SUPPORTING INFORMATION

Metal-free Synthesis of *α*-Keto-*N*-acyl sulfoximines from Sulfoximines and *α*-Bromomethyl aryl ketones under Photoredox catalysis

Navaneetha Krishnan V.,[$] Natarajan K.[$] Padma Priya V. R., Antony Haritha Mercy A., Ganesh Chandra Nandi*

Department of Chemistry, National Institute of Technology-Tiruchirappalli 620015, Tamilnadu

Email: ganeshnandi@gmail.com; nandi@nitt.edu

[$]Equal Contribution

Table of Contents

1. General information

Eosin-Y, acetonitrile, thiols, photocatalysts, and other chemicals were purchased from various suppliers and used as received. The progress of the reactions was monitored by thin-layer chromatography (TLC) using TLC silica gel 60 F_{254} plates and visualized by short-wave ultraviolet light at 254 nm and by treatment with iodine. ^{1}H (500 MHz) and ^{13}C NMR (126 MHz) spectra were recorded on a BRUKER NMR spectrophotometer. $CDCl_3$ was used as a solvent to record NMR spectra. Chemical shifts are reported in parts per million (ppm) downfield units from tetramethylsilane (TMS), and all coupling constants are reported in Hertz. The description of the signals includes the following: s = singlet, d = doublet, t = triplet, dd = doublet of doublet, td = triplet of doublet, tt = triplet of triplet, and m = multiplet. Mass spectra were recorded with Agilent QTOF G6545 spectrometer at 50,000 resolutions using ESI mode. Melting points were uncorrected. A Kessil 525 nm green LED was used for the photochemical reaction.

2. General procedure for the synthesis of Sulfoximines (2)

To a stirred solution of diaryl (or alkylaryl) sulfide (1 mmol) in MeOH (5 mL) were added $(NH_4)_2CO_3$ (1.5 equiv.) and $PhI(OAc)_2$ (2.3 equiv.), and the reaction mixture was stirred at room temperature for 3–4 h. Upon complete consumption of the sulfide, as monitored by TLC, the solvent was removed under reduced pressure. The crude material was then purified by flash column chromatography using 25–40% EtOAc/hexane as the eluent to afford the desired product.

All the sulfoximines were synthesised using the above mentioned procedure and characterisation data were exactly matching with the reported data.[1]

3. General Procedure for the Synthesis of α-Bromomethyl aryl ketones (1)

In a 100 mL round bottom flask, acetophenone (1 g, 8.3 mmol, 1.0 equiv.) was dissolved in 4 mL of acetonitrile, followed by the addition of *N*-bromosuccinimide (4.4 g, 24.9 mmol, 3.0 equiv.) and *p*-toluenesulfonic acid (1.4 g, 8.3 mmol, 1.0 equiv.). The resulting mixture was stirred at 50 °C for 24 hours. Once the reaction was completed, as checked by TLC, the solvent was removed under reduced pressure. A saturated aqueous $NaHCO_3$ solution (50 mL) was added, and the solution was extracted with dichloromethane (3 x 50 mL). The organic layers were combined and dried over Na_2SO_4. The solvent was evaporated, and the residue was purified through column chromatography (100–200 mesh

SiO_2) using 2% of EtOAc in hexane as eluent to give the desired product (**1a**) as a white solid.

A similar protocol was used to synthesize the rest of the *α*-bromomethyl aryl ketone derivatives, and the products were purified using 1-3% of EtOAc in hexane as eluent.

4. General Procedure for the Synthesis of *α*-Keto-*N*-acyl sulfoximines (3)

A 20 mL Schlenk tube containing the sulfoximine **(2a)**, (30 mg, 0.1507 mmol, 1.4 equiv.), *α*-bromomethyl aryl ketone **(1a)**, (42 mg, 0.2110 mmol, 1.0 equiv.) was dissolved in 0.7 mL of acetonitrile, followed by the addition of eosin-Y (5 mol%) under an oxygen atmosphere via balloon. The resulting mixture was stirred at room temperature in the presence of a green LED (525 nm) for 5 hours. After the completion of the reaction (checked by TLC), the reaction mixture was diluted with EtOAC and washed with water (3×15 mL), followed by brine solution (3×15 mL). The collected organic phase was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified through column chromatography (100–200 mesh SiO_2) using 25% of EtOAC in hexane as eluent to deliver *α*-keto-*N*-acyl sulfoximine (**3a)** as product.

A similar protocol was used to synthesize the rest of *α*-keto-*N*-acyl sulfoximine derivatives **(3b–3x)** and the products were purified using 15-30% of EtOAc in hexane as eluent.

5. General Procedure for the Gram Scale Synthesis of 3a

In a 100 mL round bottom flask containing the sulfoximine **(2a)**, (1.4 g, 7.033 mmol, 1.4 equiv.), *α*-bromomethyl aryl ketone **(1a)**, (1.0 g, 5.024 mmol, 1.0 equiv.) was dissolved in 7 mL of acetonitrile, followed by the addition of eosin-Y (5 mol%) under an oxygen atmosphere via balloon. The resulting mixture was stirred at room temperature in the presence of a green LED (525 nm) for 8.5 hours. After the completion of the reaction (checked by TLC), the reaction mixture was diluted with EtOAC and washed with water (3×50 mL), followed by brine solution (3×50 mL). The collected organic phase was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified through column chromatography (100–200 mesh SiO_2) using 25% of EtOAC in hexane as eluent to deliver *α*-keto-*N*-acyl sulfoximine (**3a)** as product. The product was obtained as a sticky yellow liquid **3a** (915 mg, 55%).

6. General Procedure for the Synthesis of 1,4-diarylisothiazolones 4 from 3c

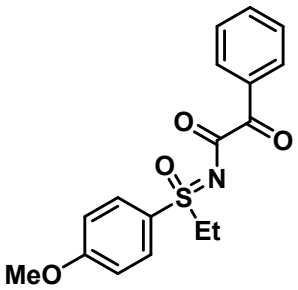
An oven-dried 15 mL pressure tube equipped with a magnetic stir bar was charged with sulfoximine **(3c)** (20 mg, 0.069 mmol, 1.0 equiv.), Et_3N (49 mg, 0.487 mmol, 7.0 equiv.), and DMF (0.7 mL). The reaction mixture was stirred at 120 °C for 8 h. After completion of the reaction, as confirmed by TLC analysis, the mixture was diluted with ethyl acetate (20 mL) and washed sequentially with ice-cold water (1 × 10 mL) and brine (1 × 5 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2, 100–200 mesh) using 15% EtOAc/hexane as the eluent to afford the corresponding 1,4-diarylisothiazolone **(4)** as a pale brown solid (15 mg, 81%).

REFERENCE

[1]. A. Tota, M. Zenzola, S. J. Chawner, S. S. John-Campbell, C. Carlucci, G. Romanazzi, L. Degennaro, J. A. Bull and R. Luisi, *Chem. Commun.,* 2017, **53**, 348–351.

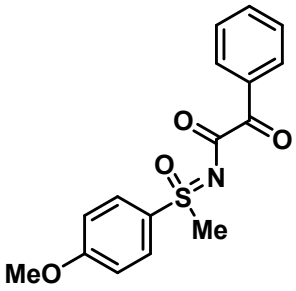
7. Analytical data of the synthesized compounds

Compound 3a



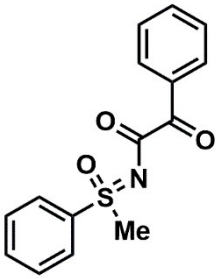
It was obtained as a sticky, pale yellow liquid. Purified via column chromatography with 25% EtOAc/Hexane as eluent. Yield: 71% (47 mg obtained from 0.2009 mmol of corresponding α-bromomethyl aryl ketone). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06 – 8.04 (m, 2H), 7.94 (d, J = 9.0 Hz, 2H), 7.59 (t, J = 7.5 Hz, 1H), 7.47 – 7.44 (m, 2H), 7.08 (d, J = 9.0 Hz, 2H), 3.89 (s, 3H), 3.62 - 3.52 (m, 2H), 1.31 (t, J = 7.5 Hz, 3H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 190.5, 173.5, 164.4, 134.2, 132.9, 130.3, 130.3, 128.7, 126.0, 115.2, 55.9, 51.6, 7.1. HRMS (ESI) calcd. for $C_{17}H_{18}NO_4S$ $[M+H]^+$ 332.0951; found 332.0966.

Compound 3b



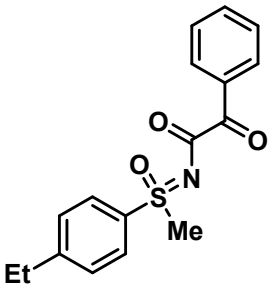
It was obtained as a white solid. Purified via column chromatography with 25% EtOAc/Hexane as eluent. Yield: 68% (32 mg obtained from 0.1507 mmol of corresponding α-bromomethyl aryl ketone), mp: 131-133 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 – 8.04 (m, 2H), 7.98 (d, J = 9.0 Hz, 2H), 7.59 (t, J = 7.5 Hz, 1H), 7.48 – 7.45 (m, 2H), 7.08 (d, J = 9.0 Hz, 2H), 3.89 (s, 3H), 3.46 (s, 3H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 190.4, 173.4, 164.5, 134.2, 132.9, 130.3, 129.5, 128.7, 128.7, 115.2, 55.9, 45.4. HRMS (ESI) calcd. for $C_{16}H_{16}NO_4S$ $[M+H]^+$ 318.0795; found 318.0780.

Compound 3c



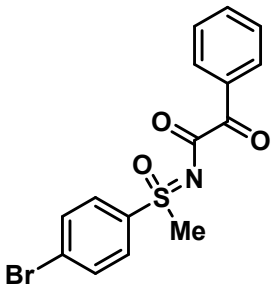
It was obtained as a white solid. Purified via column chromatography with 30% EtOAc/Hexane as eluent. Yield: 62% (27 mg obtained from 0.1507 mmol of corresponding α-bromomethyl aryl ketone), mp: 97 – 99 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 – 8.16 (m, 2H), 8.06 – 8.05 (m, 2H), 7.68 (t, J = 7.0 Hz, 1H), 7.62 – 7.59 (m, 2H), 7.51 (t, J = 7.5 Hz, 1H), 7.42 – 7.39 (m, 2H), 3.46 (s,3H) .^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 190.1, 173.3, 136.9, 134.5, 133.5, 132.8, 130.4, 130.2, 128.9, 128.9, 45.0. HRMS (ESI) calcd. for $C_{15}H_{13}NO_3SNa$ $[M+Na]^+$ 310.0508; found 310.0512.

Compound 3d



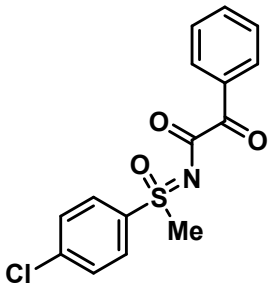
It was obtained as a sticky, yellow liquid. Purified via column chromatography with 25% EtOAc/Hexane as eluent. Yield: 61% (29 mg obtained from 0.1507 mmol of corresponding α-bromomethyl aryl ketone). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 (d, J = 8.0 Hz, 2H), 7.96 (d, J = 8.0 Hz, 2H), 7.58 (t, J = 6.5 Hz, 1H), 7.47 – 7.43 (m, 4H), 3.46 (s, 3H), 2.75 (q, J = 7.5 Hz, 2H), 1.26 (t, J = 7.0 Hz, 3H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 190.3, 173.4, 151.9, 134.7, 134.3, 132.9, 130.3, 129.5, 128.7, 127.4, 45.0, 29.0, 15.1. HRMS (ESI) calcd. for $C_{17}H_{18}NO_3S$ $[M+H]^+$ 316.1002; found 316.1012.

Compound 3e



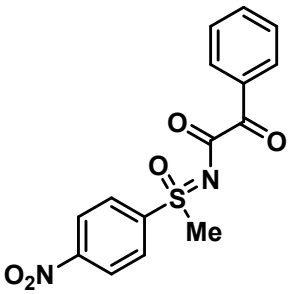
It was obtained as a white solid. Purified via column chromatography with 23% EtOAc/Hexane as eluent. Yield: 58% (32 mg obtained from 0.1507 mmol of corresponding α-bromomethyl aryl ketone), mp: 148-150 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 – 8.01 (m, 2H), 7.94 – 7.91 (m, 2H), 7.79 – 7.76 (m, 2H), 7.60 (t, J = 9.0 Hz, 1H), 7.48 – 7.45 (m, 2H), 3.46 (s, 3H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 190.0, 173.2, 136.8, 134.4, 133.4, 132.7, 130.3, 130.1, 128.9, 128.8, 44.9. HRMS (ESI) calcd. for $C_{15}H_{13}BrNO_3S$ $[M+H]^+$ 365.9794; found 365.9804.

Compound 3f



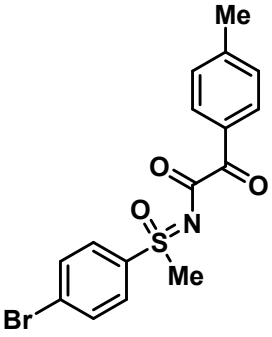
It was obtained as a orange solid. Purified via column chromatography with 20% EtOAc/Hexane as eluent. Yield: 56% (27 mg obtained from 0.1507 mmol of corresponding α-bromomethyl aryl ketone), mp: 143-144 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 – 8.03 (m, 2H), 8.01 (d, J = 9.0 Hz, 2H), 7.62 – 7.59 (m, 3H), 7.49 – 7.46 (m, 2H), 3.48 (s, 3H). ^{13}C {^{1}H} NMR 126 MHz, $CDCl_3$): δ 190.0, 173.2, 141.6, 134.4, 133.8, 132.8, 130.4, 130.3, 128.8, 128.8, 45.0. HRMS (ESI) calcd. for $C_{15}H_{13}ClNO_3S$ $[M+H]^+$ 322.0299; found 322.0280.

Compound 3g



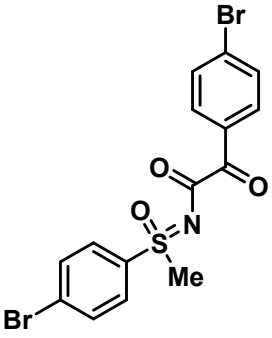
It was obtained as a white solid. Purified via column chromatography with 25% EtOAc/Hexane as eluent. Yield: 55% (27 mg obtained from 0.1507 mmol of corresponding α-bromomethyl aryl ketone), mp: 131-133 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.50 (d, J = 9.0 Hz, 2H), 8.30 (d, J = 9.0 Hz, 2H), 8.04 – 8.02 (m, 2H), 7.62 (t, J = 7.5 Hz, 1H), 7.50 – 7.47 (m, 2H), 3.51 (s, 3H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 189.6, 172.8, 143.8, 142.0, 134.6, 132.5, 130.3, 129.0, 128.9, 125.2, 44.6. HRMS (ESI) calcd. for $C_{15}H_{13}N_2O_5S$ $[M+H]^+$ 333.0540; found 333.0543.

Compound 3h



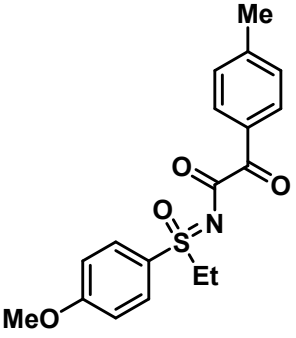
It was obtained as a sticky, yellow liquid. Purified via column chromatography with 23% EtOAc/Hexane as eluent. Yield: 67% (36 mg obtained from 0.1407 mmol of corresponding α-bromomethyl aryl ketone). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 – 7.92 (m, 4H), 7.77 (d, J = 8.5 Hz, 2H), 7.27 – 7.26 (m, 2H), 3.46 (s, 3H), 2.42 (s, 3H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 189.7, 173.5, 145.6, 136.9, 133.3, 130.4, 130.2, 130.1, 129.5, 128.8, 44.9, 22.0. HRMS (ESI) calcd. for $C_{16}H_{15}BrNO_3S$ $[M+H]^+$ 379.9951; found 379.9961.

Compound 3i



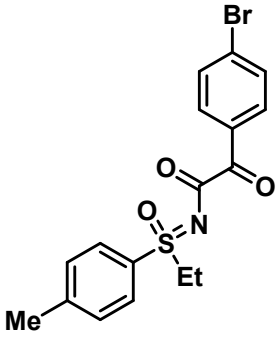
It was obtained as a sticky, yellow liquid. Purified via column chromatography with 25% EtOAc/Hexane as eluent. Yield: 61% (29 mg obtained from 0.1079 mmol of corresponding α-bromomethyl aryl ketone). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92 – 7.89 (m, 4H), 7.78 (d, J = 8.5 Hz, 2H), 7.61 (d, J = 9.0 Hz, 2H), 3.46 (s, 3H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 188.8, 172.5, 136.6, 133.4, 132.2, 131.7, 131.6, 130.2, 129.9, 128.8, 44.9. HRMS (ESI) calcd. for $C_{15}H_{12}{}^{79}Br^{81}BrNO_3S$ $[M+H]^+$ 445.8879; found 445.8889.

Compound 3j



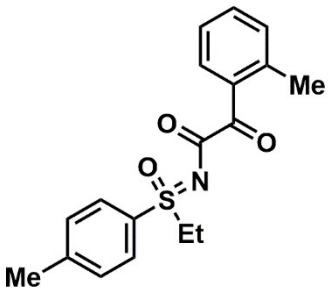
It was obtained as a sticky, yellow liquid. Purified via column chromatography with 25% EtOAc/Hexane as eluent. Yield: 65% (31 mg obtained from 0.1407 mmol of corresponding α-bromomethyl aryl ketone). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96 – 7.93 (m, 4H), 7.27 – 7.25 (m, 2H), 7.07 (d, J = 9.0 Hz, 2H), 3.89 (s, 3H), 3.61 – 3.52 (m, 2H), 2.41 (s, 3H), 1.30 (t, J = 7.0 Hz, 3H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 190.3, 173.8, 164.4, 145.3, 130.4, 130.3, 129.4, 126.1, 115.2, 112.1, 55.9, 51.6, 21.9, 7.1. HRMS (ESI) calcd. for $C_{18}H_{19}NO_4SNa$ $[M+Na]^+$ 368.0927; found 368.0938.

Compound 3k



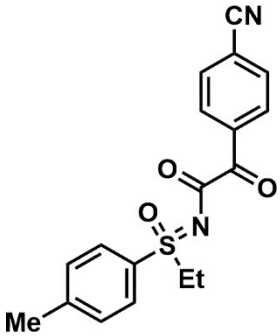
It was obtained as a sticky, pale yellow liquid. Purified via column chromatography with 25% EtOAc/Hexane as eluent. Yield: 66% (28 mg obtained from 0.1079 mmol of corresponding *α*-bromomethyl aryl ketone). ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.92 (d, *J* = 9.0 Hz, 2H), 7.88 (d, *J* = 8.5 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 3.61 – 3.49 (m, 2H), 2.46 (s, 3H), 1.30 (t, *J* = 7.5 Hz, 3H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): *δ* 189.2, 172.8, 145.8, 132.1, 132.0, 131.8, 131.7, 130.6, 129.6, 128.0, 51.4, 21.8, 7.0. HRMS (ESI) calcd. for $C_{17}H_{17}BrNO_3S$ $[M+H]^+$ 394.0107; found 394.0135.

Compound 3l



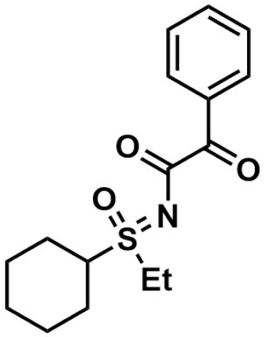
It was obtained as a sticky, pale yellow liquid. Purified via column chromatography with 32% EtOAc/Hexane as eluent. Yield: 68% (32 mg obtained from 0.1407 mmol of corresponding *α*-bromomethyl aryl ketone). ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.88 (d, *J* = 8.5 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.42 – 7.40 (m, 3H), 7.29 – 7.24 (m, 3H; $CDCl_3$; *solvent peak (1H) included)*, 3.61–3.51 (m, 2H), 2.62 (s, 3H), 2.46 (s, 3H), 1.30 (t, *J* = 7.5 Hz, 3H).^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): *δ* 192.9, 174.1, 145.7, 141.2, 133.1, 132.9, 132.1, 130.5, 129.7, 128.1, 126.5, 125.8, 51.3, 21.7, 21.7, 7.0. HRMS (ESI) calcd. for $C_{18}H_{19}NO_3SNa$ $[M+Na]^+$ 352.0978; found 352.0987.

Compound 3m



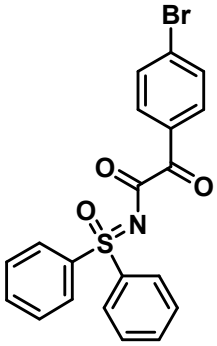
It was obtained as a sticky, yellow liquid. Purified via column chromatography with 35% EtOAc/Hexane as eluent. Yield: 63% (29 mg obtained from 0.1338 mmol of corresponding *α*-bromomethyl aryl ketone). ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 8.15 (d, *J* = 8.5 Hz, 2H), 7.87 (d, *J* = 8.5 Hz, 2H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 3.63 – 3.50 (m, 2H), 2.47 (s, 3H), 1.31 (t, *J* = 7.5 Hz, 3H).^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): *δ* 188.6, 171.9, 146.0, 136.2, 132.4, 131.8, 130.7, 130.6, 128.0, 117.9, 117.1, 51.4, 21.8, 6.9. HRMS (ESI) calcd. for $C_{18}H_{17}N_2O_3S$ $[M+H]^+$ 357.0904; found 357.0916.

Compound 3n



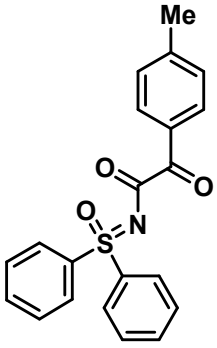
It was obtained as sticky, yellow liquid. Purified via column chromatography with 15% EtOAc/Hexane as eluent. Yield: 55% (25 mg obtained from 0.1507 mmol of corresponding α-bromomethyl aryl ketone). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 (d, J = 7.0 Hz, 2H), 7.60 (t, J = 7.5 Hz, 1H), 7.48 (t, J = 8 Hz, 2H), 3.64 – 3.47 (m, 3H), 2.29 (d, J = 13 Hz, 1H), 2.20 (d, J = 12.5 Hz, 1H), 1.99 (d, J = 15 Hz, 2H), 1.74 – 1.63 (m, 4H), 1.51 (t, J = 7.5 Hz, 3H), 1.38 – 1.35 (m, 2H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 190.7, 173.4, 134.1, 133.1, 130.2, 128.7, 61.1, 43.4, 25.3, 25.2, 25.1, 25.0, 24.7, 6.5. HRMS (ESI) calcd. for $C_{16}H_{22}NO_3S$ $[M+H]^+$ 308.1315 ; found 308.1339.

