Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Visible Light-Induced C(sp^3)-S Bond Formation

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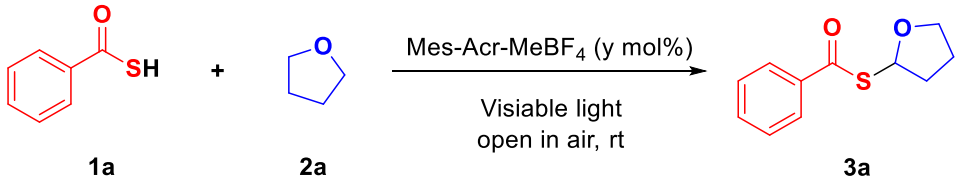
1 General information

Unless otherwise noted, all commercially available reagents and solvents were used without further additional purification. Thin layer chromatography was performed using precoated silica gel plates and visualized with UV light at 254 nm. Flash column chromatography was performed with silica gel (40-60μm). The photocatalytic reactions were performed on WATTCAS Parallel Light Reactor (WP-TEC-1020HSL). ^{1}H and ^{13}C nuclear magnetic resonance spectra (NMR) were obtained on Bruker Avance II 400 MHz, Bruker Avance III 500 MHz and Bruker Avance NEO 600M recorded in ppm (δ) downfield of TMS (δ=0) in $CDCl_3$ unless noted otherwise. Signal splitting patterns were described as singlet (s), doublet (d), triplet(t), quartet (q), quintet (quint), or multiplet (m), with coupling constants (J) in hertz (Hz). High resolution mass spectra (HRMS) were performed by an Agilent apparatus (TOF mass analyzer type) on an Electron Spray Injection (ESI) mass spectrometer. Fourier Transform Infrared Spectrometer (FT-IR) was performed on Thermo Scientific Nicolet 6700. The UV-vis spectra (UV-vis) were measured on Lambda 1050+. The fluorescence spectra were obtained with Hitachi F-7100 spectrophotometer.

2 Optimization of supplementary reaction conditions

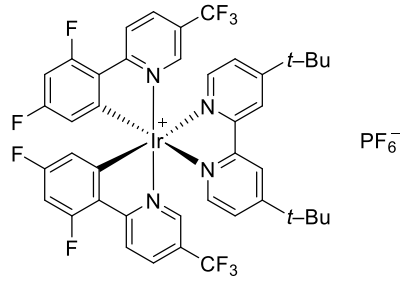
Table S1. Optimization of supplementary reaction conditions for the synthesis of **3a**[a].



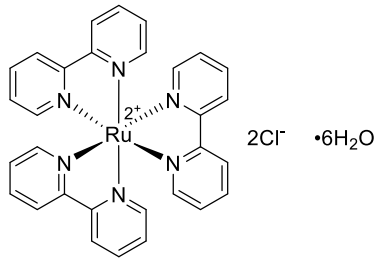
1a **2a** **3a**

Entry	Light (λ)/nm	Power/W	y/mol%	Yield[b]/%
1	White LED (6000-6500K)	20	1	65
2	700-705nm	20	1	n.d
3	660-665nm	20	1	n.d
4	595-600nm	20	1	n.d
5	540-545nm	20	1	n.d
6	495-500nm	20	1	32
7	460-465nm	20	1	71
8	425-430nm	20	1	71
9	365-370nm	20	1	68
10	425-430nm	5	1	49
11	425-430nm	10	1	57
12	425-430nm	15	1	65
13	425-430nm	20	0.1	65
14	425-430nm	20	0.5	71
15	425-430nm	20	2	53

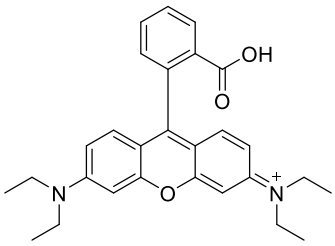
[a] Standard reaction conditions: **1a** (0.2 mmol), **2a** (1 ml), reaction for 1h at rt. [b] Isolated yield.



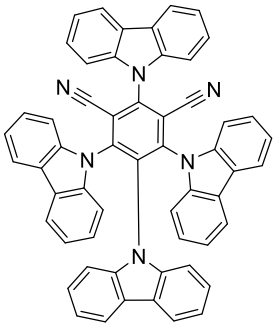
[Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$



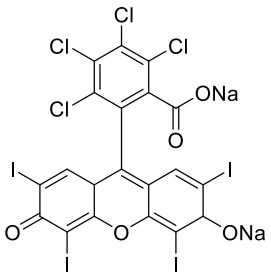
Ru(bpy)$_3$Cl$_2$•6H$_2$O



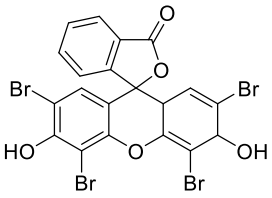
rhodamine B



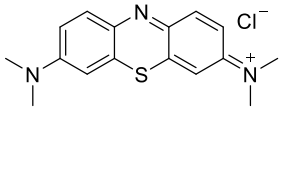
4-CzIPN



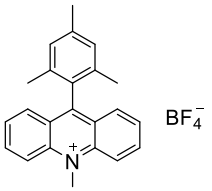
rose bengal



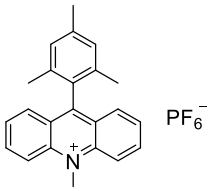
eosin Y



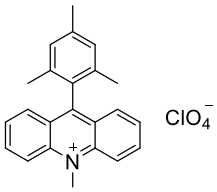
methylene blue



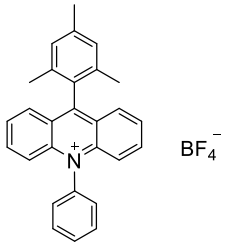
Mes-Acr-MeBF$_4$



Mes-Acr-MePF$_6$



Mes-Acr-MeClO$_4$



Mes-Acr-PhBF$_4$

Figure S1. Structure of photocatalyst

3 Details of photoreactor

The photocatalytic reaction were performed on WATTCAS Parallel Light Reactor (WP-TEC-1020HSL) with 20W 425-430nm blue COB LED.

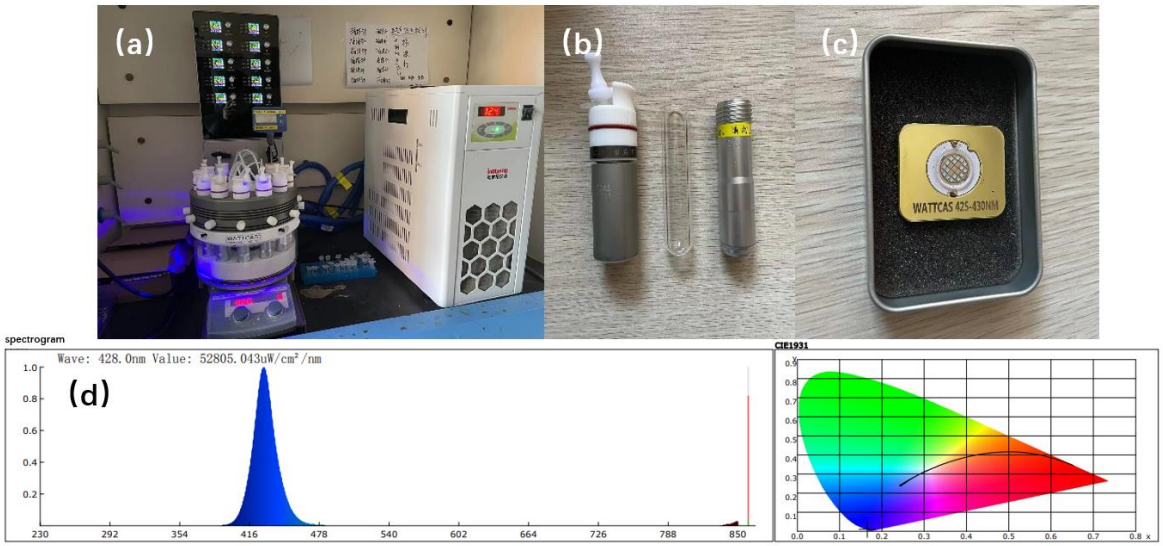
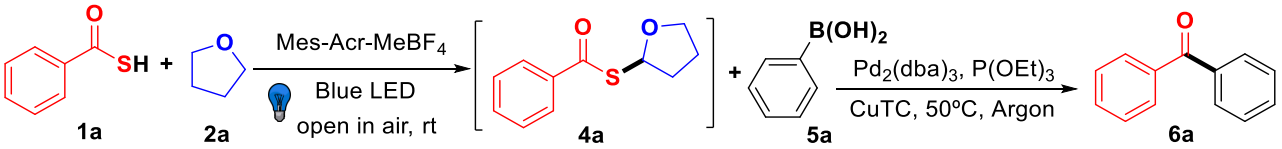


Figure S2. (a): photoreactor; (b): reaction vial; (c): chip; (d): spectrum of 425-430nm blue LED light

4 Representative procedures for the synthesis of products

To a vial containing Mes-Acr-MeBF$_4$ (0.4 mg, 0.5 mol%) in THF (3 mL) was added thiobenzoic acid (28 mg, 0.2 mmol). The mixture was stirred under 20 W blue LED (λ=425-430nm) at room temperature for 1 h and then was concentrated in vacuo. The mixture was purified with flash column chromatography (petroleum ether:ethyl acetate 14:1 to 8:1) to give the pure product **3a** (41 mg, 98% yield) as a colorless oil.

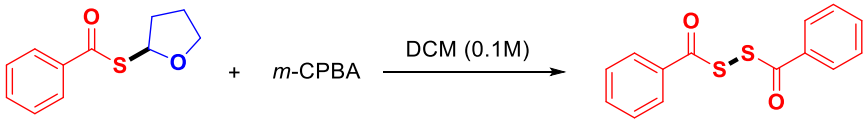


To a vial containing Mes-Acr-MeBF$_4$ (0.4 mg, 0.5 mol%) in THF (3 mL) was added thiobenzoic acid (1 equiv, 0.2 mmol). The mixture was stirred under 20 W blue LED (λ=425-430nm) at room temperature for 1 h. The reaction was transferred to a glove box filled with argon then added boronic acid (10 equiv), CuTC (1.5 equiv), $Pd_2(dba)_3$ (2.5 mol%), triethylphosphite (20 mol%). The mixture was stirred at 50°C for 24 h and then was concentrated in vacuo. The mixture was purified with flash column chromatography (petroleum ether:ethyl acetate 16:1 to 10:1) to give the pure product **6a** (26 mg, 73% yield) as a white solid.[S2]

(1) Isovaleric acid (20.5 mg, 0.2 mmol) was suspended in 1 mL DCM and stirred at room temperature. Oxalyl chloride (60 mg, 0.4 mmol) was added to this stirred solution. After stirring for 30 min, 2 μL of dimethylformamide (DMF) was added to this solution and the reaction was stirred for additional 6 h at room temperature. The solvent was evaporated to get a colorless oil as the product.[S3]

(2) To a vial containing sodium hydrosulfide hydrate (22 mg, 0.4 mmol) in MeOH (1 mL) was added the product from previous step at 0 ℃ for 1 h. Then, the mixture was stirred at room temperature for 2 h. The mixture was poured into water (2 mL) and then acidized with 1 N HCl (2 mL). The mixture was extracted with EtOAc (3×4 mL). The organic phase was washed by brine, dried over Na_2SO_4 and concentrated *in vacuo*. The product as a colorless oil was used to the visible-light induced reactions without further purification.[S4]

(3) To a vial containing Mes-Acr-MeBF$_4$ (0.4 mg, 0.5 mol%) in THF (3 mL) was added the product from previous step. The mixture was stirred under 20 W blue LED (λ=425-430nm) at room temperature for 1 h and then was concentrated *in vacuo*. The mixture was purified with flash column chromatography (petroleum ether:ethyl acetate 14:1 to 8:1) to give the pure product **3p** (19 mg, 0.1 mmol, 50% yield) as a colorless oil.

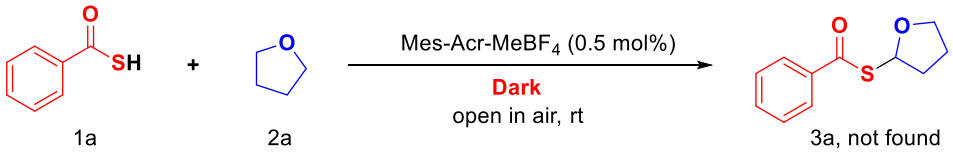


3a (0.2 mmol) **3 eq** **8, 99%, yield**

To a vial containing *m*-CPBA (104 mg, 0.6 mmol, 3 equiv) in DCM (2 mL) was added **3a** (41.6 mg, 0.2 mmol, 1 equiv). The mixture was stirred at room temperature for 24 h and then was concentrated *in vacuo*. The mixture was purified with flash column chromatography (petroleum ether:ethyl acetate 14:1 to 8:1) to give the pure product **8** (27 mg, 99% yield) as a white solid.

5 Mechanistic investigation

5.1 Dark experiment



To a vial containing Mes-Acr-$MeBF_4$ (0.4 mg, 0.5 mol%) in THF (3 mL) was added thiobenzoic acid (28 mg, 0.2 mmol). The mixture was stirred in dark at room temperature for 1 h and then was concentrated *in vacuo*. Product **3a** was not found by GC. Thus, the progress could be well controlled with/without light irradiation. (Figure S3)

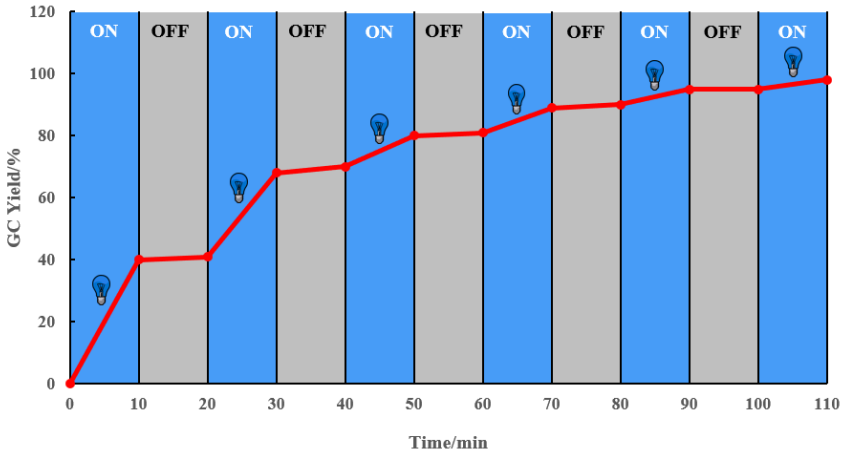
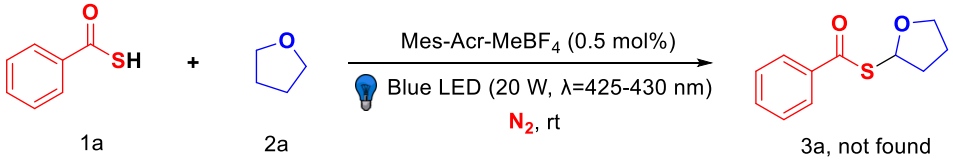


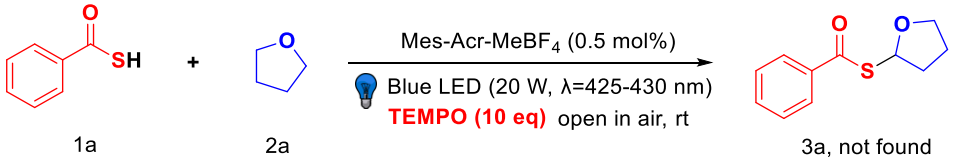
Figure S3. Light on/off experiment.

5.2 Nitrogen experiment



To a vial containing Mes-Acr-$MeBF_4$ (0.4 mg, 0.5 mol%) in THF (3 mL) was added thiobenzoic acid (28 mg, 0.2 mmol). The mixture was stirred in nitrogen at room temperature at 20W blue LED (λ=425-430 nm) for 1 h and then was concentrated *in vacuo*. Product **3a** was not found by GC.

5.3 Radical experiment



To a vial containing TEMPO (313 mg, 2 mmol, 10 equiv) in THF (3 mL) and Mes-Acr-MeBF$_4$ (0.4 mg, 0.5 mol%) was added thiobenzoic acid (28 mg, 0.2 mmol, 1 equiv). The mixture was stirred under 20 W blue LED (λ=425-430 nm) at room temperature for 1 h and then was concentrated *in vacuo*. Product **3a** was not found by GC. The corresponding adducts of tetrahydrofuran radical with TEMPO was detected by HRMS. (Figure S4)

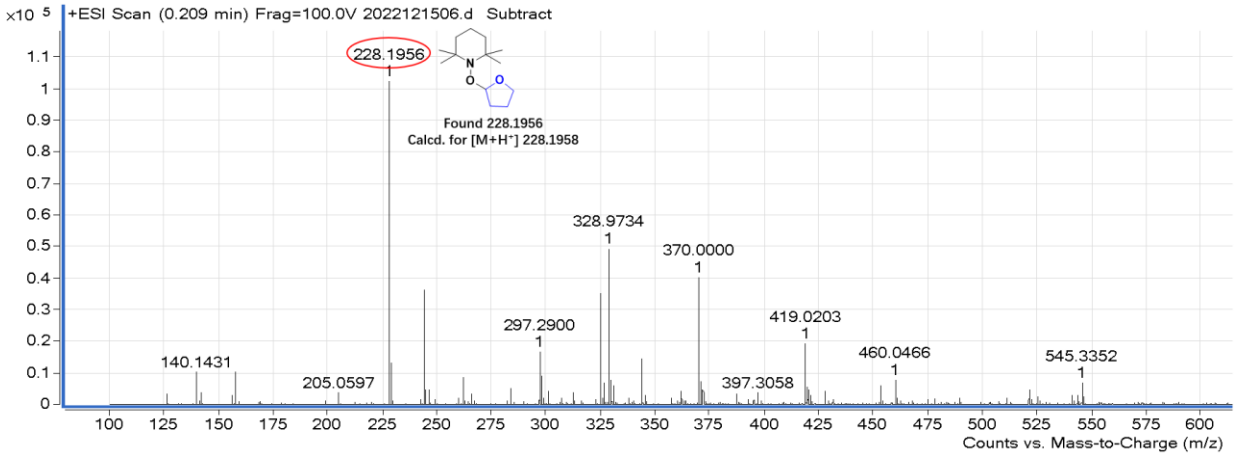
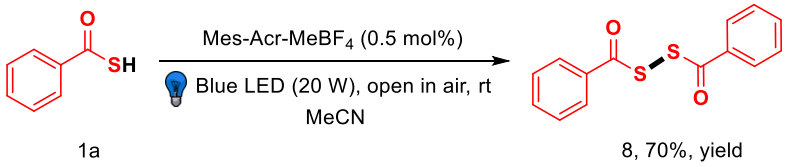


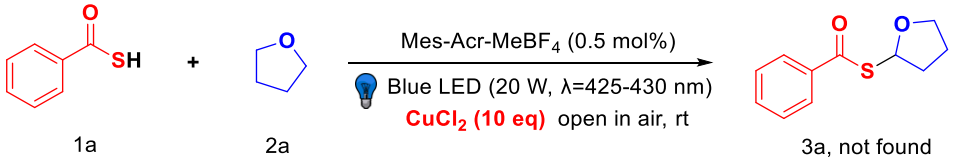
Figure S4. HRMS of radical experiment.

HRMS (ESI-TOF, *m/z*): [M+H$^+$] calcd for $C_{13}H_{26}NO_2$, 228.1958; found, 228.1956.



To a vial containing Mes-Acr-MeBF$_4$ (0.5 mol%, 0.4 mg) in MeCN (3 mL) was added thiobenzoic acid (28 mg, 0.2 mmol). The mixture was stirred under 20 W blue LED (λ=425-430 nm) at room temperature for 1 h and then was concentrated *in vacuo*. Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 16:1 to 10:1) to afford product **8** as a white solid (27 mg, 99% yield).

5.4 Single electron quenching experiment



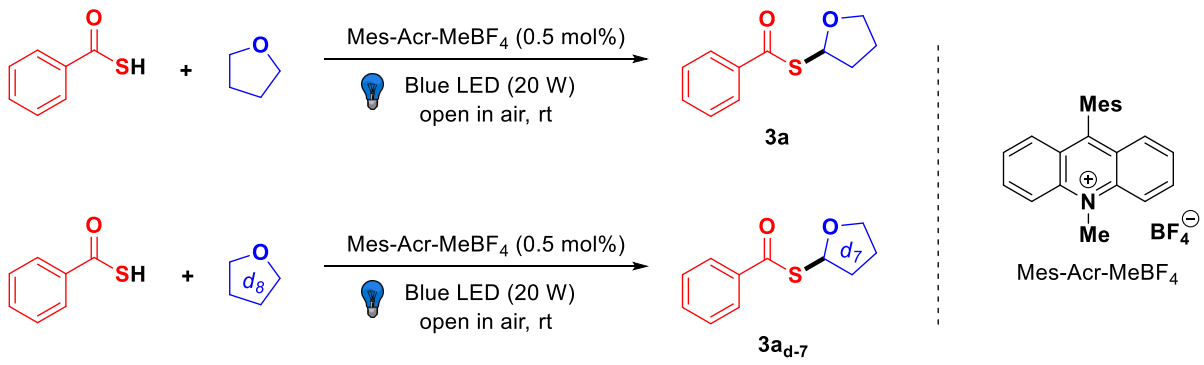
To a vial containing $CuCl_2$ (270 mg, 2 mmol, 10 equiv) in THF (3 mL) and Mes-Acr-$MeBF_4$ (0.4 mg, 0.5 mol%) was added thiobenzoic acid (28 mg, 0.2 mmol, 1 equiv). The mixture was stirred under 20 W blue LED (λ=425-430 nm) at room temperature for 1 h and then was concentrated *in vacuo*. Product **3a** was not found by GC.

5.5 Superoxide radical quenching experiment

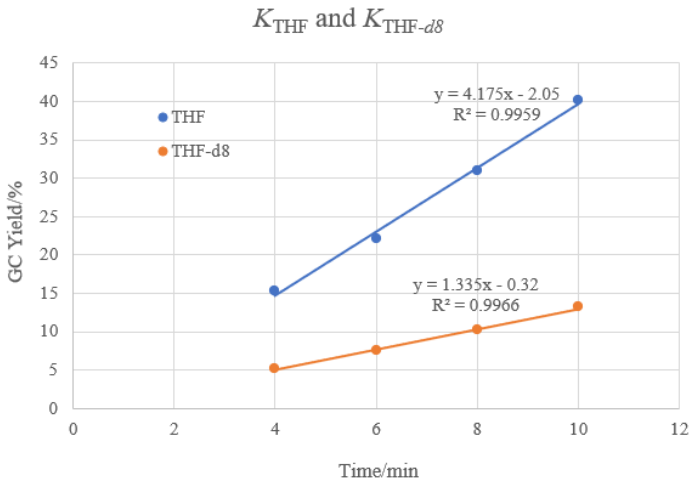
To a vial containing Benzoquinone (216 mg, 2 mmol, 10 equiv) in THF (3 mL) and Mes-Acr-$MeBF_4$ (0.4 mg, 0.5 mol%) was added thiobenzoic acid (28 mg, 0.2 mmol, 1 equiv). The mixture was stirred under 20 W blue LED (λ=425-430 nm) at room temperature for 1 h and then was concentrated *in vacuo*. Product **3a** was not found by GC.

5.6 Kinetic isotope effect experiment

Parallel kinetic isotope effect



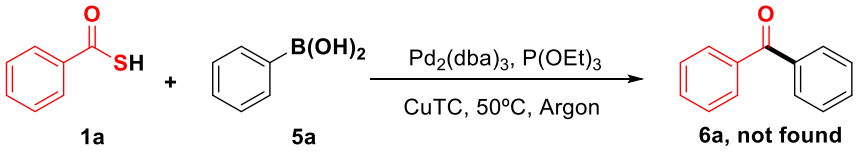
Thiobenzoic acid (28 mg, 0.2 mmol) was added to the vials containing Mes-Acr-MeBF$_4$ (0.4 mg, 0.5 mol%) in THF or THF-*d8* (3 mL). The mixtures were stirred under 20 W blue LED (λ=425-430 nm) at room temperature. Samples (500 μl) were taken every two minutes, concentrated *in vacuo*, and analyzed by GC. (Figure S5)



KIE: K_H/K_D= 4.175/1.335= 3.1

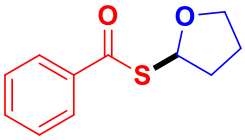
Figure S5. Initial rates of THF and THF-d_8.

5.7 Control experiment about Liebeskind-Srogl cross-coupling reaction



Thiobenzoic acid (1 equiv, 0.2mmol), boronic acid (10 equiv), CuTC (1.5 equiv) and $Pd_2(dba)_3$ (2.5 mol%) were flushed with argon in a round bottomed flask. Anhydrous THF (3ml) and triethylphosphite (20 mol%) were added. The mixture was stirred at 50℃ for 24 h and then was concentrated in vacuo. Product **6a** was not found by GC.

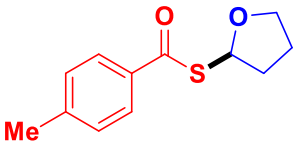
6 Characterization data of synthesized compound



3a

***S*-(tetrahydrofuran-2-yl) benzothioate (3a)** Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 14:1 to 8:1) to afford the product as a colorless oil (41 mg, 98% yield).

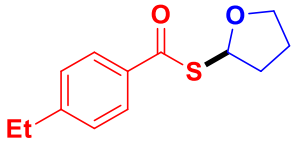
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.8 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 6.20 (dd, *J* = 7.1, 3.3 Hz, 1H), 4.05 – 3.89 (m, 2H), 2.46 (m, *J* = 16.0, 14.0, 7.3 Hz, 1H), 2.16 (m, *J* = 18.1, 15.0, 6.6 Hz, 1H), 2.10 – 1.92 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.63, 137.13, 133.50, 128.61, 127.42, 83.68, 68.48, 32.80, 24.71.
IR (KBr): v 2985, 2876, 1655, 1579, 1448, 1173, 1059, 895, 782, 695 cm^{-1}
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_{11}H_{12}O_2SNa$, 231.0456; found, 231.0458.



3b

***S*-(tetrahydrofuran-2-yl) 4-methylbenzothioate (3b)** Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 16:1 to 8:1) to afford the product as a colorless oil (37 mg, 85% yield).

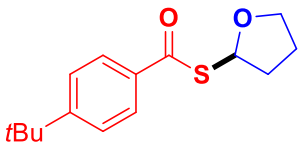
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 6.19 (dd, *J* = 7.1, 3.4 Hz, 1H), 4.03 – 3.92 (m, 2H), 2.46 (m, *J* = 16.3, 14.4, 7.4 Hz, 1H), 2.40 (s, 3H), 2.21 – 2.11 (m, 1H), 2.11 – 1.92 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.14, 144.34, 134.66, 129.25, 127.49, 83.56, 68.42, 32.81, 24.72, 21.69.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_{12}H_{14}O_2SNa$, 245.0612; found, 245.0617.



3c

***S*-(tetrahydrofuran-2-yl) 4-ethylbenzothioate (3c)** Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 16:1 to 8:1) to afford the product as a colorless oil (39 mg, 83% yield).

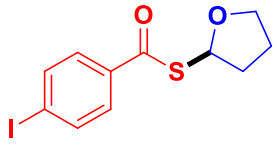
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 6.19 (dd, *J* = 7.1, 3.4 Hz, 1H), 4.04 – 3.91 (m, 2H), 2.69 (q, *J* = 7.6 Hz, 2H), 2.52 – 2.38 (m, 1H), 2.23 – 2.11 (m, 1H), 2.11 – 1.90 (m, 2H), 1.25 (t, *J* = 7.6 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.17, 150.51, 134.85, 128.08, 127.59, 83.57, 68.41, 32.82, 28.97, 24.71, 15.15.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_{13}H_{16}O_2SNa$, 259.0769; found, 259.0773.



3d

***S*-(tetrahydrofuran-2-yl) 4-(*tert*-butyl)benzothioate (3d)** Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 16:1 to 8:1) to afford the product as a colorless oil (41 mg, 79% yield).

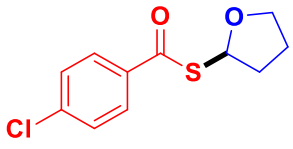
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 6.19 (dd, *J* = 7.0, 3.3 Hz, 1H), 4.03 – 3.91 (m, 2H), 2.46 (m, *J* = 16.0, 11.4, 7.3 Hz, 1H), 2.24 – 2.11 (m, 1H), 2.11 – 1.92 (m, 2H), 1.33 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.15, 157.28, 134.57, 127.32, 125.54, 83.58, 68.41, 35.17, 32.86, 31.08, 24.69.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_{15}H_{20}O_2SNa$, 287.1082; found, 287.1084.



3e

***S*-(tetrahydrofuran-2-yl) 4-iodobenzothioate (3e)** Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 18:1 to 12:1) to afford the product as a colorless oil (55 mg, 83% yield).

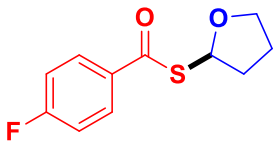
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 8.3 Hz, 2H), 6.19 (dd, *J* = 7.0, 3.2 Hz, 1H), 4.04 – 3.93 (m, 2H), 2.53 – 2.35 (m, 1H), 2.16 (m, *J* = 16.7, 8.3, 4.4 Hz, 1H), 2.10 – 1.95 (m, 2H).
^{13}C NMR (101 MHz, CDCl3) δ 190.94, 137.89, 136.48, 128.72, 101.29, 83.89, 68.53, 32.81, 24.66.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_{11}H_{11}O_2SINa$, 356.9422; found, 356.9418.



3f

***S*-(tetrahydrofuran-2-yl) 4-chlorobenzothioate (3f)** Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 18:1 to 12:1) to afford the product as a colorless oil (37 mg, 76% yield).

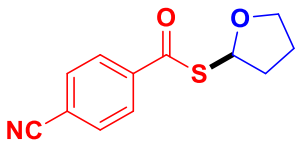
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 6.20 (dd, *J* = 7.0, 3.2 Hz, 1H), 3.98 (m, *J* = 8.4 Hz, 2H), 2.47 (m, *J* = 15.8, 7.5 Hz, 1H), 2.16 (m, *J* = 9.1, 8.5, 5.6 Hz, 1H), 2.11 – 1.93 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 190.43, 139.85, 135.49, 128.91, 128.75, 83.92, 68.52, 32.80, 24.66.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_{11}H_{11}O_2SClNa$, 265.0066; found, 265.0069.



3g

***S*-(tetrahydrofuran-2-yl) 4-fluorobenzothioate (3g)** Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 18:1 to 12:1) to afford the product as a colorless oil (31 mg, 69% yield).

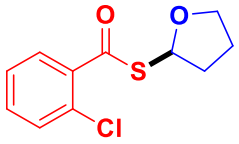
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.12 (t, *J* = 8.5 Hz, 2H), 6.20 (dd, *J* = 7.0, 3.2 Hz, 1H), 3.98 (m, *J* = 8.4 Hz, 2H), 2.47 (m, *J* = 15.7, 7.5 Hz, 1H), 2.23 – 2.12 (m, 1H), 2.03 (m, *J* = 13.7, 12.8, 6.7 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 190.05, 167.21, 164.68, 133.51, 133.48, 130.00, 129.90, 115.84, 115.62, 83.86, 68.47, 32.77, 24.66.
^{19}F NMR (376 MHz, $CDCl_3$) δ -104.58.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_{11}H_{11}O_2SFNa$, 249.0361; found, 249.0356.



3h

***S*-(tetrahydrofuran-2-yl) 4-cyanobenzothioate (3h)** Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 14:1 to 8:1) to afford the product as a colorless oil (31 mg, 66% yield).

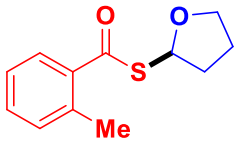
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 6.22 (dd, *J* = 7.0, 3.1 Hz, 1H), 4.09 – 3.94 (m, 2H), 2.49 (m, *J* = 16.1, 14.0, 7.4 Hz, 1H), 2.27 – 2.13 (m, 1H), 2.13 – 1.96 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 190.44, 140.22, 132.50, 127.82, 117.82, 116.70, 84.36, 68.68, 32.85, 24.59.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_{12}H_{11}NO_2SNa$, 256.0408; found, 256.0416.



