Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

Enantioselective Palladium-Catalyzed Diarylation of Unactivated Alkenes

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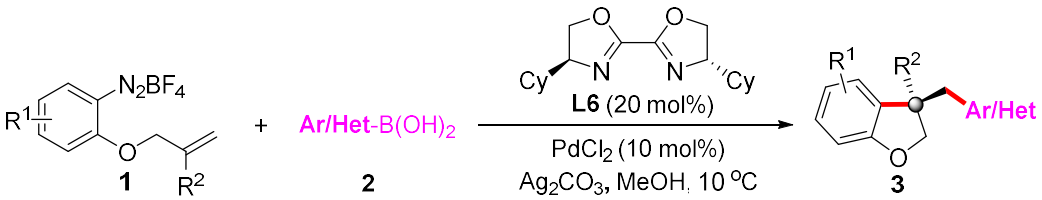
Contents

1. General Information

^{1}H and ^{13}C NMR data were recorded with Bruker ADVANCE III (400 MHz) or JNM-ECZ400S/L1 (400 MHz) spectrometers. Chemical shifts are given in ppm. The spectra are calibrated to the residual ^{1}H and ^{13}C signals of the solvents. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet-doublet (dd), quintet (quint), septet (sept), multiplet (m), and broad (b). ^{19}F NMR spectra were recorded using $CFCl_3$ as internal standard. Gas chromatography were determined with a SHIMADZU Nexis GC 2030 gas chromatography instrument with a FID detector. High-resolution mass spectra (HRMS) were recorded on DIONEX UltiMate 3000 & Bruker Compact TOF mass spectrometer. Enantiomeric excesses were determined with a SHIMADZU LC-20ADXR system using chiral stationary phase columns (DAICEL) by comparing the samples with the corresponding racemic samples. Column and elution details were specified in each entry.

Materials and Methods: Unless otherwise stated, starting materials were purchased from commercial suppliers (Adamas-beta®, Alfa, Aldrich and so on). All reactions dealing with air- or moisture-sensitive compounds were performed in the argon-filled glove box or by standard Schlenk techniques in oven-dried reaction vessels under argon atmosphere. Solvents were purchased in HPLC quality, degassed by purging thoroughly with argon and dried over activated molecular sieves of appropriate size. More sensitive compounds were stored in a desiccator or in a glove-box if required. Reactions were monitored by thin layer chromatography (TLC) using glass 0.25 mm silica gel plates. Compounds were visualized by UV-light at 254 nm and by dipping the plates in an aqueous potassium permanganate solution followed by heating. Flash column chromatography was performed over silica gel (200-400 mesh).

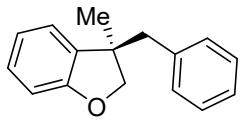
2. General Procedures



A mixture of $PdCl_2$ (10 mol %), (*4S, 4'S*)-Cy-BOX **L6** (20 mol %) and MeOH (1.0 mL) was stirred in an oven-dried vial at room temperature for 15 minutes to form the precatalyst. The resulting solution was cooled to 10 °C and charged with arenediazonium salt **1** (0.10 mmol), boronic acid **2** (0.2 mmol) and Ag_2CO_3 (0.1 mmol). Then the reaction mixture was stirred at the same temperature until the reaction was completed. The solvent was removed under vacuum and the residue was then purified by column chromatography on silica gel, eluting with petroleum ether/EtOAc = 100:1~30/1 to afford the desired dihydrobenzofuran **3**.

3. Characterization data of products

(*R*)-3-benzyl-3-methyl-2,3-dihydrobenzofuran (**3aa**)



Chemical Formula: $C_{16}H_{16}O$
Exact Mass: 224.1201

3aa was prepared according to general procedure using **1a** and **2a** and was purified by silica gel column chromatography (petroleum ether/EtOAc = 100/1~50/1) to obtain **3aa** as colorless oil (85% yield). The ^{1}H NMR data matched those reported in the literature[1]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.20 (m, 3H), 7.13 (ddd, *J* = 7.9, 7.3, 1.5 Hz, 1H), 7.00 (dd, *J* = 7.3, 2.2 Hz, 2H), 6.94 (dd, *J* = 7.4, 1.6 Hz, 1H), 6.86 (td, *J* = 7.4, 0.9 Hz, 1H), 6.80-6.74 (m, 1H), 4.50 (d, *J* = 8.7 Hz, 1H), 4.06 (d, *J* = 8.8 Hz, 1H), 3.15-2.78 (m, 2H), 1.36 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.5, 137.5, 134.8, 130.3, 128.2, 127.9, 126.4, 123.3, 120.3, 109.7, 81.9, 46.6, 46.2, 24.6.

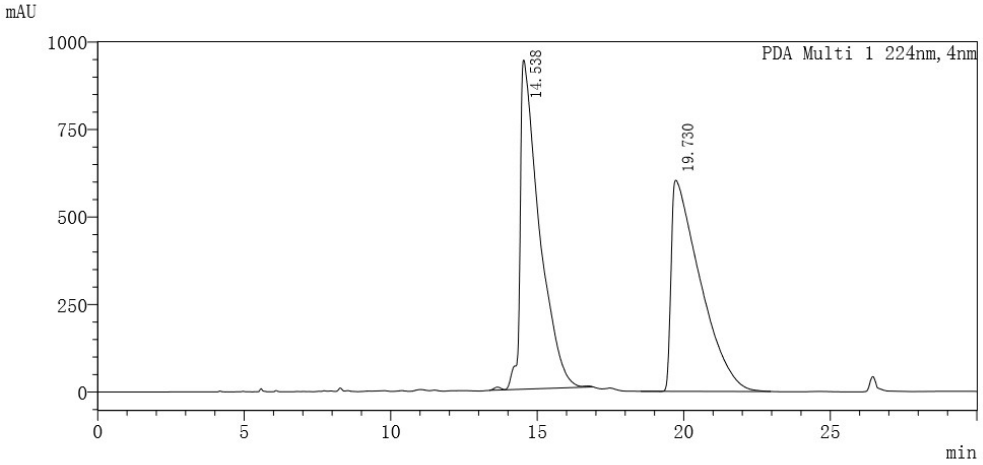
The enantiomeric purity was established by HPLC analysis using a chiral column: IA-H column, 30 °C, *n*-Hexane/*i*-Propanol = 98.8/0.2 as eluent, 254 nm, 0.75 mL/min. tR = 15 min (major), 22 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ -13.4 (c 0.75, $CHCl_3$) for 94% ee.

Determination of Absolute Configuration:

We assigned the absolute stereochemistry of the aryl-alkenylation product **3aa** via chemical correlation with the corresponding known enantimer reported by the Brown and Correia's group;[1] Both the HPLC analysis using the same conditions and the specific rotation indicated the *R* absolute stereochemistry. All other dihydrobenzofurans **3** were attributed accordingly.

〈色谱图〉



〈峰表〉

PDA Ch1 224nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	14.538	42888801	940751	0.000		M	
2	19.730	41606477	603210	0.000		M	
总计		84495277	1543961				

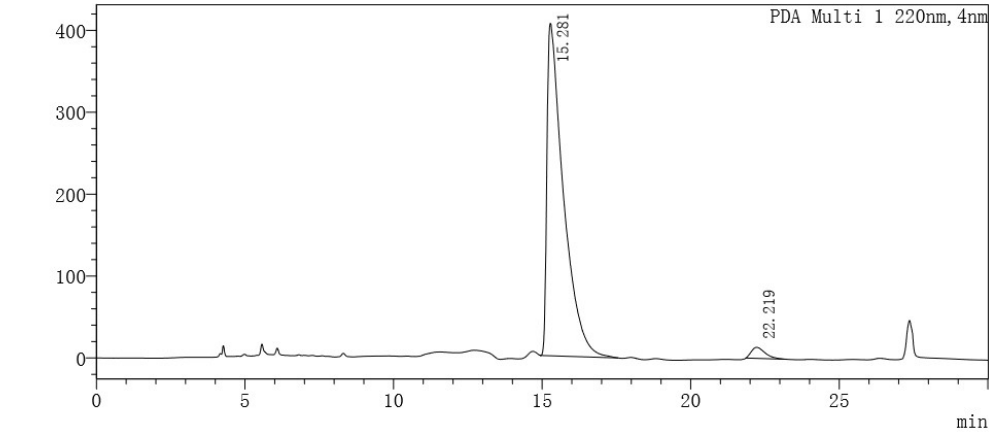
peak number

retention time

area

height

〈色谱图〉



〈峰表〉

PDA Ch1 220nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	15.281	15608551	405948	0.000		M	
2	22.219	433739	13501	0.000		M	
总计		16042290	419449				

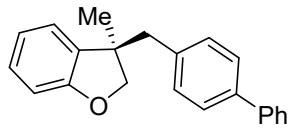
peak number

retention time

area

height

(*R*)-3-([1,1'-biphenyl]-4-ylmethyl)-3-methyl-2,3-dihydrobenzofuran (**3ab**)



Chemical Formula: $C_{22}H_{20}O$
Exact Mass: 300.1514

3ab was prepared according to general procedure using **1a** and **2b** and was purified by silica gel column chromatography (petroleum ether/EtOAc = 100/1~50/1) to obtain **3ab** as colorless oil (82% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66-7.58 (m, 2H), 7.54-7.42 (m, 4H), 7.39-7.32 (m, 1H), 7.17 (td, *J* = 7.6, 1.4 Hz, 1H), 7.12-7.06 (m, 2H), 7.00 (dd, *J* = 7.4, 1.4 Hz, 1H), 6.90 (td, *J* = 7.4, 1.0 Hz, 1H), 6.81 (ddd, *J* = 8.1, 1.0, 0.5 Hz, 1H), 4.56 (d, *J* = 8.7 Hz, 1H), 4.12 (d, *J* = 8.7 Hz, 1H), 2.97 (d, *J* = 13.2 Hz, 1H), 2.92 (d, *J* = 13.2 Hz, 1H), 1.41 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.5, 140.8, 139.3, 136.7, 134.8, 130.8, 128.7, 128.2, 127.1, 127.0, 126.6, 123.4, 120.3, 109.7, 81.9, 46.3, 46.2, 24.6;

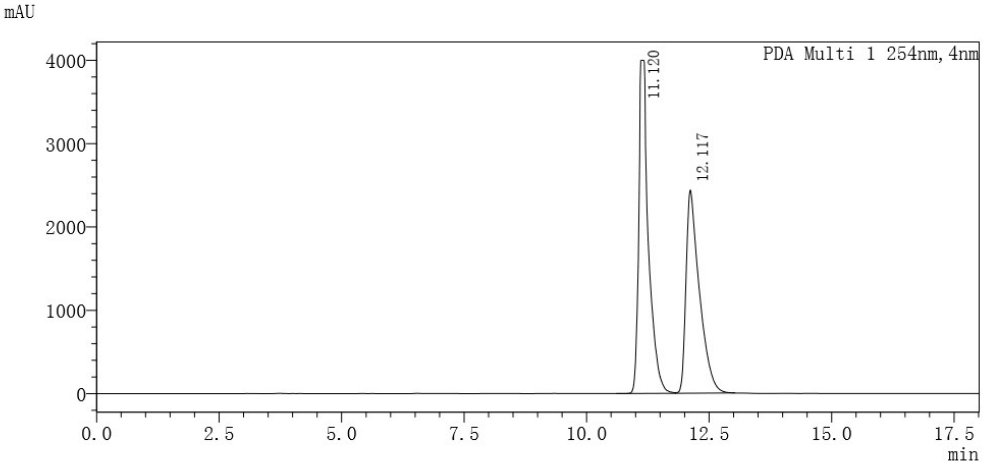
HRMS: (ESI) calcd for $C_{22}H_{20}NaO^{+}$[M+Na]$^{+}$ 232.1406; found 323.1406.

The enantiomeric purity was established by HPLC analysis using a chiral column: OJ-H column, 30 °C, *n*-Hexane/*i*-Propanol = 85/15 as eluent, 254 nm, 1 mL/min. tR = 11.1 min (major), 12.1 min (minor).

Optical Rotation: $[\alpha]_D^{30}$ -31.2 (c 0.58, $CHCl_3$) for 95% ee.

Absolute stereochemistry was determined through analogy with **3aa**.

〈色谱图〉



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	11.120	55192437	3997685	0.000		M	
2	12.117	46082408	2440031	0.000		V M	
总计		101274844	6437717				

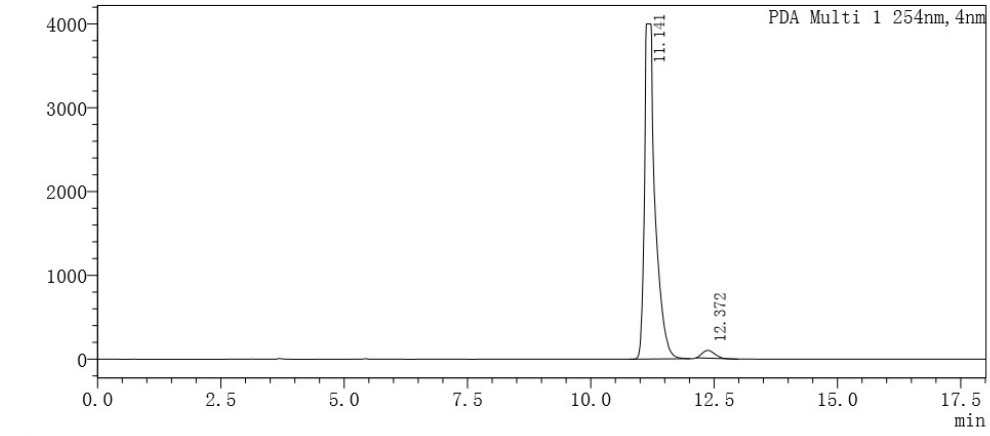
peak number

retention time

area

height

〈色谱图〉



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	11.141	60571711	3999165	0.000		M	
2	12.372	1625010	94571	0.000		M	
总计		62196721	4093736				

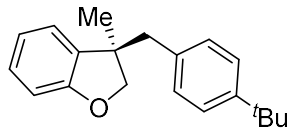
peak number

retention time

area

height

(*R*)-3-(4-(tert-butyl)benzyl)-3-methyl-2,3-dihydrobenzofuran (**3ac**)



Chemical Formula: $C_{20}H_{24}O$
Exact Mass: 280.1827

3ac was prepared according to general procedure using **1a** and **2c** and was purified by silica gel column chromatography (petroleum ether/EtOAc = 100/1~50/1) to obtain **3ac** as colorless oil (79% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.26 (m, 2H), 7.18-7.12 (m, 1H), 7.03-6.95 (m, 3H), 6.88 (td, *J* = 7.4, 1.0 Hz, 1H), 6.79 (dt, *J* = 7.9, 0.8 Hz, 1H), 4.53 (d, *J* = 8.7 Hz, 1H), 4.06 (d, *J* = 8.7 Hz, 1H), 2.90 (d, *J* = 13.2 Hz, 1H), 2.84 (d, *J* = 13.2 Hz, 1H), 1.36 (s, 3H), 1.32 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.5, 149.3, 135.3, 134.5, 130.0, 128.1, 124.9, 123.3, 120.3, 109.7, 81.8, 46.2, 45.9, 34.4, 31.4, 24.7;

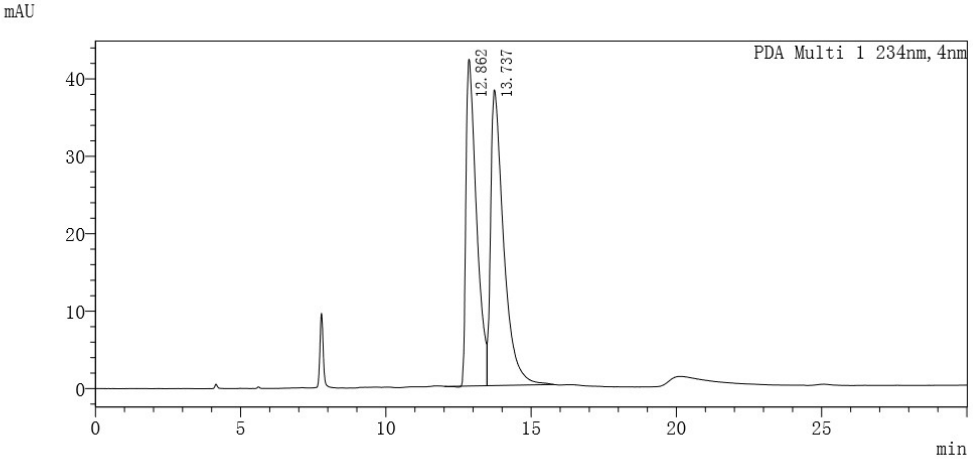
HRMS: (ESI) calcd for $C_{20}H_{24}NaO^{+}$[M+Na]$^{+}$ 303.1719; found 303.1714.

The enantiomeric purity was established by HPLC analysis using a chiral column: IA-H column, 30 °C, *n*-Hexane as eluent, 254 nm, 0.75 mL/min. tR = 12.8 min (major), 14.0 min (minor).

Optical Rotation: $[\alpha]_D^{30}$ -25.4 (c 0.35, $CHCl_3$) for 99% ee.

Absolute stereochemistry was determined through analogy with **3aa**.

〈色谱图〉



〈峰表〉

PDA Ch1 234nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	12.862	1067928	42203	0.000		M	
2	13.737	1189800	38195	0.000		V M	
总计		2257728	80398				

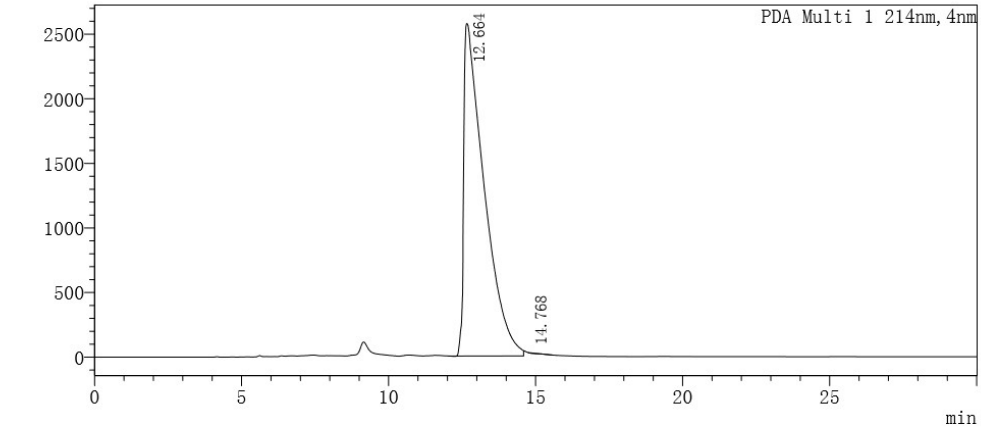
peak number

retention time

area

height

〈色谱图〉



〈峰表〉

PDA Ch1 214nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	12.664	123421424	2574686	0.000		M	
2	14.768	-67884	-356	0.000		M	
总计		123353540	2574329				

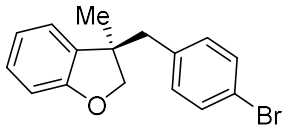
peak number

retention time

area

height

(*R*)-3-(4-bromobenzyl)-3-methyl-2,3-dihydrobenzofuran (**3ad**)



Chemical Formula: $C_{16}H_{15}BrO$
Exact Mass: 302.0306

3ad was prepared according to general procedure using **1a** and **2d** and was purified by silica gel column chromatography (petroleum ether/EtOAc = 100/1~50/1) to obtain **3ad** as colorless oil (63% yield). The ^{1}H NMR data matched those reported in the literature[2]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.31 (m, 2H), 7.14 (ddd, *J* = 8.0, 7.1, 1.7 Hz, 1H), 6.97-6.80 (m, 4H), 6.76 (dt, *J* = 8.0, 0.8 Hz, 1H), 4.45 (d, *J* = 8.8 Hz, 1H), 4.08 (d, *J* = 8.7 Hz, 1H), 2.83 (d, *J* = 2.9 Hz, 2H), 1.36 (s, 3H);

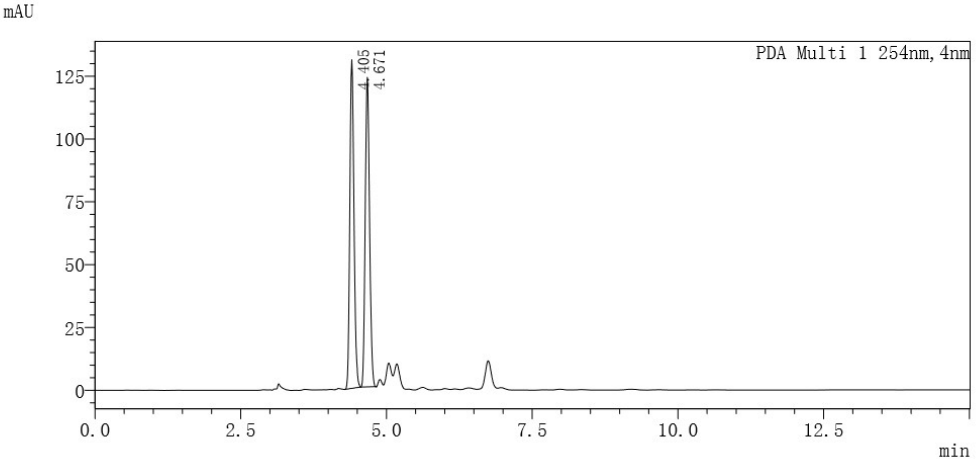
^{13}C NMR (101 MHz, $CDCl_3$): δ 159.5, 136.5, 134.1, 132.0, 131.0, 128.3, 123.3, 120.5, 120.3, 109.8, 81.8, 46.1, 24.4.

The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 97/3 as eluent, 254 nm, 1 mL/min. tR = 4.3 min (minor), 4.6 min (major).

Optical Rotation: $[\alpha]_D^{28}$ -30.2 (c 0.5, $CHCl_3$) for 93% ee.

Absolute stereochemistry was determined through analogy with **3aa**.

〈色谱图〉



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	4.405	645724	130826	0.000		M	
2	4.671	636255	123208	0.000		M	
总计		1281979	254033				

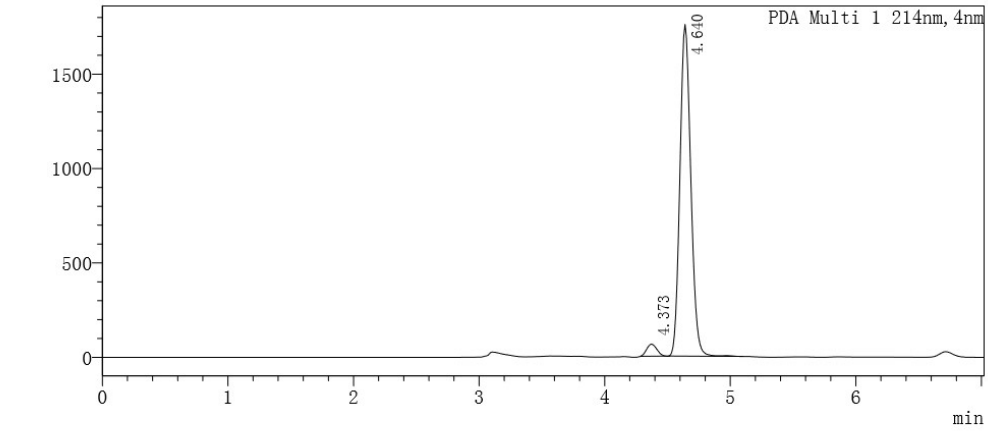
peak number

retention time

area

height

〈色谱图〉



〈峰表〉

PDA Ch1 214nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	4.373	358654	64125	0.000		M	
2	4.640	10541151	1757391	0.000		M	
总计		10899806	1821517				

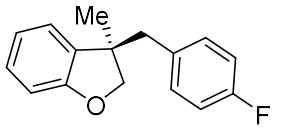
peak number

retention time

area

height

(*R*)-3-(4-fluorobenzyl)-3-methyl-2,3-dihydrobenzofuran (**3ae**)



Chemical Formula: $C_{16}H_{15}FO$
Exact Mass: 242.1107

3ae was prepared according to general procedure using **1a** and **2e** and was purified by silica gel column chromatography (petroleum ether/EtOAc = 100/1~50/1) to obtain **3ae** as colorless oil (72% yield). The ^{1}H NMR data matched those reported in the literature[1]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (ddd, *J* = 8.0, 7.2, 1.6 Hz, 1H), 6.92 (d, *J* = 7.1 Hz, 5H), 6.86 (td, *J* = 7.3, 1.0 Hz, 1H), 6.76 (dt, *J* = 8.0, 0.8 Hz, 1H), 4.47 (d, *J* = 8.7 Hz, 1H), 4.08 (d, *J* = 8.7 Hz, 1H), 2.87 (d, *J* = 13.2 Hz, 1H), 2.84 (d, *J* = 13.2 Hz, 1H), 1.37 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 161.8 (d, *J* = 244.5 Hz), 159.6, 134.3, 133.2 (d, *J* = 3.4 Hz), 131.7 (d, *J* = 7.9 Hz), 128.3, 123.3, 120.3, 114.7 (d, *J* = 21.1 Hz), 109.7, 81.8, 46.2, 45.9, 24.5;

^{19}F NMR (376 MHz, $CDCl_3$): δ -116.58;

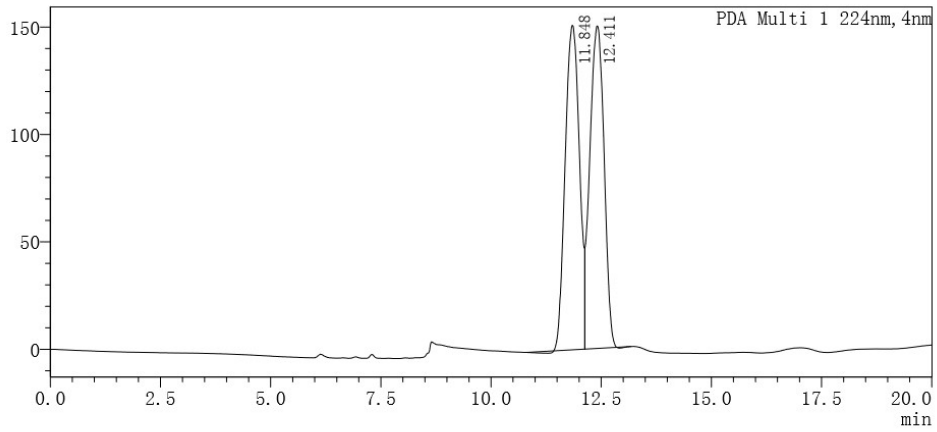
The enantiomeric purity was established by HPLC analysis using a chiral column: OD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 99.5/0.5 as eluent, 254 nm, 0.5 mL/min. tR = 11.8 min (major), 12.4 min (minor).

Optical Rotation: $[\alpha]_D^{30}$ -29.0 (c 0.23, $CHCl_3$) for 94% ee.

Absolute stereochemistry was determined through analogy with **3aa**.

<色谱图>

mAU



<峰表>

PDA Ch1 224nm

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1	11.848	3394603	151066	0.000		M	
2	12.411	3369248	150098	0.000		V M	
总计		6763851	301164				

peak number

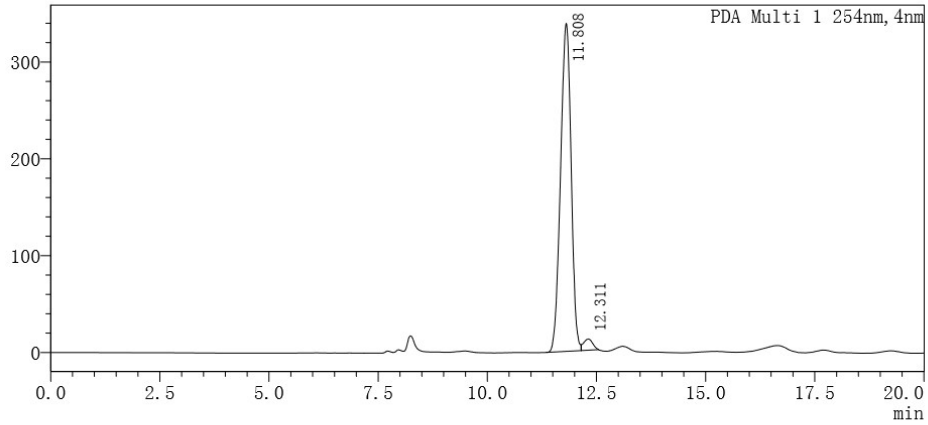
retention time

area

height

<色谱图>

mAU



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	11.808	5704432	338790	0.000		M	
2	12.311	167112	11572	0.000		V M	
总计		5871544	350362				

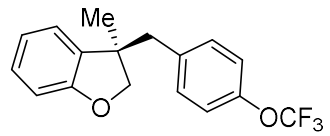
peak number

retention time

area

height

(*R*)-3-methyl-3-(4-(trifluoromethoxy)benzyl)-2,3-dihydrobenzofuran (**3af**)



Chemical Formula: $C_{17}H_{15}F_3O_2$
Exact Mass: 308.1024

3af was prepared according to general procedure using **1a** and **2f** and was purified by silica gel column chromatography (petroleum ether/EtOAc = 100/1~50/1) to obtain **3af** as colorless oil (72% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18-7.11 (m, 1H), 7.11-7.05 (m, 2H), 7.01-6.95 (m, 2H), 6.94-6.83 (m, 2H), 6.80-6.73 (m, 1H), 4.47 (d, *J* = 8.7 Hz, 1H), 4.09 (d, *J* = 8.8 Hz, 1H), 2.90 (d, *J* = 13.2 Hz, 1H), 2.86 (d, *J* = 13.2 Hz, 1H), 1.38 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.6, 148.1, 136.3, 134.3, 131.6, 128.5, 123.4, 120.6 (q, *J* = 256.7 Hz), 120.5, 109.9, 81.9, 46.3, 46.1, 24.5;

^{19}F NMR (376 MHz, $CDCl_3$): δ -57.8;

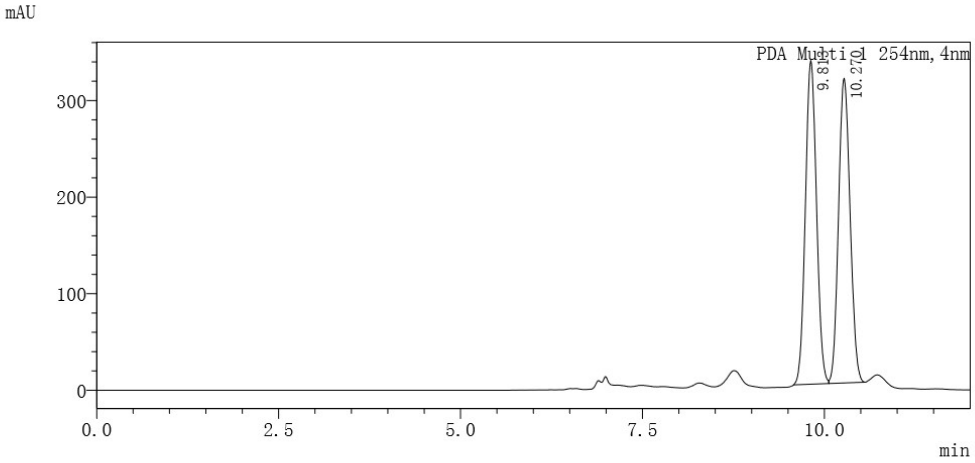
HRMS: (APCI) calcd for $C_{17}H_{15}F_3NaO_2^+$[M+Na]$^+$ 331.0916; found 331.0929.

The enantiomeric purity was established by HPLC analysis using a chiral column: OD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 99/1 as eluent, 254 nm, 0.5 mL/min. tR = 9.8 min (major), 10.2 min (minor).

Optical Rotation: $[\alpha]_D^{30}$ -24.4 (c 0.38, $CHCl_3$) for 92% ee.

Absolute stereochemistry was determined through analogy with **3aa**.

〈色谱图〉



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	9.813	3558921	335269	0.000		M	
2	10.270	3482360	315592	0.000		V M	
总计		7041281	650861				

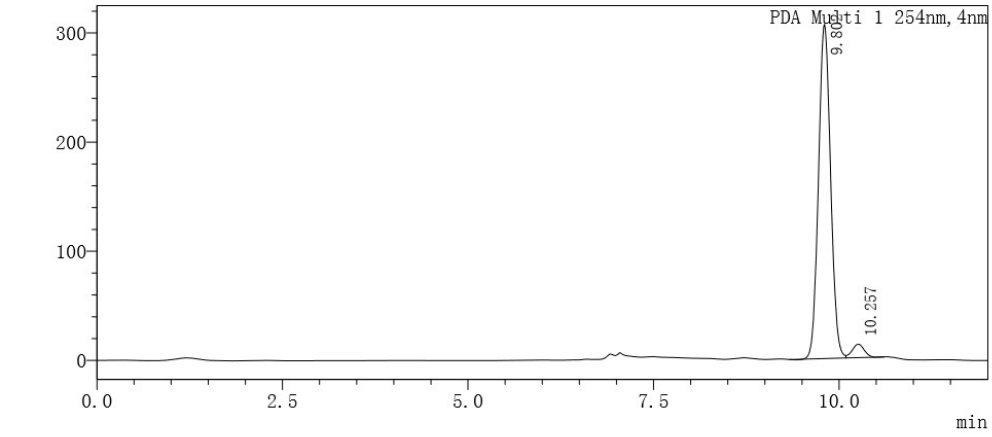
peak number

retention time

area

height

〈色谱图〉



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	9.802	3458652	306390	0.000		M	
2	10.257	138043	12365	0.000		V M	
总计		3596695	318755				

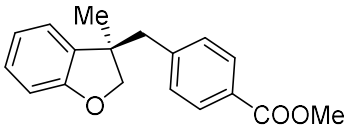
peak number

retention time

area

height

Methyl (*R*)-4-((3-methyl-2,3-dihydrobenzofuran-3-yl)methyl)benzoate (**3ag**)



Chemical Formula: $C_{18}H_{18}O_3$
Exact Mass: 282.1256

3ag was prepared according to general procedure using **1a** and **2g** and was purified by silica gel column chromatography (petroleum ether/EtOAc = 100/1~30/1) to obtain **3ag** as colorless oil (75% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.14 (ddd, *J* = 8.0, 7.1, 1.7 Hz, 1H), 7.06-6.98 (m, 2H), 6.95-6.82 (m, 2H), 6.75 (dt, *J* = 8.0, 0.8 Hz, 1H), 4.47 (d, *J* = 8.7 Hz, 1H), 4.08 (d, *J* = 8.7 Hz, 1H), 3.90 (s, 3H), 2.93 (d, *J* = 2.0 Hz, 2H), 1.38 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 167.0, 159.5, 142.9, 134.0, 130.3, 129.1, 128.4, 123.3, 120.3, 109.8, 81.8, 52.0, 46.7, 46.2, 24.5;

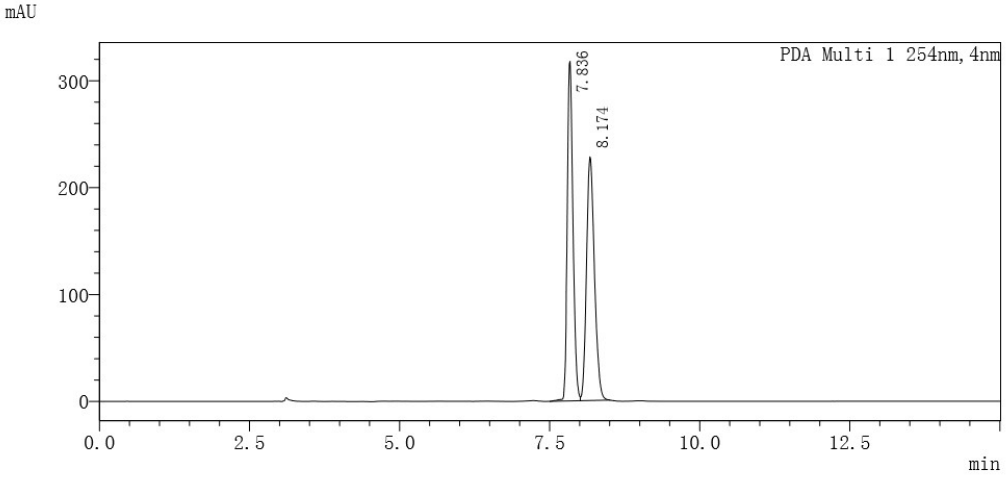
HRMS: (ESI) calcd for $C_{18}H_{19}O_3^+$[M+H]$^+$ 283.1329; found 283.1317.

The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 97/3 as eluent, 254 nm, 1 mL/min. tR = 7.8 min (minor), 8.2 min (major).

Optical Rotation: $[\alpha]_D^{28}$ -34.1 (c 0.3, $CHCl_3$) for 93% ee.

Absolute stereochemistry was determined through analogy with **3aa**.

