Supporting Information

Brønsted Acid-Catalyzed Synthesis of Sulfinamidines and Sulfinimidate Esters through Electrophilic Fluorination and Substitution

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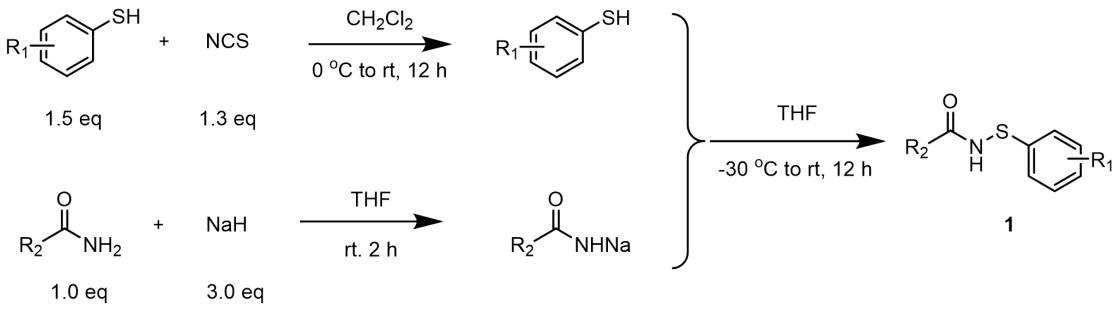
A. General information

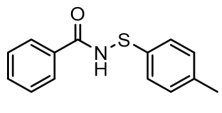
Reagents and solvents were purchased from commercial suppliers and used as received unless noted. All products were purified by flash chromatography on silica gel.Analytical thin-layer chromatography was performed with 0.25 mm coated commercial silica gel plates (TLC Silica Gel 60 F_{254}); Visualization of the developed chromatogram was performed by fluorescence. Flash chromatography was performed with silica gel (300-400 mesh). The chemical yields referred are isolated products.Proton nuclear magnetic resonance (^{1}H NMR) data were acquiredat on Bruker Ascend 400 (400 MHz) spectrometer. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; dd, doublet of doublets; dt, triplet of doublets; td, doublet of triplets; q, quartet; m, multiplet; Coupling constants J are quoted in Hz. Chemical shifts are reported in delta (δ) units. ^{1}H NMR spectra were calibrated using residual undeuterated solvent as an internal reference ($CDCl_3$: 7.26 ppm; DMSO-d6: 2.50 ppm). Carbon nuclear magnetic resonance (^{13}C NMR) data were acquired at 100 MHz on Bruker Ascend 400 spectrometer; Chemical shifts are reported in ppm relative to the center line of a triplet at 77.16 ppm for chloroform-d. Infrared (IR) data were recorded as films on potassium bromide plates on a Bruker Tensor 27 FT-IR spectrometer. Absorbance frequencies are reported in reciprocal cetimeters (cm^{-1}). HRMS (ESI) determinations were performed on a Bruker micrOTOF II spectrometer (TOF analyzer).

B. Substrates preparation and characterization

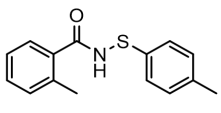
N-acylsulfenamides were synthesized according to a reported literature[1].

In an argon atmosphere, N-chlorosuccinimide (6.5 mmol, 1.3 eq.) was weighed into a 100 ml round-bottom flask filled with a stir bar and dissolved in CH_2Cl_2 (50 ml). Benzenethiol (7.5 mmol, 1.5 eq.) was added slowly at 0° C and the reaction mixture was stirred at room temperature for 12 h. The reaction solution was concentrated in a rotary evaporator. The concentrated mixture was washed with n-hexane, filtered and concentrated to afford the crude phenyl hypochlorothioite as an orange liquid, which was used directly in the next step. The benzamide (5 mmol, 1.0 eq.), NaH (15 mmol, 3.0 eq.) and dry THF (80 mL) were added to a 250 mL reaction flask in turn and stirred at room temperature for 2 h to afford the corresponding sodium salt. Then at -30 °C, crude phenyl hypochlorothione was slowly added dropwise to the sodium salt mixture. After the addition, the reaction flask was stirred at room temperature for 12 h. Ultimately, the reaction was quenched by adding 200 mL of water. The reaction mixture was extracted with ethyl acetate (2 X 100 mL), and the organic phase was washed successively with water, brine, dried over anhydrous magnesium sulfat, and concentrated in vacuo. The residue was subjected to flash column chromatography on silica gel, yielding the desired substrates.

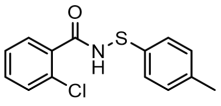




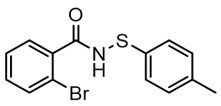
1a
70% yield



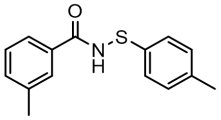
1b
66% yield



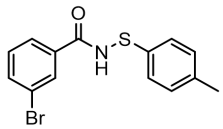
1c
69% yield



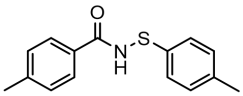
1d
65% yield



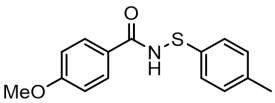
1e
69% yield



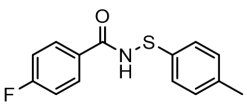
1f
68% yield



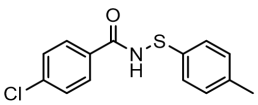
1g
74% yield



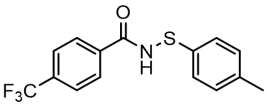
1h
72% yield



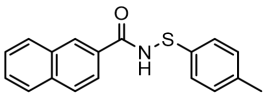
1i
73% yield



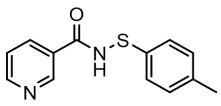
1j
70% yield



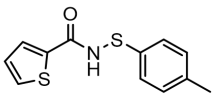
1k
55% yield



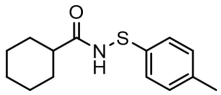
1l
70% yield



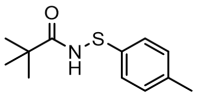
1m
45% yield



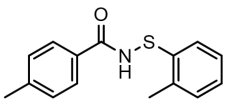
1n
68% yield



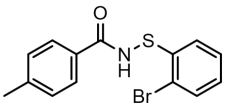
1o
72% yield



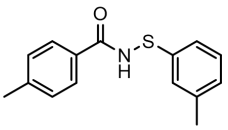
1p
76% yield



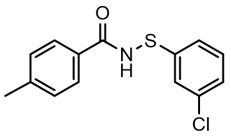
1q
73% yield



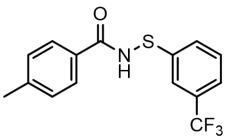
1r
70% yield



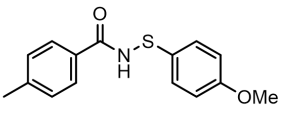
1s
71% yield



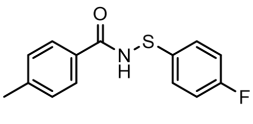
1t
67% yield



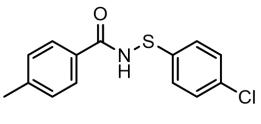
1u
65% yield



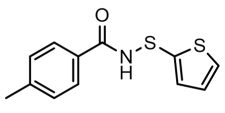
1v
75% yield



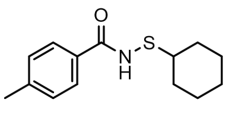
1w
66% yield



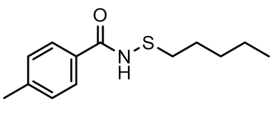
1x
68% yield



1y
36% yield

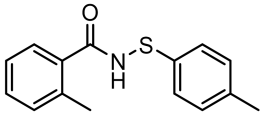


1z
52% yield



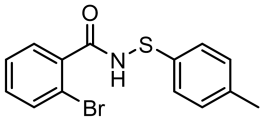
1aa
31% yield

Analytical data for reported substrates are in accordance with the literature values[1-2], and analytical data for unreported substrates are as follows:



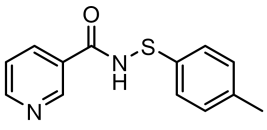
2-methyl-N-(p-tolylthio)benzamide (1b)

Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10:1 to 6:1) to afford a white solid (0.85 g 66%, m. p. 102.3-102.6 °C); **^{1}H NMR** (400 MHz, CDCl3) δ 7.39 (s, 1H), 7.29 (t, *J* = 7.4 Hz, 4H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 2.35 (s, 3H), 2.31 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.49, 137.54, 136.75, 135.07, 134.88, 131.16, 130.57, 129.79, 127.41, 126.96, 125.74, 21.13, 19.85; **IR** (KBr): 3277, 3225, 2835, 1670, 1495, 1290, 1150, 868, 755, 691cm^{-1}; **HRMS** (ESI) calcd for $C_{15}H_{15}NOS$ $[M+Na]^+$:280.0767; found:280.0766.



2-bromo-N-(p-tolylthio)benzamide (1d)

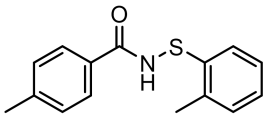
Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10:1 to 4:1) to afford a white solid (1.04 g 65%, m. p. 114.8-115.1 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.51 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.39 (dd, *J* = 7.4, 2.0 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.25 – 7.19 (m, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 2.30 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.53, 137.72, 136.73, 134.36, 133.42, 131.75, 129.73, 129.55, 127.92, 127.51, 119.35, 21.14; **IR** (KBr): 3235, 2340, 1660, 1589, 1435, 1290, 1120, 745cm^{-1}; **HRMS** (ESI) calcd for $C_{14}H_{12}BrNOS$ $[M+Na]^+$:343.9715; found: 343.9716.



N-(p-tolylthio)nicotinamide (1m)

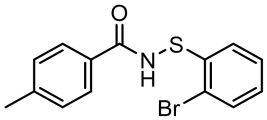
Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (1:1) to afford a white solid (0.55 g 45%, m. p. 145.2-145.5 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 8.66 (dd, *J* = 4.8, 1.7 Hz, 1H), 8.58 (s, 1H), 8.17 (d, *J* = 7.2 Hz, 1H), 7.32 (dd, *J* = 8.0, 4.8 Hz, 1H), 7.24 (d, *J* = 1.9 Hz, 2H), 7.06 (d, *J* = 8.0

Hz, 2H), 2.27 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.74, 152.72, 148.47, 137.99, 136.18, 134.57, 129.98, 129.57, 127.70, 123.79, 21.20; **IR** (KBr): 3210, 3090, 1655, 1530, 1435, 1269, 1095, 745, 697cm^{-1}; **HRMS** (ESI) calcd for $C_{13}H_{12}N_2OS$ $[M+H]^+$:245.0743; found: 245.0740.



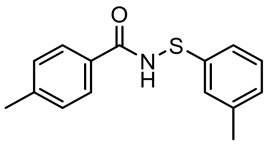
4-methyl-N-(o-tolylthio)benzamide (1q)

Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10:1 to 6:1) to afford a white solid (0.94 g 73%, m. p. 119.9-120.2 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.41 (s, 1H), 7.21 (d, *J* = 7.9 Hz, 2H), 7.19 – 7.15 (m, 1H), 7.14 – 7.11 (m, 1H), 7.11 – 7.05 (m, 2H), 2.40 (s, 3H), 2.33 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.27, 143.11, 137.40, 133.55, 130.34, 130.31, 129.44, 127.82, 126.66, 126.15, 123.87, 21.61, 19.04; **IR** (KBr): 3280, 1661, 1601, 1445, 1260, 1102, 933, 875, 745, 688cm^{-1}; **HRMS** (ESI) calcd for $C_{15}H_{15}NOS$ $[M+Na]^+$:280.0767; found: 280.0774.



N-((2-bromophenyl)thio)-4-methylbenzamide (1r)

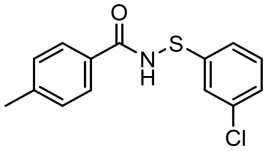
Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10:1 to 4:1) to afford a white solid (1.12 g 70%, m. p. 134.0-134.3 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.8 Hz, 2H), 7.56 (s, 1H), 7.44 (d, *J* = 7.9 Hz, 1H), 7.23 (t, *J* = 8.4 Hz, 3H), 7.08 (d, *J* = 9.5 Hz, 1H), 7.01 (t, *J* = 7.7 Hz, 1H), 2.41 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.93, 143.52, 139.25, 132.78, 130.04, 129.62, 127.99, 127.88, 127.17, 124.45, 117.64, 21.70; **IR** (KBr): 3205, 2970, 2331, 1660, 1570, 1412, 1269, 1056, 769, 675cm^{-1}; **HRMS** (ESI) calcd for $C_{14}H_{12}BrNOS$ $[M+H]^+$:321.9896; found: 321.9889.



4-methyl-N-(m-tolylthio)benzamide (1s)

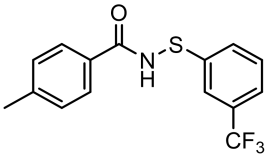
Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10:1 to 5:1) to afford a white solid (0.91 g 71%, m. p. 136.8-137.1°C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.78 (d, *J* = 7.8 Hz, 2H), 7.15 (d, *J* = 1.8 Hz,

1H), 7.14 – 7.11 (m, 2H), 7.07 (d, *J* = 7.1 Hz, 2H), 6.96 (d, *J* = 7.3 Hz, 1H), 2.36 (s, 3H), 2.25 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.39, 142.93, 138.79, 138.69, 130.30, 129.32, 128.83, 127.88, 127.55, 125.70, 122.33, 21.54, 21.41; **IR** (KBr): 3310, 3011, 1660, 1435, 1253, 1070, 823, 715, 697cm^{-1}; **HRMS** (ESI) calcd for $C_{15}H_{15}NOS$ $[M+H]^+$:258.0947; found: 258.0951.



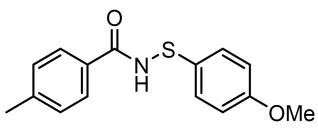
N-((3-chlorophenyl)thio)-4-methylbenzamide (1t)

Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10:1 to 6:1) to afford a white solid (0.93 g 67%, m. p. 128.2-128.5 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.18 – 7.14 (m, 3H), 7.13 (d, *J* = 7.8 Hz, 1H), 7.07 (ddt, *J* = 9.3, 7.7, 1.6 Hz, 2H), 2.38 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.38, 143.41, 141.16, 134.98, 130.06, 129.89, 129.48, 127.94, 126.55, 124.13, 122.46, 21.64; **IR** (KBr): 3315, 1663, 1598, 1465, 1261, 1095, 885, 781, 690cm^{-1}; **HRMS** (ESI) calcd for $C_{14}H_{12}ClNOS$ $[M+H]^+$:278.0401; found: 278.0408.



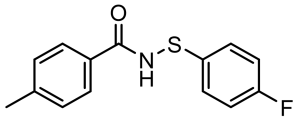
4-methyl-N-((3-(trifluoromethyl)phenyl)thio)benzamide (1u)

Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (15:1 to 10:1) to afford a white solid (1.01 g 65%, m. p. 158.4-158.7 °C); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.1 Hz, 2H), 7.71 (s, 1H), 7.47 (s, 1H), 7.45 – 7.35 (m, 3H), 7.24 (t, *J* = 9.7 Hz, 2H), 2.40 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 169.15, 143.63, 140.55, 131.52 (C-F, $^2J_{C\text{-}F}$ = 32.6 Hz), 129.94, 129.63, 129.57, 127.86, 127.80, 123.81 (C-F, $^1J_{C\text{-}F}$ = 272.7 Hz), 123.38 (C-F, $^3J_{C\text{-}F}$ = 3.7 Hz), 121.21 (C-F, $^3J_{C\text{-}F}$ = 3.8 Hz), 21.66; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.75; **IR** (KBr): 3231, 1655, 1599, 1465, 1331, 1269,1180, 1075, 697cm^{-1}; **HRMS** (ESI) calcd for $C_{15}H_{12}F_3NOS$ $[M+H]^+$:312.0664; found: 312.0669.



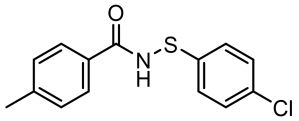
N-((4-methoxyphenyl)thio)-4-methylbenzamide (1v)

Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (5:1 to 2:1) to afford a brown solid (1.02 g 75%, m. p. 106.7-107.0 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.8 Hz, 2H), 7.16 (d, *J* = 7.7 Hz, 2H), 6.79 (d, *J* = 8.9 Hz, 2H), 3.75 (s, 3H), 2.35 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.29, 159.90, 142.80, 131.78, 130.65, 129.31, 129.26, 127.74, 114.59, 55.39, 21.53; **IR** (KBr): 3490, 3293, 3065, 1671, 1598, 1435, 1269, 1095, 808, 697, 635cm^{-1}; **HRMS** (ESI) calcd for $C_{15}H_{15}NO_2S$ $[M+H]^+$:274.0896; found: 274.0895.



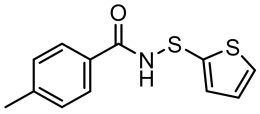
N-((4-fluorophenyl)thio)-4-methylbenzamide (1w)

Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10:1 to 6:1) to afford a white solid (0.86 g 66%, m. p. 146.3-146.6 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.8 Hz, 2H), 7.70 (s, 1H), 7.38 (dd, *J* = 8.3, 4.8 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 6.97 (t, *J* = 8.5 Hz, 2H), 2.39 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.21, 162.38 (d, $^1J_{C\text{-}F}$ = 247.4 Hz), 143.28, 133.86 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 130.32, 129.60 (d, $^3J_{C\text{-}F}$ = 8.2 Hz), 129.52, 127.80, 116.24 (d, $^2J_{C\text{-}F}$ = 22.2 Hz), 21.63; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.61 (p, J = 6.0 Hz); **IR** (KBr): 3310, 3061, 1655, 1590, 1492, 1269, 1115, 845, 697cm^{-1}; **HRMS** (ESI) calcd for $C_{14}H_{12}FNOS$ $[M+Na]^+$: 284.0516; found: 284.0511.



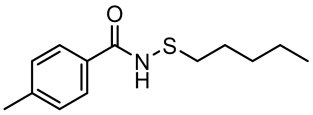
N-((4-chlorophenyl)thio)-4-methylbenzamide (1x)

Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10:1 to 6:1) to afford a white solid (0.94 g 68%, m. p. 169.5-169.8 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.66 (s, 1H), 7.23 (t, *J* = 3.0 Hz, 6H), 2.40 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.13, 143.45, 137.40, 132.89, 130.13, 129.57, 129.24, 127.83, 127.01, 21.67; **IR** (KBr): 3461, 3290, 1660, 1598, 1453,1303, 1266, 1095, 815, 685cm^{-1}; **HRMS** (ESI) calcd for $C_{14}H_{12}ClNOS$ $[M+Na]^+$:300.0220; found: 300.0221.



4-methyl-N-(thiophen-2-ylthio)benzamide (1y)

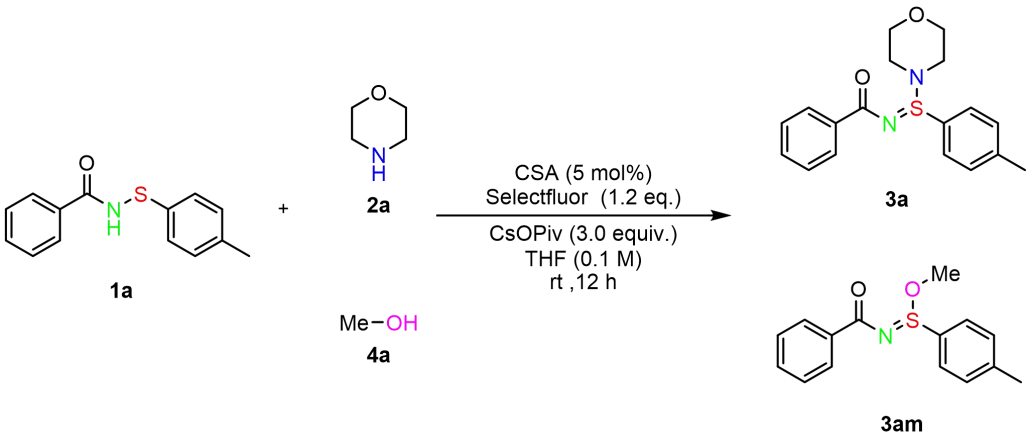
Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10:1 to 5:1) to afford a brown solid (0.45 g 36%, m. p. 135.4-135.7 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.9 Hz, 2H), 7.47 (s, 1H), 7.45 (s, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.00 – 6.97 (m, 1H), 2.37 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.61, 143.04, 136.32, 136.20, 132.56, 130.56, 129.44, 127.71, 127.53, 21.62; **IR** (KBr): 3219, 3097, 1655, 1531, 1435, 1369, 1267, 1095, 874, 725, 697cm^{-1}; HRMS (ESI) calcd for $C_{12}H_{11}NOS_2$ $[M+H]^+$:250.0355; found: 250.0358.



4-methyl-N-(pentylthio)benzamide (1aa)

Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (8:1 to 5:1) to afford a yellow solid (0.37 g 31%, m. p. 58.1-58.4 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.75 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 2.72 (t, *J* = 7.5 Hz, 2H), 2.29 (s, 3H), 1.58 – 1.44 (m, 2H), 1.33 – 1.11 (m, 4H), 0.78 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.93, 142.26, 130.76, 128.98, 127.63, 38.52, 30.69, 27.31, 22.10, 21.29, 13.79; **IR** (KBr): 3225, 3090, 1685, 1550, 1467, 1219, 1085, 899, 745, 733cm^{-1}; **HRMS** (ESI) calcd for $C_{13}H_{19}NOS$ $[M+Na]^+$:260.1080; found: 260.1075.

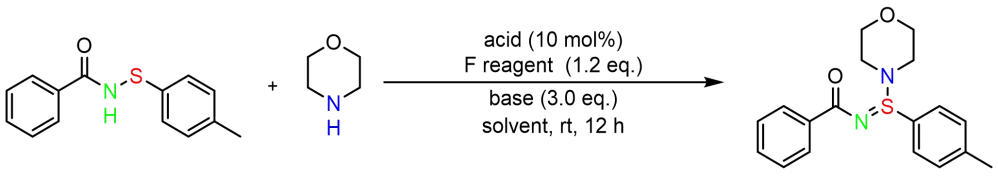
C. General procedures of Sulfilimines and Sulfinimidate Ester



General procedure for 3a. In a glovebox, a 5 mL vial equipped with a stirring bar was charged with N-(p-tolylthio)benzamide (**1a**) (0.20 mmol, 1.0 eq., 48.6 mg), Selectfluor (0.24 mmol, 1.2 eq., 85.02 mg), CSA (0.01 mmol, 5 mol%, 2.3 mg), CsOPiv (0.6 mmol, 3.0 eq., 140.42 mg), morpholine (0.30 mmol, 1.5 eq., 26.2 μL) and THF (2 mL) was then added. The reaction mixture was stirred at roon temperature for 12 h. Then the crude reaction mixture was filtered with celite and washed with ethyl acetate. The solvent was removed under reduced pressure. Finally the residue was chromatographed on silica gel to afford the desired product **3a**.

General procedure for 3am. In a glovebox, a 5 mL vial equipped with a stirring bar was charged with N-(p-tolylthio)benzamide (**1a**) (0.20 mmol, 1.0 eq. 48.6 mg), Selectfluor (0.24 mmol, 1.2 eq., 85.02 mg), CSA (0.01 mmol, 5 mol%, 2.3 mg), CsOPiv (0.6 mmol, 3.0 eq., 140.42 mg), MeOH (0.30 mmol, 1.5 eq., 12.2 μL) and THF (2 mL) was then added. The reaction mixture was stirred at roon temperature for 12 h. Then the crude reaction mixture was filtered with celite and washed with ethyl acetate. The solvent was removed under reduced pressure. Finally the residue was chromatographed on silica gel to afford the desired product **3am**.

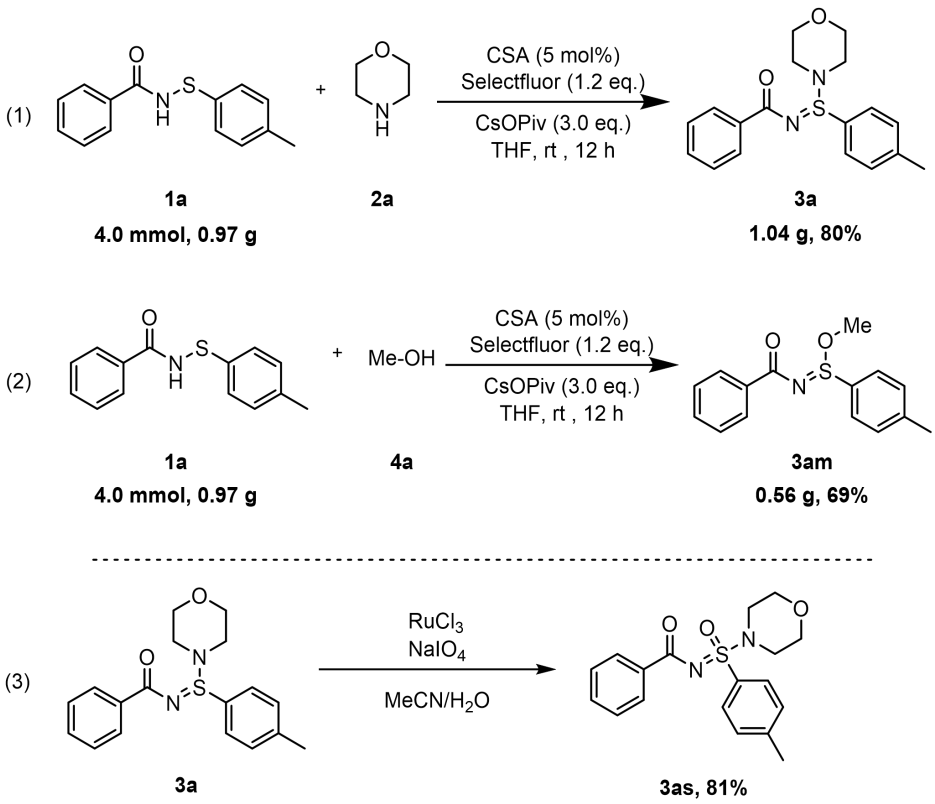
D. Reaction optimization



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

Entry	Solvent	Base	F reagents	Acid	Yield(%)[b]
1	PhMe	Cs_2CO_3	Selectfluor	CSA	trace
2	MeCN	Cs_2CO_3	Selectfluor	CSA	11
3	DCM	Cs_2CO_3	Selectfluor	CSA	30
4	THF	Cs_2CO_3	Selectfluor	CSA	44
5	1,4-dioxane	Cs_2CO_3	Selectfluor	CSA	39
6	EA	Cs_2CO_3	Selectfluor	CSA	22
7	$CHCl_3$	Cs_2CO_3	Selectfluor	CSA	26
8	THF	Na_2CO_3	Selectfluor	CSA	7
9	THF	K_2CO_3	Selectfluor	CSA	12
10	THF	NaOH	Selectfluor	CSA	16
11	THF	KOH	Selectfluor	CSA	50
12	THF	K_3PO_4	Selectfluor	CSA	57
13	THF	t-BuOK	Selectfluor	CSA	23
14	THF	CsOPiv	Selectfluor	CSA	89
15	THF	DMAP	Selectfluor	CSA	<5
16	THF	CsOPiv	Selectfluor II	CSA	61
17	THF	CsOPiv	NFSI	CSA	37
18	THF	CsOPiv	Selectfluor	TsOH	74
19	THF	CsOPiv	Selectfluor	CH_3SO_3H	70
20	THF	CsOPiv	Selectfluor	CF_3CO_2H	46
21	THF	CsOPiv	Selectfluor	H_2SO_4	38
22	THF	CsOPiv	Selectfluor	CH_3CO_2H	62
23	THF	CsOPiv	Selectfluor	/	43
24	THF	CsOPiv	Selectfluor	CSA (5 mol%)	86

E. Gram-scale synthesis and product derivatization



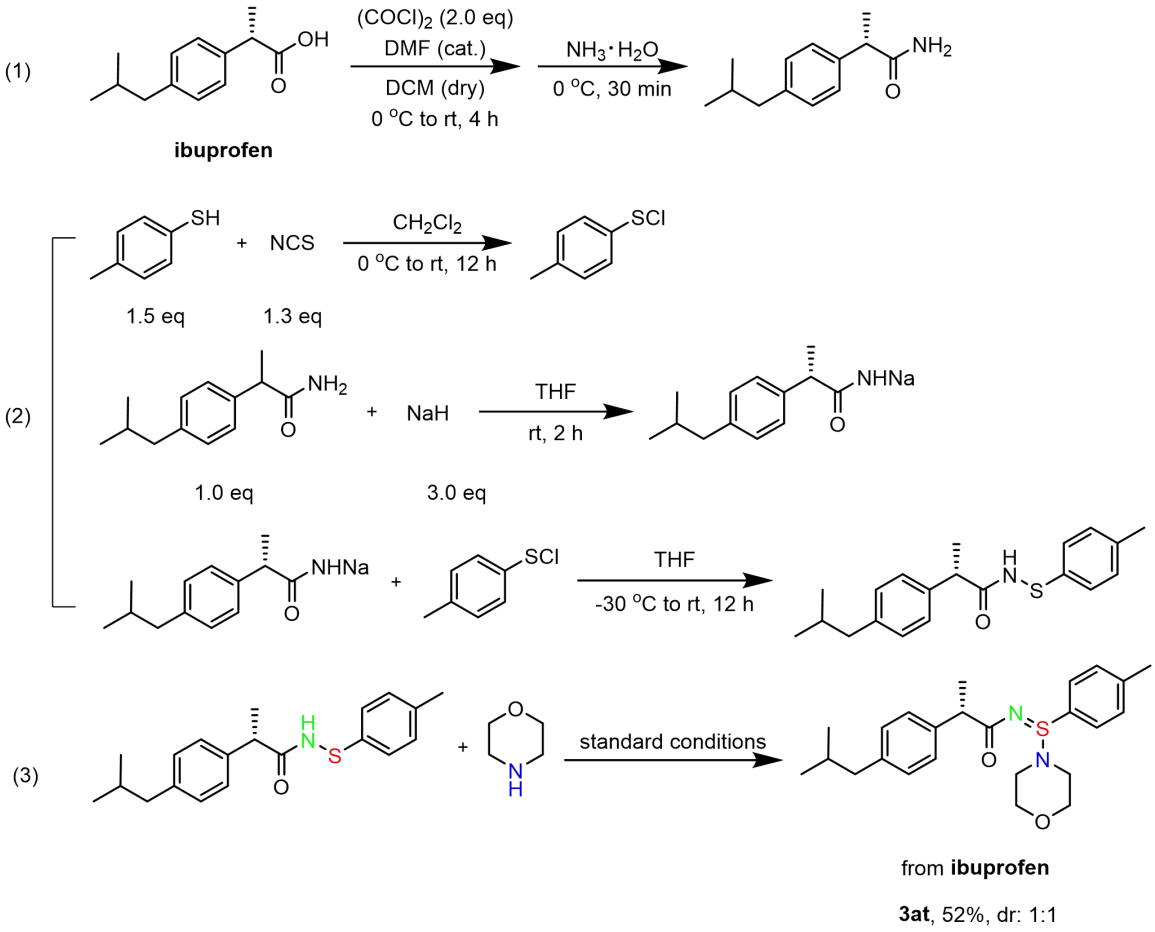
(1) In an argon atmosphere, a 150 mL round bottom flask equipped with with a stirring bar was charged with Sulfenamide **1a** (4 mmol, 1.0 eq., 0.97 g), Selectfluor (4.8 mmol, 1.2 eq., 1.7 g), CSA (0.2 mmol, 5 mol%, 46.44 mg), CsOPiv (12 mmol, 3.0 eq., 2.81 g), morpholine **2a** (6 mmol, 1.5 eq., 0.52 ml) and THF (40 ml) was added. After addition the reaction flask was stirred at room temperature for 12 h. Then the mixture was quenched with H_2O and extracted with ethylacetate (EtOAc). The combined organic layers were washed with brine, dried over Na_2SO_4 and then concentrated. The crude mixture was purified by silica gel column chromatography to afford the desired product **3a** (PE:EA = 2:1, 1.05g, 80% yield).

(2) In an argon atmosphere, a 150 mL round bottom flask equipped with with a stirring bar was charged with Sulfenamide **1a** (4 mmol, 1.0 eq., 0.97 g), Selectfluor (4.8 mmol, 1.2 eq., 1.7 g), CSA (0.2 mmol, 5 mol%, 46.44 mg), CsOPiv (12 mmol, 3.0 eq., 2.81 g), methanol **4a** (6 mmol, 1.5 eq., 0.24 ml) and THF (40 ml) was added. After addition the reaction flask was stirred at room temperature for 12 h. Then the mixture was quenched with H_2O and extracted with ethylacetate (EtOAc). The combined organic layers were washed with brine, dried over Na_2SO_4 and then concentrated. The crude mixture

was purified by silica gel column chromatography to afford the desired product **3am** (PE:EA = 5:1, 0.69g, 69% yield).

(3) To a solution of N-(morpholino(p-tolyl)-l4-sulfanylidene)benzamide (0.2 mmol, 1.0 eq., 65.65 mg) in MeCN (2 mL) was added a predissolved solution of $NaIO_4$ (1.0 mmol, 5.0 eq., 213.5 mg) in H_2O (4 mL), followed by $RuCl_3$ hydrate (0.01 mmol, 0.05 eq., 4.95 mg). After stirring at room temperature for 4 h, the reaction mixture was extracted 3x with CH_2Cl_2. The combined organic layers were dried over sodium sulfate and concentrated. Purification by silica gel chromatography (PE:EA=3:1) afforded the product **3as** (55.75 mg, 81% yield) as a yellow viscous solid. The synthesis steps were referenced in the literature[3]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 (d, J = 7.0 Hz, 2H), 7.81 (d, J = 8.3 Hz, 2H), 7.51 (t, J = 7.5 Hz, 1H), 7.45 – 7.33 (m, 4H), 3.77 (t, J = 4.7 Hz, 4H), 3.19 (t, J = 4.8 Hz, 4H), 2.44 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.75, 144.62, 135.87, 132.28, 132.21, 130.15, 129.55, 128.11 (d, J = 322.6 Hz), 128.09 (d, J = 10.0 Hz), 66.26, 45.73, 21.68; **IR** (KBr): 3040, 1677, 1495, 1396, 1168, 871, 824, 761, 698cm^{-1}; **HRMS** (ESI) calcd for $C_{18}H_{20}N_2O_3S$ $[M+H]^+$: 345.1267; found: 345.1271.

F. Late-stage functionalization of drug molecule

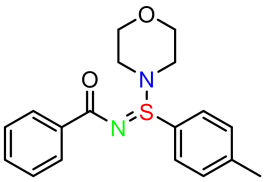


(1) A 100 mL round-bottom flask was charged with 2-(4-isobutylphenyl) propanoic acid (**ibuprofen**, 10 mmol, 1.0 eq., 2.06 g), dry CH_2Cl_2 (20 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 min. Then $(COCl)_2$ (20 mmol, 2.0 eq., 1.7 mL) was added dropwise to the reaction mixture and stirred at room temperature for 4 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step. Then the acid chloride prepared above was added dropwise to an excess of 25%-28% (v/v) ammonium hydroxide (40.0 eq.) in an ice bath. After stirring for 30 min, the precipitated product was dissolved in CH_2Cl_2, washed with water and brine, dried over Na_2SO_4, filtered, and the solvent removed. The crude product was purified by column chromatography on silica gel to afford the desired 2-(4-isobutylphenyl)propanamide. (PE:EA=1:1, 1.21g, 59%). The synthesis steps were referenced in the literature[4].

(2) In an argon atmosphere, NCS (6.5 mmol, 1.3 eq., 0.87 g) was weighed into a 100 ml round-bottom flask filled with a stir bar and dissolved in CH_2Cl_2 (50 ml). 4-methylbenzenethiol (7.5mmol, 1.5 eq., 0.93 g) was added slowly at 0^o C and the reaction mixture was stirred at room temperature for 12 h. The reaction solution was concentrated in a rotary evaporator. The concentrated mixture was washed with n-hexane, filtered and concentrated to afford the crude phenyl hypochlorothioite as an orange liquid, which was used directly in the next step.The 2-(4-isobutylphenyl)propanamide (5 mmol, 1.0 eq., 1.03 g), NaH (15 mmol, 3.0 eq.) and dry THF (80 mL) were added to a 250 mL reaction flask in turn and stirred at room temperature for 2 h to afford the corresponding sodium salt. Then at -30 °C, crude phenyl hypochlorothione was slowly added dropwise to the sodium salt mixture. After addition the reaction flask was stirred at room temperature for 12 h. Ultimately, the reaction was quenched by adding 200 mL of water. The reaction mixture was extracted with ethyl acetate (2 X 100 mL), and the organic phase was washed successively with water, brine, dried over anhydrous magnesium sulfat, and concentrated in vacuo. The residue was subjected to flash column chromatography on silica gel, yielding the desired substrate.

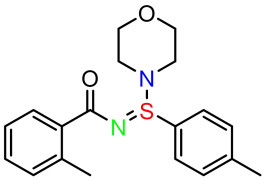
(3) In a glovebox, a 5 mL vial equipped with a stirring bar was charged with 2-(4-isobutylphenyl)-N-(p-tolylthio)propanamide (0.20 mmol, 1.0 eq., 48.6 mg), Selectfluor (0.24 mmol, 1.2 eq., 85.02 mg), CSA (0.01 mmol, 5 mol%, 2.3 mg), CsOPiv (0.6 mmol, 3.0 eq., 140.42 mg), morpholine (0.30 mmol, 1.5 eq., 26.2 μL) and THF (2 mL) was then added. The reaction mixture was stirred at roon temperature for 12 h. Then the crude reaction mixture was filtered with celite and washed with ethyl acetate. The solvent was removed under reduced pressure. Finally the residue was chromatographed on silica gel to afford the desired product **3at** (42.87 mg, 52%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.1 Hz, 1H), 7.63 (d, J = 8.1 Hz, 1H), 7.34 (dd, J = 8.0, 2.4 Hz, 2H), 7.29 (d, J = 8.2 Hz, 1H), 7.25 (s, 1H), 7.06 (dd, J = 8.0, 2.6 Hz, 2H), 3.96 – 3.85 (m, 1H), 3.65 (t, J = 4.8 Hz, 2H), 3.59 – 3.52 (m, 2H), 3.19 – 3.09 (m, 1H), 3.08 – 2.94 (m, 2H), 2.95 – 2.85 (m, 1H), 2.43 (d, J = 7.2 Hz, 2H), 2.39 (d, J = 5.9 Hz, 3H), 1.83 (dt, J = 13.5, 6.8 Hz, 1H), 1.55 (dd, J = 7.1, 4.1 Hz, 3H), 0.88 (d, J = 6.6 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 187.65 (d, J = 5.8 Hz), 142.33 (d, J = 12.2 Hz), 140.91 (d, J = 18.8 Hz), 139.57 (d, J = 1.7 Hz), 130.46, 130.04, 128.98, 128.21 (d, J = 12.1 Hz), 127.40, 66.88 (d, J = 6.6 Hz), 48.48 (d, J = 1.8 Hz), 47.35 (d, J = 15.4 Hz), 45.13, 30.28, 22.45 (d, J = 1.7 Hz), 21.40 (d, J = 3.2 Hz), 19.32 (d, J = 29.1 Hz); **IR** (KBr): 3078, 2910, 1687, 1465, 1376, 875, 821, 751, 699cm^{-1}; **HRMS** (ESI) calcd for $C_{24}H_{32}N_2O_2S$ $[M+H]^+$: 413.2257; found: 413.2260.

G. Analytical data of products



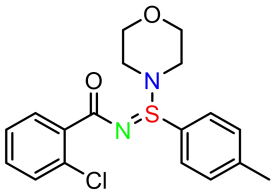
N-(morpholino(p-tolyl)-l4-sulfanylidene)benzamide (3a)

Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2:1 to 1:1) to afford a pale yellow viscous solid (57.7 mg 88%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.3 Hz, 2H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 7.1 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 3.68 (t, *J* = 4.9 Hz, 4H), 3.29 – 3.20 (m, 2H), 3.13 – 3.04 (m, 2H), 2.41 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.90, 142.54, 136.66, 131.14, 130.60, 130.10, 129.12, 128.33, 127.90, 66.92, 47.48, 21.43; **IR** (KBr): 3010, 1671, 1495, 1396, 1150, 868, 813, 760, 695cm^{-1}; **HRMS** (ESI) calcd for $C_{18}H_{20}N_2O_2S$ $[M+H]^+$: 329.1319; found: 329.1320.



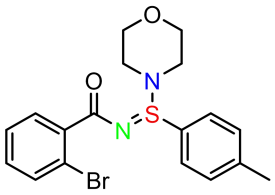
2-methyl-N-(morpholino(p-tolyl)-l4-sulfanylidene)benzamide (3b)

Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2:1 to 1:1) to afford a yellow viscous solid (56.1mg 82%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.7 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 1H), 7.19 (t, *J* = 7.0 Hz, 2H), 3.72 – 3.67 (t, 4H), 3.28 – 3.23 (m, 2H), 3.16 – 3.04 (m, 2H), 2.62 (s, 3H), 2.39 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 181.17, 142.55, 137.52, 137.48, 131.08, 130.36, 130.11, 129.72, 129.69, 128.35, 125.37, 66.96, 47.64, 21.62, 21.43; **IR** (KBr): 2998, 1670, 1418, 1390, 1105, 868, 805, 755, 691cm^{-1} ; **HRMS** (ESI) calcd for $C_{19}H_{22}N_2O_2S$ $[M+H]^+$:343.1475; found: 343.1479.



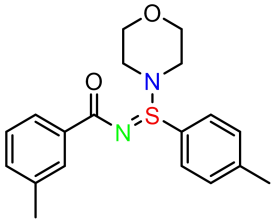
2-chloro-N-(morpholino(p-tolyl)-l4-sulfanylidene)benzamide (3c)

Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2:1 to 1:1) to afford a yellow viscous solid (68.1mg 94%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.8 Hz, 2H), 7.76 – 7.69 (m, 1H), 7.39 – 7.34 (m, 1H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.25 – 7.24 (m, 1H), 7.23 (s, 1H), 3.70 – 3.67 (t, 4H), 3.31 – 3.21 (m, 2H), 3.14 – 3.04 (m, 2H), 2.37 (s, 3H). Analytical data are in accordance with the literature values[5].



2-bromo-N-(morpholino(p-tolyl)-l4-sulfanylidene)benzamide (3d)

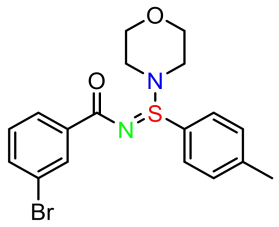
Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2:1 to 1:1) to afford a yellow viscous solid (78.8mg 97%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 0H), 7.56 (d, *J* = 8.0 Hz, 0H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 6.6 Hz, 0H), 7.17 (t, *J* = 7.7 Hz, 0H), 3.70 (t, *J* = 5.5 Hz, 1H), 3.34 – 3.25 (m, 1H), 3.14 – 3.09 (m, 1H), 2.38 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.33, 142.67, 140.21, 133.31, 130.16, 130.13, 129.93, 129.63, 128.30, 126.97, 66.85, 47.70, 21.37; **IR** (KBr): 3106, 2350, 1667, 1435, 1390, 1091, 815, 735cm^{-1}; **HRMS** (ESI) calcd for $C_{18}H_{19}BrN_2O_2S$ $[M+Na]^+$:429.0243; found:429.0226.



3-methyl-N-(morpholino(p-tolyl)-l4-sulfanylidene)benzamide (3e)

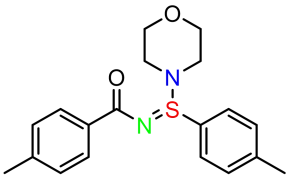
Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2:1 to 1:1) to afford a pale pink viscous solid (54.1mg 79%); **^{1}H NMR**

(400 MHz, $CDCl_3$) δ 8.06 (s, 2H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 3.70 (t, *J* = 4.8 Hz, 4H), 3.30 – 3.21 (m, 2H), 3.15 – 3.05 (m, 2H), 2.43 (s, 3H), 2.41 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.21, 142.53, 137.52, 136.55, 131.94, 130.65, 130.13, 129.68, 128.36, 127.85, 126.33, 66.96, 47.52, 21.50, 21.46; **IR** (KBr): 3125, 2910, 1657, 1435, 1390, 1095, 815, 735cm^{-1}; **HRMS** (ESI) calcd for $C_{19}H_{22}N_2O_2S$ $[M+Na]^+$: 365.1295; found:365.1288.



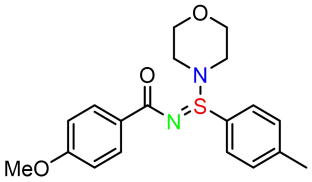
3-bromo-N-(morpholino(p-tolyl)-l4-sulfanylidene)benzamide (3f)

Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2:1) to afford a yellow viscous solid (73.9mg 91%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 8.17 (d, *J* = 7.8 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 8.1 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.28 (s, 1H), 3.69 (t, *J* = 4.0 Hz, 4H), 3.26 – 3.22 (m, 2H), 3.10 – 3.06 (m, 2H), 2.42 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.19, 142.71, 138.68, 133.89, 132.11, 130.14, 130.02, 129.48, 128.19, 127.61, 122.02, 66.81, 47.42, 21.41; **IR** (KBr): 3115, 2360, 1671, 1445, 1396, 1098, 815, 731cm^{-1}; **HRMS** (ESI) calcd for $C_{18}H_{19}BrN_2O_2S$ $[M+Na]^+$: 429.0243; found:429.0238.



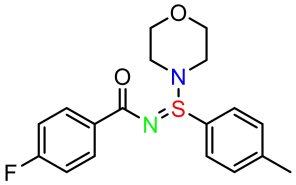
4-methyl-N-(morpholino(p-tolyl)-l4-sulfanylidene)benzamide (3g)

Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2:1 to 1:1) to afford a yellow viscous solid (56.8 mg 83%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.2 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 3.68 (t, *J* = 4.2 Hz, 4H), 3.28 – 3.19 (m, 2H), 3.13 – 3.03 (m, 2H), 2.40 (s, 3H), 2.38 (s, 3H); Analytical data are in accordance with the literature values[5].



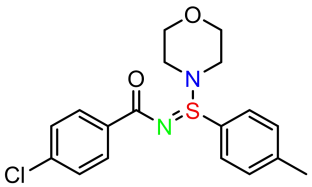
4-methoxy-N-(morpholino(p-tolyl)-l4-sulfanylidene)benzamide (3h)

Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (1:1) to afford a yellow viscous solid (58.7mg 82%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.9 Hz, 2H), 7.87 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H), 3.69 (t, *J* = 4.2 Hz, 4H), 3.29 – 3.19 (m, 2H), 3.13 – 3.03 (m, 2H), 2.42 (s, 3H); Analytical data are in accordance with the literature values[5].



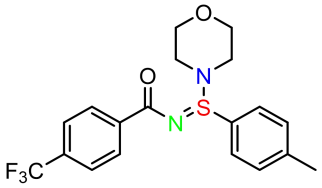
4-fluoro-N-(morpholino(p-tolyl)-l4-sulfanylidene)benzamide (3i)

Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2:1 to 1:1) to afford a yellow viscous solid (63.7 mg 92%); **^{1}H NM**R (400 MHz, $CDCl_3$) δ 8.28 – 8.24 (m, 2H), 7.86 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.07 (t, J = 8.5 Hz, 2H), 3.72 – 3.67 (m, 4H), 3.29 – 3.21 (m, 2H), 3.12 – 3.04 (m, 2H), 2.43 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.91, 164.92 (d, $^{1}J_{C\text{-}F}$ = 250.3 Hz), 142.70, 132.91 (d, $^{4}J_{C\text{-}F}$ = 2.9 Hz), 131.47 (d, $^{3}J_{C\text{-}F}$ = 8.9 Hz), 130.44, 130.19, 128.33, 114.78 (d, $^{2}J_{C\text{-}F}$ = 21.5 Hz), 66.96, 47.50, 21.49; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -109.49 (p, *J* = 7.8 Hz); **IR** (KBr): 3067, 1659, 1495, 1359, 1125, 811, 698cm^{-1}; **HRMS** (ESI) calcd for C18H19FN2O2S $[M+Na]^+$:369.1044; found:369.1043.



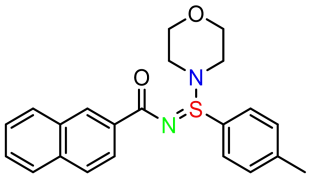
4-chloro-N-(morpholino(p-tolyl)-l4-sulfanylidene)benzamide (3j)

Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2:1 to 1:1) to afford a yellow viscous solid (65.2 mg 90%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.1 Hz, 2H), 7.86 (d, *J* = 7.9 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 4H), 3.70 (t, *J* = 4.9 Hz, 4H), 3.29 – 3.21 (m, 2H), 3.12 – 3.05 (m, 2H), 2.44 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.95, 142.79, 137.36, 135.19, 130.65, 130.39, 130.24, 128.36, 128.18, 66.99, 47.56, 29.82, 21.54. **IR** (KBr): 3289, 1671, 1453, 1313, 1095, 821, 717cm^{-1}; **HRMS** (ESI) calcd for $C_{18}H_{19}ClN_2O_2S$ $[M+Na]^+$:385.0748; found:385.0749.



N-(morpholino(p-tolyl)-l4-sulfanylidene)-4-(trifluoromethyl)benzamide (3k)

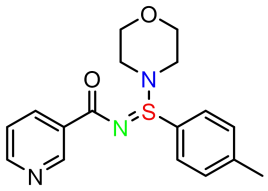
Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2:1) to afford a yellow viscous solid (76.1 mg 96%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.4 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 3.72 (t, *J* = 5.0 Hz, 4H), 3.30 – 3.25 (m, 2H), 3.16 – 3.07 (m, 2H), 2.46 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.31, 142.81, 139.97, 132.47 (C-F, $^2J_{C\text{-}F}$ = 32.2 Hz), 130.16, 130.05, 129.39, 128.20, 124.82 (C-F, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.17 (C-F, $^1J_{C\text{-}F}$ =270.6 Hz), 66.82, 47.48, 21.34; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.55; **IR** (KBr): 3235, 1665, 1465, 1330, 1180, 1075, 824, 697cm^{-1}; **HRMS** (ESI) calcd for $C_{19}H_{19}F_3N_2O_2S$ $[M+Na]^+$: 419.1012; found:419.1002.



N-(morpholino(p-tolyl)-l4-sulfanylidene)-2-naphthamide (3l)

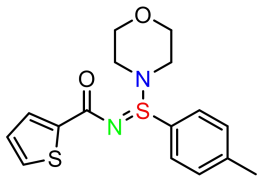
Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2:1) to afford a yellow viscous solid (62.0 mg 82%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.33 (d, *J* = 10.1 Hz, 1H), 7.99 (d, *J* = 9.2 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.87 (d, *J* = 11.7 Hz, 2H), 7.60 – 7.47 (m, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 3.73 (t, *J* = 4.2 Hz, 4H), 3.37 –

3.27 (m, 2H), 3.21 – 3.11 (m, 2H), 2.45 (s, 3H). Analytical data are in accordance with the literature values[5].



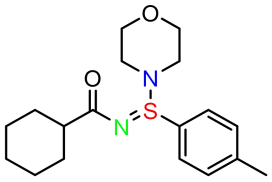
N-(morpholino(p-tolyl)-l4-sulfanylidene)nicotinamide (3m)

Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (1:2 to 1:3) to afford a yellow viscous solid (48.7 mg 74%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.43 (s, 1H), 8.65 (dd, *J* = 4.9, 1.8 Hz, 1H), 8.43 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 4.8 Hz, 1H), 3.67 (t, *J* = 4.0 Hz, 4H), 3.27 – 3.17 (m, 2H), 3.11 – 3.01 (m, 2H), 2.40 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.01, 151.60, 150.83, 142.85, 136.41, 132.08, 130.20, 129.97, 128.26, 122.97, 66.85, 47.46, 21.43; **IR** (KBr): 3096, 1675, 1440, 1369, 1195, 813, 745, 687cm^{-1}; **HRMS** (ESI) calcd for $C_{17}H_{19}N_3O_2S$ $[M+H]^+$:330.1271; found:330.1276.



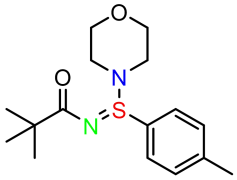
N-(morpholino(p-tolyl)-l4-sulfanylidene)thiophene-2-carboxamide (3n)

Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2:1 to 1:1) to afford a yellow viscous solid (61.5 mg 92%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.1 Hz, 2H), 7.79 (d, *J* = 3.6 Hz, 1H), 7.40 (d, *J* = 4.0 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.05 (t, *J* = 4.6 Hz, 1H), 3.68 (t, *J* = 4.6 Hz, 4H), 3.28 – 3.18 (m, 0H), 3.10 – 3.00 (m, 0H), 2.40 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.03, 142.61, 142.05, 130.44, 130.11, 130.05, 128.29, 127.42, 66.83, 47.33, 21.41; **IR** (KBr): 3106, 1659, 1455, 1369, 1098, 821, 726, 698cm^{-1}; **HRMS** (ESI) calcd for $C_{16}H_{18}N_2O_2S_2$ $[M+H]^+$:335.0883; found:335.0872.



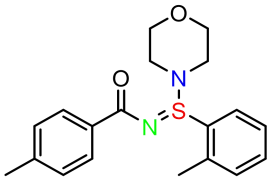
N-(morpholino(p-tolyl)-l4-sulfanylidene)cyclohexanecarboxamide (3o)

Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2:1 to 1:1) to afford a yellow viscous solid (52.1 mg 78%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 3.71 – 3.65 (m, 4H), 3.20 – 3.11 (m, 2H), 3.04 – 2.95 (m, 2H), 2.49 – 2.41 (m, 1H), 2.40 (s, 2H), 2.07 – 1.91 (m, 2H), 1.76 (d, *J* = 12.1 Hz, 2H), 1.64 (d, *J* = 11.0 Hz, 1H), 1.53 (d, *J* = 11.6 Hz, 2H), 1.31 (d, *J* = 9.3 Hz, 2H), 1.21 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.85, 142.32, 130.63, 130.11, 128.26, 66.99, 47.40, 47.22, 30.72 (d, *J* = 22.1 Hz), 26.22, 26.14 (d, *J* = 2.4 Hz), 21.45; **IR** (KBr): 3067, 1645, 1391, 1365, 1267, 1092, 816, 715, 695cm^{-1}; **HRMS** (ESI) calcd for $C_{18}H_{26}N_2O_2S$ $[M+H]^+$: 335.1788; found:335.1783.



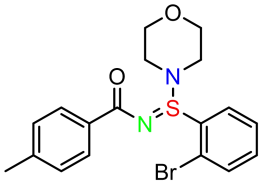
N-(morpholino(p-tolyl)-l4-sulfanylidene)pivalamide (3p)

Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2:1) to afford a yellow solid (51.8 mg 84%, m. p. 74.2-74.5 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.9 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 3.66 (t, *J* = 5.6 Hz, 4H), 3.20 – 3.11 (m, 2H), 3.03 – 2.96 (m, 2H), 2.40 (s, 3H), 1.27 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.35, 142.21, 131.10, 129.98, 128.35, 66.99, 47.34, 40.95, 28.71, 21.43; **IR** (KBr): 3445, 2965, 1867, 1571, 1476, 1317, 1195, 1081, 809, 719cm^{-1}; **HRMS** (ESI) calcd for $C_{16}H_{24}N_2O_2S$ $[M+H]^+$:309.1632; found:309.1627.



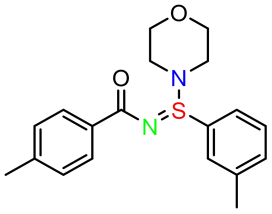
4-methyl-N-(morpholino(o-tolyl)-l4-sulfanylidene)benzamide (3q)

Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2:1) to afford a yellow viscous solid (58.2 mg 85%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 9.4 Hz, 1H), 8.16 (d, *J* = 7.9 Hz, 2H), 7.41 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 2H), 3.62 (t, *J* = 5.8 Hz, 3H), 3.29 – 3.19 (m, 2H), 3.11 – 3.01 (m, 2H), 2.57 (s, 3H), 2.38 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.48, 141.30, 138.47, 133.94, 132.05, 131.81, 131.71, 129.09, 128.55, 128.09, 126.38, 66.77, 47.05, 21.55, 19.43; **IR** (KBr): 3285, 1681, 1441, 1361, 1102, 936, 819, 715, 688cm^{-1}; **HRMS** (ESI) calcd for $C_{19}H_{22}N_2O_2S$ [M+H]$^{+}$:343.1475; found:343.1469.



N-((2-bromophenyl)(morpholino)-l4-sulfanylidene)-4-methylbenzamide (3r)

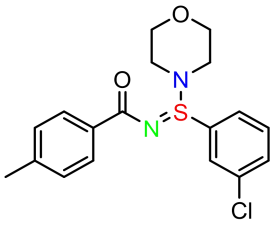
Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2:1) to afford a green solid (72.3 mg 89%, m. p. 121.7-122.0 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8.0 Hz, 1H), 8.13 (d, *J* = 7.8 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 2H), 3.64 (t, *J* = 8.8 Hz, 4H), 3.30 – 3.25 (m, 2H), 3.15 – 3.10 (m, 2H), 2.38 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.24, 141.45, 134.38, 133.98, 133.68, 133.32, 130.39, 129.05, 128.59, 127.66, 124.22, 66.71, 46.99, 21.56; **IR** (KBr): 3215, 2980, 2336, 1660, 1412, 1370, 1096, 820, 768, 677cm^{-1}; **HRMS (ESI)** calcd for $C_{18}H_{19}BrN_2O_2S$ [M+Na]$^{+}$:429.0243; found:429.0252.



