Supporting Information

Direct construction of 2,3-unsubstituted benzofurans and benzothiophenes *via* metal-free catalyzed intramolecular Friedel-Crafts reaction

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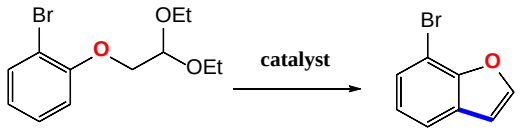
1. Screening of acids as the catalyst

Table S1. Screening of acids as the catalyst[a,b]



1d **2d**

Entry	Catalyst	Solvent	T [°C]	GC yield[b]
1	H_2SO_4	Toluene	110	trace
2	HNO_3	Toluene	110	trace
3	HCl	Toluene	110	trace
4	CF_3COOH	Toluene	110	trace
5	CF_3SO_3H	Toluene	110	trace
6	TsOH	Toluene	110	trace
7	PPA[c]	Toluene	110	23%
8	BF_3-Et_2O	Toluene	110	trace
9	H_3PO_4	Toluene	110	17%

[a] Reaction conditions: unless otherwise noted, all reactions were performed with **1d** (1 mmol), catalyst (100 μL) in 2.0 mL toluene at 110 °C for 12 h. [b] GC yield with TCE as internal standard. [c] 100 mg PPA was used.

2. GC Standard curve of 2d

Table S2. GC standard curve of 7-bromobenzofuran (**2d**) with TCE as internal reference.

GC Method: 50 °C hold for 1 min, followed by a temperature increase of 10 °C/min to 200 °C, and 30 °C/min to 300 °C, hold for 2 min (total run time: 21.3 min). Retention time: TCE 5.72 min, **2d** 12.1 min.

entry	Mass of **2d** (mg)	Mass of TCE (mg)	$y = \frac{Mass\ of\ \mathbf{2d}}{\text{Mass of TCE}}$	Area of **2d**	Area of TCE	$x = \frac{Area\ of\ \mathbf{2d}}{Area\ of\ TCE}$
1	0	0	0	0	0	0
2	9.2	32	0.2875	2358189	12180674	0.786918905
3	26.6	32	0.83125	7384301	9931586	2.221038125
4	41.2	32	1.2875	9433960	7151579	3.464410322
5	52.8	32	1.65	14638007	7461543	4.35185074
6	75.5	32	2.359375	20850021	8133414	6.427492562

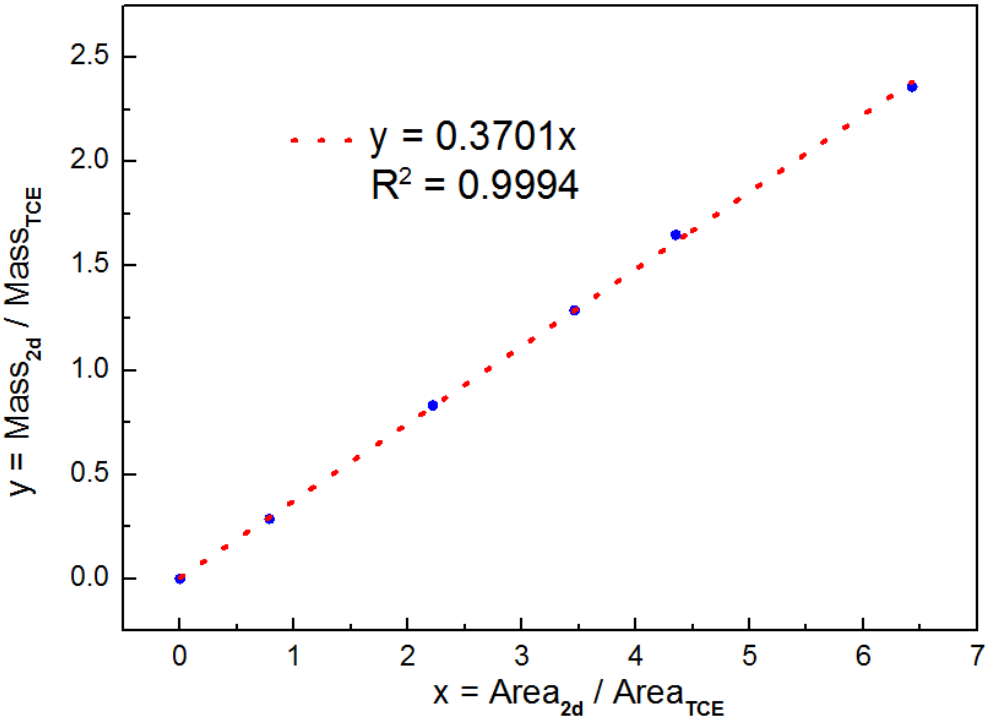


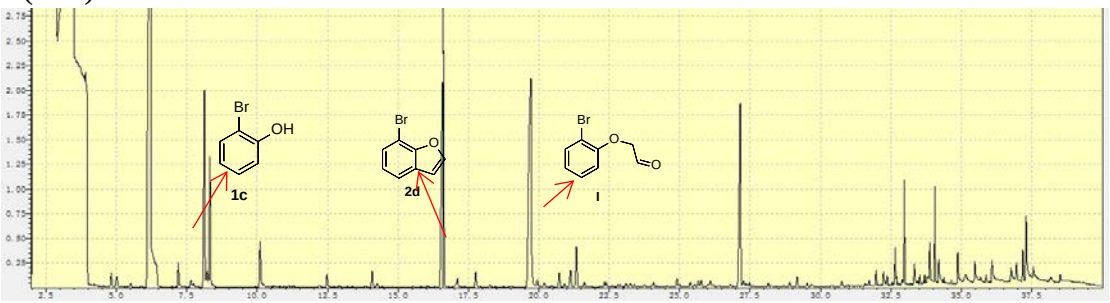
Figure S1: The standard curve of **2d** with TCE.

3. Mechanism study for the synthesis of 2d

3.1 Mechanism study for the synthesis of 2d by GC-MS

Taking **2d** as an example, when the reaction mixture was stirred for 3 h at 130 °C, we took small amount of sample for testing, and the GC-MS spectra are shown below (Figure S2).

GC (TIC):



MS spectra:

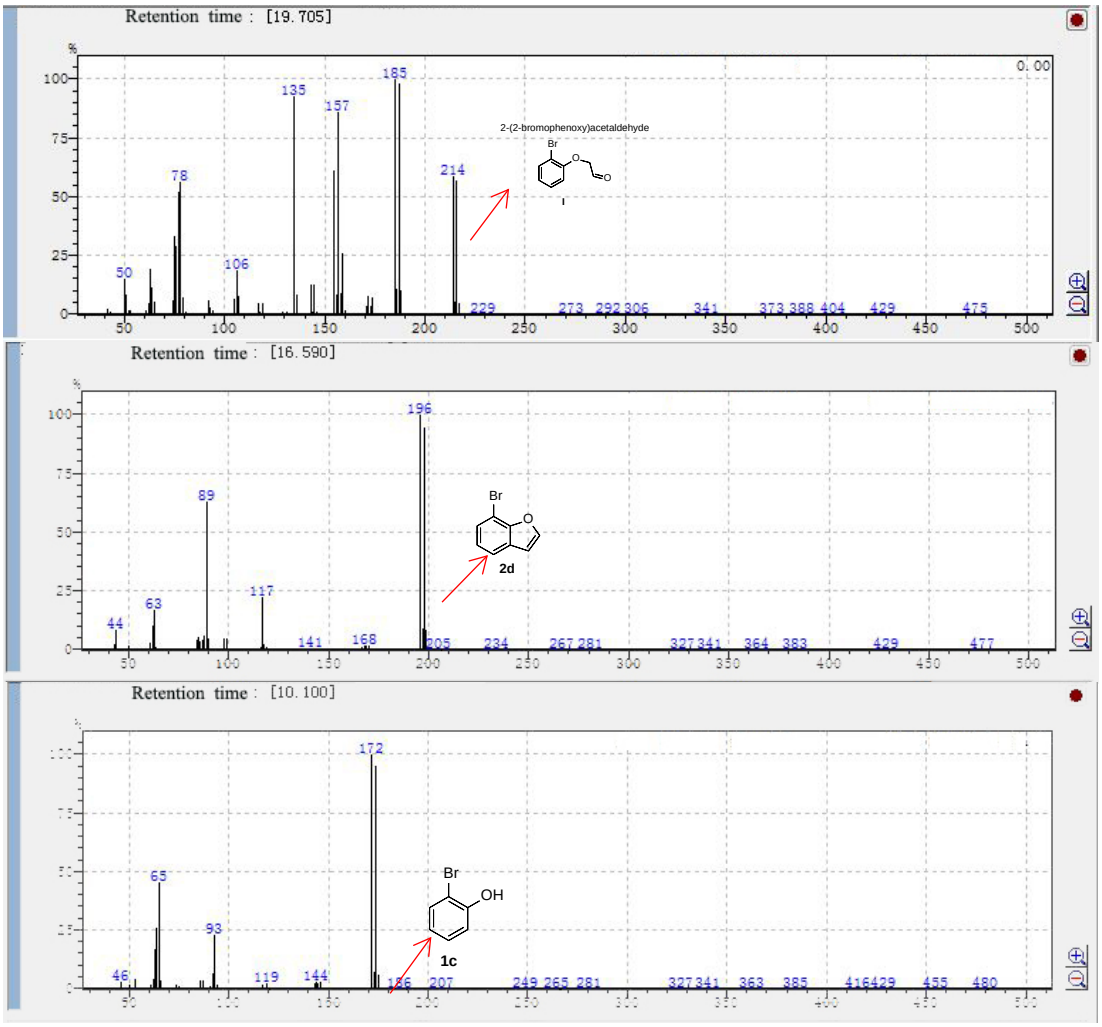


Figure S2: GC-MS data of the reaction mixture for synthesis of **2d**.

3.2 Further verification of the proposed mechanism

To a 50 mL round-bottomed flask was added 1-bromo-2-(2,2-diethoxyethoxy)benzene (**1d**) (1.4 g, 5 mmol), phosphoric acid (1.5 ml, 4.8 equiv) and chlorobenzene (15 mL). The mixture was stirred at 80 °C for 3 h. Then the mixture was cooled to room temperature, the organic layer was separated and concentrated under reduced pressure. The residue was finally purified by flash silica gel column chromatography (eluting with petroleum ether/ethyl acetate) to afford the desired intermediate I: 2-(2-bromophenoxy)acetaldehyde (360 mg, 1.67 mmol, 33% yield) as yellow liquid . ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 7.59 (dd, J = 7.9, 1.6 Hz, 1H), 7.29-7.25 (m, 1H), 6.92 (m, 1H), 6.79 (dd, J = 8.2, 1.3 Hz, 1H), 4.62 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.04, 154.23, 133.99, 128.75, 123.40, 113.67, 112.44, 73.64. GC-MS (EI) *m/z* 214. IR: 3069, 2826, 2717 (ν_{C-H} of aldehyde group), 1731 ($\nu_{C=O}$), 1586, 1442, 1282, 1240, 1055, 1028, 740, 657 cm^{-1}.

To a 10 mL Schleck tube was added 2-(2-bromophenoxy)acetaldehyde (108 mg, 0.5 mmol) isolated above, phosphoric acid (150 μL, 4.8 equiv) and chlorobenzene (1.5 mL). The mixture was stirred at 130 °C for 8 h. The GC yield is 90%. As we predicted, intermediate product I can be converted into the target product **2d** efficiently.

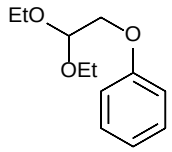
4. General information

All reagents were purchased from commercial suppliers and used without further purification unless otherwise specified. Thin layer chromatography (TLC) was performed using TLC silica gel 60 F254 glass plates. Silica gel 60 (200-300 mesh) was used for column chromatography. Proton nuclear magnetic resonance (^{1}H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectra were measured on JEOL 400YH spectrometers. Chemical shifts for hydrogens are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane (δ = 0), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constant (Hz). Detection and analysis of compounds by gas chromatography (Shimazu GC- 2010 plus) and gas chromatography mass spectrometry were performed (Shimazu GC-2010 plus and Shimazu GCMS-TQ8040). HRMS spectra were determined on a Bruker Apex IV Fourier Transform Mass Spectrometer (EI) or Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (ESI).

5. General procedure A for the preparation of starting materials

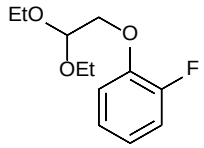
To a mixture of phenol **1** (1.0 equiv.) and K_2CO_3 or KOH (2.0 equiv.) was added DMF, and it was stirred at 60 °C for 1 h. Then 2-bromo-acetaldehyde ethyl acetal (1.5 equiv.) was added. The mixture was stirred for about 6 h under reflux until the reaction was completed based on TLC analysis. It was cooled to room temperature and extracted with EtOAc (50 mL × 3). The combined organic layers were subsequently washed with 5% NaOH aqueous solution and water, dried over $MgSO_4$ and concentrated under reduced pressure. The residual crude product was finally purified by flash silica gel column chromatography (eluting with petroleum ether/ethyl acetate) to afford the desired 2-aryloxyacetaldehyde diethyl acetals.

(2,2-Diethoxyethoxy)benzene (**1a**)[1]



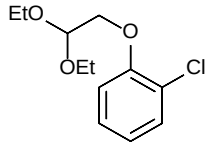
The general procedure A was followed with phenol (1.0 g, 10.6 mmol), KOH (1.19 g, 21.2 mmol) and 2-bromoacetaldehyde diethyl acetal (3.13 g, 15.9 mmol) in DMF (15 mL). **1a** was afforded as a colorless liquid (1.9 g, 9.05 mmol, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 2H), 6.97 – 6.89 (m, 3H), 4.84 (t, J = 5.2 Hz, 1H), 4.00 (d, J = 5.2 Hz, 2H), 3.80 – 3.72 (m, 2H), 3.67 – 3.59 (m, 2H), 1.24 (t, J = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.86, 129.51, 121.06, 114.73, 100.61, 68.54, 62.53, 15.43.

1-(2,2-Diethoxyethoxy)-2-fluorobenzene (**1b**)[2]



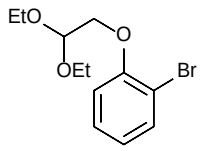
The general procedure A was followed with 2-fluorophenol (5.0 g, 44.6 mmol), K_2CO_3 (12.3 g, 89.2 mmol) and 2-bromoacetaldehyde diethyl acetal (13.18 g, 66.9 mmol) in DMF (35 mL). **1b** was afforded as a colorless liquid (7.98 g, 38 mmol, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 – 6.99 (m, 3H), 6.91 – 6.89 (m, 1H), 4.86 (t, J = 5.2 Hz, 1H), 4.07 (d, J = 5.2 Hz, 2H), 3.82 – 3.75 (m, 2H), 3.69 – 3.61 (m, 2H), 1.25 (t, J = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.76 (d, J = 246 Hz), 146.68 (d, J = 11.1 Hz), 124.16 (d, J = 3.0 Hz), 121.46 (d, J = 7.1 Hz), 116.15 (d, J = 18.2 Hz), 115.19, 100.61, 70.16, 62.93, 15.41.

1-Chloro-2-(2,2-diethoxyethoxy)benzene (**1c**)[1]



The general procedure A was followed with 2-chlorophenol (5.0 g, 38.9 mmol), K_2CO_3 (10.74 g, 77.8 mmol) and 2-bromoacetaldehyde diethyl acetal (11.5 g, 58.4 mmol) in DMF (35 mL). **1c** was afforded as a colorless liquid (6.55 g, 26.7 mmol, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, J = 7.9, 1.6 Hz, 1H), 7.29 – 7.20 (m, 1H), 6 .97 – 6.90 (m, 2H), 4.90 (t, J = 5.2 Hz, 1H), 4.08 (d, J = 5.3 Hz, 2H), 3.87 –3.80 (m, 2H), 3.75 – 3.68 (m, 2H), 1.28 (t, J = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, CDCl3) δ 154.15, 130.15, 127.71, 122.89, 121.65, 113.78, 100.53, 70.04, 63.22, 15.24.

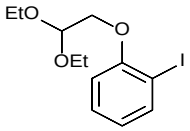
1-Bromo-2-(2,2-diethoxyethoxy)benzene (**1d**)[1]



The general procedure A was followed with 2-bromophenol (10.50 g, 60.7 mmol), K_2CO_3 (16.80 g, 121.4 mmol) and 2-bromoacetaldehyde diethyl acetal (17.95 g, 91.1 mmol) in DMF (35 mL). **1d** was afforded as a colorless liquid (14.05 g, 48.6 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, J = 7.8, 1.7 Hz, 1H), 7.24 – 7.23 (m, 1H), 6.91 – 6.89 (m, 1H), 6.86 – 6.81 (m, 1H), 4.88 (t, J = 5.2 Hz, 1H), 4.05 (d, J = 5.2 Hz, 2H), 3.85 – 3.77 (m,

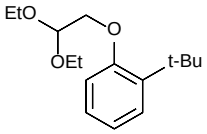
2H), 3.74 – 3.67 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.89, 113.20, 128.32, 122.02, 113.26, 112.05, 100.99, 69.96, 63.29, 15.25.

1-(2,2-Diethoxyethoxy)-2-iodobenzene (**1e**)[3]



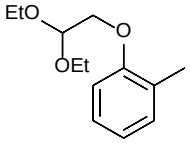
The general procedure A was followed with 2-iodophenol (5 g, 22.7 mmol), K_2CO_3 (6.27 g, 45.4 mmol) and 2-bromoacetaldehyde diethyl acetal (6.7 g, 34 mmol) in DMF (35 mL). **1e** was afforded as a colorless liquid (4.74 g, 14.08 mmol, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.28 – 7.25(m, 1H), 6.81 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.73 – 6.69 (m, 1H), 4.89 (t, *J* = 5.2 Hz, 1H), 4.03 (d, *J* = 5.2 Hz, 2H), 3.86 – 3.78 (m, 2H), 3.76 – 3.69 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.06, 139.31, 129.32, 122.66, 112.14, 100.57, 86.32, 70.00, 63.31, 15.29.

1-(*Tert*-butyl)-2-(2,2-diethoxyethoxy) benzene (**1f**)



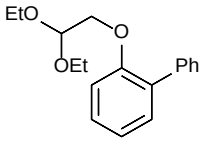
The general procedure A was followed with 2-*tert*-butylphenol (2.9 g, 19.3 mmol), K_2CO_3 (2.2 g, 38.9 mmol) and 2-bromoacetaldehyde diethyl acetal (5.7 g, 28.9 mmol) in DMF (35 mL). **1f** was afforded as a colorless liquid (2.33 g, 8.76 mmol, 45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.18 – 7.14 (m, 1H), 6.92 – 6.88 (m, 1H), 6.84 (dd, *J* = 8.2, 1.1 Hz, 1H), 4.95 (t, *J* = 5.4 Hz, 1H), 4.02 (d, *J* = 5.4 Hz, 2H), 3.81 – 3.74 (m, 2H), 3.69 – 3.62 (m, 2H), 1.40 (s, 9H), 1.25 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.33, 138.17, 127.17, 126.80, 120.67, 111.82, 100.63, 67.80, 62.28, 34.99, 29.86, 15.47. HRMS (EI) *m/z* calcd for $C_{16}H_{26}O_3$ $[M]^+$ 266.1882, found 266.1876.

1-(2,2-Diethoxyethoxy)-2-methylbenzene (**1g**)[4]



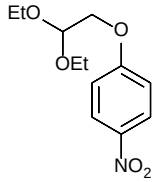
The general procedure A was followed with *o*-cresol (5.0 g, 46.3 mmol), K_2CO_3 (12.8 g, 92.6 mmol) and 2-bromoacetaldehyde diethyl acetal (13.7 g, 69.5 mmol) in DMF (35 mL). **1g** was afforded as a colorless liquid (6.7 g, 29.9 mmol, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (t, *J* = 7.0 Hz, 2H), 6.88 (td, *J* = 7.4, 0.6 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 4.88 (t, *J* = 5.3 Hz, 1H), 4.03 (d, *J* = 5.3 Hz, 2H), 3.86 – 3.74 (m, 2H), 3.73 – 3.62 (m, 2H), 2.26 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.61, 130.55, 126.74, 126.66, 120.54, 111.01, 100.68, 68.72, 62.62, 16.11, 15.25.

2-(2,2-Diethoxyethoxy)-1,1'-biphenyl (**1h**)



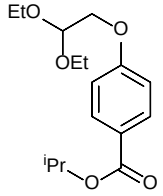
The general procedure A was followed with 2-phenylphenol (4.0 g, 23.5 mmol), K_2CO_3 (6.5 g, 47 mmol) and 2-bromoacetaldehyde diethyl acetal (6.95 g, 35.3 mmol) in DMF (35 mL). **1h** was afforded as a colorless liquid (5.5 g, 19.2 mmol, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.39 – 7.26 (m, 5H), 7.05 – 7.01 (m, 1H), 6.96 (dd, *J* = 8.2, 0.7 Hz, 1H), 4.71 (t, *J* = 5.3 Hz, 1H), 3.98 (d, *J* = 5.2 Hz, 2H), 3.71 – 3.64 (m, 2H), 3.55 – 3.47 (m, 2H), 1.17 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.57, 138.51, 131.04, 130.99, 129.77, 128.72, 127.90, 126.93, 121.38, 112.65, 100.87, 69.43, 63.17, 15.42. HRMS (EI) *m/z* calcd for $C_{18}H_{22}O_3$ $[M]^+$ 286.1569, found 286.1633.

1-(2,2-Diethoxyethoxy)-4-nitrobenzene (**1i**)[5]



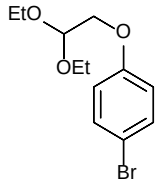
The general procedure A was followed with 4-nitrophenol (5.0 g, 36 mmol), K_2CO_3 (10 g, 72 mmol) and 2-bromoacetaldehyde diethyl acetal (10.64 g, 54 mmol) in DMF (70 mL). **1i** was afforded as a pale-yellow liquid (3.7 g, 14.5 mmol, 40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.15 (m, 2H), 7.02 – 6.97 (m, 2H), 4.86 (t, J = 5.1 Hz, 1H), 4.10 (d, J = 5.2 Hz, 2H), 3.85 – 3.74 (m, 2H), 3.70 – 3.60 (m, 2H), 1.25 (q, J = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.60, 141.63, 125.81, 114.64, 100.20, 69.08, 63.02, 15.30.

Isopropyl 4-(2,2-diethoxyethoxy) benzoate (**1j**)



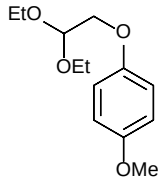
The general procedure A was followed with isopropyl 4-hydroxybenzoate (5.0 g, 27.8 mmol), K_2CO_3 (7.67 g, 55.6 mmol) and 2-bromoacetaldehyde diethyl acetal (8.2 g, 41.7 mmol) in DMF (35 mL). **1j** was afforded as a colorless liquid (6.5 g, 21.9 mmol, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.96 (m, 2H), 6.94 – 6.92 (m, 2H), 5.25 – 5.19 (m, 1H), 4.85 (t, J = 5.2 Hz, 1H), 4.05 (d, J = 5.1 Hz, 2H), 3.81 – 3.74 (m, 2H), 3.68 – 3.60 (m, 2H), 1.35 (d, J = 8Hz, 6H), 1.25 (t, J = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.89, 162.21, 131.54, 123.69, 114.18, 100.42, 68.60, 68.04, 62.87, 22.09, 15.42. HRMS (ESI) *m/z* calcd for $C_{16}H_{24}O_5$ $[M + H]^+$ 297.1702, found 297.1694.

1-Bromo-4-(2,2-diethoxyethoxy)benzene (**1k**)[1]



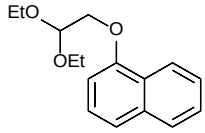
The general procedure A was followed with 4-bromophbenol (3.0 g, 17.3 mmol), KOH (1.94 g, 34.6 mmol) and 2-bromoacetaldehyde diethyl acetal (5.1 g, 25.9 mmol) in DMF (30 mL). **1k** was afforded as a colorless liquid (3.3 g, 11.4 mmol, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 2H), 6.82 – 6.80 (m, 2H), 4.82 (t, J = 5.2 Hz, 1H), 3.97 (d, J = 5.2 Hz, 2H), 3.80 – 3.72 (m, 2H), 3.67 – 3.59 (m, 2H), 1.25 (t, J = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.64, 132.15, 116.38, 113.09, 100.29, 68.63, 62.62, 15.28.

1-(2,2-Diethoxyethoxy)-4-methoxybenzene (**1l**)[1]



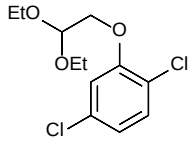
The general procedure A was followed with 4-methoxyphenol (3.0 g, 24.2 mmol), KOH (2.7 g, 48.4 mmol) and 2-bromoacetaldehyde diethyl acetal (7.15 g, 36.3 mmol) in DMF (30 mL). **1l** was afforded as a colorless liquid (5.1 g, 21.3 mmol, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 – 6.80 (m, 4H), 4.82 (t, J = 5.2 Hz, 1H), 3.97 (d, J = 5.2 Hz, 2H), 3.81 – 3.72 (m, 5H), 3.67 – 3.59 (m, 2H), 1.25 (t, J = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.87, 152.65, 115.49, 114.41, 100.41, 69.10, 62.32, 55.48, 15.19.

1-(2,2-Diethoxyethoxy)naphthalene (**1m**)[1]



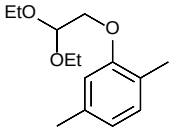
The general procedure A was followed with 1-naphthol (5.0 g, 34.7 mmol), K_2CO_3 (9.6 g, 69.4 mmol) and 2-bromoacetaldehyde diethyl acetal (10.26 g, 52.1 mmol) in DMF (35 mL). **1m** was afforded as a colorless liquid (6.25 g, 24 mmol, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 – 8.29 (m, 1H), 7.82 – 7.79 (m, 1H), 7.52 – 7.44 (m, 3H), 7.37 (t, J =8.0 Hz, 1H), 6.83 (d, J = 7.2 Hz, 1H), 5.02 (t, J = 5.3 Hz, 1H), 4.20 (d, J = 5.2 Hz, 2H), 3.88 – 3.81 (m, 2H), 3.76 – 3.68 (m, 2H), 1.30 (t, J = 8.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.21, 134.40, 127.32, 126.28, 125.70, 125.55, 125.07, 121.92, 120.46, 104.80, 100.56, 68.77, 62.60, 15.30.

2-(2,2-Diethoxyethoxy)-1,4-dichlorobenzene (**1n**)



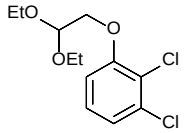
The general procedure A was followed with 2, 5-dichlorophenol (5.0 g, 30.67 mmol), K_2CO_3 (8.46 g, 61.34 mmol) and 2-bromoacetaldehyde diethyl acetal (9.06 g, 46 mmol) in DMF (35 mL). **1n** was afforded as a colorless liquid (6.2 g, 22.2 mmol, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, J = 8.4 Hz, 1H), 6.94 (d, J = 2.3 Hz, 1H), 6.88 (dd, J = 8.3, 2.3 Hz, 1H), 4.86 (t, J = 5.2 Hz, 1H), 4.03 (d, J = 5.2 Hz, 2H), 3.84 – 3.76 (m, 2H), 3.71 – 3.64 (m, 2H), 1.25 (t, J = 8.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.70, 133.06, 130.78, 121.69, 121.50, 114.23, 100.60, 70.27, 63.53, 15.43. HRMS (ESI) *m/z* calcd for $C_{12}H_{16}Cl_2O_3$ $[M + Na]^+$ 301.0374, found 301.0374.

2-(2,2-Diethoxyethoxy)-1,4-dimethylbenzene (**1o**)[6]



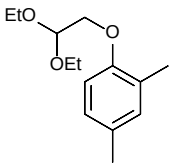
The general procedure A was followed with 2, 5-dimethylphenol (5.0 g, 40.98 mmol), K_2CO_3 (11.3 g, 81.96 mmol) and 2-bromoacetaldehyde diethyl acetal (9.06 g, 46 mmol) in DMF (35 mL). **1o** was afforded as a colorless liquid (12.1 g, 61.5 mmol, 43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, J = 7.5 Hz, 1H), 6.67 (d, J = 7.5 Hz, 1H), 6.64 (s, 1H), 4.85 (t, J = 5.3 Hz, 1H), 3.99 (d, J = 5.3 Hz, 2H), 3.82 – 3.74 (m, 2H), 3.69 – 3.61 (m, 2H), 2.30 (s, 3H), 2.19 (s, 3H), 1.25 (t, J = 6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.49, 136.48, 130.30, 123.58, 121.07, 112.08, 100.74, 68.72, 62.67, 21.32, 15.77, 15.32.

1,2-Dichloro-3-(2,2-diethoxyethoxy) benzene (**1p**)



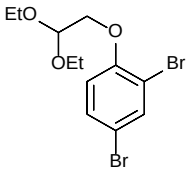
The general procedure A was followed with 2,3-dichlorophenol (3.0 g, 18.4 mmol), Cs_2CO_3 (9.0 g, 27.6 mmol) and 2-bromoacetaldehyde diethyl acetal (5.4 g, 27.6 mmol) in DMF (35 mL). **1p** was afforded as a colorless liquid (3.78 g, 13.55 mmol, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (t, J = 8.1 Hz, 1H), 7.05 (dd, J = 8.2, 1.5 Hz, 1H), 6.82 (dd, J = 8.1, 1.5 Hz, 1H), 4.85 (t, J = 5.2 Hz, 1H), 4.03 (d, J = 5.2 Hz, 2H), 3.82 – 3.75 (m, 2H), 3.70 – 3.63 (m, 2H), 1.23 (t, J = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.70, 133.06, 130.78, 121.69, 121.50, 114.23, 100.60, 70.27, 63.53, 15.43. HRMS (EI) *m/z* calcd for $C_{12}H_{16}Cl_2O_3$ $[M]^+$ 278.0476, found 278.0472.

1-(2,2-Diethoxyethoxy)-2,4-dimethylbenzene (**1q**)



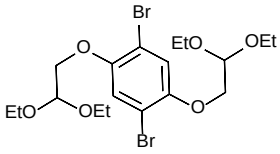
The general procedure A was followed with 2,5-dimethylphenol (5.0 g, 40.98 mmol), K_2CO_3 (11.3 g, 81.96 mmol) and 2-bromoacetaldehyde diethyl acetal (12.1 g, 61.5 mmol) in DMF (55 mL). **1q** was afforded as a colorless liquid (4.65 g, 19.54 mmol, 48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 – 6.92 (m, 2H), 6.70 (d, J = 8.1 Hz, 1H), 4.84 (t, J = 5.3 Hz, 1H), 3.88 (d, J = 5.3 Hz, 2H), 3.81 – 3.74 (m, 2H), 3.69 – 3.61 (m, 2H), 2.25 (s, 3H), 2.20 (s, 3H), 1.25 (t, J = 8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.72, 131.60, 129.94, 127.03, 126.75, 111.29, 100.87, 69.10, 62.81, 20.56, 16.28, 15.48. HRMS (EI) *m/z* calcd for $C_{14}H_{22}O_3$ $[M]^+$ 238.1569, found 238.1563.

2,4-Dibromo-1-(2,2-diethoxyethoxy) benzene (**1r**)



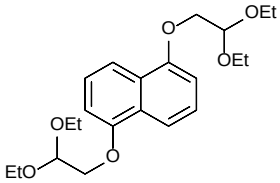
The general procedure A was followed with 2, 4-dibromophenol (3.0 g, 11.9 mmol), K_2CO_3 (3.28 g, 23.8 mmol) and 2-bromoacetaldehyde diethyl acetal (3.53 g, 17.9 mmol) in DMF (55 mL). **1r** was afforded as a colorless liquid (2.7 g, 7.34 mmol, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 2.4 Hz, 1H), 7.35 (dd, J = 8.7, 2.3 Hz, 1H), 6.79 (d, J = 8.8 Hz, 1H), 4.86 (t, J = 5.2 Hz, 1H), 4.02 (d, J = 5.2 Hz, 2H), 3.84 – 3.77 (m, 2H), 3.72 – 3.65 (m, 2H), 1.25 (t, J = 6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.51, 135.57, 131.29, 114.67, 113.37, 113.17, 100.68, 70.41, 63.63, 15.46. HRMS (EI) m/z calcd for $C_{12}H_{16}Br_2O_3$ $[M+2]^+$ 367.9466, found 367.9435.

1,4-Dibromo-2,5-bis(2,2-diethoxyethoxy)benzene (**1s**)[7]



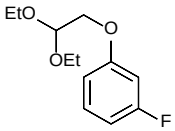
The general procedure A was followed with hydroquinone (10 g, 37.3 mmol), KOH (8.36 g, 149.2 mmol) and 2-bromoacetaldehyde diethyl acetal (3.53 g, 17.9 mmol) in DMSO (125 mL). **1s** was afforded as a white solid (13.1 g, 26.2 mmol, 70%), Mp 61.5-62.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (s, 2H), 4.84 (t, J = 5.2 Hz, 2H), 3.99 (d, J = 5.2 Hz, 4H), 3.83 – 3.75 (m, 4H), 3.71–3.65 (m, 4H), 1.25 (t, J = 7.1 Hz, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.04, 118.85, 111.10, 100.48, 71.00, 63.17, 15.27.

1,5-Bis(2,2-diethoxyethoxy)naphthalene (**1t**)[8]



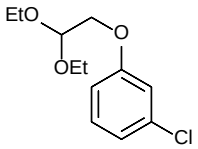
The general procedure A was followed with 1,5-dihydroxynaphthalene (5.0 g, 31.25 mmol), KOH (7 g, 125 mmol) and 2-bromoacetaldehyde diethyl acetal (9.24 g, 46.9 mmol) in DMF (125 mL). **1t** was afforded as a pale-yellow solid (2.04 g, 5.19 mmol, 17%), Mp 140.6 - 141.8 °C. ^{1}H NMR (400 MHz,) δ 7.87 (d, J = 8.4 Hz, 2H), 7.36 (t, J = 8.0 Hz, 2H), 6.85 (d, J = 7.6 Hz, 2H), 5.01 (t, J = 5.2 Hz, 2H), 4.18 (d, J = 5.2 Hz, 4H), 3.89 - 3.79 (m, 4H), 3.79 – 3.66 (m, 4H), 1.29 (t, J = 7.0 Hz, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.08, 126.82, 125.08, 114.63, 105.67, 100.65, 68.94, 62.72, 15.36.

1-(2,2-Diethoxyethoxy)-3-fluorobenzene (**1u**)



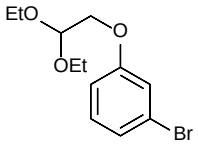
The general procedure A was followed with 3-fluorophenol (3.6 g, 32.1 mmol), K_2CO_3 (6.8 g, 49 mmol) and 2-bromoacetaldehyde diethyl acetal (5.5 g, 24.1 mmol) in DMF (15 mL). **1u** was afforded as a colorless liquid (5.5 g, 24.1 mmol, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.18 (m, 1H), 6.72 – 6.62 (m, 3H), 4.83 (t, J = 5.2 Hz, 1H), 3.99 (d, J = 5.2 Hz, 2H), 3.81 – 3.73 (m, 2H), 3.67 – 3.60 (m, 2H), 1.25 (t, J = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.62 (d, J = 246 Hz), 160.00 (d, J = 10.8 Hz), 130.26 (d, J = 10.1 Hz), 110.38 (d, J = 2.5 Hz), 107.86 (d, J = 21.3 Hz), 102.52 (d, J = 25.0 Hz), 100.40, 68.77, 62.75, 15.39. HRMS (EI) *m/z* calcd for $C_{12}H_{17}FO_3$ $[M]^+$ 228.1162, found 228.1164.

1-Chloro-3-(2,2-diethoxyethoxy)benzene (**1v**)[1]



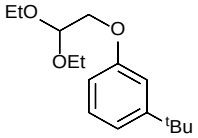
The general procedure A was followed with 3-chlorophenol (5.0 g, 38.8 mmol), KOH (4.37 g, 78 mmol) and 2-bromoacetaldehyde diethyl acetal (11.5 g, 58.4 mmol) in *N*,*N*-dimethylacetamide (DMAC) (50 mL). **1v** was afforded as a colorless liquid (5.2 g, 21.2 mmol, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.16 (m, 1H), 6.96 – 6.91 (m, 2H), 6.83 – 6.78 (m, 1H), 4.82 (t, J = 5.2 Hz, 1H), 3.99 (d, J = 5.2 Hz, 2H), 3.81 – 3.70 (m, 2H), 3.69 – 3.58 (m, 2H), 1.25 (dd, J = 8.8, 5.3 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.25, 134.72, 130.10, 121.08, 115.10, 112.97, 100.27, 68.64, 62.60, 15.24.

1-Bromo-3-(2,2-diethoxyethoxy)benzene (**1w**)[1]



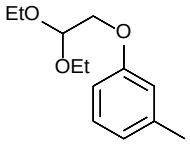
The general procedure A was followed with 3-bromophenol (3.26 g, 18.8 mmol), KOH (2.11 g, 37.6 mmol) and 2-bromoacetaldehyde diethyl acetal (5.6 g, 28.2 mmol) in DMAC (35 mL). **1w** was afforded as a colorless liquid (3.8 g, 13.1 mmol, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.07 (m, 3H), 6.87 – 6.84 (m, 1H), 4.82 (t, J = 5.2 Hz, 1H), 3.98 (d, J = 5.2 Hz, 2H), 3.80 – 3.73 (m, 2H), 3.67 – 3.59 (m, 2H), 1.25 (t, J = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.16, 130.35, 123.88, 122.54, 117.84, 113.34, 100.14, 68.48, 62.48, 15.18.

1-(*Tert*-butyl)-3-(2,2-diethoxyethoxy)benzene (**1x**)



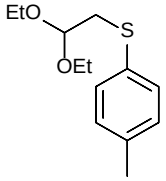
The general procedure A was followed with 3-tert-butylphenol (2.9 g, 19.3 mmol), KOH (2.16 g, 38.6 mmol) and 2-bromoacetaldehyde diethyl acetal (5.7 g, 28.95 mmol) in DMF (35 mL). **1x** was afforded as a colorless liquid (1.81 g, 6.80 mmol, 35%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.18 (m, 1H), 6.99 – 6.97 (m, 2H), 6.73 – 6.70 (m, 1H), 4.84 (t, J = 5.2 Hz, 1H), 4.00 (d, J = 5.2 Hz, 2H), 3.80 – 3.72 (m, 2H), 3.67 – 3.60 (m, 2H), 1.29 (s, 9H), 1.25 (t, J = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.53, 153.02, 129.03, 118.23, 112.74, 110.90, 100.63, 68.41, 62.52, 34.86, 31.43, 15.47. HRMS (EI) *m/z* calcd for $C_{16}H_{26}O_3$ $[M]^+$ 266.1882, found 266.1885.

1-(2,2-Diethoxyethoxy)-3-methylbenzene (**1y**)[1]



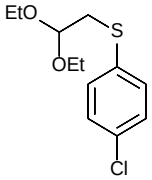
The general procedure A was followed with 3-methylphenol (5 g, 46.3 mmol), KOH (5.2 g, 92.6 mmol) and 2-bromoacetaldehyde diethyl acetal (5.7 g, 28.95 mmol) in DMF (50 mL). **1y** was afforded as a colorless liquid (7.8 g, 35 mmol, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-7.16 (m, 1H), 6.70 – 6.76 (m, 3H), 4.82 (t, J = 5.2 Hz, 1H), 3.98 (d, J = 5.3 Hz, 2H), 3.80 – 3.68 (m, 2H), 3.68 – 3.56 (m, 2H), 2.30 (s, 3H), 1.27 – 1.20 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.50, 139.40, 129.13, 121.61, 115.58, 111.53, 100.43, 68.51, 62.48, 21.36, 15.32.

(2,2-Diethoxyethyl)(*p*-tolyl)sulfane (**3a**)[4]



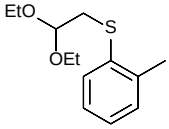
The general procedure A was followed with 4-methylbenzenethiol (2.48 g, 20 mmol), K_2CO_3 (3.3 g, 24 mmol) and 2-bromoacetaldehyde diethyl acetal (4.7 g, 24 mmol) in DMF (50 mL). **3a** was afforded as a colorless liquid (4.08 g, 17 mmol, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.2 Hz, 2H), 7.09 (d, J = 8.2 Hz, 2H), 4.62 (t, J = 5.6 Hz, 1H), 3.70 – 3.62 (m, 2H), 3.57 – 3.50 (m, 2H), 3.09 (d, J = 5.5 Hz, 2H), 2.31 (s, 3H), 1.19 (t, J = 6.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.38, 132.70, 130.24, 129.78, 101.86, 62.17, 38.17, 21.13, 15.37.

(4-Chlorophenyl) (2,2-diethoxyethyl) sulfide (**3b**)[9]



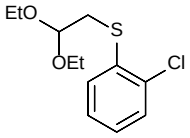
The general procedure A was followed with 4-chlorothiophenol (4.3 g, 30 mmol), K_2CO_3 (8.3 g, 45 mmol) and 2-bromoacetaldehyde diethyl acetal (8.9 g, 45 mmol) in DMF (50 mL). **3b** was afforded as a colorless liquid (7.05 g, 27 mmol, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 2H), 7.26 – 7.21 (m, 2H), 4.63 (t, J = 5.6 Hz, 1H), 3.72 – 3.62 (m, 2H), 3.59 – 3.48 (m, 2H), 3.10 (d, J = 5.5 Hz, 2H), 1.19 (t, J = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.09, 132.11, 130.71,129.02, 101.80, 62.51, 37.83, 15.31.

(2,2-Diethoxyethyl) (*o*-tolyl)sulfane (**3c**)[10]



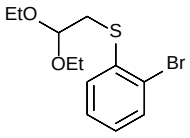
The general procedure A was followed with *o*-toluenethiol (2.48 g, 20 mmol), K_2CO_3 (3.3 g, 24 mmol) and 2-bromoacetaldehyde diethyl acetal (4.7 g, 24 mmol) in DMF (50 mL). **3c** was afforded as a colorless liquid (3.84 g, 16 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 7.9 Hz, 1H), 7.18 – 7.06 (m, 3H), 4.66 (t, J = 5.6 Hz, 1H), 3.71 – 3.64 (m, 2H), 3.59 – 3.51 (m, 2H), 3.11 (d, J = 5.6 Hz, 2H), 2.39 (s, 3H), 1.21 (t, J = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.86, 135.71, 130.22, 128.52, 126.53, 125.99, 101.66, 62.11, 36.79, 20.57, 15.38.

(2-Chlorophenyl) (2,2-diethoxyethyl) sulfane (**3d**)[9]



The general procedure A was followed with 2-chlorothiophenol (4.30 g, 30 mmol), K_2CO_3 (8.30 g, 60 mmol) and 2-bromoacetaldehyde diethyl acetal (8.9 g, 45 mmol) in DMF (50 mL). **3d** was afforded as a colorless liquid (7.52 g, 28.8 mmol, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 2H), 7.20 (td, J = 7.6, 1.4 Hz, 1H), 7.14 – 7.09 (m, 1H), 4.69 (t, J = 5.5 Hz, 1H), 3.73 – 3.65 (m, 2H), 3.60 – 3.52 (m, 2H), 3.15 (d, J = 5.5 Hz, 2H), 1.20 (t, J = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.77, 133.89, 129.79, 129.28, 127.16, 126.86, 101.74, 62.38, 36.45, 15.35.

(2-Bromophenyl)(2,2-diethoxyethyl)sulfane (**3e)**[11]

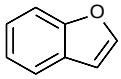


The general procedure A was followed with 2-bromothiophenol (5.67 g, 30 mmol), K_2CO_3 (8.28 g, 60 mmol) and 2-bromoacetaldehyde diethyl acetal (8.9 g, 45 mmol) in DMF (50 mL). **3e** was afforded as a colorless liquid (8.7 g, 28.5 mmol, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, J = 8.0, 1.3 Hz, 1H), 7.36 (dd, J = 7.9, 1.5 Hz, 1H), 7.29 – 7.22 (m, 1H), 7.06 – 6.99 (m, 1H), 4.70 (t, J = 5.6 Hz, 1H), 3.73 – 3.66 (m, 2H), 3.60 – 3.54 (m, 2H), 3.15 (d, J = 5.5 Hz, 2H), 1.20 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.81, 133.05, 128.88, 127.77, 126.89, 123.90, 101.65, 62.39, 36.86, 15.34.

6. General procedure B for the preparation of benzofurans and benzothiophenes

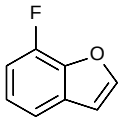
To a 25 mL Schlenk tube was added compound **1** or **3** (1 mmol), phosphoric acid (300 μL, 4.8 equiv) and chlorobenzene (3 mL). The mixture was stirred at 130 °C for 12 h. Then the mixture was cooled to room temperature, the organic layer was separated and concentrated under reduced pressure. The residual was finally purified by flash silica gel column chromatography (eluting with petroleum ether/ethyl acetate) to afford the desired products.

Benzofuran (**2a**)[12]



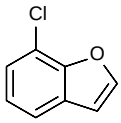
2a was afforded as a colorless liquid (104 mg, 0.88 mmol, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 2H), 7.54 – 7.49 (m, 1H), 7.34 – 7.28 (m, 1H), 7.23 (dd, J = 7.3, 1.0 Hz, 1H), 6.78 (dd, J = 2.2, 0.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.04, 144.99, 127.50, 124.32, 122.82, 121.28, 111.51, 106.65.

7-Fluorobenzofuran (**2b**)[13]



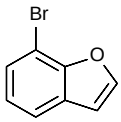
2b was afforded as a colorless liquid (67 mg, 0.49 mmol, 49%). Due to the relatively low boiling point of the compound, some products evaporated away with the chlorobenzene solvent, resulting in low yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 2.1 Hz, 1H), 7.37 (dd, J = 7.8, 0.8 Hz, 1H), 7.19 – 7.14 (m, 1H), 7.06 – 7.01 (m, 1H), 6.83 – 6.81 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.42 (d, J = 124 Hz), 145.86, 141.92, 130.96, 123.42, 116.88, 110.67, 107.12.

7-Chlorobenzofuran (**2c**)[1]



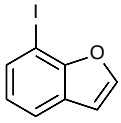
2c was afforded as a colorless liquid (108 mg, 0.71 mmol, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 2.2 Hz, 1H), 7.50 (dd, J = 7.8, 0.9 Hz, 1H), 7.30 (dd, J = 7.8, 0.9 Hz, 1H), 7.17 (t, J = 7.8 Hz, 1H), 6.82 (d, J = 2.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.70, 145.64, 129.02, 124.42, 123.66, 119.74, 116.90, 107.11.

7-Bromobenzofuran (**2d**)[14]



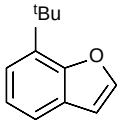
2d was afforded as a colorless liquid (173 mg, 0.88 mmol, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 2.2 Hz, 1H), 7.56 – 7.46 (m, 2H), 7.13 (t, J = 7.8 Hz, 1H), 6.85 (d, J = 2.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.05, 145.82, 128.71, 127.60, 124.18, 120.52, 107.42, 104.59.

7-Iodobenzofuran (**2e**)[3]



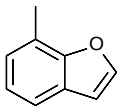
2e was afforded as a pale-yellow liquid (137 mg, 0.56 mmol, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 2.2 Hz, 1H), 7.66 (dd, J = 7.7, 0.9 Hz, 1H), 7.55 (dd, J = 7.7, 1.0 Hz, 1H), 7.00 (t, J = 7.6 Hz, 1H), 6.88 (d, J = 2.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.30, 145.34, 133.39, 127.54, 124.66, 121.45, 107.79, 75.19.

7-(*Tert*-butyl)benzofuran (**2f**)



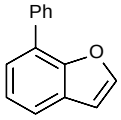
2f was afforded as a colorless liquid (148 mg, 0.85 mmol, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 2.2 Hz, 1H), 7.46 (dd, J = 7.0, 2.0 Hz, 1H), 7.20 – 7.15 (m, 2H), 6.75 (d, J = 2.1 Hz, 1H), 1.50 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.36, 144.06, 135.09, 127.99, 122.77, 120.90, 119.28, 106.49, 34.45, 29.95. HRMS (EI) *m/z* calcd for $C_{12}H_{14}O$ $[M]^+$ 174.1045, found 174.1037.

7-Methylbenzofuran (**2g**)[15]



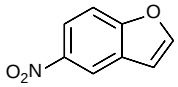
2g was afforded as a colorless liquid (96 mg, 0.73 mmol, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 2.2 Hz, 1H), 7.45 – 7.40 (m, 1H), 7.16 – 7.05 (m, 2H), 6.75 (d, J = 2.2 Hz, 1H), 2.53 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.11, 144.67, 126.94, 125.14, 122.85, 121.73, 118.70, 106.86, 15.08.

7-Phenylbenzofuran (**2h**)[3]



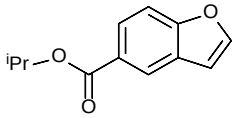
2h was afforded as a colorless liquid (121 mg, 0.62 mmol, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.85 (m, 2H), 7.68 (d, J = 2.2 Hz, 1H), 7.58 (dd, J = 7.7, 1.2 Hz, 1H), 7.52 – 7.48 (m, 2H), 7.46 (dd, J = 7.5, 1.1 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.34 – 7.30 (m, 1H), 6.83 (d, J = 2.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.35, 145.14, 136.67, 128.78, 128.75, 128.33, 127.82, 125.76, 123.98, 123.46, 120.56, 106.93.

7-Nitrobenzofuran (**2i**)[5]



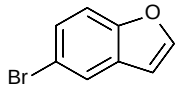
2i was afforded as a pale-yellow liquid (64 mg, 0.39 mmol, 39%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, J = 2.0 Hz, 1H), 8.25 (dd, J = 9.2, 2.4 Hz, 1H), 7.79 (d, J = 2.4 Hz, 1H), 7.60 (d, J = 9.2 Hz, 1H), 6.94 (dd, J = 2.4, 1.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.69, 147.98, 144.20, 127.80, 120.22, 117.86, 111.78, 107.59.

Isopropyl benzofuran-5-carboxylate (**2j**)



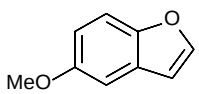
2j was afforded as a white solid (91 mg, 0.44 mmol, 44%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 1.6 Hz, 1H), 8.03 (dd, J = 8.7, 1.8 Hz, 1H), 7.69 (d, J = 2.2 Hz, 1H), 7.53 (d, J = 8.7 Hz, 1H), 6.85 (dd, J = 2.2, 0.7 Hz, 1H), 5.31 – 5.25 (m, 1H), 1.40 (d, J= 4Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.42, 157.50, 146.29, 127.47, 126.13, 126.02, 123.75, 111.28, 107.26, 68.44, 22.17. HRMS (ESI) *m/z* calcd for $C_{12}H_{12}O_3$ $[M + H]^+$ 205.0865, found 205.0864.

5-Bromobenzofuran (**2k**)[1]



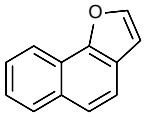
2k was afforded as a colorless liquid (185 mg, 0.94 mmol, 94%).^{1}H NMR (400 MHz,) δ 7.72 (d, J = 1.2 Hz, 1H), 7.61 (d, J = 2.2 Hz, 1H), 7.38 (d, J = 1.5 Hz, 2H), 6.71 (d, J = 2.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.66, 146.12, 129.39, 127.14, 123.81, 115.77, 112.82, 106.11.

5-Methoxybenzofuran (**2l**)[1]



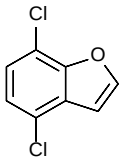
2l was afforded as a colorless liquid (70 mg, 0.47 mmol, 47%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 2.2 Hz, 1H), 7.39 (d, J = 9.0 Hz, 1H), 7.06 (d, J = 2.5 Hz, 1H), 6.90 (dd, J = 9.0, 2.6 Hz, 1H), 6.71 (dd, J = 2.2, 0.7 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.99, 149.99, 145.80, 127.86, 113.14, 111.88, 106.77, 103.57, 29.79.

Naphtho[1,2-*b*]furan (**2m**)[1]



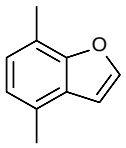
2m was afforded as a colorless liquid (138 mg, 0.82 mmol, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, J = 8.2 Hz, 1H), 7.93 (d, J = 8.2 Hz, 1H), 7.76 (d, J = 2.1 Hz, 1H), 7.66 (s, 2H), 7.61 – 7.57 (m, 1H), 7.51 – 7.46 (m, 1H), 6.90 (d, J = 2.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.71, 144.23, 131.56, 128.45, 126.45, 125.22, 123.55, 123.08, 121.64, 120.14, 119.87, 107.73.

4,7-Dichlorobenzofuran (**2n**)[1]



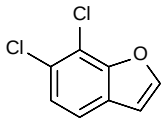
2n was afforded as a white solid (129 mg, 0.69 mmol, 69%), Mp 56.5-57.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 2.2 Hz, 1H), 7.25 (d, J = 8.4 Hz, 1H), 7.19 (d, J = 8.3 Hz, 1H), 6.92 (d, J = 2.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.77, 146.21, 128.19, 124.92, 124.82, 123.53, 115.66, 106.19.

4,7-Dimethylbenzofuran (**2o**)[6]



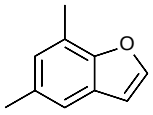
2o was afforded as a colorless liquid (108 mg, 0.74 mmol, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 2.2 Hz, 1H), 7.00 (d, J = 7.4 Hz, 1H), 6.94 (d, J = 7.4 Hz, 1H), 6.78 (d, J = 2.1 Hz, 1H), 2.50 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.69, 144.09, 128.31, 126.60, 124.88, 122.89, 118.78, 105.39, 18.34, 14.82.

6,7-Dichlorobenzofuran (**2p**)[16]



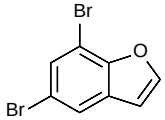
2p was afforded as a white solid (119 mg, 0.64 mmol, 64%), Mp 40.3-41.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 2.2 Hz, 1H), 7.43 (d, J = 8.3 Hz, 1H), 7.34 (d, J = 8.4 Hz, 1H), 6.81 (d, J = 2.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ151.67, 146.49, 128.74, 127.40, 125.02, 119.69, 116.26, 107.48. HRMS (EI) *m/z* calcd for $C_8H_4Cl_2O$ $[M]^+$ 185.9639, found 185.9633.

5,7-Dimethylbenzofuran (**2q**)[17]



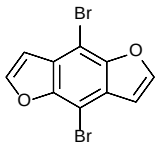
2q was afforded as a colorless liquid (124 mg, 0.85 mmol, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 2.1 Hz, 1H), 7.20 (s, 1H), 6.91 (s, 1H), 6.67 (d, J = 2.2 Hz, 1H), 2.48 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.44, 144.67, 132.13, 126.94, 126.45, 120.98, 118.31, 106.32, 21.22, 15.00.

5,7-Dibromobenzofuran (**2r**)



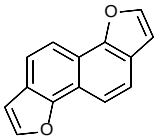
2r was afforded as a white solid (153 mg, 0.56 mmol, 56%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 2.2 Hz, 1H), 7.68 (d, J = 1.8 Hz, 1H), 7.60 (d, J = 1.8 Hz, 1H), 6.80 (d, J = 2.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.29, 146.88, 130.11, 129.73, 123.23, 116.06, 107.13, 105.06. HRMS (EI) *m/z* calcd for $C_8H_4Br_2O$ $[M]^+$ 273.8629, found 273.8622.

4,8-Dibromobenzo[1,2-*b*:4,5-*b'*]difuran (**2s**)[7]



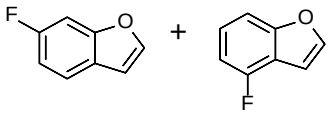
2s was afforded as a yellow solid (177 mg, 0.56 mmol, 56%), Mp 209.9-212.6 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 2.2 Hz, 2H), 6.98 (d, J = 2.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.94, 146.60, 127.19, 107.53, 93.94.

Naphtho[1,2-*b*;5,6-*b*']difuran (**2t**)[18]



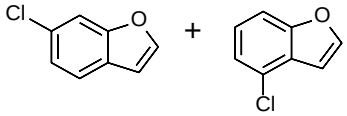
2t was afforded as a white solid (93 mg, 0.45 mmol, 45%), Mp 149.8–150.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.3 Hz, 2H), 7.79 – 7.77 (m, 4H), 6.94 (d, J = 1.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.07, 143.98, 122.62, 120.22, 119.01, 115.58, 107.70.

6- And 4-fluorobenzofuran (**2u+2u′**)[19,20]



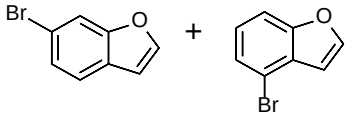
A mixture of **2u** and **2u′** were afforded as a colorless liquid (78 mg, 0.57 mmol, 57%). Due to the relatively low boiling point of the compounds, some products evaporated away with the chlorobenzene solvent, resulting in low yield. **2u**: **2u′** = 83:17. **2u** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 2.3 Hz, 1H), 7.50 (dd, J = 8.7, 5.5 Hz, 1H), 7.21 (dd, J = 9.6, 2.3 Hz, 1H), 7.02-6.97 (m, 1H), 6.74 (dd, J = 2.0, 0.8 Hz, 1H). **2u′** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 2.2 Hz, 1H), 7.30 (d, J = 8.4Hz, 1H) 7.13-7.05 (m, 1H), 6.94-6.98 (m, 1H), 6.86 (dd, J = 2.2, 0.7 Hz, 1H). **2u** ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.99 (d, J = 290 Hz), 155.05, 145.59 (d, J = 5.0Hz), 121.35 (d, J = 10.1Hz), 113.80, 111.12 (d, J = 24.2Hz), 106.37, 99.08 (d, J = 27.3Hz).

6- And 4-chlorobenzofuran (**2v+2v′**)[1]



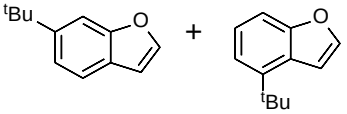
A mixture of **2v** and **2v′** were afforded as a colorless liquid (124 mg, 0.81 mmol, 81%); **2v:2v′** = 66:34. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (**2v′**, d, J = 2.2 Hz, 1H), 7.61 (**2v**, d, J = 2.2 Hz, 1H), 7.52 (**2v**, s, 1H), 7.50 (**2v′**, d, J = 8.0 Hz, 2H), 7.44 – 7.40 (**2v′**, m, 1H), 7.25 – 7.20 (**2v**, m, 2H), 6.87 (**2v′**, dd, J = 2.2, 0.8 Hz, 1H), 6.75 (**2v**, dd, J = 2.1, 0.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.71, 145.52, 134.27, 129.81, 128.71, 126.53, 124.95, 123.61, 122.79, 121.76, 112.07, 110.11, 106.57, 105.38.

6- And 4-bromobenzofuran (**2w+2w′**)[1]



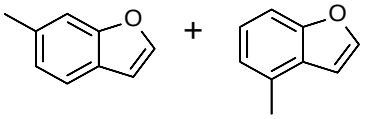
A mixture of **2w** and **2w′** were afforded as a colorless liquid (169 mg, 0.86 mmol, 86%). **2w:2w′** = 57:47. ^{1}H NMR (400 MHz,) δ 7.68 (s, 1H), 7.66 (d, J = 2.2 Hz, 1H), 7.59 (d, J = 2.2 Hz, 1H), 7.47 – 7.45 (m, 1H), 7.45 – 7.43 (m, 1H), 7.39 (d, J = 7.7 Hz, 1H), 7.35 (dd, J = 8.3, 1.5 Hz, 1H), 7.16 (t, J = 8.0 Hz, 1H), 6.81 (**2w′**, dd, J = 2.3, 0.9 Hz, 1H), 6.74 (**2w**, dd, J = 2.0, 1.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.34, 154.81, 145.64, 145.47, 129.10, 126.56, 126.26, 125.86, 125.32, 122.21, 117.64, 114,98, 114.35, 110.64, 106.94, 106.64.

6- And 4- (tert-butyl)benzofuran (**2x+2x′**)[21]



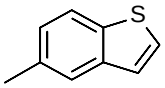
A mixture of **2x** and **2x′** was afforded as a colorless liquid (143 mg, 0.82 mmol, 82%). **2x:2x′** = 84:16. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (**2x′**, d, J = 2.3 Hz, 1H), 7.58 (**2x**, d, J = 2.3 Hz, 1H), 7.51-7.53 (**2x**, m, 2H), 7.37-7.39 (**2x′**, m, 1H), 7.31 (**2x**, dd, J = 8.2, 1.4 Hz, 1H), 7.23 (**2x′**, t, J = 8.0 Hz, 1H), 7.16 (**2x′**, dd, J = 7.5, 1.1 Hz, 1H), 7.01 (**2x′,** dd, J = 2.3, 0.9 Hz, 1H), 6.71 (**2x**, dd, J = 2.2, 1.0 Hz, 1H), 1.47 (**2x′**, s, 9H), 1.38 (**2x**, s, 9H) ^{13}C NMR (101MHz, $CDCl_3$) δ 155.40, 148.27, 144.77, 143.54, 124.78, 124.00, 120.71, 120.63, 120.46, 118.78, 109.56, 108.11, 107.63, 106.30, 35.02, 31.79, 30.79.

6- And 4-methylbenzofuran (**2y+2y'**)[1]



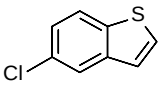
A mixture of **2y** and **2y′** were afforded as a colorless liquid (102 mg, 0.77 mmol, 77%). **2y: 2y′ =** 64: 36. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (**2y′**, d, J = 2.2 Hz, 1H), 7.55 (**2y**, d, J = 2.2 Hz, 1H), 7.47 (**2y**, d, J = 7.9 Hz, 1H), 7.38 – 7.29 (m, 2H), 7.19 (**2y′**, t, J = 7.8 Hz, 1H), 7.05 (dd, J = 13.2, 7.7 Hz, 2H), 6.82 – 6.77 (**2y′**, m, 1H), 6.76 – 6.68 (**2y**, m, 1H), 2.53 (**2y′**, s, 3H), 2.47 (**2y**, s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.46, 154.82, 144.43, 134.51, 131.22, 127.29, 124.93, 124.24, 123.05, 120.68, 111.69, 108.89, 106.44, 105.27, 21.74, 18.73.

5-Methylbenzothiophene (**4a**)[22]



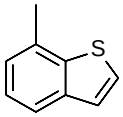
4a was afforded as a colorless liquid (80 mg, 0.54 mmol, 54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.2 Hz, 1H), 7.60 (d, J = 0.6 Hz, 1H), 7.38 (d, J = 5.4 Hz, 1H), 7.24 (d, J = 5.4 Hz, 1H), 7.16 (d, J = 8.2 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.07, 137.01, 133.96, 126.51, 126.11, 123.66, 123.62, 122.20, 21.51.

5-Chlorobenzothiophene (**4b**)[23]



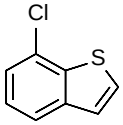
4b was afforded as a colorless liquid (80 mg, 0.50 mmol, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, J = 6.9, 5.3 Hz, 2H), 7.48 (d, J = 5.5 Hz, 1H), 7.29 (dd, J = 8.6, 2.0 Hz, 1H), 7.25 (d, J = 5.5 Hz, 1H); ^{13}C NMR (101 MHz,$CDCl_3$) δ 140.69, 137.81, 130.42, 128.27, 124.65, 123.40, 123.17, 123.11.

7-Methylbenzothiophene (**4c**)[23]



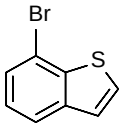
4c was afforded as a colorless liquid (90 mg, 0.61 mmol, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.9 Hz, 1H), 7.41 (d, J = 5.4 Hz, 1H), 7.35 (d, J = 5.4 Hz, 1H), 7.29 (t, J = 7.5 Hz, 1H), 7.14 (d, J = 7.2 Hz, 1H), 2.57 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.12, 139.54, 132.14, 125.91, 124.70, 124.67, 124.51, 121.35, 20.56.

7-Chlorobenzothiophene (**4d**)[23]



4d was afforded as a colorless liquid (123 mg, 0.73 mmol, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, J = 7.3, 1.6 Hz, 1H), 7.48 (d, J = 5.4 Hz, 1H), 7.38 – 7.27 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.14, 139.20, 128.06, 127.50, 125.51, 124.70, 123.99, 122.14.

