Supporting Information

PQS-Enabled Visible-Light Iridium Photoredox Catalysis in Water at Room Temperature

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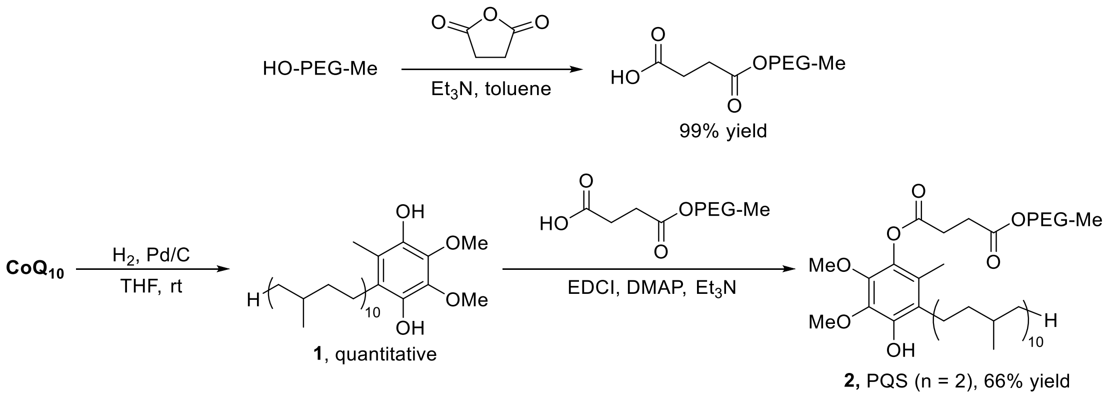
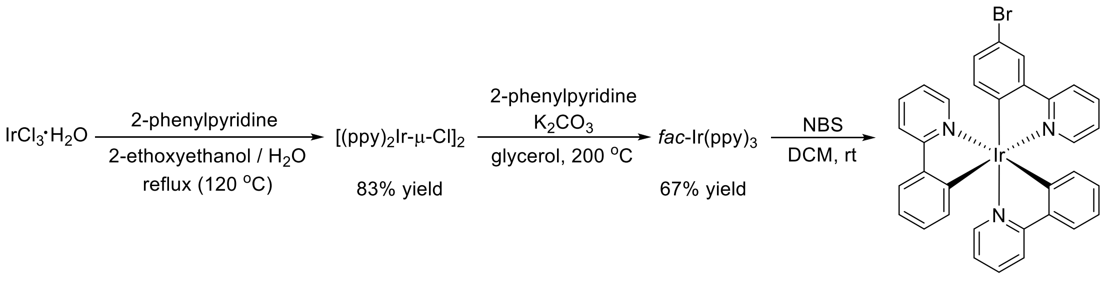
1. General Information

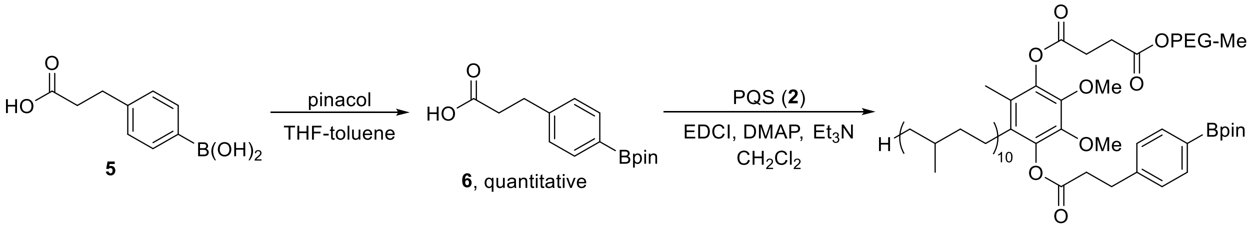
Unless otherwise noted, all commercially available reagents were used without further purification. HPLC grade water was degassed by sparging with argon prior to use. All reactions were performed under an atmosphere of argon. Photoreactions were conducted in a 5 mL microwave vial irradiated with a 5 W blue LED lamp. The LED lamp (QB-4038) is produced by Weelte lighting factory of Longgang, Shenzhen, and was purchased from Fantesen Household Light at taobao.com. NMR solvents were purchased from Cambridge Isotopes Laboratories. $CDCl_3$ was dried over activated 4 Å molecular sieves and then stored over dried 4 Å sieves. Column chromatography was carried out using Silica gel 60 (230 – 400 mesh). Analytical thin layer chromatography (TLC) was done using Silica Gel 60 F_{254} glass plates. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded at 22 °C on Varian Unity INOVA spectrometers at 400, 500, or 600 MHz. Chemical shifts in ^{1}H NMR spectra are reported in parts per million (ppm) on the δ scale from an internal standard of residual chloroform (7.26 ppm) or DMSO-d_6 (2.50 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sex = sextet, sep = septet, m = multiplet, br = broad w = weak), coupling constant in Hertz (Hz), and integration. Matrix Assisted Laser Desorption/Ionization (MALDI) analyses were recorded on a Microflex LRF MALDI TOF mass spectrometer with α-Cyano-4-hydroxycinnamic acid (CHCA) as matrix. High-resolution mass spectral analyses were obtained using a quadrupole/TOF instrument (API) for ESI and a double-focusing magnetic sector instrument for EI. A 2 wt% TPGS-750-M/H2O solution was prepared by dissolving 4 g TPGS-750-M in 196 g water (HPLC grade), followed by degassing with argon. TPGS-750-M was made as previously described,[1] and is available from Sigma-Aldrich (catalog #733857). Cryo-TEM images were obtained using a FEI Tecnai F30 300 kV field emission gun transmission electron microscope. UV-vis absorption measurements were performed using a Perkin Elmer Lambda 750 spectrophotometer at room temperature. Photoluminescence (PL) spectra were processed in the MD-5020 with Xe lamp made from Photo Technology International at room temperature. The electrochemical cyclic voltammetry (CV) was recorded on a CHI760D electrochemical workstation (Chenhua Shanghai) with Pt plate as working electrode, Pt slice as counter electrode, and a saturated calomel electrode as reference electrode in a solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, 0.1 M) in acetonitrile at a scan rate of 50 mV s^{-1}. Ferrocene/ferrocenium (Fc/Fc^+) was used as the internal reference.

2. Preparation of the PQS-Attached Photocatalyst 8





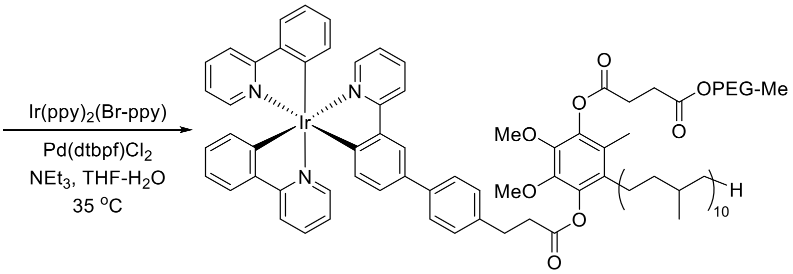
4, Ir(ppy)$_2$(Br-ppy), 98% yield



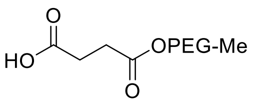
5

6, quantitative

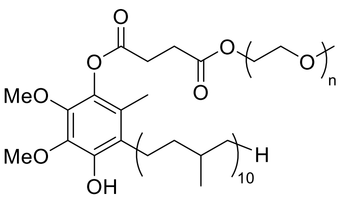
7, 87% yield



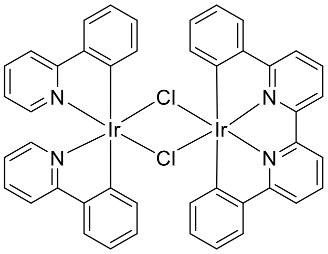
8, 80% yield



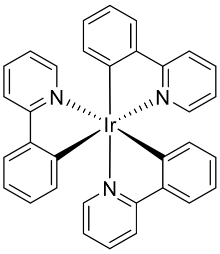
Synthesis of mono-PEGylated succinic acid. Mono-PEGylated succinic acid was prepared according to the reported procedure.[2] Poly(ethylene glycol) methyl ether-2000 (15 g, 7.5 mmol) and succinic anhydride (1.50 g, 15 mmol) were weighed into a 100 mL round-bottom flask and dissolved in toluene (7.5 mL). Triethylamine (0.53 mL, 3.75 mmol) was then added at rt with stirring. The reaction was stirred at 60 °C for 8 h. Water was added and the mixture was extracted with CH_2Cl_2. The combined organic layers were washed with 1 N HCl and brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* to afford mono-PEGylated succinic acid (15.59 g, 99% yield) as a white waxy solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.23 – 4.20 (m, 2H), 3.76 – 3.45 (s, PEG), 3.34 (s, 3H), 2.66 – 2.54 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.9, 172.1, 72.0 – 69.0 (m, PEG), 63.8, 59.0, 29.4, 28.9. Analytical data are in accordance with the literature values.[2]



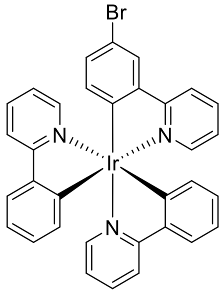
Synthesis of PQS (**2**). CoQ$_{10}$ (1.38 g, 1.6 mmol) was weighed into a 100 mL round-bottom flask and dissolved in THF (40 mL). Pd/C (5% w/w, 300 mg) was then added slowly. The well-stirred suspension was fitted to a source of hydrogen (1 atm) and stirred at 22 °C for 12 h. The mixture was filtered through a pad of Celite. The filtrate was stirred under argon at 0 °C, before mono-PEGylated succinic acid (2.1 g, 1 mmol) was added, followed by EDCI (384 mg, 2 mmol), DMAP (37 mg, 0.3 mmol) and Et_3N (101 mg, 1 mmol). The mixture was stirred at rt under argon for 12 h, before saturated aqueous NH_4Cl was added and extracted with CH_2Cl_2. The combined organic layers were washed with water and brine, dried, and concentrated *in vacuo*, affording a yellow liquid, which was purified by flash column chromatography on silica gel eluting with CH_2Cl_2 to 7% MeOH/CH_2Cl_2 gradient to afford PQS (**2**) (1.97 g, 66% yield, mixture of two regioisomers) as a white waxy solid. ^1H NMR (500 MHz, $CDCl_3$) δ 5.78 (s, 0.3H), 5.69 (s, 0.7H), 4.24 (td, *J* = 4.7, 2.3 Hz, 2H), 3.87 (s, 3H), 3.77 (s, 3H), 3.70 – 3.45 (m, PEG), 3.35 (s, 3H), 2.91 (t, *J* = 6.9 Hz, 2H), 2.79 – 2.75 (m, 2H), 2.13 (s, 1H), 2.01 (s, 2H), 1.55 – 0.99 (m, 68H), 0.95 – 0.75 (m, 33H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.1, 170.8, 145.0, 141.9, 137.6, 135.2, 124.5, 123.2, 72.0 – 69.1 (m, PEG), 64.0, 61.0, 60.7, 59.1, 39.4, 37.5, 37.5, 37.4, 37.4, 37.3, 37.2, 33.4, 33.4, 32.9, 32.8, 32.8, 29.2, 28.8, 28.0, 24.8, 24.5, 24.2, 22.8, 22.7, 19.9, 19.8, 19.8, 19.7, 19.7, 19.6, 11.8, 11.2. MS (MALDI-TOF) calcd. for $C_{152}H_{294}O_{51}Na$ (when n = 44) $[M + Na]^+$ *m/z* 2960.034, found 2960.667.



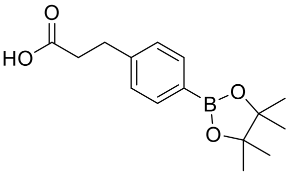
Synthesis of $[(ppy)_2Ir\text{-}\mu\text{-}Cl]_2$. $[(ppy)_2Ir\text{-}\mu\text{-}Cl]_2$ was prepared according to the reported procedure.[3] A mixture of iridium chloride hydrate (388 mg, 1.2 mmol) and 2-phenylpyridine (760 mg, 4.8 mmol) in 2-methoxyethanol/H_2O (30 mL/10 mL) was stirred at 120 °C under argon for 24 h. After cooling to rt, the resulting precipitate was filtered off, washed with water and acetone, then dried *in vacuo* to afford $[(ppy)_2Ir\text{-}\mu\text{-}Cl]_2$ (533 mg, 83% yield) as a bright yellow powder.



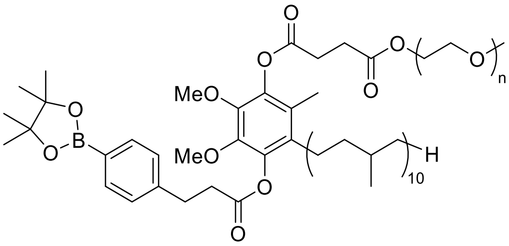
Synthesis of *fac*-$Ir(ppy)_3$ (3). $Ir(ppy)_3$ was prepared according to the reported procedure.[3] $[(ppy)_2Ir\text{-}\mu\text{-}Cl]_2$ (429 mg, 0.4 mmol), 2-phenylpyridine (186 mg, 1.2 mmol), and K_2CO_3 (554 mg, 4 mmol) were stirred in glycerol (33 mL) at 200 °C under argon for 20 h. After cooling to rt, water was added. The resulting precipitate was filtered off, washed with methanol, followed by ether and hexanes. The crude product was purified by flash column chromatography on silica gel, eluting with 1:2 hexane/ CH_2Cl_2 to afford *fac*-$Ir(ppy)_3$ (351 mg, 67% yield) as a bright yellow powder. ^1H NMR (500 MHz, DMSO-d_6) δ 8.11 (dt, *J* = 8.4, 1.1 Hz, 3H), 7.84 – 7.68 (m, 6H), 7.47 (ddd, *J* = 5.5, 1.7, 0.8 Hz, 3H), 7.11 (ddd, *J* = 7.1, 5.5, 1.3 Hz, 3H), 6.79 (ddd, *J* = 7.9, 6.9, 1.6 Hz, 3H), 6.66 (dtd, *J* = 14.4, 7.6, 1.5 Hz, 6H). Analytical data are in accordance with the literature values.[4]



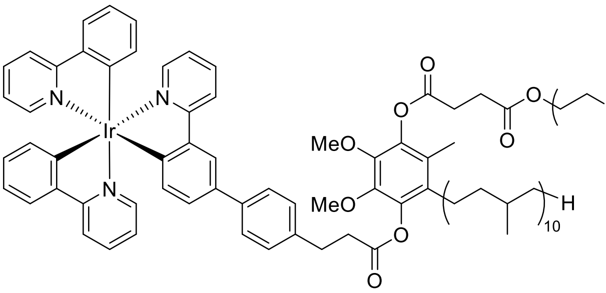
Synthesis of Ir(ppy)$_2$(Br-ppy). Ir(ppy)$_2$(Br-ppy) was prepared according to the reported procedure.[5] Ir(ppy)$_3$ (167 mg, 0.25 mmol) was dissolved in CH_2Cl_2 (38 mL). The solution was stirred vigorously in the dark at rt, while NBS (38 mg, 0.25 mmol) dissolved in CH_2Cl_2 (3 mL) was added dropwise. The mixture was kept in the dark and stirred for another 15 h. Then it was concentrated under reduced pressure, followed by the addition of ethanol. The precipitate was filtered off, washed with ethanol and ethyl ether, and dried *in vacuo* to afford Ir(ppy)$_2$(Br-ppy) and side products (180 mg) as a bright yellow powder, which was used in the Suzuki-Miyaura coupling without further purification. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.22 (t, J = 6.9 Hz, 1H), 8.17 – 8.07 (m, 2H), 7.92 (dd, J = 7.0, 2.1 Hz, 1H), 7.86 – 7.67 (m, 5H), 7.53 – 7.39 (m, 3H), 7.21 – 7.08 (m, 3H), 6.89 – 6.76 (m, 3H), 6.74 – 6.50 (m, 5H). MS (MALDI-TOF) calcd. for $C_{33}H_{23}N_3BrIr$ $[M]^+$ m/z 733.071, found 732.948. Analytical data are in accordance with the literature values.[5]



Synthesis of 3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propanoic acid (**6**). Compound **6** was prepared using a modified procedure according to the reported literature.[6] 3-(4-boronophenyl)propanoic acid (291 mg, 1.5 mmol) and pinacol (177 mg, 1.5 mmol) were weighed into a 100 mL round-bottom flask. THF (25 mL) and toluene (25 mL) were added. The resulting mixture was evaporated under reduced pressure at 45 °C to dryness. Solvents addition and evaporation were repeated two more times. The resulting residue was dried *in vacuo* to afford 3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propanoic acid (**6**, 414 mg, quantitative) as a white solid, which can be used without further purification. ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.13 (br, 1H), 7.58 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.1 Hz, 2H), 2.83 (t, J = 7.5 Hz, 2H), 2.53 (t, J = 7.6 Hz, 2H), 1.28 (s, 12H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 173.6, 144.5, 134.5, 127.8, 83.5, 34.9, 30.5, 24.7. HRMS (ESI-TOF) calcd. for $C_{15}H_{21}O_4BNa$ $[M + Na]^+$ m/z 299.1433, found 299.1418.

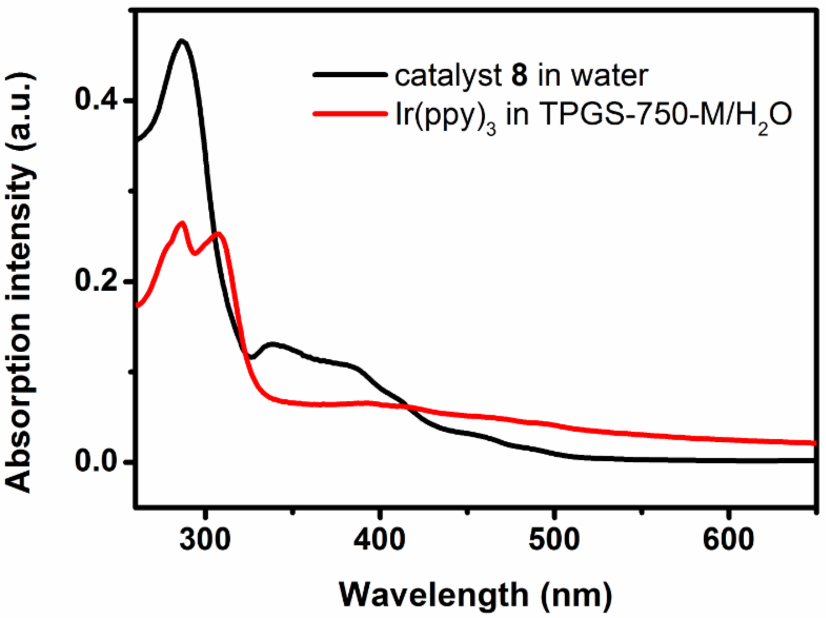


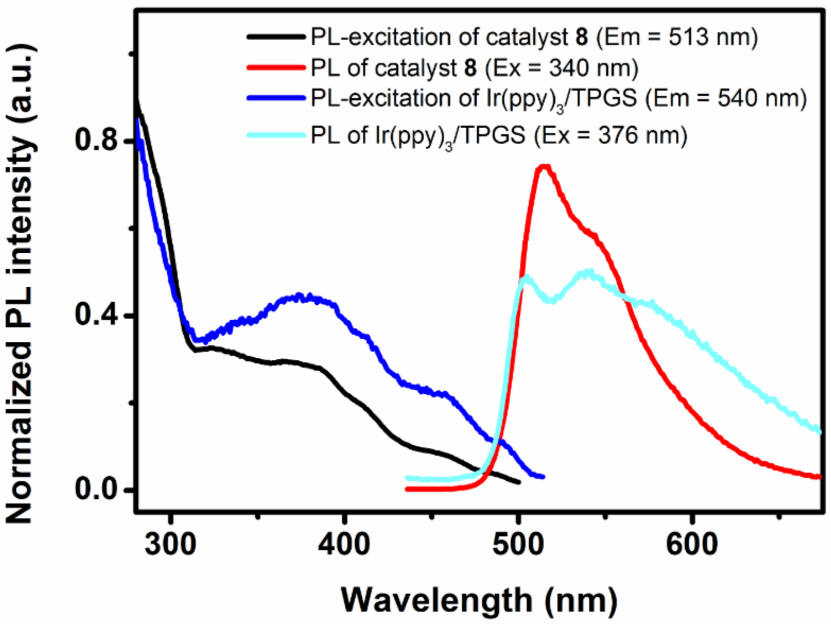
Synthesis of Compound 7. 3-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propanoic acid (**7**, 276 mg, 1.0 mmol) was dissolved in CH_2Cl_2 (10 mL) and cooled to 0 °C. PQS (**2**, 1.79 g, 0.6 mmol) was added, followed by DMAP (25 mg, 0.2 mmol), EDCI (231 mg, 1.2 mmol), and triethylamine (61 mg, 0.6 mmol). The resulting mixture was stirred at rt for 20 h, and water was then added. Water was added to the reaction mixture and extracted with CH_2Cl_2. The combined organic layers were washed with saturated $NaHCO_3$, water, brine, dried and concentrated *in* *vacuo* affording a colorless liquid, which was purified by flash column chromatography on silica gel, eluting with CH_2Cl_2 to 6% MeOH/CH_2Cl_2 gradient to afford the compound **7** (1.70 g, 87% yield) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, J = 7.9 Hz, 2H), 7.26 (d, J = 7.9 Hz, 2H), 4.27 – 4.23 (m, 2H), 3.78 (s, 3H), 3.73 (s, 3H), 3.71 – 3.46 (m, PEG), 3.36 (s, 3H), 3.09 (dd, J = 9.8, 6.1 Hz, 2H), 2.91 (dtd, J = 11.4, 8.8, 7.8, 5.5 Hz, 4H), 2.78 (t, J = 6.9 Hz, 2H), 2.04 (s, 2H), 1.95 (s, 1H), 1.57 – 0.97 (m, 80H), 0.95 – 0.66 (m, 33H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.1, 171.0, 170.3, 143.6, 143.3, 140.8, 140.3, 135.2, 135.2, 129.9, 127.8, 127.8, 124.5, 83.8, 72.0 – 69.1 (m, PEG), 64.0, 60.8, 60.7, 59.1, 39.5, 37.6, 37.6, 37.5, 37.5, 37.5, 37.5, 37.5, 37.4, 37.4, 37.2, 35.4, 33.4, 32.9, 32.9, 32.9, 32.9, 32.8, 31.2, 29.1, 28.9, 28.1, 25.0, 24.9, 24.6, 24.5, 22.8, 22.7, 19.9, 19.9, 19.8, 19.8, 19.8, 19.7, 19.7, 19.6, 19.6, 12.0. MS (MALDI-TOF) calcd. for $C_{167}H_{313}O_{54}BNa$ (when n = 44) $[M + Na]^+$ *m/z* 3218.177, found 3218.351.



Synthesis of PQS-attached iridium complex (**8**). Pd(dtbpf)Cl_2 (4 mg, 10 mol %) was weighed into a tube. THF (0.8 mL), water (0.8 mL), and triethylamine (30 mg) were added. The mixture was stirred and heated with a heat gun for 1 min. After it was cooled to rt, compound **7** (163 mg, 0.05 mmol) and Ir(ppy)$_2$(Br-ppy) (45 mg, 0.06 mmol) were added. The resulting mixture was stirred under argon at 35 °C for 18 h. After the reaction, saturated aqueous NH_4Cl was added and the mixture was extracted with CH_2Cl_2. The combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated under vacuum. The crude product was purified by flash column chromatography on silica gel, eluting with CH_2Cl_2 to 9% MeOH/CH_2Cl_2 gradient to afford catalyst **8** (150 mg, 80% yield) as a dark yellow waxy solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 8.1 Hz, 2H), 7.87 (dd, J = 14.4, 7.1 Hz, 3H), 7.71 – 7.48 (m, 9H), 7.28 (d, J = 8.6 Hz, 2H), 7.10 (d, J = 7.9 Hz, 2H), 6.87 (ddt, J = 19.9, 13.9, 7.5 Hz, 9H), 4.29 – 4.24 (m, 2H), 3.79 (s, 3H), 3.73 (s, 3H), 3.71 – 3.47 (m, PEG), 3.37 (s, 3H), 3.13 – 3.07 (m, 2H), 2.99 – 2.90 (m, 4H), 2.82 – 2.77 (m, 2H), 2.06 (s, 3H), 1.56 – 0.99 (m, 68H), 0.98 – 0.67 (m, 33H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.1, 171.2, 170.3, 166.9, 166.8, 166.7, 161.1, 161.0, 147.3, 147.2, 147.1, 144.4, 143.8, 143.7, 143.3, 143.3, 140.8, 140.7, 140.4, 137.9, 137.5, 137.2, 137.2, 136.1, 136.1, 132.3, 130.0, 129.9, 128.8, 128.7, 128.7, 126.6, 126.6, 124.5, 124.0, 122.4, 122.2, 122.1, 122.0, 120.0, 119.0, 118.9, 72.1 – 69.2 (m, PEG), 64.1, 60.8, 60.7, 59.2, 39.5, 37.7, 37.6, 37.6, 37.6, 37.5, 37.5, 37.4, 37.3, 35.7, 33.5, 32.9, 32.9, 30.7, 29.8, 29.2, 28.9, 28.1, 27.5, 24.9, 24.9, 24.6, 22.9, 22.8, 19.9, 19.9, 19.8, 12.1. MS (MALDI-TOF) calcd. for $C_{194}H_{324}O_{52}N_3Ir$ (when n = 44) $[M]^+$ *m/z* 3723.250, found 3722.598.

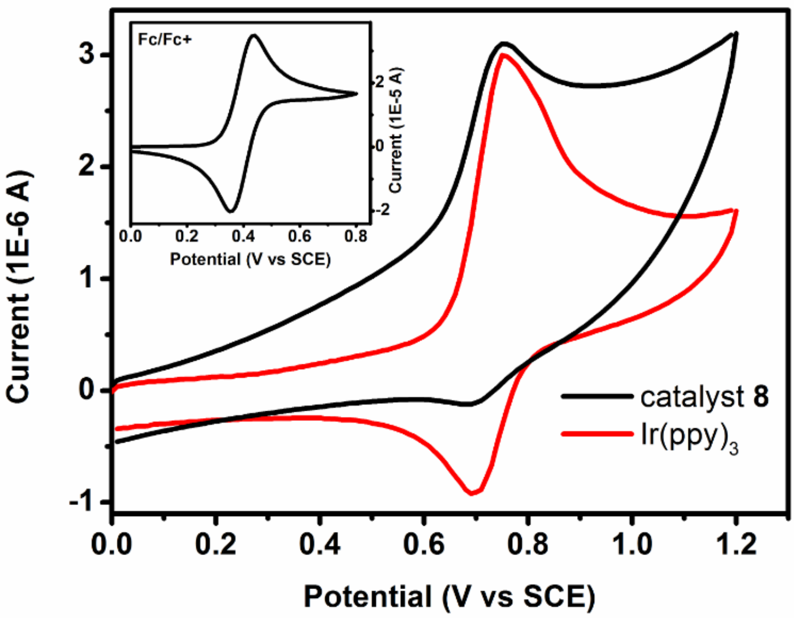
3. UV-Vis Absorptions and Photoluminescence Spectra





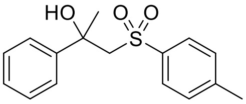
Note: For both UV-vis and photoluminescence measurements, aqueous solutions were processed with the concentration of 10 μM on the basis of Iridium content for both catalyst **8** and *fac*-Ir(ppy)$_3$/TPGS composite. The molar ratio of Ir to TPGS-750M was kept at 3:8, in accordance of the ratio as applied in the photoredox catalysis setting.

4. CV Curve of Catalyst 8 and Ir(ppy)$_3$



5. General Methods and Product Characterization

Photocatalytic difunctionalization of alkenes under micellar catalysis. Aryl sulfonyl chloride (0.375 mmol) and PQS-attached photocatalyst **8** (10 mg, 1 mol %) were added to a reaction vial containing a PTFE coated magnetic stir bar. The vial was closed with a rubber septum and sealed with parafilm. It was then evacuated and backfilled with dry argon (this operation was repeated three times). Degassed water (0.5 mL) was added, followed by alkene (0.25 mmol). The resulting mixture was stirred under the irradiation with a blue LED lamp (5 W) at rt. After a reaction time of 18 h, the mixture was diluted with EtOAc (5 mL), and filtered through a bed of silica gel layered over Celite. The bed was further washed with EtOAc to collect the product. The volatiles were removed under reduced pressure, and the crude product was purified by flash column chromatography on silica gel using hexane and ethyl acetate as eluents to afford the title compounds.



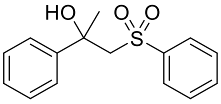
2-Phenyl-1-tosylpropan-2-ol (**11a**).

White solid, yield 90% (65 mg), R_f = 0.31 (3:7, EtOAc/hexanes).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.3 Hz, 2H), 7.33 – 7.27 (m, 2H), 7.18 (td, *J* = 7.8, 6.5, 4.1 Hz, 5H), 4.65 (br, 1H), 3.74 – 3.55 (m, 2H), 2.38 (s, 3H), 1.70 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6, 144.6, 137.4, 129.8, 128.4, 127.7, 127.2, 124.7, 73.3, 66.8, 30.9, 21.7.

Analytical data are in accordance with literature values.[7]



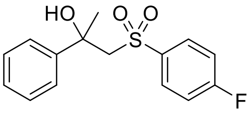
2-Phenyl-1-(phenylsulfonyl)propan-2-ol (**11b**).

White solid, yield 91% (63 mg), R_f = 0.28 (3:7, EtOAc/hexanes).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.55 (m, 2H), 7.55 – 7.50 (m, 1H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.30 – 7.26 (m, 2H), 7.21 – 7.11 (m, 3H), 4.63 (br, 1H), 3.77 – 3.60 (m, 2H), 1.70 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 140.3, 133.6, 129.2, 128.4, 127.6, 127.4, 124.7, 73.3, 66.7, 30.9.

Analytical data are in accordance with literature values.[7]



1-((4-Fluorophenyl)sulfonyl)-2-phenylpropan-2-ol (**11c**).

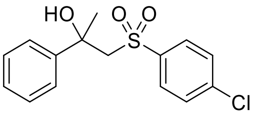
White solid, yield 83% (61 mg), R_f = 0.30 (3:7, EtOAc/hexanes).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.50 (m, 2H), 7.26 (dd, *J* = 6.6, 3.3 Hz, 2H), 7.19 (qd, *J* = 5.2, 4.4, 1.5 Hz, 3H), 7.06 – 6.98 (m, 2H), 4.56 (br, 1H), 3.80 – 3.63 (m, 2H), 1.69 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6 (d, *J* = 256.7 Hz), 144.2, 136.3 (d, *J* = 3.1 Hz), 130.6 (d, *J* = 9.7 Hz), 128.4, 127.4, 124.8, 116.4 (d, *J* = 22.8 Hz), 73.2 , 66.9, 31.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -103.6.

Analytical data are in accordance with literature values.[7]



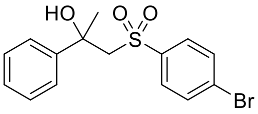
1-((4-Chlorophenyl)sulfonyl)-2-phenylpropan-2-ol (**11d**).

White solid, yield 91% (71 mg), R_f = 0.31 (3:7, EtOAc/hexanes).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 2H), 7.33 – 7.28 (m, 2H), 7.25 – 7.21 (m, 2H), 7.20 – 7.15 (m, 3H), 4.51 (br, 1H), 3.78 – 3.61 (m, 2H), 1.67 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1, 140.3, 138.6, 129.4, 129.1, 128.4, 127.4, 124.8, 73.2, 66.9, 31.2.

Analytical data are in accordance with literature values.[7]



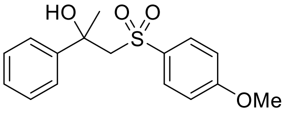
1-((4-Bromophenyl)sulfonyl)-2-phenylpropan-2-ol (**11e**).

White solid, yield 82% (73 mg), R_f = 0.37 (1:3, EtOAc/hexanes).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 2H), 7.40 – 7.35 (m, 2H), 7.25 – 7.21 (m, 2H), 7.18 (dt, *J* = 5.4, 2.5 Hz, 3H), 4.48 (br, 1H), 3.77 – 3.61 (m, 2H), 1.67 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 144.1, 139.2, 132.4, 129.2, 128.9, 128.5, 127.4, 124.8, 73.2, 66.8, 31.2.

Analytical data are in accordance with literature values.[7]

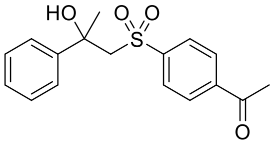


1-((4-Methoxyphenyl)sulfonyl)-2-phenylpropan-2-ol (**11f**).

White solid, yield 86% (66 mg), R_f = 0.22 (3:7, EtOAc/hexanes).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.46 (m, 2H), 7.34 – 7.26 (m, 2H), 7.18 (dddd, *J* = 13.8, 10.1, 5.6, 1.9 Hz, 3H), 6.87 – 6.76 (m, 2H), 4.66 (br, 1H), 3.83 (s, 3H), 3.72 – 3.56 (m, 2H), 1.69 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7, 144.6, 132.0, 129.9, 128.4, 127.3, 124.8, 114.4, 73.3, 66.9, 55.8, 31.0. Analytical data are in accordance with literature values.[7]

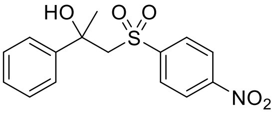


1-(4-((2-Hydroxy-2-phenylpropyl)sulfonyl)phenyl)ethan-1-one (**11g**).

White solid, yield 88% (70 mg), R_f = 0.24 (3:7, EtOAc/hexanes).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.26 – 7.21 (m, 2H), 7.14 (p, J = 3.3, 2.8 Hz, 3H), 4.47 (br, 1H), 3.81 – 3.64 (m, 2H), 2.61 (s, 3H), 1.68 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.7, 144.1, 143.9, 140.5, 128.8, 128.4, 128.1, 127.4, 124.8, 73.2, 66.8, 31.1, 27.0. Analytical data are in accordance with literature values.[7]

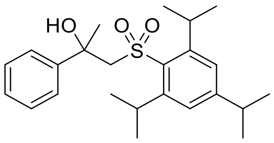


1-((4-Nitrophenyl)sulfonyl)-2-phenylpropan-2-ol (**11h**).

White solid, yield 83% (67 mg), R_f = 0.28 (3:7, EtOAc/hexanes).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.38 – 8.19 (m, 2H), 8.03 – 7.88 (m, 2H), 7.40 – 7.28 (m, 2H), 7.22 – 7.06 (m, 3H), 5.44 (br, 1H), 3.99 (d, J = 2.5 Hz, 2H), 1.60 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 149.8, 146.8, 146.4, 129.5, 127.6, 126.5, 125.0, 123.8, 71.7, 65.8, 30.0. Analytical data are in accordance with literature values.[7]



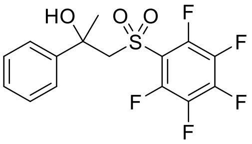
2-Phenyl-1-((2,4,6-triisopropylphenyl)sulfonyl)propan-2-ol (**11i**).

White solid, yield 72% (72 mg), R_f = 0.50 (3:7, EtOAc/hexanes).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 7.7 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.22 (t, J = 7.3 Hz, 1H), 7.15 (s, 2H), 4.69 (br, 1H), 4.15 (p, J = 6.7 Hz, 2H), 3.74 – 3.57 (m, 2H), 2.90 (p, J = 6.9 Hz, 1H), 1.89 (s, 3H), 1.39 – 1.16 (m, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 150.9, 145.7, 134.2, 128.7, 127.6, 124.7, 124.3, 74.2, 68.2, 34.5, 30.1, 29.8, 25.4, 25.1, 23.8, 23.8.

HRMS (ESI-TOF) calcd. for $C_{24}H_{34}O_3SNa$ $[M + Na]^+$ m/z 425.2126, found 425.2133.



1-((Perfluorophenyl)sulfonyl)-2-phenylpropan-2-ol (**11j**).

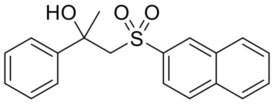
White solid, yield 84% (77 mg), R_f = 0.30 (1:4, EtOAc/hexanes).

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.42 (d, J = 7.3 Hz, 2H), 7.25 (t, J = 7.5 Hz, 2H), 7.21 – 7.15 (m, 1H), 5.63 (br, 1H), 4.18 – 3.94 (m, 2H), 1.62 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 146.1, 145.9 (m), 143.3 (m), 138.5 (m), 136.0 (m), 127.8, 126.8, 124.8, 116.3 (m), 71.7, 67.5, 30.1.

^{19}F NMR (376 MHz, DMSO-d_6) δ -136.83 (dp, *J* = 18.3, 6.9 Hz, 2F), -146.47 – -146.72 (m, 1F), -160.48 – -160.78 (m, 2F).

Analytical data are in accordance with literature values.[7]



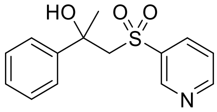
1-(Naphthalen-2-ylsulfonyl)-2-phenylpropan-2-ol (**11k**).

White solid, yield 76% (62 mg), R_f = 0.28 (3:7, EtOAc/hexanes).

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.04 (d, *J* = 1.8 Hz, 1H), 7.85 (t, *J* = 8.1 Hz, 2H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.68 – 7.61 (m, 2H), 7.58 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.28 – 7.23 (m, 2H), 7.04 (t, *J* = 7.8 Hz, 2H), 6.94 (t, *J* = 7.3 Hz, 1H), 4.68 (br, 1H), 3.84 – 3.66 (m, 2H), 1.70 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 144.3, 137.0, 135.2, 132.0, 129.9, 129.7, 129.6, 129.5, 128.2, 127.9, 127.7, 127.4, 124.7, 122.0, 73.3, 66.6, 31.1.