Compound 3o



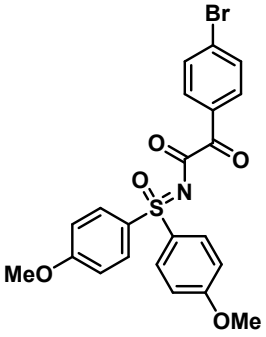
It was obtained as a sticky, yellow liquid. Purified via column chromatography with 18% EtOAc/Hexane as eluent. Yield: 63% (29 mg obtained from 0.1079 mmol of corresponding α-bromomethyl aryl ketone). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06 (d, J = 8.5 Hz, 4H), 7.93 (d, J = 8.0 Hz, 2H), 7.64 – 7.54 (m, 8H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 189.0, 172.6, 138.8, 134.0, 132.1, 131.7, 131.7, 129.8, 129.7, 127.6. HRMS (ESI) calcd. for $C_{20}H_{15}BrNO_3S$ $[M+H]^+$ 427.9951; found 427.9964.

Compound 3p



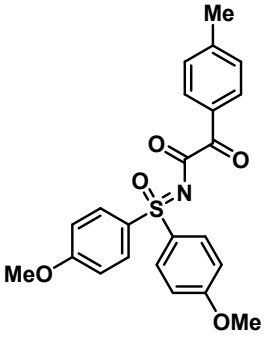
It was obtained as a sticky, yellow liquid. Purified via column chromatography with 18% EtOAc/Hexane as eluent. Yield: 67% (34 mg obtained from 0.1407 mmol of corresponding α-bromomethyl aryl ketone). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09 – 8.07 (m, 4H), 7.96 (d, J = 8.0 Hz, 2H), 7.63 – 7.59 (m, 2H), 7.57 – 7.54 (m, 4H), 7.27 – 7.26 (m, 1H), 7.26 – 7.25 (m, 1H), 2.41 (s, 3H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 189.9, 173.5, 145.4, 139.0, 133.9, 130.5, 130.4, 129.8, 129.5, 127.7, 22.0. HRMS (ESI) calcd. for $C_{21}H_{18}NO_3S$ $[M+H]^+$ 364.1002; found 364.1016.

Compound 3q



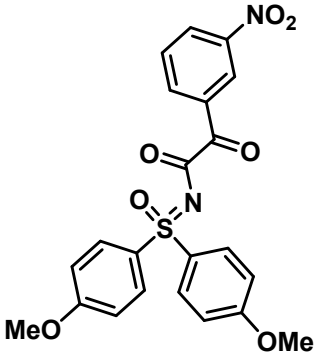
It was obtained as a sticky, yellow liquid. Purified via column chromatography with 25% EtOAc/Hexane as eluent. Yield: 65% (34 mg obtained from 0.1079 mmol of corresponding α-bromomethyl aryl ketone). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96 – 7.92 (m, 6H), 7.59 (d, J = 8.5 Hz, 2H), 6.99 (d, J = 9.0 Hz, 4H), 3.84 (s, 6H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 189.3, 172.5, 163.9, 132.0, 131.9, 131.8, 130.3, 129.7, 129.6, 115.0, 55.8. HRMS (ESI) calcd. for $C_{22}H_{19}BrNO_5S$ $[M+H]^+$ 488.0162; found 488.0179.

Compound 3r



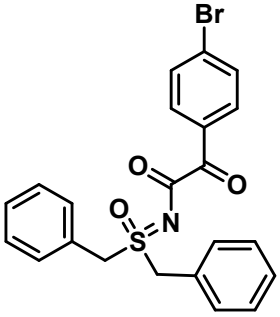
It was obtained as a sticky, yellow liquid. Purified via column chromatography with 25% EtOAc/Hexane as eluent. Yield: 67% (39 mg obtained from 0.1407 mmol of corresponding α-bromomethyl aryl ketone). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96 – 7.94 (m, 6H), 7.26 – 7.24 (m, 1H), 6.99 – 6.97 (m, 5H), 3.84 (s, 6H), 2.40 (s, 3H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 190.2, 173.4, 163.8, 145.2, 130.6, 130.5, 129.7, 129.4, 115.0, 114.3, 55.8, 21.9. HRMS (ESI) calcd. for $C_{23}H_{22}NO_5S$ $[M+H]^+$ 424.1213; found 424.1201.

Compound 3s



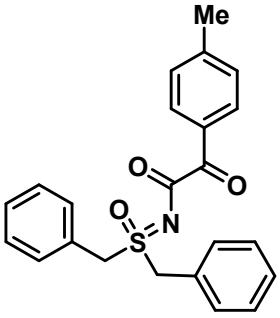
It was obtained as a sticky, yellow liquid. Purified via column chromatography with 18% EtOAc/Hexane as eluent. Yield: 62% (34 mg obtained from 0.1229 mmol of corresponding α-bromomethyl aryl ketone). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.85 (s, 1H), 8.43 – 8.39 (m, 2H), 7.96 (d, J = 9.0 Hz, 4H), 7.67 (t, J = 8.0 Hz, 1H), 7.02 (d, J = 9.0 Hz, 4H), 3.85 (s, 6H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 187.7, 171.5, 164.0, 148.4, 135.9, 134.7, 130.0, 130.0, 129.7, 128.1, 125.0, 115.1, 55.9. HRMS (ESI) calcd. for $C_{22}H_{19}N_2O_7S$ $[M+H]^+$ 455.0907; found 455.0917.

Compound 3t



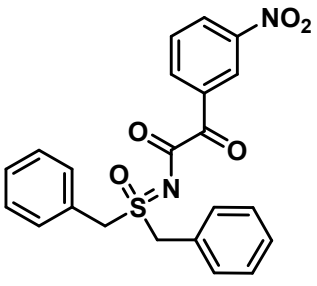
It was obtained as a sticky, pale brown liquid. Purified via column chromatography with 18% EtOAc/Hexane as eluent. Yield: 62% (30 mg obtained from 0.1079 mmol of corresponding *α*-bromomethyl aryl ketone). ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.69 (d, *J* = 9.0 Hz, 2H), 7.51 (d, *J* = 9.0 Hz, 2H), 7.47 – 7.43 (m, 10H), 4.79 (d, *J* = 13.5 Hz, 2H), 4.65 (d, *J* = 13.5 Hz, 2H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): *δ* 189.4, 172.2, 132.0, 131.76, 131.6, 131.5, 130.0, 129.6, 129.4, 125.4, 57.6. HRMS (ESI) calcd. for $C_{22}H_{19}BrNO_3S$ $[M+H]^+$ 456.0264; found 456.0250.

Compound 3u



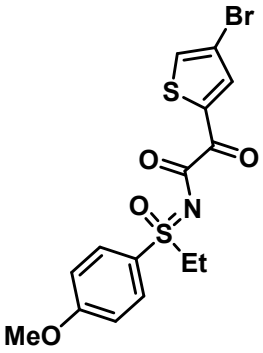
It was obtained as a sticky, pale brown liquid. Purified via column chromatography with 18% EtOAc/Hexane as eluent. Yield: 61% (33 mg obtained from 0.1407 mmol of corresponding *α*-bromomethyl aryl ketone). ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.76 (d, *J* = 8.5 Hz, 2H), 7.46 – 7.42 (m, 10H), 7.18 (d, *J* = 8.0 Hz, 2H), 4.79 (d, *J* = 13.5 Hz, 2H), 4.66 (d, *J* = 14.0 Hz, 2H), 2.39 (s, 3H).^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): *δ* 190.2, 173.3, 145.3, 131.5, 130.4, 130.3, 129.9, 129.3, 129.3, 125.6, 57.5, 21.9. HRMS (ESI) calcd. for $C_{23}H_{22}NO_3S$ $[M+H]^+$ 392.1315; found 392.1324.

Compound 3v



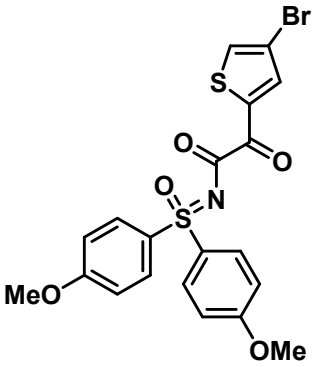
It was obtained as sticky, yellow liquid. Purified via column chromatography with 18% EtOAc/Hexane as eluent. Yield: 61% (31 mg obtained from 0.1229 mmol of corresponding *α*-bromomethyl aryl ketone). ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 8.80 – 8.79 (m, 1H), 8.42 – 8.39 (m, 1H), 8.15 – 8.13 (m, 1H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.46 – 7.43 (m, 10H), 4.82 (d, *J* = 13.5 Hz, 2H), 4.67 (d, *J* = 14.0 Hz, 2H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): *δ* 187.7, 170.8, 148.3, 135.7, 134.4, 131.4, 130.0, 129.7, 129.4, 128.0, 125.1, 124.8, 57.5. HRMS (ESI) calcd. for $C_{22}H_{19}N_2O_5S$ $[M+H]^+$ 423.1009; found 423.1021.

Compound 3w



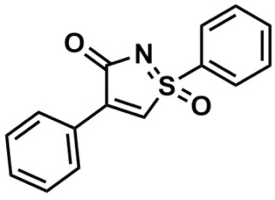
It was obtained as a sticky, yellow liquid. Purified via column chromatography with 27% EtOAc/Hexane as eluent. Yield: 63% (38 mg obtained from 0.1462 mmol of corresponding 2-bromo-1-(4-bromothiophene-2-yl)ethan-1-one). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (d, J = 9.0 Hz, 2H), 7.83 (d, J = 4.0 Hz, 1H), 7.10 (d, J = 4.5 Hz, 1H), 7.08 (d, J = 9.0 Hz, 2H), 3.89 (s, 3H), 3.65 – 3.49 (m, 2H), 1.31 (t, J = 7.5 Hz, 3H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 179.4, 170.0, 164.5, 140.0, 136.9, 131.3, 130.3, 126.0, 125.8, 115.3, 55.9, 51.4, 7.0. HRMS (ESI) calcd. for $C_{15}H_{15}BrNO_4S_2$ $[M+H]^+$ 415.9620; found 415.9634.

Compound 3x



It was obtained as a sticky, yellow liquid. Purified via column chromatography with 27% EtOAc/Hexane as eluent. Yield: 64% (46 mg obtained from 0.1462 mmol of corresponding 2-bromo-1-(4-bromothiophene-2-yl)ethan-1-one). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95 (d, J = 9.0 Hz, 4H), 7.83 (d, J = 4.0 Hz, 1H), 7.09 (d, J = 4.5 Hz, 1H), 6.99 (d, J = 9.0 Hz, 4H), 3.85 (s, 6H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 179.5, 169.7, 163.8, 163.8, 136.7, 131.2, 130.1, 129.6, 125.7, 114.9, 55.7. HRMS (ESI) calcd. for $C_{20}H_{17}BrNO_5S_2$ $[M+H]^+$ 493.9726; found 493.9748.

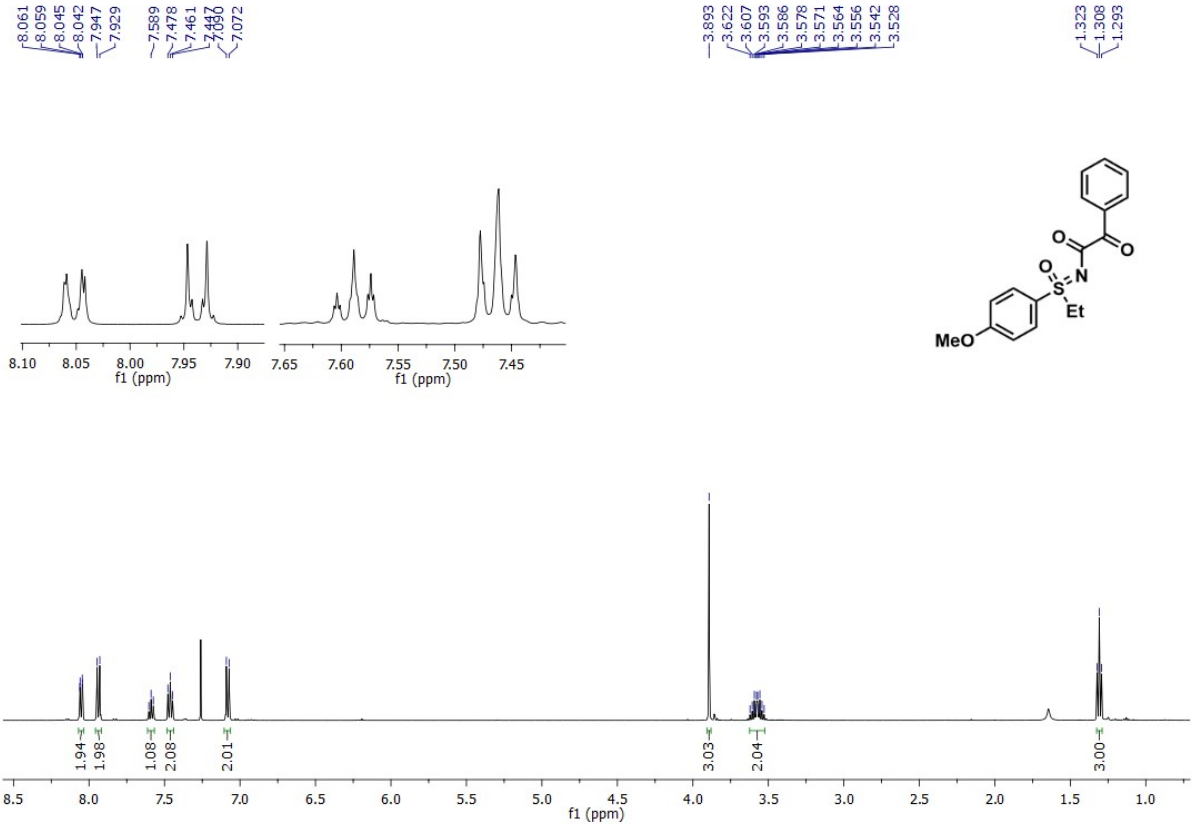
Compound 4



It was obtained as pale brown solid. Purified via column chromatography with 20% EtOAc/Hexane as eluent. Yield: 81% (15 mg obtained from 0.069 mmol of corresponding α-keto-N-acyl Sulfoximine). m.p. 128-130 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (d, J = 8.0 Hz, 2H), 7.92 (d, J = 7.0 Hz, 2H), 7.75 (t, J = 7.5 Hz, 1H), 7.66 – 7.63 (m, 2H), 7.61 (s, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.47 – 7.44 (m, 2H).^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 172.9, 149.2, 135.2, 133.6, 133.4, 132.0, 130.2, 130.0, 129.0, 128.8, 128.1. HRMS (ESI) calcd. for $C_{16}H_{12}NO_2S$ $[M+H]^+$ 270.0583; found 270.0593.

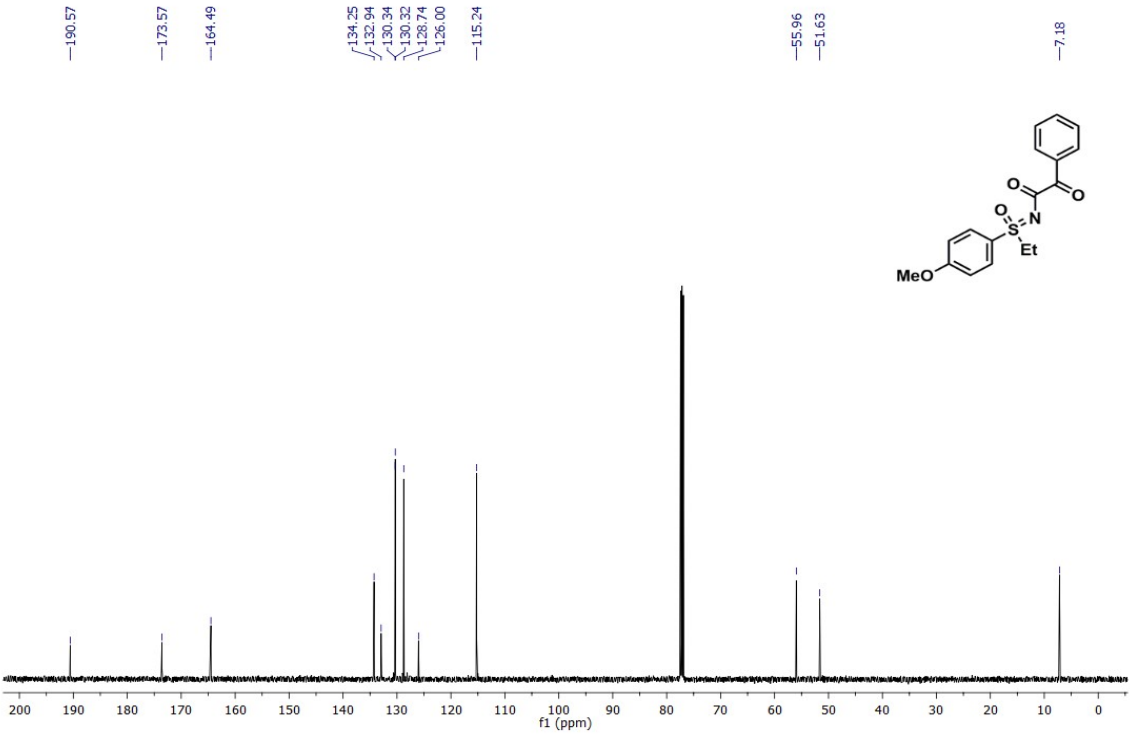
8. ^{1}H and ^{13}C NMR spectra of synthesized compounds

