Supplementary Information

A Catalyst- and Thiol-Free Protocol for Arene C–H Thioetherification *via* Photoactive Electron Donor–Acceptor Complexes

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1. General Information

1.1 Analytical Methods

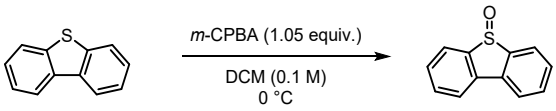
The NMR spectra were recorded on Bruker 600 MHz spectrometer and Agilent 600 MHz spectrometer. The chemical shifts (δ) in ^{1}H NMR were reported in ppm relative to tetramethylsilane (Me_4Si) as internal standard (0.0 ppm) or proton resonance resulting from incomplete deuteration of NMR solvent: $CDCl_3$ (7.26 ppm). Coupling constants (J) are expressed in hertz. ^{13}C NMR spectra were recorded at 151 MHz, and the chemical shifts (δ) were reported in ppm relative to $CDCl_3$ (77.10 ppm). ^{19}F NMR spectra were recorded at 565 MHz. The absorption spectra in solution were recorded on a UNIC 4802 UV/VIS double beam spectrophotometer in a 1.0 cm length quartz cell, all compounds were dissolved in CH_3CN and measured at 25 °C. HRMS analysis was performed on Finnigan LCQ advantage Max Series MS System. ESI-mass data was acquired using a Thermo LTQ Orbitrap XL Instrument equipped with an ESI source and controlled by Xcalibur software. GC chromatograms were recorded on Shimadzu GC-2014.

1.2 Materials

All reactions were carried out in oven-dried Schlenk tubes under argon atmosphere (purity ≥ 99.99%) unless otherwise mentioned. Other Commercial reagents were purchased from Adamas-beta, Energy Chemical, TCI and Aldrich. Organic solutions were concentrated under reduced pressure on Buchi rotary evaporator. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on silica gel (200-300 mesh). The flow photocatalytic reactor was purchased from Anhui Kexin Microfluidic Chemical Technology Co., Ltd. The LED lamps were purchased from Kessil (427 nm, 440 nm), HepatoChem (450 nm), Anhui Kemi Instrument Co., Ltd. (420 nm, 455 nm, 467 nm, 520 nm) and Bibby Scientific Ltd. (565 nm). The Photo Reaction Setup was purchased from HepatoChem.

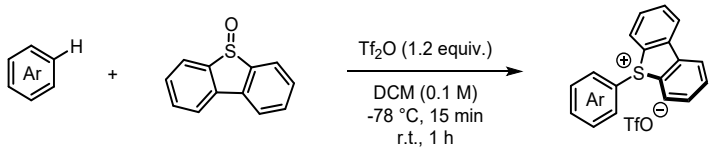
2. Procedure for the Synthesis of Substrates

A. Synthesis of Sulfoxides[1]



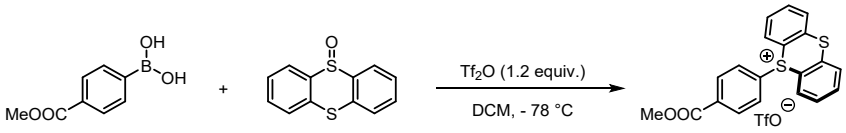
Sulfide (1.0 equiv.), was dissolved in CH_2Cl_2 (0.1 M) and cooled to 0 °C. *m*-CPBA (1.05 equiv.) was added portion wise over 30 minutes at 0 °C and the resulting suspension stirred for 2 h. The mixture was diluted with DCM, washed with brine, and dried over Na_2SO_4. Upon filtration, the organic layers were combined and concentrated on rotary evaporator. The residue was purified by silica gel column chromatography to give the product (petroleum ether/ethyl acetate = 5:1).

B. Synthesis of Aryldibenzothiophenium Salts from Arenes[1-3]



Tf_2O (1.2 equiv.) was slowly added to a stirred solution of the arene (1.0 equiv.) and the S-oxide (1.1 equiv.) in dry CH_2Cl_2 (0.1 M) at −78 °C under a argon atmosphere. The resulting solution was stirred at this temperature for 15 minutes before warming to room temperature. After stirring for 1 h, the reaction was quenched with the addition of methanol which removed the dark colour of the reaction mixture. At this point, the solvent was removed under vacuum while keeping the water bath at 30 °C. The sulfonium salt was then precipitated by the addition of cold Et_2O to the mixture while stirring (occasionally vigorous stirring was needed). The Et_2O was then decanted off and the resulting solid was washed with further portions of Et_2O. In case of an unsuccessful precipitation, the desired sulfonium salt was purified from the crude mixture by column chromatography (CH_2Cl_2/methanol = 15:1).

C. Synthesis of 5-(4-(methoxycarbonyl)phenyl)-5*H*-thianthren-5-ium trifluoromethanesulfonate



Tf_2O (1.2 mmol, 1.2 equiv.) was slowly added to a stirred solution of the (4-(methoxycarbonyl)phenyl)boronic acid (1.0 mmol, 1.0 equiv.) and the S-oxide (1.0 mmol, 1.0 equiv.) in dry DCM (4.0 mL, 0.25 M) at −78 °C under a argon atmosphere. The resulting solution was stirred at this temperature for 1 h before warming to room temperature. After stirring for 2 h, the reaction was quenched with the addition of methanol which removed the dark colour of the reaction mixture. At this point, the solvent was removed under vacuum while keeping the water bath at 30 °C. The residue was purified by silica gel column chromatography to give the product (white solid, 265 mg, 53%, CH_2Cl_2/methanol = 15:1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.86 (d, *J* = 6.9 Hz, 2H), 8.02 (d, *J* = 7.4 Hz, 2H), 7.83 – 7.79 (m, 6H), 7.23 (d, *J* = 8.4 Hz, 2H), 3.89 (s, 3H).

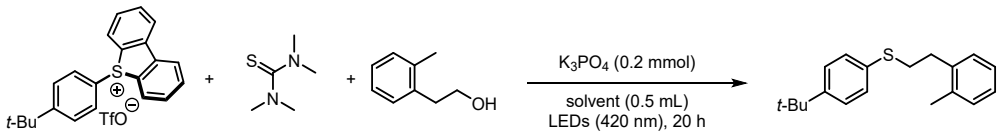
^{13}C NMR (151 MHz, Chloroform-*d*) δ 164.92, 136.76, 136.42, 134.96, 134.07, 131.13, 130.34, 130.26, 129.16, 128.20, 119.11, 52.81.

HRMS (ESI) (m/z): $[M\text{-}CF_3O_3S]^+$ Calcd for $C_{20}H_{15}O_2S_2^+$, 351.0508; found:351.0505.

Melting point: 130–132 ℃.

3. Investigation of the Key Reaction Parameters

Table S1. Screening of solvents

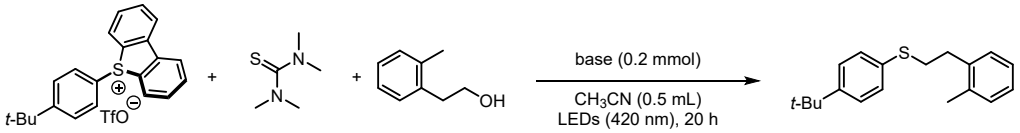


1a, 0.15 mmol **2a,** 0.3 mmol **3,** 0.1 mmol **4**

Entry	solvent	Yield of **4** (%)[a]
1	CH_3CN	81
2	Acetone	63
3	DMSO	52
4	THF	Trace
5	Dioxane	28
6	DCM	Trace
7	$CHCl_3$	Trace
8	DCE	25
9	DMF	Trace
10	DMA	Trace
11	NMP	Trace
12	0.25 mL CH_3CN+0.25 mL Acetone	80

Reaction conditions: **1a** (0.15 mmol, 1.5 equiv.), **2a** (0.3 mmol, 3.0 equiv.), **3** (0.1 mmol, 1.0 equiv.), K_3PO_4 (0.2 mmol, 2.0 equiv.), solvent (0.5 mL), stirred at room temperature for 20 h under LEDs (420 nm, 40 W) irradiation. [a]The yield was determined by GC using benzophenone as an internal standard.

Table S2. Screening of bases

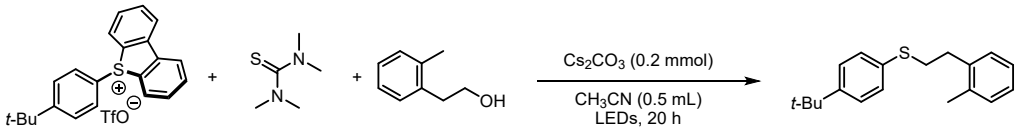


1a, 0.15 mmol **2a,** 0.3 mmol **3,** 0.1 mmol **4**

Entry	base	Yield of **4** (%)[a]
1	K_3PO_4	81
2	Cs_2CO_3	90
3	*t*-BuONa	39
4	Na_2CO_3	35
5	BTMG	72
6	DABCO	Trace
7	2,6-Lutidine	Trace
8	DBU	39
9	K_2HPO_4	21
10	KOAc	Trace

Reaction conditions: **1a** (0.15 mmol, 1.5 equiv.), **2a** (0.3 mmol, 3.0 equiv.), **3** (0.1 mmol, 1.0 equiv.), base (0.2 mmol, 2.0 equiv.), CH_3CN (0.5 mL), stirred at room temperature for 20 h under LEDs (420 nm, 40 W) irradiation. [a] The yield was determined by GC using benzophenone as an internal standard.

Table S3. Screening of light sources

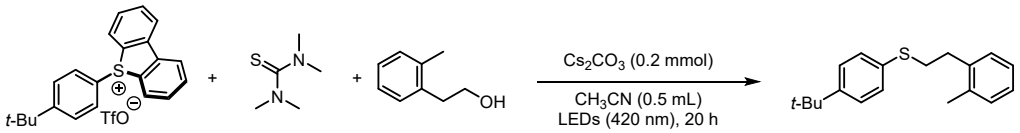


1a, 0.15 mmol **2a,** 0.3 mmol **3,** 0.1 mmol **4**

Entry	light sources	Yield of **4** (%)[a]
1	420 nm, 20 W	82
2	420 nm, 40 W	90
3	427 nm, 40 W	83
4	440 nm, 40 W	87
5	450 nm, 18 W	85
6	455 nm, 40 W	80
7	467 nm, 40 W	75
8	520 nm, 40 W	69
9	565 nm, 15 W	65

Reaction conditions: **1a** (0.15 mmol, 1.5 equiv.), **2a** (0.3 mmol, 3.0 equiv.), **3** (0.1 mmol, 1.0 equiv.), Cs_2CO_3 (0.2 mmol, 2.0 equiv.), CH_3CN (0.5 mL), stirred at room temperature for 20 h under LEDs irradiation. [a] The yield was determined by GC using benzophenone as an internal standard.

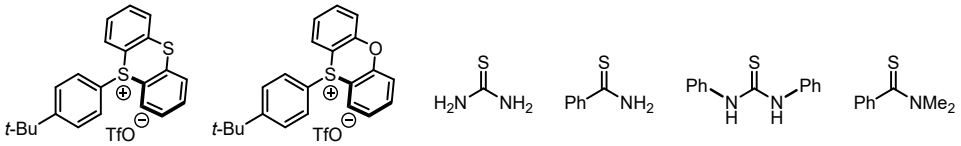
Table S4. Control experiments



1a, 0.15 mmol **2a,** 0.3 mmol **3,** 0.1 mmol **4**

Entry	variations from standard conditions	Yield of **4** (%)[a]
1	None	90 (83)[b]
2	**1b**, or **1c** instead of **1a**	66, or 47
3	**2b – 2d**, or **2e** instead of **2a**	n.d., or 7
4	**1a** (0.1 mmol), or **1a** (0.2 mmol)	56, or 91
5	**2a** (0.2 mmol), or **2a** (0.4 mmol)	58, or 90
6	CH_3CN (1 mL)	61
7	Cs_2CO_3 (0.15 mmol)	79
8	reaction time: 12 h	73
9	no base or no light	trace, or n.d.

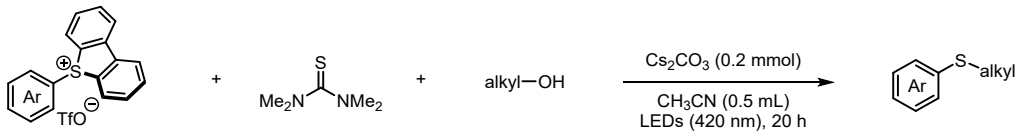
Reaction conditions: **1a** (0.15 mmol, 1.5 equiv.), **2a** (0.3 mmol, 3.0 equiv.), **3** (0.1 mmol, 1.0 equiv.), Cs_2CO_3 (0.2 mmol, 2.0 equiv.), CH_3CN (0.5 mL), stirred at room temperature for 20 h under LEDs (420 nm, 40 W) irradiation. [a] The yield was determined by GC using benzophenone as an internal standard. n.d. = not detected. [b] Isolated yield.



1b **1c** **2b** **2c** **2d** **2e**

4. General Procedure and Spectral Data

4.1 General Procedure A

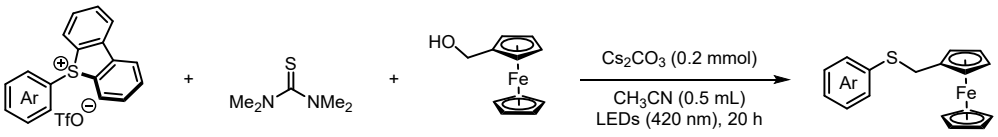


General Procedure A: A mixture of aryldibenzothiophenium salt (0.15 mmol, 1.5 equiv.), 1,1,3,3-tetramethylthiourea (0.3 mmol, 3.0 equiv.), Cs_2CO_3 (0.2 mmol, 2.0 equiv.) and corresponding alcohol (if solid, 0.1 mmol, 1.0 equiv.) were added in 10 mL Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (repeated for three times). To this solid, anhydrous CH_3CN (0.5 mL) and corresponding alcohol (if liquid., 0.1 mmol, 1.0 equiv.) were added using a gastight syringe under argon atmosphere. The reaction mixture was stirred under LEDs (420 nm, 40 W) irradiation, maintained at approximately room temperature in the air-conditioned room of 25 ℃. After 20 h, the mixture was diluted with EtOAc (approximately 4 mL), washed with brine (approximately 3 mL), and dried over Na_2SO_4. Upon filtration, the organic layers were combined and concentrated on rotary evaporator. The residue was purified by silica gel column chromatography to give the product.

4.2 General Procedure B

General Procedure B: A mixture of aryldibenzothiophenium salt (0.15 mmol, 1.5 equiv.), 1,1,3,3-tetramethylthiourea (0.3 mmol, 3.0 equiv.) and Cs_2CO_3 (0.2 mmol, 2.0 equiv.) were added in 10 mL Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (repeated for three times). To this solid, anhydrous CH_3CN (0.5 mL) and CD_3OD (0.1 mmol, 1.0 equiv., 99.8 atom%D) were added using a gastight syringe under argon atmosphere. The reaction mixture was stirred under LEDs (420 nm, 40 W) irradiation, maintained at approximately room temperature in the air-conditioned room of 25 ℃. After 20 h, the mixture was diluted with EtOAc (approximately 4 mL), washed with brine (approximately 3 mL), and dried over Na_2SO_4. Upon filtration, the organic layers were combined and concentrated on rotary evaporator. The residue was purified by silica gel column chromatography to give the product.

4.3 General Procedure C



General Procedure C: A mixture of aryldibenzothiophenium salt (0.15 mmol, 1.5 equiv.), 1,1,3,3-tetramethylthiourea (0.3 mmol, 3.0 equiv.), ferrocenemethanol (0.1 mmol, 1.0 equiv.) and Cs_2CO_3 (0.2

mmol, 2.0 equiv.) were added in 10 mL Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (repeated for three times). To this solid, anhydrous CH_3CN (0.5 mL) were added using a gastight syringe under argon atmosphere. The reaction mixture was stirred under LEDs (420 nm, 40 W) irradiation, maintained at approximately room temperature in the air-conditioned room of 25 ℃. After 20 h, the mixture was diluted with EtOAc (approximately 4 mL), washed with brine (approximately 3 mL), and dried over Na_2SO_4. Upon filtration, the organic layers were combined and concentrated on rotary evaporator. The residue was purified by silica gel column chromatography to give the product.

Reaction Setup

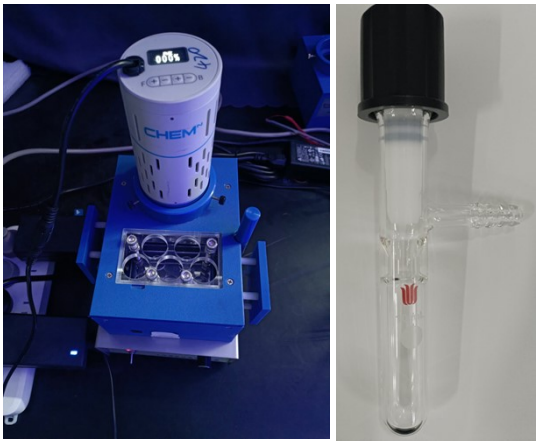
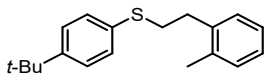


Figure S1. Photo-reaction setup and reaction tube

4.3 Characterization data for the products

(4-(*tert*-butyl)phenyl)(2-methylphenethyl)sulfane (4)



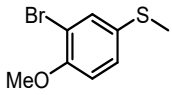
General procedure A was followed to obtain **4** (23.6 mg, 83%, petroleum ether/ethyl acetate = 20:1) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.34 (s, 4H), 7.18 – 7.10 (m, 4H), 3.23 – 3.06 (m, 2H), 2.97 – 2.87 (m, 2H), 2.28 (s, 3H), 1.32 (s, 9H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 149.4, 138.6, 136.0, 132.7, 130.3, 129.5, 129.0, 126.6, 126.1, 126.0, 34.5, 34.3, 33.3, 31.3, 19.2.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{19}H_{25}S^+$, 285.1671; found: 285.1670.

(3-bromo-4-methoxyphenyl)(methyl)sulfane (5)



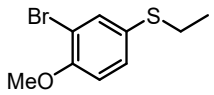
General procedure A was followed to obtain **5** (20.9 mg, 90%, petroleum ether/ethyl acetate = 15:1) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 2.1 Hz, 1H), 7.22 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.83 (d, *J* = 8.5 Hz, 1H), 3.87 (s, 3H), 2.44 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 154.3, 133.0, 130.6, 128.7, 112.4, 112.1, 56.4, 17.7.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_8H_{10}BrOS^+$, 232.9630; found: 232.9629.

(3-bromo-4-methoxyphenyl)(ethyl)sulfane (6)



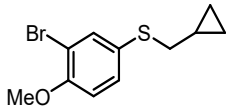
General procedure A was followed to obtain **6** (21.2 mg, 86%, petroleum ether/ethyl acetate = 15:1) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 2.2 Hz, 1H), 7.30 (dd, *J* = 7.6, 2.2 Hz, 1H), 6.82 (d, *J* = 8.5 Hz, 1H), 3.88 (s, 3H), 2.84 (q, *J* = 7.3 Hz, 2H), 1.25 (t, *J* = 7.8 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.0, 135.8, 131.7, 128.3, 112.2, 111.9, 56.3, 29.6, 14.5.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_9H_{12}BrOS^+$, 246.9787; found: 246.9785.

(3-bromo-4-methoxyphenyl)(cyclopropylmethyl)sulfane (7)

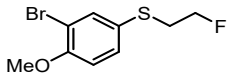


General procedure A was followed to obtain **7** (17.1 mg, 63%, petroleum ether/ethyl acetate = 15:1) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 2.3 Hz, 1H), 7.34 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.82 (d, *J* = 8.5 Hz, 1H), 3.88 (s, 3H), 2.76 (d, *J* = 7.2 Hz, 2H), 1.02 – 0.95 (m, 1H), 0.59 – 0.51 (m, 2H), 0.19 (q, *J* = 5.5, 5.0 Hz, 2H).

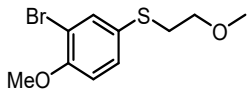
^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.0, 136.2, 132.0, 128.7, 112.1, 111.8, 56.3, 41.6, 10.9, 5.5.
HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{11}H_{14}BrOS^+$, 272.9943; found: 272.9945.

(3-bromo-4-methoxyphenyl)(2-fluoroethyl)sulfane (8)



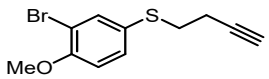
General procedure A was followed to obtain **8** (24.5 mg, 93%, petroleum ether/ethyl acetate = 15:1) as a colorless oil.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 2.2 Hz, 1H), 7.37 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.83 (d, *J* = 8.6 Hz, 1H), 4.53 (t, *J* = 6.7 Hz, 1H), 4.45 (t, *J* = 6.7 Hz, 1H), 3.88 (s, 3H), 3.10 (t, *J* = 6.7 Hz, 1H), 3.07 (t, *J* = 6.7 Hz, 1H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.8, 137.0, 132.9, 126.5, 112.3, 112.1, 81.5 (d, *J* = 172.4 Hz), 56.4, 35.5 (d, *J* = 21.4 Hz).
^{19}F NMR (565 MHz, Chloroform-*d*) δ -213.4.
HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_9H_{11}BrFOS^+$, 264.9693; found: 264.9684.

(3-bromo-4-methoxyphenyl)(2-methoxyethyl)sulfane (9)



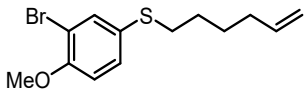
General procedure A was followed to obtain **9** (24.0 mg, 87%, petroleum ether/ethyl acetate = 15:1) as a colorless oil.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 2.2 Hz, 1H), 7.35 (dd, *J* = 8.5, 2.1 Hz, 1H), 6.83 (d, *J* = 8.5 Hz, 1H), 3.88 (s, 3H), 3.52 (t, *J* = 6.7 Hz, 2H), 3.35 (s, 3H), 3.01 (t, *J* = 6.7 Hz, 2H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.3, 136.3, 132.1, 127.6, 112.2, 111.9, 71.0, 58.7, 56.3, 35.1.
HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{10}H_{14}BrO_2S^+$, 276.9892; found: 276.9890.

(3-bromo-4-methoxyphenyl)(but-3-yn-1-yl)sulfane (10)



General procedure A was followed to obtain **10** (21.1 mg, 78%, petroleum ether/ethyl acetate = 15:1) as a colorless oil.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 2.2 Hz, 1H), 7.36 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.83 (d, *J* = 8.5 Hz, 1H), 3.88 (s, 3H), 2.96 (t, *J* = 7.4 Hz, 2H), 2.46 – 2.40 (m, 2H), 2.03 (t, *J* = 2.6 Hz, 1H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.6, 136.9, 132.8, 126.8, 112.2, 112.0, 82.1, 69.7, 56.3, 34.7, 19.4.
HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{11}H_{12}BrOS^+$, 270.9787; found: 270.9779.

(3-bromo-4-methoxyphenyl)(hex-5-en-1-yl)sulfane (11)



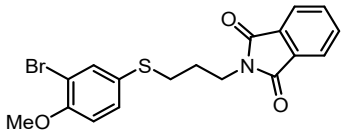
General procedure A was followed to obtain **11** (17.1 mg, 57%, petroleum ether/ethyl acetate = 15:1) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 2.3 Hz, 1H), 7.29 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.82 (d, *J* = 8.5 Hz, 1H), 5.82 – 5.73 (m, 1H), 5.03 – 4.91 (m, 2H), 3.88 (s, 3H), 2.83 (t, *J* = 7.3 Hz, 2H), 2.05 (q, *J* = 7.1 Hz, 2H), 1.63 – 1.53 (m, 2H), 1.53 – 1.46 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 154.9, 138.4, 135.7, 131.5, 128.6, 114.8, 112.2, 111.9, 56.3, 35.4, 33.2, 28.6, 27.8.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{13}H_{18}BrOS^+$, 301.0256; found: 301.0258.

2-(3-((3-bromo-4-methoxyphenyl)thio)propyl)isoindoline-1,3-dione (12)



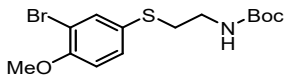
General procedure A was followed to obtain **12** (23.9 mg, 59%, petroleum ether/ethyl acetate = 10:1) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.83 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.71 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.60 (d, *J* = 2.2 Hz, 1H), 7.34 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.81 (d, *J* = 8.5 Hz, 1H), 3.87 (s, 3H), 3.80 (t, *J* = 7.0 Hz, 2H), 2.84 (t, *J* = 7.2 Hz, 2H), 1.93 (p, *J* = 7.1 Hz, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.3, 155.4, 136.7, 134.0, 132.6, 132.0, 127.4, 123.3, 112.2, 111.9, 56.3, 36.8, 33.4, 28.1.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{18}H_{17}BrNO_3S^+$, 406.0107; found: 406.0109.

***tert*-butyl (2-((3-bromo-4-methoxyphenyl)thio)ethyl)carbamate (13)**



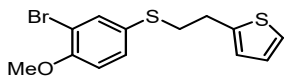
General procedure A was followed to obtain **13** (24.9 mg, 69%, petroleum ether/ethyl acetate = 3:1) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 1.8 Hz, 1H), 7.34 (dd, *J* = 8.5, 1.9 Hz, 1H), 6.82 (d, *J* = 8.5 Hz, 1H), 4.89 (s, 1H), 3.87 (s, 3H), 3.29 – 3.25 (m, 2H), 2.93 (t, *J* = 6.5 Hz, 2H), 1.42 (s, 9H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.7, 155.4, 136.6, 132.4, 126.8, 112.3, 112.0, 79.5, 56.3, 39.5, 36.0, 28.4.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{14}H_{21}BrNO_3S^+$, 362.0420; found: 362.0423.

2-(2-((3-bromo-4-methoxyphenyl)thio)ethyl)thiophene (14)



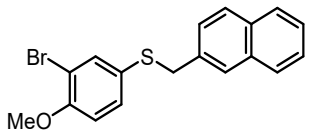
General procedure A was followed to obtain **14** (27.9 mg, 85%, petroleum ether/ethyl acetate = 15:1) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 2.3 Hz, 1H), 7.35 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.15 (d, *J* = 5.1 Hz, 1H), 6.93 (dd, *J* = 5.2, 3.5 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 6.82 (d, *J* = 3.8 Hz, 1H), 3.89 (s, 3H), 3.14 – 3.05 (m, 4H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.3, 142.5, 136.4, 132.2, 127.6, 126.8, 125.0, 123.7, 112.3, 112.0, 56.4, 37.3, 29.9.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{13}H_{14}BrOS_2^+$, 328.9664; found: 328.9668.

(3-bromo-4-methoxyphenyl)(naphthalen-2-ylmethyl)sulfane (15)



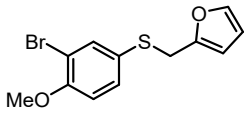
General procedure A was followed to obtain **15** (26.1 mg, 73%, petroleum ether/ethyl acetate = 20:1) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.83 – 7.80 (m, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.75 – 7.71 (m, 1H), 7.57 (d, *J* = 2.1 Hz, 1H), 7.55 (s, 1H), 7.47 – 7.44 (m, 2H), 7.41 (d, *J* = 8.5 Hz, 1H), 7.16 (dd, *J* = 8.5, 2.1 Hz, 1H), 6.71 (d, *J* = 8.5 Hz, 1H), 4.15 (s, 2H), 3.84 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.5, 137.0, 135.0, 133.2, 132.8, 132.6, 128.3, 127.7, 127.7, 127.6, 127.5, 127.0, 126.2, 125.9, 112.0, 111.8, 56.3, 41.3.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{18}H_{16}BrOS^+$, 359.0100; found: 359.0105.

2-(((3-bromo-4-methoxyphenyl)thio)methyl)furan (16)



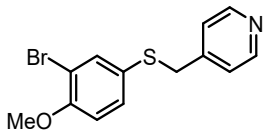
General procedure A was followed to obtain **16** (26.2 mg, 88%, petroleum ether/ethyl acetate = 15:1) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 1.9 Hz, 1H), 7.35 (s, 1H), 7.24 (dd, *J* = 10.5, 2.0 Hz, 1H), 6.79 (d, *J* = 8.6 Hz, 1H), 6.26 (s, 1H), 6.01 (s, 1H), 3.98 (s, 2H), 3.87 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.7, 150.8, 142.2, 137.6, 133.4, 126.9, 111.9, 111.6, 110.4, 108.1, 56.3, 33.4.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{12}H_{12}BrO_2S^+$, 298.9736; found: 298.9737.

4-(((3-bromo-4-methoxyphenyl)thio)methyl)pyridine (17)



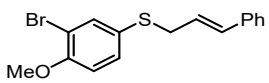
General procedure A was followed to obtain **17** (22.6 mg, 73%, petroleum ether/ethyl acetate = 2:1) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.49 (d, *J* = 6.1 Hz, 2H), 7.52 (d, *J* = 2.3 Hz, 1H), 7.14 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.08 (d, *J* = 6.1 Hz, 2H), 6.74 (d, *J* = 8.5 Hz, 1H), 3.91 (s, 2H), 3.86 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.9, 149.7, 147.1, 137.5, 133.4, 126.1, 123.9, 112.1, 111.9, 56.3, 40.0.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{13}H_{13}BrNOS^+$, 309.9896; found: 309.9896.

(3-bromo-4-methoxyphenyl)(cinnamyl)sulfane (18)



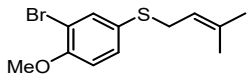
General procedure A was followed to obtain **18** (21.1 mg, 63%, petroleum ether/ethyl acetate = 15:1) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 2.0 Hz, 1H), 7.32 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.31 – 7.27 (m, 4H), 7.24 – 7.20 (m, 1H), 6.79 (d, *J* = 8.6 Hz, 1H), 6.31 (d, *J* = 15.8 Hz, 1H), 6.24 – 6.16 (m, 1H), 3.86 (s, 3H), 3.60 (d, *J* = 7.3 Hz, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.4, 137.1, 136.7, 133.0, 132.9, 128.5, 127.6, 127.4, 126.3, 125.0, 112.0, 111.7, 56.3, 39.0.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{16}H_{16}BrOS^+$, 335.0100; found: 335.0103.

(3-bromo-4-methoxyphenyl)(3-methylbut-2-en-1-yl)sulfane (19)



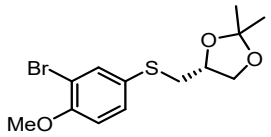
General procedure A was followed to obtain **19** (23.2 mg, 81%, petroleum ether/ethyl acetate = 15:1) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 2.2 Hz, 1H), 7.30 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.80 (d, *J* = 8.5 Hz, 1H), 5.28 – 5.22 (m, 1H), 3.88 (s, 3H), 3.43 (d, *J* = 7.8 Hz, 2H), 1.70 (s, 3H), 1.47 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.2, 136.8, 136.5, 132.5, 128.3, 119.4, 112.0, 111.6, 56.3, 34.1, 25.7, 17.6.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{12}H_{16}BrOS^+$, 287.0100; found: 287.0098.

(*R*)-4-(((3-bromo-4-methoxyphenyl)thio)methyl)-2,2-dimethyl-1,3-dioxolane (20)



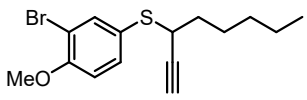
General procedure A was followed to obtain **20** (27.9 mg, 84%, petroleum ether/ethyl acetate = 7:1) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 2.2 Hz, 1H), 7.34 (dd, *J* = 8.5, 2.1 Hz, 1H), 6.82 (d, *J* = 8.5 Hz, 1H), 4.21 – 4.14 (m, 1H), 4.09 – 4.04 (m, 1H), 3.87 (s, 3H), 3.73 – 3.68 (m, 1H), 3.12 – 3.06 (m, 1H), 2.93 – 2.83 (m, 1H), 1.41 (s, 3H), 1.32 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.4, 136.3, 132.1, 127.2, 112.3, 109.6, 74.7, 68.7, 56.3, 39.0, 26.9, 25.5.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{13}H_{18}BrO_3S^+$, 333.0155; found: 333.0158.

(3-bromo-4-methoxyphenyl)(oct-1-yn-3-yl)sulfane (21)



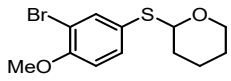
General procedure A was followed to obtain **21** (25.1 mg, 77%, petroleum ether/ethyl acetate = 15:1) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 2.2 Hz, 1H), 7.48 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.85 (d, *J* = 8.6 Hz, 1H), 3.90 (s, 3H), 3.66 – 3.60 (m, 1H), 2.35 (d, *J* = 2.4 Hz, 1H), 1.74 – 1.67 (m, 2H), 1.57 – 1.45 (m, 2H), 1.35 – 1.24 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.3, 139.2, 135.2, 125.3, 111.9, 111.6, 83.6, 72.6, 56.3, 39.7, 34.8, 31.2, 26.8, 22.5, 14.0.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{15}H_{20}BrOS^+$, 327.0413; found: 327.0414.

2-((3-bromo-4-methoxyphenyl)thio)tetrahydro-2*H*-pyran (22)



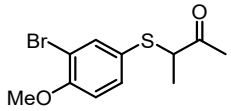
General procedure A was followed to obtain **22** (22.4 mg, 74%, petroleum ether/ethyl acetate = 10:1) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 2.2 Hz, 1H), 7.41 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.82 (d, *J* = 8.5 Hz, 1H), 5.07 – 5.02 (m, 1H), 4.19 – 4.12 (m, 1H), 3.87 (s, 3H), 3.59 – 3.52 (m, 1H), 2.02 – 1.95 (m, 1H), 1.88 – 1.73 (m, 2H), 1.67 – 1.55 (m, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.6, 137.2, 133.1, 126.9, 112.1, 111.7, 86.2, 64.6, 56.3, 31.4, 25.5, 21.6.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{12}H_{16}BrO_2S^+$, 303.0049; found: 303.0052.

3-((3-bromo-4-methoxyphenyl)thio)butan-2-one (23)



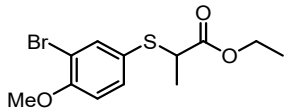
General procedure A was followed to obtain **23** (16.1 mg, 56%, petroleum ether/ethyl acetate = 8:1) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 2.2 Hz, 1H), 7.30 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.82 (d, *J* = 8.5 Hz, 1H), 3.88 (s, 3H), 3.63 (q, *J* = 7.0 Hz, 1H), 2.29 (s, 3H), 1.35 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 205.0, 156.6, 139.1, 135.0, 123.8, 112.1, 111.9, 56.3, 52.7, 26.7, 15.8.

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd for $C_{11}H_{13}BrNaO_2S^+$, 310.9712; found: 310.9716.

ethyl 2-((3-bromo-4-methoxyphenyl)thio)propanoate (24)



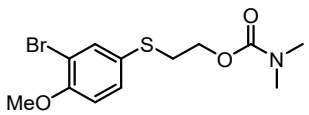
General procedure A was followed to obtain **24** (28.0 mg, 88%, petroleum ether/ethyl acetate = 10:1) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 2.2 Hz, 1H), 7.40 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.83 (d, *J* = 8.5 Hz, 1H), 4.17 – 4.06 (m, 2H), 3.88 (s, 3H), 3.63 (q, *J* = 7.1 Hz, 1H), 1.42 (d, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.5, 156.4, 139.3, 135.3, 124.6, 111.9, 111.6, 61.2, 56.3, 46.0, 17.1, 14.1.

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd for $C_{12}H_{15}BrNaO_3S^+$, 340.9817; found: 340.9820.

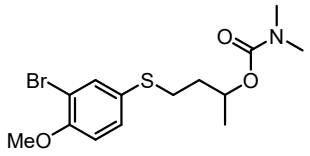
2-((3-bromo-4-methoxyphenyl)thio)ethyl dimethylcarbamate (25)



General procedure A was followed to obtain **25** (23.6 mg, 71%, petroleum ether/ethyl acetate = 3:1) as a colorless oil.

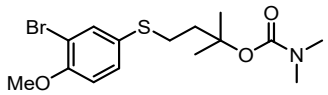
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 2.3 Hz, 1H), 7.36 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.82 (d, *J* = 8.5 Hz, 1H), 4.19 (t, *J* = 6.7 Hz, 2H), 3.87 (s, 3H), 3.05 (t, *J* = 6.7 Hz, 2H), 2.88 (s, 3H), 2.83 (s, 3H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.2, 155.3, 136.3, 132.2, 127.3, 112.2, 111.9, 63.8, 56.3, 36.4, 35.8, 34.6.
HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{12}H_{17}BrNO_3S^+$, 334.0107; found: 334.0111.

4-((3-bromo-4-methoxyphenyl)thio)butan-2-yl dimethylcarbamate (26)



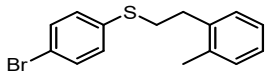
General procedure A was followed to obtain **26** (23.1 mg, 64%, petroleum ether/ethyl acetate = 3:1) as a colorless oil.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 2.1 Hz, 1H), 7.30 (dd, *J* = 8.5, 2.1 Hz, 1H), 6.81 (d, *J* = 8.5 Hz, 1H), 4.91 – 4.84 (m, 1H), 3.87 (s, 3H), 2.91 – 2.77 (m, 8H), 1.90 – 1.81 (m, 1H), 1.80 – 1.72 (m, 1H), 1.21 (d, *J* = 6.3 Hz, 3H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.2, 155.1, 135.8, 131.7, 128.2, 112.3, 112.0, 70.5, 56.4, 36.4, 36.1, 35.8, 31.6, 20.5.
HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{14}H_{21}BrNO_3S^+$, 362.0420; found: 362.0419.

4-((3-bromo-4-methoxyphenyl)thio)-2-methylbutan-2-yl dimethylcarbamate (27)



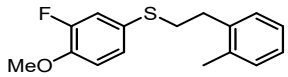
General procedure A was followed to obtain **27** (25.5 mg, 68%, petroleum ether/ethyl acetate = 3:1) as a colorless oil.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 1.8 Hz, 1H), 7.29 (dd, *J* = 8.5, 1.9 Hz, 1H), 6.82 (d, *J* = 8.5 Hz, 1H), 3.87 (s, 3H), 2.89 – 2.84 (m, 2H), 2.84 (s, 6H), 2.03 – 1.97 (m, 2H), 1.44 (s, 6H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.5, 155.0, 135.4, 131.4, 128.3, 112.2, 112.0, 80.4, 56.3, 56.3, 41.5, 36.2, 36.0, 30.2, 26.2.
HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{15}H_{23}BrNO_3S^+$, 376.0577; found: 376.0577.

(4-bromophenyl)(2-methylphenethyl)sulfane (28)



General procedure A was followed to obtain **28** (23.3 mg, 76%, petroleum ether/ethyl acetate = 20:1) as a colorless oil.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.44 – 7.39 (m, 2H), 7.24 – 7.20 (m, 2H), 7.16 – 7.12 (m, 4H), 3.13 – 3.07 (m, 2H), 2.94 – 2.89 (m, 2H), 2.28 (s, 3H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 138.1, 135.9, 135.7, 132.0, 130.8, 130.4, 129.1, 126.7, 126.2, 119.8, 34.0, 33.0, 19.3.
HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{15}H_{16}BrS^+$, 307.0151; found: 307.0153.

(3-fluoro-4-methoxyphenyl)(2-methylphenethyl)sulfane (29)



General procedure A was followed to obtain **29** (25.1 mg, 91%, petroleum ether/ethyl acetate = 15:1) as a colorless oil.

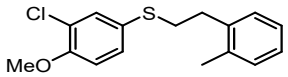
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.21 – 7.09 (m, 6H), 6.91 (t, *J* = 8.4 Hz, 1H), 3.89 (s, 3H), 3.09 – 3.00 (m, 2H), 2.96 – 2.82 (m, 2H), 2.26 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 152.2 (d, *J* = 248.5 Hz), 146.8 (d, *J* = 10.5 Hz), 138.3, 135.9, 130.4, 129.1, 127.5 (d, *J* = 6.4 Hz), 127.3 (d, *J* = 3.5 Hz), 126.6, 126.1, 118.9 (d, *J* = 18.8 Hz), 113.7 (d, *J* = 2.3 Hz), 56.3, 35.5, 33.3, 19.2.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -104.5 (t, *J* = 5.6 Hz).

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{16}H_{18}FOS^+$, 277.1057; found: 277.1049.

(3-chloro-4-methoxyphenyl)(2-methylphenethyl)sulfane (30)



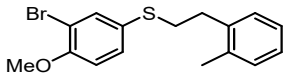
General procedure A was followed to obtain **30** (20.4 mg, 70%, petroleum ether/ethyl acetate = 15:1) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 1.7 Hz, 1H), 7.30 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.22 – 7.09 (m, 4H), 6.87 (d, *J* = 8.5 Hz, 1H), 3.90 (s, 3H), 3.30 – 2.95 (m, 2H), 2.89 – 2.82 (m, 2H), 2.25 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 154.2, 138.2, 135.9, 132.9, 131.0, 130.4, 129.1, 127.7, 126.6, 126.1, 122.8, 112.4, 56.3, 35.7, 33.3, 19.2.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{16}H_{18}ClOS^+$, 293.0761; found: 293.0764.

(3-bromo-4-methoxyphenyl)(2-methylphenethyl)sulfane (31)



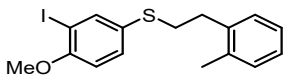
General procedure A was followed to obtain **31** (18.4 mg, 78%, petroleum ether/ethyl acetate = 15:1) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 2.2 Hz, 1H), 7.34 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.18 – 7.07 (m, 4H), 6.84 (d, *J* = 8.5 Hz, 1H), 3.90 (s, 3H), 3.25 – 2.98 (m, 2H), 2.98 – 2.77 (m, 2H), 2.25 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.1, 138.2, 135.9, 135.9, 131.7, 130.4, 129.1, 128.2, 126.6, 126.1, 112.2, 111.9, 56.4, 35.7, 33.3, 19.2.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{16}H_{18}BrOS^+$, 337.0256; found: 337.0259.

(3-iodo-4-methoxyphenyl)(2-methylphenethyl)sulfane (32)



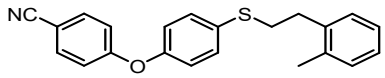
General procedure A was followed to obtain **32** (23.8 mg, 62%, petroleum ether/ethyl acetate = 15:1) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 2.2 Hz, 1H), 7.38 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.18 – 7.09 (m, 4H), 6.76 (d, *J* = 8.5 Hz, 1H), 3.88 (s, 3H), 3.04 – 2.99 (m, 2H), 2.90 – 2.84 (m, 2H), 2.25 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.4, 142.0, 138.3, 135.9, 132.9, 130.4, 129.1, 128.7, 126.6, 126.1, 111.1, 86.3, 56.5, 35.8, 33.4, 19.2.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{16}H_{18}IOS^+$, 385.0118; found: 385.0122.

4-(4-((2-methylphenethyl)thio)phenoxy)benzonitrile (33)



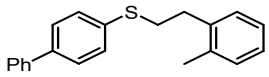
General procedure A was followed to obtain **33** (25.9 mg, 75%, petroleum ether/ethyl acetate = 15:1) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.75 – 7.59 (m, 2H), 7.42 (dd, *J* = 8.6, 1.4 Hz, 2H), 7.15 (d, *J* = 1.3 Hz, 4H), 7.01 (d, *J* = 9.0 Hz, 4H), 3.18 – 3.06 (m, 2H), 3.03 – 2.84 (m, 2H), 2.28 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 161.4, 153.4, 138.2, 135.9, 134.2, 132.8, 131.8, 130.4, 129.0, 126.7, 126.2, 121.0, 118.8, 117.9, 106.0, 34.7, 33.2, 19.3.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{22}H_{20}NOS^+$, 346.1260; found: 346.1258.

[1,1'-biphenyl]-4-yl(2-methylphenethyl)sulfane (34)



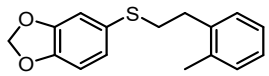
General procedure A was followed to obtain **34** (25.5 mg, 84%, petroleum ether/ethyl acetate = 20:1) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 7.4 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.49 – 7.43 (m, 5H), 7.40 – 7.34 (m, 1H), 7.21 – 7.16 (m, 3H), 3.23 – 3.14 (m, 2H), 3.06 – 2.94 (m, 2H), 2.32 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 140.4, 139.0, 138.4, 136.0, 135.5, 130.4, 129.5, 129.1, 128.9, 127.6, 127.4, 126.9, 126.7, 126.2, 33.9, 33.2, 19.3.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{21}H_{21}S^+$, 305.1358; found: 305.1359.

5-((2-methylphenethyl)thio)benzo[*d*][1,3]dioxole (35)



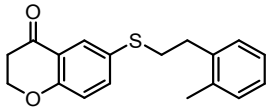
General procedure A was followed to obtain **35** (22.0 mg, 81%, petroleum ether/ethyl acetate = 15:1) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.18 – 7.10 (m, 4H), 6.96 (d, *J* = 8.7 Hz, 2H), 6.78 (d, *J* = 7.8 Hz, 1H), 5.98 (s, 2H), 3.05 – 2.99 (m, 2H), 2.91 – 2.85 (m, 2H), 2.26 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 148.0, 147.1, 138.4, 135.9, 130.3, 129.0, 128.0, 126.6, 126.1, 125.4, 112.0, 108.7, 101.3, 36.0, 33.4, 19.2.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{16}H_{17}O_2S^+$, 273.0944; found: 273.0932.

6-((2-methylphenethyl)thio)chroman-4-one (36)



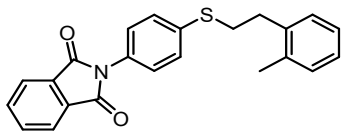
General procedure A was followed to obtain **36** (13.7 mg, 46%, petroleum ether/ethyl acetate = 10:1) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 2.4 Hz, 1H), 7.61 – 7.42 (m, 1H), 7.12 (s, 4H), 6.93 (d, *J* = 8.6 Hz, 1H), 4.54 (t, *J* = 6.5 Hz, 2H), 3.09 – 3.04 (m, 2H), 2.91 – 2.85 (m, 2H), 2.81 (t, *J* = 6.4 Hz, 2H), 2.26 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 191.2, 160.7, 138.4, 138.2, 135.9, 130.4, 129.1, 128.7, 128.5, 126.6, 126.1, 121.6, 118.8, 67.1, 37.6, 35.0, 33.2, 19.2.

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd for $C_{18}H_{18}NaO_2S^+$, 321.0920; found: 321.0921.

2-(4-((2-methylphenethyl)thio)phenyl)isoindoline-1,3-dione (37)



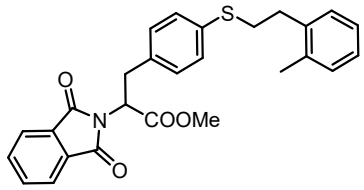
General procedure A was followed to obtain **37** (23.5 mg, 63%, petroleum ether/ethyl acetate = 5:1) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.96 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.80 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.39 (d, *J* = 8.6 Hz, 2H), 7.19 – 7.11 (m, 4H), 3.22 – 3.09 (m, 2H), 3.02 – 2.90 (m, 2H), 2.31 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.2, 138.2, 137.0, 136.0, 134.5, 131.7, 130.4, 129.4, 129.1, 129.1, 126.9, 126.7, 126.2, 123.8, 33.7, 33.0, 19.3.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{23}H_{20}NO_2S^+$, 374.1209; found: 374.1195.

methyl 2-(1,3-dioxoisoindolin-2-yl)-3-(4-((2-methylphenethyl)thio)phenyl)propanoate (38)



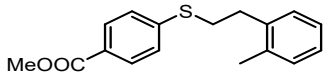
General procedure A was followed to obtain **38** (28.9 mg, 63%, petroleum ether/ethyl acetate = 3:1) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.80 – 7.73 (m, 2H), 7.71 – 7.64 (m, 2H), 7.21 – 7.15 (m, 2H), 7.12 – 7.07 (m, 5H), 7.07 – 7.03 (m, 1H), 5.19 – 5.12 (m, 1H), 3.78 (s, 3H), 3.64 – 3.49 (m, 2H), 3.03 – 2.97 (m, 2H), 2.84 – 2.74 (m, 2H), 2.19 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.3, 167.4, 138.4, 135.9, 134.7, 134.7, 134.2, 131.6, 130.3, 129.7, 129.5, 129.0, 126.6, 126.1, 123.5, 53.1, 52.9, 34.2, 33.9, 33.1, 19.2.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{27}H_{26}NO_4S^+$, 460.1577; found: 460.1585.

methyl 4-((2-methylphenethyl)thio)benzoate (39)



A mixture of corresponding arylthianthene salt (0.15 mmol, 1.5 equiv.), 1,1,3,3-tetramethylthiourea **2a** (0.3 mmol, 3.0 equiv.) and Cs_2CO_3 (0.2 mmol, 2.0 equiv) were added in 10 mL Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (repeated for three times). To this solid, 2-(*o*-tolyl)ethan-1-ol (0.1 mmol, 1.0 equiv.) and anhydrous CH_3CN (0.5 mL) were added using a gastight syringe under argon atmosphere. The reaction mixture was stirred under LEDs (420 nm, 40 W)

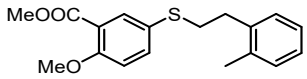
irradiation, maintained at approximately room temperature in the air-conditioned room of 25 ℃. After 20 h, the mixture was diluted with EtOAc (approximately 4 mL), washed with brine (approximately 3 mL), and dried over Na_2SO_4. Upon filtration, the organic layers were combined and concentrated on rotary evaporator. The residue was purified by silica gel column chromatography to give the product **39** (20.3 mg, 71%, petroleum ether/ethyl acetate = 15:1) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.16 (s, 4H), 3.91 (s, 3H), 3.22 – 3.16 (m, 2H), 3.00 – 2.94 (m, 2H), 2.32 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.8, 143.8, 138.0, 136.0, 130.5, 130.0, 129.1, 126.9, 126.8, 126.7, 126.2, 52.1, 32.7, 32.5, 19.3.

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd for $C_{17}H_{18}NaO_2S^+$, 309.0920; found: 309.0929.

methyl 2-methoxy-5-((2-methylphenethyl)thio)benzoate (40)



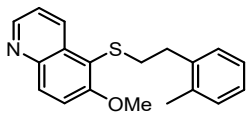
General procedure A was followed to obtain **40** (25.9 mg, 82%, petroleum ether/ethyl acetate = 10:1) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 2.5 Hz, 1H), 7.53 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.15 – 7.08 (m, 4H), 6.94 (d, *J* = 8.7 Hz, 1H), 3.91 (s, 3H), 3.89 (s, 3H), 3.09 – 3.00 (m, 2H), 2.93 – 2.83 (m, 2H), 2.24 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.0, 158.3, 138.3, 136.7, 135.9, 134.6, 130.4, 129.1, 126.6, 126.5, 126.1, 120.6, 112.8, 56.2, 52.2, 35.6, 33.4, 19.2.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{18}H_{21}O_3S^+$, 317.1206; found: 317.1212.

3-methoxy-4-((2-methylphenethyl)thio)quinoline (41)



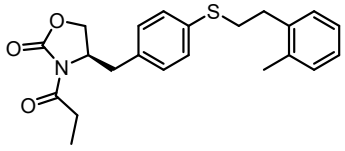
General procedure A was followed to obtain **41** (24.7 mg, 80%, petroleum ether/ethyl acetate = 7:1) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.91 (d, *J* = 8.7 Hz, 1H), 8.80 (d, *J* = 4.1 Hz, 1H), 8.15 (d, *J* = 9.3 Hz, 1H), 7.53 (d, *J* = 9.3 Hz, 1H), 7.42 (dd, *J* = 8.6, 4.1 Hz, 1H), 7.09 – 6.99 (m, 4H), 4.06 (s, 3H), 3.07 – 3.02 (m, 2H), 2.78 – 2.71 (m, 2H), 2.08 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.0, 135.8, 131.7, 128.3, 112.2, 111.9, 56.3, 29.6, 14.5.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{19}H_{20}NOS^+$, 310.1260; found: 310.1259.

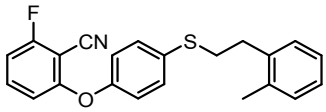
(*R*)-4-(4-((2-methylphenethyl)thio)benzyl)-3-propionyloxazolidin-2-one (42)



General procedure A was followed to obtain **42** (20.3 mg, 53%, petroleum ether/ethyl acetate = 3:1) as a colorless oil.

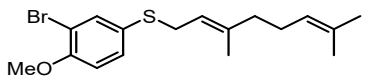
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 8.0 Hz, 2H), 7.16 – 7.12 (m, 6H), 4.69 – 4.61 (m, 1H), 4.21 (t, *J* = 8.4 Hz, 1H), 4.15 (dd, *J* = 9.1, 2.7 Hz, 1H), 3.26 (dd, *J* = 13.5, 3.3 Hz, 1H), 3.15 – 3.07 (m, 2H), 2.98 – 2.88 (m, 4H), 2.78 – 2.72 (m, 1H), 2.27 (s, 3H), 1.20 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 174.1, 153.4, 138.3, 135.9, 135.7, 133.1, 130.4, 130.0, 129.7, 129.1, 126.7, 126.2, 66.2, 55.1, 37.5, 33.9, 33.1, 29.2, 19.3, 8.3.
HRMS (ESI) (m/z): $[M+Na]^+$ Calcd for $C_{22}H_{25}NNaO_3S^+$, 406.1447; found: 406.1449.

2-fluoro-6-((2-methylphenethyl)thio)-3-phenoxybenzonitrile (43)



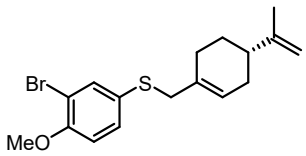
General procedure A was followed to obtain **43** (25.8 mg, 71%, petroleum ether/ethyl acetate = 15:1) as a colorless oil.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.56 – 7.36 (m, 3H), 7.15 (s, 4H), 7.05 (d, *J* = 8.7 Hz, 2H), 6.89 (t, *J* = 8.4 Hz, 1H), 6.61 (d, *J* = 8.6 Hz, 1H), 3.18 – 3.04 (m, 2H), 2.98 – 2.88 (m, 2H), 2.28 (s, 3H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 164.9, 163.2, 160.9 (d, *J* = 4.0 Hz), 152.9, 138.1, 135.9, 134.9 (d, *J* = 10.4 Hz), 133.6, 131.6, 130.4, 129.1, 126.7, 126.2, 121.0, 111.7, 111.1, 109.8 (d, *J* = 19.6 Hz), 34.6, 33.1, 19.3.
^{19}F NMR (565 MHz, Chloroform-*d*) δ -104.5 (t, *J* = 5.6 Hz).
HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{22}H_{19}FNOS^+$, 364.1166; found: 364.1163.

(*E*)-(3-bromo-4-methoxyphenyl)(3,7-dimethylocta-2,6-dien-1-yl)sulfane (44)



General procedure A was followed to obtain **44** (26.9 mg, 76%, petroleum ether/ethyl acetate = 20:1) as a colorless oil.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 2.1 Hz, 1H), 7.31 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.80 (d, *J* = 8.5 Hz, 1H), 5.26 (t, *J* = 7.8 Hz, 1H), 5.08 – 5.03 (m, 1H), 3.87 (s, 3H), 3.44 (d, *J* = 7.8 Hz, 2H), 2.04 (q, *J* = 7.7 Hz, 2H), 2.01 – 1.96 (m, 2H), 1.67 (s, 3H), 1.59 (s, 3H), 1.47 (s, 3H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.2, 140.0, 136.9, 132.7, 131.7, 128.3, 124.0, 119.3, 112.0, 111.6, 56.3, 39.6, 34.0, 26.6, 25.7, 17.7, 16.0.
HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{17}H_{24}BrOS^+$, 355.0726; found: 355.0732.

(*S*)-(3-bromo-4-methoxyphenyl)((4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl)sulfane (45)

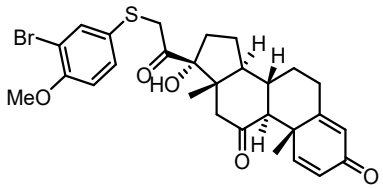


General procedure A was followed to obtain **45** (22.5 mg, 64%, petroleum ether/ethyl acetate = 20:1) as a colorless oil.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 2.3 Hz, 1H), 7.29 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.81 (d, *J* = 8.5 Hz, 1H), 5.35 (s, 1H), 4.70 (d, *J* = 16.6 Hz, 2H), 3.88 (s, 3H), 3.39 – 3.30 (m, 2H), 2.21 (d, *J* = 18.8 Hz, 2H), 2.10 – 2.02 (m, 2H), 1.91 – 1.81 (m, 2H), 1.72 (s, 3H), 1.52 – 1.42 (m, 1H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.3, 149.7, 137.4, 133.0, 132.7, 128.2, 125.6, 111.9, 111.4,

108.7, 56.3, 43.9, 40.8, 30.7, 27.6, 27.4, 20.8.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{17}H_{22}BrOS^+$, 353.0569; found: 353.0566.

(8*S*,9*S*,10*R*,13*S*,14*S*,17*R*)-17-(2-((3-bromo-4-methoxyphenyl)thio)acetyl)-17-hydroxy-10,13-dimethyl-7,8,9,10,12,13,14,15,16,17-decahydro-3*H*-cyclopenta[*a*]phenanthrene-3,11(6*H*)-dione (46)



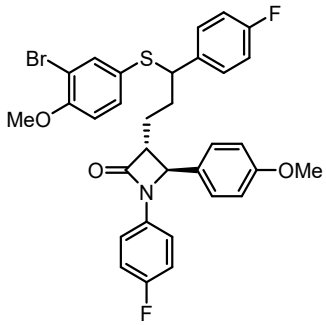
General procedure A was followed to obtain **46** (40.2 mg, 72%, CH_2Cl_2/methanol = 20:1) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 10.3 Hz, 1H), 7.61 (d, *J* = 2.2 Hz, 1H), 7.34 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.82 (d, *J* = 8.5 Hz, 1H), 6.18 (dd, *J* = 10.3, 1.8 Hz, 1H), 6.06 (s, 1H), 3.95 (d, *J* = 15.0 Hz, 1H), 3.87 (s, 3H), 3.62 (d, *J* = 15.0 Hz, 1H), 2.84 (d, *J* = 12.2 Hz, 1H), 2.78 (s, 4H), 2.77 – 2.72 (m, 1H), 2.53 – 2.45 (m, 1H), 2.40 – 2.32 (m, 2H), 2.06 (d, *J* = 12.2 Hz, 2H), 1.96 (s, 1H), 1.78 – 1.70 (m, 1H), 1.50 – 1.42 (m, 1H), 1.41 (s, 3H), 0.63 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 209.1, 205.6, 186.4, 166.6, 156.0, 155.3, 137.4, 133.3, 127.6, 126.0, 124.6, 112.2, 112.0, 88.8, 60.1, 51.7, 49.9, 49.5, 43.4, 42.3, 38.6, 36.1, 35.2, 33.6, 32.2, 23.5, 18.8, 16.0.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{28}H_{32}BrO_5S^+$, 559.1148; found: 559.1149.

(3*R*,4*S*)-3-((*R*)-3-((3-bromo-4-methoxyphenyl)thio)-3-(4-fluorophenyl)propyl)-1-(4-fluorophenyl)-4-(4-methoxyphenyl)azetidin-2-one (47)



General procedure A was followed to obtain **47** (50.5 mg, 81%, CH_2Cl_2/methanol = 30:1) as a colorless oil.

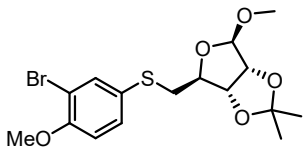
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.38 (s, 1H), 7.24 – 7.18 (m, 4H), 7.11 – 7.02 (m, 3H), 6.97 – 6.86 (m, 6H), 6.69 (d, *J* = 8.6 Hz, 1H), 4.50 (s, 1H), 3.94 (t, *J* = 7.1 Hz, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 3.06 – 3.02 (m, 1H), 2.18 – 2.11 (m, 1H), 2.05 – 1.94 (m, 2H), 1.79 (q, *J* = 9.0 Hz, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.0, 161.9 (d, *J* = 246.1 Hz), 159.9, 159.0 (d, *J* = 243.2 Hz), 156.0, 139.0, 136.9 (d, *J* = 3.1 Hz), 134.9, 133.9 (d, *J* = 2.6 Hz), 129.3 (d, *J* = 7.8 Hz), 129.3, 127.2, 125.6, 118.4 (d, *J* = 7.7 Hz), 115.8 (d, *J* = 22.6 Hz), 115.4 (d, *J* = 21.5 Hz), 114.7, 111.8, 111.5, 60.9, 60.2, 56.3, 55.4, 53.6, 33.1, 26.7.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -114.8, -118.1.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{32}H_{29}BrF_2NO_3S^+$, 624.1014; found: 624.1016.

(3a*S*,4*S*,6*R*,6a*R*)-4-(((3-bromo-4-methoxyphenyl)thio)methyl)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxole (48)



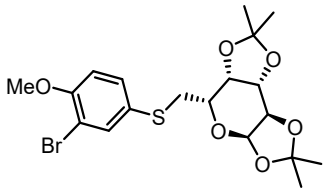
General procedure A was followed to obtain **48** (32.3 mg, 80%, petroleum ether/ethyl acetate = 3:1) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 2.4 Hz, 1H), 7.37 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.82 (d, *J* = 8.6 Hz, 1H), 4.95 (s, 1H), 4.70 (d, *J* = 5.9 Hz, 1H), 4.59 (d, *J* = 5.9 Hz, 1H), 4.16 (dd, *J* = 9.4, 6.1 Hz, 1H), 3.87 (s, 3H), 3.34 (s, 3H), 3.05 (dd, *J* = 13.5, 6.3 Hz, 1H), 2.84 (dd, *J* = 13.6, 9.4 Hz, 1H), 1.45 (s, 3H), 1.30 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.6, 136.9, 132.7, 126.6, 112.5, 112.3, 112.1, 109.6, 85.3, 85.1, 83.2, 56.4, 55.0, 39.4, 26.4, 24.9.