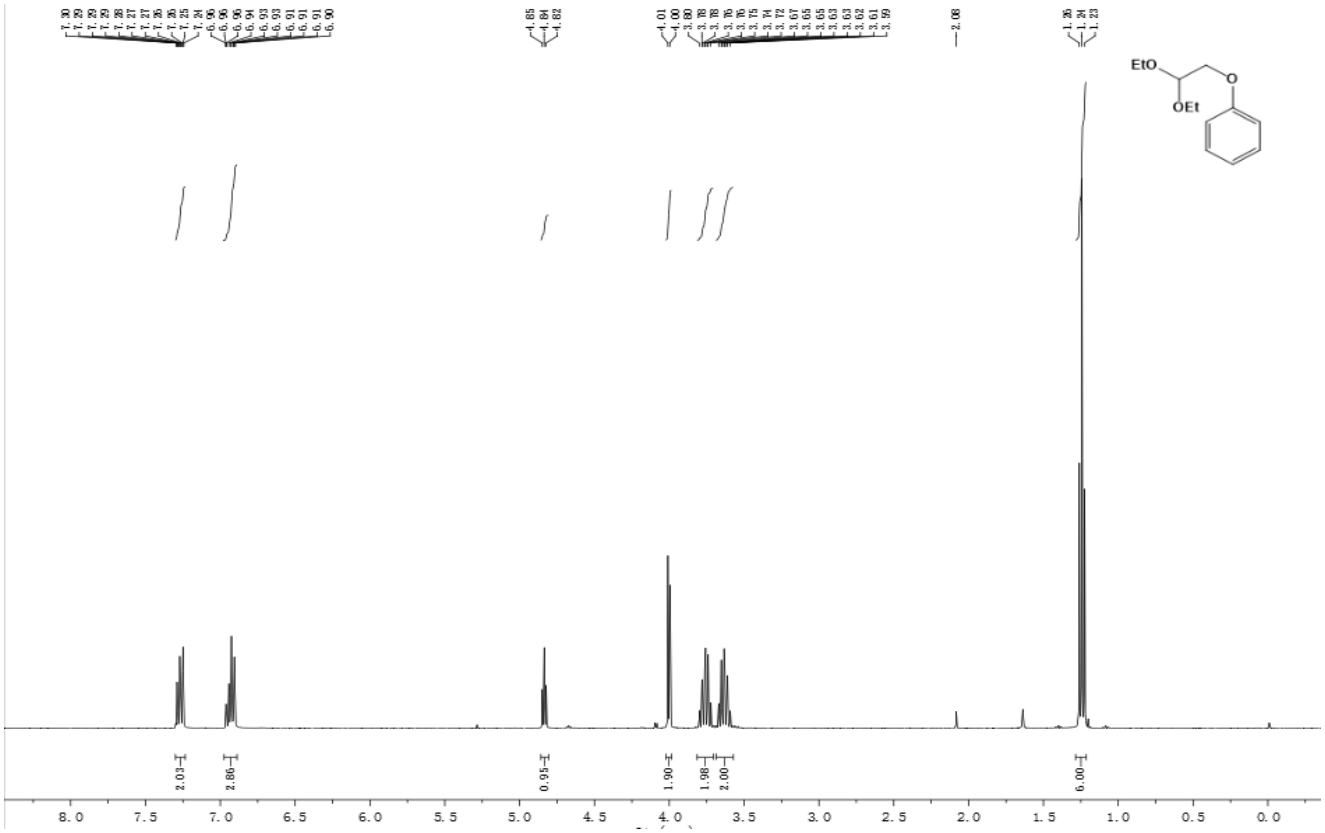
7-Bromobenzothiophene (**4e**)[3]



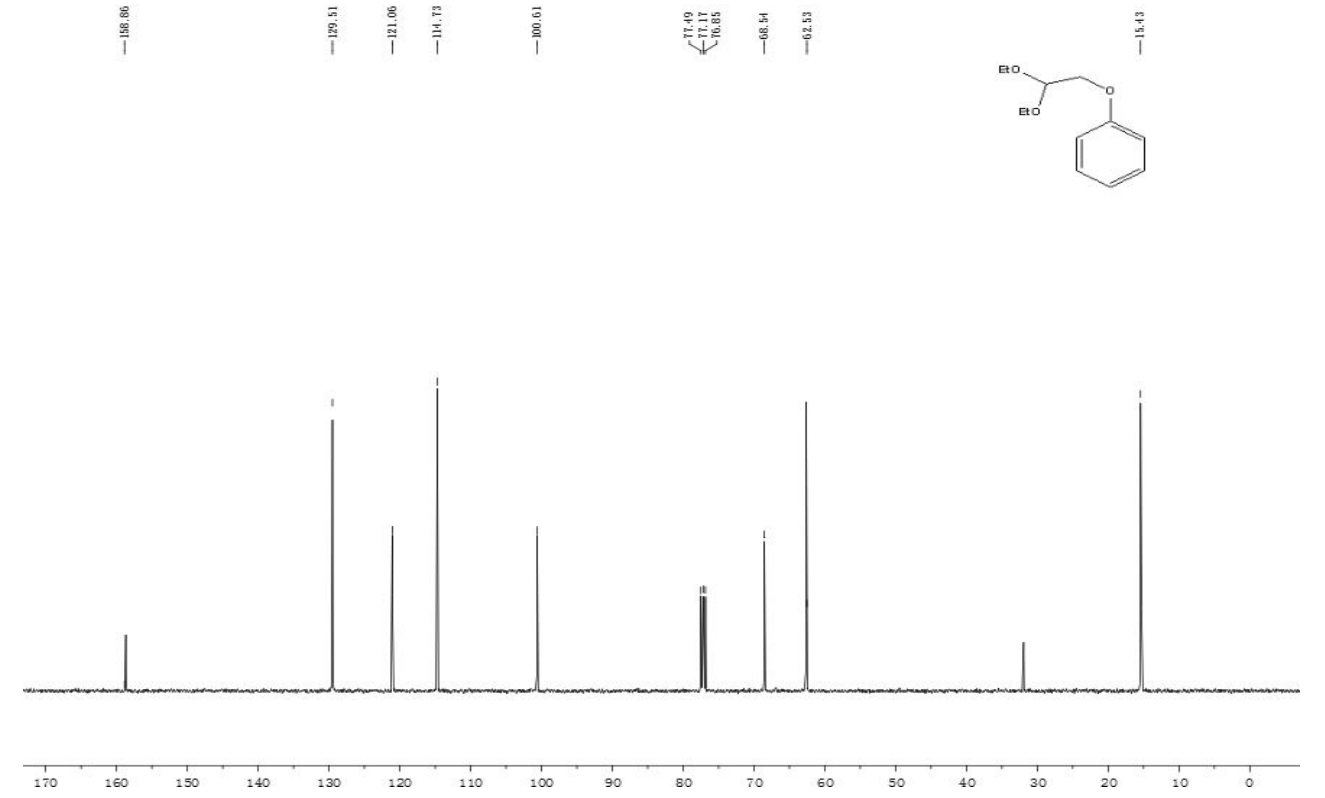
4e was afforded as a colorless liquid (170 mg, 0.8 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.0 Hz, 1H), 7.51 – 7.46 (m, 2H), 7.42 (d, J = 5.5 Hz, 1H), 7.24 (t, J = 7.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.58, 140.51, 127.29, 127.12, 125.57, 124.83, 122.61, 115.94.

7. ^{1}H and ^{13}C NMR spectra and HRMS spectra

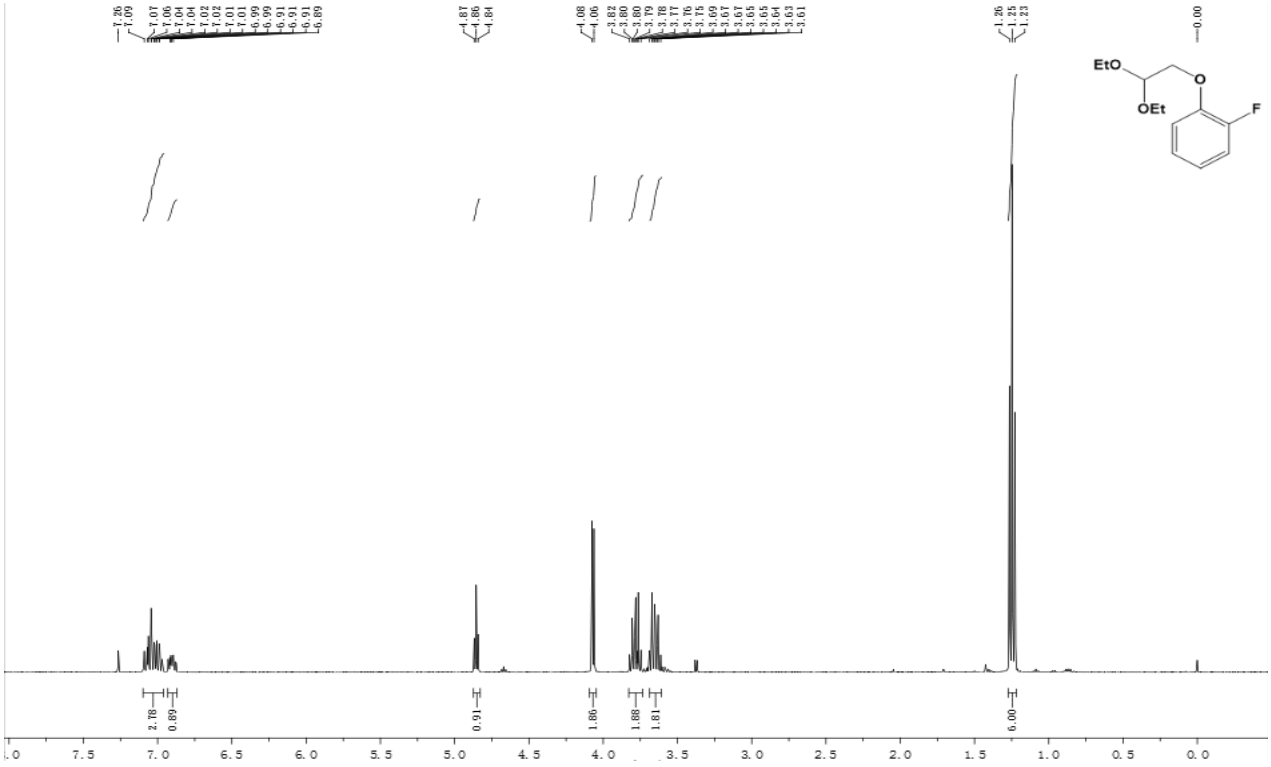
^{1}H NMR spectrum for 1a



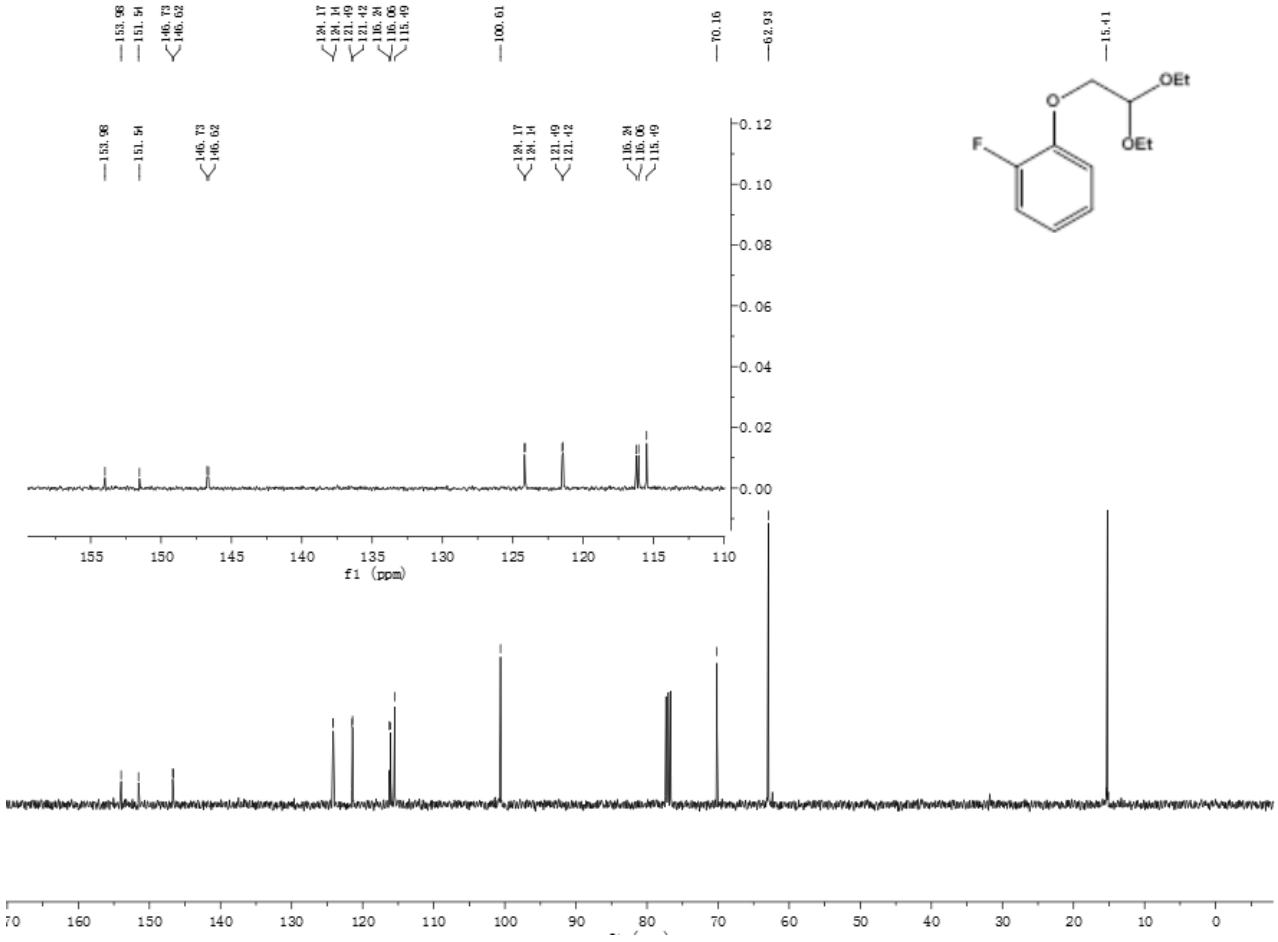
^{13}C NMR spectrum for 1a



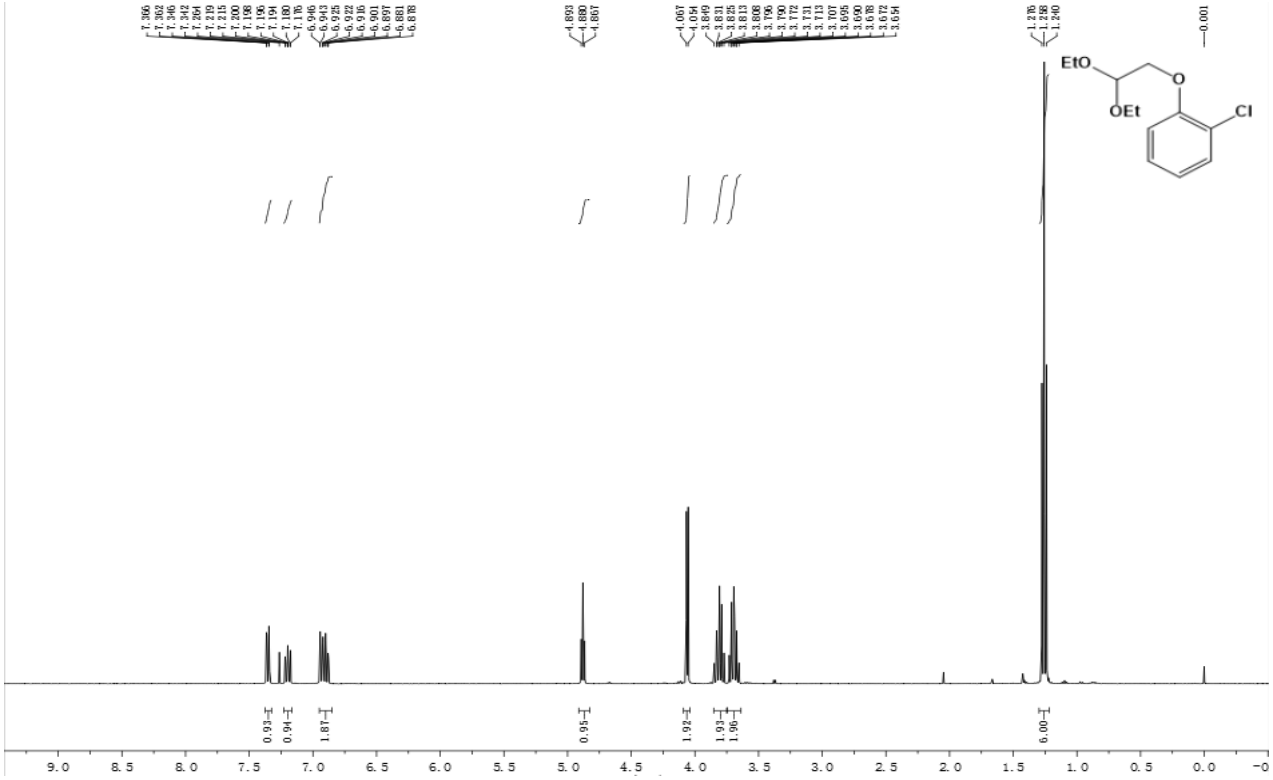
^{1}H NMR spectrum for 1b



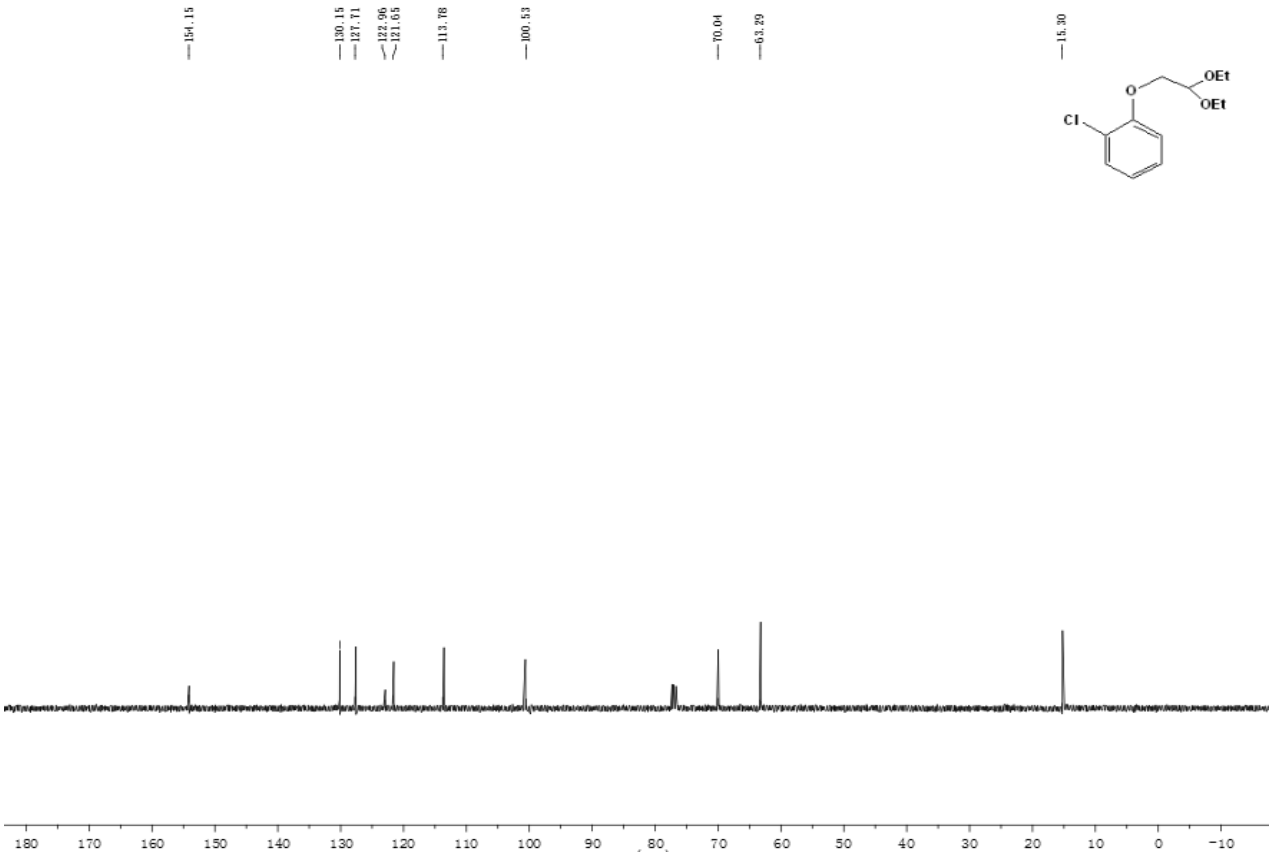
^{13}C NMR spectrum for 1b



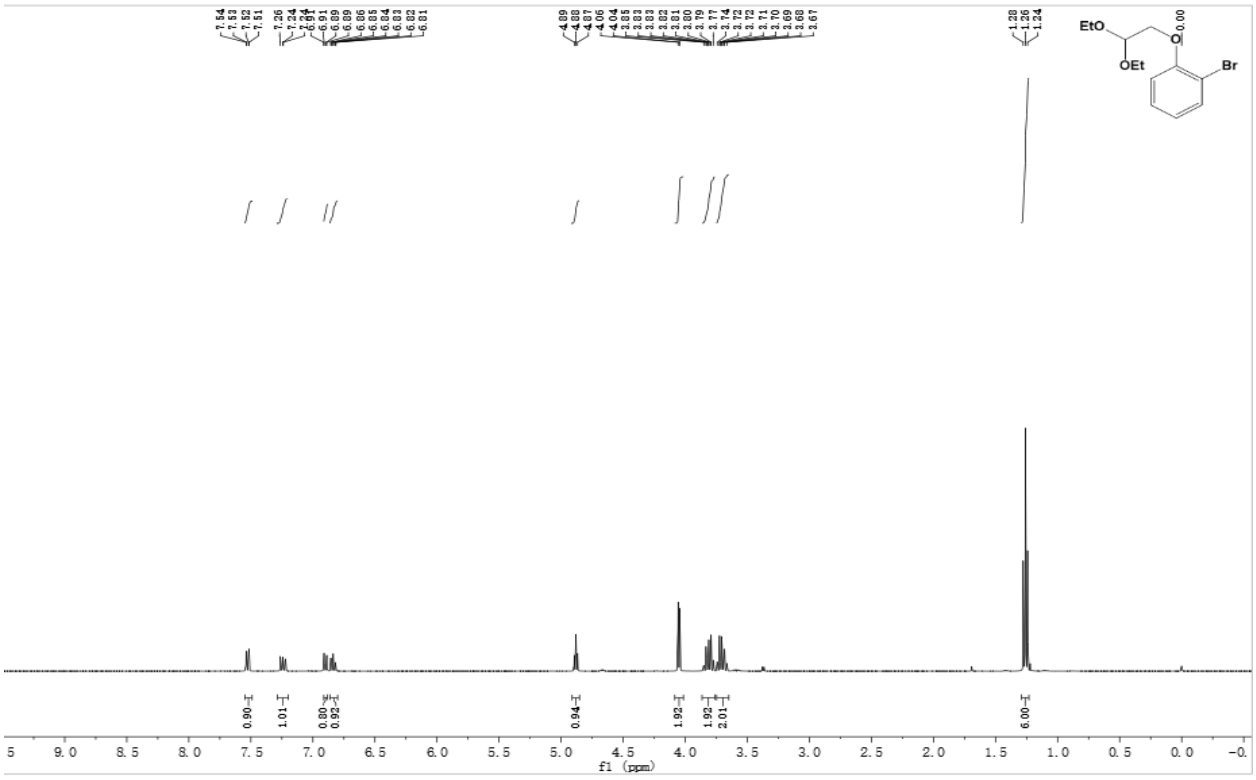
^{1}H NMR spectrum for 1c



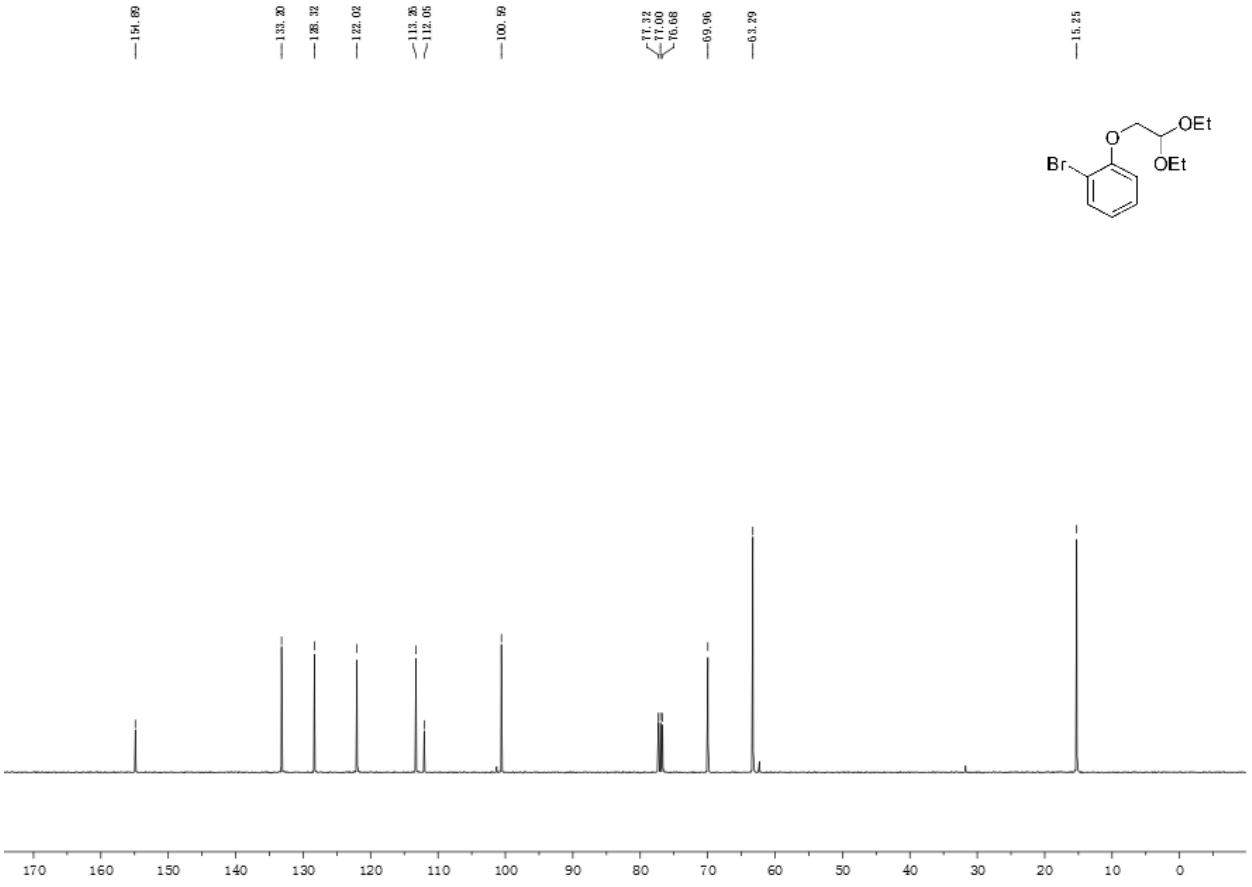
^{13}C NMR spectrum for 1c



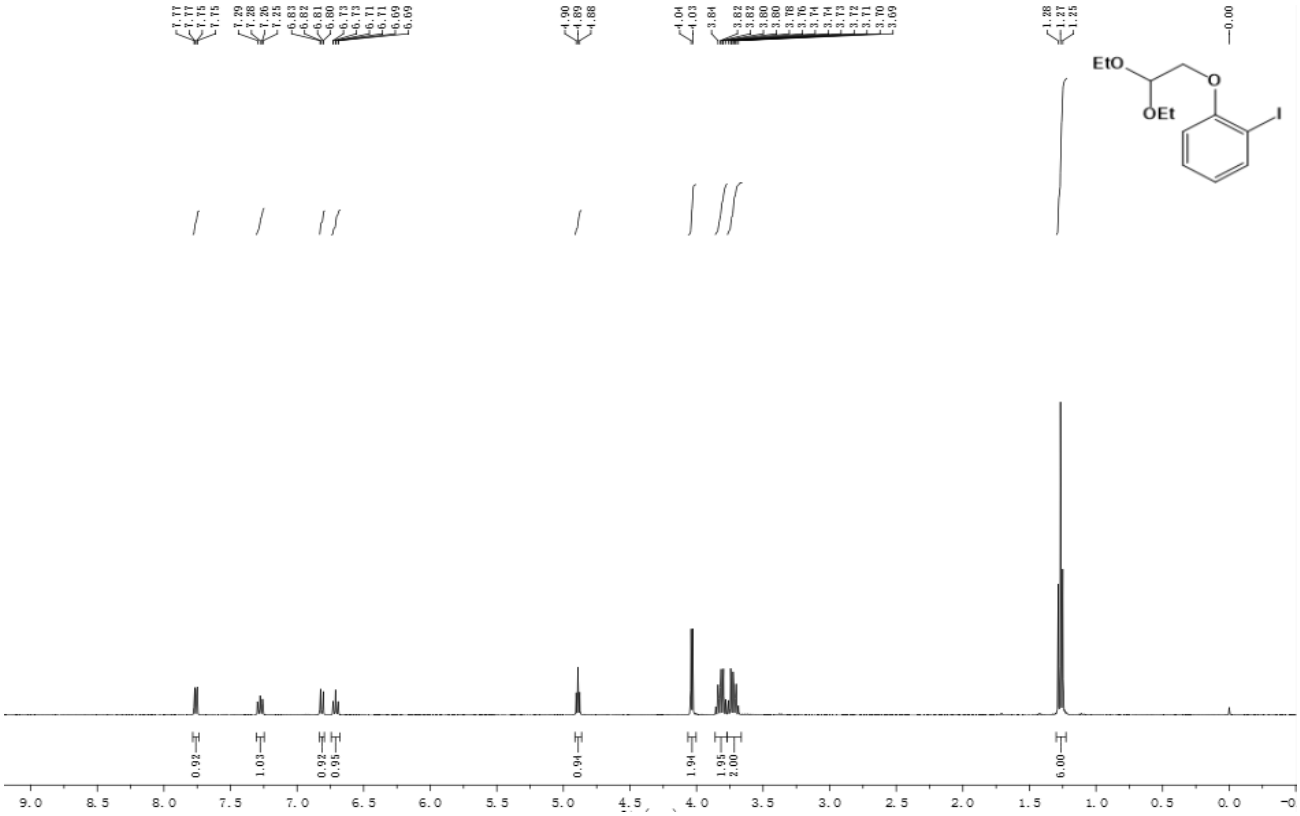
[1]H NMR spectrum for 1d



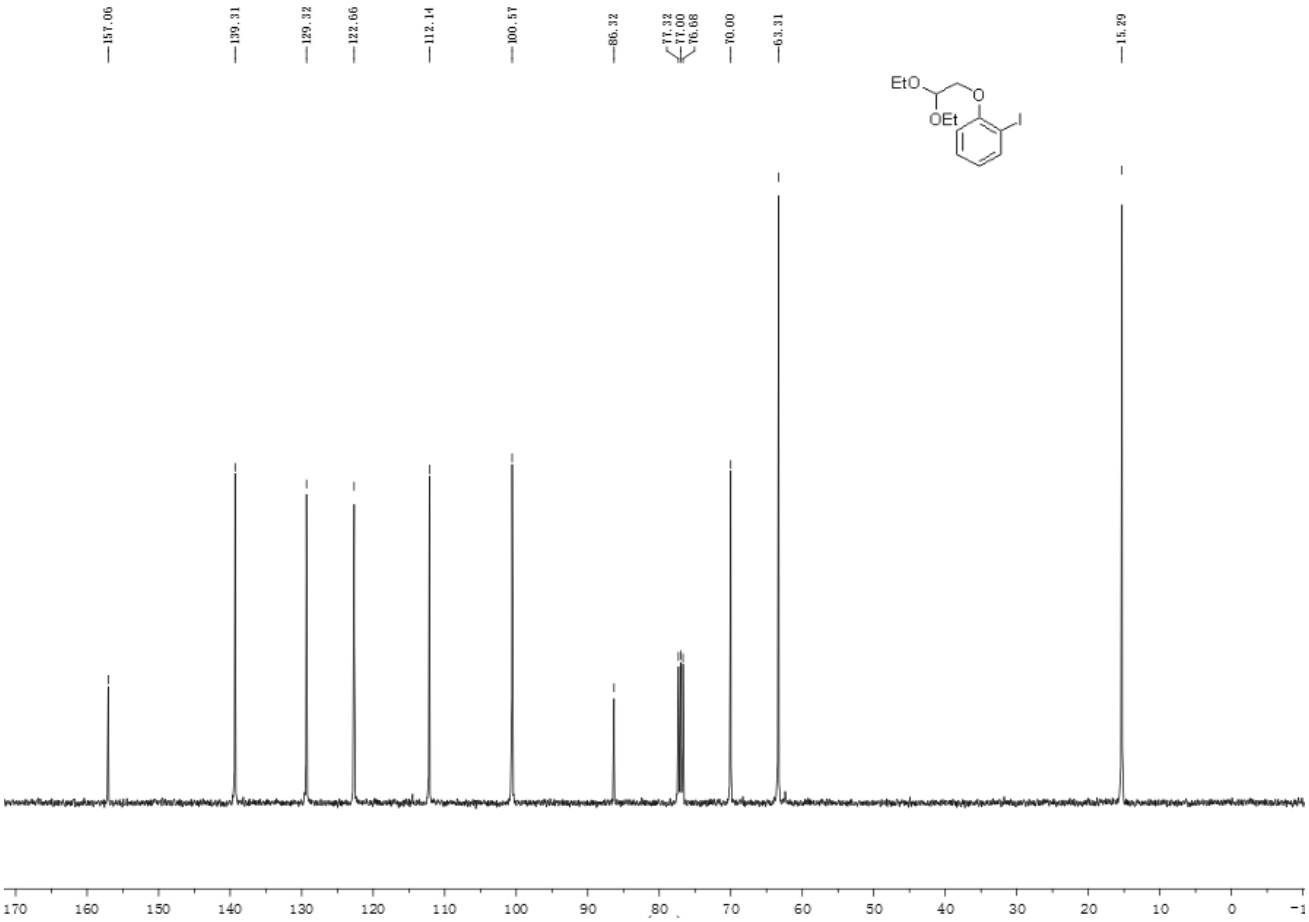
[13] C NMR spectrum for 1d



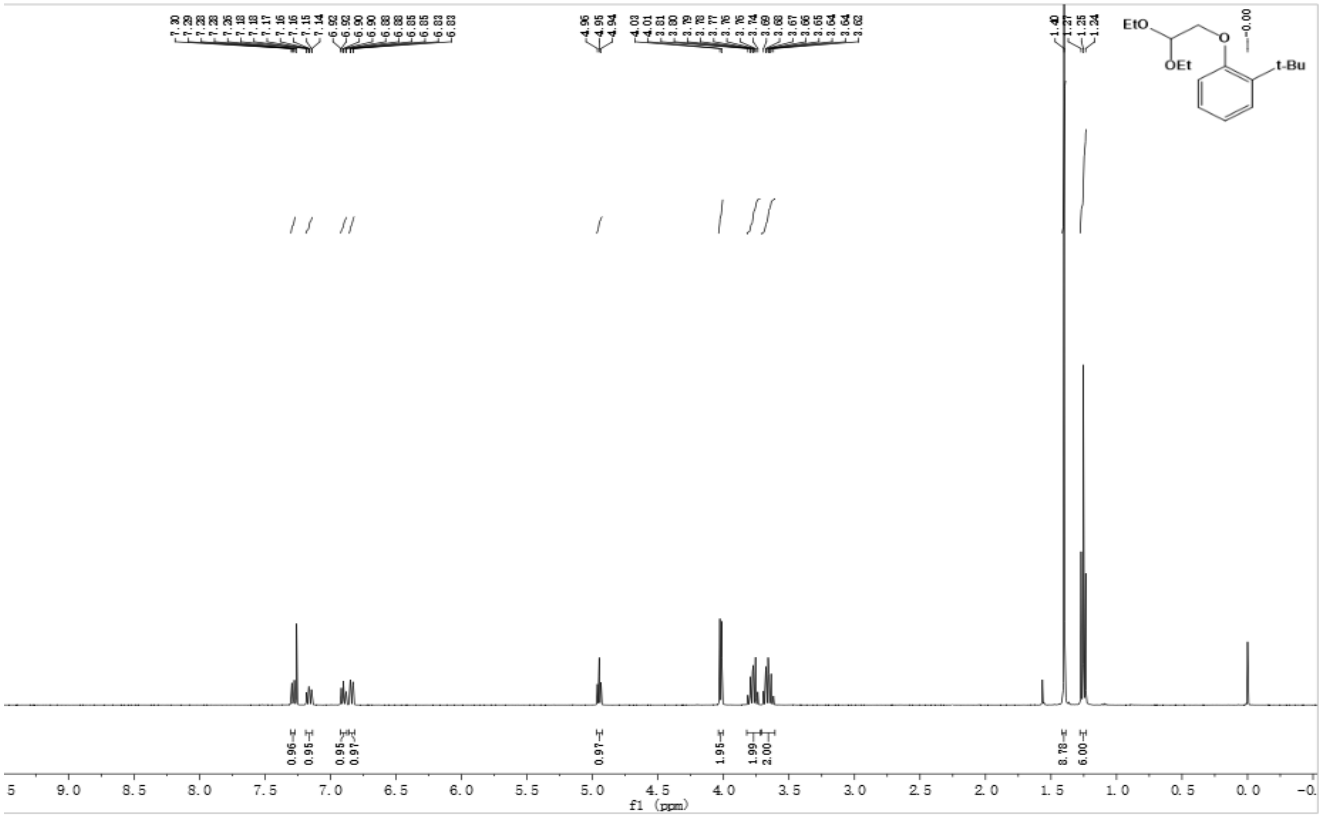
^{1}H NMR spectrum for 1e



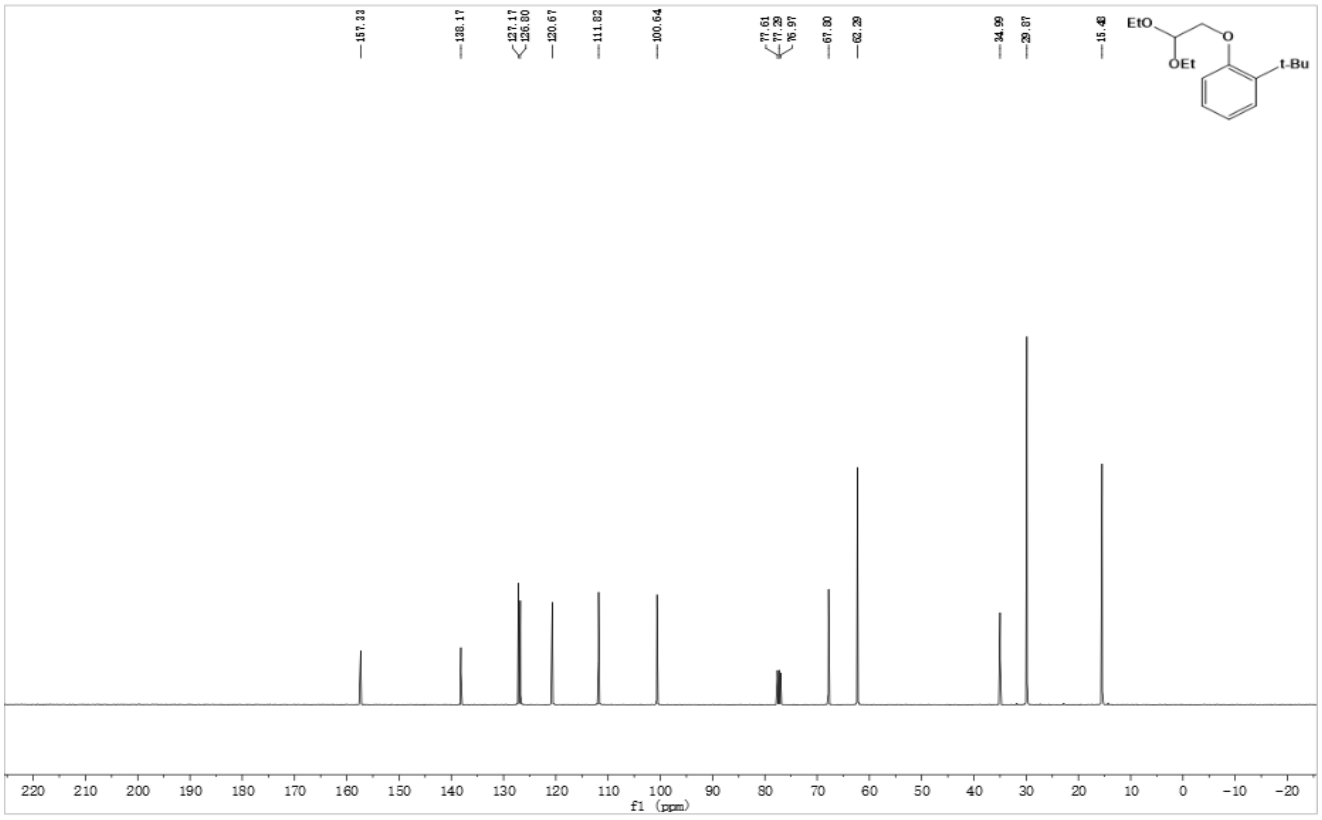
^{13}C NMR spectrum for 1e



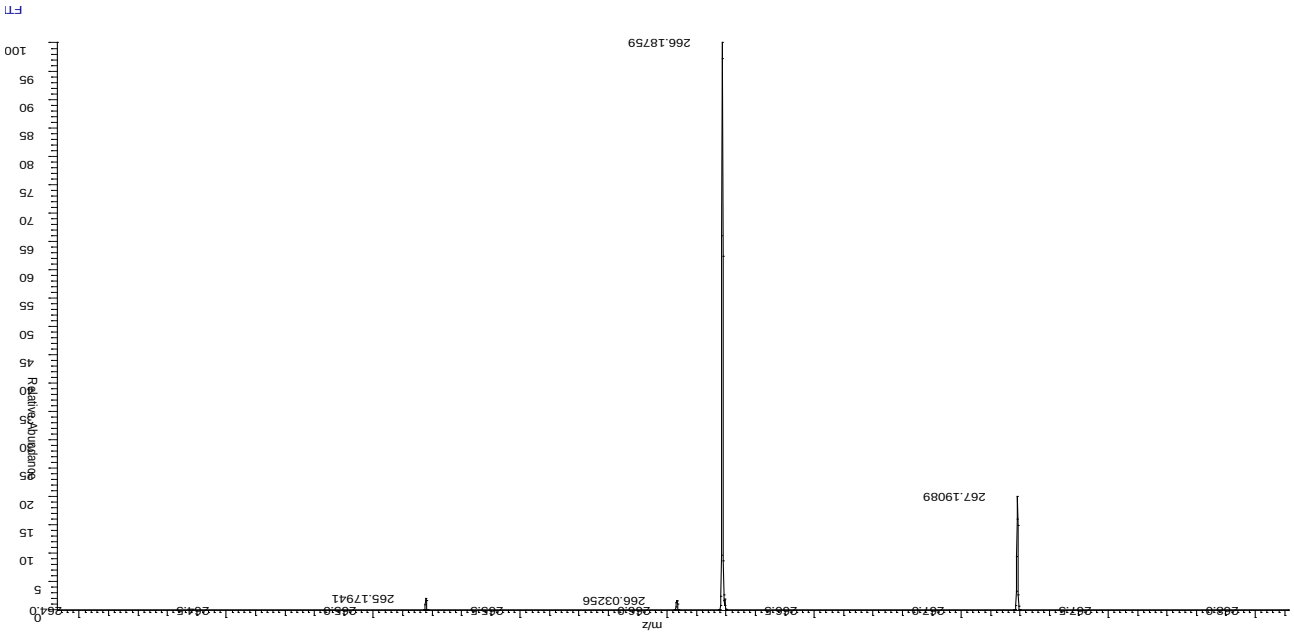
^{1}H NMR spectrum for 1f



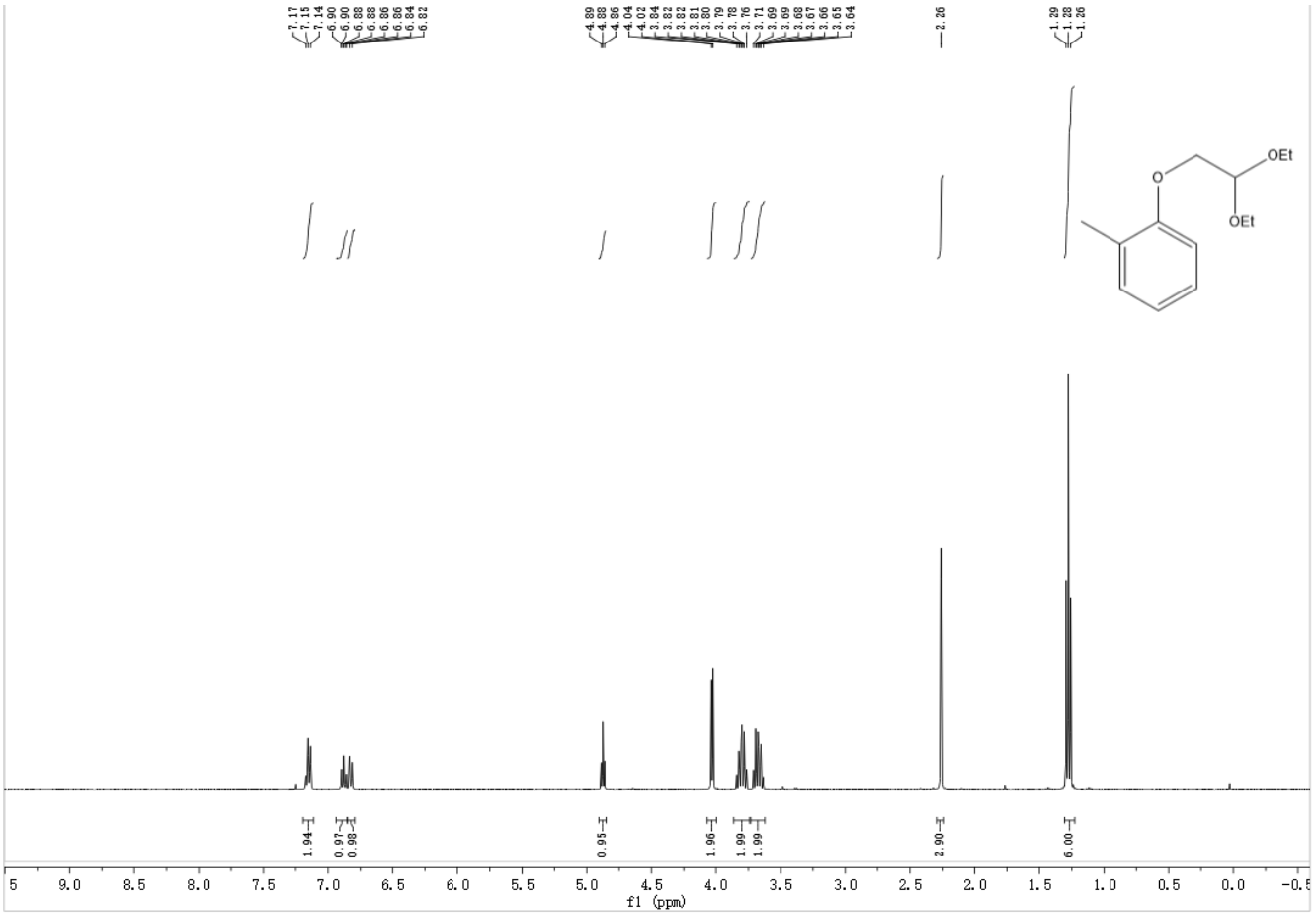
^{13}C NMR spectrum for 1f



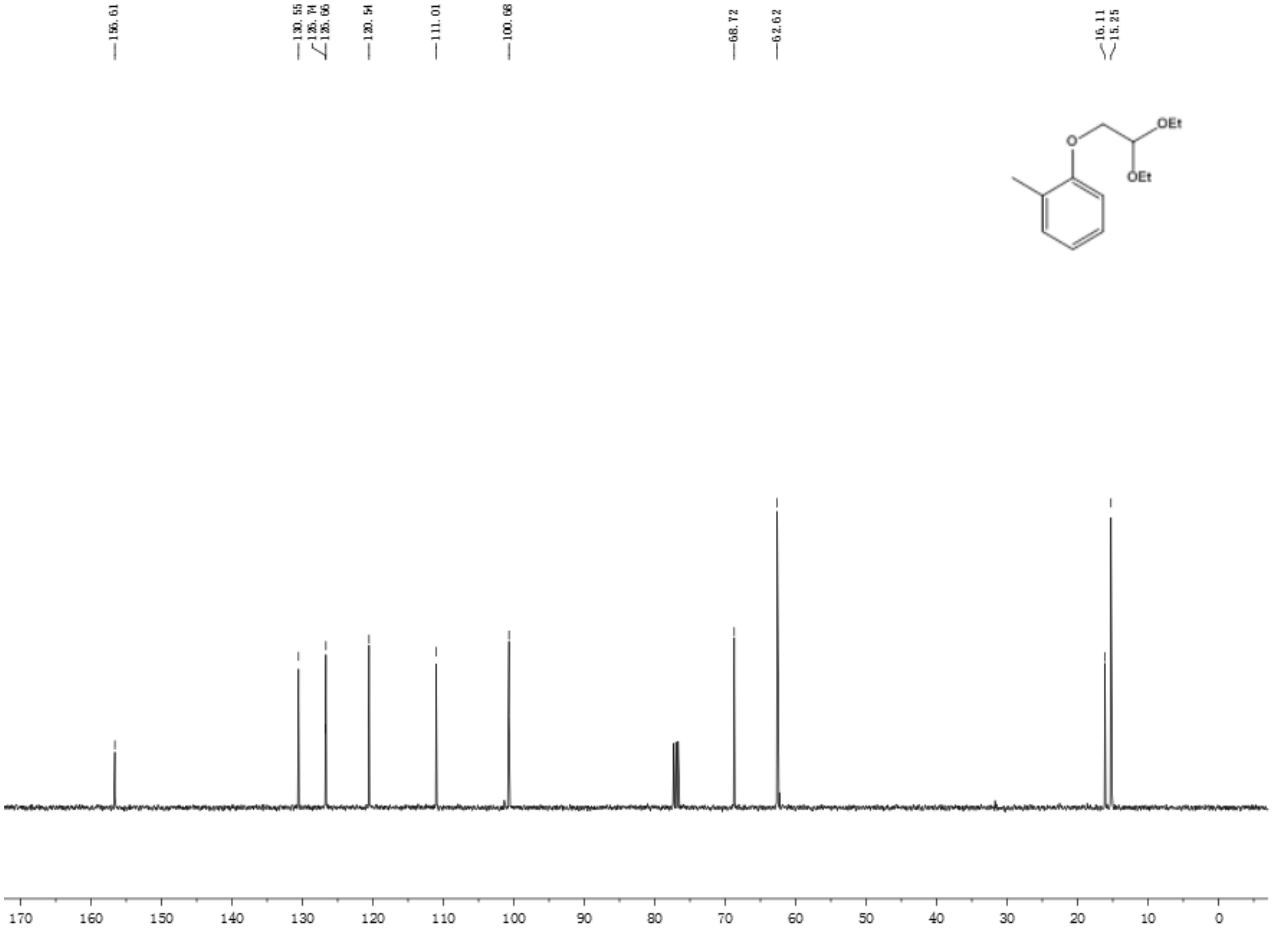
HRMS (EI) spectrum for 1f



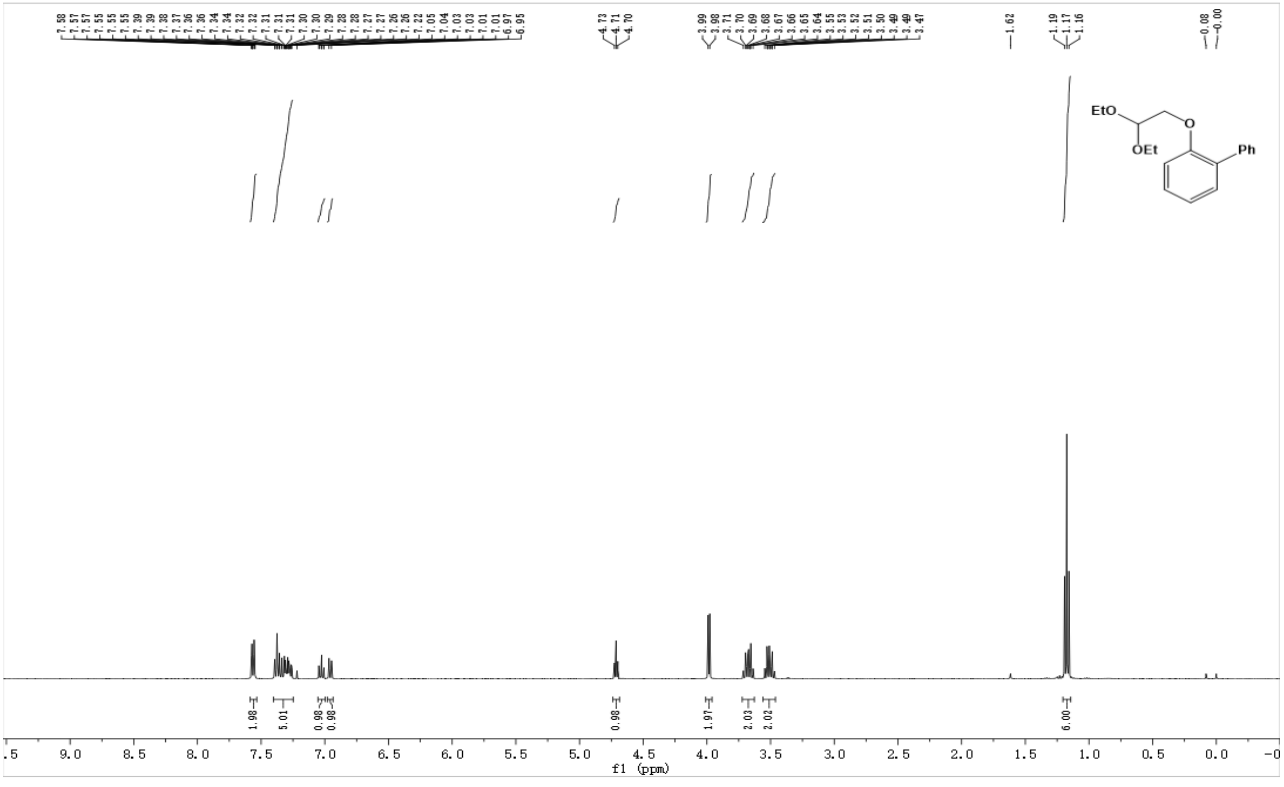
^{1}H NMR spectrum for 1g



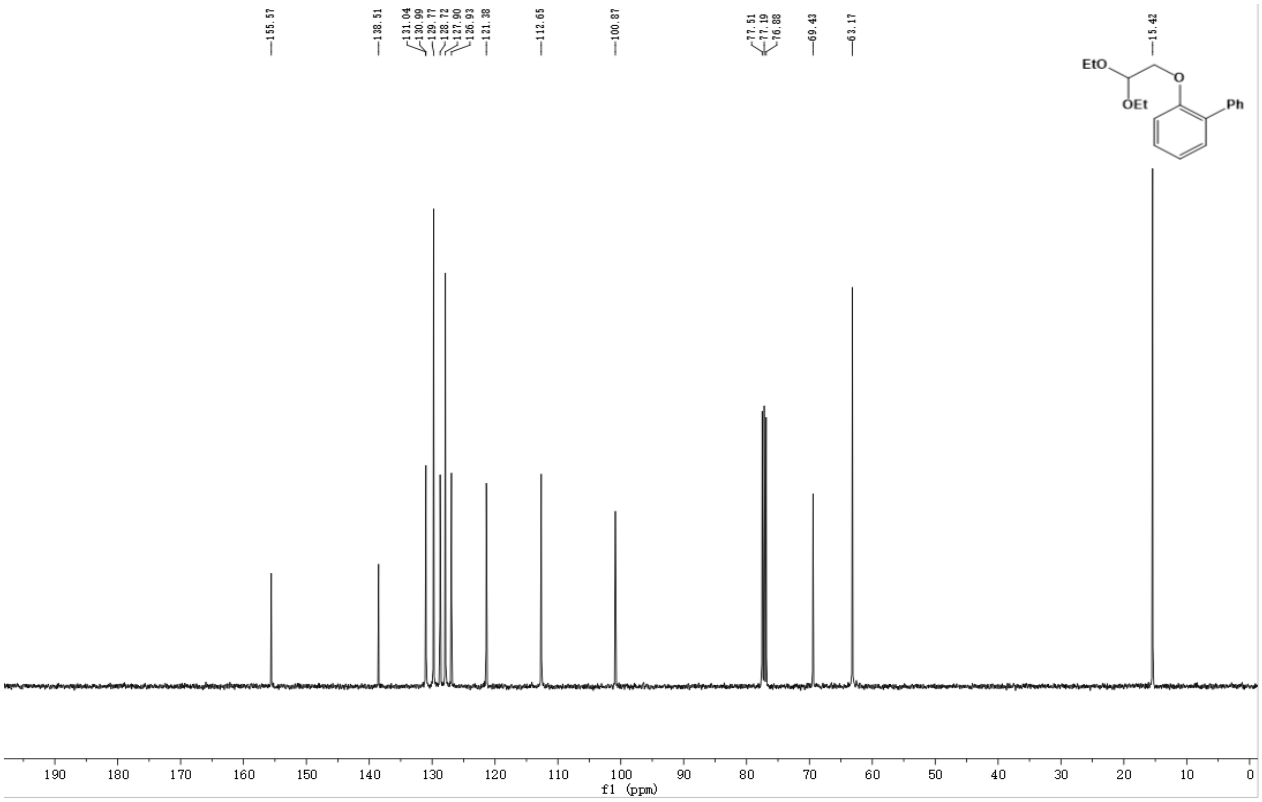
^{13}C NMR spectrum for 1g



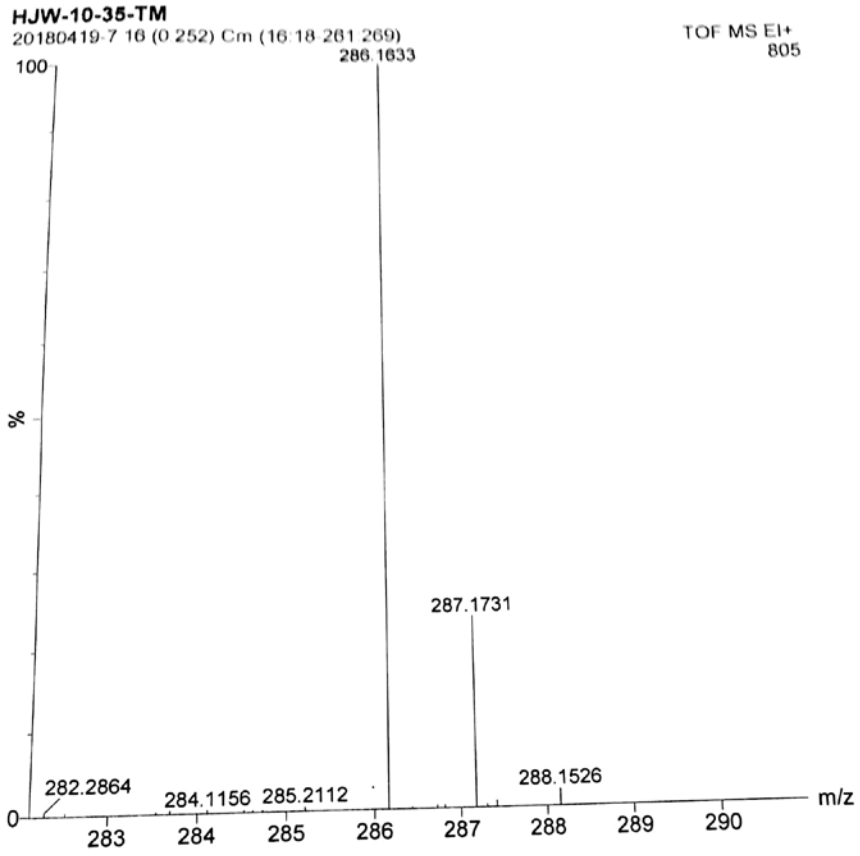
^{1}H NMR spectrum for 1h



^{13}C NMR spectrum for 1h



HRMS (EI) spectrum for 1h



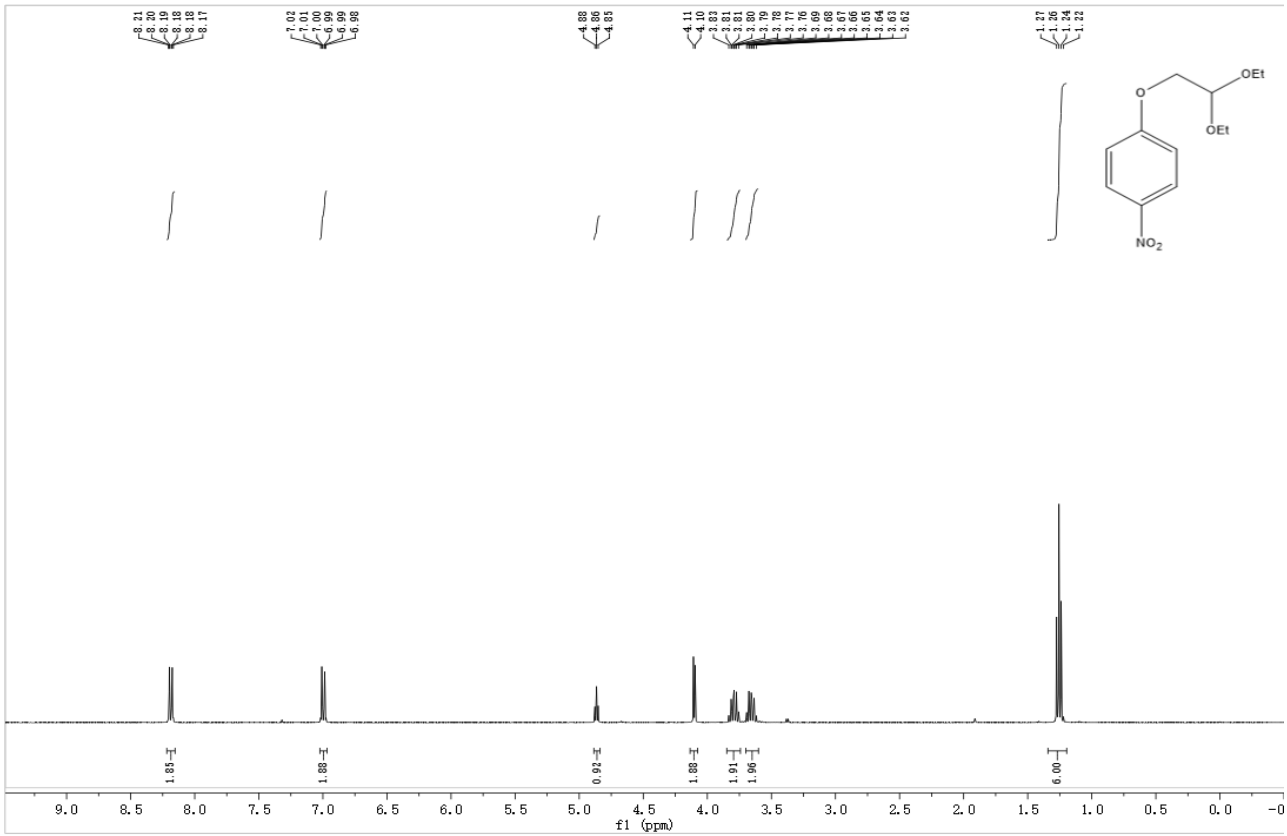
Elemental Composition Report

Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

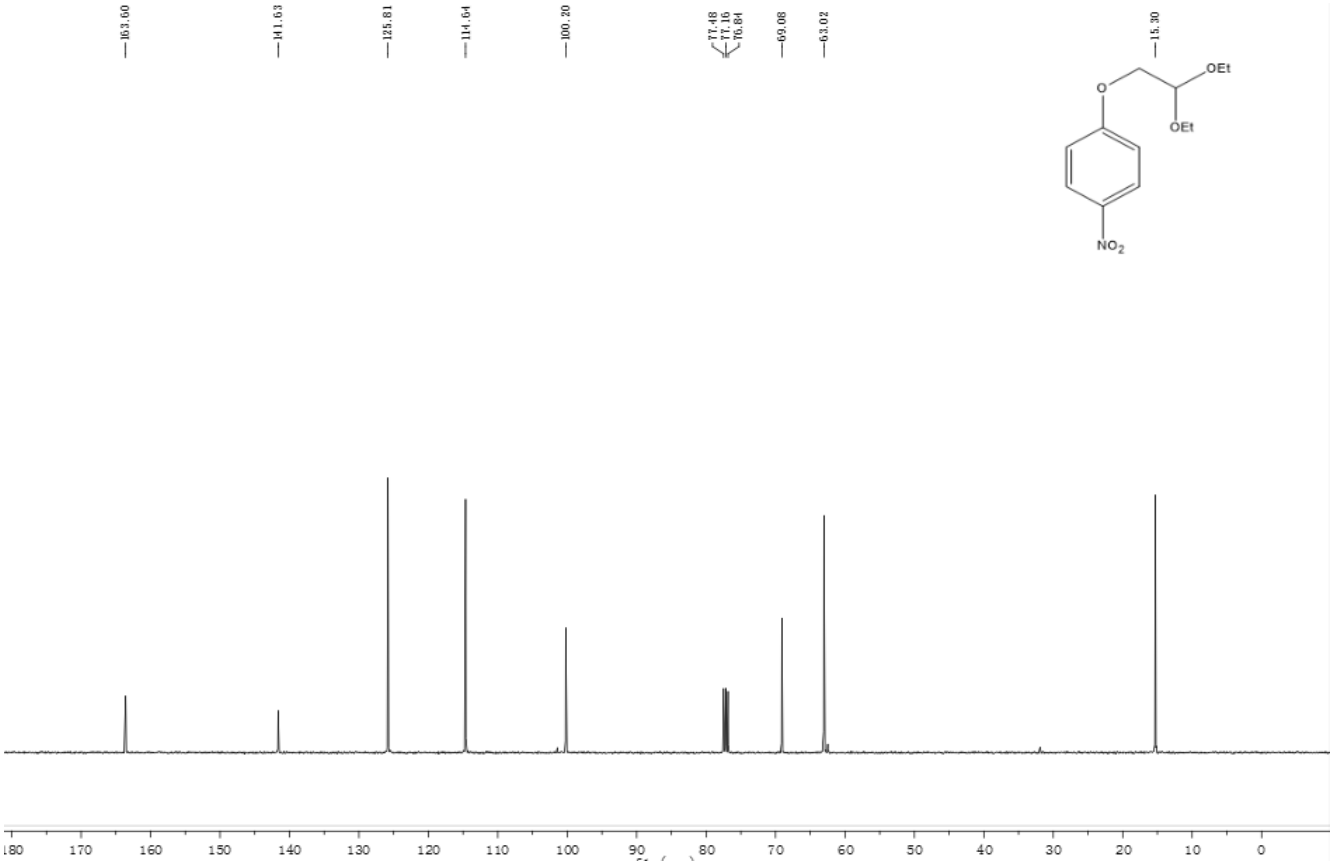
Monoisotopic Mass, Odd and Even Electron Ions
5 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)

