Electronic Supplementary Information for

Batch and Flow Synthesis of Sulfides and Sulfoxides Using Green Solvent and Oxidant Through Visible-Light Photocatalysis

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I. General Experimental Information

All reactions were performed under an atmosphere of argon and anhydrous conditions unless otherwise indicated. Acetonitrile, ethyl acetate, methanol, ethanol and pH 9 buffer (bicarbonate-based buffer) were purchased from Sigma-Aldrich Chemical Company and degassed by bubbling nitrogen gas for 30 min. Pressure tubes (13 × 100 mm, PYREXPLUS) and 50 mL flasks (Chem Glass) were dried in an oven overnight and cooled under a stream of nitrogen prior to use. All commercial reagents were used directly without further purification. The progress of the reaction was monitored on thin layer chromatographic (TLC) plates (Merck 5554 Kiesel gel 60 F254), and the spots were visualized under 254 nm ultraviolet light or by charring after dipping the TLC plate into a *p*-anisaldehyde solution (5.6 mL of *p*-anisaldehyde, 2.3 mL of acetic acid, and 3.0 mL of concentrated sulfuric acid in 200 mL of ethanol). Column chromatography was performed on silica gel (Merck 9385 Kiesel gel 60) using hexanes:EtOAc (v/v).

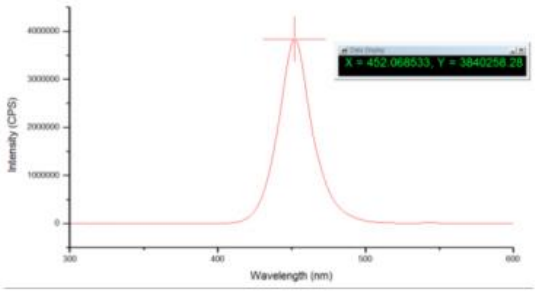
Analysis was done by using Bruker 300-500 MHz spectrometer, Shimadzu (IR Affinity-1S), Varian Carry 100 and Horiba Fluoromax-4P spectrophotometer at total-period analysis center for Ulsan chemical industry of Korea Basic Science Institute (KBSI). Infrared spectra were recorded on a Shimadzu (affinity-1S). High-resolution mass spectra (EI) were obtained on a Jeol JMS 700 HRMS at the Korea Basic Science Center (KBSI), Daegu, Korea. Accurate masses are reported for the molecular ion $[M^+]$ or $[M+H]^+$. ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded using a Bruker 300 or 400 MHz spectrometer. The chemical shift values are reported as parts per million relatives to tetramethylsilane as an internal standard unless otherwise indicated and coupling constants in Hertz. The following abbreviations are used: m (multiplet), s (singlet), brs (broad singlet), d (doublet), t (triplet), q (quartet), p (quintet), dd (doublet of doublets), dtdd (doublet of triplet of doublet of doublet), etc. The absorption spectra of the photocatalysts and the emission spectra of the visible-light sources were measured on a Varian Carry 100, Horiba Fluoromax-4P spectrophotometer. Cyclic voltammograms were recorded on a CH Instrument (CHI600E). A Vapourtec E-Series Integrated Flow chemistry system (Vapourtec Ltd., part #50-1307) and a UV-150 photochemical reactor (Vapourtec Ltd., part #50-1453) were used.

II. Reaction Setup

A. Batch reaction setup

Irradiation of photochemical reactions was carried out using two MR16 5 W blue LED spotlight lamp for milligram scale reaction (manufactured in China, commercially available in AliExpress). The picture utilized spotlight lamp and their description are given below:

MR16 5W blue LED spotlight lamp



Emission spectrum of 5W blue LED

	Specification
Power	5 W
Voltage	12 V
Wavelength	452 nm

Figure S1A. Description for 5 W blue LED spotlight lamp

For milligram scale reactions, two MR16 10 W blue LEDs spotlight lamps are positioned 3 cm away from the reaction vial using a customized reactor that was made by acrylic plate.

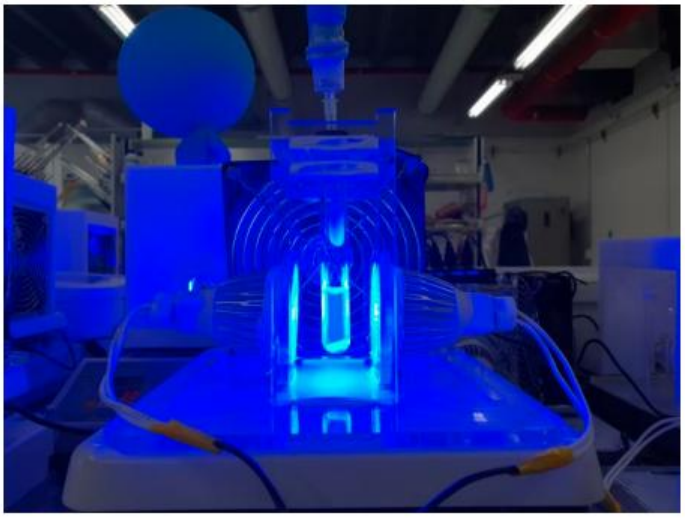


Figure S2. Milligram scale reaction set up

In the optimized reaction conditions, the reaction is not significantly affected by temperature. The fan was used or not used according to the external temperature to maintain 20 ~ 30 ºC in the reactor.

B. Flow Reaction Setup

A 450 nm light source (Vapourtec Ltd., part #50-1448) was employed. The blue LED lamps were positioned 1 cm away from the reactor without the use of filters. Temperature monitoring was conducted using an external surface sensor. Additionally, an organometallic chemistry kit (part # 50-1311) was employed. Oxygen gas injection was facilitated through a mass flow controller (Sierra SmartTrak 100).

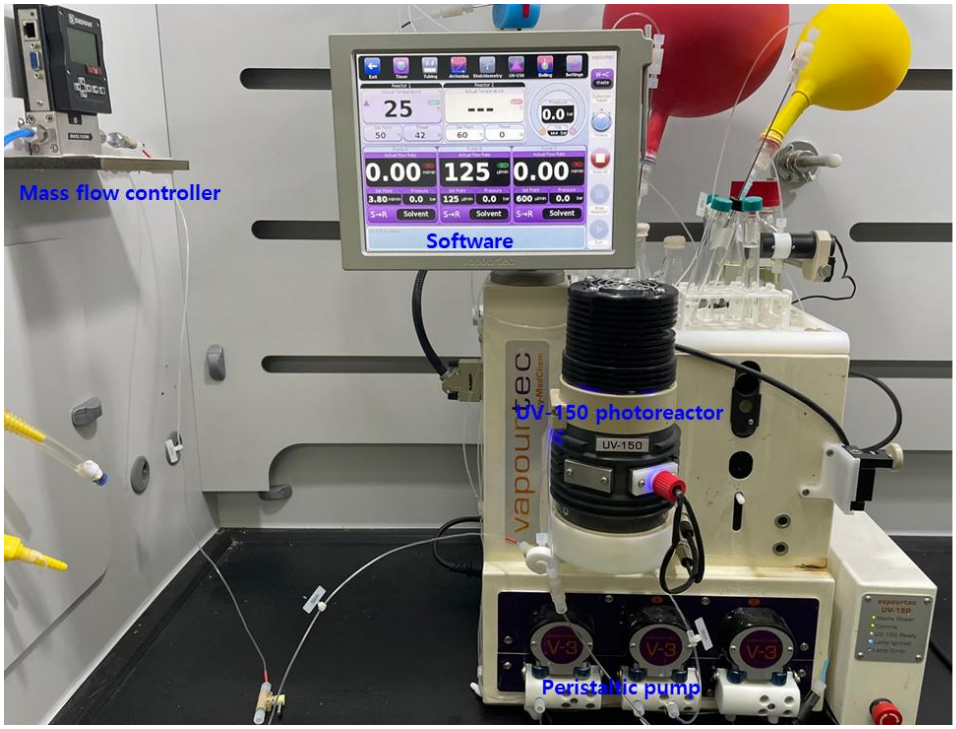
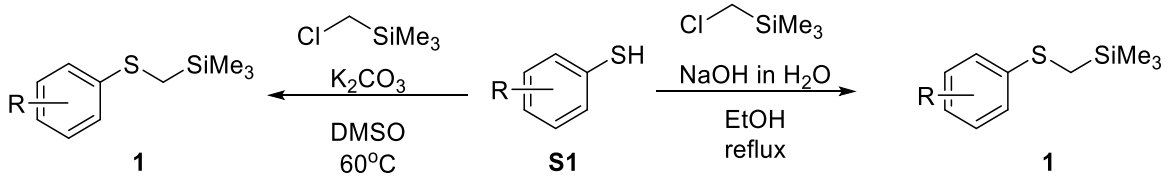


Figure S3. Picture of the overall setup for flow process using Vapourtec system.

III. Preparation and characterization data of starting materials

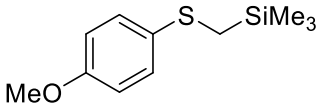
A. General procedure for preparation of α-silyl thioethers 1



All the following α-silyl thioether derivatives **1** had been prepared by following reported protocol[1]. Among these, synthesized α-silyl thioether derivatives **1** compound data were matched to previously reported paper.[1-3]

B. Characterization of α-silyl thioethers

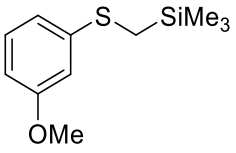
(((4-Methoxyphenyl)thio)methyl)trimethylsilane **(1a)**[1b]



1a

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.31 – 7.24 (m, 2H), 6.88 – 6.79 (m, 2H), 3.79 (s, 3H), 2.18 (s, 2H), 0.15 (s, 9H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 157.9, 130.9, 129.2, 114.6, 55.5, 20.5, -1.5.

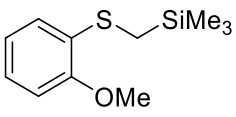
(((3-Methoxyphenyl)thio)methyl)trimethylsilane **(1b)**[3]



1b

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.19 (t, *J* = 8.0 Hz, 1H), 6.93 – 6.83 (m, 2H), 6.66 (ddd, *J* = 8.1, 2.5, 0.9 Hz, 1H), 3.80 (s, 3H), 2.20 (s, 2H), 0.19 (s, 9H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 159.9, 141.9, 129.6, 118.3, 111.4, 110.3, 55.3, 18.1, -1.5.

(((2-Methoxyphenyl)thio)methyl)trimethylsilane **(1c)**

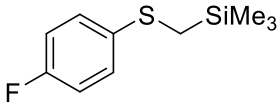


1c

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.23 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.12 (ddd, *J* = 8.0, 7.4, 1.6 Hz, 1H), 6.96 (td, *J* = 7.5, 1.3 Hz, 1H), 6.82 (dd, *J* = 8.1, 1.3 Hz, 1H), 3.90 (s, 3H), 2.06 (s,

2H), 0.19 (s, 9H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 155.9, 128.8, 125.4, 125.2, 121.3, 109.9, 55.9, 16.4, -1.4.; HRMS m/z (EI): calcd. For C_{11} (M^+) 226.0848, found 226.0849.

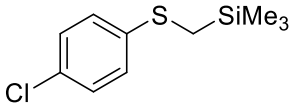
(((4-Fluorophenyl)thio)methyl)trimethylsilane **(1d)**[1b]



1d

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.32 – 7.21 (m, 2H), 7.05 – 6.91 (m, 2H), 2.18 (s, 2H), 0.17 (s, 9H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 162.6, 159.3, 135.4, 135.4, 128.4, 128.3, 116.0, 115.7, 19.6, -1.5.

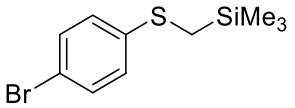
(((4-Chlorophenyl)thio)methyl)trimethylsilane **(1e)**[2b]



1e

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.26 – 7.17 (m, 4H), 2.15 (s, 2H), 0.17 (s, 9H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 139.13, 130.46, 128.84, 127.33, 18.59, -1.49.

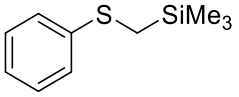
(((4-Bromophenyl)thio)methyl)trimethylsilane **(1f)**



1f

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.40 – 7.34 (m, 2H), 7.17 – 7.10 (m, 2H), 2.15 (s, 2H), 0.17 (s, 9H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 139.8, 131.7, 127.6, 118.2, 18.4, -1.5.; HRMS m/z (EI): calcd. For C_{10} (M^+) 275.9826, found 275.9830.

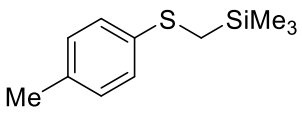
Trimethyl((phenylthio)methyl)silane **(1g)**[3]



1g

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.37 – 7.24 (m, 4H), 7.13 (ddt, *J* = 8.4, 6.2, 2.1 Hz, 1H), 2.21 (s, 2H), 0.20 (s, 9H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 140.4, 128.8, 126.1, 124.7, 18.2, -1.5.

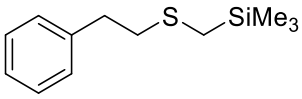
***Trimethyl((p-tolylthio)methyl)silane* (1h)**[3]



1h

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.25 – 7.19 (m, 2H), 7.14 – 7.08 (m, 2H), 2.33 (s, 3H), 2.20 (s, 2H), 0.19 (s, 9H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 136.8, 134.6, 129.6, 126.6, 21.0, 18.9, -1.5.

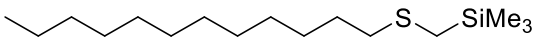
***Trimethyl((phenethylthio)methyl)silane* (1i)**[3]



1i

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.36 – 7.27 (m, 2H), 7.21 (ddt, *J* = 6.8, 3.0, 1.3 Hz, 3H), 2.97 – 2.85 (m, 2H), 2.83 – 2.69 (m, 2H), 1.83 (s, 2H), 0.11 (s, 9H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 141.0, 128.6, 128.6, 126.3, 37.9, 36.0, 18.7, -1.5.

((dodecylthio)methyl)trimethylsilane (1j)

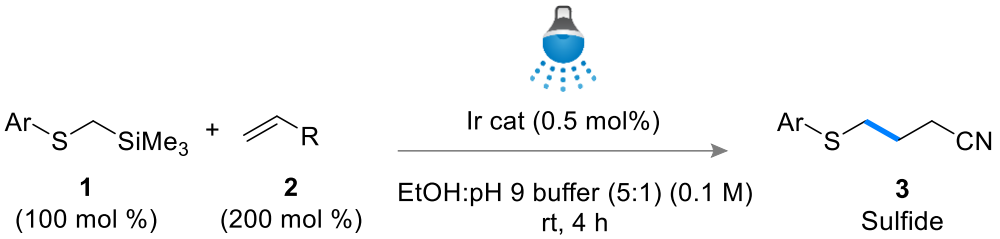


1j

^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.50 (t, *J* = 7.2 Hz, 2H), 1.76 (s, 2H), 1.58 (p, *J* = 7.2 Hz, 2H), 1.40 – 1.19 (m, 18H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.09 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 32.07, 29.81, 29.79, 29.76, 29.69, 29.50, 29.46, 29.03, 22.84, 14.27, -1.53.

IV. General Procedure and characterization data for Sulfides

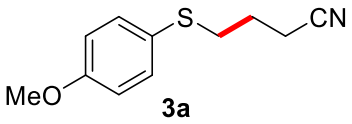
A. General procedure for Sulfides 3



To a re-sealable pressure tube (13 x 100 mm) with a tiny magnetic stir bar was charged with silane **1** (0.2 mmol, 1.0 equiv), alkene **2** (0.4 mmol, 2.0 equiv) and $[Ir(dF(CF_3)ppy)_2(dtbpy)]PF_6$ (1.2 mg, 0.010 mmol, 0.5 mol%) under argon atmosphere. Then, a mixture of degassed solvents (2 mL, 0.1 M for **1**) of EtOH:pH 9 buffer in a ratio of 5:1 was added to that pressure tube. The resultant light greenish-yellow mixture was irradiated with 2 x 5 W blue LEDs under constant stirring condition at room temperature for 4 h. After finishing the stipulated time, the solvent was removed under reduced pressure and residue was purified by flash column chromatography on silica gel to afford the corresponding sulfide product **3**.

B. Characterization data

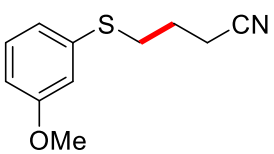
4-((4-Methoxyphenyl)thio)butanenitrile **(3a)**[4]



3a

Following the general procedures, **3a** was obtained as a colourless liquid in the yield of 92% (38.1 mg). R_f = 0.20 (Hexane:Ethyl acetate, 5:1); ^{1}H NMR (300 MHz, Chloroform-d) δ 7.42 – 7.29 (m, 2H), 6.93 – 6.79 (m, 2H), 3.80 (s, 3H), 2.91 (t, *J* = 6.8 Hz, 2H), 2.50 (t, *J* = 7.1 Hz, 2H), 1.88 (p, *J* = 7.0 Hz, 2H); ^{13}C NMR (75 MHz, Chloroform-d) δ 159.5, 134.1, 124.8, 119.3, 114.9, 55.5, 34.7, 24.9, 15.9.

4-((3-Methoxyphenyl)thio)butanenitrile **(3b)**

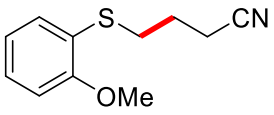


3b

Following the general procedures, **3b** was obtained as a colourless liquid in the yield of 95%

(39.4 mg). R_f = 0.20 (Hexane:Ethyl acetate, 5:1); ^{1}H NMR (300 MHz, Chloroform-d) δ 7.22 (t, *J* = 8.0 Hz, 1H), 6.97 – 6.85 (m, 2H), 6.76 (ddd, *J* = 8.3, 2.5, 0.9 Hz, 1H), 3.80 (s, 3H), 3.04 (t, *J* = 6.8 Hz, 2H), 2.52 (t, *J* = 7.1 Hz, 2H), 1.97 (tt, *J* = 7.1 Hz, 6.8Hz, 2H).; ^{13}C NMR (75 MHz, Chloroform-d) δ 160.0, 136.1, 130.0, 121.9, 119.1, 115.3, 112.3, 55.4, 32.3, 24.9, 16.0; HRMS m/z (EI): calcd. For C_{11} (M^+) 207.0718, found 207.0720.

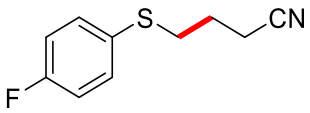
4-((2-Methoxyphenyl)thio)butanenitrile **(3c)**



3c

Following the general procedures, **3c** was obtained as a colourless liquid in the yield of 94% (39.0 mg). R_f = 0.20 (Hexane:Ethyl acetate, 5:1); ^{1}H NMR (300 MHz, Chloroform-d) δ 7.32 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.25 (ddd, *J* = 8.2, 7.5, 1.7 Hz, 1H), 6.97 – 6.84 (m, 2H), 3.90 (s, 3H), 3.01 (t, *J* = 6.8 Hz, 2H), 2.54 (t, *J* = 7.1 Hz, 2H), 1.92 (tt, *J* = 7.1, 6.8 Hz, 2H).; ^{13}C NMR (75 MHz, Chloroform-d) δ 158.3, 131.7, 128.6, 122.4, 121.2, 119.4, 110.9, 55.9, 31.3, 25.0, 16.1; HRMS m/z (EI): calcd. For C_{11} (M^+) 207.0718, found 207.0719.

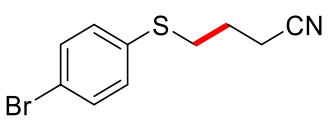
4-((4-Fluorophenyl)thio)butanenitrile **(3d)**[5]



3d

Following the general procedures, **3d** was obtained as a colourless liquid in the yield of 95% (37.1 mg). R_f = 0.20 (Hexane:Ethyl acetate, 5:1); ^{1}H NMR (300 MHz, Chloroform-d) δ 7.43 – 7.31 (m, 2H), 7.08 – 6.95 (m, 2H), 2.98 (t, *J* = 6.9 Hz, 2H), 2.51 (t, *J* = 7.0 Hz, 2H), 1.92 (tt, *J* = 6.9 Hz, 7.0Hz 2H).; ^{13}C NMR (75 MHz, Chloroform-d) δ 133.4, 133.3, 129.7, 119.1, 116.6, 116.3, 34.0, 29.8, 24.9, 16.0; ^{19}F NMR (376 MHz, Chloroform-d) δ -114.29.

4-((4-Bromophenyl)thio)butanenitrile **(3e)**[7]

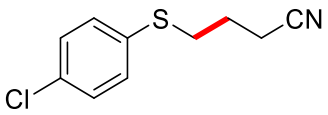


3e

Following the general procedures, **3e** was obtained as a colourless liquid in the yield of 75%

(38.4 mg). R_f = 0.25 (Hexane:Ethyl acetate, 5:1); ^{1}H NMR (300 MHz, Chloroform-d) δ 7.48 – 7.38 (m, 2H), 7.25 – 7.19 (m, 2H), 3.02 (t, *J* = 6.9 Hz, 2H), 2.51 (t, *J* = 7.0 Hz, 2H), 1.95 (tt, *J* = 7.0 , 6.9 Hz, 2H); ^{13}C NMR (75 MHz, Chloroform-d) δ 134.1, 132.4, 131.7, 120.8, 119.0, 32.7, 24.8, 16.1.

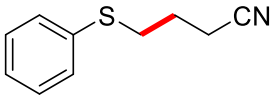
4-((4-Chlorophenyl)thio)butanenitrile **(3f)**[6]



3f

Following the general procedures, **3f** was obtained as a colourless liquid in the yield of 88% (37.3 mg). R_f = 0.30 (Hexane:Ethyl acetate, 5:1); ^{1}H NMR (300 MHz, Chloroform-d) δ 7.29 (s, 4H), 3.02 (t, *J* = 6.9 Hz, 2H), 2.51 (t, *J* = 7.0 Hz, 2H), 1.95 (tt, *J* = 7.0 Hz, 6.9 Hz, 2H); ^{13}C NMR (75 MHz, Chloroform-d) δ 133.4, 133.0, 131.5, 129.4, 119.0, 32.9, 24.8, 16.0.

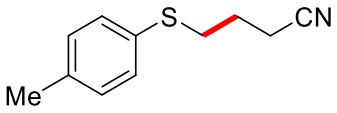
4-(Phenylthio)butanenitrile **(3g)**[4]



3g

Following the general procedures, **3g** was obtained as a colourless liquid in the yield of 90% (31.9 mg). R_f = 0.50 (Hexane:Ethyl acetate, 3:2); ^{1}H NMR (300 MHz, Chloroform-d) δ 7.39 – 7.27 (m, 4H), 7.25 – 7.19 (m, 1H), 3.04 (t, *J* = 6.8 Hz, 2H), 2.52 (t, *J* = 7.1 Hz, 2H), 1.96 (tt, *J* = 7.1, 6.8 Hz, 2H); ^{13}C NMR (75 MHz, Chloroform-d) δ 134.8, 130.3, 129.3, 126.9, 119.2, 32.7, 24.9, 16.0

4-(p-Tolylthio)butanenitrile **(3h)**[6]

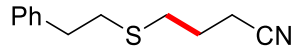


3h

Following the general procedures, **3h** was obtained as a colourless liquid in the yield of 85% (32.5 mg). R_f = 0.25 (Hexane:Ethyl acetate, 5:1); ^{1}H NMR (300 MHz, Chloroform-d) δ 7.40 – 7.23 (m, 2H), 7.17 – 7.06 (m, 2H), 2.98 (t, *J* = 6.8 Hz, 2H), 2.50 (t, *J* = 7.1 Hz, 2H), 2.33 (s,

3H), 1.92 (tt, J = 7.1, 6.8 Hz, 2H); ^{13}C NMR (75 MHz, Chloroform-d) δ 137.2, 131.1, 130.9, 130.1, 119.2, 33.4, 29.8, 24.9, 21.2, 16.0.

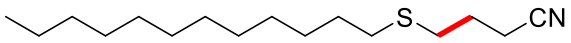
4-(Phenethylthio)butanenitrile **(3i)**[4]



3i

Following the modified general procedures (using 1 mol% of PC, methanol (0.1 M) in 16 h), **3i** was obtained as a colourless liquid in the yield of 52% (21.3 mg). R_f = 0.20 (Hexane:Ethyl acetate, 4:1); ^{1}H NMR (300 MHz, Chloroform-d) δ 7.37 – 7.27 (m, 2H), 7.26 – 7.17 (m, 3H), 2.94 – 2.84 (m, 2H), 2.82 – 2.74 (m, 2H), 2.65 (t, J = 6.9 Hz, 2H), 2.48 (t, J = 7.1 Hz, 2H), 1.92 (tt, J = 7.1, 6.9 Hz, 2H); ^{13}C NMR (75 MHz, Chloroform-d) δ 140.3, 128.7, 128.6, 126.6, 119.3, 36.3, 33.8, 30.9, 25.3, 16.1.

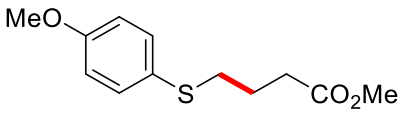
4-(dodecylthio)butanenitrile **(3j)**



3j

Following the modified general procedures (using 2 mol% of PC, methanol (0.1 M) in 32 h), **3j** was obtained as a light-yellow liquid in the yield of 60% (32.1 mg). R_f = 0.5 (Hexane:Ethyl acetate, 5:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.64 (t, J = 6.9 Hz, 2H), 2.54 – 2.46 (m, 4H), 1.93 (p, J = 7.0 Hz, 2H), 1.57 (p, J = 7.2 Hz, 2H), 1.40 – 1.20 (m, 20H), 0.87 (t, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 119.37, 32.26, 32.05, 30.75, 29.78, 29.76, 29.72, 29.65, 29.48, 29.35, 29.00, 25.37, 22.82, 16.15, 14.26.

Methyl 4-((4-methoxyphenyl)thio)butanoate **(3k)**[8]

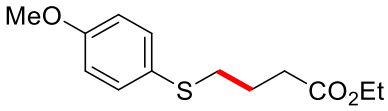


3k

Following the general procedures, **3k** was obtained as a colourless liquid in the yield of 72% (34.6 mg). R_f = 0.80 (Hexane:Ethyl acetate, 3:2); ^{1}H NMR (300 MHz, Chloroform-d) δ 7.42 – 7.29 (m, 2H), 6.90 – 6.79 (m, 2H), 3.79 (s, 3H), 3.66 (s, 3H), 2.85 (t, J = 7.1 Hz, 2H), 2.45 (t,

J = 7.3 Hz, 2H), 1.88 (tt, J = 7.2 Hz, 2H); ^{13}C NMR (75 MHz, Chloroform-d) δ 173.53, 159.00, 133.42, 125.92, 114.60, 55.35, 51.63, 35.14, 32.55, 24.41.

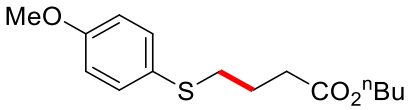
Ethyl 4-((4-methoxyphenyl)thio)butanoate **(3l)**[9]



3l

Following the general procedures, **3l** was obtained as a colourless liquid in the yield of 64% (32.5 mg). R_f = 0.70 (Hexane:Ethyl acetate, 3:2); ^{1}H NMR (300 MHz,) δ 7.34 (d, J = 8.8 Hz, 2H), 6.83 (d, J = 8.7 Hz, 2H), 4.11 (q, J = 7.1 Hz, 2H), 3.78 (s, 3H), 2.84 (t, J = 7.1 Hz, 2H), 2.43 (t, J = 7.3 Hz, 2H), 1.88 (p, J = 7.2 Hz, 2H), 1.24 (t, J = 7.1 Hz, 3H).; ^{13}C NMR (75 MHz, Chloroform-d) δ 173.07, 158.98, 133.38, 126.00, 114.59, 60.39, 55.33, 35.15, 32.84, 24.48, 14.23.

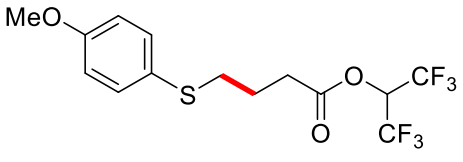
Butyl 4-((4-methoxyphenyl)thio)butanoate **(3m)**



3m

Following the general procedures, **3m** was obtained as a colourless liquid in the yield of 81% (45.7 mg). R_f = 0.70 (Hexane:Ethyl acetate, 3:2); ^{1}H NMR (300 MHz, Chloroform-d) δ 7.41 – 7.29 (m, 2H), 6.89 – 6.78 (m, 2H), 4.05 (t, J = 6.7 Hz, 2H), 3.78 (s, 3H), 2.84 (t, J = 7.1 Hz, 2H), 2.43 (t, J = 7.3 Hz, 2H), 1.87 (p, J = 7.2 Hz, 2H), 1.66 – 1.51 (m, 2H), 1.45 – 1.26 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, Chloroform-d) δ 173.25, 159.08, 133.51, 126.08, 114.68, 64.42, 55.42, 35.27, 32.95, 30.75, 24.60, 19.24, 13.82; HRMS m/z (EI): calcd. For C_{15} (M^+) 282.1290, found 282.1292.

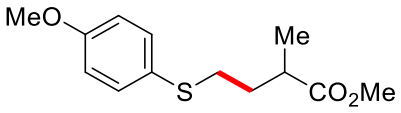
1,1,1,3,3,3-hexafluoropropan-2-yl 4-((4-methoxyphenyl)thio)butanoate **(3n)**



3n

Following the general procedures, **3n** was obtained as a light-yellow liquid in the yield of 70% (52.5 mg). R_f = 0.50 (Hexane:Ethyl acetate, 5:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.31 (m, 2H), 6.89 – 6.82 (m, 2H), 5.76 (hept, J_{HF} = 6.1 Hz, 1H), 3.80 (s, 3H), 2.85 (t, *J* = 7.0 Hz, 2H), 2.67 (t, *J* = 7.3 Hz, 2H), 1.94 (p, *J* = 7.1 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.99, 159.40, 133.93, 125.42, 121.91, 119.10, 114.83, 67.23, 66.89, 66.54, 66.20, 65.85, 55.46, 35.01, 31.81, 24.07; ^{19}F NMR (377 MHz, Chloroform-*d*) δ -73.33 (d, *J* = 6.1 Hz).

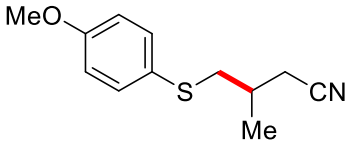
Methyl 4-((4-methoxyphenyl)thio)-2-methylbutanoate **(3o)**



3o

Following the general procedures, **3o** was obtained as a colourless liquid in the yield of 77% (39.2 mg). R_f = 0.20 (Hexane:Ethyl acetate, 5:1); ^{1}H NMR (300 MHz, Chloroform-d) δ 7.39 – 7.28 (m, 2H), 6.90 – 6.79 (m, 2H), 3.80 (s, 3H), 3.66 (s, 3H), 2.91 – 2.72 (m, 2H), 2.62 (ddd, *J* = 14.0, 7.0 Hz, 1H), 1.95 (dtd, *J* = 13.8, 8.0, 6.8 Hz, 1H), 1.74 – 1.58 (m, 1H), 1.15 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, Chloroform-d) δ 176.7, 159.1, 133.4, 126.2, 114.7, 55.5, 51.8, 38.4, 33.6, 33.2, 17.1; HRMS *m/z* (EI): calcd. For $C_{13}H_{18}O_3S$ (M^+) 254.0977, found 254.0973.

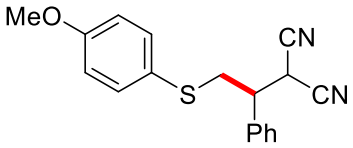
4-((4-Methoxyphenyl)thio)-3-methylbutanenitrile **(3p)**



3p

Following the general procedures, **3p** was obtained as a colourless liquid in the yield of 55% (24.3 mg). R_f = 0.25 (Hexane:Ethyl acetate, 5:1) ^{1}H NMR (300 MHz, Chloroform-d) δ 7.41 – 7.30 (m, 2H), 6.92 – 6.79 (m, 2H), 3.80 (s, 3H), 2.87 (dd, *J* = 13.6, 5.9 Hz, 1H), 2.77 (dd, *J* = 13.6, 5.8 Hz, 1H), 2.55 (dd, *J* = 16.7, 5.2 Hz, 1H), 2.42 (dd, *J* = 16.7, 6.9 Hz, 1H), 2.08 – 1.91 (m, 1H), 1.16 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, Chloroform-d) δ 159.44, 133.83, 125.45, 118.46, 114.94, 55.49, 41.98, 30.59, 23.18, 19.25; HRMS m/z (EI): calcd. For C_{12} (M^+) 221.0876, found 221.0874.

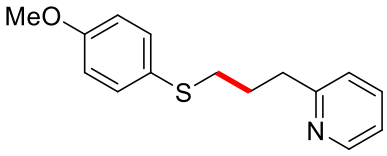
2-(2-((4-Methoxyphenyl)thio)-1-phenylethyl)malononitrile **(3q)**



3q

Following the modified general procedures (using 1 mol% of PC, methanol (0.1 M) in 16 h), **3q** was obtained as a colourless liquid in the yield of 95% (58.6 mg). R_f = 0.30 (Hexane:Ethyl acetate, 5:1).; ^{1}H NMR (300 MHz, Chloroform-d) δ 7.44 – 7.28 (m, 7H), 6.94 – 6.85 (m, 2H), 4.63 (d, *J* = 4.5 Hz, 1H), 3.83 (s, 3H), 3.42 – 3.17 (m, 3H); ^{13}C NMR (75 MHz, Chloroform-d) δ 160.1, 135.6, 134.4, 129.4, 129.4, 128.1, 123.2, 115.3, 112.1, 111.3, 55.5, 45.6, 38.3, 27.9; HRMS m/z (EI) : calcd. For $C_{18}H_{16}N_2OS$ (M^+) 308.0983, found 308.0985.

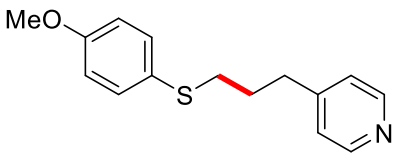
2-(3-((4-Methoxyphenyl)thio)propyl)pyridine **(3r)**



3r

Following the general procedures, **3r** was obtained as a colourless liquid in the yield of 87% (45.1 mg). R_f = 0.30 (Hexane:Ethyl acetate, 2:1); ^{1}H NMR (300 MHz, Chloroform-d) δ 8.51 (ddd, *J* = 4.9, 1.9, 1.0 Hz, 1H), 7.58 (td, *J* = 7.7, 1.9 Hz, 1H), 7.38 – 7.30 (m, 2H), 7.15 – 7.07 (m, 2H), 6.87 – 6.78 (m, 2H), 3.79 (s, 3H), 2.88 (dt, *J* = 14.3, 7.3 Hz, 4H), 2.09 – 1.95 (m, 2H); ^{13}C NMR (75 MHz, Chloroform-d) δ 161.3, 159.0, 149.4, 136.5, 133.3, 126.6, 123.1, 121.3, 114.7, 55.5, 37.1, 35.4, 29.3; HRMS m/z (EI) : calcd. For $C_{15}H_{17}NOS$ (M^+) 259.1031, found 259.1031.

4-(3-((4-Methoxyphenyl)thio)propyl)pyridine **(3s)**

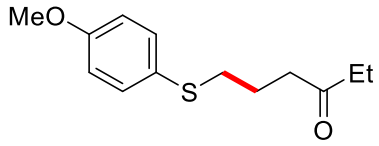


3s

Following the general procedures, **3s** was obtained as a colourless liquid in the yield of 92% (47.7 mg). R_f = 0.30 (Hexane:Ethyl acetate, 1:1); ^{1}H NMR (300 MHz, Chloroform-d) δ 8.54 –

8.46 (m, 2H), 7.41 – 7.30 (m, 2H), 7.14 – 7.06 (m, 2H), 6.92 – 6.81 (m, 2H), 3.82 (s, 3H), 2.79 (dt, J = 24.1, 7.5 Hz, 4H), 1.91 (dtd, J = 9.0, 7.5, 6.5 Hz, 2H); ^{13}C NMR (75 MHz, Chloroform-d) δ 159.05, 150.39, 149.78, 133.47, 125.93, 123.94, 114.63, 55.35, 35.09, 33.73, 29.61; HRMS m/z (EI) : calcd. For $C_{15}H_{17}NOS$ (M^+) 259.1031, found 259.1031.

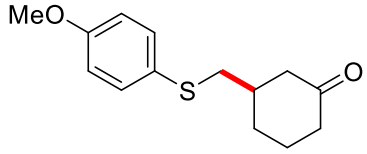
6-((4-Methoxyphenyl)thio)hexan-3-one **(3t)**



3t

Following the general procedures, **3t** was obtained as a colourless liquid in the yield of 85% (40.5 mg). R_f = 0.20 (Hexane:Ethyl acetate, 5:1); ^{1}H NMR (300 MHz, Chloroform-d) δ 7.39 – 7.27 (m, 2H), 6.89 – 6.78 (m, 2H), 3.79 (s, 3H), 2.82 (t, J = 7.0 Hz, 2H), 2.55 (t, J = 7.1 Hz, 2H), 2.40 (q, J = 7.3 Hz, 2H), 1.84 (tt, J = 7.1 Hz, 2H), 1.04 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, Chloroform-d) δ 211.05, 159.05, 133.34, 126.20, 114.72, 55.47, 40.66, 36.14, 35.34, 23.30, 7.95; HRMS m/z (EI): calcd. For C_{13} (M^+) 238.1028, found 238.1026.

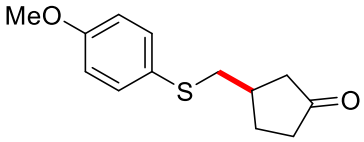
(((4-Methoxyphenyl)thio)methyl)cyclohexan-1-one **(3u)**



3u

Following the general procedures, **3u** was obtained as a colourless liquid in the yield of 82% (41.1 mg). R_f = 0.25 (Hexane:Ethyl acetate, 5:1); ^{1}H NMR (300 MHz, Chloroform-d) δ 7.39 – 7.29 (m, 2H), 6.89 – 6.76 (m, 2H), 3.79 (s, 3H), 2.90 – 2.72 (m, 2H), 2.61 – 2.48 (m, 1H), 2.41 – 2.18 (m, 2H), 2.20 (s, 2H), 2.18 – 1.87 (m, 4H), 1.69 – 1.56 (m, 1H), 1.53 – 1.33 (m, 1H). ^{13}C NMR (75 MHz, Chloroform-d) δ 211.03, 159.15, 133.49, 126.38, 114.80, 55.47, 47.31, 42.60, 41.41, 38.75, 30.56, 24.94.; HRMS m/z (EI): calcd. For C_{14} (M^+) 250.1028, found 250.1031.

3-(((4-Methoxyphenyl)thio)methyl)cyclopentan-1-one **(3v)**

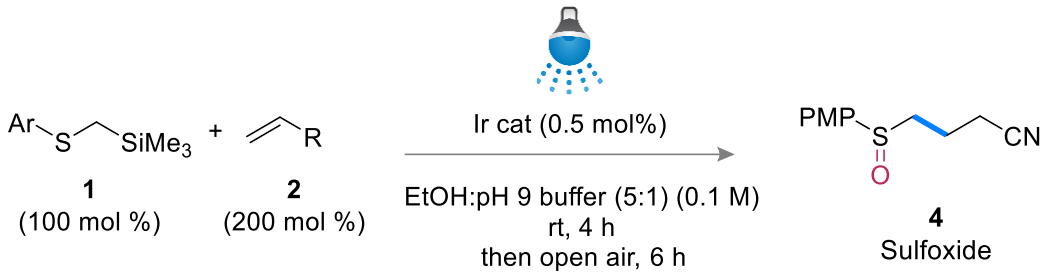


3v

Following the general procedures, **3v** was obtained as a colourless liquid in the yield of 82% (38.8 mg). R_f = 0.25 (Hexane:Ethyl acetate, 5:1); ^{1}H NMR (300 MHz, Chloroform-d) δ 7.42 – 7.31 (m, 2H), 6.91 – 6.79 (m, 2H), 3.80 (s, 3H), 3.01 – 2.83 (m, 2H), 2.52 – 2.06 (m, 5H), 2.06 – 1.88 (m, 1H), 1.77 – 1.60 (m, 1H). ^{13}C NMR (75 MHz, Chloroform-d) δ 218.61, 159.26, 133.65, 126.15, 114.82, 55.49, 44.61, 41.52, 38.46, 36.99, 28.90; HRMS m/z (EI): calcd. For C_{13} (M^+) 236.0871, found 236.0873.

V. General Procedure and characterization data for Sulfoxides

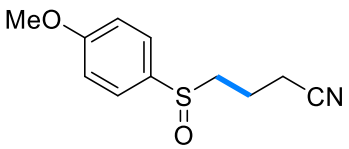
A. General procedures for Suloxides 4



To a re-sealable pressure tube (13 x 100 mm) with a tiny magnetic stir bar was charged with silane **1** (0.2 mmol, 1.0 equiv), alkene **2** (0.4 mmol, 2.0 equiv) and $[Ir(dF(CF_3)ppy)_2(dtbpy)]PF_6$ (1.2 mg, 0.010 mmol, 0.5 mol%) under argon atmosphere. Then, a mixture of degassed solvents (2 mL, 0.1 M for **1**) of EtOH:pH 9 buffer in a ratio of 5:1 was added to that pressure tube. The resultant light greenish-yellow mixture was irradiated with 2 x 5 W blue LEDs under constant stirring condition at room temperature for 4 h. After 4 h, open the cap of the tube and send 6 h reaction in Air (open cap) condition. After finishing the stipulated time, the solvent was removed under reduced pressure and residue was purified by flash column chromatography on silica gel to afford the corresponding sulfoxide product **4**.

B. Characterization data

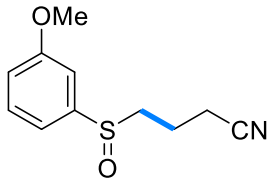
4-((4-methoxyphenyl)sulfinyl)butanenitrile **(4a)**[10]



4a

Following the general procedures, **4a** was obtained as a colourless liquid in the yield of 95% (42.4 mg). R_f = 0.20 (Hexane:Ethyl acetate, 1:4); ^{1}H NMR (400 MHz, Chloroform-d) δ 7.58 – 7.49 (m, 2H), 7.07 – 7.00 (m, 2H), 3.85 (s, 3H), 2.92 (ddd, *J* = 13.4, 8.8, 6.7 Hz, 1H), 2.83 (ddd, J = 13.6, 8.7, 5.7 Hz, 1H), 2.60 – 2.50 (m, 1H), 2.53 – 2.42 (m, 1H), 2.13 (ddq, *J* = 13.6, 8.6, 6.8 Hz, 1H), 2.05 – 1.91 (m, 1H); ^{13}C NMR (101 MHz, Chloroform-d) δ 162.27, 133.42, 125.88, 118.50, 115.05, 55.61, 54.75, 18.59, 16.54.

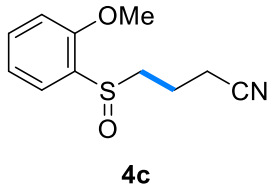
4-((3-methoxyphenyl)sulfinyl)butanenitrile **(4b)**



4b

Following the general procedures, **4b** was obtained as a colourless liquid in the yield of 74% (33.0 mg). R_f = 0.20 (Hexane:Ethyl acetate, 1:3); ^{1}H NMR (300 MHz, Chloroform-d) δ 7.44 (t, *J* = 8.0 Hz, 1H), 7.21 (dd, *J* = 2.6, 1.6 Hz, 1H), 7.11 (ddd, *J* = 7.7, 1.6, 0.9 Hz, 1H), 7.04 (ddd, *J* = 8.2, 2.6, 0.9 Hz, 1H), 3.88 (s, 3H), 3.00 (ddd, *J* = 13.4, 8.9, 6.6 Hz, 1H), 2.85 (ddd, *J* = 13.4, 8.7, 5.7 Hz, 1H), 2.66 – 2.42 (m, 2H), 2.29 – 2.09 (m, 1H), 2.09 – 1.89 (m, 1H). ^{13}C NMR (75 MHz, Chloroform-d) δ 160.63, 144.31, 130.54, 118.54, 117.70, 115.89, 108.48, 55.70, 54.60, 18.48, 16.60; HRMS m/z (EI): calcd. For C_{11} (M^+) 223.0667, found 223.0665.

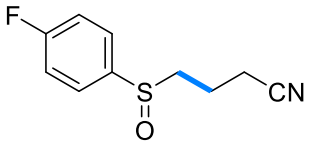
4-((2-methoxyphenyl)sulfinyl)butanenitrile **(4c)**



4c

Following the general procedures, **4c** was obtained as a colourless liquid in the yield of 92% (41.1 mg). R_f = 0.20 (Hexane:Ethyl acetate, 1:3); ^{1}H NMR (300 MHz, Chloroform-d) δ 7.74 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.4 (ddd, *J* = 8.2, 7.4, 1.7 Hz, 1H), 7.18 (ddd, *J* = 7.7, 7.4, 0.9 Hz, 1H), 6.93 (dd, *J* = 8.2, 0.9 Hz, 1H), 3.89 (s, 3H), 3.19 (ddd, *J* = 13.6, 8.3, 7.0 Hz, 1H), 2.91 (ddd, *J* = 13.6, 8.3, 5.7 Hz, 1H), 2.61 – 2.40 (m, 2H), 2.20 (m, 1H), 2.03 – 1.83 (m, 1H); ^{13}C NMR (75 MHz, Chloroform-d) δ 154.88, 132.39, 129.76, 125.45, 121.68, 118.67, 110.77, 55.82, 50.76, 18.33, 16.56; HRMS m/z (EI): calcd. For C_{11} (M^+) 223.0667, found 223.0664.

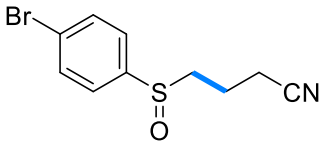
4-((4-fluorophenyl)sulfinyl)butanenitrile **(4d)**



4d

Following the general procedures, **4d** was obtained as a colourless liquid in the yield of 76% (32.1 mg). R_f = 0.20 (Hexane:Ethyl acetate, 1:1); ^{1}H NMR (400 MHz, Chloroform-d) δ 7.69 – 7.60 (m, 2H), 7.33 – 7.21 (m, 2H), 2.99 (ddd, *J* = 13.5, 8.9, 6.6 Hz, 1H), 2.85 (ddd, *J* = 13.5, 8.8, 5.6 Hz, 1H), 2.67 – 2.56 (m, 1H), 2.59 – 2.49 (m, 1H), 2.29 – 2.14 (m, 1H), 2.10 – 1.94 (m, 1H); ^{13}C NMR (101 MHz, Chloroform-d) δ 165.77, 163.26, 138.27, 138.24, 126.28, 126.19, 118.38, 117.03, 116.80, 54.82, 54.80, 18.47, 16.53. ^{19}F NMR (376 MHz, Chloroform-d) δ -107.84; HRMS m/z (EI): calcd. For C_{10} (M^+) 211.0467, found 211.0468.

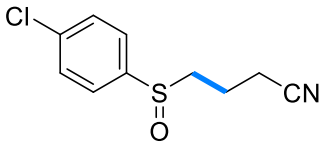
4-((4-bromophenyl)sulfinyl)butanenitrile **(4e)**



4e

Following the general procedures, **4e** was obtained as a colourless liquid in the yield of 71% (38.6 mg). R_f = 0.30 (Hexane:Ethyl acetate, 1:2); ^{1}H NMR (300 MHz, Chloroform-d) δ 7.73 – 7.66 (m, 2H), 7.52 – 7.45 (m, 2H), 2.99 (ddd, *J* = 13.6, 8.8, 6.6 Hz, 1H), 2.82 (ddd, *J* = 13.6, 8.8, 5.6 Hz, 1H), 2.65 – 2.45 (m, 2H), 2.27 – 2.11 (m, 1H), 1.99 (m, 1H); ^{13}C NMR (75 MHz, Chloroform-d) δ 142.09, 132.84, 126.01, 125.60, 118.43, 54.65, 18.47, 16.64; HRMS m/z (EI): calcd. For C_{10} (M^+) 272.9646, found 272.9644.

4-((4-chlorophenyl)sulfinyl)butanenitrile **(4f)**

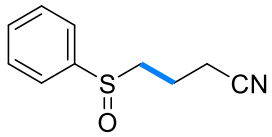


4f

Following the general procedures, **4f** was obtained as a colourless liquid in the yield of 86% (39.2 mg). R_f = 0.35 (Hexane:Ethyl acetate, 1:2); ^{1}H NMR (300 MHz, Chloroform-d) δ 7.63 –

7.43 (m, 4H), 2.98 (ddd, J = 13.5, 8.9, 6.6 Hz, 1H), 2.82 (ddd, J = 13.6, 8.7, 5.6 Hz, 1H), 2.54 (m, 2H), 2.27 – 2.11 (m, 1H), 1.98 (m, 1H); ^{13}C NMR (75 MHz, Chloroform-d) δ 141.44, 137.74, 129.89, 125.41, 118.43, 54.68, 18.46, 16.61; HRMS m/z (EI): calcd. For C_{10} (M^+) 227.0172, found 227.0169.