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd for $C_{16}H_{21}BrNaO_5S^+$, 427.0185; found: 427.0180.

(3a*R*,5*S*,5a*R*,8a*S*,8b*R*)-5-(((3-bromo-4-methoxyphenyl)thio)methyl)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran (49)



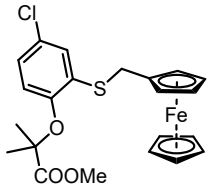
General procedure A was followed to obtain **49** (25.8 mg, 56%, petroleum ether/ethyl acetate = 3:1) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 2.2 Hz, 1H), 7.36 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 5.52 (d, *J* = 5.0 Hz, 1H), 4.59 (dd, *J* = 7.9, 2.4 Hz, 1H), 4.33 (d, *J* = 8.0 Hz, 1H), 4.28 (dd, *J* = 5.0, 2.4 Hz, 1H), 3.86 (s, 3H), 3.78 (t, *J* = 7.0 Hz, 1H), 3.06 (dd, *J* = 7.0, 2.7 Hz, 2H), 1.44 (s, 3H), 1.33 (s, 3H), 1.29 (d, *J* = 5.6 Hz, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.3, 136.1, 132.0, 127.7, 112.3, 112.0, 109.3, 108.6, 96.7, 71.3, 70.9, 70.5, 66.3, 56.4, 35.2, 26.0, 25.7, 24.9, 24.4.

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd for $C_{19}H_{25}BrNaO_6S^+$, 483.0447; found: 483.0442.

methyl 2-(4-chloro-2-((ferrocenylmethyl)thio)phenoxy)-2-methylpropanoate (50)



General procedure C was followed to obtain **50** (30.2 mg, 66%, petroleum ether/ethyl acetate = 10:1) as a yellow oil.

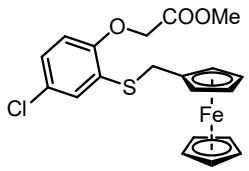
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.19 (d, *J* = 2.6 Hz, 1H), 7.00 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.70 (d,

J = 8.7 Hz, 1H), 4.29 – 4.12 (m, 9H), 3.84 (s, 2H), 1.61 (s, 6H), 1.27 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 174.1, 151.6, 132.2, 127.9, 127.6, 125.6, 118.6, 80.7, 69.2, 68.3, 61.6, 32.3, 25.1, 14.1.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{22}H_{24}ClFeO_3S^+$, 459.0479; found: 459.0475.

methyl 2-(4-chloro-2-((ferrocenylmethyl)thio)phenoxy)acetate (51)



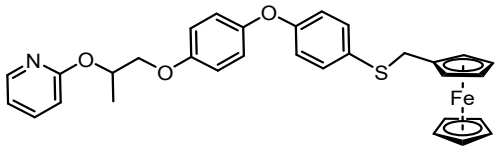
General procedure C was followed to obtain **51** (30.5 mg, 71%, petroleum ether/ethyl acetate = 15:1) as a yellow oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.25 (d, *J* = 2.5 Hz, 1H), 7.09 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.66 (d, *J* = 8.7 Hz, 1H), 4.67 (s, 2H), 4.20 – 4.15 (m, 7H), 4.10 (s, 2H), 3.93 (s, 2H), 3.80 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.8, 154.3, 129.8, 128.4, 127.1, 126.7, 113.1, 68.9, 68.9, 68.1, 66.1, 52.3, 33.0.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{20}H_{20}ClFeO_3S^+$, 431.0166; found: 431.0164.

2-((1-(4-(4-((ferrocenylmethyl)thio)phenoxy)phenoxy)propan-2-yl)oxy)pyridine (52)



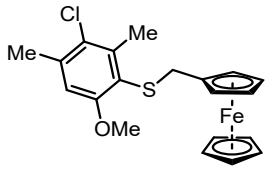
A mixture of arylthianthene salt (0.15 mmol, 1.5 equiv.), 1,1,3,3-tetramethylthiourea (0.3 mmol, 3.0 equiv.), ferrocenemethanol (0.1 mmol, 1.0 equiv.) and Cs_2CO_3 (0.2 mmol, 2.0 equiv.) were added in 10 mL Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (repeated for three times). To this solid, anhydrous CH_3CN (0.5 mL) were added using a gastight syringe under argon atmosphere. The reaction mixture was stirred under LEDs (420 nm, 40 W) irradiation, maintained at approximately room temperature in the air-conditioned room of 25 ℃. After 20 h, the mixture was diluted with EtOAc (approximately 4 mL), washed with brine (approximately 3 mL), and dried over Na_2SO_4. Upon filtration, the organic layers were combined and concentrated on rotary evaporator. The residue was purified by silica gel column chromatography to give the product **52** (38.0 mg, 69%, petroleum ether/ethyl acetate = 10:1) as a yellow oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.15 (dd, *J* = 5.4, 1.9 Hz, 1H), 7.60 – 7.54 (m, 1H), 7.28 (d, *J* = 8.7 Hz, 2H), 6.96 – 6.90 (m, 4H), 6.86 (d, *J* = 7.0 Hz, 1H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.74 (d, *J* = 8.3 Hz, 1H), 5.62 – 5.55 (m, 1H), 4.19 (dd, *J* = 9.9, 5.3 Hz, 1H), 4.13 (s, 5H), 4.10 – 4.02 (m, 5H), 3.82 (s, 2H), 1.48 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 163.2, 157.8, 155.4, 150.0, 146.8, 138.7, 133.4, 129.3, 120.8, 118.0, 116.8, 115.9, 111.7, 71.1, 69.3, 68.8, 68.8, 68.1, 36.6, 17.0.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{31}H_{30}FeNO_3S^+$, 552.1290; found: 552.1286.

(3-chloro-6-methoxy-2,4-dimethylphenyl)(ferrocenylmethyl)sulfane (53)



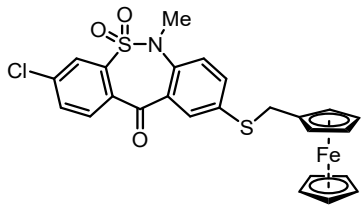
General procedure C was followed to obtain **53** (24.0 mg, 60%, petroleum ether/ethyl acetate = 10:1) as a yellow oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.65 (s, 1H), 4.12 (s, 5H), 4.05 (s, 2H), 3.99 (s, 2H), 3.86 (s, 3H), 3.66 (s, 2H), 2.44 (s, 3H), 2.38 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.4, 141.7, 137.4, 126.9, 121.3, 110.9, 68.9, 68.8, 68.1, 56.2, 35.3, 21.6, 19.7.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{20}H_{22}ClFeOS^+$, 401.0424; found: 401.0420.

3-chloro-9-((ferrocenylmethyl)thio)-6-methyldibenzo[*c*,*f*][1,2]thiazepin-11(6*H*)-one 5,5-dioxide (54)



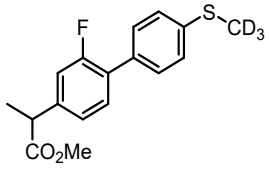
General procedure C was followed to obtain **54** (39.7 mg, 74%, petroleum ether/ethyl acetate = 2:1) as a yellow oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.24 (s, 1H), 7.94 (d, *J* = 1.9 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.68 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 1H), 4.28 – 4.15 (m, 9H), 3.95 (s, 2H), 3.32 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 189.1, 139.2, 138.8, 138.3, 135.9, 135.7, 134.2, 133.4, 133.3, 132.0, 131.0, 125.5, 125.0, 69.4, 69.2, 68.6, 39.1, 34.8.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{25}H_{21}ClFeNO_3S_2^+$, 537.9995; found: 537.9991.

methyl 2-(2-fluoro-4'-((methyl-*d*$_3$)thio)-[1,1'-biphenyl]-4-yl)propanoate (55)



General procedure B was followed to obtain **55** (29.5 mg, 96%, petroleum ether/ethyl acetate = 15:1) as a colorless oil.

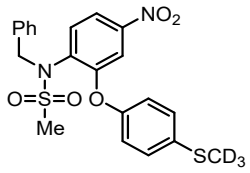
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 6.7 Hz, 2H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.12 (dd, *J* = 13.5, 9.7 Hz, 2H), 3.76 (q, *J* = 7.2 Hz, 1H), 3.70 (s, 3H), 1.53 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 174.4, 159.7 (d, *J* = 248.4 Hz), 141.8 (d, *J* = 7.6 Hz), 138.2, 132.1, 130.5 (d, *J* = 4.0 Hz), 129.3 (d, *J* = 3.1 Hz), 127.2 (d, *J* = 13.3 Hz), 126.4, 123.6 (d, *J* = 3.2 Hz), 115.3 (d, *J* = 23.6 Hz), 52.2, 44.9, 18.4.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -117.4.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{17}H_{15}D_3FO_2S^+$, 308.1194; found: 308.1196.

***N*-benzyl-*N*-(2-(4-((methyl-d_3)thio)phenoxy)-4-nitrophenyl)methanesulfonamide (56)**



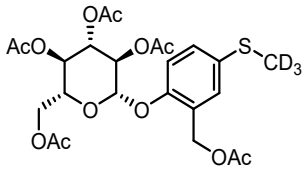
General procedure B was followed to obtain **56** (38.0 mg, 85%, petroleum ether/ethyl acetate = 5:1) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.77 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.56 (d, *J* = 2.5 Hz, 1H), 7.36 – 7.31 (m, 3H), 7.28 (s, 5H), 7.00 (d, *J* = 8.8 Hz, 2H), 4.91 (s, 2H), 3.09 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.5, 151.7, 148.0, 136.2, 135.3, 134.3, 134.1, 129.0, 128.8, 128.7, 128.3, 120.6, 117.7, 111.9, 54.0, 40.5.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{21}H_{18}D_3N_2O_5S_2^+$, 448.1075; found: 448.1072.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(2-(acetoxymethyl)-4-((methyl-d_3)thio)phenoxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (57)



General procedure B was followed to obtain **57** (30.0 mg, 55%, CH_2Cl_2/methanol = 30:1) as a colorless oil.

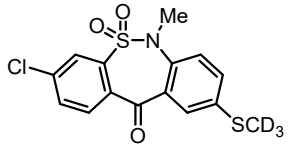
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.26 (s, 1H), 7.18 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.02 (d, *J* = 8.6 Hz, 1H), 5.29 – 5.26 (m, 2H), 5.20 – 5.13 (m, 1H), 5.08 (d, *J* = 13.0 Hz, 1H), 5.02 – 4.98 (m, 2H), 4.26 (dd, *J* = 12.3, 5.3 Hz, 1H), 4.17 (dd, *J* = 12.3, 2.5 Hz, 1H), 3.86 – 3.79 (m, 1H), 2.09 (s, 3H), 2.09 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 2.03 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.6, 170.5, 170.2, 169.4, 169.3, 152.6, 133.0, 128.7, 128.5, 127.2, 117.0, 99.7, 72.6, 72.1, 71.0, 68.3, 61.9, 60.8, 20.9, 20.7, 20.6.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{24}H_{28}D_3O_{12}S^+$, 546.1719; found: 546.1721.

$[\alpha]_D^{15}$ = -21.6 (c = 0.31, CH_2Cl_2).

3-chloro-6-methyl-9-((methyl-d_3)thio)dibenzo[*c*,*f*][1,2]thiazepin-11(6*H*)-one 5,5-dioxide (58)



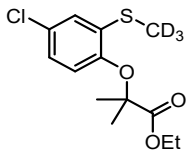
General procedure B was followed to obtain **58** (34.9 mg, 98%, petroleum ether/ethyl acetate = 2:1) as a yellow oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.11 (s, 1H), 7.96 – 7.88 (m, 2H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.28 – 7.24 (m, 1H), 3.31 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 189.1, 138.8, 138.3, 138.3, 137.5, 134.1, 133.3, 133.3, 133.0, 131.2, 128.7, 125.6, 125.3, 39.1.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{15}H_{10}D_3ClNO_3S_2^+$, 357.0208; found: 357.0206.

ethyl 2-(4-chloro-2-((methyl-*d*$_3$)thio)phenoxy)-2-methylpropanoate (59)



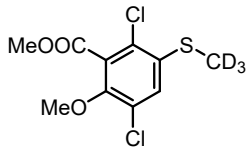
General procedure B was followed to obtain **59** (18.3 mg, 63%, petroleum ether/ethyl acetate = 15:1) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.02 (d, *J* = 2.5 Hz, 1H), 6.95 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.68 (d, *J* = 8.6 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 1.60 (s, 6H), 1.26 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 174.1, 150.7, 133.7, 128.1, 124.7, 124.4, 118.2, 80.7, 61.6, 25.0, 14.1.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{13}H_{15}D_3ClO_3S^+$, 292.0848; found: 292.0850.

methyl 2,5-dichloro-6-methoxy-3-((methyl-*d*$_3$)thio)benzoate (60)



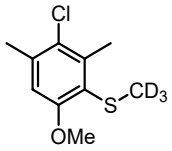
General procedure B was followed to obtain **60** (20.1 mg, 71%, petroleum ether/ethyl acetate = 15:1) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.18 (s, 1H), 3.96 (s, 3H), 3.87 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 164.9, 150.6, 135.5, 130.9, 127.5, 127.2, 127.0, 62.4, 53.0.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{10}H_8D_3Cl_2O_3S^+$, 283.9989; found: 283.9990.

(3-chloro-6-methoxy-2,4-dimethylphenyl)(methyl-*d*$_3$)sulfane (61)



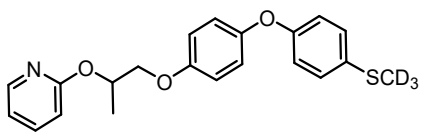
General procedure B was followed to obtain **61** (18.0 mg, 82%, petroleum ether/ethyl acetate = 15:1) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.66 (s, 1H), 3.88 (s, 3H), 2.63 (s, 3H), 2.38 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.3, 140.7, 137.1, 127.0, 122.7, 111.0, 56.1, 21.5, 19.4.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{10}H_{11}D_3ClOS^+$, 220.0637; found: 220.0640.

2-((1-(4-(4-((methyl-*d*$_3$)thio)phenoxy)phenoxy)propan-2-yl)oxy)pyridine (62)



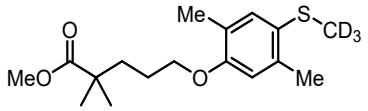
A mixture of arylthianthene salt (0.15 mmol, 1.5 equiv.), 1,1,3,3-tetramethylthiourea (0.3 mmol, 3.0 equiv.) and Cs_2CO_3 (0.2 mmol, 2.0 equiv.) were added in 10 mL Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (repeated for three times). To this solid, anhydrous CH_3CN (0.5 mL) and CD_3OD (0.1 mmol, 1.0 equiv., 99.8 atom%D) were added using a gastight syringe under argon atmosphere. The reaction mixture was stirred under LEDs (420 nm, 40 W) irradiation, maintained at approximately room temperature in the air-conditioned room of 25 ℃. After 20 h, the mixture was diluted with EtOAc (approximately 4 mL), washed with brine (approximately 3 mL), and dried over Na_2SO_4. Upon filtration, the organic layers were combined and concentrated on rotary evaporator. The residue was purified by silica gel column chromatography to give the product **67** (22.6 mg, 61%, petroleum ether/ethyl acetate = 10:1) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.17 – 8.13 (m, 1H), 7.60 – 7.54 (m, 1H), 7.23 (d, *J* = 8.7 Hz, 2H), 6.97 – 6.90 (m, 4H), 6.89 – 6.82 (m, 3H), 6.74 (d, *J* = 8.4 Hz, 1H), 5.62 – 5.55 (m, 1H), 4.18 (dd, *J* = 9.9, 5.3 Hz, 1H), 4.07 (dd, *J* = 9.9, 4.8 Hz, 1H), 1.48 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 163.1, 156.7, 155.3, 150.3, 146.7, 138.8, 131.2, 129.5, 120.6, 118.4, 116.8, 115.8, 111.7, 71.1, 69.3, 17.0.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{21}H_{19}D_3NO_3S^+$, 371.1503; found: 371.1501.

methyl 5-(2,5-dimethyl-4-((methyl-*d*$_3$)thio)phenoxy)-2,2-dimethylpentanoate (63)



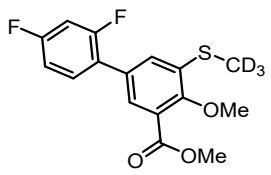
A mixture of aryldibenzothiophenium salt (0.2 mmol, 2.0 equiv.), 1,1,3,3-tetramethylthiourea (0.3 mmol, 3.0 equiv.) and Cs_2CO_3 (0.2 mmol, 2.0 equiv.) were added in 10 mL Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (repeated for three times). To this solid, anhydrous CH_3CN (0.5 mL) and CD_3OD (0.1 mmol, 1.0 equiv., 99.8 atom%D) were added using a gastight syringe under argon atmosphere. The reaction mixture was stirred under LEDs (420 nm, 40 W) irradiation, maintained at approximately room temperature in the air-conditioned room of 25 ℃. After 20 h, the mixture was diluted with EtOAc (approximately 4 mL), washed with brine (approximately 3 mL), and dried over Na_2SO_4. Upon filtration, the organic layers were combined and concentrated on rotary evaporator. The residue was purified by silica gel column chromatography to give the product **68** (18.2 mg, 58%, petroleum ether/ethyl acetate = 15:1) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.06 (s, 1H), 6.63 (s, 1H), 3.90 (t, *J* = 5.6 Hz, 2H), 3.66 (s, 3H), 2.35 (s, 3H), 2.18 (s, 3H), 1.76 – 1.67 (m, 4H), 1.22 (s, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 178.3, 155.6, 136.2, 131.0, 126.8, 125.0, 113.2, 68.2, 51.7, 42.1, 37.1, 25.2, 25.2, 20.3, 15.7.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{17}H_{24}D_3O_3S^+$, 314.1864; found: 314.1867.

methyl 2',4'-difluoro-4-methoxy-5-((methyl-*d*$_3$)thio)-[1,1'-biphenyl]-3-carboxylate (64)



General procedure B was followed to obtain **64** (29.8 mg, 91%, petroleum ether/ethyl acetate = 15:1)

as a colorless oil.

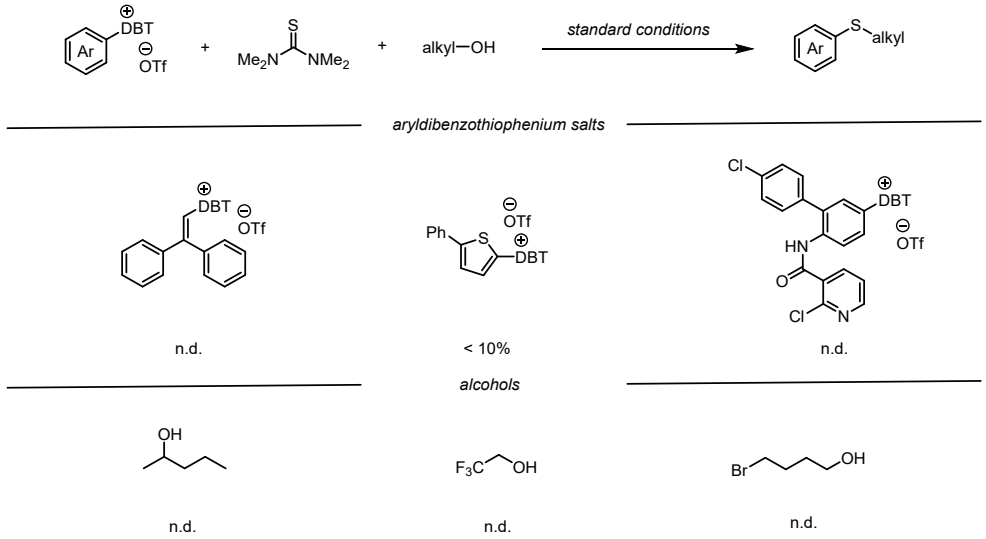
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 1.1 Hz, 1H), 7.39 (d, *J* = 6.6 Hz, 2H), 6.93 (d, *J* = 26.3 Hz, 2H), 3.95 (s, 3H), 3.93 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.0, 162.5 (dd, *J* = 249.6, 12.1 Hz), 159.6 (dd, *J* = 250.5, 11.9 Hz), 156.1, 135.3, 131.3 (dd, *J* = 9.4, 4.6 Hz), 131.2, 129.6, 127.9, 124.6, 123.9 (dd, *J* = 13.7, 3.9 Hz), 111.7 (dd, *J* = 21.1, 3.8 Hz), 104.5 (t, *J* = 25.9 Hz), 61.6, 52.4.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.5 (d, *J* = 7.9 Hz), -113.2 (d, *J* = 7.8 Hz).

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{16}H_{12}D_3F_2O_3S^+$, 328.0893; found: 328.0895.

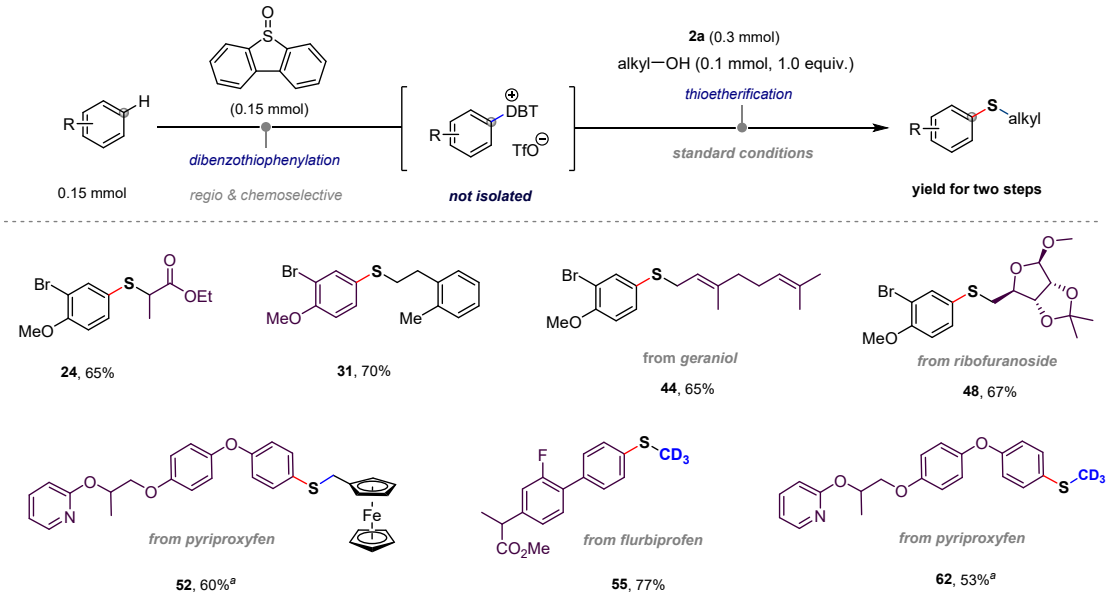
Unsuccessful Substrates



Scheme S1. Unsuccessful Substrates; n.d. = not detected.

5. Synthetic Applications

5.1 Two-step one-pot for arene C-H thioetherification[4]

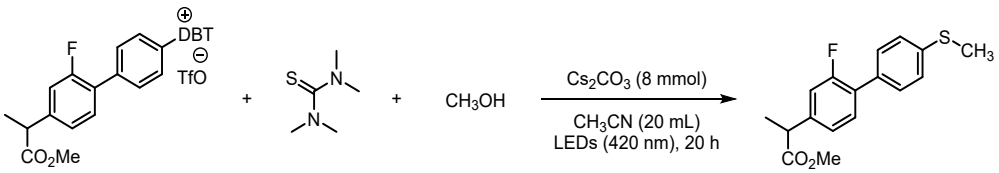


Scheme S2. Two-step one-pot for arene C-H thioetherificatio. [a]arylthianthene salt as substrate.

Tf_2O (0.15 mmol, 1.5 equiv) was slowly added to a stirred solution of the arene (0.15 mmol, 1.5 equiv.) and dibenzothiophene *S*-oxide (0.15 mmol, 1.5 equiv.) in CH_2Cl_2 (0.1 M) at −78 °C under argon atmosphere. The resulting solution was stirred at −78 °C for 15 minutes before warming to room temperature. After stirring for 1-3 hours and confirming that the reaction is complete through TLC monitoring, add Cs_2CO_3 (0.15 mmol, 1.5 equiv.) to neutralize the acid produced during the reaction. Subsequently, remove the solvent under vacuum. Then, to these mixtures, add 1,1,3,3-tetramethylthiourea 2a (0.3 mmol, 3.0 equiv.) and Cs_2CO_3 (0.2 mmol, 2.0 equiv.). The tube was evacuated and filled with argon (repeated for three times). To this solid, anhydrous CH_3CN (0.5 mL) and corresponding alcohol (0.1 mmol, 1.0 equiv.) were added using a gastight syringe under argon atmosphere. The reaction mixture was stirred under LEDs (420 nm, 40 W) irradiation, maintained at approximately room temperature in the air-conditioned room of 25 ℃. After 20 h, the mixture was diluted with EtOAc (approximately 4 mL), washed with brine (approximately 3 mL), and dried over Na_2SO_4. Upon filtration, the organic layers were combined and concentrated on rotary evaporator. The residue was purified by silica gel column chromatography to give the product.

5.2 Gram-scale methylthiolation of Flurbiprofen and its subsequent derivatization

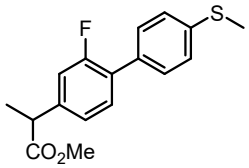
A. Synthesis of methyl 2-(2-fluoro-4'-(methylthio)-[1,1'-biphenyl]-4-yl)propanoate



65, 6 mmol **2a**, 12 mmol 4 mmol **66**, 91%, 1.1 g

A mixture of aryldibenzothiophenium salt **65** (6.0 mmol, 1.5 equiv.), 1,1,3,3-tetramethylthiourea **2a** (12.0 mmol, 3.0 equiv.) and Cs_2CO_3 (8 mmol, 2.0 equiv.) were added in 100 mL Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (repeated for three times). To this solid, anhydrous CH_3CN (20 mL) and methanol (4 mmol, 1.0 equiv.) were added using a gastight syringe under argon atmosphere. The reaction mixture was stirred under LEDs (420 nm, 40 W) irradiation, maintained at approximately room temperature in the air-conditioned room of 25 ℃. After 20 h, the mixture was diluted with EtOAc (approximately 50 mL), washed with brine (approximately 50 mL), and dried over Na_2SO_4. Upon filtration, the organic layers were combined and concentrated on rotary evaporator. The residue was purified by silica gel column chromatography to give the product **66** (colorless oil, 1.1 g, 91%, petroleum ether/ethyl acetate = 15:1).

methyl 2-(2-fluoro-4'-(methylthio)-[1,1'-biphenyl]-4-yl)propanoate (66)



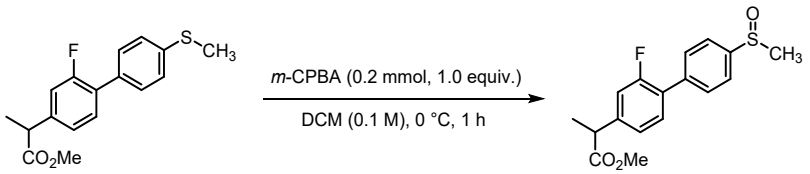
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 6.7 Hz, 2H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.5 Hz, 2H), 7.16 – 7.09 (m, 2H), 3.76 (q, *J* = 7.2 Hz, 1H), 3.70 (s, 3H), 2.52 (s, 3H), 1.53 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 174.4, 159.7 (d, *J* = 248.5 Hz), 141.8 (d, *J* = 7.6 Hz), 138.2, 132.2, 130.5 (d, *J* = 3.9 Hz), 129.3 (d, *J* = 3.0 Hz), 127.2 (d, *J* = 13.4 Hz), 126.4, 123.6 (d, *J* = 3.2 Hz), 115.3 (d, *J* = 23.5 Hz), 52.2, 44.9, 18.4, 15.7.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -117.4.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{17}H_{18}FO_2S^+$, 305.1006; found: 305.1010.

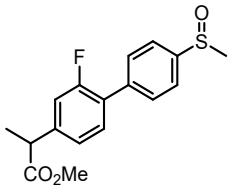
B. Synthesis of methyl 2-(2-fluoro-4'-(methylsulfinyl)-[1,1'-biphenyl]-4-yl)propanoate



66, 0.2 mmol **67**, 87%

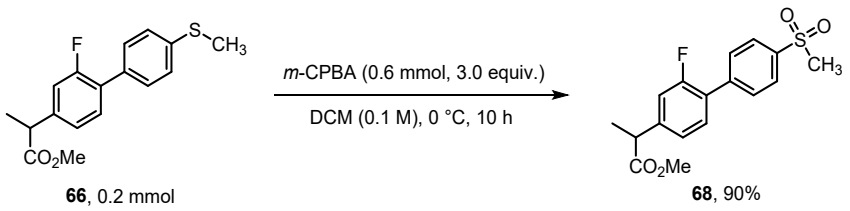
A mixture of methyl 2-(2-fluoro-4'-(methylthio)-[1,1'-biphenyl]-4-yl)propanoate **66** (0.2 mmol, 1.0 equiv.), *m*-CPBA (0.2 mmol, 1.0 equiv.) and DCM (2 mL, 0.1 M) were added in 10 mL Schlenk tube equipped with a stirring bar. The resulting solution was stirred at 0 °C. After 1 h, the mixture was diluted with EtOAc (approximately 4 mL), washed with brine (approximately 3 mL), and dried over Na_2SO_4. Upon filtration, the organic layers were combined and concentrated on rotary evaporator. The residue was purified by silica gel column chromatography to give the product **67** (colorless oil, 55.7 mg, 87%, petroleum ether/ethyl acetate = 10:1).

methyl 2-(2-fluoro-4'-(methylsulfinyl)-[1,1'-biphenyl]-4-yl)propanoate (67)



^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 7.9 Hz, 1H), 7.77 – 7.62 (t, *J* = 6.8 Hz, 1H), 7.55 (t, *J* = 6.8 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.24 (t, *J* = 7.7 Hz, 1H), 7.16 (d, *J* = 11.5 Hz, 1H), 7.13 (d, *J* = 10.5 Hz, 1H), 3.78 (q, *J* = 7.2 Hz, 1H), 3.72 (s, 3H), 2.51 (s, 3H), 1.55 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 174.2, 159.2 (d, *J* = 246.8 Hz), 145.0, 143.6 (d, *J* = 5.5 Hz), 132.8, 131.6 (d, *J* = 3.2 Hz), 130.9 (d, *J* = 24.7 Hz), 129.7, 124.1 (d, *J* = 16.3 Hz), 123.6, 115.1 (d, *J* = 23.1 Hz), 52.3, 45.0, 42.5, 18.4.
^{19}F NMR (565 MHz, Chloroform-*d*) δ -113.7.
HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{17}H_{18}FO_3S^+$, 321.0955; found: 321.0957.

C. Synthesis of methyl 2-(2-fluoro-4'-(methylsulfonyl)-[1,1'-biphenyl]-4-yl)propanoate

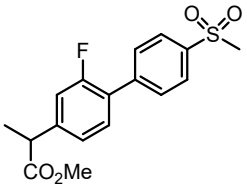


66, 0.2 mmol

68, 90%

A mixture of methyl 2-(2-fluoro-4'-(methylthio)-[1,1'-biphenyl]-4-yl)propanoate **66** (0.2 mmol, 1.0 equiv.), *m*-CPBA (0.6 mmol, 3.0 equiv.) and DCM (2 mL, 0.1 M) were added in 10 mL Schlenk tube equipped with a stirring bar. The resulting solution was stirred at 0 °C. After 1 h, the mixture was diluted with EtOAc (approximately 4 mL), washed with brine (approximately 3 mL), and dried over Na_2SO_4. Upon filtration, the organic layers were combined and concentrated on rotary evaporator. The residue was purified by silica gel column chromatography to give the product **68** (colorless oil, 60.5 mg, 90%, petroleum ether/ethyl acetate = 10:1).

methyl 2-(2-fluoro-4'-(methylsulfonyl)-[1,1'-biphenyl]-4-yl)propanoate (68)



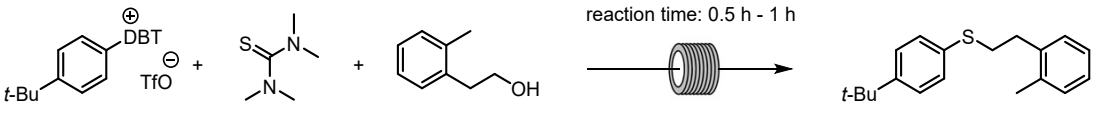
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 6.9 Hz, 2H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 9.6 Hz, 1H), 7.16 (d, *J* = 11.6 Hz, 1H), 3.78 (q, *J* = 7.2 Hz, 1H), 3.70 (s, 3H), 3.10 (s, 3H), 1.54 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 174.2, 159.7 (d, *J* = 249.9 Hz), 143.5 (d, *J* = 7.7 Hz), 141.1, 139.5, 130.7 (d, *J* = 3.3 Hz), 129.8 (d, *J* = 3.1 Hz), 127.6, 125.9 (d, *J* = 12.9 Hz), 124.0 (d, *J* = 3.2 Hz), 115.6 (d, *J* = 23.4 Hz), 52.3, 45.0, 44.6, 18.4.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -117.1.

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{17}H_{18}FO_4S^+$, 337.0904; found: 337.0907.

5.3 Synthesis of thioethers using a continuous-flow process



1a, 1.5 mmol **2a,** 3 mmol **3,** 1 mmol **4** 77% (1 h), 62% (0.5 h) trace (0.5 h, in batch)

A 25 mL round bottom flask equipped with a magnetic stir bar was charged with aryldibenzothiophenium salt **1a** (1.5 mmol, 1.5 equiv.), 1,1,3,3-tetramethylthiourea **2a** (3.0 mmol, 3.0 equiv.), Cs_2CO_3 (2.0 mmol, 2.0 equiv.) and 2-(*o*-tolyl)ethan-1-ol **3** (1.0 mmol, 1.0 equiv.). The reagents were dissolved in anhydrous CH_3CN and the total volume of the solution was adjusted to 5 mL. The resulting mixture bubbled with an argon balloon for 20 min. After that, the reaction solution was introduced to the flow apparatus (Supplementary Figure S2). The flow apparatus was purged with degassed argon to remove the air first. The syringe pump was then connected to the reaction mixture and the 3.6 mL PFA microreactor coil (internal diameter of 1.0 mm) with a 5 psi back-pressure regulator (BPR). The reaction was placed under LEDs (420 nm, 40 W). When the syringe was fully empty, a crude sample (1 mL) was taken from the collected solution and analyzed by determined through GC analysis.

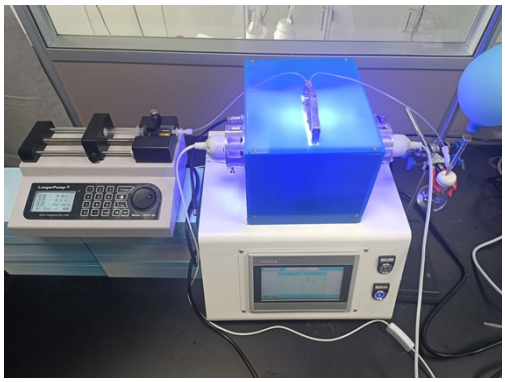
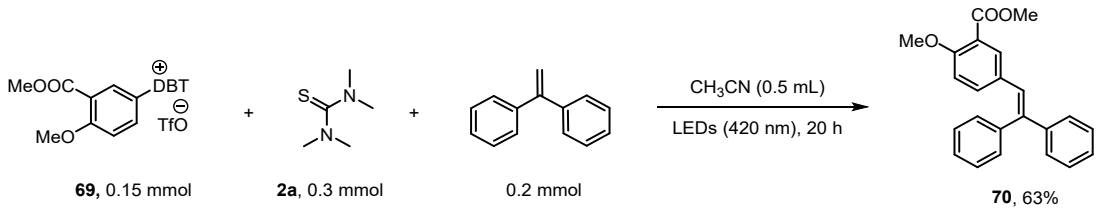


Figure S2. Flow set-up with light irradiation

6. Preliminary Mechanistic Studies

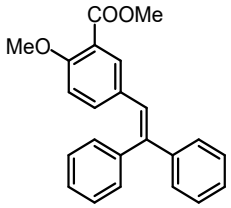
6.1 Aryl radical trapping experiment



69, 0.15 mmol **2a**, 0.3 mmol 0.2 mmol **70**, 63%

A mixture of aryldibenzothiophenium salt **69** (0.15 mmol, 1.0 equiv.) and 1,1,3,3-tetramethylthiourea **2a** (0.3 mmol, 2.0 equiv.) were added in 10 mL Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (repeated for three times). To this solid, anhydrous CH_3CN (0.5 mL) and ethene-1,1-diyldibenzene (0.2 mmol) were added using a gastight syringe under argon atmosphere. The reaction mixture was stirred under LEDs (420 nm, 40 W) irradiation, maintained at approximately room temperature in the air-conditioned room of 25 ℃. After 20 h, the mixture was diluted with EtOAc (approximately 4 mL), washed with brine (approximately 3 mL), and dried over Na_2SO_4. Upon filtration, the organic layers were combined and concentrated on rotary evaporator. The residue was purified by silica gel column chromatography to give the product **70** (white solid, 21.7 mg, 63%, petroleum ether/ethyl acetate = 10:1).

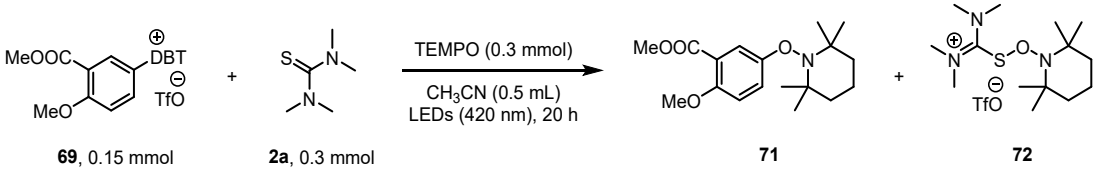
methyl 5-(2,2-diphenylvinyl)-2-methoxybenzoate[5] (70)



^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 2.4 Hz, 1H), 7.39 – 7.26 (m, 8H), 7.21 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.04 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.93 (s, 1H), 6.71 (d, *J* = 8.8 Hz, 1H), 3.84 (s, 3H), 3.81 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.39, 157.84, 143.11, 141.90, 140.25, 134.16, 133.29, 130.31, 129.64, 128.86, 128.26, 127.50, 127.45, 127.42, 126.47, 119.45, 111.58, 56.00, 51.89.

6.2 TEMPO experiment



69, 0.15 mmol **2a**, 0.3 mmol **71** **72**

A mixture of aryldibenzothiophenium salt **69** (0.15 mmol, 1.0 equiv.), 1,1,3,3-tetramethylthiourea **2a** (0.3 mmol, 2.0 equiv.), Cs_2CO_3 (0.2 mmol) and TEMPO (0.3 mmol, 2.0 equiv) were added in 10 mL Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (repeated for

three times). To this solid, anhydrous CH_3CN (0.5 mL) were added using a gastight syringe under argon atmosphere. The reaction mixture was stirred under LEDs (420 nm, 40 W) irradiation, maintained at approximately room temperature in the air-conditioned room of 25 ℃. After 20 h, the reaction mixture was sent for HRMS analysis, the compounds **71** and **72** were detected by HRMS.

HRMS (ESI) (m/z): [**71**+H]$^+$ Calcd for $C_{18}H_{28}NO_4^+$, 322.2013; found: 322.2012.

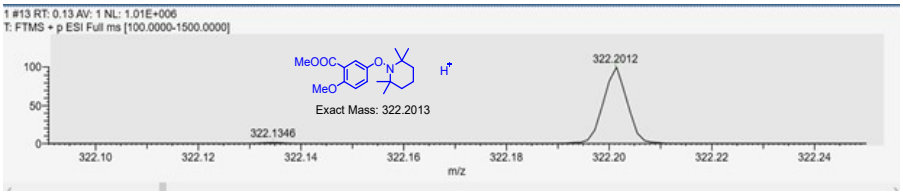


Figure S3. Compounds **71** were detected by HRMS

HRMS (ESI) (m/z): [**72**-CF_3O_3S]$^+$ Calcd for $C_{14}H_{30}N_3OS^+$, 288.2014; found: 288.2015.

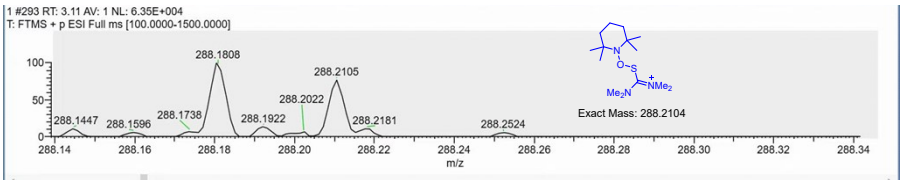
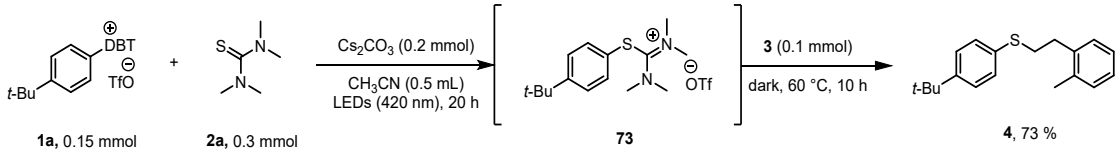


Figure S4. Compounds **72** were detected by HRMS

6.3 Control experiments



A mixture of aryldibenzothiophenium salt **1a** (0.15 mmol, 1.5 equiv.), 1,1,3,3-tetramethylthiourea **2a** (0.3 mmol, 3.0 equiv.) and Cs_2CO_3 (0.2 mmol, 2.0 equiv.) were added in 10 mL Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (repeated for three times). To this solid, anhydrous CH_3CN (0.5 mL) were added using a gastight syringe under argon atmosphere. The reaction mixture was stirred under LEDs (420 nm, 40 W) irradiation, maintained at approximately room temperature in the air-conditioned room of 25 ℃. After 20 h, a small amount of the reaction solution was taken out for HRMS analysis, and compound **73** was detected. Then, 2-(*o*-tolyl)ethan-1-ol **3** (0.1 mmol, 1.0 equiv.) was added to the reaction mixture and heated to 60℃ with stirring in the dark. After 10 h, the mixture was diluted with EtOAc (approximately 4 mL), washed with brine (approximately 3 mL), and dried over Na_2SO_4. Upon filtration, the organic layers were combined and concentrated on rotary evaporator. The residue was purified by silica gel column chromatography to give the product **4** (colorless oil, 20.7 mg, 73%, petroleum ether/ethyl acetate = 20:1).

HRMS (ESI) (m/z): [**73**-X]$^+$ Calcd for $C_{15}H_{25}N_2S^+$, 265.1733; found: 265.1726.

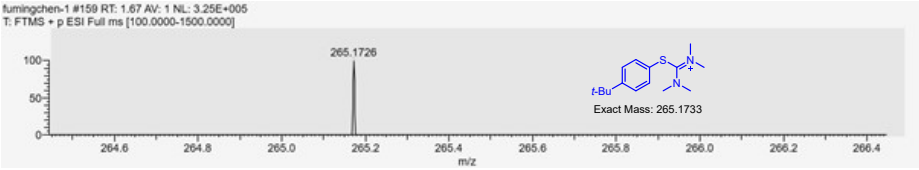


Figure S5. Compounds **73** were detected by HRMS

6.4 ^{1}H NMR spectrometry of titration experiments

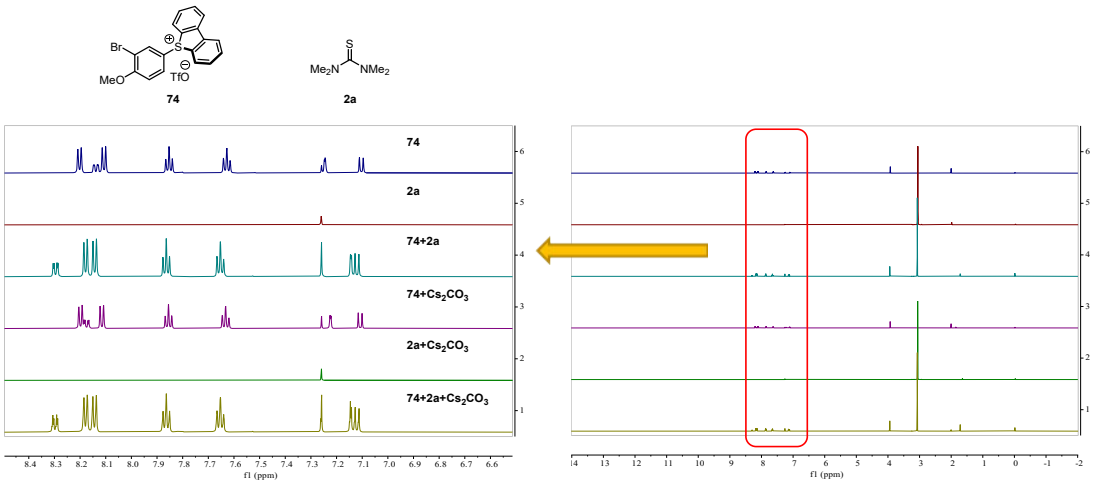


Figure S6. ^{1}H NMR spectrometry of titration experiments. The compound is dissolved in acetonitrile solution. [**74**] = 0.3 M, [**2a**] = 0.6 M, [$\mathbf{Cs_2CO_3}$] = 0.4 M. After 10 minutes, the solvent was removed in vacuo. The solid residue was dissolved in chloroform-*d* for testing.

6.5 UV-vis absorption spectra

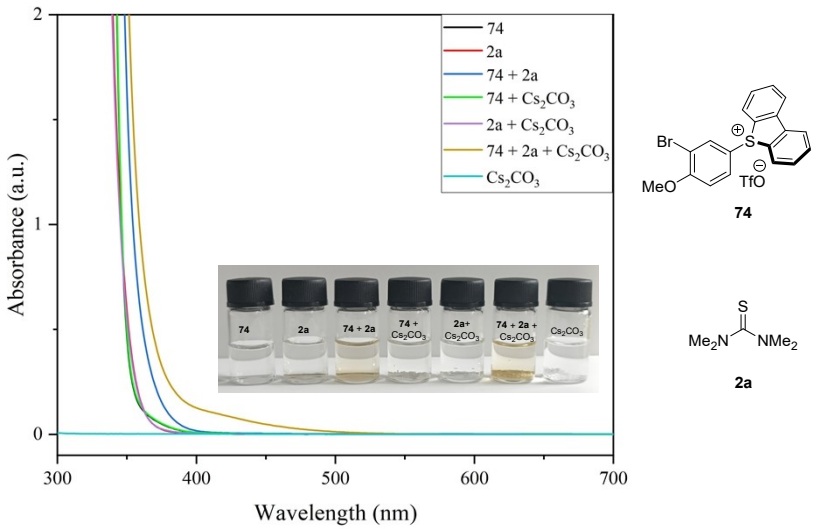


Figure S7. The absorption spectra in solution were recorded on a UNIC 4802 UV/VIS double beam spectrophotometer in a 1.0 cm length quartz cell. All compounds were dissolved in CH_3CN and measured at 25 °C. [**74**] = 0.3 M, [**2a**] = 0.6 M, [$\mathbf{Cs_2CO_3}$] = 0.4 M.

6.6 Job's plot

The absorbance values at 420 nm were monitored and plotted as a function of molar fraction of **74** and **2a** in CH_3CN. A parabolic curve with a maximum absorbance value at 50% mol fraction was obtained, indicating a 1:1 EDA complex between **74** and **2a**.

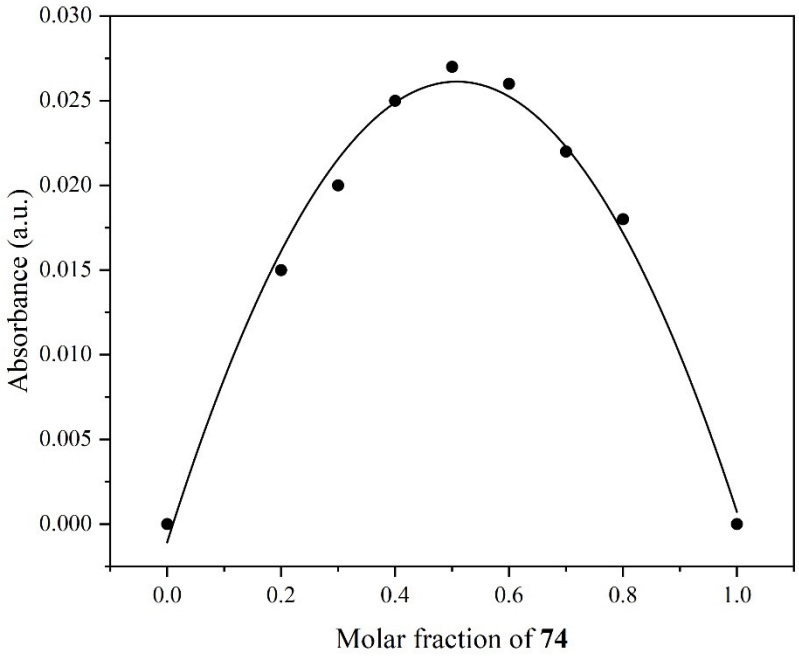


Figure S8. Job's plot.

7. References

[1] A. Dewanji, L. van Dalsen, J. Rossi-Ashton, E. Gasson, G. Crisenza, D. J. Procter, *Nat. Chem.* **2023**, *15*, 43–52;

[2] M. Zhang, B. Wang, Y. Cao, Y. Liu, Z. Wang, Q. Wang, *Org. Lett.* **2022**, *24*, 8895–8900.

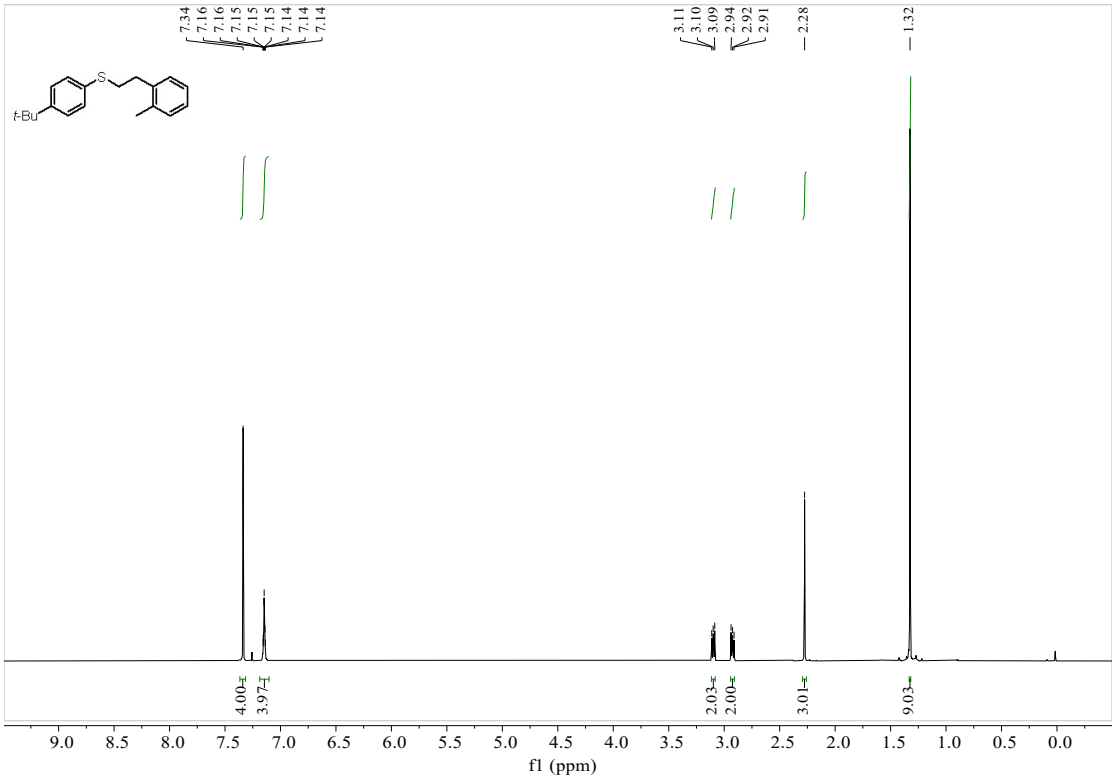
[3] B. Li, K. Wang, H. Yue, A. Drichel, J. Lin, Z. Su, M. Rueping, *Org. Lett.* **2022**, *24*, 7434–7439.

[4] T. Michiyuki, S. L. Homölle, N. K. Pandit, L. Ackermann, *Angew. Chem. Int. Ed.* **2024**, *63*, e202401198.

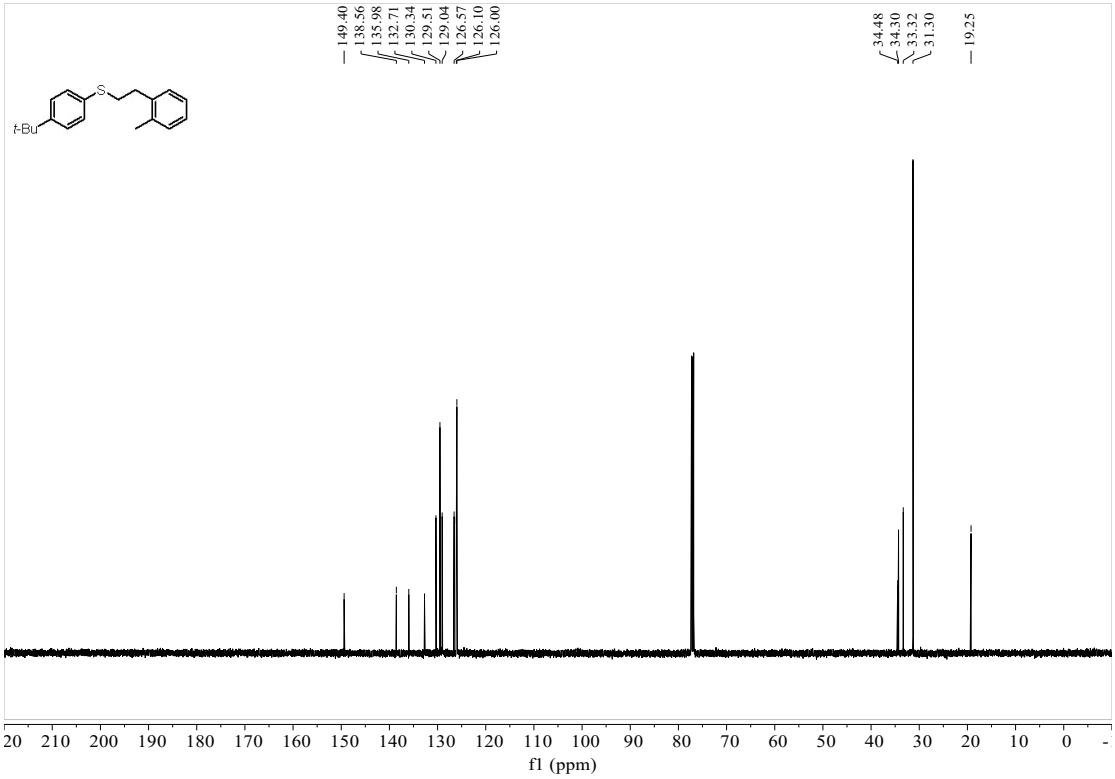
[5] Y. Wang, L. Zhao, X. Hao, K. Jin, R. Zhang, C. Duan, Y. Li, *Org. Biomol. Chem.* **2024**, *22*, 2451-2455.