3i

***S*-(tetrahydrofuran-2-yl) 2-chlorobenzothioate (3i)** Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 18:1 to 12:1) to afford the product as a colorless oil (35 mg, 73% yield).

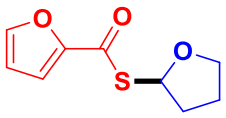
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.41 (m, *J* = 9.5, 8.0, 1.5 Hz, 2H), 7.31 (m, *J* = 7.4, 1.5 Hz, 1H), 6.18 (dd, *J* = 7.0, 3.2 Hz, 1H), 4.05 – 3.92 (m, 2H), 2.48 (m, *J* = 16.1, 14.1, 7.4 Hz, 1H), 2.17 (m, *J* = 13.2, 7.6, 5.7, 3.3 Hz, 1H), 2.11 – 1.92 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.55, 137.47, 132.25, 130.87, 130.83, 129.31, 126.67, 84.37, 68.66, 32.89, 24.60.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_{11}H_{11}O_2SClNa$, 265.0066; found, 265.0071.



3j

***S*-(tetrahydrofuran-2-yl) 2-methylbenzothioate (3j)** Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 16:1 to 8:1) to afford the product as a colorless oil (32 mg, 71% yield).

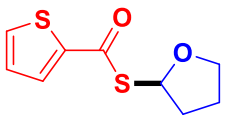
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.23 (t, *J* = 5.8 Hz, 2H), 6.13 (dd, *J* = 6.8, 3.2 Hz, 1H), 4.04 – 3.91 (m, 2H), 2.51 (s, 3H), 2.49 – 2.39 (m, 1H), 2.19 – 2.09 (m, 1H), 2.09 – 1.92 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 193.59, 137.34, 137.16, 131.75, 131.64, 128.71, 125.71, 83.81, 68.44, 32.73, 24.74, 20.72.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_{12}H_{14}O_2SNa$, 245.0612; found, 245.0620.



3k

***S*-(tetrahydrofuran-2-yl) furan-2-carbothioate (3k)** Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 14:1 to 8:1) to afford the product as a colorless oil (31 mg, 83% yield).

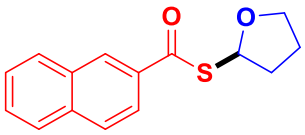
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.19 (d, *J* = 3.5 Hz, 1H), 6.56 – 6.50 (m, 1H), 6.22 (dd, *J* = 7.1, 3.3 Hz, 1H), 4.03 – 3.93 (m, 2H), 2.54 – 2.34 (m, 1H), 2.24 – 2.11 (m, 1H), 2.11 – 1.91 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 179.88, 150.87, 146.27, 115.97, 112.27, 83.07, 68.43, 32.78, 24.62.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_9H_{10}O_3SNa$, 221.0248; found, 221.0252.



3l

***S*-(tetrahydrofuran-2-yl) thiophene-2-carbothioate (3l)** Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 14:1 to 8:1) to afford the product as a colorless oil (36 mg, 85% yield).

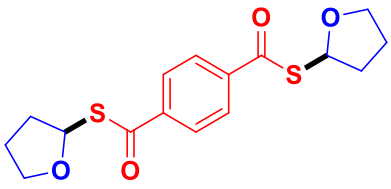
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 3.8 Hz, 1H), 7.62 (d, *J* = 4.9 Hz, 1H), 7.10 (t, *J* = 4.4 Hz, 1H), 6.22 (dd, *J* = 7.1, 3.2 Hz, 1H), 4.05 – 3.91 (m, 2H), 2.46 (m, *J* = 16.0, 14.1, 7.3 Hz, 1H), 2.22 – 2.11 (m, 1H), 2.11 – 1.91 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 183.38, 142.34, 132.96, 131.36, 127.86, 84.02, 68.47, 32.81, 24.62.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_9H_{10}O_2S_2Na$, 237.0020; found, 237.0023.



3m

***S*-(tetrahydrofuran-2-yl) naphthalene-2-carbothioate (3m)** Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 14:1 to 8:1) to afford the product as a colorless oil (27 mg, 52% yield).

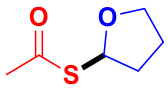
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.97 (t, *J* = 7.3 Hz, 2H), 7.87 (dd, *J* = 8.4, 3.1 Hz, 2H), 7.57 (m, *J* = 14.8, 7.0 Hz, 2H), 6.27 (dd, *J* = 7.1, 3.3 Hz, 1H), 4.10 – 3.92 (m, 2H), 2.50 (m, *J* = 20.8, 7.7 Hz, 1H), 2.28 – 2.15 (m, 1H), 2.15 – 1.76 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.48, 135.84, 134.51, 132.45, 129.60, 128.95, 128.51, 128.47, 127.82, 126.90, 123.23, 83.83, 68.50, 32.89, 24.72.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_{15}H_{14}O_2SNa$, 281.0612; found, 281.0620.



3n

***S,S*-bis(tetrahydrofuran-2-yl) benzene-1,4-bis(carbothioate) (3n)** Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 8:1 to 4:1) to afford the product as a colorless oil (53 mg, 79% yield).

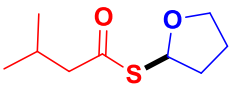
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 4H), 6.21 (dd, *J* = 7.0, 3.1 Hz, 2H), 4.08 – 3.93 (m, 4H), 2.48 (m, *J* = 14.9, 7.5 Hz, 2H), 2.23 – 2.13 (m, 2H), 2.10 – 1.98 (m, 5H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 190.92, 140.65, 127.58, 84.10, 68.58, 32.85, 24.62.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_{16}H_{18}O_4S_2Na$, 361.0544; found, 361.0551.



3o

***S*-(tetrahydrofuran-2-yl) ethanethioate (3o)** Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 16:1 to 8:1) to afford the product as a colorless oil (22 mg, 75% yield).

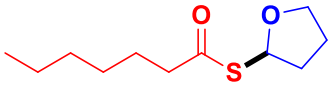
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.99 (dd, *J* = 7.1, 3.1 Hz, 1H), 3.96 – 3.88 (m, 2H), 2.43 – 2.35 (m, 1H), 2.34 (s, 3H), 2.09 – 2.01 (m, 1H), 1.99 – 1.91 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 195.58, 83.31, 68.32, 32.39, 31.15, 24.70.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_6H_{10}O_2SNa$, 169.0299; found, 169.0297.



3p

***S*-(tetrahydrofuran-2-yl) 3-methylbutanethioate (3p)** Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 16:1 to 8:1) to afford the product as a colorless oil (23 mg, 60% yield).

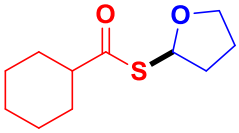
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.99 (dd, *J* = 7.2, 3.1 Hz, 1H), 3.98 – 3.85 (m, 2H), 2.45 – 2.41 (m, 2H), 2.41 – 2.31 (m, 1H), 2.18 (m, *J* = 20.5, 10.2, 5.3 Hz, 1H), 2.06 – 1.90 (m, 3H), 0.96 (dd, *J* = 6.7, 1.8 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.62, 83.07, 68.31, 53.43, 32.58, 26.25, 24.70, 22.35, 22.32.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_9H_{16}O_2SNa$, 211.0769; found, 211.0768.



3q

***S*-(tetrahydrofuran-2-yl) heptanethioate (3q)** Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 16:1 to 8:1) to afford the product as a colorless oil (32 mg, 73% yield).

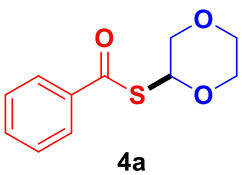
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.40 – 5.25 (m, 1H), 4.09 – 3.88 (m, 2H), 2.70 (t, *J* = 7.4 Hz, 2H), 2.30 (m, *J* = 19.8, 12.4, 6.9 Hz, 1H), 2.17 – 1.97 (m, 2H), 1.97 – 1.84 (m, 1H), 1.79 – 1.63 (m, 2H), 1.29 (s, 6H), 0.88 (t, *J* = 6.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 197.89, 89.39, 67.87, 42.52, 32.37, 31.36, 28.59, 25.45, 24.35, 22.40, 13.97.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_{11}H_{20}O_2SNa$, 239.1082; found, 239.1084.



3r

***S*-(tetrahydrofuran-2-yl) cyclohexanecarbothioate (3r)** Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 16:1 to 8:1) to afford the product as a colorless oil (30 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.34 – 5.26 (m, 1H), 4.07 – 3.86 (m, 2H), 2.68 (t, *J* = 11.3 Hz, 1H), 2.28 (m, *J* = 12.9, 6.0 Hz, 1H), 2.12 – 1.86 (m, 5H), 1.80 (m, *J* = 12.5 Hz, 2H), 1.67 (m, *J* = 9.5 Hz, 1H), 1.51 (m, *J* = 12.2 Hz, 2H), 1.27 (m, *J* = 9.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 200.65, 89.31, 67.87, 51.58, 32.36, 29.57, 29.38, 25.52, 25.43, 25.38, 24.35.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_{11}H_{18}O_2SNa$, 237.0925; found, 237.0921.

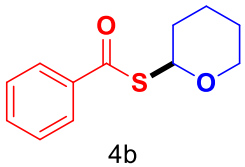


4a

***S*-(1,4-dioxan-2-yl) benzothioate (4a)** Purified via flash column chromatography on silica gel (from petroleum

ether:ethyl acetate 14:1 to 8:1) to afford the product as a colorless oil (25 mg, 56% yield).

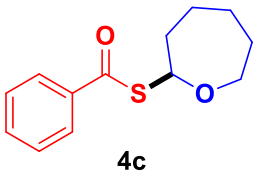
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.7 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 5.93 (t, *J* = 3.0 Hz, 1H), 4.11 – 4.05 (m, 2H), 3.87 (dd, *J* = 12.0, 3.6 Hz, 1H), 3.82 – 3.72 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 189.70, 136.74, 133.82, 128.73, 127.57, 78.89, 70.41, 66.73, 63.91.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_{11}H_{12}O_3SNa$, 247.0405; found, 247.0419.



4b

***S*-(tetrahydro-2H-pyran-2-yl) benzothioate (4b)** Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 14:1 to 8:1) to afford the product as a colorless oil (34 mg, 76% yield).

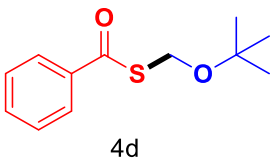
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 5.93 (t, *J* = 4.6 Hz, 1H), 3.95 (m, *J* = 11.6, 7.6, 3.9 Hz, 1H), 3.88 – 3.69 (m, 1H), 2.11 (m, *J* = 12.9, 8.7, 4.2 Hz, 1H), 1.89 (m, *J* = 13.1, 5.5 Hz, 1H), 1.83 – 1.74 (m, 2H), 1.71 – 1.58 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 190.24, 137.14, 133.51, 128.61, 127.48, 80.90, 65.91, 31.65, 25.42, 21.81.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_{12}H_{114}O_2SNa$, 245.0612; found, 245.0617.



4c

***S*-(oxepan-2-yl) benzothioate (4c)** Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 14:1 to 8:1) to afford the product as a colorless oil (33 mg, 69% yield).

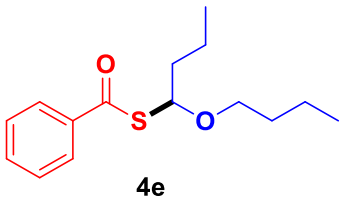
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.3 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 5.91 (dd, *J* = 11.4, 5.2 Hz, 1H), 3.79 (m, *J* = 7.3, 3.7 Hz, 2H), 2.26 (m, *J* = 8.3, 7.0, 3.9 Hz, 1H), 2.06 – 1.92 (m, 1H), 1.91 – 1.64 (m, 5H), 1.49 – 1.35 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.15, 137.25, 133.38, 128.56, 127.46, 83.54, 66.16, 35.46, 30.58, 28.38, 25.64.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_{13}H_{16}O_2SNa$, 259.0769; found, 259.0772.



4d

***S*-(tert-butoxymethyl) benzothioate (4d)** Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 18:1 to 10:1) to afford the product as a colorless oil (28 mg, 63% yield).

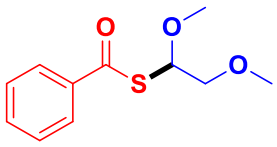
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 5.22 (s, 2H), 1.30 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 190.61, 137.02, 133.52, 128.61, 127.51, 75.96, 62.79, 27.72.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_{12}H_{16}O_2SNa$, 247.0769; found, 265.0773.



4e

***S*-(1-butoxybutyl) benzothioate (4e)** Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 16:1 to 8:1) to afford the product as a colorless oil (29 mg, 55% yield).

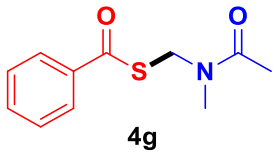
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.2 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 5.62 (dd, *J* = 7.3, 5.6 Hz, 1H), 3.69 (m, *J* = 9.4, 6.5 Hz, 1H), 3.49 (m, *J* = 9.4, 6.5 Hz, 1H), 2.10 – 1.98 (m, 1H), 1.98 – 1.84 (m, 1H), 1.59 – 1.55 (m, 4H), 1.39 (m, *J* = 10.7, 5.4 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 192.38, 133.43, 128.60, 127.43, 85.73, 69.18, 39.16, 31.47, 19.35, 19.28, 13.84, 13.70.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_{15}H_{22}O_2SNa$, 289.1238; found, 289.1244.



4f

***S*-(1,2-dimethoxyethyl) benzothioate (4f)** Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 16:1 to 8:1) to afford the product as a colorless oil (26 mg, 58% yield).

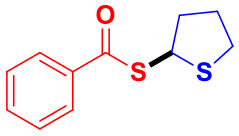
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.3 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 5.70 (dd, *J* = 5.4, 4.2 Hz, 1H), 3.82 – 3.73 (m, 2H), 3.47 (d, *J* = 2.1 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.36, 136.76, 133.78, 128.70, 127.53, 85.28, 75.08, 59.48, 57.22.
HRMS (ESI-TOF, *m/z*): $[M+K]^+$ calcd for $C_{11}H_{14}O_3SK$, 265.0301; found, 265.0297.



4g

***S*-((*N*-methylacetamido)methyl) benzothioate (4g)** Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 2:1 to 1:1) to afford the product as a colorless oil (33 mg, 75% yield).

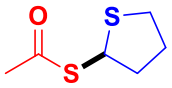
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.88 (m, 2H), 7.67 – 7.55 (m, 1H), 7.55 – 7.42 (m, 2H), 5.10 (d, *J* = 4.7 Hz, 2H), 3.05 (d, *J* = 53.7 Hz, 3H), 2.18 (d, *J* = 61.8 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.85, 171.55, 134.05, 133.73, 128.82, 128.70, 127.52, 127.46, 50.64, 46.60, 36.04, 21.69, 21.58.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_{11}H_{13}NO_2SNa$, 246.0565; found, 246.0555.



4h

***S*-(tetrahydrothiophen-2-yl) benzothioate (4h)** Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 14:1 to 8:1) to afford the product as a colorless oil (35 mg, 79% yield).

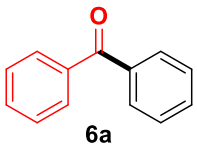
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 4.29 (dd, *J* = 12.5, 6.2 Hz, 1H), 3.34 (dd, *J* = 10.9, 6.1 Hz, 1H), 2.99 (t, *J* = 6.6 Hz, 2H), 2.88 (dd, *J* = 10.9, 6.5 Hz, 1H), 2.43 (m, *J* = 12.0, 6.0 Hz, 1H), 2.11 (m, *J* = 13.8, 7.0 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.50, 136.87, 133.57, 128.68, 127.25, 46.10, 37.03, 36.62, 29.85.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_{11}H_{12}OS_2Na$, 247.0027; found, 247.0032.



4i

***S*-(tetrahydrothiophen-2-yl) ethanethioate (4i)** Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 14:1 to 8:1) to afford the product as a colorless oil (26 mg, 80% yield).

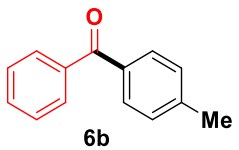
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.14 – 3.99 (m, 1H), 3.23 (dd, *J* = 11.0, 6.1 Hz, 1H), 2.93 (t, *J* = 6.8 Hz, 2H), 2.76 (dd, *J* = 10.9, 6.7 Hz, 1H), 2.34 (s, 3H), 2.33 – 2.28 (m, 1H), 1.99 (m, *J* = 14.2, 7.2 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 195.35, 46.01, 36.82, 36.38, 30.71, 29.73.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_6H_{10}OS_2Na$, 185.0071; found, 185.0079.



6a

Benzophenone (6a) Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 16:1 to 10:1) to afford the product as a white solid (26 mg, 73% yield).

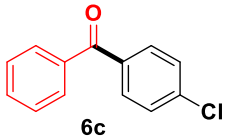
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.75 (m, 2H), 7.70 – 7.66 (m, 2H), 7.65 – 7.58 (m, 3H), 7.52 – 7.46 (m, 2H).
Compound **6a** is known compound, and the proton spectrum is fully consistent with literature reported.[S5]



6b

4-Methylbenzophenone (6b) Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 16:1 to 10:1) to afford the product as a white solid (28 mg, 71% yield).

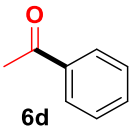
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.76 (m, 2H), 7.75 – 7.69 (m, 2H), 7.60 – 7.55 (m, 1H), 7.47 (t, J = 7.7 Hz, 2H), 7.28 (d, J = 7.8 Hz, 2H), 2.44 (s, 3H).
Compound **6b** is known compound, and the proton spectrum is fully consistent with literature reported.[S5]



6c

4-Chlorobenzophenone (6c) Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 16:1 to 10:1) to afford the product as a white solid (30 mg, 70% yield).

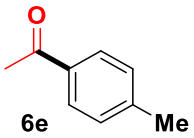
1H NMR (400 MHz, $CDCl_3$)) δ 7.76 (t, J = 7.0 Hz, 4H), 7.59 (t, J = 7.0 Hz, 1H), 7.52-7.42 (m, 4H).[S5]
Compound **6c** is known compound, and the proton spectrum is fully consistent with literature reported.



6d

Acetophenone (6d) Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 30:1 to 20:1) to afford the product as a colorless liquid (13 mg, 52% yield).

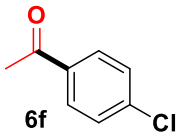
1H NMR (400 MHz, $CDCl_3$)) δ 7.97 (d, J = 8.0 Hz, 2H), 7.57 (t, J = 7.8 Hz, 1H), 7.47 (t, J = 7.2 Hz, 2H), 2.62 (s, 3H).
Compound **6d** is known compound, and the proton spectrum is fully consistent with literature reported.[S6]



6e

1-(*p*-Tolyl)ethan-1-one (6e) Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 30:1 to 20:1) to afford the product as a colorless liquid (14 mg, 51% yield).

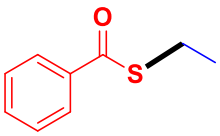
1H NMR (400 MHz, $CDCl_3$)) δ 7.86 (d, J = 8.1 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 2.58 (s, 3H), 2.41 (s, 3H).
Compound **6e** is known compound, and the proton spectrum is fully consistent with literature reported.[S7]



6f

1-(4-Chlorophenyl)ethan-1-one (6f) Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 30:1 to 20:1) to afford the product as a colorless liquid (16 mg, 51% yield).

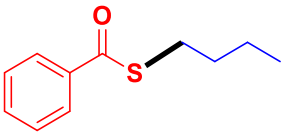
1H NMR (400 MHz, $CDCl_3$)) δ 7.90 (d, J = 8.6 Hz, 2H), 7.44 (d, J = 8.6 Hz, 2H), 2.59 (s, 3H).
Compound **6f** is known compound, and the proton spectrum is fully consistent with literature reported.[S6]



7a

***S*-ethyl benzothioate (7a)** Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 20:1 to 10:1) to afford the product as a colorless oil (17 mg, 51% yield).

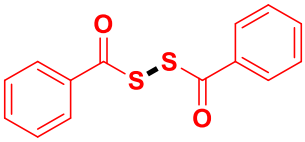
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.90 (m, 2H), 7.56 (m, *J* = 7.4 Hz, 1H), 7.44 (m, *J* = 7.6 Hz, 2H), 3.08 (q, *J* = 7.4 Hz, 2H), 1.36 (t, *J* = 7.4 Hz, 3H).
Compound **7a** is known compound, and the proton spectrum is fully consistent with literature reported.[S8]



7b

***S*-butyl benzothioate (7b)** Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 20:1 to 10:1) to afford the product as a colorless oil (13 mg, 32% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 7.90 (m, 2H), 7.59 (m, *J* = 7.4 Hz, 1H), 7.47 (m, *J* = 7.7 Hz, 2H), 3.11 (t, *J* = 7.3 Hz, 2H), 1.77 – 1.56 (m, 2H), 1.56 – 1.43 (m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H).
Compound **7b** is known compound, and the proton spectrum is fully consistent with literature reported.[S9]



8

Benzoic dithioperoxyanhydride (8) Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 16:1 to 10:1) to afford the product as a white solid (27 mg, 99% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.7 Hz, 2H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 2H).
Compound **8** is known compound, and the proton spectrum is fully consistent with literature reported.[S10]

7 Reference

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(S6) X. Zhu, Y. Liu, C. Liu, H. Yang, H. Fu, *Green Chem.* **2020**, *22*, 4357-4363.

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(S8) L. Steemers, L. Wijsman, J. H. van Maarseveen, *Adv. Synth. Catal.* **2018**, *360*, 4241-4245.

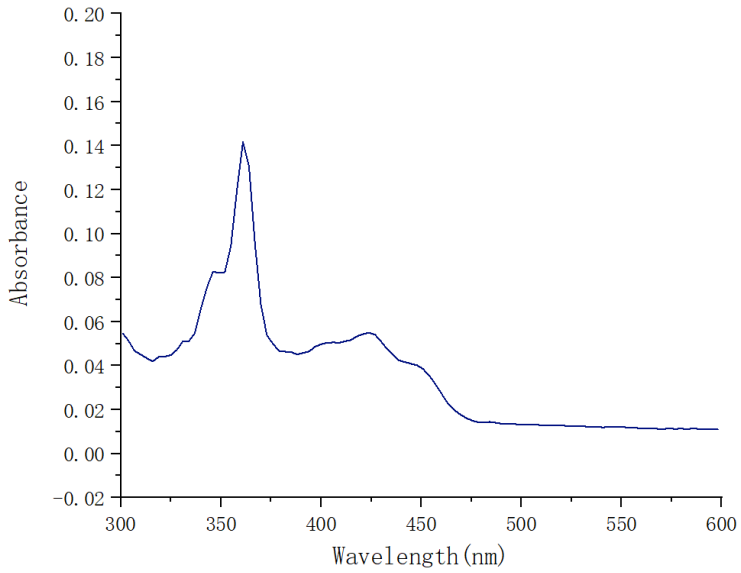
(S9) J. Zeng, Y. Liu, P. A. Hsieh, Y. Huang, C. Yi, S. S. Badsara, C. F. Lee, *Green Chem.* **2014**, *16*, 2644-2652.

(S10) P. Qiu, X. Duan, M. Li, Y. Zheng, W. Song, *Org. Lett.* **2022**, *24*, 2733-2737.

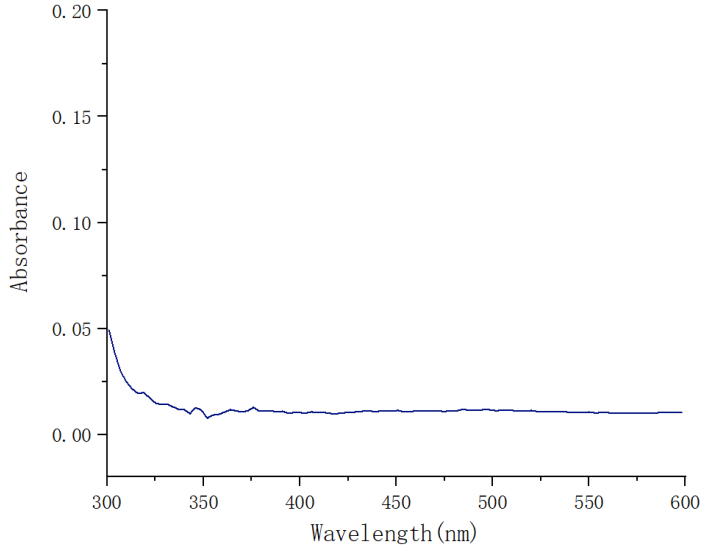
8 UV-Vis spectra:

The UV-vis spectra (UV-vis) were measured on Lambda 1050+. In general, sample (1×10^{-5} M in THF) was added in a 4.5 cm quartz cuvette.

1) Mes-Acr-MeBF_4 (1×10^{-5} M) in THF



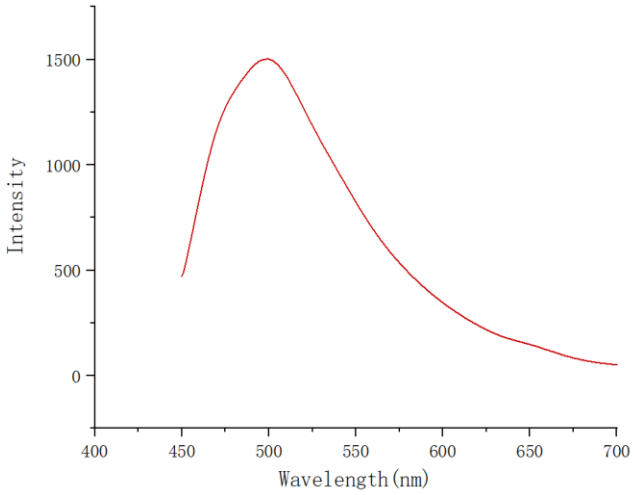
2) **3a** (1×10^{-5} M) in THF



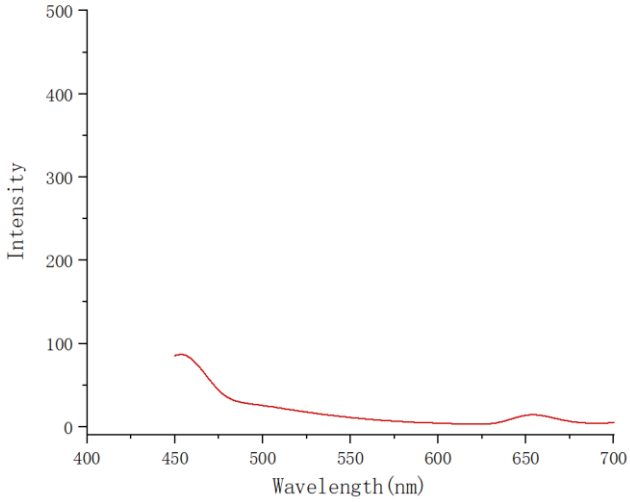
9 Fluorescence emission spectrum:

Emission intensities results were monitored by an F-7100 spectrophotometer. All samples were excited at 402nm and the emission intensity was collected at 450-700 nm. In general, sample (1×10^{-5} M in THF) was added in a 4.5 cm quartz cuvette.