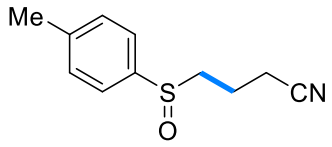
4-(phenylsulfinyl)butanenitrile **(4g)**[11]



4g

Following the general procedures, **4g** was obtained as a colourless liquid in the yield of 80% (30.9 mg). R_f = 0.30 (Hexane:Ethyl acetate, 1:2); ^{1}H NMR (300 MHz, Chloroform-d) δ 7.72 – 7.46 (m, 5H), 2.99 (ddd, J = 13.4, 8.8, 6.6 Hz, 1H), 2.84 (ddd, J = 13.4, 8.7, 5.7 Hz, 1H), 2.65 – 2.41 (m, 2H), 2.29 – 2.09 (m, 1H), 2.08 – 1.94 (m, 1H); ^{13}C NMR (75 MHz, Chloroform-d) δ 142.90, 131.48, 129.59, 123.97, 118.54, 54.64, 18.51, 16.64.

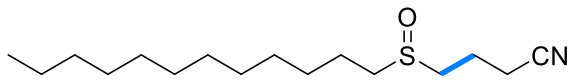
4-(p-tolylsulfinyl)butanenitrile **(4h)**



4h

Following the general procedures, **4h** was obtained as a colourless liquid in the yield of 88% (36.5 mg). R_f = 0.20 (Hexane:Ethyl acetate, 1:2); ^{1}H NMR (300 MHz, Chloroform-d) δ 7.53 – 7.44 (m, 2H), 7.41 – 7.28 (m, 2H), 2.95 (ddd, J = 13.4, 8.8, 6.7 Hz, 1H), 2.81 (ddd, J = 13.4, 8.8, 5.7 Hz, 1H), 2.62 – 2.42 (m, 2H), 2.41 (s, 3H), 2.25 – 2.05 (m, 1H), 2.05 – 1.89 (m, 1H); ^{13}C NMR (75 MHz, Chloroform-d) δ 141.99, 139.58, 130.23, 123.97, 118.56, 54.64, 21.49, 18.48, 16.59; HRMS m/z (EI): calcd. For C_{11} (M^+) 207.0718, found 207.0714.

4-(dodecylsulfinyl)butanenitrile **(4j)**

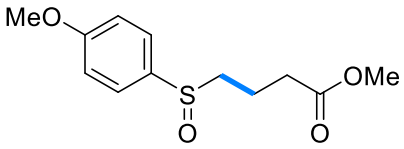


4j

Following the modified general procedures (using 2 mol% of PC, methanol (0.1 M) in 32 h),

4j was obtained as a white solid in the yield of 56% (31.9 mg). R_f = 0.2 (Hexane:Ethyl acetate, 1:3); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.87 – 2.53 (m, 6H), 2.28 – 2.14 (m, 2H), 1.83 – 1.69 (m, 2H), 1.51 – 1.20 (m, 18H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 118.62, 53.09, 50.19, 29.71, 29.63, 29.44, 29.28, 28.92, 22.80, 22.67, 19.47, 16.71, 15.46, 14.24.

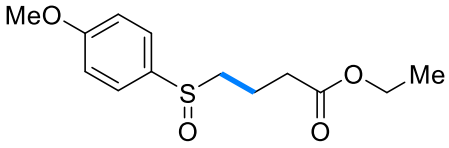
Methyl 4-((4-methoxyphenyl)sulfinyl)butanoate **(4k)**



4k

Following the general procedures, **4k** was obtained as a colourless liquid in the yield of 82% (42.0 mg). R_f = 0.20 (Hexane:Ethyl acetate, 1:2); ^{1}H NMR (400 MHz, Chloroform-d) δ 7.58 – 7.50 (m, 2H), 7.04 – 6.96 (m, 2H), 3.83 (s, 3H), 3.63 (s, 3H), 2.87 – 2.75 (m, 2H), 2.43 (td, *J* = 7.1, 1.5 Hz, 2H), 2.09 – 1.83 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-d) δ 172.82, 162.00, 134.24, 125.95, 114.81, 56.06, 55.52, 51.72, 32.53, 17.79; HRMS m/z (EI): calcd. For C_{12} (M^+) 256.0769, found 256.0771.

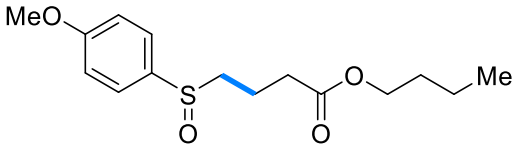
Ethyl 4-((4-methoxyphenyl)sulfinyl)butanoate **(4l)**[10]



4l

Following the general procedures, **4l** was obtained as a colourless liquid in the yield of 55% (29.7 mg). R_f = 0.20 (Hexane:Ethyl acetate, 1:2); ^{1}H NMR (400 MHz, Chloroform-d) δ 7.56 – 7.46 (m, 2H), 7.01 – 6.93 (m, 2H), 3.80 (s, 3H), 2.81 – 2.69 (m, 2H), 2.53 (t, *J* = 7.0 Hz, 2H), 2.36 (q, *J* = 7.3 Hz, 2H), 2.00 – 1.77 (m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-d) δ 172.44, 162.05, 134.25, 126.03, 114.85, 60.65, 56.18, 55.56, 32.85, 17.87, 14.21.

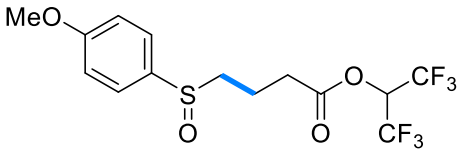
Butyl 4-((4-methoxyphenyl)sulfinyl)butanoate **(4m)**



4m

Following the general procedures, **4m**was obtained as a colourless liquid in the yield of 59% (35.2 mg). R_f = 0.20 (Hexane:Ethyl acetate, 3:2); ^{1}H NMR (500 MHz, Chloroform-d) δ 7.54 (dd, *J* = 8.6, 1.4 Hz, 2H), 7.00 (dd, *J* = 8.6, 1.5 Hz, 2H), 4.03 (t, *J* = 6.4 Hz, 2H), 3.87 – 3.78 (m, 3H), 2.81 (t, *J* = 7.5 Hz, 2H), 2.42 (t, *J* = 7.2 Hz, 2H), 2.01 (dp, *J* = 14.5, 7.2 Hz, 1H), 1.91 (dp, *J* = 14.2, 7.1 Hz, 1H), 1.56 (p, *J* = 6.8 Hz, 2H), 1.33 (h, *J* = 7.3 Hz, 2H), 0.93 – 0.87 (m, 3H); ^{13}C NMR (126 MHz, Chloroform-d) δ 172.59, 162.08, 134.41, 126.02, 114.89, 64.60, 56.27, 55.60, 32.90, 30.64, 19.17, 17.92, 13.76; HRMS m/z (FAB): calcd. For C_{15} (M^+) 299.1317, found 299.1315.

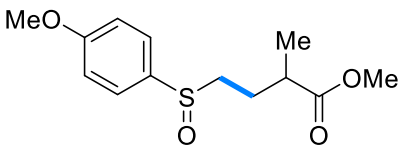
1,1,1,3,3,3-hexafluoropropan-2-yl 4-((4-methoxyphenyl)sulfinyl)butanoate **(4n)**



4n

Following the general procedures, **4n** was obtained as a light-yellow in the yield of 69% (33.1 mg). R_f = 0.20 (Hexane:Ethyl acetate, 1:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 8.7 Hz, 2H), 7.03 (d, *J* = 8.7 Hz, 2H), 5.73 (hept, J_{HF} = 5.9 Hz, 1H), 3.85 (s, 3H), 2.81 (tt, *J* = 9.4, 5.2 Hz, 2H), 2.68 (t, *J* = 7.1 Hz, 2H), 2.14 (dp, *J* = 14.5, 7.3 Hz, 1H), 2.02 (tt, *J* = 14.6, 7.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.40, 162.27, 134.10, 125.98, 121.84, 119.01, 115.05, 67.33, 66.98, 66.64, 66.29, 65.92, 55.67, 55.47, 32.04, 17.55; ^{19}F NMR (377 MHz, Chloroform-*d*) δ -73.30 (d, *J* = 6.1 Hz).

Methyl 4-((4-methoxyphenyl)sulfinyl)-2-methylbutanoate **(4o)**

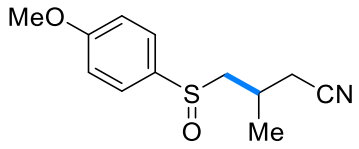


4o

Following the general procedures, **4o** was obtained as a colourless liquid in the yield of 73%

(39.5 mg) (dr: 1.1:1). R_f = 0.20 (Hexane:Ethyl acetate, 1:1); ^{1}H NMR (500 MHz, Chloroform-d) δ 7.56 – 7.49 (m, 2H), 7.04 – 6.97 (m, 2H), 3.84 (s, 3H), 3.64 (s, 1.6H), 3.63 (s, 1.4H), 2.82 – 2.70 (m, 2H), 2.61 – 2.46 (m, 1H), 2.05 – 1.73 (m, 2H), 1.16 (d, *J* = 2.2 Hz, 1.6H),1.15 (d, *J* = 2.2 Hz, 1.4); ^{13}C NMR (126 MHz, Chloroform-d) δ 175.91, 162.07, 162.03, 134.53, 134.28, 126.00, 114.85, 55.58, 54.91, 54.59, 51.87, 38.67, 38.41, 26.17, 25.66, 17.25, 17.20.

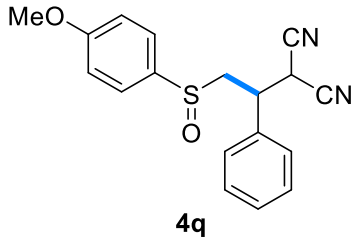
4-((4-Methoxyphenyl)sulfinyl)-3-methylbutanenitrile **(4p)**



4p

Following the general procedures, **4p** was obtained as a colourless liquid in the yield of 45% (21.3 mg) (dr: 1.16:1). R_f = 0.20 (Hexane:Ethyl acetate, 1:2); ^{1}H NMR (400 MHz, Chloroform-d) δ 7.61 – 7.52 (m, 2H), 7.07 – 6.99 (m, 2H), 3.85 (s, 3H), 2.92 – 2.77 (m, 1H), 2.77 – 2.65 (m, 1H), 2.66 – 2.50 (m, 2H), 2.50 – 2.40 (m, 1H), 1.33 (d, *J* = 5.6 Hz, 1.4H), 1.23 (d, *J* = 6.8 Hz, 1.6H); ^{13}C NMR (101 MHz, Chloroform-d) δ 162.27, 134.48, 134.02, 125.83, 125.77, 117.56, 115.07, 115.06, 63.35, 62.58, 55.60, 26.63, 26.26, 24.63, 23.51, 19.85, 19.13; HRMS m/z (EI): calcd. For C_{12} (M^+) 237.0824, found 237.0824.

2-(2-((4-Methoxyphenyl)sulfinyl)-1-phenylethyl)malononitrile (4q)

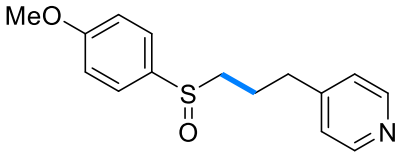


4q

Following the modified general procedures (using 1 mol% of PC, methanol (0.1 M) in 16 h), **4q** was obtained as a yellow liquid in the yield of 81% (52.5 mg) (dr = 1.1:1). R_f = 0.20 (Hexane:Ethyl acetate, 1:5); ^{1}H NMR (400 MHz, Chloroform-d) δ 7.61 – 7.56 (m, 1H), 7.54 – 7.49 (m, 1H), 7.49 – 7.35 (m, 4H), 7.29 – 7.25 (m, 1H), 7.08 – 7.02 (m, 2H), 4.98 (d, *J* = 5.4 Hz, 0.5H), 4.74 (d, *J* = 4.9 Hz, 0.5H), 4.00 – 3.93 (m, 0.5H), 3.87 (s, 3H), 3.64 – 3.58 (m, 0.5H), 3.53 (dd, *J* = 13.7, 9.1 Hz, 0.5H), 3.38 (dd, *J* = 13.4, 7.3 Hz, 0.5H), 3.13 (dd, *J* = 13.3, 7.3 Hz, 1H), 3.18 (dd, *J* = 13.7, 4.0 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-d) δ 162.72, 162.61, 135.17, 135.00, 133.80, 131.89, 129.76, 129.61, 129.55, 129.50, 128.20, 128.01, 126.09,

125.94, 115.35, 115.33, 111.61, 111.52, 111.48, 111.43, 58.86, 56.22, 55.71, 42.24, 40.51, 29.59, 28.92; HRMS m/z (EI): calcd. For C_{18} (M^+) 324.0932, found 324.0929.

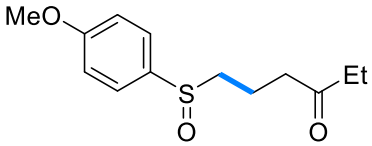
4-(3-((4-Methoxyphenyl)sulfinyl)propyl)pyridine **(4s)**



4s

Following the general procedures, **4s** was obtained as a colourless liquid in the yield of 60% (33.0 mg). R_f = 0.20 (Hexane:Ethyl acetate, 1:1); ^{1}H NMR (500 MHz, Chloroform-d) δ 8.45 (s, 2H), 7.52 – 7.45 (m, 2H), 7.07 – 7.01 (m, 2H), 7.01 – 6.95 (m, 2H), 3.88 – 3.78 (m, 3H), 2.81 – 2.63 (m, 4H), 2.07 – 1.98 (m, 1H), 1.96 – 1.85 (m, 1H); ^{13}C NMR (126 MHz, Chloroform-d) δ 162.03, 149.92, 149.46, 134.31, 125.88, 123.83, 114.85, 56.05, 55.56, 33.83, 22.65; HRMS m/z (EI): calcd. For C_{15} (M^+) 275.0980, found 275.0977.

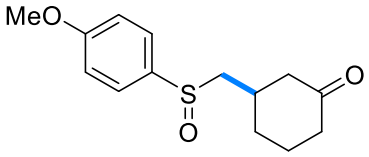
6-((4-Methoxyphenyl)sulfinyl)hexan-3-one **(4t)**



4t

Following the general procedures, **4t** was obtained as a colourless liquid in the yield of 85% (43.2 mg). R_f = 0.20 (Hexane:Ethyl acetate, 1:2); ^{1}H NMR (400 MHz, Chloroform-d) δ 7.54 – 7.46 (m, 2H), 7.01 – 6.93 (m, 2H), 3.80 (s, 3H), 2.81 – 2.69 (m, 2H), 2.53 (t, J = 7.0 Hz, 2H), 2.36 (q, J = 7.3 Hz, 2H), 2.00 – 1.77 (m, 2H), 0.98 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-d) δ 210.12, 161.97, 134.33, 125.94, 114.79, 56.22, 55.52, 40.42, 35.91, 16.72, 7.72; HRMS m/z (FAB): calcd. For C_{13} (M^+) 255.1055, found 255.1058.

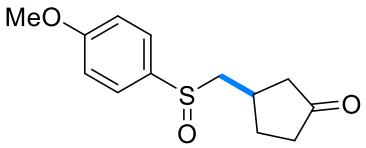
3-(((4-Methoxyphenyl)sulfinyl)methyl)cyclohexan-1-one **(4u)**



4u

Following the general procedures, **4u** was obtained as a colourless liquid in the yield of 85% (45.3 mg) (dr: 1:1). R_f = 0.20 (Hexane:Ethyl acetate, 1:2); ^{1}H NMR (300 MHz, Chloroform-d) δ 7.62 – 7.51 (m, 2H), 7.06 – 6.96 (m, 2H), 3.86 (s, 3H), 2.97 – 2.75 (m, 1H), 2.73 – 2.49 (m, 2H), 2.48 – 2.34 (m, 2H), 2.34 – 2.17 (m, 2H), 2.16 – 1.98 (m, 2H), 1.84 – 1.64 (m, 1H), 1.66 – 1.48 (m, 1H);^{13}C NMR (101 MHz, Chloroform-d) δ 209.42, 162.18, 134.84, 134.66, 125.91, 114.99, 114.98, 64.50, 64.20, 55.60, 47.48, 46.80, 41.16, 41.11, 34.29, 34.03, 31.24, 30.29, 24.64, 24.58; HRMS m/z (EI): calcd. For C_{14} (M^+) 266.0977, found 266.0980.

3-(((4-Methoxyphenyl)sulfinyl)methyl)cyclopentan-1-one **(4v)**

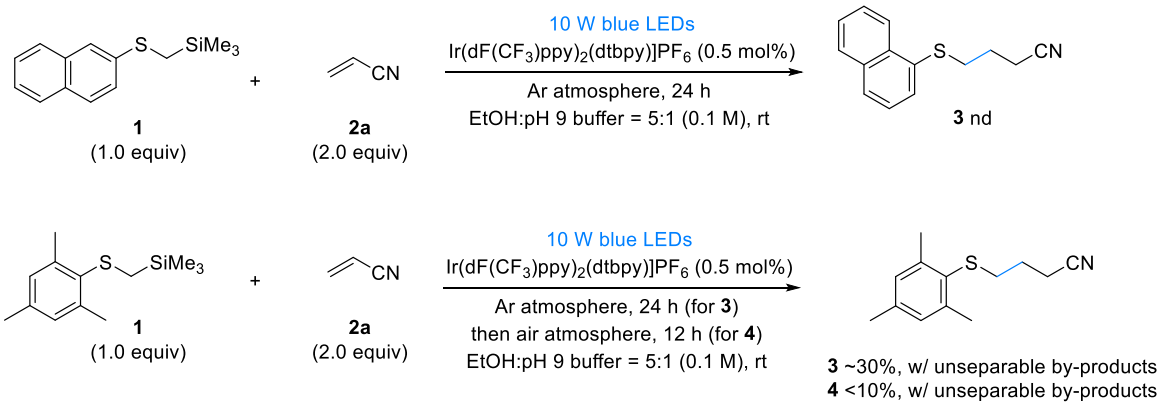


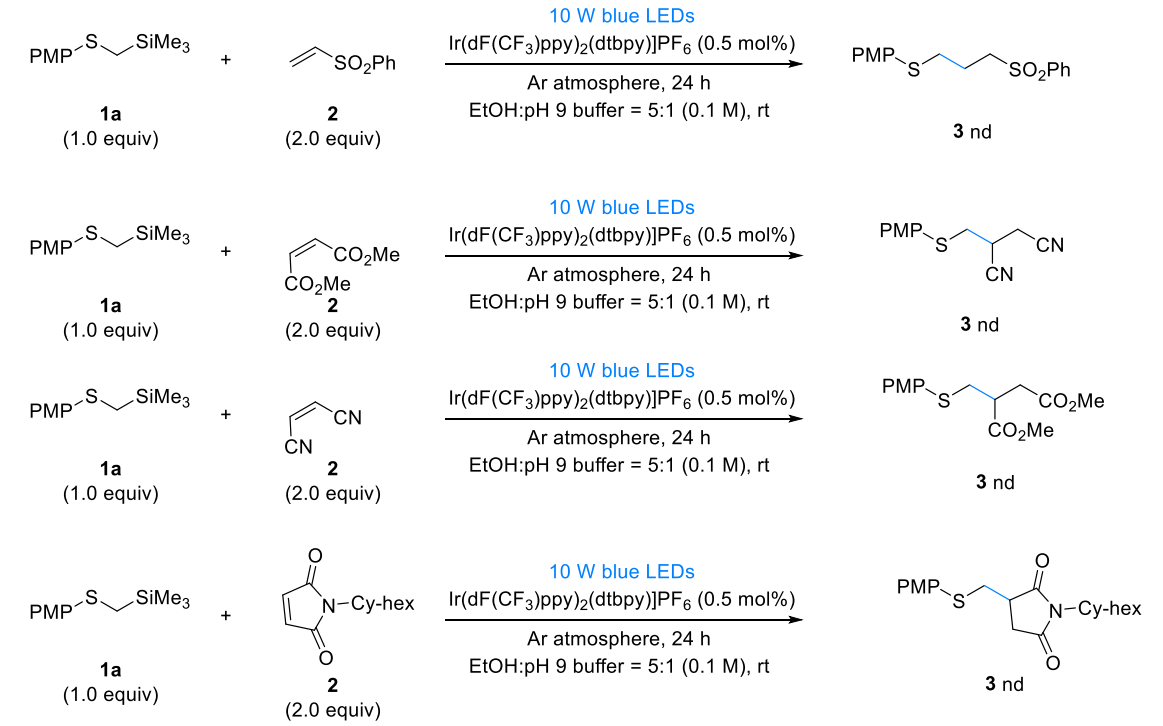
4v

Following the general procedures, **4v** was obtained as a colourless liquid in the yield of 78% (39.4 mg) (dr: 1:1). R_f = 0.20 (Hexane:Ethyl acetate, 1:2); ^{1}H NMR (300 MHz, Chloroform-d) δ 7.65 – 7.52 (m, 2H), 7.09 – 6.96 (m, 2H), 3.86 (s, 3H), 3.07 – 2.95 (m, 1H), 2.85 – 2.56 (m, 2.5H), 2.48 – 2.10 (m, 3.5H), 2.08 – 1.83 (m, 1H), 1.69 (m, 1H); ^{13}C NMR (75 MHz, Chloroform-d) δ 217.04, 162.19, 134.72, 134.49, 130.11, 125.87, 125.49, 114.99, 114.98, 63.36, 63.04, 55.58, 44.46, 44.15, 38.11, 38.04, 32.13, 31.77, 29.58, 29.26; HRMS m/z (EI): calcd. For C_{13} (M^+) 252.0820, found 252.0823.

VI. Unsuccessful Substrate scope

Scheme S1. Unsuccessful Substrate scope





[a]Reaction conditions: 1 (0.2 mmol), 2 (0.4 mol), catalyst (0.5 mol%), and solvent (0.1 M) irradiated with 10 W blue LED (452 nm) at room temperature under argon in a pressure tube.

VII. General Procedure for Flow Process

A. General procedure for the synthesis of sulfide 3a from 1a and 2a in flow process

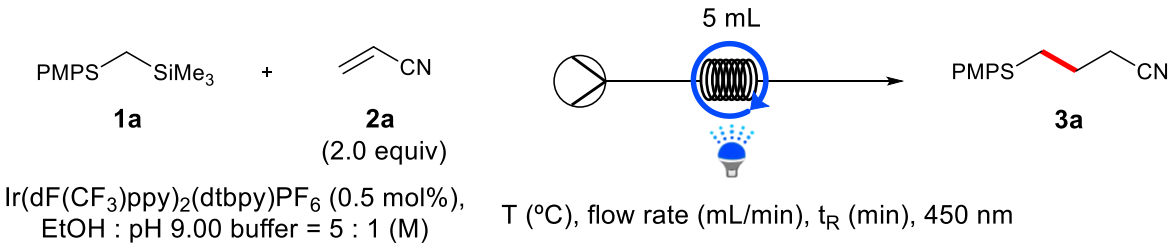
For a 0.2 mmol scale reaction, a flame-dried 16 x 125 mm reaction tube (Fisher Scientific, part # 14-962-26G) was filled with photocatalyst $Ir(dF(CF_3)ppy)_2(dtbpy)PF_6$ (0.003 mmol, 3.4 mg) and purged by nitrogen gas. After that, degassed solvent (EtOH : pH 9.00 buffer = 5 :1) (up to 3–4 mL), followed by $PMPSCH_2TMS$ **1a** (0.6 mmol, 0.138 mL) and acrylonitrile **2a** (1.2 mmol, 0.078 mL) was charged in the reaction tube. To make a total volume of the reaction solution 6 mL, solvent was added to the reaction tube until it reached the same level of a reference reaction tube filled with 6 mL of solvent. The reaction solution, with an argon balloon, was added at a flow rate of 0.125 mL/min using the peristaltic pump of the Vapourtec E-series. After 40 minutes, depending on the reaction mixture volume, 2 mL of the solution from the central part of the injected solution was collected to avoid dilution effects. The collected crude mixture was analyzed by ^1H NMR spectroscopy using 1,3-benzodioxole as an internal standard. After analysis, the product **3a** was purified by flash column chromatography.

B. General procedure for the synthesis of sulfoxide 4a from 1a and 2a in flow process

For a 0.2 mmol scale reaction, a flame-dried 16 x 125 mm reaction tube (Fisher Scientific, part # 14-962-26G) was filled with photocatalyst $Ir(dF(CF_3)ppy)_2(dtbpy)PF_6$ (0.003 mmol, 3.4 mg) and purged by nitrogen gas. After that, degassed solvent (EtOH : pH 9.00 buffer = 5 :1) (up to 3–4 mL), followed by $PMPSCH_2TMS$ **1a** (0.6 mmol, 0.138 mL) and acrylonitrile **2a** (1.2 mmol, 0.078 mL) was charged in the reaction tube. To make a total volume of the reaction solution 6 mL, solvent was added to the reaction tube until it reached the same level of a reference reaction tube filled with 6 mL of solvent. The reaction solution with an argon balloon, was added at a flow rate of 0.125 mL/min using the peristaltic pump of Vapourtec E-series. At the same time, the oxygen gas was injected to the second part of the reactor using a mass flow controller. After 40 + 15 minutes, depending on the reaction mixture volume, 2 mL of the solution from the central part of the injected solution was collected to avoid dilution effects. The collected crude mixture was analyzed by ^1H NMR spectroscopy using 1,3-benzodioxole as an internal standard. After analysis, the product **3a** was purified by flash column chromatography.

VIII. Optimization of the reaction conditions for sulfide 3a in flow process

Table S1. Optimization of the reaction conditions for sulfide **3a** in flow process



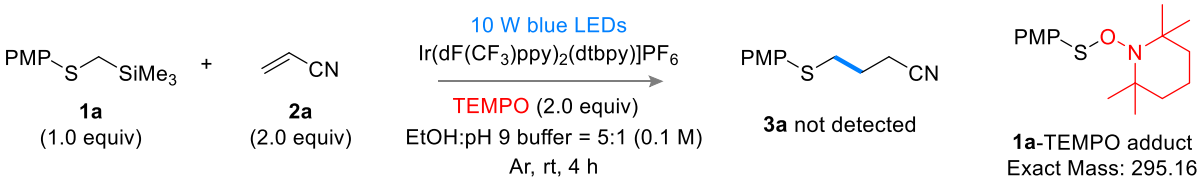
entry	flow rate (mL/min)	c (M)	t_R (min)	T (ºC)	yield of **3a**[b] (%)
1	0.100	0.1	50	25	91
2	**0.125**	**0.1**	**40**	**25**	**98(96)**[c]
3	0.166	0.1	30	25	89 / 90
4	0.250	0.1	20	25	67
5	0.500	0.1	10	25	38
6	**0.125**	**0.05**	**40**	**25**	**96(92)**[c]
7	0.166	0.05	30	25	85
8	0.250	0.05	20	25	64
9	0.250	0.1	20	35	83
10	**0.250**	**0.1**	**20**	**50**	**92(88)**[c]
11	0.250	0.1	20	60	92
12	0.250	0.1	20	70	89

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (200 equiv), catalyst (0.5 mol%). Flow rate (mL/min), solvent (M), residence time (min) and temperature (°C) are noted in the table. [b]Yields determined by ^{1}H NMR analysis of the crude mixture using 1,3-benzodioxole as the internal standard. [c]Isolated yield by flash column chromatography.

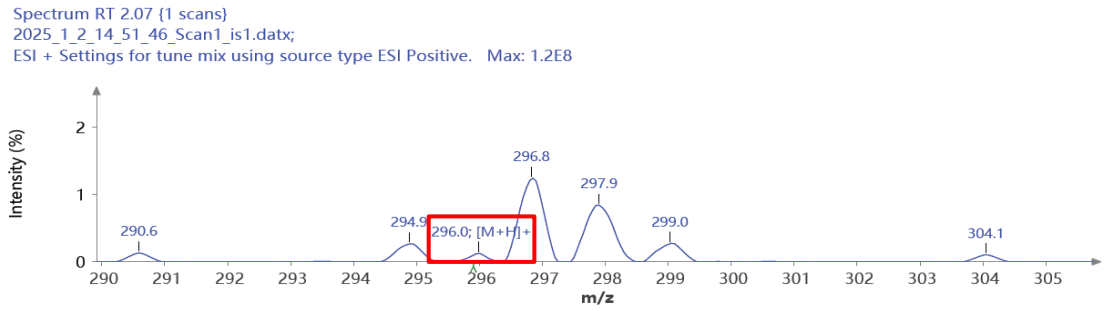
IX. Mechanistic Studies

A. Radical Trapping Experiment

In radical-trapping experiments using 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) as radical scavenger, sulfide **3a** was not detected, indicating that a radical mechanism is involved in the reaction and the alkyl radical species were trapped by TEMPO. After the reaction time was elapsed, 98 % of starting material **1a** was observed to remain, and a trace amount of **1a**-TEMPO adduct was detected by LRMS (Calc. $[M+H]^+$: 296.16 / Found. $[M+H]^+$: 296.0).



entry	1a	3a
1	98	nd



B. Deuterium Labeling Experiment

To identify the proton source in the reaction, control experiments were performed using methanol-D instead of methanol while keeping other conditions unchanged. The presence of deuterium atom in the final crude product was confirmed by ^{1}H NMR spectroscopy (**Figure S4**). When we replaced the solvent using deuterated methanol, as expected we got up to 100% deuterium incorporated product **3a.** This study proves that the proton source was from solvent.

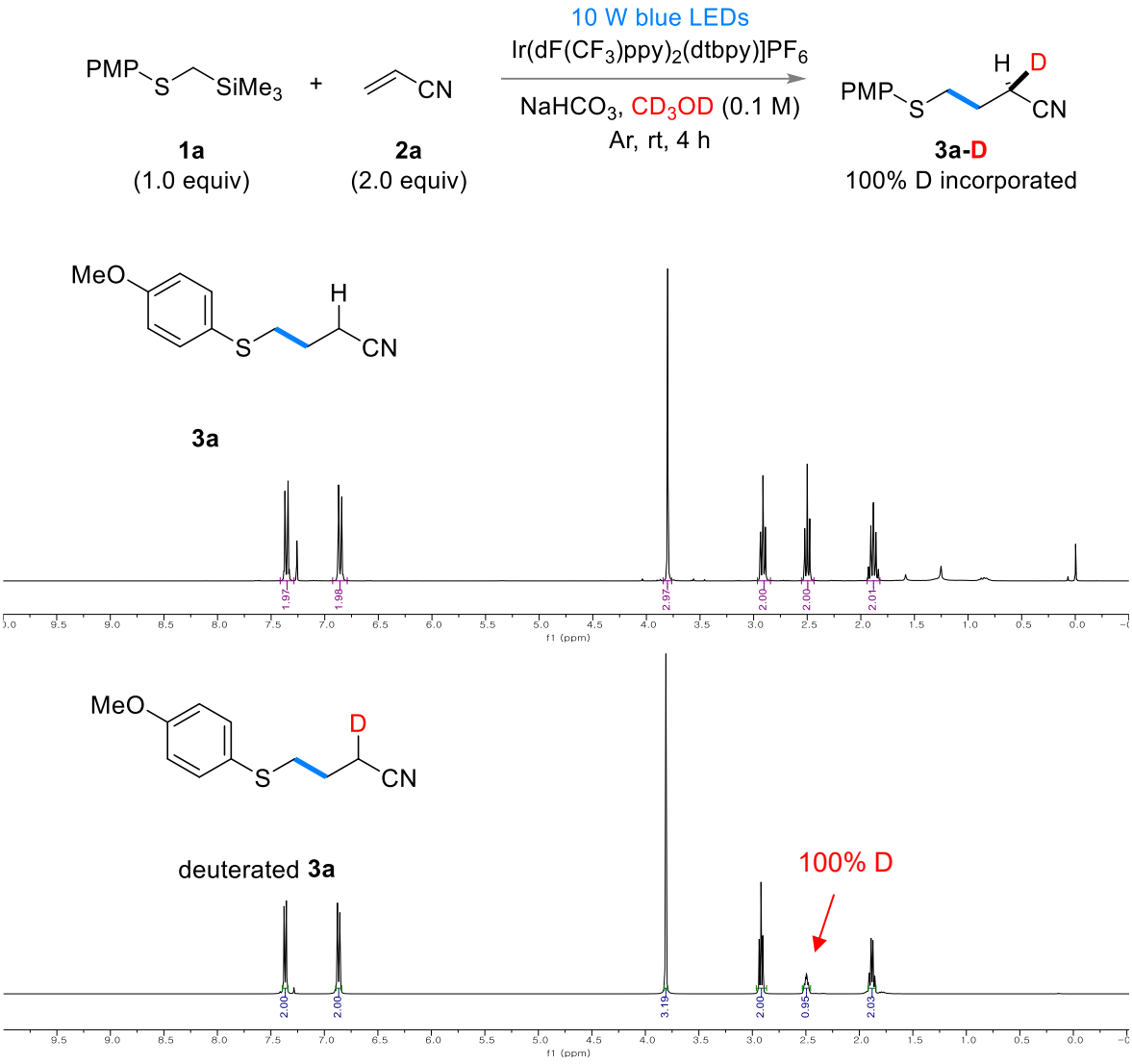


Figure S4 Comparison between **3a** and deuterated-**3a**

C. Luminescence Quenching Experiment

Catalyst $Ir(dF(CF_3)ppy)_2(dtbpy)PF_6$ was excited at 435 nm in MeCN solution and the emission intensity were observed. MeCN was degassed with a stream of argon gas for 30 min. In a typical experiment, the emission spectrum of a 1.0×10^{-4} M solution of $Ir(dF(CF_3)ppy)_2(dtbpy)PF_6$ in MeCN solution was recorded. Then, **1a** or **2a** was added to the measured solution in a quartz cuvette and the emission spectrum of the sample was measured. I0 and I signify the intensities of the emission in the absence and presence of the quencher around 480-500 nm, respectively. As shown in **Figure S5**, the steady decrease in the emission intensity of the catalyst solution with increasing gradually the amount of **1a** supports that the reaction mechanism occurs through a reductive quenching cycle. However, the prescence of 2a

did not quench the photocatalyst as shown in **Figure S6.** Stern-volmer plot also provided to shows the reaction between photocatalysts and the quencher **1a** or **2a.**

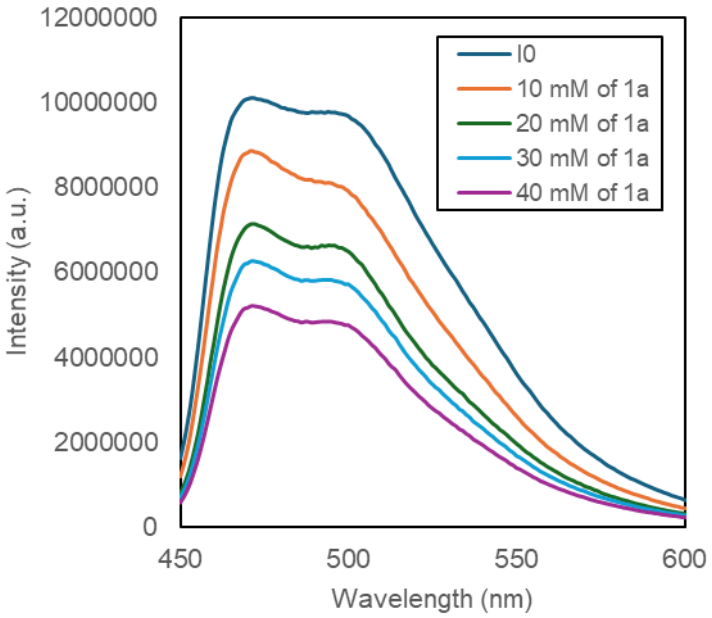


Figure S5 Emission spectra of $Ir(dF(CF_3)ppy)_2(dtbpy)PF_6$ and **1a**

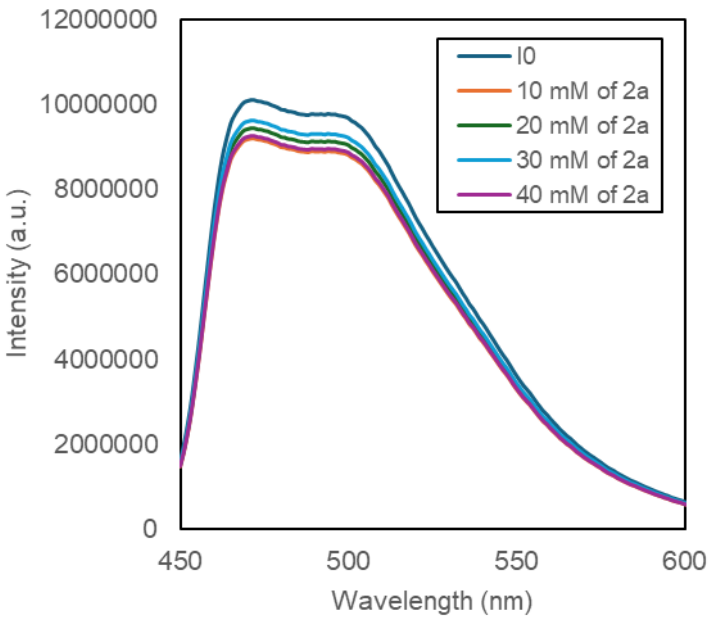


Figure S6 Emission spectra of $Ir(dF(CF_3)ppy)_2(dtbpy)PF_6$ and **2a**

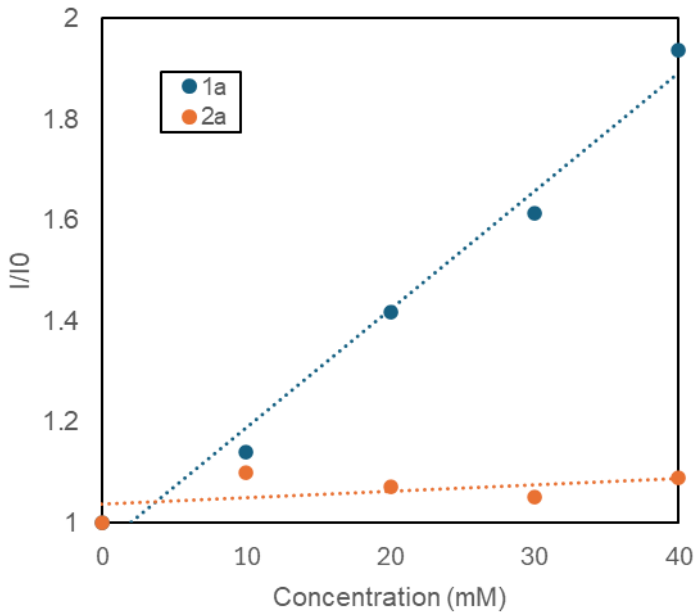


Figure S7 Stern-volmer plot

D. Cyclic Voltammetry Experiment

Electrochemical study was performed using a CH Instrument (CHI600E). The redox potentials of the substrates (vs Ag/AgCl) were determined through cyclic voltammetry using a 5.0 mM solution of that material in 0.1 M solution of Bu_4NPF_6 in MeCN (purged with N_2 for 30 min). Measurements employed a glassy carbon disk electrode (surface area: 7.065 mm^2, polished with alumina polishing pad), platinum wire counter electrode, and Ag/AgCl reference electrode (3.0 M NaCl). Initial potential was 0 V to +2.5 V (oxidative) with a scan rate of 50 mV/s in room temperature. The obtained value was onset potential and referenced to Ag/AgCl and converted to SCE by subtracting 0.032 V.

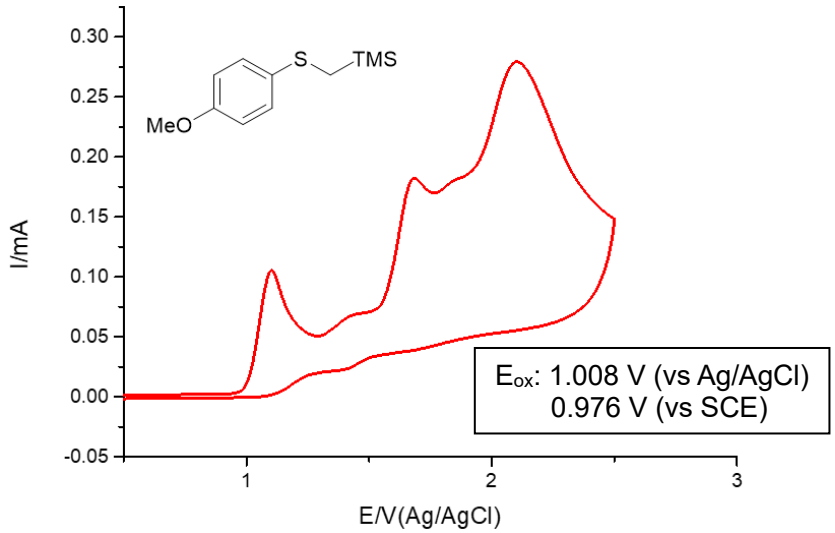


Figure S8. Cyclic voltammogram study for **1a** (5.0 mM of **1a** in 0.1 M solution of Bu_4NPF_6 in MeCN, initial potential was 0 V to +2.5 V (vs Ag/AgCl)

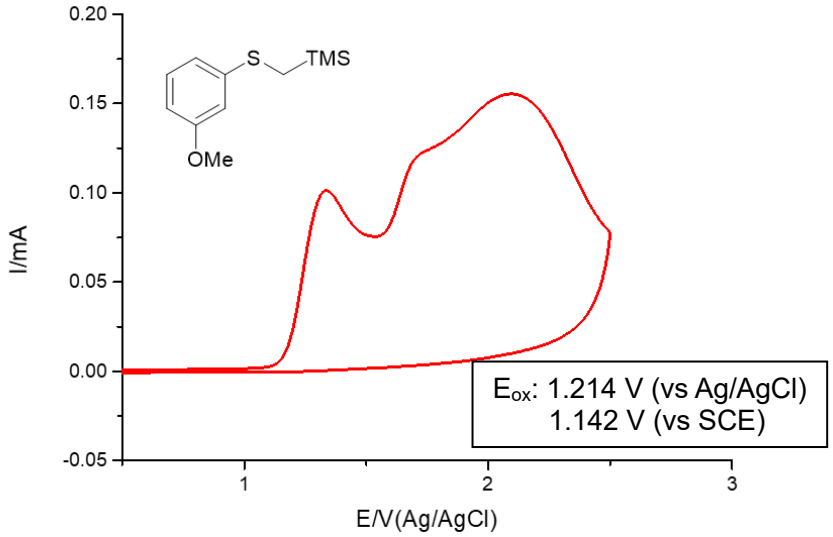


Figure S9. Cyclic voltammogram study for **1b** (5.0 mM of **1a** in 0.1 M solution of Bu_4NPF_6 in MeCN, initial potential was 0 V to +2.5 V (vs Ag/AgCl)

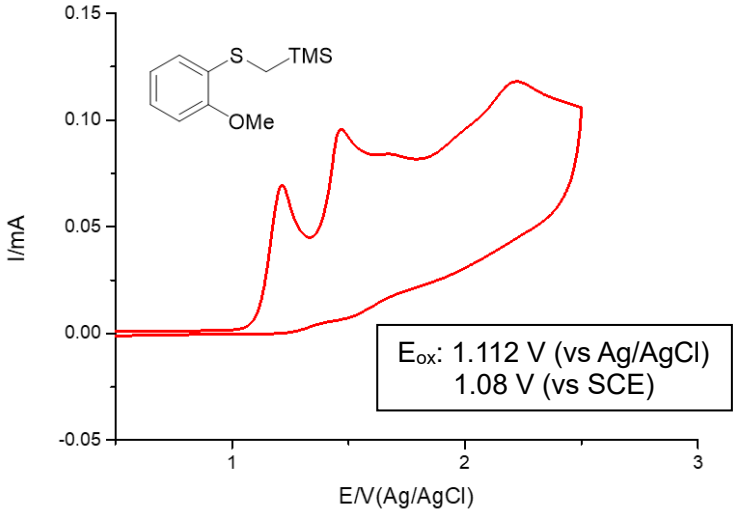


Figure S10. Cyclic voltammogram study for **1c** (5.0 mM of **1a** in 0.1 M solution of Bu_4NPF_6 in MeCN, initial potential was 0 V to +2.5 V (vs Ag/AgCl)

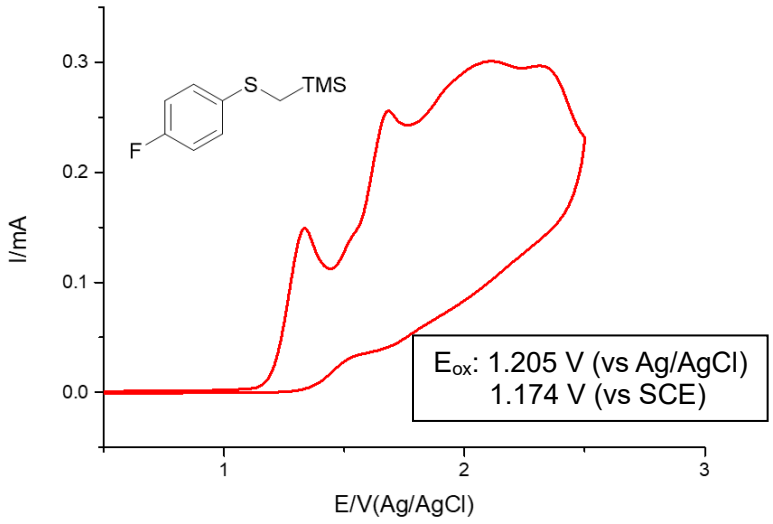


Figure S11. Cyclic voltammogram study for **1d** (5.0 mM of **1a** in 0.1 M solution of Bu_4NPF_6 in MeCN, initial potential was 0 V to +2.5 V (vs Ag/AgCl)

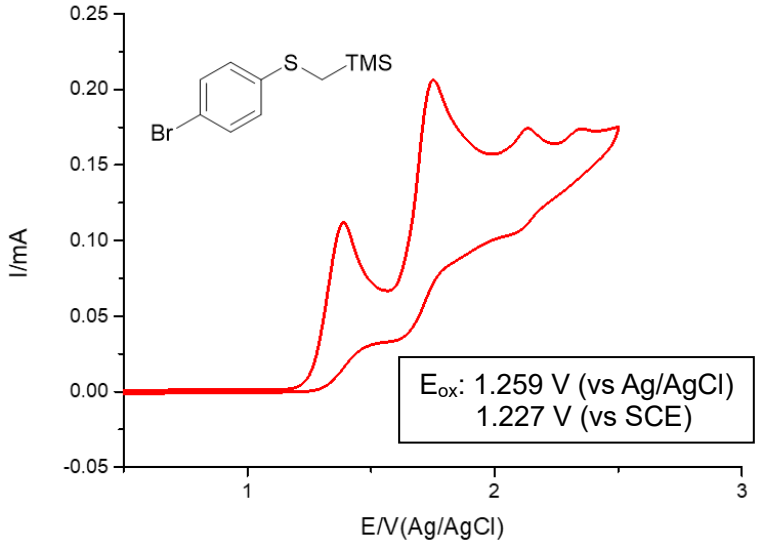


Figure S12. Cyclic voltammogram study for **1e** (5.0 mM of **1a** in 0.1 M solution of Bu_4NPF_6 in MeCN, initial potential was 0 V to +2.5 V (vs Ag/AgCl)

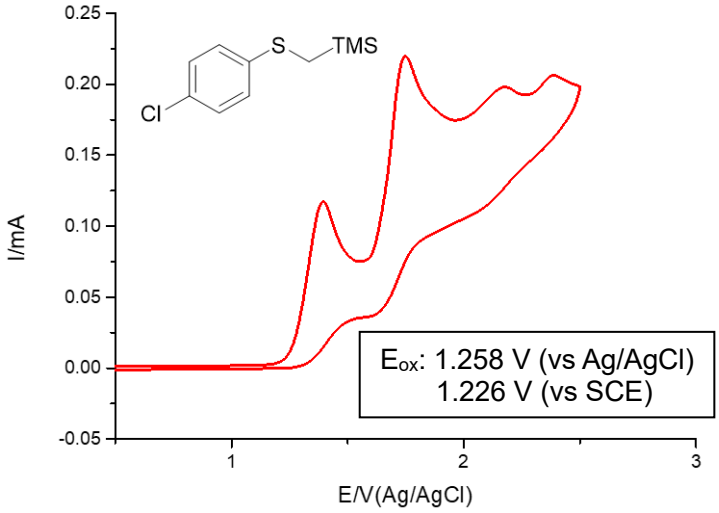


Figure S13. Cyclic voltammogram study for **1f** (5.0 mM of **1a** in 0.1 M solution of Bu_4NPF_6 in MeCN, initial potential was 0 V to +2.5 V (vs Ag/AgCl)

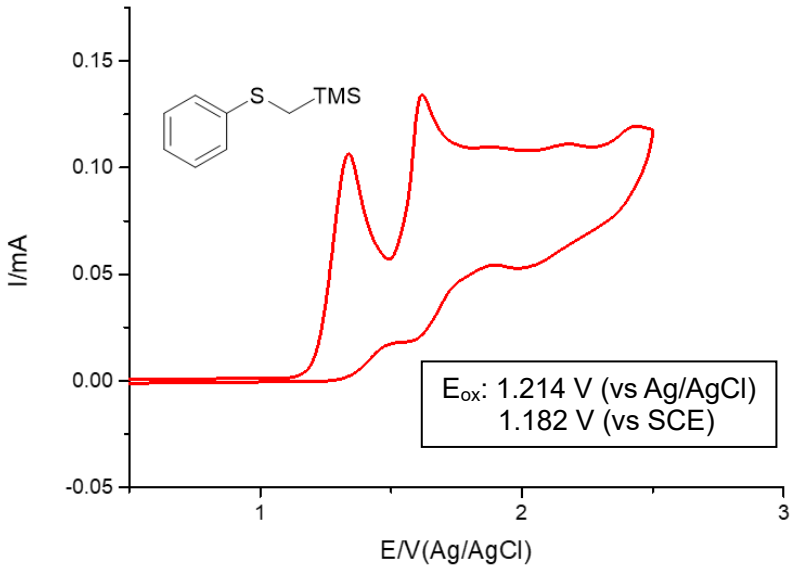


Figure S14. Cyclic voltammogram study for **1g** (5.0 mM of **1a** in 0.1 M solution of Bu_4NPF_6 in MeCN, initial potential was 0 V to +2.5 V (vs Ag/AgCl)

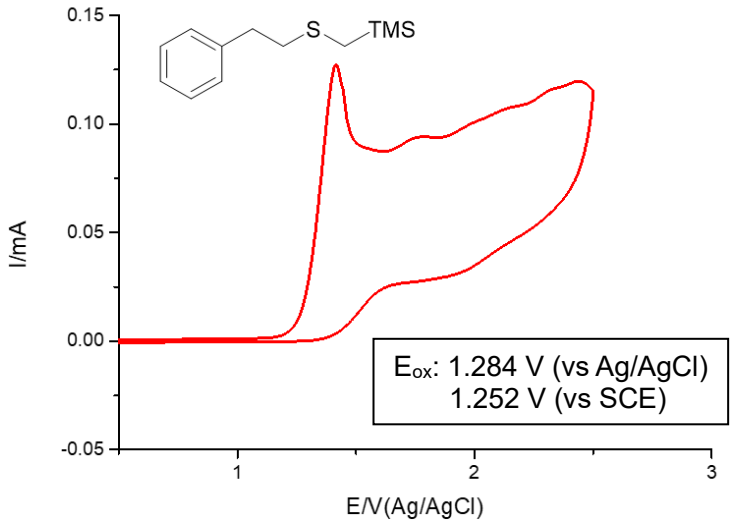


Figure S15. Cyclic voltammogram study for **1i** (5.0 mM of **1a** in 0.1 M solution of Bu_4NPF_6 in MeCN, initial potential was 0 V to +2.5 V (vs Ag/AgCl)

This is the stacked CV data of several α-thioalkyl substrates that were synthesized through previous literature.[12,13] These substrates oxidation potential then compared with **1a**.