Minimum:	70.00				-1.5		
Maximum:	100.00		200.0	100.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula
286.1633	100.00	286.1629	0.4	1.2	7.5	1	C18 H24 N S

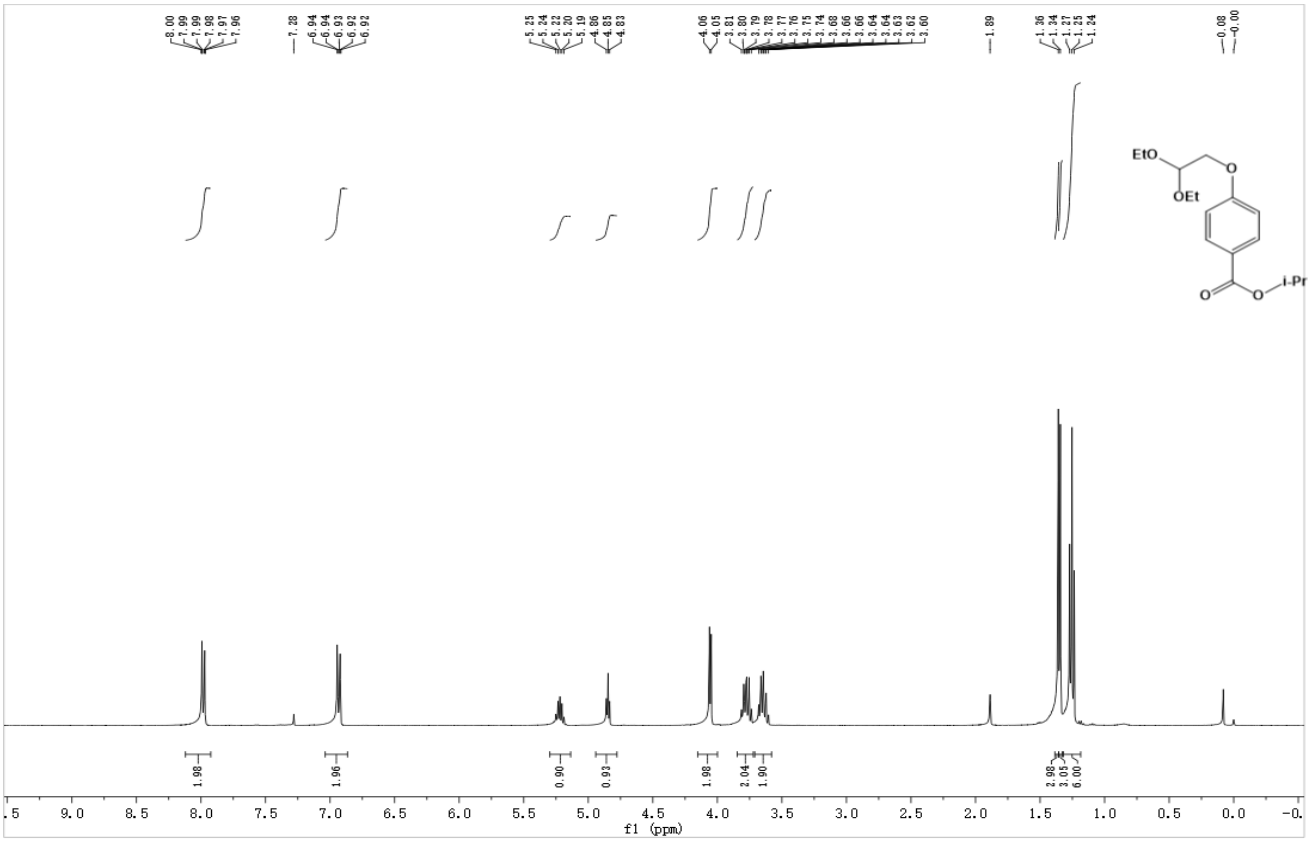
^{1}H NMR spectrum for 1i



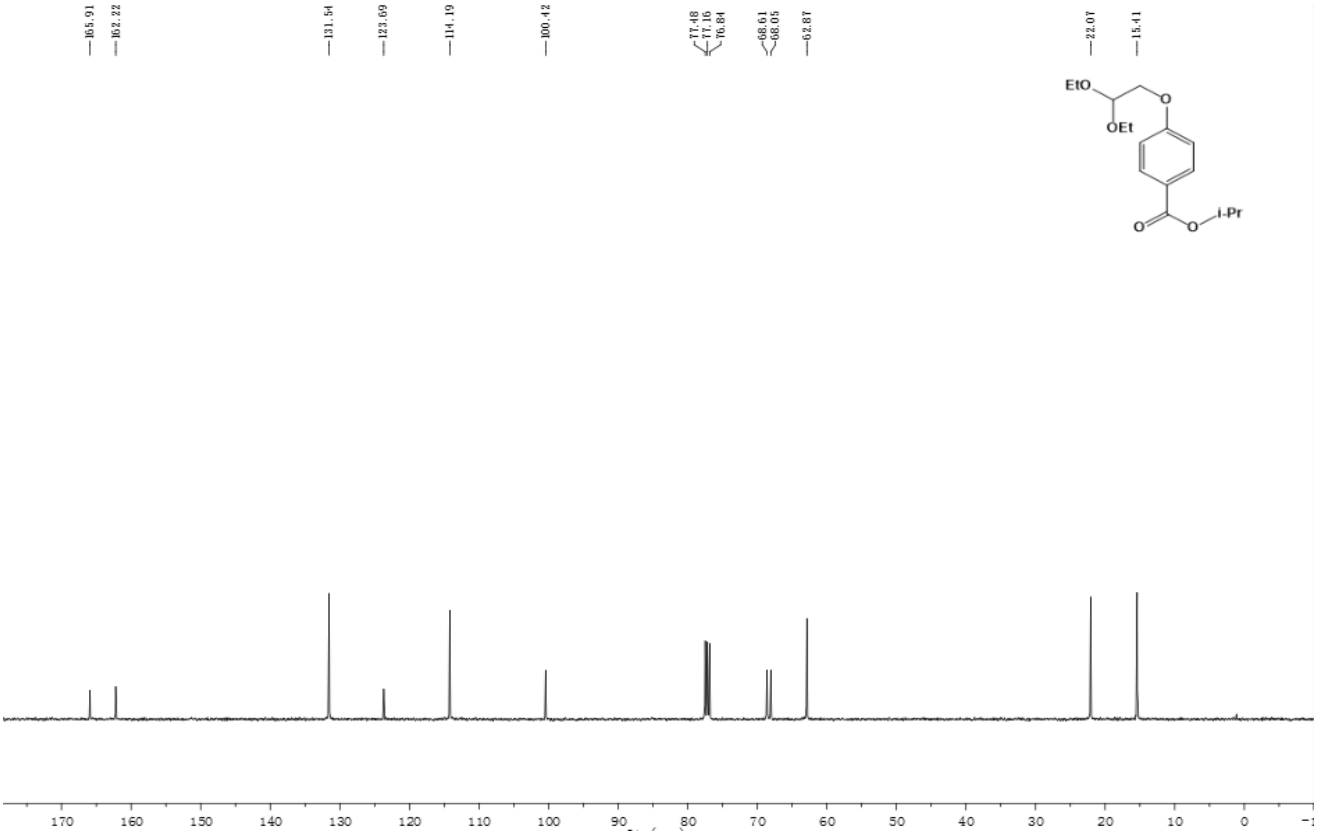
^{13}C NMR spectrum for 1i



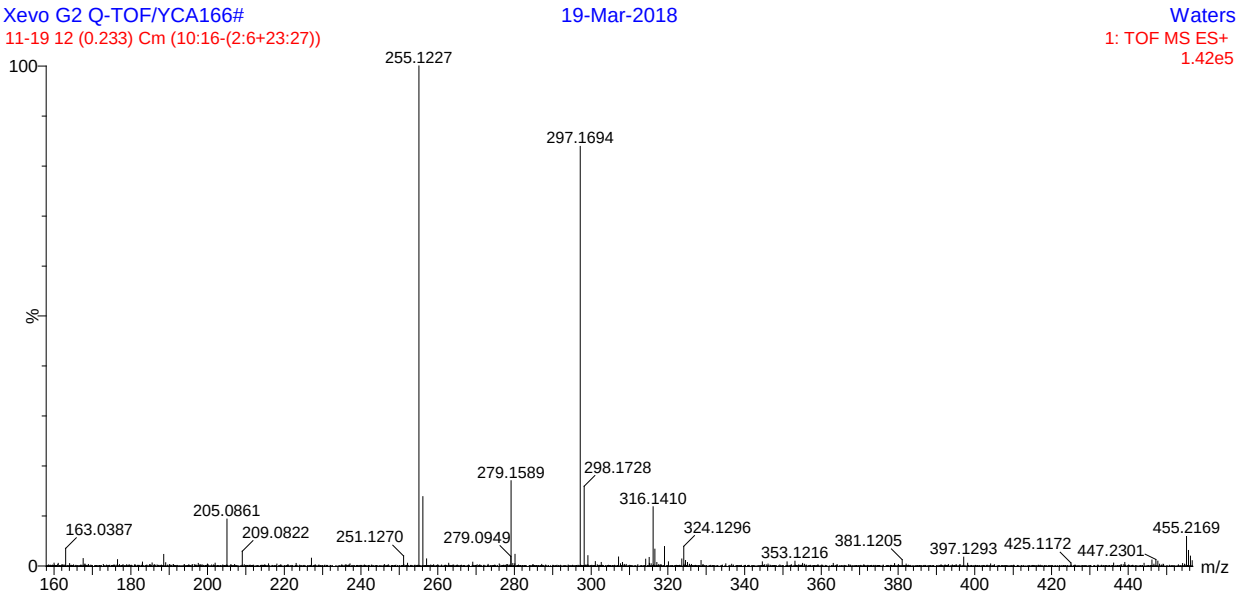
^{1}H NMR spectrum for 1j



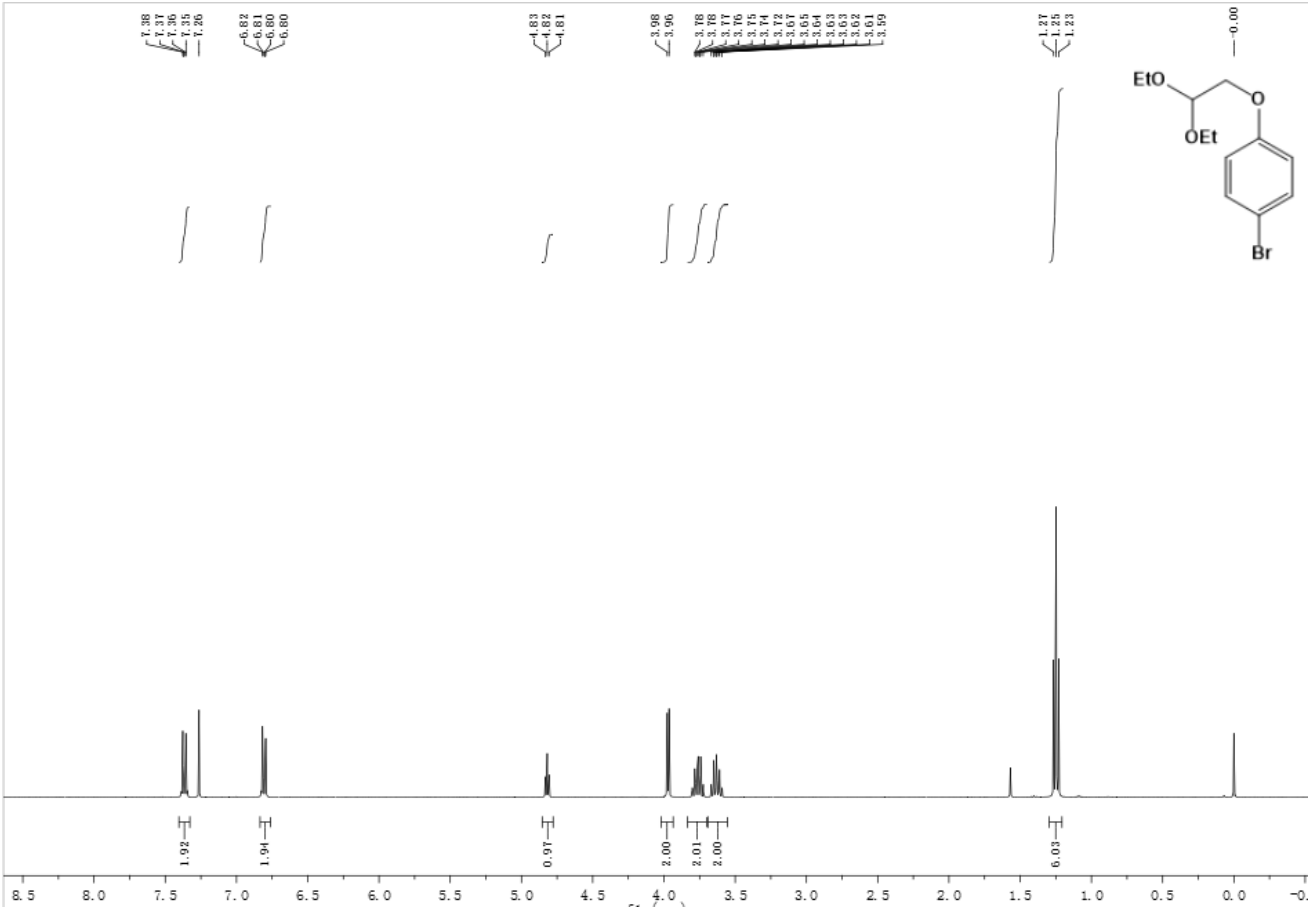
^{13}C NMR spectrum for 1j



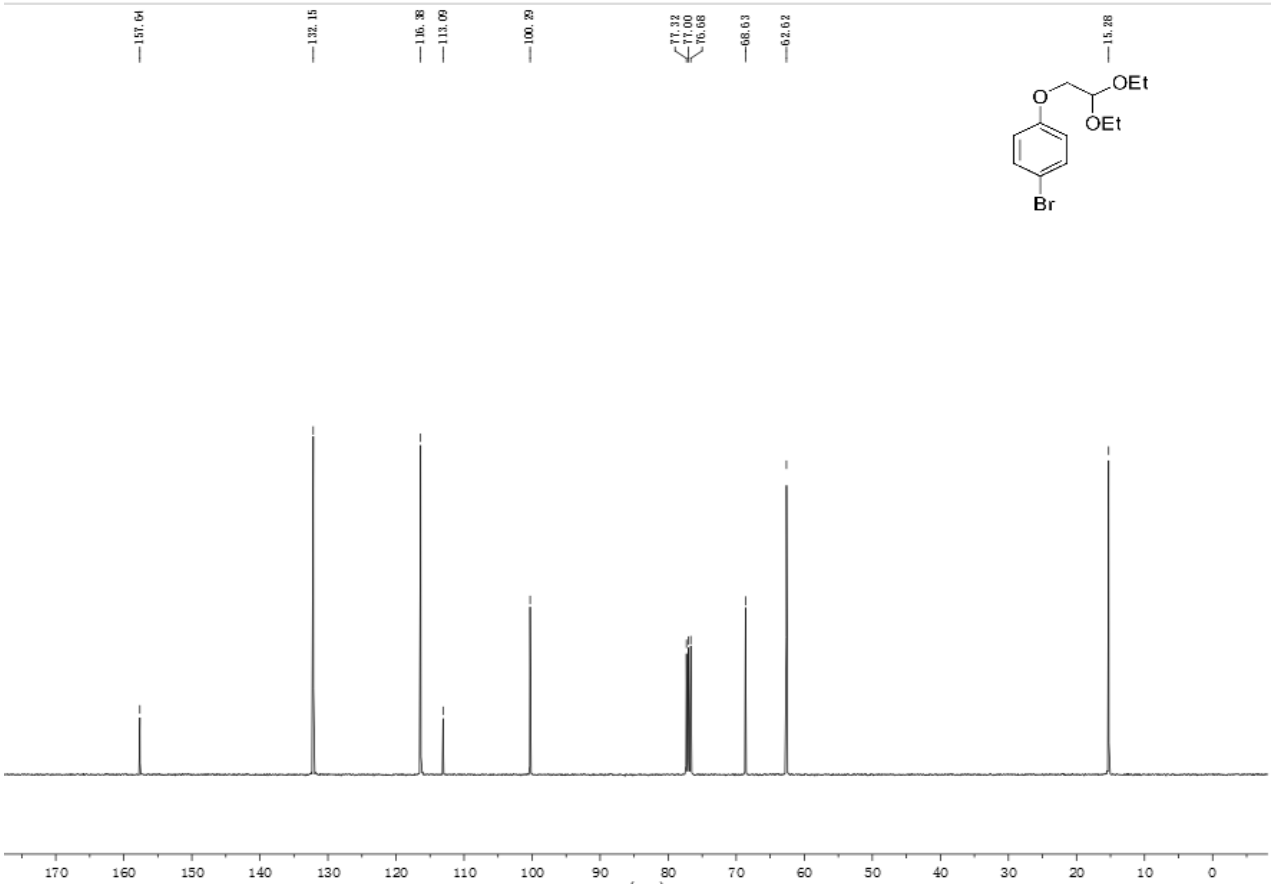
HRMS (ESI) spectrum for 1j



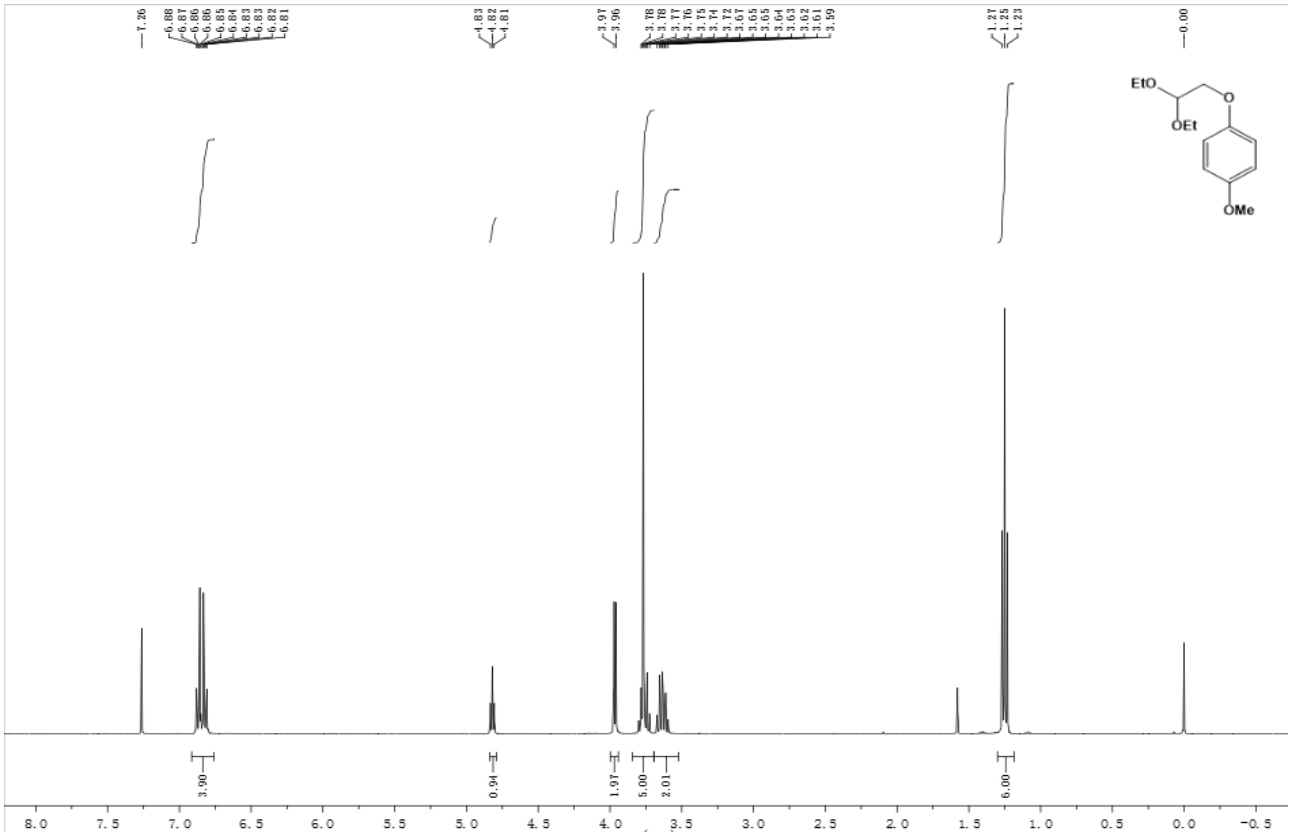
^{1}H NMR spectrum for 1k



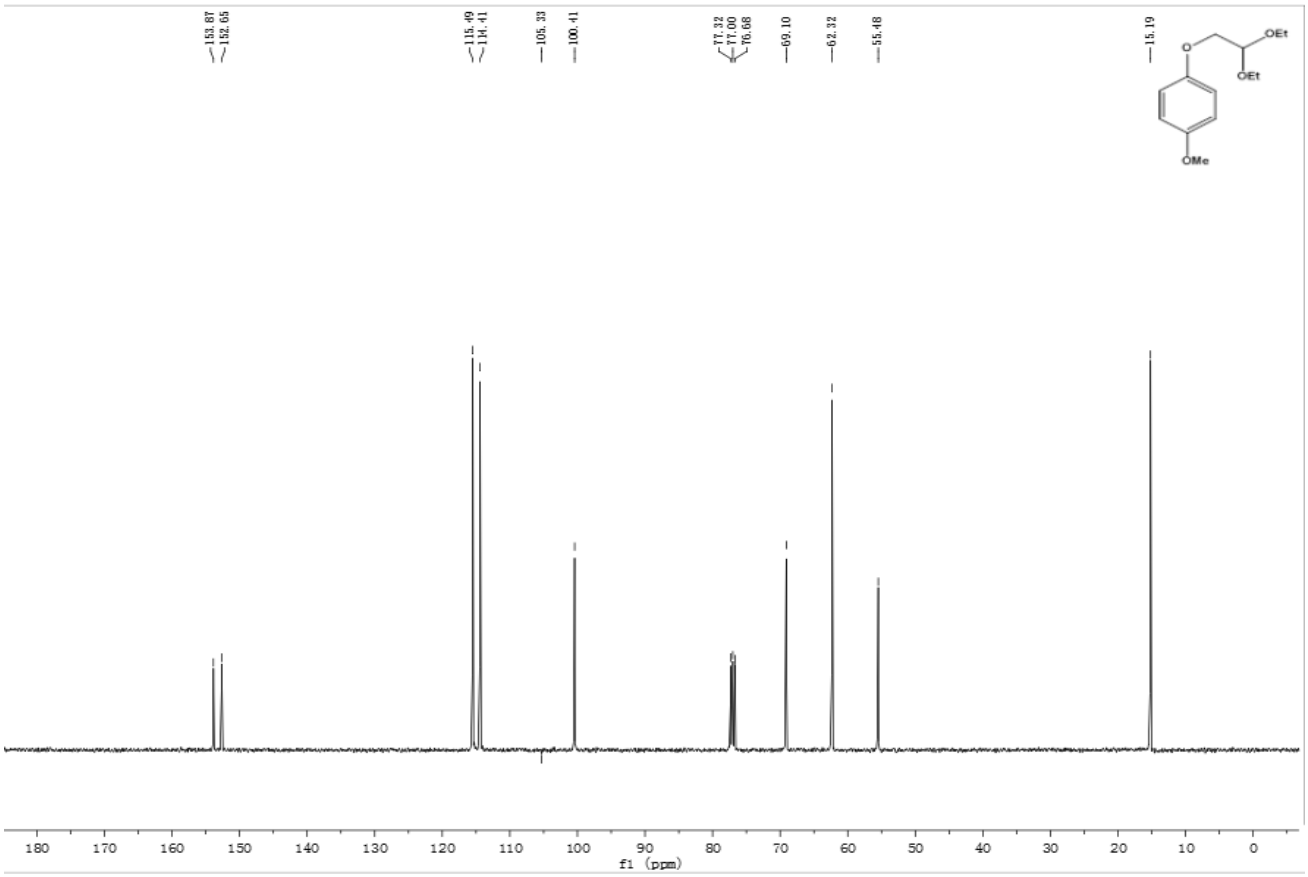
^{13}C NMR spectrum for 1k



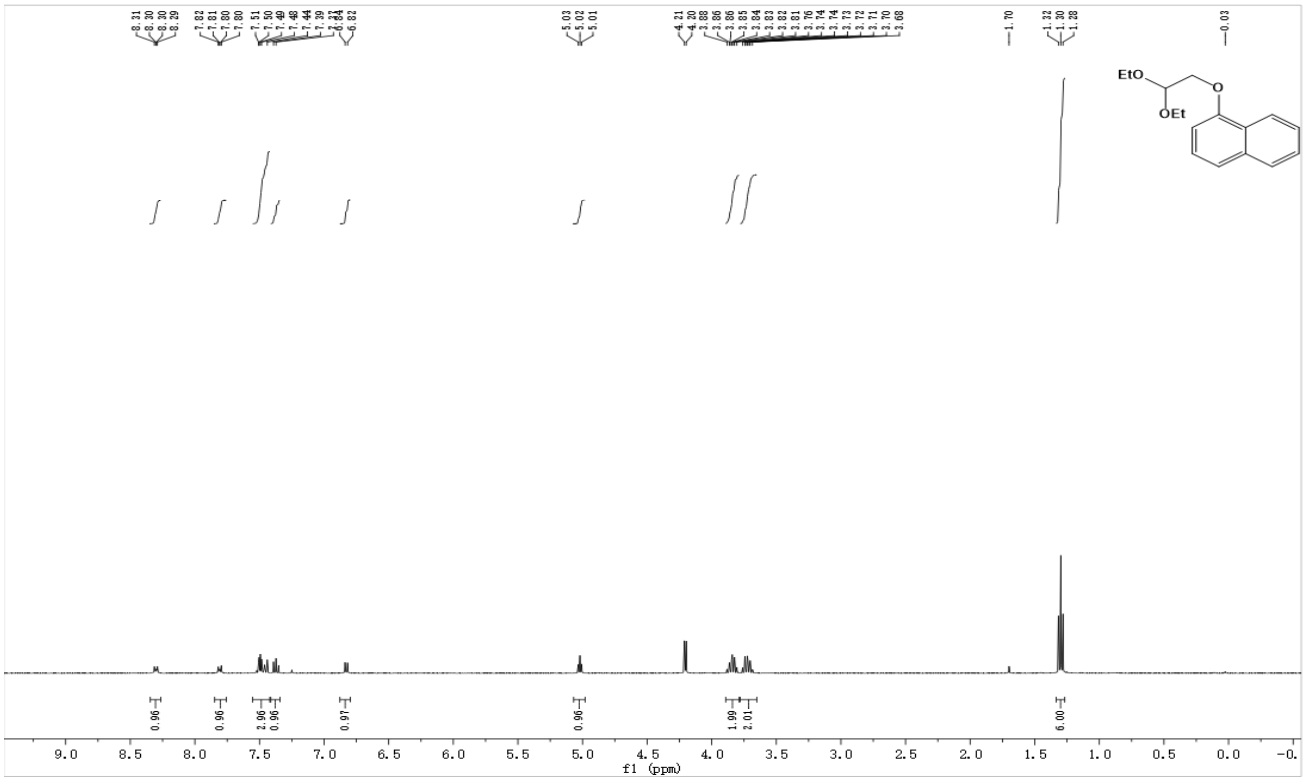
[1]H NMR spectrum for 1l



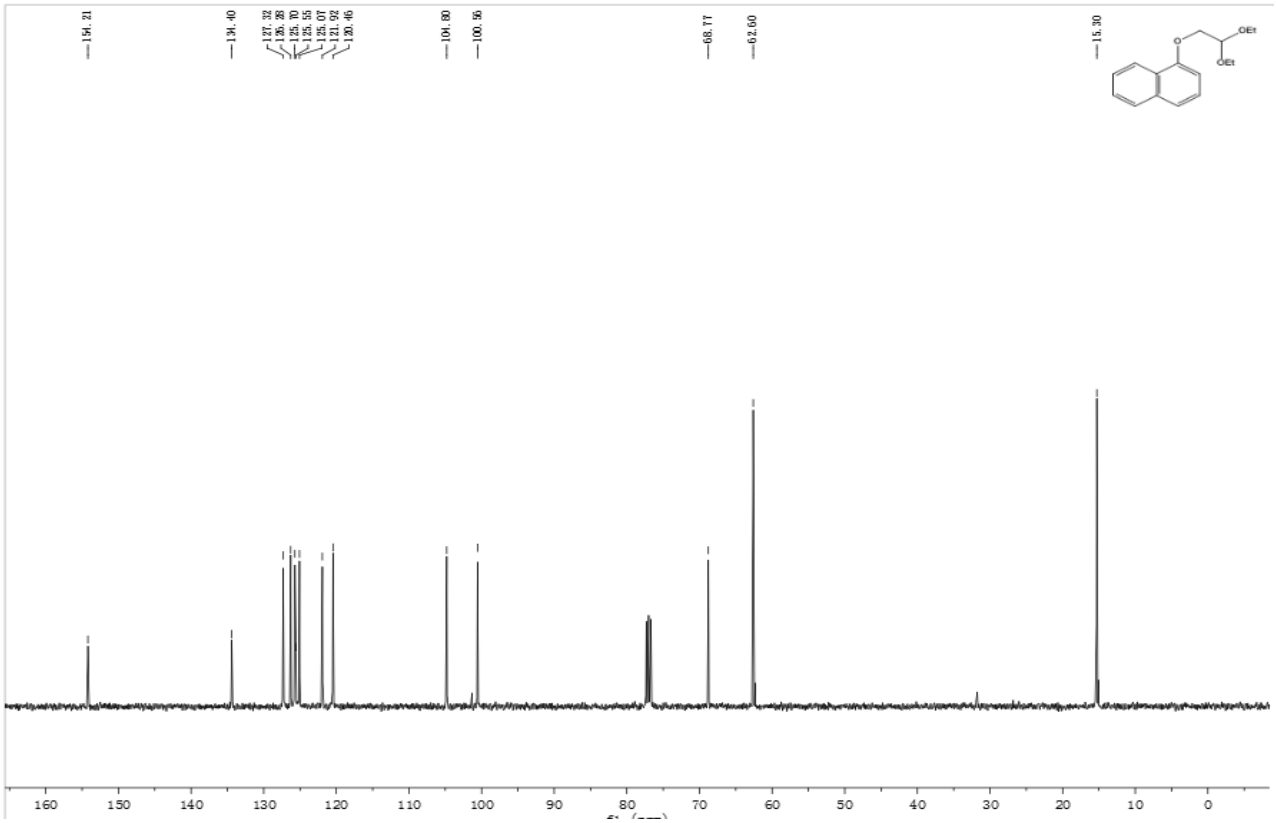
[13]C NMR spectrum for 1l



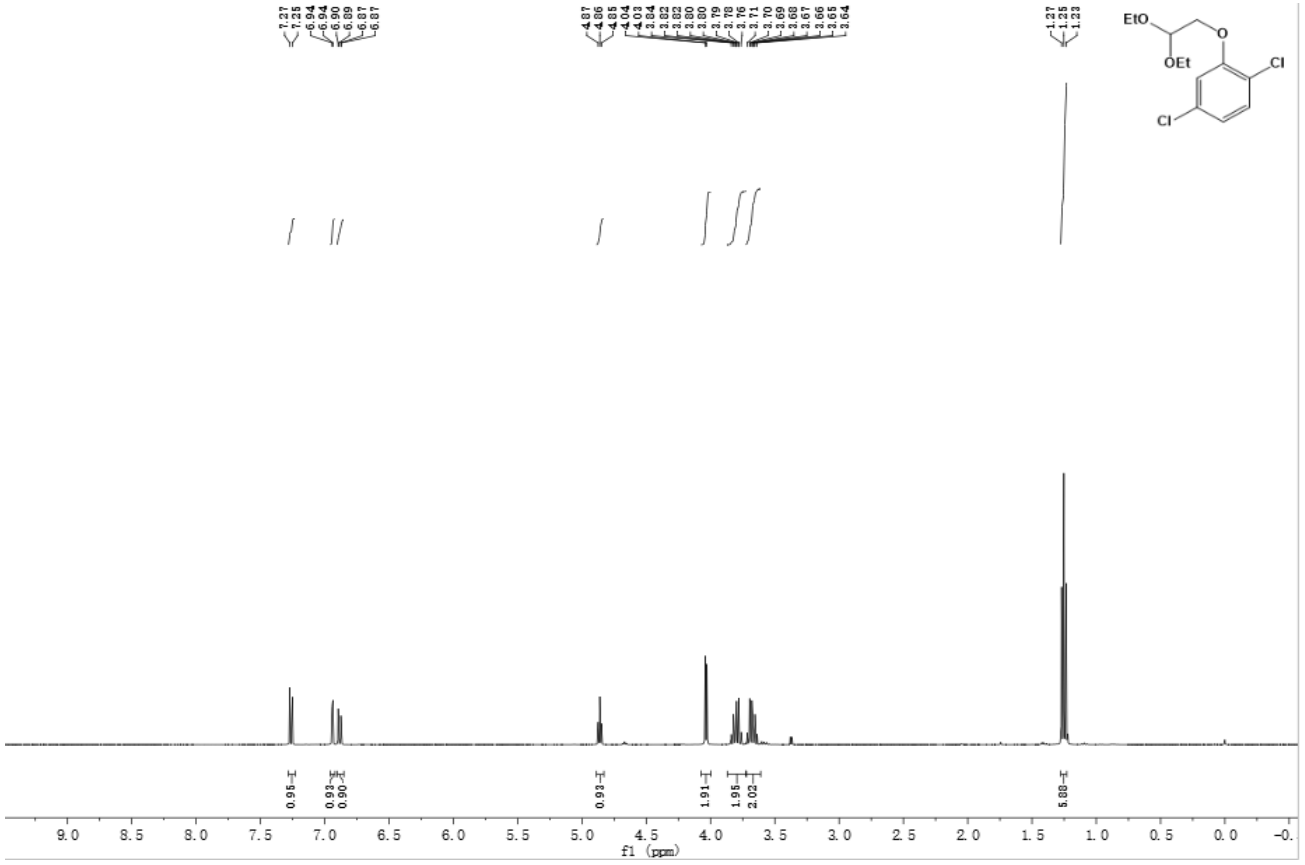
^{1}H NMR spectrum for 1m



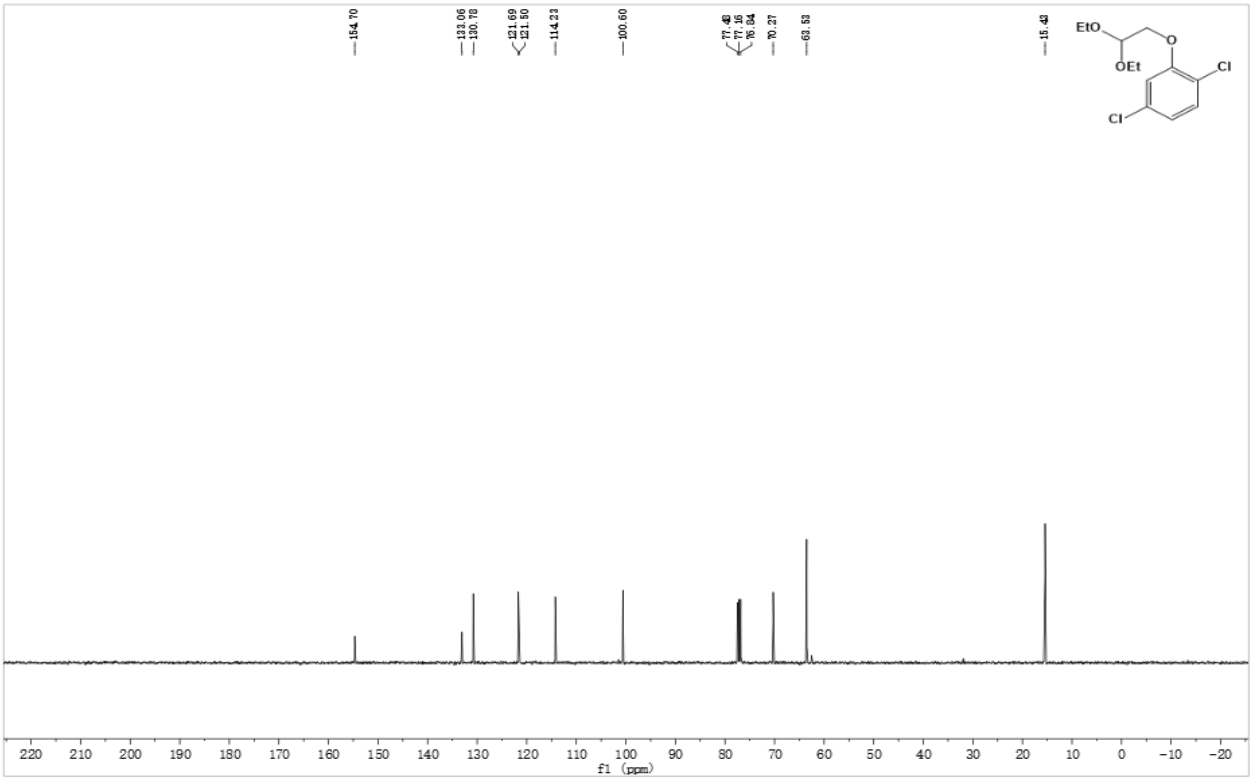
^{13}C NMR spectrum for 1m



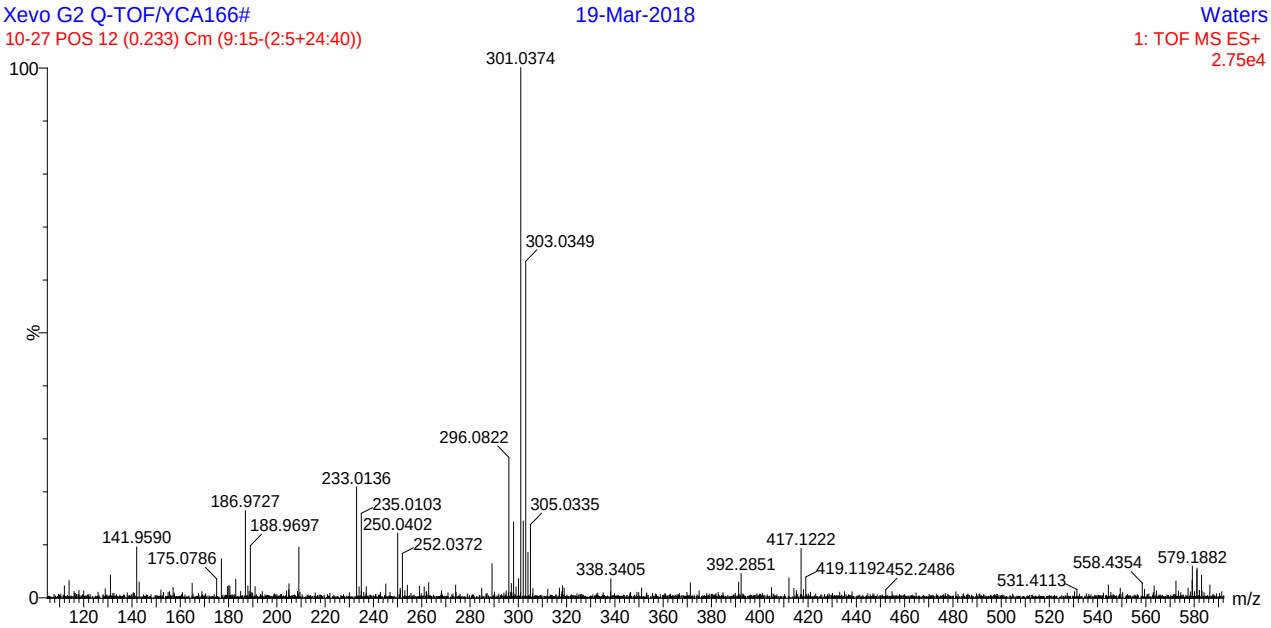
^{1}H NMR spectrum for 1n



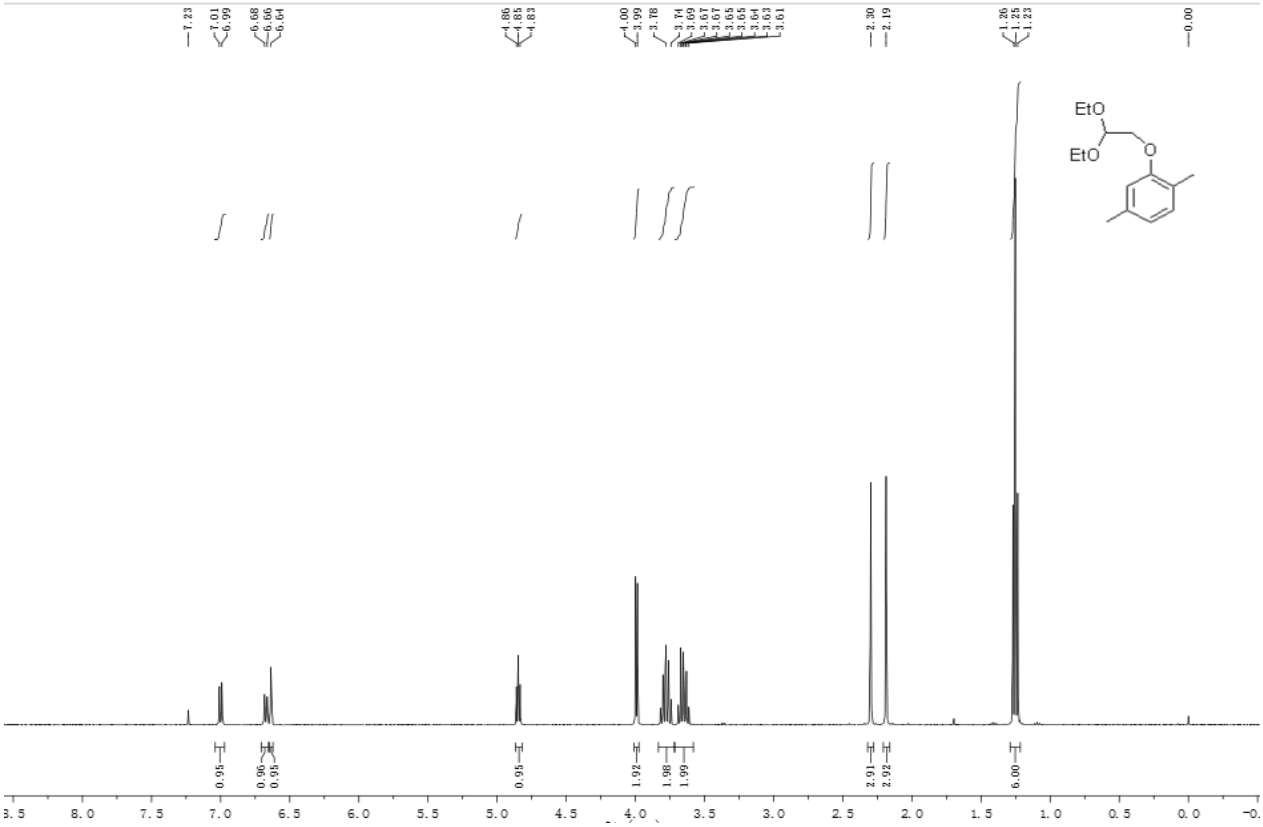
^{13}C NMR spectrum for 1n



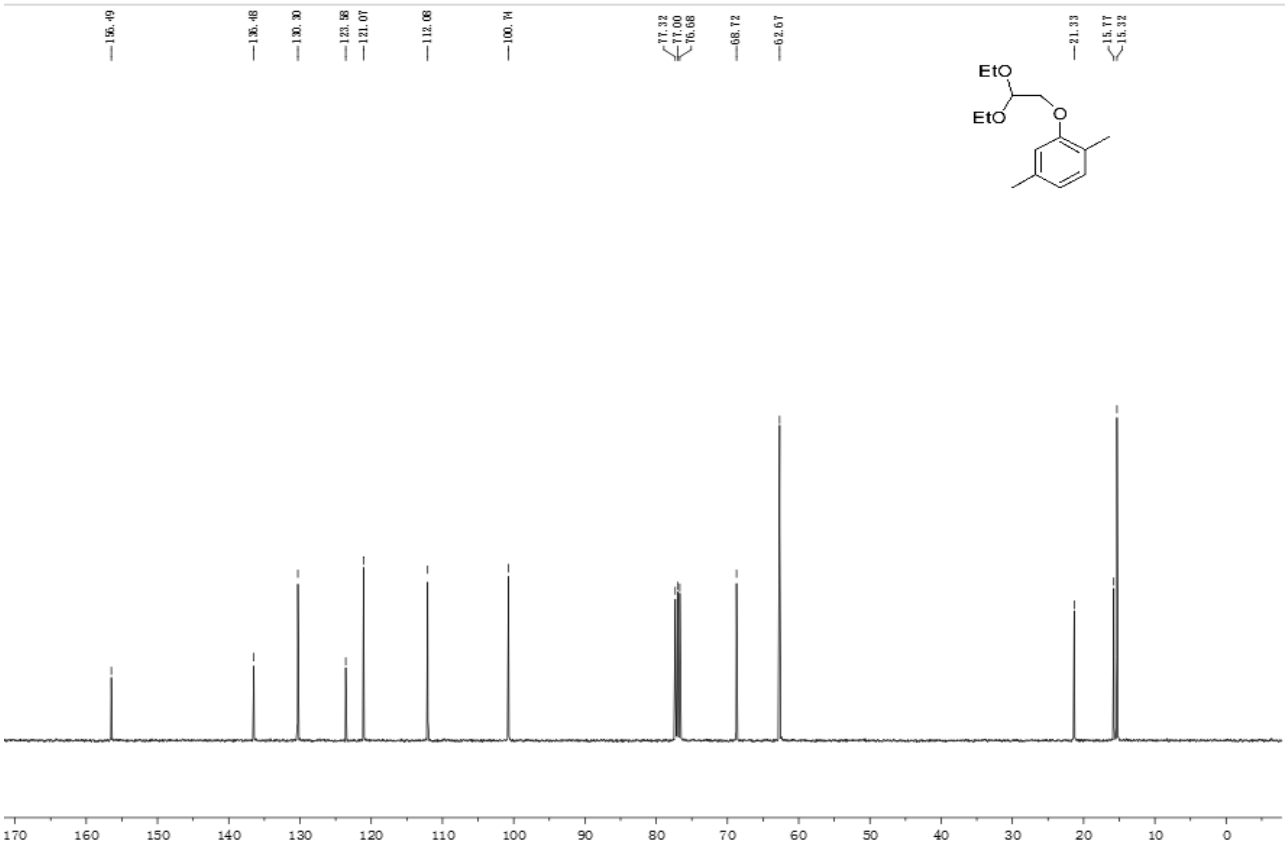
HRMS (ESI) spectrum for 1n



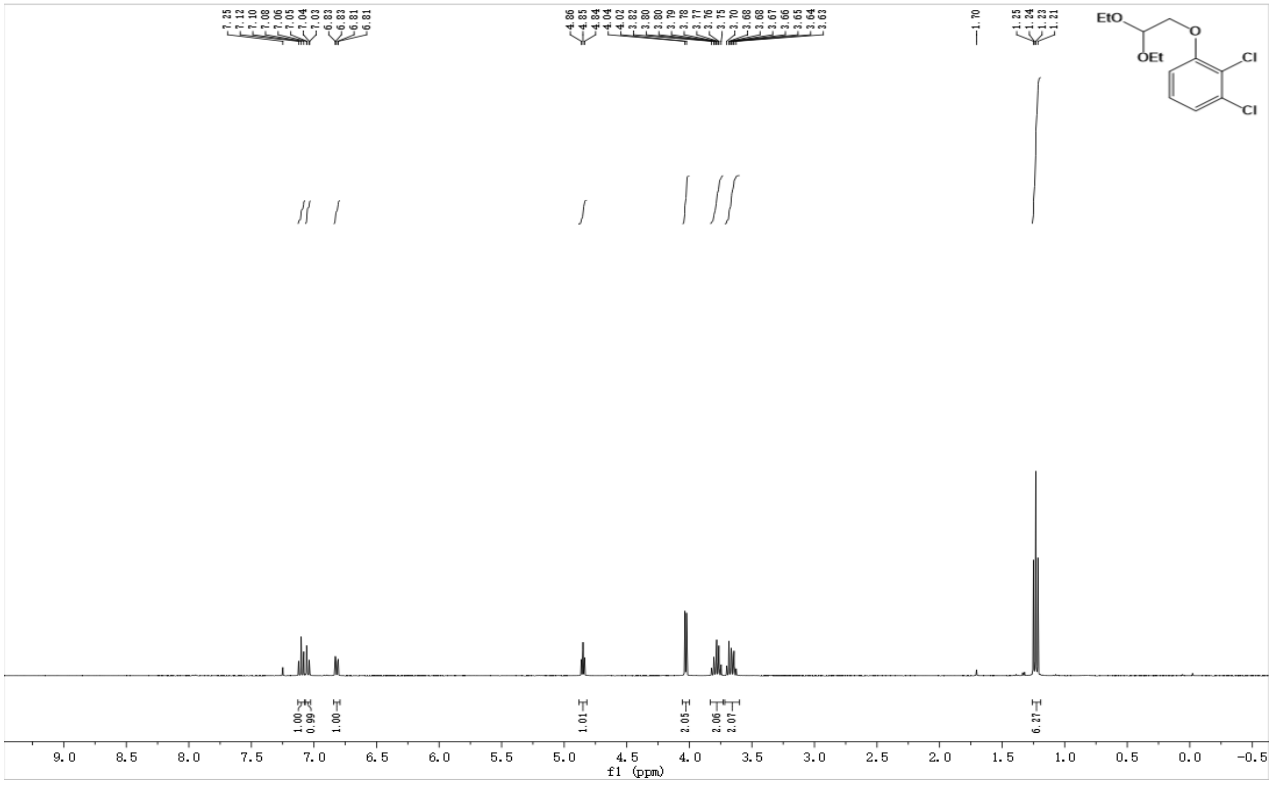
^{1}H NMR spectrum for 1o



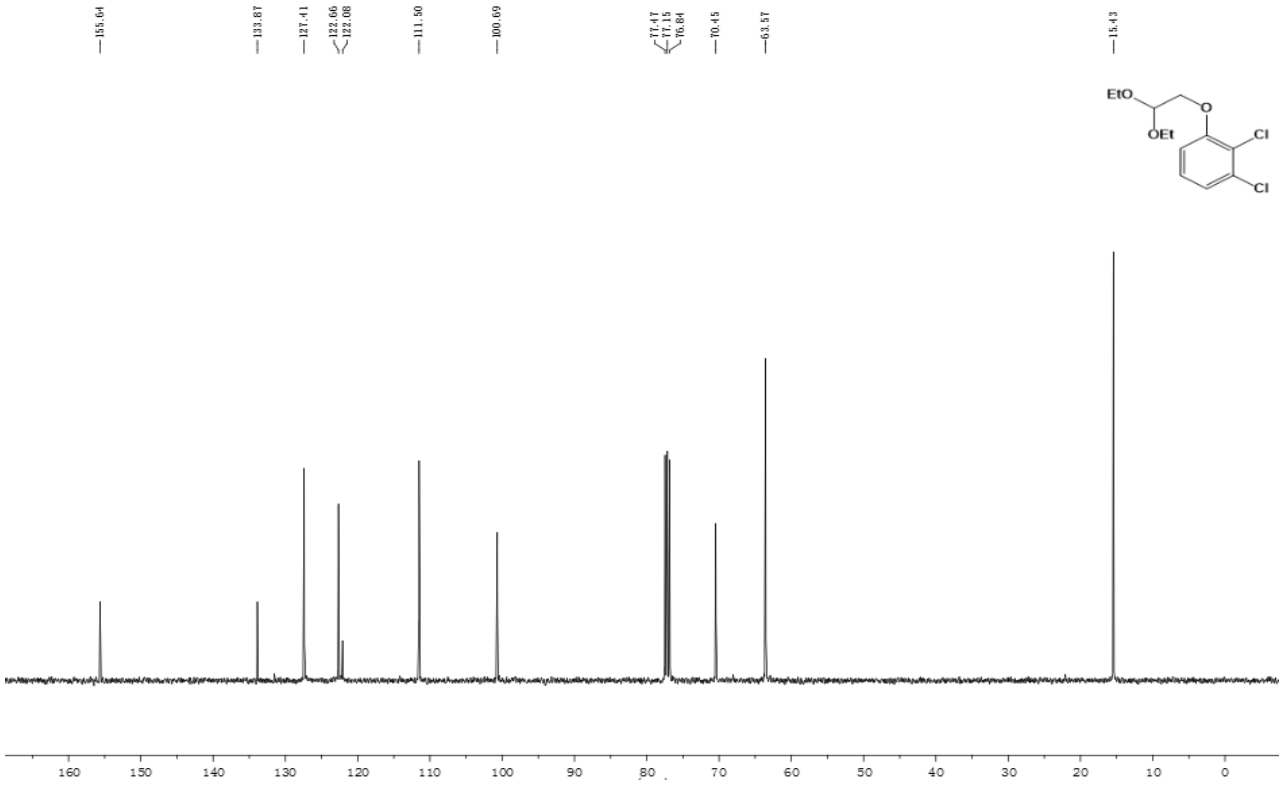
^{13}C NMR spectrum for 1o



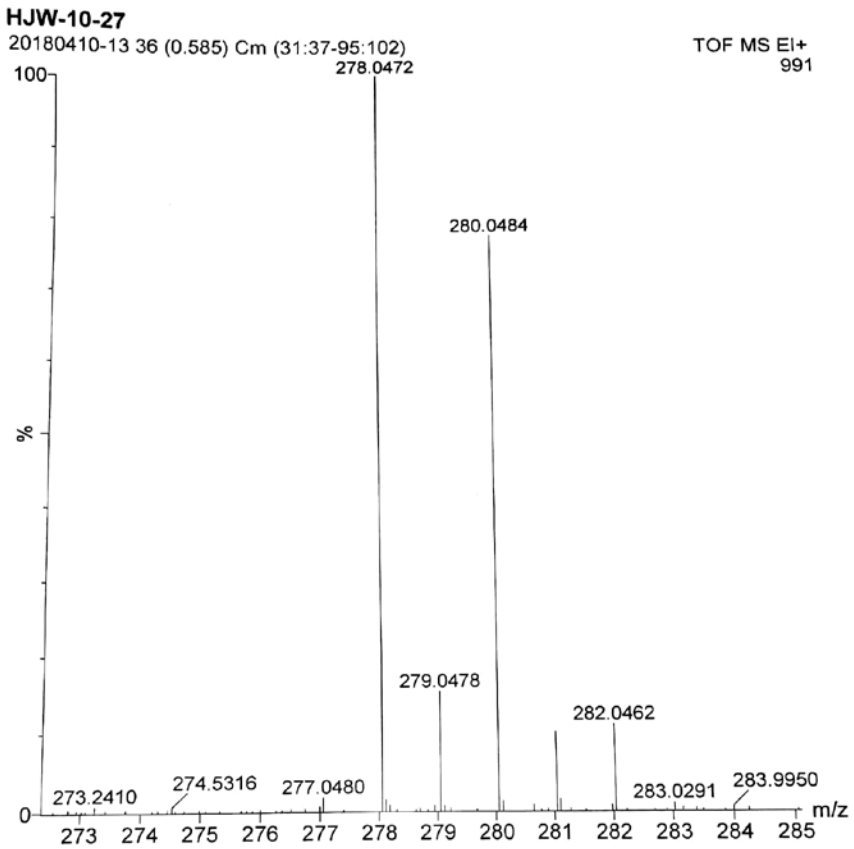
^{1}H NMR spectrum for 1p



^{13}C NMR spectrum for 1p



HRMS (EI) spectrum for 1p



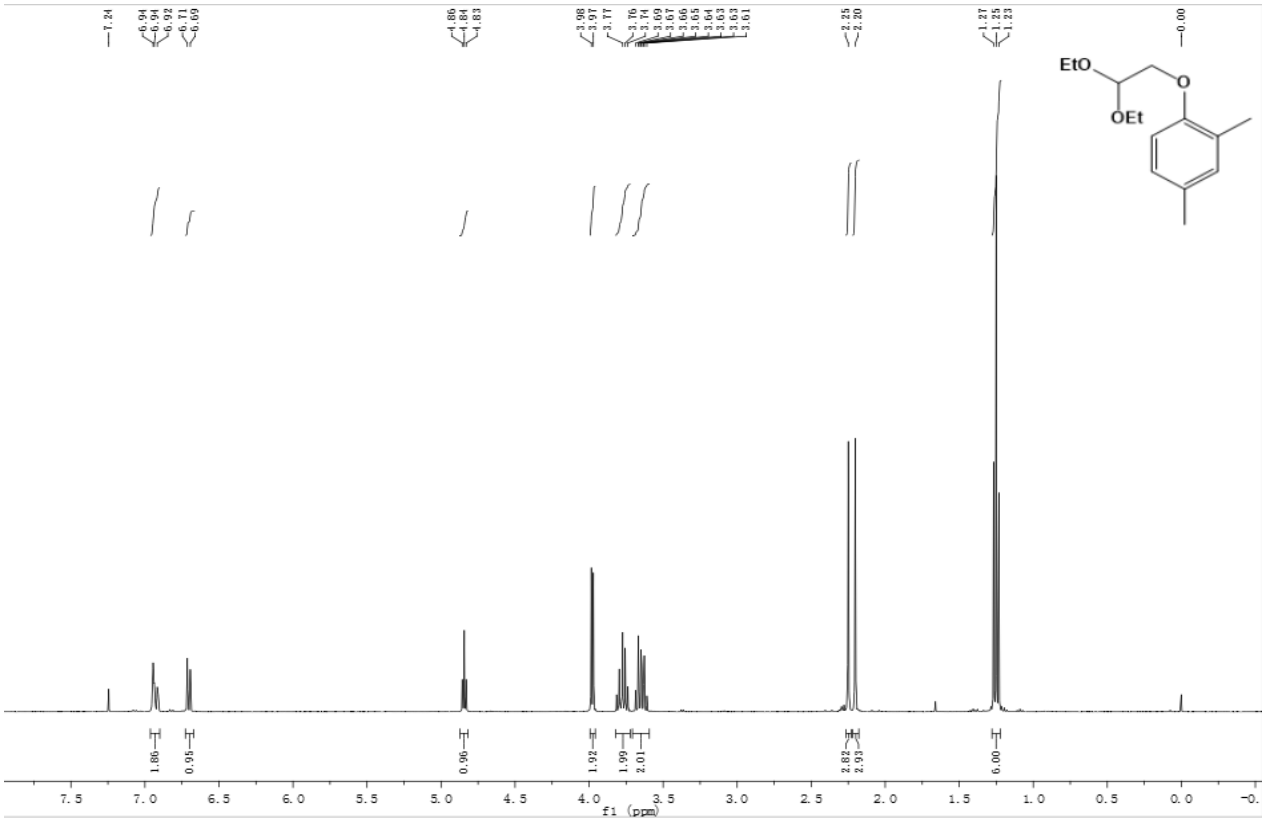
Elemental Composition Report

Multiple Mass Analysis: 2 mass(es) processed
Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