4-methyl-N-(morpholino(m-tolyl)-l4-sulfanylidene)benzamide (3s)

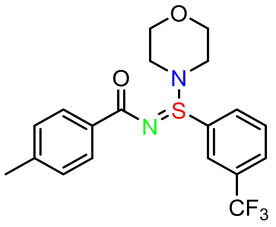
Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (1:1) to afford a brown viscous solid (60.2 mg 88%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.8 Hz, 2H), 7.79 (d, *J* = 6.9 Hz, 2H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 7.6

Hz, 1H), 7.22 (d, J = 7.9 Hz, 2H), 3.70 (t, J = 4.8 Hz, 4H), 3.30 – 3.22 (m, 2H), 3.13 – 3.06 (m, 2H), 2.45 (s, 3H), 2.40 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.09, 141.48, 139.56, 133.88, 133.71, 132.68, 129.21, 129.19, 128.65, 125.50, 66.93, 47.55, 21.64, 21.62; **IR** (KBr): 3025, 1660, 1445, 1353, 1079, 825, 715, 688cm^{-1}; **HRMS** (ESI) calcd for $C_{19}H_{22}N_2O_2S$ [M+H]$^+$:343.1475; found:343.1457.



N-((3-chlorophenyl)(morpholino)-l4-sulfanylidene)-4-methylbenzamide (3t)

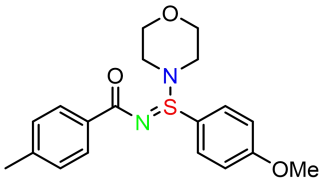
Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2:1 to 1:1) to afford a yellow viscous solid (66.6 mg 92%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (d, J = 7.8 Hz, 2H), 8.00 (d, J = 2.4 Hz, 1H), 7.85 (d, J = 7.0 Hz, 1H), 7.47 (d, J = 7.4 Hz, 2H), 7.21 (d, J = 7.8 Hz, 2H), 3.69 (t, J = 4.9 Hz, 4H), 3.29 – 3.20 (m, 2H), 3.14 – 3.04 (m, 2H), 2.38 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.00, 141.63, 136.14, 135.45, 133.41, 131.92, 130.47, 129.11, 128.63, 128.29, 126.60, 66.76, 47.58, 21.55; **IR** (KBr): 3315, 1685, 1466, 1360, 1095, 885, 827, 781, 690cm^{-1}; **HRMS** (ESI) calcd for $C_{18}H_{19}ClN_2O_2S$ [M+H]$^+$:363.0929; found:363.0926.



4-methyl-N-(morpholino(3-(trifluoromethyl)phenyl)-l4-sulfanylidene)benzamide (3u)

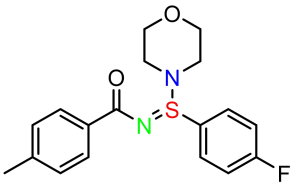
Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2:1 to 1:1) to afford a yellow viscous solid (74.5 mg 94%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 8.25 (d, J = 8.0 Hz, 1H), 8.16 (d, J = 7.8 Hz, 2H), 7.85 (d, J = 7.8 Hz, 1H), 7.75 (t, J = 7.9 Hz, 1H), 7.26 (d, J = 8.0 Hz, 2H), 3.75 (t, J = 5.0 Hz, 4H), 3.37 – 3.28 (m, 2H), 3.18 – 3.11 (m, 2H), 2.43 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.29, 141.93, 136.05, 133.36, 132.07 (C-F, $^2J_{C\text{-}F}$ = 33.3 Hz), 131.96, 130.10, 129.24, 128.81, 128.62 (C-F, $^3J_{C\text{-}F}$ = 3.6 Hz), 125.57 (C-F, $^3J_{C\text{-}F}$ = 4.0 Hz),

123.45 (C-F, $^{1}J_{C\text{-}F}$ = 272.8 Hz), 66.90, 47.79, 21.66; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.58; **IR** (KBr): 3241, 1658, 1455, 1366, 1269, 1185, 1095, 697cm^{-1}; **HRMS** (ESI) calcd for $C_{19}H_{19}F_3N_2O_2S$ $[M+H]^+$: 397.1193 ;found:397.1182. HRMS (ESI) calcd for $C_{19}H_{19}F_3N_2O_2S$ $[M+H]^+$:397.1193; found:397.1182.



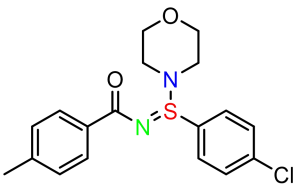
N-((4-methoxyphenyl)(morpholino)-l4-sulfanylidene)-4-methylbenzamide (3v)

Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (1:1) to afford a yellow solid (58.0 mg 81%, m. p. 120.1-120.4 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (t, *J* = 8.5 Hz, 2H), 7.91 (t, *J* = 8.9 Hz, 2H), 7.21 (t, *J* = 8.5 Hz, 2H), 7.04 (t, *J* = 8.9 Hz, 2H), 3.85 (s, 3H), 3.68 (t, *J* = 4.8 Hz, 4H), 3.22 (m, 2H), 3.07 (m, 2H), 2.40 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.77, 162.44, 141.30, 133.98, 130.05, 129.11, 128.55, 124.61, 114.75, 66.88, 55.58, 47.24, 21.53; **IR** (KBr): 3298, 3065, 1675, 1436, 1369, 1099, 808, 698, 639cm^{-1}; **HRMS** (ESI) calcd for $C_{19}H_{22}N_2O_3S$ $[M+Na]^+$:381.1244; found:381.1226.



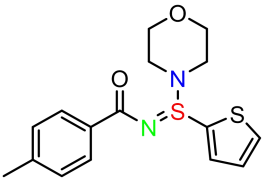
(Z)-N-((4-fluorophenyl)(morpholino)-l4-sulfanylidene)-4-methylbenzamide (3w)

Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2:1) to afford a yellow solid (62.3 mg 90%, m. p. 108.7-109.0 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.9 Hz, 2H), 8.00 (dd, *J* = 8.7, 5.1 Hz, 2H), 7.22 (t, *J* = 8.1 Hz, 4H), 3.68 (t, *J* = 4.9 Hz, 4H), 3.29 – 3.19 (m, 2H), 3.12 – 3.03 (m, 2H), 2.38 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.96, 164.75 (d, $^{1}J_{C\text{-}F}$ = 253.7 Hz), 141.60, 133.59, 130.79 (d, $^{3}J_{C\text{-}F}$ = 9.0 Hz), 129.53 (d, $^{4}J_{C\text{-}F}$ = 3.1 Hz), 129.13, 128.64, 116.63 (d, $^{2}J_{C\text{-}F}$ = 22.6 Hz), 66.84, 47.44, 21.57; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -107.25 (dt, *J* = 13.9, 7.1 Hz); **IR** (KBr): 3065, 1655, 1392, 1373, 1105, 845, 701cm^{-1}; **HRMS** (ESI) calcd for $C_{18}H_{19}FN_2O_2S$ $[M+Na]^+$:369.1044; found:369.1040.



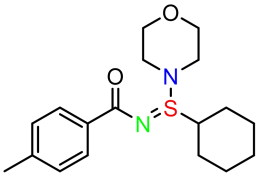
N-((4-chlorophenyl)(morpholino)-l4-sulfanylidene)-4-methylbenzamide (3x)

Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2:1 to 1:1) to afford a yellow solid (67.3 mg 93%, m. p. 96.3-96.6 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.8 Hz, 2H), 7.93 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 3.67 (t, *J* = 4.8 Hz, 4H), 3.28 – 3.19 (m, 2H), 3.11 – 3.03 (m, 2H), 2.37 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.97, 141.60, 138.25, 133.49, 132.62, 129.79, 129.56, 129.10, 128.62, 66.79, 47.50, 21.56; **IR** (KBr): 3298, 1665, 1598, 1450, 1391, 1099, 813, 736, 685cm^{-1}; **HRMS** (ESI) calcd for $C_{18}H_{19}ClN_2O_2S$ $[M+Na]^+$:385.0748; found:385.0747.



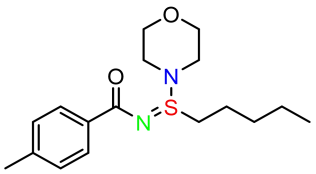
4-methyl-N-(morpholino(thiophen-2-yl)-l4-sulfanylidene)benzamide (3y)

Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2:1 to 1:1) to afford a yellow viscous solid (59.5 mg 89%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.2 Hz, 2H), 7.66 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.54 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.24 – 7.15 (m, 3H), 3.70 (t, *J* = 4.8 Hz, 4H), 3.30 – 3.22 (m, 2H), 3.21 – 3.14 (m, 2H), 2.38 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.86, 141.63, 136.02, 133.24, 132.97, 131.49, 129.22, 128.64, 128.62, 66.90, 47.10, 21.60; **IR** (KBr): 3107, 1661, 1405, 1369, 1102, 814, 720, 691cm^{-1}; **HRMS** (ESI) calcd for $C_{16}H_{18}N_2O_2S_2$ $[M+H]^+$:335.0882; found:335.0879.



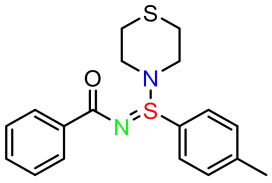
N-(cyclohexyl(morpholino)-l4-sulfanylidene)-4-methylbenzamide (3z)

Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2:1) to afford a yellow solid (56.1 mg 84%, m. p. 134.6-134.9 °C); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 7.9 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 3.78 – 3.69 (m, 4H), 3.32 – 3.23 (m, 2H), 3.17 (d, *J* = 10.8 Hz, 1H), 3.14 – 3.05 (m, 2H), 2.35 (s, 3H), 2.20 (d, *J* = 13.7 Hz, 1H), 2.08 (d, *J* = 16.8 Hz, 1H), 1.87 (s, 2H), 1.69 (d, *J* = 11.2 Hz, 1H), 1.53 – 1.30 (m, 5H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 178.39, 141.11, 133.97, 129.01, 128.55, 66.84, 54.41, 48.12, 27.63 (d, *J* = 33.1 Hz), 25.44, 25.12, 21.55; **IR** (KBr): 3097, 1675, 1395, 1366， 1095, 816, 745, 733cm^{-1}; **HRMS** (ESI) calcd for $C_{18}H_{26}N_2O_2S$ $[M+H]^+$:335.1788; found:335.1792.



5-methyl-N-(morpholino(pentyl)-l4-sulfanylidene)benzamide (3aa)

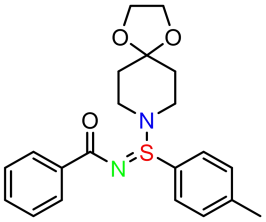
Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2:1 to 1:1) to afford a yellow viscous solid (55.4 mg 86%); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 7.8 Hz, 2H), 3.78 – 3.65 (m, 4H), 3.35 – 3.20 (m, 2H), 3.17 – 3.10 (m, 2H), 3.05 (t, *J* = 7.6 Hz, 2H), 2.36 (s, 3H), 1.82 – 1.62 (m, 2H), 1.48 – 1.34 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 178.27, 141.26, 133.66, 128.85 (d, *J* = 102.4 Hz), 128.81 (d, *J* = 39.1 Hz), 66.90, 47.84, 46.22, 30.54, 23.62, 22.26, 21.57, 13.85; **IR** (KBr): 3097, 1675, 1469, 1219, 1095, 816, 745, 733cm^{-1}; **HRMS** (ESI) calcd for $C_{17}H_{26}N_2O_2S$ $[M+Na]^+$:345.1607; found:345.1611.



N-(thiomorpholino(p-tolyl)-l4-sulfanylidene)benzamide (3ab)

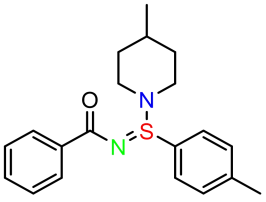
Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (3:1) to afford a yellow viscous solid (59.2 mg 86%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.7 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 6.8 Hz, 1H), 7.42 (t, *J* = 7.3

Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 3.55 – 3.47 (m, 2H), 3.45 – 3.36 (m, 2H), 2.65 (t, *J* = 5.3 Hz, 4H), 2.42 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.77, 142.45, 136.67, 131.14, 131.13, 130.11, 129.07, 128.27, 127.90, 50.00, 28.09, 21.43; **IR** (KBr): 3020, 1675, 1396, 1371, 1099, 815, 761, 696cm^{-1}; **HRMS** (ESI) calcd for $C_{18}H_{20}N_2OS_2$ $[M+Na]^+$:367.0909; found:367.0902.



N-((1,4-dioxa-8-azaspiro[4.5]decan-8-yl)(p-tolyl)-l4-sulfanylidene)benzamide (3ac)

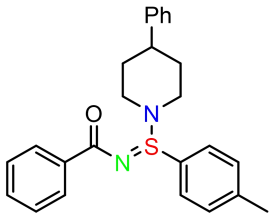
Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2:1) to afford a yellow viscous solid (70.7 mg 92%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 6.9 Hz, 2H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 6.9 Hz, 1H), 7.37 (t, *J* = 7.1 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 3.83 (s, 4H), 3.37 – 3.26 (m, 2H), 3.23 – 3.12 (m, 2H), 2.37 (s, 3H), 1.72 (t, *J* = 5.8 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.55, 142.11, 136.73, 131.48, 130.85, 129.92, 128.98, 127.95, 127.70, 106.00, 64.23, 45.80, 35.21, 21.29; **IR** (KBr): 3015, 1665, 1391, 1362, 1124, 879, 761, 696cm^{-1}; **HRMS** (ESI) calcd for $C_{21}H_{24}N_2O_3S$ $[M+H]^+$:385.1580; found:385.1584.



N-((4-methylpiperidin-1-yl)(p-tolyl)-l4-sulfanylidene)benzamide (3ad)

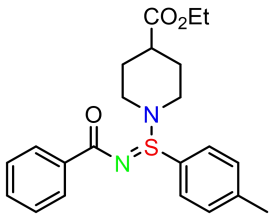
Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (3:1) to afford a white solid (58.5 mg 86%, m. p. 129.5-129.8 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 6.6 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.47 – 7.38 (m, 3H), 7.34 (d, *J* = 8.1 Hz, 2H), 3.74 (d, *J* = 12.7 Hz, 1H), 3.22 (td, *J* = 12.0, 2.7 Hz, 1H), 2.97 (d, *J* = 12.0 Hz, 1H), 2.68 (td, *J* = 12.2, 2.9 Hz, 1H), 2.42 (s, 3H), 1.76 (d, *J* = 12.7 Hz, 1H), 1.58 (d, *J* = 13.6 Hz, 1H), 1.49 – 1.39(m, 1H), 1.33 (qd, *J* = 12.0, 4.0 Hz, 1H), 1.14 – 1.03 (m, 1H), 0.90 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.77, 142.00, 136.95, 131.80, 130.94, 129.97, 129.10, 128.18, 127.86, 51.72, 44.46, 34.50 (d, *J*

= 79.9 Hz), 30.17, 21.59 (d, *J* = 31.9 Hz); **IR** (KBr): 3022, 1671, 1455, 1370, 726, 693cm^{-1}; **HRMS** (ESI) calcd for $C_{20}H_{24}N_2OS$ $[M+Na]^+$: 363.1502; found:363.1501.



N-((4-phenylpiperidin-1-yl)(p-tolyl)-l4-sulfanylidene)benzamide (3ae)

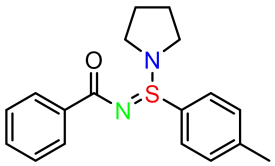
Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (5:1 to 4:1) to afford a yellow viscous solid (76.4 mg 95%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 6.8 Hz, 2H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.50 (t, *J* = 6.5 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.1 Hz, 1H), 7.17 (d, *J* = 6.7 Hz, 2H), 3.94 (d, *J* = 11.6 Hz, 1H), 3.42 (t, *J* = 11.2 Hz, 1H), 3.14 (d, *J* = 11.3 Hz, 1H), 2.90 – 2.79 (m, 1H), 2.59 (t, *J* = 12.0 Hz, 1H), 2.44 (s, 3H), 2.00 (d, *J* = 12.3 Hz, 1H), 1.96 – 1.86 (m, 1H), 1.81 (d, *J* = 13.2 Hz, 1H), 1.60 – 1.73 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.61, 145.08, 142.04, 136.83, 131.52, 130.89, 129.92, 129.03, 128.42, 128.09, 127.77, 126.61, 126.36, 48.30 (d, *J* = 735.9 Hz), 41.61, 33.48 (d, *J* = 95.4 Hz), 21.30; **IR** (KBr): 3018, 1670, 1498, 1395, 1365, 1149, 877, 721, 689cm^{-1}; **HRMS** (ESI) calcd for $C_{25}H_{26}N_2OS$ $[M+H]^+$:403.1839; found:403.1846.



ethyl-1-(N-benzoyl-S-(p-tolyl)sulfinimidoyl)piperidine-4-carboxylate (3af)

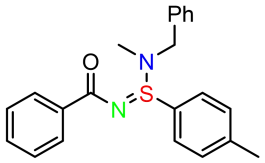
Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2:1) to afford a pale yellow viscous solid (72.5 mg 91%); **^{1}H NM**R (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 6.8 Hz, 2H), 7.81 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 6.9 Hz, 1H), 7.36 (t, *J* = 7.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 4.04 (q, *J* = 7.1 Hz, 2H), 3.73 (d, *J* = 12.3 Hz, 1H), 3.27 – 3.18 (m, 1H), 2.98 (d, *J* = 12.2 Hz, 1H), 2.74 – 2.64 (m, 1H), 2.36 (s, 3H), 2.34 – 2.25 (m, 1H), 2.01 (d, *J* = 12.4 Hz,

1H), 1.88 – 1.77 (m, 2H), 1.63 – 1.51 (m, 1H), 1.16 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.63, 174.01, 142.05, 136.57, 131.26, 130.86, 129.88, 128.91, 128.00, 127.69, 60.43, 47.07 (d, *J* = 691.9 Hz), 40.11, 28.38 (d, *J* = 74.5 Hz), 21.23, 14.04; **IR** (KBr): 3032, 1750, 1678, 1310, 1125, 721, 689cm^{-1}; **HRMS** (ESI) calcd for $C_{22}H_{26}N_2O_3S$ $[M+H]^+$:399.1737; found:399.1738.



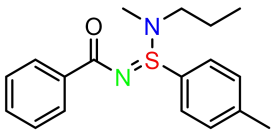
N-(pyrrolidin-1-yl(p-tolyl)-l4-sulfanylidene)benzamide (3ag)

Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (4:1 to 3:1) to afford a yellow viscous solid (53.1 mg 85%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 7.4 Hz, 2H), 7.85 (d, *J* = 7.9 Hz, 2H), 7.42 (m, 3H), 7.31 (d, *J* = 8.0 Hz, 2H), 3.44 – 3.21 (m, 4H), 2.39 (s, 3H), 1.80 (t, *J* = 6.1 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.71, 141.68, 136.90, 133.01, 130.84, 129.86, 129.01, 127.79, 127.76, 47.40, 25.53, 21.31; **IR** (KBr): 3016, 1651, 1398, 1370, 720, 685cm^{-1}; **HRMS** (ESI) calcd for $C_{18}H_{20}N_2OS$ $[M+H]^+$:313.1369; found:313.1364.



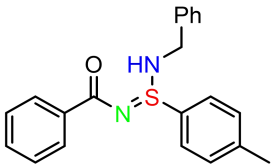
O-((benzyl(methyl)amino)(p-tolyl)-l4-sulfanylidene)benzamide (3ah)

Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (5:1) to afford a pale yellow viscous solid (63.7 mg 88%); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.34 (d, *J* = 6.6 Hz, 2H), 7.95 (d, *J* = 8.3 Hz, 2H), 7.50 – 7.43 (m, 3H), 7.40 – 7.28 (m, 7H), 4.59 (d, *J* = 14.1 Hz, 1H), 4.19 (d, *J* = 14.1 Hz, 1H), 2.56 (s, 3H), 2.44 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 177.84, 139.57 (d, *J* = 549.1 Hz), 134.49 (d, *J* = 195.0 Hz), 134.38 (d, *J* = 479.5 Hz), 134.36 (d, *J* = 465.2 Hz), 131.04, 129.61, 129.54 (d, *J* = 92.6 Hz), 128.59 (d, *J* = 2.5 Hz), 128.19 (d, *J* = 55.4 Hz), 128.05 (d, *J* = 38.7 Hz), 127.77, 126.55, 57.69, 34.02, 21.38; **IR** (KBr): 3033, 1661, 1453, 1378, 711, 687cm^{-1}; **HRMS** (ESI) calcd for $C_{22}H_{22}N_2OS$ $[M+Na]^+$:385.1345; found:385.1344 .



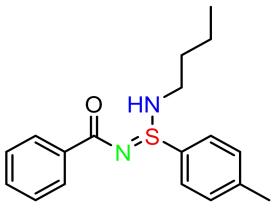
N-((methyl(propyl)amino)(p-tolyl)-l4-sulfanylidene)benzamide (3ai)

Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (5:1 to 4:1) to afford a pale yellow viscous solid (46.5 mg 74%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 6.5 Hz, 2H), 7.86 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 7.1 Hz, 1H), 7.41 (t, *J* = 7.2 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 3.43 – 3.34 (m, 1H), 3.10 – 3.00 (m, 1H), 2.60 (s, 3H), 2.42 (s, 3H), 1.70 – 1.59 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.83, 142.12, 136.98, 132.55, 131.02, 130.02, 129.16, 128.31, 127.94, 55.98, 34.29, 21.69, 21.51, 11.46; **IR** (KBr): 3019, 1657, 1459, 1381, 722, 689cm^{-1}; **HRMS** (ESI) calcd for $C_{18}H_{22}N_2OS$ $[M+Na]^+$:337.1345; found:337.1344.



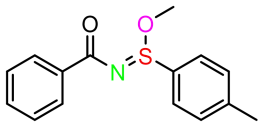
N-((benzylamino)(p-tolyl)-l4-sulfanylidene)benzamide (3aj)

Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (3:1) to afford a yellow solid (66.8 mg 96%, m. p. 114.4-114.7 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 6.9 Hz, 2H), 7.96 (d, *J* = 8.3 Hz, 2H), 7.50 (t, *J* = 7.3 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.25 – 7.19 (m, 4H), 5.88 (dd, *J* = 8.4, 4.2 Hz, 1H), 4.16 (dd, *J* = 13.4, 4.0 Hz, 1H), 3.84 (dd, *J* = 13.4, 8.3 Hz, 1H), 2.43 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.80, 142.10, 137.27, 136.69, 131.39, 131.08, 130.02, 129.01, 128.51, 128.39, 128.15, 127.85, 127.58, 44.43, 21.38; **IR** (KBr): 3430, 3036, 1667, 1468, 860, 702, 675cm^{-1}; **HRMS** (ESI) calcd for $C_{21}H_{20}N_2OS$ $[M+H]^+$:349.1369; found:349.1370.



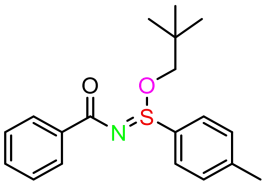
N-((butylamino)(p-tolyl)-l4-sulfanylidene)benzamide (3ak)

Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (3:1 to 2:1) to afford a yellow solid (58.4 mg 93%, m. p. 83.4-83.7 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 7.3 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.47 (t, *J* = 7.0 Hz, 1H), 7.41 (t, *J* = 7.3 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 5.22 (dd, *J* = 8.0, 4.3 Hz, 1H), 3.07 – 2.97 (m, 1H), 2.72 – 2.59 (m, 1H), 2.41 (s, 3H), 1.48 – 1.38 (m, 2H), 1.30 – 1.20 (m, 2H), 0.78 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.85, 141.94, 136.87, 131.81, 131.07, 130.00, 128.95, 128.02, 127.89, 40.58, 31.88, 21.42, 19.99, 13.70; **IR** (KBr): 3395, 3019, 1657, 1461, 843, 712, 670cm^{-1}; **HRMS** (ESI) calcd for $C_{18}H_{22}N_2OS$ $[M+Na]^+$:337.1345; found:337.1347.



Methyl N–(benzoyl)-4-methylphenylsulfinimidate (3am)

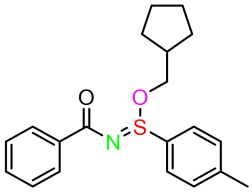
Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (5:1 to 4:1) to afford a yellow viscous solid (36.0 mg 66%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 7.3 Hz, 2H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.45 (d, *J* = 7.7 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 3.63 (s, 3H), 2.47 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.52, 144.02, 135.97, 132.72, 131.95, 130.29, 129.62, 128.83 (d, *J* = 224.6 Hz), 128.11, 52.36, 21.73; **IR** (KBr): 3031, 1669, 1466, 1379, 726, 689cm^{-1}; **HRMS** (ESI) calcd for $C_{15}H_{15}NO_2S$ $[M+H]^+$:274.0896; found:274.0895.



2,2-dimethylpropyl N–(benzoyl)-4-methylphenylsulfinimidate (3an)

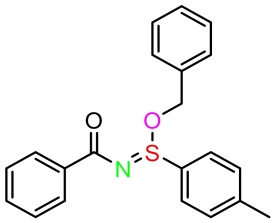
Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (6:1 to 5:1) to afford a yellow viscous solid (52.7 mg 80%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.4 Hz, 2H), 7.93 (d, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 6.9 Hz, 2H), 7.44 (d, *J* = 7.7 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 1H), 3.91 (d, *J* = 9.9 Hz, 1H), 3.47 (d, *J* = 9.2 Hz, 1H), 2.46 (s, 3H), 0.87 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.40, 143.63, 136.20, 133.68, 131.76, 130.16, 129.54, 128.03,

127.91, 32.23, 29.79, 26.40, 21.65; **IR** (KBr): 3024, 1665, 1463, 1379, 1152, 726, 692cm^{-1}; **HRMS** (ESI) calcd for $C_{19}H_{23}NO_2S$ $[M+H]^+$:330.1522; found:330.1519.



Cyclopentanemethyl N–(benzoyl)-4-methylphenylsulfinimidate (3ao)

Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (6:1 to 5:1) to afford a yellow viscous solid (53.9 mg 79%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.6 Hz, 2H), 7.91 (d, *J* = 7.9 Hz, 2H), 7.48 (t, *J* = 7.3 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 4.15 – 4.07 (m, 1H), 3.77 – 3.69 (m, 1H), 2.42 (s, 3H), 2.23 – 2.10 (m, 1H), 1.75 – 1.60 (m, 2H), 1.49 (s, 2H), 1.21 – 1.08 (m, 0H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.12, 143.41, 135.91, 133.37, 131.54, 129.94, 129.29, 127.79, 127.58, 71.30, 39.30, 29.10, 25.10, 21.38; **IR** (KBr): 3023, 2910, 1661, 1457, 1291, 1019, 713, 679cm^{-1}; **HRMS** (ESI) calcd for $C_{20}H_{23}NO_2S$ $[M+Na]^+$:364.1342; found:364.1345.



Benzyl N–(benzoyl)-4-methylphenylsulfinimidate (3ap)

Prepared according to general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (5:1) to afford a yellow viscous solid (58.7 mg 84%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 7.8 Hz, 2H), 7.90 (d, *J* = 7.8 Hz, 2H), 7.53 (t, *J* = 6.5 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 7.9 Hz, 2H), 7.32 (s, 4H), 5.32 (d, *J* = 11.2 Hz, 1H), 4.91 (d, *J* = 11.2 Hz, 1H), 2.44 (s, 3H) ; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.56, 143.80, 135.76 (d, *J* = 38.1 Hz), 133.45, 132.16, 131.86, 129.85 (d, *J* = 60.3 Hz), 129.74, 128.84, 128.70, 128.62, 127.95 (d, *J* = 17.8 Hz), 127.01, 69.65, 21.58; **IR** (KBr): 3031, 1659, 1457, 1295, 1035, 710, 675cm^{-1}; **HRMS** (ESI) calcd for $C_{21}H_{19}NO_2S$ $[M+Na]^+$:372.1029; found:372.1.

H. References

[1] (a) X.-S. Zhang, X.-H. Zhang, *Phosphorus, Sulfur, and Silicon and the Related Elements.,* 2016*,* 191, 89- 94. (b) M. Iwasaki, T. Fujii, A. Yamamoto, K. Nakajima and Y. Nishihara, *Chem. Asian. J*., 2014, 9, 58-62. (c) X. Lei, Y. Wang, E. Fan and Z. Sun, *Org. Lett*., 2019, 21, 5, 1484–1487.

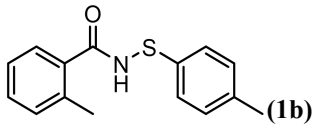
[2] (a) J.-J. Tang, N. Yan, Y. Zhang, Y. Wang, M. Bao and X. Yu, *Green Chem.,* 2023, 25, 7529-7533. (b) X. Lu, G. Huang, J. Ye, M. Adnan Bashir, J. Su, K. Yang, F. Liang and X. Xu, *Org. Lett.,* 2023, 25, 12, 2151–2156. (c) G. Huang, X. Lu, *ChemRxiv*., 2023, doi:10.26434/chemrxiv-2023-p1732. (d). A. Yoshimura, C. L. Makitalo, M. E. Jarvi, M. T. Shea, P. S. Postnikov, G. T. Rohde, V. V. Zhdankin, A. Saito and M. S. Yusubov, *Molecules*., 2019, 24(5), 979. (e) N. S. Greenwood, A. T. Champlin and J. A. Ellman, *J. Am. Chem. Soc.,* 2022, 144(39), 17808-17814. (f) Z. Bai, S. Zhu, Y. Hu, P. Yang, X. Chu, G. He, H. Wang and G. Chen, *Nat. Commun*., 2022, 13, 6445. (g) L. Ma, L. Bai, Z. Yu and Q. Shen, *Chirality.,* 2022, 34(9), 1191-1196.

[3] N. S. Greenwood, J. A. Ellman, *Org. Lett.,* 2023, 25, 4759−4764.

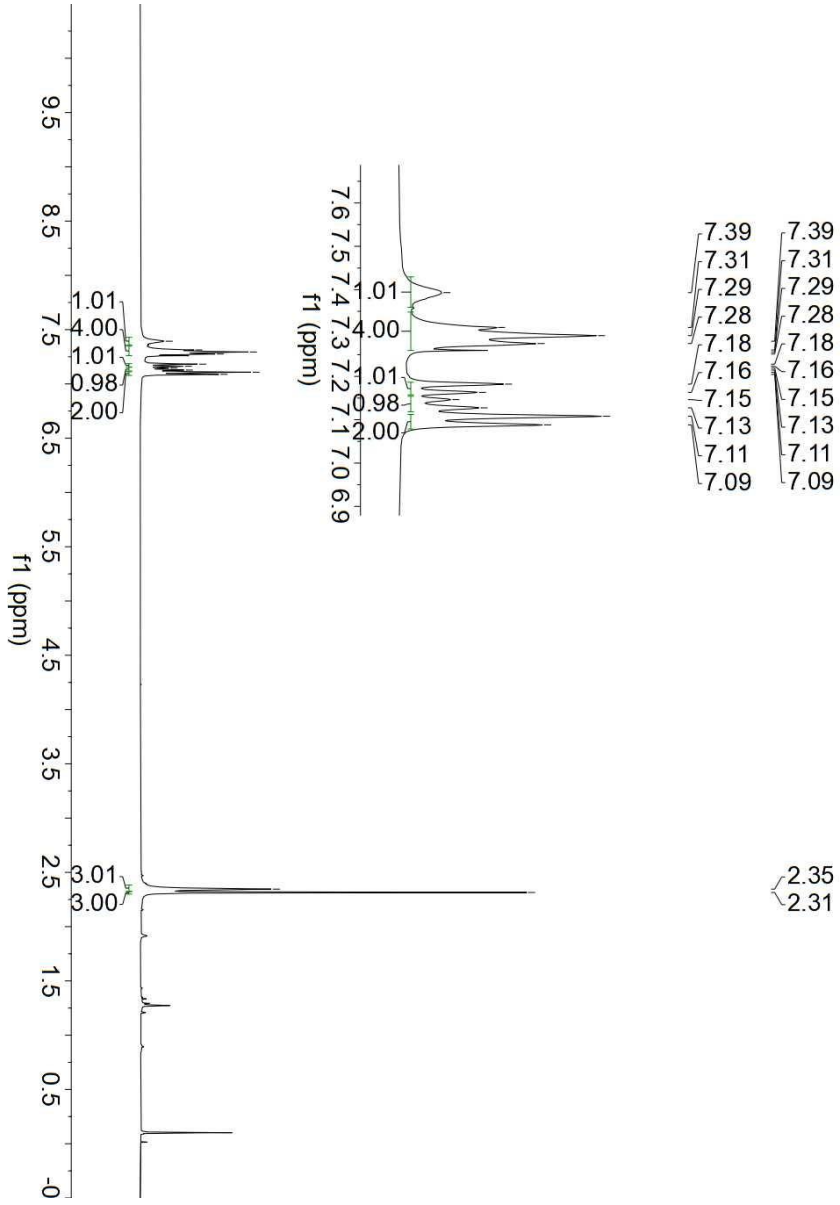
[4] A. K. Jain, M. G. Gund, D. C. Desai, N. Borhade, S. P. Senthilkumar, M. Dhiman, N. K. Mangu, S. V. Mali, N. P. Dubash, S. Halder and A. Satyam, *Bioorganic Chemistry*., 2013, 49, 40-48.

[5] G. Huang, J. Ye, M. Adnan Bashir, Y. Chen, W. Chen and X. Lu, *J. Org. Chem*., 2023, 88, 16, 11728–11734.

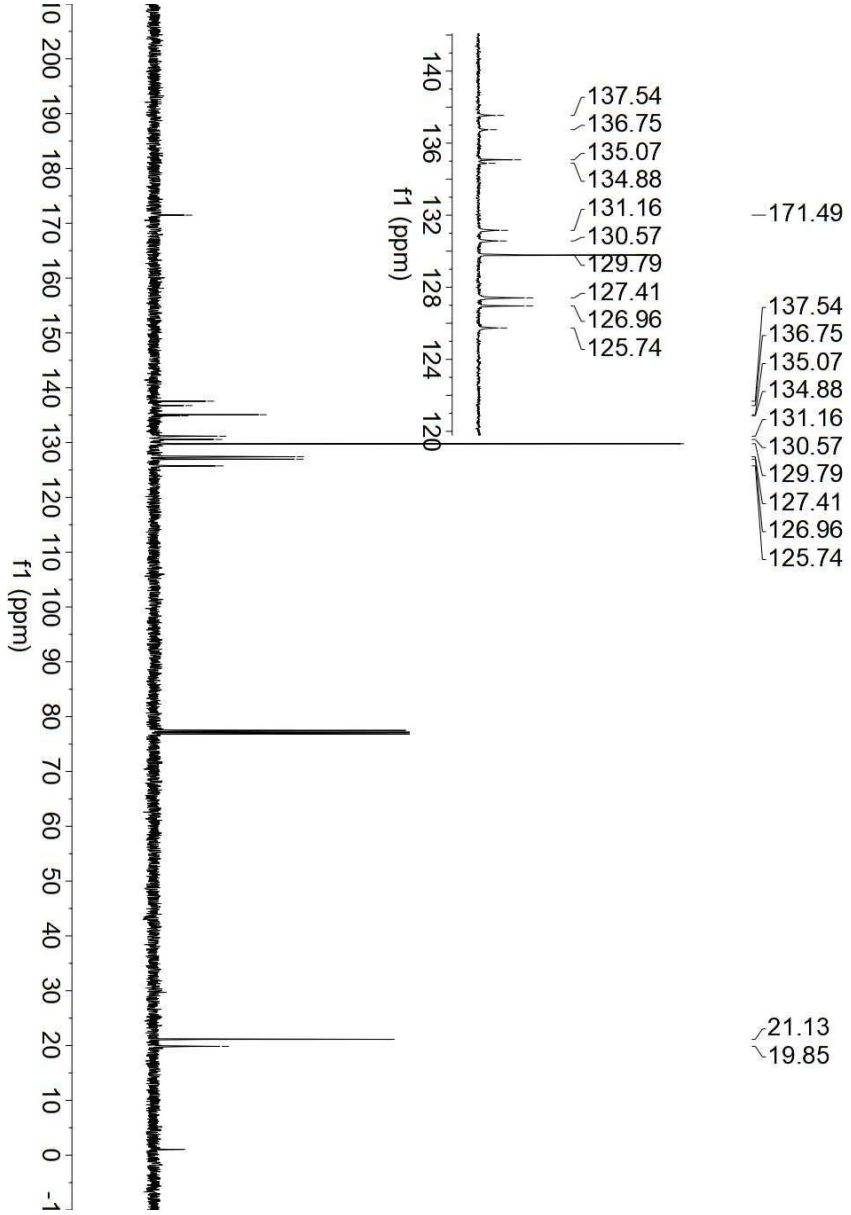
I. NMR spectra

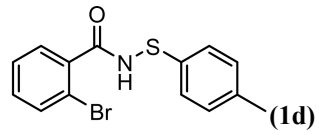


^{1}H NMR (400 MHz, Chloroform-d)



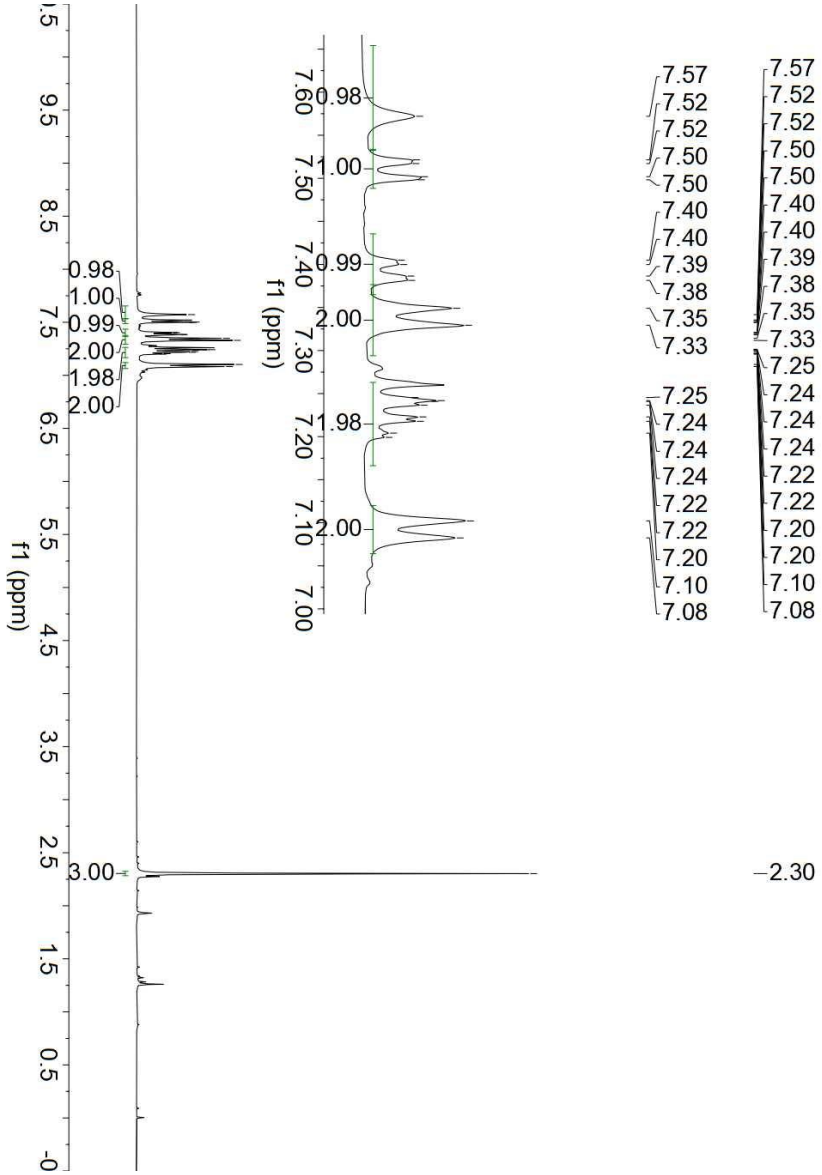
^{13}C NMR (100 MHz, Chloroform-*d*)





(1d)

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



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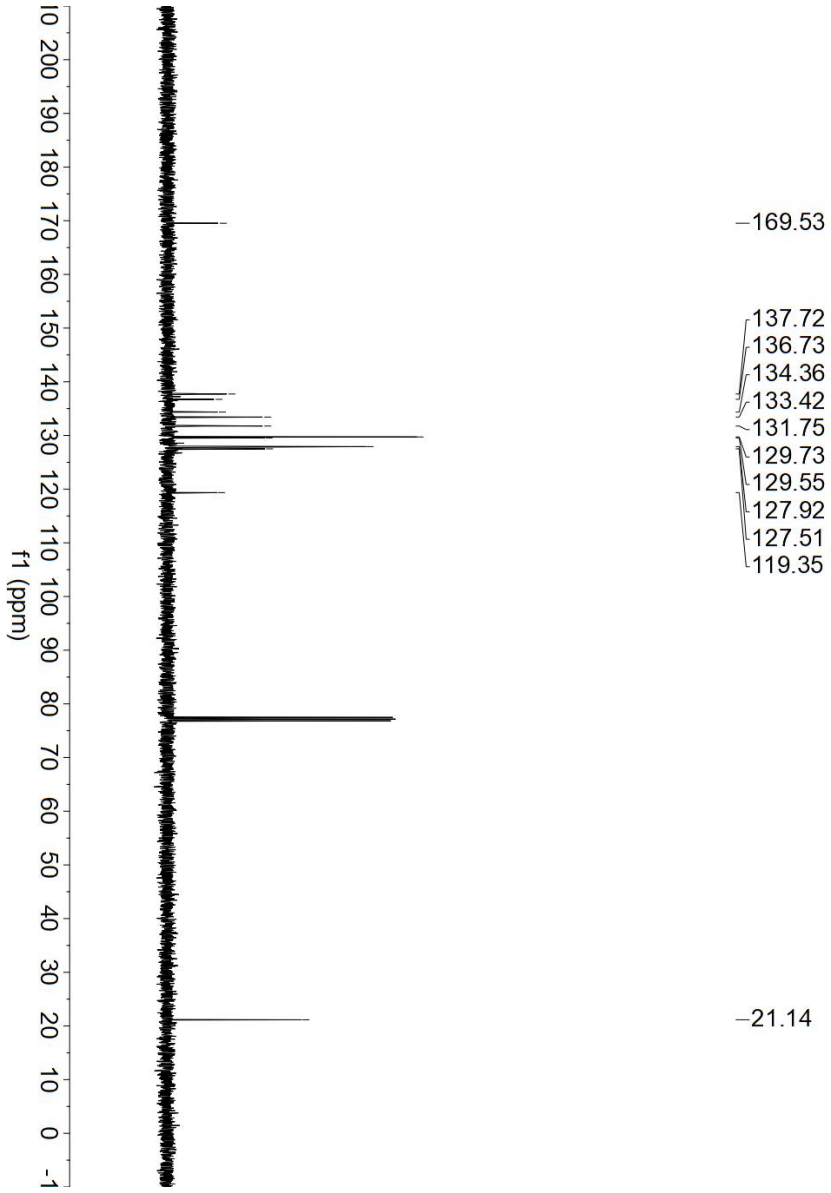

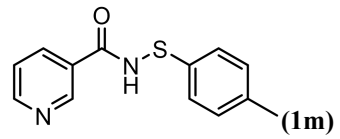

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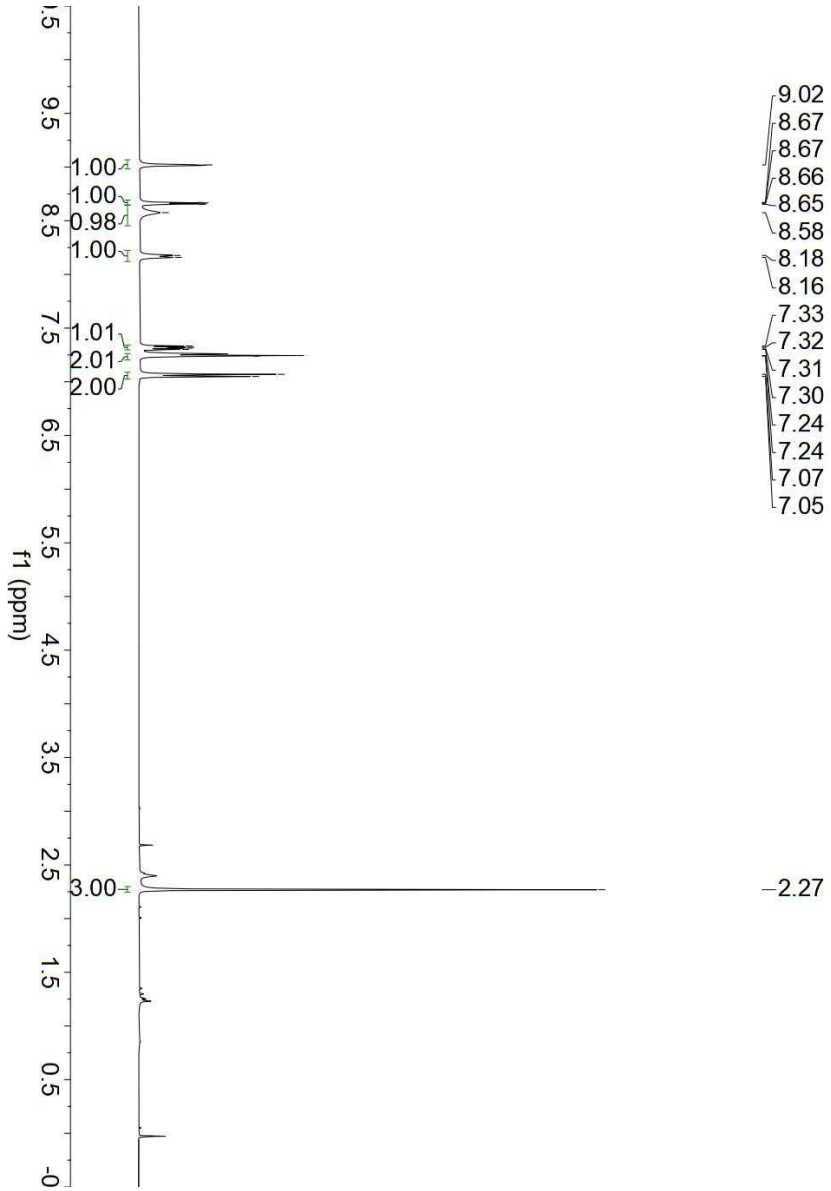

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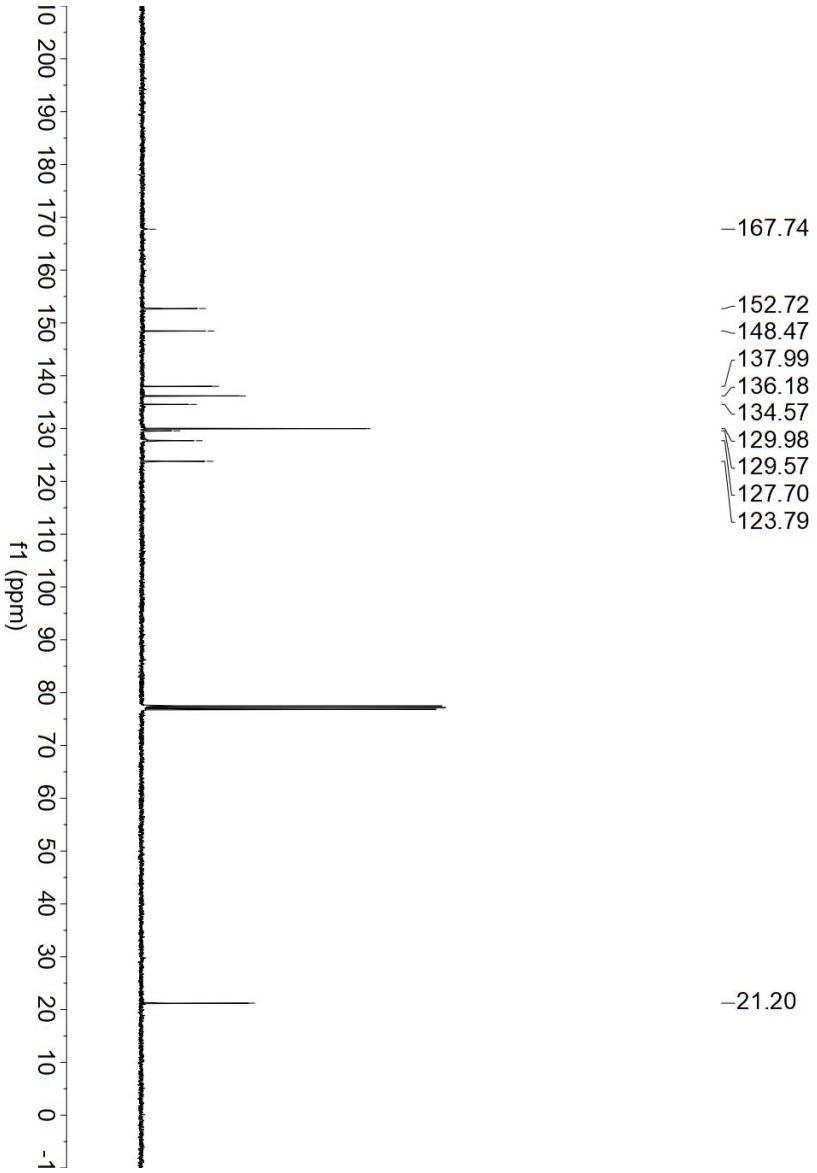

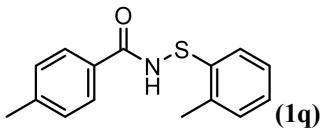

(1q)

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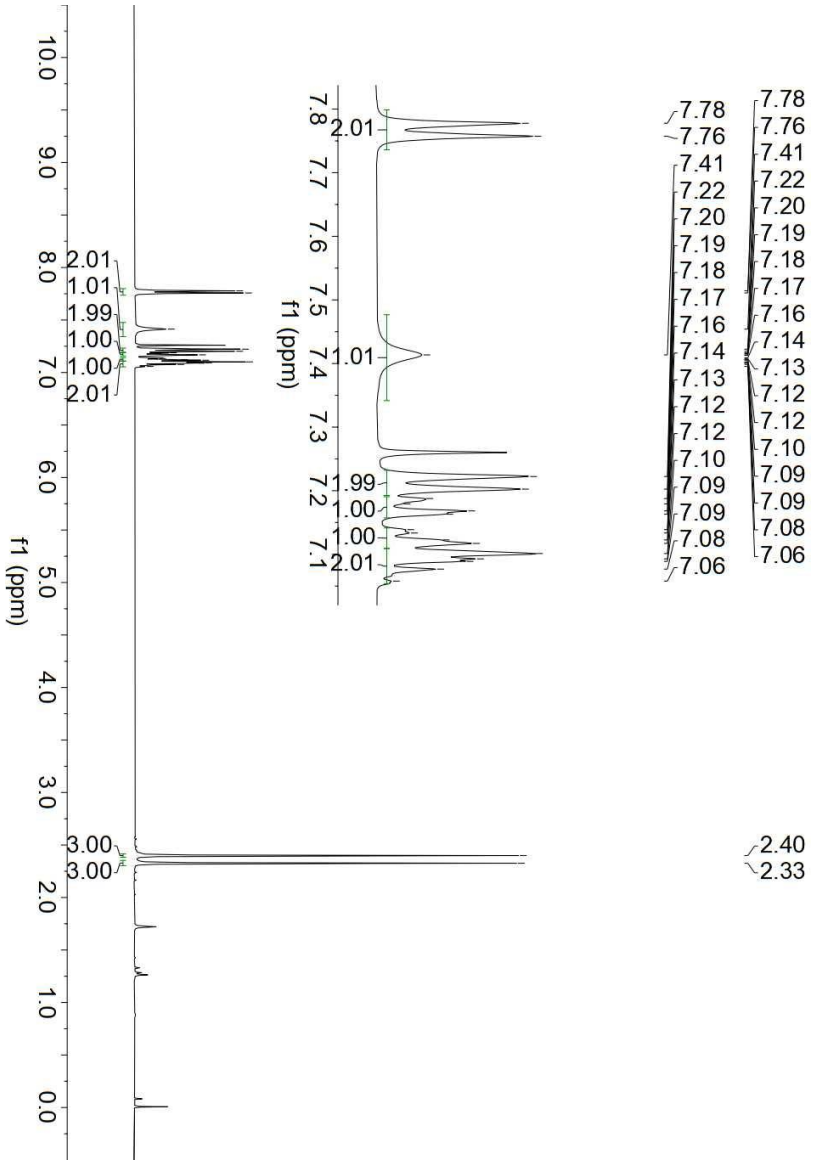

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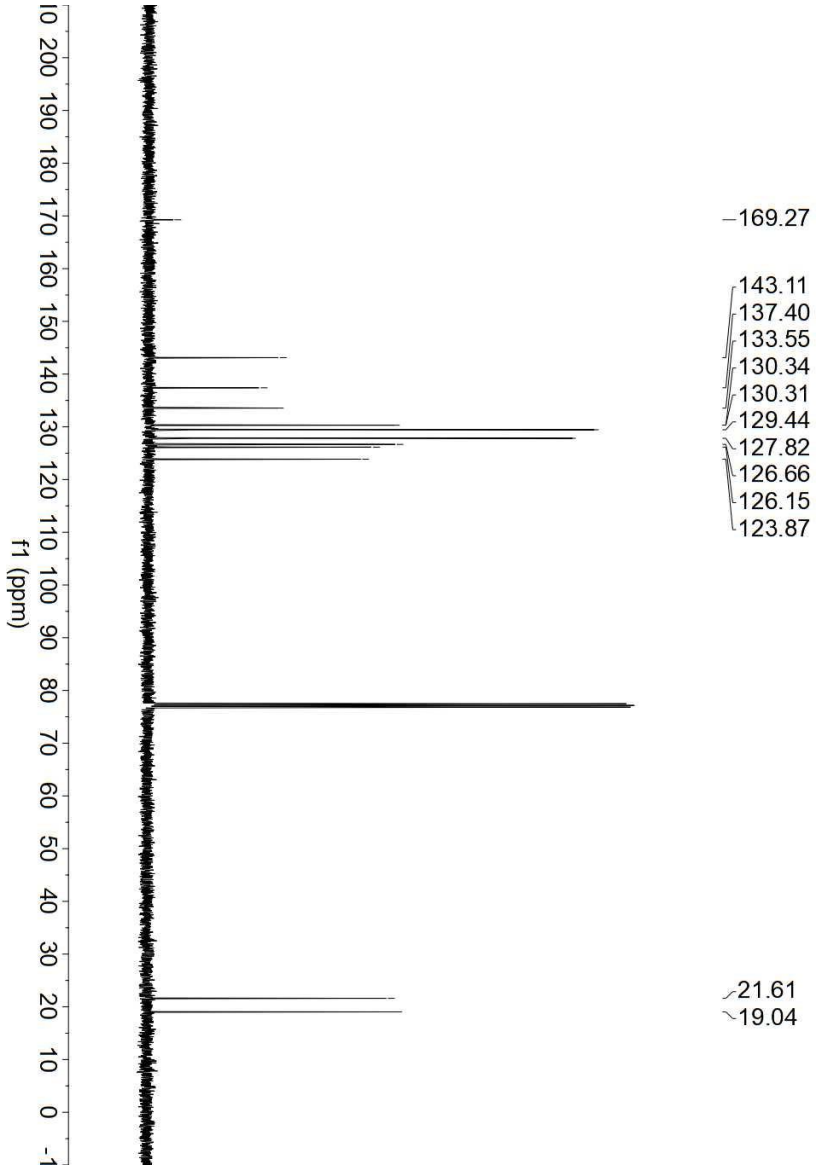

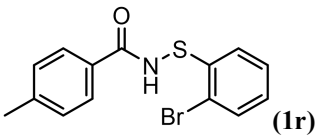

(1r)

