

## Supporting Information

### Electrochemically Enhanced Deoxygenative Cross-Coupling of Aryl Ketones with Heteroarenes through in-situ Generated Benzyl Carbocations

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## General Information

Unless otherwise noted, all electrochemical reactions for products preparation were handled under air, and performed in an undivided electrolysis cell (ElectraSyn 2.0). Aryl ketones **1a-1q**, the corresponding O-, S-, N-heteroarenes were purchased from Aladdin Ltd. (Shanghai, China), J&K Scientific, and TCI (Shanghai) Development Co., Ltd. Graphite plates (immersed in electrolyte  $\approx 1 \times 1$  cm), copper plates ( $\approx 1 \times 1$  cm), and other electrodes ( $\approx 1 \times 1$  cm) were used for reaction optimization and substrate scope studies. HPLC grade solvents, *N,N'*-dimethylformamide (DMF), dichloromethane (DCM), acetonitrile (MeCN), and tetrahydrofuran (THF) were purchased from commercial sources and used without further purification. The new products were fully characterized by using  $^1\text{H}$ ,  $^{13}\text{C}$  NMR and HRMS.  $^1\text{H}$  NMR spectra were recorded on a Bruker GPX 400 MHz spectrometer. Chemical shifts ( $\delta$ ) were reported in parts per million (ppm,  $\delta$ ) relative to residual chloroform (7.26 ppm for  $^1\text{H}$  NMR; 77.0 ppm for  $^{13}\text{C}$  NMR), Coupling constants were reported in Hertz.  $^1\text{H}$  NMR assignment abbreviations were the following: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), and multiplet (m).  $^{13}\text{C}$  NMR spectra were recorded at 101 MHz on the same spectrometer and reported in ppm. Known products were analyzed by GC-MS,  $^1\text{H}$  NMR and verified by comparison with literature data. Melting points were measured on an SGW-4A microscopic melting point apparatus. High resolution mass spectra (HRMS) were recorded on a Waters Acquity UPLC Class I/Xevo G2 Q-ToF MS by using electrospray ionization (ESI) with a TOF mass analyzer.

## Graphic presentation of reaction.

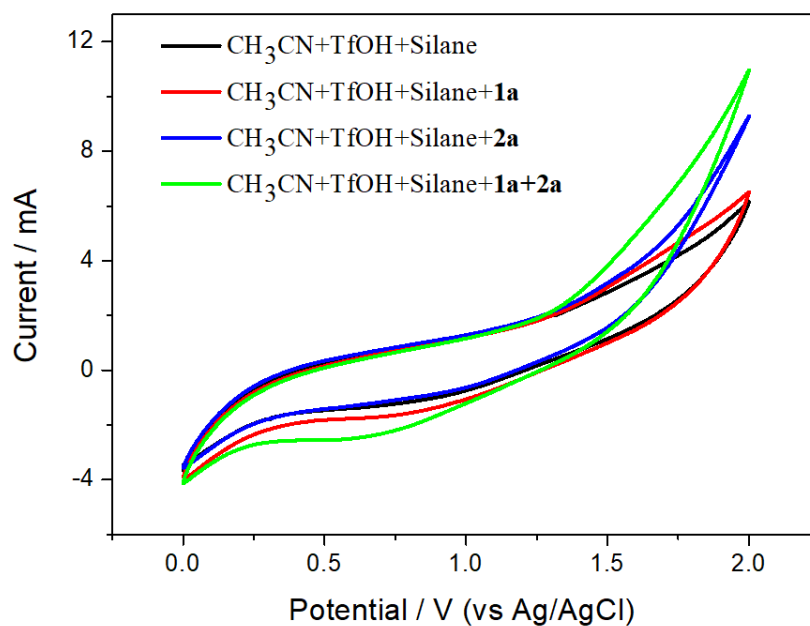


**Figure S1.** Typical reaction set-up of electrochemical reaction of aryl ketones and heteroarenes.

## Controlled electrochemical studies of benzophenone and benzofuran

Notably, triflic acid, a super strong acid in organic media, can help stabilize benzylic carbocations even in organic media, which also serves as an efficient supporting electrolyte for the electrochemical reactions. Cyclic voltammetry (CV) measurements were performed to study the electrical behavior of **1a** and **2a** (Figure S2). Surprisingly, the initial current was around 4.5 mA even without an applied potential and substrates, such a phenomenon possibly arose from the reaction of triflic acid and  $\text{CH}_3\text{CN}$ .<sup>17-18</sup> The proton from triflic acid and the hydride from silane could work synergistically to reduce the carbonyl group, which could cause the current signal. Besides that, the CV investigation shows that benzophenone **1a** and benzofuran **2a** exhibit electrochemical reactivity at oxidative potentials with onset  $\sim 1.2\text{--}1.3$  V vs Ag/AgCl. The mixture of **1a** and **2a** (green) shows an increased anodic current compared to the independent study of **1a** (red) and **2a** (blue), which is consistent with the occurrence of the rapid cross-coupling between benzyl carbocations and heteroarenes. It is also clear that the cross-coupling reaction between **1a** and **2a** (green) outcompetes the carbonyl deoxygenative reduction reaction (red). The increasing tendency to the applied potential of the carbonyl deoxygenative reduction reaction (red) probably suggests that the increased

generation of benzyl carbocation and the reduction of benzyl carbocation in the presence of silane.



**Figure S2.** Electrochemical behaviors of **1a** and **2a** by CV techniques at scan rate 100 mv/s, vs (Ag/AgCl).

## Reaction Conditions Optimization

**Table S1.** Optimization for electrochemical reaction of **1a** and **2a**.<sup>a</sup>

Entry	Anode	Cathode	Acid	Silane	Current (mA)	Time (h)	Solvent (5.0 mL)	Yield of <b>3a</b> (%)
1	Graphite	Cu	CF <sub>3</sub> SO <sub>3</sub> H	0.25	0	3	CH <sub>3</sub> CN	68
2	Graphite	Cu	CF <sub>3</sub> SO <sub>3</sub> H	0.25	2	3	CH <sub>3</sub> CN	73
3	Graphite	Cu	CF <sub>3</sub> SO <sub>3</sub> H	0.25	5	3	CH <sub>3</sub> CN	75
4	Graphite	Cu	CF <sub>3</sub> SO <sub>3</sub> H	0.25	10	3	CH <sub>3</sub> CN	100 (82)
5	Graphite	Cu	CF <sub>3</sub> SO <sub>3</sub> H	0.25	10	0.5	CH <sub>3</sub> CN	76
6	Graphite	Cu	CF <sub>3</sub> SO <sub>3</sub> H	0.25	10	1	CH <sub>3</sub> CN	83
7	Graphite	Cu	CF <sub>3</sub> SO <sub>3</sub> H	0.25	10	2	CH <sub>3</sub> CN	92
8	Graphite	Cu	CF <sub>3</sub> SO <sub>3</sub> H	0.25	10	3	CH <sub>3</sub> CN	100



9	Graphite	Cu	CF <sub>3</sub> SO <sub>3</sub> H	0.25	10	3	CH <sub>2</sub> Cl <sub>2</sub>	0
10	Graphite	Cu	CF <sub>3</sub> SO <sub>3</sub> H	0.25	10	3	THF	0
11	Graphite	Cu	CF <sub>3</sub> SO <sub>3</sub> H	0.25	10	3	DMF	0
12	Glass carbon	Cu	CF <sub>3</sub> SO <sub>3</sub> H	0.25	10	3	CH <sub>3</sub> CN	94
13	Graphite	C	CF <sub>3</sub> SO <sub>3</sub> H	0.25	10	3	CH <sub>3</sub> CN	100
14	Graphite	Cu	None	0.25	10	3	CH <sub>3</sub> CN	0
15	Graphite	Cu	CF <sub>3</sub> COOH	0.25	10	3	CH <sub>3</sub> CN	0
16	Graphite	Cu	CH <sub>3</sub> COOH	0.25	10	3	CH <sub>3</sub> CN	0
17	Graphite	Cu	TsOH	0.25	10	3	CH <sub>3</sub> CN	0
18	Graphite	Cu	H <sub>2</sub> SO <sub>4</sub>	0.25	10	3	CH <sub>3</sub> CN	0
19 <sup>b</sup>	Graphite	Cu	0.5mmol	0.25	10	3	CH <sub>3</sub> CN	68
20 <sup>c</sup>	Graphite	Cu	0.75mmol	0.25	10	3	CH <sub>3</sub> CN	100
21	Graphite	Cu	CF <sub>3</sub> SO <sub>3</sub> H	0	10	3	CH <sub>3</sub> CN	0
22	Graphite	Cu	CF <sub>3</sub> SO <sub>3</sub> H	0.5	10	3	CH <sub>3</sub> CN	100 (83)
23 <sup>d</sup>	-	-	CF <sub>3</sub> SO <sub>3</sub> H	0.25	50 °C	3	CH <sub>3</sub> CN	71
24 <sup>d</sup>	-	-	CF <sub>3</sub> SO <sub>3</sub> H	0.25	70 °C	3	CH <sub>3</sub> CN	77
25 <sup>d</sup>	-	-	CF <sub>3</sub> SO <sub>3</sub> H	0.25	90 °C	3	CH <sub>3</sub> CN	81

<sup>a</sup> Reaction condition: **1a**, 0.5 mmol, **2a**, 2.0 equiv. 1.0 mmol, CF<sub>3</sub>SO<sub>3</sub>H, 1.8 equiv. 0.90 mmol, hydrosilane, 0.50 equiv. 0.25 mmol, Solvent, CH<sub>3</sub>CN, 5.0 mL; 10 mA, 3.0 h at room temperature. Yields was determined GC by using 50 μL of dodecane as internal standard and isolated yield was given in parenthesis. <sup>b</sup> 1.0 equiv. CF<sub>3</sub>SO<sub>3</sub>H. <sup>c</sup> 1.5 equiv. CF<sub>3</sub>SO<sub>3</sub>H. <sup>d</sup> Reactions were performed in a 25 mL seal Schlenk.

## General procedure for electrochemically enhanced cross-coupling reactions

The reactions were performed in an undivided ElectraSyn 2.0 vial (10 mL), which was equipped with graphite plate (anode, ≈1 x 1 cm) and Cu plate (cathode, ≈1 x 1 cm) as electrodes. To this electrolysis vial, aryl ketone (0.5 mmol, 1.0 equiv.), 1,1,3,3-Tetramethyldisiloxane (0.25 mmol, 0.5 equiv.), heteroarene (1.0 mmol, 2.0 equiv.), CH<sub>3</sub>CN (5.0 mL), and triflic acid (0.9 mmol, 1.8 equiv.) were added. The mixture was electrolyzed under 10 mA constant current at room temperature with rigid magnetic stirring, and the reaction was monitored by thin layer chromatography (TLC) after 3 hours till aryl ketone was completely converted. Then, a partial solution was filtered through a short silica gel column for GC and GC-MS analysis. The combined solution

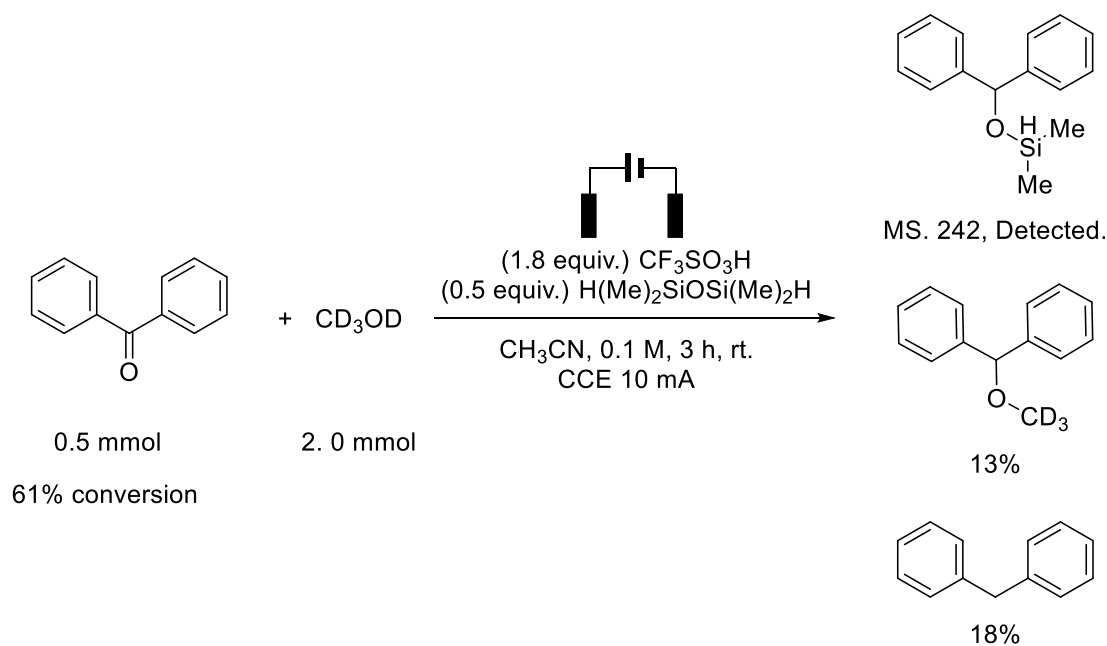
was concentrated under reduced pressure and purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the desired cross-coupling products.

## Procedure for synthesis of 2-benzhydrylbenzofuran (**3a**)

To an undivided ElectraSyn 2.0 cell (10 mL), graphite plate (anode,  $\approx 2 \times 1$  cm) and Cu plate (cathode,  $\approx 2 \times 1$  cm) was equipped as electrodes. Benzophenone (**1a**, 1.0 mmol, 182.2 mg), 1,1,3,3-Tetramethyldisiloxane (0.5 mmol, 67.2 mg), benzofuran (**2a**, 2.0 mmol, 236.4 mg), CH<sub>3</sub>CN (10.0 mL, 0.1 M), and triflic acid (1.8 mmol, 270.1 mg) were added subsequently to the electrolysis cell. The mixture was electrolyzed under 10 mA constant current at room temperature with rigid magnetic stirring for 3 hours, and TLC showed that benzophenone **1a** was completely converted. The reaction was filtrated through celites and a partial solution was submitted for GC and GC-MS analysis. The combined filtrate was concentrated under reduced pressure and purified by column chromatography on silica gel using petroleum ether as eluent, affording **3a** a white solid in 83% isolated yield, 236.0 mg.

**Note:** When the reaction was performed in 0.2 M (1.0 mmol **1a** in 5.0 mL CH<sub>3</sub>CN), or 0.125 M (1.0 mmol **1a** in 8.0 mL CH<sub>3</sub>CN), trace amount of diphenylmethane was observed as side product in the reaction mixture.

## Deoxygenative cross-coupling of **1a** and CD<sub>3</sub>OD



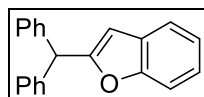
**Scheme S1.** Deoxygenative cross-coupling of **1a** with CD<sub>3</sub>OD.

To an undivided ElectraSyn 2.0 cell (10 mL), graphite plate (anode,  $\approx 2 \times 1$  cm) and

Cu plate (cathode,  $\approx 2 \times 1$  cm) was equipped as electrodes. Benzophenone (**1a**, 0.5 mmol, 91.2 mg), 1,1,3,3-Tetramethyldisiloxane (0.25 mmol, 36.6 mg),  $\text{CD}_3\text{OD}$  (2.0 mmol, 72.1 mg),  $\text{CH}_3\text{CN}$  (5.0 mL, 0.1 M), and triflic acid (0.9 mmol, 135.1 mg) were added subsequently to the electrolysis cell. The mixture was electrolyzed under 10 mA constant current at room temperature with rigid magnetic stirring for 3 hours. The reaction was filtrated through a short silica gel column, and a partial solution was submitted for GC and GC-MS analysis. The products distribution was summarized in Scheme S1.

## Analytical Data

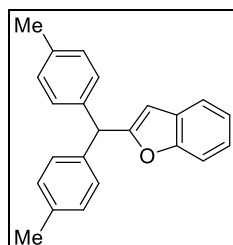
### 2-diphenylmethylbenzofuran<sup>1,2</sup> (**3a**):



From benzophenone (0.5 mmol, 91.1 mg) and benzofuran (1.0 mmol, 118.1 mg), **3a** was obtained according the general procedure using petroleum ether as eluent to give a white solid in 82% yield, 116.5 mg. **3a** was further analyzed by GC-MS,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and verified by comparison with literature data.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.46 (d,  $J = 7.2$  Hz, 1H), 7.40 (d,  $J = 7.6$  Hz, 1H), 7.33-7.15 (m, 12H), 6.27 (s, 1H), 5.58 (s, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  160.0, 155.2, 144.1, 142.3, 141.1, 129.2, 128.9, 128.9, 128.8, 128.7, 128.6, 128.6, 128.5, 128.4, 127.6, 127.3, 127.1, 126.8, 124.3, 124.1, 123.8, 122.7, 122.4, 120.7, 120.7, 111.5, 111.2, 105.7, 51.4, 47.7.

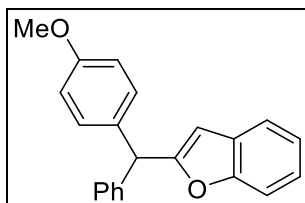
### 2-(di-p-tolylmethyl)benzofuran (**3b**):



From 4,4'-dimethylbenzophenone (0.5 mmol, 105.1 mg) and benzofuran (**2a**, 1.0 mmol, 118.1 mg), **3b** was obtained according the general procedure using petroleum ether as eluent to give a yellow oil in 32% yield, 50.0 mg.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 (dd,  $J$  = 23.2, 7.5 Hz, 2H), 7.17–7.09 (m, 2H), 7.07–7.02 (m, 8H), 6.19 (s, 1H), 5.43 (s, 1H), 2.26 (s, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  160.4, 155.1, 138.3, 136.5, 129.3, 128.7, 128.5, 123.7, 122.5, 120.6, 111.2, 105.4, 50.6, 21.1. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{23}\text{H}_{21}\text{O}^+$  313.1592; found 313.1589.

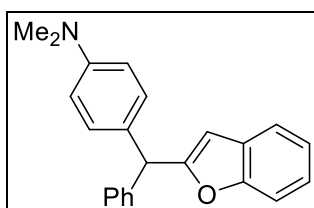
**2-((4-methoxyphenyl)(phenyl)methyl)benzofuran<sup>5</sup> (3c):**



From 4-methoxybenzophenone (0.5 mmol, 106.1 mg) and benzofuran (**2a**, 1.0 mmol, 118.1 mg), **3c** was obtained according the general procedure (EtOAc/petroleum ether=1:49) to give a colorless oil in 36% yield, 56.8 mg. **3c** was analyzed by GC-MS,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and verified by comparison with literature data.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49–7.44 (m, 1H), 7.43–7.38 (m, 1H), 7.29 (ddt,  $J$  = 9.0, 4.2, 1.6 Hz, 3H), 7.24–7.10 (m, 6H), 6.88–6.81 (m, 2H), 6.25 (d,  $J$  = 0.8 Hz, 1H), 5.53 (s, 1H), 3.79 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  160.3, 158.5, 155.1, 141.4, 133.2, 129.9, 128.8, 128.5, 128.5, 126.9, 123.7, 122.6, 120.3, 113.9, 111.1, 105.5, 55.2, 50.5.

**(2-benzofuryl) (4-dimethylaminophenyl)phenylmethane<sup>4</sup> (3d):**

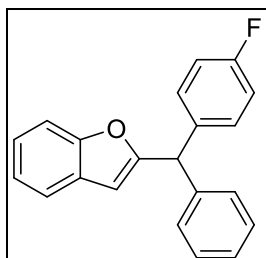


From 4-(dimethylamino)benzophenone (0.5 mmol, 112.6 mg) and benzofuran (**2a**, 1.0 mmol, 118.1 mg), **3d** was obtained according the general procedure (EtOAc/petroleum ether=1:49) to give a colorless oil in 33% yield, 54.6mg. **3d** was further analyzed by GC-MS,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and verified by comparison with literature data.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41 (dt,  $J$  = 15.6, 7.4 Hz, 2H), 7.33–7.26 (m, 2H), 7.25–7.13 (m, 6H), 7.07 (t,  $J$  = 9.8 Hz, 2H), 6.67 (t,  $J$  = 7.3 Hz, 2H), 6.25 (s, 1H), 5.45 (d,  $J$  = 26.0 Hz, 1H), 2.89 (d,  $J$  = 7.7 Hz, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  160.9, 155.1, 149.5,

141.7, 129.5, 128.9, 128.8, 128.6, 128.4, 126.7, 123.5, 122.5, 120.5, 112.6, 111.1, 105.3, 50.4, 40.6.