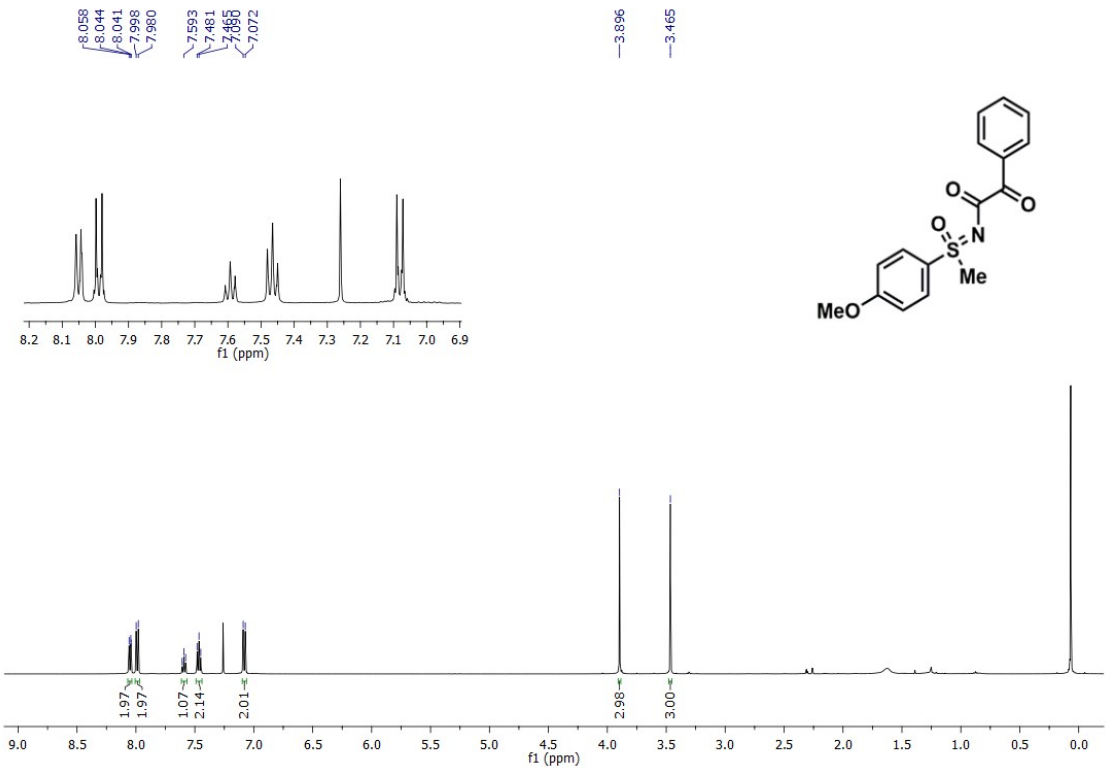
^{1}H NMR of 3a



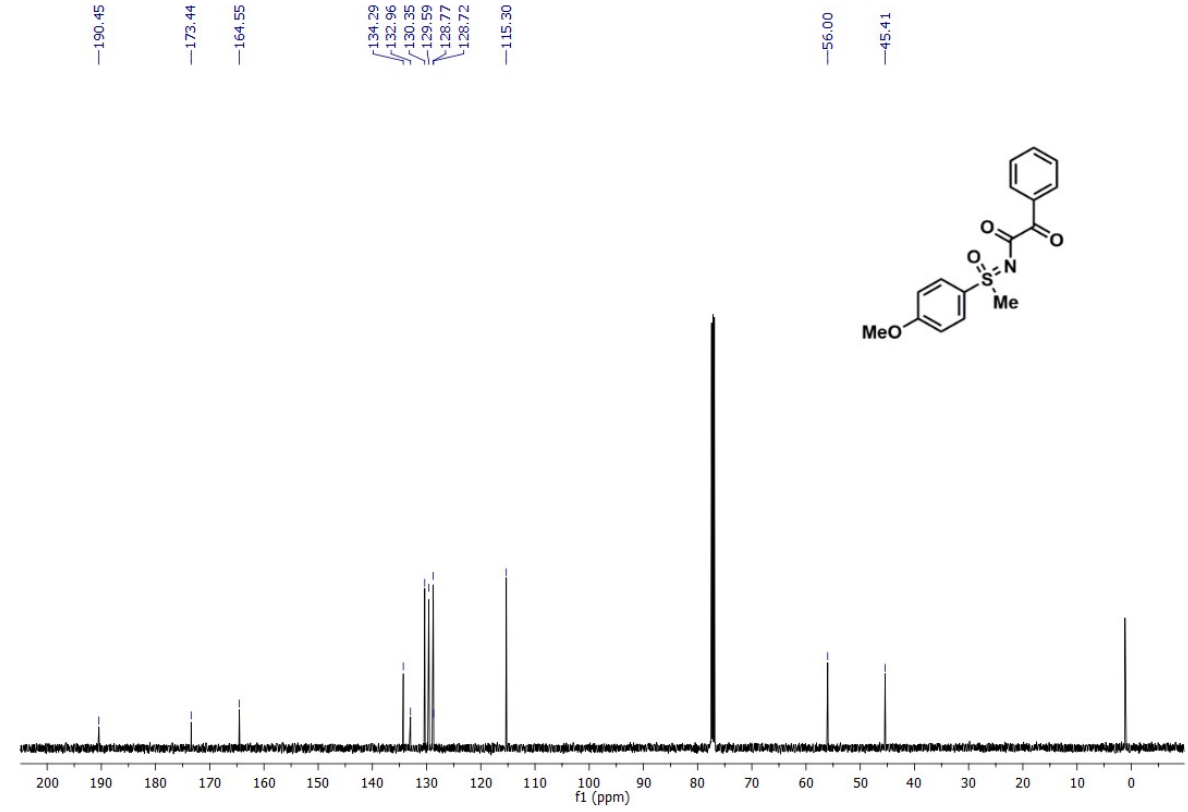
^{13}C {^{1}H} NMR of 3a

^{1}H NMR of 3b

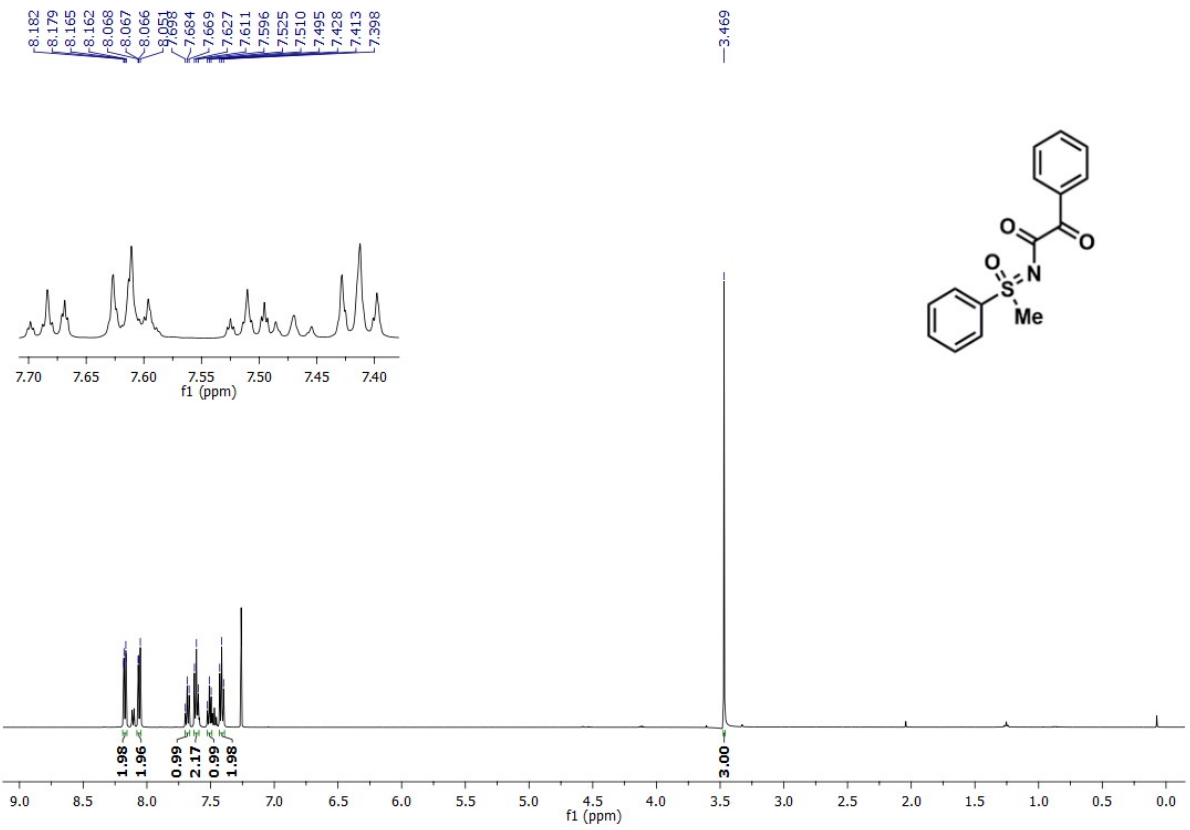




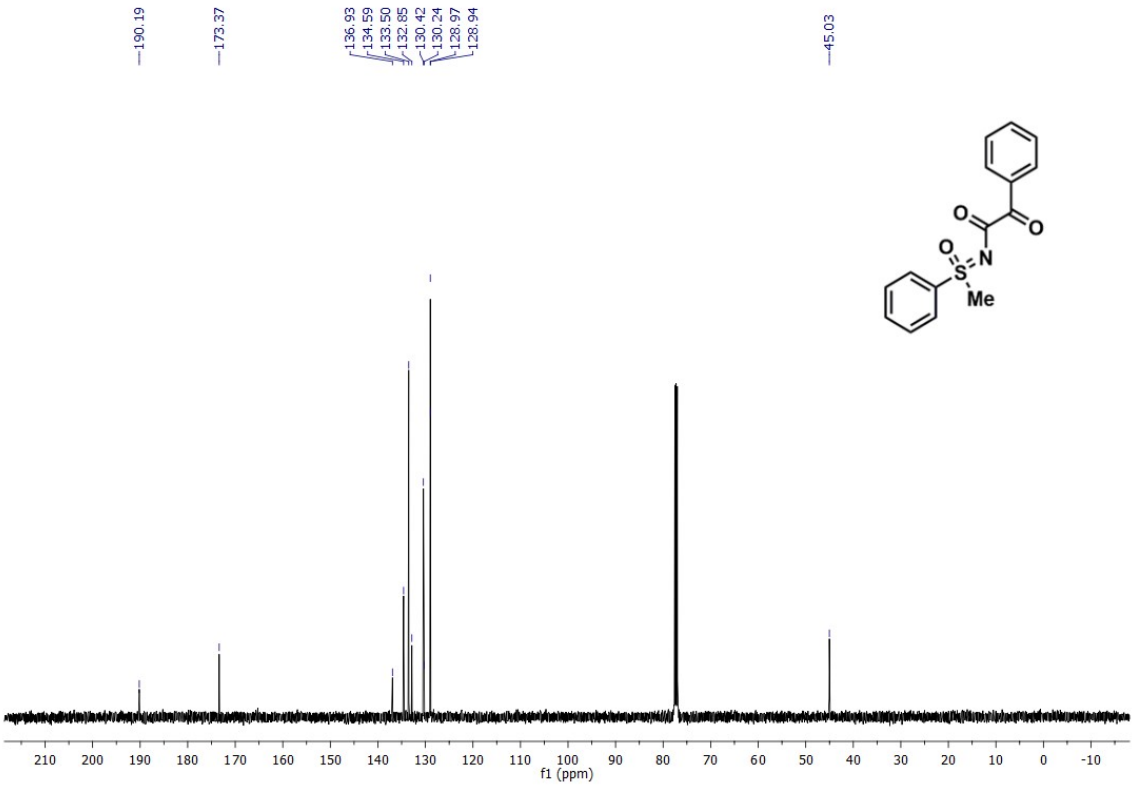
^{13}C {^{1}H} NMR of 3b



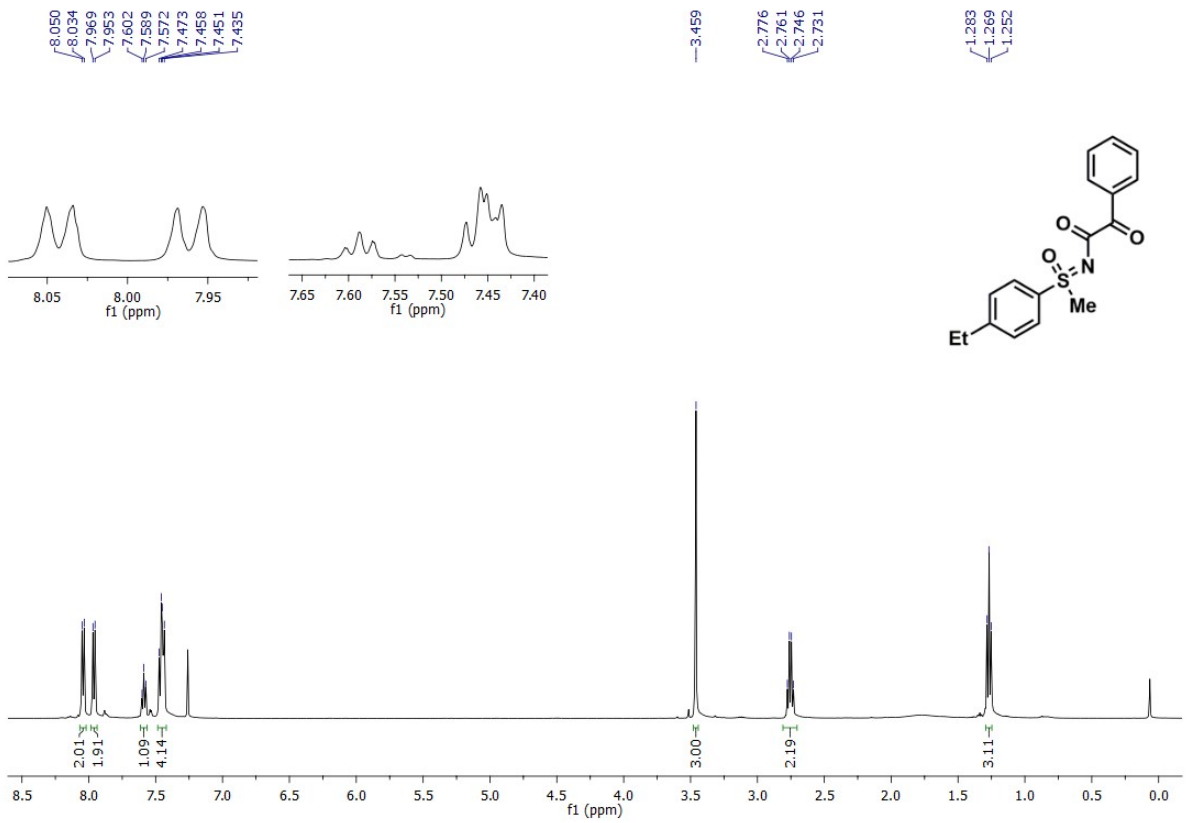
^{1}H NMR of 3c



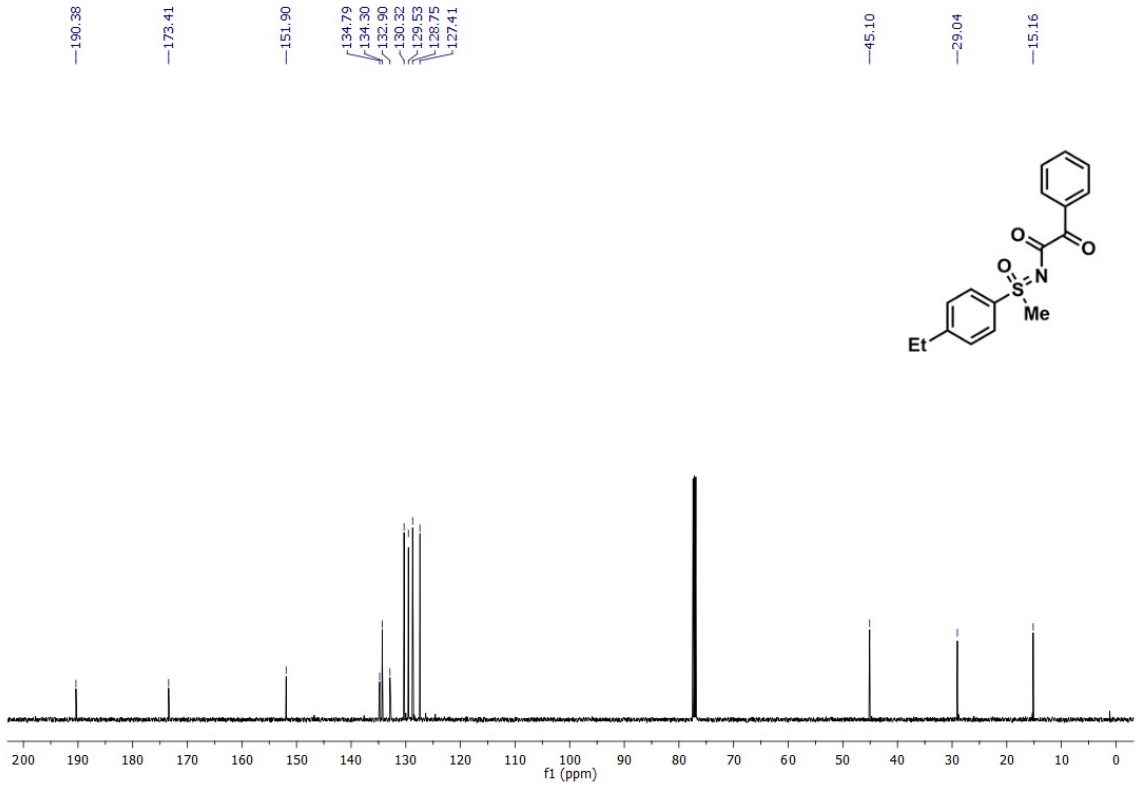
^{13}C {^{1}H} NMR of 3c



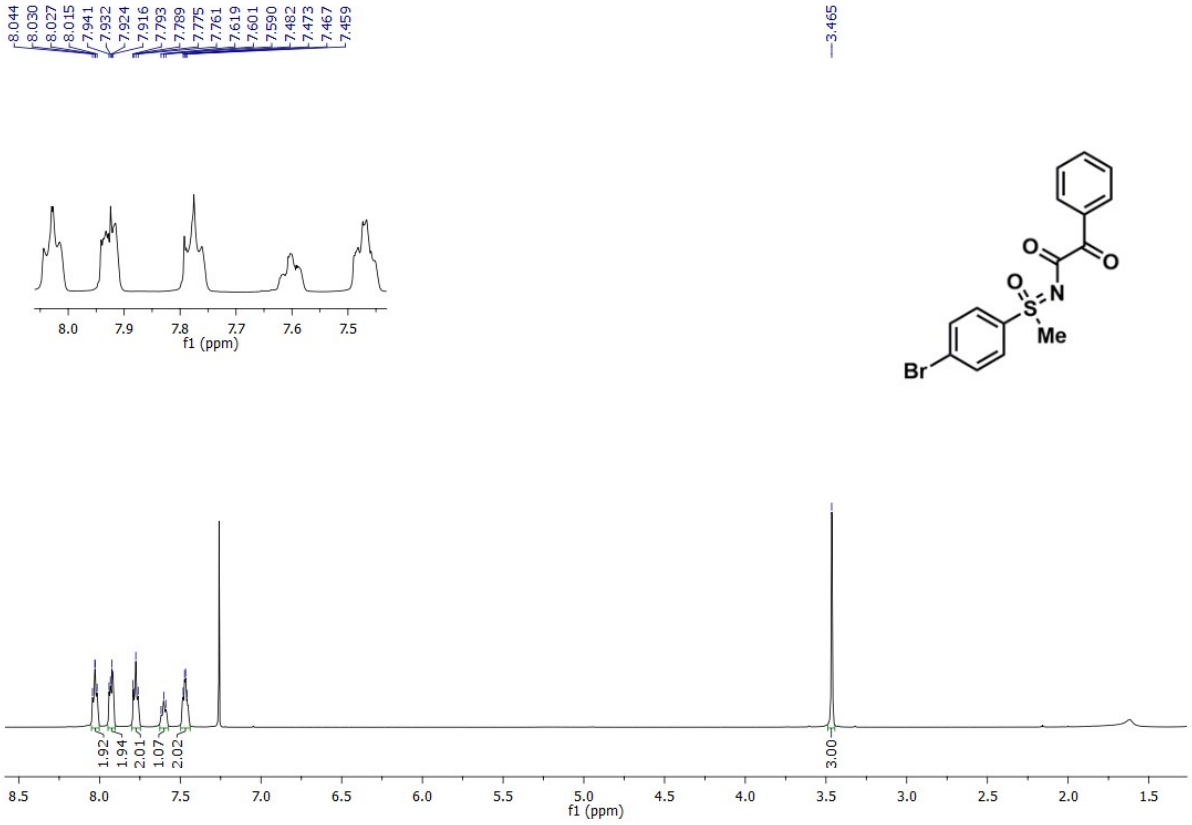
^{1}H NMR of 3d



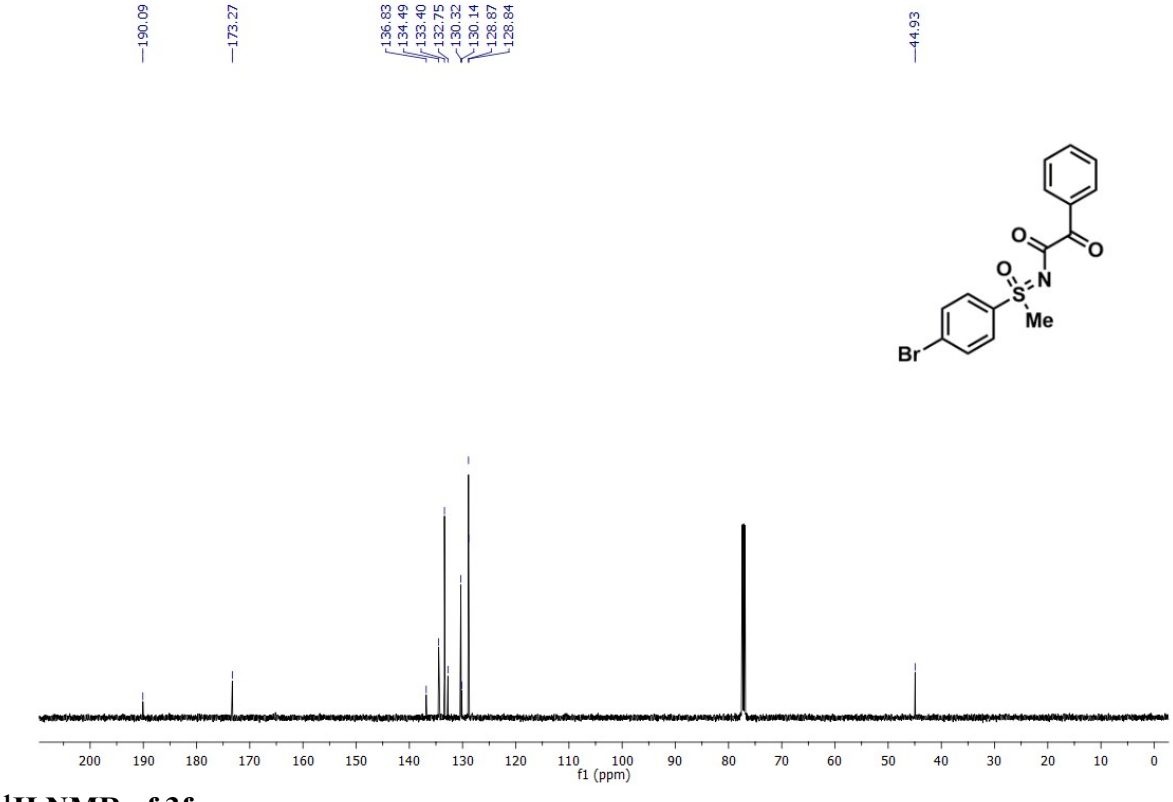
^{13}C {^{1}H} NMR of 3d