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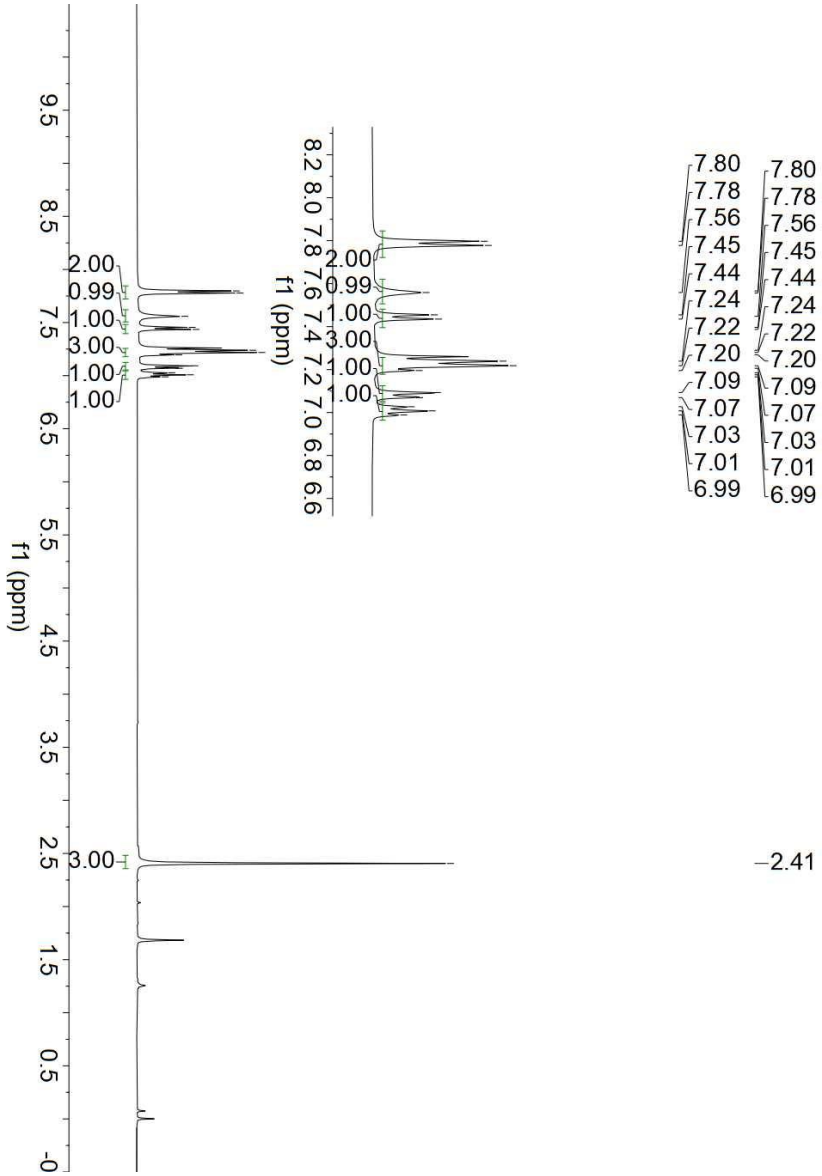
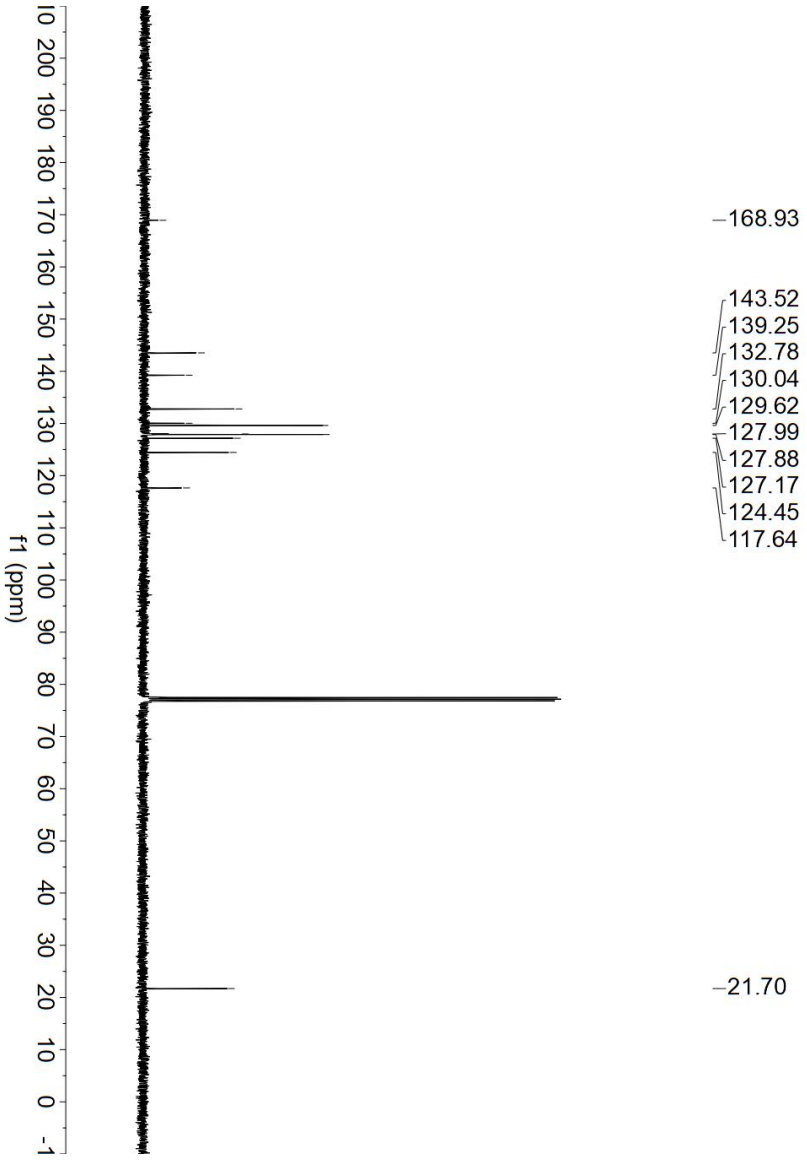
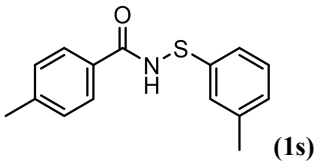


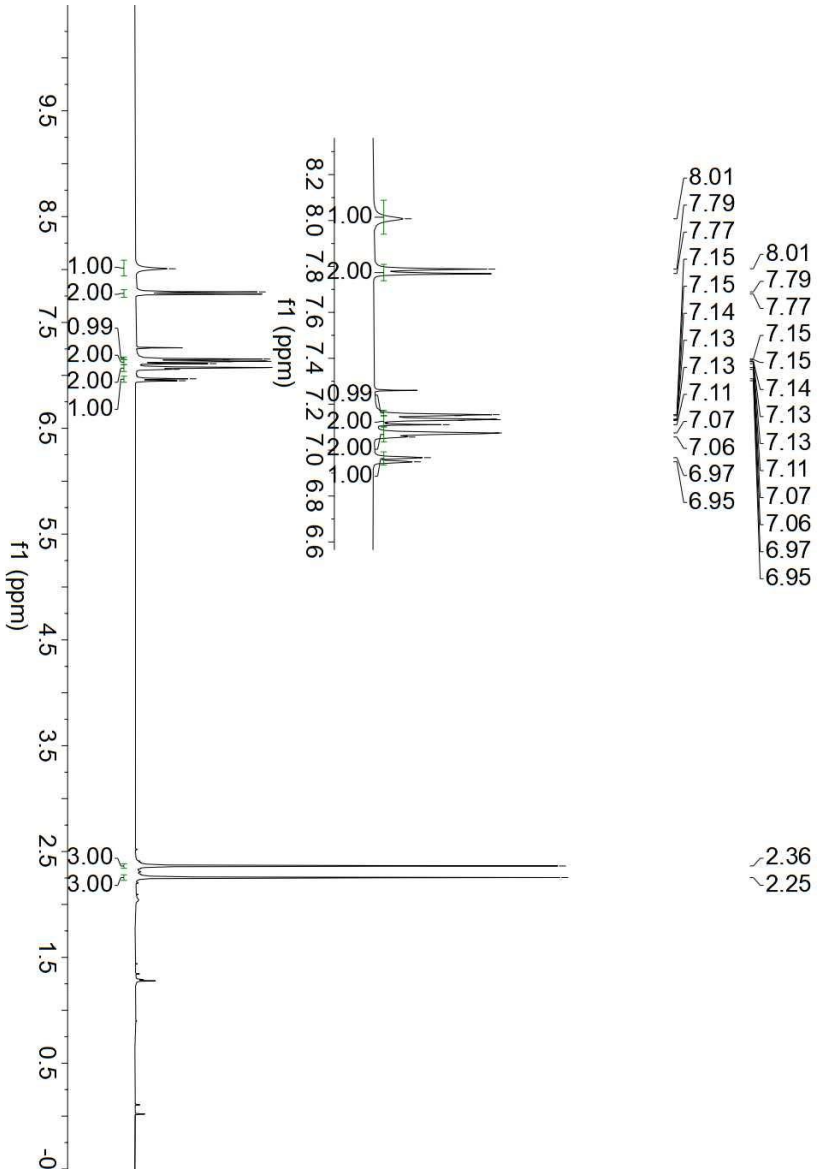
^{13}C NMR (100 MHz, Chloroform-*d*)



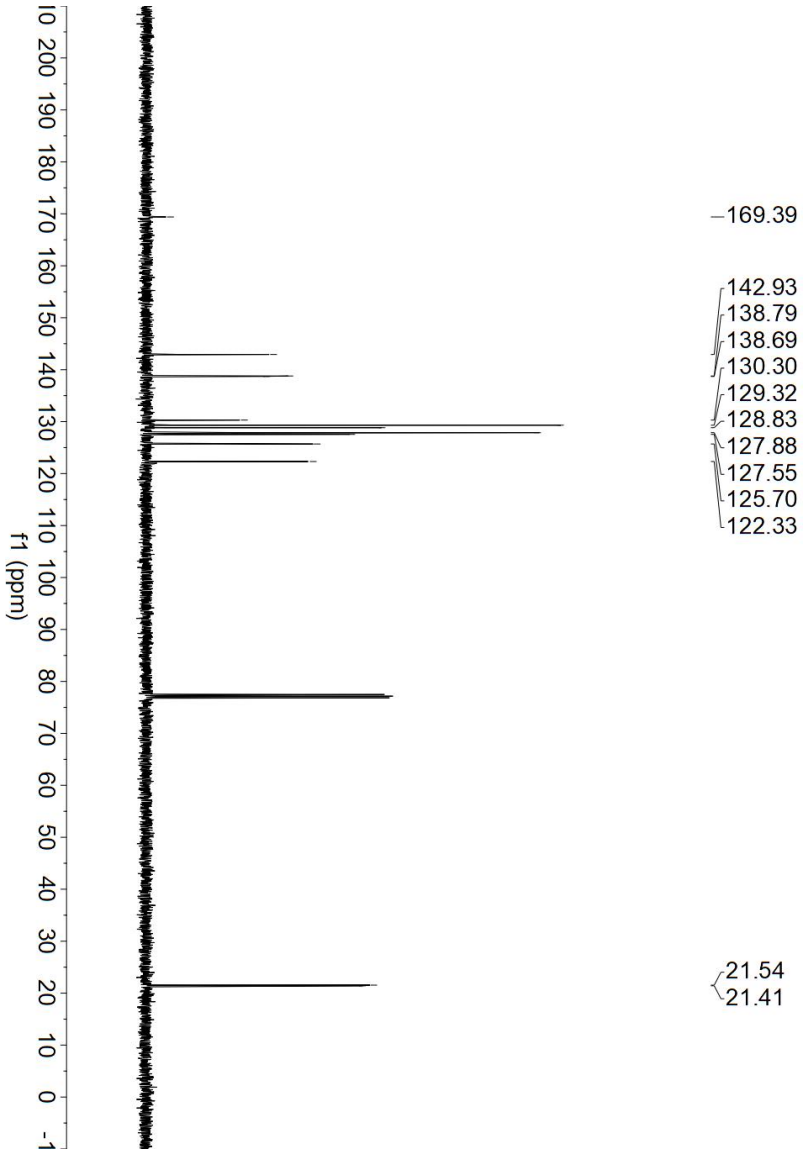


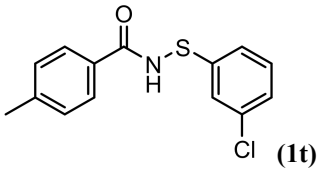
(1s)

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



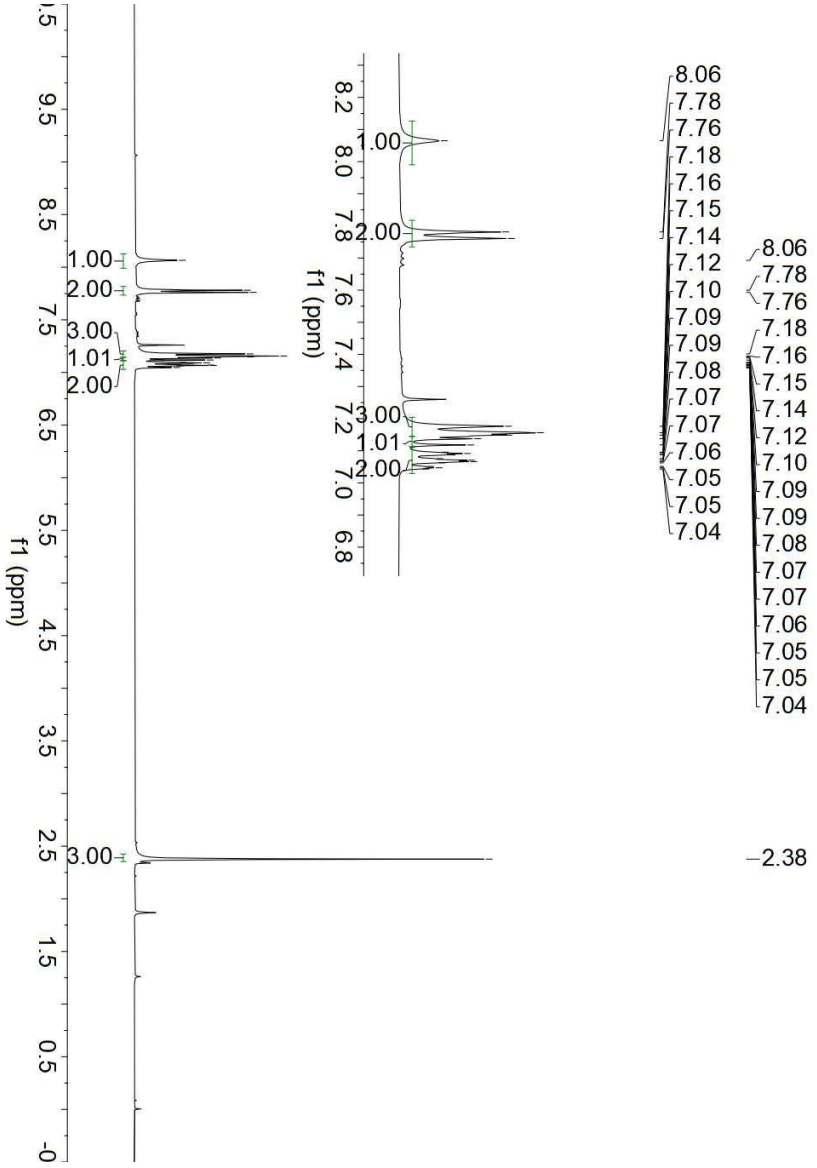
^{13}C NMR (100 MHz, Chloroform-*d*)



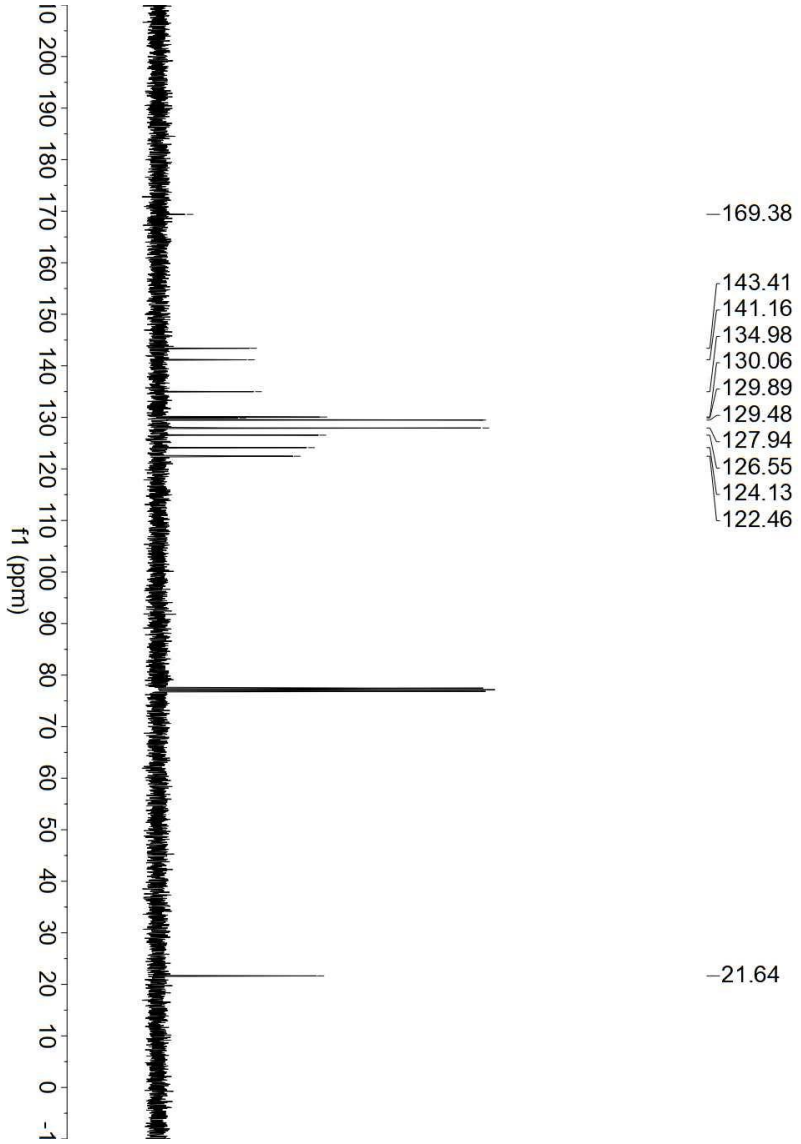


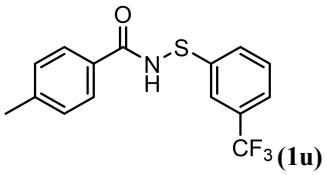
(1t)

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



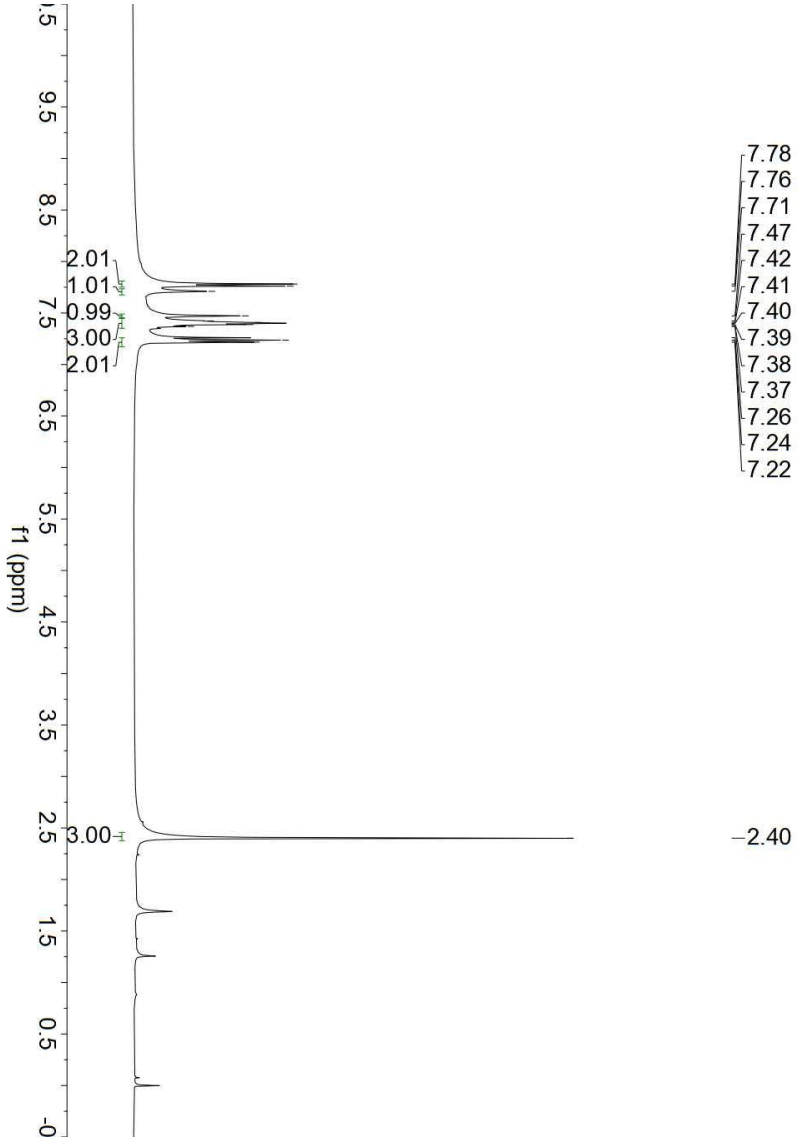
^{13}C NMR (100 MHz, Chloroform-*d*)



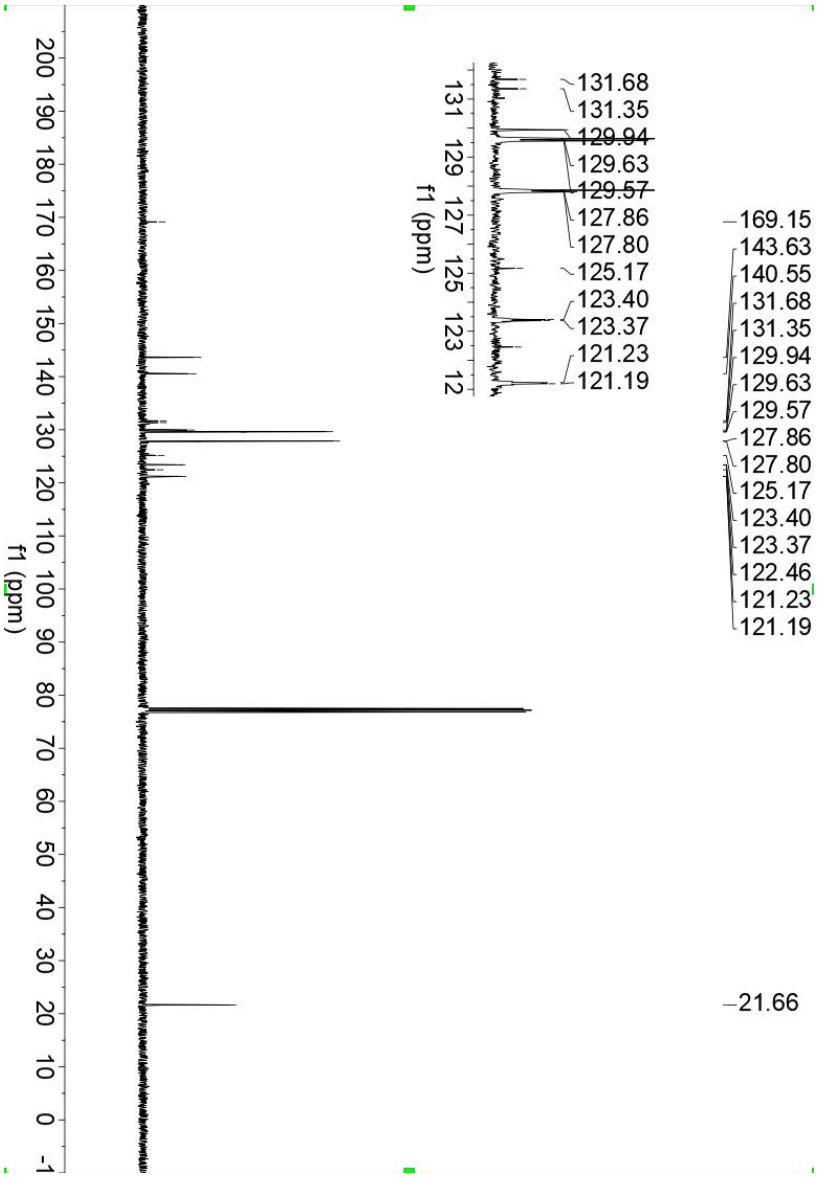


(1u)

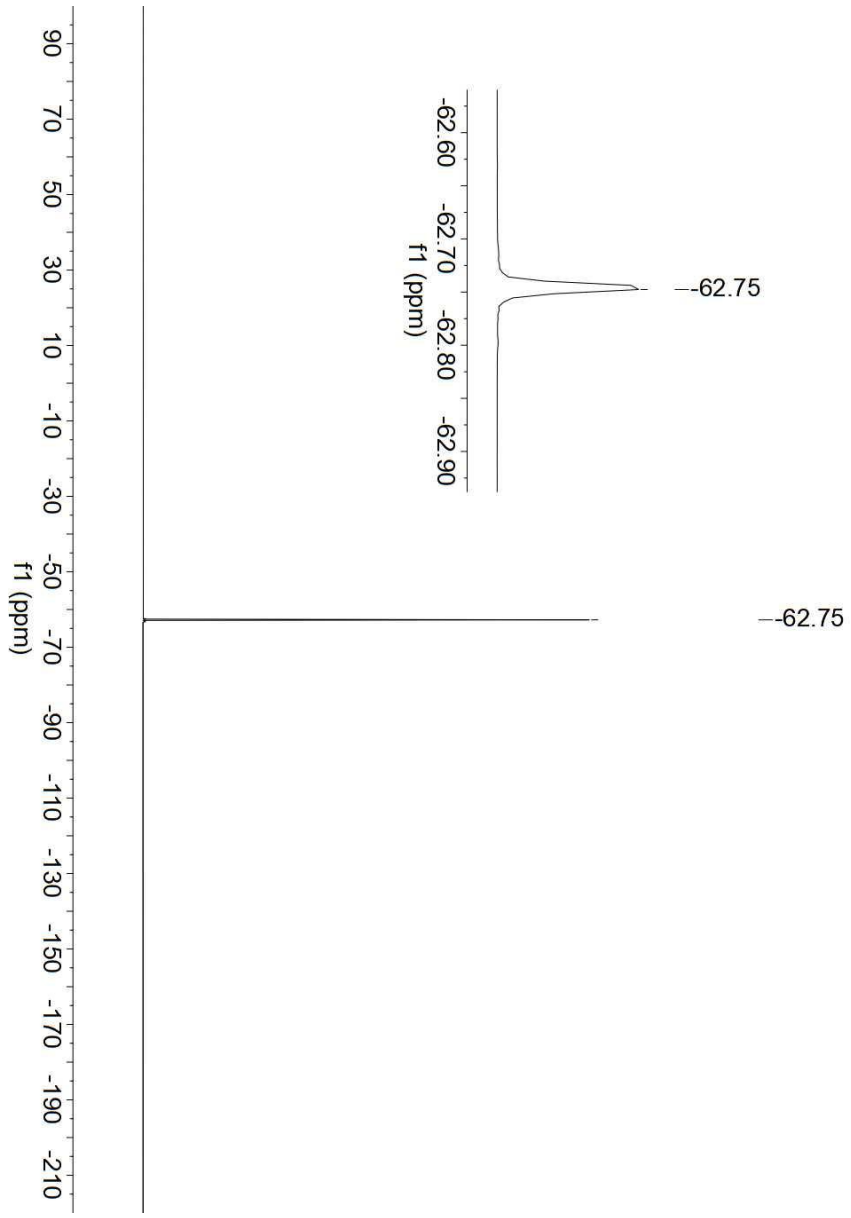
^{1}H NMR (400 MHz, Chloroform-d)

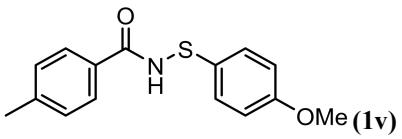


^{13}C NMR (100 MHz, Chloroform-*d*)



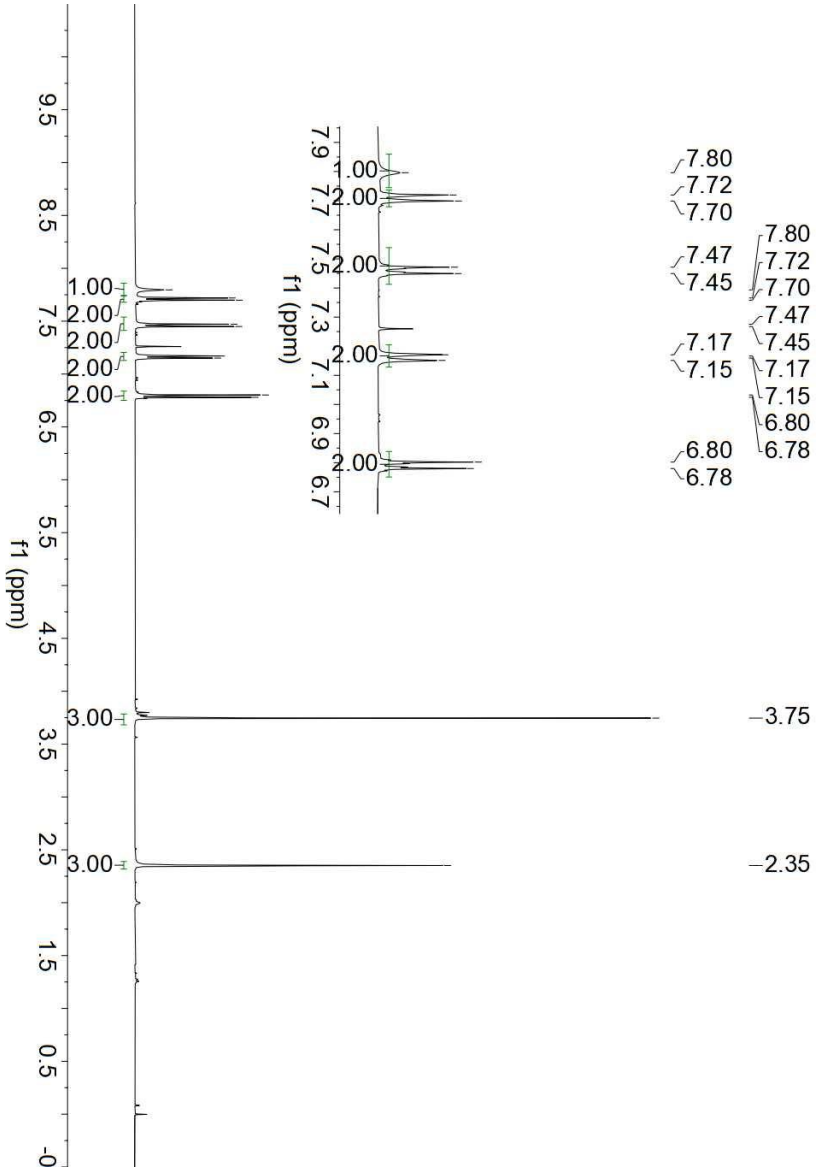
^{19}F NMR (376 MHz, Chloroform-*d*)



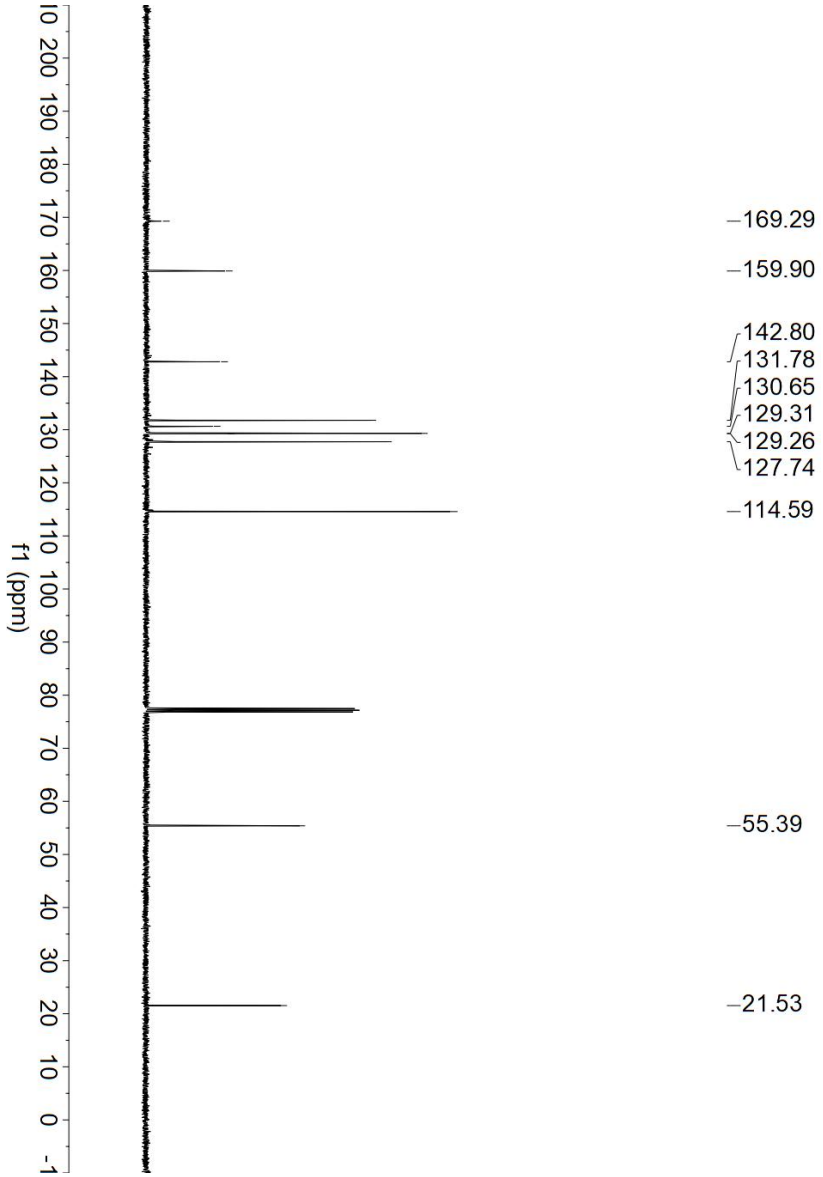


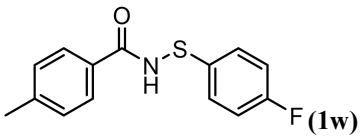
(1v)

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



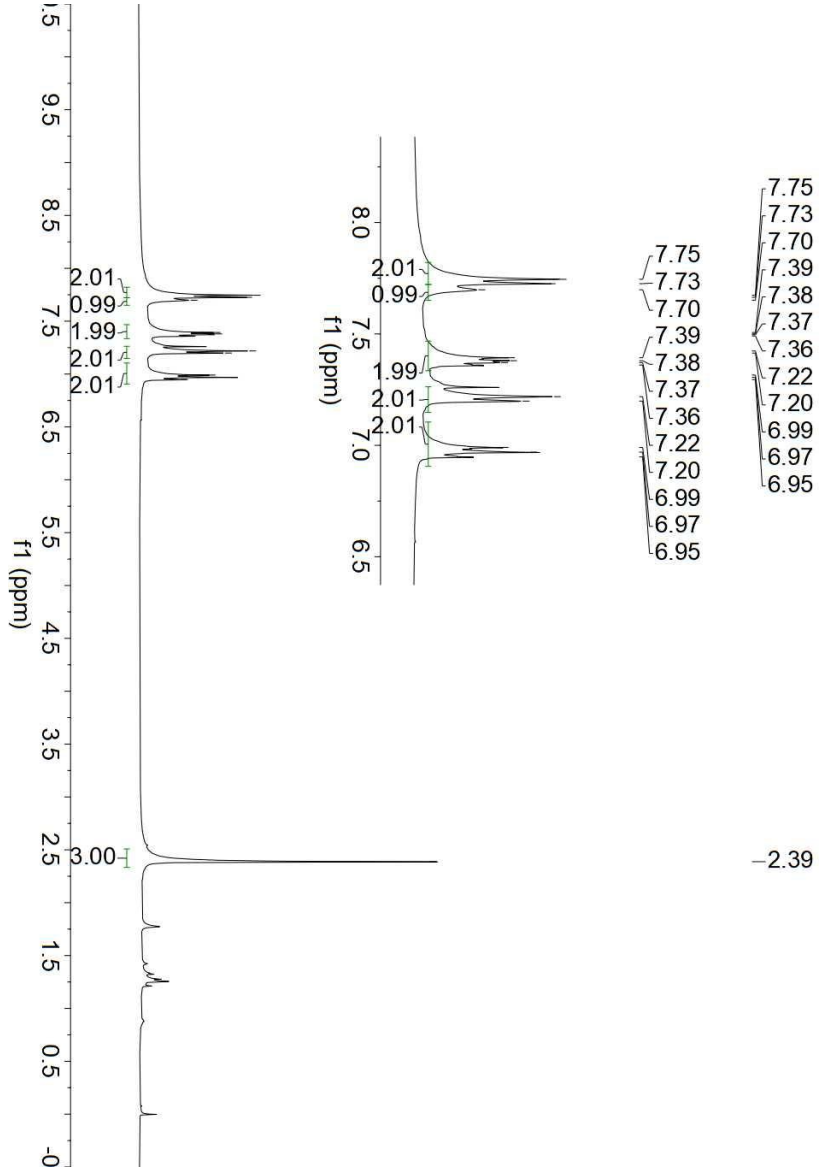
^{13}C NMR (100 MHz, Chloroform-*d*)



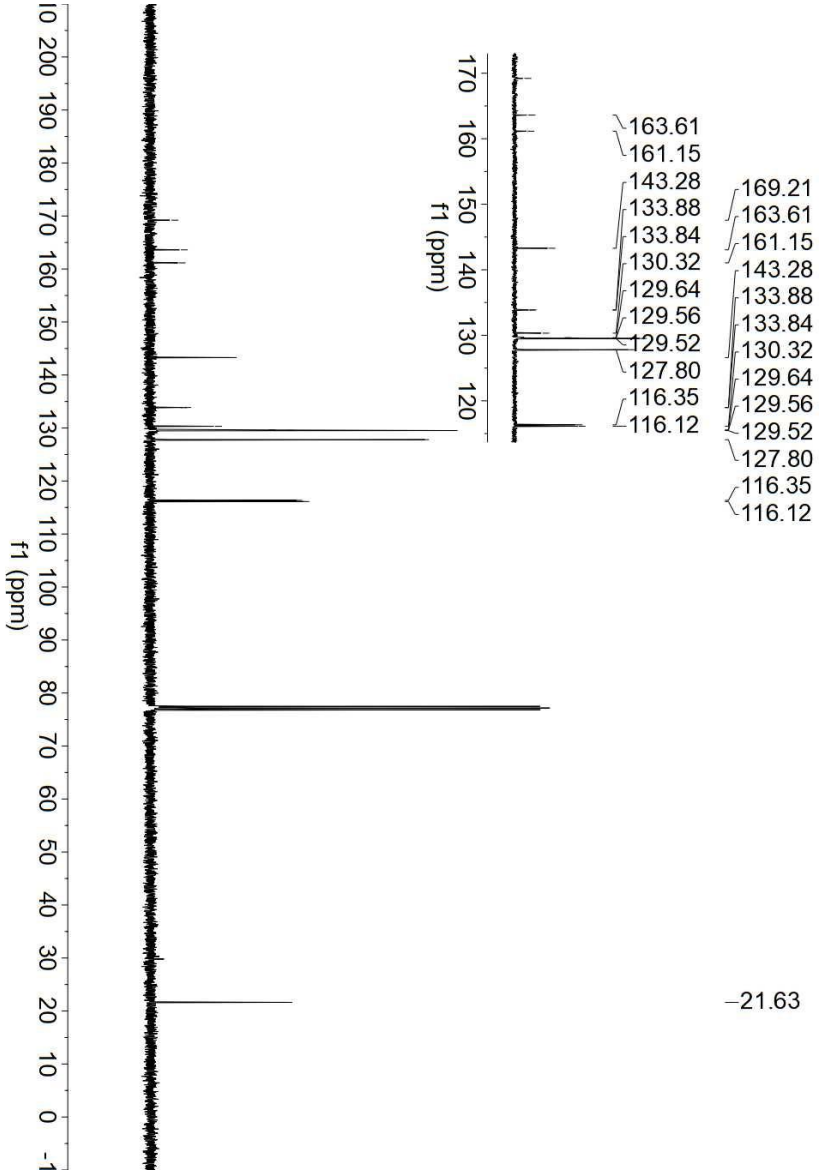


(1w)

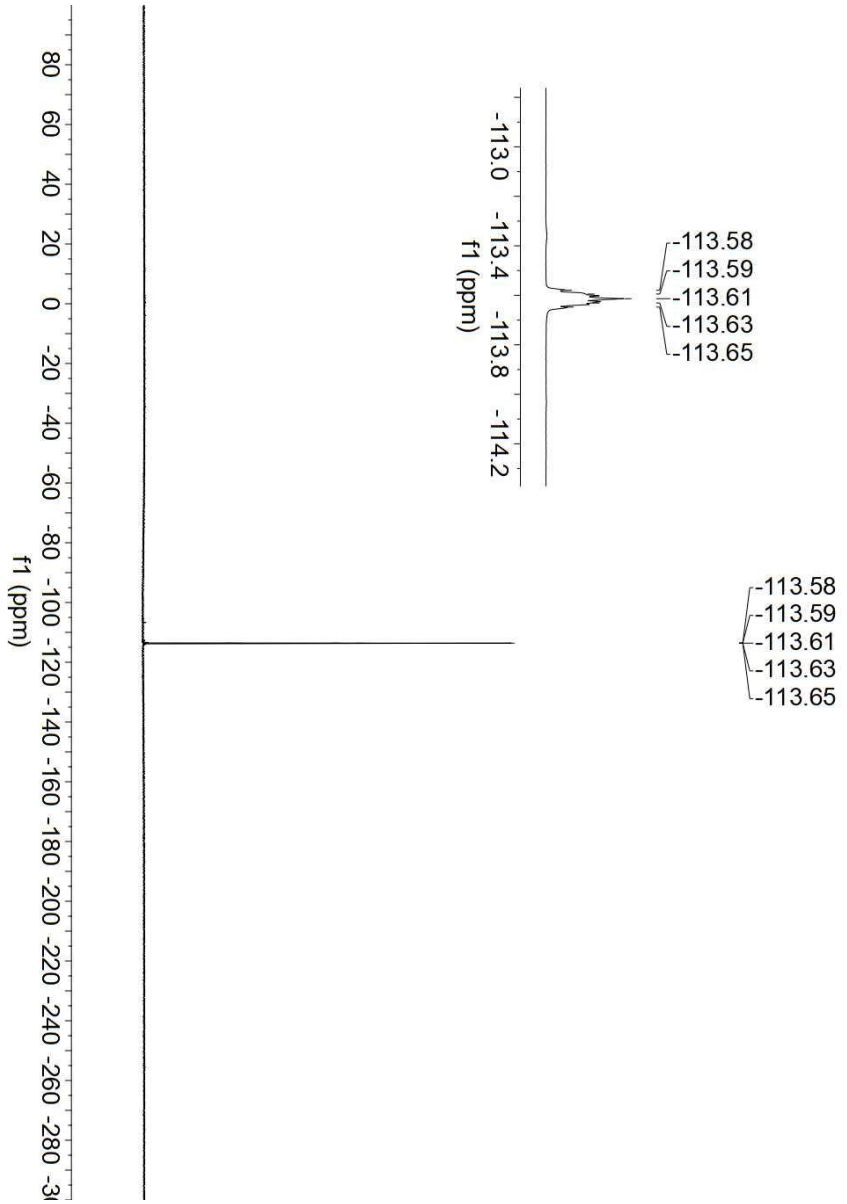
1H NMR (400 MHz, Chloroform-d)

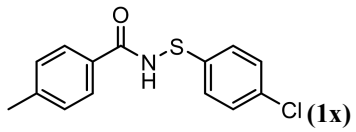


^{13}C NMR (100 MHz, Chloroform-*d*)



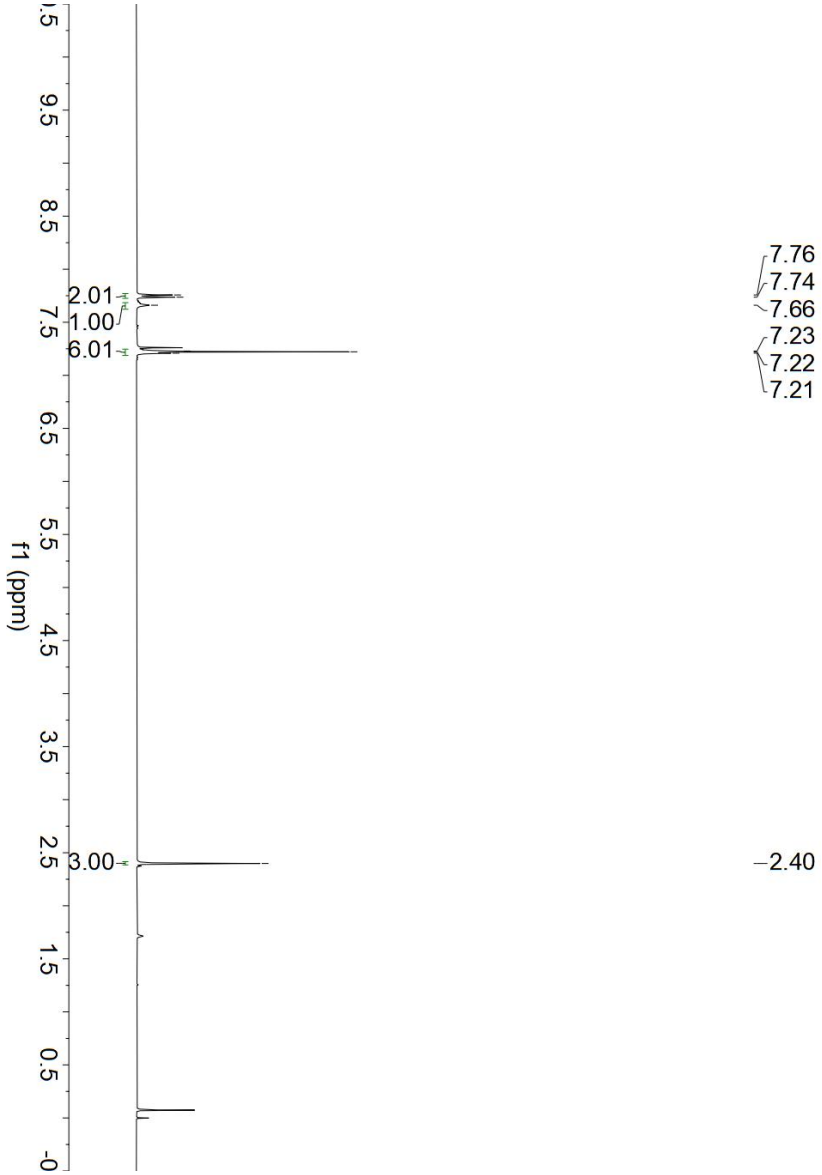
^{19}F NMR (376 MHz, Chloroform-*d*)



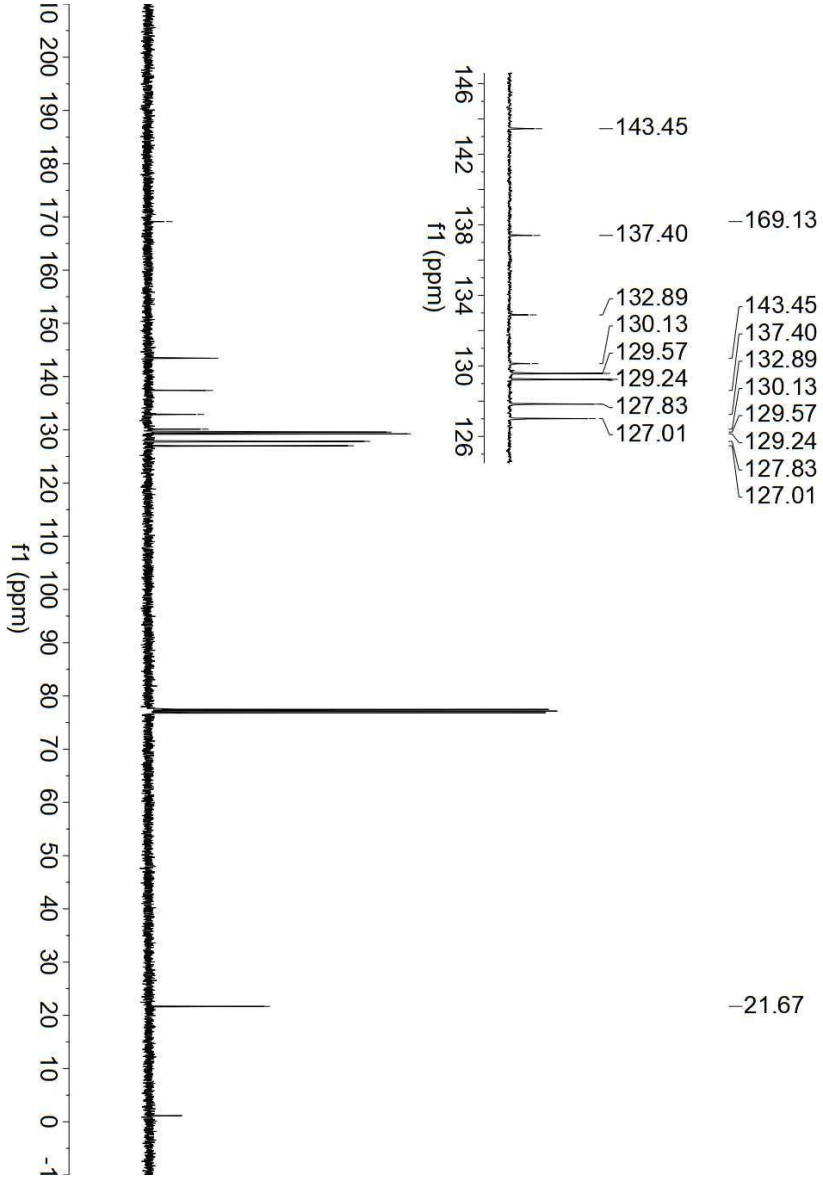


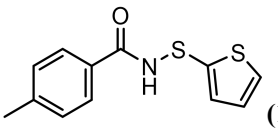
(1x)

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



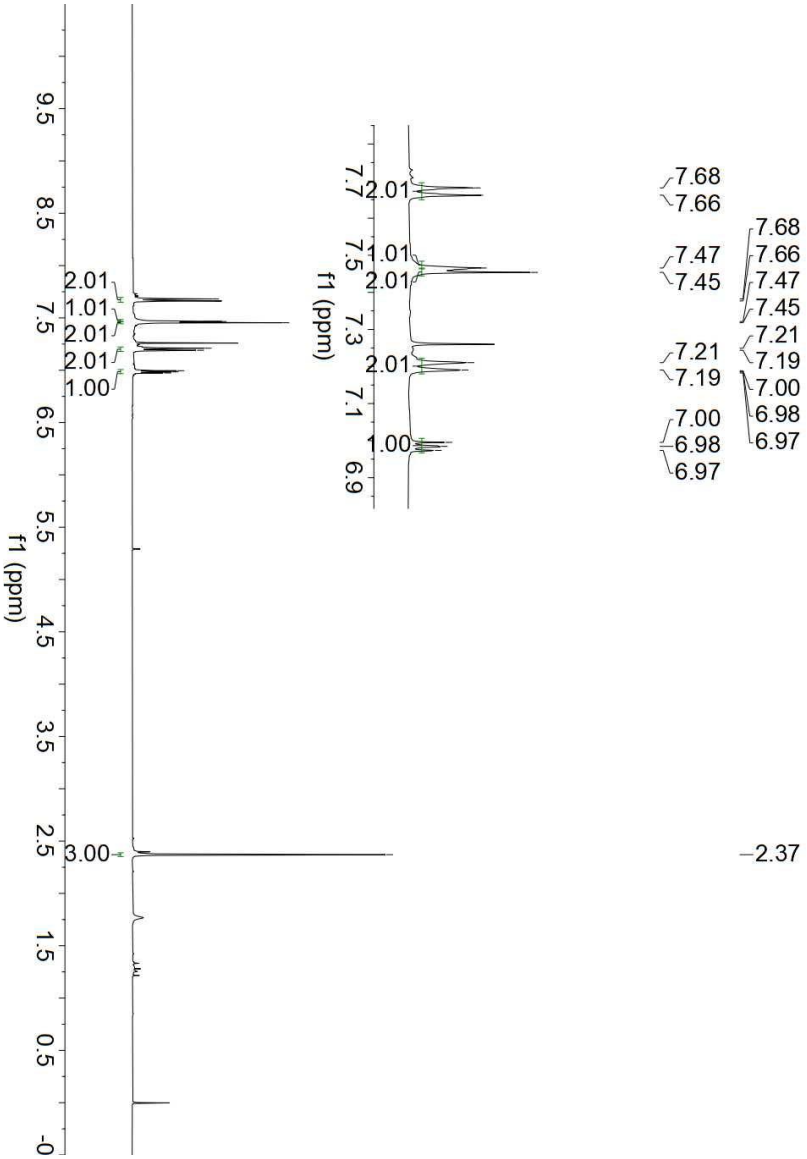
^{13}C NMR (100 MHz, Chloroform-*d*)



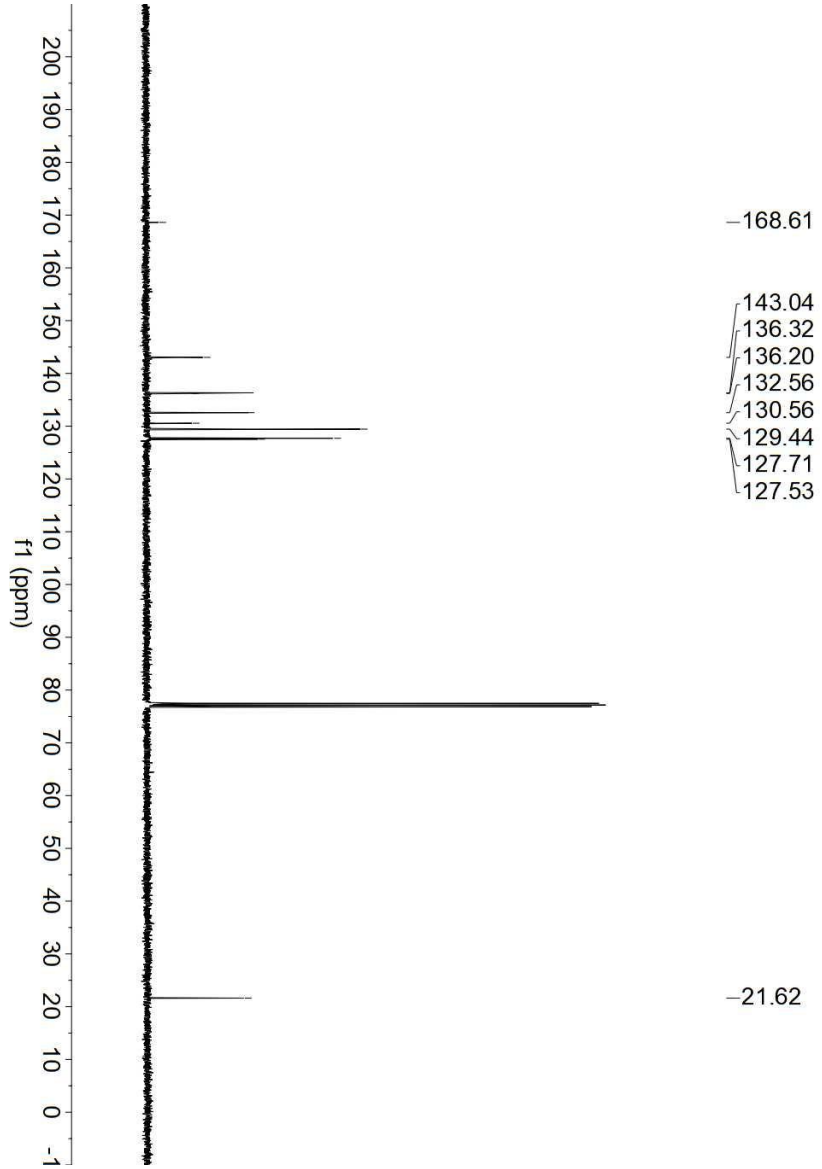


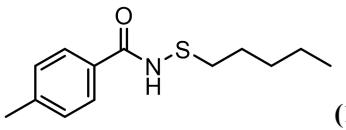
(1y)

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



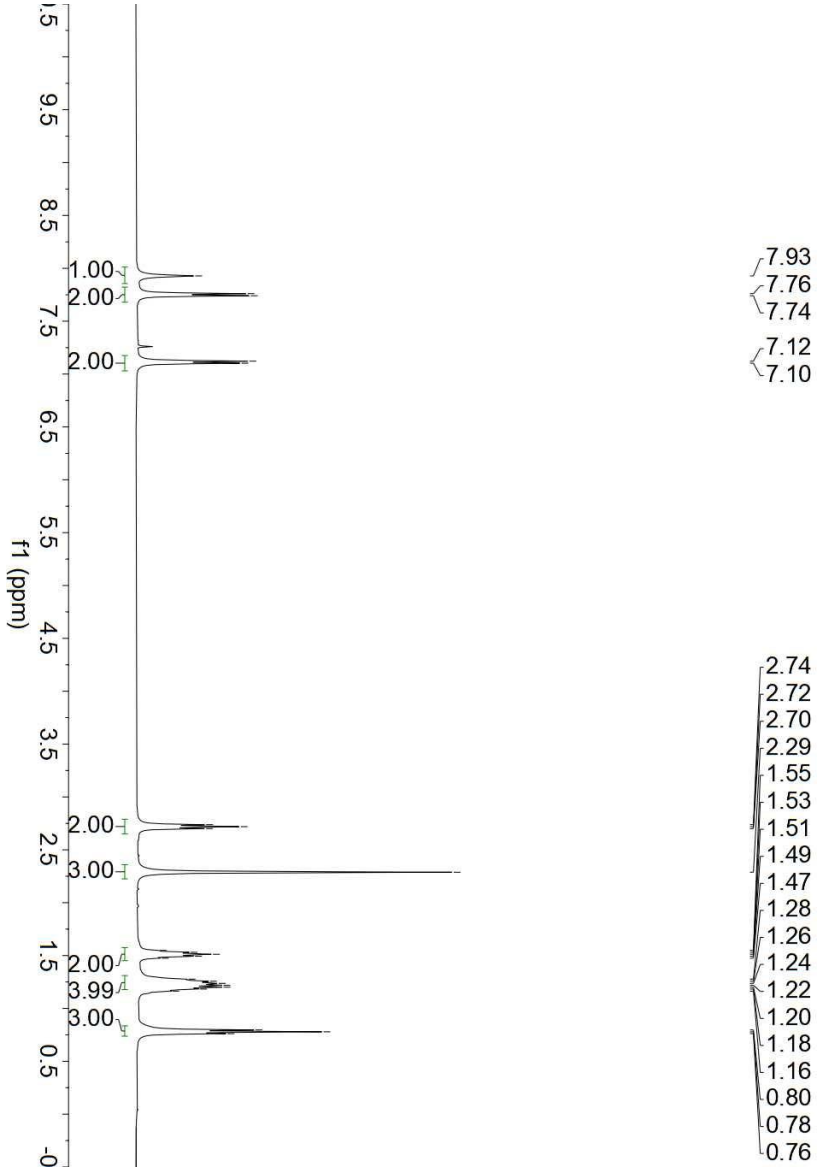
^{13}C NMR (100 MHz, Chloroform-*d*)