〈色谱图〉



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	7.836	2094398	317763	0.000		M	
2	8.174	2094584	228006	0.000		V M	
总计		4188983	545768				

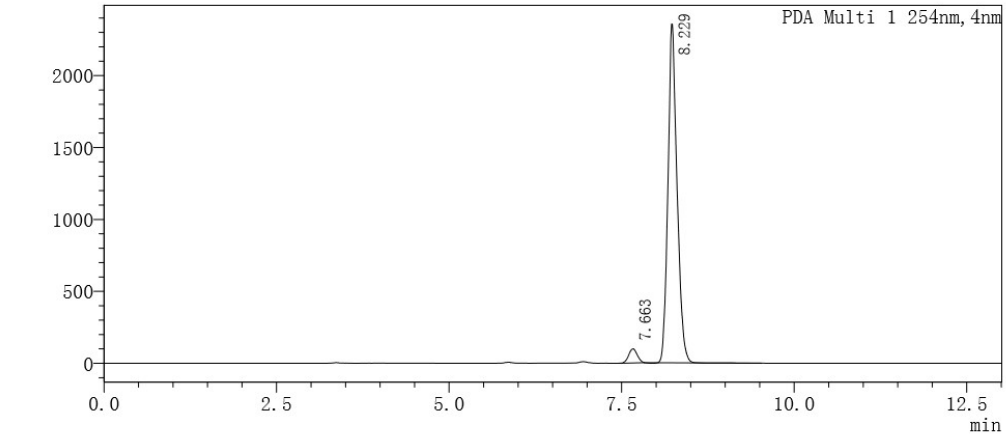
peak number

retention time

area

height

〈色谱图〉



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	7.663	844966	98944	0.000		M	
2	8.229	21447204	2354743	0.000		M	
总计		22292170	2453688				

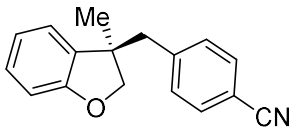
peak number

retention time

area

height

(*R*)-4-((3-methyl-2,3-dihydrobenzofuran-3-yl)methyl)benzonitrile (**3ah**)



Chemical Formula: $C_{17}H_{15}NO$
Exact Mass: 249.1154

3ah was prepared according to general procedure using **1a** and **2h** and was purified by silica gel column chromatography (petroleum ether/EtOAc = 100/1~30/1) to obtain **3ah** as colorless oil (50% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.46 (m, 2H), 7.19-7.08 (m, 1H), 7.04-6.98 (m, 2H), 6.92-6.82 (m, 2H), 6.73 (dt, *J* = 7.9, 0.8 Hz, 1H), 4.43 (d, *J* = 8.8 Hz, 1H), 4.10 (d, *J* = 8.9 Hz, 1H), 2.93 (d, *J* = 13.2 Hz, 1H), 2.89 (d, *J* = 13.2 Hz, 1H), 1.40 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.5, 143.1, 133.4, 131.6, 130.9, 128.6, 123.2, 120.5, 118.9, 110.5, 109.9, 81.7, 47.0, 46.3, 24.4;

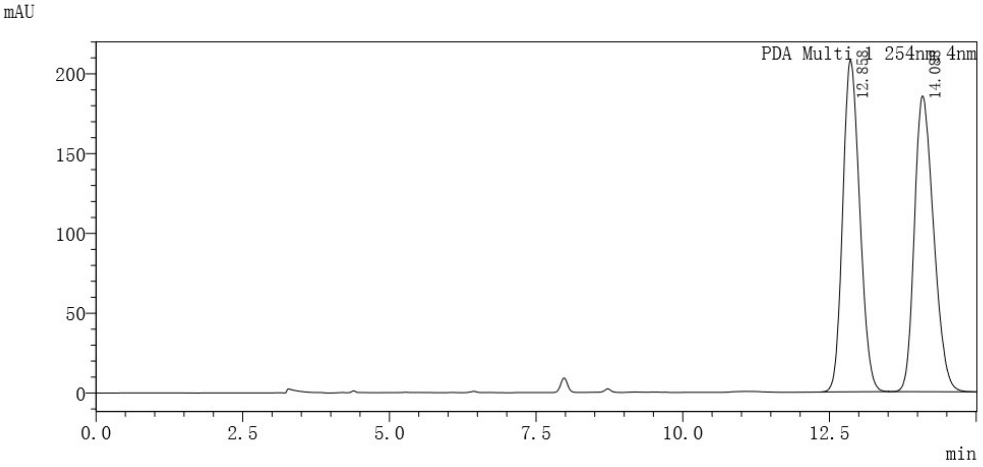
HRMS: (ESI) calcd for $C_{17}H_{15}NaNO^+$[M+Na]$^+$ 272.1046; found 272.1044.

The enantiomeric purity was established by HPLC analysis using a chiral column: OD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 98/2 as eluent, 254 nm, 1 mL/min. tR = 12.8 min (major), 14.1 min (minor).

Optical Rotation: $[\alpha]_D^{30}$ -29.8 (c 0.2, $CHCl_3$) for 96% ee.

Absolute stereochemistry was determined through analogy with **3aa**.

〈色谱图〉



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	12.858	4196621	207830	0.000		M	
2	14.088	4242168	185394	0.000		M	
总计		8438789	393224				

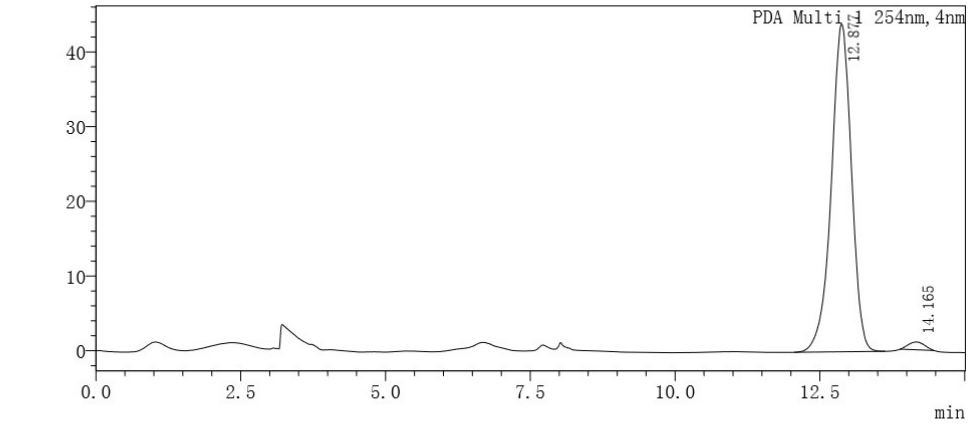
peak number

retention time

area

height

〈色谱图〉



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	12.877	1065815	43884	0.000		M	
2	14.165	20424	1054	0.000		M	
总计		1086239	44938				

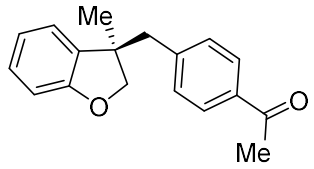
peak number

retention time

area

height

(*R*)-1-(4-((3-methyl-2,3-dihydrobenzofuran-3-yl)methyl)phenyl)ethan-1-one (**3ai**)



Chemical Formula: $C_{18}H_{18}O_2$
Exact Mass: 266.1307

3ai was prepared according to general procedure using **1a** and **2i** and was purified by silica gel column chromatography (petroleum ether/EtOAc = 100/1~30/1) to obtain **3ai** as colorless oil (91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88-7.76 (m, 2H), 7.17-7.08 (m, 1H), 7.06-7.01 (m, 2H), 6.97- 6.81 (m, 2H), 6.74 (dt, *J* = 8.1, 0.7 Hz, 1H), 4.46 (d, *J* = 8.7 Hz, 1H), 4.07 (d, *J* = 8.8 Hz, 1H), 2.94 (d, *J* = 13.2 Hz, 1H), 2.90 (d, *J* = 13.2 Hz, 1H), 2.56 (s, 3H), 1.37 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 197.8, 159.5, 143.2, 135.5, 134.0, 130.5, 128.4, 128.0, 123.3, 120.4, 109.8, 81.8, 46.7, 46.3, 26.5, 24.5;

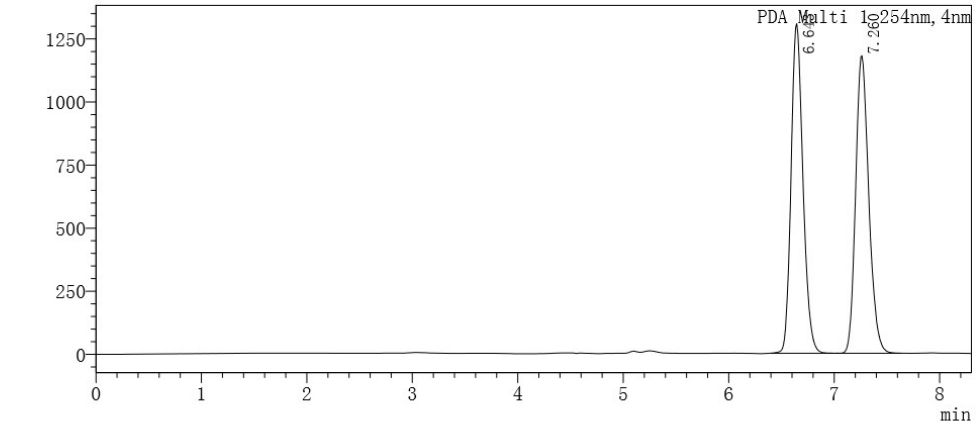
HRMS: (ESI) calcd for $C_{18}H_{18}NaO_2^+$[M+Na]$^+$ 289.1199; found 289.1193.

The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 90/10 as eluent, 254 nm, 1 mL/min. tR = 6.6 min (minor), 7.2 min (major).

Optical Rotation: $[\alpha]_D^{30}$ -41.7 (c 0.23, $CHCl_3$) for 94% ee.

Absolute stereochemistry was determined through analogy with **3aa**.

〈色谱图〉



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	6.643	10226235	1306393	0.000		M	
2	7.260	10202715	1179234	0.000		M	
总计		20428949	2485628				

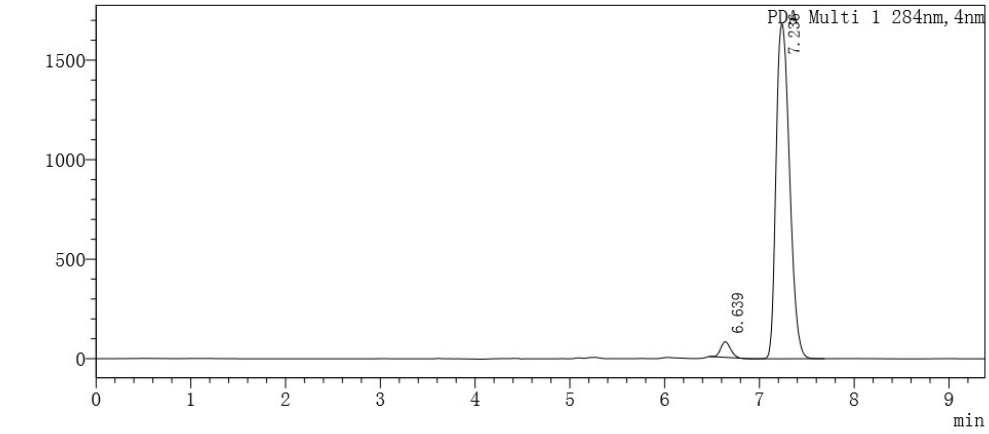
peak number

retention time

area

height

〈色谱图〉



〈峰表〉

PDA Ch1 284nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	6.639	558895	78386	0.000		M	
2	7.236	16708239	1682879	0.000		M	
总计		17267134	1761264				

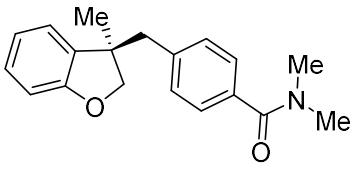
peak number

retention time

area

height

(*R*)-N,N-dimethyl-4-((3-methyl-2,3-dihydrobenzofuran-3-yl)methyl)benzamide (**3aj**)



Chemical Formula: $C_{19}H_{21}NO_2$
Exact Mass: 295.1572

3aj was prepared according to general procedure using **1a** and **2j** and was purified by silica gel column chromatography (petroleum ether/EtOAc = 100/1~30/1) to obtain **3aj** as colorless oil (91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.38 (m, 1H), 7.32-7.27 (m, 2H), 7.16-7.09 (m, 1H), 7.03-6.98 (m, 2H), 6.94-6.90 (m, 1H), 6.85 (td, *J* = 7.4, 1.0 Hz, 1H), 6.77-6.72 (m, 1H), 4.47 (d, *J* = 8.8 Hz, 1H), 4.06 (d, *J* = 8.7 Hz, 1H), 3.03 (bs, 6H), 2.89 (d, *J* = 2.1 Hz, 2H), 1.36 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.6, 159.5, 139.2, 134.4, 130.2, 128.3, 128.3, 127.0, 126.8, 123.3, 120.3, 109.7, 81.8, 46.5, 46.2, 24.4;

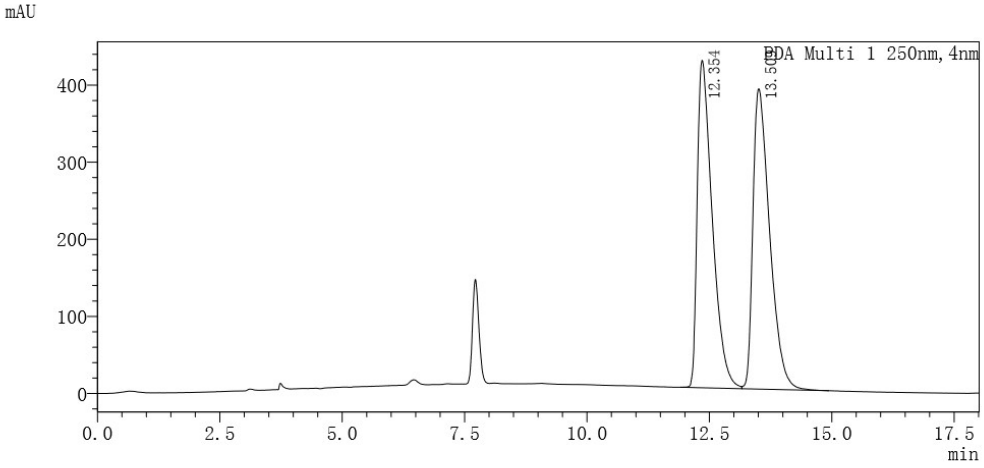
HRMS: (ESI) calcd for $C_{19}H_{21}NNaO_2^+$[M+Na]$^+$ 318.1465; found 318.4166.

The enantiomeric purity was established by HPLC analysis using a chiral column: OJ-H column, 30 °C, *n*-Hexane/*i*-Propanol = 85/15 as eluent, 254 nm, 1 mL/min. tR = 12.3 min (major), 13.5 min (minor).

Optical Rotation: $[\alpha]_D^{30}$ -28.2 (c 0.35, $CHCl_3$) for 92% ee.

Absolute stereochemistry was determined through analogy with **3aa**.

〈色谱图〉



〈峰表〉

PDA Ch1 250nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	12.354	9084411	424953	0.000		M	
2	13.509	9283903	389558	0.000		V M	
总计		18368314	814511				

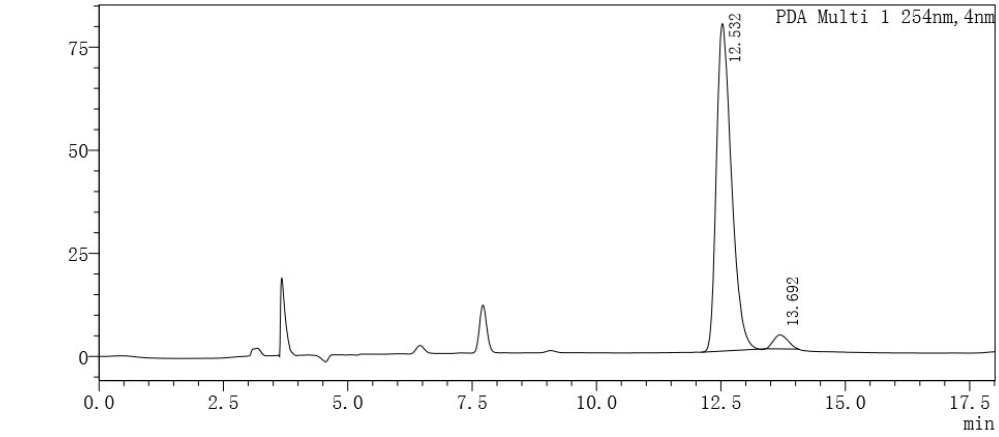
peak number

retention time

area

height

〈色谱图〉



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	12.532	1679560	79444	0.000		M	
2	13.692	68934	3432	0.000		M	
总计		1748493	82876				

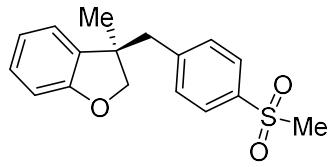
peak number

retention time

area

height

(*R*)-3-methyl-3-(4-(methylsulfonyl)benzyl)-2,3-dihydrobenzofuran (**3ak**)



Chemical Formula: $C_{17}H_{18}O_3S$
Exact Mass: 302.0977

3ak was prepared according to general procedure using **1a** and **2k** and was purified by silica gel column chromatography (petroleum ether/EtOAc = 100/1~30/1) to obtain **3ak** as colorless oil (65% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.3 Hz, 1H), 7.20-7.06 (m, 3H), 6.96-6.81 (m,2H), 6.78-6.69 (m, 1H), 4.45 (d, *J* = 8.8 Hz, 1H), 4.10 (d, *J* = 8.8 Hz, 1H), 3.04 (s, 3H), 2.96 (d, *J* = 1.1 Hz, 2H), 1.39 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.6, 144.2, 138.8, 133.6, 131.3, 128.7, 127.0, 123.4, 120.6, 110.0, 81.8, 46.7, 46.4, 44.6, 24.5;

HRMS: (ESI) calcd for $C_{17}H_{18}NaO_3S^+$[M+Na]$^+$ 325.0869; found 325.0864.

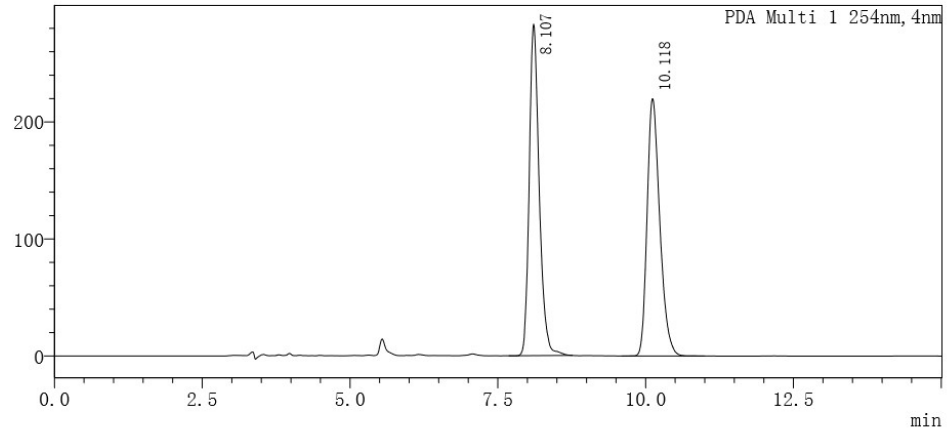
The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 70/30 as eluent, 254 nm, 1 mL/min. tR = 8.1 min (minor), 10.1 min (major).

Optical Rotation: $[\alpha]_D^{30}$ -24.1 (c 0.42, $CHCl_3$) for 90% ee.

Absolute stereochemistry was determined through analogy with **3aa**.

〈色谱图〉

mAU



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	8.107	3327200	283535	0.000		M	
2	10.118	3278109	219863	0.000		M	
总计		6605309	503397				

peak number

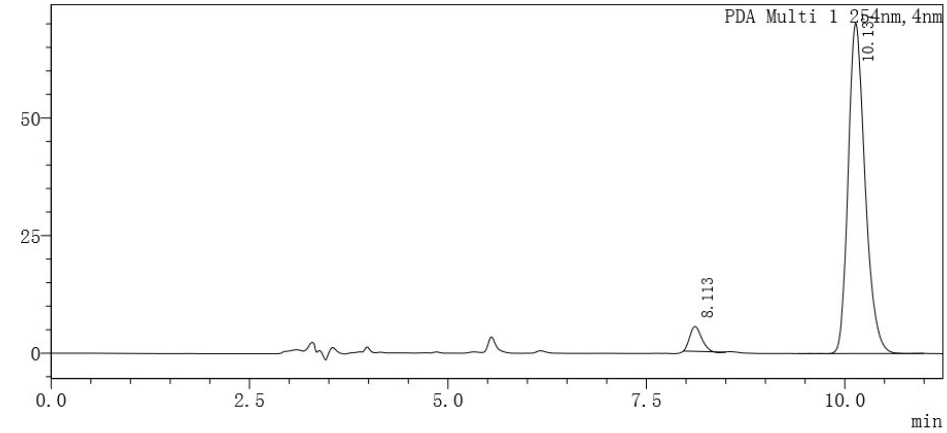
retention time

area

height

〈色谱图〉

mAU



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	8.113	53587	5266	0.000		M	
2	10.137	1038409	70205	0.000		M	
总计		1091995	75471				

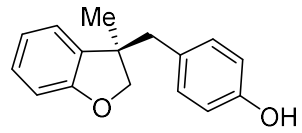
peak number

retention time

area

height

(*R*)-4-((3-methyl-2,3-dihydrobenzofuran-3-yl)methyl)phenol (**3al**)



Chemical Formula: $C_{16}H_{16}O_2$
Exact Mass: 240.1150

3al was prepared according to general procedure using **1a** and **2l** and was purified by silica gel column chromatography (petroleum ether/EtOAc = 100/1~30/1) to obtain **3al** as colorless oil (81% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13 (ddd, *J* = 8.0, 7.4, 1.5 Hz, 1H), 6.94 (dd, *J* = 7.4, 1.5 Hz, 1H), 6.90-6.82 (m, 3H), 6.79-6.73 (m, 1H), 6.73-6.66 (m, 2H), 4.48 (d, *J* = 8.7 Hz, 1H), 4.07 (d, *J* = 8.7 Hz, 1H), 2.83 (d, *J* = 13.2 Hz, 1H), 2.79 (d, *J* = 13.2 Hz, 1H), 1.35 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.5, 154.2, 134.8, 131.4, 129.7, 128.1, 123.4, 120.3, 114.8, 109.7, 81.9, 46.3, 45.8, 24.6;

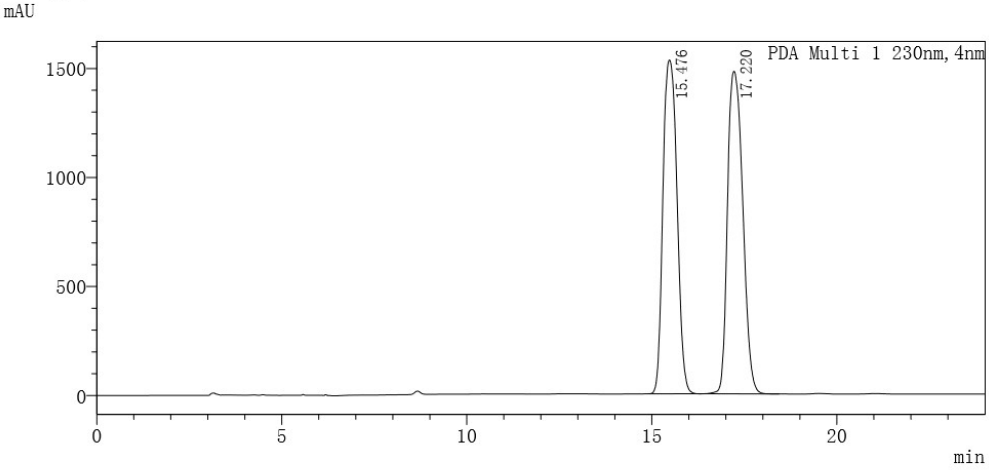
HRMS: (ESI) calcd for $C_{16}H_{15}O_2^-$[M-H]$^-$ 239.1078; found 239.1076.

The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 95/5 as eluent, 254 nm, 1 mL/min. tR = 15.4 min (major), 17.3 min (minor).

Optical Rotation: $[\alpha]_D^{30}$ -23.9 (c 0.45, $CHCl_3$) for 94% ee.

Absolute stereochemistry was determined through analogy with **3aa**.

〈色谱图〉



〈峰表〉

PDA Ch1 230nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	15.476	40530200	1531314	0.000		M	
2	17.220	42467195	1479441	0.000		M	
总计		82997395	3010755				

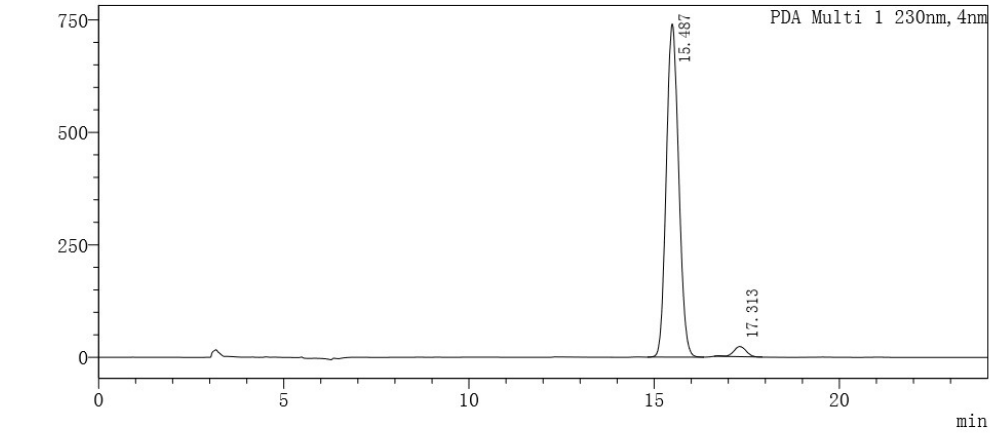
peak number

retention time

area

height

〈色谱图〉



〈峰表〉

PDA Ch1 230nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	15.487	17263812	740573	0.000		M	
2	17.313	534647	22744	0.000		M	
总计		17798459	763317				

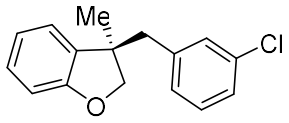
peak number

retention time

area

height

(*R*)-3-(3-chlorobenzyl)-3-methyl-2,3-dihydrobenzofuran (**3am**)



Chemical Formula: $C_{16}H_{15}ClO$
Exact Mass: 258.0811

3am was prepared according to general procedure using **1a** and **2m** and was purified by silica gel column chromatography (petroleum ether/EtOAc = 100/1~30/1) to obtain **3am** as colorless oil (75% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24-7.10 (m, 3H), 6.99-6.82 (m, 4H), 6.77 (dt, *J* = 8.0, 0.8 Hz, 1H), 4.47 (d, *J* = 8.8 Hz, 1H), 4.08 (d, *J* = 8.8 Hz, 1H), 2.88 (d, *J* = 13.2 Hz, 1H), 2.83 (d, *J* = 13.2 Hz, 1H), 1.37 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.5, 139.5, 134.2, 133.7, 130.3, 129.1, 128.5, 128.4, 126.7, 123.3, 120.4, 109.8, 81.7, 46.3, 46.2, 24.4;

HRMS: (ESI) calcd for $C_{16}H_{15}ClNaO^+$ $[M+Na]^+$ 281.0704; found 281.0702.

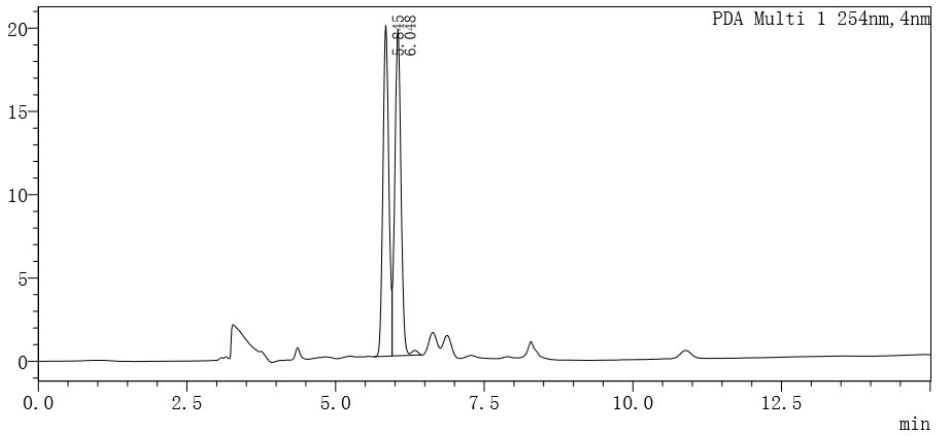
The enantiomeric purity was established by HPLC analysis using a chiral column: OD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 98/2 as eluent, 254 nm, 1 mL/min. tR = 5.8 min (major), 6.0 min (minor).

Optical Rotation: $[\alpha]_D^{30}$ -38.0 (c 0.25, $CHCl_3$) for 93% ee.

Absolute stereochemistry was determined through analogy with **3aa**.

〈色谱图〉

mAU



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	5.845	137957	19871	0.000		M	
2	6.048	140522	19600	0.000		V M	
总计		278479	39471				

peak number

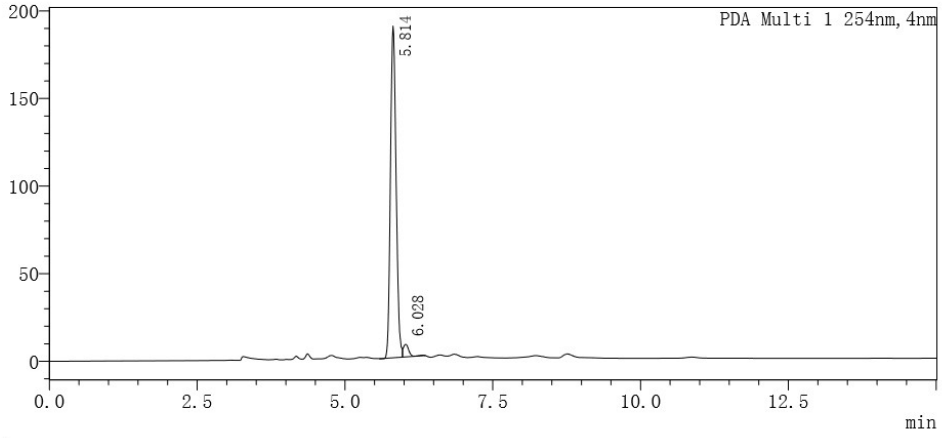
retention time

area

height

〈色谱图〉

mAU



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	5.814	1255885	189384	0.000		M	
2	6.028	45261	7192	0.000		V M	
总计		1301146	196576				

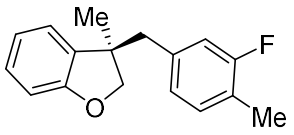
peak number

retention time

area

height

(*R*)-3-(3-fluoro-4-methylbenzyl)-3-methyl-2,3-dihydrobenzofuran (**3an**)



Chemical Formula: $C_{17}H_{17}FO$
Exact Mass: 256.1263

3an was prepared according to general procedure using **1a** and **2n** and was purified by silica gel column chromatography (petroleum ether/EtOAc = 100/1~30/1) to obtain **3an** as colorless oil (72% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (ddd, *J* = 8.0, 7.3, 1.5 Hz, 1H), 7.07-7.00 (m, 1H), 6.98-6.94 (m, 1H), 6.88 (td, *J* = 7.4, 1.0 Hz, 1H), 6.77 (dt, *J* = 8.0, 0.8 Hz, 1H), 6.70-6.60 (m, 2H), 4.47 (d, *J* = 8.7 Hz, 1H), 4.07 (d, *J* = 8.7 Hz, 1H), 2.86 (d, *J* = 13.2 Hz, 1H), 2.82 (d, *J* = 13.2 Hz, 1H), 2.24 (d, *J* = 1.8 Hz, 3H), 1.37 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 160.8 (d, *J* = 244.2 Hz), 159.5, 137.1 (d, *J* = 7.2 Hz), 134.50, 130.8 (d, *J* = 5.6 Hz), 128.3, 125.7 (d, *J* = 3.3 Hz), 123.2, 122.7 (d, *J* = 17.2 Hz), 120.4, 116.7 (d, *J* = 22.0 Hz), 109.7, 81.8, 46.2, 46.1, 24.6, 14.2 (d, *J* = 3.5 Hz);

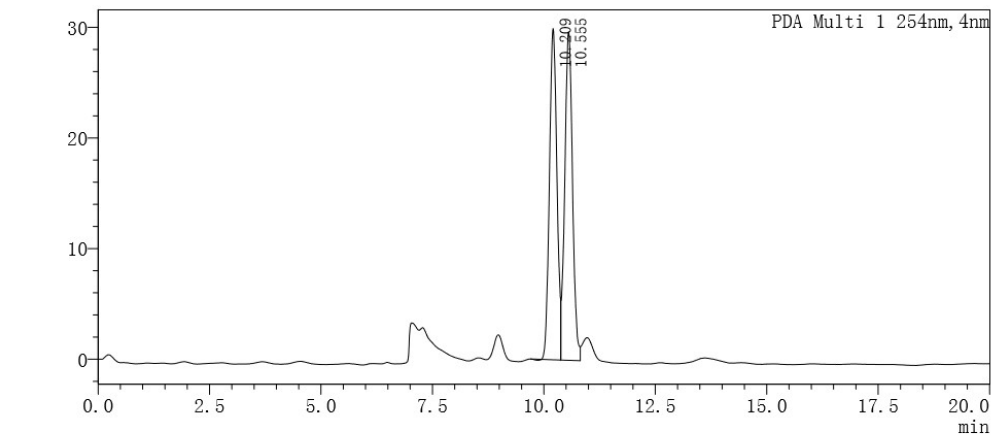
HRMS: (APCI) calcd for $C_{17}H_{17}FNaO^+$ $[M+Na]^+$ 279.1156; found 279.1152.

The enantiomeric purity was established by HPLC analysis using a chiral column: OD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 99/1 as eluent, 254 nm, 0.5 mL/min. tR = 10.3 min (major), 10.5 min (minor).

Optical Rotation: $[\alpha]_D^{30}$ -29.9 (c 0.29, $CHCl_3$) for 94% ee.

Absolute stereochemistry was determined through analogy with **3aa**.

〈色谱图〉



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	10.209	347894	29957	0.000		M	
2	10.555	358681	29691	0.000		V M	
总计		706575	59648				

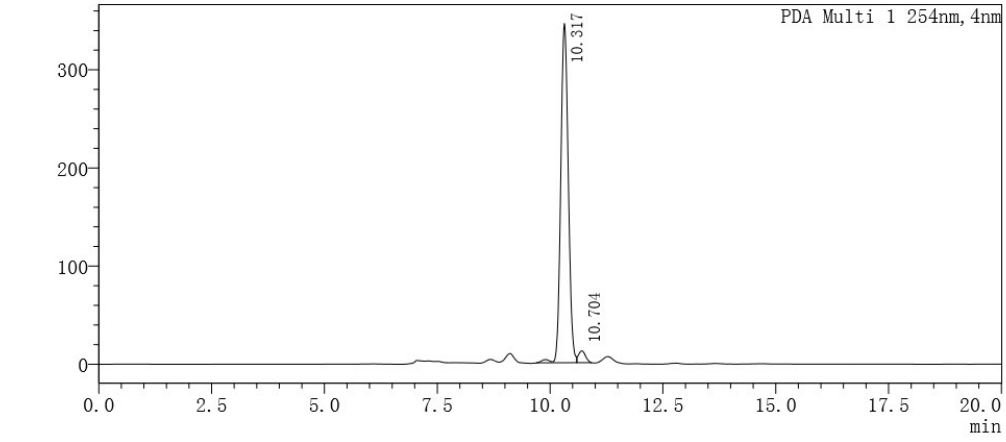
peak number

retention time

area

height

〈色谱图〉



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	10.317	4013492	345810	0.000		M	
2	10.704	128053	12056	0.000		V M	
总计		4141545	357867				

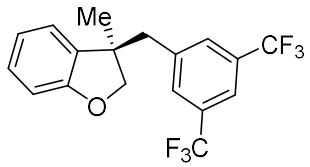
peak number

retention time

area

height

(*R*)-3-(3,5-bis(trifluoromethyl)benzyl)-3-methyl-2,3-dihydrobenzofuran (**3ao**)



Chemical Formula: $C_{18}H_{14}F_6O$
Exact Mass: 360.0949

3ao was prepared according to general procedure using **1a** and **2o** and was purified by silica gel column chromatography (petroleum ether/EtOAc = 100/1~30/1) to obtain **3ao** as colorless oil (27% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73-7.68 (m, 1H), 7.27-7.20 (m, 2H), 7.15 (ddd, *J* = 8.1, 7.0, 1.9 Hz, 1H), 6.94-6.82 (m, 2H), 6.70 (dt, *J* = 8.1, 0.8 Hz, 1H), 4.40 (d, *J* = 8.9 Hz, 1H), 4.12 (d, *J* = 8.9 Hz, 1H), 2.95 (s, 2H), 1.42 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.6, 139.8, 132.7, 131.1, 130.8, 130.2, 128.9, 123.3 (q, *J* = 272.3 Hz), 123.2, 120.6, 110.1, 81.5, 46.7, 46.3, 23.9;

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.81;

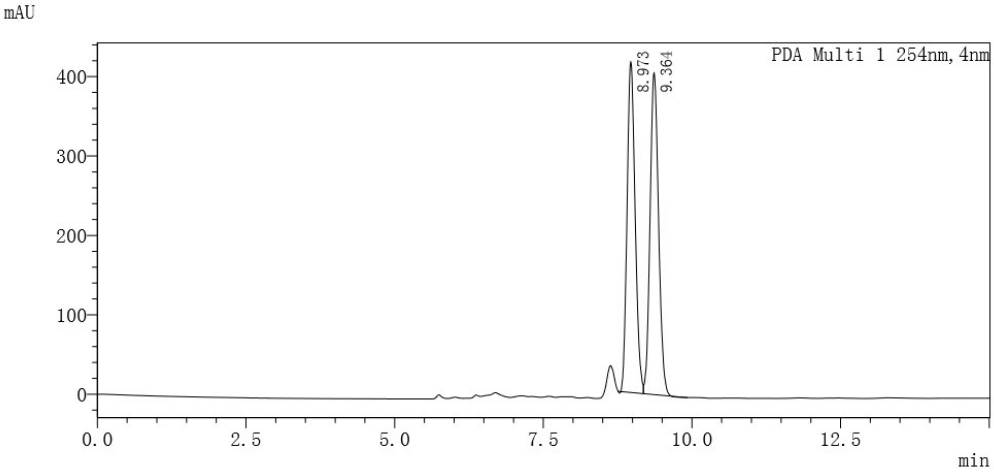
HRMS: (APCI) calcd for $C_{18}H_{15}F_6O^+$ $[M+H]^+$ 361.1022; found 361.1036.

The enantiomeric purity was established by HPLC analysis using a chiral column: OD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 98/2 as eluent, 254 nm, 0.5 mL/min. tR = 8.9 min (minor), 9.3 min (major).

Optical Rotation: $[\alpha]_D^{30}$ -201.4 (c 0.03, $CHCl_3$) for 88% ee.

Absolute stereochemistry was determined through analogy with **3aa**.

