

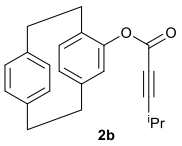


4-Hydroxy[2.2]paracyclophane[1] (**1**, 1 equiv.), DMAP (0.15 equiv.), and the desired propiolic acid (1.5 equiv.) were dissolved in dry DCM (0.02 M) under an argon atmosphere. DCC (1 M in DCM, 1.5 equiv.) was added turning the reactions dark yellow and cloudy. The mixtures were stirred at rt for 4-16 h, followed by filtration through a short plug of silica gel with DCM washings. The filtrates were concentrated under reduced pressure and the crudes products were purified by silica gel column chromatography to afford the products as amorphous solids.



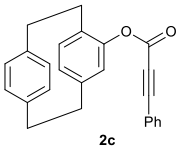
2a

*Compound **2a**:* According to **GP1**, starting from compound **1** (1 equiv., 736 mg, 3.28 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:9) gave compound **2a** (712 mg, 2.45 mmol, 75%) as an amorphous white solid. This compound has been previously characterized by our team:[2] ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.95 (dd, J = 7.8, 1.9 Hz, 1H), 6.56-6.41 (m, 5H), 6.06 (d, J = 1.3 Hz, 1H), 3.23-2.93 (m, 7H), 2.72 (ddd, J = 12.6, 10.1, 5.4 Hz, 1H), 2.09 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.6 (C), 148.4 (C), 141.8 (C), 139.5 (C), 139.1 (C), 135.4 (CH), 133.4 (CH), 132.9 (CH), 132.4 (CH), 131.2 (C), 130.7 (CH), 129.7 (CH), 127.6 (CH), 87.7 (C), 72.3 (C), 35.3 (CH_2), 34.9 (CH_2), 34.2 (CH_2), 31.5 (CH_2), 4.1 (CH_3) ppm. IR (neat): 2987, 2959, 2929, 2900, 2856, 2234, 1721, 1412, 1240, 1222, 1103, 1086, 1043, 899, 740, 716 cm^{-1}. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{20}H_{19}O_2$: 291.1380; found: 291.1386.



2b

*Compound **2b***: According to **GP1**, starting from compound **1** (1 equiv., 200 mg, 0.89 mmol); flash chromatography on silica gel (EtOAc/Cy, 9:1) gave compound **2b** (185 mg, 0.58 mmol, 65%) as an amorphous white solid. This compound has been previously characterized by our team:[2] ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.97 (dd, J = 7.8, 1.6 Hz, 1H), 6.61-6.38 (m, 5H), 6.08 (s, 1H), 3.30-2.90 (m, 7H), 2.87-2.63 (m, 2H), 1.30 (d, J = 6.9 Hz, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.8 (C), 148.5 (C), 141.7 (C), 139.5 (C), 139.0 (C), 135.3 (CH), 133.3 (CH), 132.8 (CH), 132.3 (CH), 131.2 (C), 130.6 (CH), 129.7 (CH), 127.6 (CH), 96.5 (C), 72.1 (C), 35.2 (CH_2), 34.8 (CH_2), 34.2 (CH_2), 31.5 (CH_2), 21.7 ($2CH_3$), 20.6 (CH) ppm. IR (neat): 2978, 2931, 2855, 2246, 1723, 1219, 1161, 1003, 716 cm^{-1}. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{22}H_{23}O_2$: 319.1693; found: 319.1698.

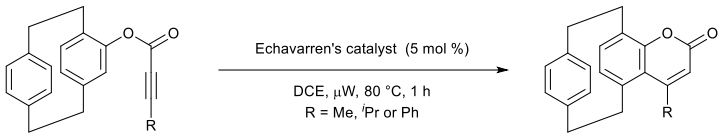


2c

*Compound **2c*** According to **GP1**, starting from compound **1** (1 equiv., 250 mg, 1.11 mmol); flash chromatography on silica gel Cy/EtOAc 14:1) gave compound **2c** (320 mg, 0.908 mmol, 81%) as an amorphous yellow solid. This compound has been previously characterized by our team:[2] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69-7.61 (m, 2H), 7.55-7.47 (m, 1H), 7.46-7.38 (m, 2H), 7.03 (dd, J = 7.8, 1.8 Hz, 1H), 6.61-6.50 (m, 4H), 6.48 (dd, J =

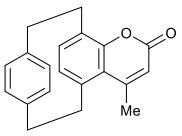
7.8, 1.7 Hz, 1H), 6.20-6.10 (m, 1H), 3.28 (ddd, *J* = 13.0, 9.9, 2.6 Hz, 1H), 3.22-3.15 (m, 1H), 3.16-2.96 (m, 5H), 2.77 (ddd, *J* = 13.4, 10.3, 5.6 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.9 (C), 148.5 (C), 141.8 (C), 139.5 (C), 139.1 (C), 135.1 (CH), 133.4 (CH), 133.2 (2CH), 132.8 (CH), 132.4 (CH), 131.3 (C), 130.9 (CH), 130.9 (CH), 129.7 (CH), 128.6 (2CH), 127.6 (CH), 119.4 (C), 88.6 (C), 80.4 (C), 35.2 (CH_2), 34.8 (CH_2), 34.2 (CH_2), 31.5 (CH_2) ppm. IR (neat): 2928, 2852, 2219, 1721, 1490, 1281, 1153, 1084, 918, 758 cm^{-1}. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{25}H_{21}O_2$: 353.1536; found: 353.1544.

General Procedure for the cyclization reactions (GP2)



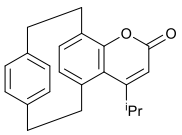
2a-c 3a-c

A 20 mL microwave vial was charged with Echavarren's catalyst (0.05 equiv.) under an Argon atmosphere. Dry DCE (0.1 M) was then added, and the resulting mixture was stirred at rt for 5 min. Compound **2** (1 equiv.) was finally added. The tube was sealed, then evacuated and refilled with argon three times. The solution was irradiated in a microwave reactor at 80 °C for 1h. At the end of the reaction, the mixture was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography. Products **3a-c** were isolated as amorphous solids.



3a

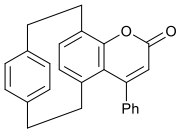
*Compound **3a***: According to **GP2**, starting from compound **2a** (1 equiv., 700 mg, 2.41 mmol); flash chromatography on silica gel (EtOAc/Cy, 2:8) gave compound **3a** (469 mg, 1.62 mmol, 67%) as an amorphous white solid. This compound has been previously characterized by our team:[2] ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 6.74 (d, *J* = 7.7 Hz, 1H), 6.63 (d, *J* = 7.7 Hz, 1H), 6.56 (ddd, *J* = 9.9, 8.0, 1.8 Hz, 2H), 6.45 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.24 (d, *J* = 1.2 Hz, 1H), 6.20 (dd, *J* = 7.8, 2.0 Hz, 1H), 3.76-3.55 (m, 2H), 3.31-3.13 (m, 2H), 3.07 (ddd, *J* = 13.3, 10.8, 2.9 Hz, 1H), 2.95 (dt, *J* = 14.6, 9.2 Hz, 1H), 2.75 (ddd, *J* = 13.4, 10.8, 5.0 Hz, 1H), 2.63 (dt, *J* = 13.4, 9.3 Hz, 1H), 2.50 (d, *J* = 1.2 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.7 (C), 153.3 (C), 153.1 (C), 139.8 (C), 139.7 (C), 137.7 (C), 135.9 (CH), 133.1 (CH), 132.2 (CH), 131.9 (CH), 129.0 (CH), 128.6 (C), 127.1 (CH), 121.9 (C), 116.0 (CH), 36.9 (CH_2), 35.3 (CH_2), 33.7 (CH_2), 30.1 (CH_2), 22.6 (CH_3) ppm. IR (neat): 2924, 2854, 2248, 1721, 1573, 1415, 1355, 1191, 1042, 914, 730, 720 cm^{-1}. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{20}H_{19}O_2$: 291.1380; found: 291.1385.



3b

*Compound **3b***: According to **GP2**, starting from compound **2b** (1 equiv., 180 mg, 0.57 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:9) gave compound **3b** (160 mg, 0.502 mmol, 89%) as an amorphous white solid. This compound has been previously characterized by our team:[2] ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 6.72 (d, *J* = 7.7 Hz, 1H), 6.62 (d, *J* = 7.7 Hz, 1H), 6.56 (ddd, *J* = 7.2, 5.0, 1.8 Hz, 2H), 6.46 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.37 (d, *J* = 0.7 Hz, 1H), 6.16 (dd, *J* = 7.8, 1.9 Hz, 1H), 3.74-3.49 (m, 2H), 3.37 (p, *J* = 6.7 Hz, 1H), 3.26-3.12 (m, 2H), 3.07 (ddd, *J* = 13.2, 10.9, 2.8 Hz, 1H), 2.99 (dt, *J* = 14.8, 9.1 Hz, 1H), 2.72 (ddd, *J* = 13.4, 10.8, 5.1 Hz, 1H), 2.61 (dt, *J* = 13.4, 9.0 Hz, 1H), 1.42 (d, *J* = 6.5 Hz, 3H), 1.11 (d, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 163.5 (C), 161.5 (C), 153.7 (C), 139.7 (C), 139.2 (C), 137.5 (C), 135.5 (CH), 133.0 (CH), 132.1 (CH), 132.0 (CH), 128.9 (CH), 128.7 (C), 127.1 (CH), 120.3 (C), 111.7 (CH), 37.9

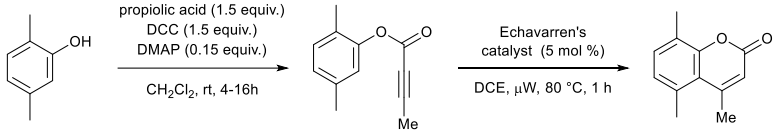
(CH_2), 35.5 (CH_2), 33.7 (CH_2), 30.3 (CH), 30.2 (CH_2), 24.1 (CH_3), 20.8 (CH_3) ppm. IR (neat): 2965, 2931, 2854, 1718, 1571, 1456, 1358, 1176, 1027, 918, 863, 682 cm^{-1}. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{22}H_{23}O_2$: 319.1693; found: 319.1697.



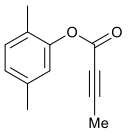
3c

*Compound **3c***: According to **GP2**, starting from compound **2c** (1 equiv., 310 mg, 0.88 mmol); flash chromatography on silica gel (EtOAc/Cy, 2:8) gave compound **3c** (180 mg, 0.51 mmol, 58%) as an amorphous white solid. This compound has been previously characterized by our team:[2] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80-7.18 (br m, 5H), 6.80 (d, *J* = 7.7 Hz, 1H), 6.65 (d, *J* = 7.9 Hz, 1H), 6.61 (d, *J* = 7.7 Hz, 1H), 6.47 (s, 2H), 6.34 (s, 1H), 6.32 (d, *J* = 7.9 Hz, 1H), 3.69 (ddd, *J* = 13.3, 10.5, 2.8 Hz, 1H), 3.22 (ddd, *J* = 13.0, 10.5, 5.0 Hz, 1H), 3.10 (ddd, *J* = 13.3, 10.8, 2.9 Hz, 1H), 2.88-2.65 (m, 2H), 2.49 (ddd, *J* = 14.1, 9.7, 8.0 Hz, 1H), 2.40-2.25 (m, 1H), 2.18 (ddd, *J* = 13.3, 9.5, 8.0 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.9 (C), 156.1 (C), 154.2 (C), 141.3 (C), 139.5 (C), 138.4 (C), 138.0 (C), 136.6 (CH), 132.9 (CH), 132.2 (CH), 131.7 (CH), 129.6 (CH), 128.9 (br, 4CH), 128.3 (CH and C), 126.9 (CH), 120.6 (C), 115.9 (CH), 36.2 (CH_2), 35.1 (CH_2), 33.8 (CH_2), 30.0 (CH_2) ppm. IR (neat): 2938, 2856, 2248, 1716, 1568, 1446, 1415, 1355, 1183, 1038, 910, 730 cm^{-1}. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{25}H_{21}O_2$: 353.1535; found: 353.1545.

Synthesis and characterization of coumarin 6

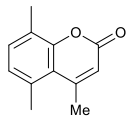


S0 6



S0

*Compound **S0*** According to **GP1**, starting from commercially available 2,5-dimethylphenol (1 equiv., 250 mg, 0.26 mL, 2.046 mmol); flash chromatography on silica gel (Cy/CH_2Cl_2 7:3) gave compound **S0** (214 mg, 1.14 mmol, 56%) as an amorphous yellow solid. This compound has been previously characterized by our team:[2] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (d, *J* = 7.7 Hz, 1H), 6.97 (d, *J* = 7.7 Hz, 1H), 6.86 (s, 1H), 2.32 (s, 3H), 2.16 (s, 3H), 2.07 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.9 (C), 148.4 (C), 137.0 (C), 130.9 (CH), 127.2 (CH), 126.7 (C), 122.2 (CH), 87.7 (C), 72.1 (C), 20.8 (CH_3), 15.7 (CH_3), 3.9 (CH_3) ppm. IR (neat): 2233, 1725, 1508, 1251, 1229, 1203, 1106, 1042, 886, 810, 741 cm^{-1}. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{12}H_{13}O_2$: 189.0910; found: 189.0912.

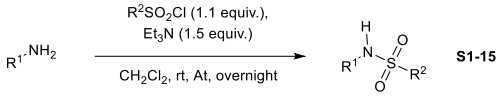


6

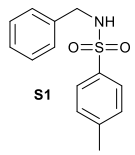
*Compound **6***: According to **GP2**, starting from compound **S0** (1 equiv., 180 mg, 0.96 mmol); flash chromatography on silica gel (EtOAc/Cy, 2:8) gave compound **6** (132 mg, 0.70 mmol, 73%) as an amorphous white solid. This compound has been previously characterized by our team:[2] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.25 – 6.16 (m, 1H), 2.67 (s, 3H), 2.60 (d, *J* = 1.1 Hz, 3H), 2.39 (s, 3H) ppm.^{13}C NMR (125 MHz, $CDCl_3$) δ 160.4 (C), 154.5 (C), 153.2 (C), 134.1 (C), 132.2 (CH), 127.6 (CH), 124.8 (C), 118.9 (C), 116.2 (CH), 25.2 (CH_3), 24.3 (CH_3), 16.0 (CH_3) ppm. IR (neat): 1703, 1585, 1411, 1206, 1136, 1064, 920, 819 cm^{-1}. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{12}H_{13}O_2$: 189.0910; found: 189.0909.

Synthesis and characterization of sulfonamides 4a-t

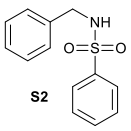
General Procedure for the tosylation reactions (GP3)



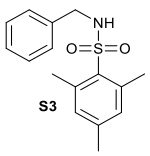
A flame-dried vial was charged with the desired amine (1 equiv.), triethylamine (1.5 equiv.) and DCM (0.1 M) under an argon atmosphere. The appropriate sulphonyl chloride (1.1 equiv.) was then added, and the resulting mixture was stirred at rt overnight. Water was then added, the immiscible phases were separated, and the aqueous layer was extracted with DCM (3x). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography. The expected products were isolated as amorphous solids unless otherwise specified.



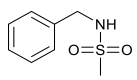
*Compound **S1**.* According to **G3**, starting from benzylamine (1 equiv., 0.408 mL, 3.73 mmol) and tosyl chloride (1.1 equiv., 783 mg, 4.106 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:9) gave compound **S1** (966 mg, 3.7 mmol, 99 %) as a pinkish solid. This compound has been previously characterized by our team:[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (d, J = 7.4 Hz, 2H), 7.33 – 7.26 (m, 5H), 7.19 (d, J = 7.4 Hz, 2H), 4.59 (br s, 1H), 4.13 (d, J = 6.2 Hz, 2H), 2.44 (s, 3H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 143.6, 136.9, 136.3, 129.8, 128.7, 128.0, 127.9, 127.2, 47.3, 21.5 ppm. Spectroscopic data are consistent with the literature data for this compound.[4]



*Compound **S2**.* According to **G3**, starting from benzylamine (1 equiv., 400 mg, 0.408 mL, 3.73 mmol) and benzenesulfonyl chloride (1.1 equiv., 725 mg, 0.52 mL, 4.106 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:9) gave compound **S2** (914 mg, 3.7 mmol, 99 %) as an amorphous white solid. This compound has been previously characterized by our team:[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 (d, J = 7.7 Hz, 2H), 7.58 (t, J = 7.0 Hz, 1H), 7.51 (m, 2H), 7.34 – 7.25 (m, 3H), 7.18 (d, J = 6.9 Hz, 2H), 4.86 – 4.58 (m, 1H), 4.14 (d, J = 6.0 Hz, 2H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 140.0, 136.2, 132.9, 129.3, 128.9, 128.1, 128.0, 127.2, 47.4 ppm. Spectroscopic data are consistent with the literature data for this compound.[5]

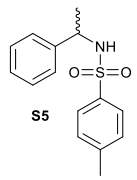


*Compound **S3**.* According toto **G3**, starting from benzylamine (1 equiv., 300 mg, 0.306 mL, 2.8 mmol) and 2-mesitylenesulfonyl chloride (1.1 equiv., 674 mg, 3.08 mmol); flash chromatography on silica gel (EtOAc/Cy, 2:8) gave compound **S3** (717 mg, 2.48 mmol, 89 %) as an amorphous white solid. This compound has been previously characterized by our team:[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 – 7.22 (m, 3H), 7.20 – 7.14 (m, 2H), 6.96 (s, 2H), 4.72 (t, J = 5.9 Hz, 1H), 4.07 (d, J = 6.2 Hz, 2H), 2.64 (s, 6H), 2.31 (s, 3H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 141.8, 138.6, 135.8, 132.9, 131.5, 128.1, 127.4, 46.3, 22.4, 20.4 ppm. Spectroscopic data are consistent with the literature data for this compound.[6]



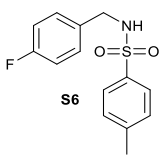
S4

*Compound **S4**.* According to **G3**, starting from benzylamine (1 equiv., 0.26 mL, 2.3 mmol) and mesyl chloride (1.1 equiv., 0.20 mL, 2.6 mmol); flash chromatography on silica gel (EtOAc/Cy, 2:8) gave compound **S4** (300 mg, 1.62 mmol, 69 %) as a colourless oil. This compound has been previously characterized by our team:[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 – 7.23 (m, 5H), 4.57 (s, 1H), 4.26 (d, J = 6.0 Hz, 2H), 2.81 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 136.6, 129.0, 128.2, 127.9, 47.3, 41.2 ppm. Spectroscopic data are consistent with the literature data for this compound.[7]



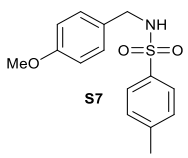
S5

*Compound (±)-**S5**.* According to **G3**, starting from DL-alpha-methylbenzylamine (1 equiv., 0.213 mL, 1.65 mmol) and tosyl chloride (1 equiv., 314 mg, 1.65 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:9) gave compound (±)-**S5** (448 mg, 1.63 mmol, 99 %) as a white solid. This compound has been previously characterized by our team:[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (d, J = 8.3 Hz, 2H), 7.19 (m, 5H), 7.12 – 7.07 (m, 2H), 5.06 – 4.76 (br m, 1H), 4.46 (p, J = 6.9 Hz, 1H), 2.38 (s, 3H), 1.42 (d, J = 6.9 Hz, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 143.3, 142.1, 137.7, 129.6, 128.7, 127.6 (br), 127.2, 126.2, 53.7, 23.7, 21.6 ppm. Spectroscopic data are consistent with the literature data for this compound.[8]



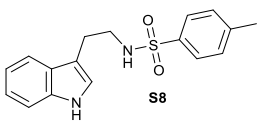
S6

*Compound **S6**.* According to **G3**, starting from 4-fluorobenzylamine (1 equiv., 0.18 mL, 1.6 mmol) and tosyl chloride (1.1 equiv., 335 mg, 1.76 mmol); flash chromatography on silica gel (EtOAc/Cy, 2:8) gave compound **S6** (442 mg, 1.58 mmol, 99 %) as a white solid. This compound has been previously characterized by our team:[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 7.9 Hz, 2H), 7.16 (dd, J = 8.3, 5.5 Hz, 2H), 6.95 (t, J = 8.5 Hz, 2H), 4.86 (s, J = 40.1 Hz, 1H), 4.08 (d, J = 6.2 Hz, 2H), 2.43 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 162.5 (d, J = 246.6 Hz), 143.8, 136.9, 132.2 (d, J = 2.9 Hz), 129.9, 129.7 (d, J = 8.3 Hz), 127.3, 115.7 (d, J = 21.5 Hz), 46.7, 21.7 ppm. ^{19}F NMR (471 MHz, $CDCl_3$): δ −114.3 (F) ppm. Spectroscopic data are consistent with the literature data for this compound.[9]



S7

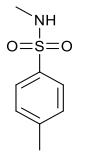
*Compound **S7**.* According to **G3**, starting from 4-methoxybenzylamine (1 equiv., 0.19 mL, 1.46 mmol) and tosyl chloride (1.1 equiv., 306 mg, 1.604 mmol); flash chromatography on silica gel (EtOAc/Cy, 2:8) gave compound **S7** (421 mg, 1.44 mmol, 99 %) as a white solid. This compound has been previously characterized by our team:[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 7.11 (d, J = 8.6 Hz, 2H), 6.82 – 6.78 (m, 2H), 4.54 (t, J = 5.8 Hz, 1H), 4.05 (d, J = 6.1 Hz, 2H), 3.78 (s, 3H), 2.44 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$: δ 159.3, 143.5, 136.8, 129.7, 129.3, 128.2, 127.2, 114.1, 55.3, 46.8, 21.6 ppm. Spectroscopic data are consistent with the literature data for this compound.[5]



S8

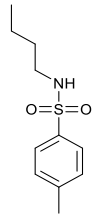
*Compound **S8**.* According to **G3**, starting from tryptamine (1 equiv., 250 mg, 1.56 mmol) and tosyl chloride (1.1 equiv., 327 mg, 1.72 mmol); flash chromatography on silica gel (EtOAc/Cy, 3:7) gave compound **S8** (380 mg, 1.209 mmol, 77 %) as a pinkish solid. This compound has been previously characterized by our team:[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06 (s, 1H), 7.63 (d, J = 8.3 Hz, 2H), 7.41 (d, J = 7.9 Hz, 1H), 7.35 (d, J = 8.2 Hz, 1H), 7.24 – 7.16 (m, 3H), 7.09 – 7.03 (m, 1H), 6.97 (d, J = 2.2 Hz, 1H), 4.42 (t, J = 6.0 Hz, 1H), 3.27 (q, J = 6.5 Hz, 2H), 2.93 (t, J = 6.6 Hz, 2H), 2.40 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR

(125 MHz, $CDCl_3$): δ 143.3, 136.7, 136.4, 129.6, 127.0, 126.8, 122.6, 122.3, 119.5, 118.5, 111.6, 111.3, 43.0, 25.5, 21.5 ppm. Spectroscopic data are consistent with the literature data for this compound.[10]



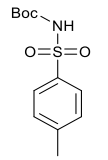
S9

*Compound **S9**.* According to **G3**, starting from methylamine (33 wt. % in absolute ethanol, 1 equiv., 300 mg, 3.19 mmol) and tosyl chloride (1.1 equiv., 668 mg, 3.51 mmol); compound **S9** (300 mg, 1.62 mmol, 51 %) was isolated as a white solid. This compound has been previously characterized by our team:[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 – 7.70 (m, 2H), 7.36 – 7.26 (m, 2H), 4.51 (s, 1H), 2.64 (s, 3H), 2.43 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 143.6, 135.8, 129.8, 127.3, 29.4, 21.6 ppm. Spectroscopic data are consistent with the literature data for this compound.[11]



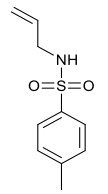
S10

*Compound **S10**.* According to **G3**, starting from butylamine (1 equiv., 200 mg, 0.27 mL, 2.73 mmol) and tosyl chloride (1 equiv., 521 mg, 2.73 mmol); solvent evaporation gave compound S10 (615 mg, 2.71 mmol, 99 %) as a clear oil. **S10** was used in the next synthetic step without further purification. This compound has been previously characterized by our team:[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 4.39 (t, *J* = 5.6 Hz, 1H), 2.86 (dd, *J* = 13.6, 6.8 Hz, 2H), 2.36 (s, 3H), 1.42 – 1.32 (m, 2H), 1.22 (dq, *J* = 14.5, 7.3 Hz, 2H), 0.78 (t, *J* = 7.3 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 143.3, 137.1, 129.7, 127.1, 42.9, 31.6, 21.5, 19.7, 13.5 ppm. Spectroscopic data are consistent with the literature data for this compound.[12]



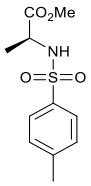
S11

*Compound **S11**.* This intermediate was prepared according to the following procedure: PTSA (1 equiv., 2 g, 11.68 mmol), Et_3N (1.1 equiv., 1.3 g, 1.79 mL, 12.85 mmol) and DMAP (0.1 equiv., 0.14 g, 1.17 mmol) was dissolved in DCE (12 mL) at room temperature under an argon atmosphere. Boc_2O (1.15 equiv., 2.93 g, 2.87 mL, 13.43 mmol) was added and the resulting mixture was stirred at rt overnight. Water was then added, the immiscible phases were separated, and the aqueous layer was extracted with DCM (3x). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was triturated in heptane to afford **S11** (2.87 g, 10.58 mmol, 91%) as a white amorphous solid. ^{1}H NMR (500 MHz, $CDCl_3$): 7.90 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 2.45 (s, 3H), 1.38 (s, 9H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 149.0, 144.7, 135.9, 129.5, 128.2, 84.1, 27.9, 21.6. Spectroscopic data are consistent with the literature data for this compound.[12]

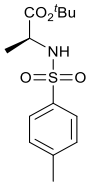


S12

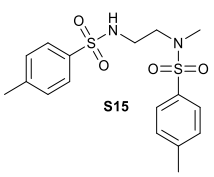
*Compound **S12**.* According to **G3**, starting from allylamine (1 equiv., 500 mg, 0.66 mL, 8.76 mmol) and tosyl chloride (1 equiv., 1.67 g, 8.76 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:9 then 2:8) gave compound **S12** (1.54 g, 7.28 mmol, 83 %) as a white solid. This compound has been previously characterized by our team:[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 5.72 (ddt, *J* = 16.2, 10.3, 5.8 Hz, 1H), 5.17 (dd, *J* = 17.1, 1.5 Hz, 1H), 5.09 (dd, *J* = 10.2, 1.1 Hz, 1H), 4.61 (s, 1H), 3.58 (t, *J* = 6.0 Hz, 2H), 2.43 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 143.5, 137.0, 133.0, 129.7, 127.2, 117.7, 45.8, 21.5 ppm. Spectroscopic data are consistent with the literature data for this compound. [13]


S13

*Compound (S)-**S13**.* This intermediate was prepared according to the following procedure: to a solution of (2S)-1-methoxy-1-oxopropan-2-aminium chloride (1 equiv., 500 mg, 3.58 mmol), Et_3N (2.2 equiv., 797.48 mg, 1.095 mL, 7.88 mmol) and DMAP (0.005 equiv., 2.19 mg, 0.018 mmol), in DCM (10 mL), was added a solution of *p*-toluene sulfonyl chloride (1.2 equiv., 819.49 mg, 4.3 mmol) in DCM (10 mL) at 0 °C under an argon atmosphere. The resulting mixture was warmed-up to rt and stirred overnight. Water was then added, the immiscible phases were separated, and the aqueous layer was extracted with Et_2O (3x). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (eluent: EtOAc/heptane 3:7) to afford **S13** (840 mg, 3.26 mmol, 91%) as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 – 7.62 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 5.19 (d, *J* = 8.2 Hz, 1H), 3.99 (dq, *J* = 14.4, 7.2 Hz, 1H), 3.54 (s, 3H), 2.42 (s, 3H), 1.38 (d, *J* = 7.2 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 172.6, 143.7, 136.7, 129.6, 127.2, 52.6, 51.4, 21.5, 19.8 ppm. $[\alpha]_D^{20}$ −37 (c 0.22, $CHCl_3$). Spectroscopic data are consistent with the literature data for this compound.[14]

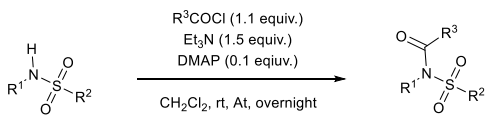

S14

*Compound (S)-**S14**.* According to **G3**, starting from tert-butyl (2*S*)-2-aminopropanoate (1 equiv., 726.01 mg, 5 mmol) and tosyl chloride (1 equiv., 953.2 mg, 5 mmol); flash chromatography on silica gel (EtOAc/heptane, 3:7) gave compound **S14** (1.47 g, 4.9 mmol, 98%) as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 5.18 (d, *J* = 8.6 Hz, 1H), 3.84 (dq, *J* = 8.5, 7.2 Hz, 1H), 2.40 (s, 3H), 1.34 (d, *J* = 7.2 Hz, 3H), 1.27 (s, 9H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 171.3, 143.5, 136.8, 129.6, 127.3, 82.4, 51.9, 27.6, 21.5, 20.1 ppm. $[\alpha]_D^{20}$ −32 (c 0.2, $CHCl_3$). Spectroscopic data are consistent with the literature data for this compound.[15]


S15

*Compound **S15**.* According to **G3**, starting from N-methylethylenediamine (1 equiv., 0.12 mL, 1.35 mmol) and tosyl chloride (2 equiv., 728 mg, 2.70 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:1) gave compound **S15** (226 mg, 0.59 mmol, 44 %) as a white solid. This compound has been previously characterized by our team:[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.32 (t, *J* = 8.3 Hz, 4H), 4.94 (dd, *J* = 14.3, 5.8 Hz, 1H), 3.13 (q, *J* = 5.8 Hz, 2H), 3.03 (t, *J* = 5.8 Hz, 2H), 2.65 (s, 3H), 2.44 (s, 3H), 2.42 (s, 3H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): *δ* 143.9, 143.6, 136.6, 133.7, 129.9, 129.8, 127.4, 127.2, 49.8, 41.4, 36.1, 21.57, 27.56 ppm. IR (neat) : ν 3308, 2882, 2254, 1598, 1453, 1333, 1159, 1090, 1048, 906, 730 cm^{-1}. HRMS (ESI-Orbitrap) : *m/z* [M-H$^+$] calcd for $C_{17}H_{21}N_2O_4S_2$: 381.0948; found : 381.0954.

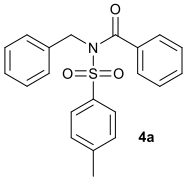
*<u>General Procedure for the benzoylation reactions (**GP4**)</u>*



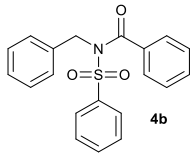
S1-15 4a-t

A round-bottomed flask containing the desired precursor (**S1-15**, 1 equiv.), DMAP (0.1 eq) and triethylamine (1.5 equiv.) dissolved in DCM (0.1 M), was cooled to 0 °C. Benzoyl chloride (1.5 equiv.) was then added dropwise. The reaction was warmed up to rt and stirred overnight. Water was then added, the immiscible phases were separated, and the aqueous layer was extracted with DCM (3x). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The

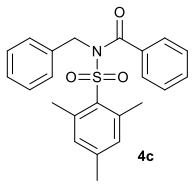
crude residue was purified by silica gel column chromatography. Products were **4a-t** isolated as amorphous solids unless otherwise specified. as a white solid.



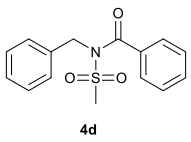
Compound **4a**. According to **GP4**, starting from N-benzyl-4-methylbenzene-1-sulfonamide (**S1**, 1 equiv., 1.05 g, 4.02 mmol), and benzoyl chloride (1.5 equiv., 0.7 mL, 6.03 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:9) gave compound **4a** (1.14 g, 3.13 mmol, 78 %) as a white solid. This compound has been previously characterized by our team:[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (d, J = 8.3 Hz, 2H), 7.49 – 7.42 (m, 3H), 7.33 (t, J = 7.7 Hz, 2H), 7.26 – 7.18 (m, 7H), 4.98 (s, 2H), 2.41 (s, 3H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 171.6, 144.7, 136.3, 136.0, 135.0, 131.7, 129.4, 128.6, 128.5, 128.3, 128.2, 128.0, 127.8, 51.2, 21.6 ppm. Spectroscopic data are consistent with the literature data for this compound.[16]



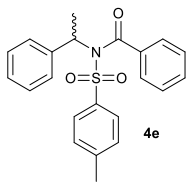
*Compound **4b**.* According to **GP4**, starting from N-benzylbenzenesulfonamide (**S2**, 1 equiv., 980 mg, 3.96 mmol) and benzoyl chloride (1.5 equiv., 0.69 mL, 5.94 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:9) gave compound **4b** (1.3 g, 3.69 mmol, 93 %) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 – 7.70 (m, 2H), 7.59 (t, J = 7.5 Hz, 1H), 7.51 – 7.41 (m, 5H), 7.37 – 7.34 (m, 2H), 7.29 – 7.24 (m, 3H), 7.23 – 7.19 (m, 2H), 5.03 (s, 2H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 171.5, 138.8, 136.0, 134.7, 133.6, 131.8, 128.7, 128.6, 128.4, 128.2, 127.9, 127.8, 51.3 ppm. Spectroscopic data are consistent with the literature data for this compound.[17]



*Compound **4c**.* According to **GP4**, starting from *N*-benzyl-2,4,6-trimethylbenzene-1-sulfonamide (**S3**, 1 equiv., 150 mg, 0.52 mmol) and benzoyl chloride (1.5 equiv., 0.09 mL, 0.78 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:9) gave compound **4c** (122 mg, 0.31 mmol, 60 %) as a white solid. This compound has been previously characterized by our team:[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 – 7.36 (m, 1H), 7.35 – 7.21 (m, 9H), 6.93 (s, 2H), 5.02 (s, 2H), 2.62 (s, 6H), 2.29 (s, 3H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 171.3, 143.7, 140.4, 136.5, 135.2, 133.0, 132.1, 131.1, 128.6, 128.1, 127.8, 127.7, 127.4, 50.2, 22.4, 21.0 ppm. IR (neat): ν 2977, 2255, 1681, 1603, 1344, 1278, 1165, 1056, 911, 733 cm^{-1}. HRMS (ESI-Orbitrap): *m/z* [M+H$^+$] calcd for $C_{23}H_{24}NO_3S$: 394.1471; found: 394.1467.

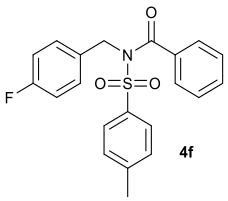


*Compound **4d**.* According to **GP4**, starting from *N*-benzylmethanesulfonamide (**S4**, 1 equiv., 150 mg, 0.81 mmol) and benzoyl chloride (1.5 equiv., 0.14 mL, 1.22 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:9 to 2:8) gave compound **4d** (222 mg, 0.77 mmol, 95 %) as a white solid. This compound has been previously characterized by our team:[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70 – 7.60 (m, 2H), 7.56 (t, J = 7.5 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.38 – 7.27 (m, 3H), 7.21 – 7.11 (m, 2H), 4.99 (s, 2H), 3.04 (s, 3H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 172.6, 135.6, 133.8, 132.3, 129.0, 128.9, 128.4, 128.1, 52.2, 42.9 ppm. Spectroscopic data are consistent with the literature data for this compound.[18]

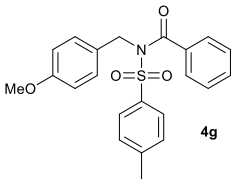


*Compound (±)-**4e**.* According to **GP4**, starting from 4-methyl-*N*-(1-phenylethyl)benzene-1-sulfonamide ((±)-**S5**, 1 equiv., 448 mg, 1.63 mmol) and benzoyl chloride (1.5 equiv., 0.28 mL, 2.44 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:9) gave compound (±)-**4e** (600 mg, 1.58 mmol, 97 %) as a white solid. This compound has been previously characterized by our team:[3] ^{1}H NMR (500 MHz, CDkCl$_3$): δ 7.51 (d, J = 8.3 Hz, 2H), 7.41 (t, J = 7.3 Hz, 1H), 7.34 – 7.24 (m, 9H), 7.19 (d, J = 8.1 Hz, 2H), 5.48 (q, J = 7.0 Hz, 1H), 2.41 (s, 3H), 1.91 (d, J = 7.1 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ

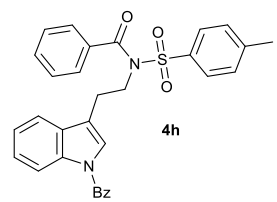
172.3, 144.6, 139.3, 136.6, 136.3, 131.4, 129.4, 128.9, 128.4, 128.2, 127.9, 127.82, 127.77, 58.7, 21.8, 18.6 ppm. Spectroscopic data are consistent with the literature data for this compound.[19]



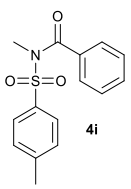
*Compound **4f**.* According to **GP4**, starting from *N*-[(4-fluorophenyl)methyl]-4-methylbenzene-1-sulfonamide (**S6**, 1 equiv., 200 mg, 0.72 mmol) and benzoyl chloride (1.5 equiv., 0.12 mL, 1.074 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:9) gave compound **4f** (273 mg, 0.71 mmol, 99 %) as a white solid. This compound has been previously characterized by our team:[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.3 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.44 – 7.41 (m, 2H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.25 – 7.19 (m, 4H), 6.95 (t, *J* = 8.7 Hz, 2H), 4.94 (s, 2H), 2.42 (s, 3H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 171.5, 162.4 (d, *J* = 246.7 Hz), 144.8, 135.9, 135.0, 132.0 (d, *J* = 3.1 Hz), 131.8, 130.0 (d, *J* = 8.2 Hz), 129.5, 128.4, 128.3, 128.2, 115.5 (d, *J* = 21.6 Hz, 2CH), 50.3, 21.6 ppm. ^{19}F NMR (471 MHz, DMSO): δ - 114.24 (F) ppm. Spectroscopic data are consistent with the literature data for this compound.[19]



*Compound **4g**.* According to **GP4**, starting from *N*-[(4-methoxyphenyl)methyl]-4-methylbenzene-1-sulfonamide (**S7**, 1 equiv., 200 mg, 0.67 mmol) and benzoyl chloride (1.5 equiv., 0.17 mL, 1.43 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:9) gave compound **4g** (255.17 mg, 0.65 mmol, 94 %) as a white solid. This compound has been previously characterized by our team:[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.3 Hz, 2H), 7.49 – 7.41 (m, 3H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.7 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 4.92 (s, 2H), 3.78 (s, 3H), 2.41 (s, 3H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 171.6, 159.2, 144.6, 136.0, 135.0, 131.7, 129.5, 129.4, 128.4, 128.31, 128.25, 128.19, 113.9, 55.3, 50.7, 21.6 ppm. IR (neat): ν 2981, 1686, 1613, 1598, 1514, 1447, 1357, 1249, 1167, 1087, 1033, 955, 814, 731 cm^{-1}. HRMS (ESI-Orbitrap): *m/z* [M+H^{+}] calcd for $C_{22}H_{22}NO_4S$: 396.1264; found: 396.1257.

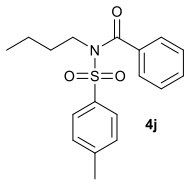


*Compound **4h**.* According to **GP4**, starting from *N*-[2-(1H-indol-3-yl)ethyl]-4-methylbenzene-1-sulfonamide (**S8**, 1 equiv., 200 mg, 0.64 mmol) and benzoyl chloride (1.5 equiv., 0.11 mL, 0.95 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:9) gave compound **4h** (158 mg, 0.302 mmol, 48 %) as a white solid. This compound has been previously characterized by our team:[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.37 (d, *J* = 8.3 Hz, 1H), 7.75 – 7.67 (m, 4H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.40 (qd, *J* = 5.6, 2.7 Hz, 1H), 7.37 – 7.32 (m, 1H), 7.25 – 7.17 (m, 8H), 7.04 (s, 1H), 4.17 – 4.04 (m, 2H), 3.14 – 2.99 (m, 2H), 2.39 (s, 3H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 171.4, 168.4, 144.9, 136.3, 136.0, 134.8, 134.5, 131.9, 131.4, 130.4, 129.5, 129.2, 128.7, 128.4, 128.1, 127.7, 125.8, 125.2, 123.9, 118.6, 117.5, 116.6, 47.6, 25.6, 21.6 ppm. IR (neat): ν 2924, 2255, 1683, 1600, 1453, 1376, 1356, 1167, 910, 732 cm^{-1}. HRMS (ESI-Orbitrap): *m/z* [M+H^{+}] calcd for $C_{31}H_{27}N_2O_4S$: 523.1686; found : 523.1678.

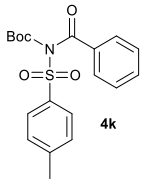


*Compound **4i**.* According to **GP4**, starting from *N*-methyl-*p*-toluenesulfonamide (**S9**, 1 equiv., 150 mg, 0.81 mmol) and benzoyl chloride (1.5 equiv., 0.14 mL, 1.22 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:9) gave compound **4i** (242 mg, 0.81 mmol, quantitative) as a white solid. This compound has been previously characterized by our team:[3] ^{1}H NMR (500 MHz, $CDCl_3$ δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.68 – 7.48 (m, 3H), 7.41 (dd, *J* = 10.8, 4.5 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 3.28 (s, 3H), 2.44 (s, 3H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$):

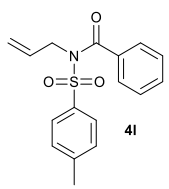
δ 171.5, 144.9, 135.1, 134.4, 132.0, 129.6, 128.50, 128.47, 128.44, 128.3, 35.6, 21.7 ppm. Spectroscopic data are consistent with the literature data for this compound.[20]



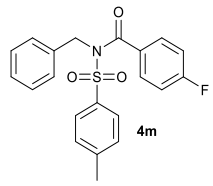
*Compound **4j**.* According to **GP4**, starting from *N*-butyl-4-methylbenzene-1-sulfonamide (**S10**, 1 equiv., 250 mg, 1.1 mmol) and benzoyl chloride (1.5 equiv., 0.19 mL, 1.65 mmol); flash chromatography on silica gel (EtOAc/Pentane, 2:8) gave compound **4j** (262 mg, 0.079 mmol, 72 %) as an off-white solid. This compound has been previously characterized by our team:[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.53 – 7.48 (m, 3H), 7.44 – 7.37 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 3.84 – 3.75 (m, 2H), 2.45 (s, 3H), 1.67 (dt, *J* = 15.1, 7.5 Hz, 2H), 1.27 (dt, *J* = 14.8, 7.4 Hz, 2H), 0.86 (t, *J* = 7.4 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 171.6, 144.6, 136.2, 135.4, 131.6, 129.5, 128.4, 128.2, 128.1, 47.9, 31.7, 21.6, 19.8, 13.5 ppm. Spectroscopic data are consistent with the literature data for this compound.[21]



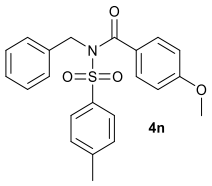
*Compound **4k**.* According to **GP4**, starting from **S11** (1 equiv., 1.36 g, 5 mmol) and benzoyl chloride (1 equiv., 0.58 mL, 5 mmol); flash chromatography on silica gel (EtOAc/heptane, 2:8) gave compound **4k** (400 mg, 1.06 mmol, 21%) as an off-white solid. ^{1}H NMR (500 MHz, $CDCl_3$): 8.11 – 8.01 (m, 4H), 7.69 – 7.64 (m, 1H), 7.53 (t, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 2.47 (s, 3H), 1.24 (s, 9H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 167.4, 148.6, 145.1, 136.0, 134.7, 133.6, 130.7, 129.5, 128.9, 85.5, 27.6, 21.7 ppm. Spectroscopic data are consistent with the literature data for this compound.[22]



*Compound **4l**.* According to **GP4**, starting from 4-methyl-*N*-(prop-2-en-1-yl)benzene-1-sulfonamide (**S12**, 1 equiv., 300 mg, 1.42 mmol) and benzoyl chloride (1.5 equiv., 0.25 mL, 2.13 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:9) gave compound **4l** (421 mg, 1.33 mmol, 94 %) as a white solid. This compound has been previously characterized by our team:[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.43 – 7.37 (m, 3H), 7.32 – 7.26 (m, 2H), 7.23 (d, J = 8.0 Hz, 2H), 5.76 (ddt, *J* = 17.0, 10.4, 5.7 Hz, 1H), 5.10 (ddd, *J* = 18.2, 13.8, 1.1 Hz, 2H), 4.34 (d, *J* = 5.7 Hz, 2H), 2.37 (s, 3H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 171.4, 144.8, 136.1, 134.9, 132.8, 131.6, 129.5, 128.7, 128.2, 128.0, 118.8, 50.3, 21.7 ppm. Spectroscopic data are consistent with the literature data for this compound.[23]

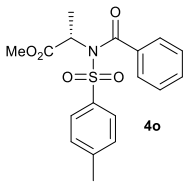


*Compound **4m**.* According to **GP4**, starting from *N*-benzyl-4-methylbenzene-1-sulfonamide (**S1**, 1 equiv., 150 mg, 0.57 mmol) and 4-fluorobenzoyl chloride (1.5 equiv., 0.10 mL, 0.86 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:9) gave compound **4m** (226 mg, 0.57 mmol, quantitative) as a white solid. This compound has been previously characterized by our team:[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.56 – 7.45 (m, 2H), 7.35 – 7.16 (m, 7H), 7.09 – 6.94 (m, 2H), 4.92 (s, 2H), 2.42 (s, 3H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 170.6, 164.8 (d, *J* = 253.5 Hz), 144.8, 136.0, 135.6, 131.2 (d, *J* = 3.4 Hz), 131.1 (d, *J* = 9.1 Hz), 129.5, 128.6, 128.3, 128.0, 127.8, 115.3 (d, *J* = 22.1 Hz), 51.1, 21.6 ppm. ^{19}F NMR (471 MHz, $CDCl_3$): δ −106.3 (F) ppm. Spectroscopic data are consistent with the literature data for this compound.[19]

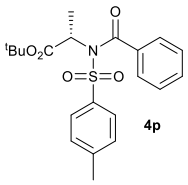


*Compound **4n**.* According to **GP4**, starting from *N*-benzyl-4-methylbenzene-1-sulfonamide (**S1**, 1 equiv., 150 mg, 0.57 mmol) and 4-methoxybenzoyl chloride (1.5 equiv., 0.12 mL, 0.86 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:9) gave compound **4n** (182 mg, 0.46 mmol, 80 %) as a white solid. This compound has been previously characterized by our team:[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62

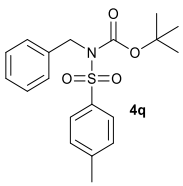
(d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 8.9 Hz, 2H), 7.25 – 7.19 (m, 7H), 6.85 (d, *J* = 8.9 Hz, 2H), 4.89 (s, 2H), 3.83 (s, 3H), 2.42 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 171.3, 162.9, 144.5, 136.1, 135.8, 131.3, 129.5, 128.5, 128.4, 128.1, 127.7, 127.2, 113.5, 55.4, 51.4, 21.6 ppm. Spectroscopic data are consistent with the literature data for this compound.[24]



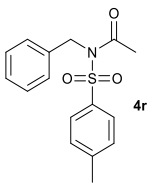
*Compound (S)-**4o**.* According to **GP4**, starting from **S13** (1 equiv., 204 mg, 0.79 mmol) and benzoyl chloride (1 equiv., 0.09 mL, 0.79 mmol); flash chromatography on silica gel (EtOAc/Pentane, 2:8) gave compound **4o** (220 mg, 0.61 mmol, 77 %) as an off-white solid. ^1H NMR (500 MHz, $CDCl_3$): 7.65 (d, *J* = 8.4 Hz, 2H), 7.44 – 7.39 (m, 1H), 7.32 (t, *J* = 4.1 Hz, 2H), 7.27 (dd, *J* = 10.4, 4.9 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 5.05 (q, *J* = 7.0 Hz, 1H), 3.81 (s, 3H), 2.41 (s, 3H), 1.78 (d, *J* = 7.0 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 170.6, 170.5, 144.9, 135.9, 134.6, 131.1, 129.3, 128.7, 128.1, 127.6, 56.7, 52.8, 21.7, 17.0 ppm. $[\alpha]_D^{20}$ −98 (c 0.2, $CHCl_3$). HRMS (ESI-Orbitrap): *m/z* [M+H$^+$] calcd for calcd for $C_{18}H_{19}NO_5S$: 362.1062; found: 362.1059.



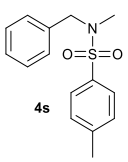
*Compound (S)-**4p**.* According to **GP4**, starting from **S14** (1 equiv., 300 mg, 1.0 mmol) and benzoyl chloride (1equiv., 0.12 mL, 1.0 mmol); flash chromatography on silica gel (EtOAc/Pentane, 2:8) gave compound **4p** (340 mg, 0.84 mmol, 84 %) as an off-white solid. ^1H NMR (500 MHz, $CDCl_3$): 7.65 (d, *J* = 8.3 Hz, 2H), 7.40 (td, *J* = 7.3, 1.5 Hz, 1H), 7.32 – 7.24 (m, 4H), 7.21 (d, *J* = 8.3 Hz, 2H), 4.93 (q, *J* = 7.0 Hz, 1H), 2.41 (s, 3H), 1.73 (d, *J* = 7.0 Hz, 3H), 1.51 (s, 9H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 170.4, 168.8, 144.7, 136.4, 135.0, 130.8, 129.3, 128.6, 127.9, 127.4, 82.4, 57.5, 27.9, 21.6, 16.9 ppm. $[\alpha]_D^{20}$ −92 (c 0.18, $CHCl_3$). HRMS (ESI-Orbitrap): *m/z* [M+H$^+$] calcd for $C_{21}H_{25}NO_5S$: 404.1532; found: 404.1525.



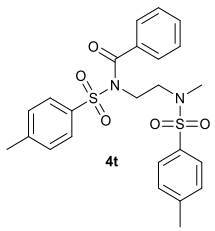
*Synthesis of Compound **4q**.* A round-bottomed flask containing *N*-benzyl-4-methylbenzene-1-sulfonamide (**S1**, 1 equiv., 150 mg, 0.57 mmol), and DMAP (0.1 equiv., 7 mg, 0.057 mmol), dissolved in THF (5 mL), was cooled to 0 °C. Boc_2O (1.5 equiv., 0.18 mL, 0.86 mmol) was then added. The reaction was warmed up to rt and stirred overnight. Water was then added, and the resulting aqueous mixture was extracted with DCM (3x). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography eluent: EtOAc/Cyclohexane 1:9) to afford compound **4q** (124 mg, 0.34 mmol, 60 %) as a white solid. This compound has been previously characterized by our team:[3] ^1H NMR (500 MHz, $CDCl_3$): *δ* 7.59 – 7.53 (m, 2H), 7.43 – 7.38 (m, 2H), 7.37 – 7.27 (m, 3H), 7.21 (d, *J* = 8.0 Hz, 2H), 5.04 (s, 2H), 2.41 (s, 3H), 1.31 (s, 9H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): *δ* 151.1, 144.1, 137.4, 137.1, 129.1, 128.5, 128.2, 128.1, 127.7, 84.5, 49.7, 27.9, 21.6 ppm. Spectroscopic data are consistent with the literature data for this compound.[25]



*Compound **4r**.* According to **GP4**, starting from *N*-benzyl-4-methylbenzene-1-sulfonamide (**S1**, 1 equiv., 150 mg, 0.57 mmol) and acetyl chloride (1.5 equiv., 0.06 mL, 0.86 mmol); flash chromatography on silica gel (EtOAc/Cy, 2:8) gave compound **4r** (168 mg, 0.55 mmol, 96 %) as a white solid. This compound has been previously characterized by our team:[3] ^1H NMR (500 MHz, $CDCl_3$): *δ* 7.61 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 7.3 Hz, 2H), 7.35 – 7.23 (m, 5H), 5.08 (s, 2H), 2.42 (s, 3H), 2.29 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): *δ* 170.4, 144.9, 136.7, 136.5, 129.8, 128.6, 128.0, 127.8, 49.5, 24.9, 21.6 ppm. Spectroscopic data are consistent with the literature data for this compound.[26]



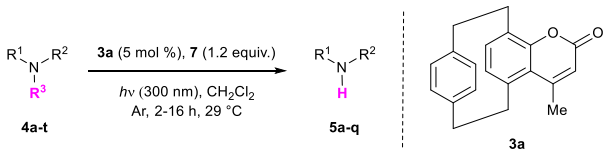
*Synthesis of Compound **4s***. A round-bottomed flask *N*-benzyl-4-methylbenzene-1-sulfonamide (**S1**, 1 equiv., 100 mg, 0.38 mmol), K_2CO_3 (6 equiv., 317 mg, 2.3 mmol), and DMF (5 mL), was cooled to 0 °C. MeI (1.5 equiv., 0.04 mL, 0.57 mmol) was then added. The reaction was warmed up to RT and stirred overnight. Water was then added, and the resulting aqueous mixture was extracted with DCM (3x). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography eluent: EtOAc/Cyclohexane 1:9) to afford compound **4s** (104 mg, 0.38 mmol, quantitative yield) as a white solid. This compound has been previously characterized by our team:[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73 (d, J = 8.2 Hz, 2H), 7.36 (m, 3H), 7.35 – 7.28 (m, 4H), 4.12 (s, 2H), 2.58 (s, 3H), 2.46 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 143.5, 135.7, 134.2, 129.8, 128.6, 128.4, 127.9, 127.5, 54.1, 34.3, 21.6 ppm. Spectroscopic data are consistent with the literature data for this compound.[27]



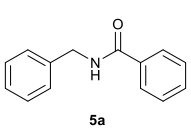
*Compound **4t***. According to **GP4**, starting from *N*,4-dimethyl-*N*-(2-((4-methylphenyl)sulfonamido)ethyl)-benzenesulfonamide (**S15**, 1 equiv., 150 mg, 0.26 mmol) and benzoyl chloride (1.5 equiv., 0.05 mL, 0.39 mmol); flash chromatography on silica gel (EtOAc/Cy, 2:8) gave compound **4t** (126 mg, 0.26 mmol, quantitative yield) as a white solid. This compound has been previously characterized by our team:[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (d, J = 8.3 Hz, 2H), 7.61 (d, J = 8.2 Hz, 2H), 7.50 – 7.44 (m, 3H), 7.37 (t, J = 7.7 Hz, 2H), 7.30 (t, J = 8.0 Hz, 4H), 4.03 (t, J = 6.5 Hz, 2H), 3.25 (t, J = 6.5 Hz, 2H), 2.74 (s, 3H), 2.43 (s, 3H), 2.43 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 171.5, 145.1, 143.6, 135.6, 134.8, 134.1, 131.6, 129.8, 129.7, 128.5, 128.2, 127.4, 49.6, 45.3, 36.0, 21.7, 21.6 ppm. IR (neat) : ν 3068, 2980, 1688, 1598, 1345, 1163, 1089, 910, 731 cm^{-1}. HRMS (ESI-Orbitrap): *m/z* [M+H$^+$] calcd for $C_{24}H_{27}N_2O_5S_2$: 487.1356; found : 487.1343.

Synthesis and characterization of compounds 5a-k and 5q

General procedure for the photodesulfonylation reactions (GP5)



A flame dried vial was charged with the desired compound 4 (1 equiv.), Hantzsch ester 7 (1.2 equiv.), and photocatalyst **3a** (0.05 equiv.) under argon atmosphere. Dry CH_2Cl_2 (0.05 M) was then added, and the resulting mixture was stirred at rt for 5 min. The tube was then sealed and evacuated and refilled with argon three times. The reaction mixture was irradiated under at 300 nm in a Rayonet chamber for 2 h (T = 29 °C). Water was then added. The immiscible phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (3x). The combined organic phases were washed with brine (2x), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography. Product **5a-q** were isolated as amorphous solids unless otherwise specified.



*Compound **5a** (Table 3, entry 1)*. According to **GP5**, starting from **4a** (1 equiv., 50 mg, 0.14 mmol); flash chromatography on silica gel (EtOAc/Cy, 7:3) gave compound **5a** (19 mg, 0.09 mmol, 65% yield) as a white solid. This compound has been previously

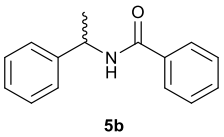
characterized by our team:[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 – 7.76 (m, 2H), 7.54 – 7.47 (m, 1H), 7.43 (m, 2H), 7.36 (d, *J* = 4.5 Hz, 4H), 7.30 (dq, *J* = 8.7, 4.2 Hz, 1H), 6.39 (br, s, 1H), 4.66 (d, *J* = 5.7 Hz, 2H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 167.4, 138.1, 134.4, 131.6, 128.8, 128.6, 128.0, 127.7, 126.9, 44.2 ppm. Spectroscopic data are consistent with the literature data for this compound.[28]

*Compound **5a** (scale-up).* According to **GP5**, starting from **4a** (1 equiv., 500 mg, 1.4 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:8) gave compound **5a** (165 mg, 0.78 mmol, 57% yield) as a white solid.

*Compound **5a** (Table 3, entry 2).* According to **GP5**, starting from **4b** (1 equiv., 50 mg, 0.14 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:8) gave compound **5a** (18 mg, 0.08 mmol, 59% yield) as a white solid.

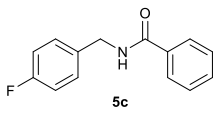
*Compound **5a** (Table 3, entry 3).* According to **GP5**, starting from **4c** (1 equiv., 50 mg, 0.13 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:8) gave compound **5a** (3 mg, 0.014 mmol, 11% yield) as a white solid.

*Compound **5a** (Table 3, entry 4).* According to **GP5**, starting from **4d** (1 equiv., 50 mg, 0.17 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:8) gave traces of compound **5a**.



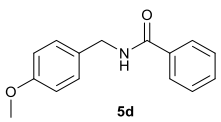
5b

*Compound **5b** (Table 3, entry 5).* According to **GP5**, starting from **4e** (1 equiv., 150 mg, 0.4 mmol); flash chromatography on silica gel (EtOAc/Cy, 2:8) gave compound **5b** (64 mg, 0.28 mmol, 72% yield) as a white solid. This compound has been previously characterized by our team:[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (dd, *J* = 5.2, 3.4 Hz, 2H), 7.52 – 7.46 (m, 1H), 7.45 – 7.32 (m, 5H), 7.31 – 7.24 (m, 2H), 6.33 (br s, 1H), 5.34 (p, *J* = 7.0 Hz, 1H), 1.61 (d, *J* = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 166.6, 143.0, 134.5, 131.5, 128.7, 128.6, 127.5, 126.9, 126.2, 49.2, 21.7 ppm. Spectroscopic data are consistent with the literature data for these compounds.[16]



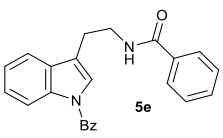
5c

*Compound **5c** (Table 3, entry 6).* According to **GP5**, starting from **4f** (1 equiv., 50 mg, 0.13 mmol); flash chromatography on silica gel (EtOAc/Cy, 2:8) gave compound **5c** (18 mg, 0.07 mmol, 60% yield) as a white solid. This compound has been previously characterized by our team:[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 – 7.76 (m, 2H), 7.51 (m, 1H), 7.44 (m, 2H), 7.37 – 7.31 (m, 2H), 7.07 – 7.01 (m, 2H), 6.40 (s, 1H), 4.63 (d, *J* = 5.7 Hz, 2H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 167.3, 162.3 (d, *J* = 245.9 Hz), 134.2, 134.0 (d, *J* = 3.3 Hz), 131.7, 129.6 (d, *J* = 8.2 Hz), 128.7, 126.9, 115.6 (d, *J* = 21.4 Hz), 43.4 ppm. ^{19}F NMR (471 MHz, $CDCl_3$): δ - 114.8 (F) ppm. Spectroscopic data are consistent with the literature data for this compound.[29]

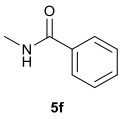


5d

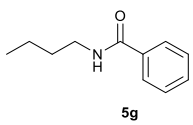
*Compound **5d** (Table 3, entry 7).* According to **GP5**, starting from **4g** (1 equiv., 50 mg, 0.13 mmol); flash chromatography on silica gel (EtOAc/Cy, 2:8) gave compound **5d** (19 mg, 0.07 mmol, 61% yield) as a white solid. This compound has been previously characterized by our team:[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 – 7.76 (m, 2H), 7.53 – 7.48 (m, 1H), 7.46 – 7.40 (m, 2H), 7.32 – 7.27 (m, 2H), 6.92 – 6.86 (m, 2H), 6.31 (s, 1H), 4.59 (d, *J* = 5.5 Hz, 2H), 3.81 (s, 3H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 167.2, 159.1, 134.4, 131.5, 130.2, 129.4, 128.6, 126.9, 114.2, 55.3, 43.7 ppm. Spectroscopic data are consistent with the literature data for this compound.[29]



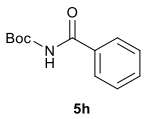
*Compound **5e** (Table 3, entry 8).* According to **GP5**, starting from **4h** (1 equiv., 50 mg, 0.10 mmol); flash chromatography on silica gel (EtOAc/Cy, 2:8) gave compound **5e** (19 mg, 0.05 mmol, 54% yield) as a white solid. This compound has been previously characterized by our team:[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.41 (d, J = 8.2 Hz, 1H), 7.67 (t, J = 6.4 Hz, 4H), 7.64 (d, J = 7.7 Hz, 1H), 7.58 (t, J = 7.5 Hz, 1H), 7.54 – 7.37 (m, 6H), 7.35 (t, J = 7.5 Hz, 1H), 7.15 (s, J = 8.8 Hz, 1H), 6.26 (s, 1H), 3.77 (q, J = 6.8 Hz, 2H), 3.03 (t, J = 6.8 Hz, 2H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 168.3, 167.3, 136.3, 134.3, 134.2, 131.7, 131.4, 130.5, 128.8, 128.5, 128.44, 128.43, 126.6, 125.2, 124.8, 123.8, 118.9, 118.8, 116.5, 39.4, 25.0 ppm. IR (neat): ν 3346, 3066, 2930, 2489, 1679, 1644, 1537, 1453, 1378, 1357, 908, 712 cm^{-1}. HRMS (ESI-Orbitrap) : *m/z* [M+H$^+$] calcd for $C_{24}H_{21}N_2O_2$: 369.1598; found : 369.1594.