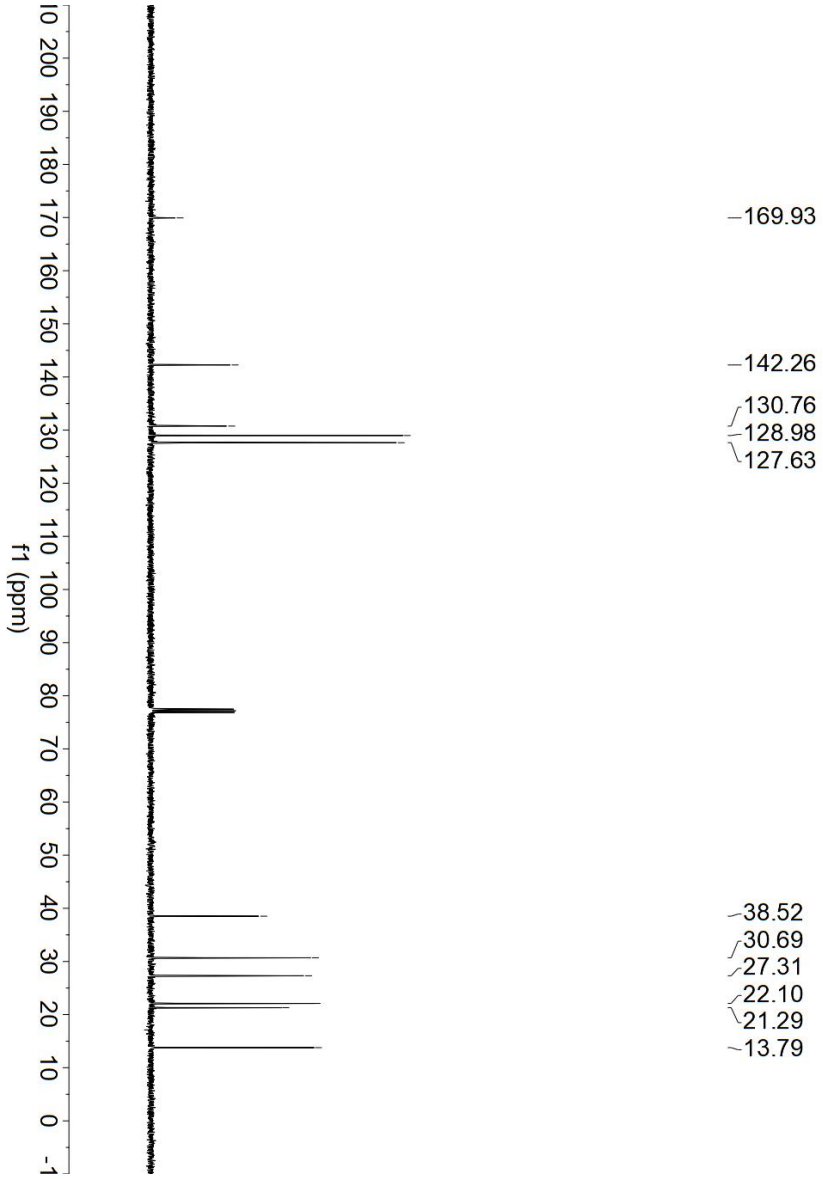


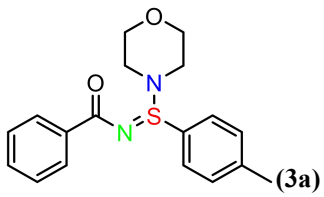
(1aa)

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

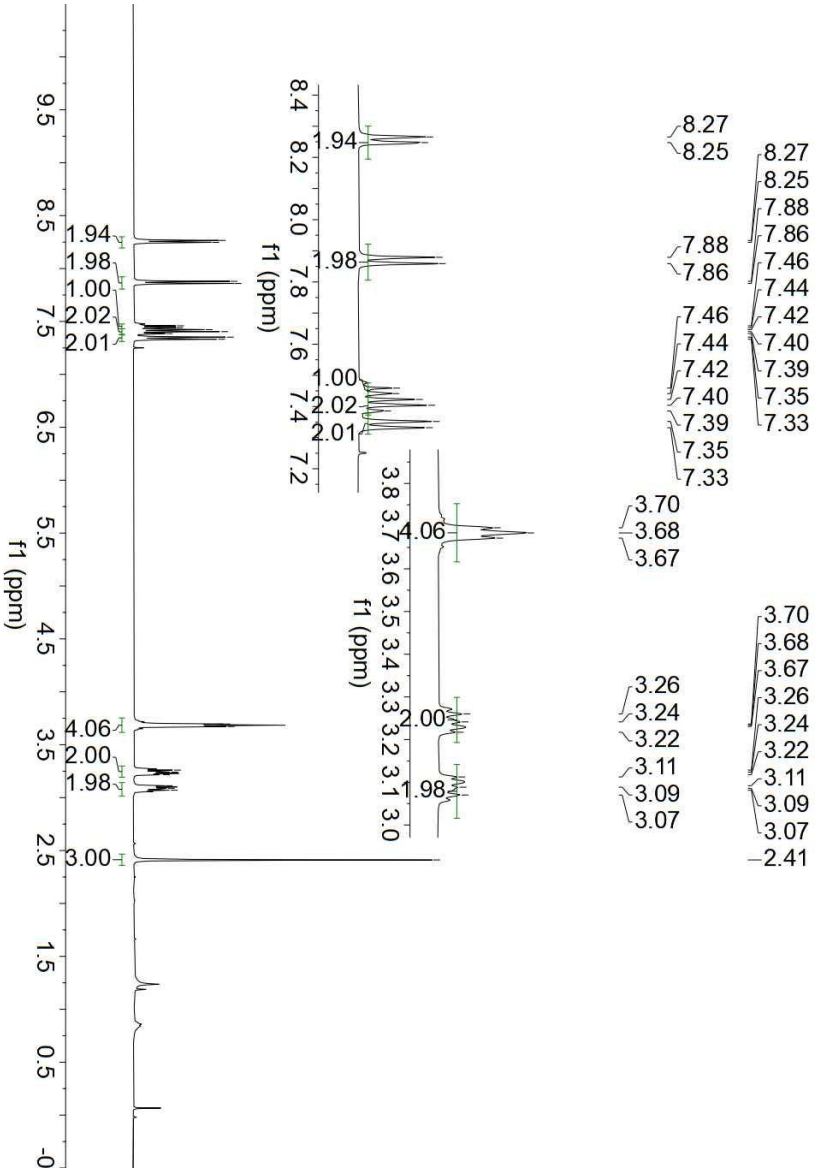


^{13}C NMR (100 MHz, Chloroform-*d*)

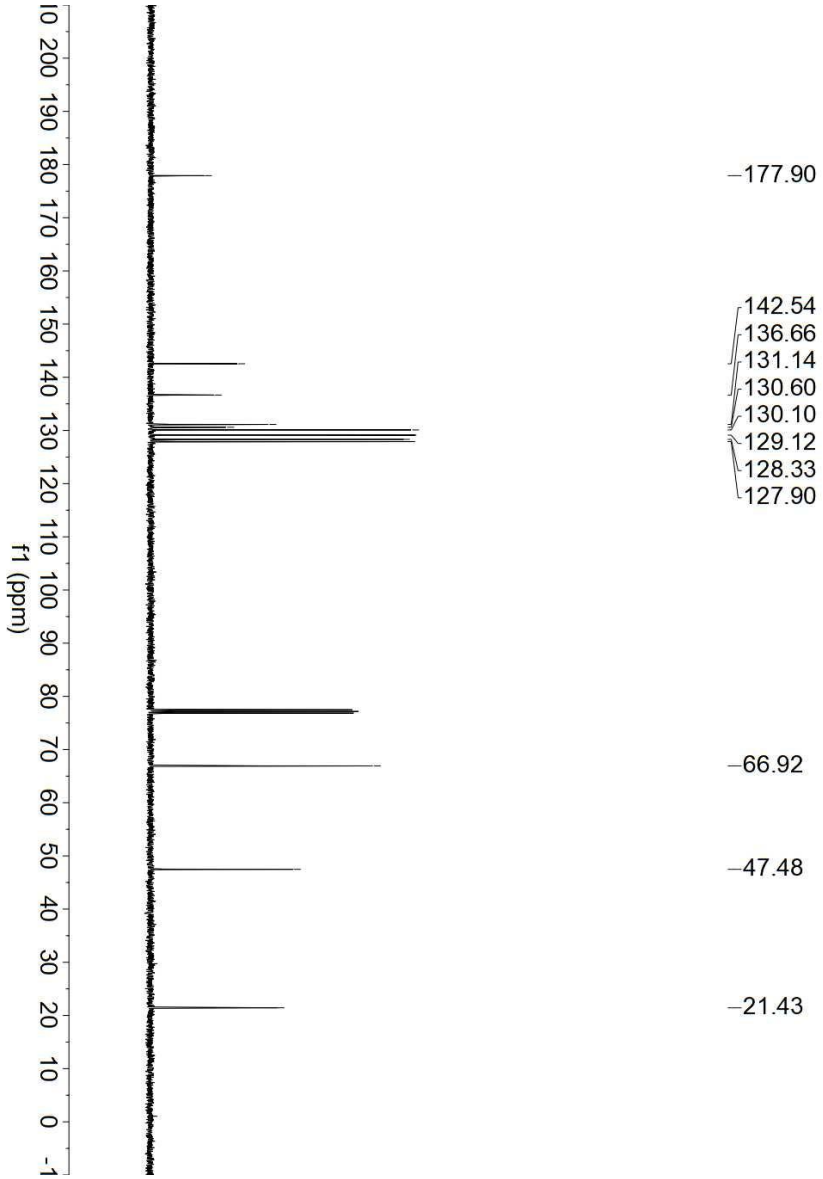


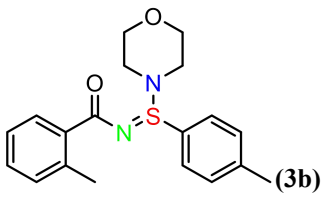


^{1}H NMR (400 MHz, Chloroform-*d*)



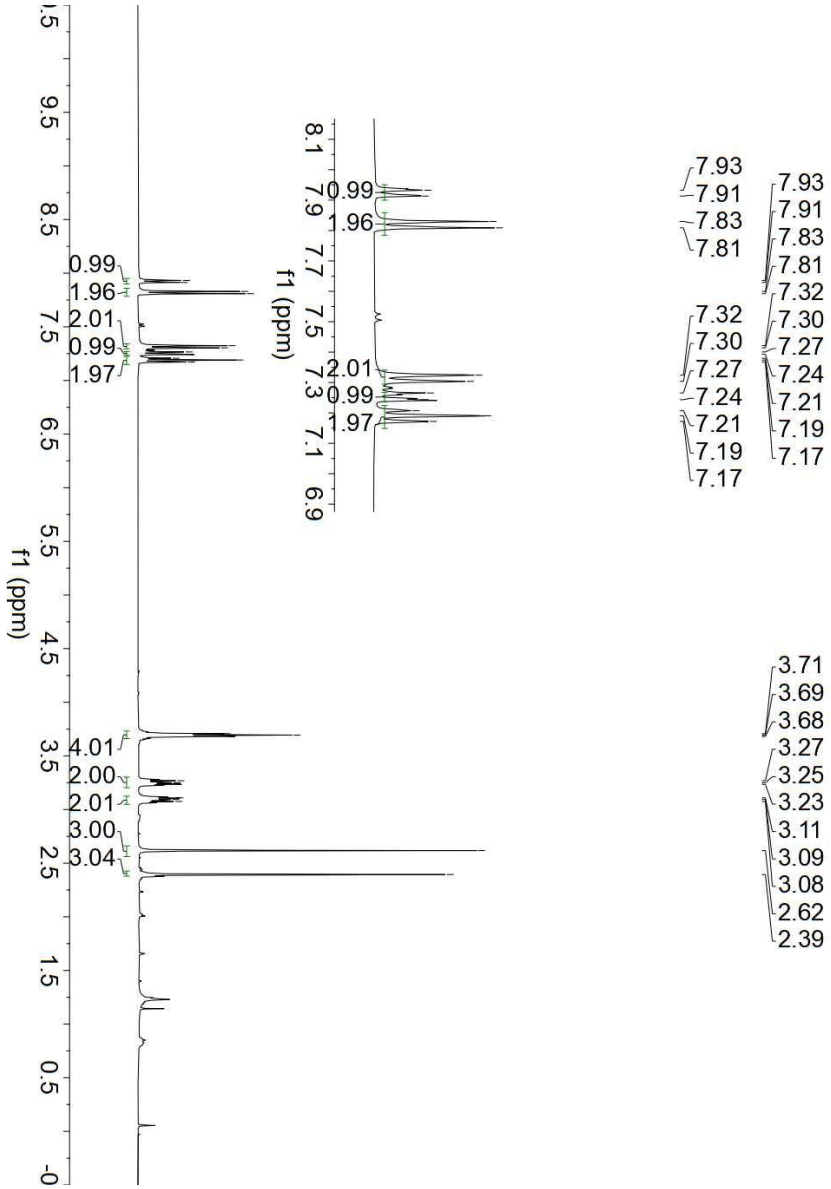
^{13}C NMR (100 MHz, Chloroform-*d*)



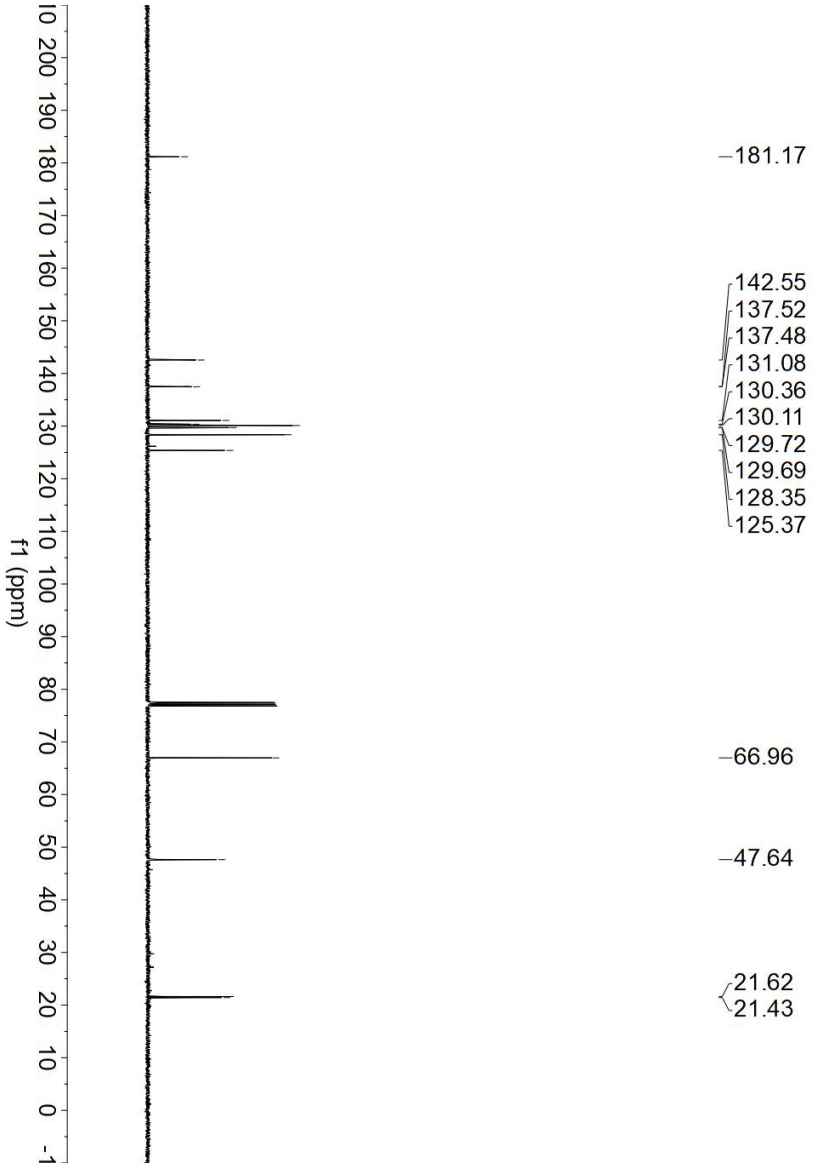


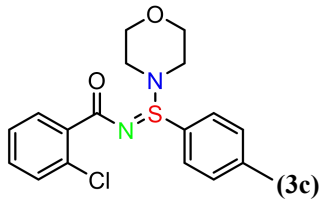
(3b)

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



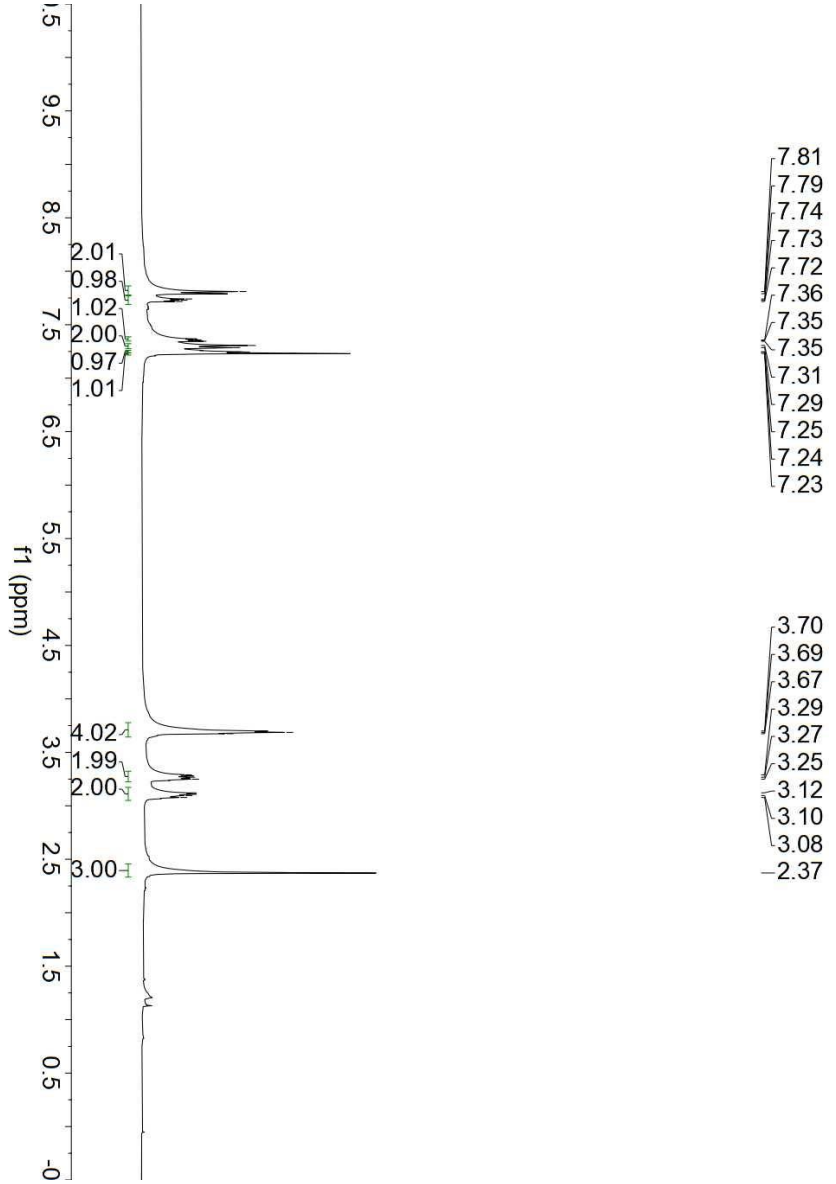
^{13}C NMR (100 MHz, Chloroform-*d*)

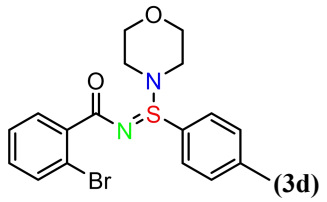




(3c)

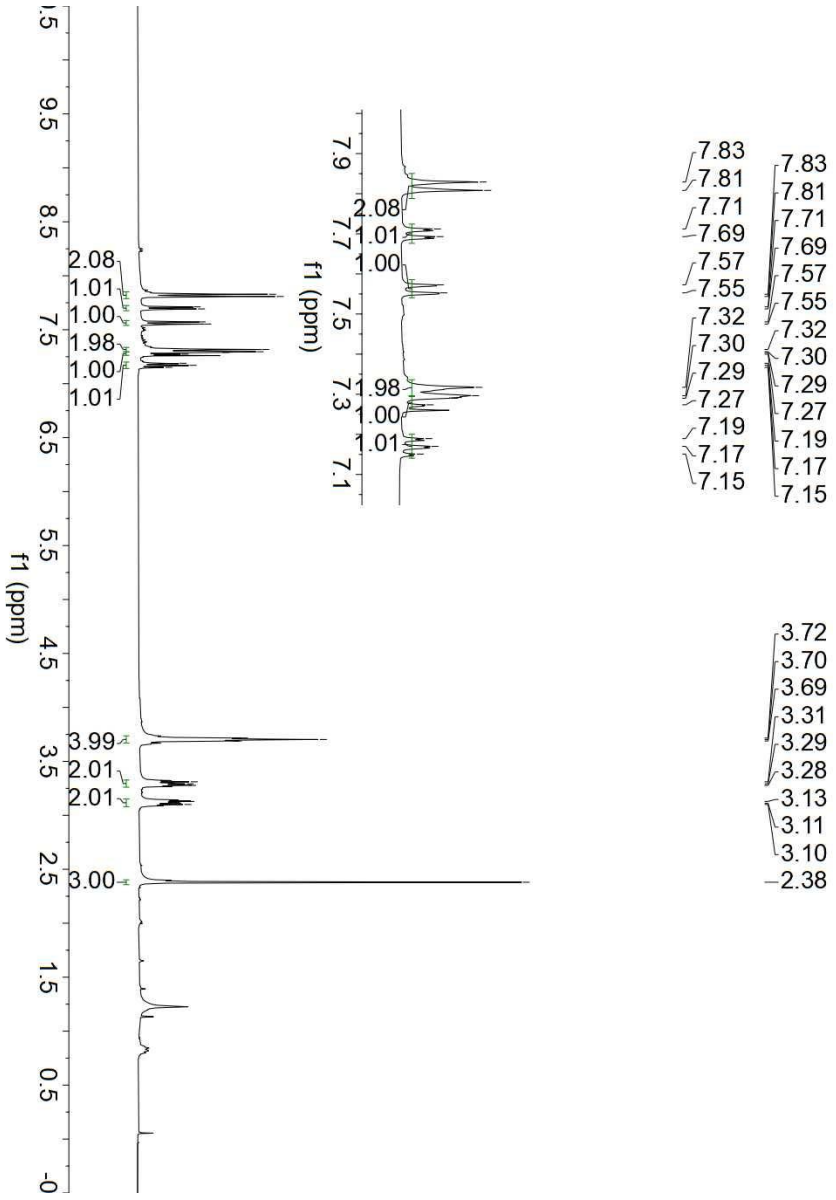
^{1}H NMR (400 MHz, Chloroform-*d*)



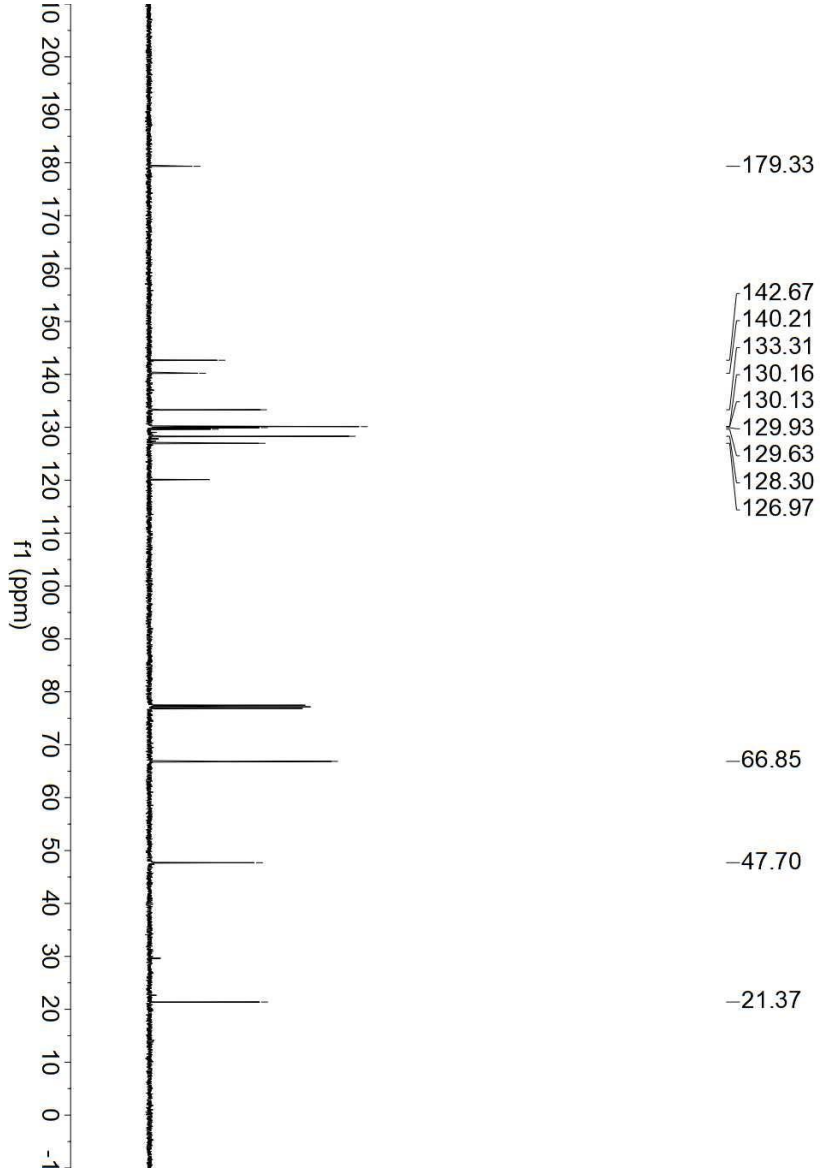


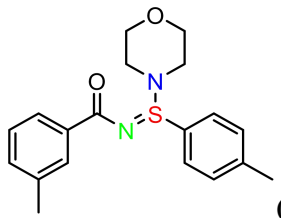
(3d)

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



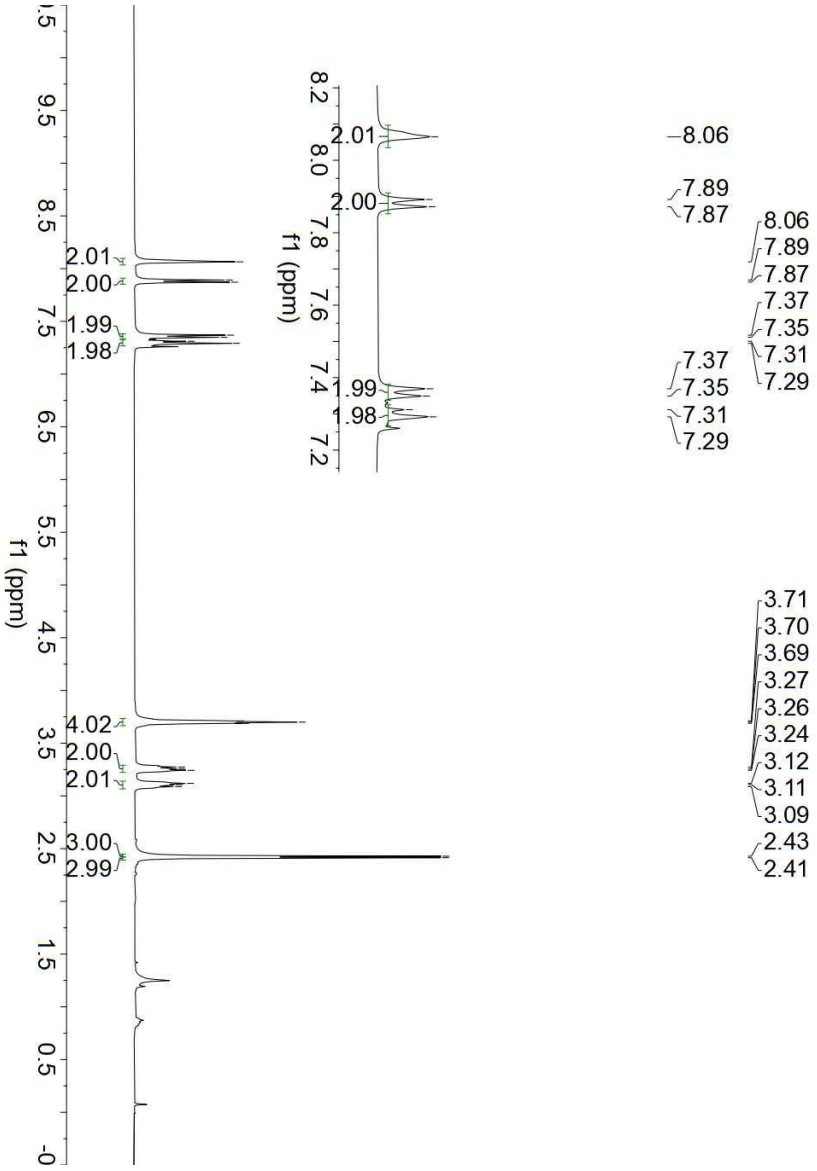
^{13}C NMR (100 MHz, Chloroform-*d*)



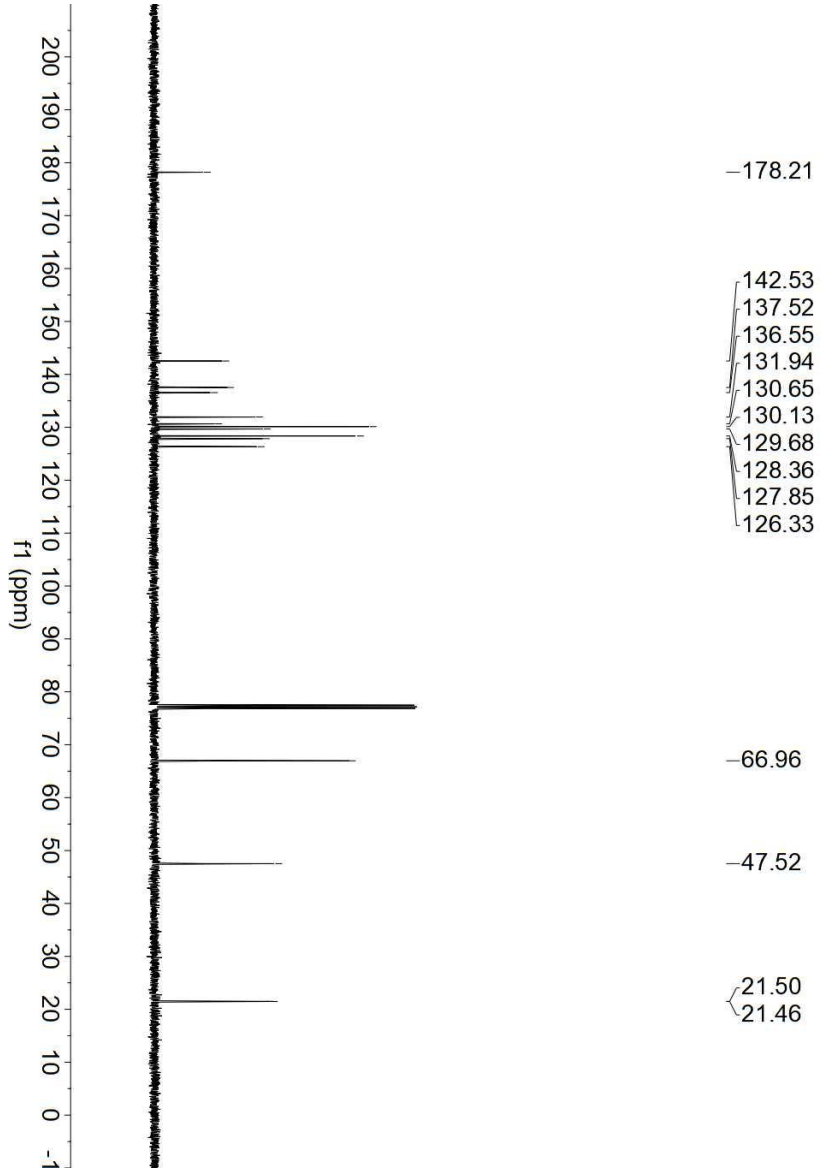


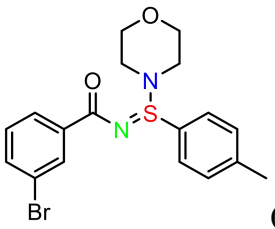
(3e)

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



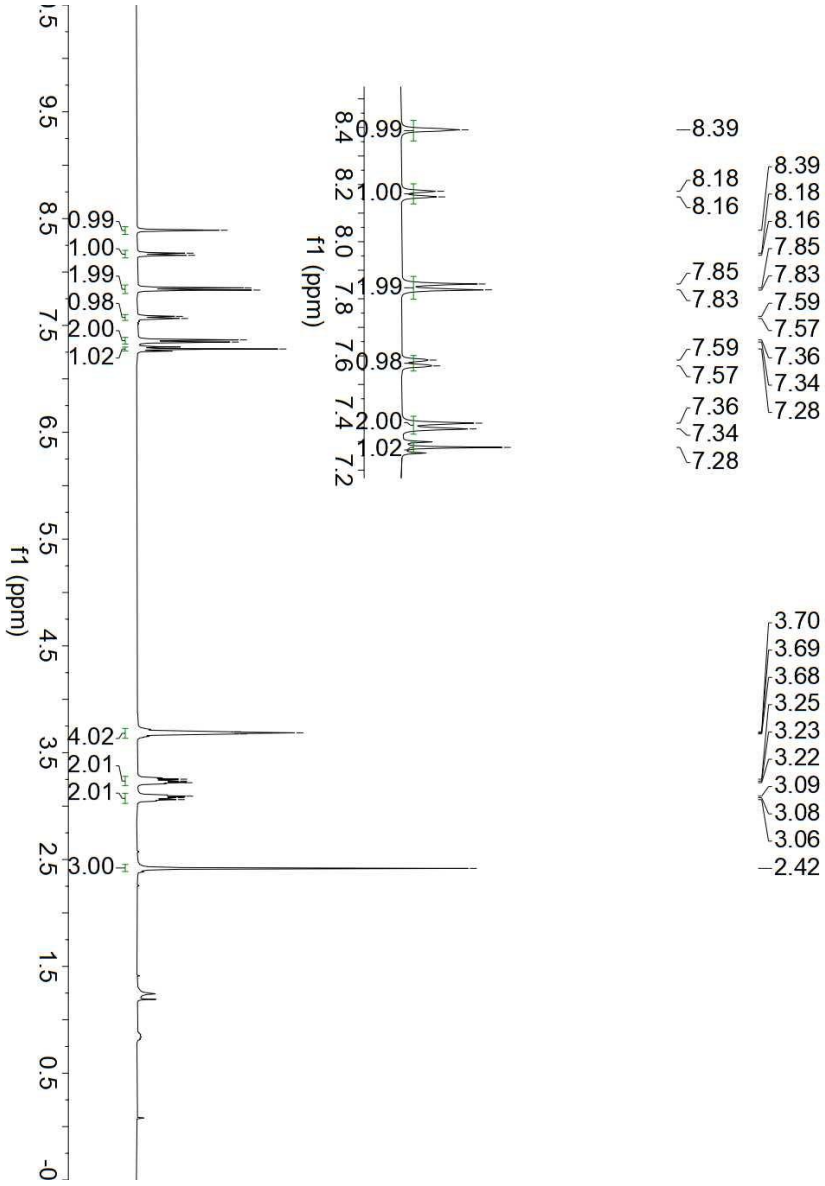
^{13}C NMR (100 MHz, Chloroform-*d*)



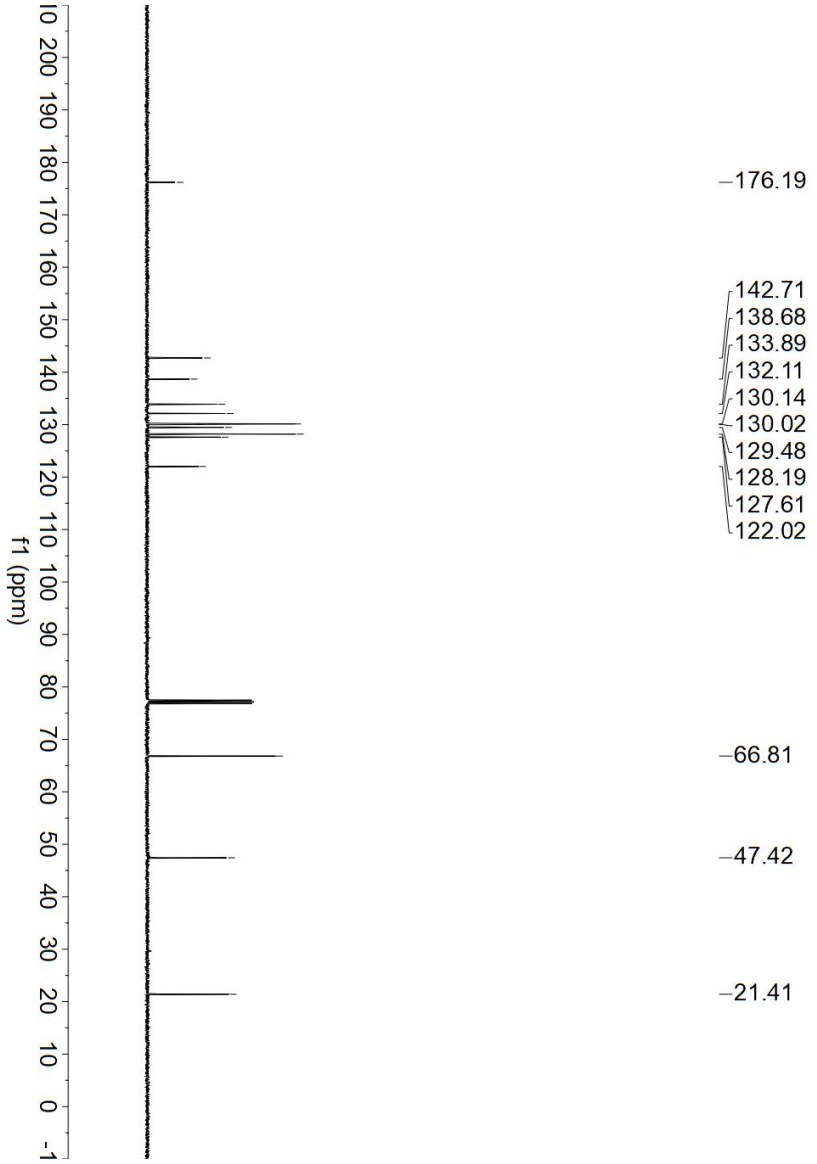


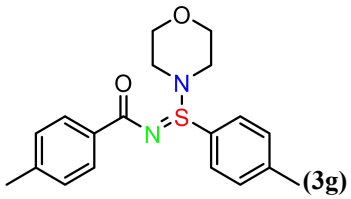
(3f)

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



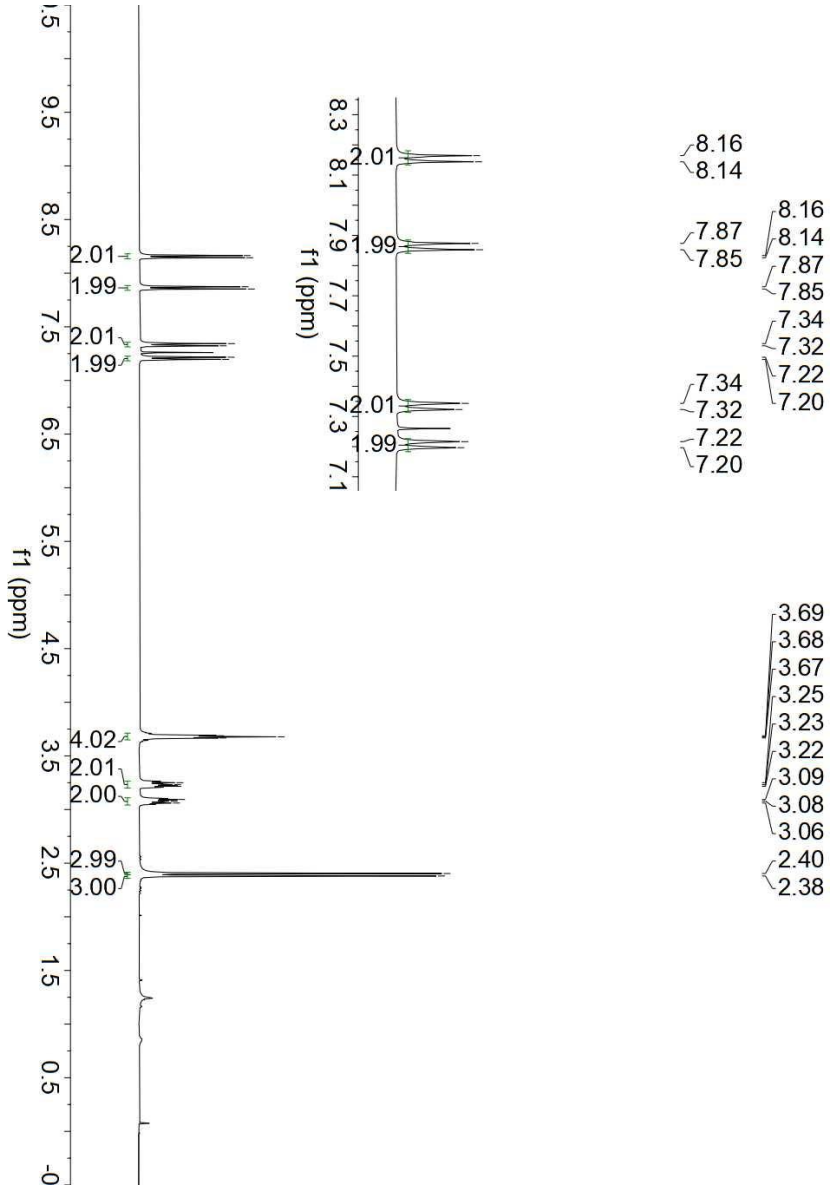
^{13}C NMR (100 MHz, Chloroform-*d*)

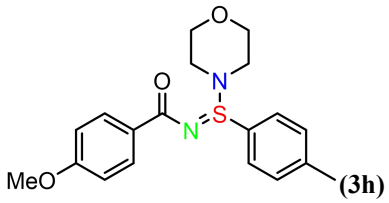




(3g)

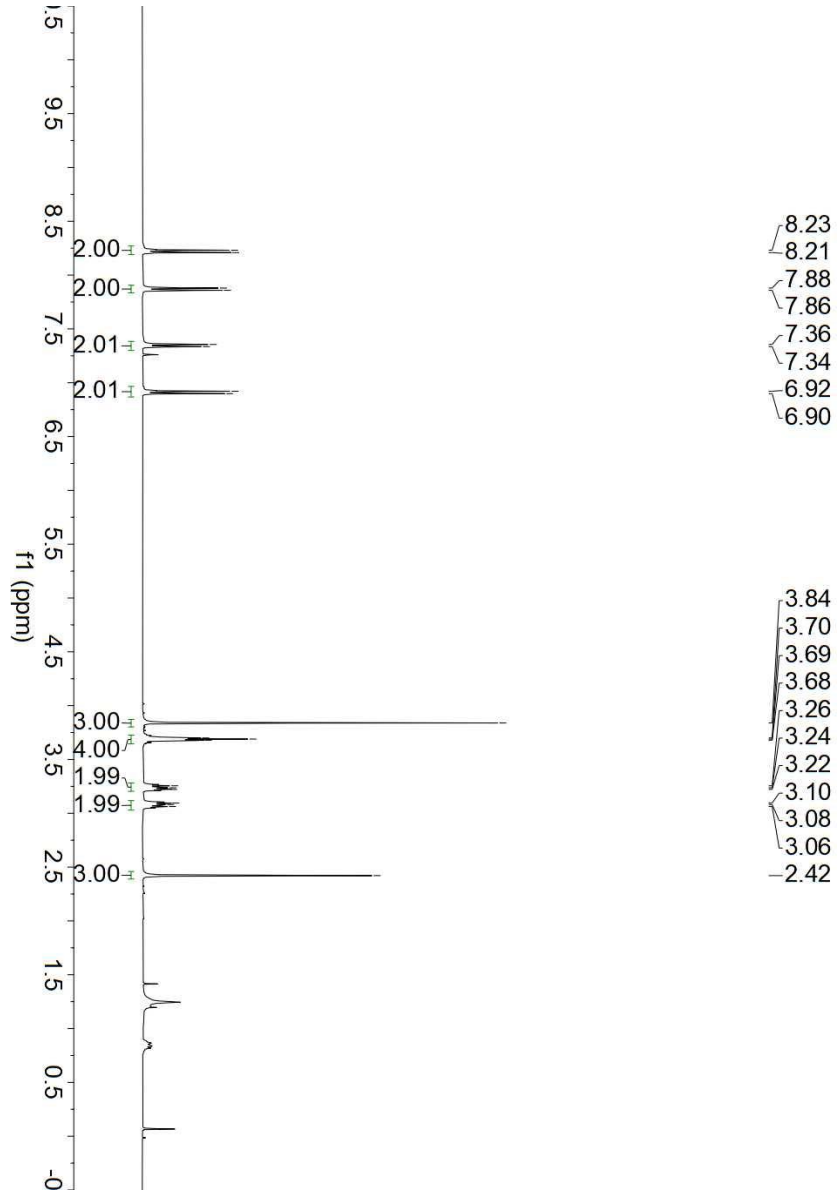
^{1}H NMR (400 MHz, Chloroform-*d*)

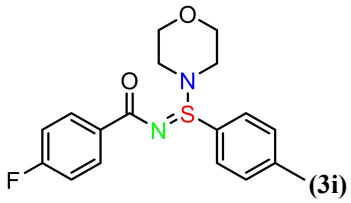




(3h)

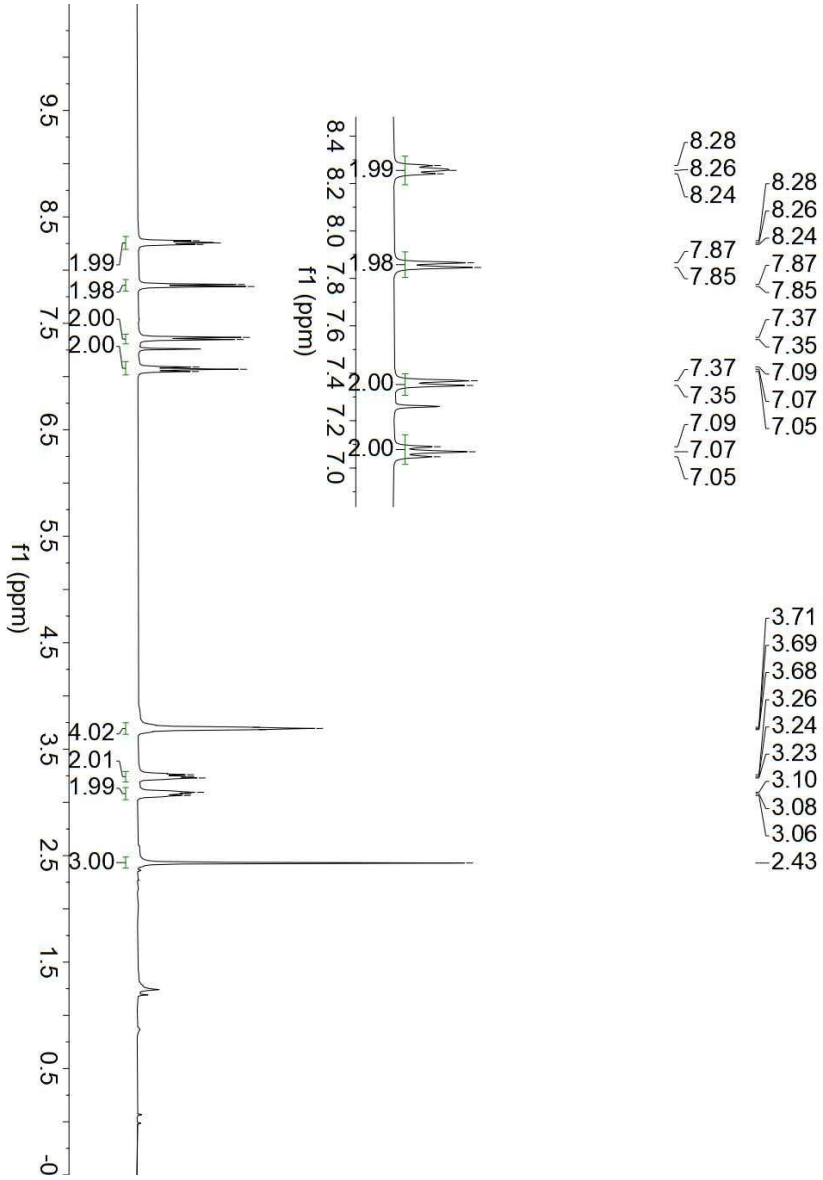
^{1}H NMR (400 MHz, Chloroform-*d*)



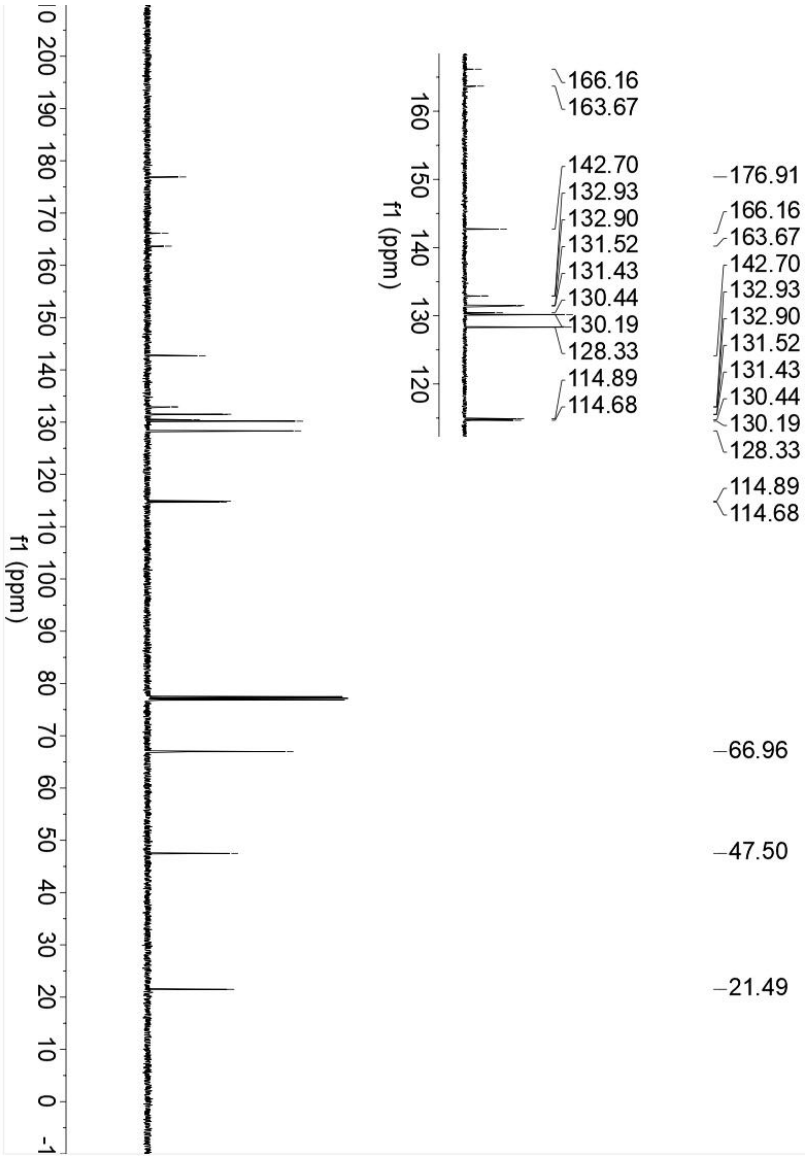


(3i)

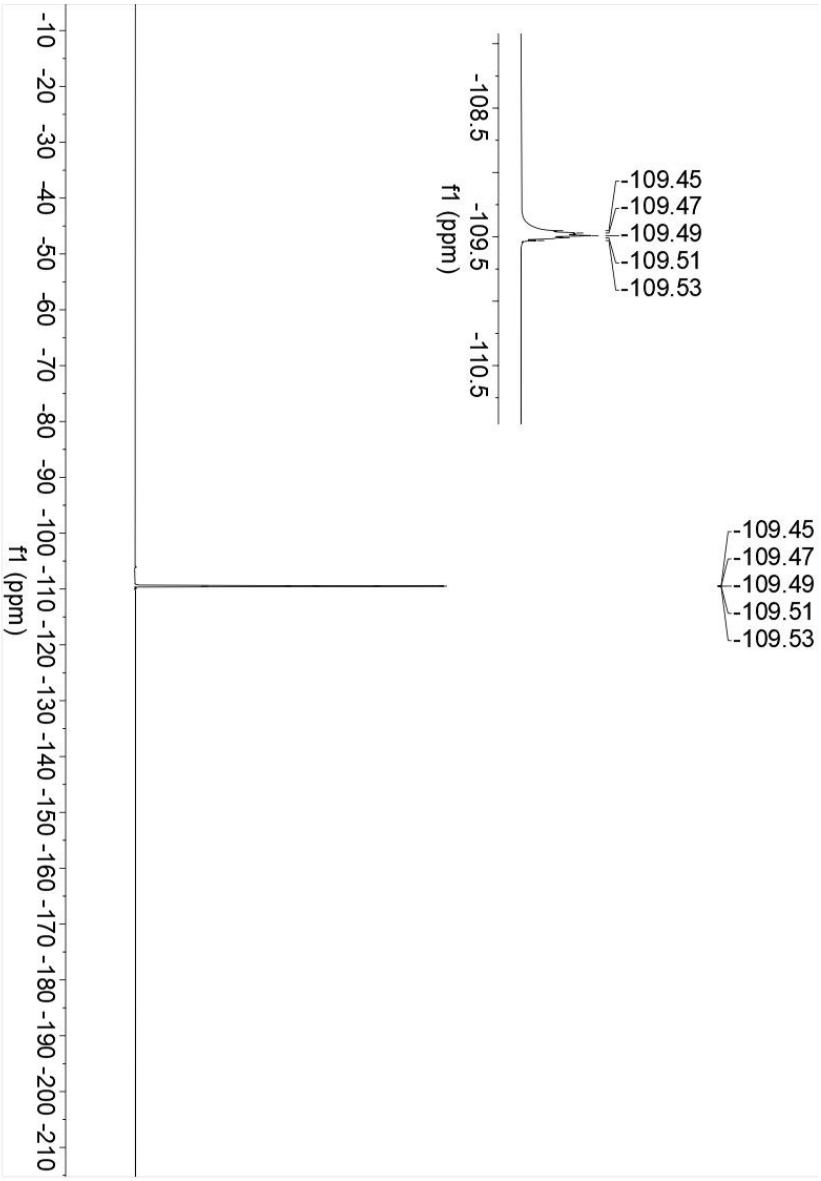
^{1}H NMR (400 MHz, Chloroform-*d*)

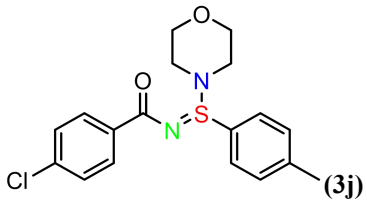


^{13}C NMR (100 MHz, Chloroform-*d*)



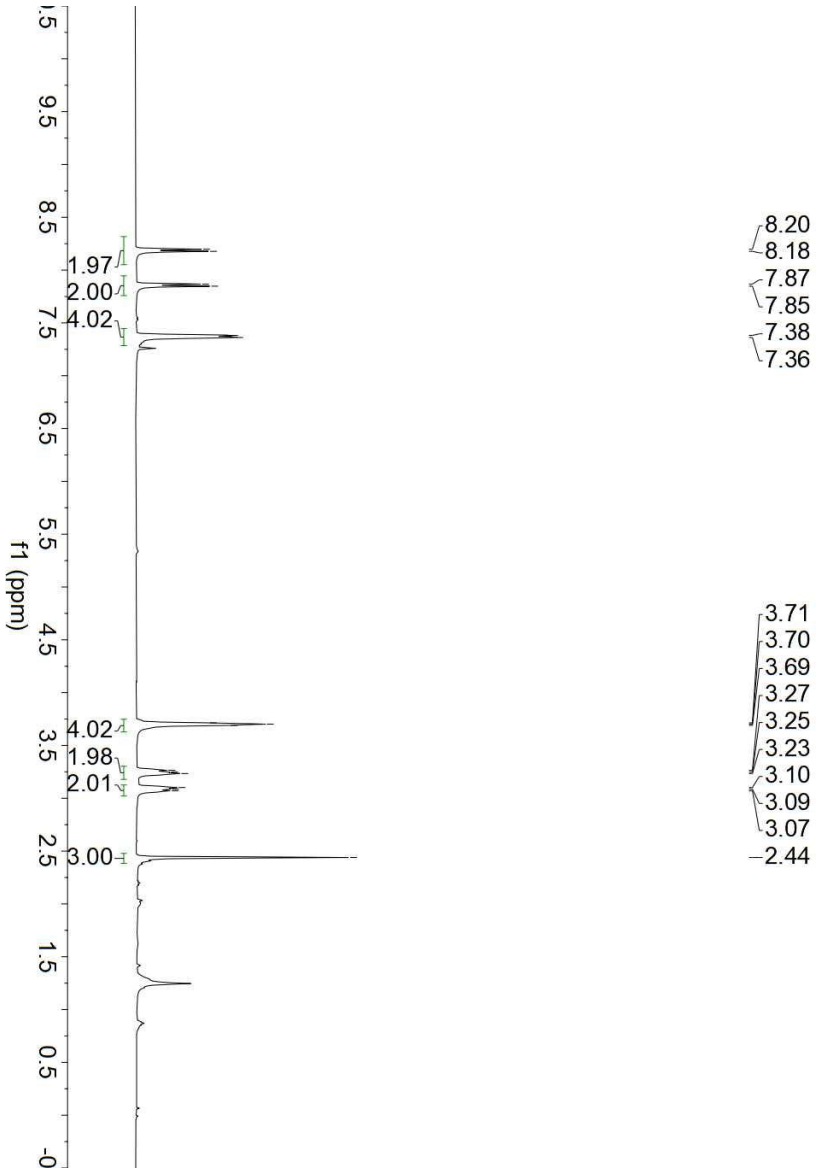
^{19}F NMR (376 MHz, Chloroform-*d*)