1) Mes-Acr-MeBF_4 (1×10^{-5} M) in THF

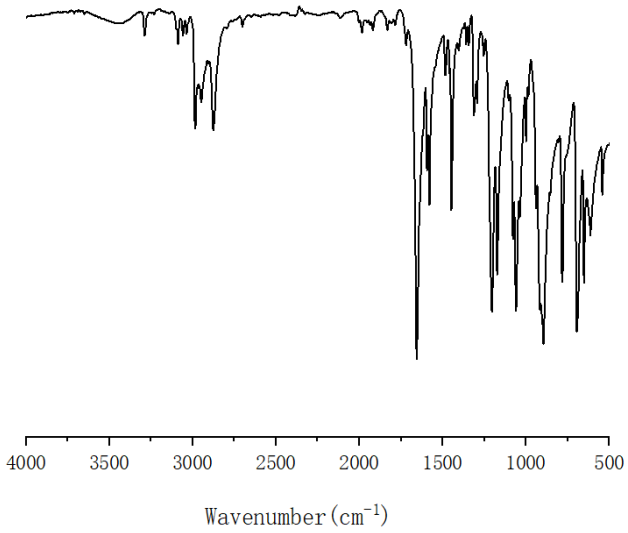


2) **3a** (1×10^{-5} M) in THF



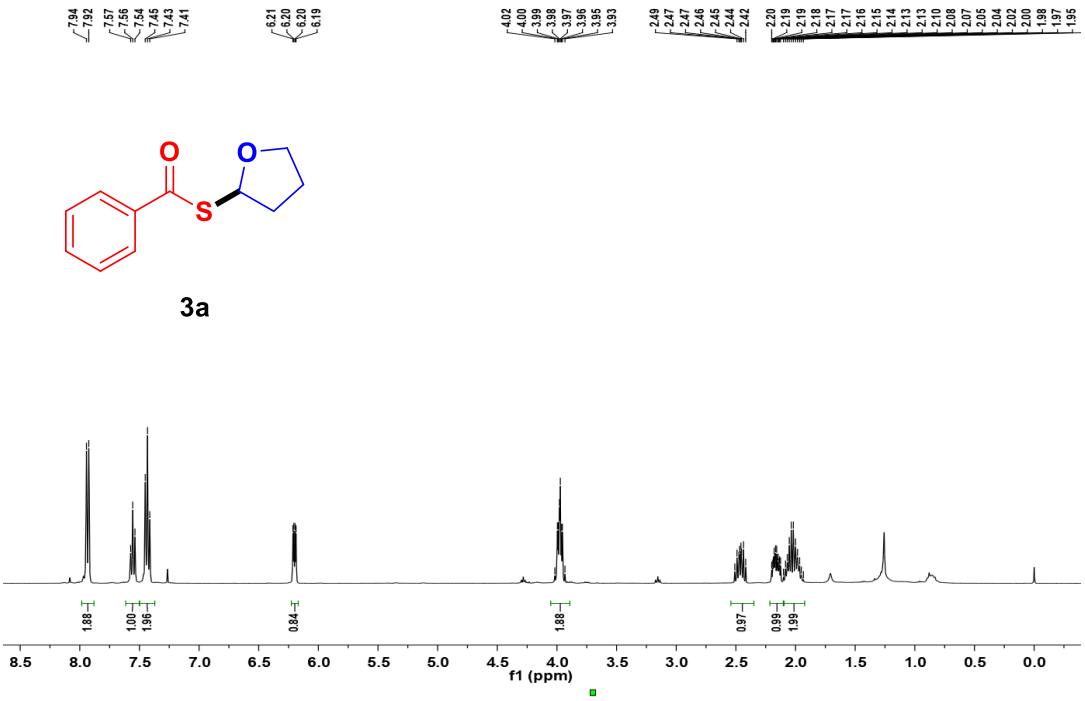
10 FT-IR spectra

FT-IR spectra of 3a

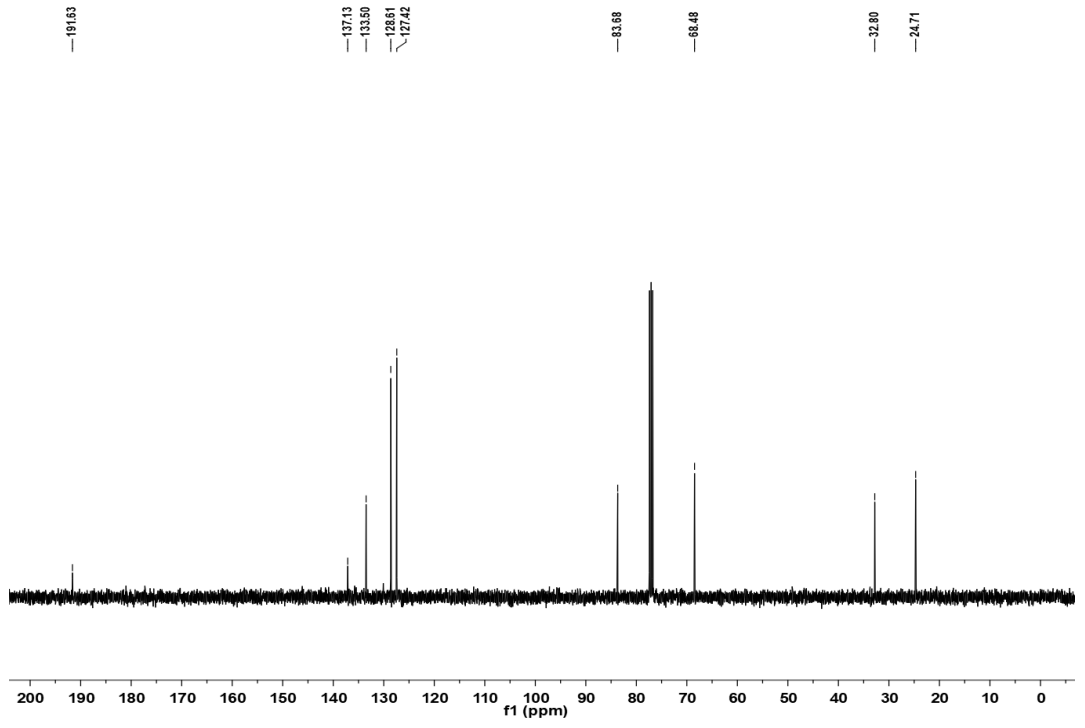


11 NMR spectra

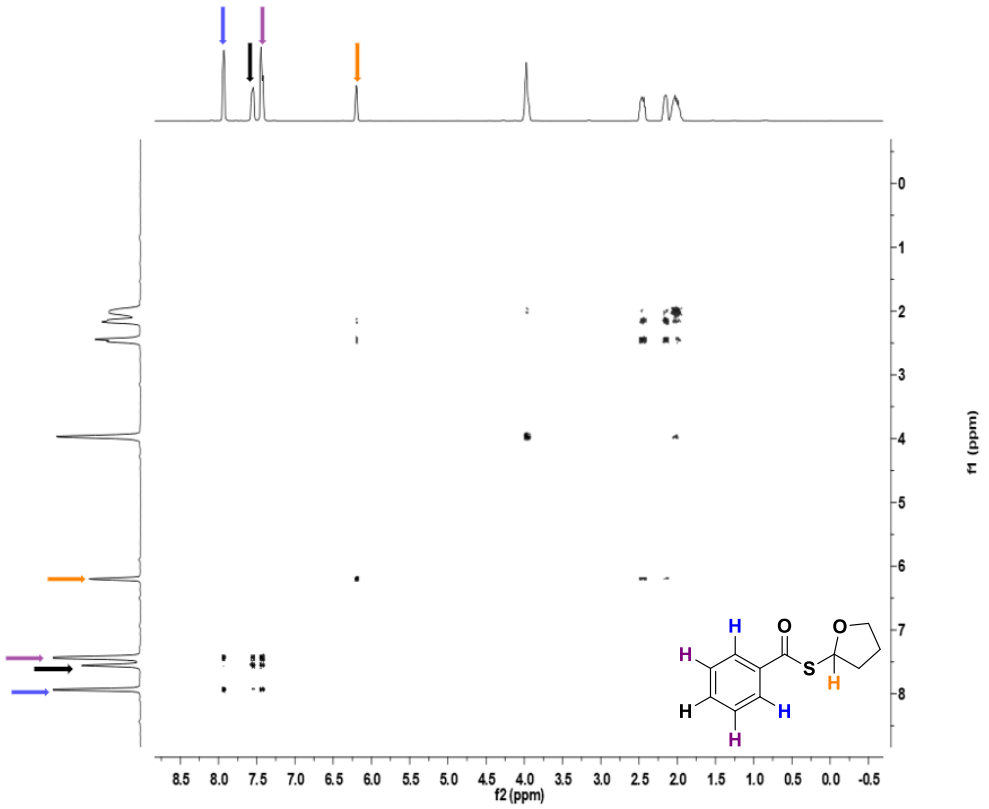
^{1}H NMR (400 MHz, $CDCl_3$) of 3a



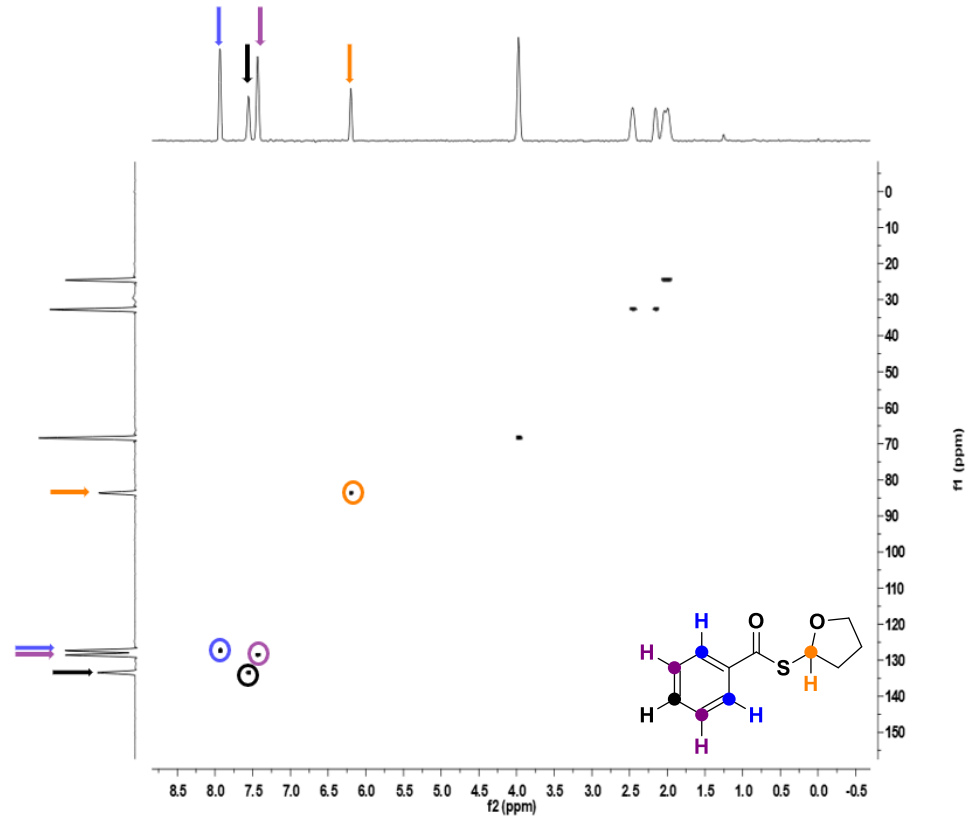
^{13}C NMR (101 MHz, $CDCl_3$) of 3a



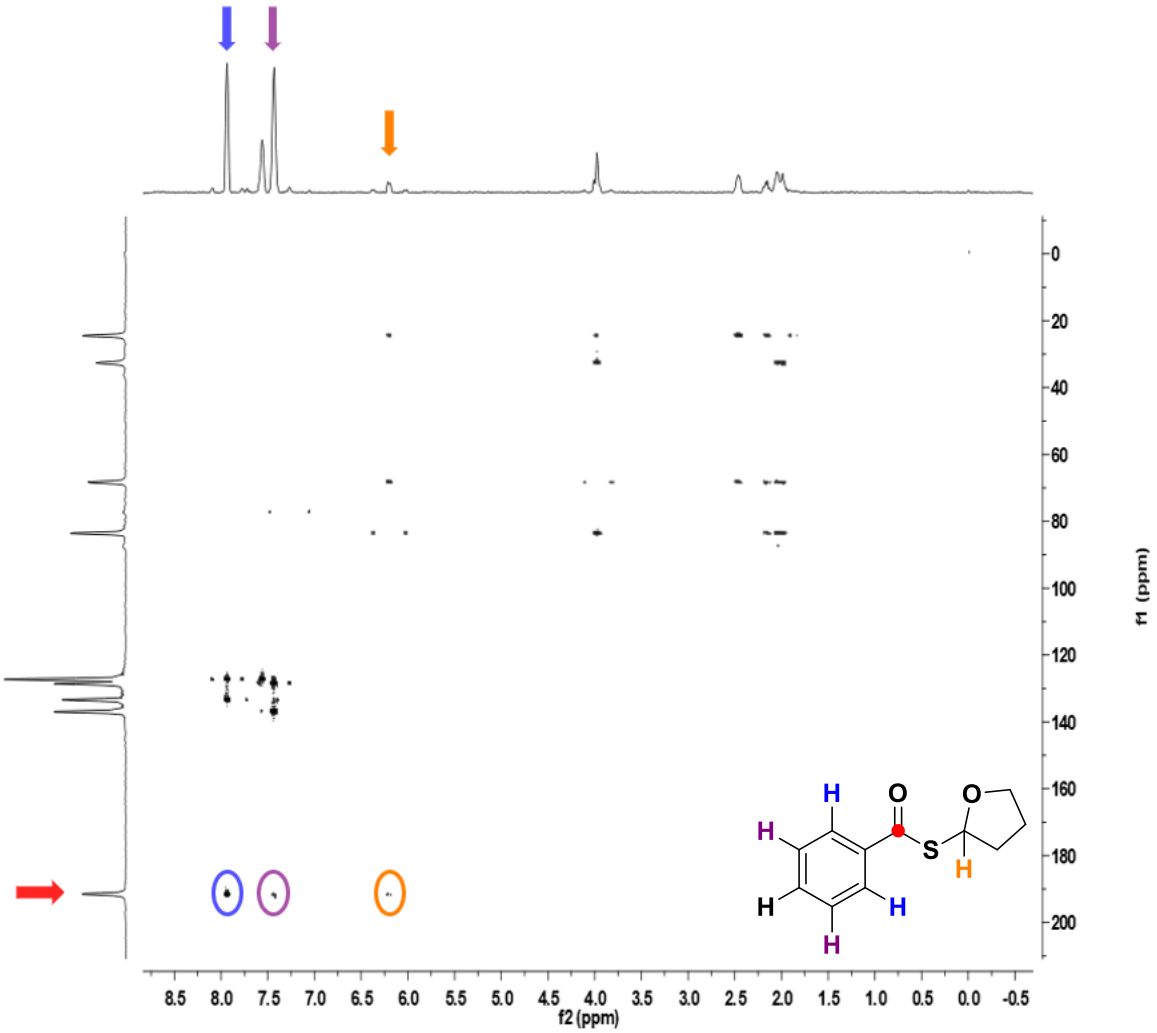
g-COSY spectra of 3a



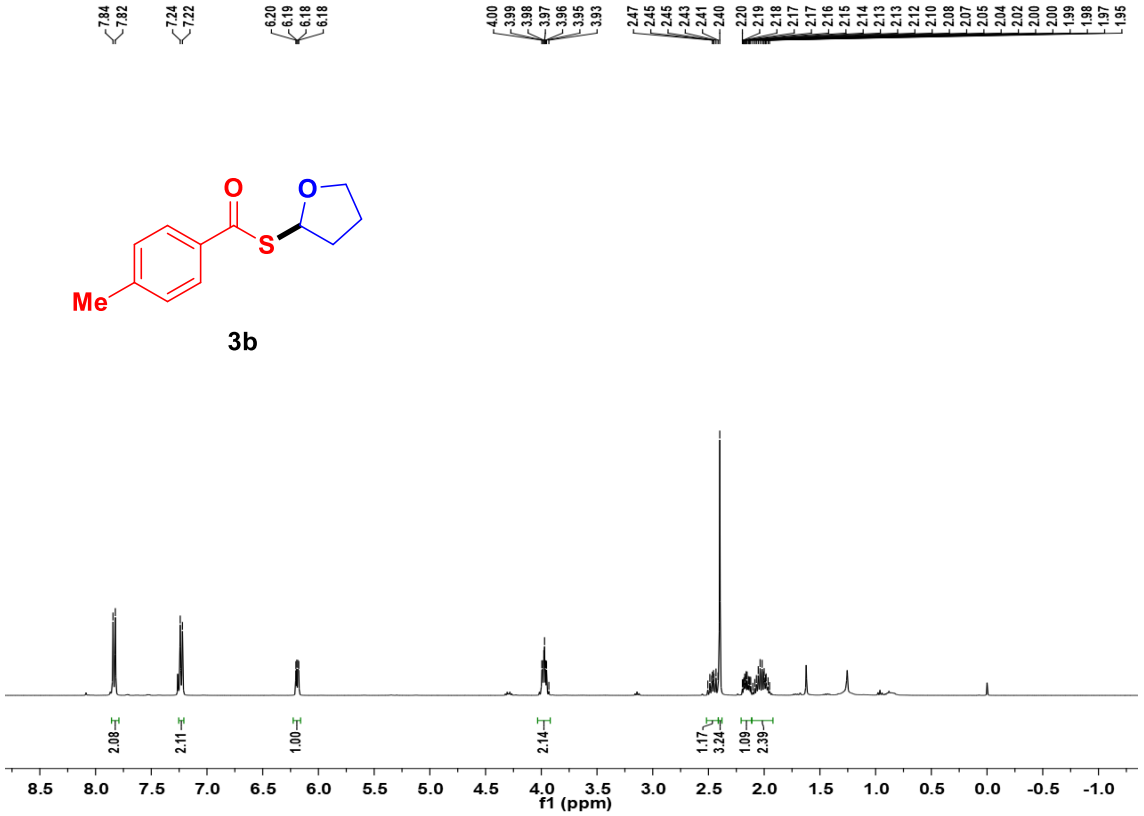
HSQC spectra of 3a



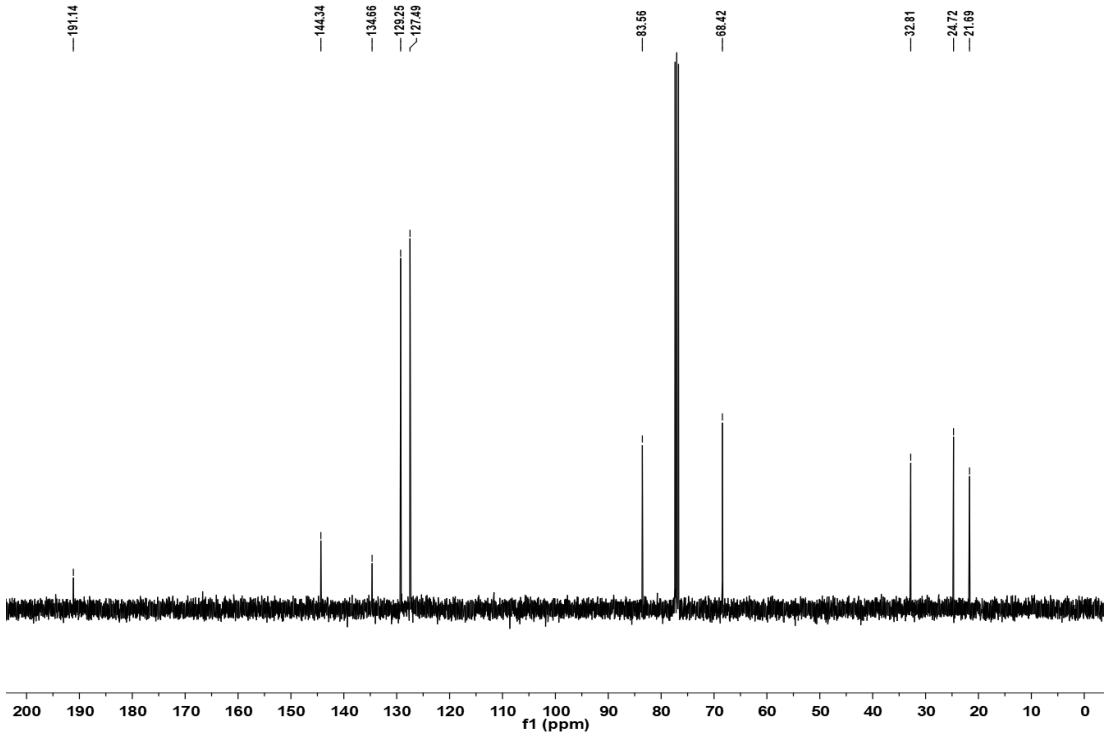
HMBC spectra of 3a



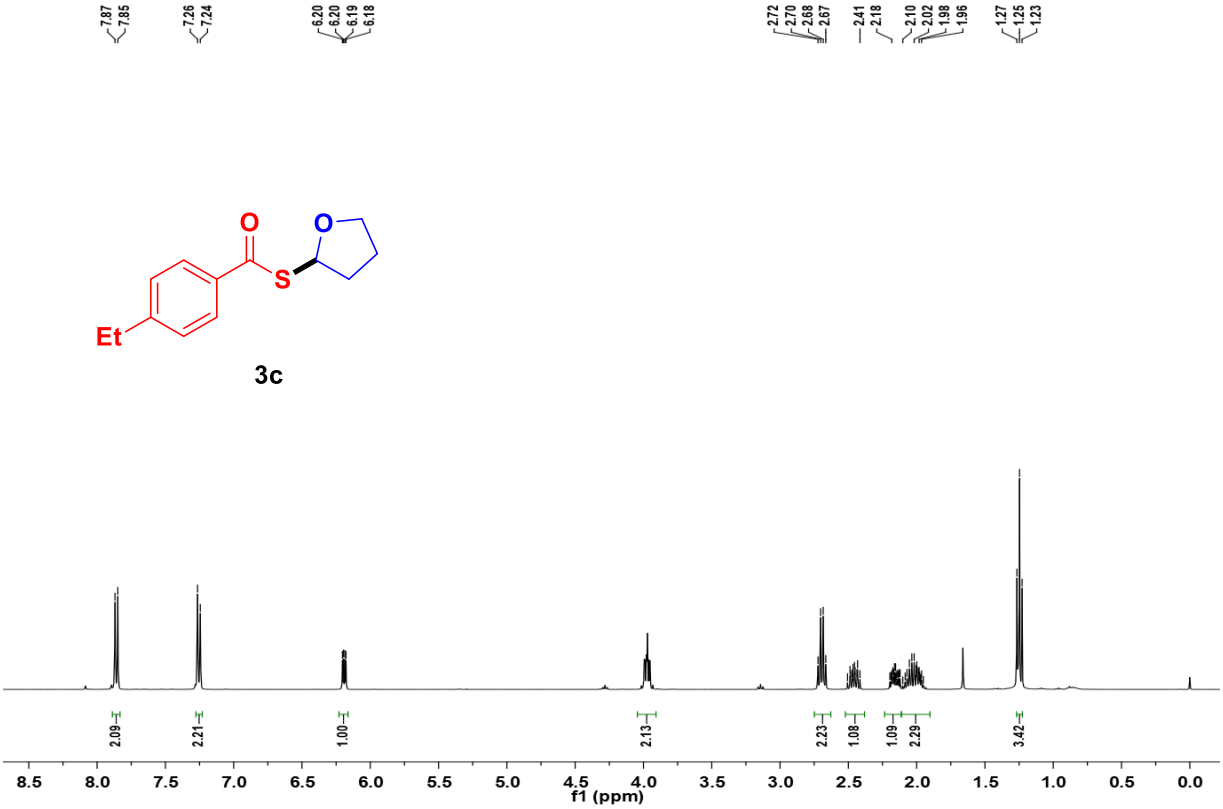
^{1}H NMR (400 MHz, $CDCl_3$) of 3b



^{13}C NMR (101 MHz, $CDCl_3$) of 3b

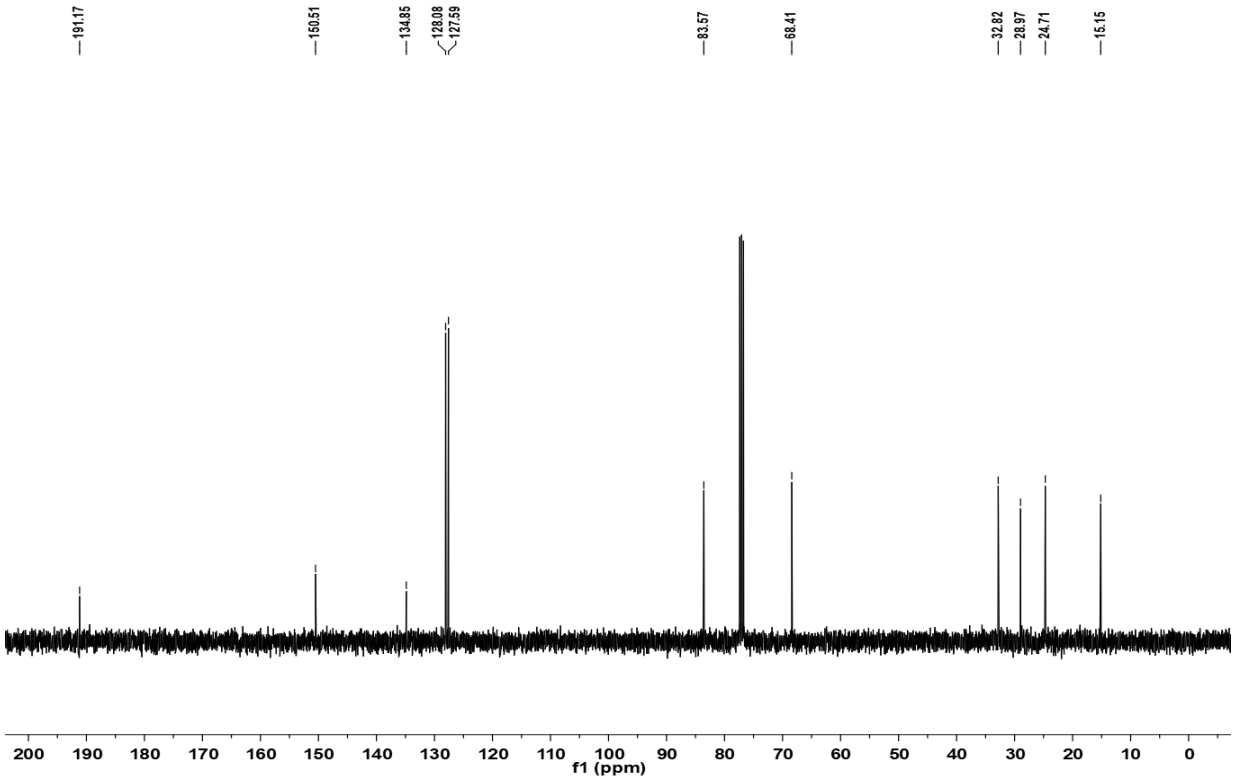


^{1}H NMR (400 MHz, $CDCl_3$) of 3c

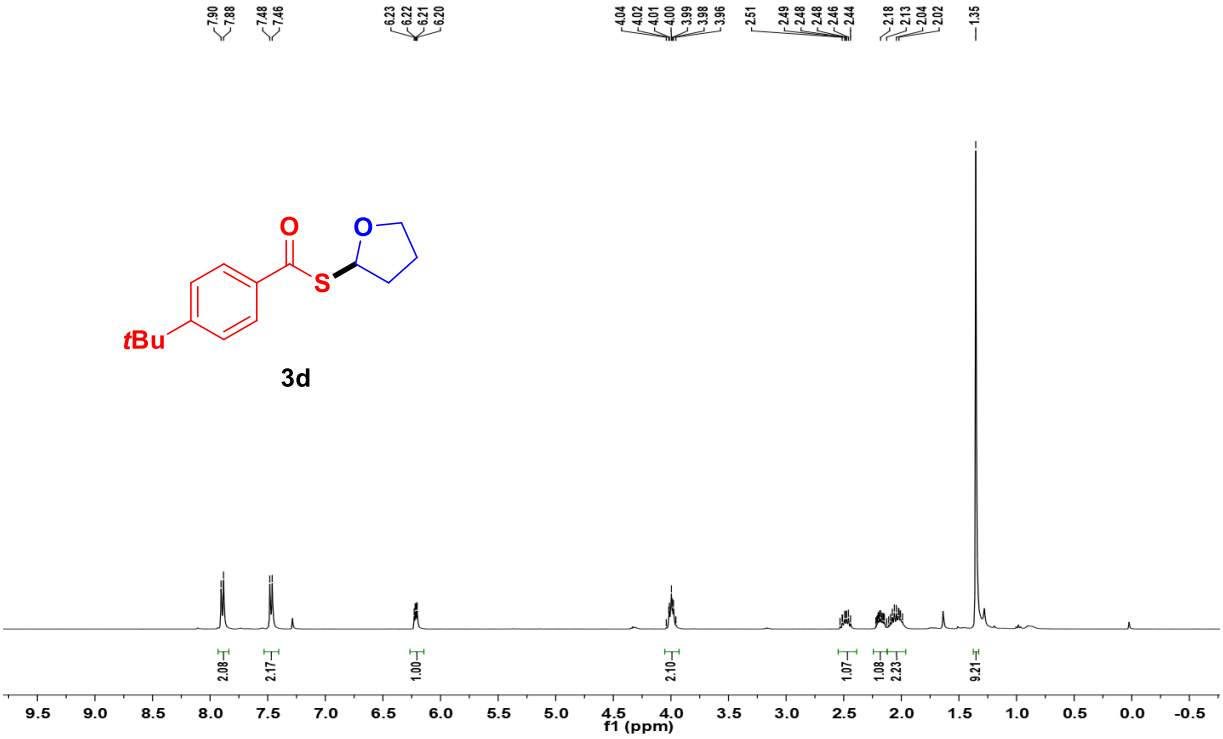


3c

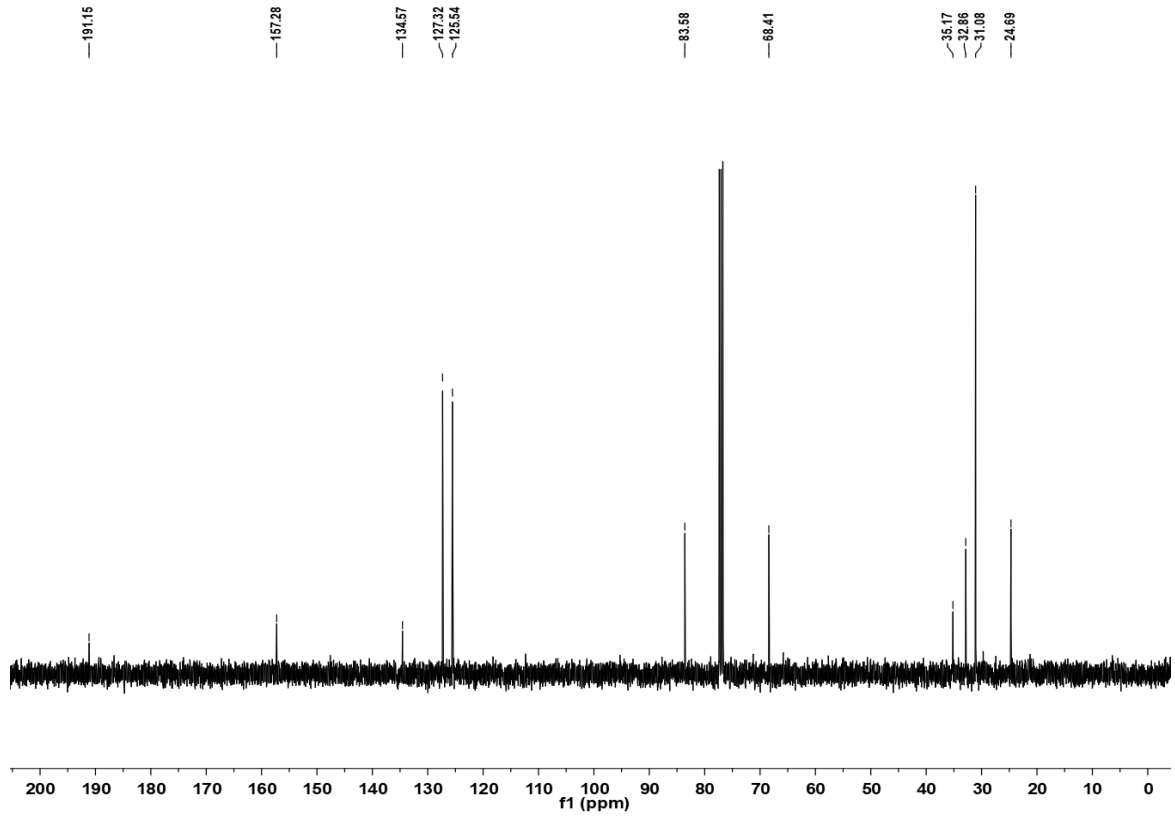
^{13}C NMR (101 MHz, $CDCl_3$) of 3c