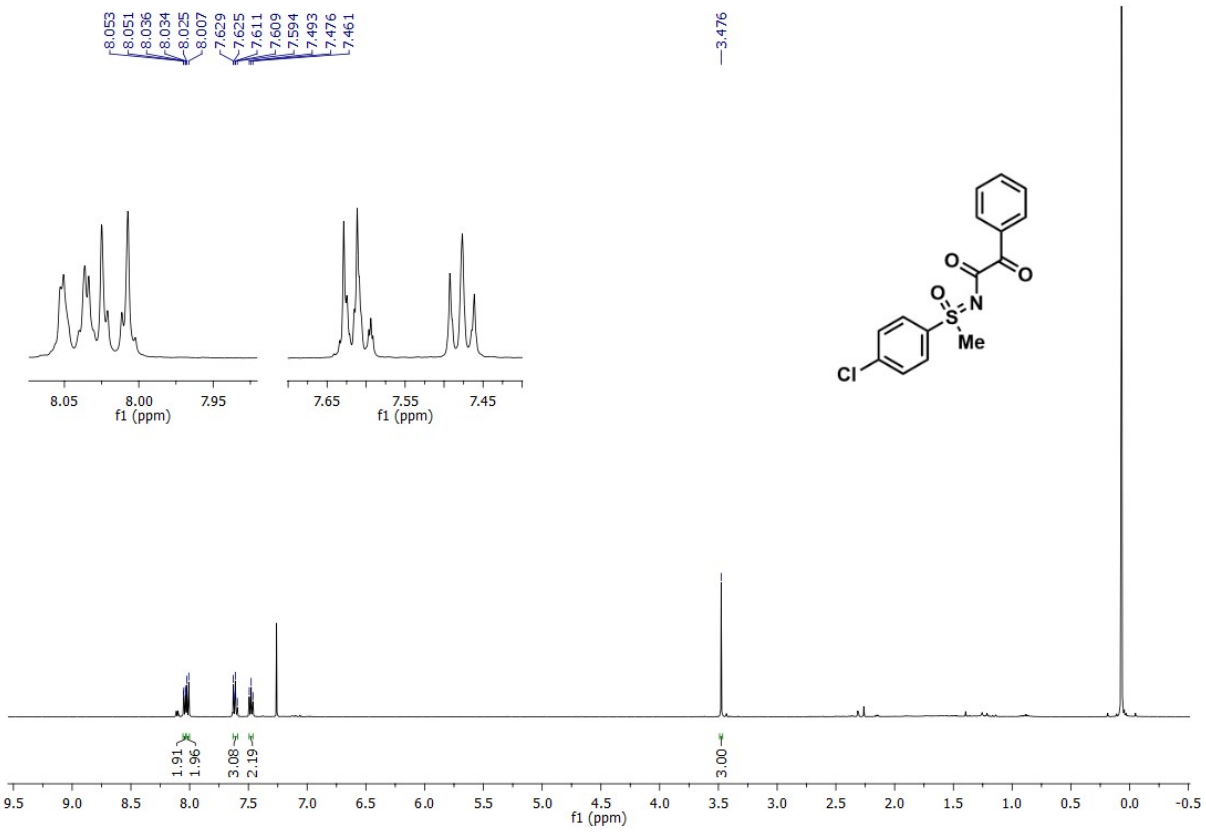
^{1}H NMR of 3e



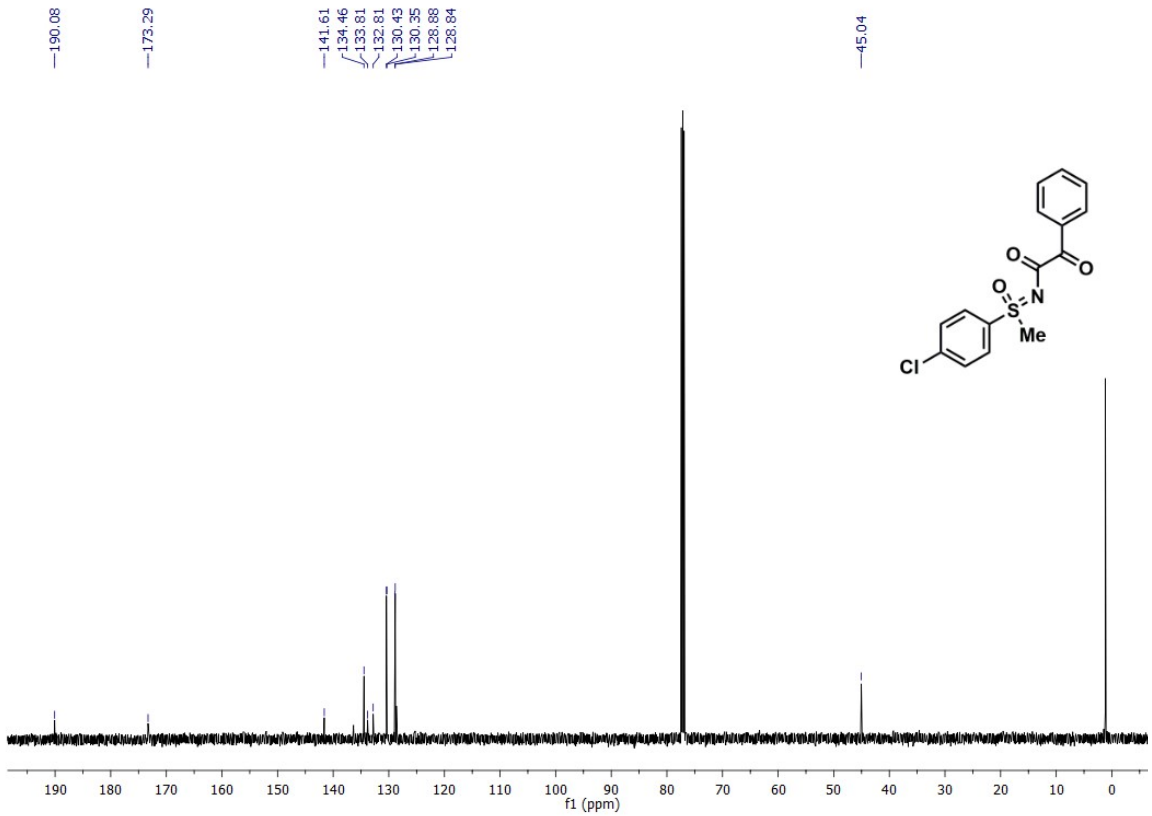
^{13}C {^{1}H} NMR of 3e



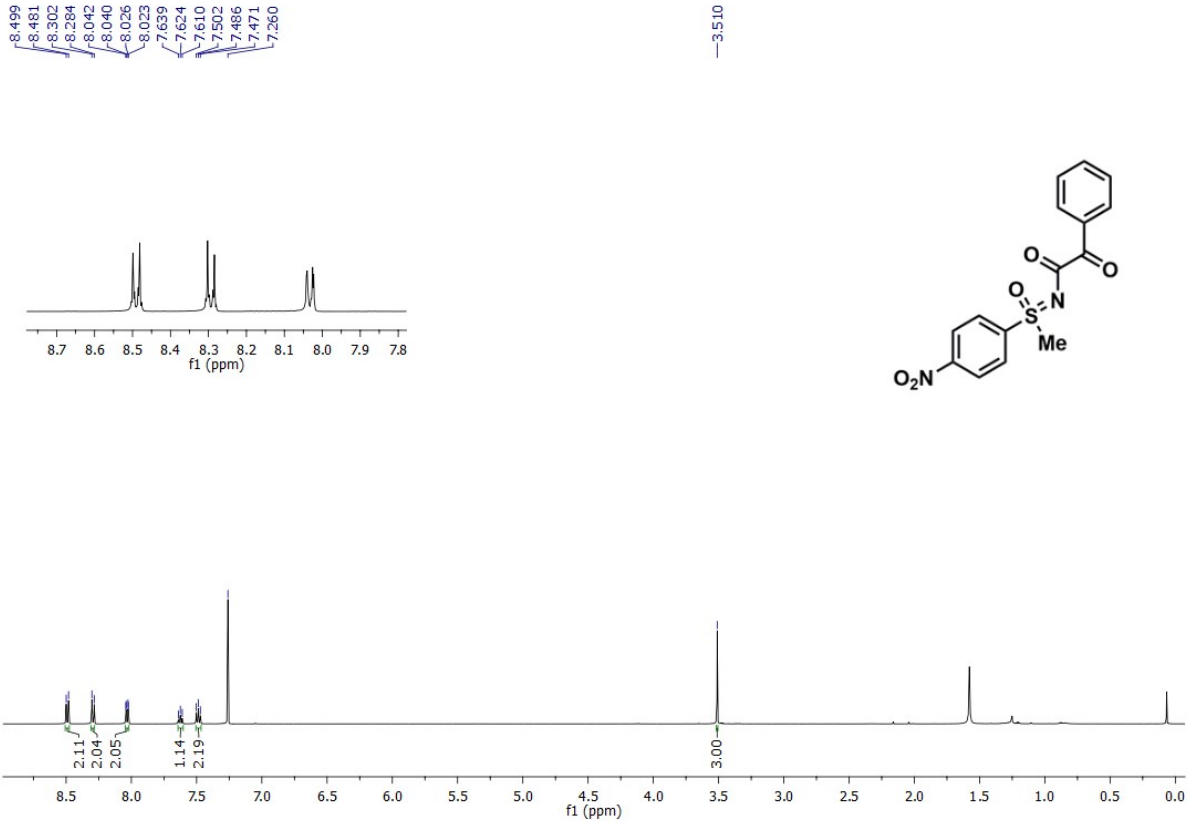
^{1}H NMR of 3f



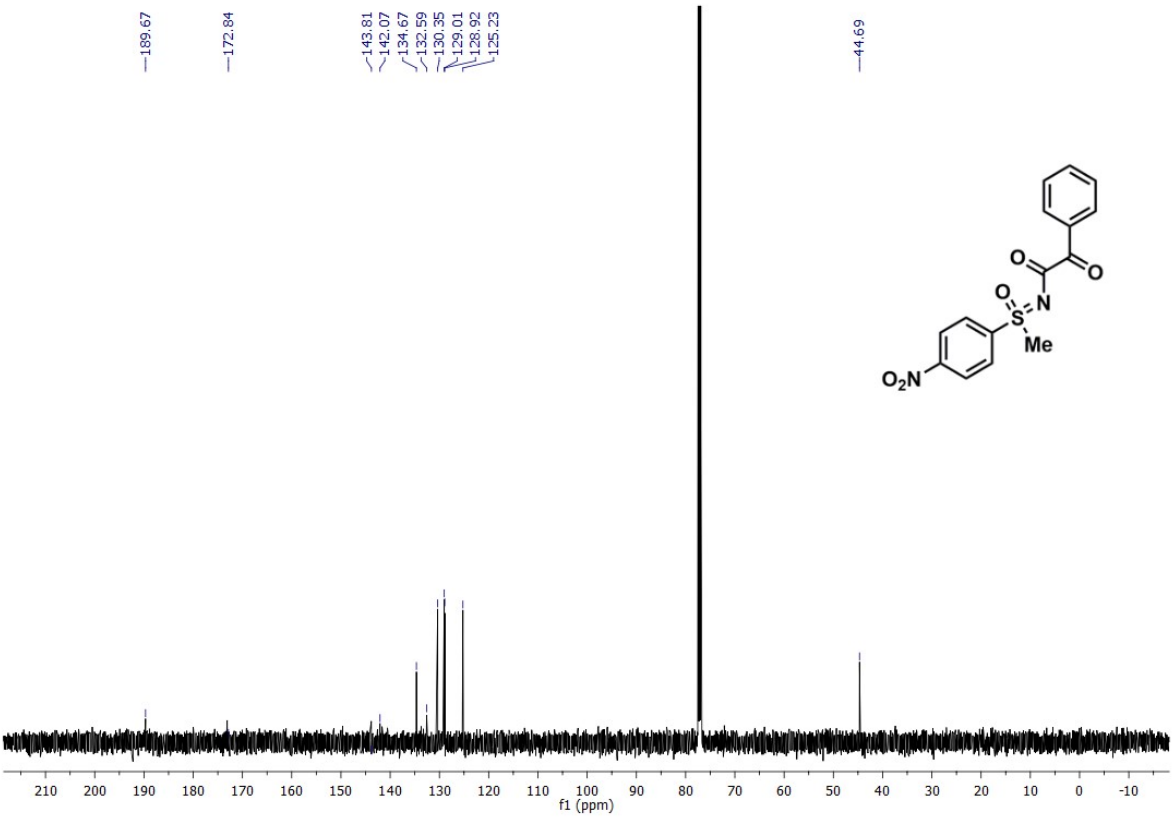
^{13}C {^{1}H} NMR of 3f



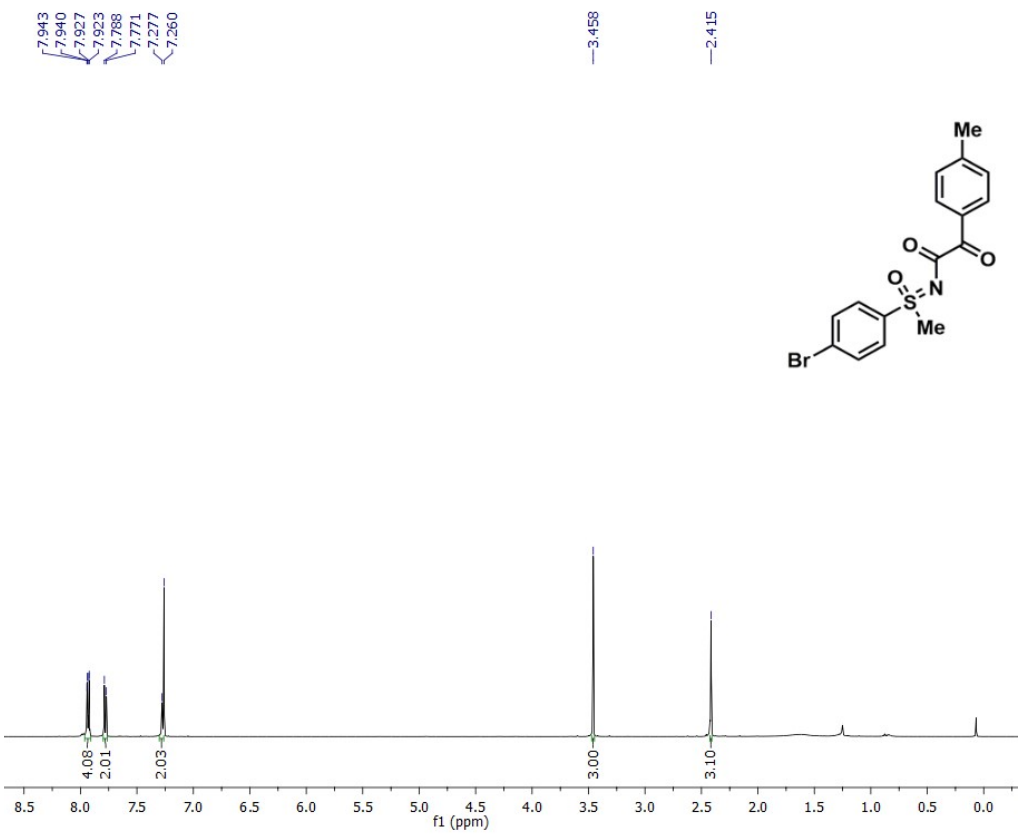
^{1}H NMR of 3g



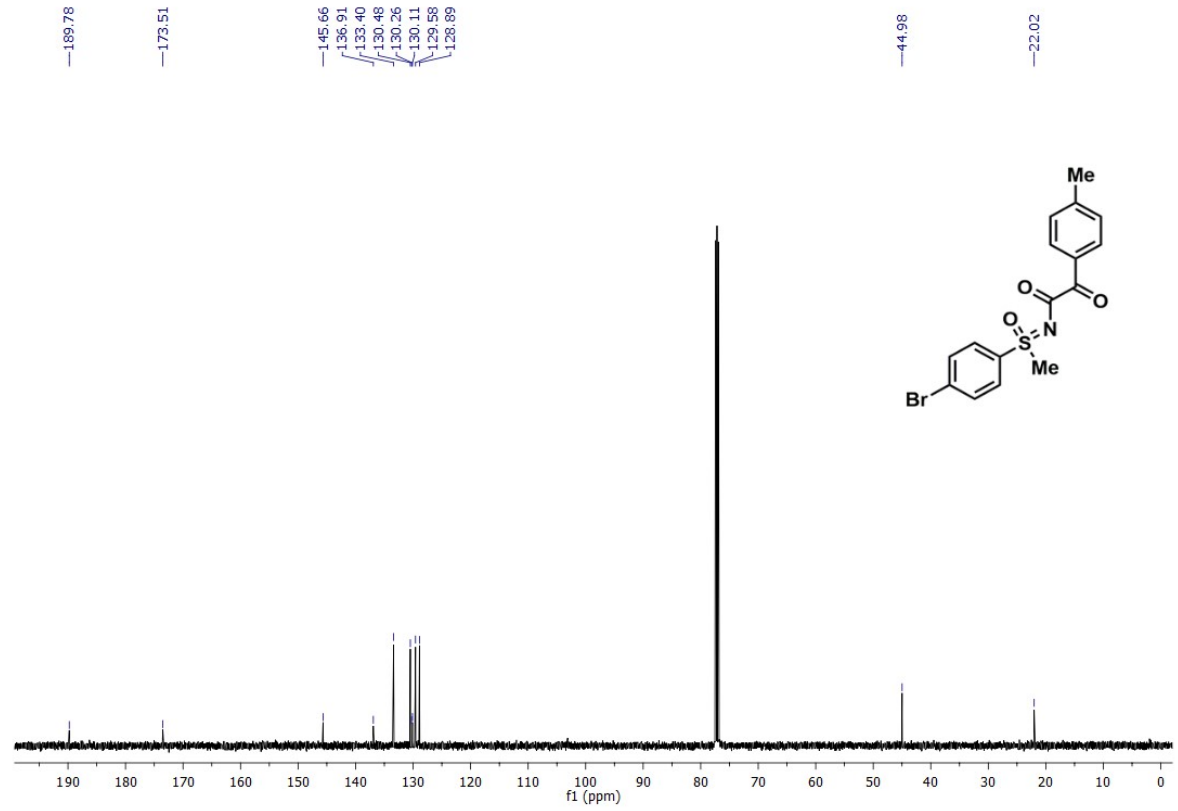
^{13}C {^{1}H} NMR of 3g



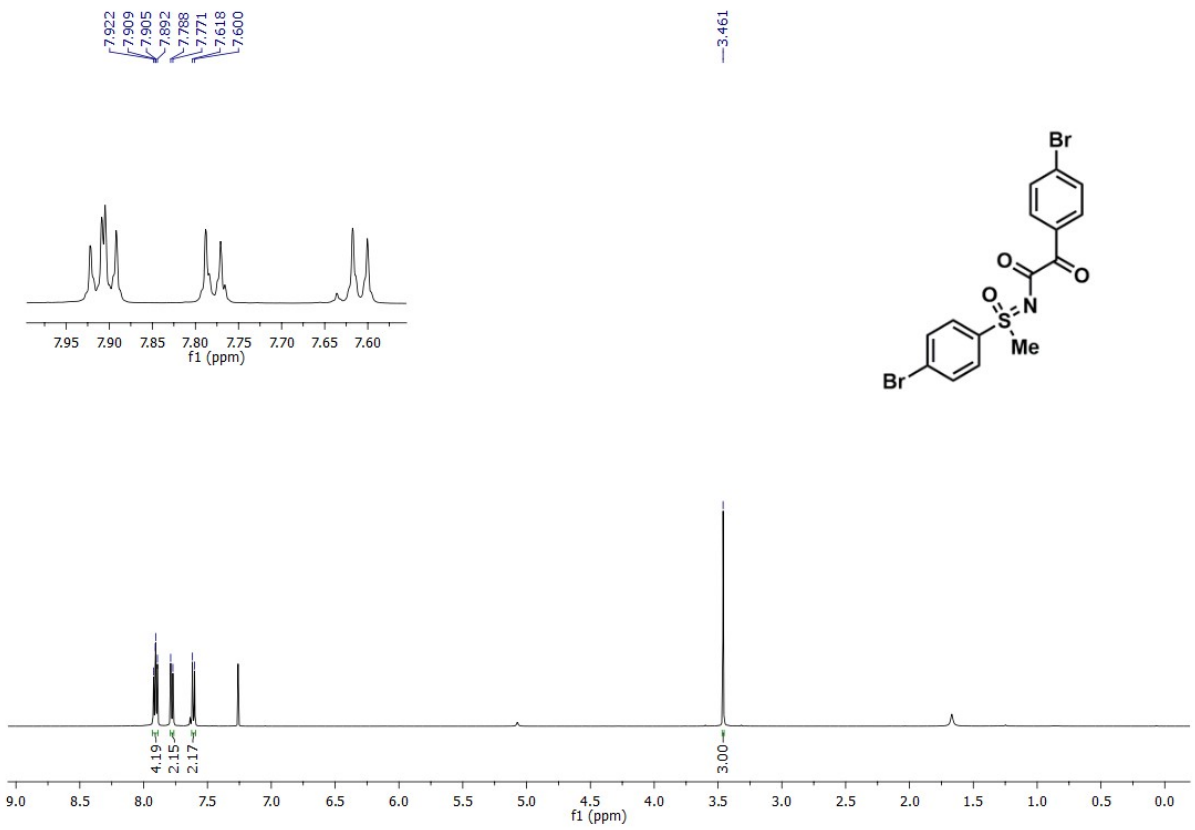
^{1}H NMR of 3h



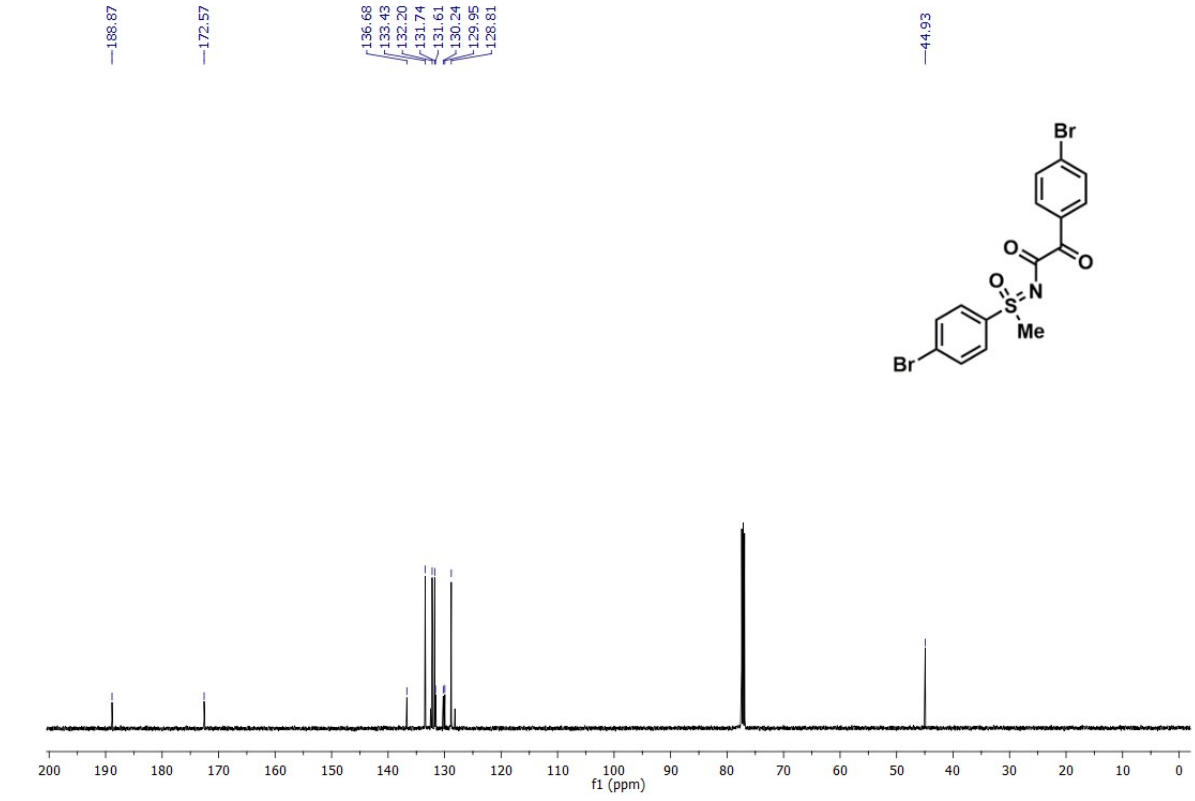
^{13}C {^{1}H} NMR of 3h