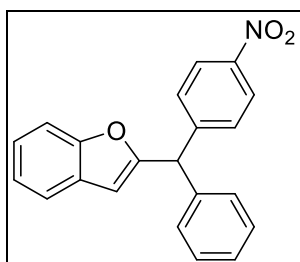
**2-((4- fluorophenyl)(phenyl)methyl)benzofuran<sup>13</sup> (3e):**



From 4-fluorobenzophenone (0.5 mmol, 100.1 mg) and benzofuran (**2a**, 1.0 mmol, 118.1 mg), **3e** was obtained according the general procedure (petroleum ether). The regioselectivity was determined by using GC and GC-Mass analysis (20:1), and purified using petroleum ether to give a colorless oil in 58% yield, 87.7 mg.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.42–7.37 (m, 1H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.26 (t, *J* = 7.2 Hz, 2H), 7.20 (t, *J* = 5.1 Hz, 1H), 7.15–7.08 (m, 6H), 6.97–6.91 (m, 2H), 6.20 (d, *J* = 9.3 Hz, 1H), 5.49 (s, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 162.5, 154.9, 141.5, 140.5, 128.6, 127.4, 123.4, 122.5, 120.5, 111.0, 102.0, 39.3, 35.6, 31.6, 31.2, 22.6, 20.4, 14.1. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>16</sub>FO<sup>+</sup> 303.1185; found 303.1192.

**2-((4-nitrophenyl)(phenyl)methyl)benzofuran (3f):**

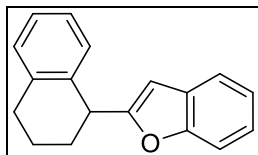


From 4-nitrobenzophenone (0.5 mmol, 113.6 mg) and benzofuran (**2a**, 1.0 mmol, 118.1 mg), **3f** was obtained according the general procedure (EtOAc/petroleum ether=1:49) to give a brown oil in 59% yield, 97.2 mg.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.21–8.04 (m, 2H), 7.41 (t, *J* = 9.6 Hz, 2H), 7.31 (dt, *J* = 15.7, 5.6 Hz, 4H), 7.27–7.21 (m, 3H), 7.21–7.11 (m, 2H), 6.25 (s, 1H), 5.60 (s, 1H); <sup>13</sup>C NMR

(101 MHz, CDCl<sub>3</sub>)  $\delta$  158.0, 156.0, 155.2, 154.3, 148.5, 147.1, 142.1, 139.5, 129.8, 129.0, 128.8, 128.7, 128.1, 127.7, 124.3, 123.9, 123.0, 120.9, 111.2, 106.2, 51.1. HRMS (ESI)  $m/z$ : [M+H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>16</sub>NO<sub>3</sub><sup>+</sup> 330.1130; found 330.1125.

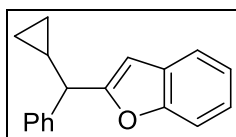
### 2-(1,2,3,4-tetrahydro-1-naphthalenyl)benzofuran<sup>6</sup> (**3g**)



From 1-tetralone (0.5 mmol, 73.1 mg) and benzofuran (**2a**, 1.0 mmol, 118.1 mg), **3g** was obtained according the general procedure (petroleum ether). The regioselectivity was determined by using GC and GC-Mass analysis (5.9:1), and purified using petroleum ether to give a yellow oil in 75% yield, 93.2 mg. **3g** was analyzed by GC-MS, <sup>1</sup>H NMR, <sup>13</sup>C NMR and verified by comparison with literature data.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.54–7.34 (m, 2H), 7.29–6.99 (m, 6H), 6.18 (s, 1H), 4.32 (t,  $J$  = 5.7 Hz, 1H), 2.98–2.73 (m, 2H), 2.36–2.20 (m, 1H), 2.17–2.05 (m, 1H), 1.93–1.64 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  162.4, 154.8, 137.4, 135.8, 129.9, 129.4, 128.7, 126.7, 125.7, 123.3, 122.5, 120.9, 111.0, 104.1, 39.1, 29.4, 28.5, 20.3; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  162.4, 154.8, 137.4, 135.8, 129.9, 129.4, 128.7, 126.7, 125.7, 123.3, 122.5, 120.4, 110.9, 104.1, 39.1, 29.4, 28.5, 20.3.

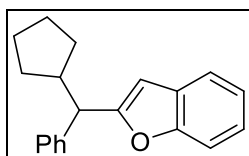
### 2-(cyclopropyl(phenyl)methyl)benzofuran<sup>2</sup> (**3h**):



From cyclopropyl phenyl ketone (0.5 mmol, 73.1 mg) and benzofuran (**2a**, 1.0 mmol, 118.1 mg), **3h** was obtained according the general procedure (petroleum ether). The regioselectivity was determined by using GC and GC-Mass analysis (6.3:1), and purified using petroleum ether to give a colorless oil in 19% yield, 23.6 mg. **3h** was analyzed by GC-MS, <sup>1</sup>H NMR, <sup>13</sup>C NMR and verified by comparison with literature data.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55–7.46 (m, 1H), 7.43–7.29 (m, 4H), 7.25 (s, 2H), 7.23–7.15 (m, 2H), 6.62 (s, 1H), 3.38 (d,  $J$  = 9.4 Hz, 1H), 1.57–1.33 (m, 2H), 0.79–0.52 (m, 2H), 0.38 (ddt,  $J$  = 22.3, 9.4, 4.6 Hz, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.0, 154.9, 141.7, 128.7, 128.5, 128.4, 128.05, 128.0, 126.7, 123.4, 122.5, 120.5, 111.1, 102.9, 50.2, 15.6, 5.3, 4.6.

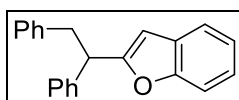
### 2-(cyclopentyl(phenyl)methyl)benzofuran (**3i**):



From cyclopentylphenylmethanone (0.5 mmol, 87.1 mg) and benzofuran (**2a**, 1.0 mmol, 118.1 mg), **3i** was obtained according the general procedure (petroleum ether) to give a colorless oil in 75% yield, 103.6 mg.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43–7.37 (m, 1H), 7.35–7.26 (m, 4H), 7.24–7.20 (m, 1H), 7.17 (t,  $J$  = 6.4 Hz, 1H), 7.14–7.03 (m, 2H), 6.42 (s, 1H), 3.69 (t,  $J$  = 10.7 Hz, 1H), 2.75–2.46 (m, 1H), 1.45–1.32 (m, 2H), 1.28–1.19 (m, 2H), 1.09 (ddd,  $J$  = 24.5, 15.1, 11.5 Hz, 2H), 0.79 (ddd,  $J$  = 13.8, 13.0, 8.0 Hz, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.3, 154.7, 142.2, 128.4, 128.3, 126.6, 123.2, 122.4, 120.4, 111.0, 102.3, 52.0, 44.0, 32.0, 31.8, 25.3, 25.1. HRMS (ESI) ( $m/z$ ):  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{20}\text{H}_{21}\text{O}^+$  277.1592; found 277.1586.

### 2-(1,2-diphenylethyl)benzofuran<sup>2</sup> (**3j**):

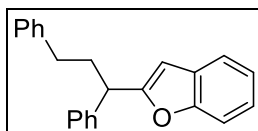


From 2-phenylacetophenone (0.5 mmol, 98.1 mg) and benzofuran (**2a**, 1.0 mmol, 118.1 mg), **3j** was obtained according the general procedure (petroleum ether) to give a colorless oil in 67% yield, 100.2 mg. **3j** was analyzed by GC-MS,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and verified by comparison with literature data.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55–7.38 (m, 2H), 7.31–6.88 (m, 10H), 6.45 (d,  $J$  = 1.0 Hz, 1H), 4.35 (t,  $J$  = 7.7 Hz, 1H), 3.57 (dd,  $J$  = 13.7, 7.5 Hz, 1H), 3.25 (dd,  $J$  = 13.7, 8.1 Hz, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  160.1, 154.8, 141.3, 139.4, 129.0, 129.0, 128.6, 128.5,

128.4, 128.2, 128.2, 128.1, 128.1, 126.9, 126.2, 123.5, 122.5, 120.6, 111.0, 103.2, 47.8, 40.9.

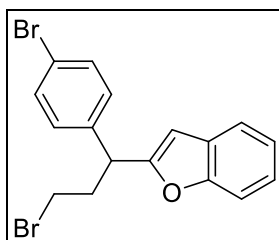
**2-(1,3-diphenylpropyl)benzofuran (3k):**



From 1,3-diphenyl-2-propen-1-one (0.5 mmol, 104.1 mg) and benzofuran (**2a**, 1.0 mmol, 118.1 mg), **3k** was obtained according the general procedure (petroleum ether) [using 1.0 equiv. tetramethyldisiloxane (1.0 mmol, 134.3 mg)]. The regioselectivity was determined by using GC and GC-Mass analysis (6.0:1), and purified using petroleum ether to give a yellow oil in 51% yield, 79.8 mg.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45–7.38 (m, 1H), 7.32 (d,  $J$  = 7.8 Hz, 1H), 7.28–7.22 (m, 6H), 7.20 (d,  $J$  = 7.5 Hz, 1H), 7.16 (d,  $J$  = 5.5 Hz, 1H), 7.13–7.05 (m, 5H), 6.38 (s, 1H), 3.99 (t,  $J$  = 7.5 Hz, 1H), 2.56 (p,  $J$  = 7.8 Hz, 2H), 2.34–2.16 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  160.9, 154.8, 141.7, 141.6, 128.7, 128.6, 128.5, 128.5, 128.1, 128.0, 126.9, 126.0, 123.5, 122.5, 120.5, 111.0, 102.6, 45.0, 36.0, 33.7. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{23}\text{H}_{21}\text{O}^+$  313.1592; found 313.1585.

**2-(3-bromo-1-(4-bromophenyl)propyl)benzofuran (3l):**



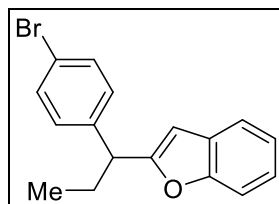
From 3-bromo-1-(4-bromophenyl)propan-1-one (0.5 mmol, 146.0 mg) and benzofuran (1.0 mmol, 118.1 mg), **3l** was obtained according the general procedure. The regioselectivity was determined by using GC and GC-Mass analysis (5.6:1), and purified using petroleum ether to give a yellow oil in 27% yield, 53.2 mg. Meanwhile, **3m** was obtained in the same reaction mixture with C2:C3 regioselectivity as 3.3:1,



and was isolated by using column chromatography (EtOAc/petroleum ether=1:99) to give a yellow oil in 31% yield, 49.1 mg.

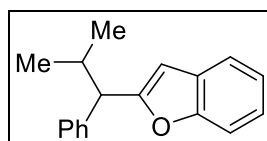
**3l:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46–7.41 (m, 3H), 7.28–7.24 (m, 2H), 7.18 (t,  $J$  = 3.4 Hz, 2H), 7.16 (d,  $J$  = 2.8 Hz, 1H), 6.45 (s, 1H), 3.90 (dd,  $J$  = 13.3, 5.7 Hz, 1H), 2.23 (qt,  $J$  = 13.4, 6.8 Hz, 1H), 2.03–1.89 (m, 1H), 0.97–0.91 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  160.4, 154.8, 141.2, 140.9, 131.6, 129.8, 123.5, 122.6, 120.5, 111.0, 102.6, 47.0, 27.4, 12.3. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{15}\text{Br}_2\text{O}^+$  392.9490; found 392.9504.

**2-(1-(4-bromophenyl)propyl)benzofuran (3m):**



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 (ddd,  $J$  = 9.1, 5.1, 3.6 Hz, 1H), 7.45–7.35 (m, 3H), 7.27–7.19 (m, 2H), 7.17–7.14 (m, 2H), 6.45 (s, 1H), 3.90 (dd,  $J$  = 13.9, 6.3 Hz, 1H), 2.29–2.16 (m, 1H), 2.02–1.88 (m, 1H), 0.94 (t,  $J$  = 7.4 Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  160.5, 154.8, 141.0, 131.6, 131.6, 129.8, 129.8, 128.5, 123.6, 122.6, 120.6, 120.5, 111.0, 102.6, 46.7, 27.4, 12.3. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{16}\text{BrO}^+$  315.0385; found 315.0390.

**2-(2-methyl-1-phenylpropyl)benzofuran (3n):**

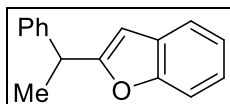


From isobutyrophenone (0.5 mmol, 74.1 mg) and benzofuran (1.0 mmol, 118.1 mg), **3n** was prepared according the general procedure, and the regioselectivity was determined by using GC and GC-Mass analysis (4.9:1). **3n** was isolated by using column chromatography (petroleum ether) to give a colorless oil in 32% yield, 40.1 mg.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42–7.35 (m, 1H), 7.34–7.24 (m, 1H), 7.15–7.05 (m, 5H), 7.04–6.97 (m, 2H), 6.33 (s, 1H), 4.19–4.06 (m, 1H), 2.46 (dt,  $J$  = 12.1, 8.1 Hz, 1H), 1.29–1.16 (m, 3H), 0.79 (q,  $J$  = 6.9 Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  160.6, 154.7, 141.5,

128.5, 128.4, 126.6, 123.2, 122.4, 120.4, 111.0, 102.8, 54.1, 32.1, 21.7, 21.2. HRMS (ESI)  $m/z$ :  $[M+H]^+$  Calcd for  $C_{18}H_{19}O^+$  251.1436; found 251.1433.

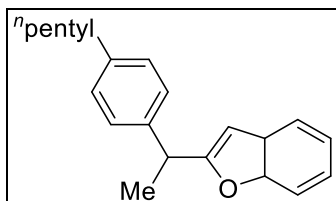
### 2-(1-phenylethyl)benzofuran<sup>2,3</sup> (**3o**)



From acetophenone (0.5 mmol, 105.1 mg) and benzofuran (**2a**, 1.0 mmol, 118.1 mg), **3o** was obtained according the general procedure, and the regioselectivity was determined by using GC and GC-Mass analysis (4.9:1). Purification of the mixture using petroleum ether gave **3o** as a colorless oil in 71 yield, 156 mg. **3o** was analyzed by GC-MS,  $^1H$  NMR,  $^{13}C$  NMR and verified by comparison with literature data.

$^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.51–7.41 (m, 1H), 7.41–7.34 (m, 1H), 7.33–7.25 (m, 4H), 7.17 (dddd,  $J$  = 21.3, 15.5, 9.5, 6.9 Hz, 3H), 6.42 (s, 1H), 4.28–4.19 (m, 1H), 1.68 (dd,  $J$  = 7.2, 3.4 Hz, 3H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  162.2, 154.9, 143.4, 128.7, 128.6, 128.6, 127.5, 127.4, 126.8, 123.5, 122.5, 120.5, 111.0, 102.2, 39.7, 20.4.

### 2-(1-(4-pentylphenyl)ethyl)-3a,7a-dihydrobenzofuran (**3p**)

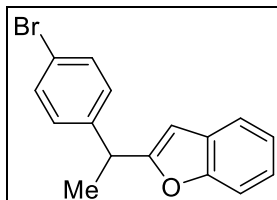


From 4'-n-amyacetophenone (0.5 mmol, 95.1 mg) and benzofuran (**2a**, 1.0 mmol, 118.1 mg), **3p** was obtained according the general procedure. The regioselectivity was determined by using GC and GC-Mass analysis (11.1:1), and purified using petroleum ether to give **3p** as a colorless oil in 78% yield, 114.1 mg.

$^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.42–7.35 (m, 1H), 7.34–7.24 (m, 1H), 7.15–7.05 (m, 5H), 7.04–6.97 (m, 1H), 6.33 (s, 1H), 4.19–4.06 (m, 1H), 2.46 (dt,  $J$  = 12.1, 8.1 Hz, 3H), 1.69–1.55 (m, 2H), 1.50 (dd,  $J$  = 14.6, 7.0 Hz, 2H), 1.29–1.16 (m, 4H), 0.79 (t,  $J$  = 6.9 Hz, 3H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  162.5, 154.9, 141.5, 140.5, 128.6, 127.4, 123.4, 122.5,

120.5, 111.0, 102.0, 39.3, 35.6, 31.6, 31.2, 22.6, 20.4, 14.1. HRMS (ESI)  $m/z$ :  $[M+H]^+$   
Calcd for  $C_{21}H_{25}O^+$  293.1906, found 293.1920.

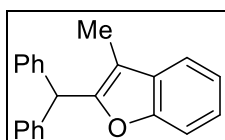
### 2-(1-(4-bromophenyl)ethyl)benzofuran (3q)



From 4'-bromoacetophenone (0.5 mmol, 99.5 mg) and benzofuran (1.0 mmol, 118.1 mg), **3q** was obtained according the general procedure. The regioselectivity was determined by using GC and GC-Mass analysis (3.1:1), and purified using EtOAc/petroleum ether (1:99) to give a yellow oil in 83% yield, 125.1 mg.

$^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.51–7.43 (m, 2H), 7.40–7.36 (m, 2H), 7.27–7.24 (m, 1H), 7.21 (d,  $J$  = 1.6 Hz, 1H), 7.18–7.13 (m, 2H), 6.44 (s, 1H), 4.28–4.13 (m, 1H), 1.67 (dd,  $J$  = 7.2, 2.8 Hz, 3H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  161.3, 154.9, 142.3, 141.3, 131.7, 131.6, 129.3, 129.2, 128.5, 123.6, 122.6, 120.6, 111.0, 102.3, 39.2, 20.2. HRMS (ESI)  $m/z$ :  $[M+H]^+$  calcd for  $C_{16}H_{14}BrO^+$  301.0228; found 301.0222.

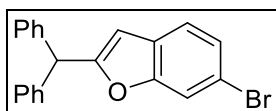
### 2-benzhydryl-3-methylbenzofuran (4a)



From benzophenone (**1a**, 0.5 mmol, 91.1 mg) and 3-methylbenzofuran (1.0 mmol, 132.2 mg), **4a** was obtained according the general procedure (petroleum ether) to give a white solid in 72% yield, 108.0 mg. Melting point: 69.5–71.2 °C.

$^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.40–7.34 (m, 1H), 7.32–7.26 (m, 1H), 7.21 (t,  $J$  = 6.4 Hz, 3H), 7.15 (dd,  $J$  = 11.7, 4.6 Hz, 7H), 7.11 (dd,  $J$  = 8.8, 5.1 Hz, 2H), 5.56 (s, 1H), 2.05 (s, 3H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  154.2, 153.3, 141.3, 130.3, 129.1, 128.5, 126.8, 123.7, 122.2, 119.1, 111.7, 111.2, 49.0, 8.2. HRMS (ESI)  $m/z$ :  $[M+H]^+$  Calcd for  $C_{22}H_{19}O^+$  299.1436; found 299.1427.

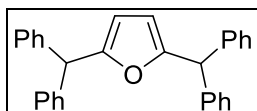
### 2-benzhydryl-6-bromobenzofuran (**4b**):



From benzophenone (**1a**, 0.5 mmol, 91.1 mg) and 6-bromobenzofuran (1.0 mmol, 98.5 mg), **4b** was obtained according the general procedure for 8 hours. Purification by using petroleum ether to give **4b** as a white solid in 47% yield, 85.3 mg. Melting point: 141.6-143.2 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 (d,  $J$  = 1.8 Hz, 1H), 7.27 (d,  $J$  = 6.9 Hz, 4H), 7.24–7.22 (m, 2H), 7.21–7.17 (m, 3H), 7.14 (d,  $J$  = 7.0 Hz, 3H), 6.15 (s, 1H), 5.50 (s, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.4, 153.9, 140.7, 130.5, 128.9, 128.7, 128.7, 127.2, 126.9, 126.6, 123.3, 115.7, 112.6, 105.2, 51.3. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{21}\text{H}_{16}\text{BrO}^+$  363.0385; found 363.0398.

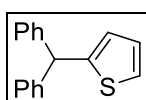
### 2, 5-dibenzhydrylfuran<sup>14</sup> (**4c**):



From benzophenone (**1a**, 0.5 mmol, 91.1 mg) and furan (1.0 mmol, 68 mg), **4c** was obtained according the general procedure (petroleum ether) to give a yellow oil in 78% yield, 285.6mg. **4c** was analyzed by GC-MS,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and verified by comparison with literature data.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30–7.18 (m, 14H), 7.17–7.09 (m, 8H), 5.80 (d,  $J$  = 3.2 Hz, 2H), 5.39 (s, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  156.1, 141.9, 128.8, 128.3, 126.6, 108.9, 77.4, 77.0, 76.73, 50.9.

### 2-benzhydrylthiophene<sup>7</sup> (**4d**):

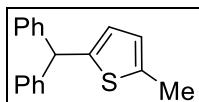


From benzophenone (0.5 mmol, 91.1 mg) and thiophene (1.0 mmol, 84.1 mg), **4d** was obtained according the general procedure (petroleum ether) to give a colorless oil in 55 yield, 68.8 mg. **4d** was analyzed by GC-MS,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and verified by

comparison with literature data.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31–7.22 (m, 9H), 7.25–7.17 (m, 4H), 7.18–7.10 (m, 7H), 5.80 (s, 2H), 5.39 (s, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.9, 143.8, 129.0, 128.8, 128.4, 128.4, 126.7, 126.6, 126.4, 124.6, 52.2.