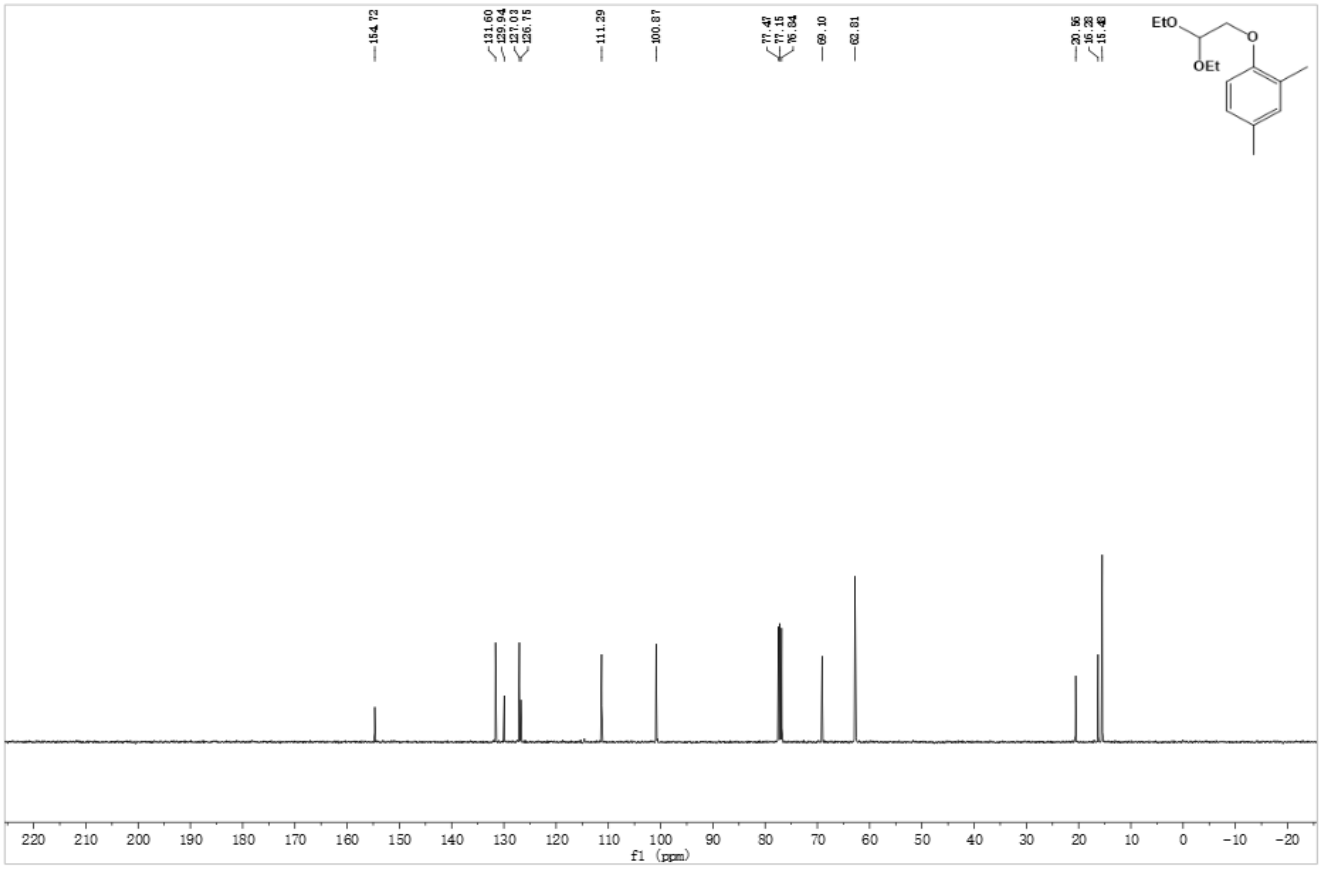
Monoisotopic Mass, Odd and Even Electron Ions
22 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)

Minimum:	70.00				-1.5		
Maximum:	100.00		200.0	100.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula
278.0472	100.00	278.0477	-0.5	-1.6	4.0	1	C12 H16 O3 Cl2

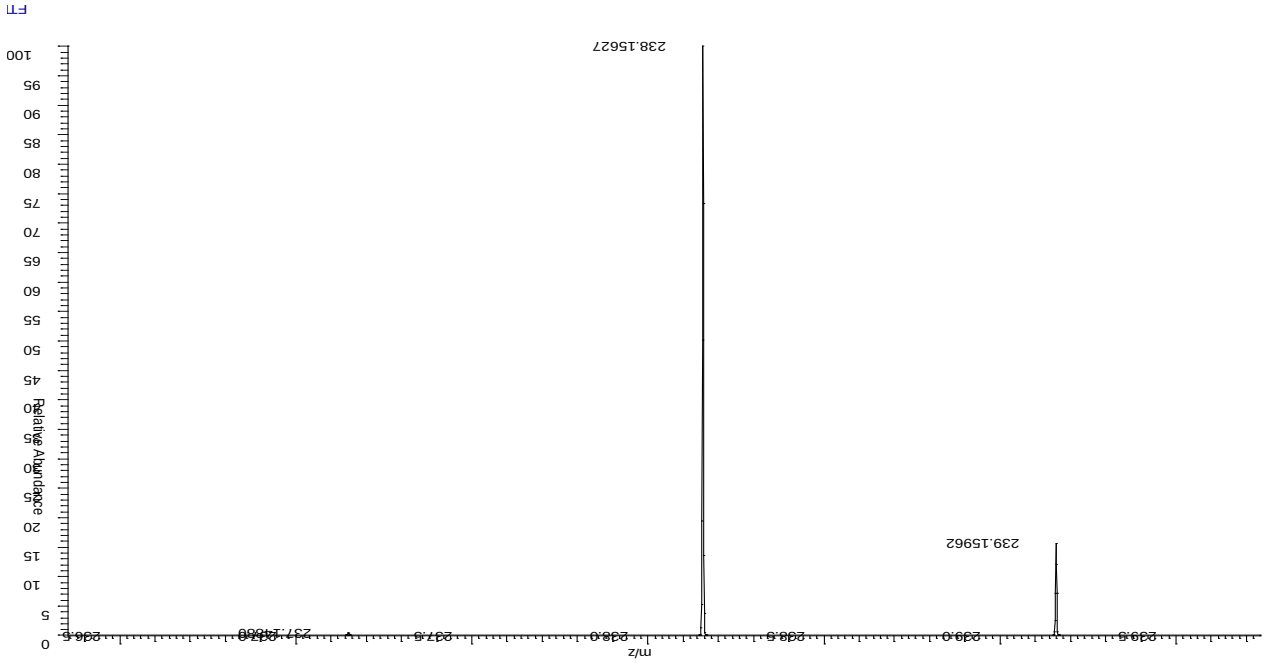
^{1}H NMR spectrum for 1q



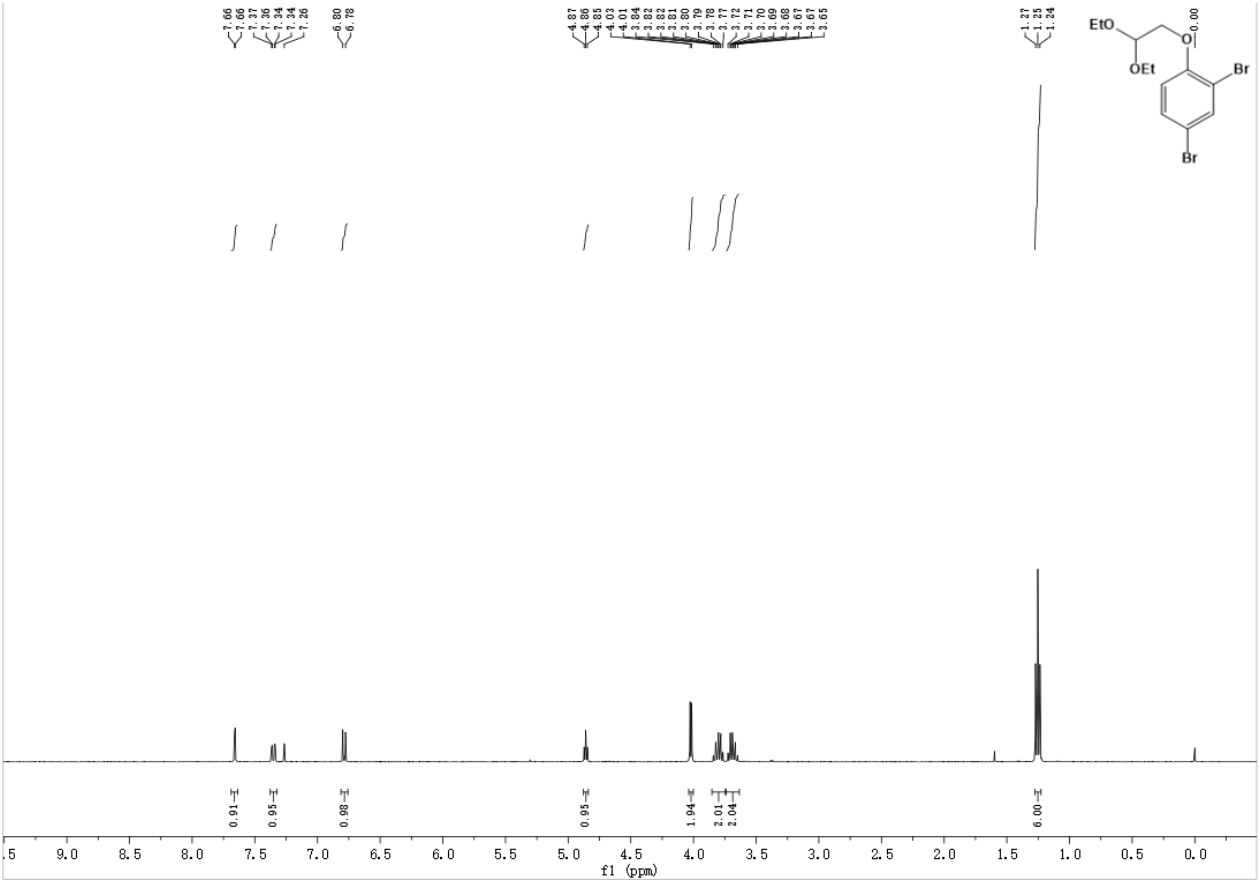
^{13}C NMR spectrum for 1q



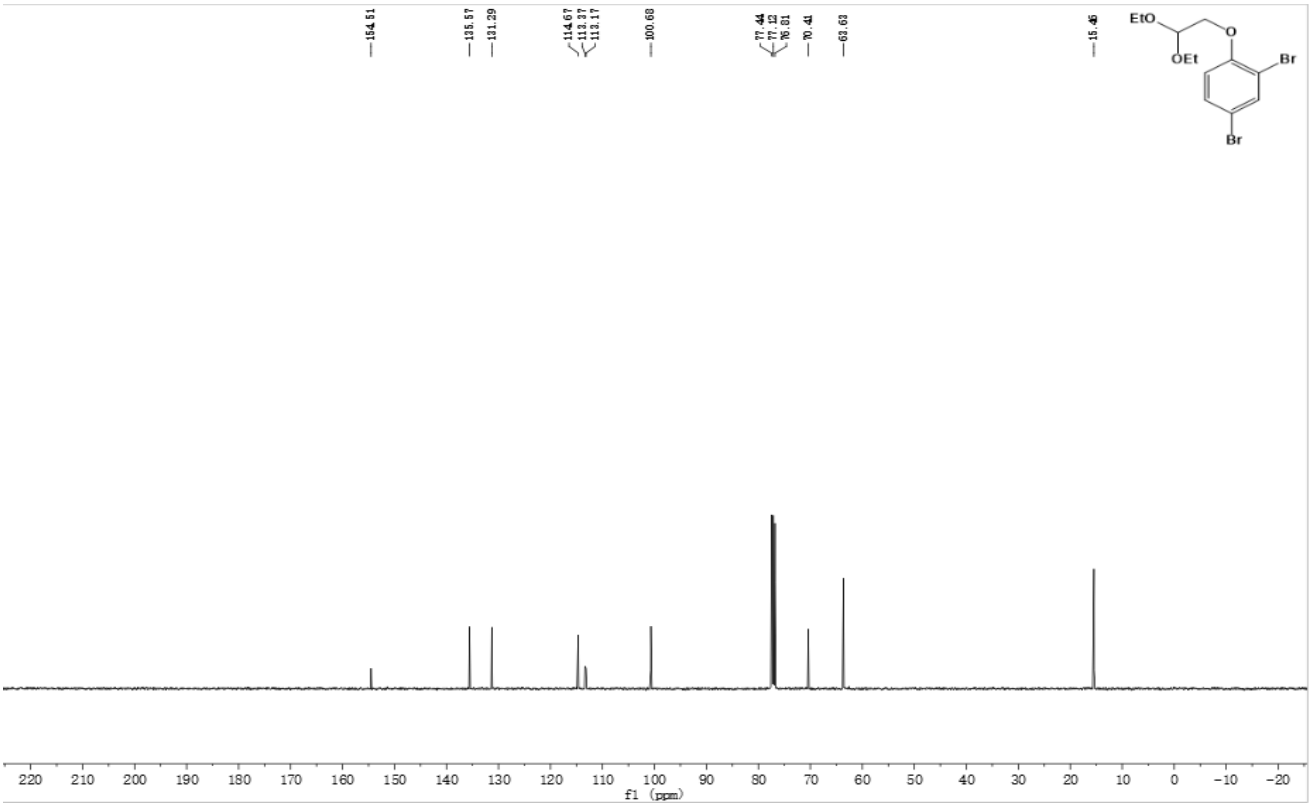
HRMS (EI) spectrum for 1q



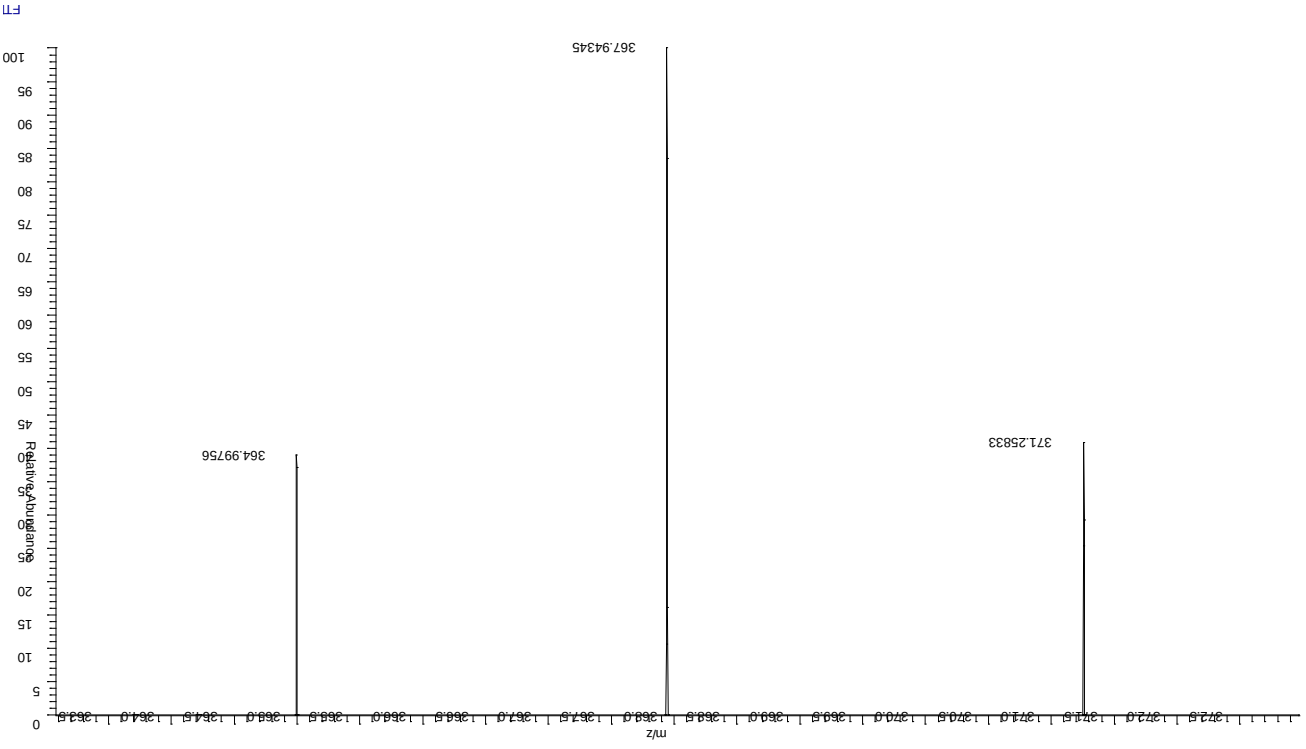
^{1}H NMR spectrum for 1r



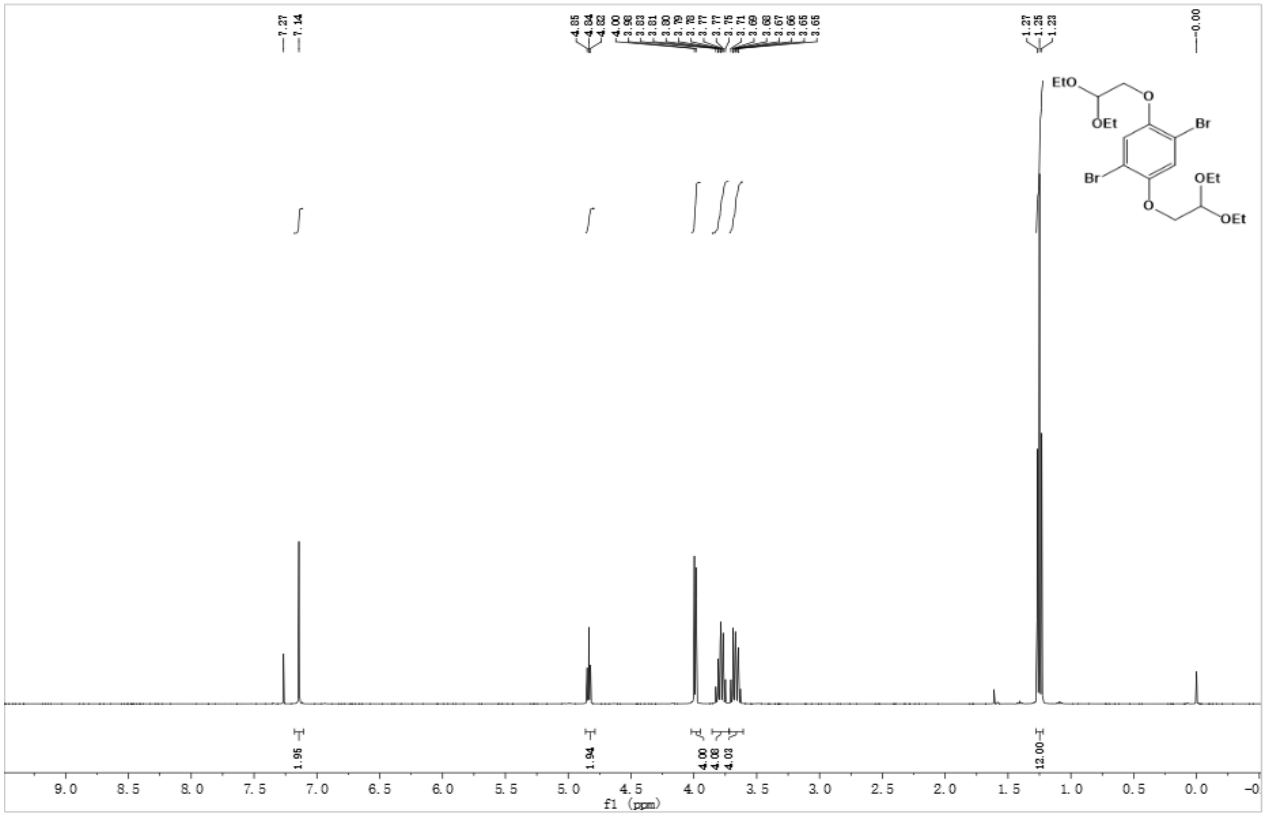
^{13}C NMR spectrum for 1r



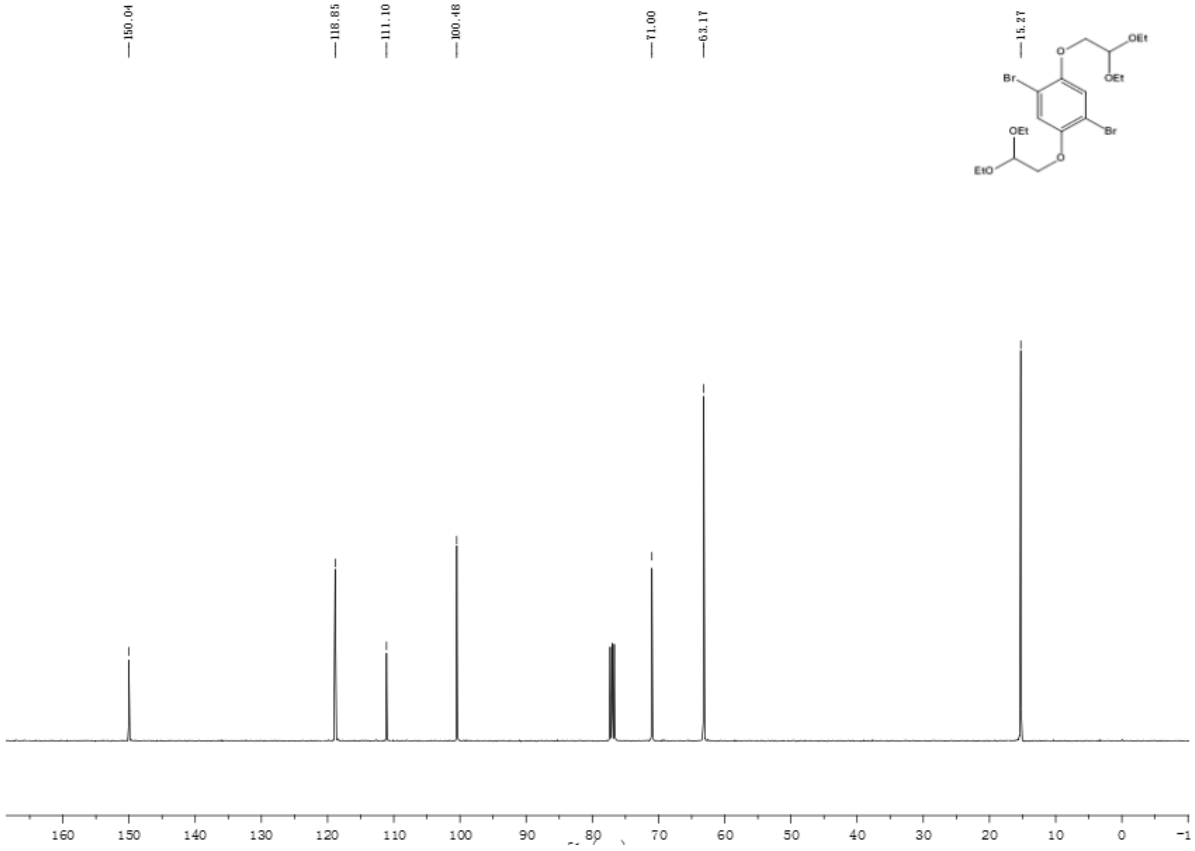
HRMS (EI) spectrum for 1r



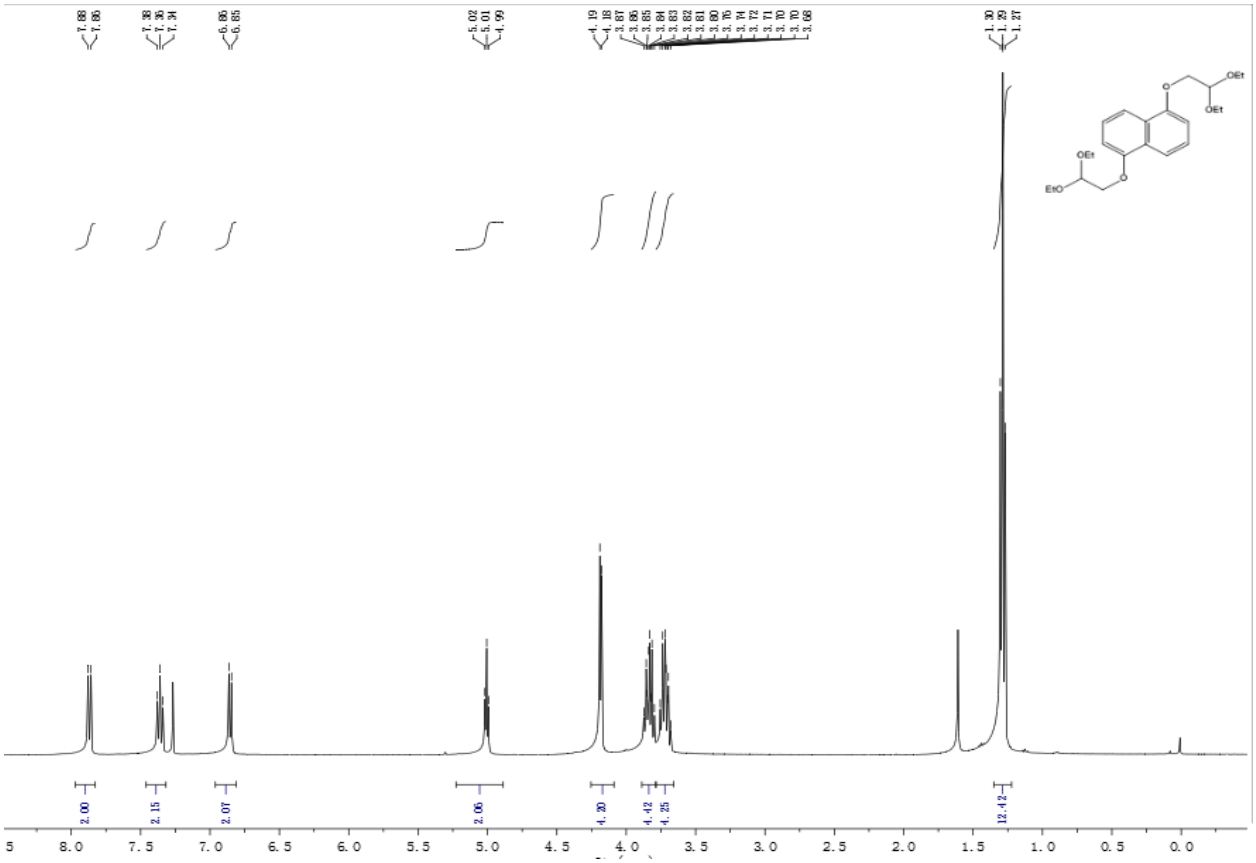
^{1}H NMR spectrum for 1s



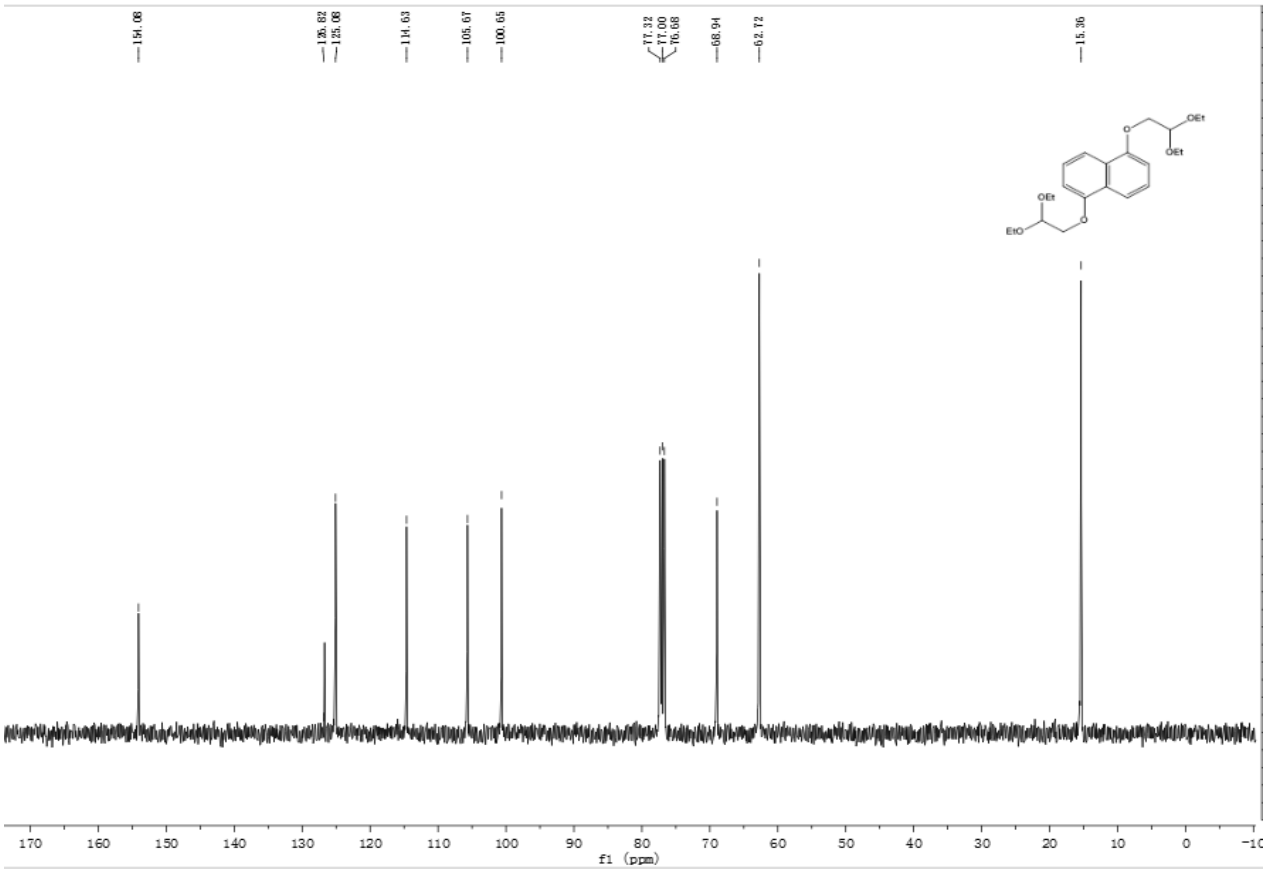
^{13}C NMR spectrum for 1s



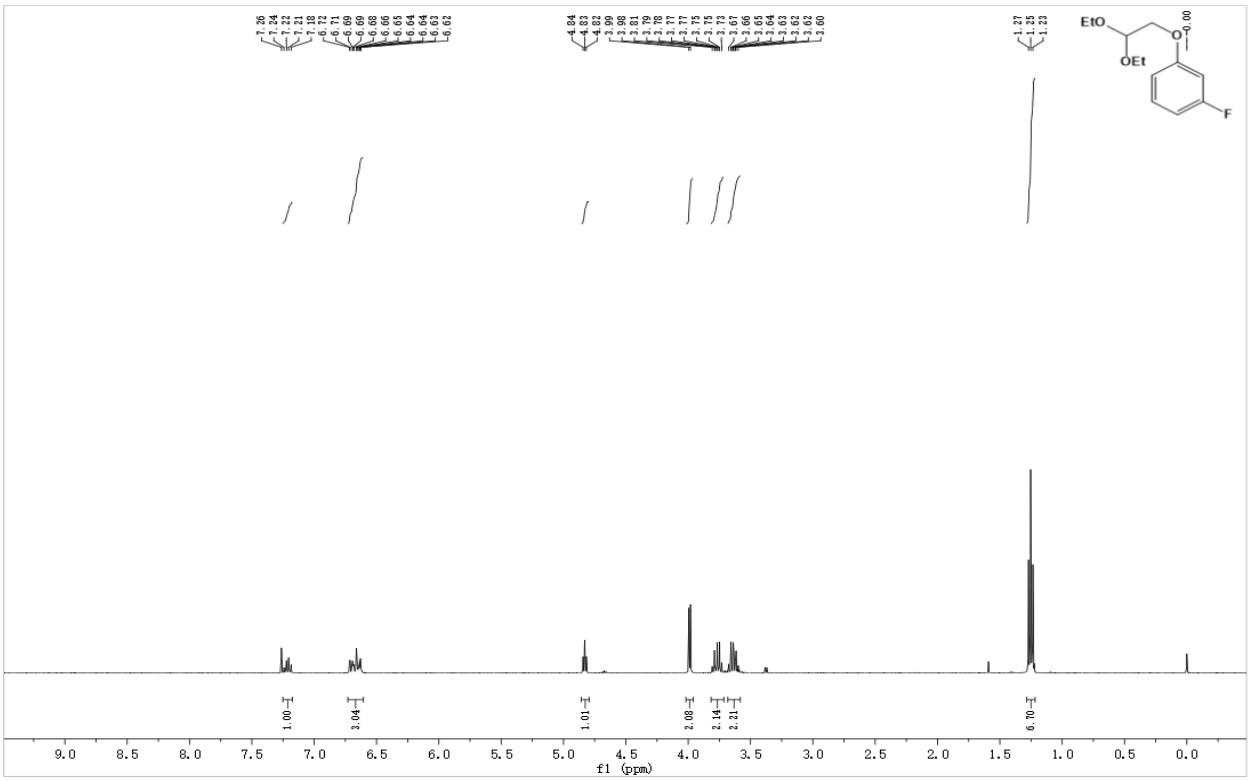
^{1}H NMR spectrum for 1t



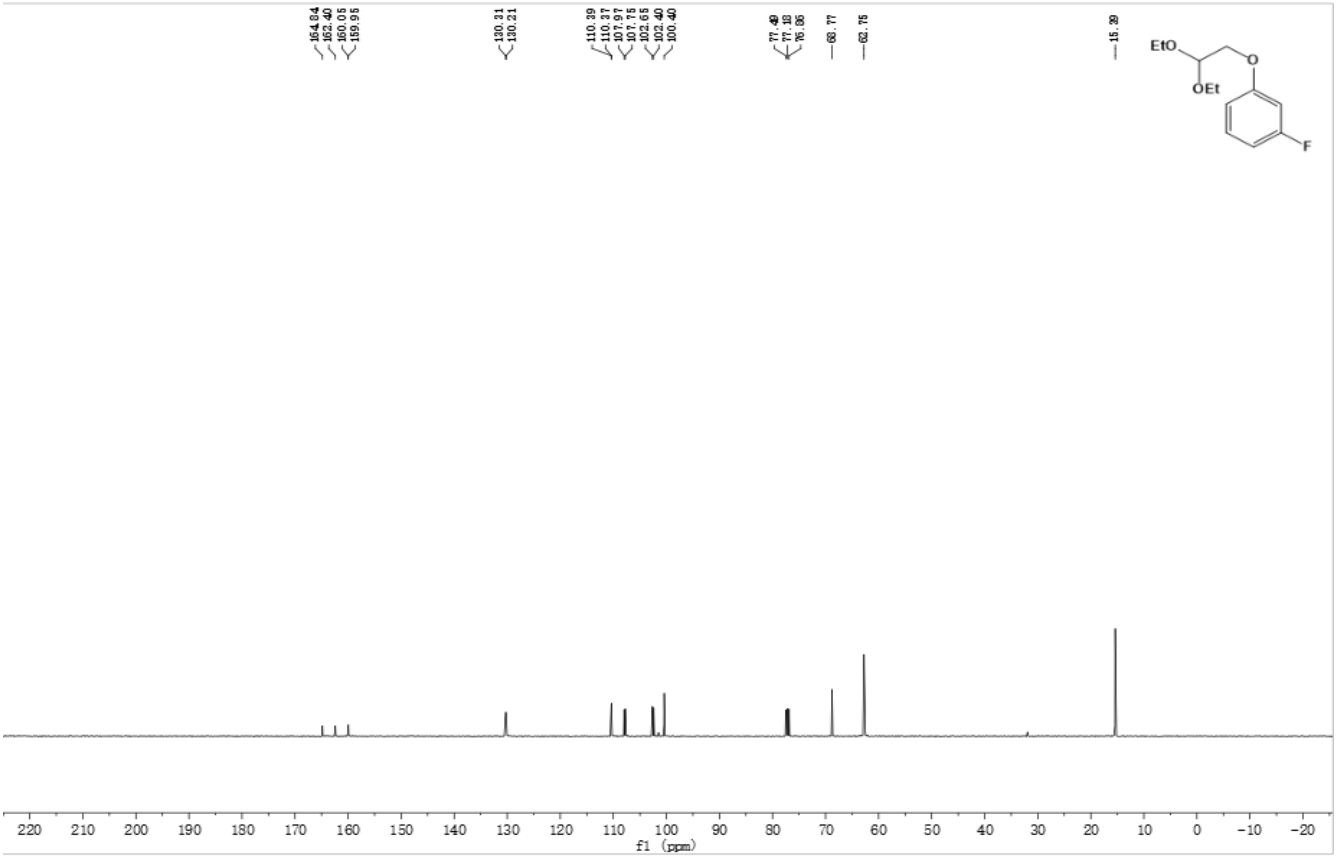
^{13}C NMR spectrum for 1t



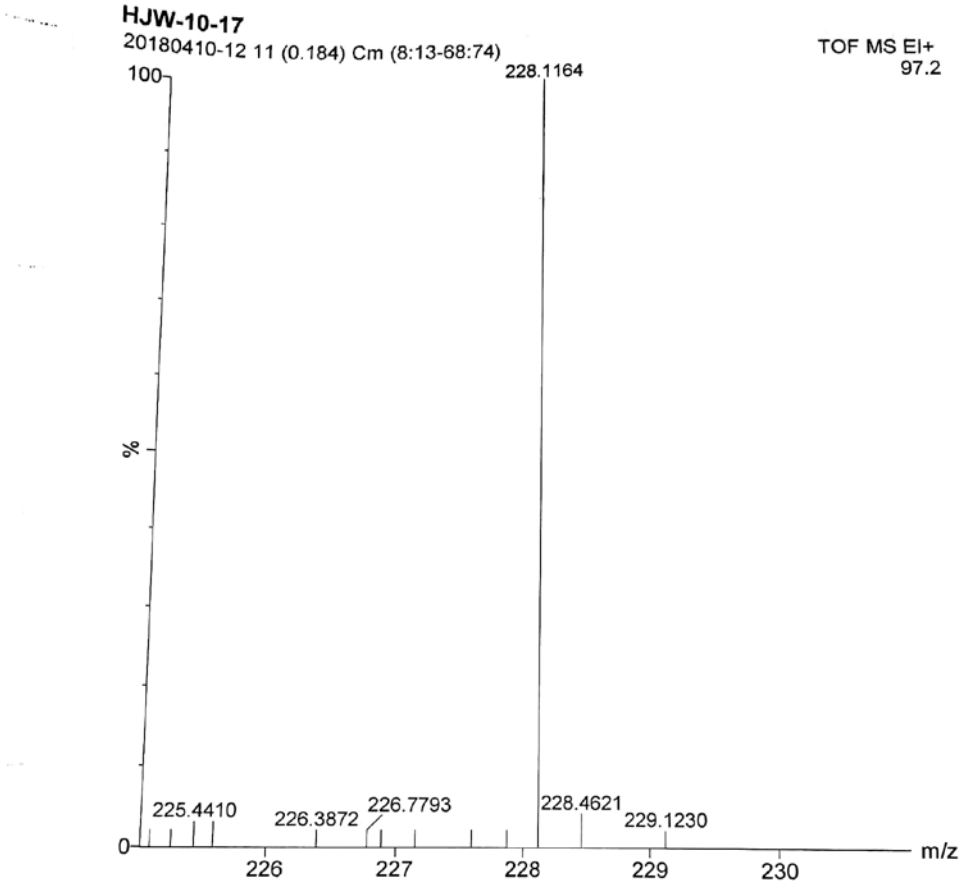
^{1}H NMR spectrum for 1u



^{13}C NMR spectrum for 1u



HRMS (EI) spectrum for 1u



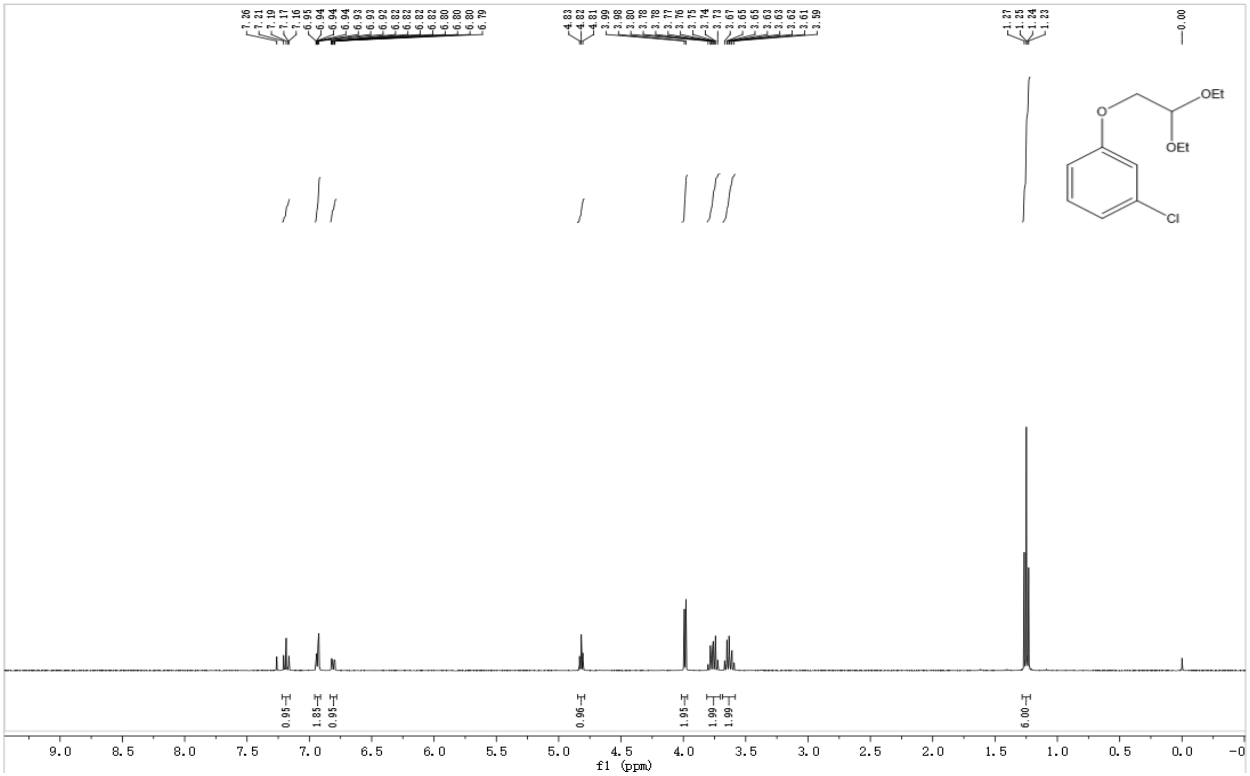
Elemental Composition Report

Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

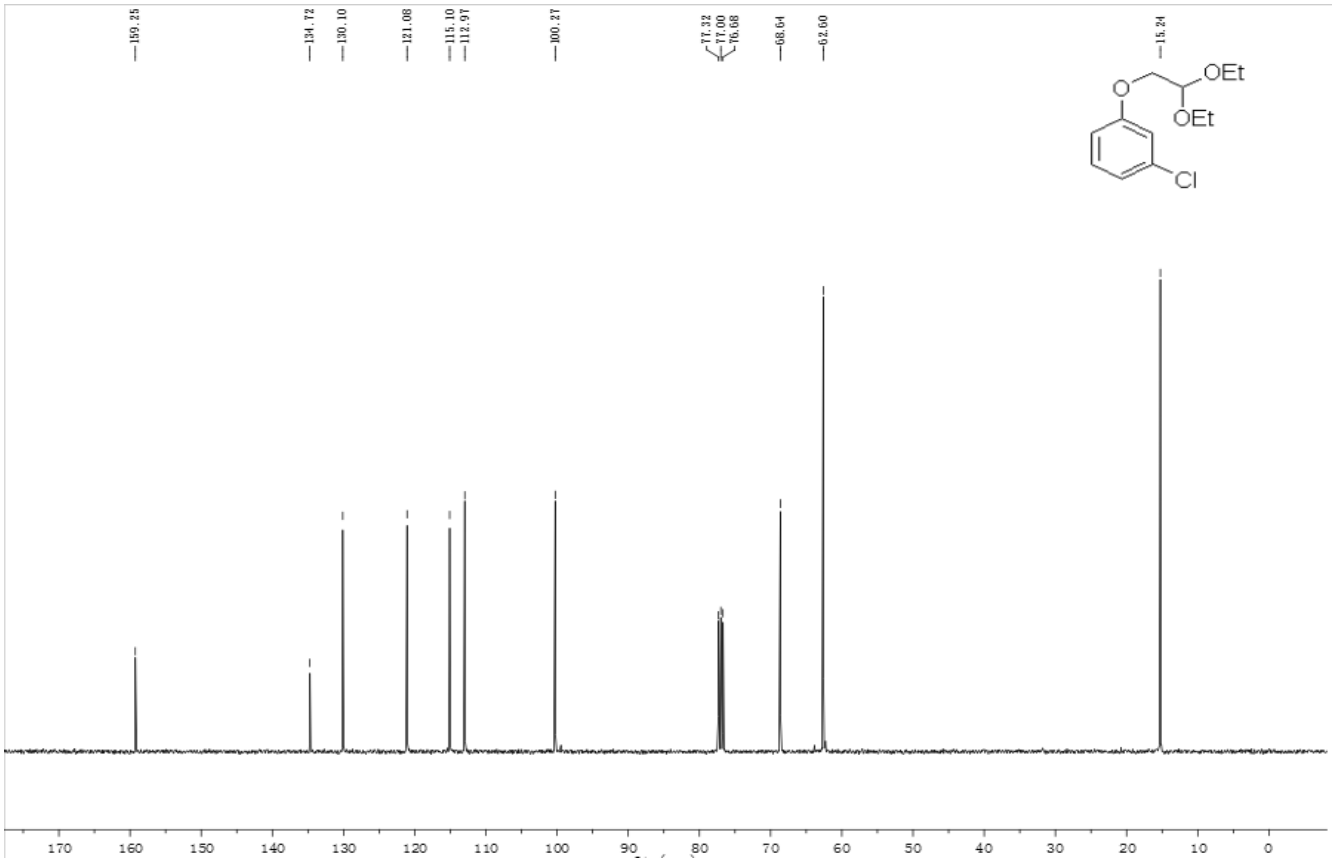
Monoisotopic Mass, Odd and Even Electron Ions
29 formula(e) evaluated with 10 results within limits (up to 50 closest results for each mass)

Minimum:	70.00				-1.5		
Maximum:	100.00		200.0	100.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula
228.1164	100.00	228.1162	0.2	1.0	4.0	4	C12 H17 O3 F

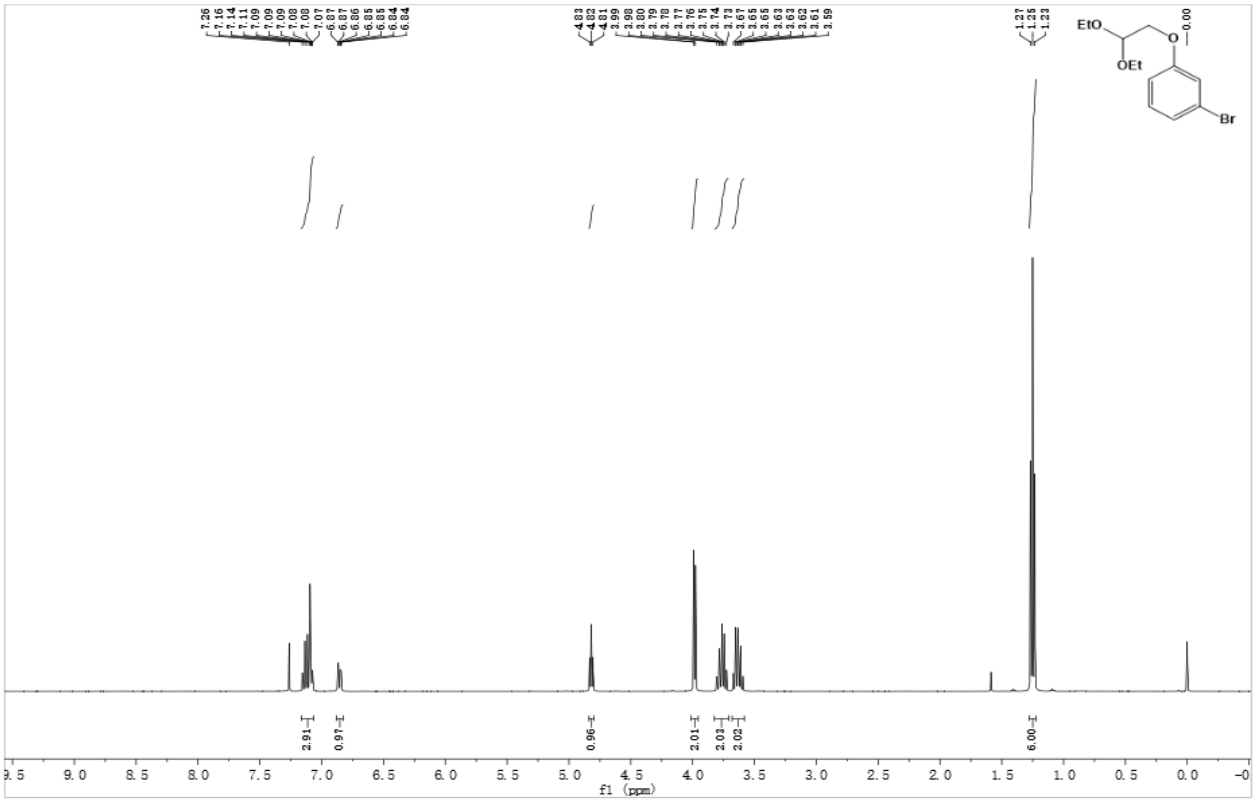
^{1}H NMR spectrum for 1v



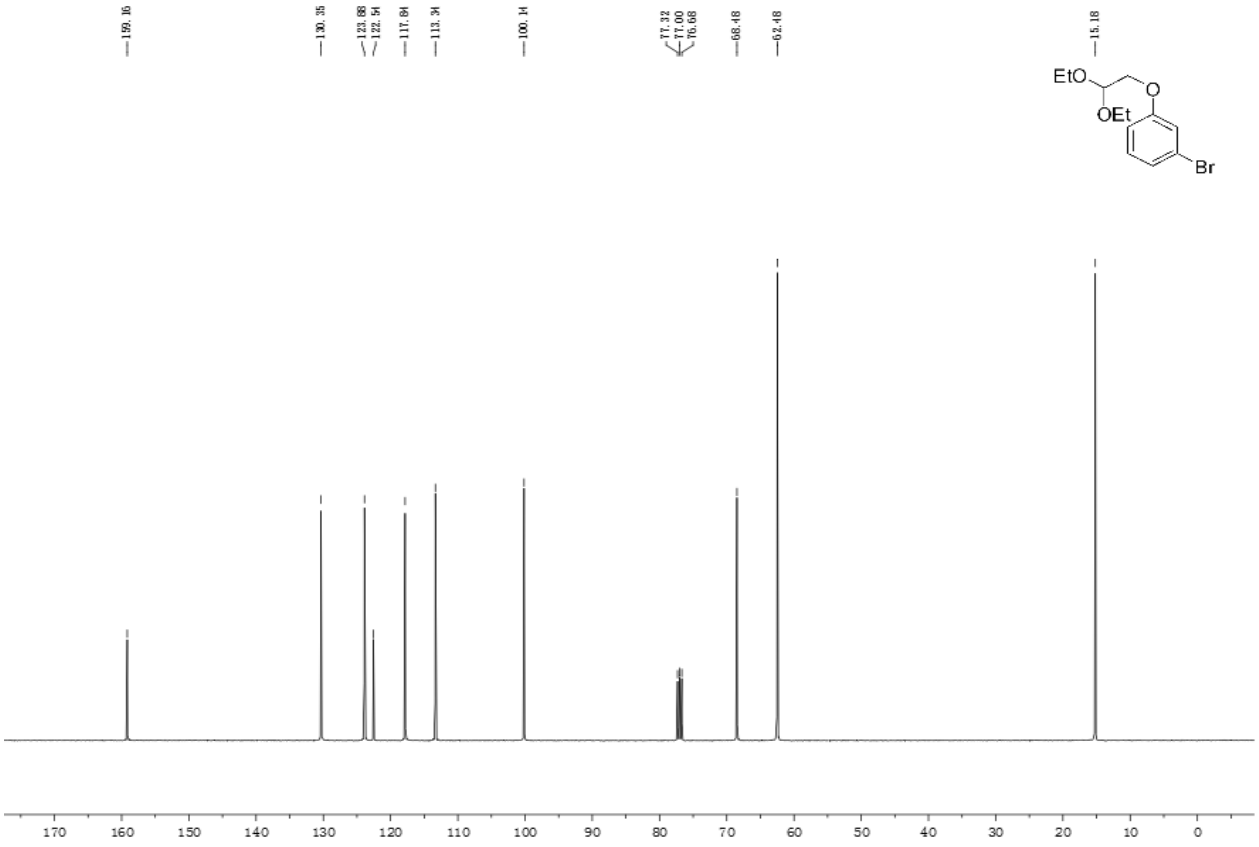
^{13}C NMR spectrum for 1v



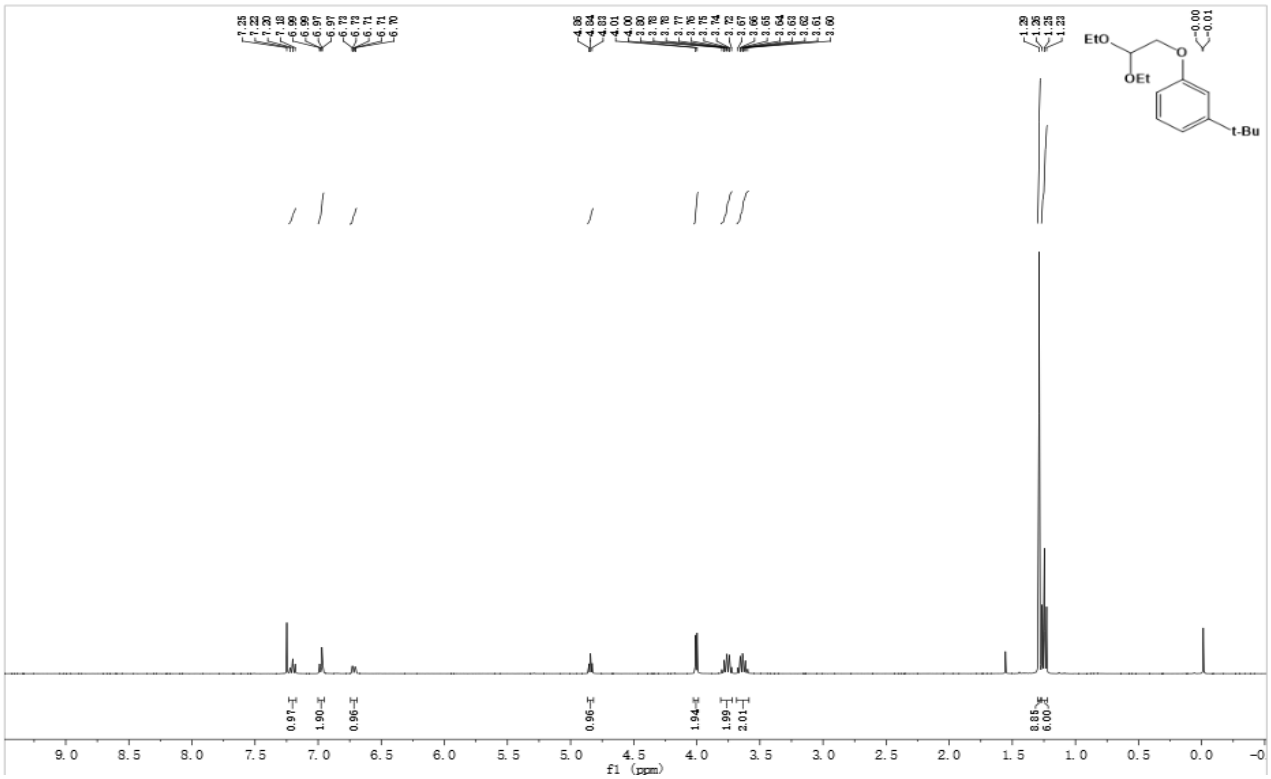
^{1}H NMR spectrum for 1w



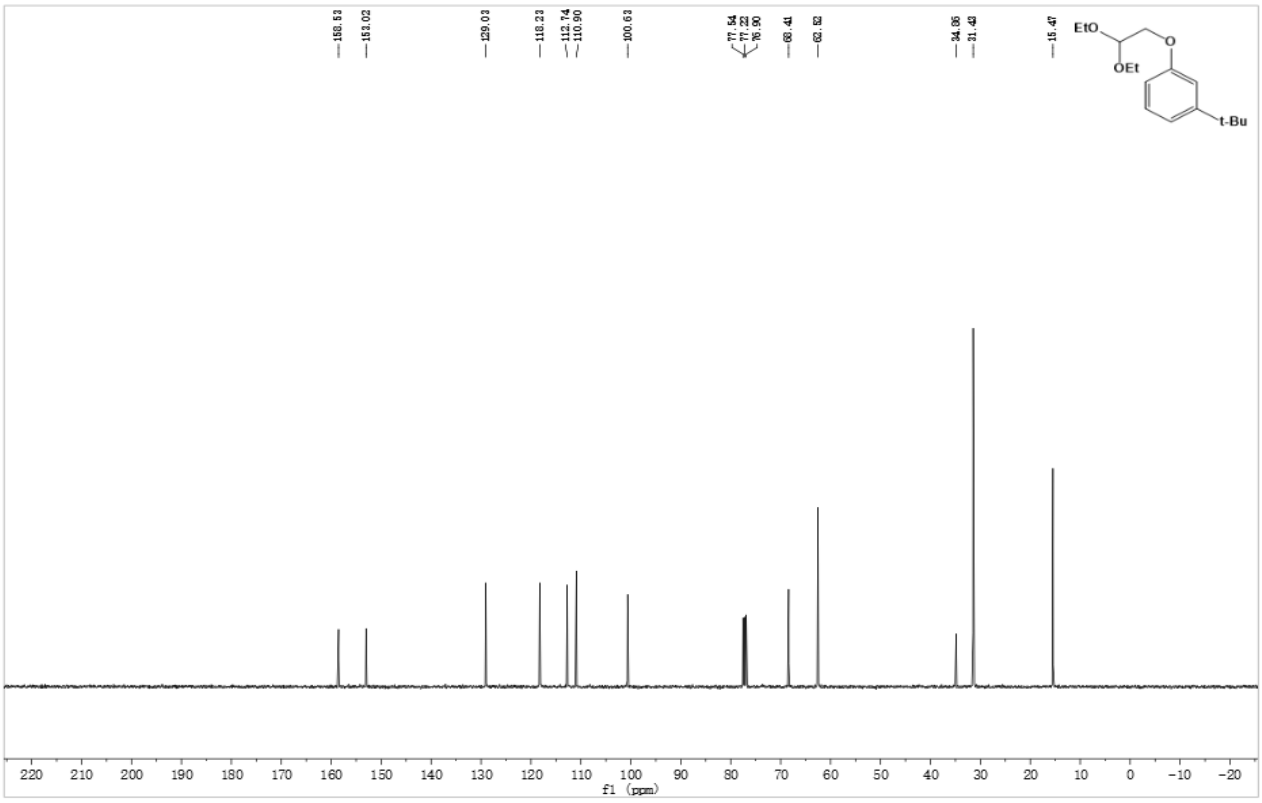
^{13}C NMR spectrum for 1w



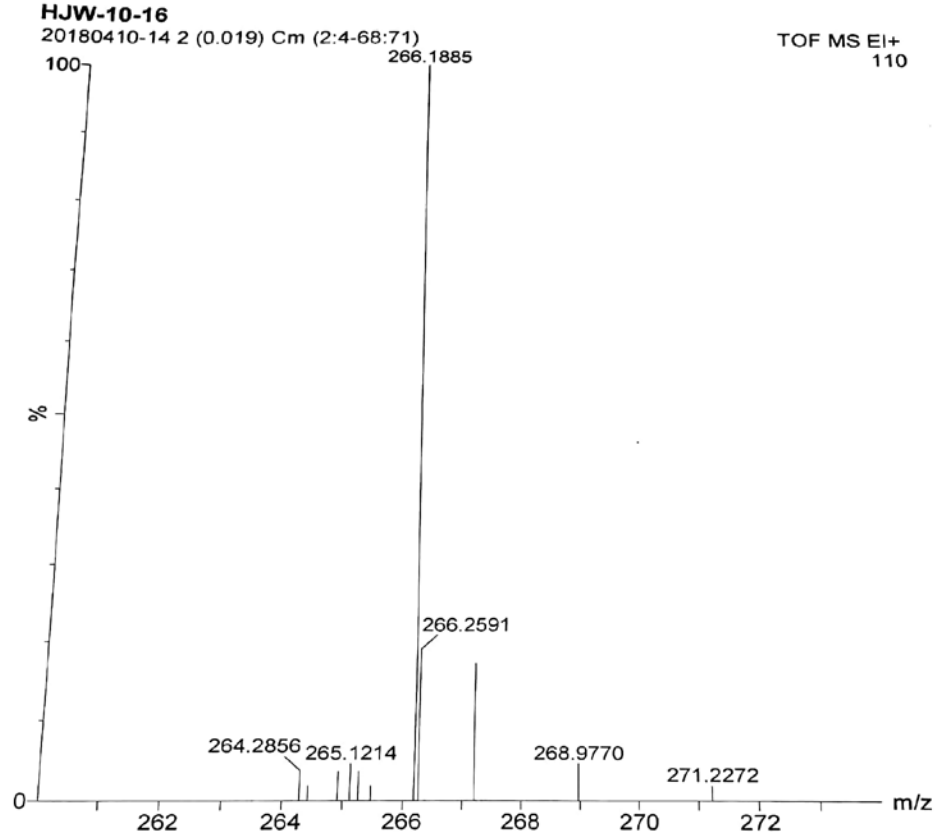
^{1}H NMR spectrum for 1x



^{13}C NMR spectrum for 1x



HRMS (EI) spectrum for 1x



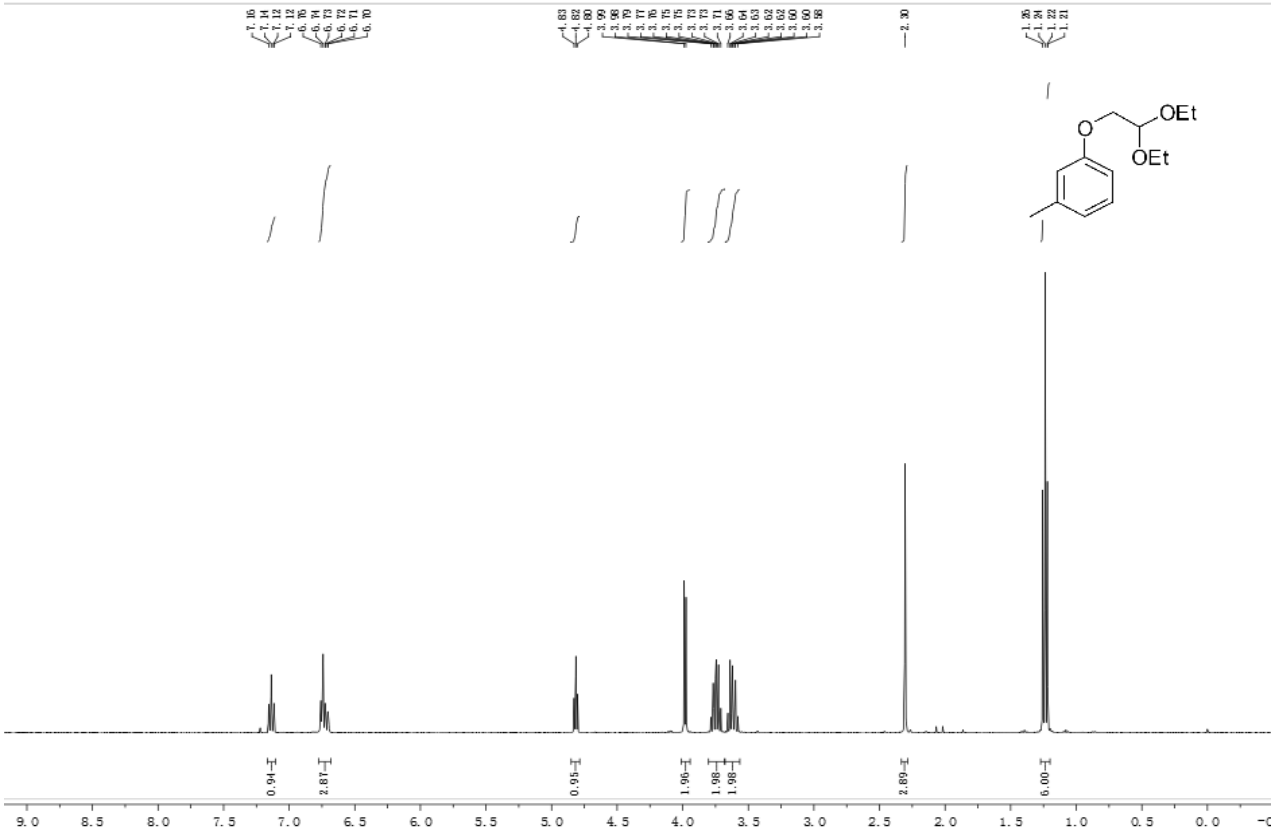
Elemental Composition Report

Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

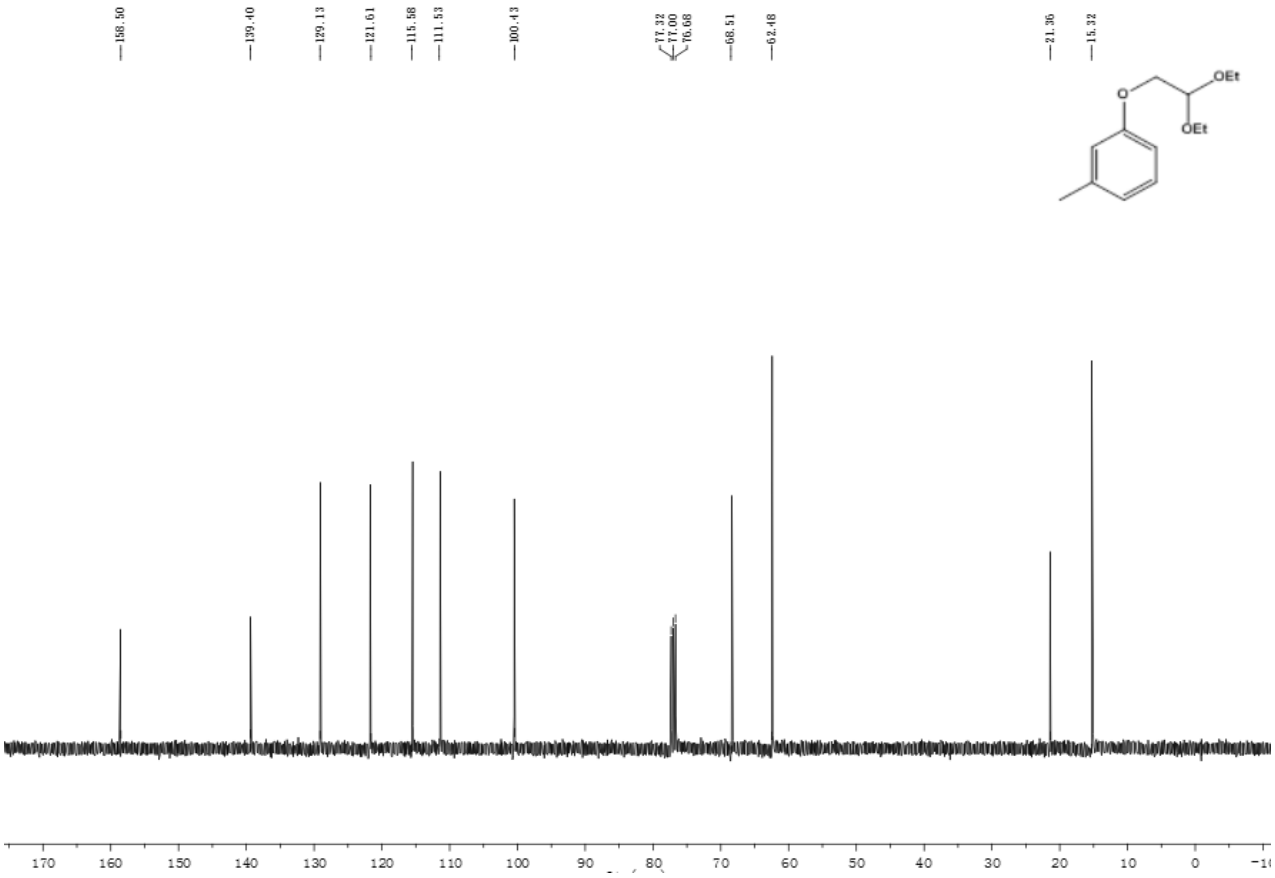
Monoisotopic Mass, Odd and Even Electron Ions
9 formula(e) evaluated with 3 results within limits (up to 50 closest results for each mass)