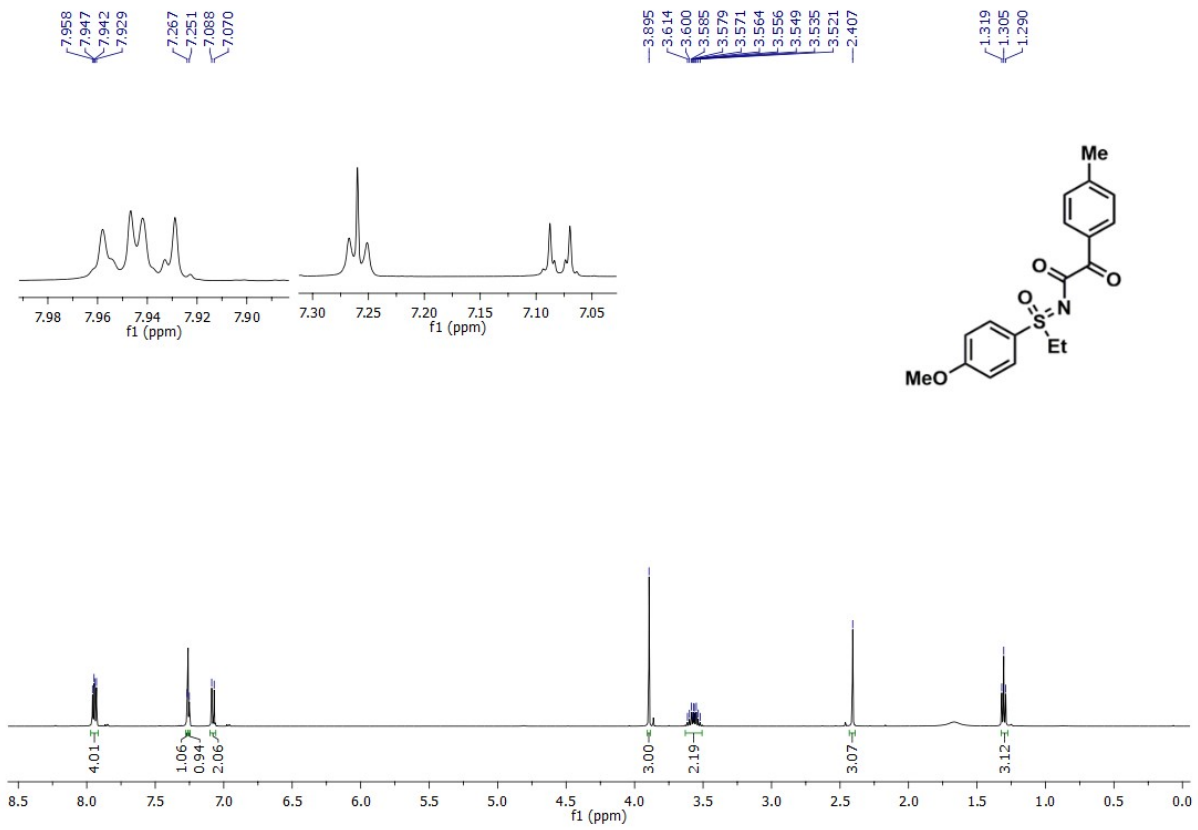
^{1}H NMR of 3i



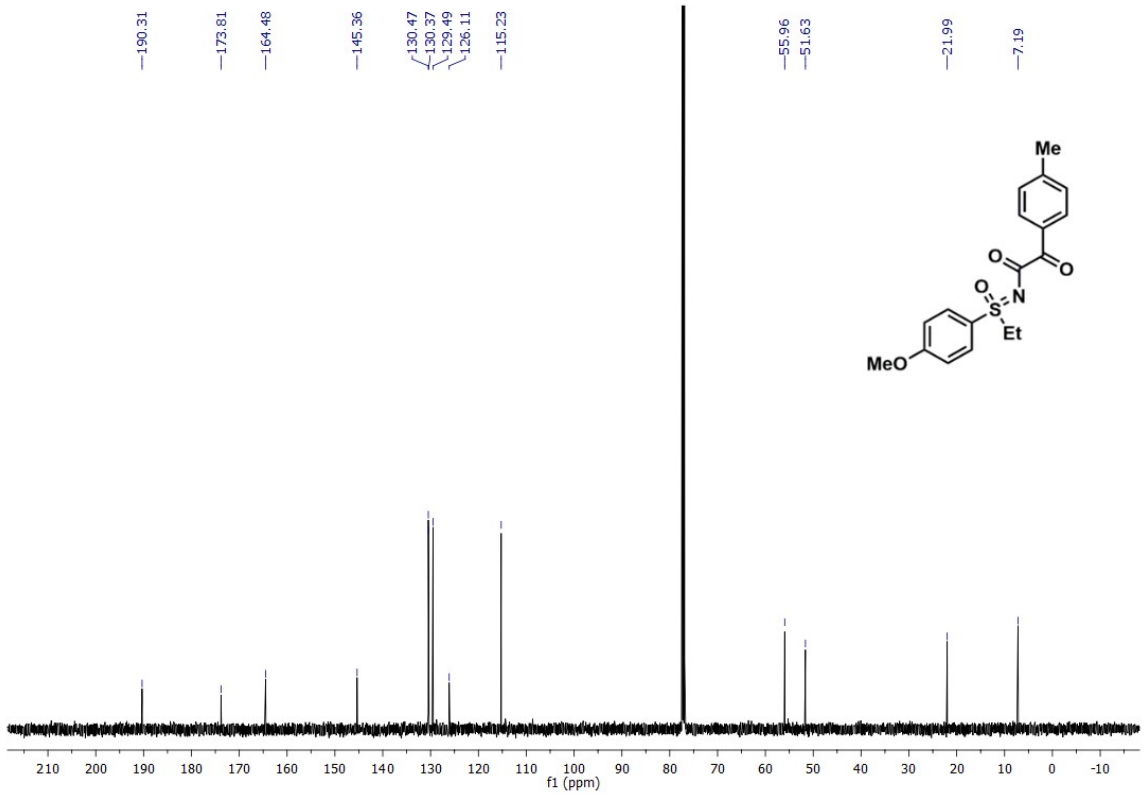
^{13}C {^{1}H} NMR of 3i



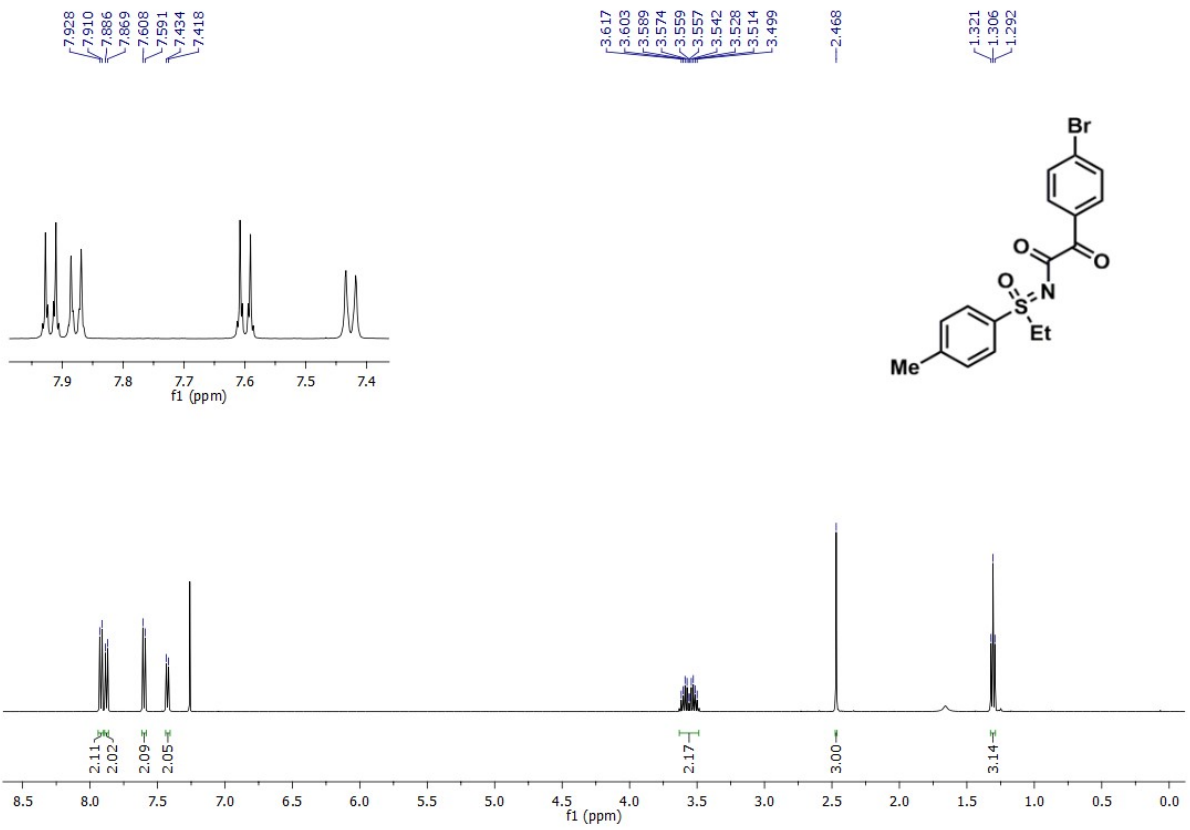
^{1}H NMR of 3j



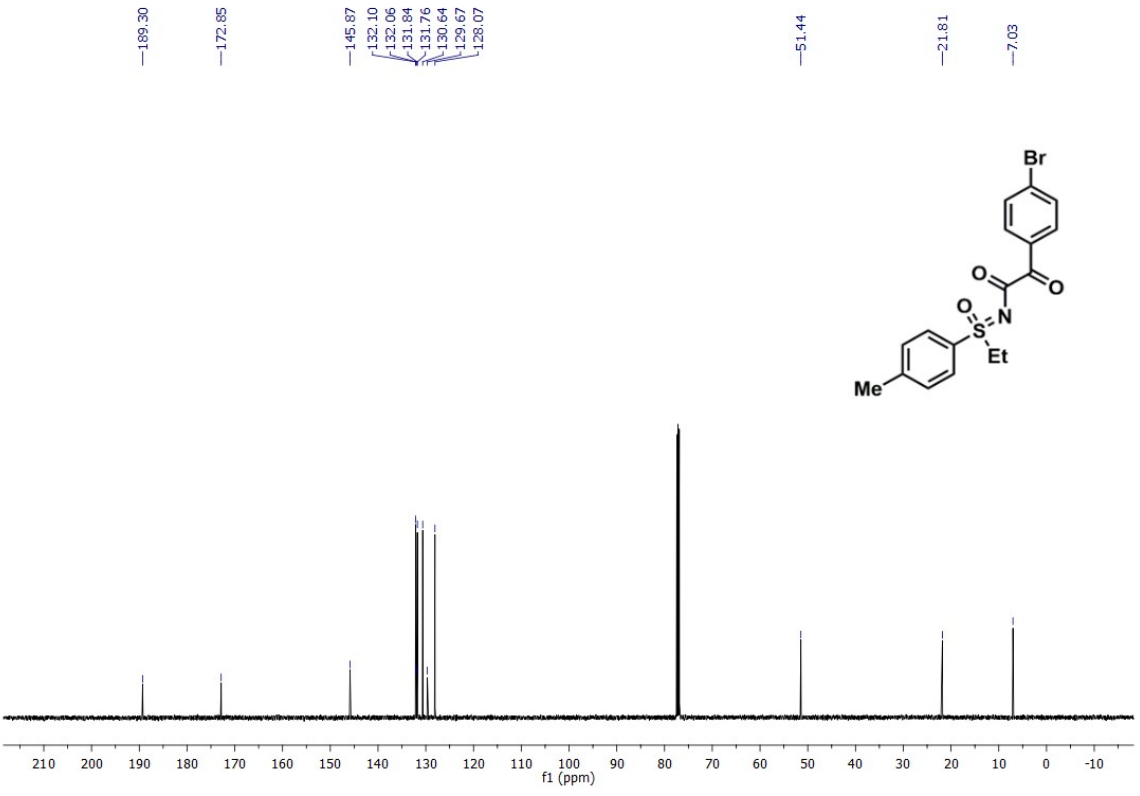
^{13}C {^{1}H} NMR of 3j



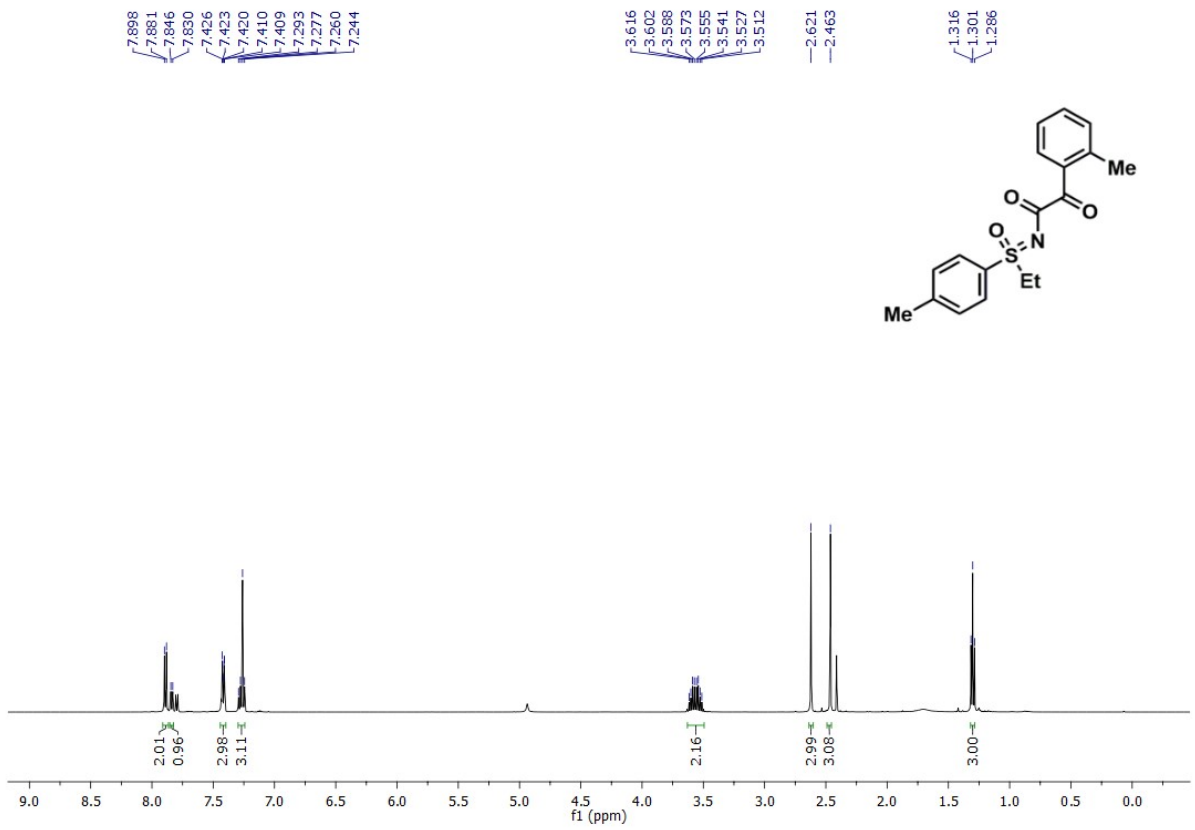
^{1}H NMR of 3k



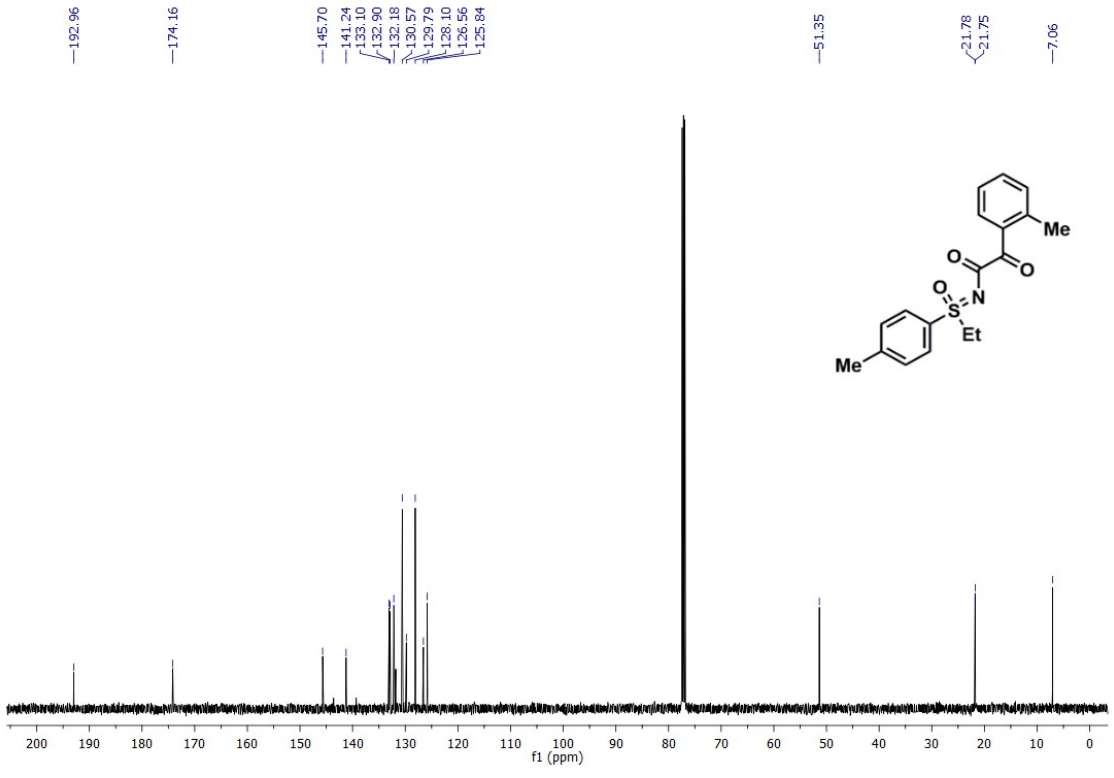
^{13}C {^{1}H} NMR of 3k



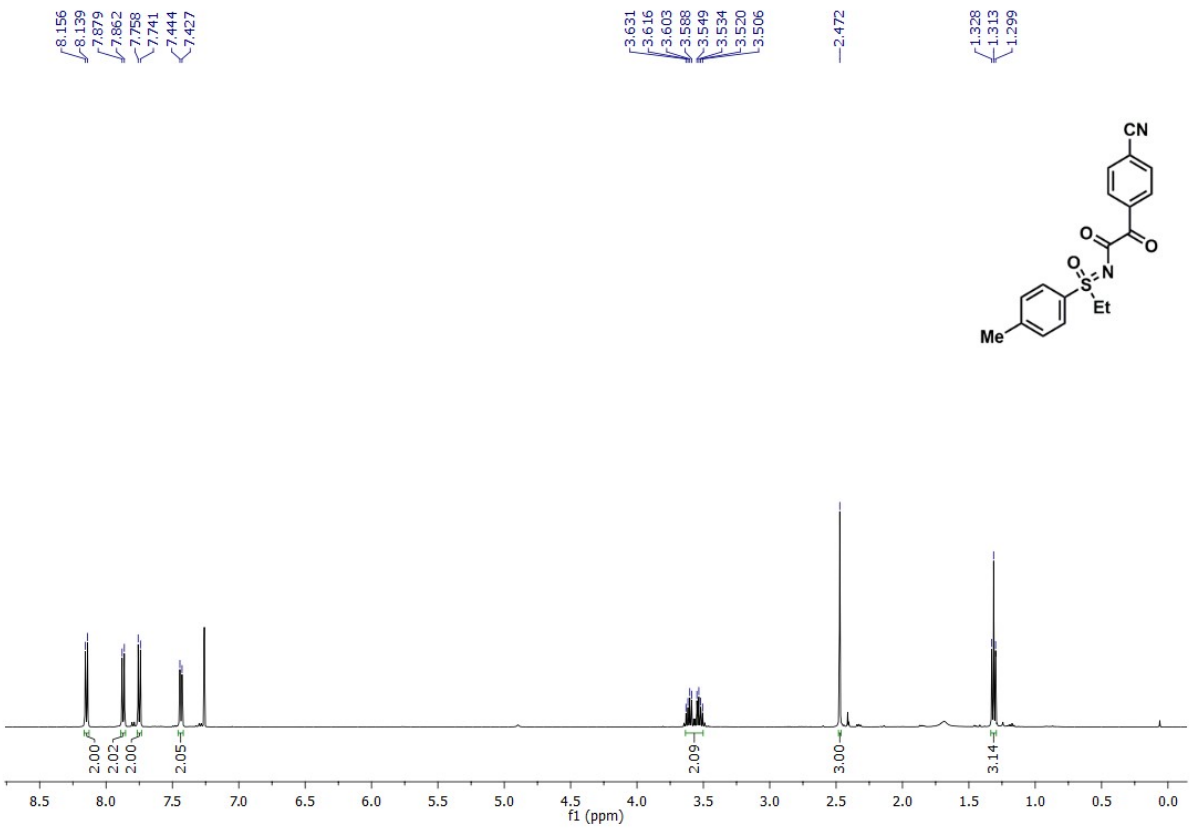
^{1}H NMR of 3l



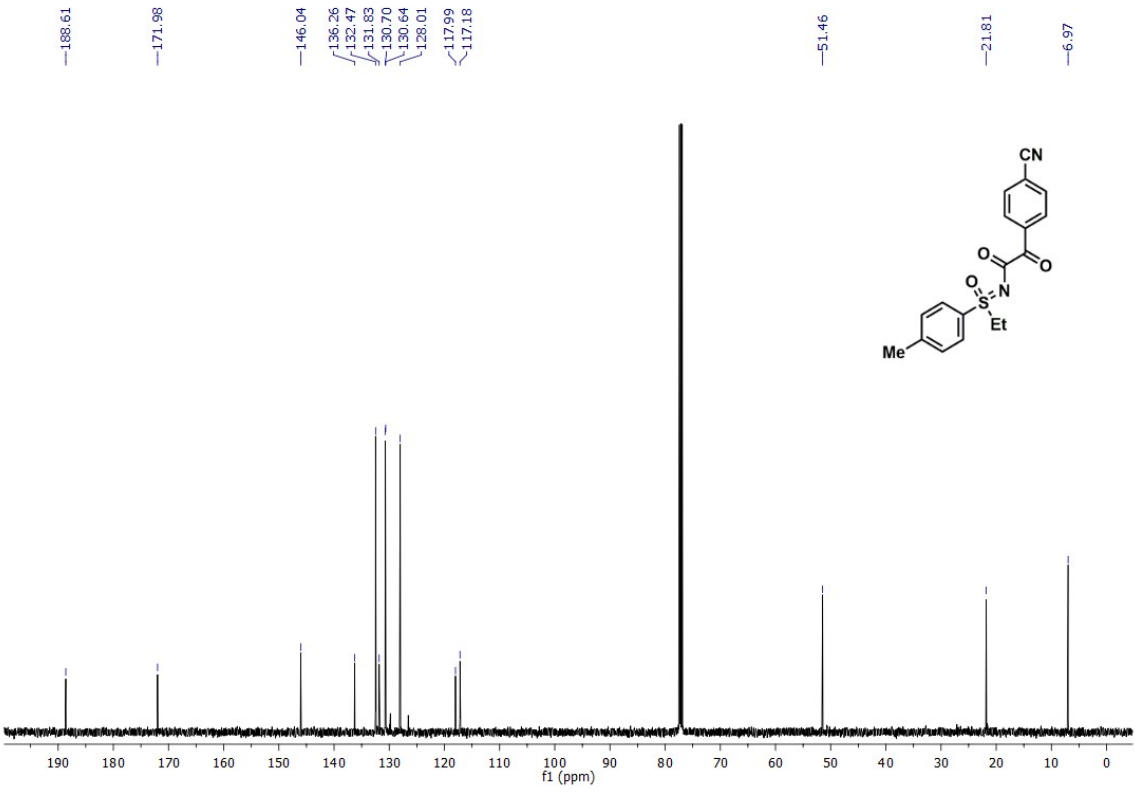
^{13}C {^{1}H} NMR of 3l