Analytical data are in accordance with literature values.[7]



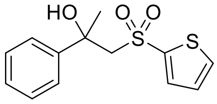
2-Phenyl-1-(pyridin-3-ylsulfonyl)propan-2-ol (**11l**).

Yellowish solid, yield 61% (42 mg), R_f = 0.20 (1:1, EtOAc/hexanes).

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.74 (d, *J* = 2.3 Hz, 1H), 8.70 (d, *J* = 4.8 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.19 (m, 3H), 7.15 (p, *J* = 3.9, 3.2 Hz, 3H), 4.41 (br, 1H), 3.77 (ddd, *J* = 65.1, 15.0, 0.8 Hz, 2H), 1.68 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 153.8, 148.8, 143.7, 136.8, 135.3, 128.5, 127.7, 124.9, 123.6, 73.1, 67.2, 31.3.

HRMS (ESI-TOF) calcd. for $C_{14}H_{15}NO_3SNa$ [M + Na]$^+$ *m/z* 300.0670, found 300.0661.



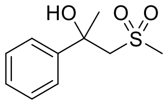
2-Phenyl-1-(thiophen-2-ylsulfonyl)propan-2-ol (**11m**).

White solid, yield 82% (58 mg), R_f = 0.23 (1:3, EtOAc/hexanes).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.58 (dd, *J* = 4.9, 1.3 Hz, 1H), 7.36 – 7.31 (m, 2H), 7.27 – 7.16 (m, 4H), 6.95 – 6.88 (m, 1H), 4.45 (br, 1H), 3.87 – 3.70 (m, 2H), 1.72 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 144.4, 141.4, 134.3, 134.3, 128.5, 127.9, 127.4, 124.7, 73.3, 68.2, 30.9.

HRMS (ESI-TOF) calcd. for $C_{13}H_{14}O_3S_2Na$ [M+ Na]$^+$ *m/z* 305.0282, found 305.0269.



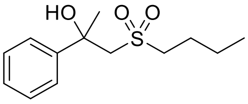
1-(Methylsulfonyl)-2-phenylpropan-2-ol (**11n**).

Colorless viscous oil, yield 62% (33 mg), R_f = 0.18 (3:7, EtOAc/hexanes).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.47 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.34 – 7.27 (m, 1H), 4.36 (br, 1H), 3.51 (dd, *J* = 101.2, 15.0 Hz, 2H), 2.42 (s, 3H), 1.72 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 144.7, 128.8, 127.8, 124.9, 72.6, 65.7, 43.1, 30.6.

Analytical data are in accordance with literature values.[7]



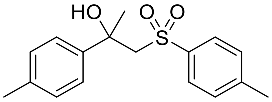
1-(*n*-Butylsulfonyl)-2-phenylpropan-2-ol (**11o**).

Colorless viscous oil, yield 69% (44 mg), R$_f$ = 0.34 (3:7, EtOAc/hexanes).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.51 – 7.43 (m, 2H), 7.38 (dd, *J* = 8.6, 6.9 Hz, 2H), 7.34 – 7.27 (m, 1H), 4.53 (br, 1H), 3.44 (dd, *J* = 118.6, 14.8 Hz, 2H), 2.45 – 2.34 (m, 2H), 1.73 (s, 3H), 1.68 – 1.52 (m, 2H), 1.24 (h, *J* = 7.3 Hz, 2H), 0.82 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 144.9, 128.7, 127.7, 124.8, 72.7, 63.3, 63.3, 54.8, 54.8, 30.6, 23.7, 21.5, 13.4.

HRMS (ESI-TOF) calcd. for $C_{13}H_{20}O_3SNa$ [M + Na]$^+$ *m/z* 279.1031, found 279.1029.



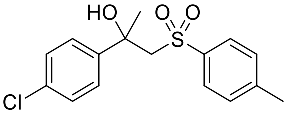
2-(*p*-Tolyl)-1-tosylpropan-2-ol (**11p**).

White solid, yield 76% (58 mg), R$_f$ = 0.33 (3:7, EtOAc/hexanes).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.47 (d, *J* = 8.3 Hz, 2H), 7.15 (dd, *J* = 8.0, 4.9 Hz, 4H), 6.97 (d, *J* = 8.0 Hz, 2H), 4.58 (br, 1H), 3.71 – 3.55 (m, 2H), 2.39 (s, 3H), 2.28 (s, 3H), 1.68 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 144.5, 141.7, 137.5, 137.0, 129.7, 129.0, 127.7, 124.7, 73.2, 66.9, 30.9, 21.7, 21.0.

HRMS (ESI-TOF) calcd. for $C_{17}H_{20}O_3SNa$ [M + Na]$^+$ *m/z* 327.1031, found 327.1019.



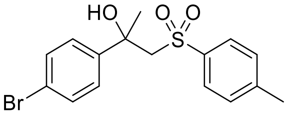
2-(4-Chlorophenyl)-1-tosylpropan-2-ol (**11q**).

White solid, yield 75% (61 mg), R$_f$ = 0.27 (3:7, EtOAc/hexanes).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.43 (d, *J* = 8.3 Hz, 2H), 7.21 – 7.13 (m, 4H), 7.13 – 7.07 (m, 2H), 4.69 (s, 1H), 3.71 – 3.55 (m, 2H), 2.41 (s, 3H), 1.64 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 144.9, 142.9, 137.1, 133.3, 129.9, 128.4, 127.7, 126.4, 72.9, 66.5, 31.1, 21.7.

Analytical data are in accordance with literature values.[7]



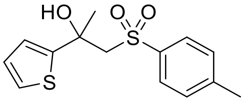
2-(4-Bromophenyl)-1-tosylpropan-2-ol (**11r**).

White solid, yield 74% (68 mg), R$_f$ = 0.27 (3:7, EtOAc/hexanes).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.41 (d, *J* = 8.3 Hz, 2H), 7.26 – 7.21 (m, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 7.12 – 7.08 (m, 2H), 4.70 (br, 1H), 3.72 – 3.55 (m, 2H), 2.42 (s, 3H), 1.63 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 144.9, 143.4, 137.0, 131.3, 129.9, 127.6, 126.7, 121.5, 72.9, 66.4, 31.2, 21.8.

HRMS (EI) calcd. for $C_{16}H_{17}BrO_3S$ [M]$^+$ *m/z* 368.0082, found 368.0086.



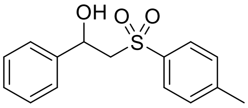
2-(Thiophen-2-yl)-1-tosylpropan-2-ol (**11s**).

Yellowish viscous oil, yield 64% (47 mg), R_f = 0.29 (3:7, EtOAc/hexanes).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.12 (dd, *J* = 5.0, 1.2 Hz, 1H), 6.81 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.76 (dd, *J* = 3.6, 1.2 Hz, 1H), 4.82 (br, 1H), 3.70 – 3.57 (m, 2H), 2.41 (s, 3H), 1.82 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.2, 144.9, 137.6, 130.0, 127.7, 126.9, 124.8, 123.1, 72.6, 67.3, 31.3, 21.7.

HRMS (ESI-TOF) calcd. for $C_{14}H_{16}O_3S_2Na$ $[M + Na]^+$ *m/z* 319.0439, found 319.0426.



1-Phenyl-2-tosylethan-1-ol (**11t**).

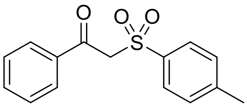
White solid, yield 51% (35 mg), R_f = 0.28 (3:7, EtOAc/hexanes).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.34 – 7.22 (m, 5H), 5.24 (d, *J* = 10.1 Hz, 1H), 3.75 (d, *J* = 1.9 Hz, 1H), 3.47 (dd, *J* = 14.4, 10.2 Hz, 1H), 3.31 (dd, *J* = 14.4, 1.8 Hz, 1H), 2.46 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 145.3, 140.8, 136.3, 130.2, 128.8, 128.4, 128.1, 125.7, 68.6, 64.1, 21.8.

Analytical data are in accordance with literature values.[7]

Photocatalytic sulfonylation of enols under micellar catalysis conditions. Sulfonyl chloride (0.375 mmol) and PQS-attached photocatalyst **8** (10 mg, 1 mol %) were added to a reaction vial containing a PTFE coated magnetic stir bar. The vial was closed with a rubber septum and sealed with parafilm. It was then evacuated and backfilled with dry argon (this operation was repeated three times). Degassed water (0.5 mL) was added, followed by enol acetate (0.25 mmol). The resulting mixture was stirred under the irradiation with a blue LED lamp (5 W) at rt. After a reaction time of 12 h, the mixture was diluted with EtOAc (5 mL), and filtered through a bed of silica gel layered over Celite. The bed was further washed with EtOAc to collect all the product. The volatiles were removed under reduced pressure, and the crude product was purified by flash column chromatography on silica gel using hexane and ethyl acetate as eluents to afford the title compounds.



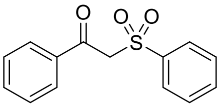
1-Phenyl-2-tosylethan-1-one (**13a**).

White solid, yield 86% (59 mg), R_f = 0.29 (3:7, EtOAc/hexanes).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 4.72 (s, 2H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.1, 145.3, 135.7, 135.7, 134.3, 129.8, 129.3, 128.8, 128.6, 63.6, 21.7.

Analytical data are in accordance with literature values.[8]



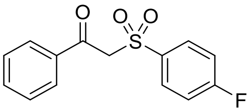
1-Phenyl-2-(phenylsulfonyl)ethan-1-one (**13b**).

White solid, yield 93% (61 mg), $R_f = 0.25$ (3:7, EtOAc/hexanes).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (ddd, *J* = 14.4, 8.5, 1.3 Hz, 4H), 7.68 – 7.59 (m, 2H), 7.54 (t, *J* = 7.7 Hz, 2H), 7.47 (t, *J* = 7.8 Hz, 2H), 4.74 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.1, 138.9, 135.8, 134.5, 134.3, 129.4, 129.3, 129.0, 128.7, 63.6.

Analytical data are in accordance with literature values.[9]



2-((4-Fluorophenyl)sulfonyl)-1-phenylethan-1-one (**13c**).

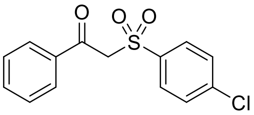
White solid, yield 92% (64 mg), $R_f = 0.27$ (1:3, EtOAc/hexanes).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.86 (m, 4H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.21 (t, *J* = 8.5 Hz, 2H), 4.74 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.1, 166.3 (d, *J* = 257.5 Hz), 135.7, 134.8 (d, *J* = 3.2 Hz), 134.6, 131.8 (d, *J* = 9.7 Hz), 129.4, 129.1, 116.7 (d, *J* = 22.7 Hz), 63.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -102.4.

Analytical data are in accordance with literature values.[10]



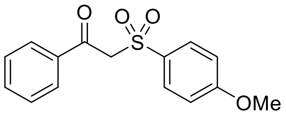
2-((4-Chlorophenyl)sulfonyl)-1-phenylethan-1-one (**13d**).

White solid, yield 85% (63 mg), $R_f = 0.36$ (3:7, EtOAc/hexanes).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.4 Hz, 2H), 7.83 (d, *J* = 8.7 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.56 – 7.44 (m, 4H), 4.74 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.0, 141.3, 137.2, 135.7, 134.7, 130.3, 129.7, 129.4, 129.1, 63.5.

Analytical data are in accordance with literature values.[8]



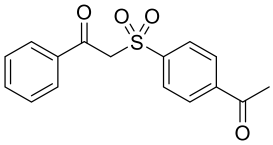
2-((4-Methoxyphenyl)sulfonyl)-1-phenylethan-1-one (**13e**).

White solid, yield 75% (54 mg), $R_f = 0.19$ (3:7, EtOAc/hexanes).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.89 (m, 2H), 7.84 – 7.75 (m, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.00 – 6.95 (m, 2H), 4.71 (s, 2H), 3.86 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.4, 164.2, 135.9, 134.4, 131.0, 130.3, 129.4, 128.9, 114.5, 63.9, 55.8.

Analytical data are in accordance with literature values.[8]

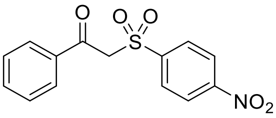


2-((4-Acetylphenyl)sulfonyl)-1-phenylethan-1-one (**13f**).

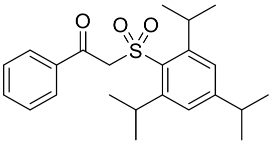
White solid, yield 81% (61 mg), $R_f = 0.29$ (2:3, EtOAc/hexanes).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.6 Hz, 2H), 8.00 (d, *J* = 8.6 Hz, 2H), 7.96 – 7.90 (m, 2H), 7.66 – 7.61 (m, 1H), 7.52 – 7.46 (m, 2H), 4.78 (s, 2H), 2.65 (s, 3H).

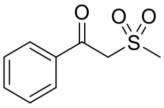
^{13}C NMR (101 MHz, CDCl$_3$) δ 196.7, 187.9, 142.4, 141.3, 135.7, 134.7, 129.4, 129.2, 129.1, 129.0, 63.3, 27.1.
Analytical data are in accordance with literature values.[11]



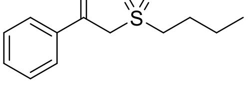
2-((4-nitrophenyl)sulfonyl)-1-phenylethan-1-one (**13g**).
White solid, yield 95% (73 mg), R$_f$ = 0.27 (3:7, EtOAc/hexanes).
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.45 (d, J = 8.8 Hz, 2H), 8.22 (d, J = 8.8 Hz, 2H), 7.96 (d, J = 7.7 Hz, 2H), 7.68 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.7 Hz, 2H), 5.61 (s, 2H).
^{13}C NMR (101 MHz, DMSO-d_6) δ 189.1, 150.5, 144.9, 135.4, 134.4, 129.9, 129.0, 128.8, 124.4, 61.8.
Analytical data are in accordance with literature values.[8]



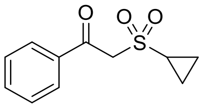
1-Phenyl-2-((2,4,6-triisopropylphenyl)sulfonyl)ethan-1-one (**13h**).
White solid, yield 83% (80 mg), R$_f$ = 0.50 (3:7, EtOAc/hexanes).
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.01 (d, J = 7.8 Hz, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.18 (s, 2H), 4.80 (s, 2H), 3.98 (p, J = 6.7 Hz, 2H), 2.91 (p, J = 6.9 Hz, 1H), 1.24 (dd, J = 9.9, 6.8 Hz, 18H).
^{13}C NMR (101 MHz, CDCl$_3$) δ 188.2, 154.3, 151.6, 136.1, 134.4, 132.4, 129.6, 128.9, 124.2, 65.3, 34.3, 29.9, 25.0, 23.6.
HRMS (ESI-TOF) calcd. for $C_{23}H_{30}O_3SNa$ [M + Na]$^+$ m/z 409.1813, found 409.1805.



2-(Methylsulfonyl)-1-phenylethan-1-one (**13i**).
White solid, yield 94% (47 mg), R$_f$ = 0.28 (2:3, EtOAc/hexanes).
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.99 (d, J = 7.8 Hz, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.7 Hz, 2H), 4.61 (s, 2H), 3.14 (s, 3H).
^{13}C NMR (101 MHz, CDCl$_3$) δ 189.2, 135.6, 134.7, 129.2, 129.0, 61.2, 41.8.
Analytical data are in accordance with literature values.[8]



2-(Butylsulfonyl)-1-phenylethan-1-one (**13j**).
White solid, yield 99% (59 mg), R$_f$ = 0.31 (3:7, EtOAc/hexanes).
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.00 (d, J = 8.1 Hz, 2H), 7.63 (t, J = 7.5 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 4.56 (s, 2H), 3.28 – 3.20 (m, 2H), 1.85 (td, J = 11.7, 9.9, 6.1 Hz, 2H), 1.48 (h, J = 7.4 Hz, 2H), 0.96 (t, J = 7.4 Hz, 3H).
^{13}C NMR (101 MHz, CDCl$_3$) δ 189.4, 135.8, 134.7, 129.4, 129.1, 59.6, 53.6, 23.9, 21.7, 13.6.
Analytical data are in accordance with literature values.[12]



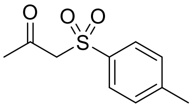
2-(Cyclopropylsulfonyl)-1-phenylethan-1-one (**13k**).

Colorless viscous oil, yield 95% (53 mg), R_f = 0.20 (3:7, EtOAc/hexanes).

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.00 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 4.64 (s, 2H), 2.74 (tt, *J* = 7.9, 4.8 Hz, 1H), 1.25 (tt, *J* = 6.7, 2.8 Hz, 2H), 1.09 – 1.04 (m, 2H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 188.9, 135.9, 134.6, 129.3, 129.0, 61.0, 31.0, 5.6.

Analytical data are in accordance with literature values.[8]



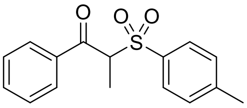
1-Tosylpropan-2-one (**13l**).

Colorless oil, yield 72% (38 mg), R_f = 0.22 (3:7, EtOAc/hexanes).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 4.13 (s, 2H), 2.44 (s, 3H), 2.39 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 196.2, 145.6, 135.8, 130.1, 128.3, 68.0, 31.6, 21.8.

Analytical data are in accordance with literature values.[13]



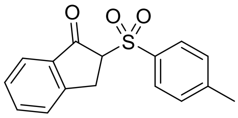
1-Phenyl-2-tosylpropan-1-one (**13m**).

White solid, yield 76% (55 mg), R_f = 0.33 (3:7, EtOAc/hexanes).

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.00 – 7.94 (m, 2H), 7.69 – 7.63 (m, 2H), 7.62 – 7.57 (m, 1H), 7.51 – 7.44 (m, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 5.15 (q, *J* = 6.9 Hz, 1H), 2.43 (s, 3H), 1.55 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 192.7, 145.5, 136.4, 134.1, 133.1, 129.9, 129.6, 129.3, 128.8, 65.1, 21.8, 13.3.

Analytical data are in accordance with literature values.[8]



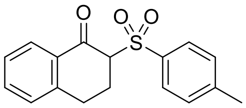
2-Tosyl-2,3-dihydro-*1H*-inden-1-one (**13n**).

White solid, yield 77% (55 mg), R_f = 0.23 (3:7, EtOAc/hexanes).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 7.7 Hz, 1H), 7.62 (td, *J* = 7.7, 1.1 Hz, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.42 – 7.31 (m, 3H), 4.26 (dd, *J* = 8.4, 3.4 Hz, 1H), 3.81 (dd, *J* = 18.2, 3.3 Hz, 1H), 3.53 (dd, *J* = 18.2, 8.4 Hz, 1H), 2.44 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 194.7, 152.0, 145.5, 136.0, 136.0, 134.7, 129.9, 129.4, 128.3, 126.5, 125.0, 68.9, 28.3, 21.9.

Analytical data are in accordance with literature values.[8]



2-Tosyl-3,4-dihydronaphthalen-1(*2H*)-one (**13o**).

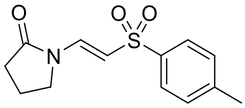
White solid, yield 73% (55 mg), $R_f = 0.31$ (3:7, EtOAc/hexanes).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.51 (td, *J* = 7.5, 1.4 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 6.7 Hz, 1H), 4.08 (t, *J* = 5.7 Hz, 1H), 3.52 (ddd, *J* = 16.9, 9.8, 4.7 Hz, 1H), 2.98 (dt, *J* = 17.0, 5.4 Hz, 1H), 2.87 (dtd, *J* = 14.2, 5.9, 4.8 Hz, 1H), 2.65 (ddt, *J* = 14.9, 10.2, 5.1 Hz, 1H), 2.46 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 188.9, 145.2, 143.7, 136.1, 134.6, 131.9, 129.8, 129.3, 129.1, 128.1, 127.2, 69.8, 26.7, 23.8, 21.9.

Analytical data are in accordance with literature values.[8]

Photocatalytic sulfonylation of an enamide in micellar media. 4-Methylbenzenesulfonyl chloride (72 mg, 0.375 mmol), Na_2HPO_4 (107 mg, 0.75 mmol), and PQS-attached photocatalyst **8** (10 mg, 1 mol %) were added to a reaction vial containing a PTFE coated magnetic stir bar. The vial was closed with a rubber septum and sealed with parafilm. It was then evacuated and backfilled with dry argon (this operation was repeated three times). Degassed water (0.5 mL) was added, followed by *N*-vinylpyrrolidone (0.25 mmol). The resulting mixture was stirred under the irradiation with a blue LED lamp (5 W) at rt. After a reaction time of 12 h, the mixture was diluted with EtOAc (5 mL), and filtered through a bed of silica gel layered over Celite. The bed was further washed with EtOAc to collect the product. The volatiles were removed under reduced pressure, and the crude product was purified by flash column chromatography on silica gel using hexane and ethyl acetate as eluents to afford the compound **15**.



(*E*)-1-(2-Tosylvinyl)pyrrolidin-2-one (**15**).

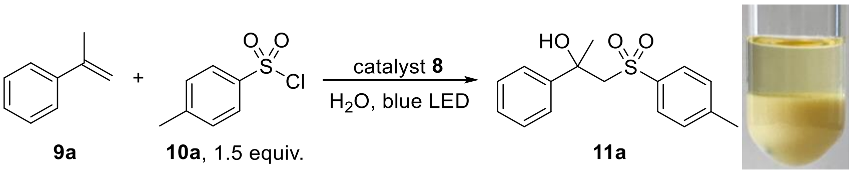
Yellowish solid, yield 24% (16 mg), $R_f = 0.15$ (1:1, EtOAc/hexanes).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 13.8 Hz, 1H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 5.72 (d, *J* = 13.8 Hz, 1H), 3.49 (t, *J* = 7.3 Hz, 2H), 2.54 (t, *J* = 8.2 Hz, 2H), 2.15 (p, *J* = 7.8 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 174.3, 144.1, 139.2, 135.9, 130.0, 127.4, 110.9, 45.3, 30.8, 21.7, 17.6.

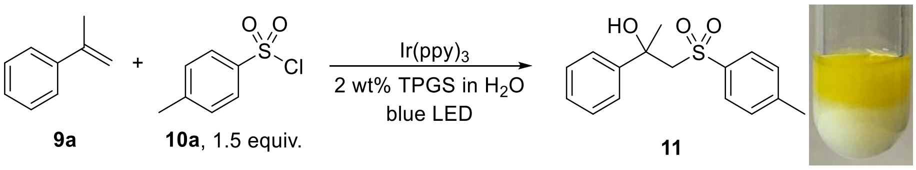
Analytical data are in accordance with literature values.[14]

6. Catalyst Recycling



4-Methylbenzenesulfonyl chloride (72 mg, 0.375 mmol) and PQS-attached photocatalyst **8** (10 mg, 1 mol %) were added to a reaction vial containing a PTFE coated magnetic stir bar. The vial was closed with a rubber septum and sealed with Parafilm. It was then evacuated and backfilled with dry argon (this operation was repeated three times). Degassed water (0.5 mL) was added, followed by α-methylstyrene (30 mg, 0.25 mmol). The resulting mixture was stirred under the irradiation with a blue LED lamp (5 W) at rt. After completion, the product was exacted with methyl *t*-butyl ether (0.5 mL x 3). The solvent was removed under reduced pressure, and the crude product was purified by flash column chromatography on silica gel to afford the pure product **11a** (65 mg, 90% yield).

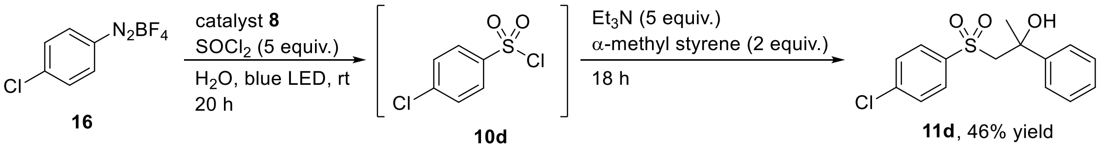
To the aqueous phase containing the catalyst was added 4-methylbenzenesulfonyl chloride (72 mg, 0.375 mmol). The mixture was then deoxygenated by three freeze-pump-thaw cycles before the addition of α-methylstyrene (30 mg, 0.25 mmol). Triethylamine (26 mg, 0.25 mmol, 1 equiv) was added. The resulting mixture was stirred under the irradiation with a blue LED lamp (5 W) at rt. The work up was conducted in exactly the same way as described for the first cycle, and the aqueous phase containing the catalyst was reused to start the next cycle. This reaction was repeated nine more times, each using the above substrates. Before the sixth run, 5 mg PQS-attached photocatalyst **8** (5 mg, 0.5 mol %) was added to the aqueous medium.



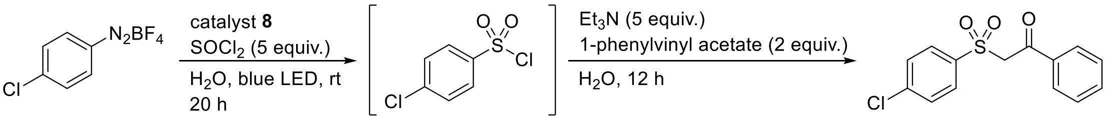
4-Methylbenzenesulfonyl chloride (72 mg, 0.375 mmol) and Ir(ppy)$_3$ (2 mg, 1 mol %) were added to a reaction vial containing a PTFE coated magnetic stir bar. The vial was closed with a rubber septum and sealed with parafilm. It was then evacuated and backfilled with dry argon (this operation was repeated three times). TPGS-750-M (2 wt %) in water (0.5 mL) was added, followed by α-methylstyrene (30 mg, 0.25 mmol). The resulting mixture was stirred under the irradiation with a blue LED lamp (5 W) at rt. After completion, the product was exacted with methyl *t*-butyl ether (0.5 mL x 3). The solvent was removed under reduced pressure, and the crude product was purified by flash column chromatography on silica gel to afford the pure product **11a** (60 mg, 83% yield).

To the aqueous phase was added 4-methylbenzenesulfonyl chloride (72 mg, 0.375 mmol). The mixture was then deoxygenated by three freeze-pump-thaw cycles before the addition of α-methylstyrene (30 mg, 0.25 mmol). Triethylamine (26 mg, 0.25 mmol, 1 equiv) was then added. The resulting mixture was stirred under the irradiation with a blue LED lamp (5 W) at rt. The work up was conducted in exactly the same way as described for the first cycle, and the aqueous phase was reused to start the next cycle.

7. 2-Step, 1-Pot Synthesis



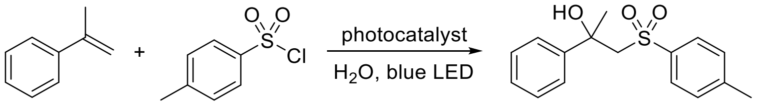
4-Chlorobenzenediazonium tetrafluoroborate (**16**, 57 mg, 0.25 mmol) and PQS-attached photocatalyst **8** (10 mg, 1 mol %) were added to a reaction vial containing a PTFE coated magnetic stir bar. The vial was closed with a rubber septum and sealed with Parafilm. It was then evacuated and backfilled with dry argon (this operation was repeated three times). Then, degassed water (0.5 mL) was added. Thionyl chloride (91 µL, 1.25 mmol) was added dropwise by syringe at 0 ^{o}C while stirring. The resulting mixture was stirred under the irradiation with a blue LED lamp (5 W) at rt. After a reaction time of 20 h, triethylamine (174 µL, 1.25 mmol) was added dropwise at 0 ^{o}C while stirring, followed by α-methylstyrene (30 mg, 0.5 mmol). The resulting mixture was then stirred under the irradiation with a blue LED lamp (5 W) at rt for another 18 h. The mixture was diluted with EtOAc (5 mL), and filtered through a bed of silica gel layered over Celite. The bed was further washed with EtOAc to collect additional product. The volatiles were removed under reduced pressure, and the crude product was purified by flash column chromatography on silica gel using hexane and ethyl acetate as eluents to afford the pure product **11d** in 46% yield.



16 **10d** **13d**, 62% yield

4-Chlorobenzenediazonium tetrafluoroborate (**16**, 57 mg, 0.25 mmol) and PQS-attached photocatalyst **8** (10 mg, 1 mol %) were added to a reaction vial containing a PTFE coated magnetic stir bar. The vial was closed with a rubber septum and sealed with Parafilm. It was then evacuated and backfilled with dry argon (this operation was repeated three times). Then, degassed water (0.5 mL) was added. Thionyl chloride (91 μL, 1.25 mmol) was added dropwise by syringe at 0 °C while stirring. The resulting mixture was stirred under the irradiation with a blue LED lamp (5 W) at rt. After a reaction time of 20 h, triethylamine (174 μL, 1.25 mmol) was added dropwise at 0 °C while stirring, followed by 1-phenylvinyl acetate (30 mg, 0.5 mmol). The resulting mixture was then stirred under the irradiation with a blue LED lamp (5 W) at rt for another 12 h. The mixture was diluted with EtOAc (5 mL), and filtered through a bed of silica gel layered over Celite. The bed was further washed with EtOAc to collect the product. The volatiles were removed under reduced pressure, and the crude product was purified by flash column chromatography on silica gel using hexane and ethyl acetate as eluents to afford the pure product **13d** in 62% yield.

8. E Factor Determination



9a **10a** extracted with 0.3 mL MTBE
11a, 76% isolated yield

4-Methylbenzenesulfonyl chloride (72 mg, 0.375 mmol) and PQS-attached photocatalyst **8** (10 mg, 1 mol %) were added to a reaction vial containing a PTFE coated magnetic stir bar. The vial was closed with a rubber septum and sealed with parafilm. It was then evacuated and backfilled with dry argon (this operation was repeated three times). Degassed water (0.5 mL) was added, followed by α-methylstyrene (30 mg, 0.25 mmol). The resulting mixture was stirred under the irradiation with a blue LED lamp (5 W) at rt. After completion, the product was exacted with methyl *tert*-butyl ether (0.3 mL). The solvent was removed under reduced pressure, and the crude product was purified by flash column chromatography on silica gel to afford the pure product **11a** (55 mg, 76% yield).

$$\begin{aligned}\text{E factor} &= \frac{total\ organic\ solvent\ wastes\ (kg)}{product\ (kg)} \\ &= \frac{MTBE\ (extraction)}{isolated\ pure\ product} \\ &= \frac{222.2\ mg}{55\ mg} \\ &= 4.0\end{aligned}$$

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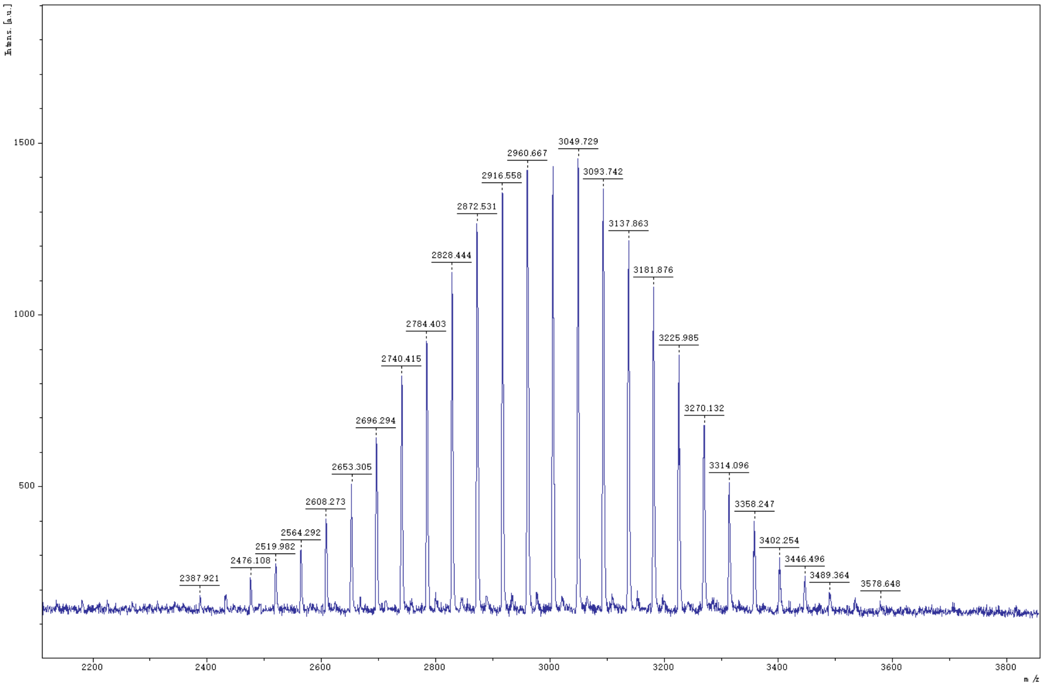
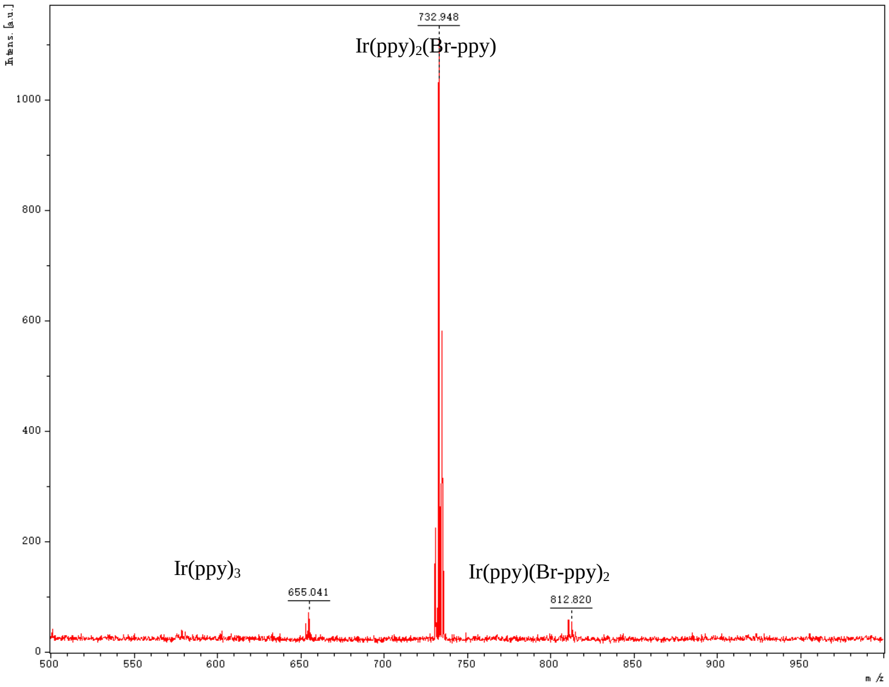
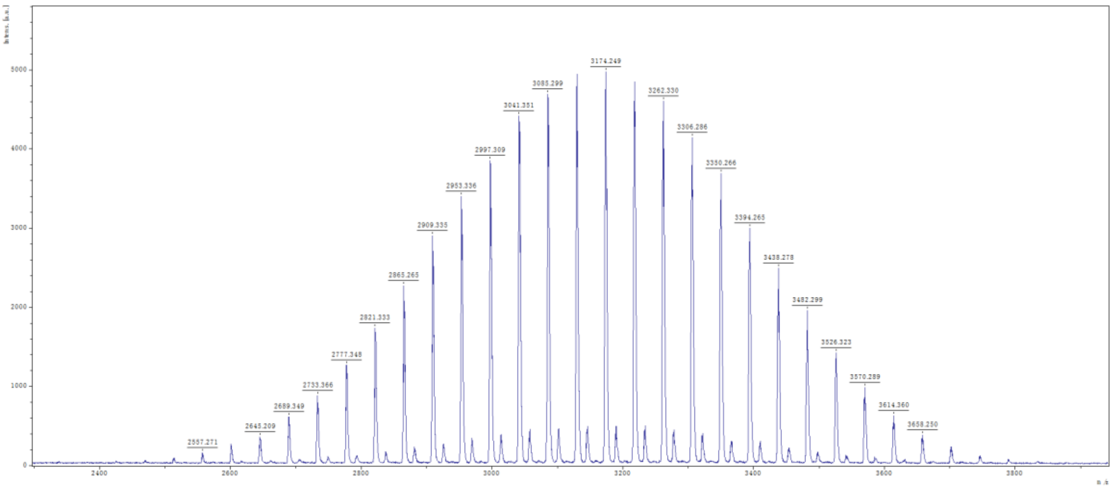
10. MALDI-TOF Spectra



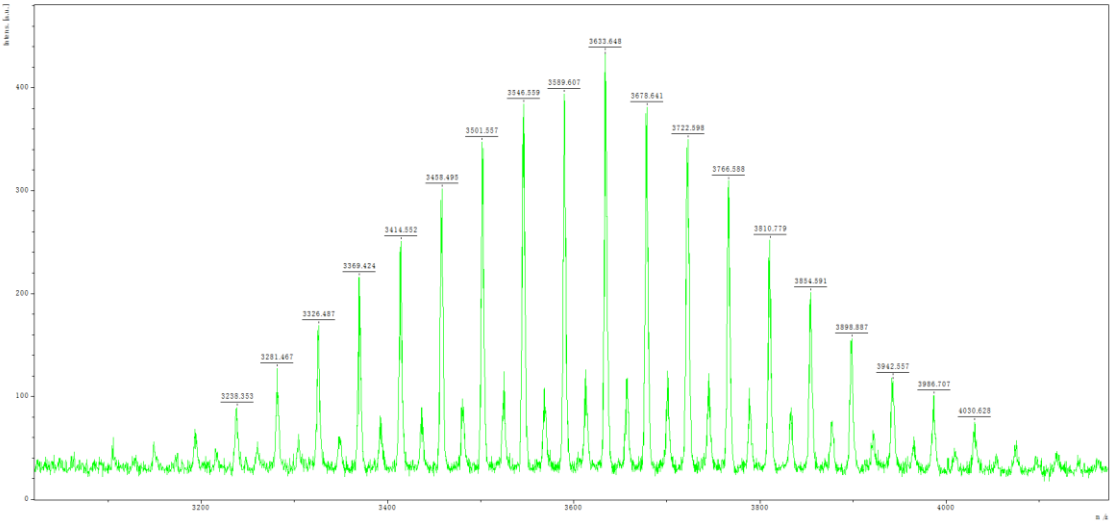
MS (MALDI-TOF) spectrum of PQS (**2**)