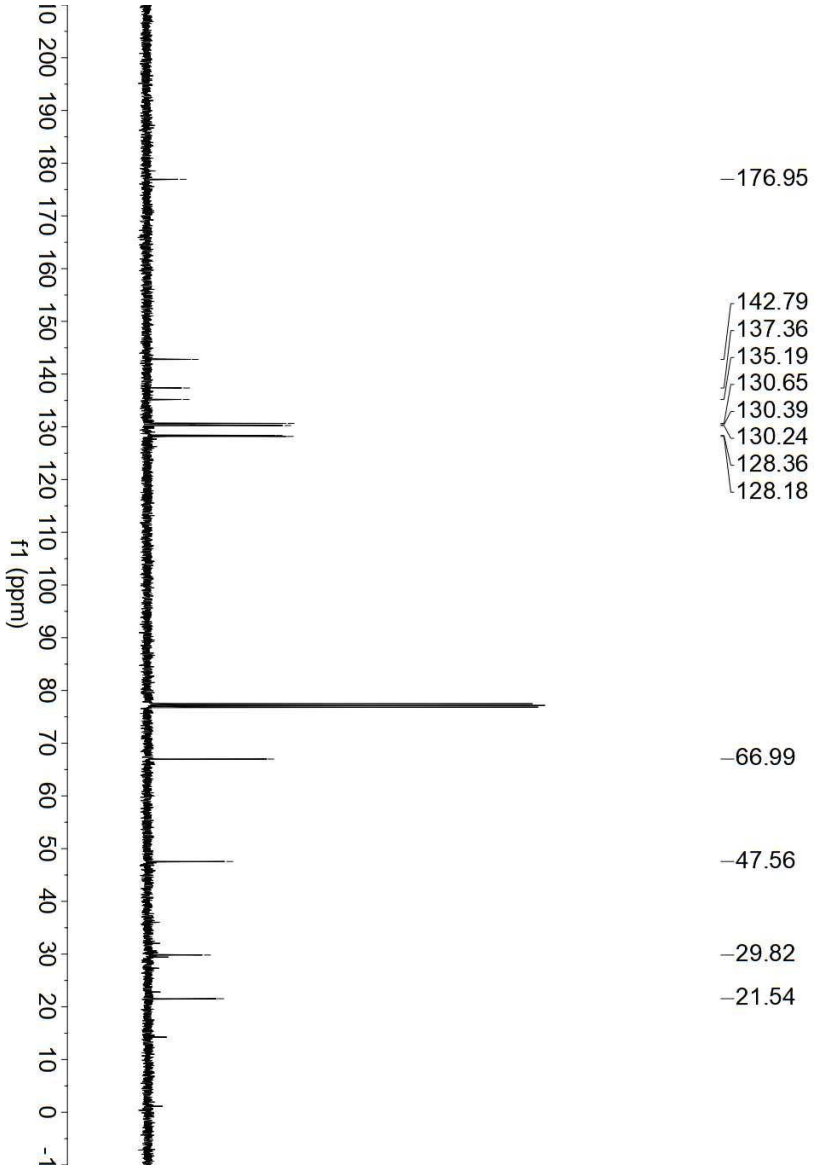


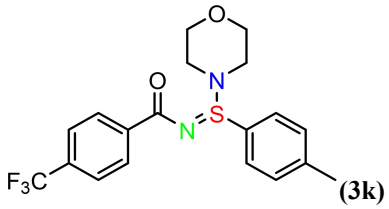
(3j)

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



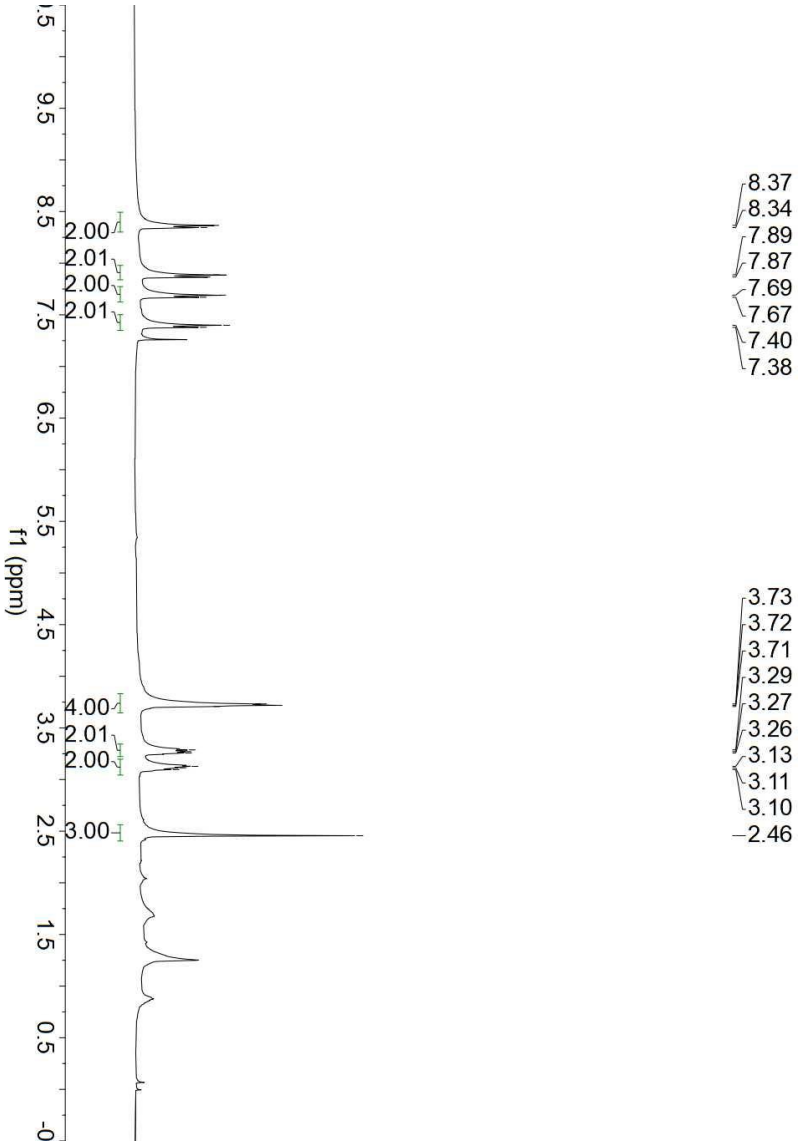
^{13}C NMR (100 MHz, Chloroform-*d*)



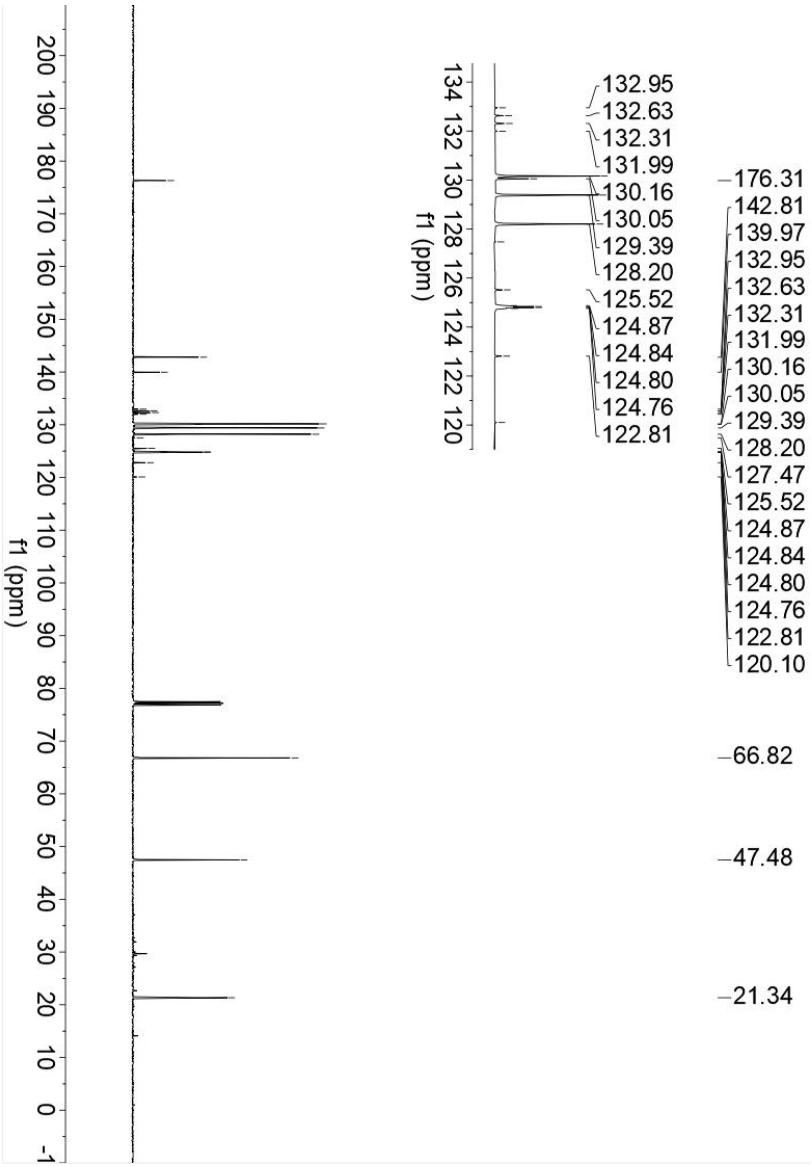


(3k)

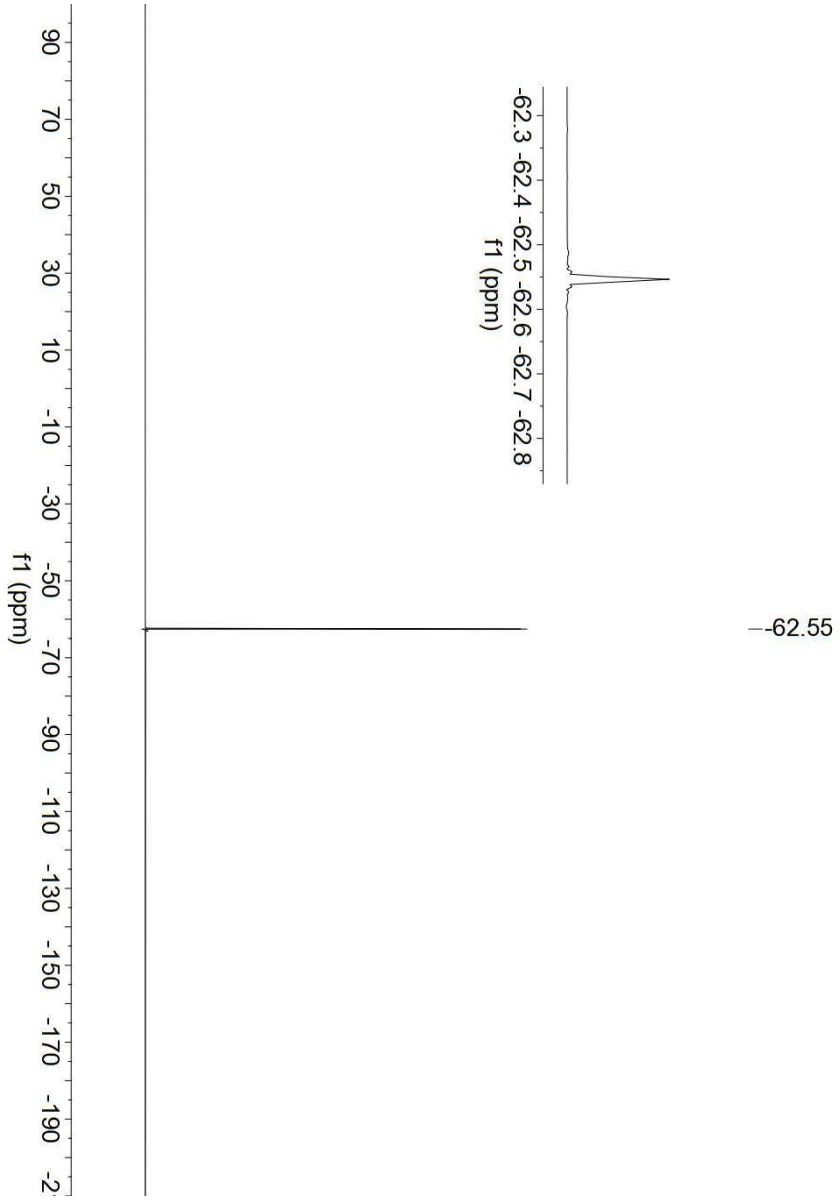
^{1}H NMR (400 MHz, Chloroform-*d*)

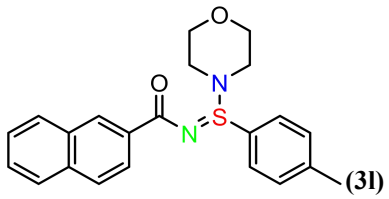


^{13}C NMR (100 MHz, Chloroform-*d*)



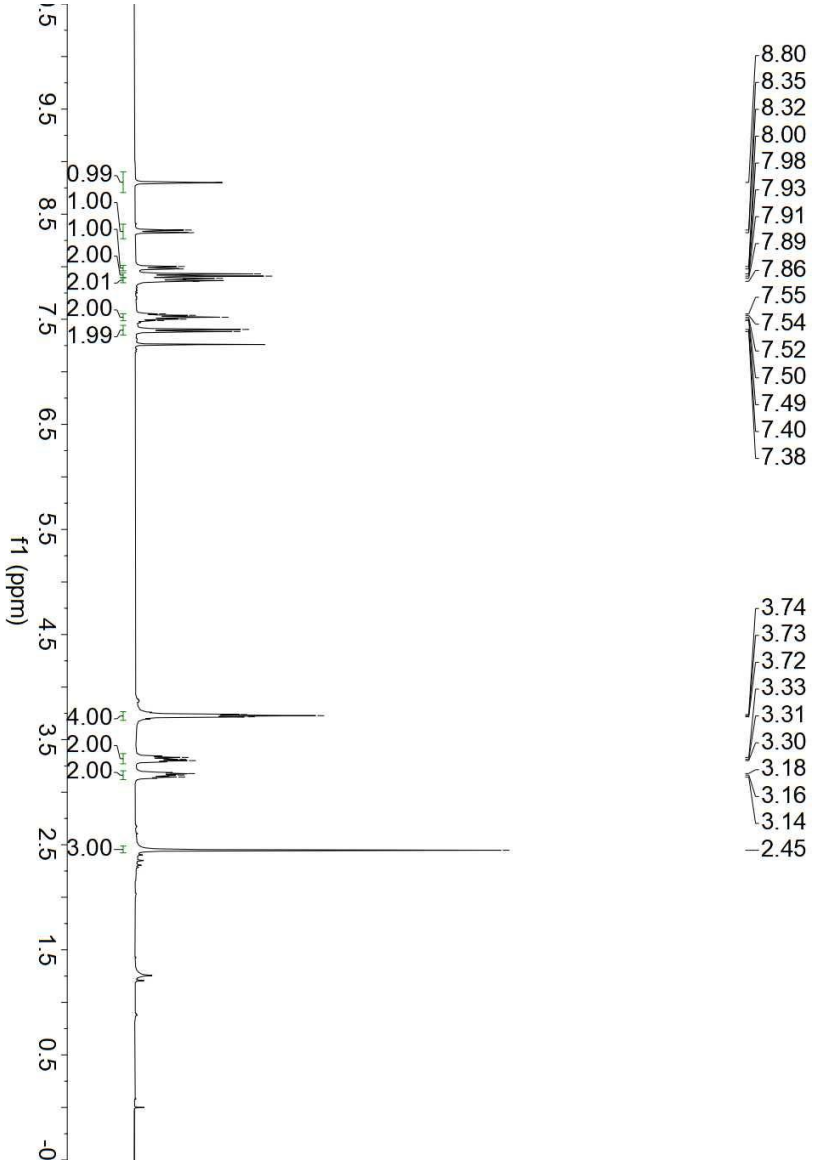
^{19}F NMR (376 MHz, Chloroform-*d*)

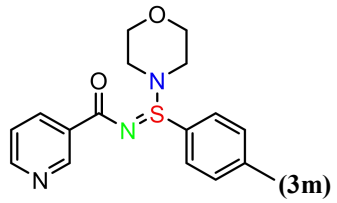




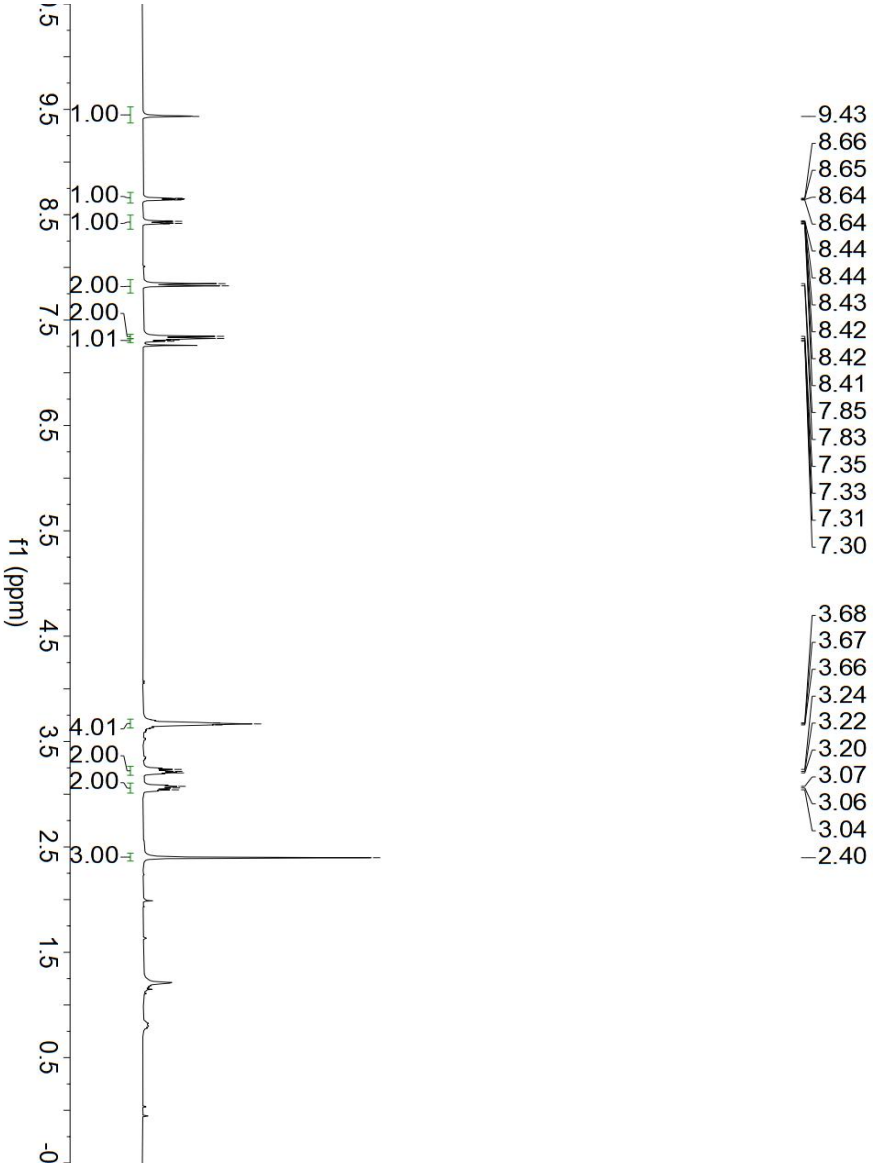
(3l)

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

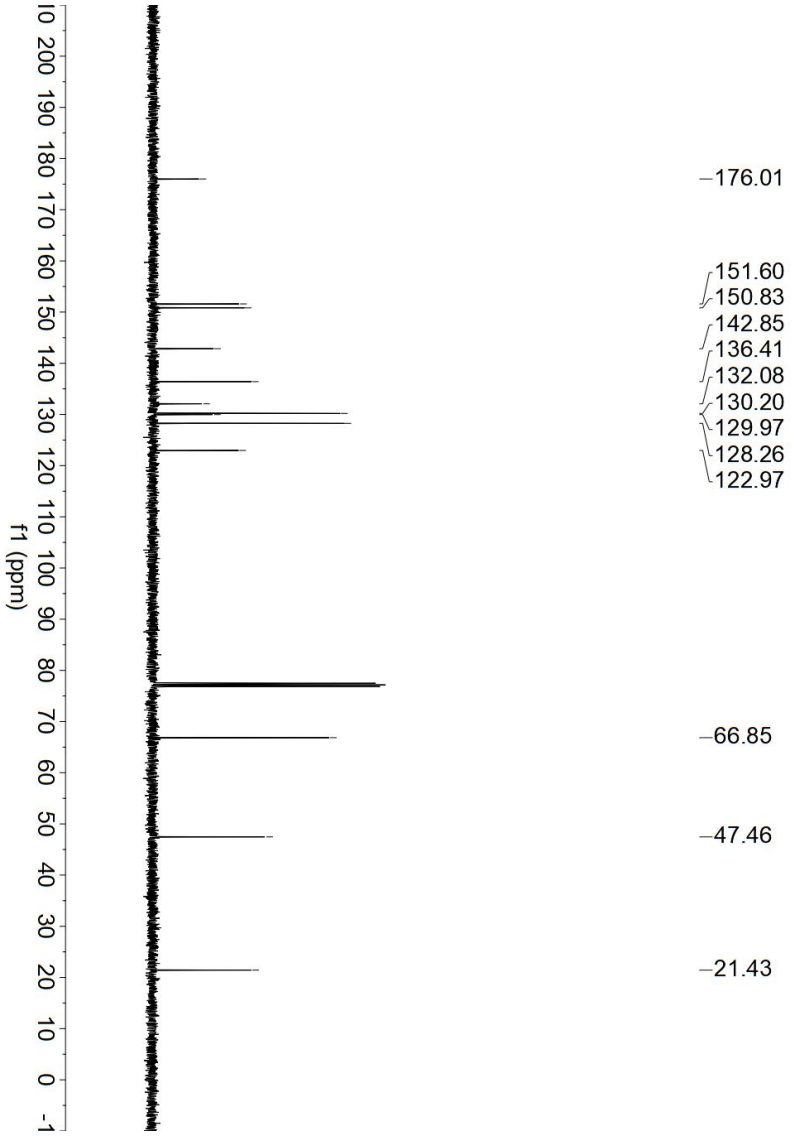


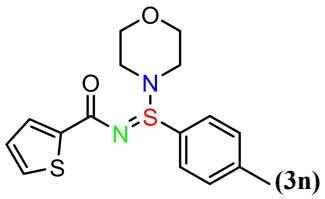


^{1}H NMR (400 MHz, Chloroform-*d*)



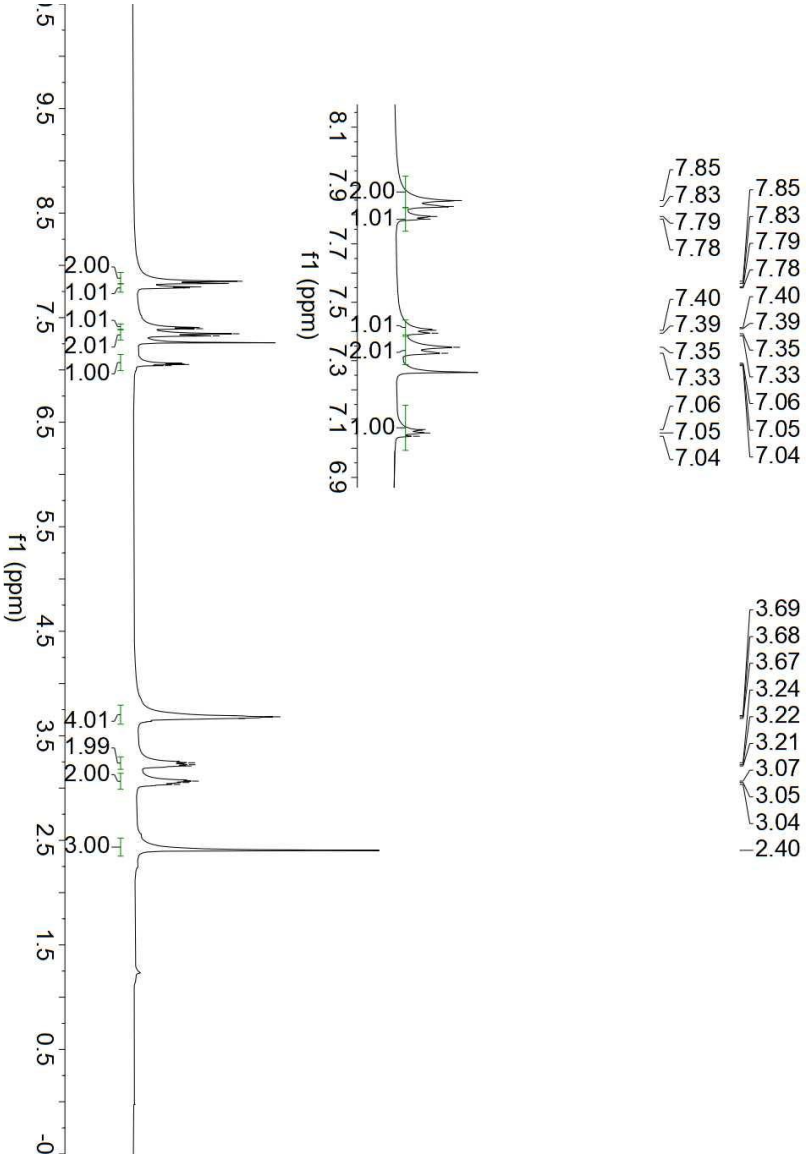
^{13}C NMR (100 MHz, Chloroform-*d*)



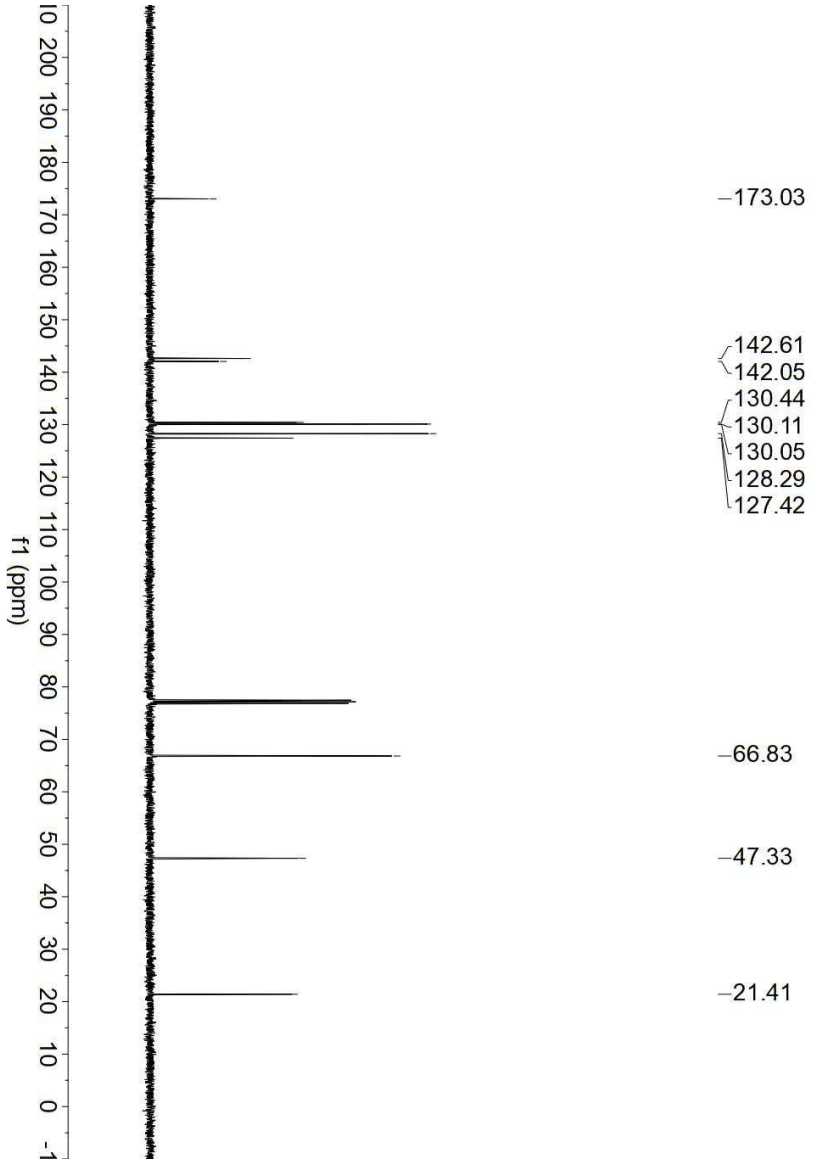


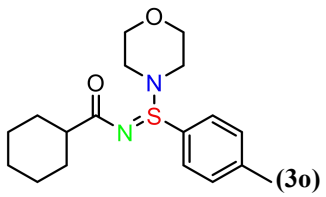
(3n)

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



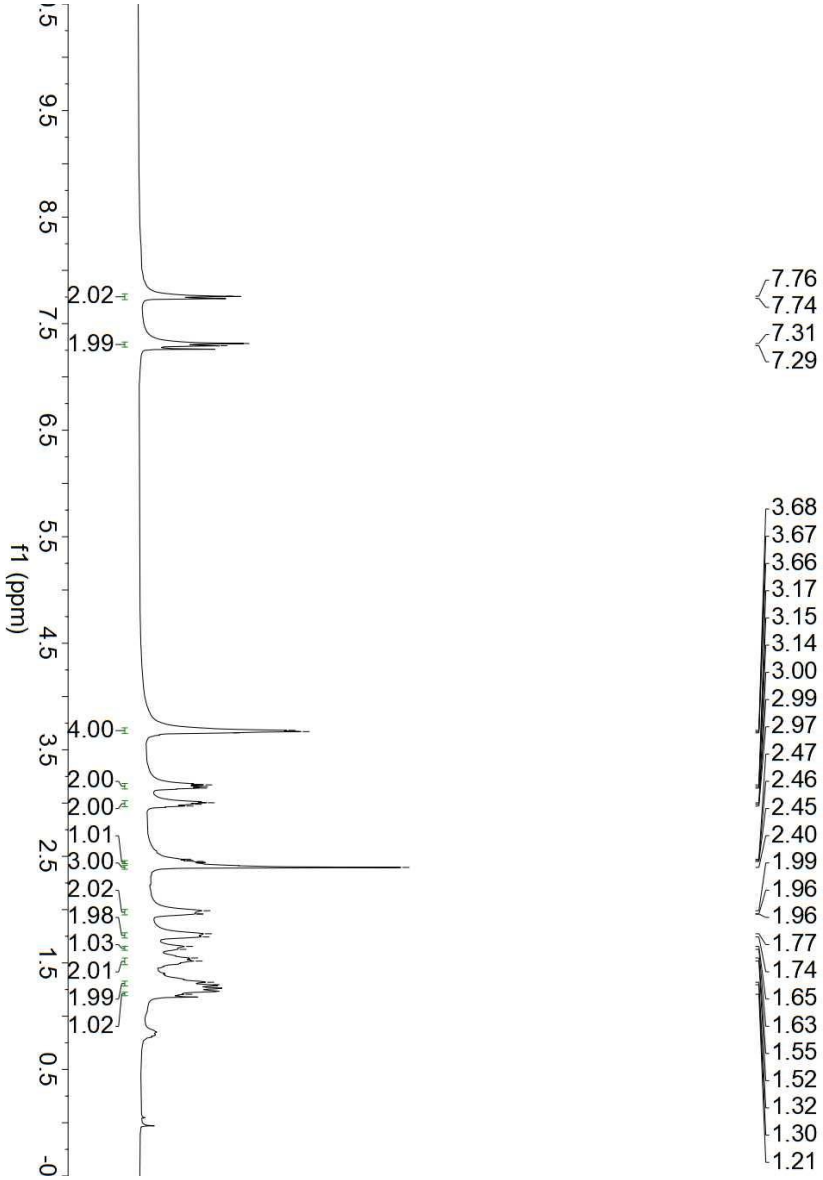
^{13}C NMR (100 MHz, Chloroform-*d*)



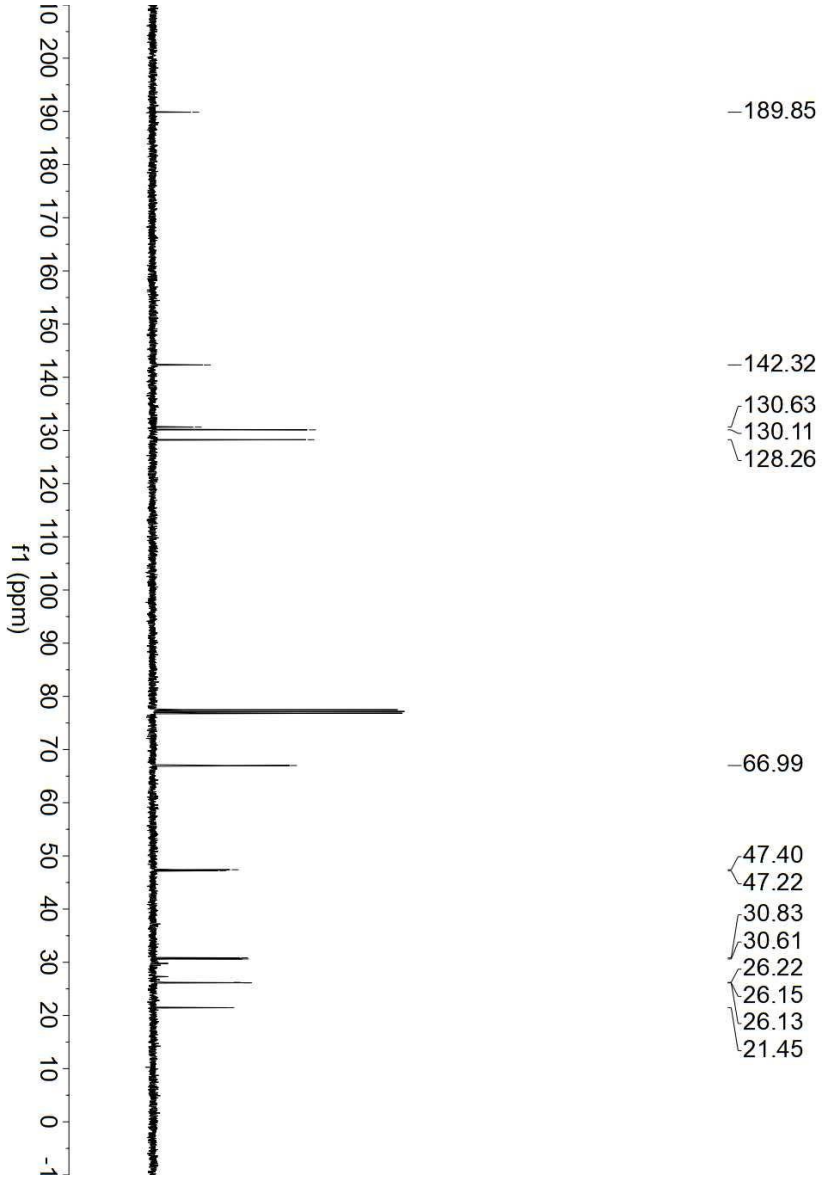


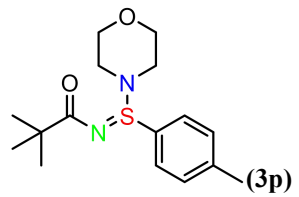
(3o)

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



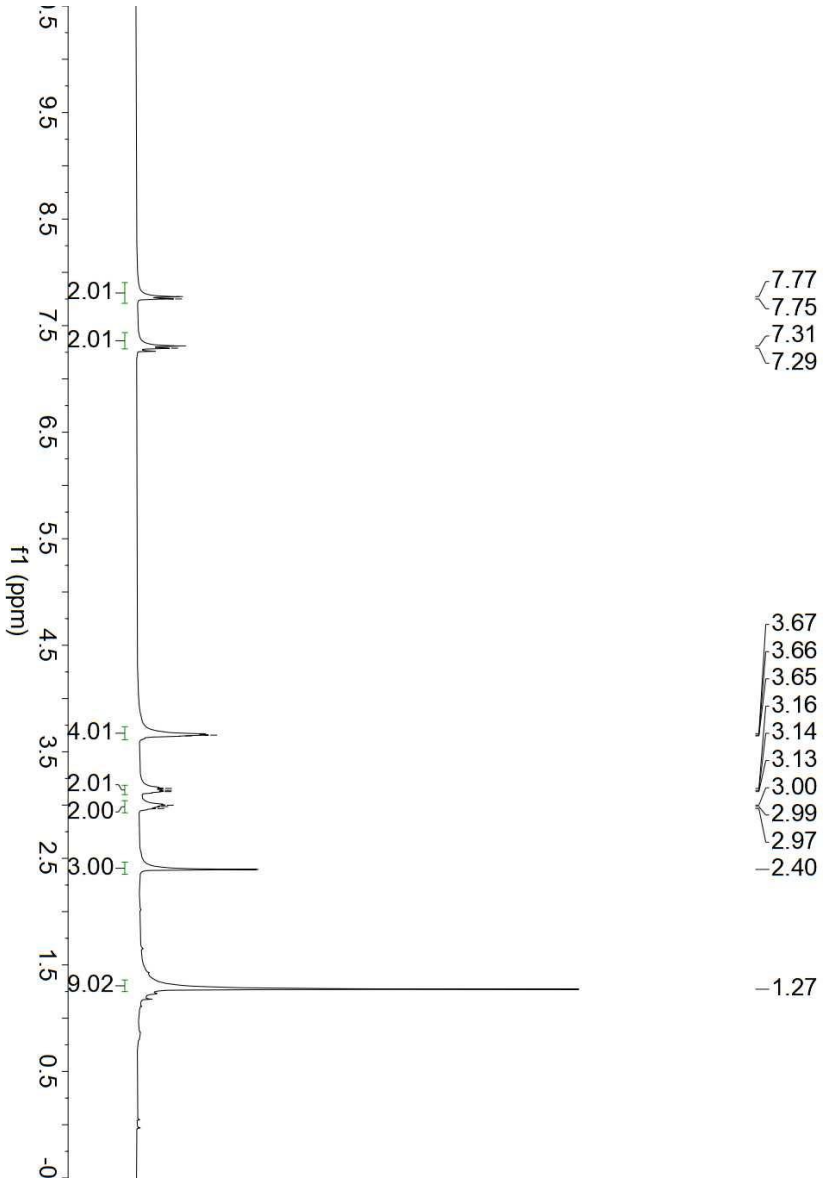
^{13}C NMR (100 MHz, Chloroform-*d*)



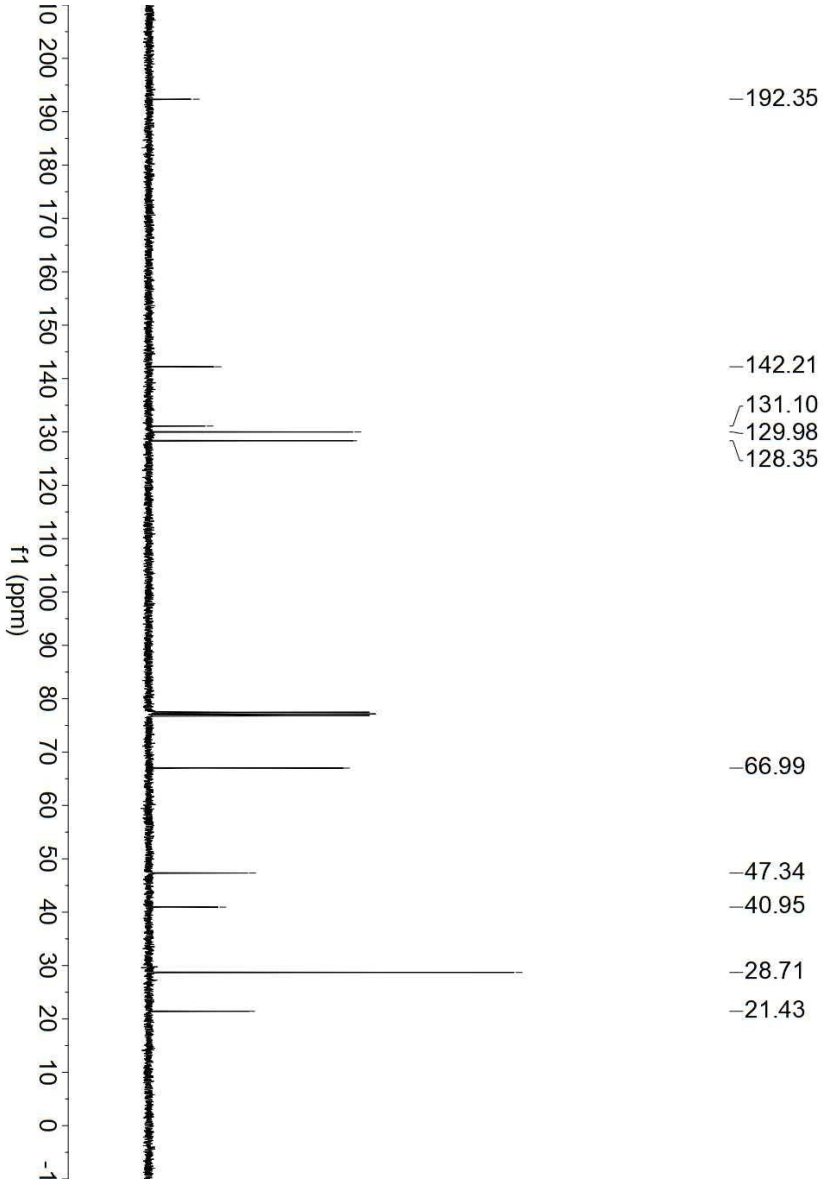


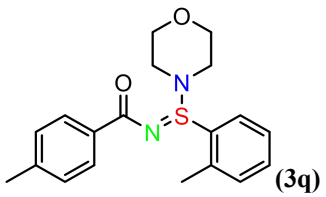
(3p)

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



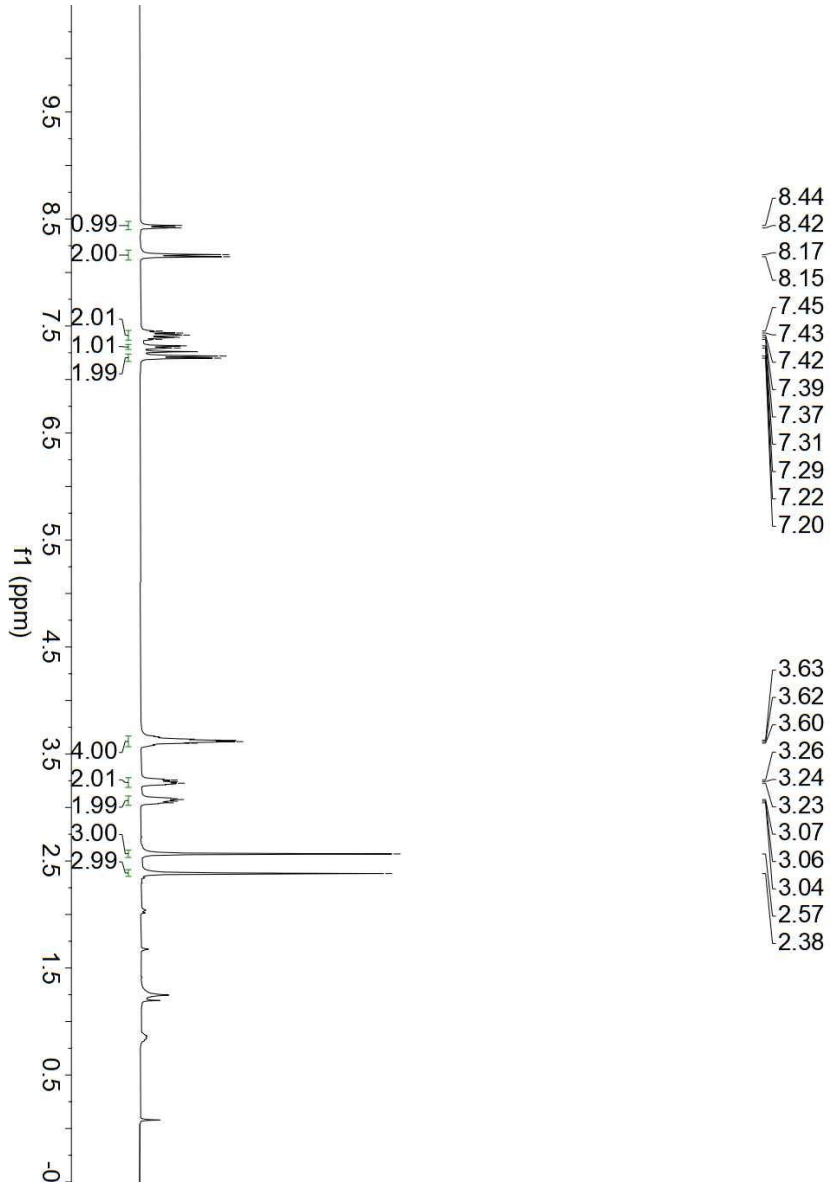
^{13}C NMR (100 MHz, Chloroform-*d*)



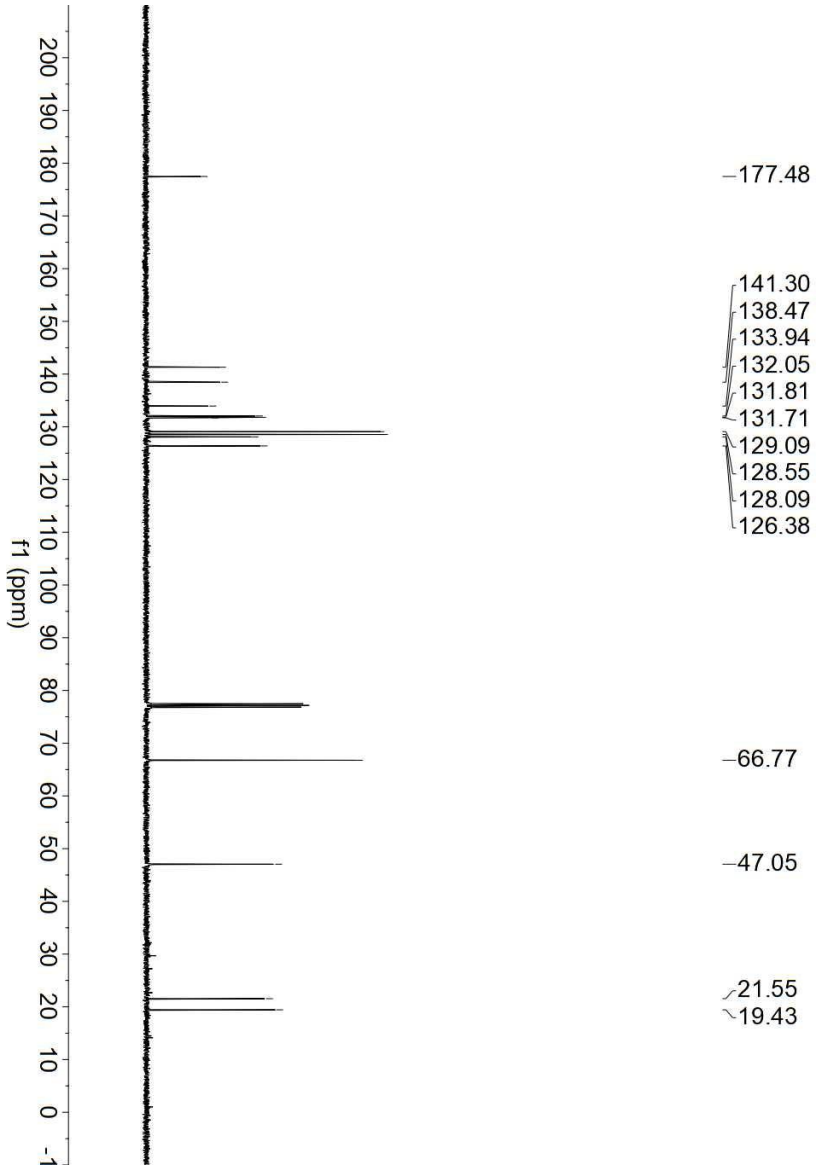


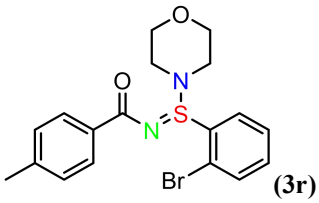
(3q)

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



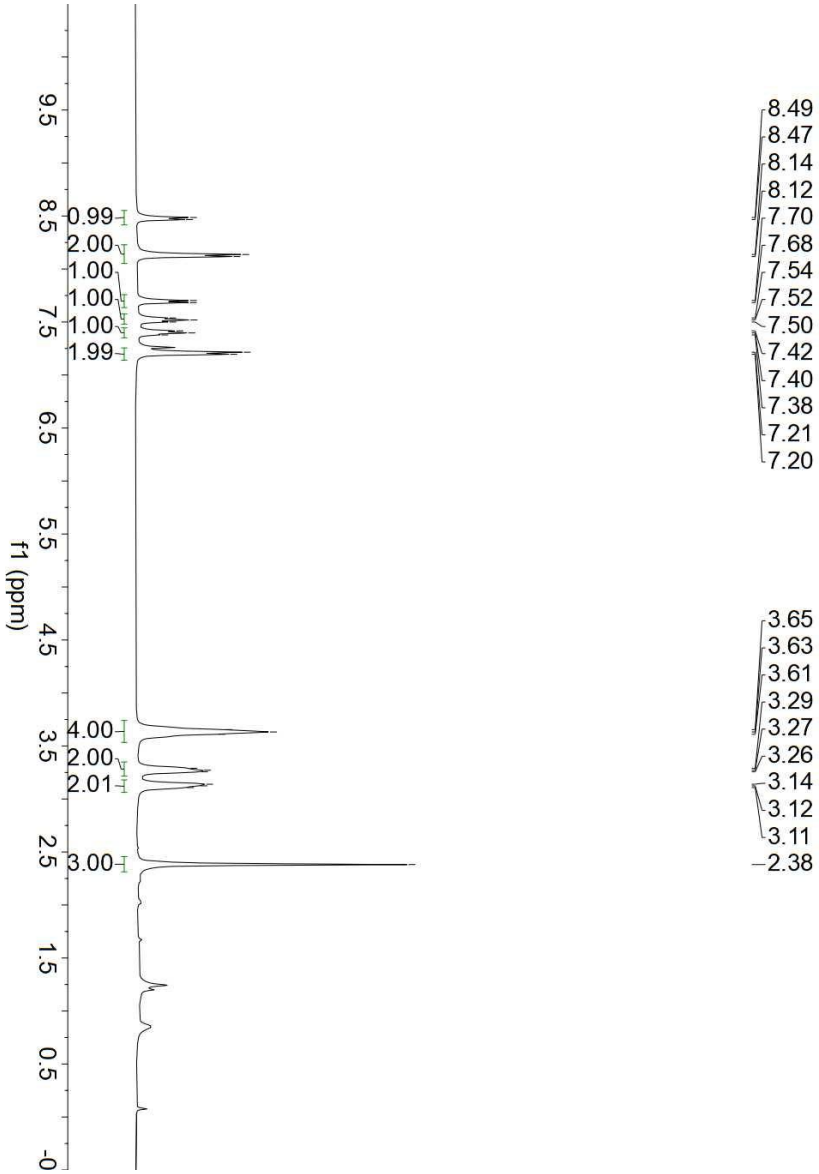
^{13}C NMR (100 MHz, Chloroform-*d*)



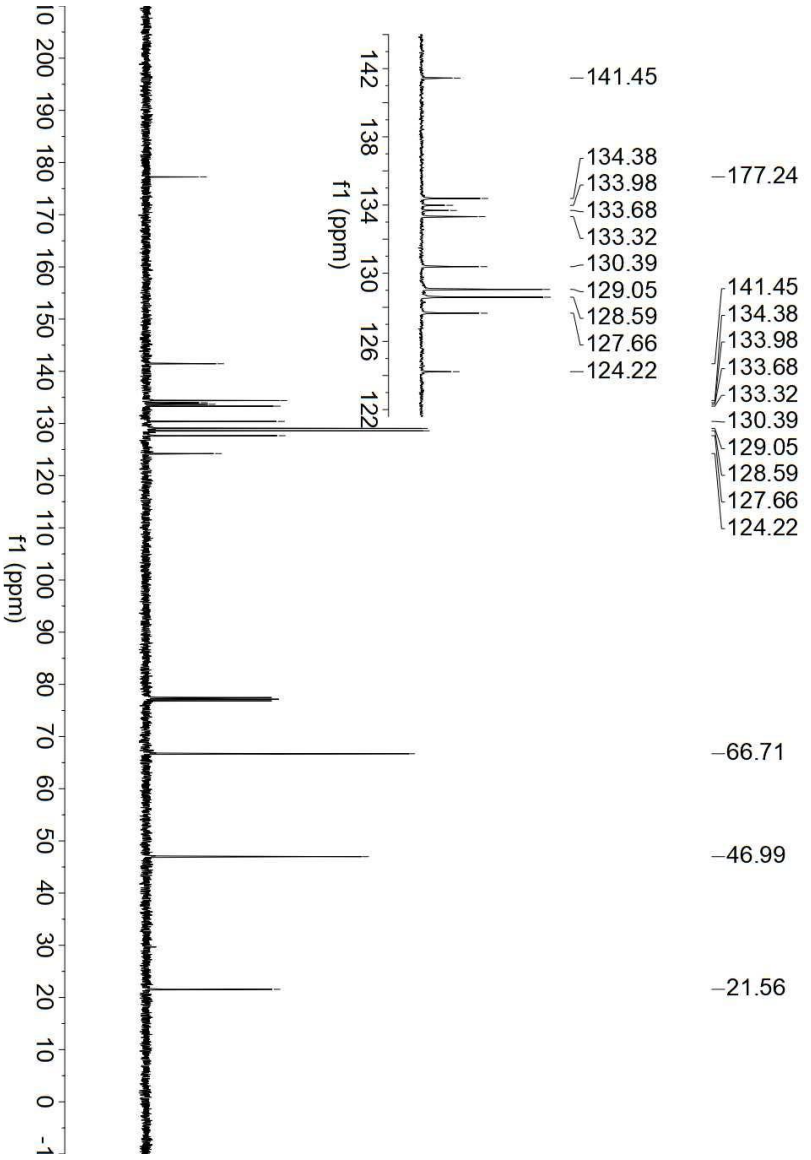


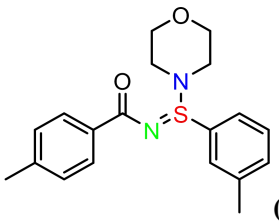
(3r)

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



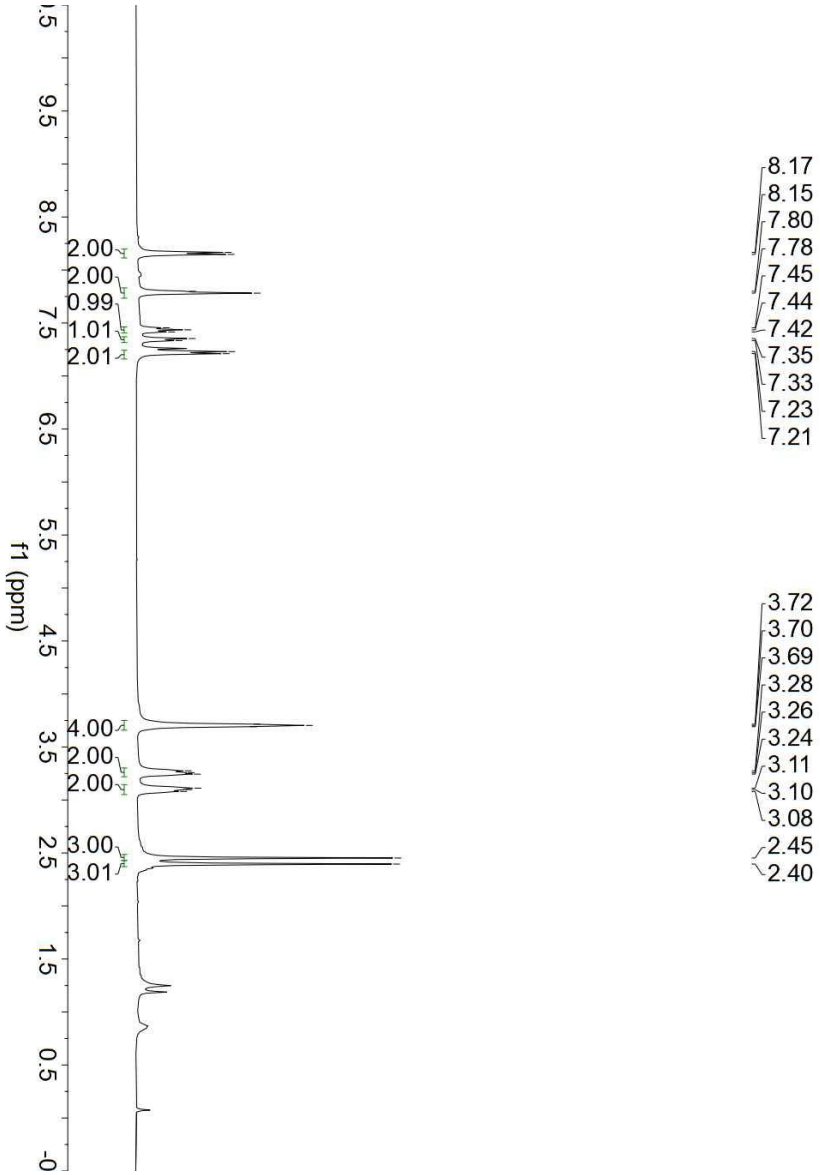
^{13}C NMR (100 MHz, Chloroform-*d*)