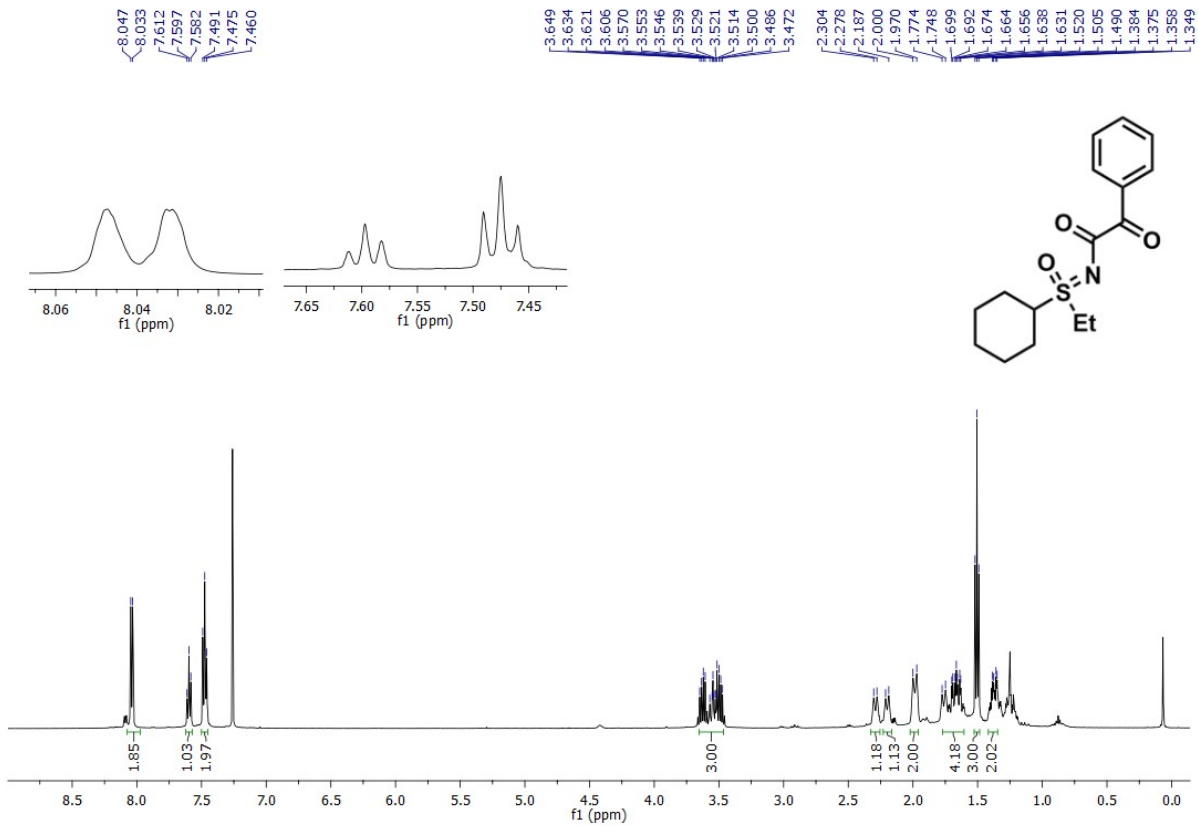
^{1}H NMR of 3m



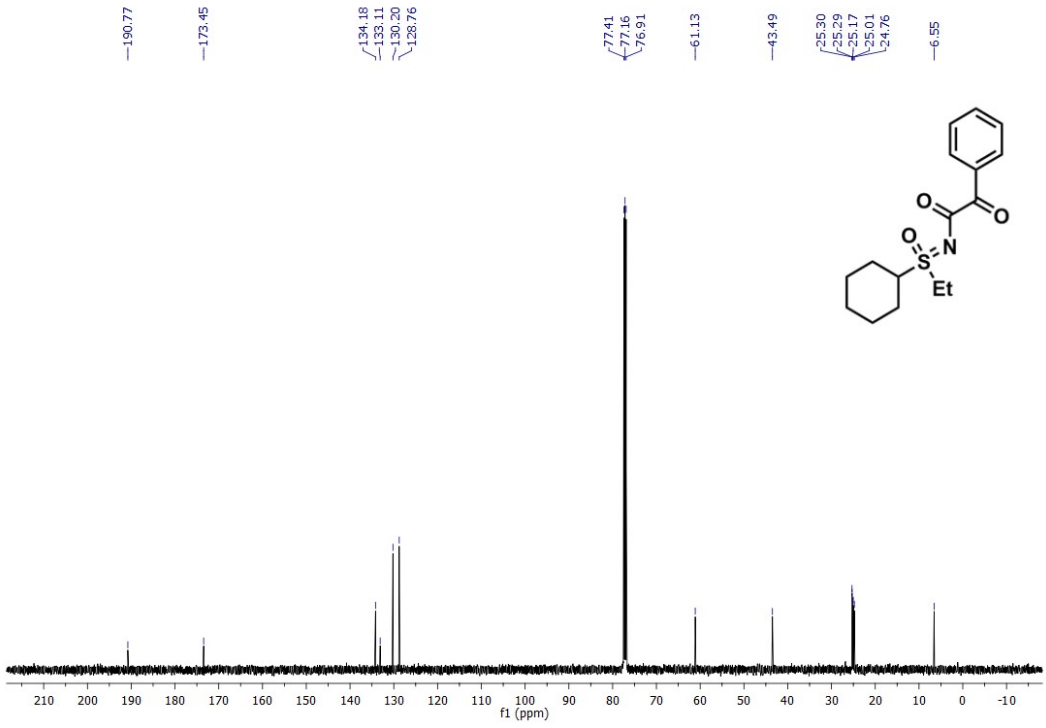
^{13}C {^{1}H} NMR of 3m



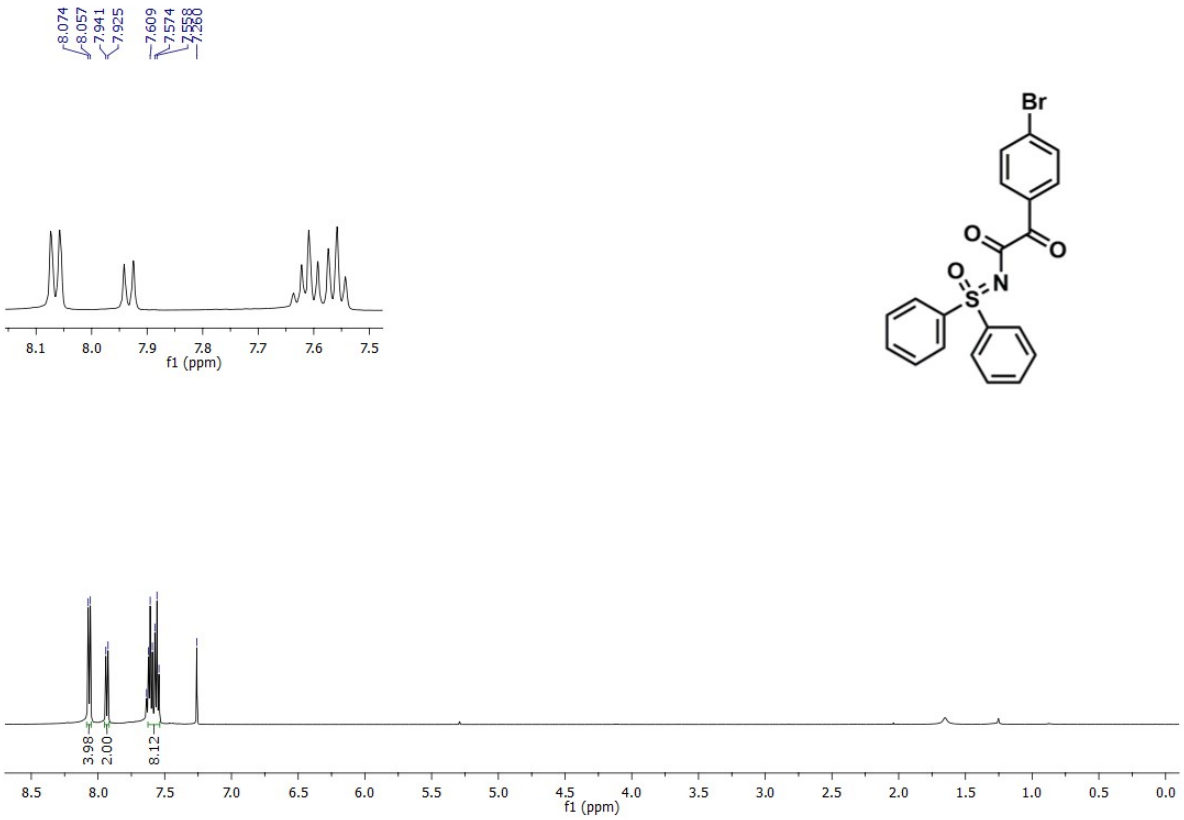
^{1}H NMR of 3n



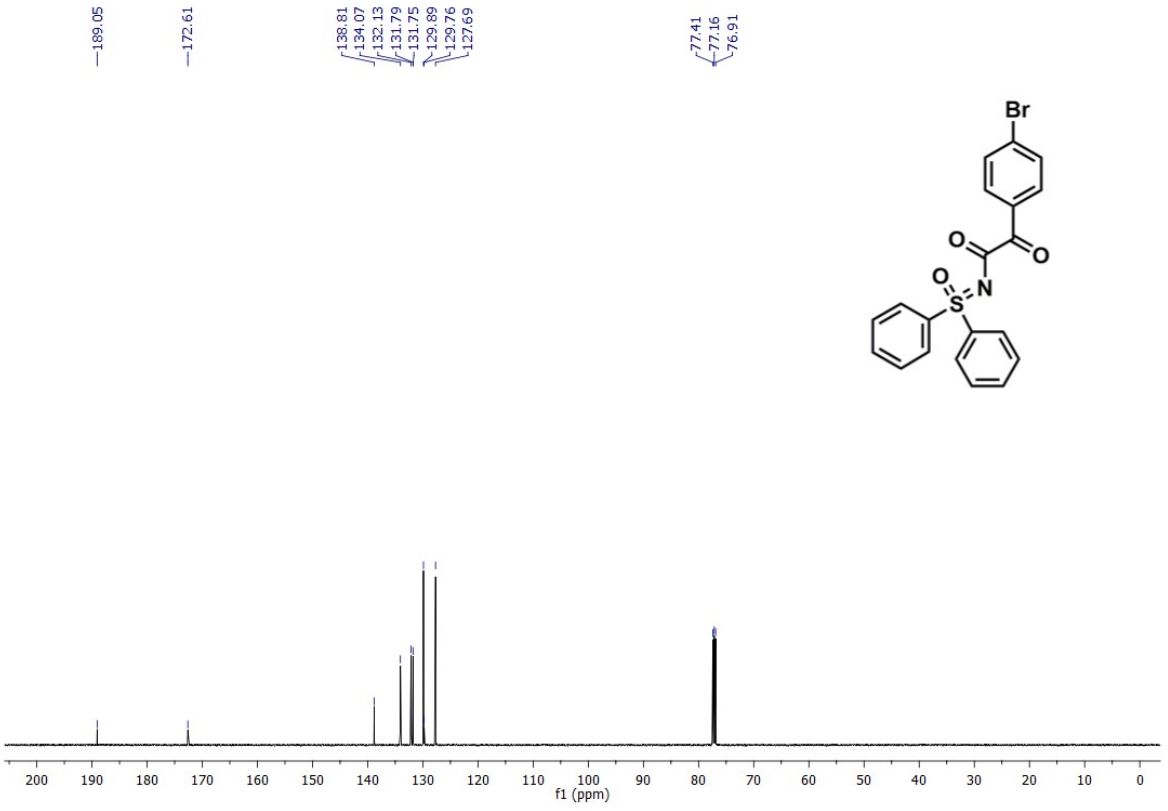
^{13}C {^{1}H} NMR of 3n



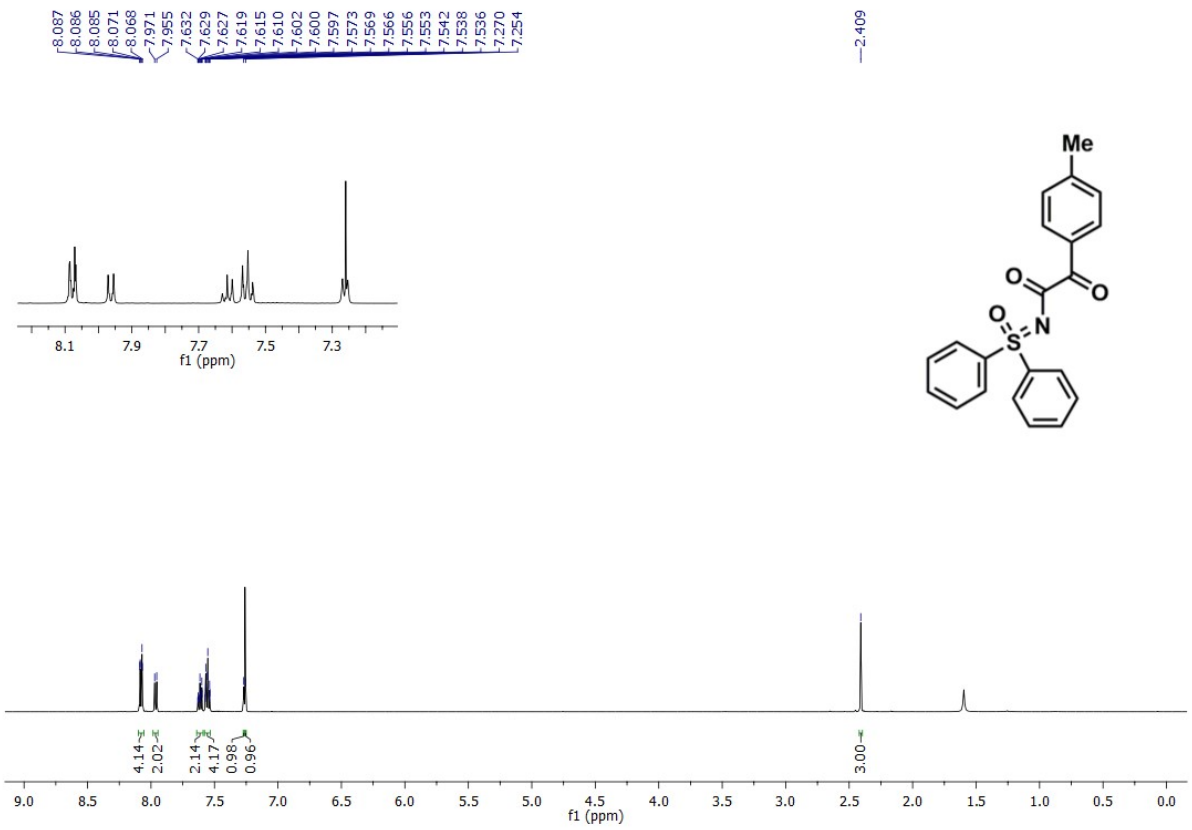
^{1}H NMR of 3o



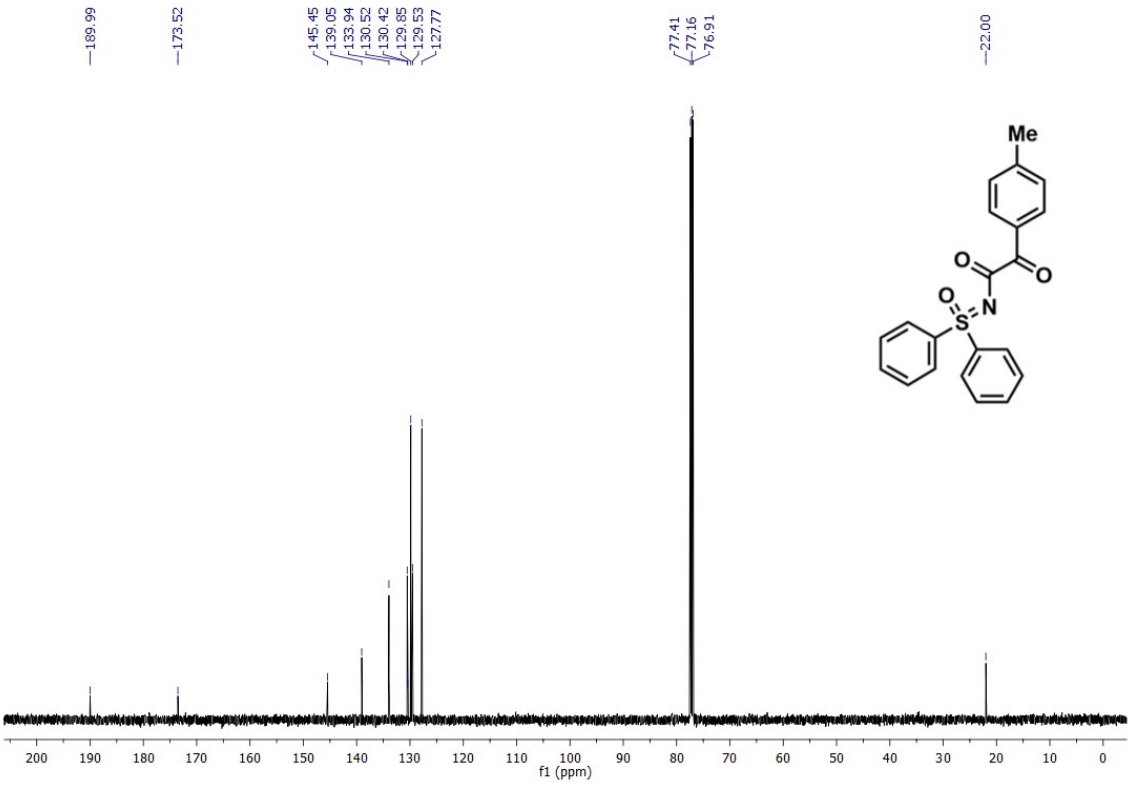
^{13}C {^{1}H} NMR of 3o



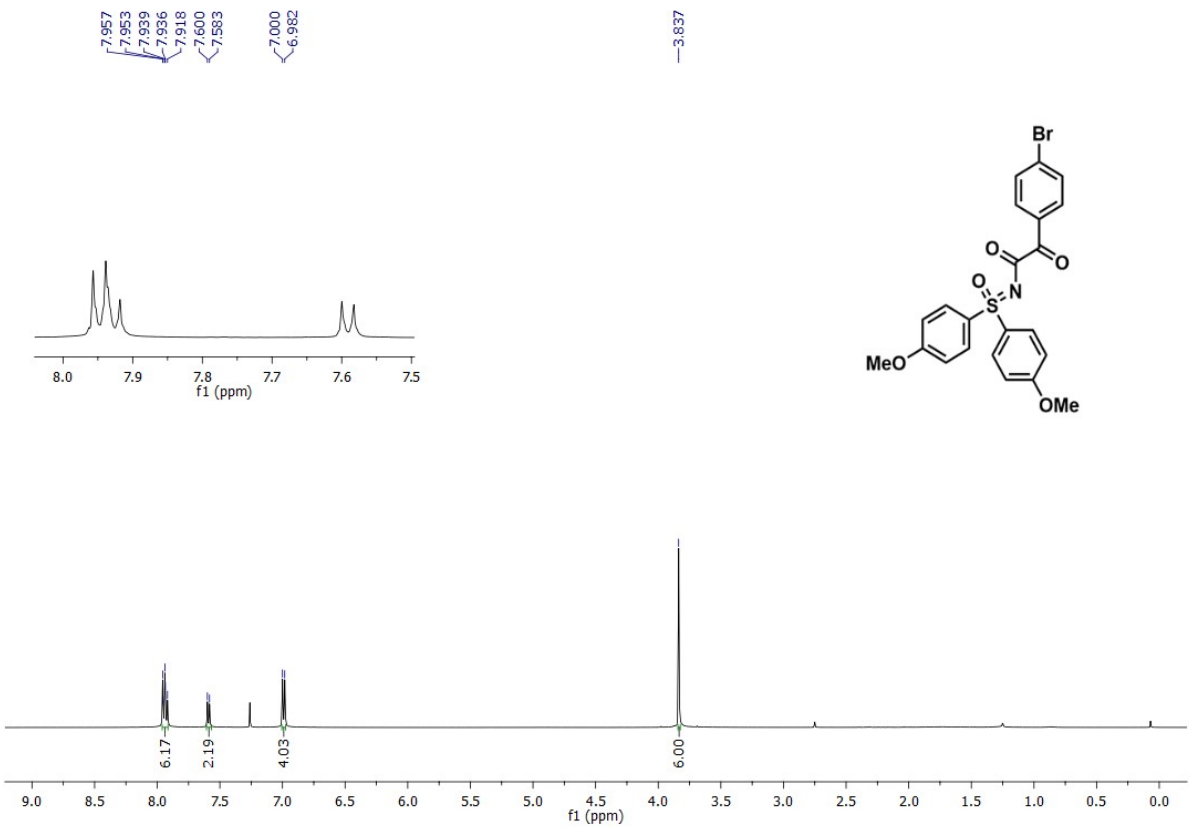
^{1}H NMR of 3p



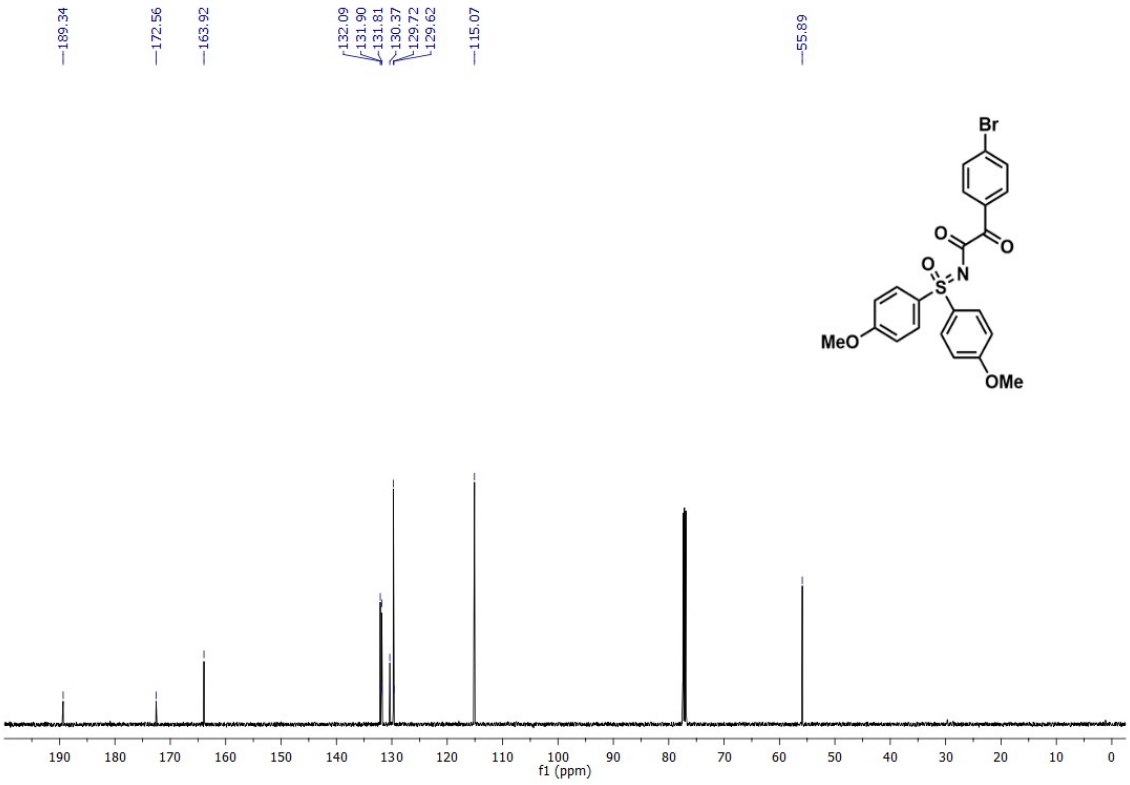
^{13}C {^{1}H} NMR of 3p