〈色谱图〉



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	8.973	3928331	416799	0.000		M	
2	9.364	4020014	405646	0.000		V M	
总计		7948345	822445				

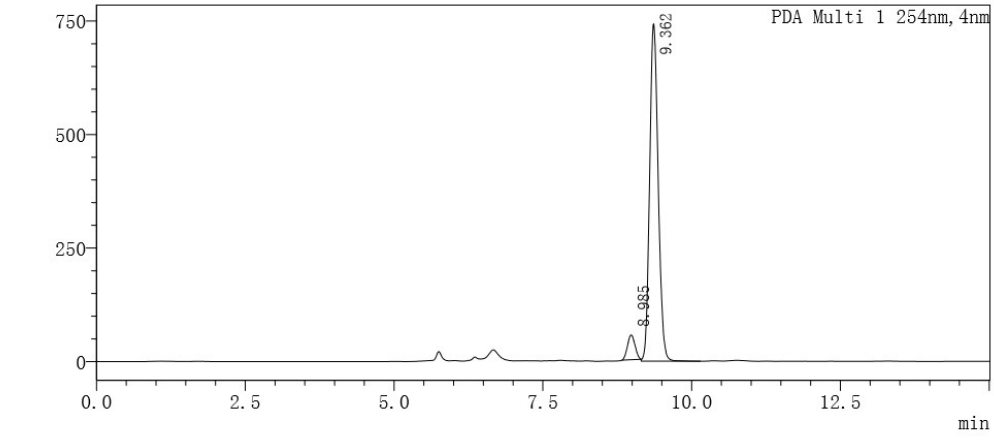
peak number

retention time

area

height

〈色谱图〉



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	8.985	478007	54531	0.000		M	
2	9.362	7404470	743166	0.000		M	
总计		7882477	797697				

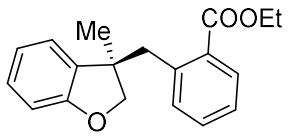
peak number

retention time

area

height

Ethyl (R)-2-((3-methyl-2,3-dihydrobenzofuran-3-yl)methyl)benzoate (**3ap**)



Chemical Formula: $C_{19}H_{20}O_3$
Exact Mass: 296.1412

3ap was prepared according to general procedure using **1a** and **2p** and was purified by silica gel column chromatography (petroleum ether/EtOAc = 100/1~30/1) to obtain **3ap** as colorless oil (53% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (dd, *J* = 7.5, 1.9 Hz, 1H), 7.35-7.22 (m, 2H), 7.17-7.04 (m, 1H), 6.95-6.79 (m, 3H), 6.72 (dd, *J* = 8.1, 0.8 Hz, 1H), 4.46 (d, *J* = 8.8 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 4.09 (d, *J* = 8.8 Hz, 1H), 3.70 (d, *J* = 13.1 Hz, 1H), 3.19 (d, *J* = 13.1 Hz, 1H), 1.36 (s, 3H), 1.35 (t, *J* = 3.6 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 168.0, 159.6, 138.8, 134.4, 132.5, 131.5, 131.0, 130.4, 128.1, 126.4, 123.5, 120.2, 109.6, 82.3, 60.9, 46.8, 42.3, 24.9, 14.2;

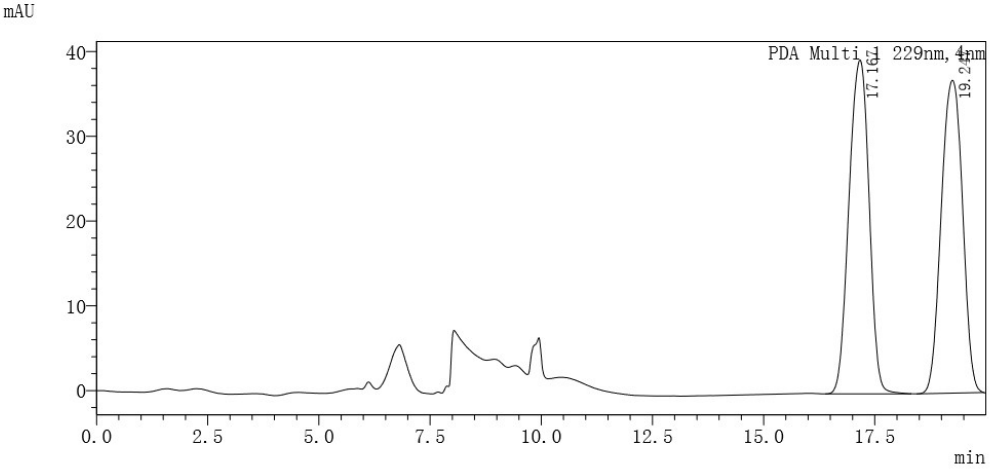
HRMS: (ESI) calcd for $C_{19}H_{20}NaO_3^+$ $[M+Na]^+$ 319.1305; found 319.1300.

The enantiomeric purity was established by HPLC analysis using a chiral column: OD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 99.5/0.5 as eluent, 254 nm, 0.5 mL/min. tR = 17.1 min (major), 19.2 min (minor).

Optical Rotation: $[\alpha]_D^{30}$ -97.9 (c 0.05, $CHCl_3$) for 90% ee.

Absolute stereochemistry was determined through analogy with **3aa**.

〈色谱图〉



〈峰表〉

PDA Ch1 229nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	17.167	1239409	39384	0.000			
2	19.247	1230395	36912	0.000			
总计		2469804	76296				

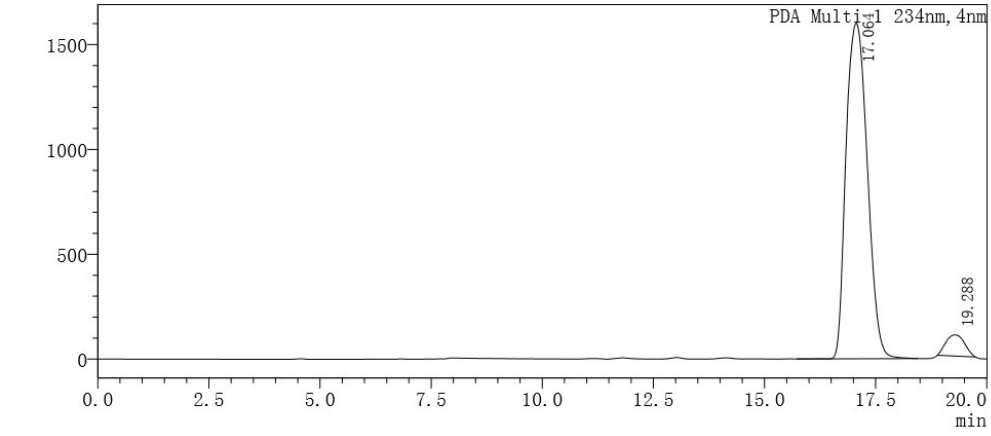
peak number

retention time

area

height

〈色谱图〉



〈峰表〉

PDA Ch1 234nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	17.064	53507884	1600927	0.000		M	
2	19.288	2963965	101405	0.000		M	
总计		56471849	1702332				

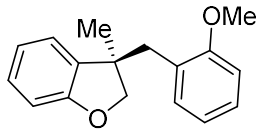
peak number

retention time

area

height

(*R*)-3-(2-methoxybenzyl)-3-methyl-2,3-dihydrobenzofuran (**3aq**)



Chemical Formula: $C_{17}H_{18}O_2$
Exact Mass: 254.1307

3aq was prepared according to general procedure using **1a** and **2q** and was purified by silica gel column chromatography (petroleum ether/EtOAc = 100/1~30/1) to obtain **3aq** as colorless oil (43% yield). The ^{1}H NMR data matched those reported in the literature[1]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (ddd, *J* = 8.2, 7.3, 1.8 Hz, 1H), 7.12 (ddd, *J* = 8.0, 7.4, 1.4 Hz, 1H), 7.01 (ddd, *J* = 7.4, 1.5, 0.5 Hz, 1H), 6.92-6.78 (m, 4H), 6.76 (dt, *J* = 8.0, 0.8 Hz, 1H), 4.57 (d, *J* = 8.6 Hz, 1H), 4.06 (d, *J* = 8.6 Hz, 1H), 3.74 (s, 3H), 3.05 (d, *J* = 13.2 Hz, 1H), 2.91 (d, *J* = 13.2 Hz, 1H), 1.34 (s, 3H);

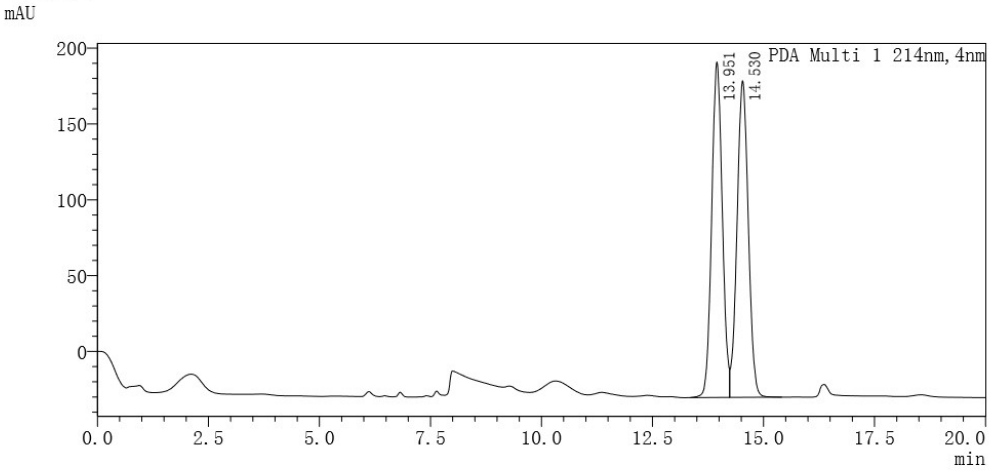
^{13}C NMR (101 MHz, $CDCl_3$): δ 159.5, 157.9, 135.5, 132.1, 127.9, 127.7, 126.3, 123.2, 120.1, 119.9, 110.3, 109.5, 82.4, 55.0, 46.7, 39.3, 24.9;

The enantiomeric purity was established by HPLC analysis using a chiral column: OD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 99.5/0.5 as eluent, 254 nm, 0.5 mL/min. tR = 14.0 min (major), 14.5 min (minor).

Optical Rotation: $[\alpha]_D^{30}$ **-**249.0 (c 0.02, $CHCl_3$) for 90% ee.

Absolute stereochemistry was determined through analogy with **3aa**.

〈色谱图〉



〈峰表〉

PDA Ch1 214nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	13.951	3684184	221247	0.000		M	
2	14.530	3690388	208769	0.000		V M	
总计		7374572	430016				

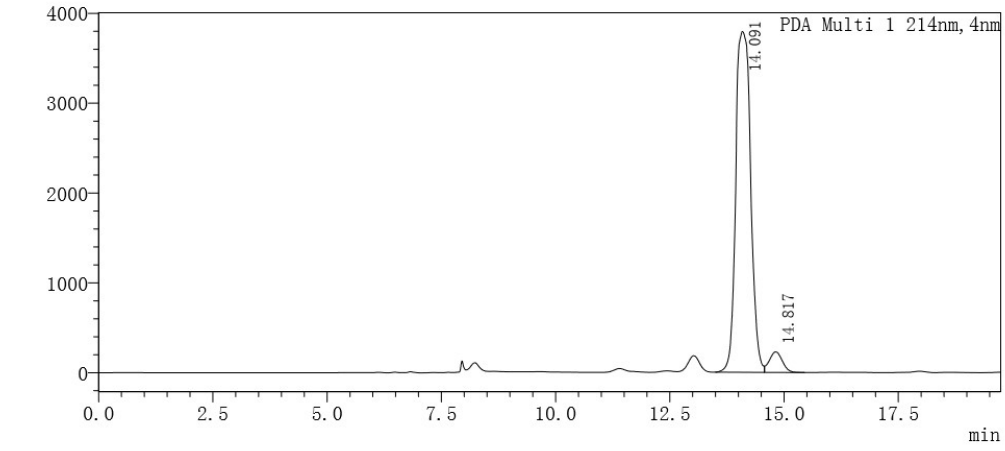
peak number

retention time

area

height

〈色谱图〉



〈峰表〉

PDA Ch1 214nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	14.091	86070441	3792636	0.000		M	
2	14.817	4502195	228853	0.000		V M	
总计		90572636	4021489				

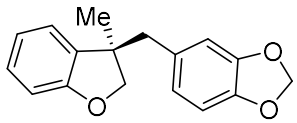
peak number

retention time

area

height

(*R*)-5-((3-methyl-2,3-dihydrobenzofuran-3-yl)methyl)benzo[d][1,3]dioxole (**3ar**)



Chemical Formula: $C_{17}H_{16}O_3$
Exact Mass: 268.1099

3ar was prepared according to general procedure using **1a** and **2r** and was purified by silica gel column chromatography (petroleum ether/EtOAc = 100/1~30/1) to obtain **3ar** as colorless oil (78% yield). The ^{1}H NMR data matched those reported in the literature[1]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18-7.09 (m, 1H), 6.94-6.99 (m, 1H), 6.90-6.84 (m, 1H), 6.79-6.74 (m, 1H), 6.71-6.66 (m, 1H), 6.48-6.41 (m, 2H), 5.93-5.91 (m, 2H), 4.47 (d, *J* = 8.6 Hz, 1H), 4.06 (d, *J* = 8.6 Hz, 1H), 2.83 (d, *J* = 13.2 Hz, 1H), 2.78 (d, *J* = 13.2 Hz, 1H), 1.35 (s, 3H);

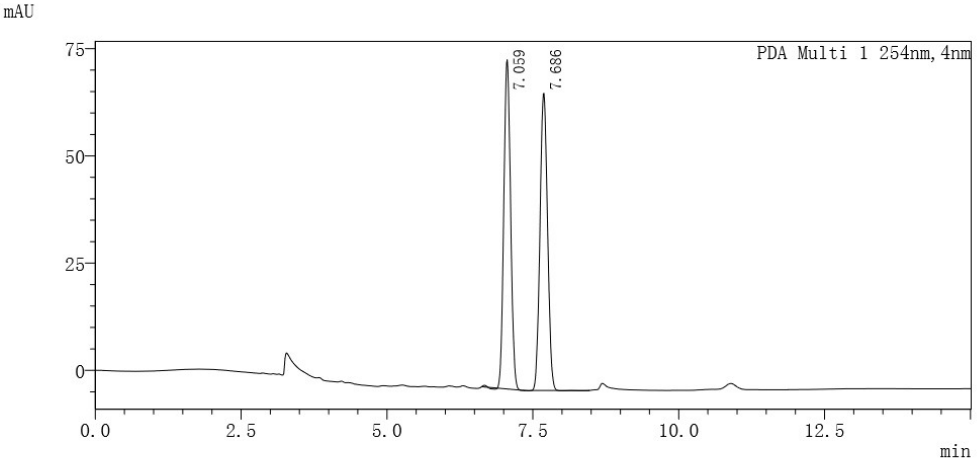
^{13}C NMR (101 MHz, $CDCl_3$): δ 159.5, 147.2, 146.2, 134.7, 131.3, 128.2, 123.4, 123.3, 123.3, 120.3, 110.6, 109.7, 107.8, 100.8, 81.8, 46.35, 46.33, 24.7;

The enantiomeric purity was established by HPLC analysis using a chiral column: OD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 98/2 as eluent, 254 nm, 1 mL/min. tR = 7.0 min (major), 7.7 min (minor).

Optical Rotation: $[\alpha]_D^{30}$ -170.0 (c 0.03, $CHCl_3$) for 92% ee.

Absolute stereochemistry was determined through analogy with **3aa**.

〈色谱图〉



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	7.059	617673	76802	0.000		M	
2	7.686	621121	69320	0.000		M	
总计		1238794	146122				

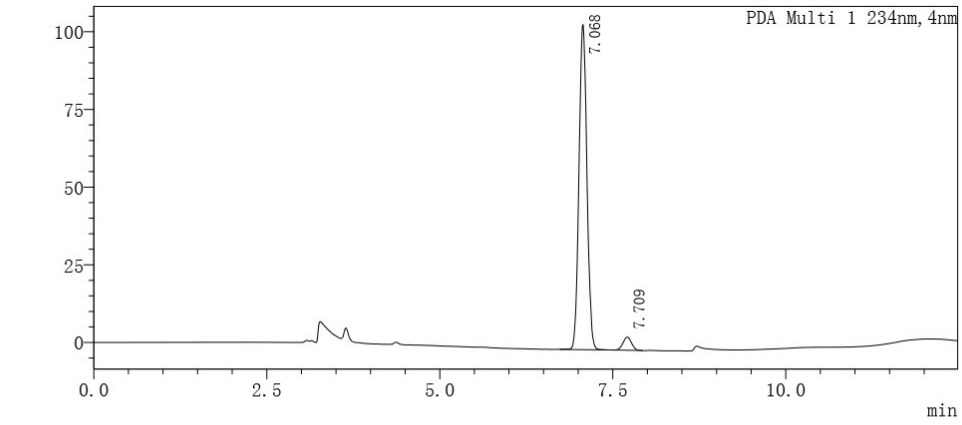
peak number

retention time

area

height

〈色谱图〉



〈峰表〉

PDA Ch1 234nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	7.068	834286	104700	0.000		M	
2	7.709	36153	4221	0.000		M	
总计		870438	108921				

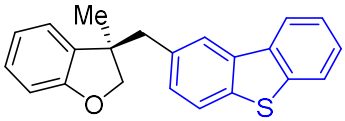
peak number

retention time

area

height

(*R*)-3-(dibenzo[*b,d*]thiophen-2-ylmethyl)-3-methyl-2,3-dihydrobenzofuran (**3as**)



Chemical Formula: $C_{22}H_{18}OS$
Exact Mass: 330.1078

3as was prepared according to general procedure using **1a** and **2s** and was purified by silica gel column chromatography (petroleum ether/EtOAc = 100/1~20/1) to obtain **3as** as colorless oil (91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18-8.01 (m, 1H), 7.91-7.82 (m, 1H), 7.78-7.69 (m, 2H), 7.55-7.39 (m, 2H), 7.19 (ddd, *J* = 8.0, 7.3, 1.5 Hz, 1H), 7.11 (dd, *J* = 8.1, 1.8 Hz, 1H), 6.99 (ddd, *J* = 7.3, 1.5, 0.5 Hz, 1H), 6.91 (td, *J* = 7.4, 1.0 Hz, 1H), 6.81 (dt, *J* = 8.0, 0.8 Hz, 1H), 4.59 (d, *J* = 8.7 Hz, 1H), 4.14 (d, *J* = 8.7 Hz, 1H), 3.07 (d, *J* = 3.9 Hz, 2H), 1.45 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.6, 139.7, 137.6, 135.4, 135.3, 134.5, 133.8, 129.2, 128.3, 126.6, 124.3, 123.5, 123.1, 122.8, 122.1, 121.4, 120.3, 109.8, 81.9, 46.7, 46.4, 24.4;

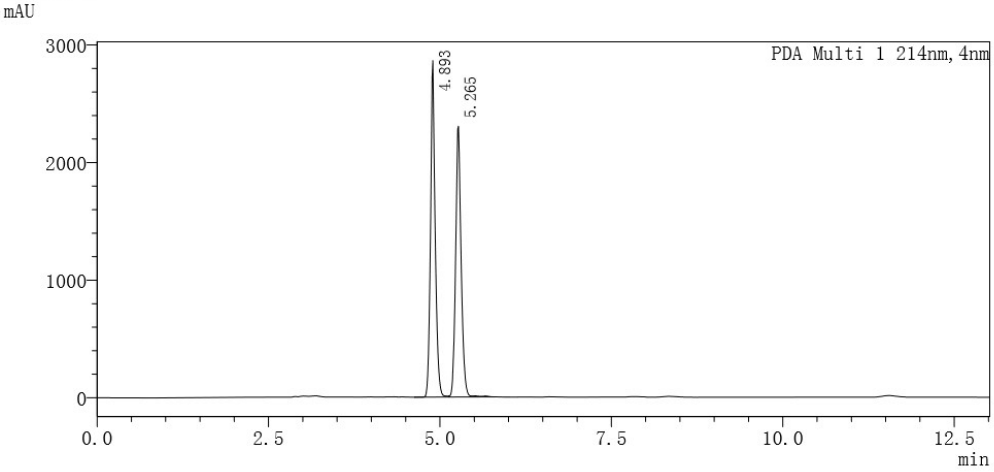
HRMS: (ESI) calcd for $C_{22}H_{18}SNaO^{+}$[M+Na]$^{+}$ 353.0971; found 353.0971.

The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 90/10 as eluent, 254 nm, 1 mL/min. tR = 4.8 min (minor), 5.2 min (major).

Optical Rotation: $[\alpha]_D^{30}$ -35.0 (c 0.6, $CHCl_3$) for 94% ee.

Absolute stereochemistry was determined through analogy with **3aa**.

〈色谱图〉



〈峰表〉

PDA Ch1 214nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	4.893	13496960	2862516	0.000		M	
2	5.265	12846684	2302530	0.000		V M	
总计		26343645	5165046				

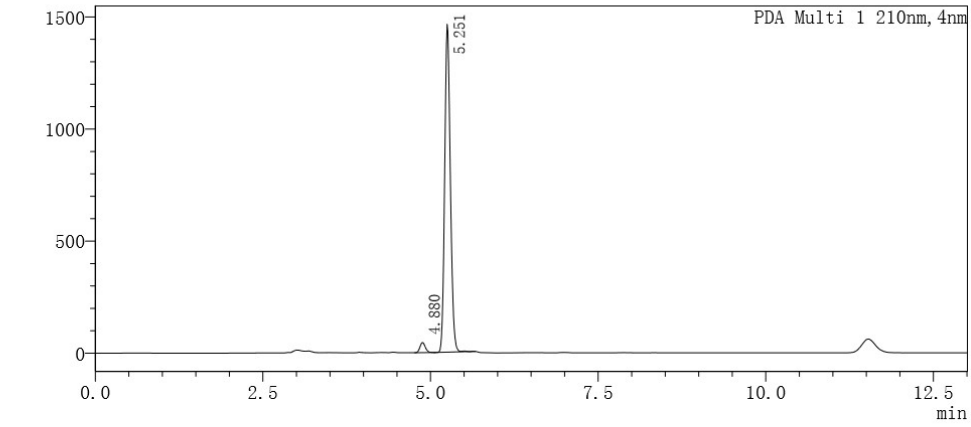
peak number

retention time

area

height

〈色谱图〉



〈峰表〉

PDA Ch1 210nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	4.880	250171	44859	2.847		M	
2	5.251	8537617	1463223	97.153		M	
总计		8787789	1508082				

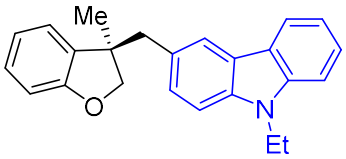
peak number

retention time

area

height

(*R*)-9-ethyl-3-((3-methyl-2,3-dihydrobenzofuran-3-yl)methyl)-9H-carbazole (**3at**)



Chemical Formula: $C_{24}H_{23}NO$
Exact Mass: 341.1780

3at was prepared according to general procedure using **1a** and **2t** and was purified by silica gel column chromatography (petroleum ether/EtOAc = 100/1~20/1) to obtain **3at** as colorless oil (67% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.75 (d, *J* = 1.6 Hz, 1H), 7.48 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.41 (dt, *J* = 8.2, 1.0 Hz, 1H), 7.30 (d, *J* = 8.3 Hz, 1H), 7.26-7.10 (m, 3H), 7.02 (dd, *J* = 7.3, 1.5 Hz, 1H), 6.91 (td, *J* = 7.4, 1.0 Hz, 1H), 6.85-6.78 (m, 1H), 4.64 (d, *J* = 8.6 Hz, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 4.11 (d, *J* = 8.6 Hz, 1H), 3.35-2.84 (m, 2H), 1.44 (d, *J* = 5.1 Hz, 6H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.6, 140.1, 138.8, 135.2, 128.2, 128.1, 127.8, 125.5, 123.5, 122.8, 122.7, 121.9, 120.3, 120.2, 118.6, 109.7, 108.4, 107.7, 82.0, 46.6, 46.5, 37.5, 24.6, 13.8;

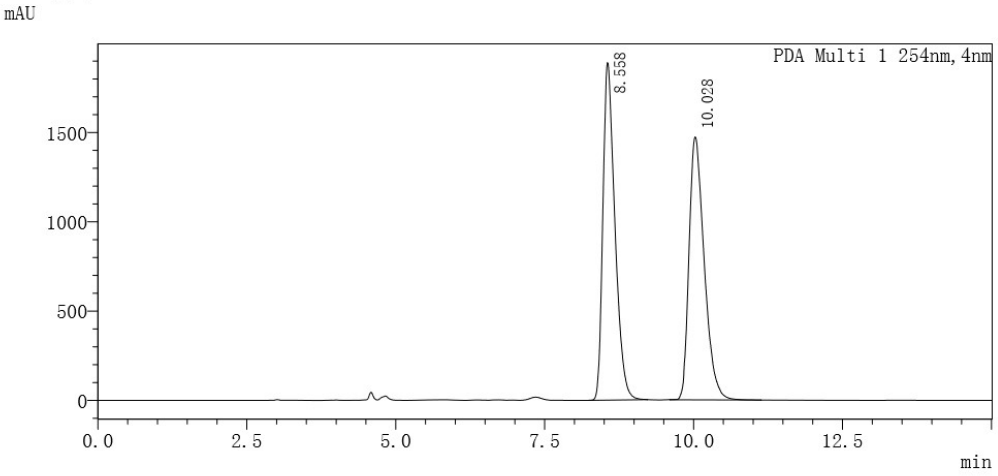
HRMS: (ESI) calcd for $C_{24}H_{24}NO^{+}$[M+H]$^{+}$ 342.1852; found 342.1836.

The enantiomeric purity was established by HPLC analysis using a chiral column: OD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 95/5 as eluent, 254 nm, 1 mL/min. tR = 8.5 min (major), 10.1 min (minor).

Optical Rotation: $[\alpha]_D^{30}$ -29.4 (c 0.5, $CHCl_3$) for 95% ee.

Absolute stereochemistry was determined through analogy with **3aa**.

〈色谱图〉



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	8.558	26501160	1891030	0.000		M	
2	10.028	26087413	1473453	0.000		M	
总计		52588573	3364483				

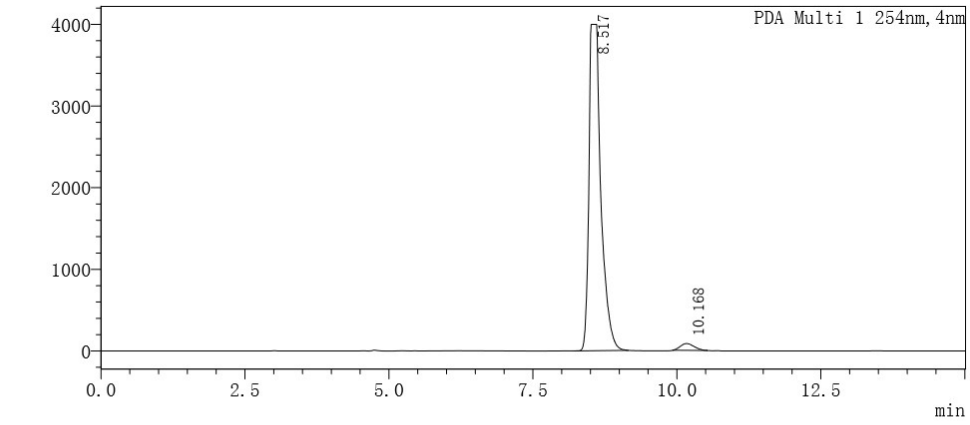
peak number

retention time

area

height

〈色谱图〉



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	8.517	57588425	3997396	0.000		M	
2	10.168	1410369	84428	0.000		M	
总计		58998795	4081825				

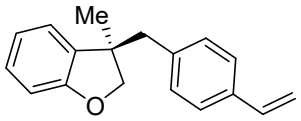
peak number

retention time

area

height

(*R*)-3-methyl-3-(4-vinylbenzyl)-2,3-dihydrobenzofuran (**3au**)



Chemical Formula: $C_{18}H_{18}O$
Exact Mass: 250.1358

3au was prepared according to general procedure using **1a** and **2u** and was purified by silica gel column chromatography (petroleum ether/EtOAc = 100/1~50/1) to obtain **3au** as colorless oil (49% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, *J* = 8.1 Hz, 2H), 7.14 (ddd, *J* = 7.9, 7.3, 1.5 Hz, 1H), 7.02-6.93 (m, 3H), 6.87 (td, *J* = 7.4, 1.0 Hz, 1H), 6.78 (dt, *J* = 7.9, 0.7 Hz, 1H), 6.70 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.72 (dd, *J* = 17.6, 1.0 Hz, 1H), 5.22 (dd, *J* = 10.9, 0.9 Hz, 1H), 4.50 (d, *J* = 8.7 Hz, 1H), 4.07 (d, *J* = 8.7 Hz, 1H), 2.88 (d, *J* = 4.4 Hz, 2H), 1.36 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.5, 137.2, 136.5, 135.8, 134.7, 130.5, 128.2, 125.8, 123.4, 120.3, 113.4, 109.7, 81.9, 46.3, 46.2, 24.5;

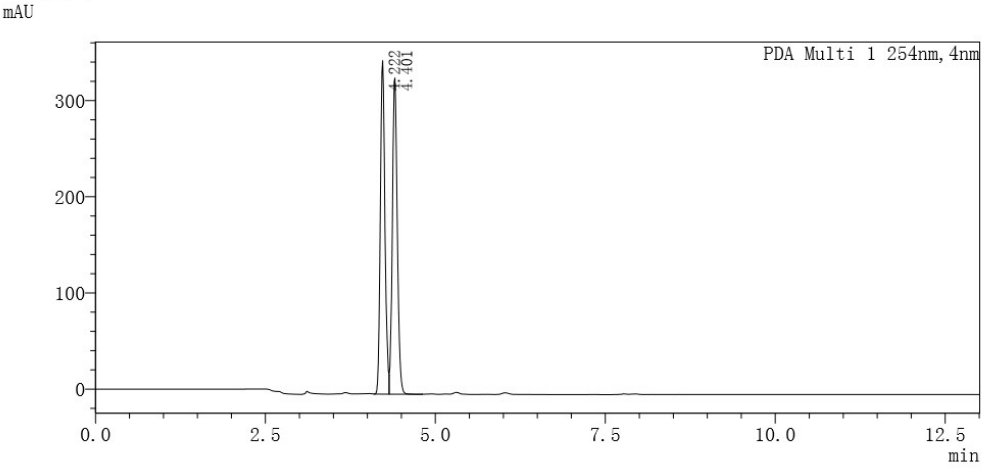
HRMS: (ESI) calcd for $C_{18}H_{18}NaO^+$[M+Na]$^+$ 273.1250; found 273.1261.

The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 97/3 as eluent, 254 nm, 1 mL/min. tR = 4.1 min (minor), 4.3 min (major).

Optical Rotation: $[\alpha]_D^{30}$ -128.8 (c 0.1, $CHCl_3$) for 89% ee.

Absolute stereochemistry was determined through analogy with **3aa**.

〈色谱图〉



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	4.222	1643483	346833	0.000		M	
2	4.401	1657365	328786	0.000		V M	
总计		3300849	675619				

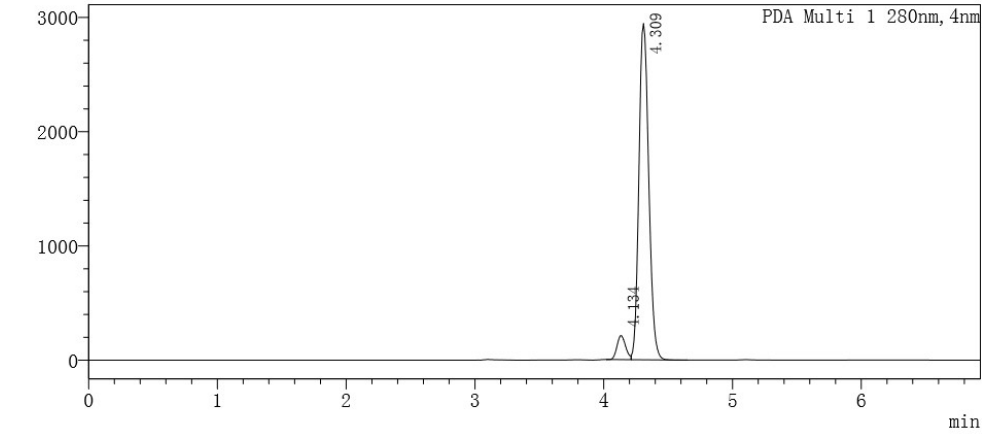
peak number

retention time

area

height

〈色谱图〉



〈峰表〉

PDA Ch1 280nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	4.134	984661	210118	0.000		M	
2	4.309	15616988	2945720	0.000		V M	
总计		16601649	3155839				

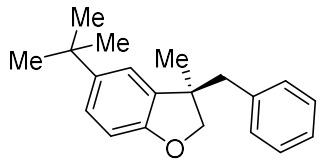
peak number

retention time

area

height

(*R*)-3-benzyl-5-(tert-butyl)-3-methyl-2,3-dihydrobenzofuran (**3ba**)



Chemical Formula: $C_{20}H_{24}O$
Exact Mass: 280.1827

3ba was prepared according to general procedure using **1b** and **2a** and was purified by silica gel column chromatography (petroleum ether/EtOAc = 100/1~20/1) to obtain **3ba** as colorless oil (74% yield). The ^{1}H NMR data matched those reported in the literature[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.22 (m, 3H), 7.17 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.02-6.96 (m, 2H), 6.81 (dd, *J* = 2.2, 0.5 Hz, 1H), 6.72 (dd, *J* = 8.4, 0.5 Hz, 1H), 4.49 (d, *J* = 8.6 Hz, 1H), 4.11 (d, *J* = 8.6 Hz, 1H), 2.89 (s, 2H), 1.36 (s, 3H), 1.28 (s, 9H);

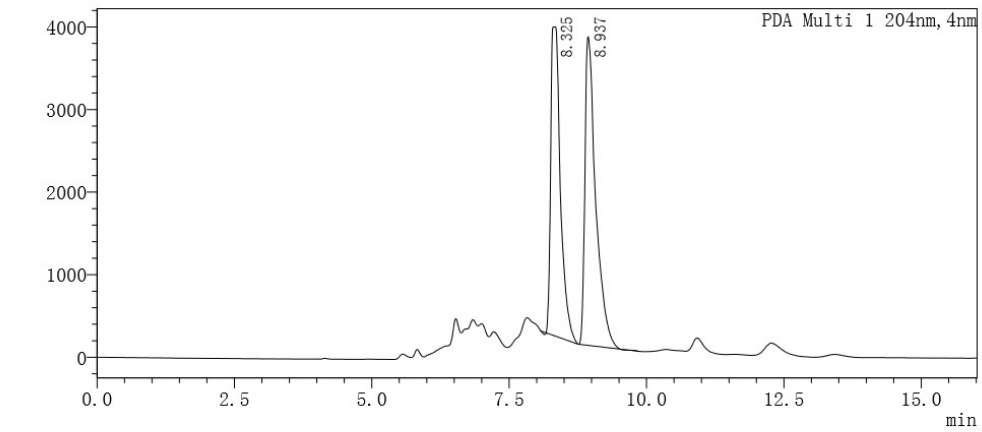
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 143.0, 137.6, 133.9, 130.5, 127.8, 126.3, 124.8, 120.6, 108.7, 82.7, 46.6, 46.3, 34.3, 31.6, 23.9.

The enantiomeric purity was established by HPLC analysis using a chiral column: IA-H column, 30 °C, *n*-Hexane as eluent, 254 nm, 0.75 mL/min. tR = 8.2 min (major), 9.0 min (minor).

Optical Rotation: $[\alpha]_D^{30}$ -16.2 (c 0.23, $CHCl_3$) for 93% ee.

Absolute stereochemistry was determined through analogy with **3aa**.

〈色谱图〉



〈峰表〉

PDA Ch1 204nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	8.325	45894577	3739520	0.000		M	
2	8.937	51003873	3738475	0.000		M	
总计		96898449	7477994				

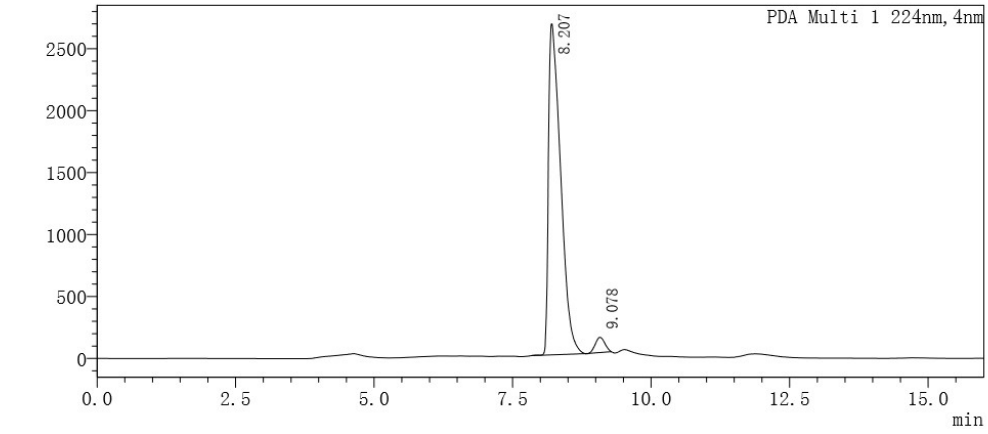
peak number

retention time

area

height

〈色谱图〉



〈峰表〉

PDA Ch1 224nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	8.207	40663157	2672368	0.000		M	
2	9.078	1470857	123550	0.000		M	
总计		42134014	2795918				

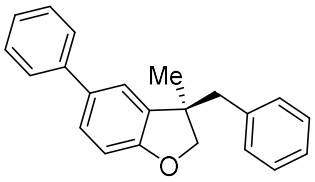
peak number

retention time

area

height

(*R*)-3-benzyl-3-methyl-5-phenyl-2,3-dihydrobenzofuran (**3ca**)



Chemical Formula: $C_{22}H_{20}O$
Exact Mass: 300.1514

3ca was prepared according to general procedure using **1c** and **2a** and was purified by silica gel column chromatography (petroleum ether/EtOAc = 100/1~20/1) to obtain **3ca** as colorless oil (85% yield). The ^{1}H NMR data matched those reported in the literature[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.49 (m, 2H), 7.46-7.37 (m, 3H), 7.34-7.26 (m, 4H), 7.12 (d, *J* = 2.0 Hz, 1H), 7.08-7.02 (m, 2H), 6.86 (d, *J* = 8.2 Hz, 1H), 4.58 (d, *J* = 8.7 Hz, 1H), 4.15 (d, *J* = 8.7 Hz, 1H), 2.97 (d, *J* = 13.2 Hz, 1H), 2.93 (d, *J* = 13.2 Hz, 1H), 1.42 (s, 3H);

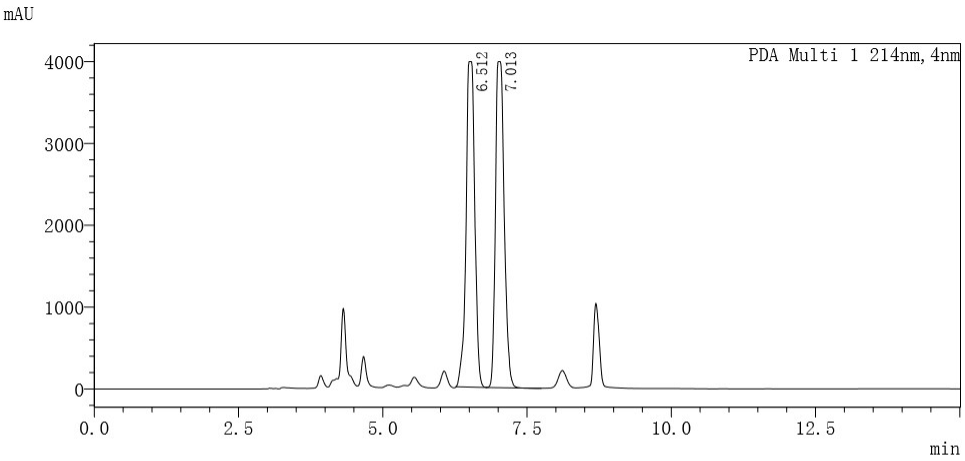
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 141.4, 137.5, 135.3, 133.8, 130.4, 128.6, 127.9, 127.3, 126.8, 126.5, 126.5, 122.3, 109.8, 82.5, 46.7, 46.3, 24.4.