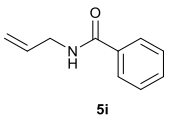
*Compound **5f** (Table 3, entry 9).* According to **GP5**, starting from **4i** (1 equiv., 50 mg, 0.17 mmol); flash chromatography on silica gel (EtOAc/Cy, 3:7) gave compound **5f** (14 mg, 0.10 mmol, 58% yield) as a white solid. This compound has been previously characterized by our team:[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (dd, J = 5.2, 3.2 Hz, 2H), 7.53 – 7.46 (m, 1H), 7.46 – 7.38 (m, 2H), 6.11 (s, 1H), 3.02 (d, J = 4.9 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 168.3, 134.7, 131.4, 128.6, 126.8, 26.9 ppm. Spectroscopic data are consistent with the literature data for this compound.[30]



*Compound **5g** (Table 3, entry 10).* According to **GP5**, starting from **4j** (1 equiv., 50 mg, 0.15 mmol); flash chromatography on silica gel (EtOAc/Cy, 2:8) gave compound **5g** (15 mg, 0.085 mmol, 56% yield) as a colourless oil. This compound has been previously characterized by our team:[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 – 7.72 (m, 2H), 7.51 – 7.46 (m, 1H), 7.45 – 7.40 (m, 2H), 6.13 (s, 1H), 3.46 (td, J = 7.2, 5.8 Hz, 2H), 1.64 – 1.55 (m, 2H), 1.42 (dq, J = 14.6, 7.3 Hz, 2H), 0.96 (t, J = 7.4 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 167.5, 134.9, 131.3, 128.6, 126.8, 39.8, 31.8, 20.2, 13.8 ppm. Spectroscopic data are consistent with the literature data for this compound.[31]

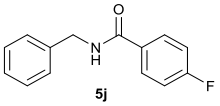


*Compound **5h** (Table 3, entry 11).* According to **GP5**, starting from **4k** (1 equiv., 100 mg, 0.27 mmol); flash chromatography on silica gel (EtOAc/Cy, 3:7) gave compound **5h** (50 mg, 0.25 mmol, 84% yield) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 (s, 1H), 7.84 – 7.75 (m, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.7 Hz, 2H), 1.54 (s, 9H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 165.2, 149.5, 133.4, 132.8, 128.8, 128.8, 127.5, 82.8, 28.0 ppm. Spectroscopic data are consistent with the literature data for this compound.[32]

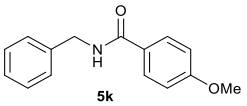


*Compound **5i** (Table 3, entry 12).* According to **GP5**, starting from **4l** (1 equiv., 50 mg, 0.16 mmol); flash chromatography on silica gel (EtOAc/Cy, 3:7) gave compound **5i** (20 mg, 0.12 mmol, 78% yield) as a colourless oil. This compound has been previously characterized by our team:[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 – 7.75 (m, 2H), 7.54 – 7.47 (m, 1H), 7.46 – 7.40 (m, 2H), 6.19 (s, 1H), 5.95 (ddt, J = 17.0, 10.3, 5.7 Hz, 1H), 5.27 (ddd, J = 17.1, 3.0, 1.6 Hz, 1H), 5.19 (ddd, J = 10.2, 2.7, 1.3 Hz, 1H), 4.10 (tt, J = 5.7, 1.5 Hz, 2H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 167.3, 134.5, 134.2, 131.5, 128.6, 126.9, 116.7, 42.4 ppm. Spectroscopic data are consistent with the literature data for this compound.[33]

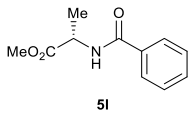
*Compound **5j** (Table 3, entry 13).* According to **GP5**, starting from **4m** (1 equiv., 50 mg, 0.16 mmol); flash chromatography on silica gel (EtOAc/Cy, 1:9) gave compound **5j** (16 mg, 0.07 mmol, 54% yield) as



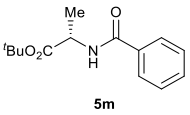
a white solid. This compound has been previously characterized by our team:[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 – 7.77 (m, 2H), 7.39 – 7.33 (m, 4H), 7.34 – 7.29 (m, 1H), 7.14 – 7.08 (m, 2H), 6.36 (s, 1H), 4.64 (d, J = 5.6 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 163.7, 162.7 (d, J = 252.0 Hz), 135.9, 128.4 (d, J = 3.3 Hz), 127.2 (d, J = 8.9 Hz,), 126.8, 125.9, 125.7, 113.6 (d, J = 21.9 Hz), 42.2 ppm. ^{19}F NMR (471 MHz, $CDCl_3$): δ −108.1 (F) ppm. Spectroscopic data are consistent with the literature data for this compound.[34]



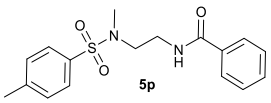
*Compound **5k** (Table 3, entry 14).* According to **GP5**, starting from **4n** (1 equiv., 50 mg, 0.13 mmol); flash chromatography on silica gel (EtOAc/Cy, 2:8) gave compound **5k** (12 mg, 0.05 mmol, 39% yield) as a white solid. This compound has been previously characterized by our team:[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (d, J = 8.7 Hz, 2H), 7.36 (d, J = 4.3 Hz, 4H), 7.33 – 7.29 (m, 1H), 6.92 (d, J = 8.7 Hz, 2H), 6.31 (s, 1H), 4.65 (d, J = 5.6 Hz, 2H), 3.85 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 166.9, 162.2, 138.4, 128.8, 128.8, 128.0, 127.6, 126.6, 113.8, 55.4, 44.1 ppm. Spectroscopic data are consistent with the literature data for this compound.[35]



*Compound (S)-**5l** (Table 3, entry 15).* According to **GP5**, starting from **4o** (1 equiv., 50 mg, 0.14 mmol); flash chromatography on silica gel (EtOAc/Cy, 3:7) gave compound **5l** (10 mg, 0.05 mmol, 36% yield) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 (d, J = 7.4 Hz, 2H), 7.51 (t, J = 7.3 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 6.75 (d, J = 5.1 Hz, 1H), 4.81 (p, J = 7.2 Hz, 1H), 3.79 (s, 3H), 1.53 (d, J = 7.1 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 173.7, 166.8, 133.9, 131.7, 128.6, 128.6, 127.0, 52.6, 48.4, 18.7, 18.8 ppm. $[\alpha]_D^{20}$ −18 (c 0.26, $CHCl_3$). Spectroscopic data are consistent with the literature data for this compound.[36]



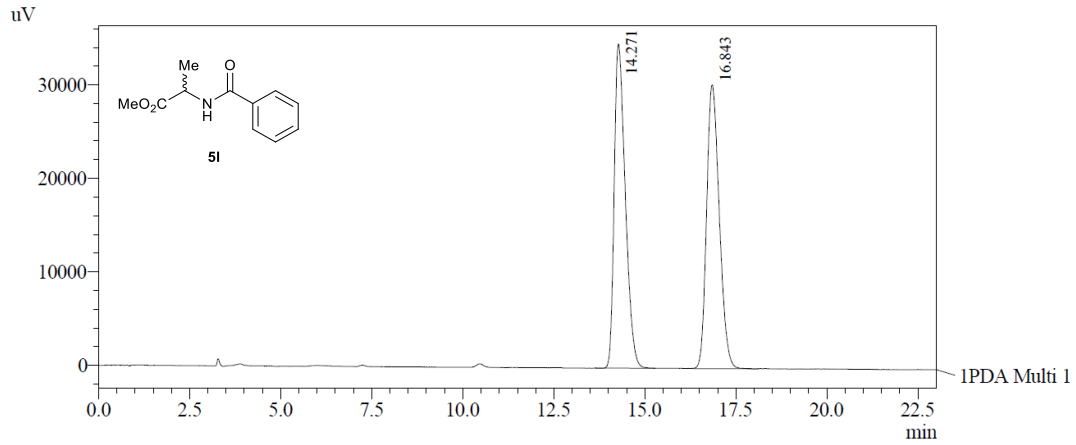
*Compound (S)-**5m** (Table 3, entry 16).* According to **GP5**, starting from **4p** (1 equiv., 50 mg, 0.12 mmol); flash chromatography on silica gel (EtOAc/Cy, 3:7) gave compound **5m** (9 mg, 0.036 mmol, 30% yield) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 (dd, J = 5.2, 3.3 Hz, 2H), 7.52 – 7.45 (m, 1H), 7.46 – 7.40 (m, 2H), 6.78 (d, J = 5.7 Hz, 1H), 4.67 (t, J = 7.1 Hz, 1H), 1.50 (s, 9H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 172.5, 166.6, 134.1, 131.6, 128.5, 127.0, 82.2, 49.0, 28.0, 18.9 ppm. $[\alpha]_D^{20}$ +30 (c 0.46, $CHCl_3$). Spectroscopic data are consistent with the literature data for this compound.[37]



*Compound **5q** (Scheme 3).* According to **GP5**, starting from **4t** (1 equiv., 50 mg, 0.10 mmol); flash chromatography on silica gel (EtOAc/Cy, 2:8 to 1:1) gave compound **5q** (21 mg, 0.063 mmol, 61% yield) as a white solid. This compound has been previously characterized by our team:[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 – 7.82 (m, 2H), 7.68 (d, J = 8.3 Hz, 2H), 7.50 (t, J = 7.3 Hz, 1H), 7.44 (t, J = 7.4 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 6.93 (s, 1H), 3.62 (dd, J = 11.0, 5.2 Hz, 2H), 3.26 – 3.20 (m, 2H), 2.84 (s, 3H), 2.43 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 166.7, 142.8, 133.2, 133.0, 130.5, 128.9, 127.6, 126.3, 126.0, 48.3, 36.9, 34.7, 20.5 ppm. IR (neat): ν 3383, 2885, 2253, 1649, 1537, 1336, 1160, 906, 730 cm^{-1}. HRMS (ESI-Orbitrap) : *m/z* [M+H$^+$] calcd for $C_{17}H_{21}N_2O_3S$: 333.1267; found : 333.1256.

HPLC analyses

HPLC analyses were performed on a Shimadzu chromatograph equipped with a diode array UV/VIS detector. Chiral separations were realized on a Chiralpack ID column (250 x 4,6 mm) [conditions: eluent = ^{i}PrOH/heptane 2:8; flow = 1 mL/min; λ = 254 nm].



1 PDA Multi 1 / 254nm 4nm

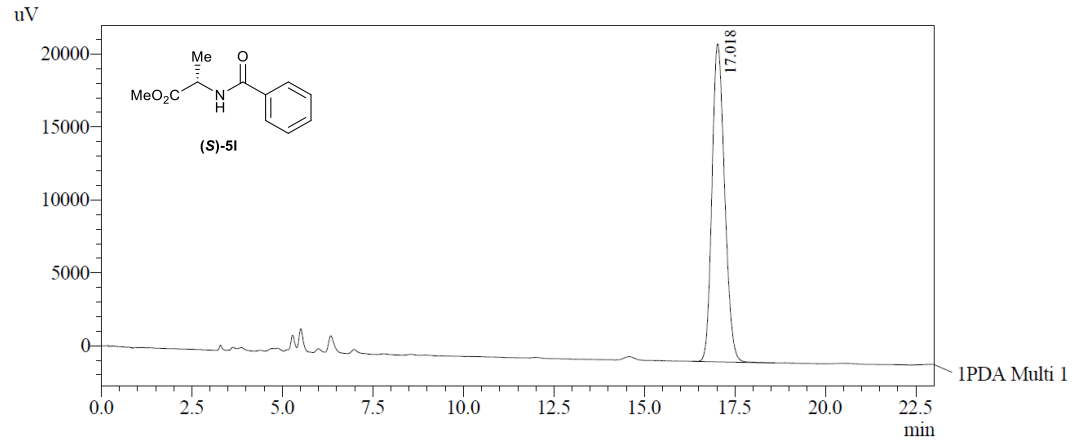
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.271	734693	34683	49.958	53.321
2	16.843	735928	30363	50.042	46.679
Total		1470621	65046	100.000	100.000

Figure **S1**. HPLC analysis of racemic compound **5l**.

This reference substrate was synthesized according to a previously described procedure.[22]



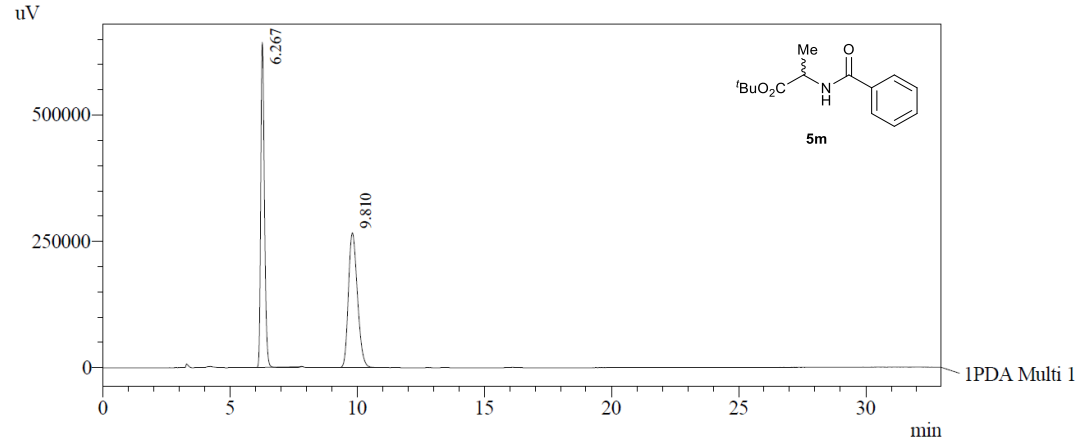
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.018	530386	21802	100.000	100.000
Total		530386	21802	100.000	100.000

Figure **S2**. HPLC analysis of compound (*S*)-**5l**.



1 PDA Multi 1 / 210nm 4nm

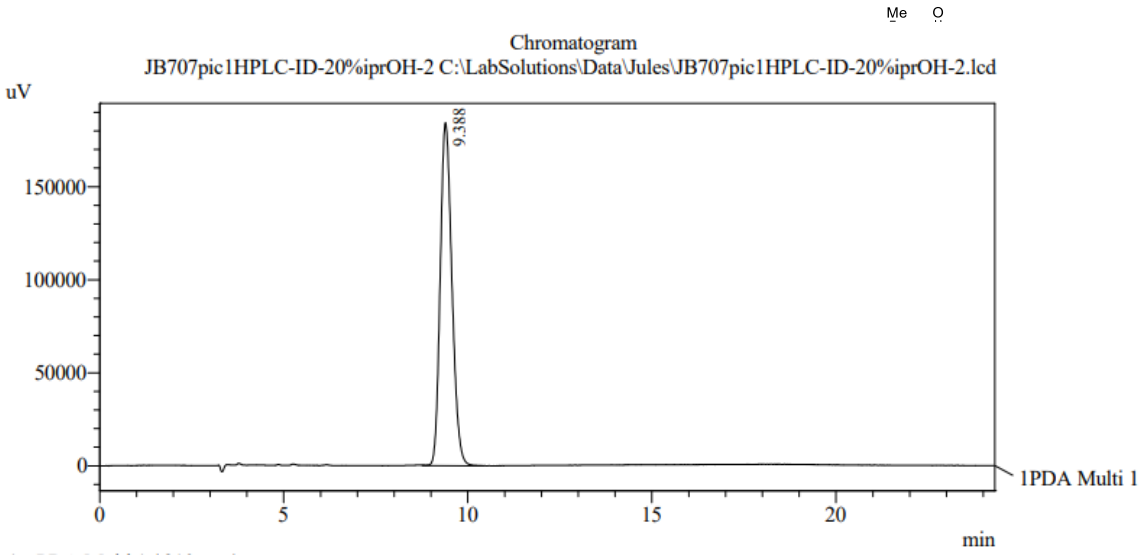
PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.267	6433475	643253	49.480	70.693
2	9.810	6568699	266672	50.520	29.307
Total		13002175	909925	100.000	100.000

Figure **S3**. HPLC analysis of racemic compound **5m**.

This reference substrate was synthesized according to a previously described procedure.[38]



PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.388	4073176	184270	100.000	100.000
Total		4073176	184270	100.000	100.000

Figure **S4**. HPLC analysis of compound (*S*)-**5m**.

UV-Vis Absorption spectra

Absorption spectra were recorded on a UV-2700 spectrophotometer (Shimadzu). The photophysical measurements were performed on air-equilibrated solutions (C = 10^{-4} M), using quartz cuvettes with 1 cm optical path length. CH_2Cl_2 was employed as solvent to perform the analyses.

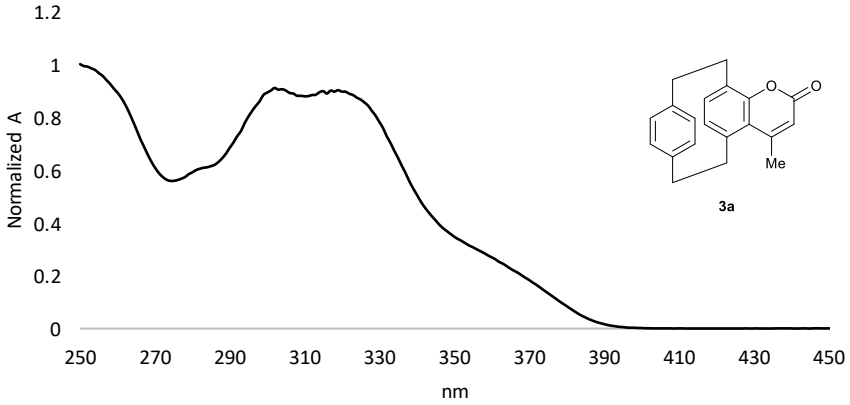


Figure **S5**. Absorption spectrum of compound **3a**

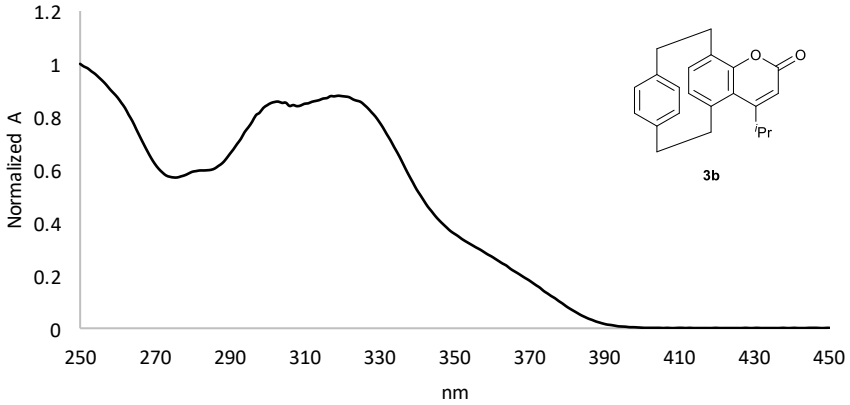


Figure **S6**. Absorption spectrum of compound **3b**

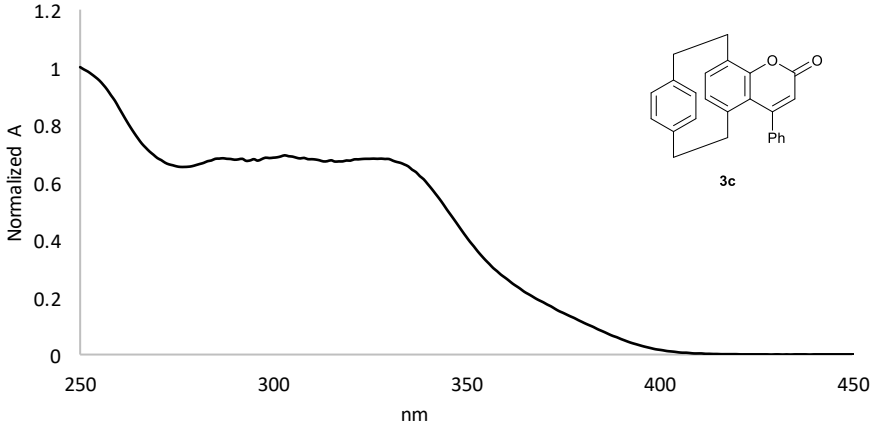


Figure **S7**. Absorption spectrum of compound **3c**

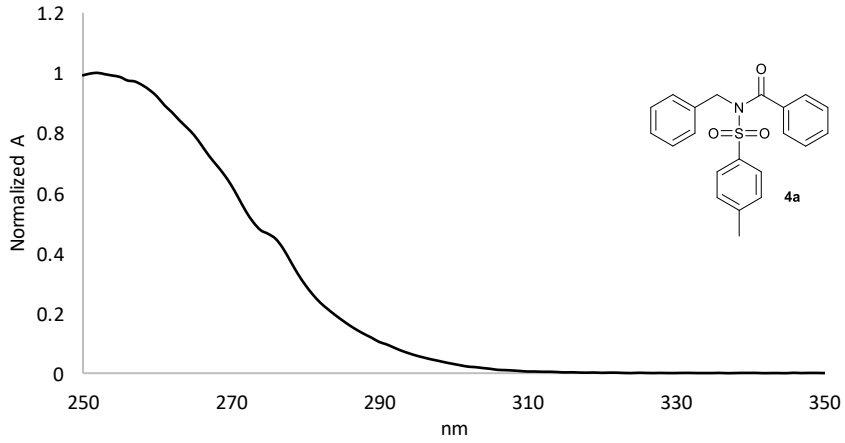


Figure **S8**. Absorption spectrum of compound **4a**

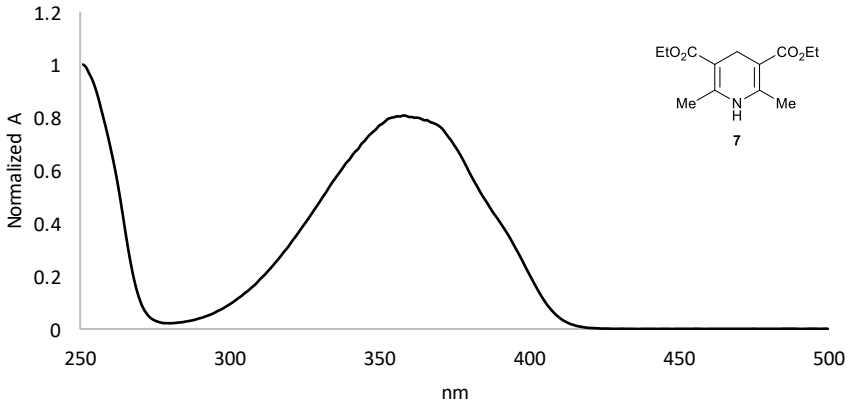


Figure **S9**. Absorption spectrum of compound **7**

Fluorescence emission spectra of catalysts 3a-c

Fluorescence emission spectra were recorded on a F-7000 fluorescence spectrometer (Hitachi), respectively. The photophysical measurements were performed on air-equilibrated solutions (C = 10^{-4} M), using quartz cuvettes with 1 cm optical path length. CH_2Cl_2 was employed as solvent to perform the analyses.

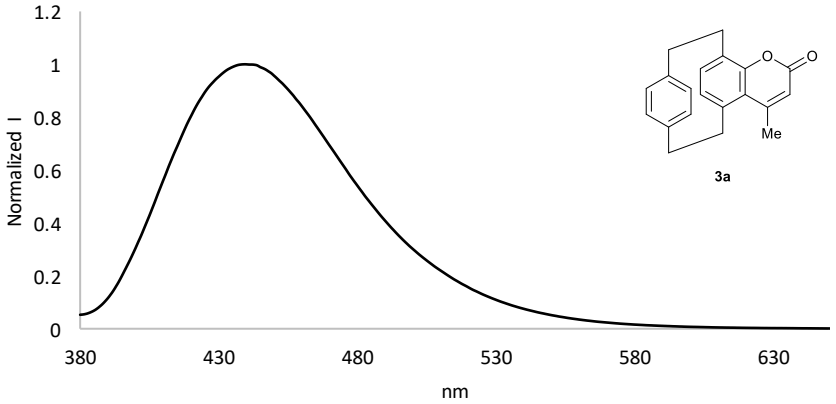


Figure **S10**. Fluorescence emission of compound **3a** (λ_{ex} = 350 nm; λ_{max} = 443 nm)

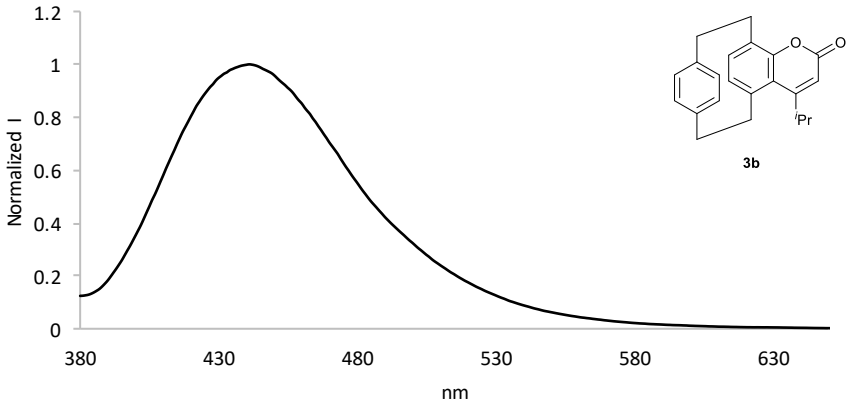


Figure **S11**. Fluorescence emission of compound **3b** (λ_{ex} = 350 nm; λ_{max} = 441 nm)

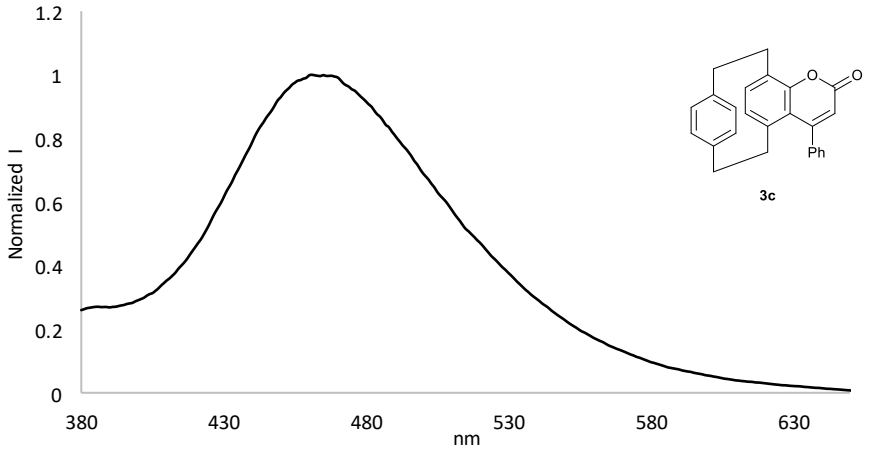
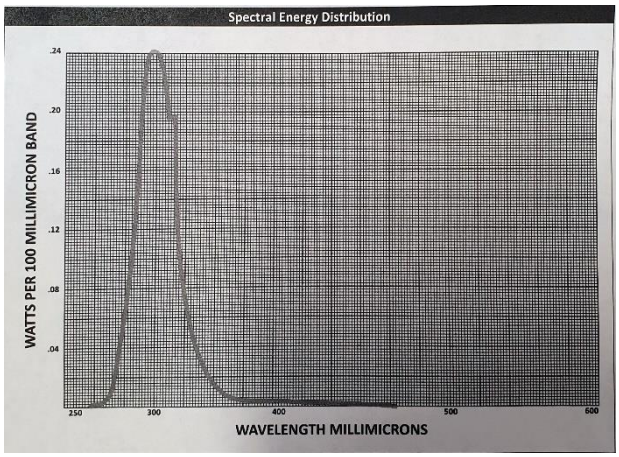


Figure **S12**. Fluorescence emission of compound **3c** (λ_{ex} = 340 nm; λ_{max} = 460 nm)

Photochemical apparatus

All photochemical transformations have been performed in a Rayonet RPR-200 photochemical reactor (manufacturer: The Southern New England Ultraviolet Co) equipped with eight 300 nm lamps (12''in length, 14 w. Manufacturer: The Southern New England Ultraviolet Co, reference: RPR-3000A). Enclosure dimensions: 12'' x 15'' x 16 ''. Lamp chamber dimensions: 10'' diameter x 15'' deep. Power consumption 400 watts. Borosilicate glass vials were employed to perform the reactions.



Cyclic Voltammetry

All electrochemical experiments were performed at room temperature using Autolab PGstat101 potentiostat from Metrohm using a 5mL glass three electrode cell. Data acquisition was performed with NOVA software. Solvent was deoxygenated with argon bubbling for 5 min prior to the analyses. The working electrode was polished using a mechanical grinder (LaboPol-2 bench-top polisher, manufacturer: Struers) on polishing cloths with alumina (Al_2O_3), then rinsed with water.

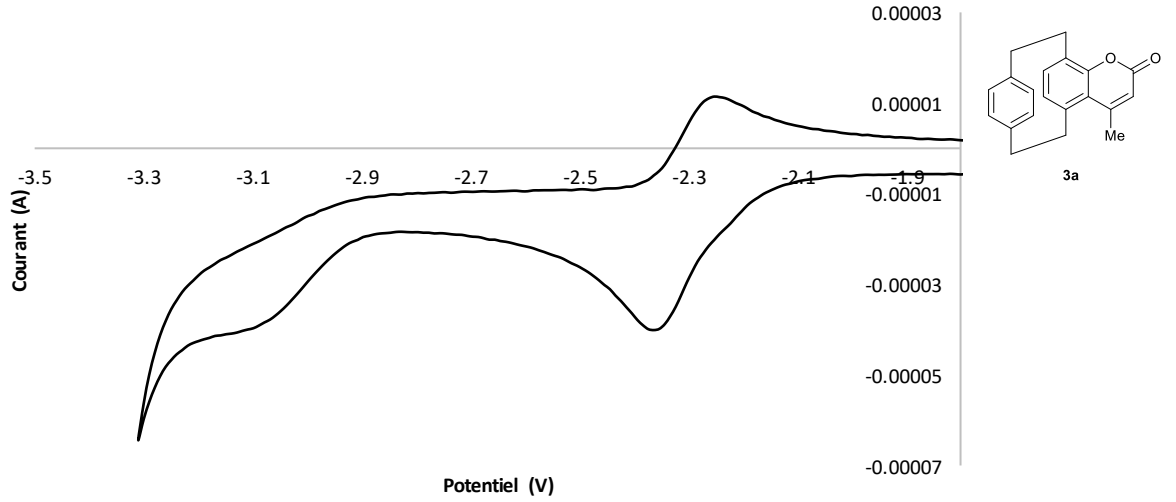


Figure **S13 Cathodic reduction of 3a.** IUPAC plotting convention. Condition of the analysis: WE: C; RE: Pt in a Fc^+/Fc equimolar solution; CE: Pt; supporting electrolyte: Bu_4NPF_6 0.15 M; analyte: **3a**, 1 mM; solvent: acetonitrile. Initial potential: -0.5 V; oxidative scan (from 0.5 to -3.3 V); Scan rate 0.1 V s^{-1}. A reversible reduction peak was observed at -2.28 V.

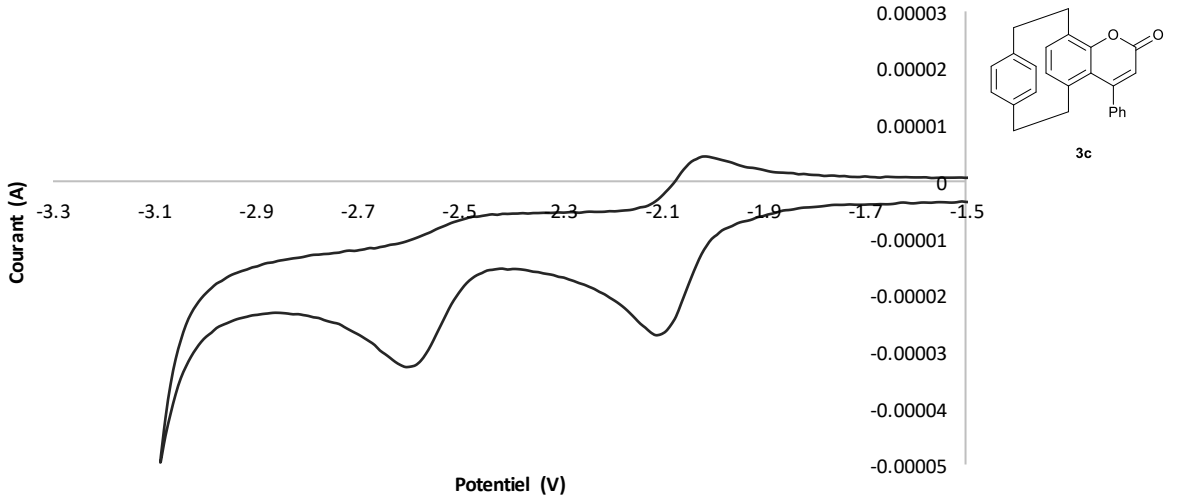


Figure **S14. Cathodic reduction of 3c.** IUPAC plotting convention. Condition of the analysis: WE: C; RE: Pt in a Fc^+/Fc equimolar solution; CE: Pt; supporting electrolyte: Bu_4NPF_6 0.15 M; analyte: **3c**, 1 mM; solvent: acetonitrile. Initial potential: -0.5 V; oxidative scan (from 0.5 to -3.1 V); Scan rate 0.1 V s^{-1}. A reversible reduction peak was observed at -2.05 V, together with an irreversible peak at -2.59 V (inflection point potentials value = -2.53 V).

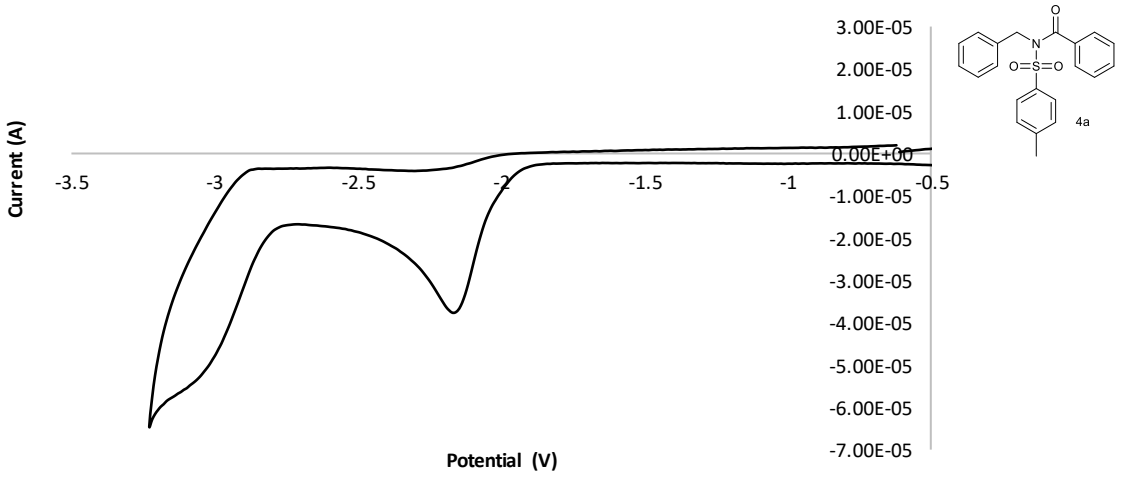


Figure **S15. Cathodic reduction of 4a** IUPAC plotting convention. Condition of the analysis: WE: C; RE: Pt in a Fc^+/Fc equimolar solution; CE: Pt; supporting electrolyte: Bu_4NPF_6 0.15 M; analyte: **4a**, 1 mM; solvent: acetonitrile. Initial potential: -0.5 V; oxidative scan (from 0.5 to -3.2 V); Scan rate 0.1 V s^{-1}. An irreversible reduction peak was observed for **4a** at -2.16 V (inflection point potentials value = -2.05 V).

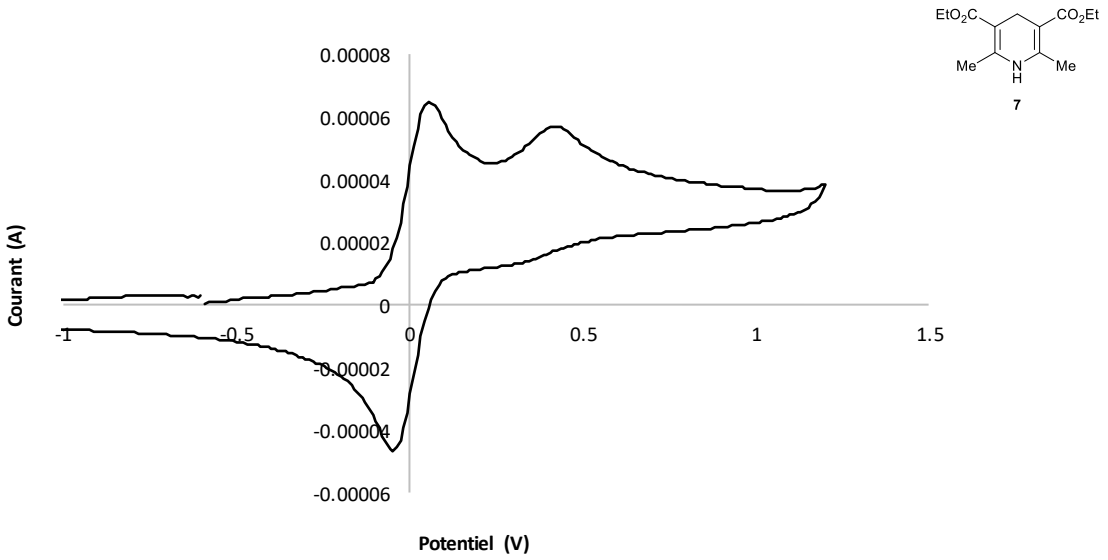


Figure **S16. Anodic oxidation of 7**. IUPAC plotting convention. Condition of the analysis: WE: C; RE: Pt in a Fc^+/Fc equimolar solution; CE: Pt; supporting electrolyte: Bu_4NPF_6 0.15 M; analyte: **7**, 1 mM; solvent: acetonitrile. Initial potential: -0.5 V; oxidative scan (from 1.2 to -3.2 V); Scan rate 0.1 V s^{-1}. An irreversible oxidation peak was observed at 0.45 V (inflection point potentials value = 0.33 V).

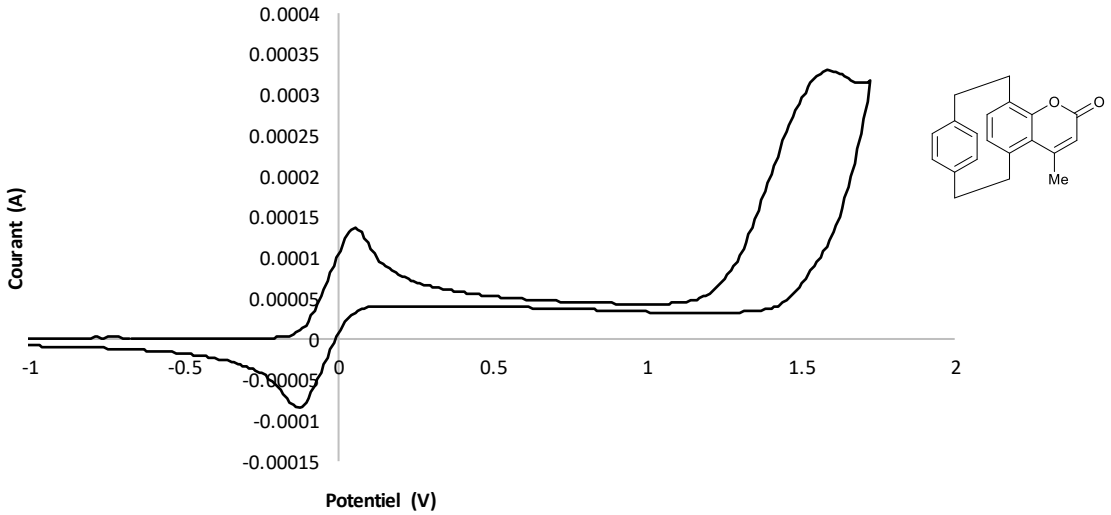


Figure **S17. Anodic oxidation of 3a**. IUPAC plotting convention. Condition of the analysis: WE: C; RE: Pt in a Fc^+/Fc equimolar solution; CE: Pt; supporting electrolyte: Bu_4NPF_6 0.15 M; analyte: **3a**, 1 mM; solvent: acetonitrile. Initial potential: -0.5 V; oxidative scan (from 1.2 to -2.6 V); Scan rate 0.1 V s^{-1}. An irreversible oxidation peak was observed at 1.60 V (inflection point potentials value = 1.32 V).

Excitation energy of the photocatalysts

The E* energy was determined based on the normalized absorption and emission spectra of compounds **3a** and **3c** (10^{-4} M solutions in MeCN). The following equation was used to estimate E*:

$$\lambda_{int} = (\lambda_{abs}^{max} + \lambda_{em}^{max})/2$$

Compound	λ_{int} (nm)	E* (eV)
3a	382	3.24
3c	401	3.09

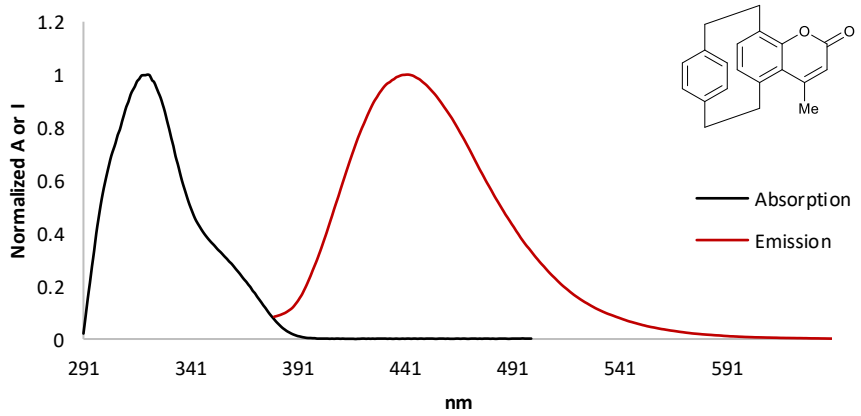


Figure **S17.** Normalized absorption and emission bands of **3a** in MeCN (λ_{abs} = 360; λex = 350 nm; λ_{em} = 442 nm)

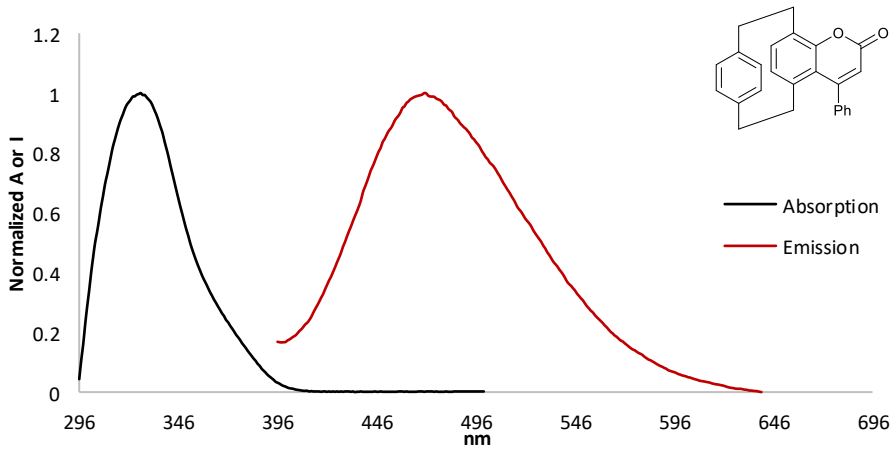


Figure **S19.** Normalized absorption and emission bands of **3c** in MeCN (λ_{abs} = 368; λex = 350 nm; λ_{em} = 471 nm)

Photoinduced electron-transfer thermodynamics

*ET between catalyst **3a** and substrate **4a***

The determination of the free energy change ΔG_{ET} for the electron transfer (ET) reaction

$$(D^* - A) \rightarrow (D^{\bullet+} - A^{\bullet-})$$

between an excited-state donor (D* = **3a**) and a ground-state acceptor (A = **4a**) is generally based on the Weller equation,[39] which is given by

$$\Delta G_{ET} = e\big(E(D^{\bullet+}/D) - E(A/A^{\bullet-})\big) - E^*(D) + \Delta E_{Coulombic}$$

Where $E(D^{\bullet+}/D)$ and $E(A/A^{\bullet-})$ are the reduction potential of the electron donor and acceptor, respectively, $E^*(D)$ is the energy of the singlet excited state of D, and $\Delta E_{Coulombic}$ accounts for the free energy gained upon bringing the charged products at ET distance minus the free energy for the same process but for the neutral reactants. This last term is often small ($|\Delta E_{Coulombic}| \lesssim 0.1$ eV) and thus will not be taken into account in the following calculations.

$$\Delta G_{ET}(eV) = \big(1.32 - (-2.05)\big) - 3.24) = 0.13\ eV$$

Note that, for irreversible oxidation or reduction processes, the standard potentials were extracted from cyclic voltammetry data by approximating the inflexion point potentials values to the standard electrochemical.[40] The inflection point potentials were determined from the zero points of the second derivatives at the rising spans of the anodic waves of the voltammograms, *i.e.,* the potentials where $\partial^2 i/\partial E^2 = 0$ at $\partial E/\partial t$ = constant.

On the basis of these considerations, we concluded that an electron transfer between **3a** and **4a** is likely to be thermodynamically unfavourable both at the ground and excited states ($\Delta G_{ET} > 0$).

*ET between catalyst **3a** and Hantzsch ester **7***

The determination of the free energy change ΔG_{ET} for the electron transfer (ET) reaction

$$(A^* - D) \rightarrow (A^{\bullet-} - D^{\bullet+})$$

between an excited-state acceptor (A* = **3a**) and a ground-state donor (D = **7**), as before, is based on the Weller equation.[39] Here again, $\Delta E_{Coulombic}$ was not taken into account in the calculations, the standard potentials were extracted from cyclic voltammetry data by approximating the inflexion point potentials values to the standard electrochemical.[40]

$$\Delta G_{ET} = e\big(E(D^{\bullet+}/D) - E(A/A^{\bullet-})\big) - E^*(D) + \Delta E_{Coulombic}$$

$$\Delta G_{ET}(eV) = \big(0.33 - (-2.28)\big) - 3.24) = -0.63\ eV$$

We concluded that an electron transfer between **3a** and **7** is likely to be thermodynamically unfavourable at the ground state, but favourable at the excited state (ΔG_{ET} <0).

*ET between catalyst **3c** and Hantzsch ester **7***

The determination of the free energy change ΔG_{ET} for the electron transfer (ET) reaction

$$(A^* - D) \rightarrow (A^{\bullet-} - D^{\bullet+})$$

between an excited-state acceptor (A* = **3c**) and a ground-state donor (D = **7**), as before, is based on the Weller equation.[39] Here again, $\Delta E_{Coulombic}$ was not taken into account in the calculations, and the standard potentials were extracted from cyclic voltammetry data by approximating the inflexion point potentials values to the standard electrochemical.[40]

$$\Delta G_{ET} = e\big(E(\mathrm{D}^{\bullet+}/\mathrm{D}) - E(\mathrm{A}/\mathrm{A}^{\bullet-})\big) - E^*(\mathrm{D}) + \Delta E_{Coulombic}$$

$$\Delta G_{ET}(eV) = \big(0.33 - (-2.05)\big) - 3.09) = -0.71\ eV$$

On the basis of these considerations, we concluded that an electron transfer between **3c** and **7** is likely to be thermodynamically unfavourable at the ground state, but favourable at the excited state (ΔG_{ET} <0).

EPR studies

EPR measurements were performed using a Bruker Elexsys 500 EPR spectrometer (Bruker, Wissembourg, France), operating at X-band (9.85 GHz) and equipped with a SHQ high-sensitivity cavity and a Variable Temperature Unit (Bruker ER4141VTM) for low temperature experiments.

Acquisition and analysis of EPR spectra was performed using Bruker Xepr software and further processing, including simulation, was performed using Matlab and the EasySpin toolbox.[41]

In situ sample irradiation (300 nm) was performed during acquisition using an arc lamp source with grating monochromator and light guide (Spectral Luminator, Oriel Instrument, Palaiseau, France). EPR tubes used are from Wilmad-Labglass SP SCIENCEWARE (ref: 707-SQ-100M).

The magnetic field at the sample position was corrected using a Bruker weak pitch standard sample for which the g-value is accurately known. The g-values were determined from the corrected magnetic field at the center of the EPR line and the microwave frequency read from the frequency meter. Routinely, g-values were measured with a reproducibility of ± 0.0001.

Photodesulfonylation reaction promoted by pCp-based coumarins

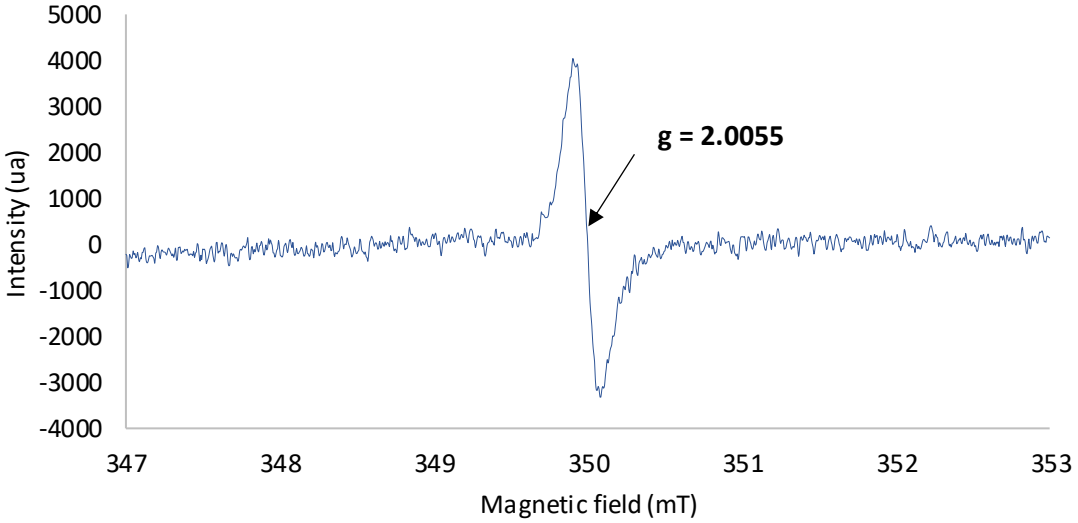


Figure S20. EPR spectroscopy of a solution of **3a** (5 mol %), **4a** (1 equiv.) and **7** (1.2 equiv.) in CH_2Cl_2 (0.05 M) under irradiation at 300 nm (T = 294 K). Analysis settings: microwave power = 40 mW; modulation frequency: 100 kHz; modulation amplitude: 0.15 mT; receiver gain: 60 dB; time constant = 40.96 ms; conversion time = 40.96 ms; data points: 1024; sweep width = 10 mT; sweep time = 41.94 s. The figure presents the sum of 24 experimental spectra. This figure also appears in the main article (figure 1).

Generation of arylsulfonyl radicals

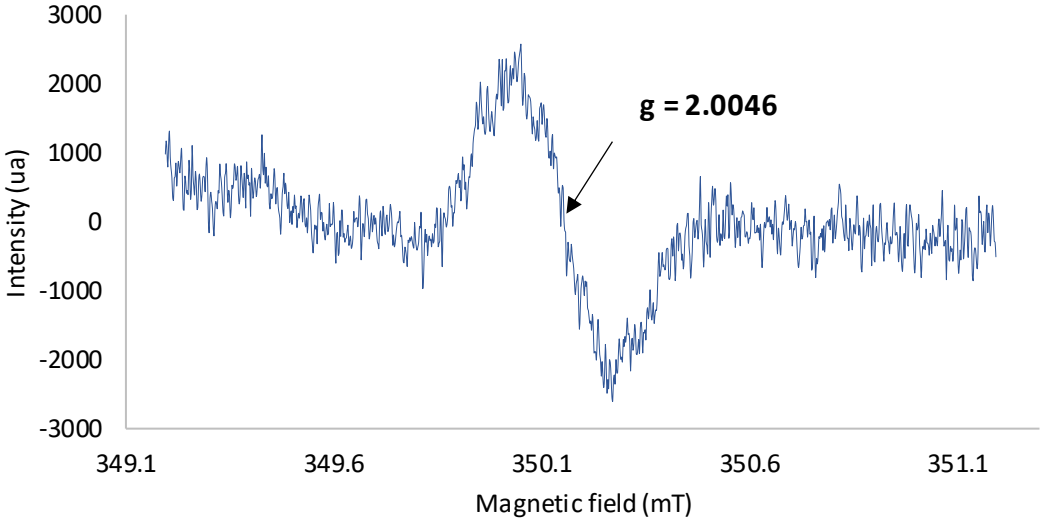


Figure S21. EPR spectroscopy of a solution of tosylchloride (1 equiv.), triethylsilane (1 equiv.) and diterbutylperoxyde (1 equiv.) in CH_2Cl_2 (0.3 mM) under irradiation at 300 nm (T = 294 K). Analysis settings: microwave power: 40 mW; modulation frequency: 100 kHz; modulation amplitude: 0.15 mT; receiver gain: 60 dB; time constant: 81.92 ms; conversion time: 81.92 ms; data points: 1024; sweep width: 2 mT; sweep time: 83.89 s. The figure presents the sum of 24 experimental spectra.

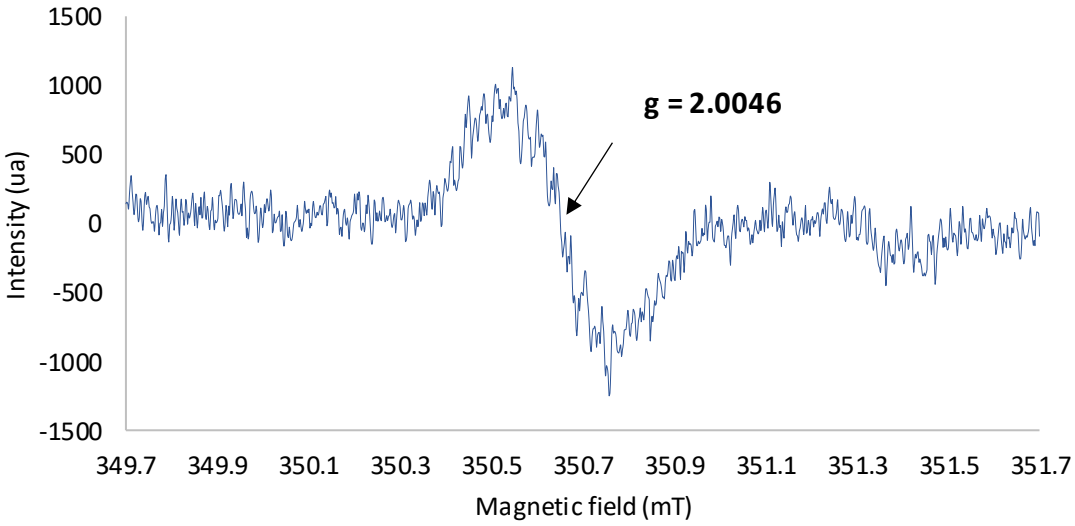


Figure S22. EPR spectroscopy of a solution of tosylchloride (1 equiv.), triethylsilane (1 equiv.) and diterbutylperoxyde (1 equiv.) in toluene (0.3 mM) under irradiation at 300 nm (T = 294 K). Analysis settings: microwave power 1 mW; modulation amplitude: 0.15 mT; receiver gain: 60 dB; time constant, 40.96 ms; conversion time, 40.96 ms; data points: 1024; sweep width, 2 mT; sweep time, 41.94 s. The figure presents the sum of 10 experimental spectra.

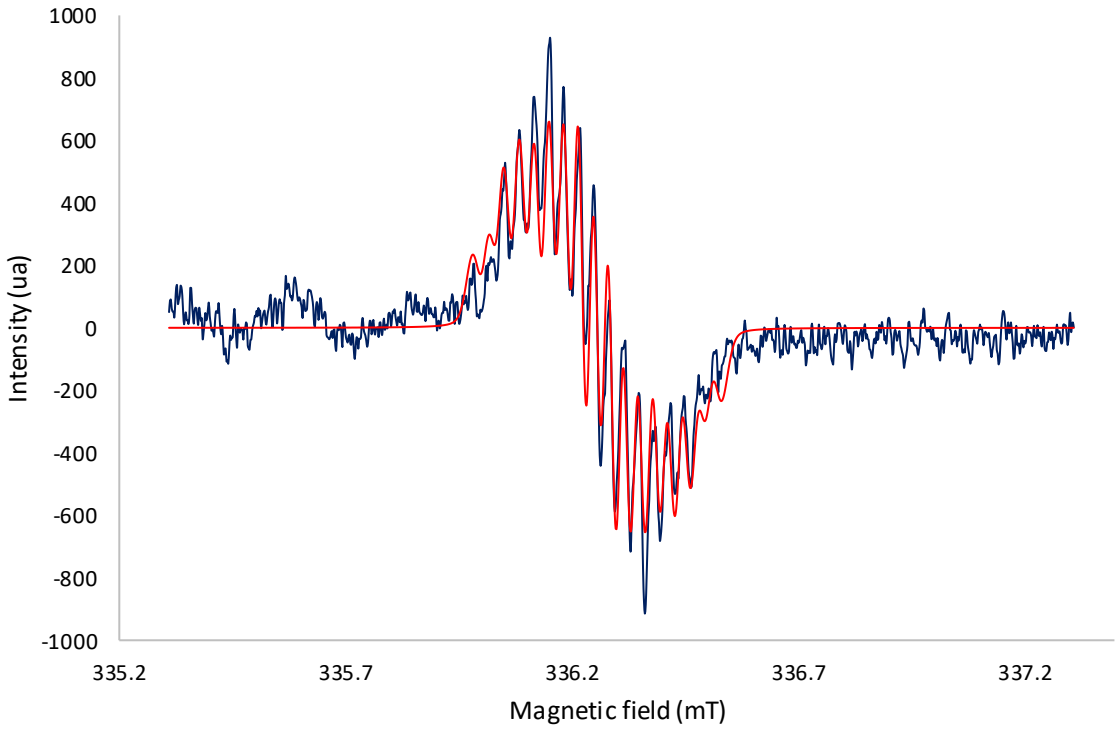


Figure S23. EPR spectroscopy (blue line) and simulation (red line) of a solution of tosylchloride (1 equiv.), triethylsilane (1 equiv.) and diterbutylperoxyde (1 equiv.) in toluene (0.3 mM) under irradiation at 300 nm (T = 193K). Analysis settings: microwave power, 1 mW; modulation frequency, 100 kHz; modulation amplitude, 0.15 mT; receiver gain,60 dB; time constant, 40.96 ms; conversion time, 40.96 ms; data points, 1024; sweep width, 2 mT; sweep time, 41.94 s. The simulation parameters used are listed in Table S1.

Table S1: EPR characteristic values (g-factor and hyperfin coupling constants (a_H)) of the simulated $ArSO_2^{\bullet}$ radical obtained in figure S23.

g	$a_{H\ ortho}$ (2 H)	$a_{H\ meta}$ (2 H)	$a_{H\ methyl}$ (3 H)
2.0046	3.609 MHz/0.129 mT	0.932 MHz/0.033 mT	1.870 MHz/0.067 mT

Theoretical investigations

The density functional theory (DFT) and time-dependent density functional dependent theory (TD-DFT) calculations were performed using Gaussian 16 package.[42] Since the excited-state properties are related to different HF exchange percentage, exchange-correlation (XC) functionals, including B3LYP (20% HF), PBE0 (25% HF), and M06-2X (56% HF) functionals, as well as long-range functionals of ωB97XD and CAM-B3LYP, were investigated. ωB97XD functional was selected eventually owing to the smallest absolute deviation between theoretical and experimental values (data not shown).

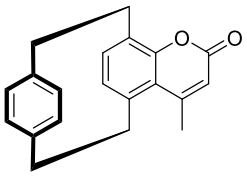
Thus, the ωB97XD with the 6-311G+(p,d)[43] basis set was used to optimize the ground state (S0) geometries of all molecules. The optimized structures were further characterized by harmonic vibrational frequency analysis to confirm that real local minima without any imaginary frequency were reached at the same computational level. The results of vibration analysis showed that there is no imaginary frequency for all reactants and products. Then, the thermodynamic correction was applied for each reactant and product at 298.15 K. The free energy was obtained by adding the single point energy to the Gibbs free energy correction value.

As for excited states, unrestricted DFT (UDFT)/ωB97XD/6-311G+(p,d) and TDDFT/ωB97XD/6-311G+(p,d) were used to optimize geometries of lowest singlet excited state (S1) and lowest singlet excited state (T1), and to calculate their energies. For all calculations, a DCM solvent environment using a conductor-like polarizable continuum model (CPCM) was added.

The EPR/NMR module of the ORCA (v4.2.1) code[44,45] was then exploited to compute the g-tensor. Organic radicals were geometry optimized using the double-hybrid density functional theory (DHDFT) B2PLYP-D3 method[46] and def2-TZVP[47] basis sets as implemented in ORCA in combination with the resolution of identity (RI) by using the AutoAux keyword to automatically build the auxiliary basis set. Hyperfine coupling tensors were calculated using B3LYP and EPR-III[48] basis sets, disregarding contributions from spin–orbit coupling.

Coordinates of geometry-optimised compounds

Electronic energies (E_{corr}) are corrected by addition of zero-point energies estimated from frequency calculations. They are given in atomic unit.