Minimum:	70.00				-1.5		
Maximum:	100.00		200.0	100.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula
266.1885	100.00	266.1882	0.3	1.1	4.0	1	C16 H26 O3

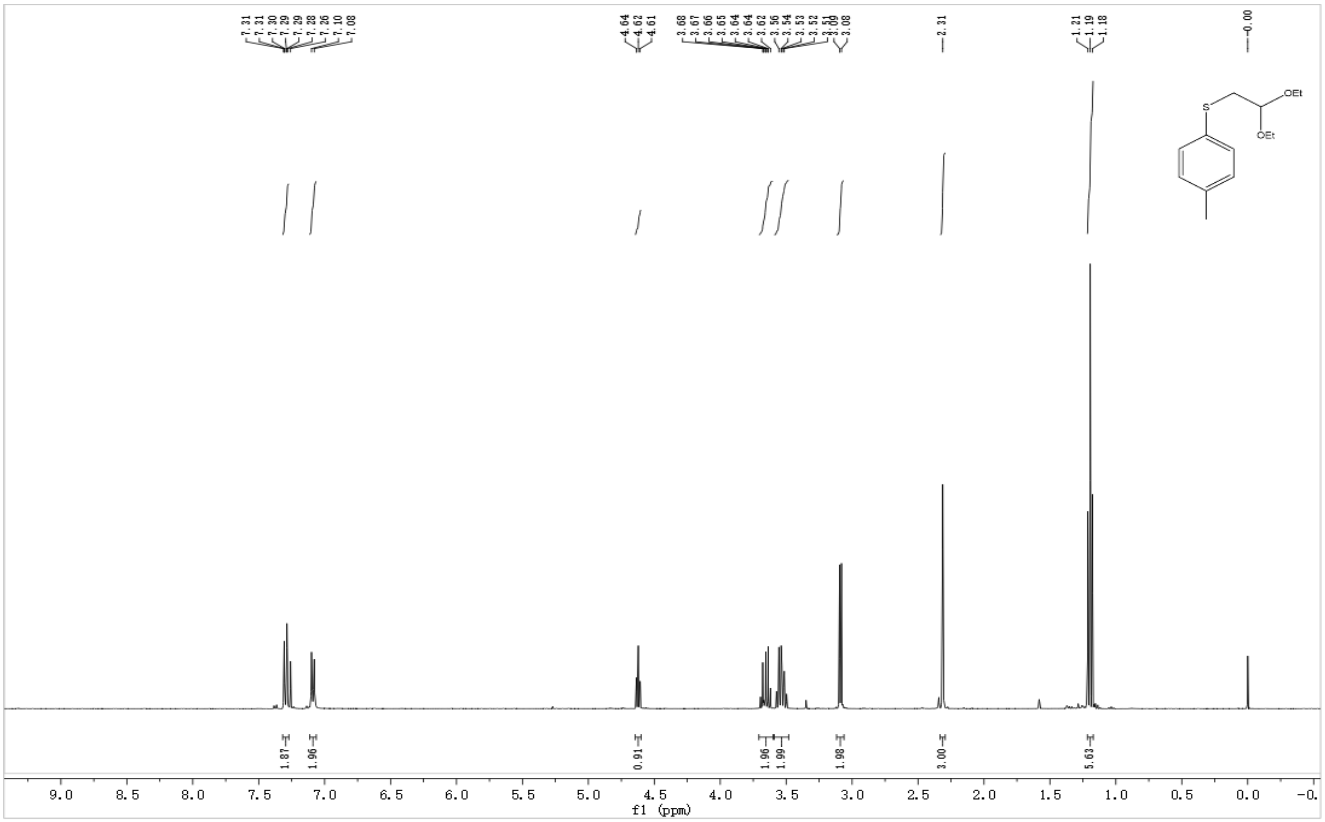
^{1}H NMR spectrum for 1y



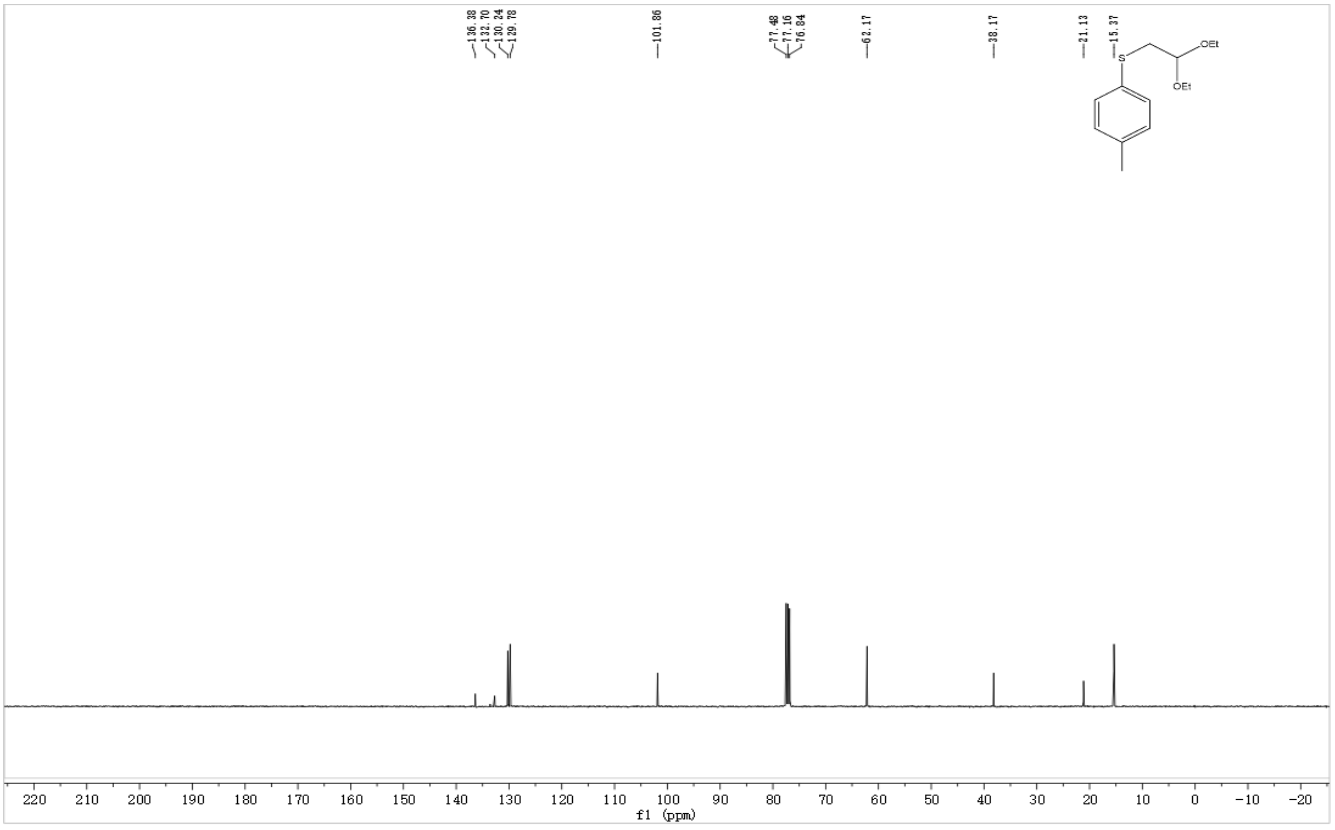
^{13}C NMR spectrum for 1y



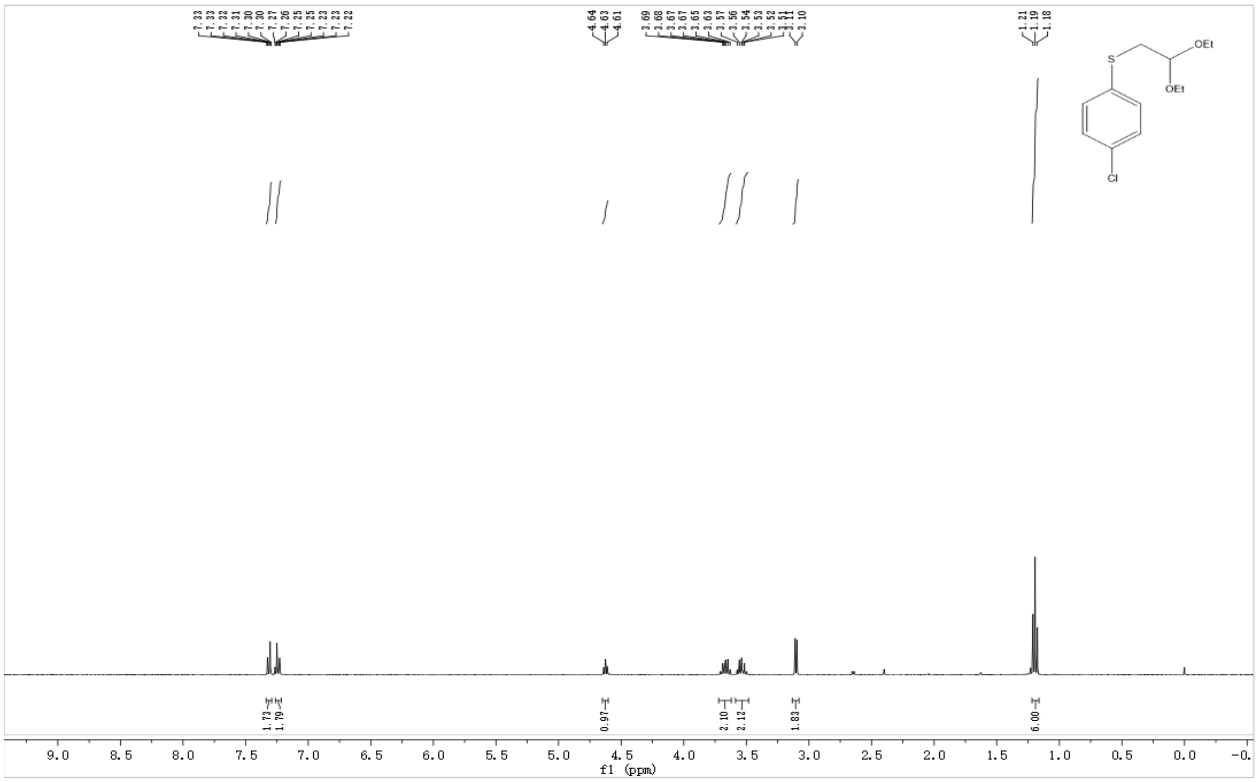
^{1}H NMR spectrum for 3a



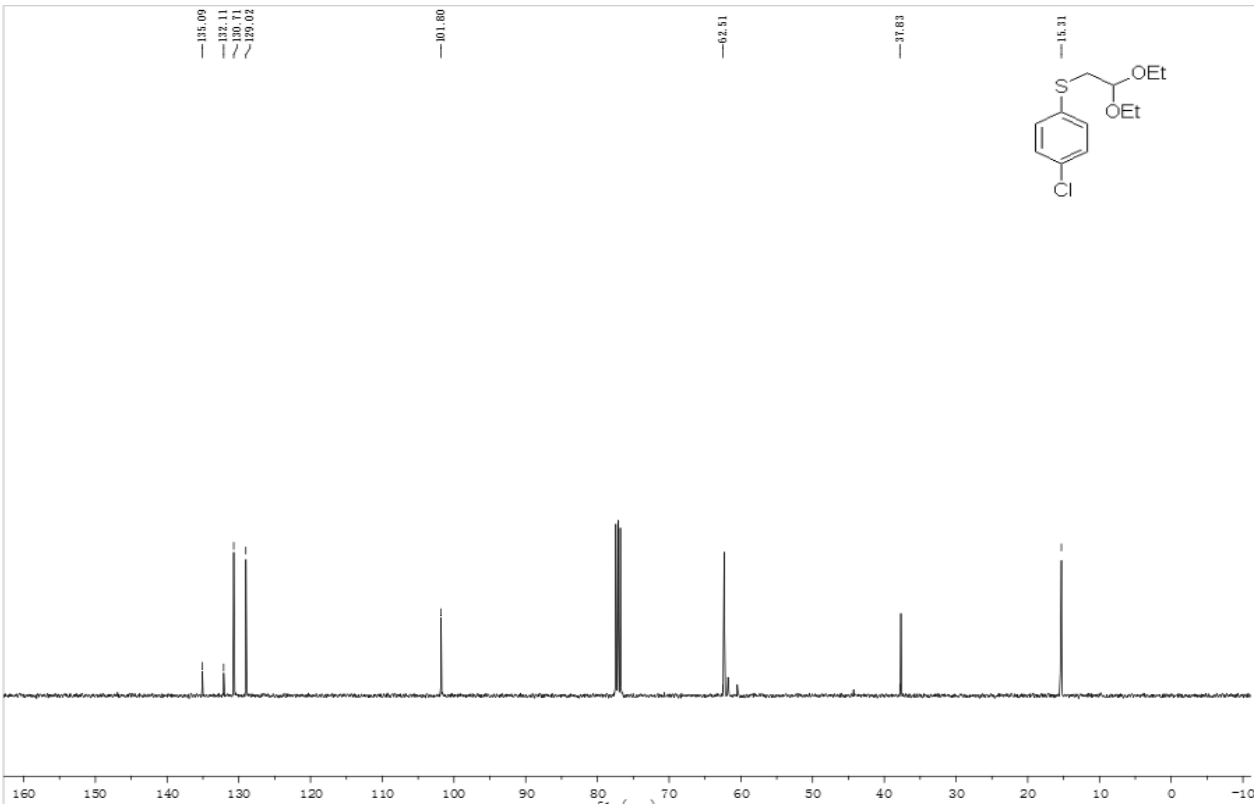
^{13}C NMR spectrum for 3a



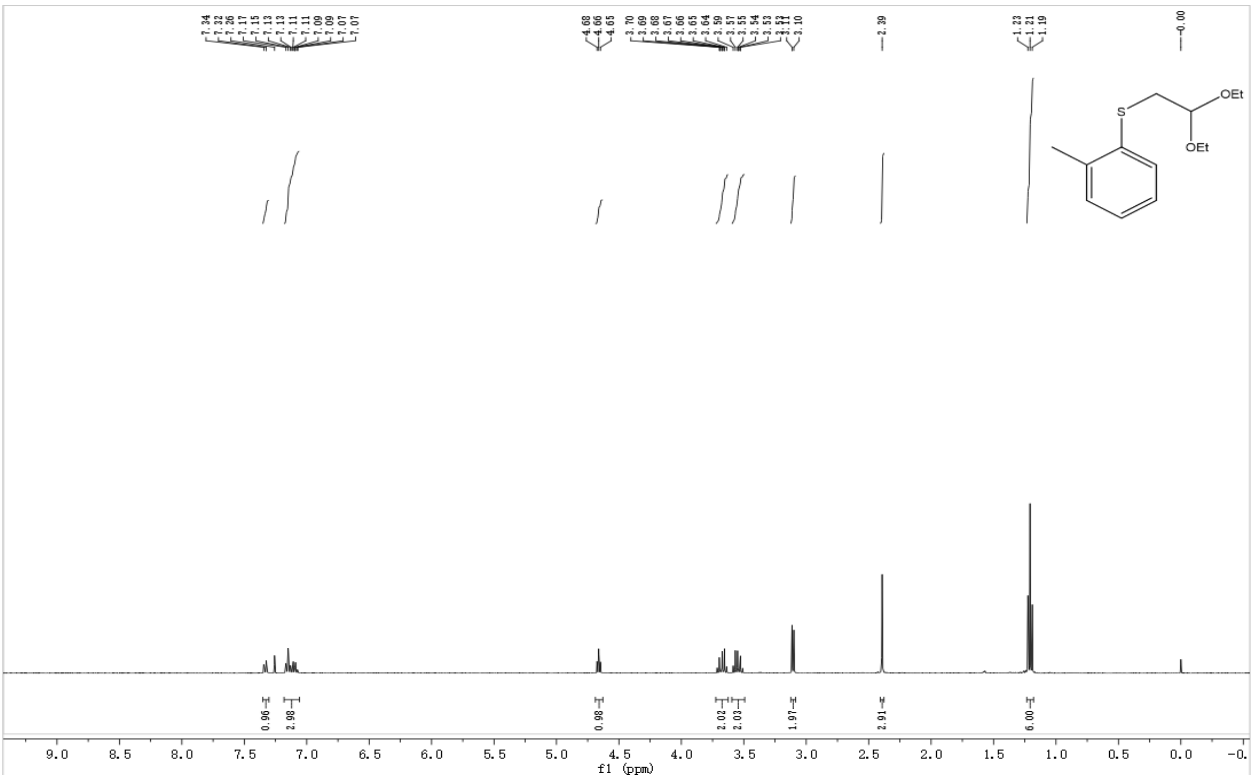
^{1}H NMR spectrum for 3b



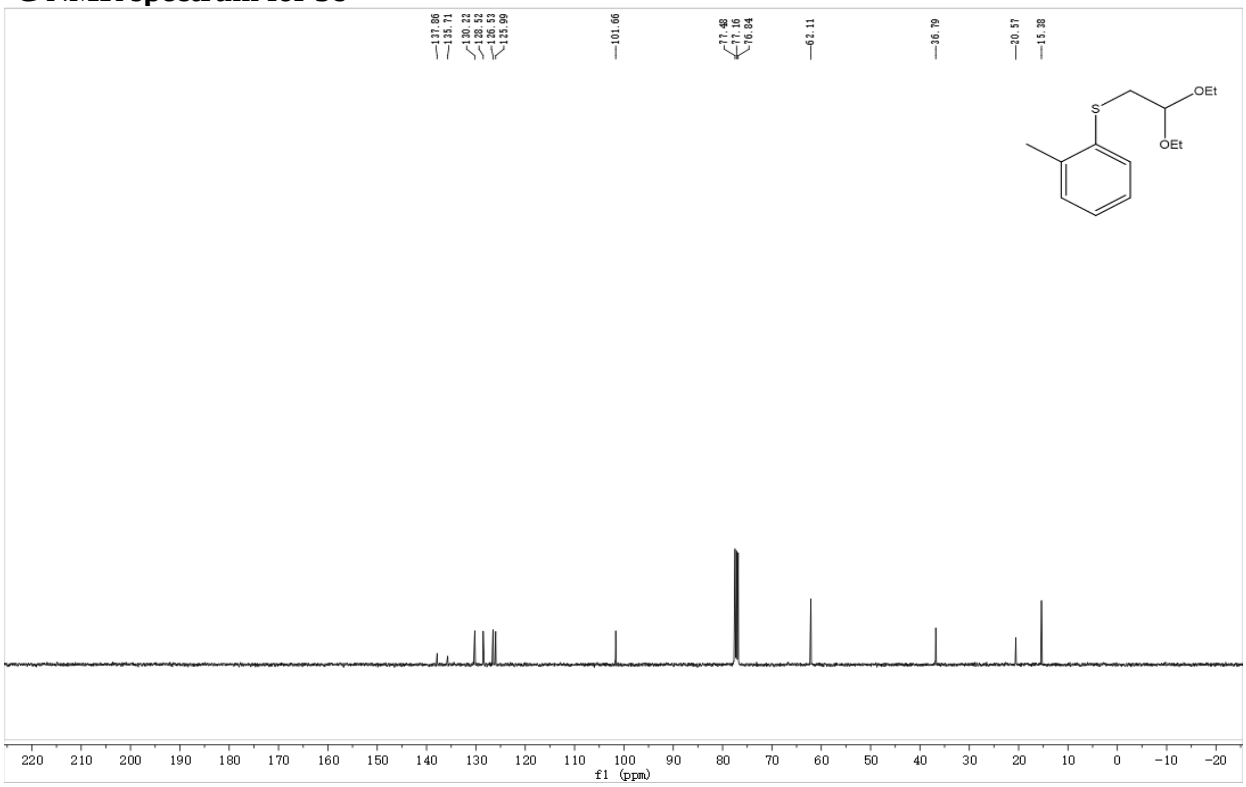
^{13}C NMR spectrum for 3b



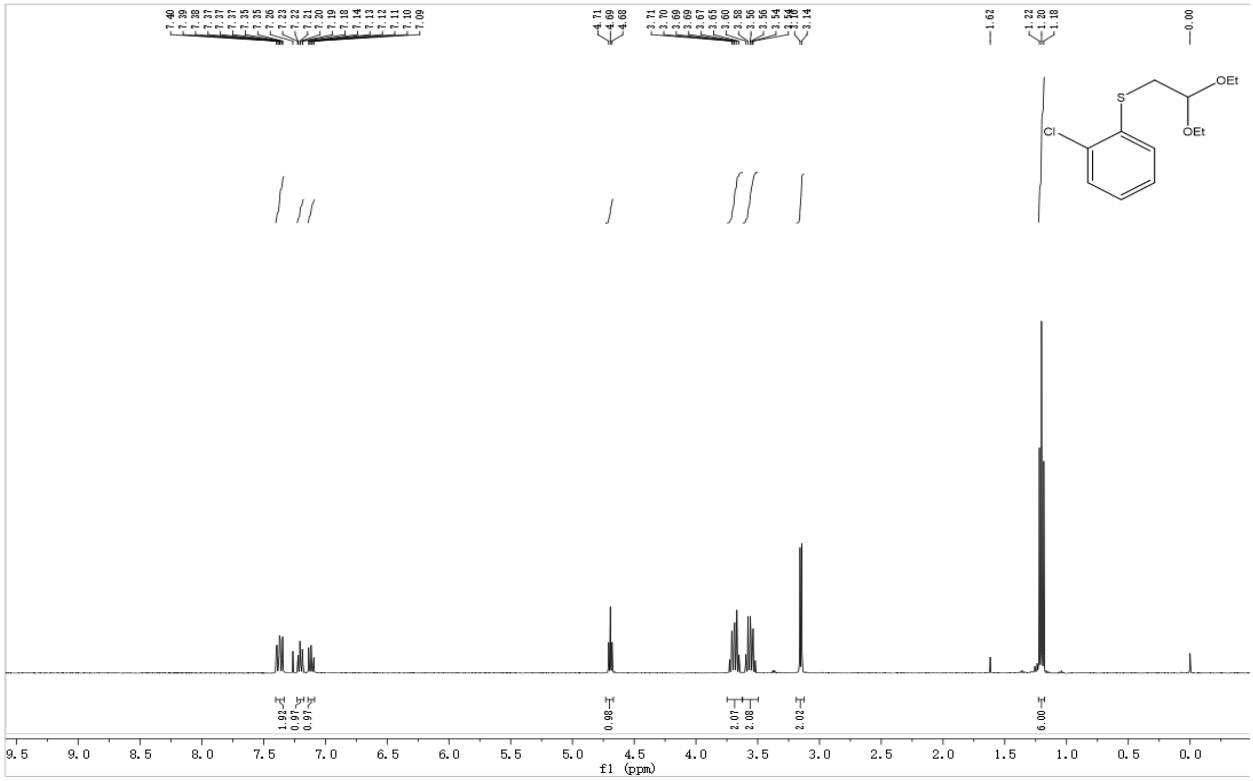
^{1}H NMR spectrum for 3c



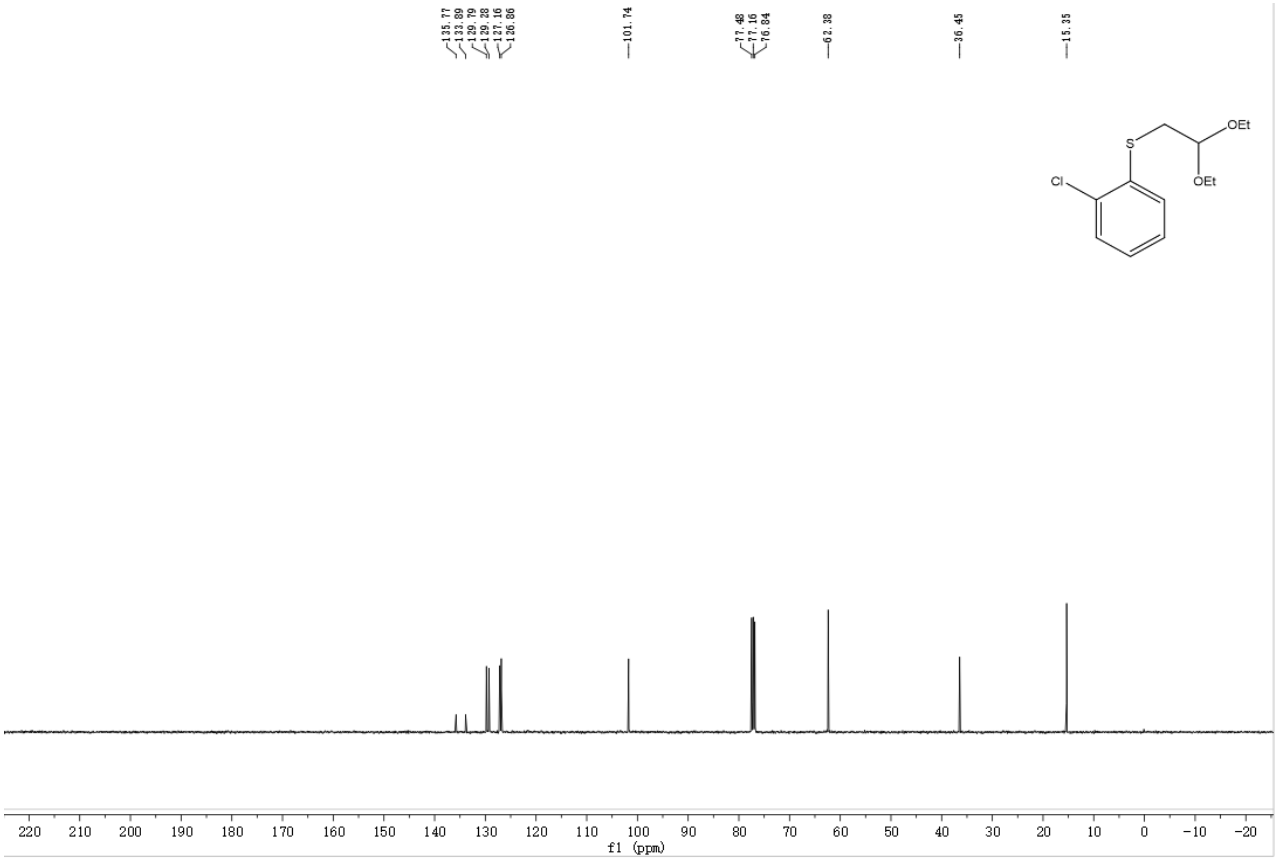
^{13}C NMR spectrum for 3c



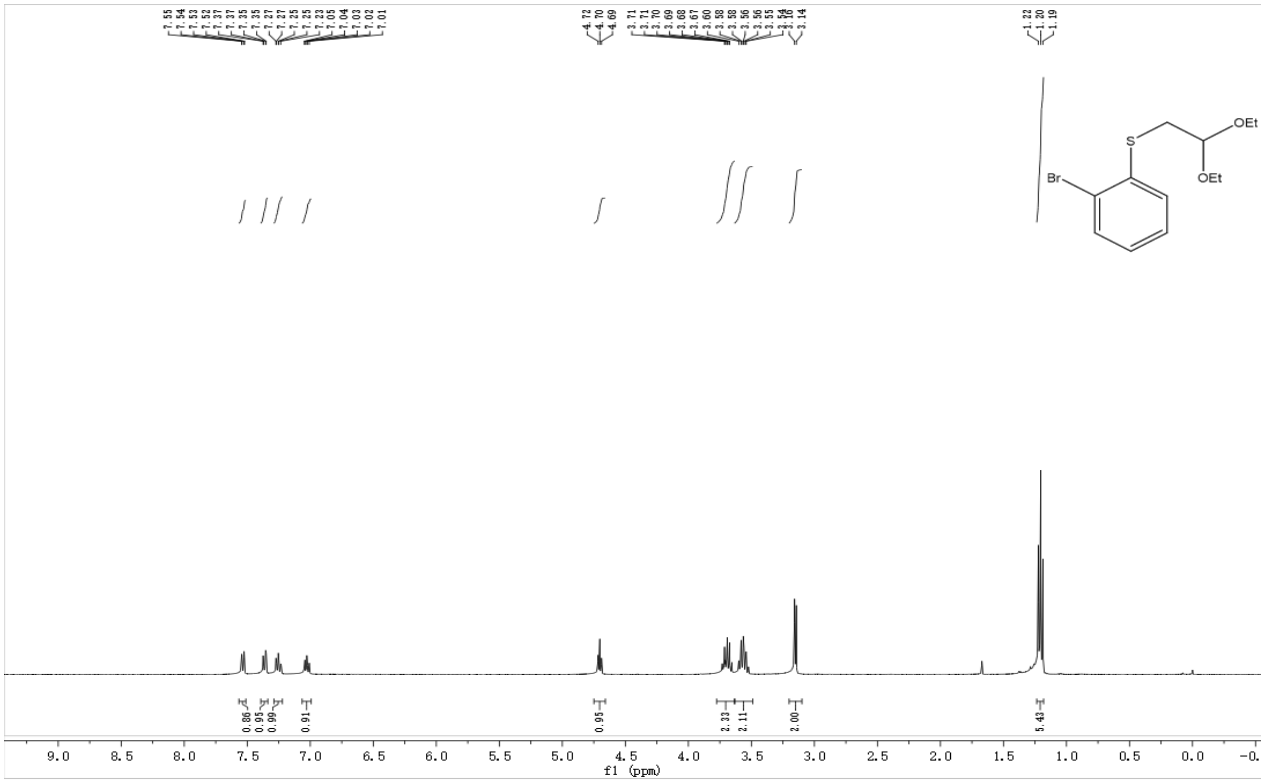
^{1}H NMR spectrum for 3d



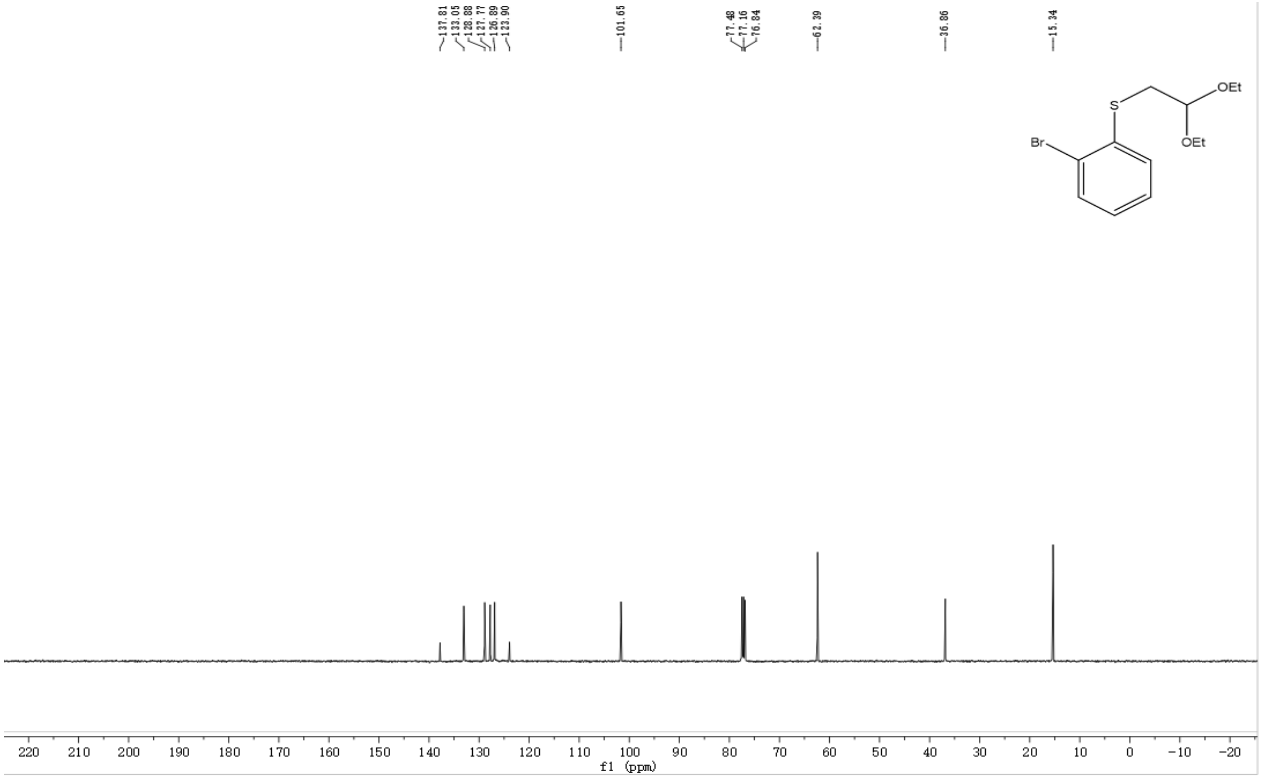
^{13}C NMR spectrum for 3d



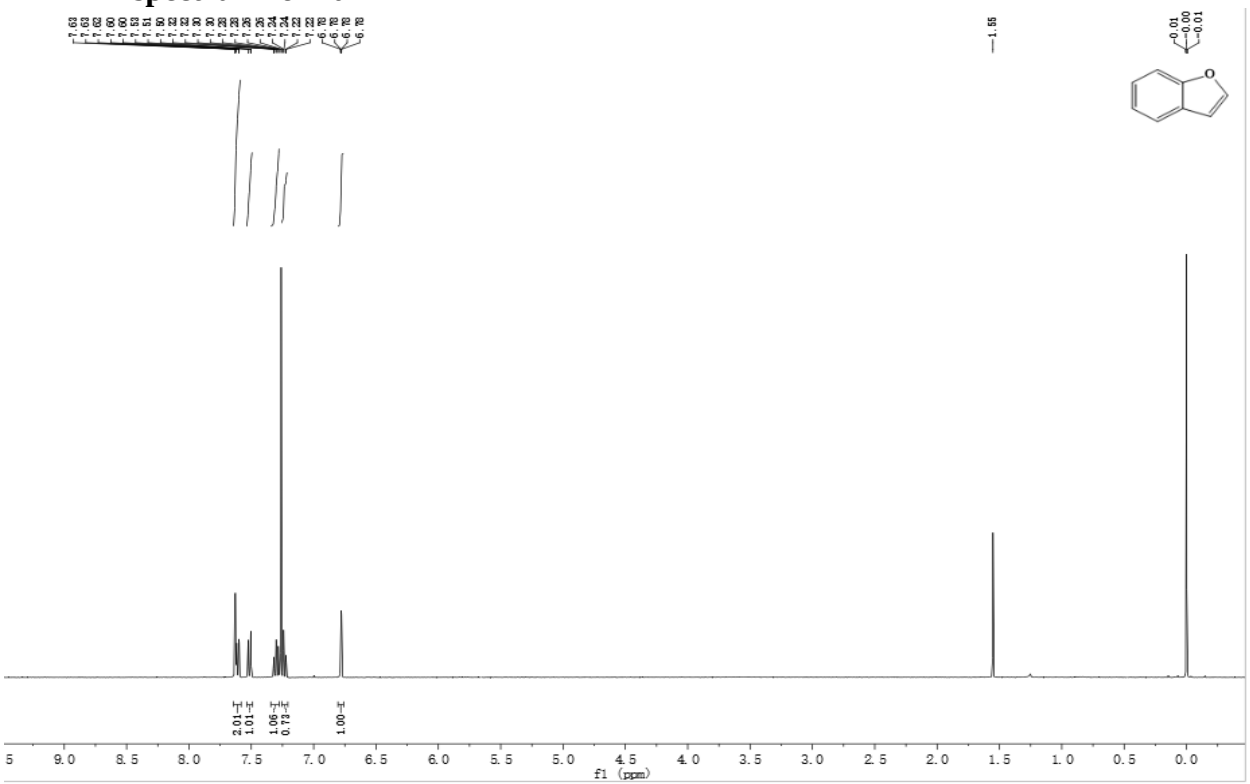
^{1}H NMR spectrum for 3e



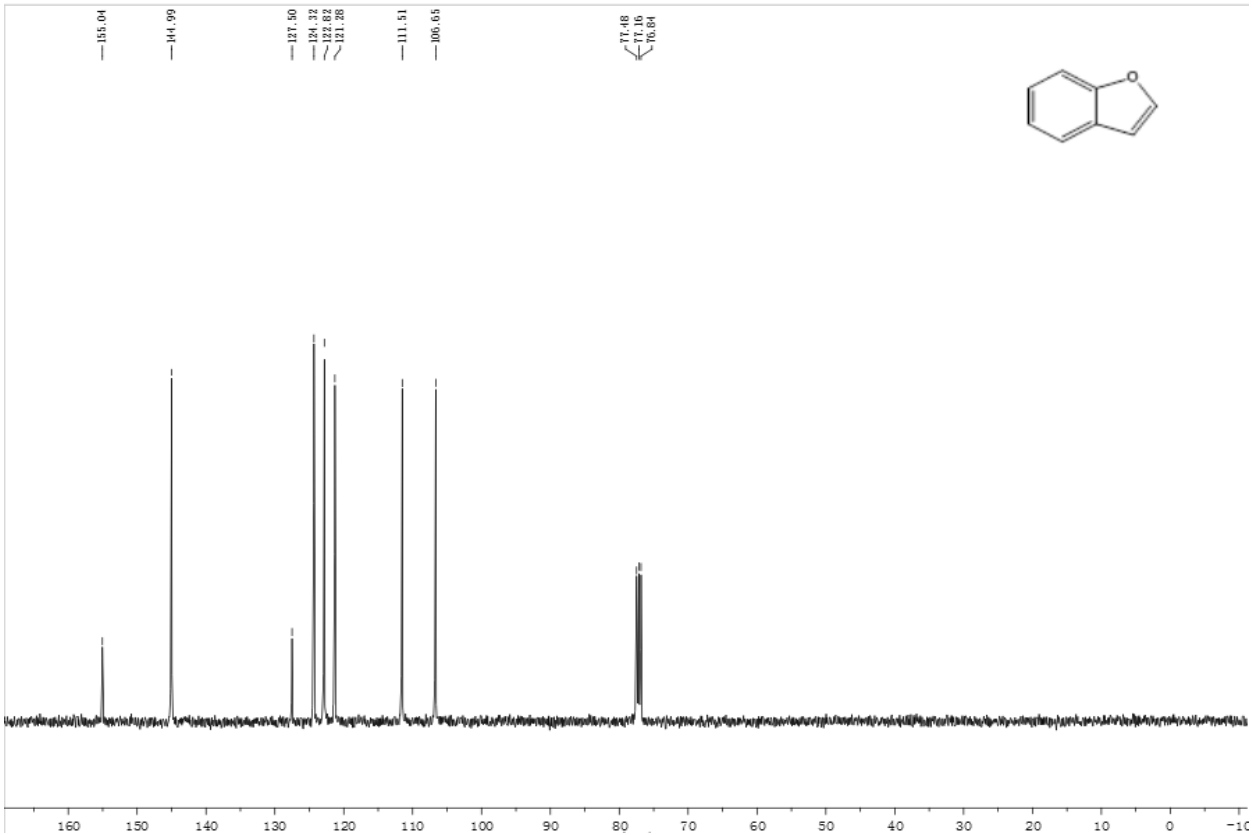
^{13}C NMR spectrum for 3e



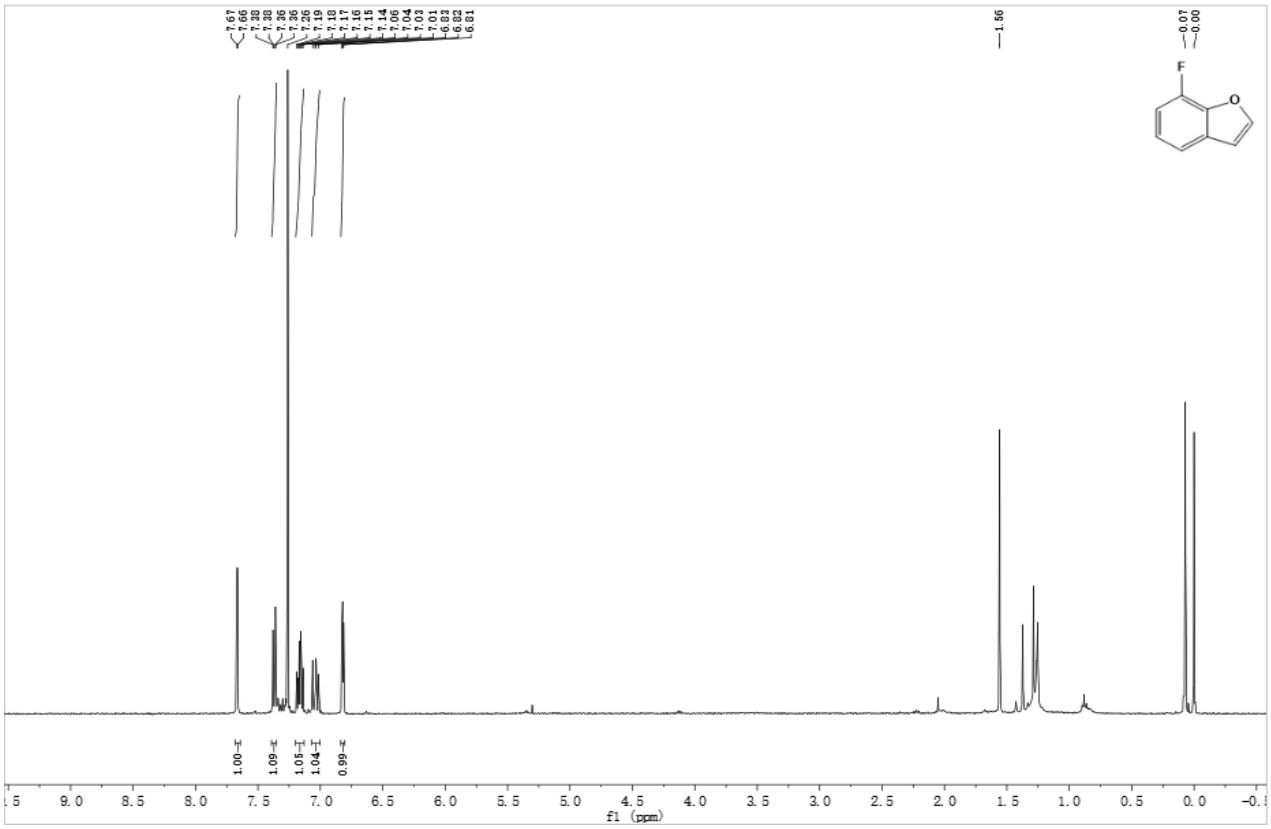
^{1}H NMR spectrum for 2a



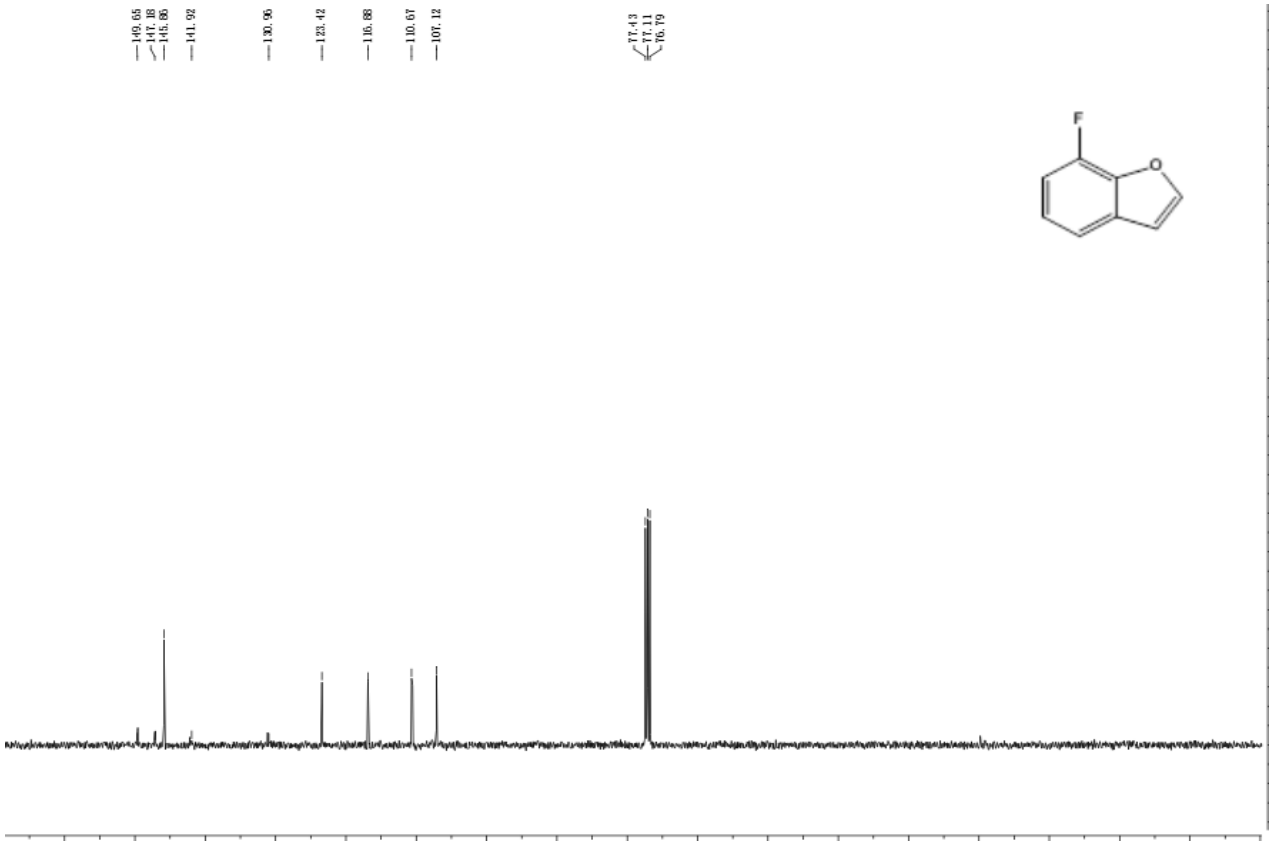
^{13}C NMR spectrum for 2a



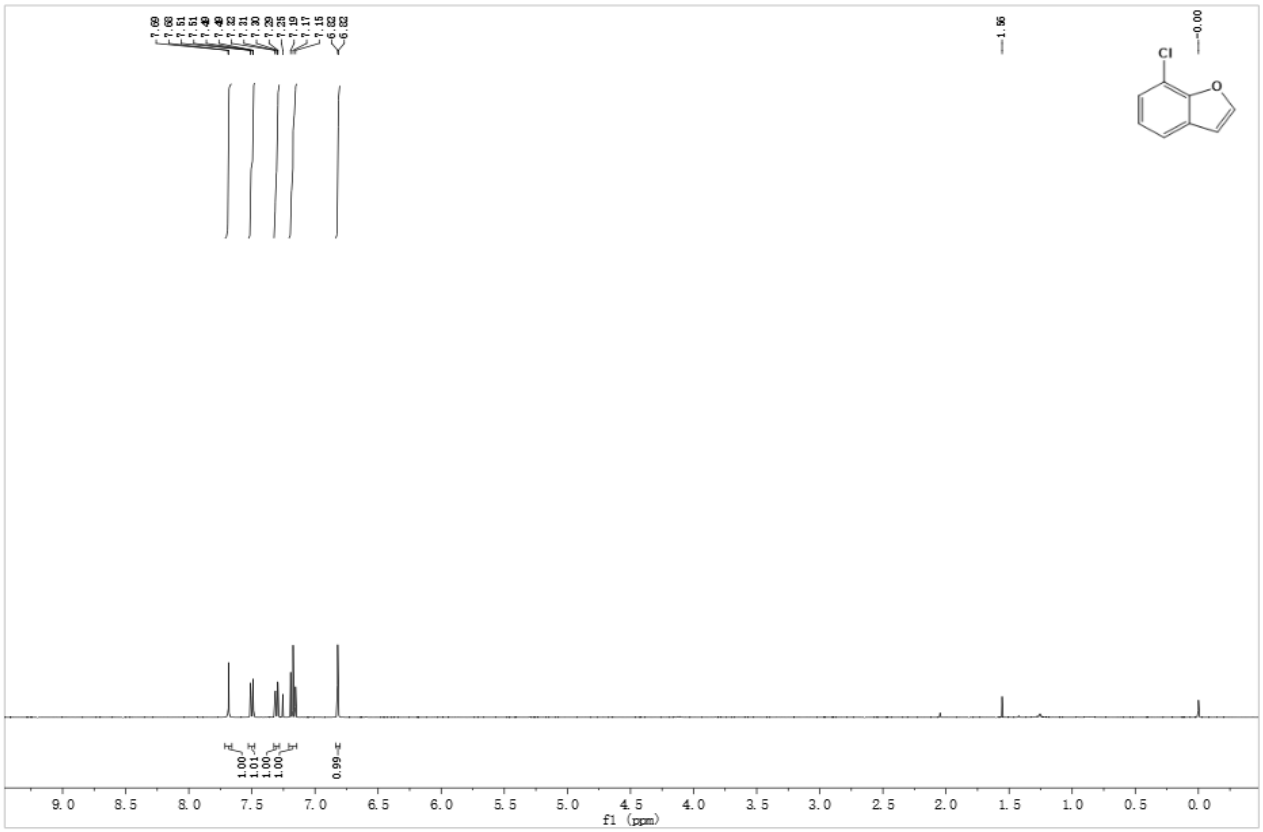
^{1}H NMR spectrum for 2b



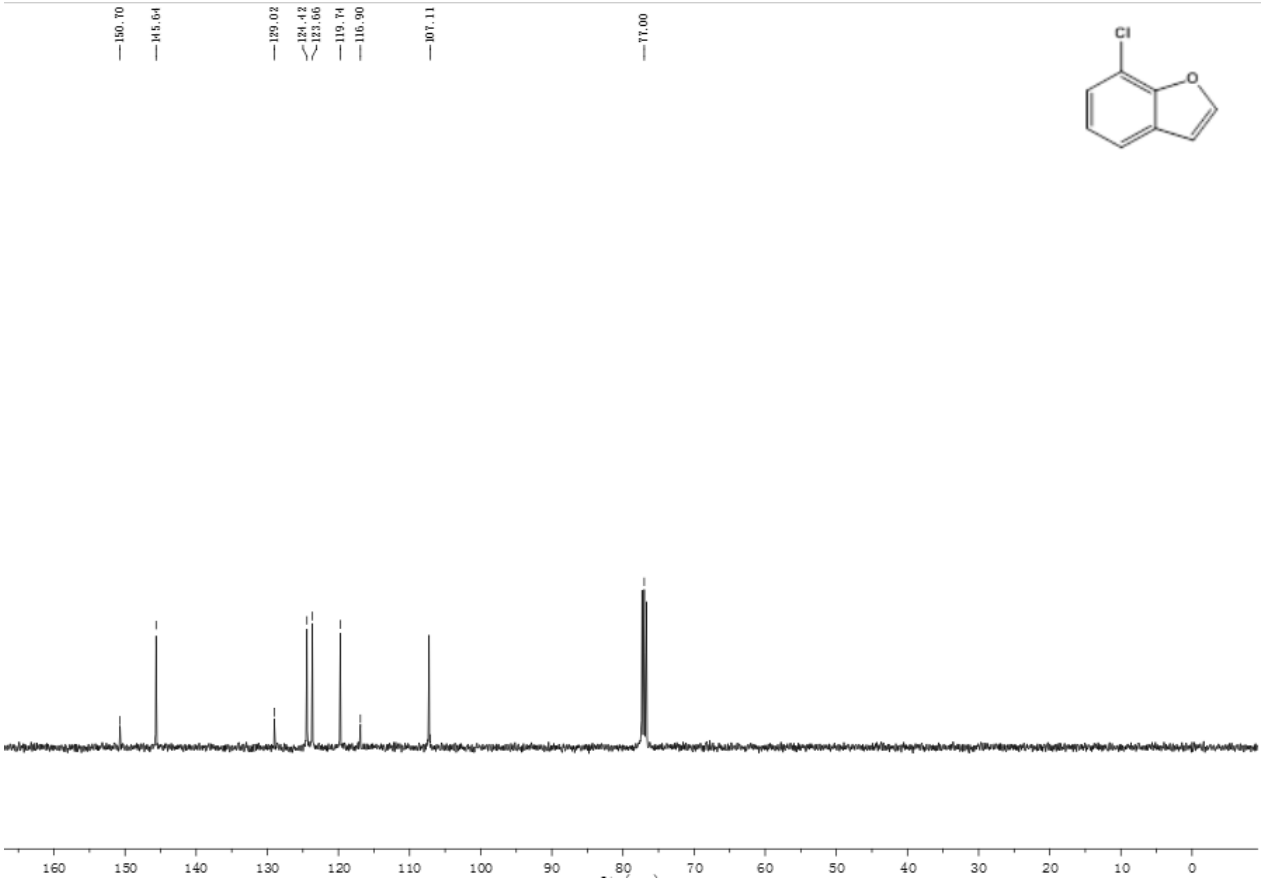
^{13}C NMR spectrum for 2b



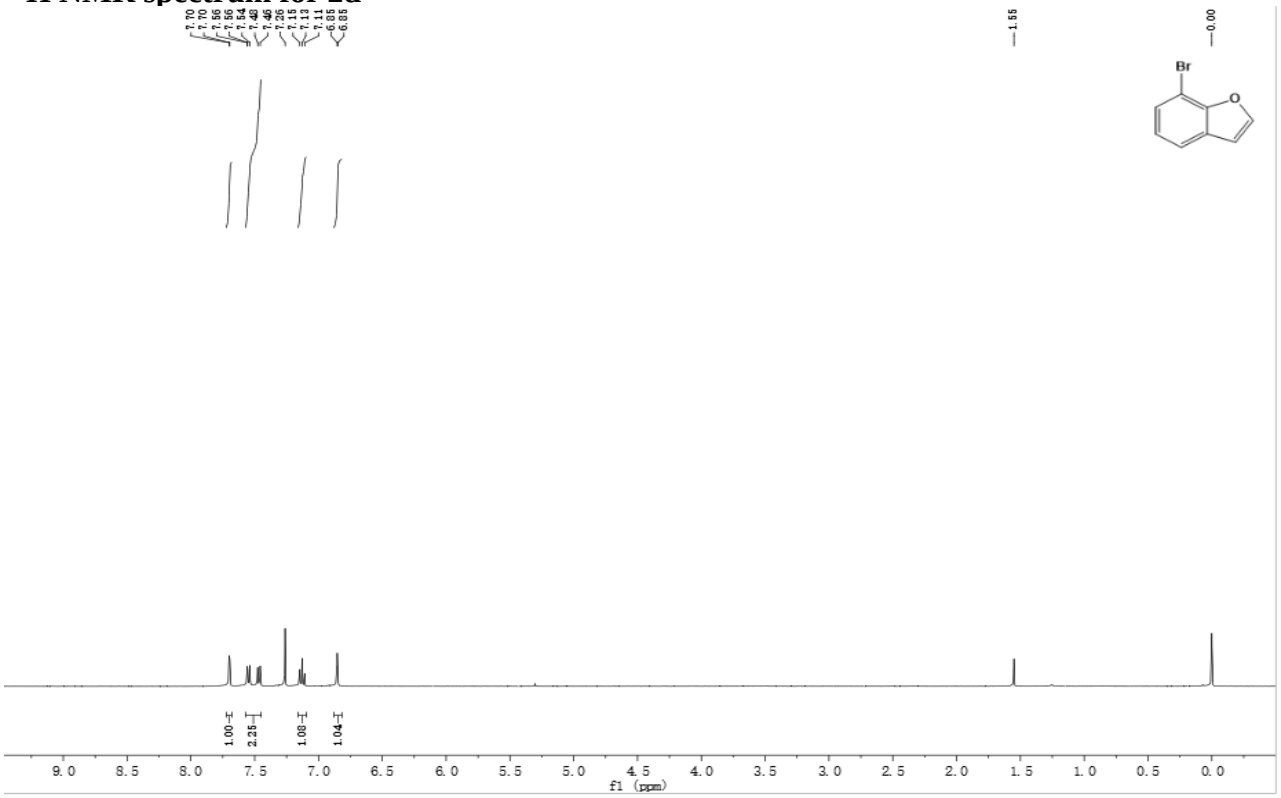
^{1}H NMR spectrum for 2c



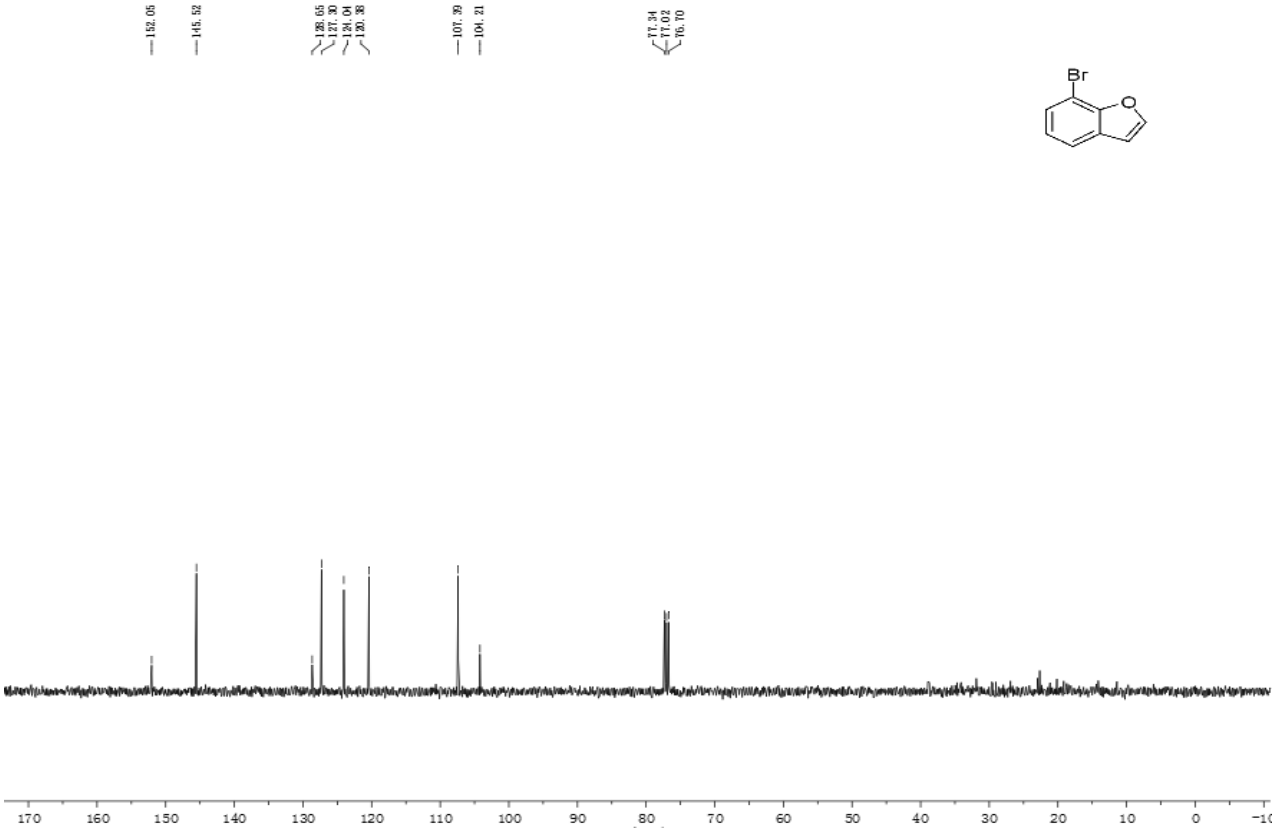
^{13}C NMR spectrum for 2c