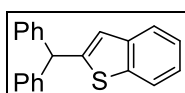
#### 2-(diphenylmethyl)-5-methylthiophene<sup>8</sup> (**4e**):



From benzophenone (0.5 mmol, 91.1 mg) and 2-methylthiophene (1.0 mmol, 98.2 mg), **4e** was obtained according the general procedure (petroleum ether) to give a colorless oil in 31% yield, 41 mg. **4e** was analyzed by GC-MS,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and verified by comparison with literature data.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.22 (dd,  $J$  = 10.4, 4.4 Hz, 4H), 7.15 (dd,  $J$  = 7.1, 4.3 Hz, 6H), 6.49 (d,  $J$  = 2.4 Hz, 2H), 6.37 (d,  $J$  = 3.2 Hz, 2H), 5.51 (s, 1H), 2.33 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  144.4, 142.8, 137.9, 127.8, 127.3, 125.6, 125.1, 123.5, 51.2, 14.3.

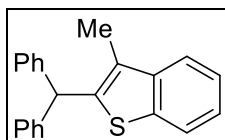
#### 2-benzhydrylbenzo[*b*]thiophene<sup>5</sup> (**4f**):



From benzophenone (0.5 mmol, 91.1 mg) and benzo[*b*]thiophene (1.0 mmol, 134.2 mg), **4f** was obtained according the general procedure (petroleum ether) to give a white solid in 53% yield, 79.5 mg. **4f** was analyzed by GC-MS,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and verified by comparison with literature data.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83 (d,  $J$  = 8.0 Hz, 1H), 7.54–7.41 (m, 1H), 7.33–7.08 (m, 12H), 6.71 (d,  $J$  = 0.9 Hz, 1H), 5.73 (d,  $J$  = 9.1 Hz, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  142.7, 140.8, 139.2, 138.5, 129.2, 128.6, 126.7, 125.2, 124.3, 124.0, 122.8, 122.8, 51.4.

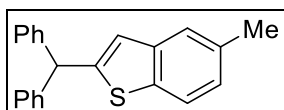
#### 2-benzhydryl-3-methylbenzo[*b*]thiophene (**4g**):



From benzophenone (0.5 mmol, 91.1 mg) and 3-methylbenzo[b]thiophene (1.0 mmol, 148.2 mg), **4g** was obtained according the general procedure (petroleum ether) to give a white solid in 72% yield, 113.2 mg. Melting point: 98.7–100.2 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 (dd,  $J$  = 19.6, 7.9 Hz, 2H), 7.33 (dd,  $J$  = 12.2, 4.2 Hz, 1H), 7.30–7.26 (m, 4H), 7.23 (dd,  $J$  = 6.7, 5.4 Hz, 7H), 5.85 (s, 1H), 2.26 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  143.1, 142.4, 141.0, 139.0, 129.2, 129.1, 128.5, 128.0, 126.9, 124.0, 123.8, 122.3, 121.5, 50.6, 12.1. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{22}\text{H}_{19}\text{S}^+$ : 315.1208; found 315.1215.

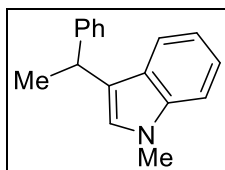
#### 2-benzhydryl-5-methylbenzo[b]thiophene (**4h**):



From benzophenone (0.5 mmol, 91.1 mg) and 5-methylthianaphthene (1.0 mmol, 148.2 mg), **4h** was obtained according the general procedure. The regioselectivity was determined by using GC and GC-Mass (C2:C3=20:1), and purified using petroleum ether to give a white solid in 82% yield, 128.9 mg. Melting point: 126.9–128.1 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 (d,  $J$  = 8.2 Hz, 1H), 7.30–7.16 (m, 6H), 7.17–7.11 (m, 2H), 7.12–7.05 (m, 3H), 7.03 (dd,  $J$  = 13.6, 7.6 Hz, 1H), 6.61 (s, 1H), 5.93–5.46 (m, 1H), 2.71–1.91 (m, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  142.8, 138.9, 138.7, 137.9, 133.7, 129.1, 128.5, 126.6, 126.1, 125.4, 122.6, 122.4, 51.3, 21.6. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{22}\text{H}_{19}\text{S}^+$  315.1208; found 315.1223.

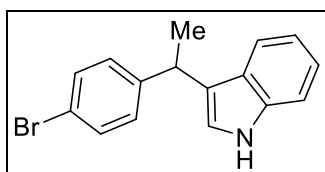
#### 1-methyl-3-(1-phenylethyl)-1H-indole<sup>16</sup> (**4i**):



From acetophenone (0.5 mmol, 60.1 mg) and 1-methyl-1H-indole (1.0 mmol, 131.2

mg), **4i** was obtained according to a modified condition from general procedure (under electrolysis at 2.0 mA for 3.0 hours). Purification by column chromatography using EtOAc/petroleum ether (1:99) as eluent gave **4i** as a yellow oil in 53% yield, 62.4 mg.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 (dt,  $J$  = 8.1, 1.0 Hz, 1H), 7.32–7.19 (m, 5H), 7.20–7.10 (m, 2H), 6.97 (ddd,  $J$  = 8.0, 6.9, 1.1 Hz, 1H), 6.79 (d,  $J$  = 1.0 Hz, 1H), 4.35 (q,  $J$  = 7.1 Hz, 1H), 3.67 (s, 3H), 1.68 (d,  $J$  = 7.2 Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.1, 137.5, 128.4, 127.6, 127.4, 126.1, 126.0, 121.6, 120.1, 119.9, 118.8, 109.2, 37.0, 32.7, 22.6.

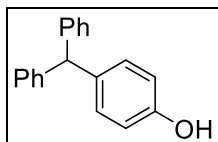
**(R)-3-(1-(4-bromophenyl)ethyl)-1H-indole<sup>15</sup>(4j):**



From 1-(4-bromophenyl)ethan-1-one (0.5 mmol, 99.6 mg) and 1H-indole (1.0 mmol, 117.2 mg), **4j** was obtained according to a modified condition from general procedure (under electrolysis at 2.0 mA for 3.0 hours). Purification by column chromatography using EtOAc/petroleum ether (1:99) as eluent gave **4j** as a colorless oil in 58% yield, 87.1 mg.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (s, 1H), 7.40–7.30 (m, 2H), 7.35–7.26 (m, 2H), 7.19–7.09 (m, 3H), 7.06–6.94 (m, 2H), 4.31 (q,  $J$  = 7.1 Hz, 1H), 1.66 (d,  $J$  = 7.2 Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.9, 136.6, 131.3, 129.2, 126.6, 122.1, 121.1, 120.6, 119.5, 119.3, 111.1, 36.4, 22.2.

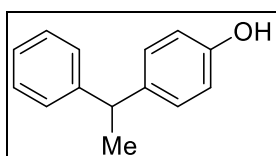
**4-benzhydrylpheno<sup>9</sup> (4k):**



From benzophenone (0.5 mmol, 91.1 mg) and phenol (1.0 mmol, 94.1 mg), **4k** was obtained according the general procedure (EtOAc/petroleum ether=3:47) to give a yellow oil in 86% yield, 112 mg. **4k** was analyzed by GC-MS,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and verified by comparison with literature data.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35–7.16 (m, 6H), 7.15–7.04 (m, 4H), 6.99 (dd,  $J$  = 16.8, 8.0 Hz, 2H), 6.73 (d,  $J$  = 8.4 Hz, 2H), 5.48 (s, 1H), 4.92 (s, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.9, 144.3, 136.4, 130.6, 129.4, 128.3, 126.3, 115.2, 56.0.

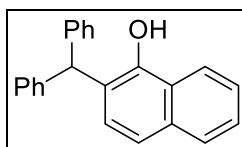
**4-(1-phenylethyl)phenol<sup>11</sup> (4l):**



From acetophenone (0.5 mmol, 105.1 mg) and phenol (1.0 mmol, 94.1 mg), **4l** was obtained according the general procedure (EtOAc/petroleum ether=3:47) to give a yellow oil in 87 yield, 86.2mg. **4l** was analyzed by GC-MS,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and verified by comparison with literature data.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38–7.04 (m, 7H), 6.82–6.61 (m, 2H), 5.18 (s, 1H), 4.08 (d,  $J$  = 7.2 Hz, 1 H), 1.60 (d,  $J$  = 7.2 Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.7, 146.8, 138.8, 128.8, 128.4, 127.6, 126.0, 115.2, 44.0, 22.1.

**2-benzhydrylnaphthalen-1-ol<sup>12</sup> (4m):**

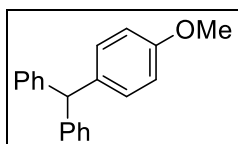


From benzophenone (**1a**, 0.5 mmol, 91.1 mg) and 1-naphthol (1.0 mmol, 144.1 mg), **4m** was obtained according the general procedure (EtOAc/petroleum ether=3:47) to give a colorless oil in 82% yield, 127 mg. **4m** was analyzed by GC-MS,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and verified by comparison with literature data.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.22 (dd,  $J$  = 7.9, 1.7 Hz, 1H), 7.91 (dd,  $J$  = 8.1, 1.5 Hz, 1H), 7.53–7.33 (m, 3H), 7.32–7.01 (m, 9H), 6.76–6.49 (m, 2H), 6.17 (s, 1H), 5.39 (s, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  150.4, 144.0, 132.9, 132.52, 129.7, 128.4, 127.6, 126.7, 126.3, 124.9, 124.8, 124.4, 122.2, 107.8, 52.8.

**(4-methoxyphenyl)diphenylmethane<sup>10</sup> (4n):**

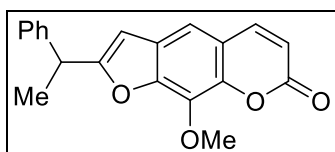




From benzophenone (0.5 mmol, 91.1 mg) and anisole (1.0 mmol, 108.1 mg), **4n** was obtained according the general procedure (EtOAc/petroleum ether=1:49) to give a colorless oil in 64% yield, 87.7mg. **4n** was analyzed by GC-MS,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and verified by comparison with literature data.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27 (dd,  $J$  = 8.2, 6.7 Hz, 4H), 7.23–7.15 (m, 2H), 7.14–7.06 (m, 4H), 7.06–6.98 (m, 2H), 6.82 (dd,  $J$  = 8.6, 1.7 Hz, 2H), 5.50 (s, 1H), 3.77 (d,  $J$  = 1.0 Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.1, 144.3, 136.1, 130.4, 129.4, 128.3, 126.3, 113.7, 56.1, 55.26.

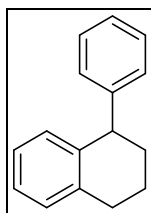
#### 9-methoxy-2-(1-phenylethyl)-7H-furo[3,2-g]chromen-7-one (**4o**):



From acetophenone (0.5 mmol, 105.1 mg) and 8-methoxypsoralen (1.0 mmol, 216.2 mg), **4o** was obtained according the general procedure (EtOAc/petroleum ether=3:17) to give a colorless oil in 46% yield, 73.8 mg.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 (t,  $J$  = 20.1 Hz, 1H), 7.55–7.39 (m, 1H), 7.26–7.20 (m, 2H), 7.14 (dd,  $J$  = 11.1, 7.4 Hz, 3H), 6.43 (d,  $J$  = 2.2 Hz, 1H), 6.23 (d,  $J$  = 10.0 Hz, 1H), 4.86–4.71 (m, 1H), 4.18 (s, 3H), 1.72 (d,  $J$  = 7.3 Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  160.2, 148.0, 145.8, 144.1, 143.9, 140.9, 131.5, 130.6, 128.7, 128.6, 127.2, 126.5, 125.2, 114.1, 106.2, 61.5, 38.3, 20.1. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{20}\text{H}_{17}\text{O}_4^+$  321.1127; found 321.1139.

#### 1-phenyl-1,2,3,4-tetrahydronaphthalene<sup>19</sup> (**4p**)



From 1,4-diphenylbutan-1-one **1p** (0.5 mmol, 112.1 mg), **4p** was obtained according the general procedure (petroleum ether) to give a colorless oil in 73% yield, 76.1 mg.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32–7.24 (m, 2H), 7.23–7.18 (m, 1H), 7.16–7.08 (m, 4H), 7.03 (ddd,  $J$  = 7.7, 6.2, 2.5 Hz, 1H), 6.84 (d,  $J$  = 7.7 Hz, 1H), 4.13 (t,  $J$  = 6.7 Hz, 1H), 3.00–2.80 (m, 2H), 2.23–2.11 (m, 1H), 1.89 (dddd,  $J$  = 15.7, 12.6, 7.1, 3.0 Hz, 2H), 1.77 (dddd,  $J$  = 14.1, 8.5, 6.0, 2.4 Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.5, 139.4, 137.6, 130.2, 129.0, 128.9, 128.2, 126.0, 125.9, 125.6, 45.6, 33.3, 29.8, 21.0.

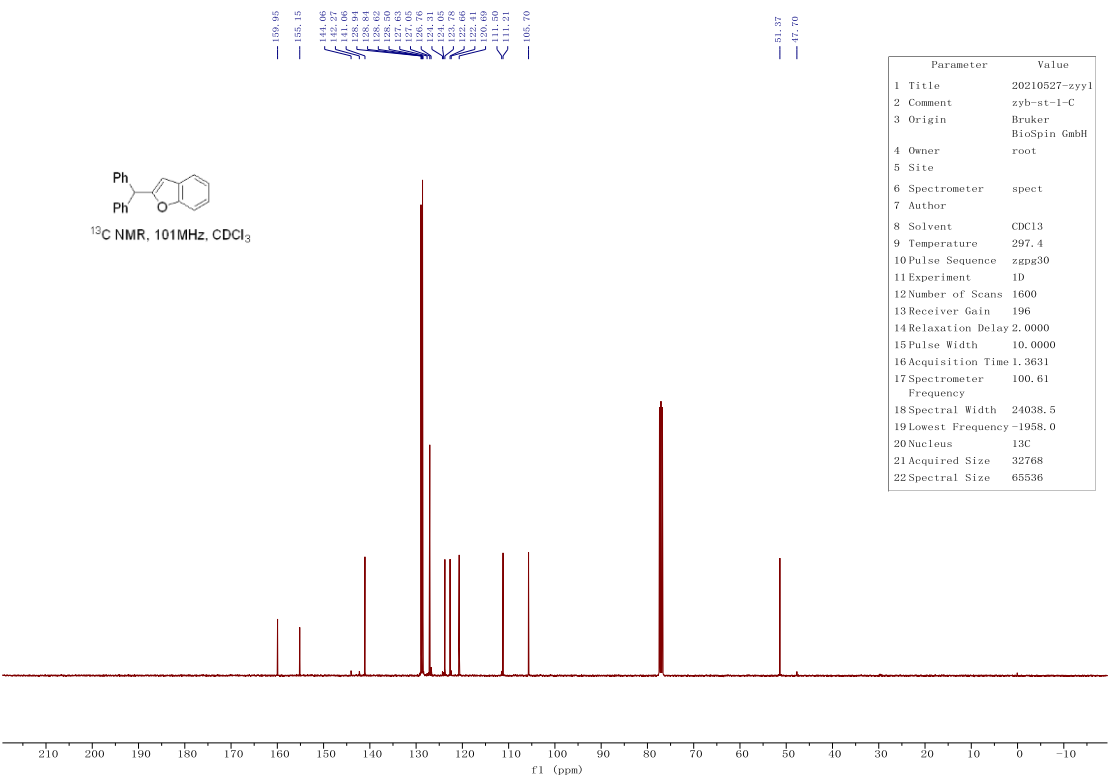
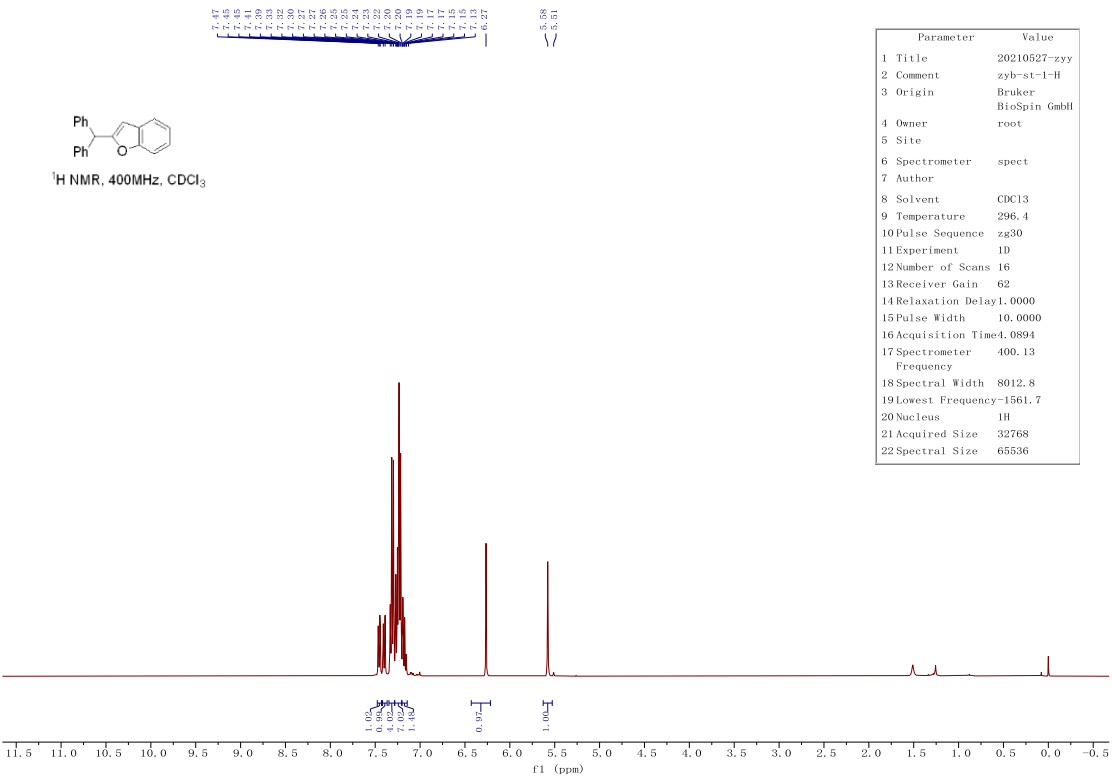
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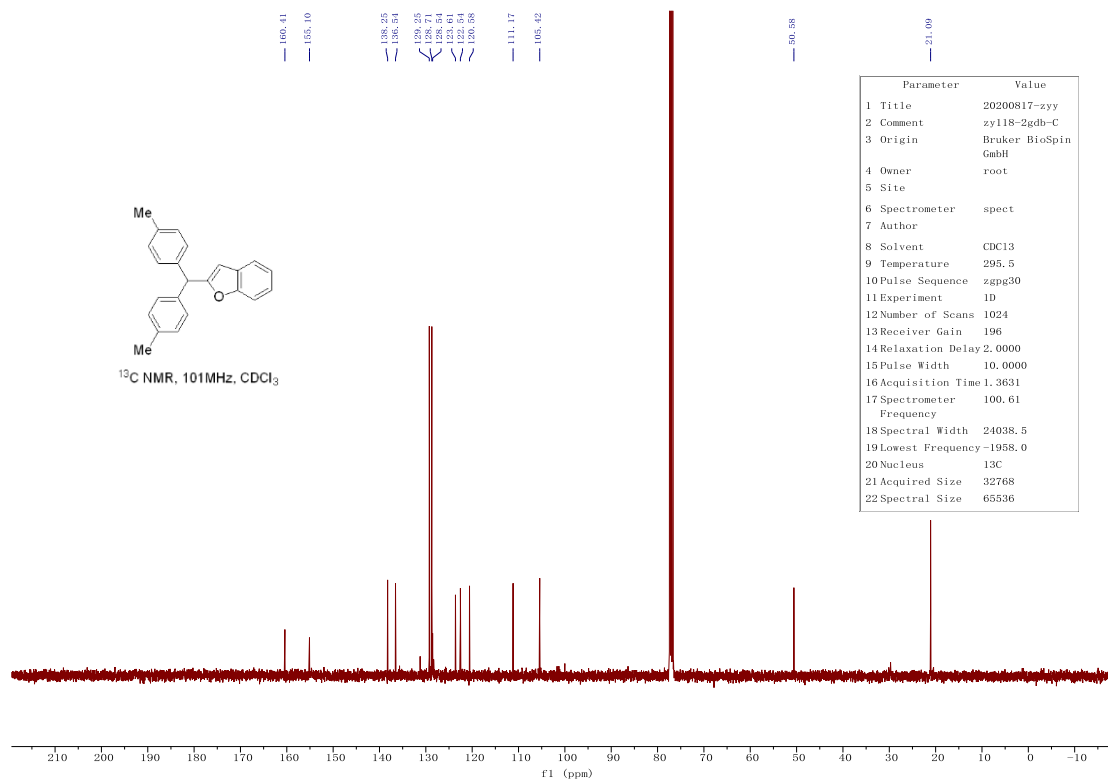
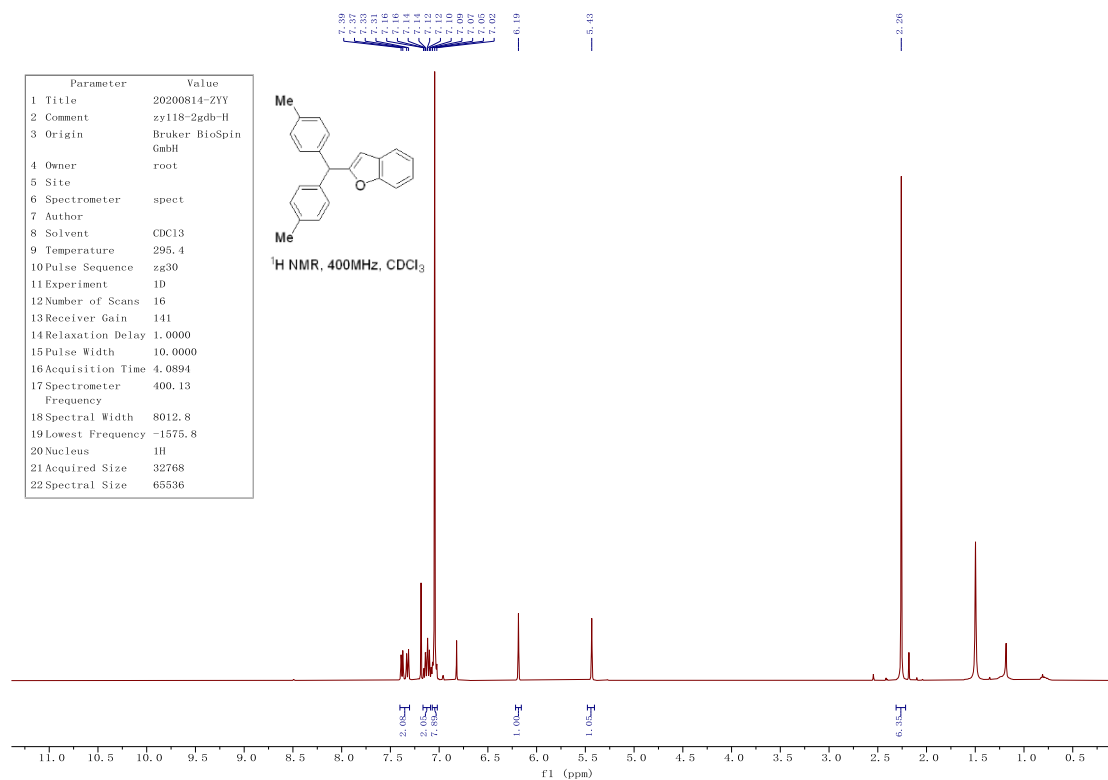
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# NMR Spectra