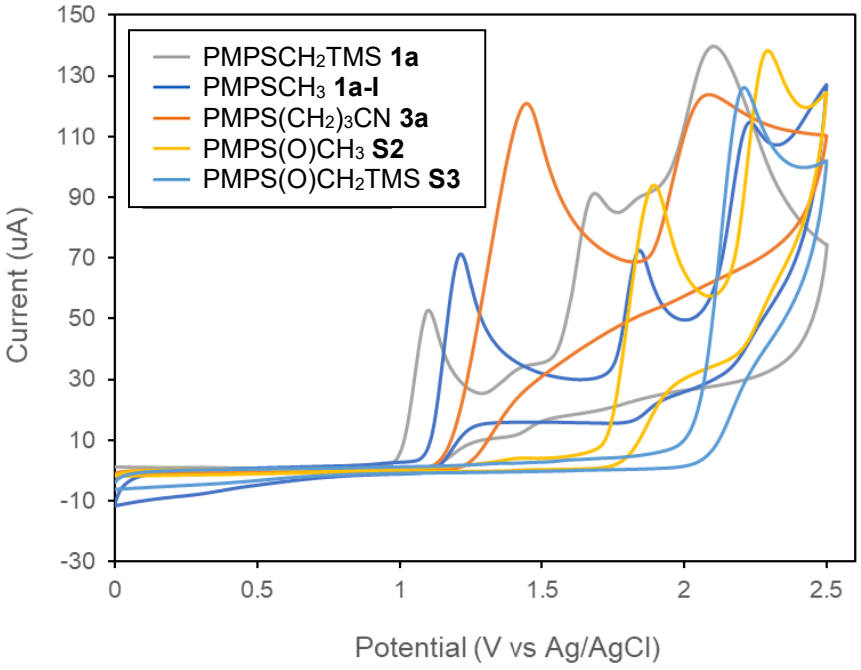
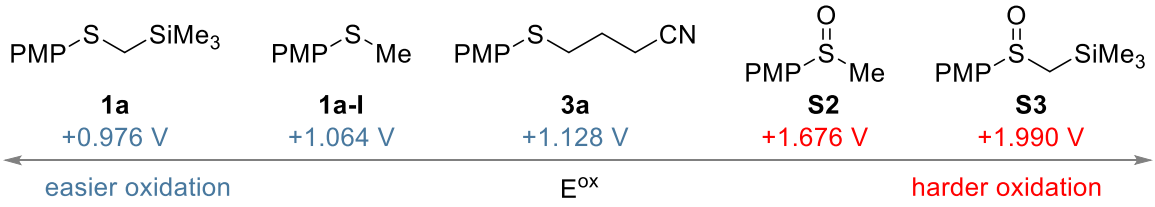


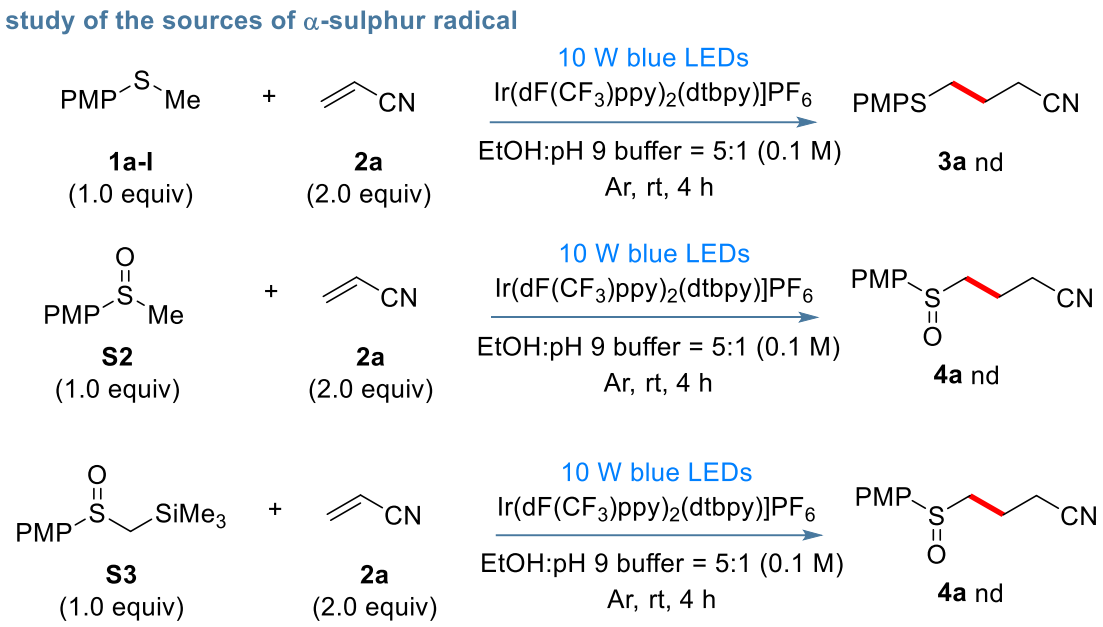
Figure S16 Cyclic voltammogram study for several α-thioalkyl substrates (5.0 mM of substrates in 0.1 M solution of Bu_4NPF_6 in MeCN, initial potential was 0 V to +2.5 V (vs Ag/AgCl)

From these voltammograms we can arrange based on the oxidation potential of the several α-thioalkyl substrates



E. Study of the source of α-thioalkyl radical

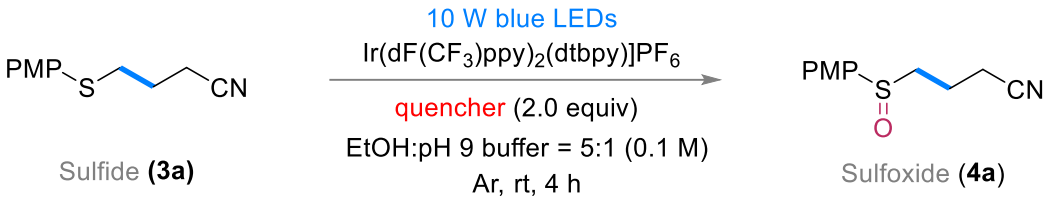
When we tried reaction using the different α-thioalkyl substrates instead of **1a**, no product was observed.



F. Controlled experiments for oxygen mediated oxidation

The oxidation of sulfide **3** to sulfoxide **4** can be achieved by using oxygen as an oxidant. The high reactivity of oxygen in a presence of visible light makes the additional control experiment need to be tried. $Ir(dF(CF_3)ppy)_2(dtbpy)PF_6$ as a photocatalyst also plays an important role in this oxidation step. $Ir(dF(CF_3)ppy)_2(dtbpy)PF_6$ have sufficient energy to oxidize sulfide **3**, reduce oxygen to produce superoxide radical anion, and also transfer energy to generate singlet oxygen. In the presence of 1,4-dimethoxybenzene (have low oxidation potential) and benzoquinone (known as a superoxide scavenger), only 45% of **4a** yield were obtained by using 1,4-dimethoxybenzene (Table S2, entry 2) and cannot observed product **4a** while using benzoquinone (Table S2, entry 3). This suggests the electron transfer between sulfide and oxygen with is Ir as a photocatalyst was proceeds. Next, we are focusing on trapping singlet oxygen using DABCO and sodium azide (Table S2, entries 5-6). No product 4a was detected in the presence of DABCO, and only 26% of product 4a was obtained with sodium azide. These results suggest that energy transfer between $Ir(dF(CF_3)ppy)_2(dtbpy)PF_6$ and oxygen was also proceeded.

Table S2 Mechanistic investigation on the formation of sulfoxide



entry	quencher	inhibited species	yield (%)
1	-	-	95
2	1,4-dimethoxybenzene	$R_2S^{\bullet+}$	45 [a]
3	Benzoquinone	$O_2^{\bullet-}$	nd
4	DABCO	$^1O_2$	nd [a]
5	NaN_3	$^1O_2$	26

[a]NMR yield (IS = styrene), nd = not detected

G. Quantum yield experiment

a. Determination of light intensity at 452 nm

The photon flux of the photoreactor and quantum yield at this reaction were determined by standard ferrioxalate actinometry.[14] In a dark condition, a 0.15 M solution of ferrioxalate was prepared by dissolving 736.8 mg (1.5 mmol) of potassium ferrioxalate trihydrate in 10.0 mL of 0.05 M H_2SO_4. A buffered solution of phenanthroline was prepared of 5.0 mg of 1,10-phenanthroline and 1.125 g of sodium acetate in 5.0 mL of 0.5 M H_2SO_4. Then 2.0 mL of the ferrioxalate solution was placed in a 8.0 mL screw cap reaction tube (batch system) or 0.04" 5 ml PFA tubing (flow system) and irradiated for 90.0 seconds at λ = 452 nm using a 5 W blue LED (batch system) or 28 W COB blue LED strip (flow system) to determine the photon flux of the spectrophotometer. After irradiation, 0.35 mL of the phenanthroline solution was added to the tube and allowed to rest for 1 hours in dark condition to allow the formation of $[Fe(phen)_3]^{2+}$. The absorbance of the solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm measured.

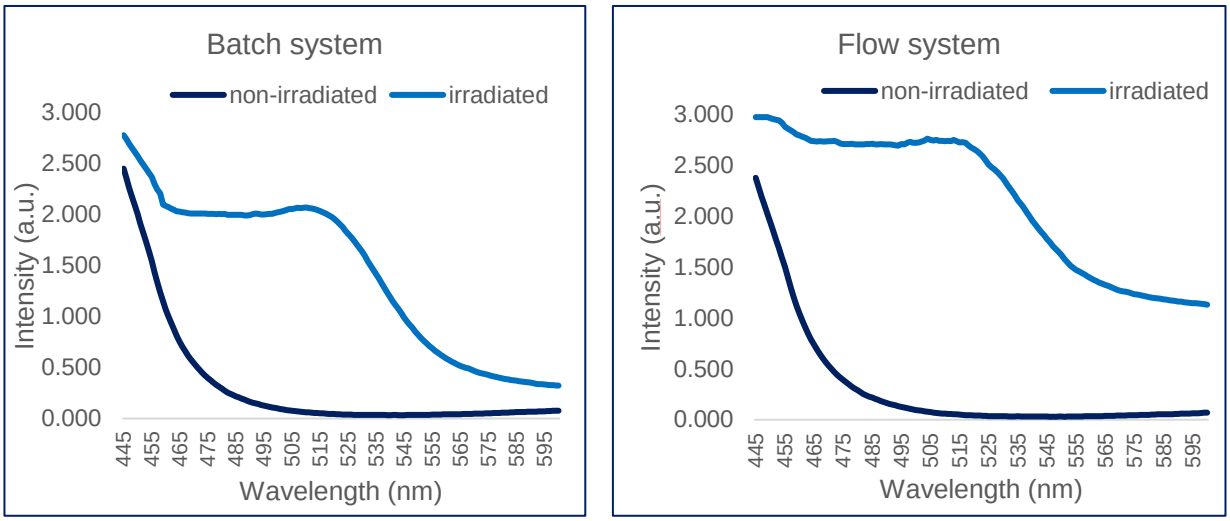


Figure S17. Irradiated and non-irradiated sample absorption of $[Fe(phen)_3]^{2+}$ in batch and flow process.

Batch system : From the measurement using UV-VIS spectrometer, conversion was calculated using eq 1.

$$mol\ (Fe^{2+}) = \frac{V\ \mathrm{X}\ \Delta A}{\mathrm{l}\ \mathrm{X}\ \varepsilon} \qquad \text{(eq 1)}$$

Where V is the total volume (0.00235 L) of the solution after addition of phenanthroline, ΔA (2.007) is the difference between the irradiated sample (2.068) and the dark sample (0.061) in absorbance at 510 nm, l is the path length (1.0 cm), and ε is the molar absorptivity at 510 nm (11,100 L mol^{-1} cm^{-1}).[15,16] The photon flux can be calculated using eq 2.

$$Photon\ flux = \frac{mol\ (Fe^{2+})}{\Phi\ (Fe^{2+})\ \mathrm{X}\ t\ \mathrm{X}\ f} \qquad \text{(eq 2)}$$

Where Φ is the quantum yield for the ferrioxalate actinometer (0.845 for a 0.15 M solution at λ = 458 nm)[16], t is the irradiation time (90.0 s), and f ($f = 1 - 10^{-A} = 0.9967$) is the fraction of light absorbed at λ = 452 nm (A = 2.491). The photon flux was calculated to be 4.973 X 10^{-9} Einstein s^{-1}.

Sample calculation:

$$mol\ (Fe^{2+}) = \frac{0.00235\ L\ \text{X}\ 2.007}{1\ cm\ \text{X}\ 11100\ L\ mol^{-1}cm^{-1}} = 4.249\ \text{X}\ 10^{-7}\ mol$$

$$Photon\ flux = \frac{4.249\ \text{X}\ 10^{-7}\ mol}{0.845\ X\ 90.0\ X\ 0.9967} = 5.606\ X\ 10^{-9}\ einstein\ s^{-1}$$

Flow system : From the measurement using UV-VIS spectrometer, conversion was calculated using eq 1.

$$mol\ (Fe^{2+}) = \frac{V\ \text{X}\ \Delta A}{\text{l}\ \text{X}\ \varepsilon} \qquad \text{(eq 1)}$$

Where V is the total volume (0.00235 L) of the solution after addition of phenanthroline, ΔA (2.673) is the difference between the irradiated sample (2.733) and the dark sample (0.060) in absorbance at 510 nm, l is the path length (1.0 cm), and ε is the molar absorptivity at 510 nm (11,100 L mol^{-1} cm^{-1}).[15,16]The photon flux can be calculated using eq 2.

$$Photon\ flux = \frac{mol\ (Fe^{2+})}{\Phi\ (Fe^{2+})\ \text{X}\ t\ \text{X}\ f} \qquad \text{(eq 2)}$$

Where Φ is the quantum yield for the ferrioxalate actinometer (0.845 for a 0.15 M solution at λ = 458 nm)[16], t is the irradiation time (90.0 s), and f ($f = 1 - 10^{-A} = 0.9989$) is the fraction of light absorbed at λ = 452 nm (A = 2.947). The photon flux was calculated to be 4.973 X 10^{-9} Einstein s^{-1}.

Sample calculation:

$$mol\ (Fe^{2+}) = \frac{0.00235\ L\ \text{X}\ 2.673}{1\ cm\ \text{X}\ 11100\ L\ mol^{-1}cm^{-1}} = 5.659\ \text{X}\ 10^{-7}\ mol$$

$$Photon\ flux = \frac{5.659\ \text{X}\ 10^{-7}\ mol}{0.845\ X\ 90.0\ X\ 0.9989} = 7.449\ X\ 10^{-9}\ einstein\ s^{-1}$$

b. Quantum yield measurement

The reaction was conducted in accordance with the general procedure as mentioned before in batch and flow system respectively. The quantum yield was determined using eq 3.

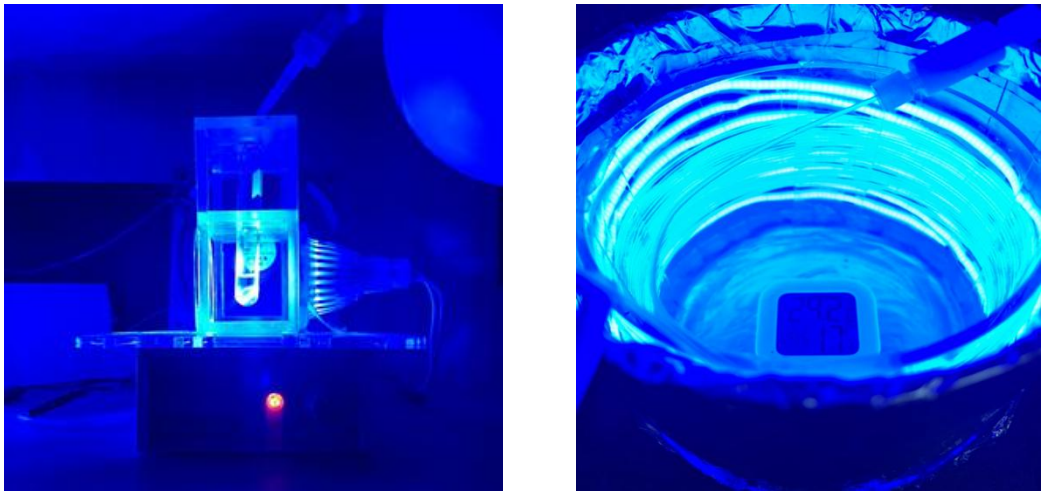


Figure S18. Picture of measuring photon flux in a batch and flow photoreactor

Sample Calculation (batch):

$$Quantum\ yield\ (\Phi) = \frac{mol\ of\ P}{Photon\ flux\ \mathrm{X}\ t\ \mathrm{X}\ f} \qquad \text{(eq 3)}$$

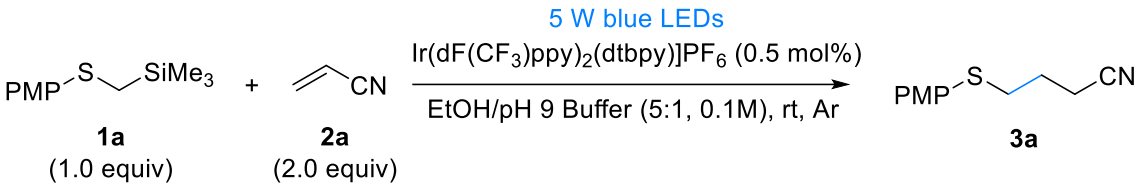
$$Quantum\ yield\ (\Phi) = \frac{a\ mol}{5.606\ \mathrm{X}\ 10^{-9}\ einstein\ s^{-1}\ \mathrm{X}\ b\ s\ \mathrm{X}\ 0.9967}$$

Sample Calculation (flow):

$$Quantum\ yield\ (\Phi) = \frac{mol\ of\ P}{Photon\ flux\ \mathrm{X}\ t\ \mathrm{X}\ f} \qquad \text{(eq 3)}$$

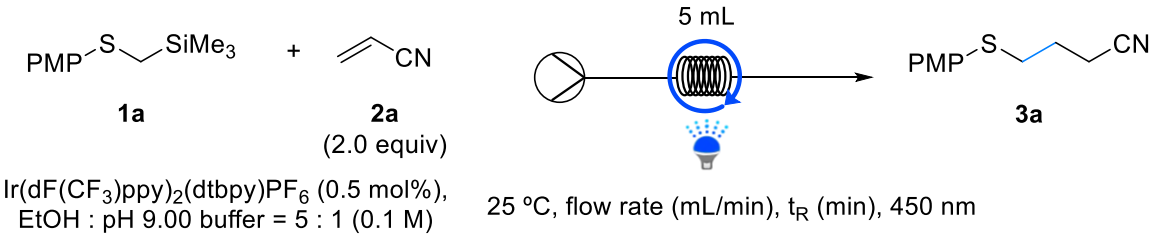
$$Quantum\ yield\ (\Phi) = \frac{a\ mol}{7.449\ \mathrm{X}\ 10^{-9}\ einstein\ s^{-1}\ \mathrm{X}\ b\ s\ \mathrm{X}\ 0.9989}$$

Table S3. Quantum yield experiment in batch system



entry	time (min)	**1a** (%)	**3a** (%)	Φ
1	10	94	3.5	**2.087**
2	20	80	12	**3.579**
3	30	78	16	**3.182**

Table S4. Quantum yield experiment in flow system

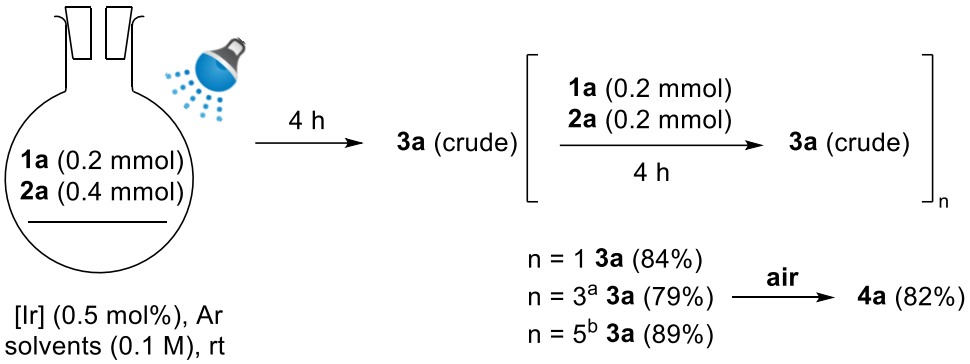


entry	flow rate (mL/min)	t_R (min)	**1a** (%)	**3a** (%)	Φ
1	4.000	1.25	90	6.5	**23.2950**
2	2.000	2.5	87	9	**16.1272**
3	0.500	10	80	16	**7.1676**
4	0.125	40	25	73	**8.1756**

The quantum yield studies indicate that the reaction mechanism include radical propagation step (Φ>1) and when comparing the two reaction configurations, the flow process exhibits superior photocatalytic performance than the batch process.

X. Reusability of reaction components

A. General procedure for 2-6 cycle experiments



[Ir] = $Ir(dF(CF_3)ppy)_2(dtbpy)PF_6$, solvents =EtOH : pH 9.00 buffer = 5 : 1

To a re-sealable pressure tube (13 x 100 mm) with a tiny magnetic stir bar was charged with silane **1a** (0.2 mmol, 1.0 equiv), alkene **2a** (0.4 mmol, 2.0 equiv) and $[Ir(dF(CF_3)ppy)_2(dtbpy)]PF_6$ (1.2 mg, 0.001 mmol, 0.5 mol%) under argon atmosphere. Then, a mixture of degassed solvents (2 mL, 0.1 M for **1a**) of EtOH:pH 9 buffer in a ratio of 5:1 was added to that pressure tube. The resultant light greenish-yellow mixture was irradiated with 2 x 5 W blue LEDs under constant stirring condition at room temperature for 4 h. After finishing 4 h reaction, addition of silane **1a** (0.2 mmol, 1.0 equiv) and alkene **2a** (0.2 mmol, 1.0 equiv) were conducted for the next cycle. Then, a mixture was irradiated with 2 x 5 W blue LEDs under argon atmosphere at room temperature for 4 h. The repeating procedure was conducted every 2 cycle with addition of $[Ir(dF(CF_3)ppy)_2(dtbpy)]PF_6$ (1.2 mg, 0.001 mmol, 0.5 mol%). After finishing the stipulated time, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to afford the corresponding sulfide product **3a**. Following the general procedure for 2, 4 and 6 cycles, **3a** was obtained as a colorless liquid in the yield of 84%, 79%, and 85% respectively.

Sulfoxide **4a** was obtained as a colorless liquid in 82% yield after 4 cycles under blue LED irradiation in air for 24 hours.

XI. Calculation of Green Chemistry Metrics

To evaluate the green chemistry aspects of the developed reaction, we calculated the green chemistry metrics, including Atom Economy (AE), Atom Efficiency (AEf), Reaction Mass Efficiency (RME), E-Factor, and Process Mass Intensity (PMI).[17] Additionally, we compared these metrics with two other efficient synthetic methods for sulfoxides. The chemistry metrics were calculated using the formulas provided below.

$$\text{Atom Economy (AE)}(\%) = \frac{\text{Molecular Weight of Desired Product}}{\text{Sum of Molecular Weights of All Reactants}} \times 100$$

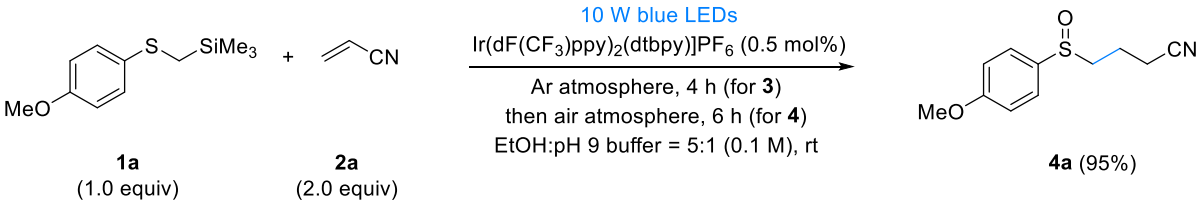
$$\text{Atom Efficiency (AEf) } (\%) = \text{Atom Economy (AE)}(\%) \times \text{yeild}$$

$$\text{Reaction Mass Efficiency (RME) } (\%) = \frac{\text{Mass of Desired Product}}{\text{Mass of Reactants Used}} \times 100$$

$$\text{E} - \text{Factor} = \frac{\text{Mass of Waste (kg)}}{\text{Mass of Product (kg)}}$$

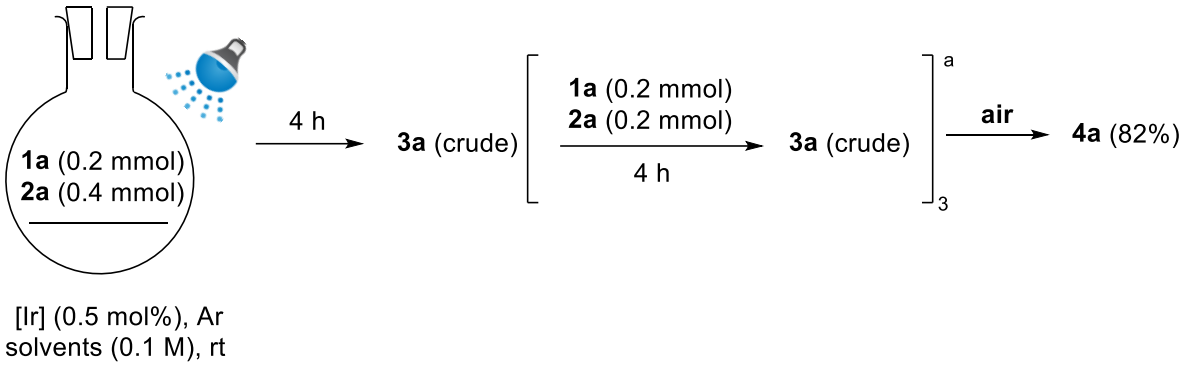
$$\text{Process Mass Intensity (PMI)} = \frac{\text{Total Mass of Inputs (Reactants, Solvents, etc.)}}{\text{Mass of Desired Product}}$$

A. our work



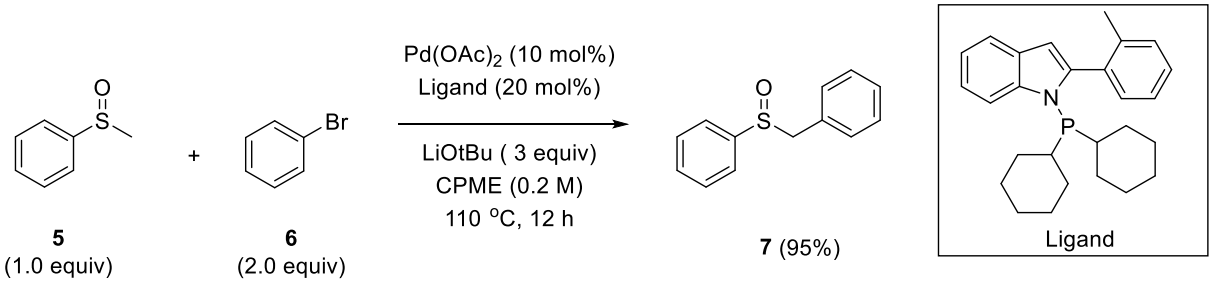
	mmol	mg	MW	**Green Chemistry Metrics**	
1a	0.2	45.28	226.41	AE (%)	61.15%
2a	0.4	21.22	53.06	AEf (%)	58.10%
4a	0.19	42.43	223.29	RME (%)	63.80%
catalyst	0.001	1.1	1121.91	E-Factor	31.59
solvent		1315		PMI	32.29

B. our work (alkene, catalyst, and solvent re-use conditions)



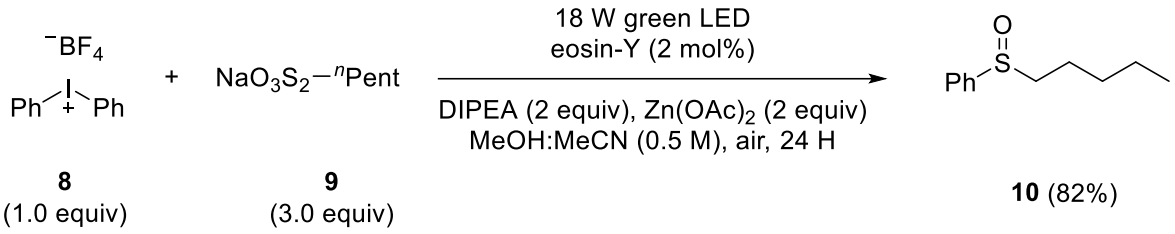
	mmol	mg	MW	Green Chemistry Metrics	
1a	0.8	181.13	226.41	AE (%)	76.28%
2a	1.0	53.06	53.06	AEf (%)	62.55%
4a	0.656	146.48	223.29	RME (%)	62.54%
catalyst	0.003	3.3	1121.91	E-Factor	9.60
solvent		1315		PMI	10.60

C. Walsh group work (2013 JACS)[18]



	mmol	mg	MW	Green Chemistry Metrics	
5	0.2	24	140.2	AE (%)	35.21%
6	0.4	62.8	157.01	AEf (%)	33.45%
7	0.19	41	216.3	RME (%)	27.08%
catalyst	0.02	4.48	224.51	E-Factor	23.78
Ligand	0.04	16.3	403.55	PMI	24.78
LiOtBu	0.6	48.3	8005		
solvent		860			

D. Jiang group work (2017 ACS catal.)[19]



8 (1.0 equiv) + **9** (3.0 equiv) → **10** (82%)

	mmol	mg	MW	**Green Chemistry Metrics**	
8	0.2	73.58	367.92	AE (%)	12.18%
9	0.6	123.75	206.25	AEf (%)	10.00%
10	0.164	32.19	196.31	RME (%)	9.98%
catalyst	0.004	2.6	647.89	E-Factor	18.84
$Zn(OAc)_2$	0.4	51.7	183.48	PMI	19.92
DIPEA	0.1	73.4	129.25		
solvent		316.2			

E. Comparison of Green Chemistry Metrics

	AE (%)	AEf (%)	RME (%)	E-Factor	PMI
Our work	61.15%	58.10%	63.80%	31.59	32.29
Our work (re-use condition)	76.28%	62.55%	62.54%	9.60	10.60
Walsh group work (2013 JACS)	35.21%	33.45%	27.08%	23.78	24.78
Jiang group work (2017 ACS catal.)	12.18%	10.00%	9.98%	18.84	19.92

XII. References

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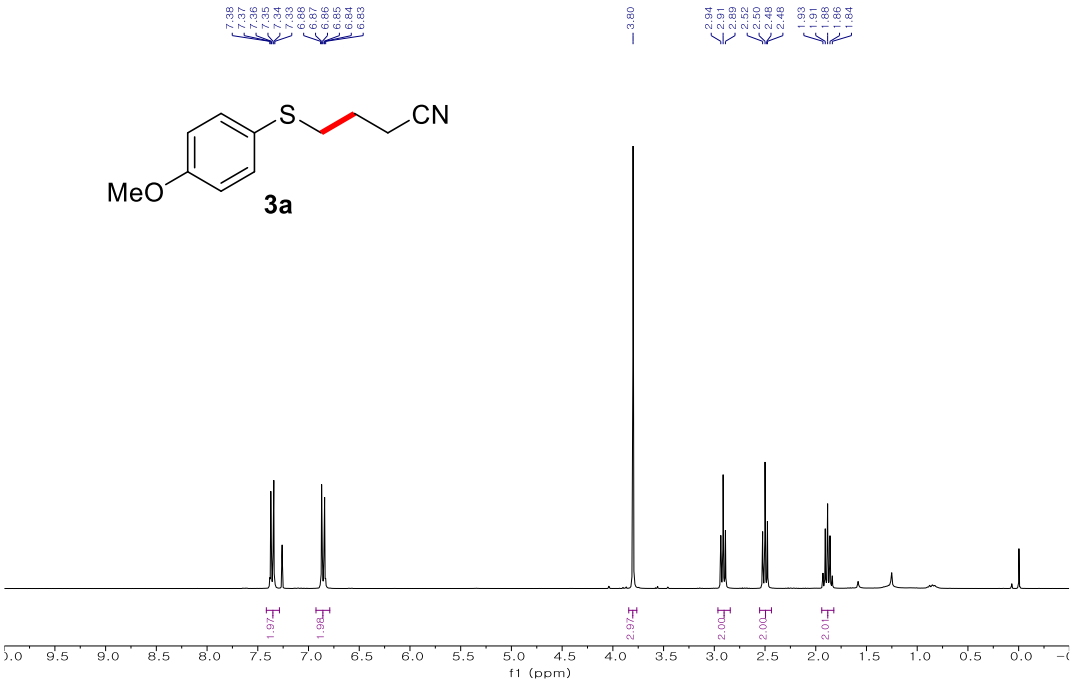
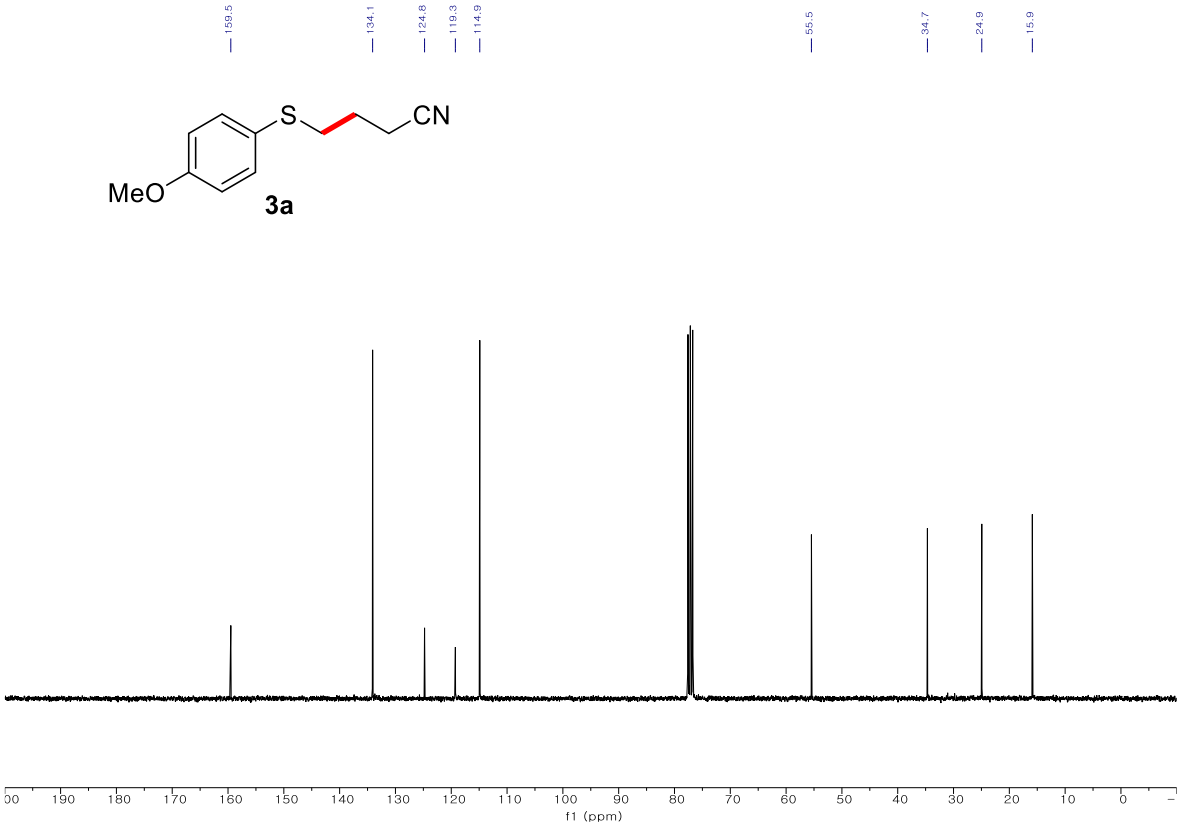
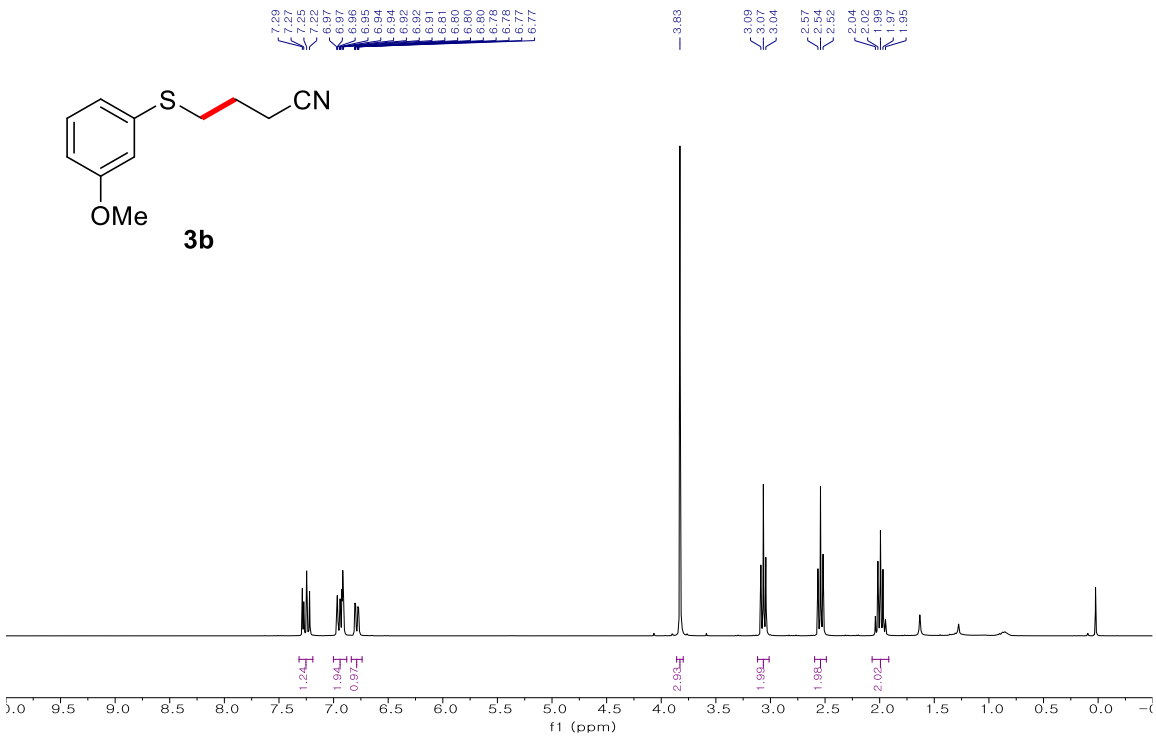
XIII. ^{1}H, ^{13}C and ^{19}F NMR Spectra



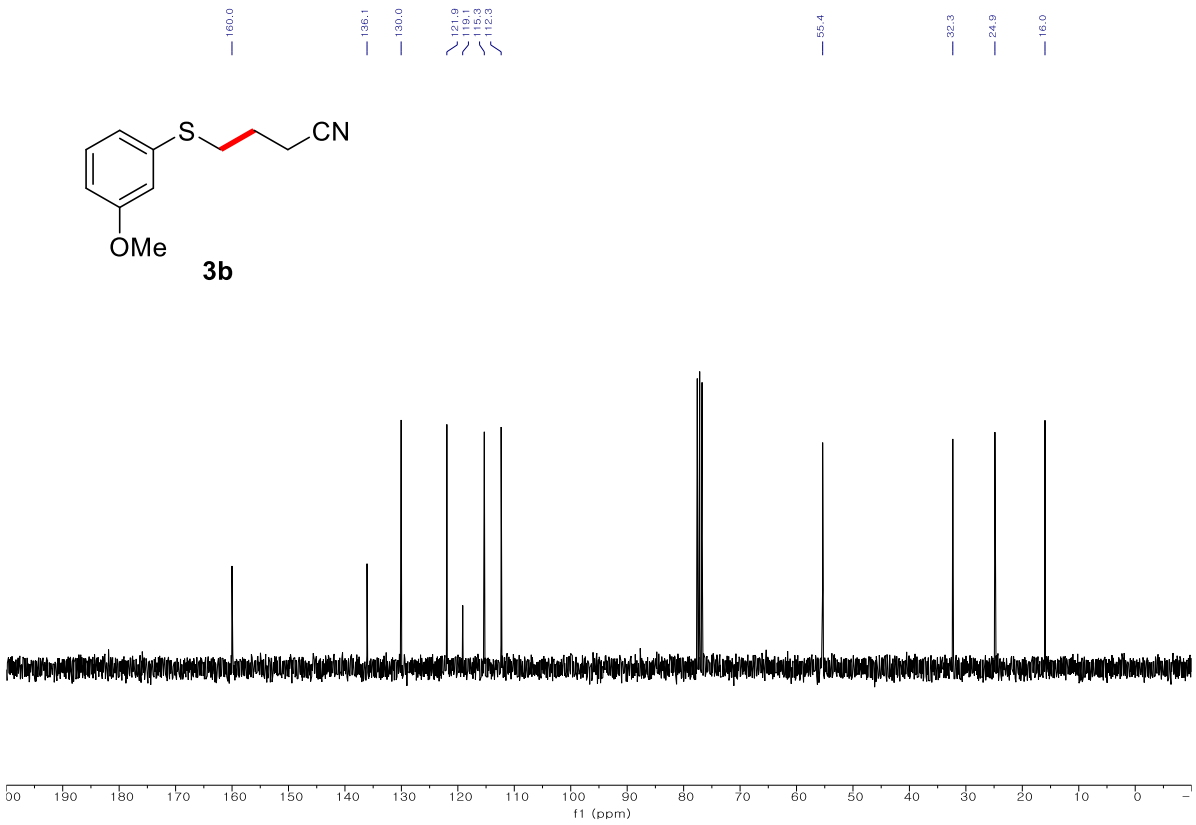
^{1}H-NMR (300 MHz, Chloroform-d) of **3a**



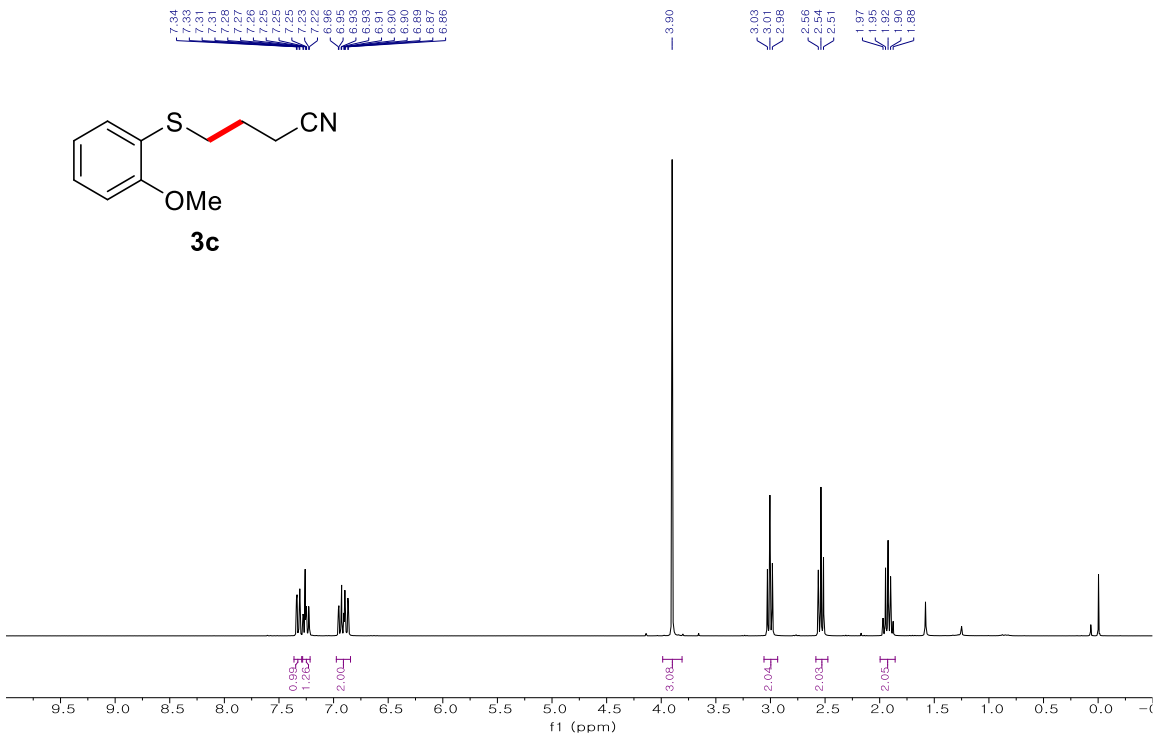
^{13}C-NMR (75 MHz, Chloroform-d) of **3a**



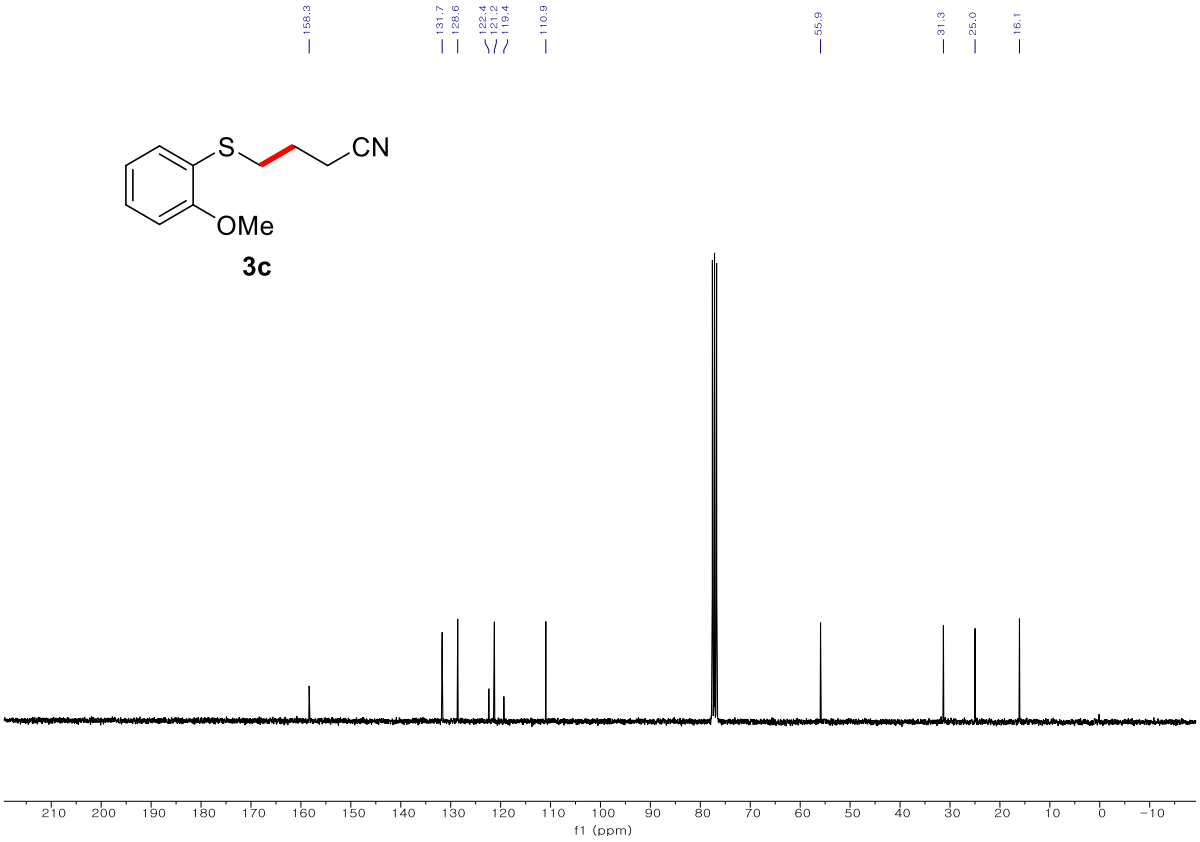
^{1}H-NMR (300 MHz, Chloroform-d) of **3b**