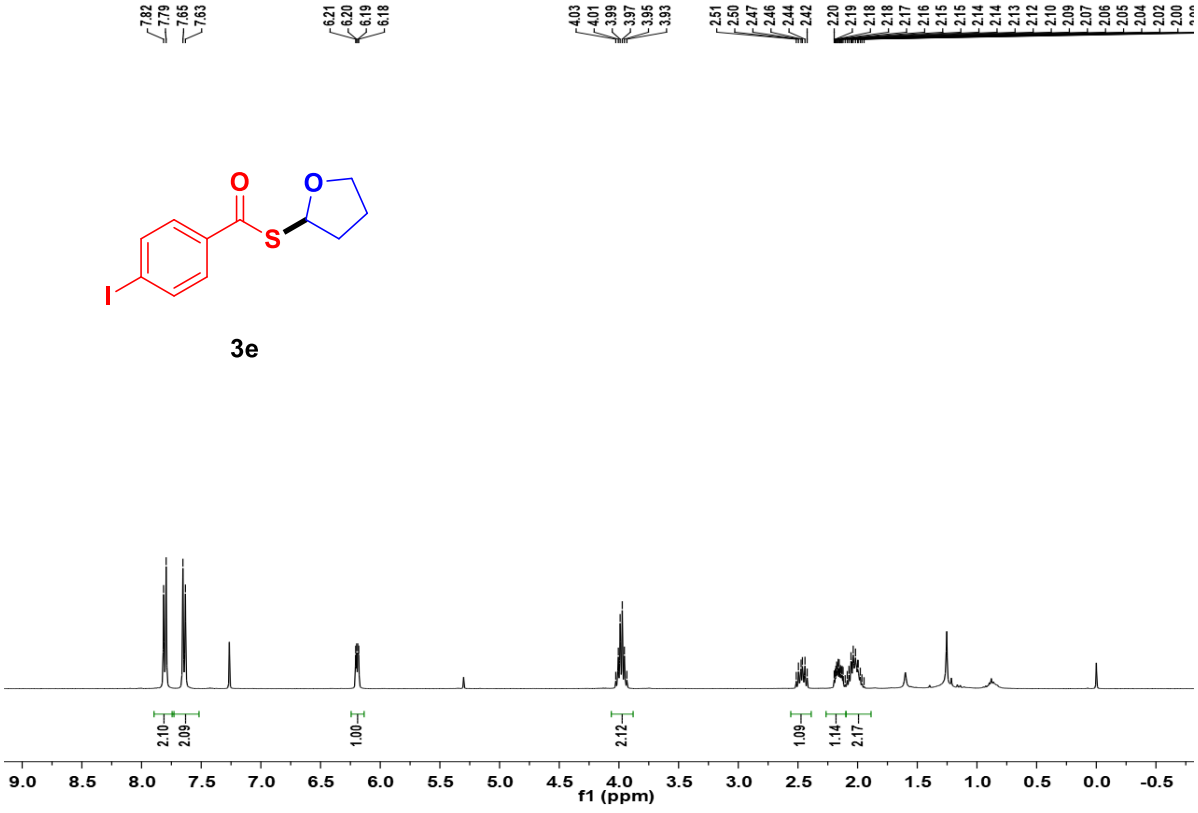
^{1}H NMR (400 MHz, $CDCl_3$) of 3d



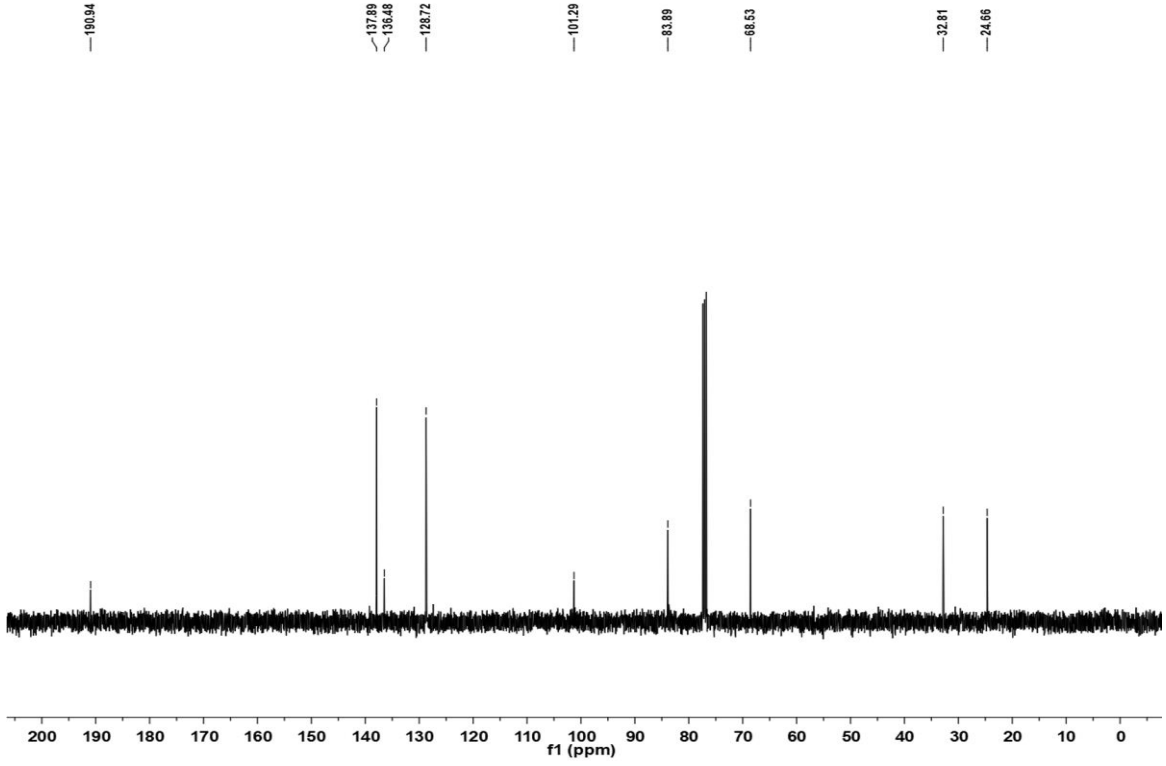
^{13}C NMR (101 MHz, $CDCl_3$) of 3d



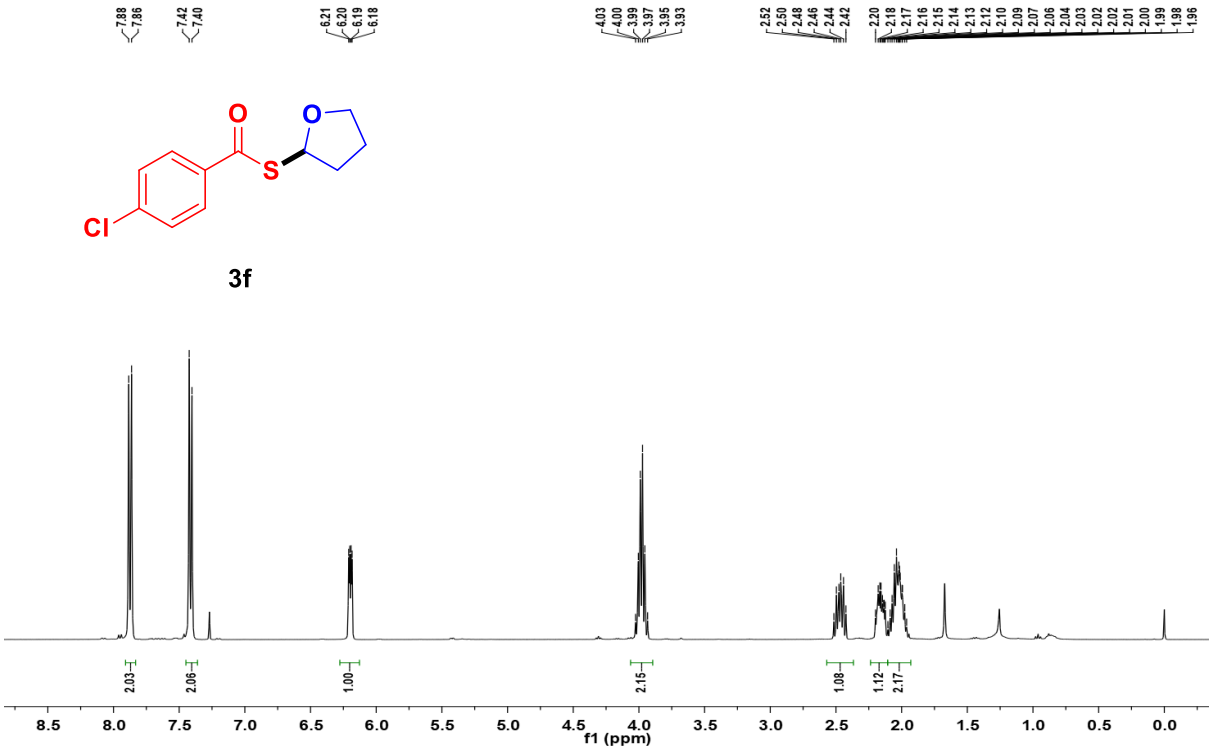
^{1}H NMR (400 MHz, $CDCl_3$) of 3e



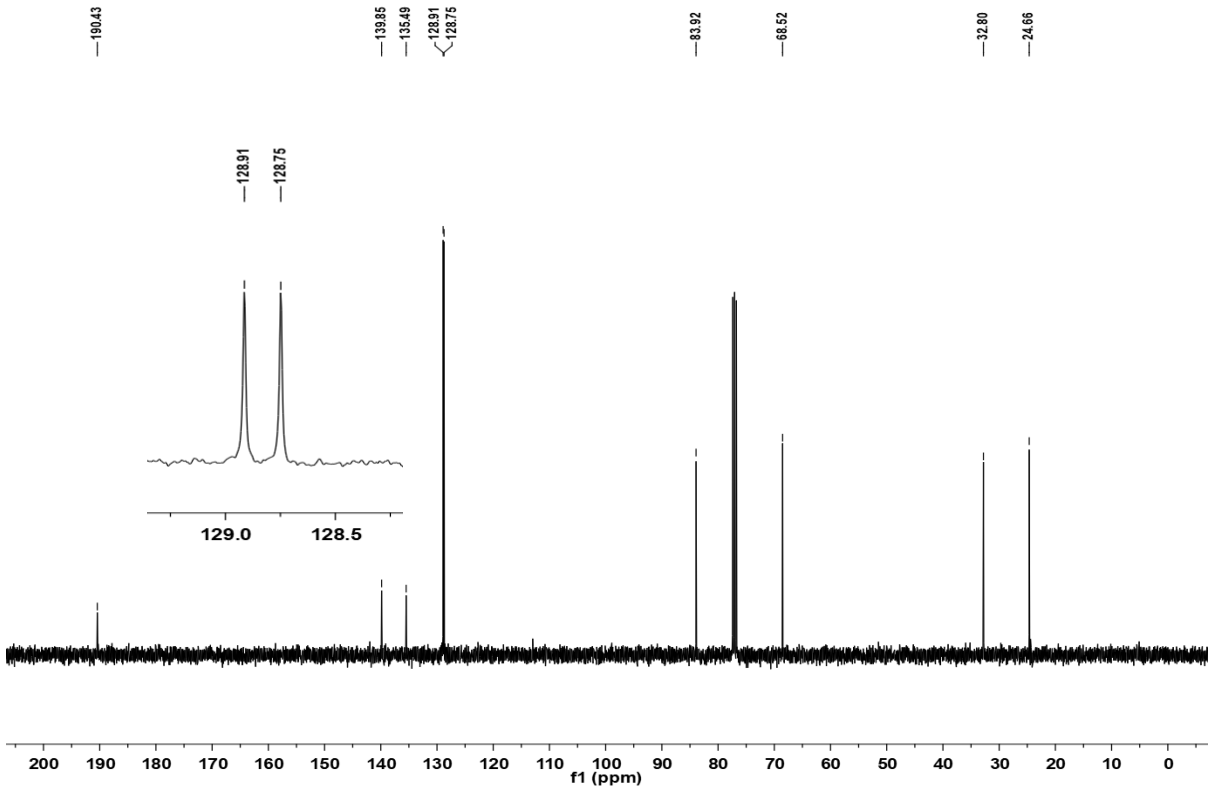
^{13}C NMR (101 MHz, $CDCl_3$) of 3e



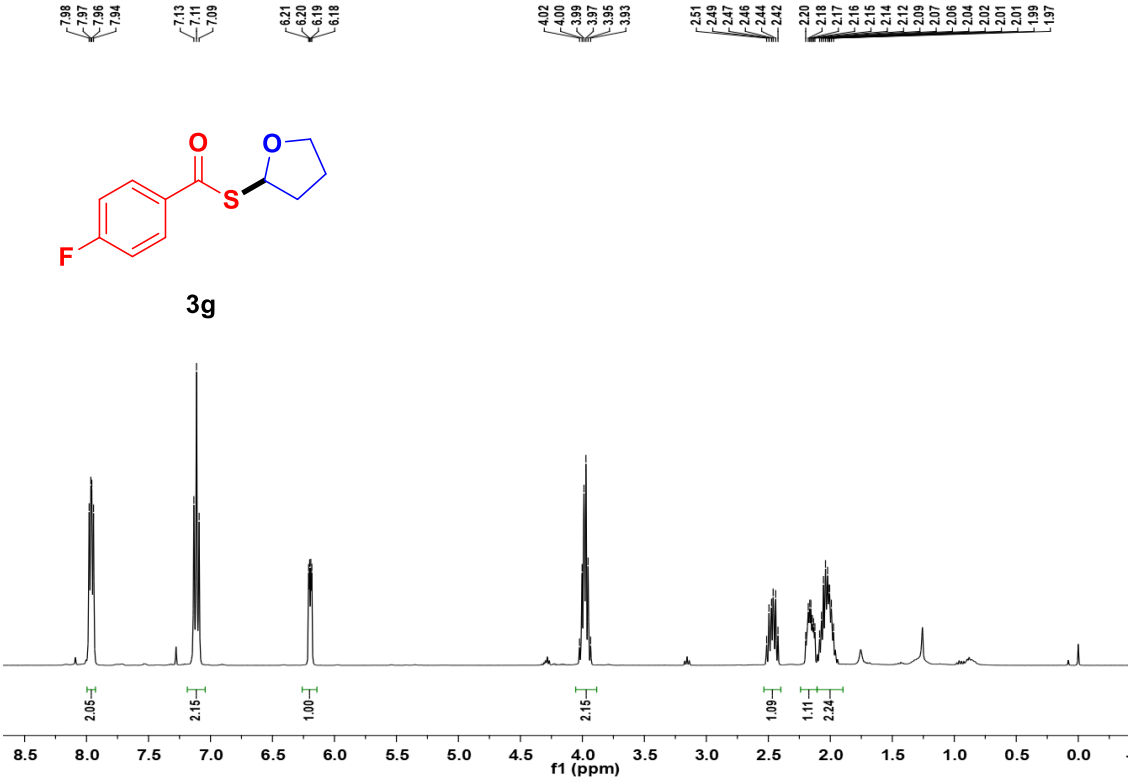
^{1}H NMR (400 MHz, $CDCl_3$) of 3f



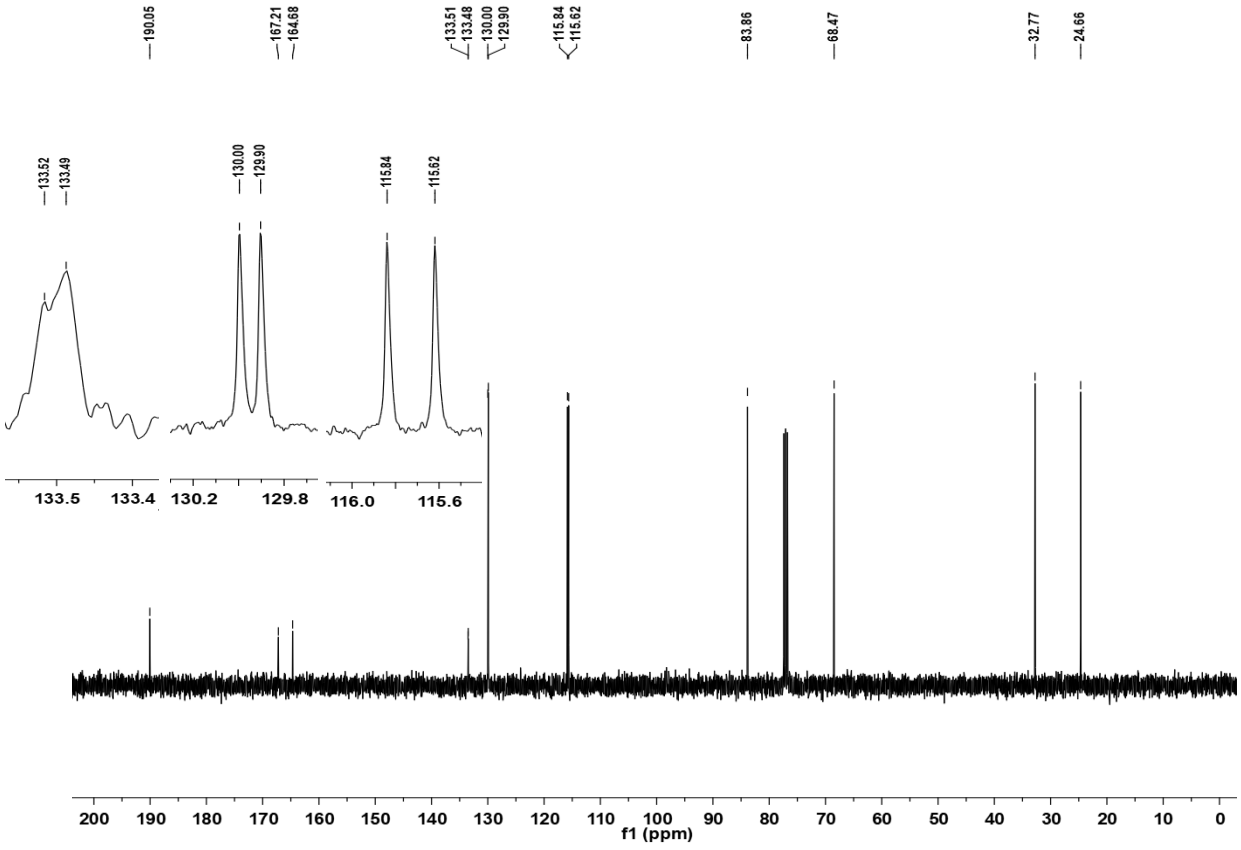
^{13}C NMR (101 MHz, $CDCl_3$) of 3f



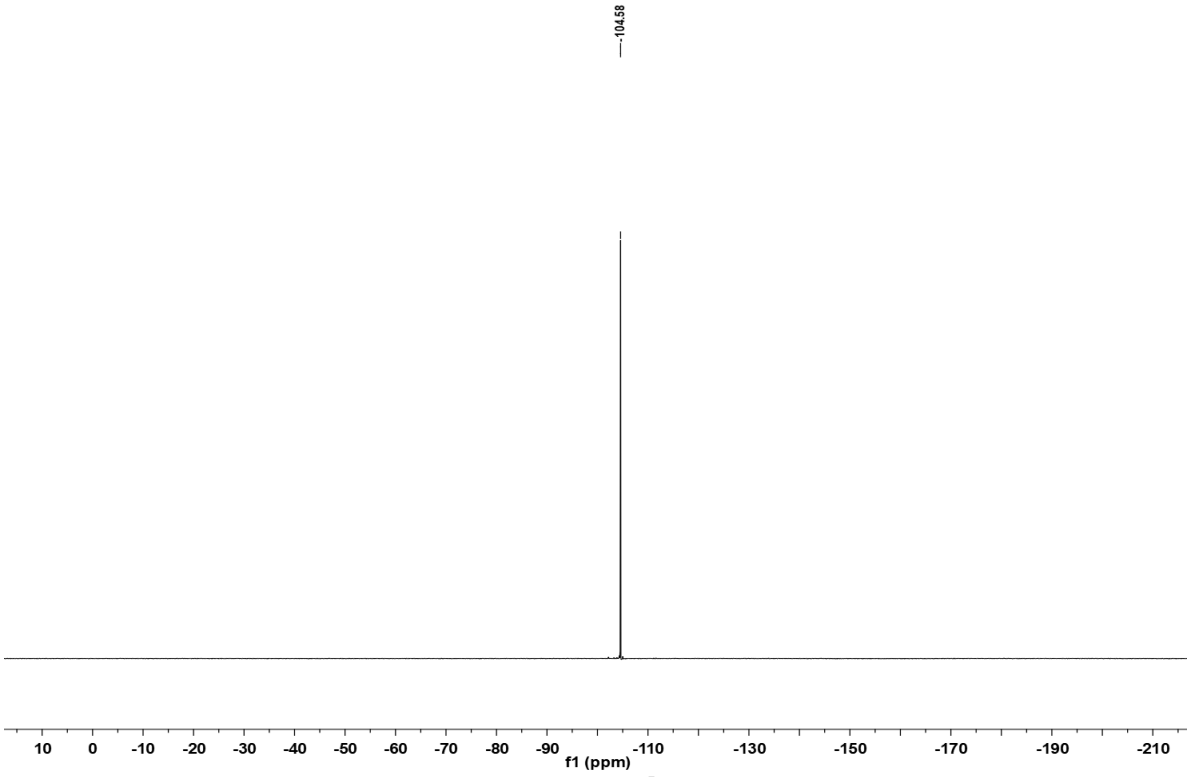
^{1}H NMR (400 MHz, $CDCl_3$) of 3g



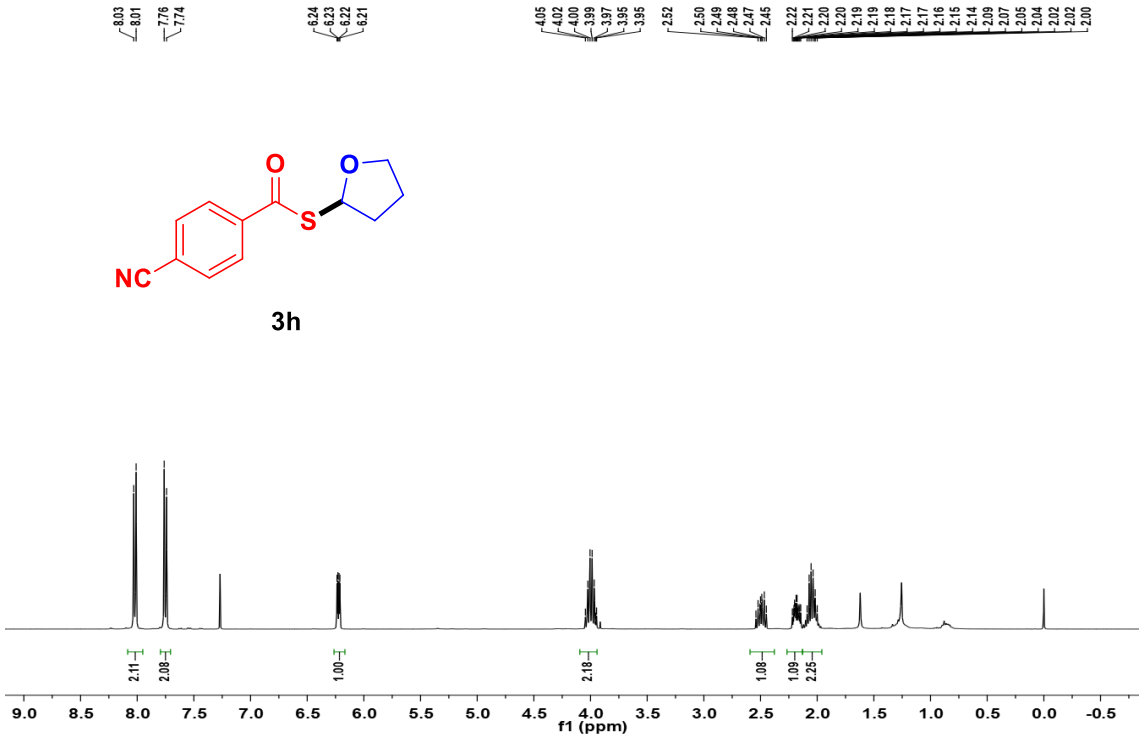
^{13}C NMR (101 MHz, $CDCl_3$) of 3g



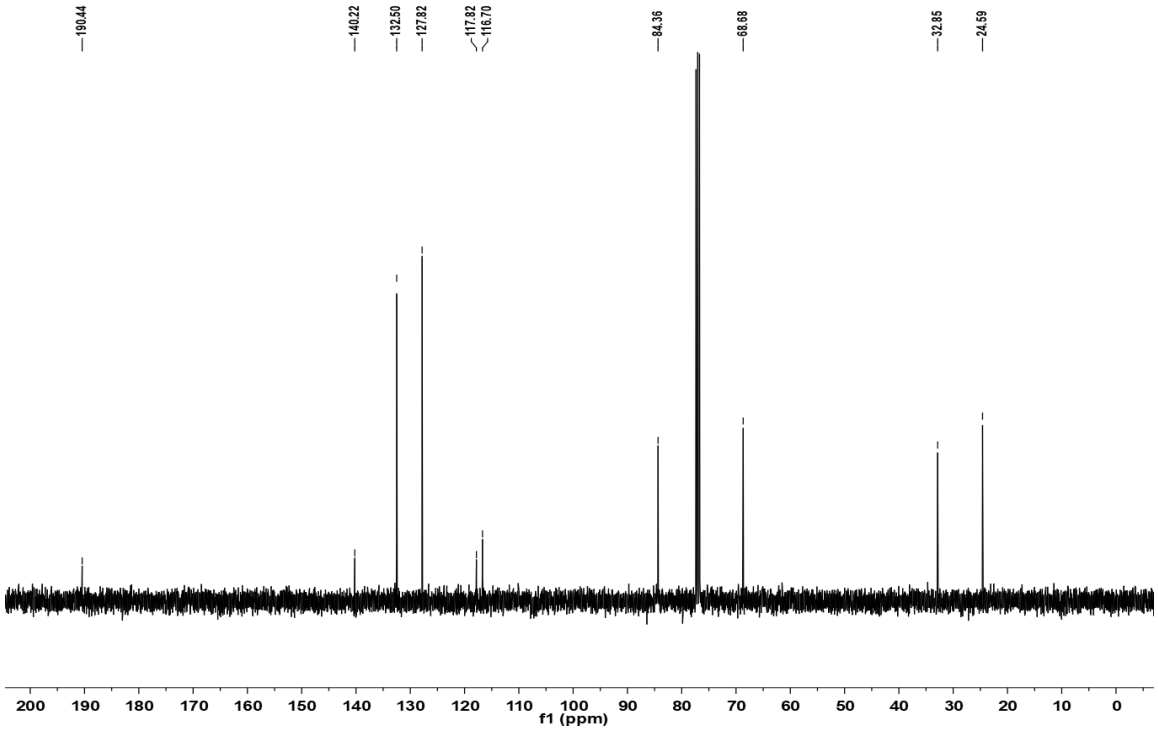
^{19}F NMR (376 MHz, $CDCl_3$) of 3g



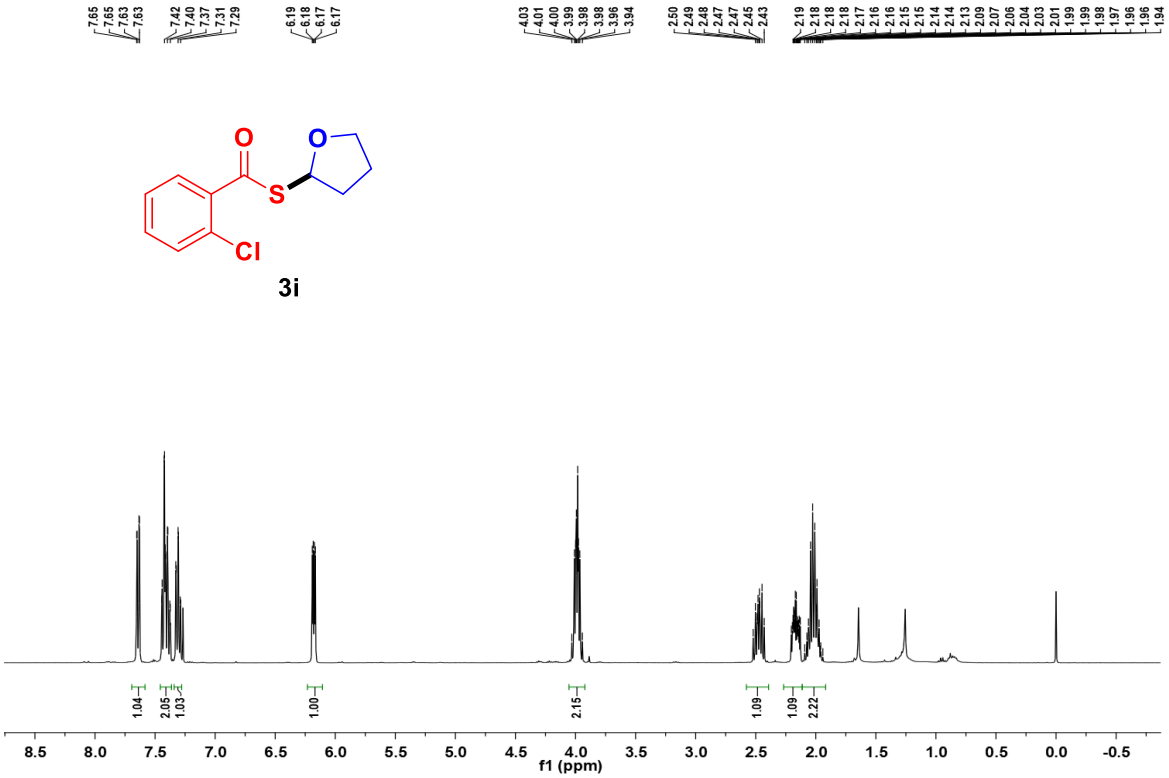
^{1}H NMR (400 MHz, $CDCl_3$) of 3h



^{13}C NMR (101 MHz, $CDCl_3$) of 3h

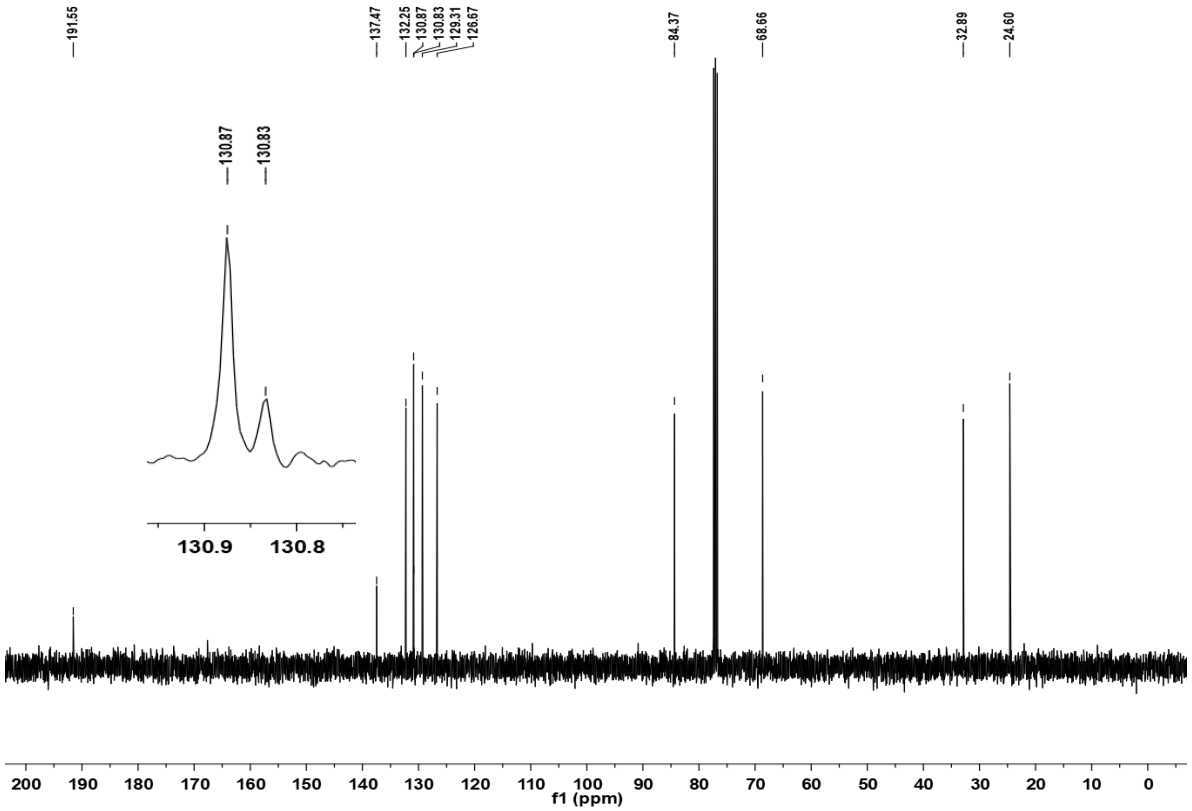


^{1}H NMR (400 MHz, $CDCl_3$) of 3i