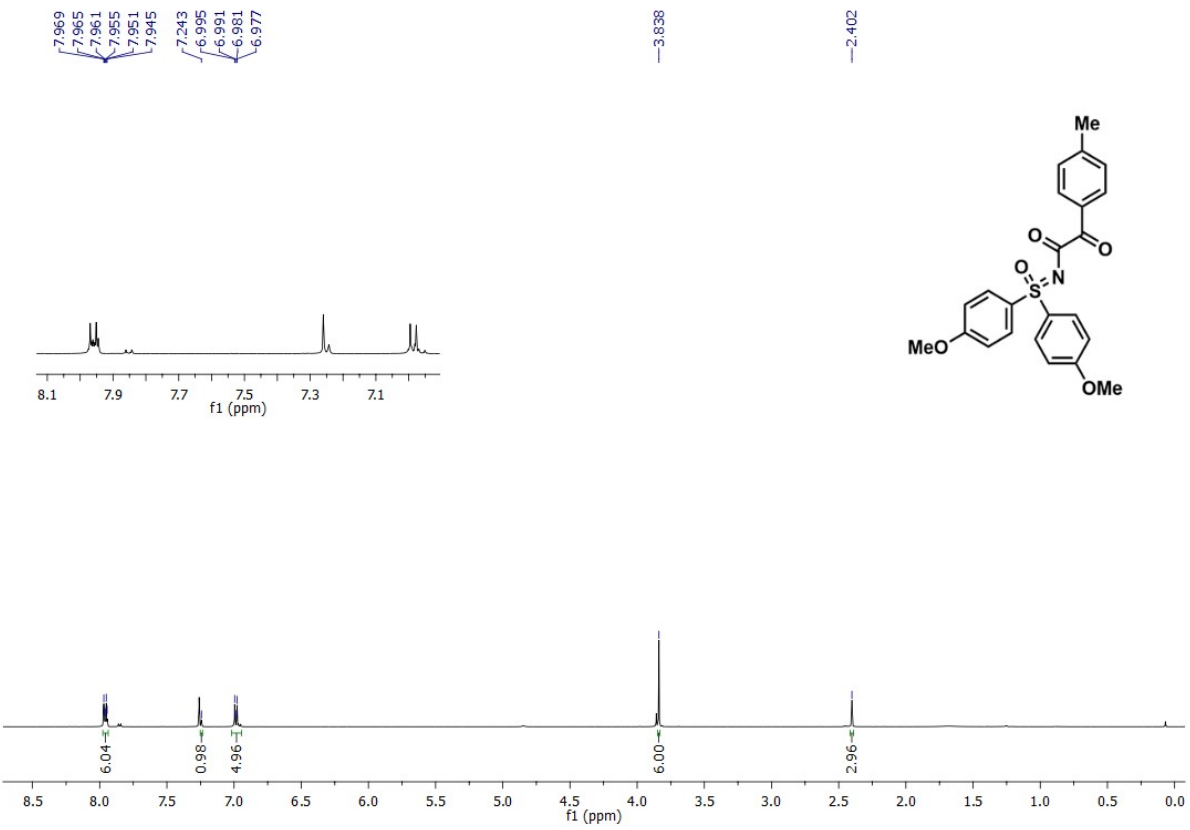
^{1}H NMR of 3q



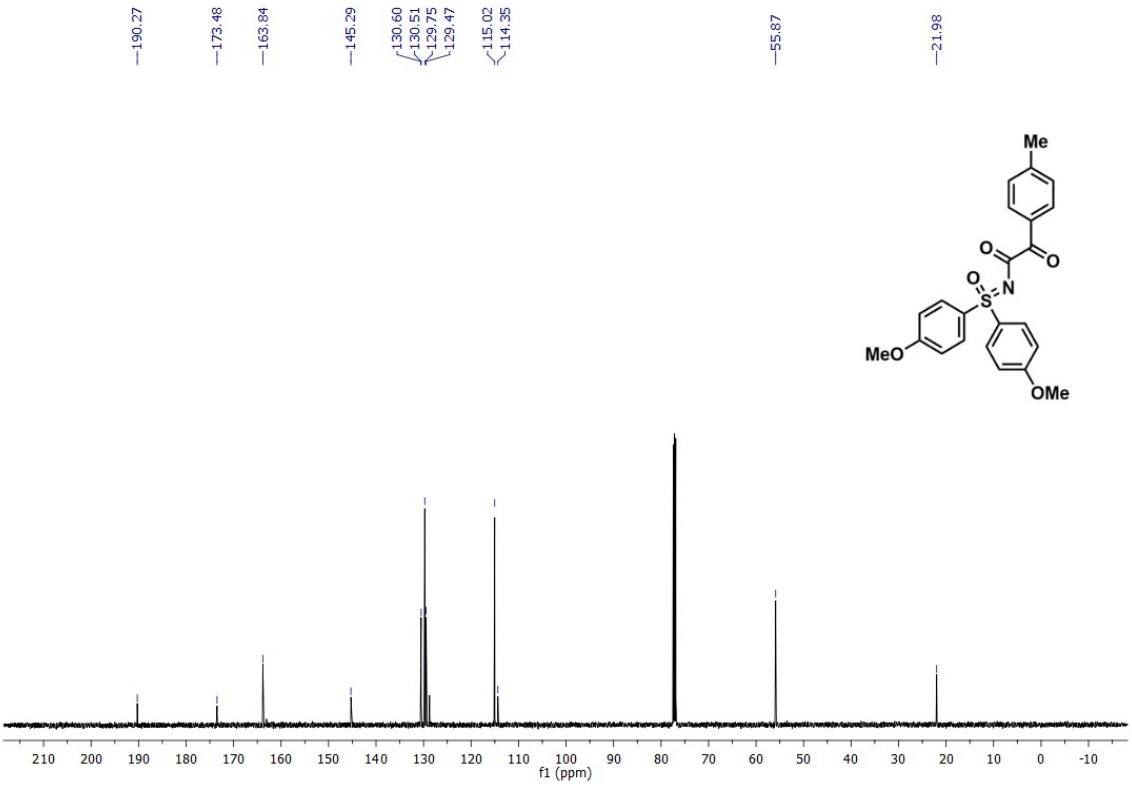
^{13}C {^{1}H} NMR of 3q



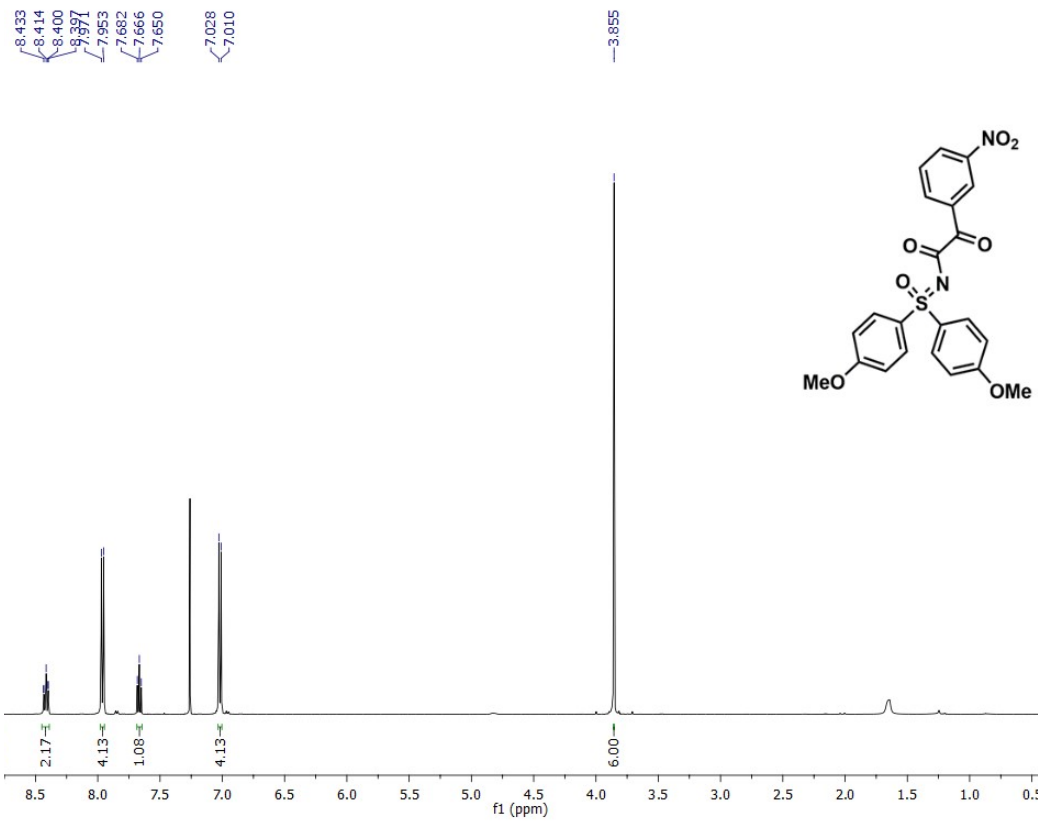
^{1}H NMR of 3r



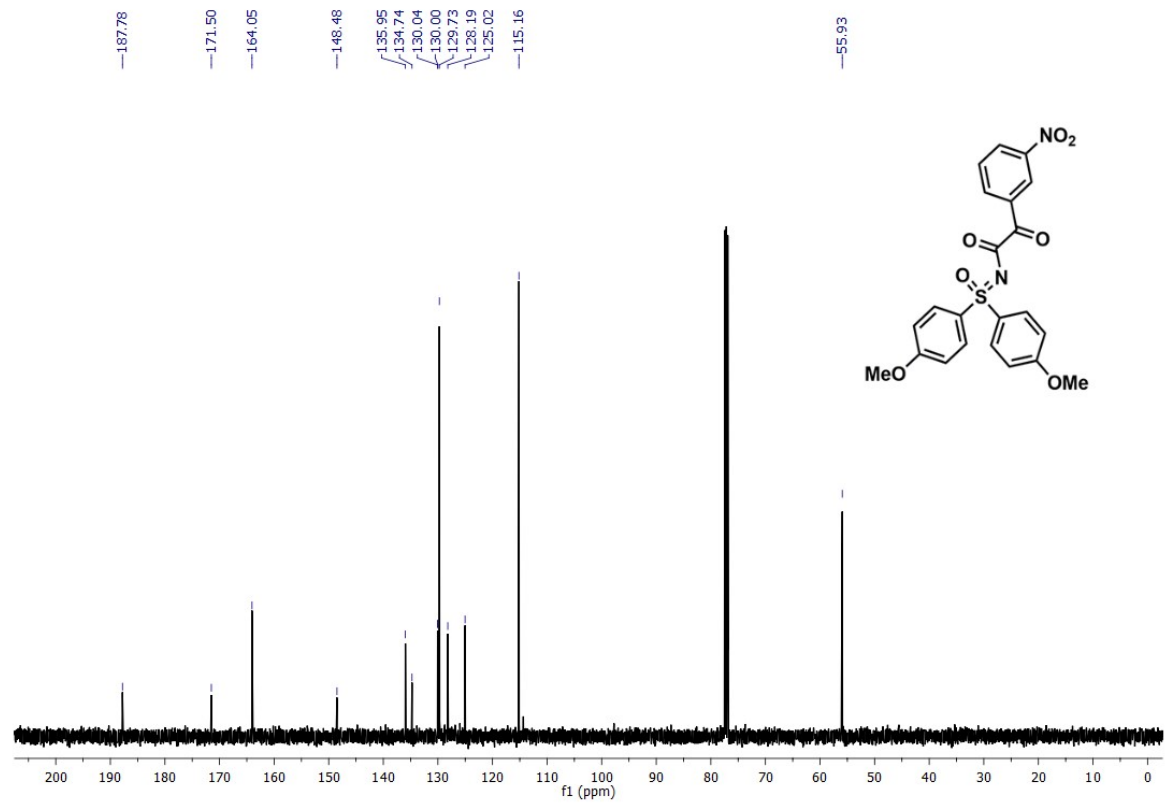
^{13}C {^{1}H} NMR of 3r



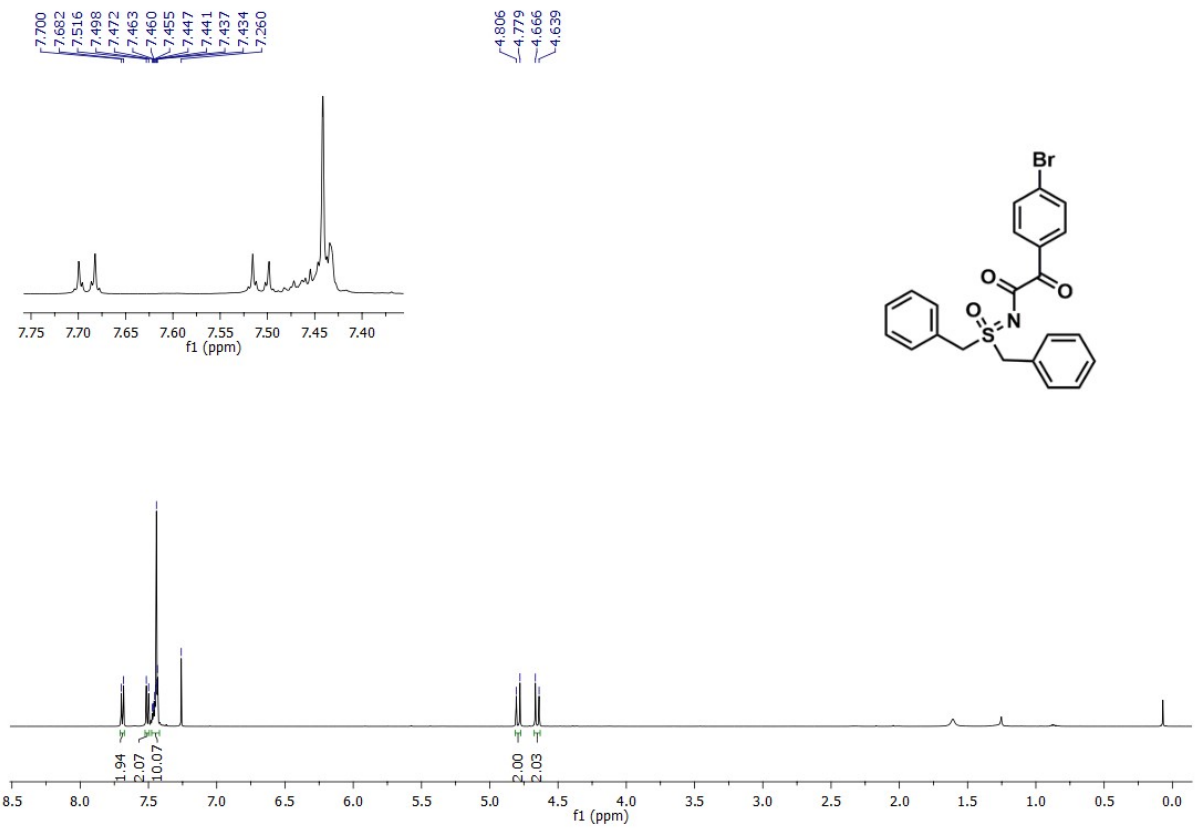
^{1}H NMR of 3s



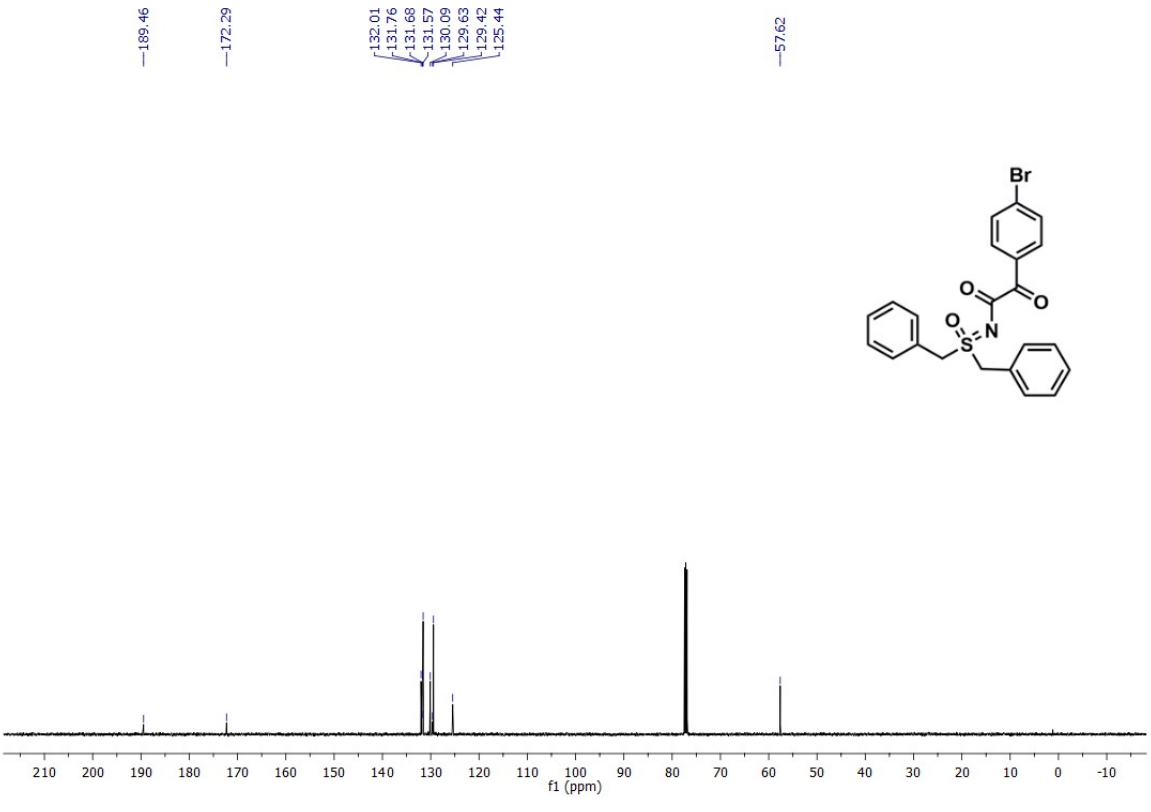
^{13}C {^{1}H} NMR of 3s



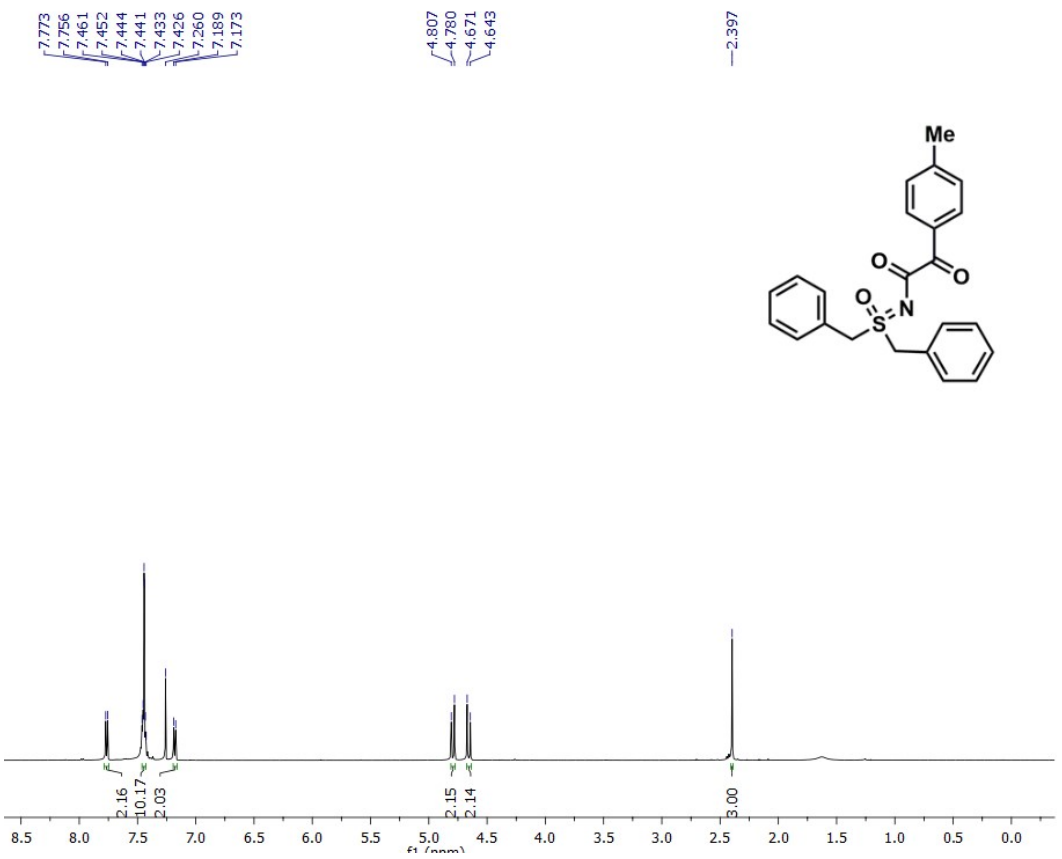
^{1}H NMR of 3t



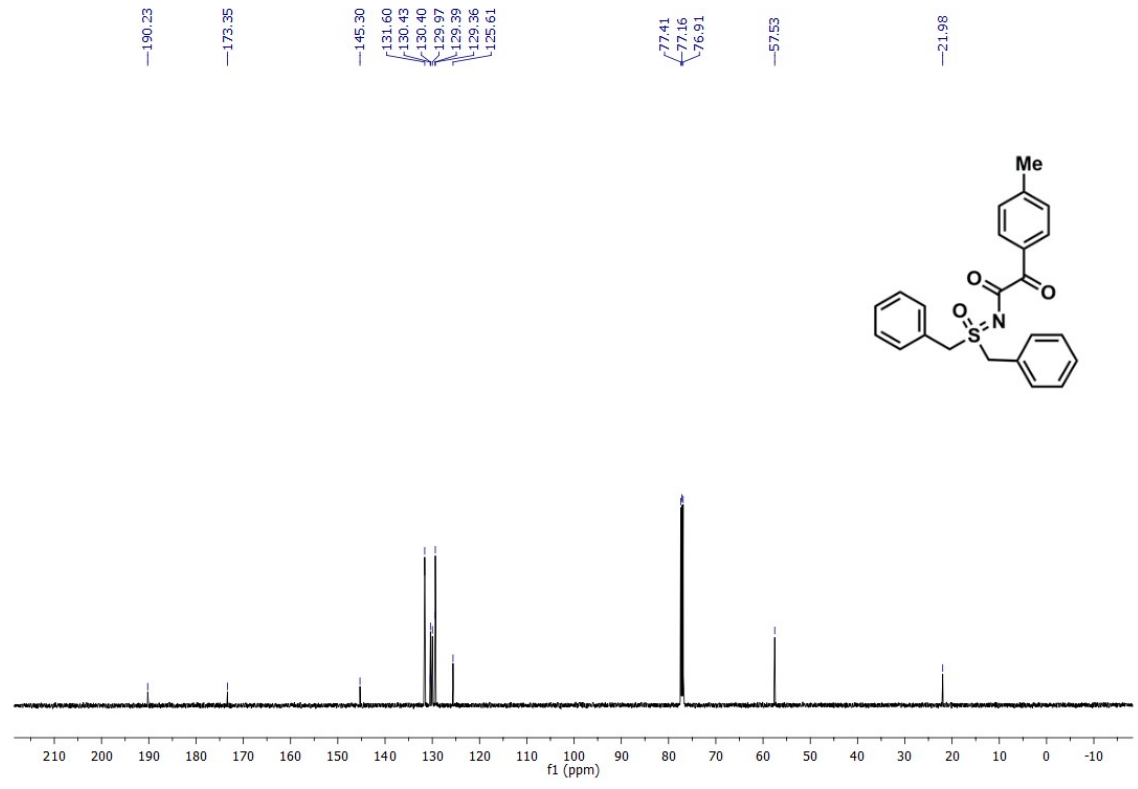
^{13}C {^{1}H} NMR of 3t