^{13}C-NMR (75 MHz, Chloroform-d) of **3b**



^{1}H-NMR (300 MHz, Chloroform-d) of **3c**



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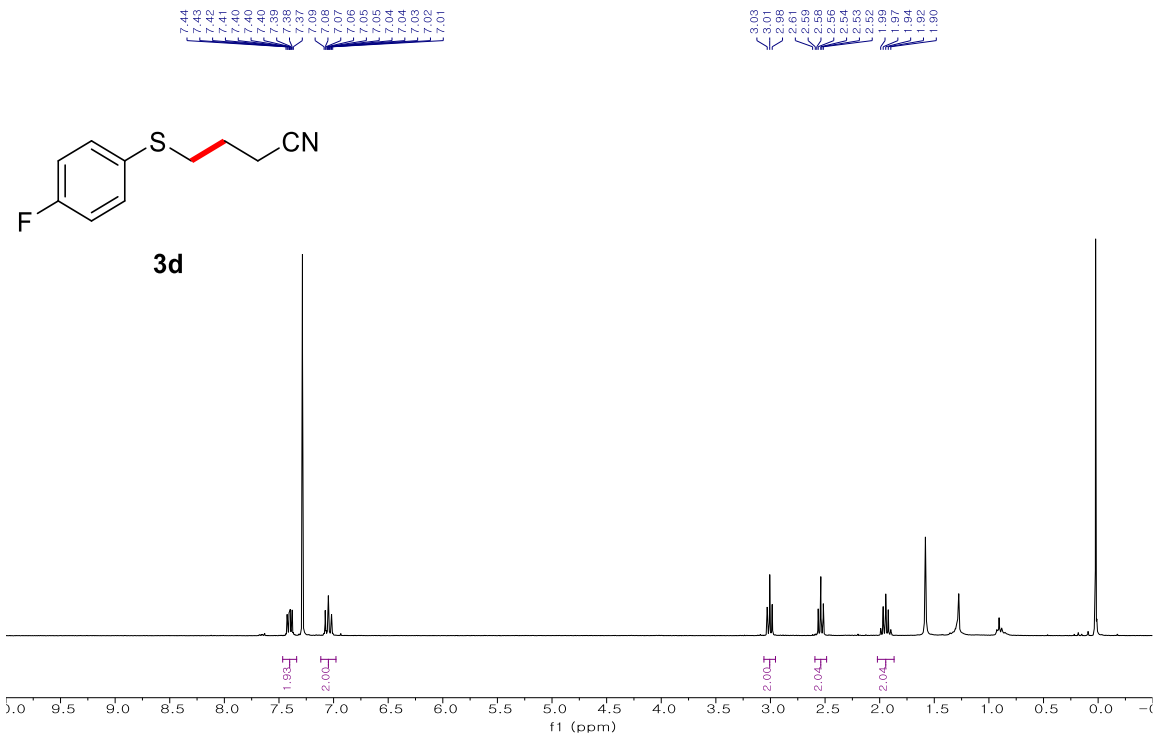
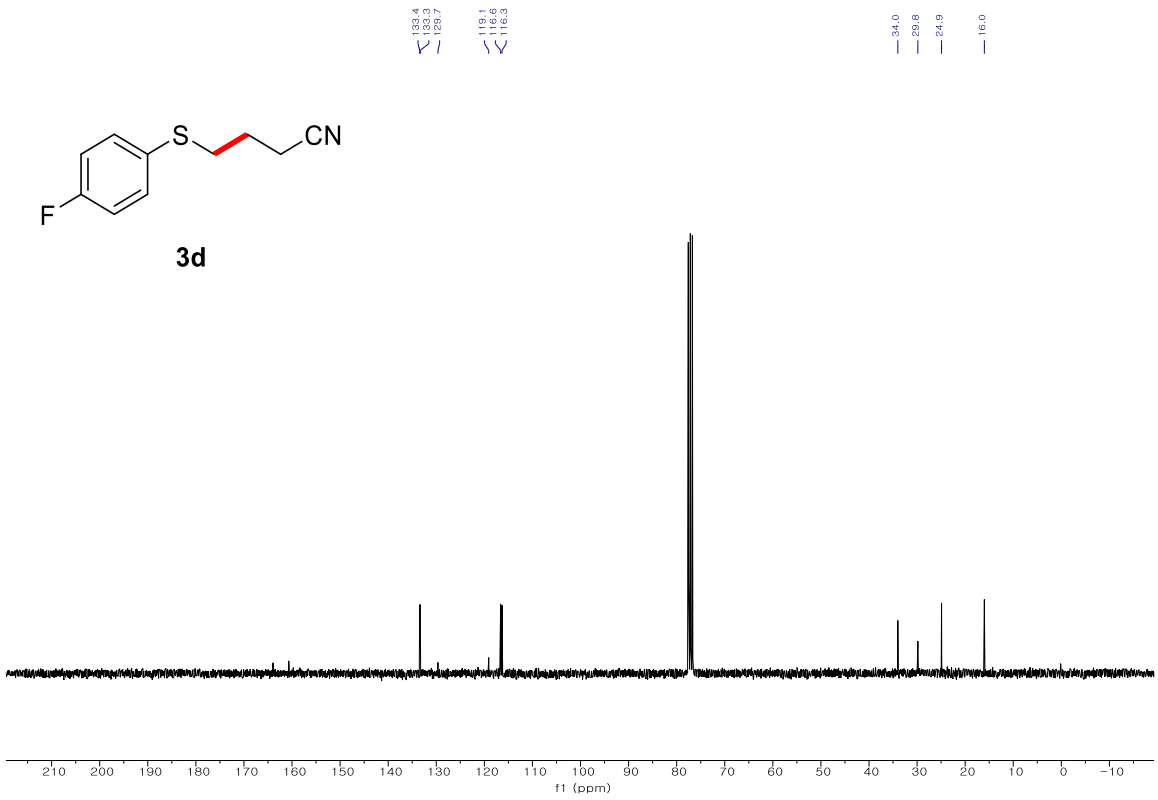
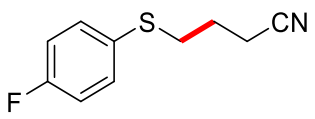


^{1}H-NMR (300 MHz, Chloroform-d) of **3d**



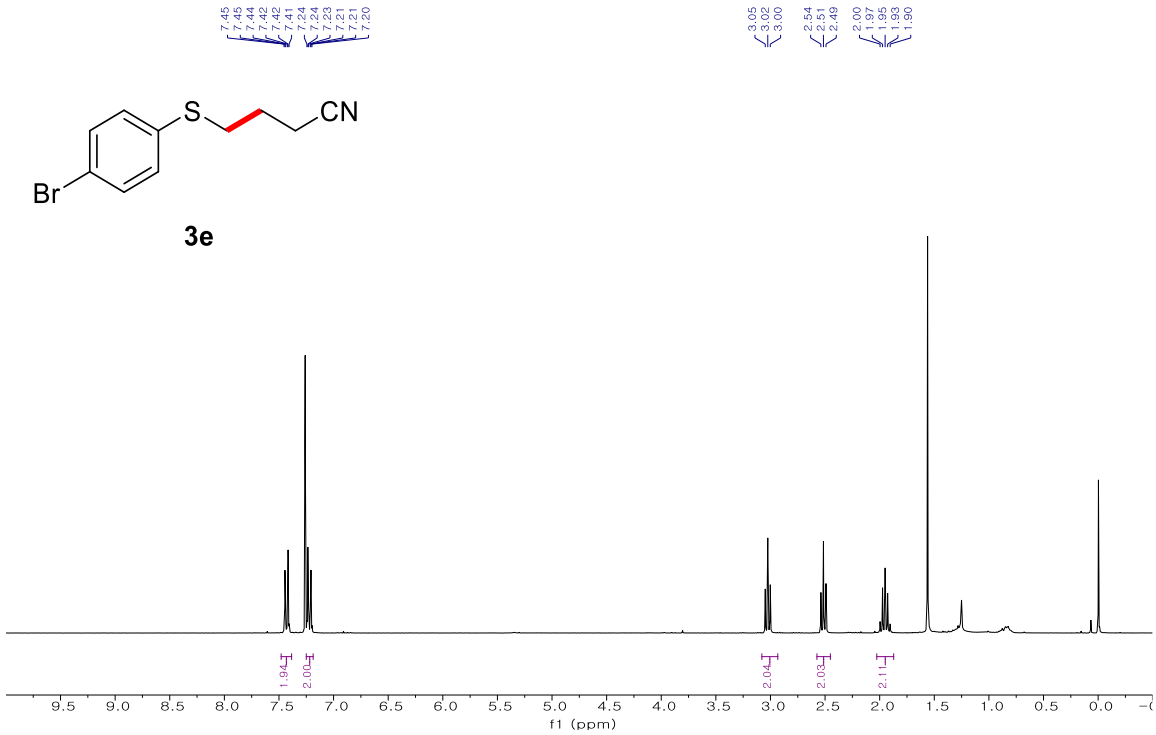
^{13}C-NMR (75 MHz, Chloroform-d) of **3d**



3d

^{19}F-NMR (MHz, Chloroform-d) of **3d**

^{13}C-NMR (75 MHz, Chloroform-d) of **3e**



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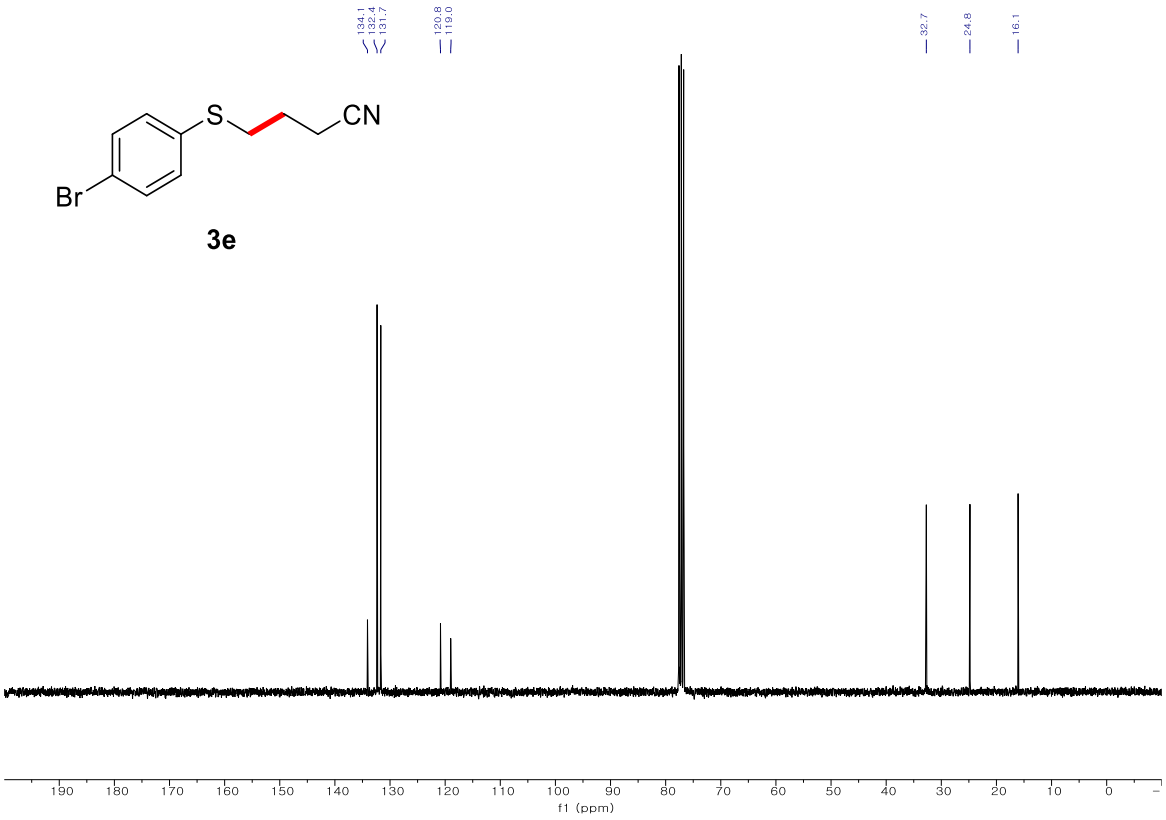
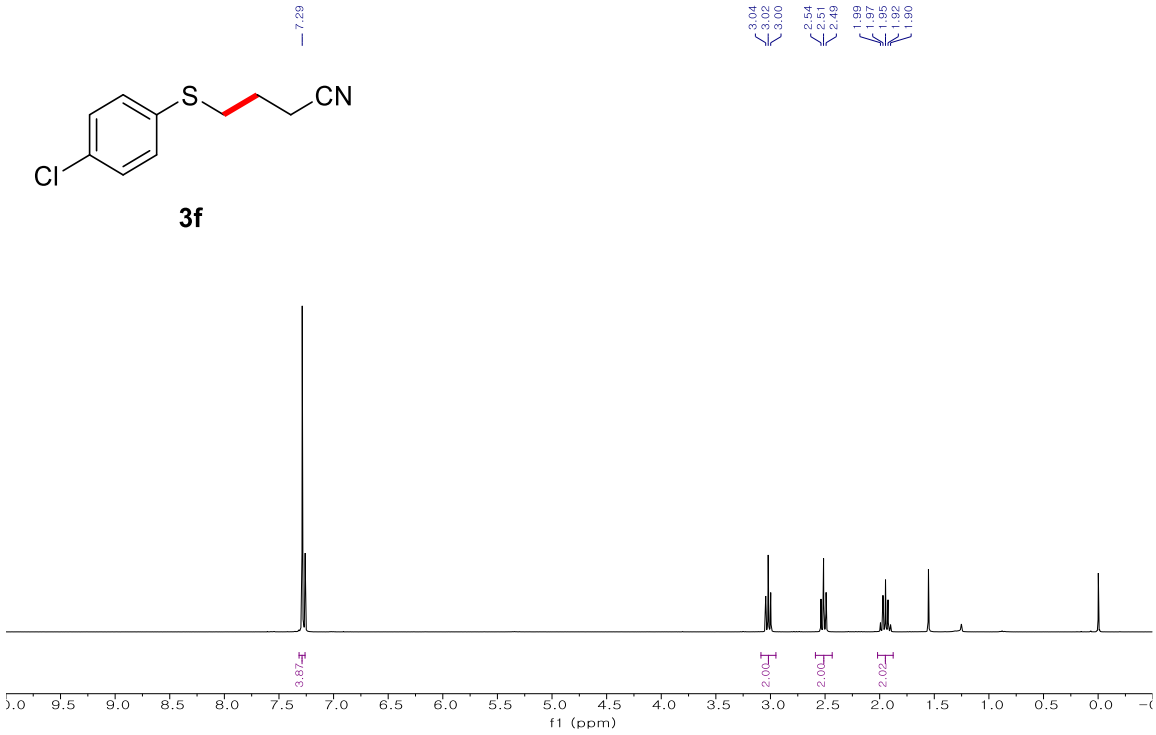
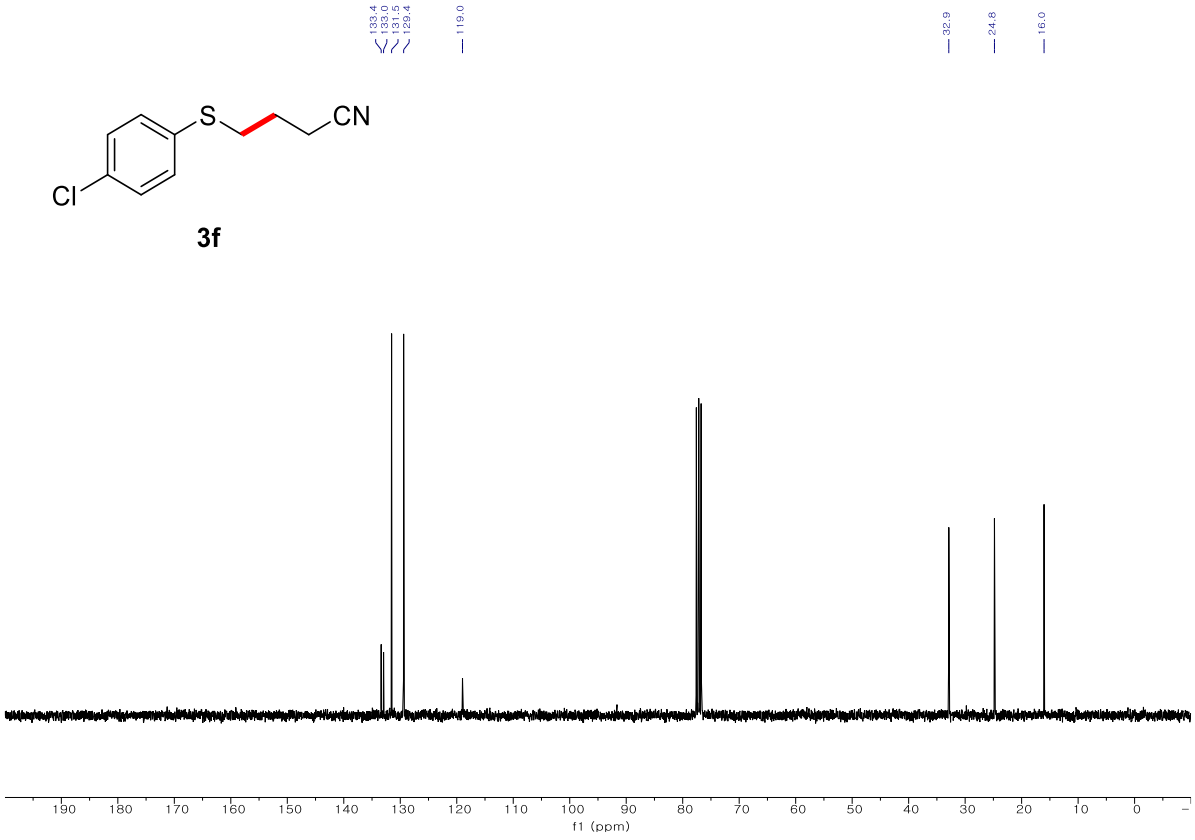


^{13}C-NMR (75 MHz, Chloroform-d) of **3e**



^{1}H-NMR (300 MHz, Chloroform-d) of **3f**



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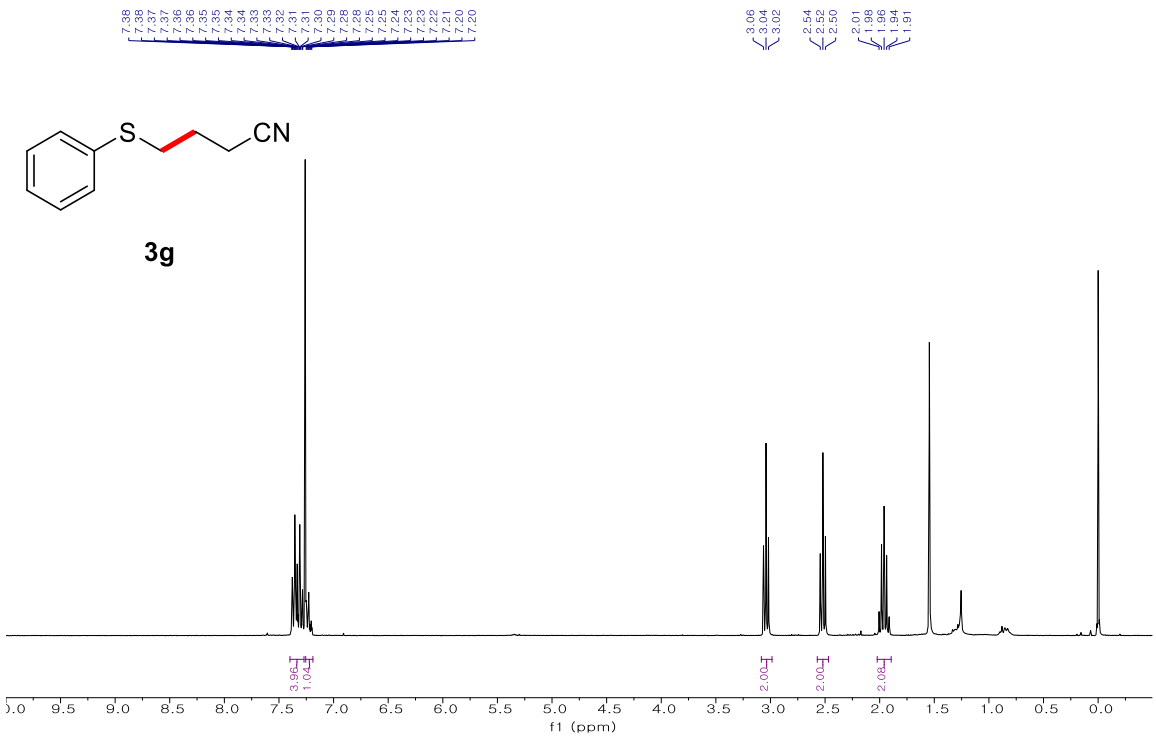
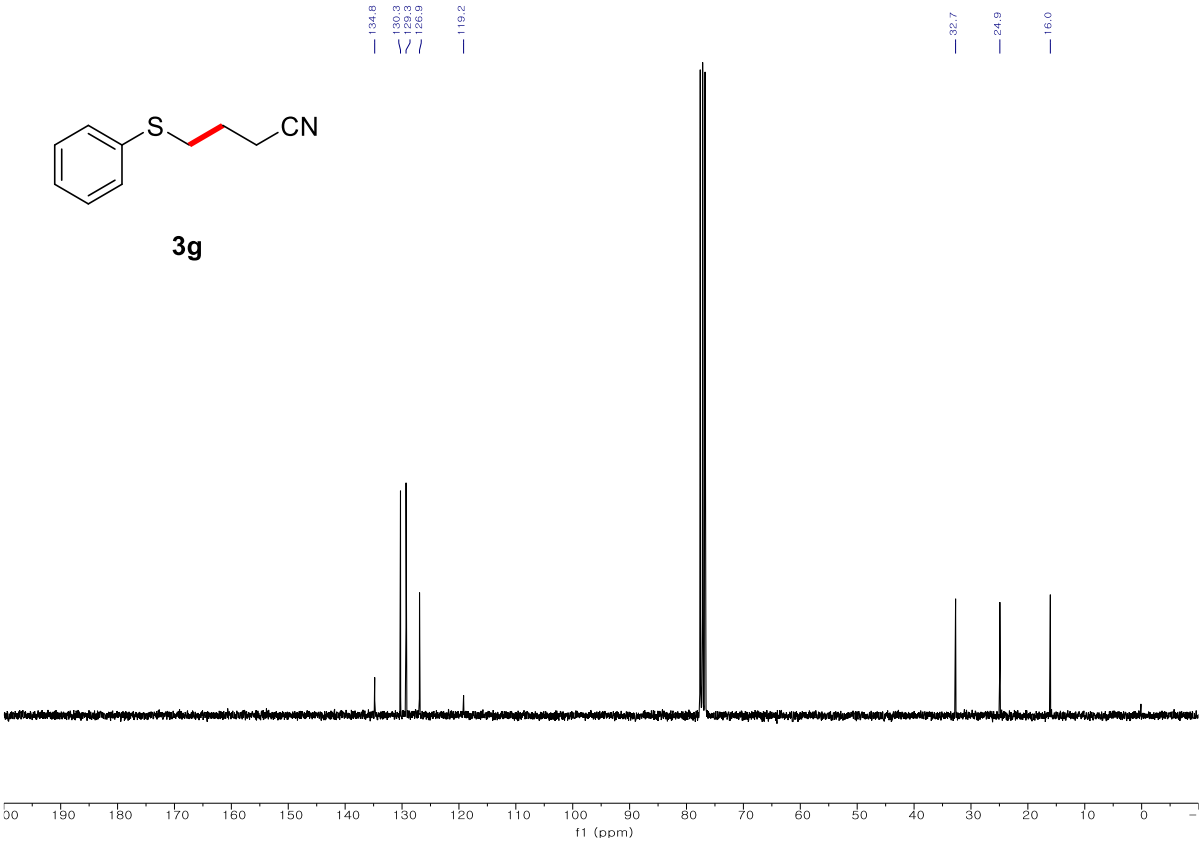
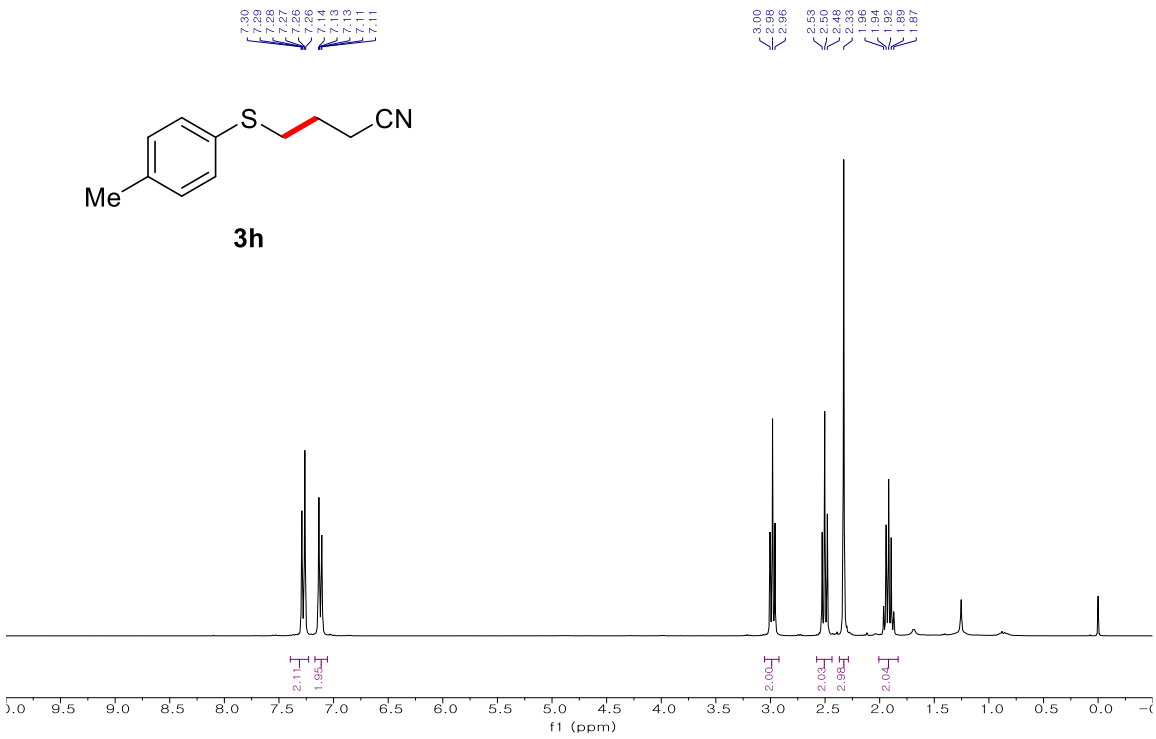


^{1}H-NMR (300 MHz, Chloroform-d) of **3g**



^{13}C-NMR (75 MHz, Chloroform-d) of **3g**



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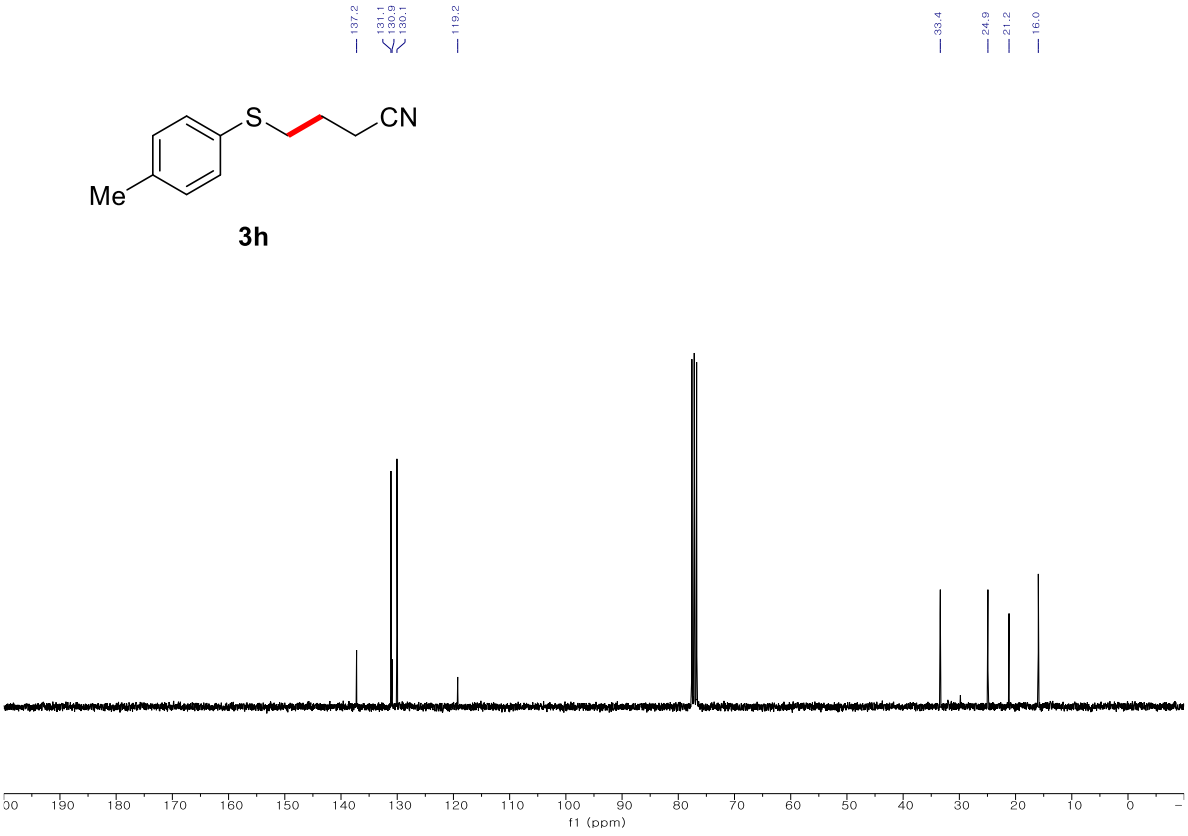

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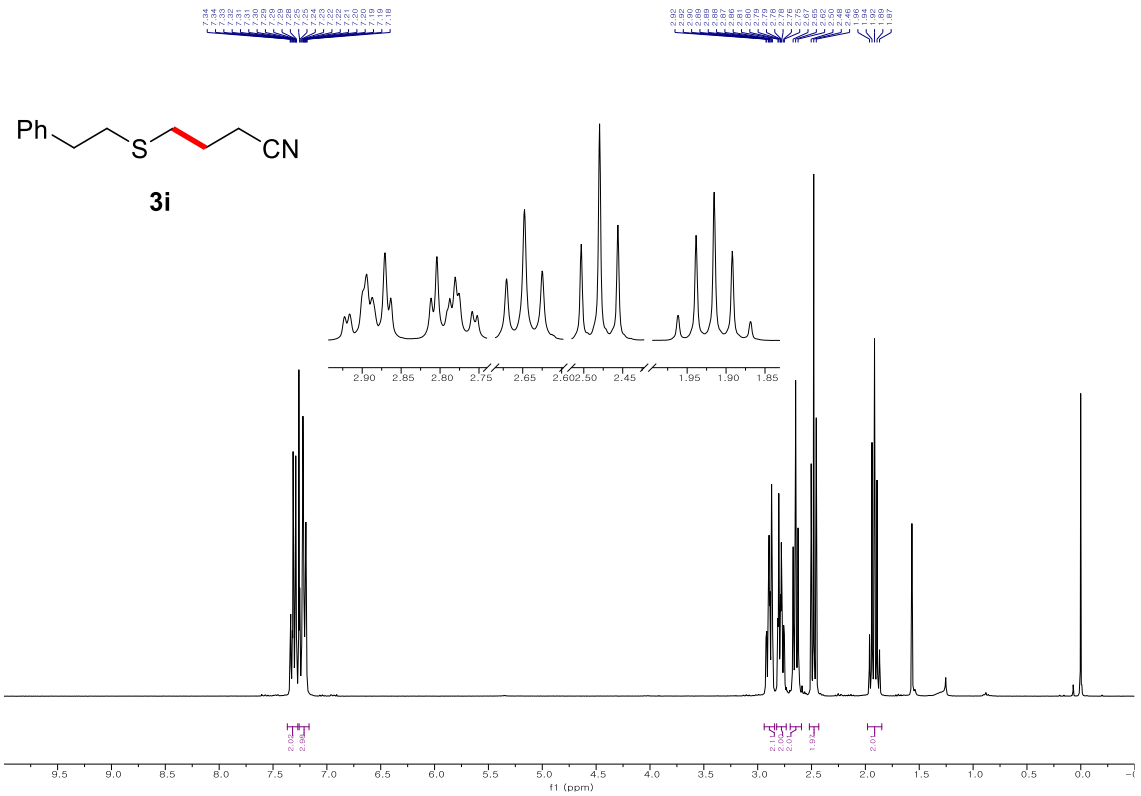
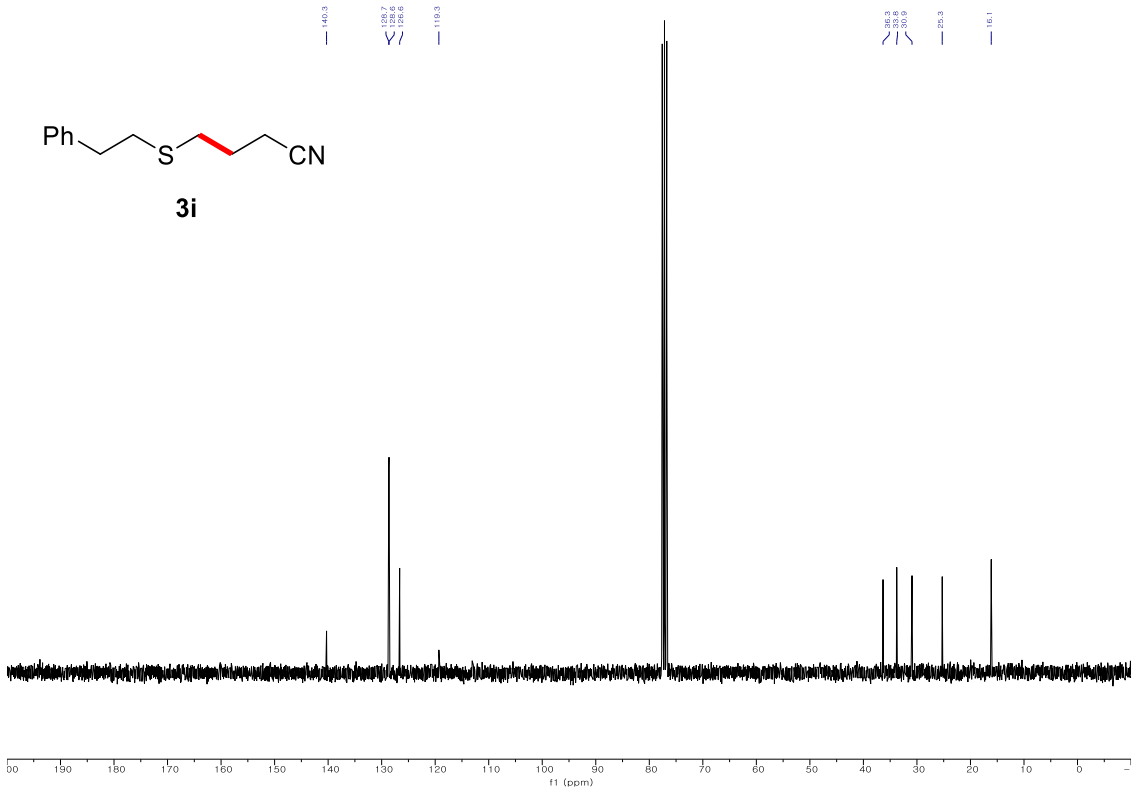


^{1}H-NMR (300 MHz, Chloroform-d) of **3i**



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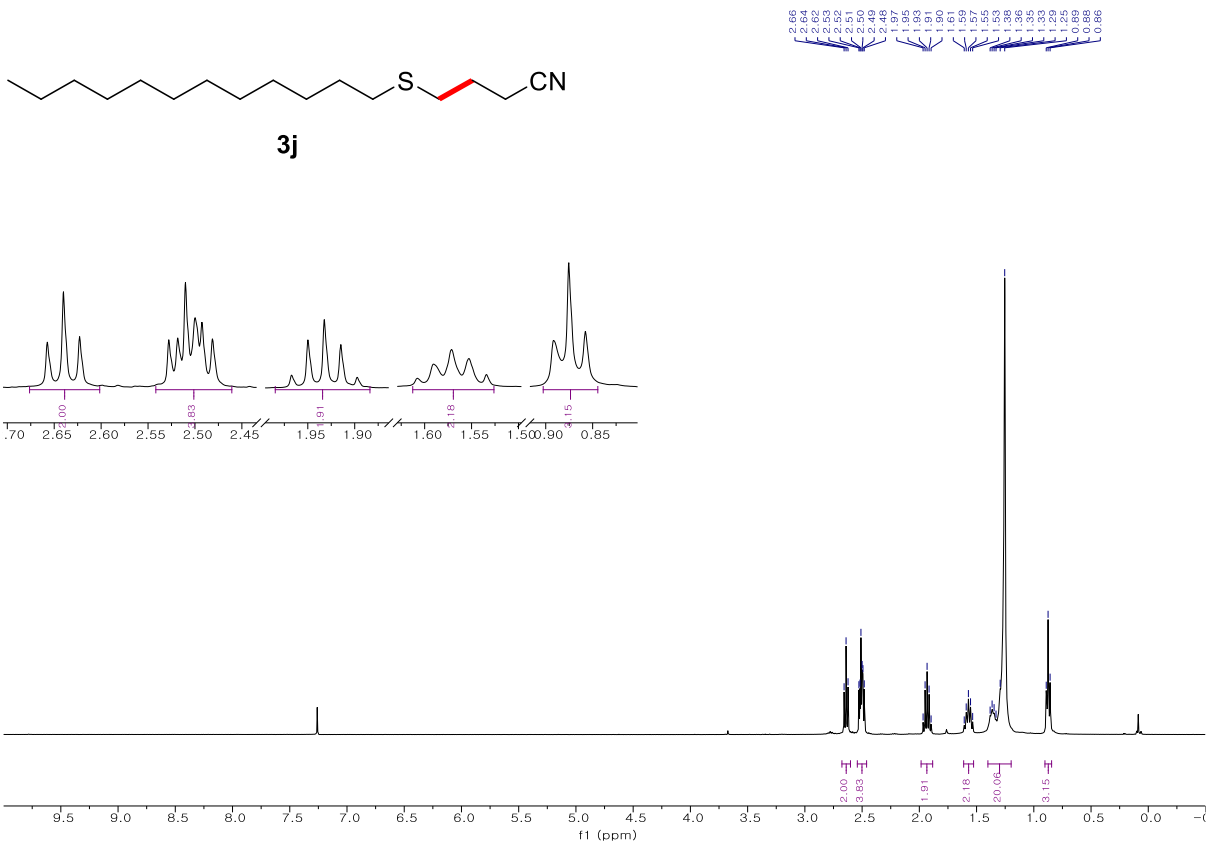

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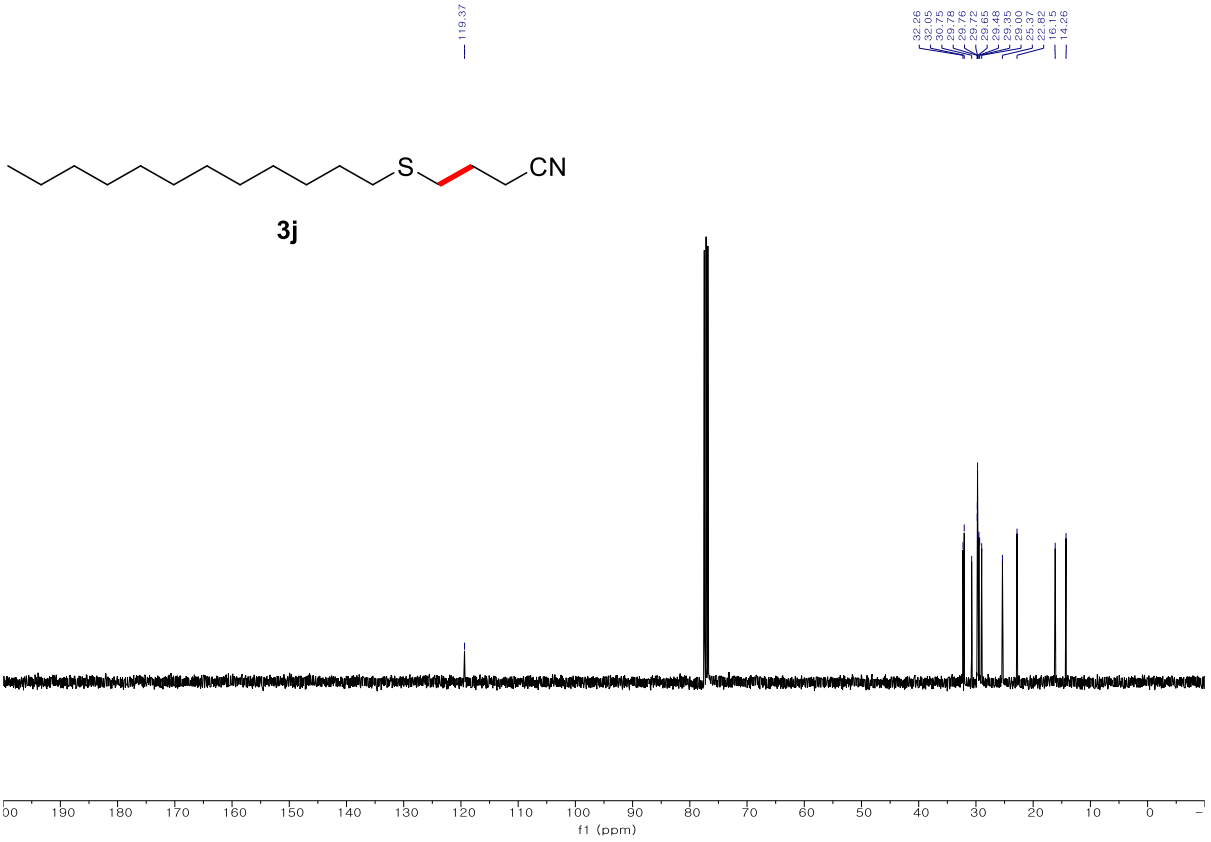
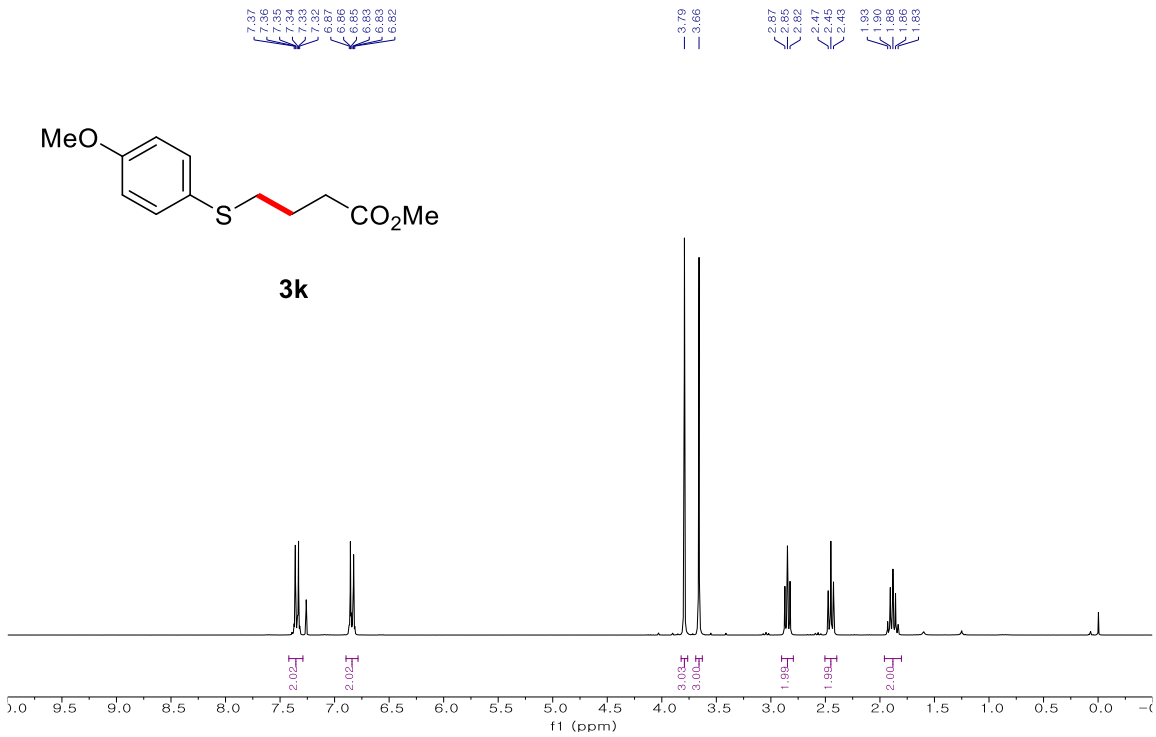
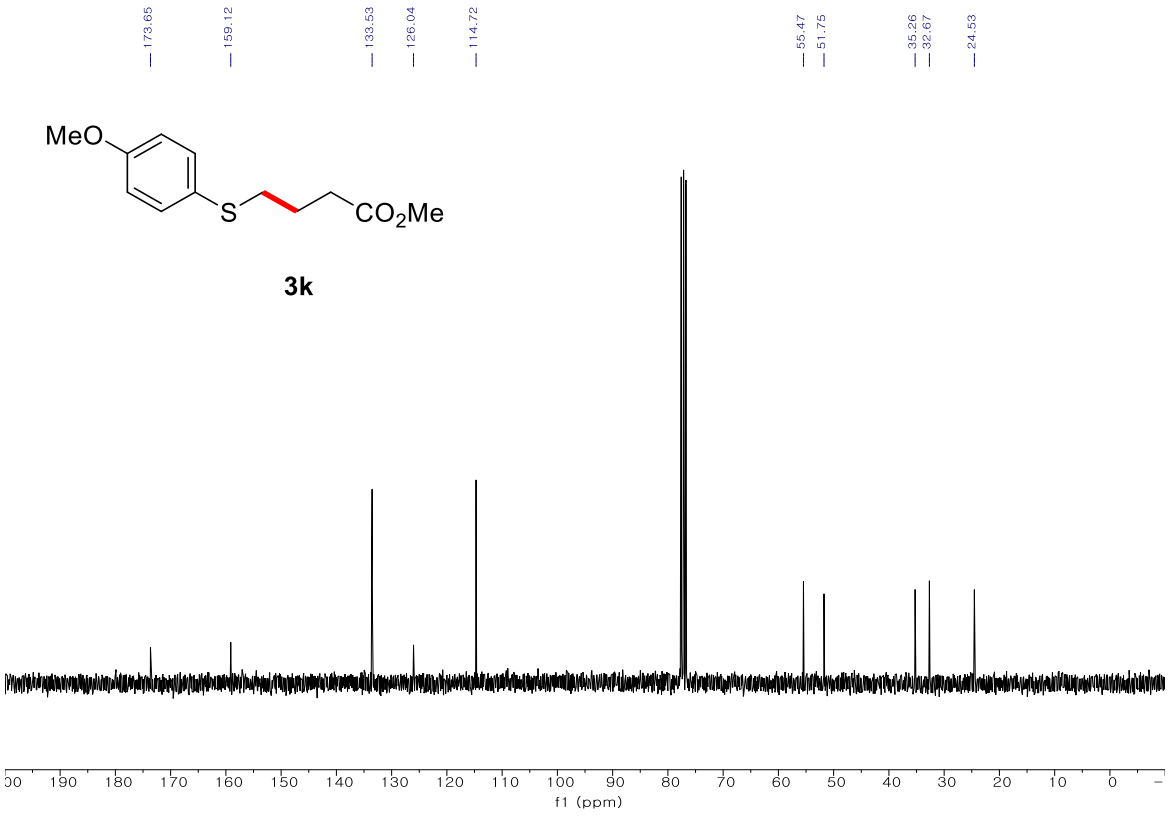