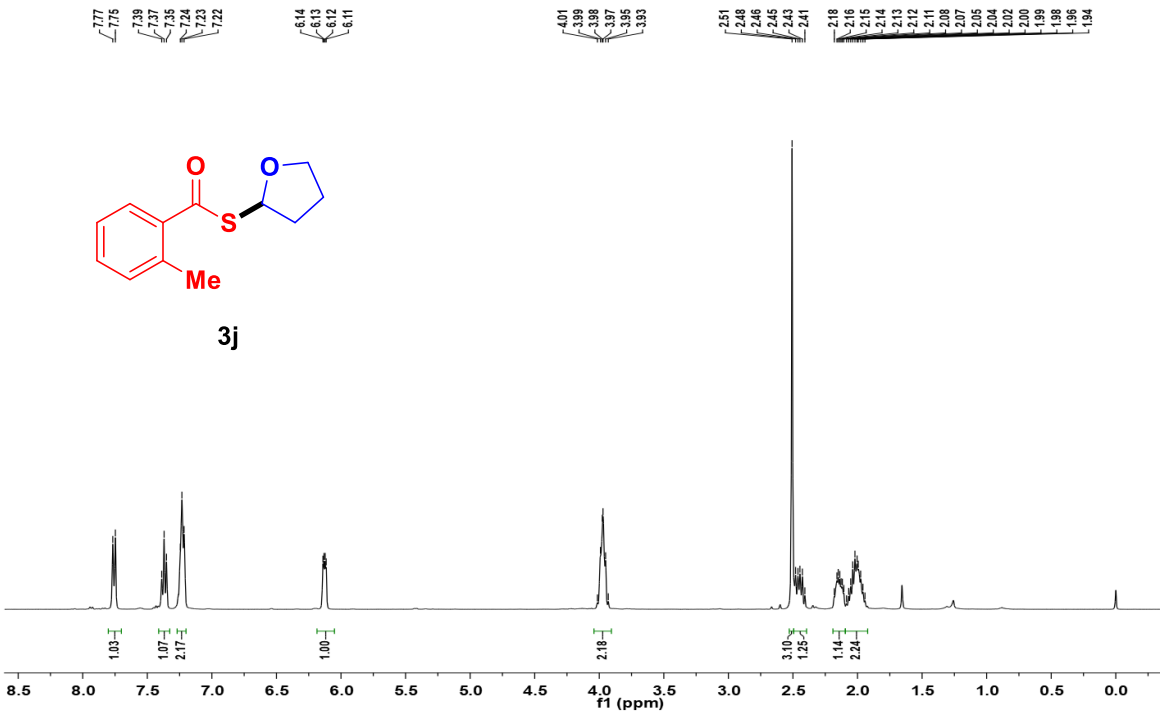


3i

^{13}C NMR (101 MHz, $CDCl_3$) of 3i

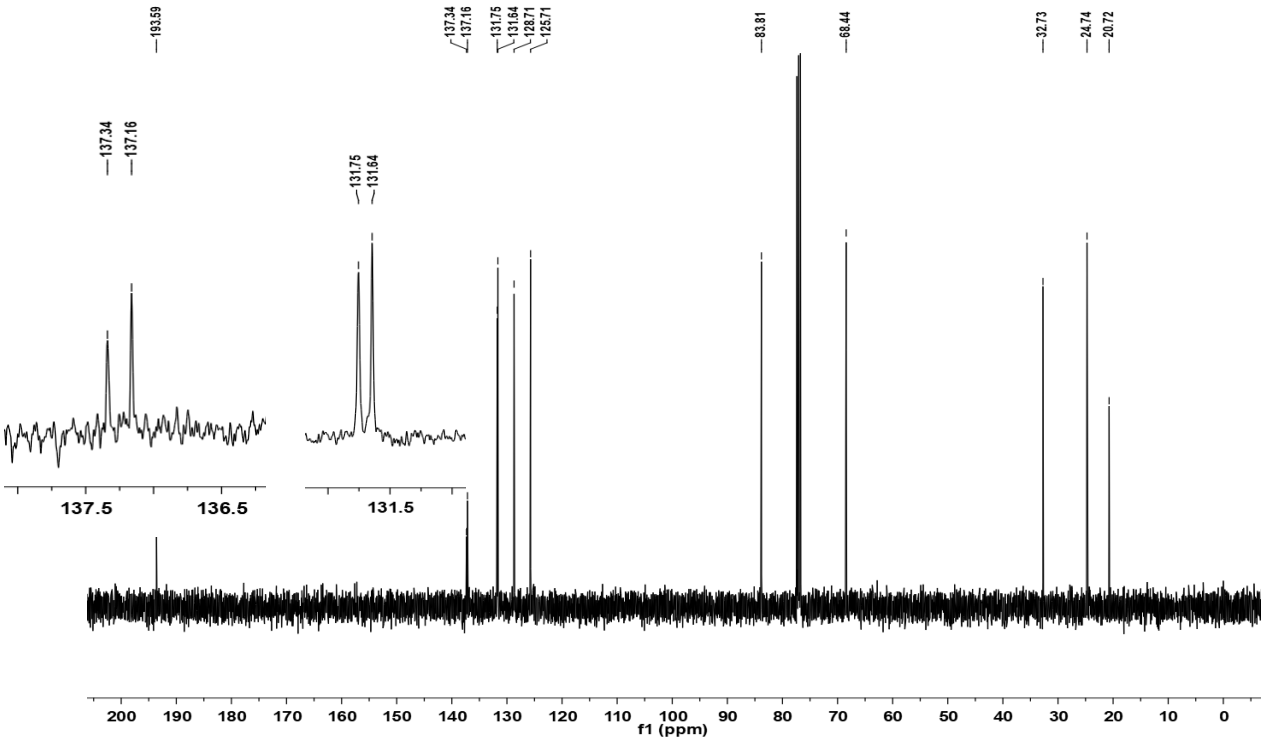


^{1}H NMR (400 MHz, $CDCl_3$) of 3j

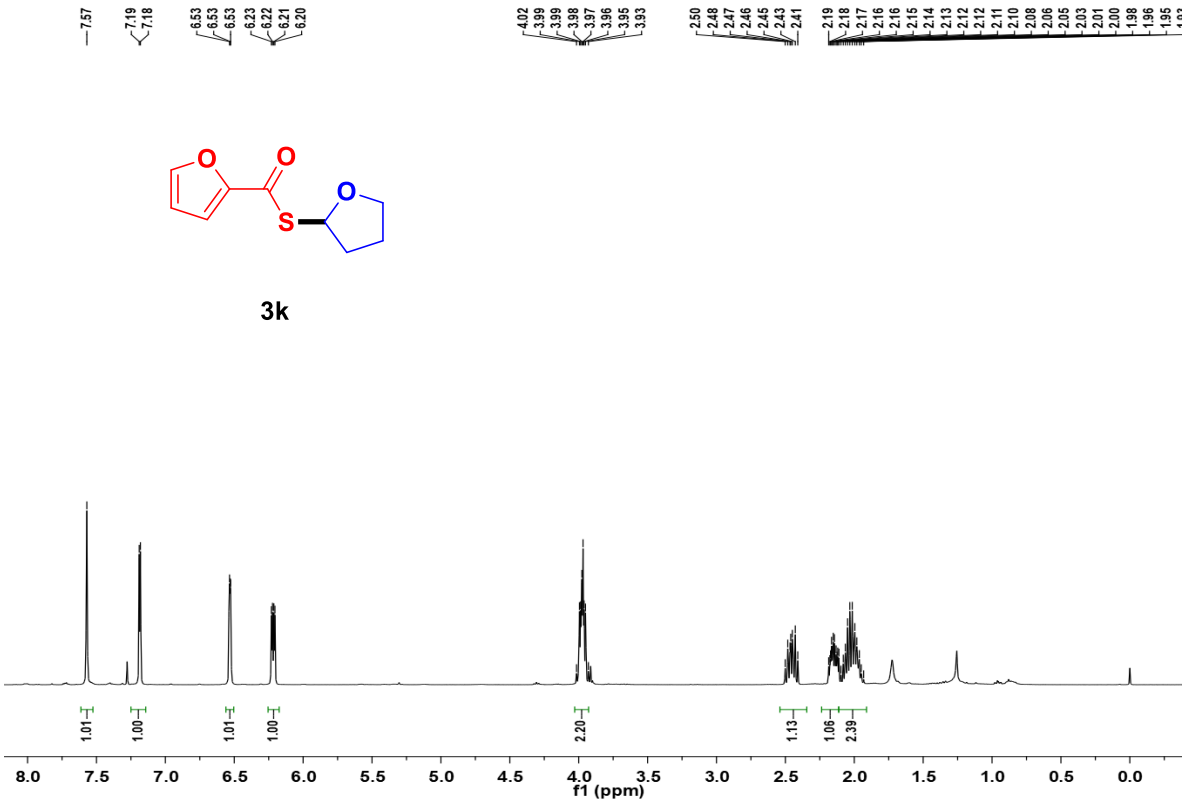


3j

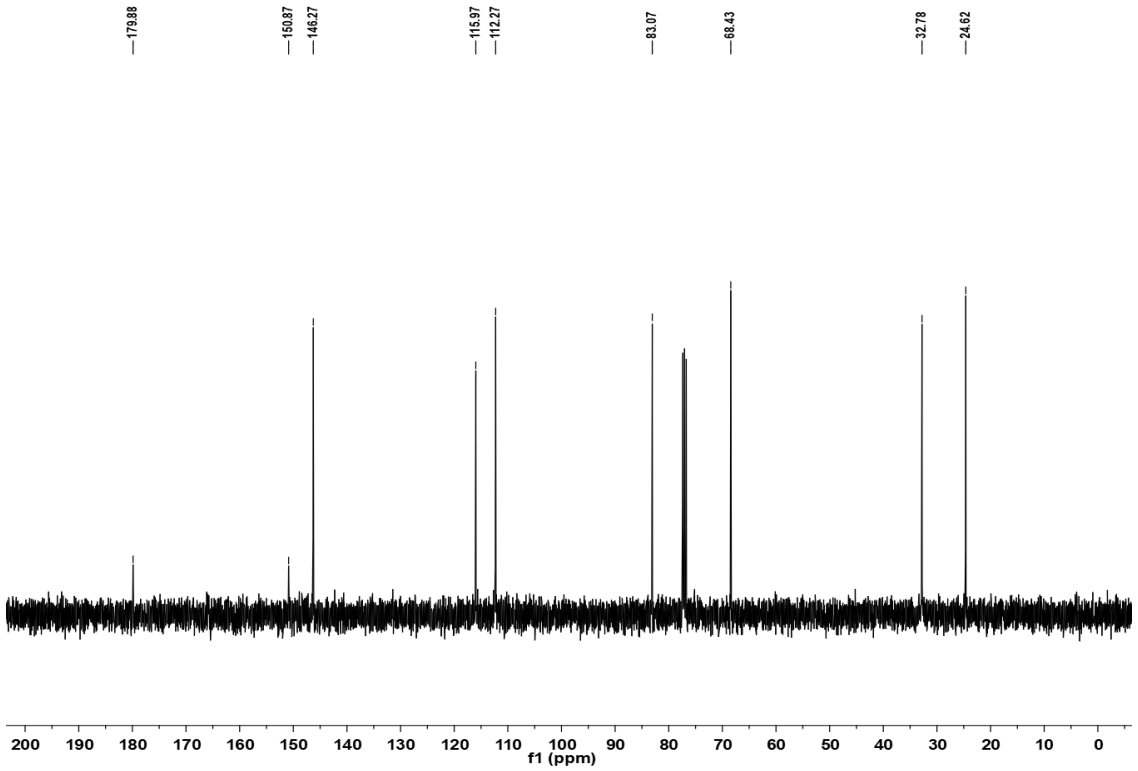
^{13}C NMR (101 MHz, $CDCl_3$) of 3j



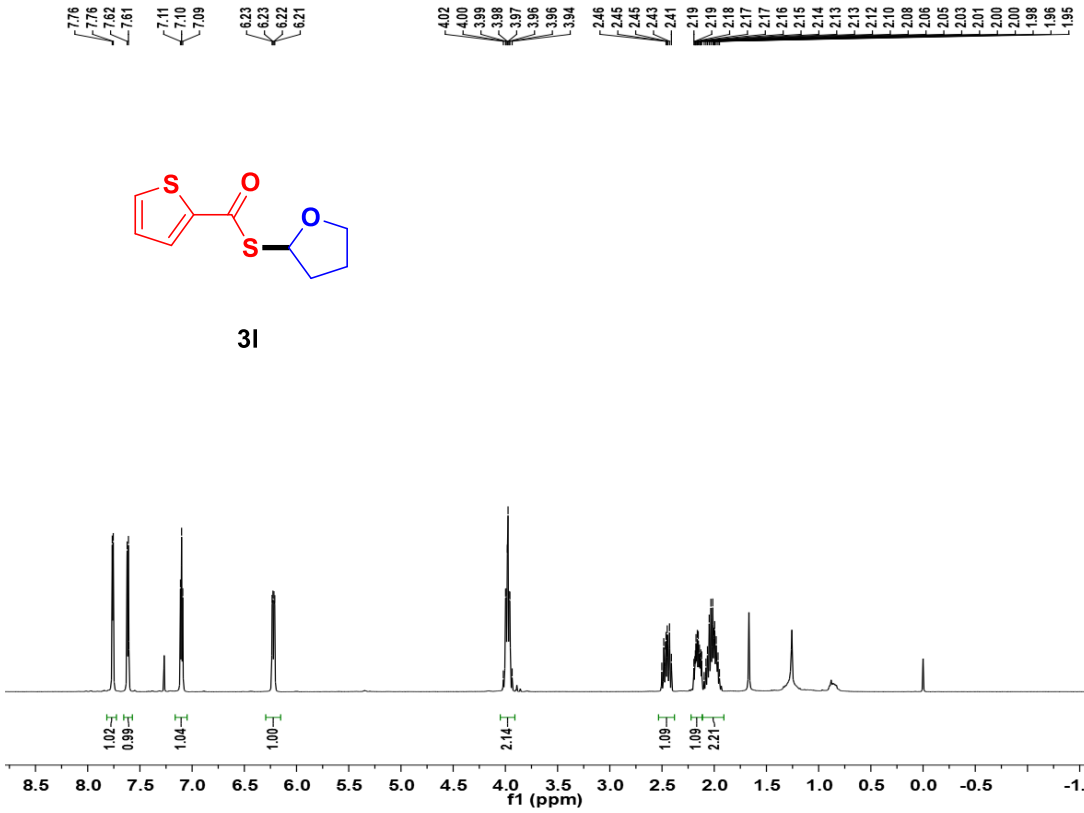
^{1}H NMR (400 MHz, $CDCl_3$) of 3k



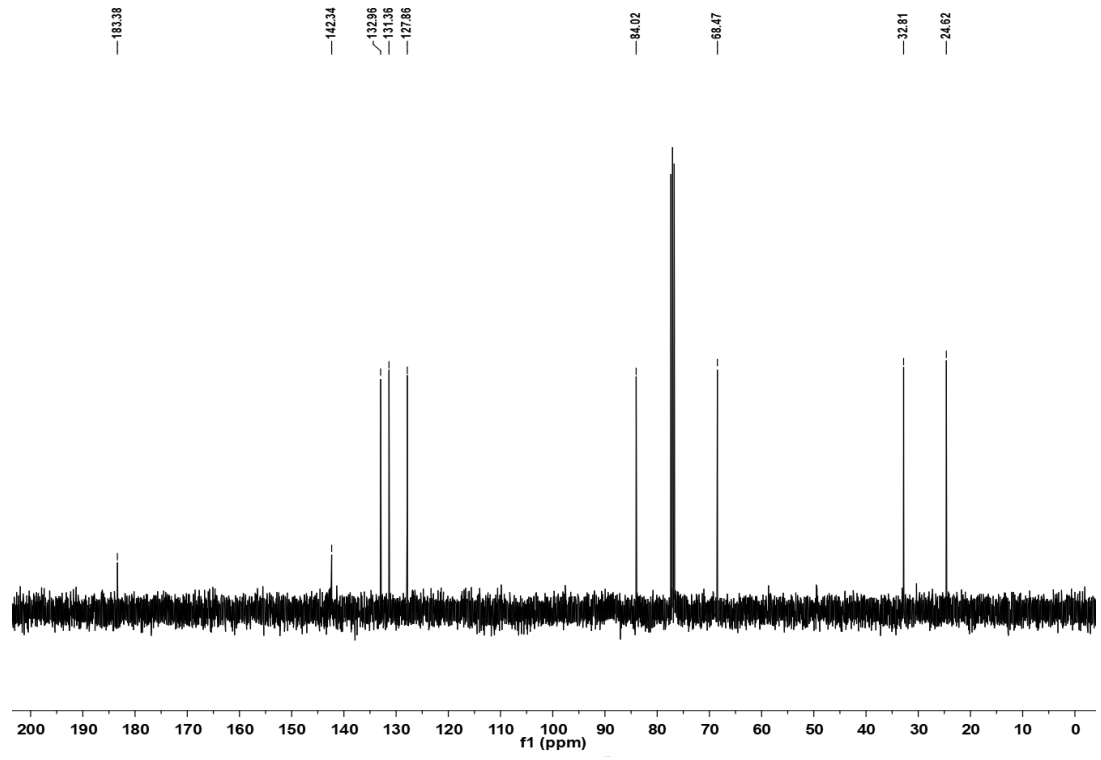
^{13}C NMR (101 MHz, $CDCl_3$) of 3k



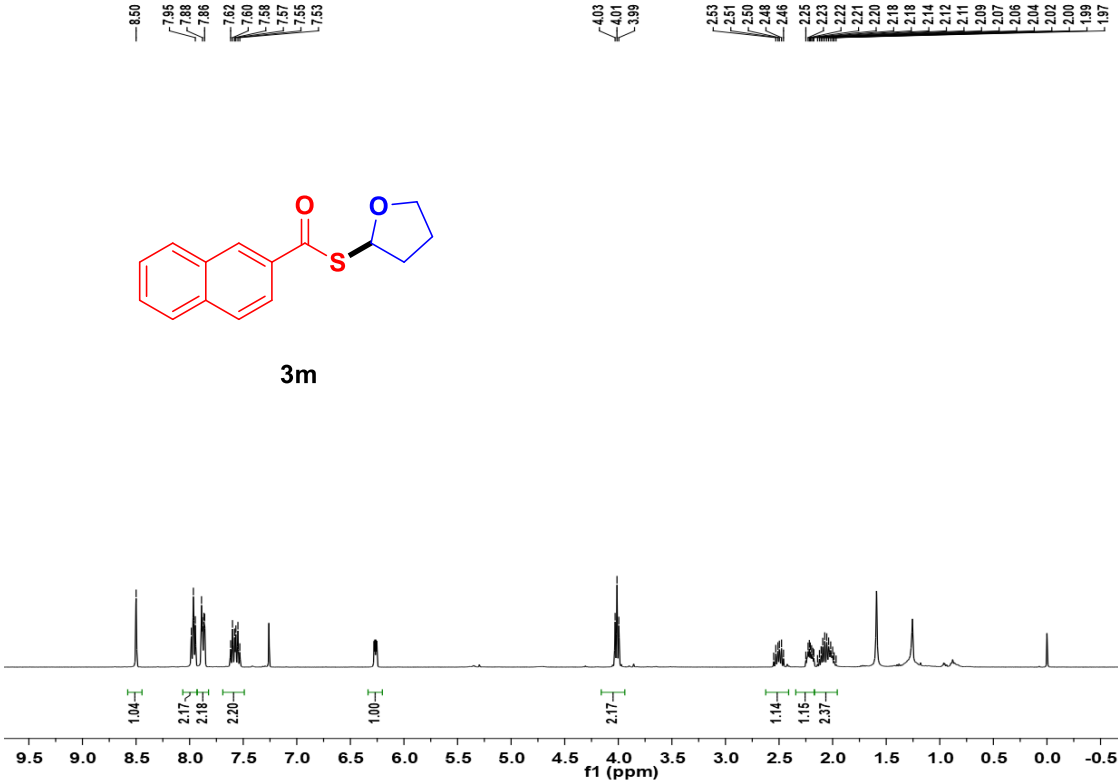
^{1}H NMR (400 MHz, $CDCl_3$) of 3l



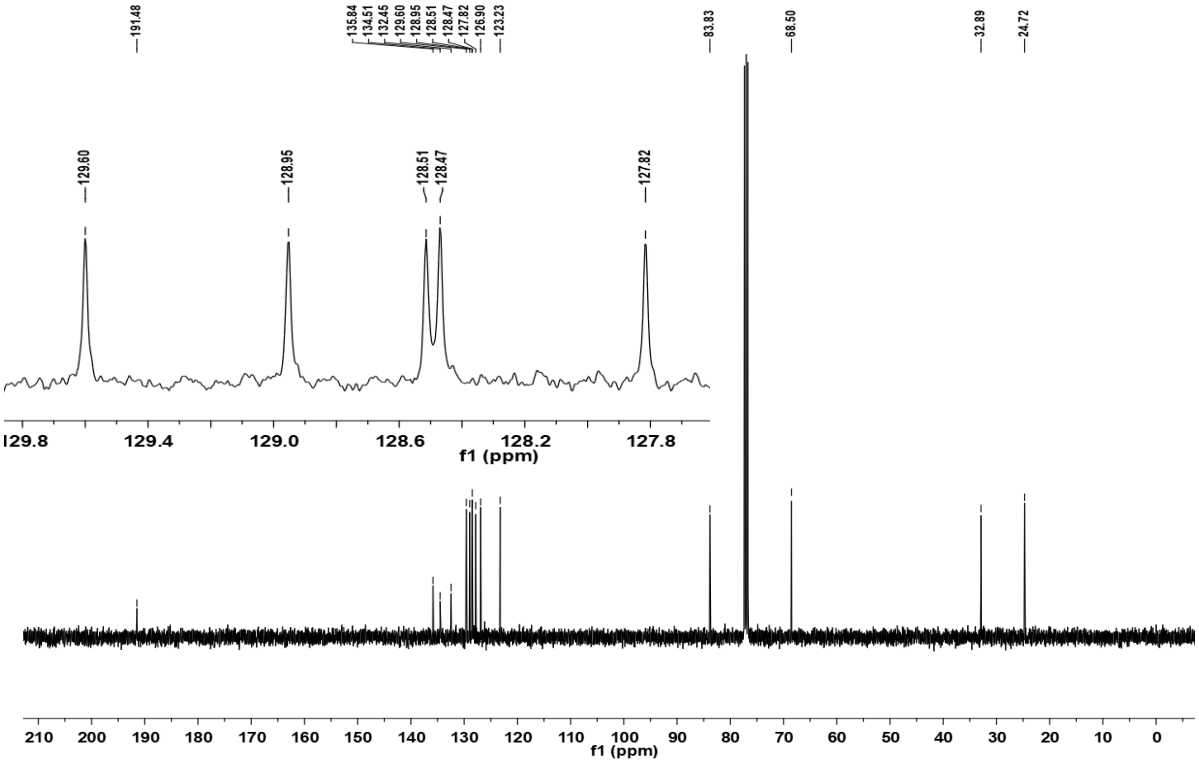
^{13}C NMR (101 MHz, $CDCl_3$) of 3l



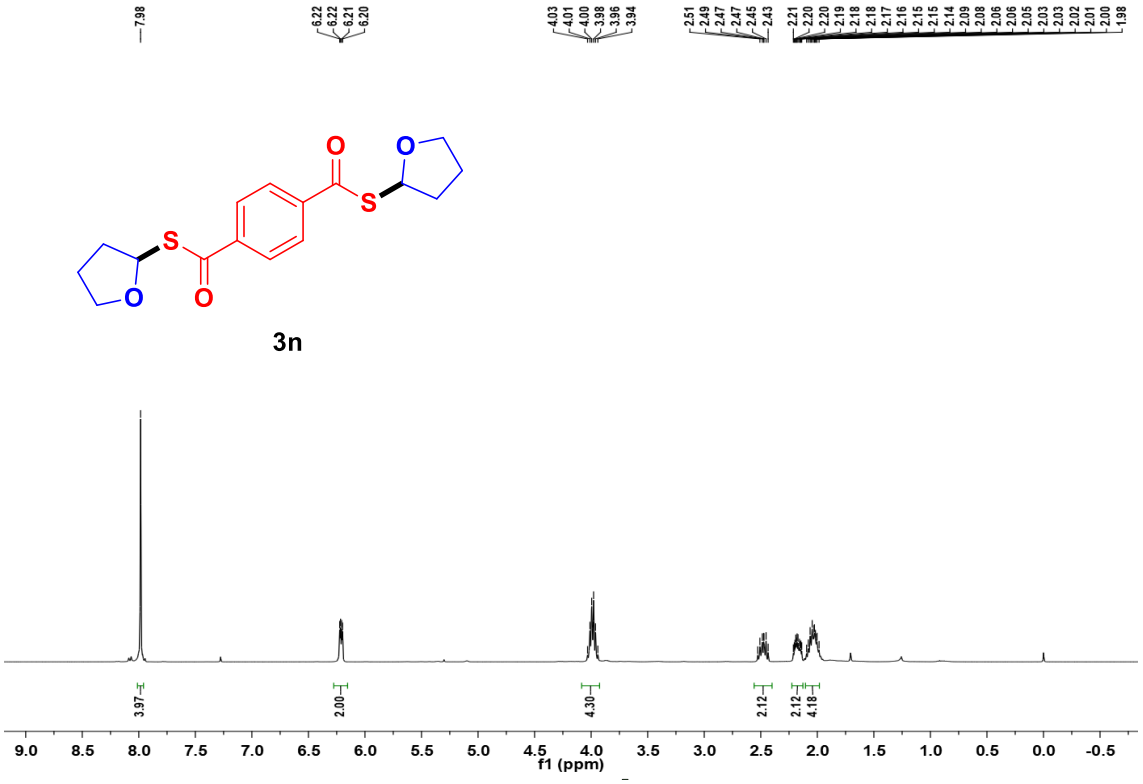
^{1}H NMR (400 MHz, $CDCl_3$) of 3m



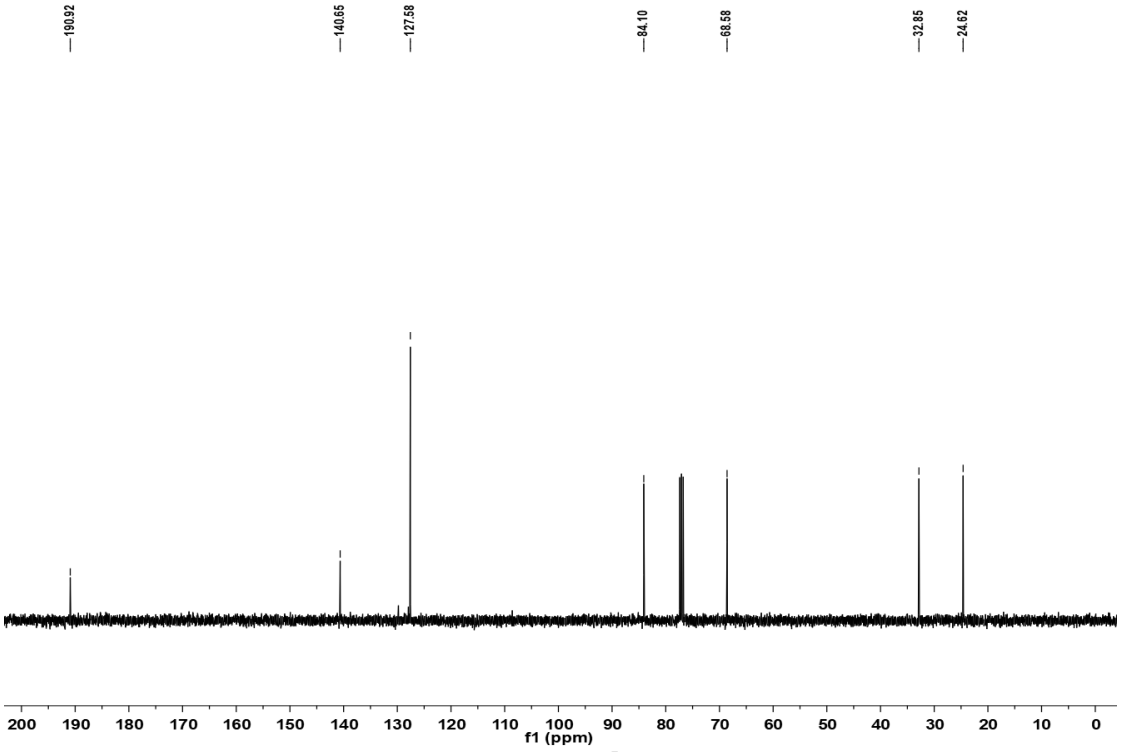
^{13}C NMR (101 MHz, $CDCl_3$) of 3m



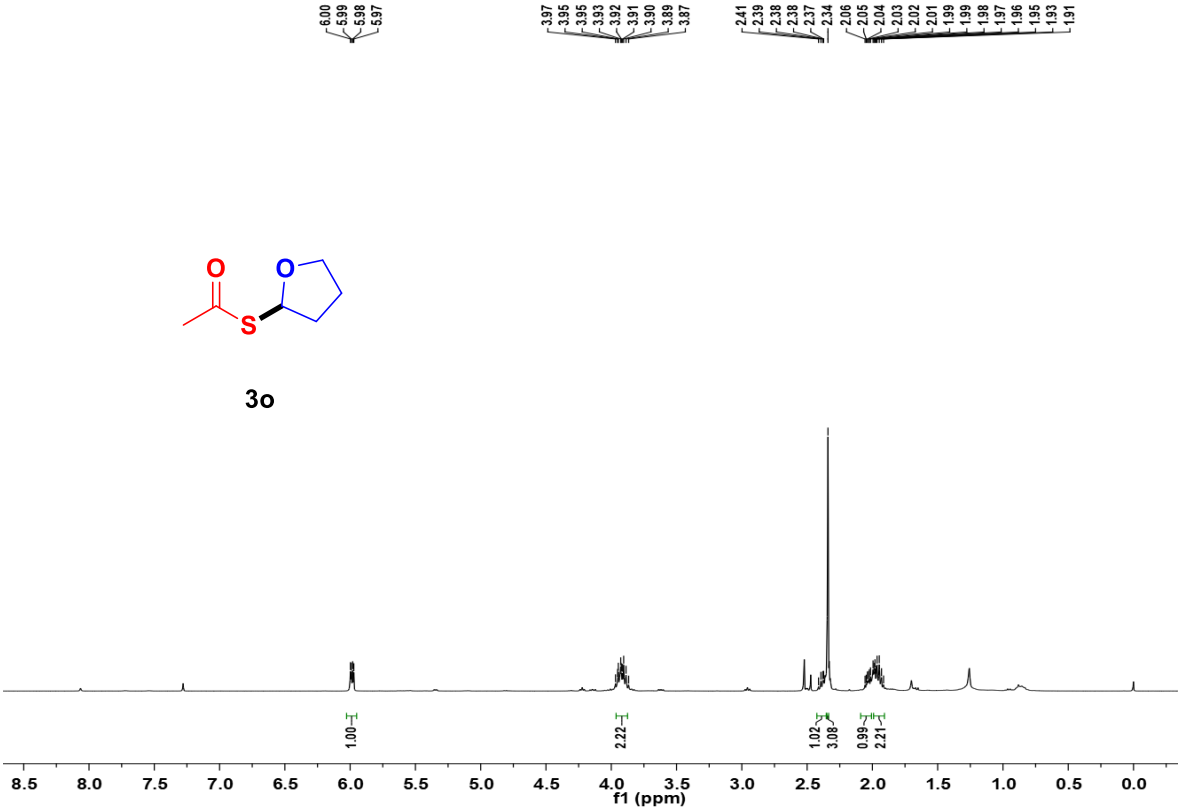
^{1}H NMR (400 MHz, $CDCl_3$) of 3n



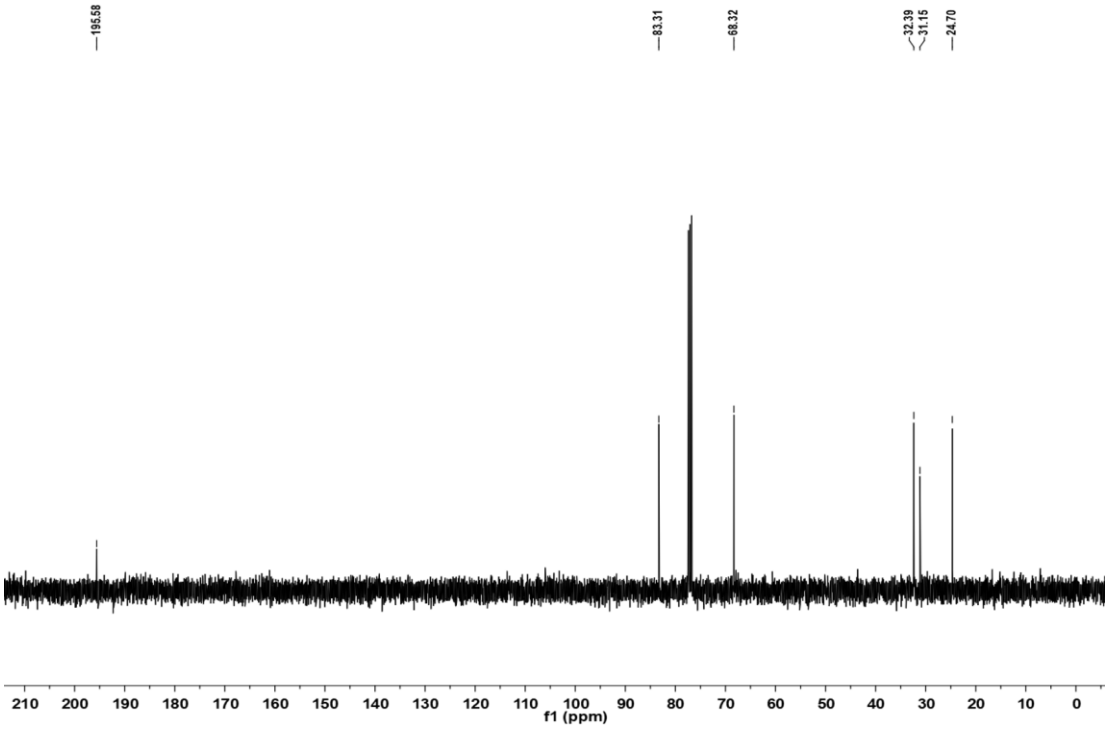
^{13}C NMR (101 MHz, $CDCl_3$) of 3n