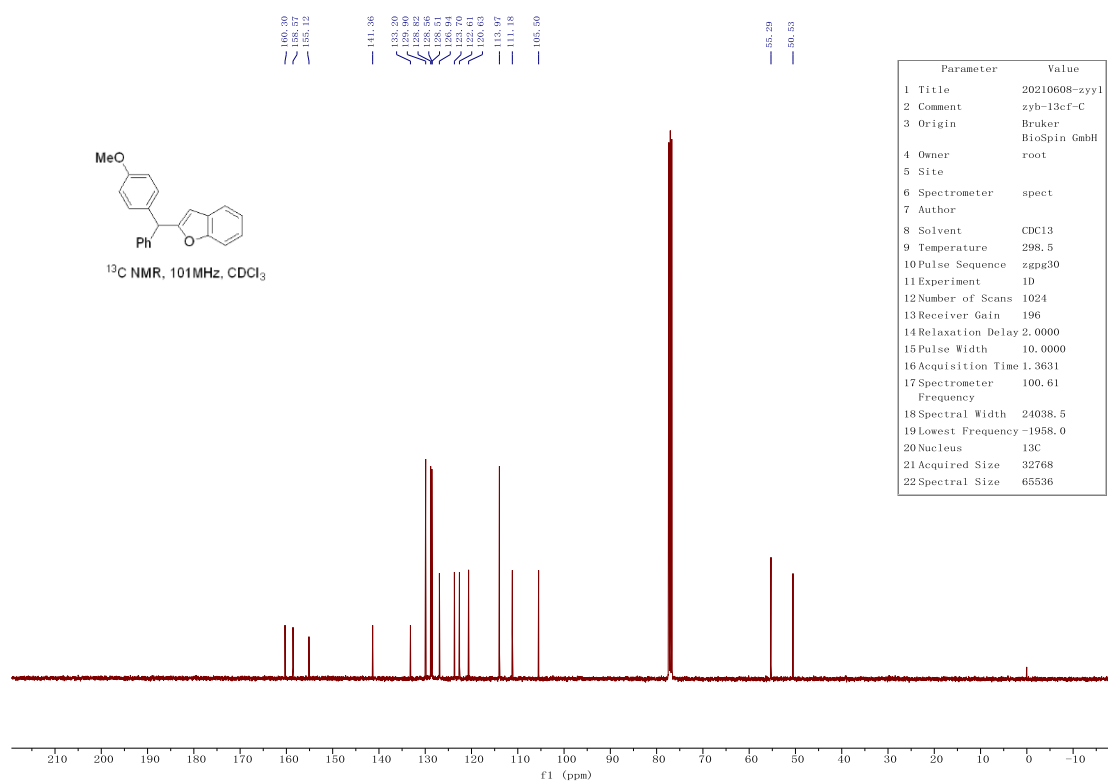
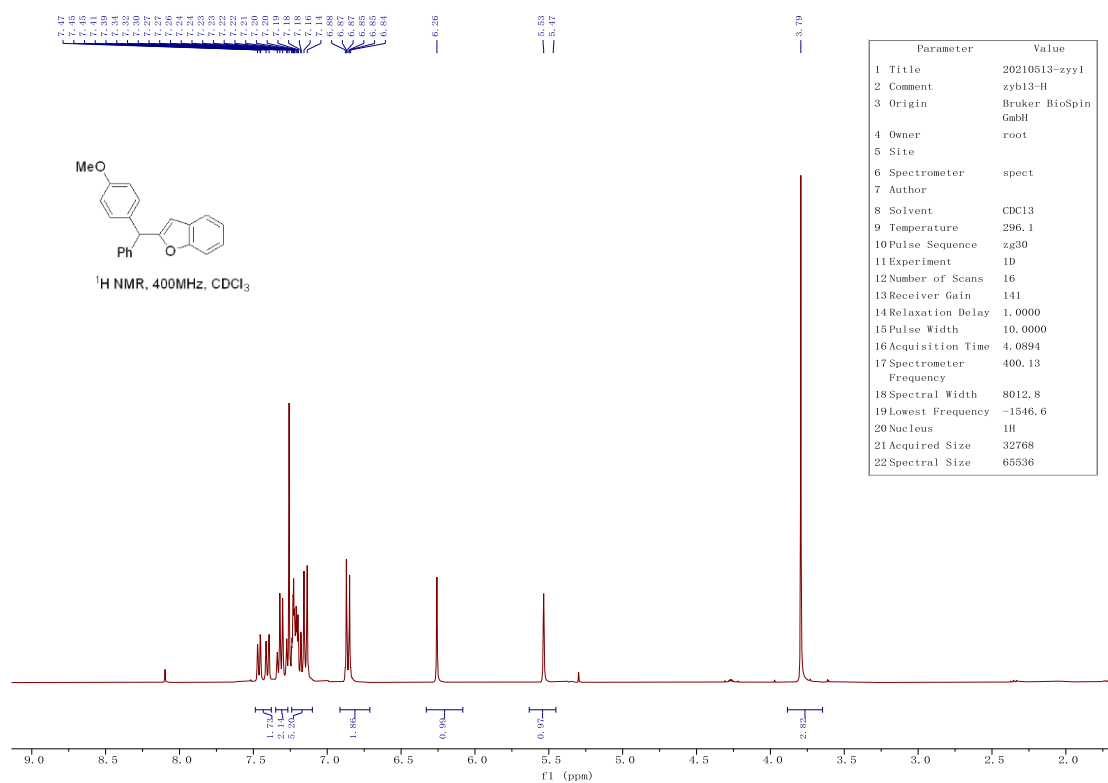
## 2-diphenylmethylbenzofuran (3a):



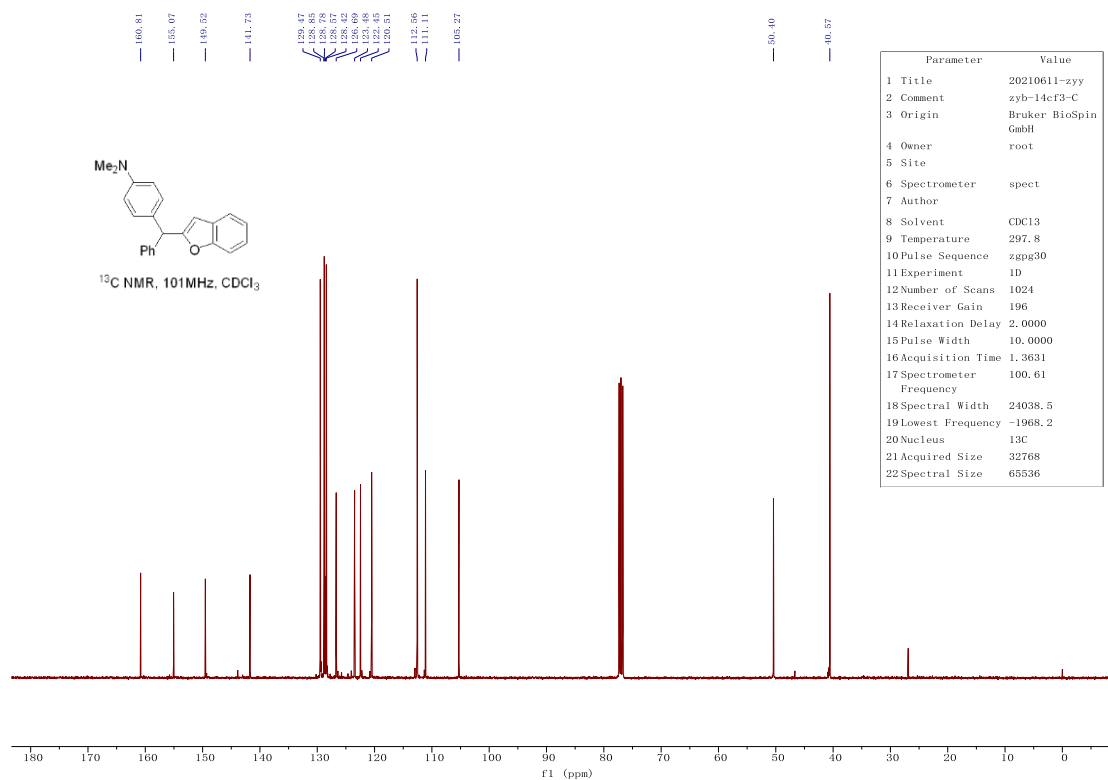
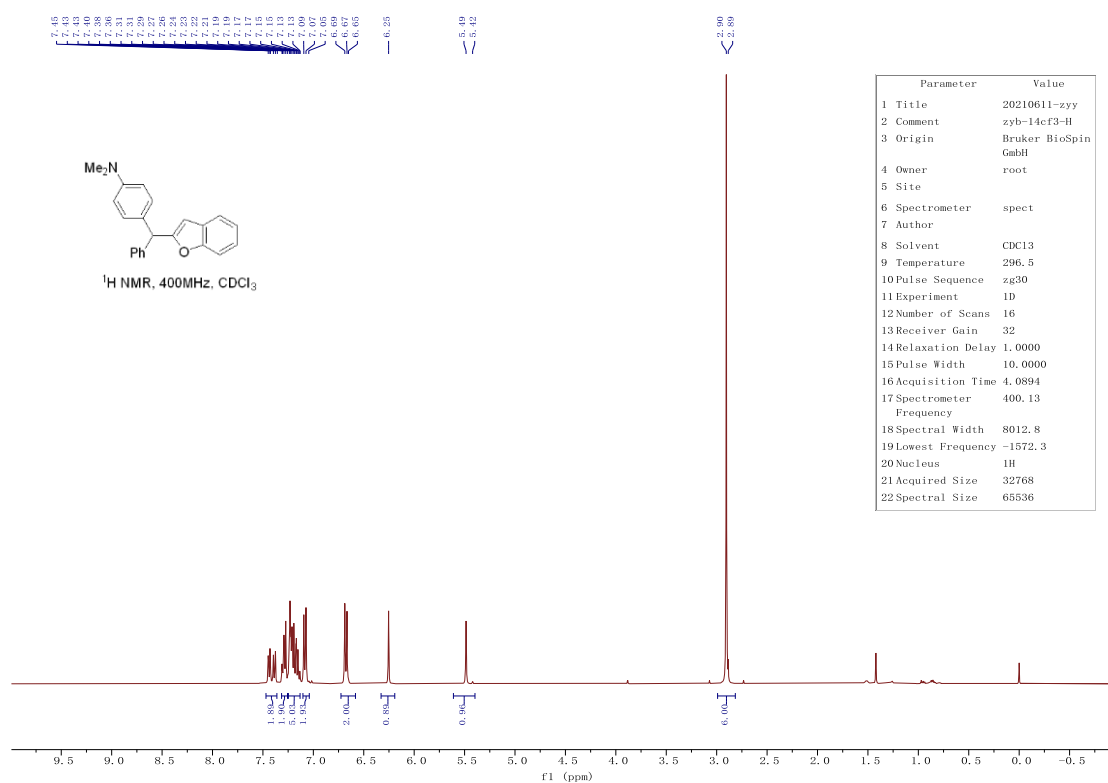
## 2-(di-p-tolylmethyl)benzofuran (3b):



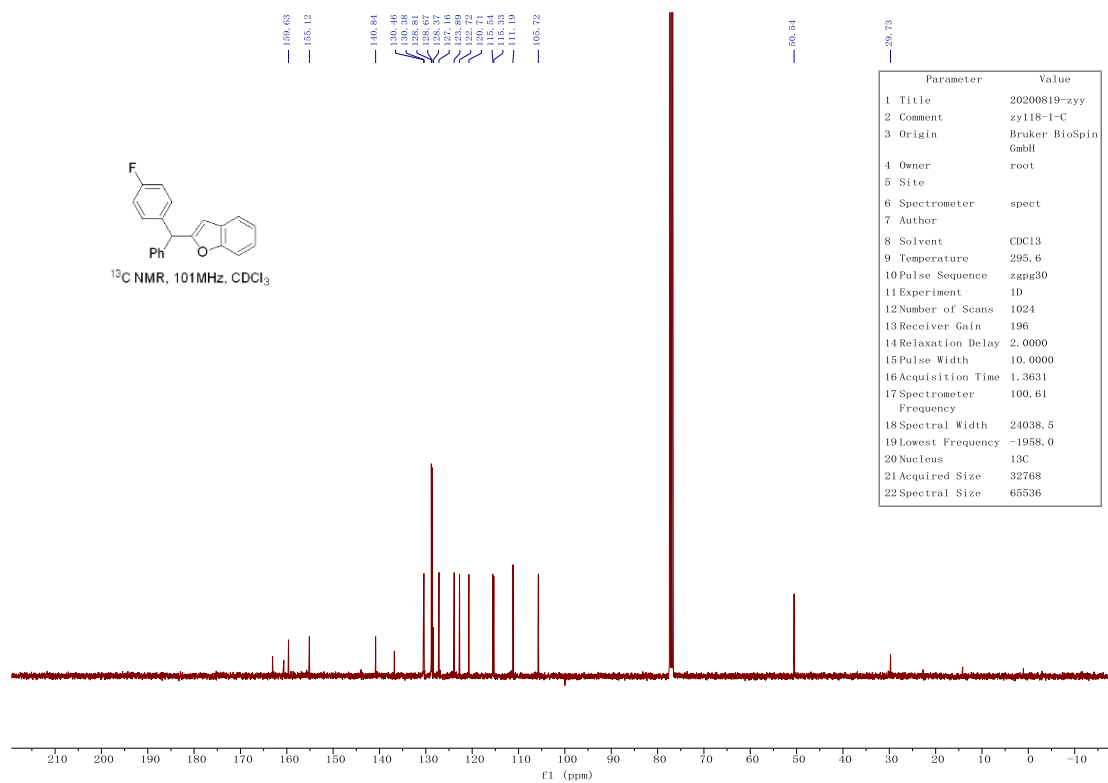
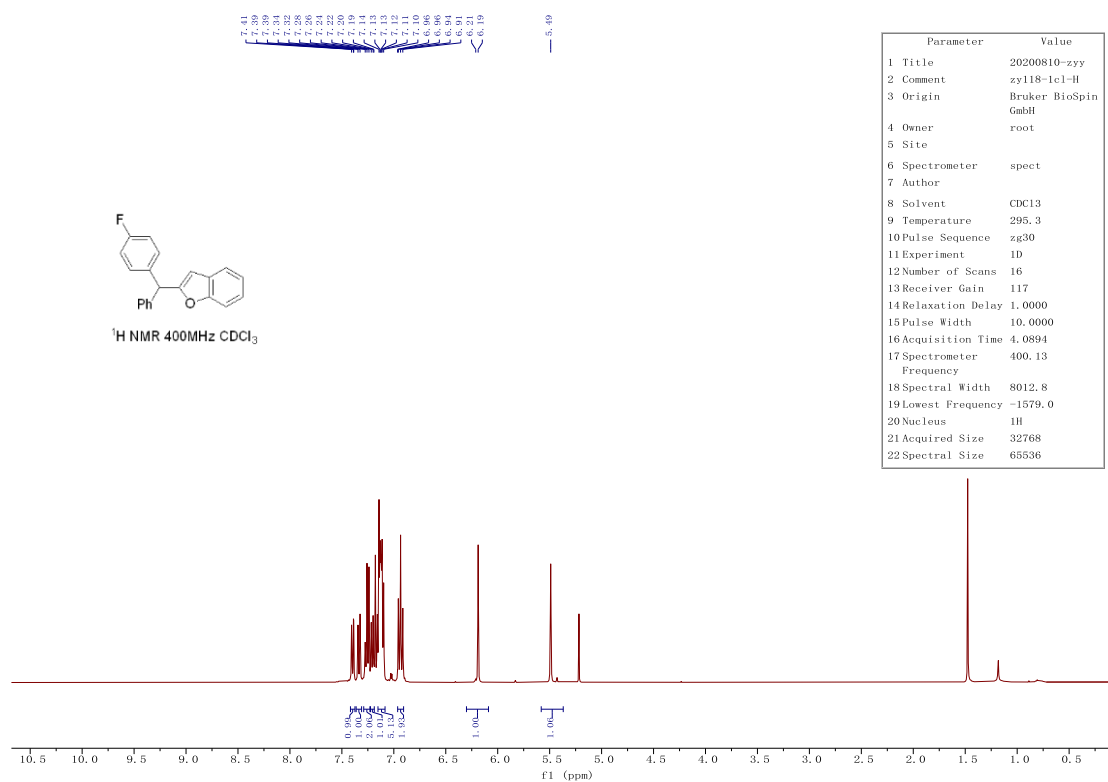
## 2-((4-methoxyphenyl)(phenyl)methyl)benzofuran (3c):