MS (MALDI-TOF) spectrum of Ir(ppy)$_2$(Br-ppy) and side products

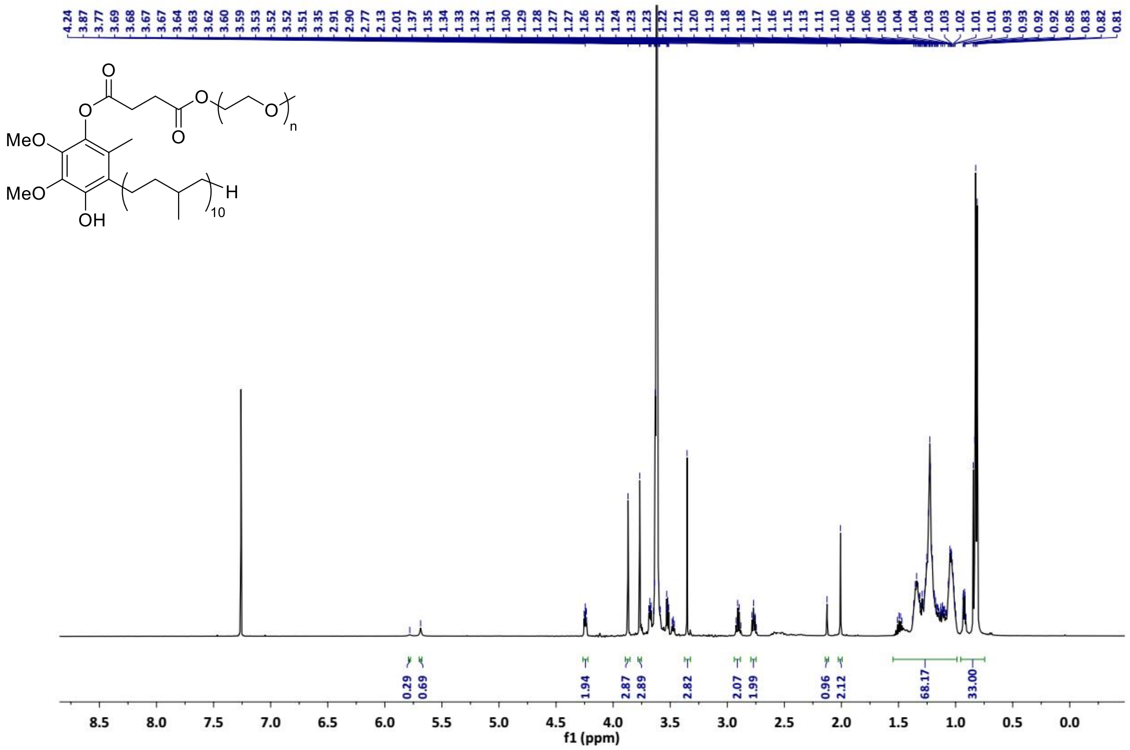


MS (MALDI-TOF) spectrum of compound **7**

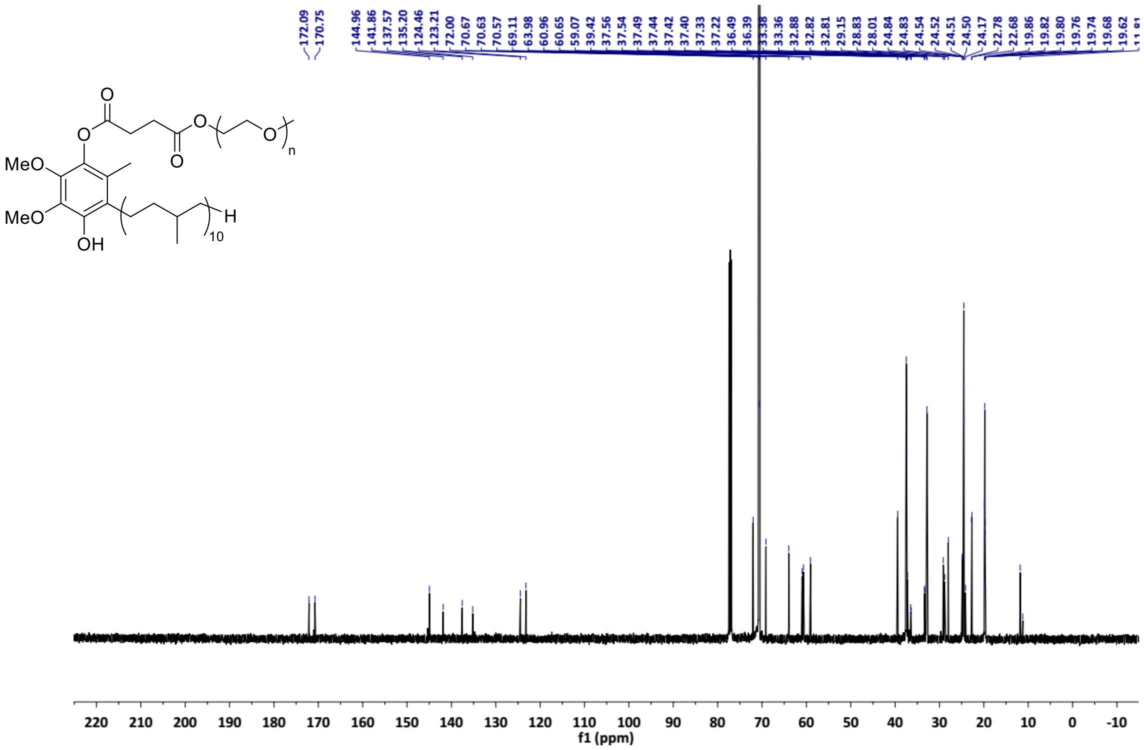


MS (MALDI-TOF) spectrum of PQS-attached photocatalyst **8**

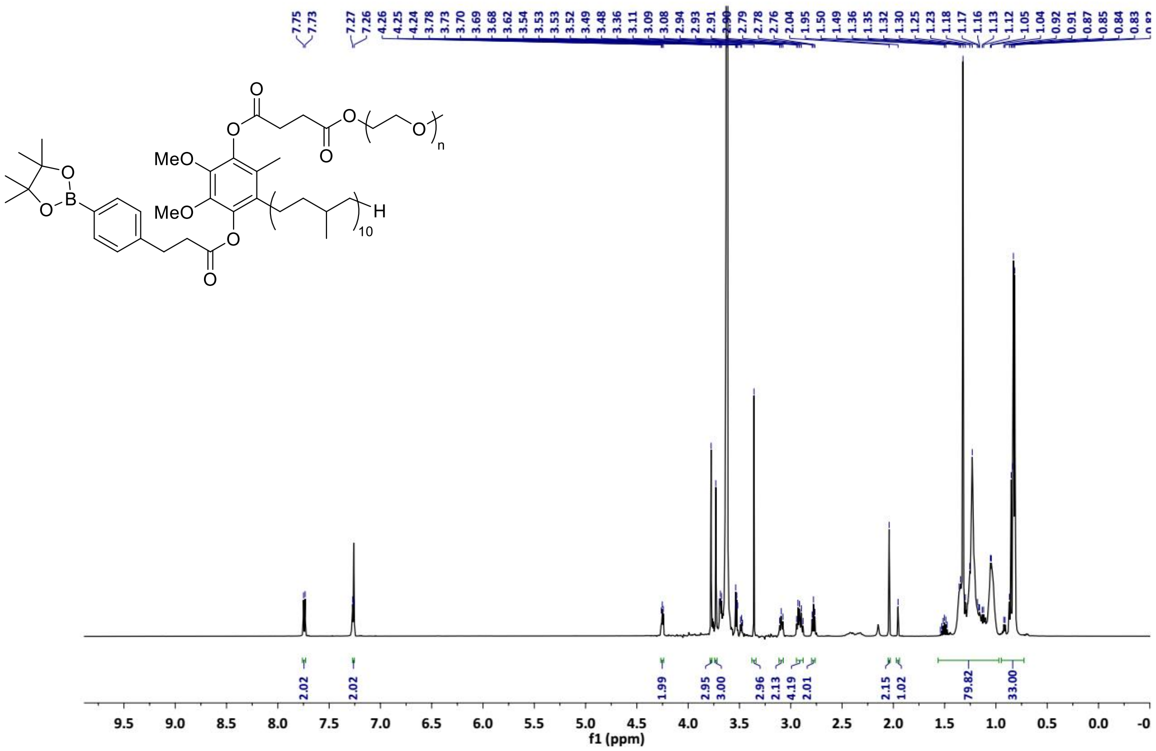
11. NMR Spectra



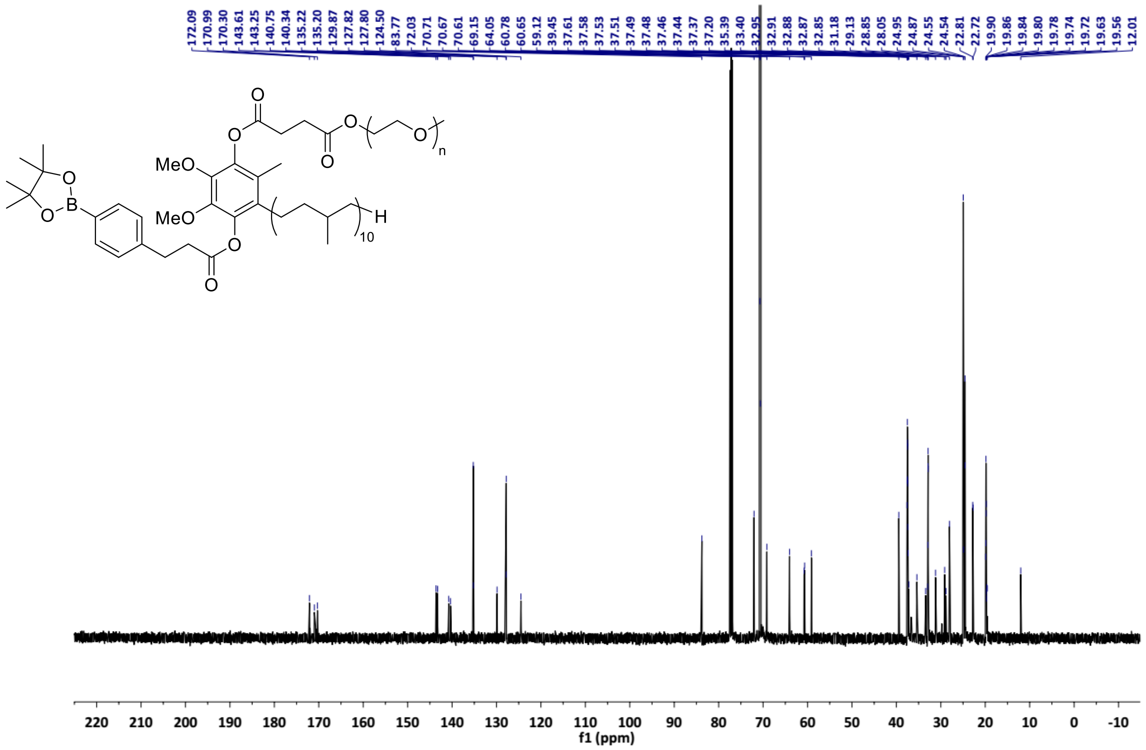
^{1}H NMR spectrum (500 MHz, CDCl$_3$) of PQS (**2**)



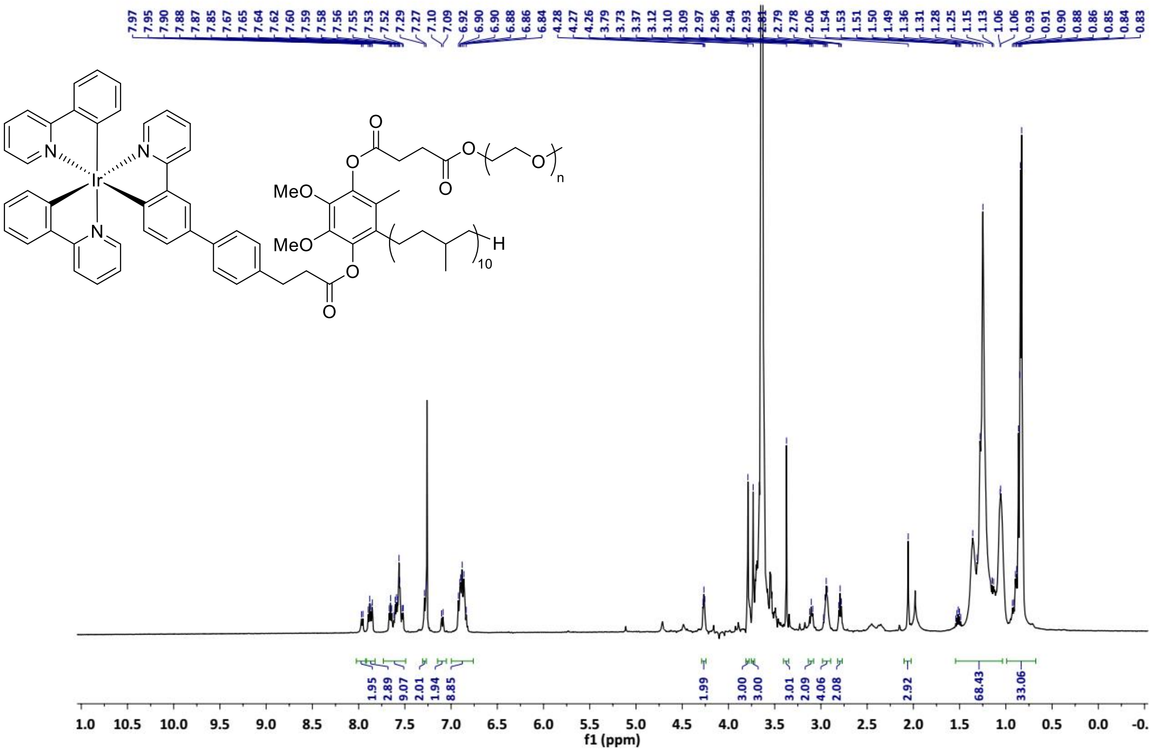
^{13}C NMR spectrum (126 MHz, CDCl$_3$) of PQS (**2**)



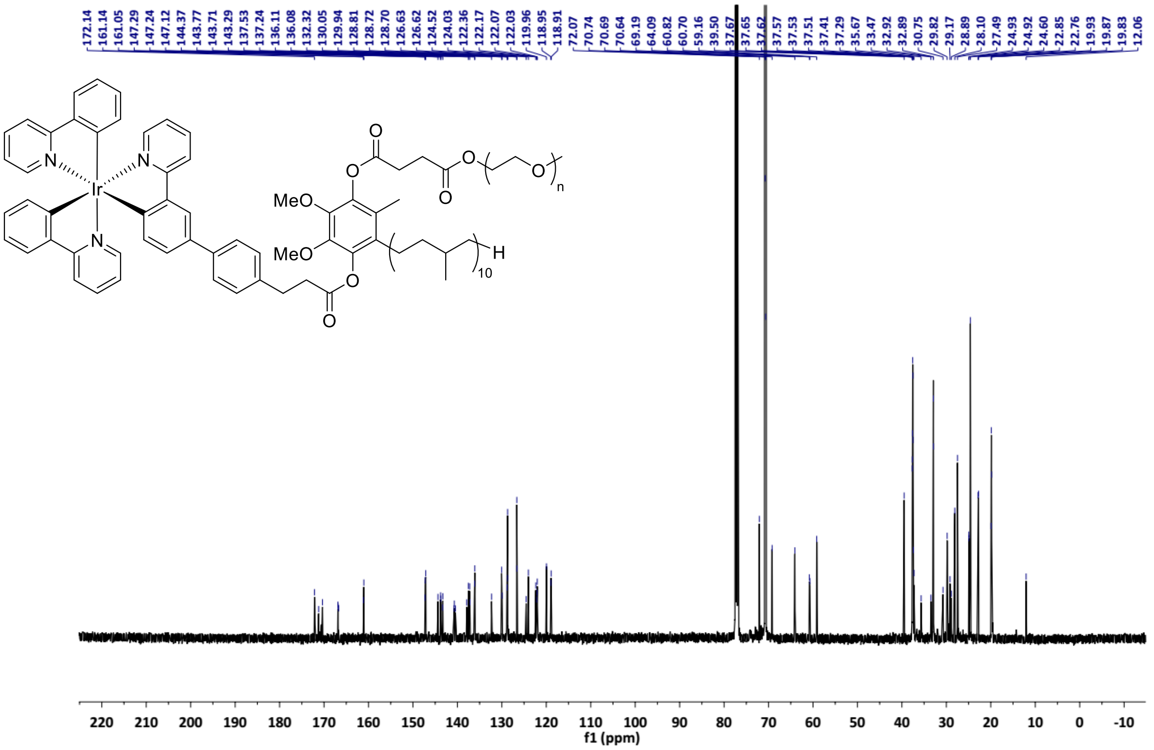
^{1}H NMR spectrum (500 MHz, CDCl$_3$) of compound **7**



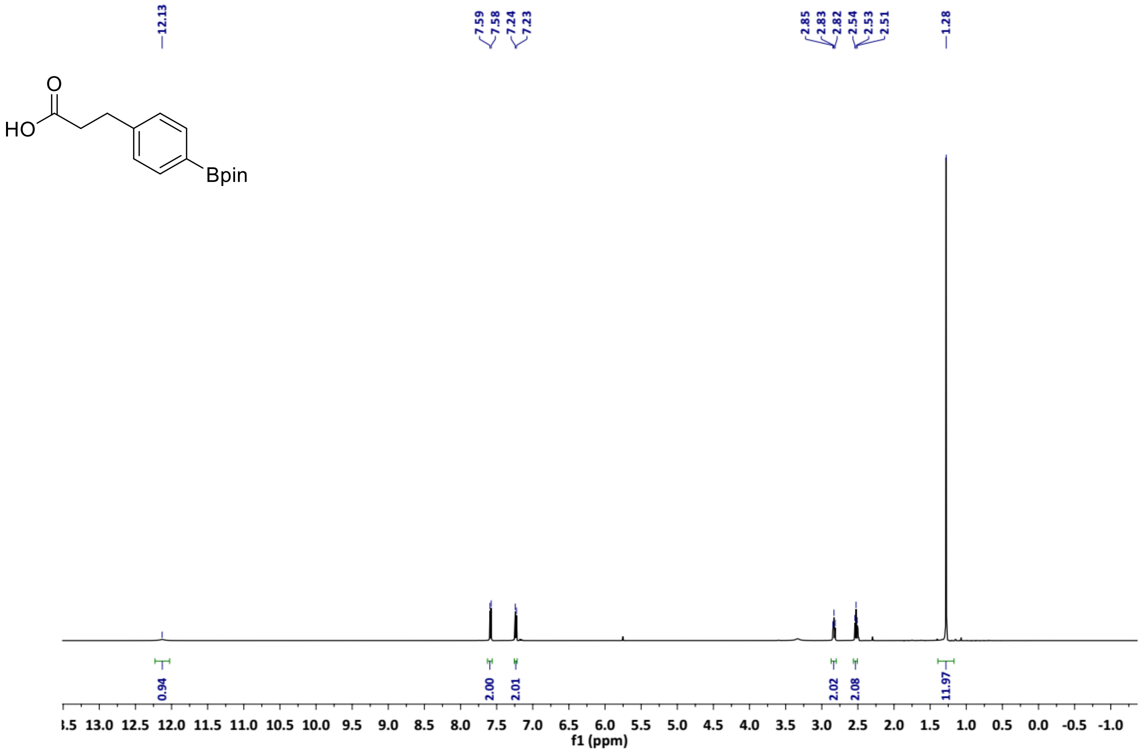
^{13}C NMR spectrum (126 MHz, CDCl$_3$) of compound **7**



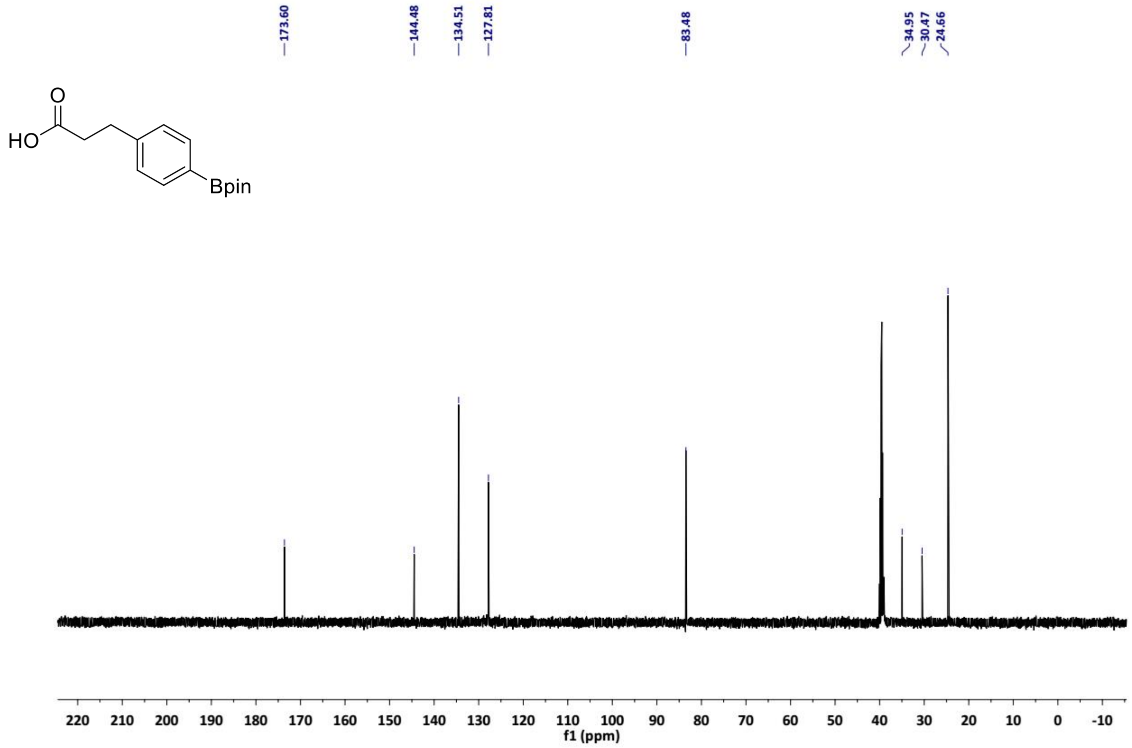
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of catalyst **8**



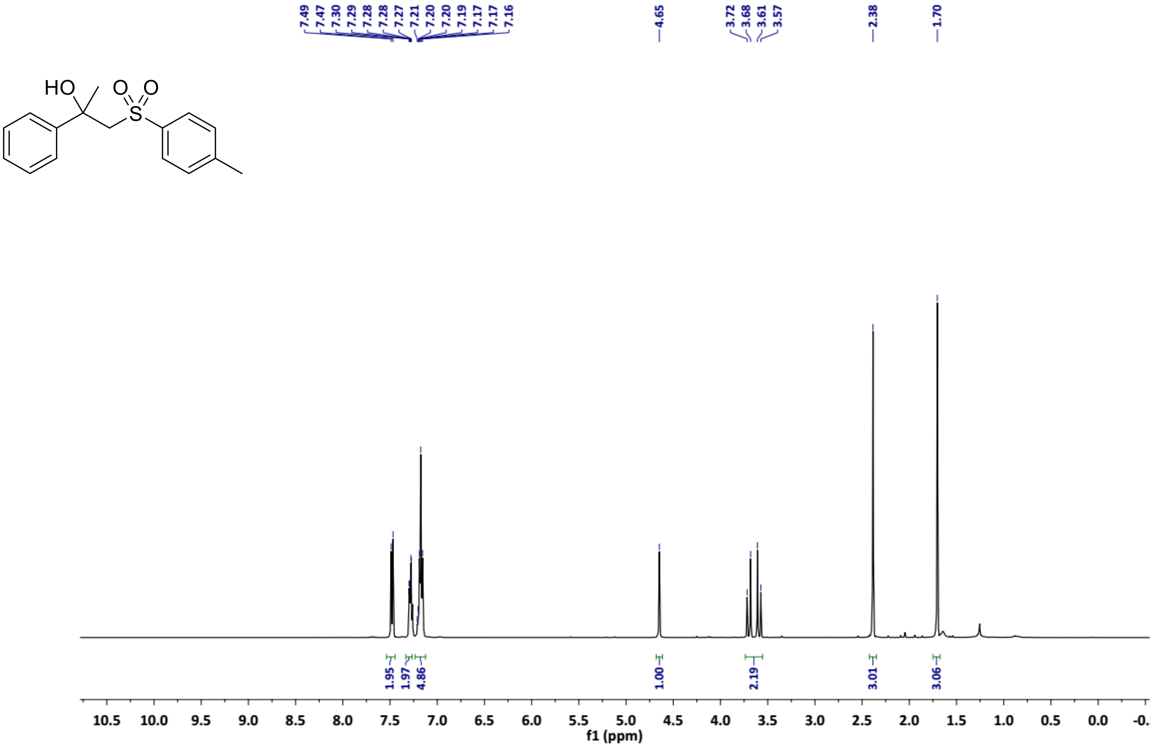
^{13}C NMR spectrum (126 MHz, $CDCl_3$) of catalyst **8**



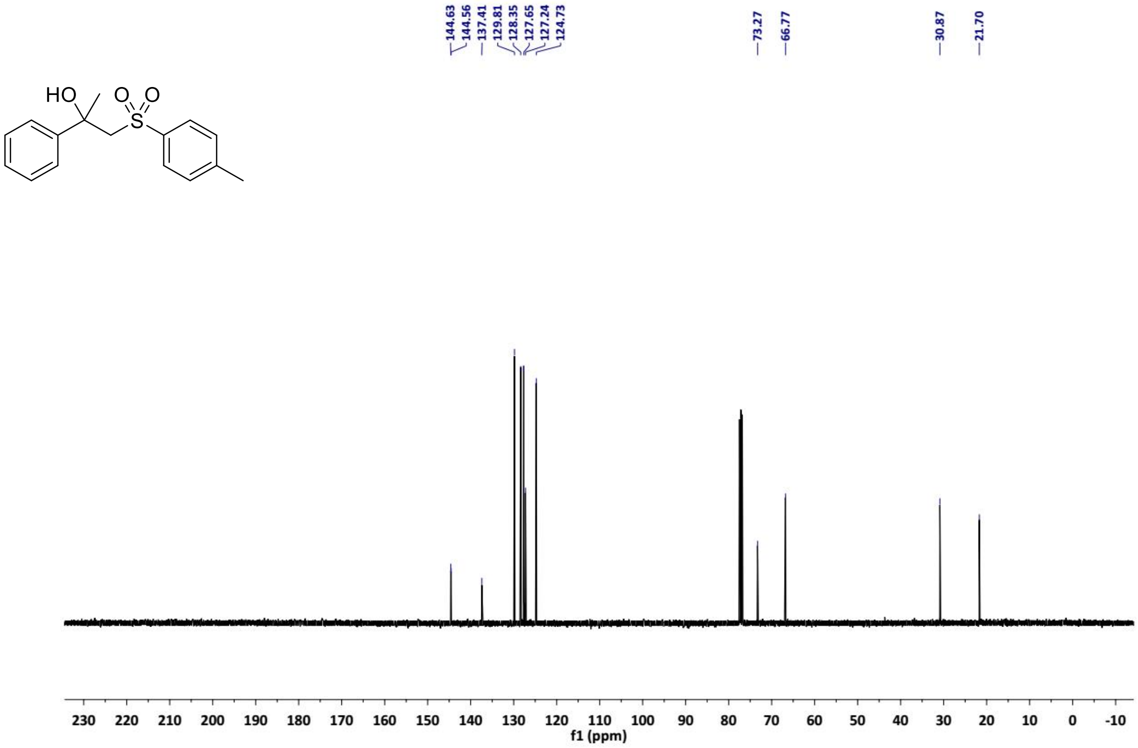
^{1}H NMR spectrum (500 MHz, DMSO-d_6) of compound **6**



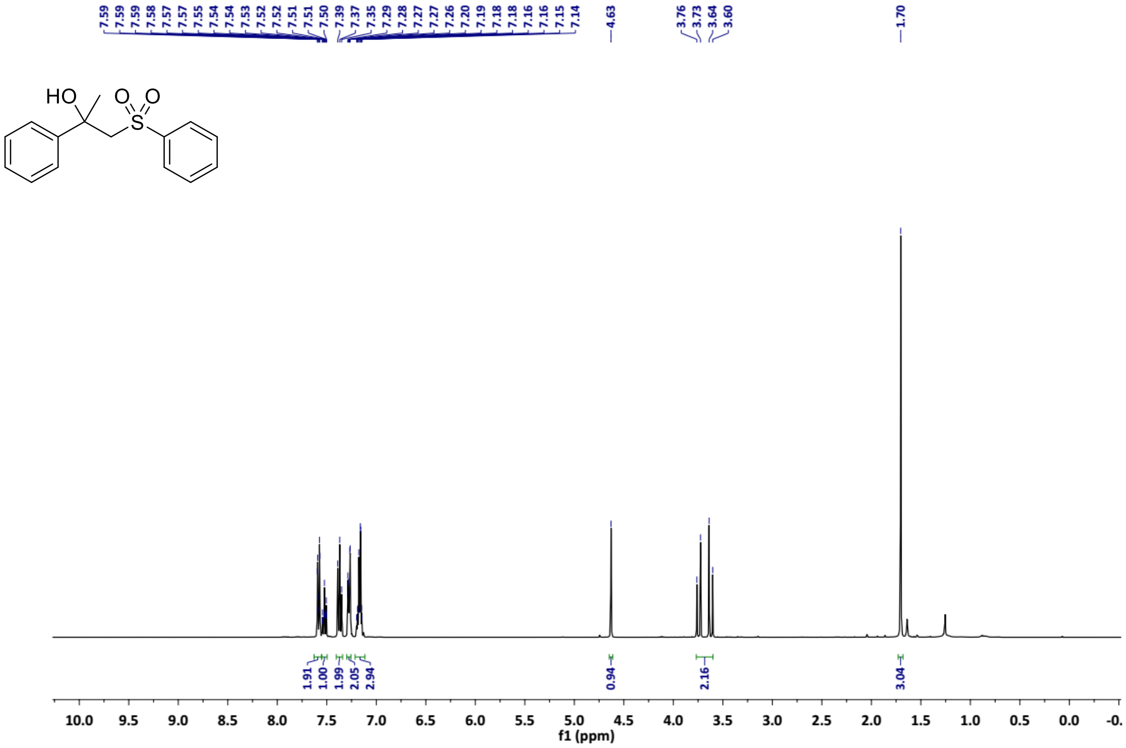
^{13}C NMR spectrum (126 MHz, DMSO-d_6) of compound **6**



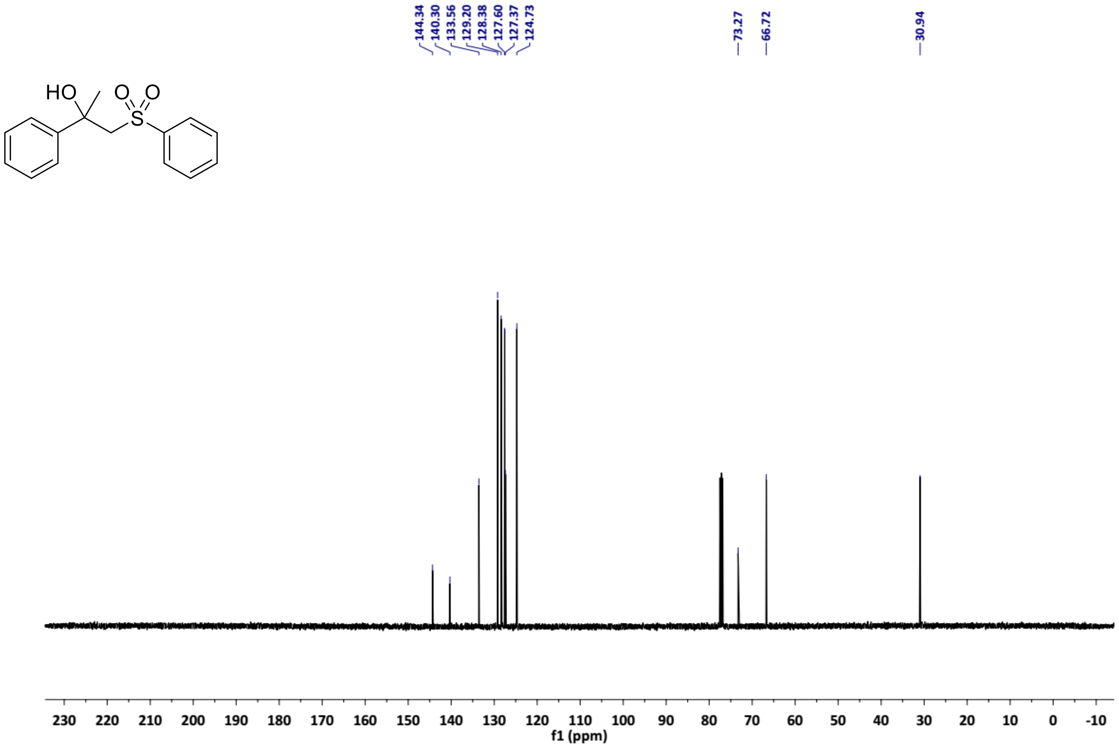
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **11a**



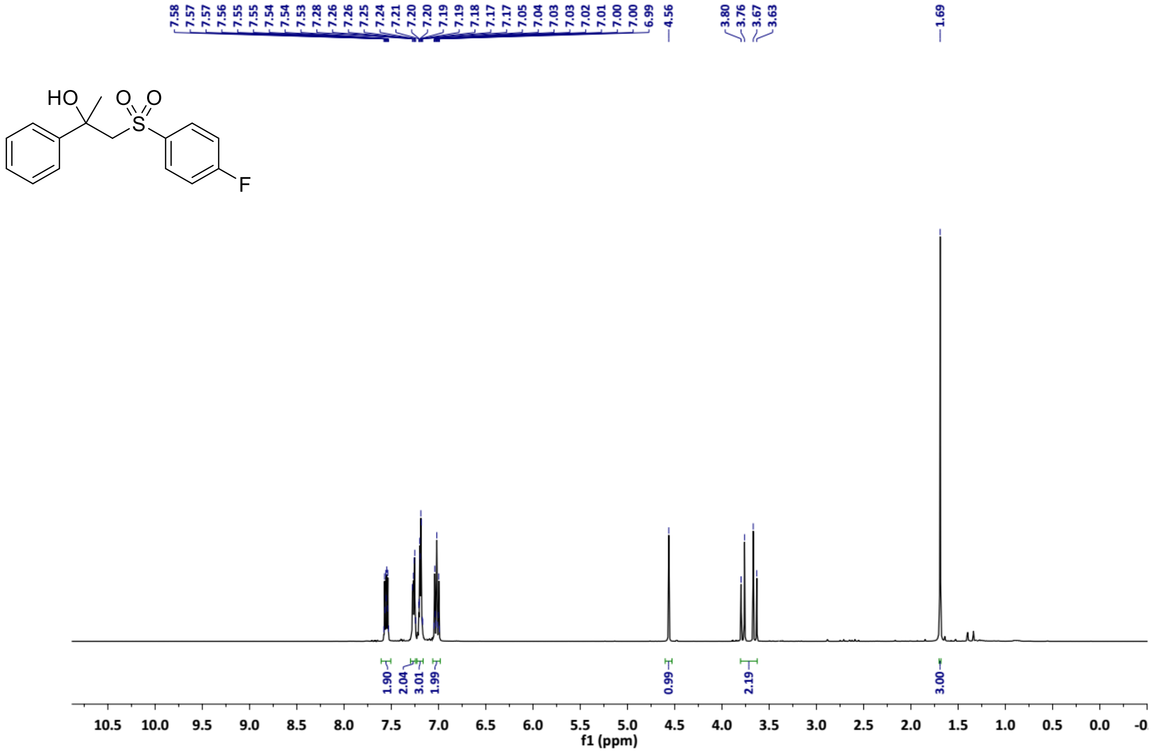
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **11a**



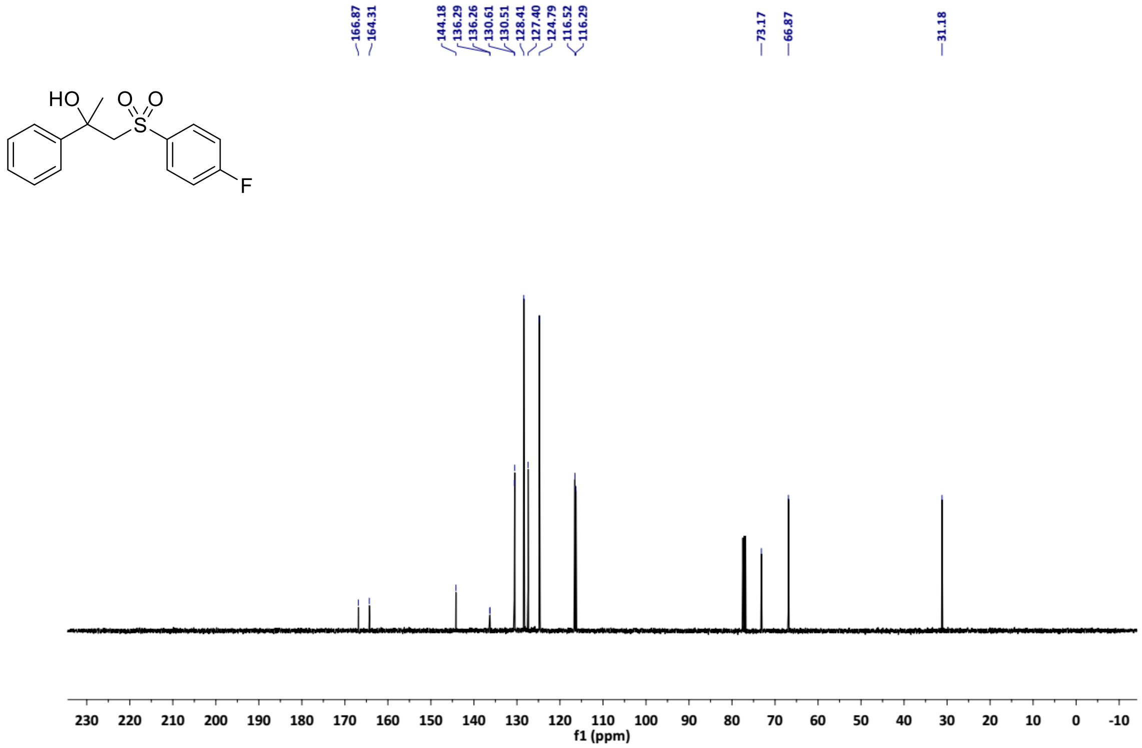
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **11b**