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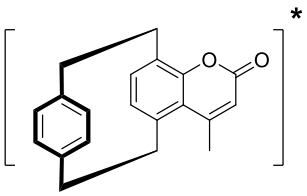

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C -1.58547000 -2.30153100 1.12320800
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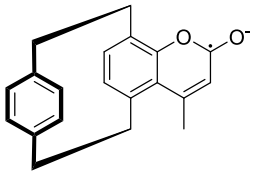

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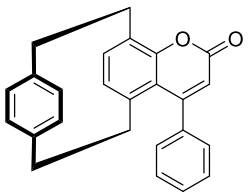

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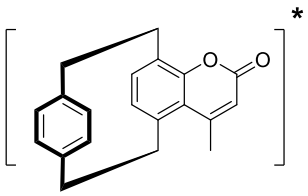

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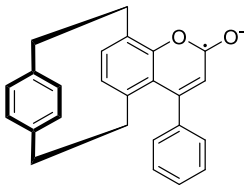

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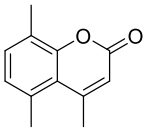

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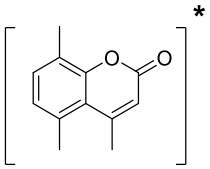
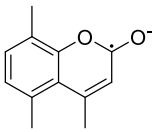
H 2.80139800 -2.08816100 -0.88263400
H 3.91864800 -1.05546000 0.00018400

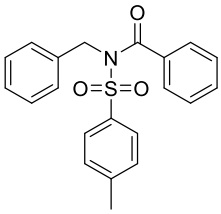


E_{corr} = -614.540977 (T1)
C 2.39898000 1.13299700 -0.00019100
C 1.96313600 -0.17699500 0.00006100
C 0.52577800 -0.45178400 0.00006200
C -0.33073700 0.72625300 -0.00015900
C 0.13285800 2.02648600 -0.00045700
C 1.52201900 2.22492600 -0.00048100
H 3.46786700 1.32509100 -0.00018000
C -0.06602200 -1.70847800 0.00014500
H 1.91662100 3.23592200 -0.00070600
C -2.35168100 -0.56996400 0.00052000
C -1.54900700 -1.74104900 0.00059500
H -2.07736600 -2.68645200 0.00106200
O -1.71331200 0.63469200 -0.00016500
O -3.57816400 -0.55484100 0.00040200
C 0.59663700 -3.05927000 0.00016700
H 1.22361800 -3.22034600 -0.88127200
H 1.22004900 -3.22194200 0.88390200
H -0.16452600 -3.84217000 -0.00204000
C -0.82568100 3.18763100 -0.00073600
H -1.47533300 3.16481300 -0.88079100
H -1.47529200 3.16526800 0.87936100
H -0.27805900 4.13248600 -0.00099200
C 3.00303200 -1.26664200 0.00027700
H 2.92848100 -1.90848600 0.88203100
H 2.93017200 -1.90715000 -0.88260900
H 3.99969600 -0.82049900 0.00151900

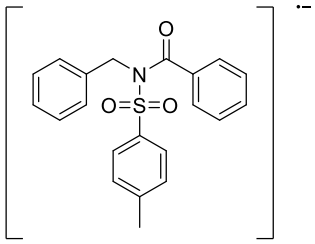


E_{corr} = -614.722336
C 2.48295000 0.94687800 -0.00004900
C 1.92598900 -0.32996700 0.00016900
C 0.49359400 -0.48095800 0.00011200
C -0.25493500 0.74190200 -0.00010900
C 0.31467900 2.01081800 -0.00030300
C 1.71157300 2.10802900 -0.00028900
H 3.56707400 1.03733600 -0.00001300
C -0.25510300 -1.69670200 0.00021300
H 2.18638900 3.08532600 -0.00045400
C -2.39054600 -0.42646100 0.00001900
C -1.67841900 -1.62009300 0.00019300
H -2.26765300 -2.53144400 0.00029100
O -1.63371600 0.75119800 -0.00019000
O -3.62577100 -0.23598400 0.00003000
C 0.33354700 -3.08887800 0.00019200
H 0.94951800 -3.29642600 -0.88125400
H 0.94977300 -3.29639400 0.88145500
H -0.47766900 -3.82247200 0.00032200
C -0.55971400 3.23799900 -0.00054400
H -1.21327300 3.26432500 -0.87893300
H -1.21332600 3.26463000 0.87779700
H 0.05312200 4.14361900 -0.00068200
C 2.88877500 -1.49808100 0.00053300

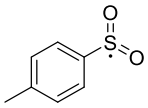
H 2.77537400 -2.13562200 0.88189000
H 2.77532300 -2.13627400 -0.88034000
H 3.91690500 -1.12521800 0.00037300



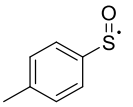
E_{corr} = -1489.878221
C 3.83277900 -2.08553500 0.96689000
C 4.95473900 -1.46620400 0.42374200
C 4.81707500 -0.64520100 -0.68998100
C 3.56203700 -0.43941700 -1.25236400
C 2.43729000 -1.05662500 -0.71275300
C 2.58034100 -1.88354900 0.40009600
C 1.08095000 -0.81722300 -1.33502600
N 0.03006400 -0.54244300 -0.33451200
C 0.15744200 0.44589000 0.63677200
C 1.19336500 1.49539800 0.38818600
O -0.54440500 0.46216200 1.62632600
C 1.15735900 2.29214200 -0.75332600
C 2.11672500 3.28086100 -0.93333300
C 3.11590500 3.46326300 0.01719800
C 3.14379800 2.67189700 1.16154300
C 2.17606300 1.69575400 1.35459700
C -2.68771800 -0.68441600 -0.06814000
C -3.04483600 0.05431300 -1.19059600
C -4.19954800 0.81822800 -1.14427700
C -5.00177300 0.84310000 0.00094200
C -4.61340600 0.08855100 1.10904300
C -3.45473900 -0.67499100 1.08662000
C -6.27175200 1.64801800 0.02473100
S -1.23163600 -1.68839000 -0.14279400
O -1.23574300 -2.43364800 -1.39070000
O -1.06455000 -2.42178400 1.09596900
H 3.93270400 -2.72605700 1.83593200
H 5.93071600 -1.61998600 0.86999800
H 5.68472700 -0.15236500 -1.11398100
H 3.45397000 0.22395400 -2.10452800
H 1.70876300 -2.36012900 0.83827300
H 1.12433700 0.00549000 -2.04778000
H 0.75576500 -1.69646100 -1.89015600
H 0.37824500 2.14968700 -1.49443600
H 2.08472000 3.90723600 -1.81710900
H 3.87098000 4.22662800 -0.13173400
H 3.91998300 2.81531000 1.90406700
H 2.19190000 1.07304600 2.24152900
H -2.43113900 0.03679000 -2.08368300
H -4.48453600 1.40336500 -2.01169500
H -5.22015200 0.10390200 2.00762600
H -3.14330100 -1.24532900 1.95206300
H -6.16881700 2.56591100 -0.55712200
H -7.09208600 1.07022800 -0.41201300
H -6.55605000 1.91075800 1.04489800



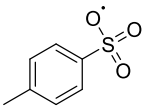
E_{corr} = -1489.962422
$g_{calculated}$ = 2.0050
$A_{calculated(iso)}$ = 0.14 mT
C -5.10796100 -1.07099500 -0.35048700
C -5.61441500 0.11825500 -0.86844600
C -4.92035500 1.30714100 -0.67111000
C -3.72377600 1.30472500 0.03898400
C -3.20744500 0.11888600 0.55670400
C -3.91272100 -1.06808800 0.35829900
C -1.89413500 0.11824100 1.30354600
N -0.73125800 -0.22908600 0.47805500
C -0.31329600 0.68003200 -0.58921100
C 0.52616300 1.75210500 -0.15862700
O -0.70278400 0.48276000 -1.77245800
C 0.99268400 1.90291700 1.17835700
C 1.80909800 2.95943200 1.53643800
C 2.20670400 3.92007600 0.59876200
C 1.75769400 3.79001700 -0.71990300
C 0.93931300 2.74085500 -1.09747100
C 1.50942100 -1.56999700 0.06854700
C 2.36148000 -1.21758400 1.10838700
C 3.70558500 -1.01211400 0.83758400
C 4.20811200 -1.14831900 -0.45873200
C 3.32901000 -1.50613000 -1.48258800
C 1.98173100 -1.72248000 -1.22767800
C 5.67196300 -0.94076400 -0.73907500
S -0.22380400 -1.79262500 0.41124000
O -0.39907200 -2.36119400 1.75035800
O -0.79590200 -2.56915500 -0.68637700
H -5.64621600 -2.00083000 -0.49805400
H -6.54715600 0.11726900 -1.42157600
H -5.30932300 2.23699400 -1.07133700
H -3.17939800 2.23239300 0.18693500
H -3.51938300 -1.99780400 0.75801600
H -1.69613700 1.11360500 1.71035900
H -1.92953700 -0.57701600 2.14423200
H 0.71349100 1.16687100 1.92318600
H 2.14943500 3.03890700 2.56499900
H 2.84770100 4.74521600 0.88808000
H 2.05595100 4.52374700 -1.46357200
H 0.60132400 2.65055500 -2.12333100
H 1.97681100 -1.10083500 2.11411200
H 4.37400400 -0.73207800 1.64487900
H 3.70121100 -1.61127200 -2.49617200
H 1.29895000 -1.99065300 -2.02377400
H 6.10210300 -0.19774900 -0.06463800
H 6.22343000 -1.87547900 -0.59709300
H 5.83534400 -0.61278000 -1.76735500



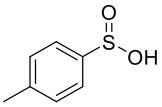
E_{corr} = -819.406666
$g_{calculated}$ = 2.0048
C 1.69898300 -1.20234000 -0.00015900
C 0.31417000 -1.21559000 0.07419200
C -0.35873400 0.00000100 0.09167700
C 0.31416800 1.21559200 0.07419100
C 1.69898200 1.20234400 -0.00016000
C 2.41018300 0.00000300 -0.03500600
H 2.23547800 -2.14413300 -0.03392300
H -0.23175700 -2.15043200 0.09754100
H -0.23176100 2.15043200 0.09753900
H 2.23547500 2.14413800 -0.03392500
S -2.14597400 -0.00000100 0.24269100
O -2.65767200 1.27809000 -0.28083500
O -2.65767000 -1.27809200 -0.28083700
C 3.91288100 -0.00000100 -0.08227400
H 4.32162700 -0.00014600 0.93286400
H 4.29272000 -0.88680100 -0.59239300
H 4.29273700 0.88692800 -0.59215200



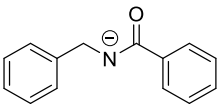
E_{corr} = -744.225357
$g_{calculated}$ = 2.0088
C 1.28718500 -1.20296100 -0.01183500
C -0.09285400 -1.06977600 -0.00576400
C -0.65321700 0.20613700 -0.00069100
C 0.16233400 1.33954800 -0.00310000
C 1.54023000 1.18576500 -0.00914700
C 2.12504800 -0.08365700 -0.01053700
H 1.72420600 -2.19601600 -0.01965300
H -0.73789300 -1.94056200 -0.00793500
H -0.27338600 2.33353500 -0.00338100
H 2.17300100 2.06685500 -0.01469200
S -2.40316800 0.44706200 0.00396300
O -3.05003800 -0.92127500 0.00568400
C 3.62076800 -0.24152000 0.01499100
H 3.98134600 -0.28290000 1.04761500
H 3.93032800 -1.16393100 -0.47995300
H 4.11643100 0.59901300 -0.47437900



E_{corr} = -894.578640
$g_{calculated}$ = 2.0089
O -2.39737800 -0.79696100 1.12228000
S -1.89939200 0.07099200 0.00209300
C -0.14301900 0.04290300 -0.00025100
O -2.40088100 -0.78974700 -1.12224700
O -2.36424400 1.43589800 0.00698400
C 0.51342200 -1.18750800 -0.00311000
C 0.55863200 1.24223600 -0.00355100
C 1.89598600 -1.20280200 -0.00850200
H -0.04568000 -2.11550000 -0.00362900
C 1.94561200 1.20274600 -0.00893500
H 0.03038100 2.18706300 -0.00427000
C 2.63225000 -0.01194900 -0.00920000
H 2.41600500 -2.15416100 -0.01368000
H 2.50106000 2.13365000 -0.01467200
C 4.13410300 -0.04993700 0.01131400
H 4.49048600 -0.24965300 1.02639100
H 4.51537900 -0.84478400 -0.63275700
H 4.56075400 0.89986500 -0.31360900

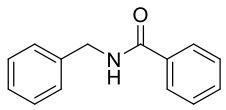


E_{corr} = -820.013705
C 1.72315900 -1.20225100 -0.00310300
C 0.33778000 -1.21284000 0.06147000
C -0.34146300 0.00000500 0.09019400
C 0.33779100 1.21284900 0.06147100
C 1.72317000 1.20225300 -0.00310300
C 2.43439000 -0.00000100 -0.03220300
H 2.26047600 -2.14364400 -0.03619600
H -0.20878500 -2.14794900 0.07440600
H -0.20877000 2.14796000 0.07440700
H 2.26049300 2.14364400 -0.03619600
S -2.11032800 -0.00000500 0.19659100
O -2.61850400 1.26444600 -0.32255800
O -2.61849900 -1.26444100 -0.32256000
H -2.33766200 -0.00000500 1.53871500
C 3.93754400 -0.00000600 -0.07213700
H 4.34103700 -0.00015500 0.94508500
H 4.32012100 -0.88682200 -0.58026600
H 4.32013200 0.88695400 -0.58000500

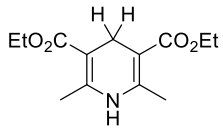


E_{corr} = -670.577875
C -4.89289200 0.23799900 0.38832800
C -4.90678400 -1.09107300 -0.02635500
C -3.71744400 -1.69064400 -0.42842900
C -2.52636200 -0.96950500 -0.41782000
C -2.49969000 0.36336300 -0.00732100
C -3.70008000 0.95302800 0.39747300
C -1.22631600 1.18291900 -0.03429100
N -0.03207400 0.37735000 0.04218400
C 1.08311900 1.05835800 -0.07094700
C 2.35972200 0.23177200 0.00648200
O 1.21215700 2.30783000 -0.23771800
C 2.34166200 -1.14818500 0.22699500
C 3.52437600 -1.87579600 0.29114300
C 4.75181000 -1.23527700 0.13452300
C 4.78230800 0.13796700 -0.08487900
C 3.59497100 0.86208800 -0.14659500
H -5.81175000 0.71661000 0.71074800
H -5.83409100 -1.65368700 -0.03123800
H -3.71562100 -2.72713400 -0.75017500
H -1.59623500 -1.43586900 -0.72018500
H -3.69801000 1.98814500 0.72825000
H -1.24118600 1.79229300 -0.95496500
H -1.27432400 1.92151600 0.78239700

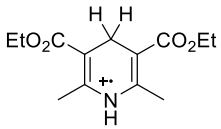
H 1.38315200 -1.63830300 0.34739600
H 3.49050000 -2.94662500 0.46396900
H 5.67511400 -1.80267800 0.18399000
H 5.73278900 0.64693900 -0.20799300
H 3.60652400 1.93260400 -0.31558500



E_{corr} = -671.068770
C -2.92606600 0.11875100 1.07532600
C -3.07152000 -1.17324000 0.57647000
C -2.37911400 -1.55077800 -0.56828600
C -1.54075000 -0.64219500 -1.20668000
C -1.38896200 0.64982700 -0.71223600
C -2.09085700 1.02412200 0.43309200
C -0.46272700 1.62806700 -1.40498000
C 1.30724400 1.70901200 0.38292300
C 1.51400900 0.22958100 0.24242800
O 1.87581000 2.35001500 1.26055400
C 2.02764700 -0.31739100 -0.93090300
C 2.22012500 -1.69039300 -1.03051600
C 1.88606700 -2.51946000 0.03495500
C 1.37935900 -1.97205100 1.21010000
C 1.20414900 -0.59875600 1.31873300
H -3.46325300 0.41991500 1.96782900
H -3.71890400 -1.88182500 1.08076300
H -2.48050500 -2.55715800 -0.95900600
H -0.98086700 -0.94871000 -2.08453000
H -1.97082800 2.02574000 0.83380600
H 0.07750600 1.11747300 -2.20448900
H -1.04657700 2.41980000 -1.87852800
H 2.28431300 0.32733900 -1.76453900
H 2.62754200 -2.11251800 -1.94202300
H 2.02473300 -3.59146200 -0.04812000
H 1.12086900 -2.61602000 2.04284500
H 0.80910500 -0.16685500 2.23126000
N 0.46989400 2.30020800 -0.50299200
H 0.34951400 3.29213700 -0.36131300



E_{corr} = -862.217665
C 1.26293000 -0.74072900 0.00015300
C 1.22182000 -2.09455600 -0.00001500
N -0.00001900 -2.73433000 -0.00020900
C -1.22185200 -2.09454500 -0.00030100
C -1.26294900 -0.74071600 -0.00017700
C -0.00000500 0.09735600 0.00013000
C 2.39905700 -3.02590400 0.00000400
C -2.39909700 -3.02588400 -0.00055300
C -2.54863600 -0.03908400 -0.00034500
C 2.54863000 -0.03911100 0.00039200
O -2.37058400 1.29452000 0.00015900
O -3.65993500 -0.53729200 -0.00067200
O 2.37060300 1.29450000 0.00020500
O 3.65992200 -0.53733600 0.00025700
C -3.55178600 2.11073500 0.00013400
C 3.55182000 2.11069200 0.00011900
C 3.10617500 3.55494600 -0.00001800
C -3.10611300 3.55498000 0.00066900
H -0.00002400 -3.74089400 -0.00028500
H 0.00011000 0.76605600 -0.86748000
H -0.00011100 0.76576700 0.86796400
H 3.02548200 -2.85579700 0.87570700
H 2.06731000 -4.06582700 -0.00014500
H 3.02566400 -2.85561100 -0.87553300
H -2.06735700 -4.06580900 -0.00032000
H -3.02589600 -2.85557600 0.87483800
H -3.02532500 -2.85578900 -0.87640300
H -4.14751100 1.87215900 -0.88423500
H -4.14791700 1.87163000 0.88408600
H 4.14775000 1.87192400 0.88429900
H 4.14773700 1.87175700 -0.88402200
H 3.98300000 4.20657800 -0.00010100
H 2.51082300 3.77962500 -0.88775300
H 2.51085300 3.77980600 0.88769000
H -3.98292500 4.20662900 0.00066100
H -2.51097500 3.77947300 0.88859500
H -2.51056600 3.78000200 -0.88684800



E_{corr} = -862.011015
$g_{calculated}$ = 2.0036
C 1.25544200 -0.75355800 -0.00003800
C 1.22695600 -2.12629600 -0.00014300
N 0.00000200 -2.72372000 -0.00017600
C -1.22695400 -2.12629800 -0.00012800
C -1.25544200 -0.75356000 -0.00004600
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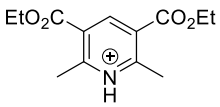

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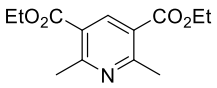

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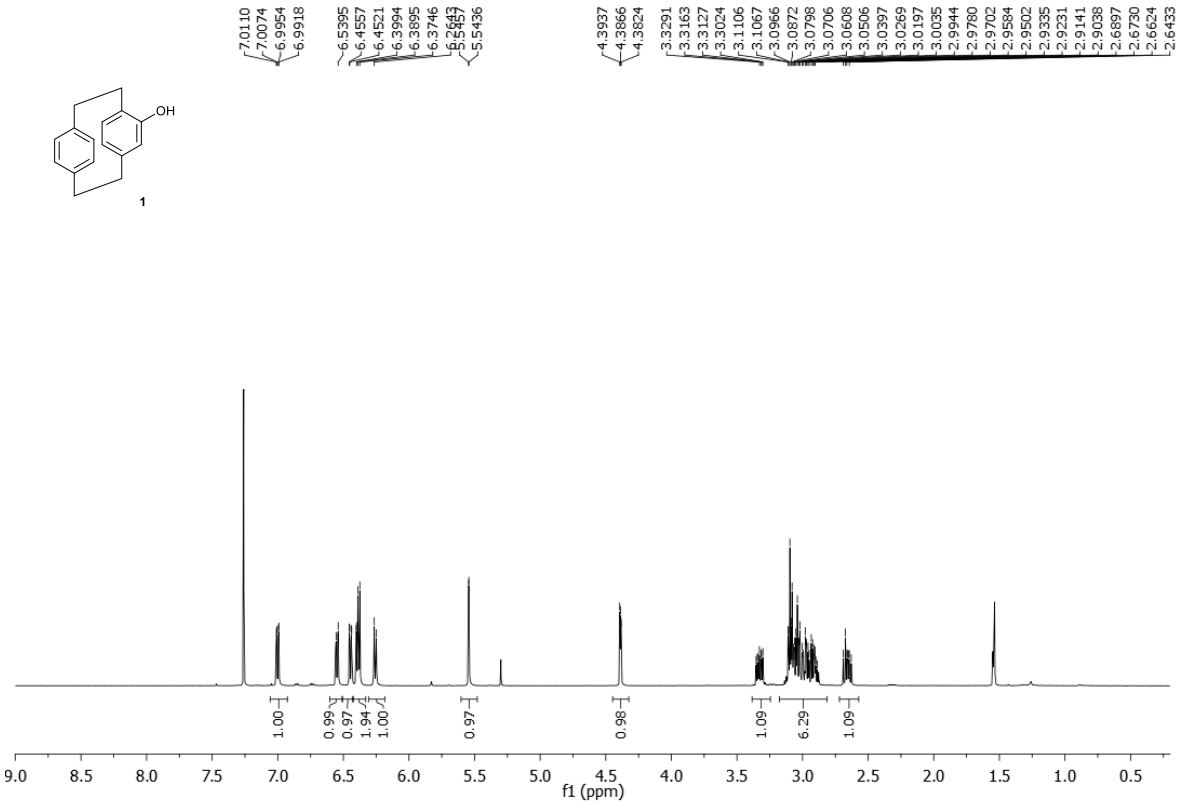
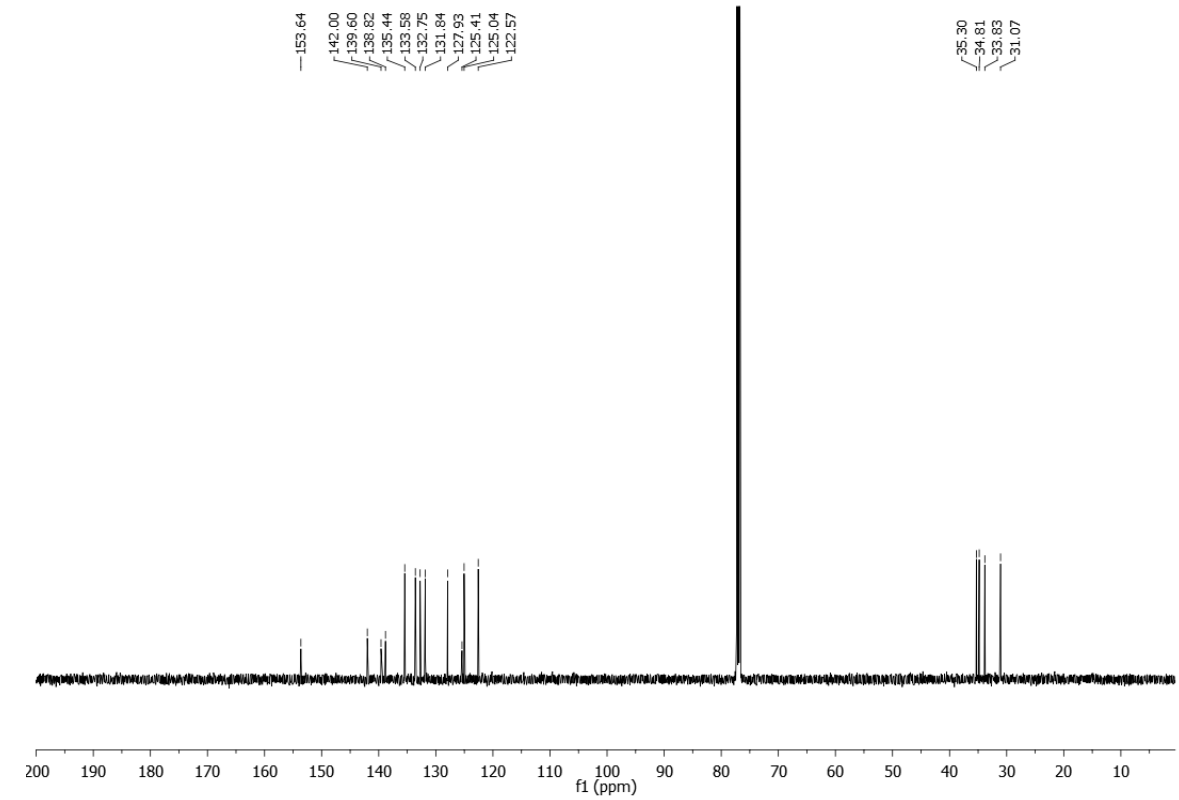
^{1}H NMR and ^{13}C NMR spectra

*4-Hydroxy[2.2]paracyclophane (**1**)*

^{1}H NMR (500 MHz, $CDCl_3$)

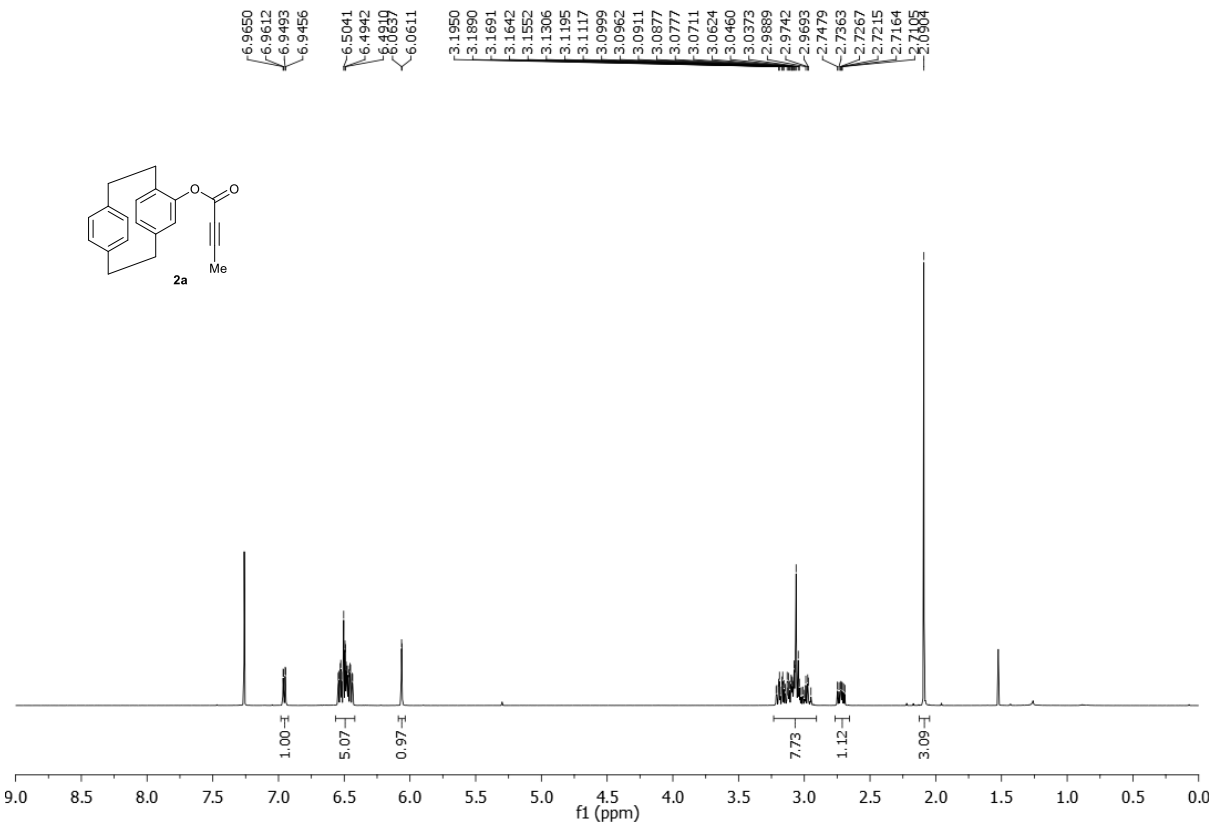


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

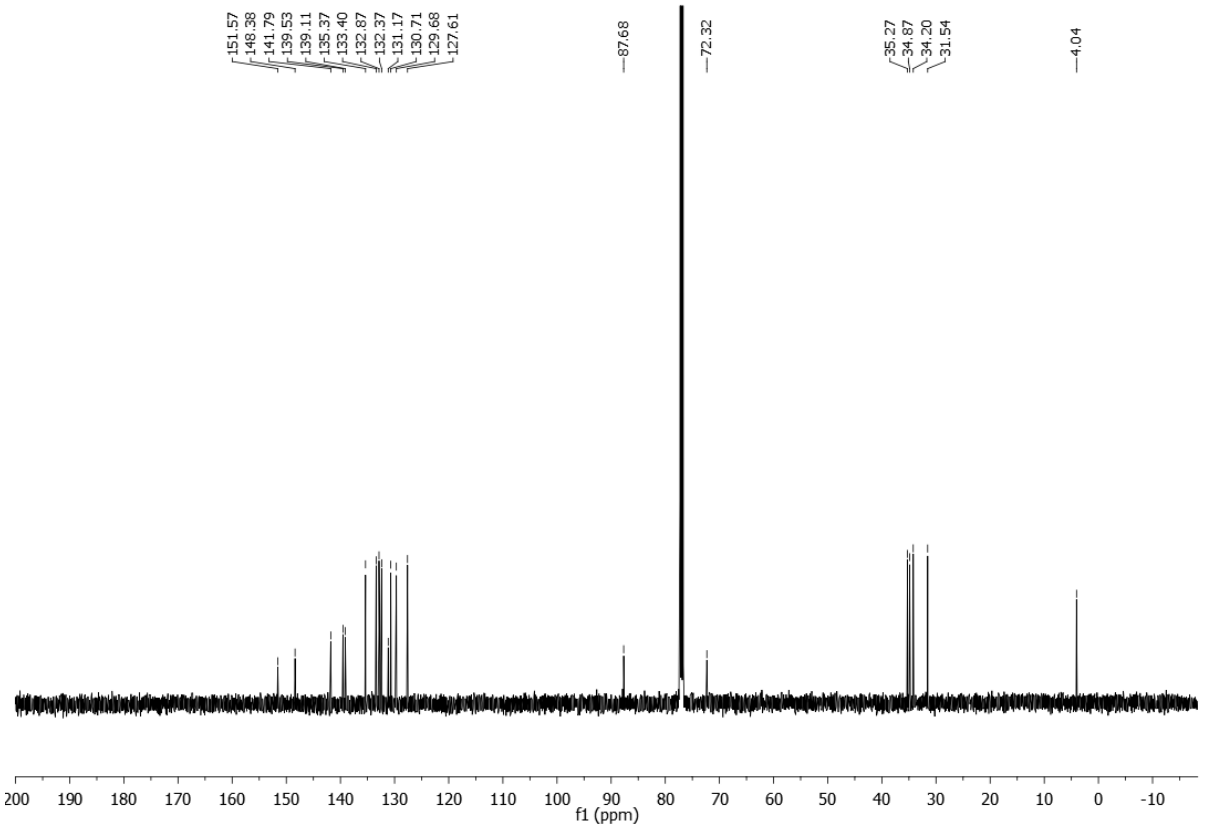


*Tricyclo[8.2.2.2^{4,7}]hexadeca-1(12),4(16),5,7(15),10,13-hexaen-5-yl but-2-ynoate (**2a**)*

^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)



*Tricyclo[8.2.2.2^{4,7}]hexadeca-1(12),4,6,10,13,15-hexaen-5-yl 4-methylpent-2-ynoate (**2b**)*

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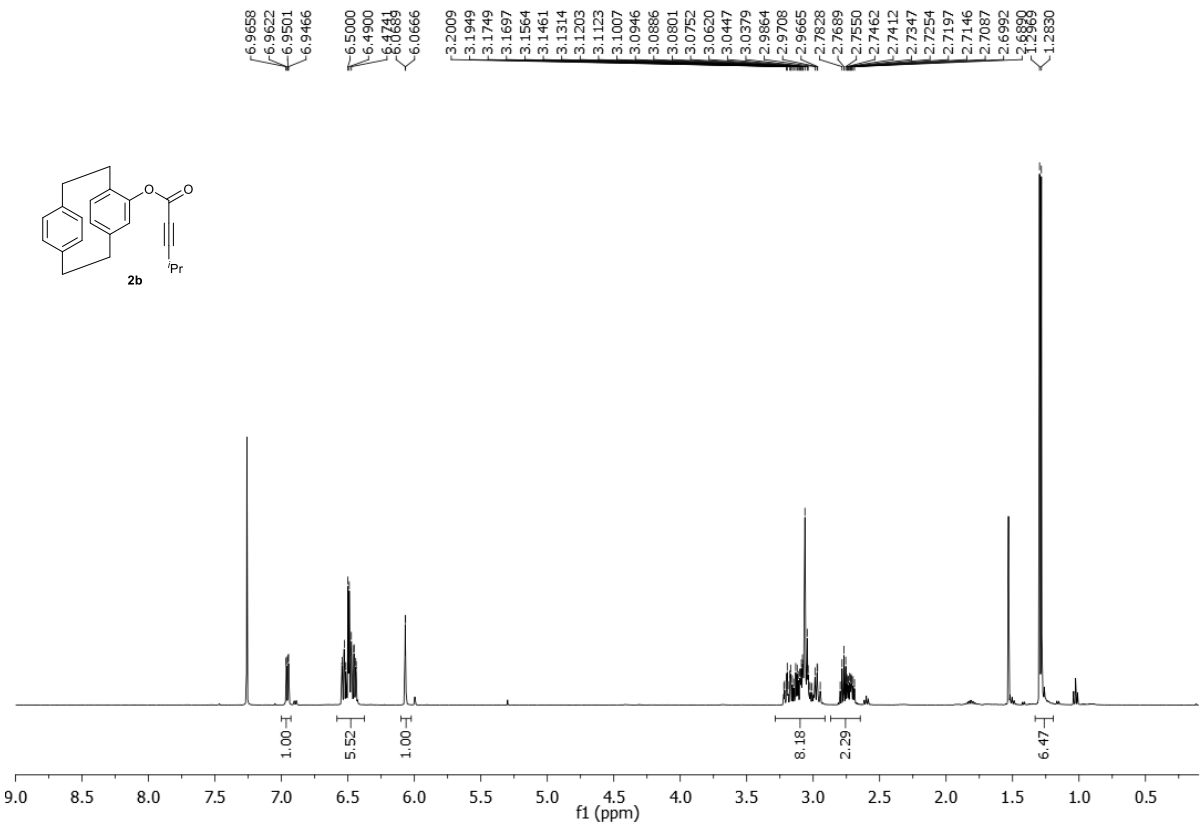
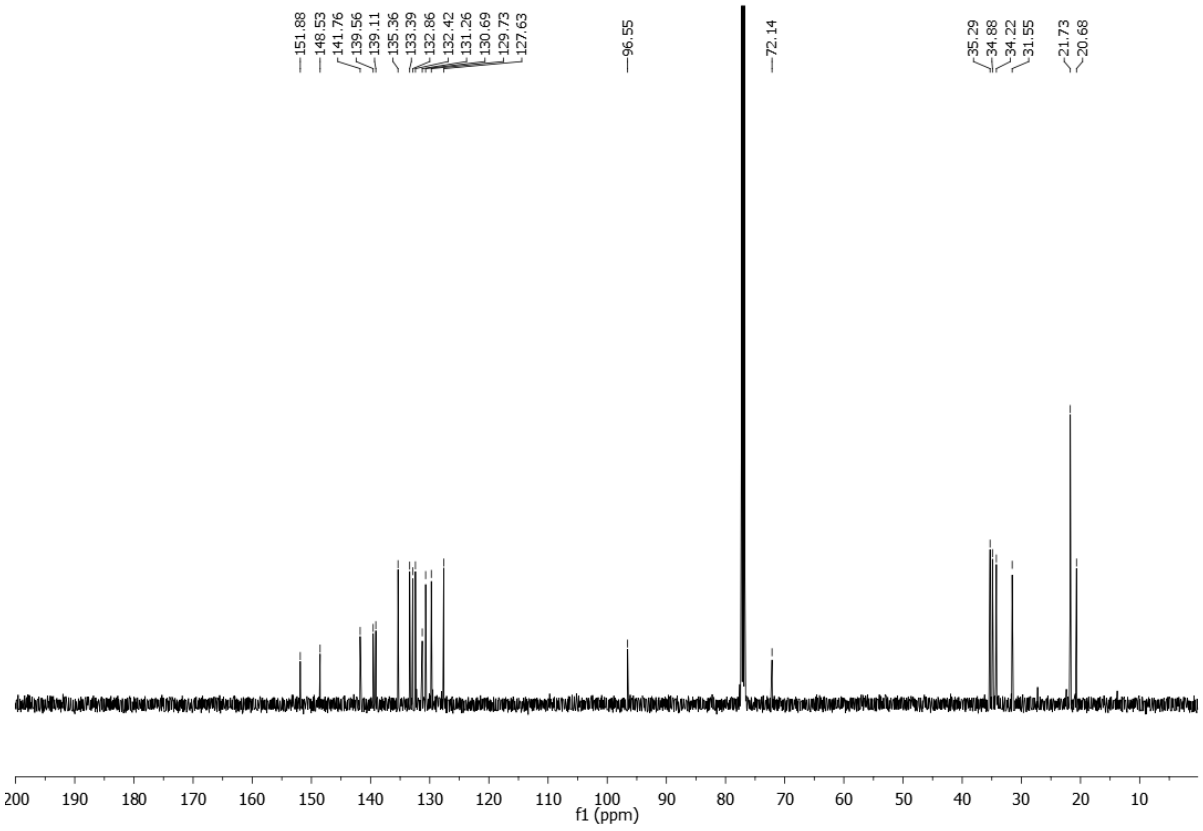


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)



*Tricyclo[8.2.2.2^{4,7}]hexadeca-1(12),4,6,10,13,15-hexaen-5-yl 3-phenylprop-2-ynoate (**2c**)*

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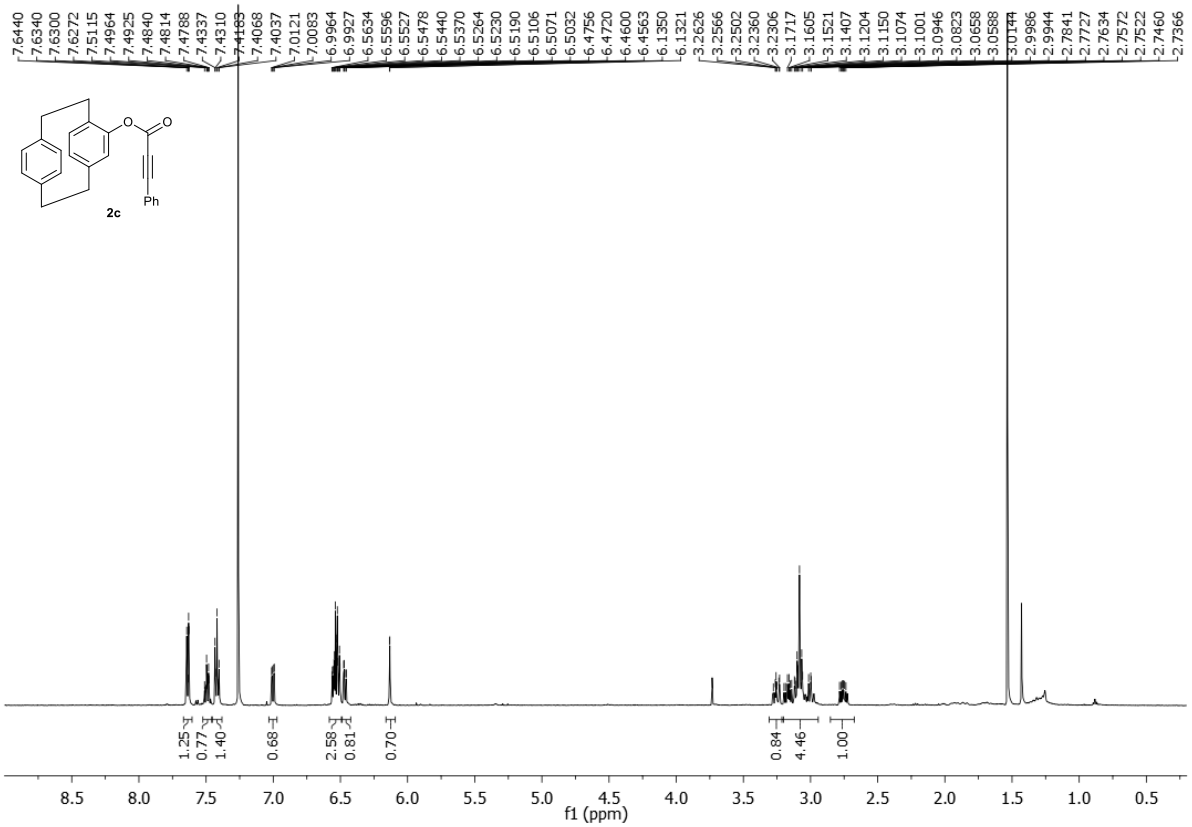
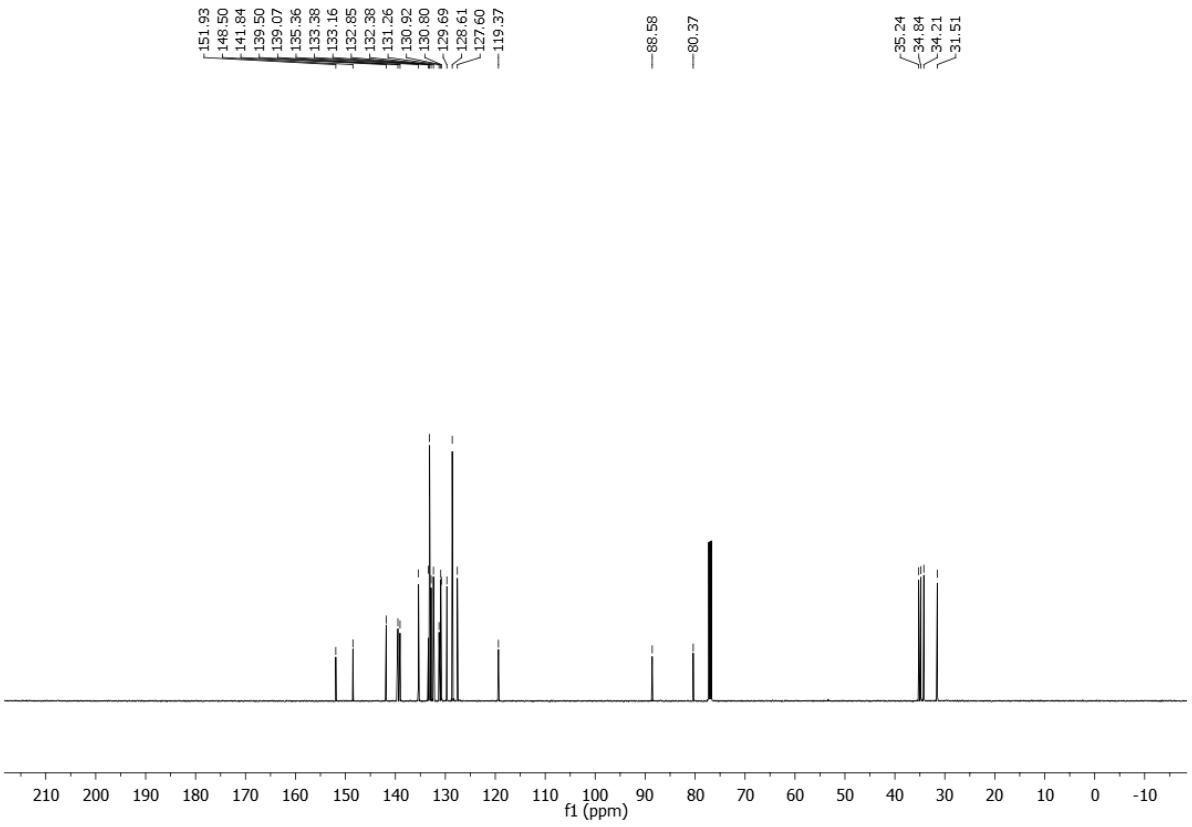
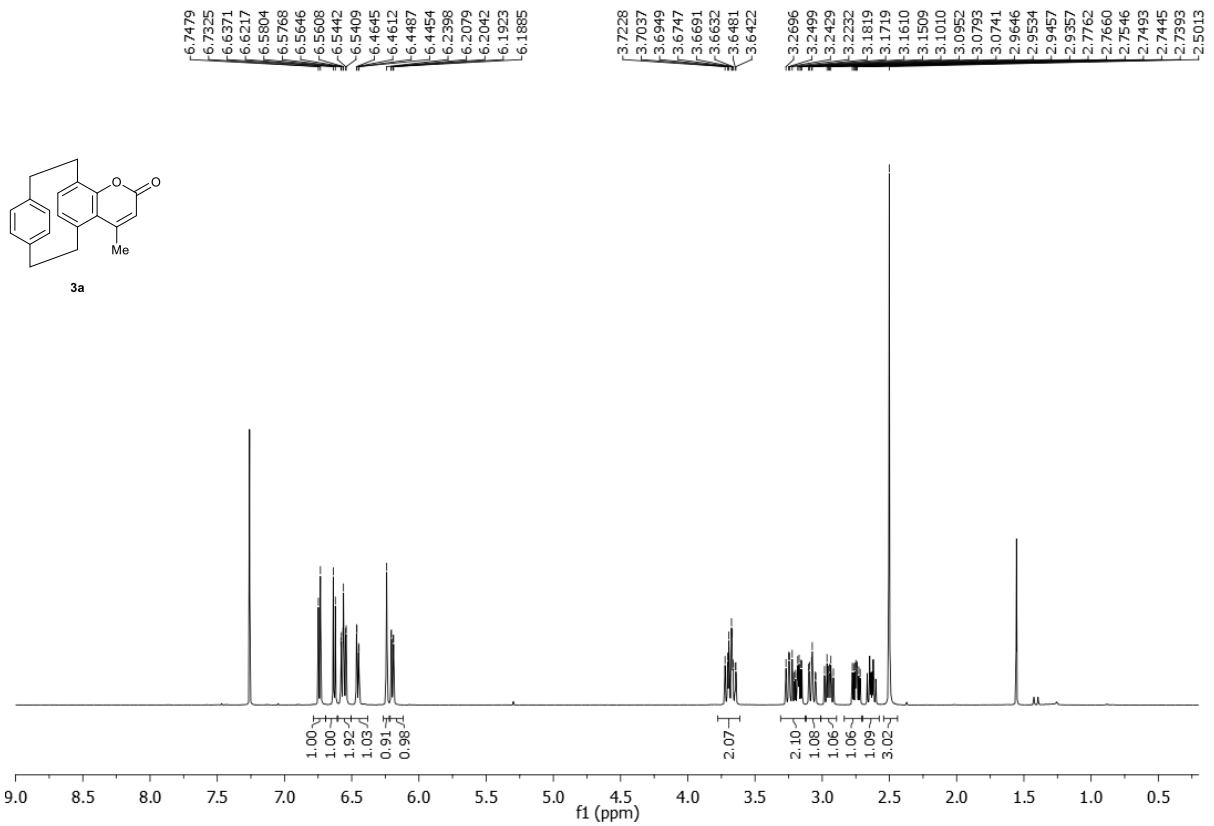


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

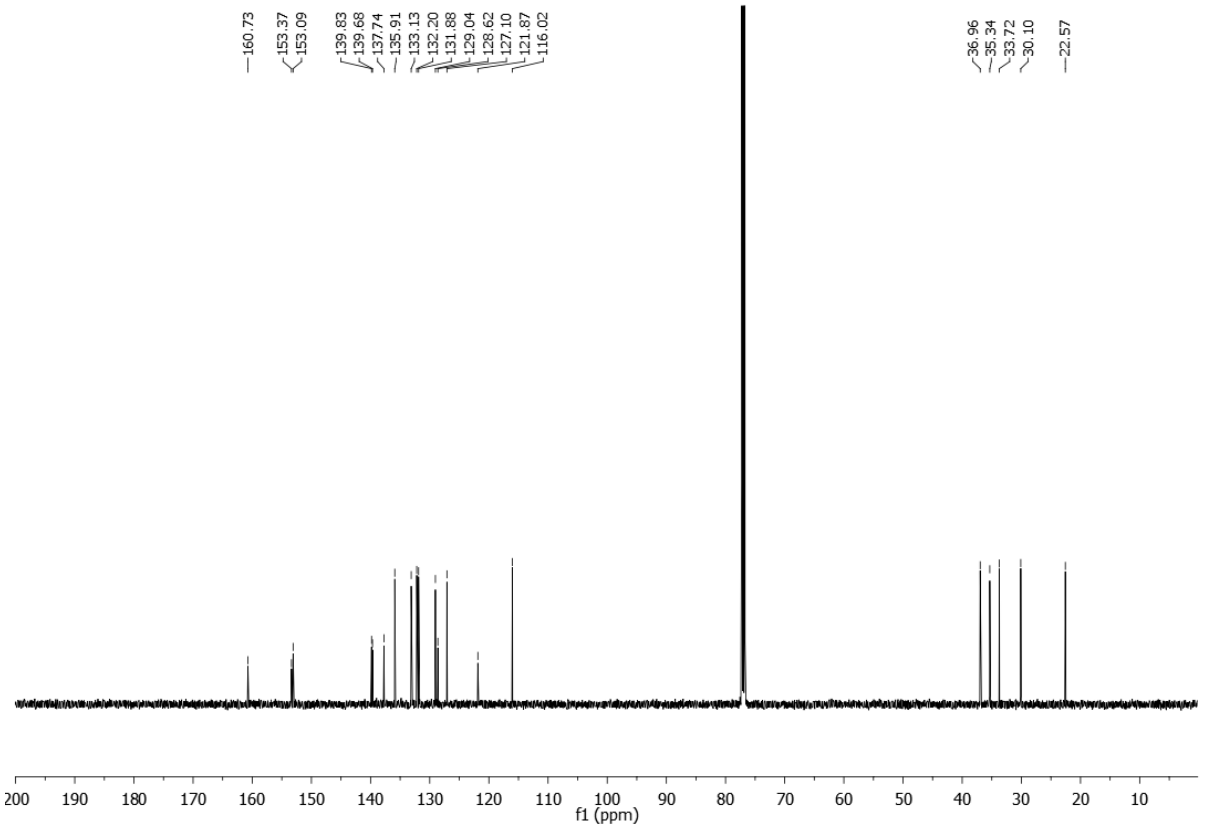


*pCp-based coumarin 3**a***

^{1}H NMR (500 MHz, $CDCl_3$)

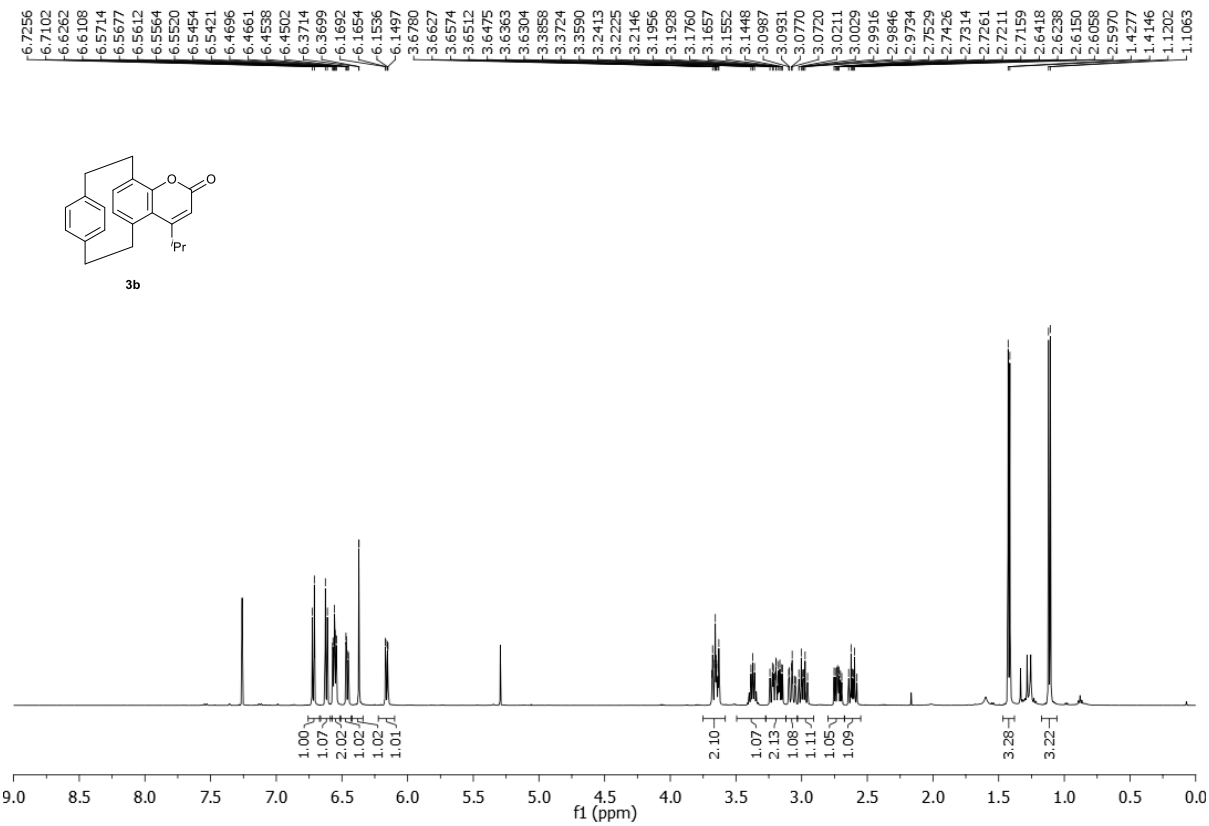


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)



*pCp-based coumarin 3**b***

^{1}H NMR (500 MHz, $CDCl_3$)



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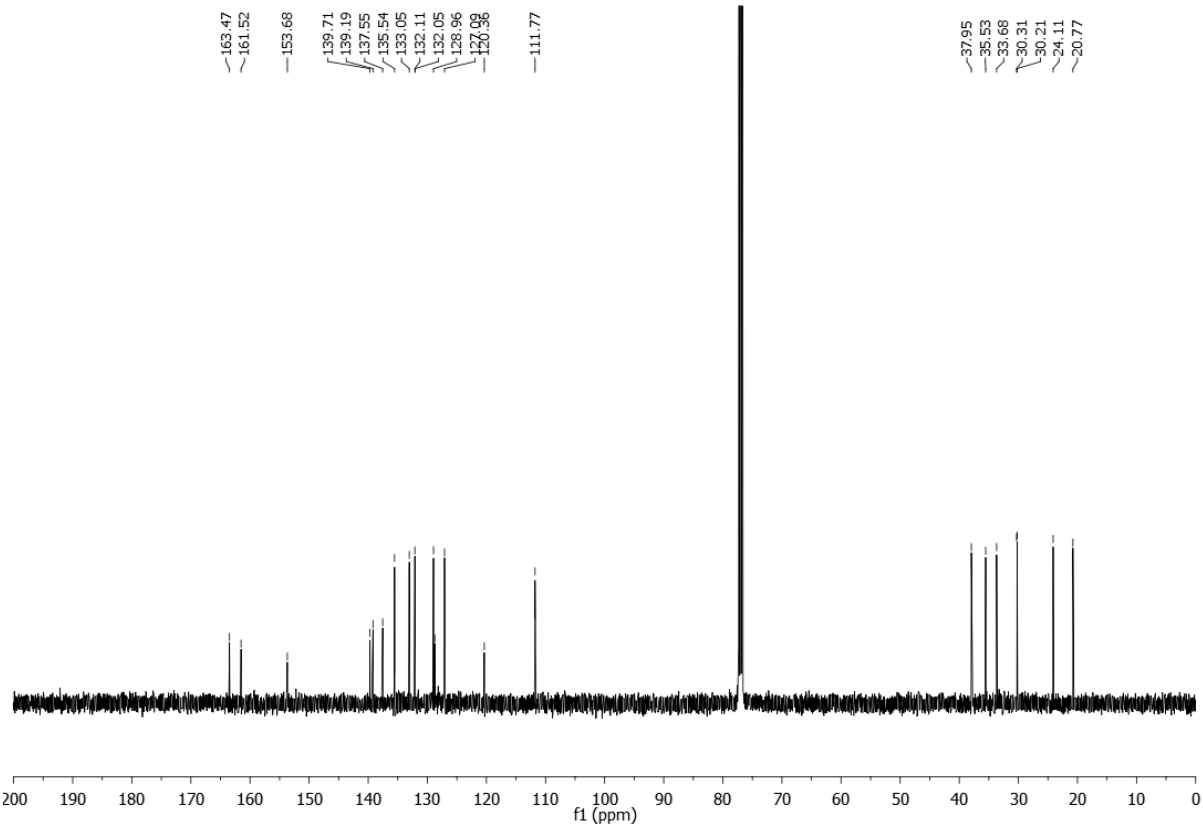

pCp-based coumarin 3c

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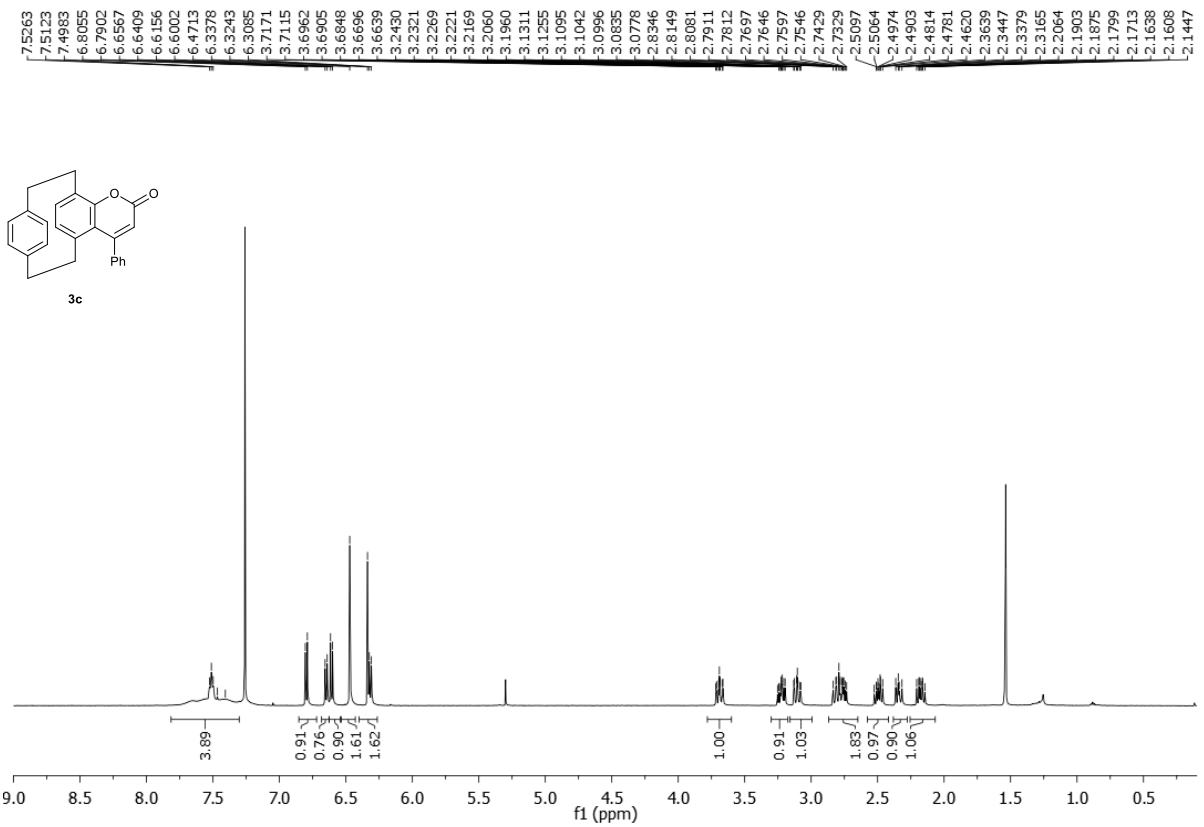

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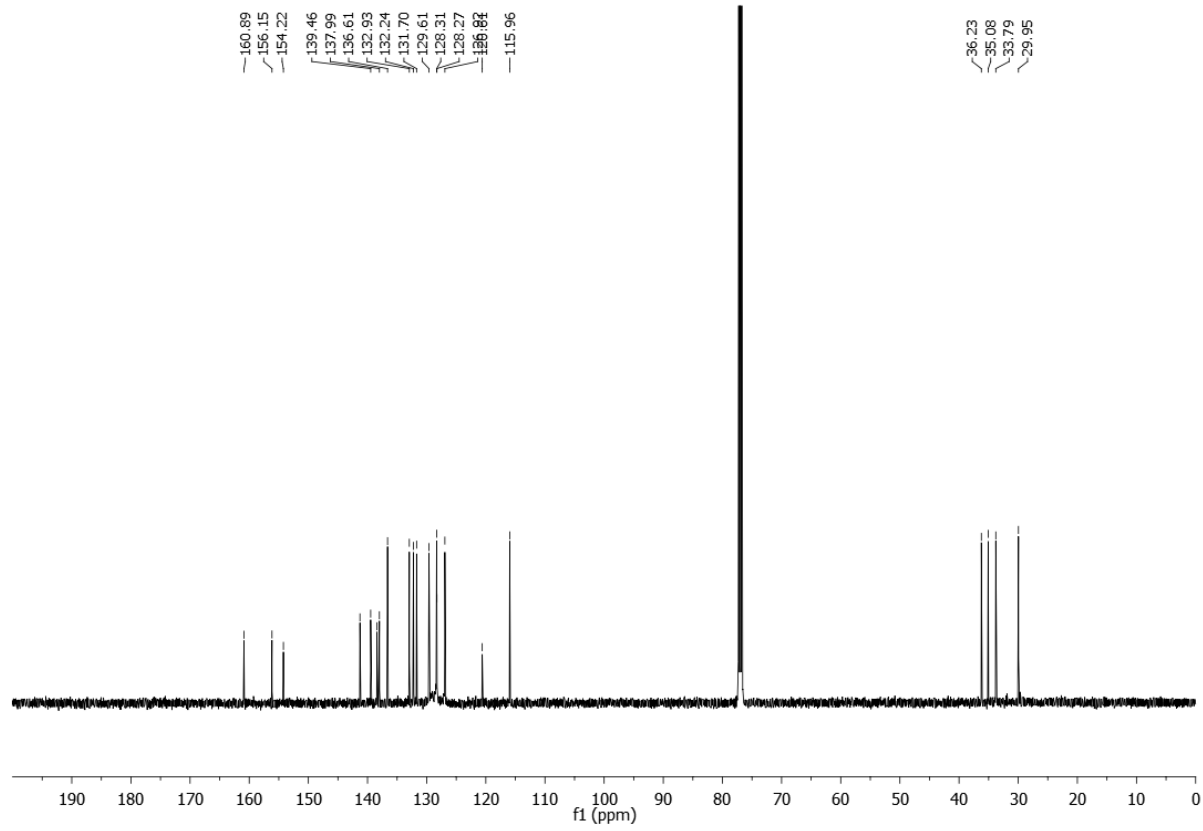
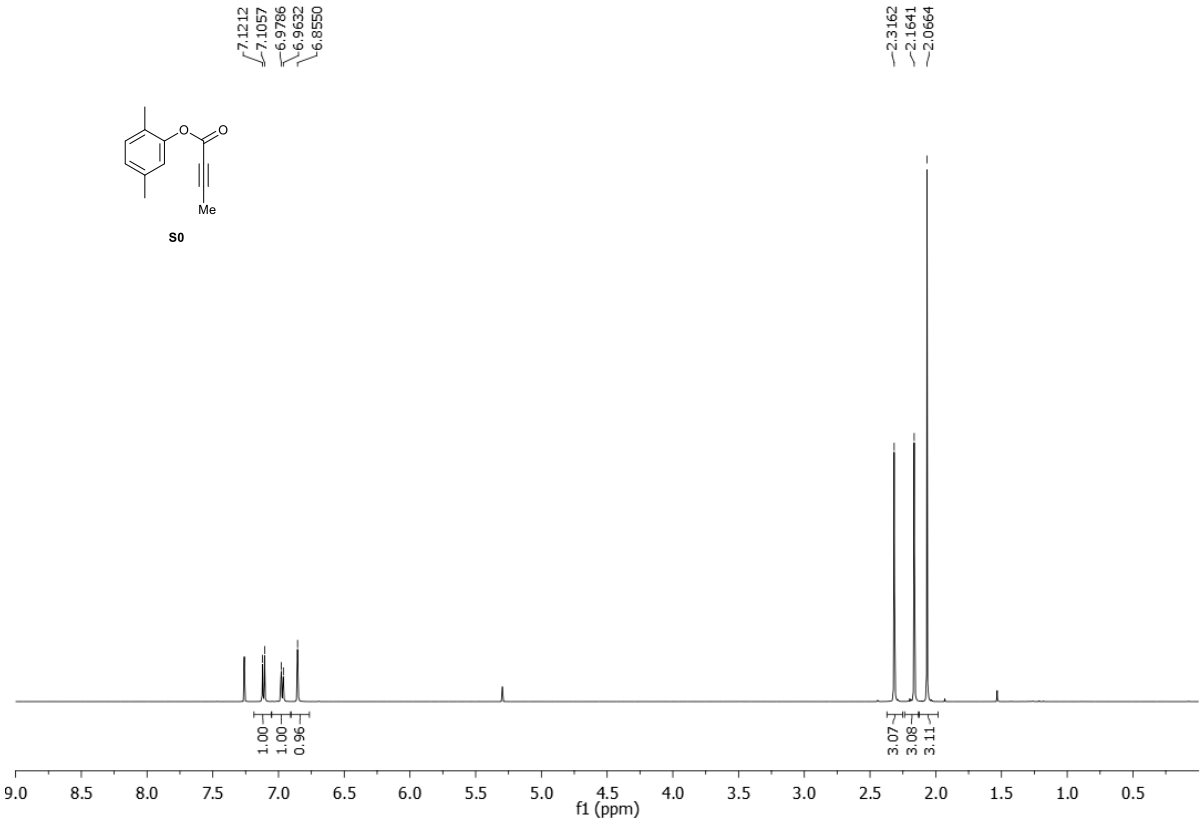
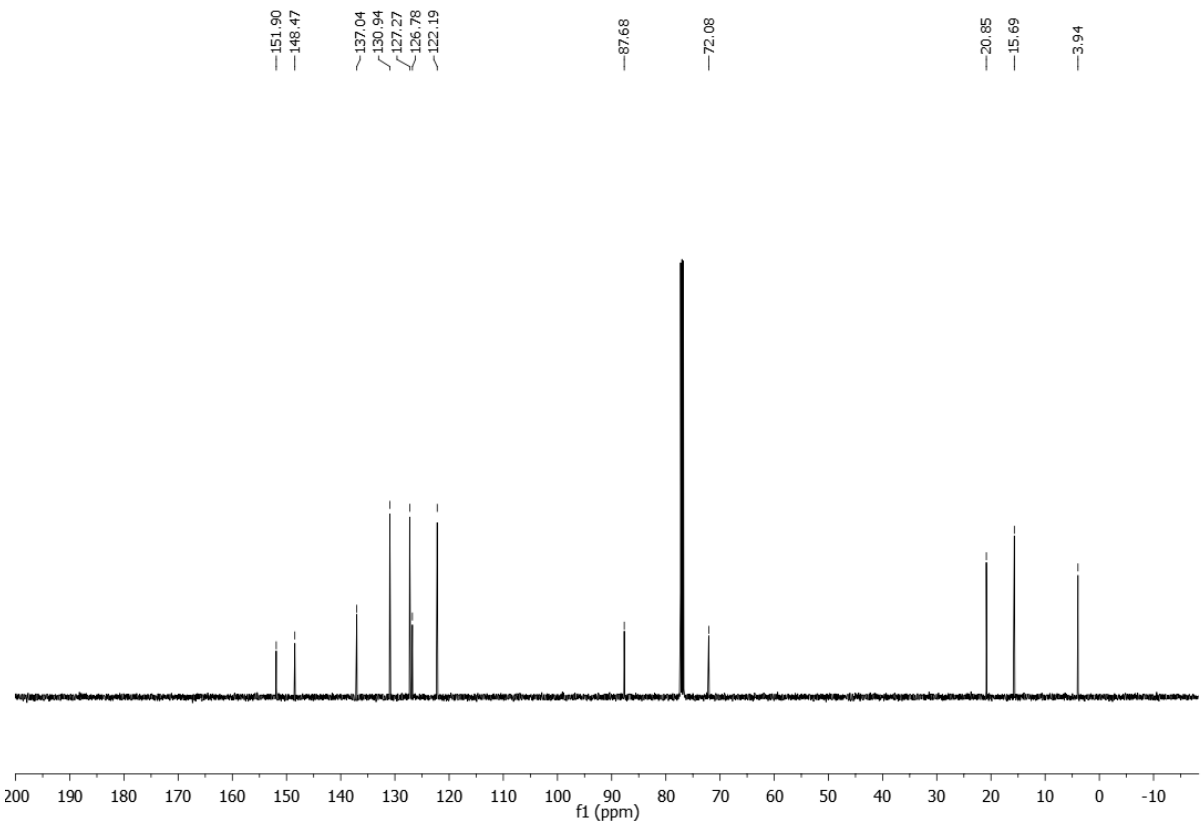


*2,5-Simethylphenyl but-2-ynoate (**S0**)*

^{1}H NMR (500 MHz, $CDCl_3$)