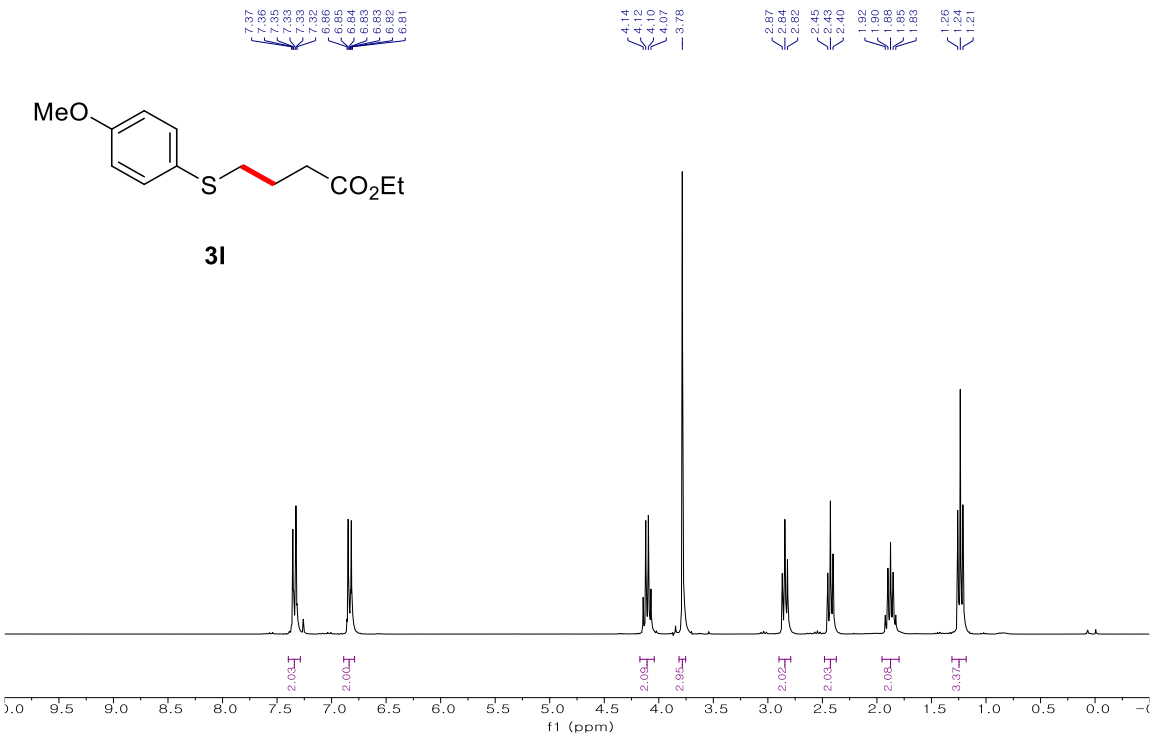
^{13}C-NMR (101 MHz, Chloroform-d) of **3j**



^{1}H-NMR (300 MHz, Chloroform-d) of **3k**



^{13}C-NMR (75 MHz, Chloroform-d) of **3k**



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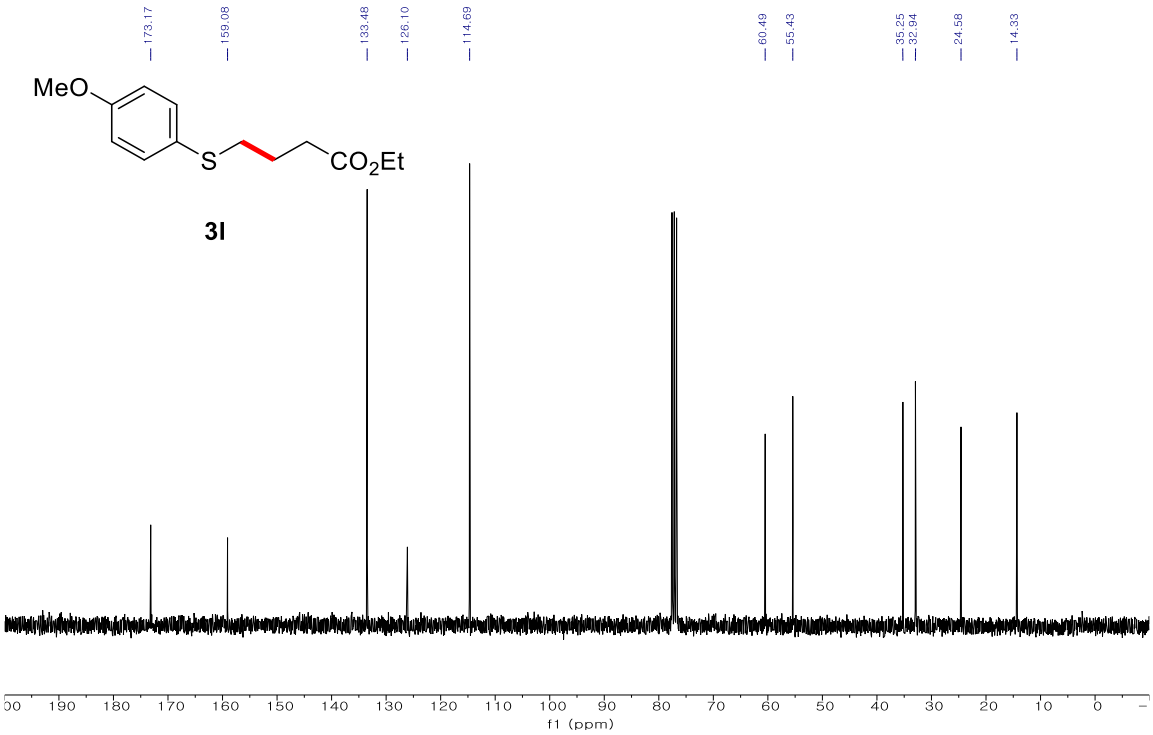

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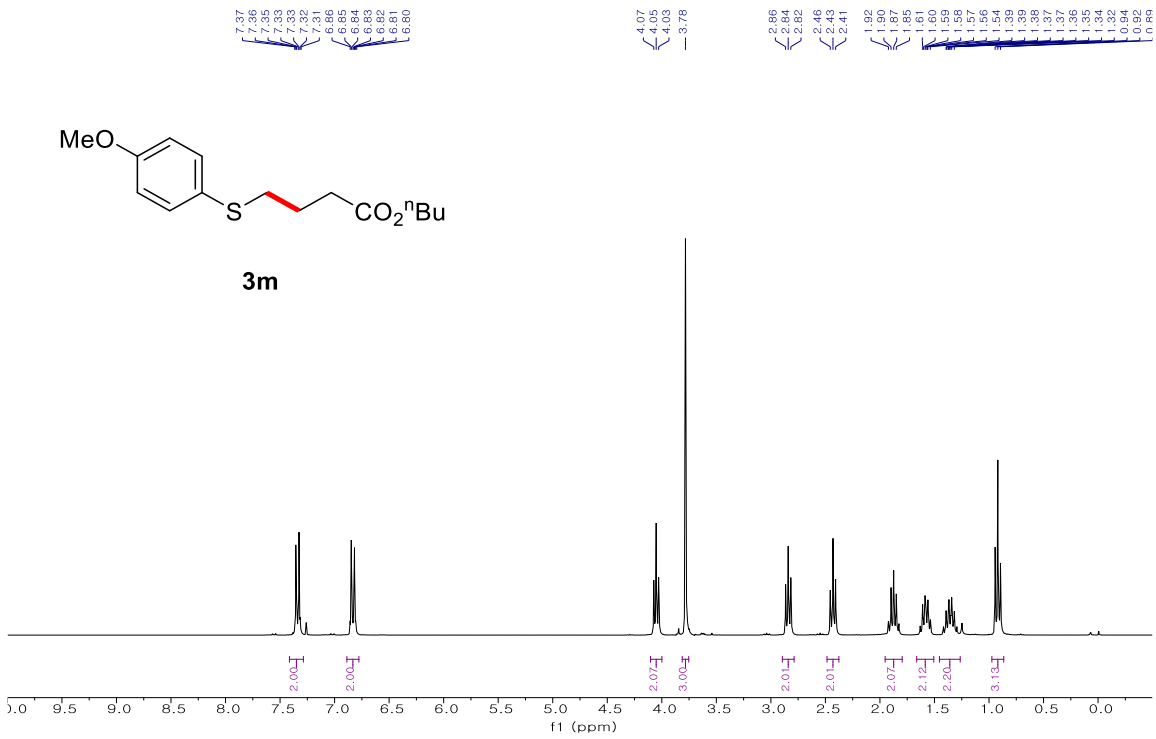

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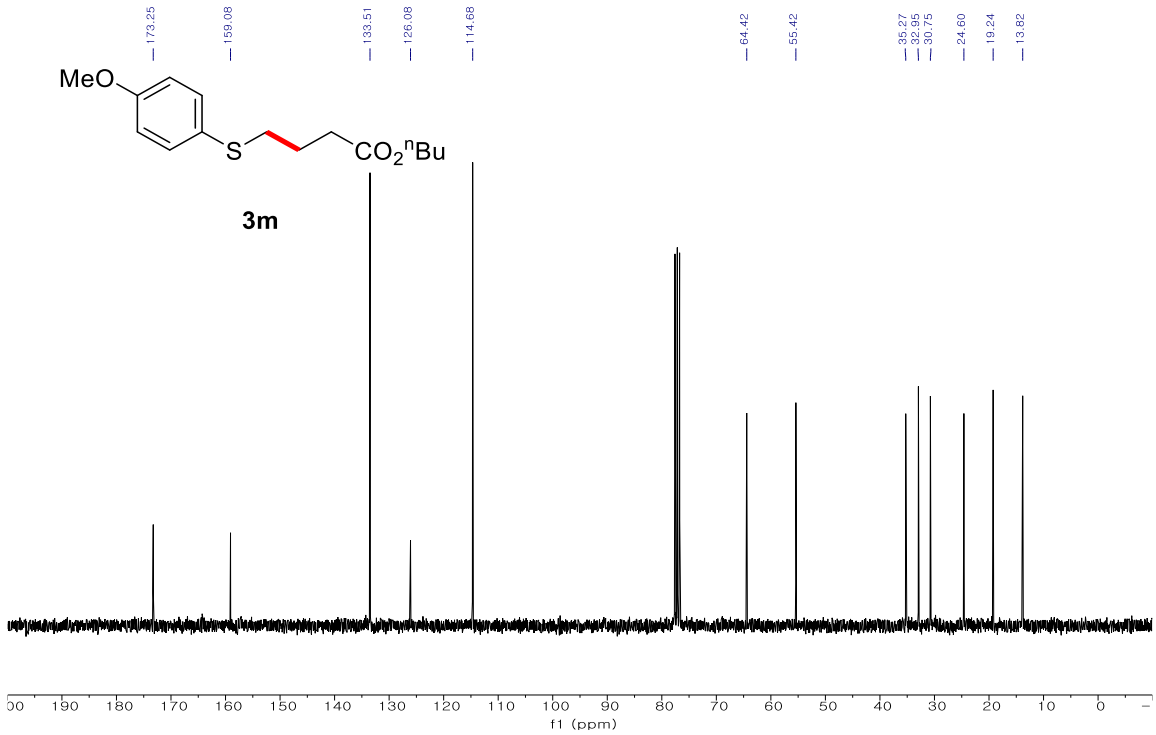
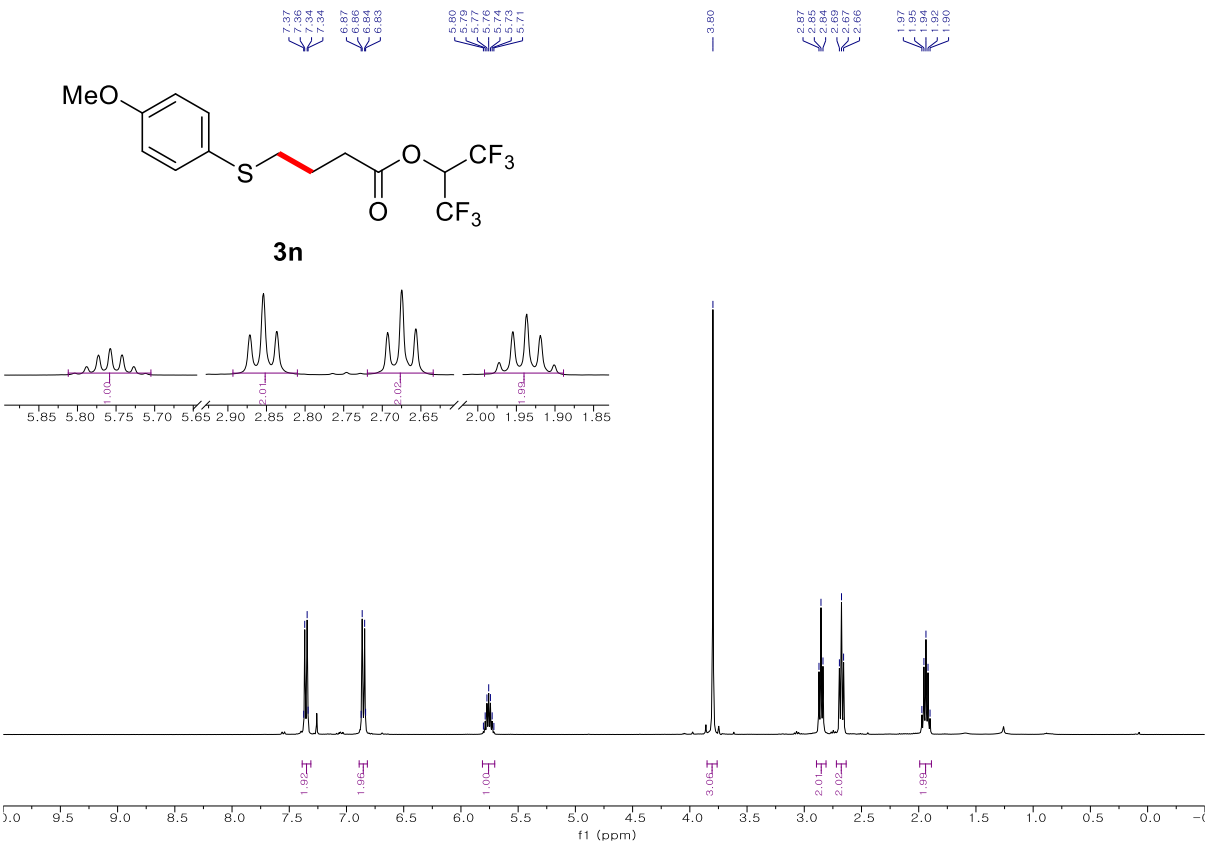
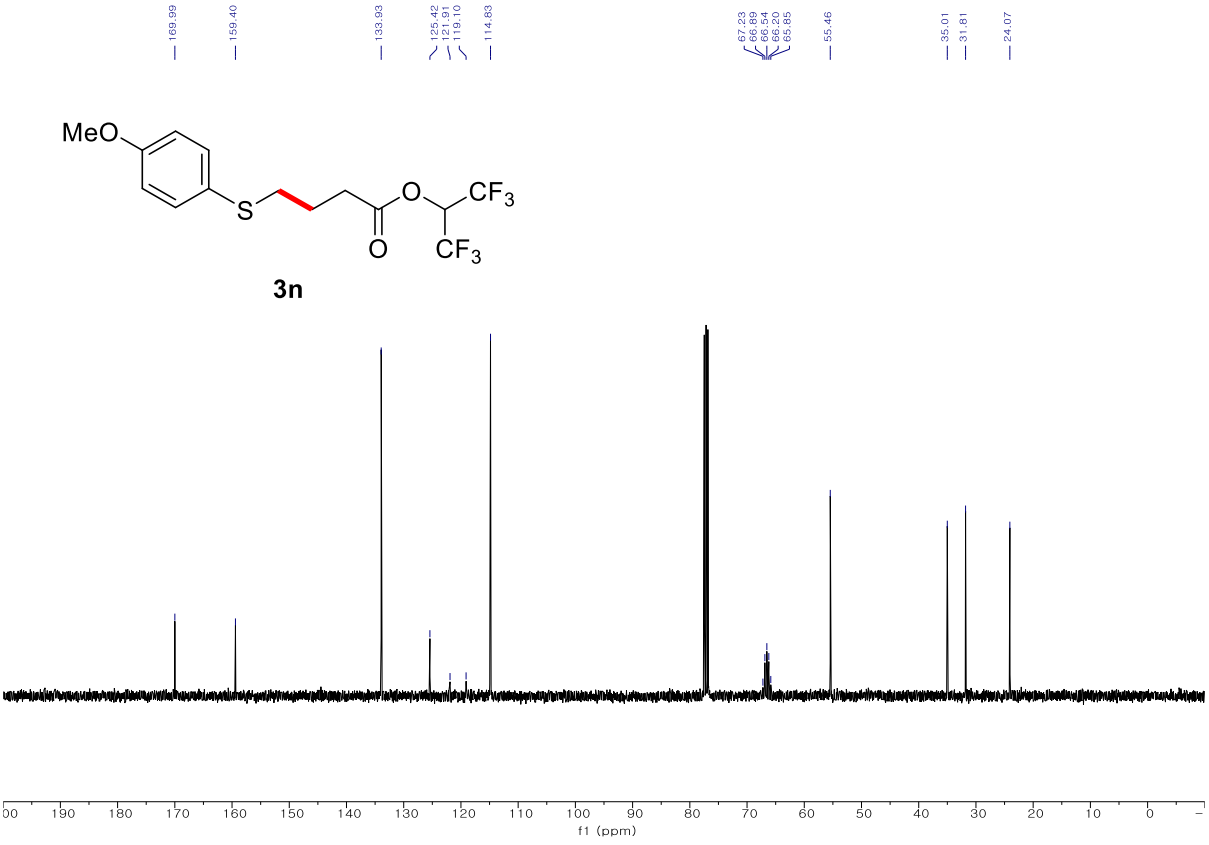


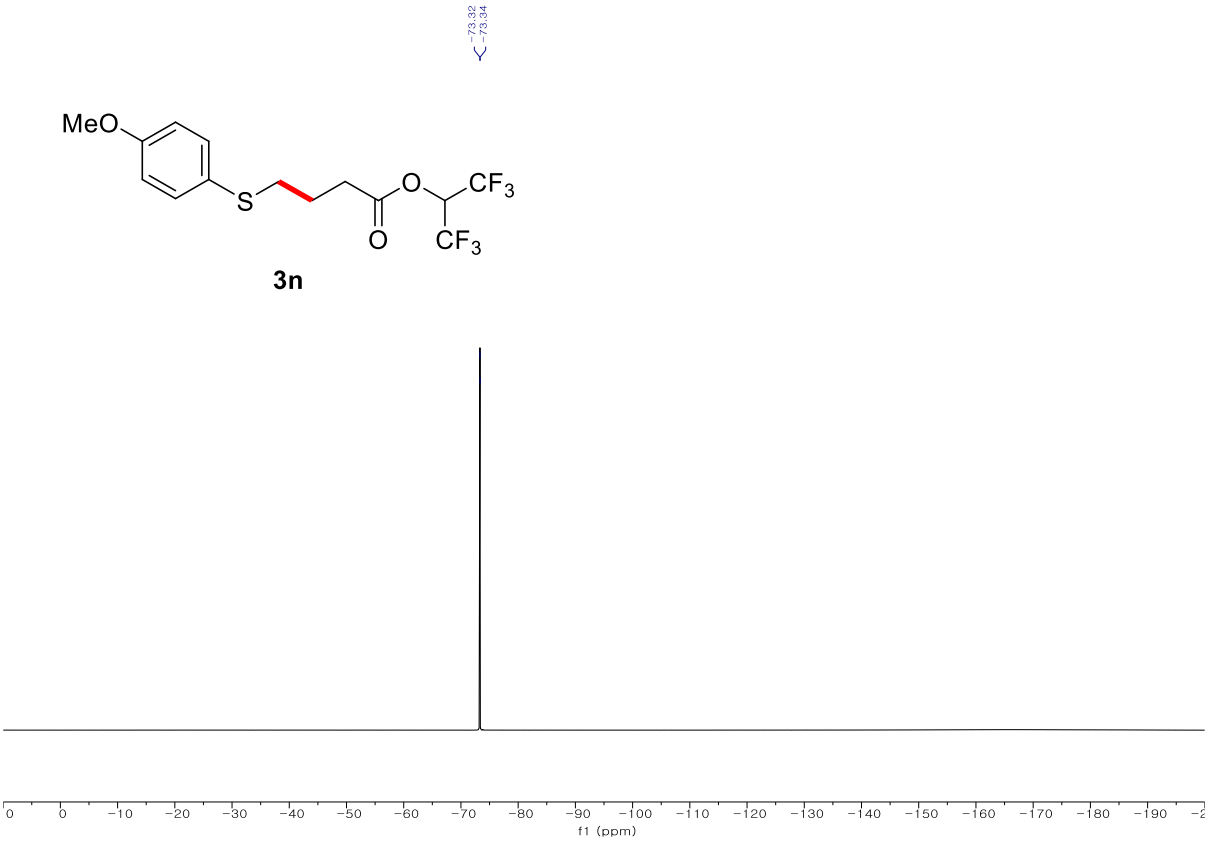
^{13}C-NMR (75 MHz, Chloroform-d) of **3m**



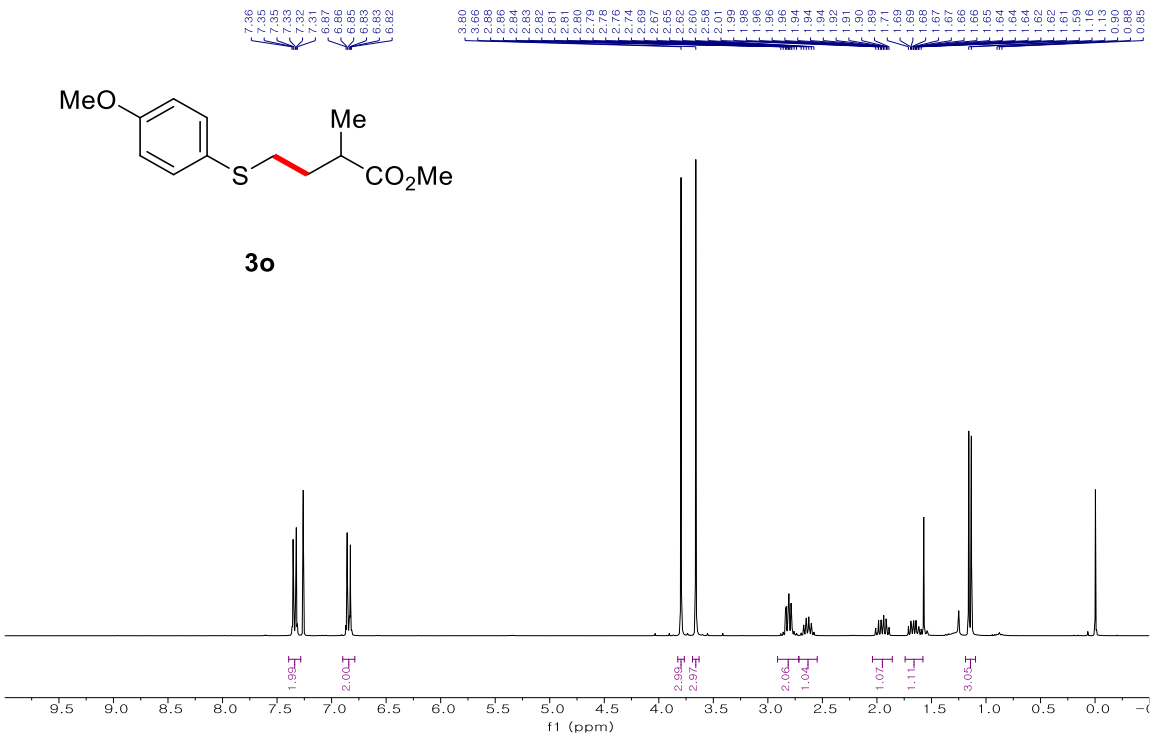
^{1}H-NMR (400 MHz, Chloroform-d) of **3n**



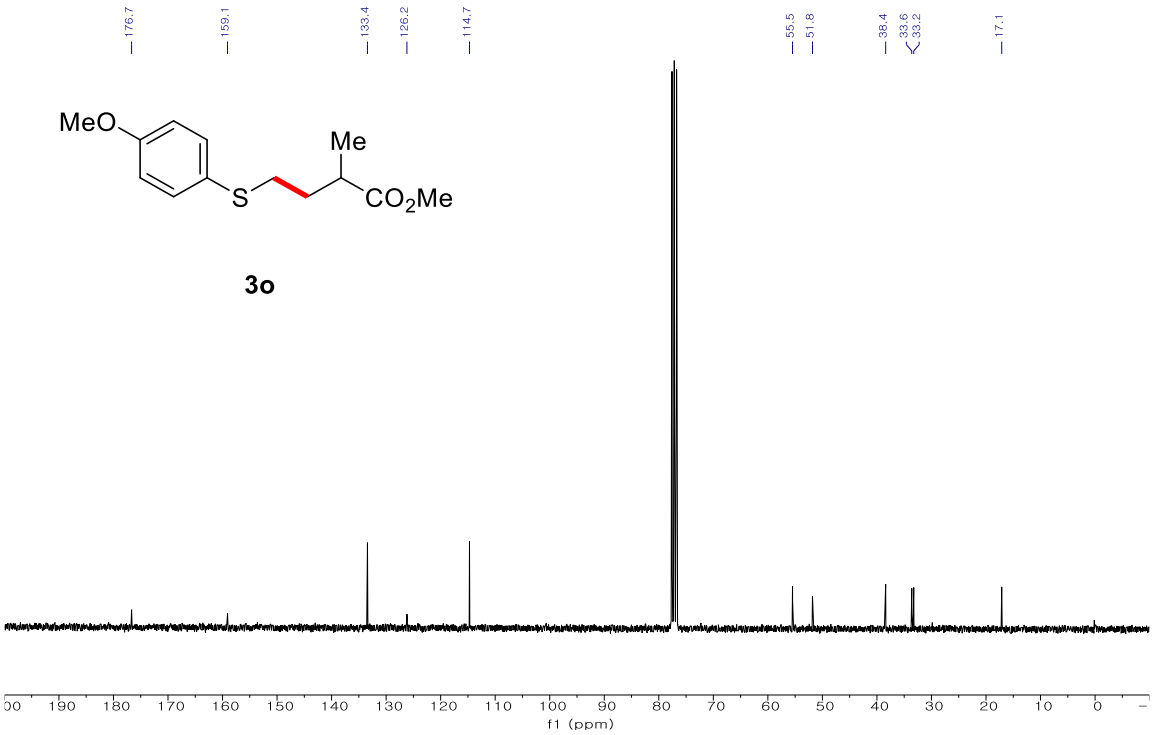
^{13}C-NMR (101 MHz, Chloroform-d) of **3n**



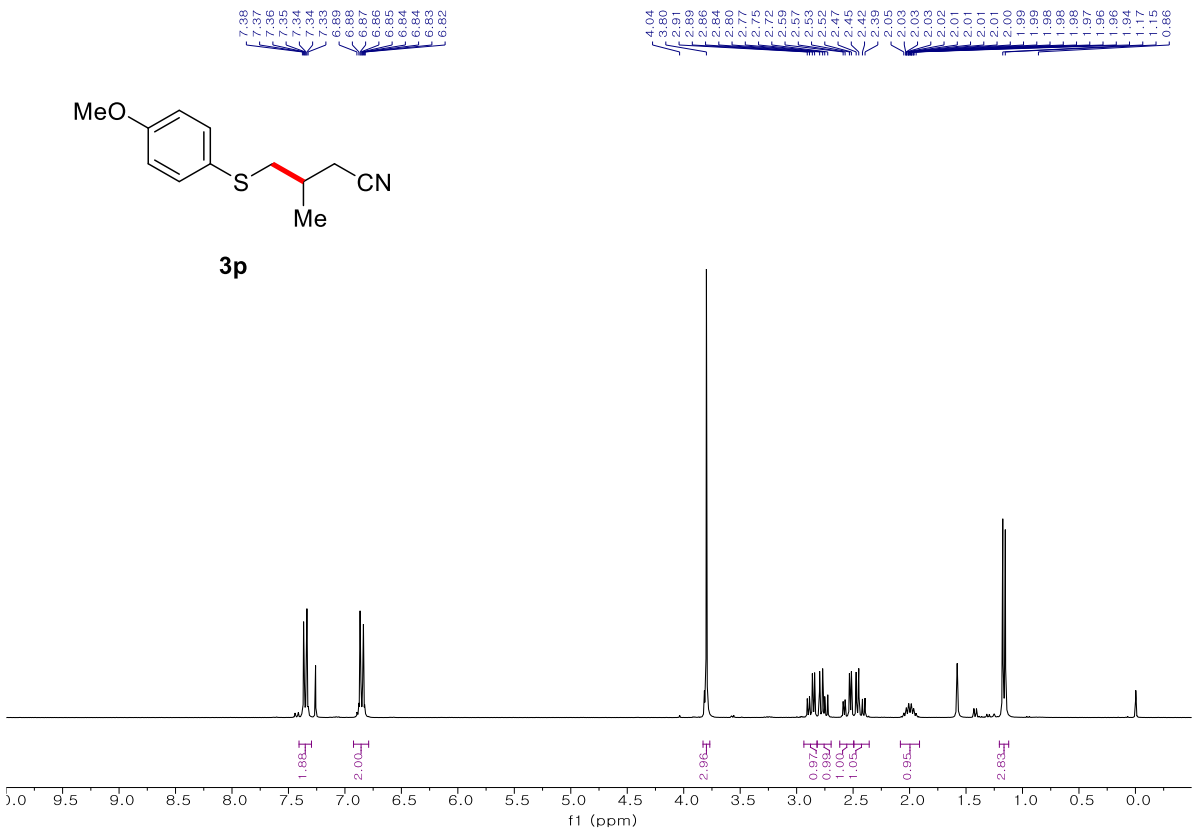
^{19}F-NMR (377 MHz, Chloroform-d) of **3n**



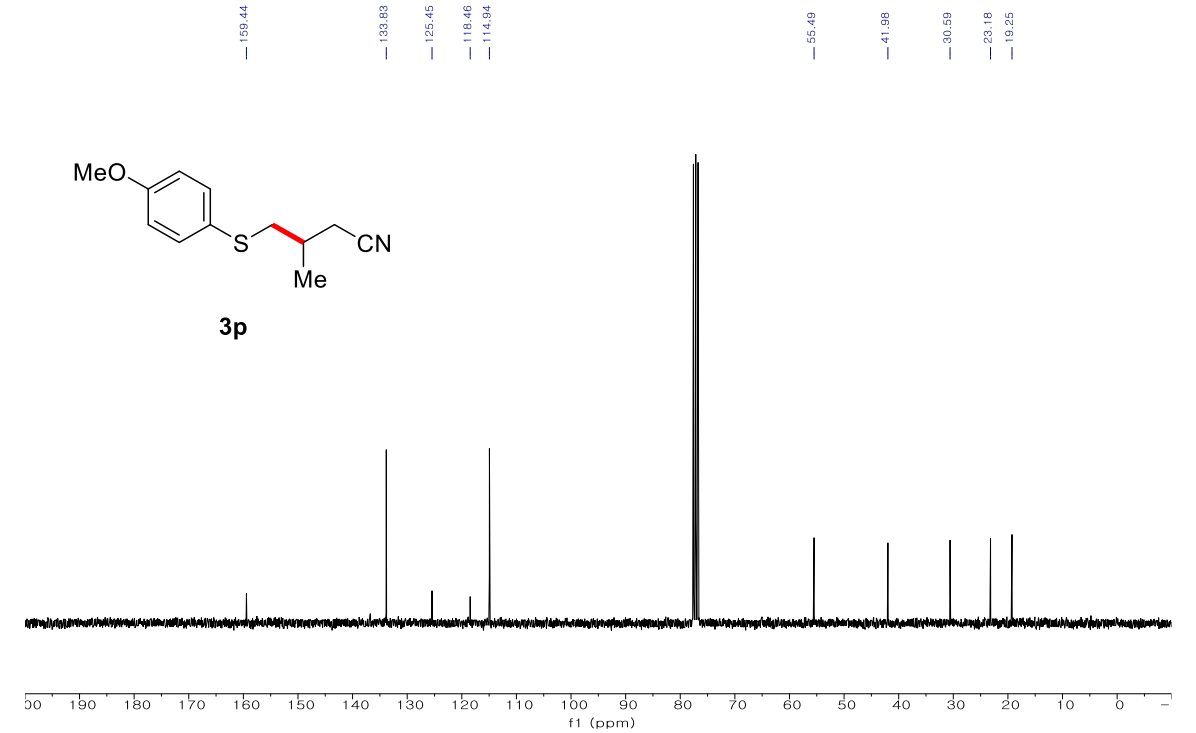
^{1}H-NMR (300 MHz, Chloroform-d) of **3o**



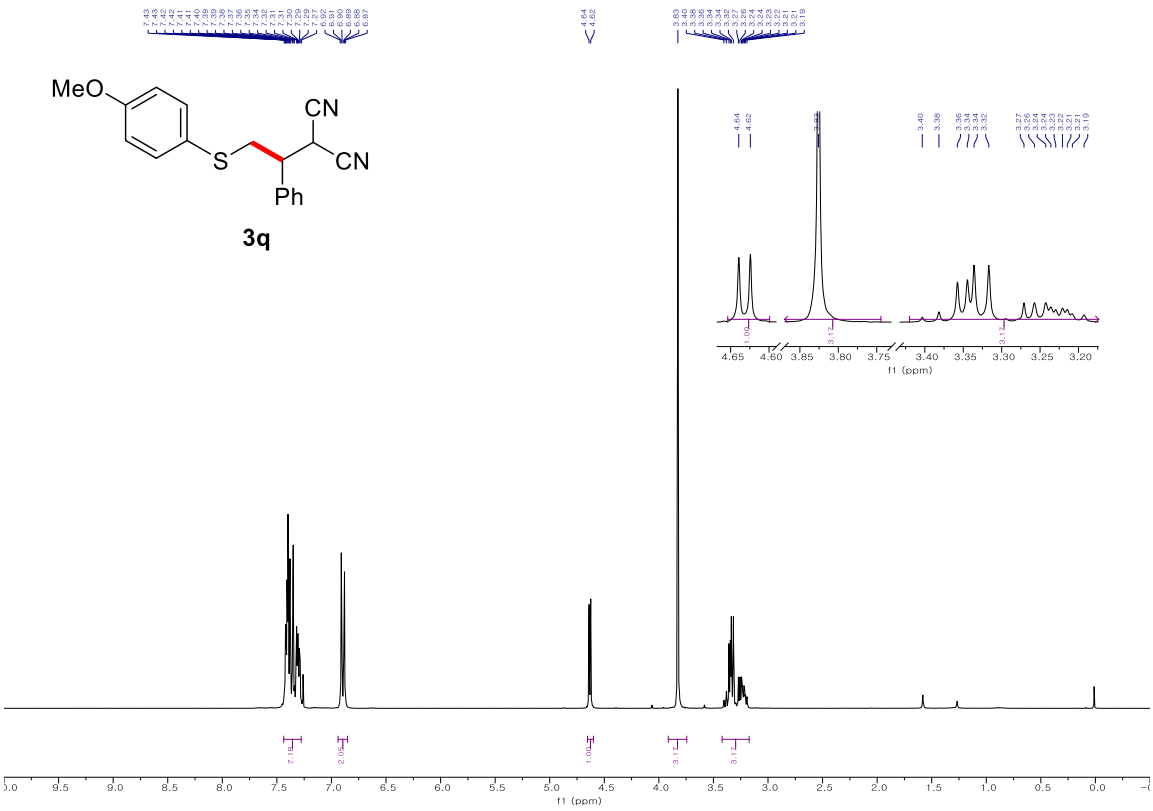
^{13}C-NMR (75 MHz, Chloroform-d) of **3o**



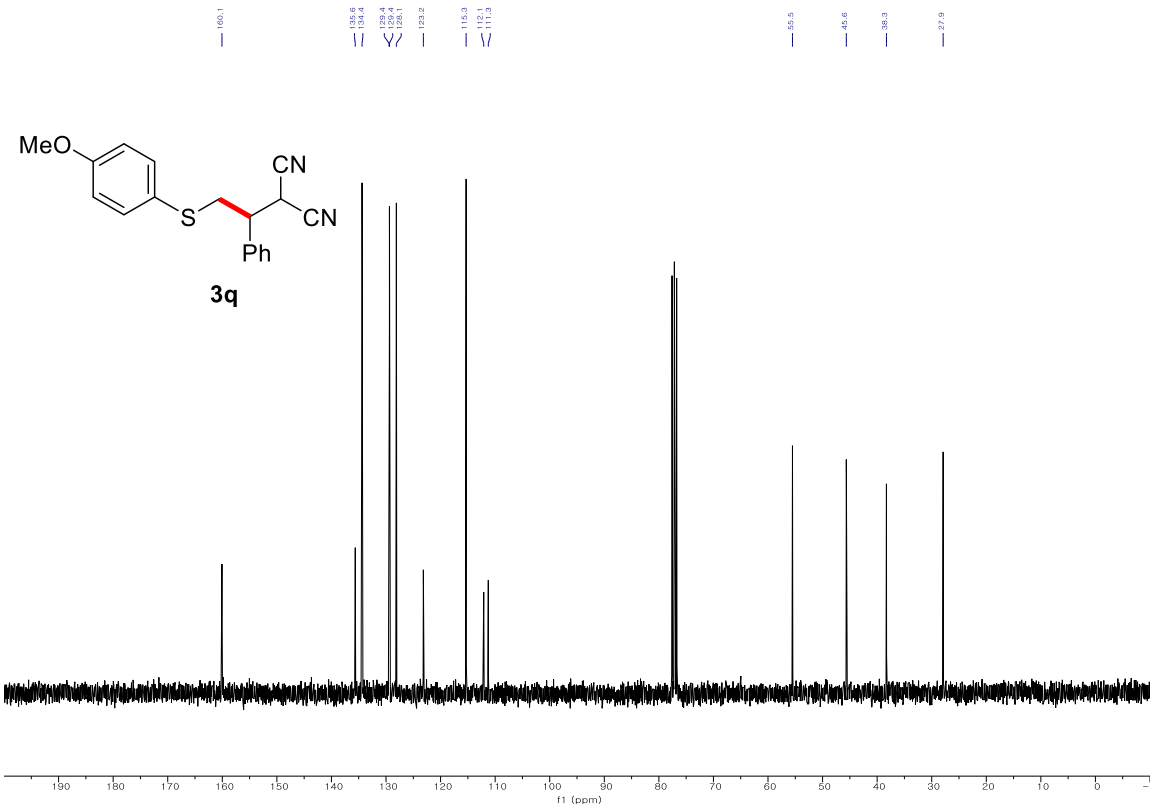
^{1}H-NMR (300 MHz, Chloroform-d) of **3p**



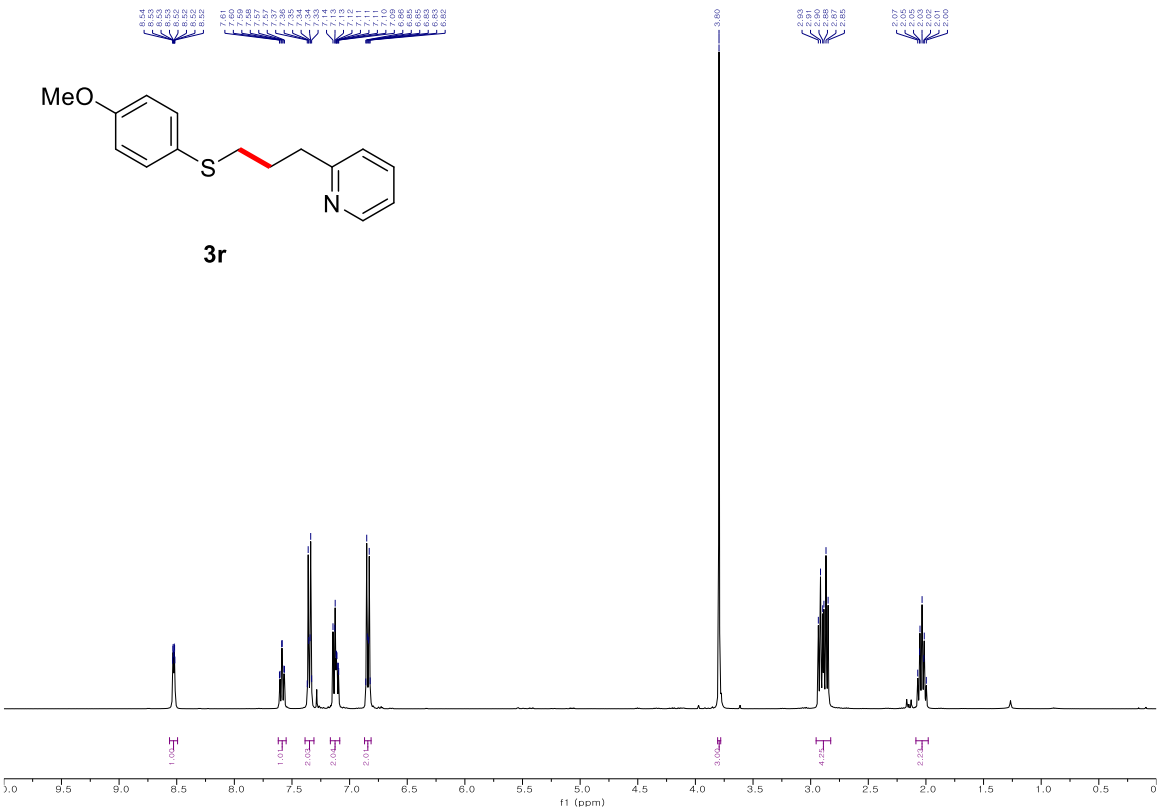
^{13}C-NMR (75 MHz, Chloroform-d) of **3p**



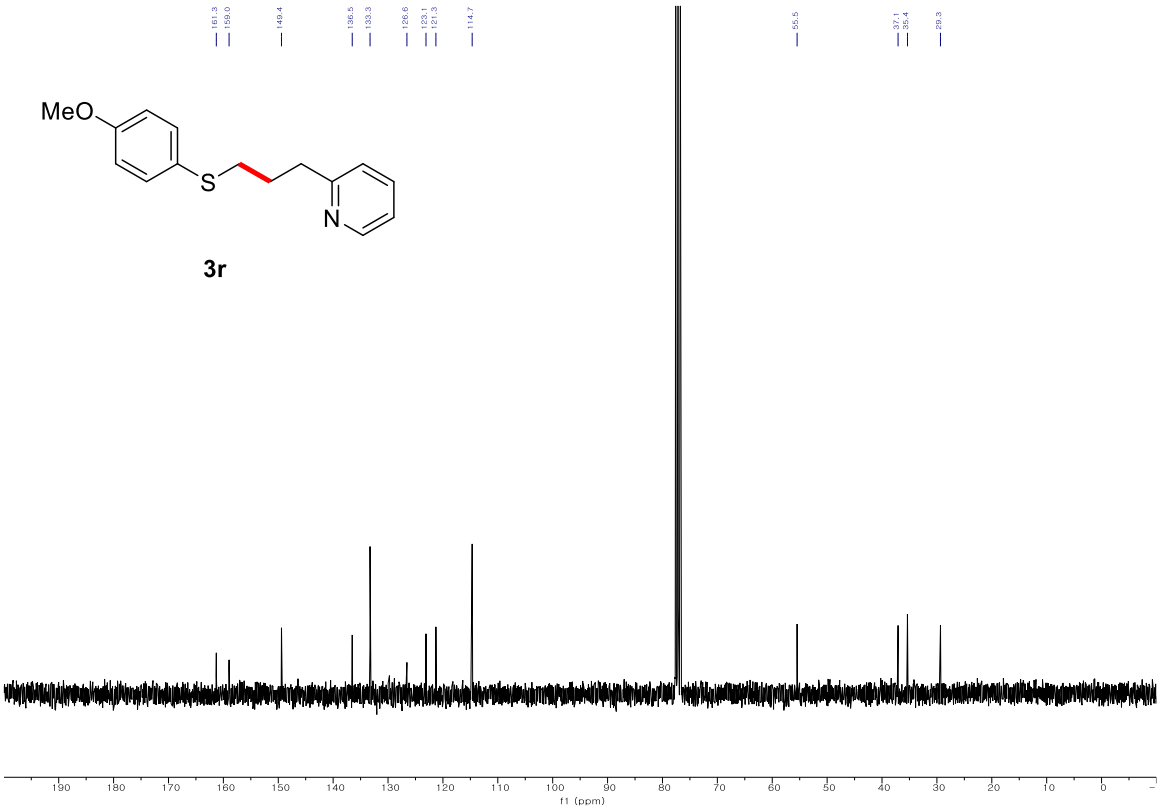
^{1}H-NMR (300 MHz, Chloroform-d) of **3q**



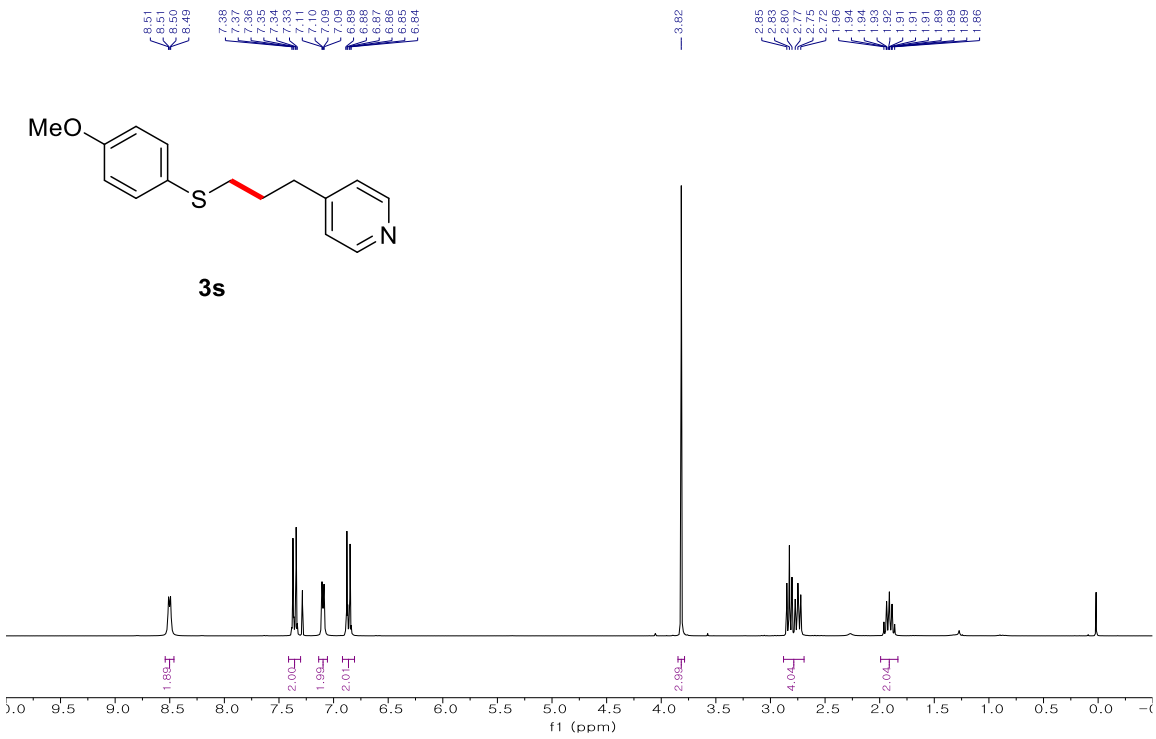
^{13}C-NMR (75 MHz, Chloroform-d) of **3q**



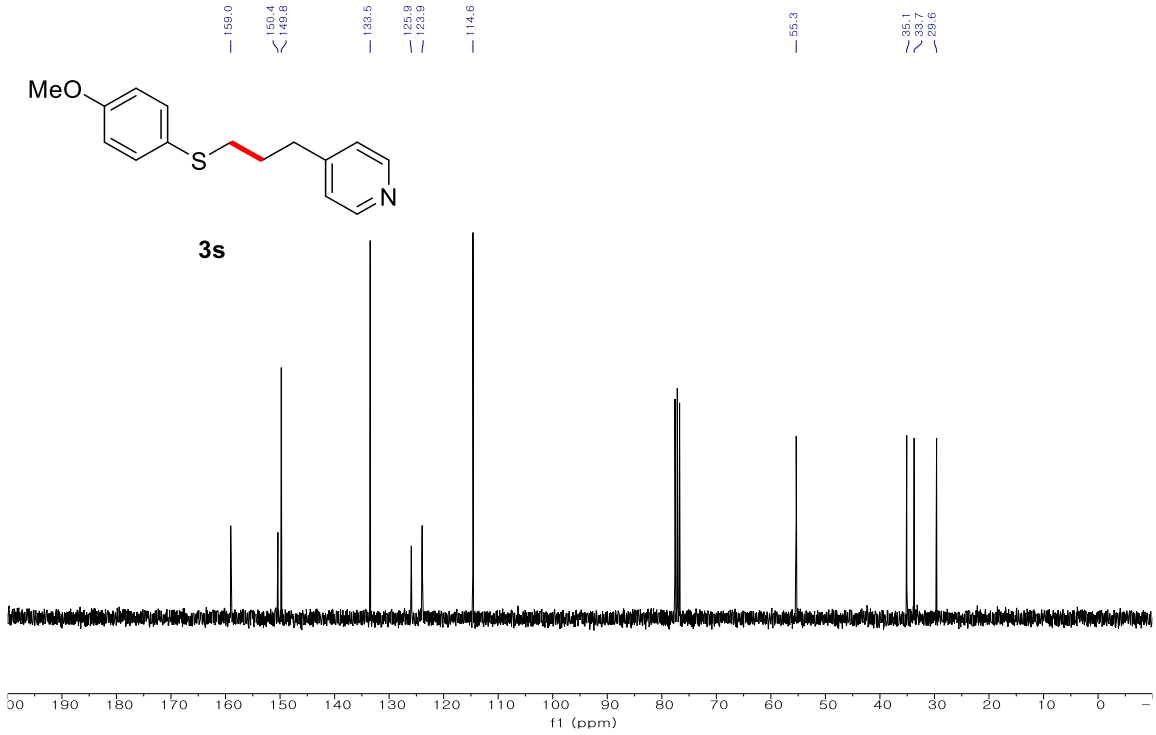
^{1}H-NMR (300 MHz, Chloroform-d) of **3r**