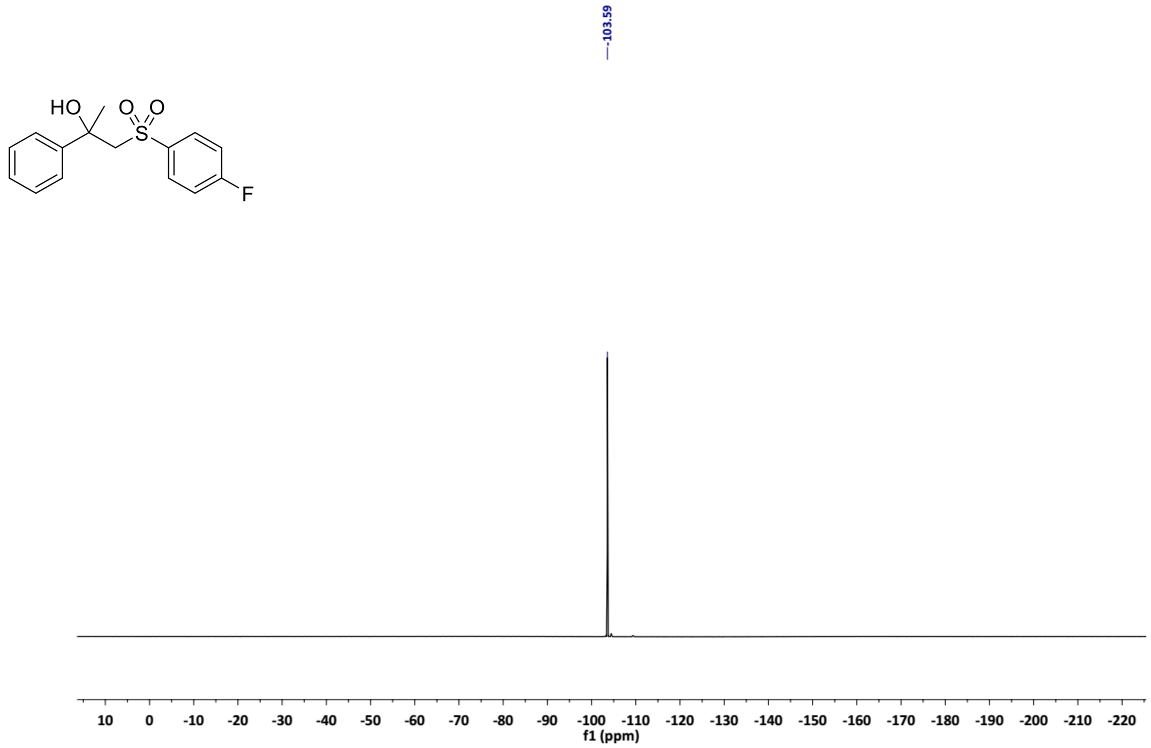
^{13}C NMR spectrum (101 MHz, CDCl$_3$) of **11b**



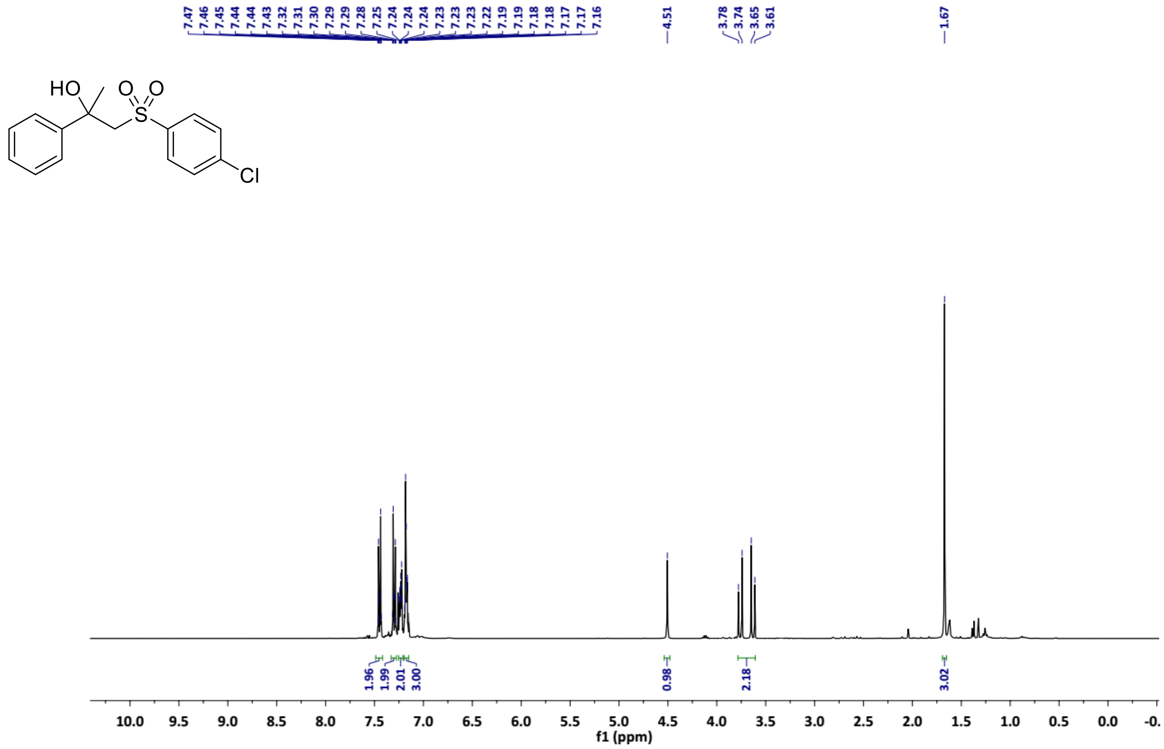
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **11c**



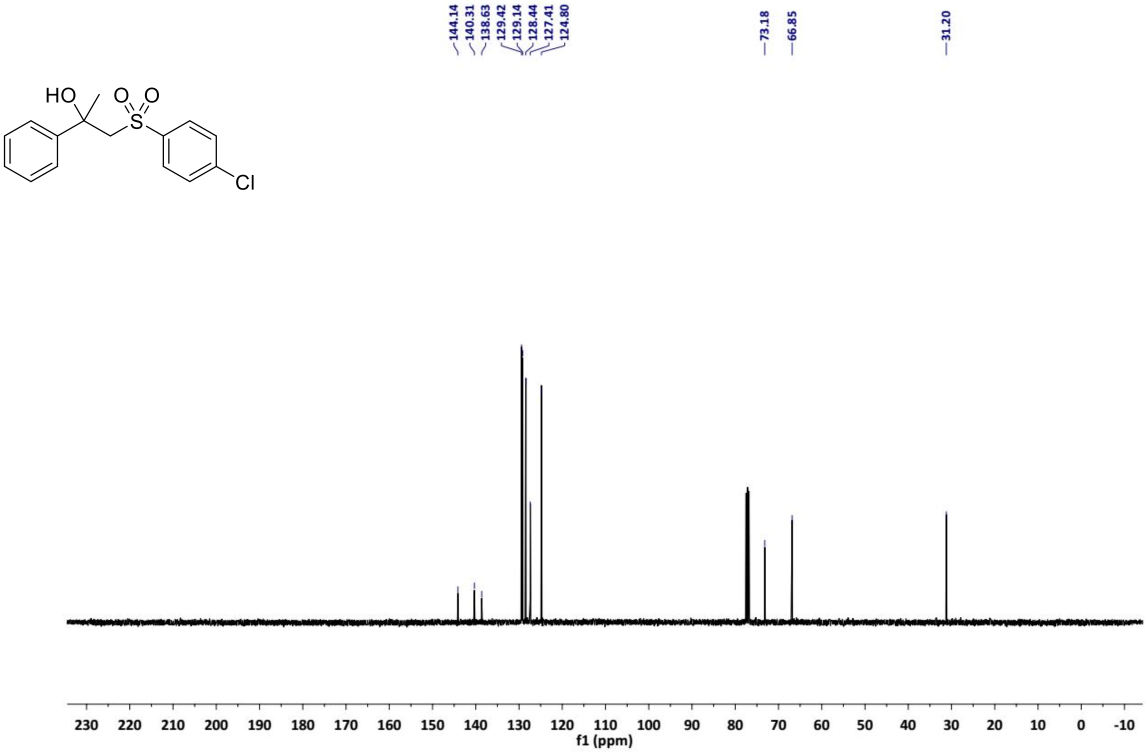
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **11c**



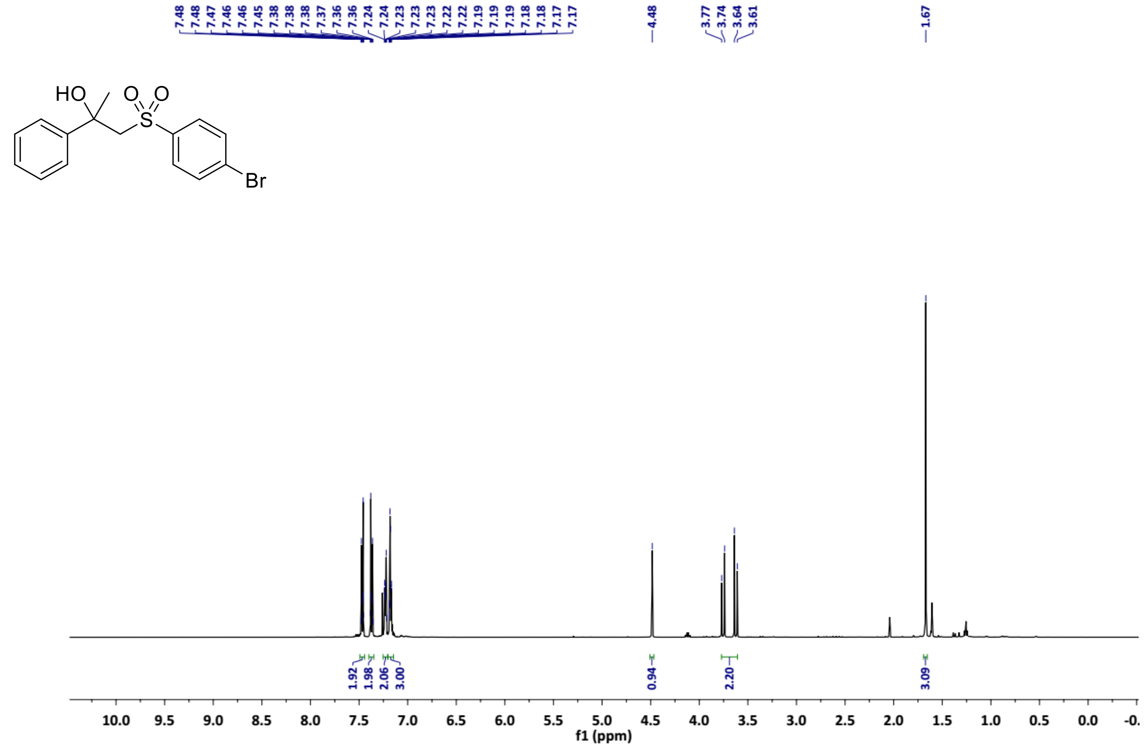
^{19}F NMR spectrum (376 MHz, CDCl$_3$) of **11d**



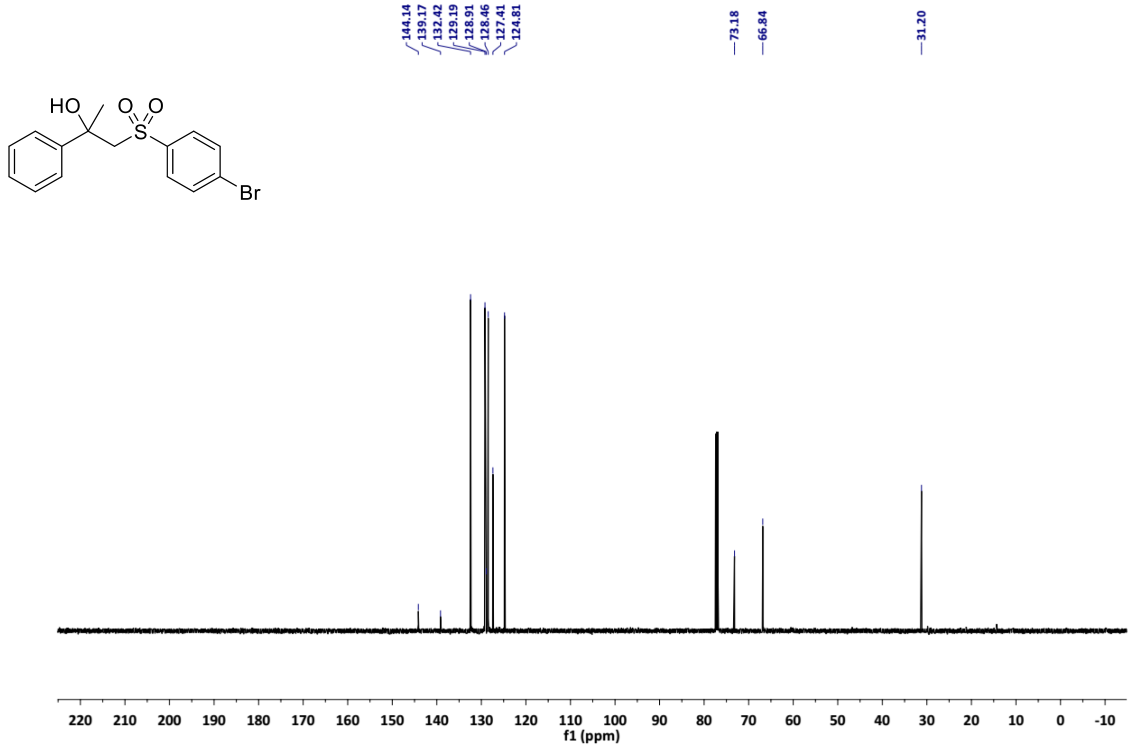
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **11d**



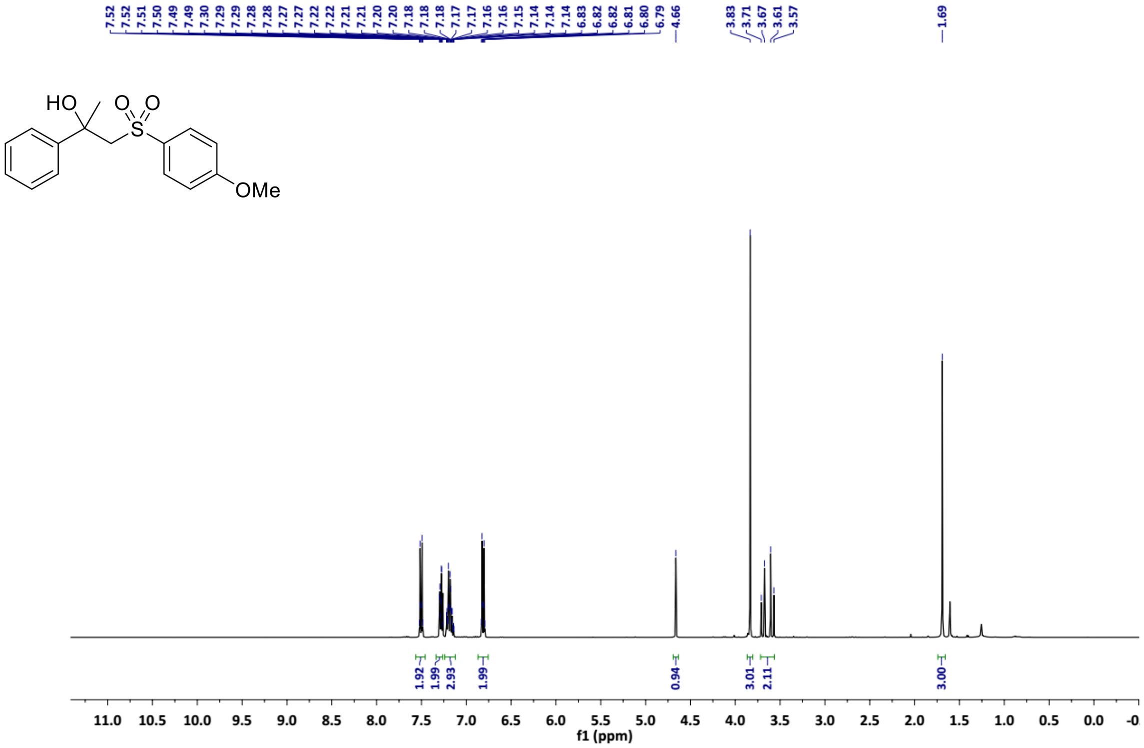
^{13}C NMR spectrum (101 MHz, CDCl$_3$) of **11d**



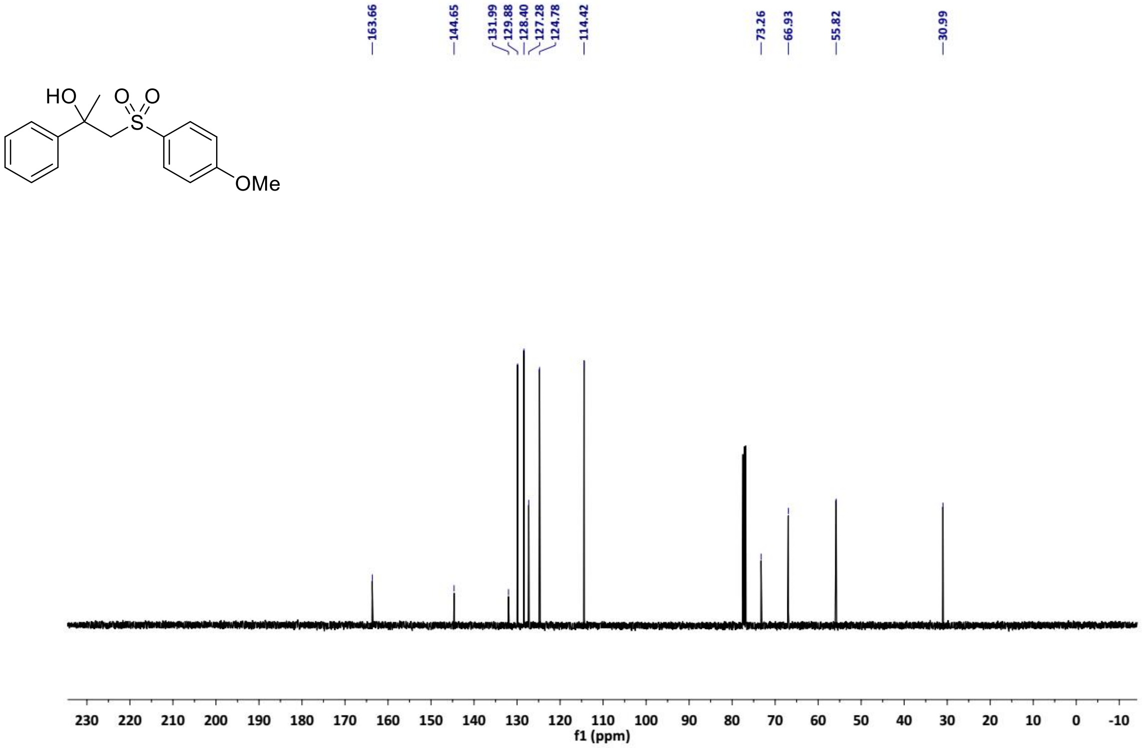
^{1}H NMR spectrum (500 MHz, CDCl$_3$) of **11e**



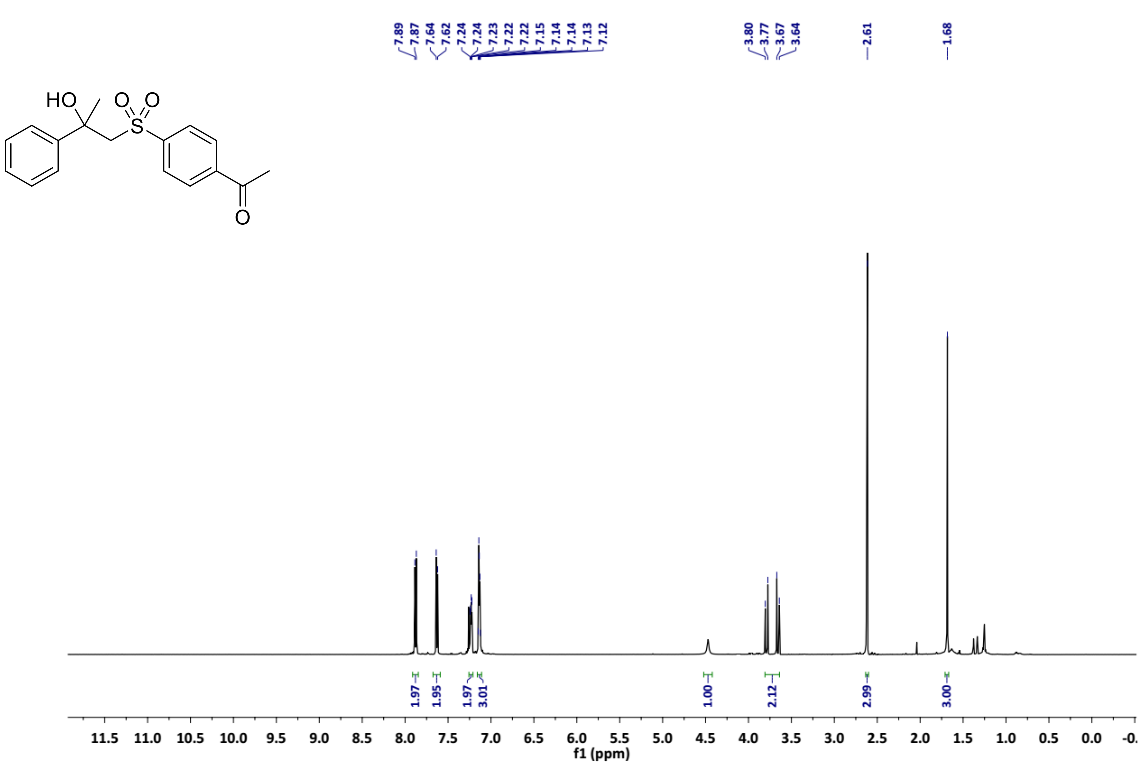
^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **11e**



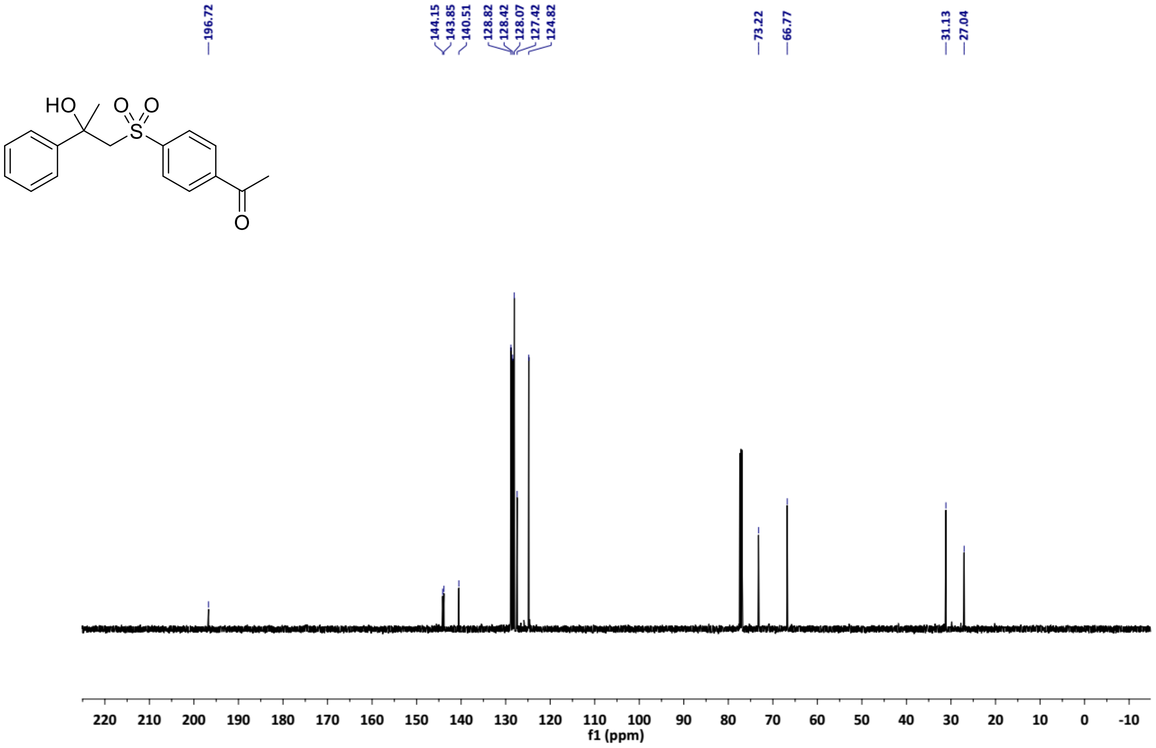
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **11f**



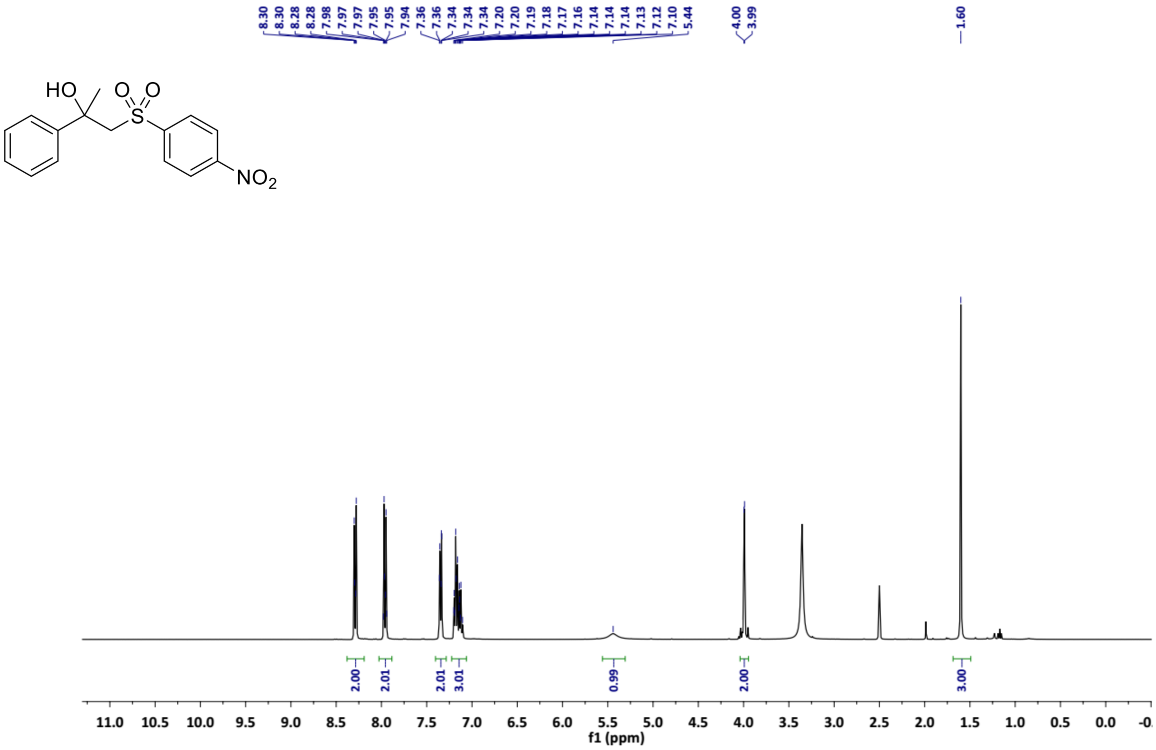
^{13}C NMR spectrum (101 MHz, CDCl$_3$) of **11f**



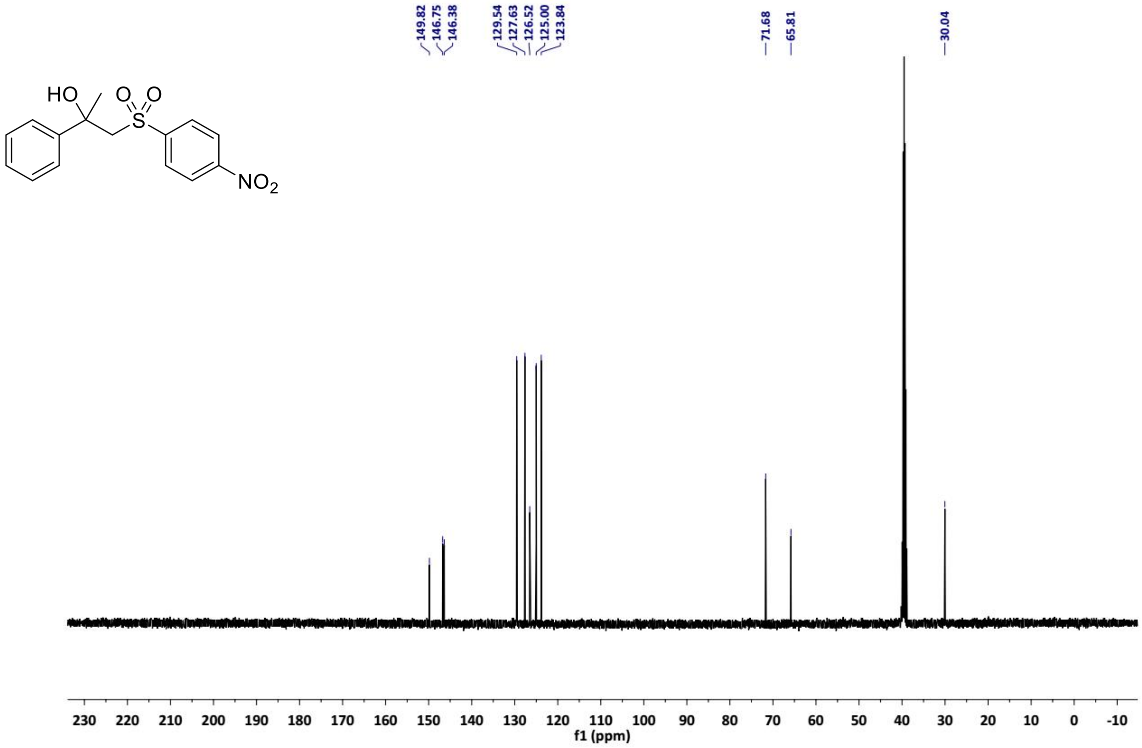
^{1}H NMR spectrum (500 MHz, CDCl$_3$) of **11g**



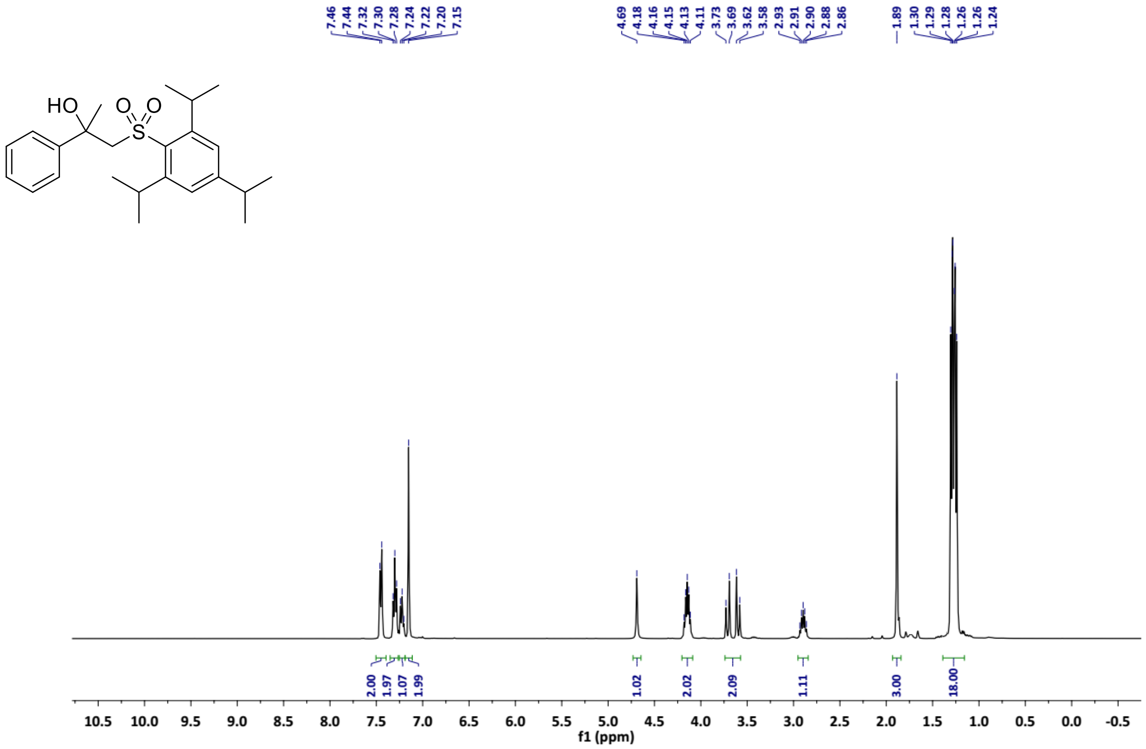
^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **11g**



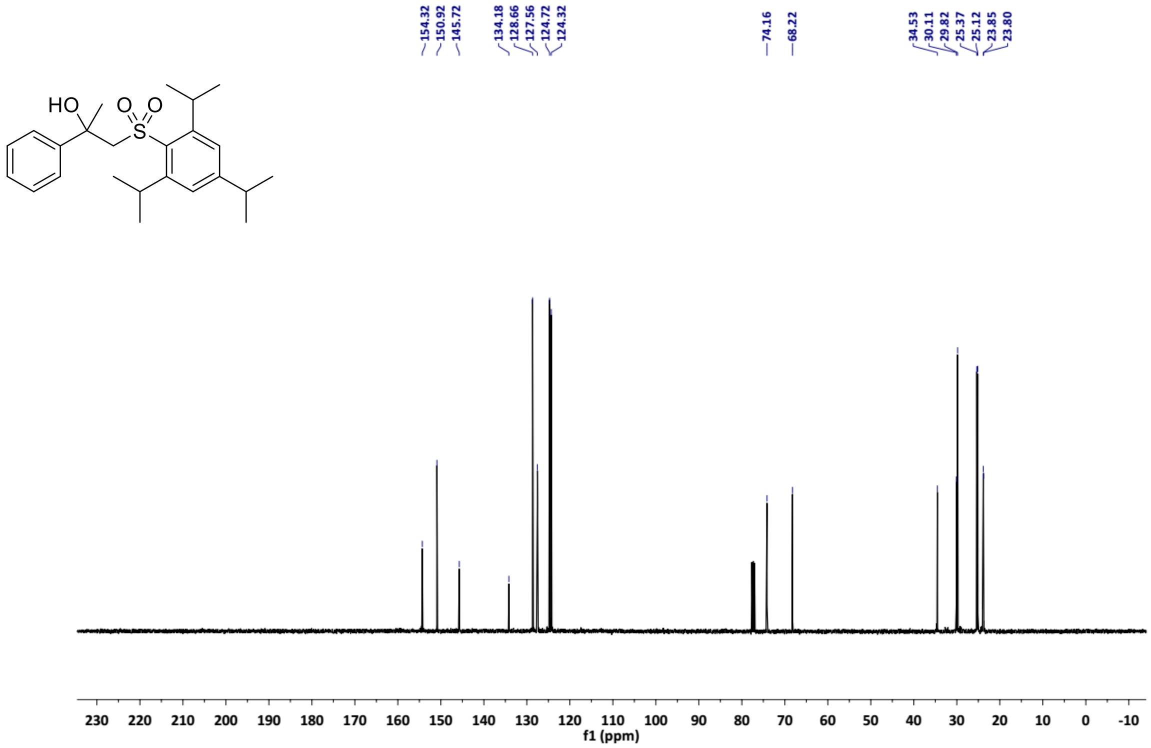
^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **11h**



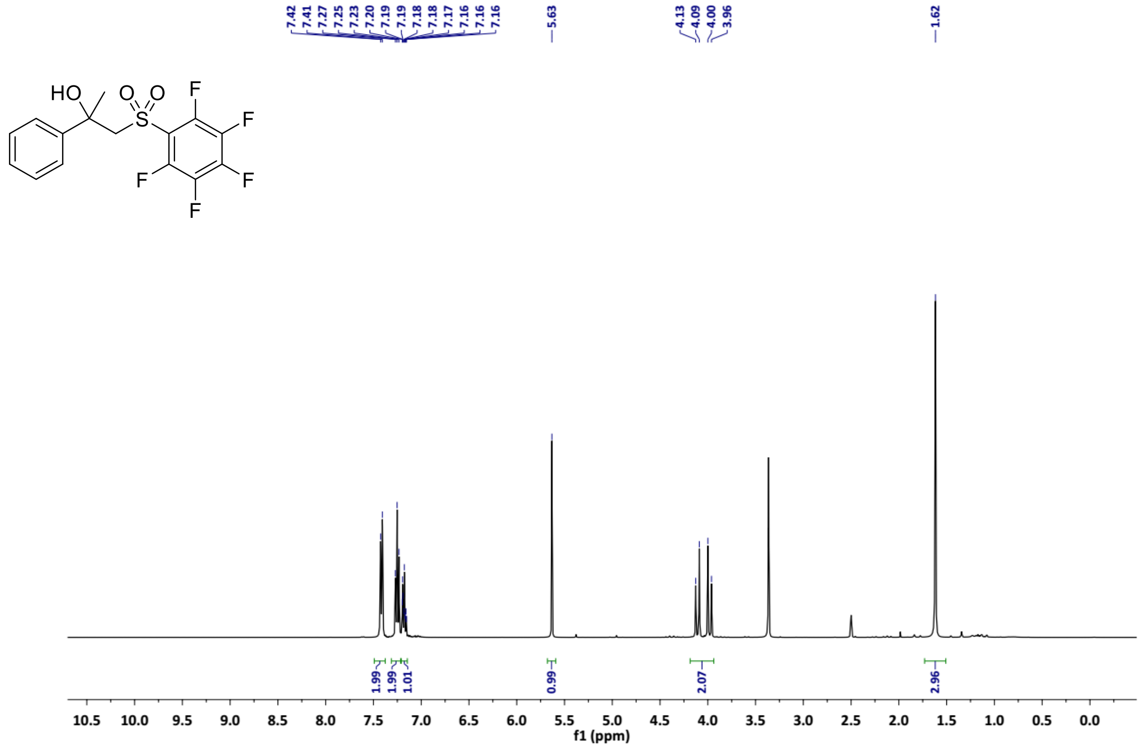
^{13}C NMR spectrum (101 MHz, DMSO-*d*$_6$) of **11h**