The enantiomeric purity was established by HPLC analysis using a chiral column: OD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 98/2 as eluent, 254 nm, 1 mL/min. tR = 6.5 min (minor), 7.0 min (major).

Optical Rotation: $[\alpha]_D^{30}$ 63.2 (c 0.58, $CHCl_3$) for 93% ee.

Absolute stereochemistry was determined through analogy with **3aa**.

〈色谱图〉



〈峰表〉

PDA Ch1 214nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	6.512	41622642	3976464	0.000		M	
2	7.013	41860205	3983283	0.000		M	
总计		83482847	7959748				

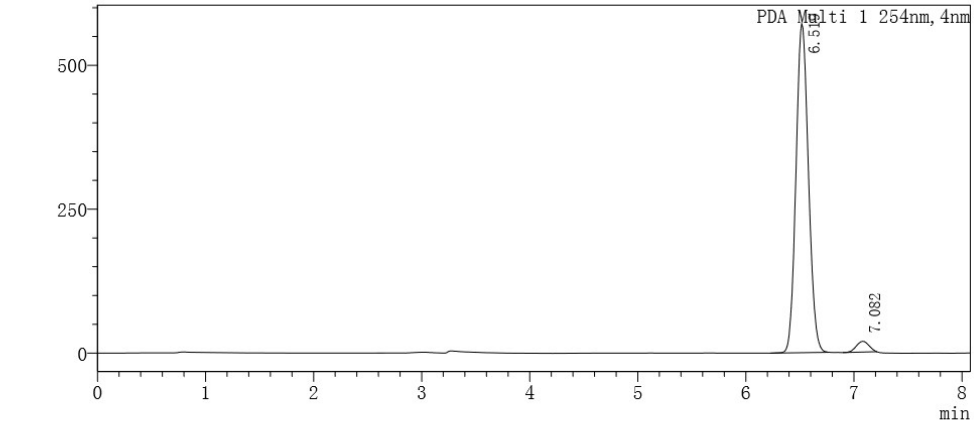
peak number

retention time

area

height

〈色谱图〉



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	6.519	4583713	572119	0.000		M	
2	7.082	152124	18772	0.000		M	
总计		4735838	590892				

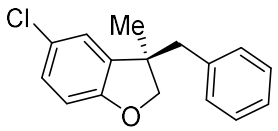
peak number

retention time

area

height

(*R*)-3-benzyl-5-chloro-3-methyl-2,3-dihydrobenzofuran (**3da**)



Chemical Formula: $C_{16}H_{15}ClO$
Exact Mass: 258.0811

3da was prepared according to general procedure using **1d** and **2a** and was purified by silica gel column chromatography (petroleum ether/EtOAc = 100/1~20/1) to obtain **3da** as colorless oil (88% yield). The ^{1}H NMR data matched those reported in the literature[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.21 (m, 3H), 7.09 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.04-6.97 (m, 2H), 6.89 (d, *J* = 2.3 Hz, 1H), 6.68 (d, *J* = 8.5 Hz, 1H), 4.53 (d, *J* = 8.8 Hz, 1H), 4.09 (d, *J* = 8.8 Hz, 1H), 2.90 (d, *J* = 13.3 Hz, 1H), 2.86(d, *J* = 13.3 Hz, 1H), 1.35 (s, 3H);

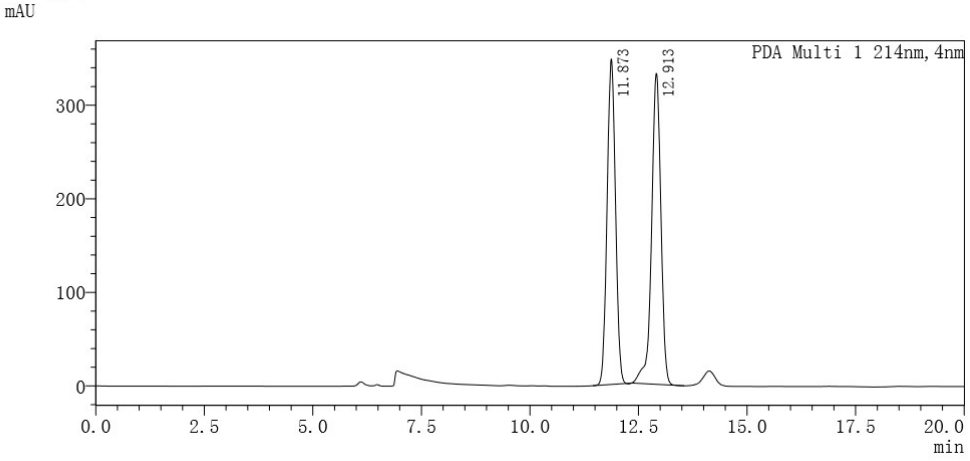
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 137.0, 136.8, 130.3, 128.0, 126.7, 125.0, 123.6, 110.7, 82.3, 46.5, 46.5, 24.5;

The enantiomeric purity was established by HPLC analysis using a chiral column: OD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 99/1 as eluent, 254 nm, 0.5 mL/min. tR = 11.8 min (minor), 12.9 min (major).

Optical Rotation: $[\alpha]_D^{30}$ 10.0 (c 0.5, $CHCl_3$) for 95% ee.

Absolute stereochemistry was determined through analogy with **3aa**.

〈色谱图〉



〈峰表〉

PDA Ch1 214nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	11.873	4680407	347965	0.000		M	
2	12.913	4970158	332323	0.000		M	
总计		9650565	680288				

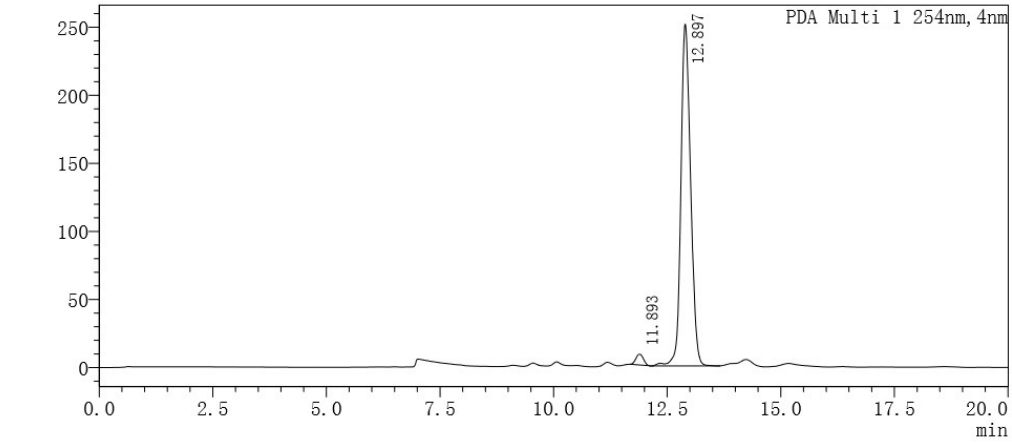
peak number

retention time

area

height

〈色谱图〉



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	11.893	90445	8026	0.000		M	
2	12.897	3740484	251170	0.000		M	
总计		3830929	259196				

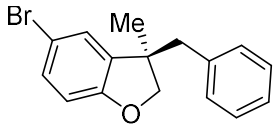
peak number

retention time

area

height

(*R*)-3-benzyl-5-bromo-3-methyl-2,3-dihydrobenzofuran (**3ea**)



Chemical Formula: $C_{16}H_{15}BrO$
Exact Mass: 302.0306

3ea was prepared according to general procedure using **1e** and **2a** and was purified by silica gel column chromatography (petroleum ether/EtOAc = 100/1~20/1) to obtain **3ea** as colorless oil (69% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.20 (m, 4H), 7.06-6.96 (m, 3H), 6.64 (d, *J* = 8.4 Hz, 1H), 4.52 (d, *J* = 8.8 Hz, 1H), 4.08 (d, *J* = 8.8 Hz, 1H), 2.90 (d, *J* = 13.3 Hz, 1H), 2.84 (d, *J* = 13.3 Hz, 1H), 1.35 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 137.3, 137.0, 130.9, 130.3, 128.0, 126.7, 126.5, 112.1, 111.3, 82.3, 46.55, 46.51, 24.5;

HRMS: (ESI) calcd for $C_{16}H_{15}BrNaO^{+}$[M+Na]$^{+}$ 325.0198; found 325.0199.

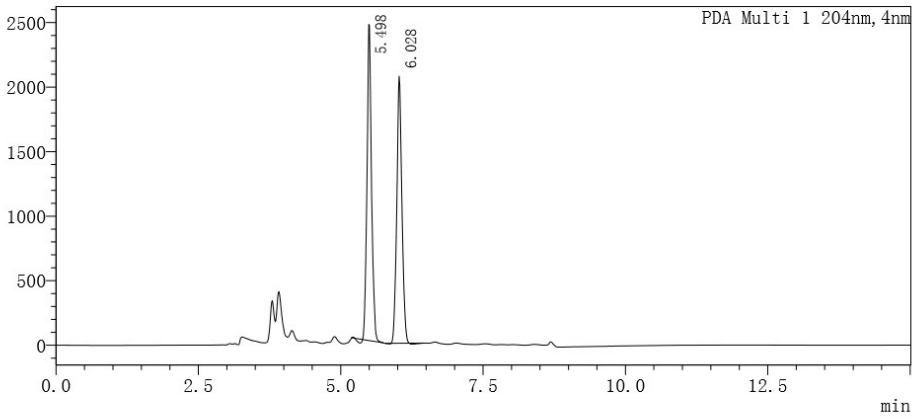
The enantiomeric purity was established by HPLC analysis using a chiral column: OD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 98/2 as eluent, 254 nm, 1 mL/min. tR = 5.5 min (minor), 6.0 min (major).

Optical Rotation: $[\alpha]_D^{30}$ 33.5(c 0.33, $CHCl_3$) for 96% ee.

Absolute stereochemistry was determined through analogy with **3aa**.

〈色谱图〉

mAU



〈峰表〉

PDA Ch1 204nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	5.498	13247978	2450498	0.000		M	
2	6.028	12804997	2070537	0.000		M	
总计		26052975	4521035				

peak number

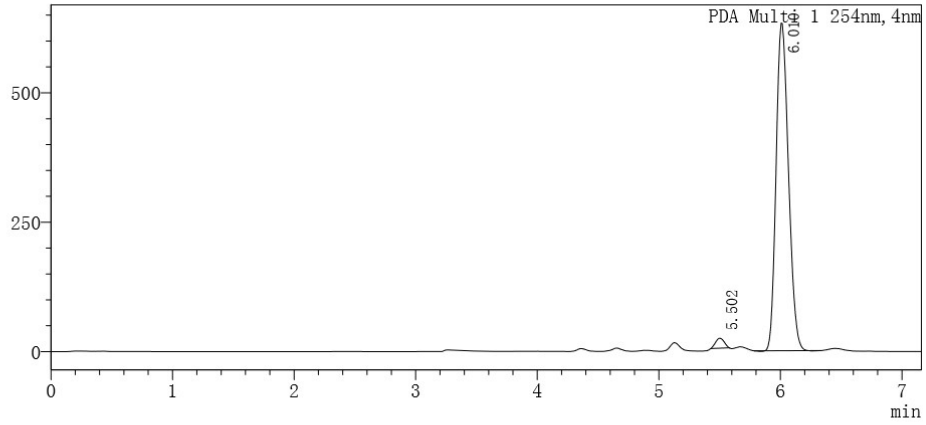
retention time

area

height

〈色谱图〉

mAU



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	5.502	95340	19300	0.000		M	
2	6.010	4472119	633166	0.000		M	
总计		4567459	652466				

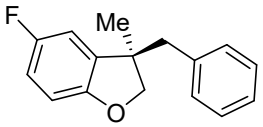
peak number

retention time

area

height

(*R*)-3-benzyl-5-fluoro-3-methyl-2,3-dihydrobenzofuran (**3fa**)



Chemical Formula: $C_{16}H_{15}FO$
Exact Mass: 242.1107

3fa was prepared according to general procedure using **1f** and **2a** and was purified by silica gel column chromatography (petroleum ether/EtOAc = 100/1~20/1) to obtain **3fa** as colorless oil (69% yield). The ^{1}H NMR data matched those reported in the literature[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.21 (m, 3H), 7.04-6.97 (m, 2H), 6.85-6.76 (m, 1H), 6.69-6.60 (m, 2H), 4.52 (d, *J* = 8.7 Hz, 1H), 4.09 (d, *J* = 8.7 Hz, 1H), 2.90 (d, *J* = 13.3 Hz, 1H), 2.85 (d, *J* = 13.3 Hz, 1H), 1.35 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4 (d, *J* = 237.0 Hz), 155.4, 137.1, 136.3 (d, *J* = 7.6 Hz), 130.3, 128.0, 126.6, 114.3 (d, *J* = 24.2 Hz), 110.5 (d, *J* = 24.6 Hz), 109.8 (d, *J* = 8.5 Hz), 82.5, 46.7, 46.4, 24.4;

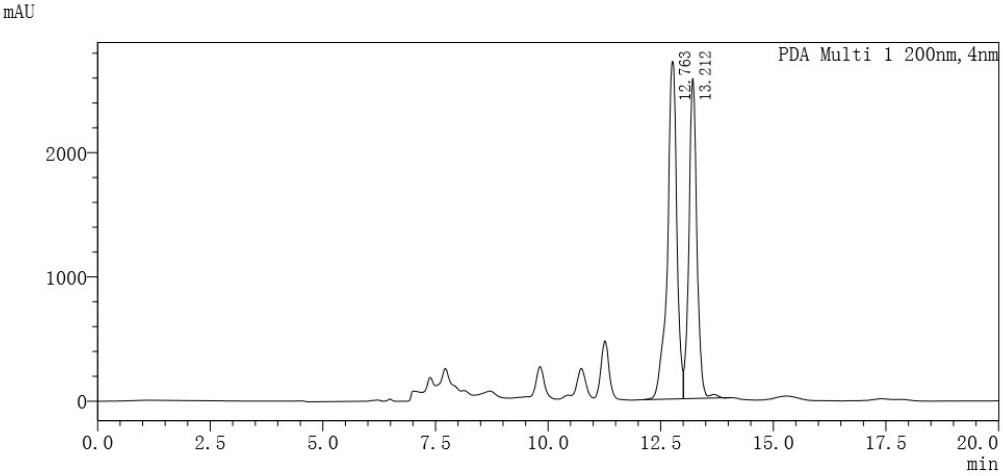
^{19}F NMR (376 MHz, $CDCl_3$) δ -124.03;

The enantiomeric purity was established by HPLC analysis using a chiral column: OD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 99/1 as eluent, 254 nm, 0.5 mL/min. tR = 12.7 min (minor), 13.2 min (major).

Optical Rotation: $[\alpha]_D^{30}$ -29.9 (c 0.4, $CHCl_3$) for 96% ee.

Absolute stereochemistry was determined through analogy with **3aa**.

〈色谱图〉



〈峰表〉

PDA Ch1 200nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	12.763	39557409	2718128	0.000		M	
2	13.212	31664985	2575854	0.000		V M	
总计		71222394	5293982				

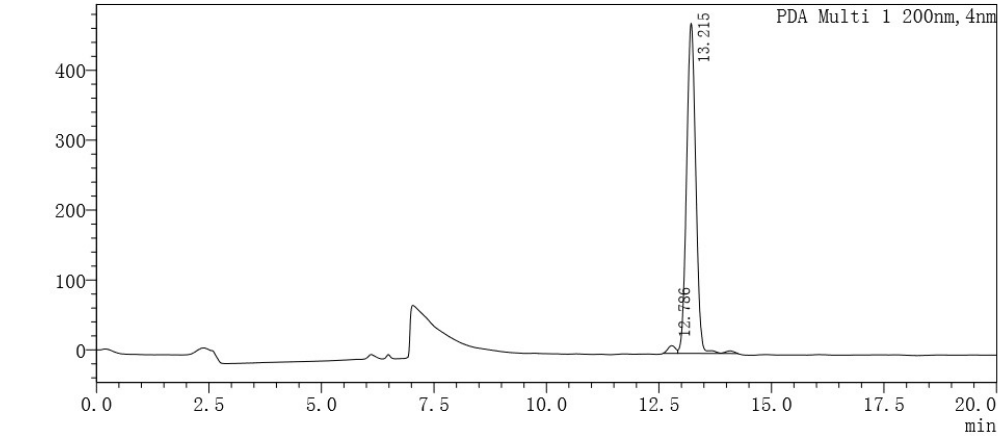
peak number

retention time

area

height

〈色谱图〉



〈峰表〉

PDA Ch1 200nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	12.786	131627	11169	0.000		M	
2	13.215	6718412	472298	0.000		V M	
总计		6850038	483467				

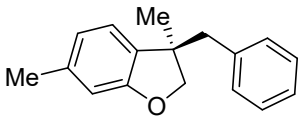
peak number

retention time

area

height

(*R*)-3-benzyl-3,6-dimethyl-2,3-dihydrobenzofuran (**3ga**)



Chemical Formula: $C_{17}H_{18}O$
Exact Mass: 238.1358

3ga was prepared according to general procedure using **1g** and **2a** and was purified by silica gel column chromatography (petroleum ether/EtOAc = 100/1~20/1) to obtain **3ga** as colorless oil (76% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.20 (m, 3H), 7.07-7.01 (m, 2H), 6.83 (d, *J* = 7.5 Hz, 1H), 6.69 (m, 1H), 6.62 (m, 1H), 4.50 (d, *J* = 8.7 Hz, 1H), 4.06 (d, *J* = 8.7 Hz, 1H), 2.90 (d, *J* = 13.3 Hz, 1H), 2.86 (d, *J* = 13.3 Hz, 1H), 2.33 (s, 3H), 1.34 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 138.3, 137.7, 131.9, 130.4, 127.9, 126.4, 122.9, 121.0, 110.4, 82.2, 46.6, 45.9, 24.6, 21.5;

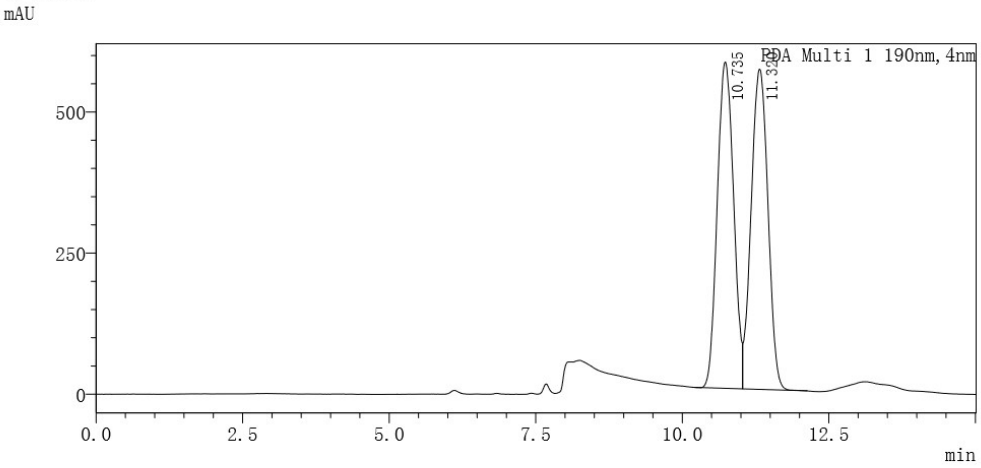
HRMS: (ESI) calcd for $C_{17}H_{18}NaO^+$[M+Na]$^+$ 261.1250; found 261.1276.

The enantiomeric purity was established by HPLC analysis using a chiral column: OD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 99.5/0.5 as eluent, 254 nm, 0.5 mL/min. tR = 10.6 min (major), 11.2 min (minor).

Optical Rotation: $[\alpha]_D^{30}$ -11.6 (c 0.38, $CHCl_3$) for 93% ee.

Absolute stereochemistry was determined through analogy with **3aa**.

〈色谱图〉



〈峰表〉

PDA Ch1 190nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	10.735	11225019	578119	0.000		M	
2	11.320	11307822	567462	0.000		V M	
总计		22532840	1145581				

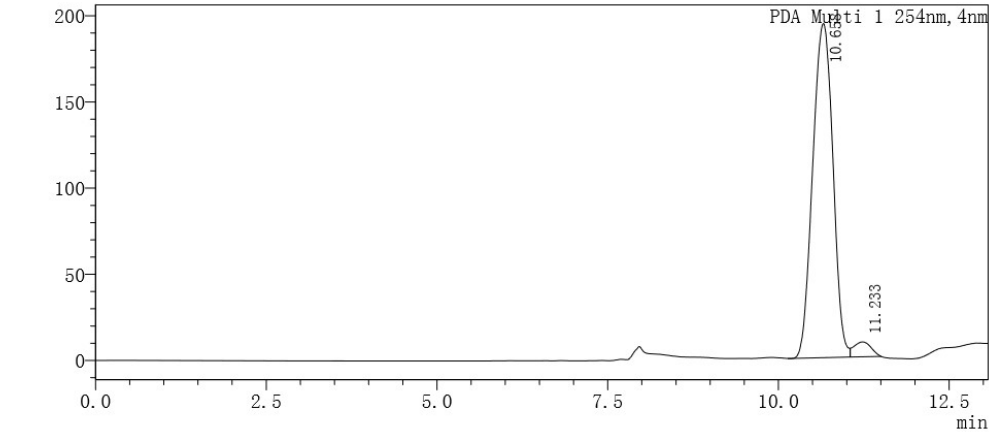
peak number

retention time

area

height

〈色谱图〉



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	10.658	3998661	193927	0.000		M	
2	11.233	150595	8640	0.000		V M	
总计		4149257	202567				

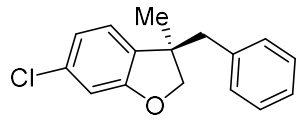
peak number

retention time

area

height

(*R*)-3-benzyl-6-chloro-3-methyl-2,3-dihydrobenzofuran (**3ha**)



Chemical Formula: $C_{16}H_{15}ClO$
Exact Mass: 258.0811

3ha was prepared according to general procedure using **1h** and **2a** and was purified by silica gel column chromatography (petroleum ether/EtOAc = 100/1~20/1) to obtain **3ha** as colorless oil (80% yield). The ^{1}H NMR data matched those reported in the literature[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.21 (m, 3H), 7.04-6.95 (m, 2H), 6.88-6.73 (m, 3H), 4.53 (d, *J* = 8.7 Hz, 1H), 4.11 (d, *J* = 8.7 Hz, 1H), 2.89 (d, *J* = 13.2 Hz, 1H), 2.85 (d, *J* = 13.2 Hz, 1H), 1.35 (s, 3H);

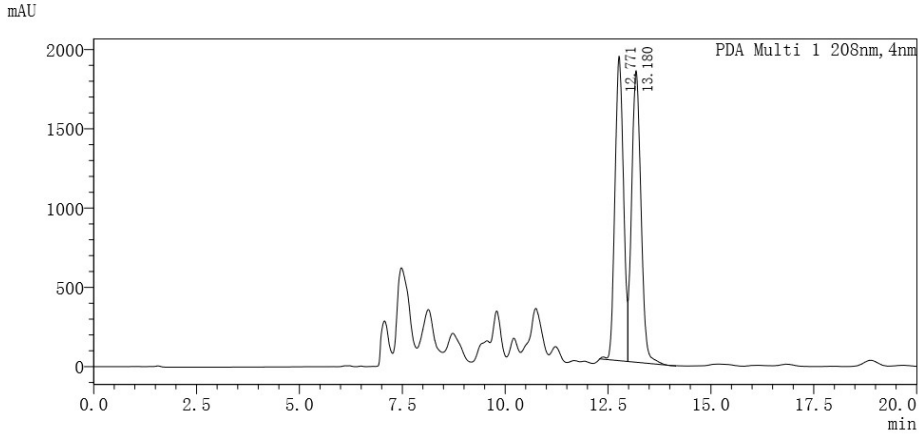
^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 137.1, 133.4, 130.3, 128.0, 126.6, 124.0, 120.3, 110.4, 82.7, 46.5, 45.9, 24.5;

The enantiomeric purity was established by HPLC analysis using a chiral column: OD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 99/1 as eluent, 254 nm, 0.5 mL/min. tR = 12.8 min (major), 13.2 min (minor).

Optical Rotation: $[\alpha]_D^{30}$ -41.9 (c 0.25, $CHCl_3$) for 94% ee.

Absolute stereochemistry was determined through analogy with **3aa**.

〈色谱图〉



〈峰表〉

PDA Ch1 208nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	12.771	27830524	1921293	48.978		M	
2	13.180	28991975	1839093	51.022		V M	
总计		56822499	3760386				

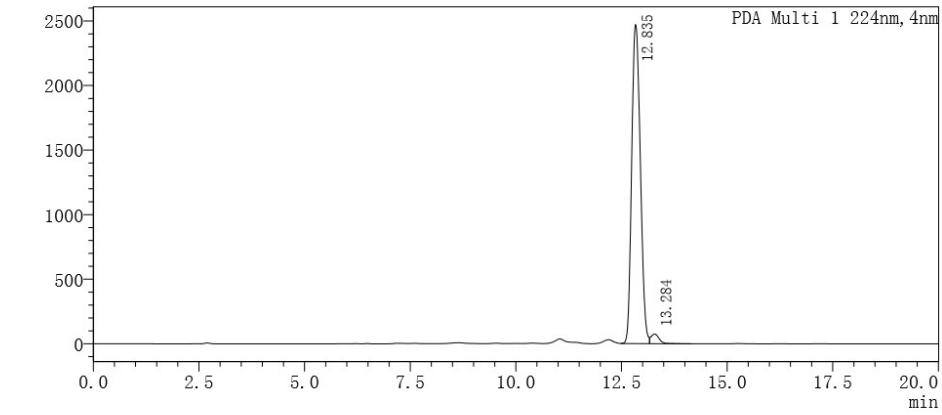
peak number

retention time

area

height

〈色谱图〉



〈峰表〉

PDA Ch1 224nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	12.835	35277167	2471813	0.000		M	
2	13.284	987039	74610	0.000		V M	
总计		36264206	2546423				

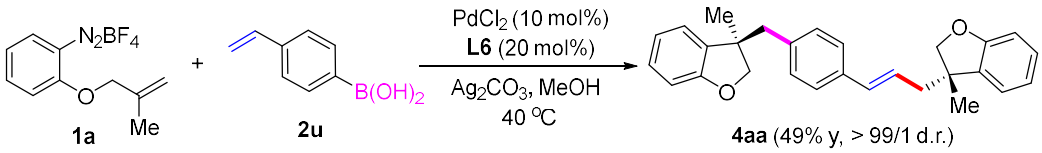
peak number

retention time

area

height

(*S*)-3-methyl-3-((*E*)-3-(4-(((*R*)-3-methyl-2,3-dihydrobenzofuran-3 yl)methyl)phenyl) allyl)-2,3-dihydrobenzofuran (**4aa**)



4aa was prepared according to general procedure using **1a** (0.4 mmol, 104.8 mg) and **2u** (0.1 mmol, 14.9 mg) and was purified by silica gel column chromatography (petroleum ether/EtOAc = 100/1~30/1) to obtain **4aa** as colorless oil (17.4 mg, 44% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.11 (m, 5H), 7.01-6.87 (m, 5H), 6.81 (ddt, *J* = 15.5, 8.0, 0.7 Hz, 2H), 6.50-6.35 (m, 1H), 6.09 (dt, *J* = 15.7, 7.5 Hz, 1H), 4.51 (d, *J* = 8.7 Hz, 1H), 4.46 (d, *J* = 8.7 Hz, 1H), 4.18 (d, *J* = 8.6 Hz, 1H), 4.08 (d, *J* = 8.7 Hz, 1H), 3.05-2.80 (m, 2H), 2.53 (dd, *J* = 7.6, 1.3 Hz, 2H), 1.42 (s, 3H), 1.38 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.5, 136.7, 135.5, 134.9, 134.8, 133.1, 130.5, 128.2, 125.7, 125.2, 123.3, 122.9, 120.5, 120.3, 109.7, 82.0, 81.8, 46.3, 46.3, 45.6, 44.2, 25.0, 24.6;

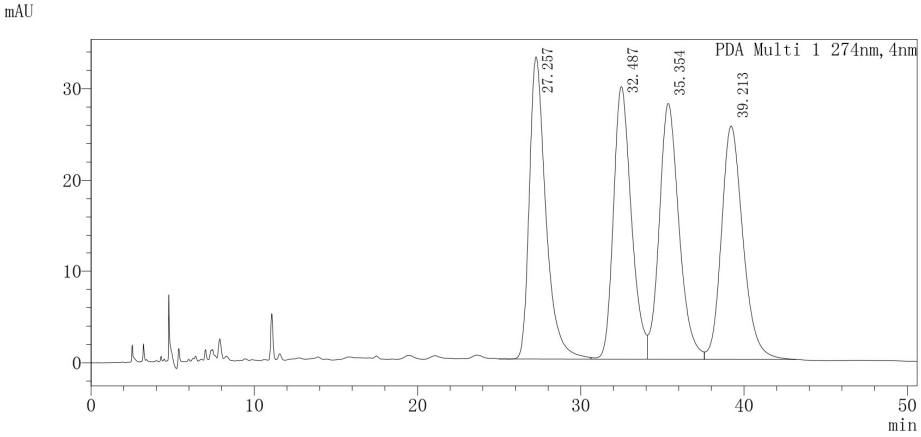
HRMS: (ESI) calcd for $C_{28}H_{28}NaO_2^+$[M+Na]$^+$ 419.1982; found 419.1971;

The enantiomeric purity was established by HPLC analysis using a chiral column: OJ-H column, 30 °C, *n*-Hexane/*i*-Propanol = 95/5 as eluent, 254 nm, 1 mL/min. tR = 27.3 min, 32.5 min, 35.4 min, 39.2 min.

Optical Rotation: $[\alpha]_D^{30}$ -24.1 (c 0.4, $CHCl_3$) for 92% ee.

Absolute stereochemistry was determined through analogy with **3aa**.

〈色谱图〉



〈峰表〉

PDA Ch1 274nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	27.257	2322186	33055	24.941		M	
2	32.487	2275318	29847	24.438		V M	
3	35.354	2362690	28005	25.376		V M	
4	39.213	2350467	25566	25.245		V M	
总计		9310661	116473				

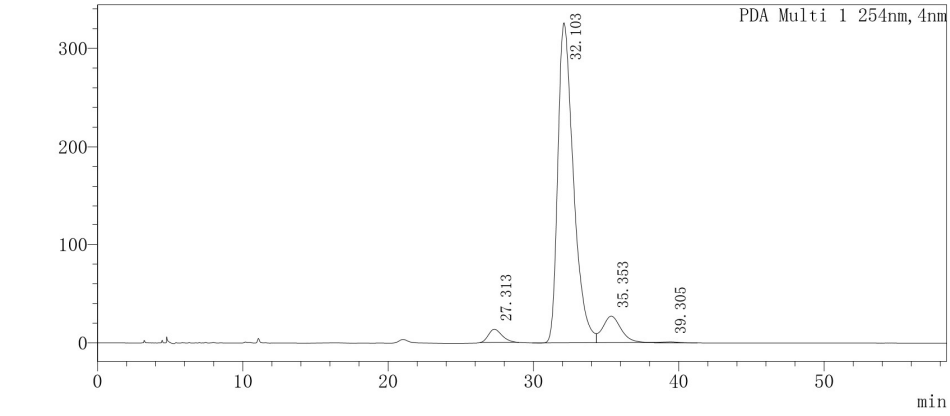
peak number

retention time

area

height

〈色谱图〉



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	27.313	874348	13405	0.000		M	
2	32.103	24316349	325782	0.000		M	
3	35.353	2354198	26912	0.000		V M	
4	39.305	104516	1125	0.000		M	
总计		27649410	367224				

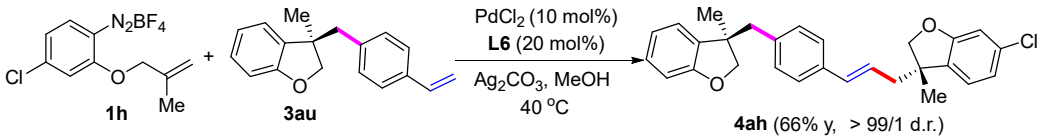
peak number

retention time

area

height

(*S*)-5-chloro-3-methyl-3-((*E*)-3-(4-(((*R*)-3-methyl-2,3-dihydrobenzofuran-3-yl)methyl)phenyl)allyl)-2,3-dihydrobenzofuran (**4ah**)



4ah was prepared according to general procedure using **3au** (0.1 mmol, 25.0 mg) and **1h** (0.2 mmol, 60.0 mg) and was purified by silica gel column chromatography (petroleum ether/EtOAc = 100/1~30/1) to obtain **4ah** as colorless oil (28.4 mg, 66% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22-7.09 (m, 3H), 7.00 (d, *J* = 7.9 Hz, 1H), 6.98-6.90 (m, 3H), 6.89-6.84 (m, 2H), 6.80-6.73 (m, 2H), 6.37 (d, *J* = 15.6 Hz, 1H), 6.03 (dt, *J* = 15.4, 7.5 Hz, 1H), 4.47 (t, *J* = 8.5 Hz, 2H), 4.18 (d, *J* = 8.7 Hz, 1H), 4.06 (d, *J* = 8.7 Hz, 1H), 2.86 (d, *J* = 5.8 Hz, 2H), 2.47 (dt, *J* = 7.7, 1.5 Hz, 2H), 1.38 (s, 3H), 1.35 (s, 3H);

^{13}C NMR (400 MHz, $CDCl_3$): δ 160.5, 159.6, 136.9, 135.5, 134.8, 133.7, 133.6, 130.7, 128.3, 125.8, 124.8, 123.6, 123.4, 120.7, 120.4, 110.6, 109.8, 82.8, 81.9, 46.4, 46.4, 45.5, 44.3, 25.2, 24.7;

HRMS: (APCI) calcd for $C_{28}H_{28}ClO_2^+$[M+H]$^+$ 431.1772; found 431.1766;

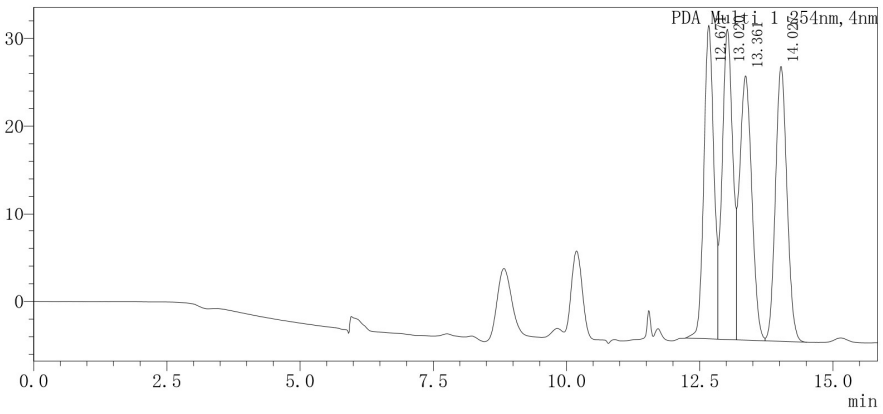
The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 95/5 as eluent, 254 nm, 0.5 mL/min. tR = 12.7 min, 13.0 min, 13.4 min, 14.0 min.

Optical Rotation: $[\alpha]_D^{30}$ -32.6 (c 0.2, $CHCl_3$) for 92% ee.

Absolute stereochemistry was determined through analogy with **3aa**.