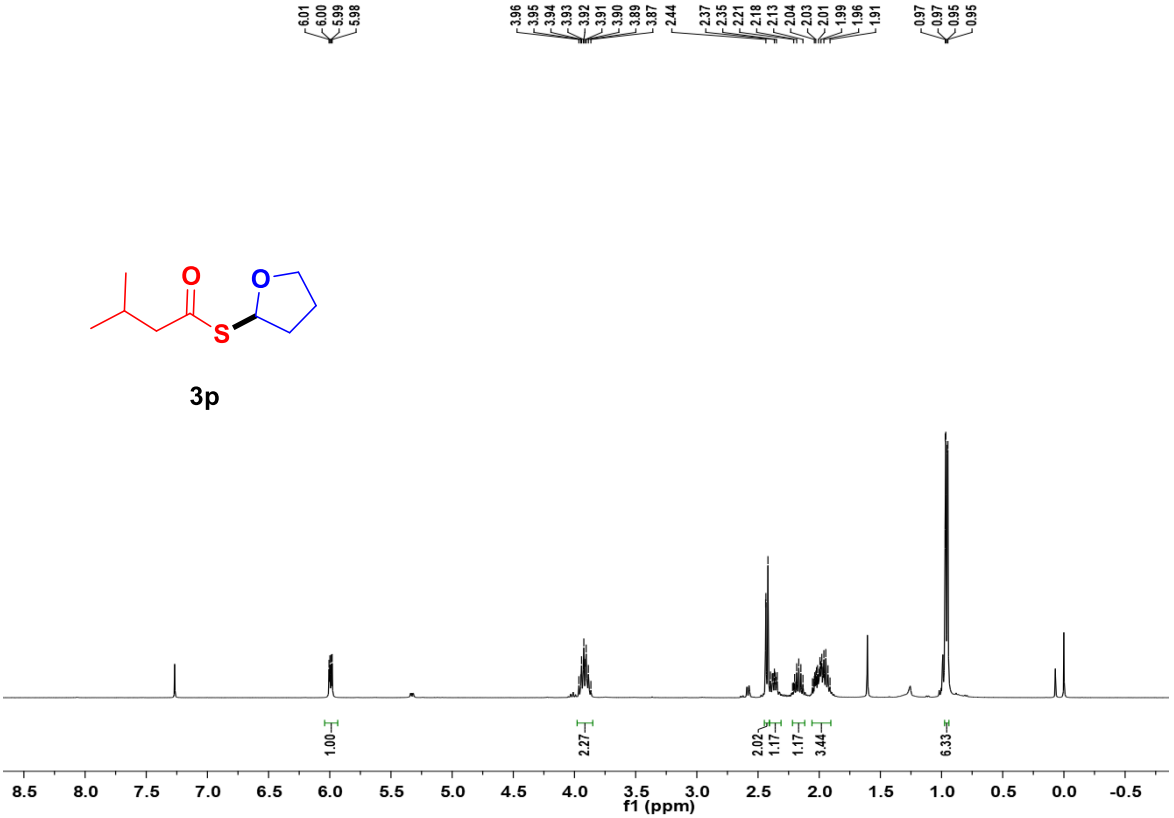
^{1}H NMR (400 MHz, $CDCl_3$) of 3o



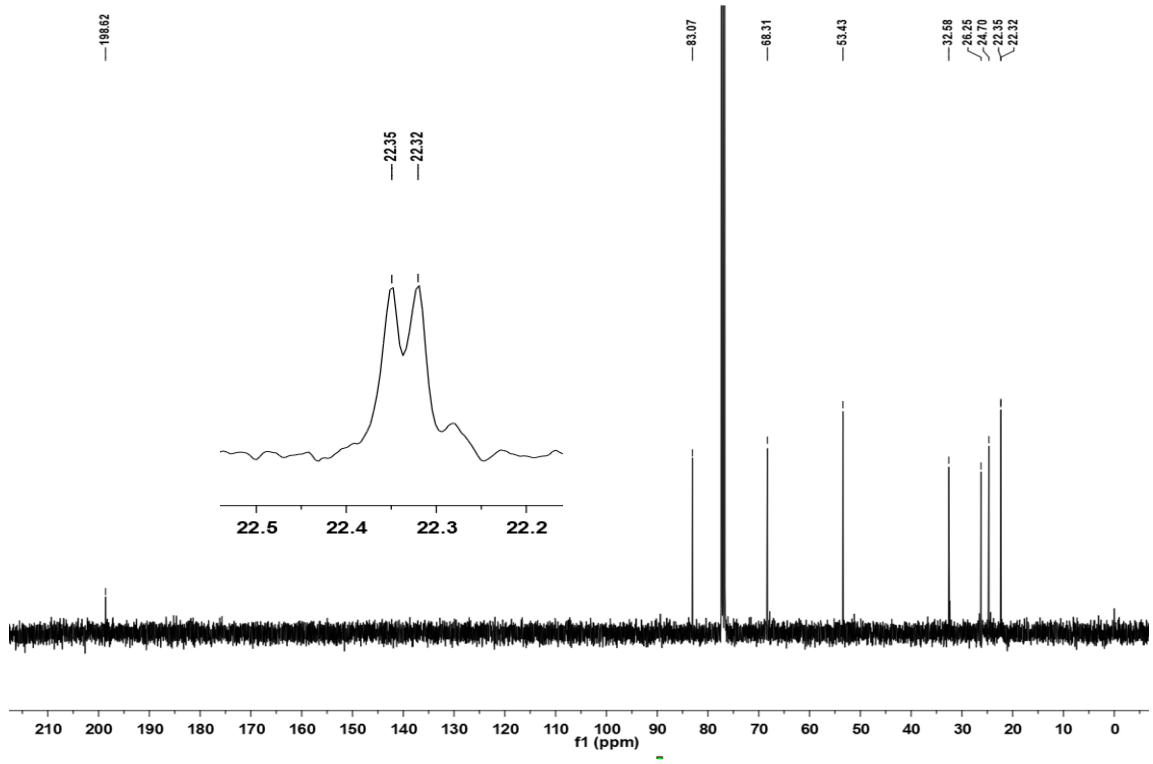
^{13}C NMR (101 MHz, $CDCl_3$) of 3o



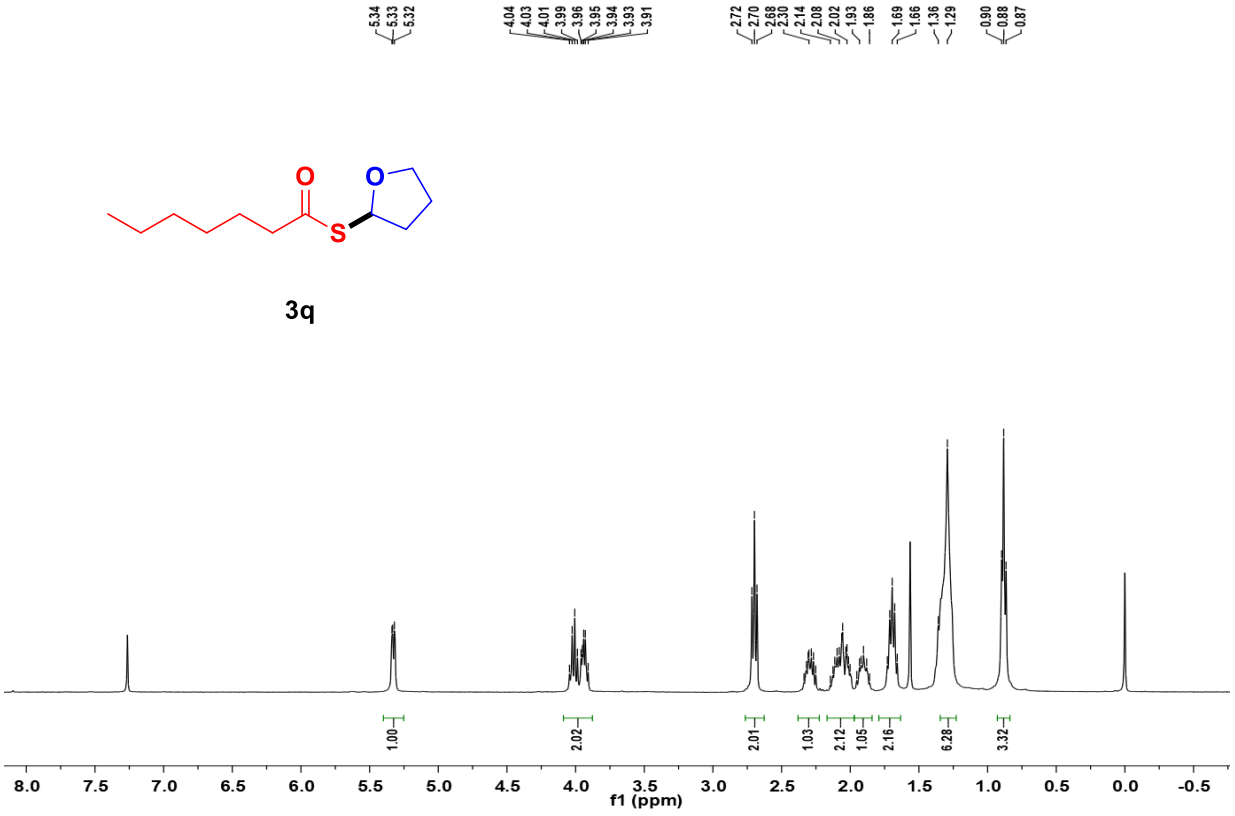
^{1}H NMR (400 MHz, $CDCl_3$) of 3p



^{13}C NMR (101 MHz, $CDCl_3$) of 3p

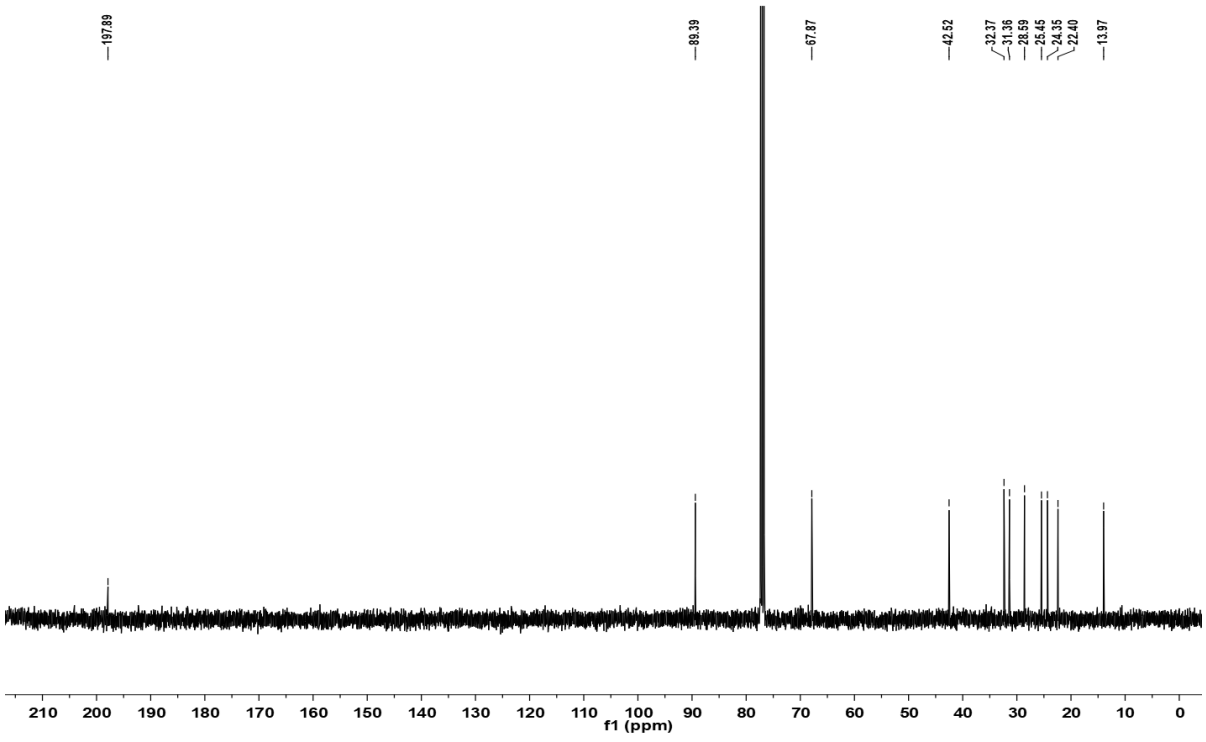


^{1}H NMR (400 MHz, $CDCl_3$) of 3q

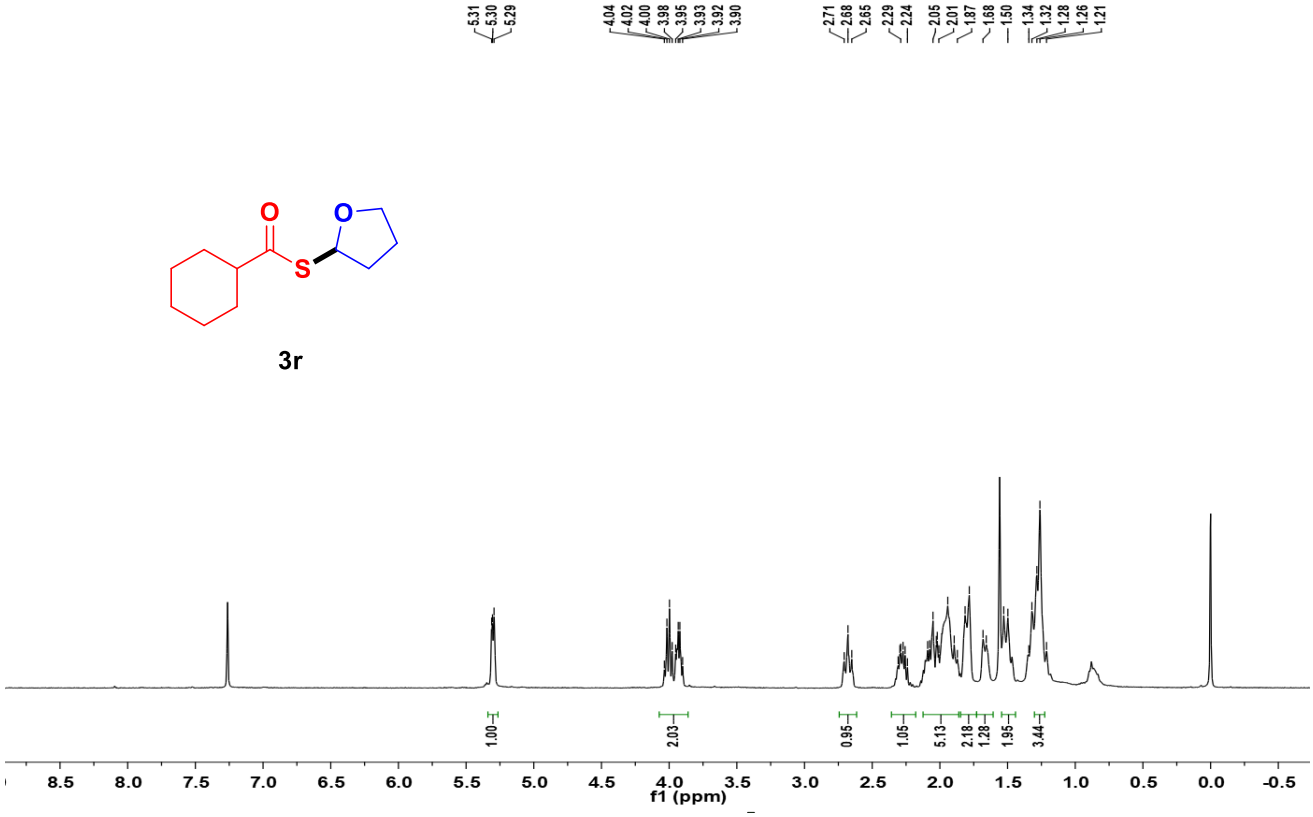


3q

^{13}C NMR (101 MHz, $CDCl_3$) of 3q

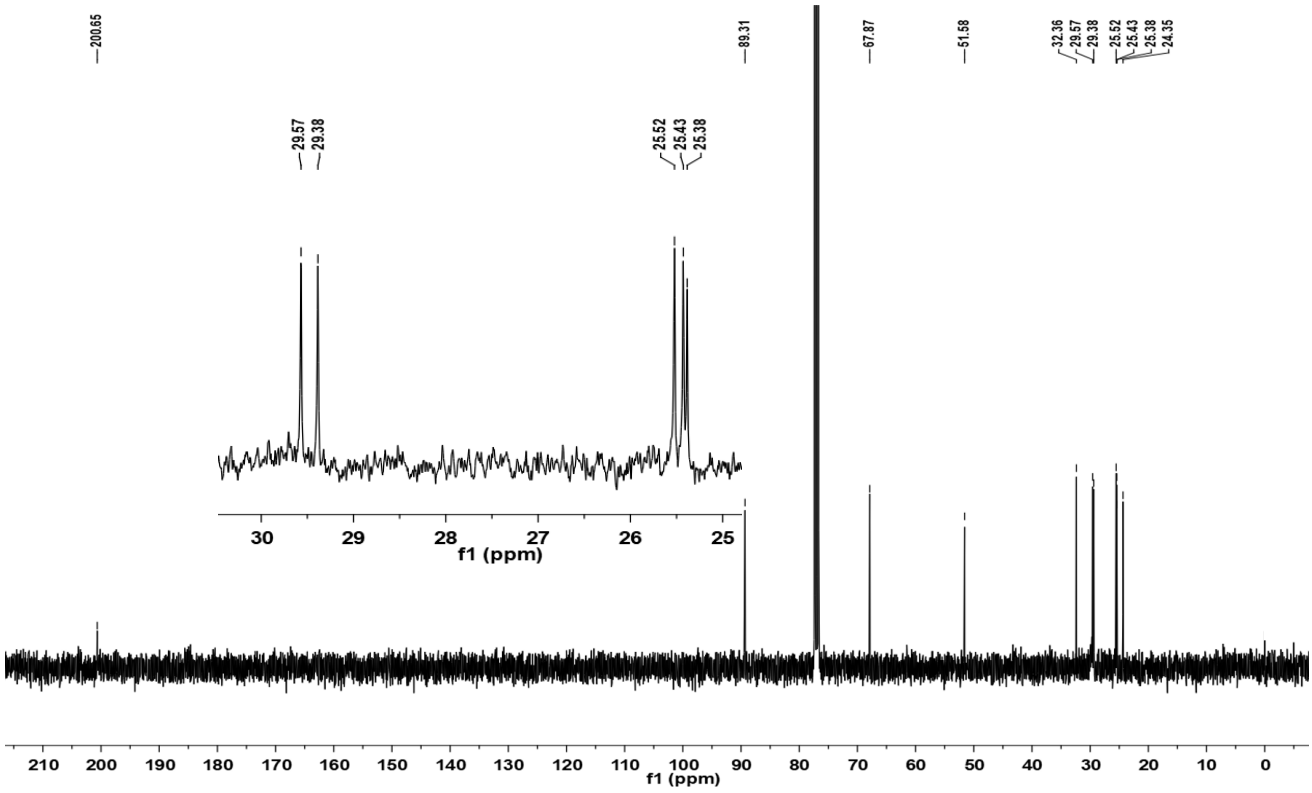


^{1}H NMR (400 MHz, $CDCl_3$) of 3r

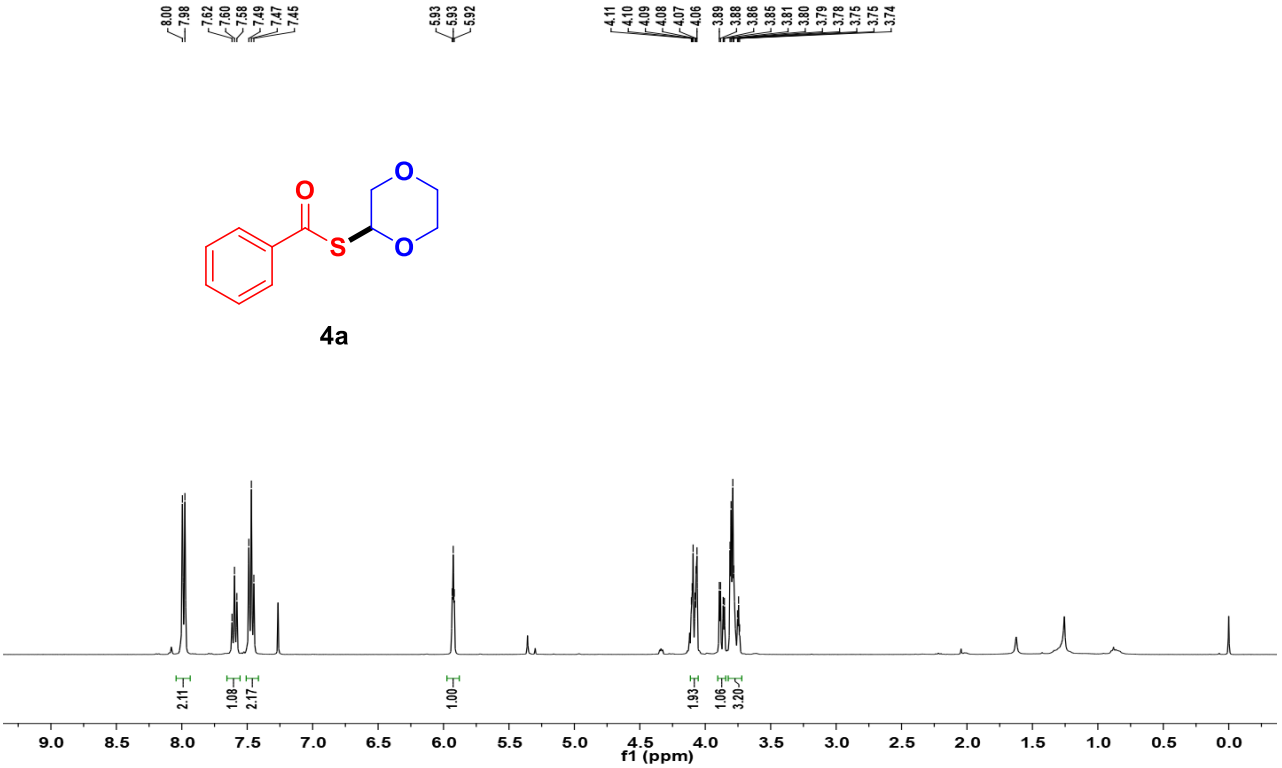


3r

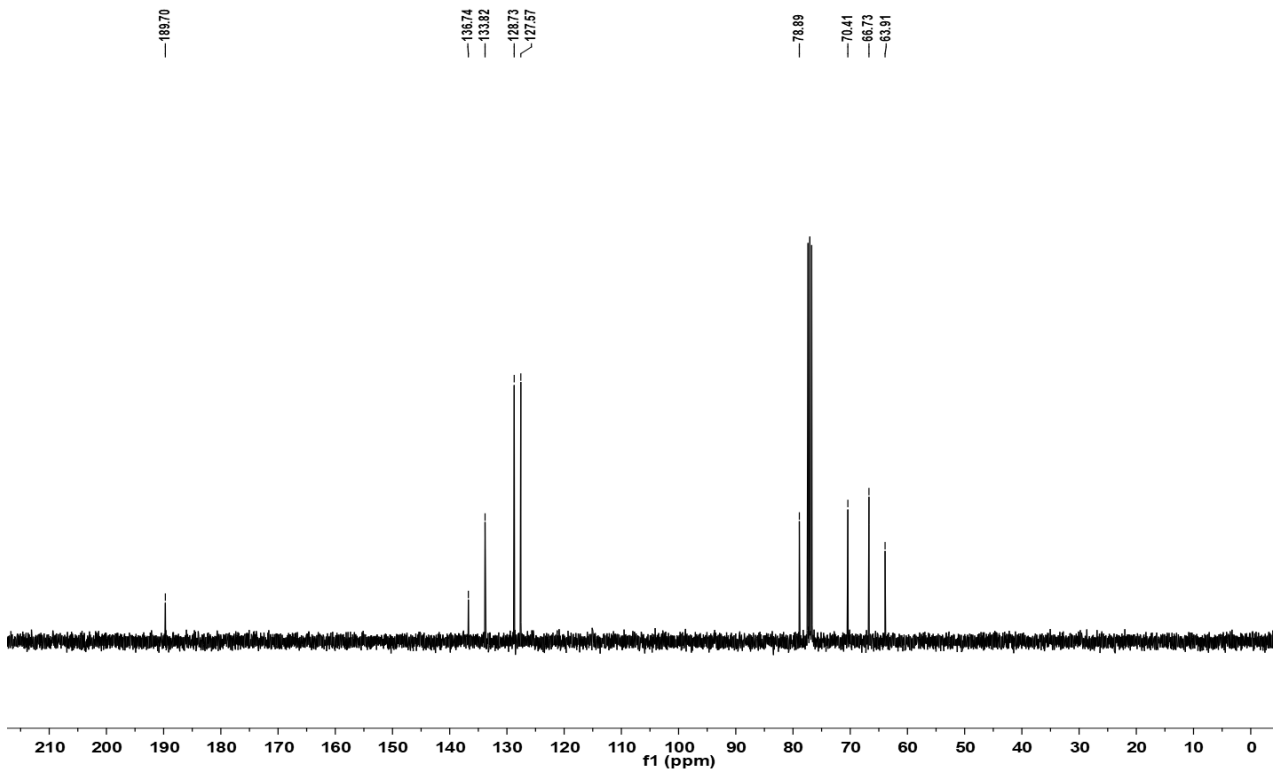
^{13}C NMR (101 MHz, $CDCl_3$) of 3r



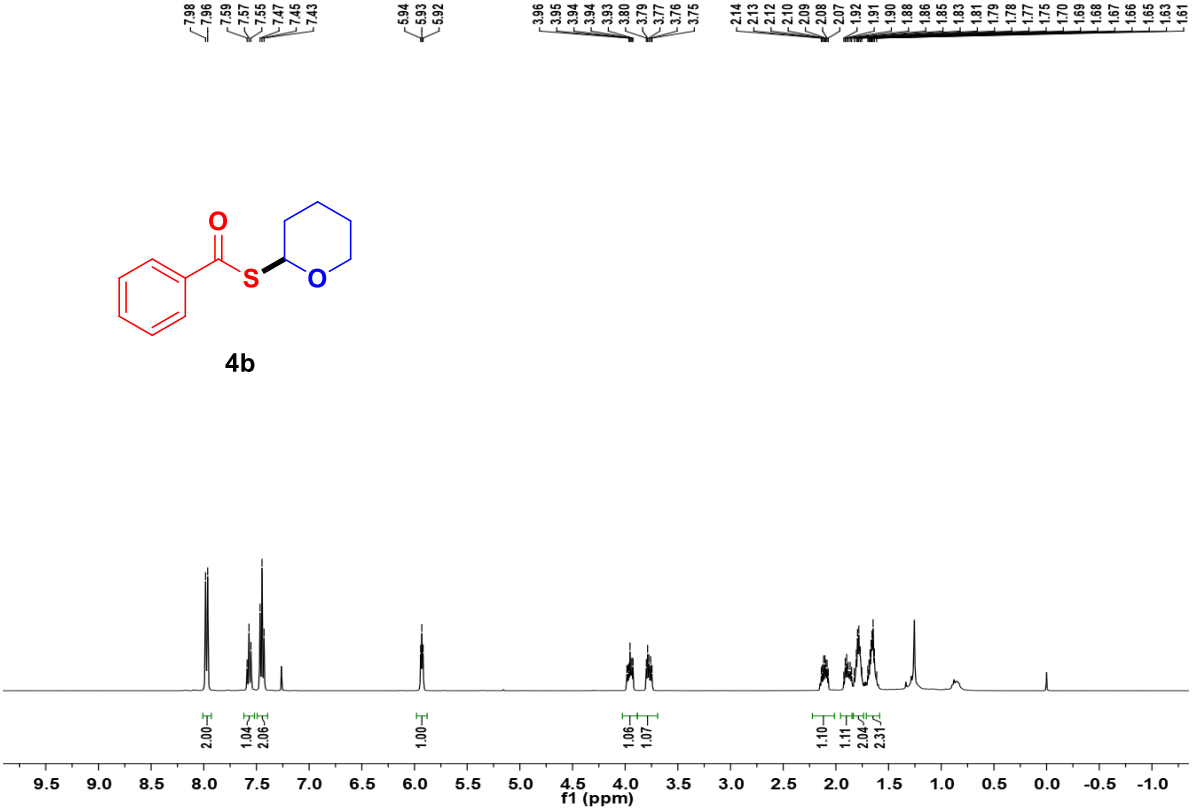
^{1}H NMR (400 MHz, $CDCl_3$) of 4a



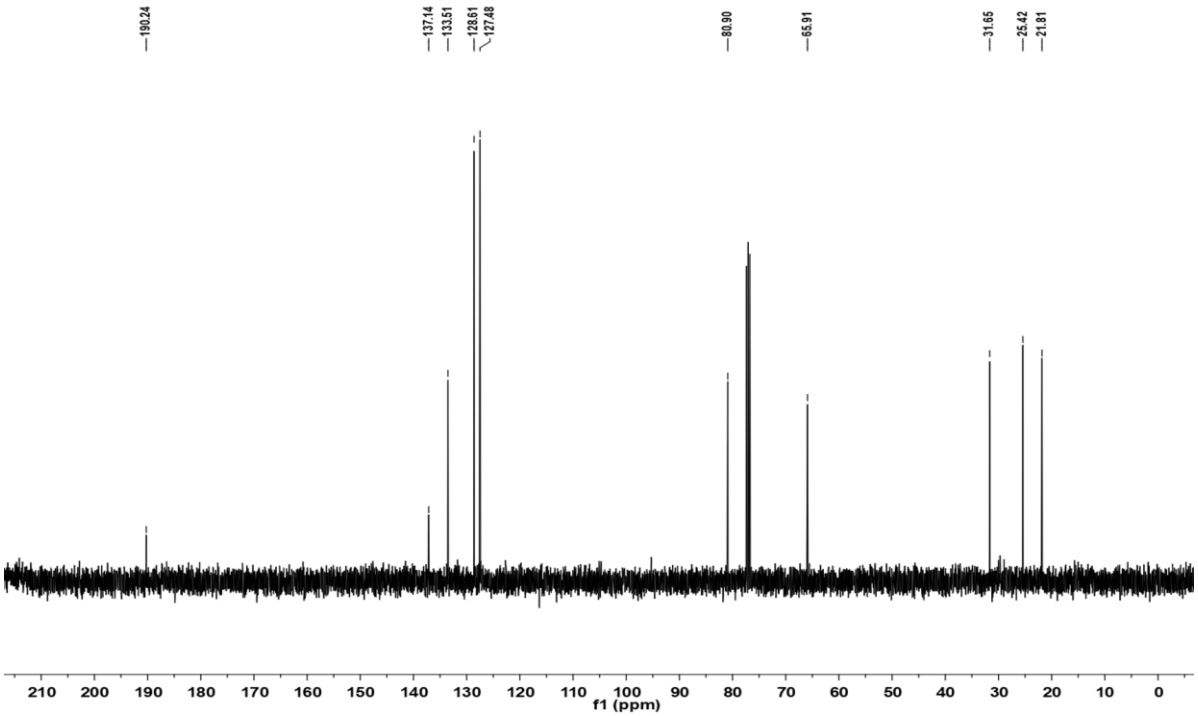
^{13}C NMR (101 MHz, $CDCl_3$) of 4a



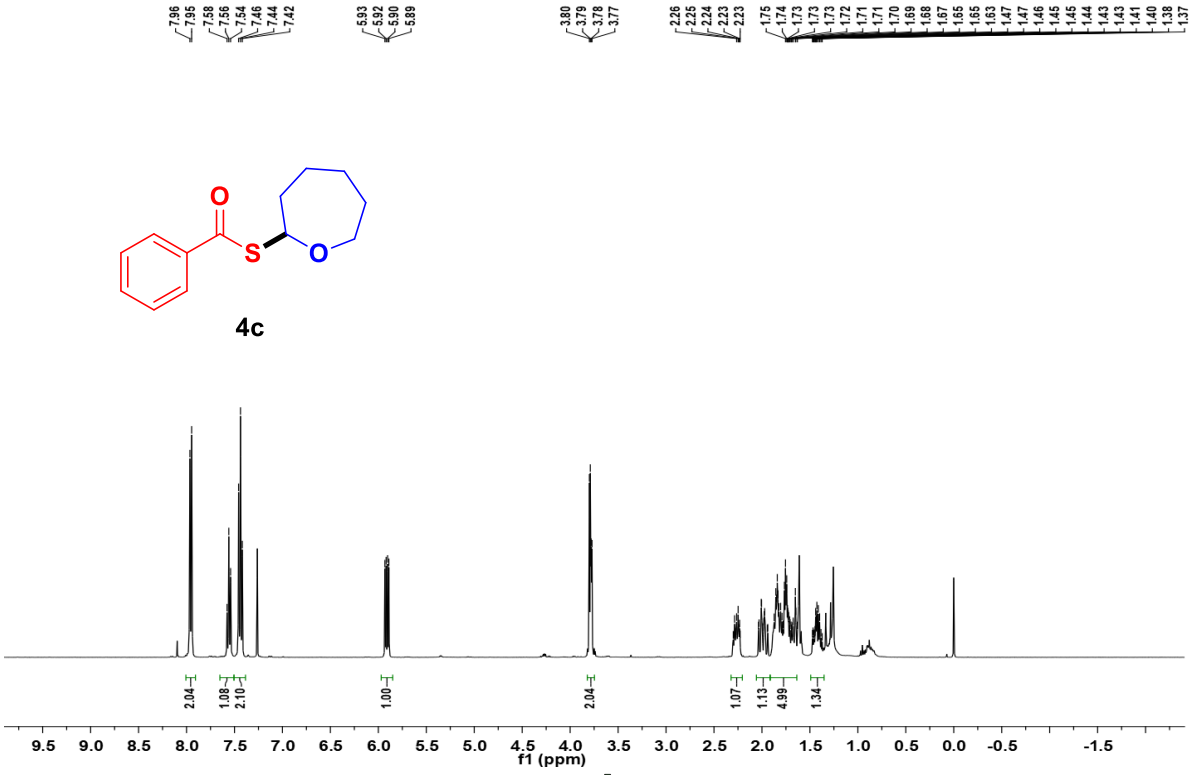
^{1}H NMR (400 MHz, $CDCl_3$) of 4b



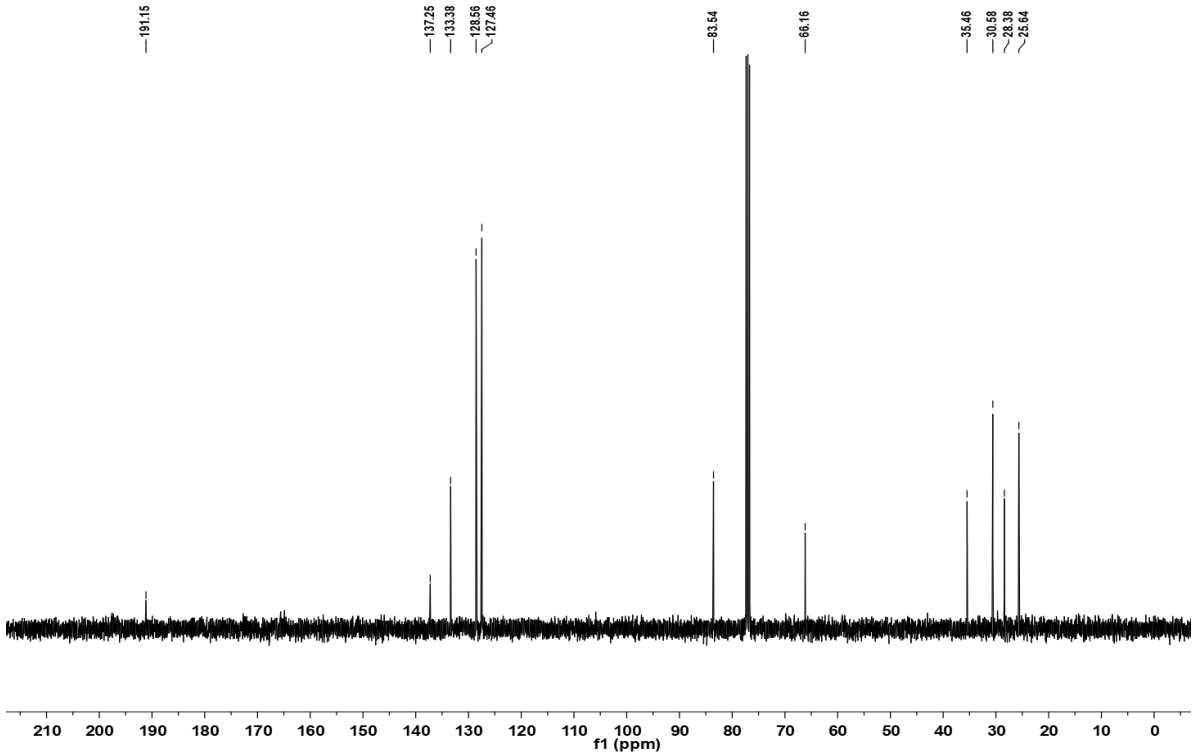