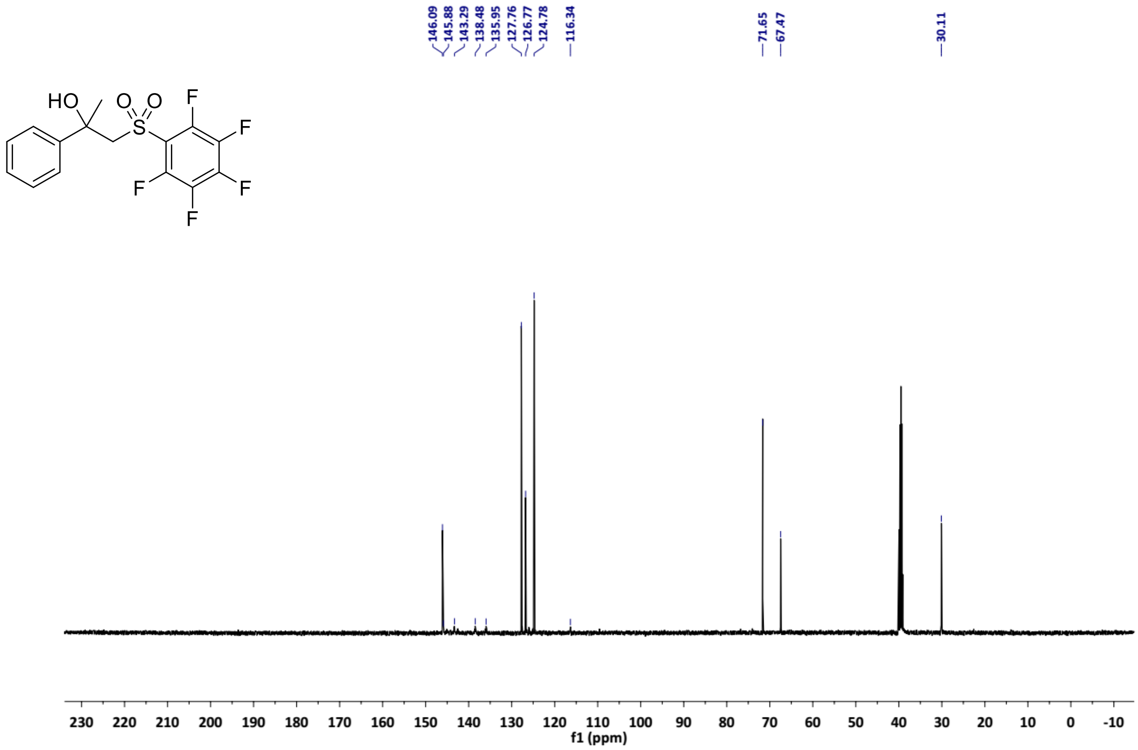
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **11i**



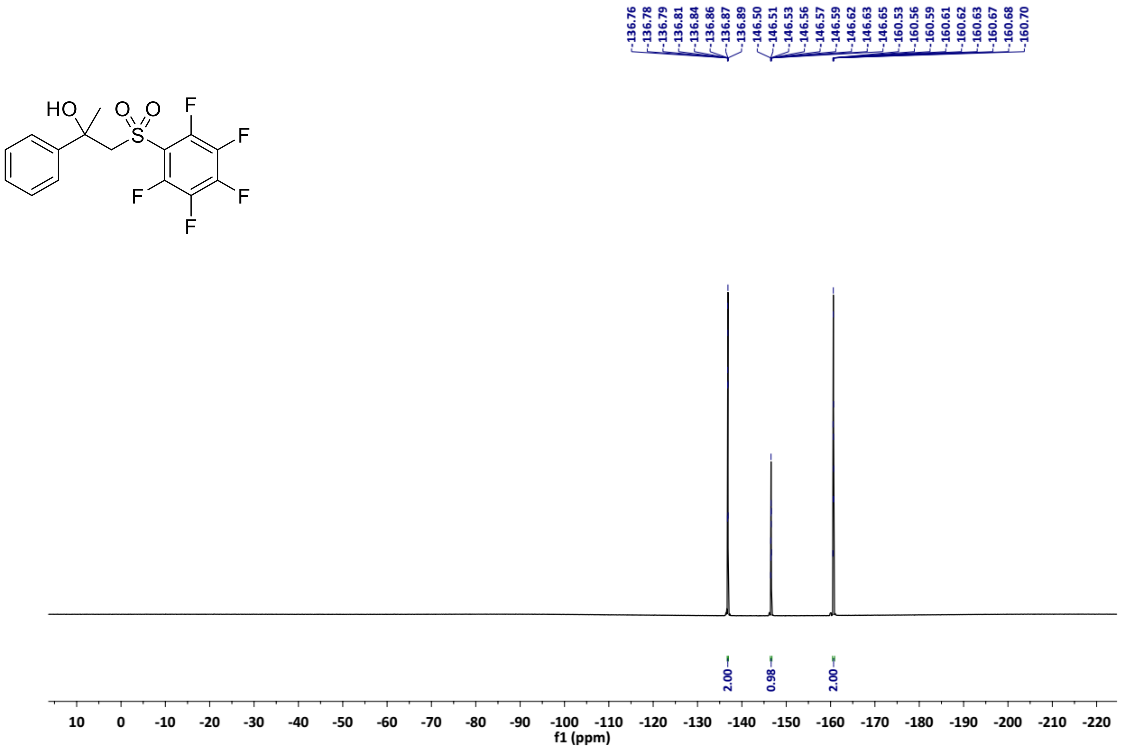
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **11i**



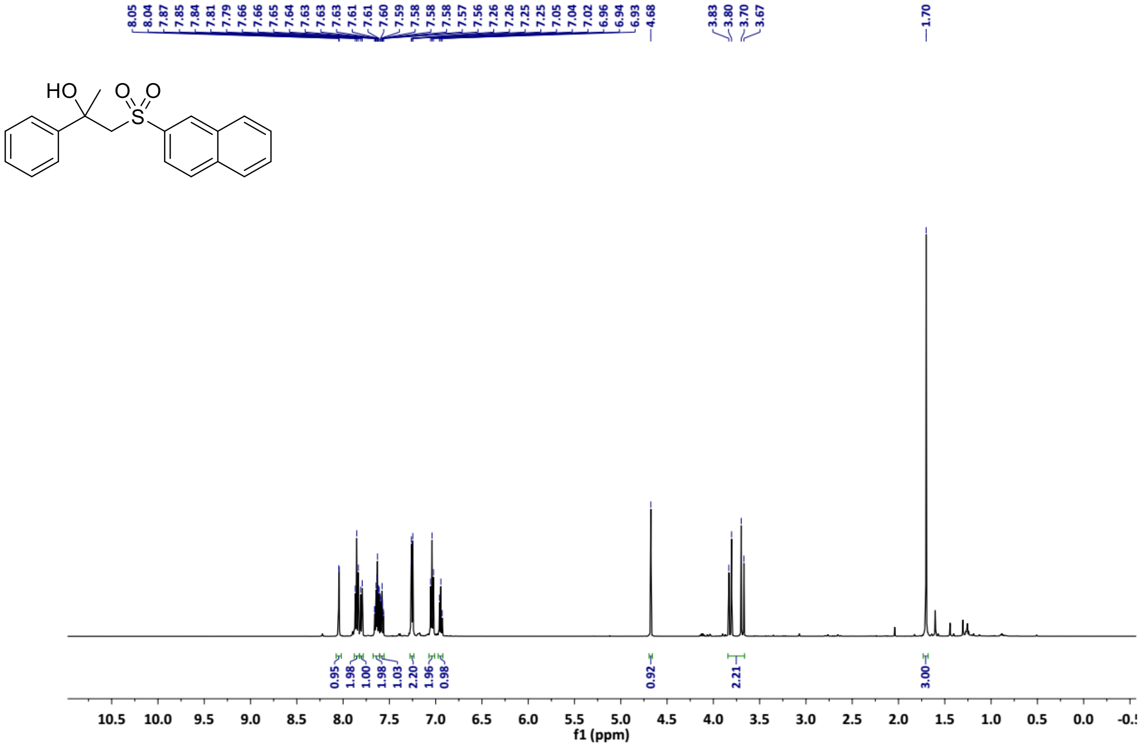
^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **11j**



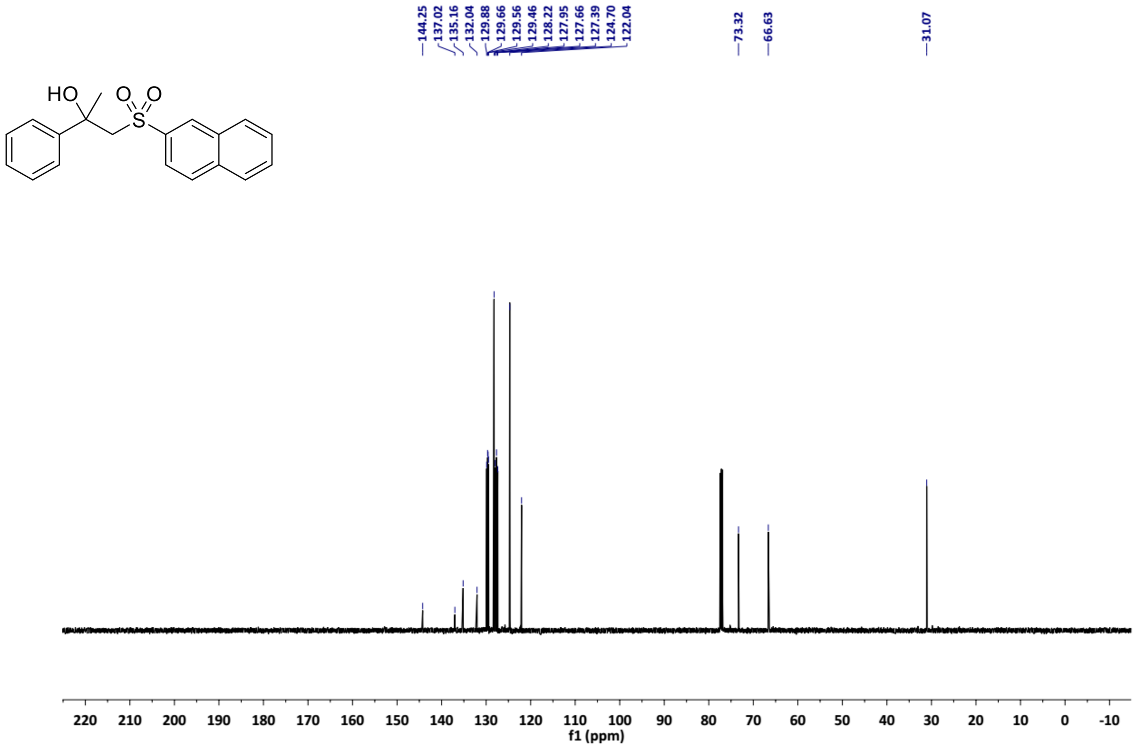
^{13}C NMR spectrum (101 MHz, DMSO-d_6) of **11j**



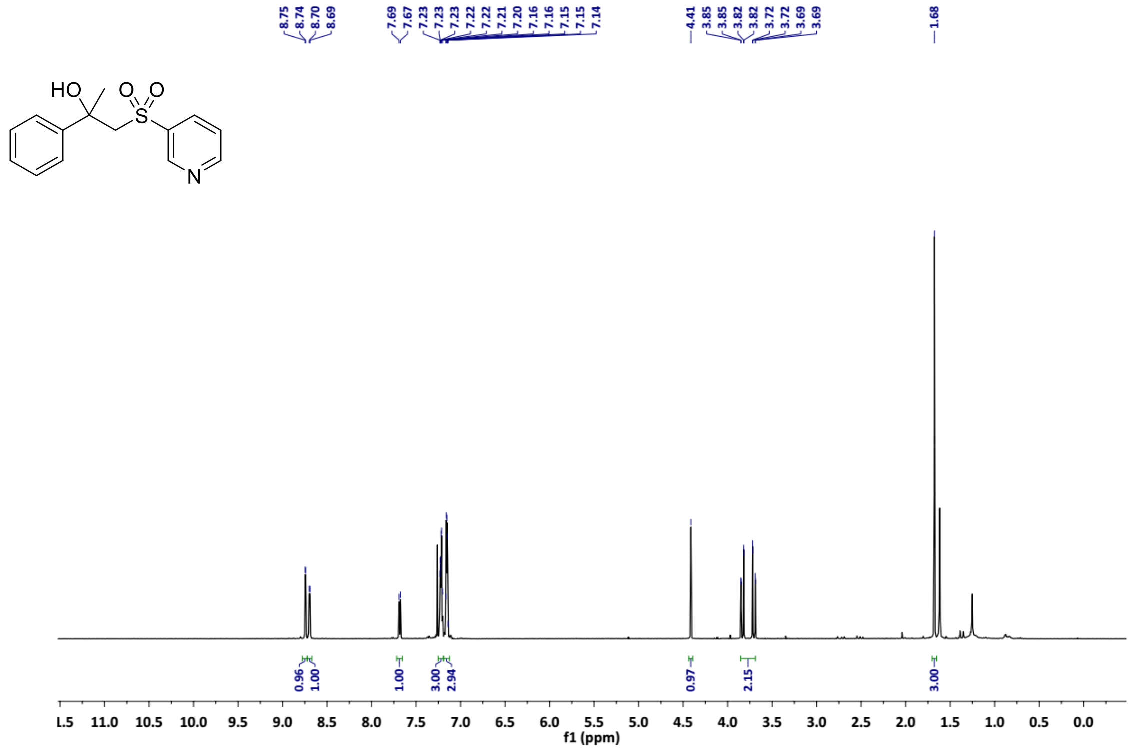
^{19}F NMR spectrum (376 MHz, DMSO-d_6) of **11j**



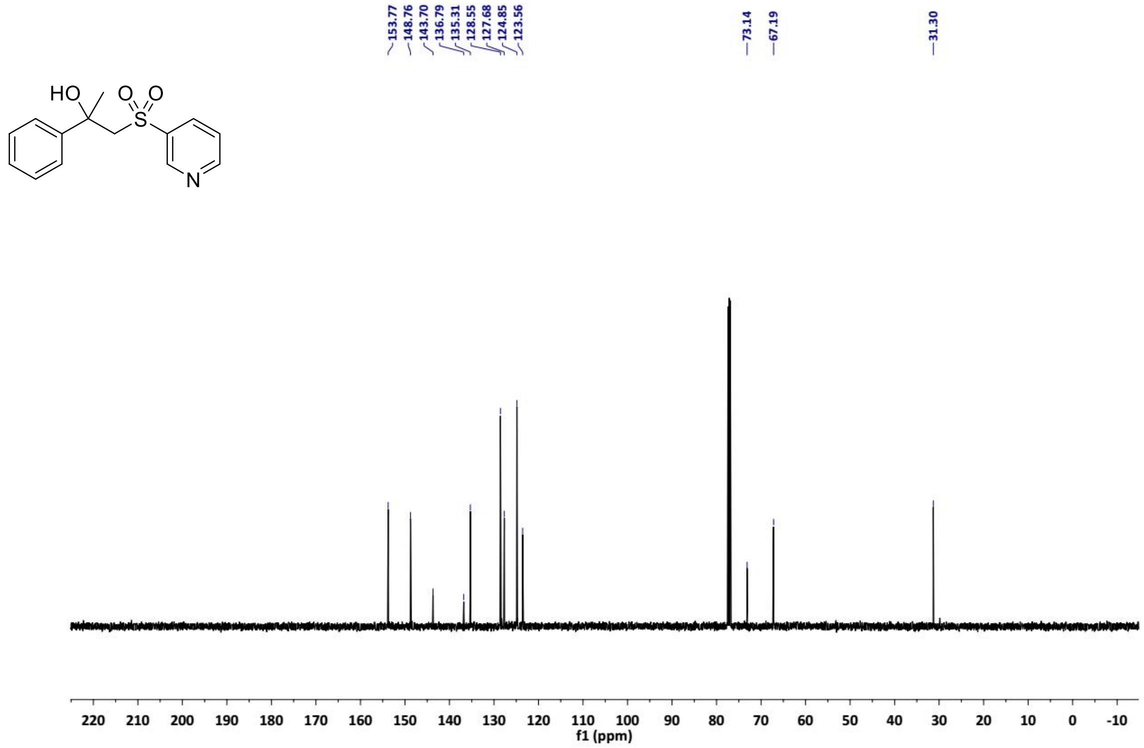
^{1}H NMR spectrum (500 MHz, CDCl$_3$) of **11k**



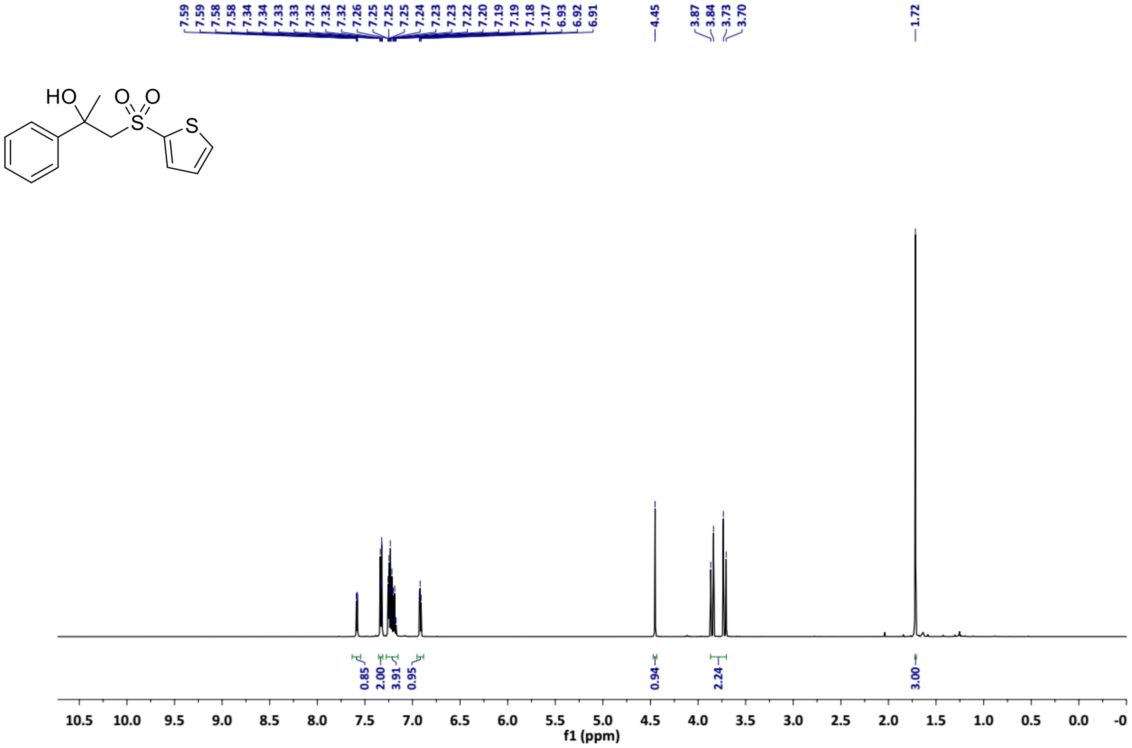
^{13}C NMR spectrum (126 MHz, CDCl$_3$) of **11k**



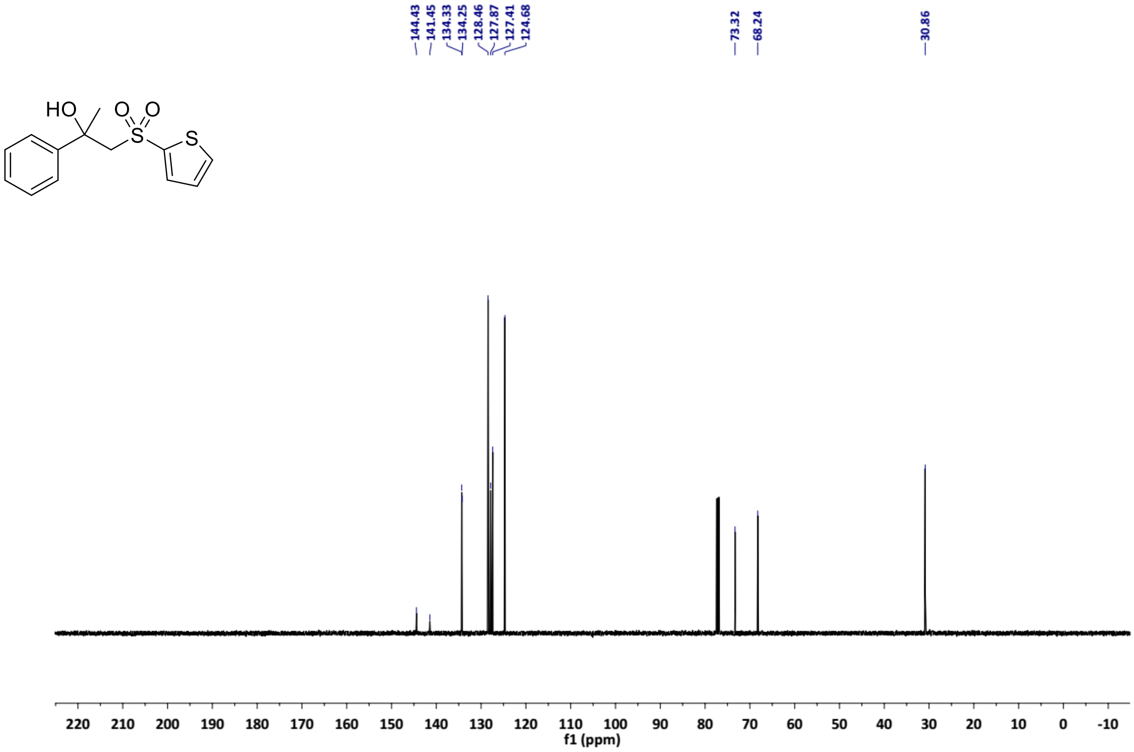
^{1}H NMR spectrum (500 MHz, CDCl$_3$) of **11l**



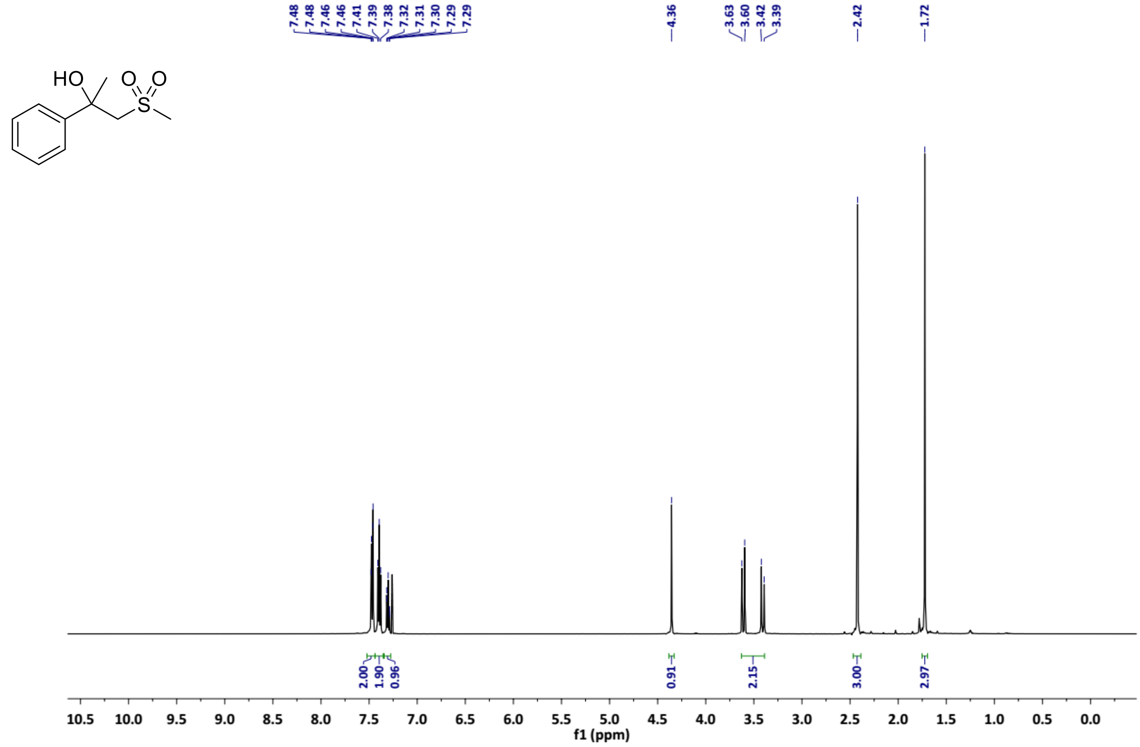
^{13}C NMR spectrum (126 MHz, CDCl$_3$) of **11l**



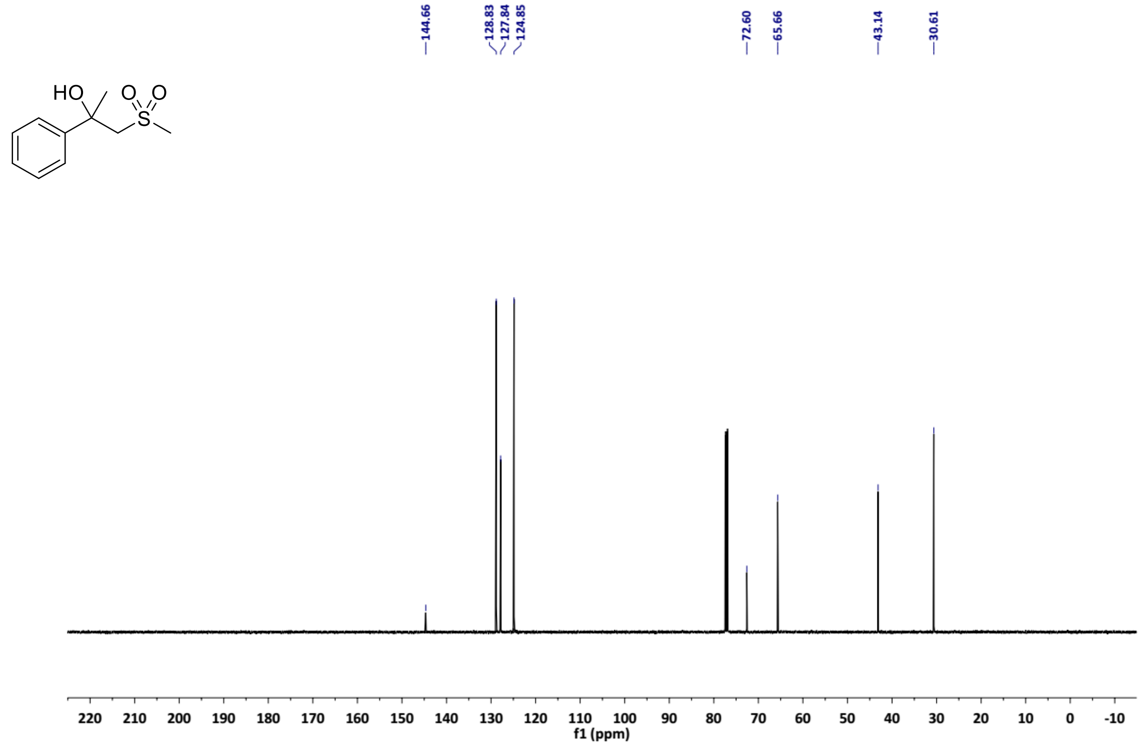
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **11m**



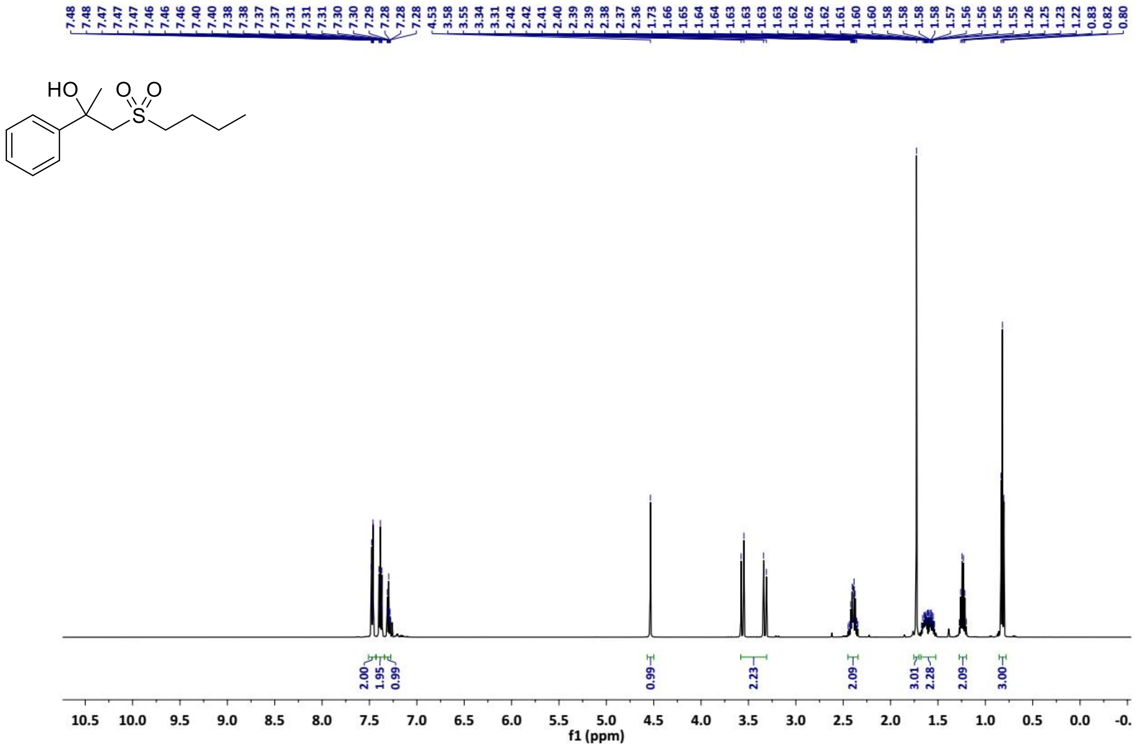
^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **11m**



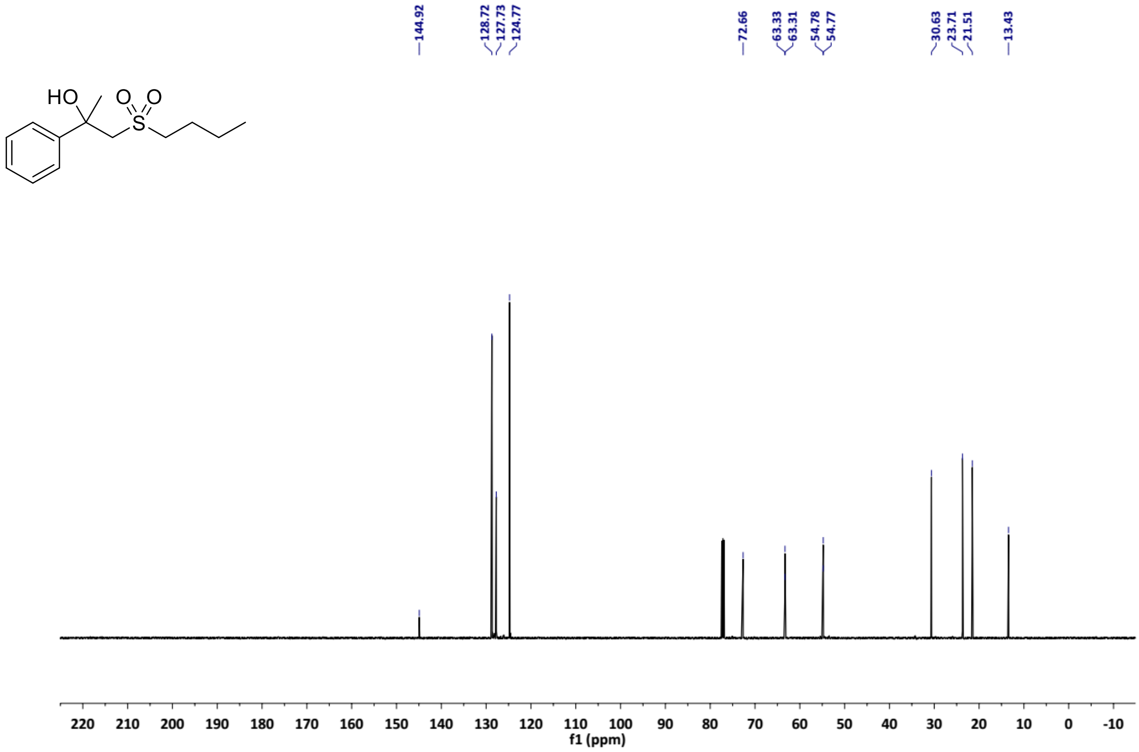
^{1}H NMR spectrum (500 MHz, CDCl$_3$) of **11n**



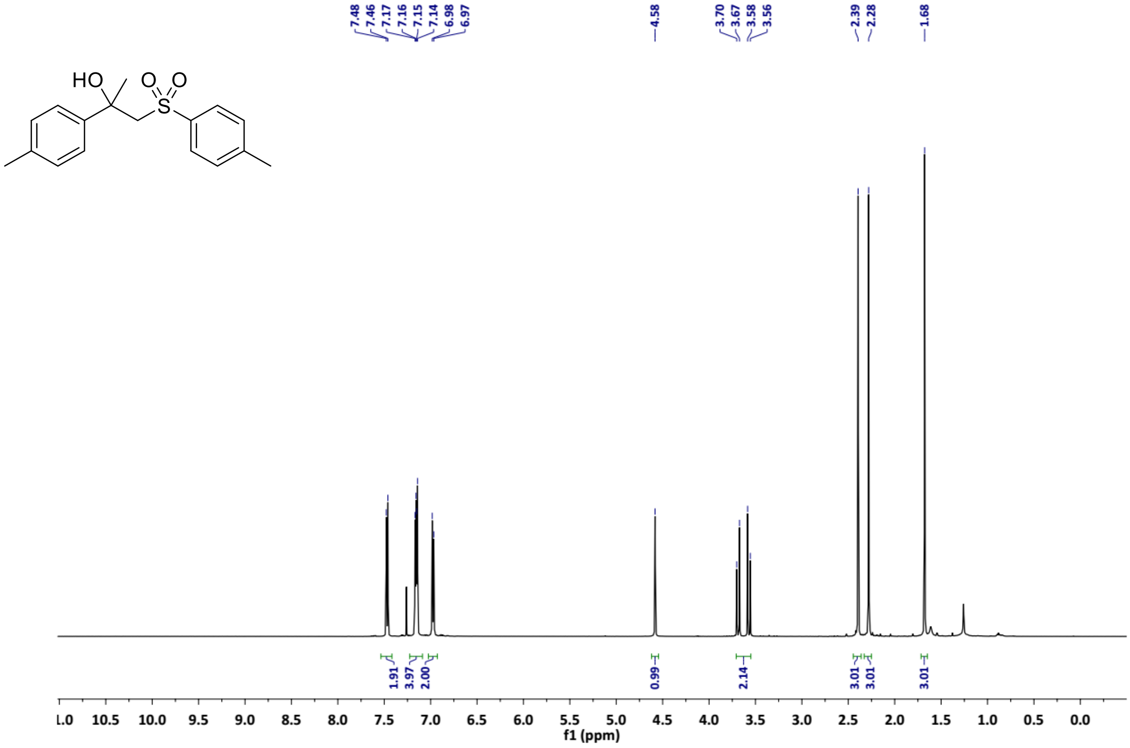
^{13}C NMR spectrum (126 MHz, CDCl$_3$) of **11n**