〈色谱图〉

mAU



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	12.671	466840	35749	24.440		M	
2	13.020	497663	35361	26.054		V M	
3	13.361	474674	30121	24.851		V M	
4	14.027	470933	31360	24.655		V M	
总计		1910110	132590				

peak number

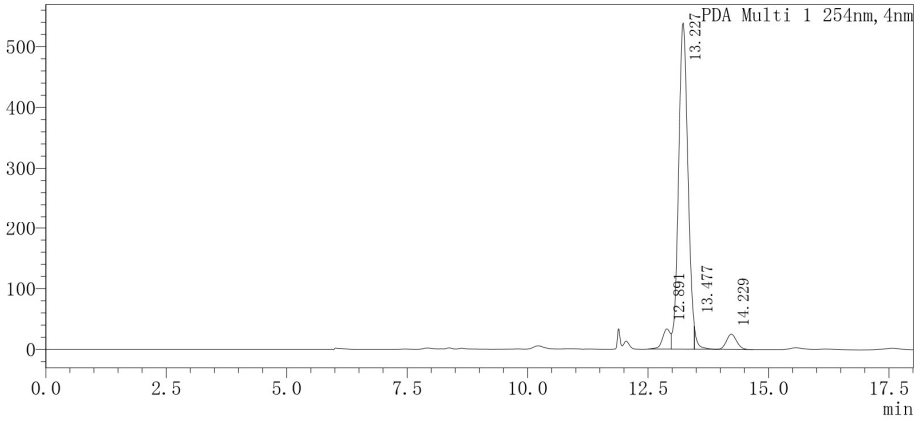
retention time

area

height

〈色谱图〉

mAU



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	12.891	383968	33240	0.000		M	
2	13.227	7252663	538845	0.000		V M	
3	13.477	127849	30860	0.000		V M	
4	14.229	368805	25067	0.000		M	
总计		8133286	628012				

peak number

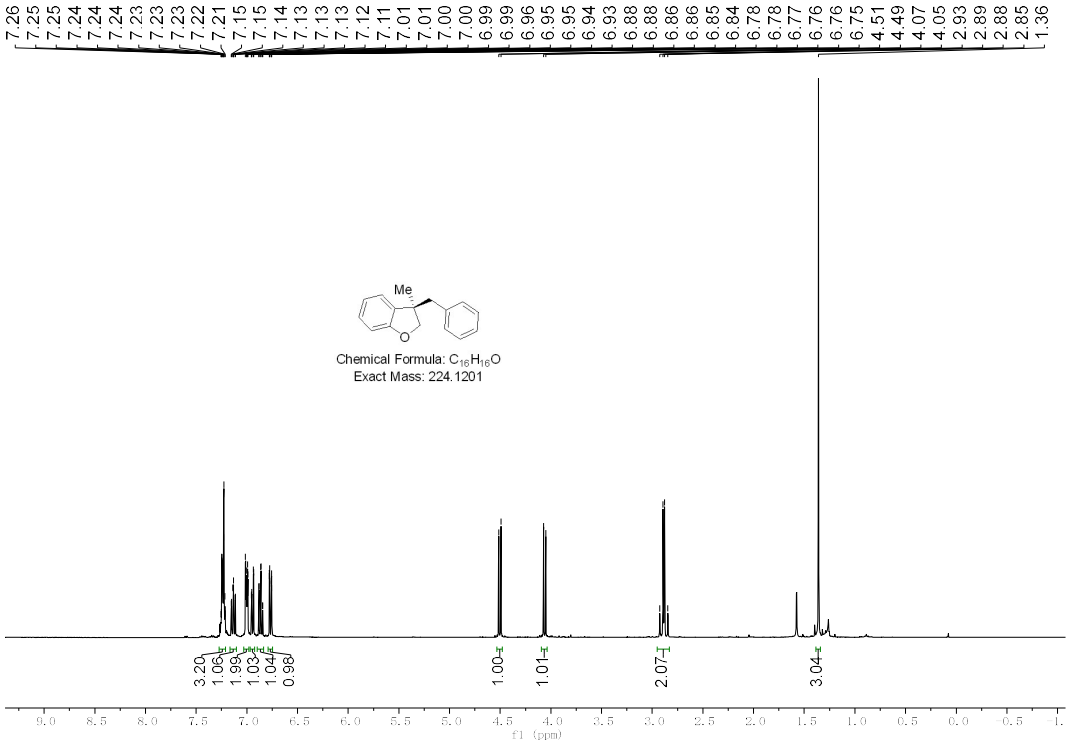
retention time

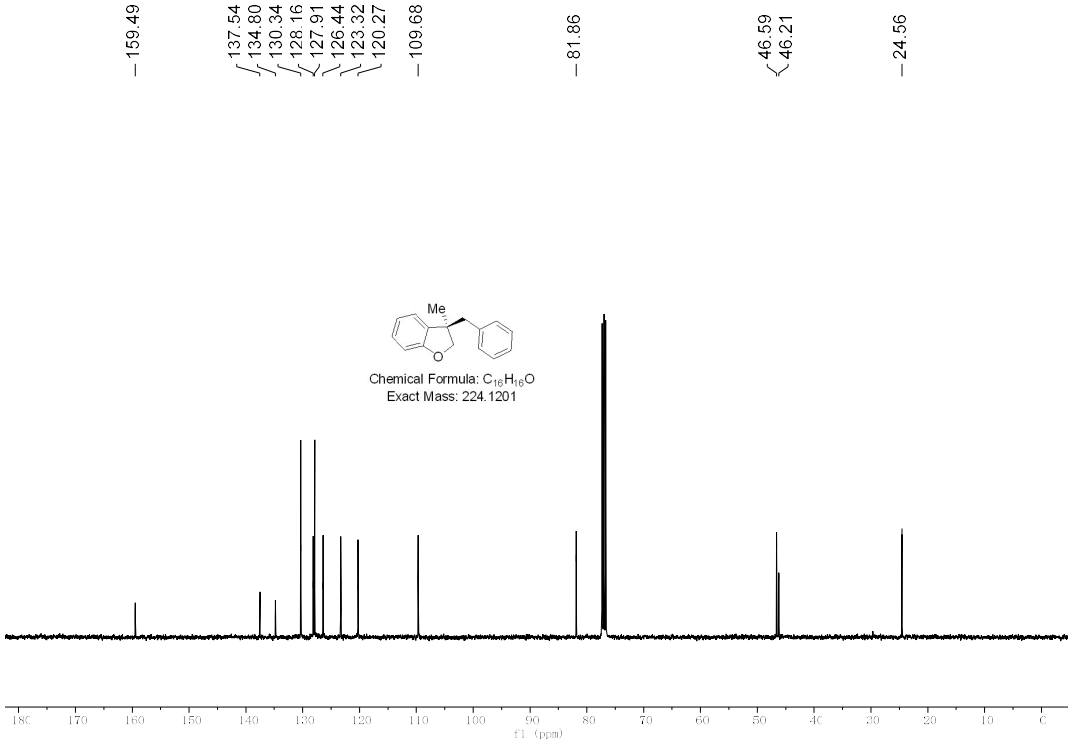
area

height

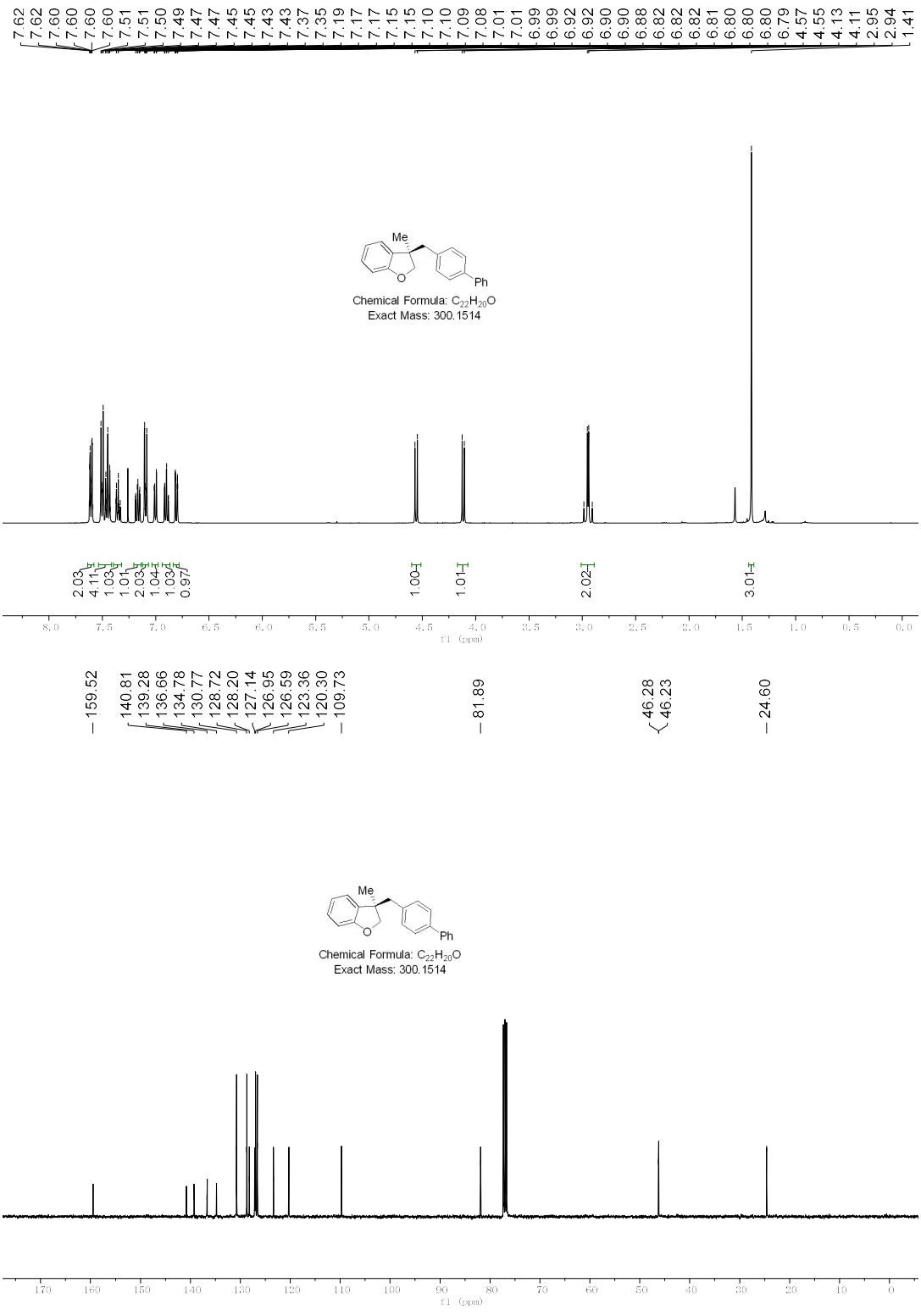
5. Copies of the ^{1}H, ^{13}C and ^{19}F NMR spectra

3aa

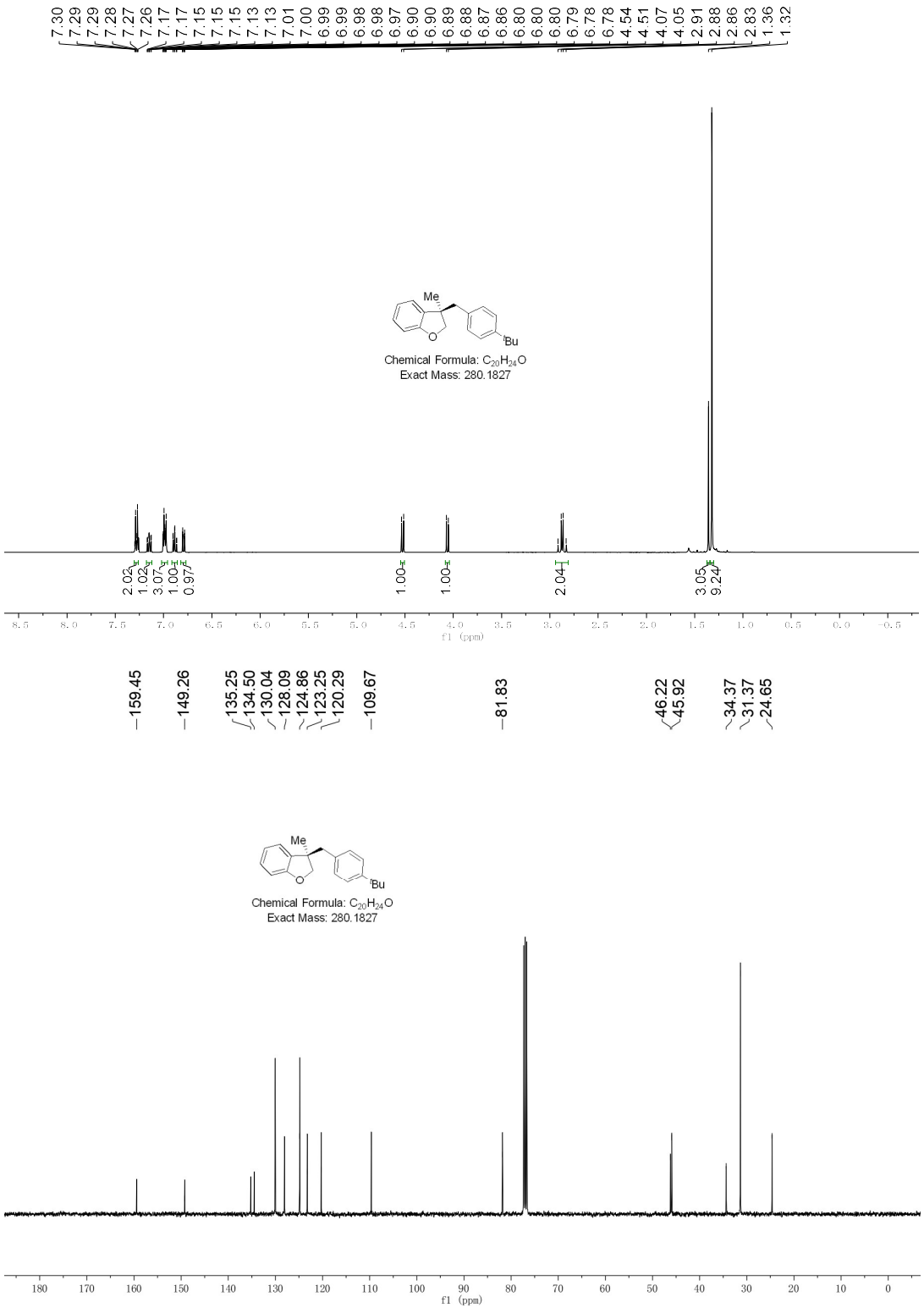




3ab


7.62 7.62 7.60 7.60 7.60 7.60 7.51 7.51 7.50 7.49 7.47 7.47 7.45 7.45 7.43 7.43 7.37 7.35 7.19 7.17 7.17 7.15 7.15 7.10 7.10 7.09 7.08 7.01 7.01 6.99 6.99 6.92 6.90 6.90 6.88 6.82 6.82 6.82 6.81 6.80 6.80 6.80 6.79 4.57 4.55 4.13 4.11 2.95 2.94 1.41
Me
Ph
Chemical Formula: C22H20O
Exact Mass: 300.1514
2.03 4.11 1.03 1.01 2.03 1.04 1.03 0.97 1.00 1.01 2.02 3.01
f1 (ppm)
159.52 140.81 139.28 136.66 134.78 130.77 128.72 128.20 127.14 126.95 126.59 123.36 120.30 109.73 81.89 46.28 46.23 24.60
Me
Ph
Chemical Formula: C22H20O
Exact Mass: 300.1514
f1 (ppm)

3ac


7.30
7.29
7.29
7.28
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7.17
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7.15
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7.01
7.00
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6.98
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6.87
6.86
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6.80
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6.79
6.78
6.78
4.54
4.51
4.07
4.05
2.91
2.88
2.86
2.83
1.36
1.32
Me
tBu
Chemical Formula: C20H24O
Exact Mass: 280.1827
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1.02
3.07
1.00
0.97
1.00
1.00
2.04
3.05
9.24
f1 (ppm)
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149.26
135.25
134.50
130.04
128.09
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123.25
120.29
109.67
81.83
46.22
45.92
34.37
31.37
24.65
Me
tBu
Chemical Formula: C20H24O
Exact Mass: 280.1827
f1 (ppm)

3ad


7.37
7.36
7.35
7.34
7.34
7.33
7.16
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7.14
7.14
7.14
7.14
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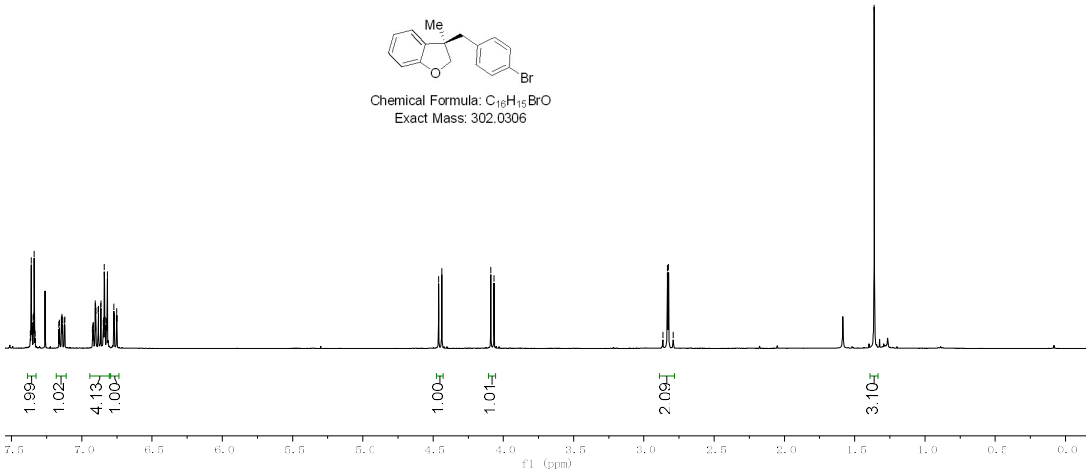
Me
O
Br
Chemical Formula: C16H15BrO
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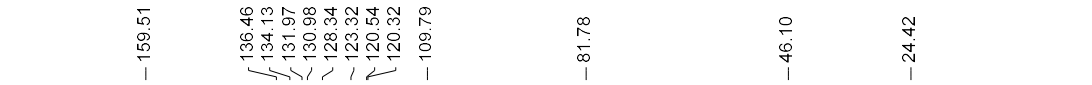
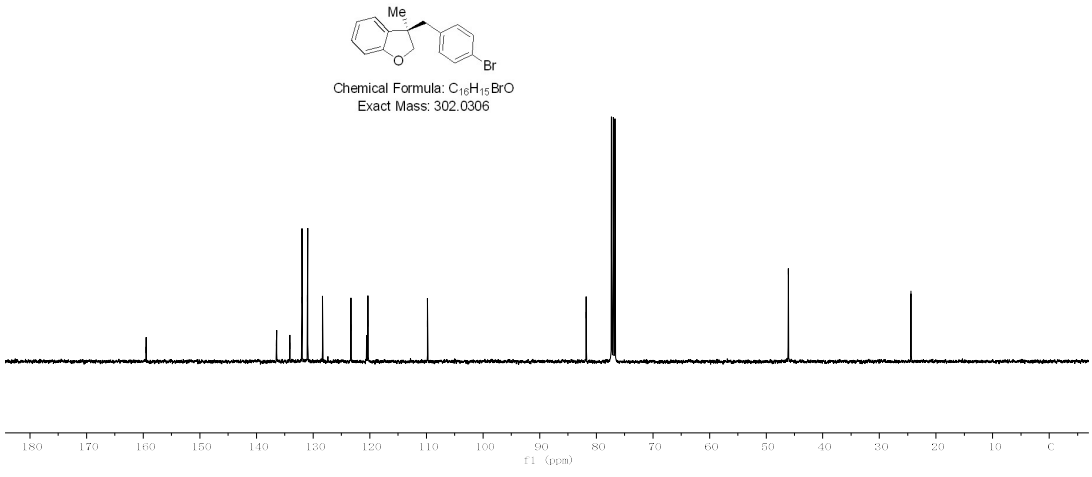
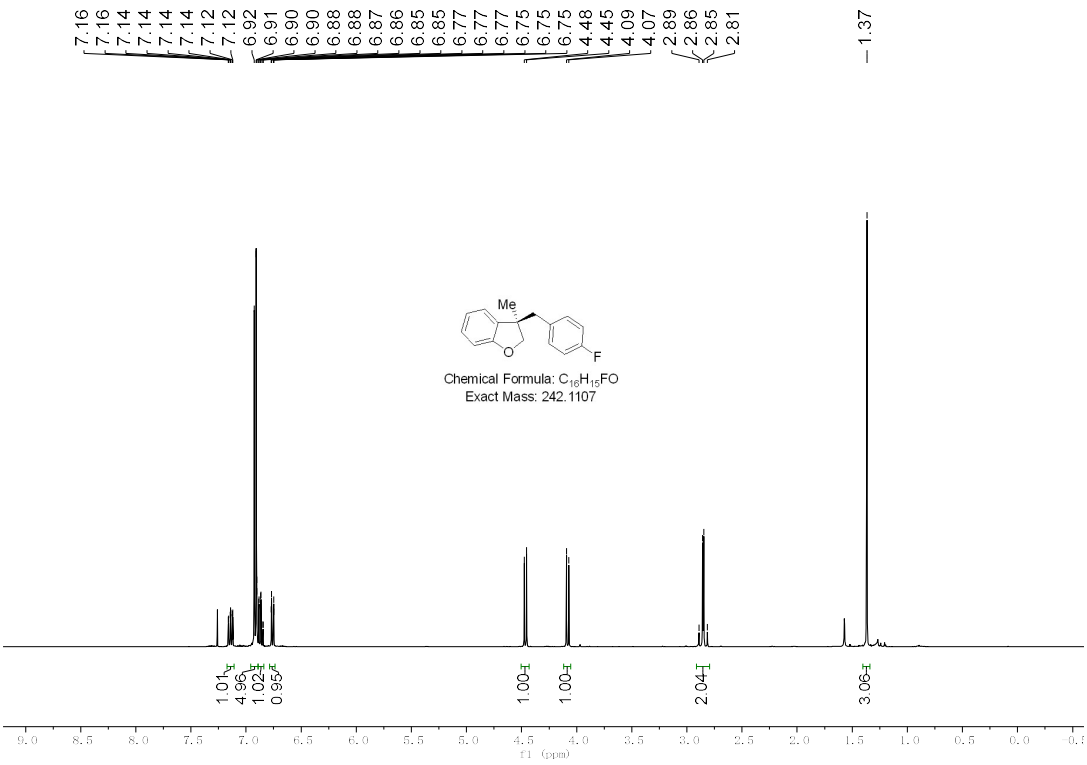
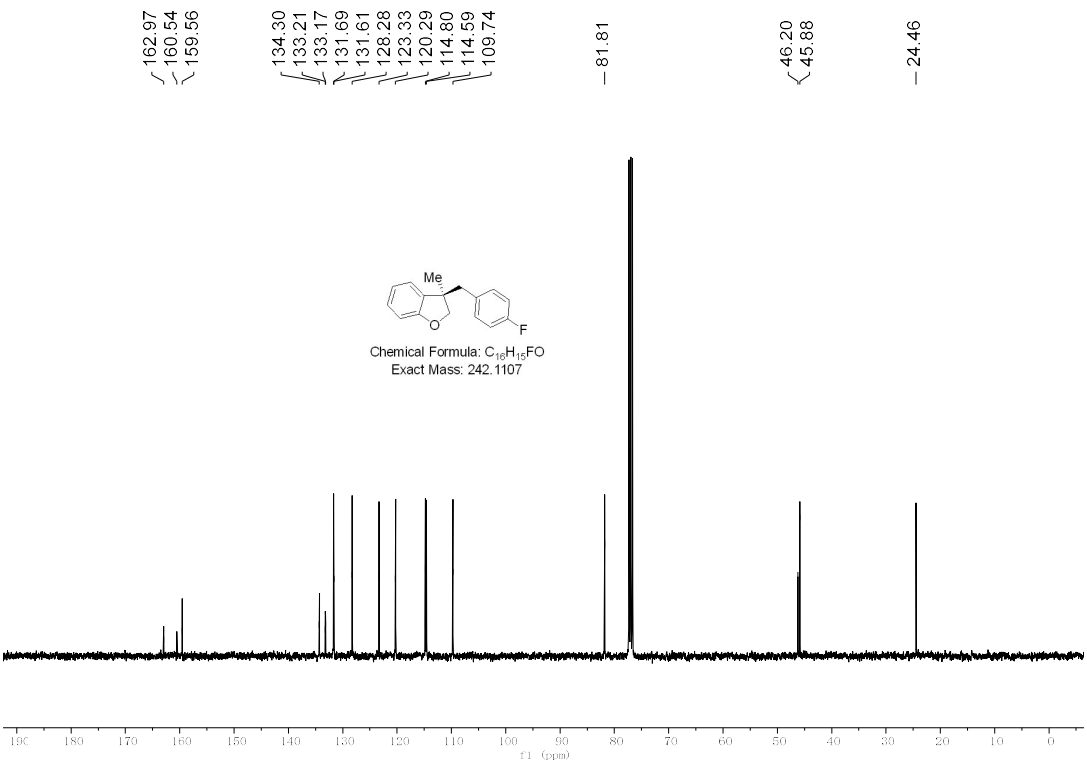
1.00
1.00
1.01
2.09
3.10
f1 (ppm)

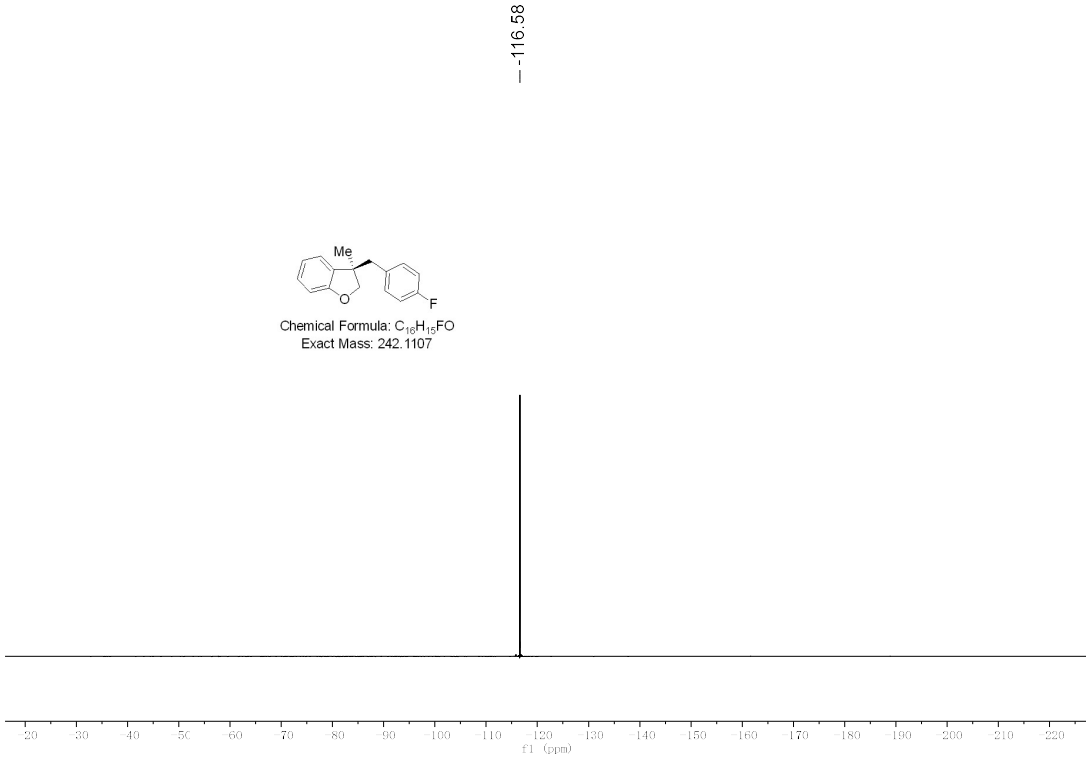

159.51
136.46
134.13
131.97
130.98
128.34
123.32
120.54
120.32
109.79
81.78
46.10
24.42


Me
O
Br
Chemical Formula: C16H15BrO
Exact Mass: 302.0306
f1 (ppm)

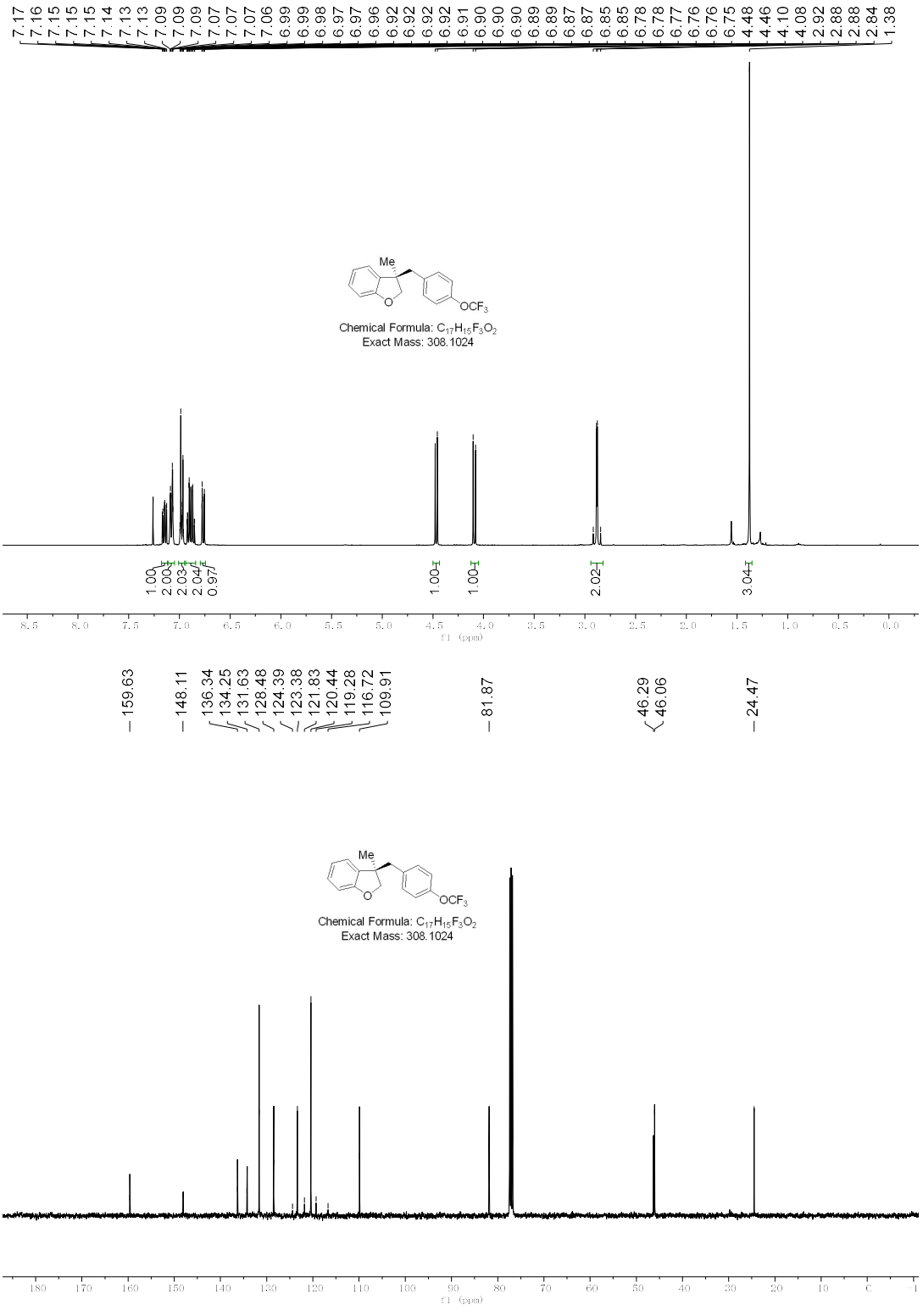
3ae

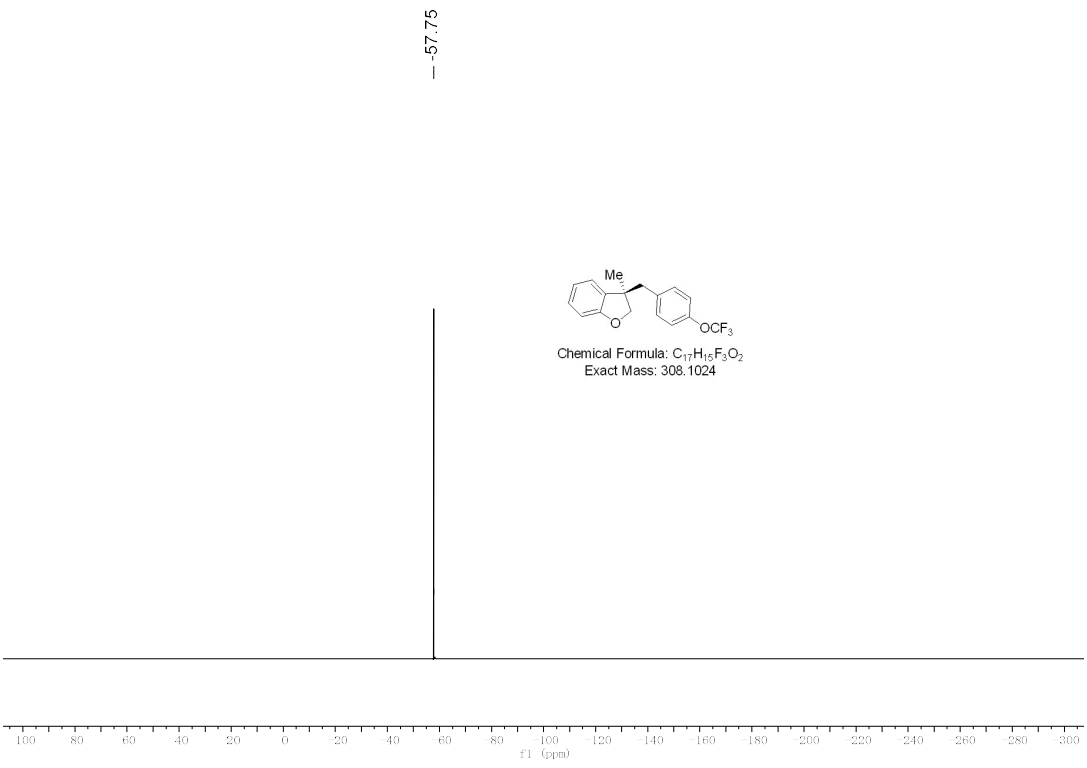

7.16
7.16
7.14
7.14
7.14
7.14
7.12
7.12
6.92
6.91
6.90
6.90
6.88
6.88
6.87
6.86
6.85
6.85
6.77
6.77
6.75
6.75
6.75
4.48
4.45
4.09
4.07
2.89
2.86
2.85
2.81
1.37
Me
O
F
Chemical Formula: C16H15FO
Exact Mass: 242.1107
1.01
4.96
1.02
0.95
1.00
1.00
2.04
3.06
f1 (ppm)


162.97
160.54
159.56
134.30
133.21
133.17
131.69
131.61
128.28
123.33
120.29
114.80
114.59
109.74
81.81
46.20
45.88
24.46
Me
O
F
Chemical Formula: C16H15FO
Exact Mass: 242.1107
f1 (ppm)

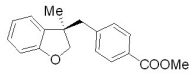

-116.58
Me
O
F
Chemical Formula: C16H15FO
Exact Mass: 242.1107
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
f1 (ppm)

3af

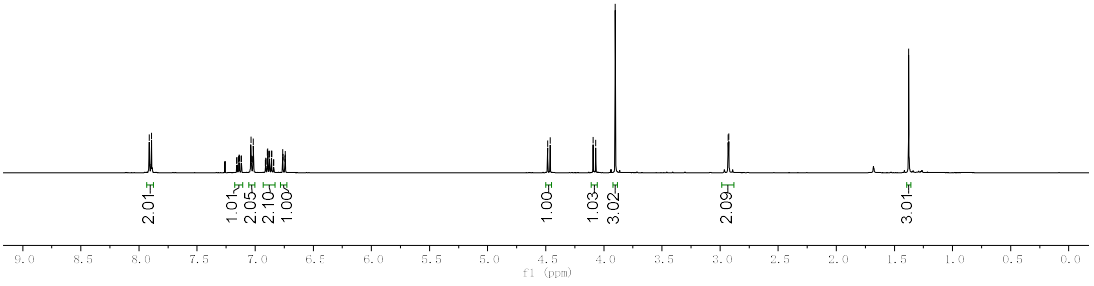

7.17
7.16
7.15
7.15
7.15
7.14
7.13
7.13
7.09
7.09
7.09
7.07
7.07
7.07
7.06
6.99
6.99
6.98
6.97
6.97
6.96
6.92
6.92
6.92
6.92
6.91
6.90
6.90
6.90
6.89
6.89
6.87
6.87
6.85
6.85
6.78
6.77
6.76
6.76
6.75
4.48
4.46
4.10
4.08
2.92
2.88
2.88
2.84
1.38
Me
OCF3
Chemical Formula: C17H15F3O2
Exact Mass: 308.1024
1.00
2.00
2.03
2.04
0.97
1.00
1.00
2.02
3.04
f1 (ppm)
159.63
148.11
136.34
134.25
131.63
128.48
124.39
123.38
121.83
120.44
119.28
116.72
109.91
81.87
46.29
46.06
24.47
Me
OCF3
Chemical Formula: C17H15F3O2
Exact Mass: 308.1024
f1 (ppm)

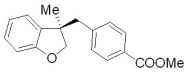

-57.75
Me
O
OCF3
Chemical Formula: C17H15F3O2
Exact Mass: 308.1024
100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
f1 (ppm)