**(2-benzofuryl) (4-dimethylaminophenyl)phenylmethane (3d):**

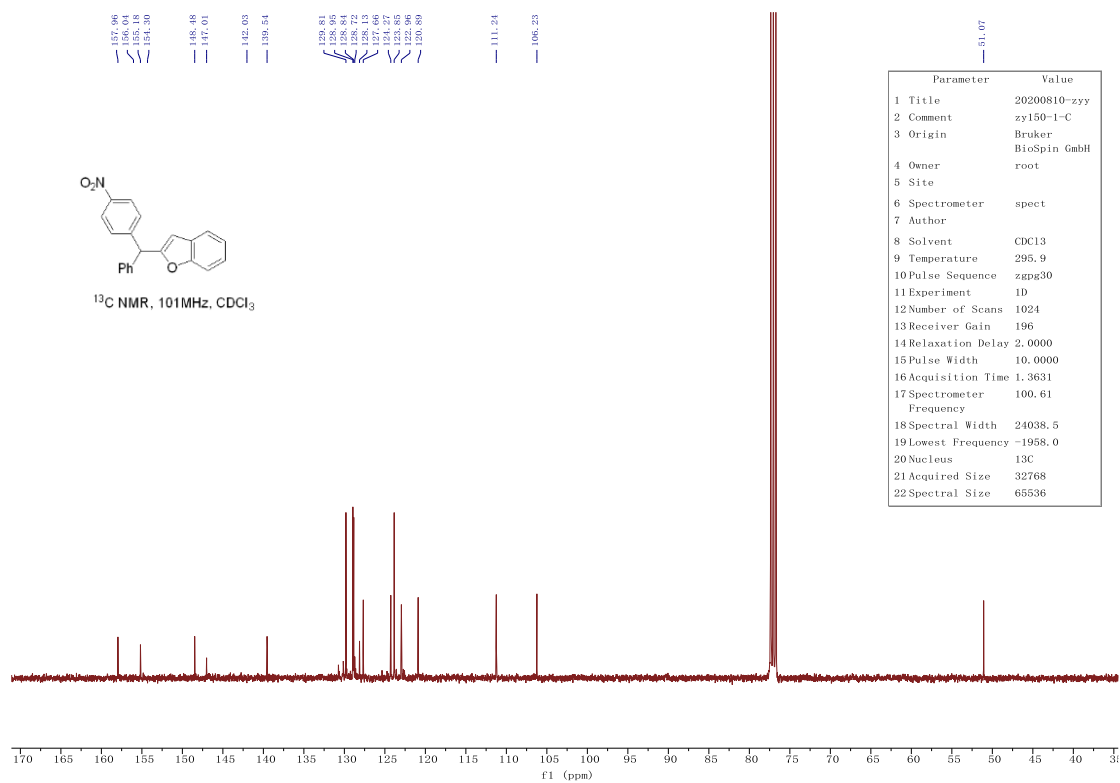
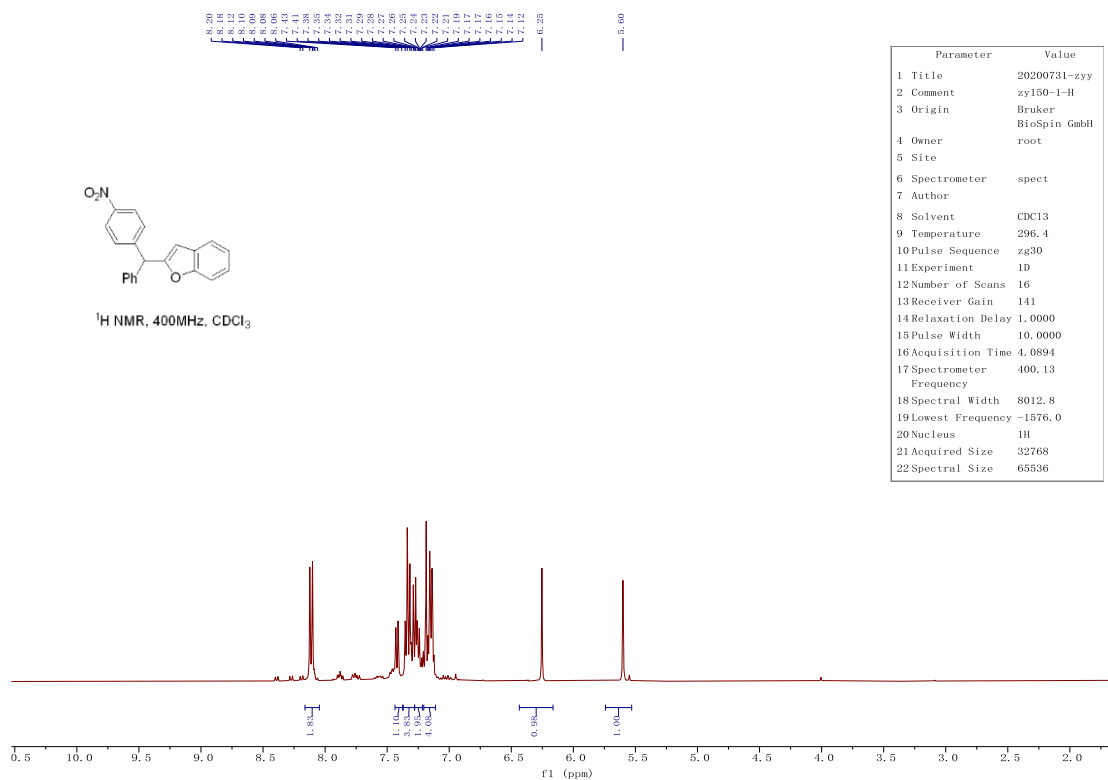


## 2-((4- fluorophenyl)(phenyl)methyl)benzofuran (3e):

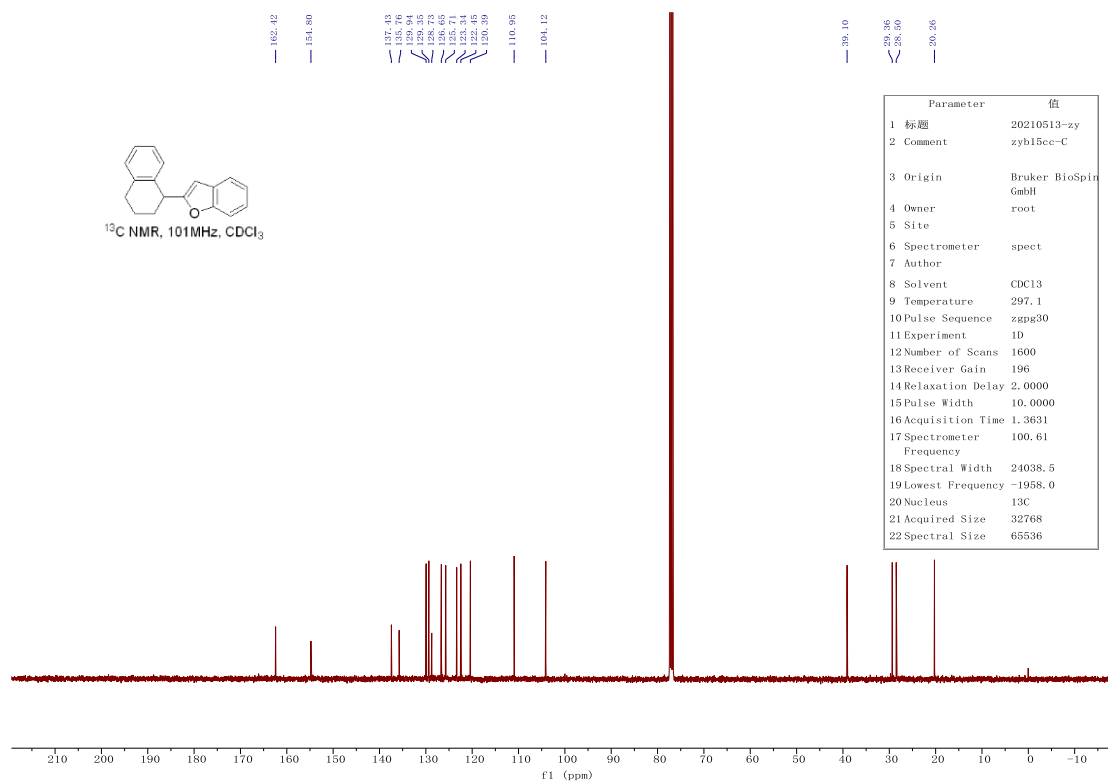
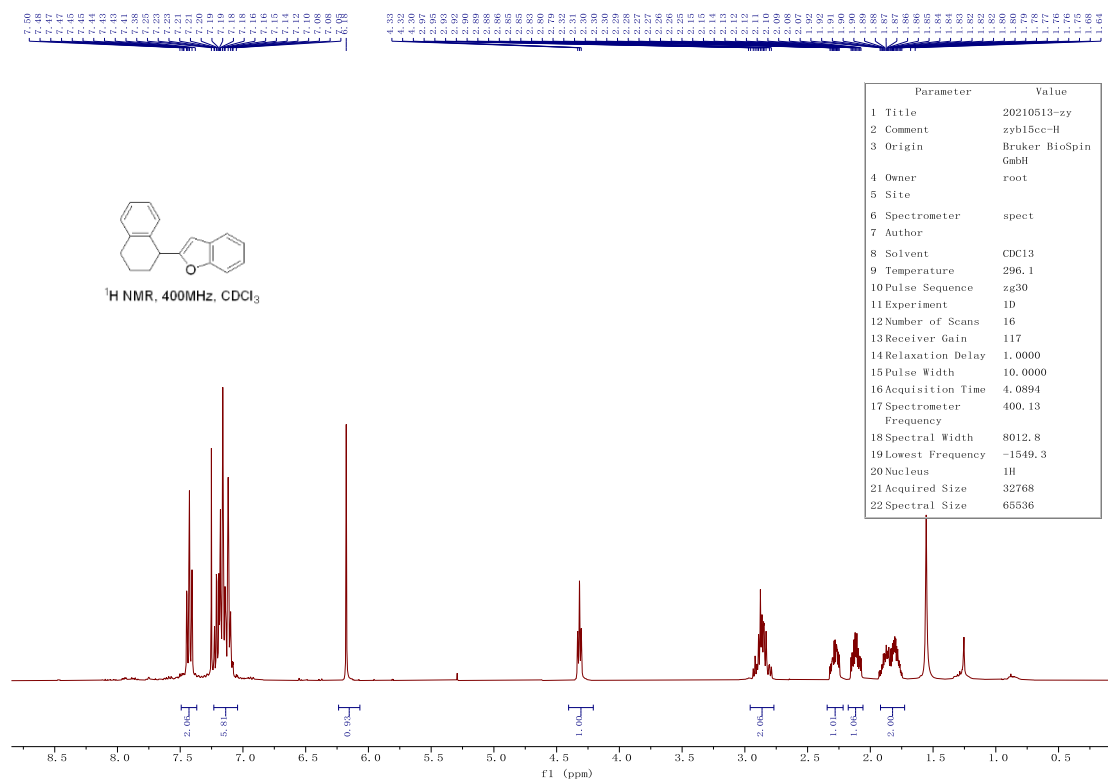




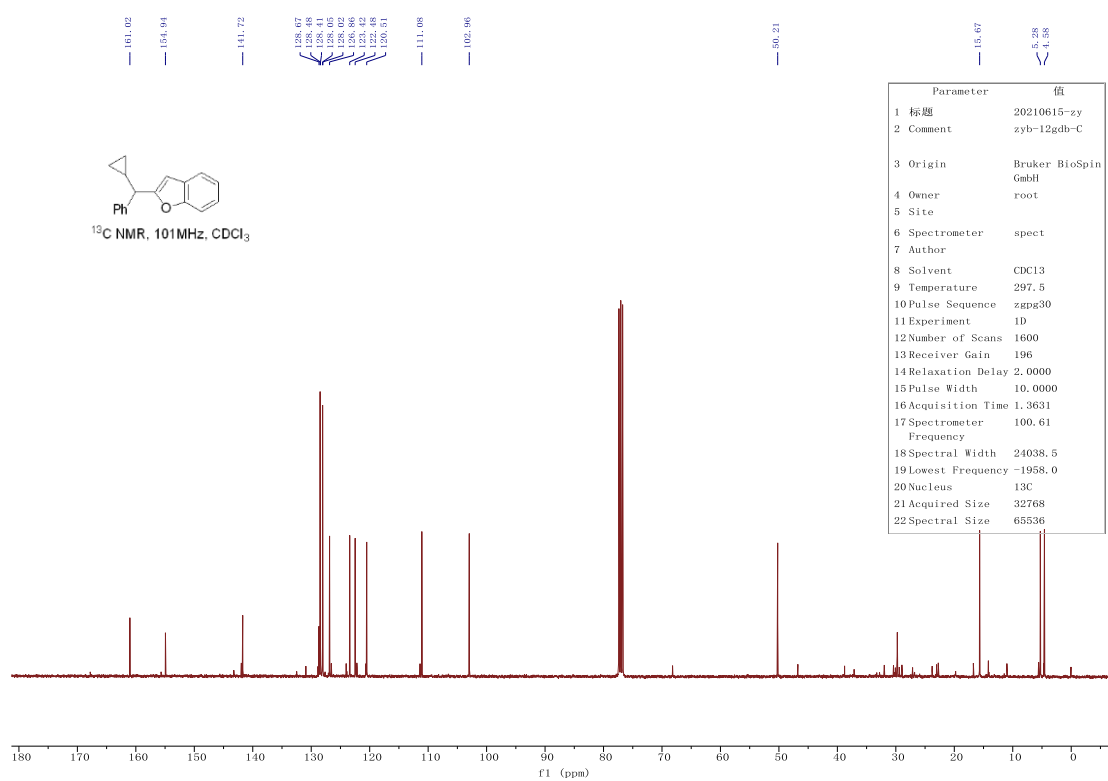
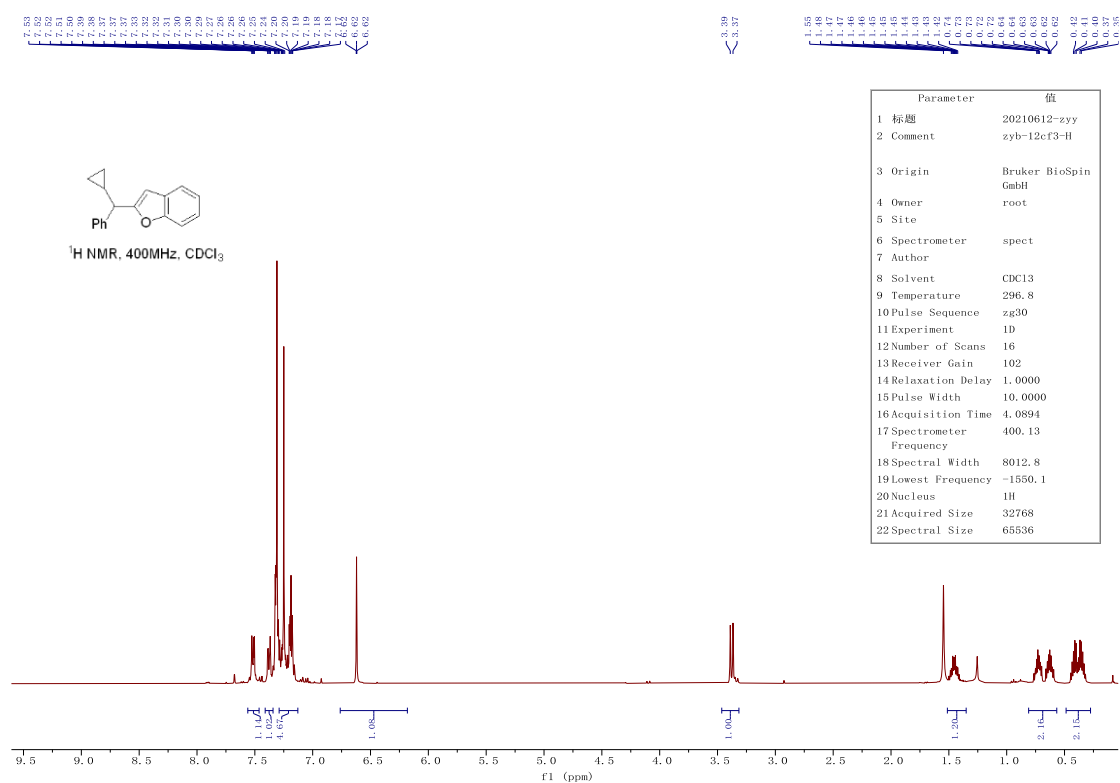
## 2-((4-nitrophenyl)(phenyl)methyl)benzofuran (3f):



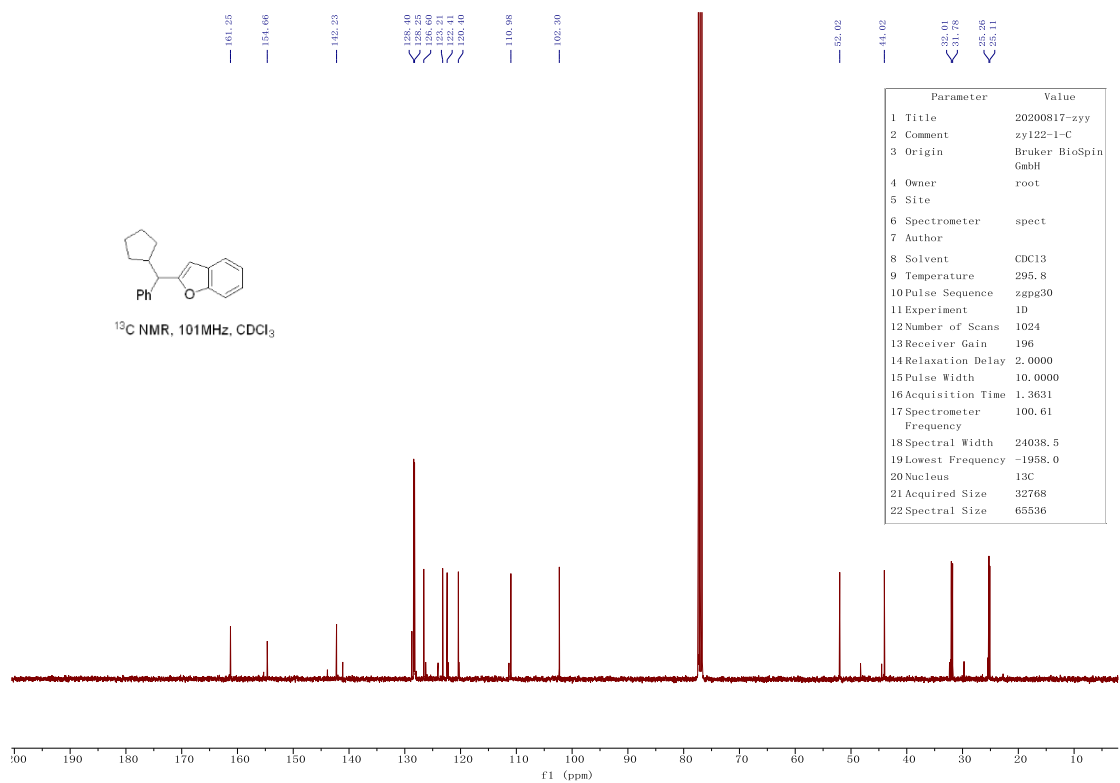
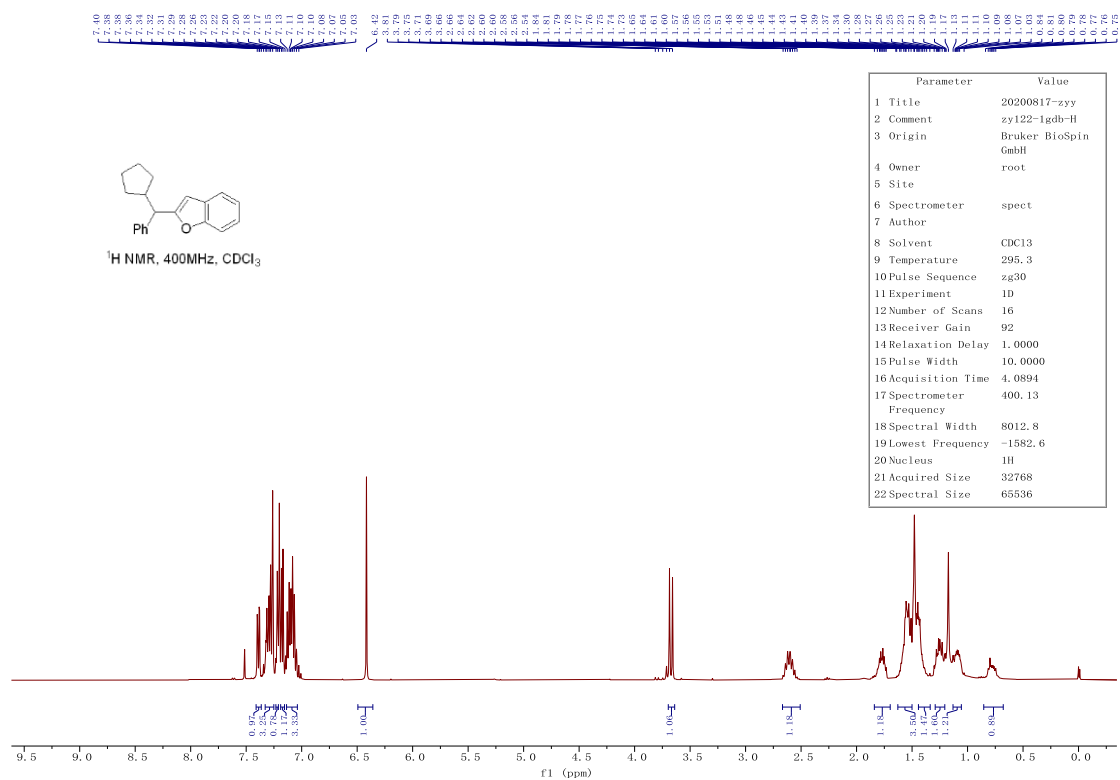
## 2-(1,2,3,4-tetrahydro-1-naphthalenyl)benzofuran(3g)