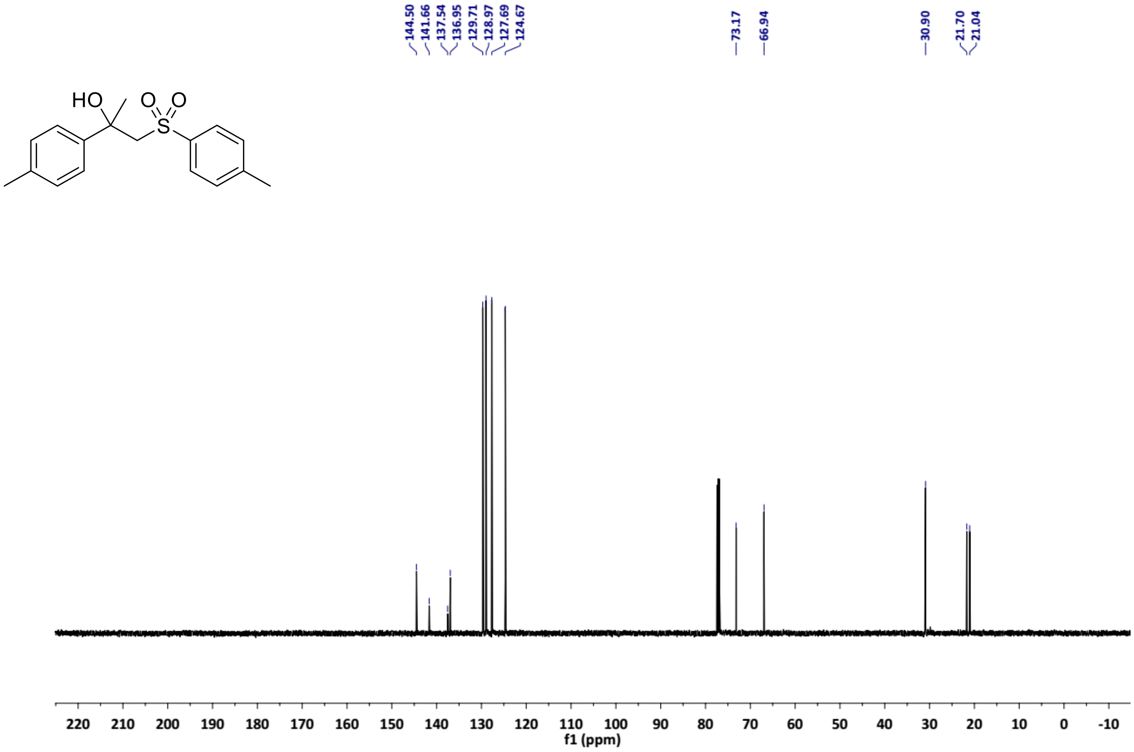
^{1}H NMR spectrum (500 MHz, CDCl$_3$) of **11o**



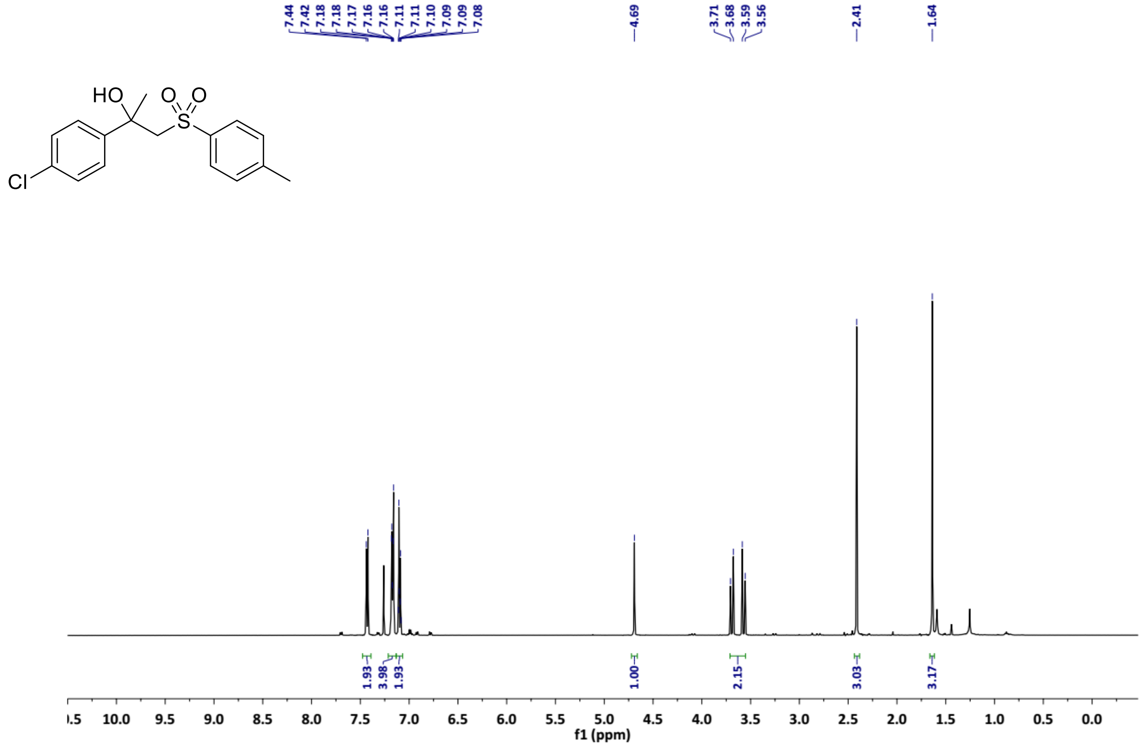
^{13}C NMR spectrum (126 MHz, CDCl$_3$) of **11o**



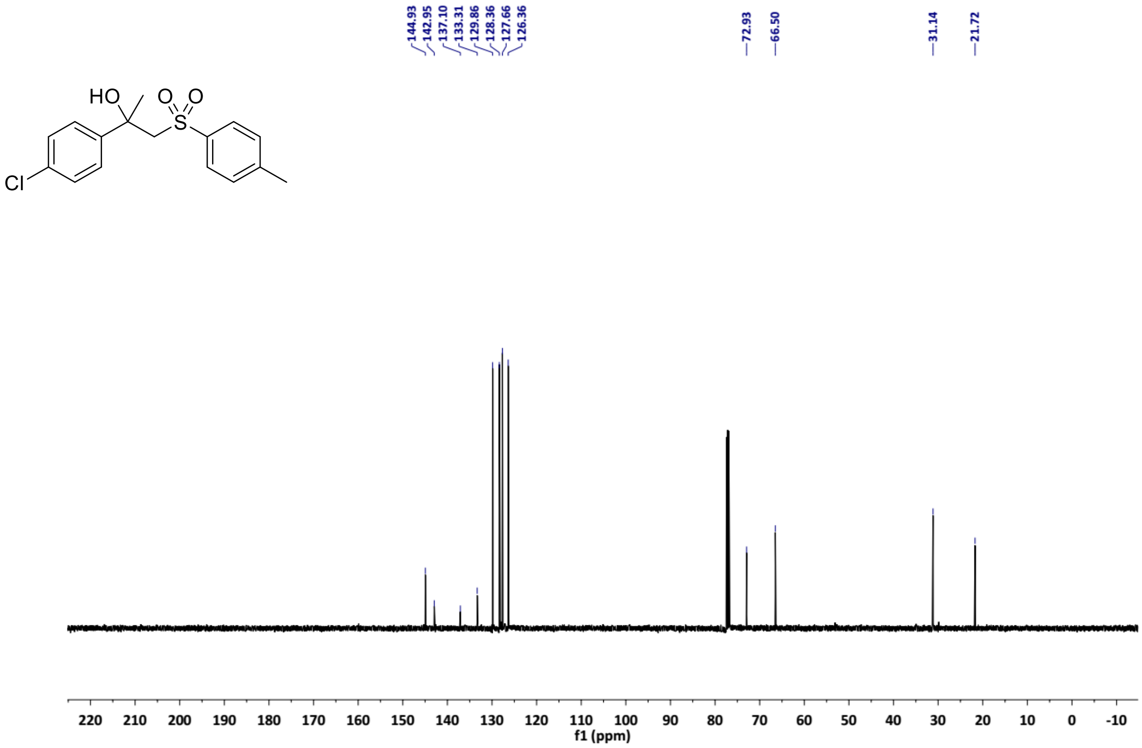
^{1}H NMR spectrum (500 MHz, CDCl$_3$) of **11p**



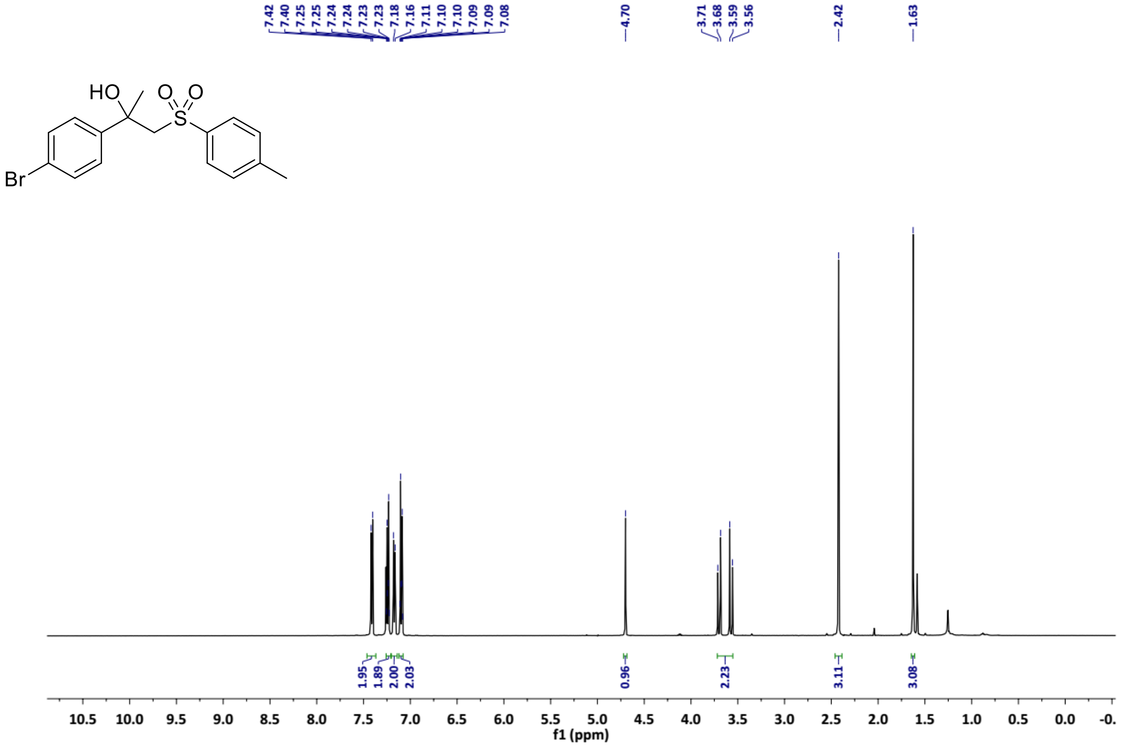
^{13}C NMR spectrum (126 MHz, CDCl$_3$) of **11p**



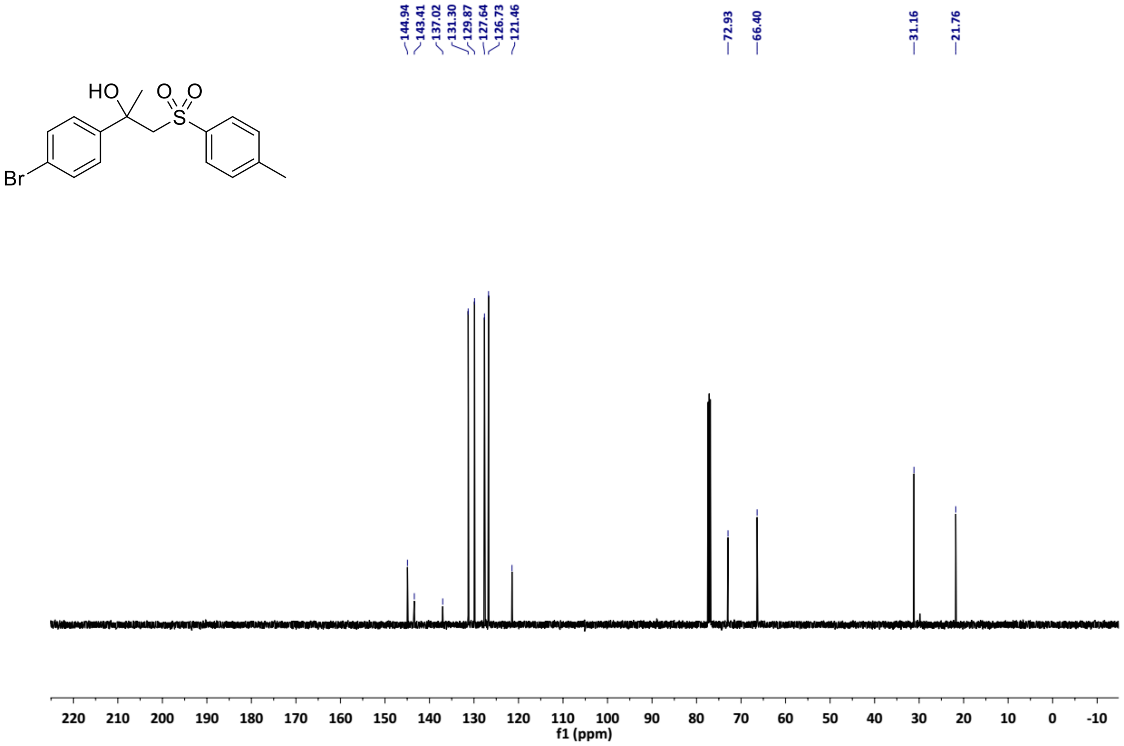
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **11q**



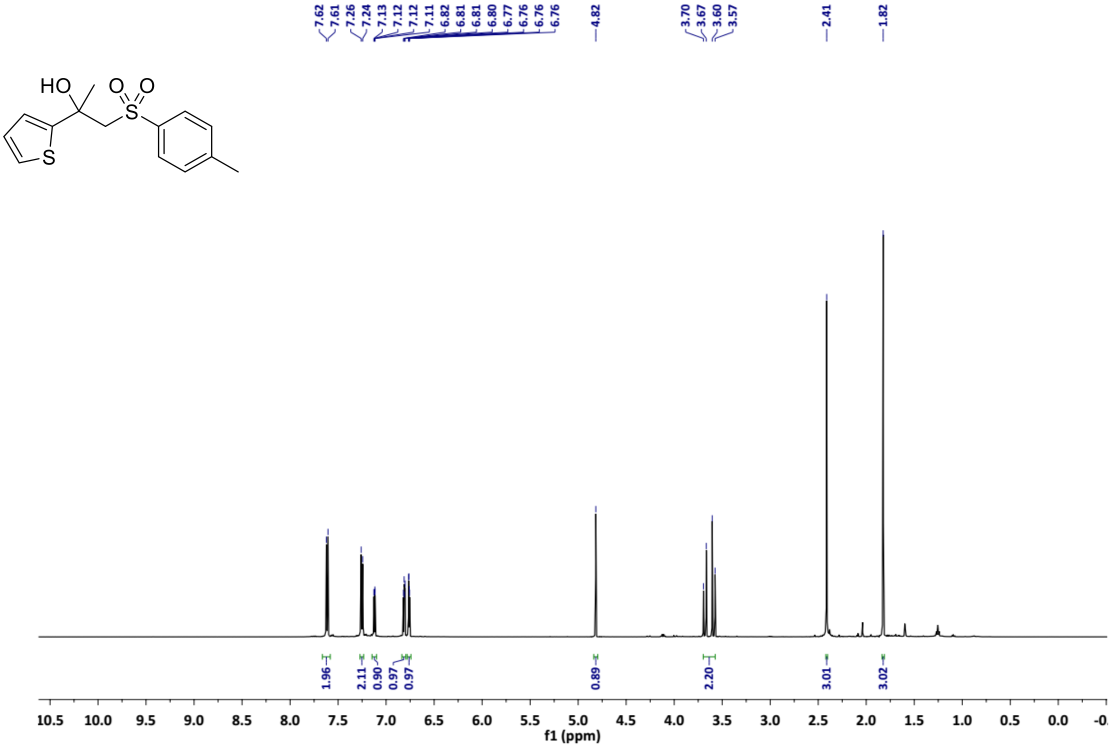
^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **11q**



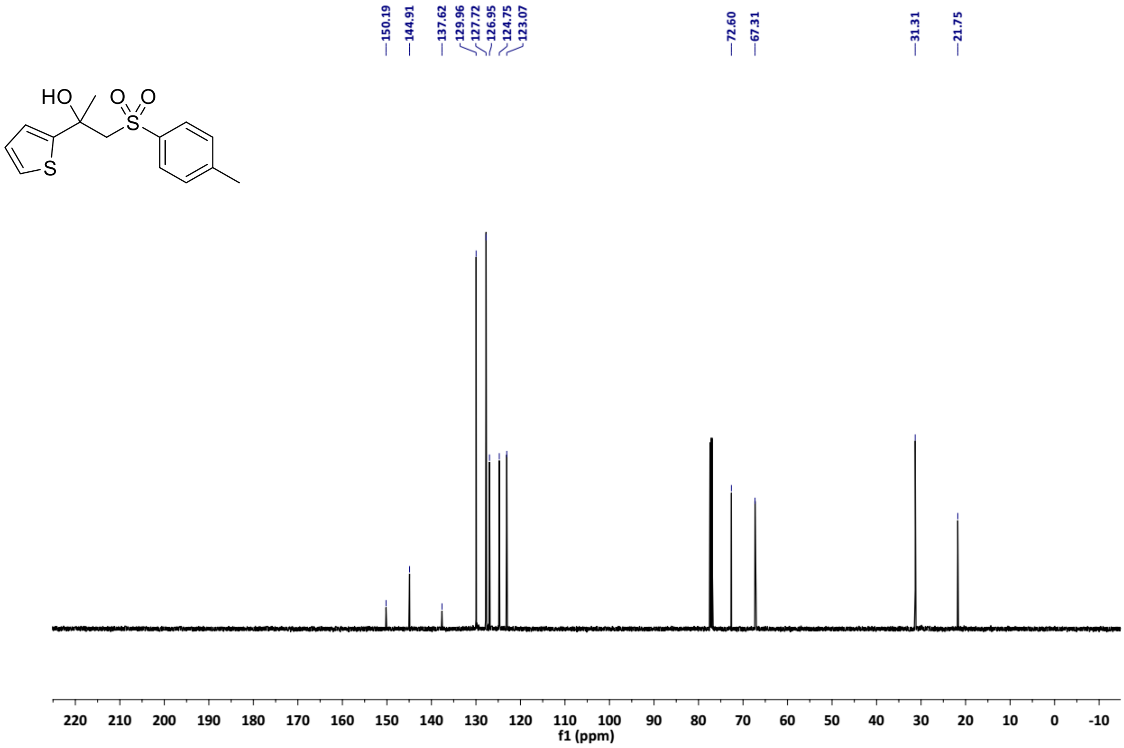
^{1}H NMR spectrum (500 MHz, CDCl$_3$) of **11r**



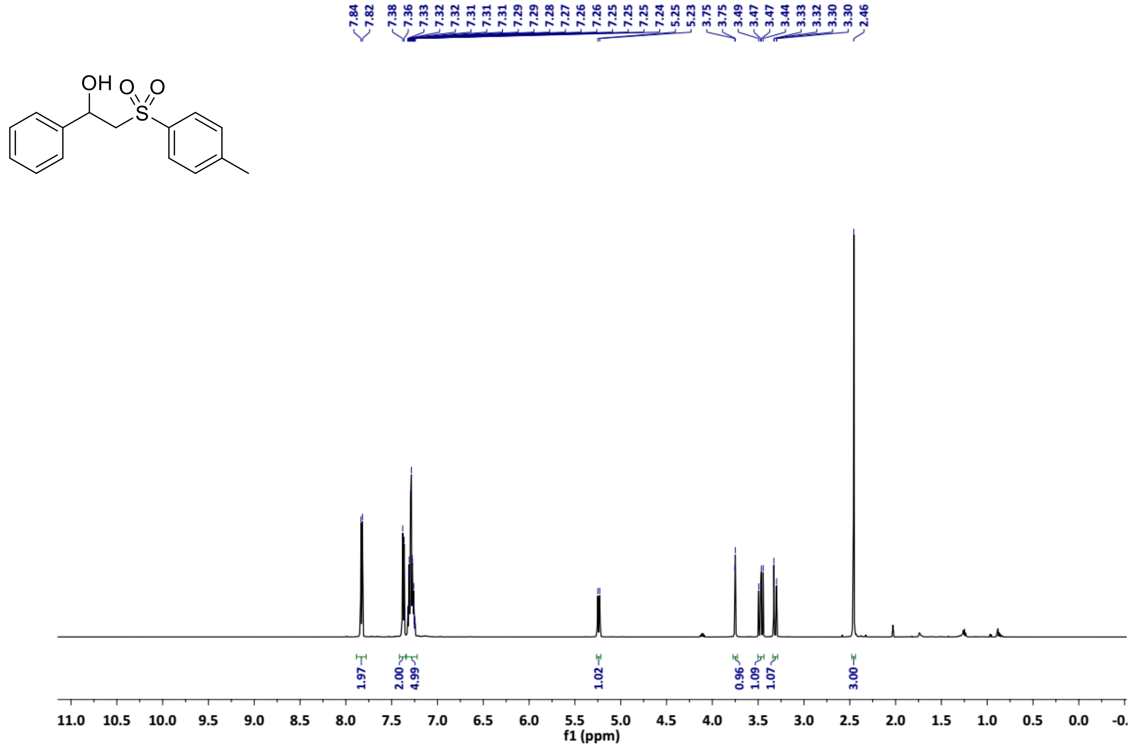
^{13}C NMR spectrum (126 MHz, CDCl$_3$) of **11r**



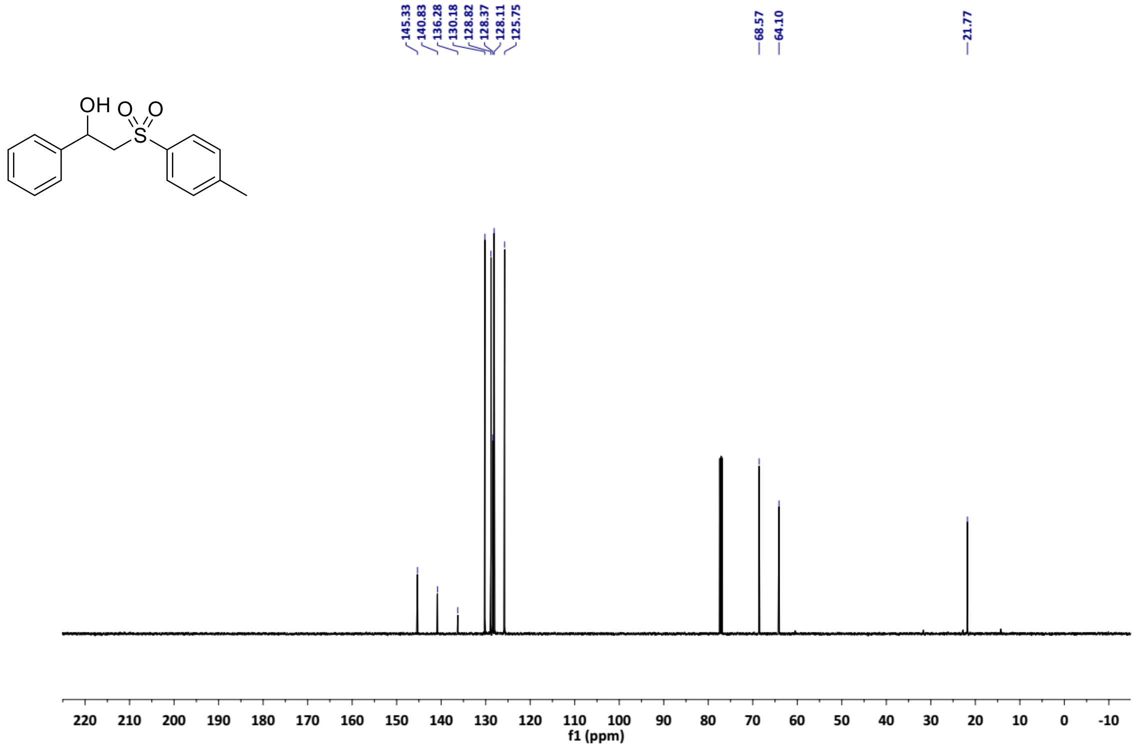
^{1}H NMR spectrum (500 MHz, CDCl$_3$) of **11s**



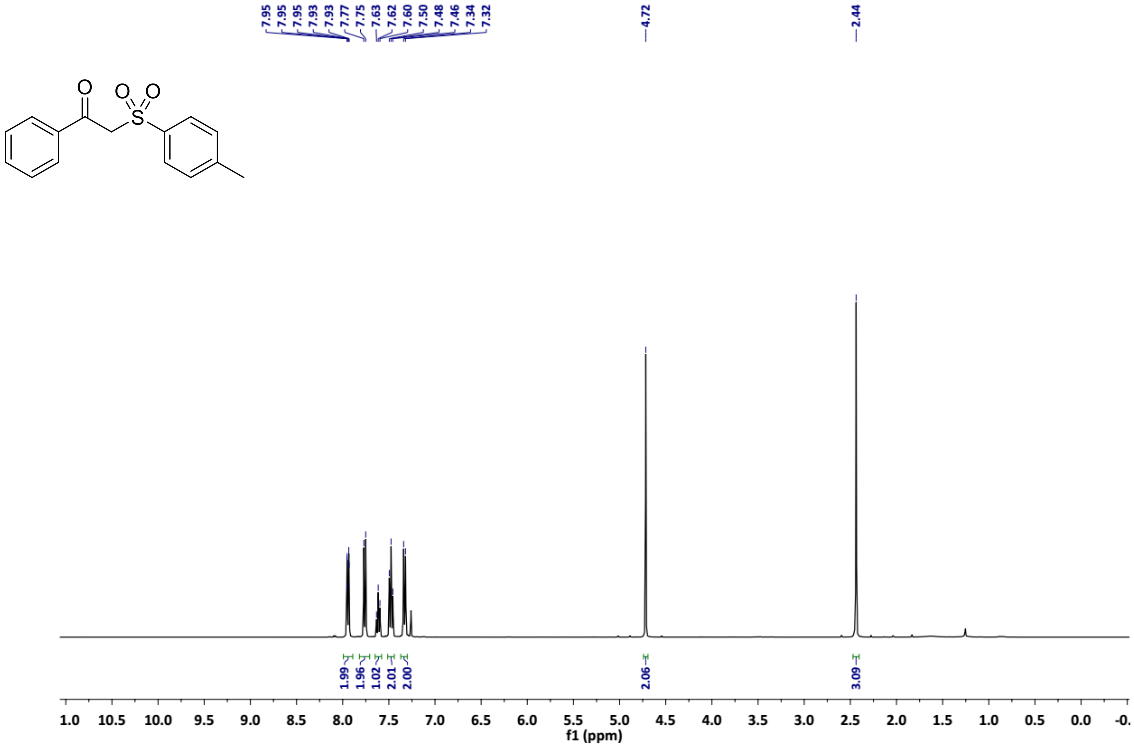
^{13}C NMR spectrum (126 MHz, CDCl$_3$) of **11s**



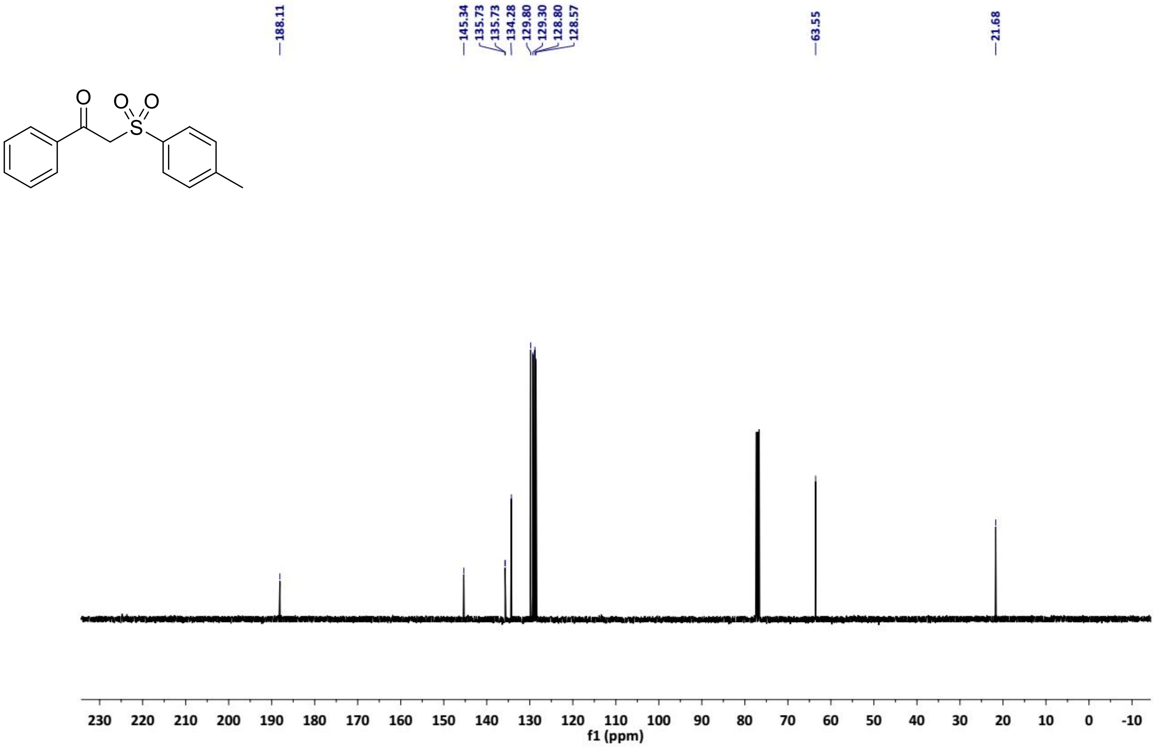
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **11t**



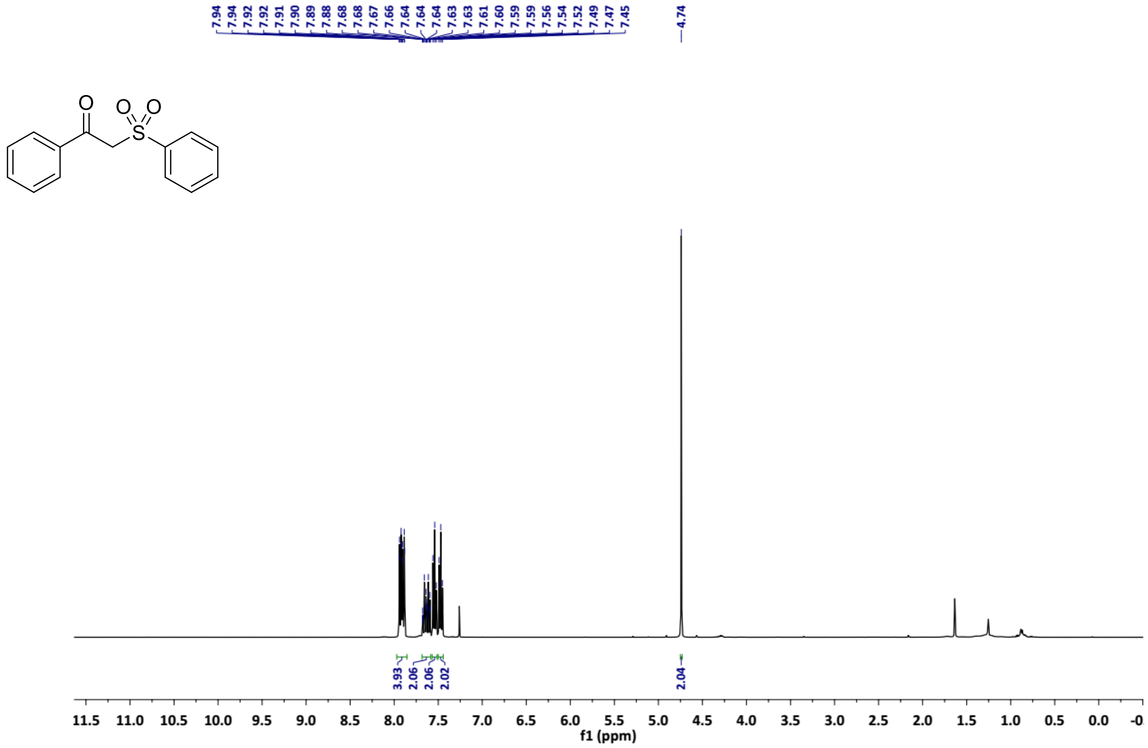
^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **11t**



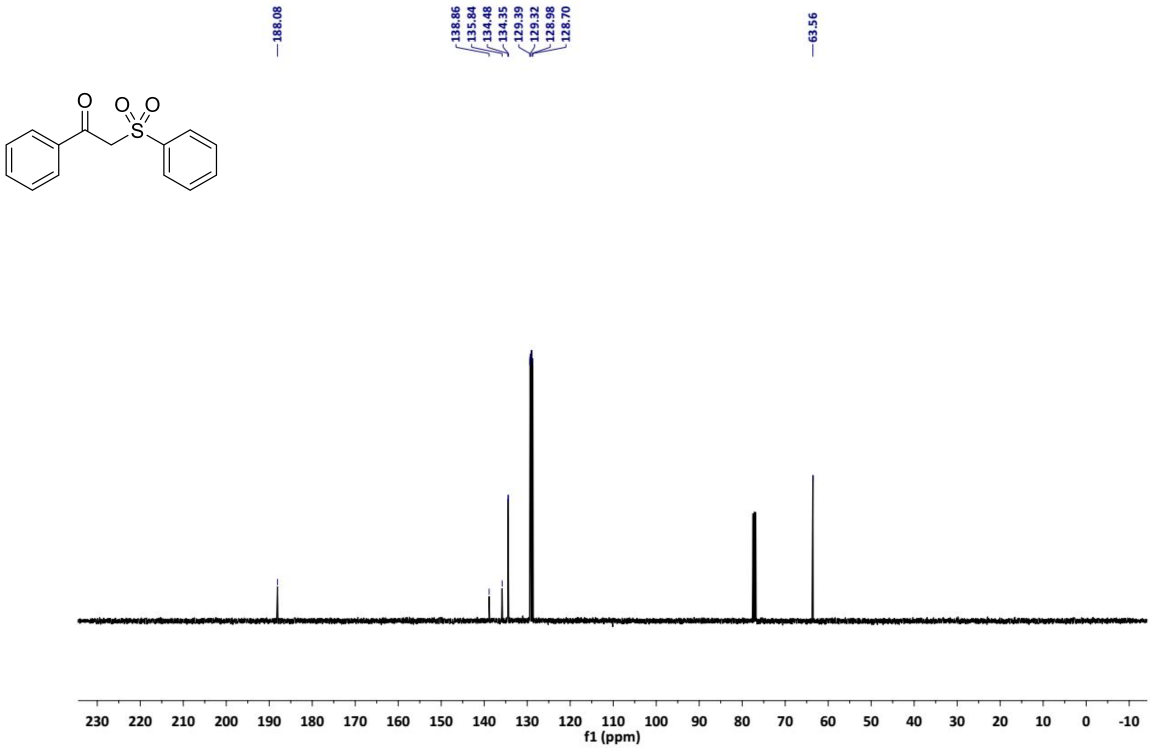
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **13a**



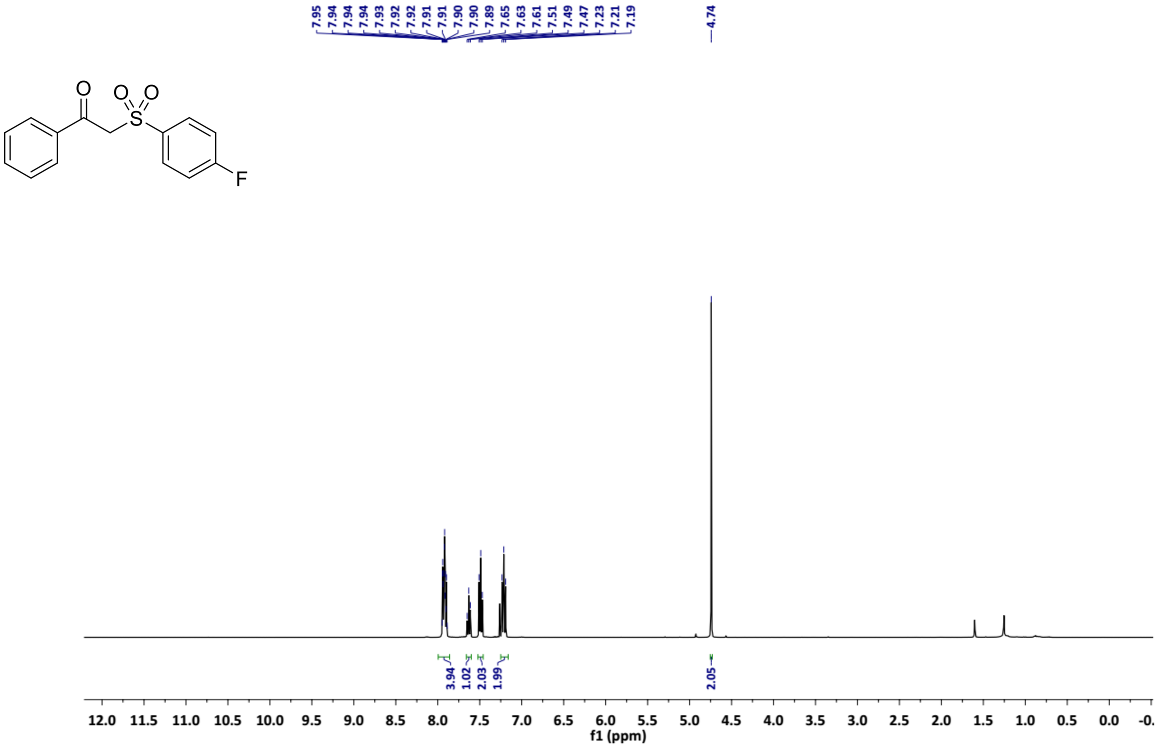
^{13}C NMR spectrum (101 MHz, CDCl$_3$) of **13a**