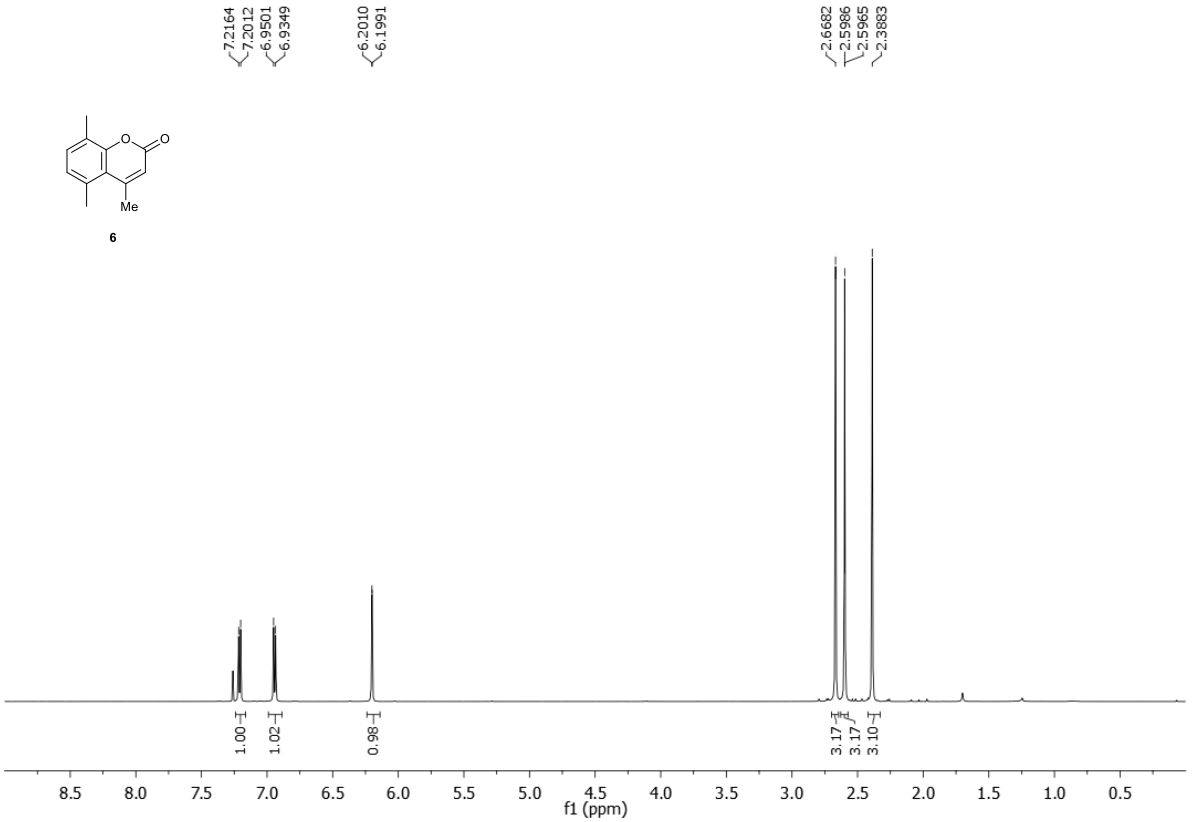


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)



*4,5,8-Trimethyl-2H-chromen-2-one (**6**)*

^{1}H NMR (500 MHz, $CDCl_3$)



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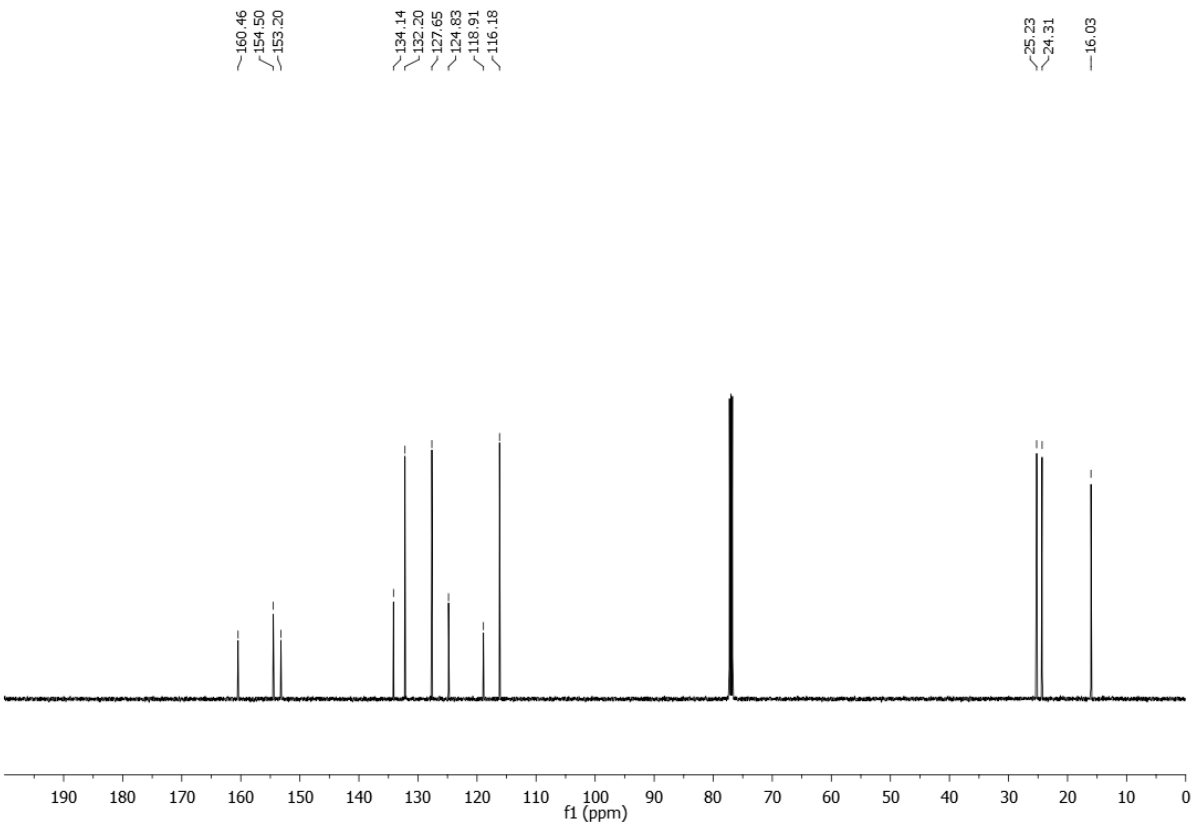
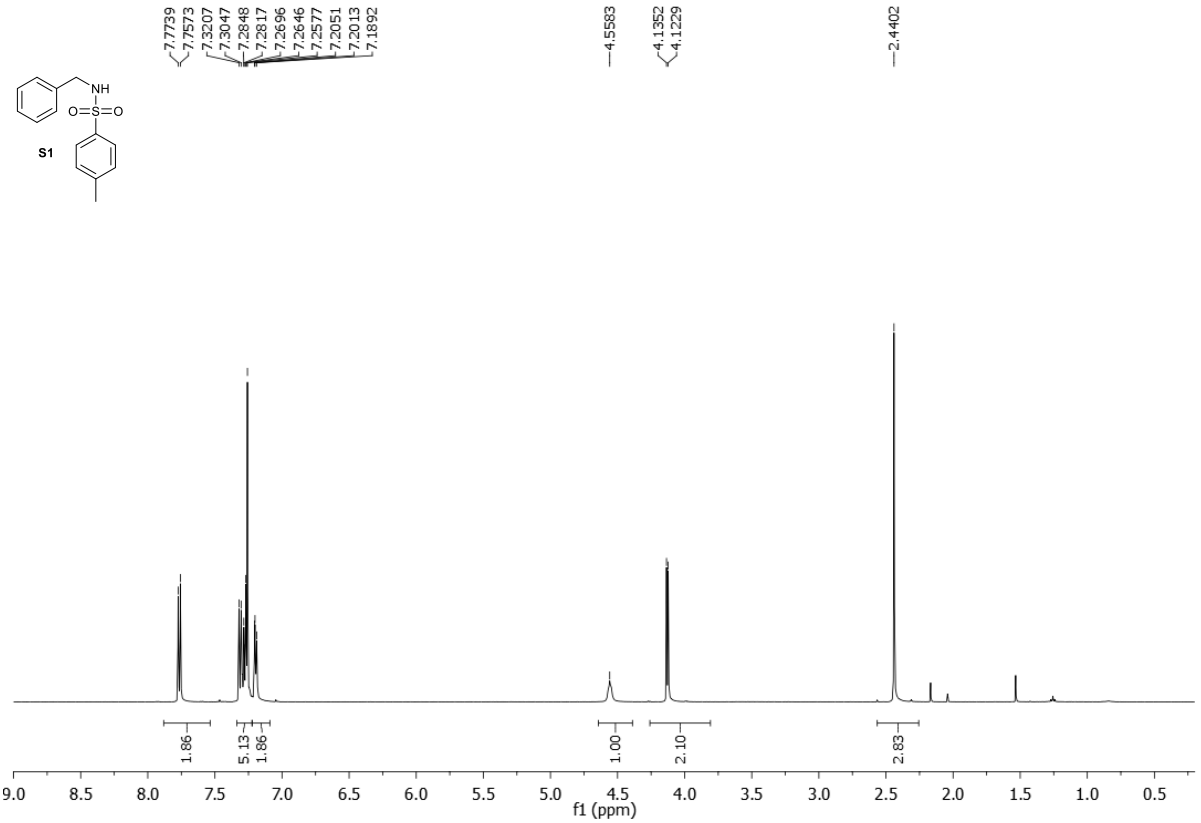
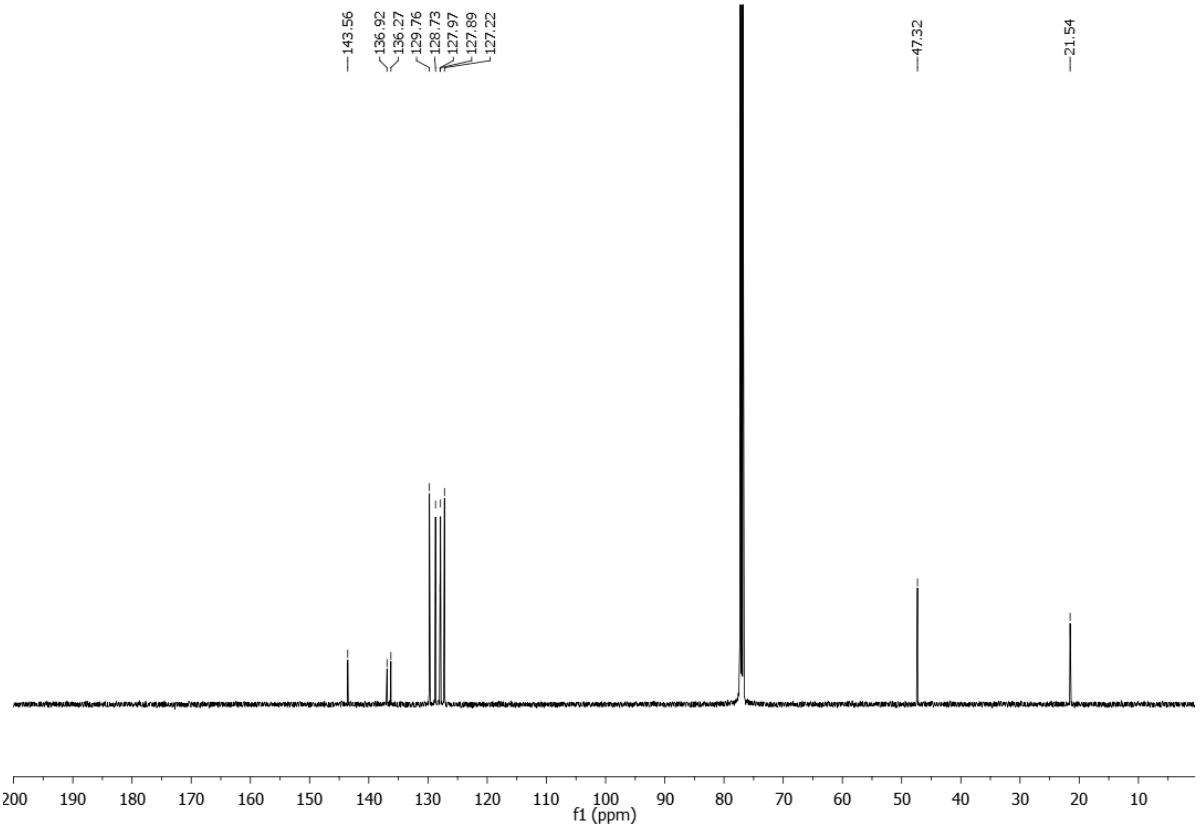


*N-benzyl-4-methylbenzene-1-sulfonamide (**S1**)*

^{1}H NMR (500 MHz, $CDCl_3$)

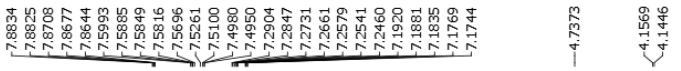


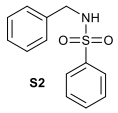
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

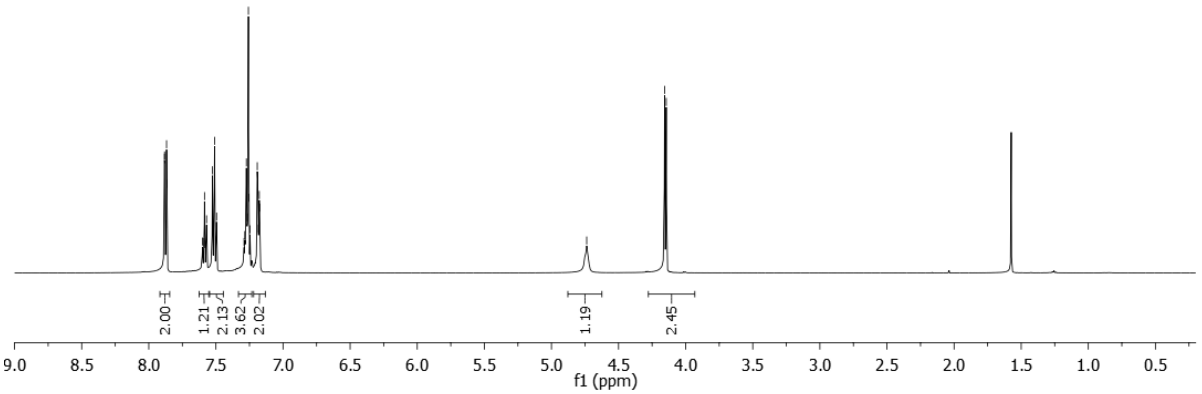


*N-benzylbenzenesulfonamide (**S2**)*

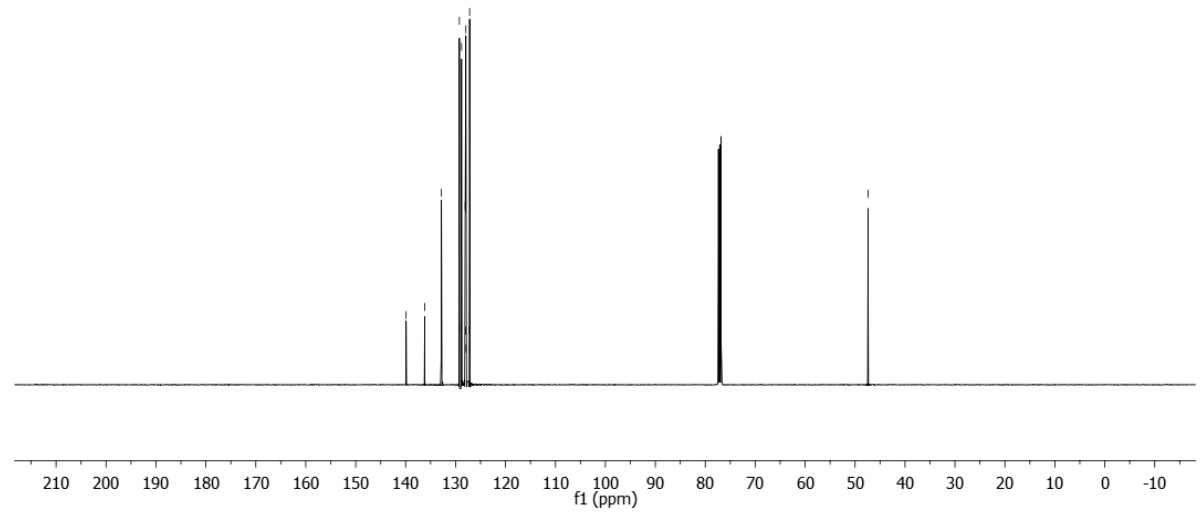
^{1}H NMR (500 MHz, $CDCl_3$)





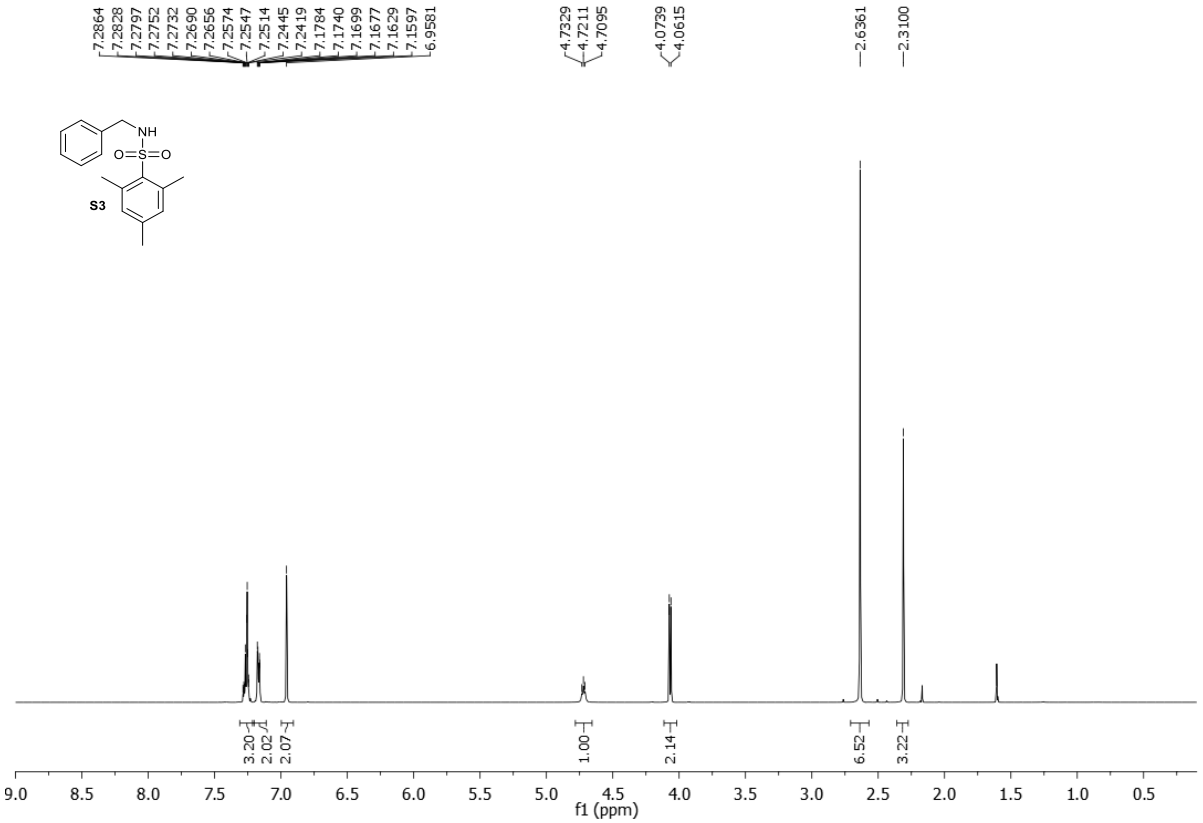


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

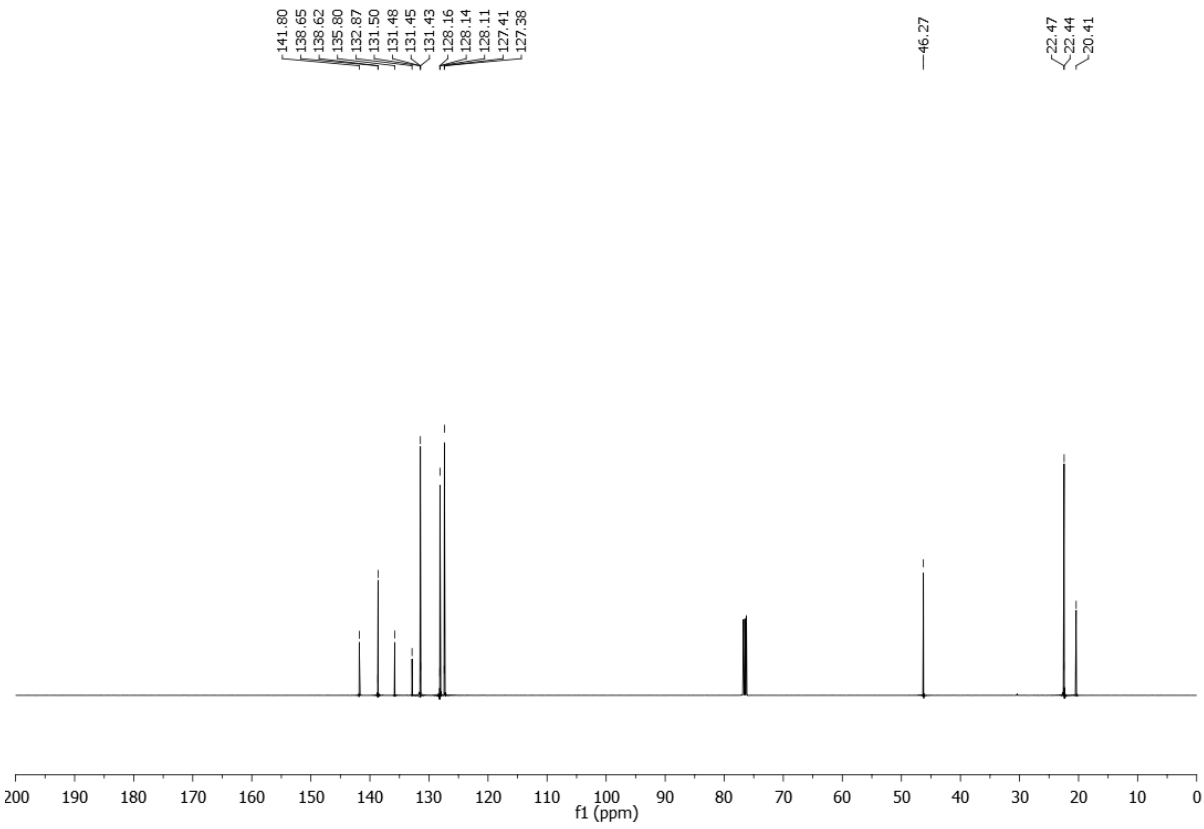


*N-benzyl-2,4,6-trimethylbenzene-1-sulfonamide (**S2**)*

^{1}H NMR (500 MHz, $CDCl_3$)

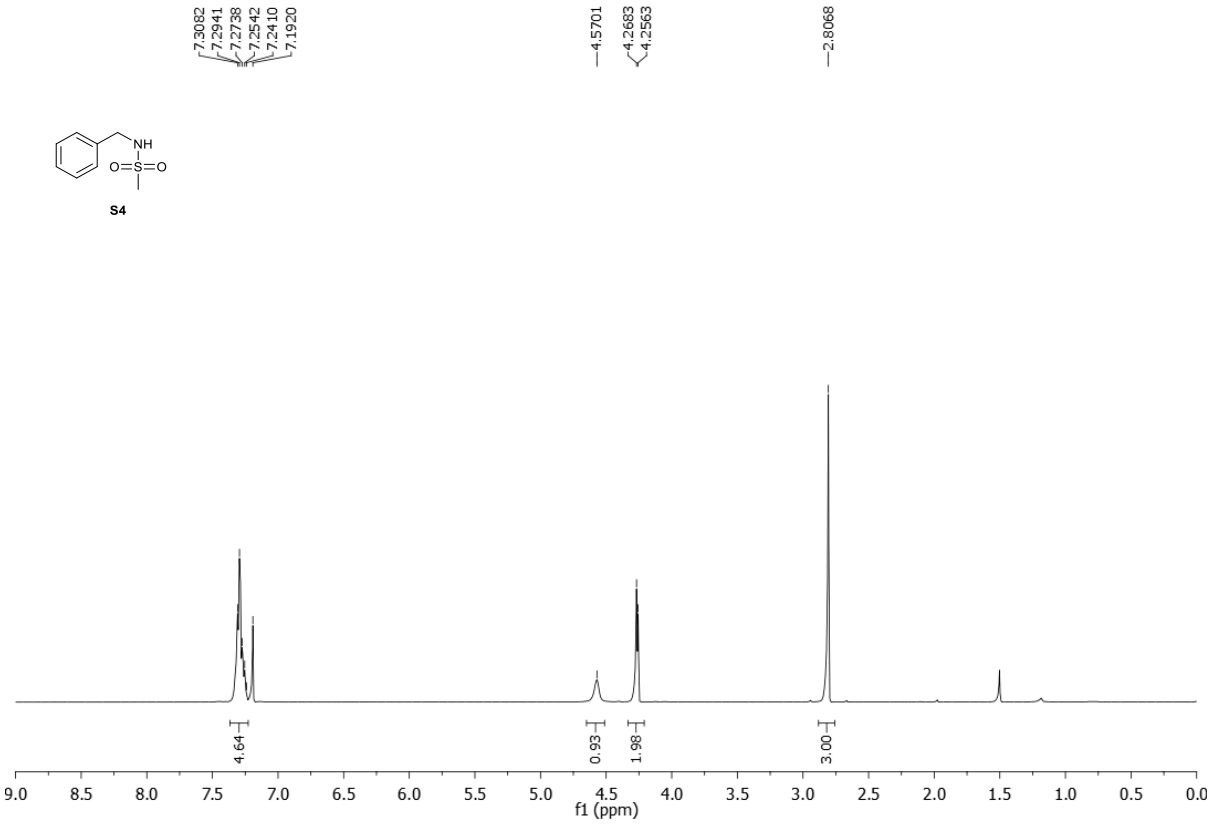


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

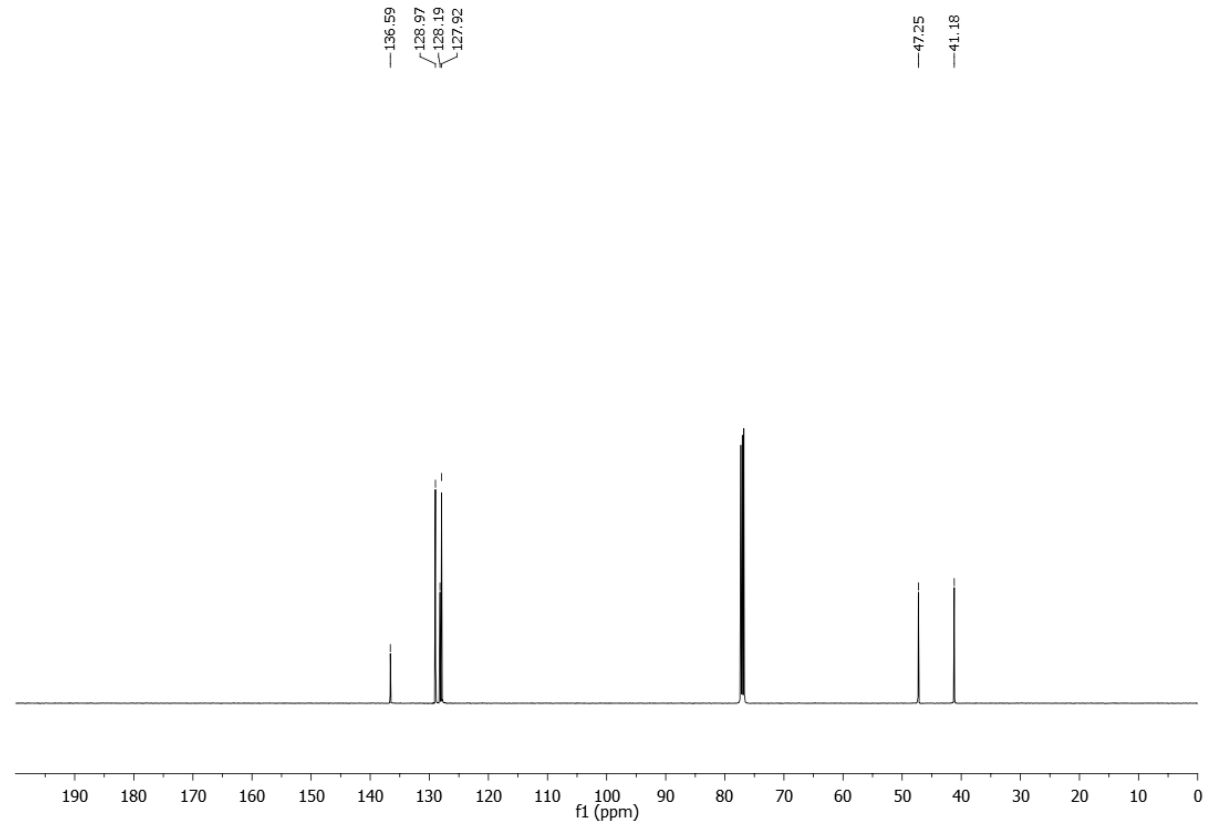


*N-benzylmethanesulfonamide (**S4**)*

^{1}H NMR (500 MHz, $CDCl_3$)

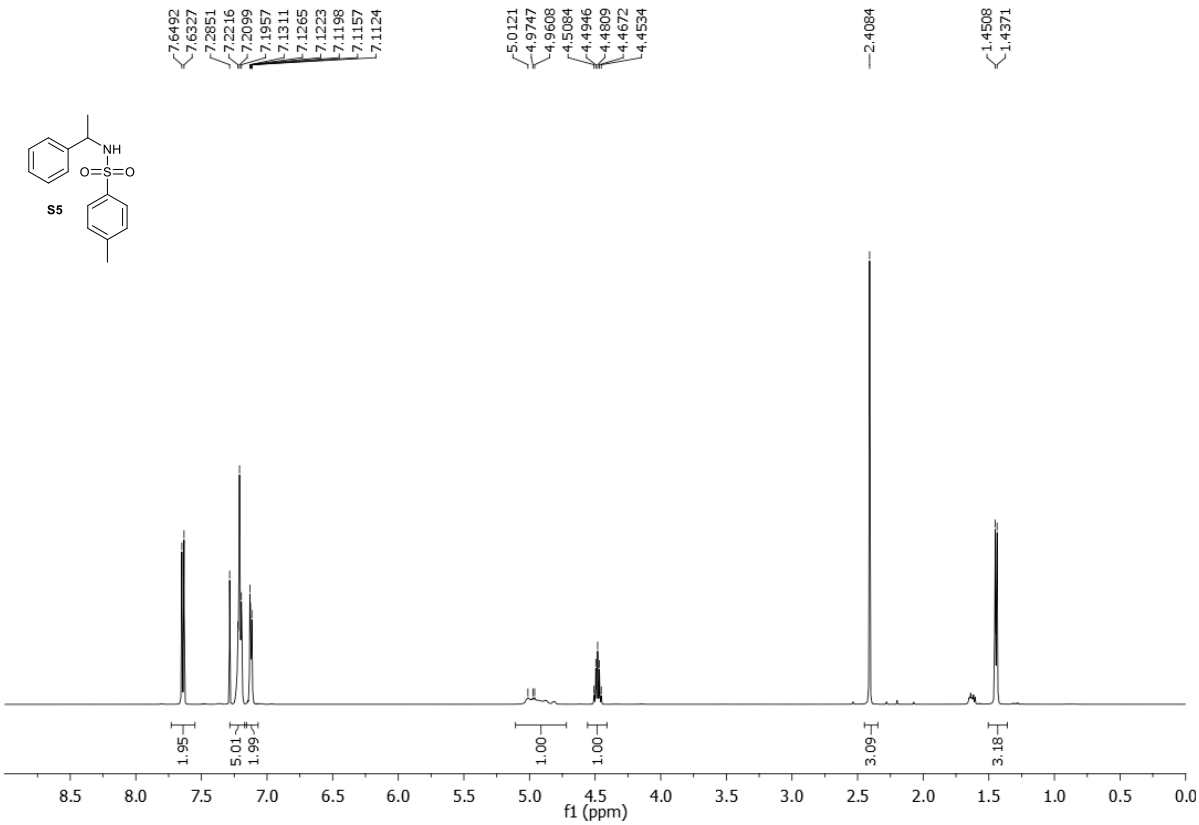


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

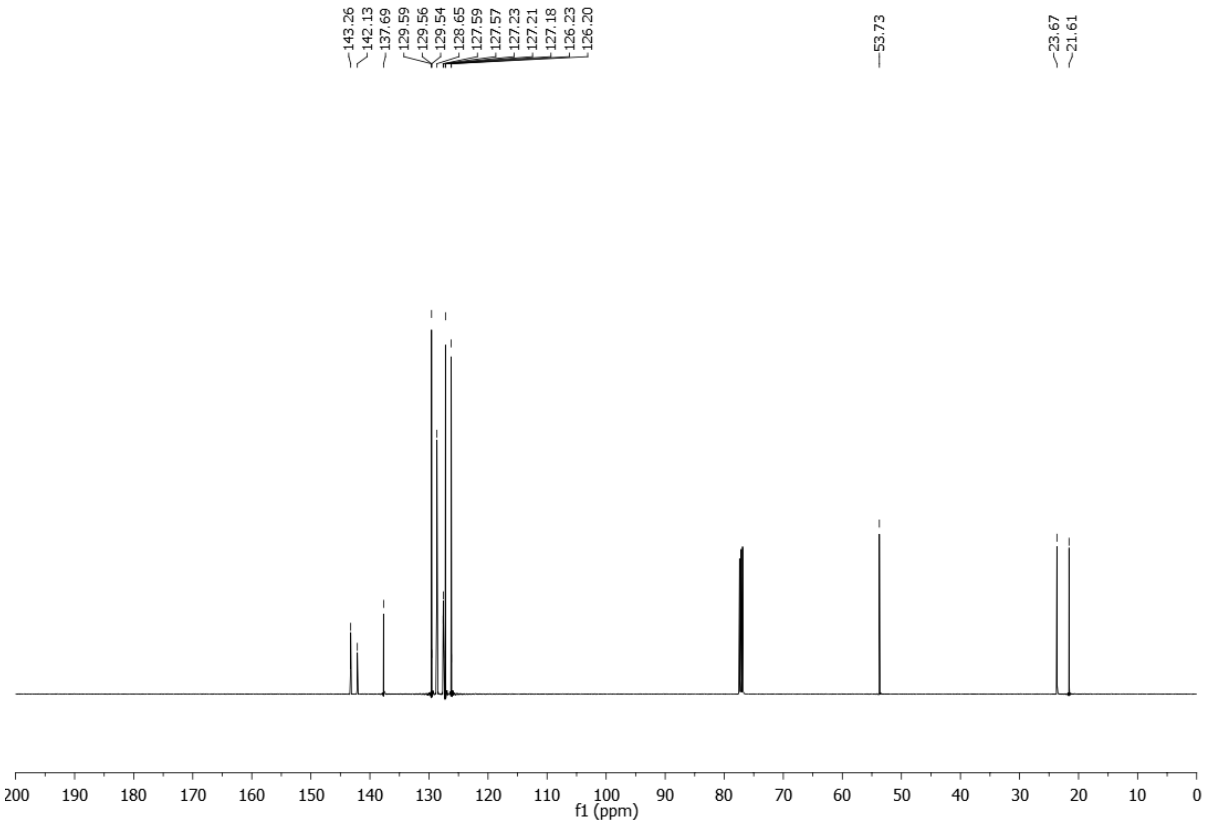


*4-Methyl-N-(1-phenylethyl)benzene-1-sulfonamide (**S5**)*

^{1}H NMR (500 MHz, $CDCl_3$)

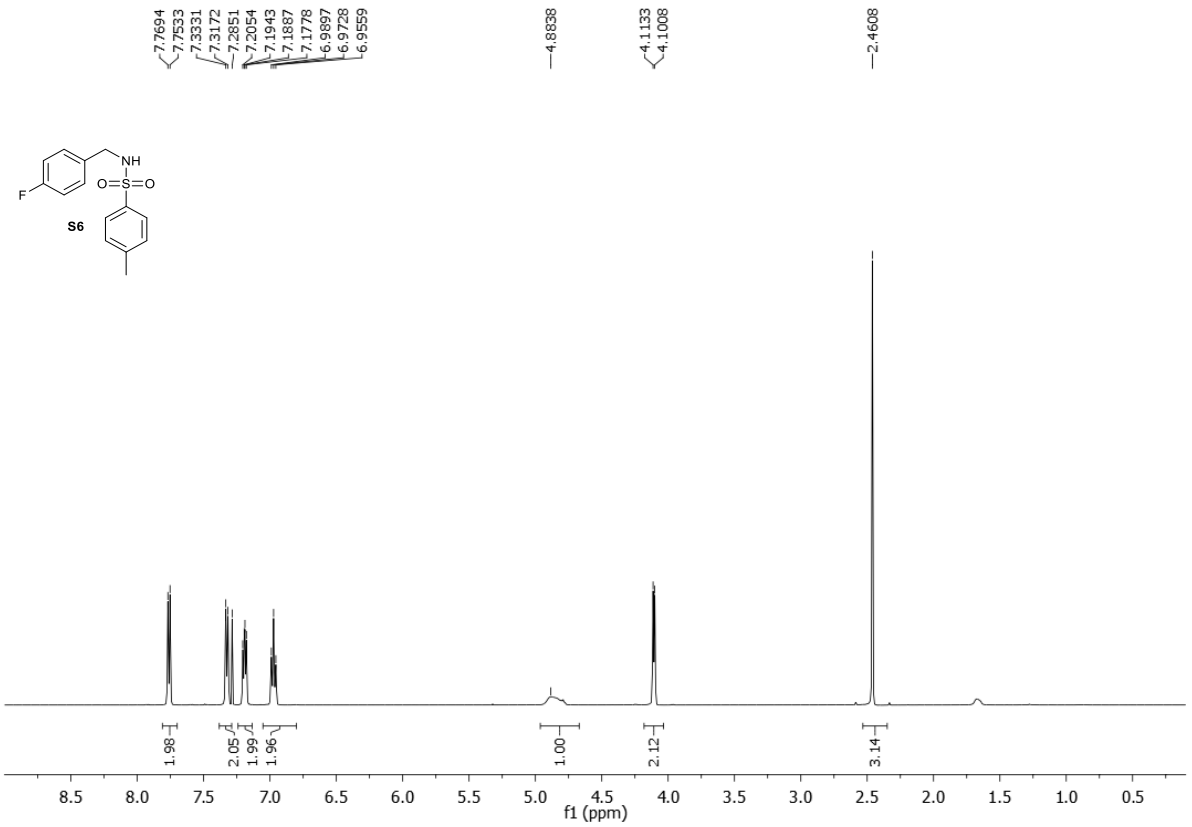


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

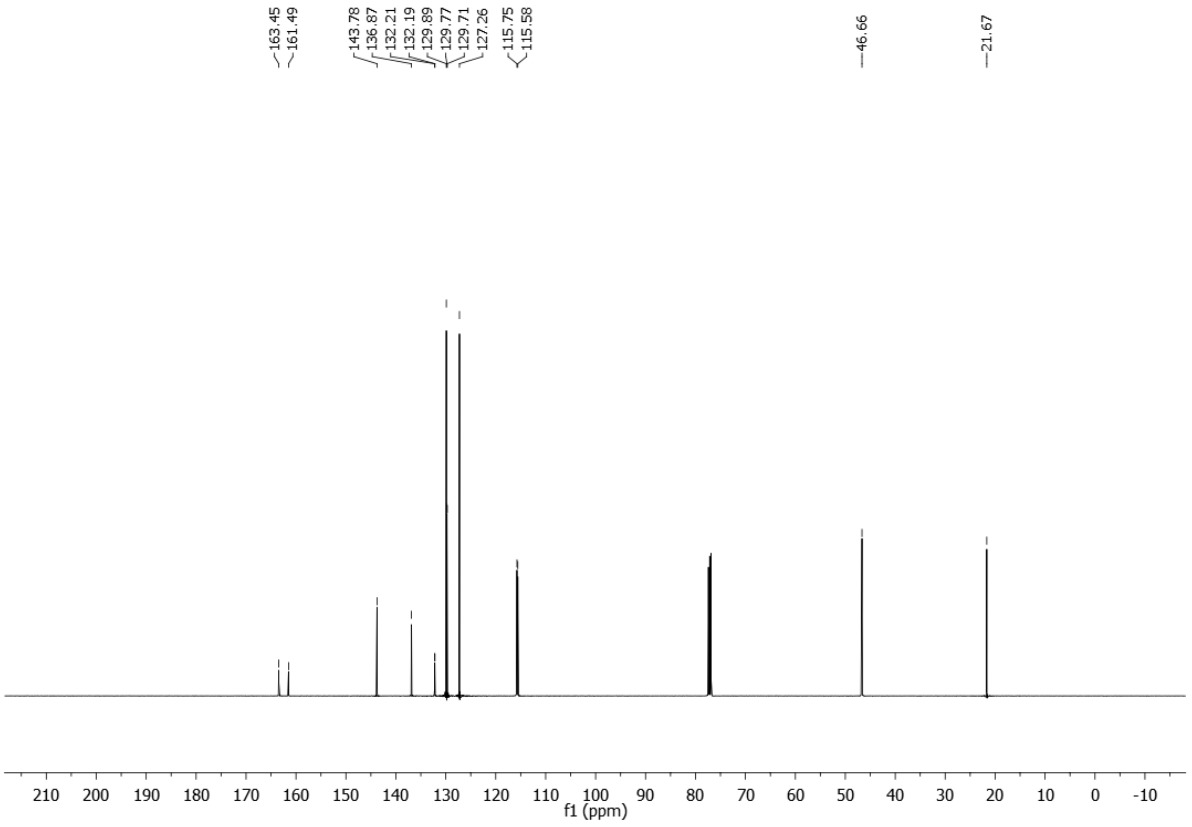


*N-[(4-fluorophenyl)methyl]-4-methylbenzene-1-sulfonamide (**S6**)*

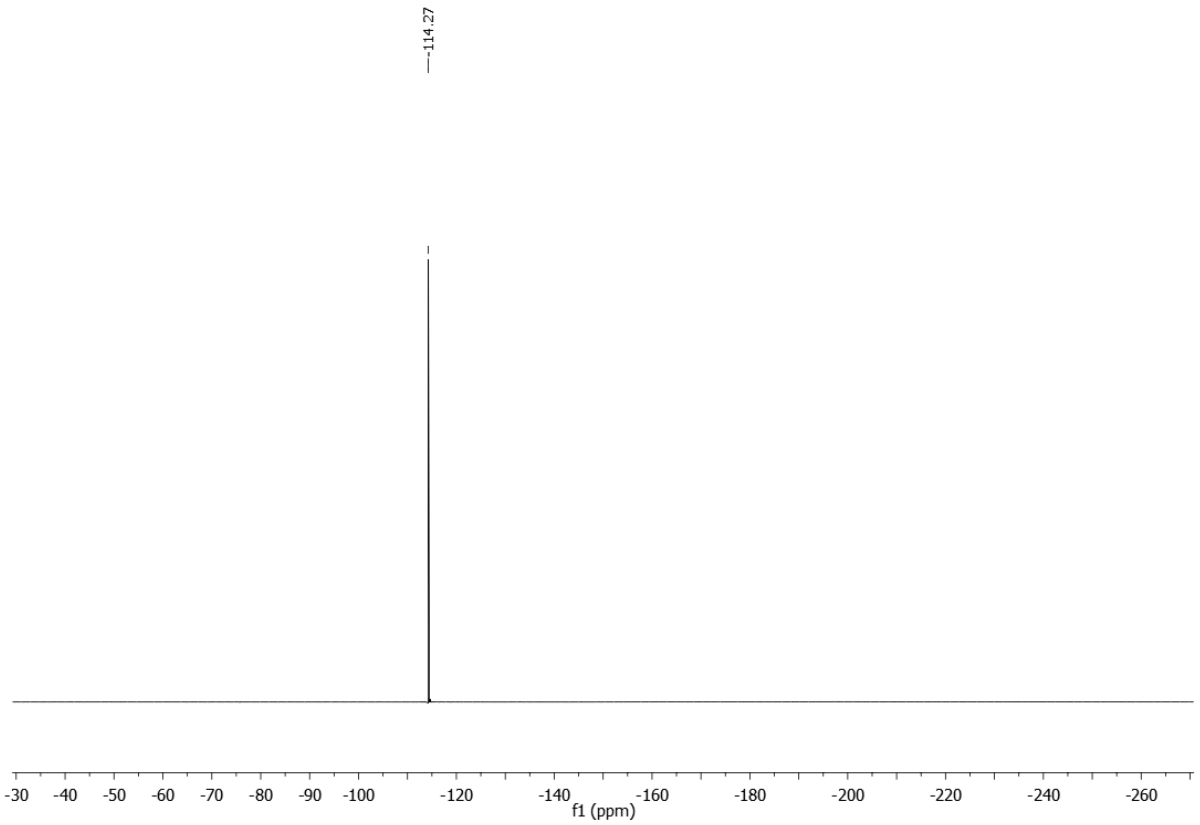
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

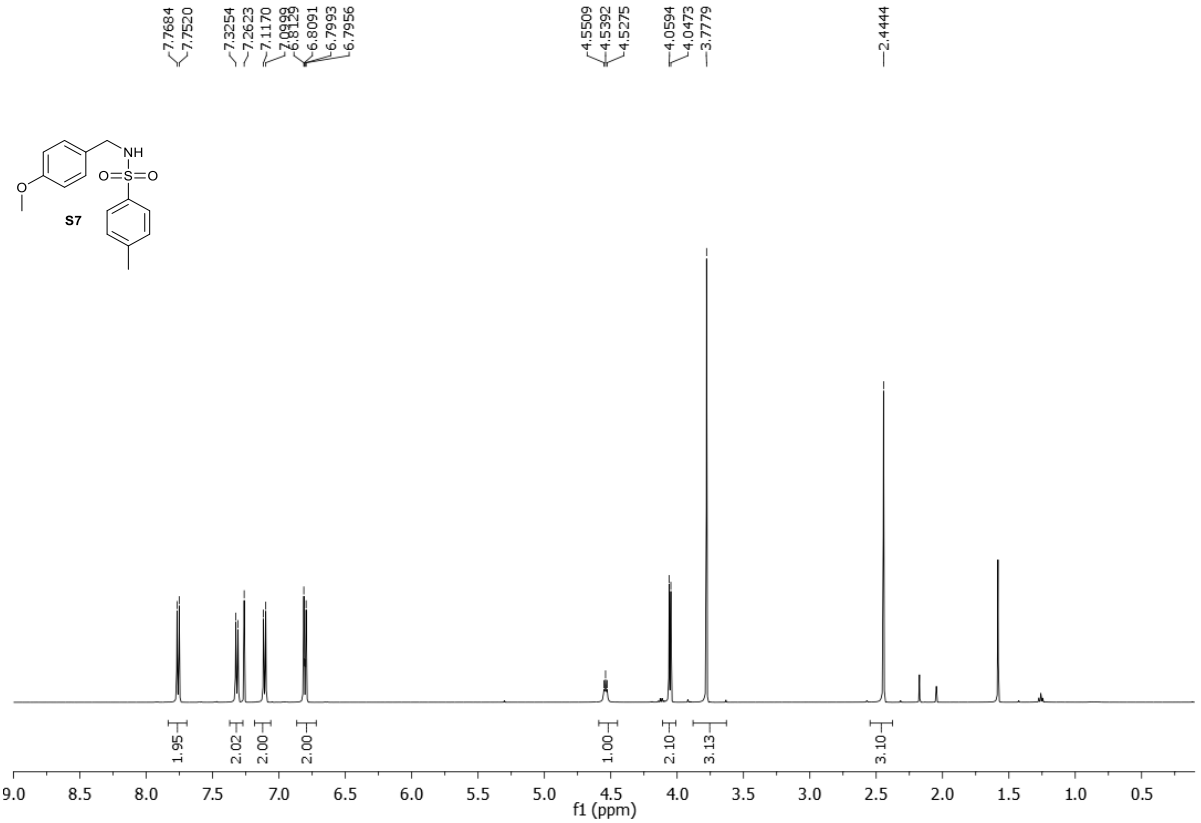


^{19}F NMR (471 MHz, $CDCl_3$)

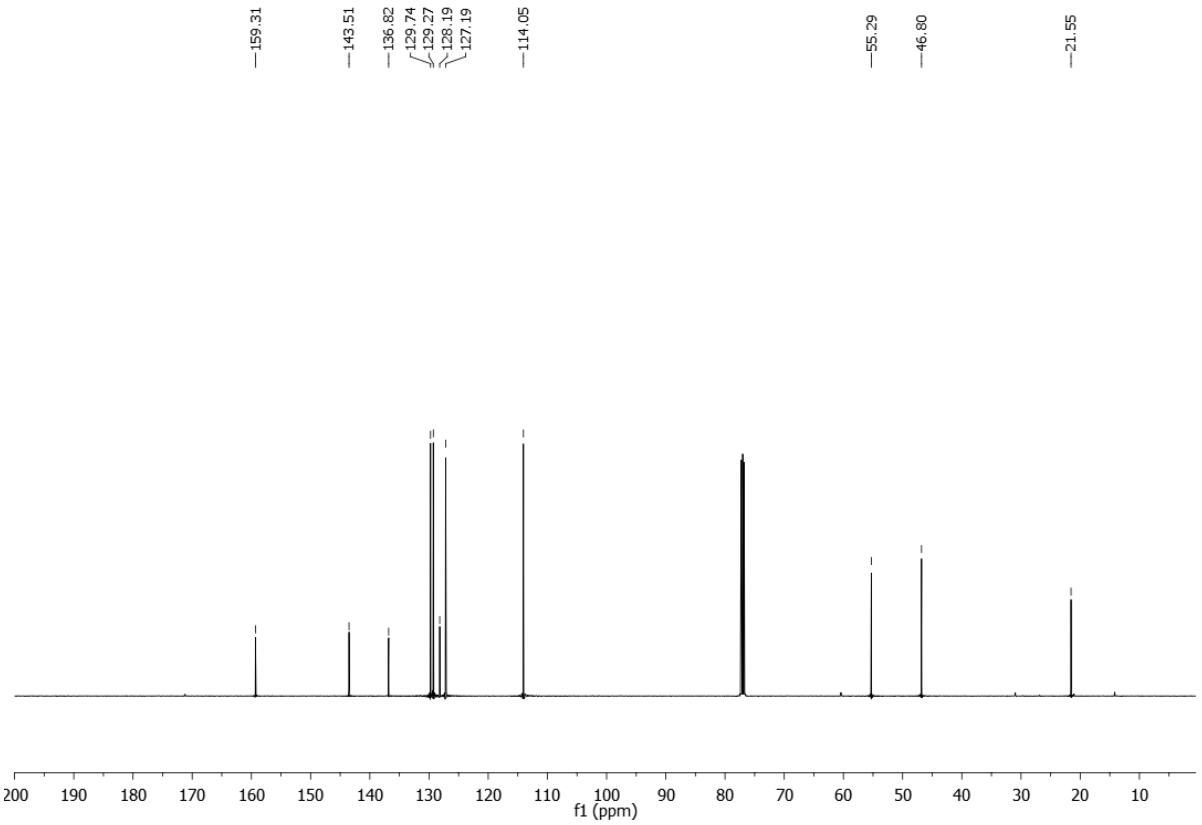


*N-[(4-methoxyphenyl)methyl]-4-methylbenzene-1-sulfonamide (**S7**)*

^{1}H NMR (500 MHz, $CDCl_3$)

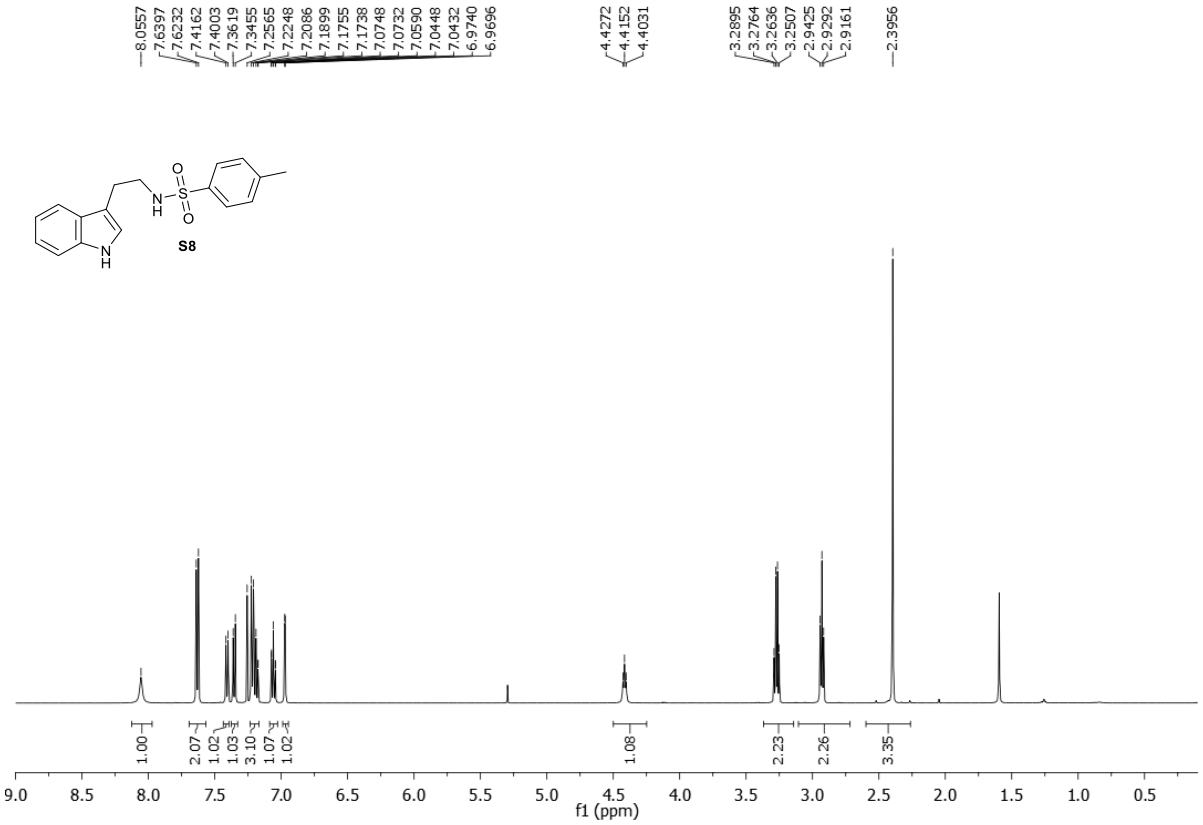


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

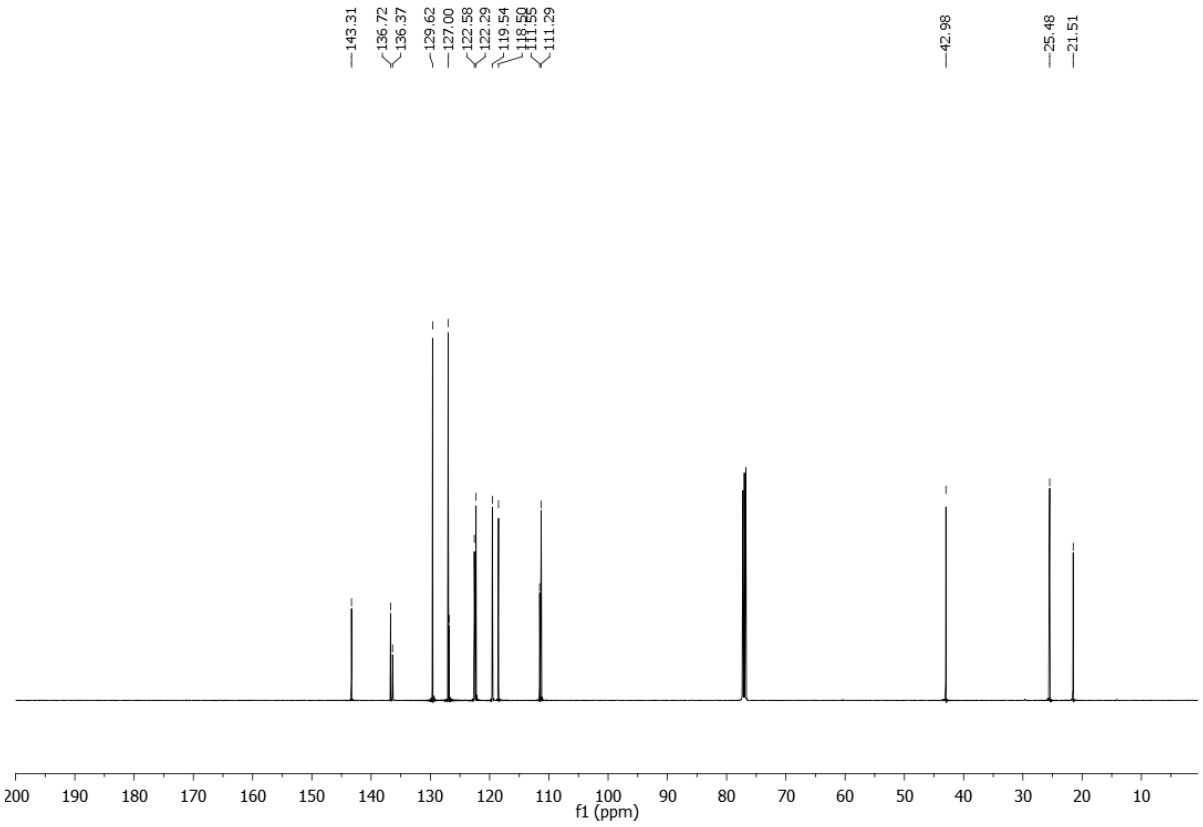


*N-[2-(1H-indol-3-yl)ethyl]-4-methylbenzene-1-sulfonamide (**S8**)*

^{1}H NMR (500 MHz, $CDCl_3$)

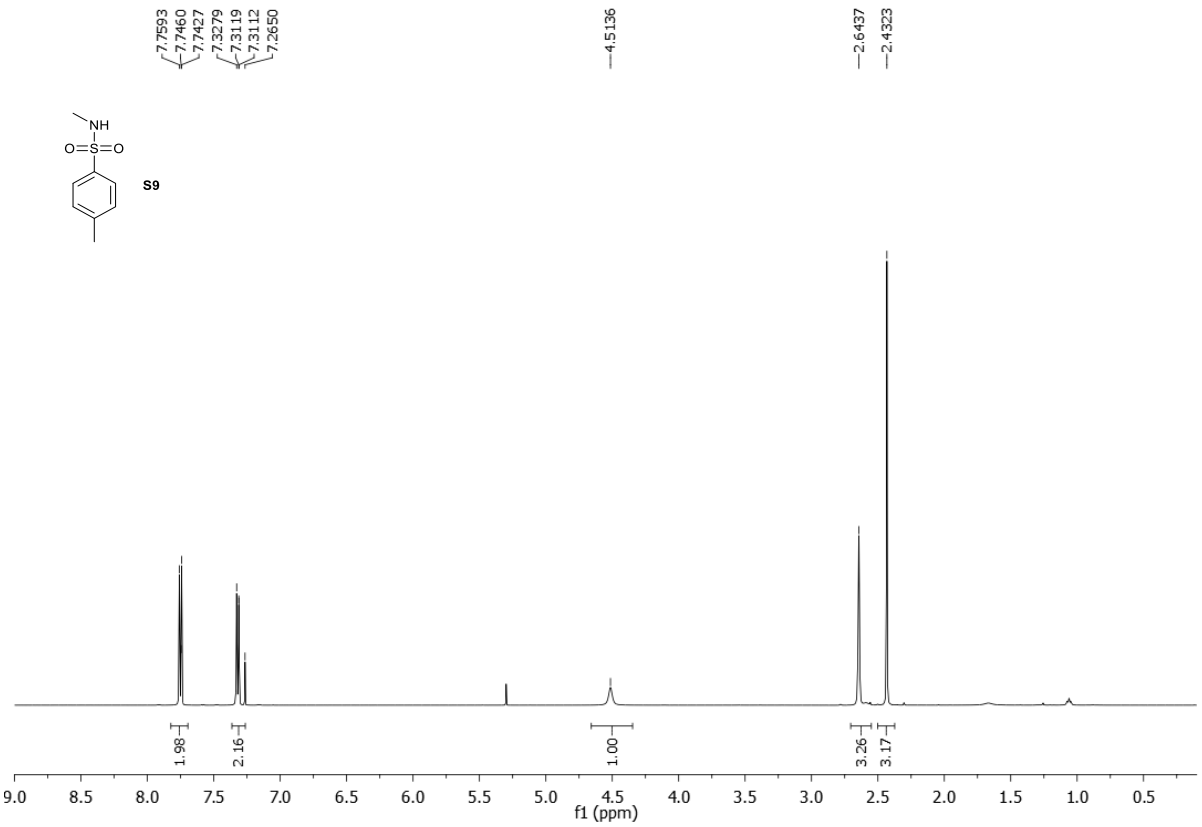


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

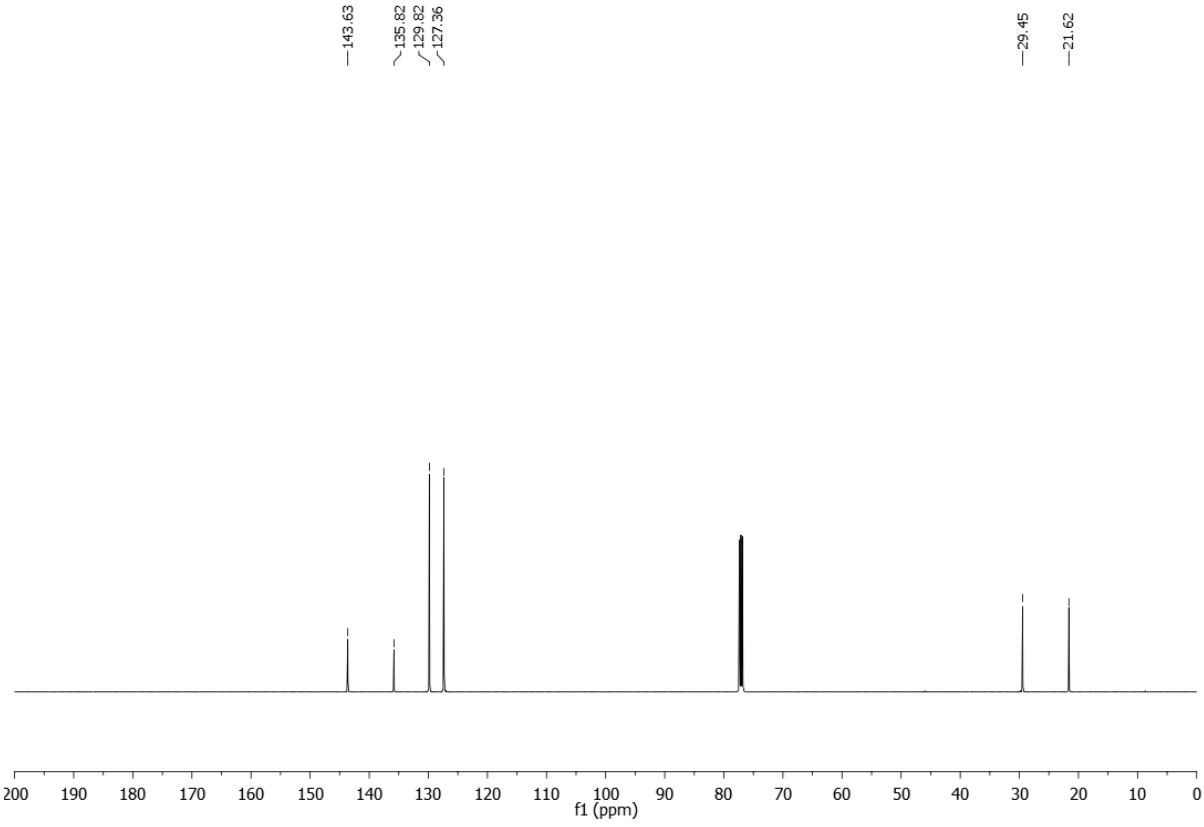


*N,4-dimethylbenzenesulfonamide (**S9**)*

^{1}H NMR (500 MHz, $CDCl_3$)