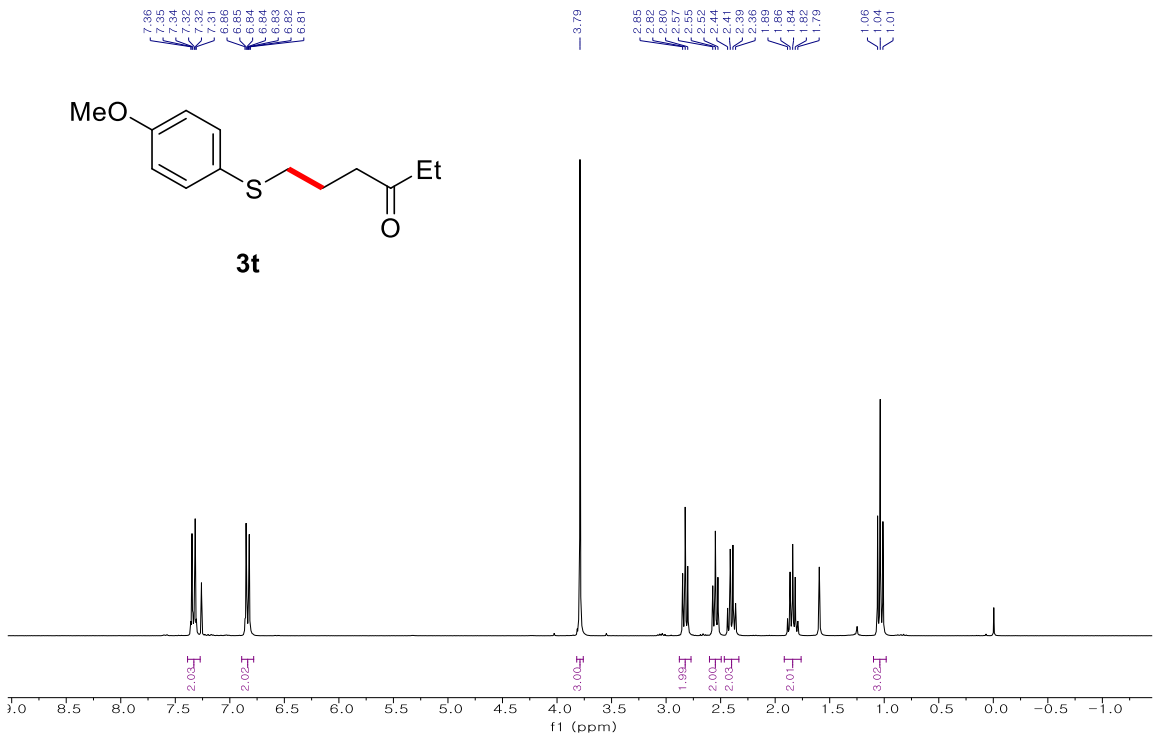
^{13}C-NMR (75 MHz, Chloroform-d) of **3r**



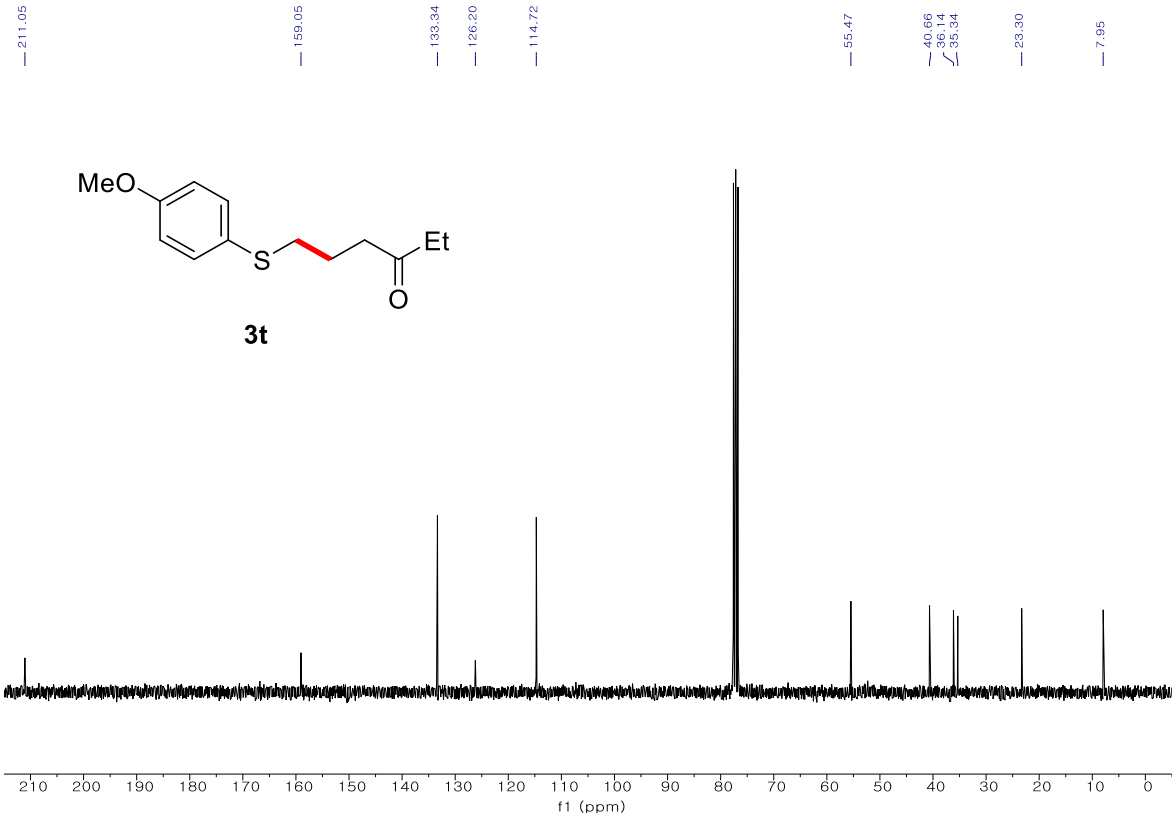
^{1}H-NMR (300 MHz, Chloroform-d) of **3s**



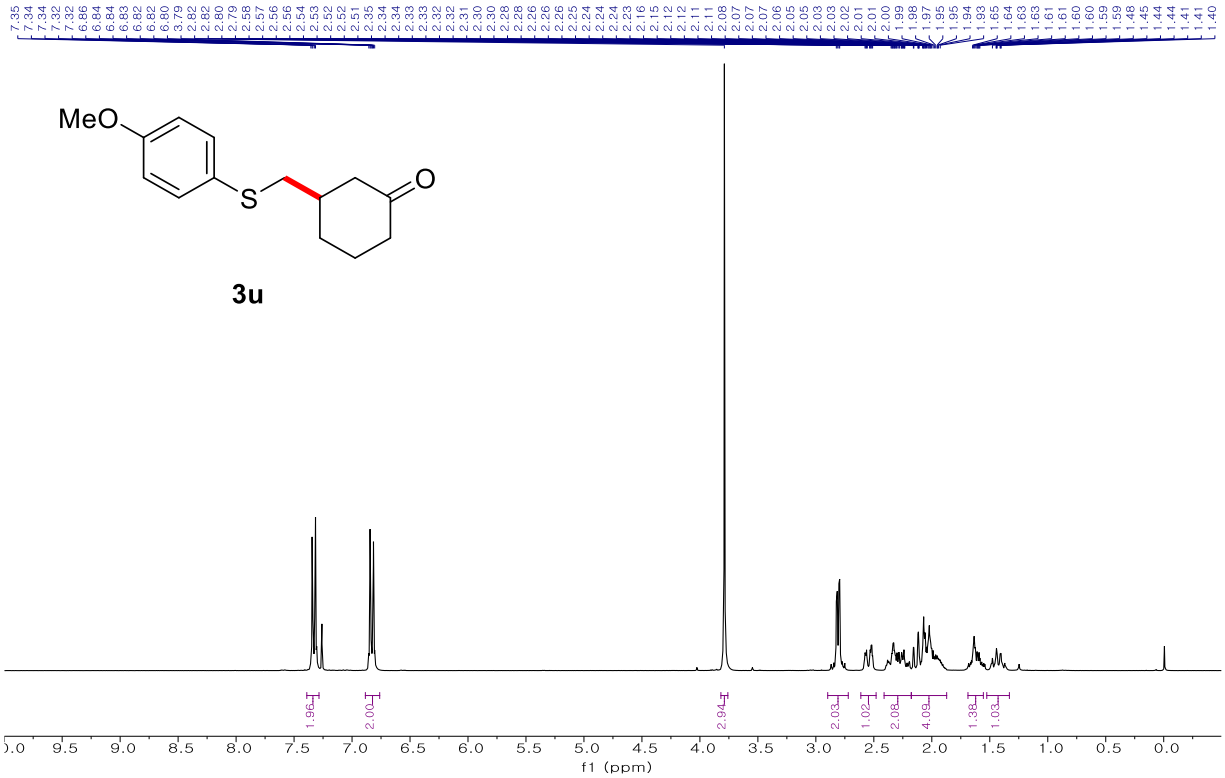
^{13}C-NMR (75 MHz, Chloroform-d) of **3s**



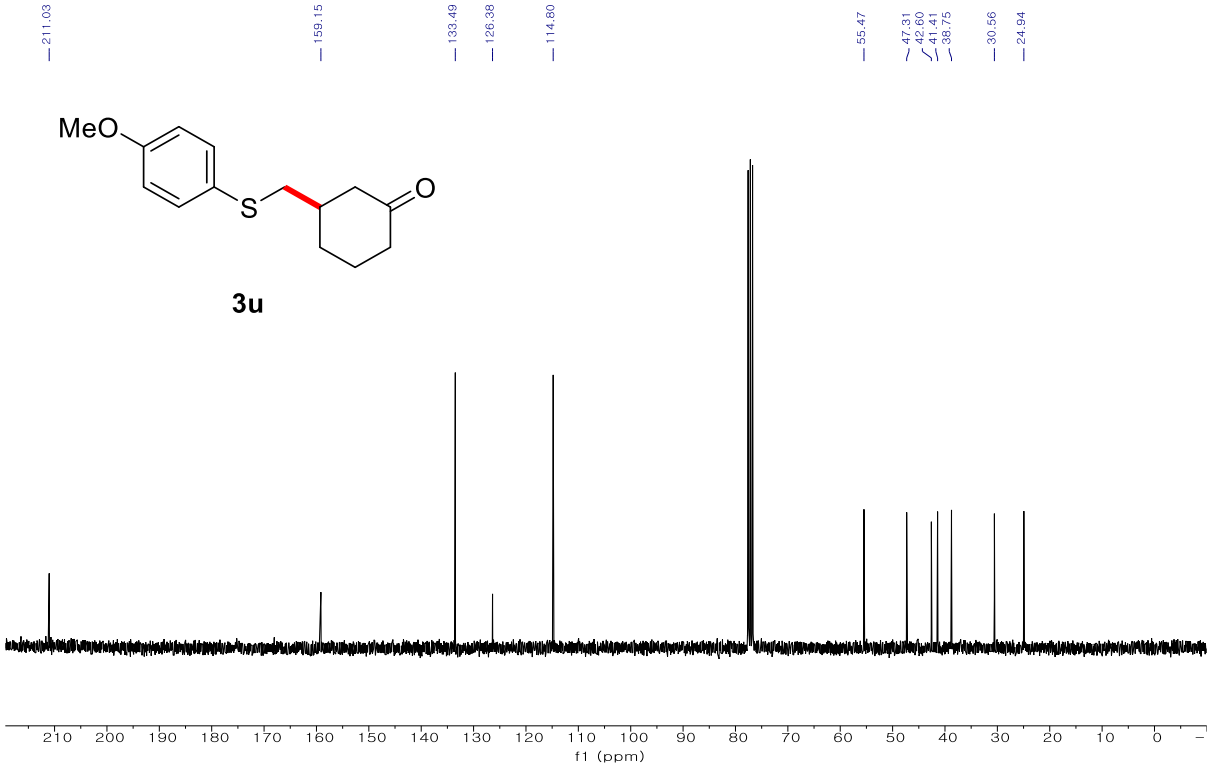
^{1}H-NMR (300 MHz, Chloroform-d) of **3t**



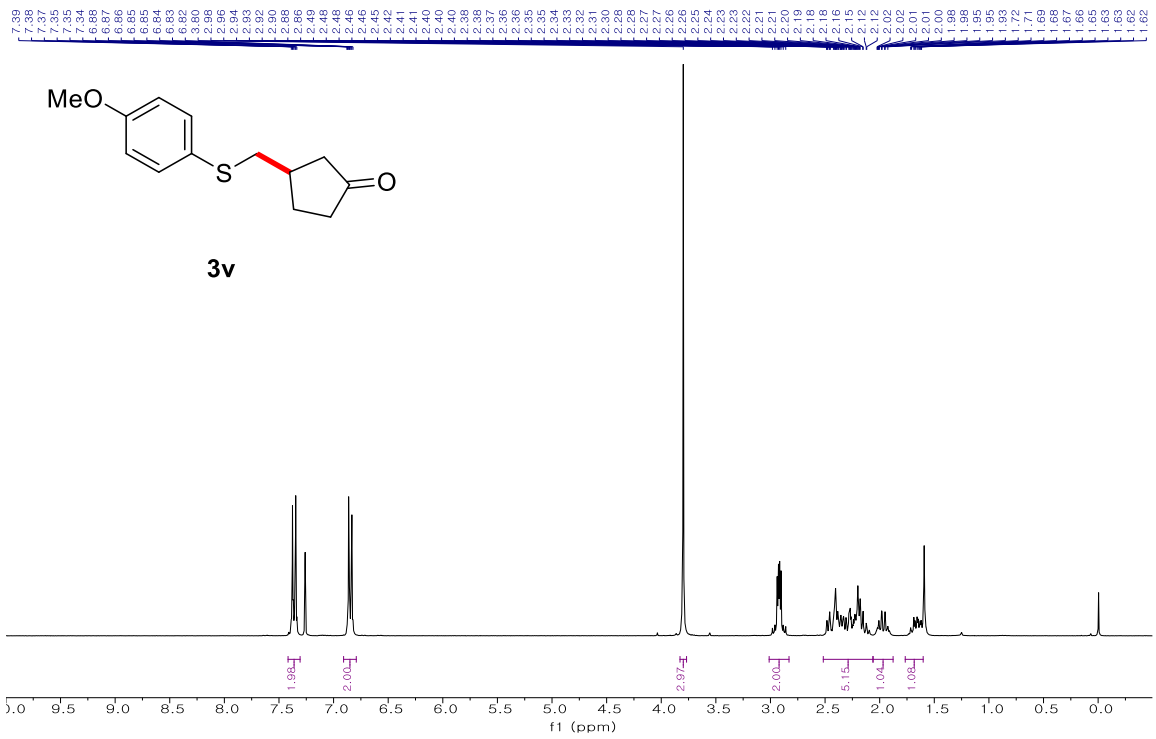
^{13}C-NMR (75 MHz, Chloroform-d) of **3t**



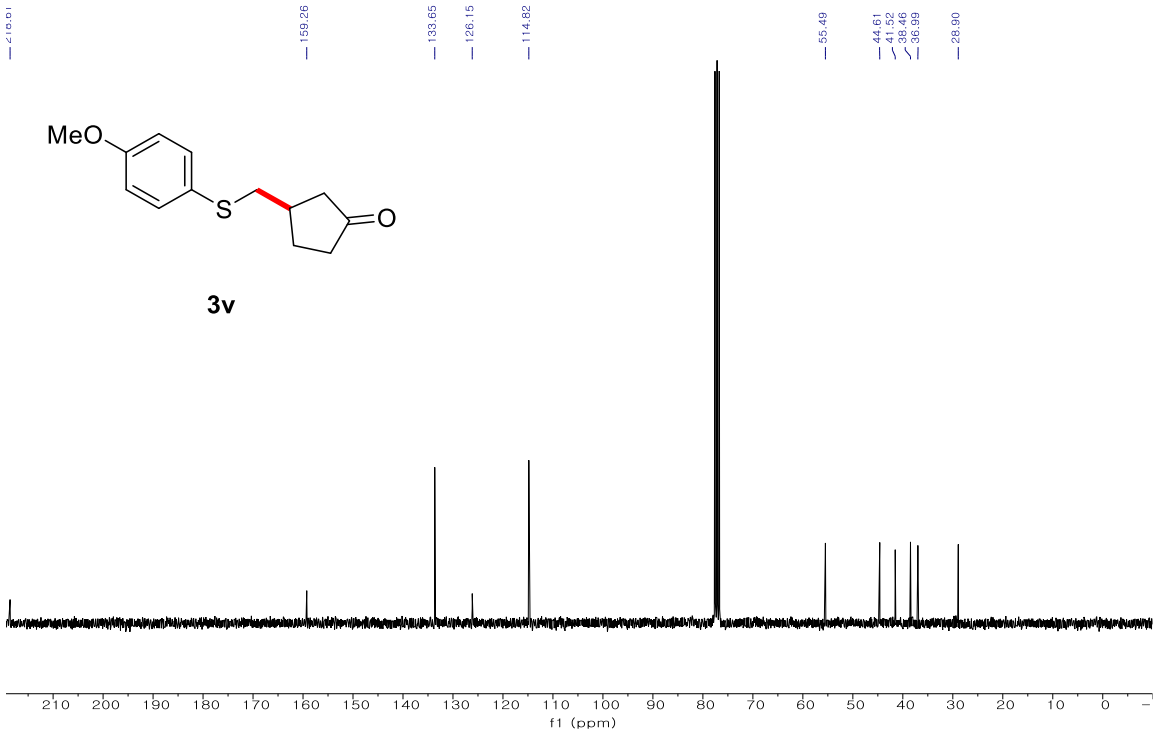
^{1}H-NMR (300 MHz, Chloroform-d) of **3u**



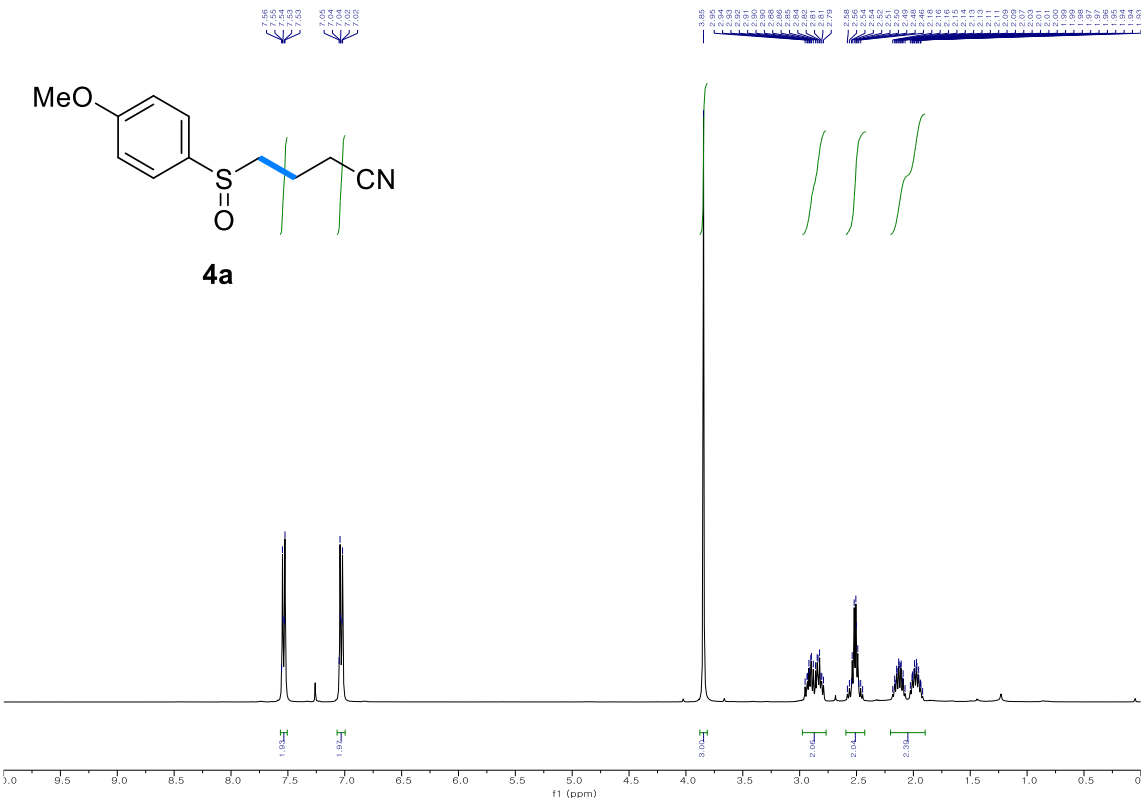
^{13}C-NMR (75 MHz, Chloroform-d) of **3u**



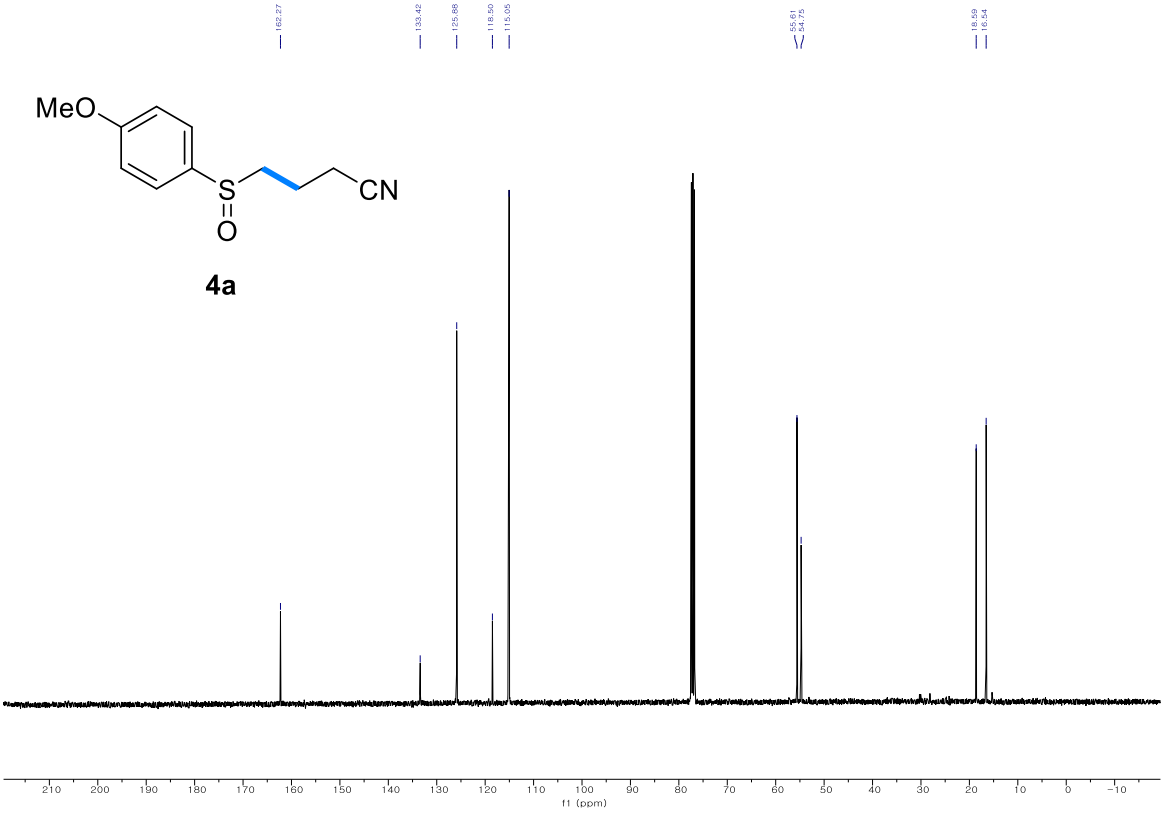
^{1}H-NMR (300 MHz, Chloroform-d) of **3v**



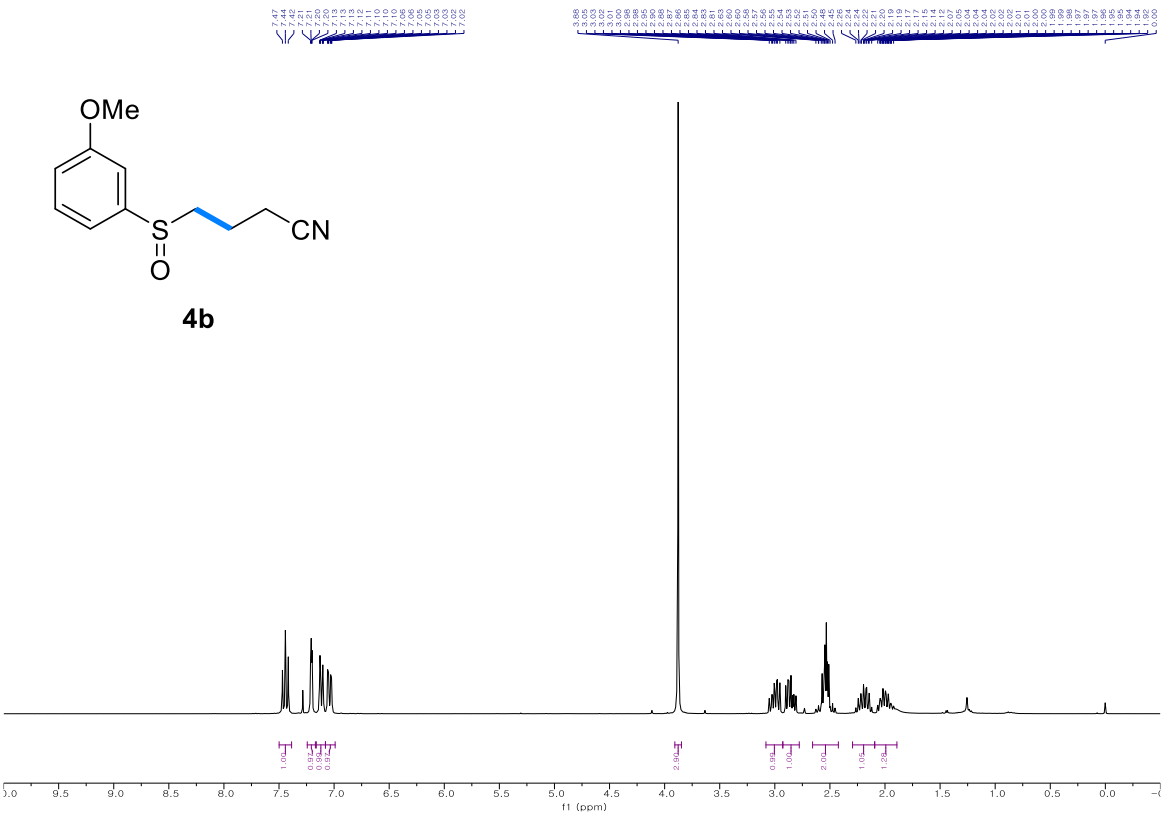
^{13}C-NMR (75 MHz, Chloroform-d) of **3v**



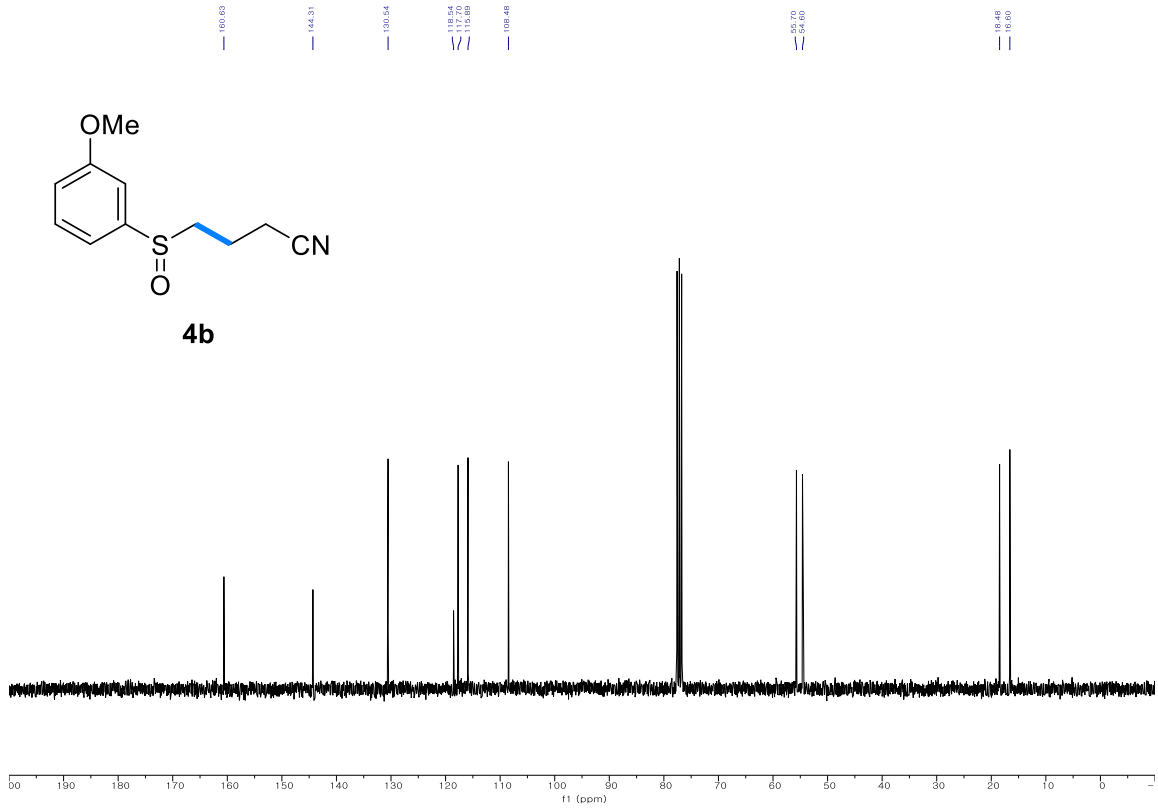
^{1}H-NMR (400 MHz, Chloroform-d) of **4a**



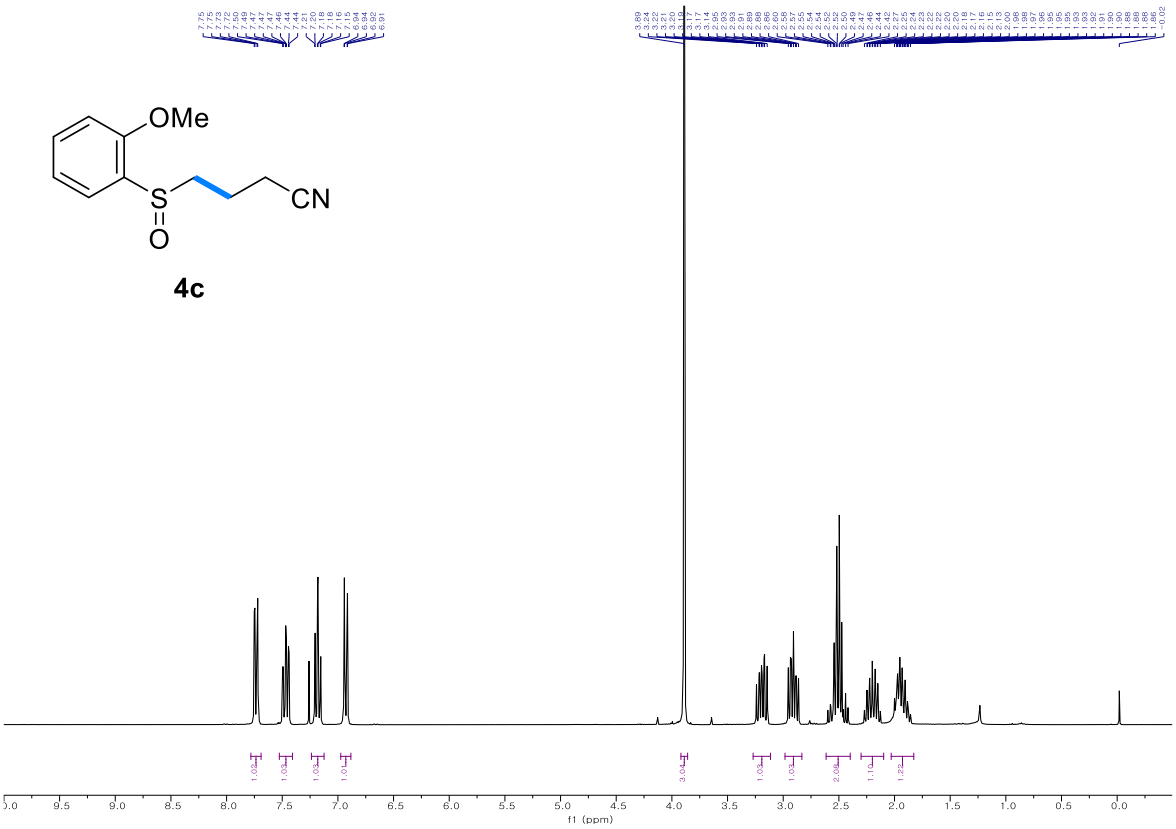
^{13}C-NMR (101 MHz, Chloroform-d) of **4a**



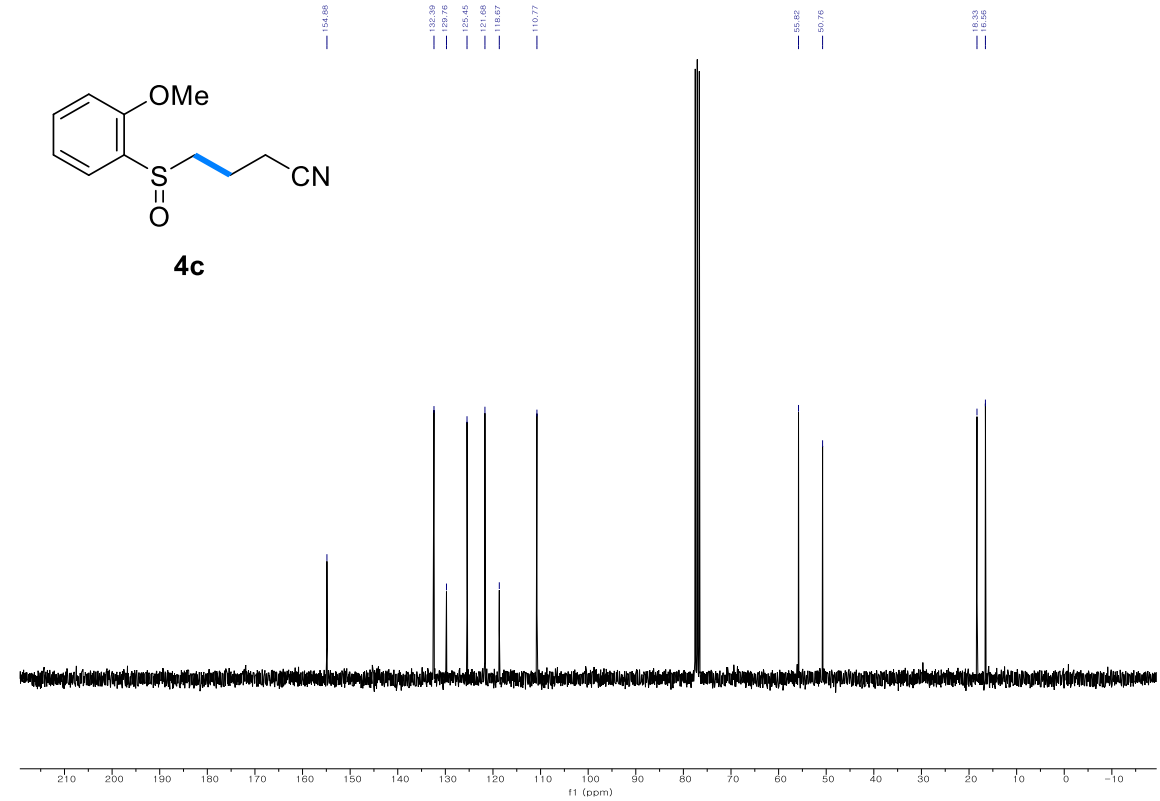
^{1}H-NMR (300 MHz, Chloroform-d) of **4b**



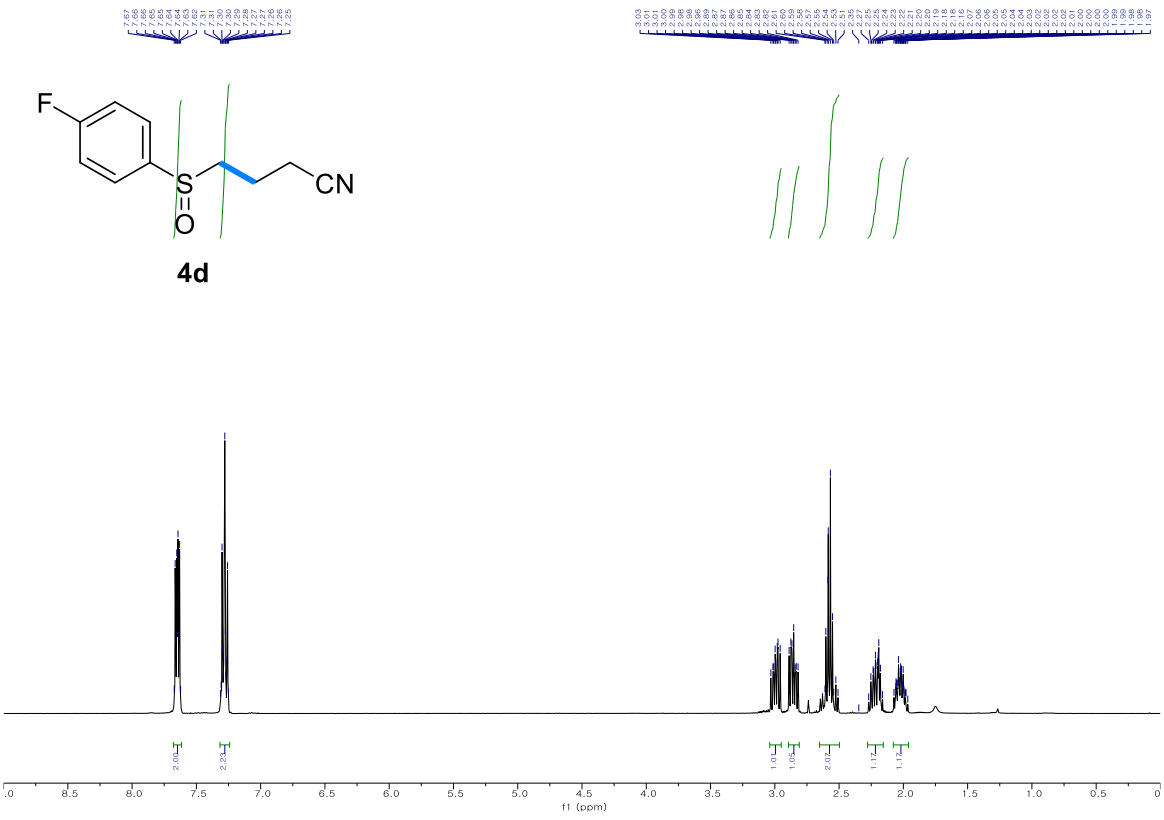
^{13}C-NMR (75 MHz, Chloroform-d) of **4b**



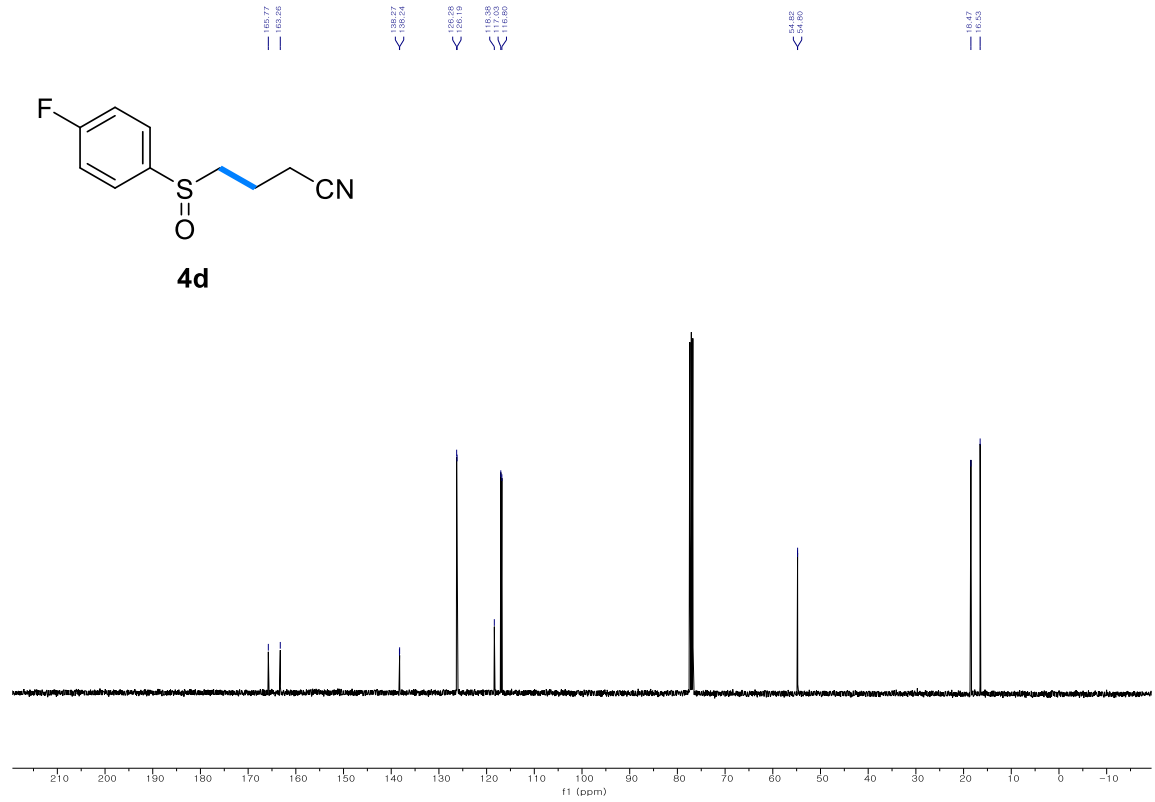
^{1}H-NMR (300 MHz, Chloroform-d) of **4c**



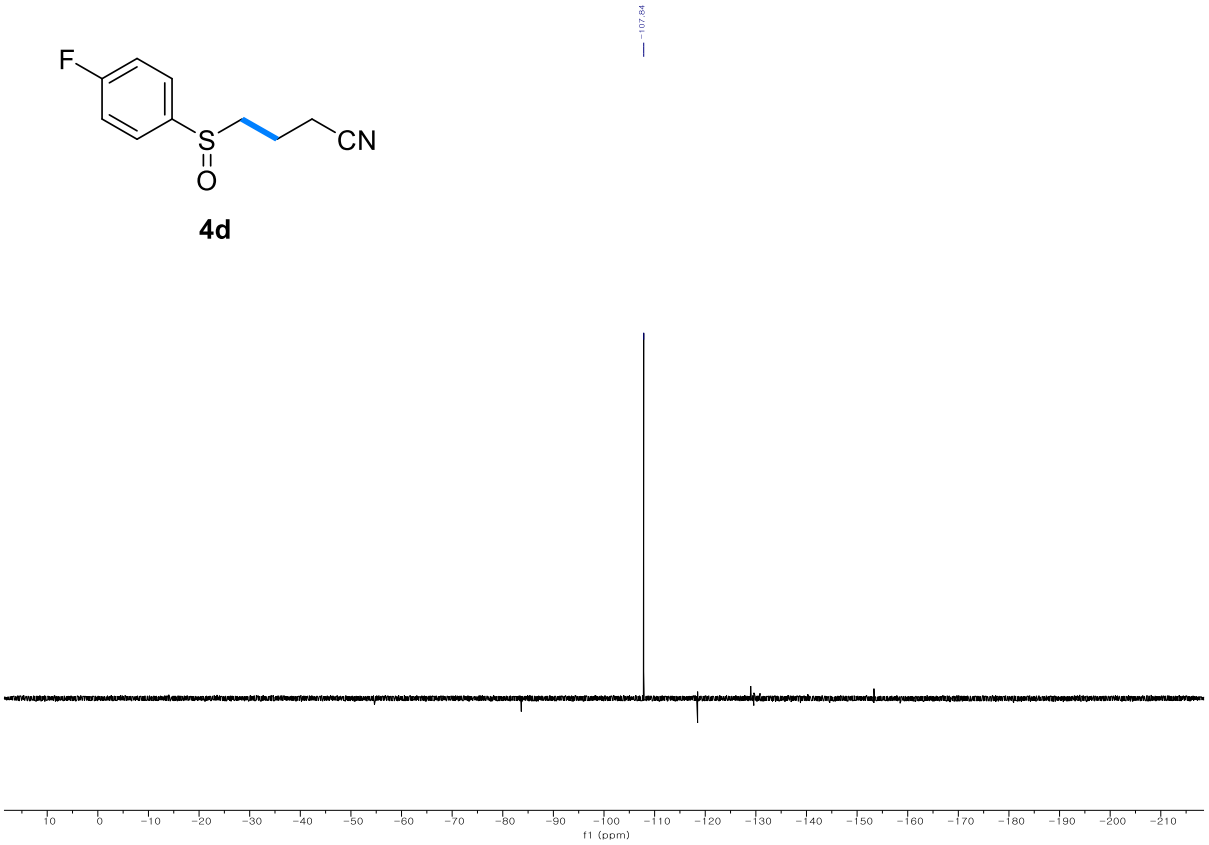
^{13}C-NMR (75 MHz, Chloroform-d) of **4c**



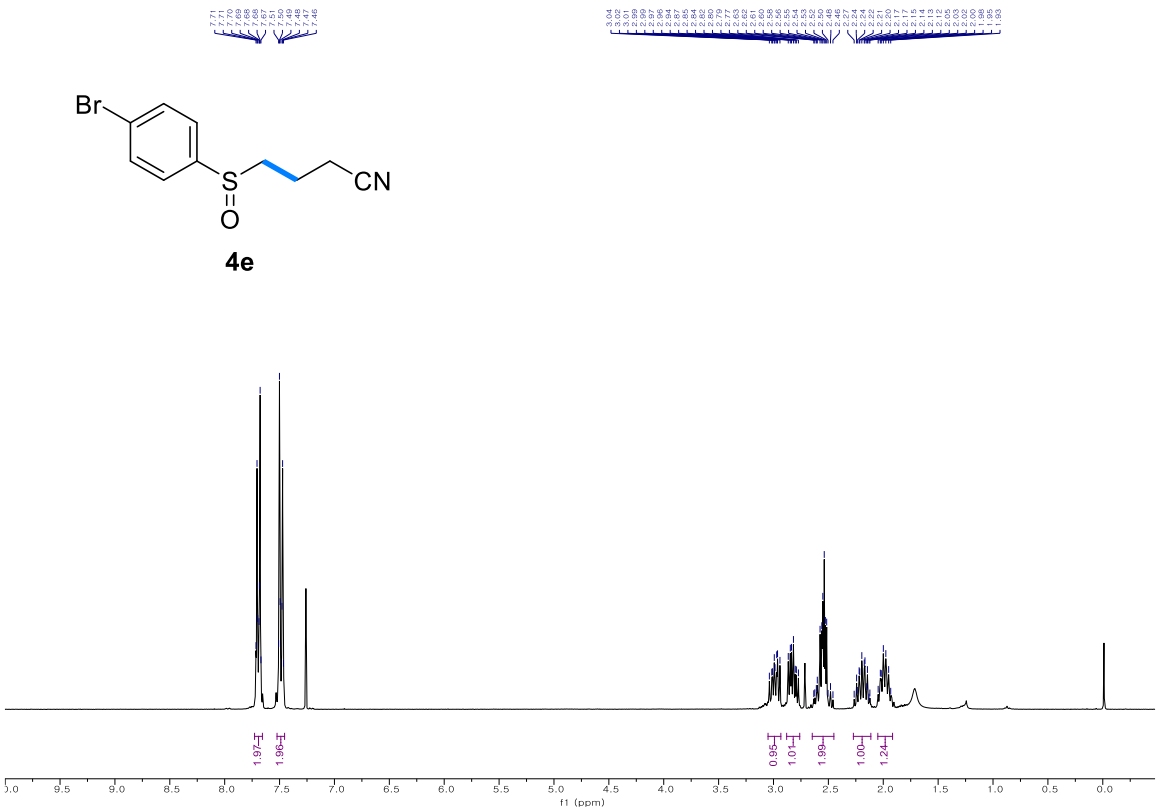
^{1}H-NMR (400 MHz, Chloroform-d) of **4d**