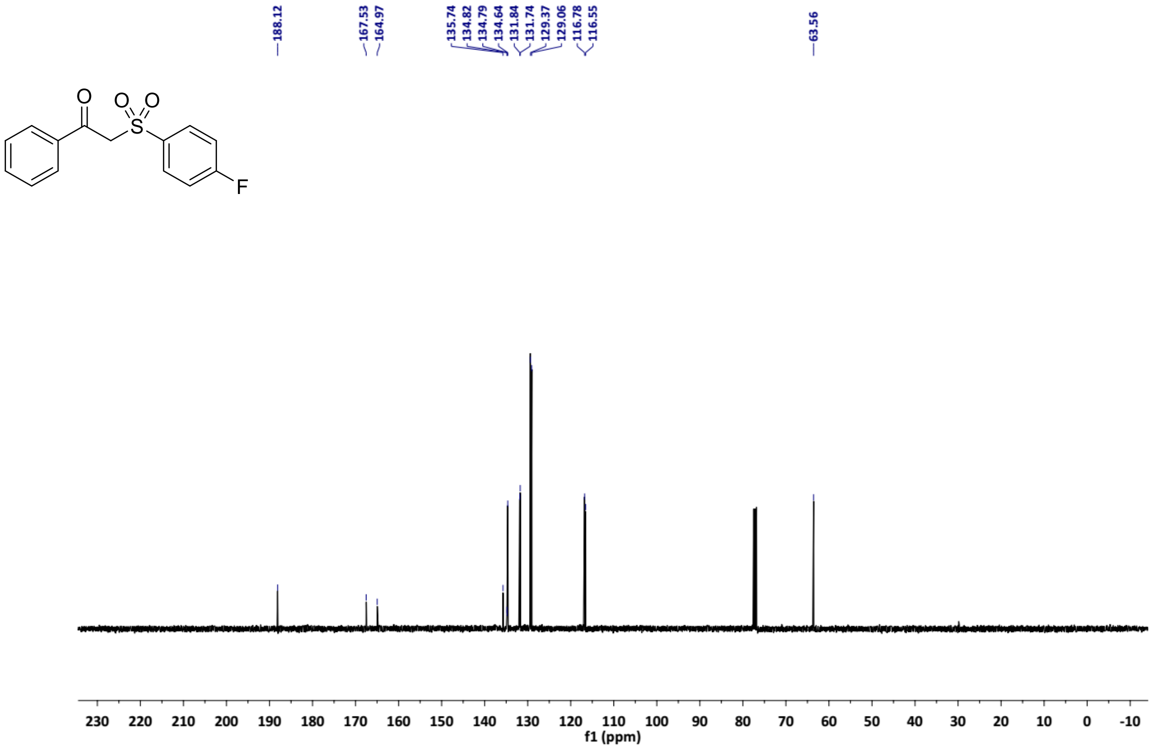
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **13b**



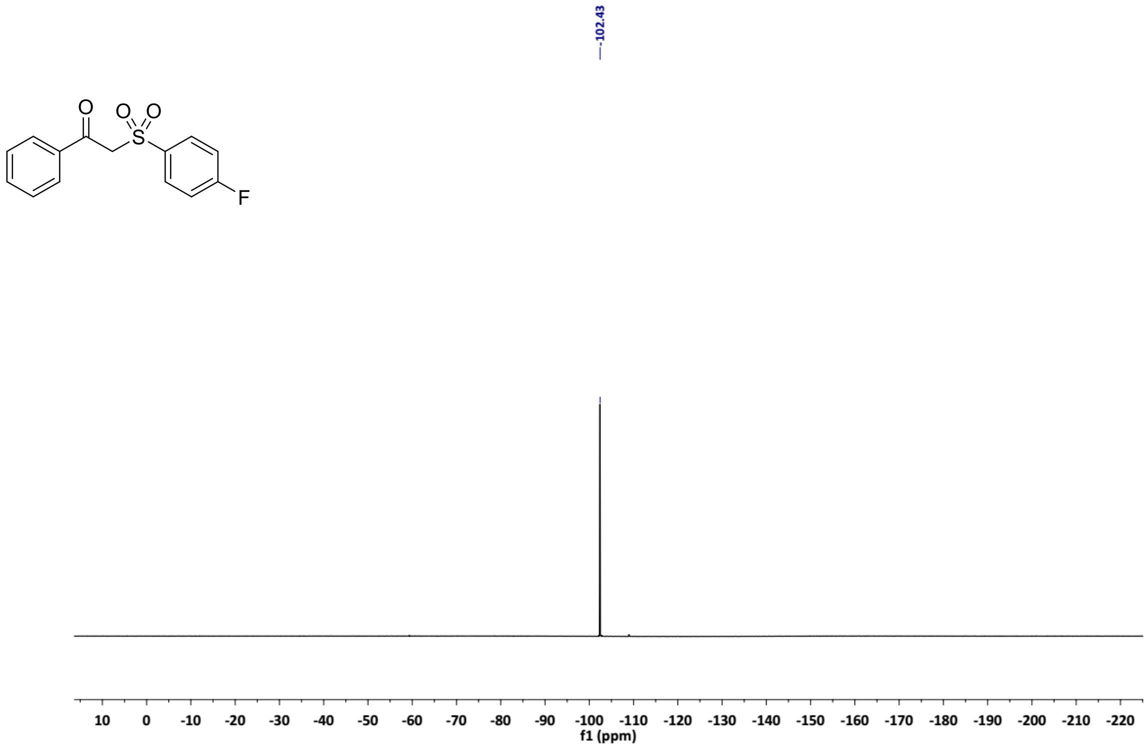
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **13b**



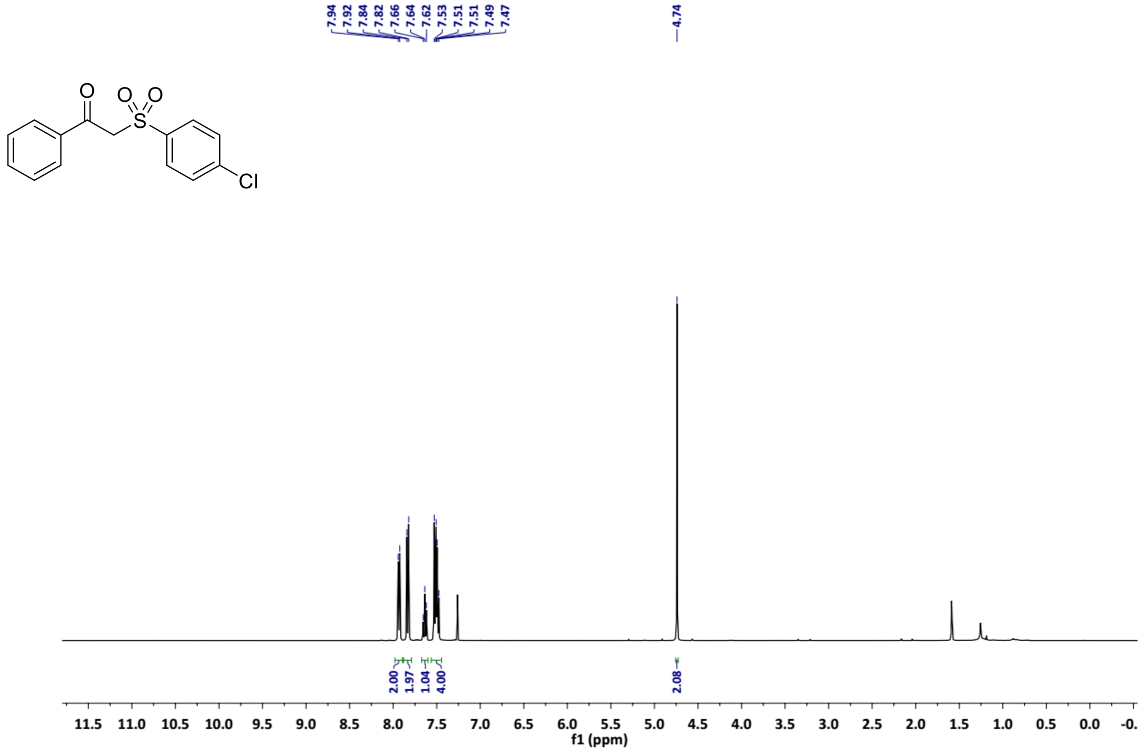
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **13c**



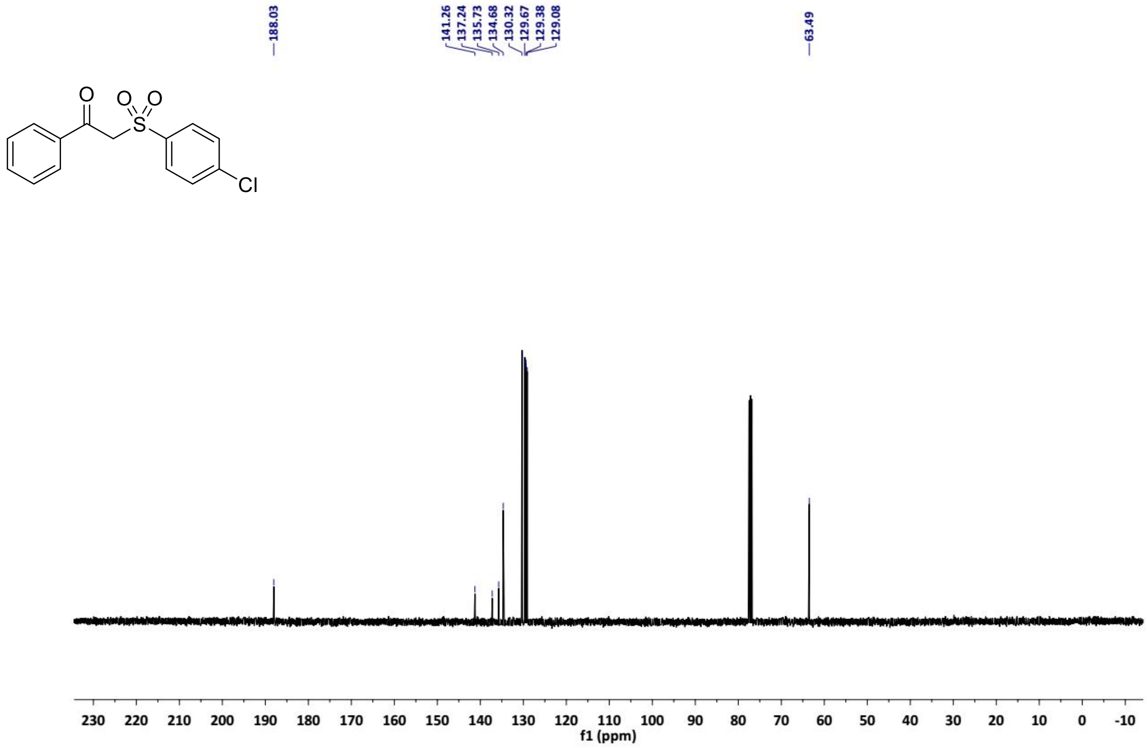
^{13}C NMR spectrum (101 MHz, CDCl$_3$) of **13c**



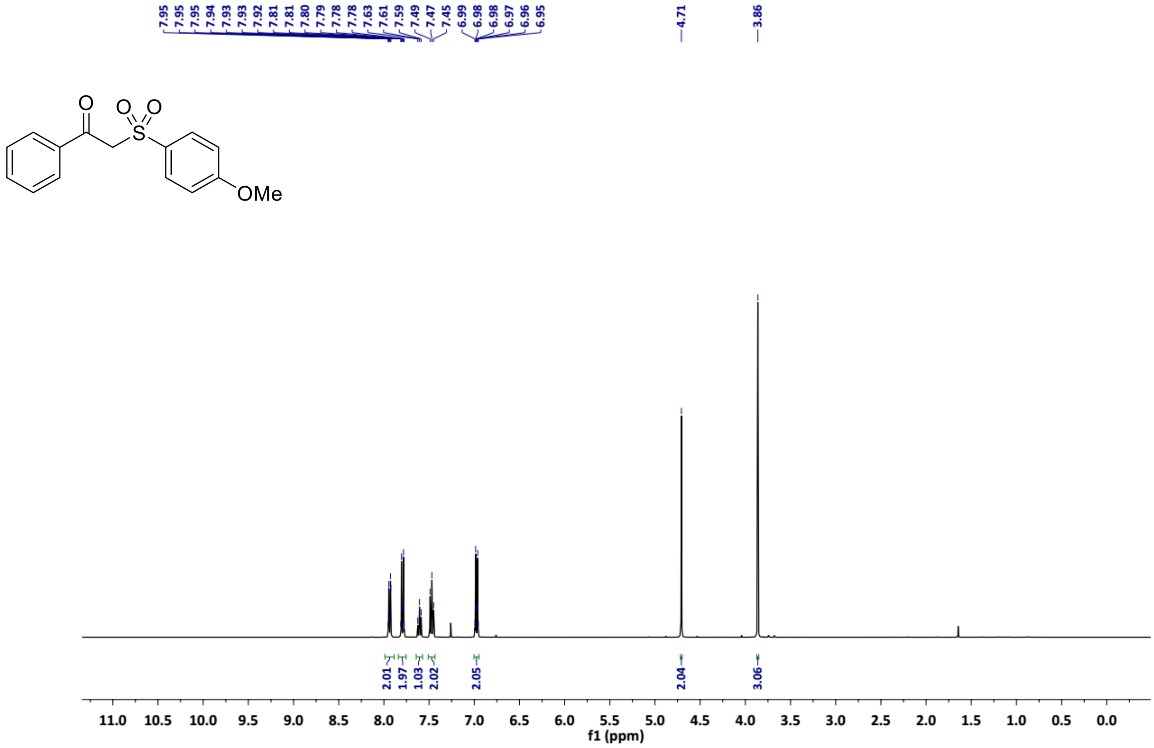
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **13c**



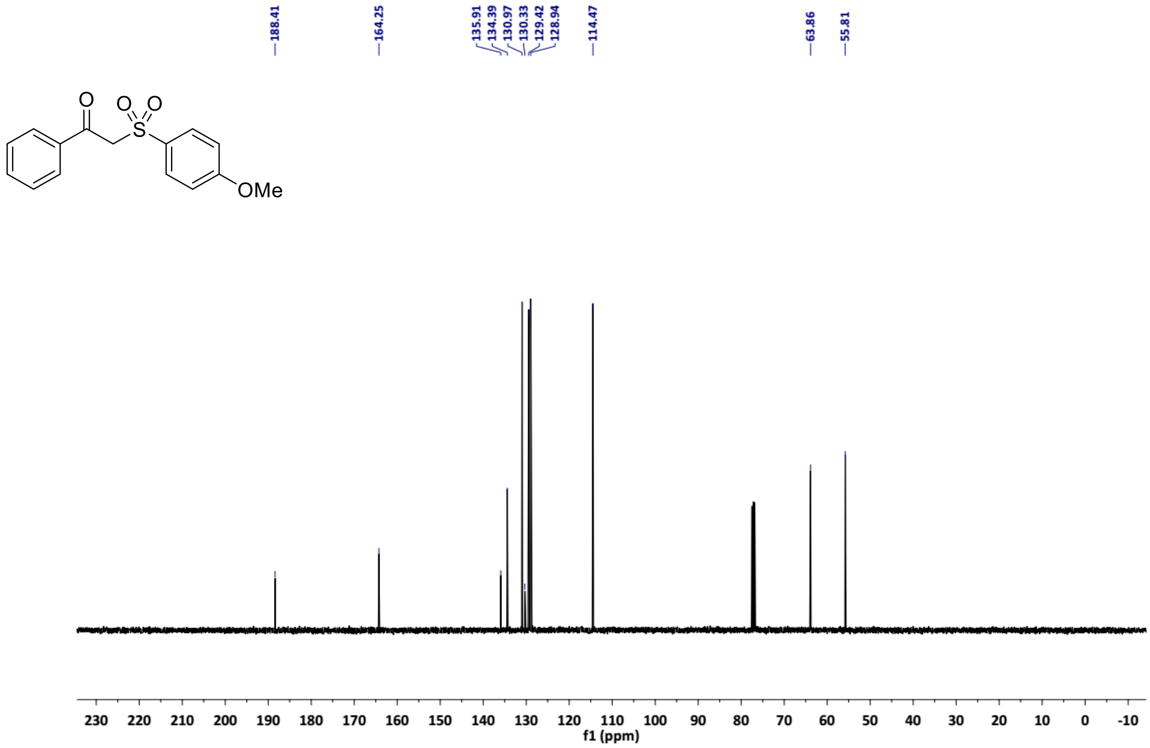
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **13d**



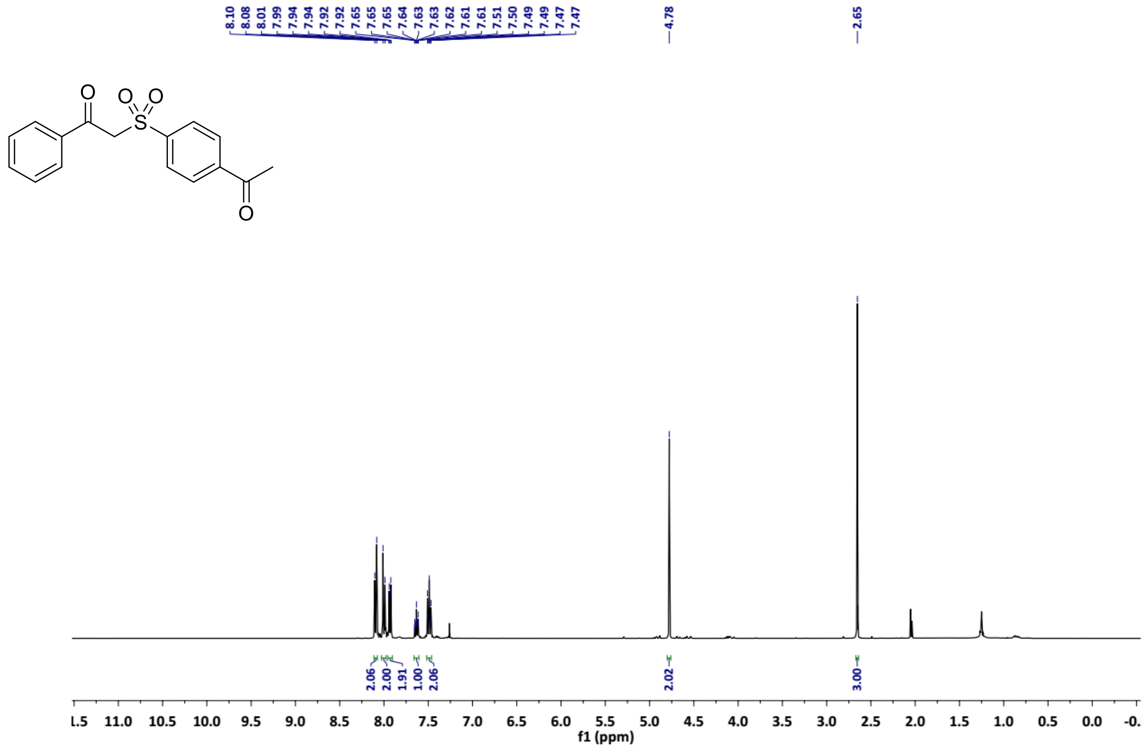
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **13d**



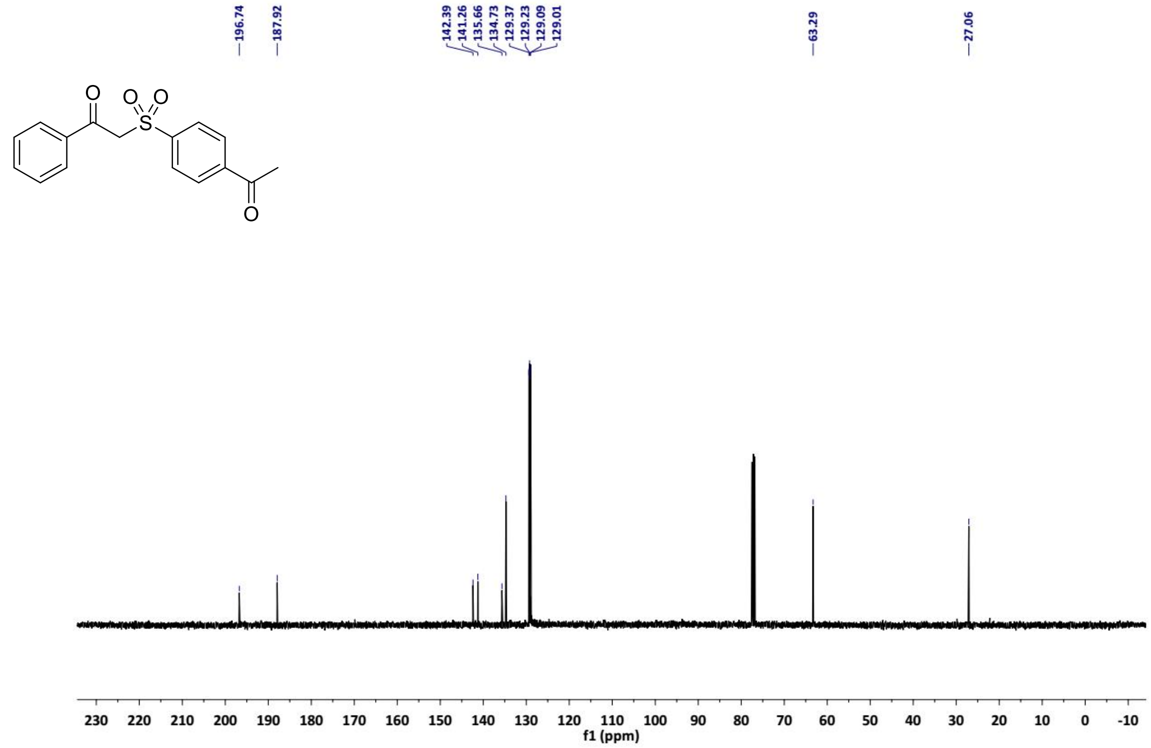
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **13e**



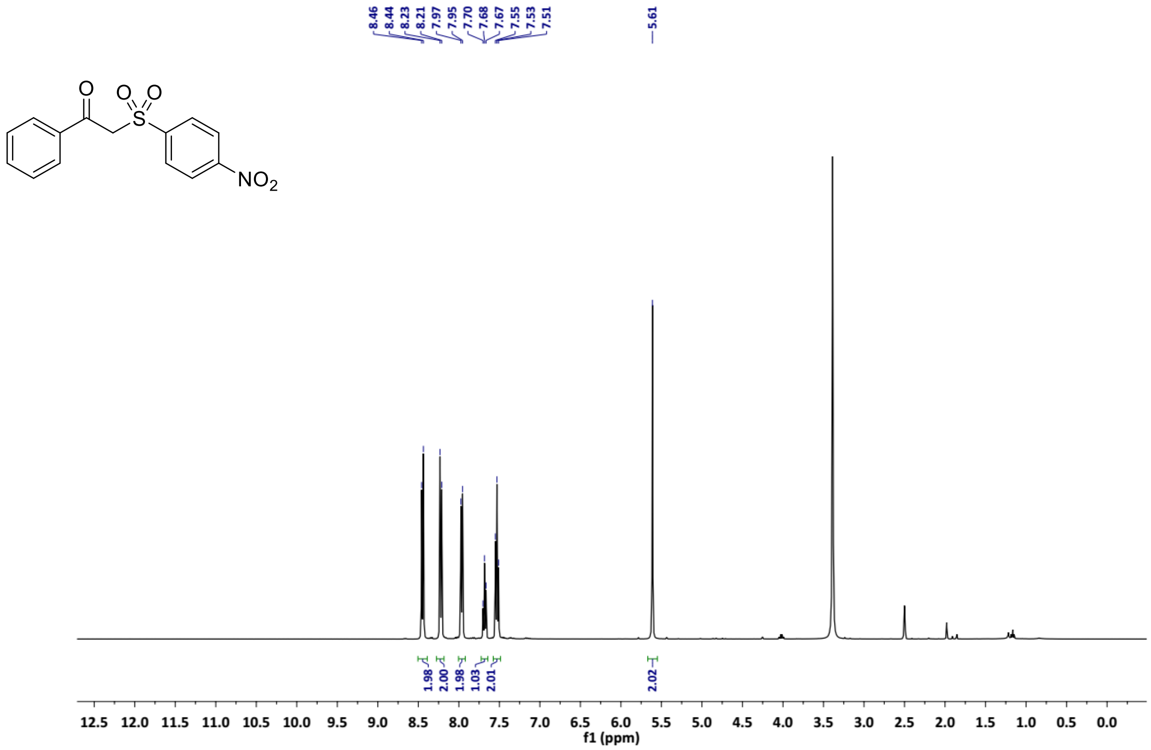
^{13}C NMR spectrum (101 MHz, CDCl$_3$) of **13e**



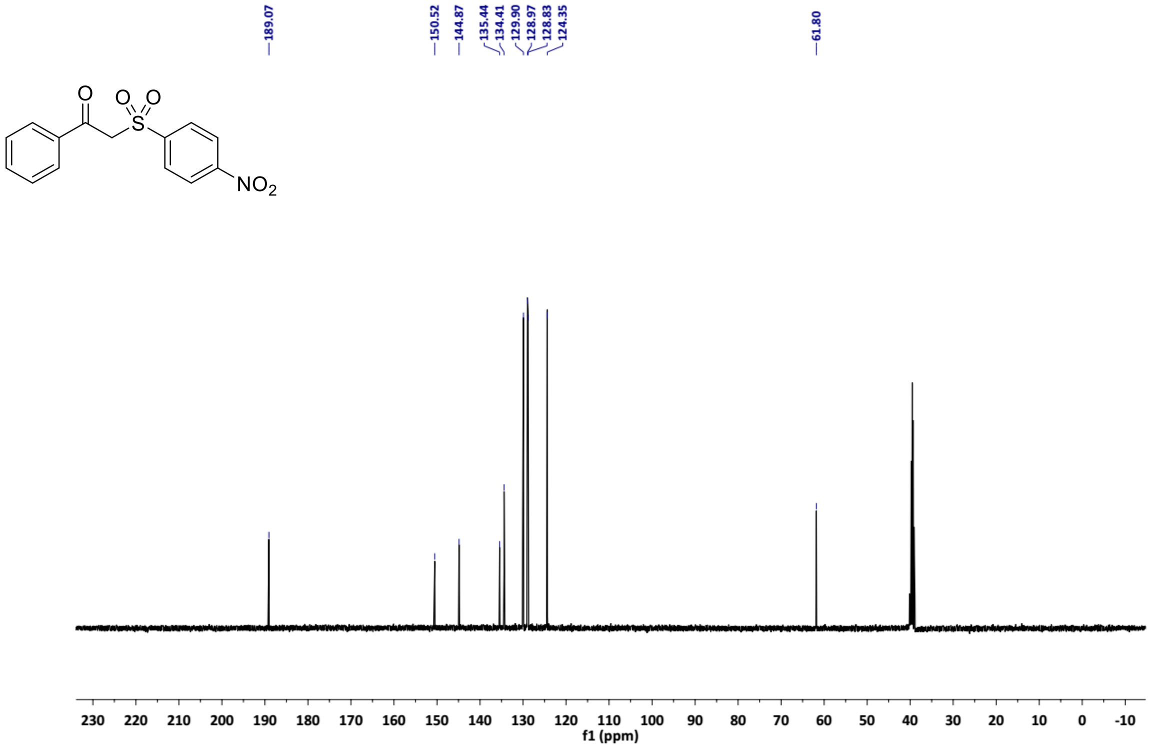
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **13f**



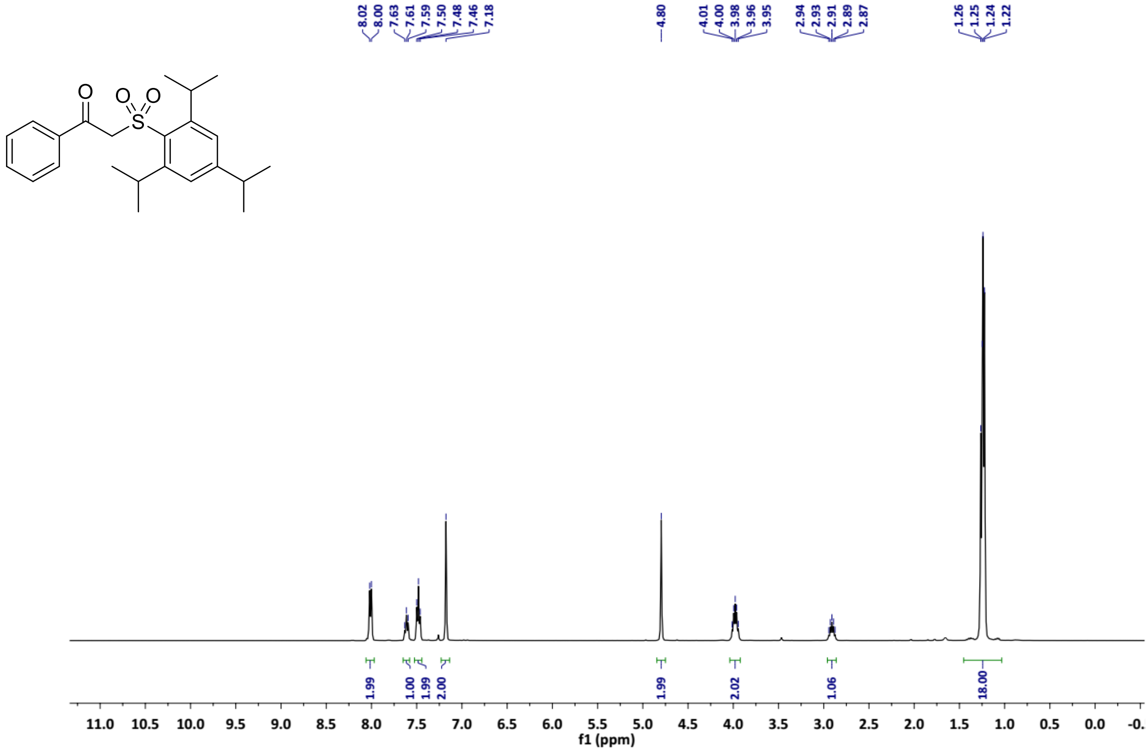
^{13}C NMR spectrum (101 MHz, CDCl$_3$) of **13f**



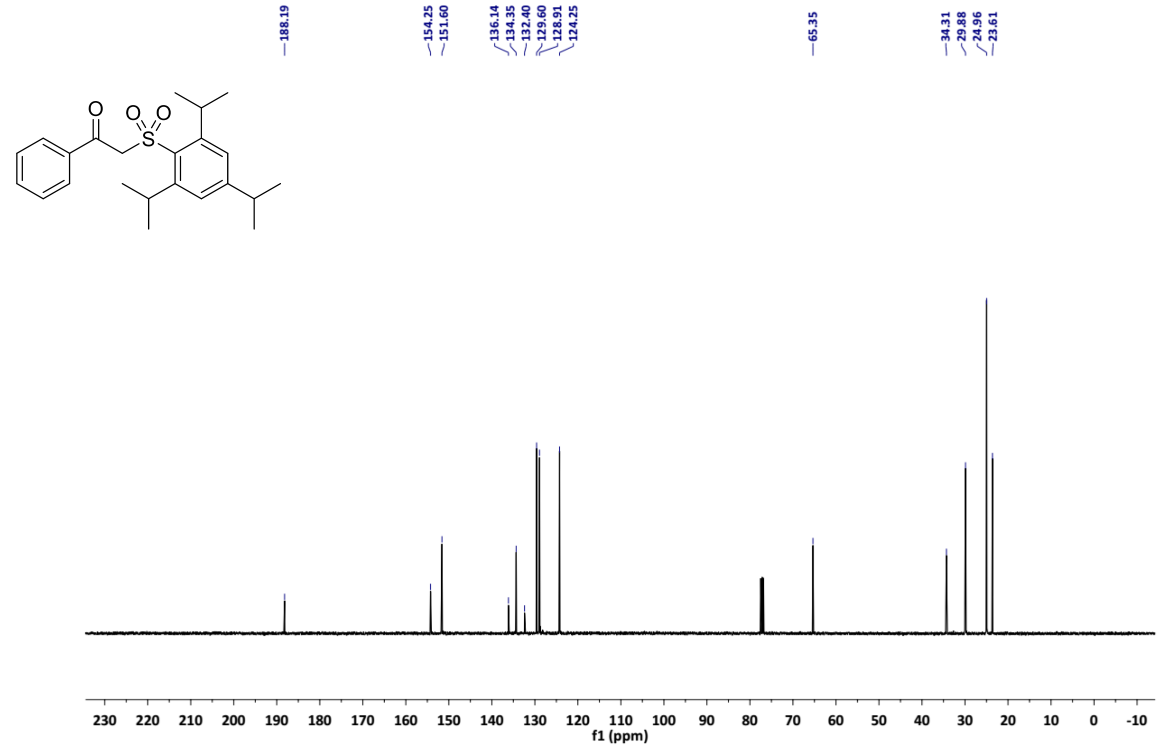
^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **13g**



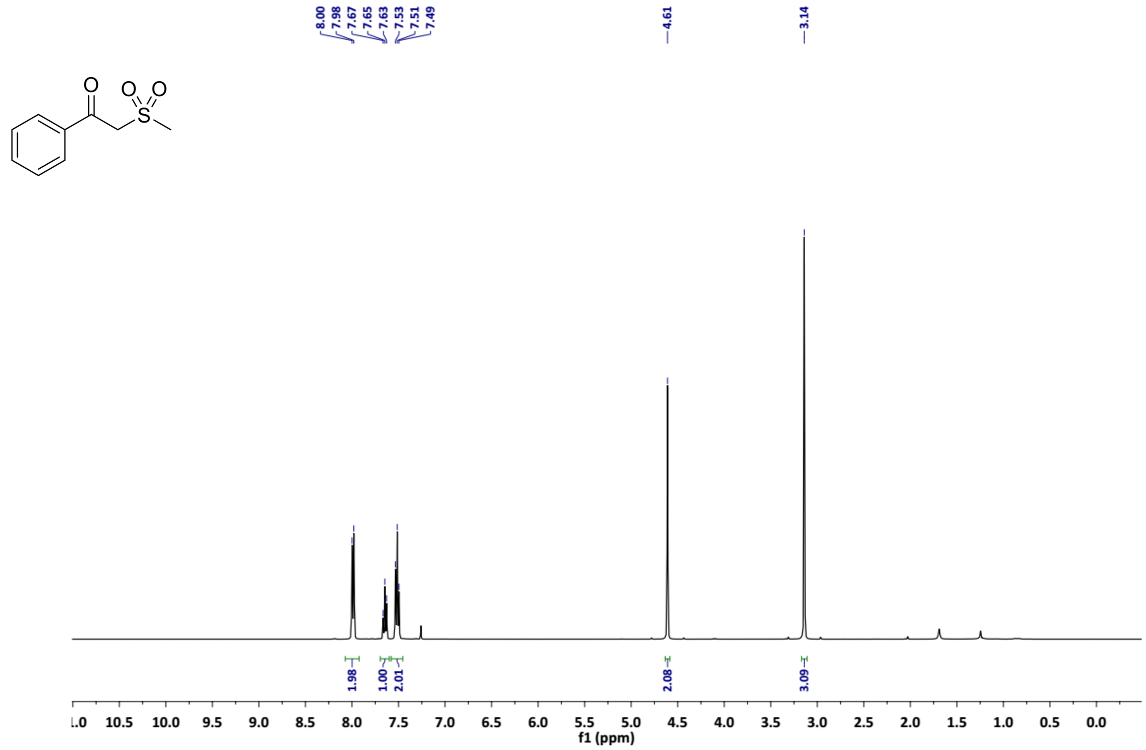
^{13}C NMR spectrum (101 MHz, DMSO-d_6) of **13g**



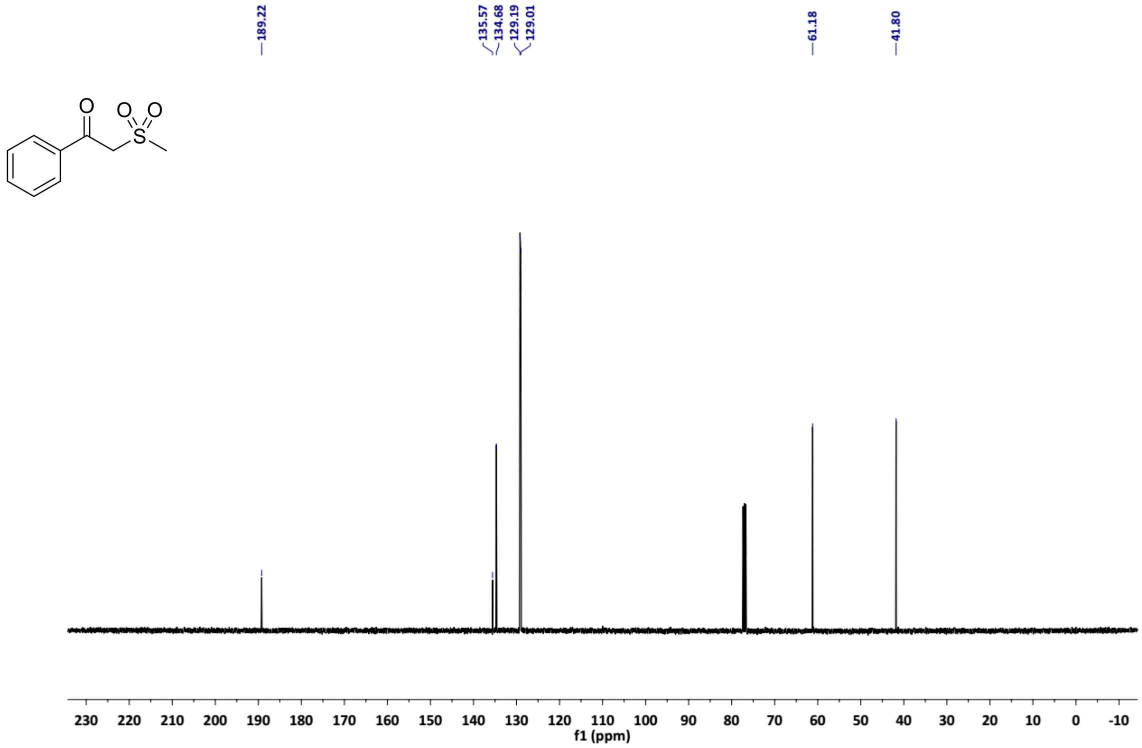
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **13h**