8. NMR Spectra

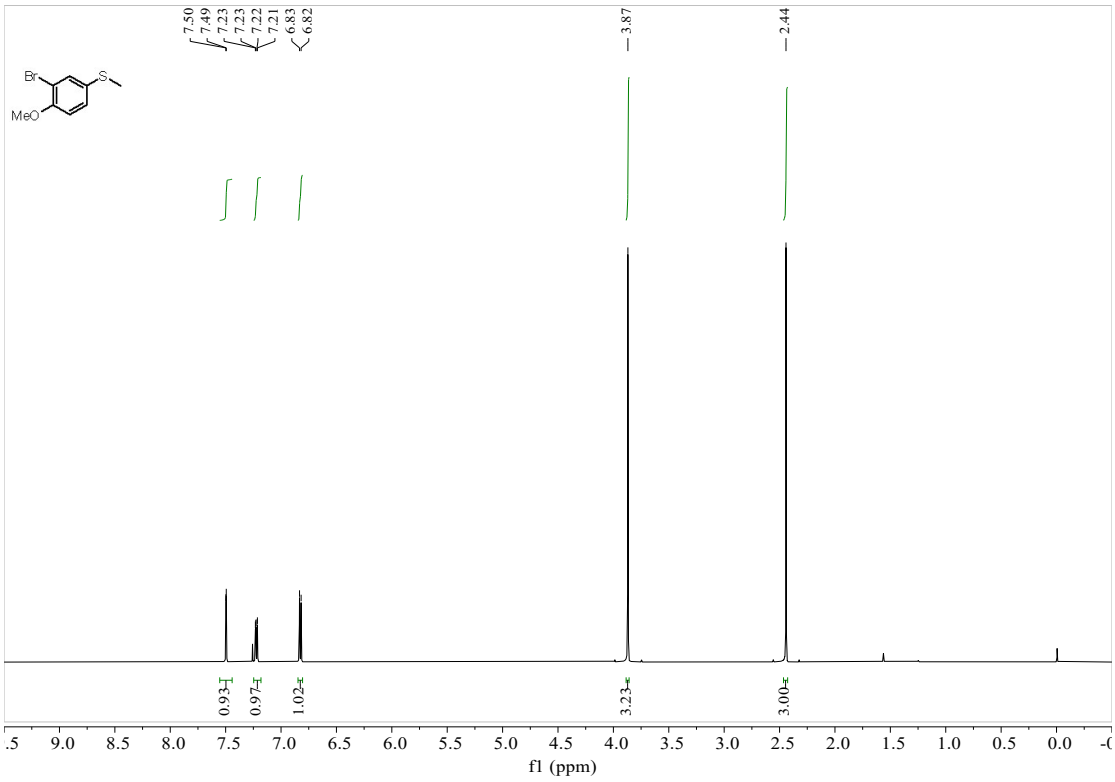
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 4



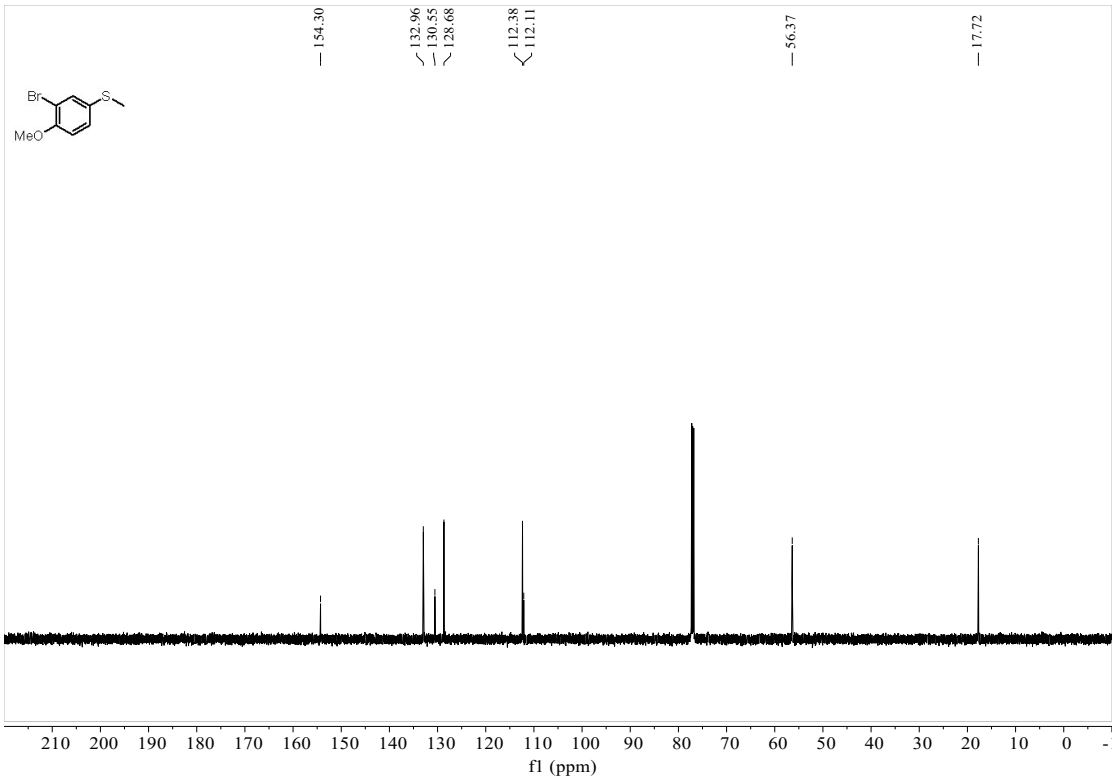
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 4



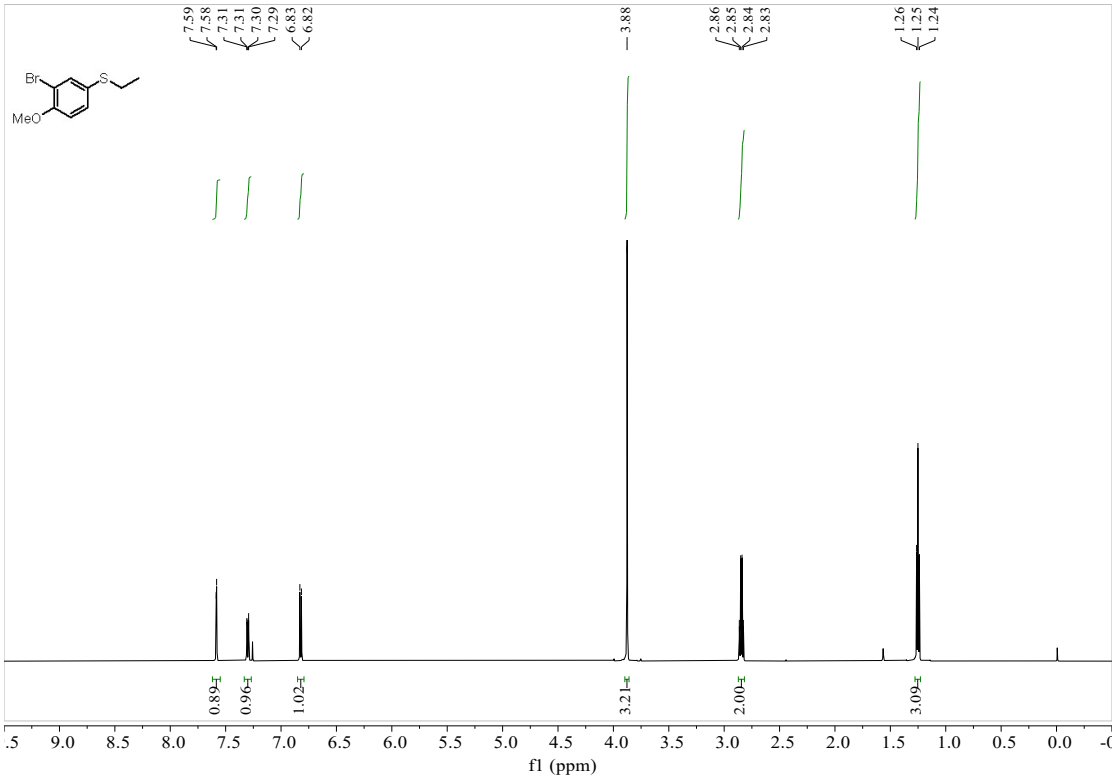
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 5



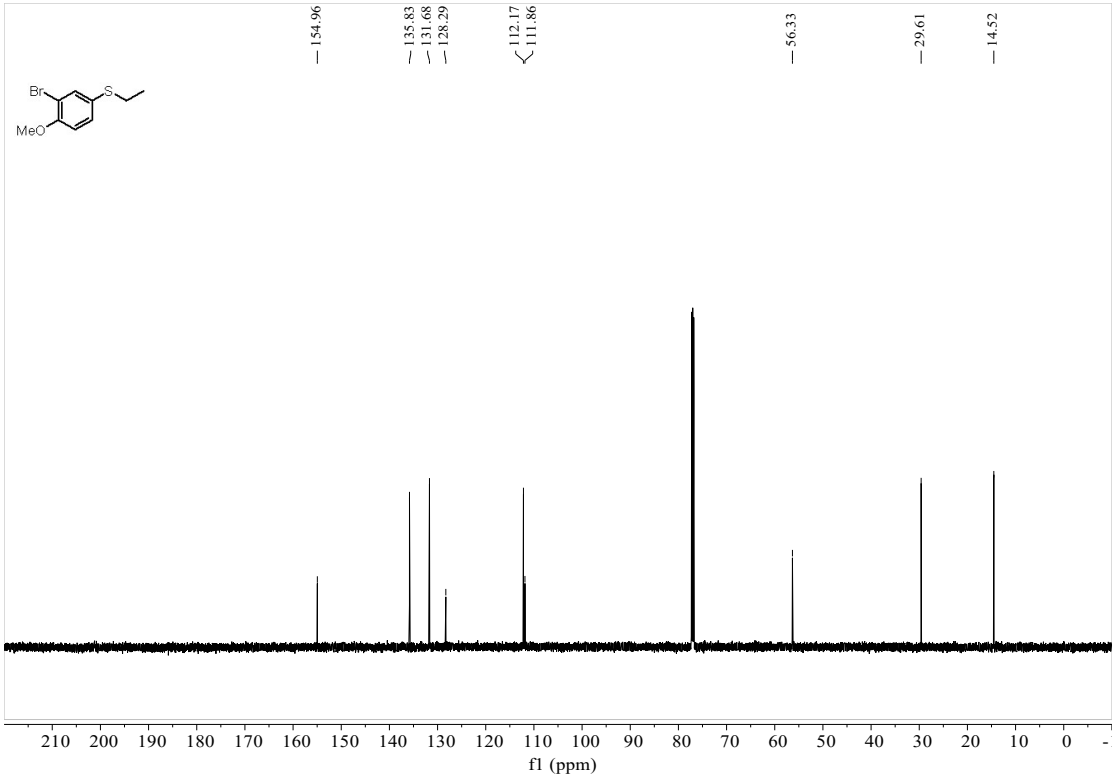
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 5



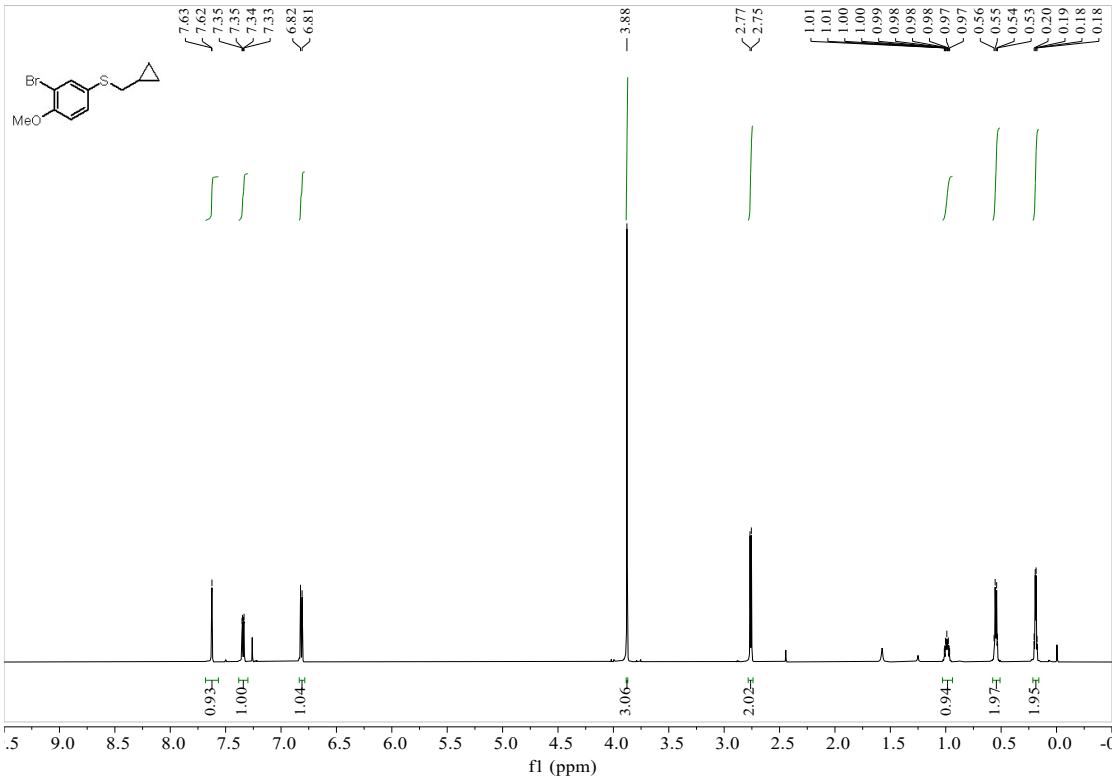
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 6



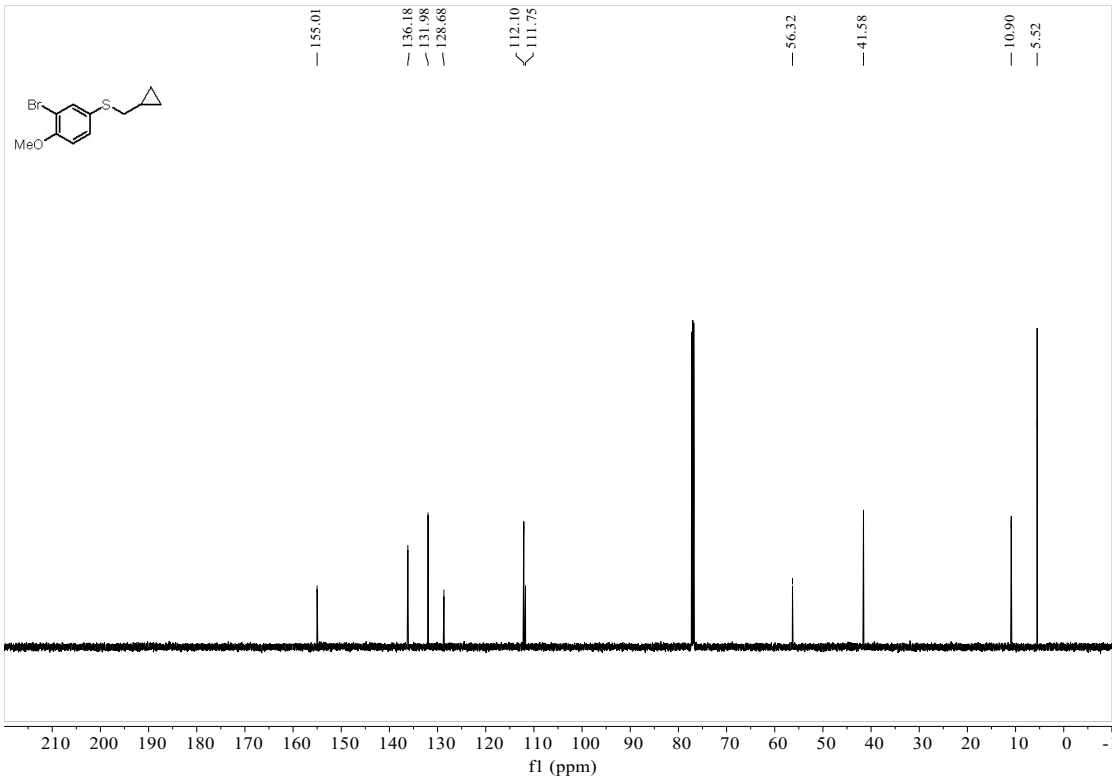
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 6



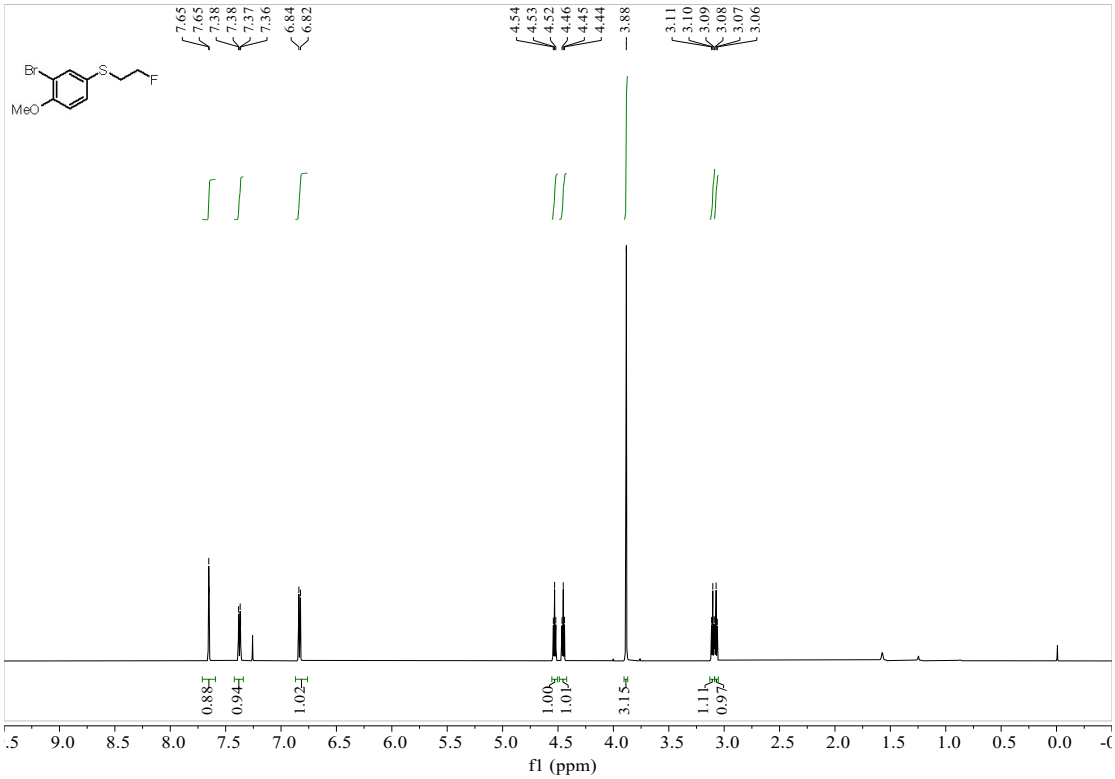
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 7



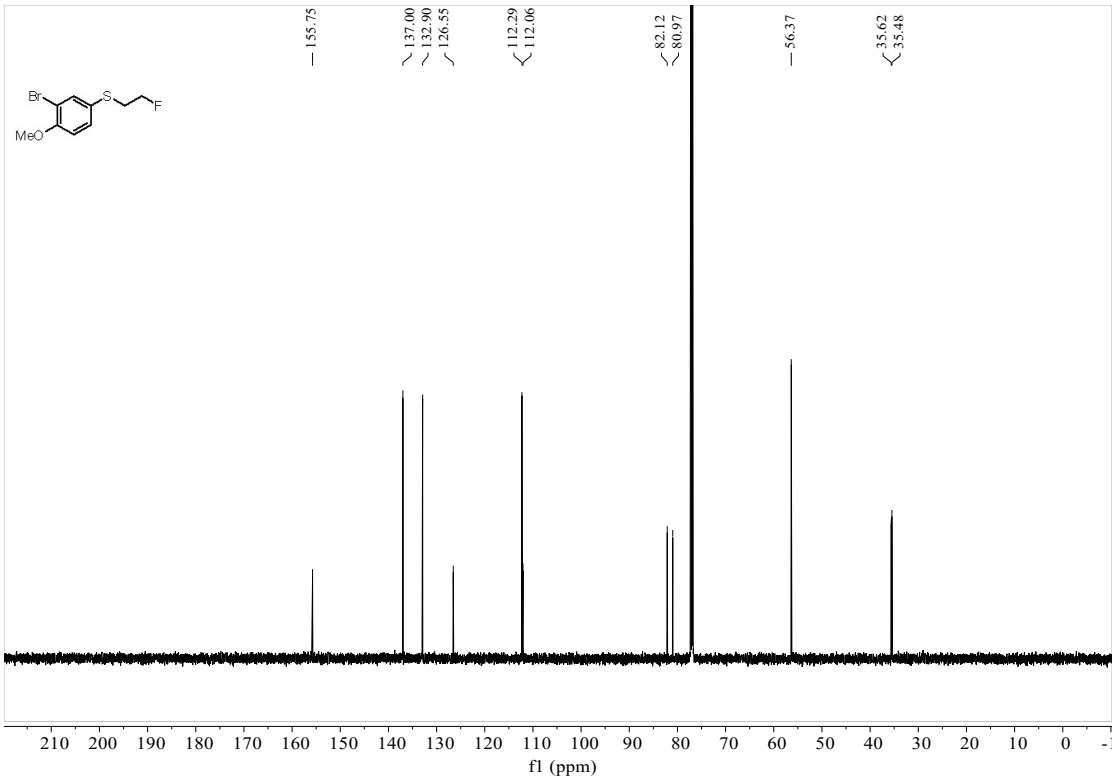
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 7



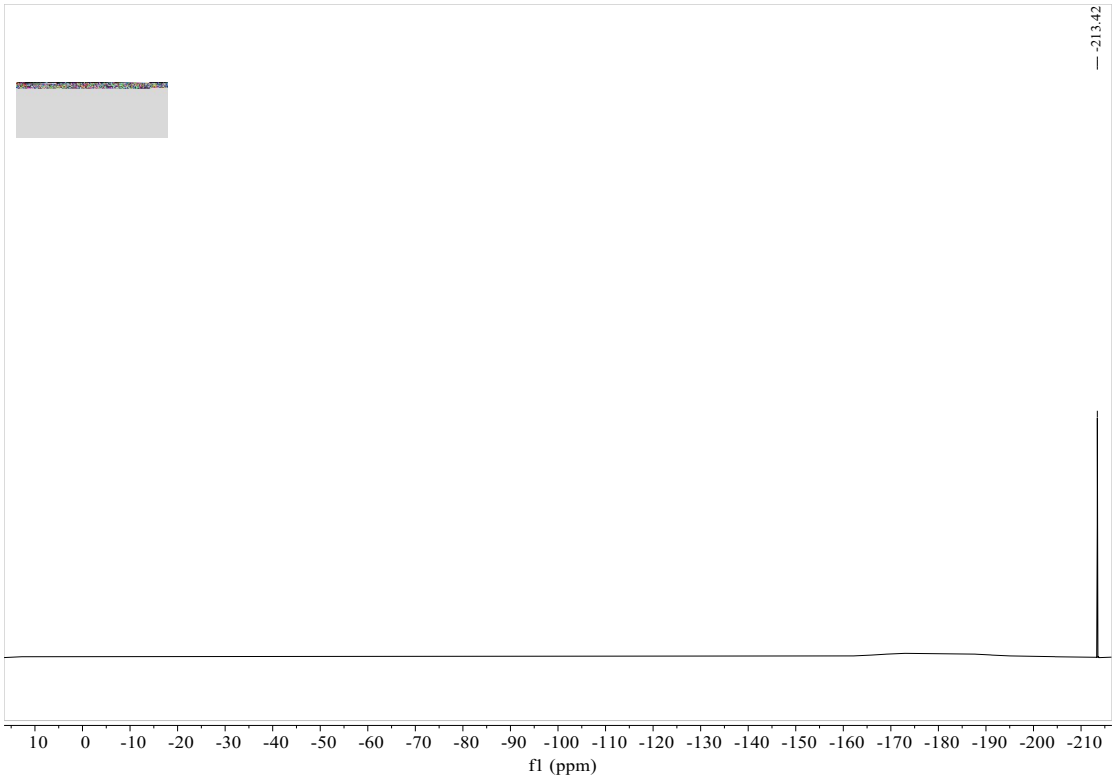
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 8



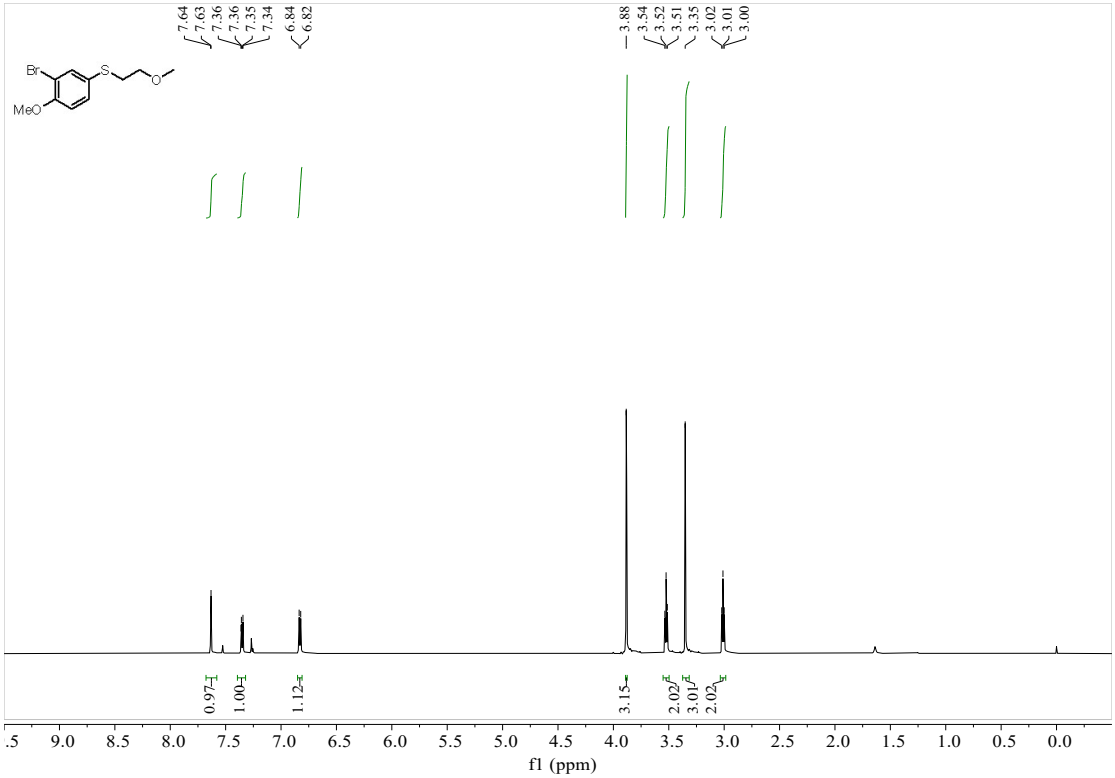
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 8



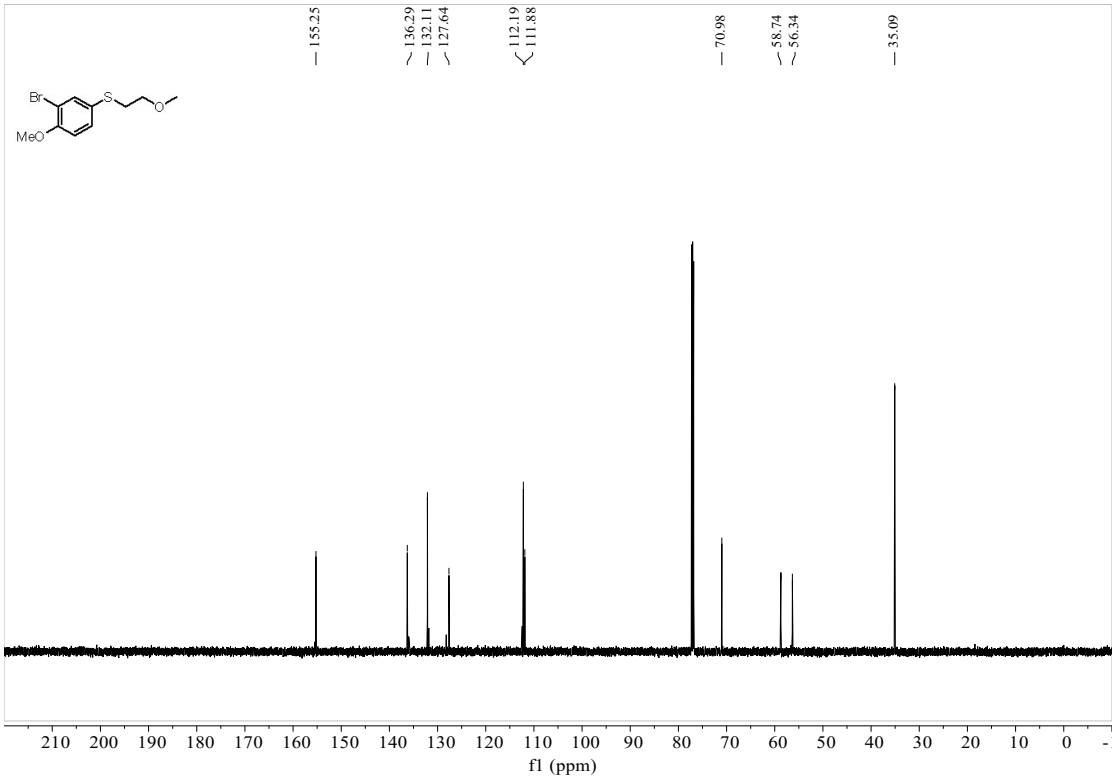
^{19}F NMR (565 MHz, Chloroform-*d*) spectrum of compound 8



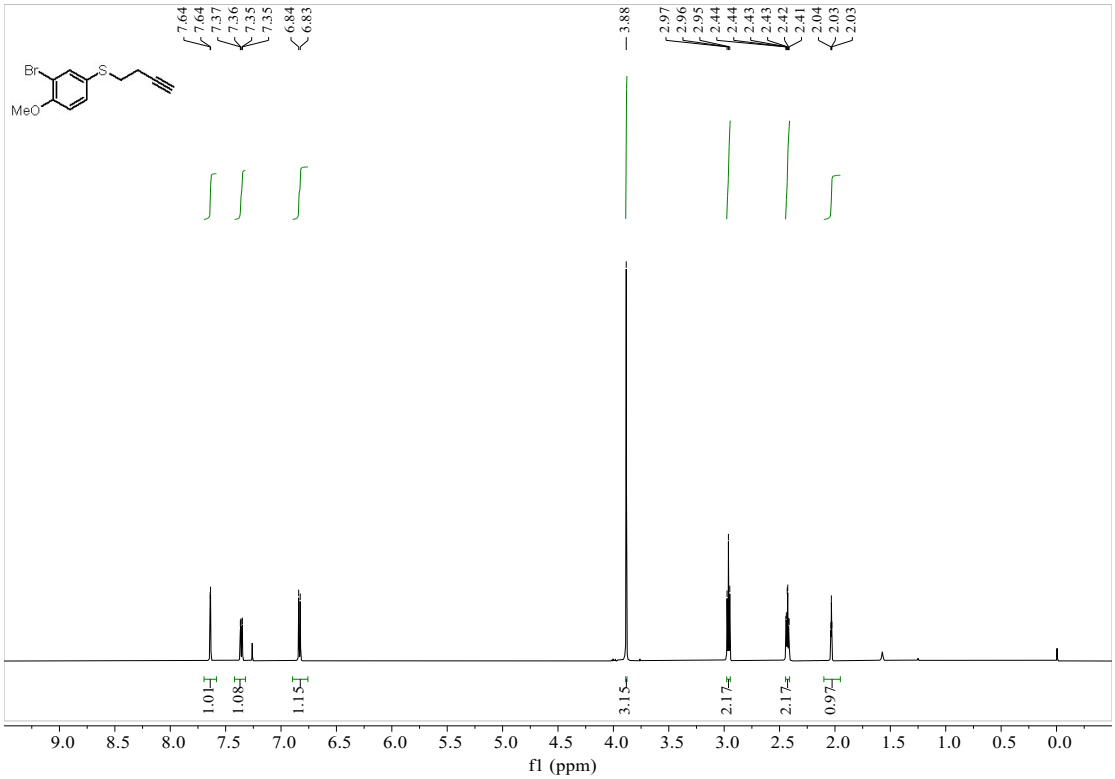
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 9



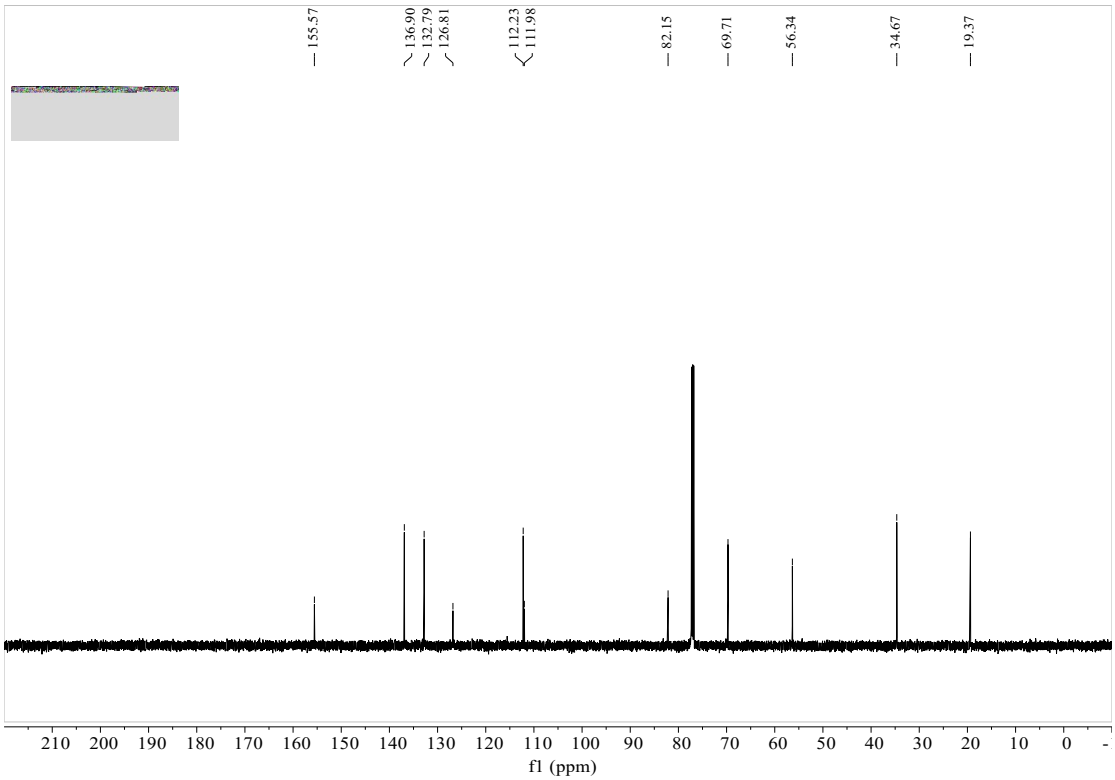
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 9



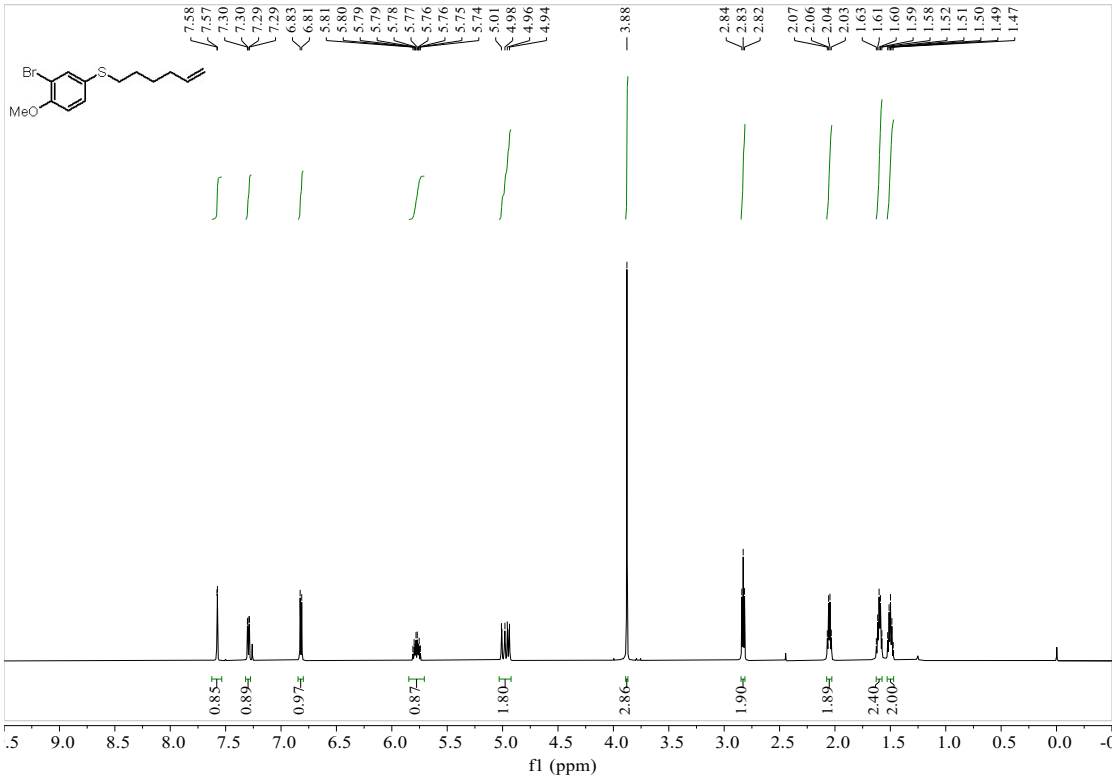
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 10



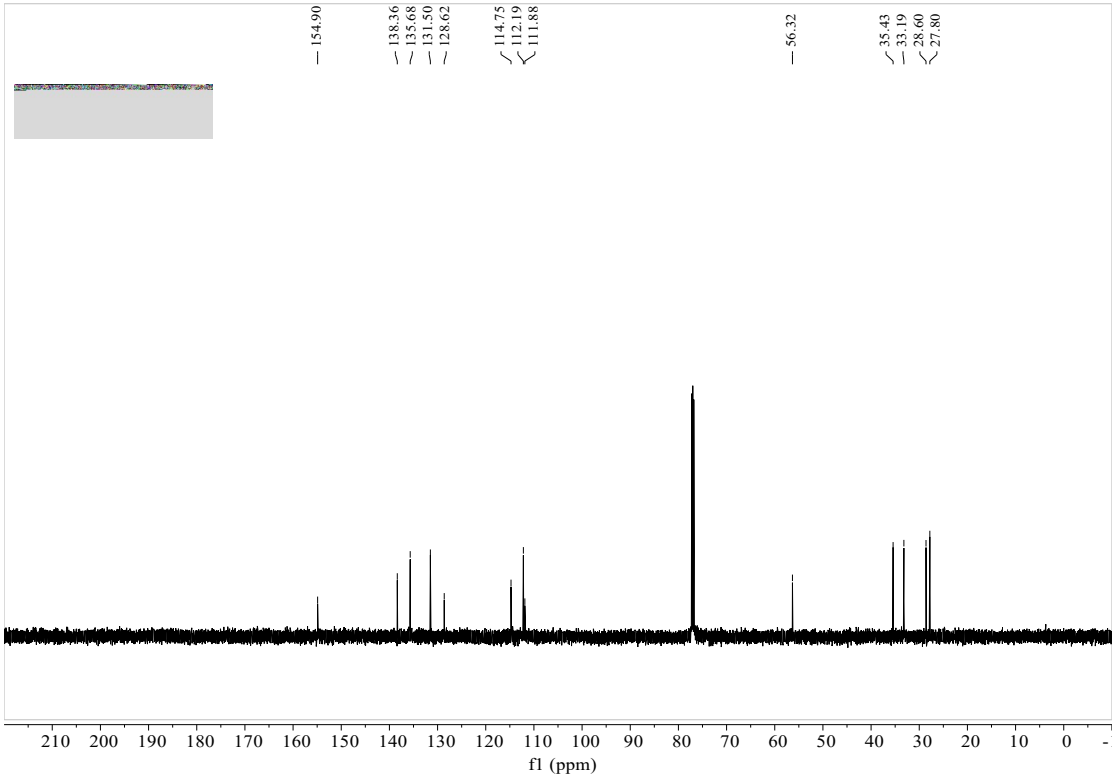
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 10



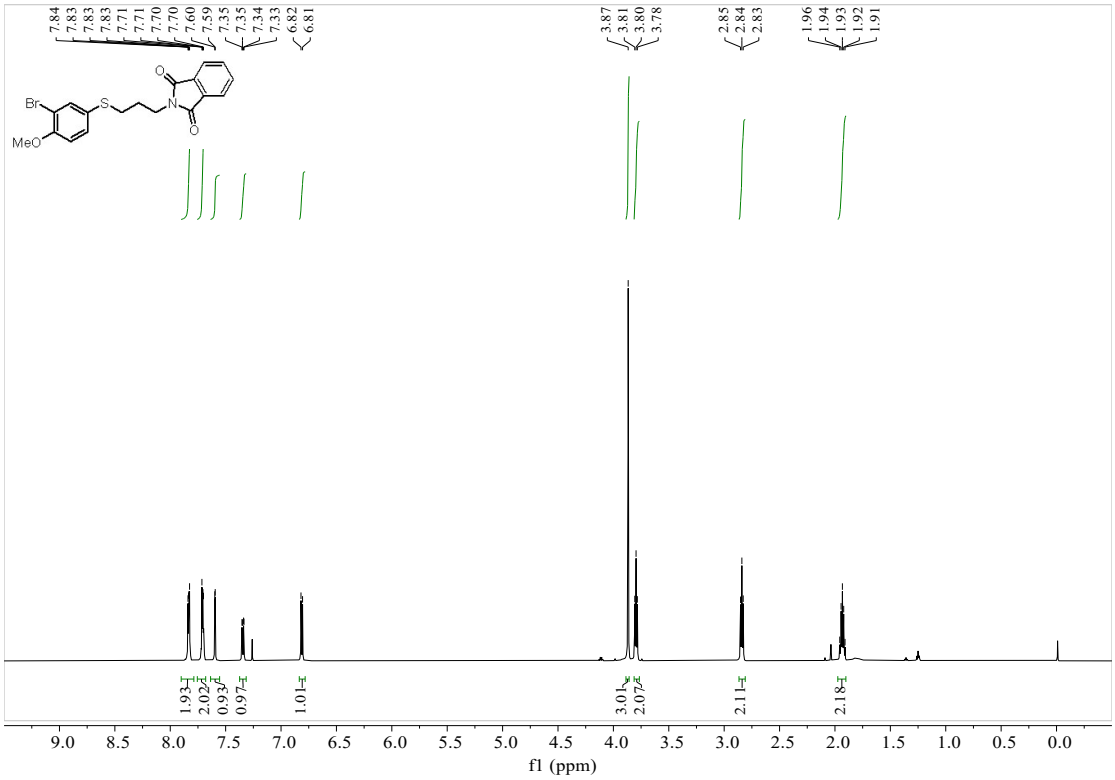
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 11



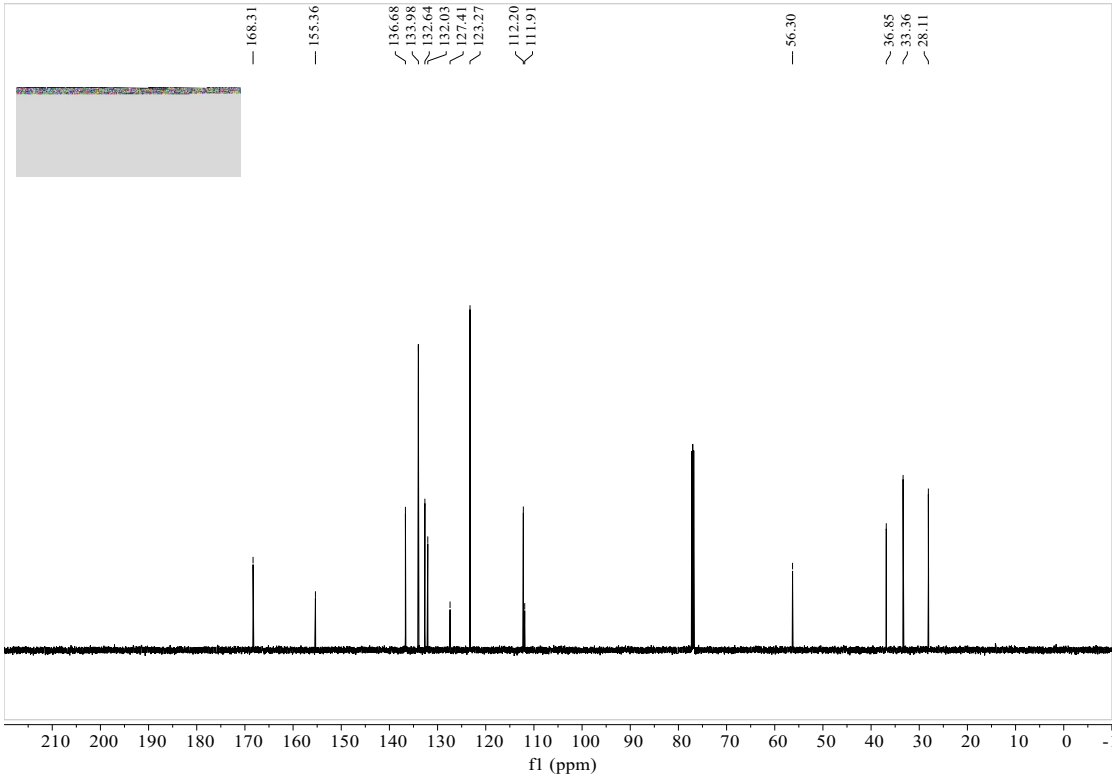
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 11



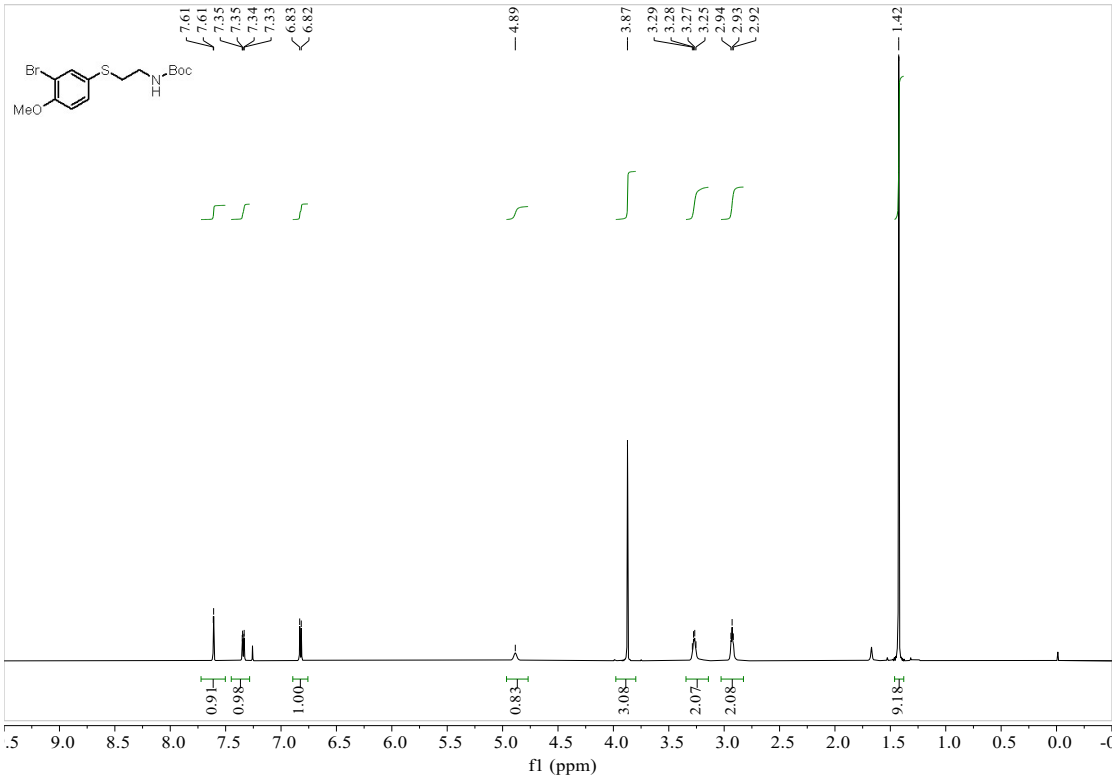
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 12



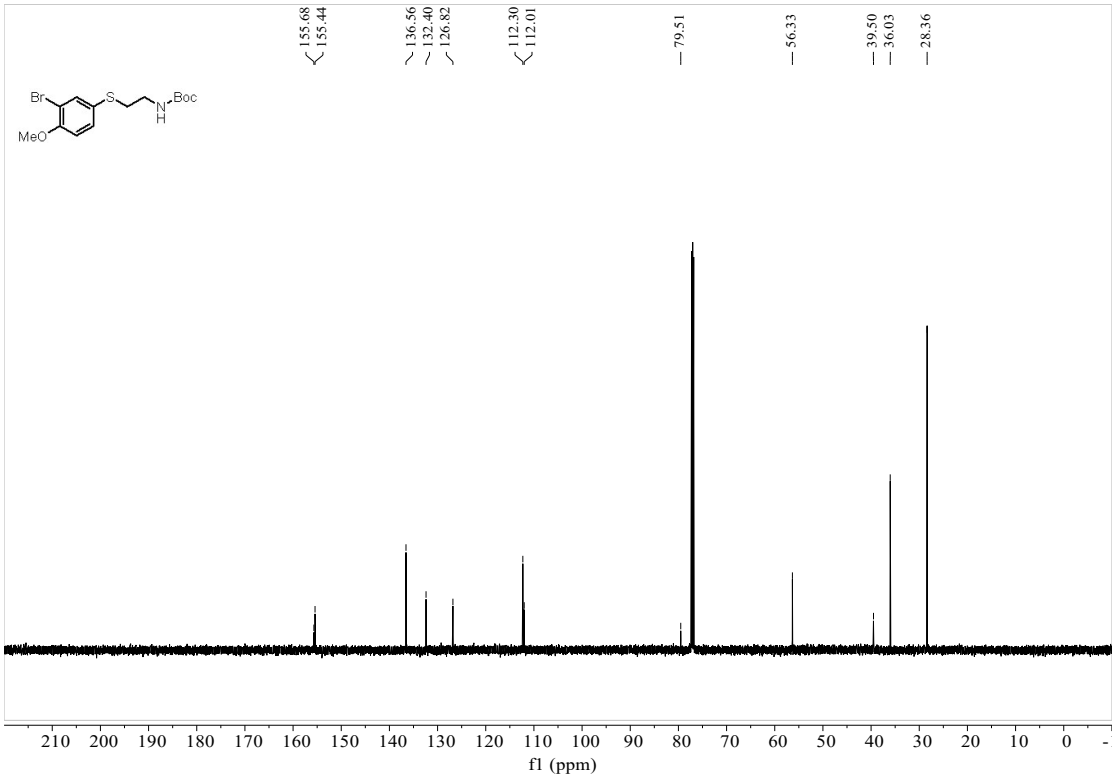
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 12



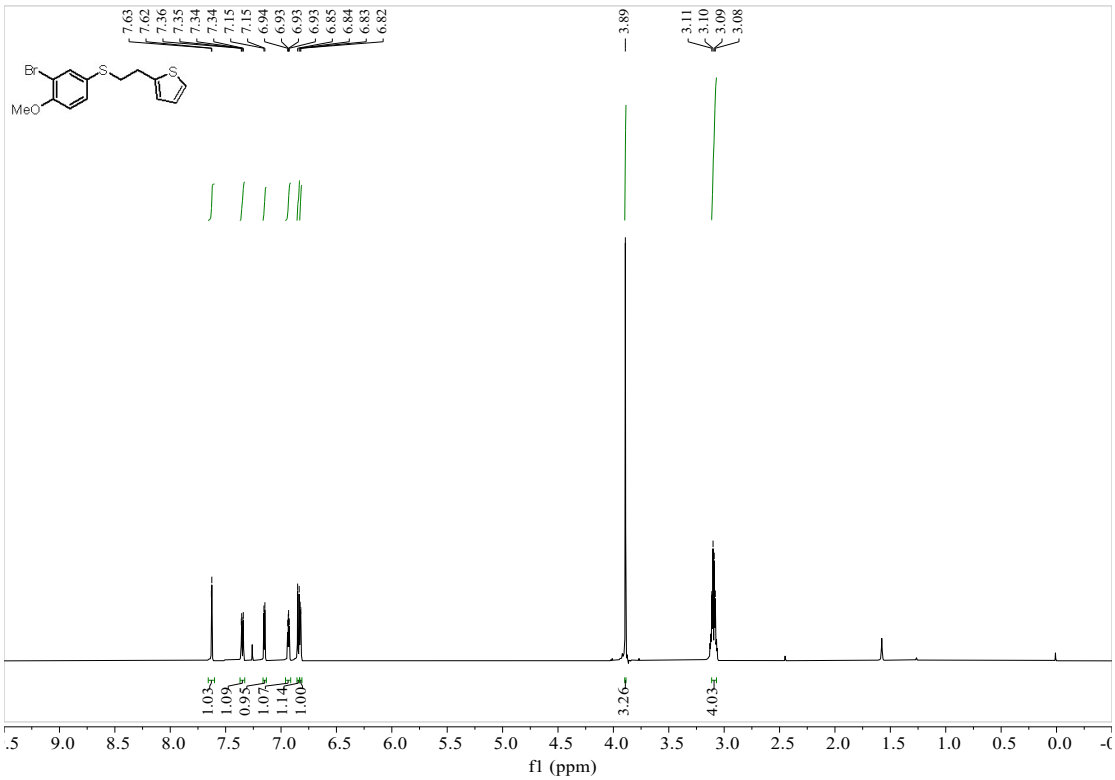
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 13



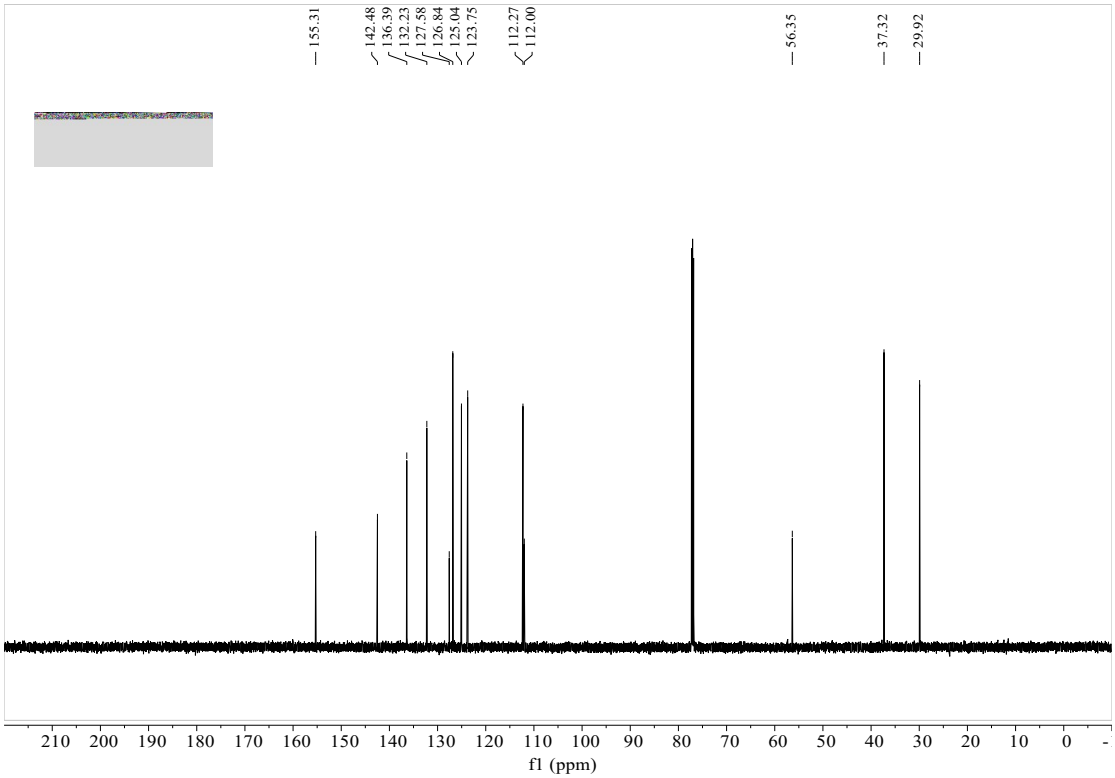
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 13



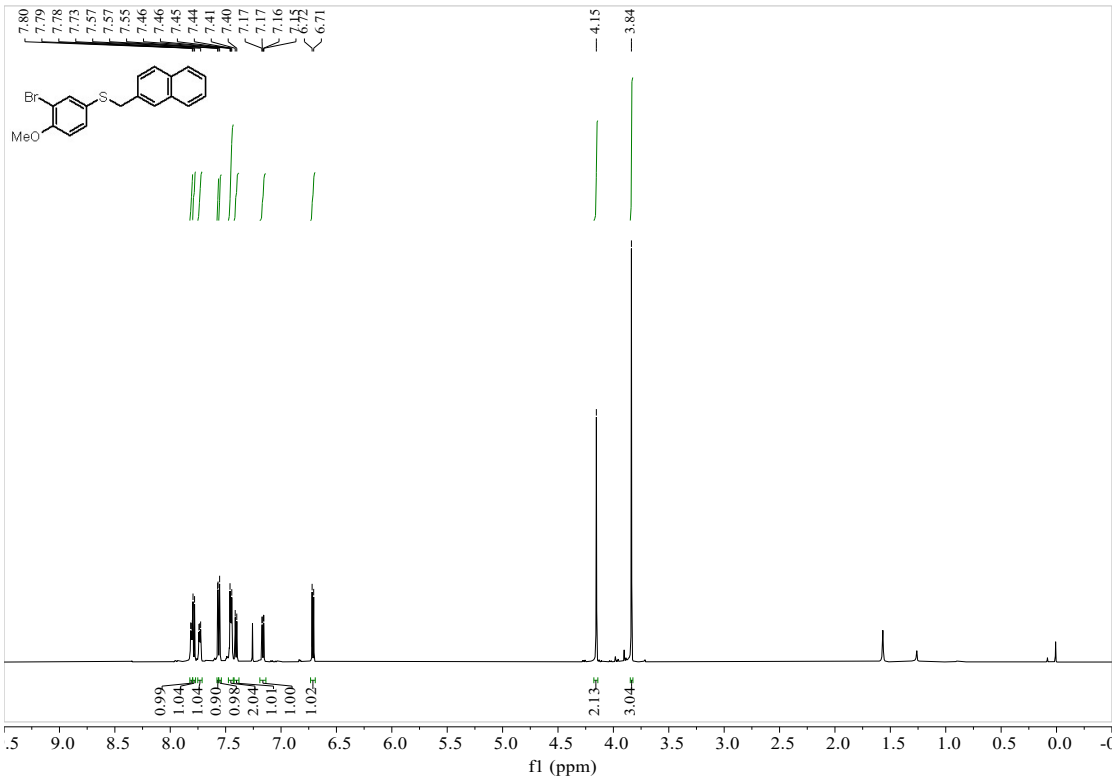
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 14



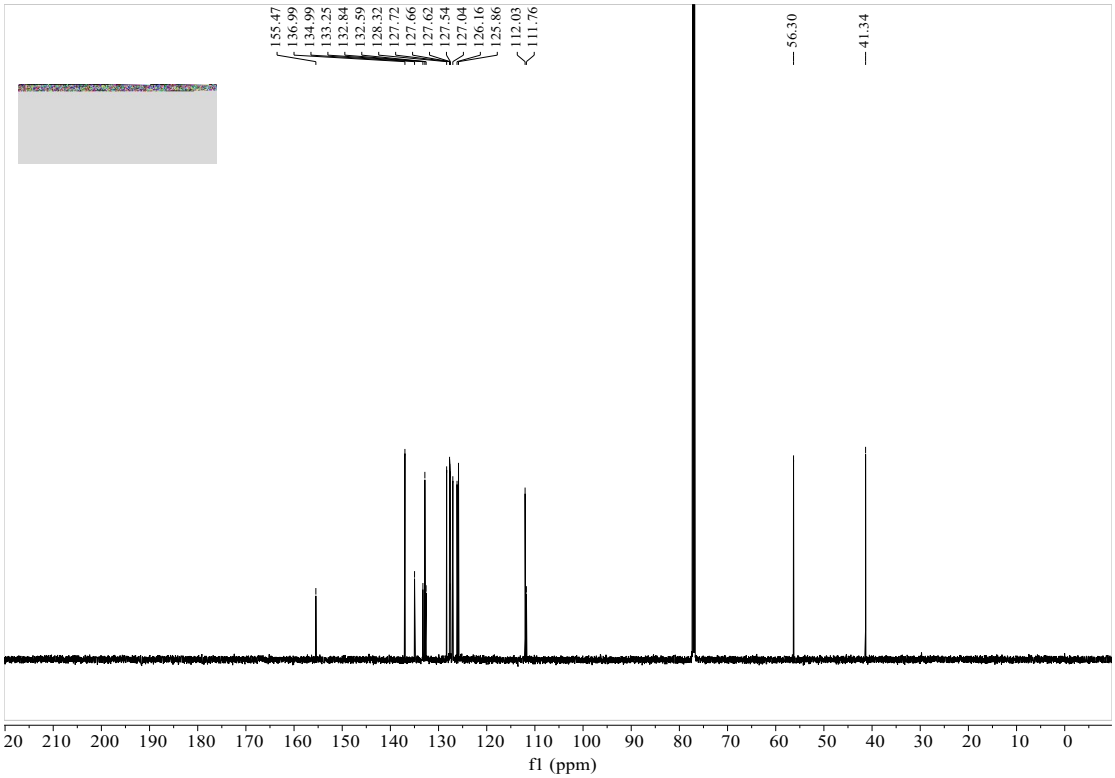
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 14



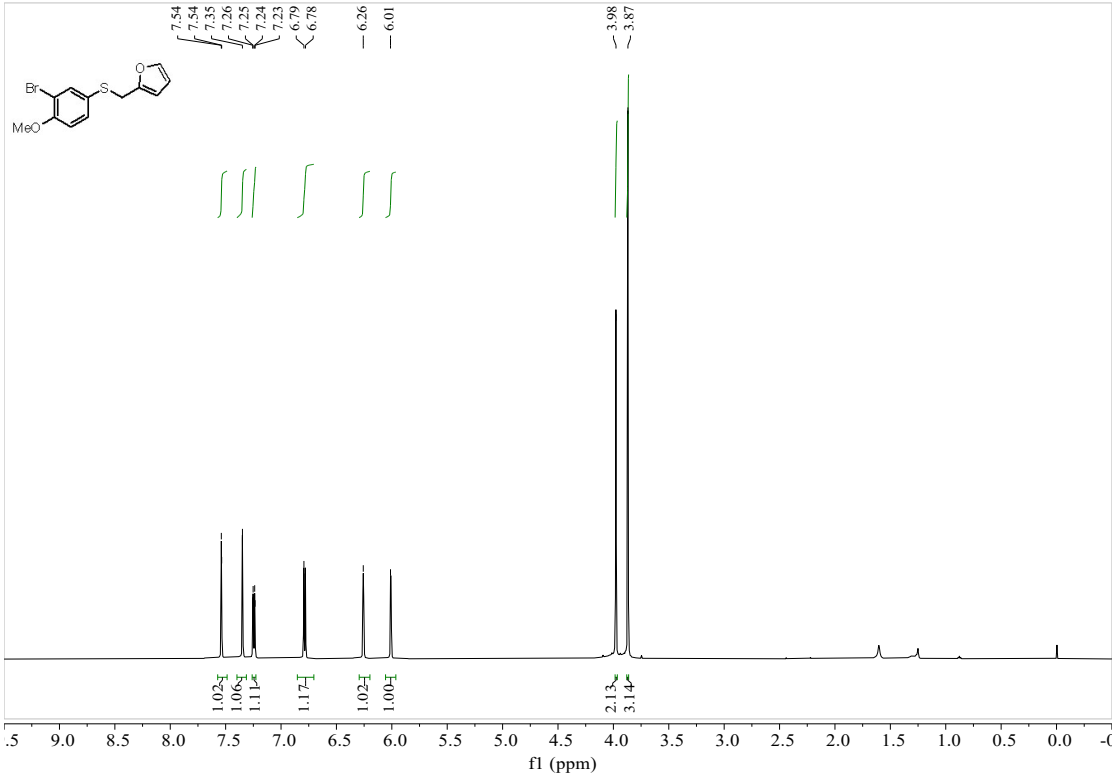
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 15



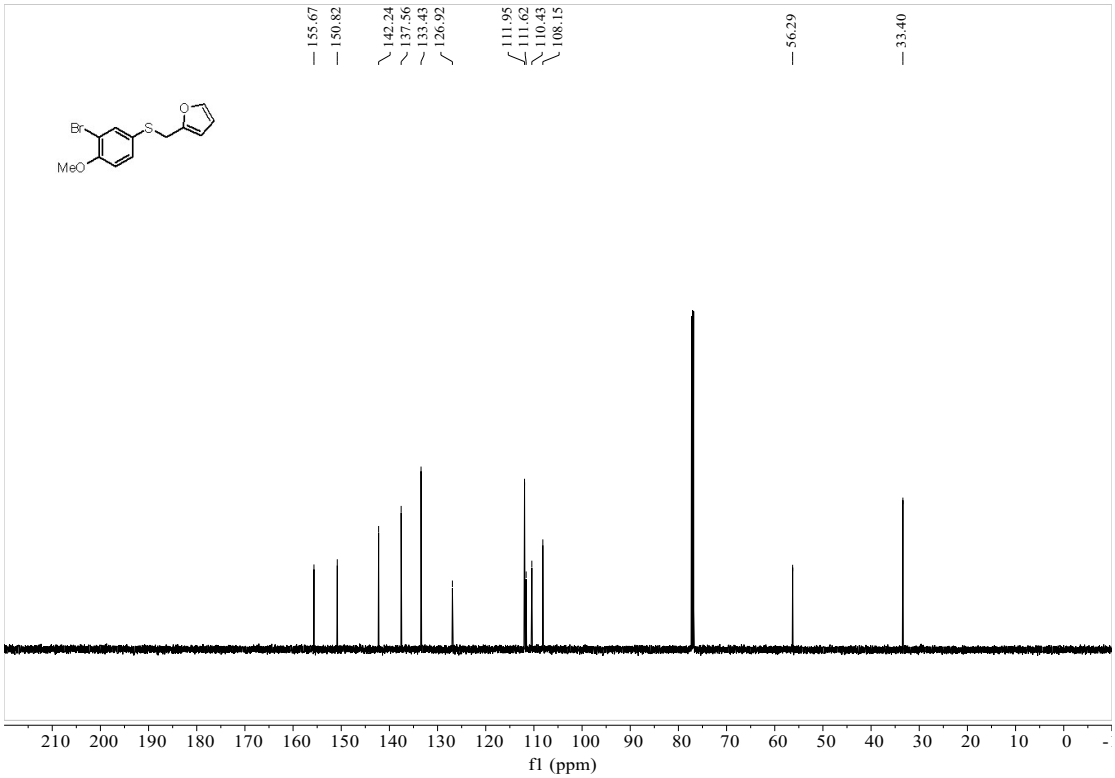
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 15