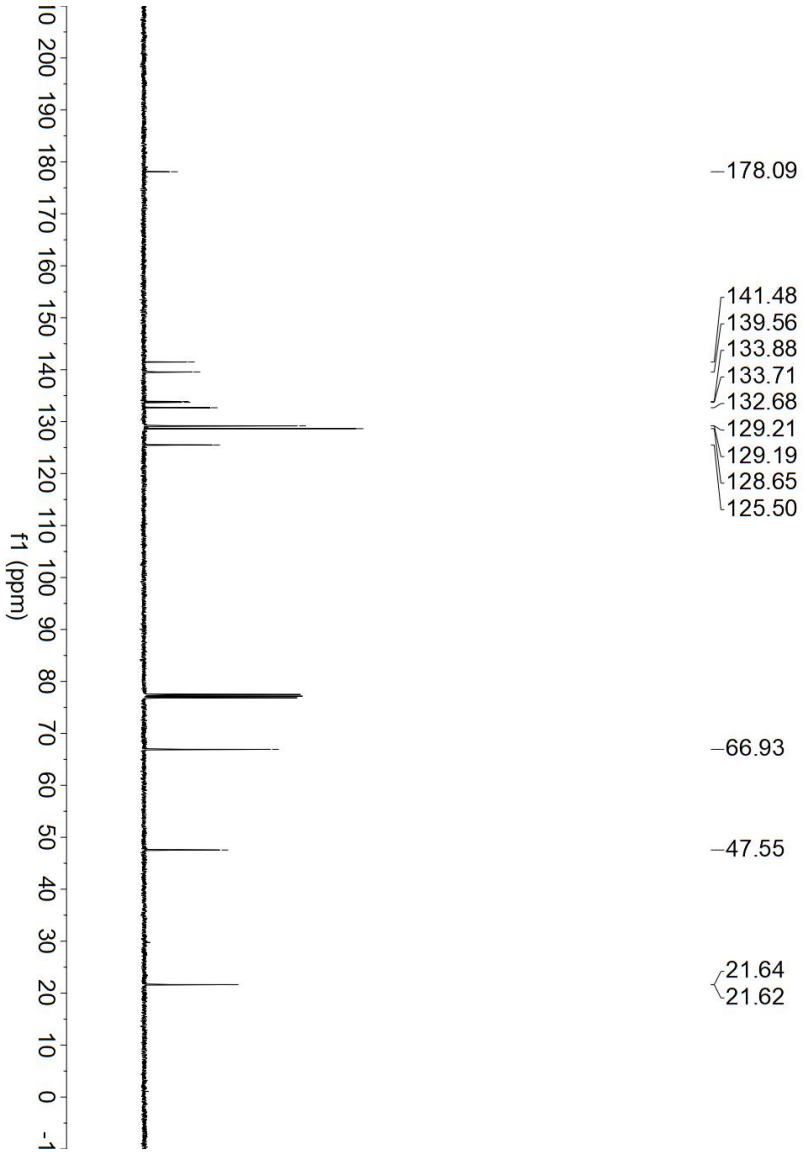


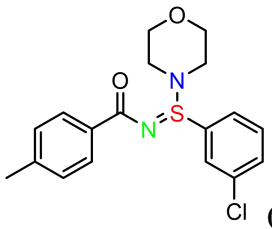
(3s)

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



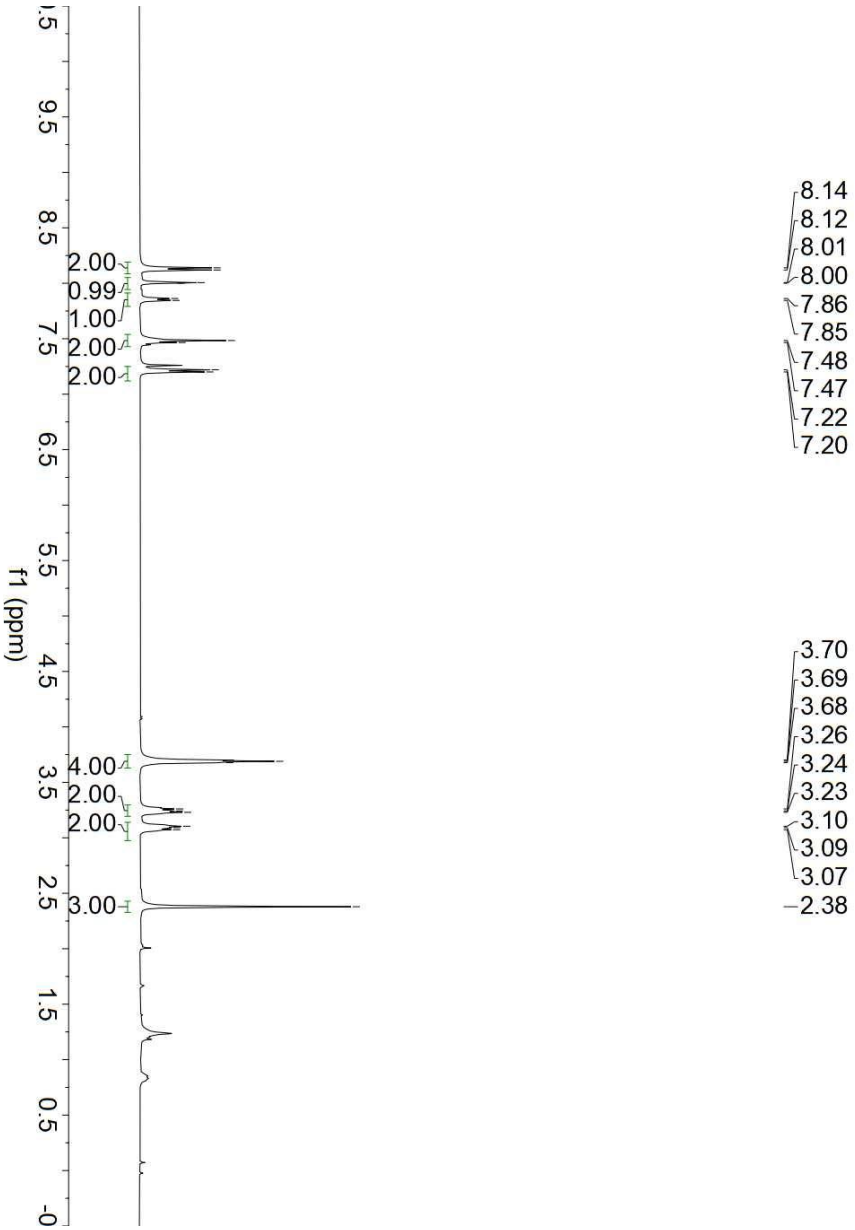
^{13}C NMR (100 MHz, Chloroform-*d*)



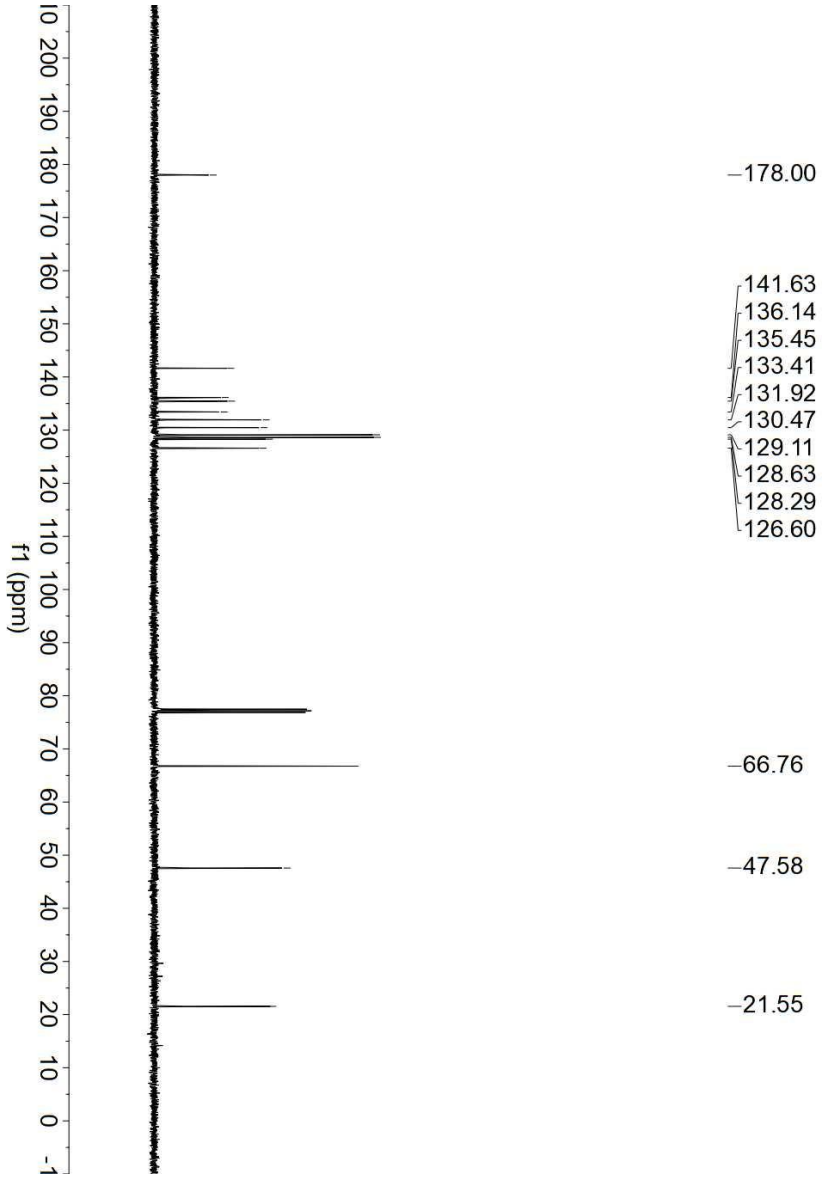


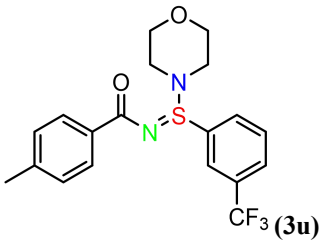
(3t)

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



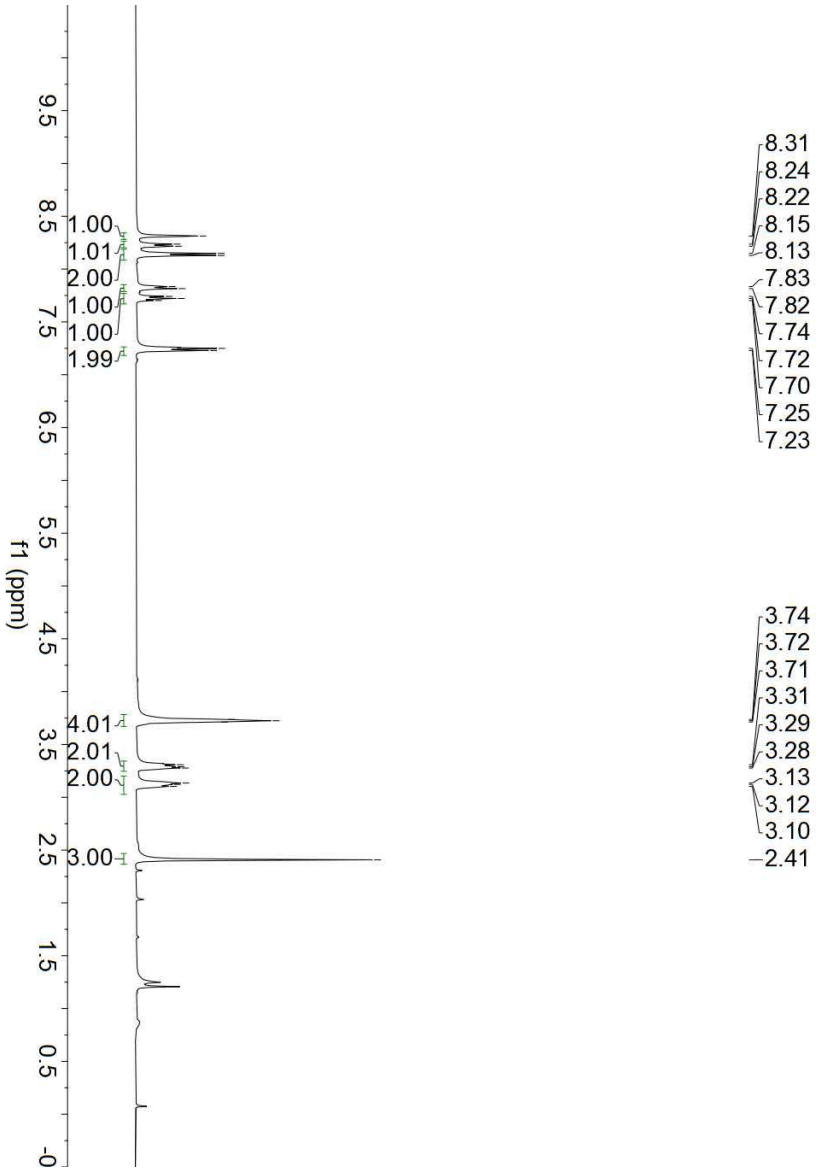
^{13}C NMR (100 MHz, Chloroform-*d*)



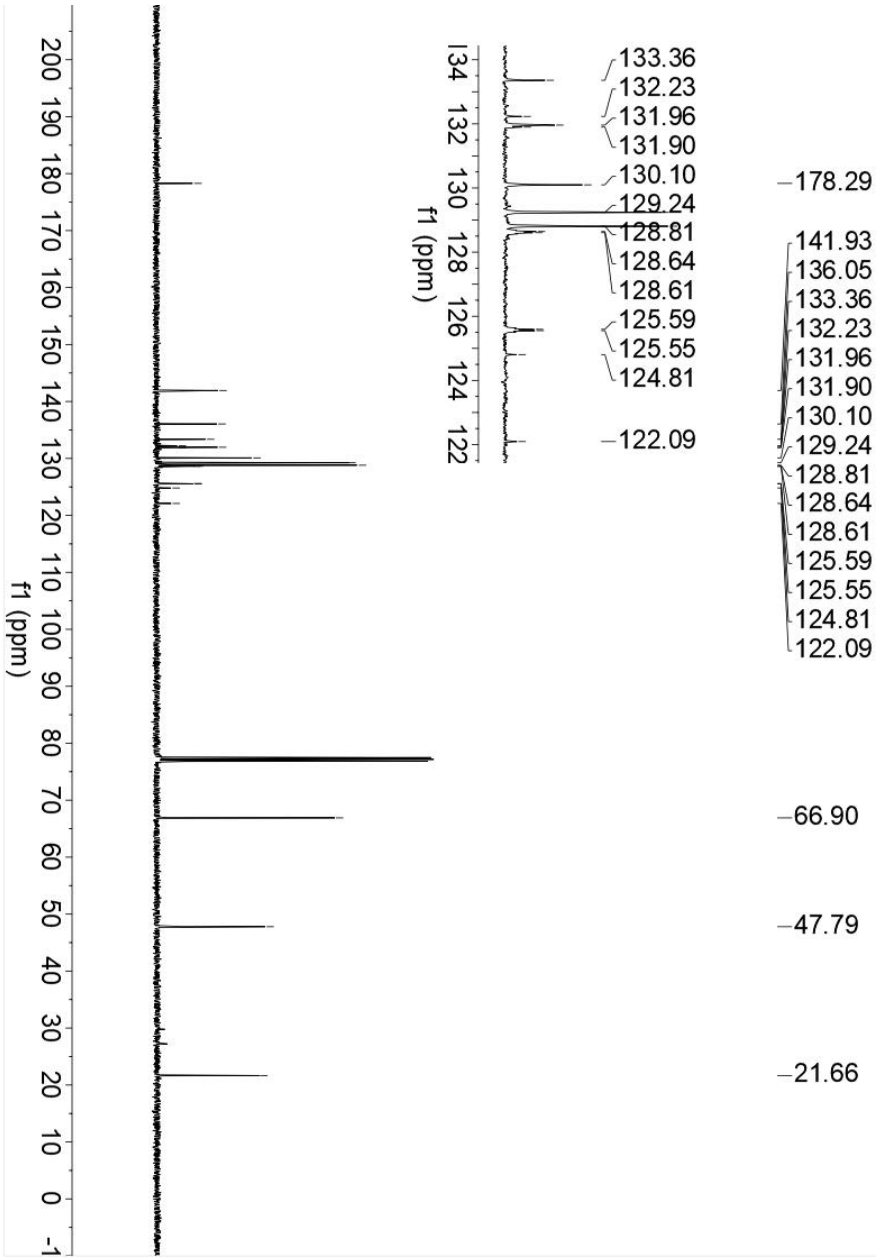


(3u)

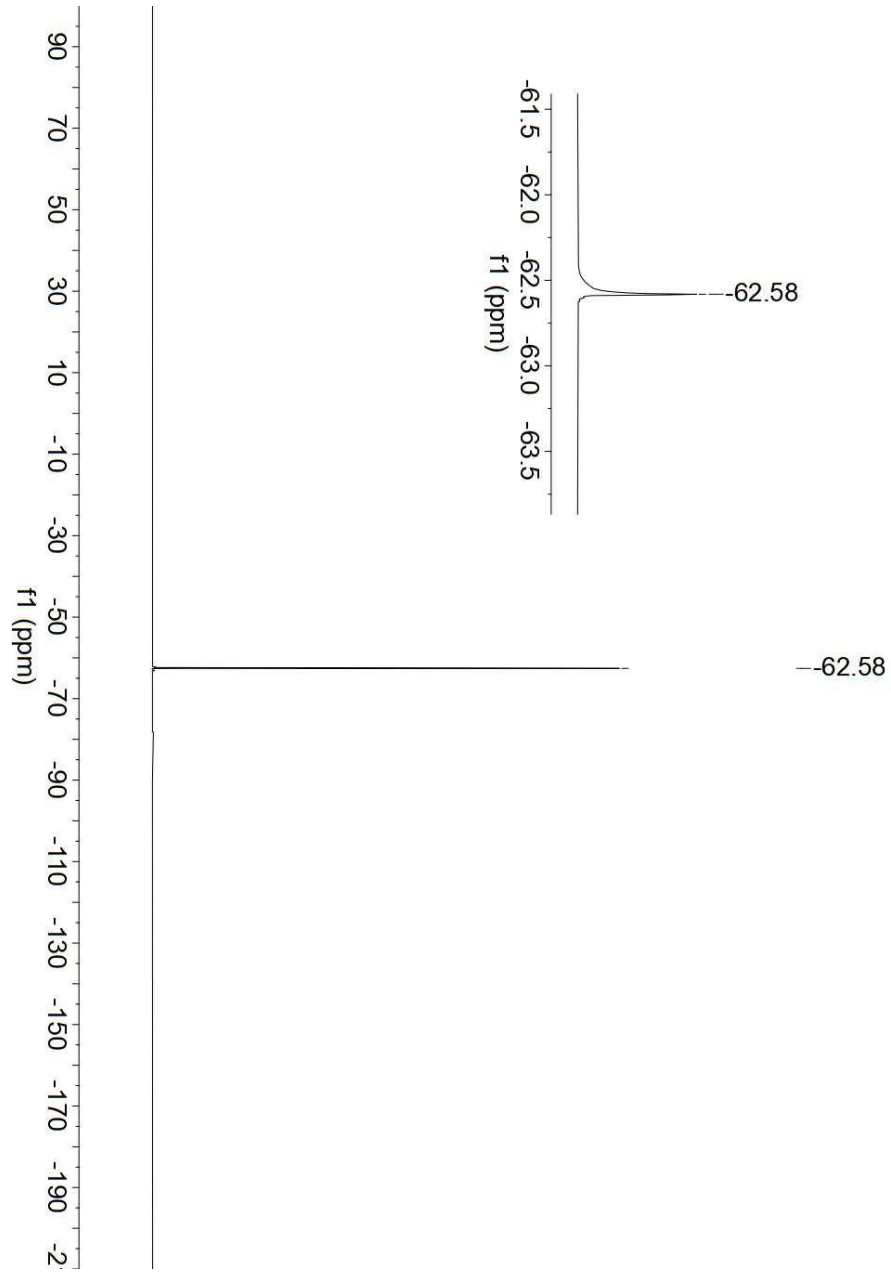
^{1}H NMR (400 MHz, Chloroform-*d*)

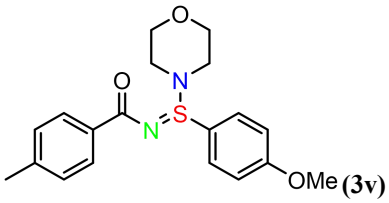


^{13}C NMR (100 MHz, Chloroform-*d*)



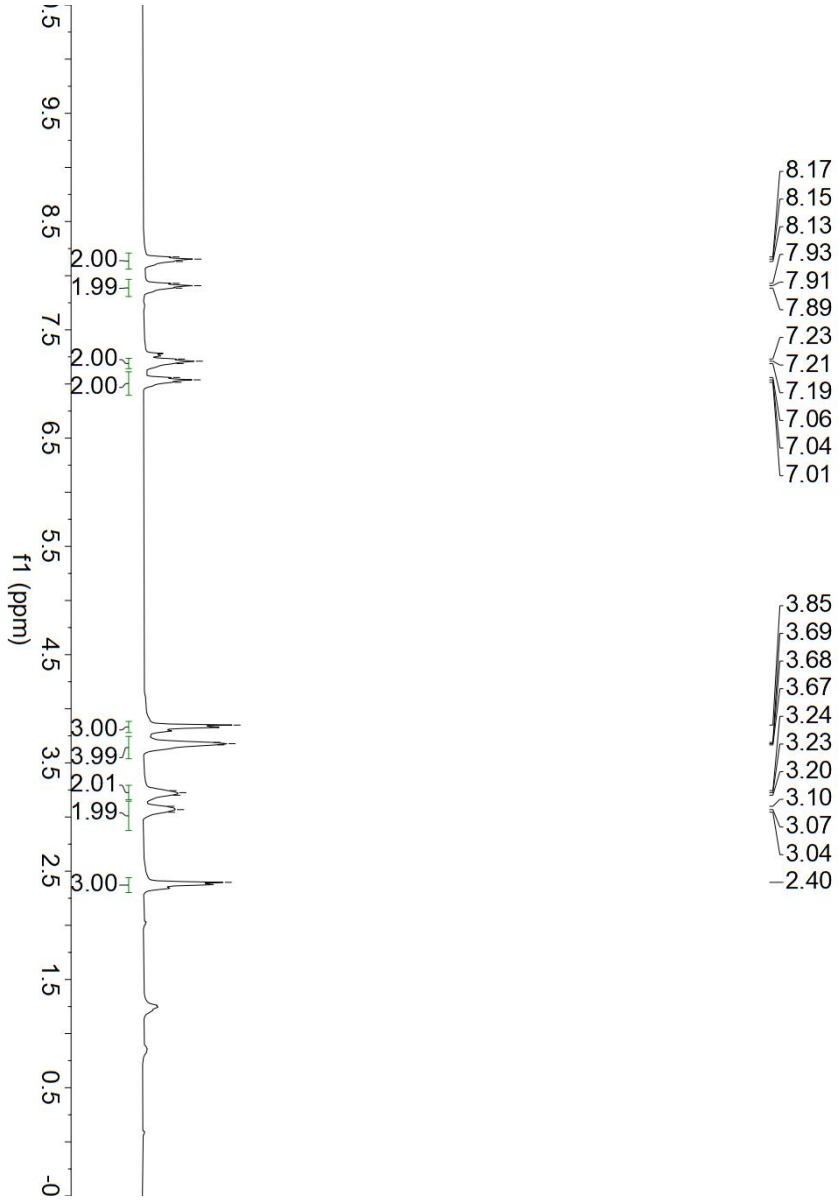
^{19}F NMR (376 MHz, Chloroform-*d*)



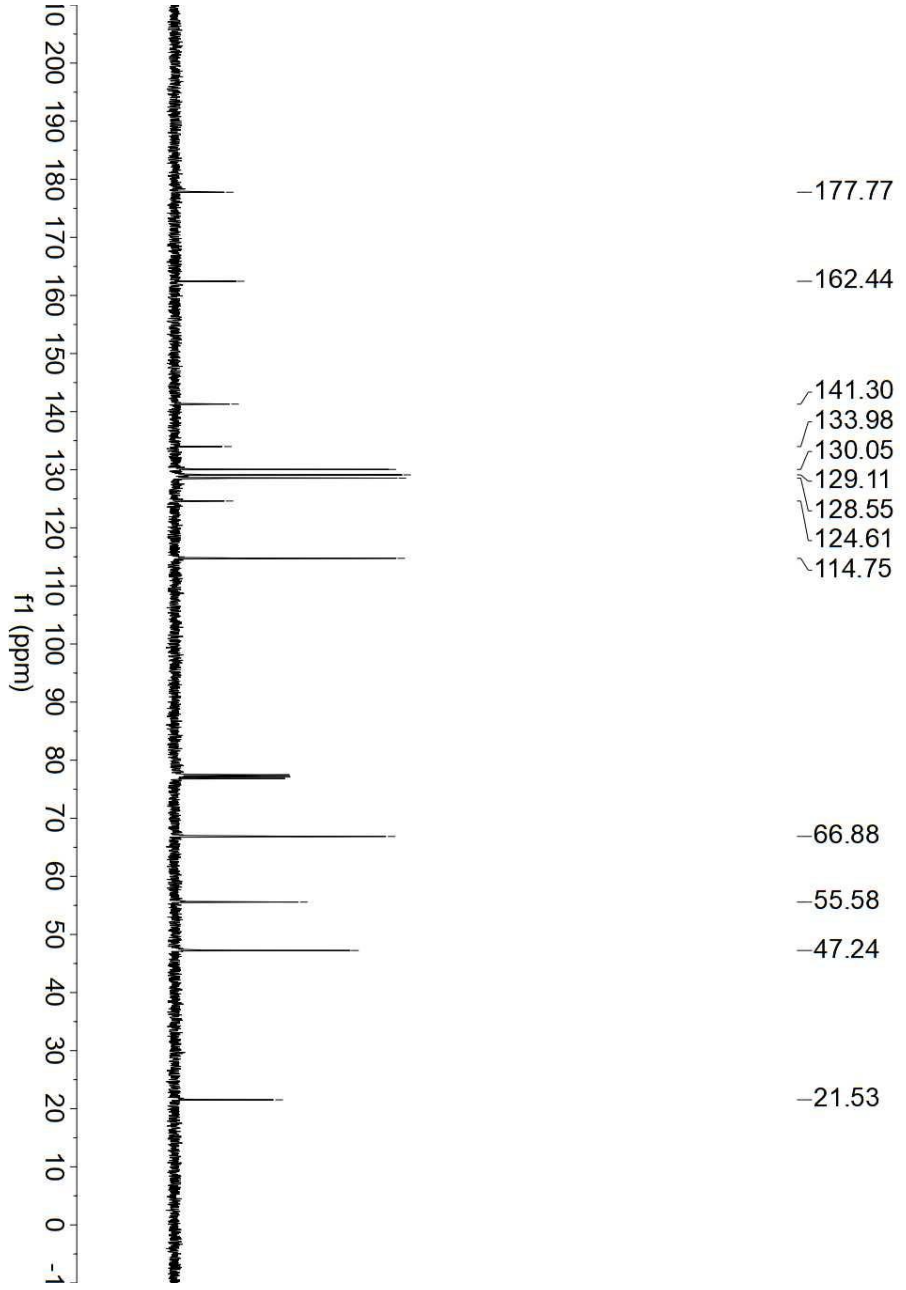


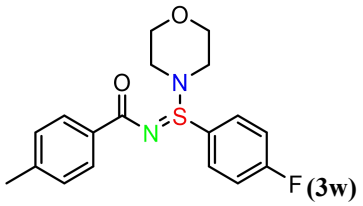
(3v)

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



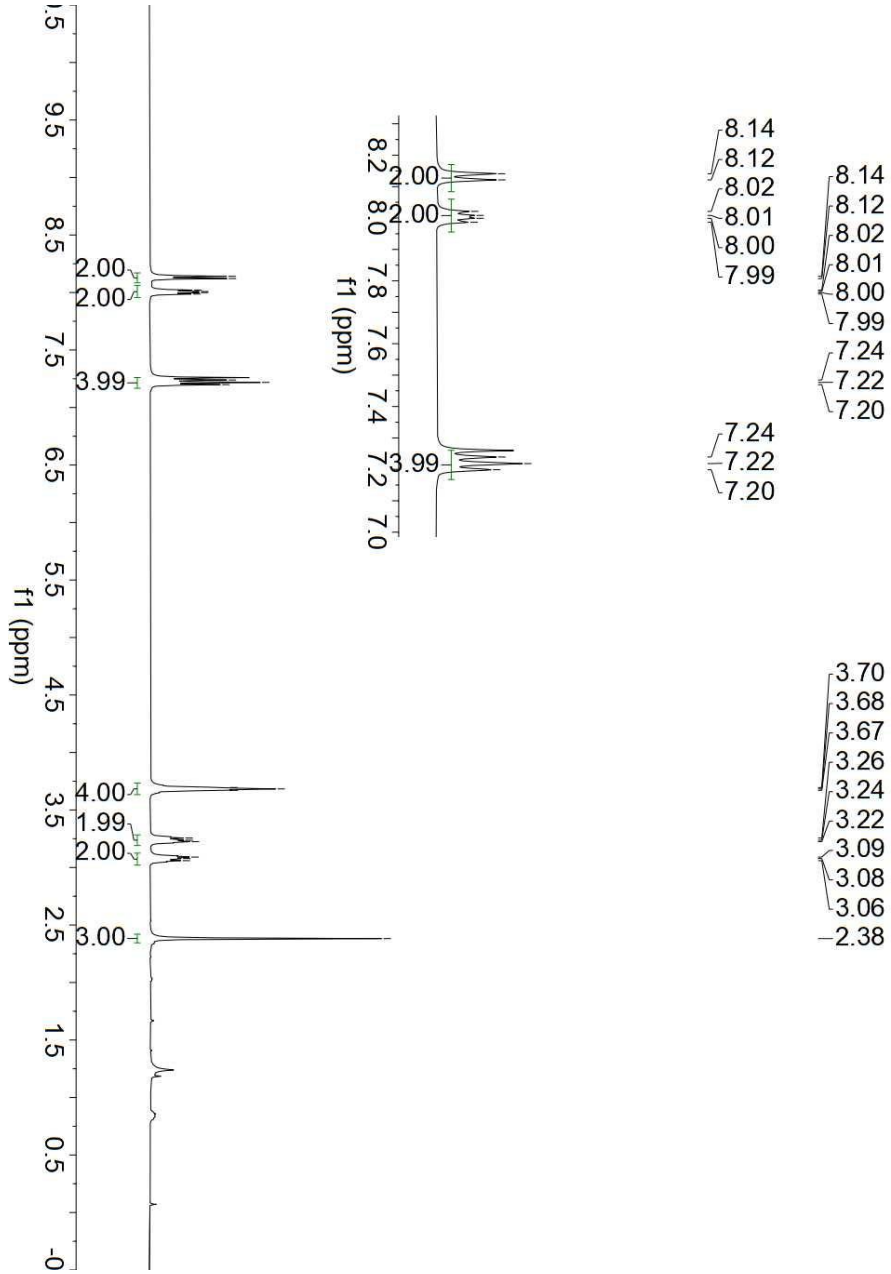
^{13}C NMR (100 MHz, Chloroform-*d*)



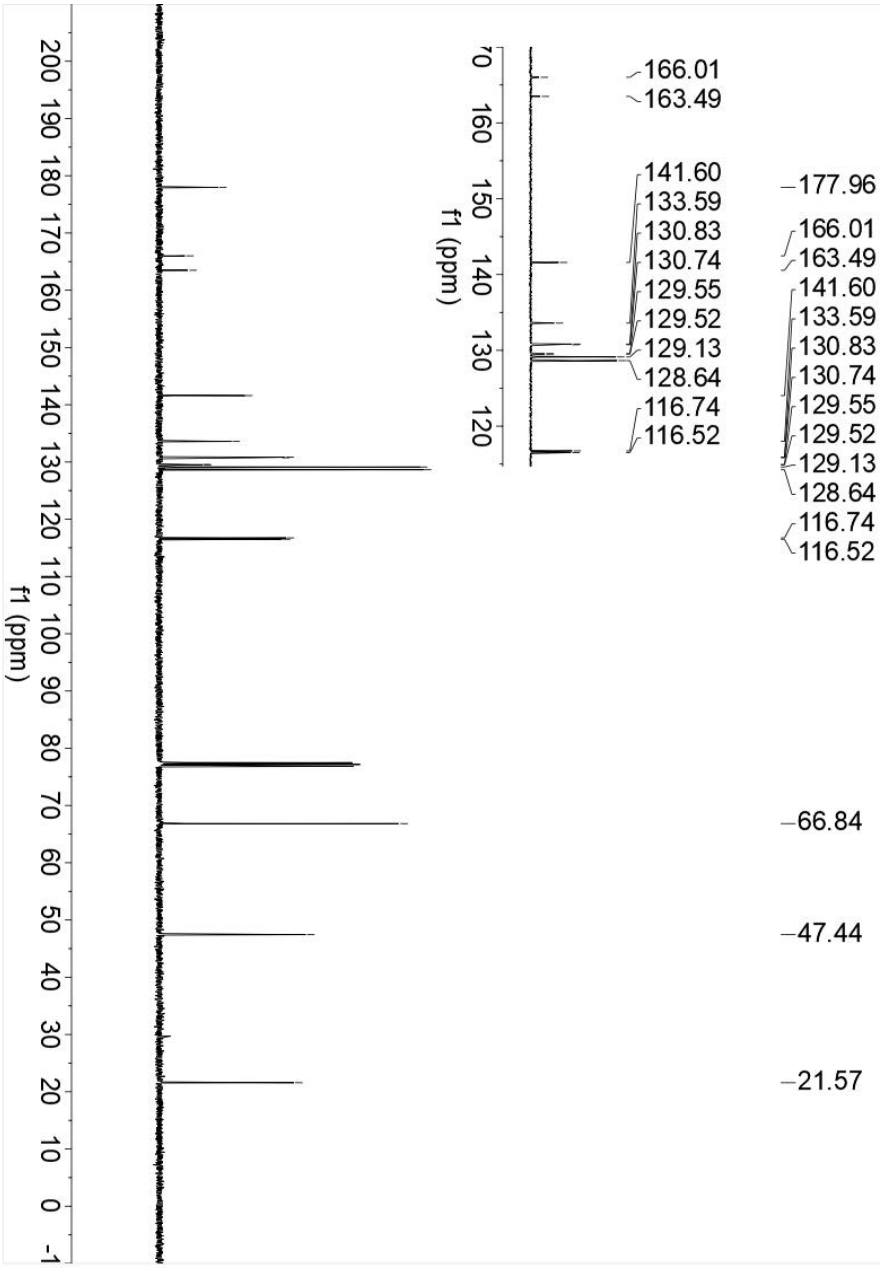


(3w)

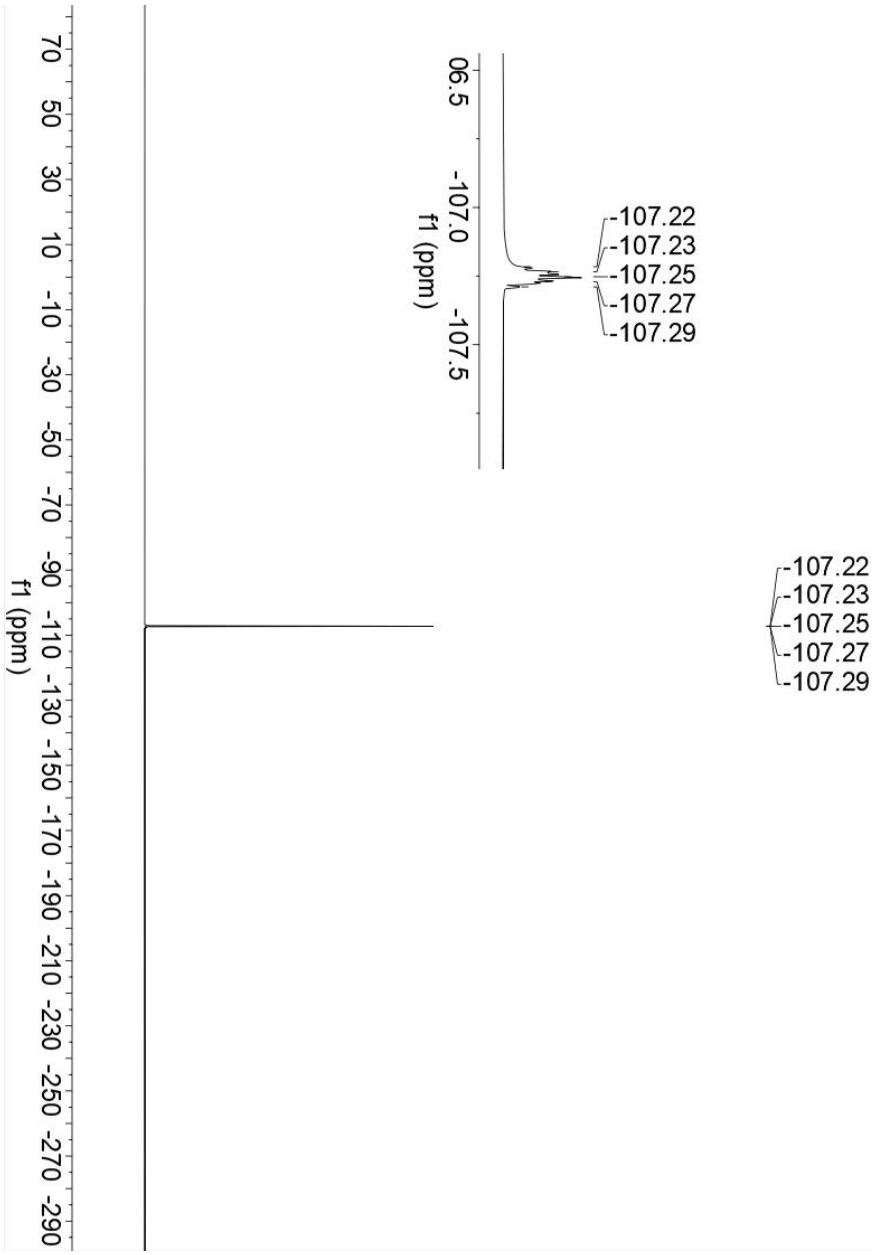
^{1}H NMR (400 MHz, Chloroform-d)

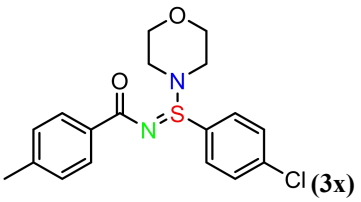


^{13}C NMR (100 MHz, Chloroform-*d*)



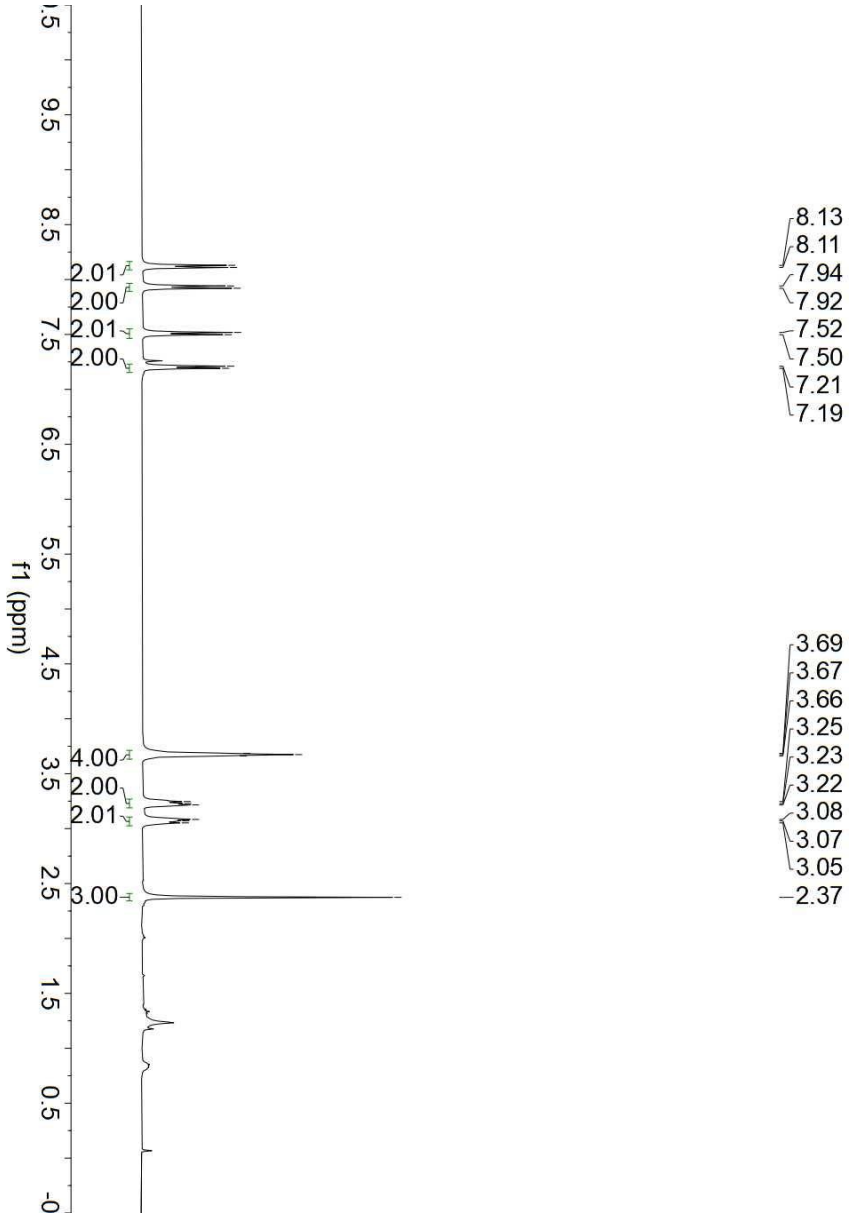
^{19}F NMR (376 MHz, Chloroform-d)



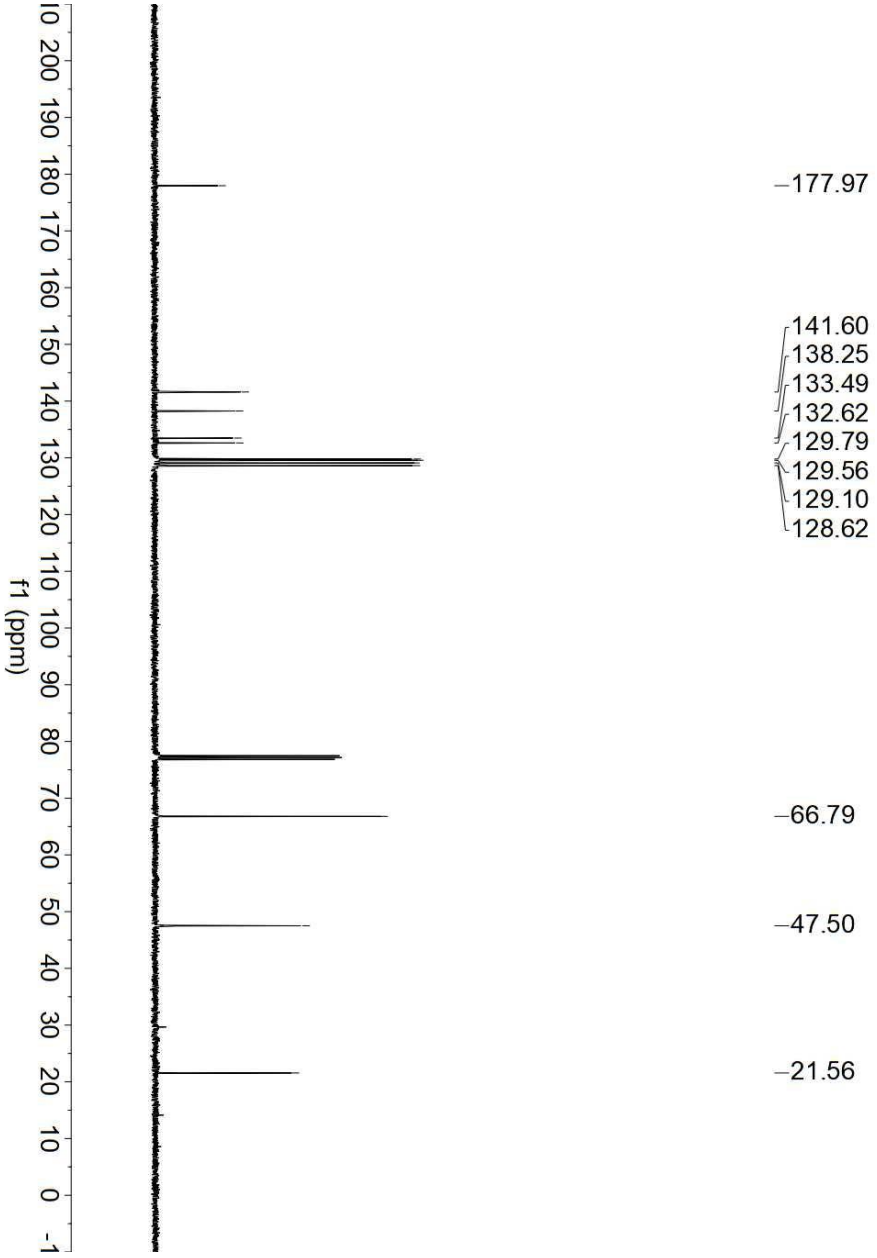


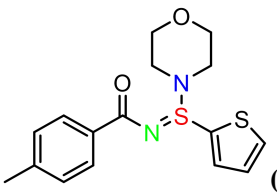
(3x)

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



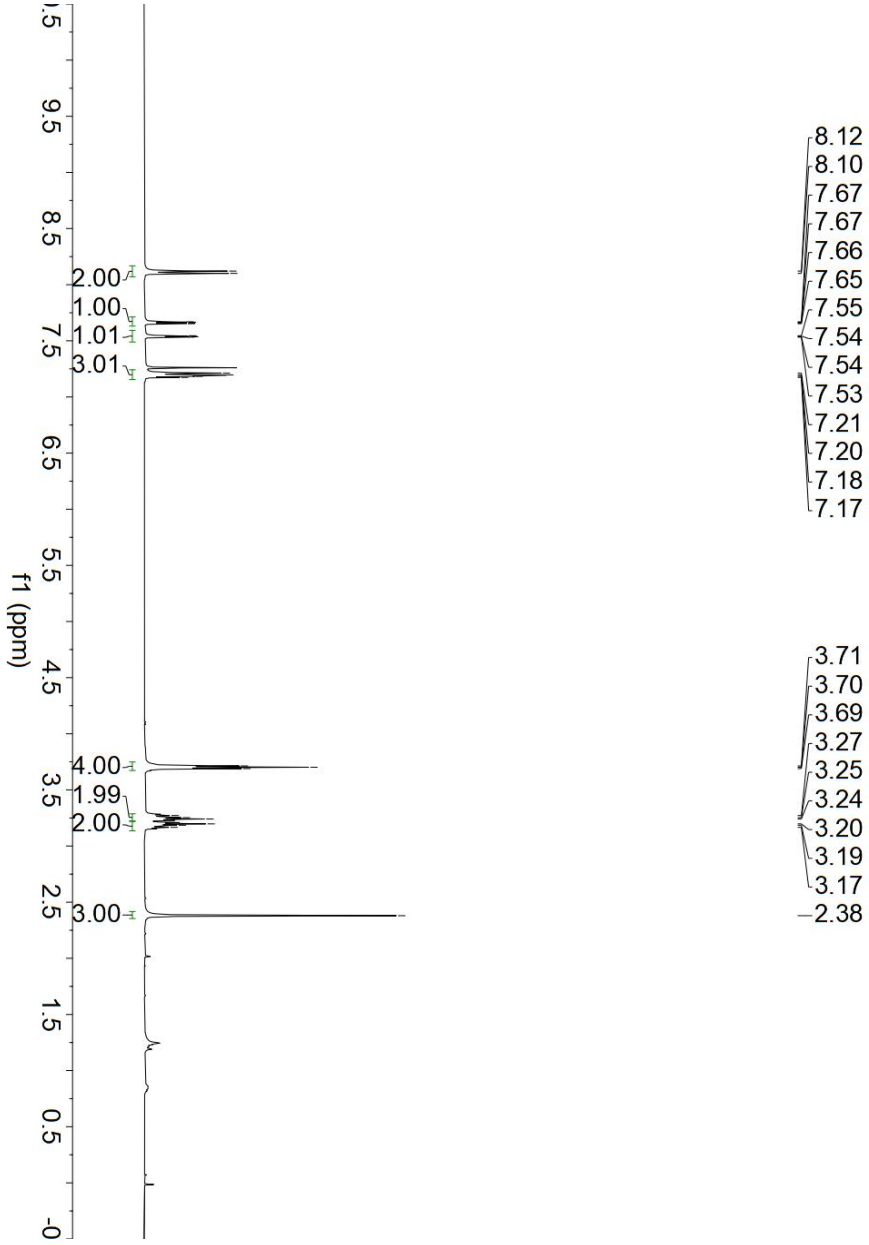
^{13}C NMR (100 MHz, Chloroform-d)



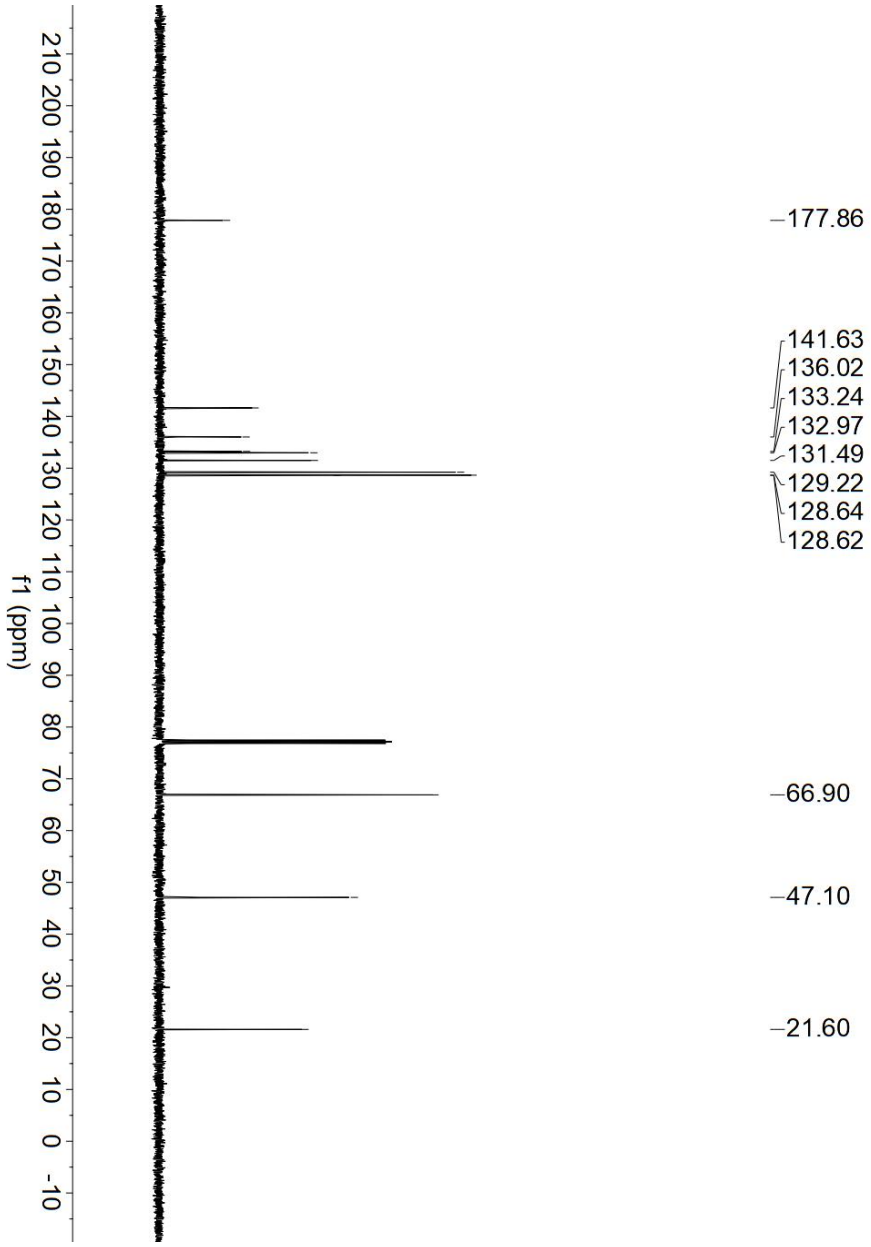


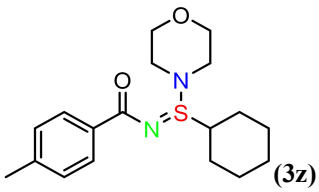
(3y)

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



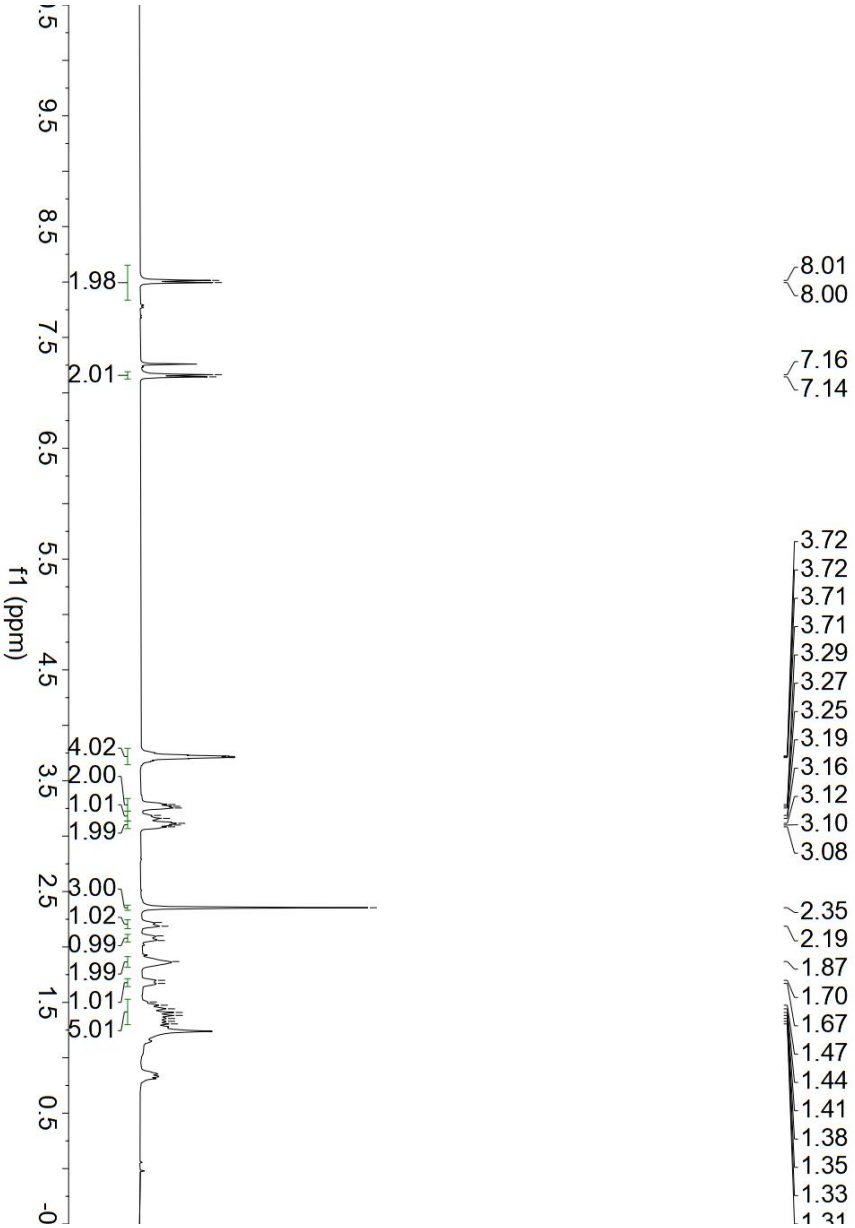
^{13}C NMR (100 MHz, Chloroform-d)