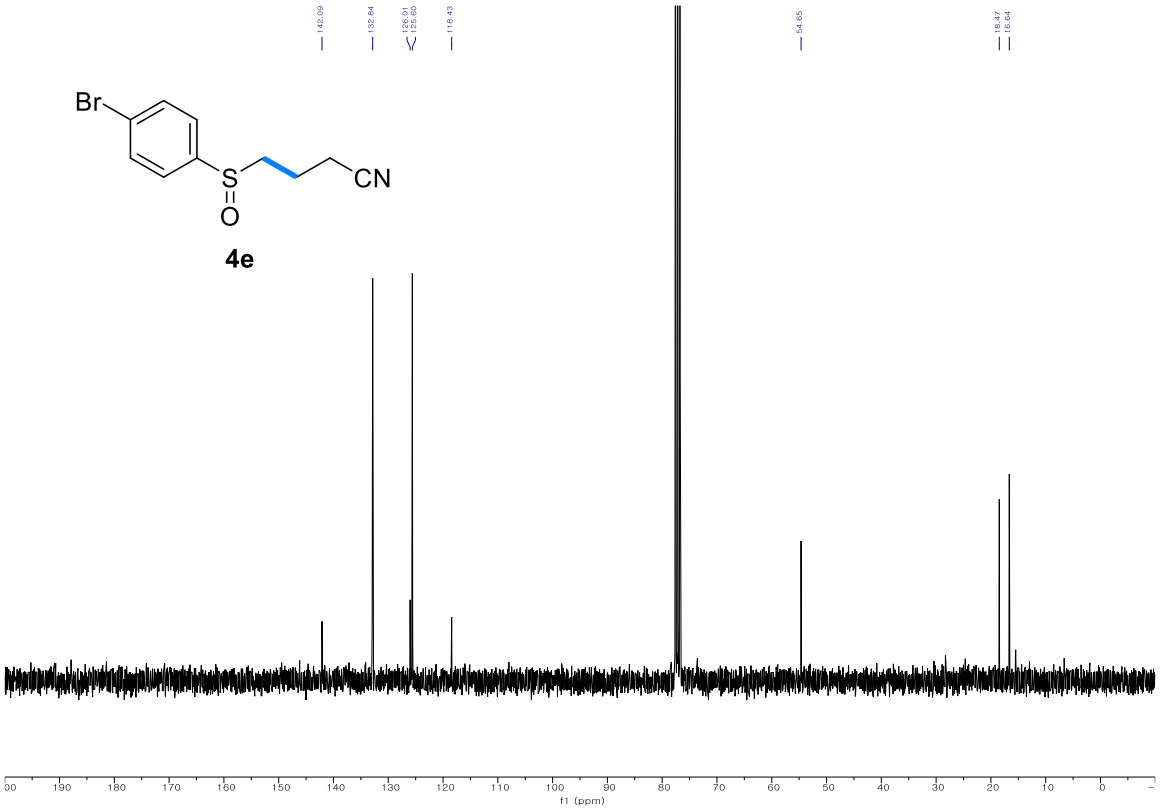
^{13}C-NMR (101 MHz, Chloroform-d) of **4d**



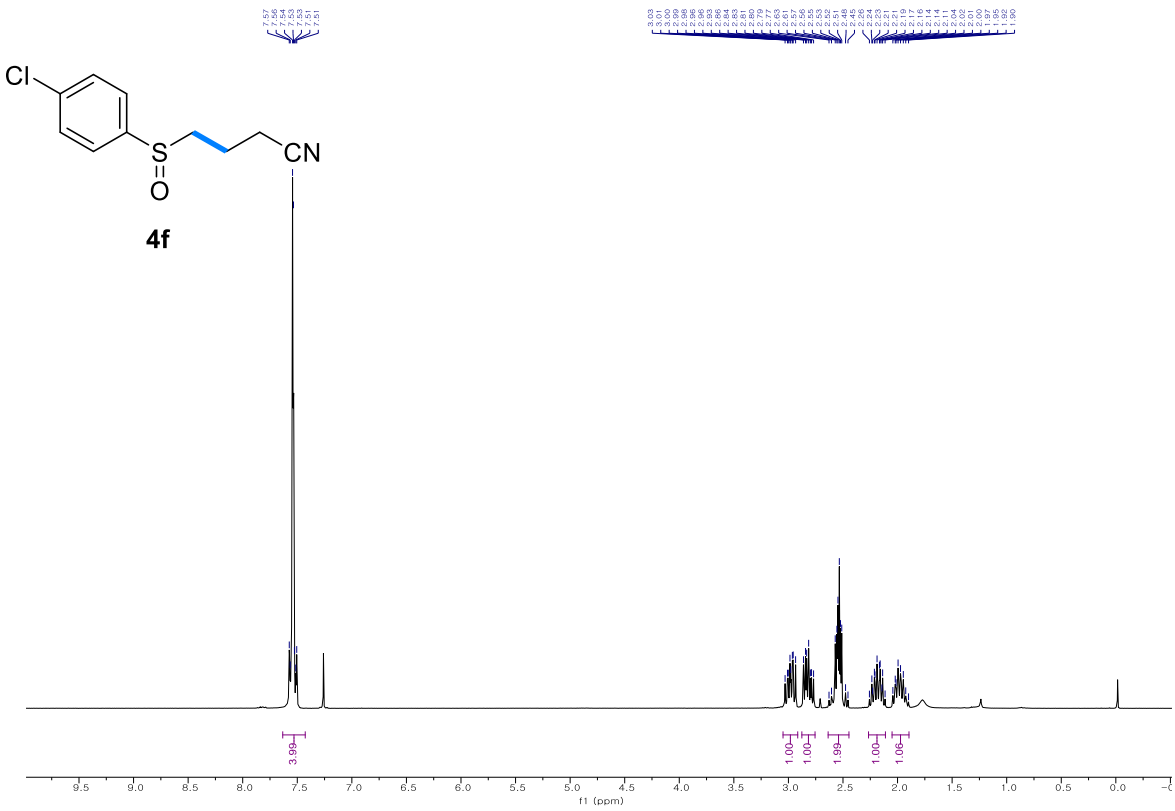
^{19}F-NMR (376 MHz, Chloroform-d) of **4d**



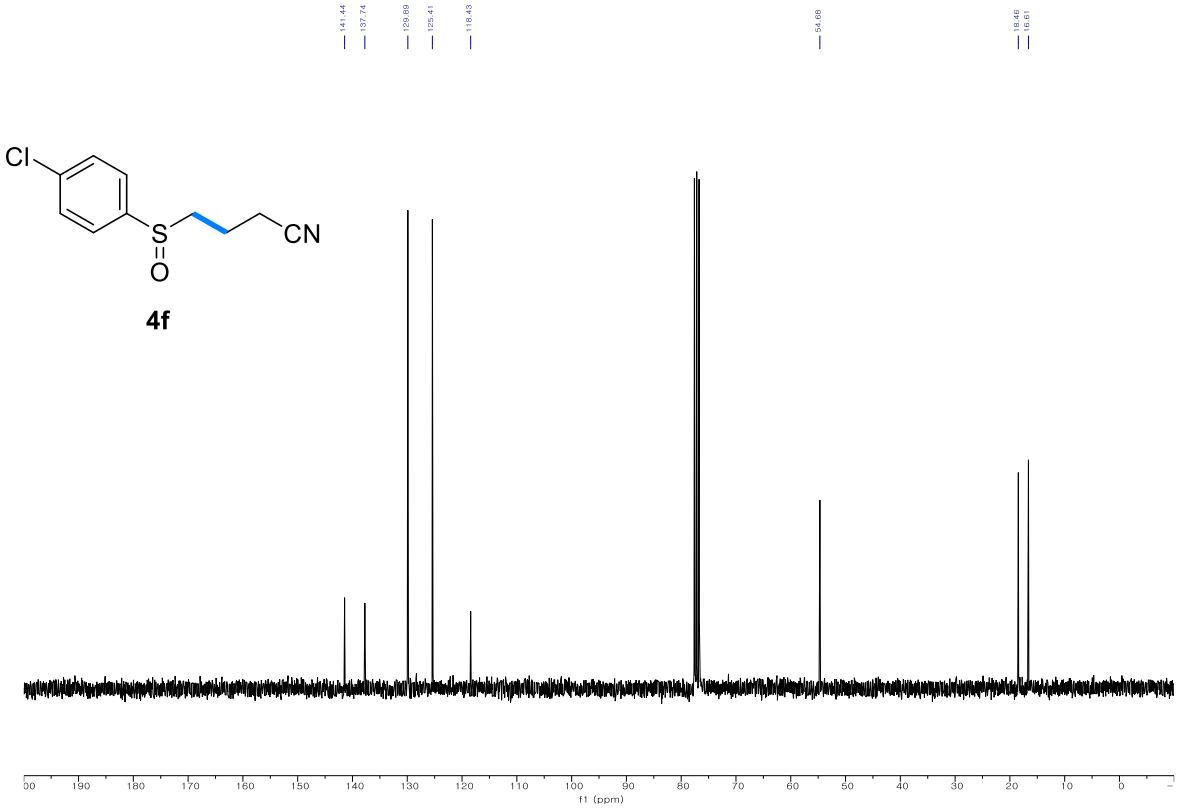
^{1}H-NMR (300 MHz, Chloroform-d) of **4e**



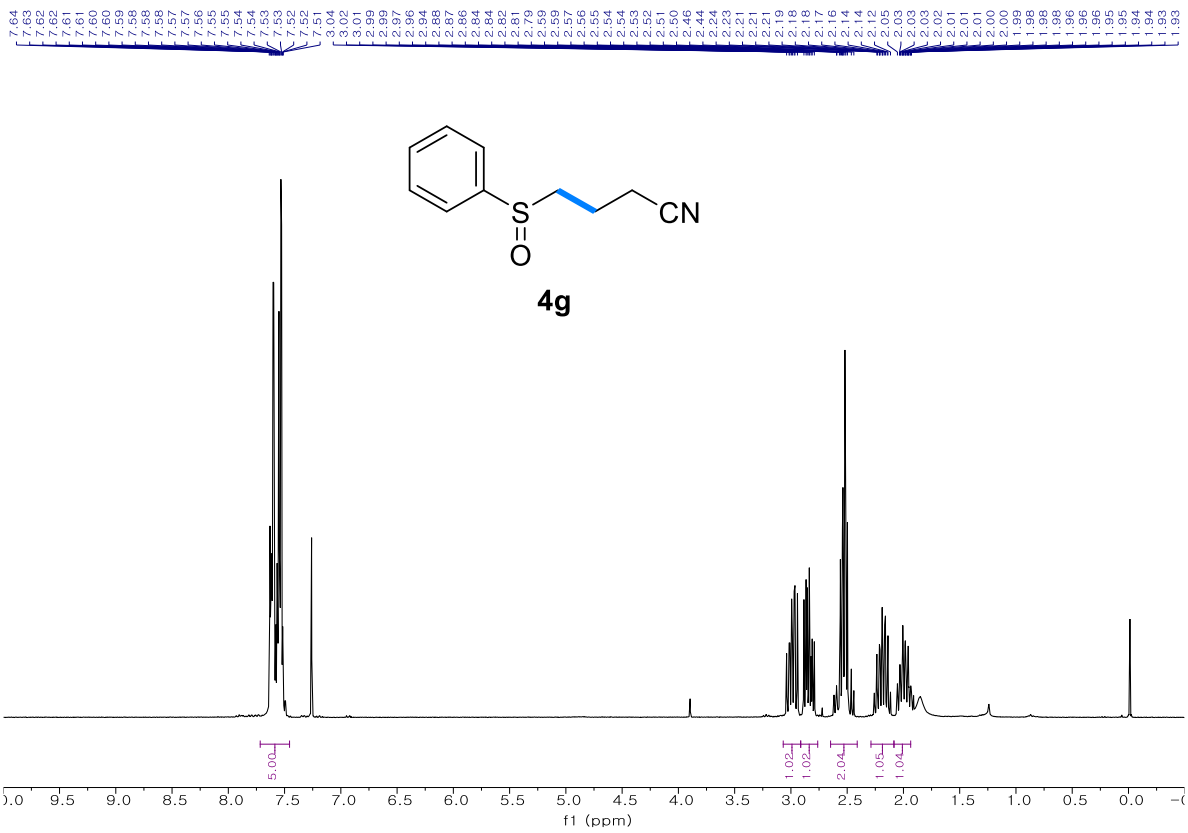
^{13}C-NMR (75 MHz, Chloroform-d) of **4e**



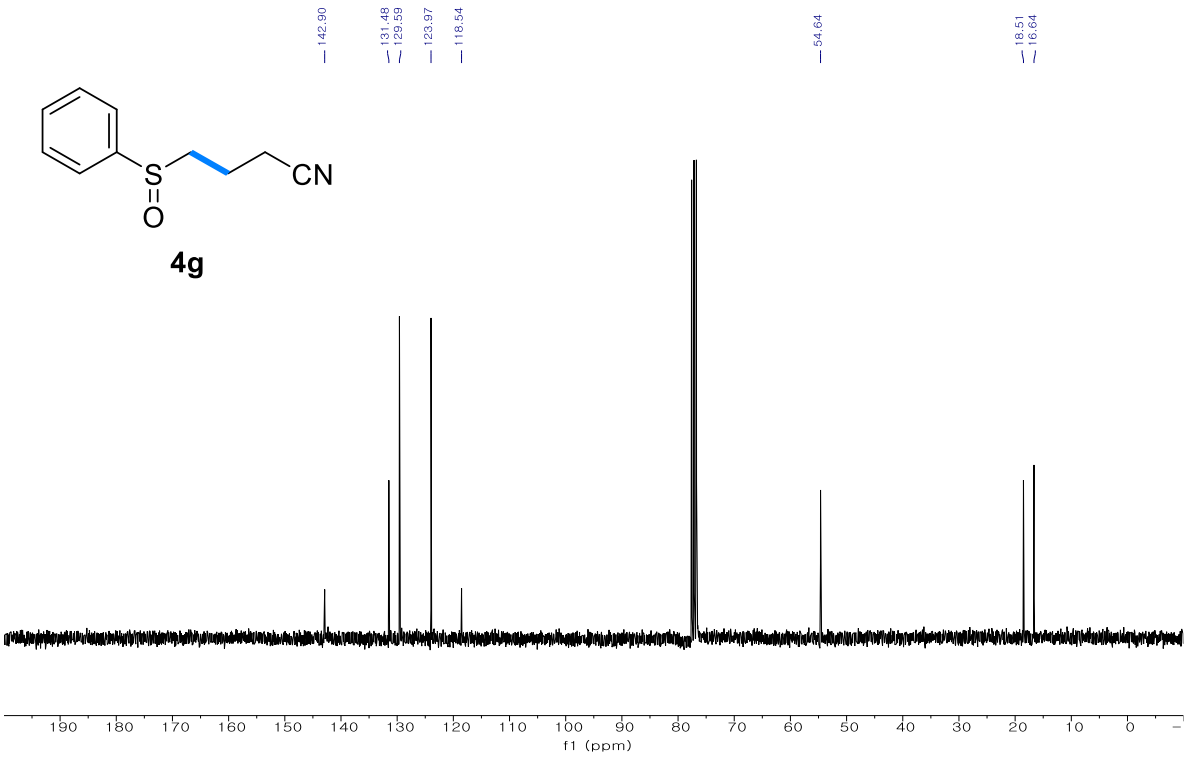
^{1}H-NMR (300 MHz, Chloroform-d) of **4f**



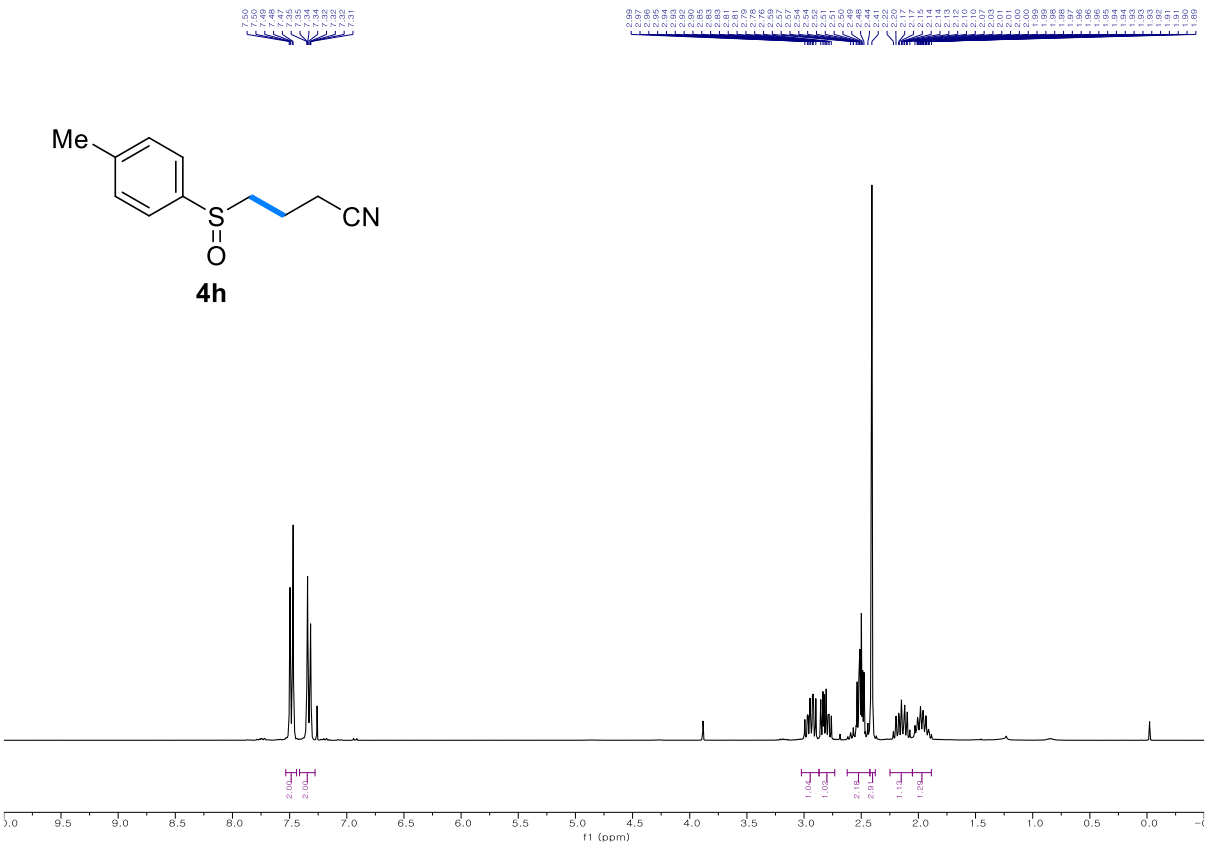
^{13}C-NMR (75 MHz, Chloroform-d) of **4f**



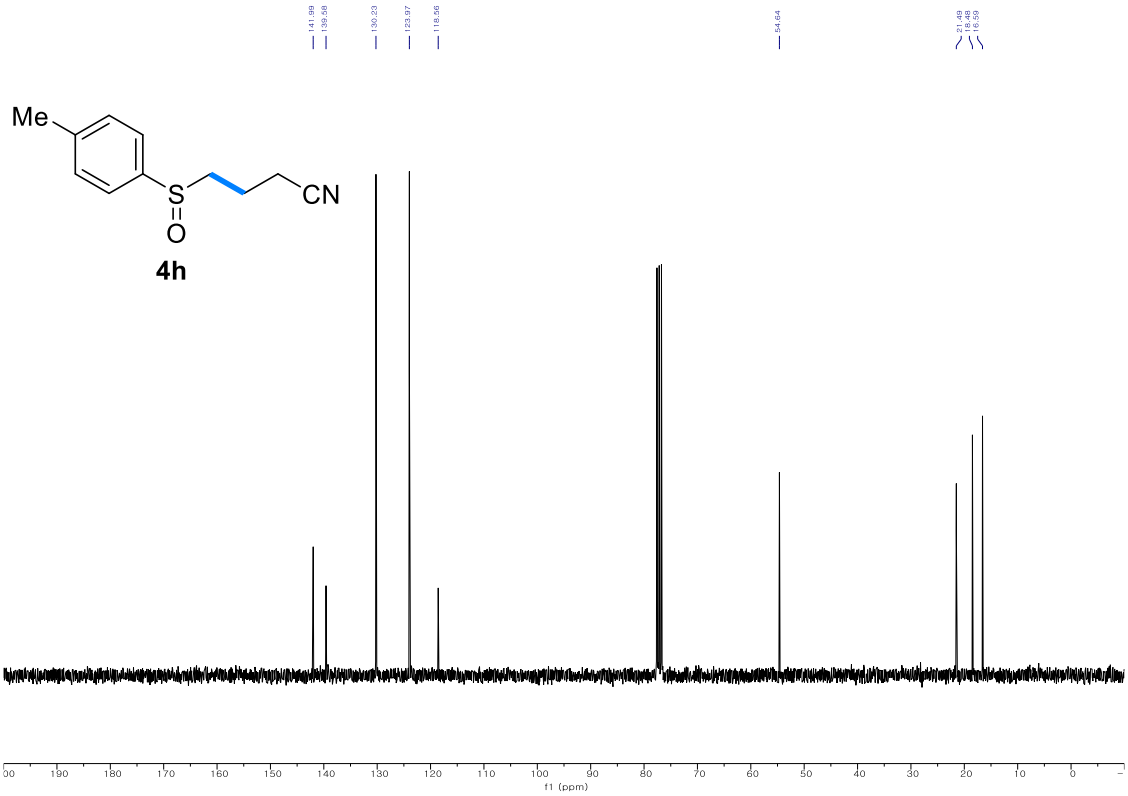
^{1}H-NMR (300 MHz, Chloroform-d) of **4g**



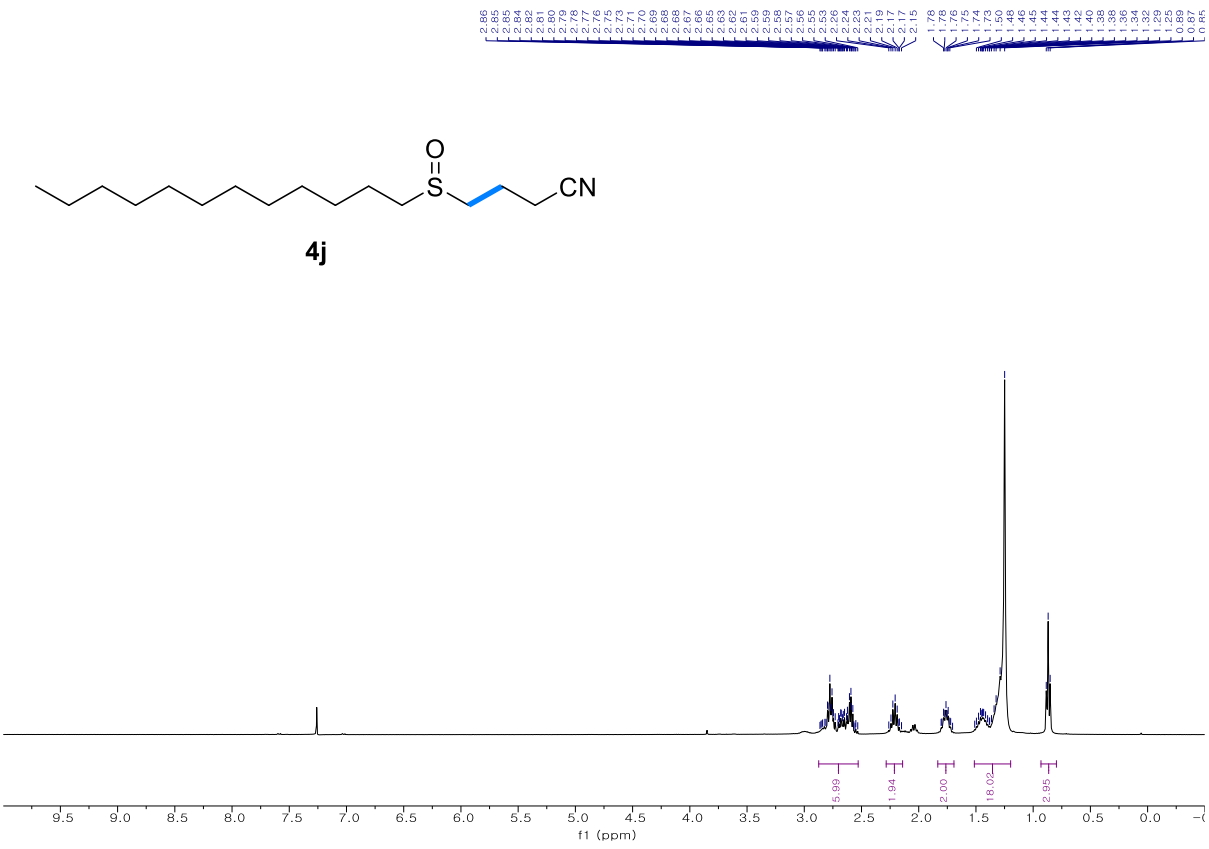
^{13}C-NMR (75 MHz, Chloroform-d) of **4g**



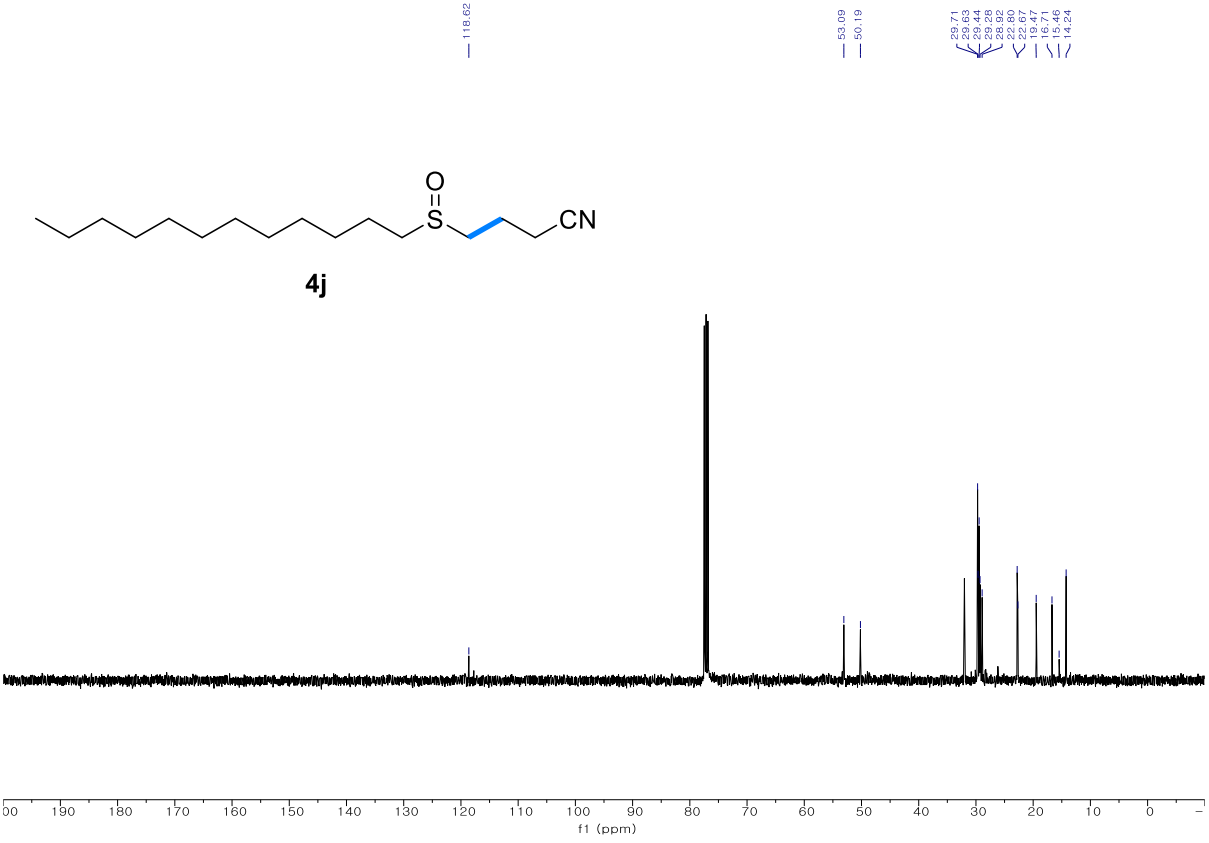
^{1}H-NMR (300 MHz, Chloroform-d) of **4h**



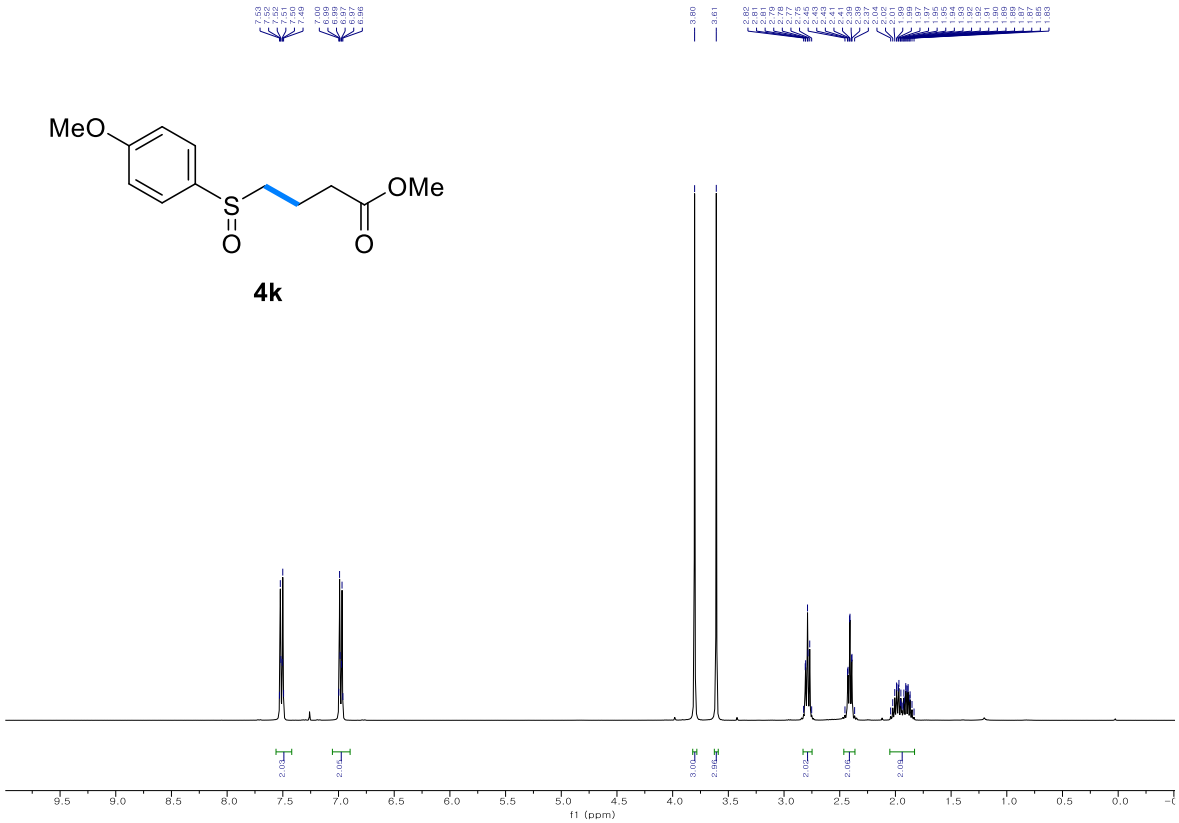
^{13}C-NMR (75 MHz, Chloroform-d) of **4h**



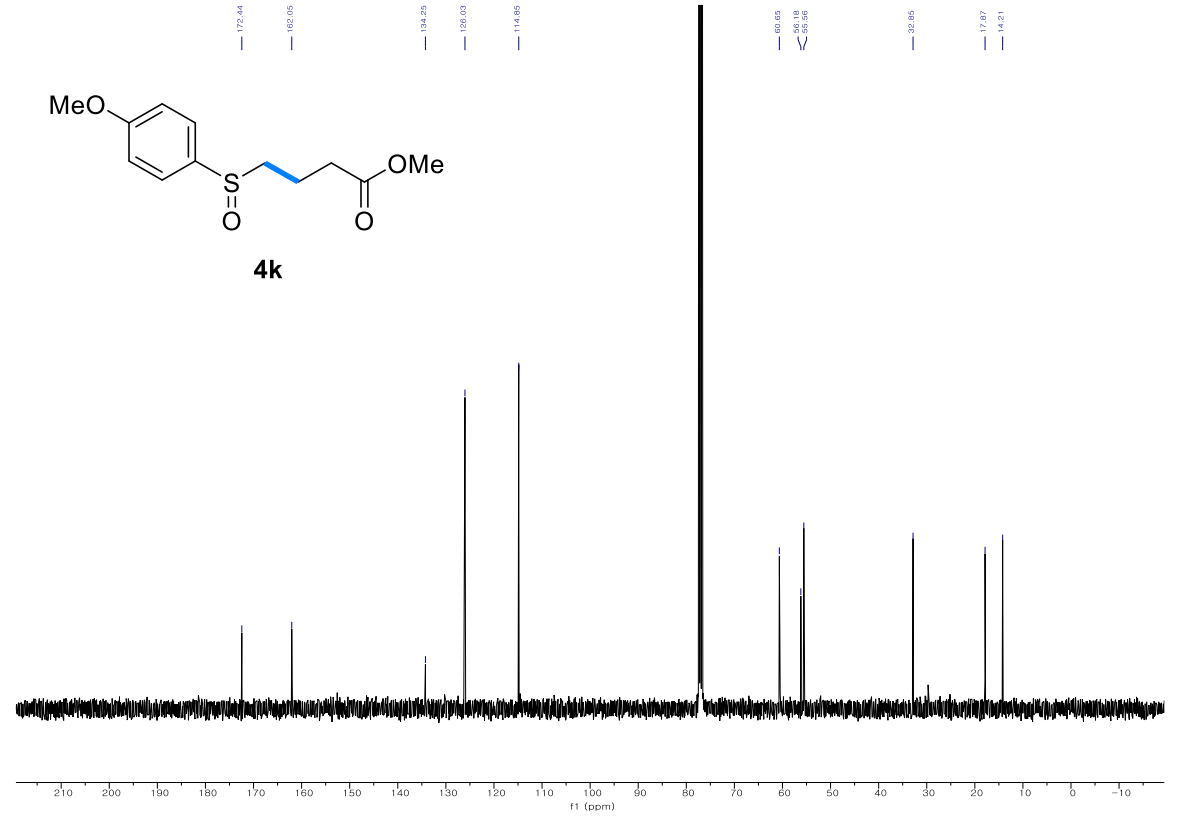
^{1}H-NMR (400 MHz, Chloroform-d) of **4j**



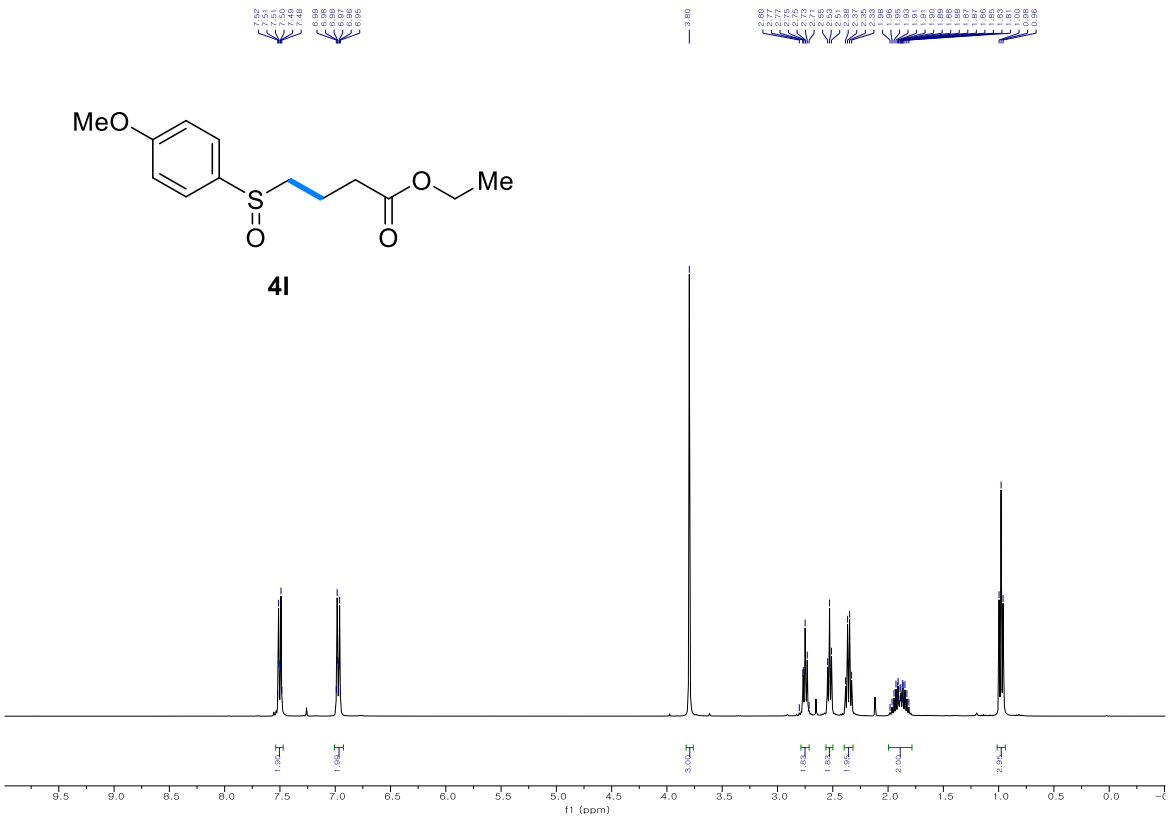
^{13}C-NMR (101 MHz, Chloroform-d) of **4j**



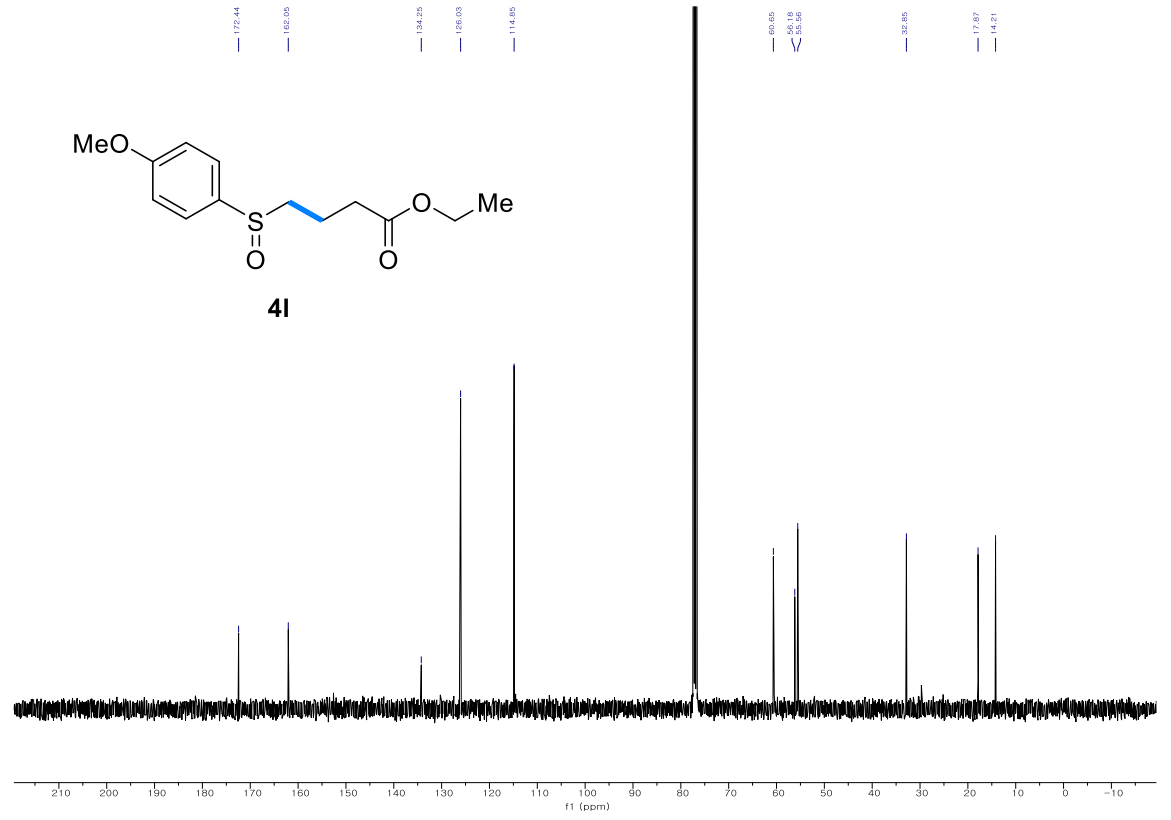
^{1}H-NMR (400 MHz, Chloroform-d) of **4k**



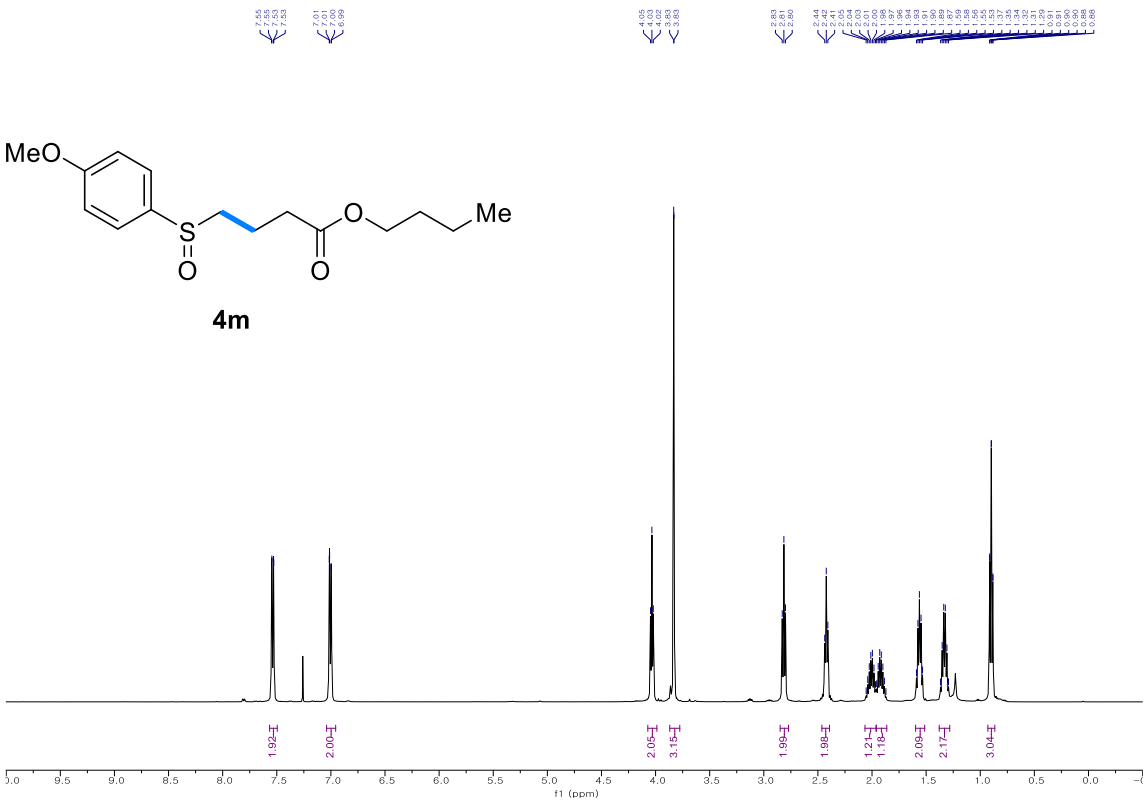
^{13}C-NMR (101 MHz, Chloroform-d) of **4k**



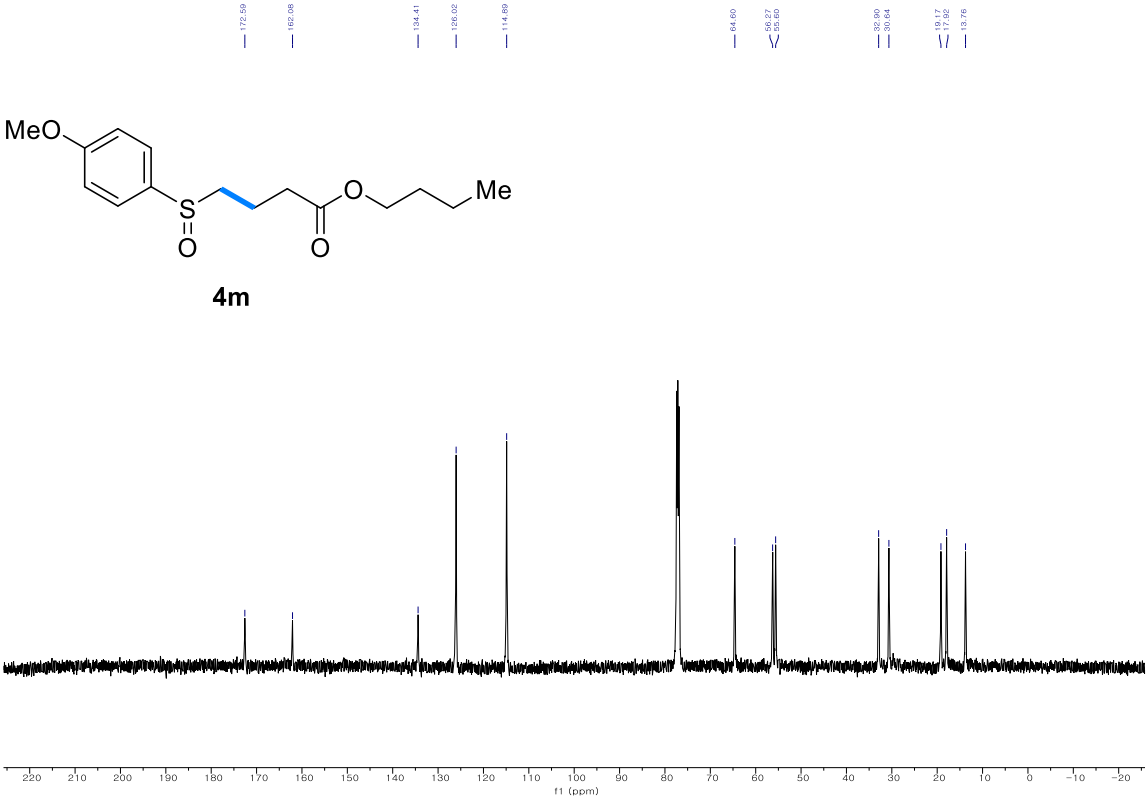
^{1}H-NMR (400 MHz, Chloroform-d) of **4l**



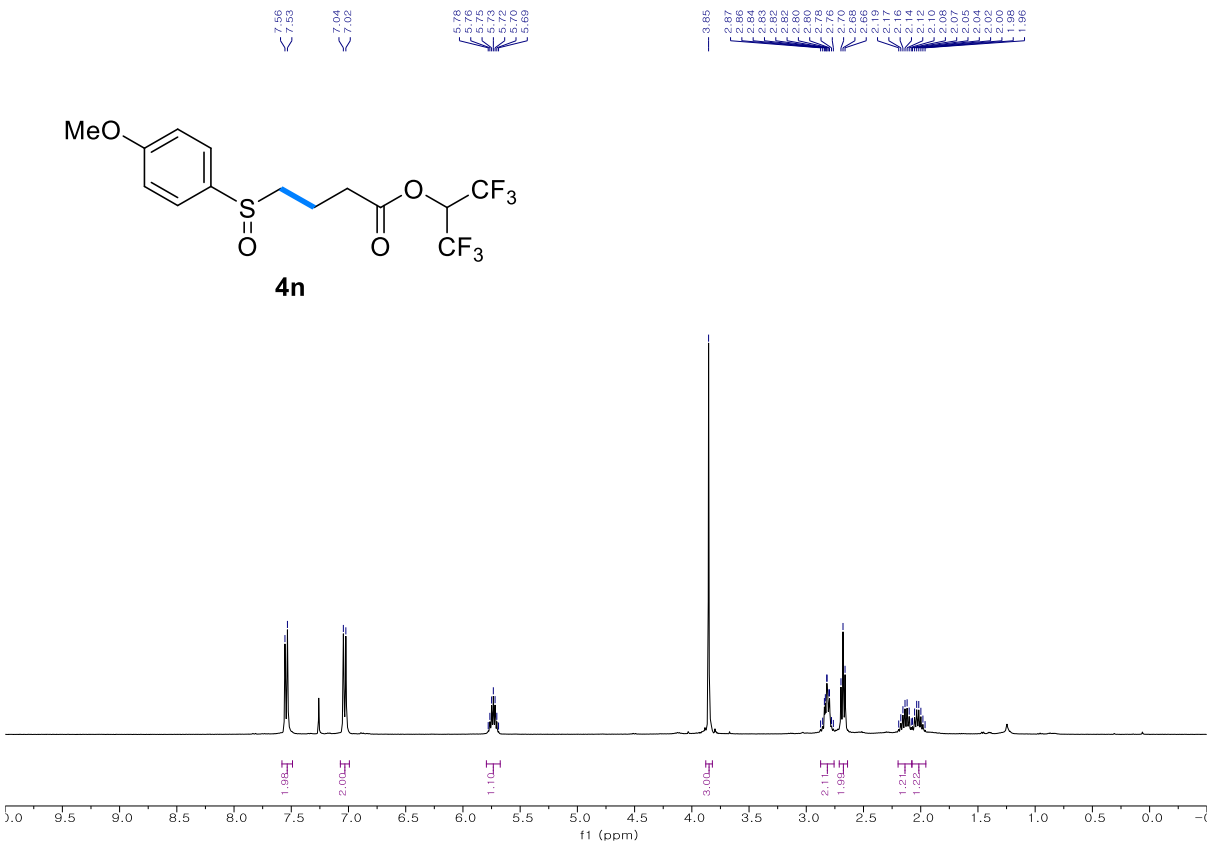
^{13}C-NMR (101 MHz, Chloroform-d) of **4l**