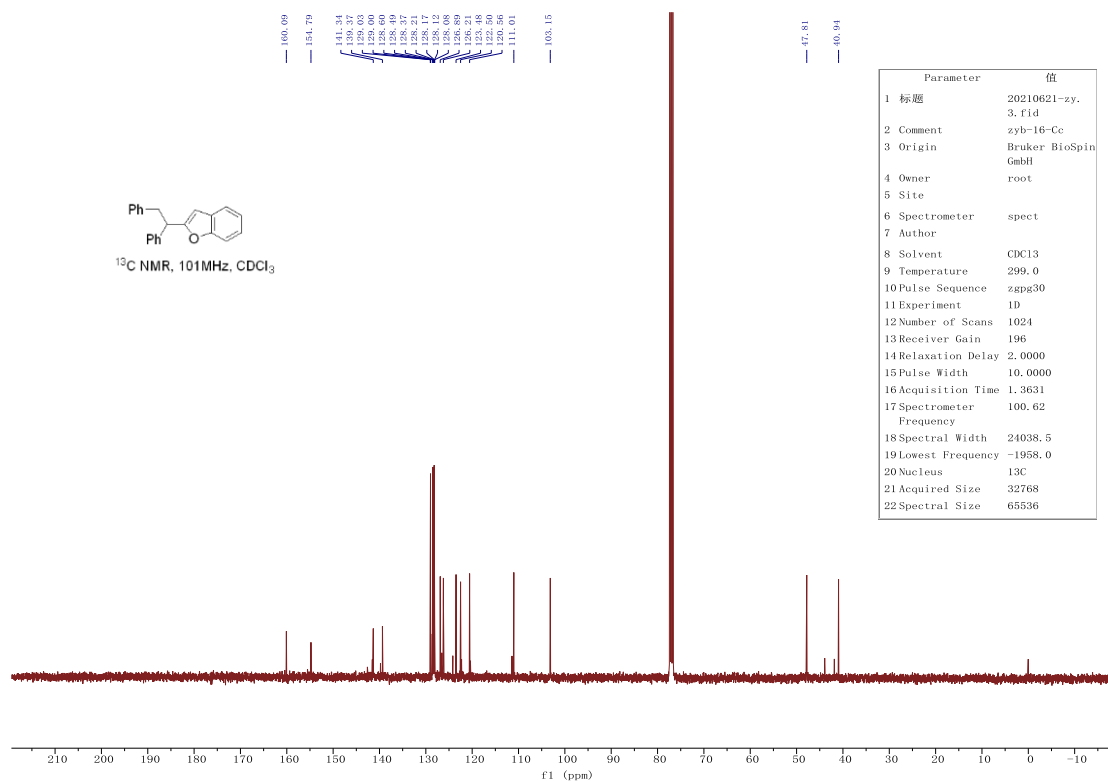
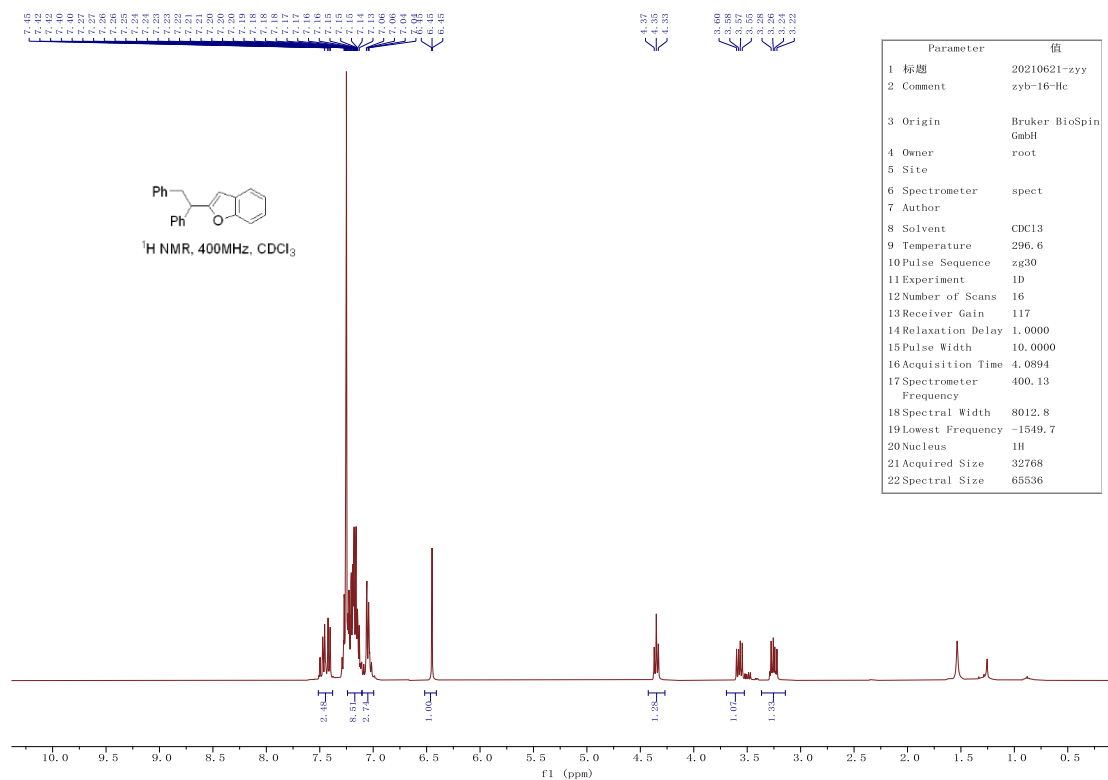
## 2-(cyclopropyl(phenyl)methyl)benzofuran (3h):



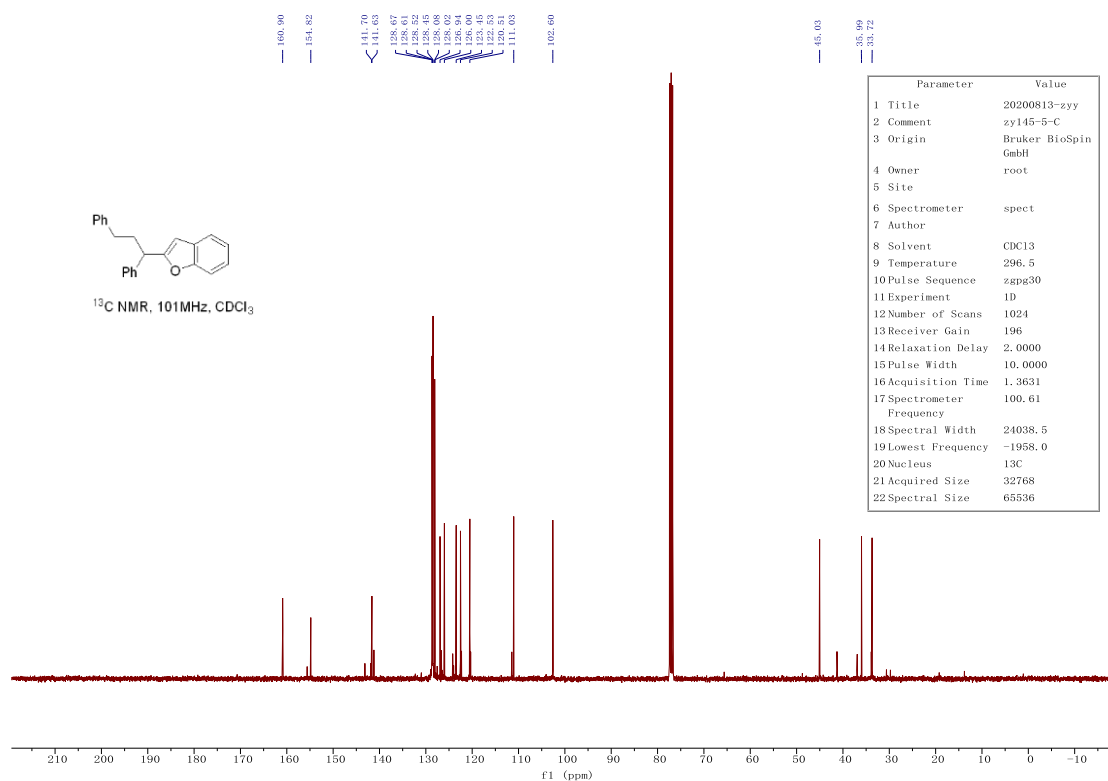
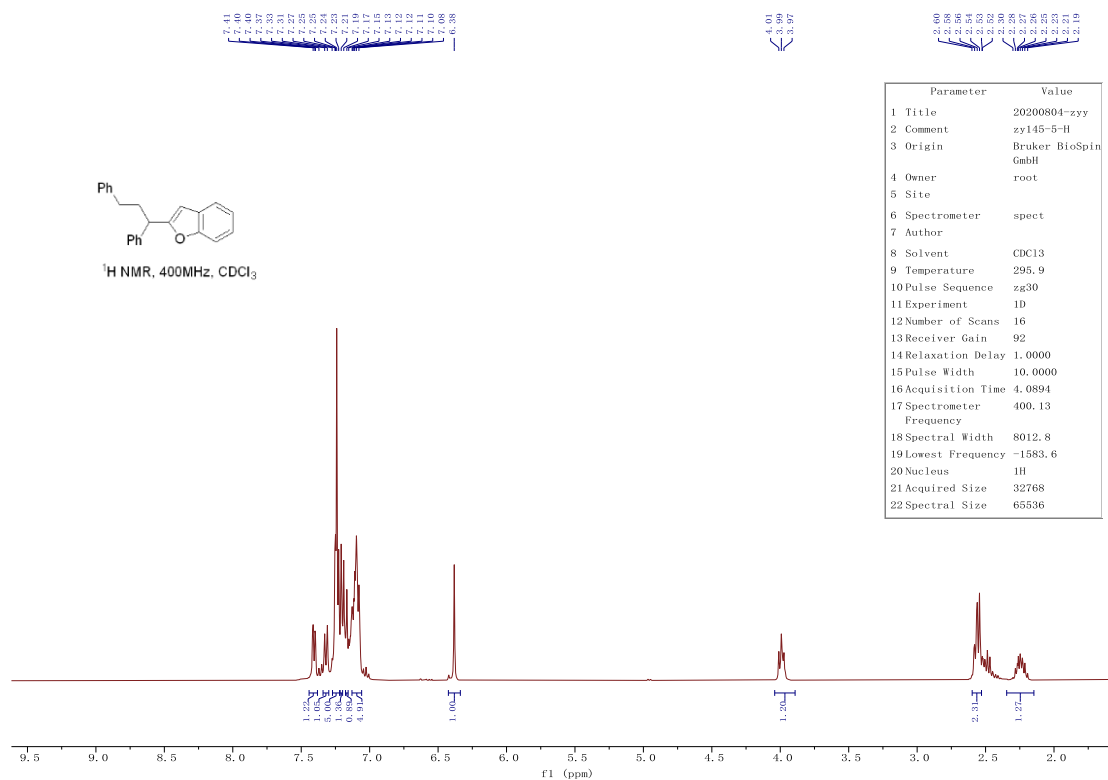
## 2-(cyclopentyl(phenyl)methyl)benzofuran (3i):



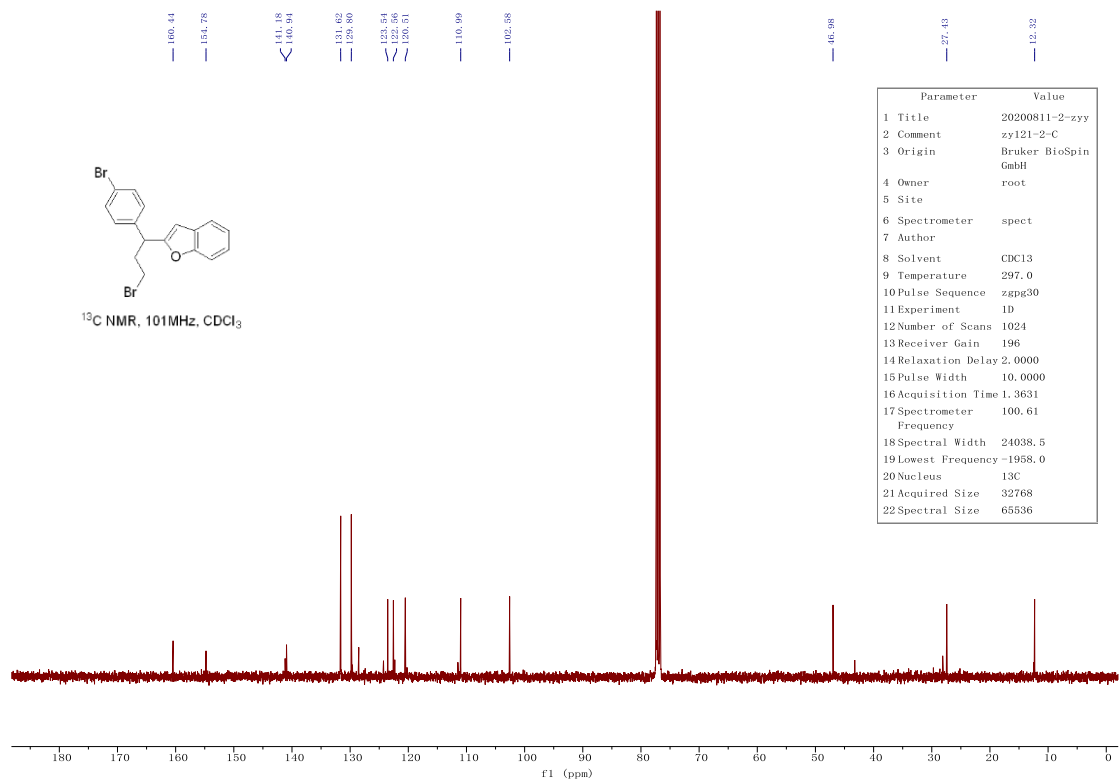
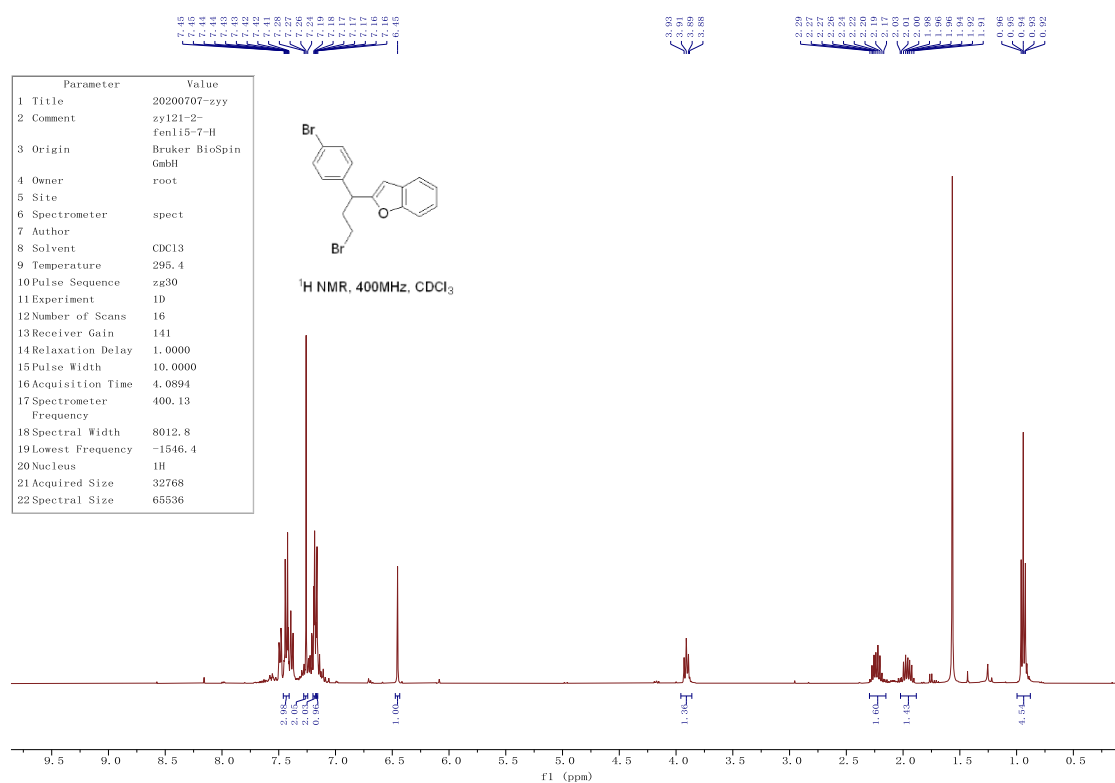
## 2-(1,2-diphenylethyl)benzofuran (3j):



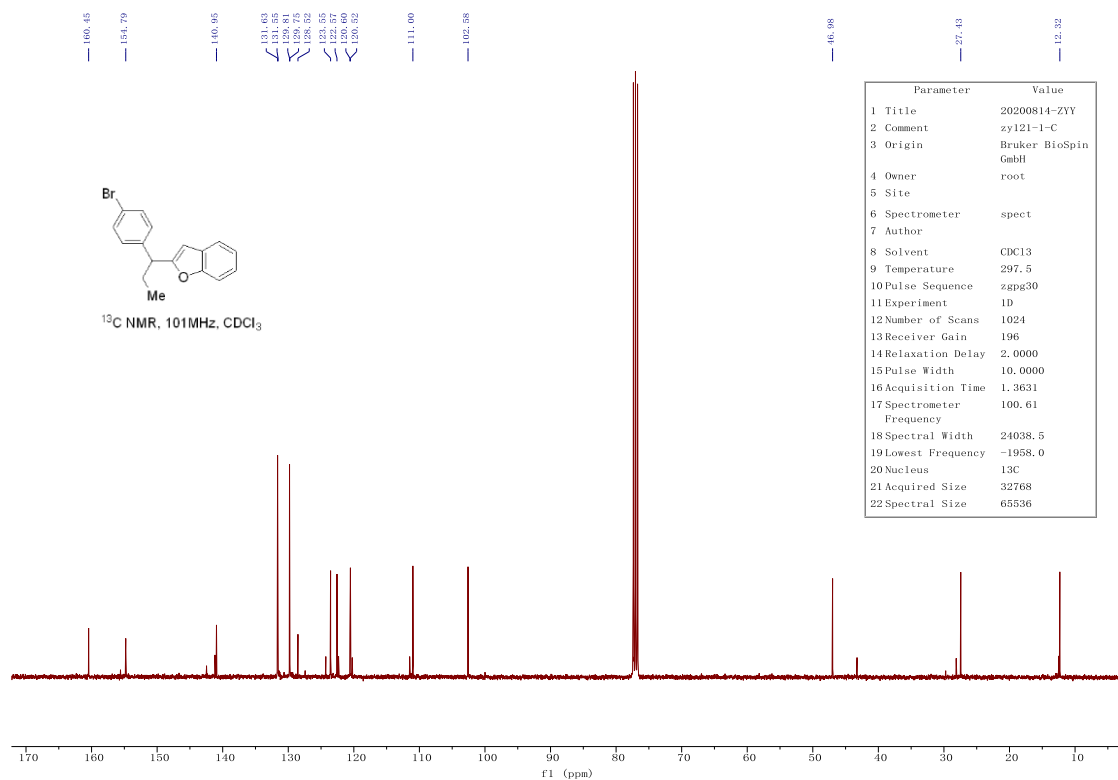
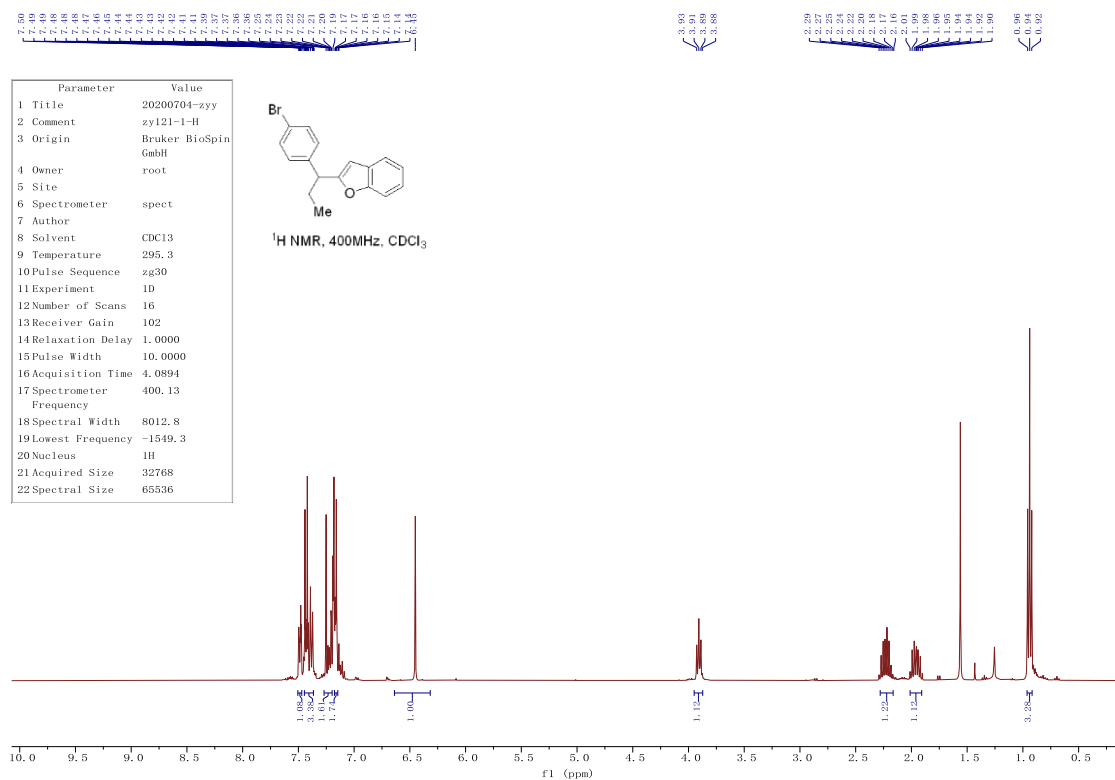
## 2-(1,3-diphenylpropyl)benzofuran (3k):