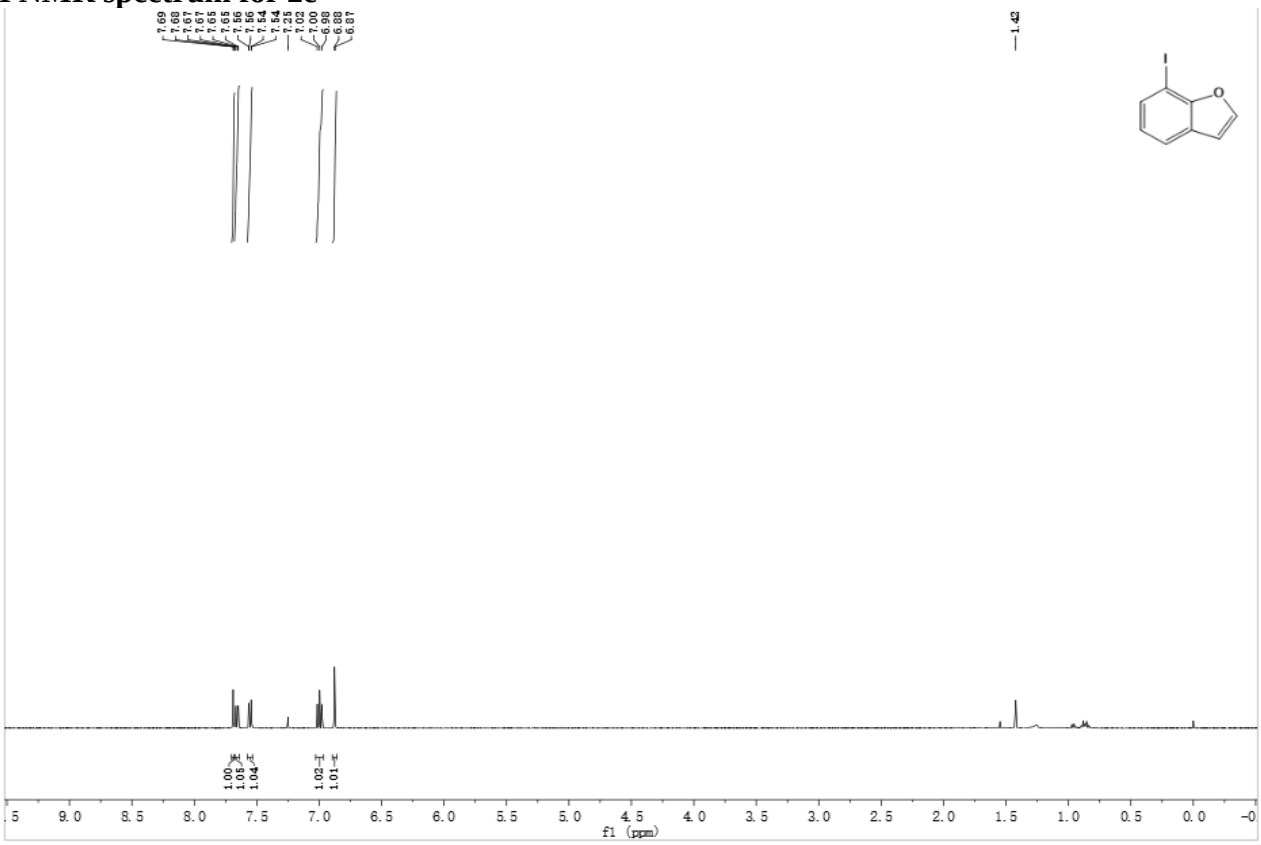
^{1}H NMR spectrum for 2d



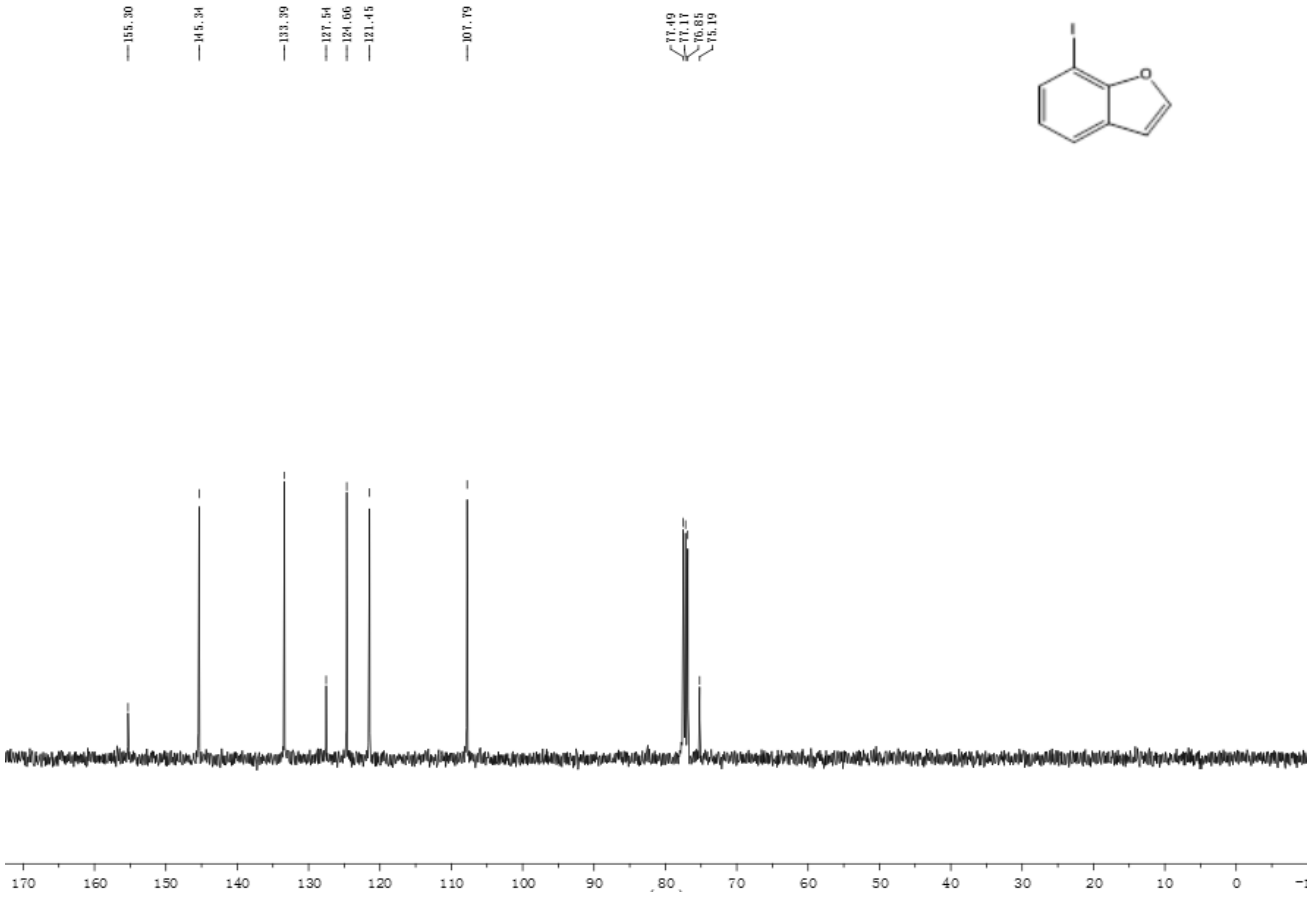
^{13}C NMR spectrum for 2d



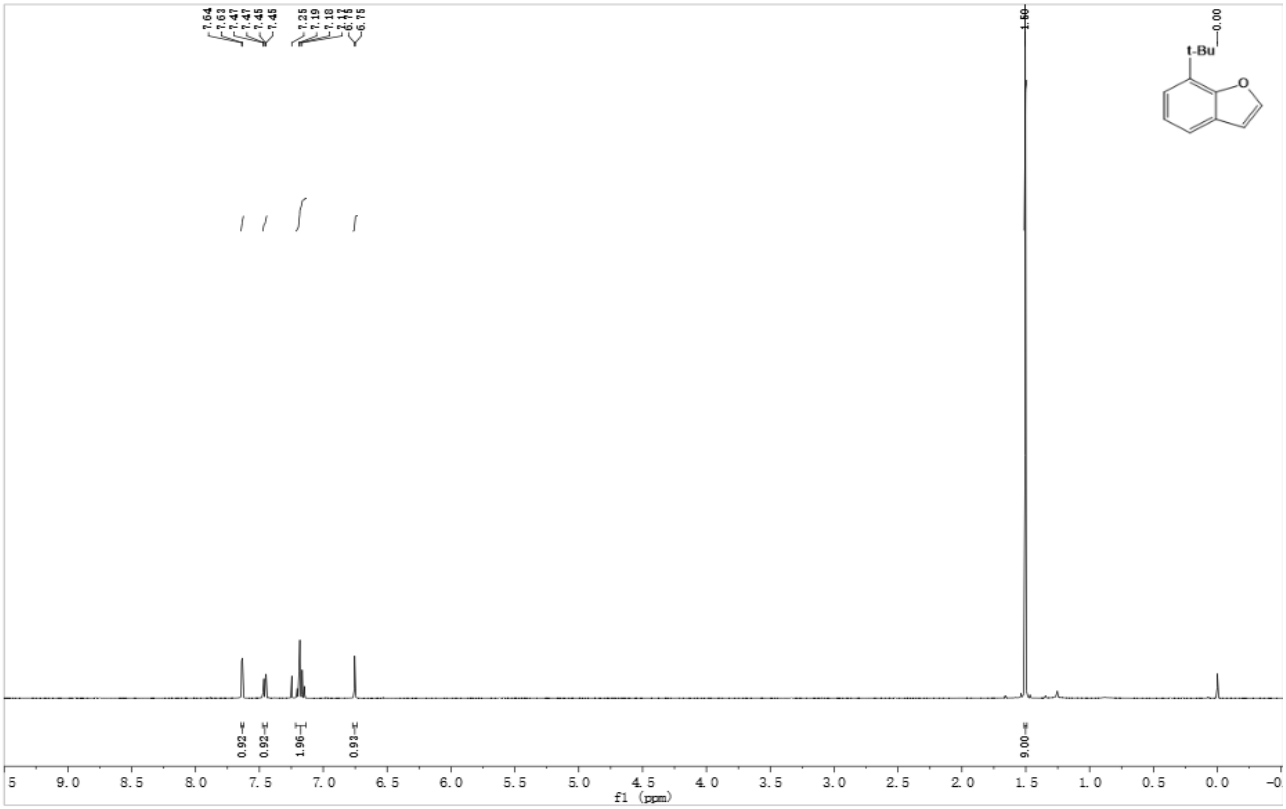
^{1}H NMR spectrum for 2e



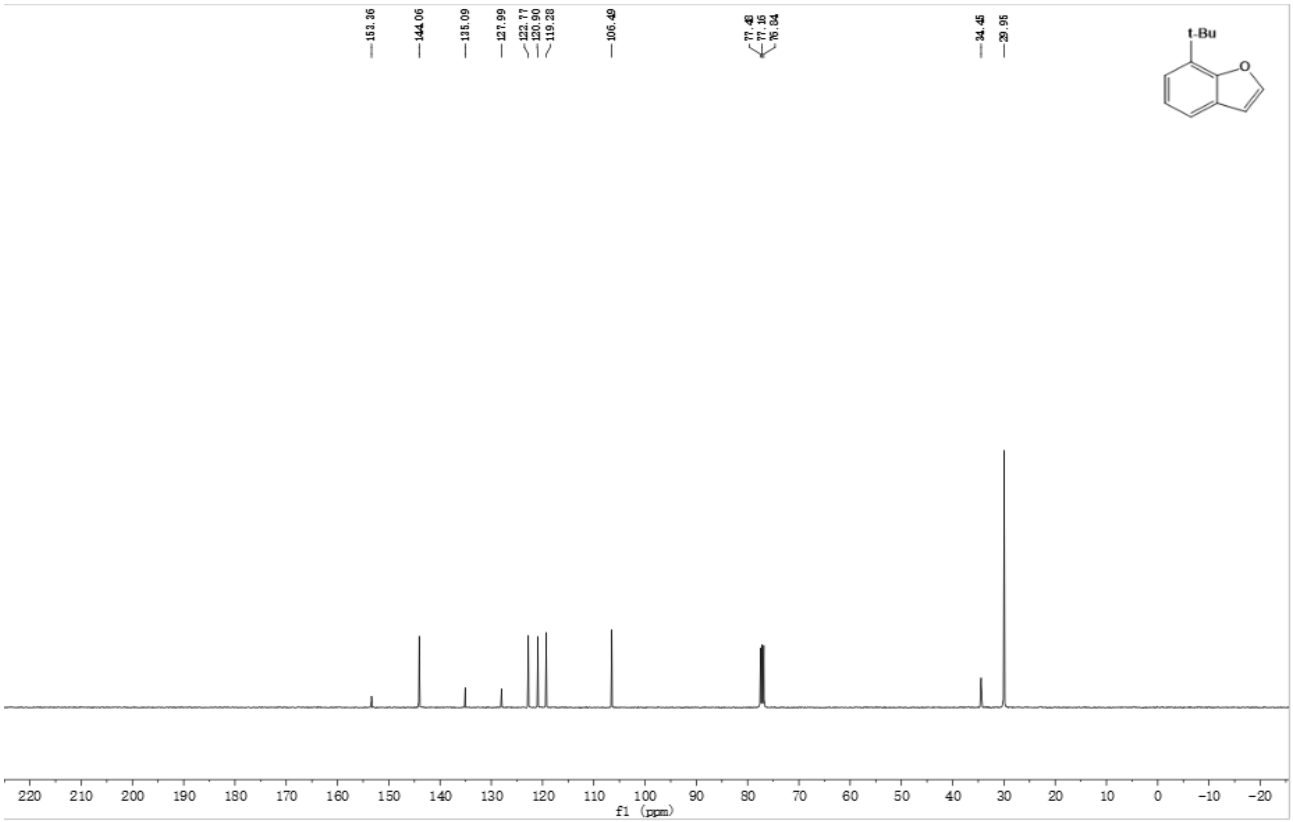
^{13}C NMR spectrum for 2e



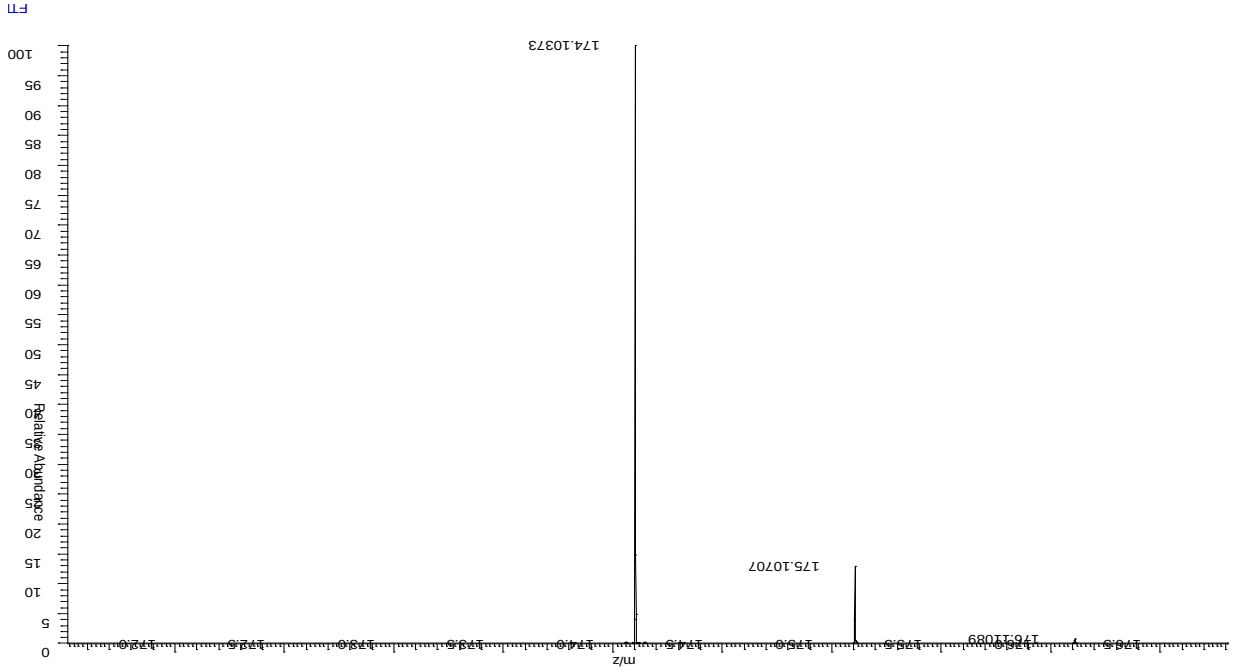
^{1}H NMR spectrum for 2f



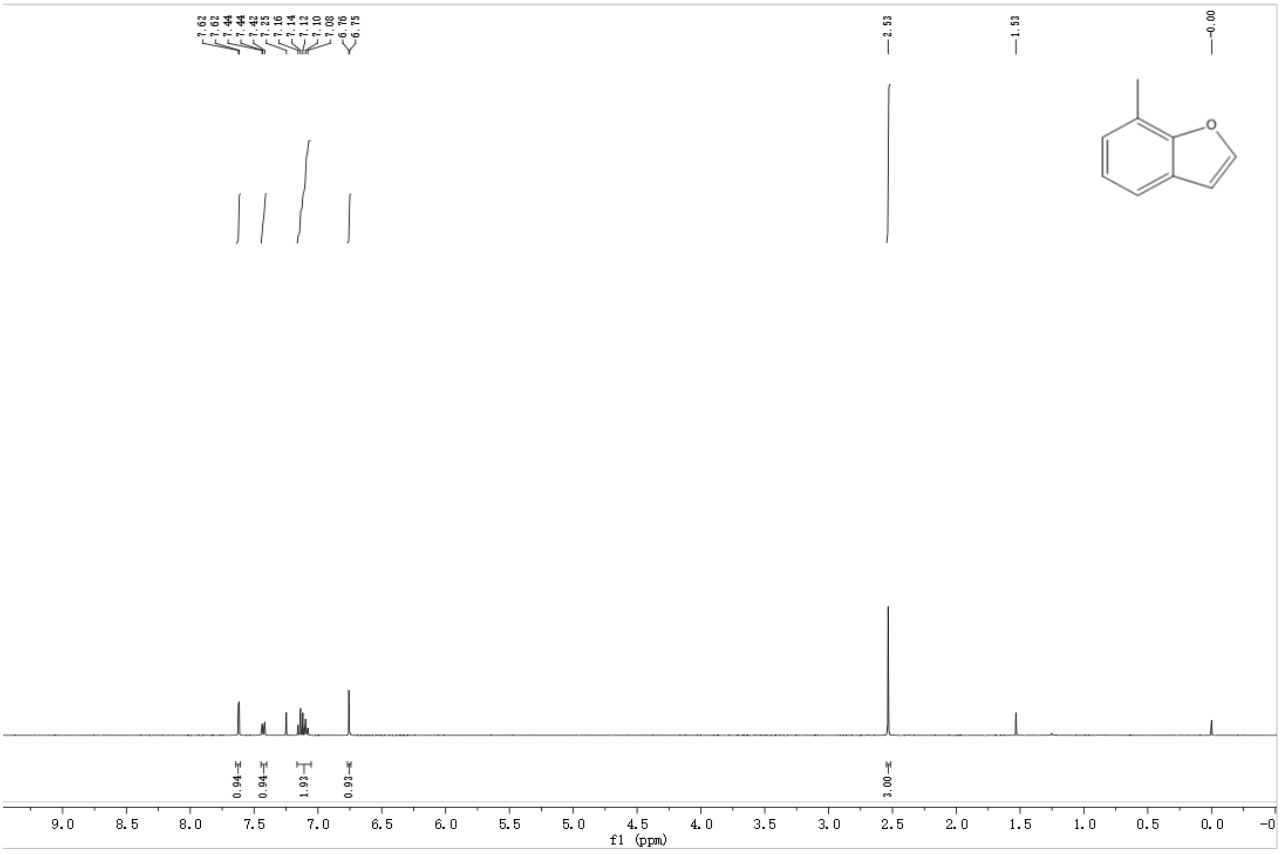
^{13}C NMR spectrum for 2f



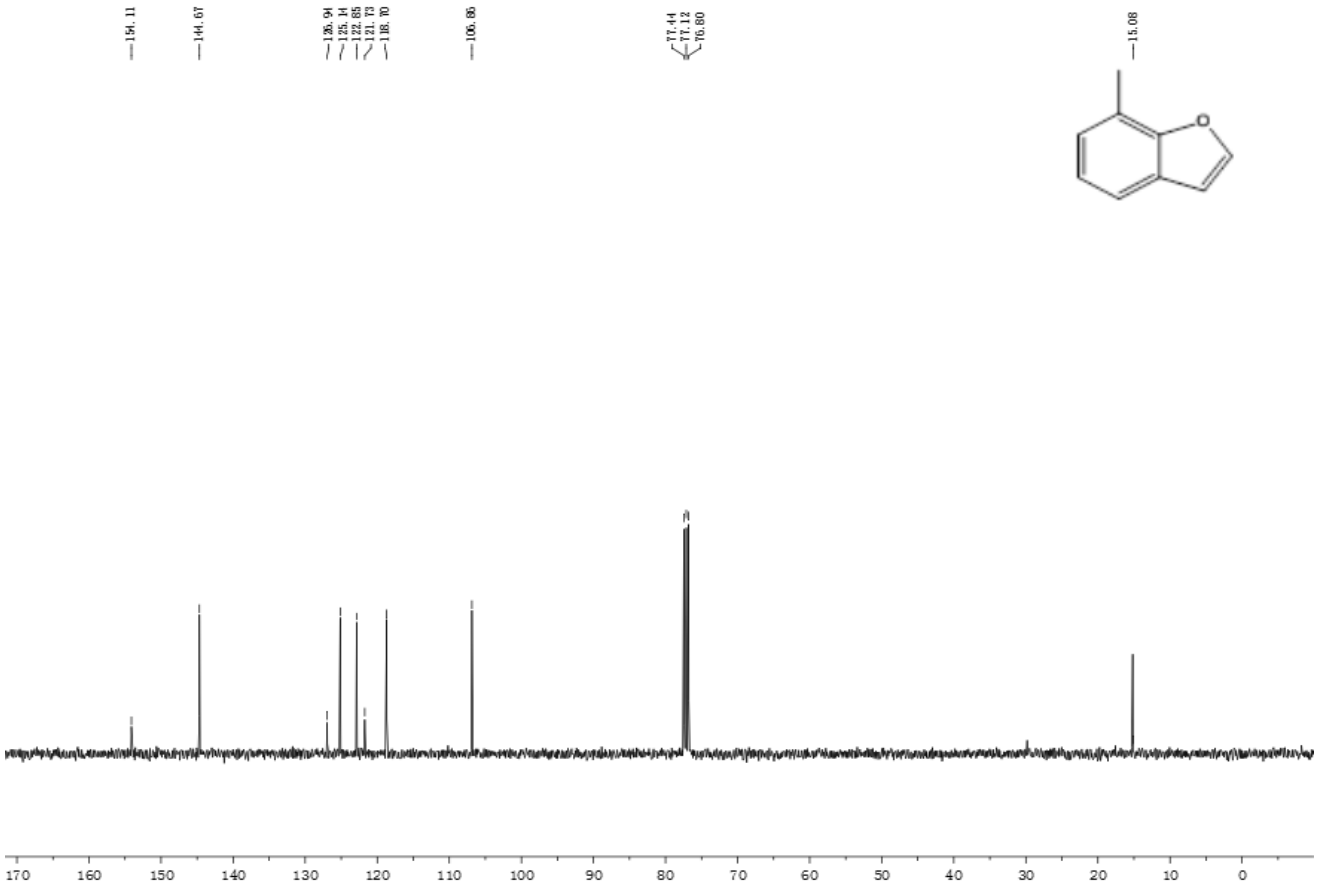
HRMS (EI) spectrum for 2f



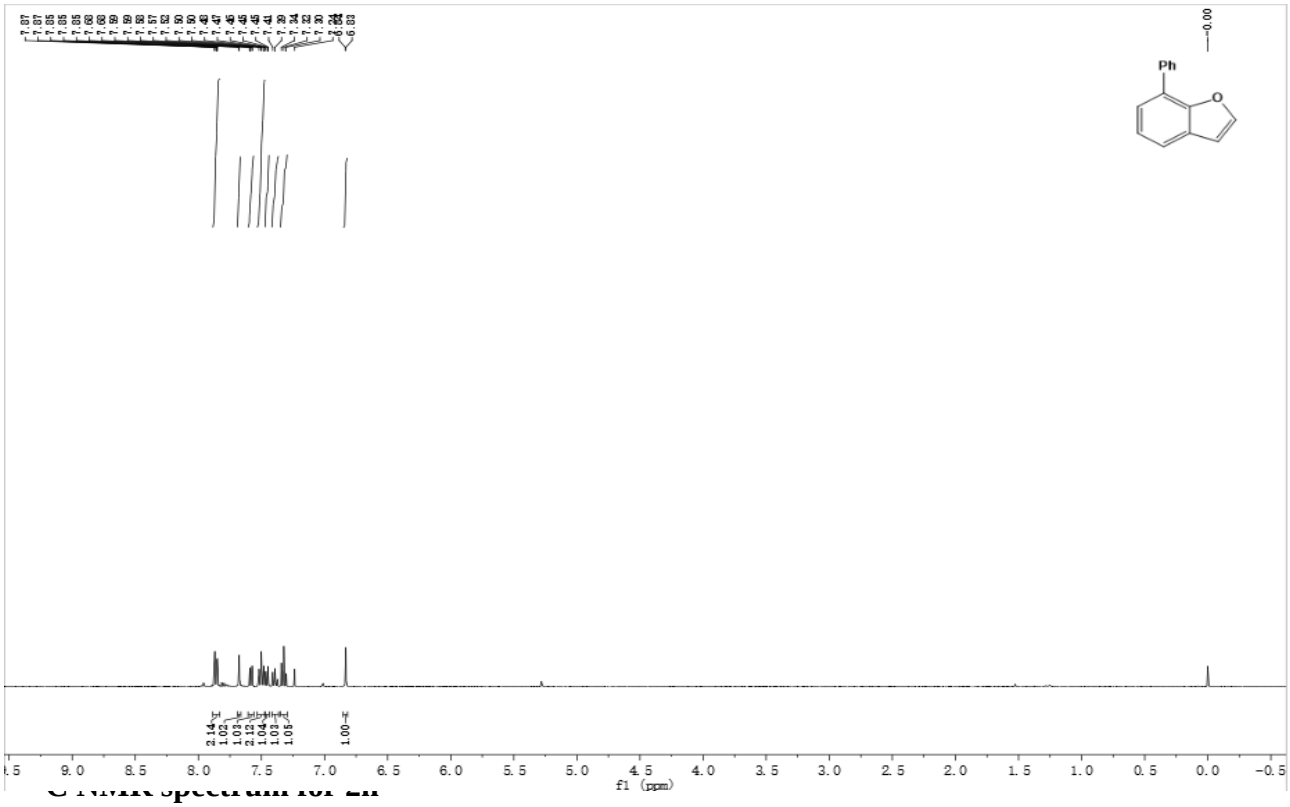
^{1}H NMR spectrum for 2g



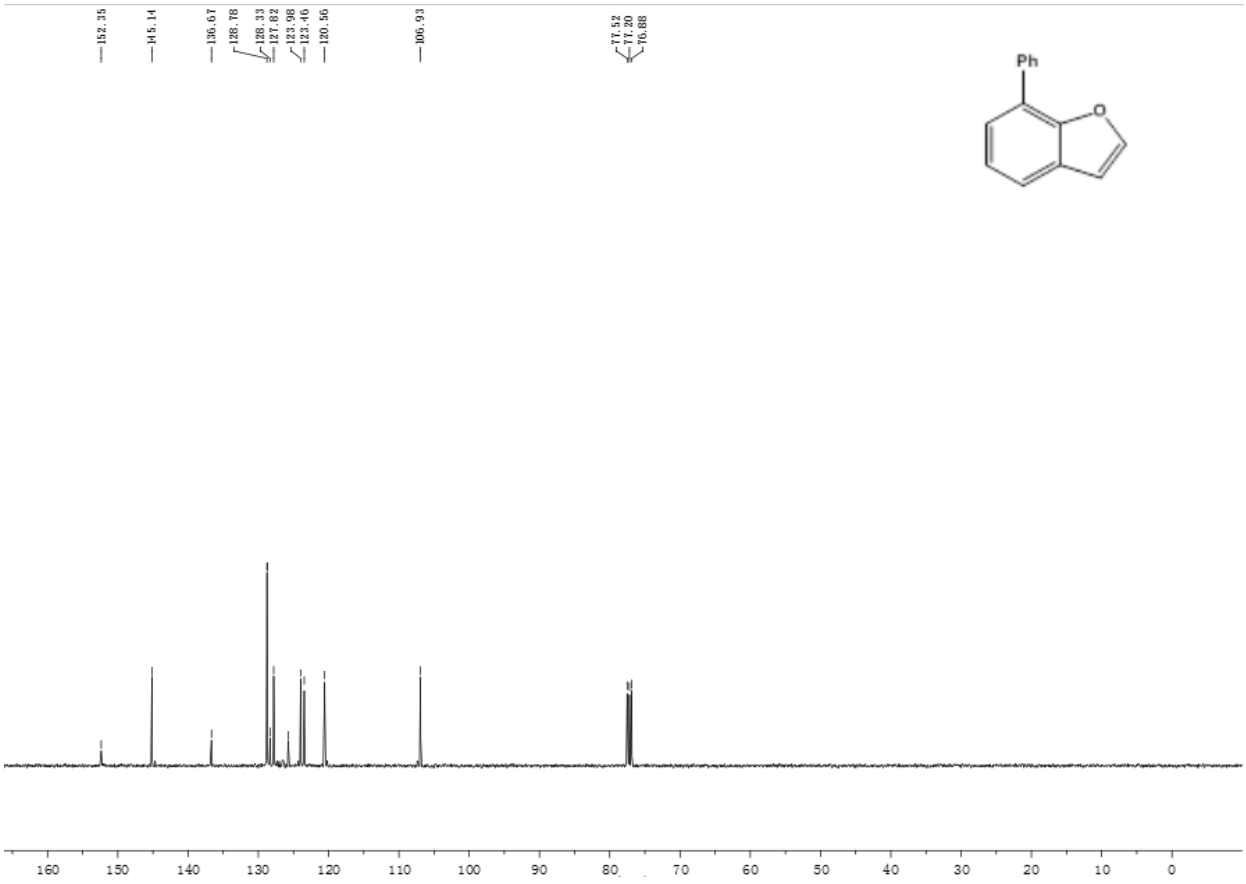
^{13}C NMR spectrum for 2g



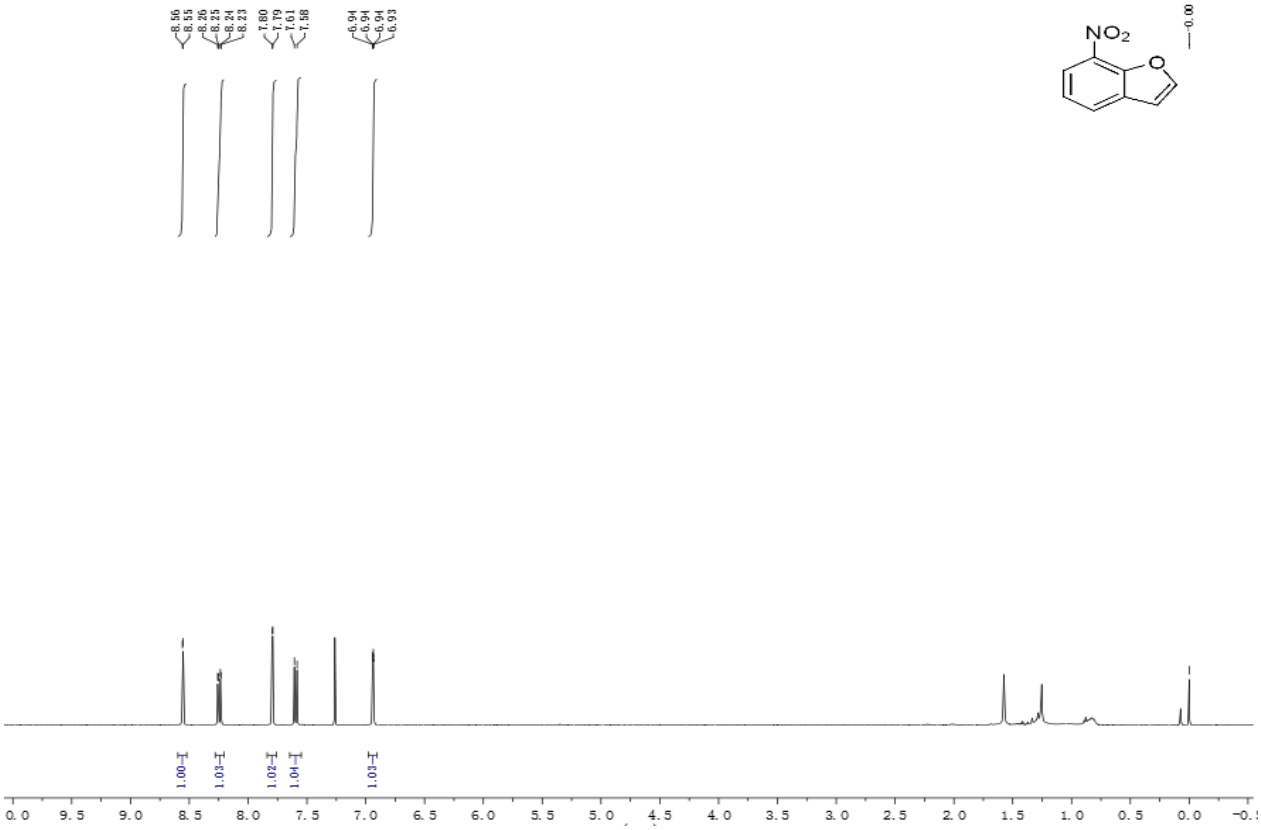
^{1}H NMR spectrum for 2h



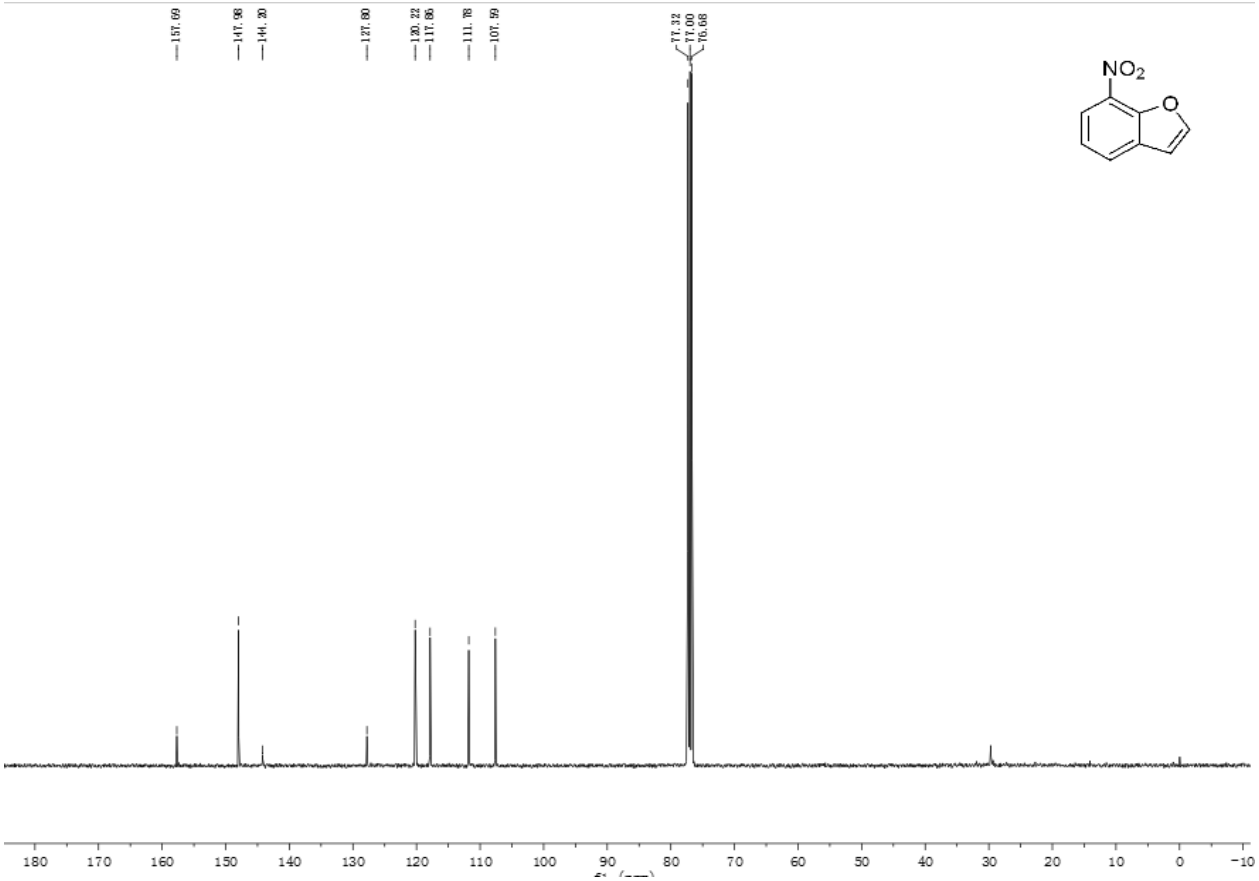
C NMR spectrum for 2h



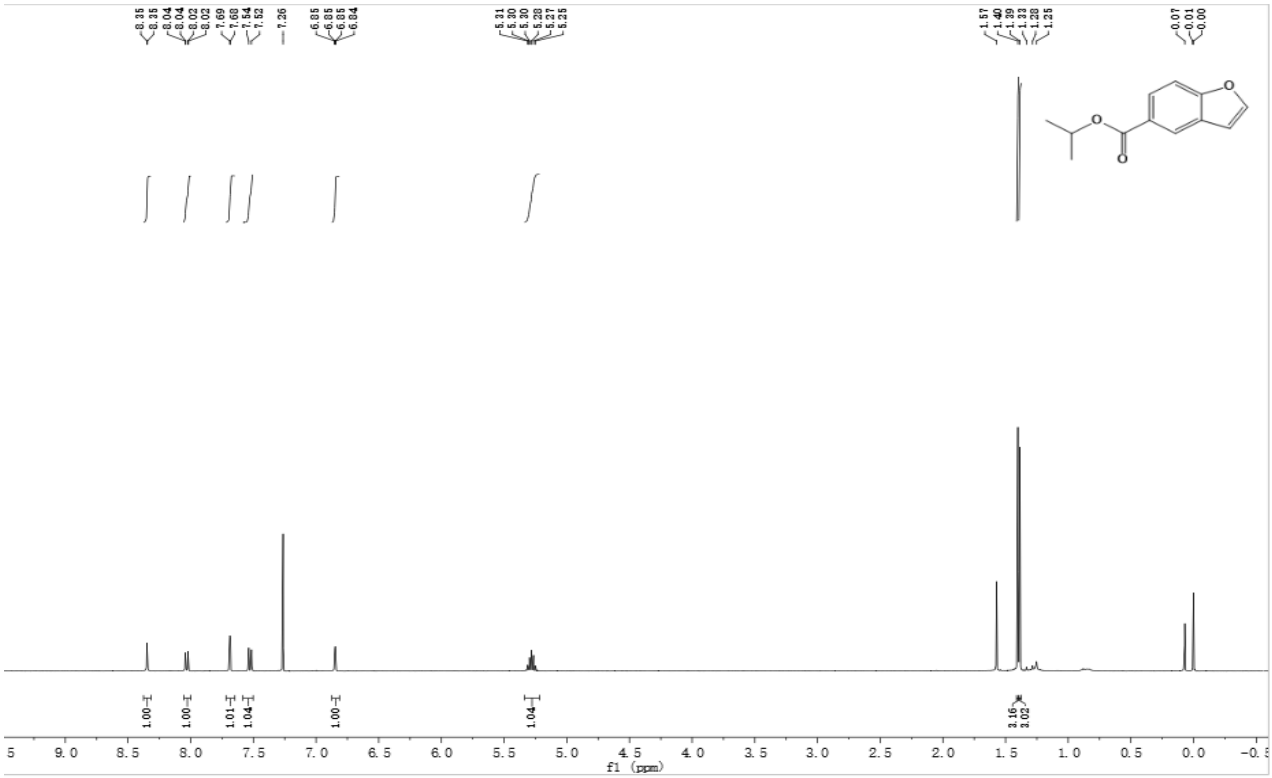
^{1}H NMR spectrum for 2i



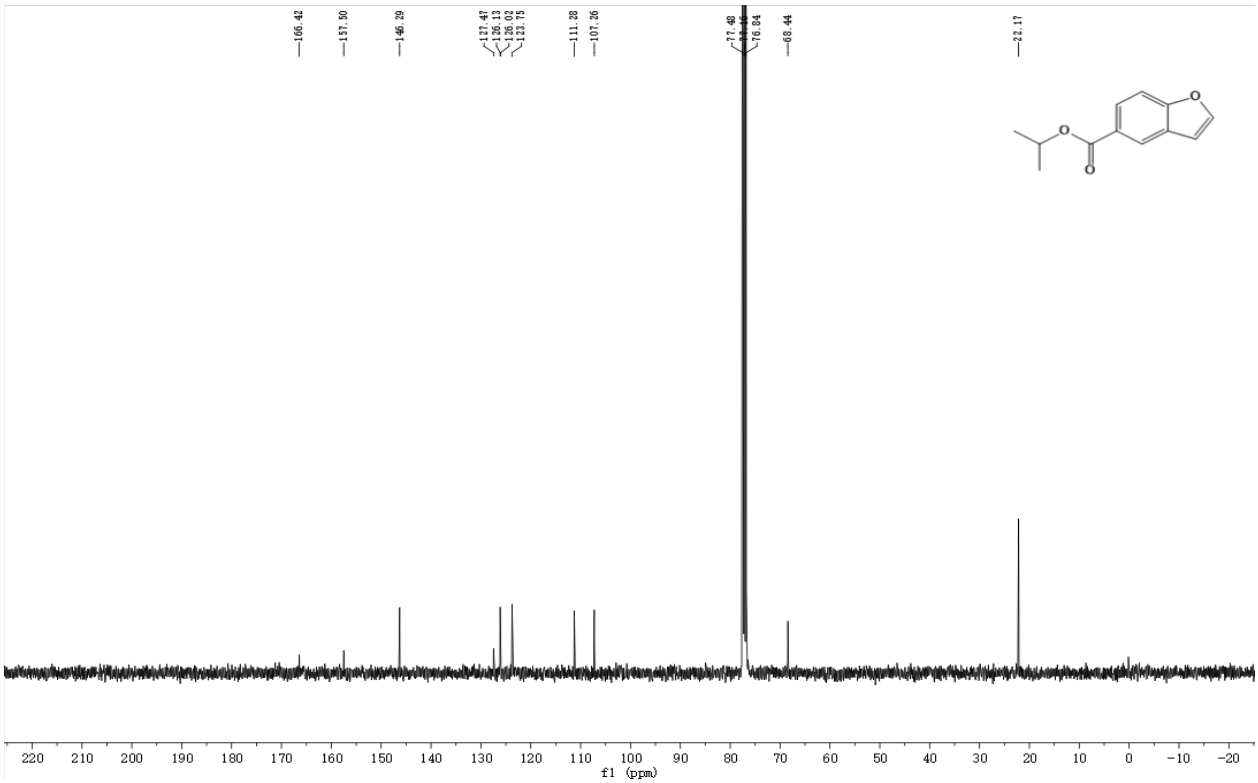
^{13}C NMR spectrum for 2i



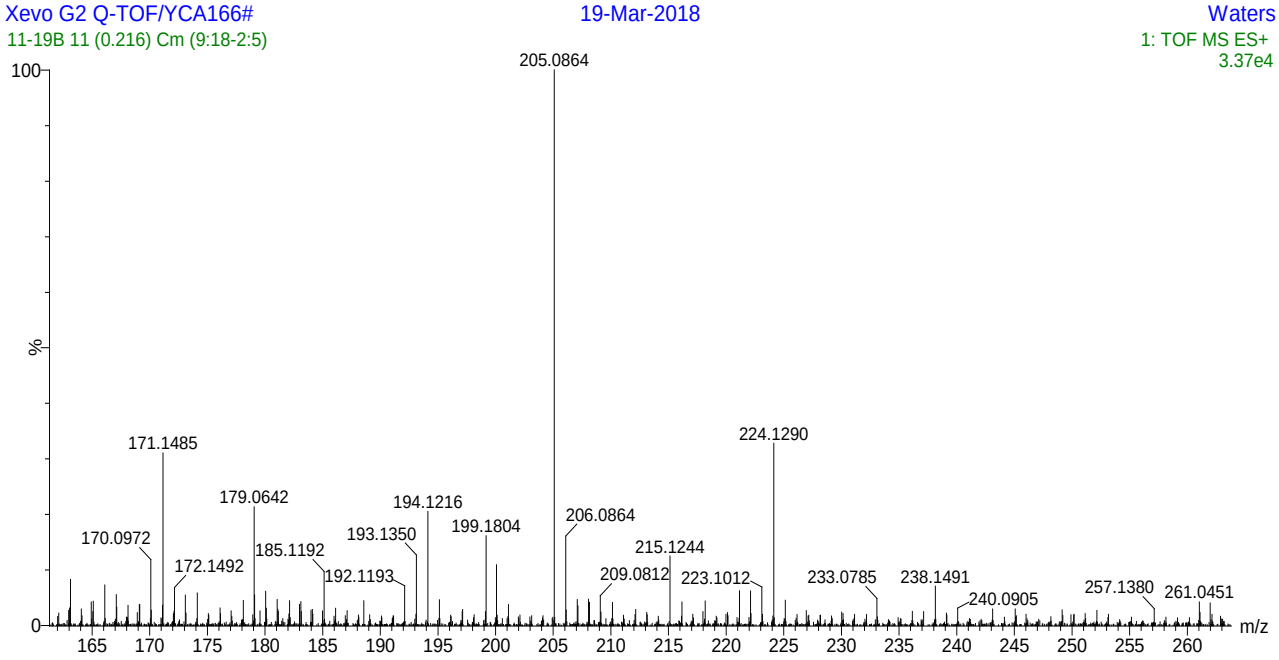
^{1}H NMR spectrum for 2j



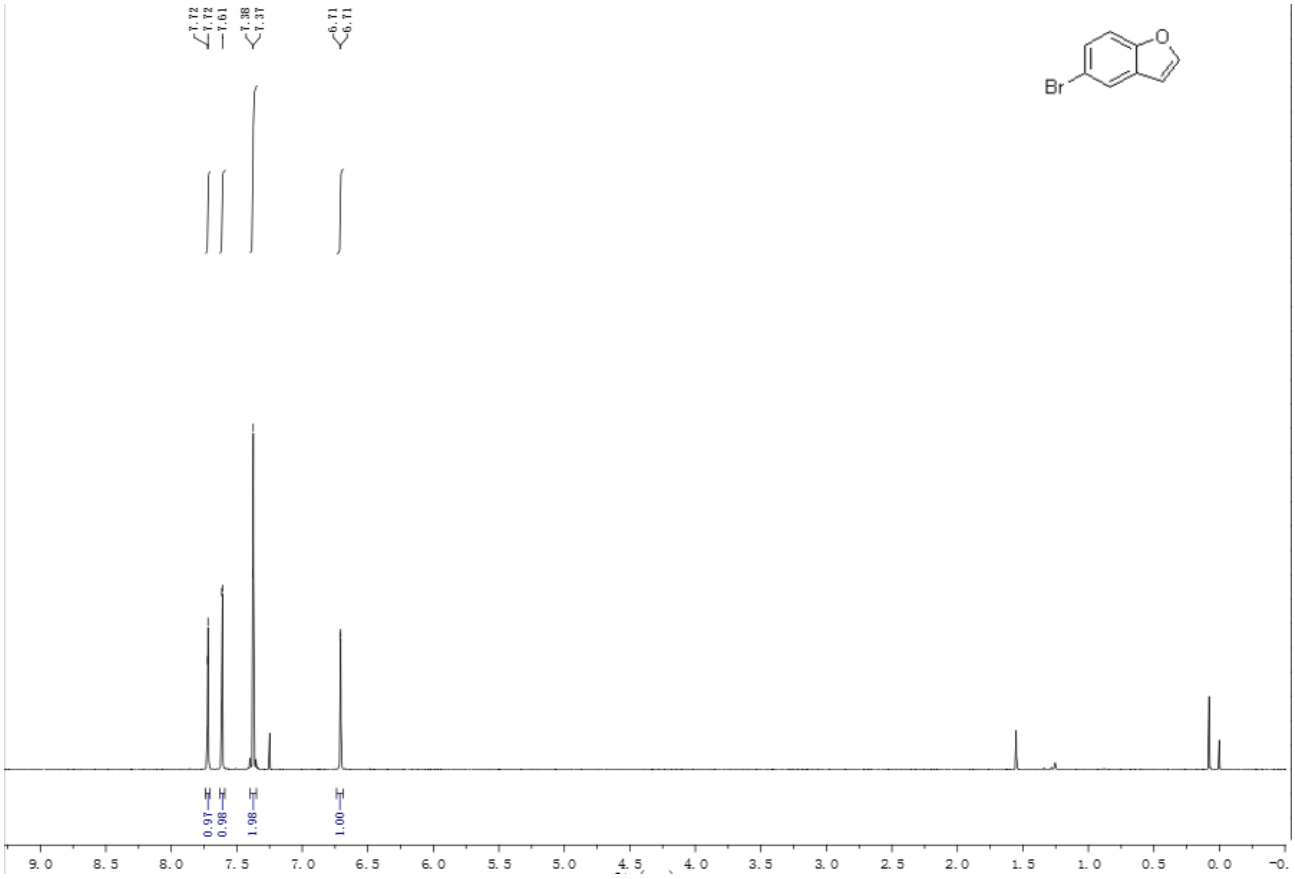
^{13}C NMR spectrum for 2j



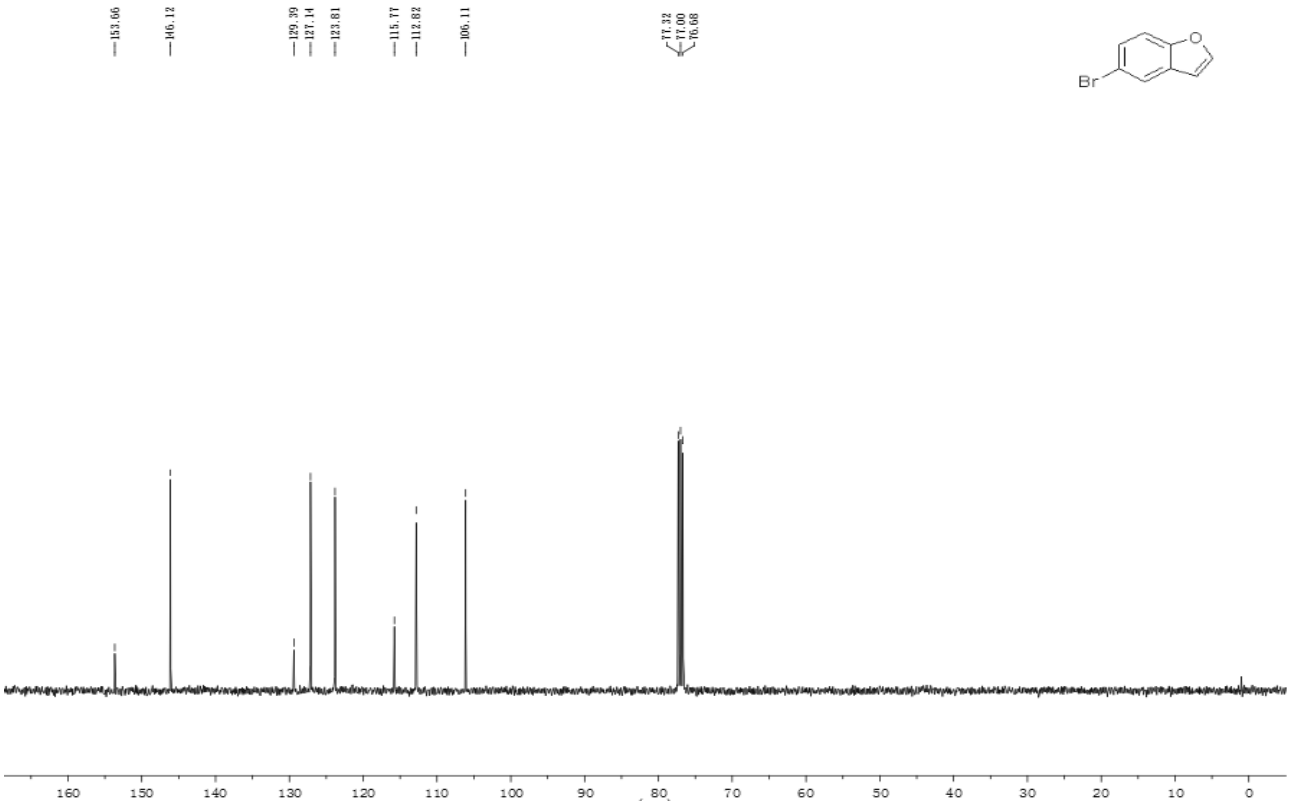
HRMS (ESI) spectrum for 2j



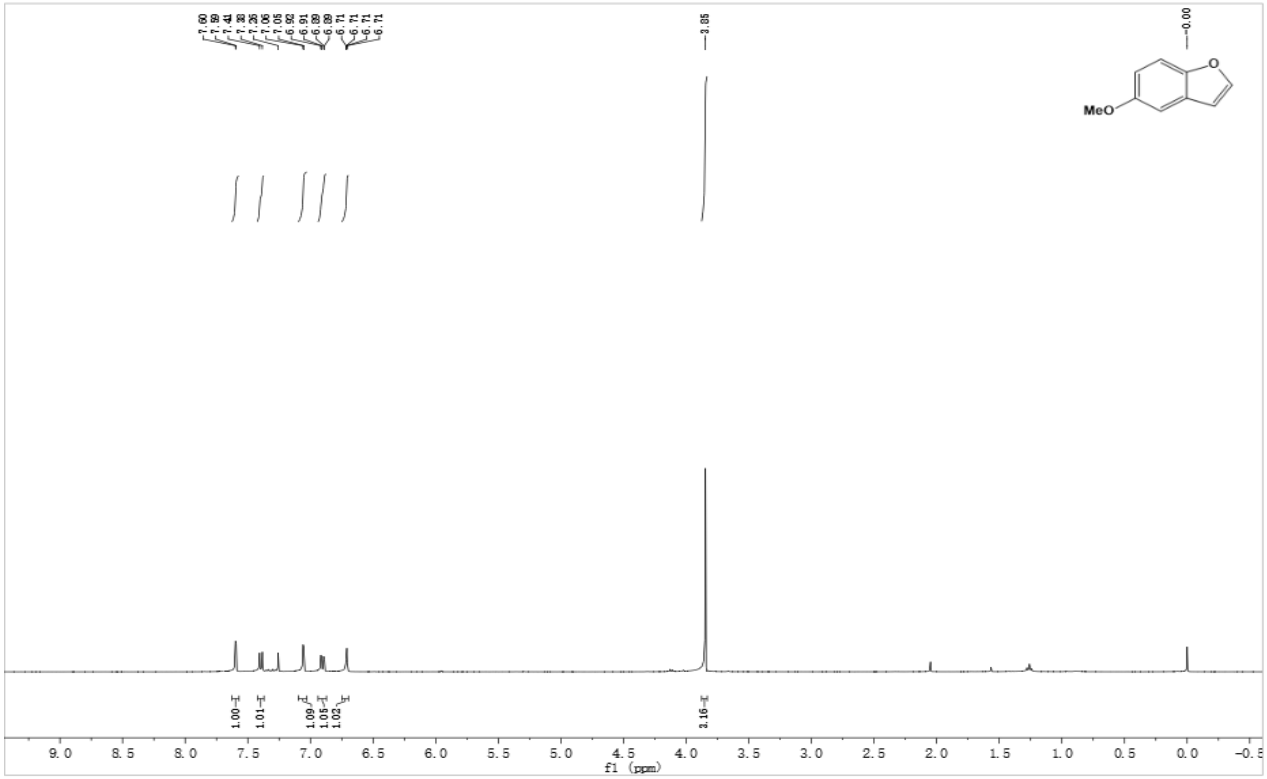
^{1}H NMR spectrum for 2k



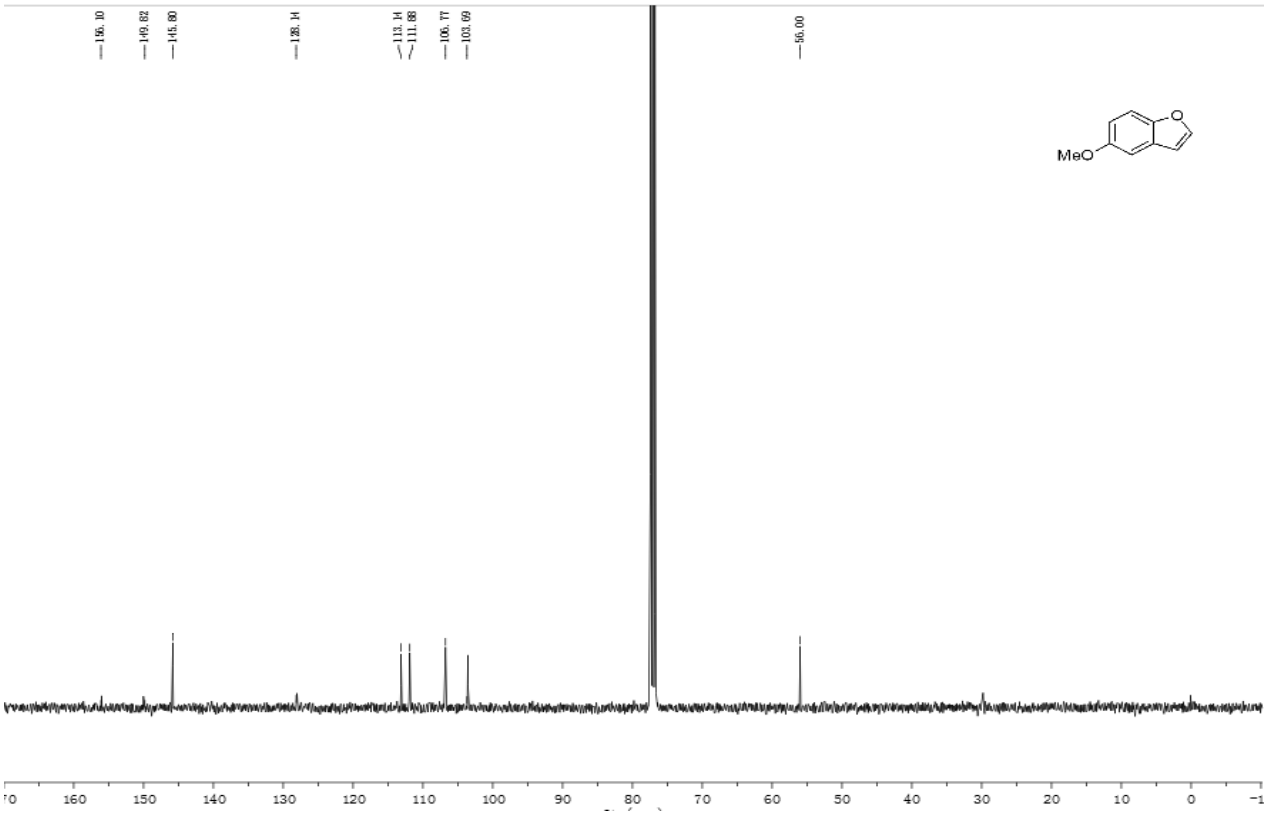
^{13}C NMR spectrum for 2k



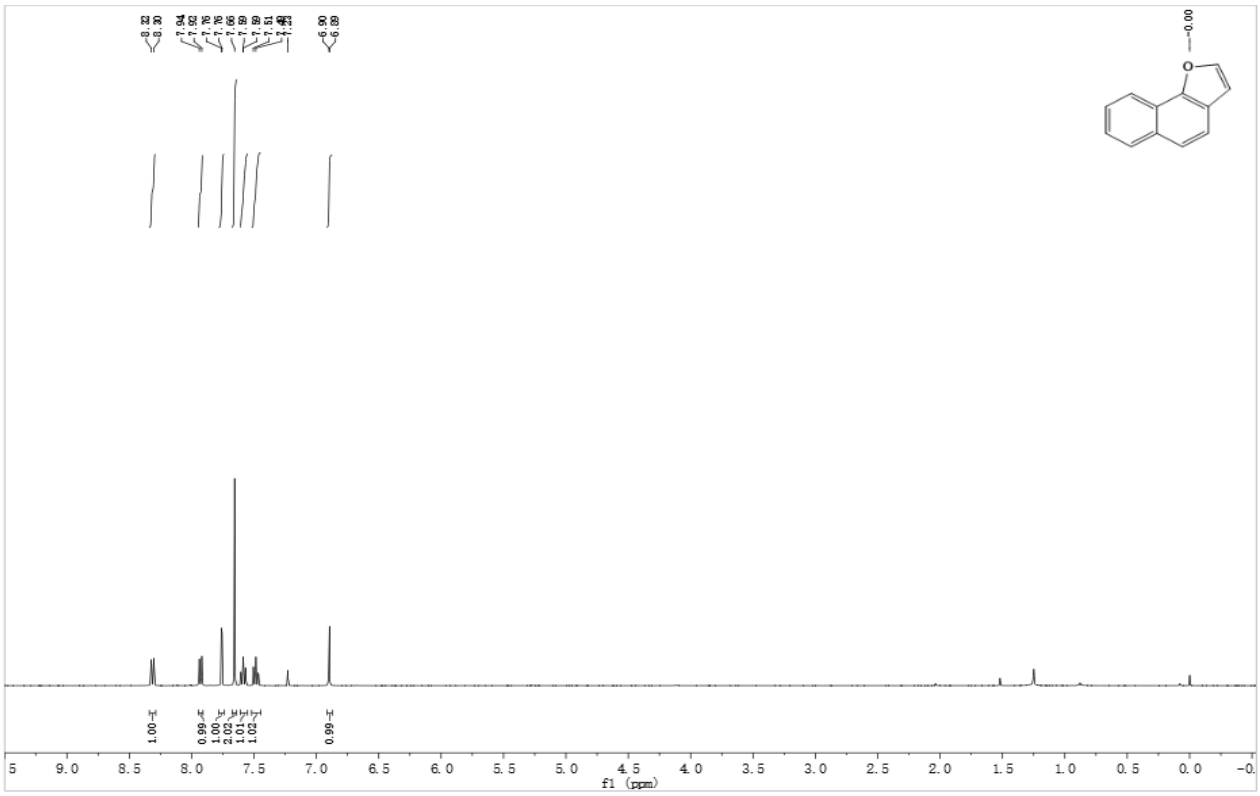
^{1}H NMR spectrum for 2l



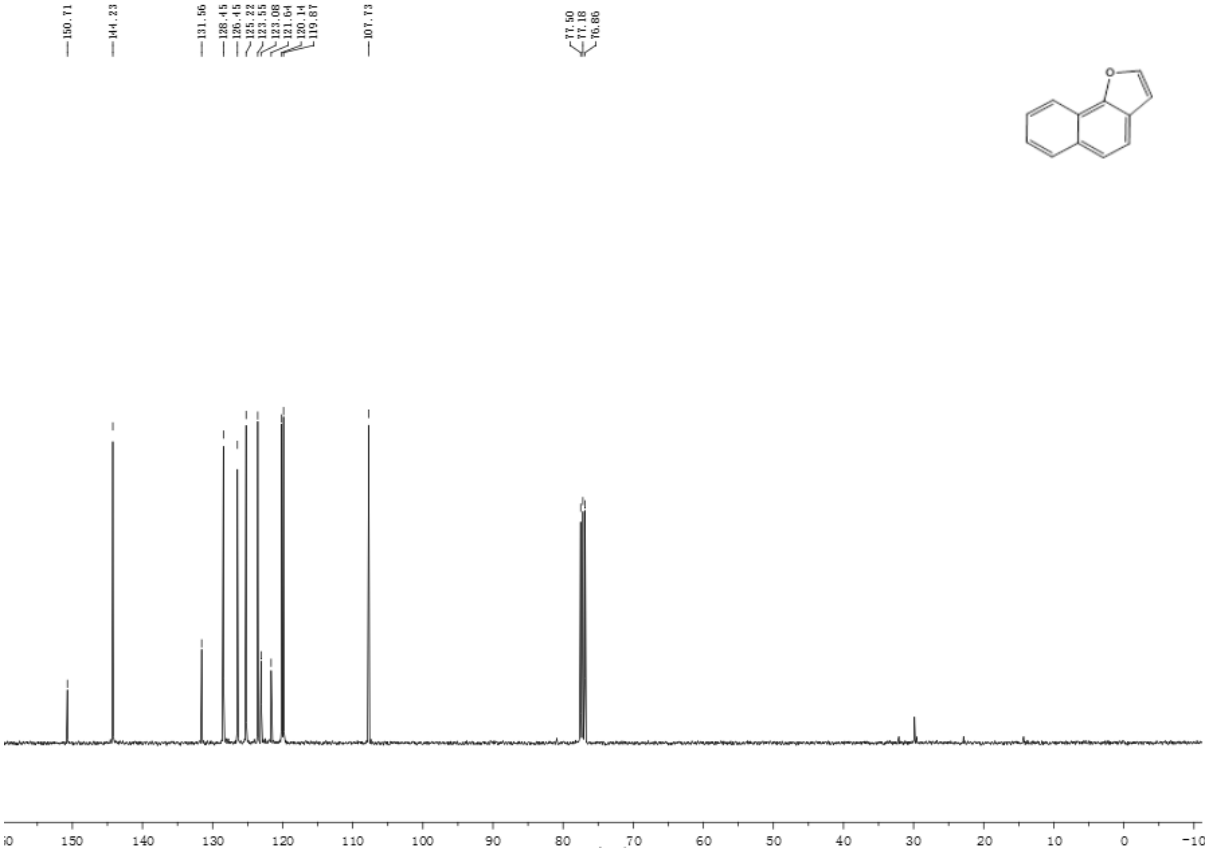
^{13}C NMR spectrum for 2l



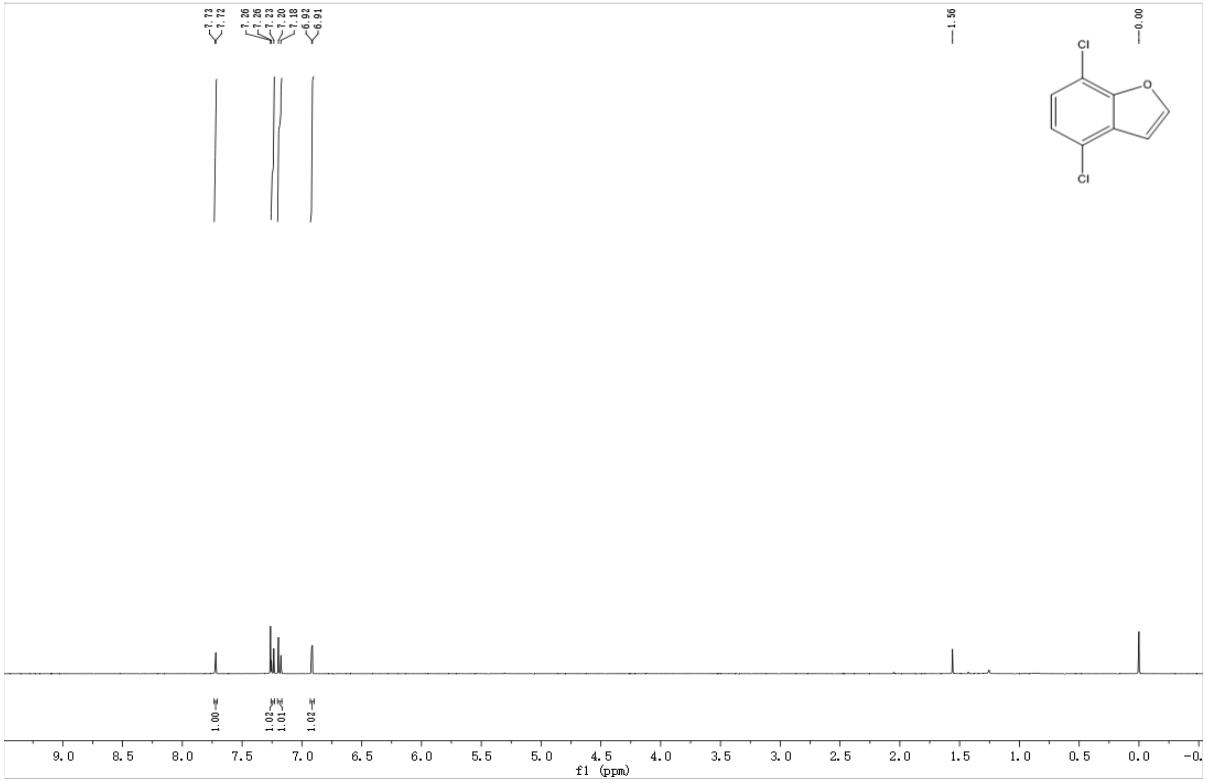