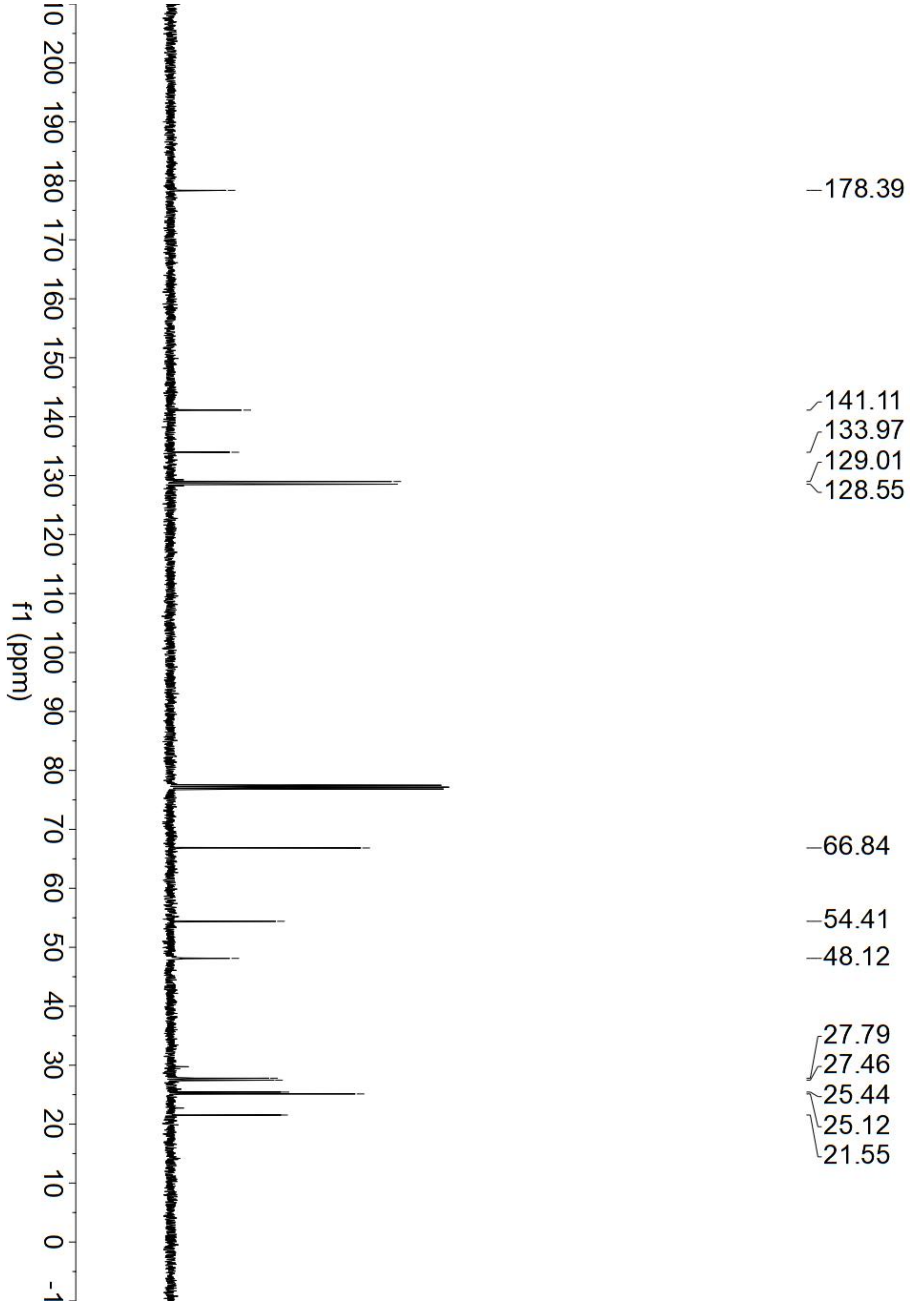


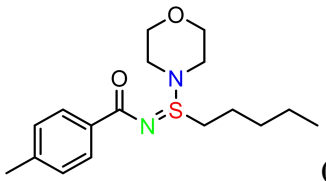
(3z)

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



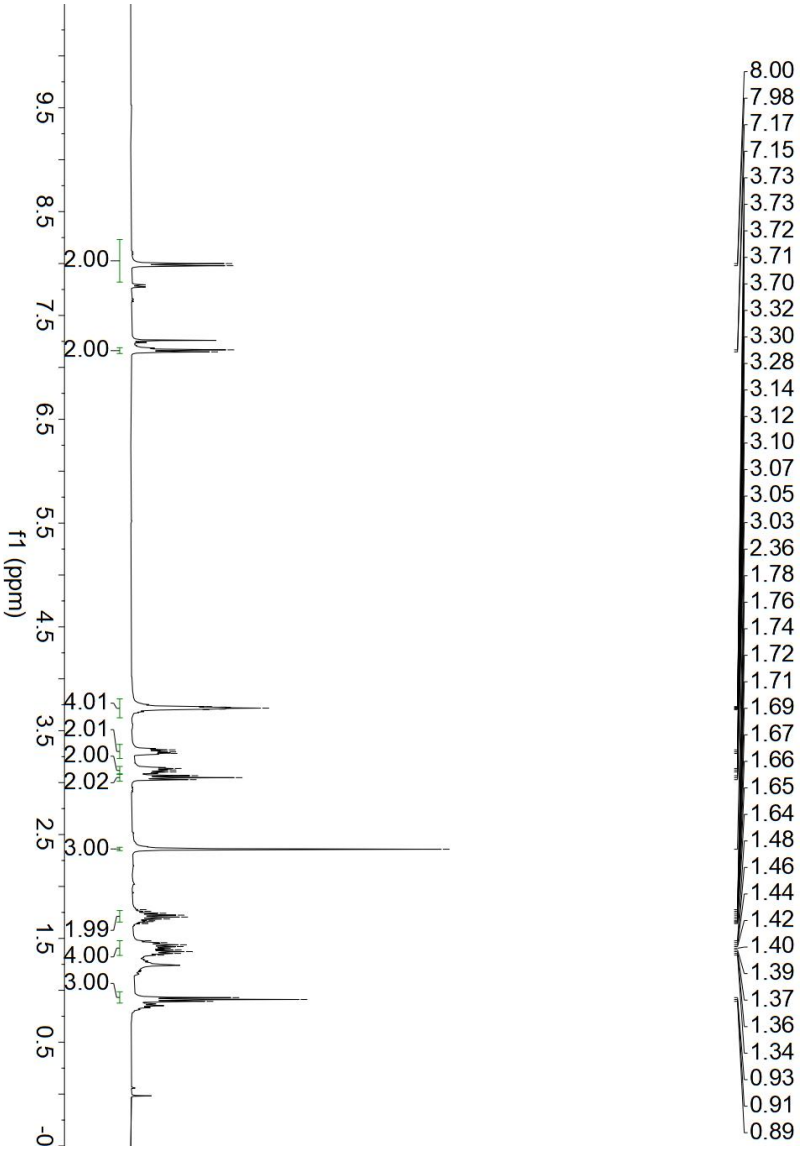
^{13}C NMR (100 MHz, Chloroform-d)



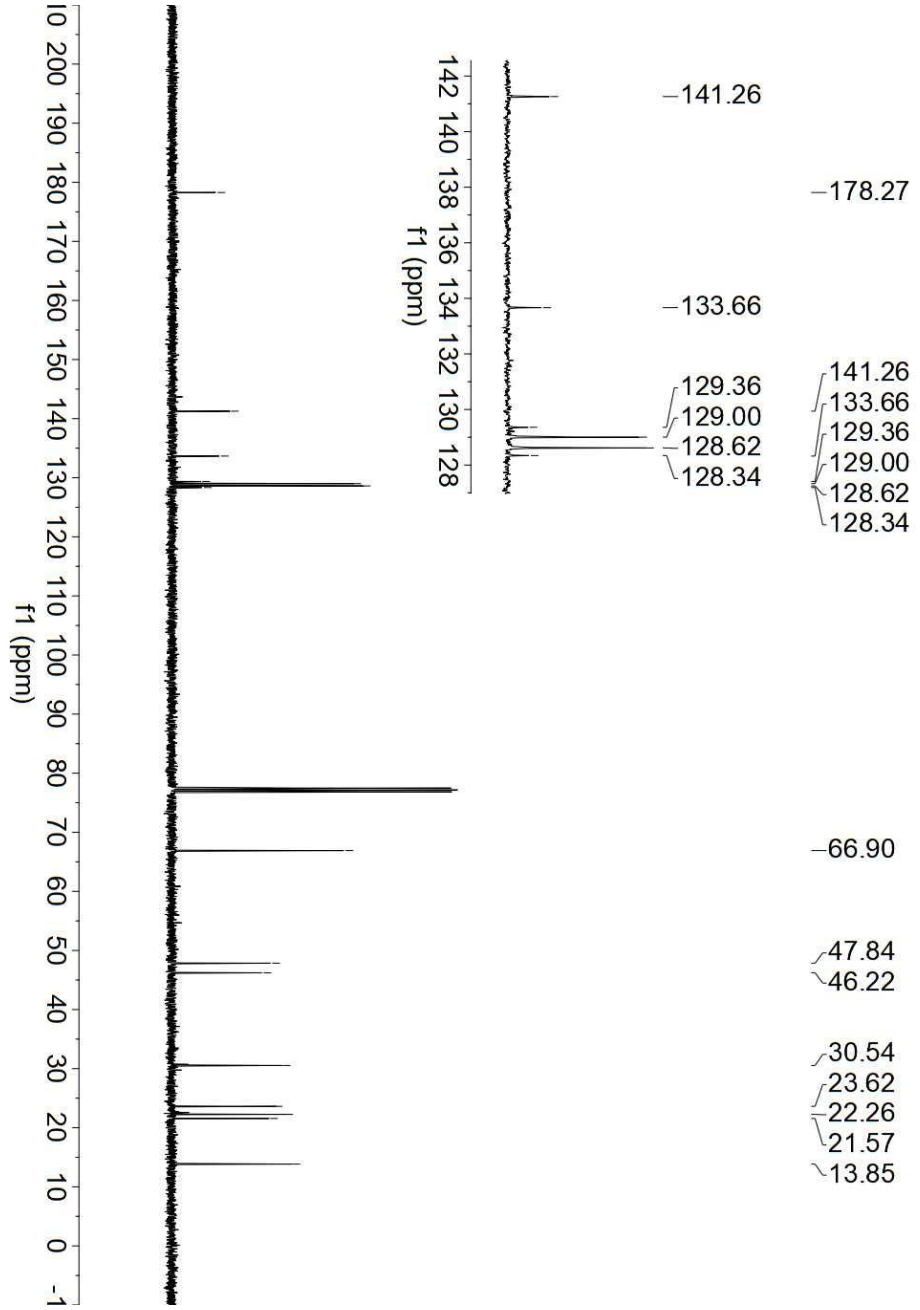


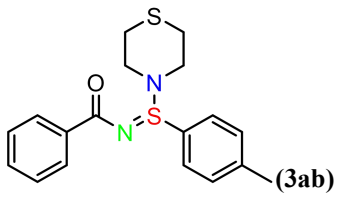
(3aa)

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



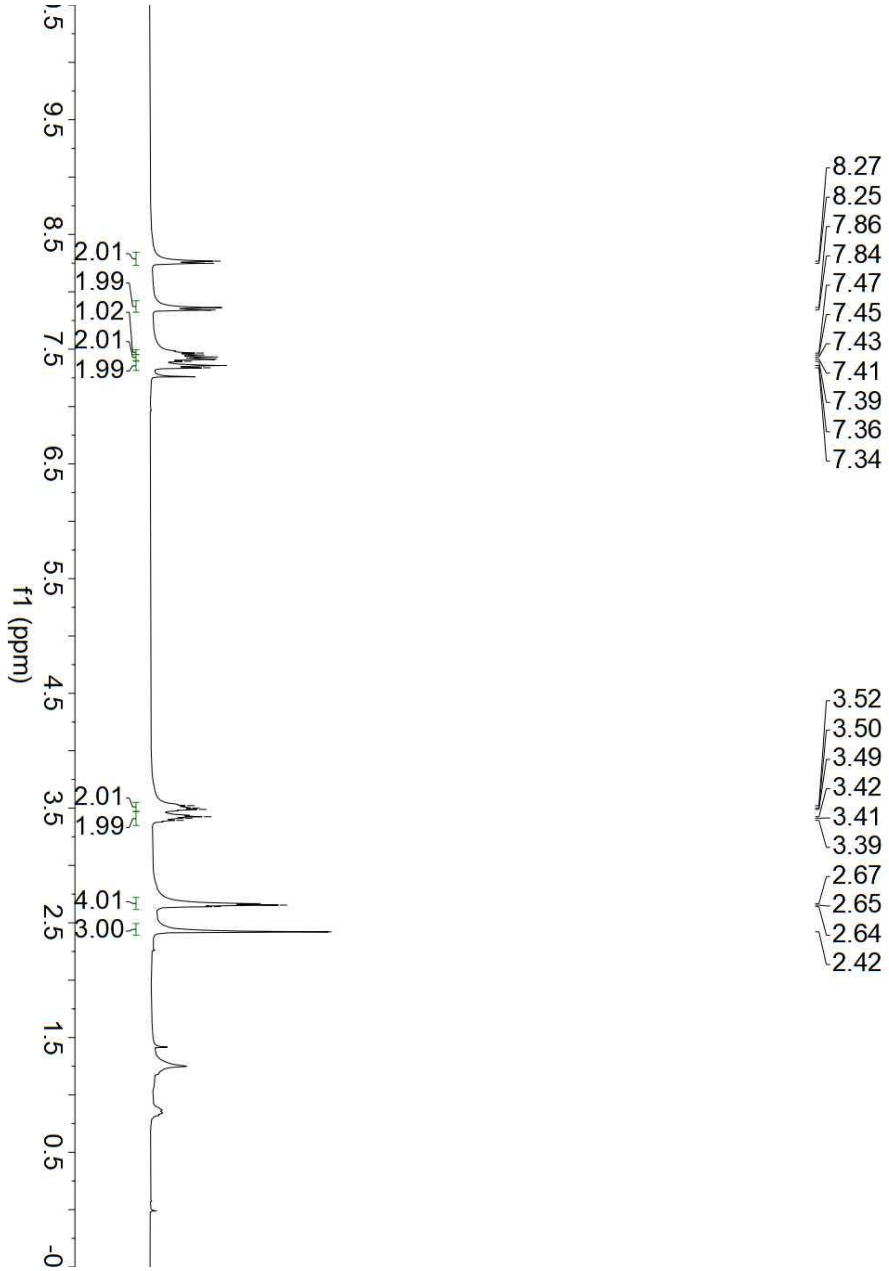
^{13}C NMR (100 MHz, Chloroform-d)



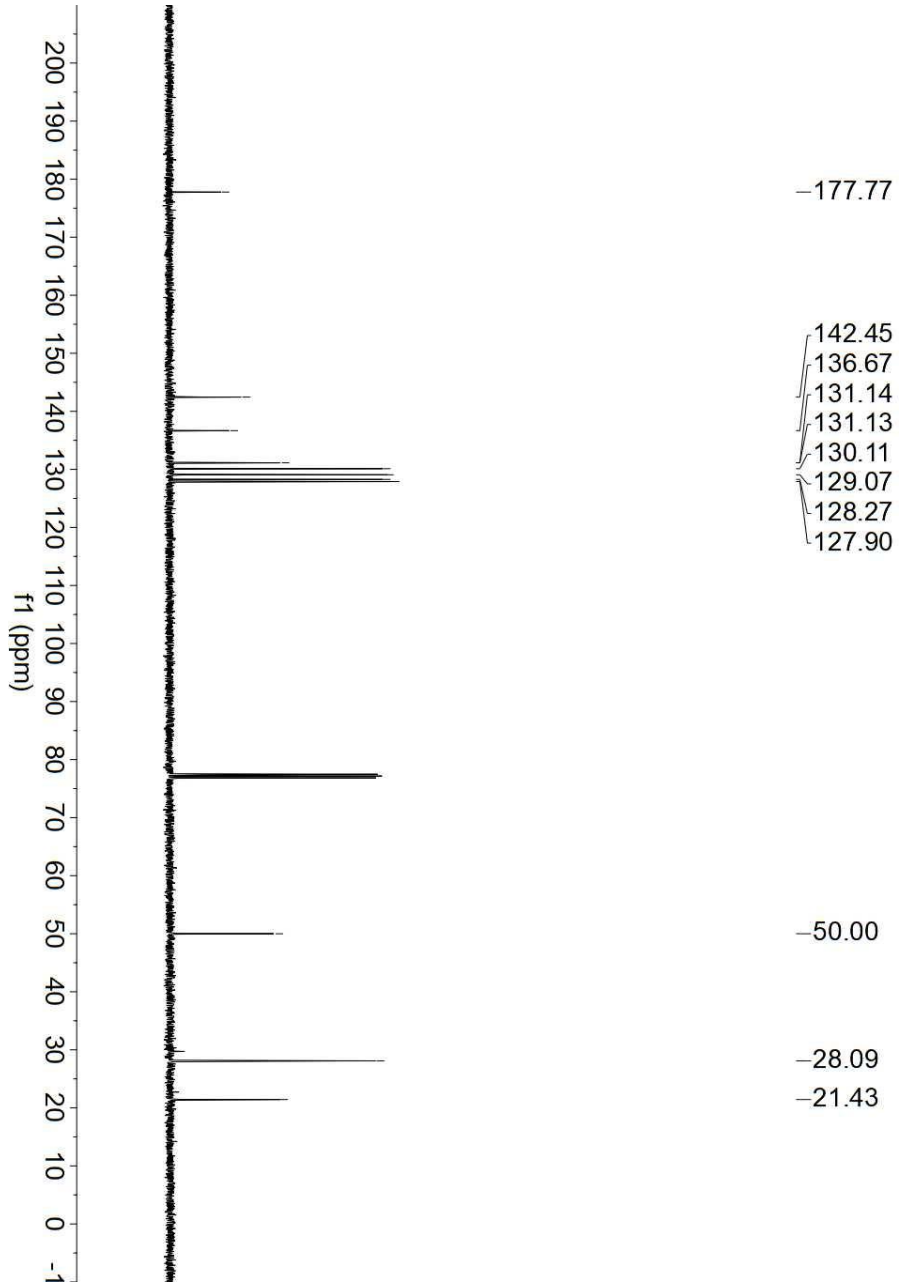


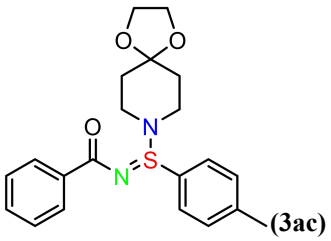
(3ab)

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

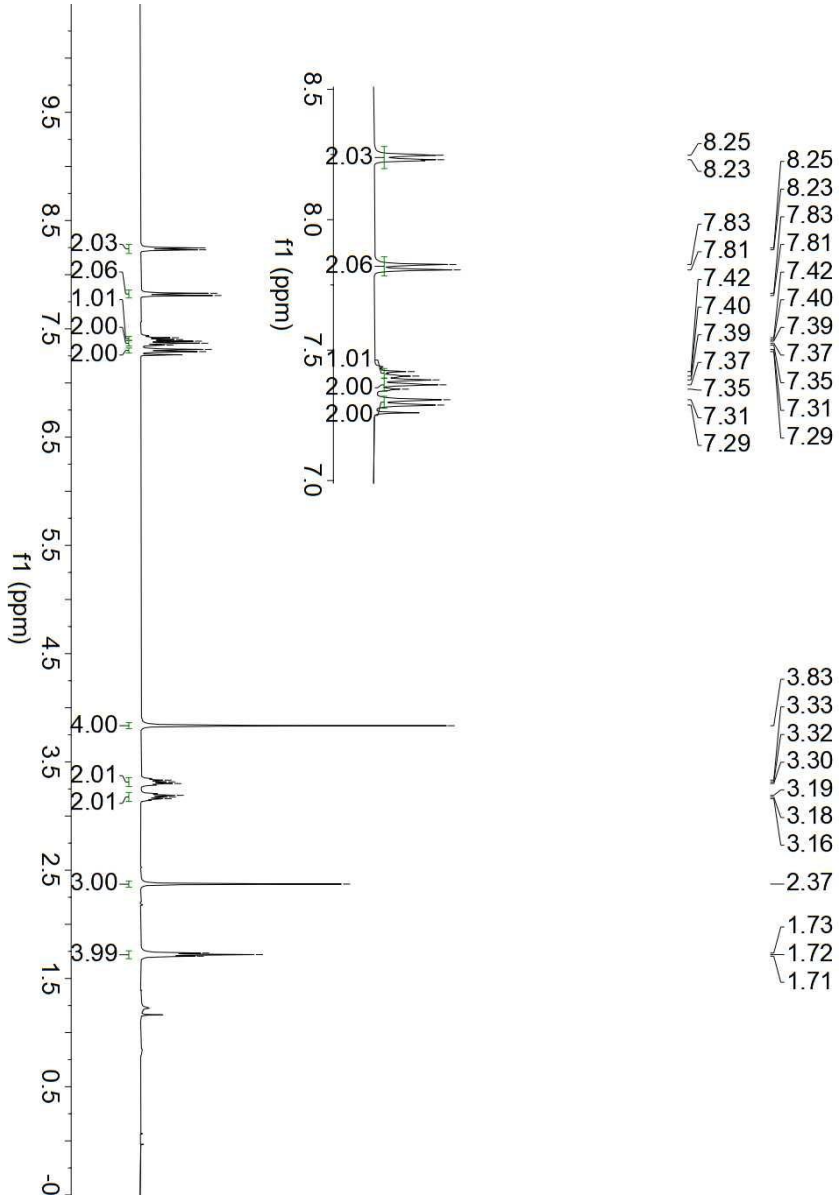


^{13}C NMR (100 MHz, Chloroform-d)

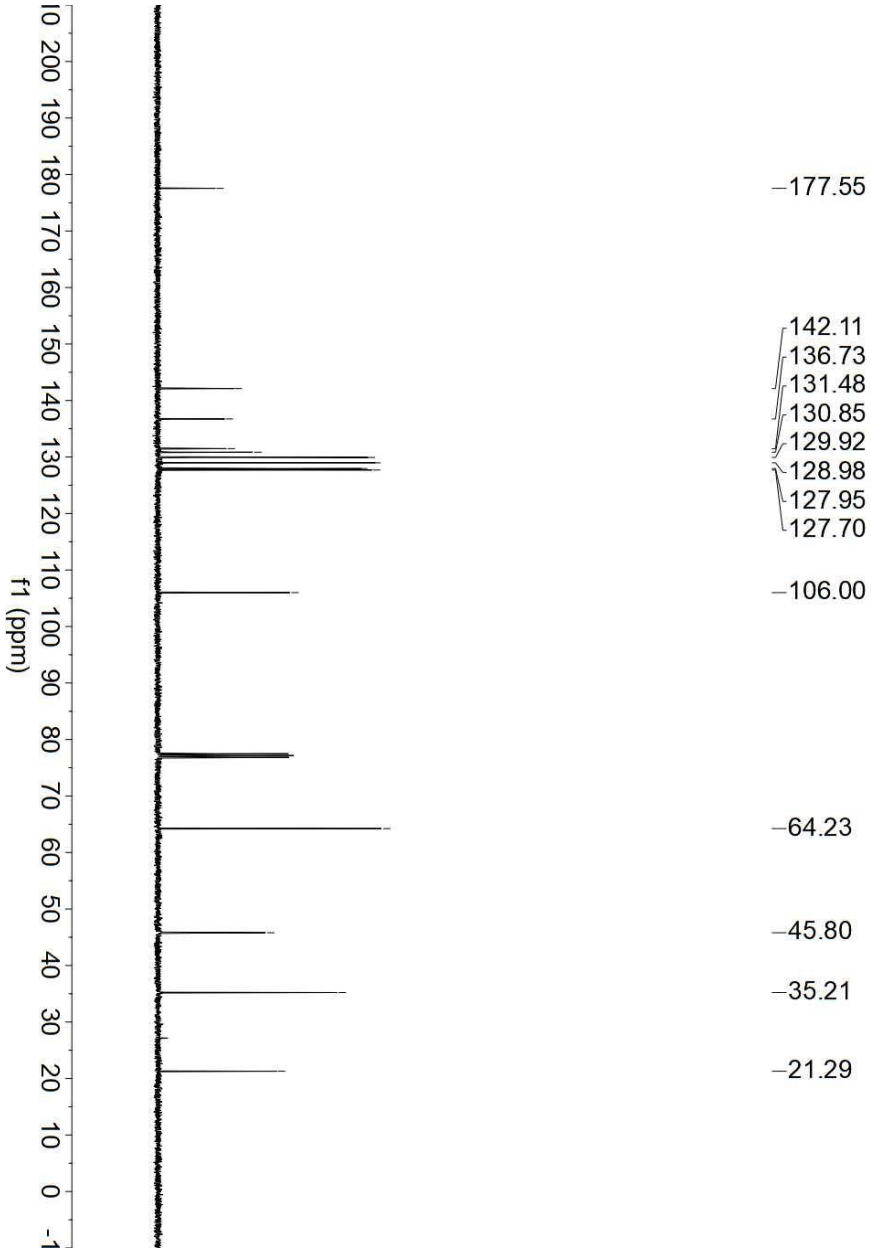


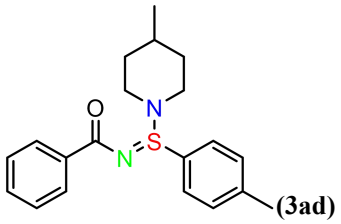


^{1}H NMR (400 MHz, Chloroform-d)



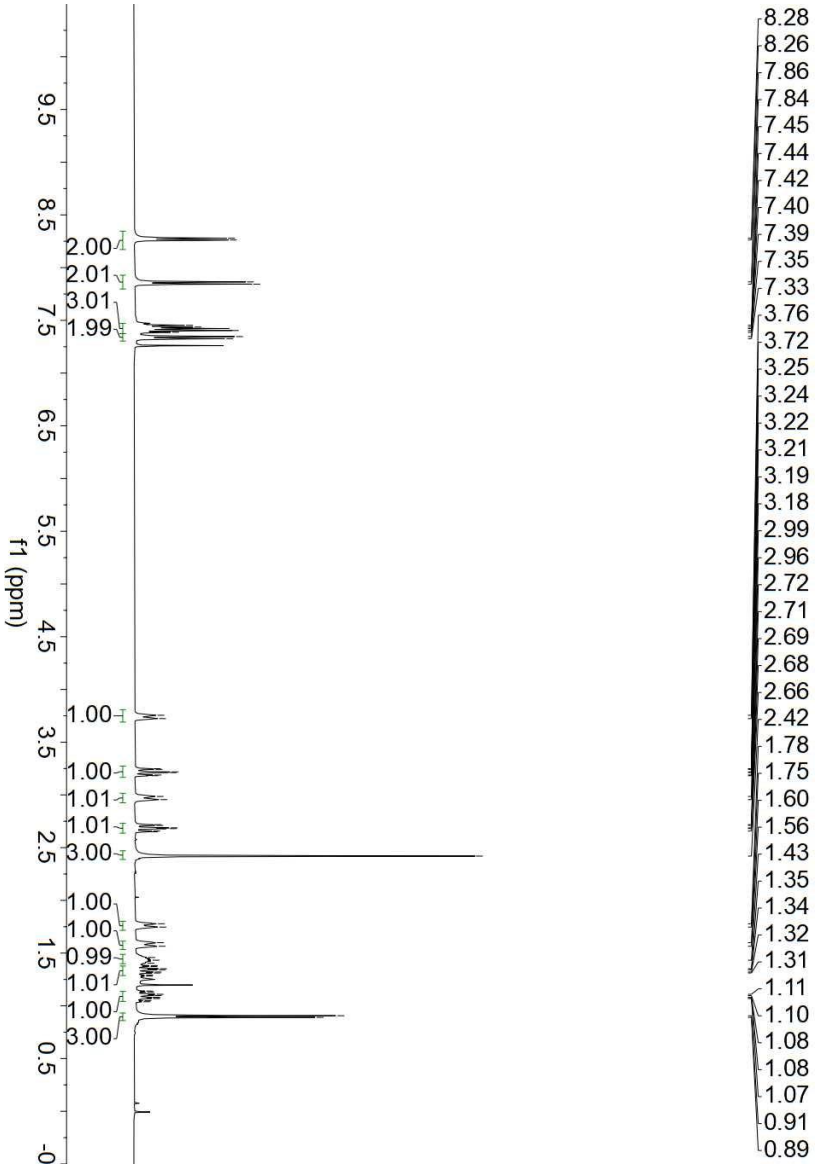
^{13}C NMR (100 MHz, Chloroform-d)



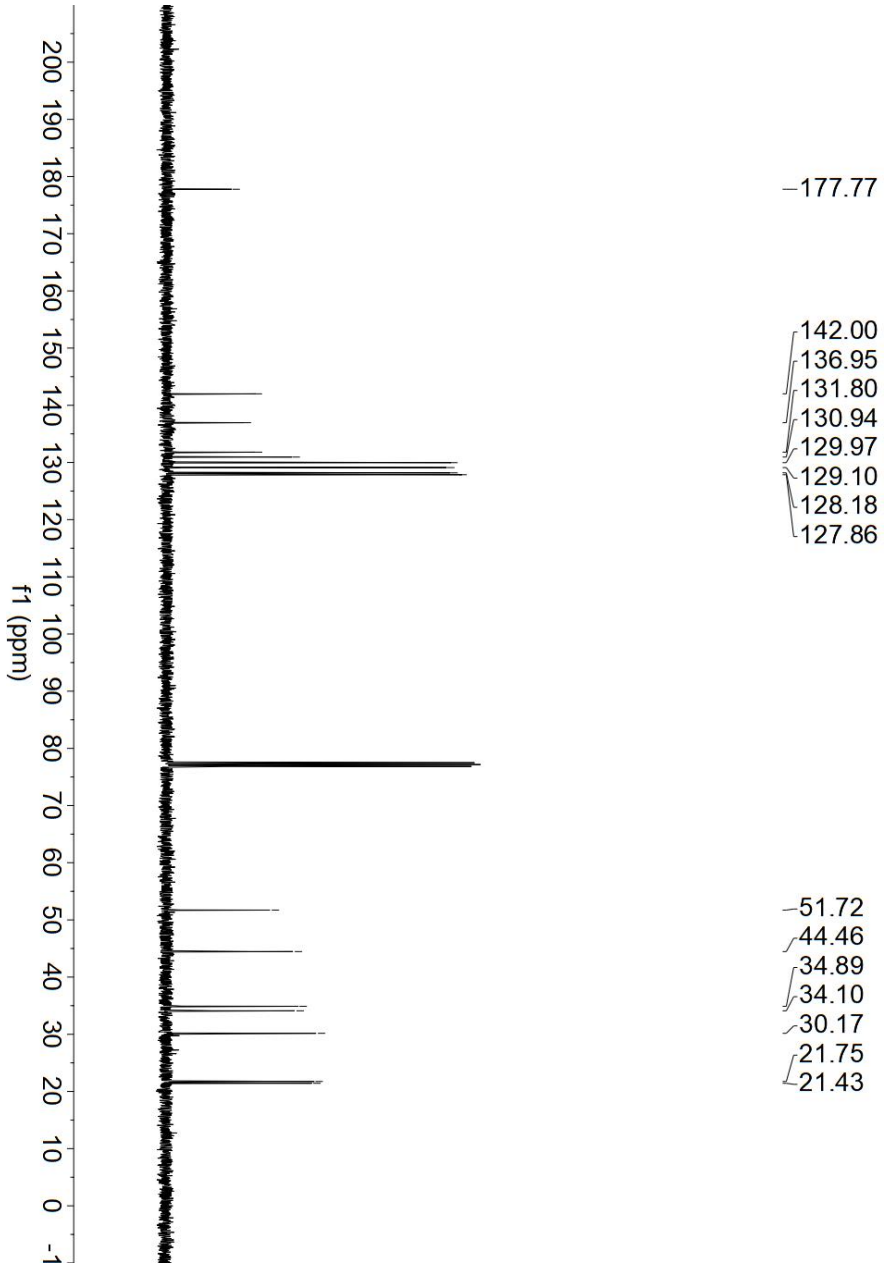


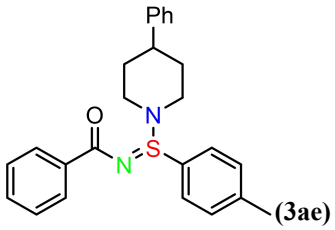
(3ad)

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

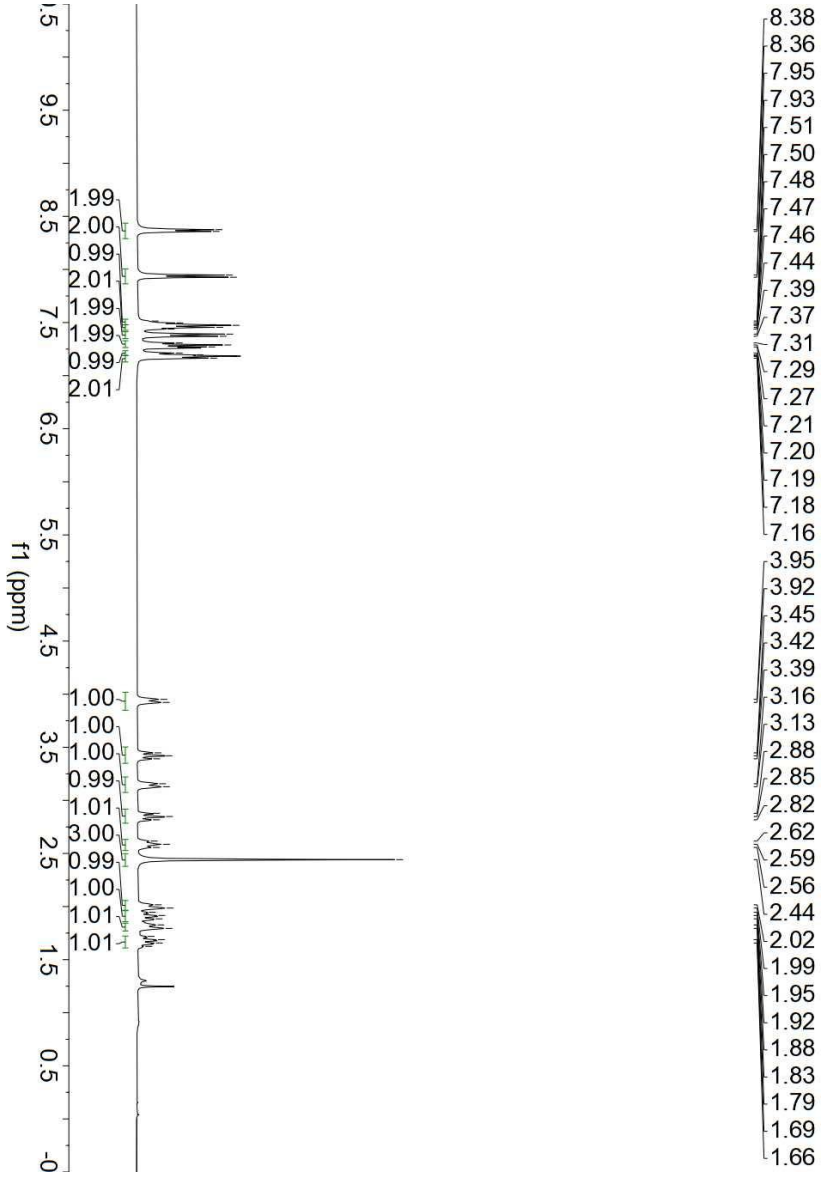


^{13}C NMR (100 MHz, Chloroform-d)

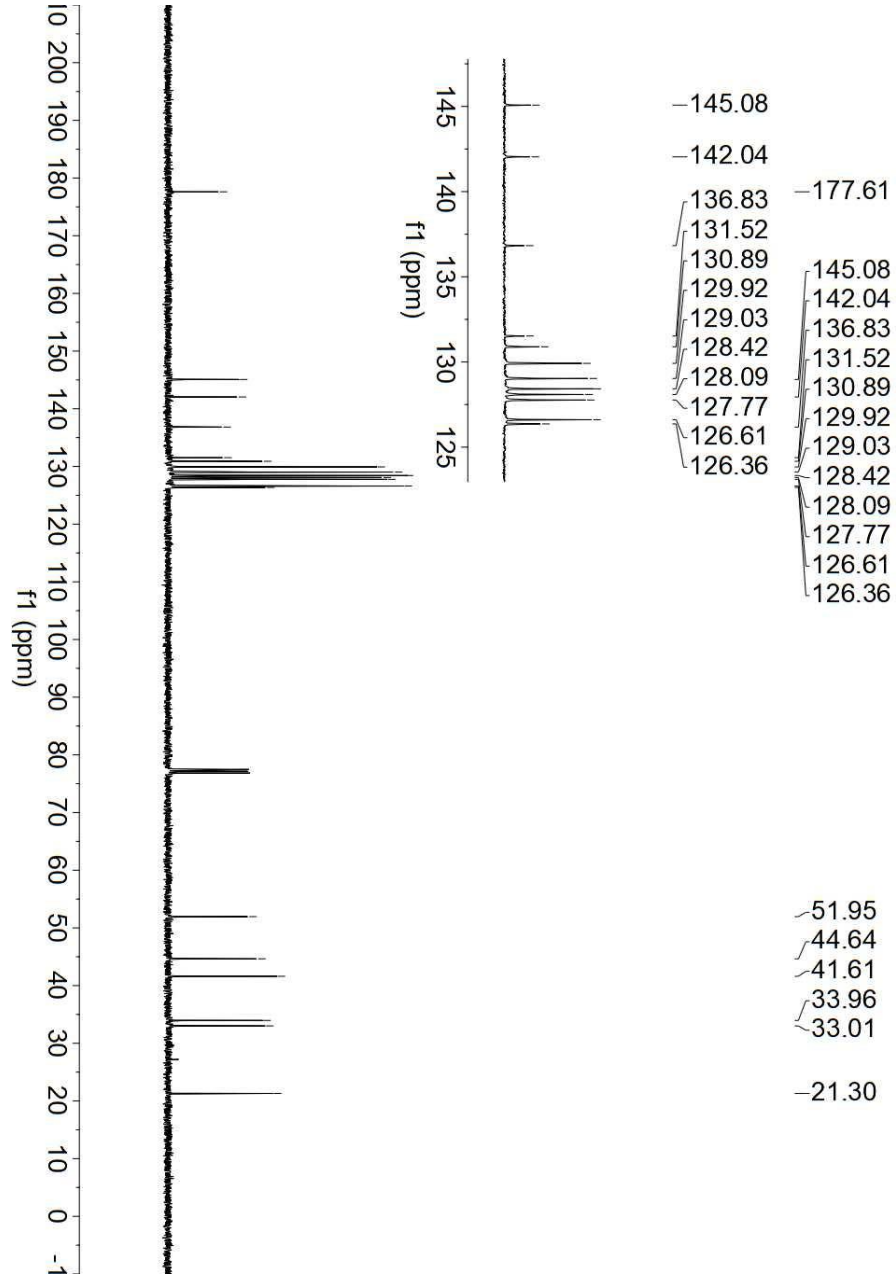


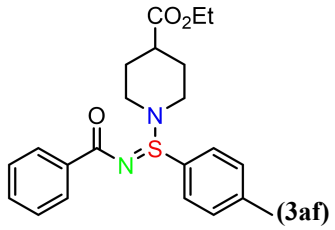


^{1}H NMR (400 MHz, Chloroform-d)

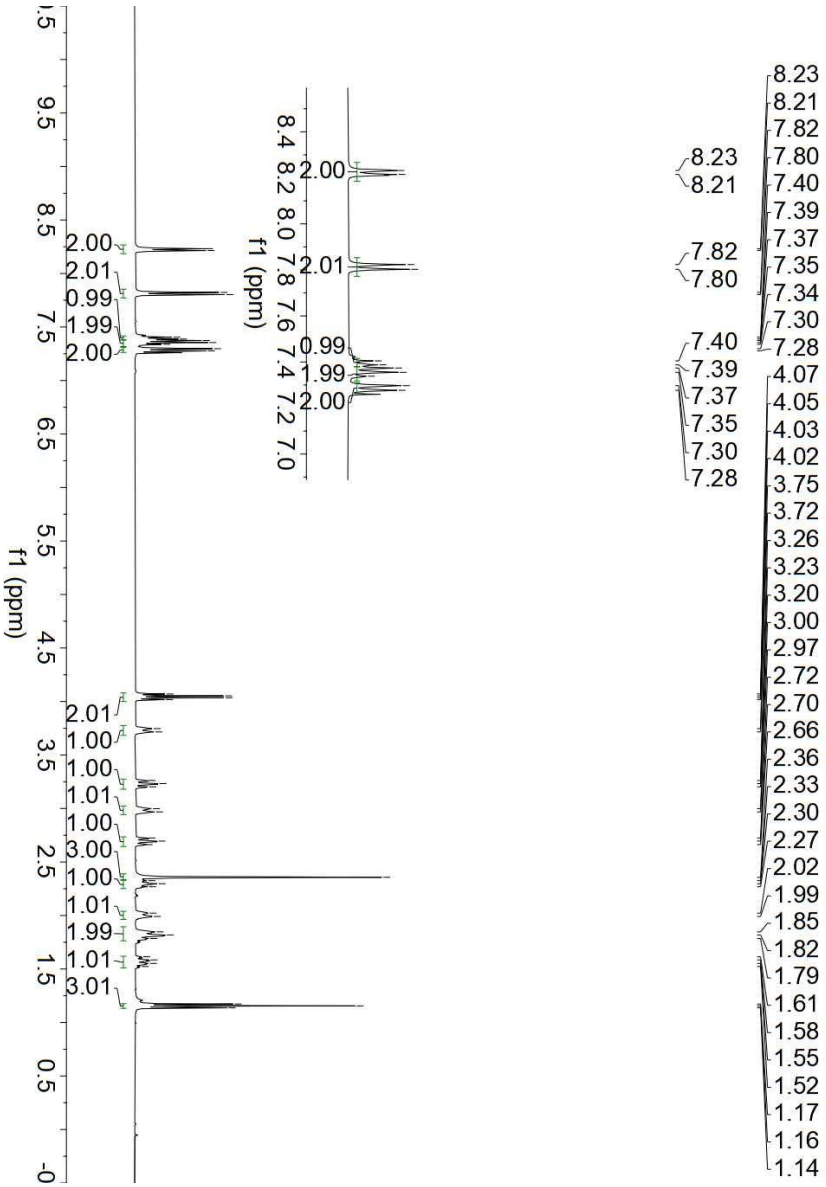


^{13}C NMR (100 MHz, Chloroform-d)

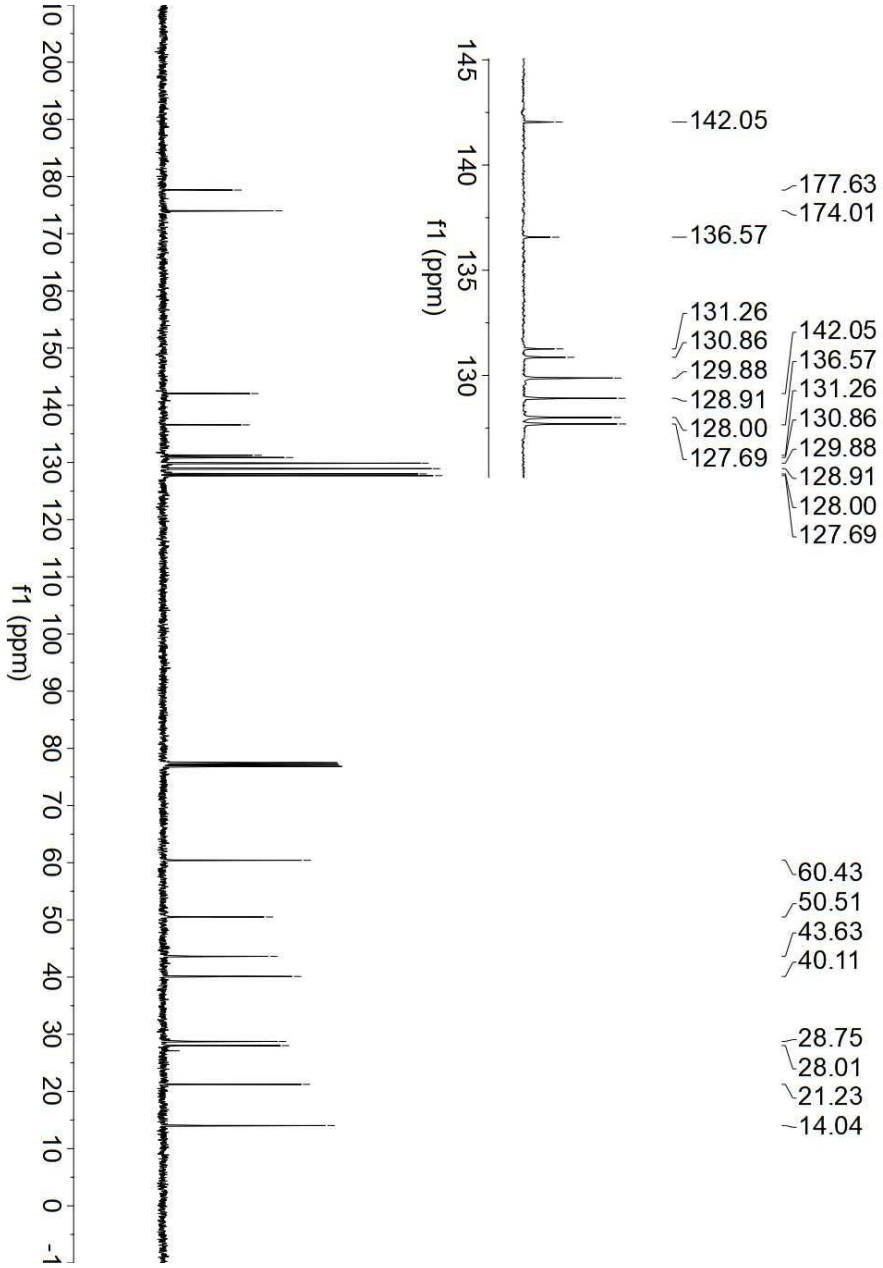


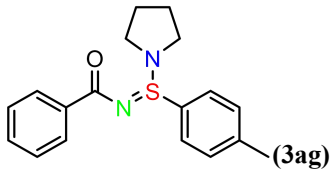


^{1}H NMR (400 MHz, Chloroform-d)



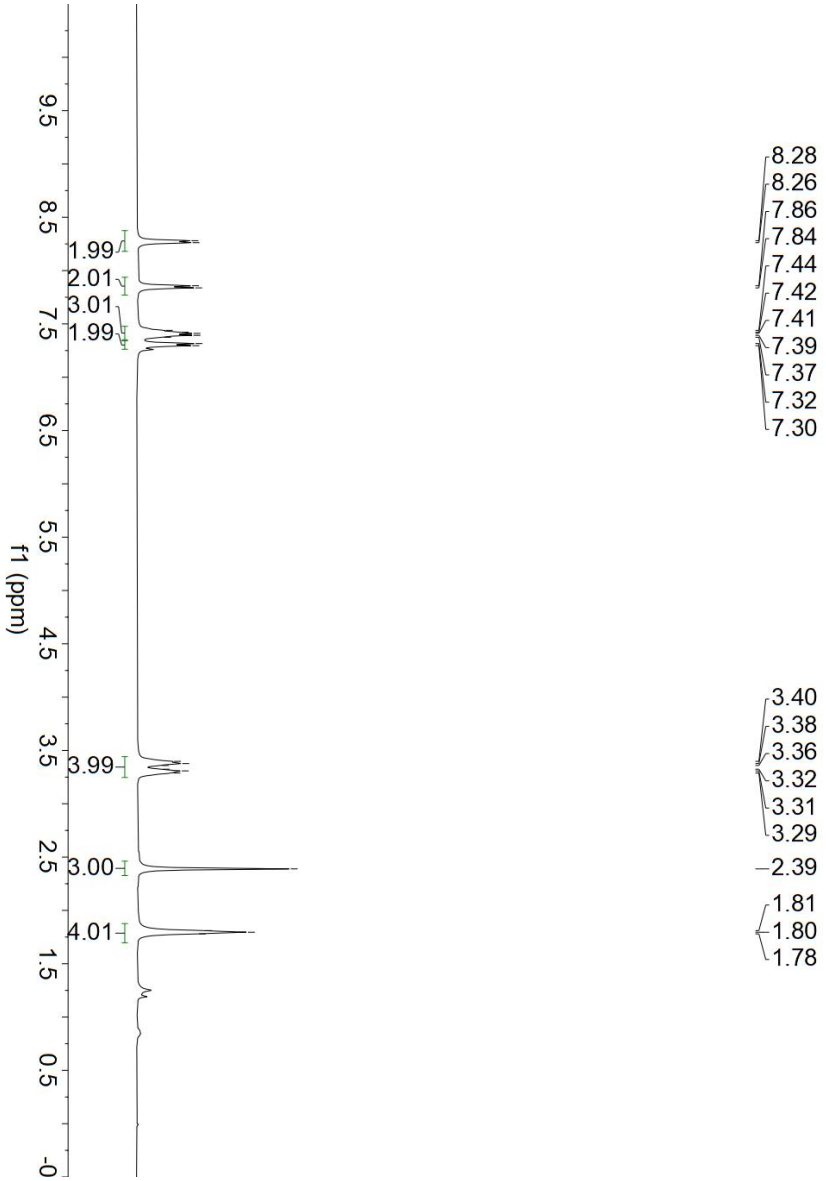
^{13}C NMR (100 MHz, Chloroform-d)



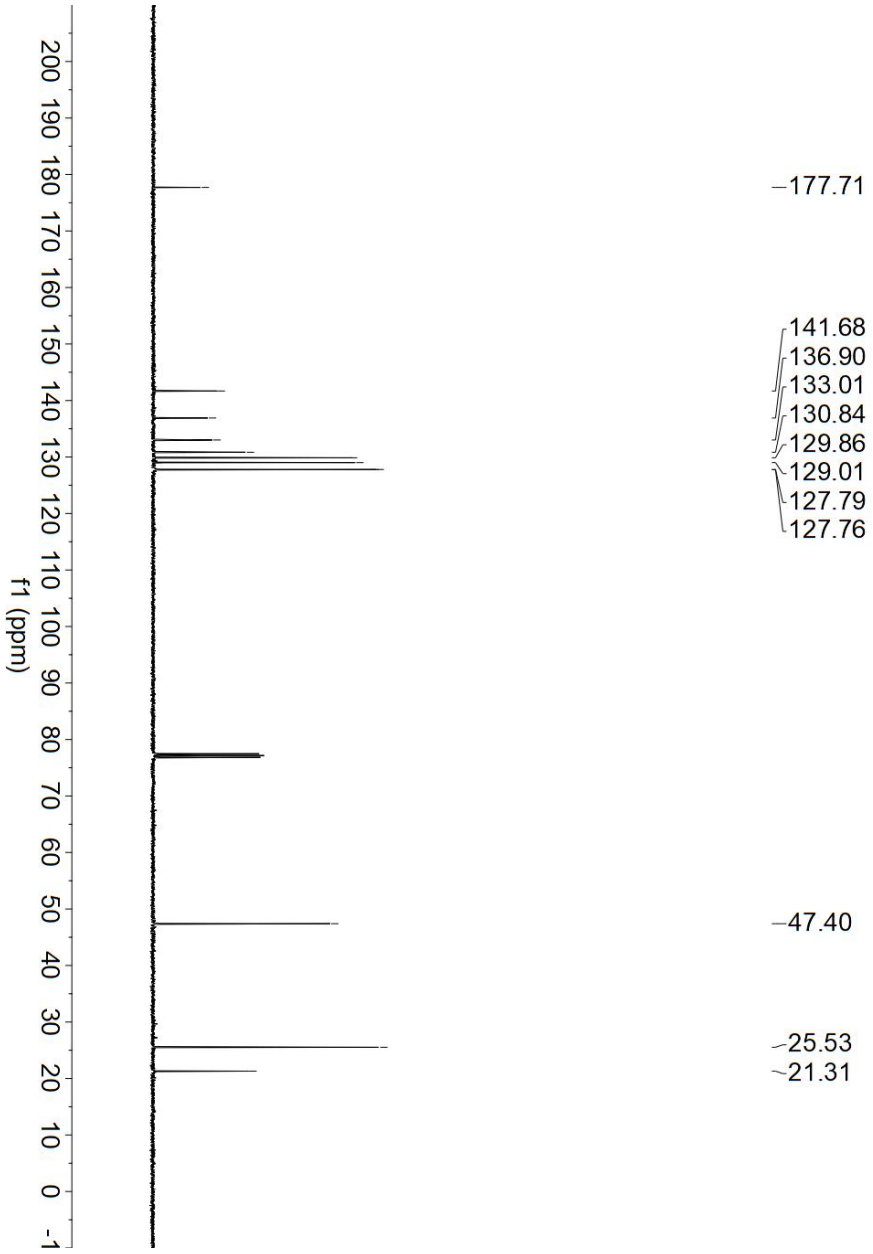


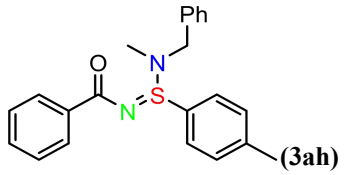
(3ag)

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

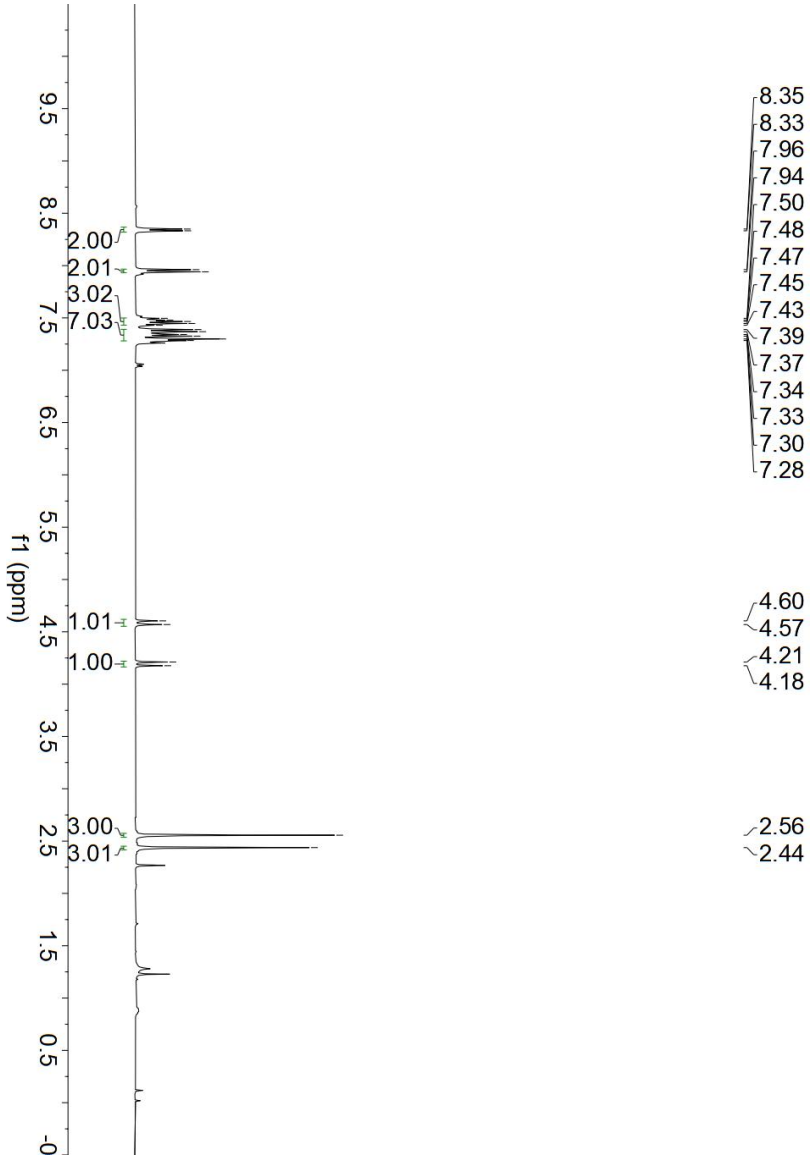


^{13}C NMR (100 MHz, Chloroform-d)

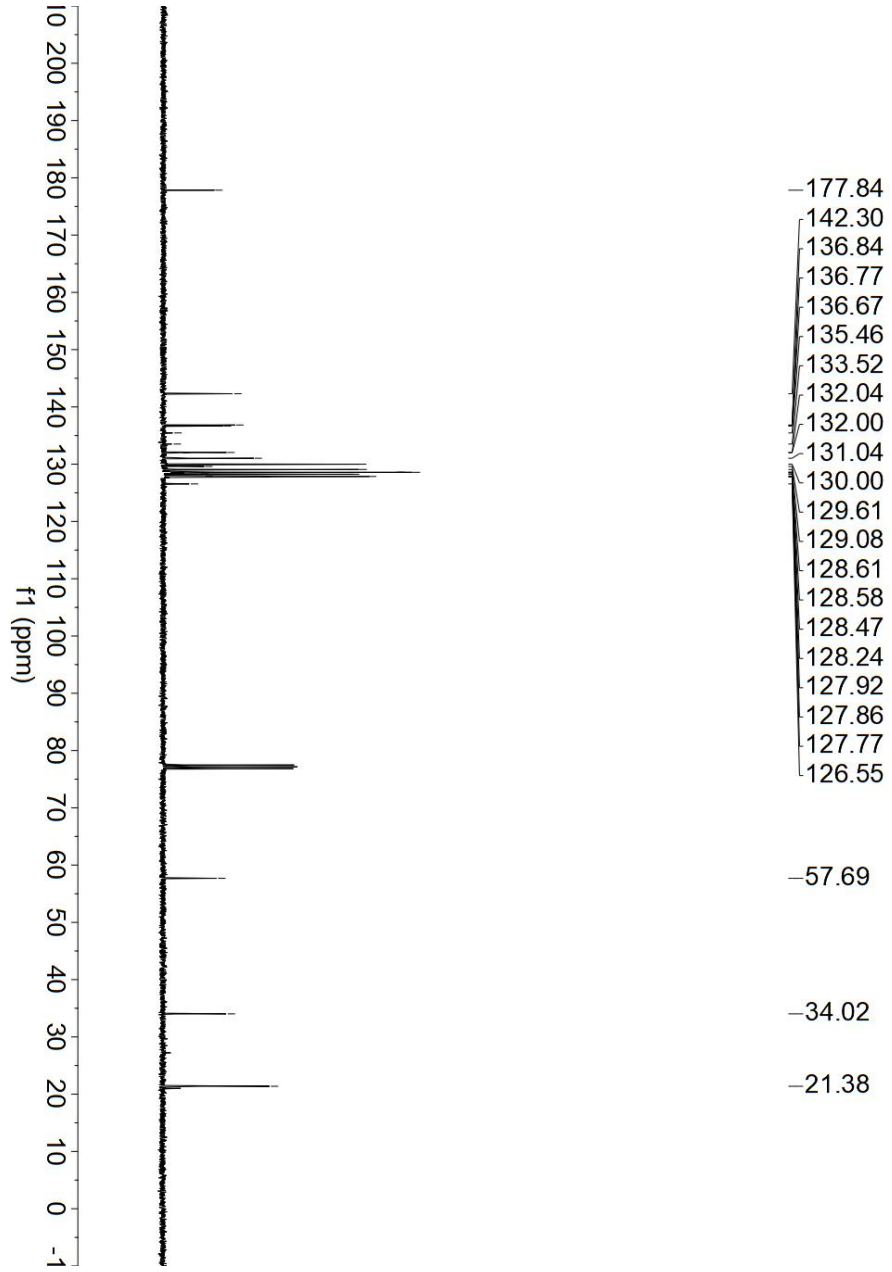


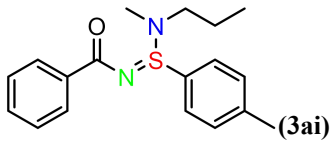


^{1}H NMR (400 MHz, Chloroform-d)