## 2-(3-bromo-1-(4-bromophenyl)propyl)benzofuran (3l):

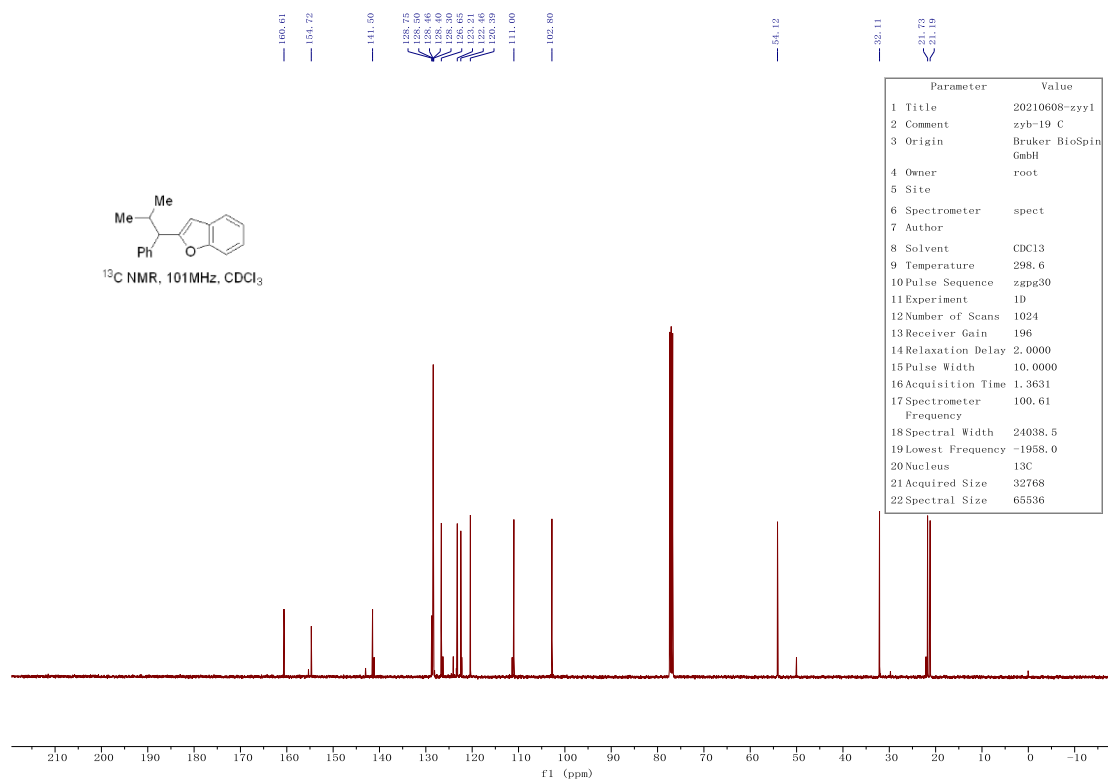
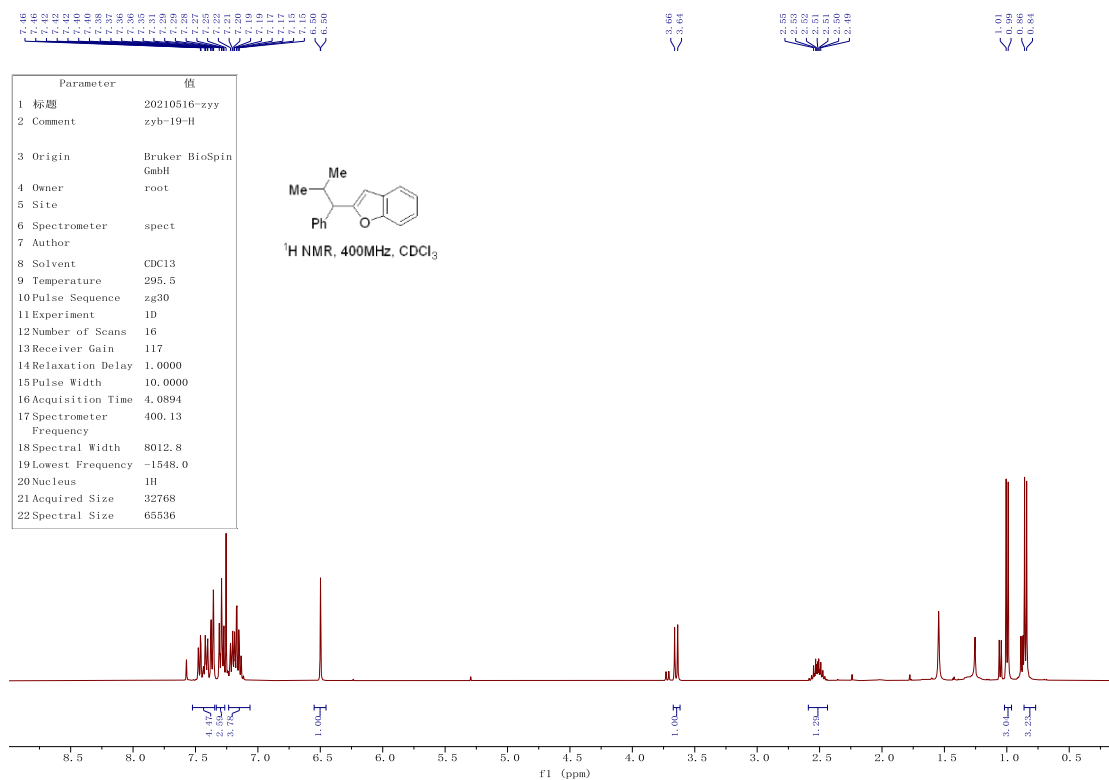


## 2-(1-(4-bromophenyl)propyl)benzofuran (3m):

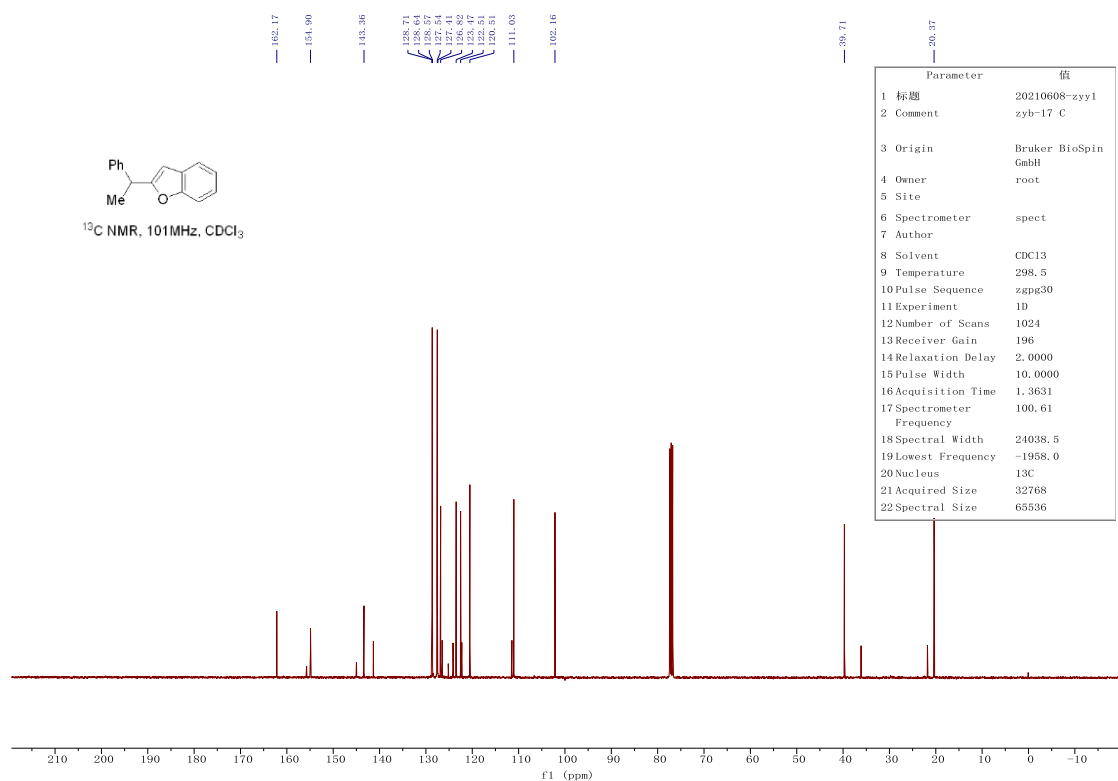
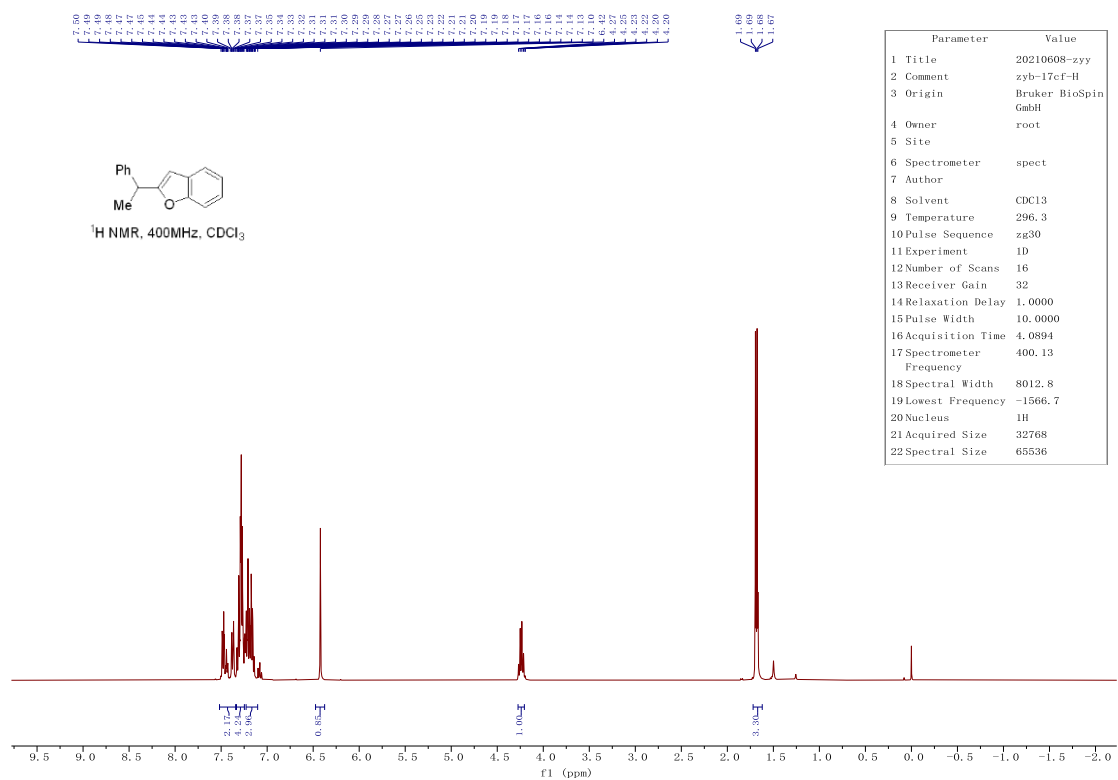




## 2-(2-methyl-1-phenylpropyl)benzofuran (3n):



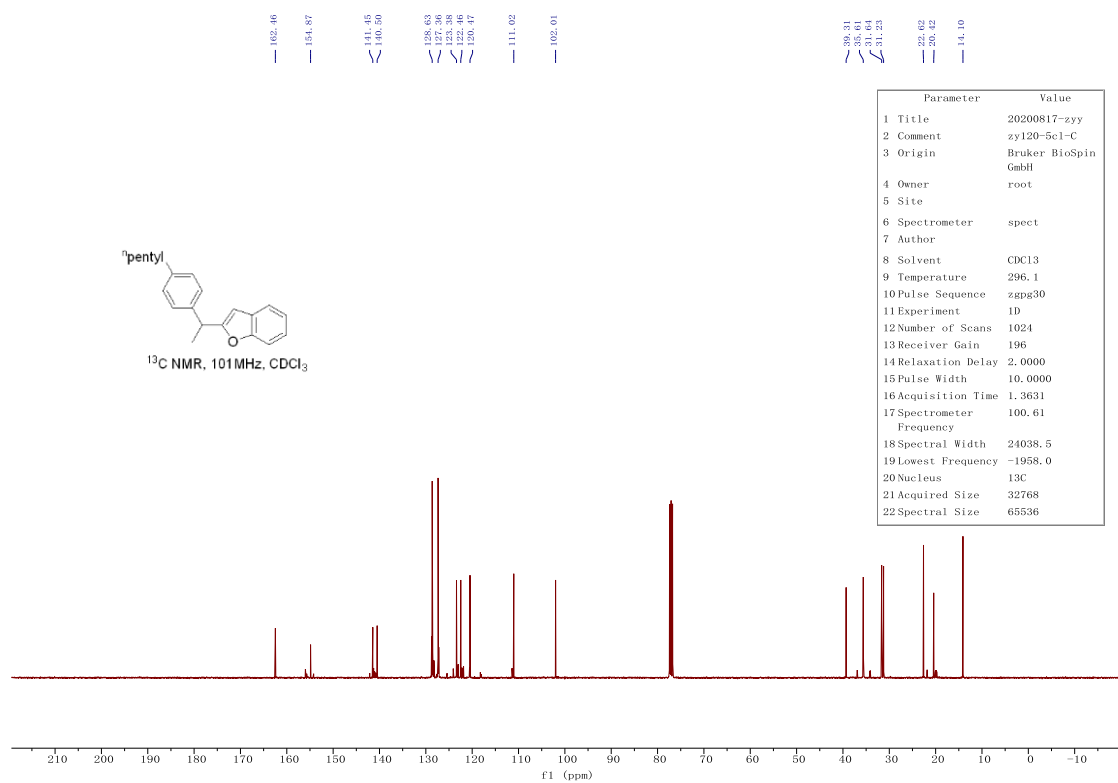
## 2-(1-phenylethyl)benzofran (3o)



Chemical structure: CCCCCc1ccc(cc1)C2(C)c3ccccc3oc2

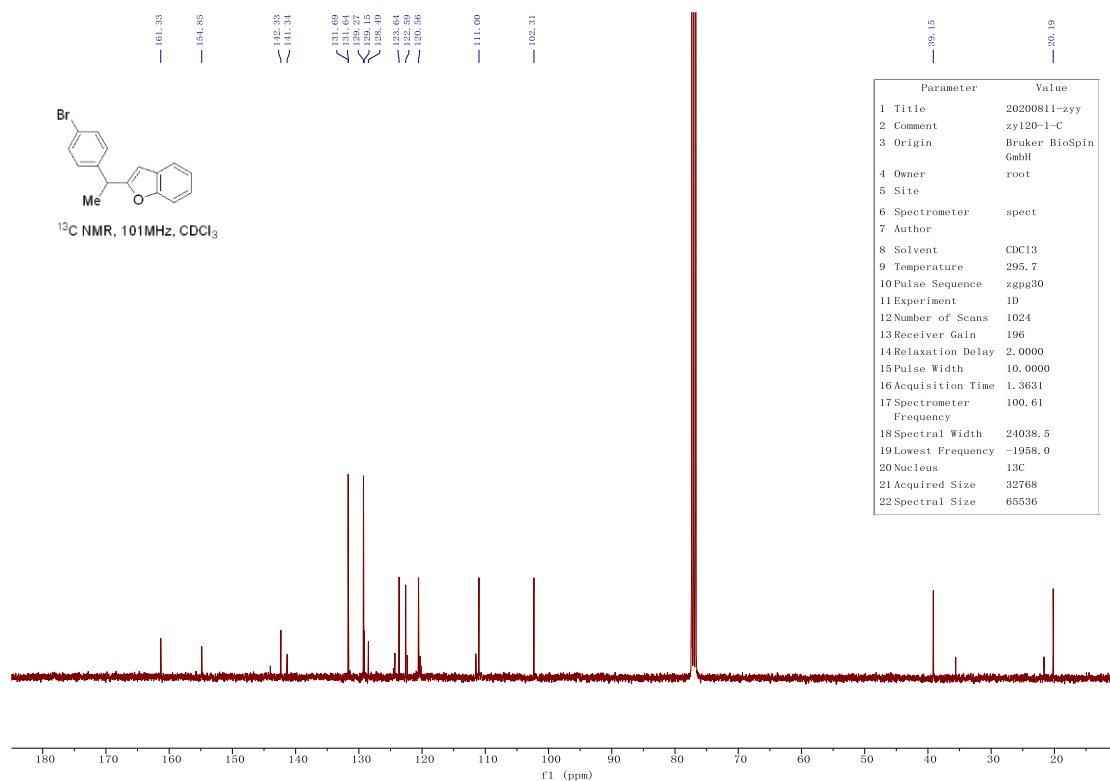
<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) showing peaks and integration values:

Chemical Shift (ppm)	Integration
~7.4	0.92
~7.3	0.86
~7.2	0.92
~6.5	0.9
~4.2	1.00
~2.6	2.12
~1.8	3.20
~1.6	2.18
~1.4	4.18
~1.1	3.40

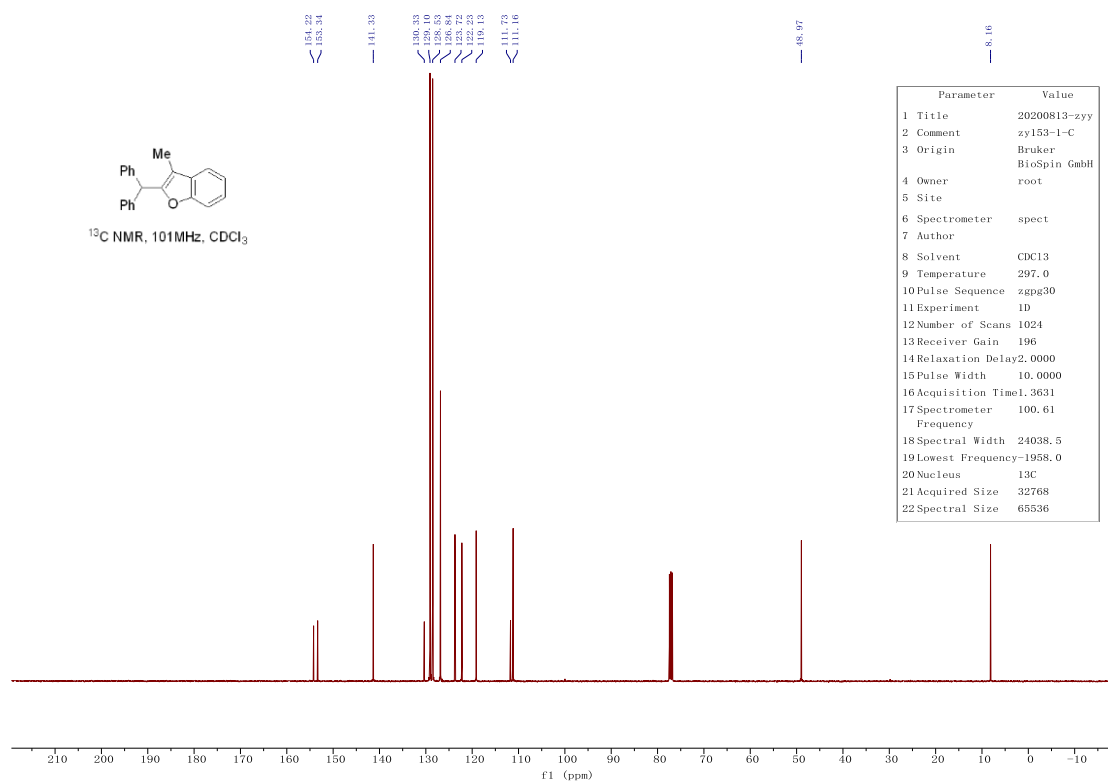
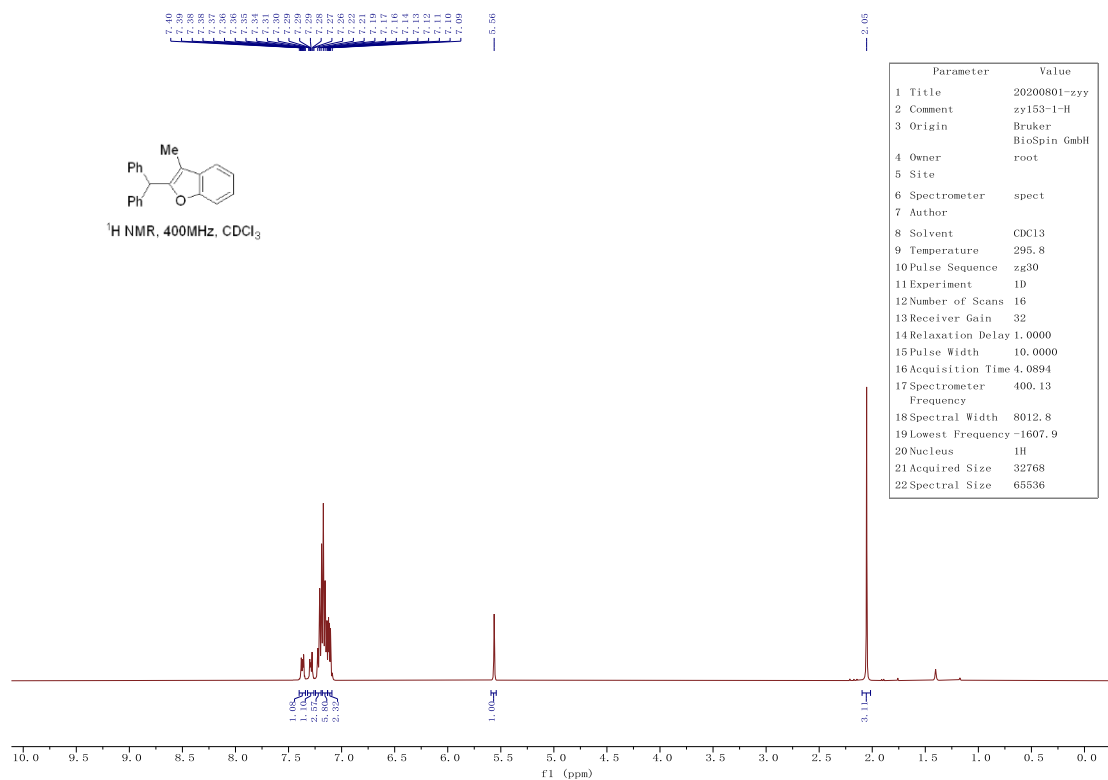