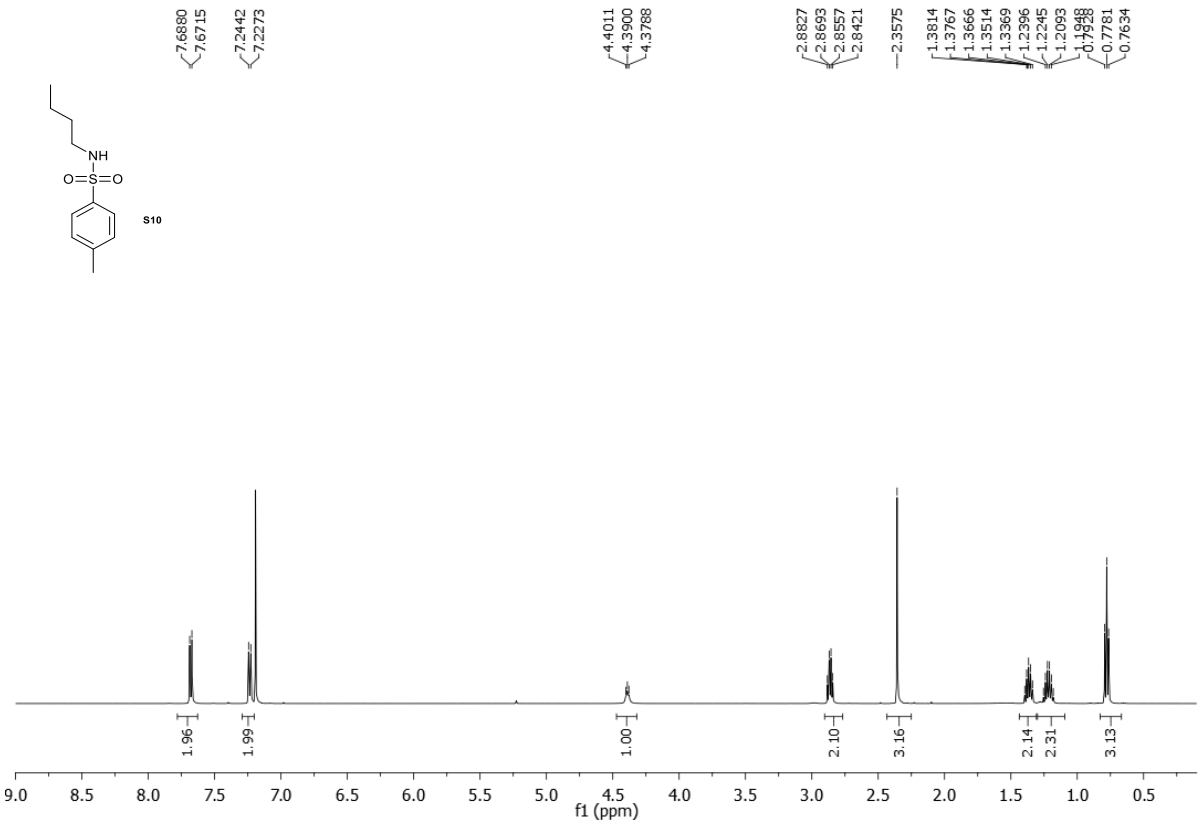


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

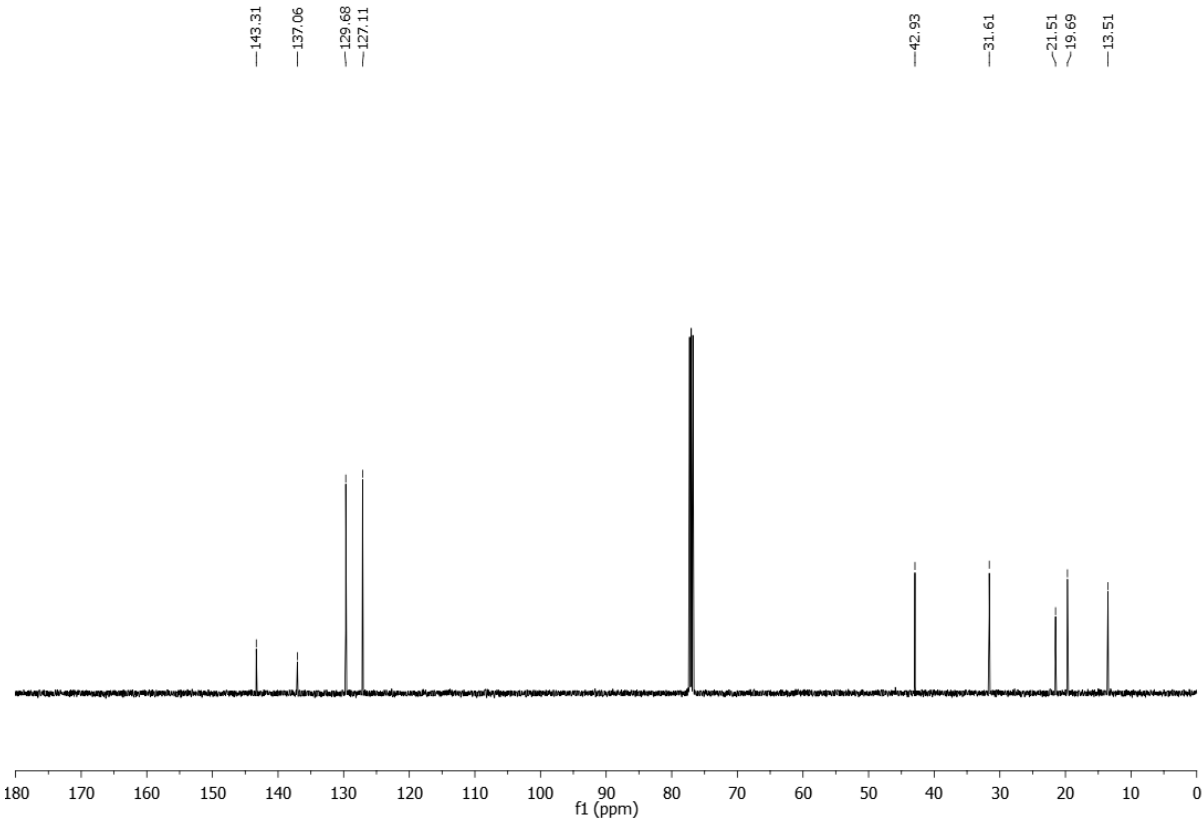


*N-butyl-4-methylbenzenesulfonamide (**S10**)*

^{1}H NMR (500 MHz, $CDCl_3$)

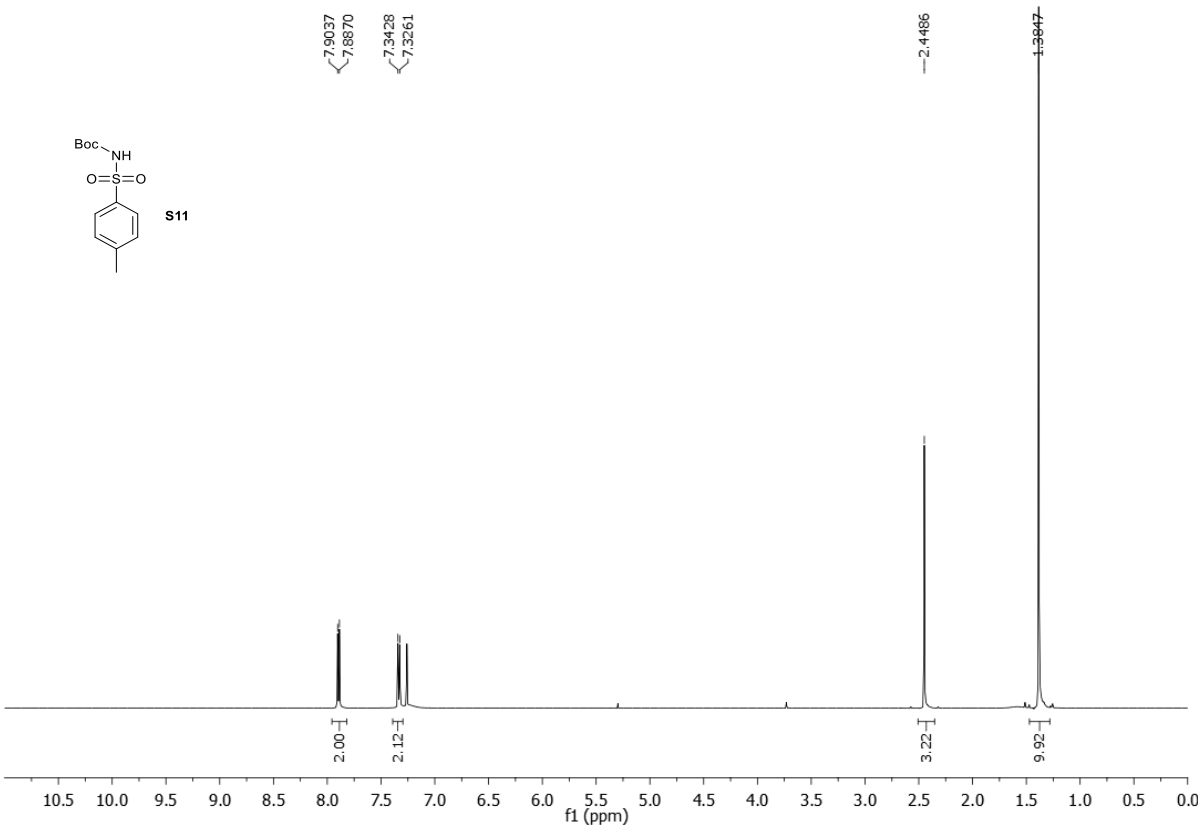


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

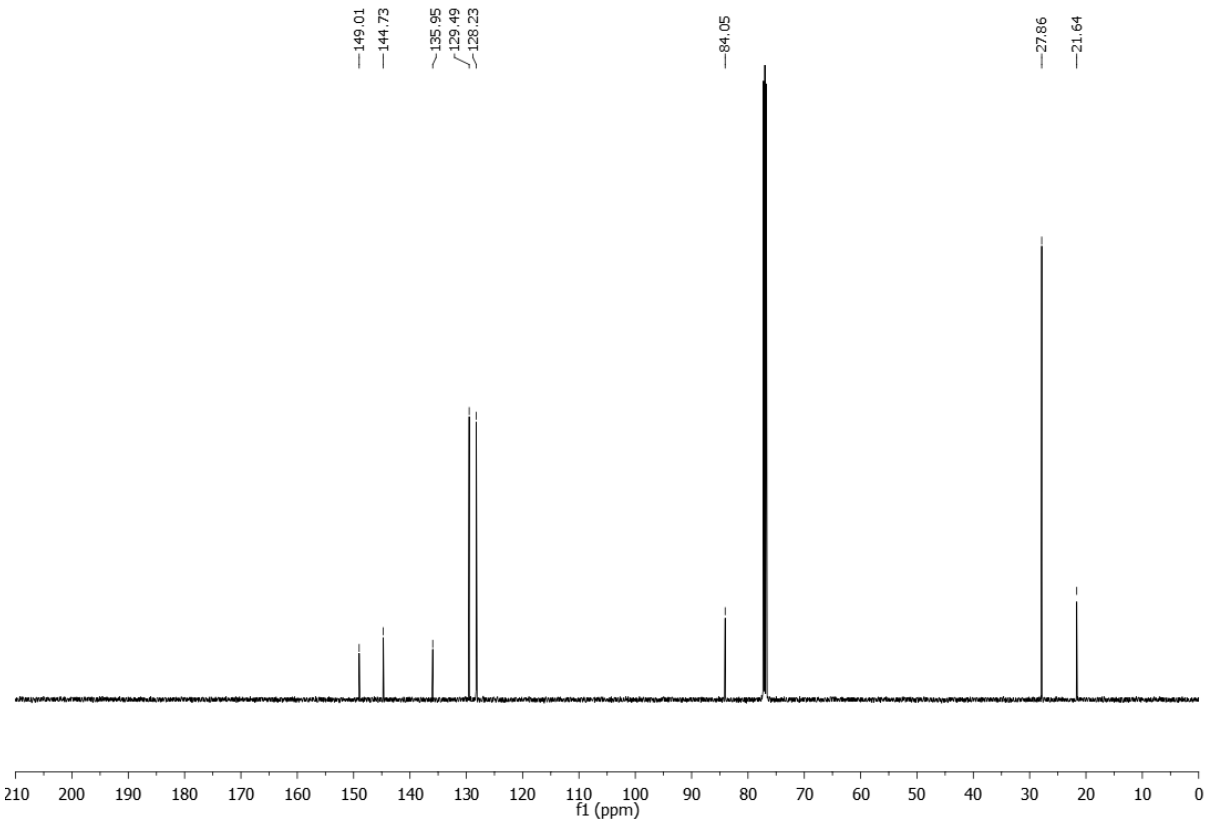


*N-tert-butyl tosylcarbamate (**S11**)*

^{1}H NMR (500 MHz, $CDCl_3$)

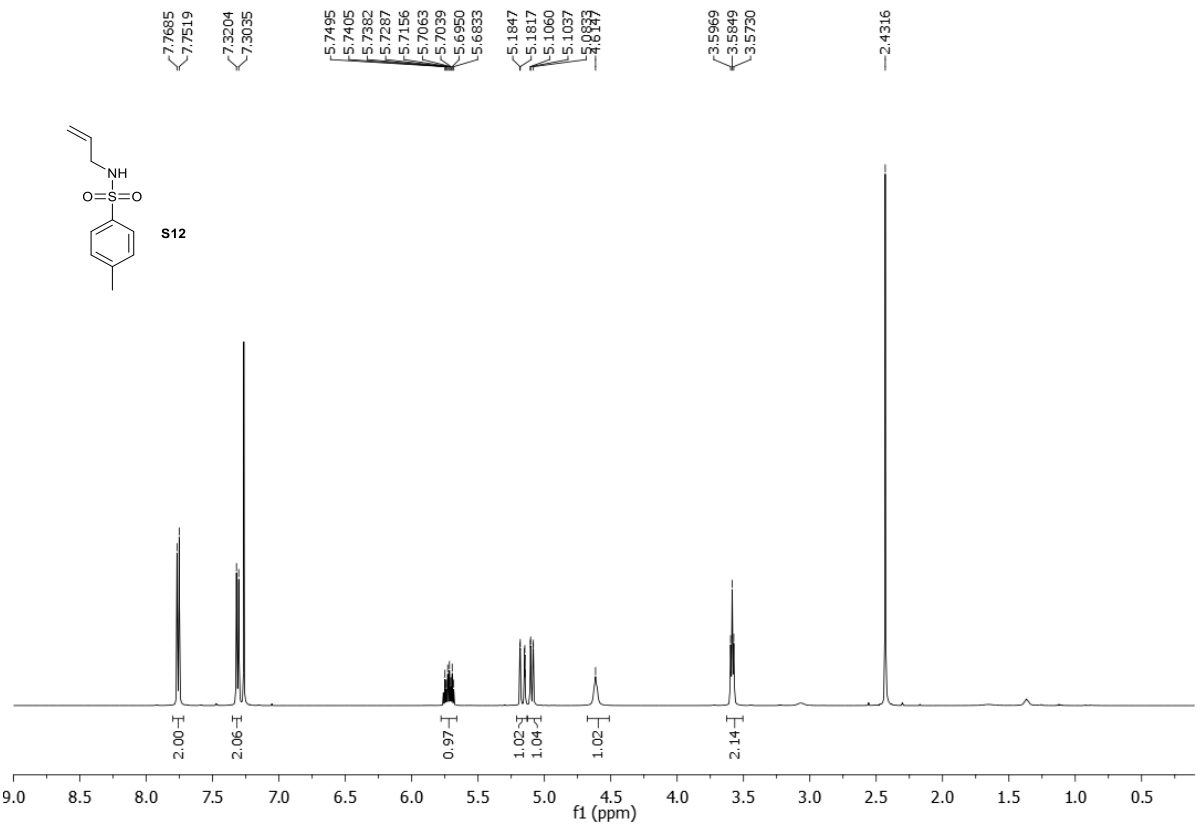


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

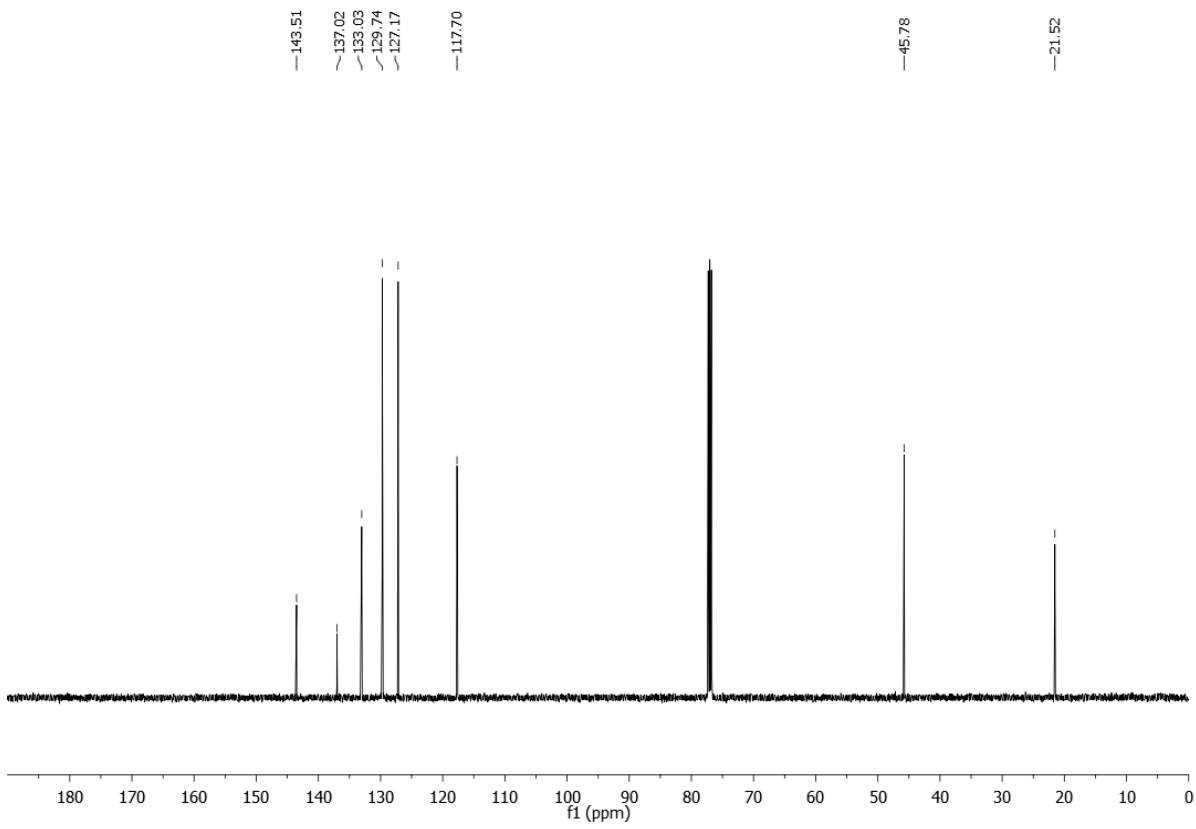


*N-allyl-4-methylbenzenesulfonamide (**S12**)*

^{1}H NMR (500 MHz, $CDCl_3$)

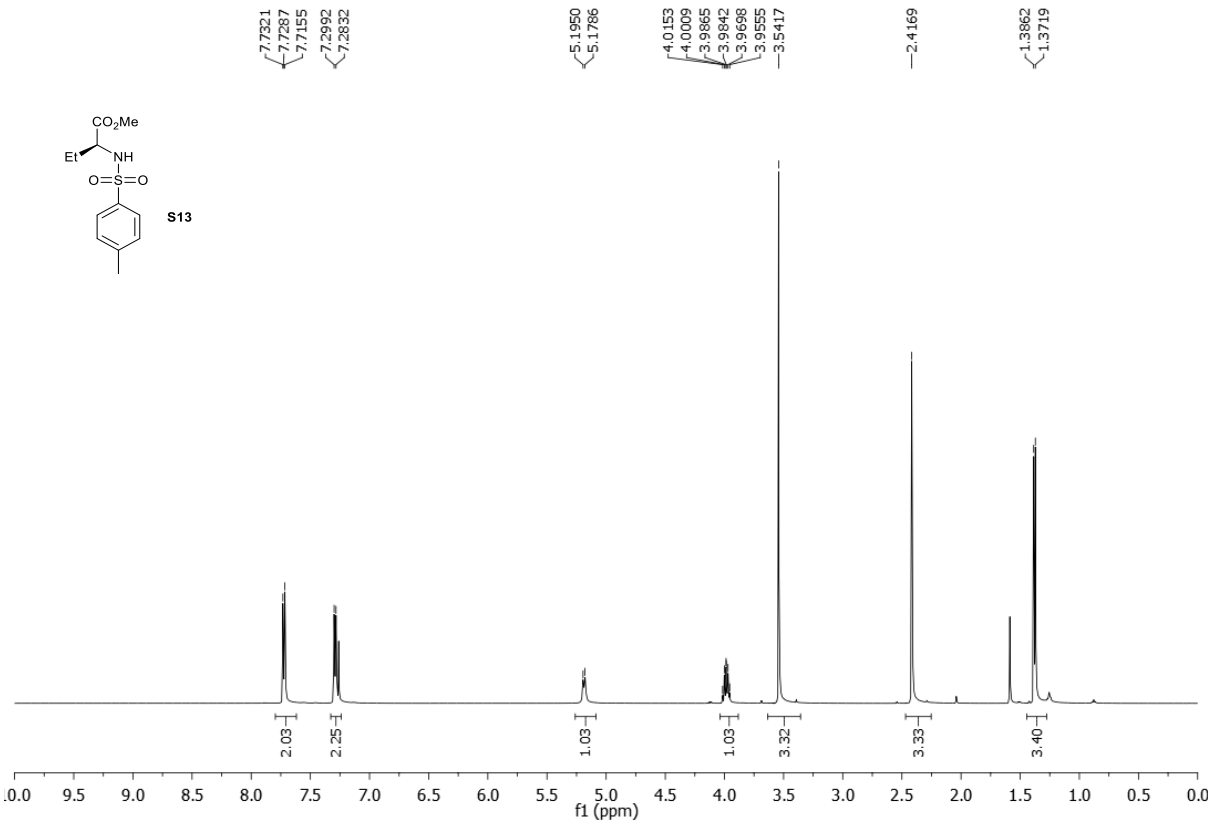


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

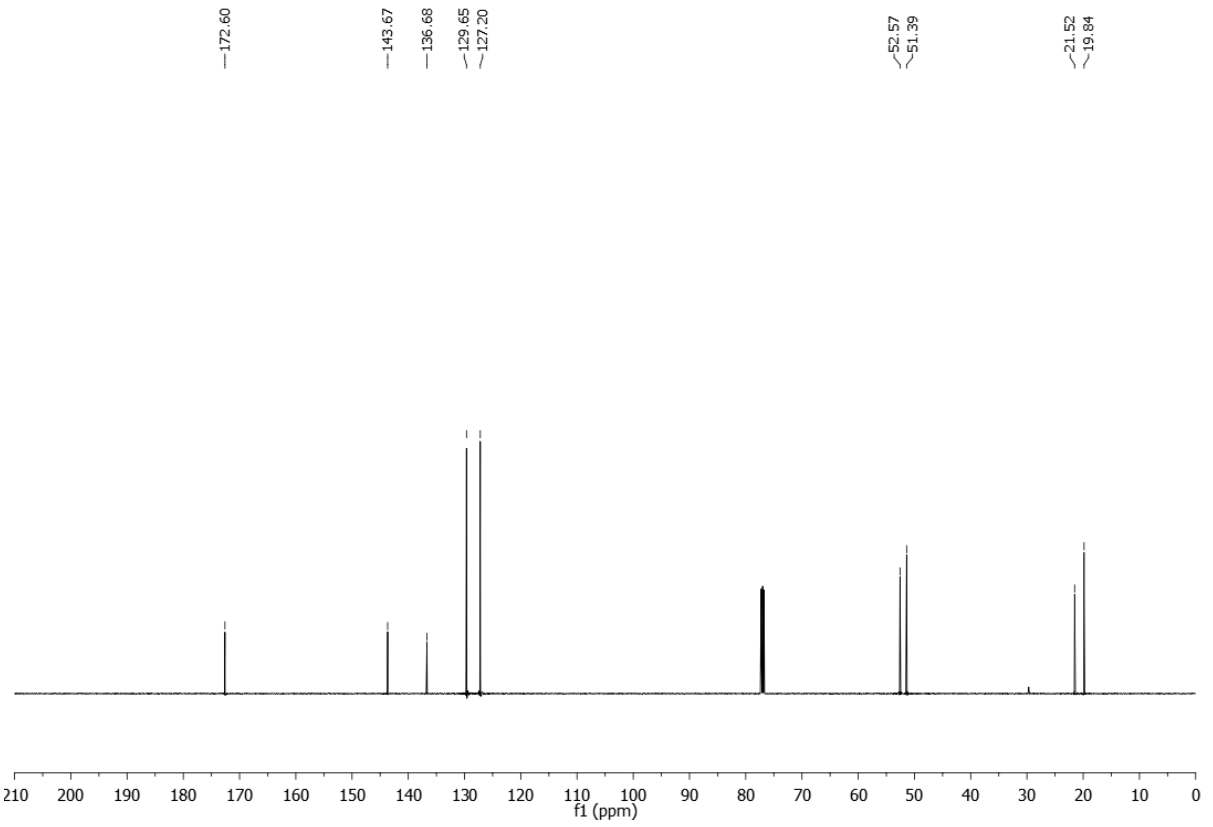


*Methyl (S)-2-((4-methylphenyl)sulfonamido)butanoate (**S13**)*

^{1}H NMR (500 MHz, $CDCl_3$)

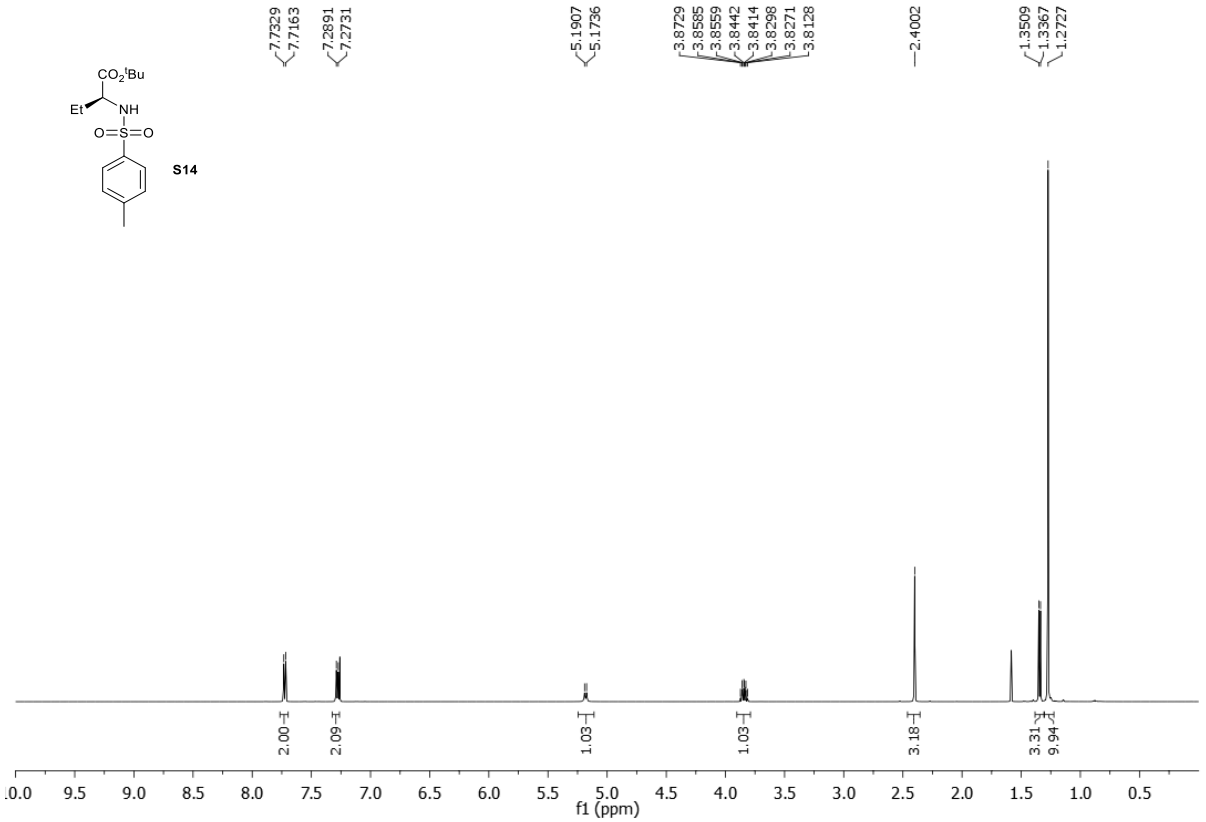


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

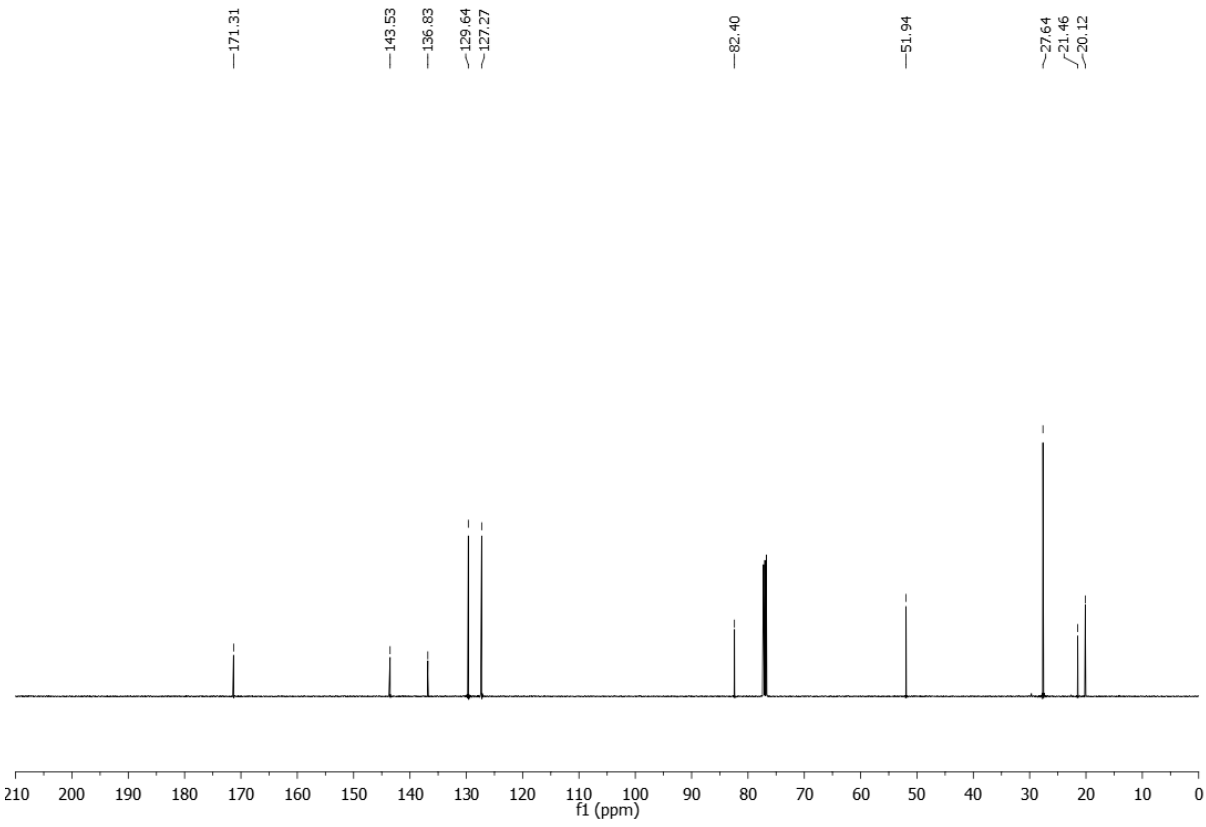


*tert-Butyl (S)-2-((4-methylphenyl)sulfonamido)butanoate (**S14**)*

^{1}H NMR (500 MHz, $CDCl_3$)

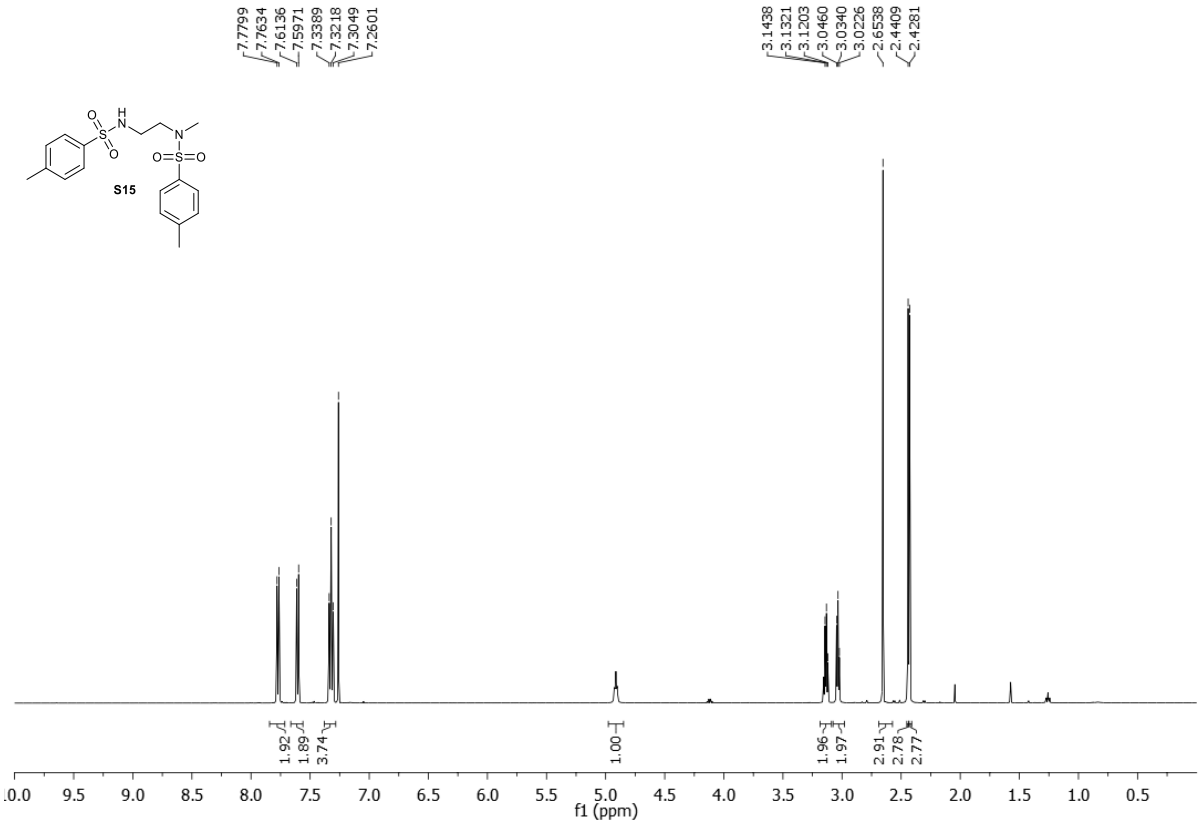


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

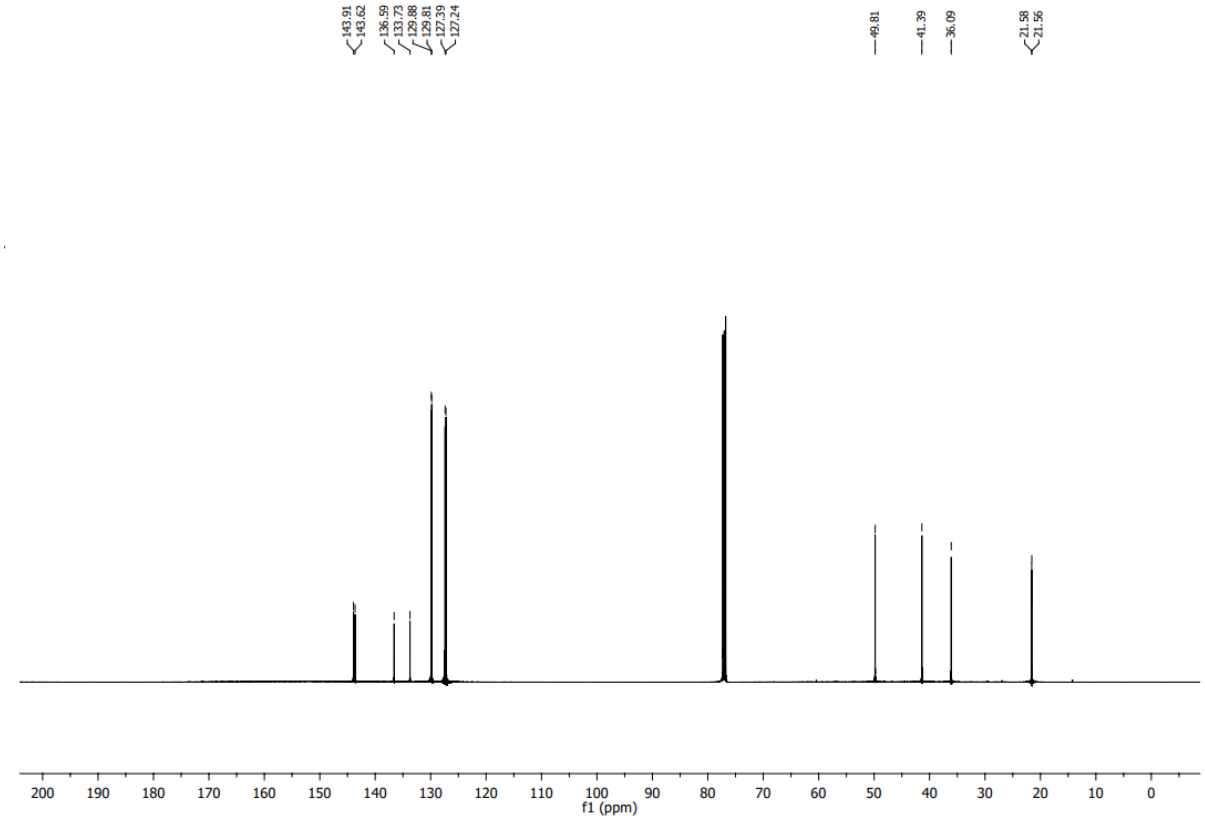


*N,4-dimethyl-N-(2-((4-methylphenyl)sulfonamido)ethyl)benzenesulfonamide (**S15**)*

^{1}H NMR (500 MHz, $CDCl_3$)

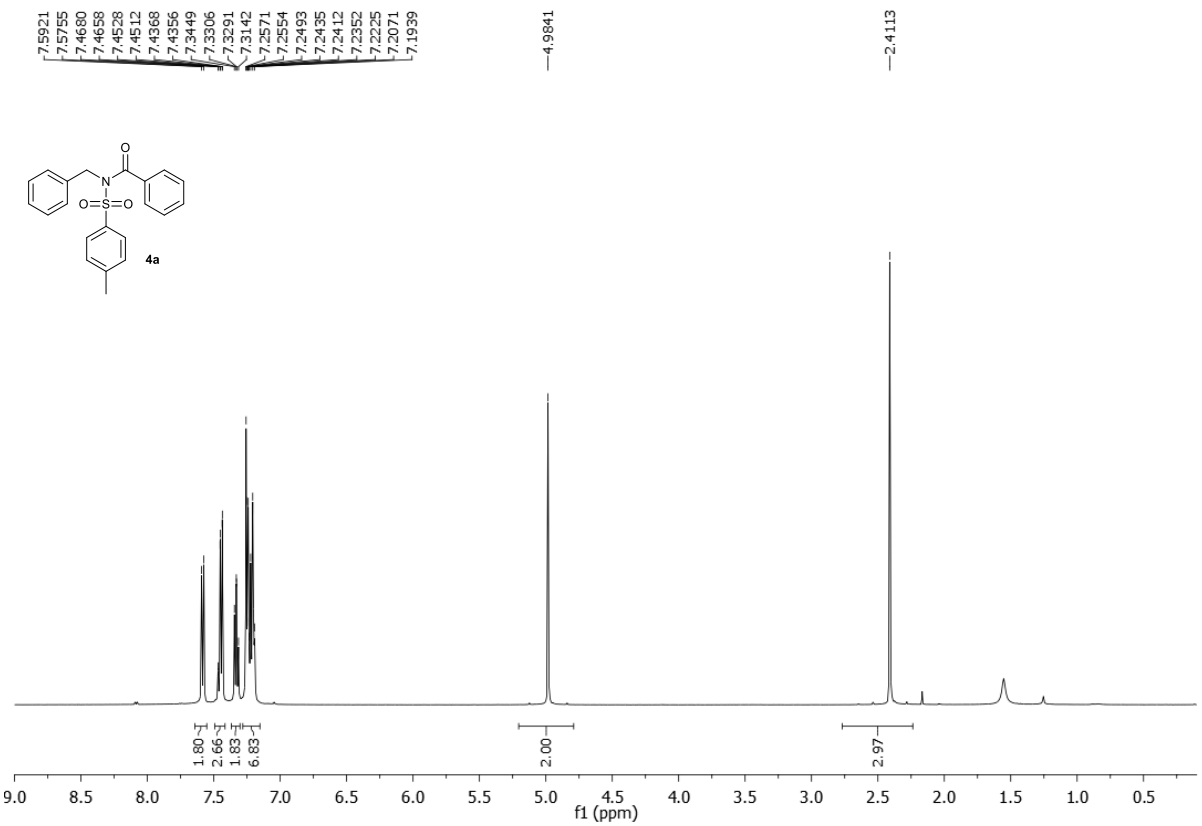


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

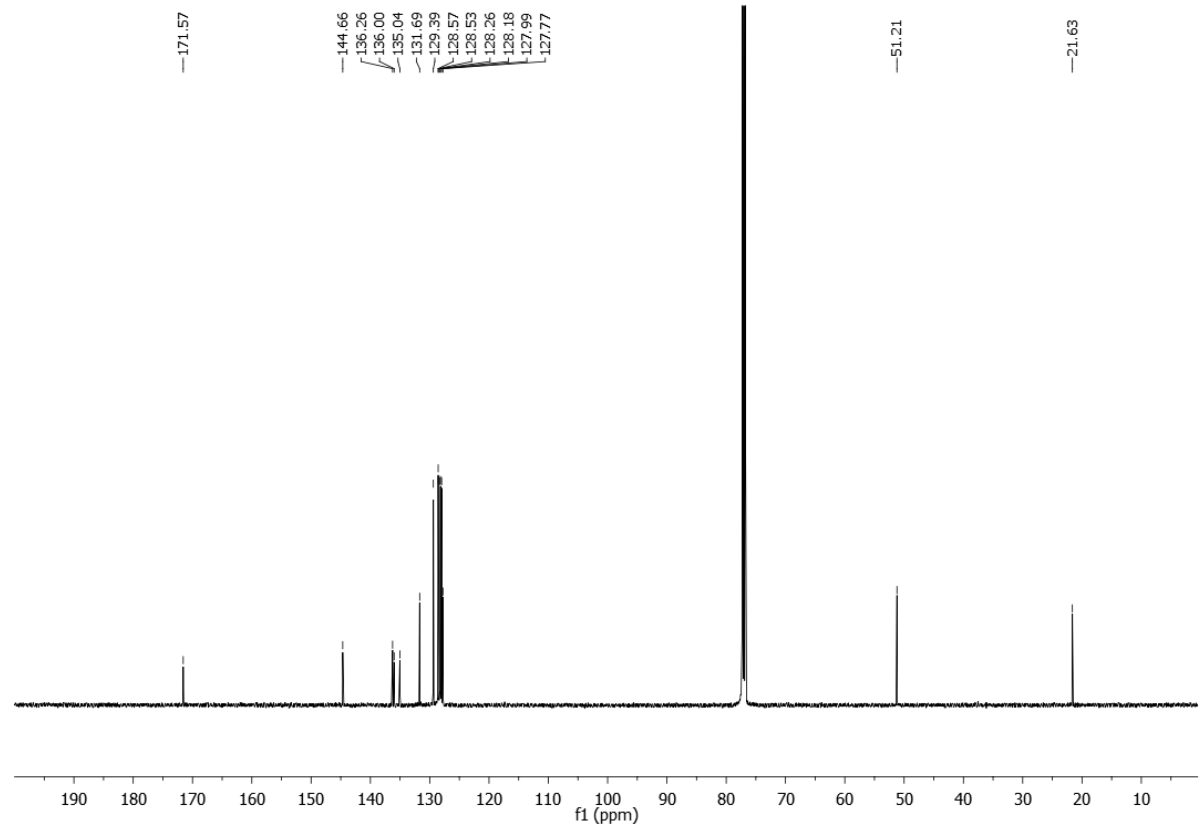


*N-benzyl-N-(4-methylbenzenesulfonyl)benzamide (**4a**)*

^{1}H NMR (500 MHz, $CDCl_3$)

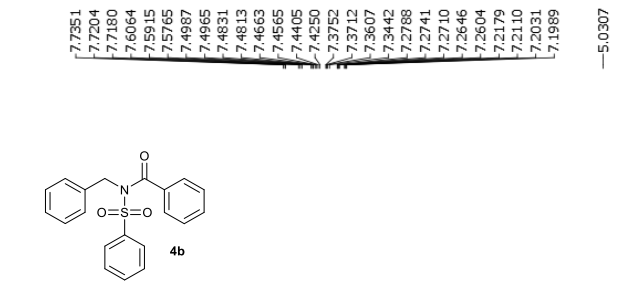


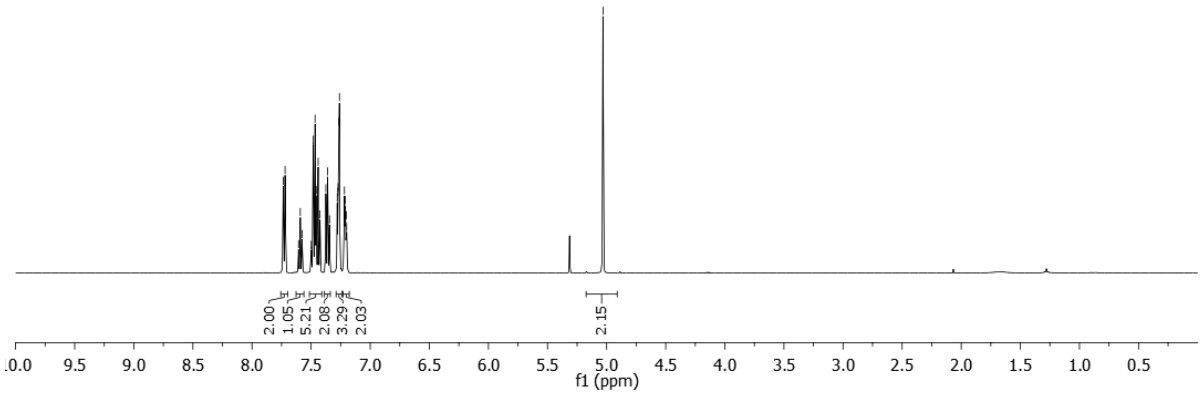
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)



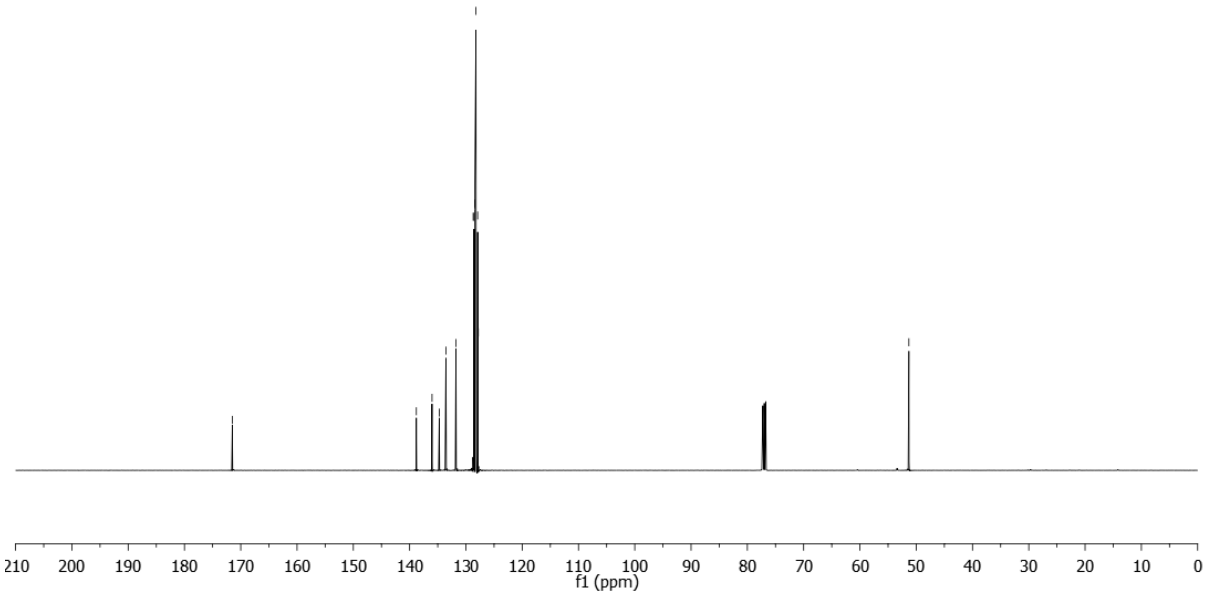
*N-(benzenesulfonyl)-N-benzylbenzamide (**4b**)*

^{1}H NMR (500 MHz, $CDCl_3$)



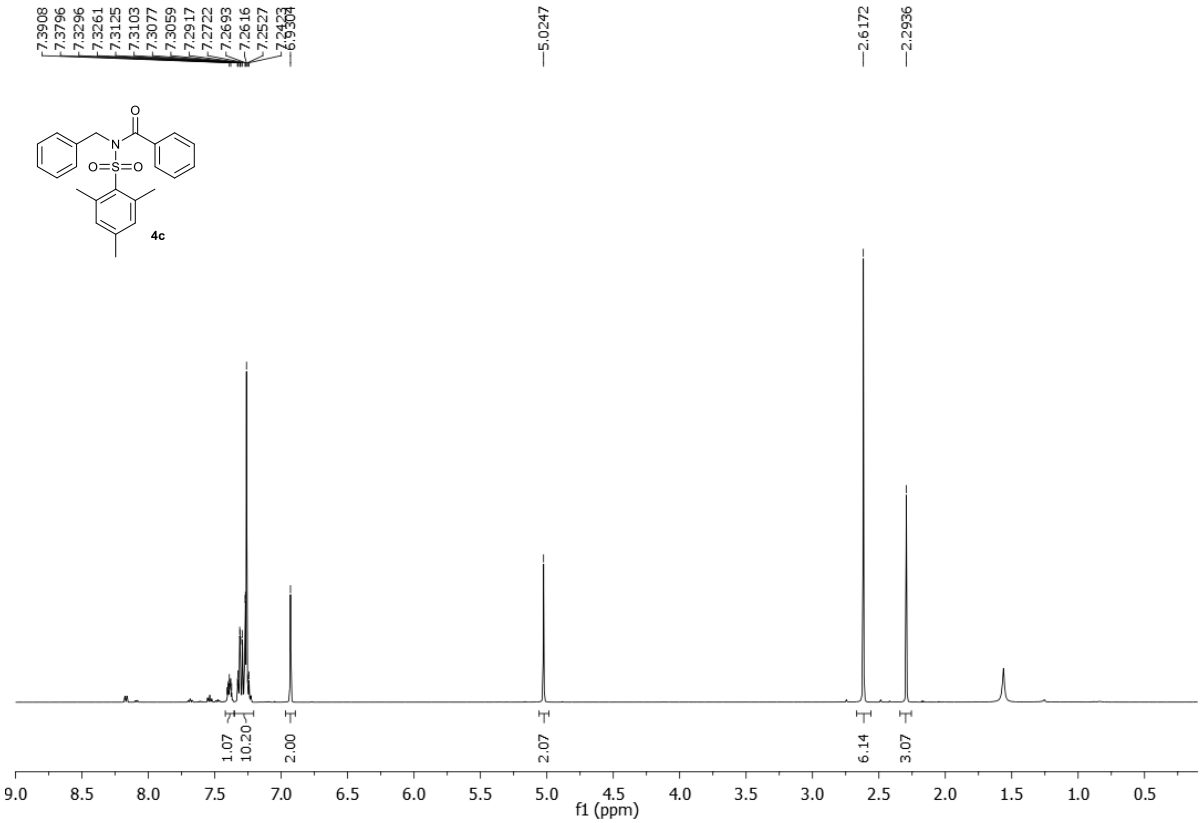


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

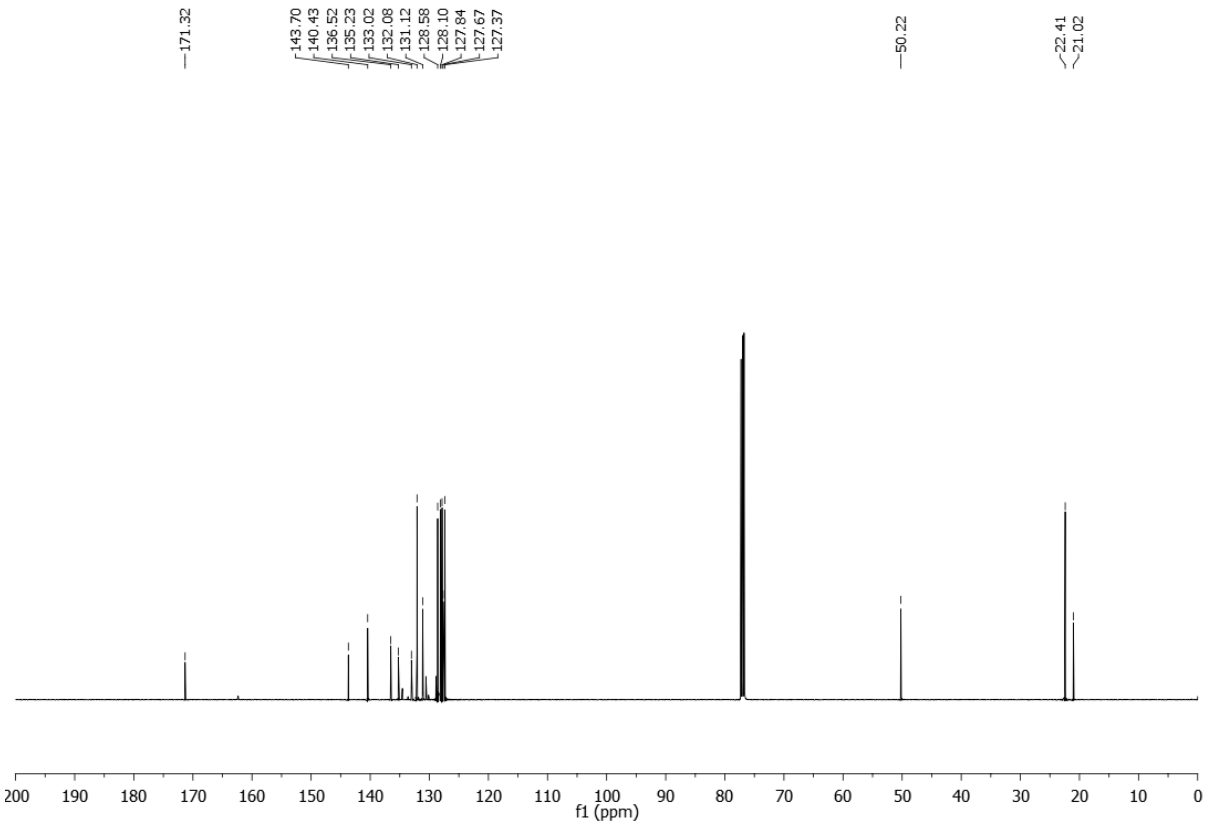


*N-benzyl-N-(2,4,6-trimethylbenzenesulfonyl)benzamide (**4c**)*

^{1}H NMR (500 MHz, $CDCl_3$)

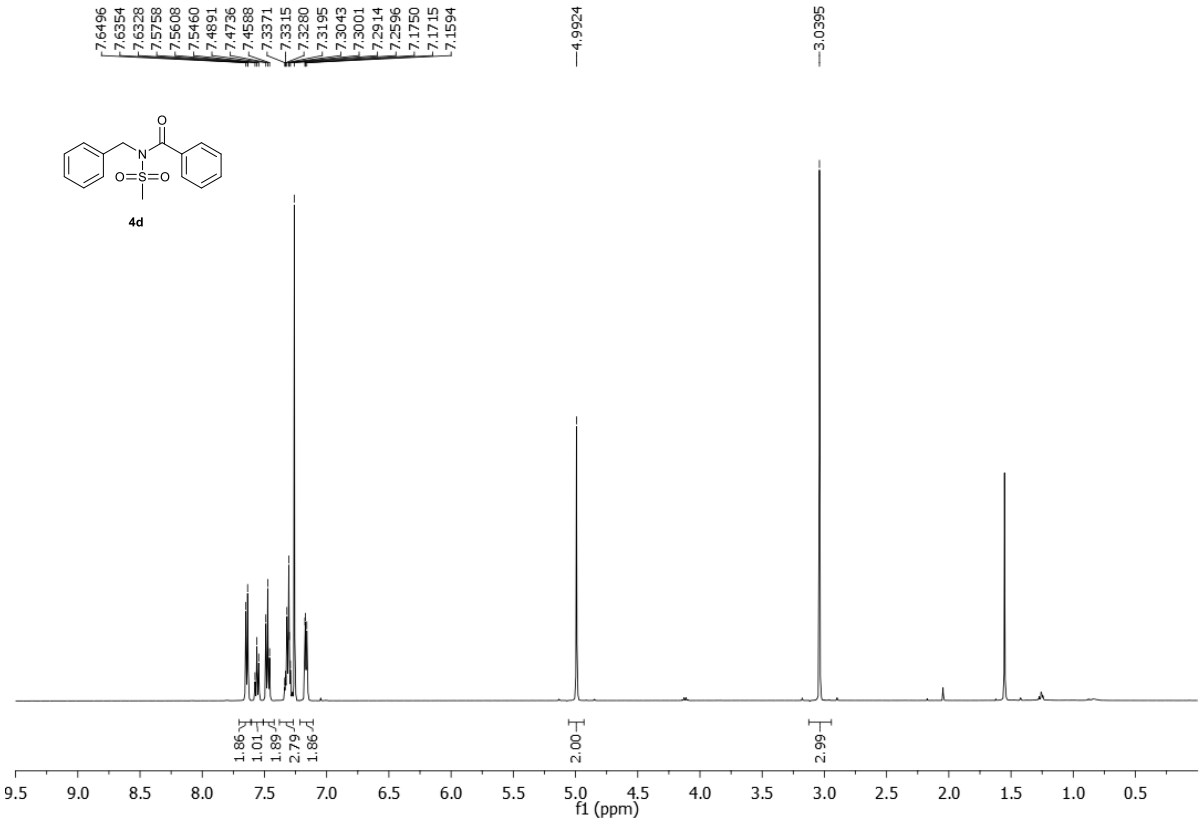


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

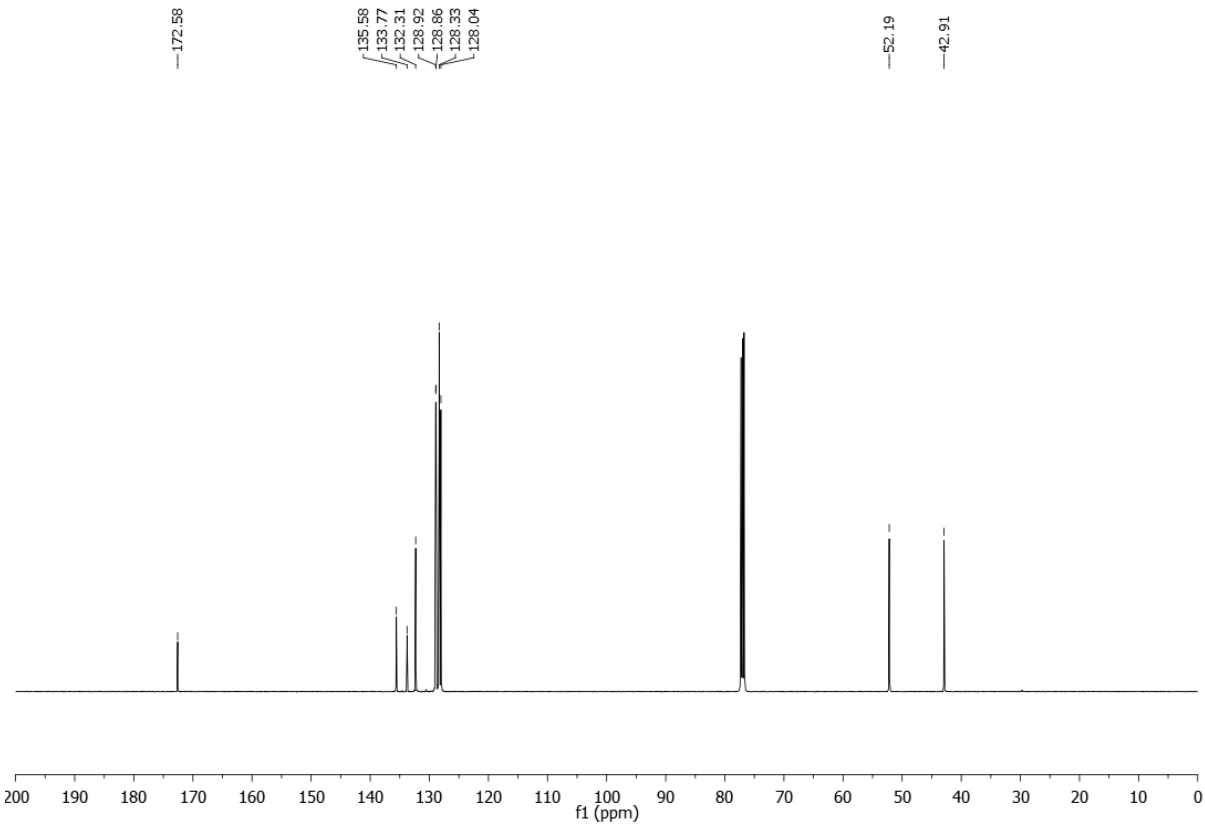


*N-benzyl-N-(methylsulfonyl)benzamide (**4d**)*

^{1}H NMR (500 MHz, $CDCl_3$)