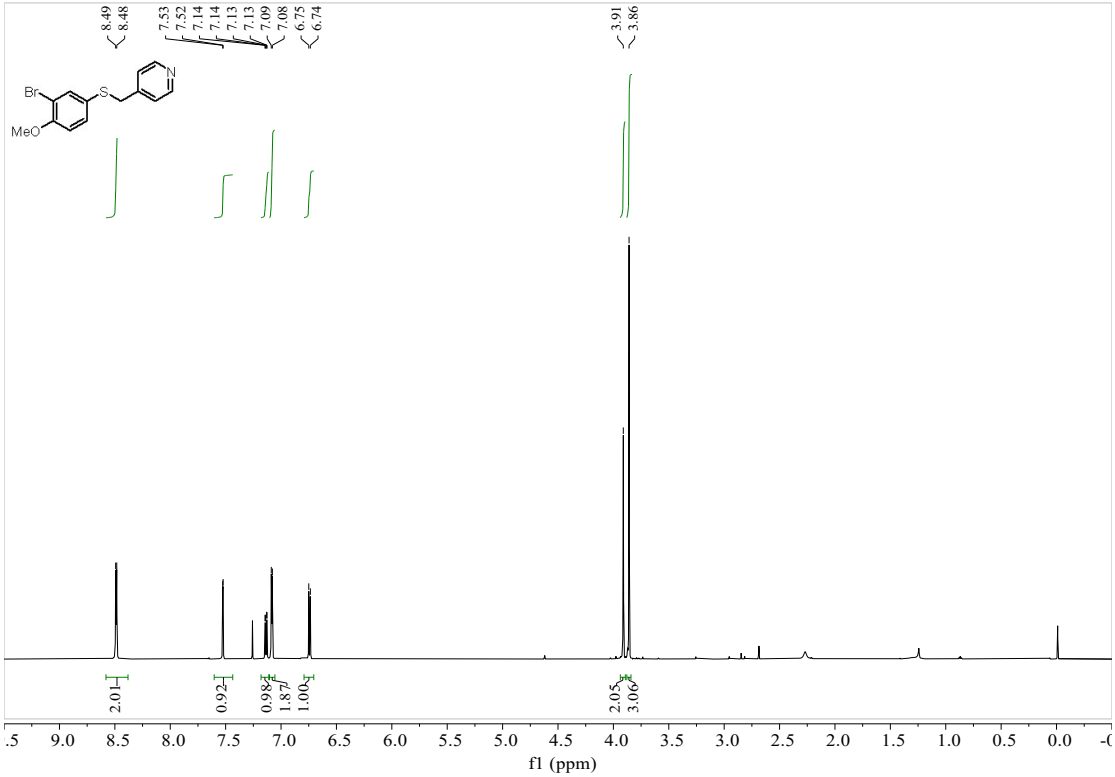
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 16



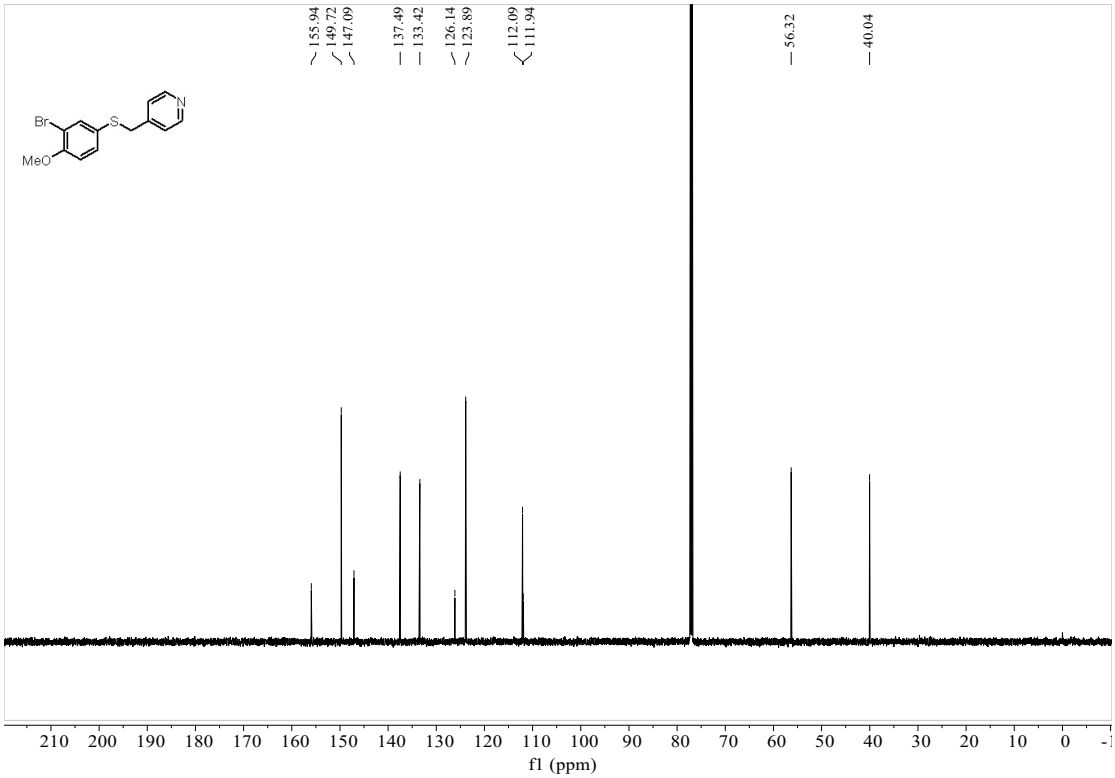
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 16



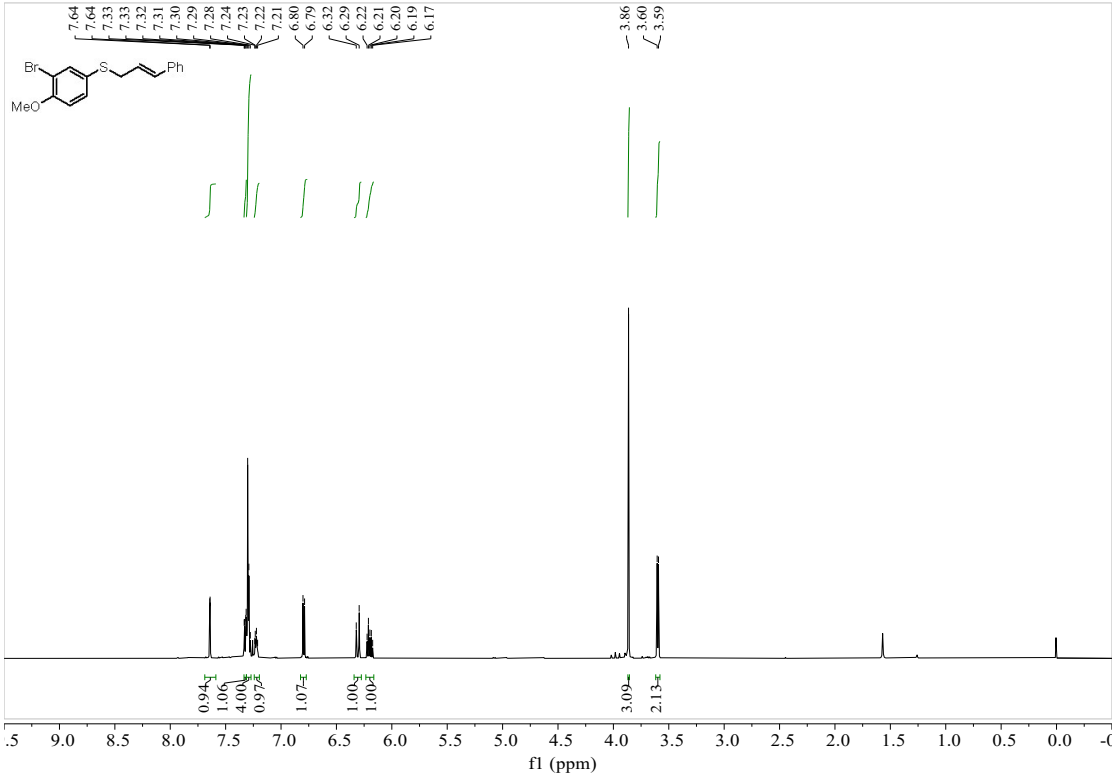
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 17



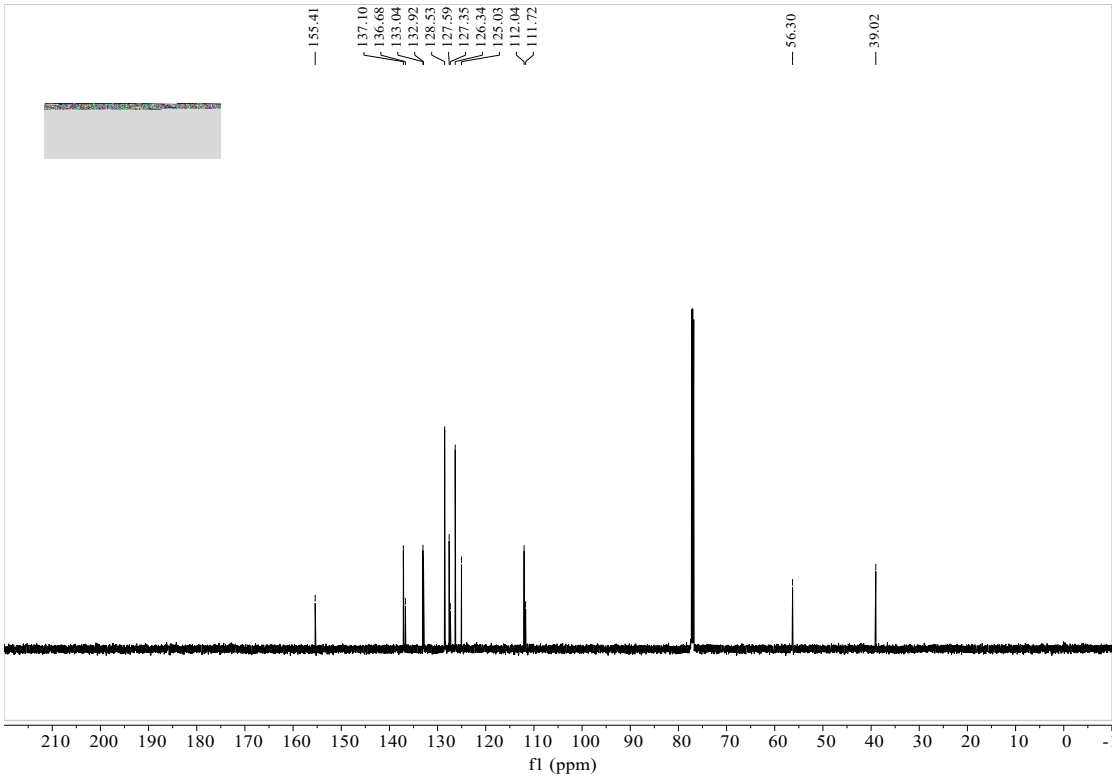
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 17



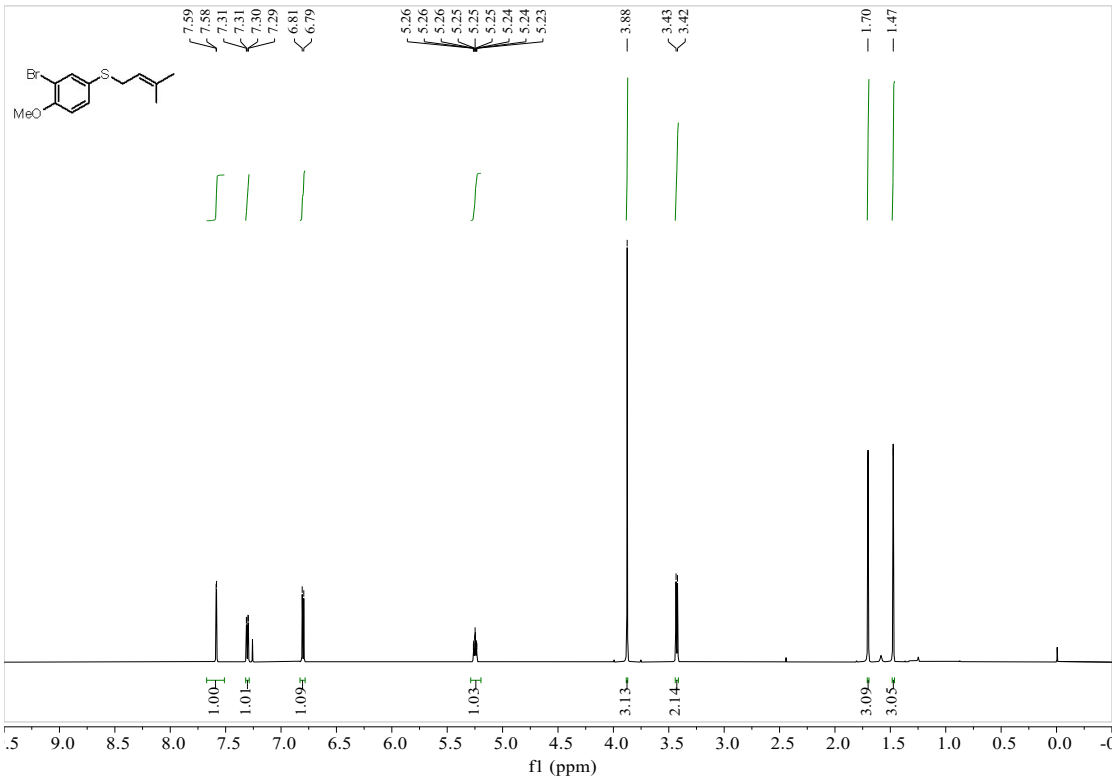
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 18



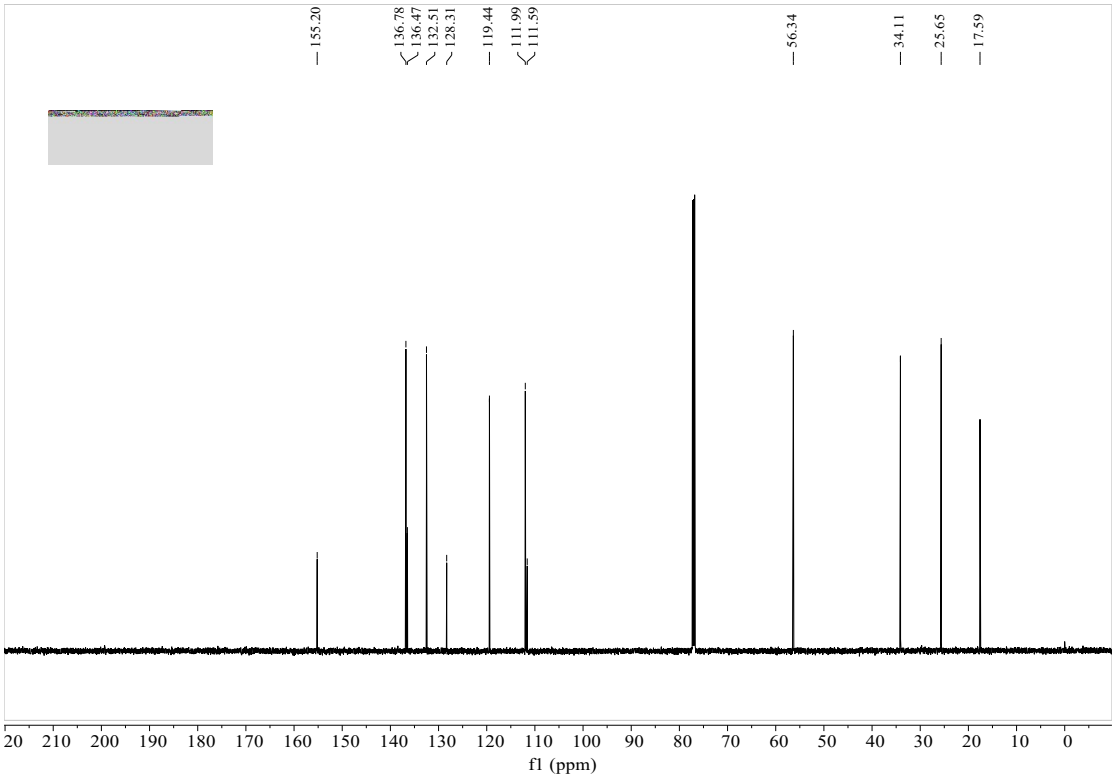
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 18



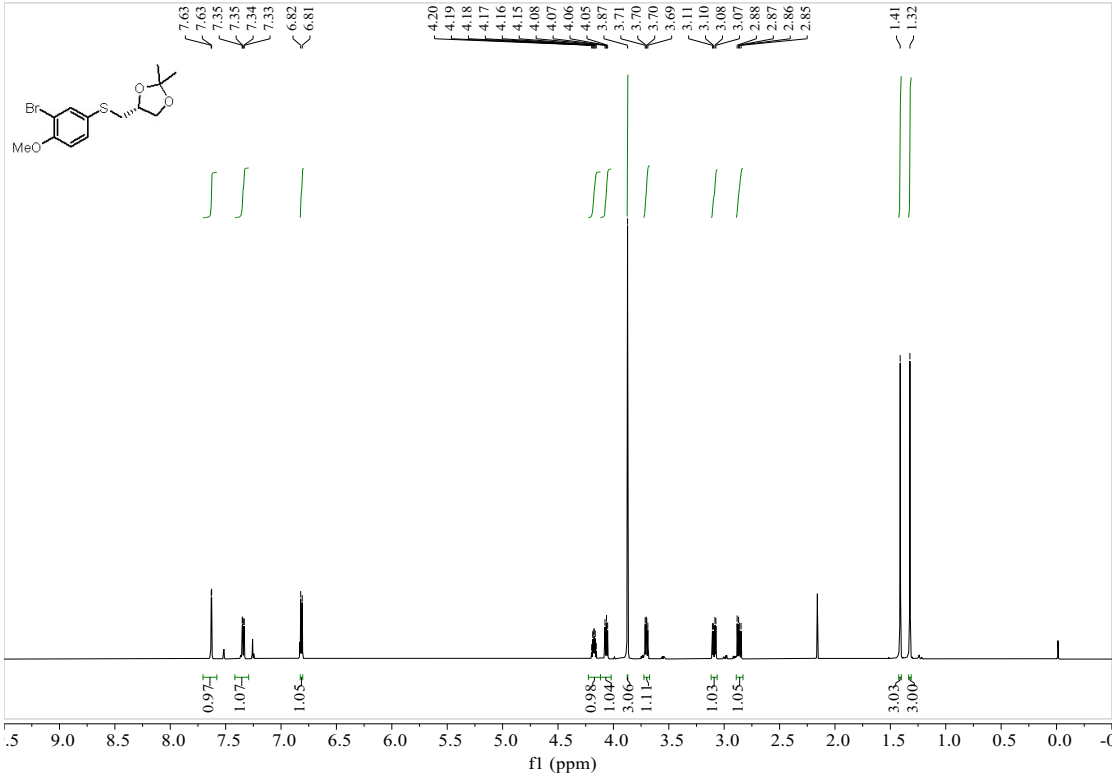
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 19



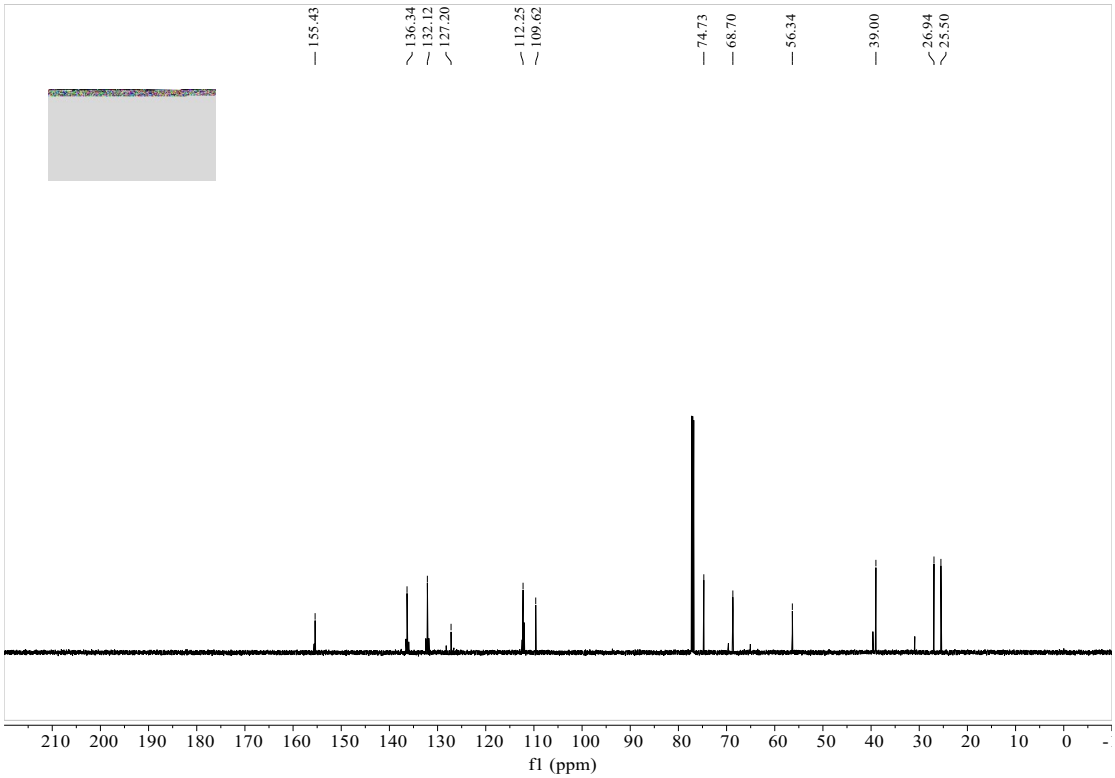
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 19



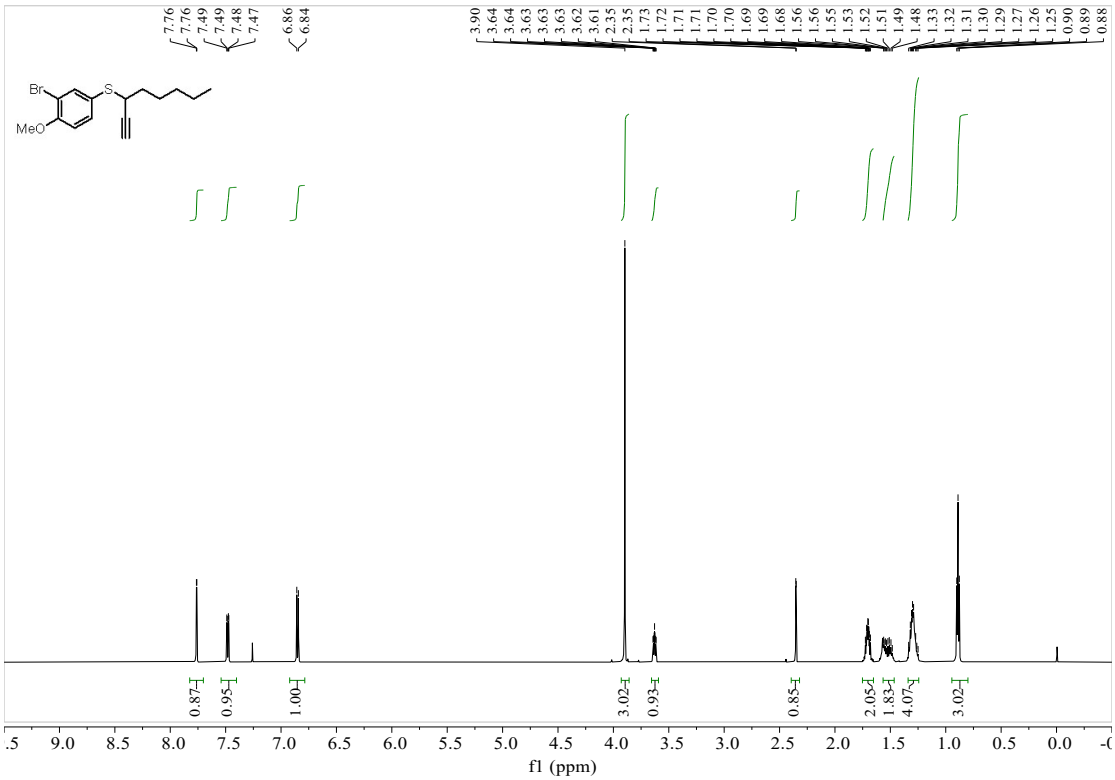
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 20



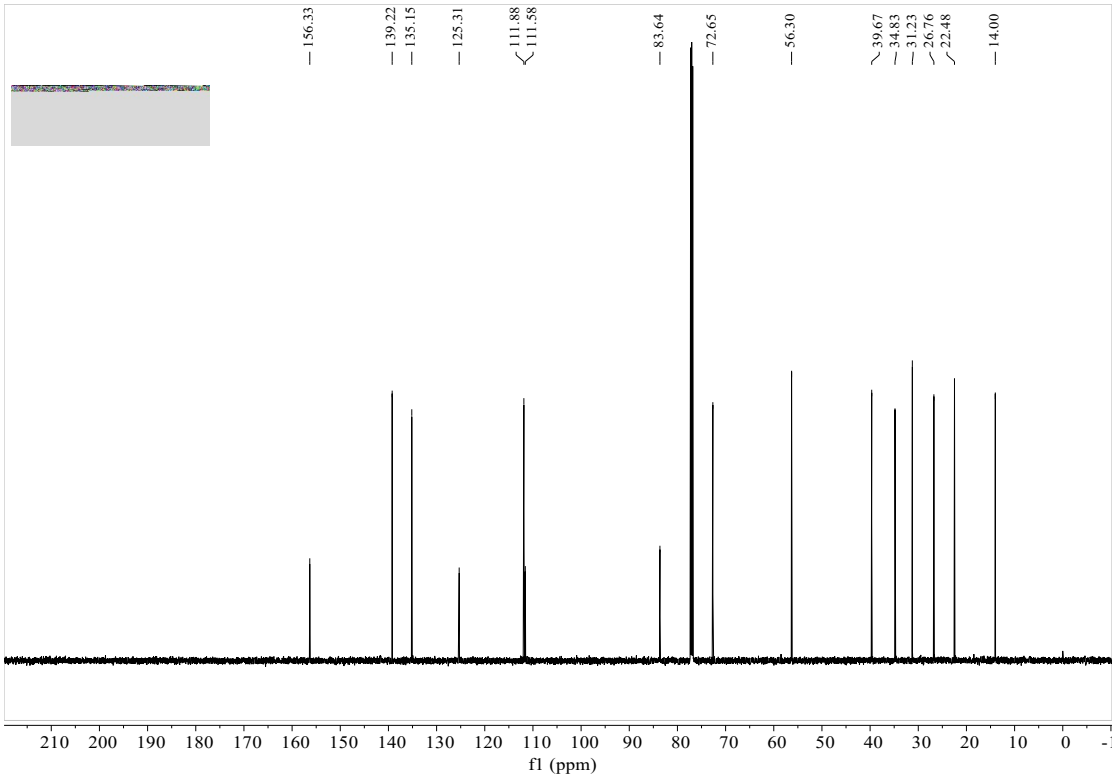
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 20



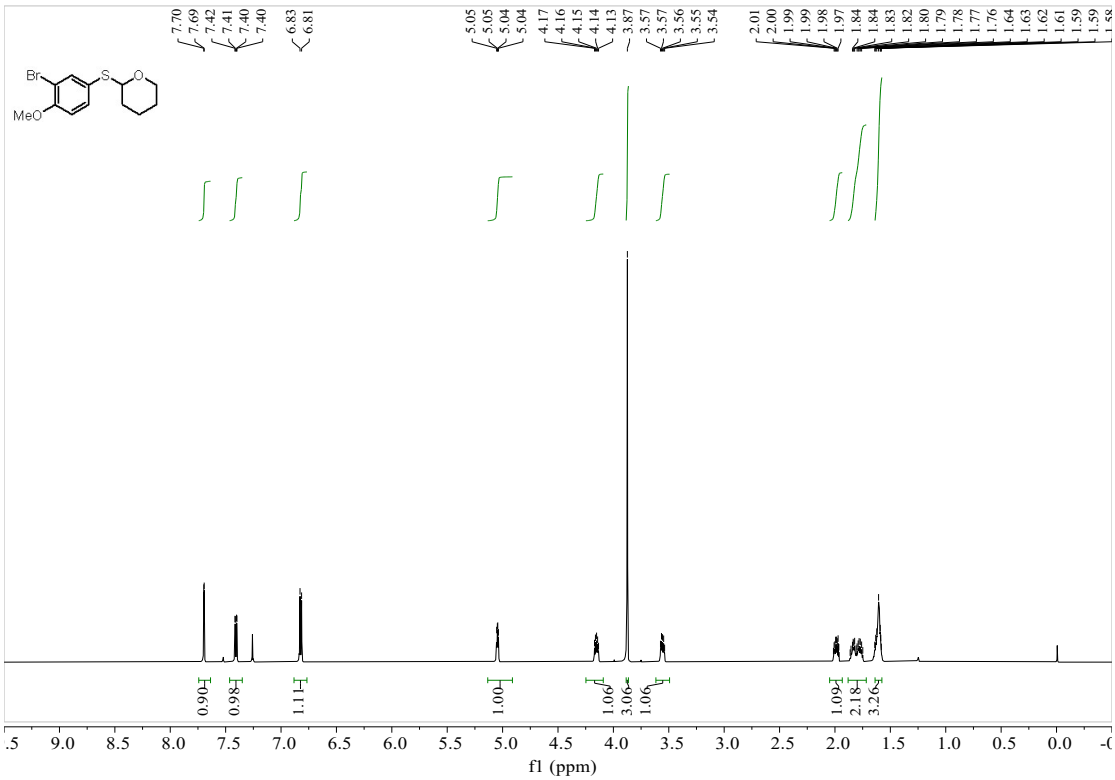
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 21



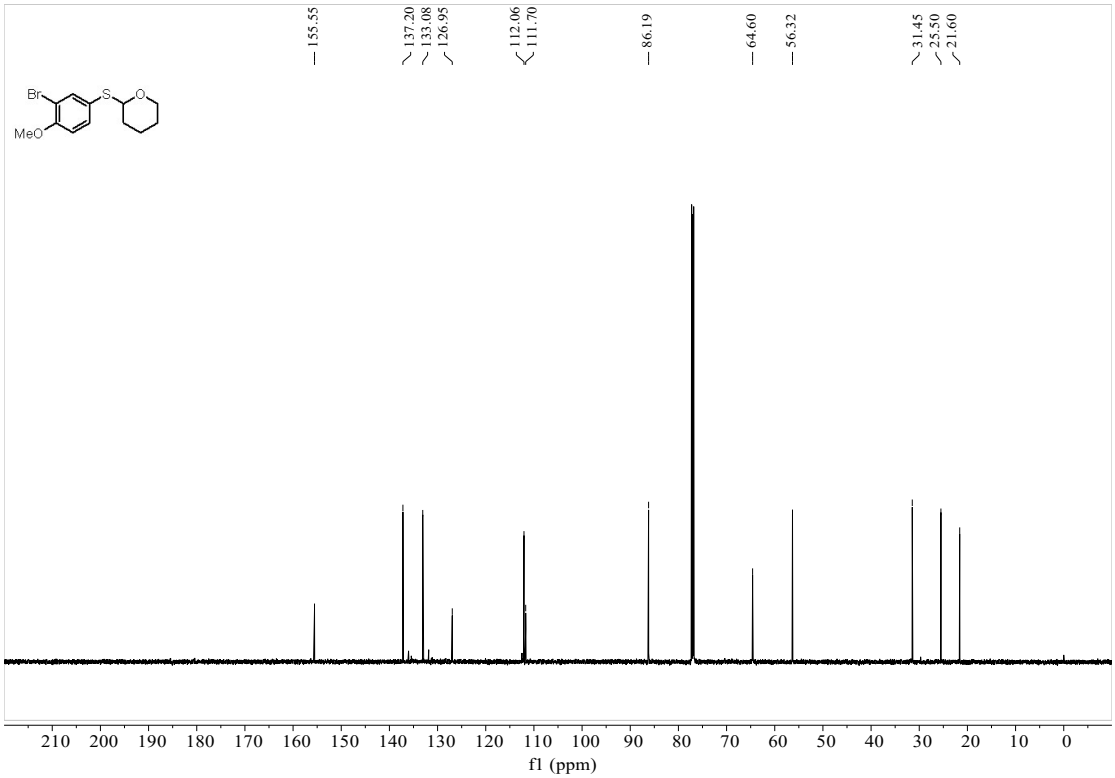
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 21



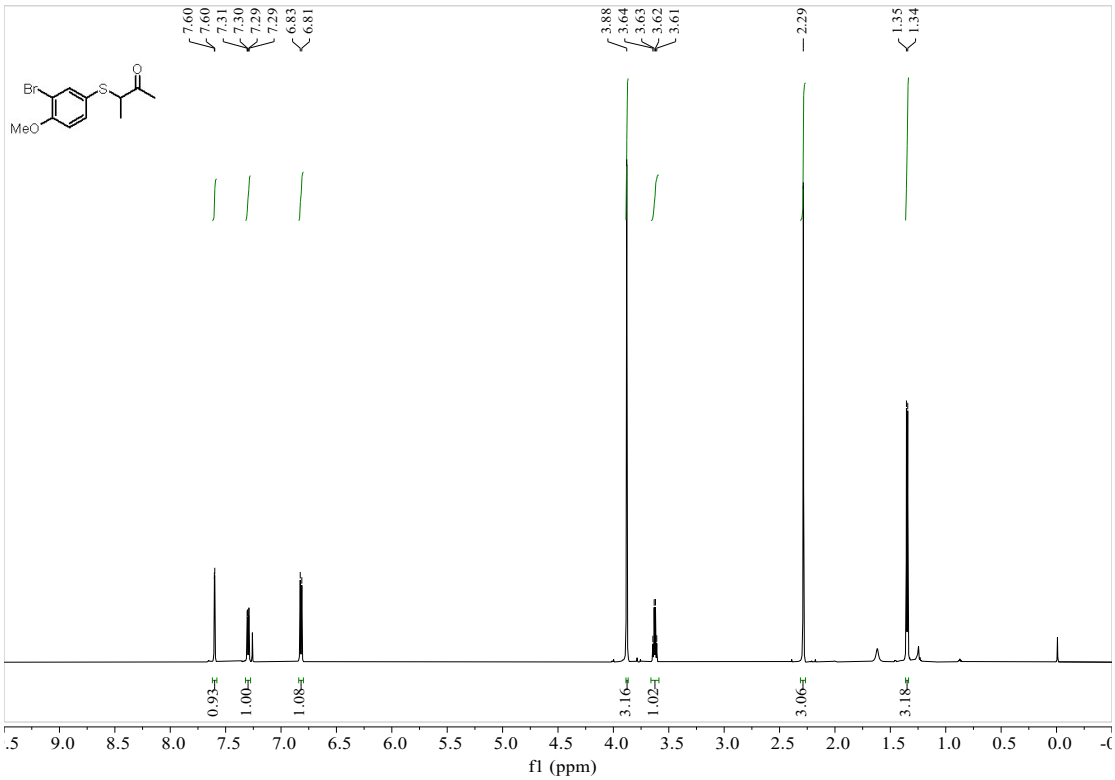
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 22



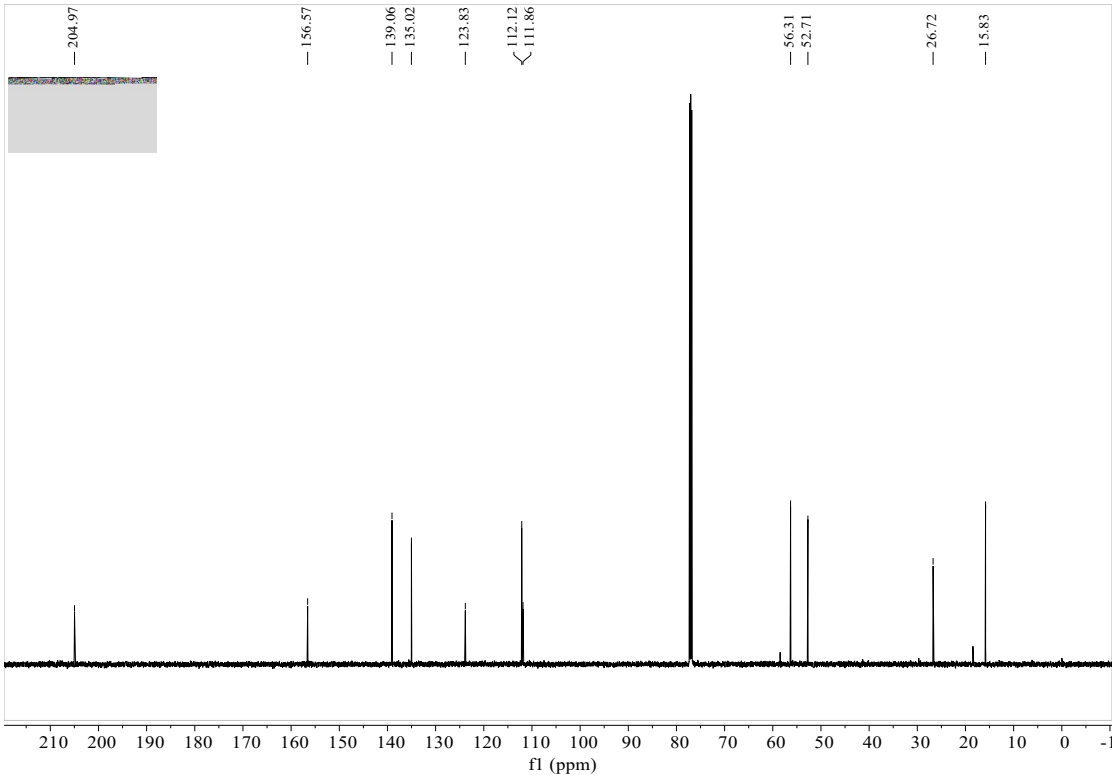
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 22



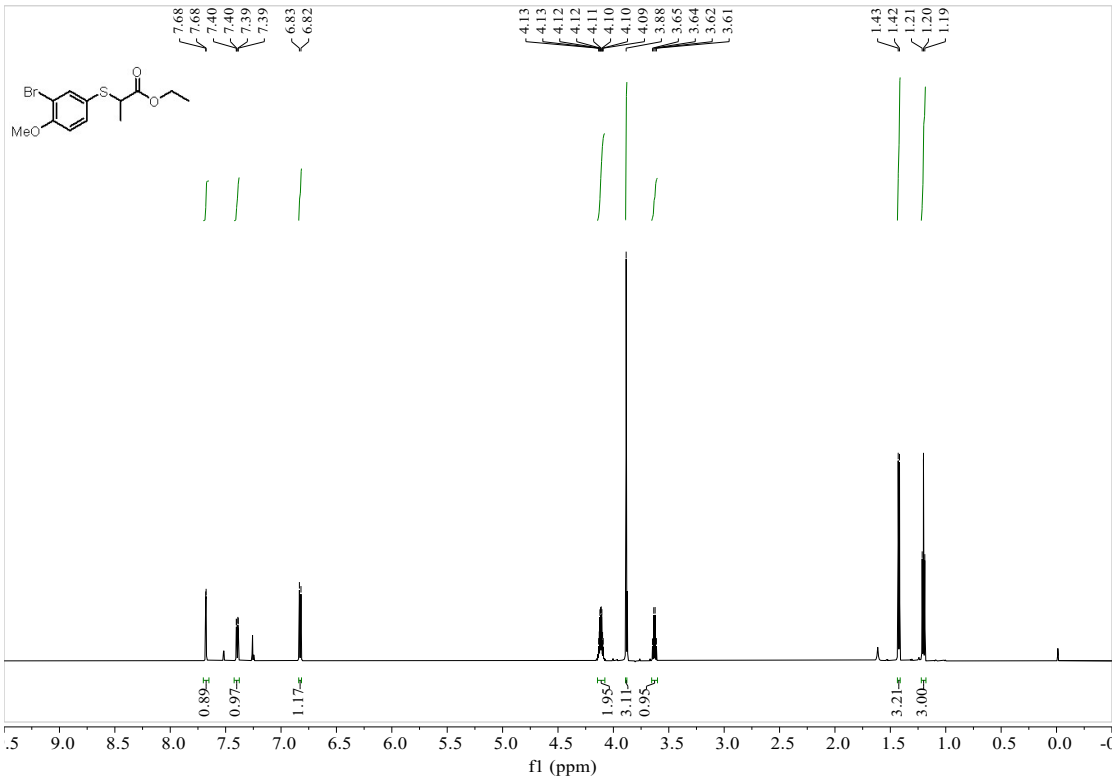
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 23



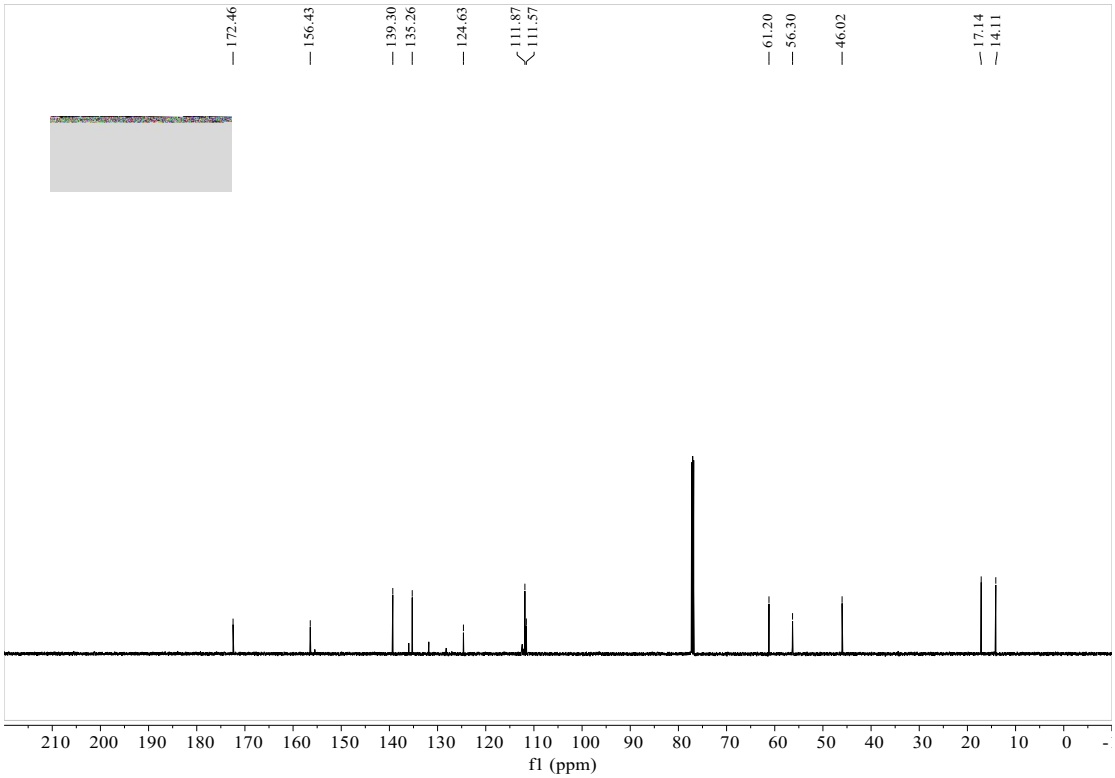
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 23



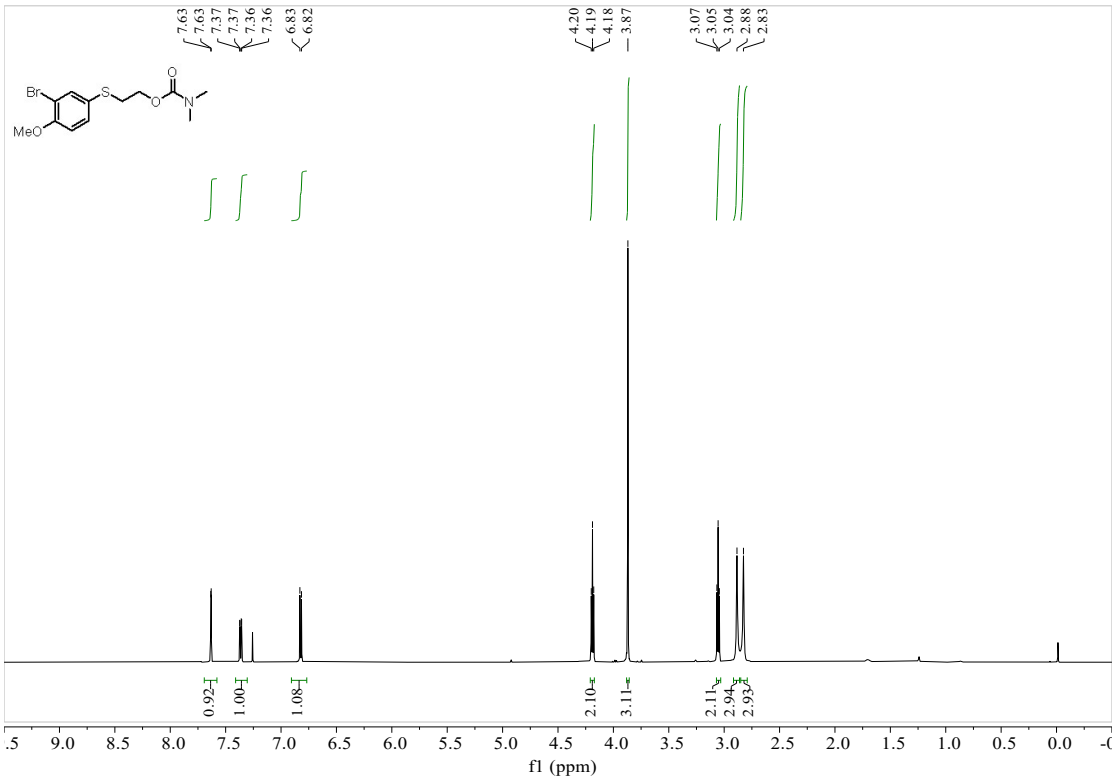
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 24



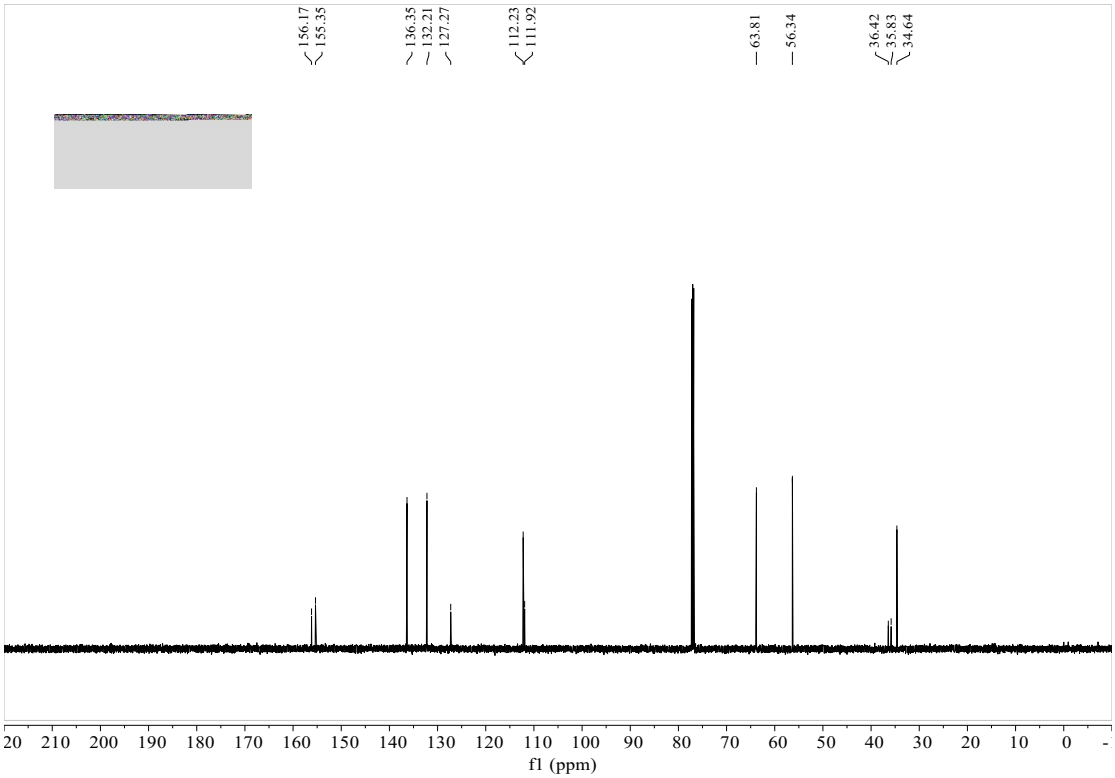
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 24



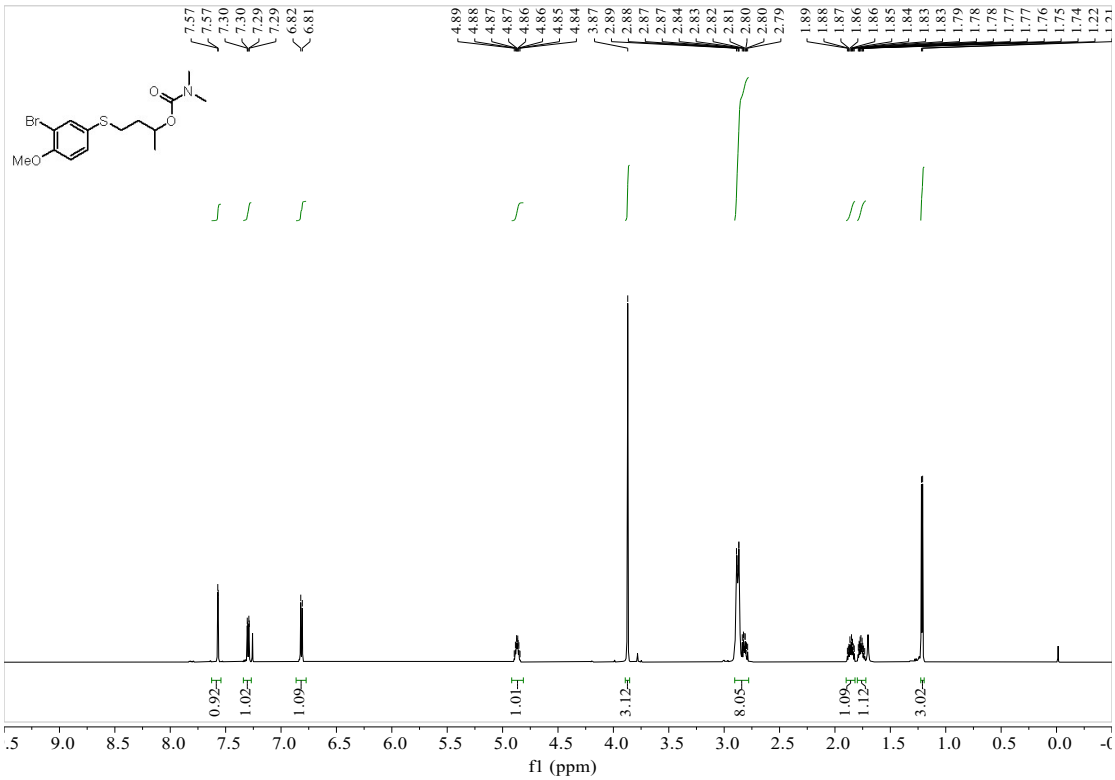
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 25



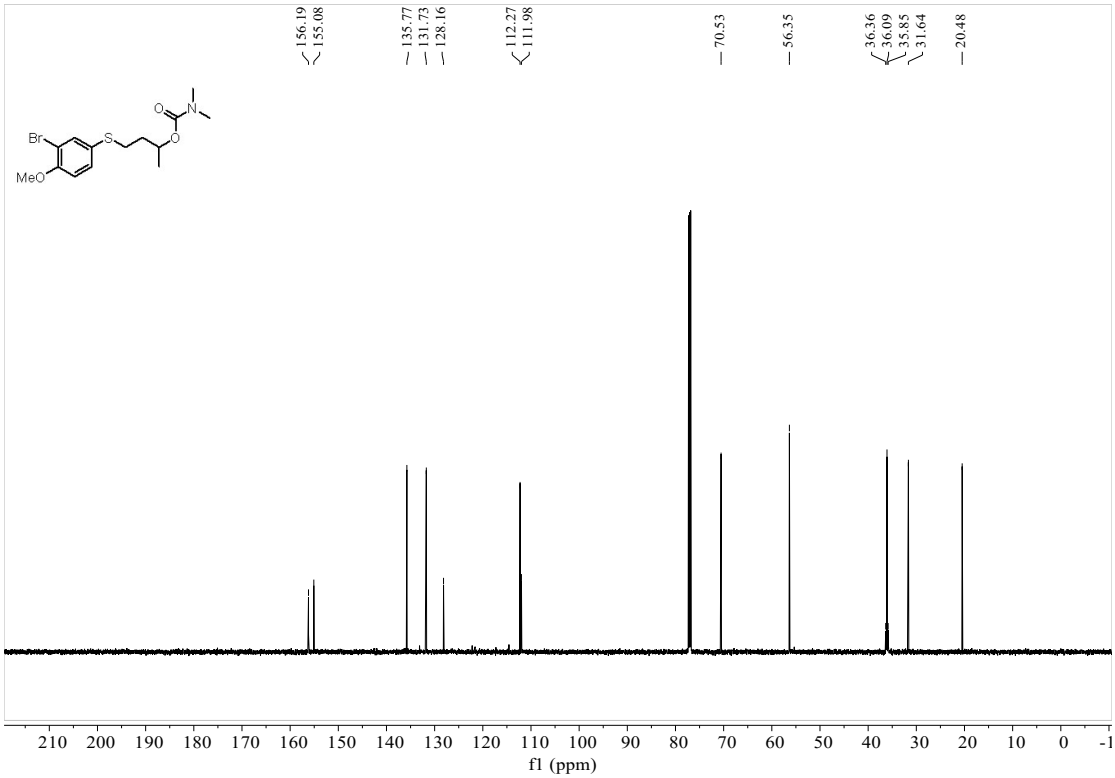
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 25



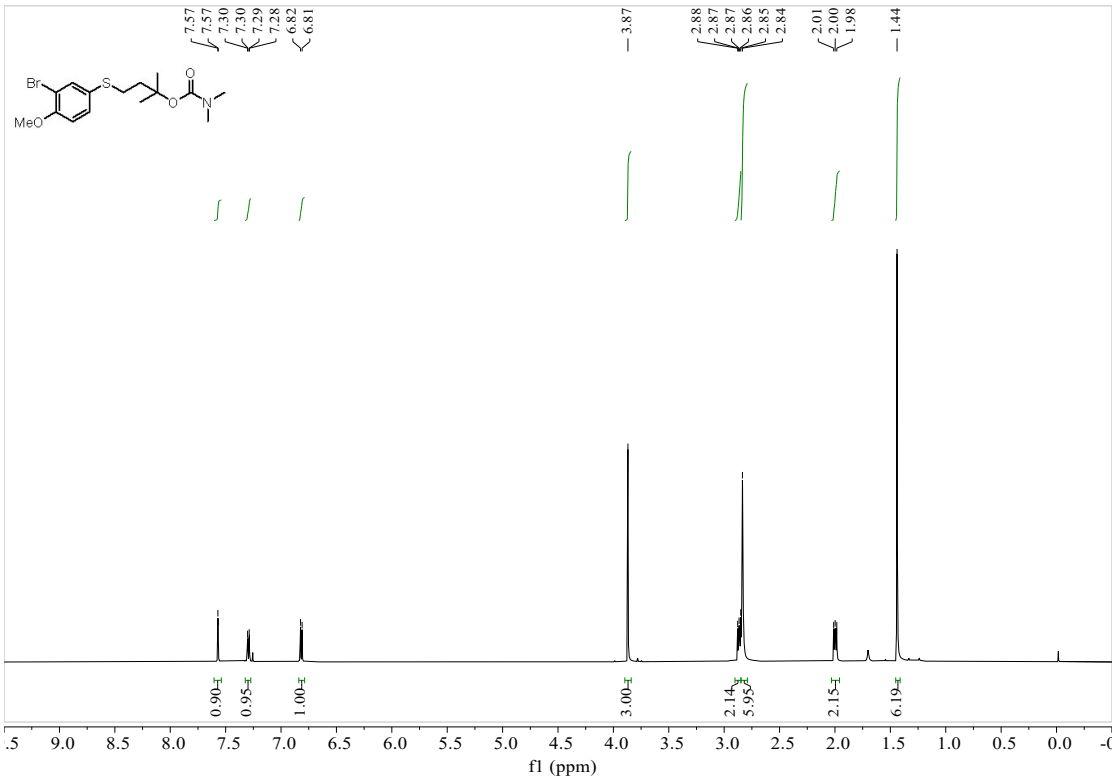
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 26



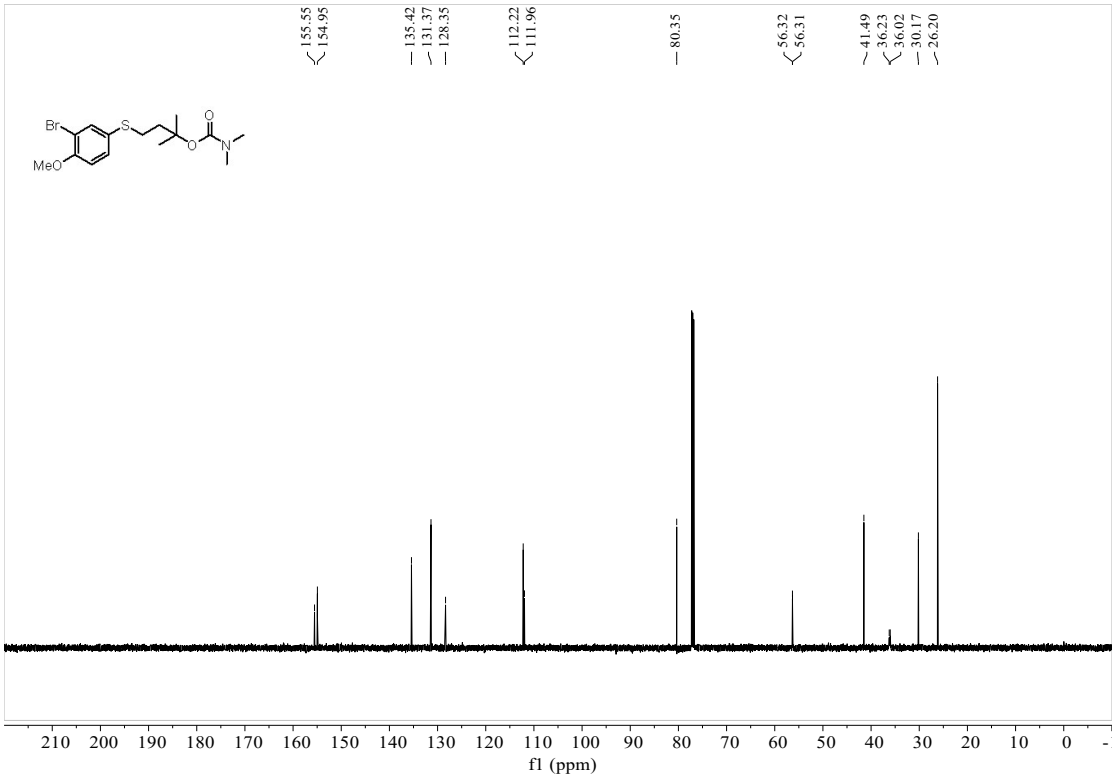
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 26