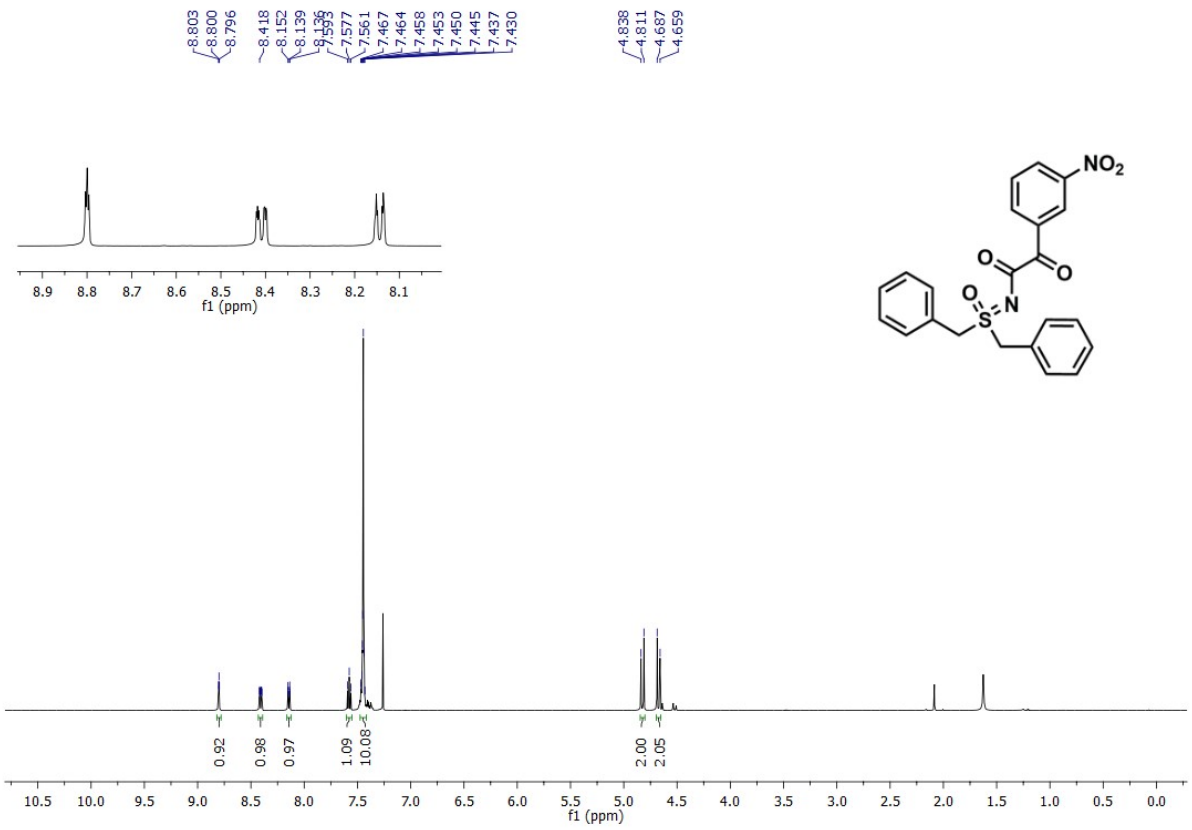
^{1}H NMR of 3u



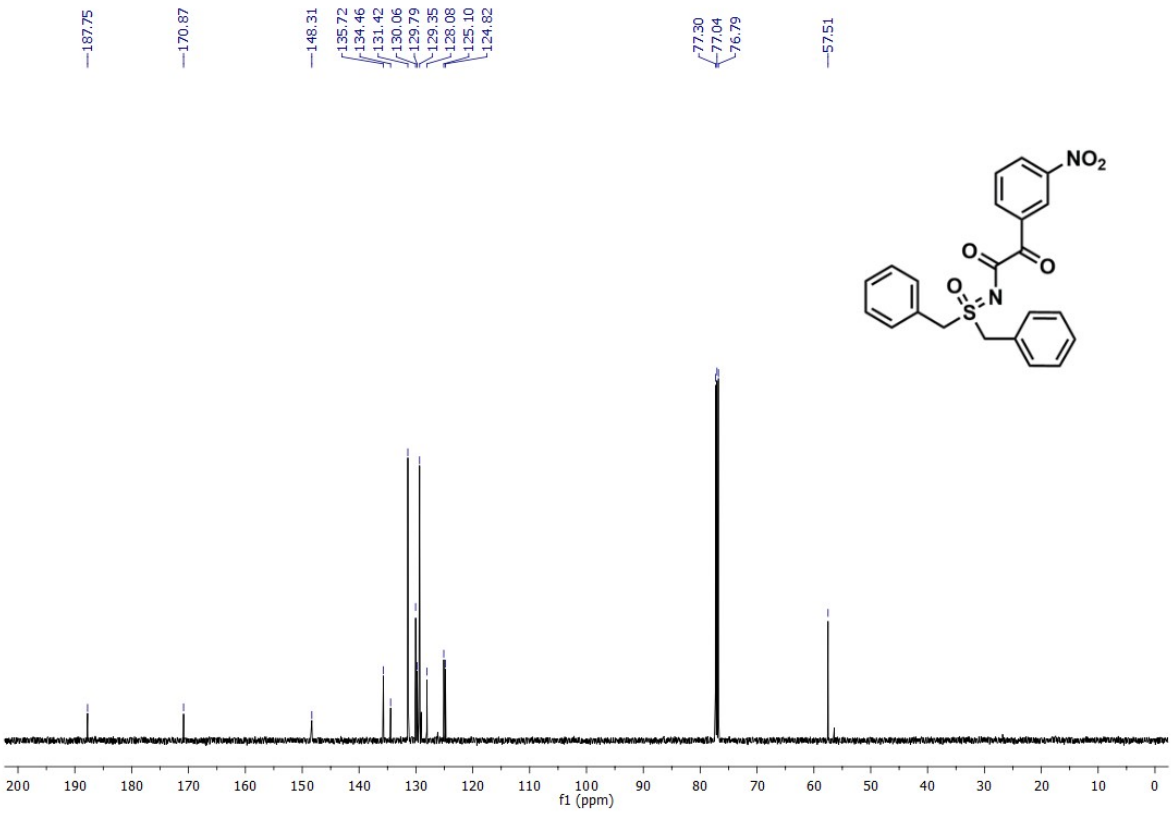
^{13}C {^{1}H} NMR of 3u



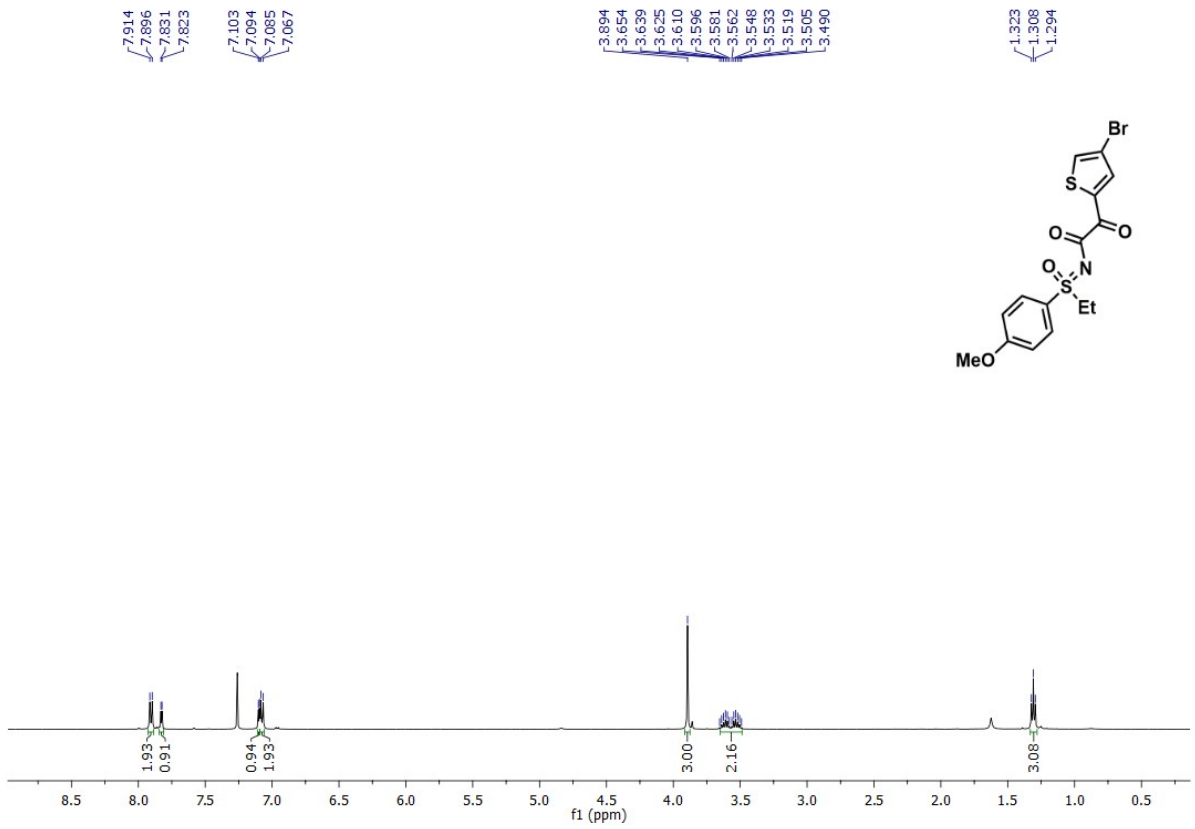
^{1}H NMR of 3v



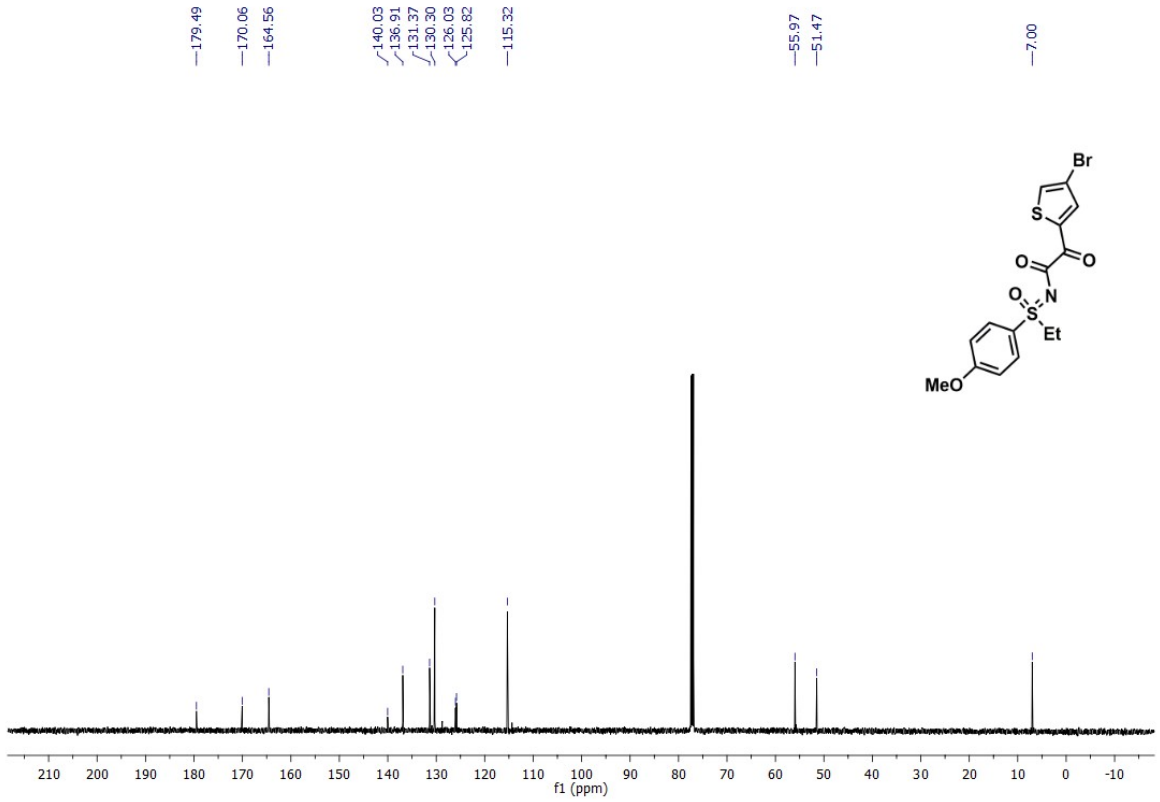
^{13}C {^{1}H} NMR of 3v



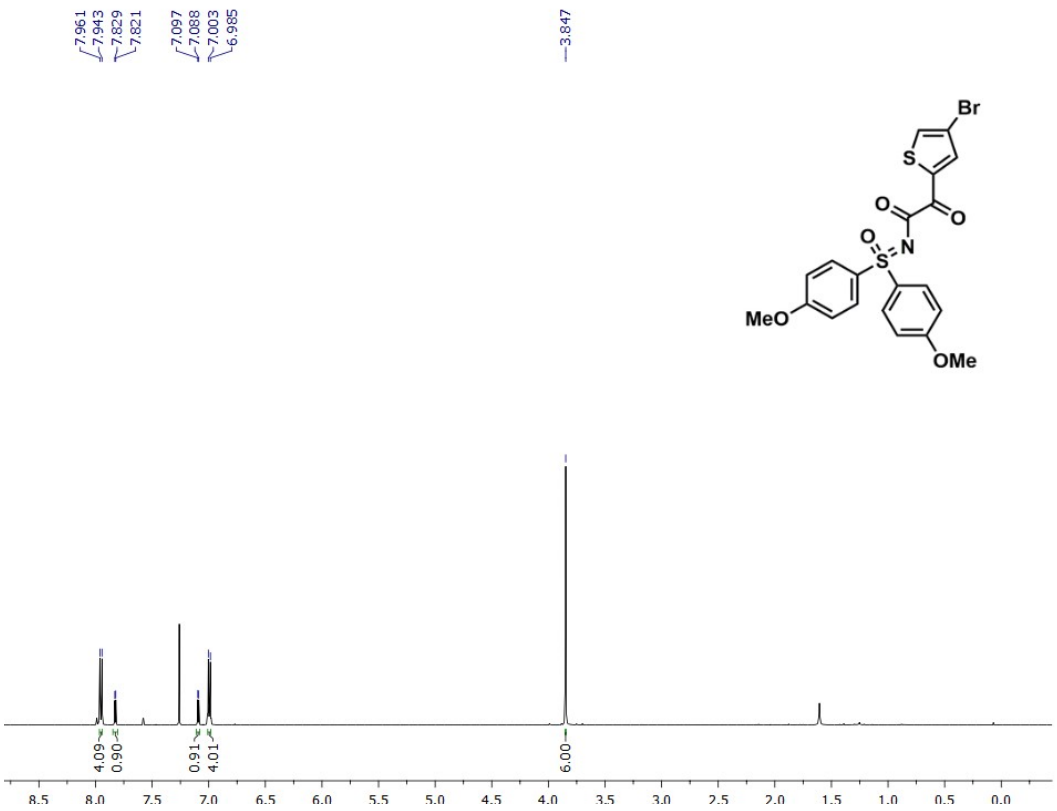
^{1}H NMR of 3w



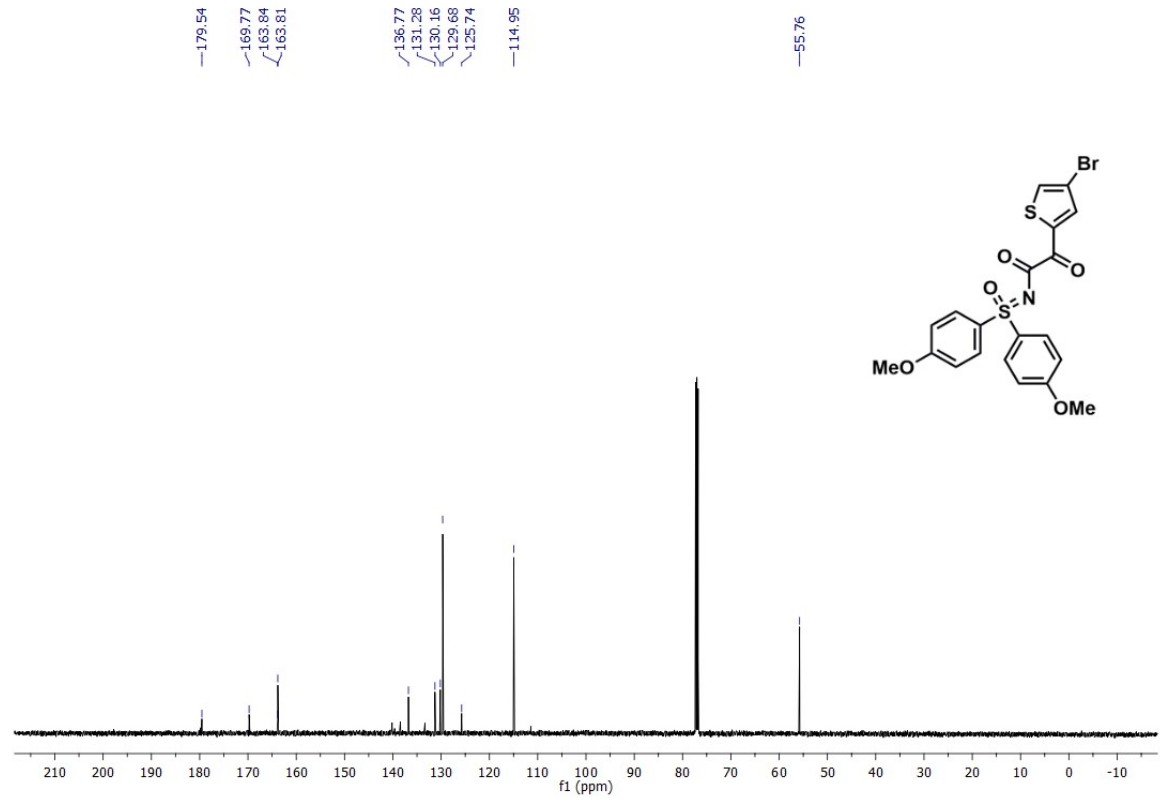
^{13}C {^{1}H} NMR of 3w



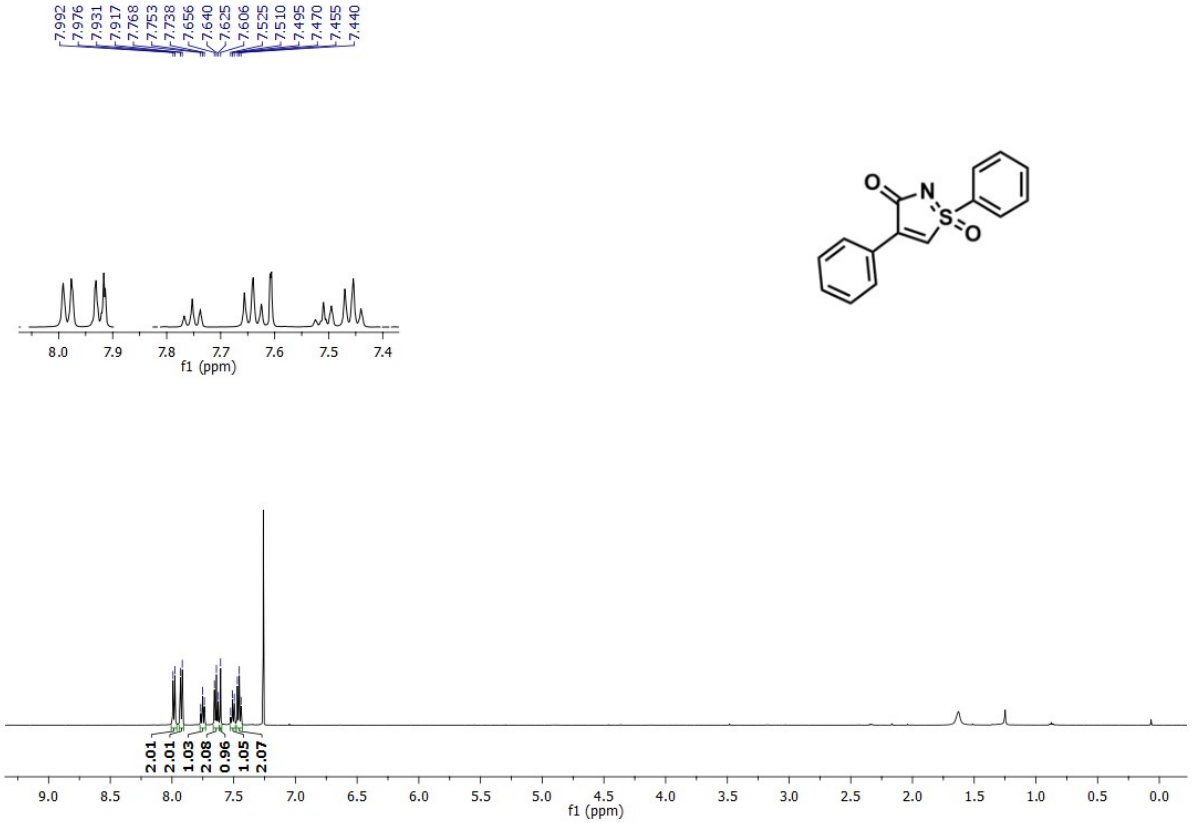
^{1}H NMR of 3x



^{13}C {^{1}H} NMR of 3x



^{1}H NMR of 4



^{13}C {^{1}H} NMR of 4