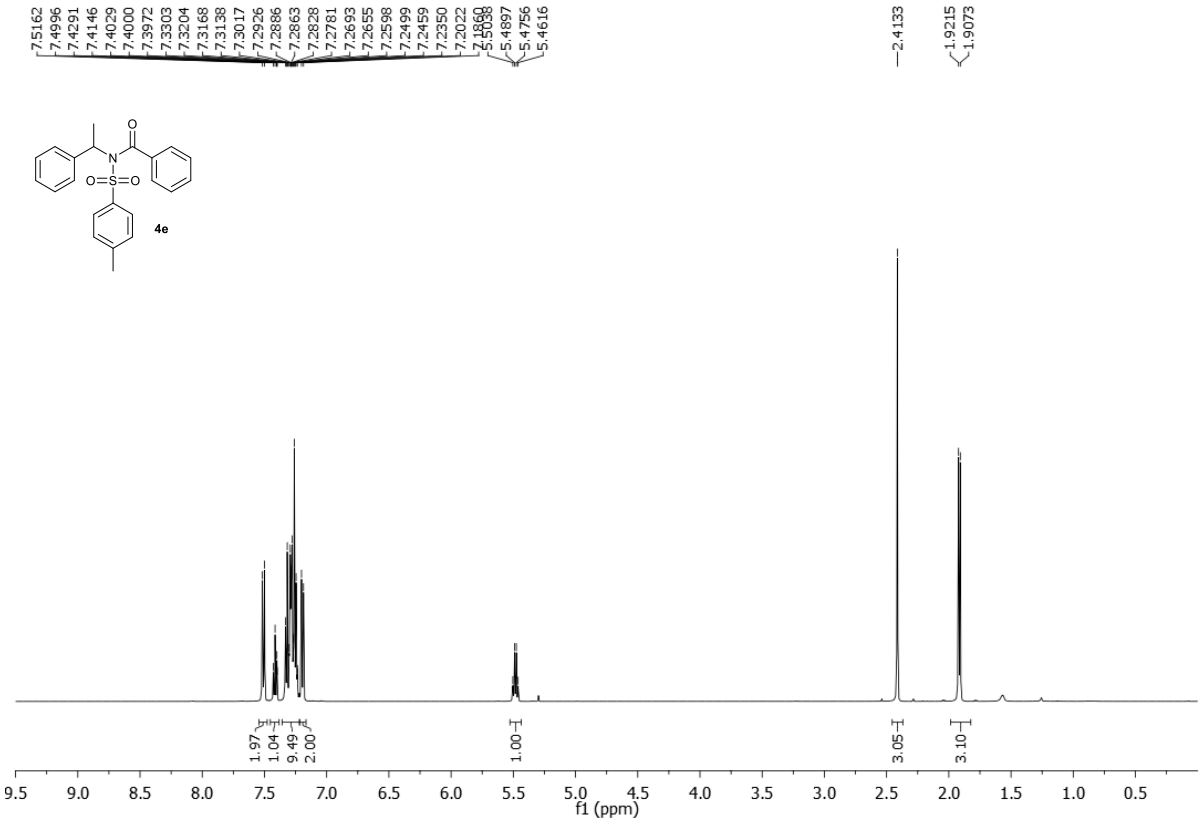


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

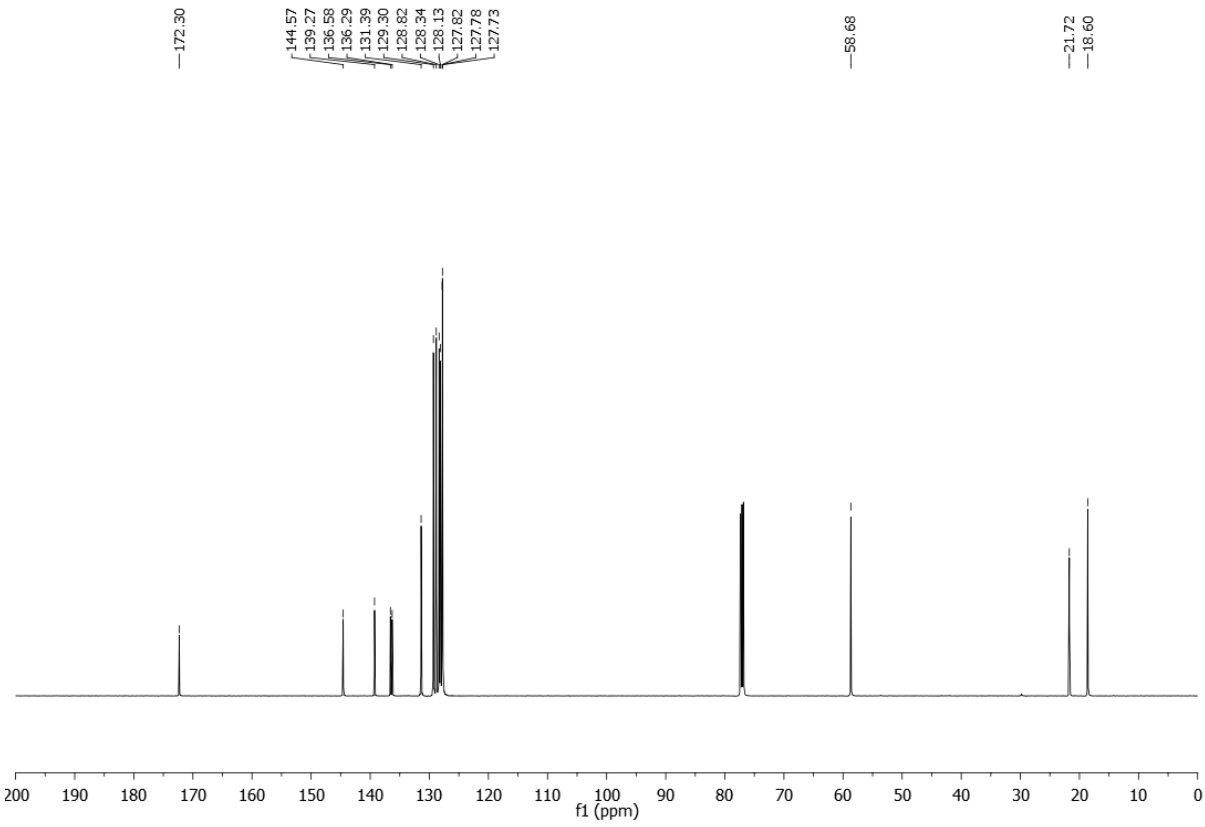


*N-(4-methylbenzenesulfonyl)-N-(1-phenylethyl)benzamide (**4e**)*

^{1}H NMR (500 MHz, $CDCl_3$)

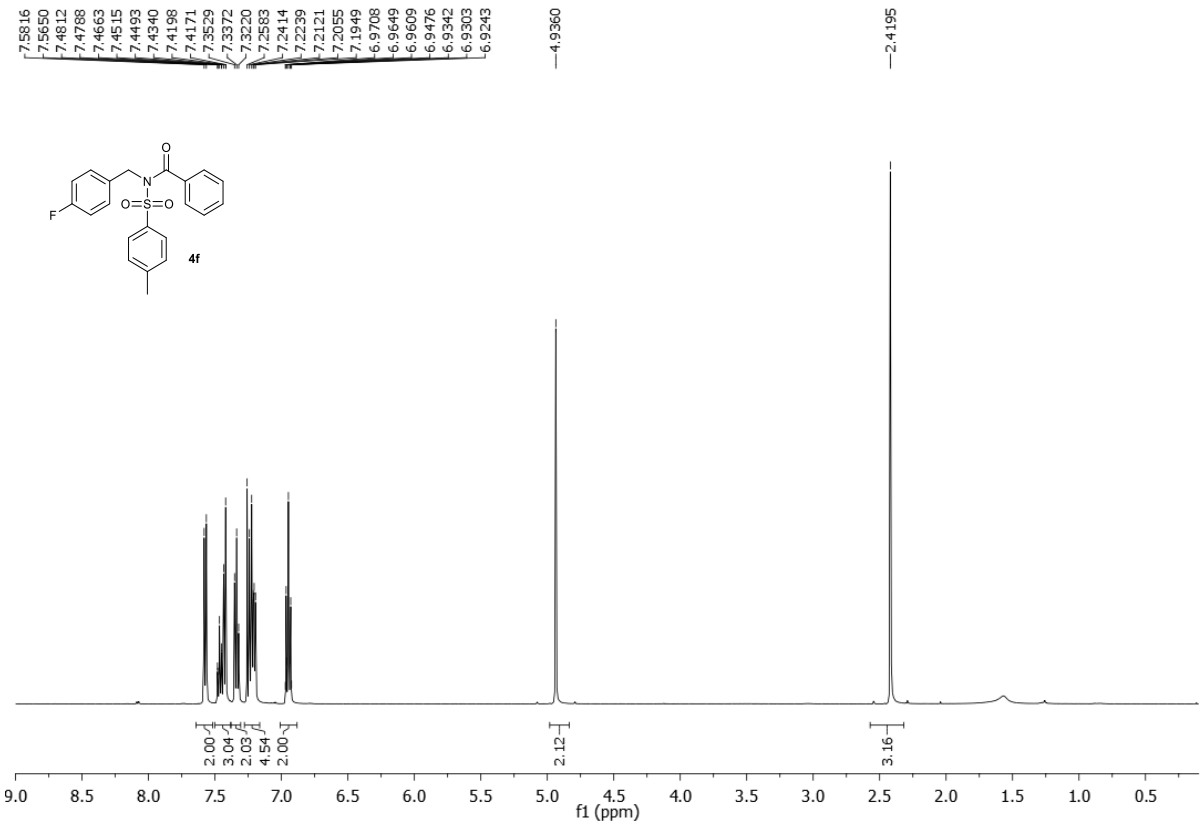


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

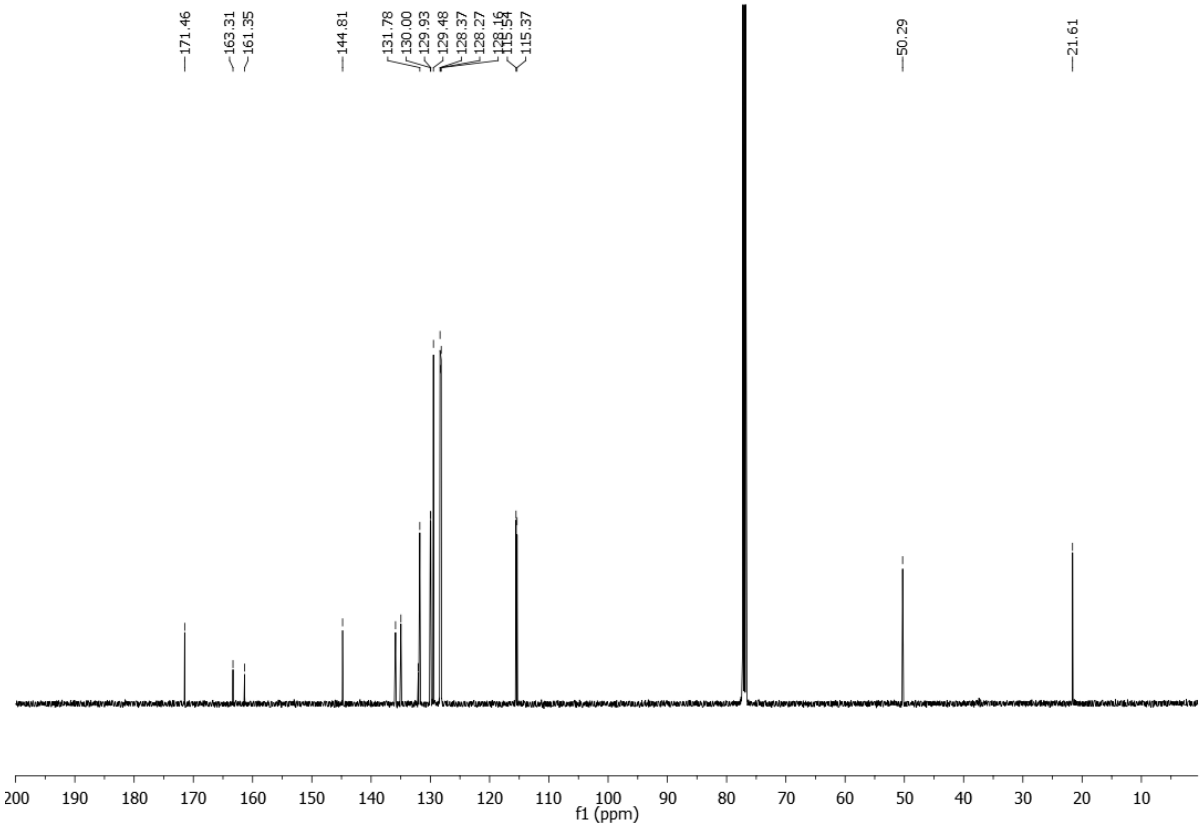


*N-[(4-fluorophenyl)methyl]-N-(4-methylbenzenesulfonyl)benzamide (**4f**)*

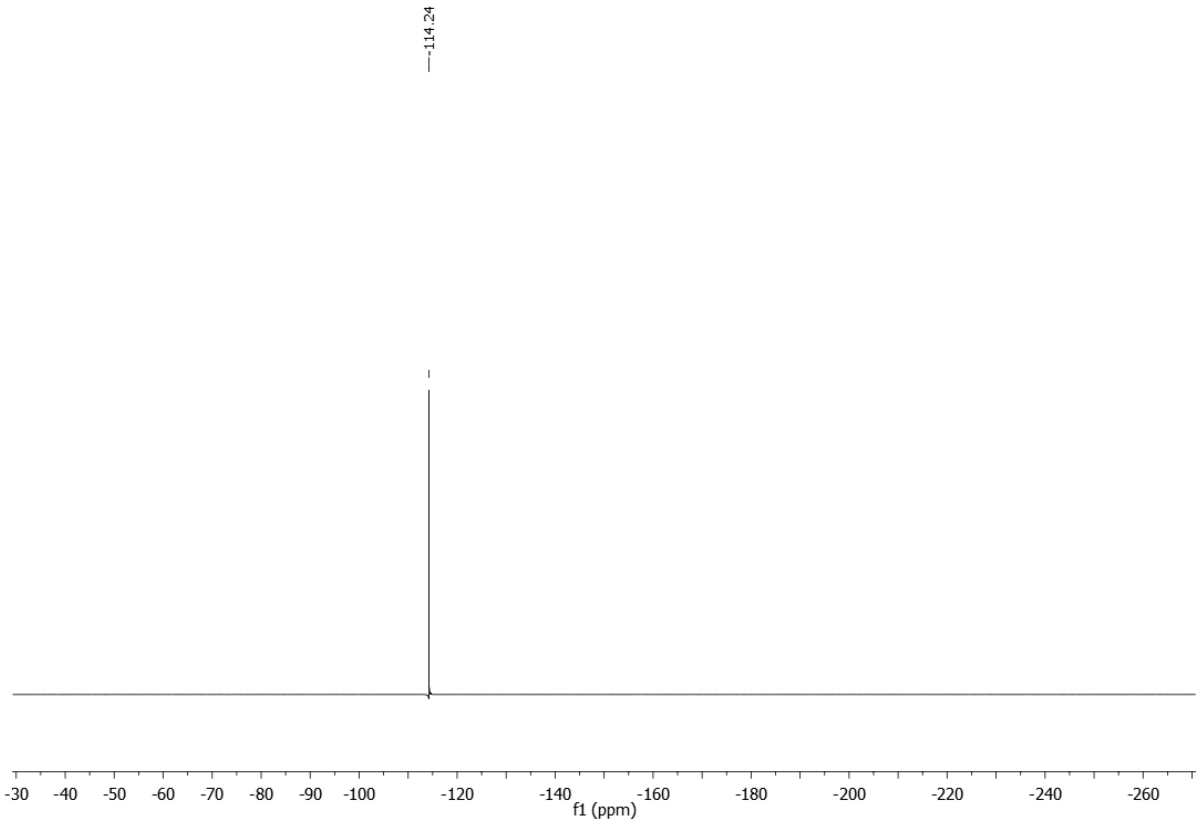
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

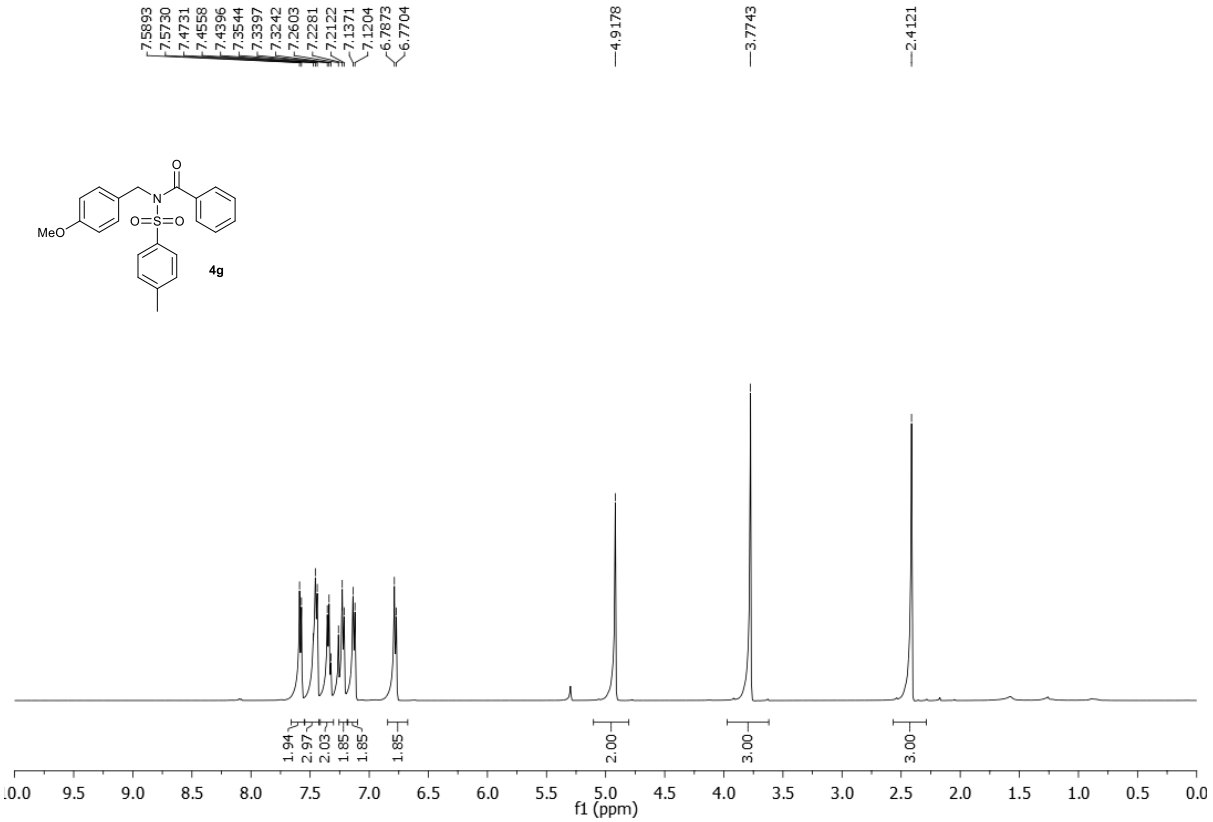


^{19}F NMR (471 MHz, $CDCl_3$)

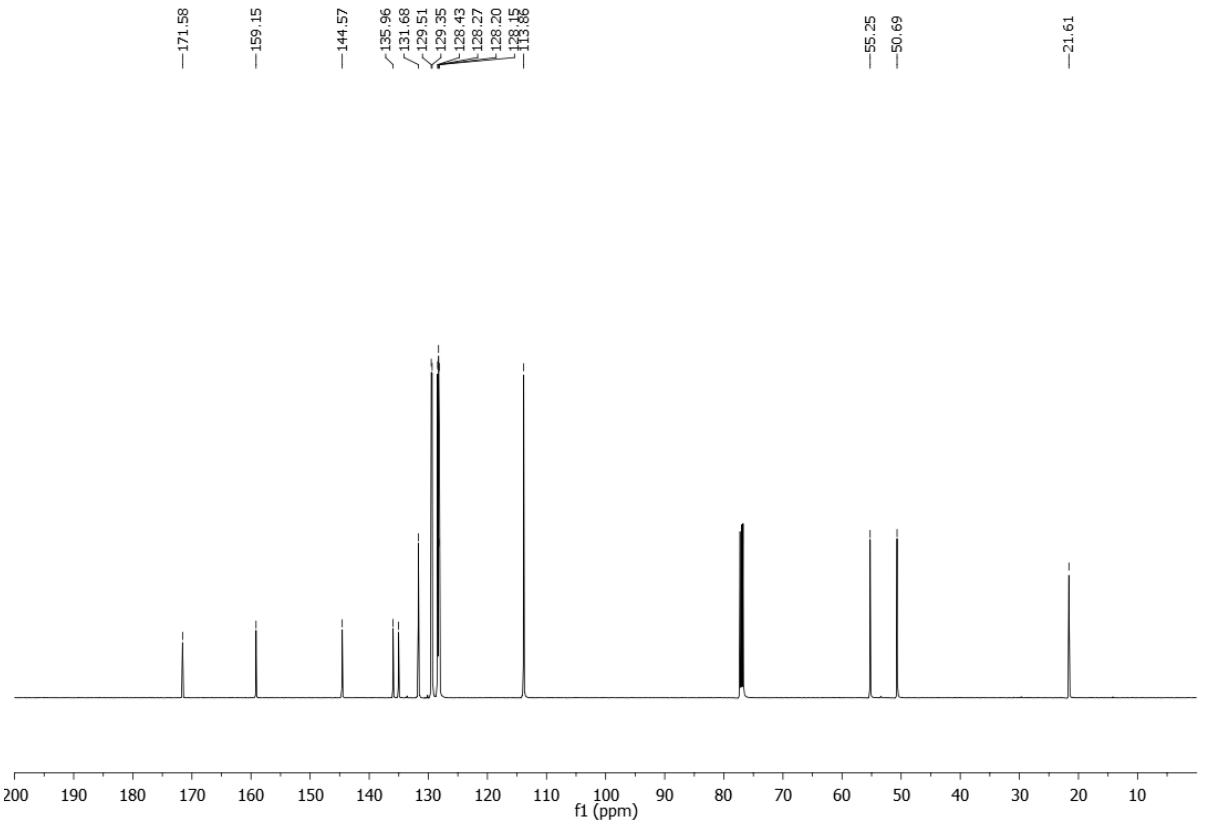


*N-(4-methoxybenzyl)-N-tosylbenzamide (**4g**)*

^{1}H NMR (500 MHz, $CDCl_3$)

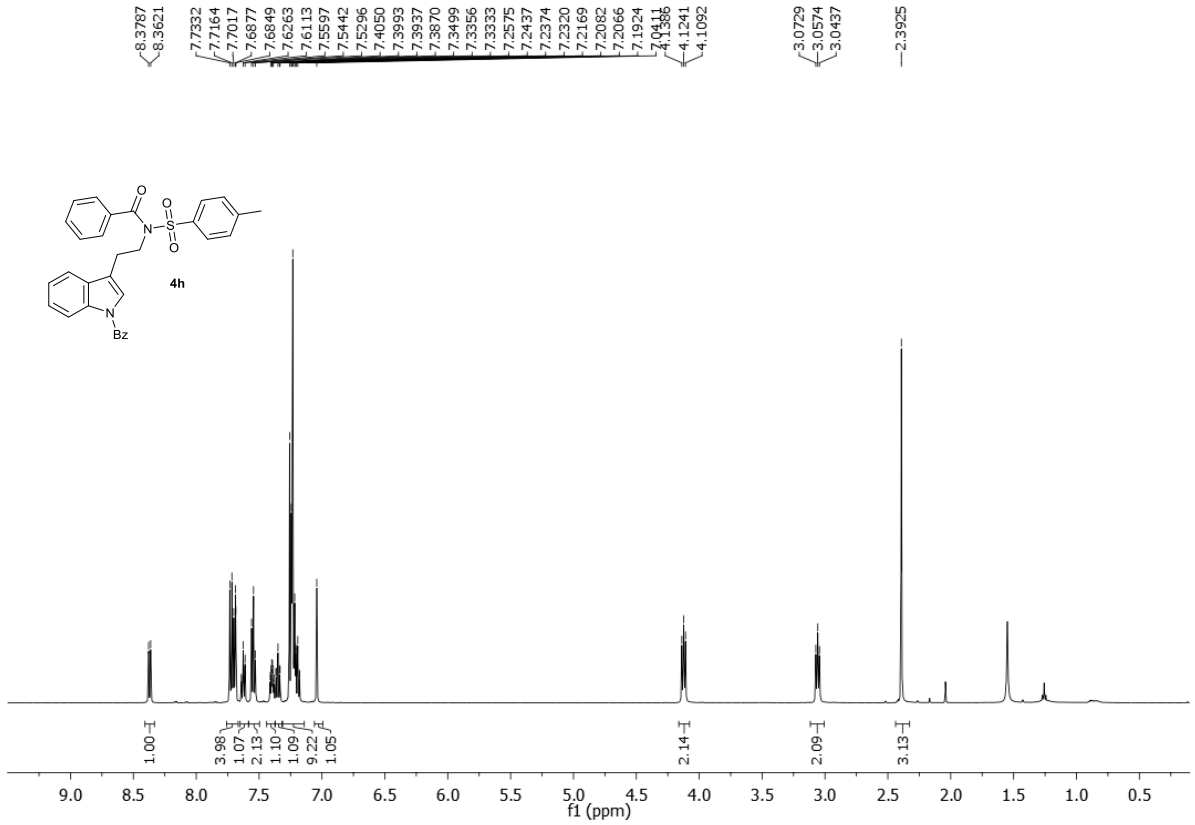


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

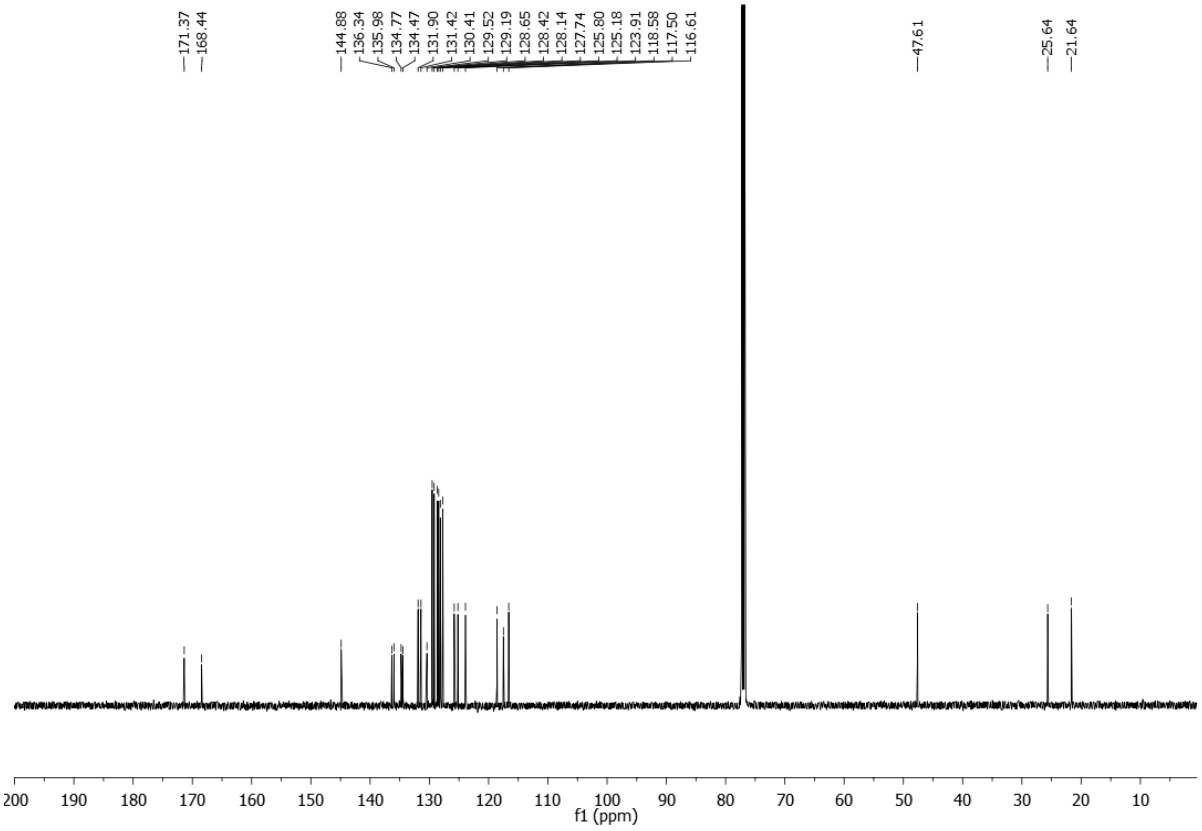


*N-[2-(1-benzoyl-1H-indol-3-yl)ethyl]-N-(4-methylbenzenesulfonyl)benzamide (**4h**)*

^{1}H NMR (500 MHz, $CDCl_3$)

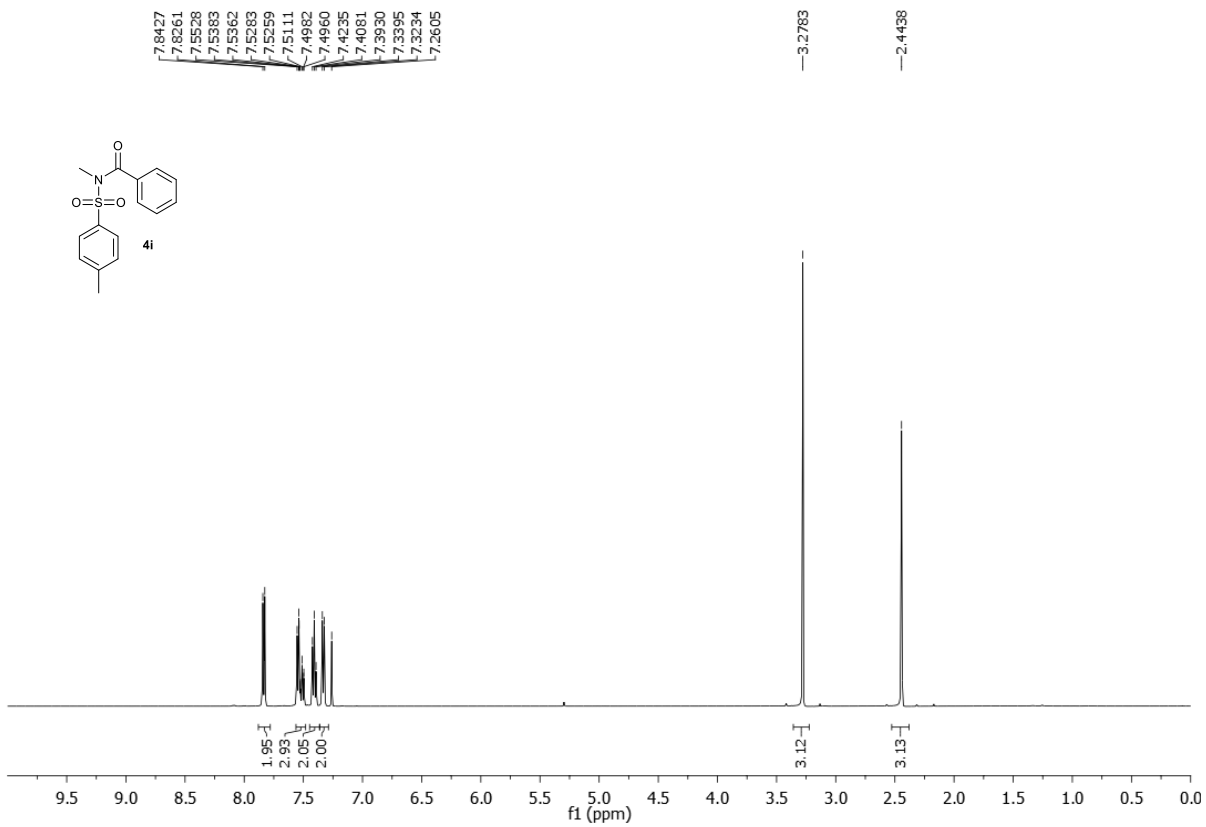


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

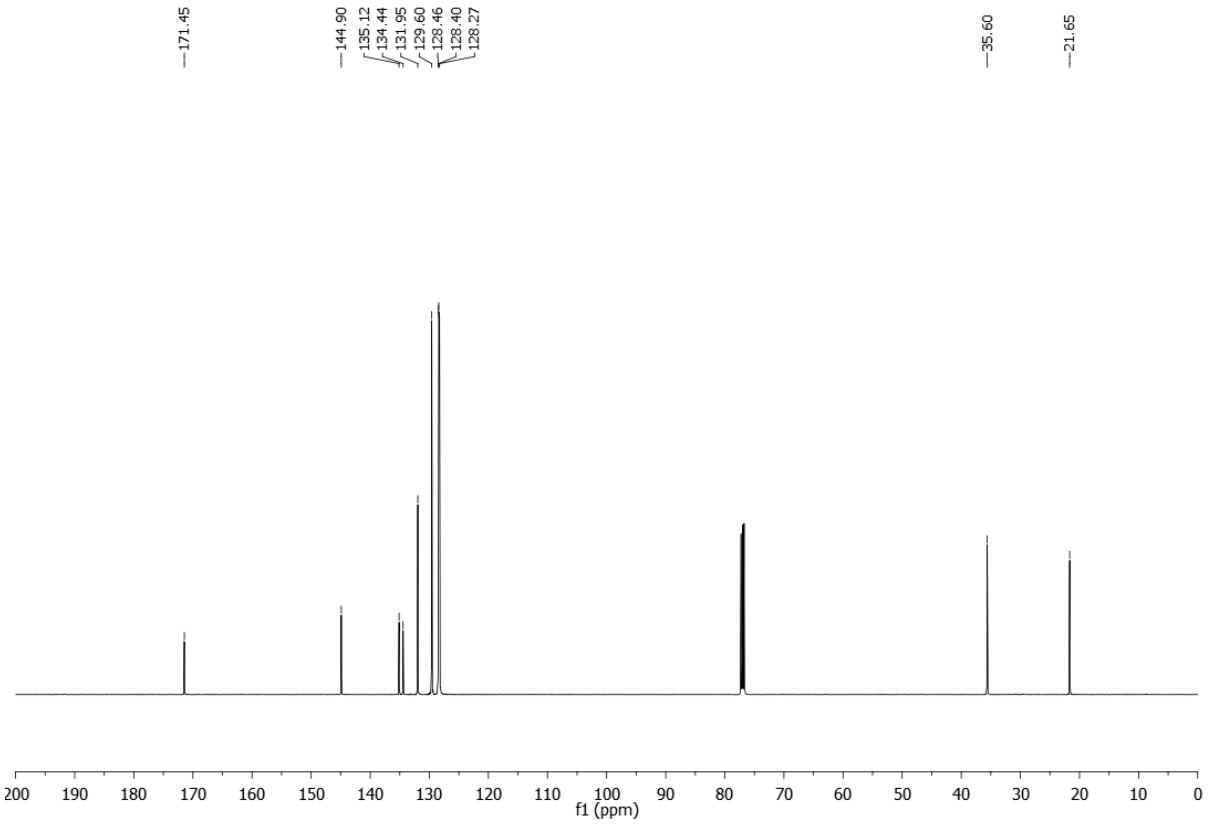


*N-methyl-N-tosylbenzamide (**4i**)*

^{1}H NMR (500 MHz, $CDCl_3$)

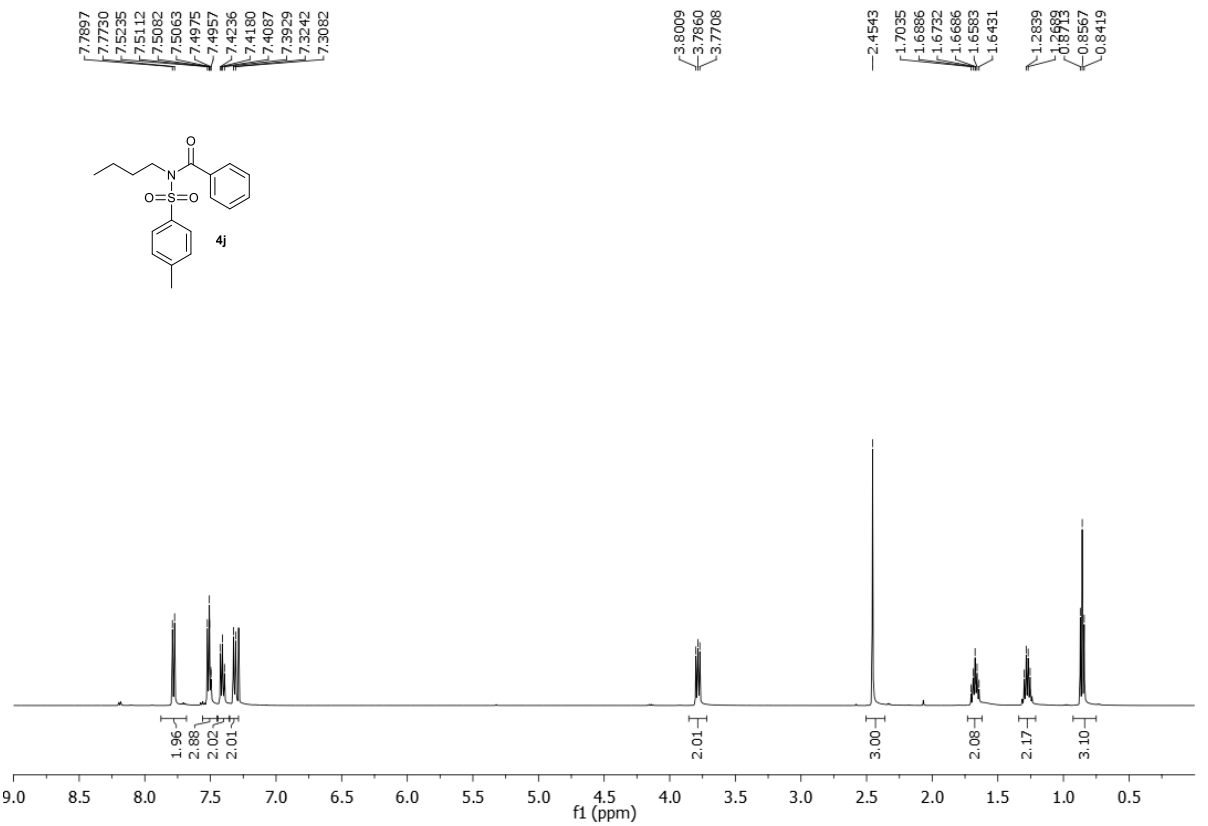


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

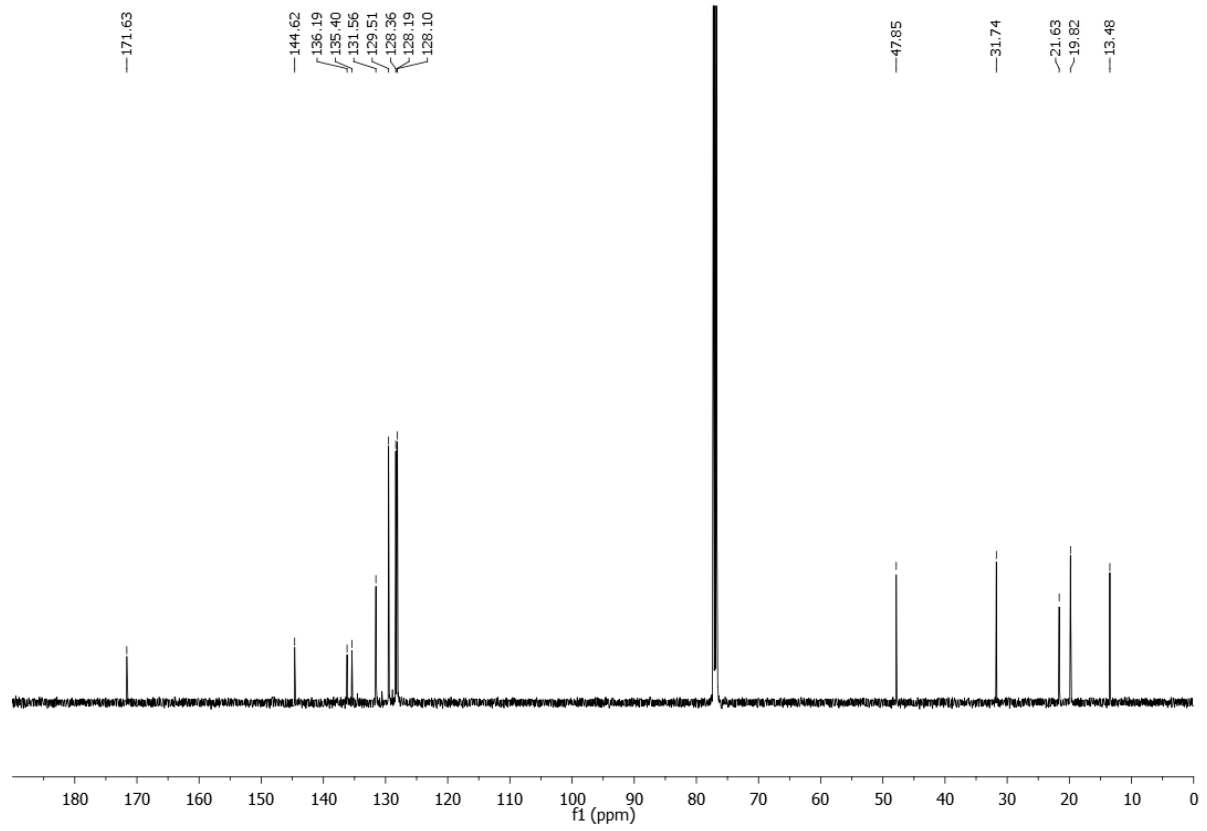


*N-butyl-N-tosylbenzamide (**4j**)*

^{1}H NMR (500 MHz, $CDCl_3$)

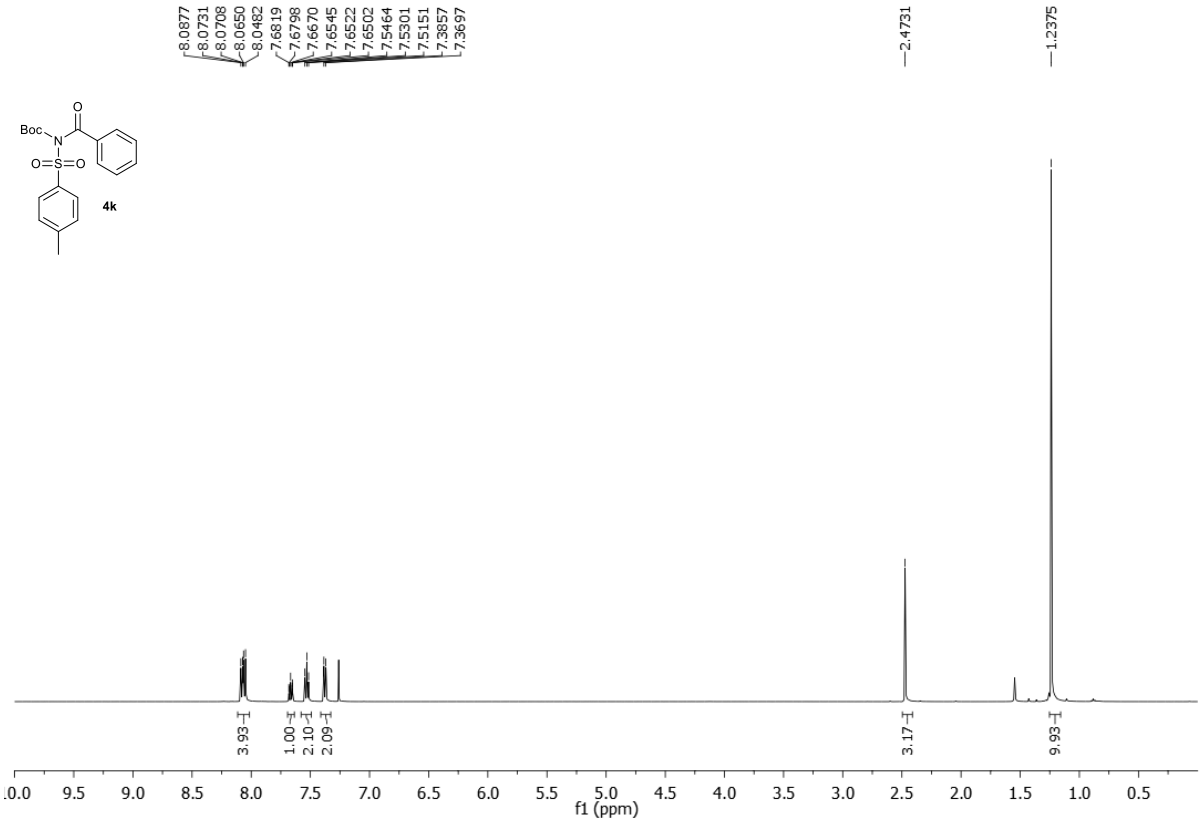


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

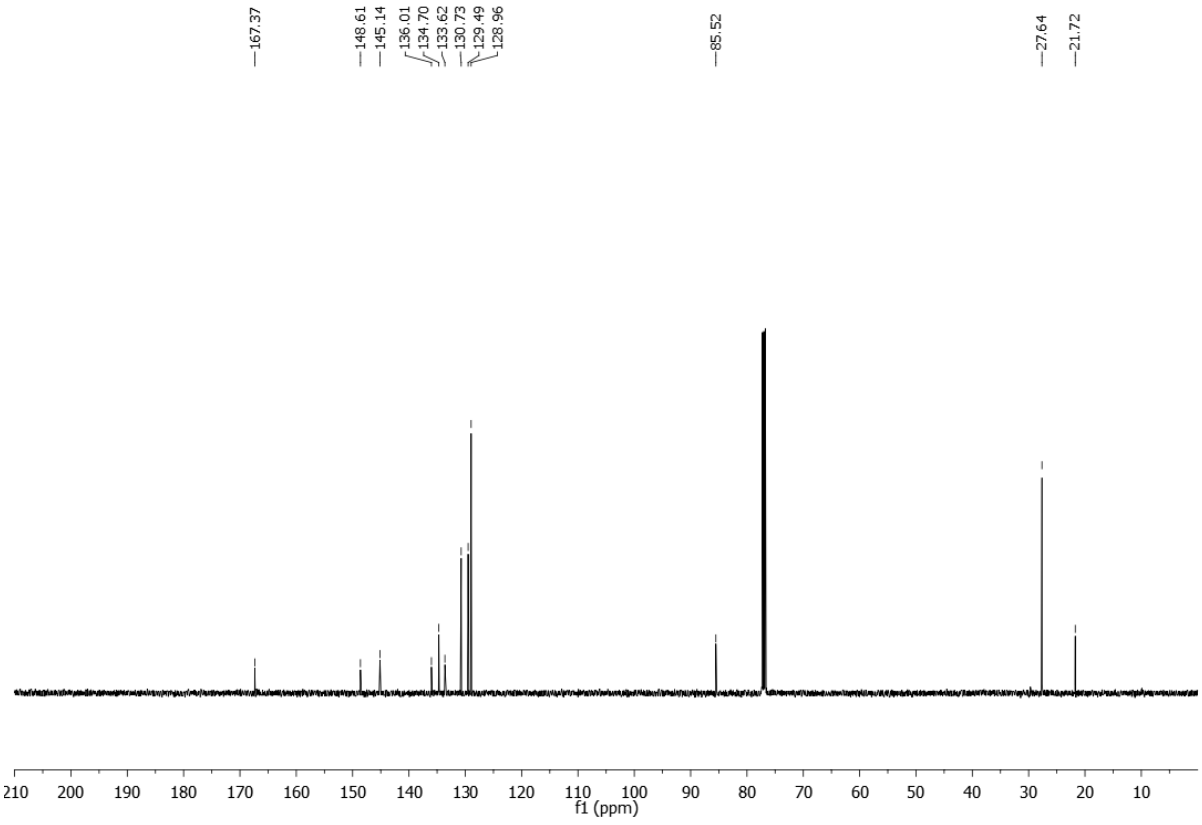


*tert-Butyl benzoyl(tosyl)carbamate (**4k**)*

^{1}H NMR (500 MHz, $CDCl_3$)

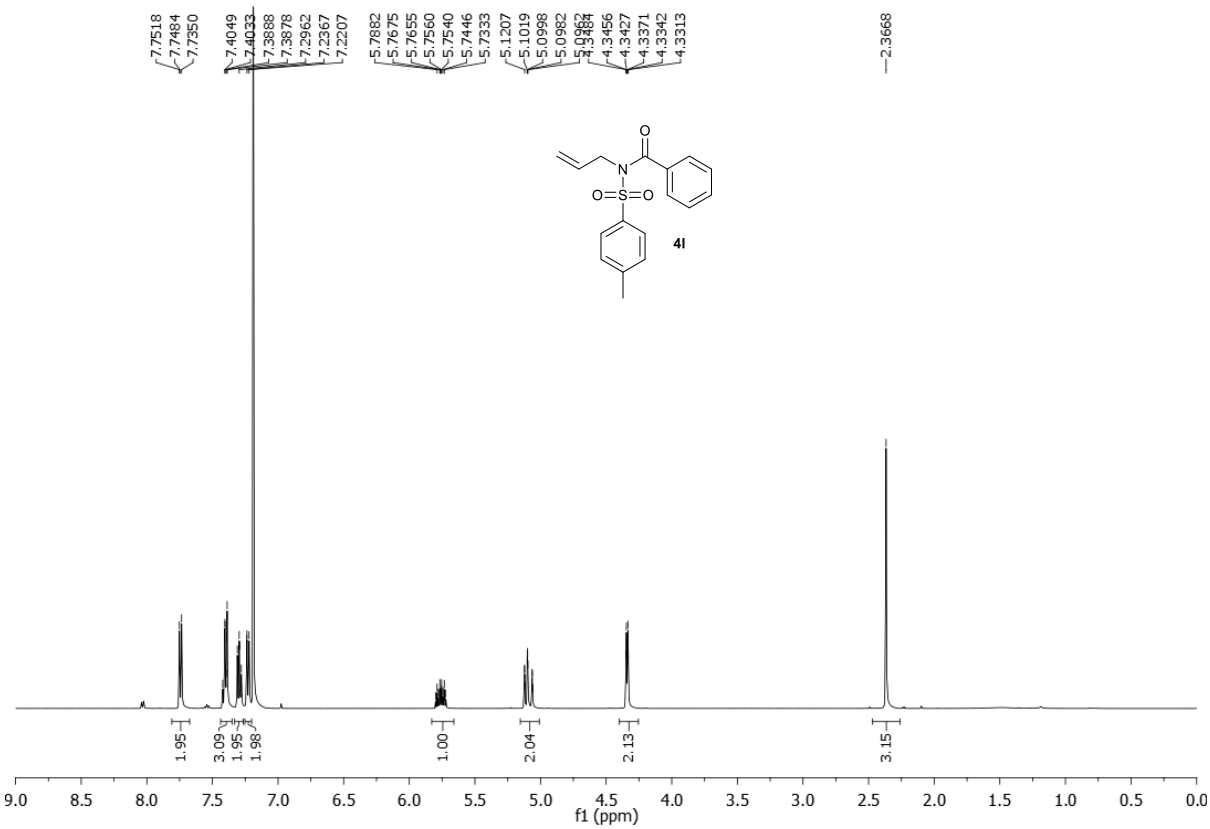


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

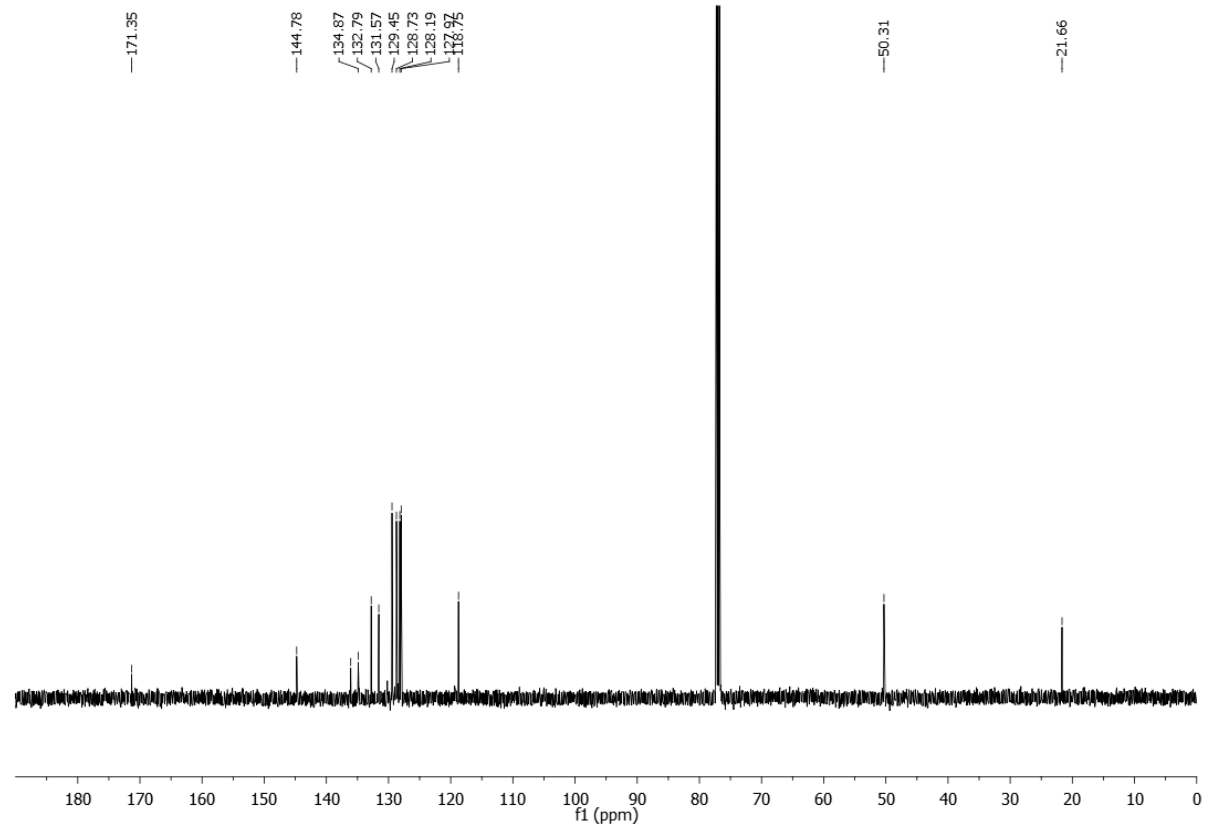


*N-allyl-N-tosylbenzamide (**4l**)*

^{1}H NMR (500 MHz, $CDCl_3$)

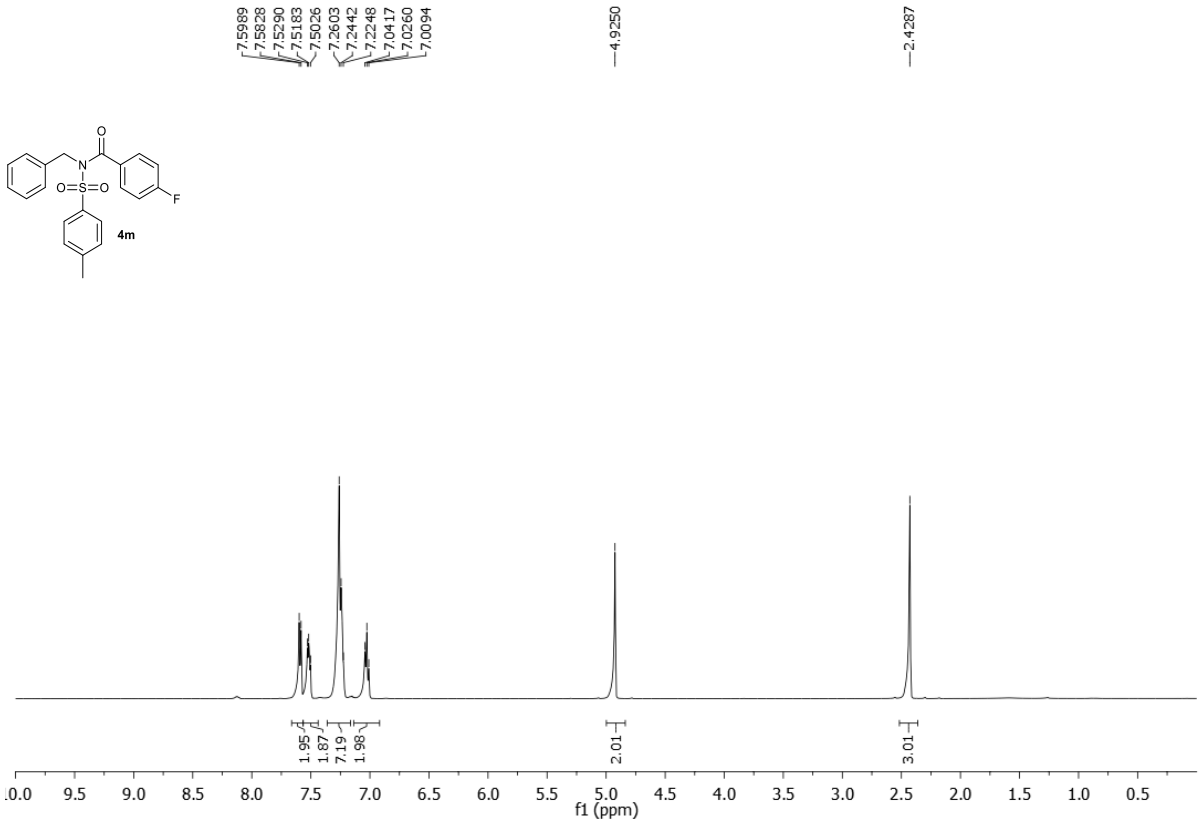


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

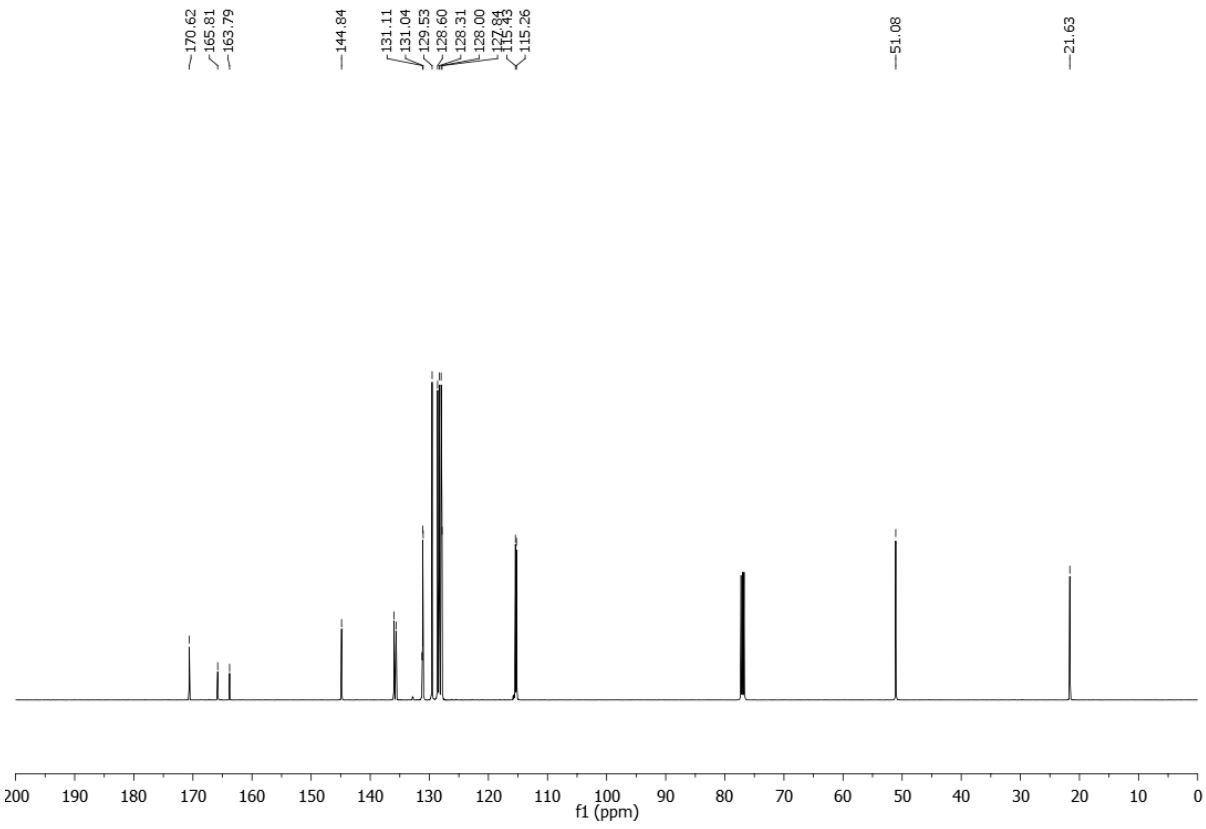


*N-benzyl-4-fluoro-N-(4-methylbenzenesulfonyl)benzamide (**4m**)*

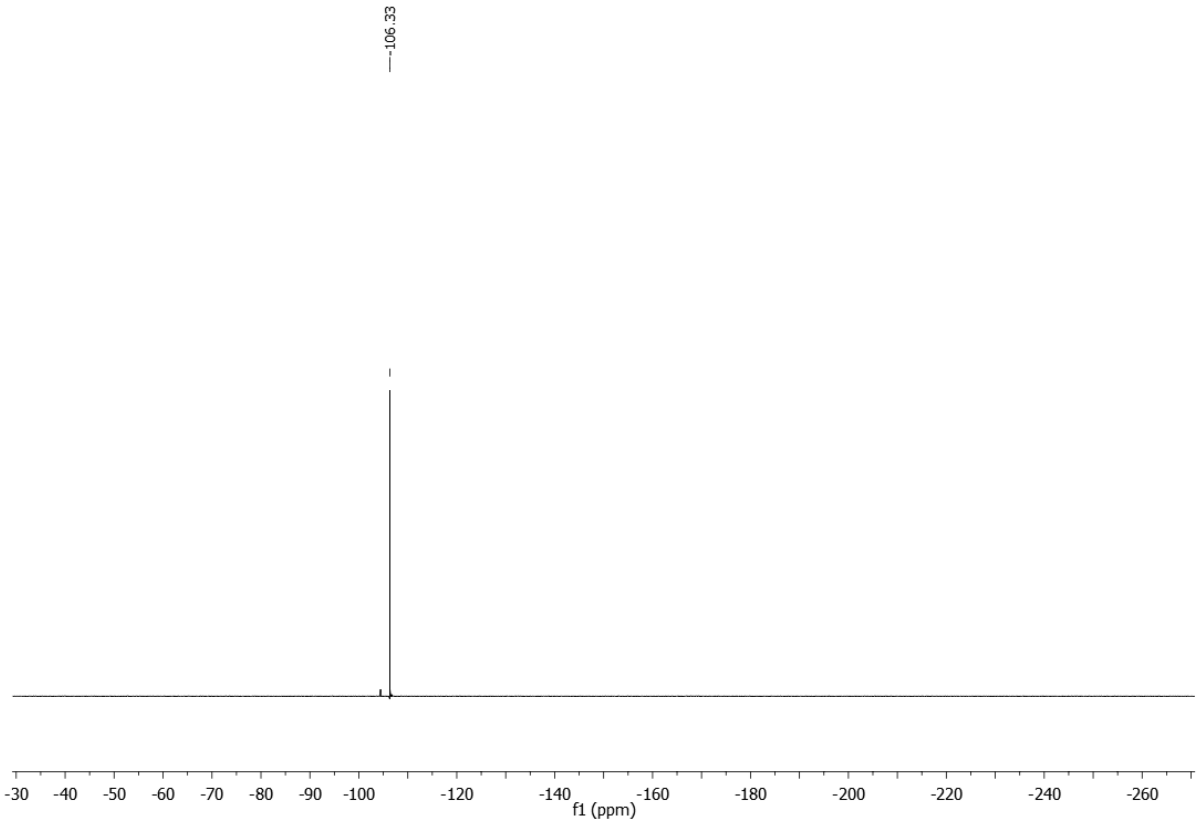
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

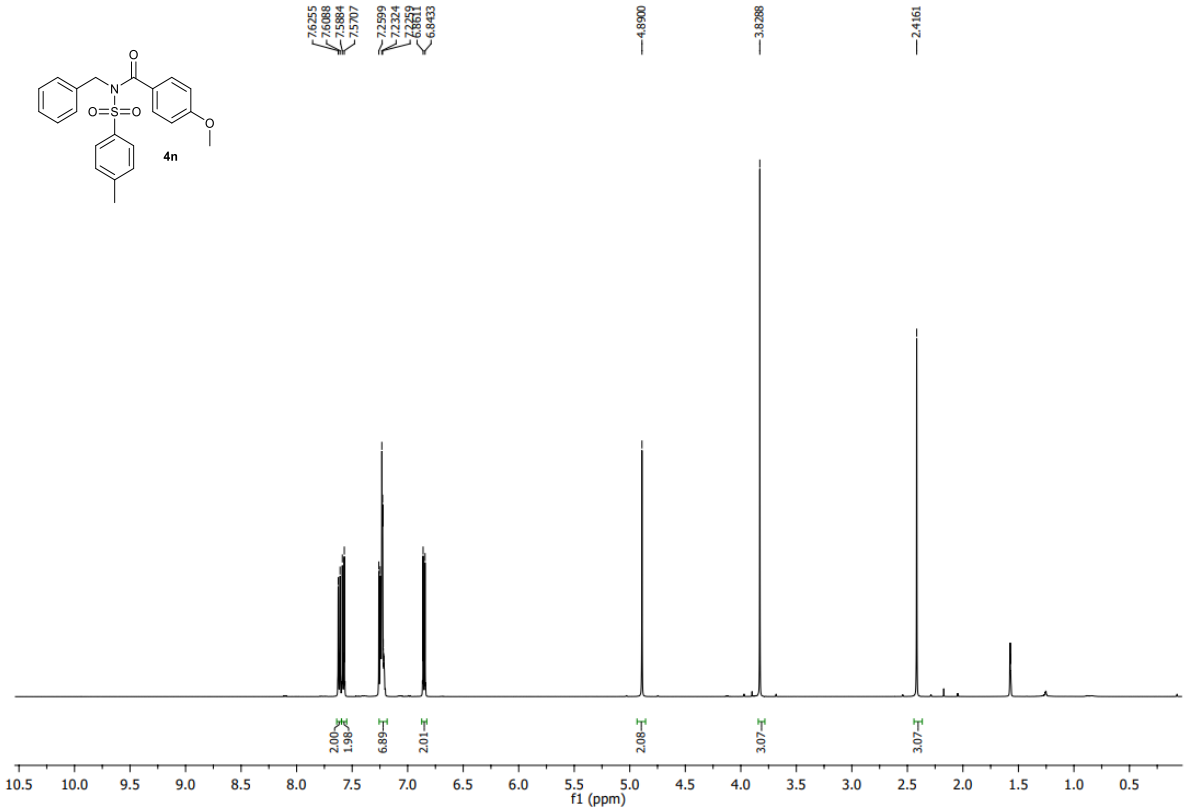


^{19}F NMR (471 MHz, $CDCl_3$)