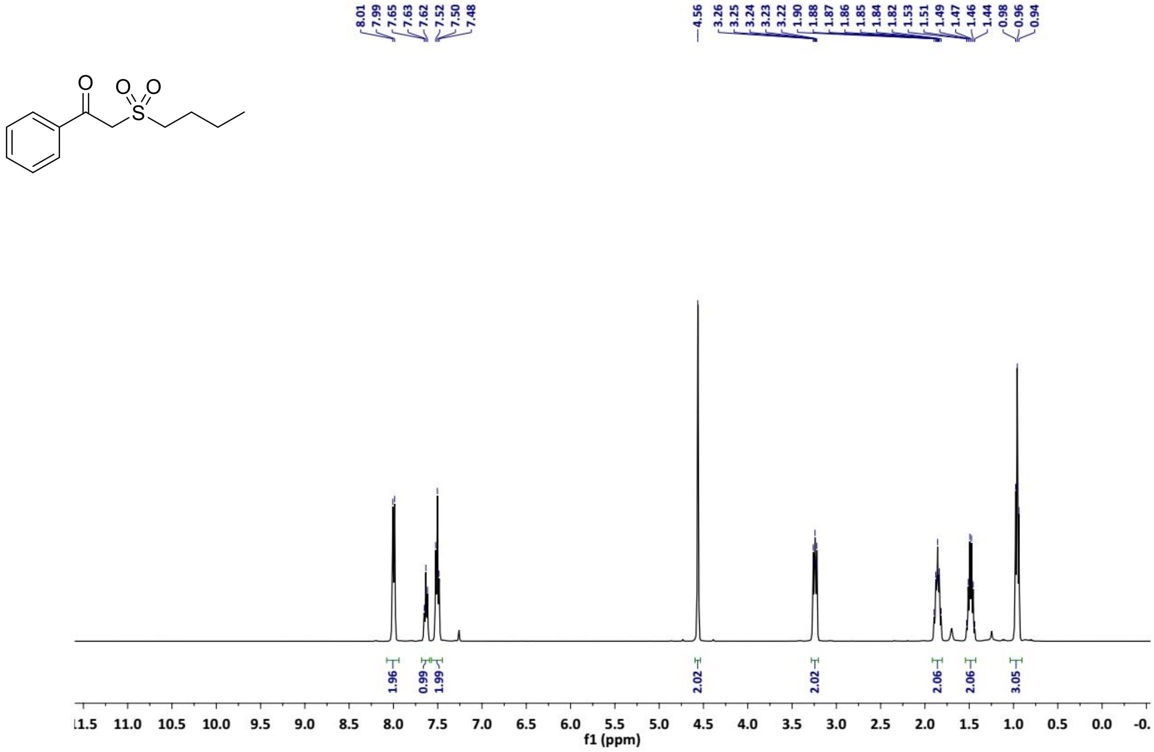
^{13}C NMR spectrum (101 MHz, CDCl$_3$) of **13h**



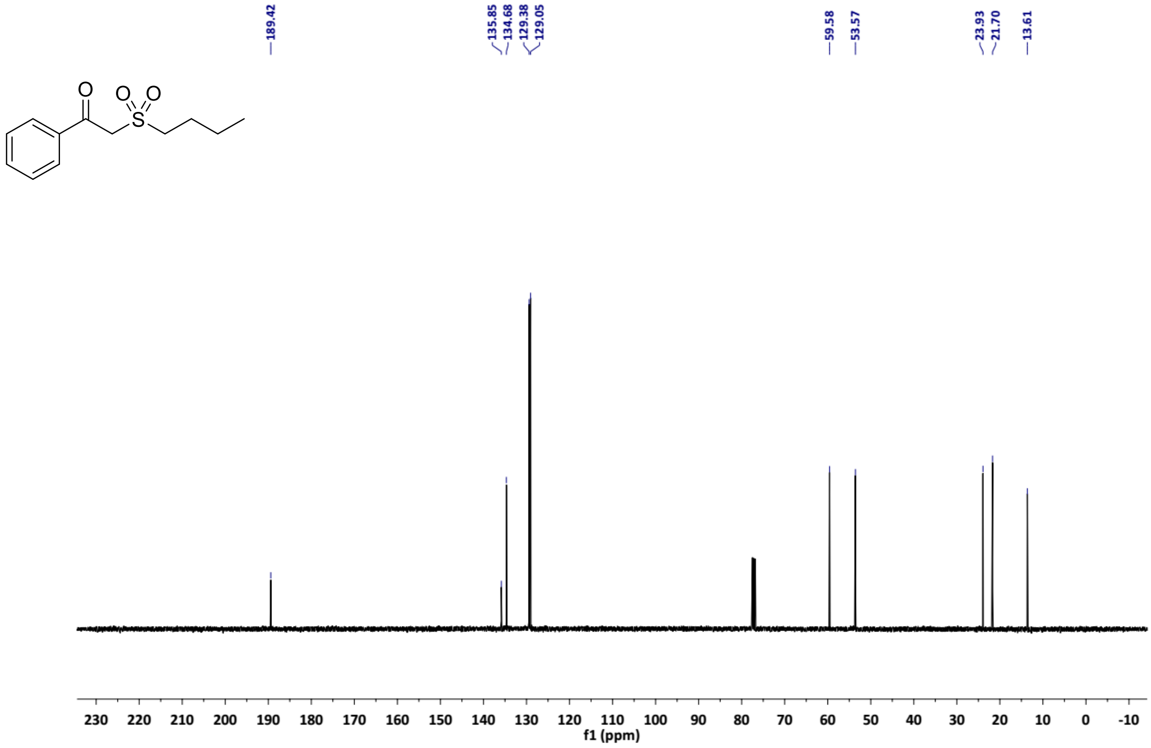
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **13i**



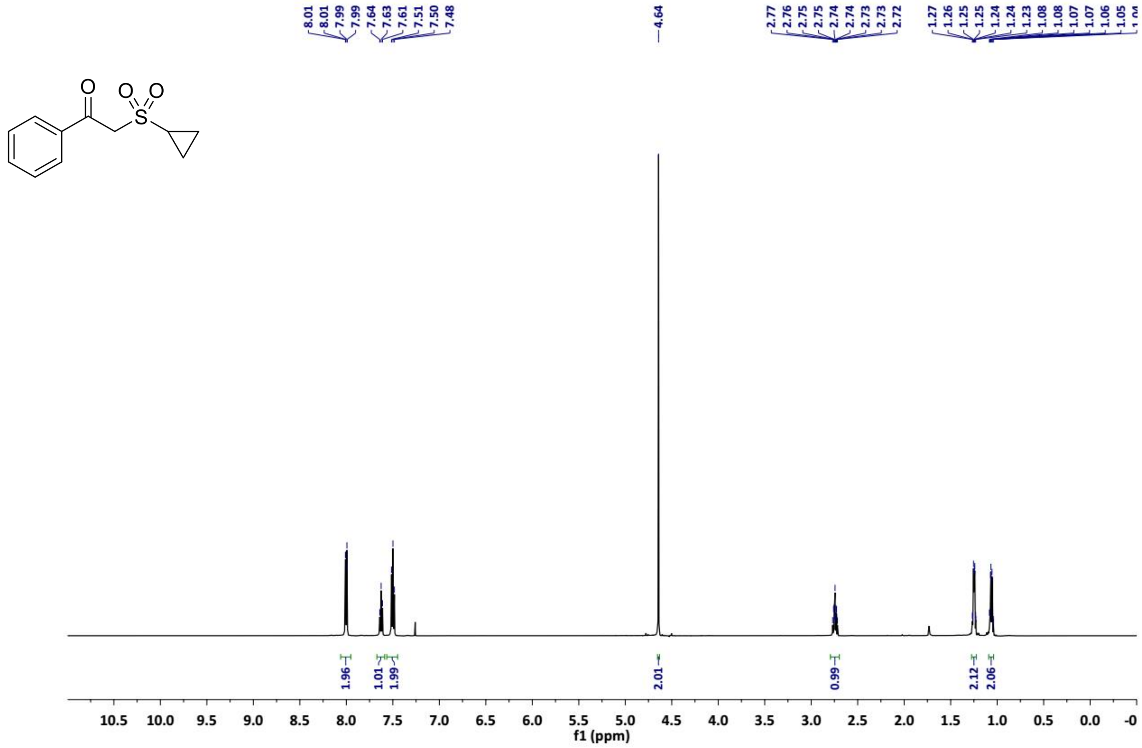
^{13}C NMR spectrum (101 MHz, CDCl$_3$) of **13i**



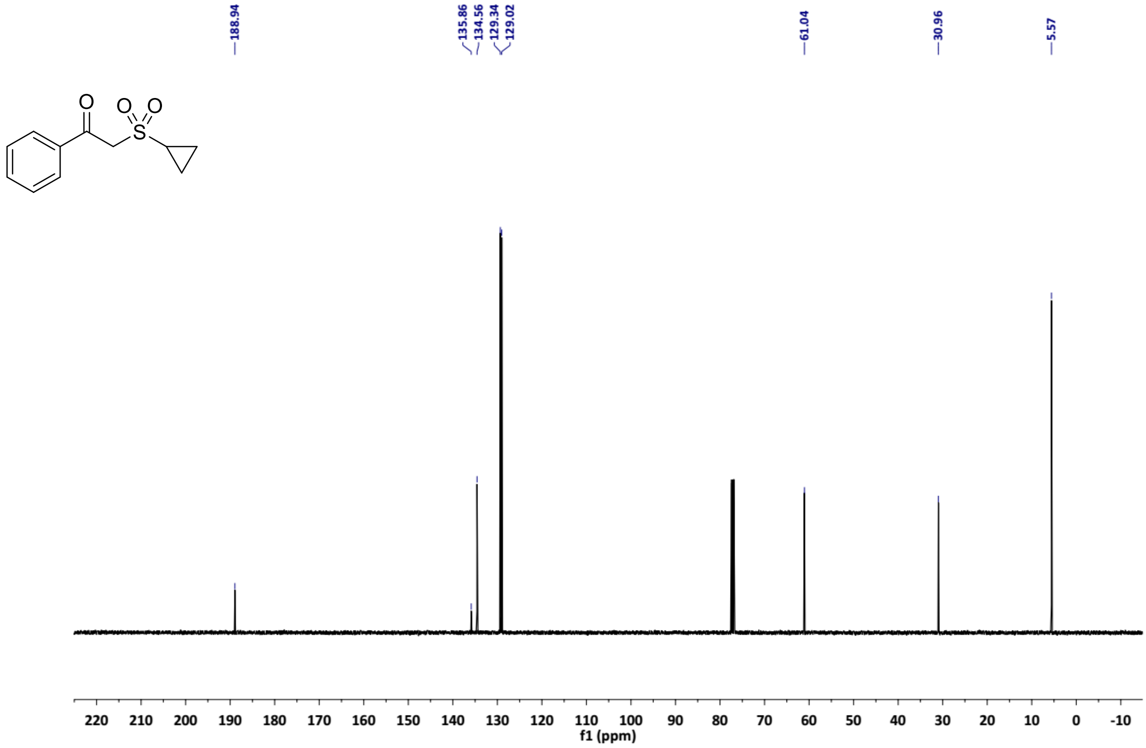
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **13j**



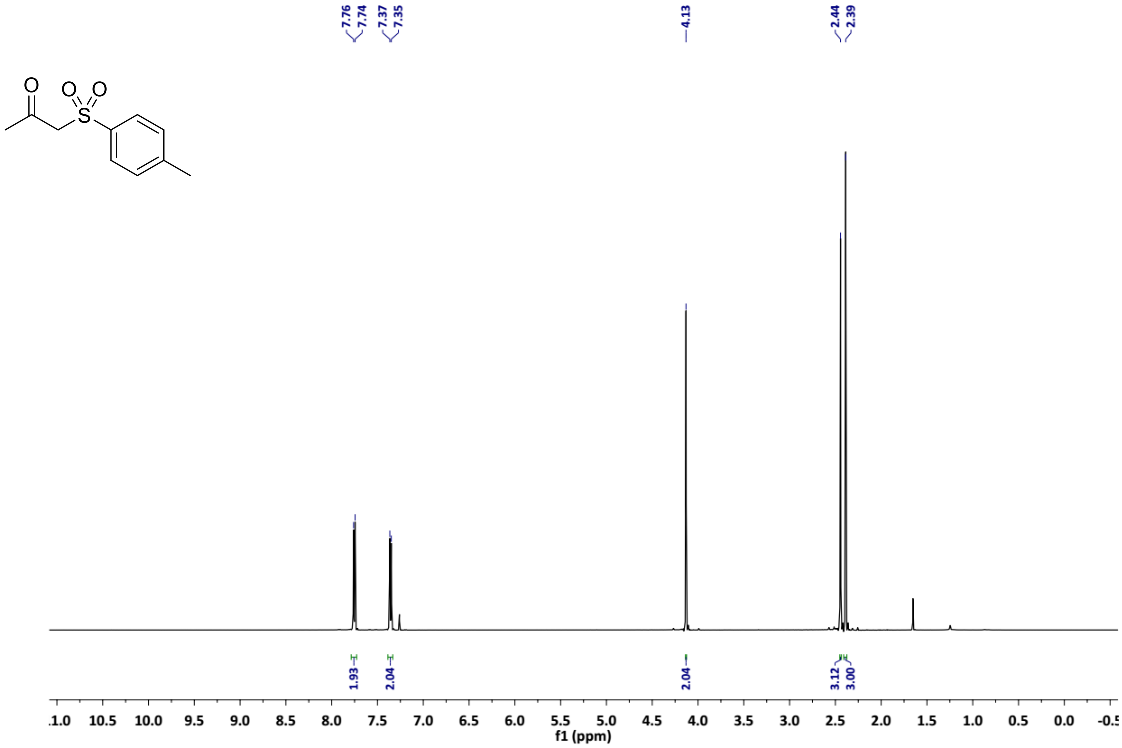
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **13j**



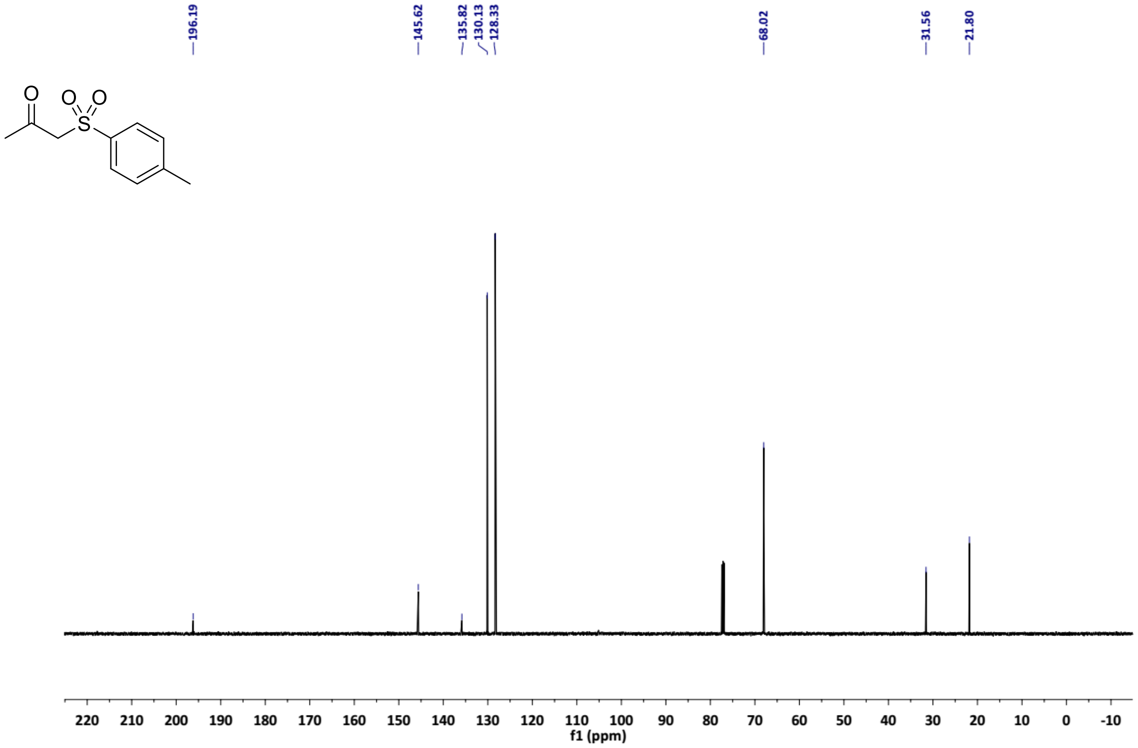
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **13k**



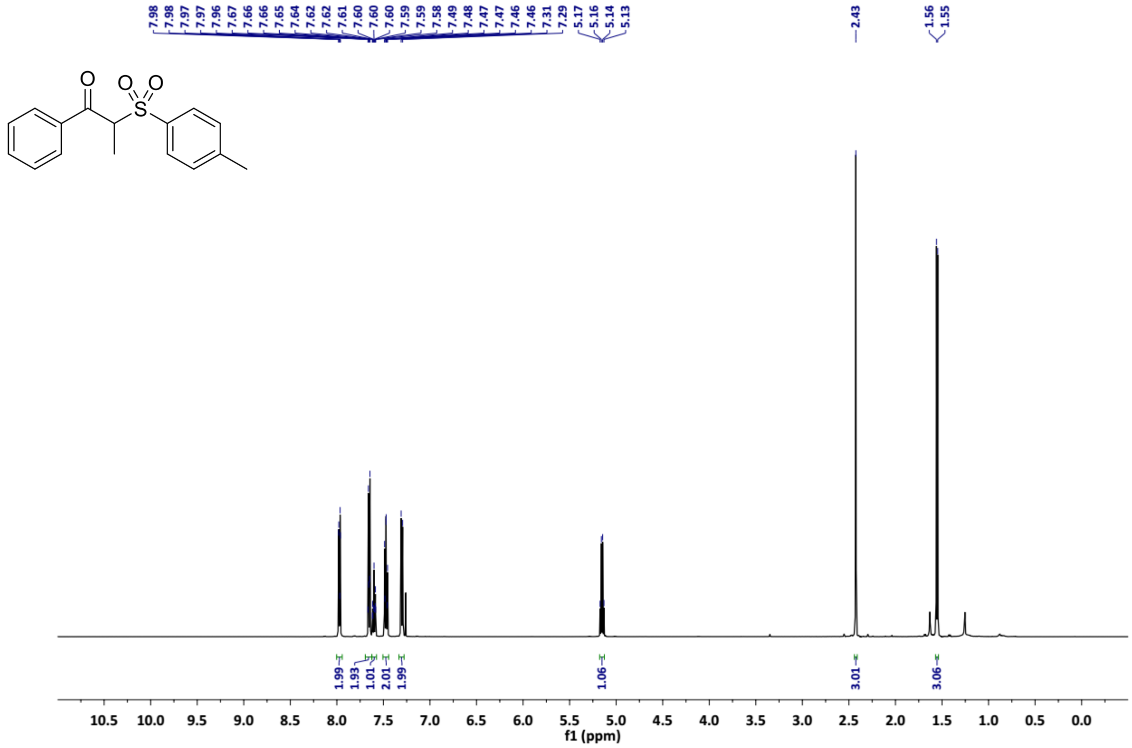
^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **13k**



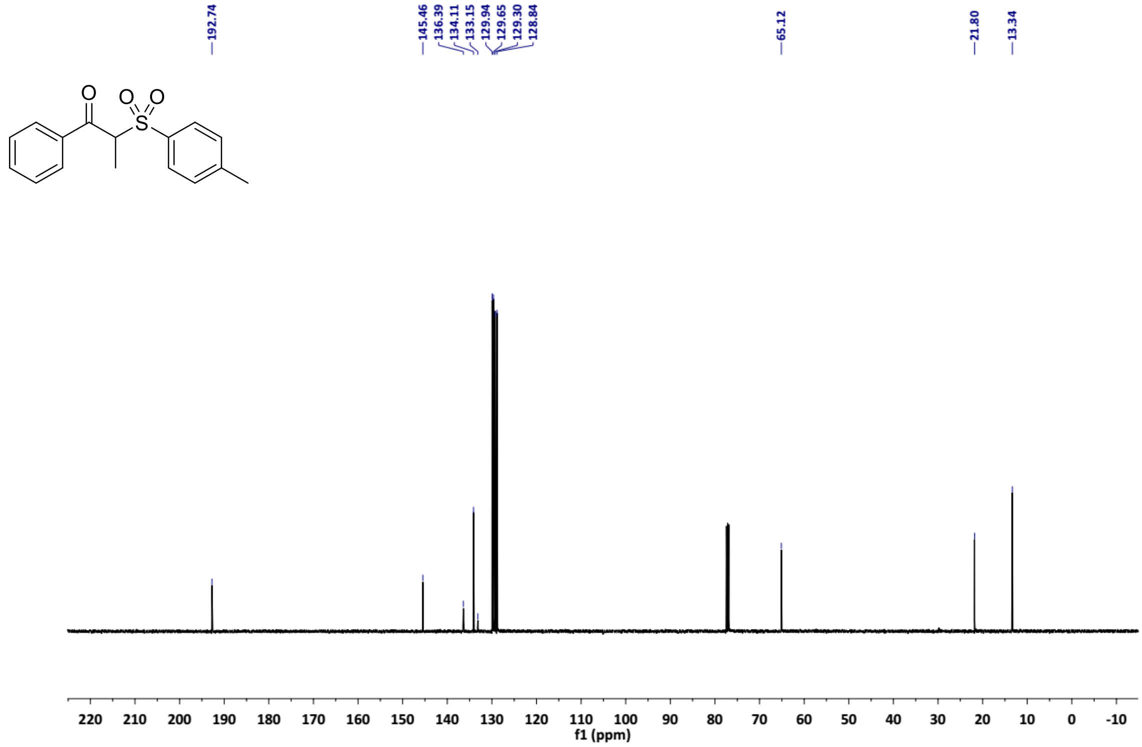
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **13l**



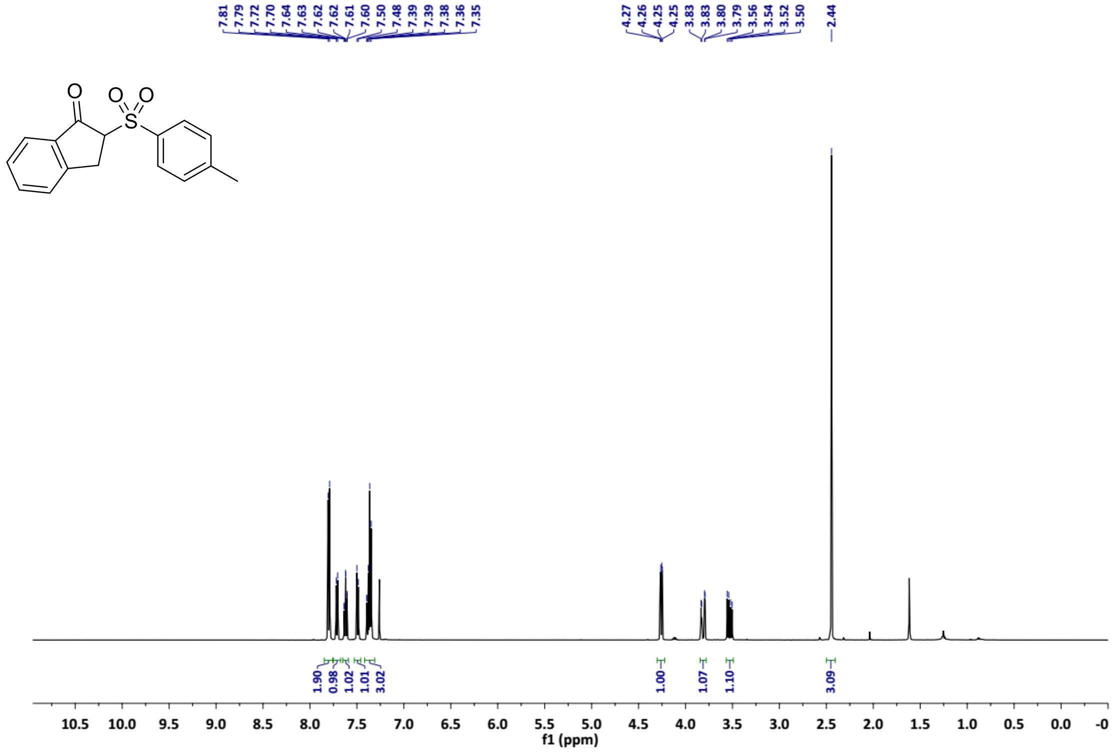
^{13}C NMR spectrum (126 MHz, CDCl$_3$) of **13l**



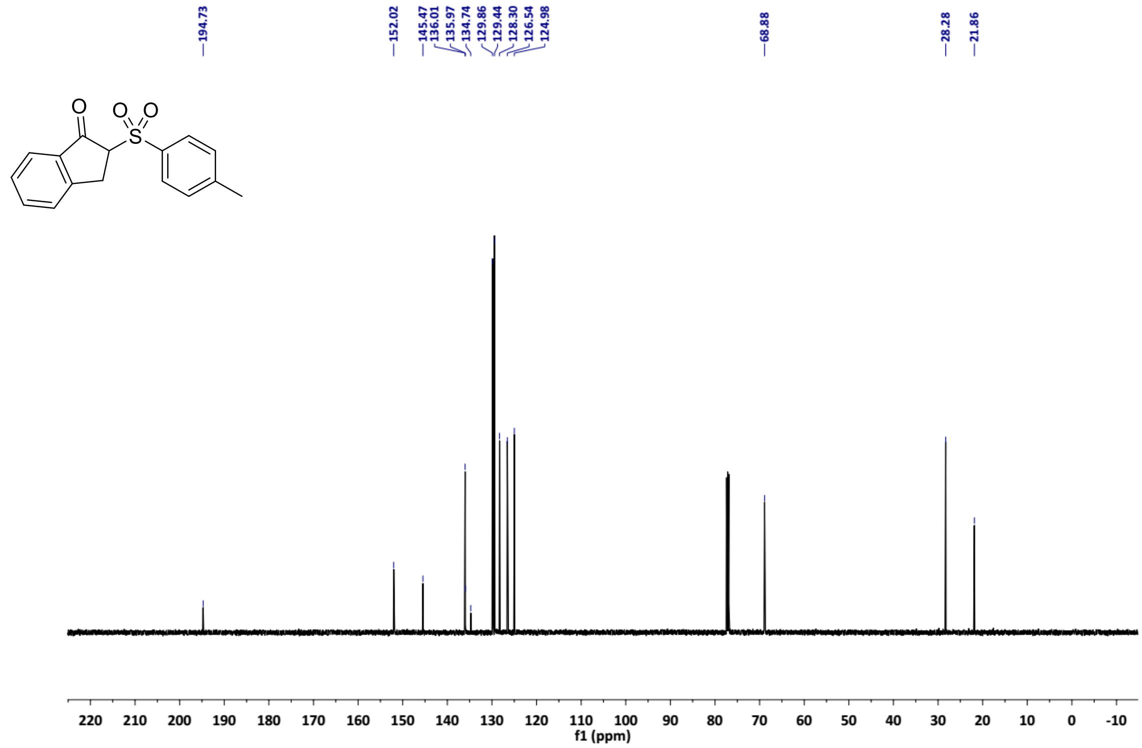
^{1}H NMR spectrum (500 MHz, CDCl$_3$) of **13m**



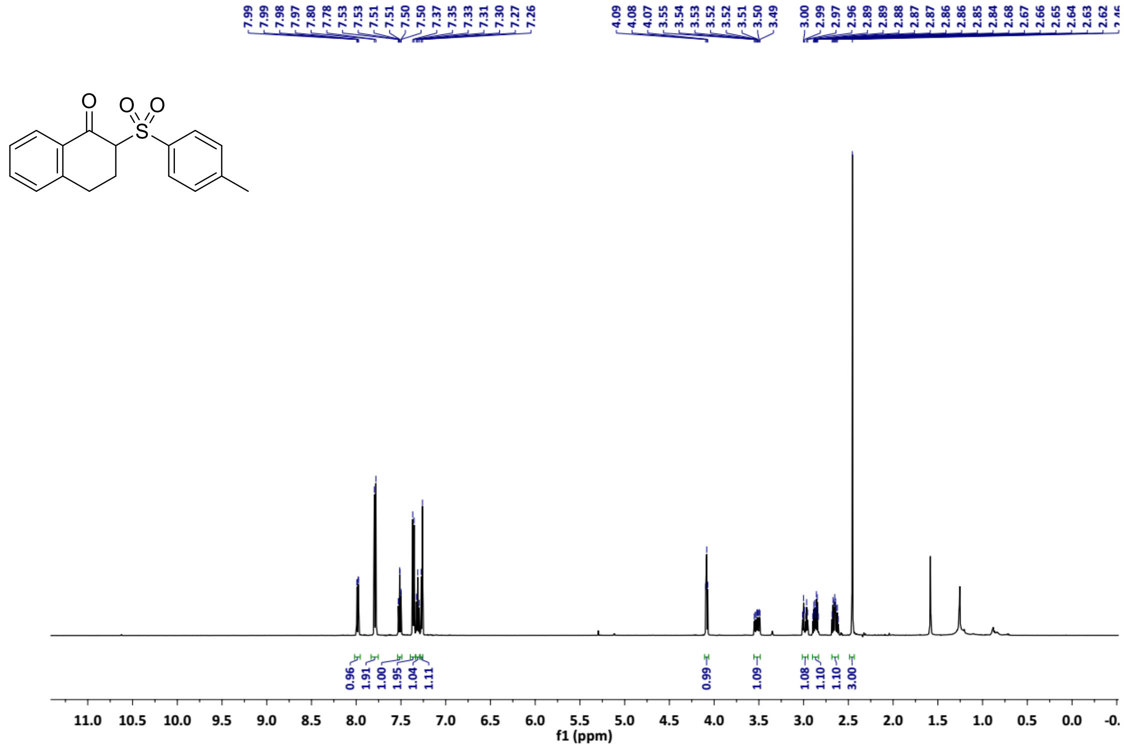
^{13}C NMR spectrum (126 MHz, CDCl$_3$) of **13m**



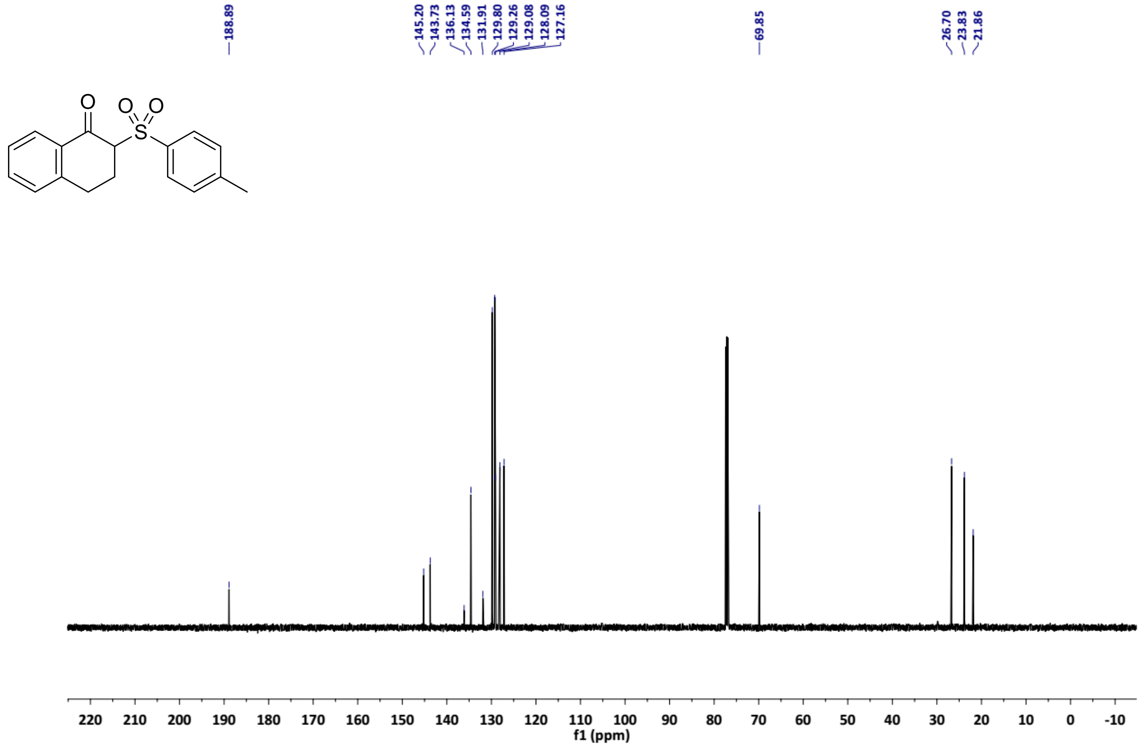
^{1}H NMR spectrum (500 MHz, CDCl$_3$) of **13n**



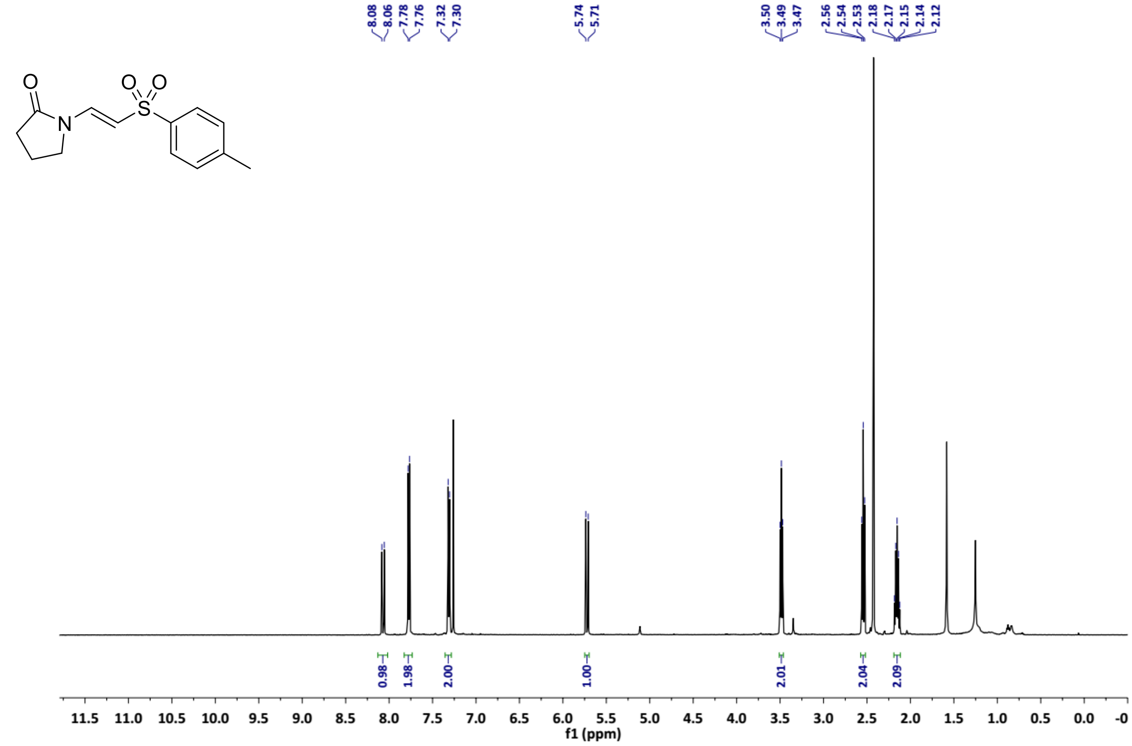
^{13}C NMR spectrum (126 MHz, CDCl$_3$) of **13n**



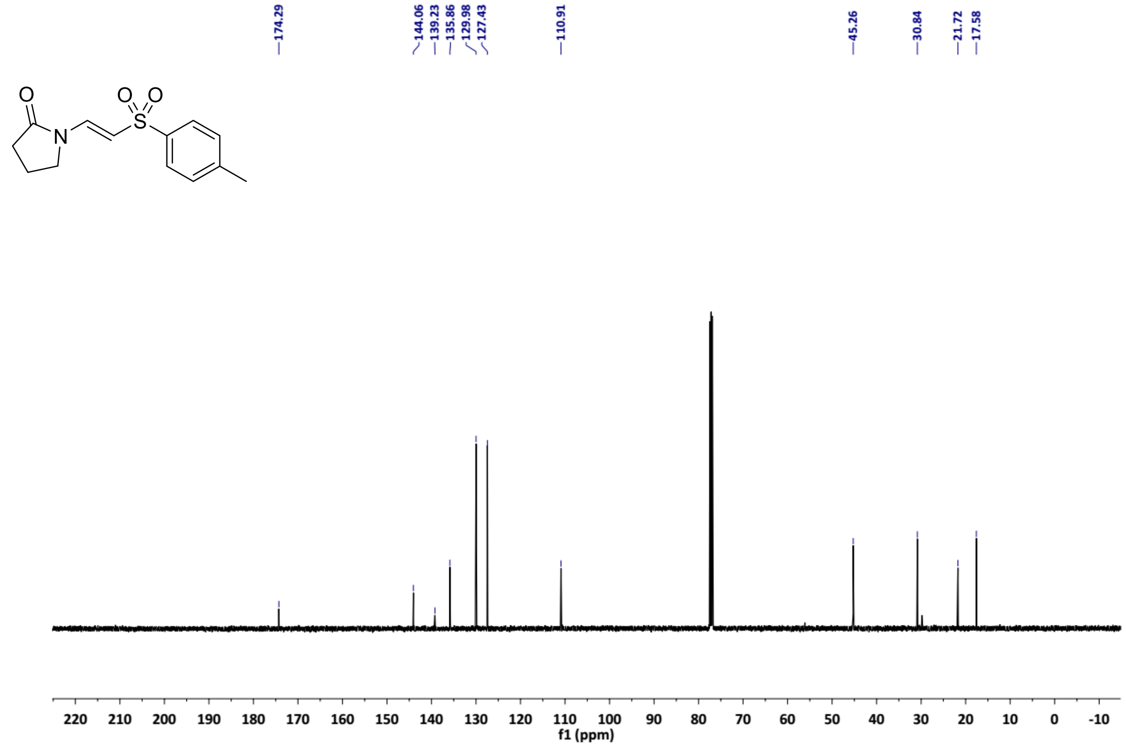
^{1}H NMR spectrum (500 MHz, CDCl$_3$) of **13o**



^{13}C NMR spectrum (126 MHz, CDCl$_3$) of **13o**



^{1}H NMR spectrum (500 MHz, CDCl$_3$) of **15**



^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **15**