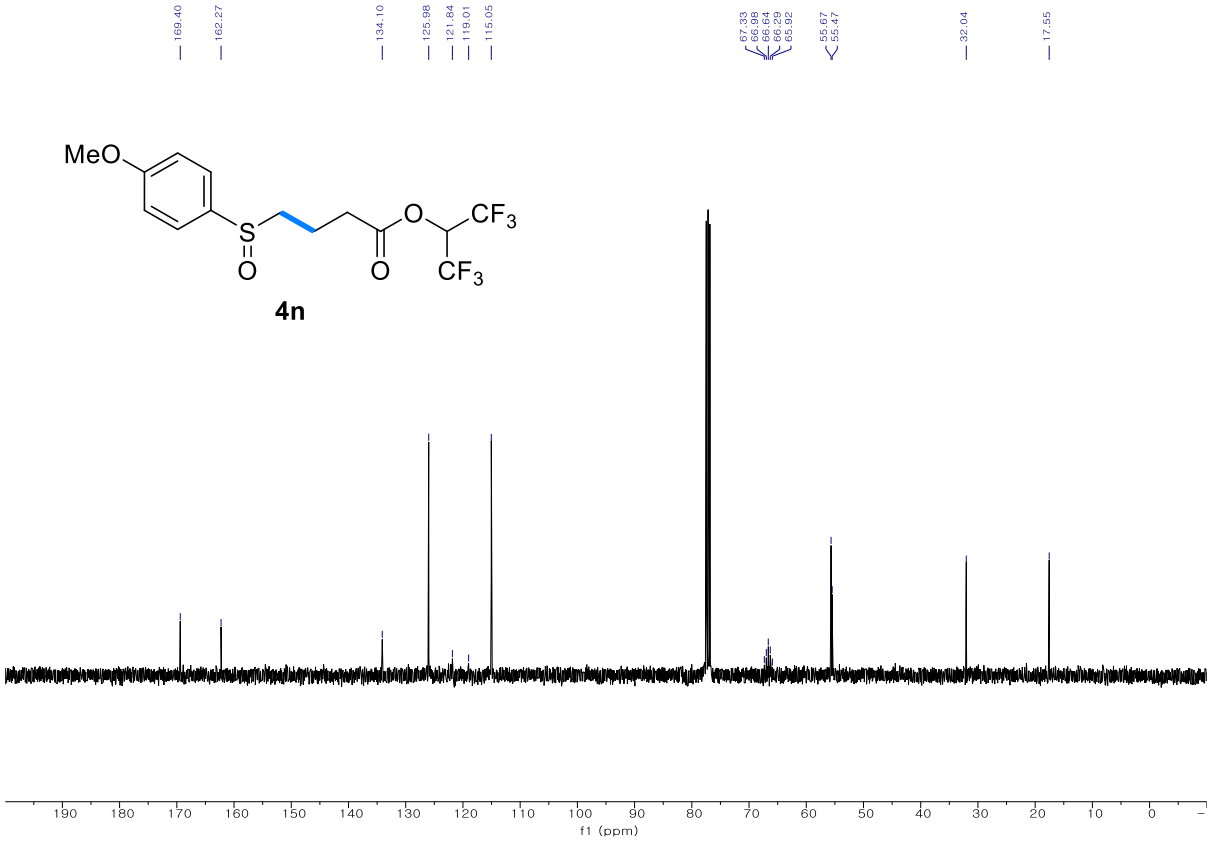
^{1}H-NMR (500 MHz, Chloroform-d) of **4m**



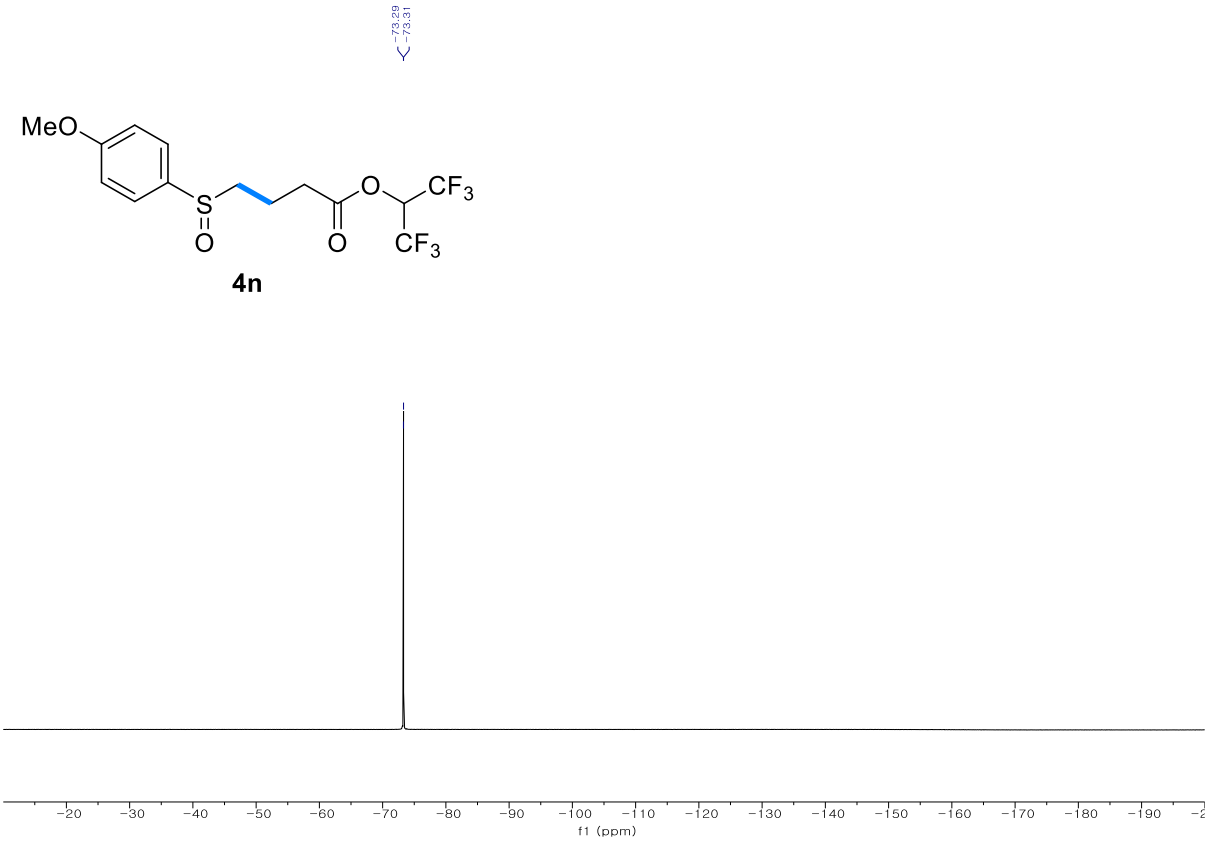
^{13}C-NMR (126 MHz, Chloroform-d) of **4m**



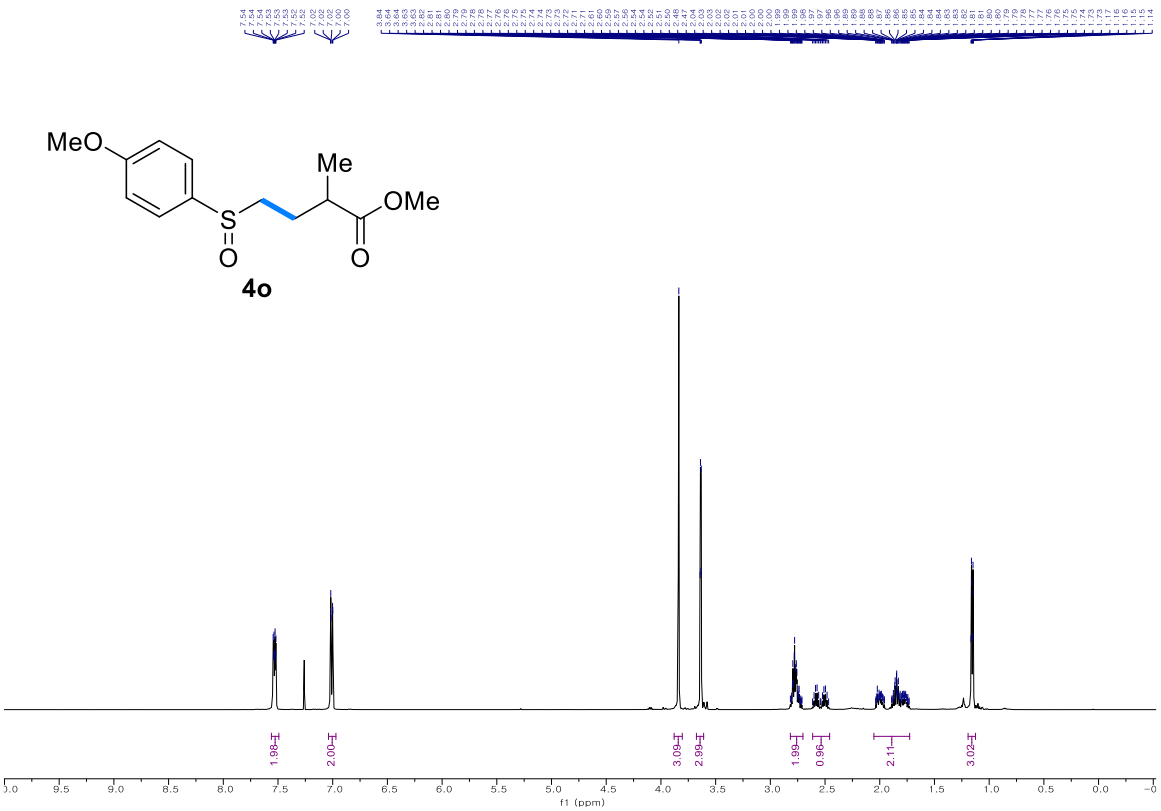
^{1}H-NMR (400 MHz, Chloroform-d) of **4n**



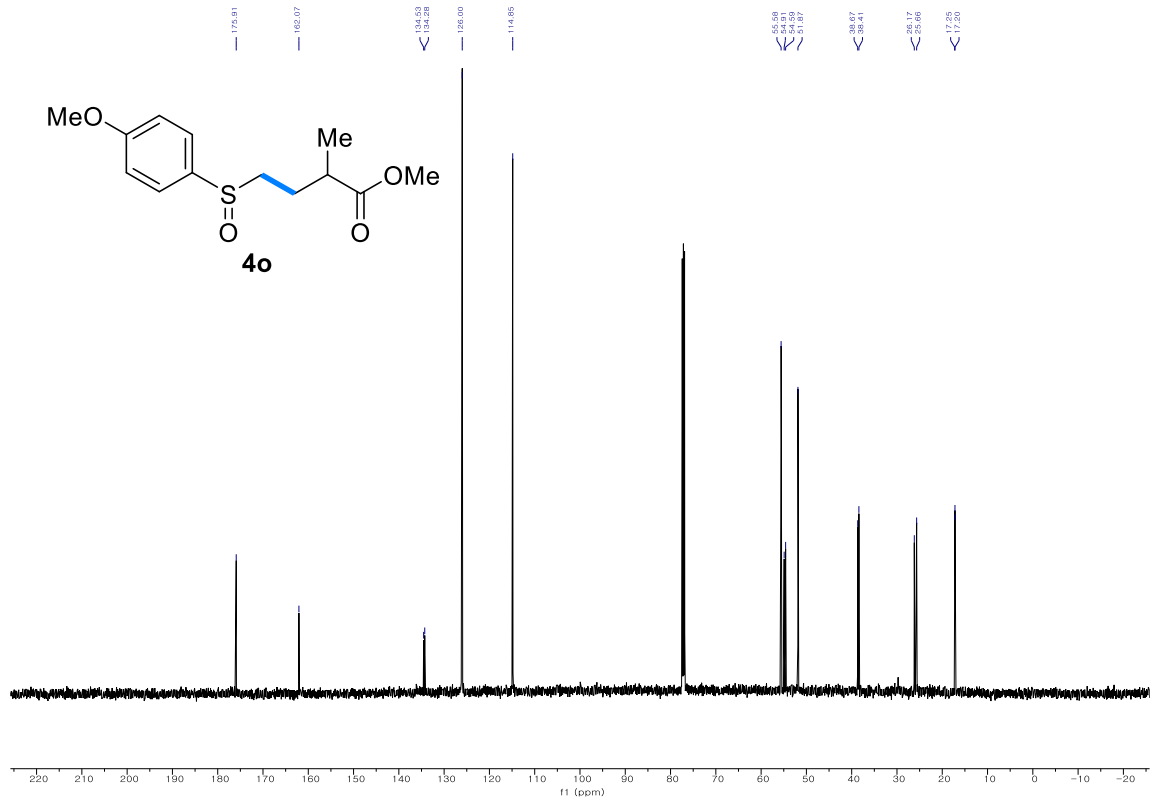
^{13}C-NMR (101 MHz, Chloroform-d) of **4n**



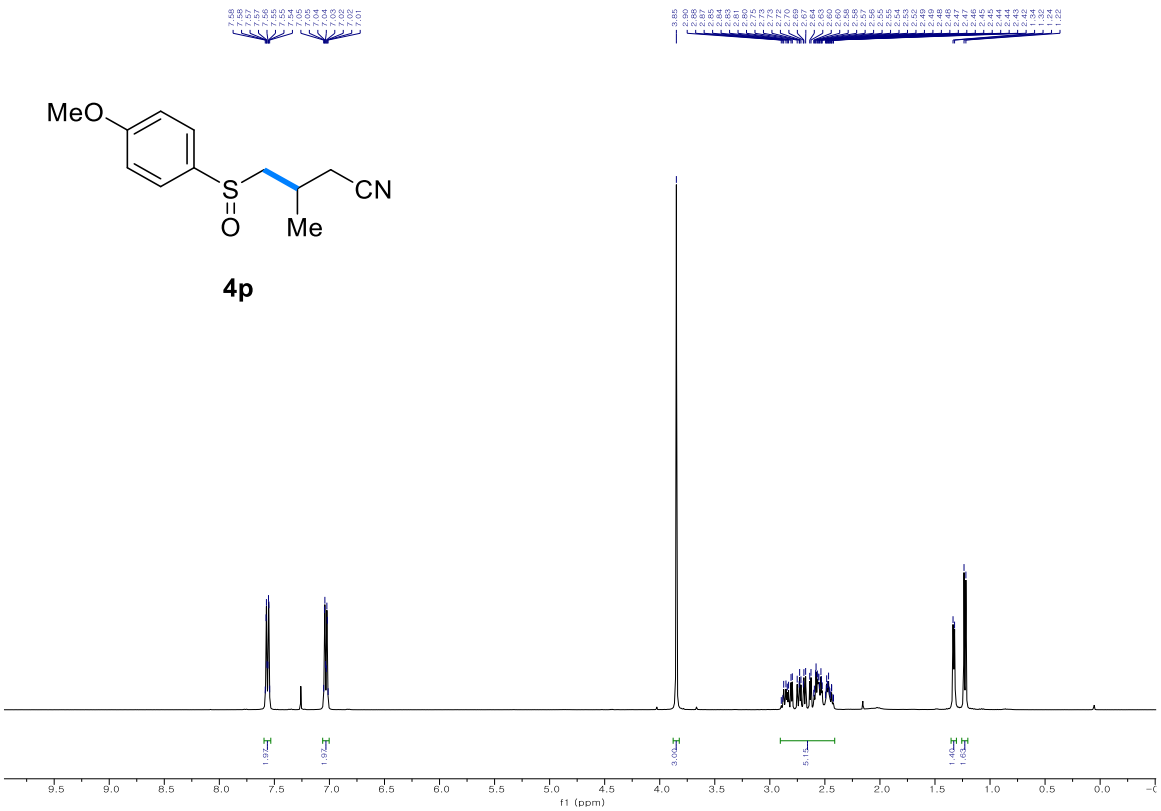
^{19}F-NMR (377 MHz, Chloroform-d) of **4n**



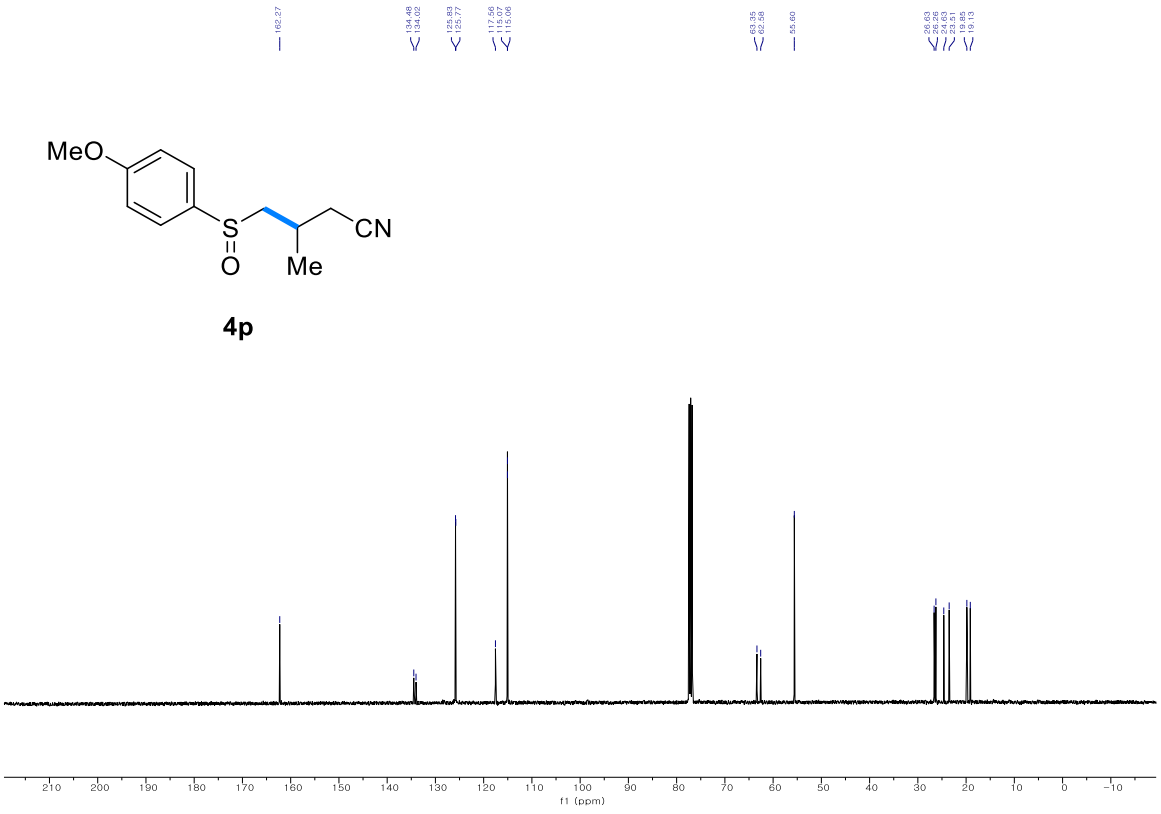
1H-NMR (500 MHz, Chloroform-d) of **4o**



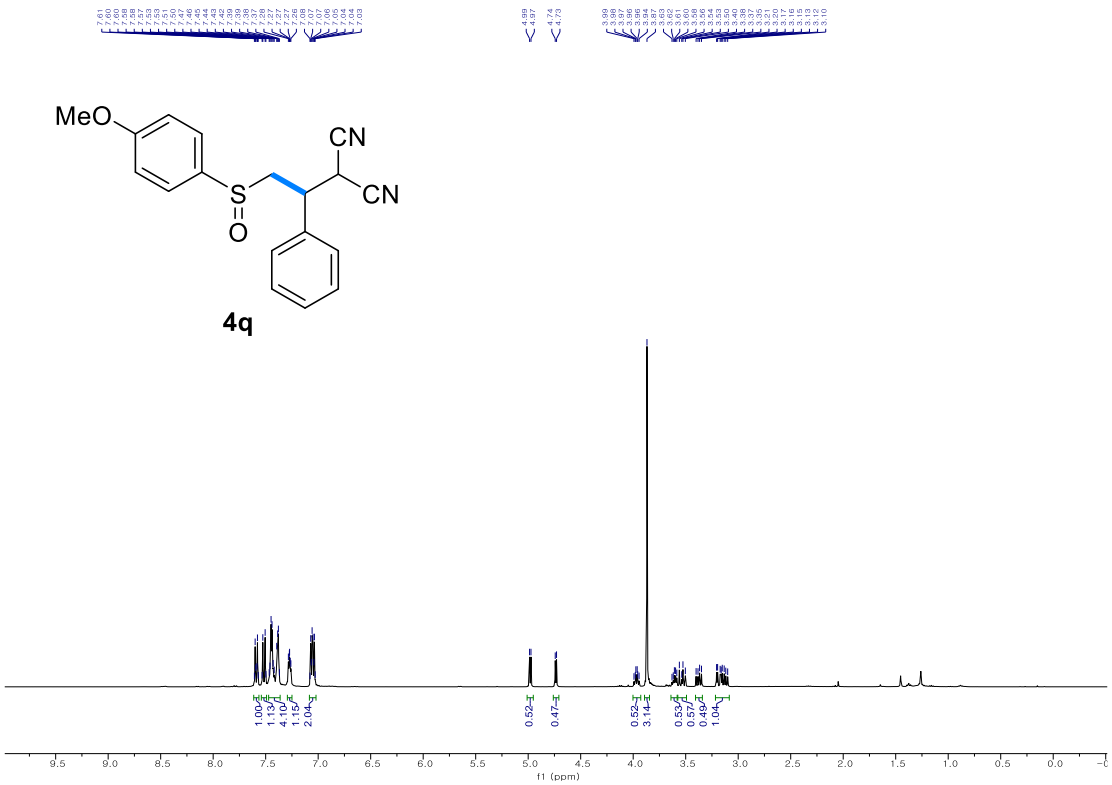
^{13}C-NMR (126 MHz, Chloroform-d) of **4o**



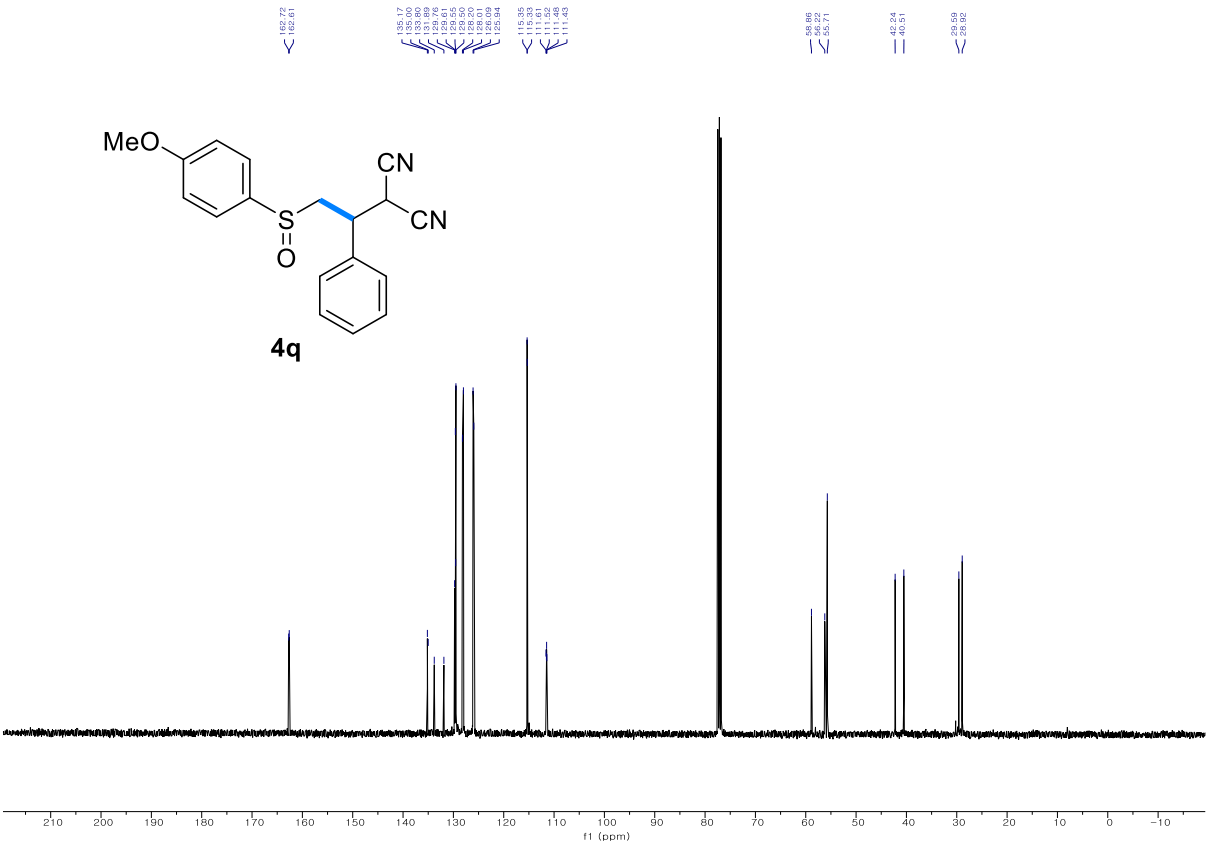
^{1}H-NMR (400 MHz, Chloroform-d) of **4p**



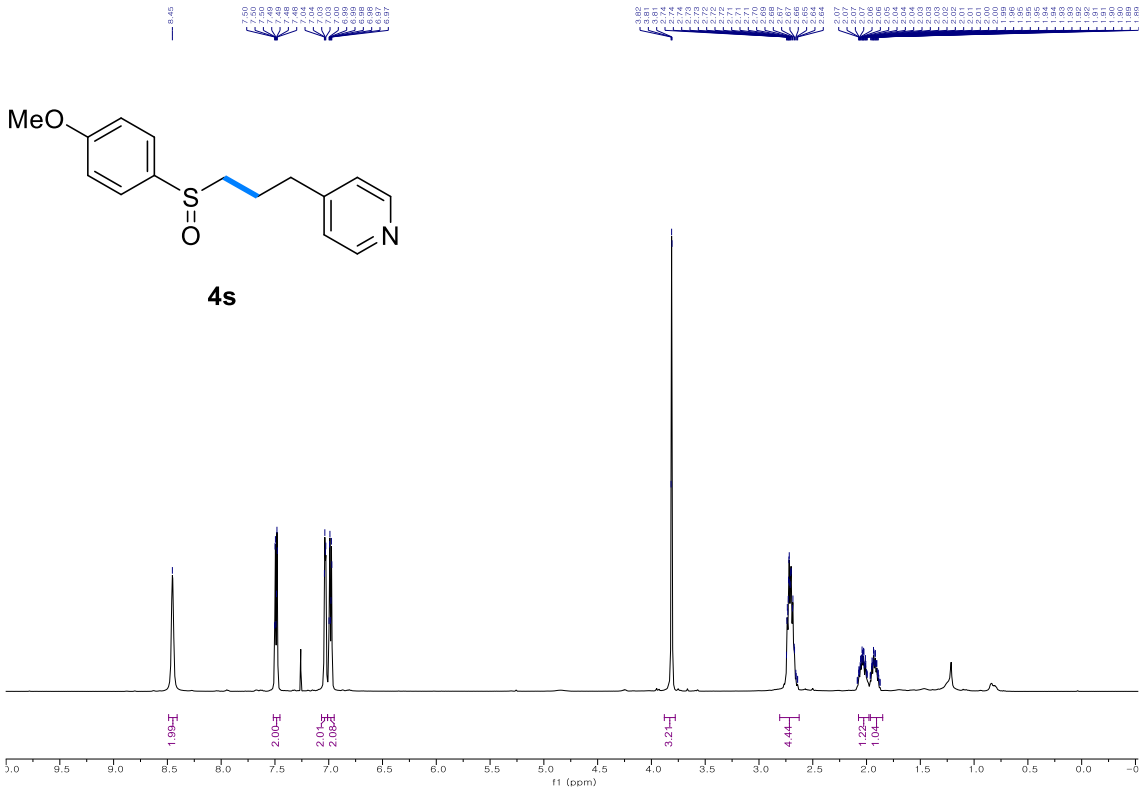
^{13}C-NMR (101 MHz, Chloroform-d) of **4p**



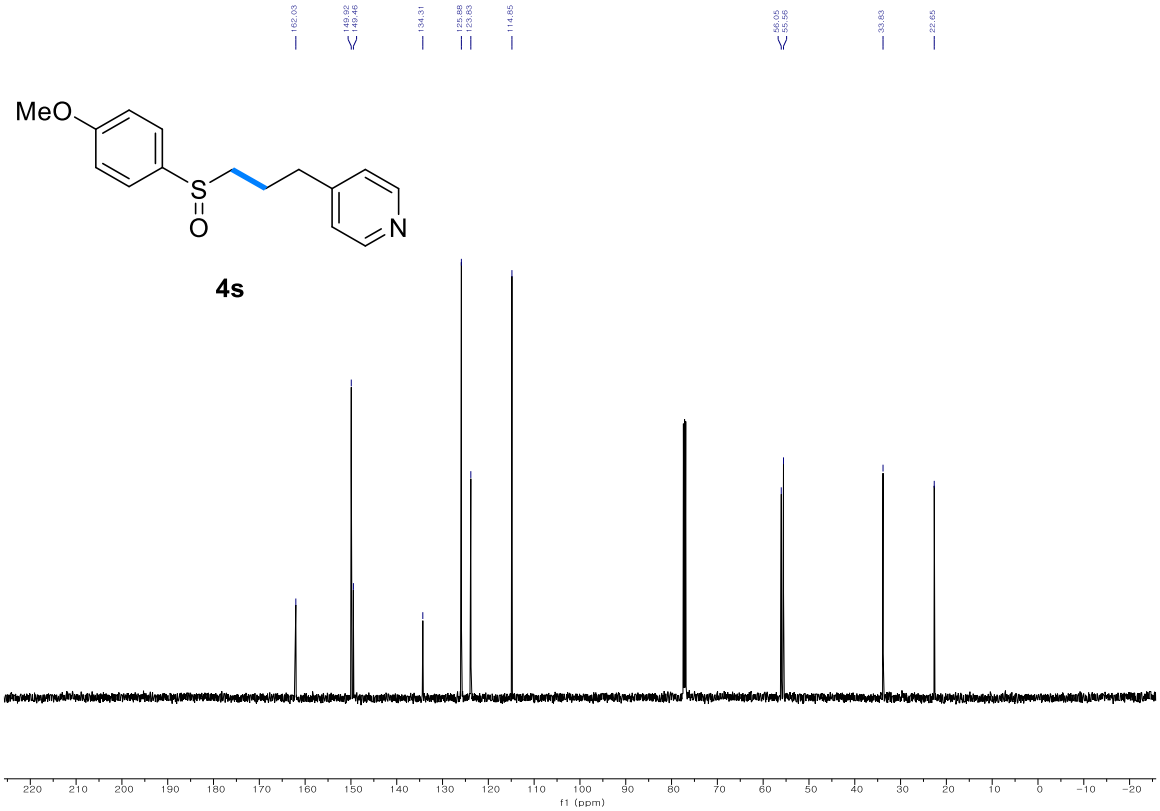
^{1}H-NMR (400 MHz, Chloroform-d) of **4q**



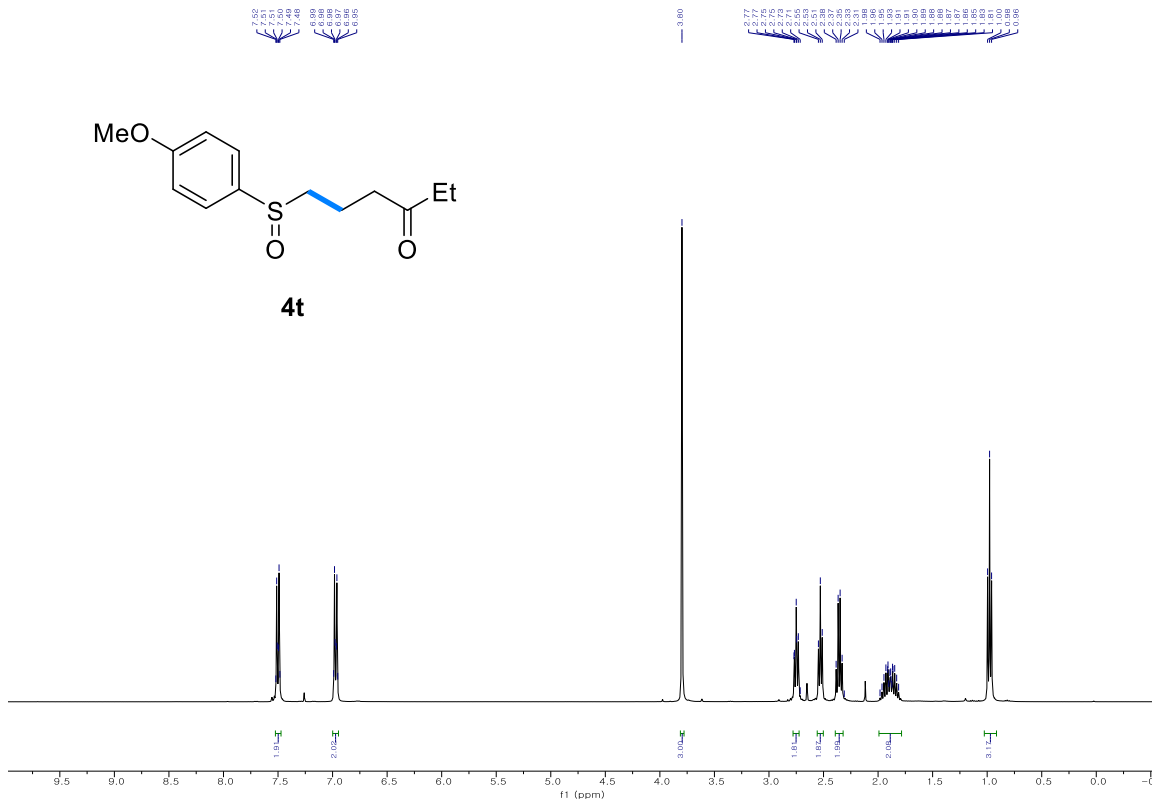
^{13}C-NMR (101 MHz, Chloroform-d) of **4q**



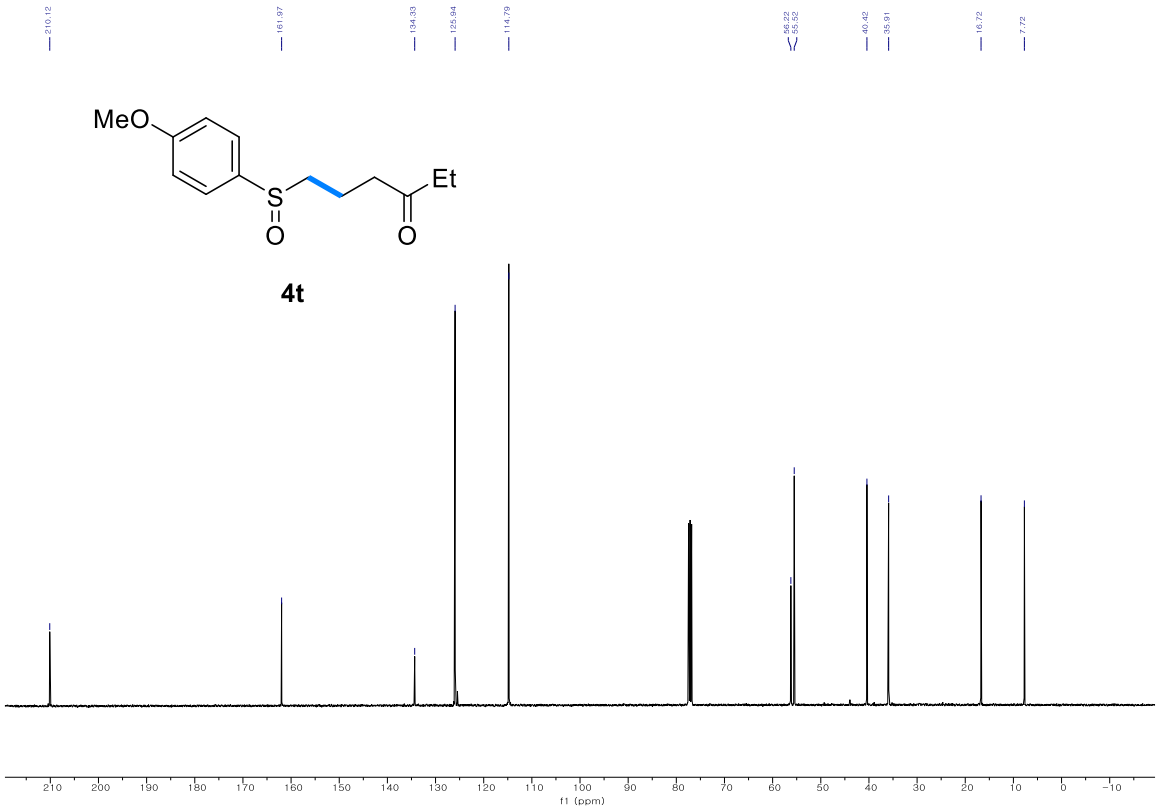
^{1}H-NMR (500 MHz, Chloroform-d) of **4s**



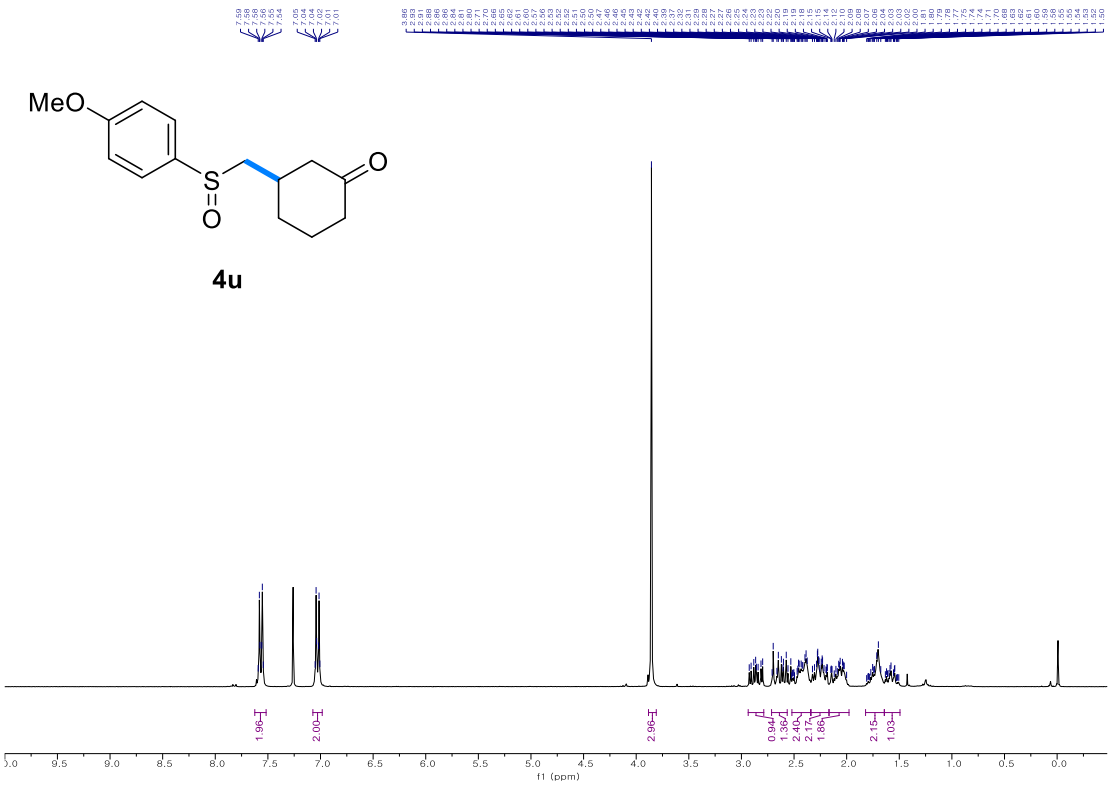
^{13}C-NMR (126 MHz, Chloroform-d) of **4s**



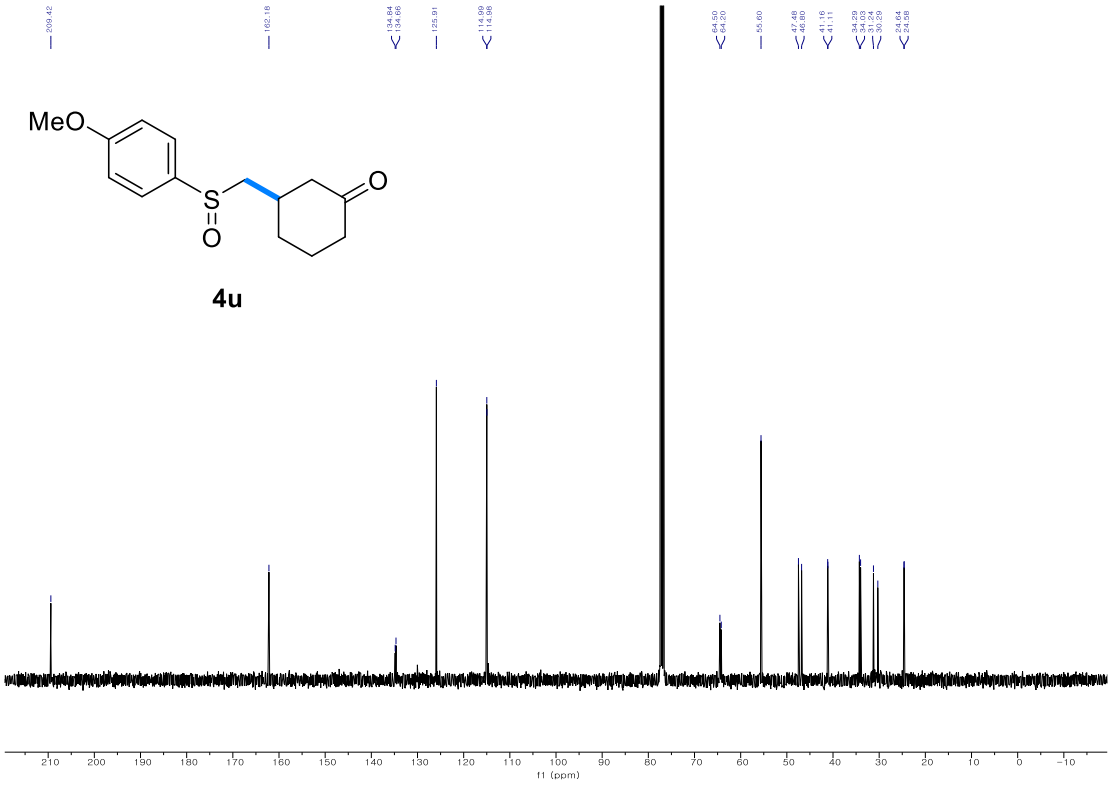
^{1}H-NMR (400 MHz, Chloroform-d) of **4t**



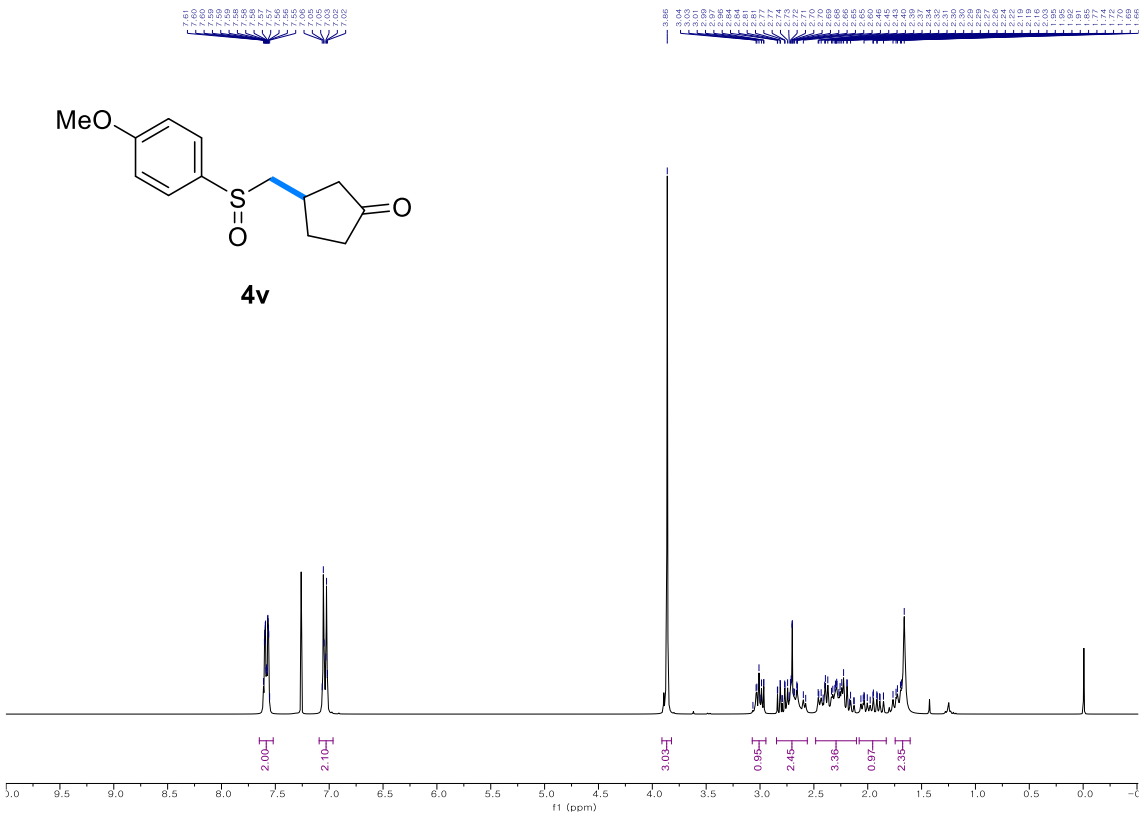
^{13}C-NMR (101 MHz, Chloroform-d) of **4t**



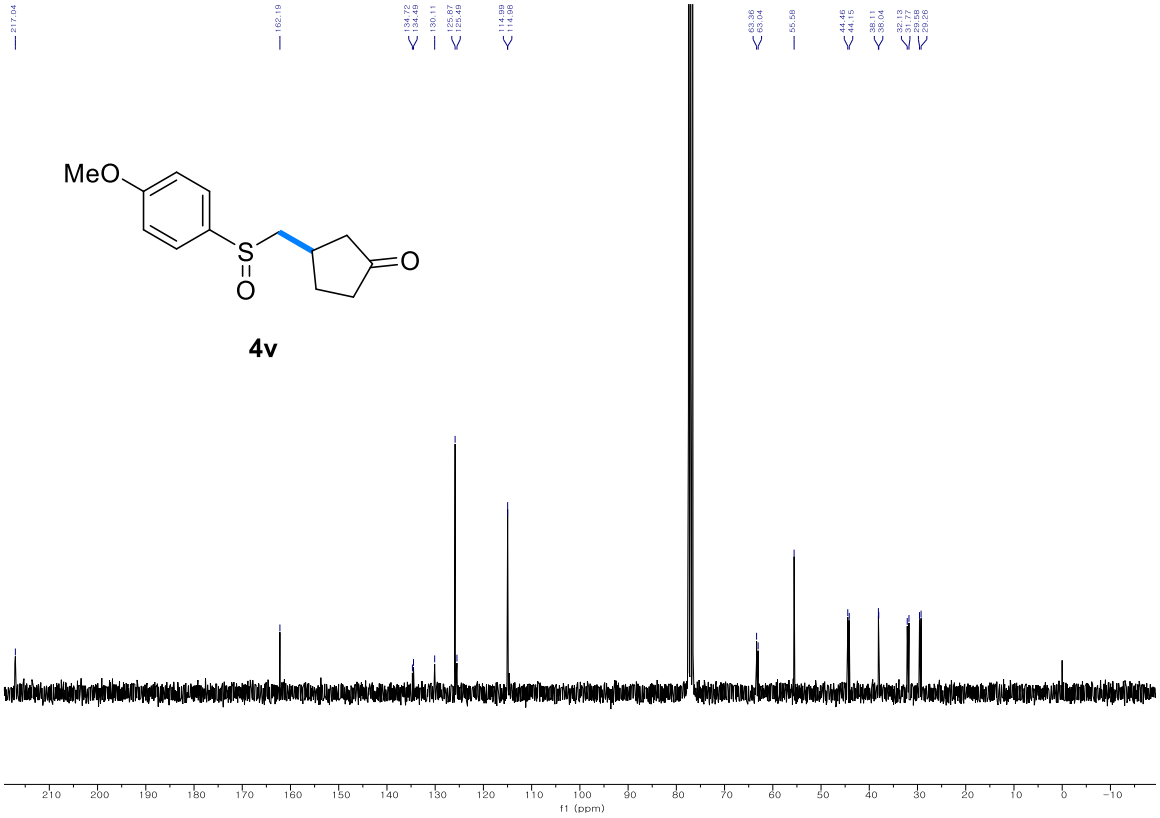
^{1}H-NMR (300 MHz, Chloroform-d) of **4u**



^{13}C-NMR (101 MHz, Chloroform-d) of **4u**



^{1}H-NMR (300 MHz, Chloroform-d) of **4v**



^{13}C-NMR (75 MHz, Chloroform-d) of **4v**