3ag

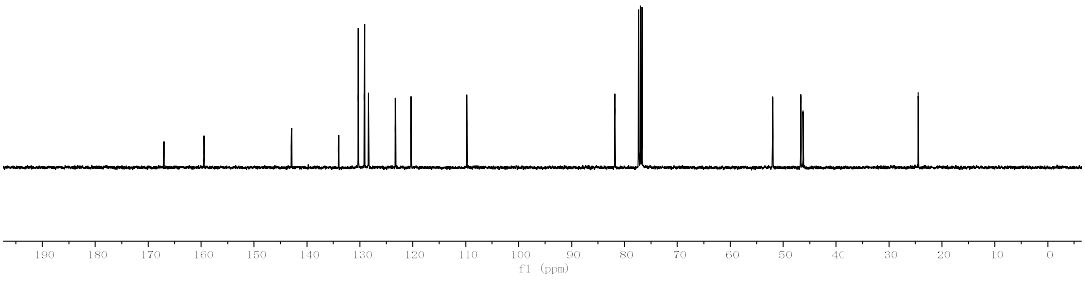


Chemical Formula: $C_{18}H_{18}O_3$
Exact Mass: 282.1256

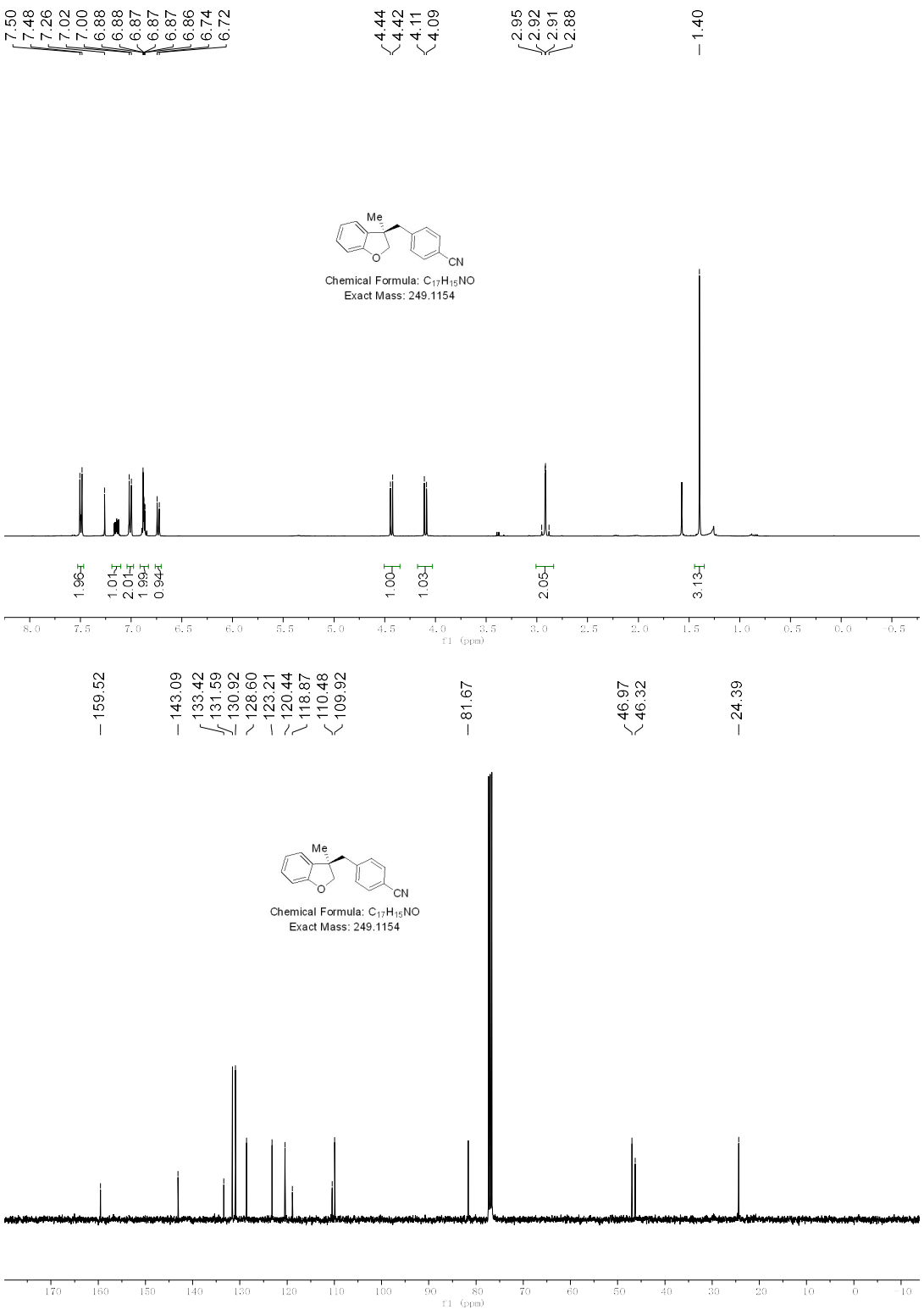




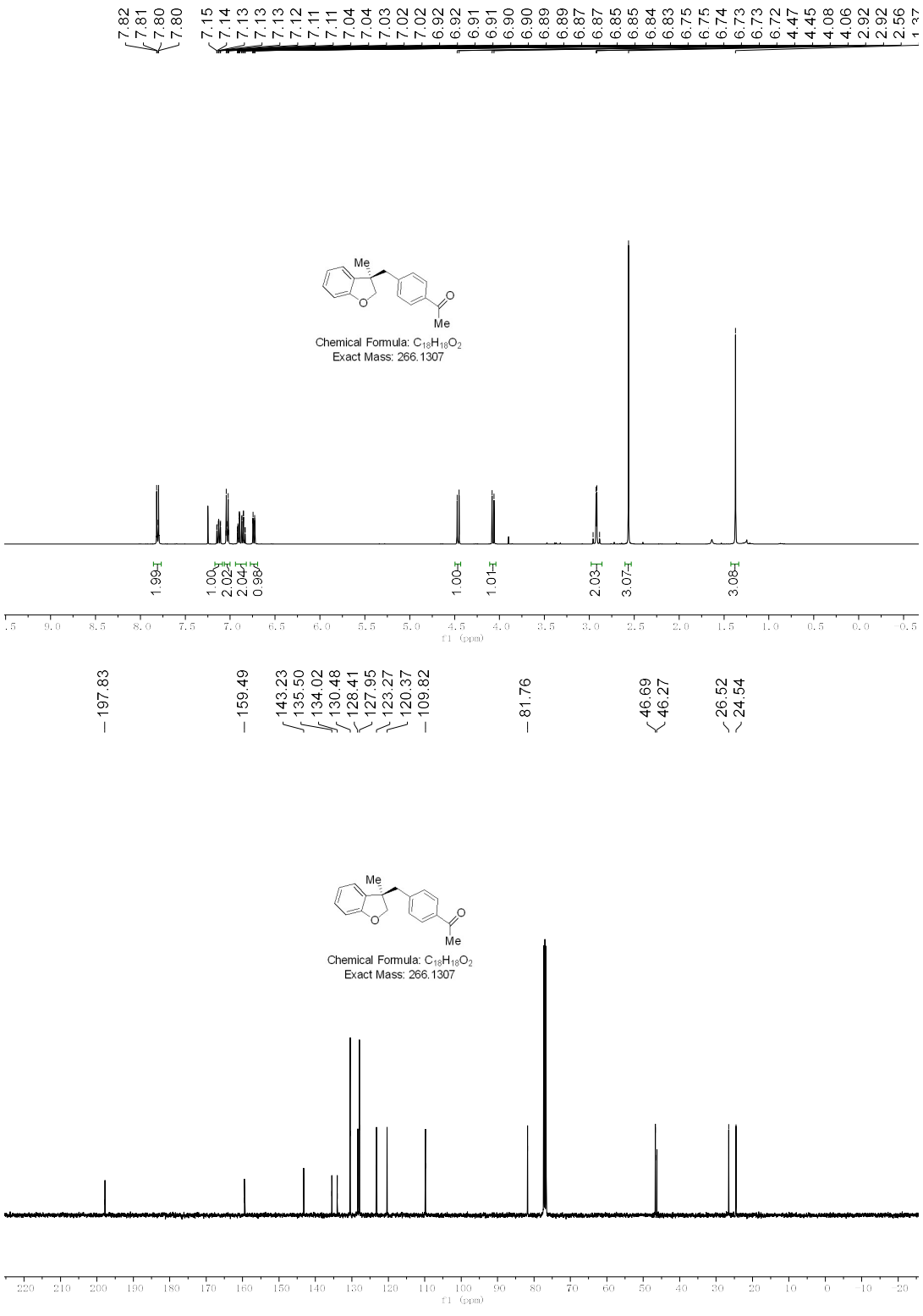
Chemical Formula: $C_{18}H_{18}O_3$
Exact Mass: 282.1256



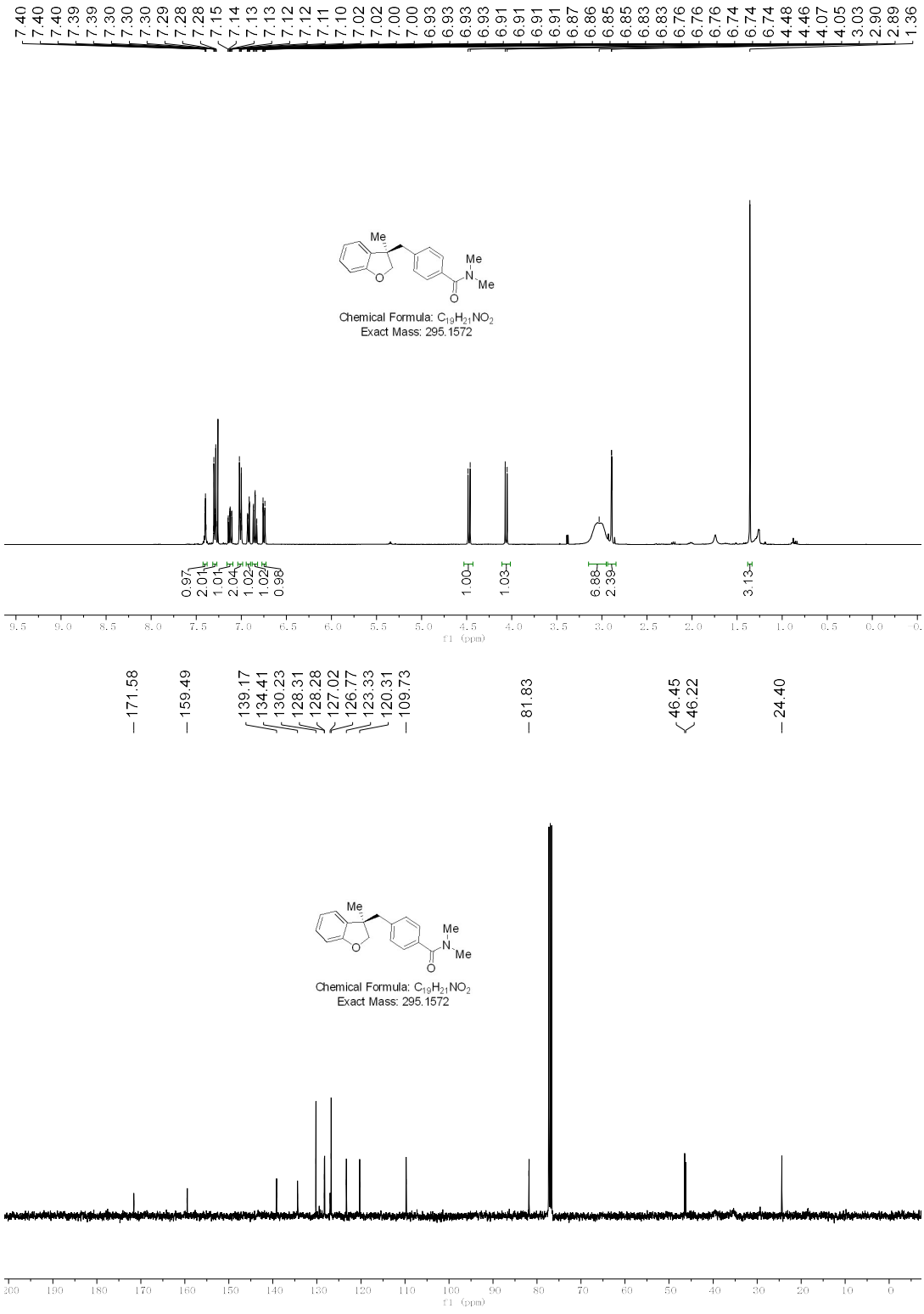
3ah


7.50
7.48
7.26
7.02
7.00
6.88
6.88
6.87
6.87
6.87
6.86
6.74
6.72
4.44
4.42
4.11
4.09
2.95
2.92
2.91
2.88
1.40
Me
CN
Chemical Formula: C17H15NO
Exact Mass: 249.1154
1.96
1.01
2.01
1.99
0.94
1.00
1.03
2.05
3.13
f1 (ppm)
159.52
143.09
133.42
131.59
130.92
128.60
123.21
120.44
118.87
110.48
109.92
81.67
46.97
46.32
24.39
Me
CN
Chemical Formula: C17H15NO
Exact Mass: 249.1154
f1 (ppm)

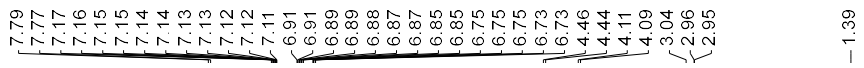
3ai

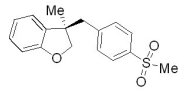

7.82
7.81
7.80
7.80
7.15
7.14
7.13
7.13
7.13
7.12
7.11
7.11
7.04
7.04
7.03
7.02
7.02
6.92
6.92
6.91
6.91
6.90
6.90
6.89
6.89
6.87
6.87
6.85
6.85
6.84
6.83
6.75
6.75
6.74
6.73
6.73
6.72
4.47
4.45
4.08
4.06
2.92
2.92
2.56
Me
O
Me
Chemical Formula: C18H18O2
Exact Mass: 266.1307
1.99
1.00
2.02
2.04
0.98
1.00
1.01
2.03
3.07
3.08
f1 (ppm)
197.83
159.49
143.23
135.50
134.02
130.48
128.41
127.95
123.27
120.37
109.82
81.76
46.69
46.27
26.52
24.54
Me
O
Me
Chemical Formula: C18H18O2
Exact Mass: 266.1307
f1 (ppm)

3aj

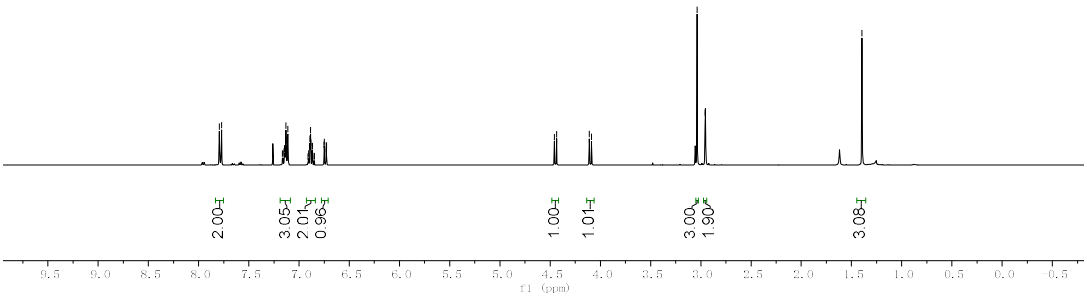

7.40 7.40 7.40 7.39 7.39 7.30 7.30 7.30 7.29 7.28 7.28 7.15 7.14 7.13 7.13 7.12 7.12 7.11 7.10 7.02 7.02 7.00 7.00 6.93 6.93 6.93 6.91 6.91 6.91 6.87 6.86 6.85 6.85 6.83 6.83 6.76 6.76 6.76 6.74 6.74 6.74 4.48 4.46 4.07 4.05 3.03 2.90 2.89 1.36
Me
Me
N
Me
O
Chemical Formula: C19H21NO2
Exact Mass: 295.1572
0.97 2.01 1.01 2.04 1.02 1.02 0.98 1.00 1.03 6.88 2.39 3.13
f1 (ppm)
171.58 159.49 139.17 134.41 130.23 128.31 128.28 127.02 126.77 123.33 120.31 109.73 81.83 46.45 46.22 24.40
Me
Me
N
Me
O
Chemical Formula: C19H21NO2
Exact Mass: 295.1572
f1 (ppm)

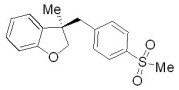
3ak



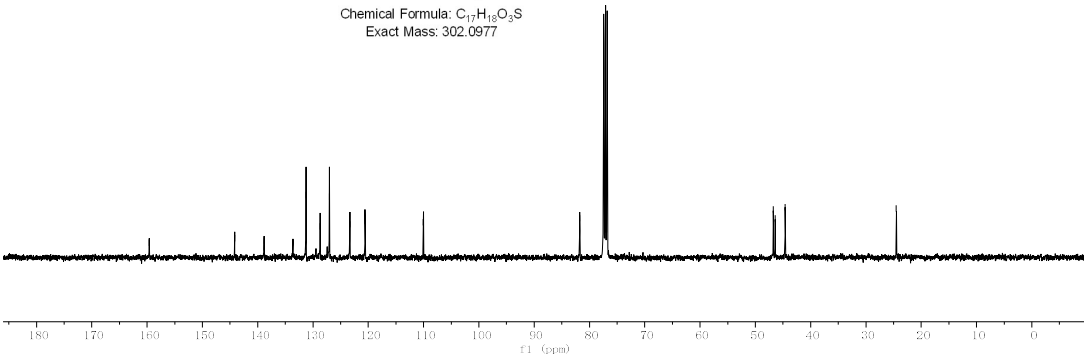


Chemical Formula: $C_{17}H_{18}O_3S$
Exact Mass: 302.0977

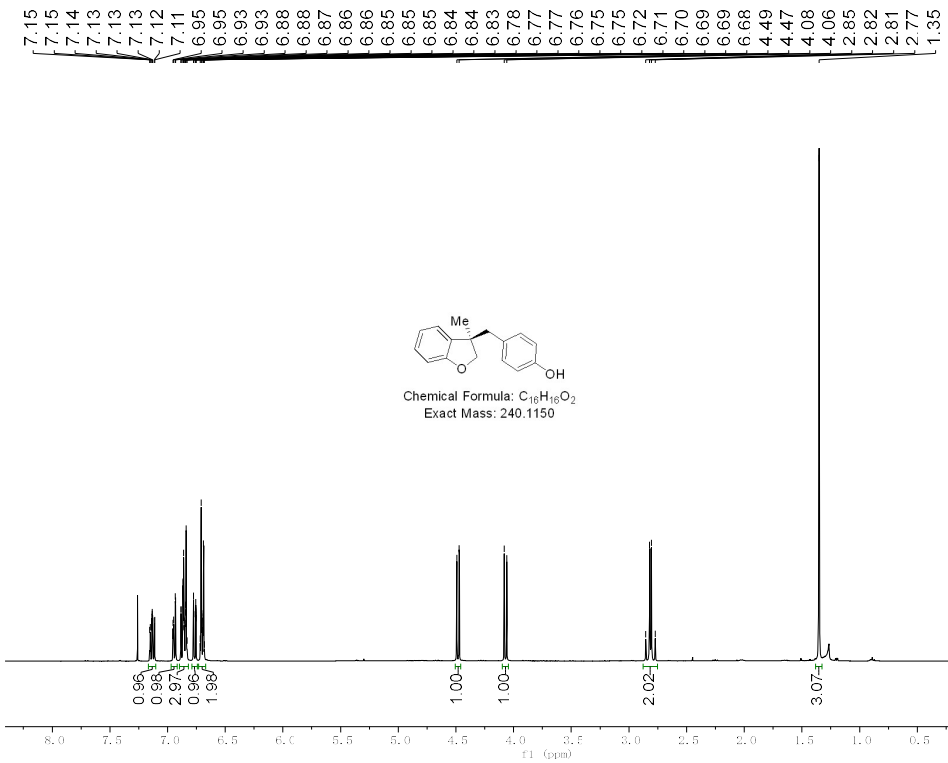


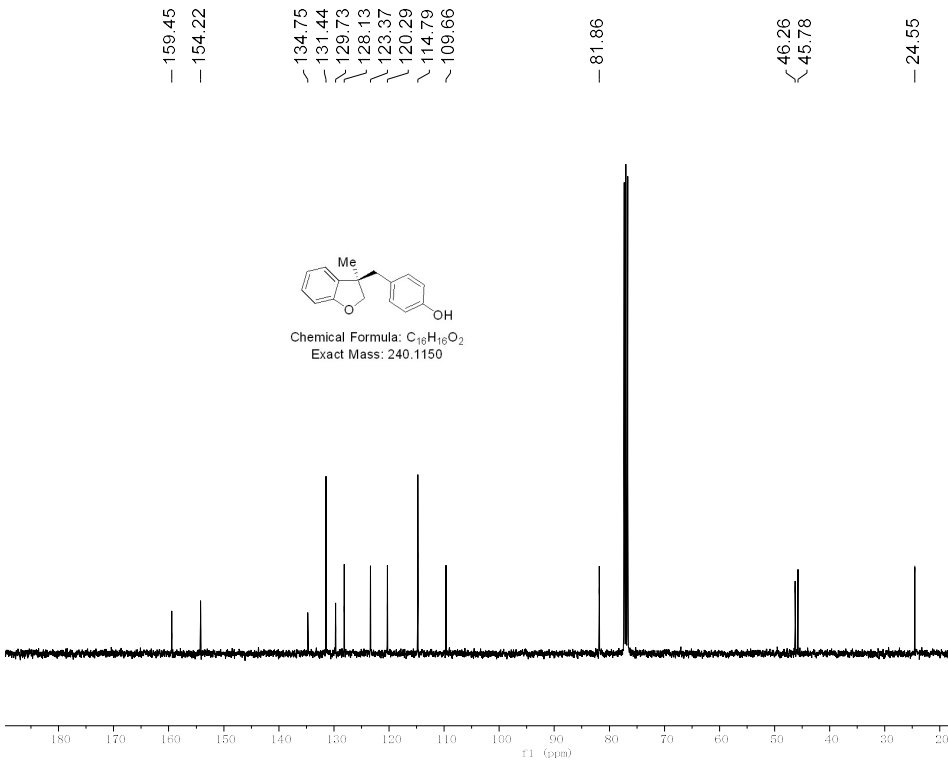


Chemical Formula: $C_{17}H_{18}O_3S$
Exact Mass: 302.0977

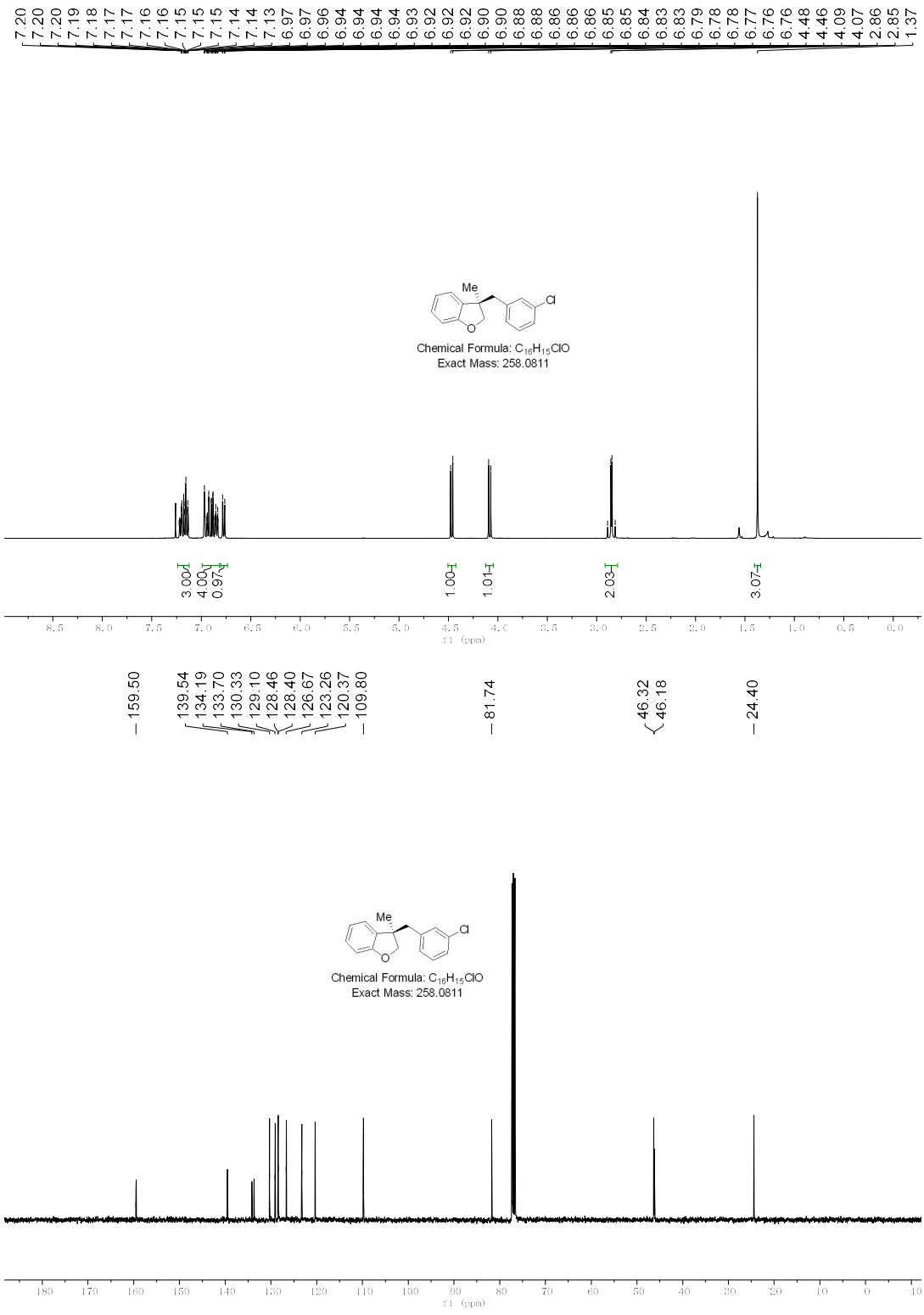


3al

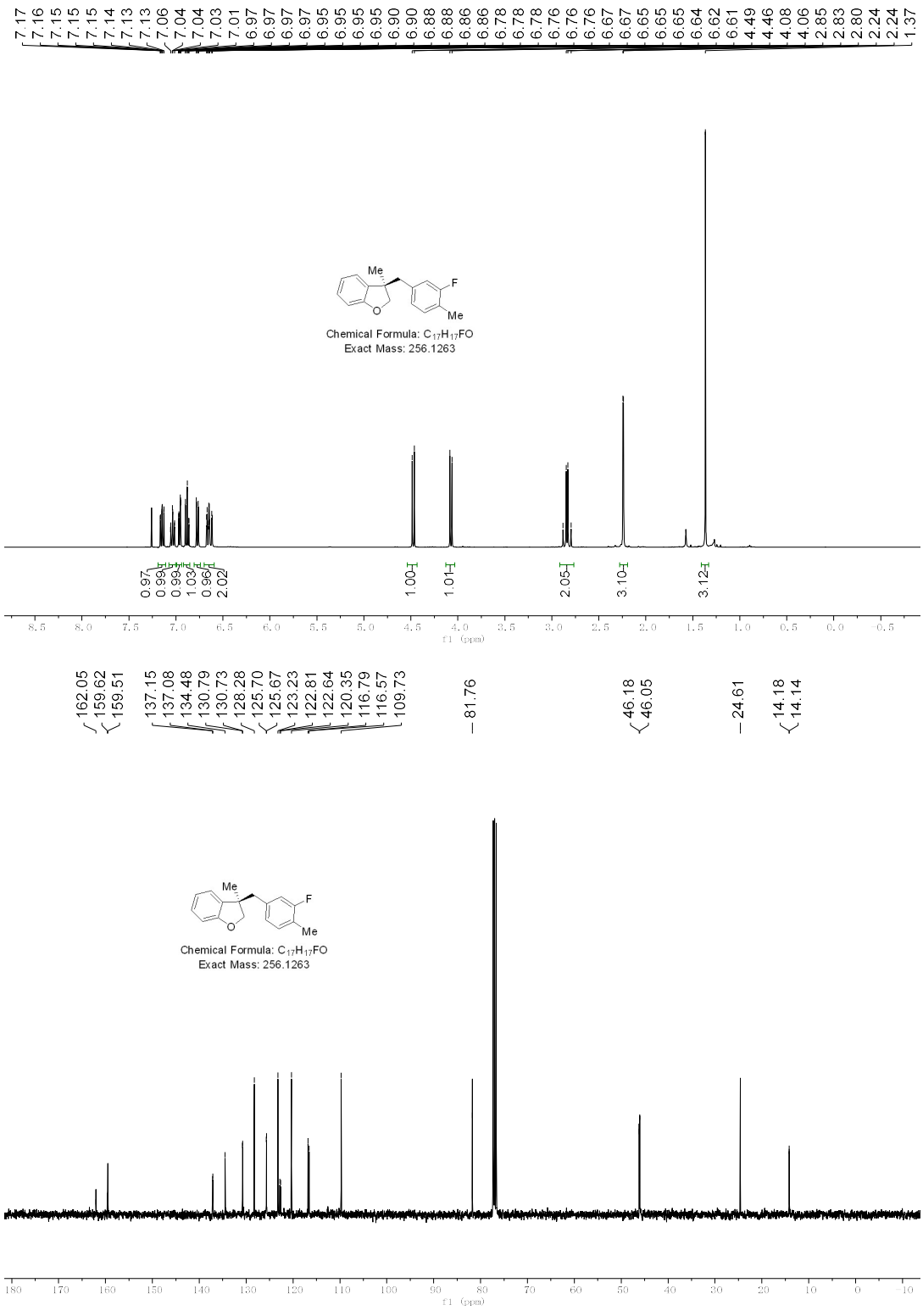

7.15
7.15
7.14
7.13
7.13
7.13
7.12
7.11
6.95
6.95
6.93
6.93
6.88
6.88
6.87
6.86
6.86
6.85
6.85
6.85
6.84
6.84
6.83
6.78
6.77
6.77
6.76
6.75
6.75
6.72
6.71
6.70
6.69
6.69
6.68
4.49
4.47
4.08
4.06
2.85
2.82
2.81
2.77
1.35
Me
OH
Chemical Formula: C16H16O2
Exact Mass: 240.1150
0.96
0.98
2.97
0.96
1.98
1.00
1.00
2.02
3.07
f1 (ppm)

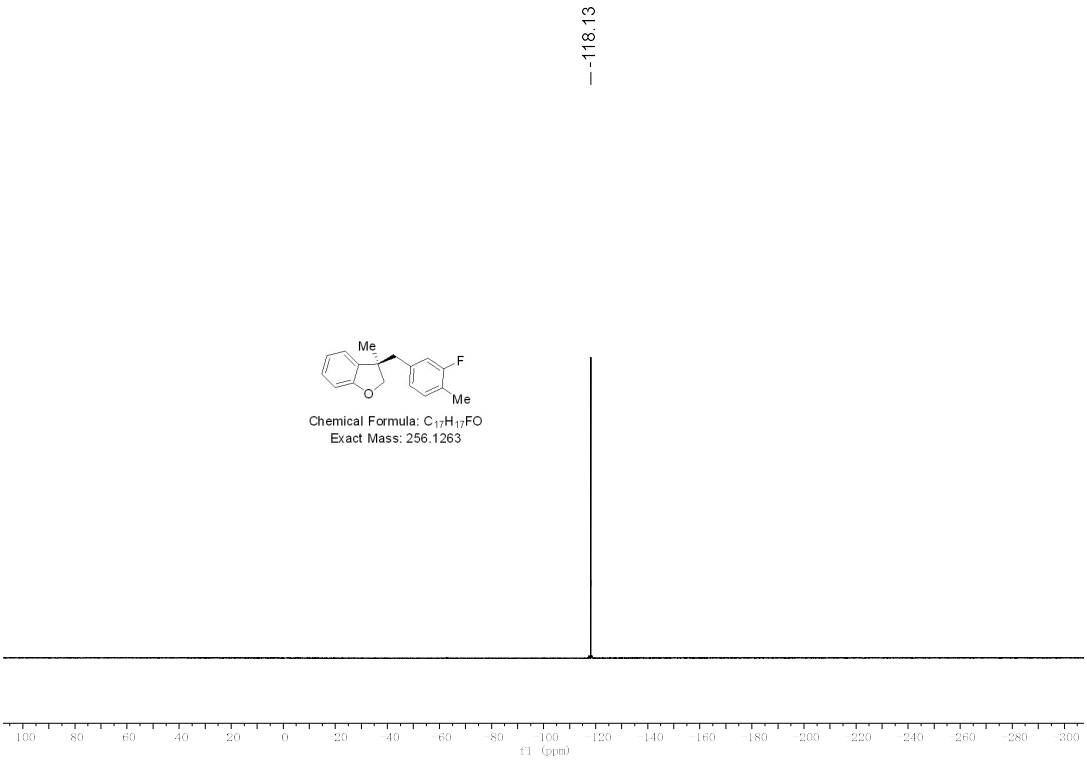

159.45
154.22
134.75
131.44
129.73
128.13
123.37
120.29
114.79
109.66
81.86
46.26
45.78
24.55
Me
OH
Chemical Formula: C16H16O2
Exact Mass: 240.1150
f1 (ppm)

3am

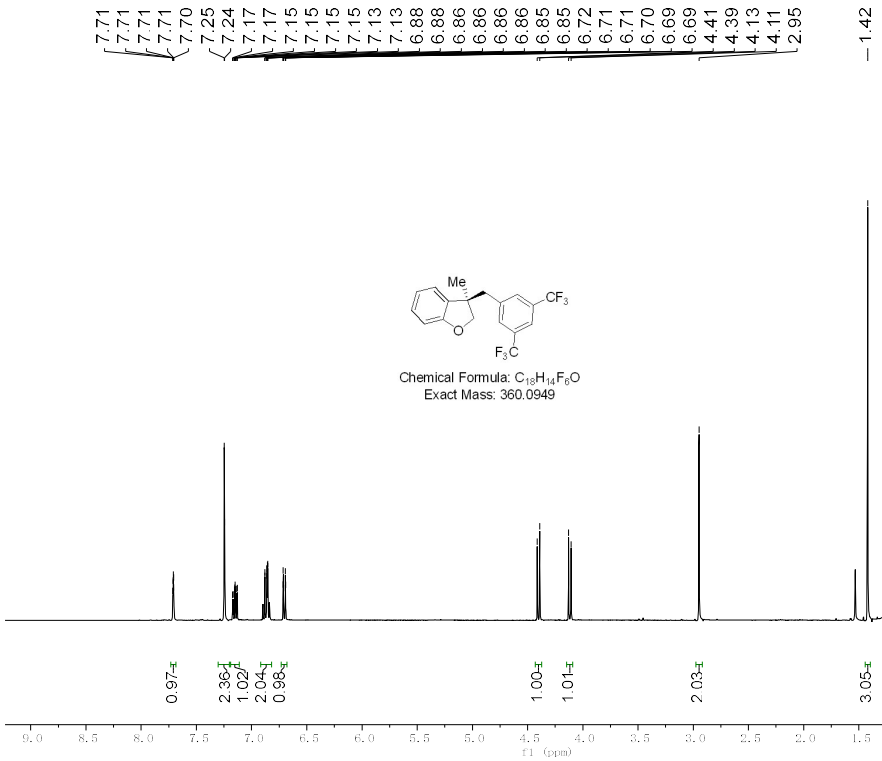

7.20 7.20 7.20 7.19 7.18 7.17 7.17 7.16 7.16 7.15 7.15 7.15 7.14 7.14 7.13 6.97 6.97 6.96 6.94 6.94 6.94 6.94 6.93 6.92 6.92 6.90 6.90 6.88 6.88 6.86 6.86 6.86 6.85 6.85 6.84 6.83 6.83 6.79 6.78 6.78 6.77 6.76 6.76 4.48 4.46 4.09 4.07 2.86 2.85 1.37
Me
Cl
O
Chemical Formula: C16H15ClO
Exact Mass: 258.0811
3.00
4.00
0.97
1.00
1.01
2.03
3.07
f1 (ppm)
159.50
139.54
134.19
133.70
130.33
129.10
128.46
128.40
126.67
123.26
120.37
109.80
81.74
46.32
46.18
24.40
Me
Cl
O
Chemical Formula: C16H15ClO
Exact Mass: 258.0811
f1 (ppm)

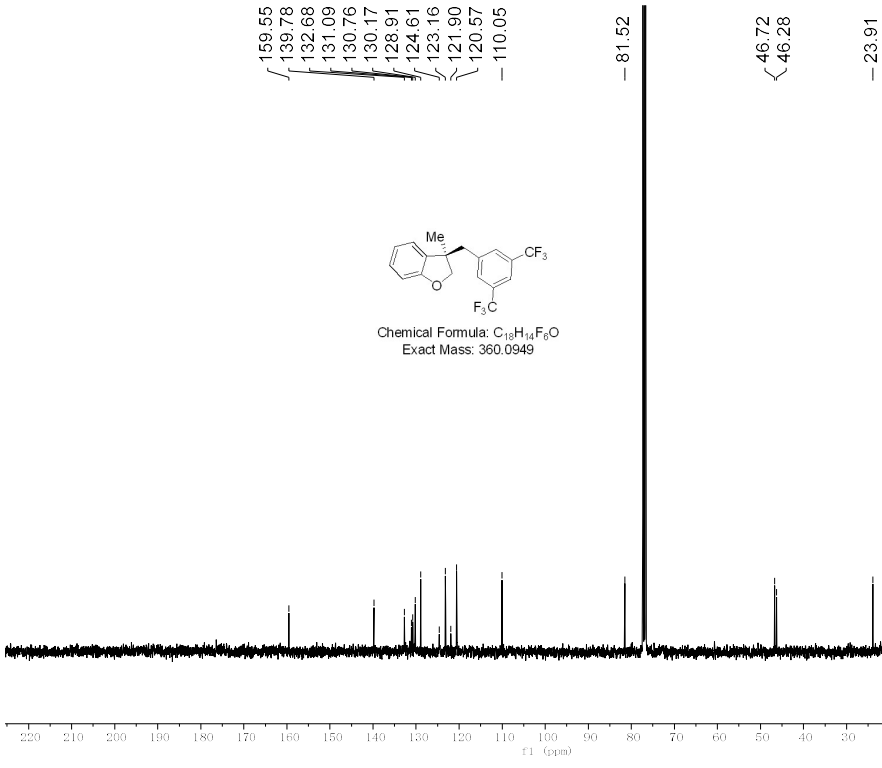
3an

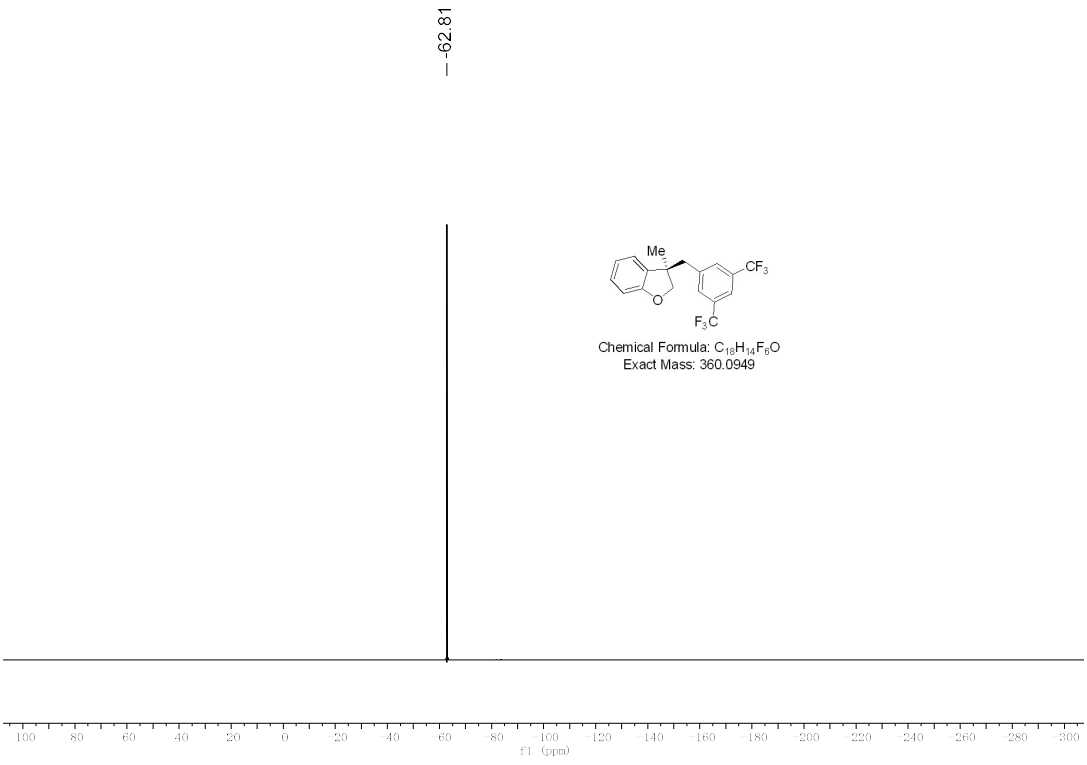

7.17 7.16 7.15 7.15 7.15 7.14 7.13 7.13 7.06 7.04 7.04 7.03 7.01 6.97 6.97 6.97 6.97 6.95 6.95 6.95 6.95 6.90 6.90 6.88 6.88 6.86 6.86 6.78 6.78 6.78 6.76 6.76 6.76 6.67 6.67 6.65 6.65 6.65 6.64 6.62 6.61 4.49 4.46 4.08 4.06 2.85 2.83 2.80 2.24 2.24 1.37
Me
F
Me
O
Chemical Formula: C17H17FO
Exact Mass: 256.1263
0.97 0.99 0.99 1.03 0.96 2.02 1.00 1.01 2.05 3.10 3.12
f1 (ppm)
162.05 159.62 159.51 137.15 137.08 134.48 130.79 130.73 128.28 125.70 125.67 123.23 122.81 122.64 120.35 116.79 116.57 109.73 81.76 46.18 46.05 24.61 14.18 14.14
Me
F
Me
O
Chemical Formula: C17H17FO
Exact Mass: 256.1263
f1 (ppm)