^{13}C NMR (101 MHz, $CDCl_3$) of 4b



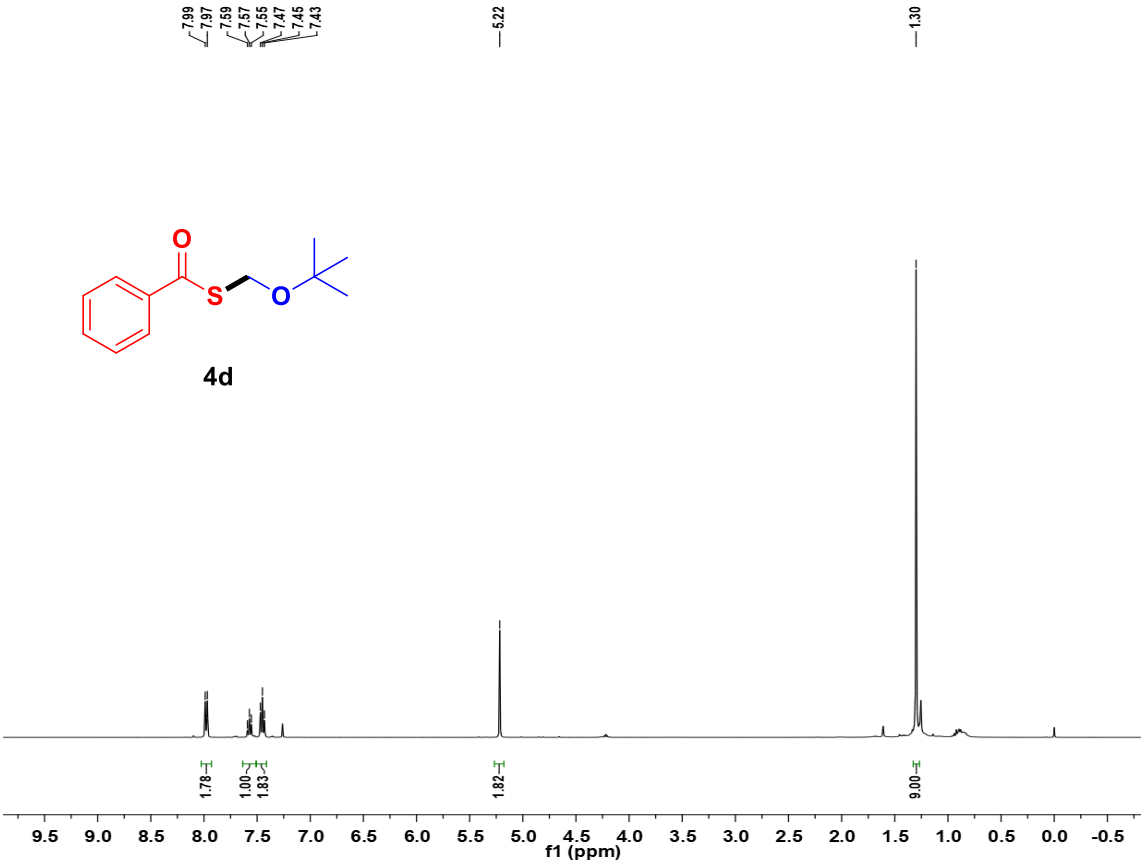
^{1}H NMR (400 MHz, $CDCl_3$) of 4c



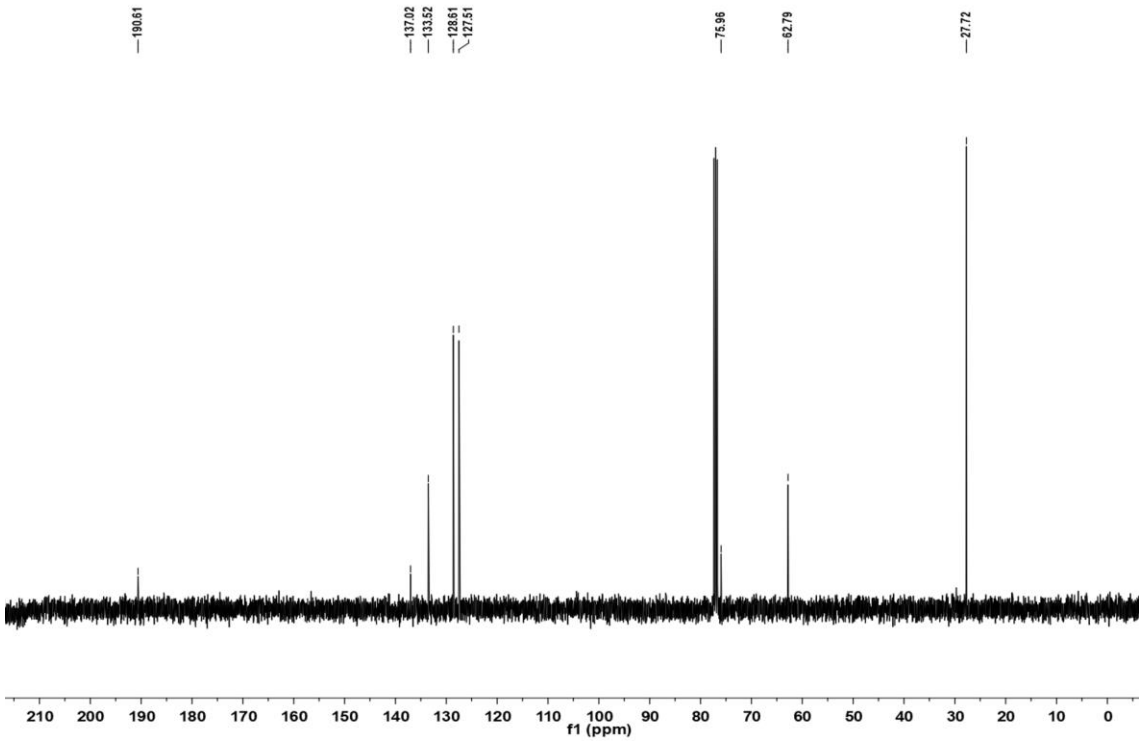
^{13}C NMR (101 MHz, $CDCl_3$) of 4c



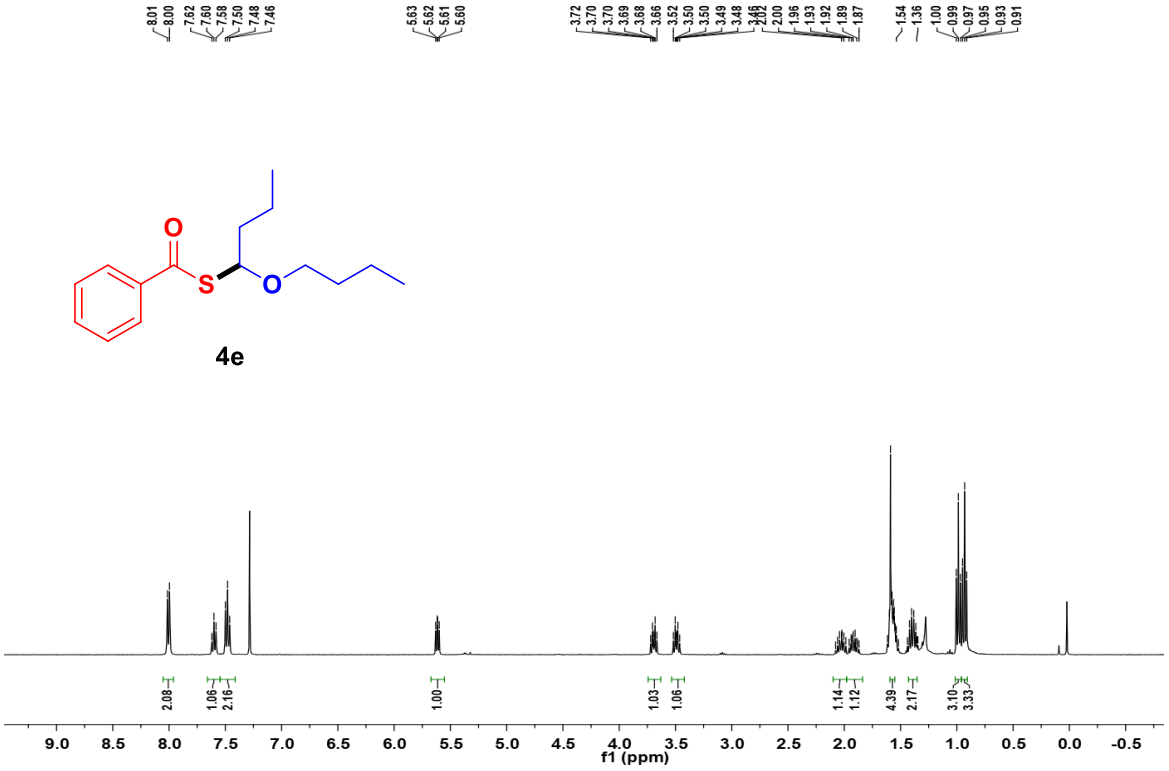
^{1}H NMR (400 MHz, $CDCl_3$) of 4d



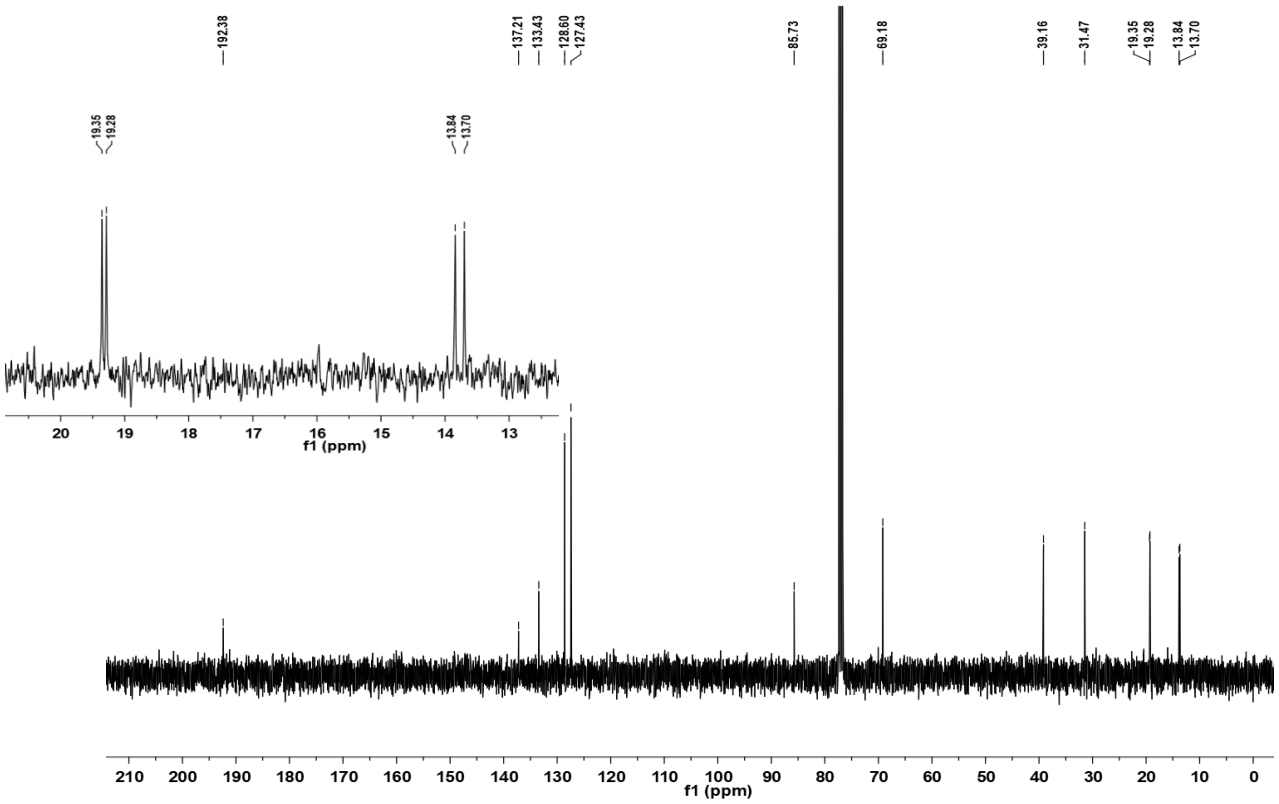
^{13}C NMR (101 MHz, $CDCl_3$) of 4d



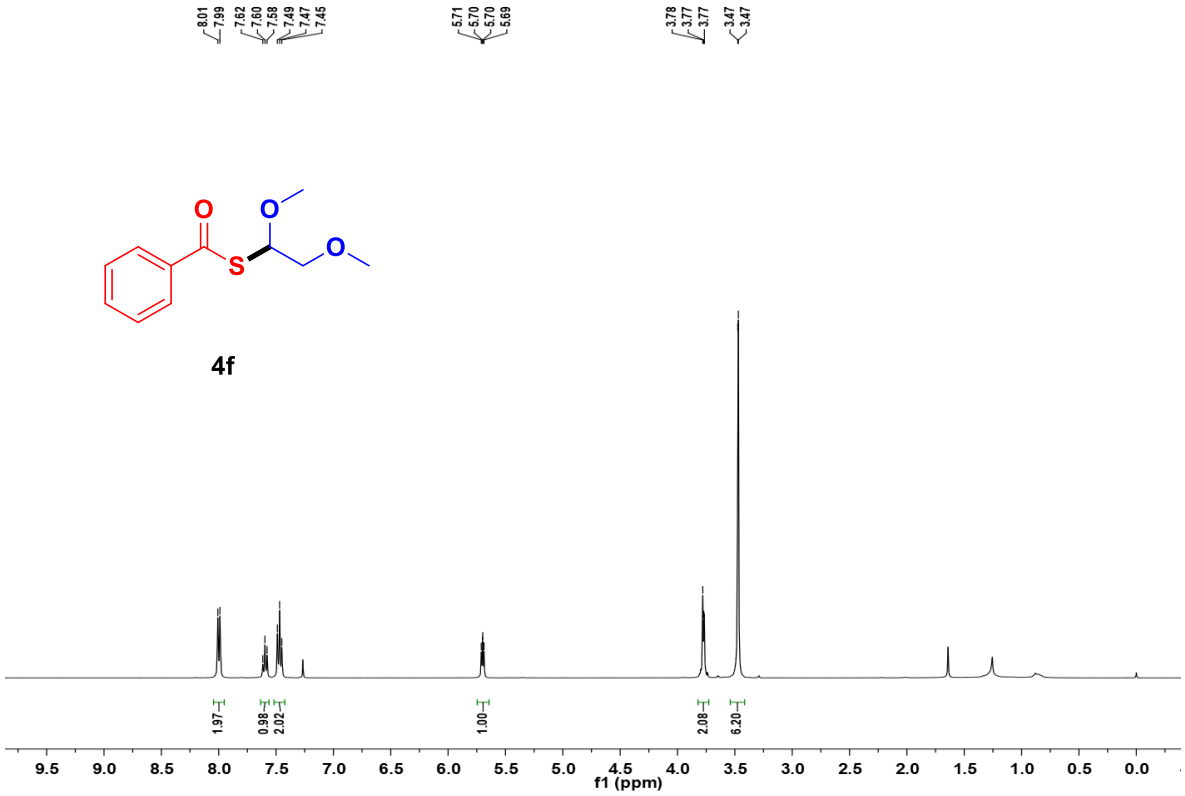
^{1}H NMR (400 MHz, $CDCl_3$) of 4e



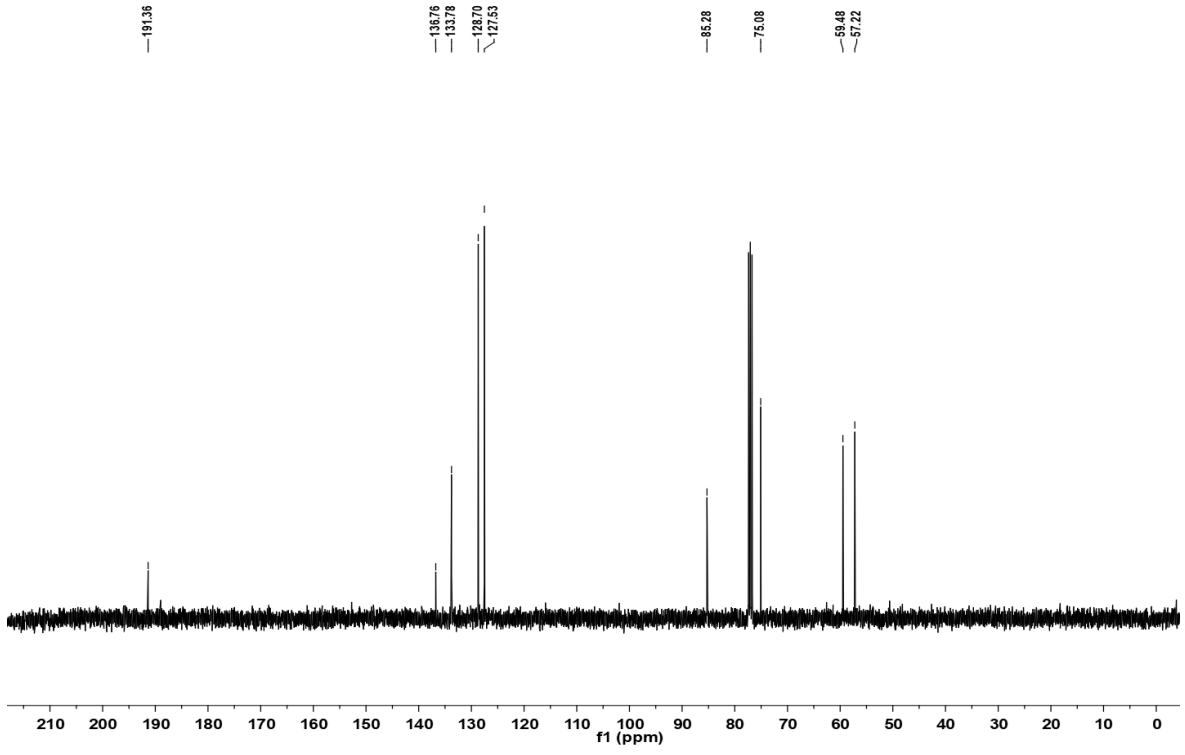
^{13}C NMR (101 MHz, $CDCl_3$) of 4e



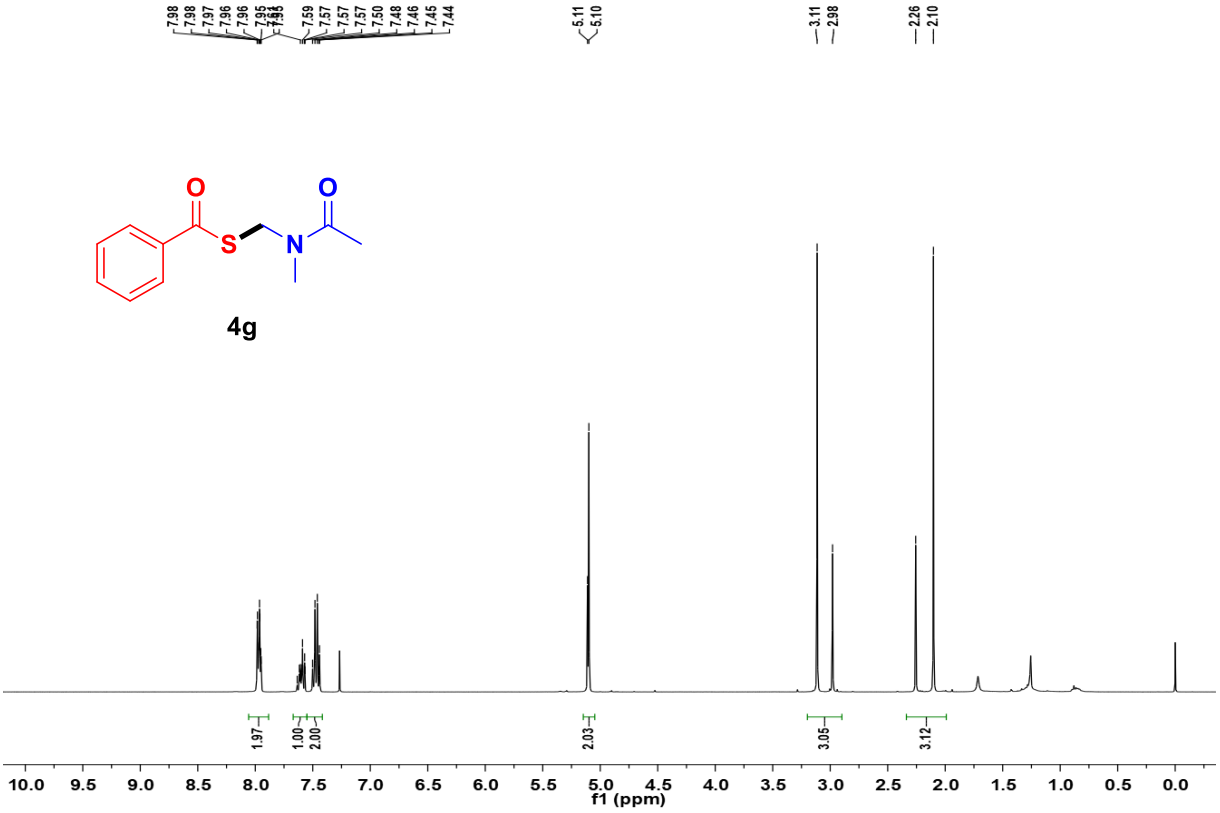
^{1}H NMR (400 MHz, $CDCl_3$) of 4f



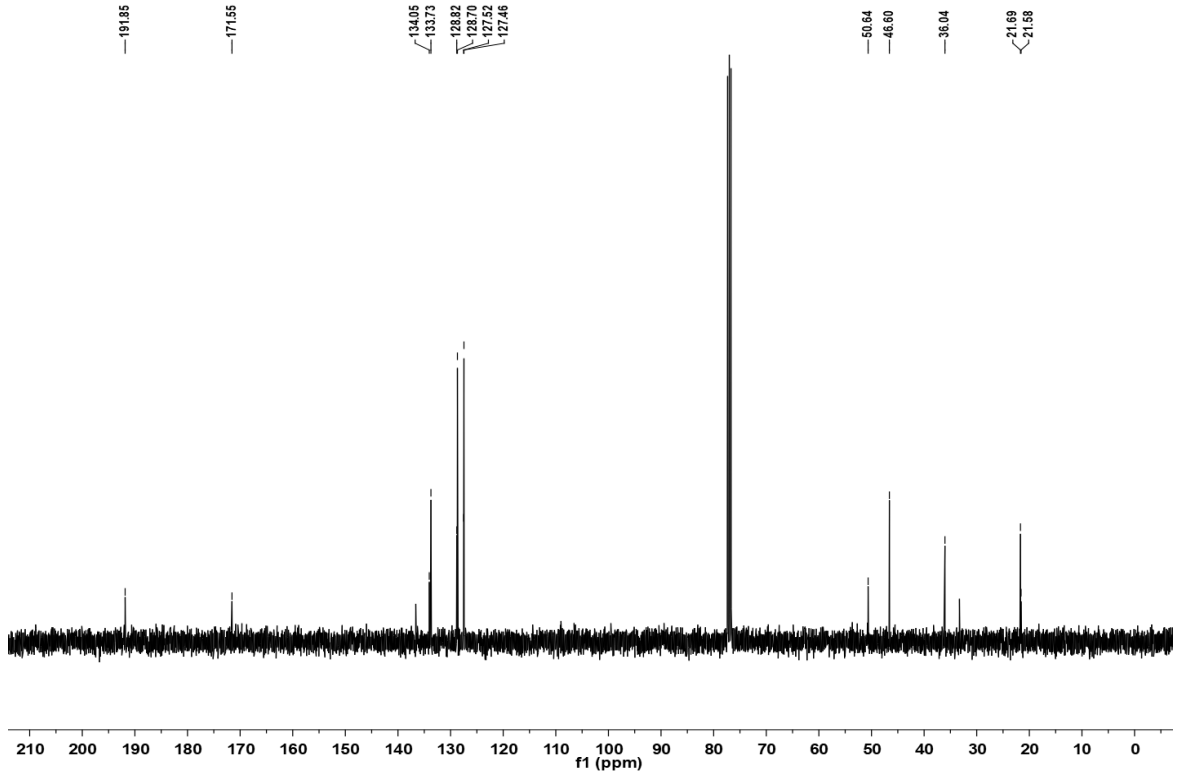
^{13}C NMR (101 MHz, $CDCl_3$) of 4f



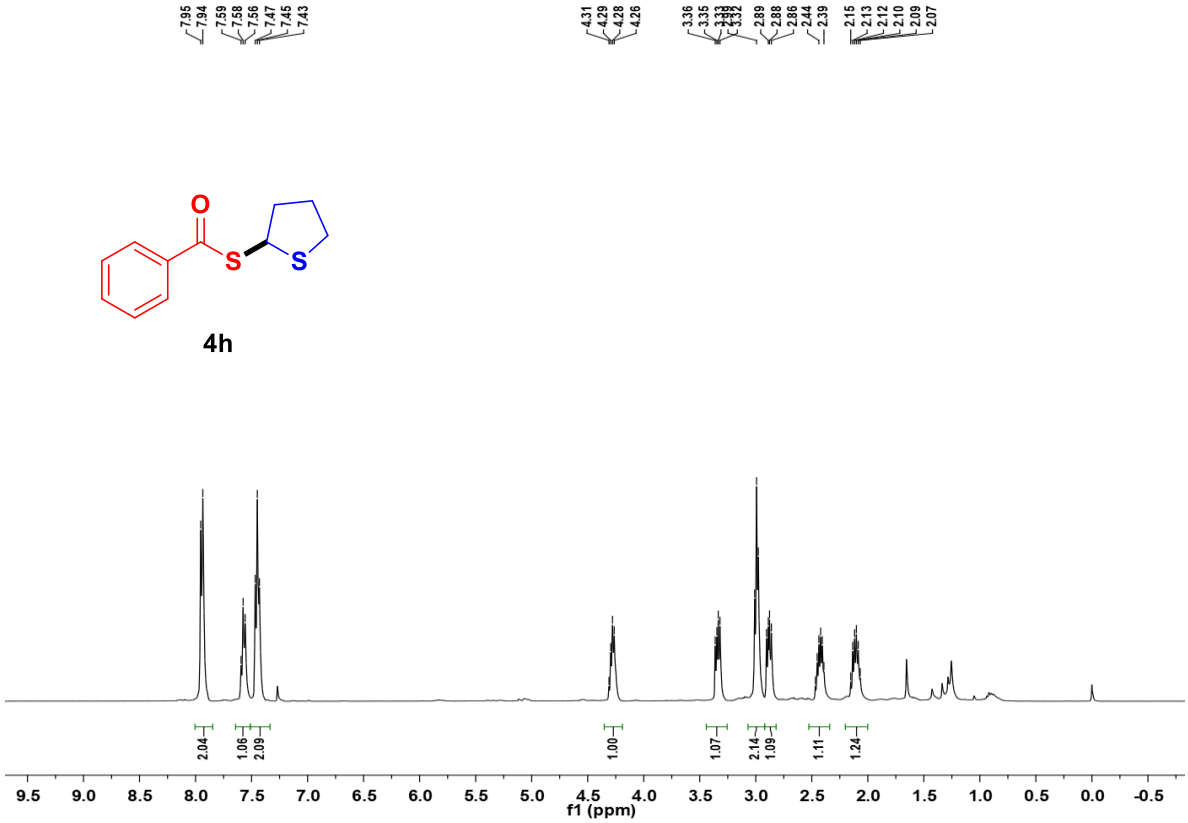
^{1}H NMR (400 MHz, $CDCl_3$) of 4g



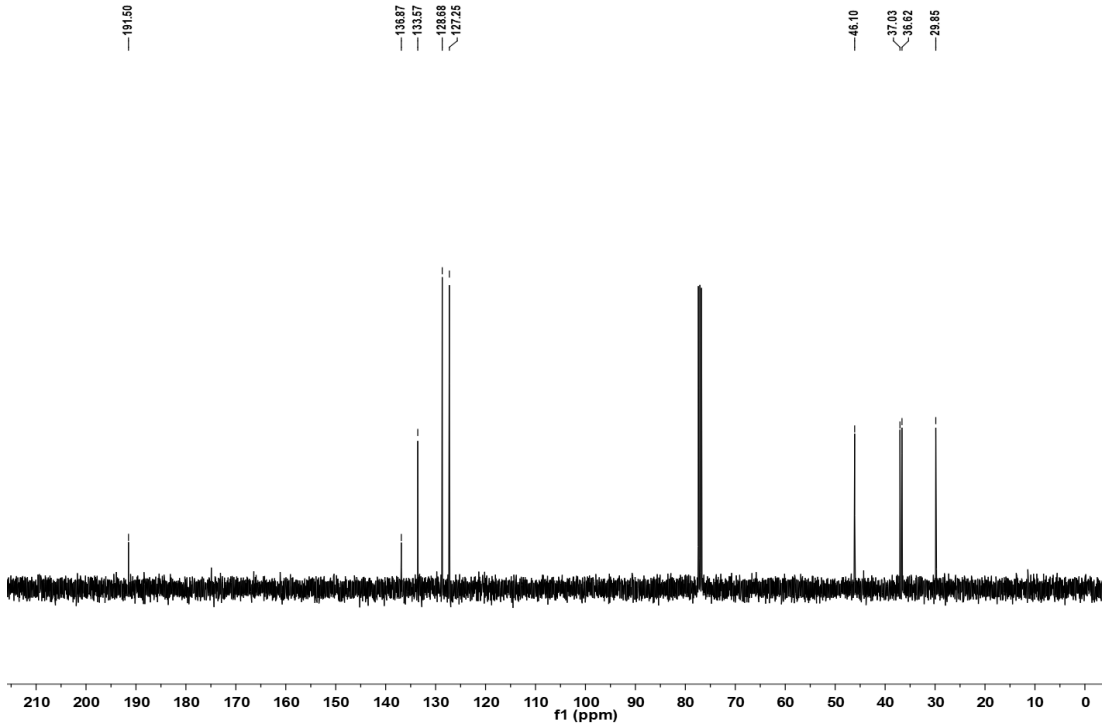
^{13}C NMR (101 MHz, $CDCl_3$) of 4g



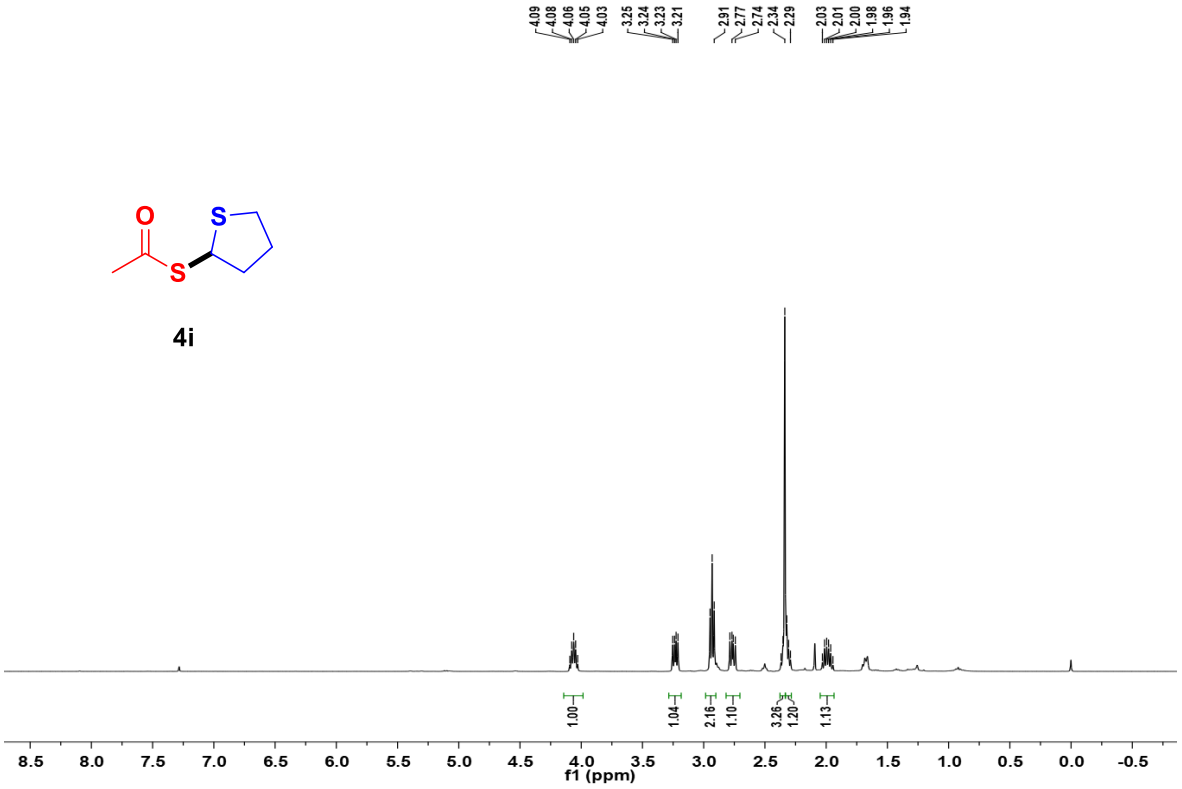
^{1}H NMR (400 MHz, $CDCl_3$) of 4h