^{1}H NMR spectrum for 2m



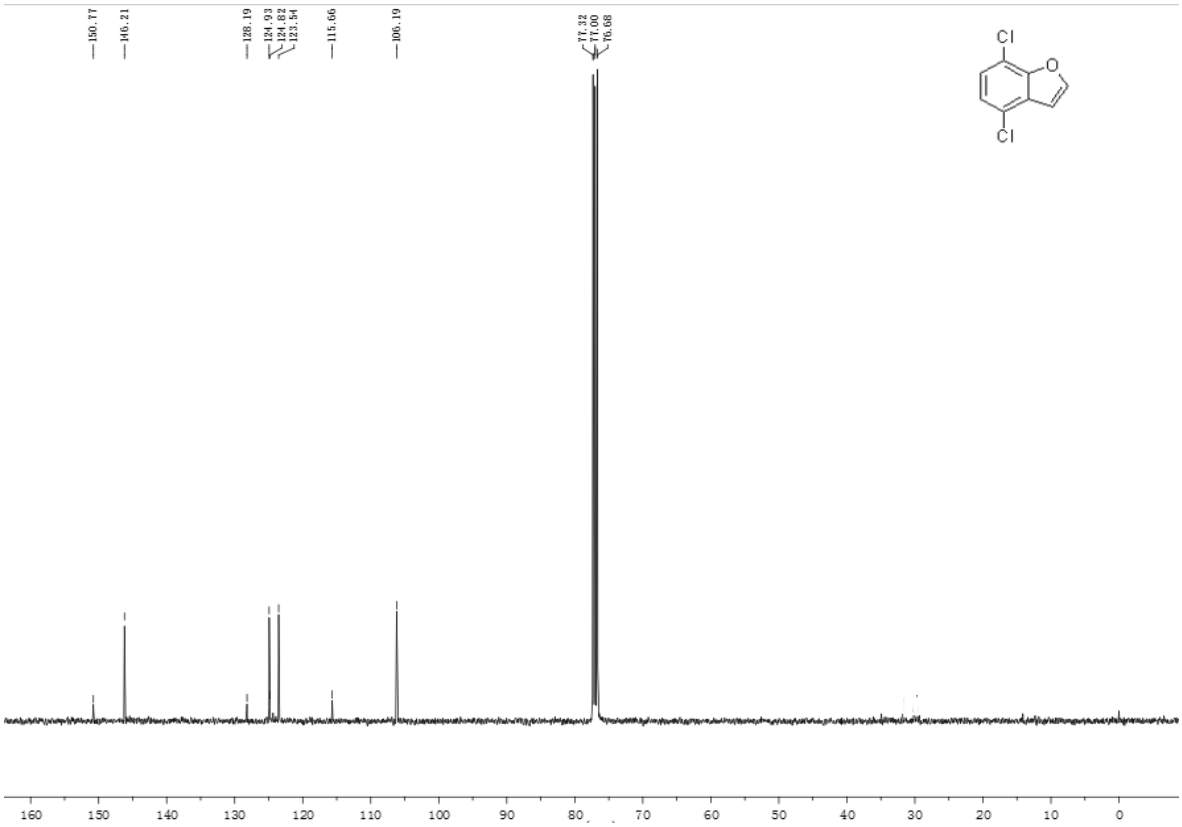
^{13}C NMR spectrum for 2m



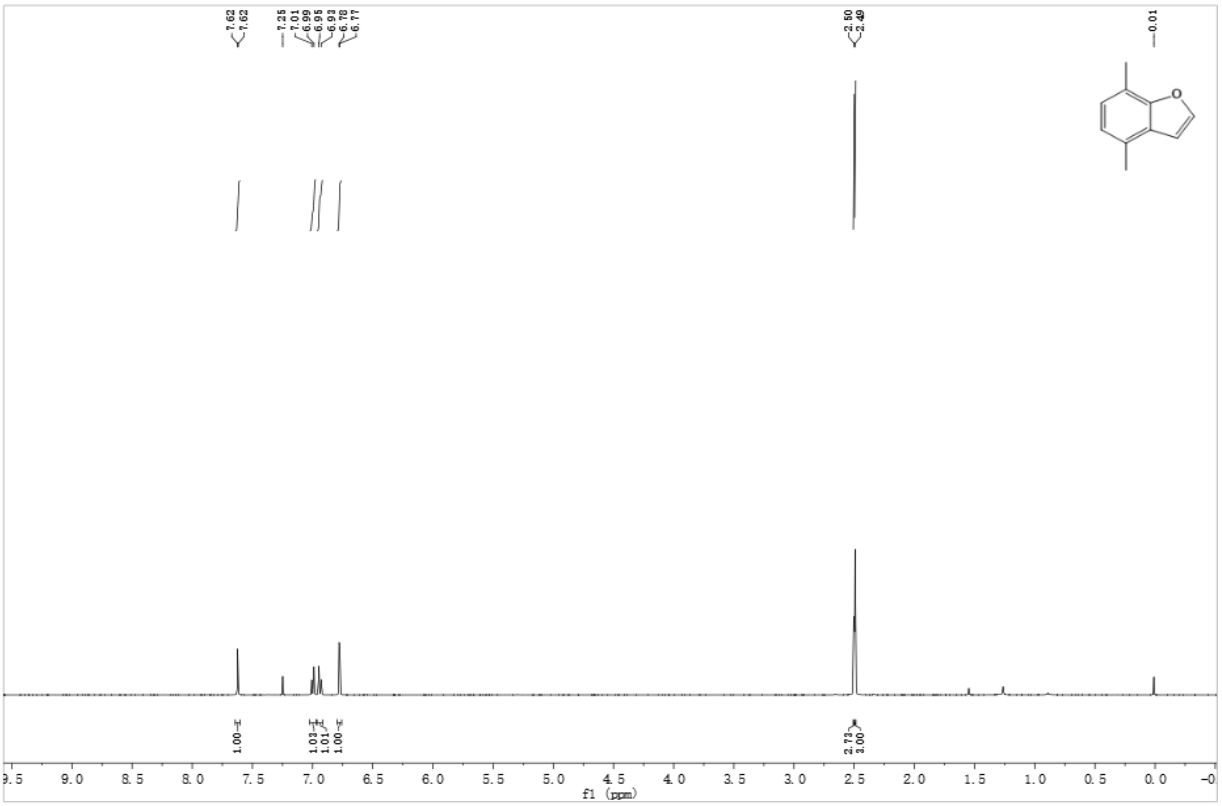
^{1}H NMR spectrum for 2n



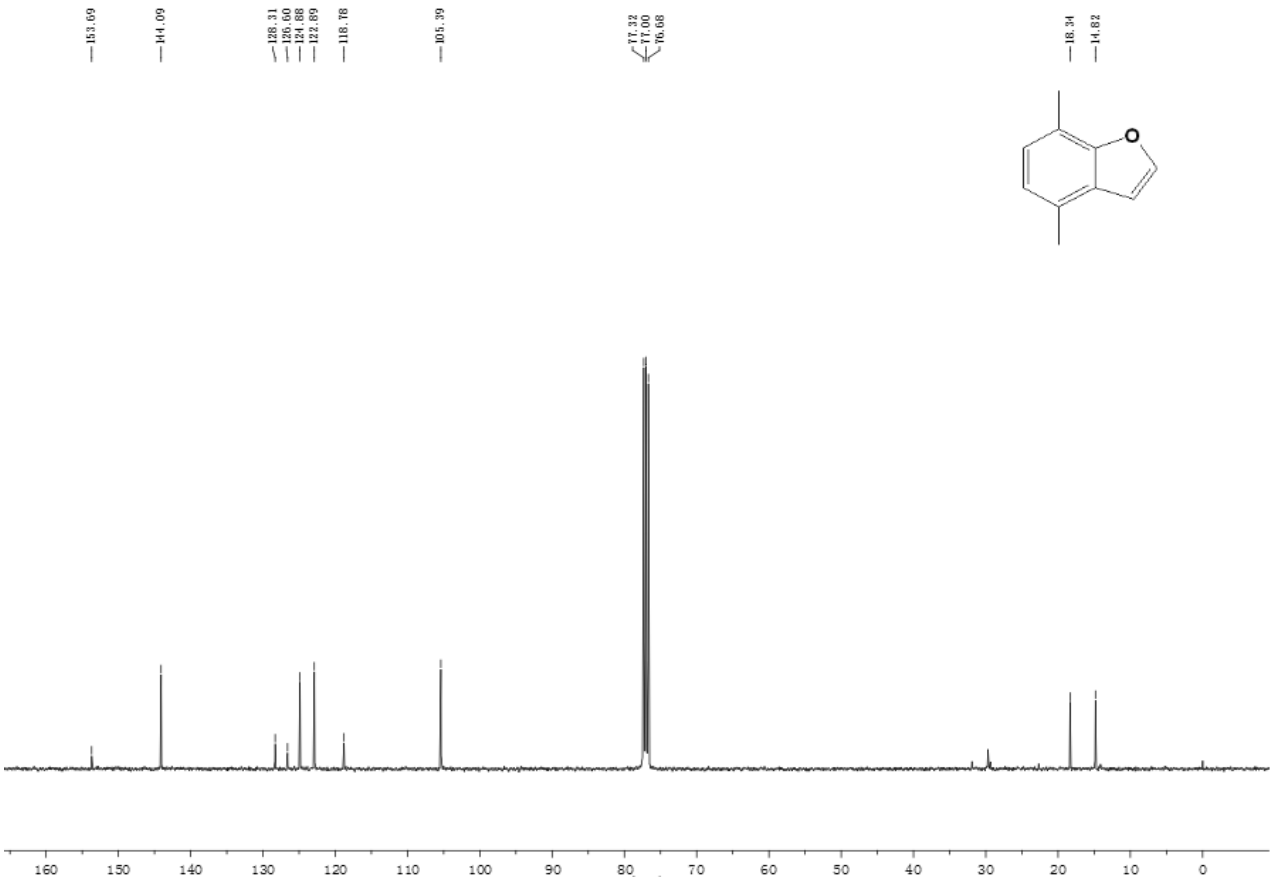
^{13}C NMR spectrum for 2n



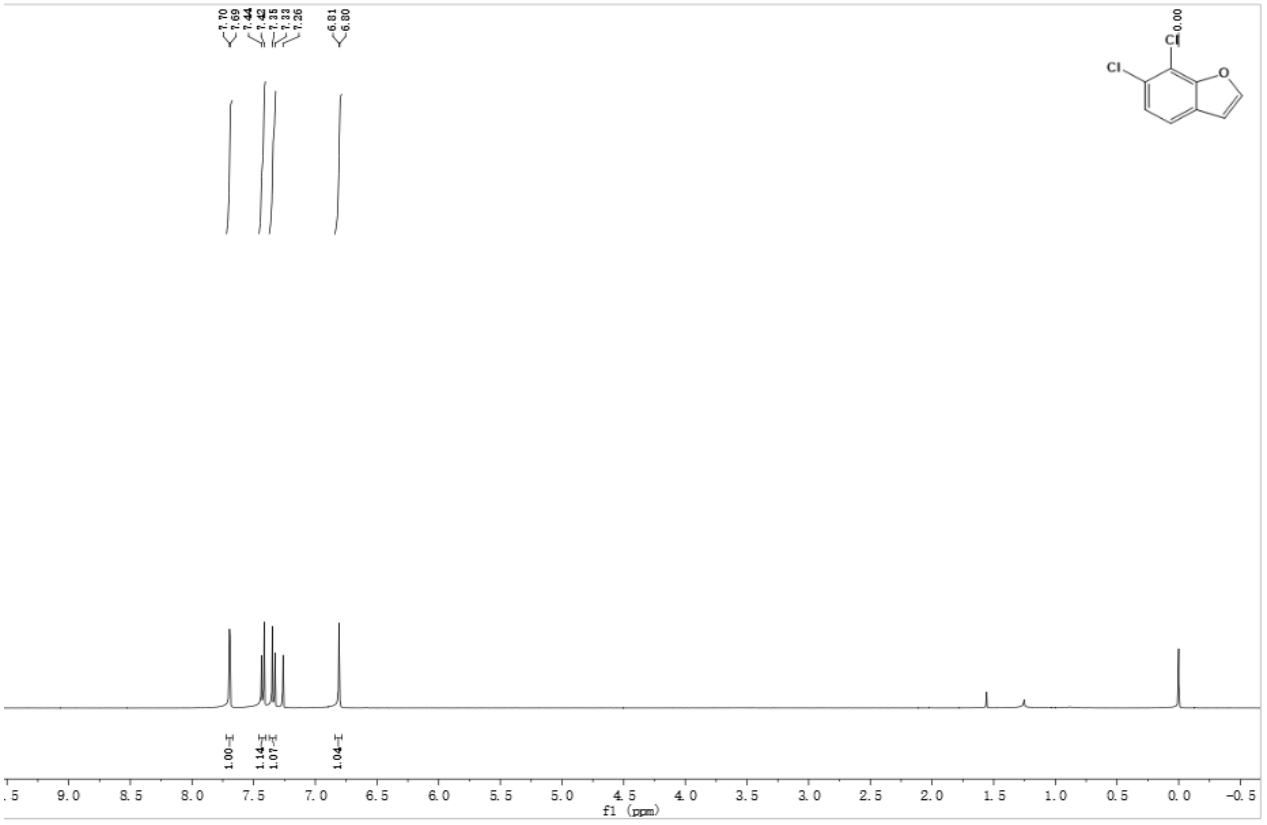
^{1}H NMR spectrum for 2o

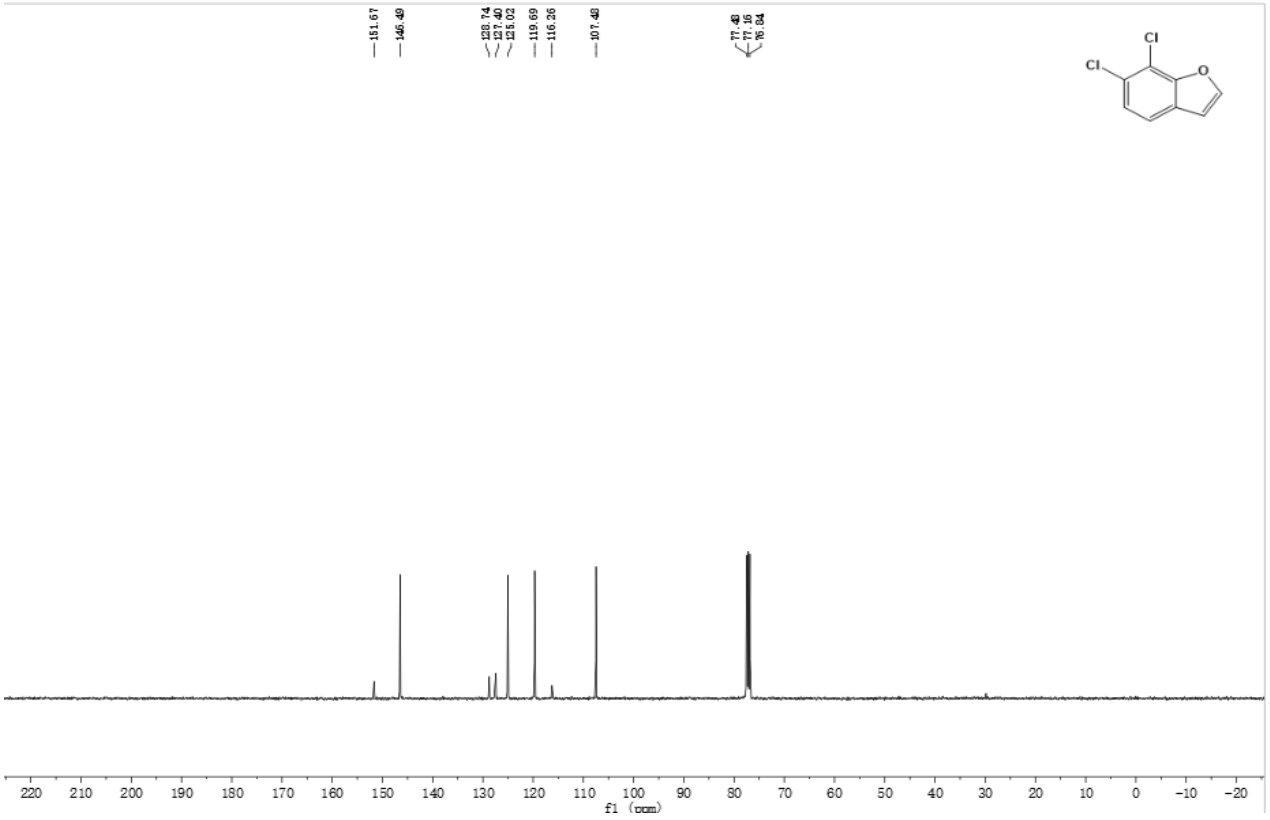


^{13}C NMR spectrum for 2o



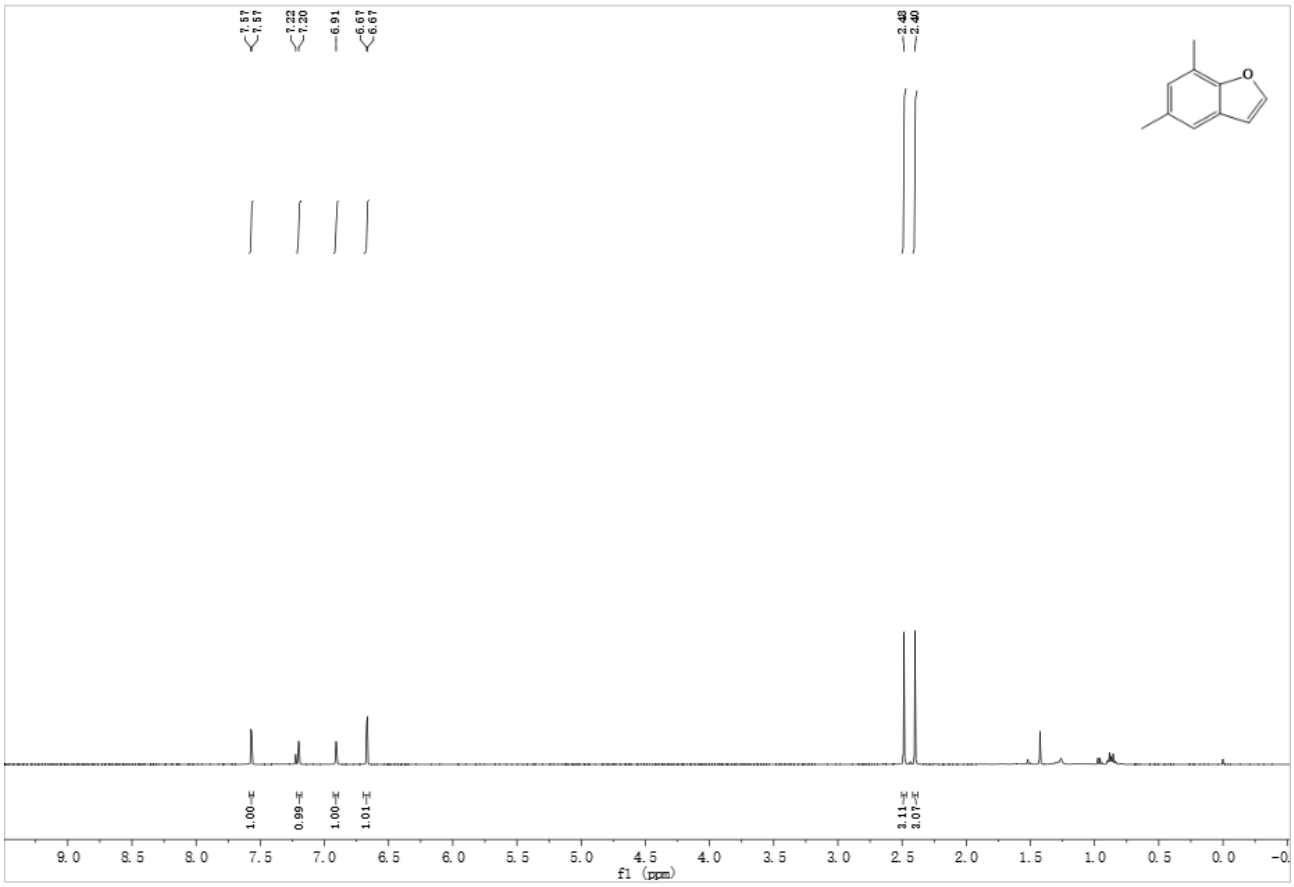
^{1}H NMR spectrum for 2p



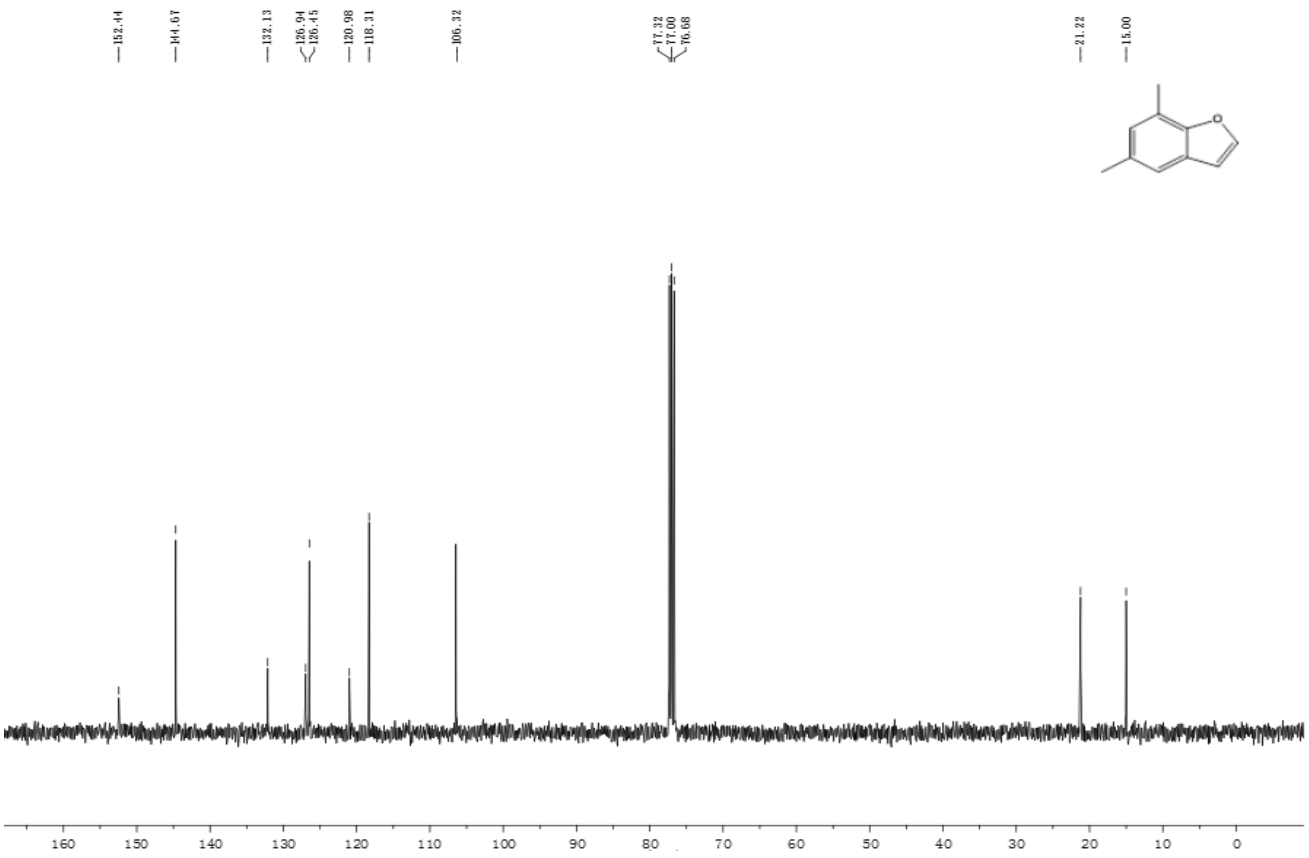


HRMS (EI) spectrum for 2p

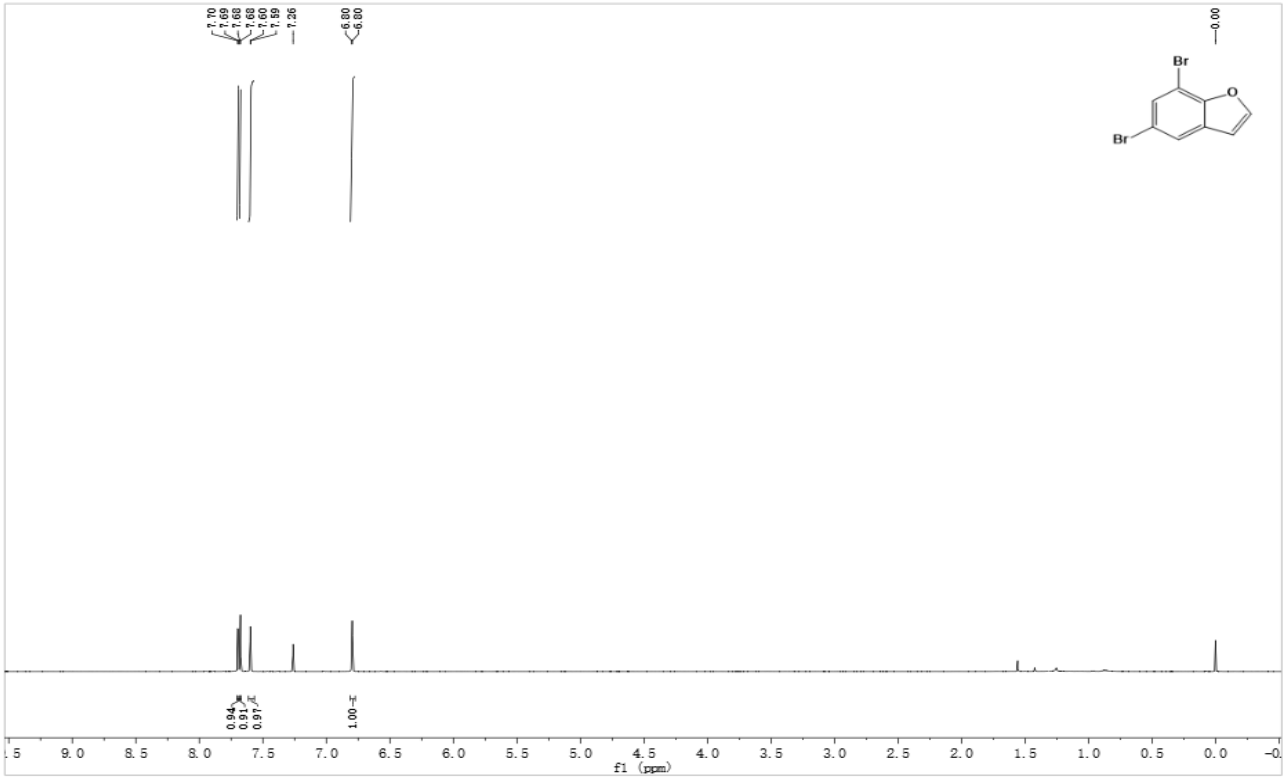
^{1}H NMR spectrum for 2q



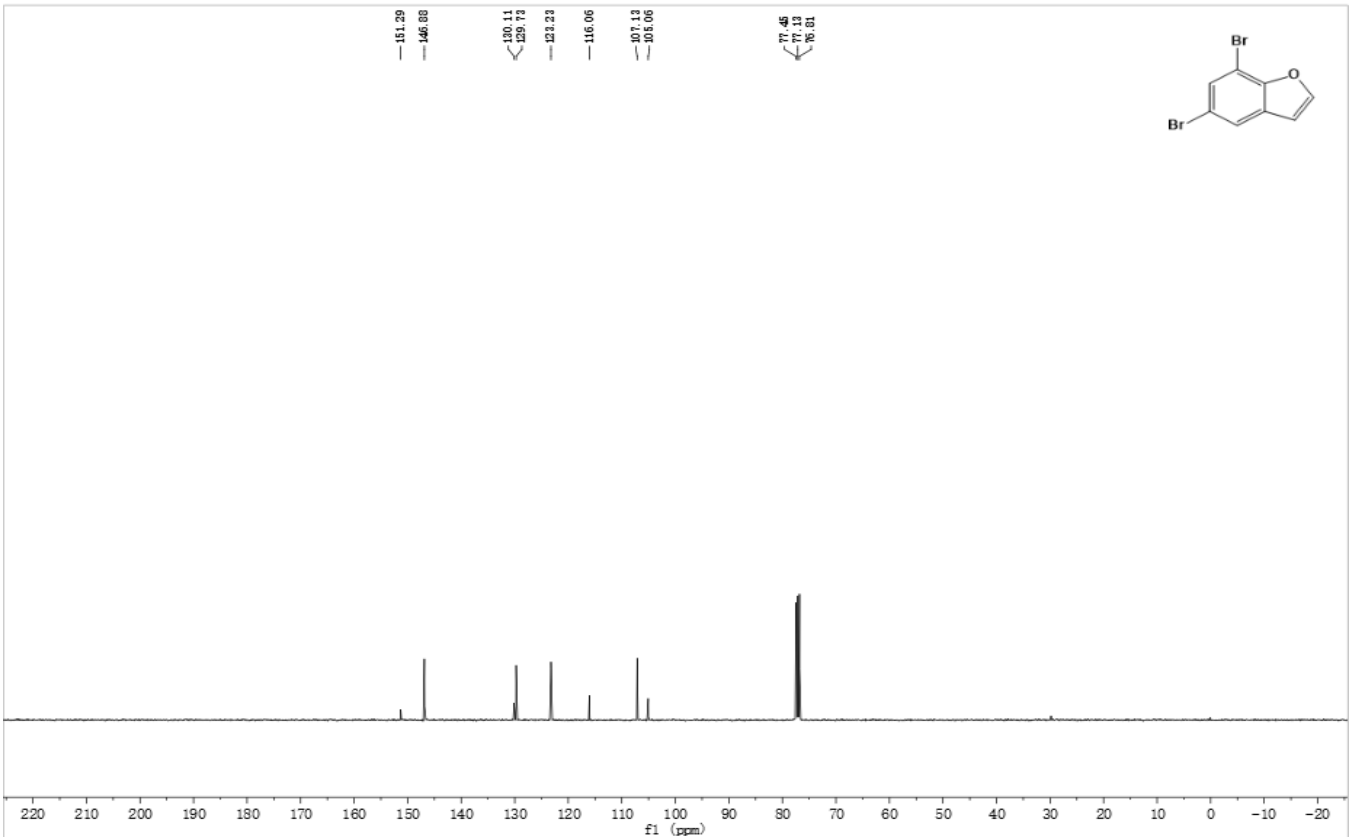
^{13}C NMR spectrum for 2q



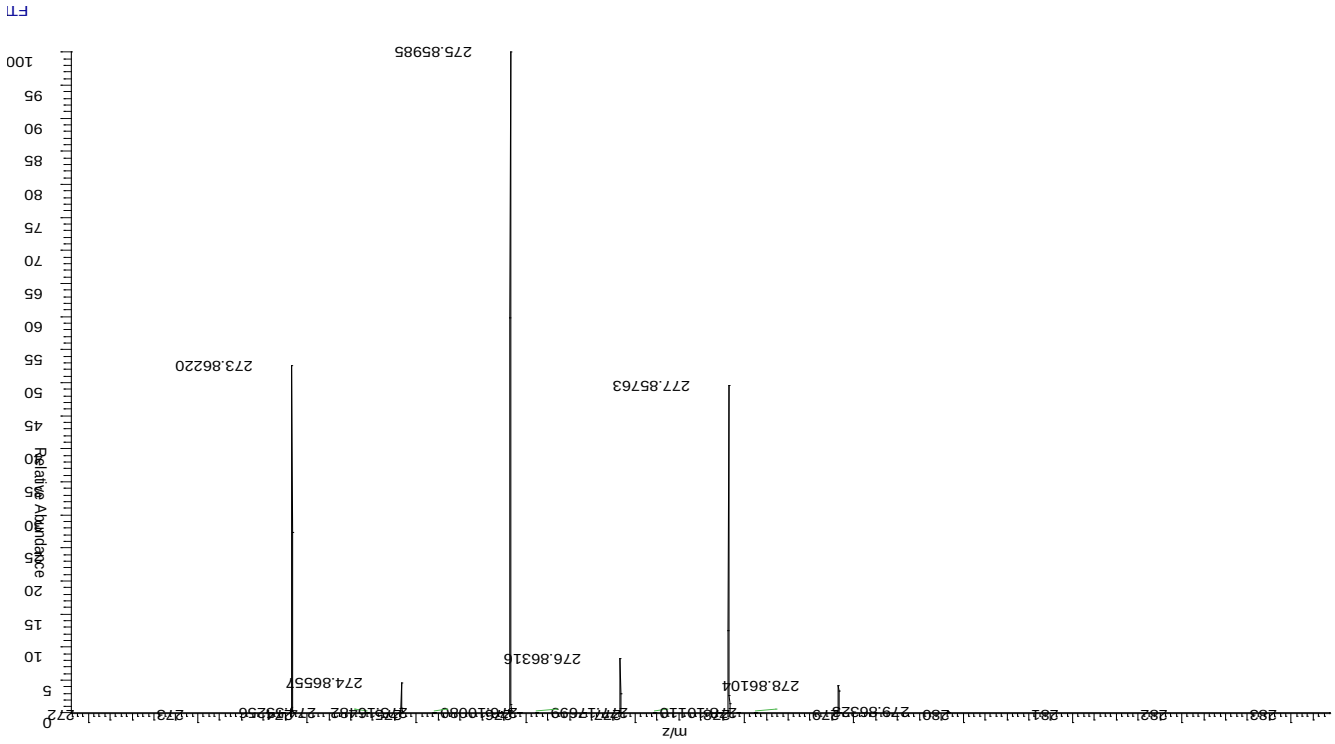
^{1}H NMR spectrum for 2r



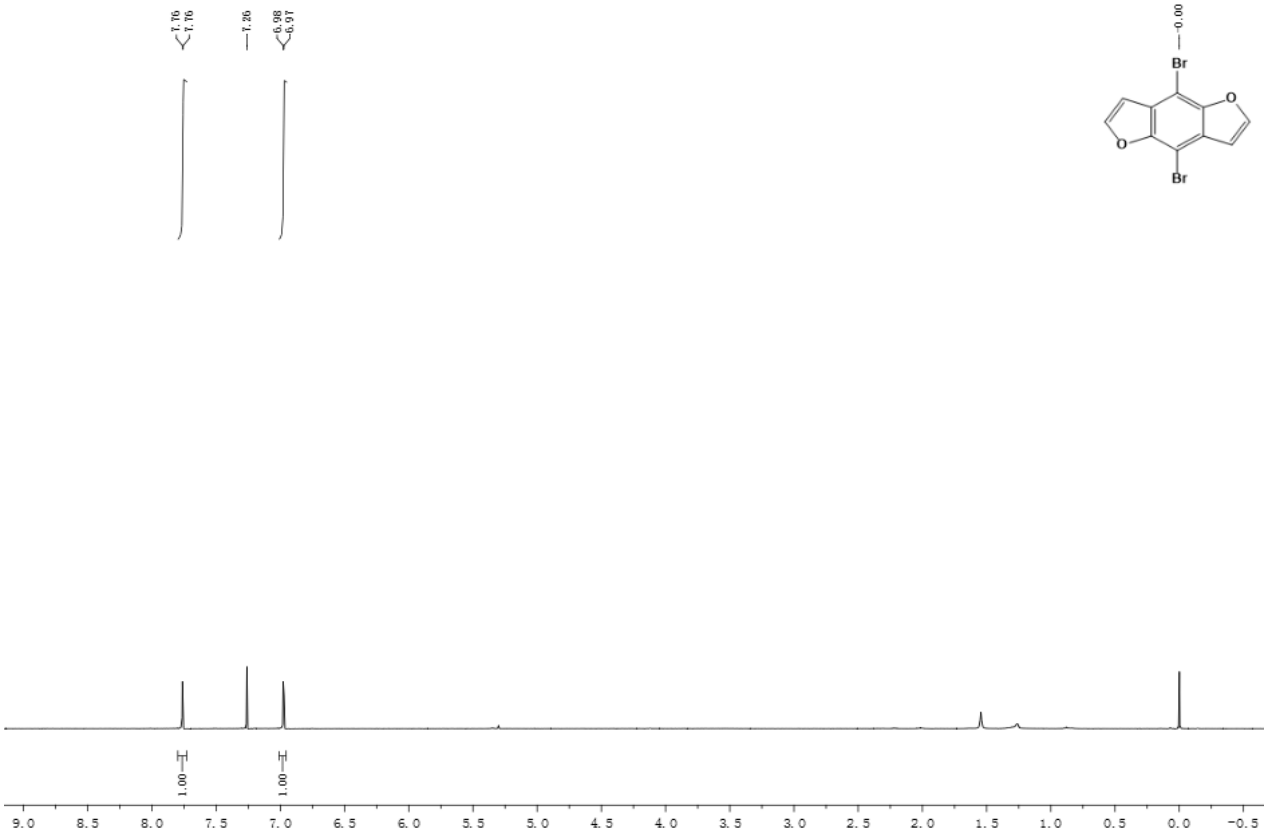
^{13}C NMR spectrum for 2r



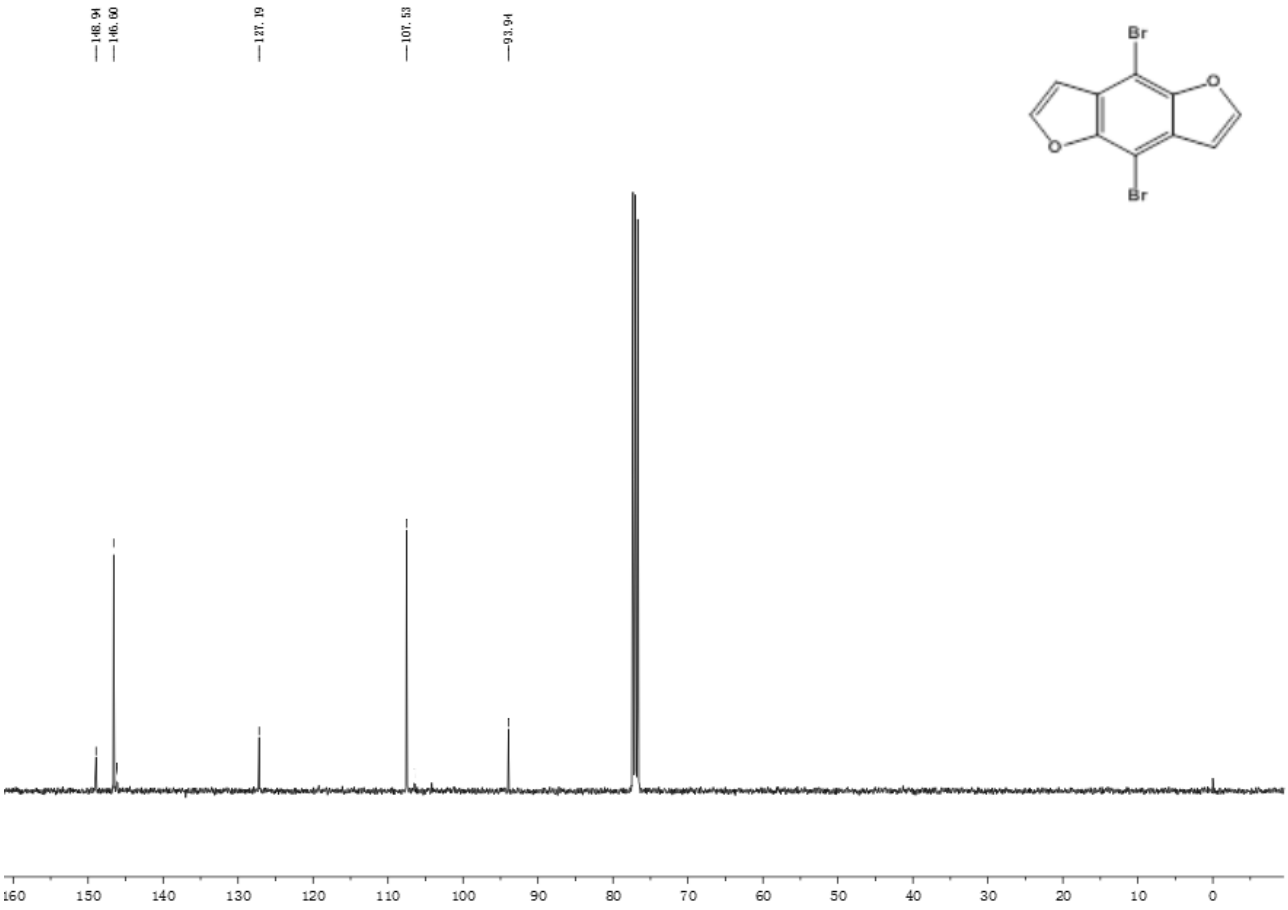
HRMS (EI) spectrum for 2r



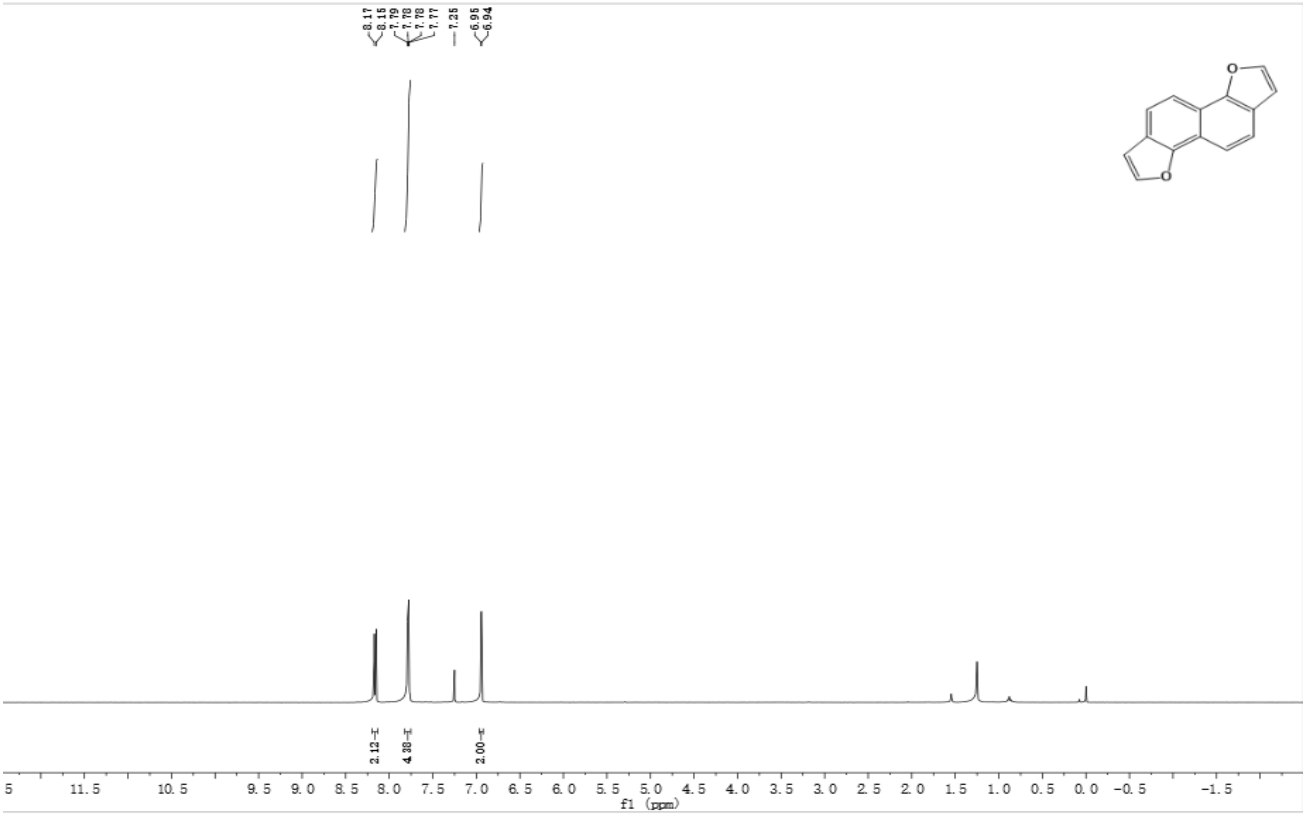
^{1}H NMR spectrum for 2s



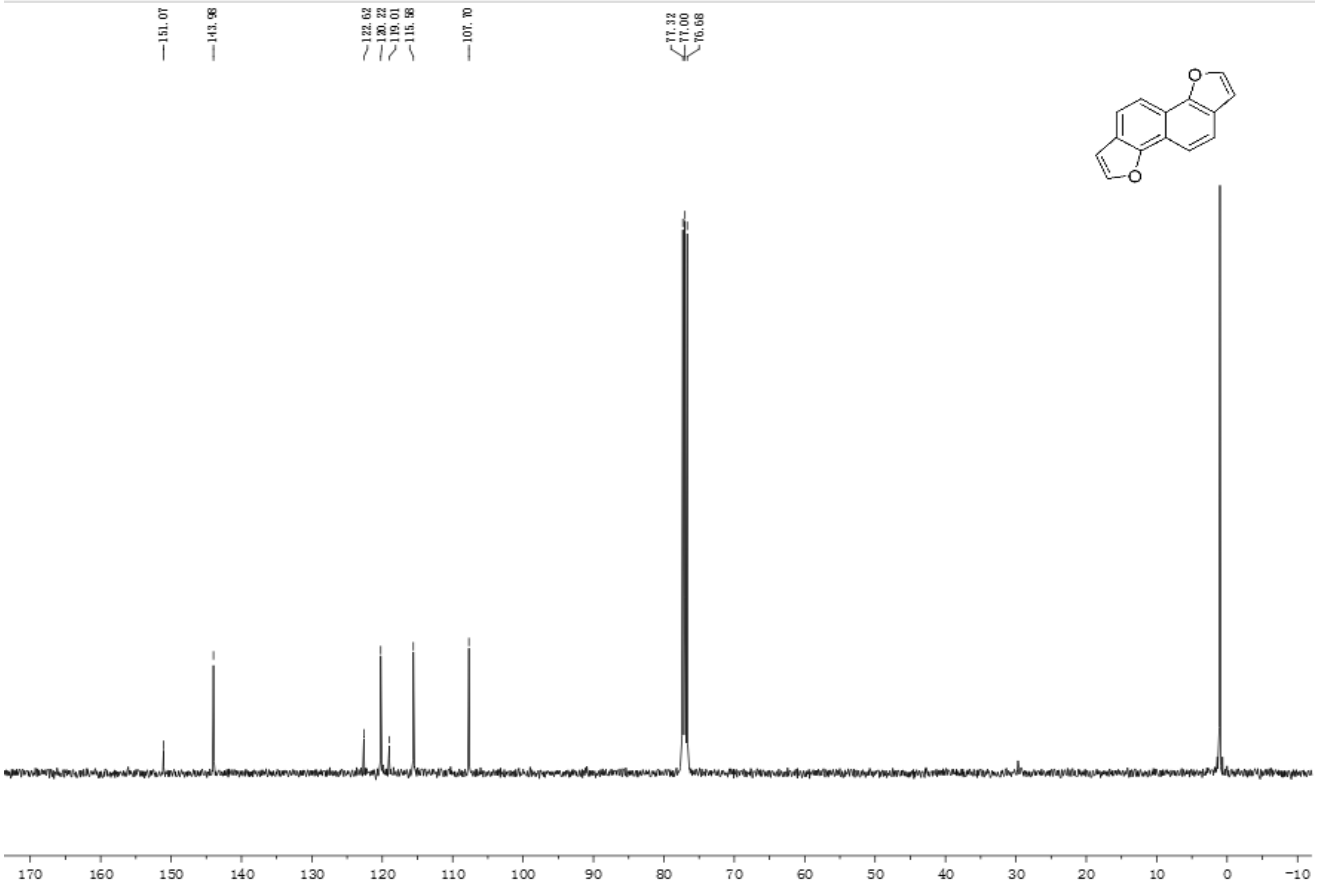
^{13}C NMR spectrum for 2s



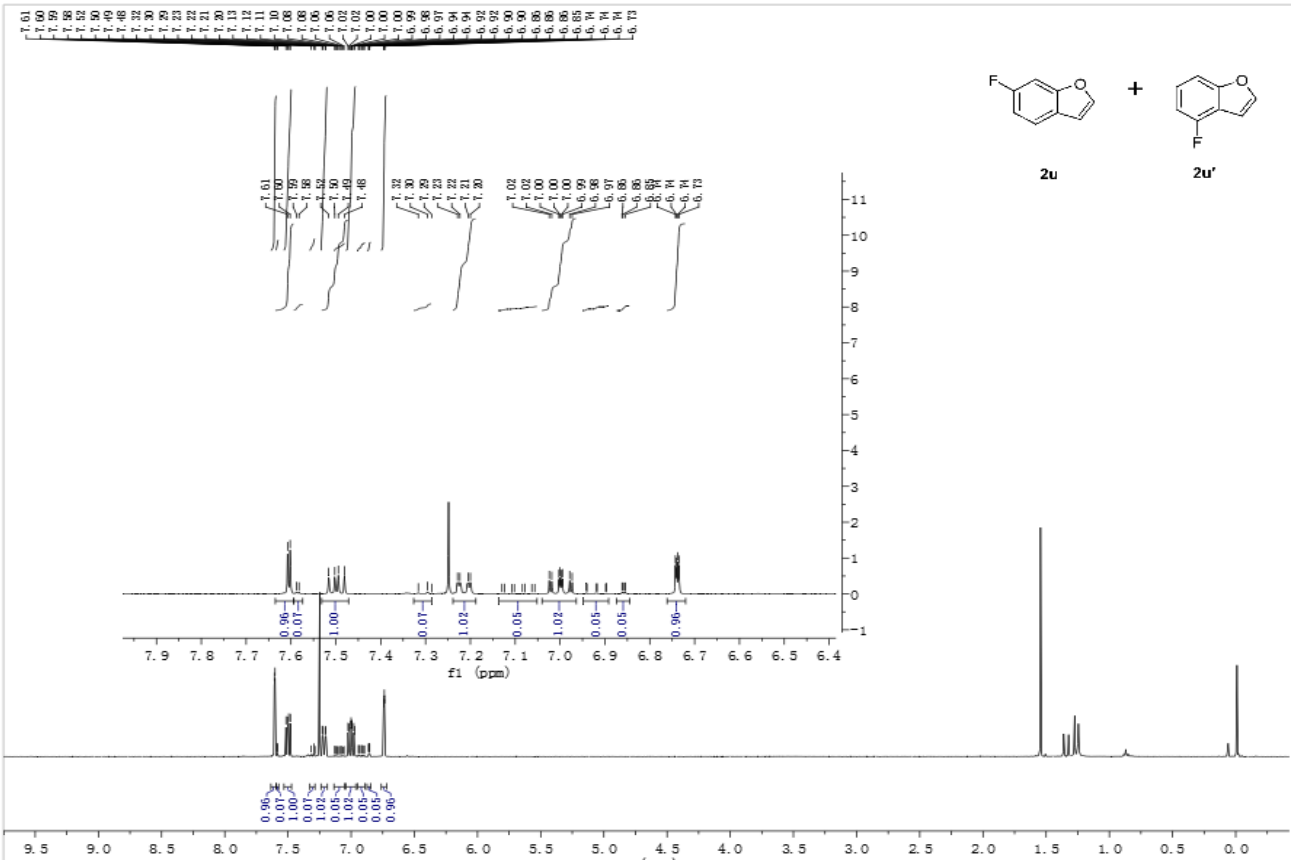
^{1}HNMR spectrum for 2t



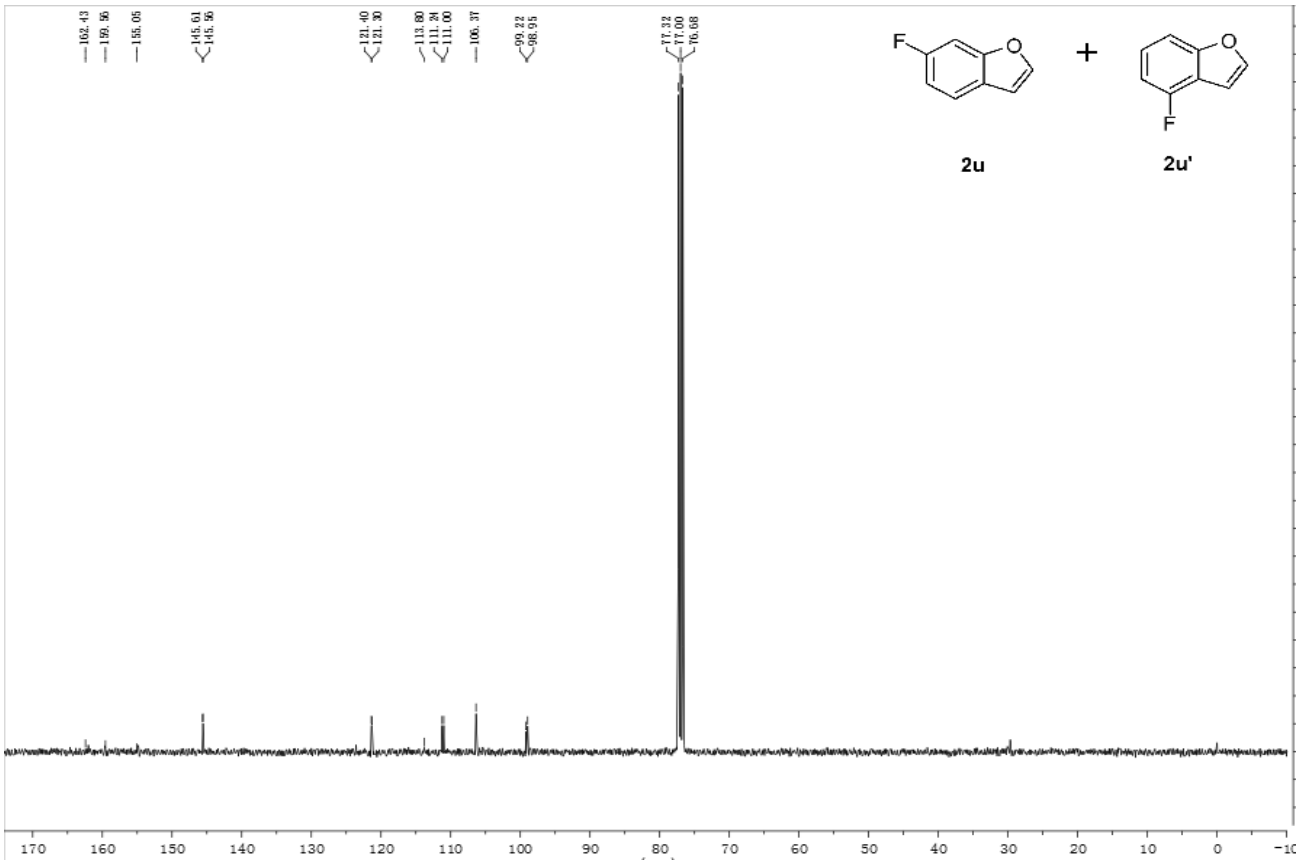
^{13}C NMR spectrum for 2t



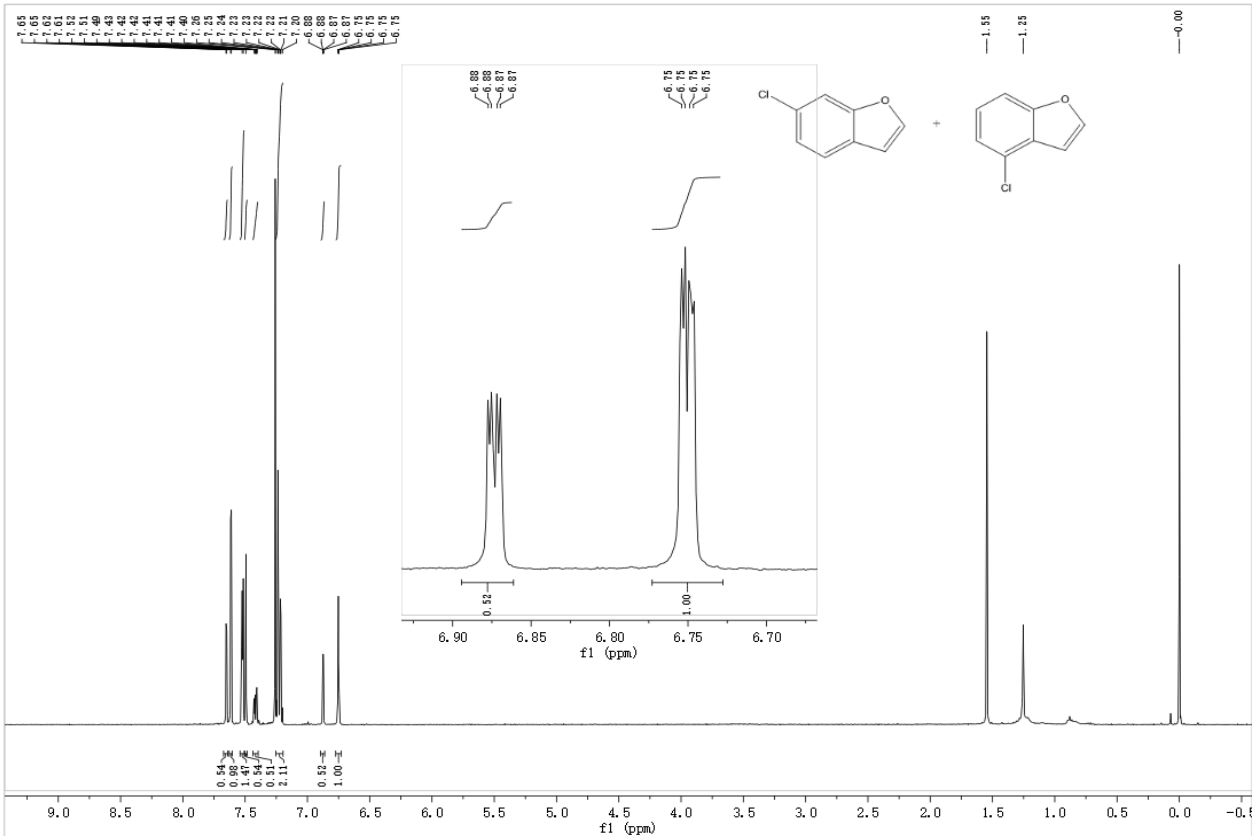
^{1}H NMR spectrum for 2u and 2u′



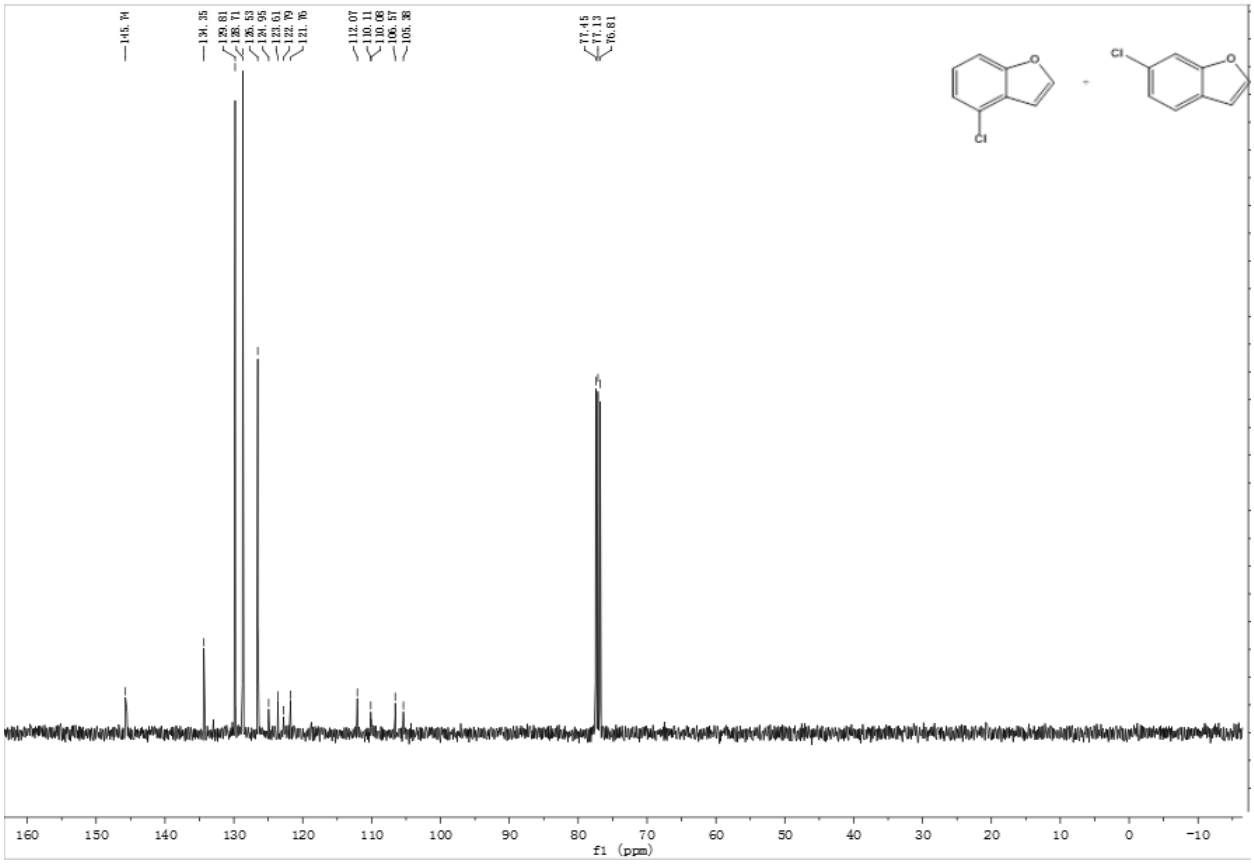
^{13}C NMR spectrum for 2u and 2u′



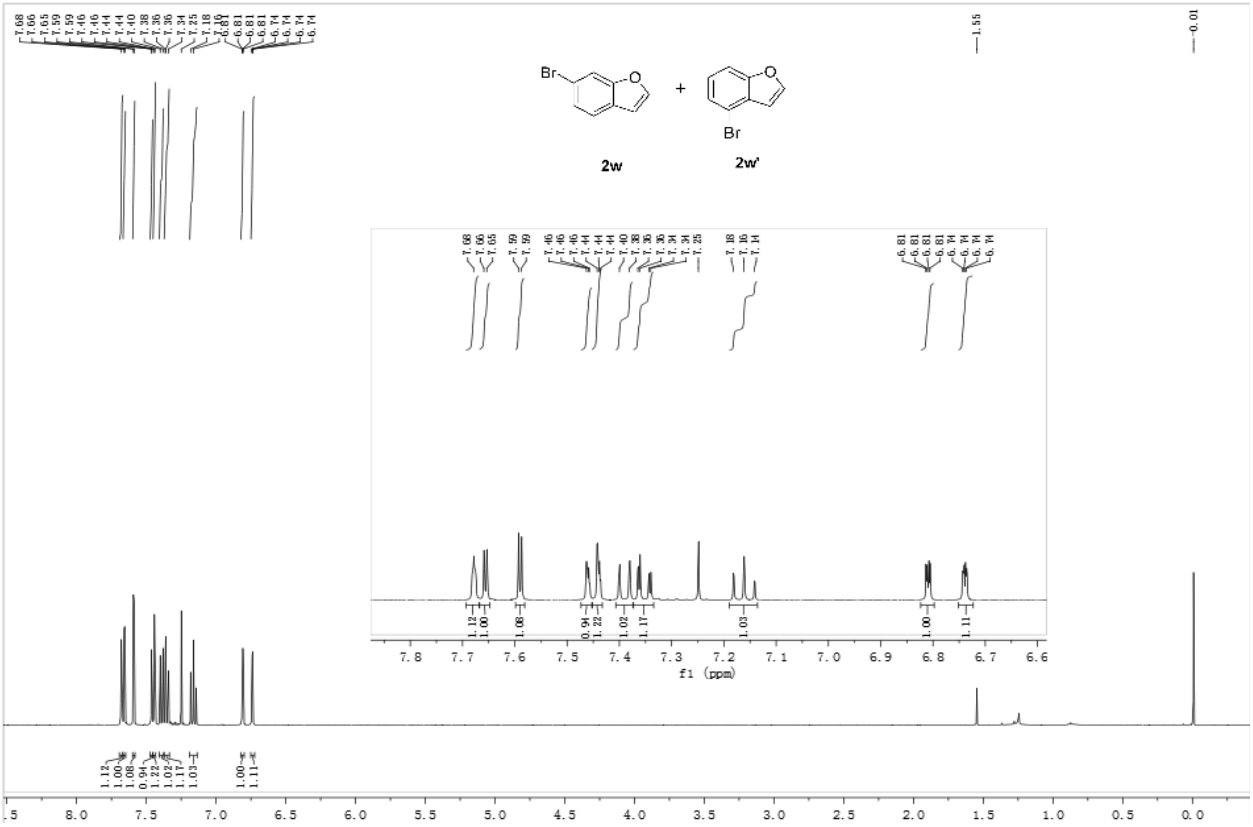
^{1}H NMR spectrum for 2v and 2v′



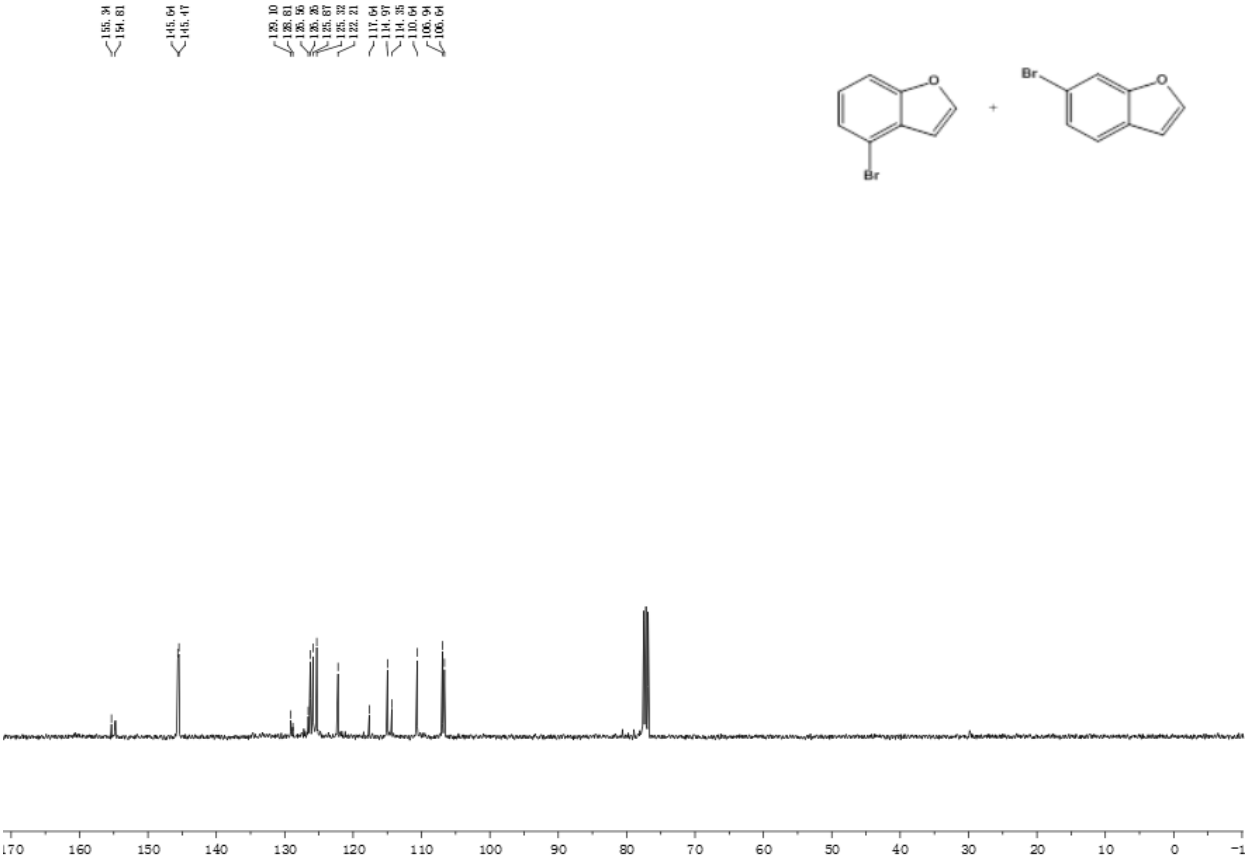
^{13}C NMR spectrum for 2v and 2v′