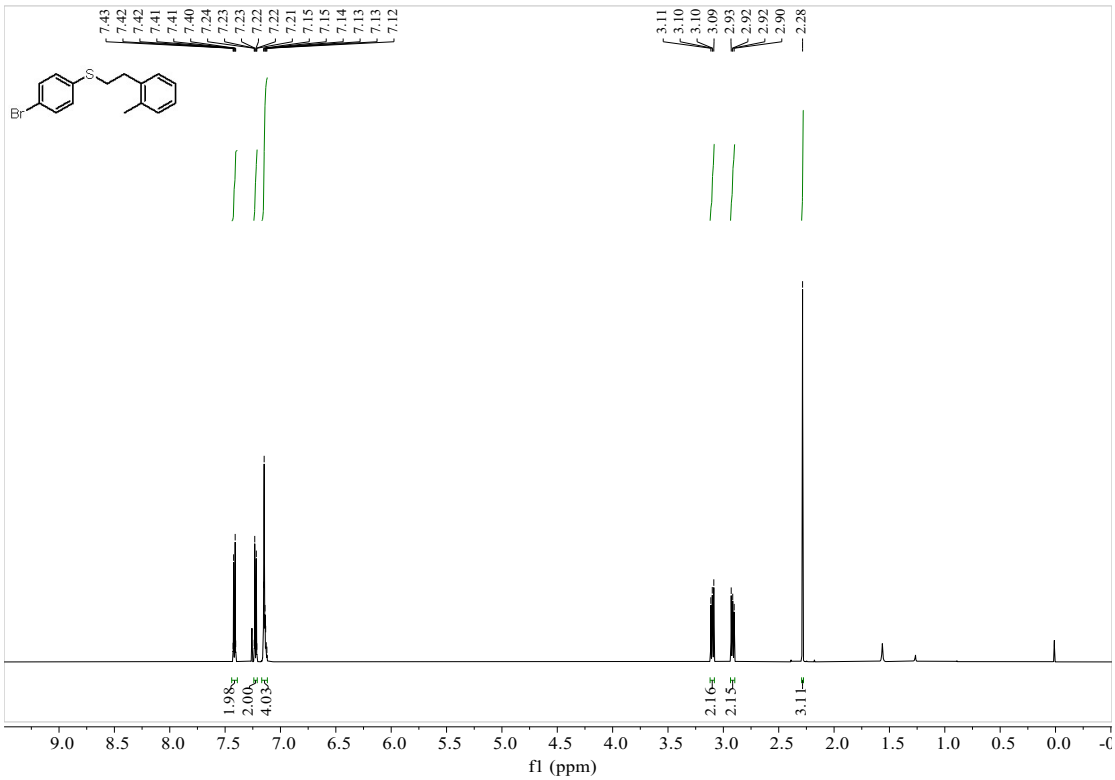
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 27



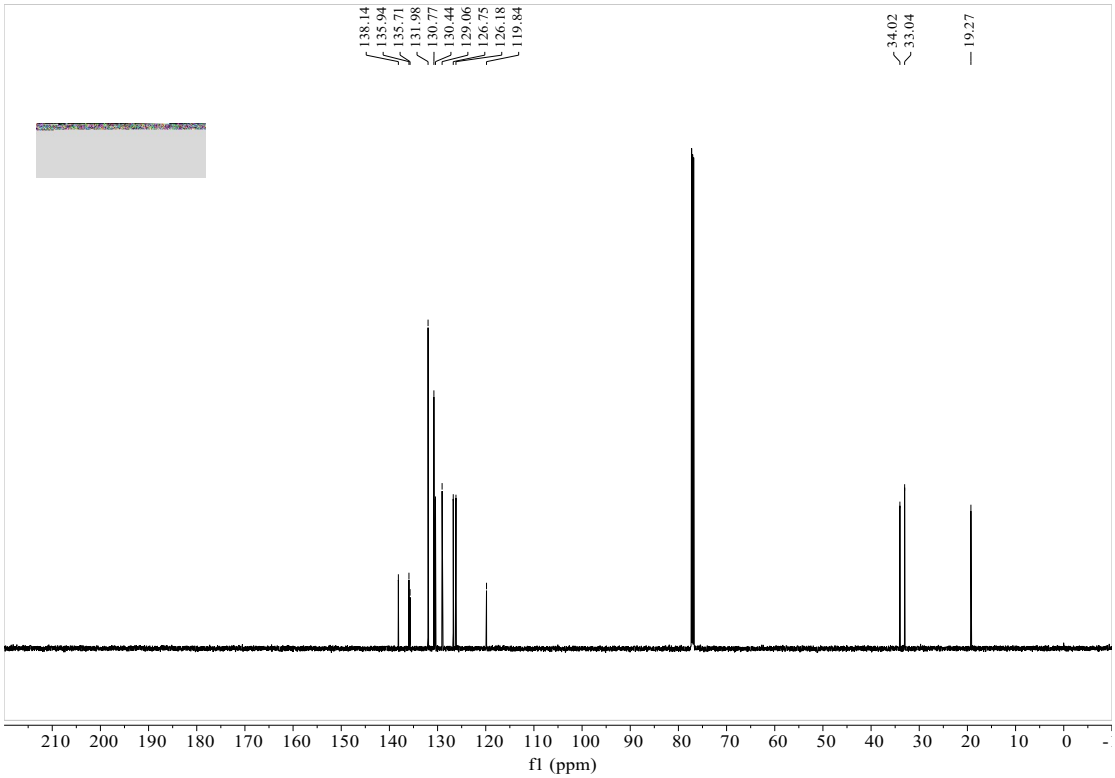
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 27



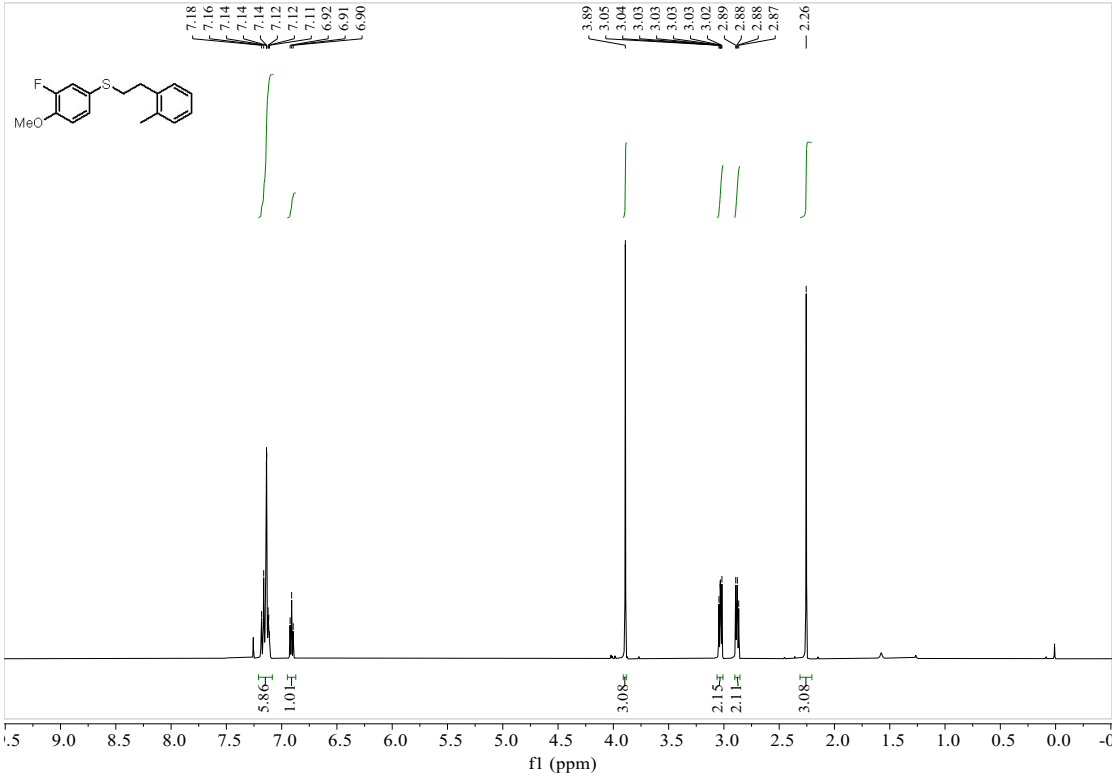
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 28



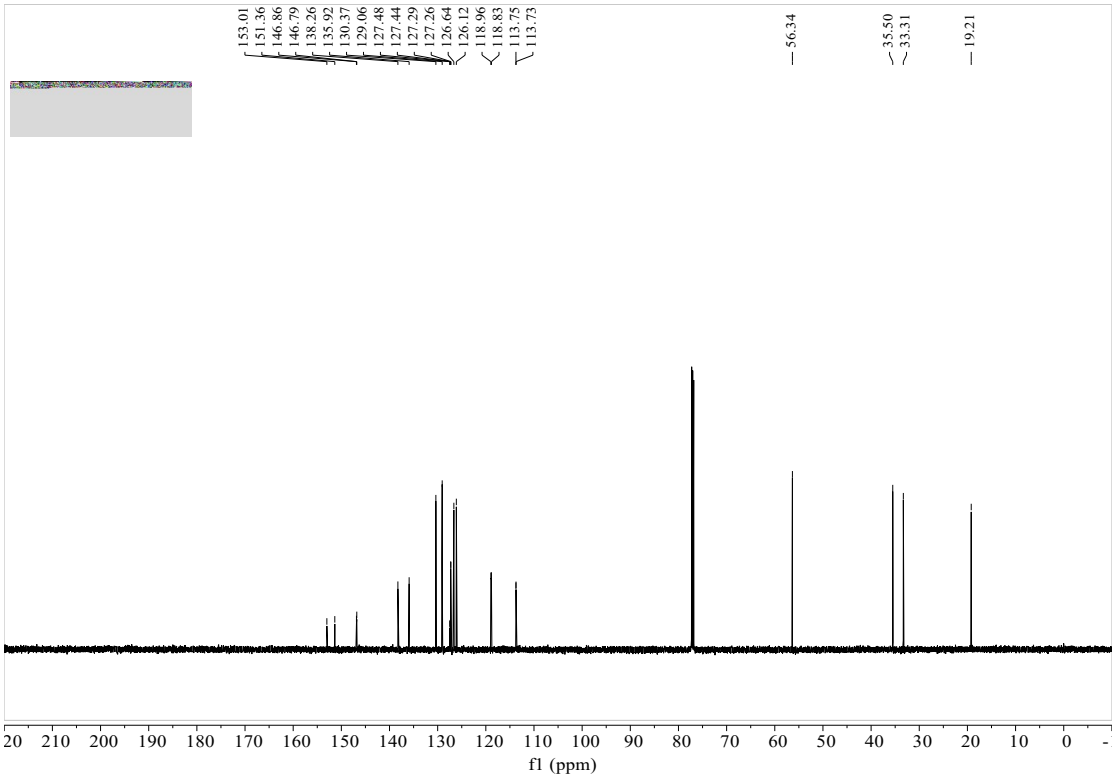
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 28



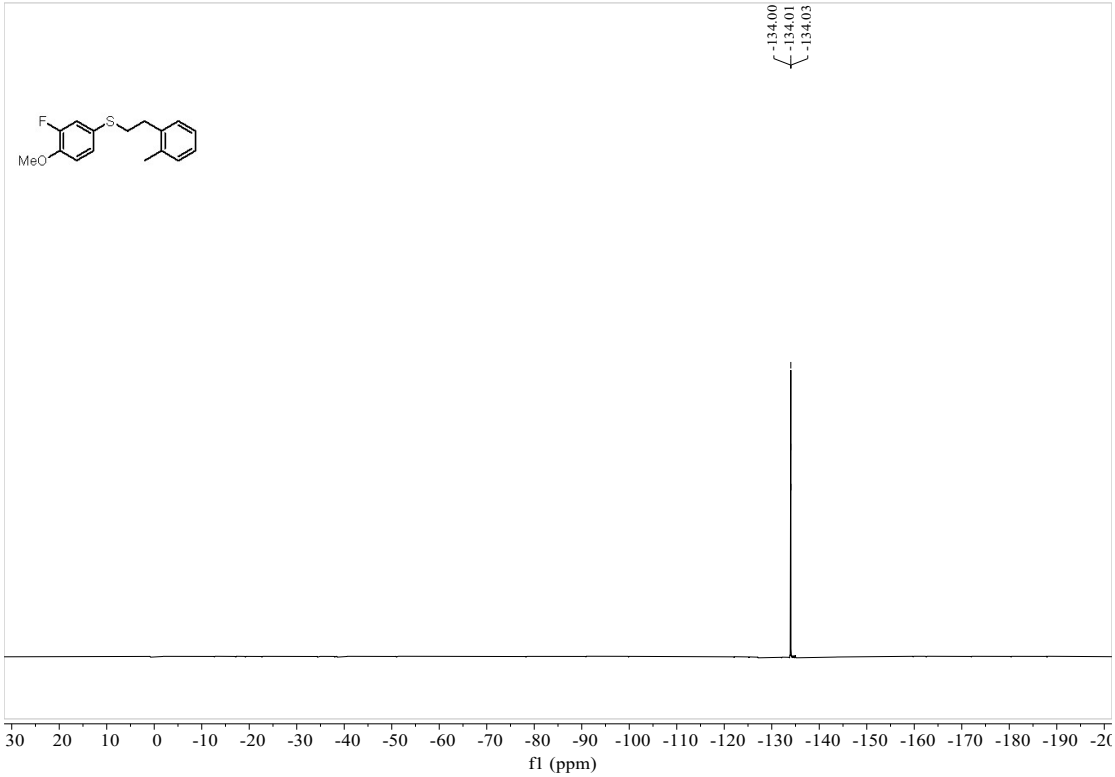
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 29



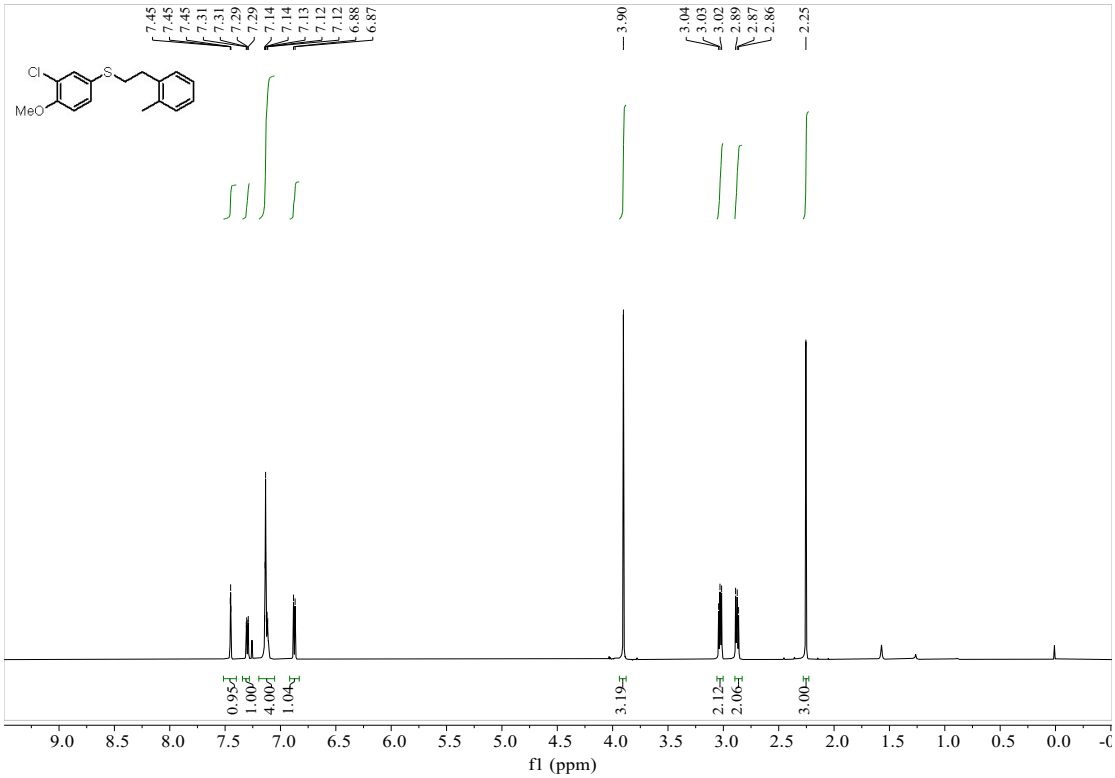
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 29



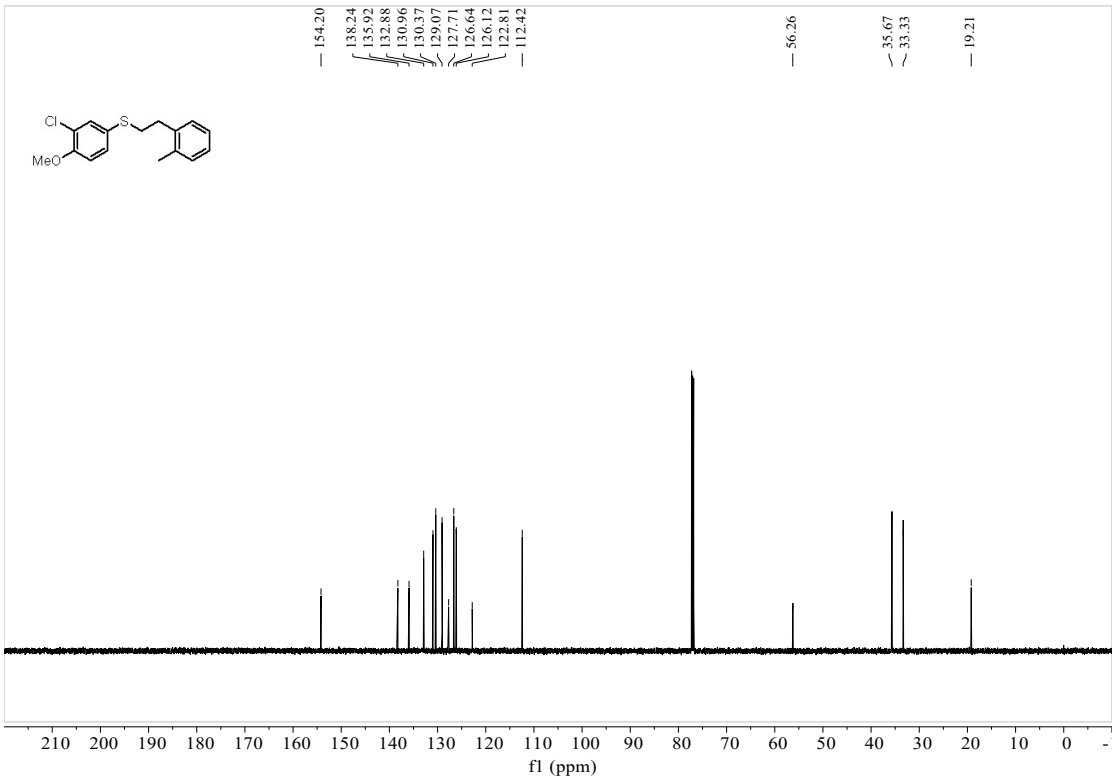
^{19}F NMR (565 MHz, Chloroform-*d*) spectrum of compound 29



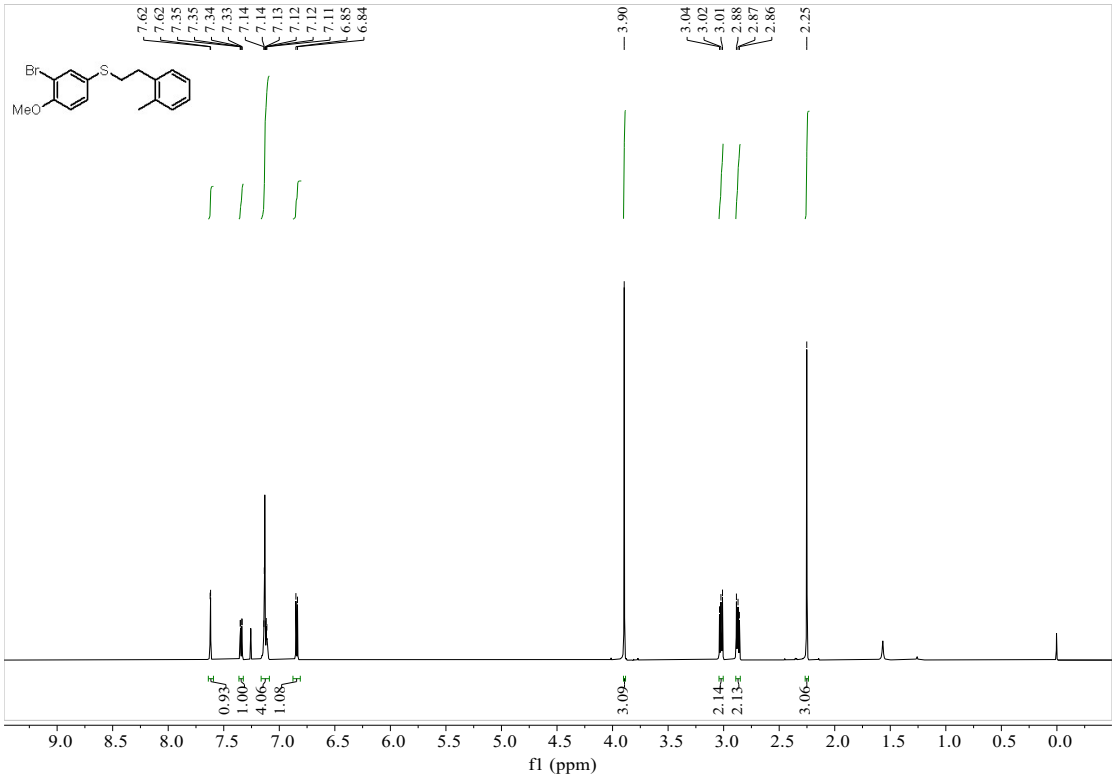
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 30



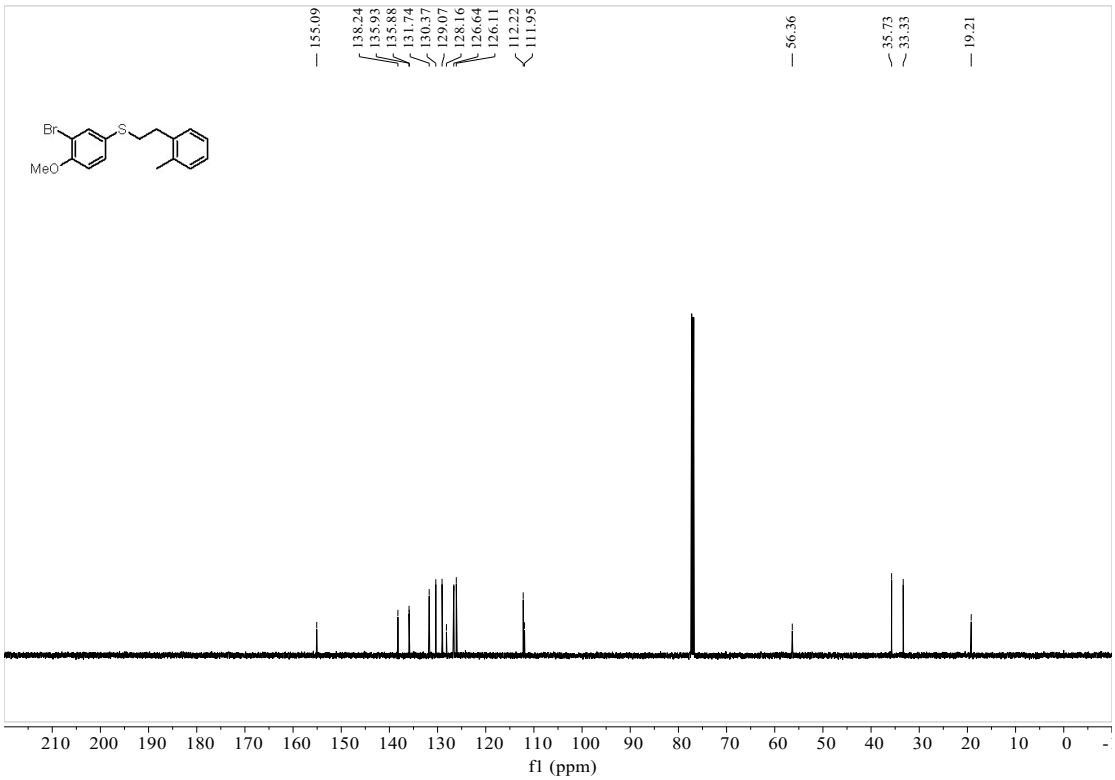
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 30



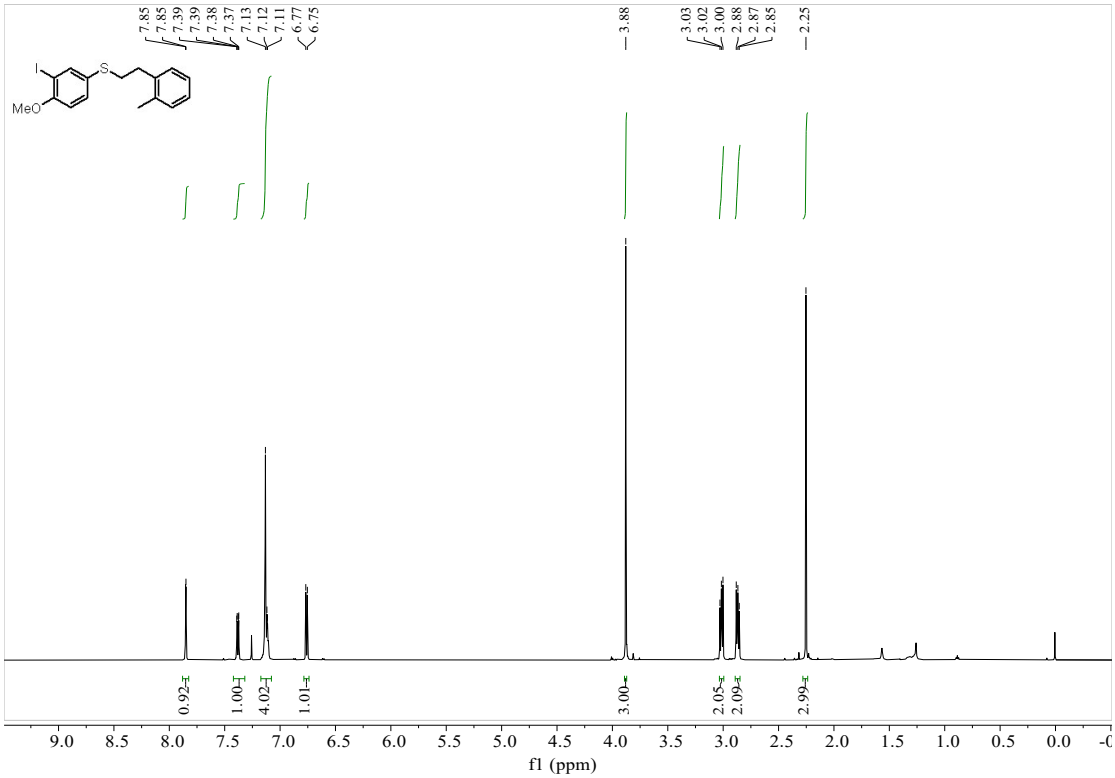
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 31



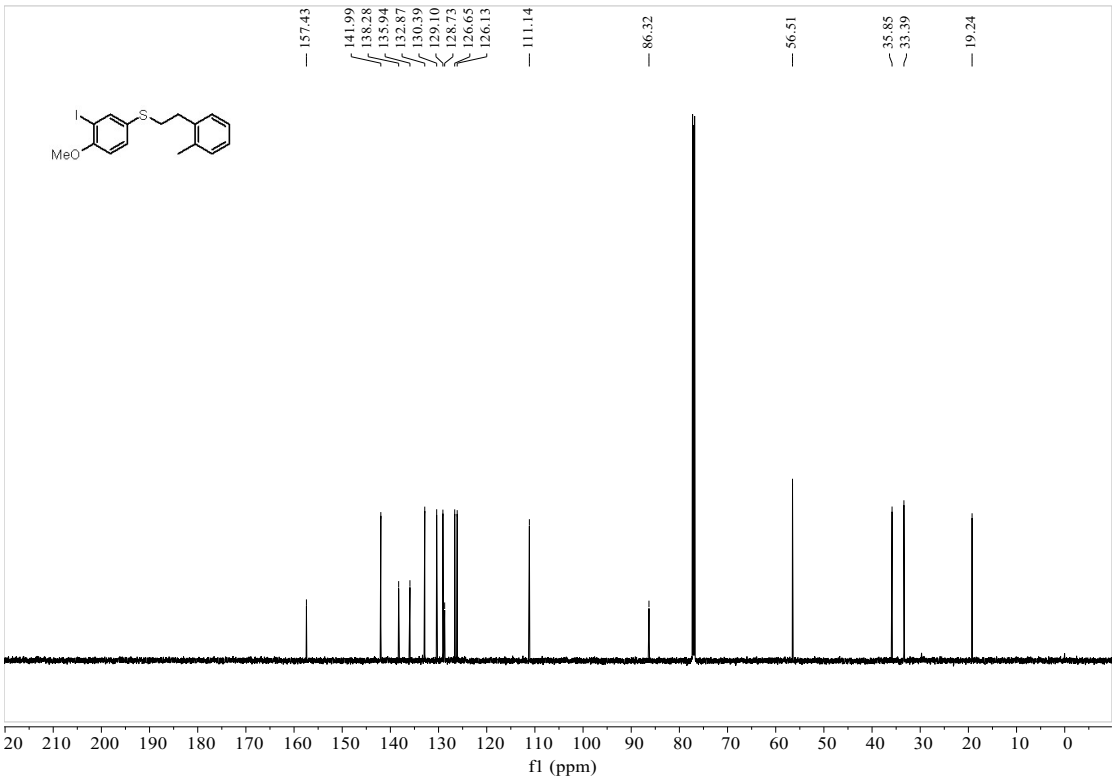
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 31



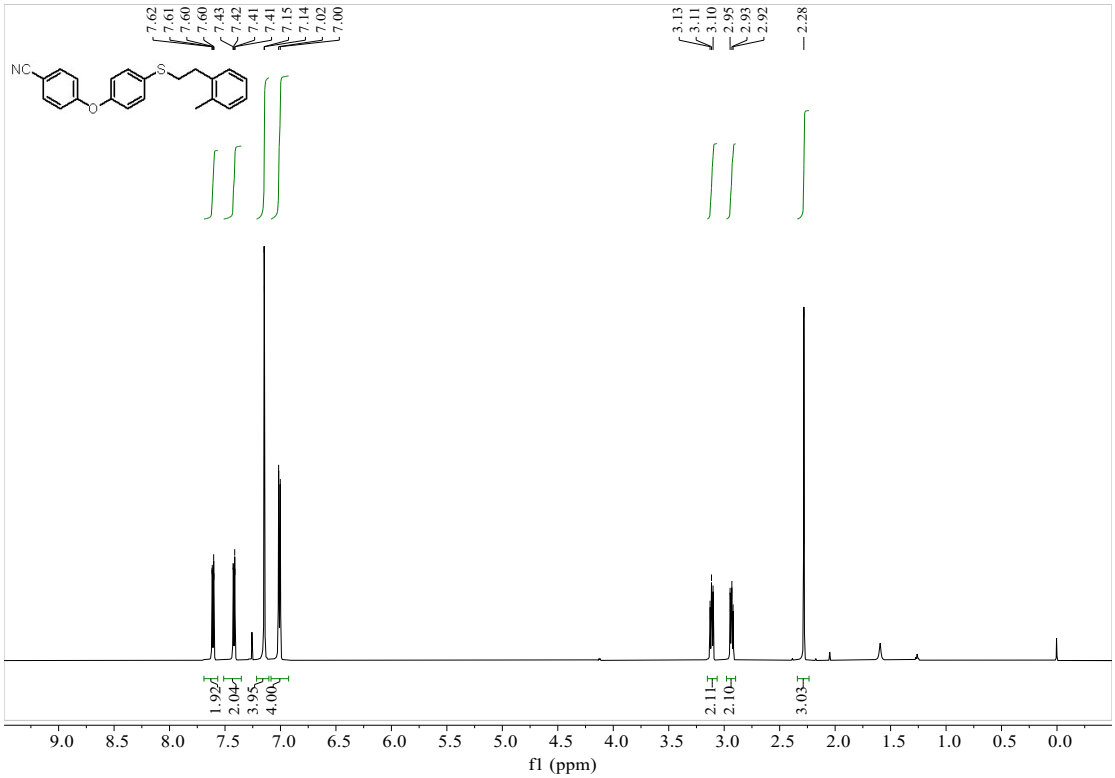
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 32



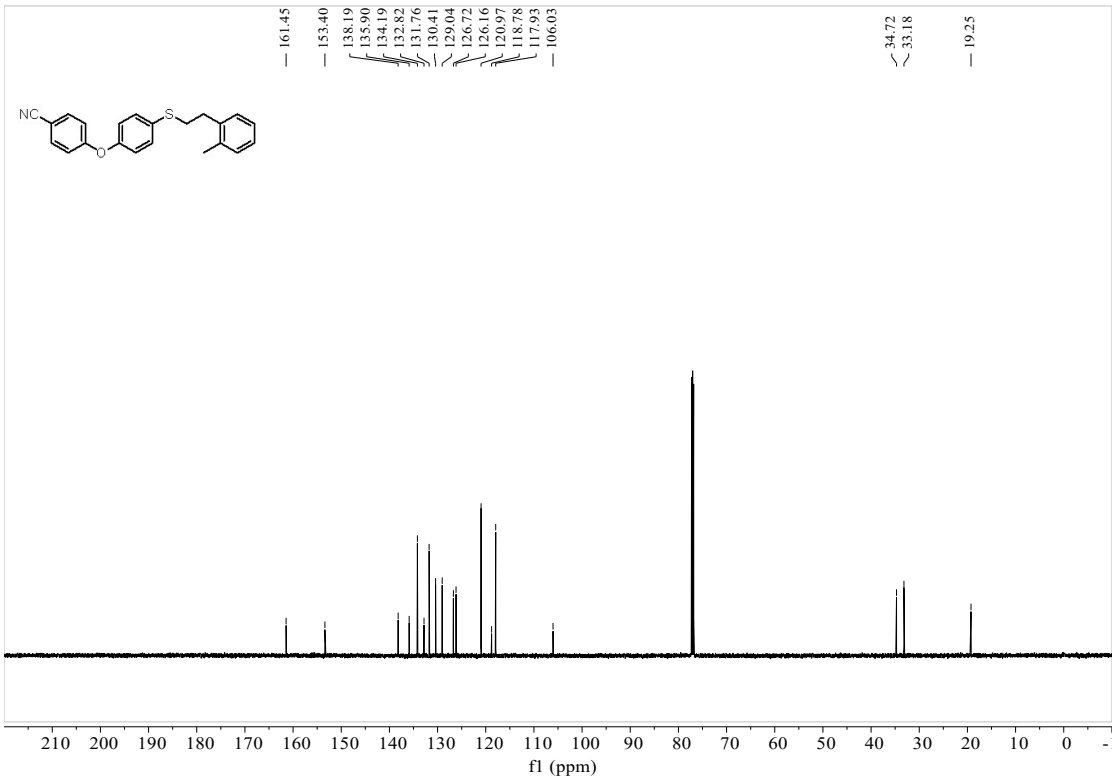
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 32



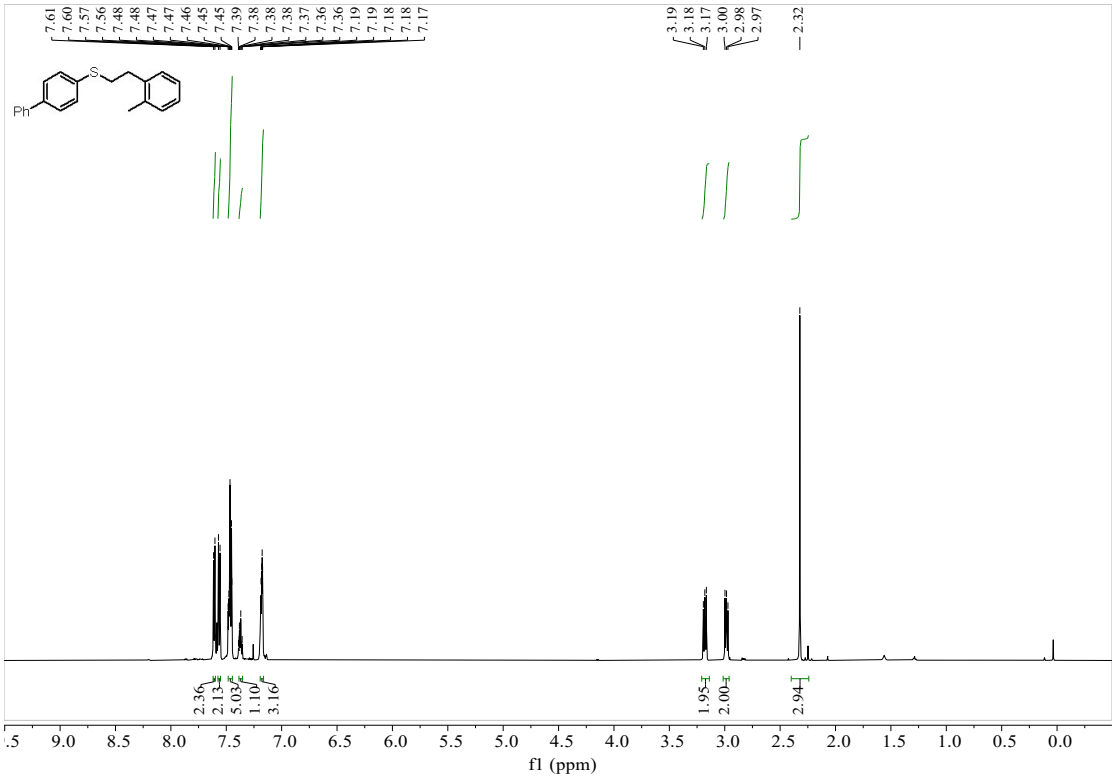
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 33



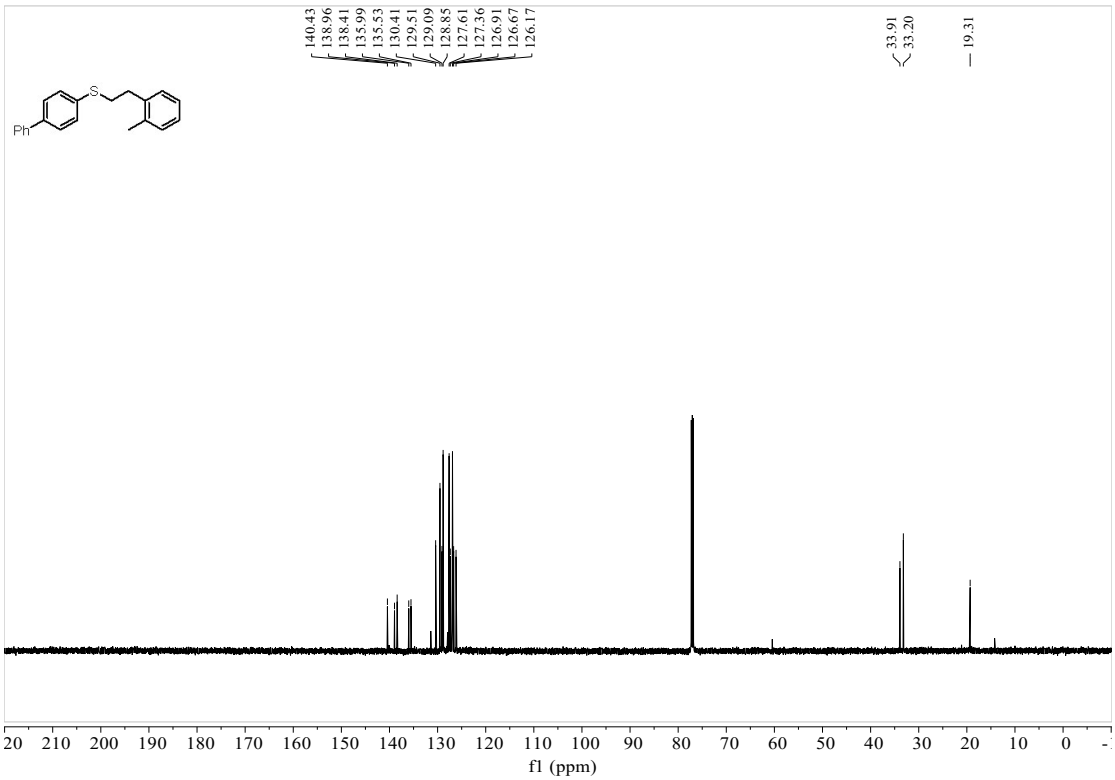
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 33



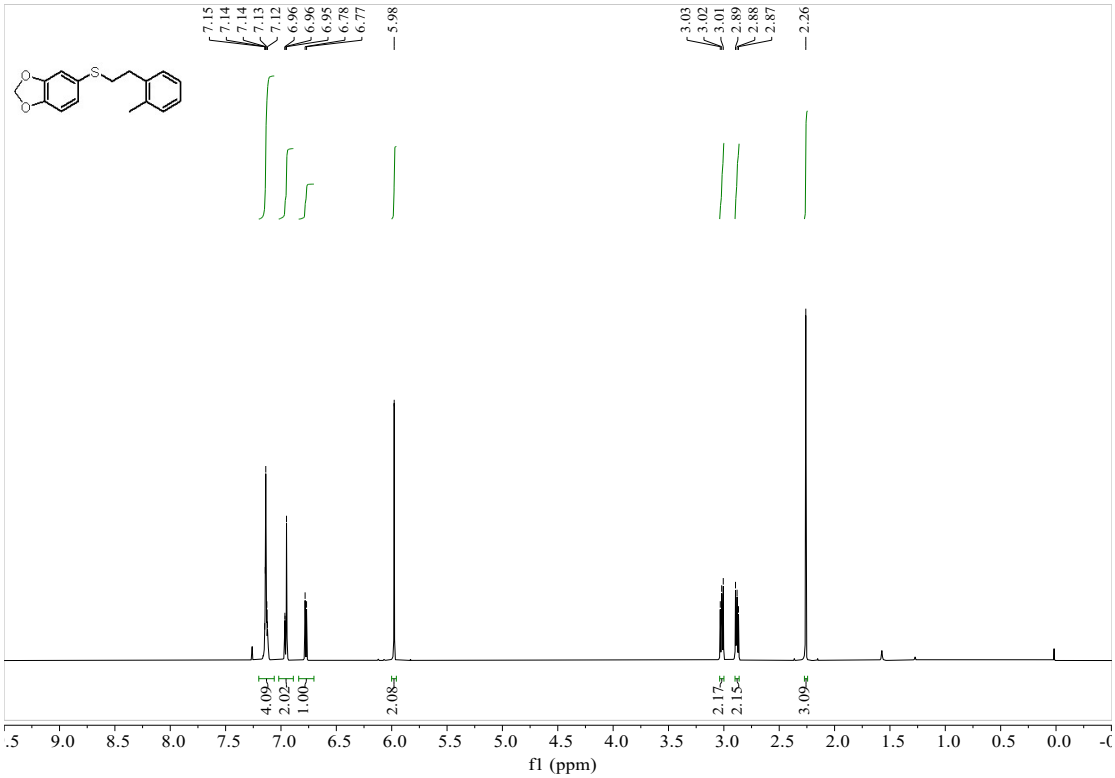
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 34



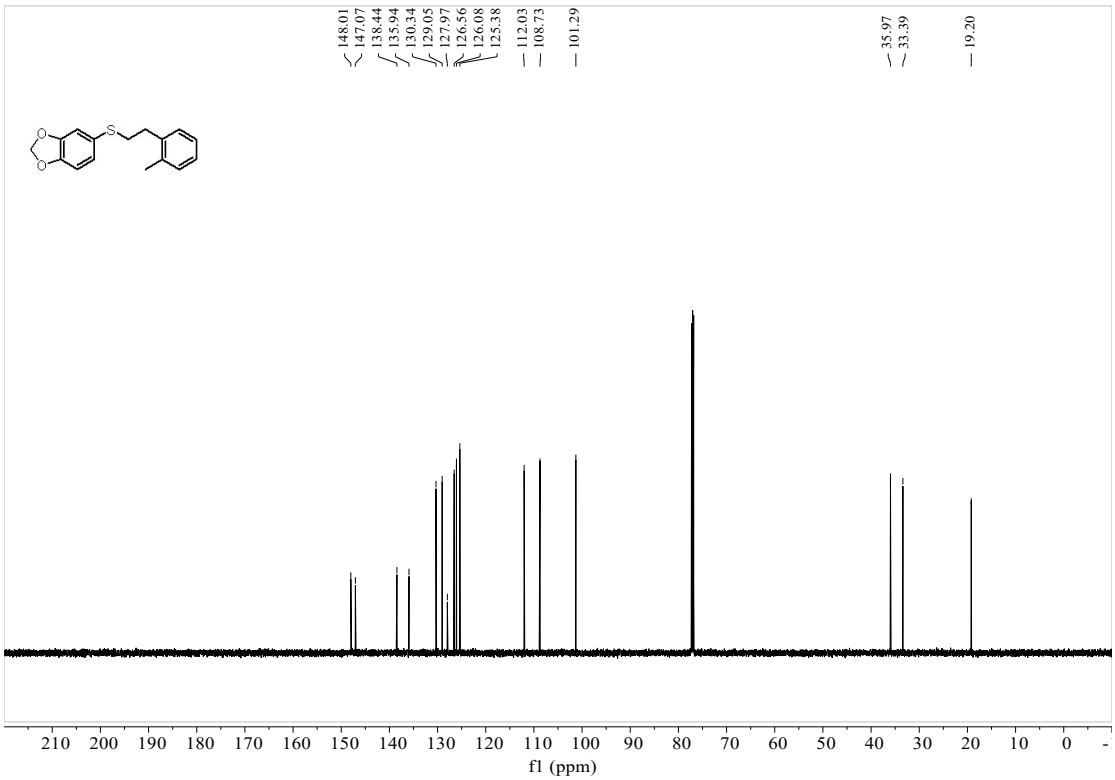
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 34



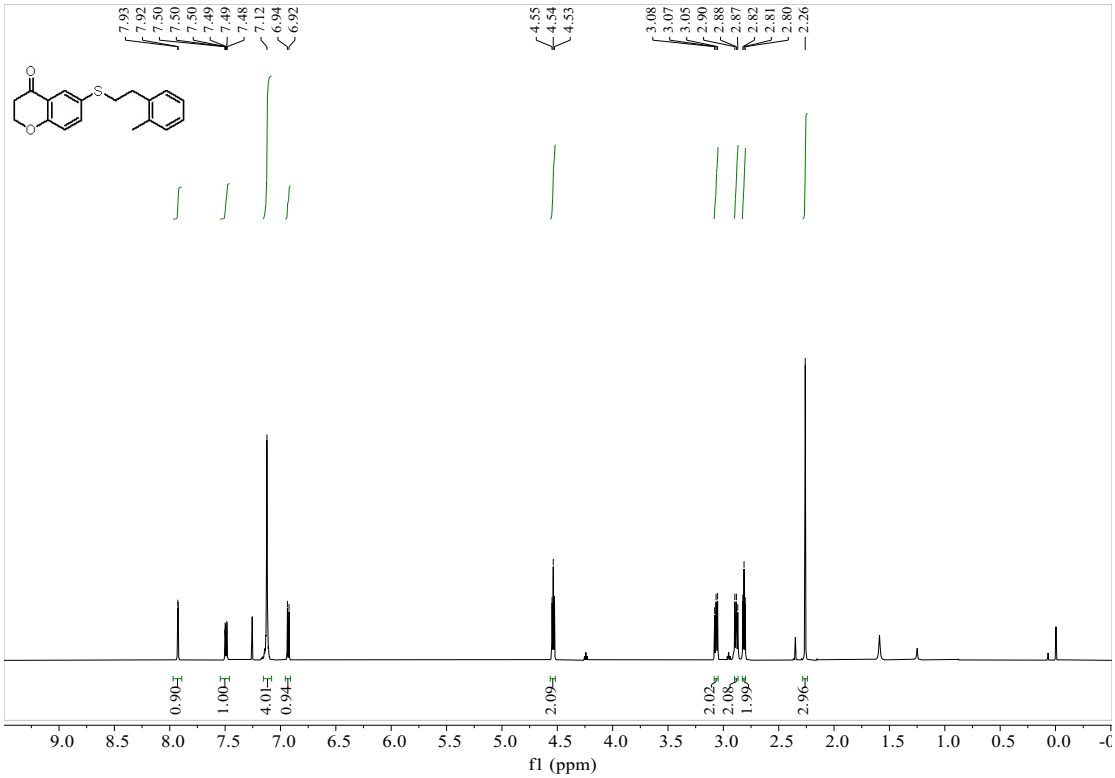
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 35



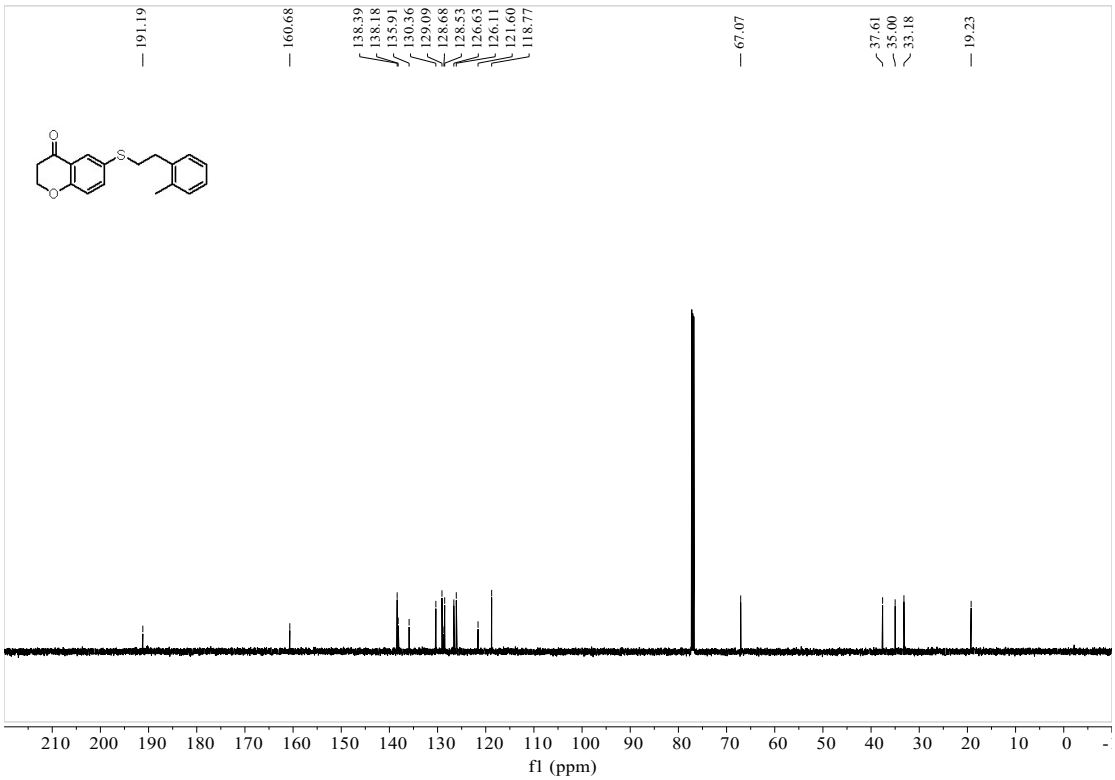
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 35



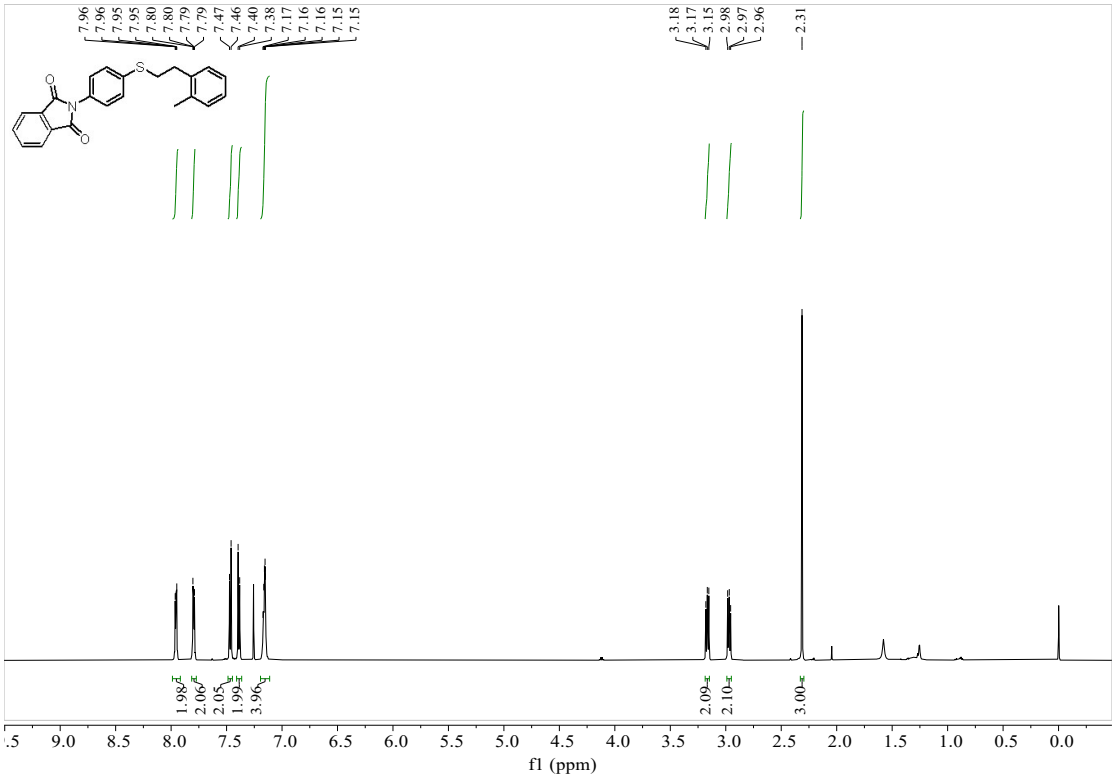
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 36



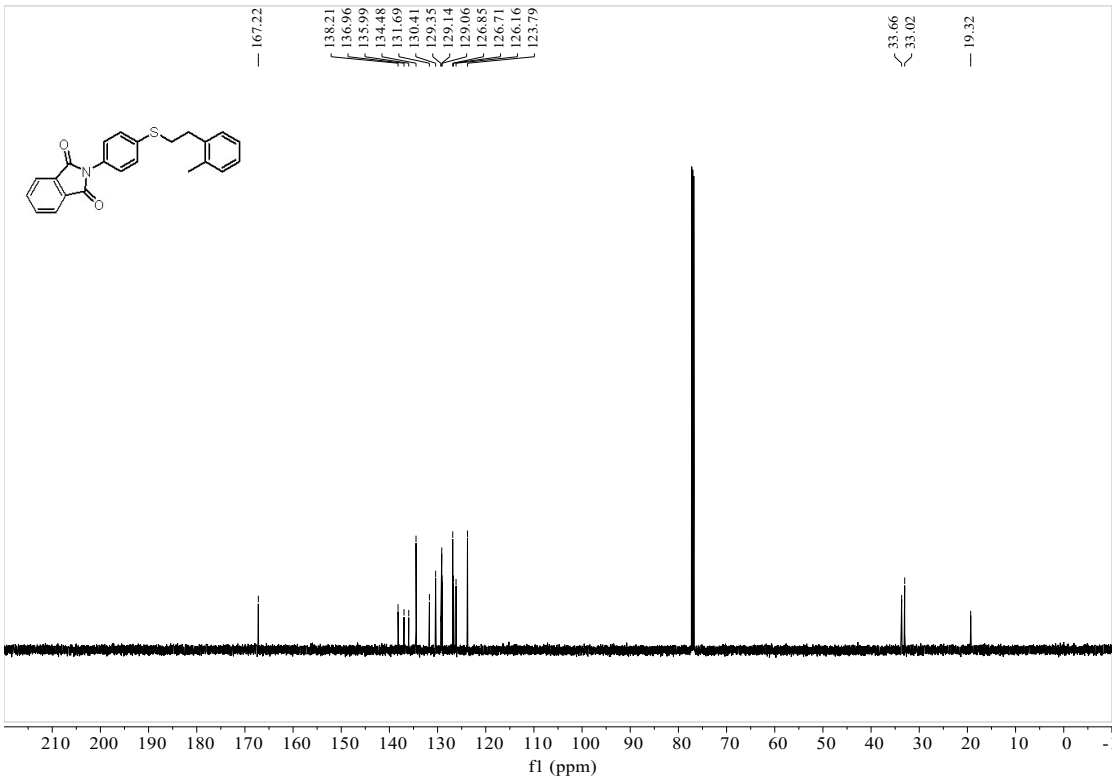
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 36



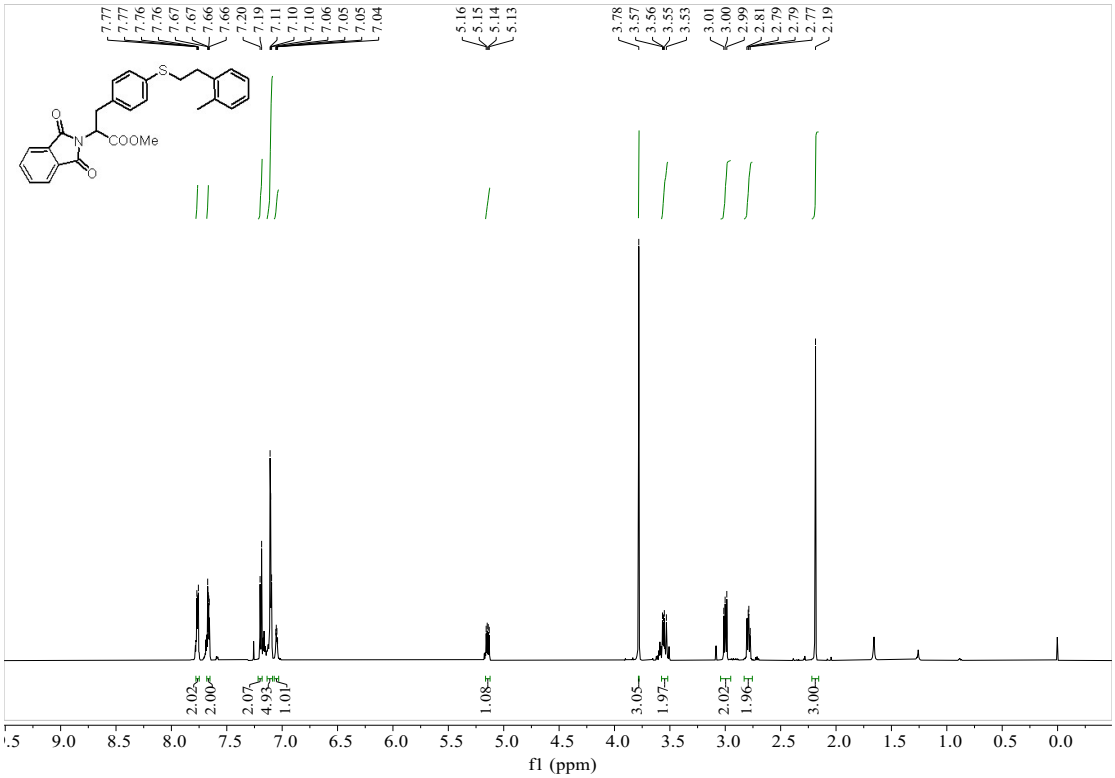
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 37



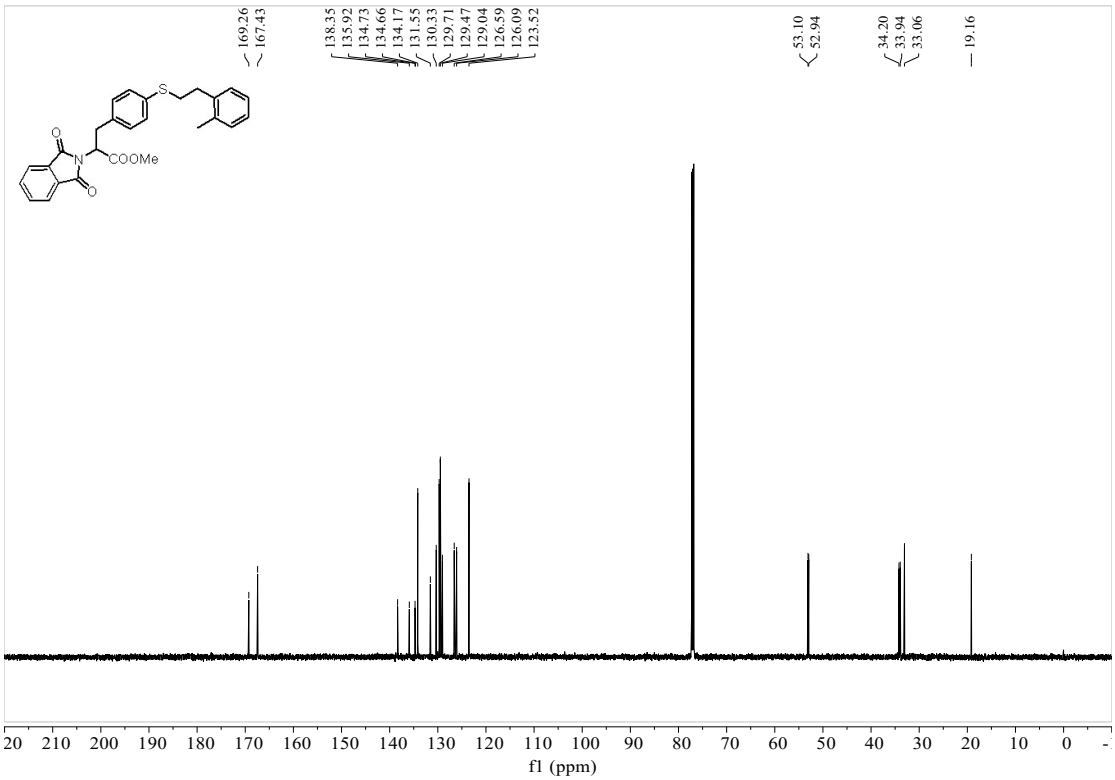
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 37