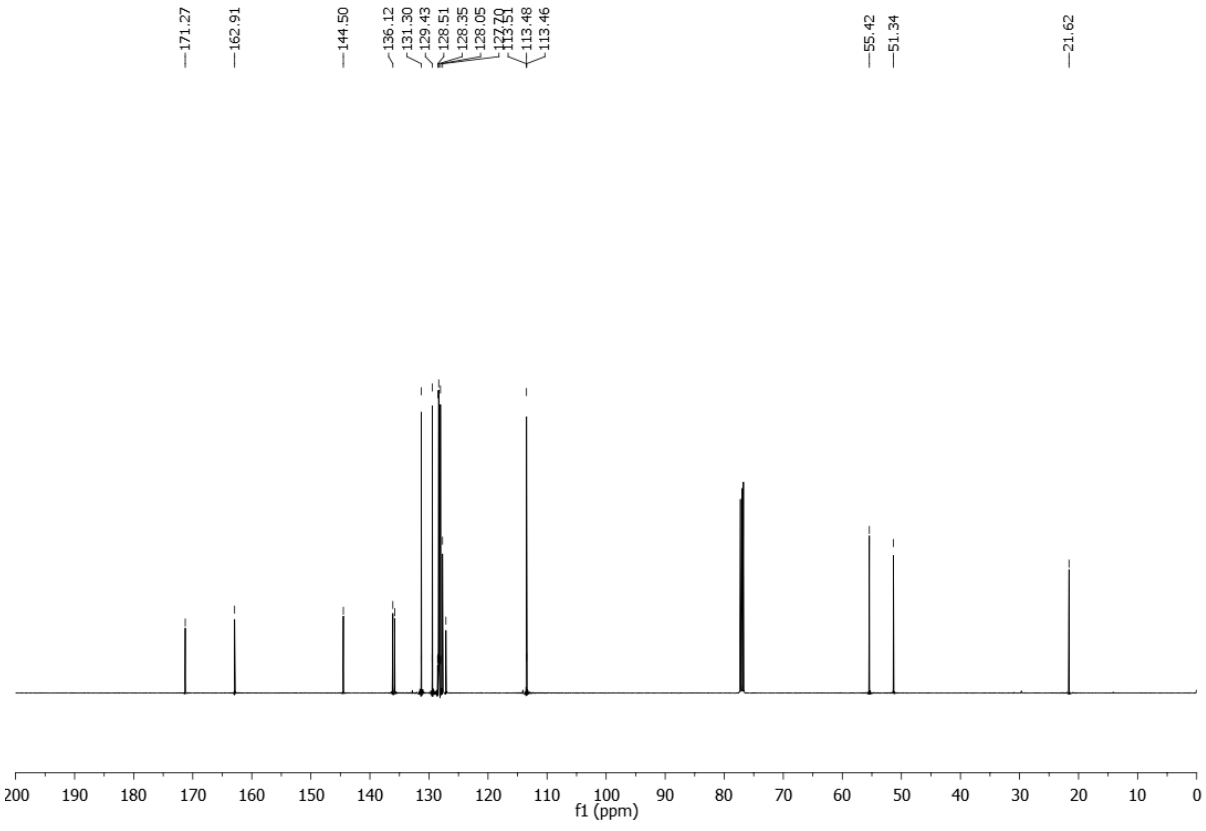


*N-benzyl-4-methoxy-N-(4-methylbenzenesulfonyl)benzamide (**4n**)*

^{1}H NMR (500 MHz, $CDCl_3$)

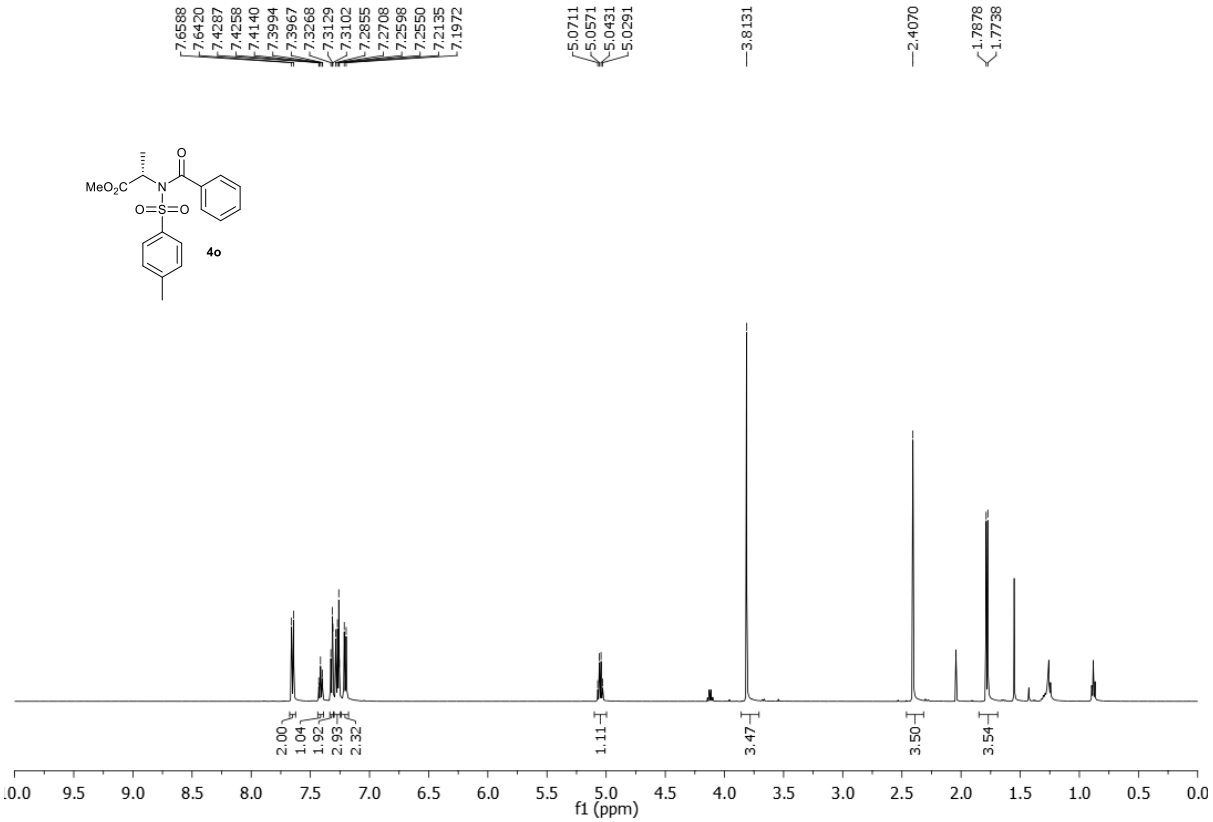


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

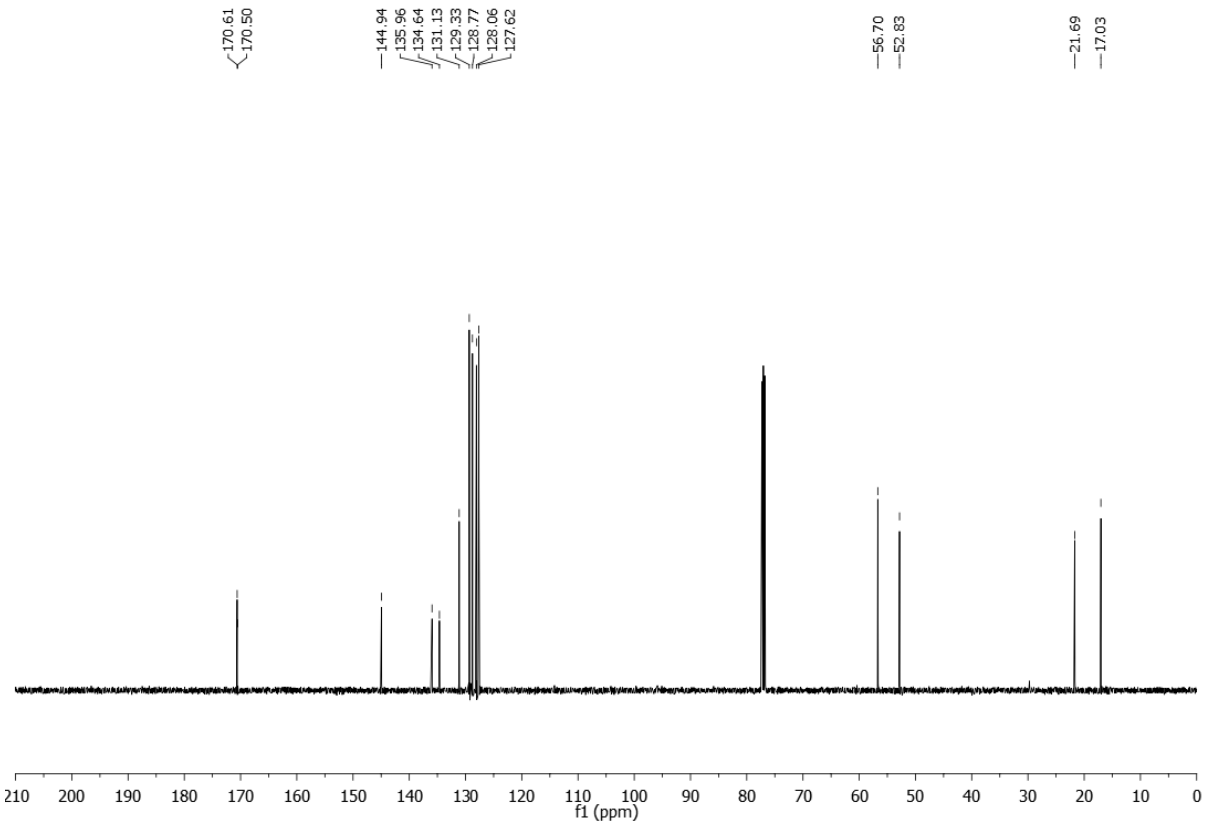


*methyl N-benzoyl-N-tosyl-L-alaninate (**4o**)*

^{1}H NMR (500 MHz, $CDCl_3$)

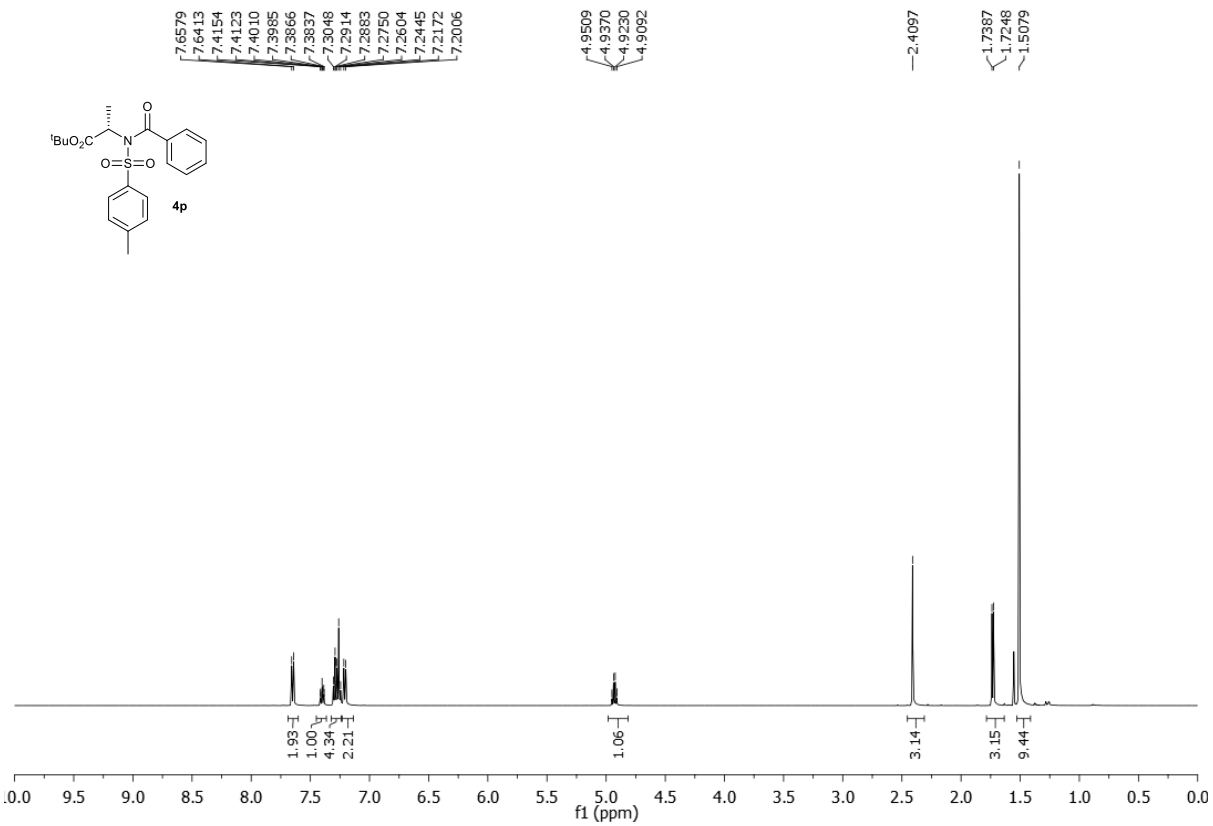


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

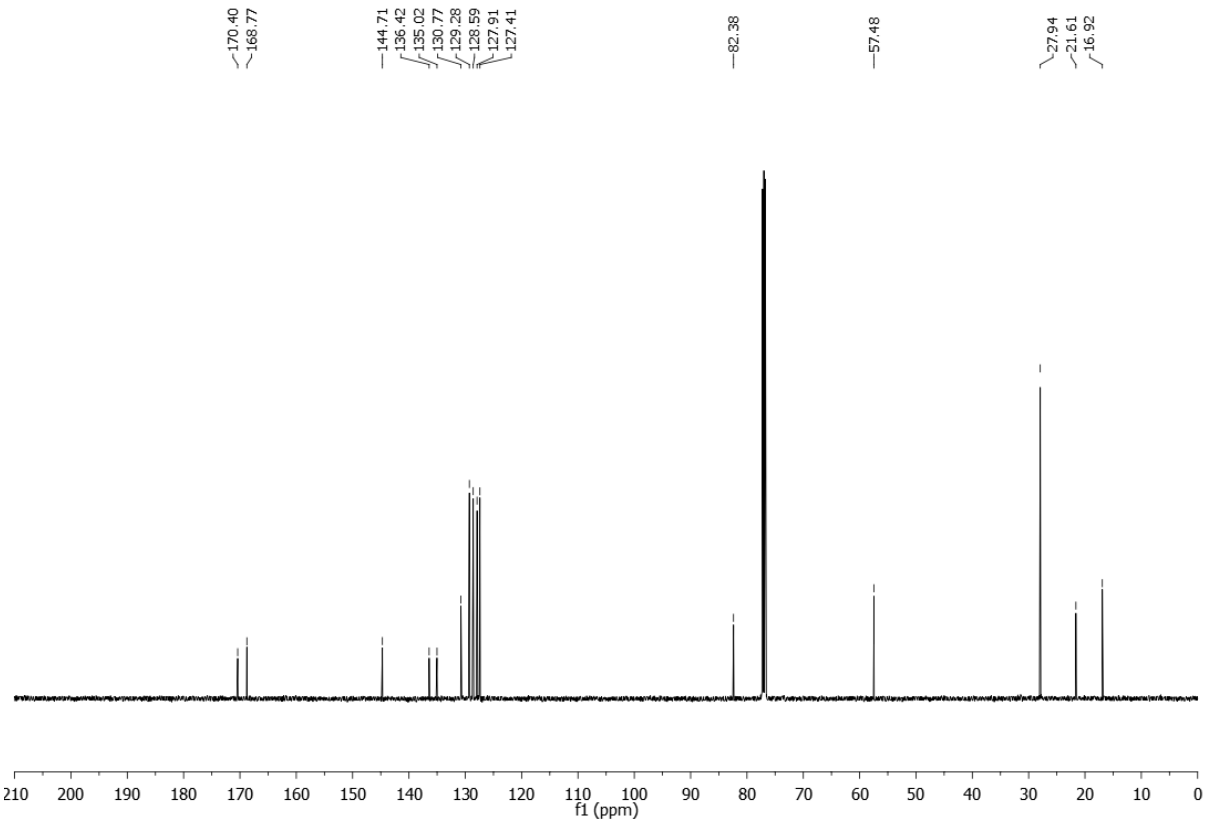


*tert-Butyl benzoyl(tosyl)carbamate (**4p**)*

^{1}H NMR (500 MHz, $CDCl_3$)

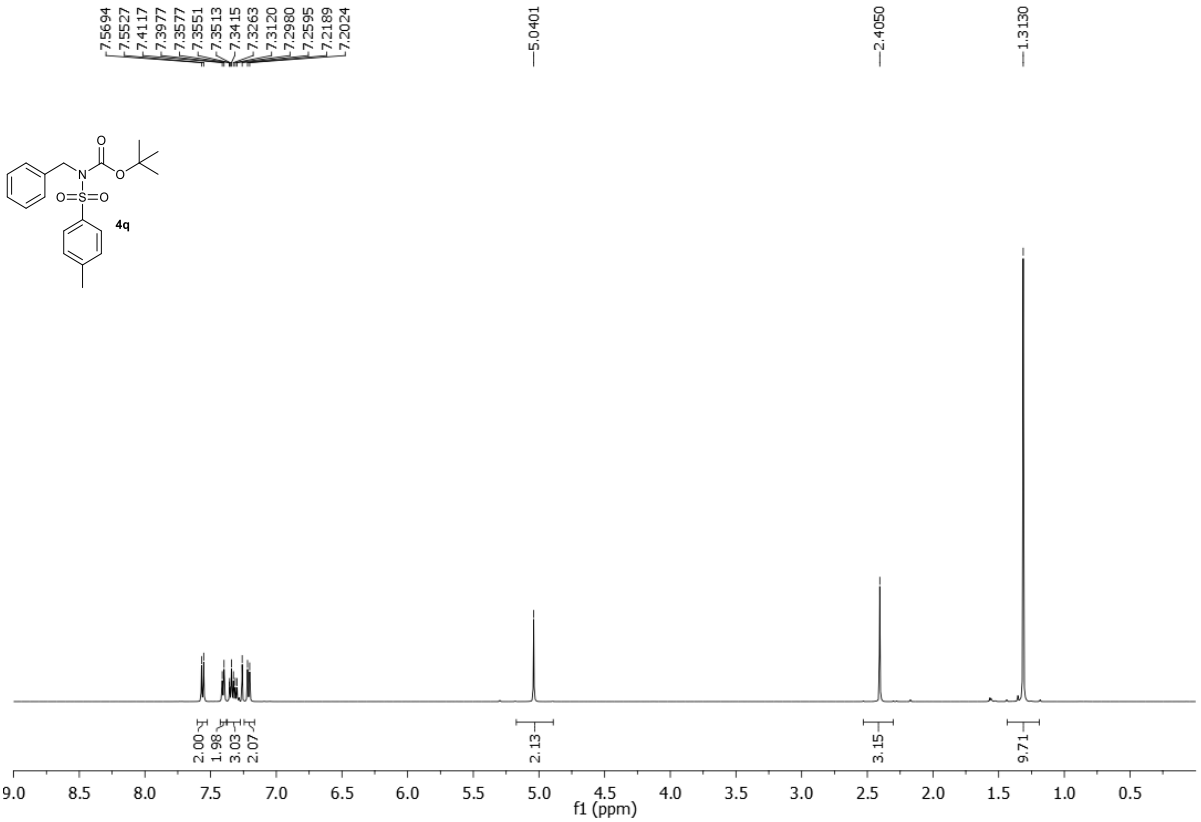


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

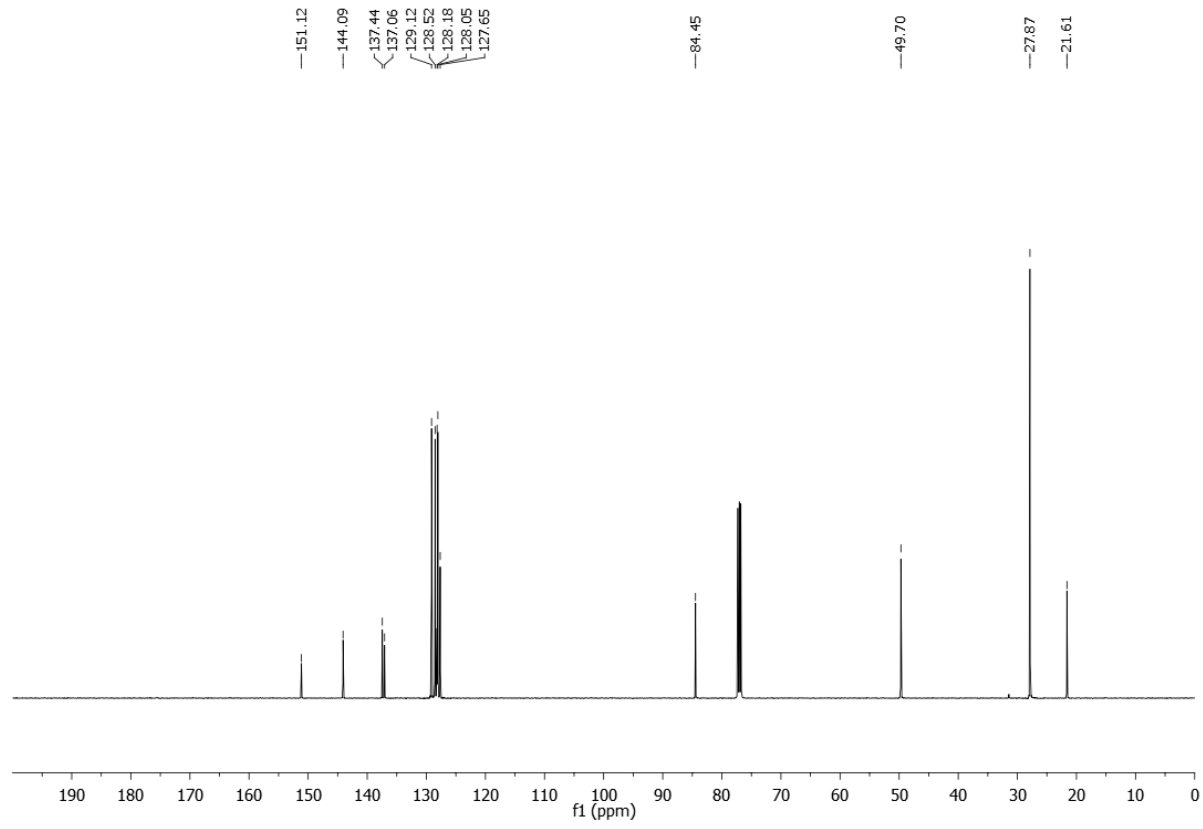


*tert-Butyl benzyl(tosyl)carbamate (**4q**)*

^{1}H NMR (500 MHz, $CDCl_3$)

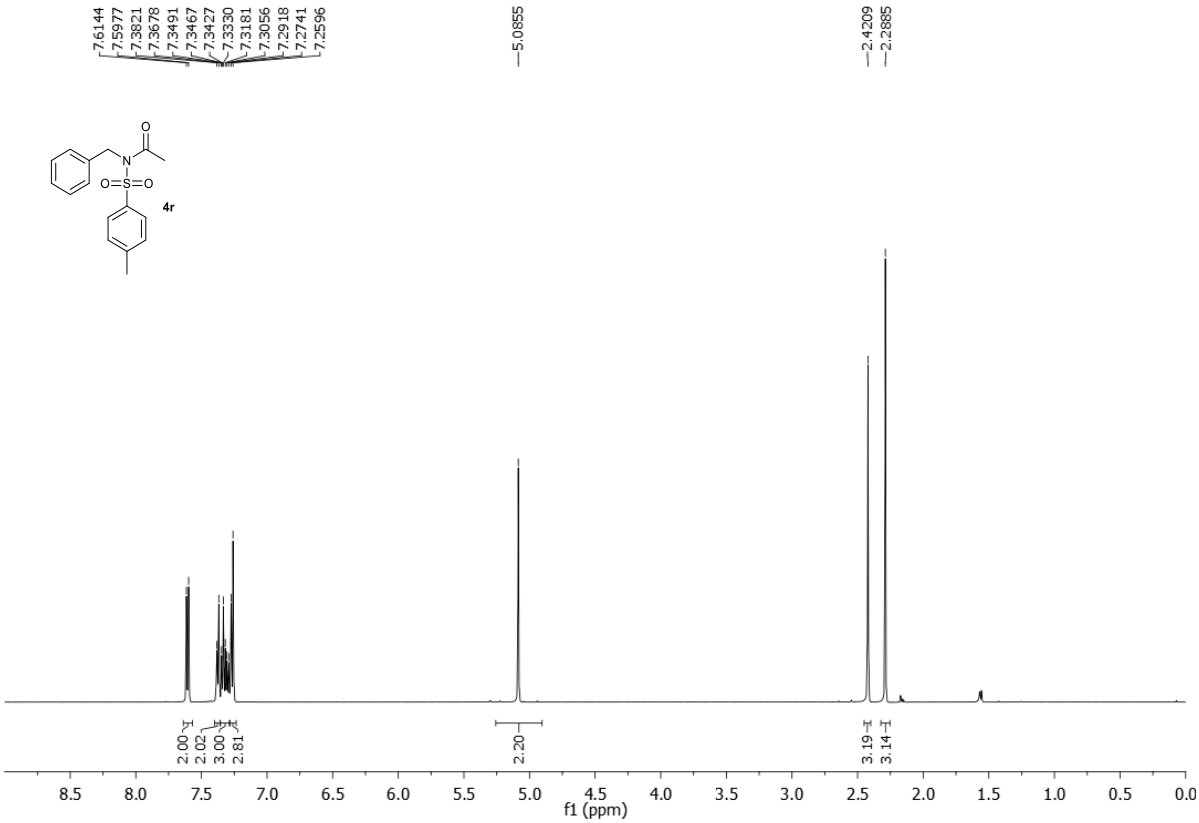


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

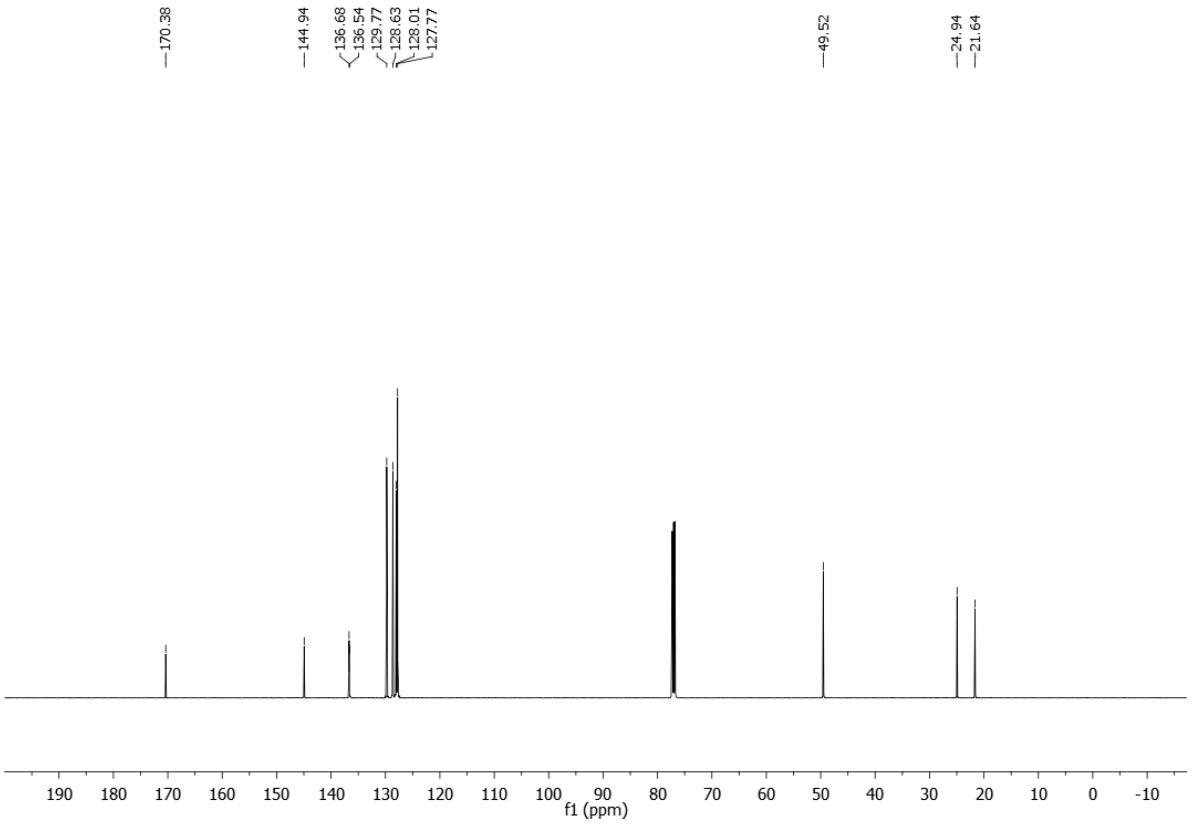


*tert-Butyl benzyl(tosyl)carbamate (**4r**)*

^{1}H NMR (500 MHz, $CDCl_3$)

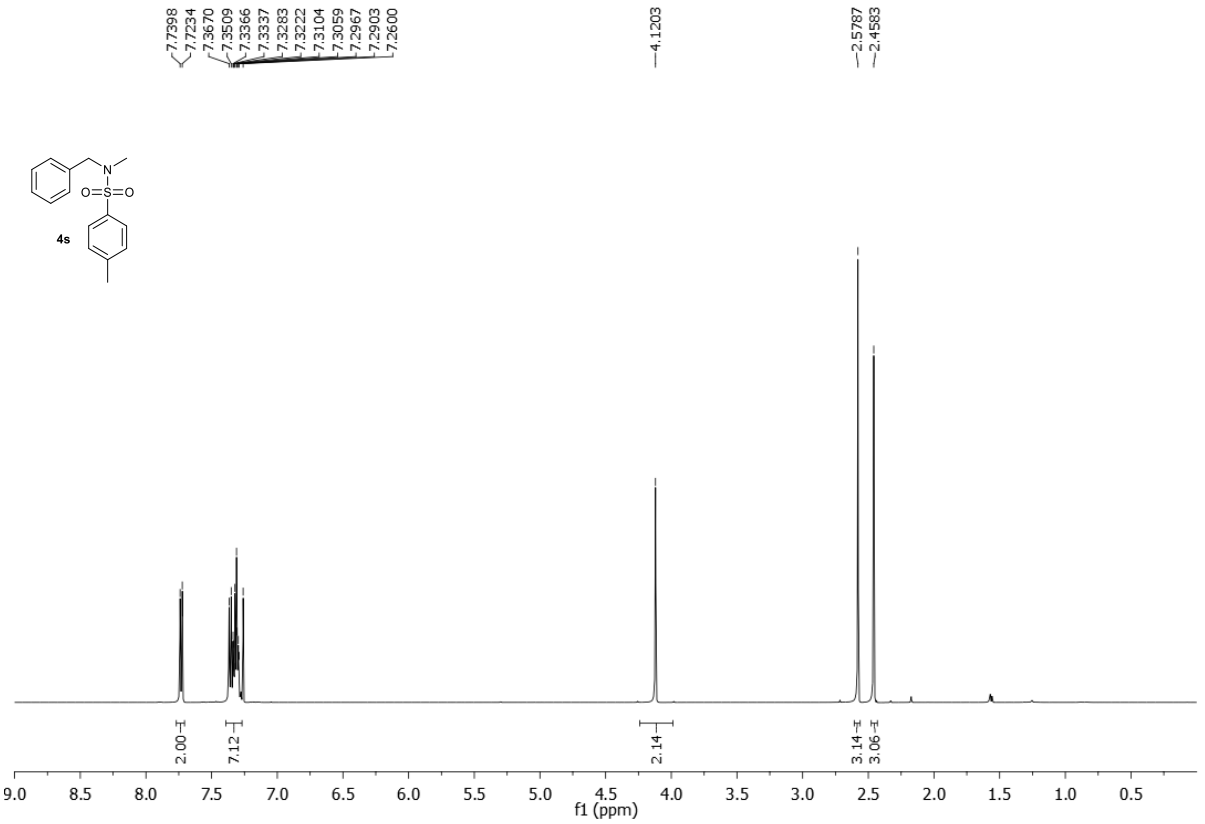


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

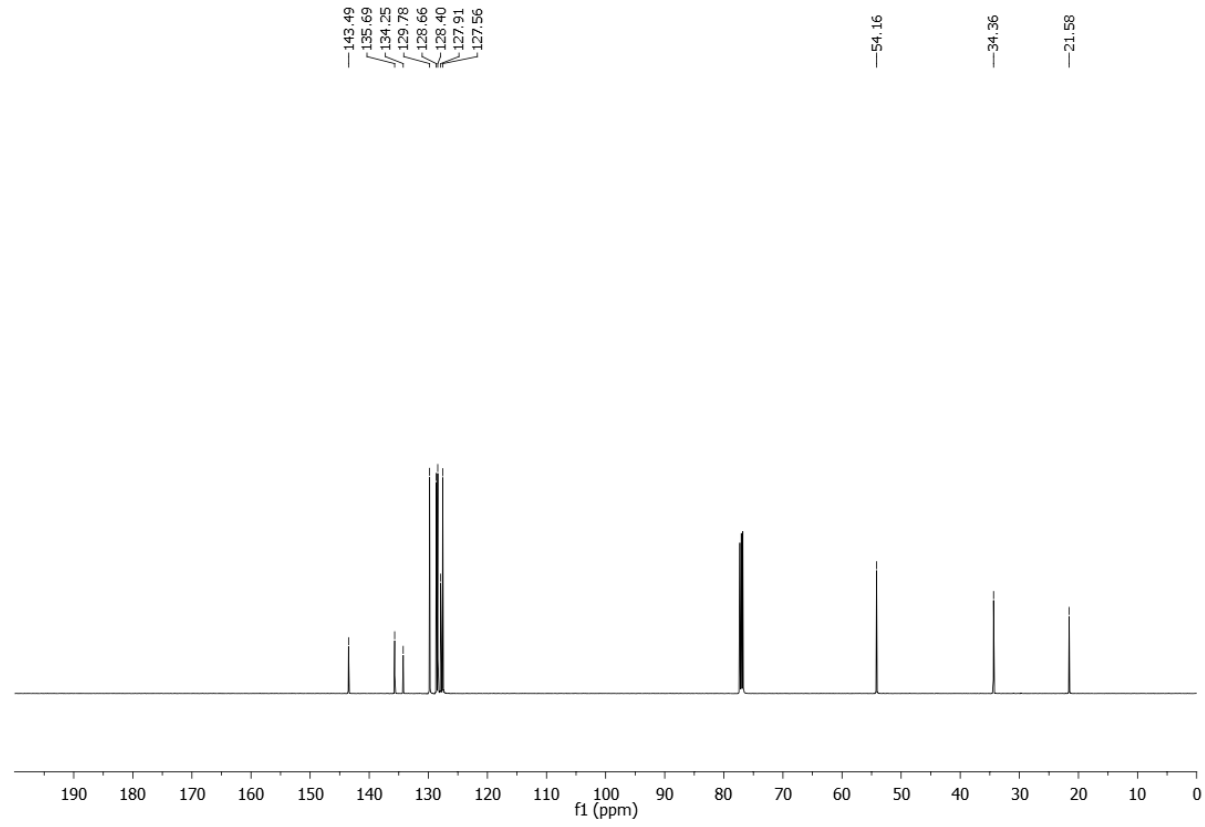


*N-benzyl-N,4-dimethylbenzene-1-sulfonamide (**4s**)*

^{1}H NMR (500 MHz, $CDCl_3$)

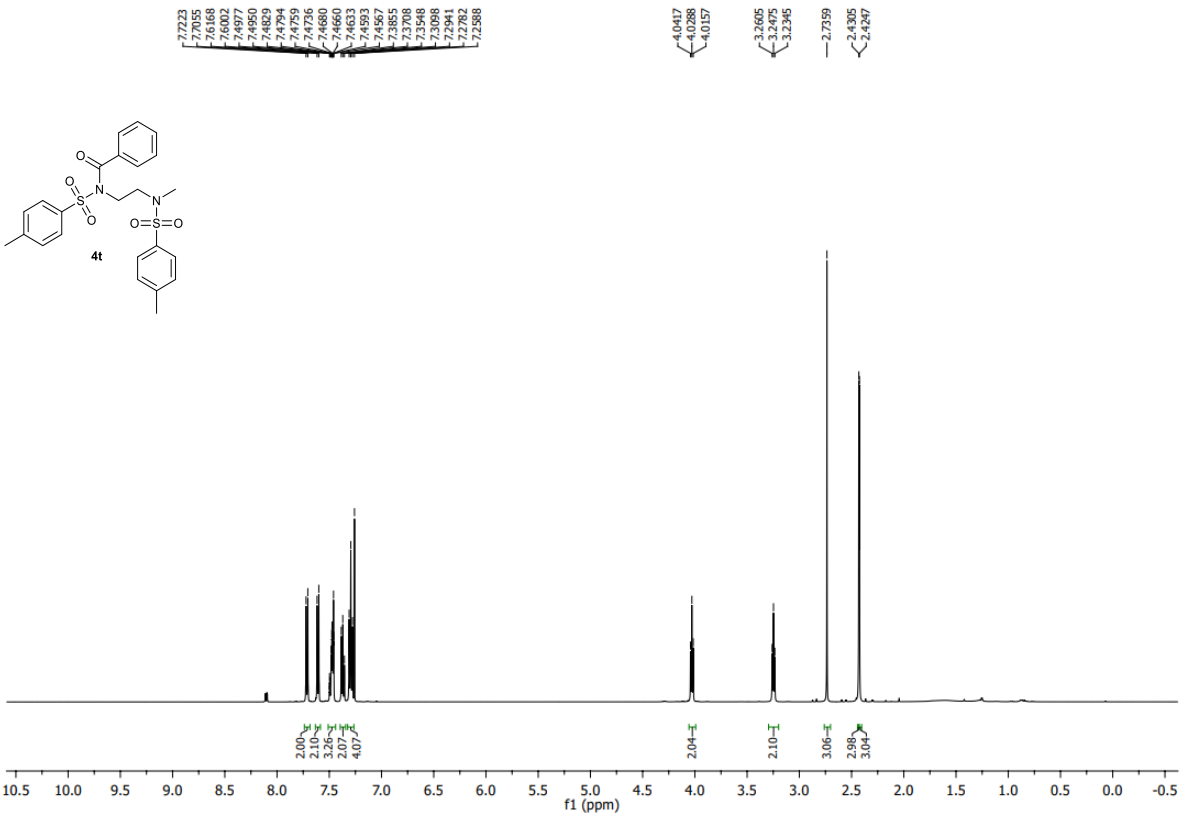


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

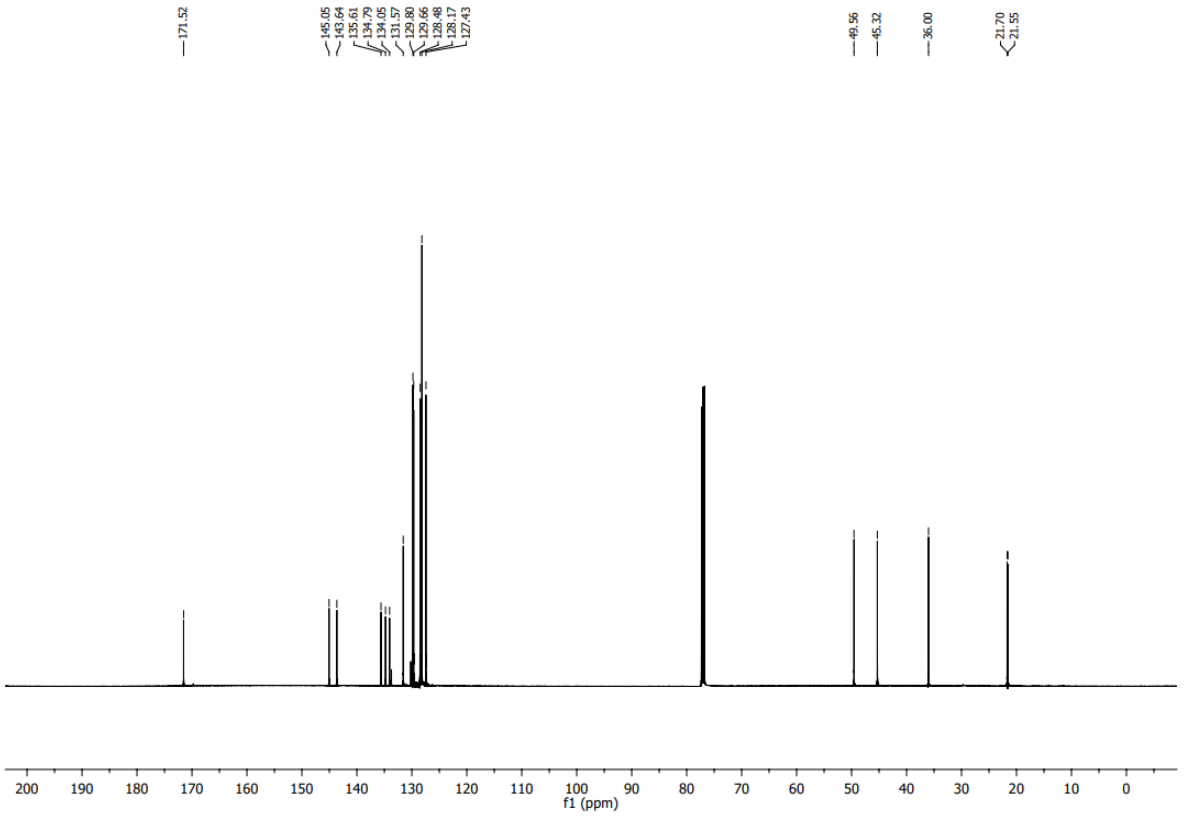


*N-(2-((N,4-dimethylphenyl)sulfonamido)ethyl)-N-tosylbenzamide (**4t**)*

^{1}H NMR (500 MHz, $CDCl_3$)

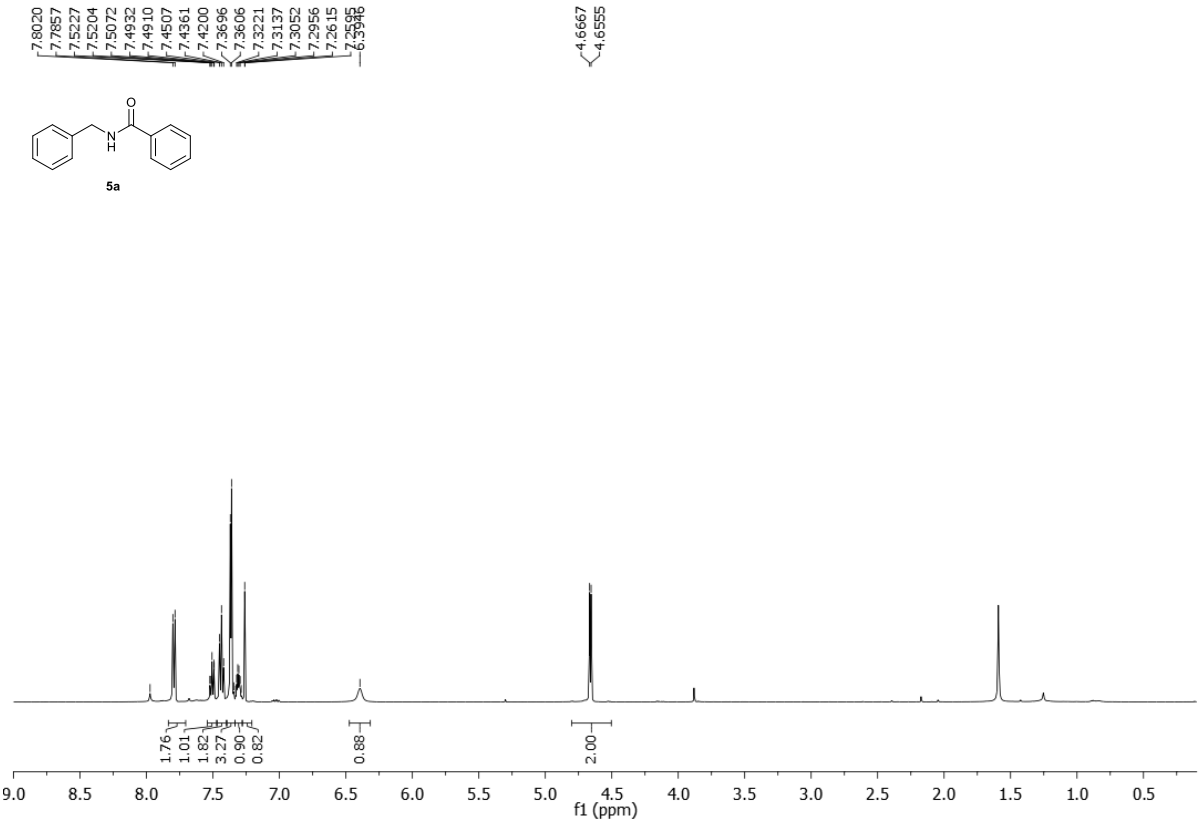


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

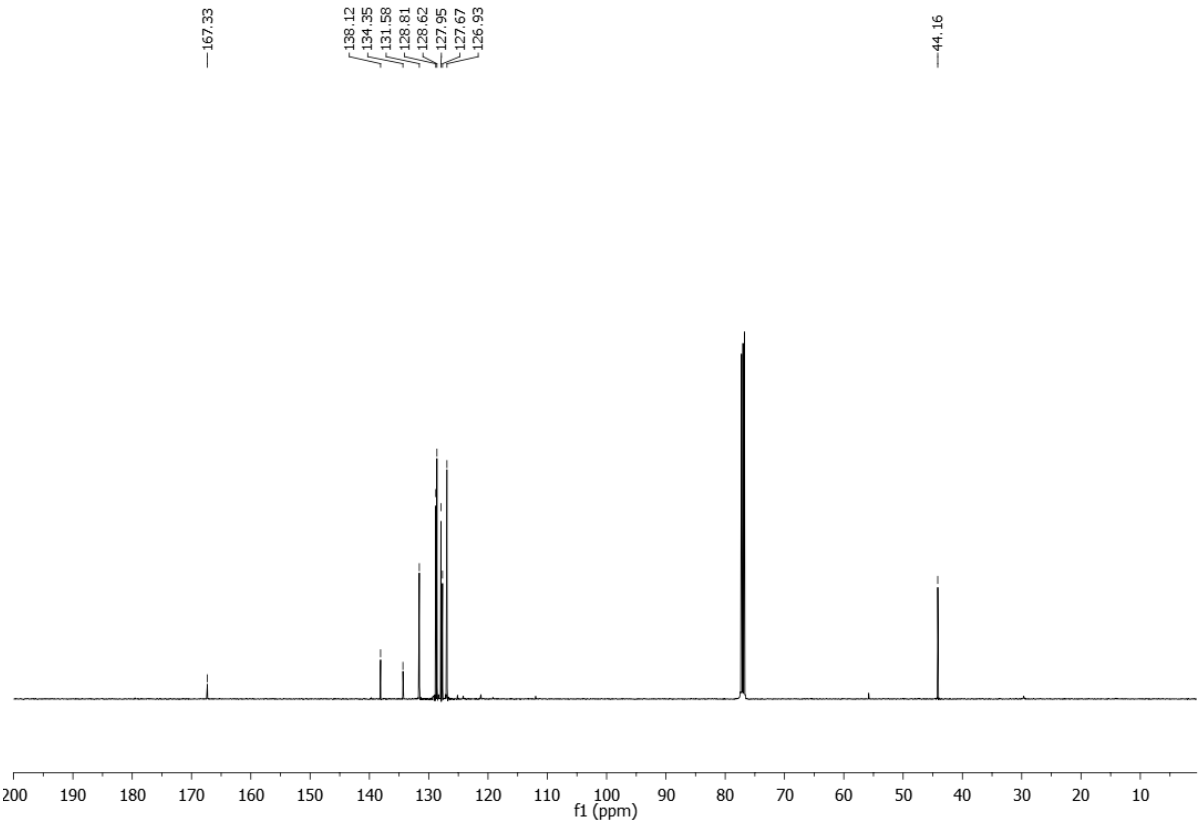


*N-benzylbenzamide (**5a**)*

^{1}H NMR (500 MHz, $CDCl_3$)

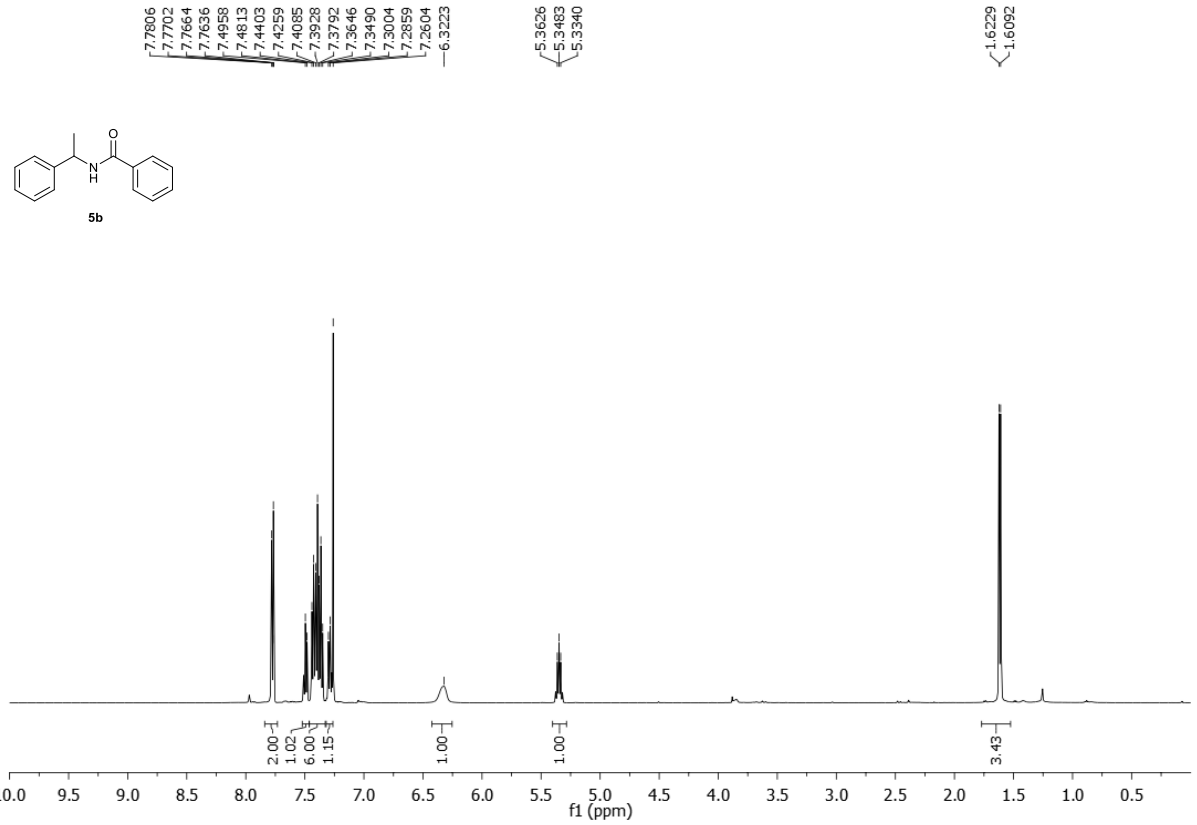


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

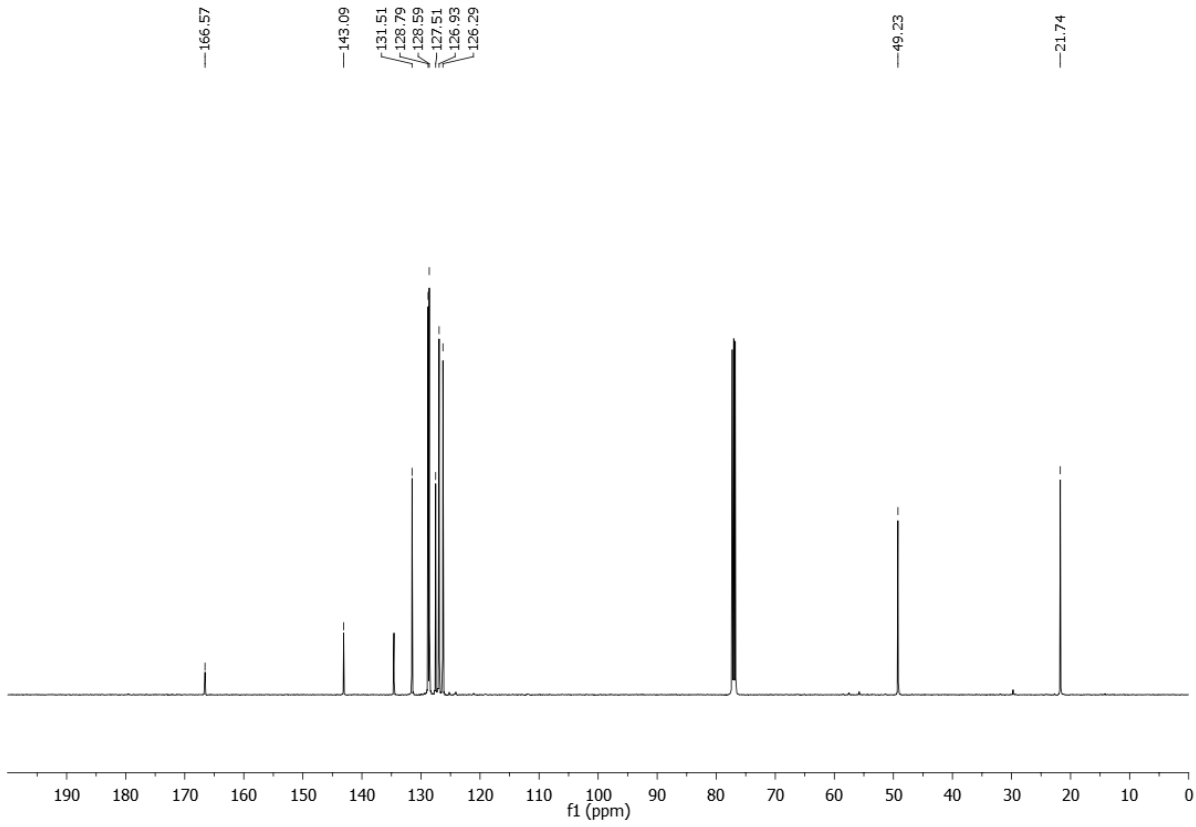


*N-(1-phenylethyl)benzamide (**5b**)*

^{1}H NMR (500 MHz, $CDCl_3$)

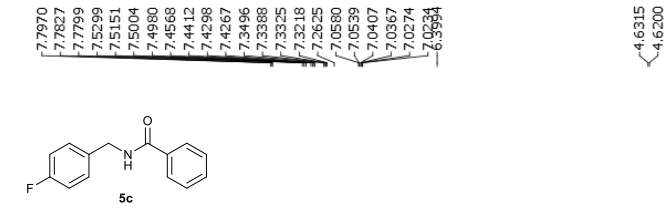


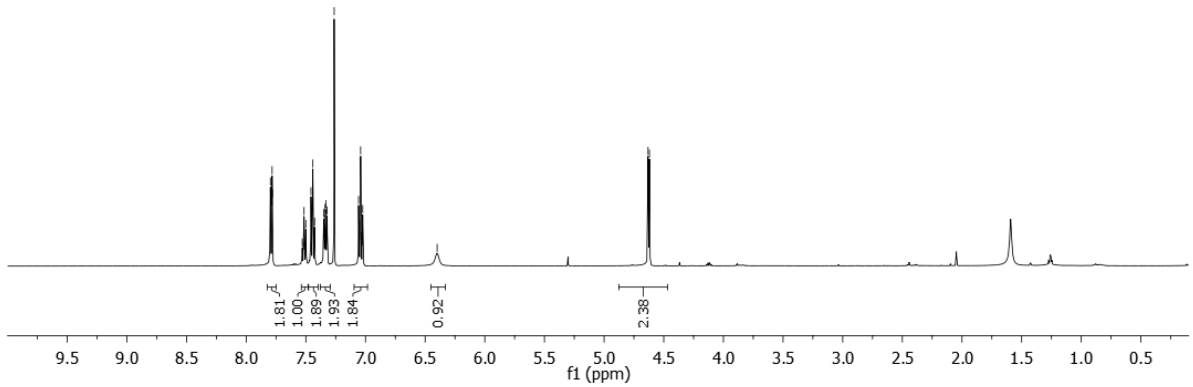
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)



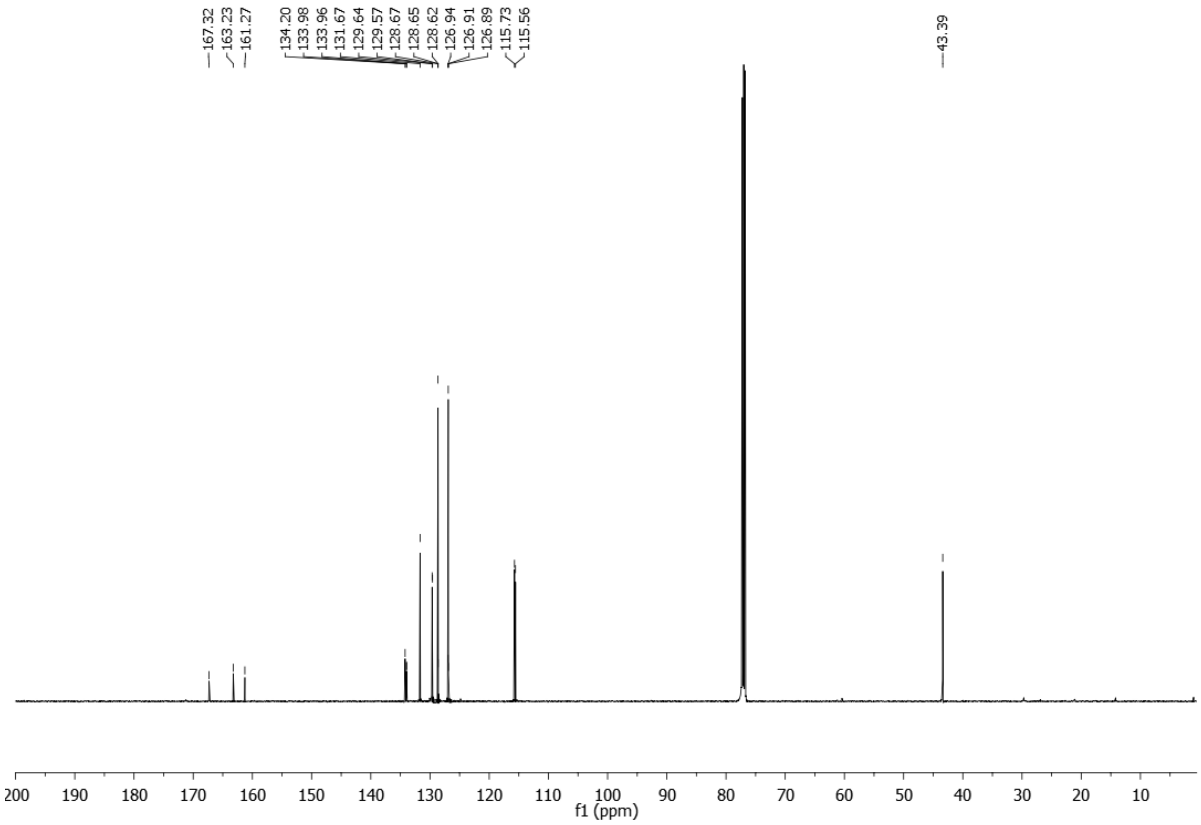
*N-[(4-fluorophenyl)methyl]benzamide (**5c**)*

^{1}H NMR (500 MHz, $CDCl_3$)

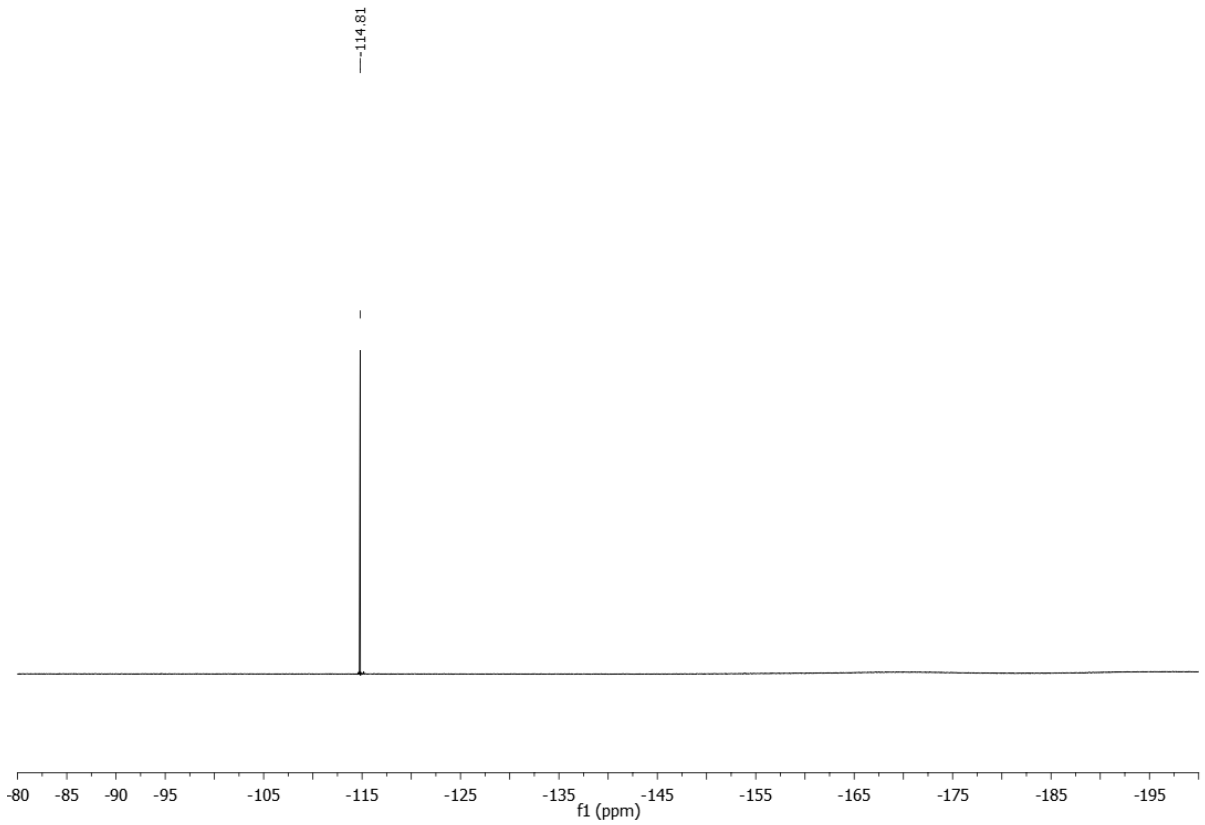




^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

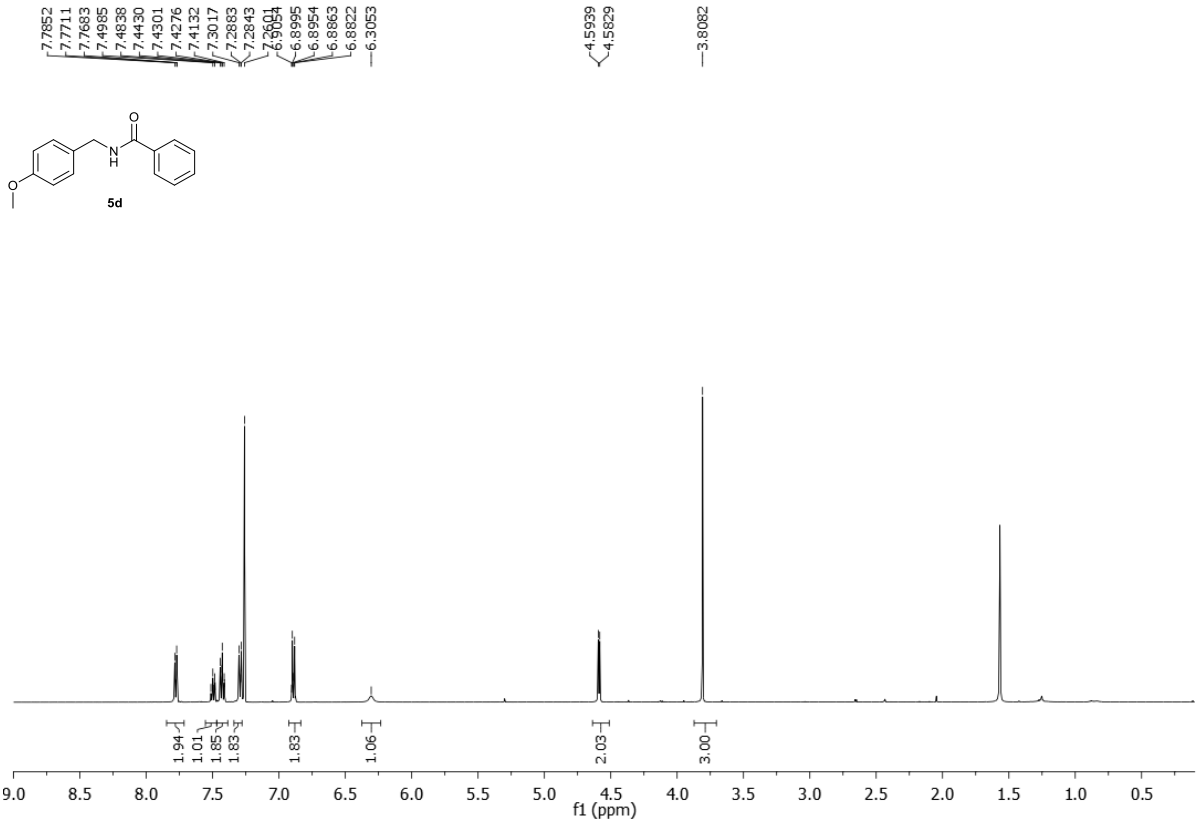


^{19}F NMR (471 MHz, $CDCl_3$)