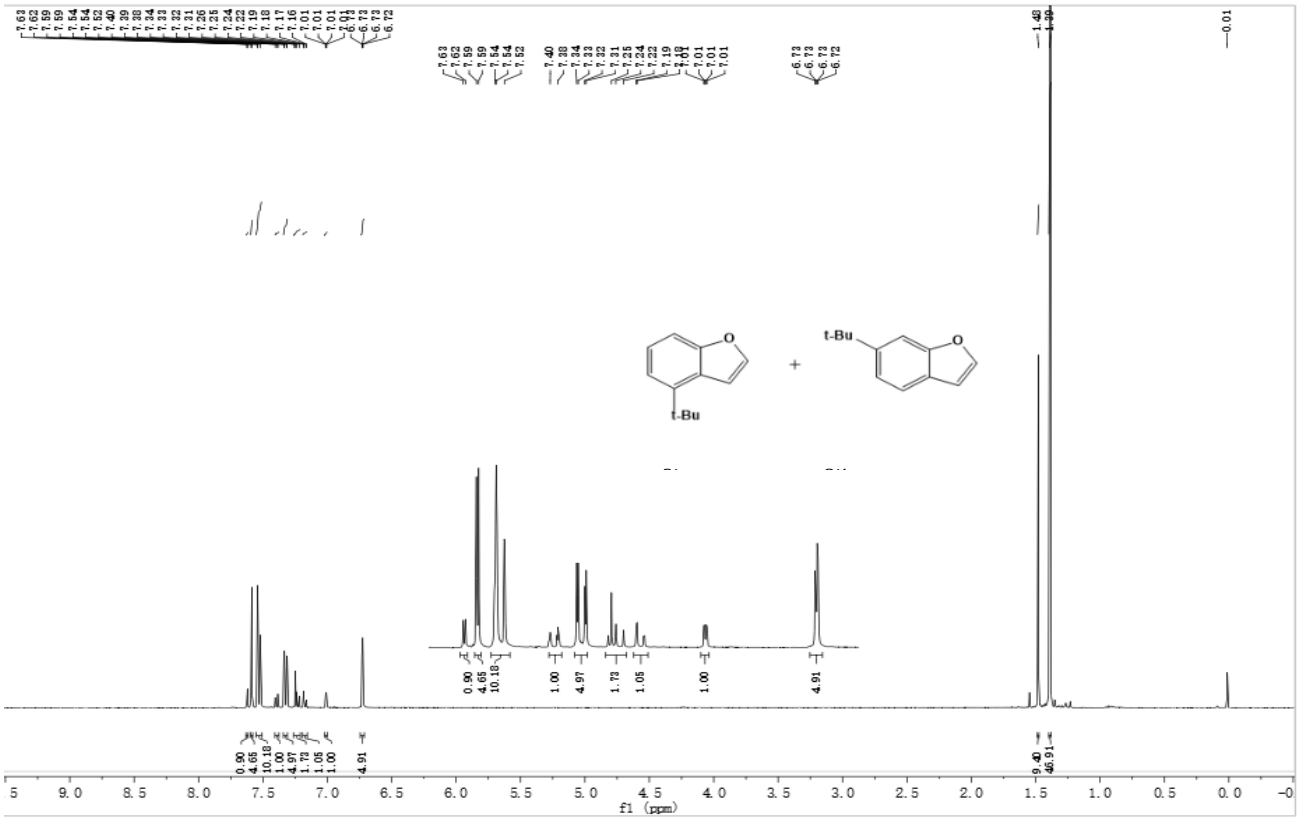
^{1}H NMR spectrum for 2w and 2w′



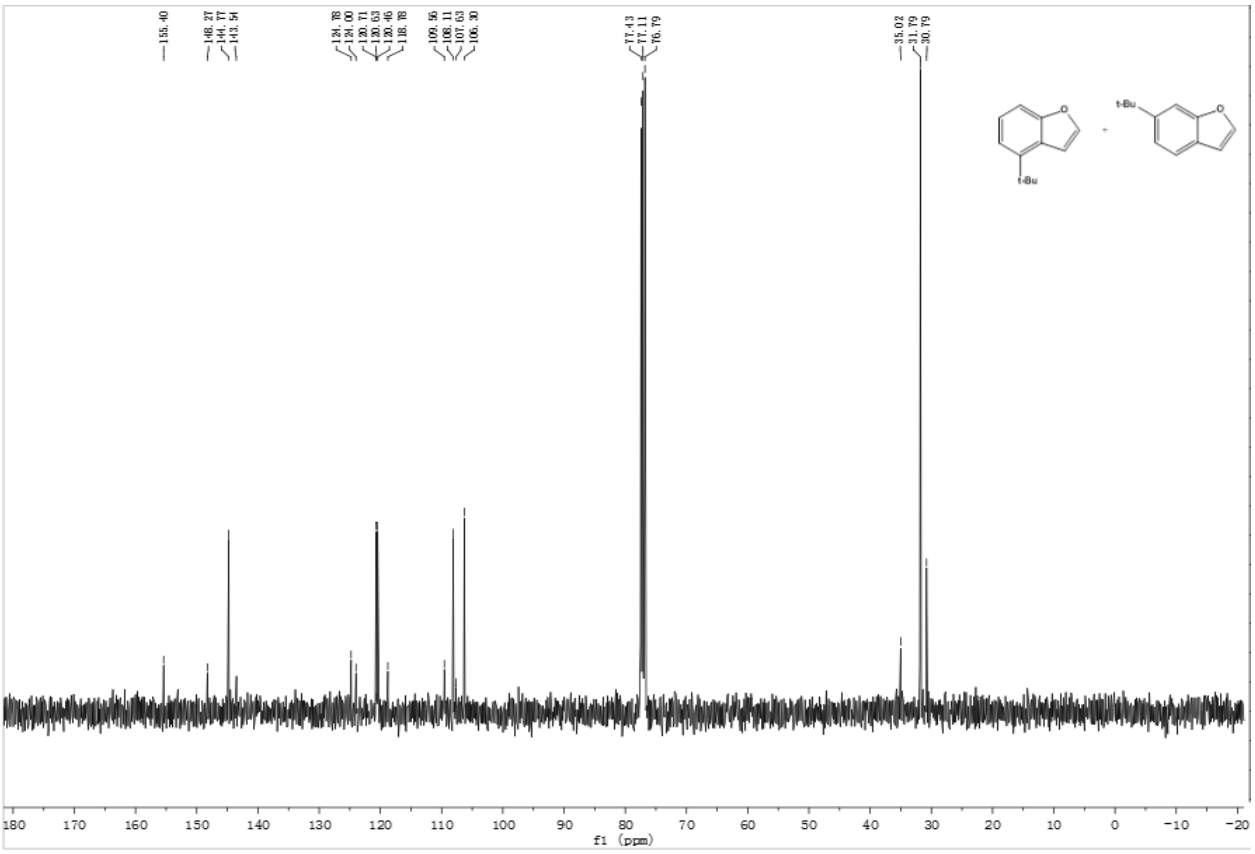
^{13}C NMR spectrum for 2w and 2w′



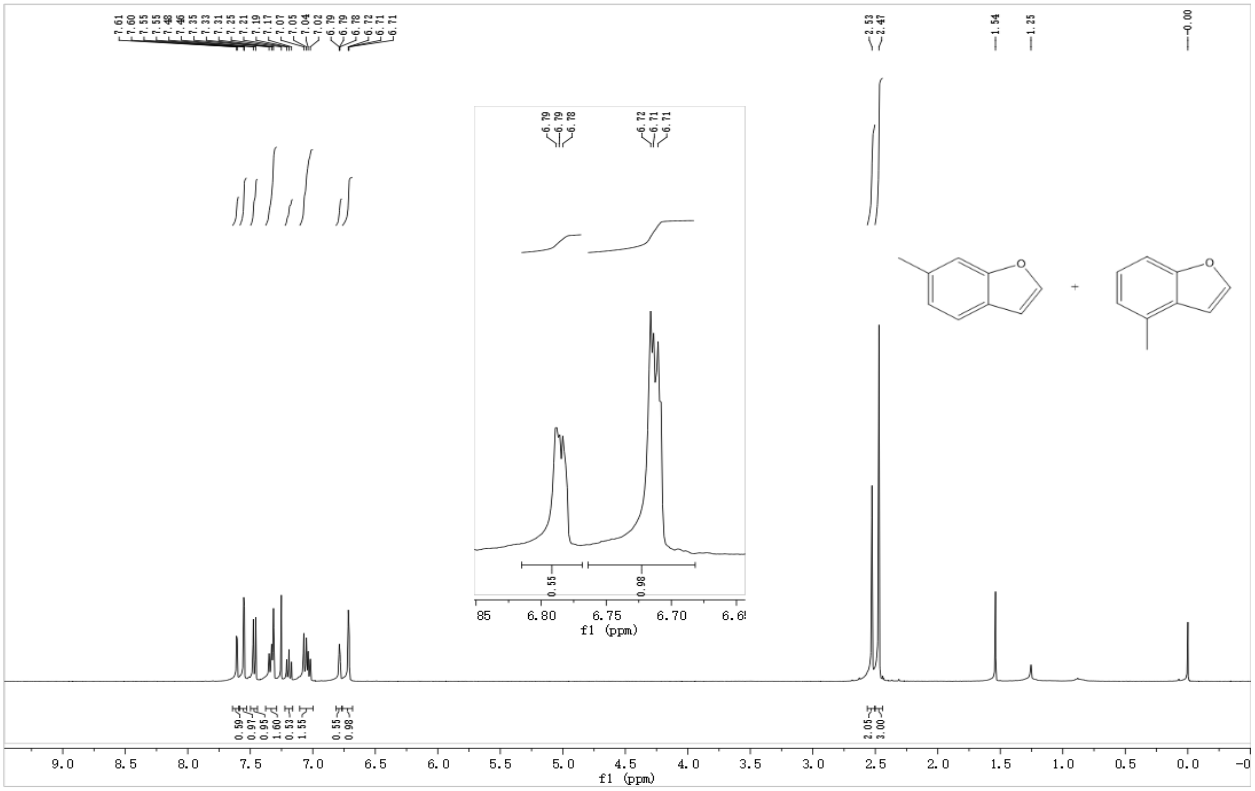
^{1}H NMR spectrum for 2x and 2x′



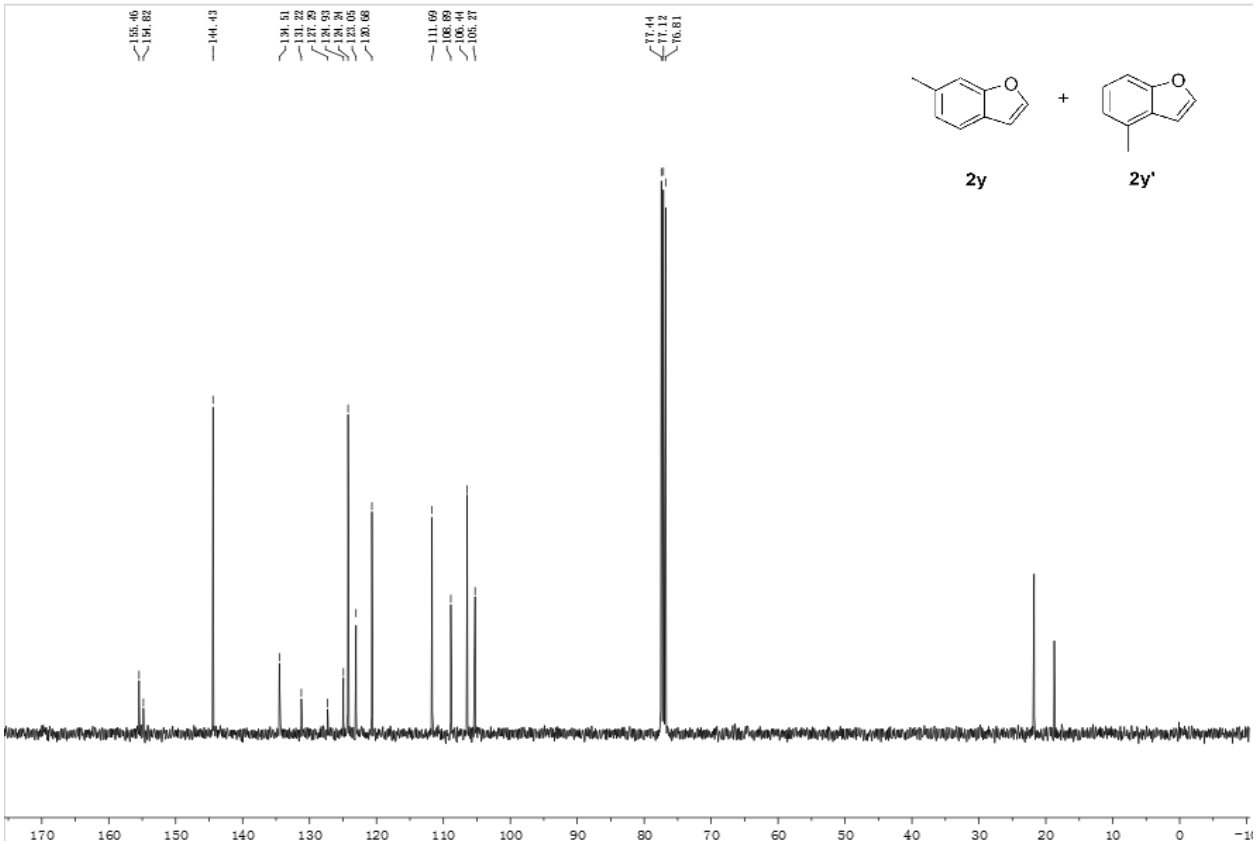
^{13}C NMR spectrum for 2x and 2x′



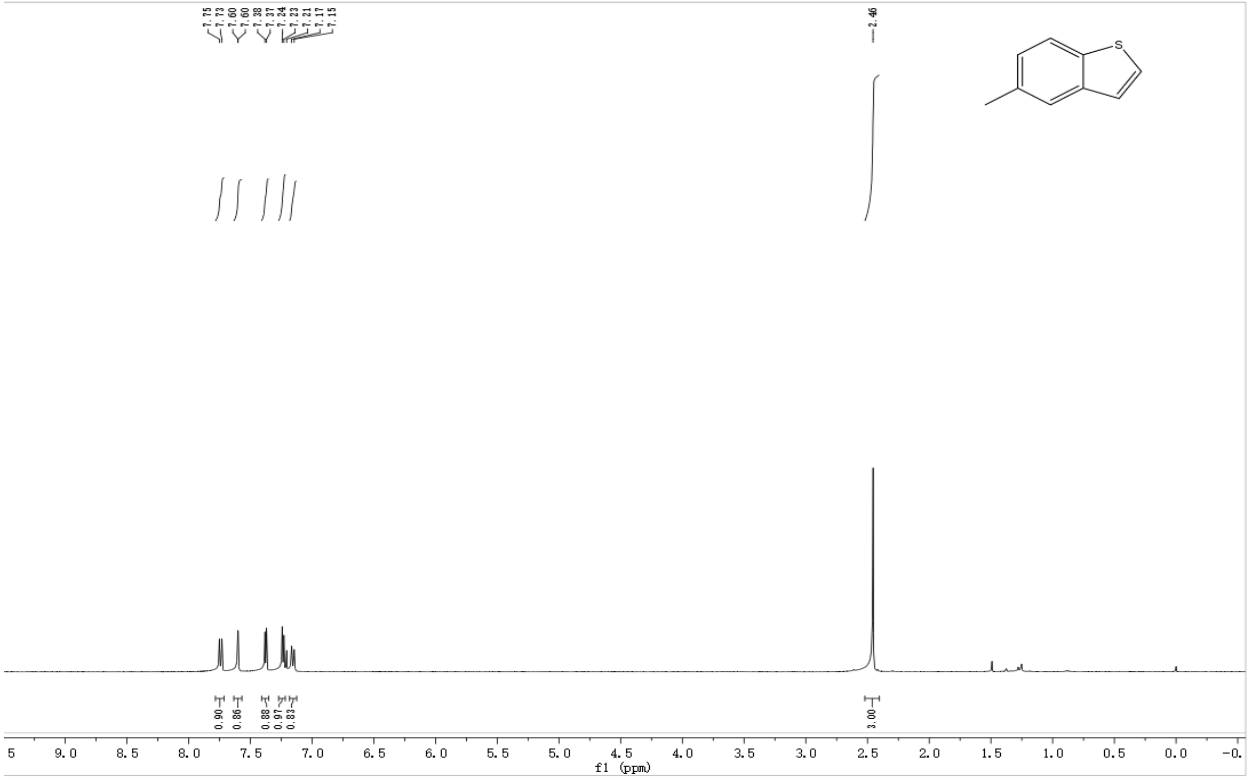
^{1}H NMR spectrum for 2y and 2y′



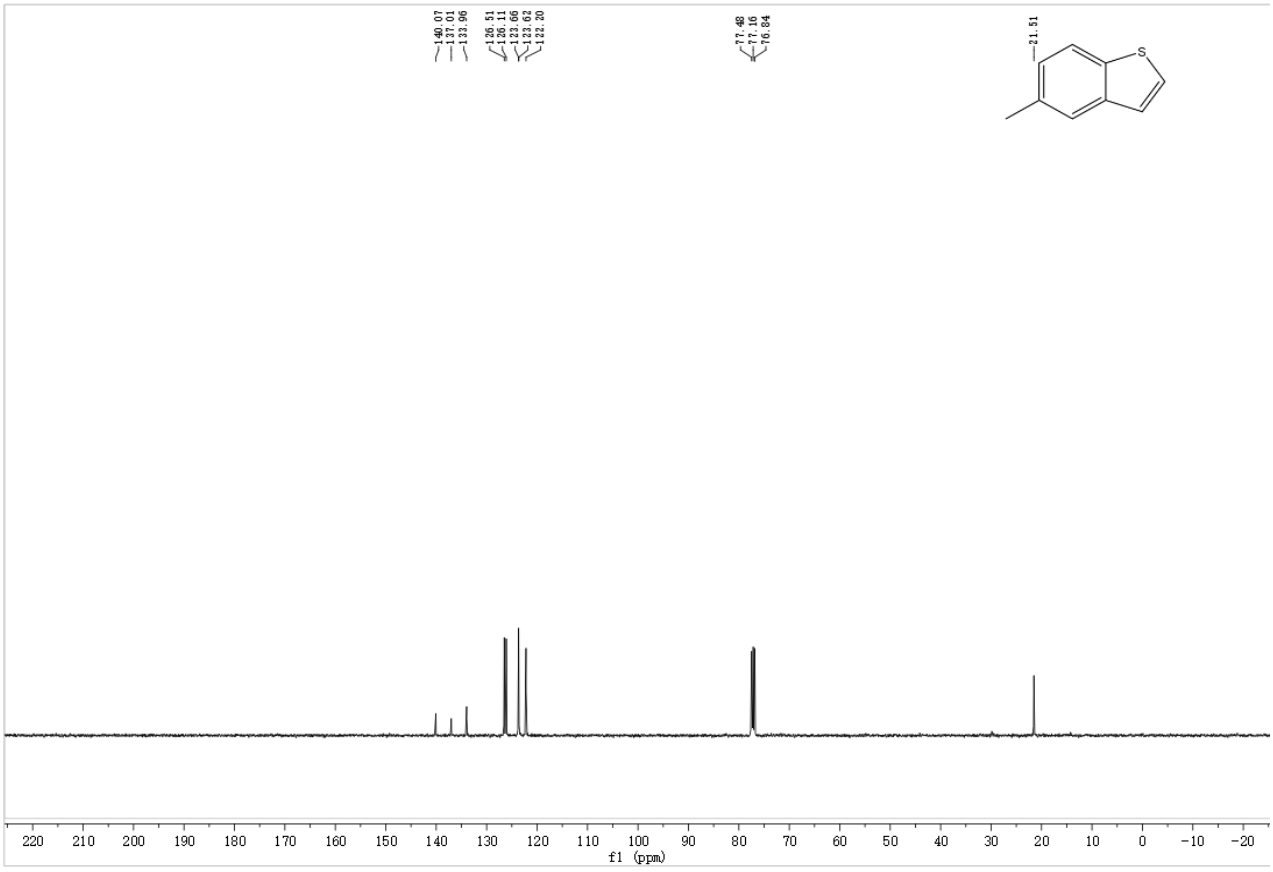
^{13}C NMR spectrum for 2y and 2y′



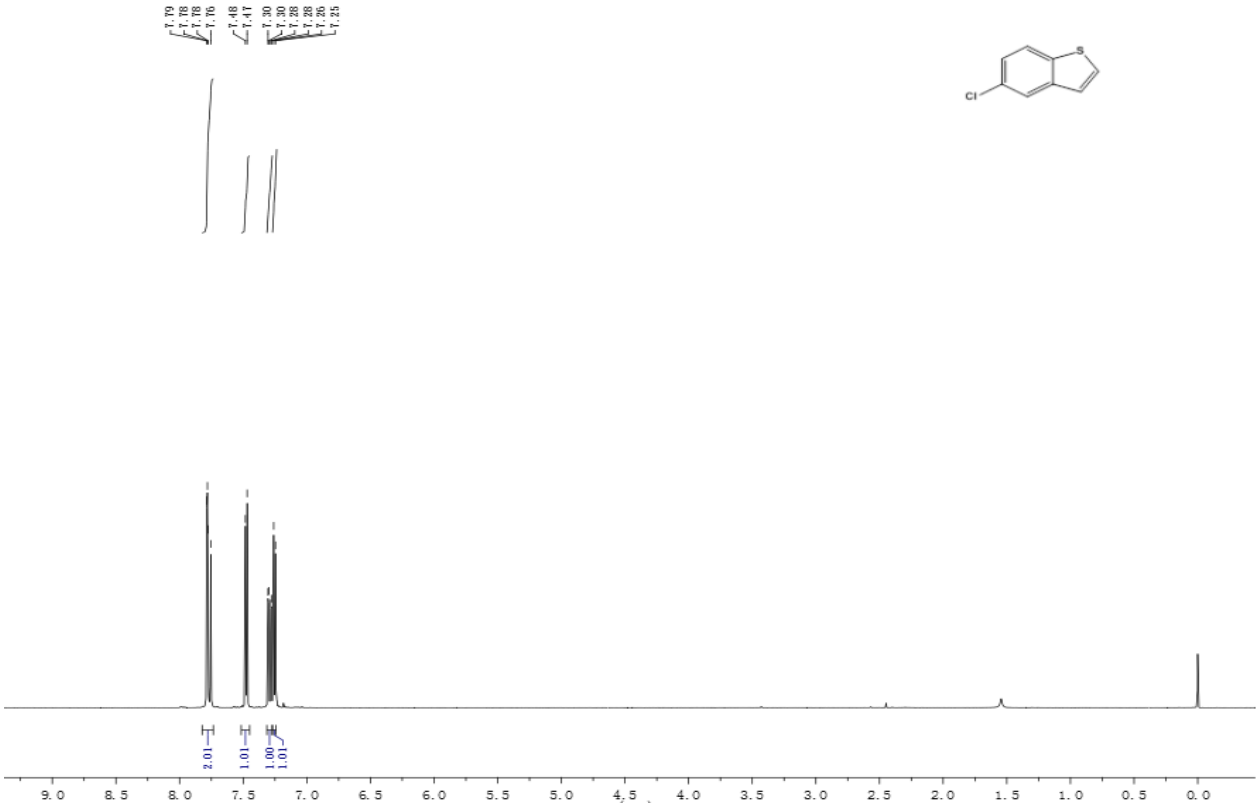
^{1}H NMR spectrum for 4a



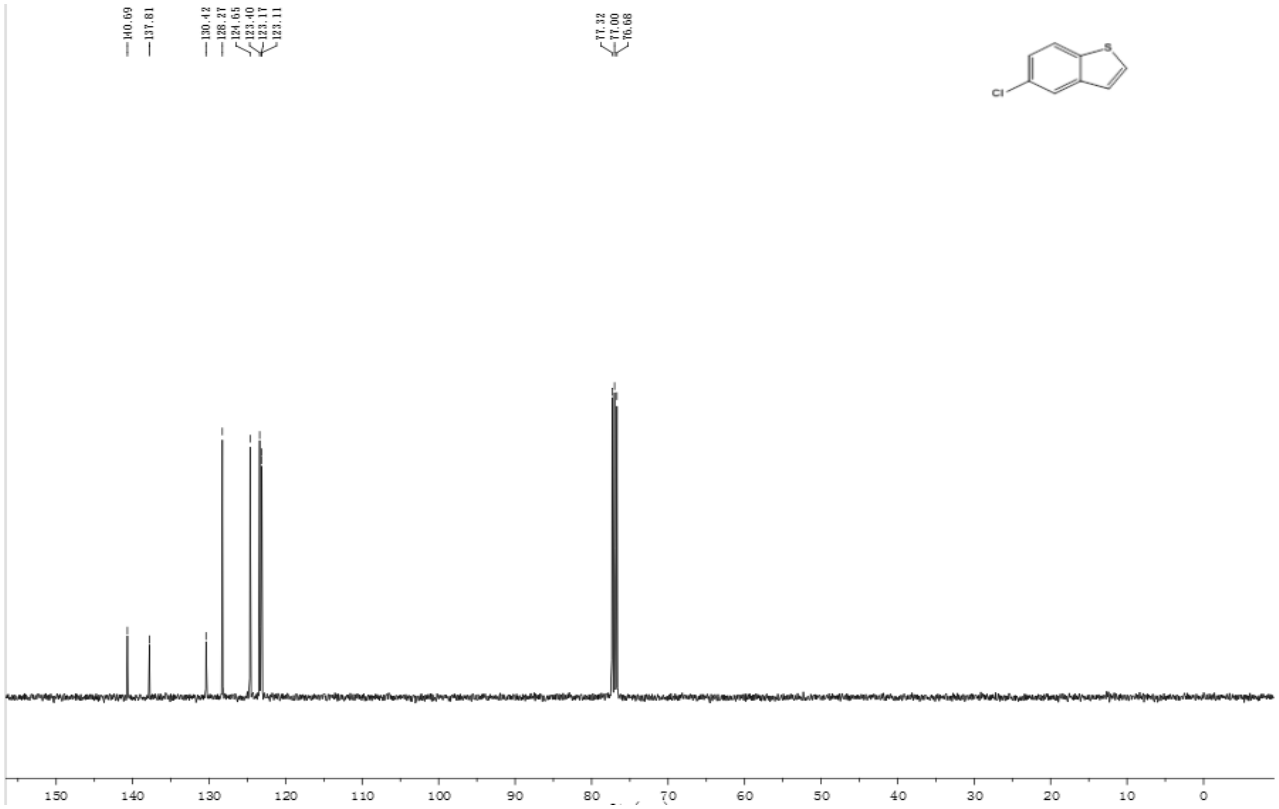
^{13}C NMR spectrum for 4a



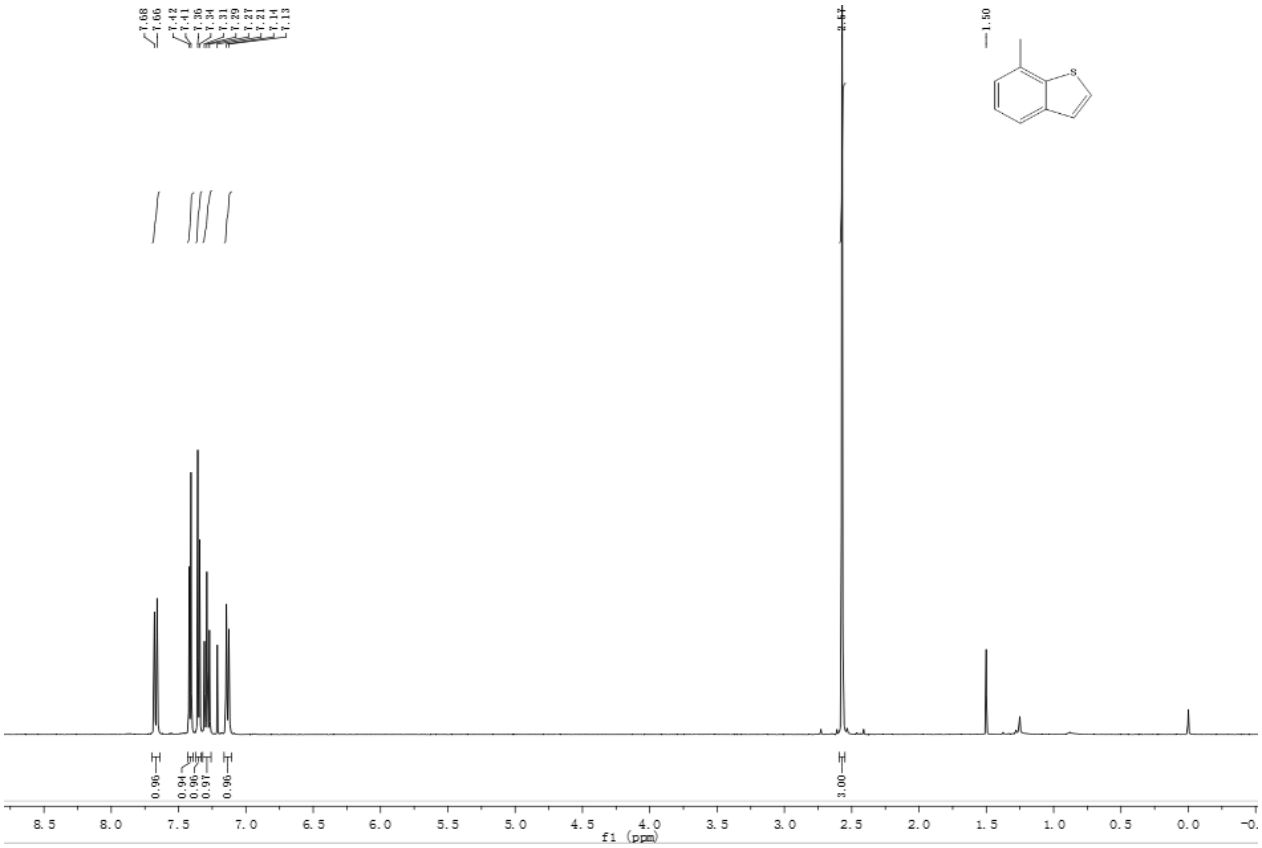
^{1}H NMR spectrum for 4b



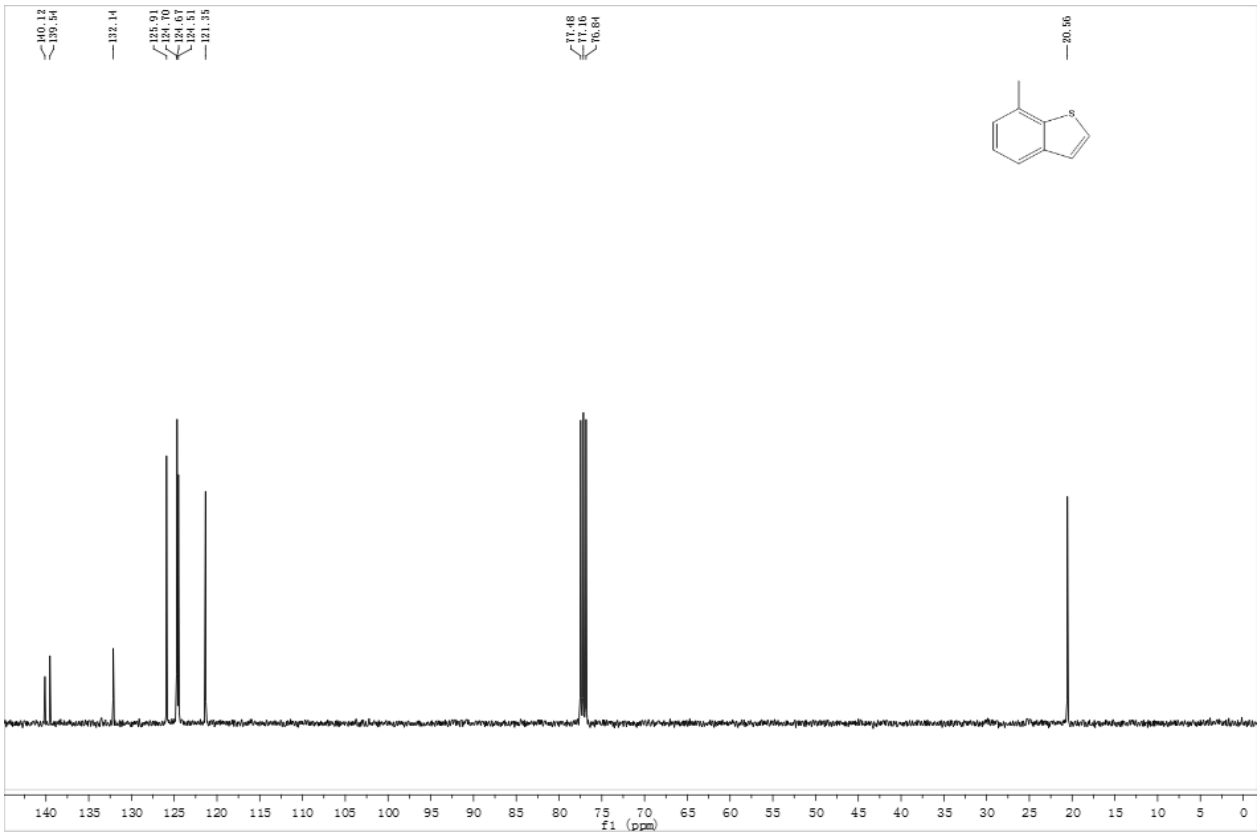
^{13}C NMR spectrum for 4b



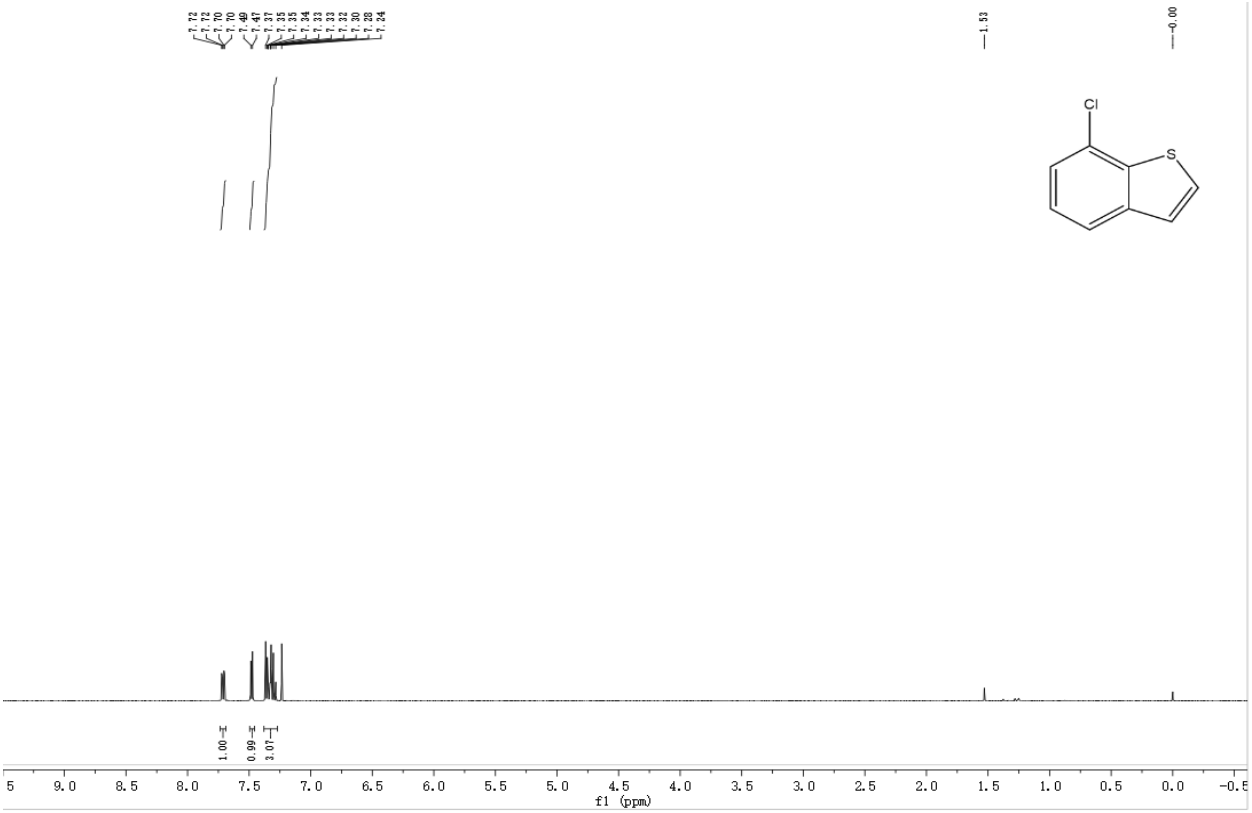
^{1}H NMR spectrum for 4c



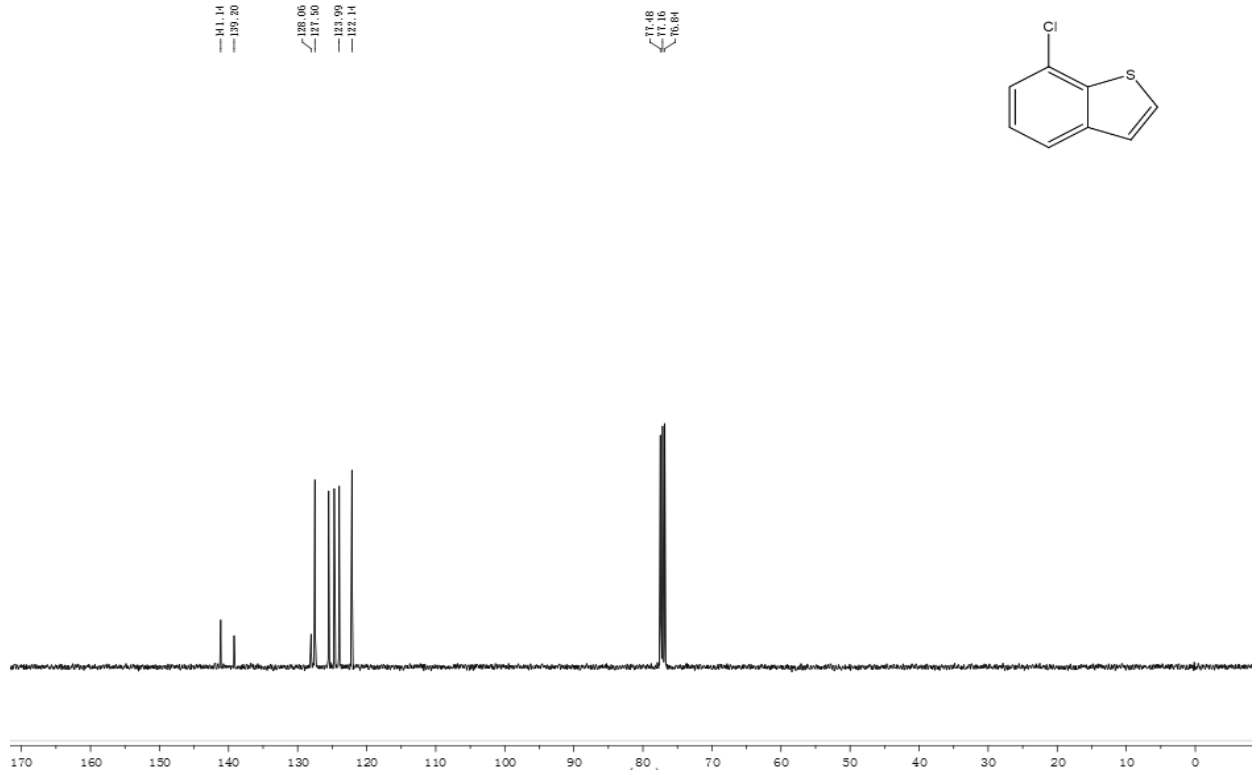
^{13}C NMR spectrum for 4c



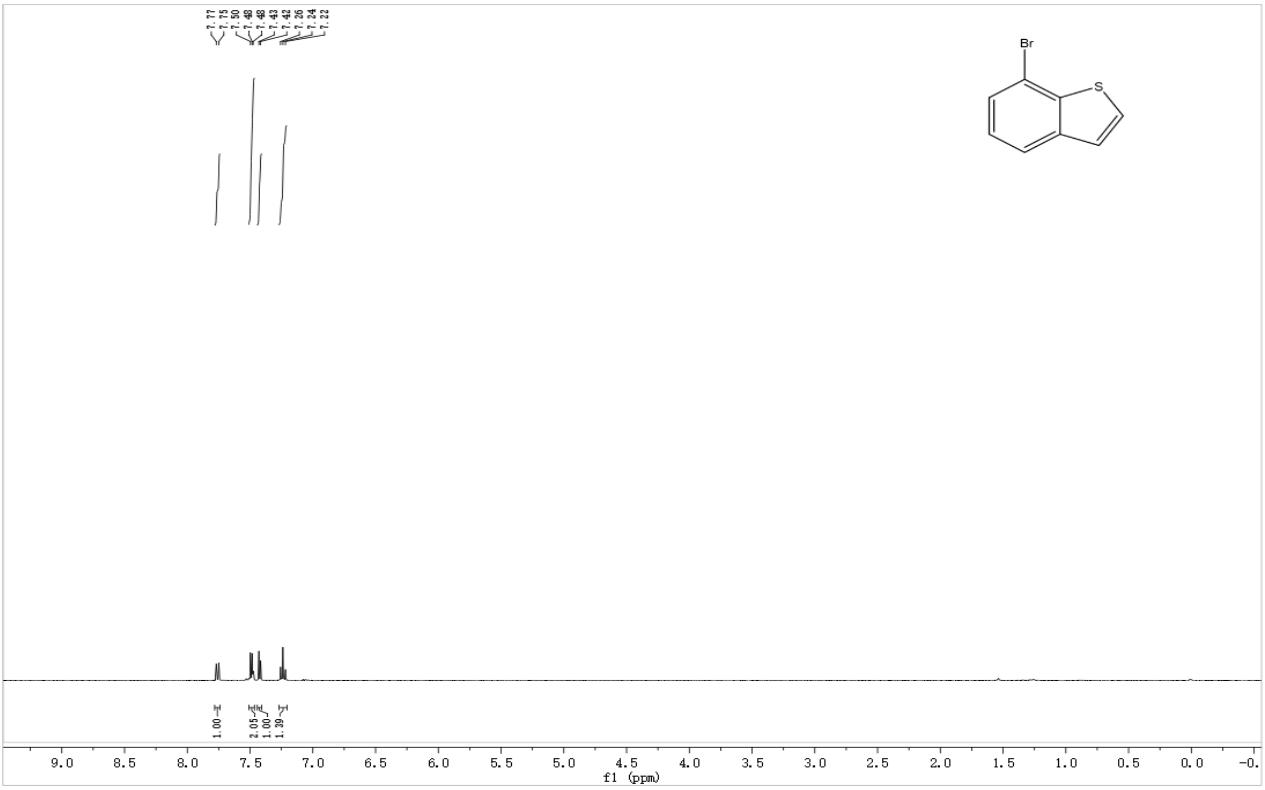
^{1}H NMR spectrum for4d



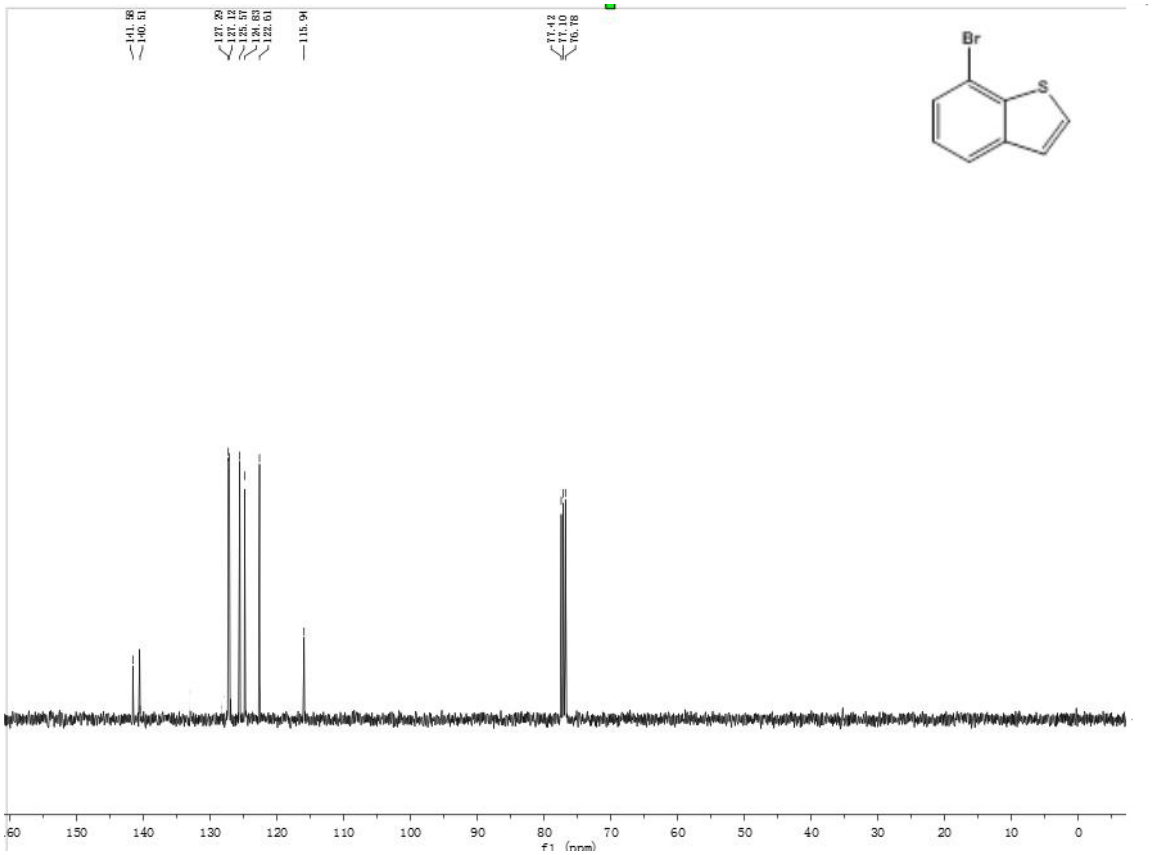
^{13}C NMR spectrum for 4d



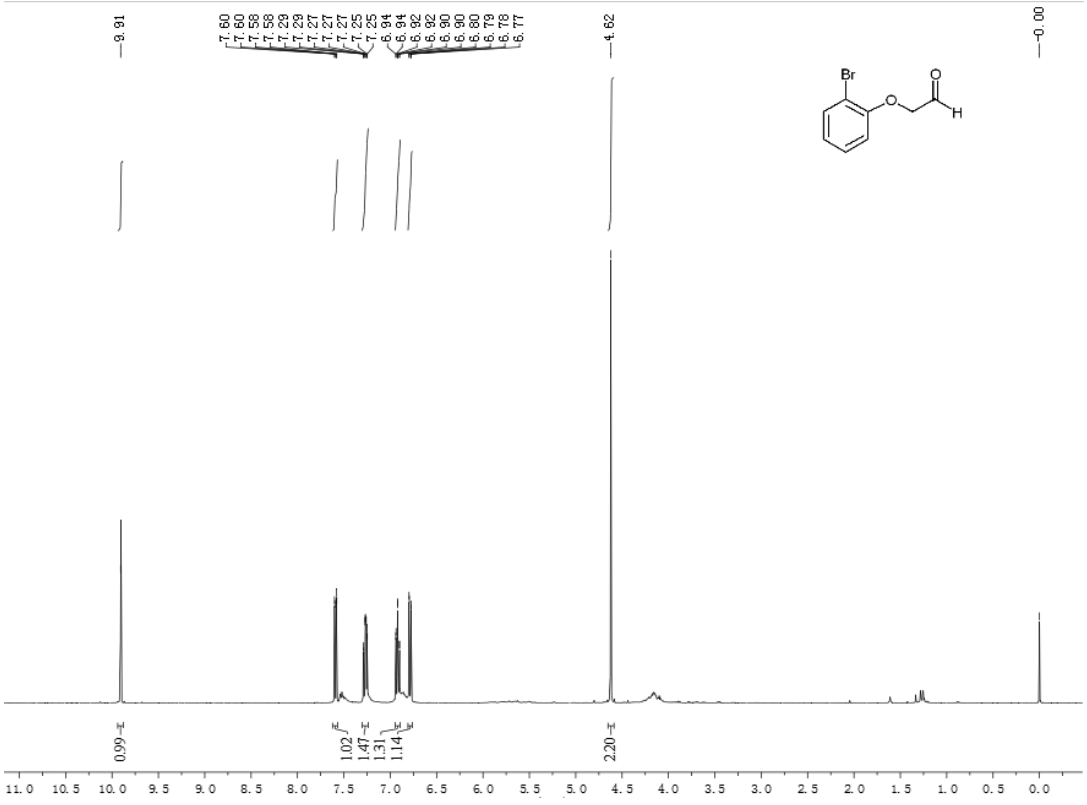
^{1}H NMR spectrum for 4e



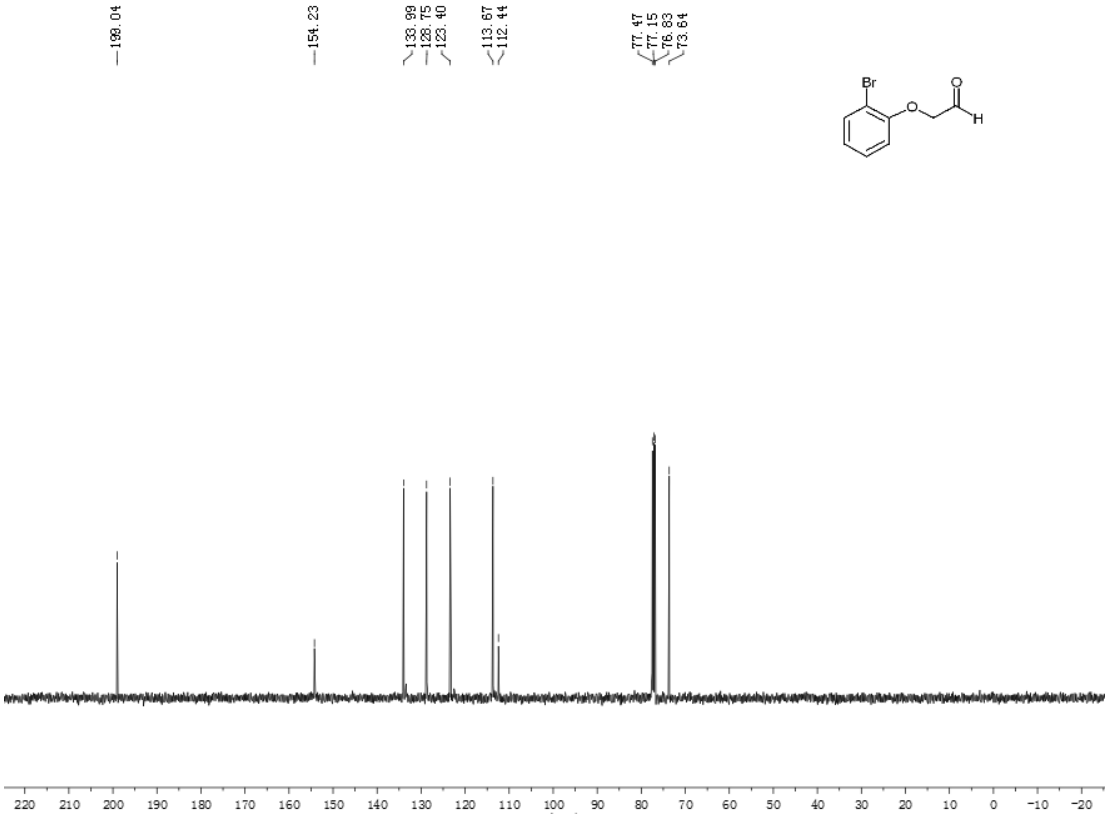
^{13}C NMR spectrum for 4e



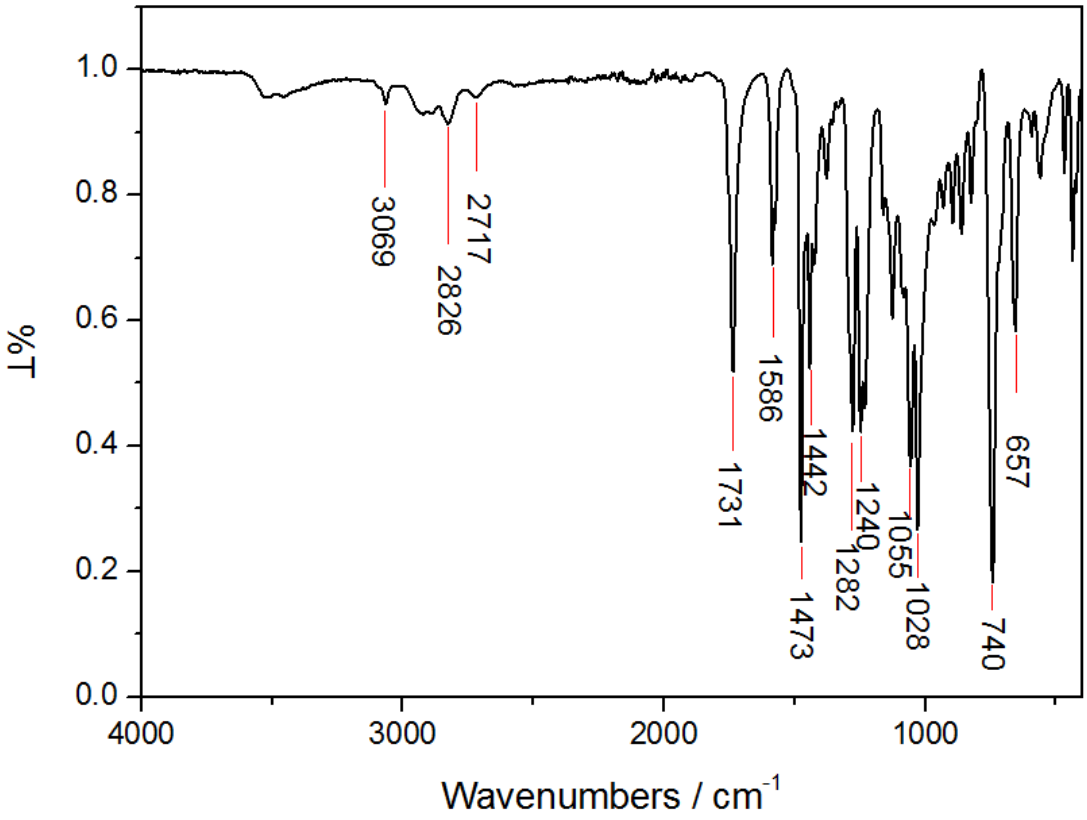
^{1}H NMR spectrum for aldehyde intermediate I



^{13}C NMR spectrum for aldehyde intermediate I



Infrared absorption spectrum of aldehyde intermediate I



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