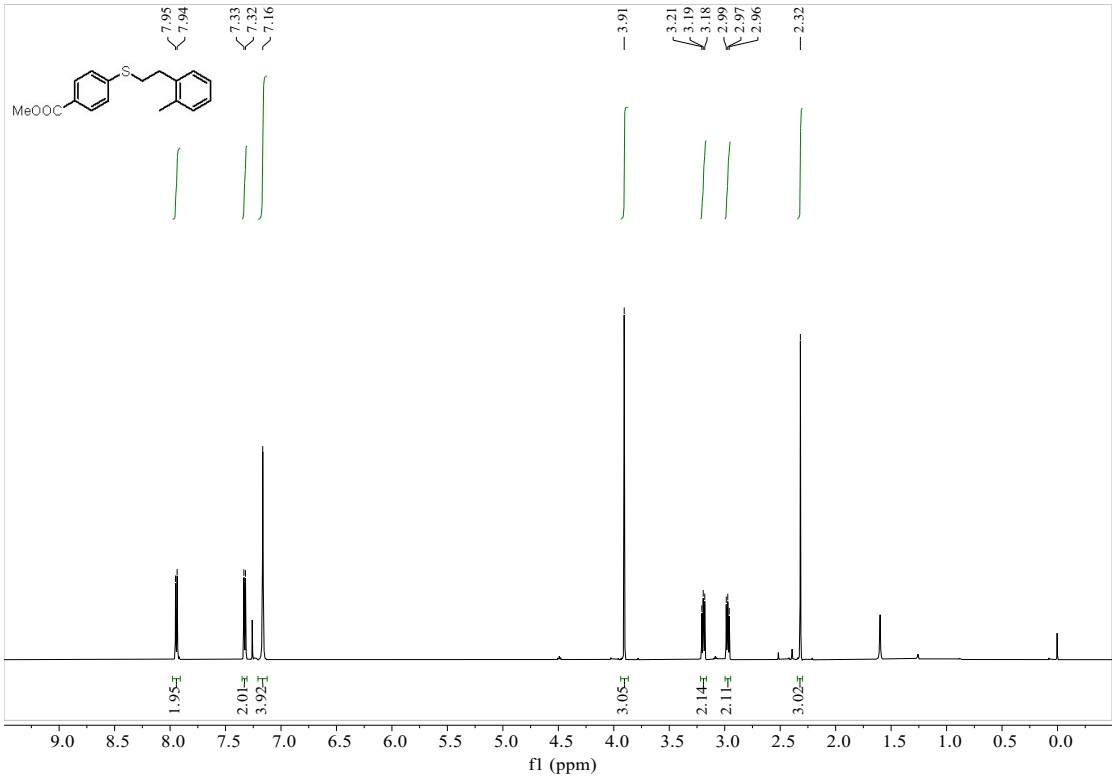
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 38



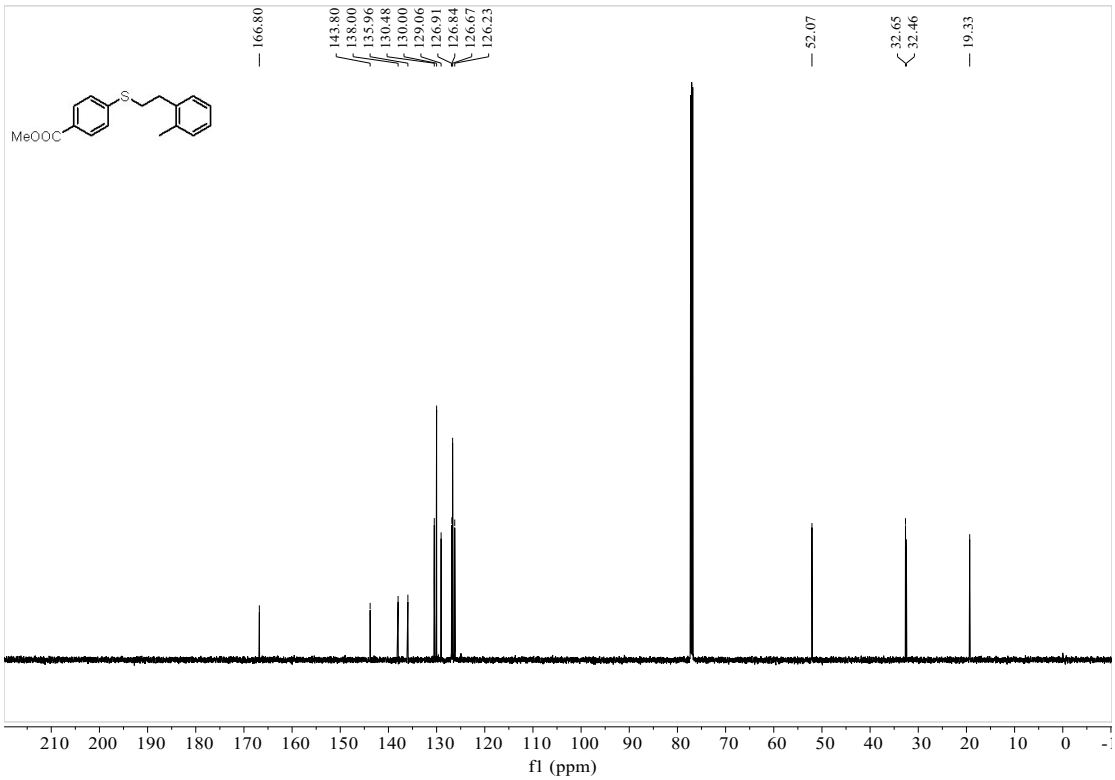
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 38



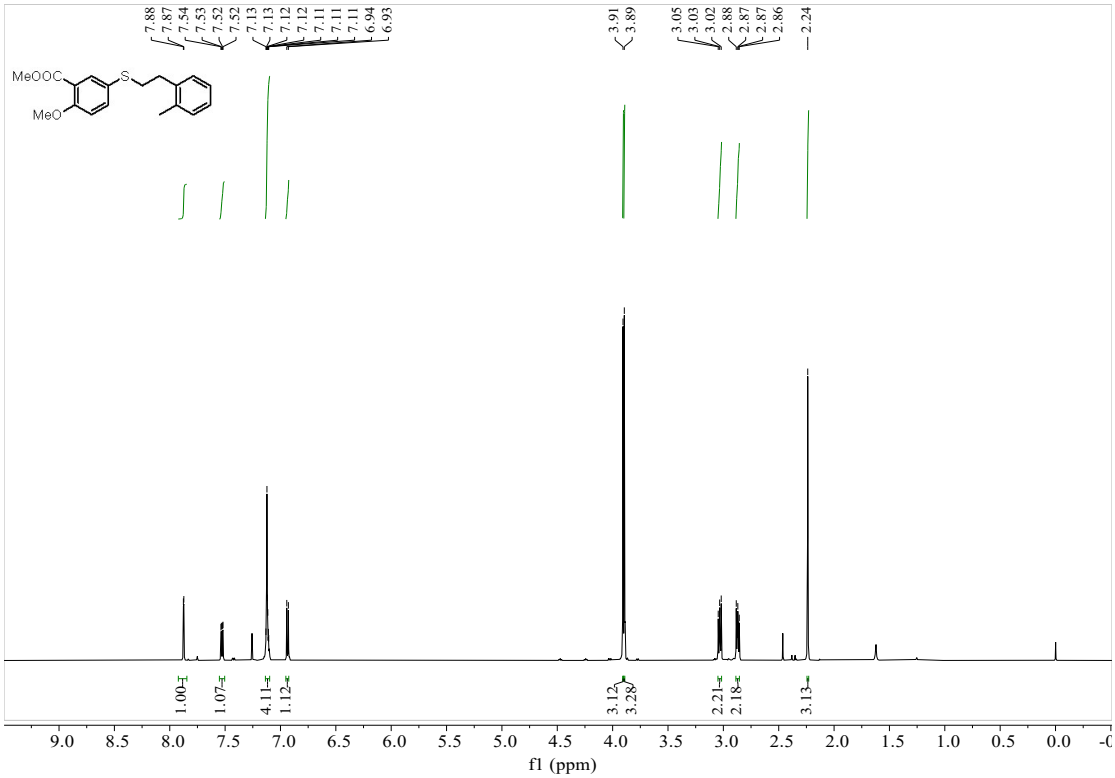
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 39



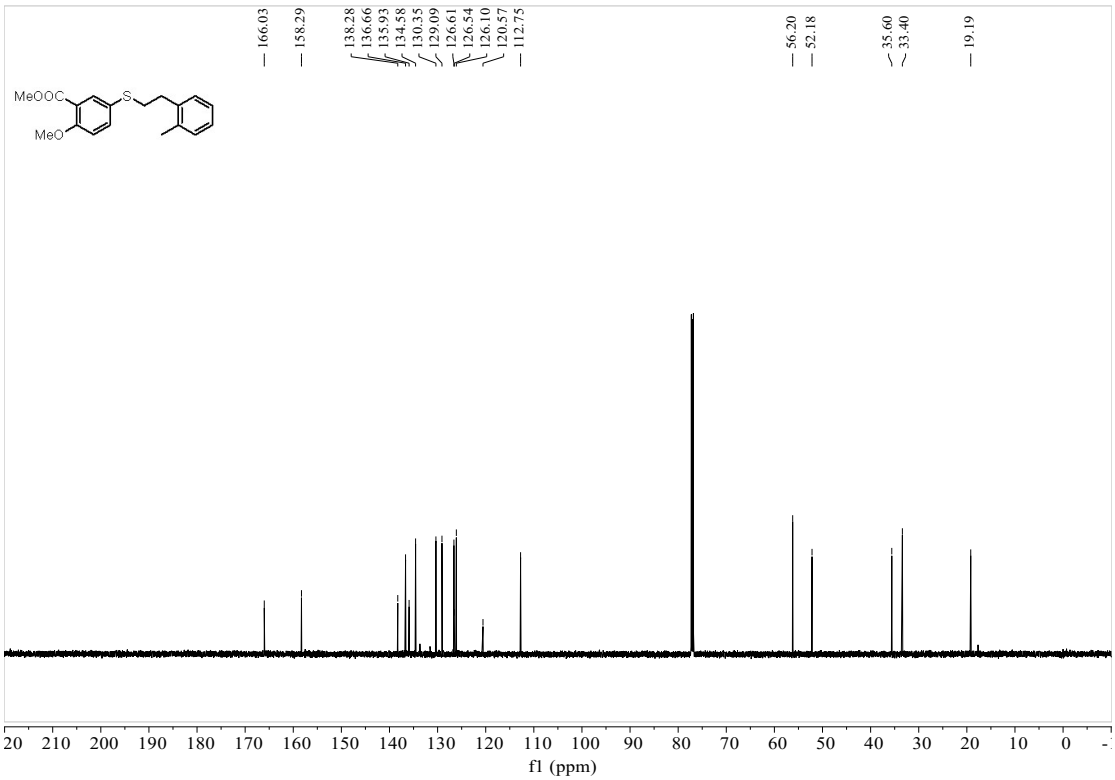
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 39



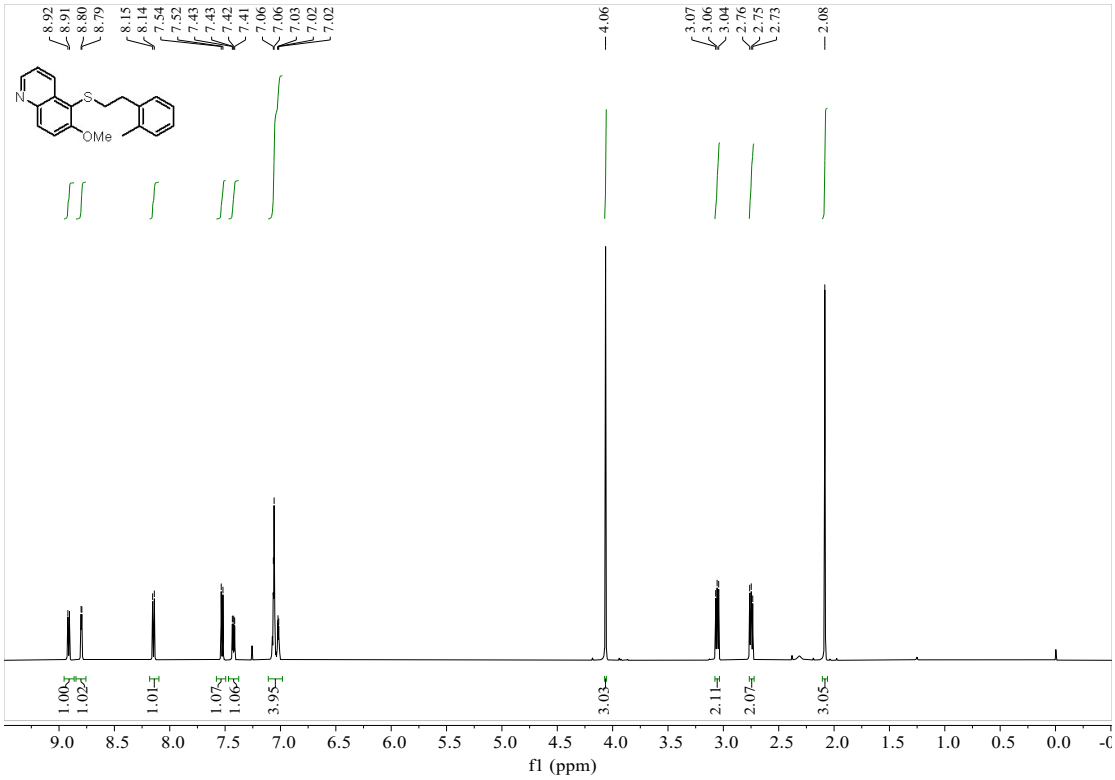
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 40



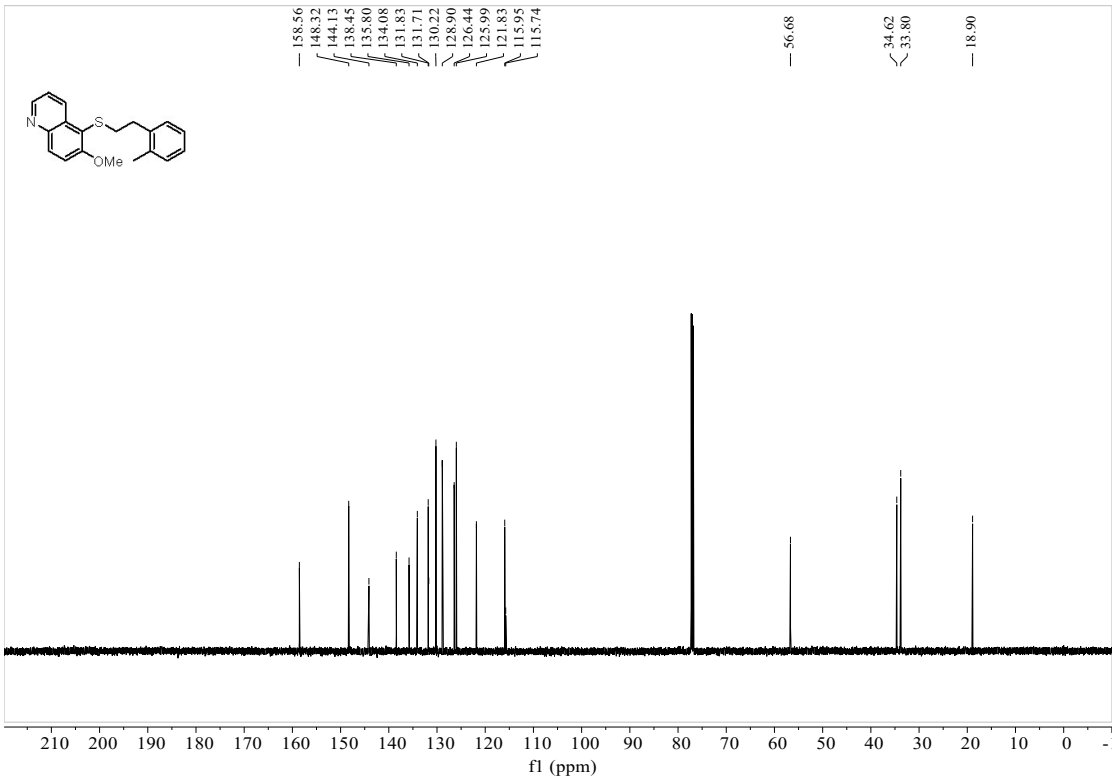
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 40



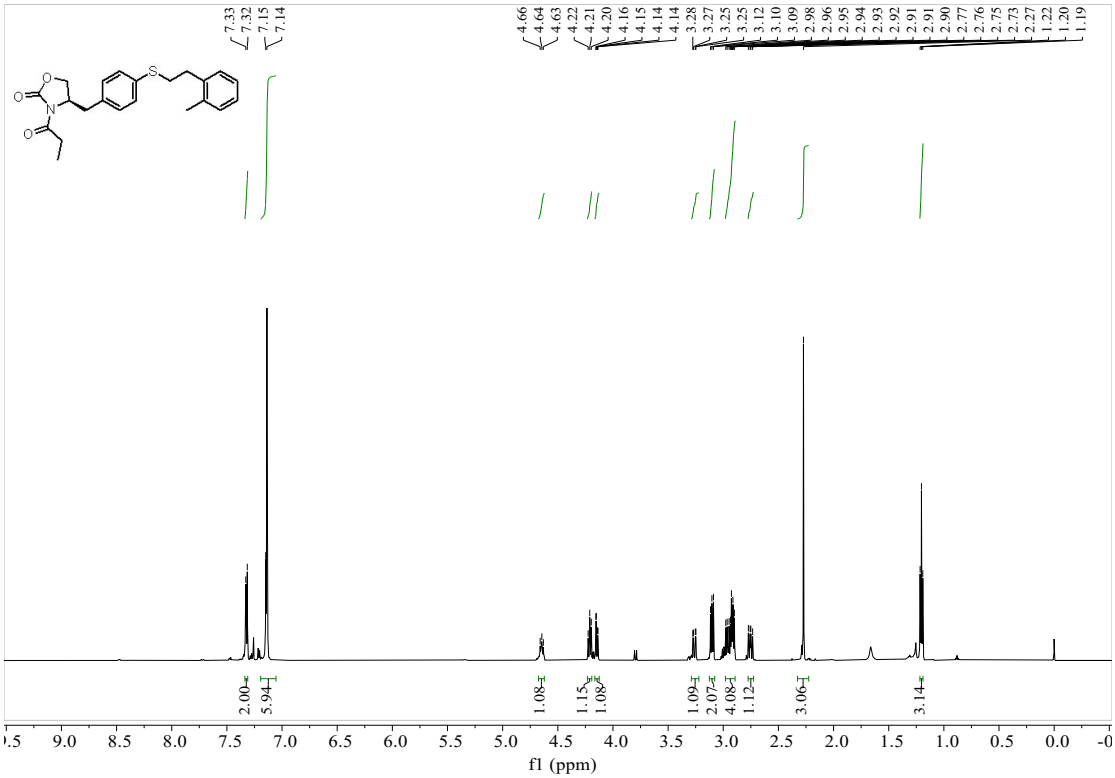
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 41



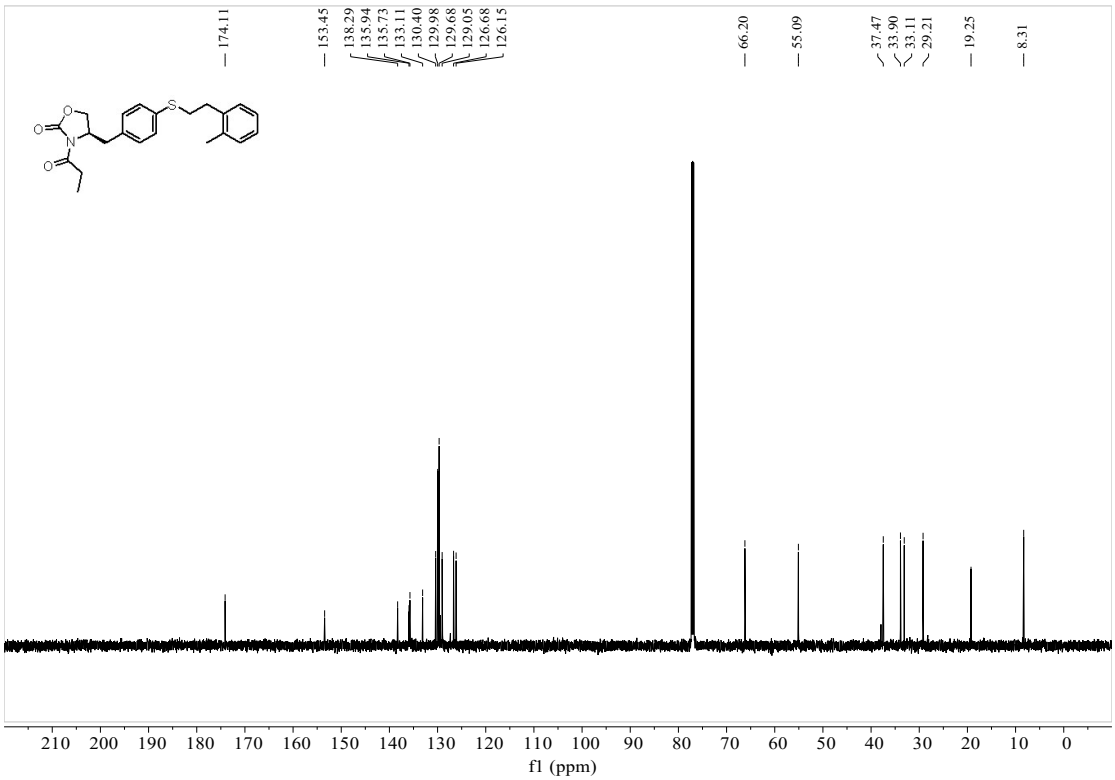
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 41



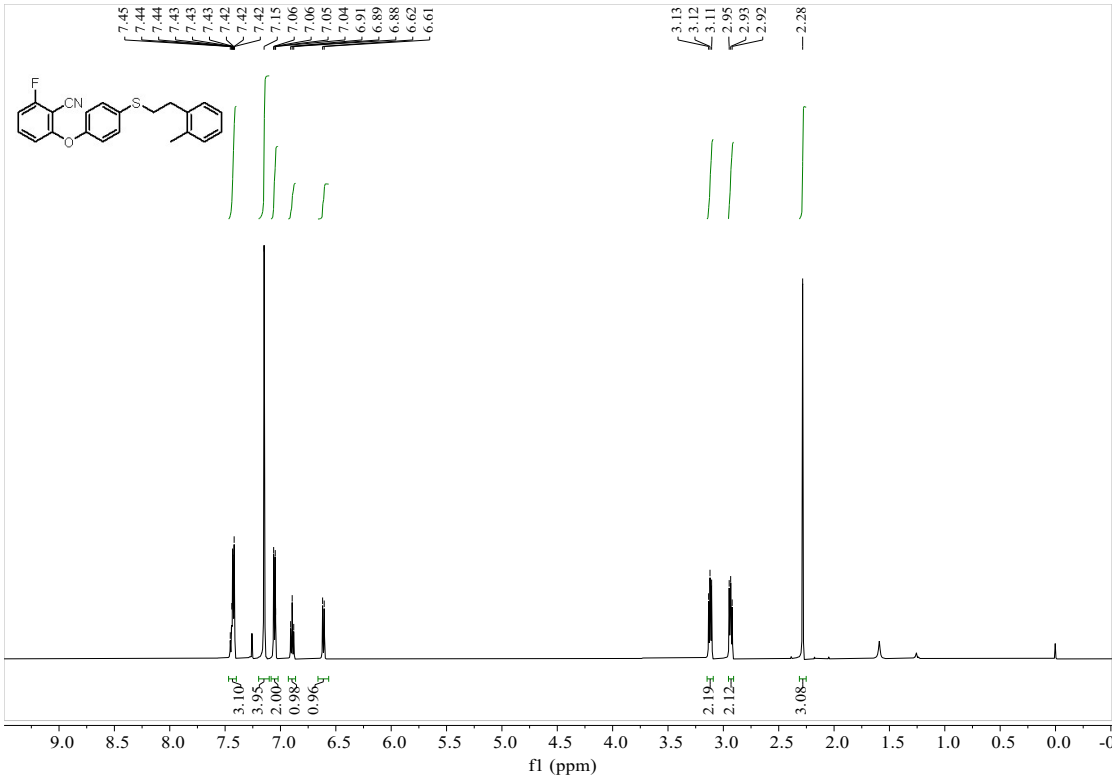
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 42



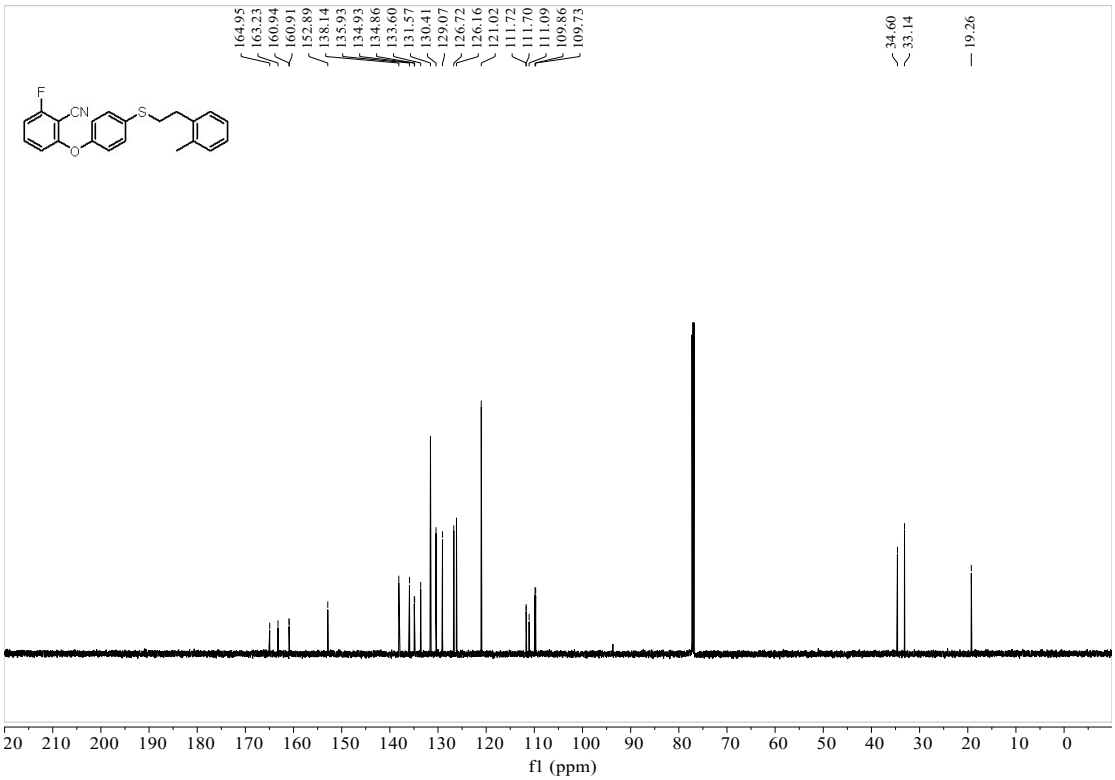
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 42



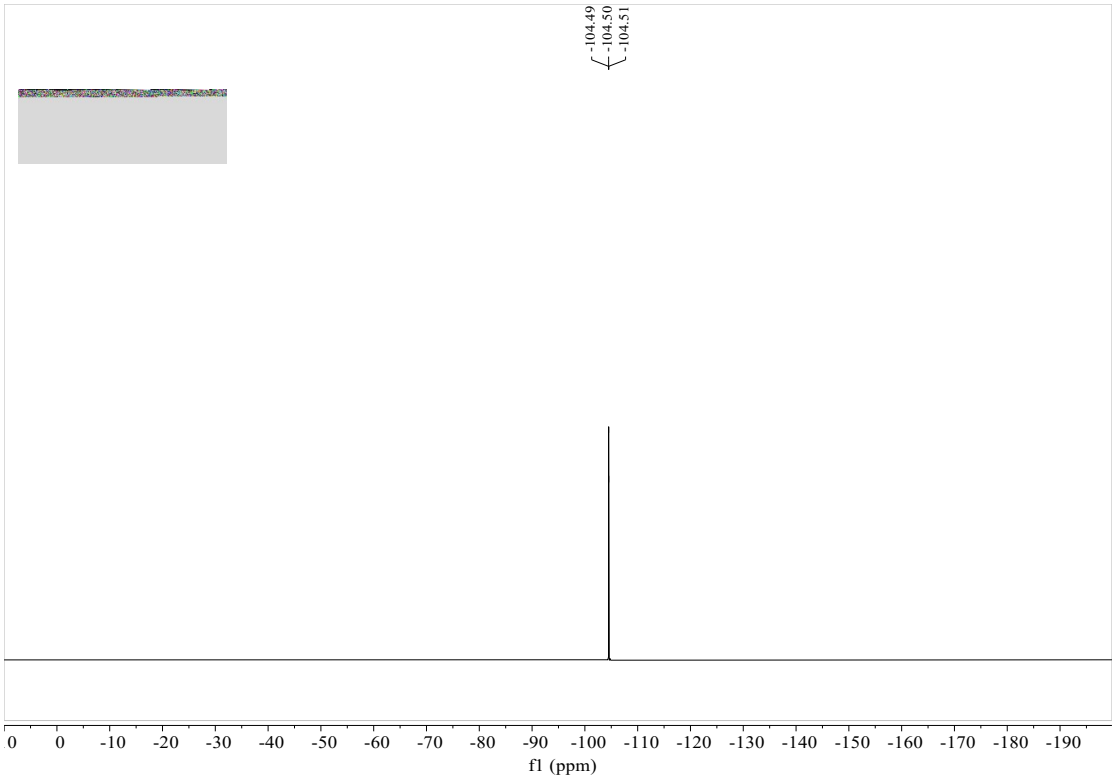
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 43



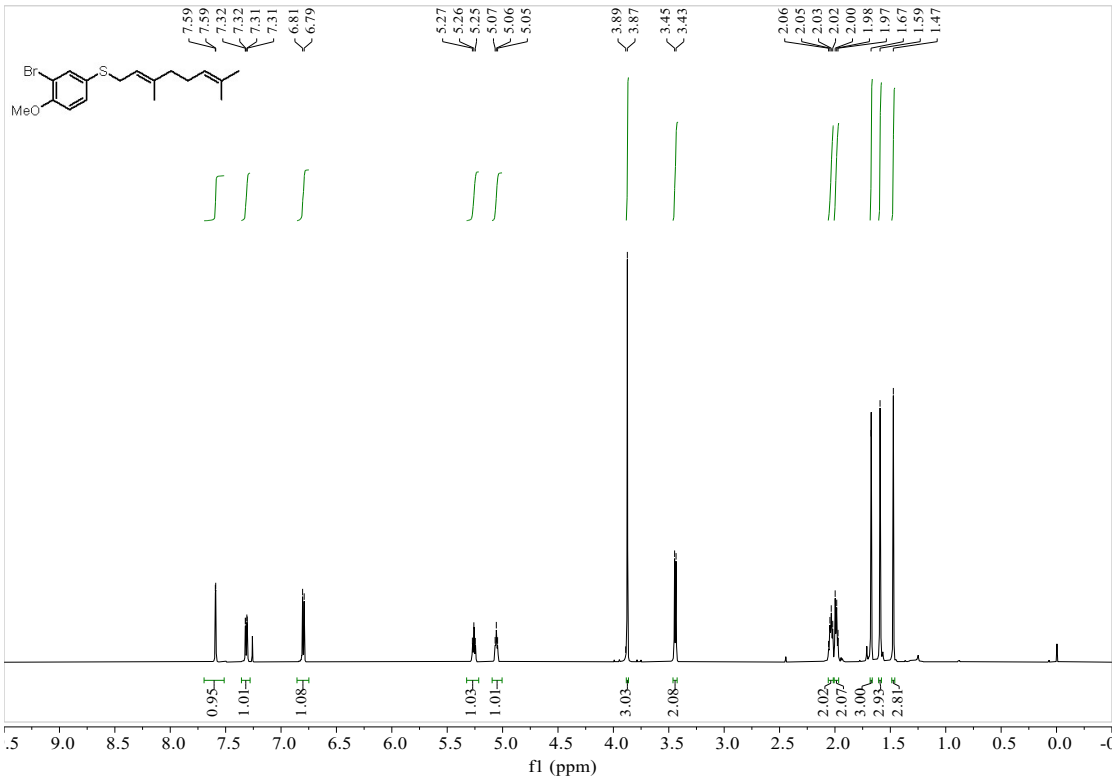
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 43



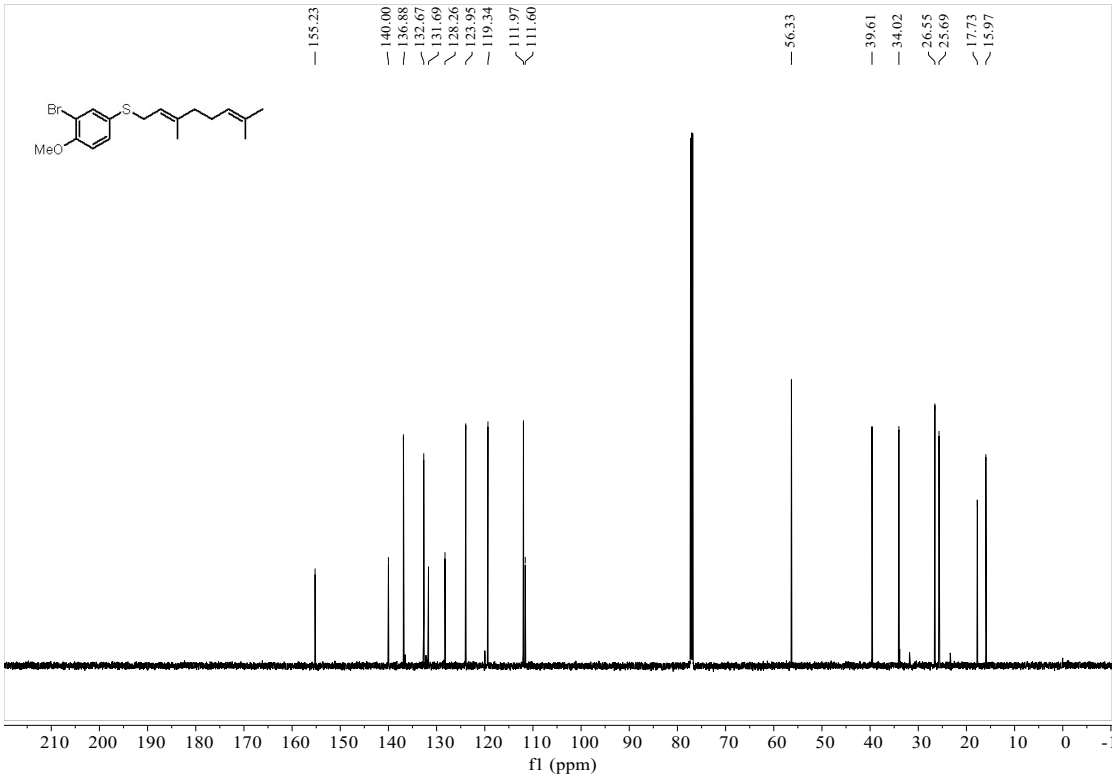
^{19}F NMR (565 MHz, Chloroform-*d*) spectrum of compound 43



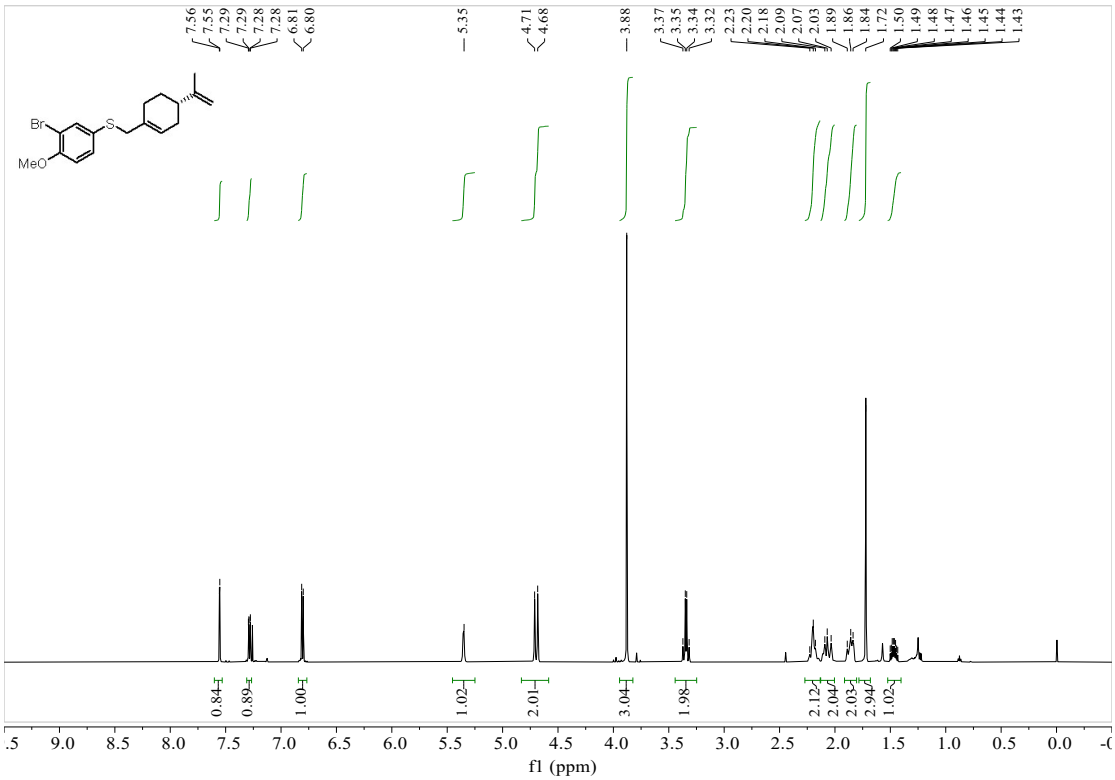
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 44



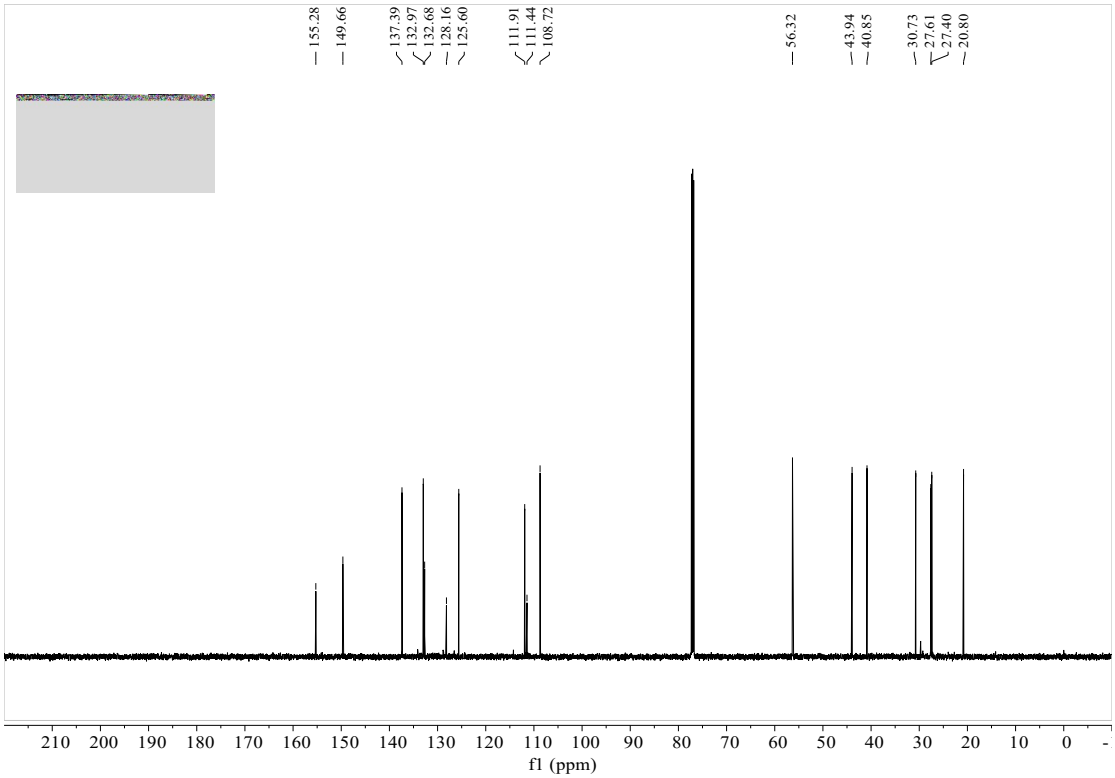
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 44



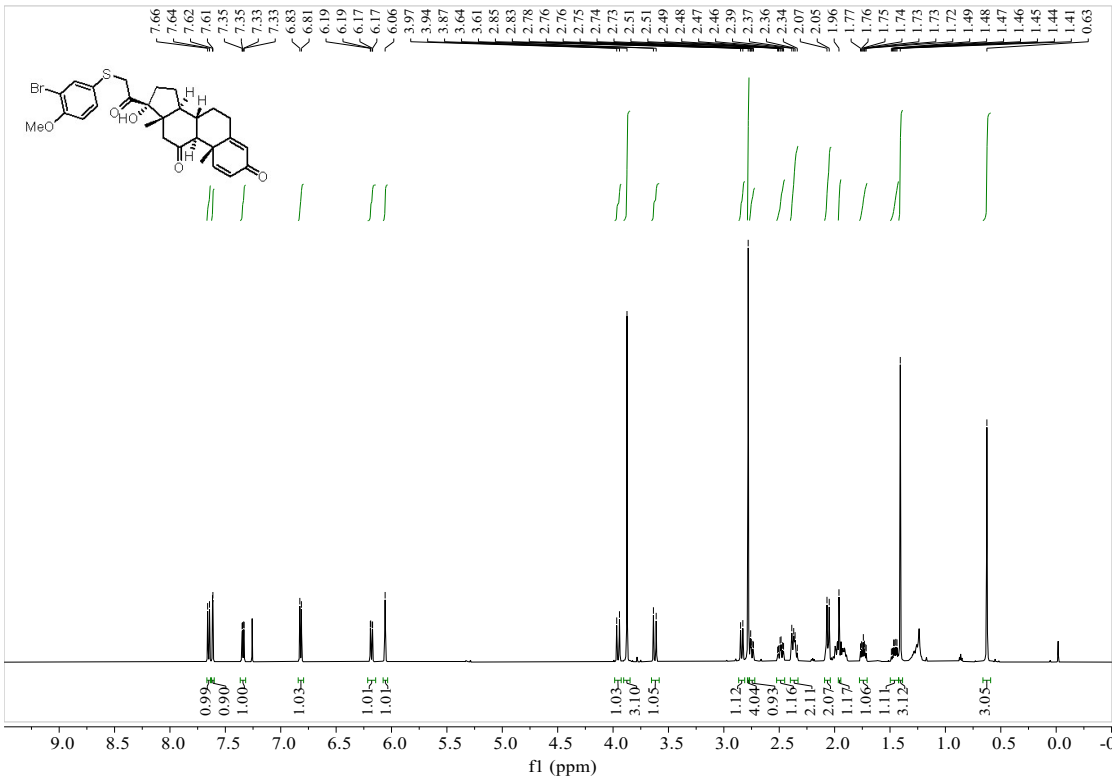
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 45



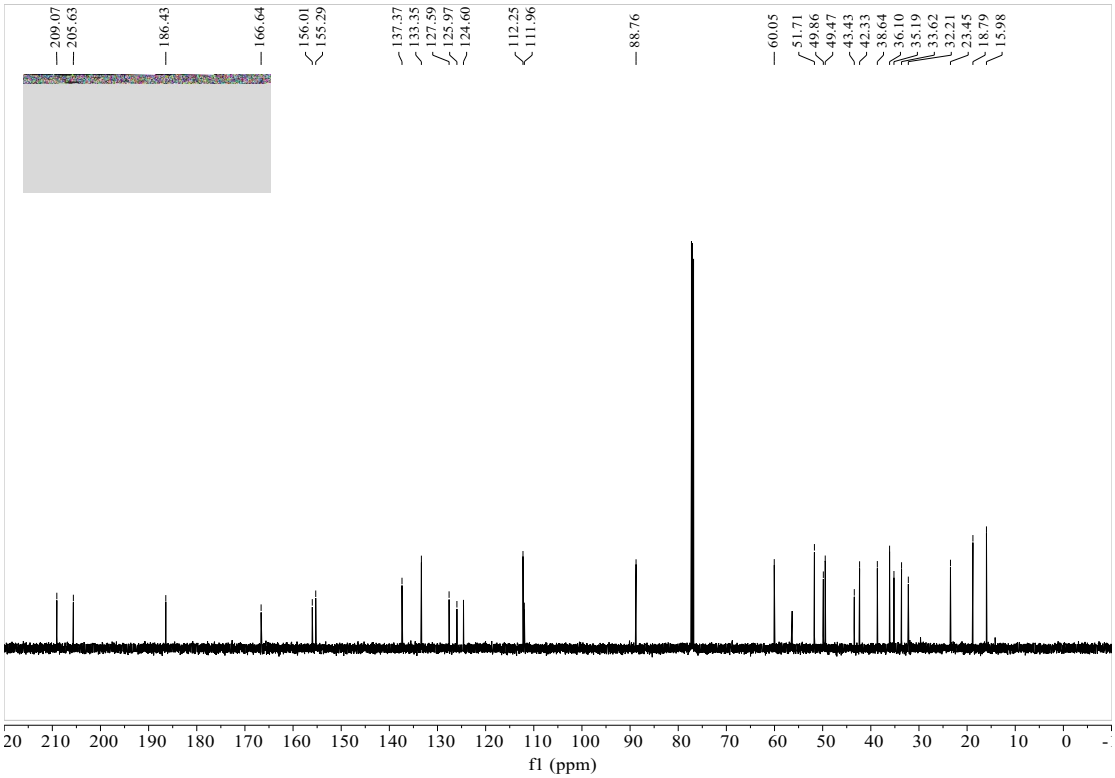
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 45



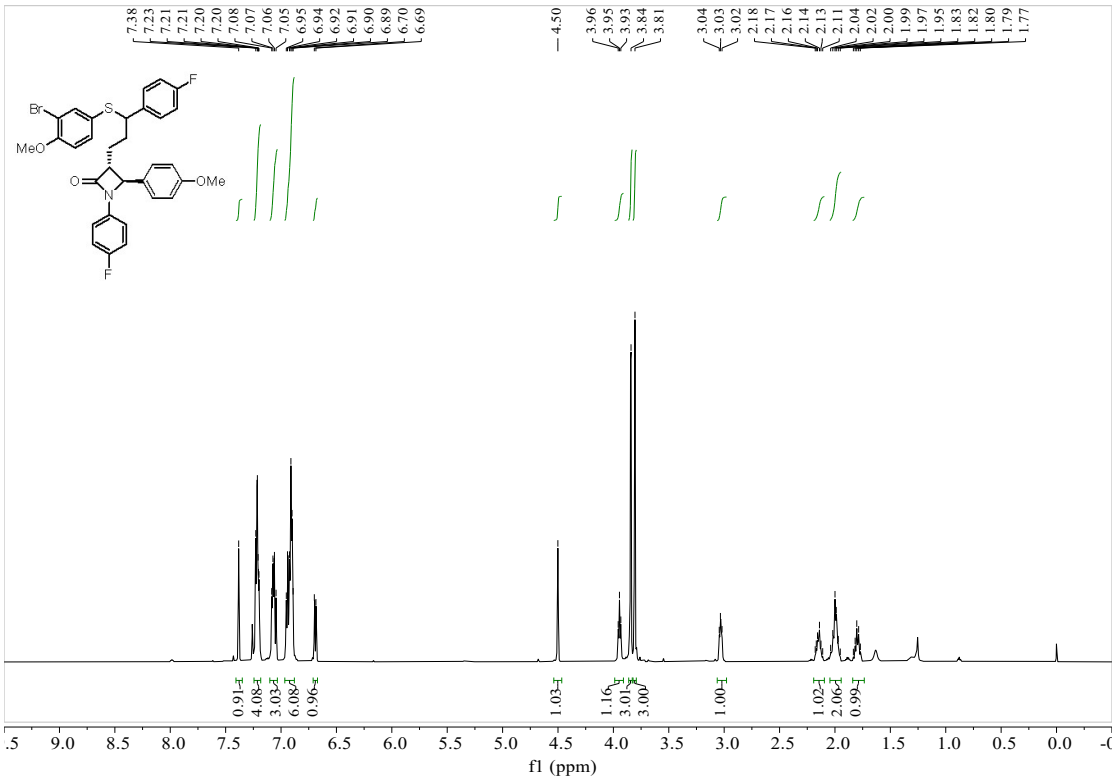
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 46



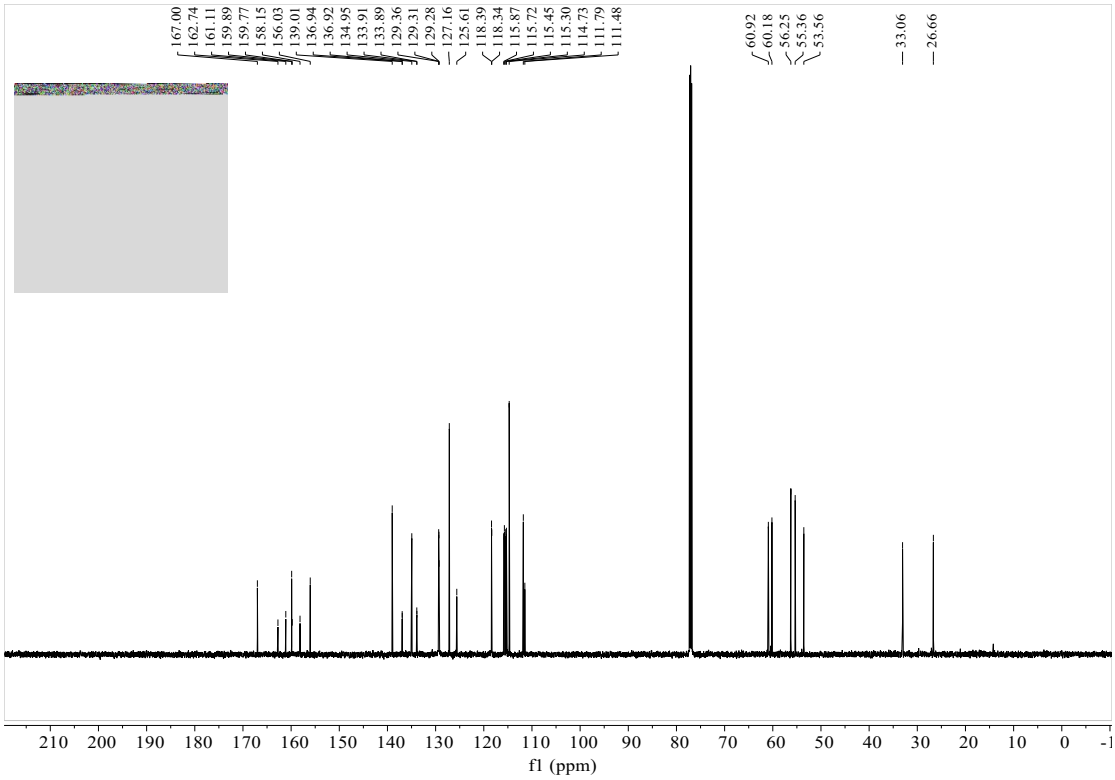
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 46



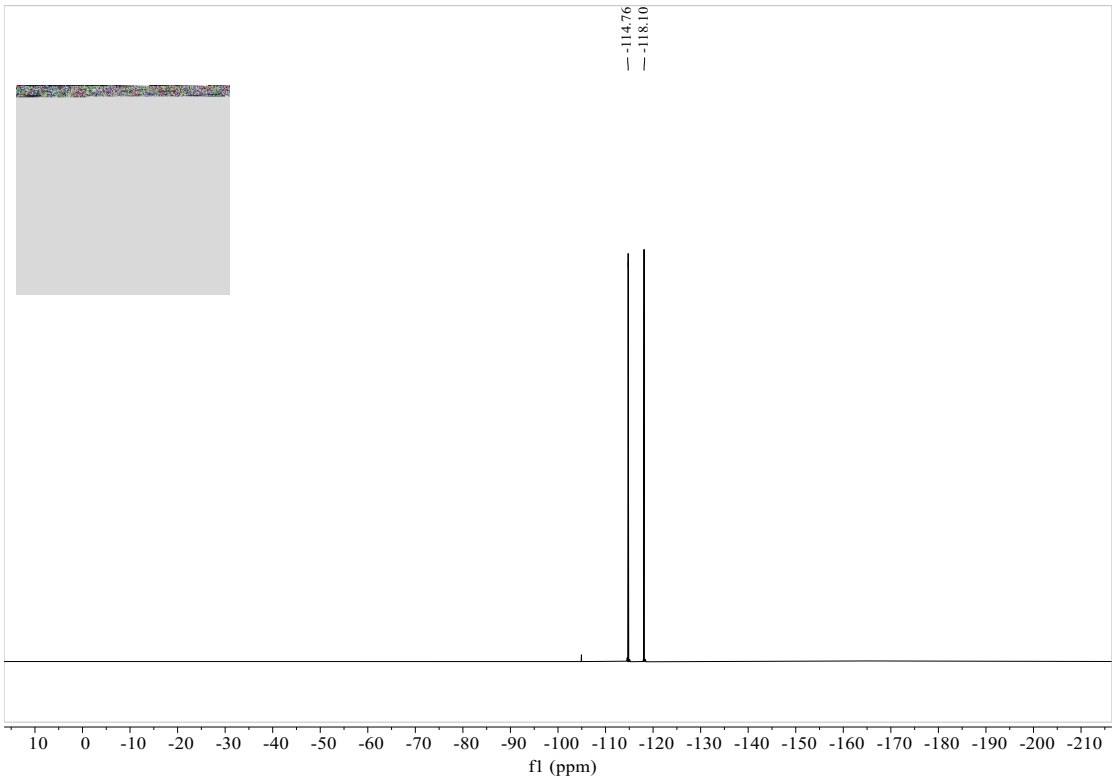
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 47



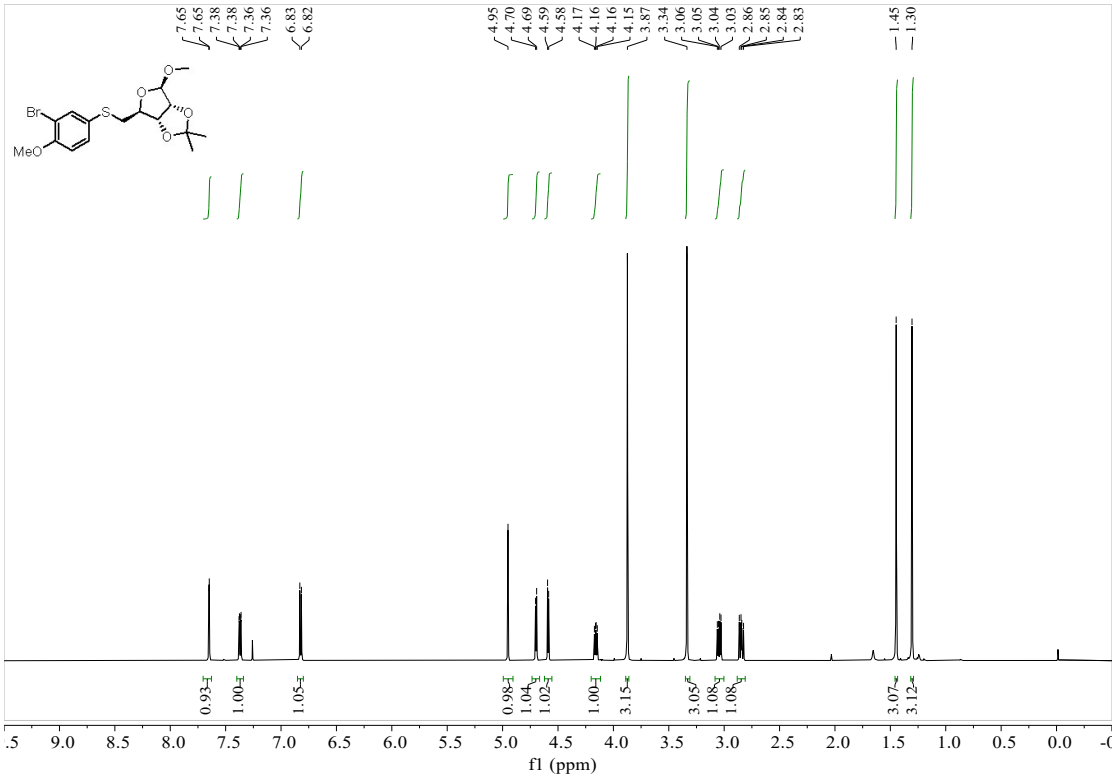
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 47



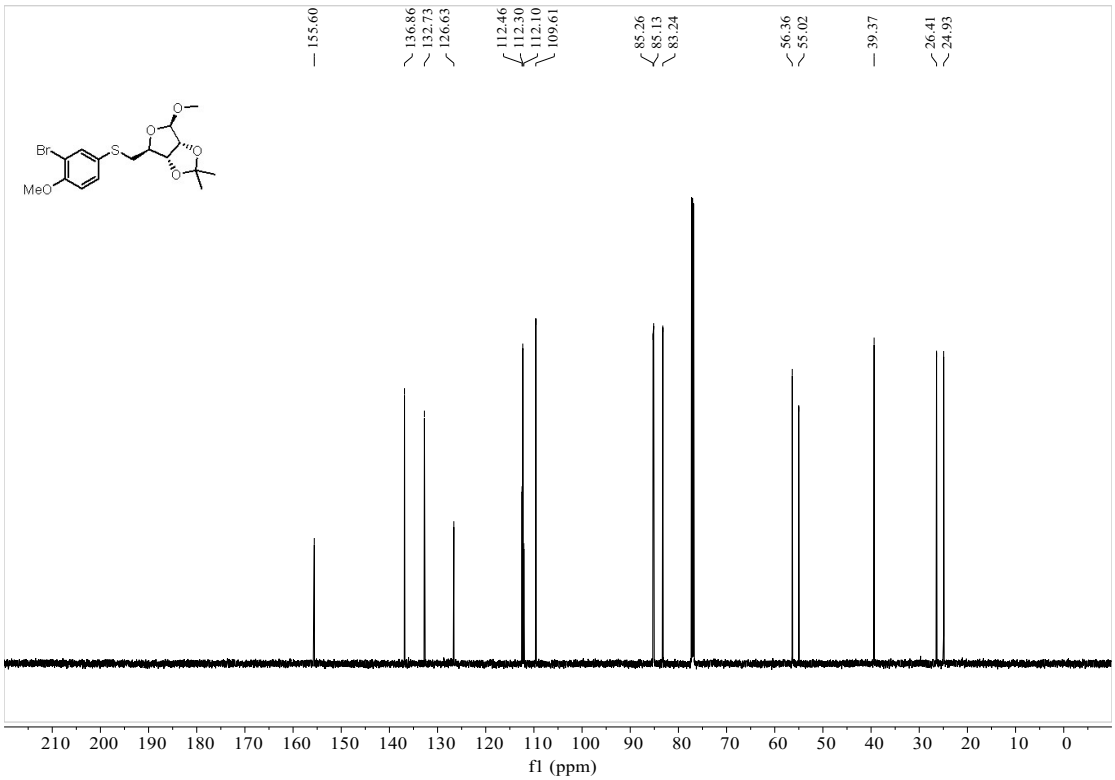
^{19}F NMR (565 MHz, Chloroform-*d*) spectrum of compound 47



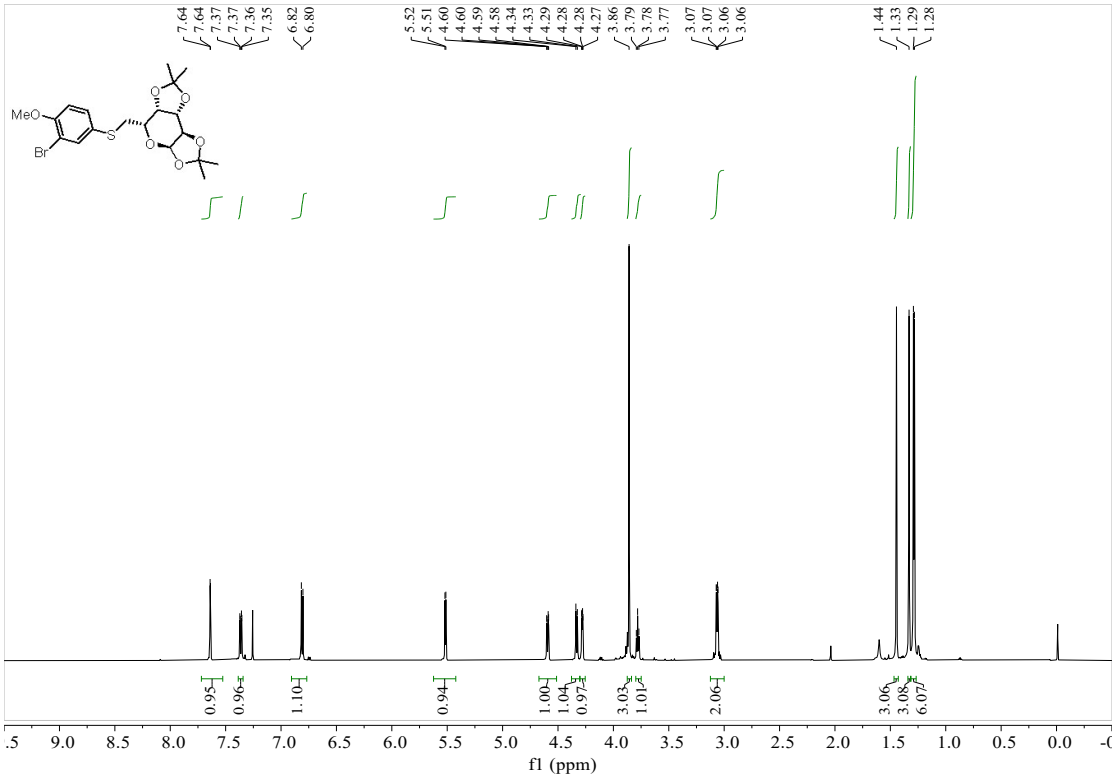
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 48