-118.13
Me
F
O
Me
Chemical Formula: C17H17FO
Exact Mass: 256.1263
100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
f1 (ppm)

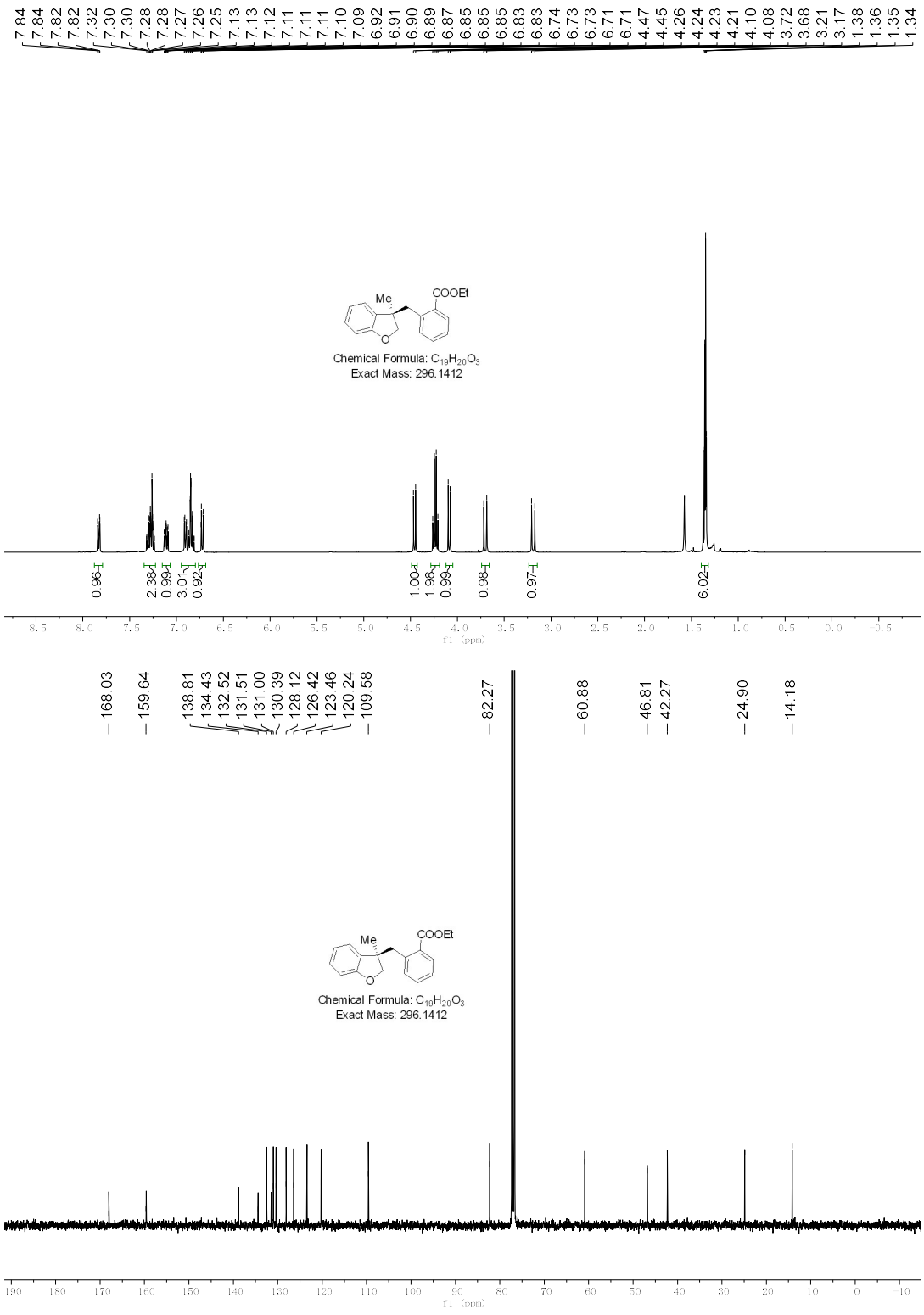
3ao


7.71
7.71
7.71
7.71
7.70
7.25
7.24
7.17
7.17
7.15
7.15
7.15
7.15
7.13
7.13
6.88
6.88
6.86
6.86
6.86
6.86
6.85
6.85
6.72
6.71
6.71
6.70
6.69
6.69
4.41
4.39
4.13
4.11
2.95
1.42
Me
CF3
F3C
Chemical Formula: C18H14F6O
Exact Mass: 360.0949
0.97
2.36
1.02
2.04
0.98
1.00
1.01
2.03
3.05
f1 (ppm)

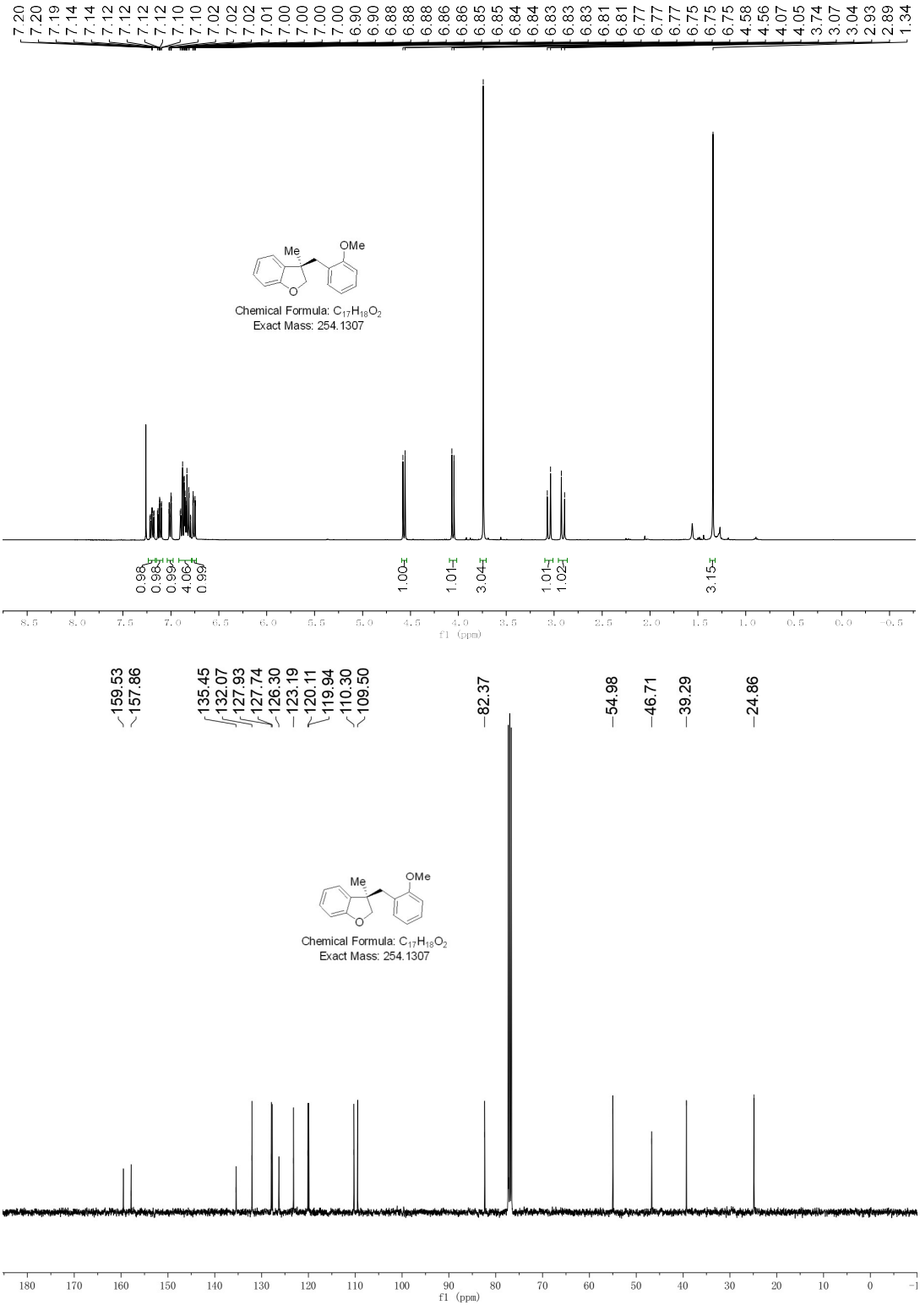

159.55
139.78
132.68
131.09
130.76
130.17
128.91
124.61
123.16
121.90
120.57
110.05
81.52
46.72
46.28
23.91
Me
CF3
F3C
Chemical Formula: C18H14F6O
Exact Mass: 360.0949
f1 (ppm)


-62.81
Me
CF3
O
F3C
Chemical Formula: C18H14F6O
Exact Mass: 360.0949
100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
f1 (ppm)

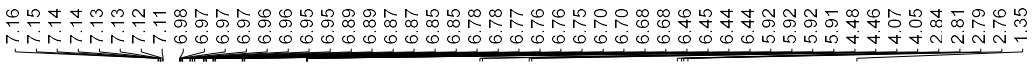
3ap

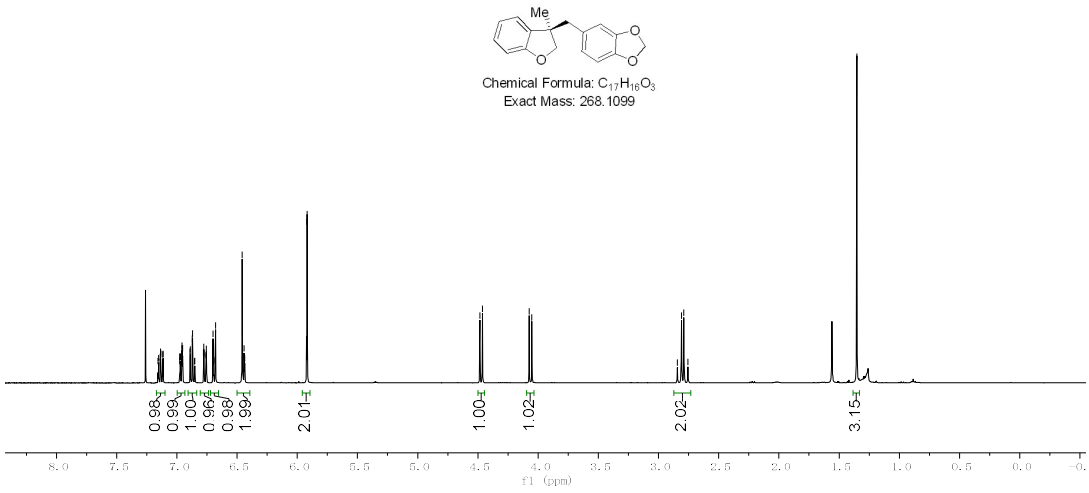

7.84
7.84
7.82
7.82
7.32
7.30
7.30
7.28
7.28
7.27
7.26
7.25
7.13
7.13
7.12
7.11
7.11
7.11
7.10
7.09
6.92
6.91
6.90
6.89
6.87
6.85
6.85
6.85
6.83
6.83
6.74
6.73
6.73
6.71
6.71
4.47
4.45
4.26
4.24
4.23
4.21
4.10
4.08
3.72
3.68
3.21
3.17
1.38
1.36
1.35
1.34
Me
COOEt
Chemical Formula: C19H20O3
Exact Mass: 296.1412
0.96
2.38
0.99
3.01
0.92
1.00
1.98
0.99
0.98
0.97
6.02
f1 (ppm)
168.03
159.64
138.81
134.43
132.52
131.51
131.00
130.39
128.12
126.42
123.46
120.24
109.58
82.27
60.88
46.81
42.27
24.90
14.18
Me
COOEt
Chemical Formula: C19H20O3
Exact Mass: 296.1412
f1 (ppm)

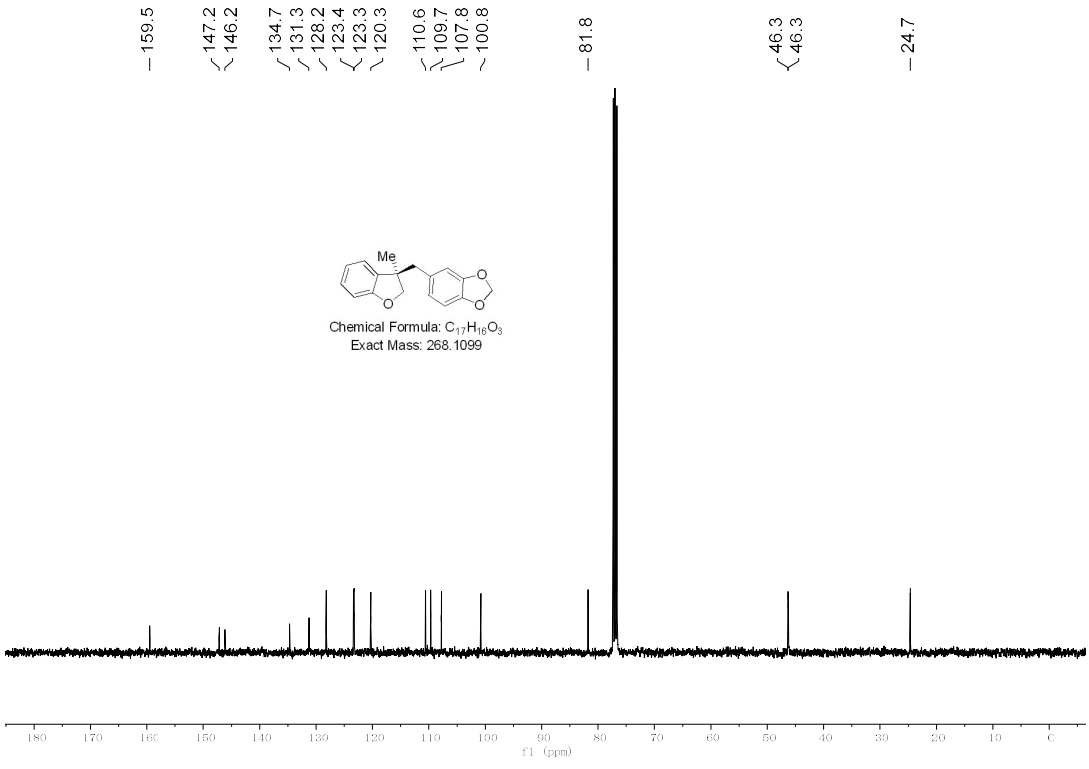
3aq


7.20 7.20 7.19 7.14 7.14 7.12 7.12 7.12 7.12 7.10 7.10 7.02 7.02 7.02 7.01 7.00 7.00 7.00 7.00 6.90 6.90 6.88 6.88 6.88 6.86 6.86 6.85 6.85 6.84 6.84 6.83 6.83 6.81 6.81 6.77 6.77 6.75 6.75 6.75 4.58 4.56 4.07 4.05 3.74 3.07 3.04 2.93 2.89 1.34
Me
OMe
Chemical Formula: C17H18O2
Exact Mass: 254.1307
0.98 0.96 0.99 4.06 0.99
1.00 1.01 3.04 1.01 1.02 3.15
f1 (ppm)
159.53 157.86 135.45 132.07 127.93 127.74 126.30 123.19 120.11 119.94 110.30 109.50 82.37 54.98 46.71 39.29 24.86
Me
OMe
Chemical Formula: C17H18O2
Exact Mass: 254.1307
f1 (ppm)

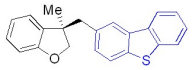
3ar


7.16
7.15
7.14
7.14
7.13
7.13
7.12
7.11
6.98
6.97
6.97
6.97
6.96
6.96
6.95
6.95
6.89
6.89
6.87
6.87
6.85
6.85
6.78
6.78
6.77
6.76
6.76
6.75
6.70
6.70
6.68
6.68
6.46
6.45
6.44
6.44
5.92
5.92
5.91
4.48
4.46
4.07
4.05
2.84
2.81
2.79
2.76
1.35

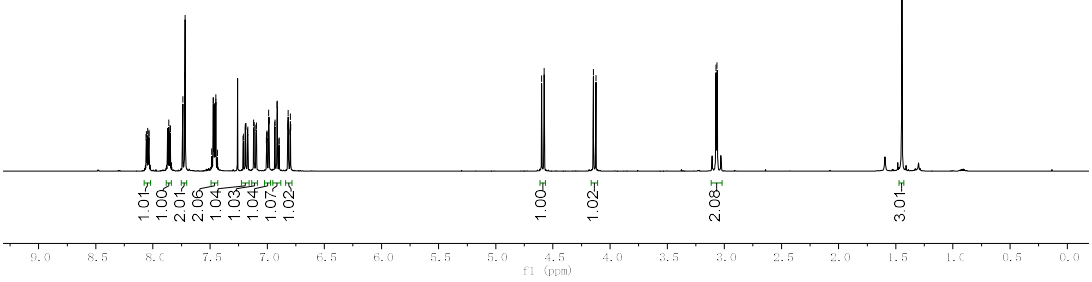

Me
Chemical Formula: C17H16O3
Exact Mass: 268.1099
0.98
0.99
1.00
0.98
0.98
1.99
2.01
1.00
1.02
2.02
3.15
f1 (ppm)

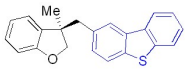

159.5
147.2
146.2
134.7
131.3
128.2
123.4
123.3
120.3
110.6
109.7
107.8
100.8
81.8
46.3
46.3
24.7
Me
Chemical Formula: C17H16O3
Exact Mass: 268.1099
f1 (ppm)

3as

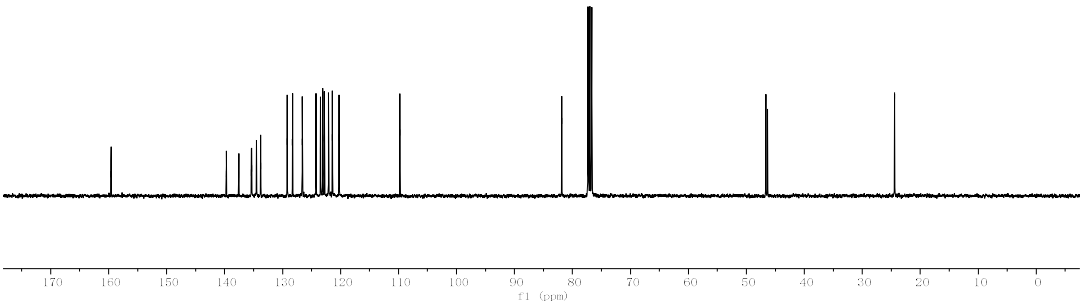


Chemical Formula: $C_{22}H_{18}OS$
Exact Mass: 330.1078

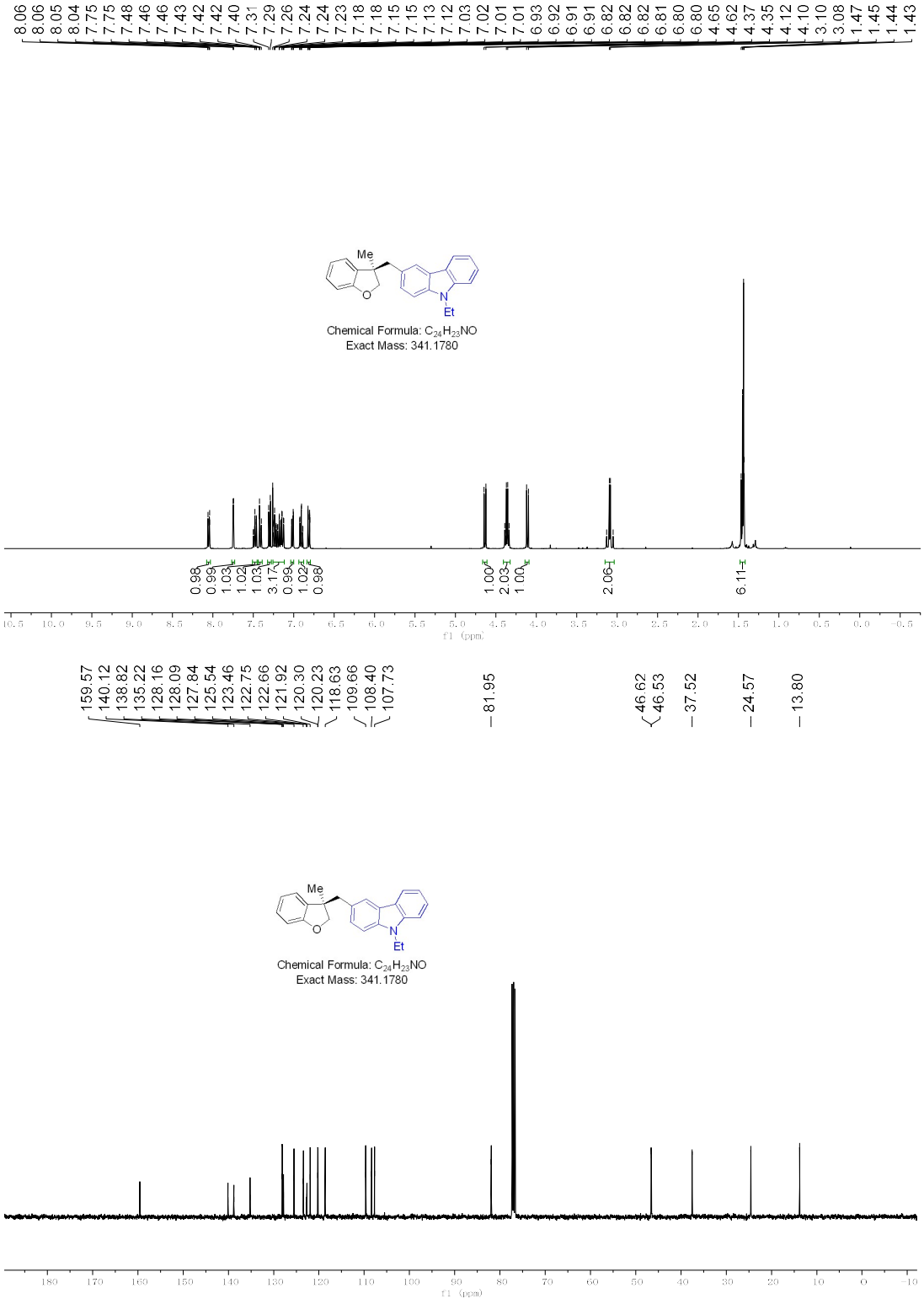




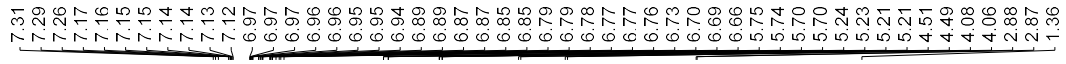
Chemical Formula: $C_{22}H_{18}OS$
Exact Mass: 330.1078

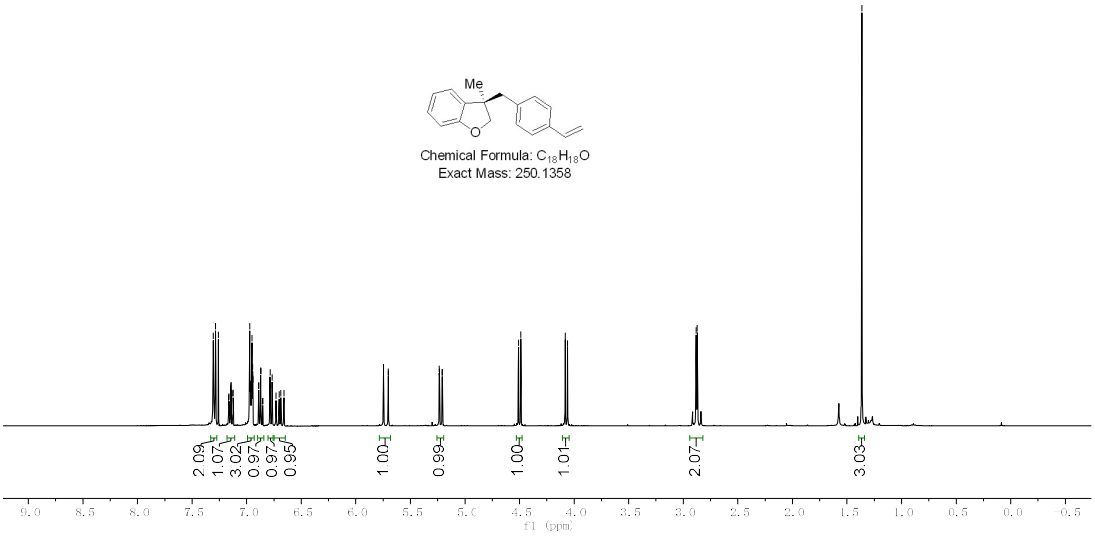


3at

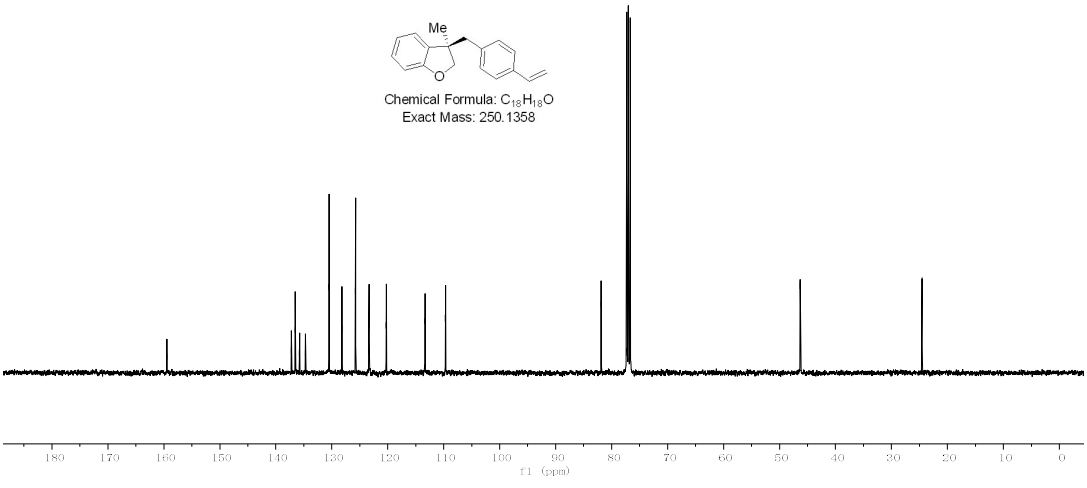

8.06 8.06 8.05 8.04 7.75 7.75 7.48 7.46 7.46 7.43 7.42 7.42 7.40 7.31 7.29 7.26 7.24 7.24 7.23 7.18 7.15 7.15 7.13 7.12 7.03 7.02 7.01 7.01 6.93 6.92 6.91 6.91 6.82 6.82 6.82 6.81 6.80 6.80 4.65 4.62 4.37 4.35 4.12 4.10 3.10 3.08 1.47 1.45 1.44 1.43
Me
O
N
Et
Chemical Formula: C24H23NO
Exact Mass: 341.1780
0.98 0.99 1.03 1.02 1.03 3.17 0.99 1.02 0.98
1.00 2.03 1.00
2.06
6.11
f1 (ppm)
159.57 140.12 138.82 135.22 128.16 128.09 127.84 125.54 123.46 122.75 122.66 121.92 120.30 120.23 118.63 109.66 108.40 107.73
81.95
46.62 46.53
37.52
24.57
13.80
Me
O
N
Et
Chemical Formula: C24H23NO
Exact Mass: 341.1780
f1 (ppm)

3au

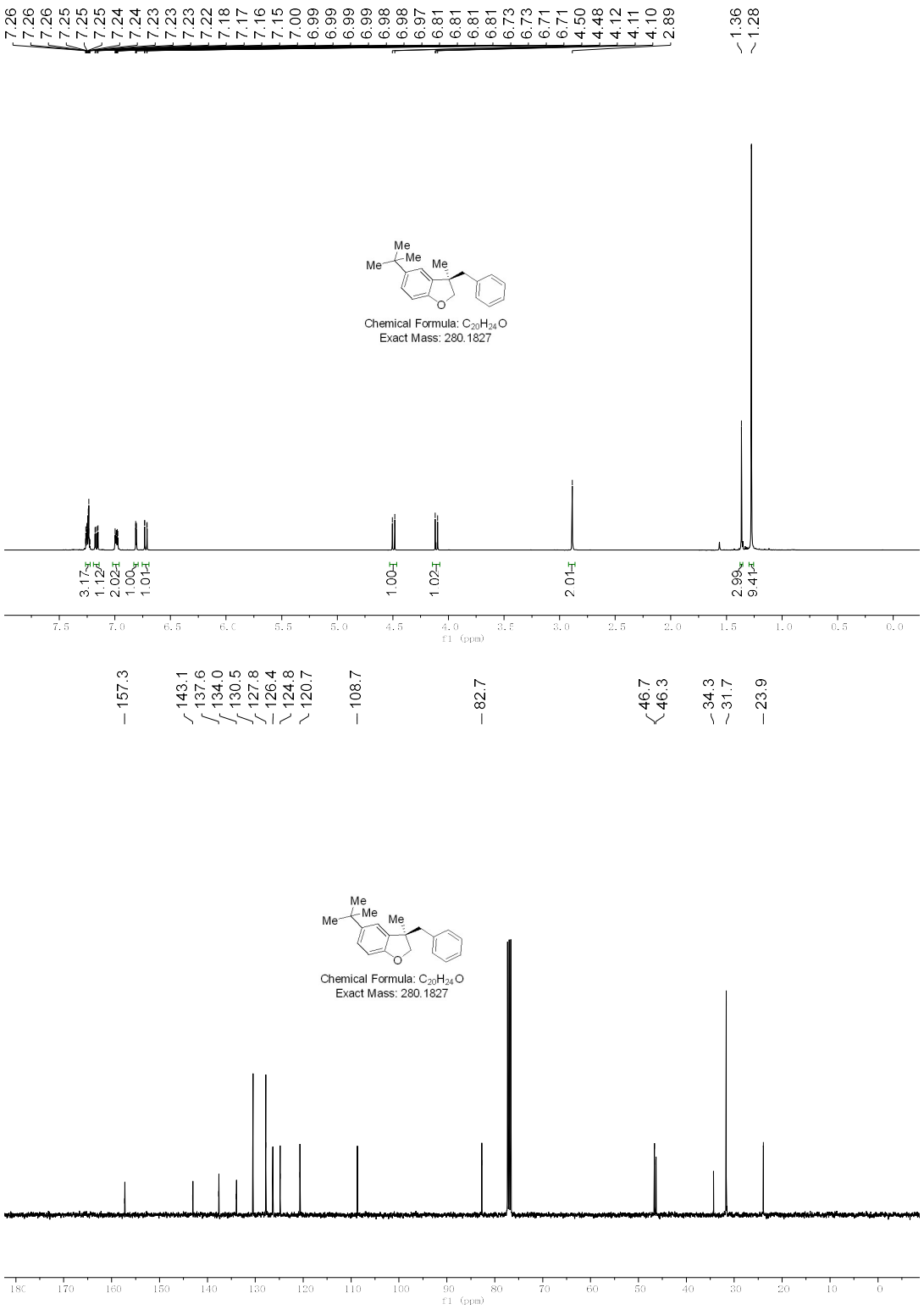

7.31
7.29
7.26
7.17
7.16
7.15
7.15
7.14
7.14
7.13
7.12
6.97
6.97
6.97
6.96
6.96
6.95
6.95
6.94
6.89
6.89
6.87
6.87
6.85
6.85
6.79
6.79
6.78
6.77
6.77
6.76
6.73
6.70
6.69
6.66
5.75
5.74
5.70
5.70
5.24
5.23
5.21
5.21
4.51
4.49
4.08
4.06
2.88
2.87
1.36


Me
O
Chemical Formula: C18H18O
Exact Mass: 250.1358
2.09
1.07
3.02
0.97
0.97
0.95
1.00
0.99
1.00
1.01
2.07
3.03
f1 (ppm)

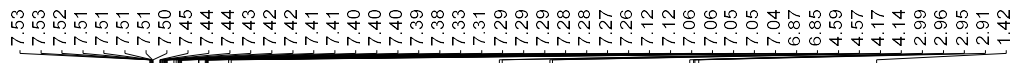

159.47
137.24
136.52
135.77
134.69
130.51
128.18
125.76
123.35
120.27
113.36
109.70
81.86
46.32
46.24
24.54

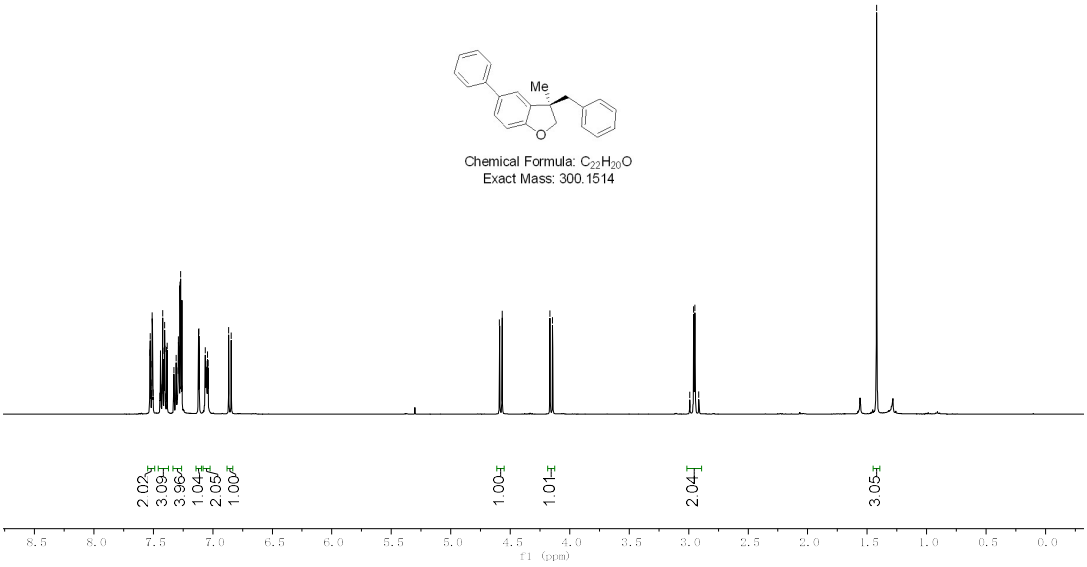

Me
O
Chemical Formula: C18H18O
Exact Mass: 250.1358
f1 (ppm)

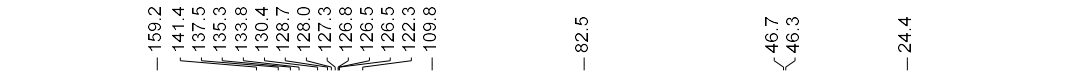
3ba

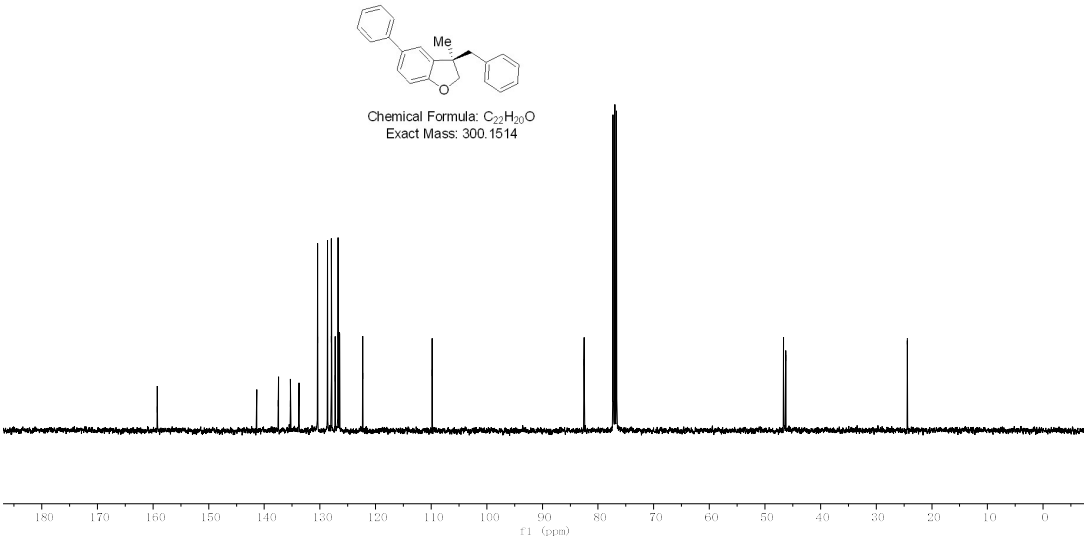

7.26
7.26
7.26
7.25
7.25
7.25
7.24
7.24
7.23
7.23
7.23
7.22
7.18
7.17
7.16
7.15
7.00
6.99
6.99
6.99
6.99
6.98
6.98
6.97
6.81
6.81
6.81
6.81
6.73
6.73
6.71
6.71
4.50
4.48
4.12
4.11
4.10
2.89
1.36
1.28
Me
Me
Me
Me
O
Chemical Formula: C20H24O
Exact Mass: 280.1827
3.17
1.12
2.02
1.00
1.01
1.00
1.02
2.01
2.99
9.41
f1 (ppm)
157.3
143.1
137.6
134.0
130.5
127.8
126.4
124.8
120.7
108.7
82.7
46.7
46.3
34.3
31.7
23.9
Me
Me
Me
Me
O
Chemical Formula: C20H24O
Exact Mass: 280.1827
f1 (ppm)