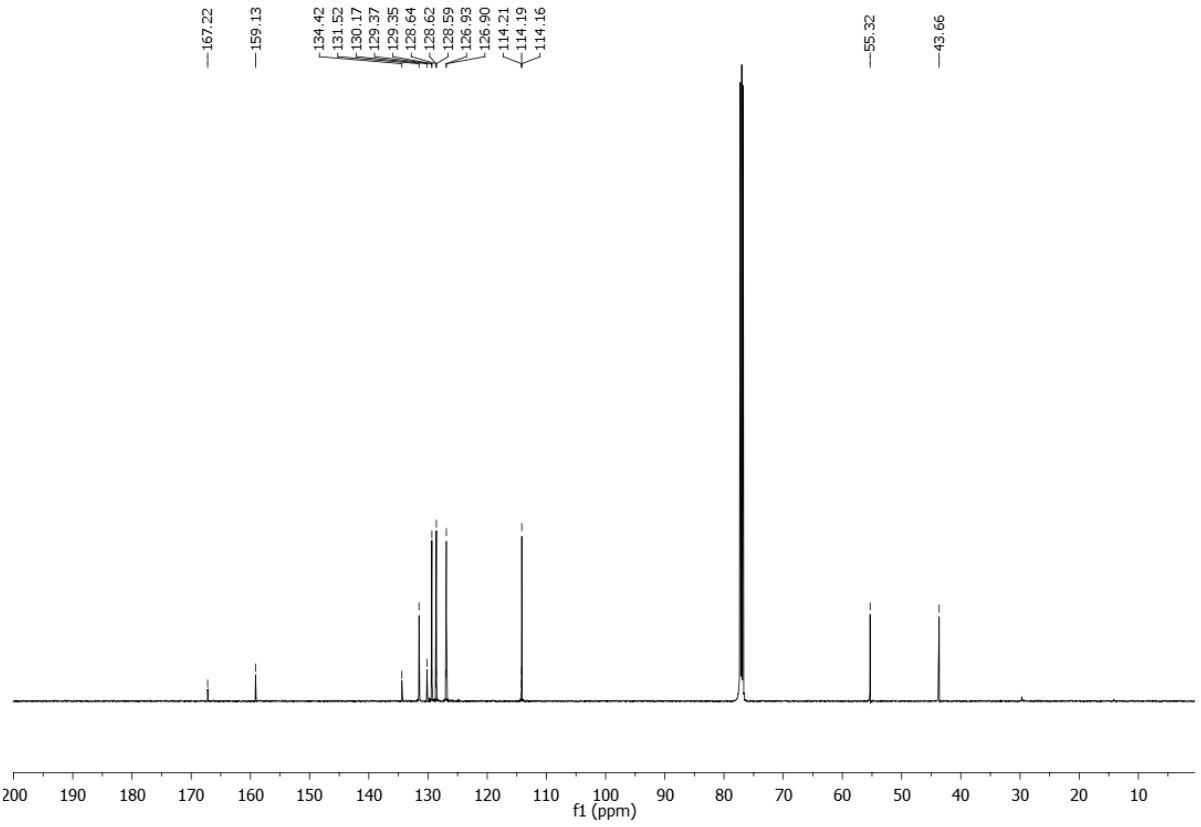


*N-[(4-methoxyphenyl)methyl]benzamide (**5d**)*

^{1}H NMR (500 MHz, $CDCl_3$)

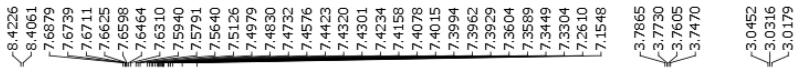


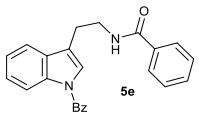
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

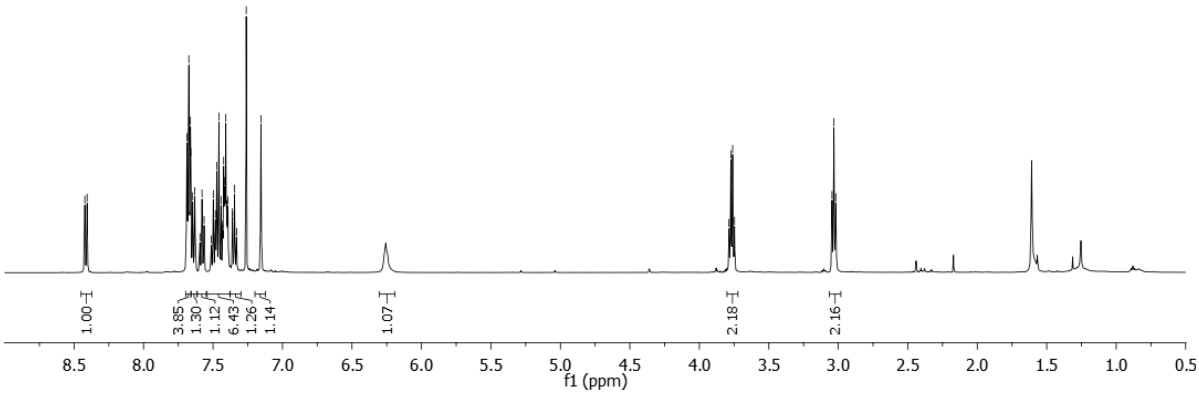


*N-[2-(1-benzoyl-1H-indol-3-yl)ethyl]benzamide (**5e**)*

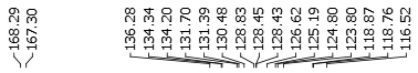
^{1}H NMR (500 MHz, $CDCl_3$)

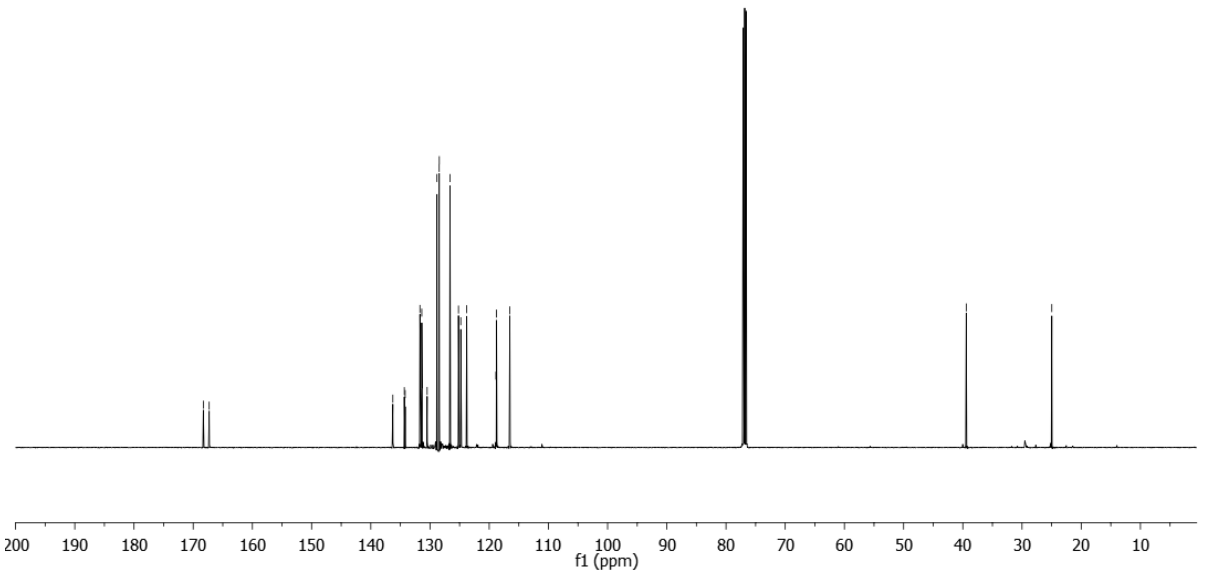






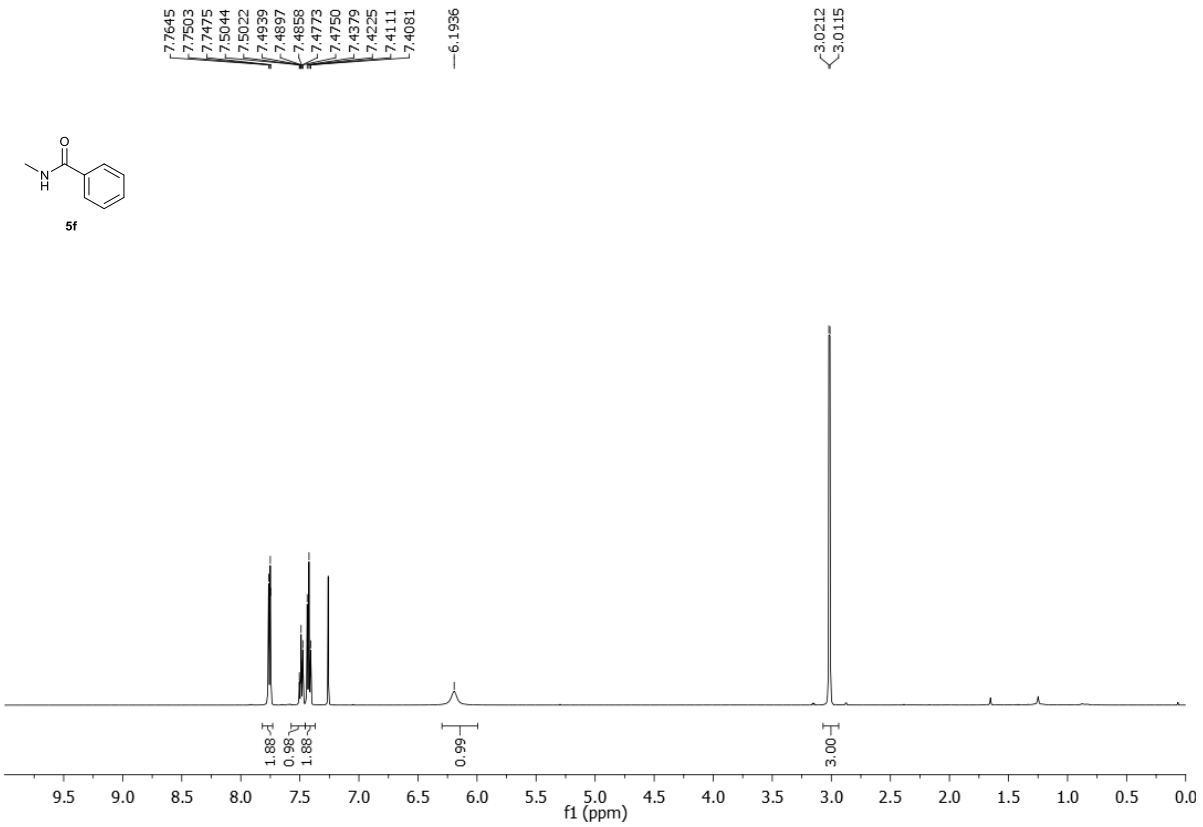
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)



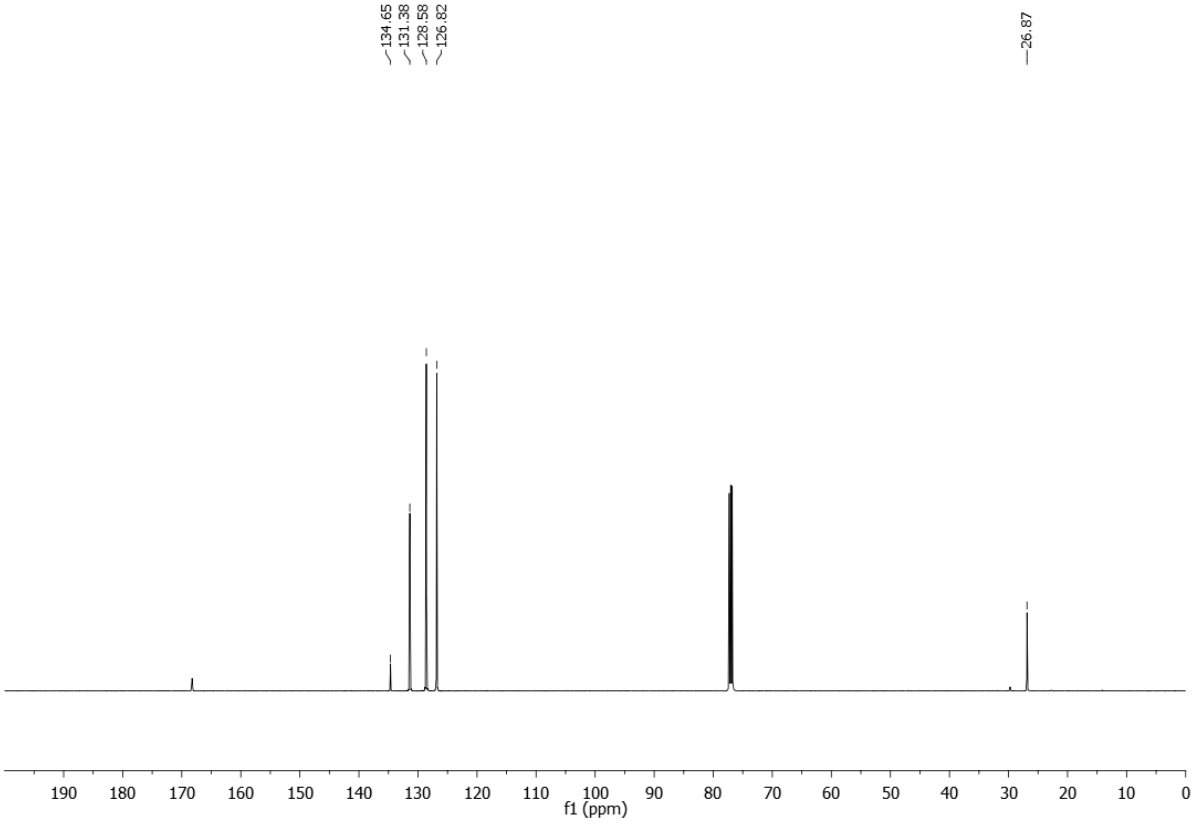


*N-methylbenzamide (**5f**)*

^{1}H NMR (500 MHz, $CDCl_3$)

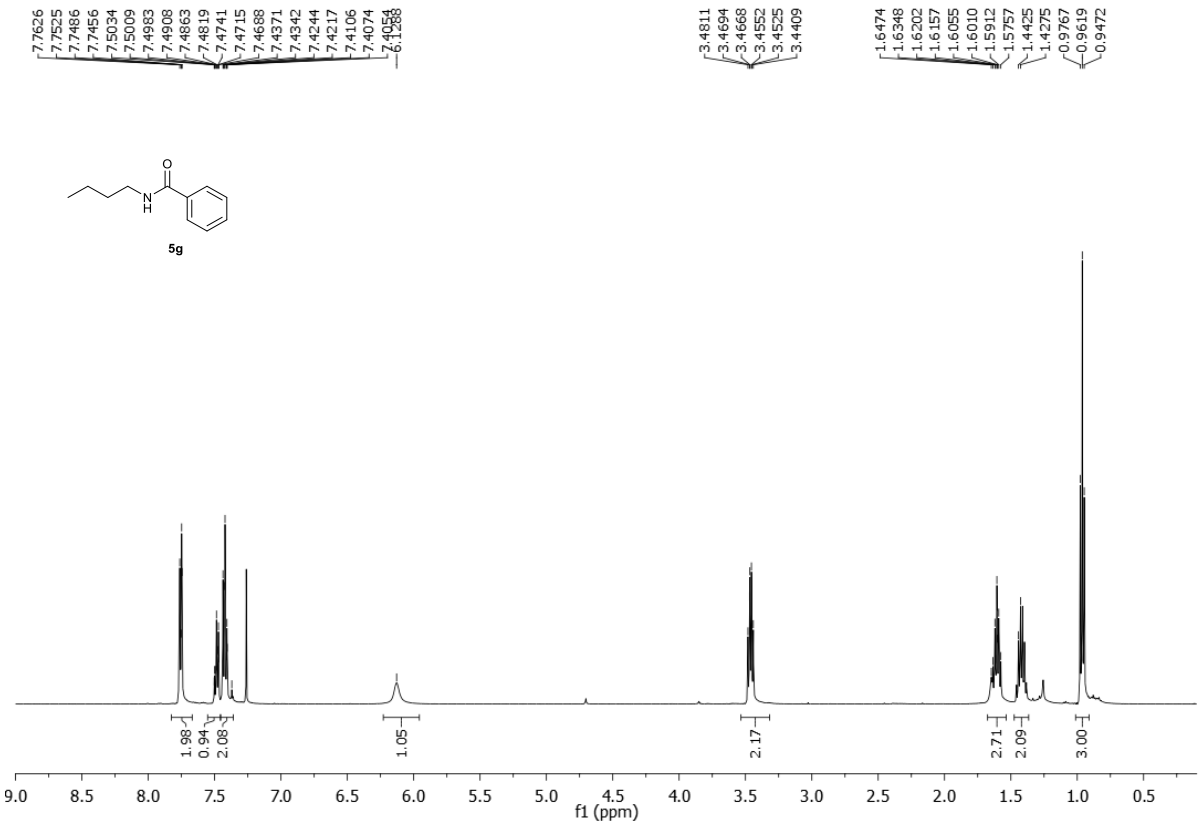


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

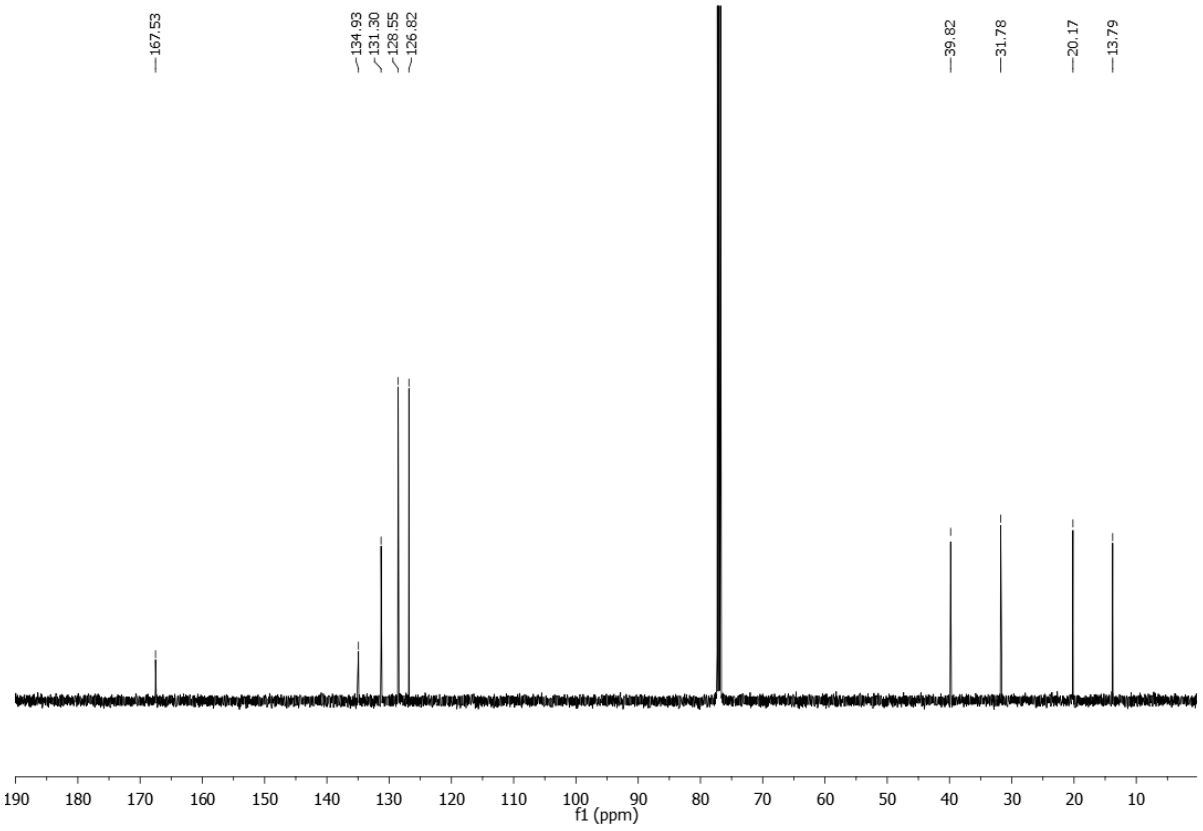


*N-butylbenzamide (**5g**)*

^{1}H NMR (500 MHz, $CDCl_3$)

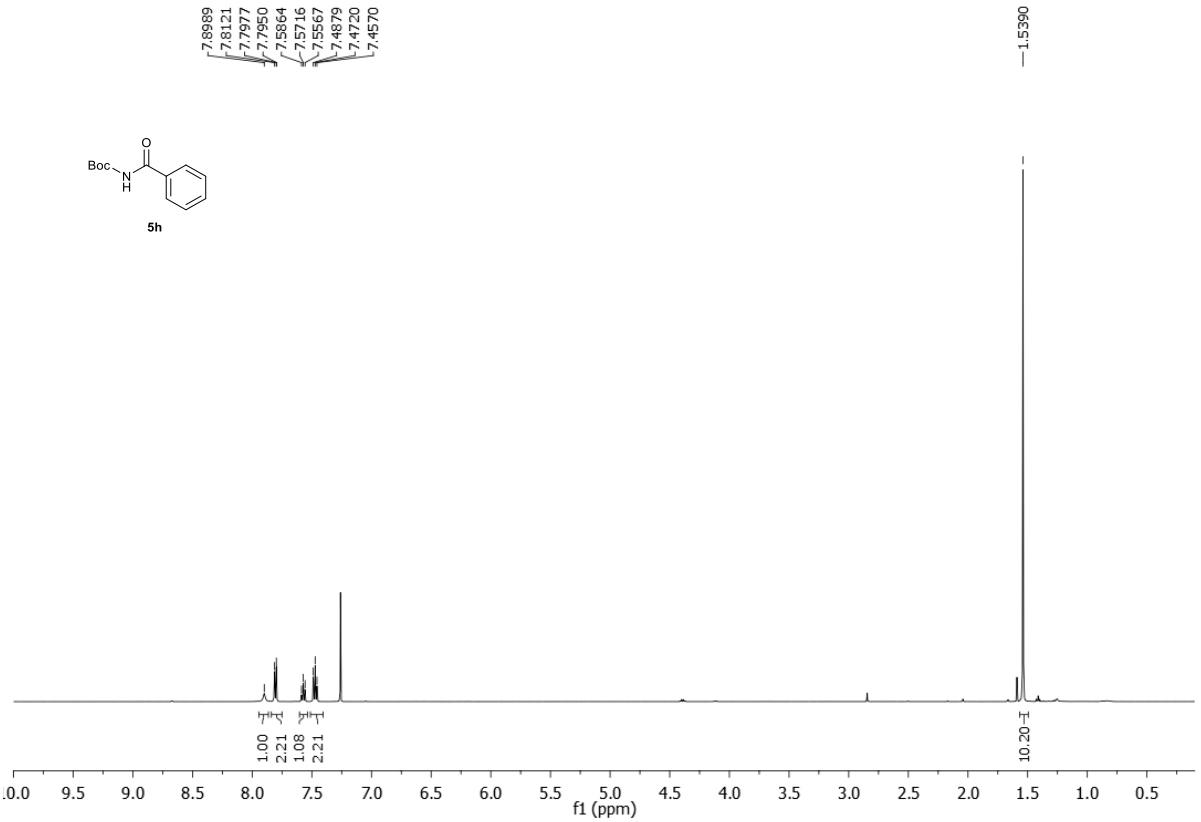


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

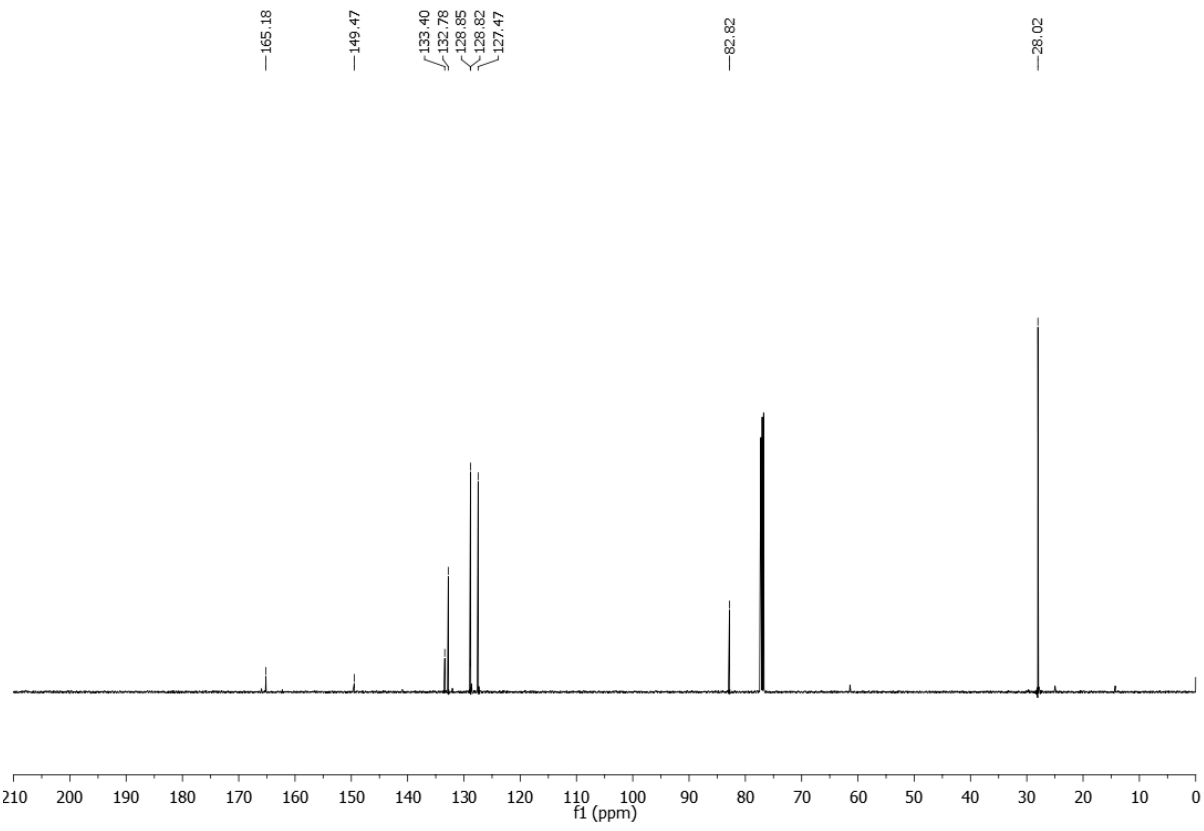


*tert-Butyl benzoylcarbamate (**5h**)*

^{1}H NMR (500 MHz, $CDCl_3$)

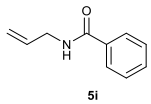


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

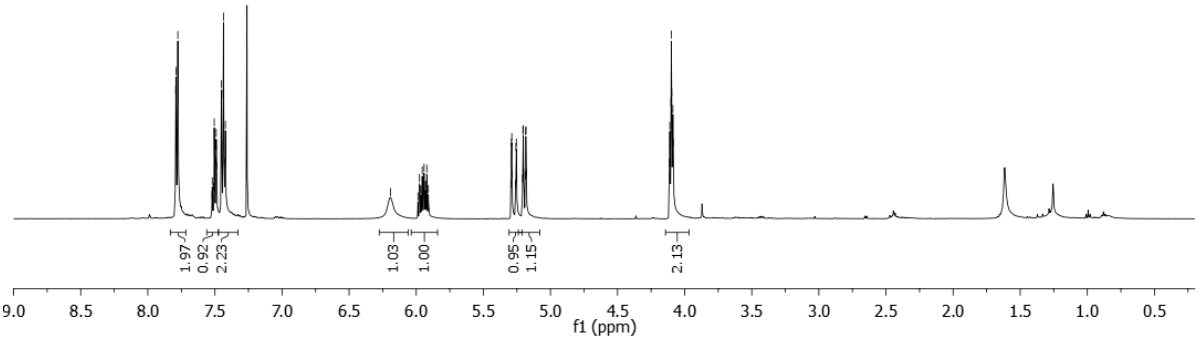


*N-allylbenzamide (**5i**)*

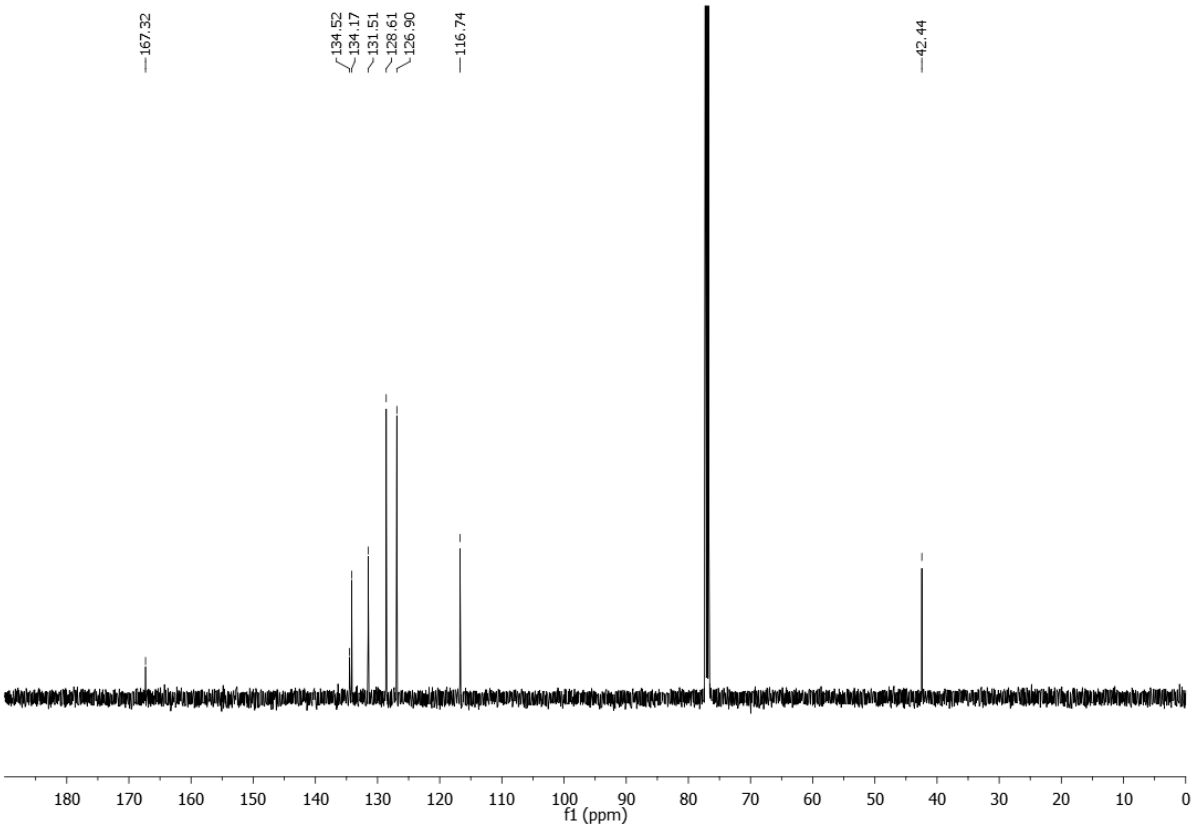
^{1}H NMR (500 MHz, $CDCl_3$)



5i

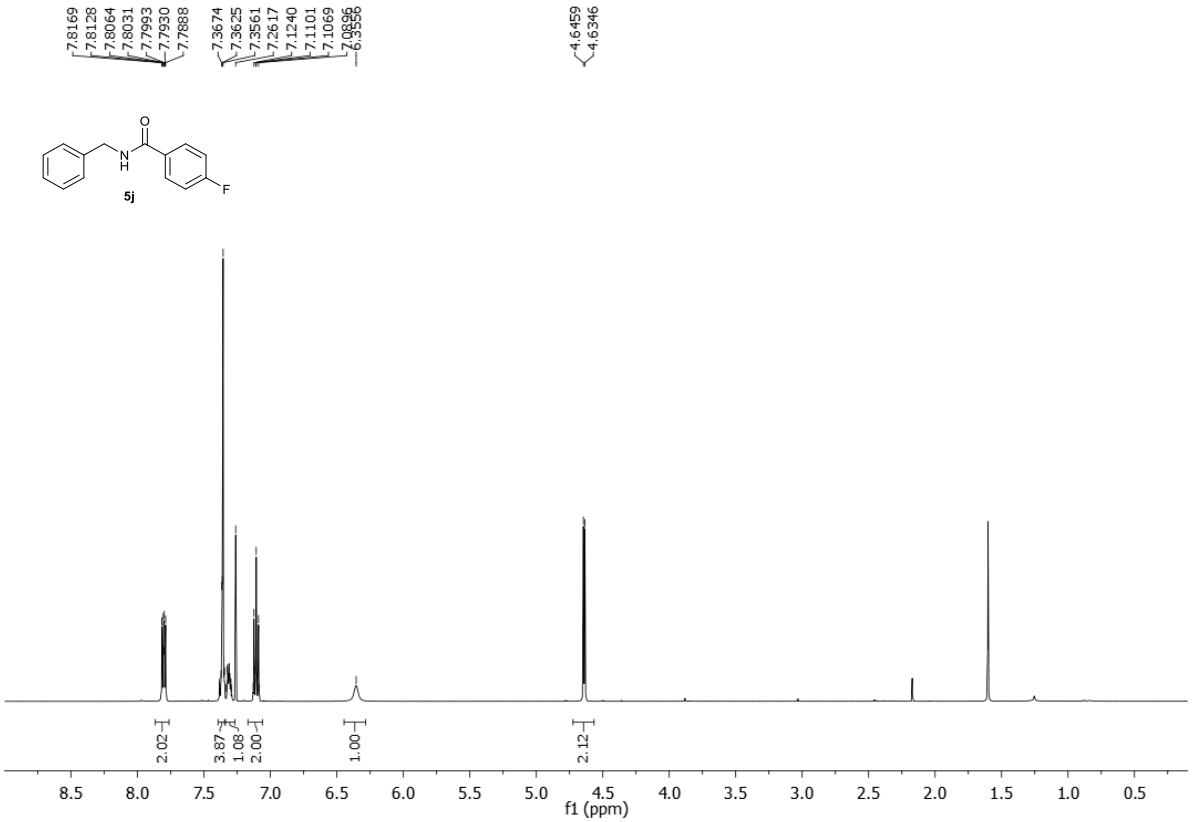


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

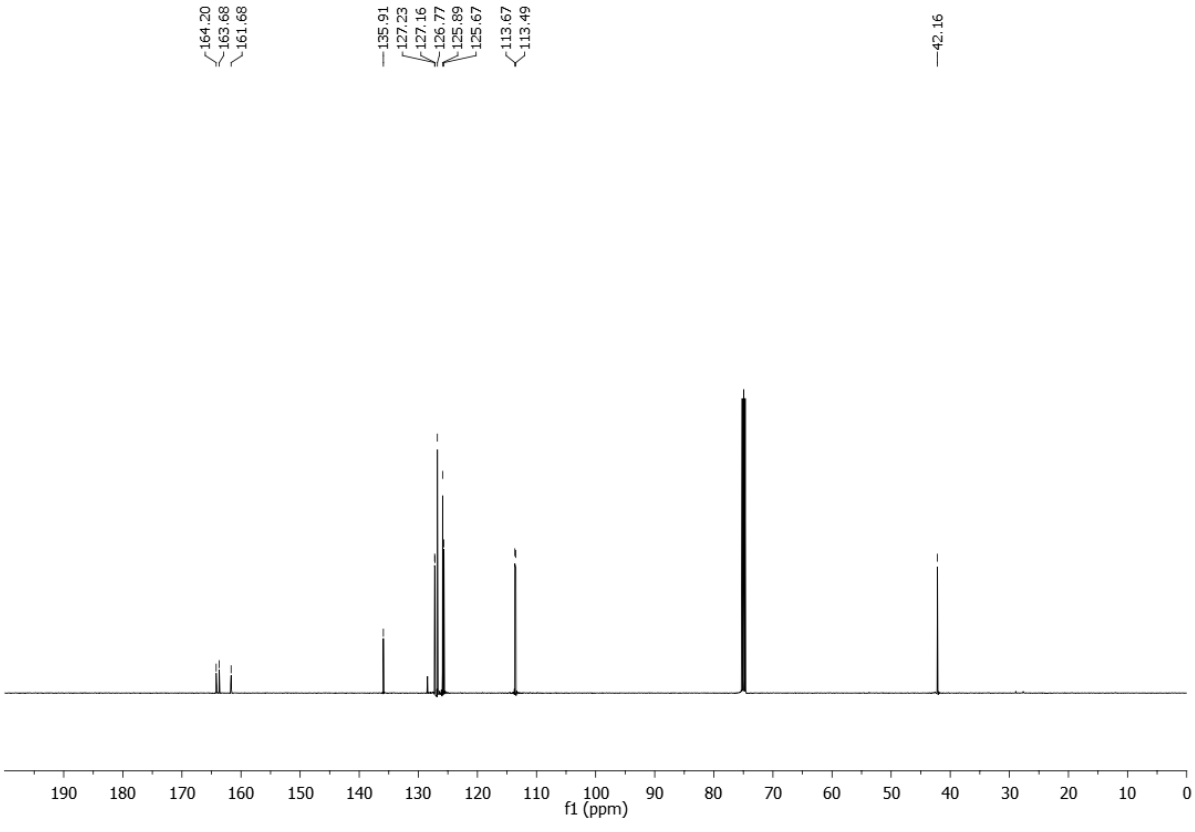


*N-benzyl-4-fluorobenzamide (**5j**)*

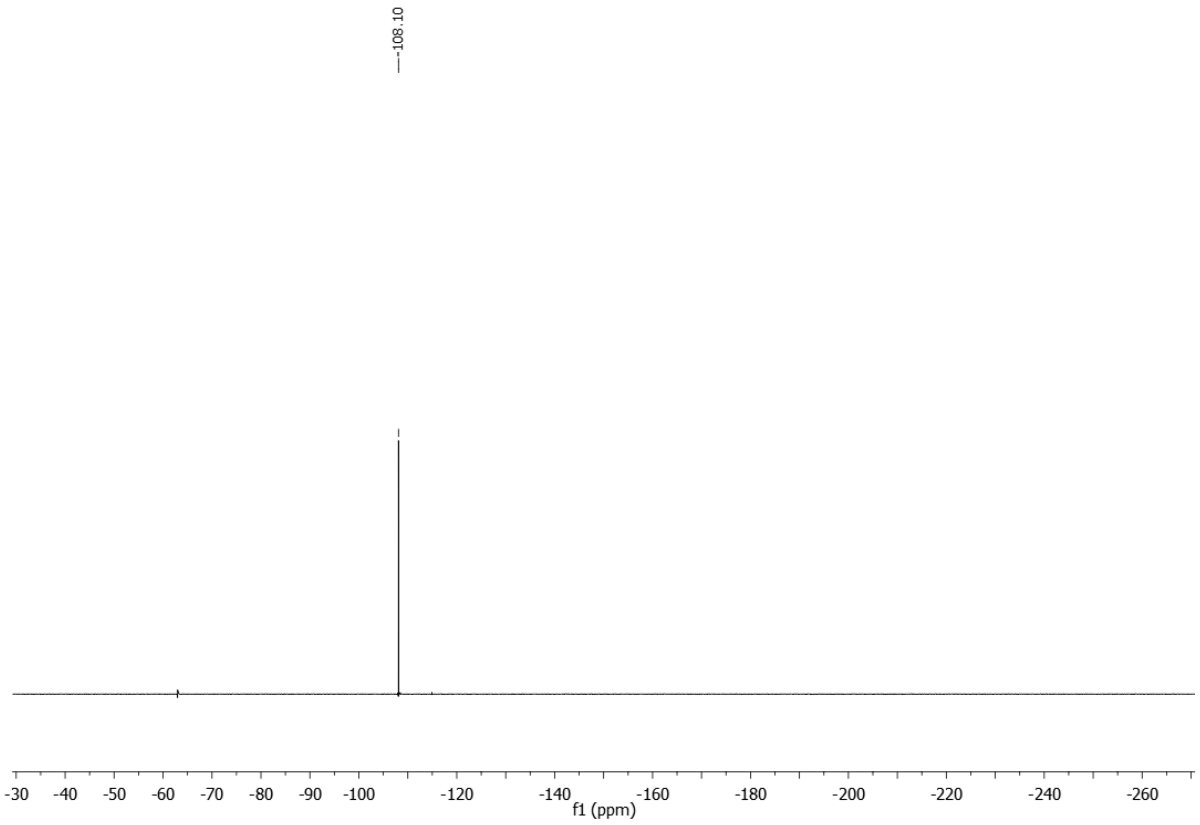
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

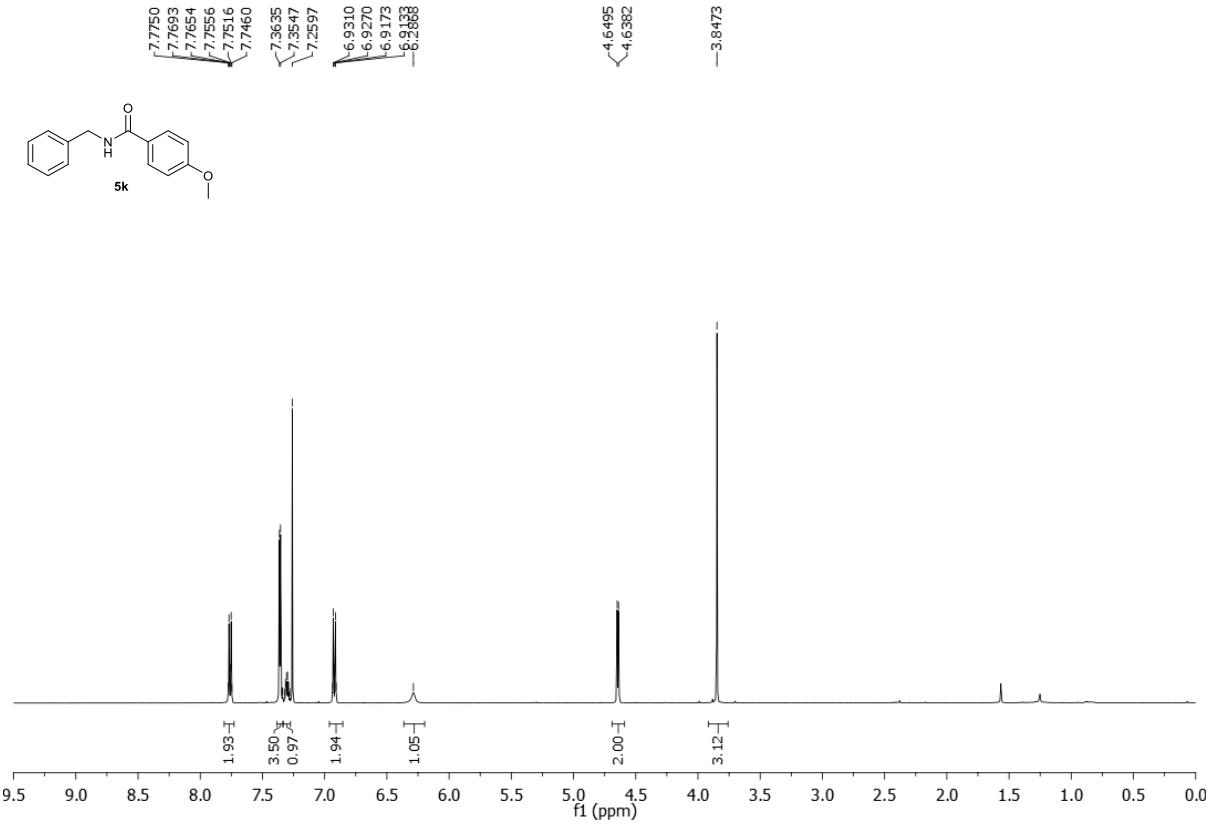


^{19}F NMR (471 MHz, $CDCl_3$)

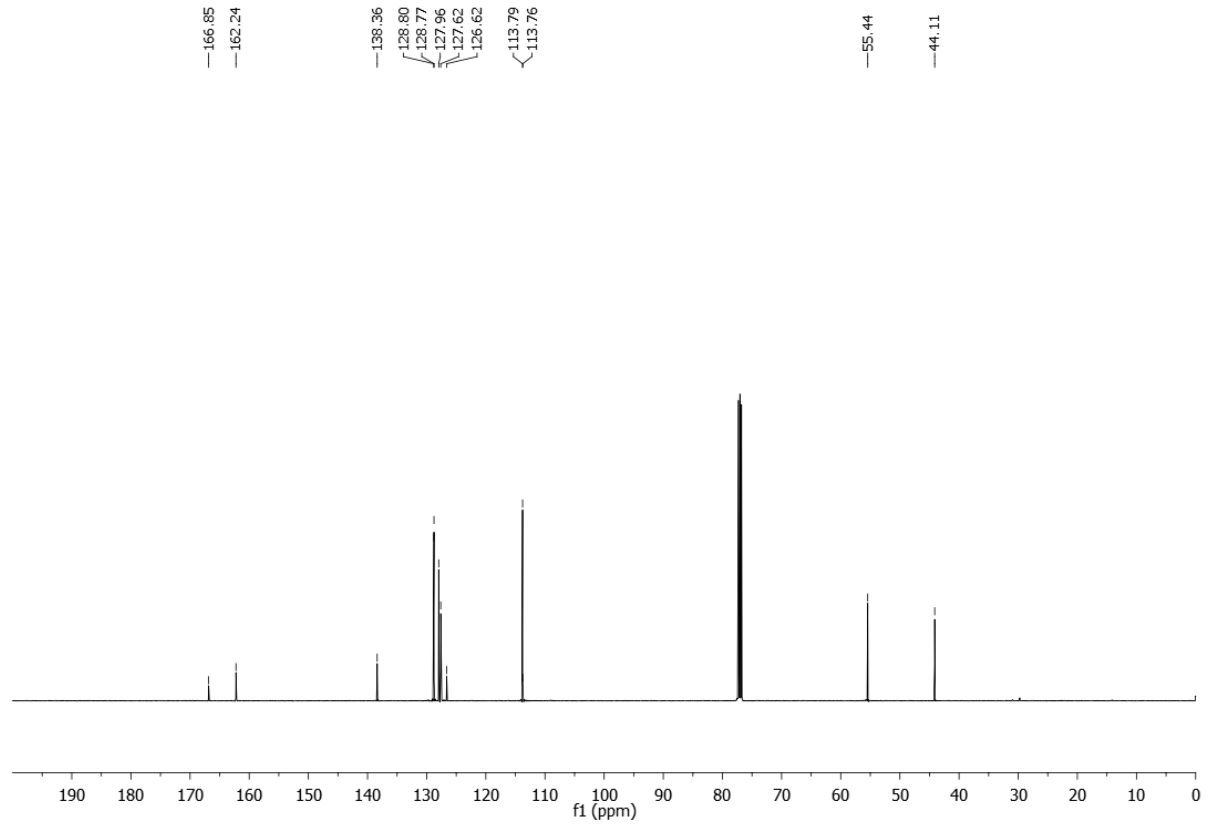


*N-benzyl-4-methoxybenzamide (**5k**)*

^{1}H NMR (500 MHz, $CDCl_3$)

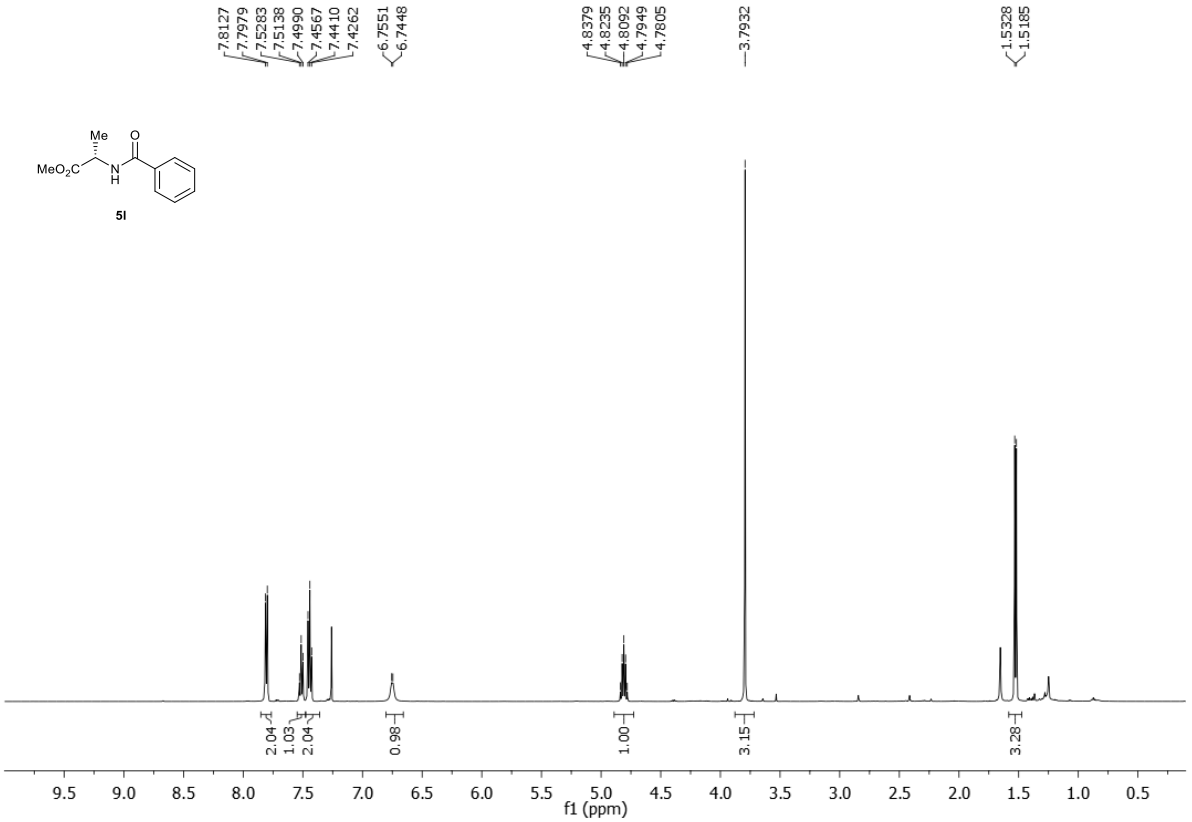


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

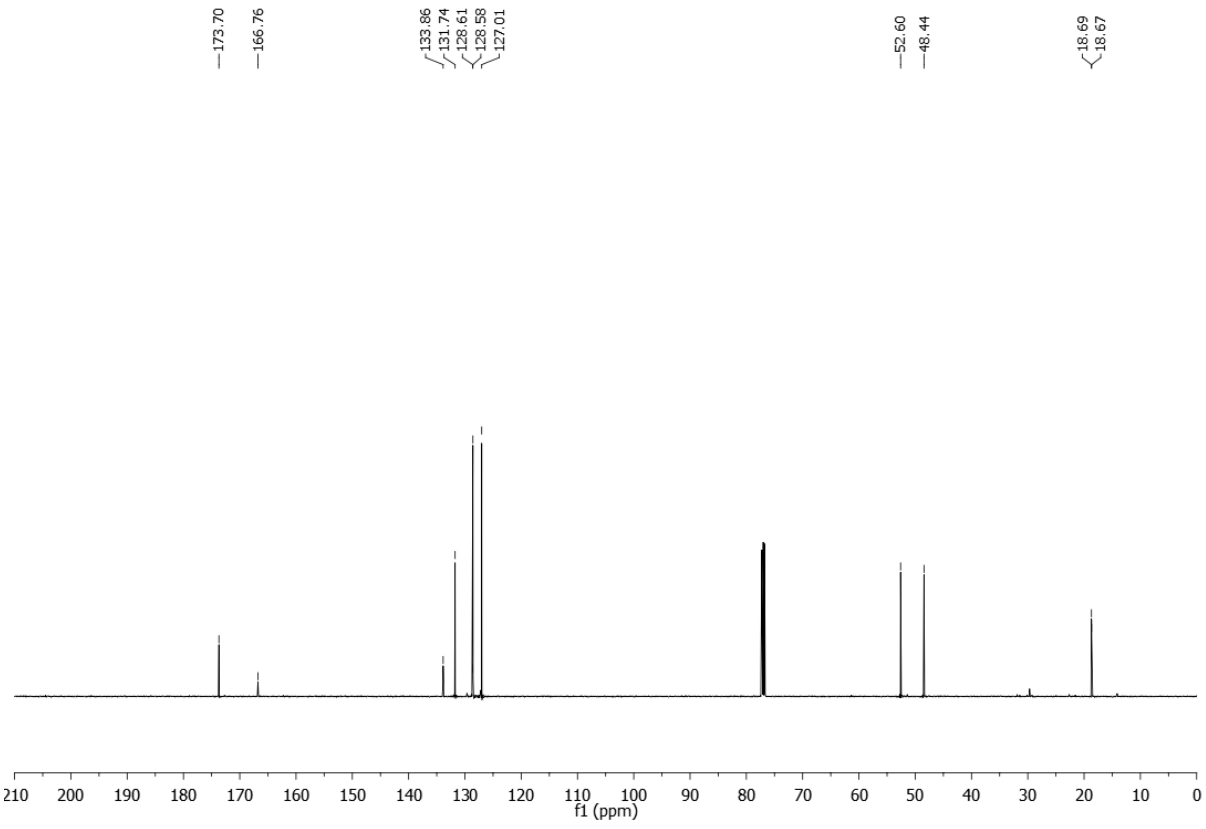


*Methyl benzoyl-L-alaninate (**5l**)*

^{1}H NMR (500 MHz, $CDCl_3$)

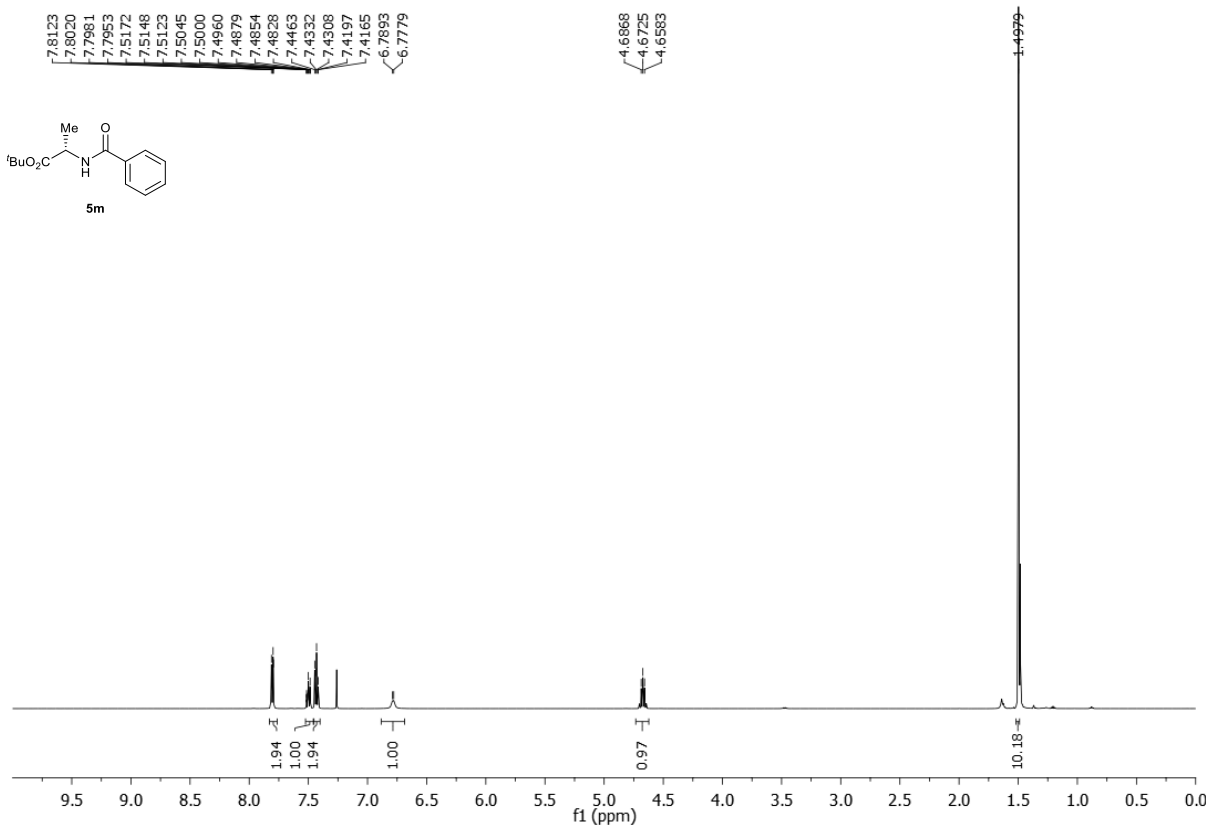


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

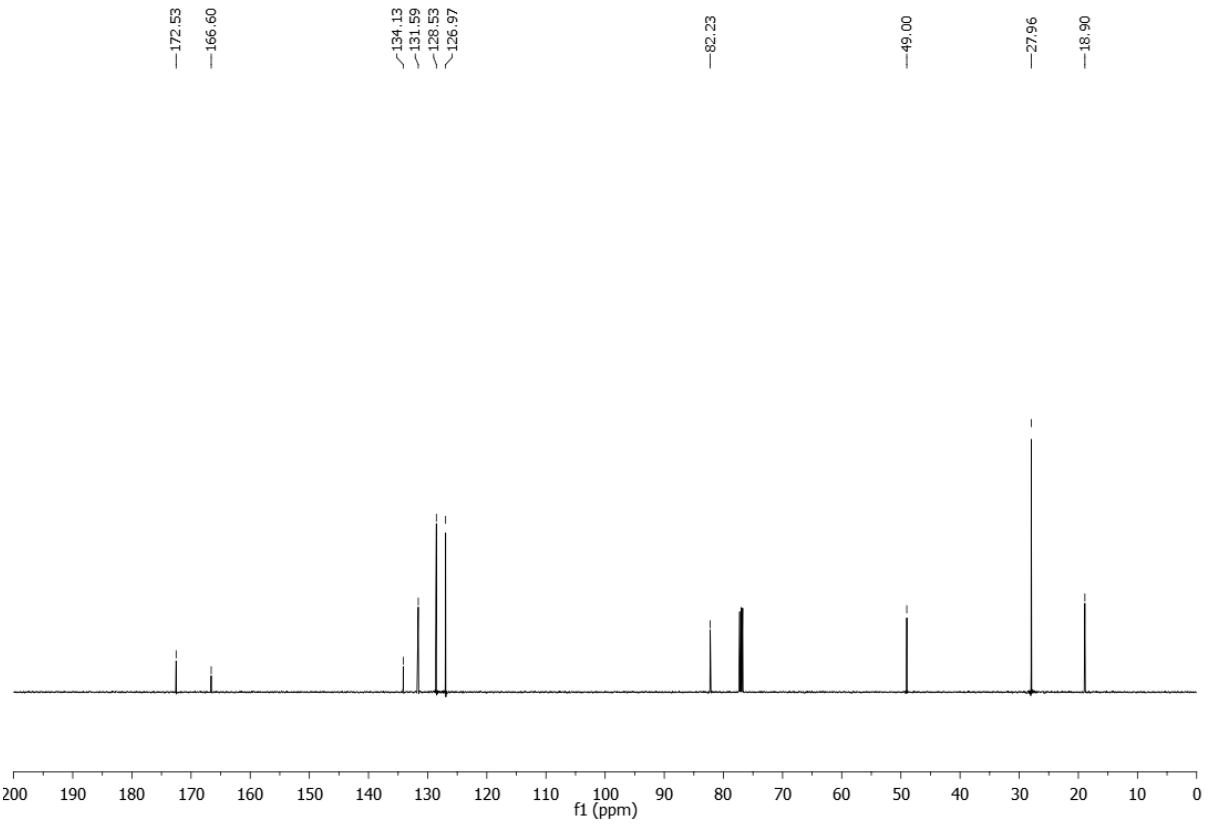


*tert-Butyl benzoyl-L-alaninate (**5m**)*

^{1}H NMR (500 MHz, $CDCl_3$)

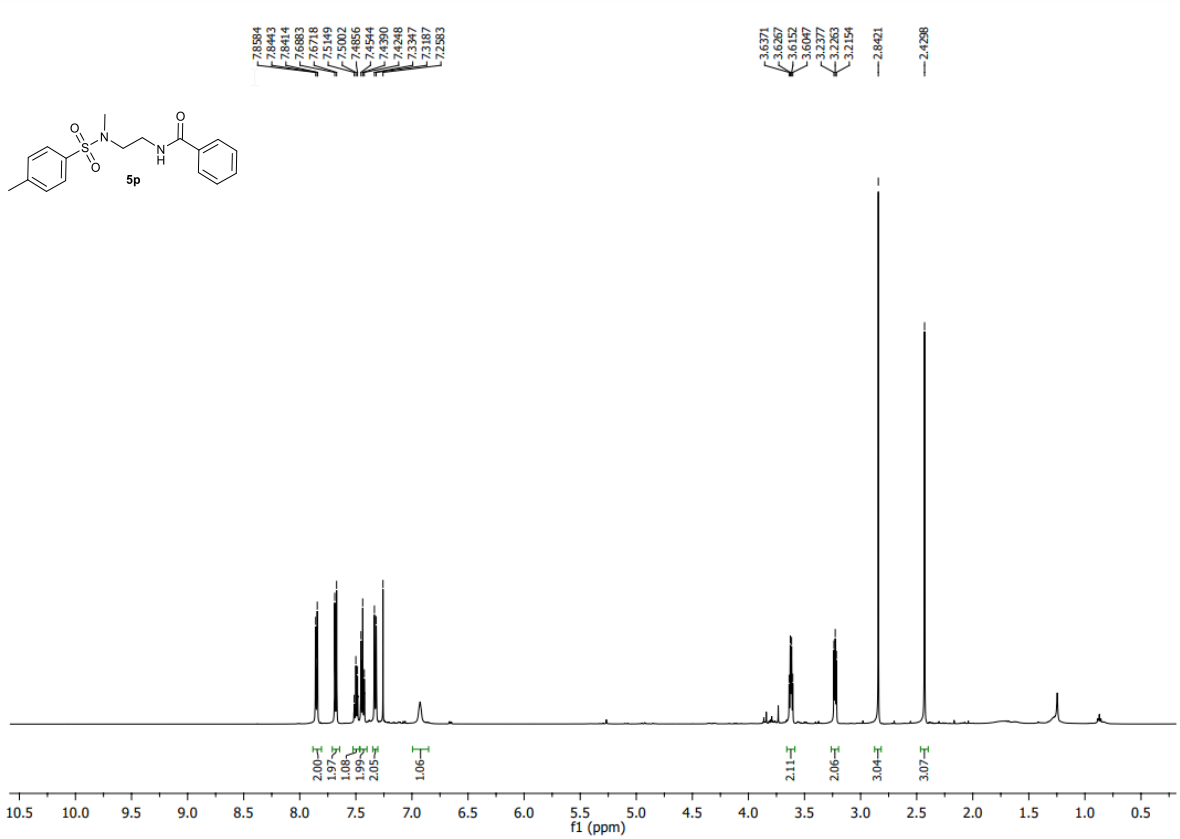


^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)



*N-(2-((N,4-dimethylphenyl)sulfonamido)ethyl)-N-tosylbenzamide (**5q**)*

^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)