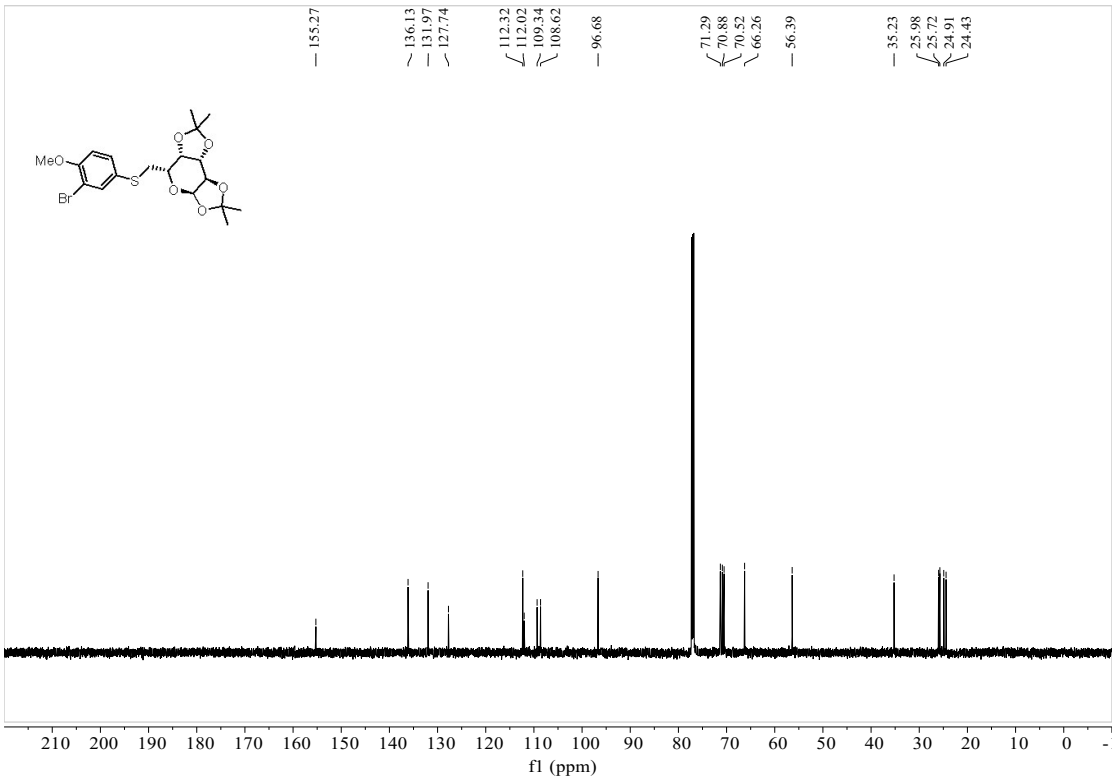
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 48



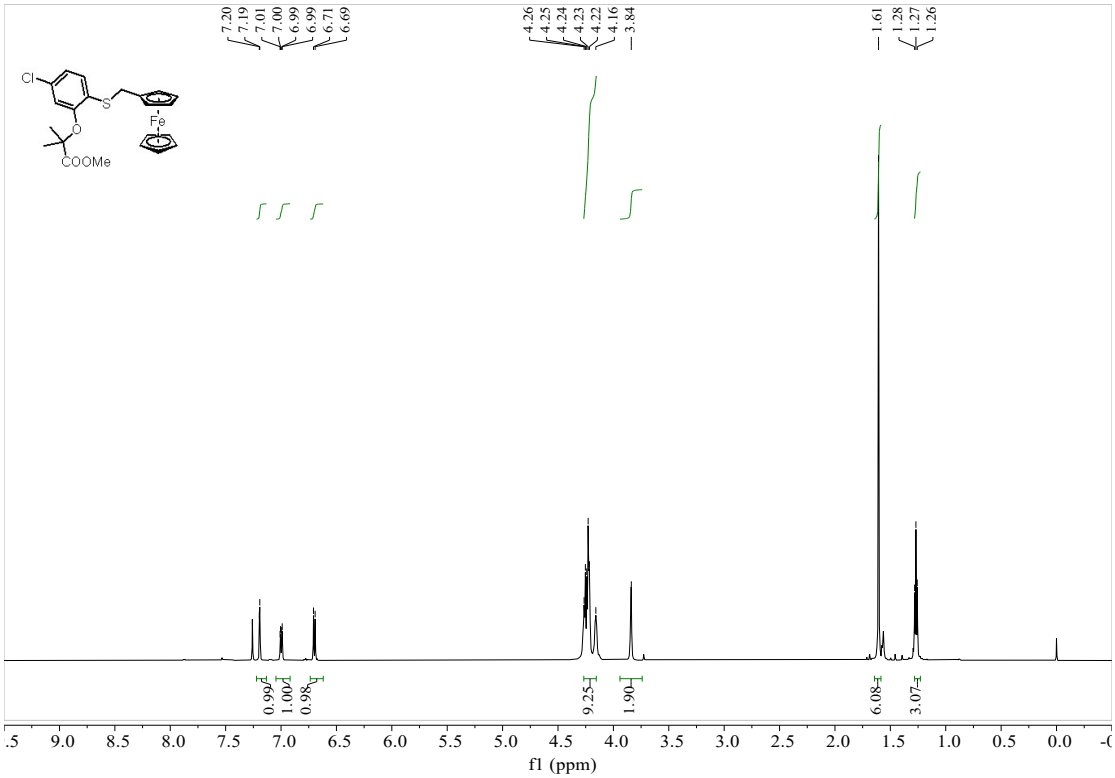
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 49



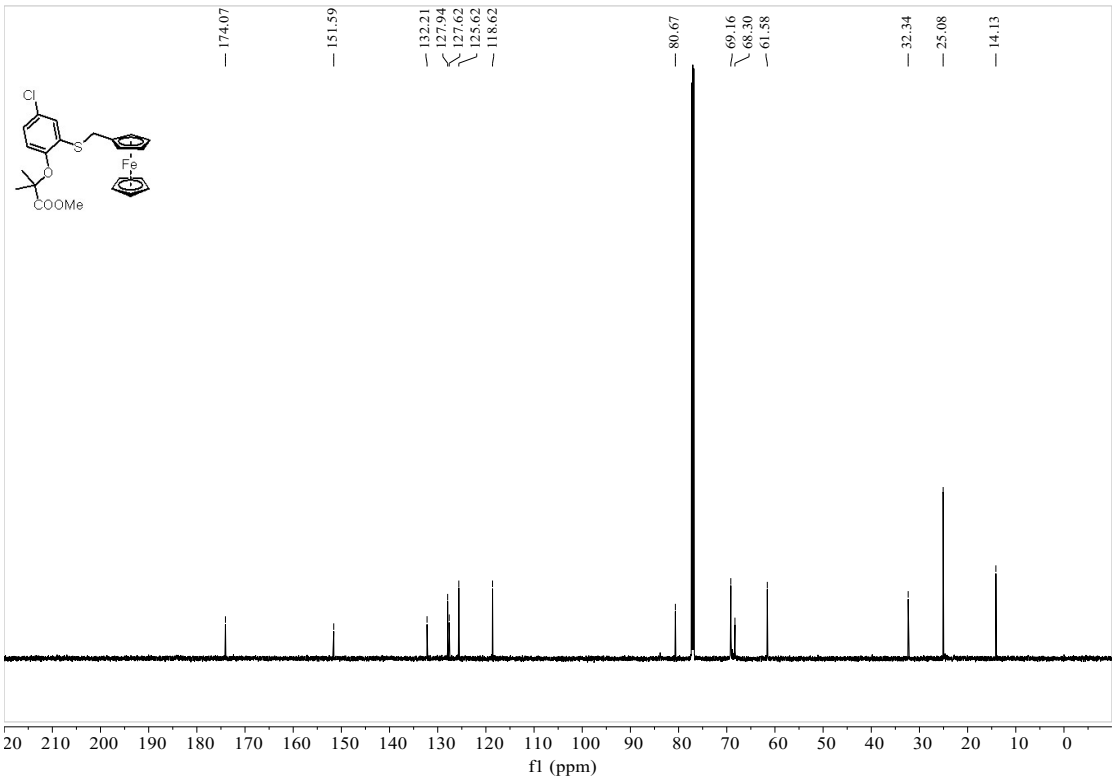
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 49



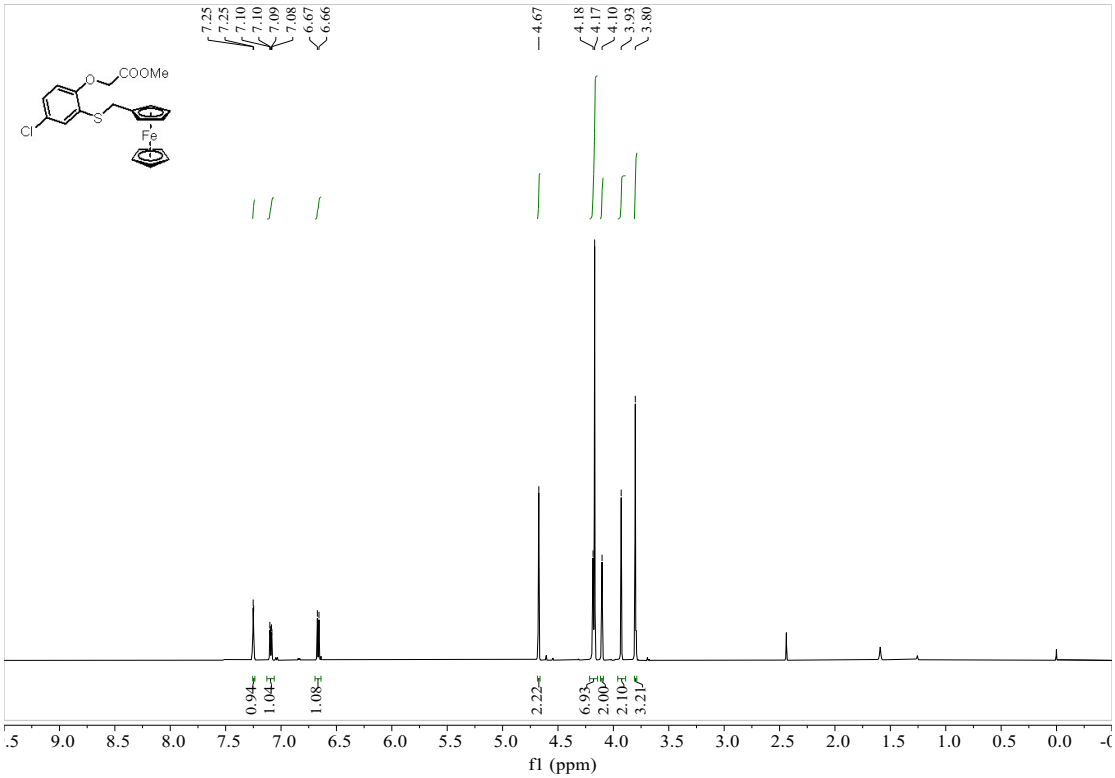
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 50



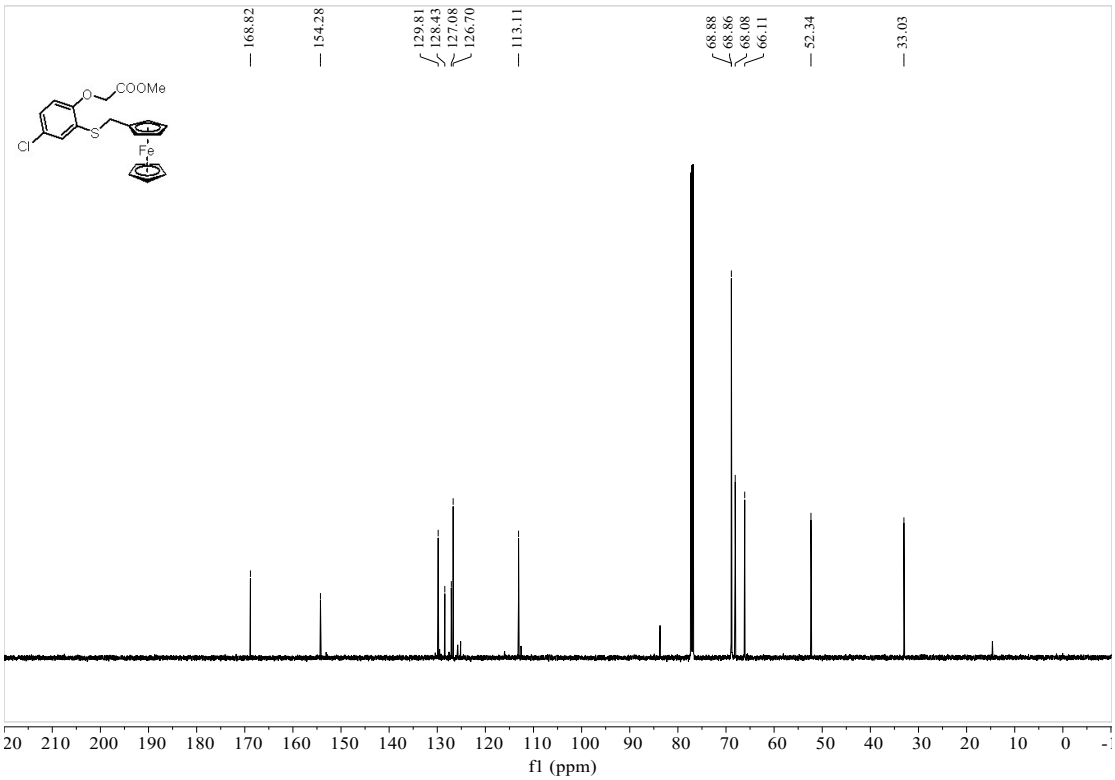
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 50



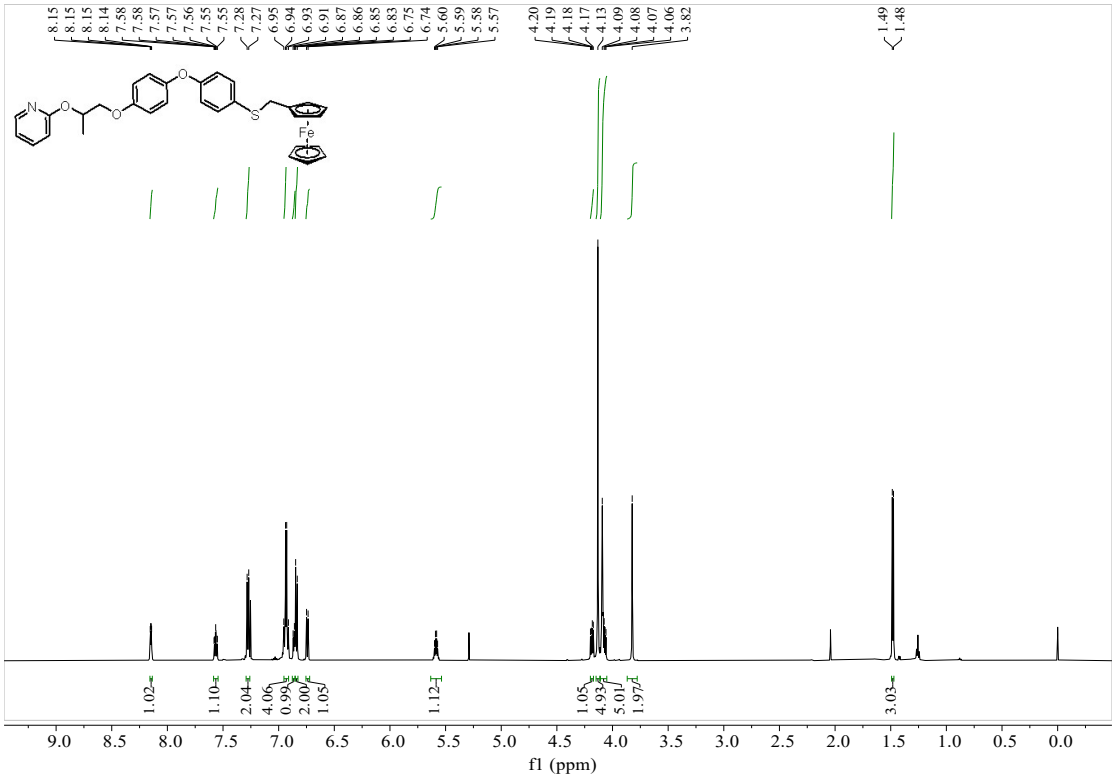
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 51



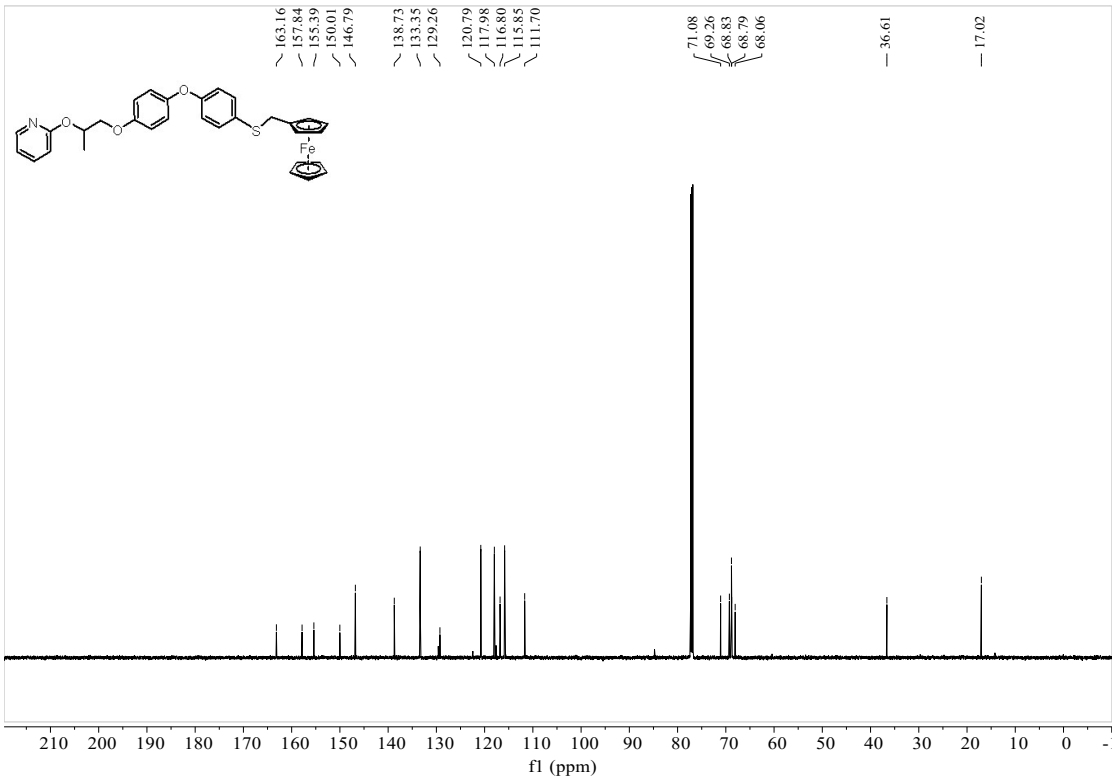
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 51



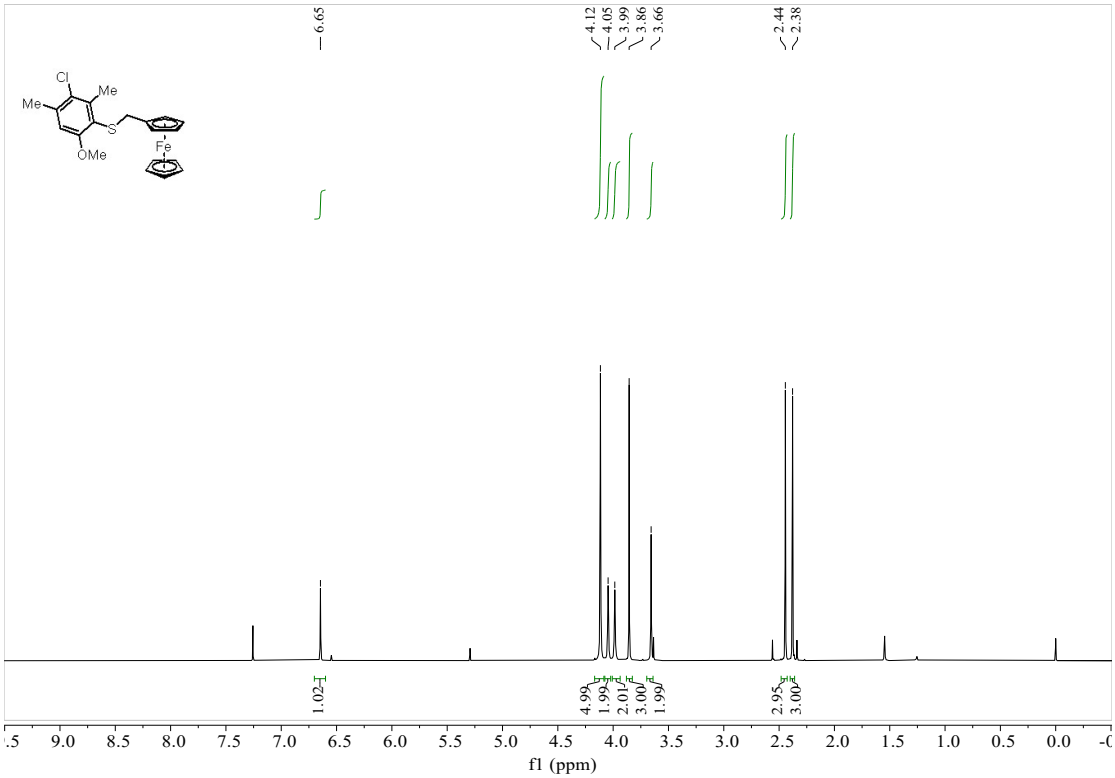
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 52



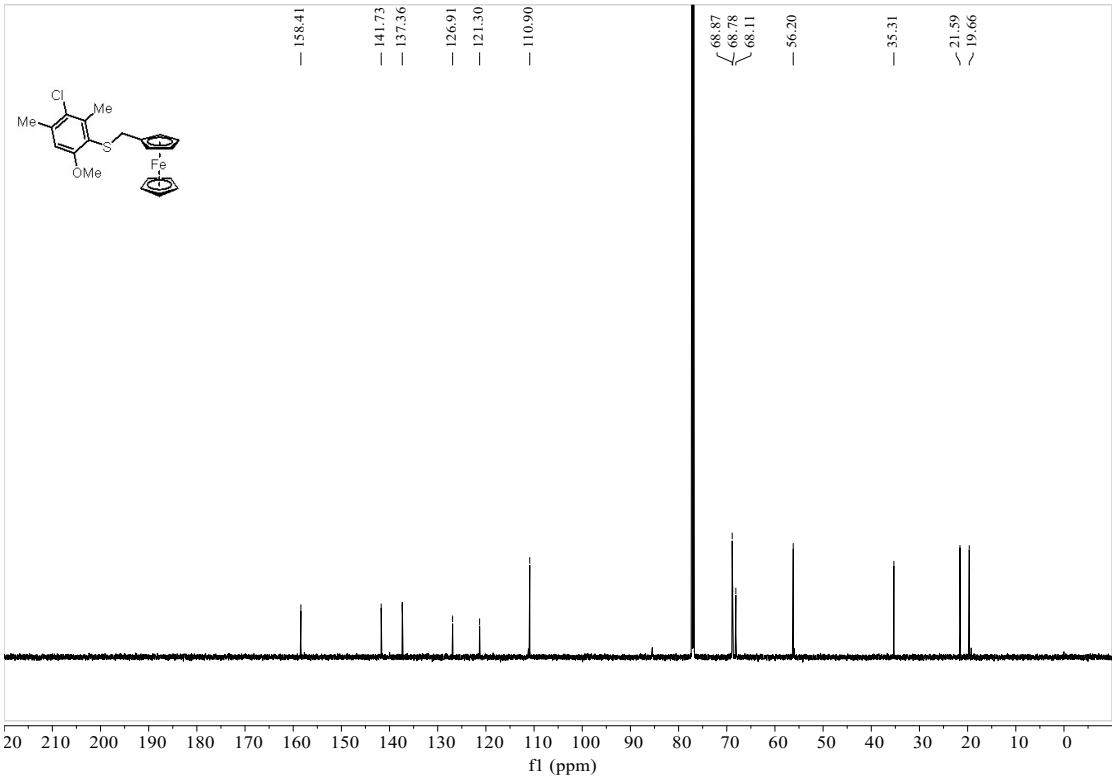
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 52



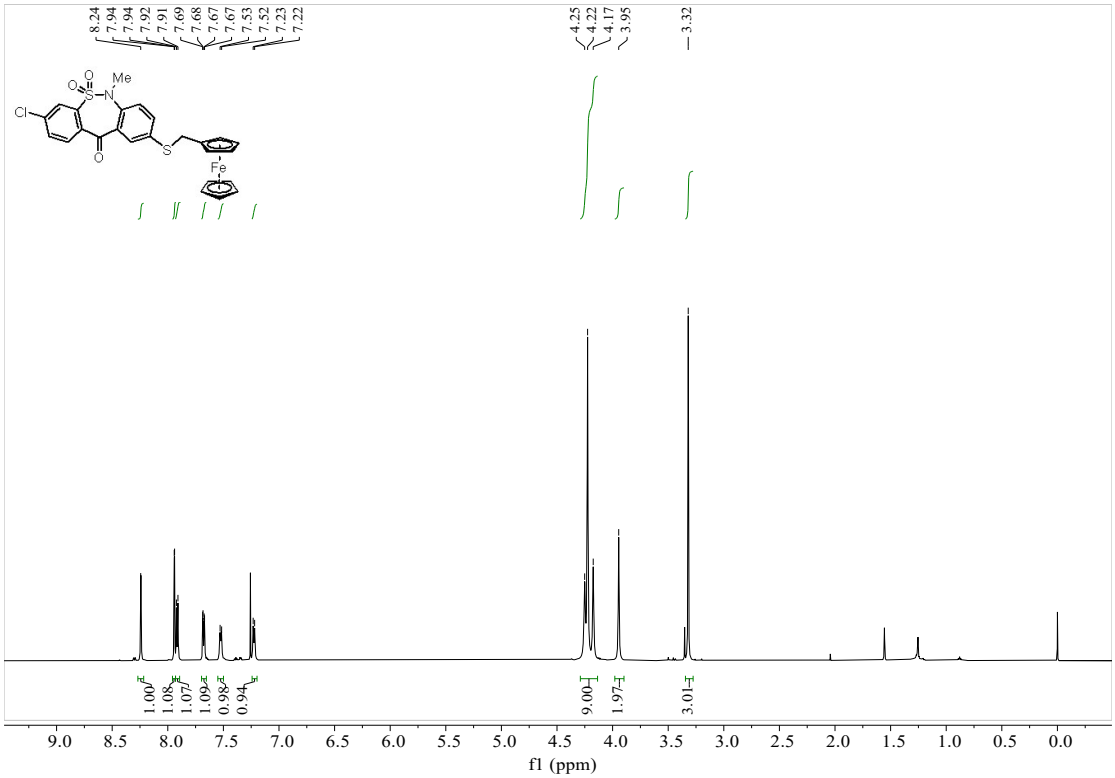
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 53



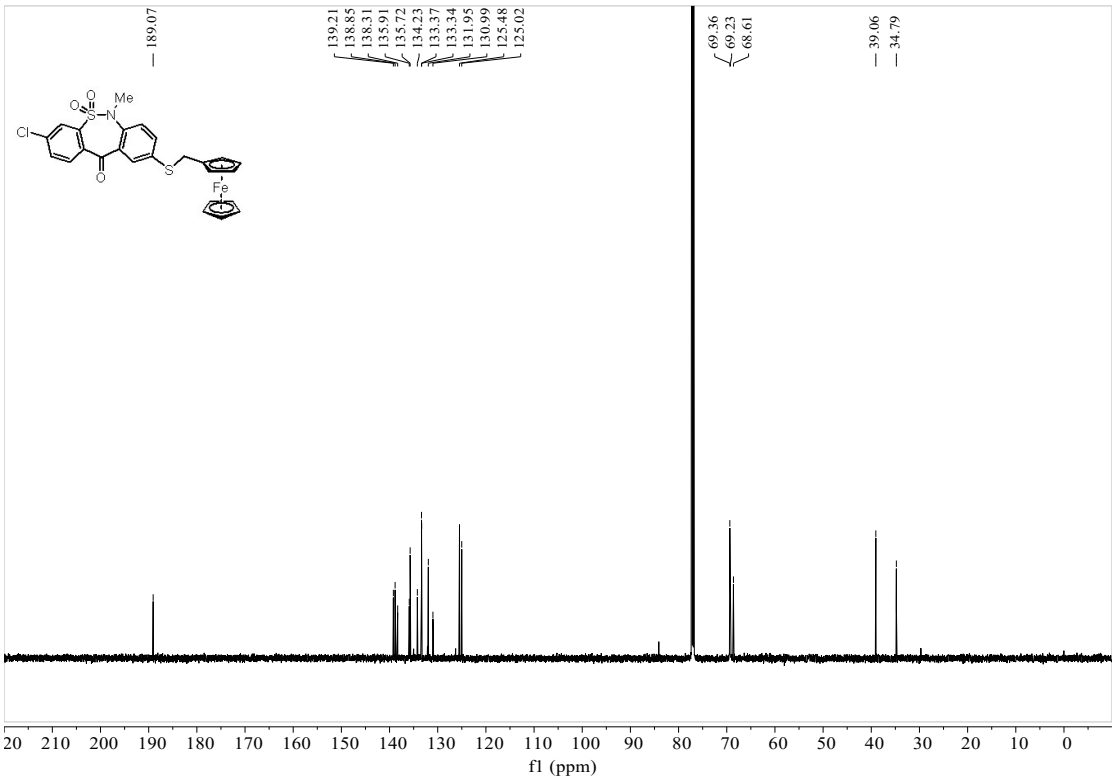
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 53



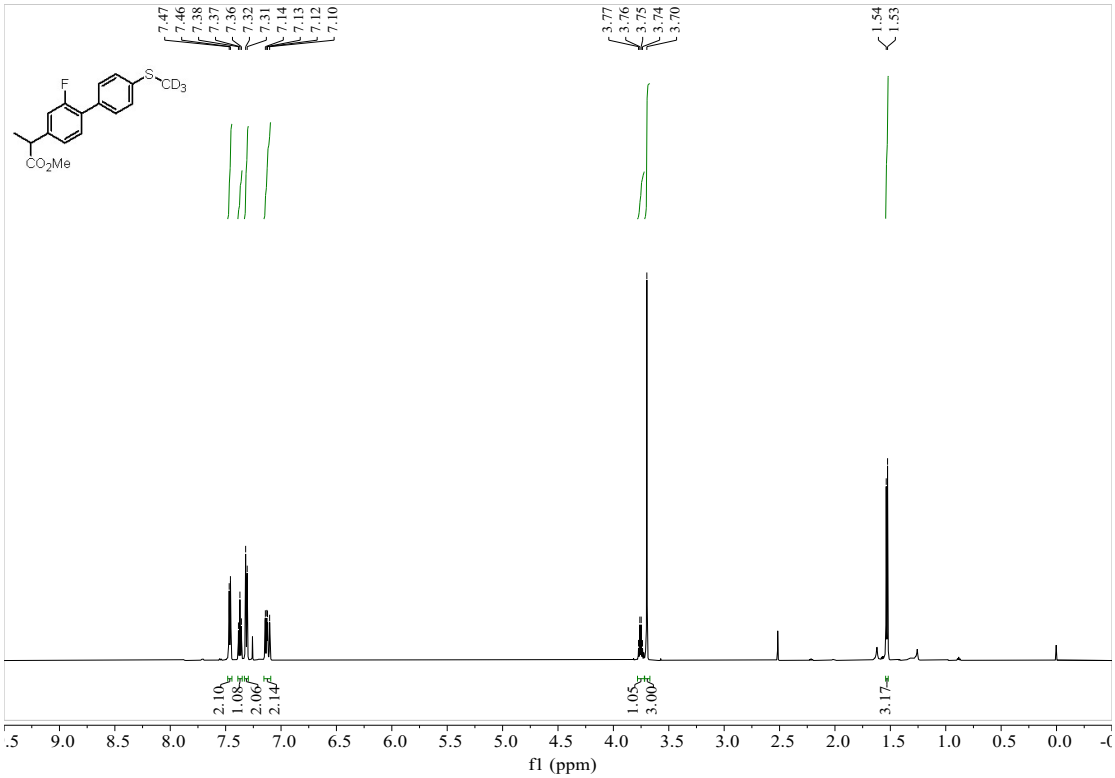
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 54



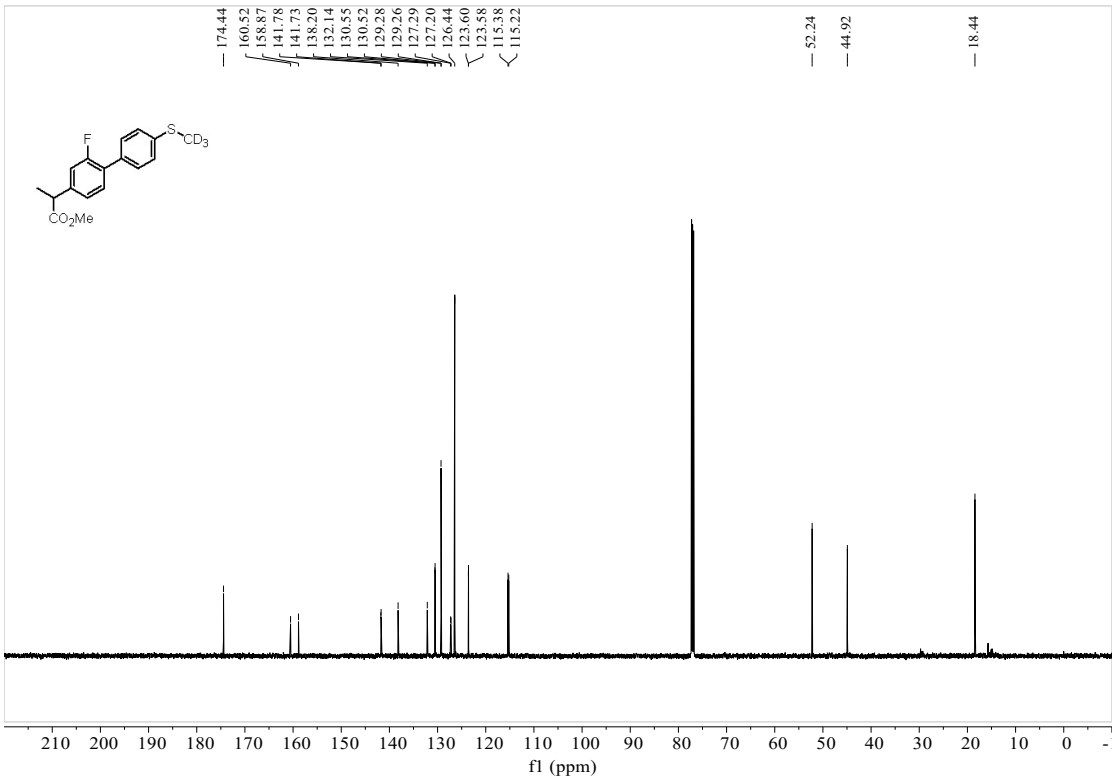
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 54



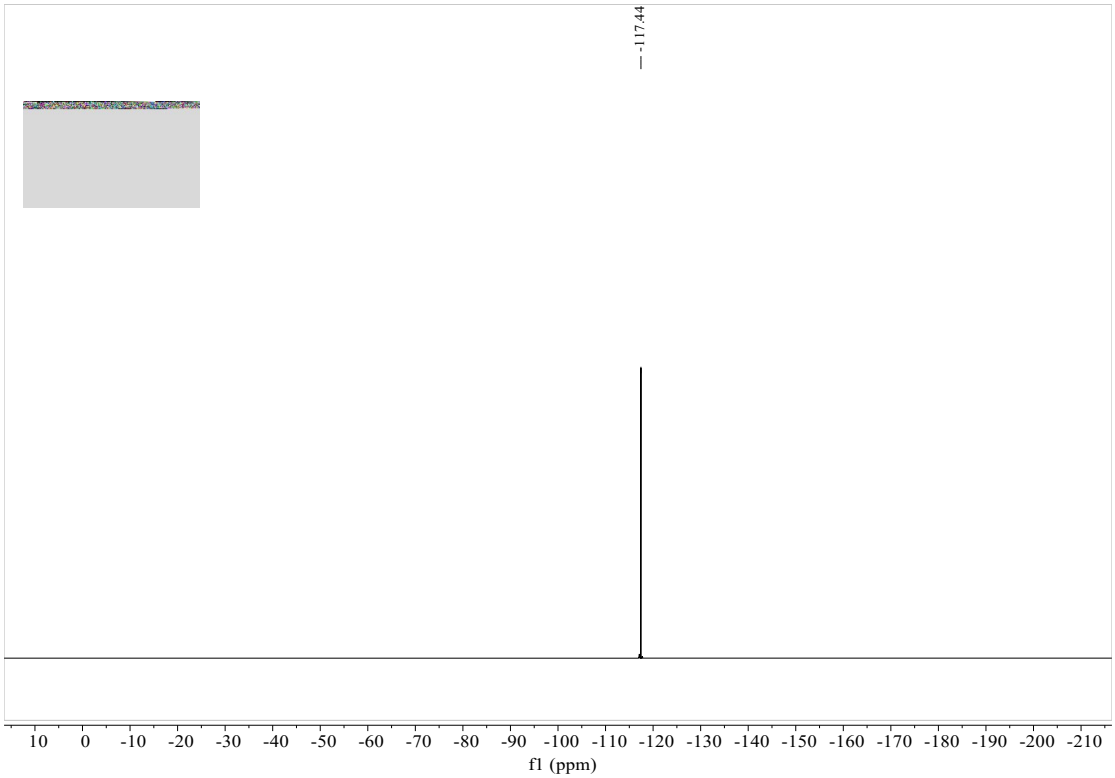
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 55



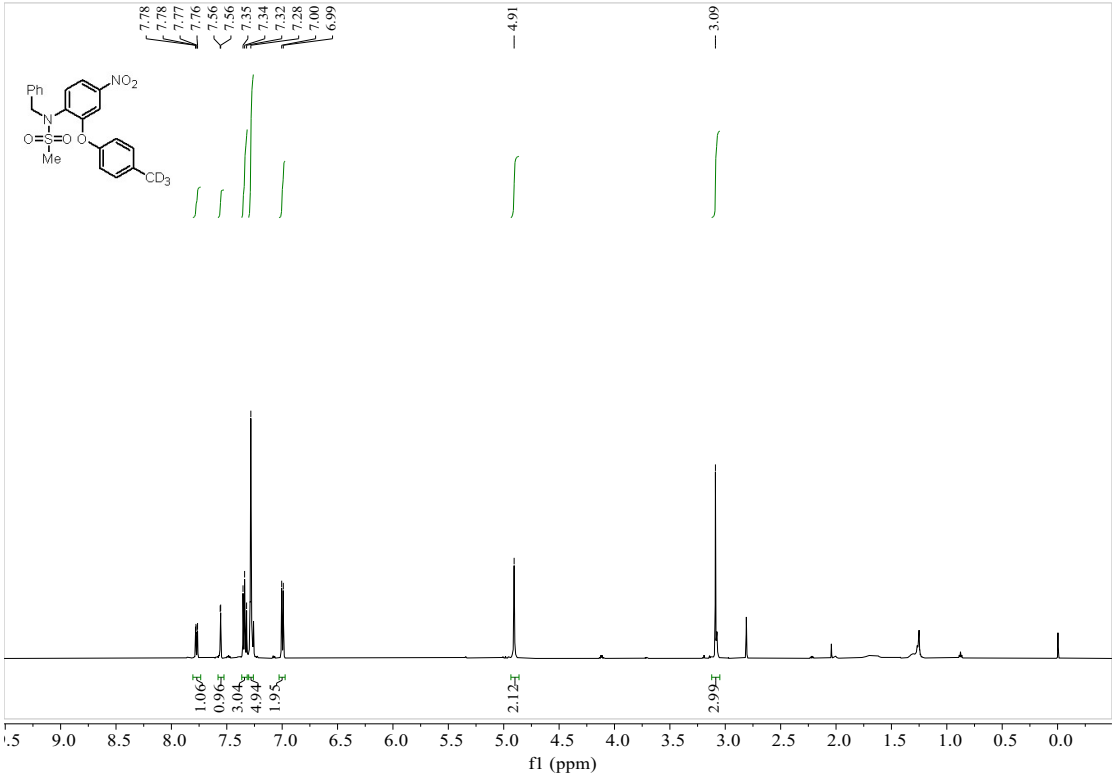
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 55



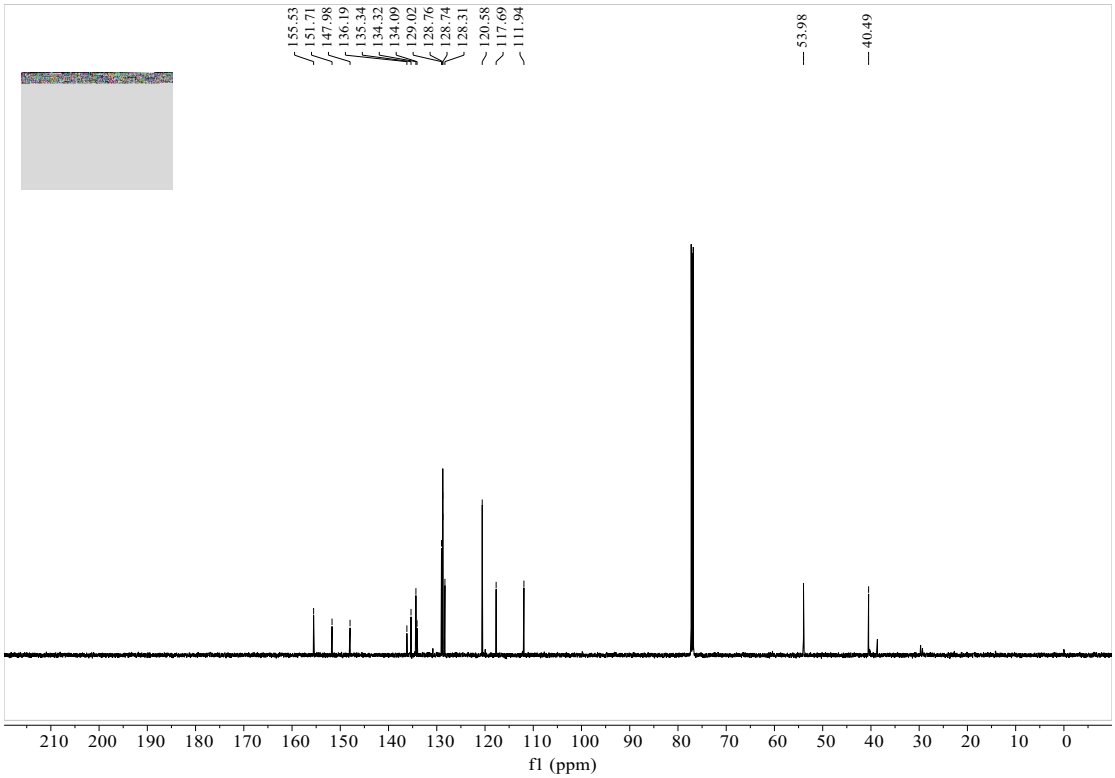
^{19}F NMR (565 MHz, Chloroform-*d*) spectrum of compound 55



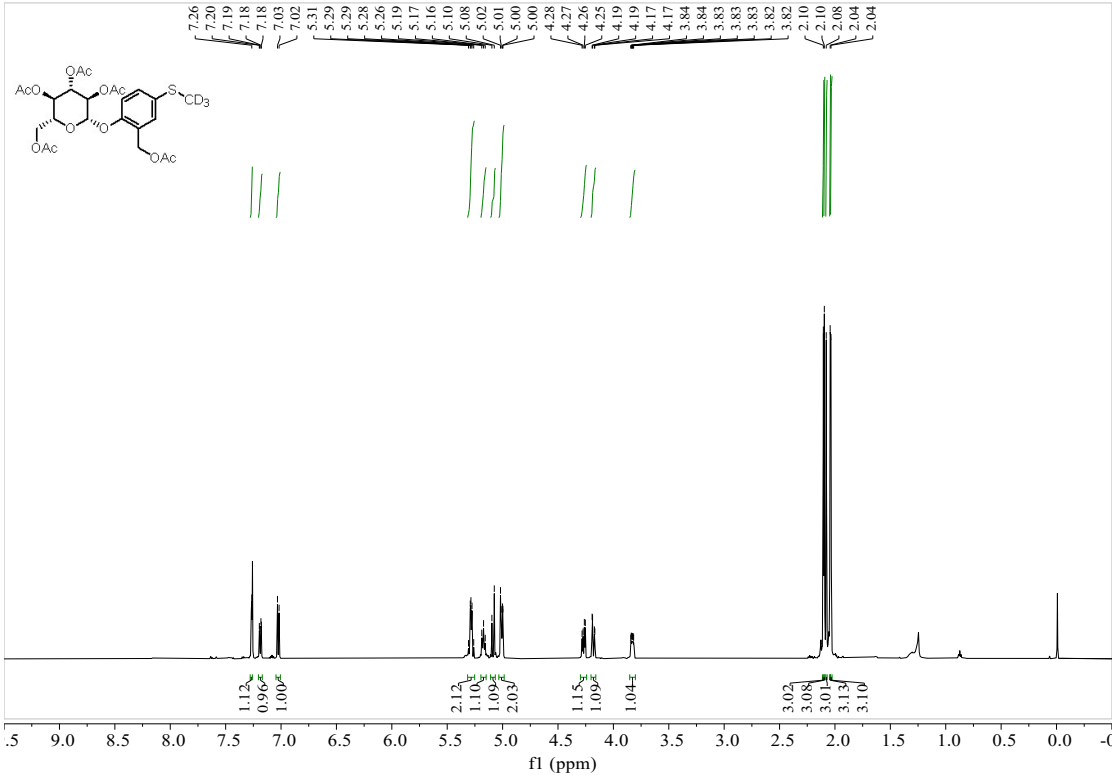
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 56



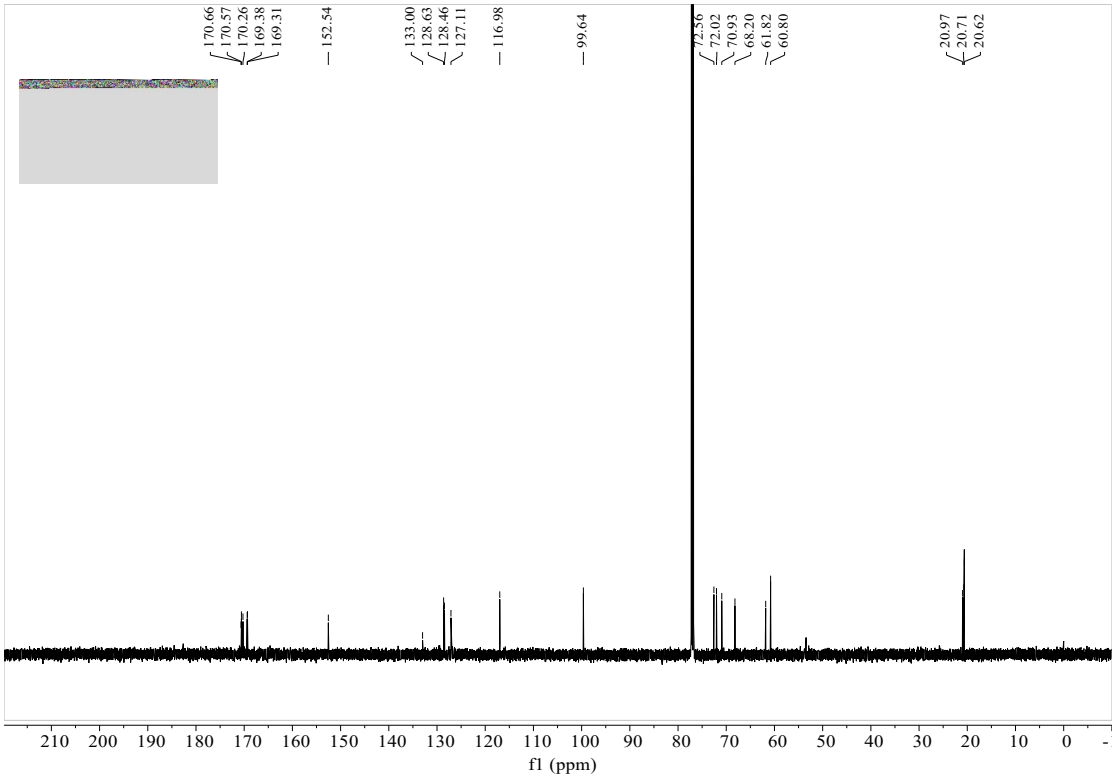
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 56



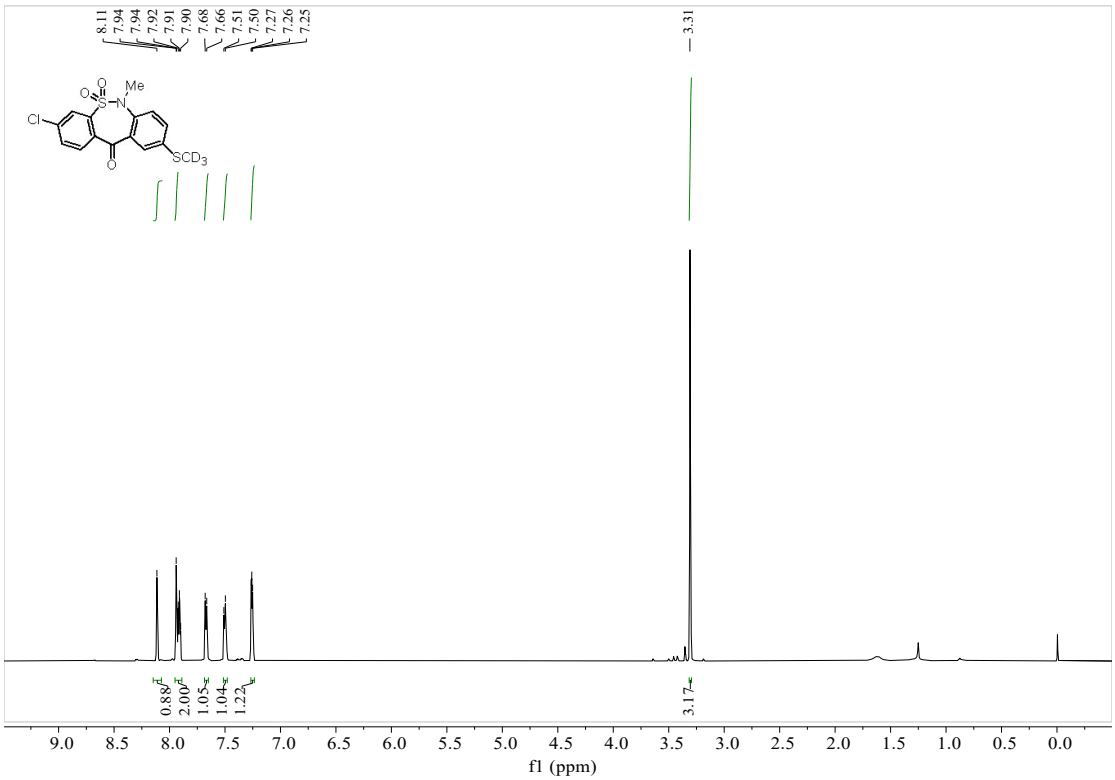
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 57



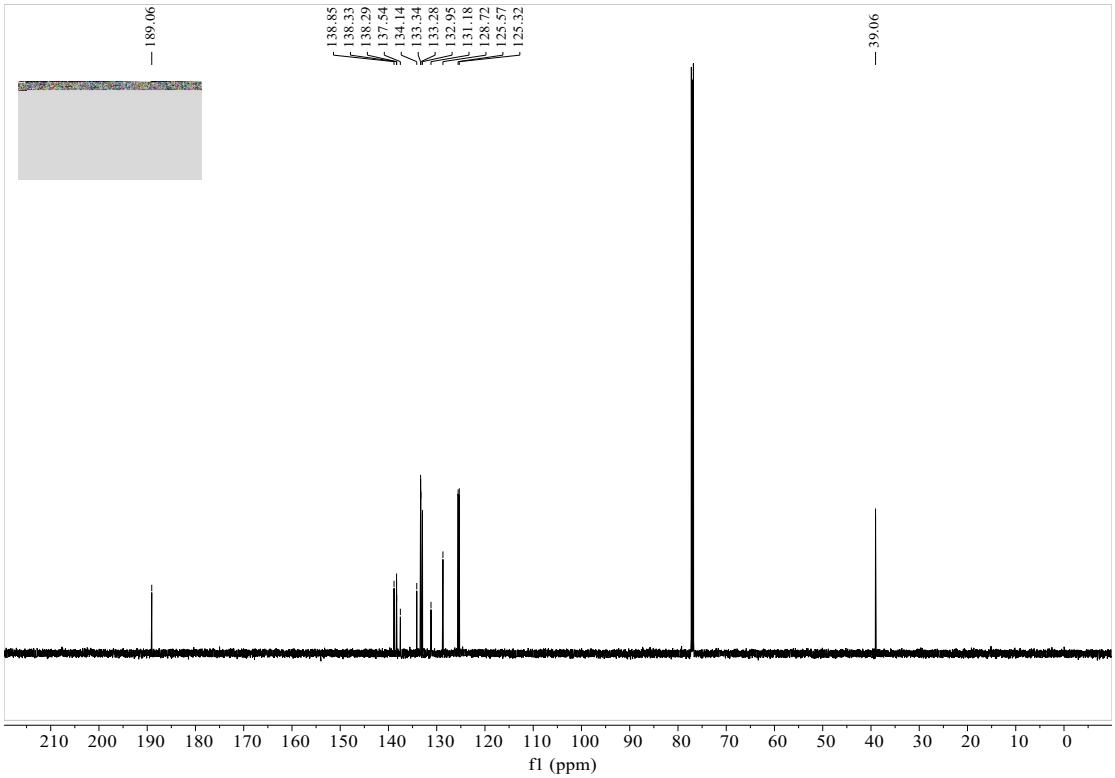
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 57



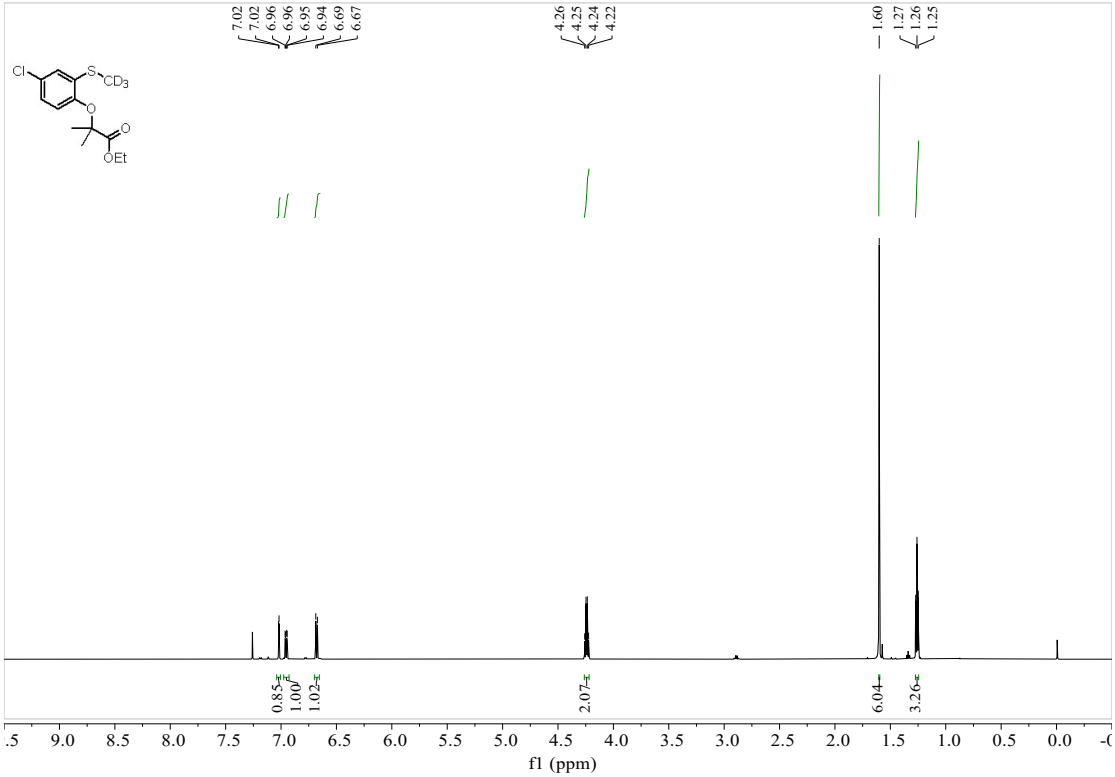
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 58



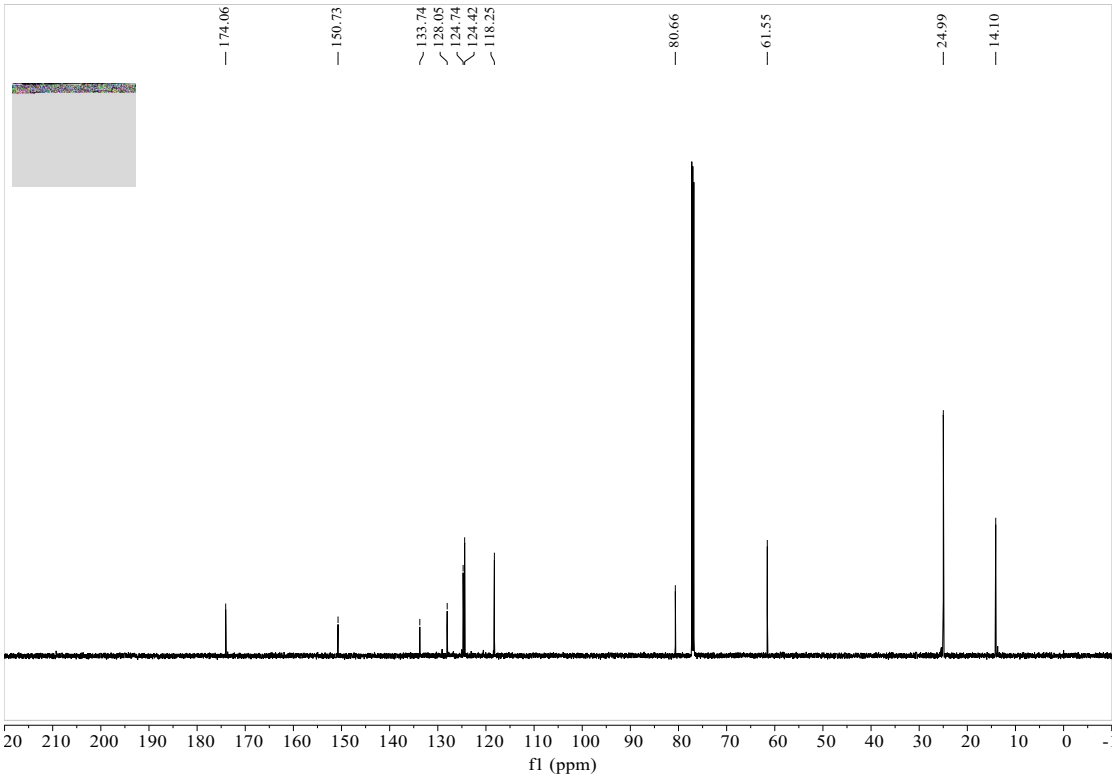
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 58



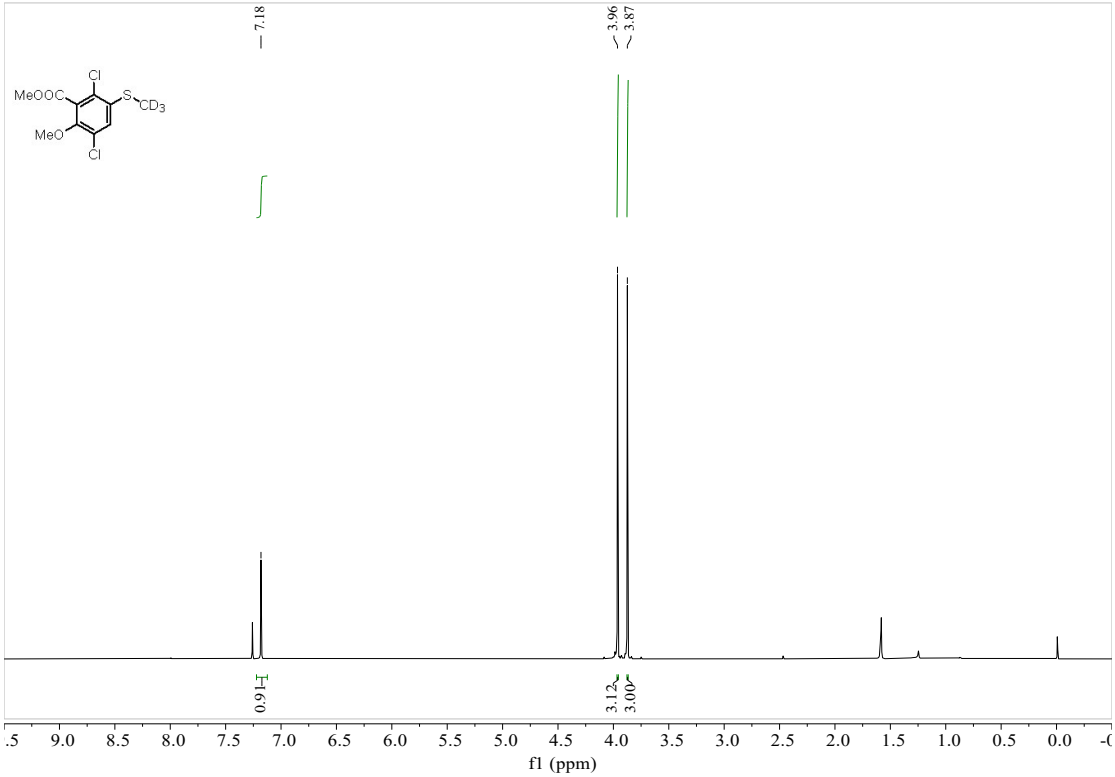
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 59