3ca

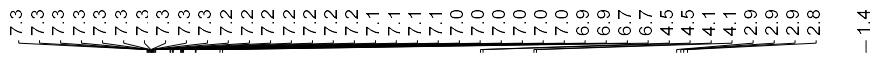

7.53
7.53
7.52
7.51
7.51
7.51
7.51
7.50
7.45
7.44
7.44
7.43
7.42
7.42
7.41
7.41
7.40
7.40
7.40
7.39
7.38
7.33
7.31
7.29
7.29
7.29
7.28
7.28
7.27
7.26
7.12
7.06
7.06
7.05
7.05
7.04
6.87
6.85
4.59
4.57
4.17
4.14
2.99
2.96
2.95
2.91
1.42

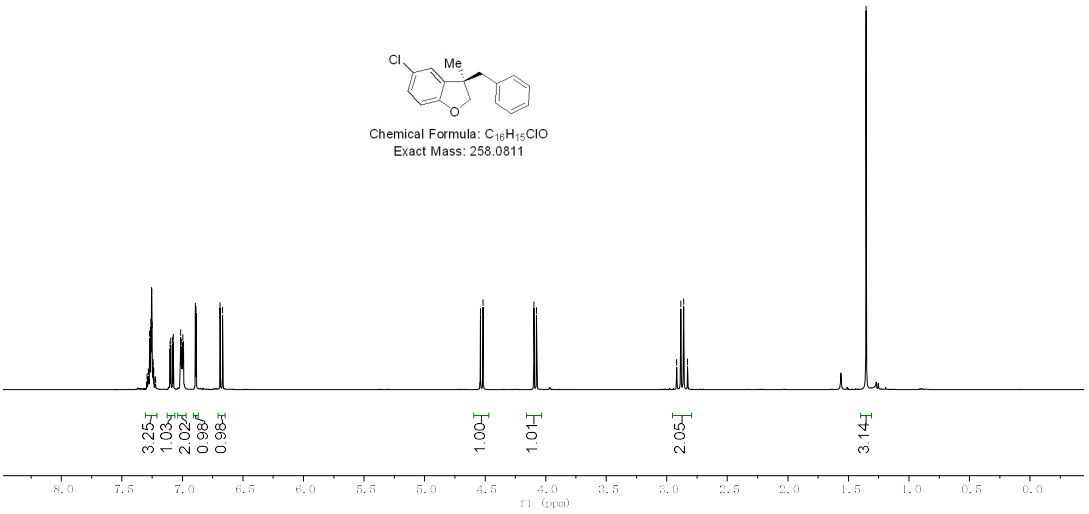

Me
O
Chemical Formula: C22H20O
Exact Mass: 300.1514
2.02
3.09
3.96
1.04
2.05
1.00
1.00
1.01
2.04
3.05
f1 (ppm)


159.2
141.4
137.5
135.3
133.8
130.4
128.7
128.0
127.3
126.8
126.5
126.5
122.3
109.8
82.5
46.7
46.3
24.4

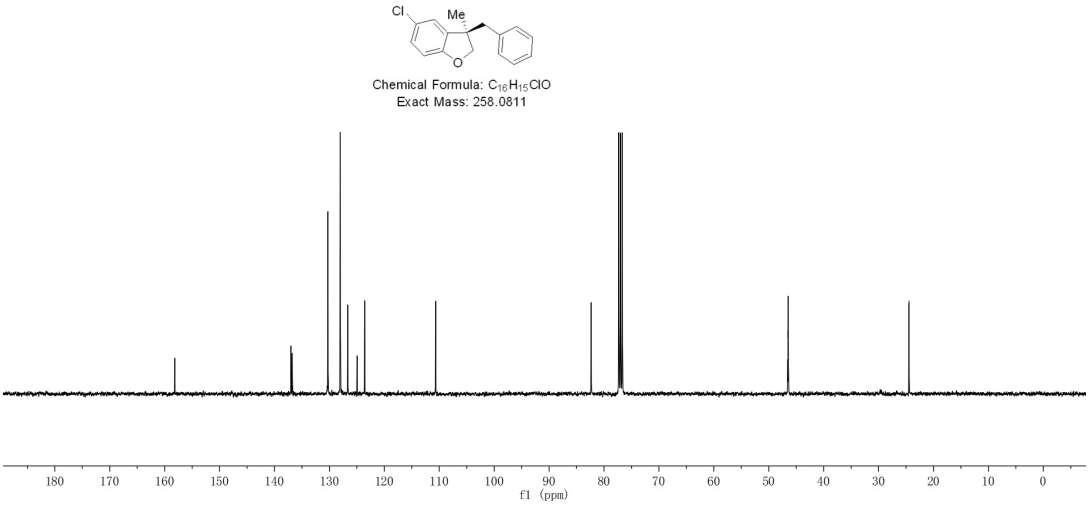

Me
O
Chemical Formula: C22H20O
Exact Mass: 300.1514
f1 (ppm)

3da

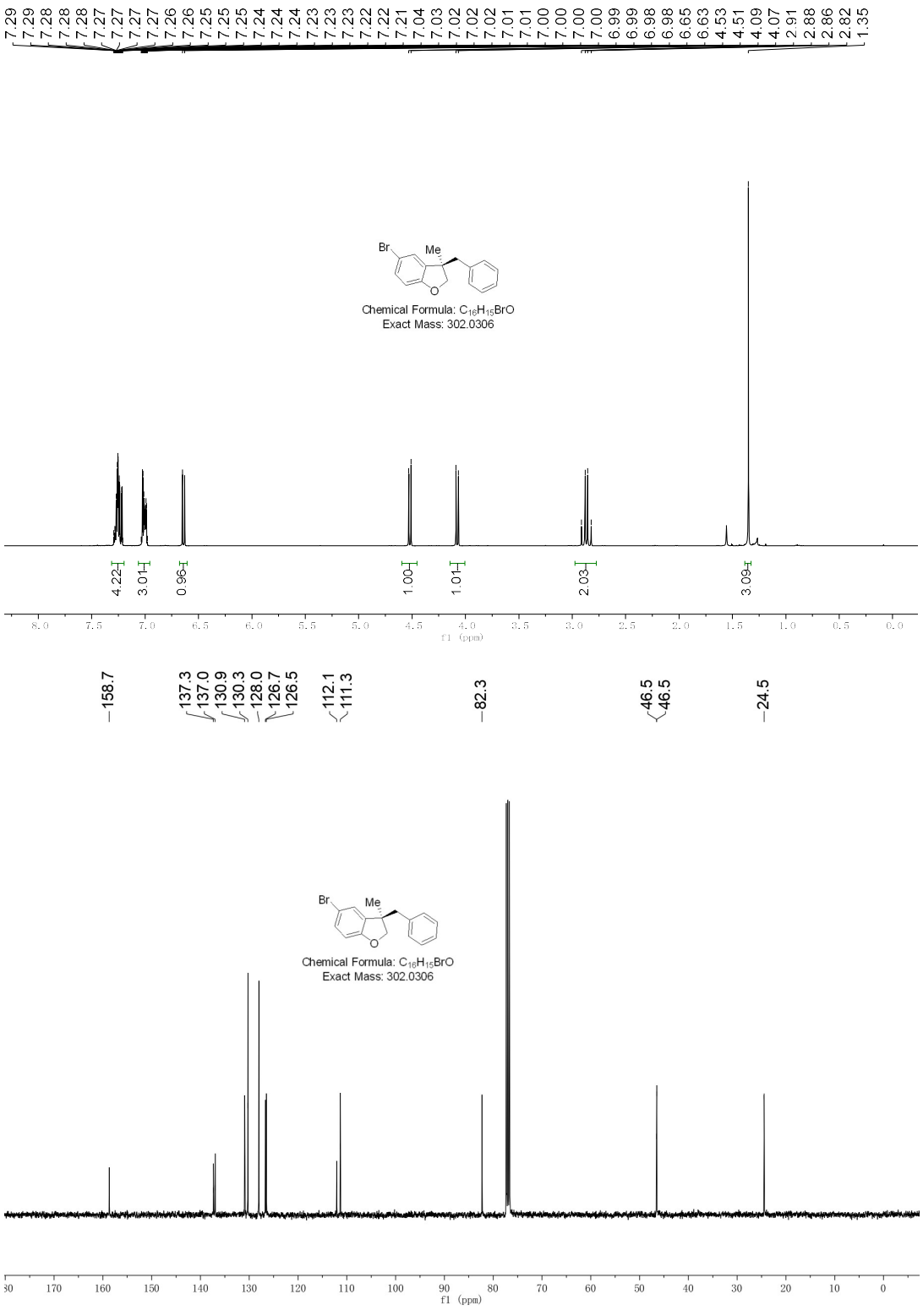

7.3
7.3
7.3
7.3
7.3
7.3
7.3
7.3
7.3
7.2
7.2
7.2
7.2
7.2
7.2
7.2
7.1
7.1
7.1
7.1
7.0
7.0
7.0
7.0
7.0
7.0
6.9
6.9
6.7
6.7
4.5
4.5
4.1
4.1
2.9
2.9
2.9
2.8
1.4


Cl
Me
O
Chemical Formula: C16H15ClO
Exact Mass: 258.0811
3.25
1.03
2.02
0.98
0.98
1.00
1.01
2.05
3.14
f1 (ppm)

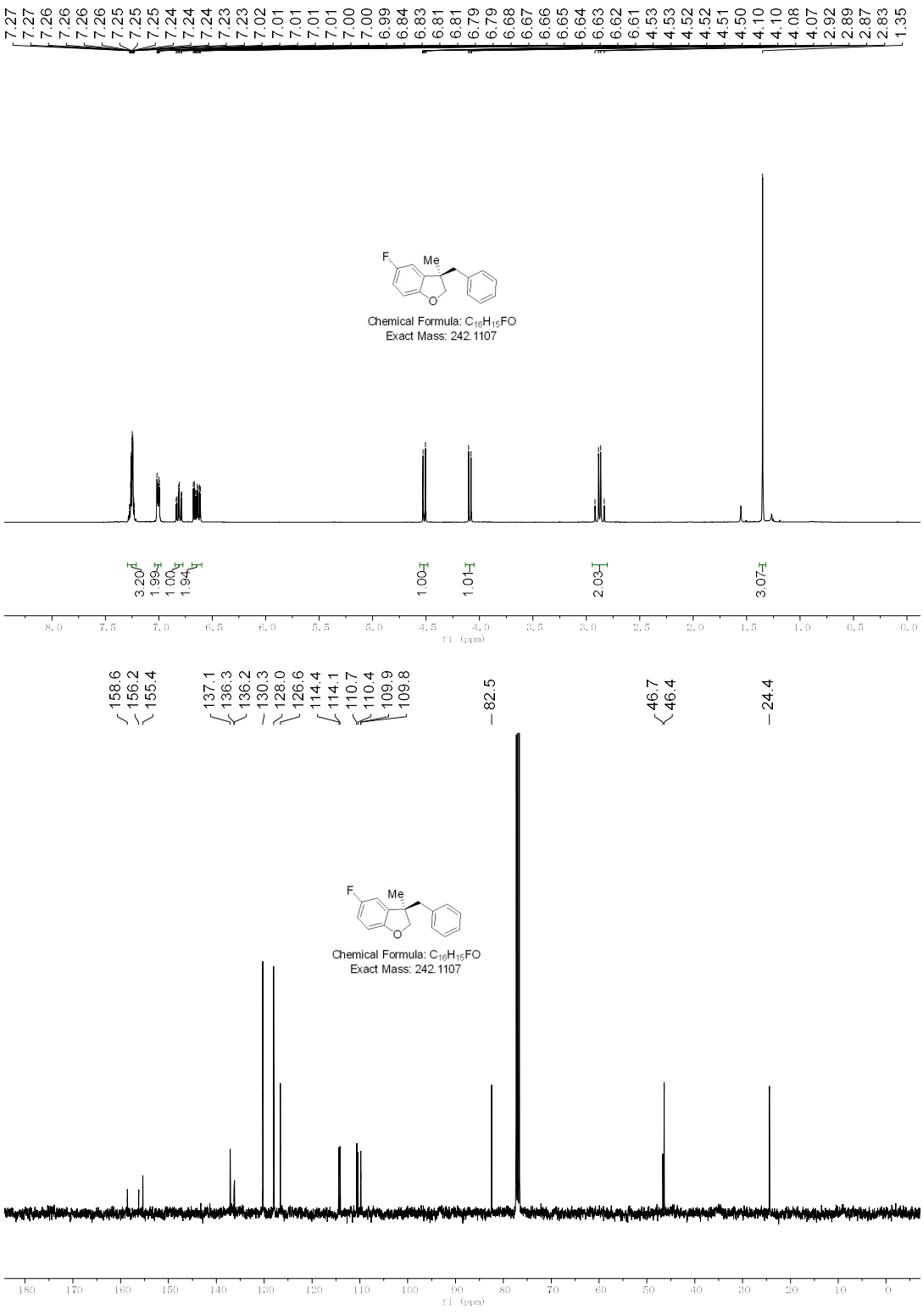

158.2
137.0
136.8
130.3
128.0
126.7
125.0
123.6
110.7
82.3
46.5
46.5
24.5

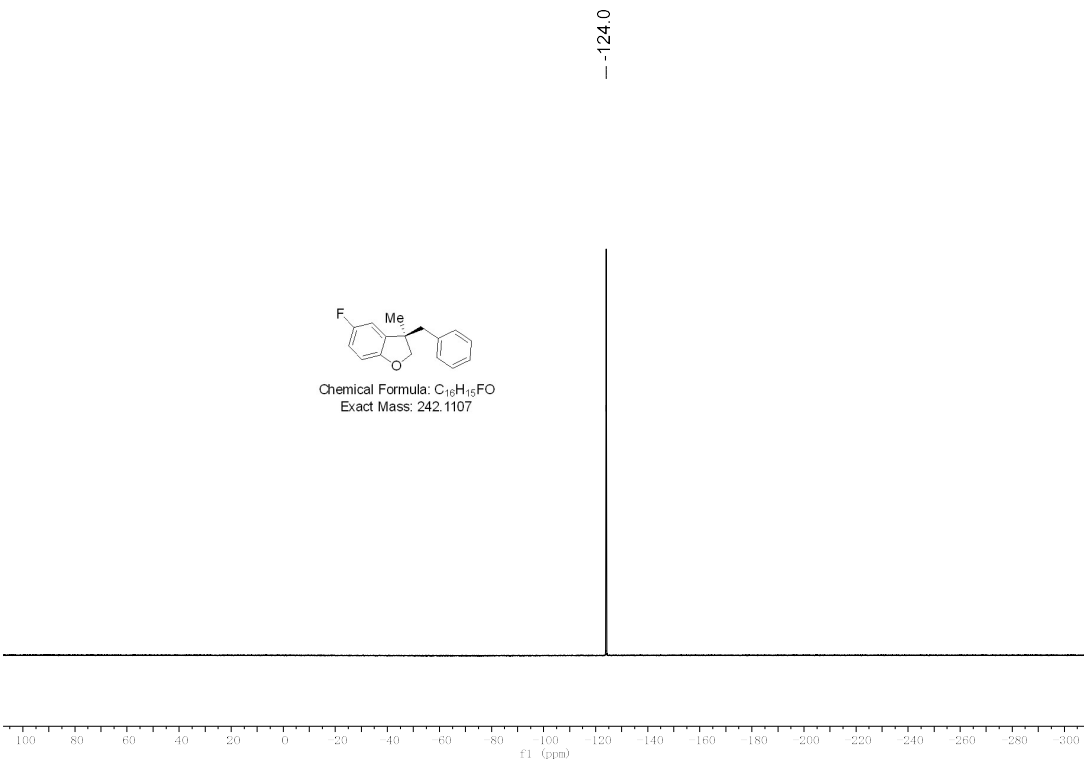

Cl
Me
O
Chemical Formula: C16H15ClO
Exact Mass: 258.0811
f1 (ppm)

3ea

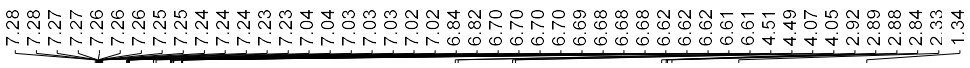

7.29 7.29 7.28 7.28 7.27 7.27 7.27 7.26 7.26 7.25 7.25 7.25 7.24 7.24 7.24 7.23 7.23 7.23 7.22 7.22 7.21 7.04 7.03 7.02 7.02 7.02 7.01 7.01 7.00 7.00 7.00 7.00 6.99 6.99 6.98 6.98 6.65 6.63 4.53 4.51 4.09 4.07 2.91 2.88 2.86 2.82 1.35
Br
Me
O
Chemical Formula: C16H15BrO
Exact Mass: 302.0306
4.22
3.01
0.96
1.00
1.01
2.03
3.09
f1 (ppm)
158.7
137.3
137.0
130.9
130.3
128.0
126.7
126.5
112.1
111.3
82.3
46.5
46.5
24.5
Br
Me
O
Chemical Formula: C16H15BrO
Exact Mass: 302.0306
f1 (ppm)

3fa


7.27 7.27 7.26 7.26 7.26 7.26 7.25 7.25 7.25 7.24 7.24 7.24 7.23 7.23 7.02 7.01 7.01 7.01 7.01 7.00 7.00 6.99 6.84 6.83 6.81 6.81 6.79 6.79 6.68 6.67 6.66 6.65 6.64 6.63 6.62 6.61 4.53 4.53 4.52 4.52 4.51 4.50 4.10 4.10 4.08 4.07 2.92 2.89 2.87 2.83 1.35
F
Me
O
Chemical Formula: C16H15FO
Exact Mass: 242.1107
3.20 1.99 1.00 1.94 1.00 1.01 2.03 3.07
f1 (ppm)
158.6 156.2 155.4 137.1 136.3 136.2 130.3 128.0 126.6 114.4 114.1 110.7 110.4 109.9 109.8 82.5 46.7 46.4 24.4
F
Me
O
Chemical Formula: C16H15FO
Exact Mass: 242.1107
f1 (ppm)


-124.0
F
Me
O
Chemical Formula: C16H15FO
Exact Mass: 242.1107
100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
f1 (ppm)

3ga


7.28
7.28
7.27
7.27
7.26
7.26
7.26
7.25
7.25
7.24
7.24
7.24
7.23
7.23
7.04
7.04
7.03
7.03
7.03
7.02
7.02
6.84
6.82
6.70
6.70
6.70
6.69
6.68
6.68
6.68
6.62
6.62
6.62
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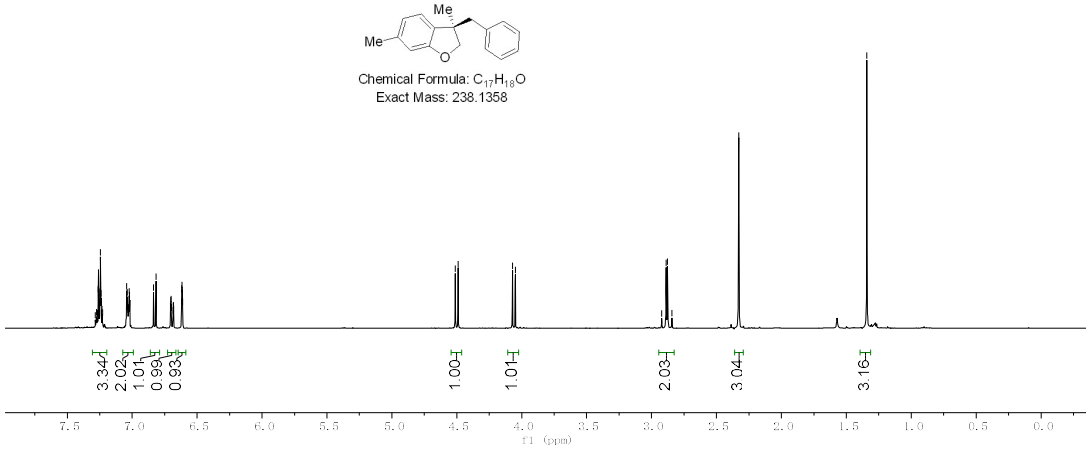
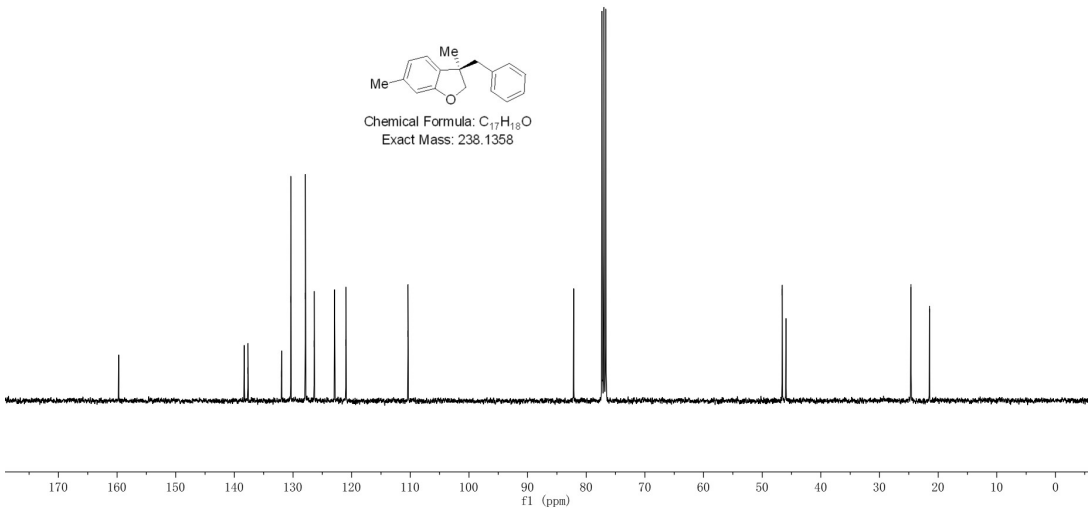
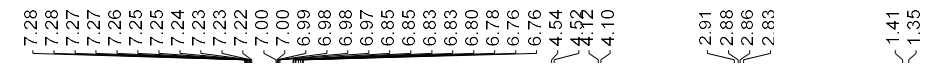
2.92
2.89
2.88
2.84
2.33
1.34


Me
Me
O
Chemical Formula: C17H18O
Exact Mass: 238.1358
3.34
2.02
1.01
0.99
0.93
1.00
1.01
2.03
3.04
3.16
f1 (ppm)


159.7
138.3
137.7
132.0
130.4
127.9
126.4
122.9
121.0
110.4
82.2
46.6
45.9
24.6
21.5


Me
Me
O
Chemical Formula: C17H18O
Exact Mass: 238.1358
f1 (ppm)

3ha


7.28
7.28
7.27
7.27
7.26
7.25
7.25
7.24
7.23
7.23
7.22
7.00
7.00
6.99
6.98
6.98
6.97
6.85
6.85
6.83
6.83
6.80
6.78
6.76
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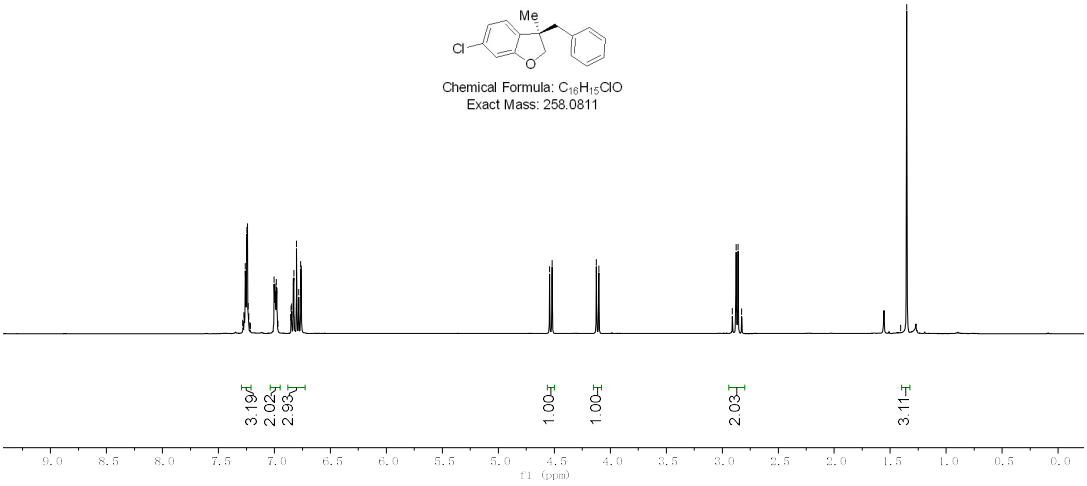
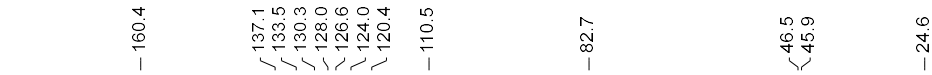
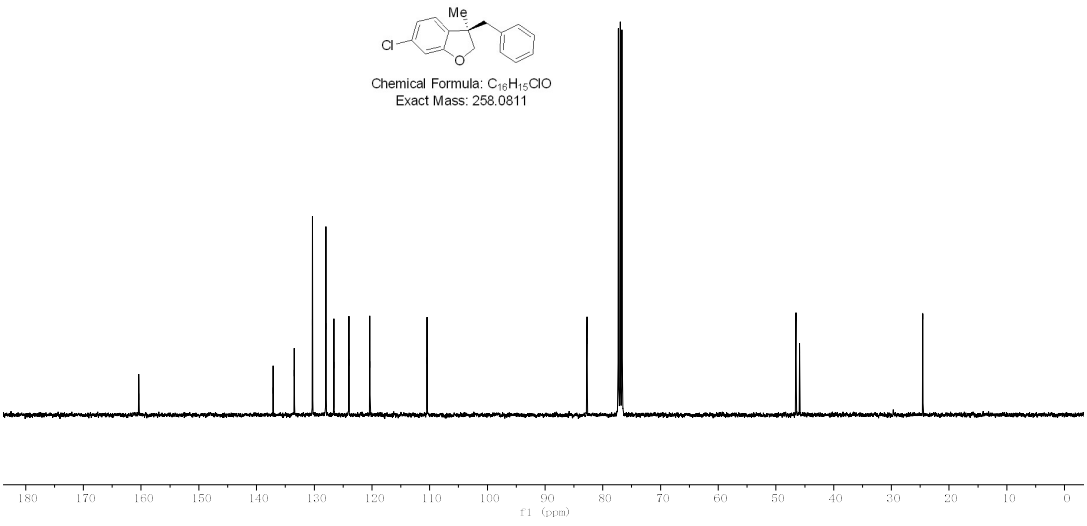
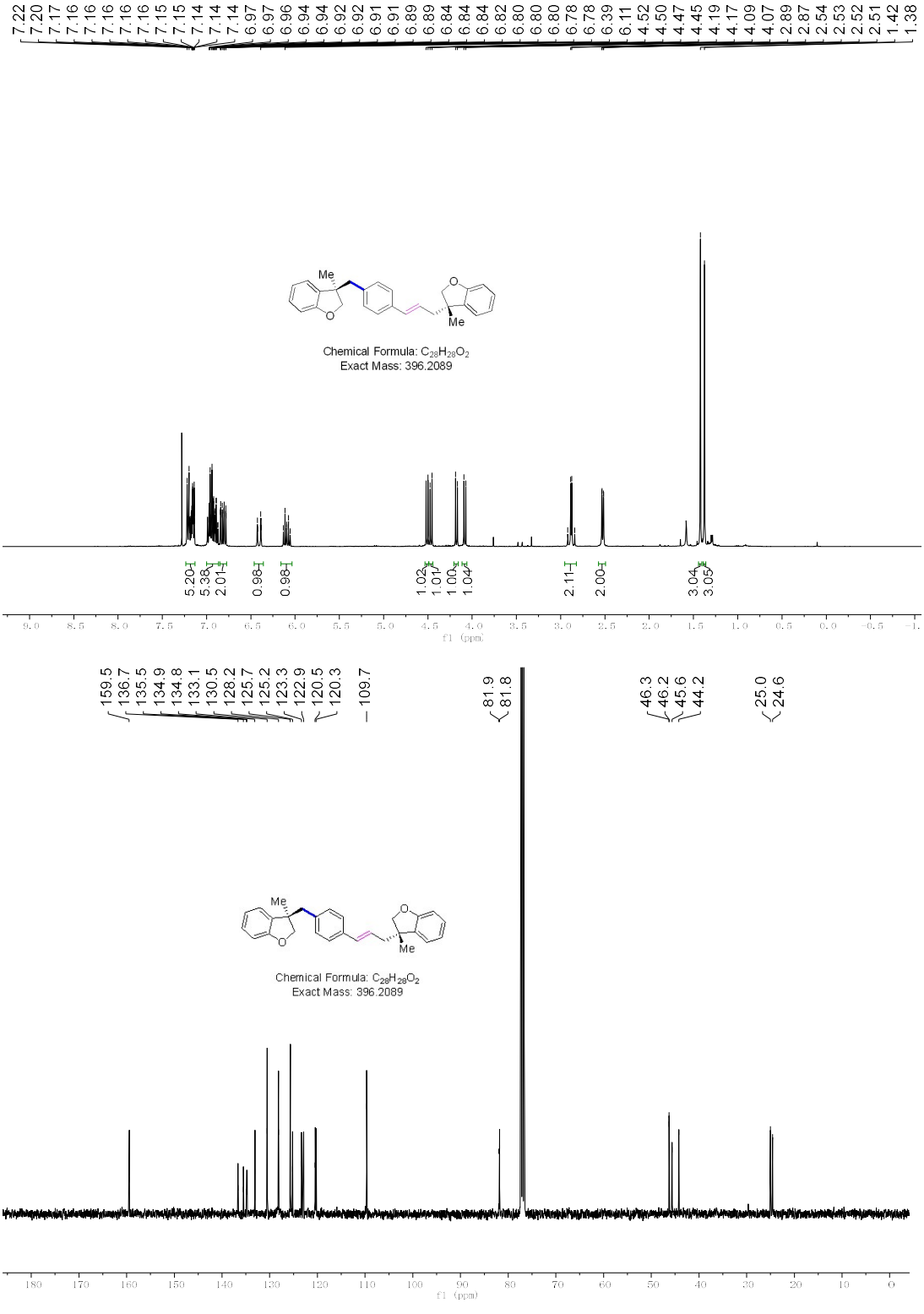
4.10
2.91
2.88
2.86
2.83
1.41
1.35


Me
Cl
O
Chemical Formula: C16H15ClO
Exact Mass: 258.0811
3.19
2.02
2.93
1.00
1.00
2.03
3.11
f1 (ppm)

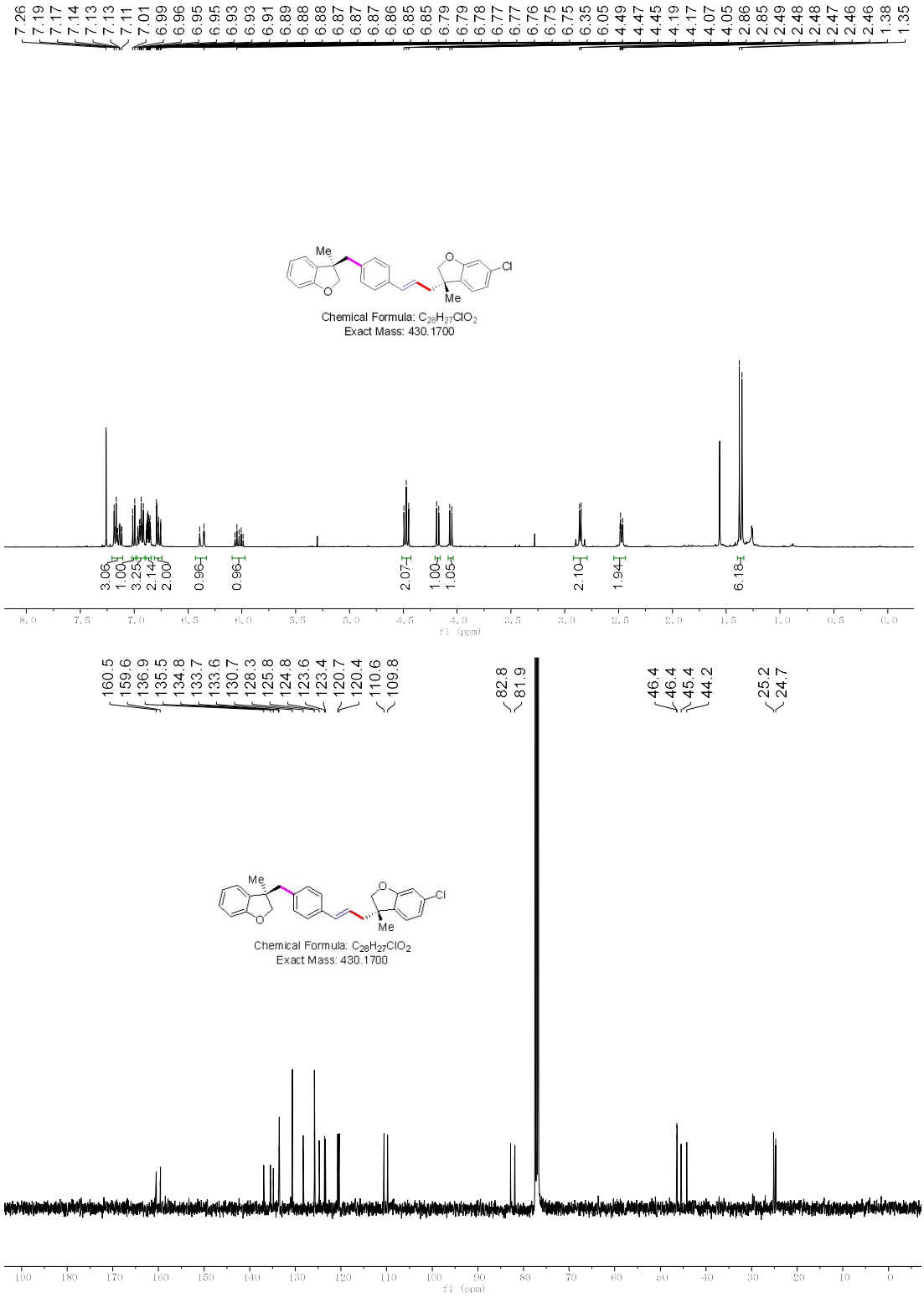

160.4
137.1
133.5
130.3
128.0
126.6
124.0
120.4
110.5
82.7
46.5
45.9
24.6


Me
Cl
O
Chemical Formula: C16H15ClO
Exact Mass: 258.0811
f1 (ppm)

4aa


7.22
7.20
7.17
7.16
7.16
7.16
7.16
7.16
7.15
7.15
7.14
7.14
7.14
6.97
6.97
6.96
6.94
6.94
6.92
6.92
6.91
6.91
6.89
6.89
6.84
6.84
6.84
6.82
6.80
6.80
6.80
6.78
6.78
6.39
6.11
4.52
4.50
4.47
4.45
4.19
4.17
4.09
4.07
2.89
2.87
2.54
2.53
2.52
2.51
1.42
1.38
Me
O
O
Me
Chemical Formula: C28H28O2
Exact Mass: 396.2089
5.20
5.38
2.01
0.98
0.98
1.02
1.01
1.00
1.04
2.11
2.00
3.04
3.05
f1 (ppm)
159.5
136.7
135.5
134.9
134.8
133.1
130.5
128.2
125.7
125.2
123.3
122.9
120.5
120.3
109.7
81.9
81.8
46.3
46.2
45.6
44.2
25.0
24.6
Me
O
O
Me
Chemical Formula: C28H28O2
Exact Mass: 396.2089
f1 (ppm)

4ah


7.26 7.19 7.17 7.14 7.13 7.13 7.11 7.01 6.99 6.96 6.95 6.95 6.93 6.93 6.91 6.89 6.88 6.88 6.87 6.87 6.87 6.86 6.85 6.85 6.79 6.79 6.78 6.77 6.77 6.76 6.75 6.75 6.35 6.05 4.49 4.47 4.45 4.19 4.17 4.07 4.05 2.86 2.85 2.49 2.48 2.48 2.47 2.46 2.46 1.38 1.35
Me
O
Cl
O
Me
Chemical Formula: C28H27ClO2
Exact Mass: 430.1700
3.06 1.00 3.25 2.14 2.00 0.96 0.96 2.07 1.00 1.05 2.10 1.94 6.18
f1 (ppm)
160.5 159.6 136.9 135.5 134.8 133.7 133.6 130.7 128.3 125.8 124.8 123.6 123.4 120.7 120.4 110.6 109.8
82.8 81.9
46.4 46.4 45.4 44.2
25.2 24.7
Me
O
Cl
Me
Chemical Formula: C28H27ClO2
Exact Mass: 430.1700
f1 (ppm)

6. References

[1] (a) You, W. and Brown, M. K., *J. Am. Chem. Soc.*, 2015, **137**, 14578. (b) Zhang, Z., Xu, B., Qian, Y., Wu, L., Wu, Y., Zhou, L., Liu, Y. and Zhang, J., *Angew. Chem. Int. Ed.*, 2018, **57**, 10373. (c) Carmona, R. C., Köster, O. D. and Correia, C. R. D., *Angew. Chem. Int. Ed.*, 2018, **57**, 12067.

[2] Grigg, R., Sansano, J. M., Santhakumar, V., Sridharan, V., Thangavelanthum, R., Thornton-Pett, M. and Wilson, D., *Tetrahedron*, 1997, **53**, 11803.