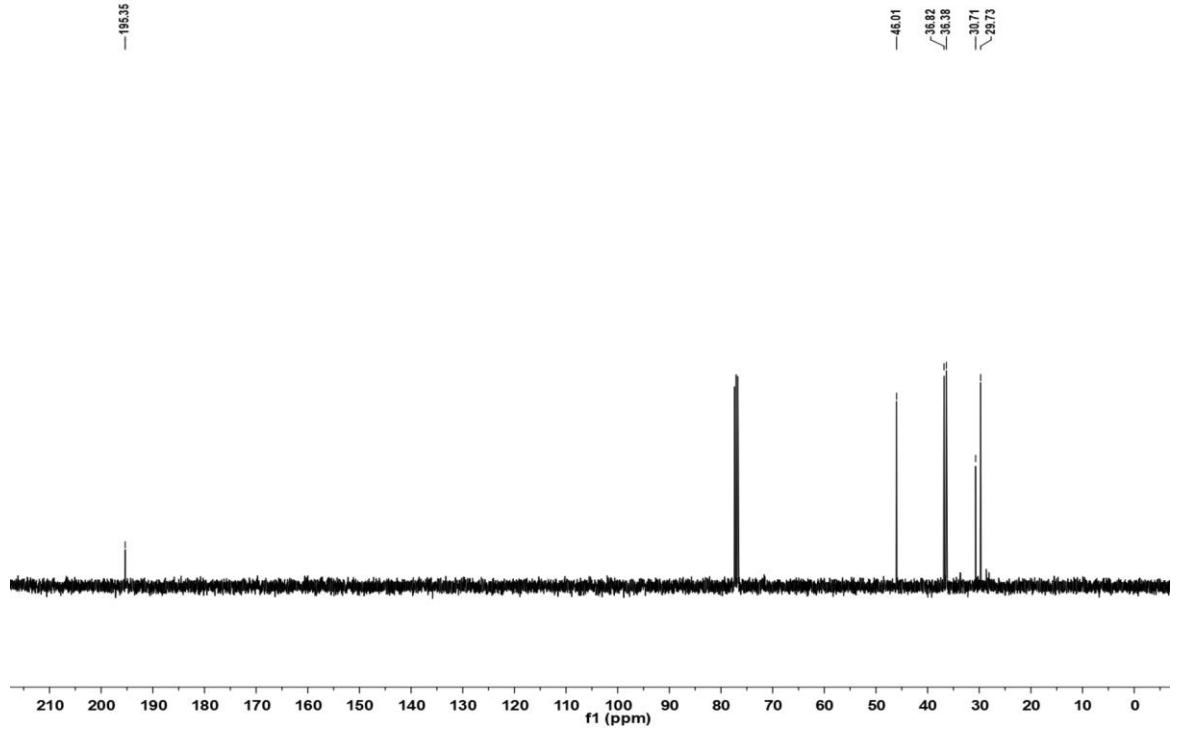
^{13}C NMR (101 MHz, $CDCl_3$) of 4h



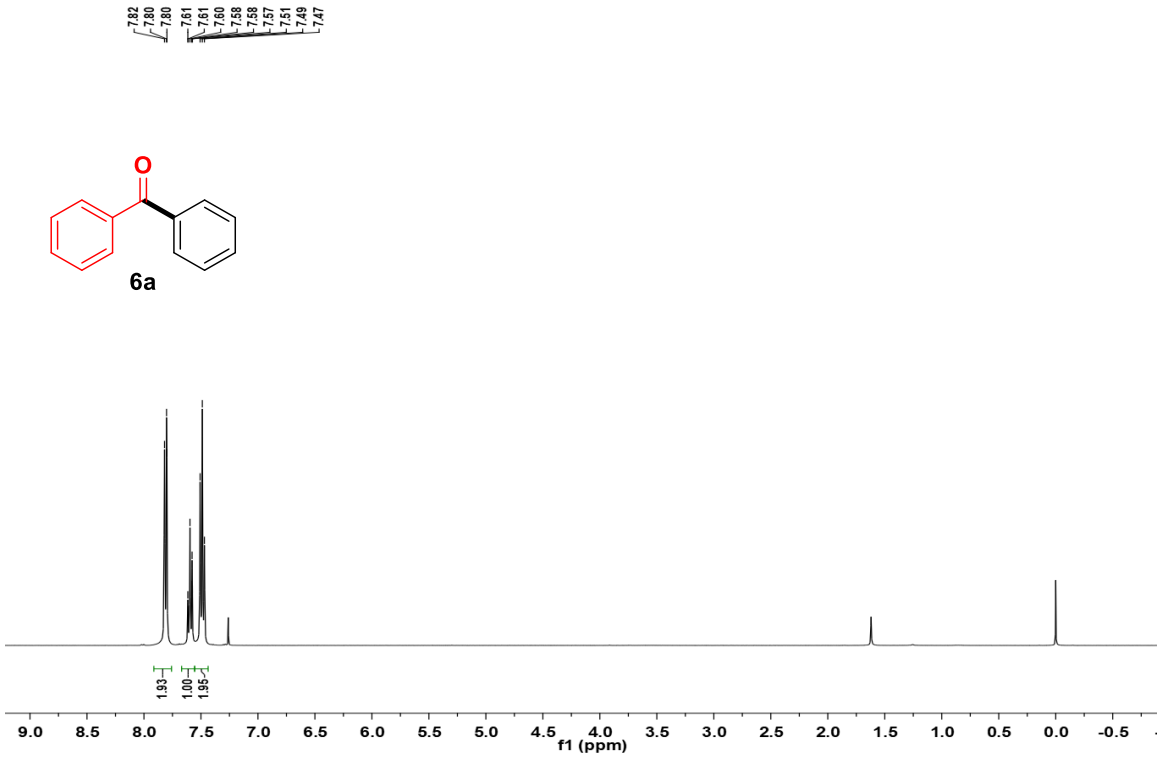
^{1}H NMR (400 MHz, $CDCl_3$) of 4i



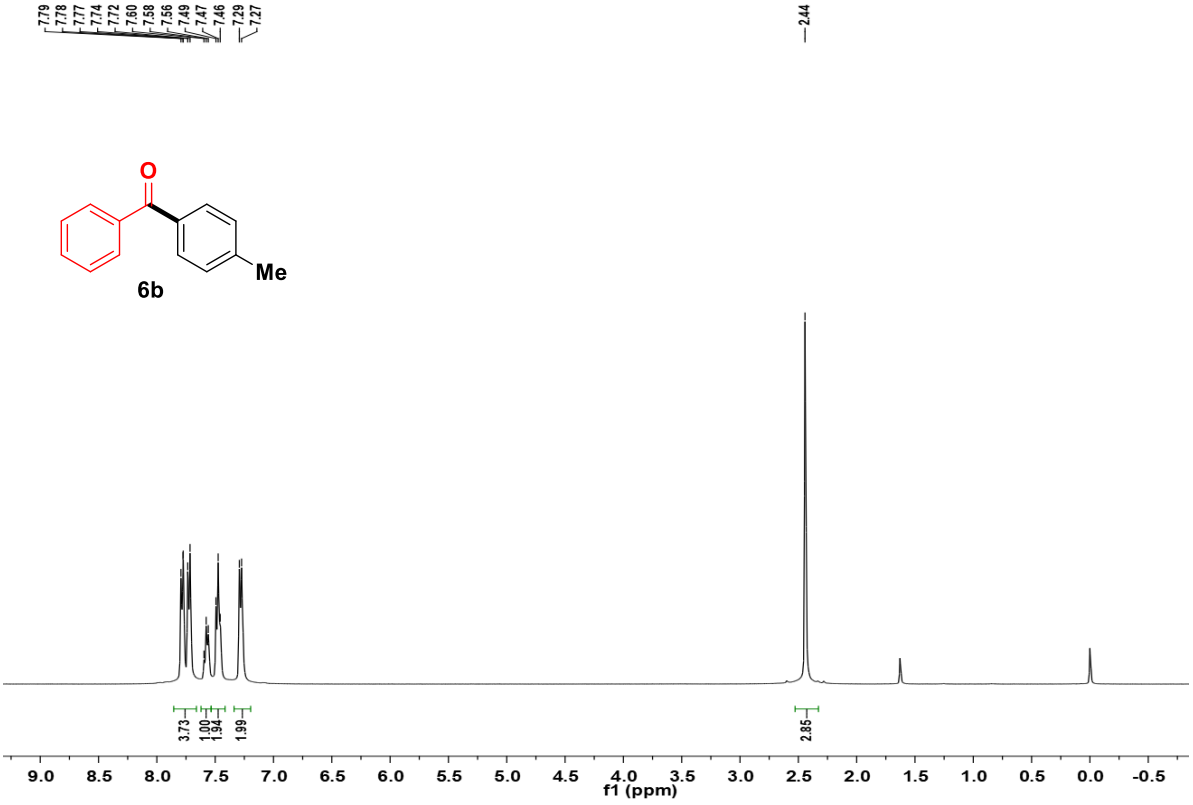
^{13}C NMR (101 MHz, $CDCl_3$) of 4i



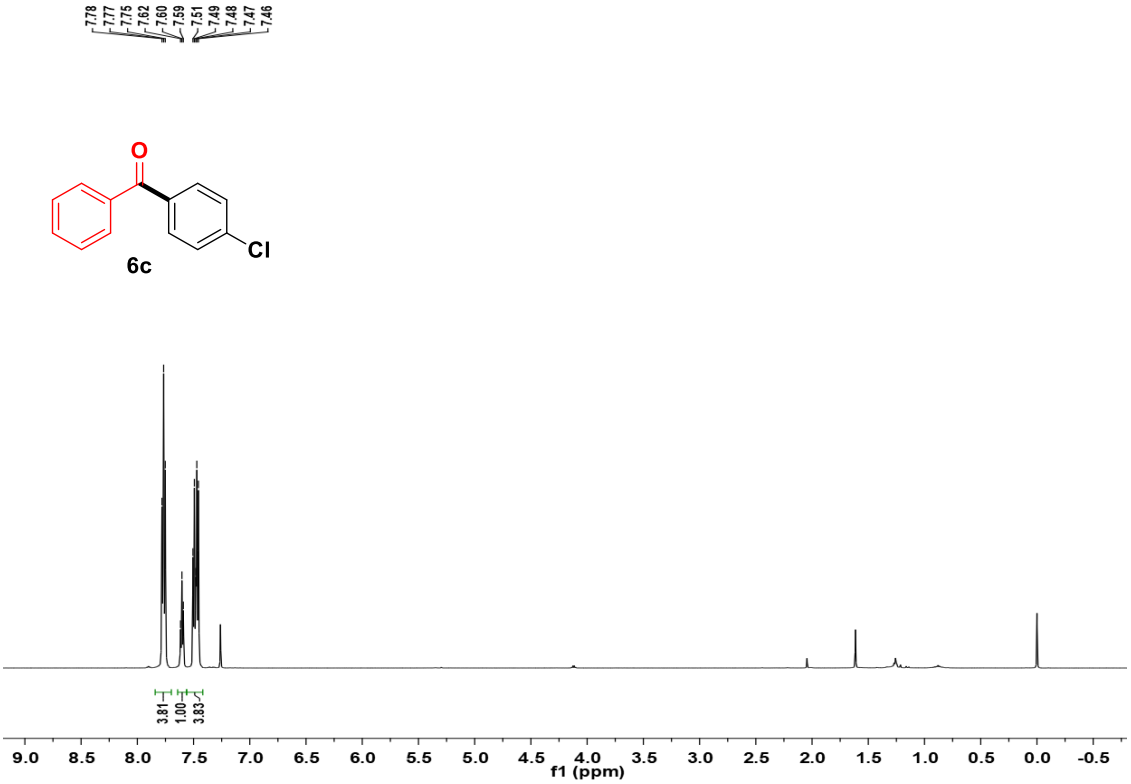
^{1}H NMR (400 MHz, $CDCl_3$) of 6a



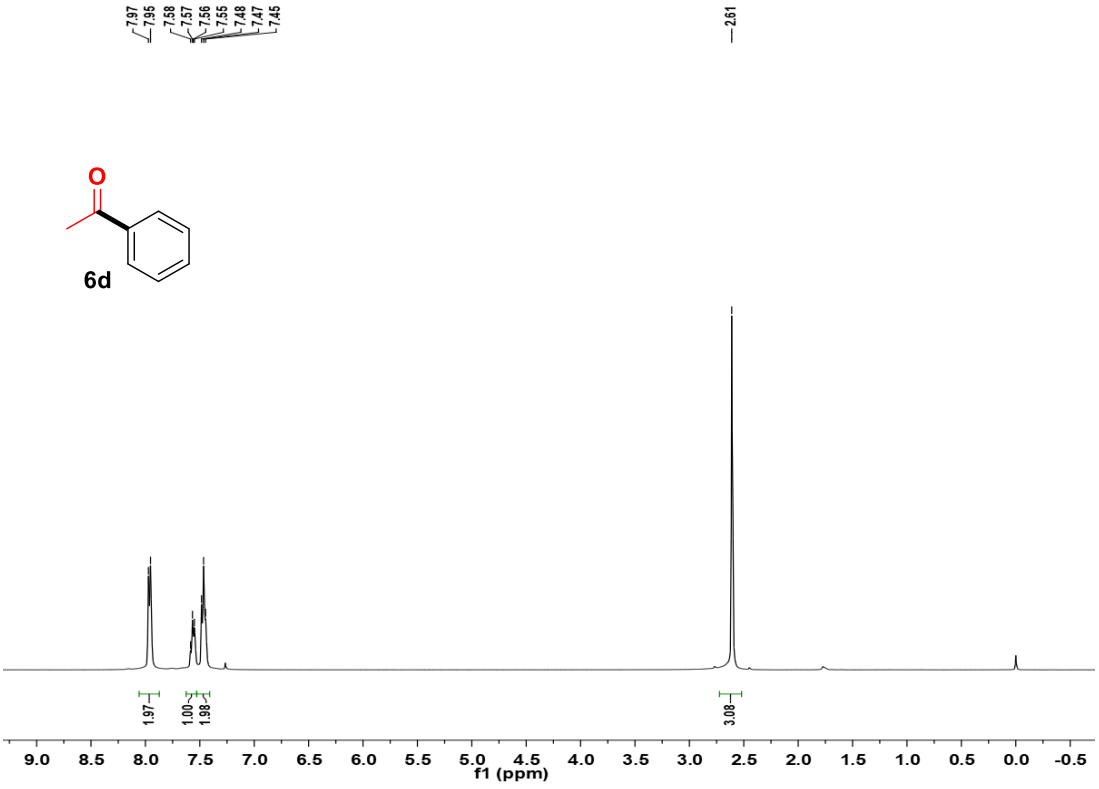
^{1}H NMR (400 MHz, $CDCl_3$) of 6b



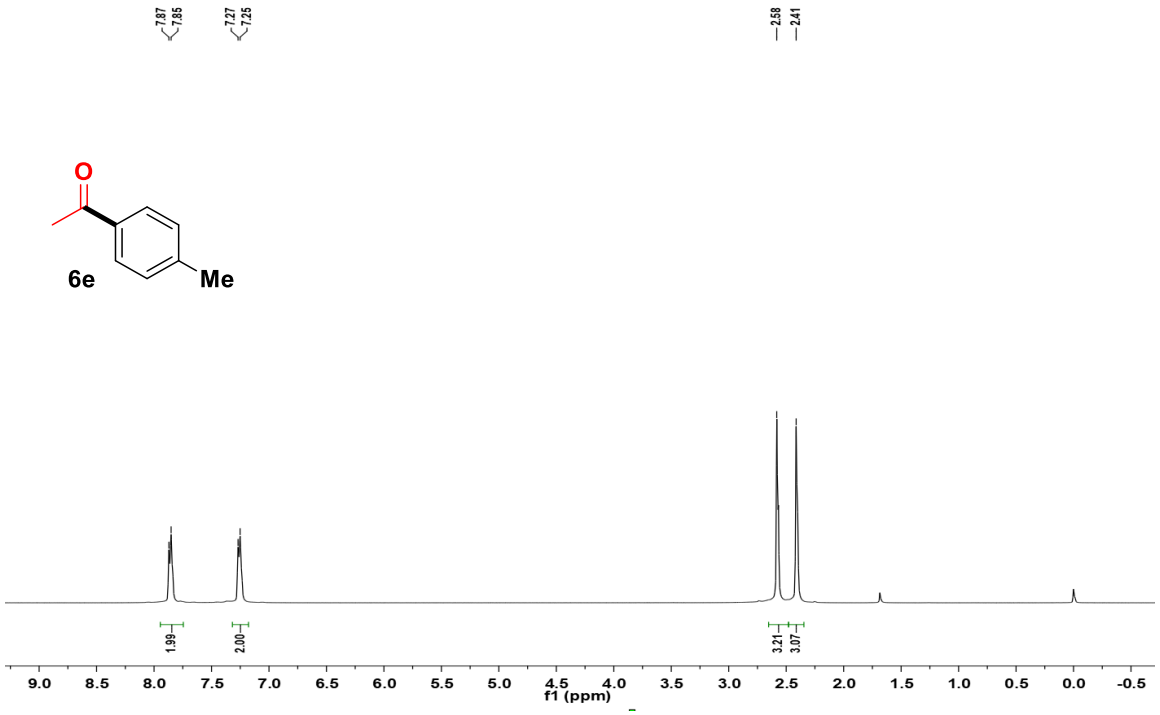
^{1}H NMR (400 MHz, $CDCl_3$) of 6c



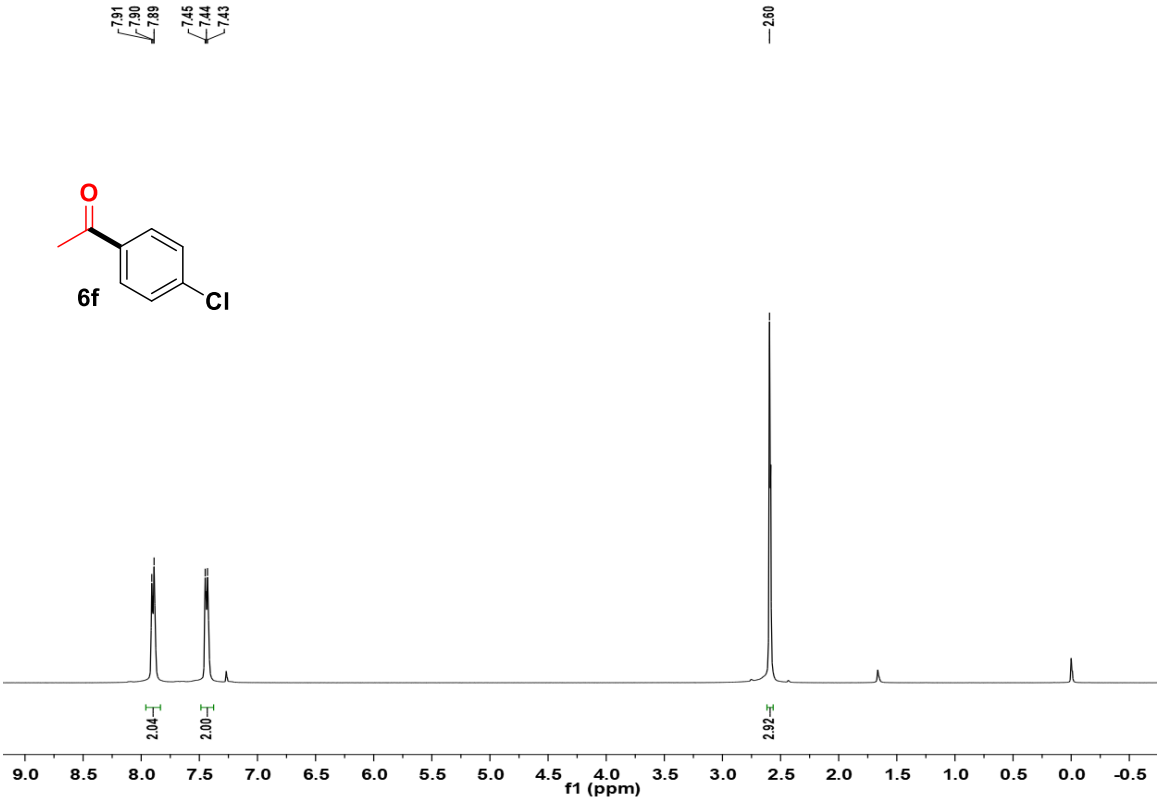
^{1}H NMR (400 MHz, $CDCl_3$) of 6d



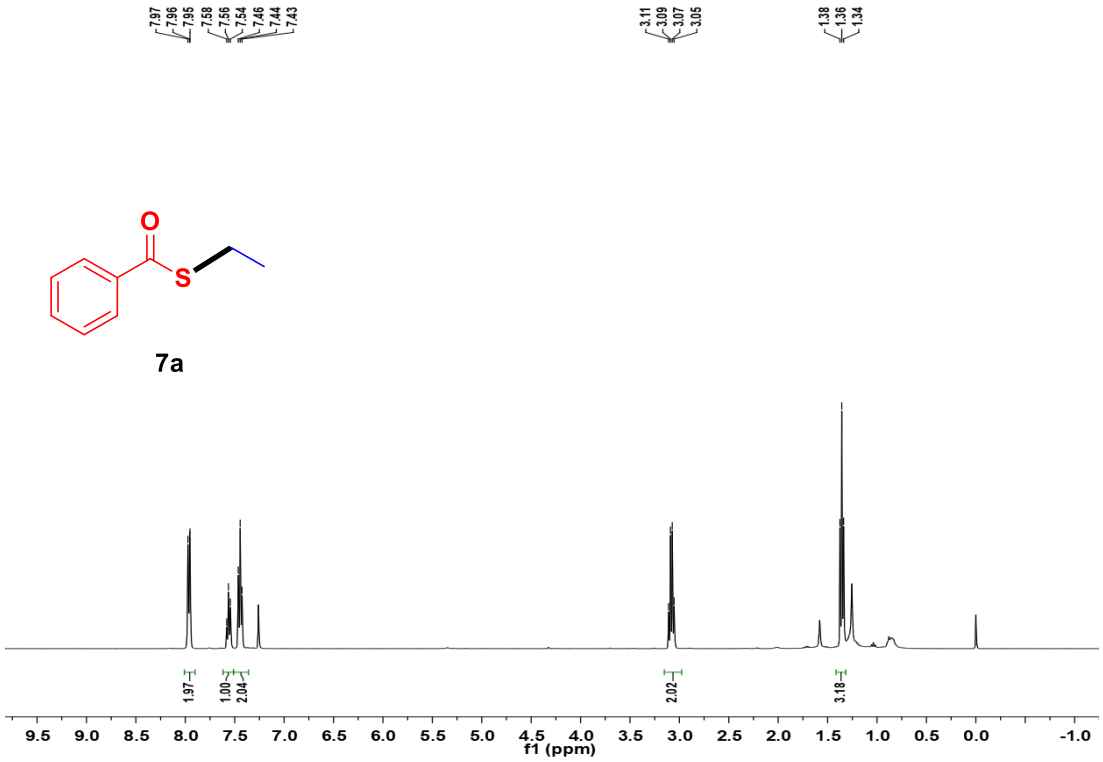
^{1}H NMR (400 MHz, $CDCl_3$) of 6e



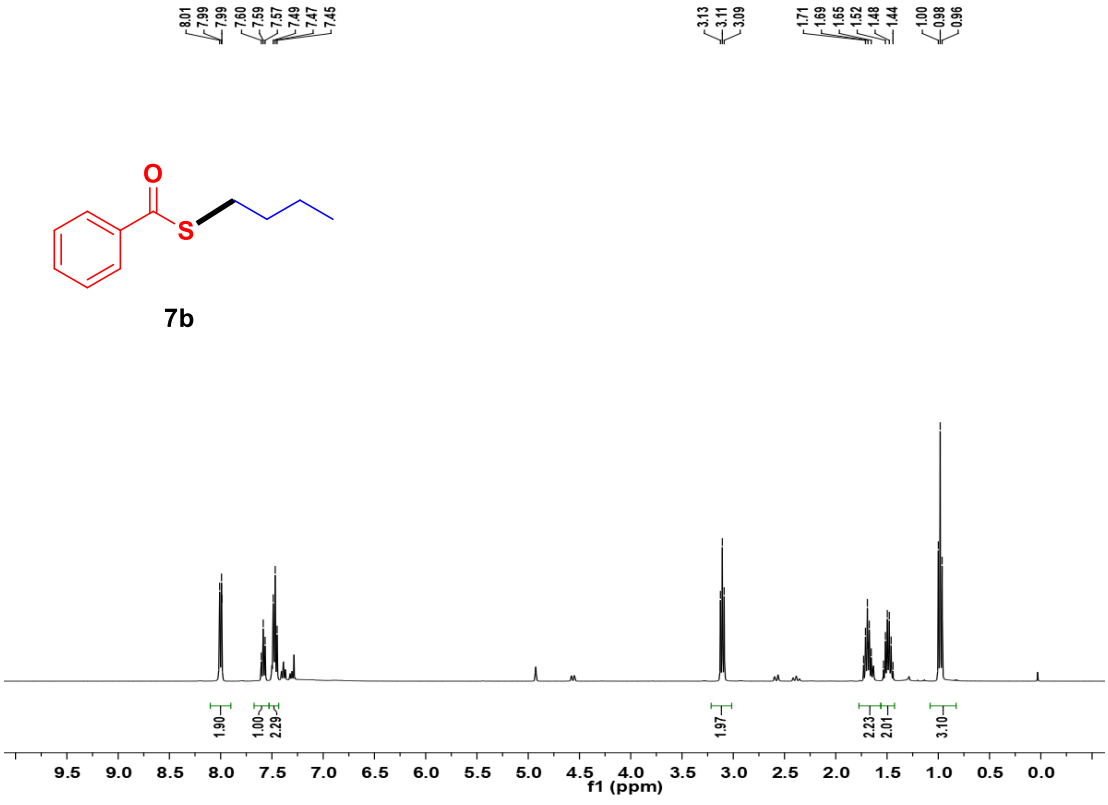
^{1}H NMR (400 MHz, $CDCl_3$) of 6f



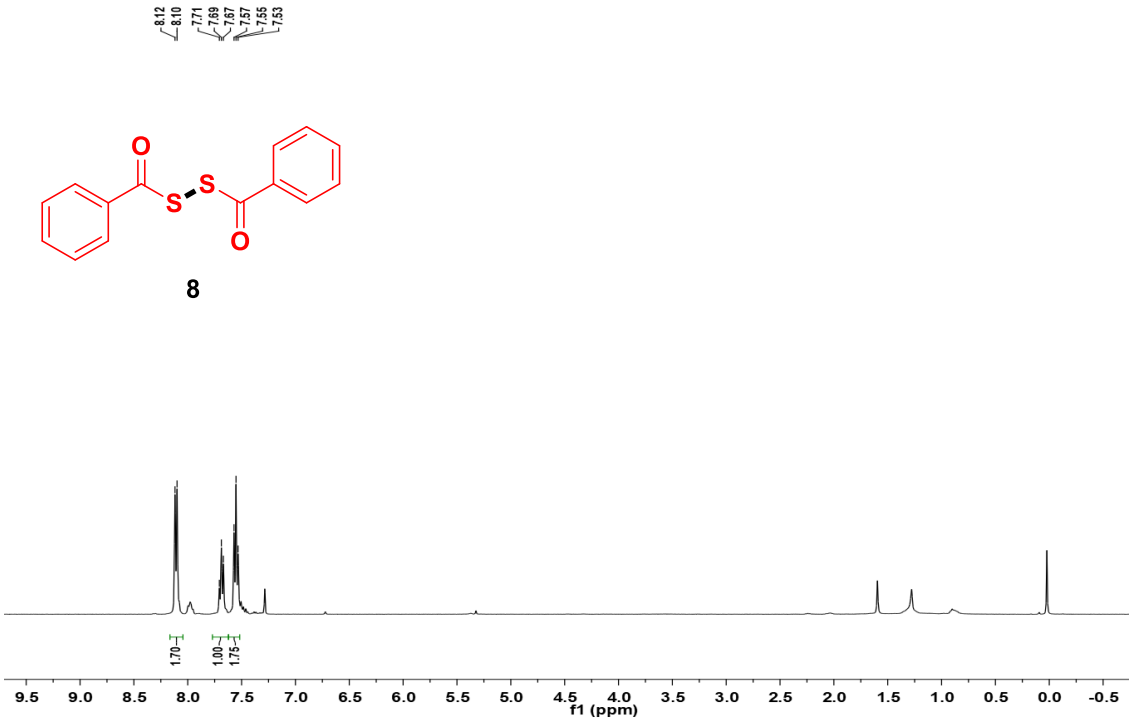
^{1}H NMR (400 MHz, $CDCl_3$) of 7a



^{1}H NMR (400 MHz, $CDCl_3$) of 7b



^{1}H NMR (400 MHz, $CDCl_3$) of 8



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