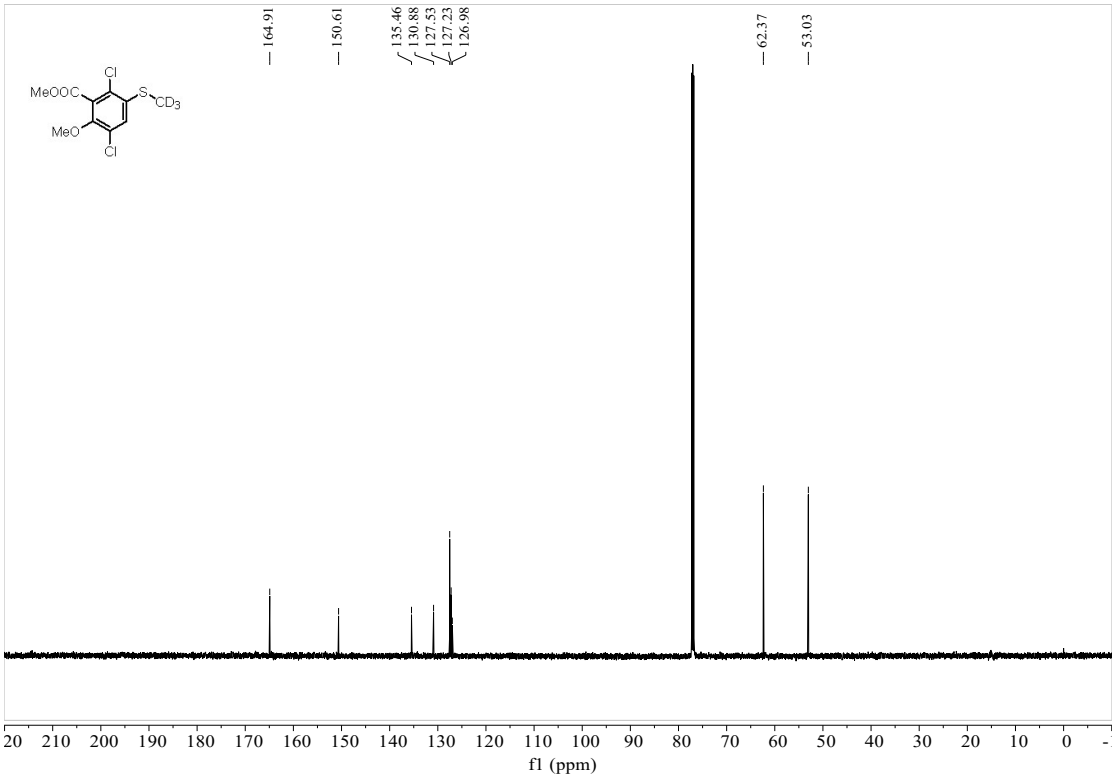
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 59



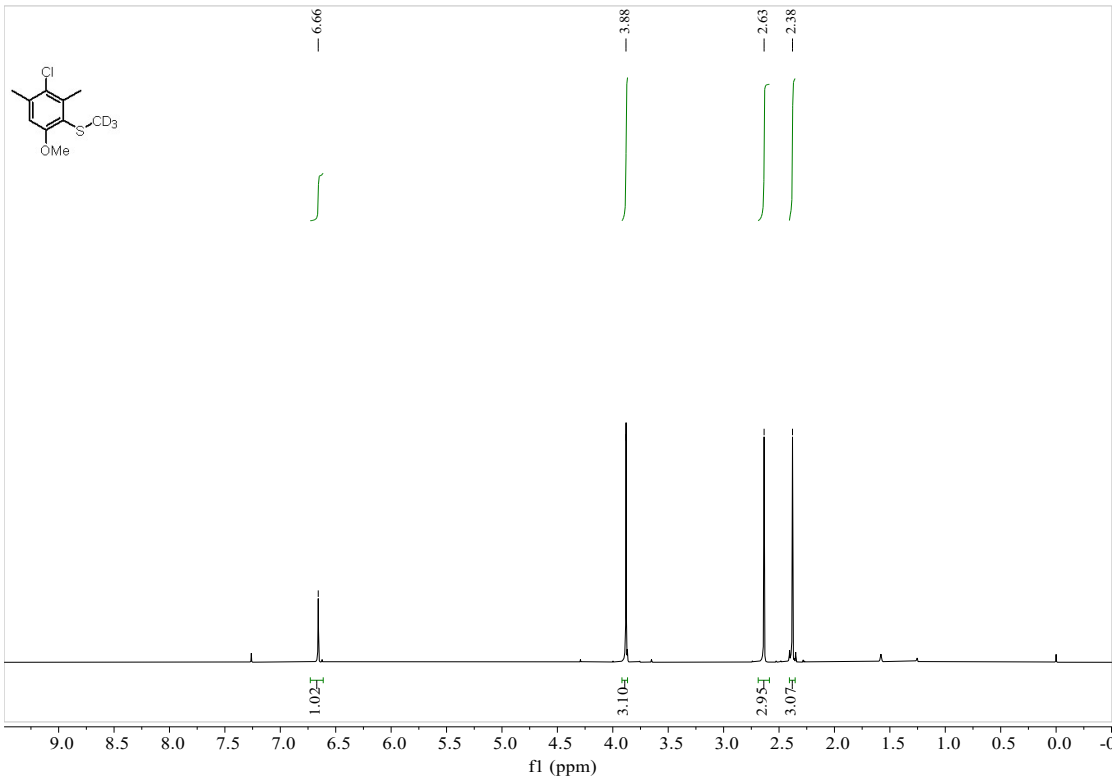
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 60



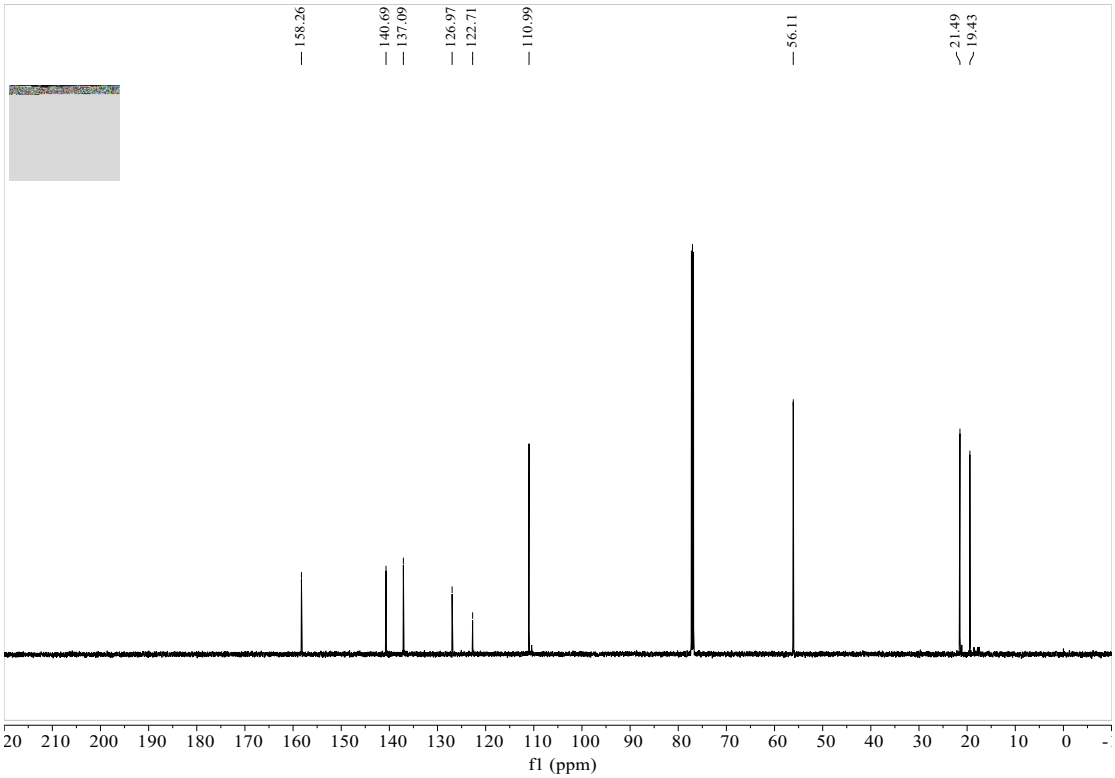
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 60



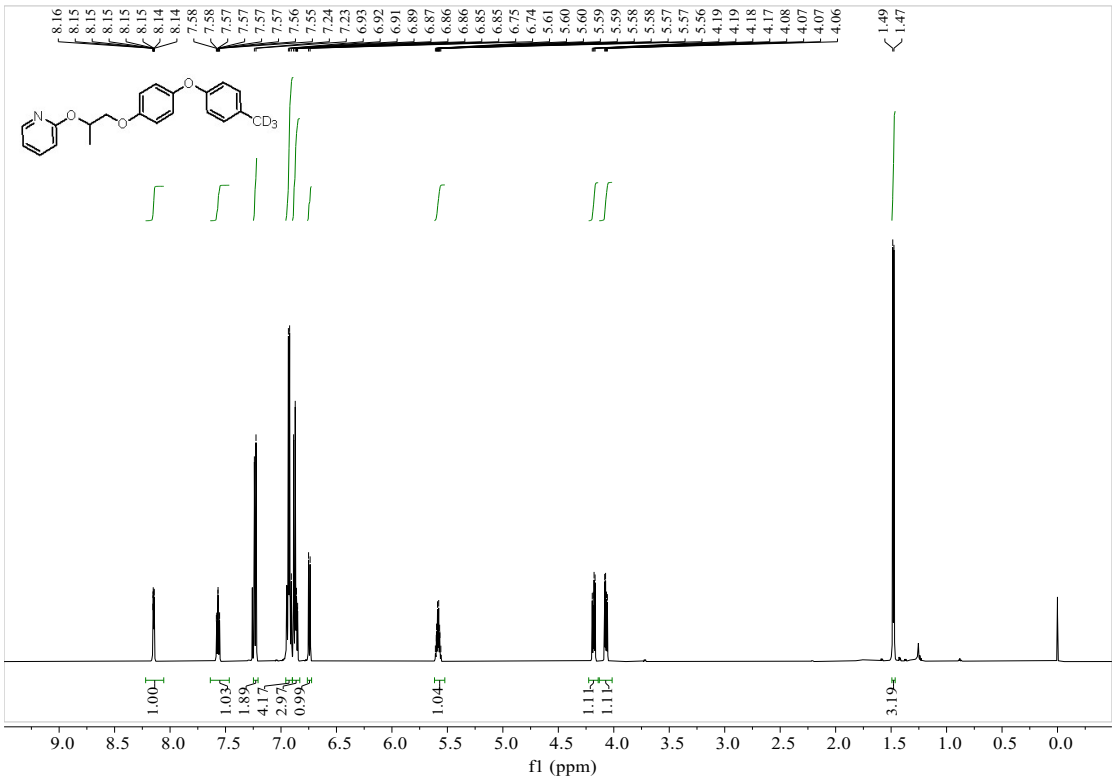
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 61



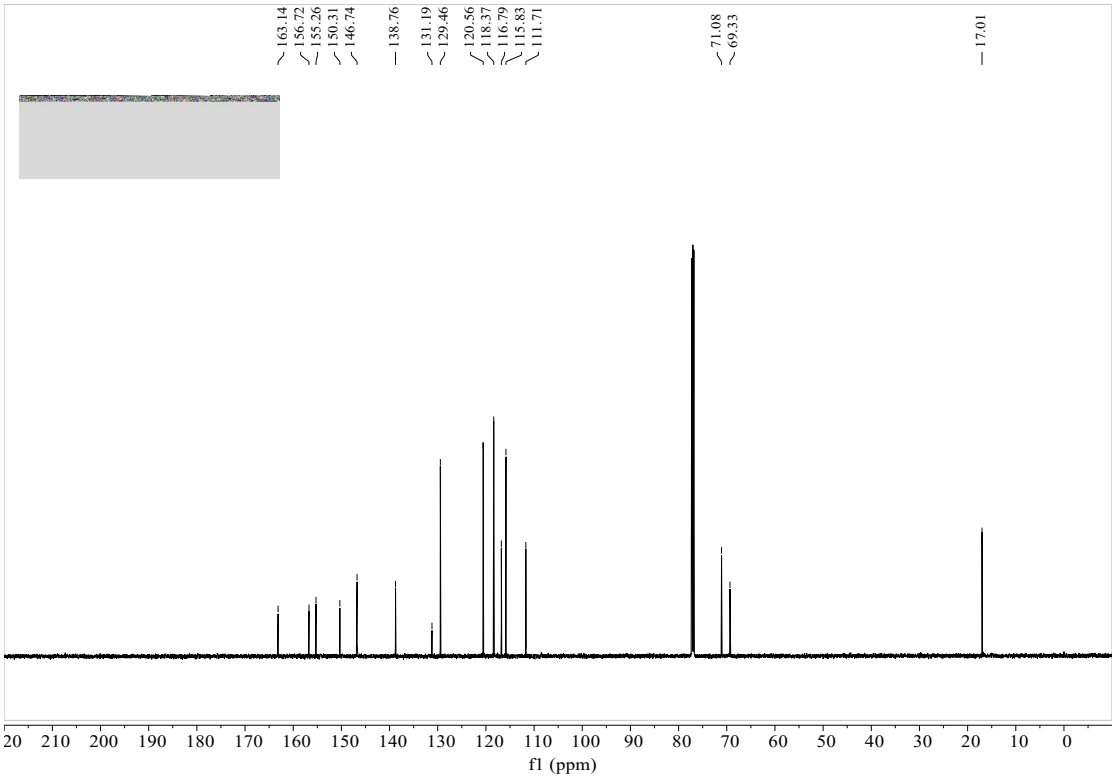
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 61



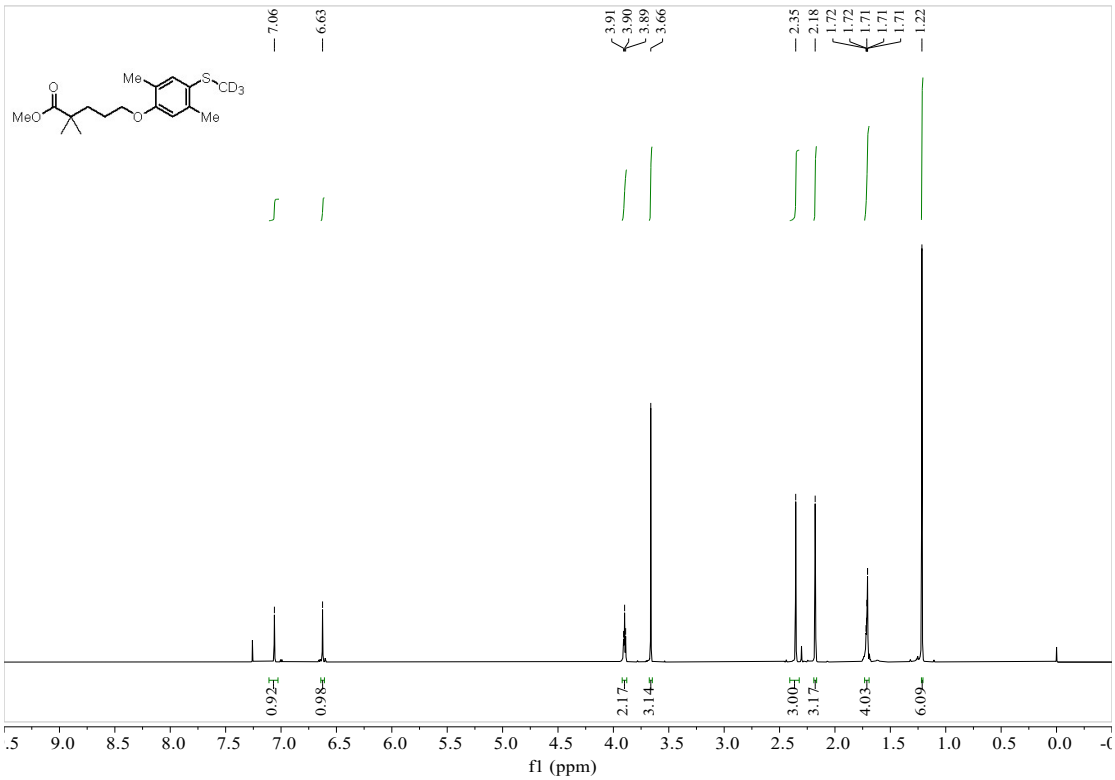
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 62



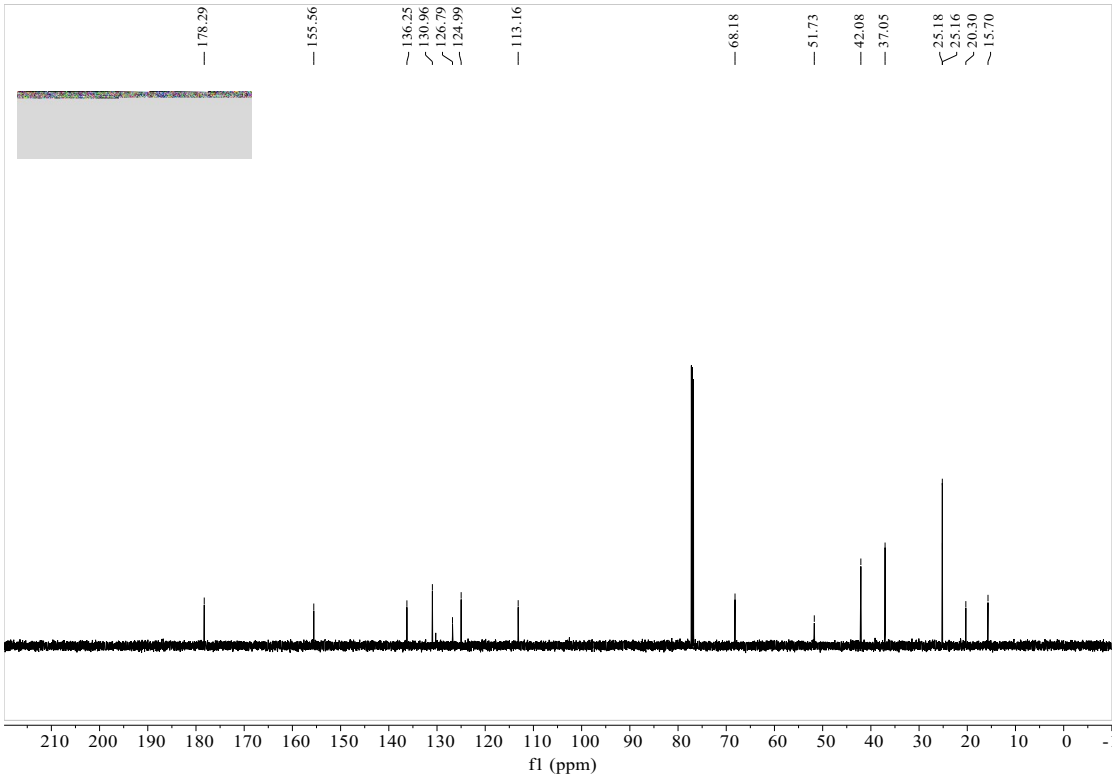
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 62



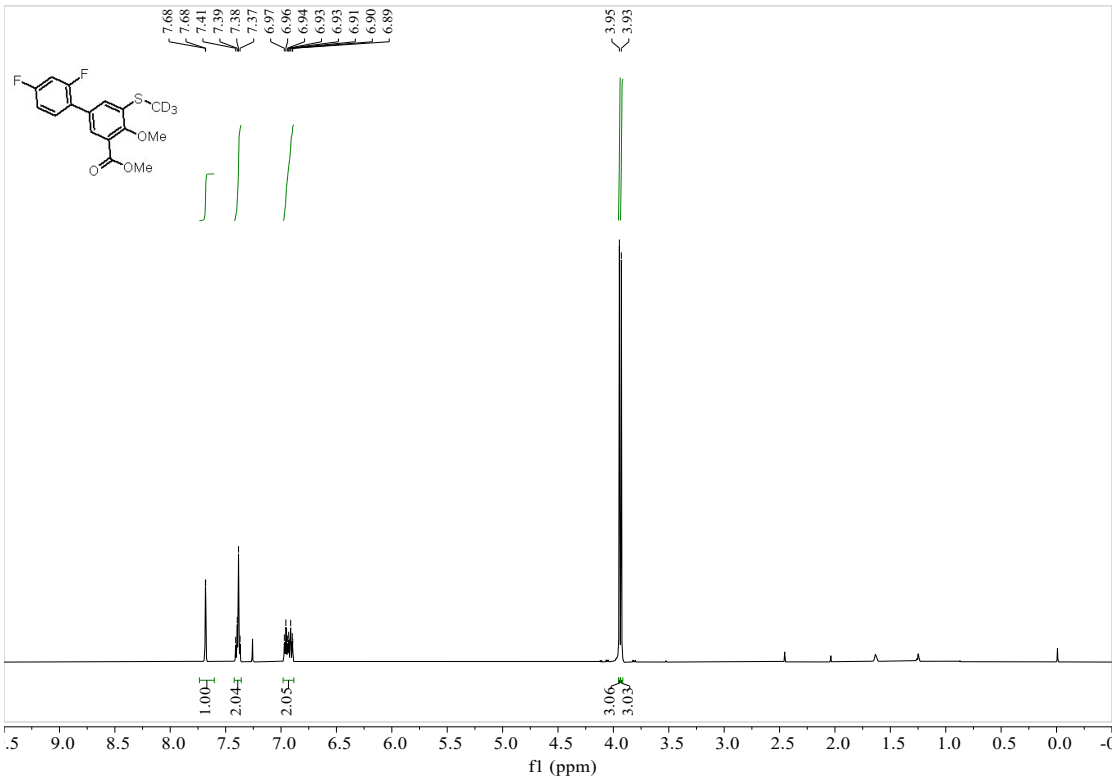
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 63



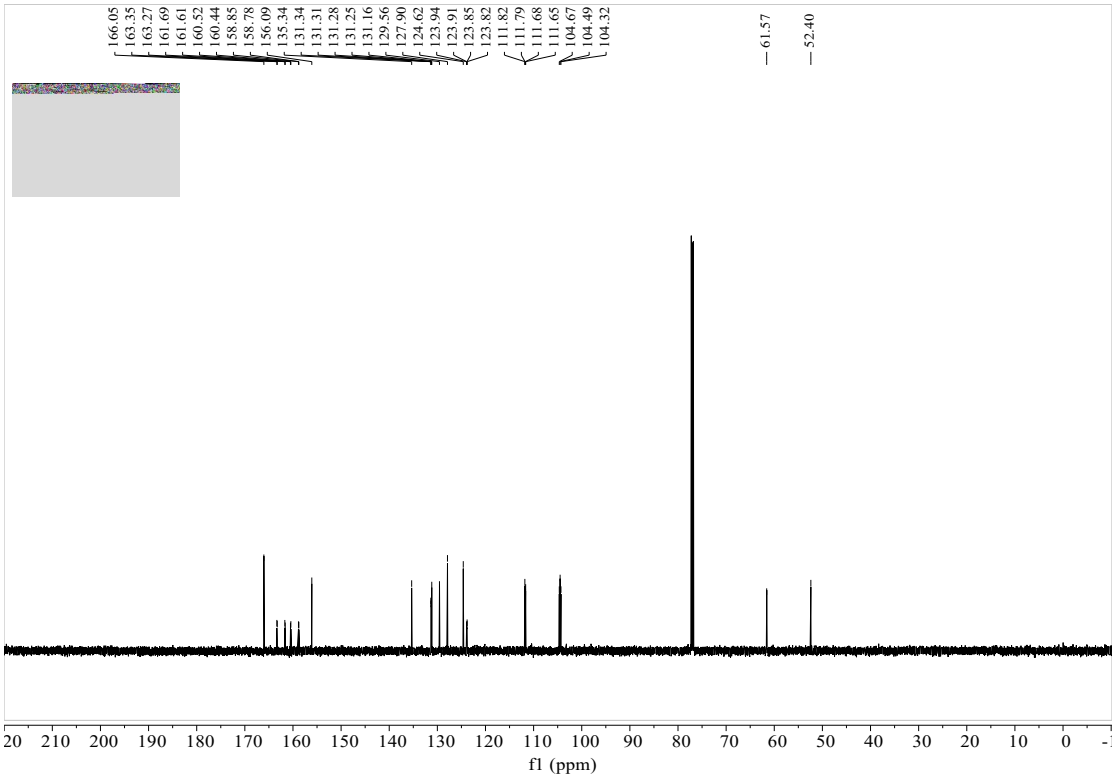
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 63



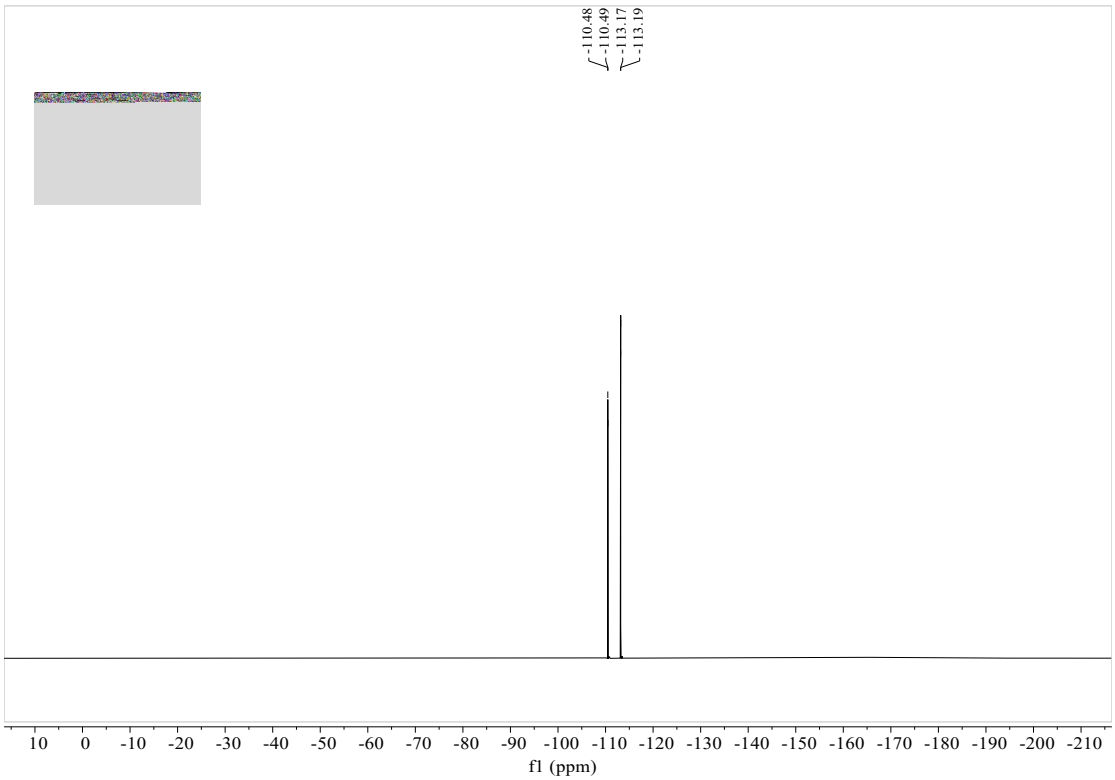
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 64



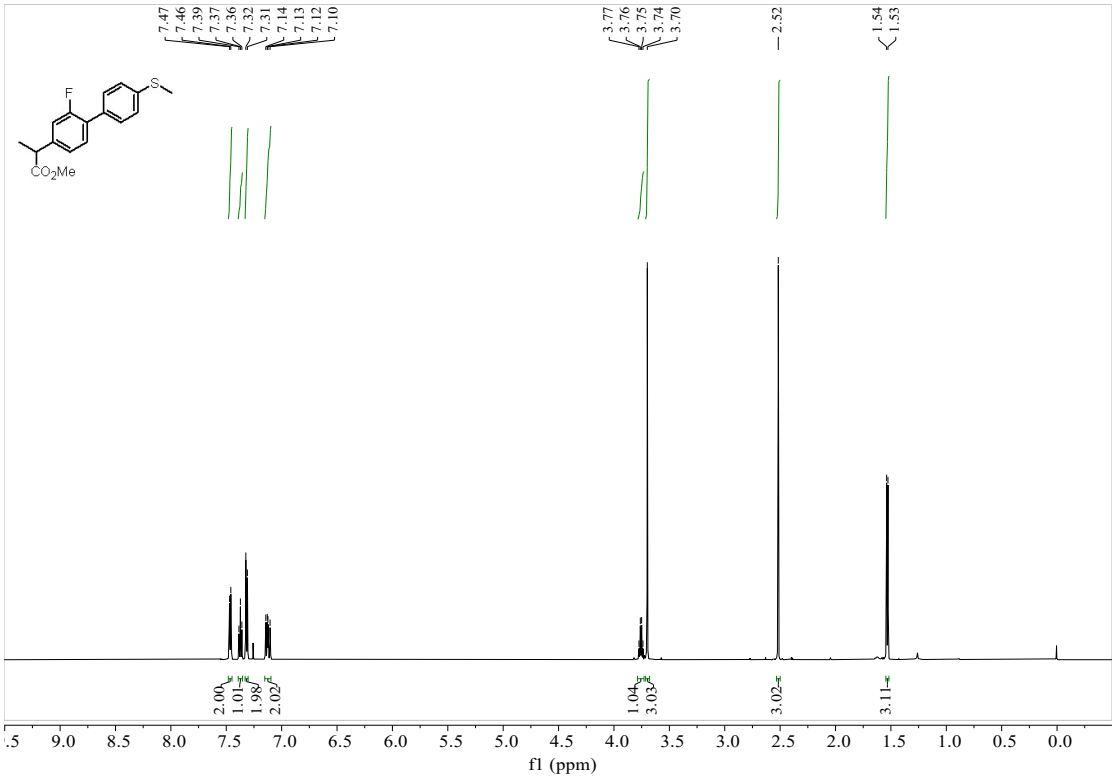
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 64



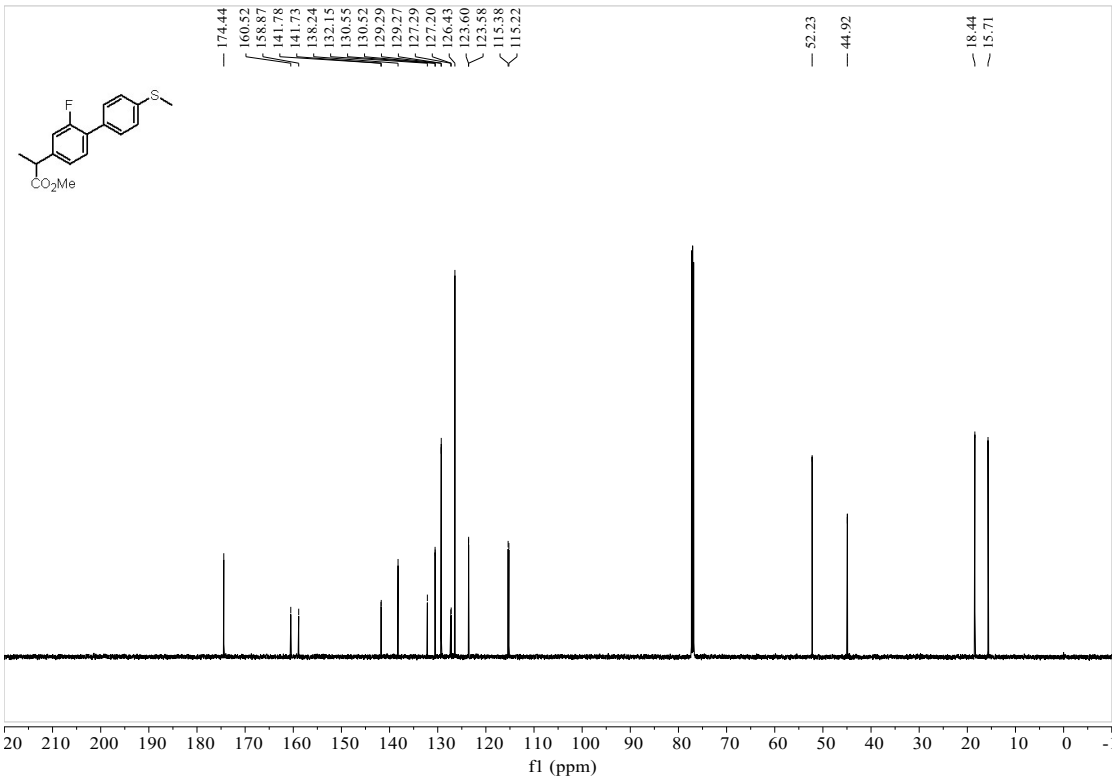
^{19}F NMR (565 MHz, Chloroform-*d*) spectrum of compound 64



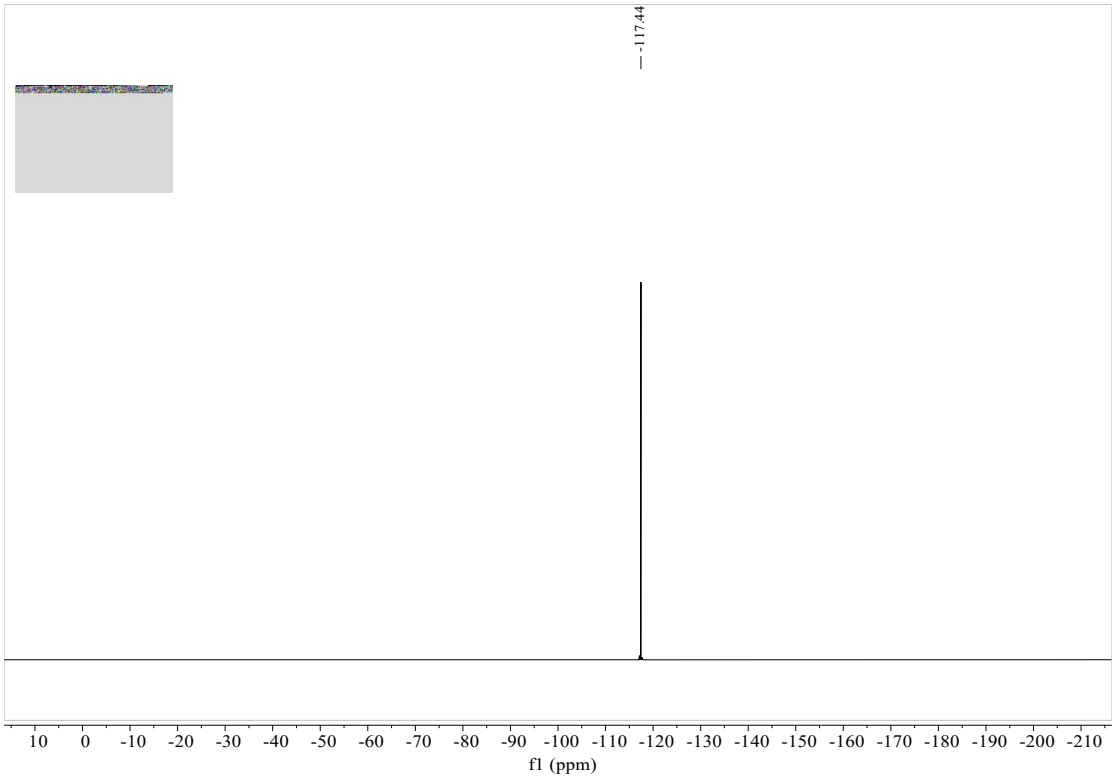
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 66



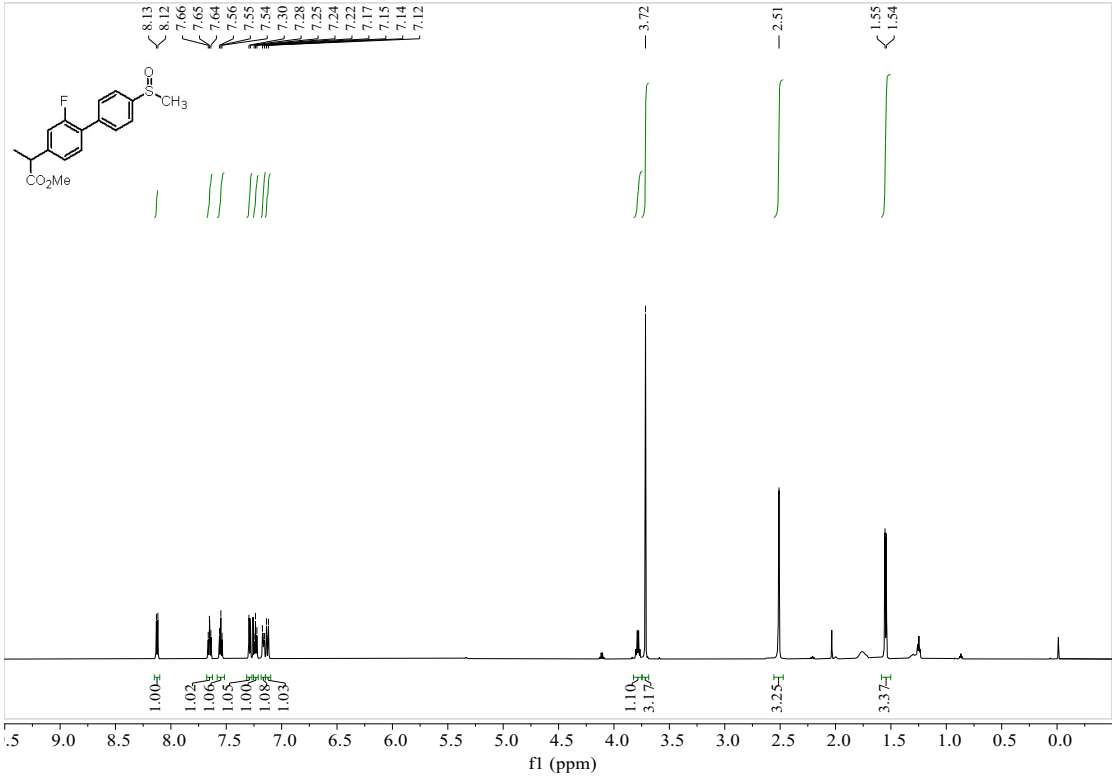
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 66



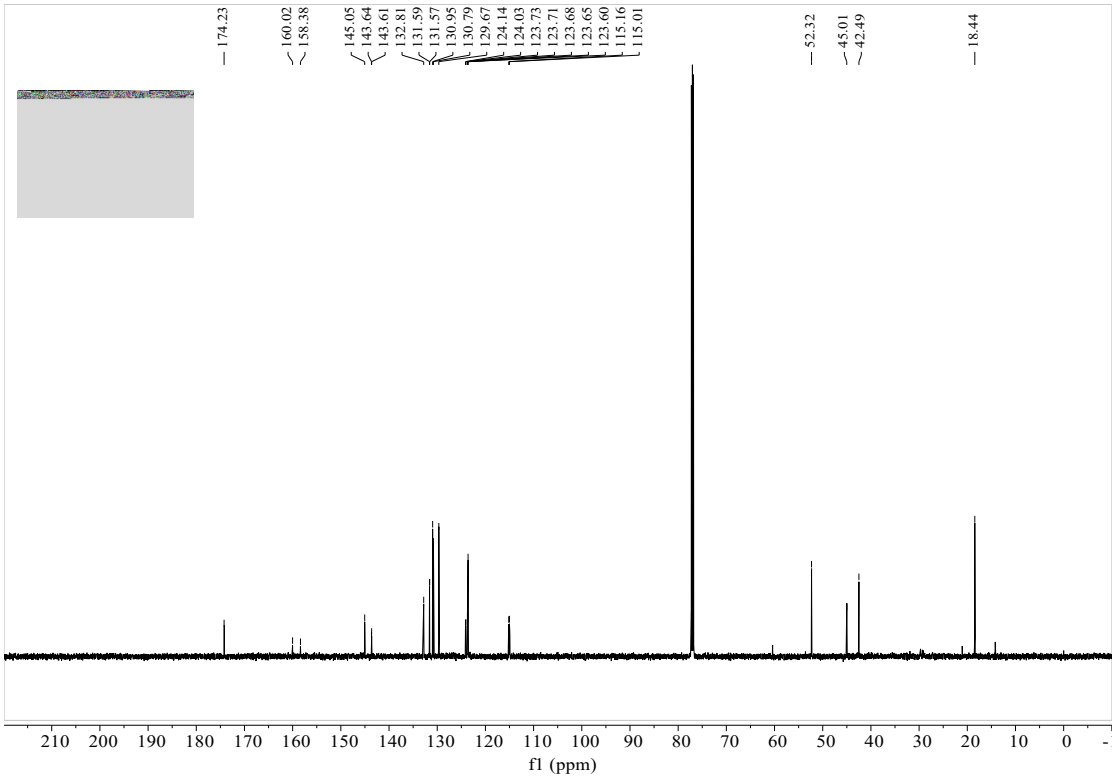
^{19}F NMR (565 MHz, Chloroform-*d*) spectrum of compound 66



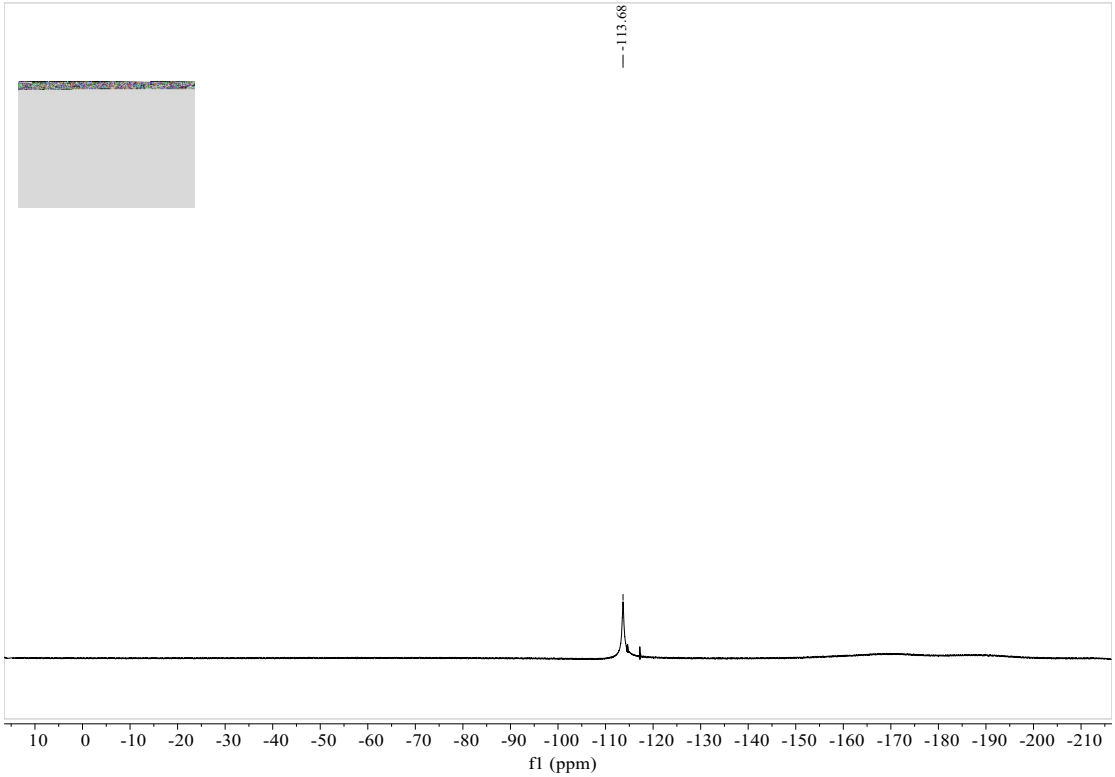
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 67



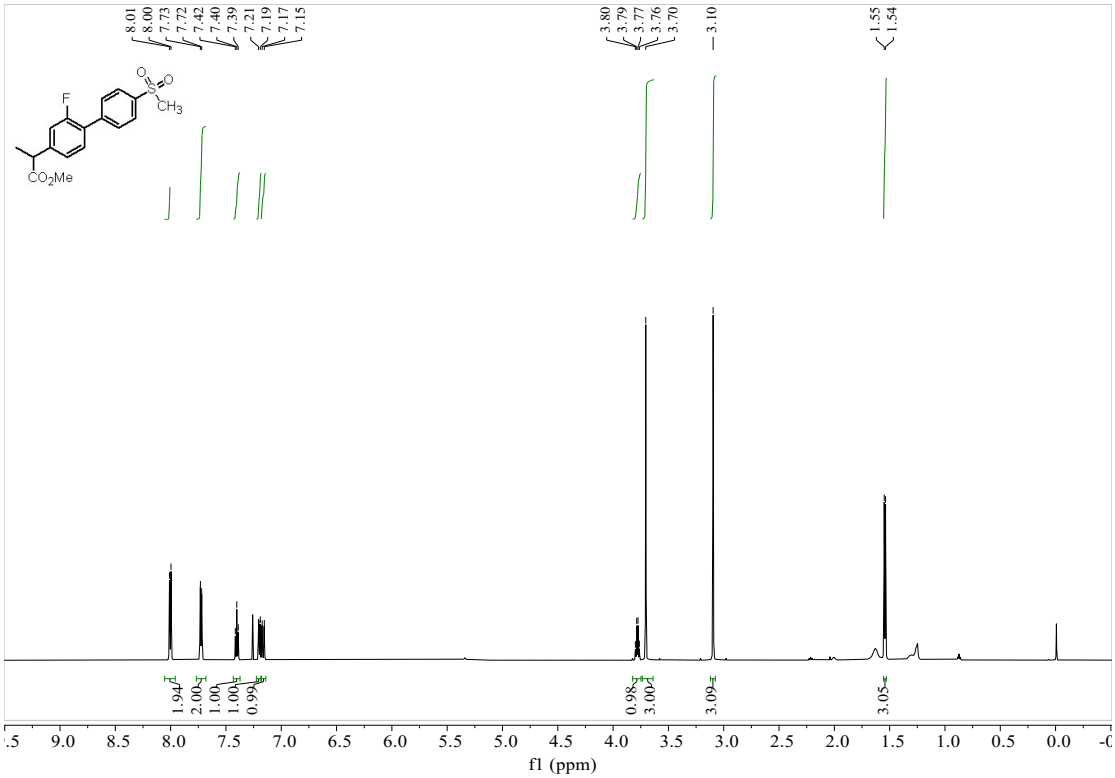
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 67



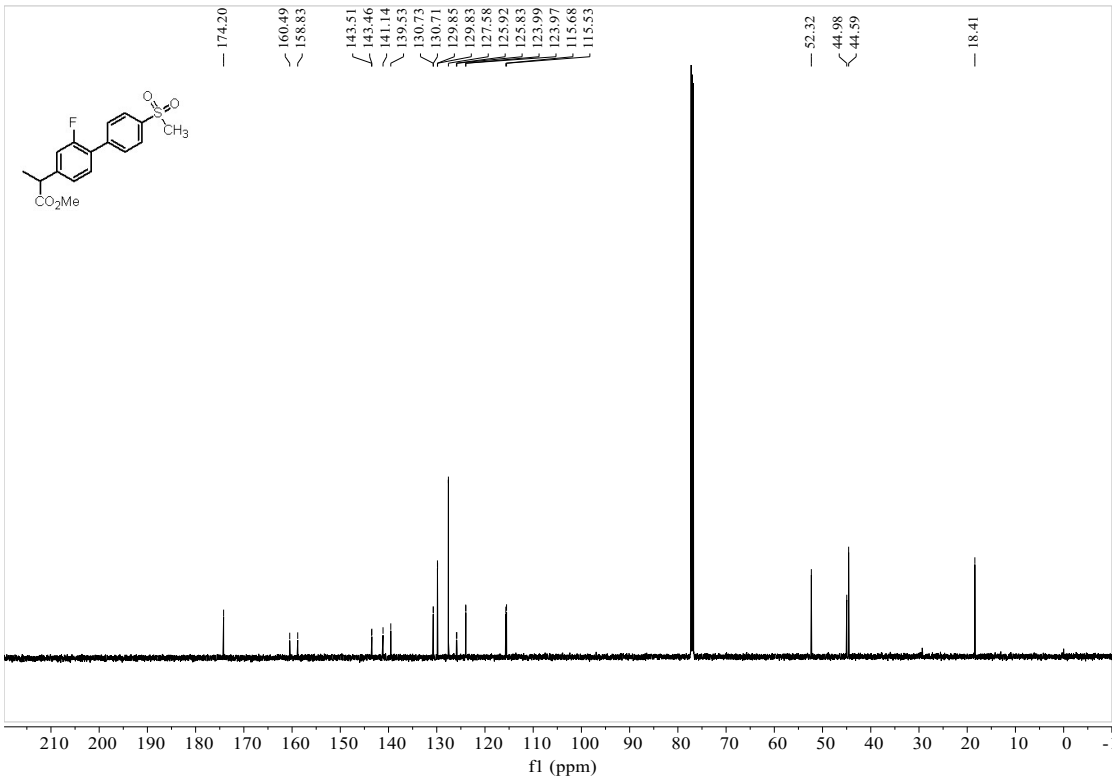
^{19}F NMR (565 MHz, Chloroform-*d*) spectrum of compound 67



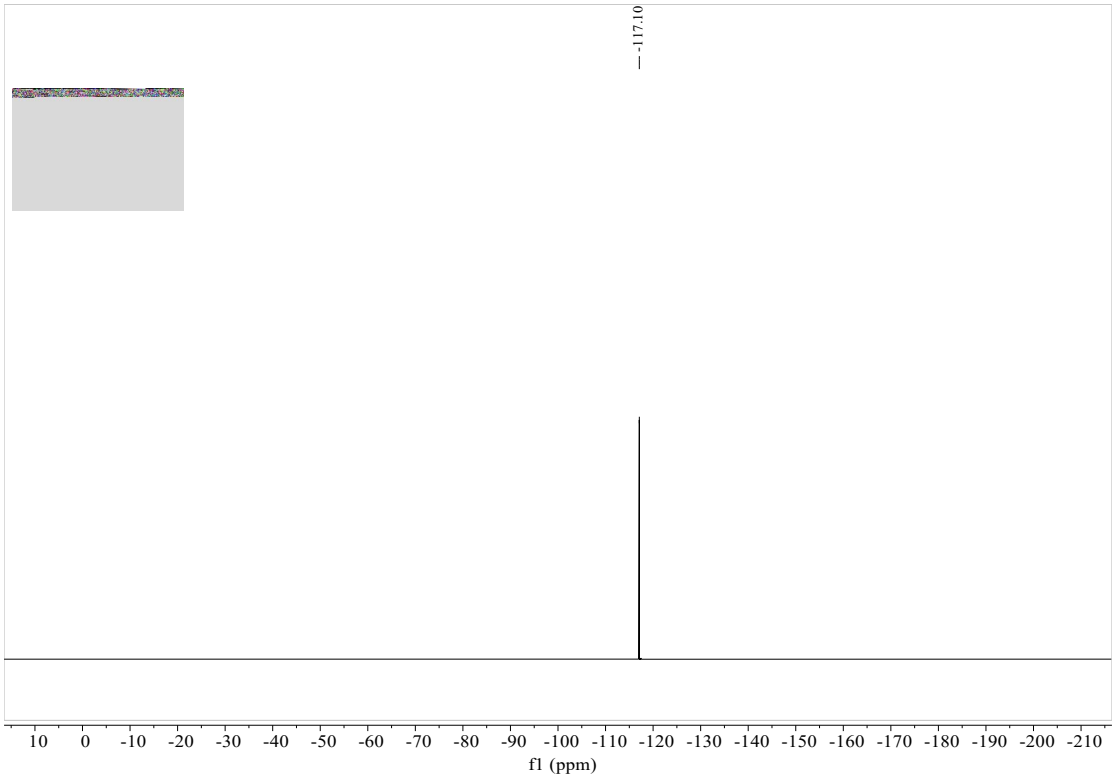
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 68



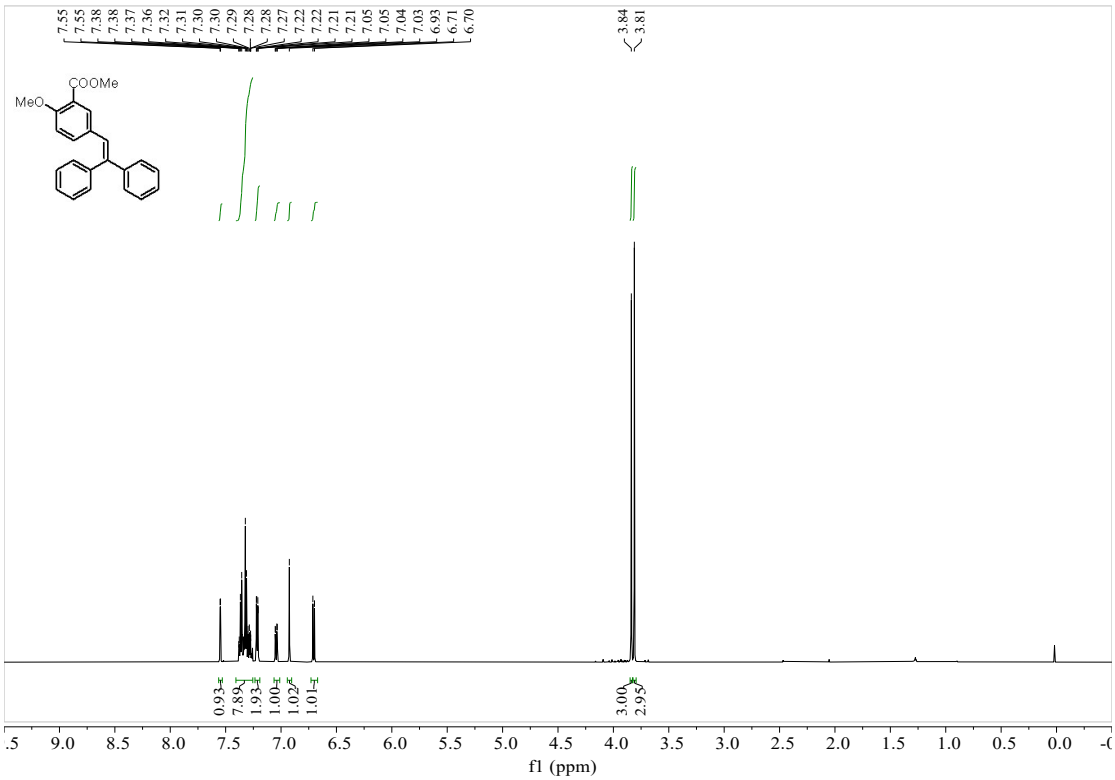
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 68



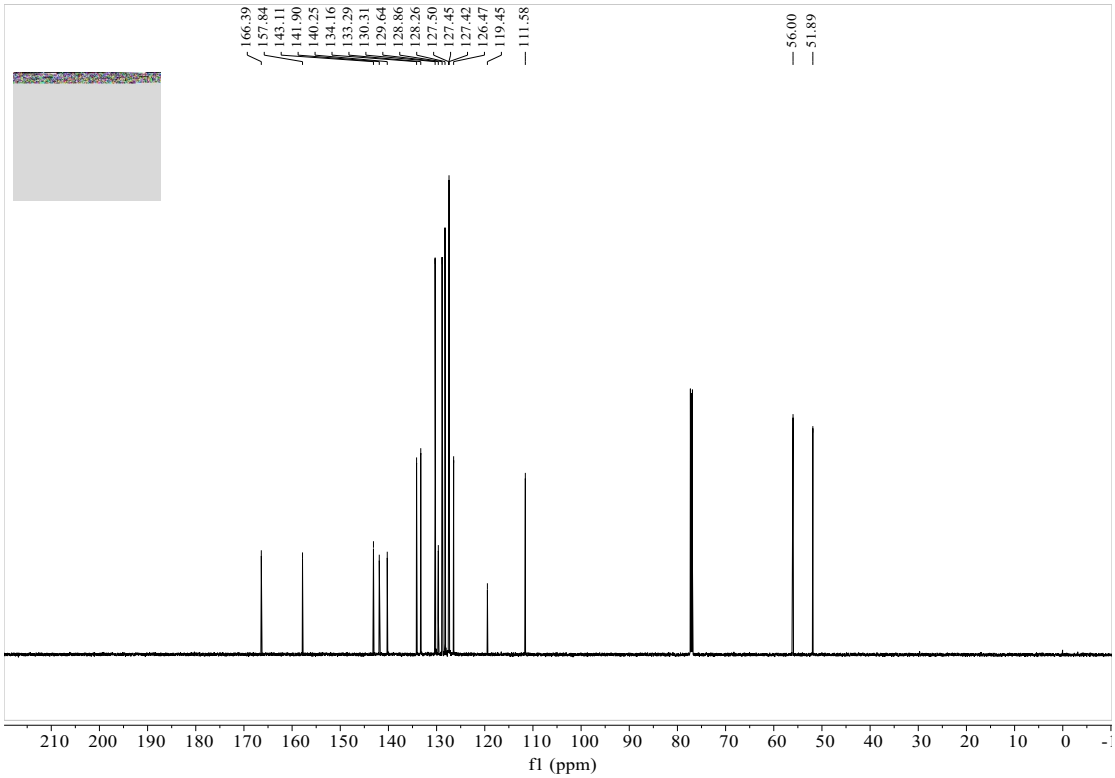
^{19}F NMR (565 MHz, Chloroform-*d*) spectrum of compound 68



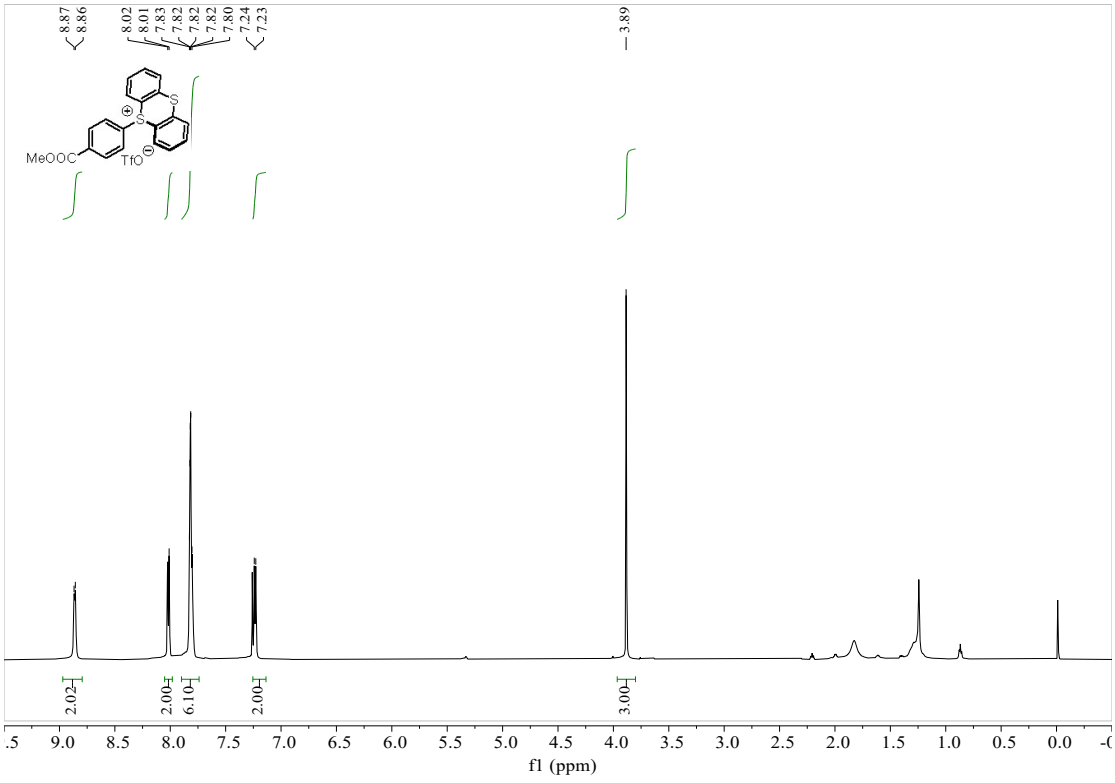
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 70



^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 70



^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 5-(4-(methoxycarbonyl)phenyl)-5*H*-thianthren-5-ium trifluoromethanesulfonate



^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 5-(4-(methoxycarbonyl)phenyl)-5*H*-thianthren-5-ium trifluoromethanesulfonate