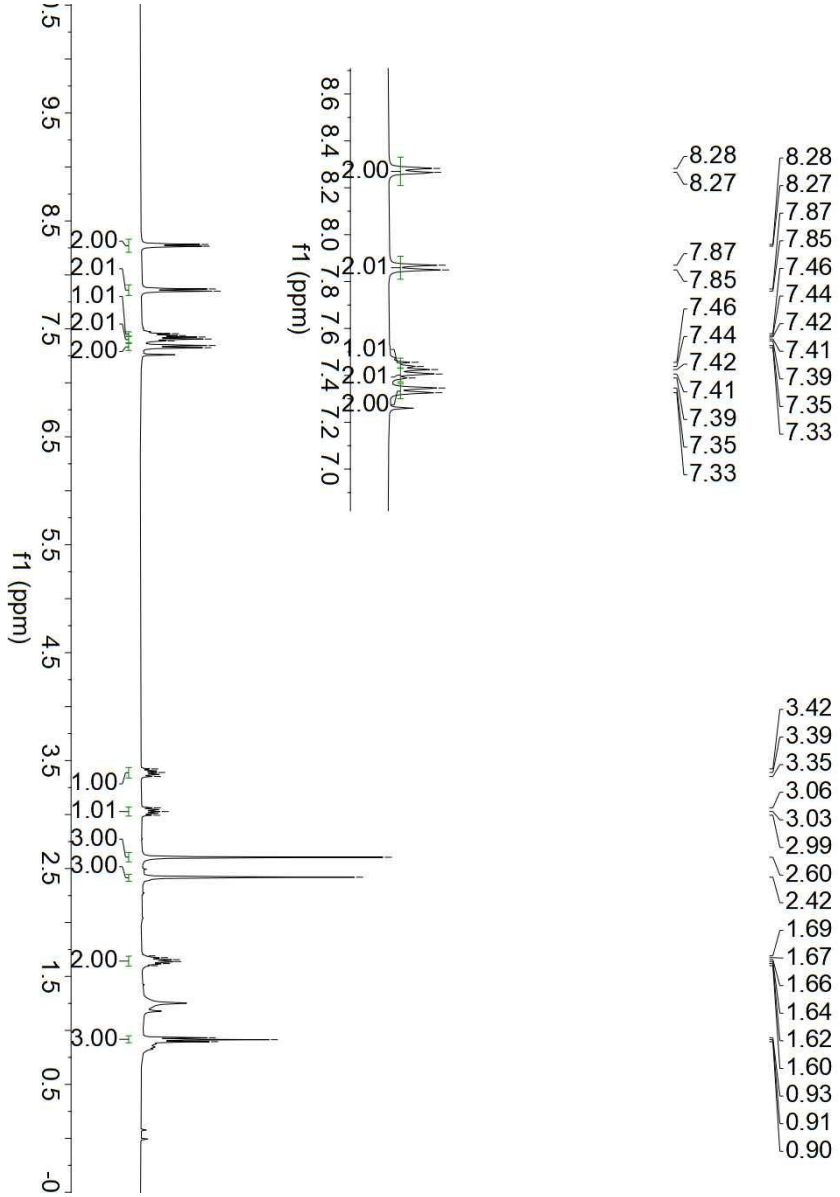


^{13}C NMR (100 MHz, Chloroform-d)

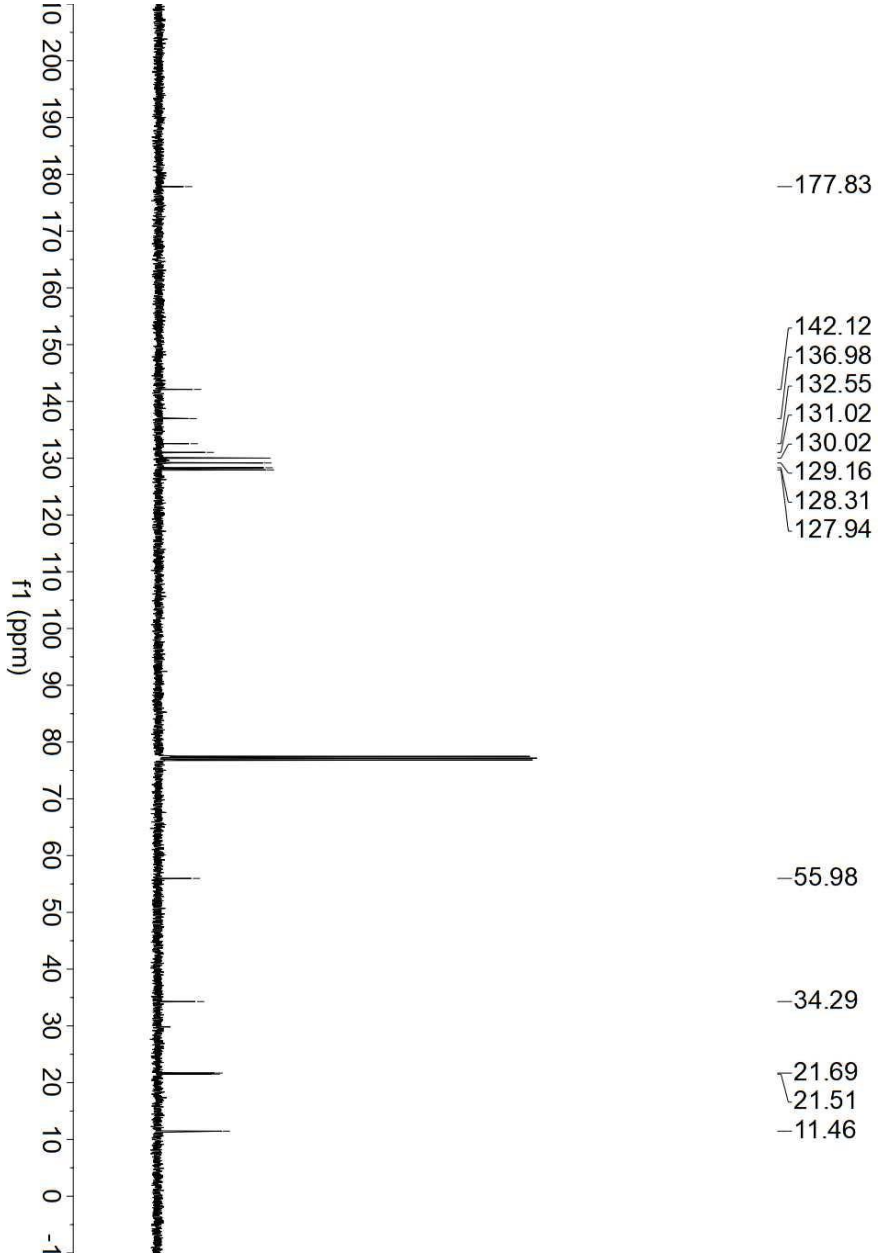


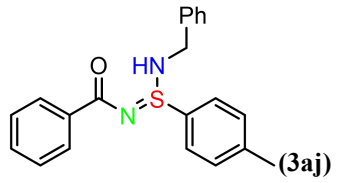


^{1}H NMR (400 MHz, Chloroform-*d*)

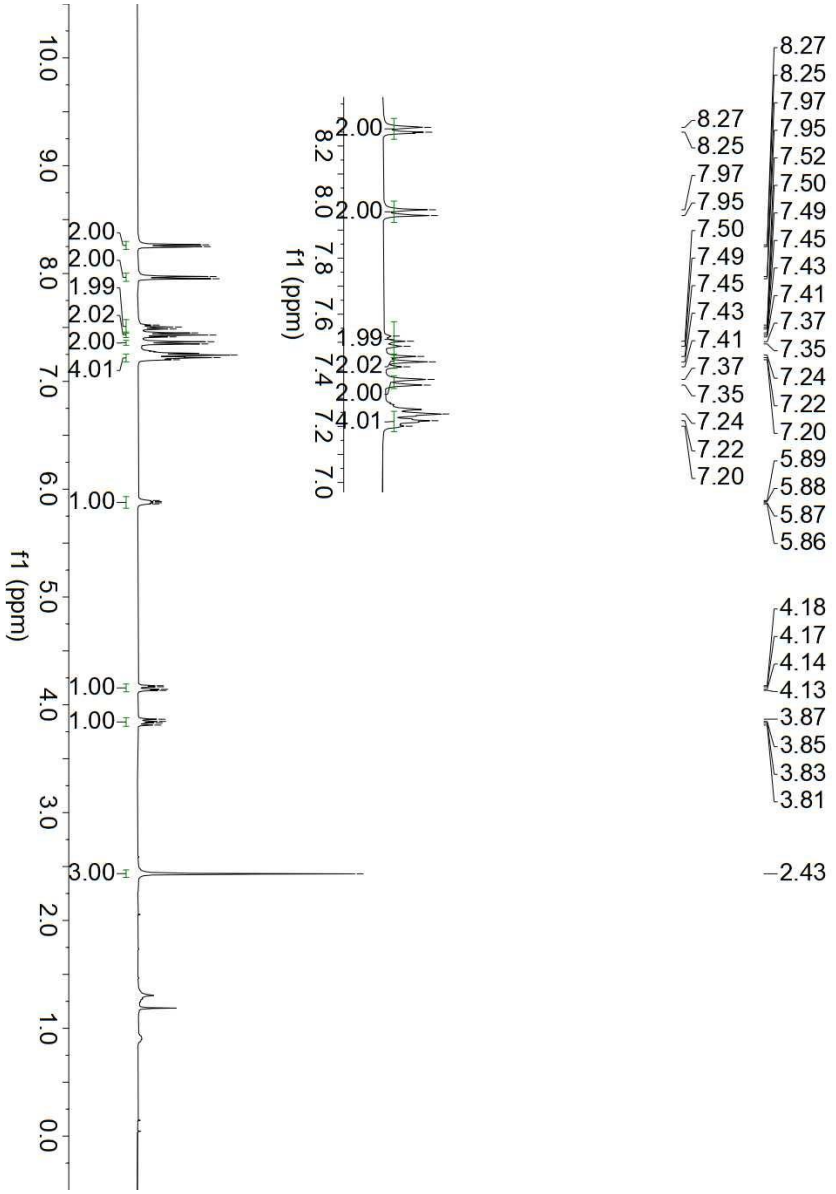


^{13}C NMR (100 MHz, Chloroform-d)

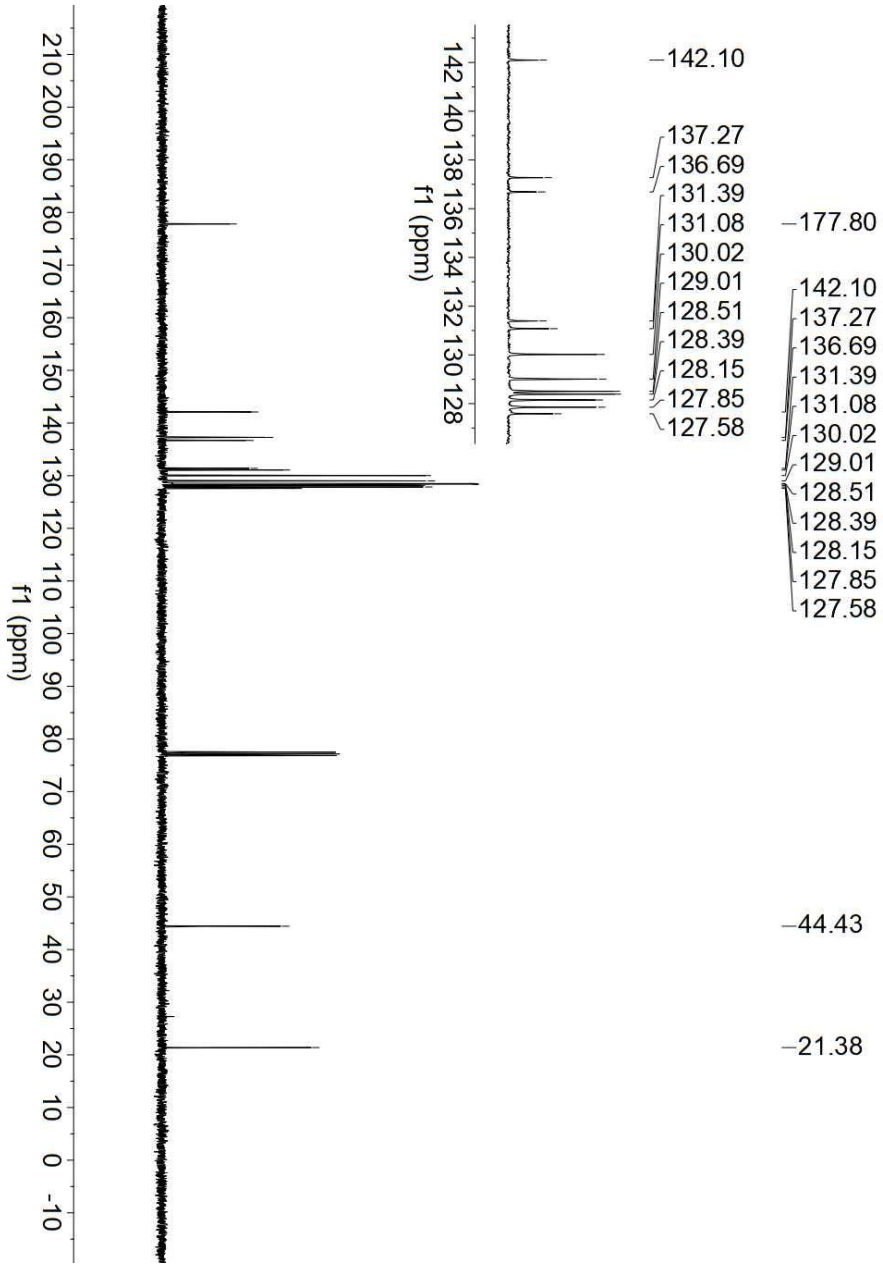


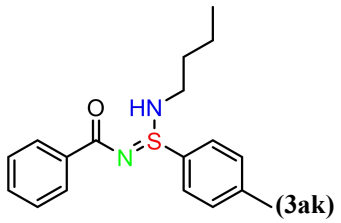


^{1}H NMR (400 MHz, Chloroform-*d*)

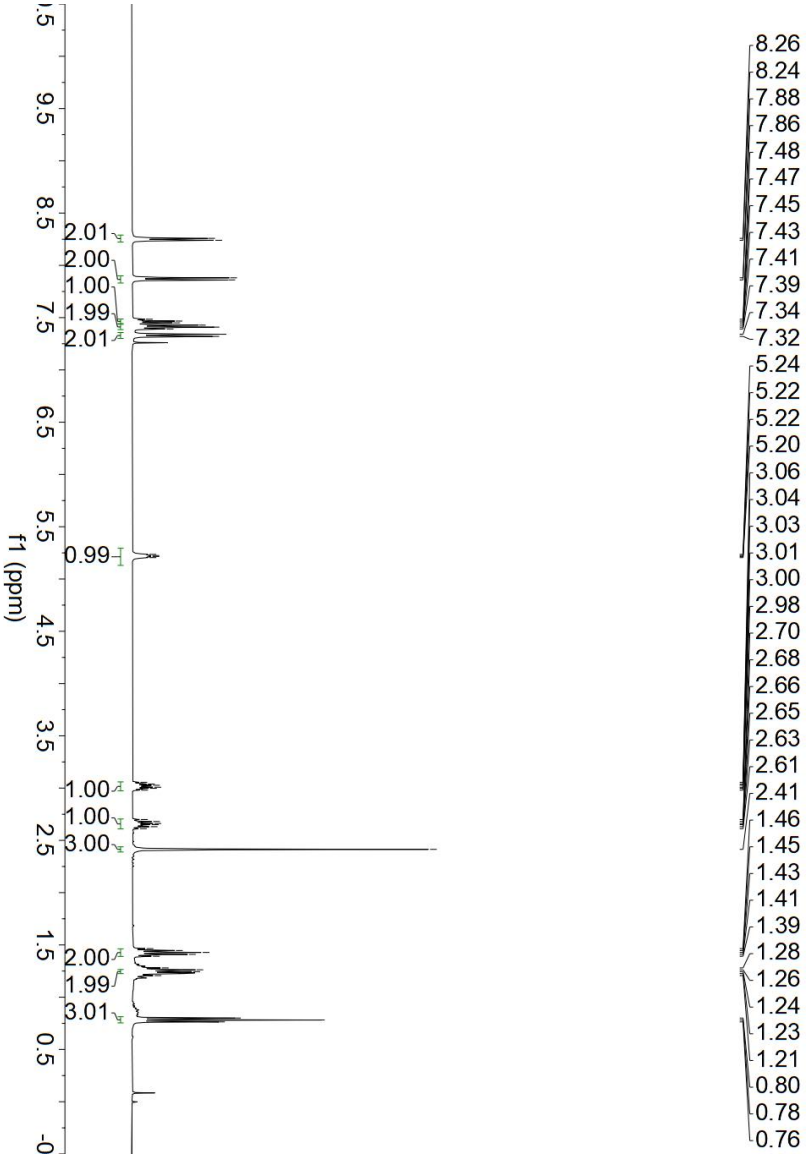


^{13}C NMR (100 MHz, Chloroform-d)

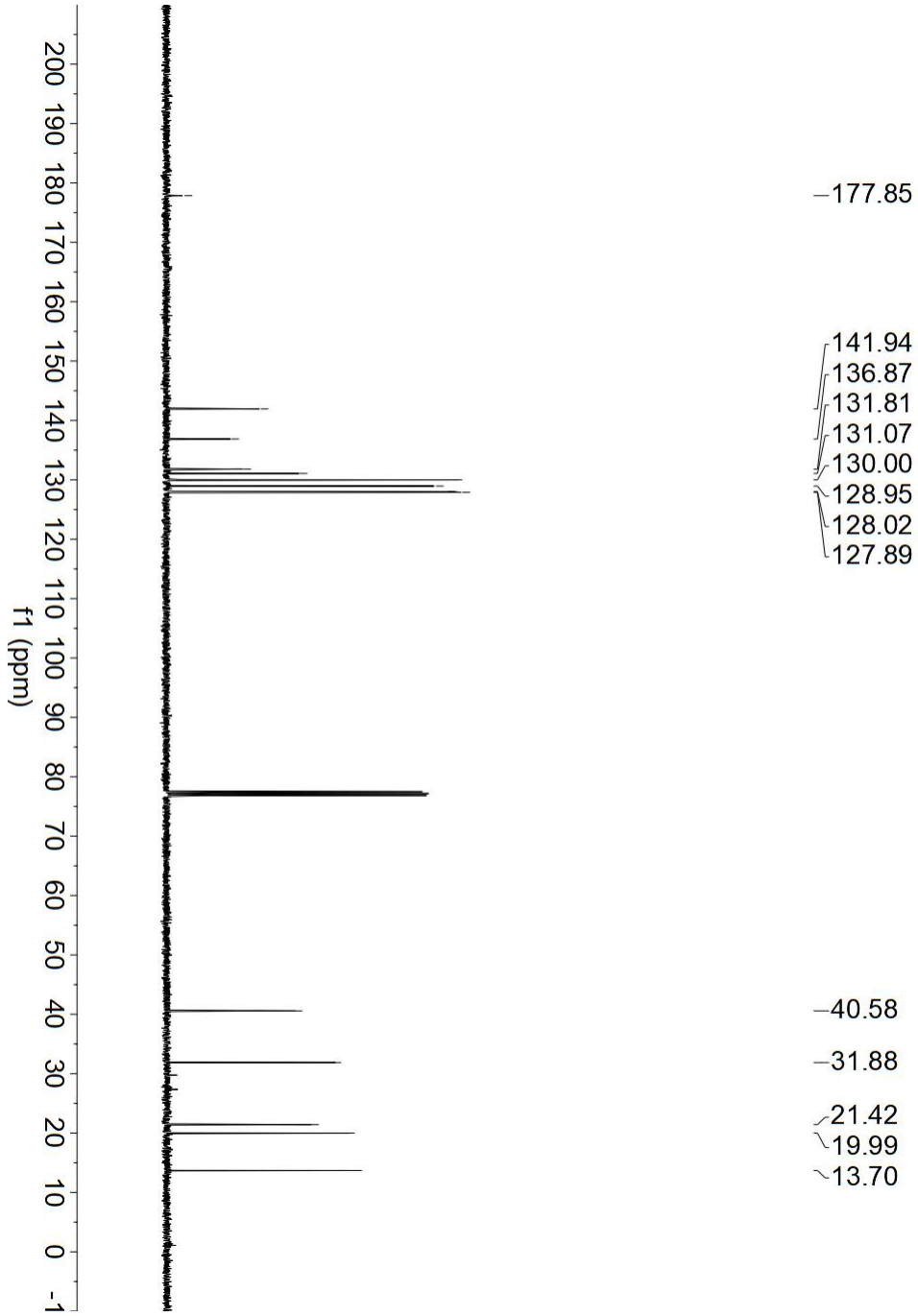


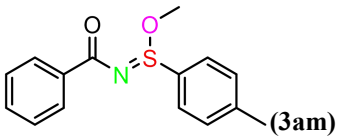


^{1}H NMR (400 MHz, Chloroform-d)



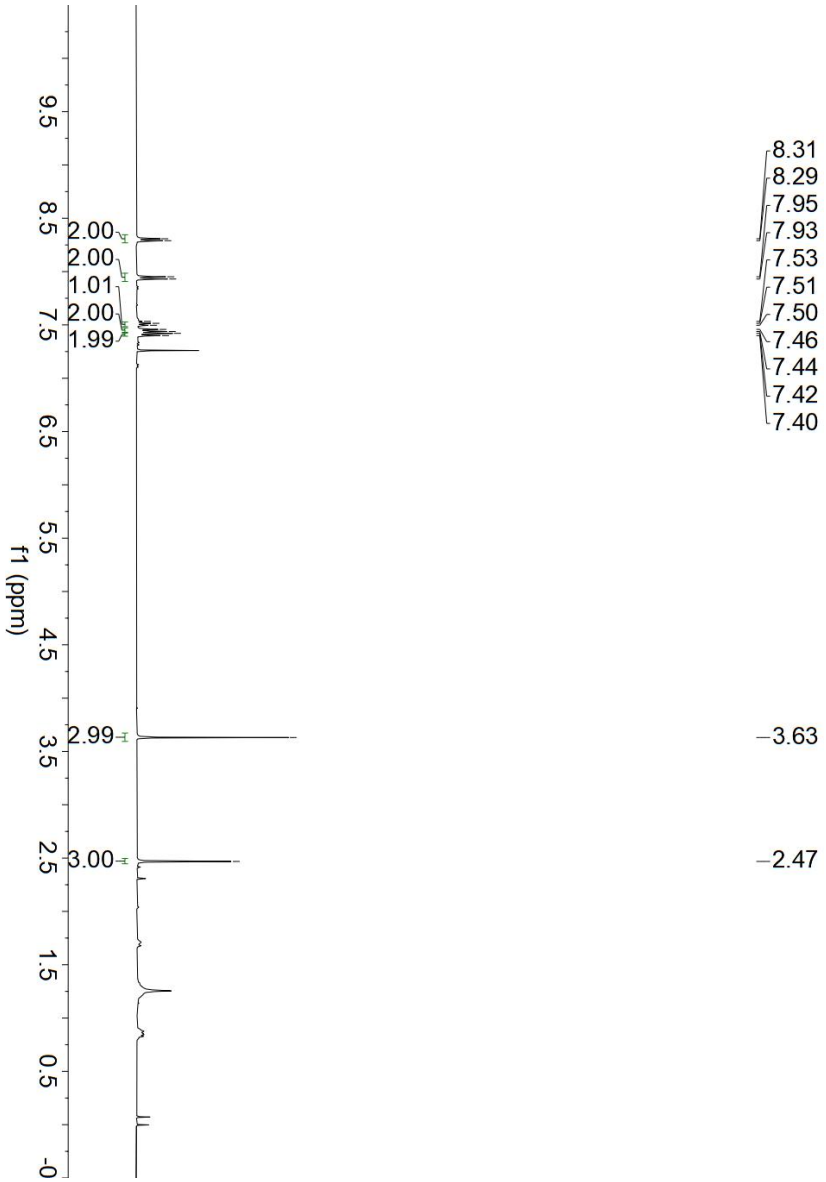
^{13}C NMR (100 MHz, Chloroform-d)



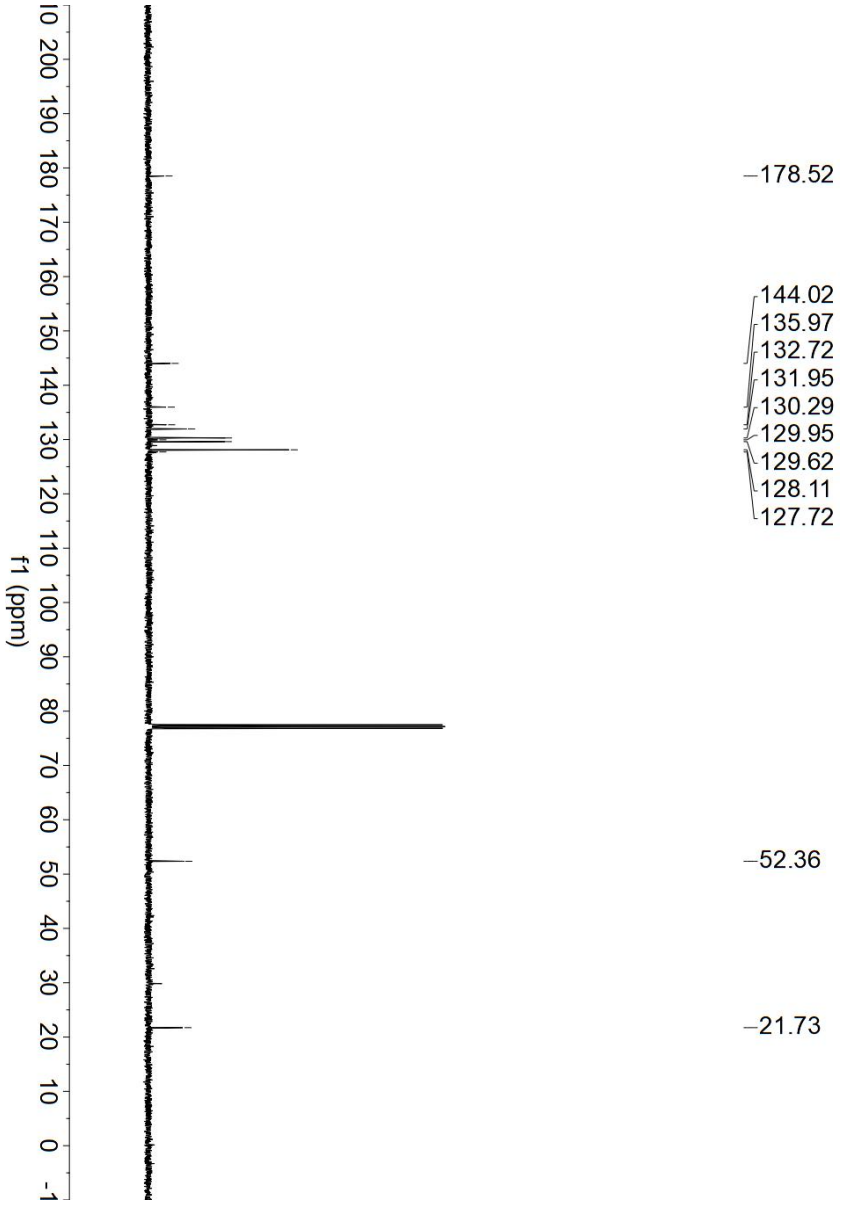


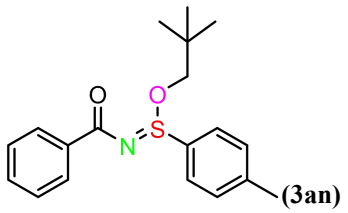
(3am)

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



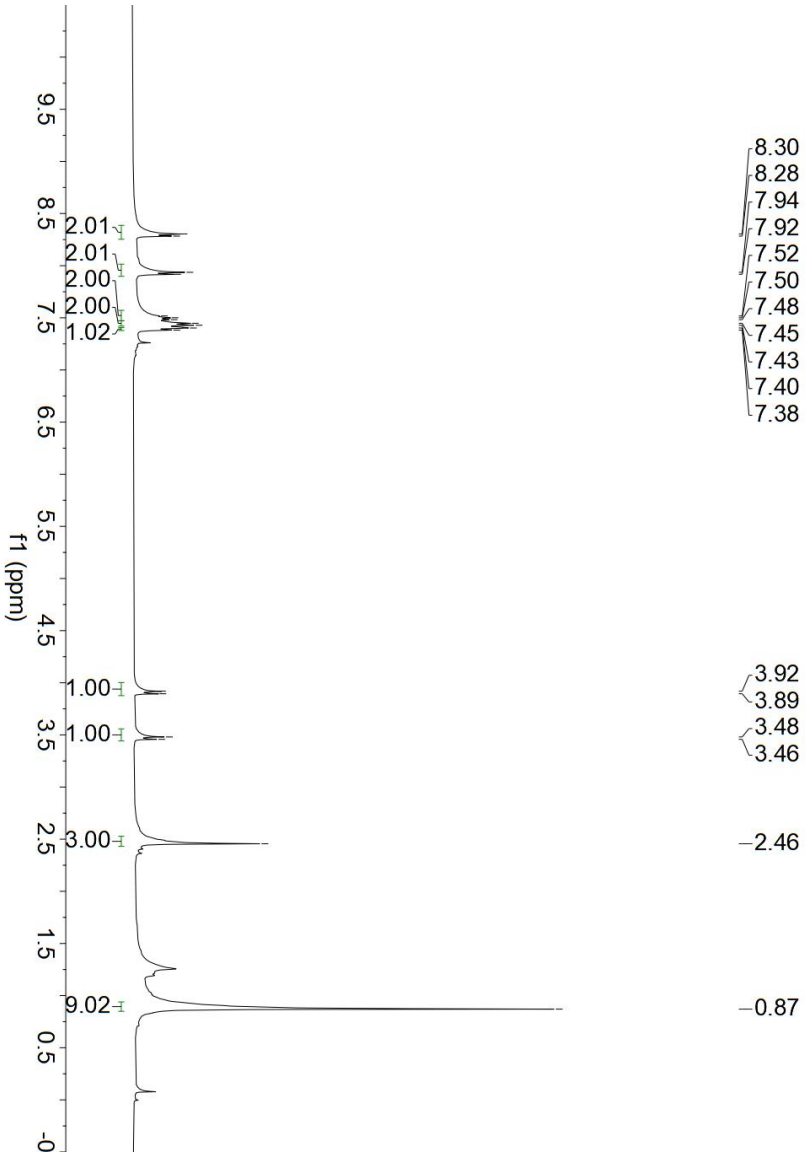
^{13}C NMR (100 MHz, Chloroform-*d*)



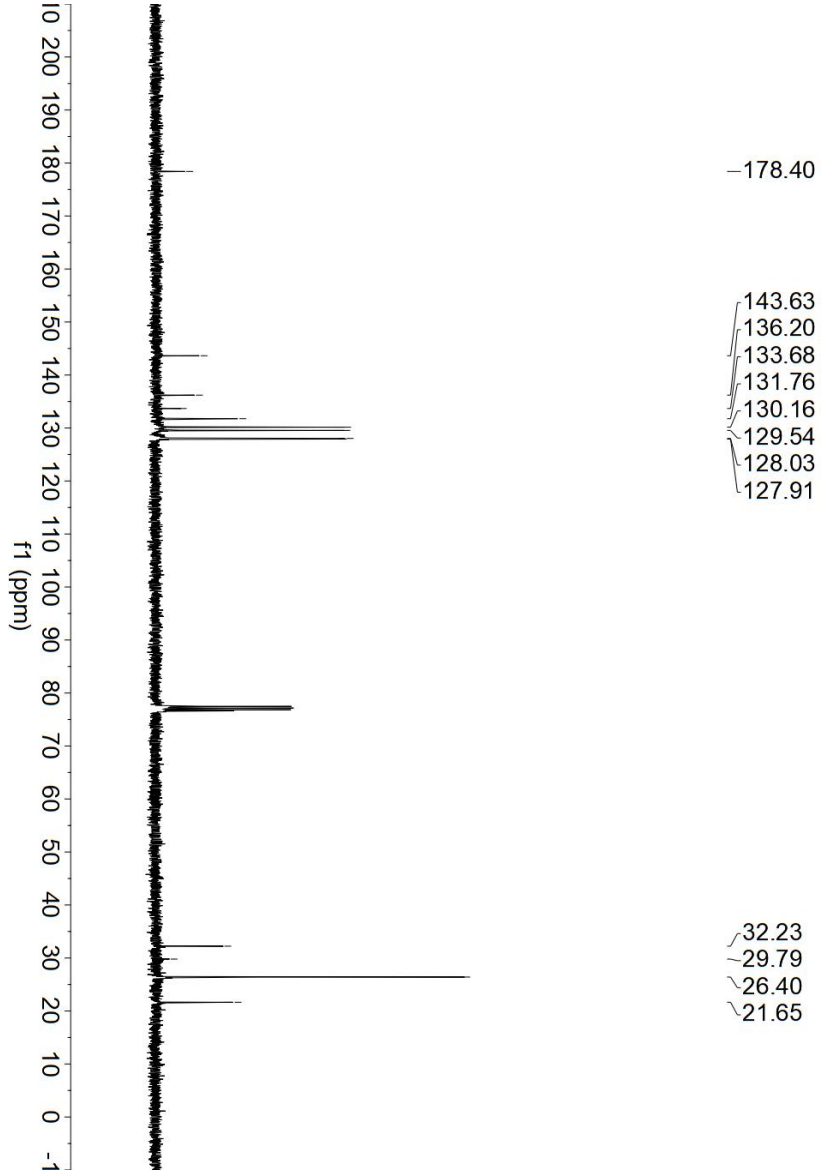


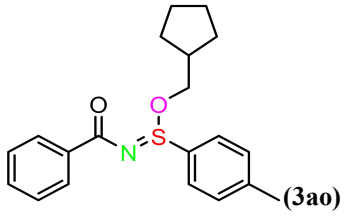
(3an)

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

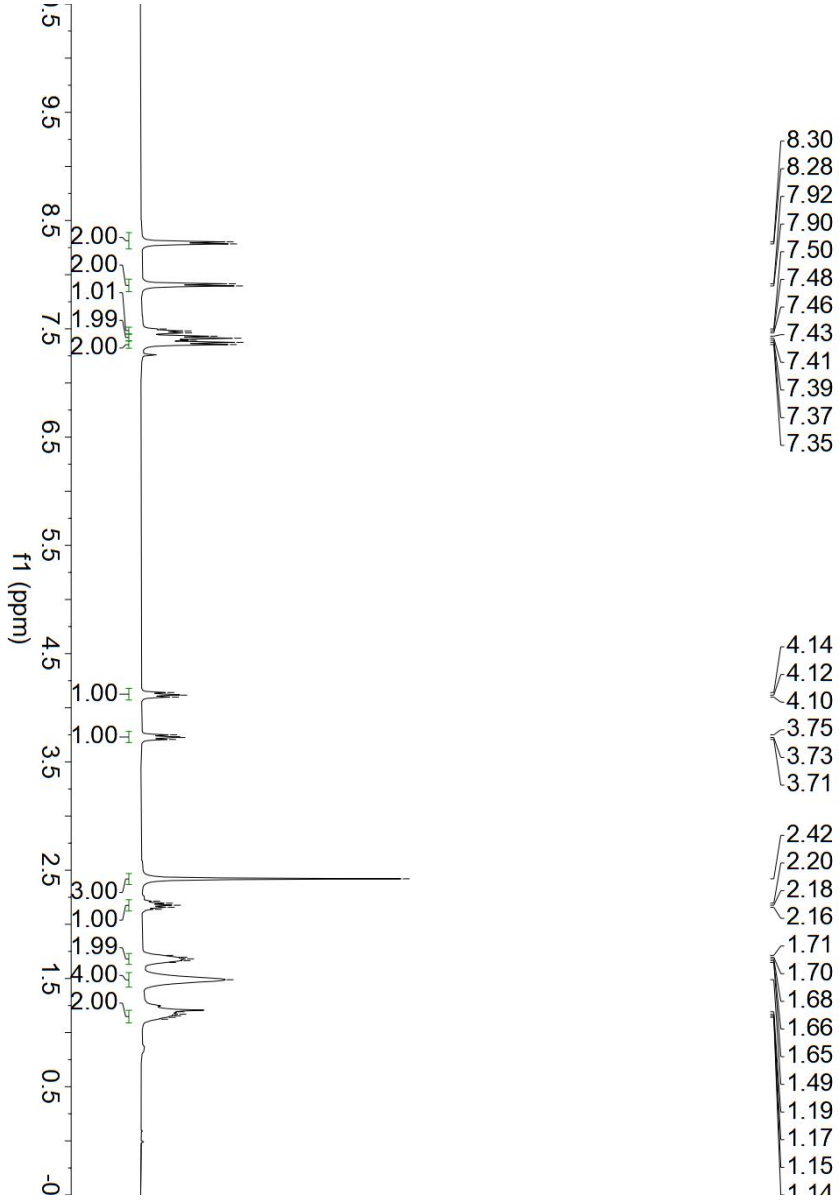


^{13}C NMR (100 MHz, Chloroform-*d*)

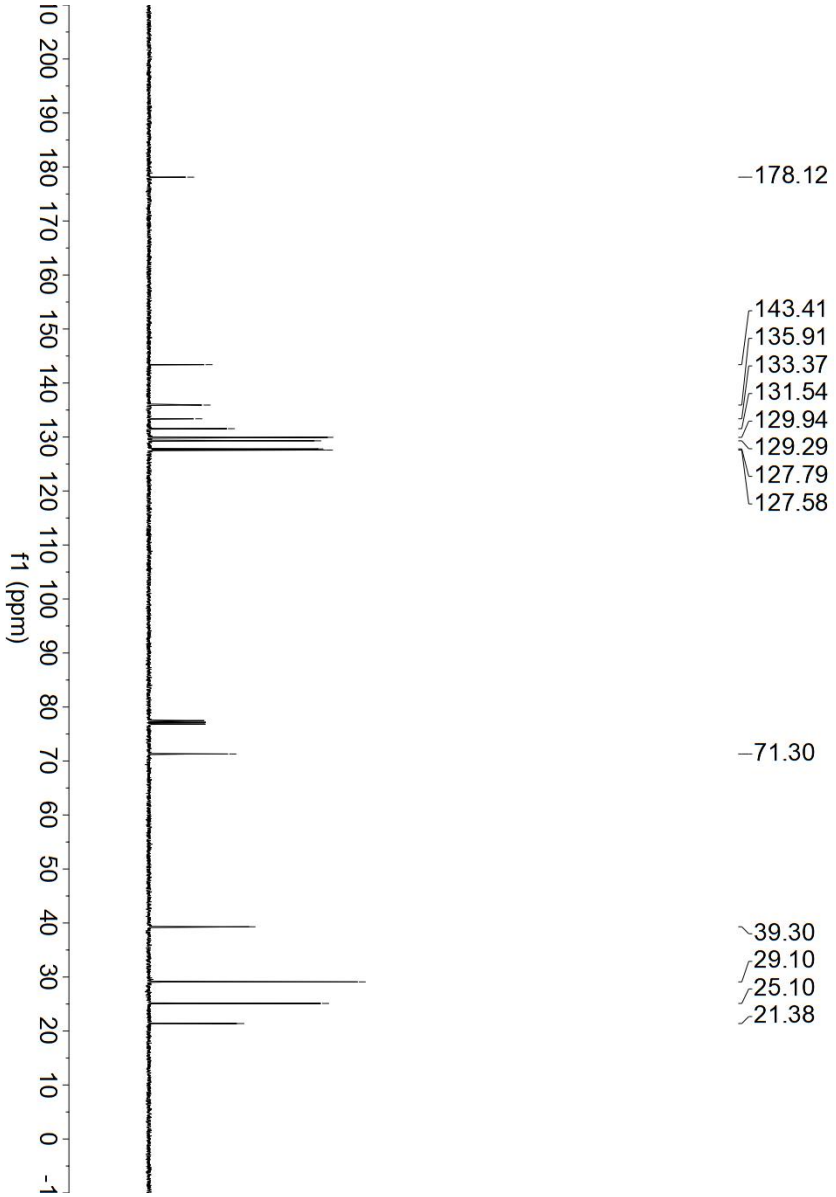


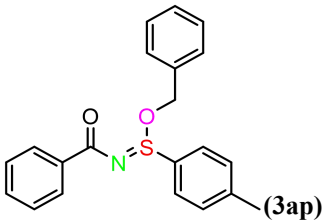


^{1}H NMR (400 MHz, Chloroform-*d*)



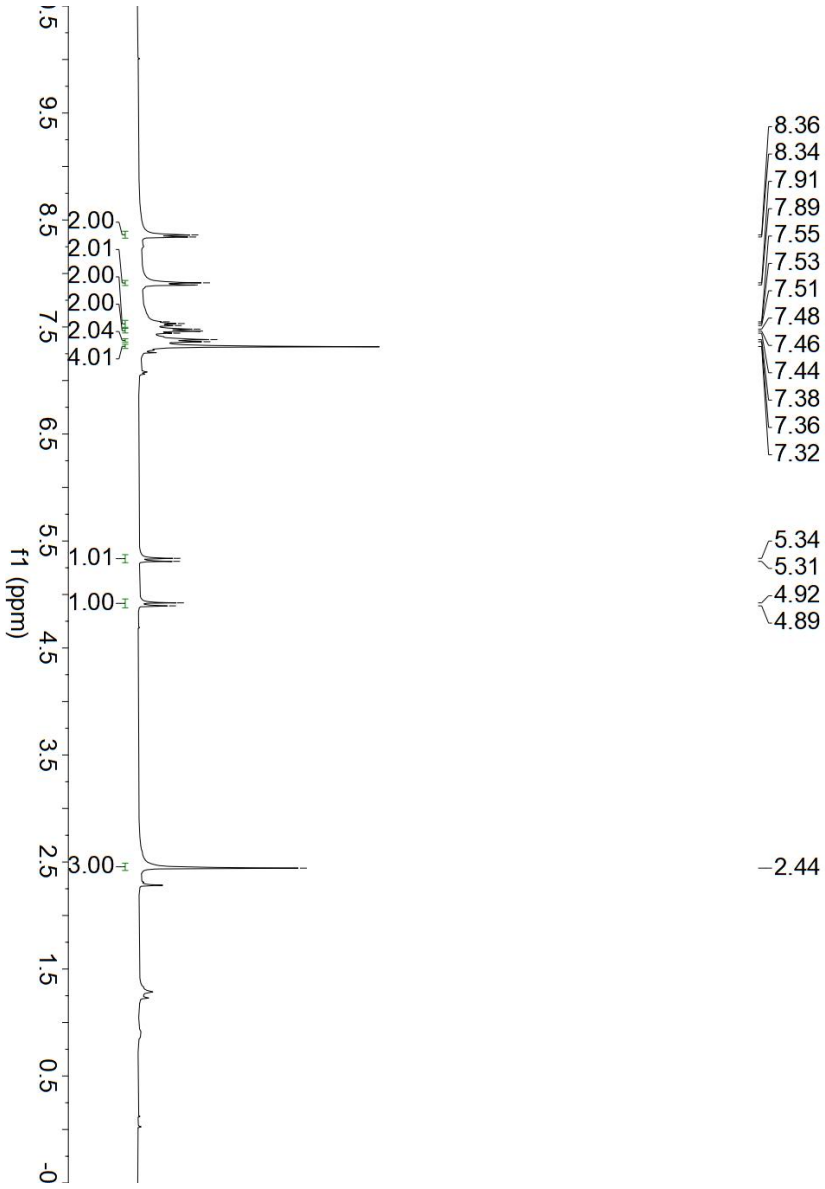
^{13}C NMR (100 MHz, Chloroform-*d*)



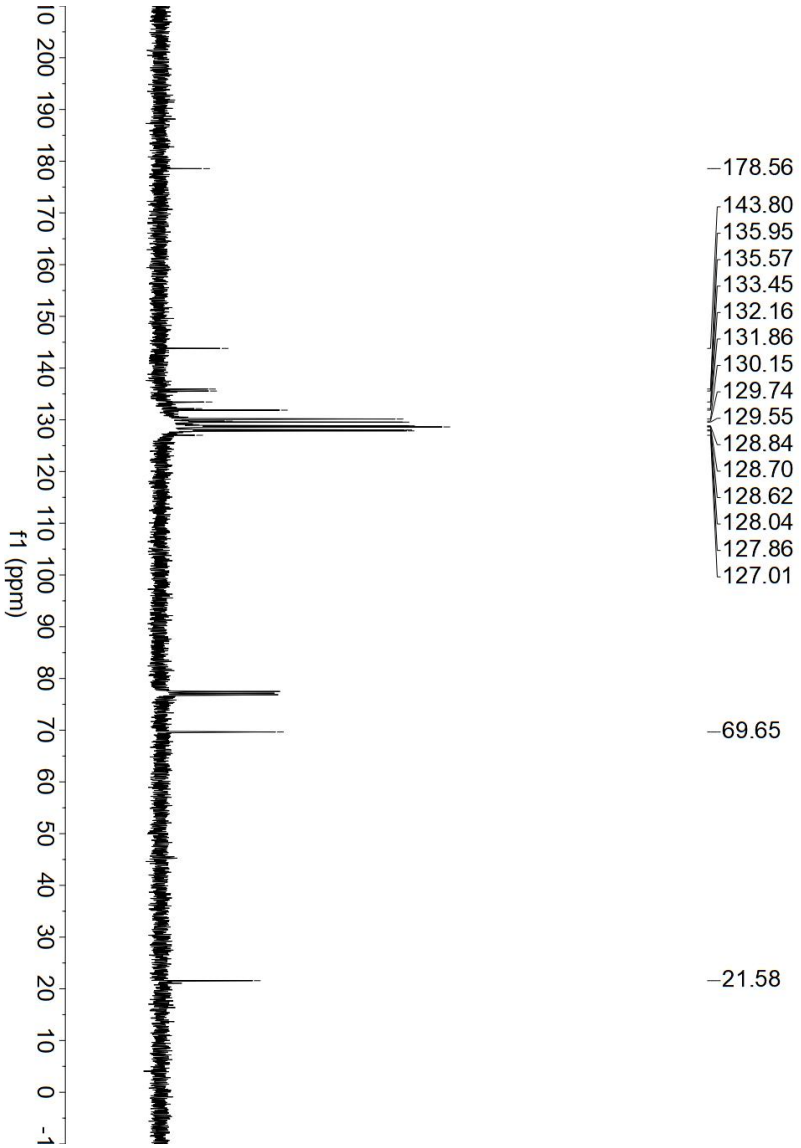


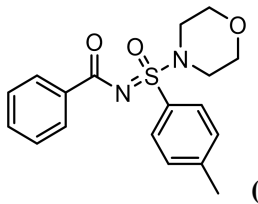
(3ap)

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



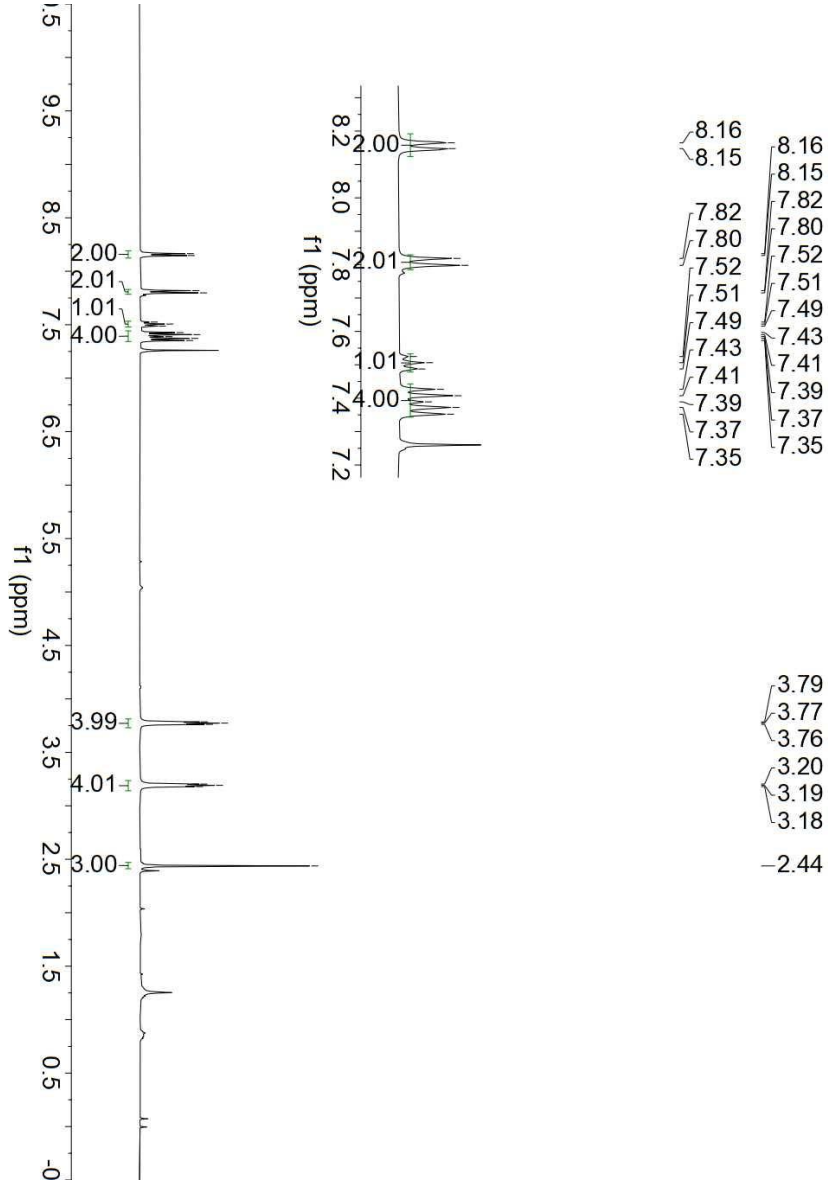
^{13}C NMR (100 MHz, Chloroform-*d*)



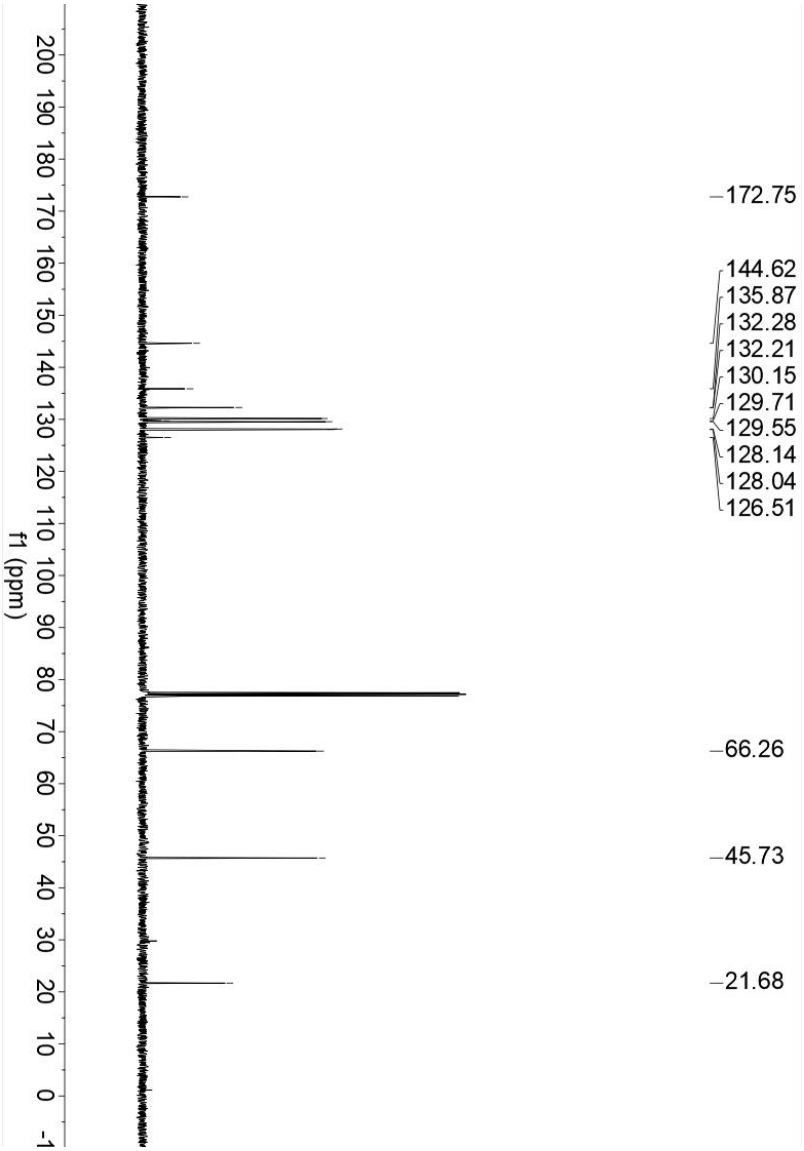


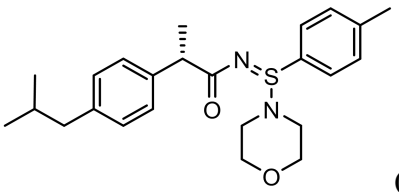
(3as)

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



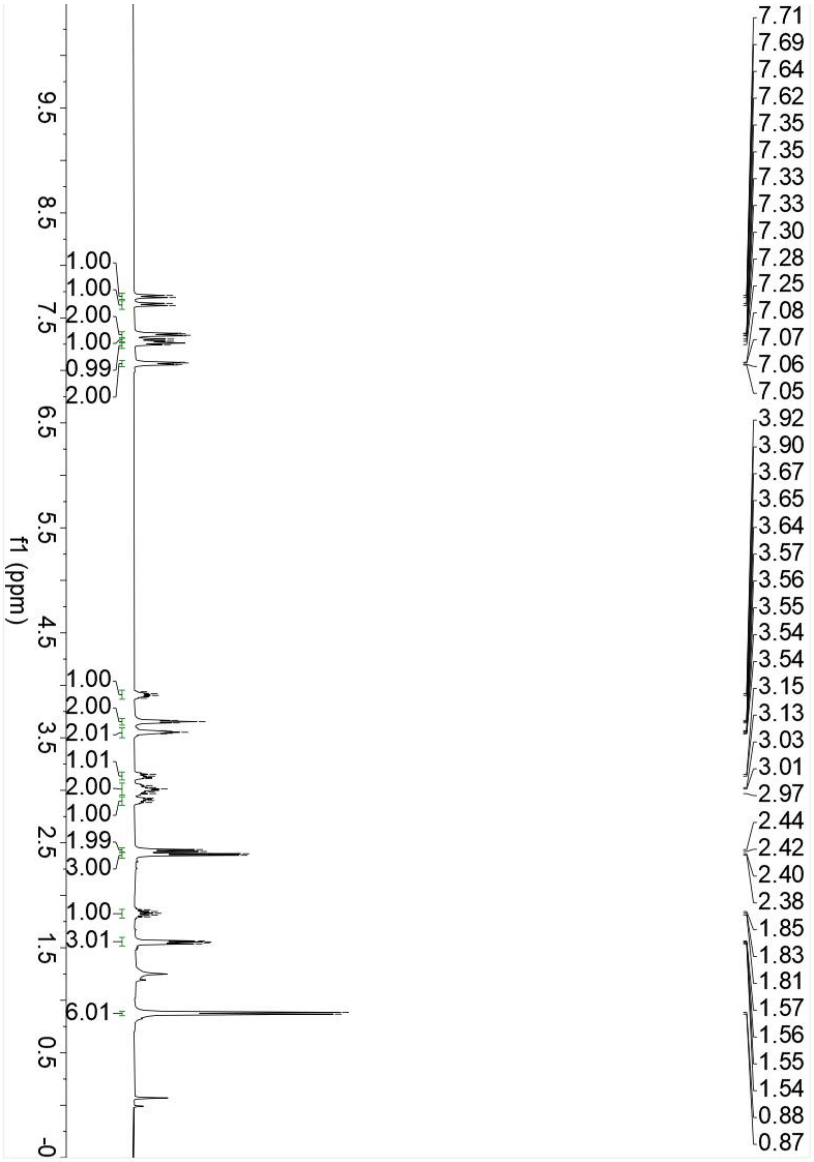
^{13}C NMR (100 MHz, Chloroform-*d*)





(3at)

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



^{13}C NMR (100 MHz, Chloroform-*d*)