**1H NMR, 400MHz, CDCl<sub>3</sub>**

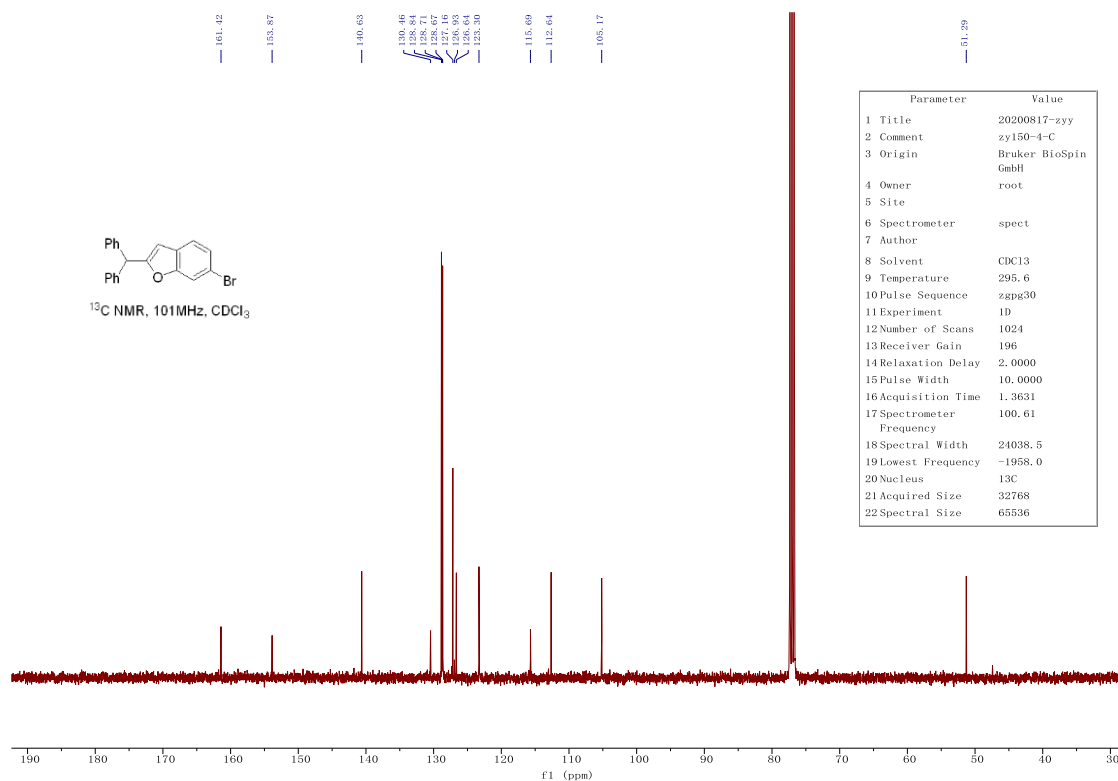
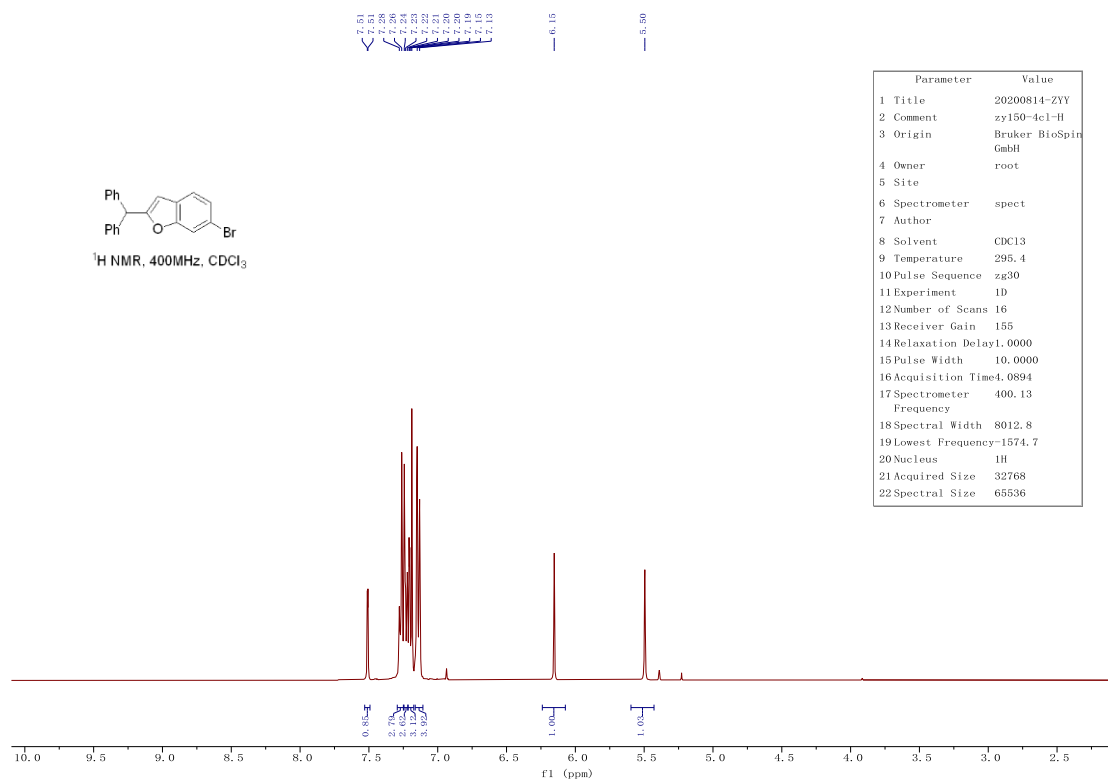
Parameter	Value
1 Title	20200628-zyy
2 Comment	zyl20-1fenli3-4
3 Origin	Broker BioSpin GmbH
4 Owner	root
5 Site	
6 Spectrometer	spect
7 Author	
8 Solvent	CDCl <sub>3</sub>
9 Temperature	295.4
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	16
13 Receiver Gain	117
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	4.0894
17 Spectrometer Frequency	400.13
18 Spectral Width	8012.8
19 Lowest Frequency	-1548.3
20 Nucleus	<sup>1</sup> H
21 Acquired Size	32768
22 Spectral Size	65536



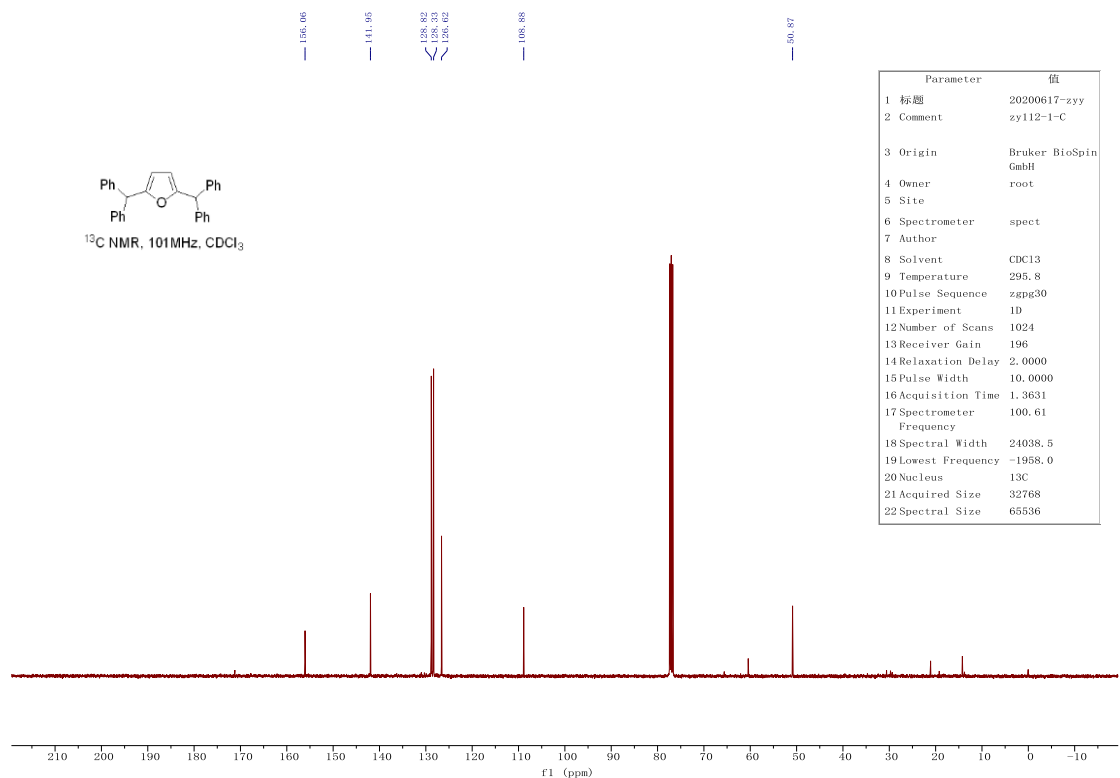
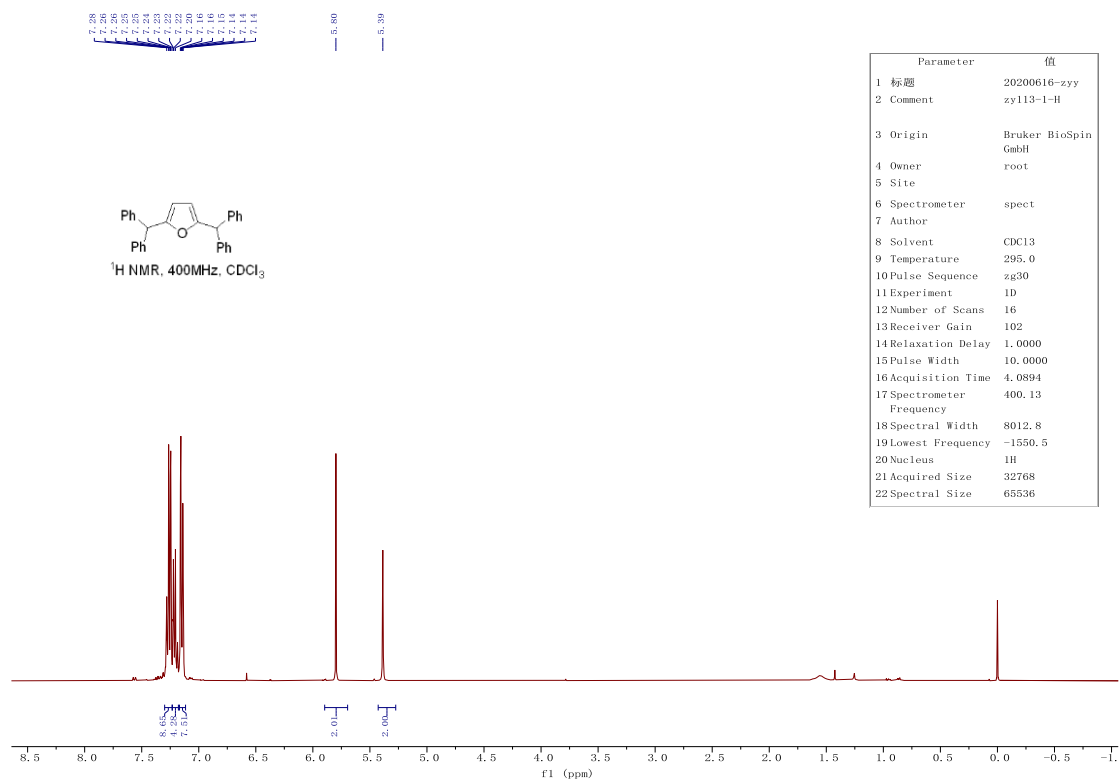
## 2-benzhydryl-3-methylbenzofuran (4a):



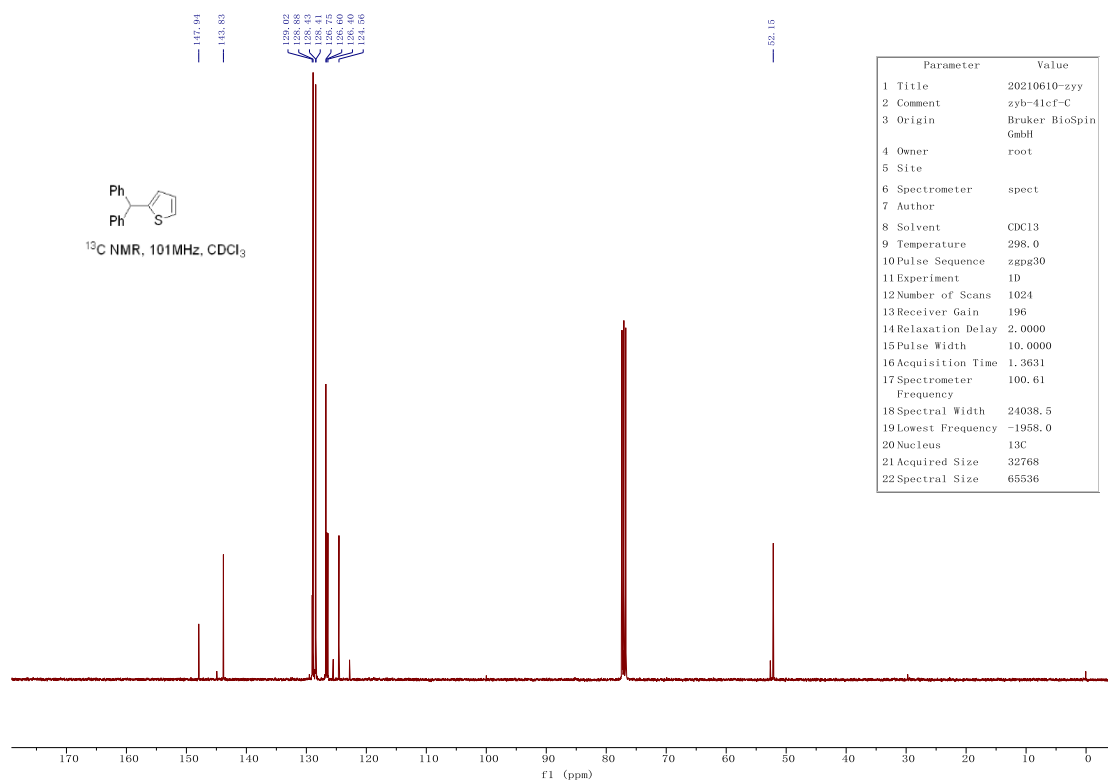
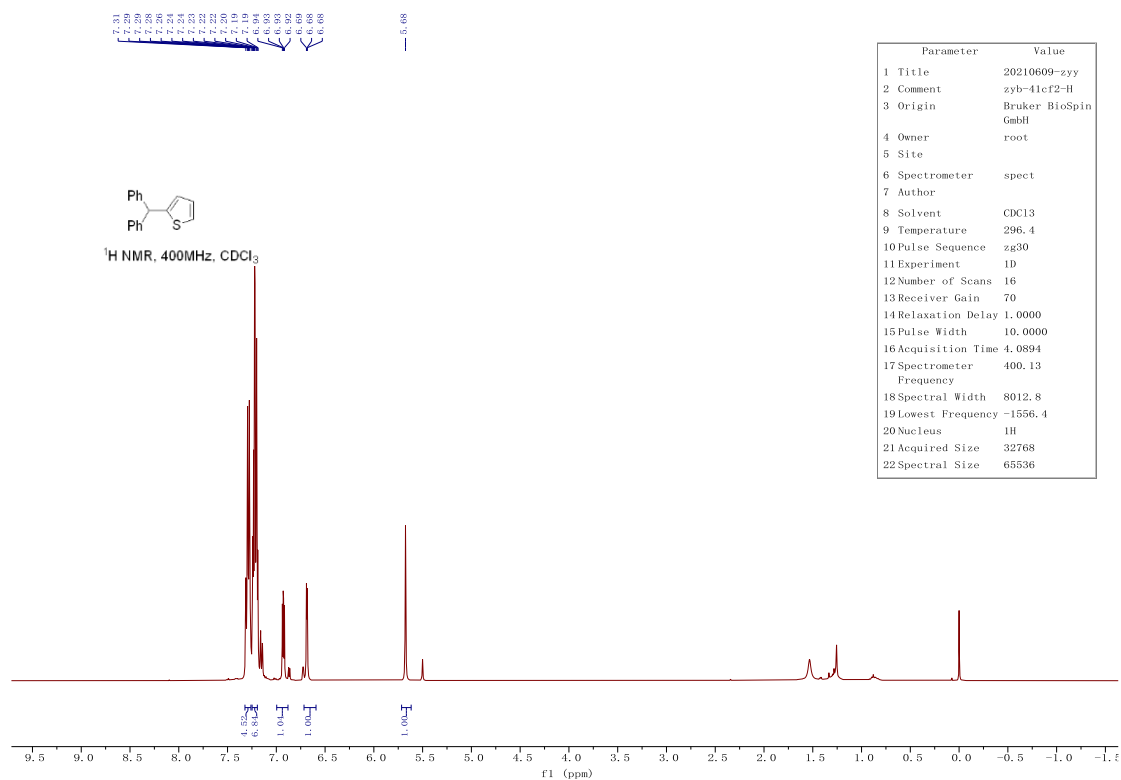
## 2-benzhydryl-6-bromobenzofuran (4b):



## 2, 5-dibenzhydrylfuran (4c):

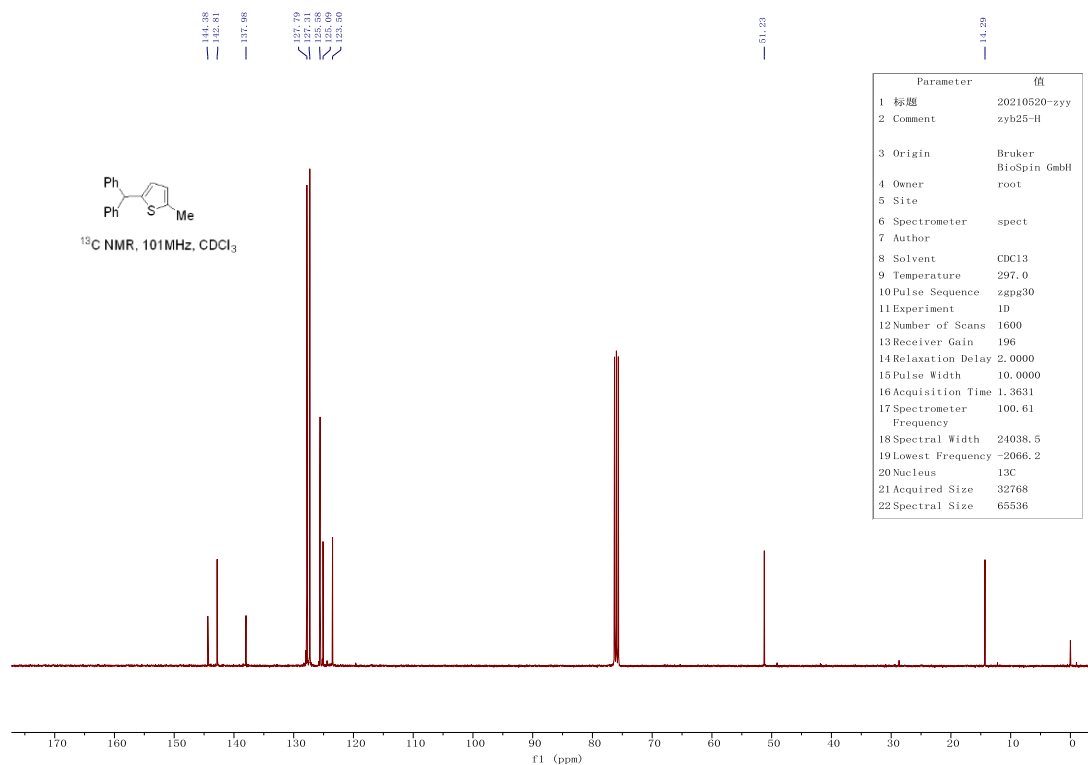
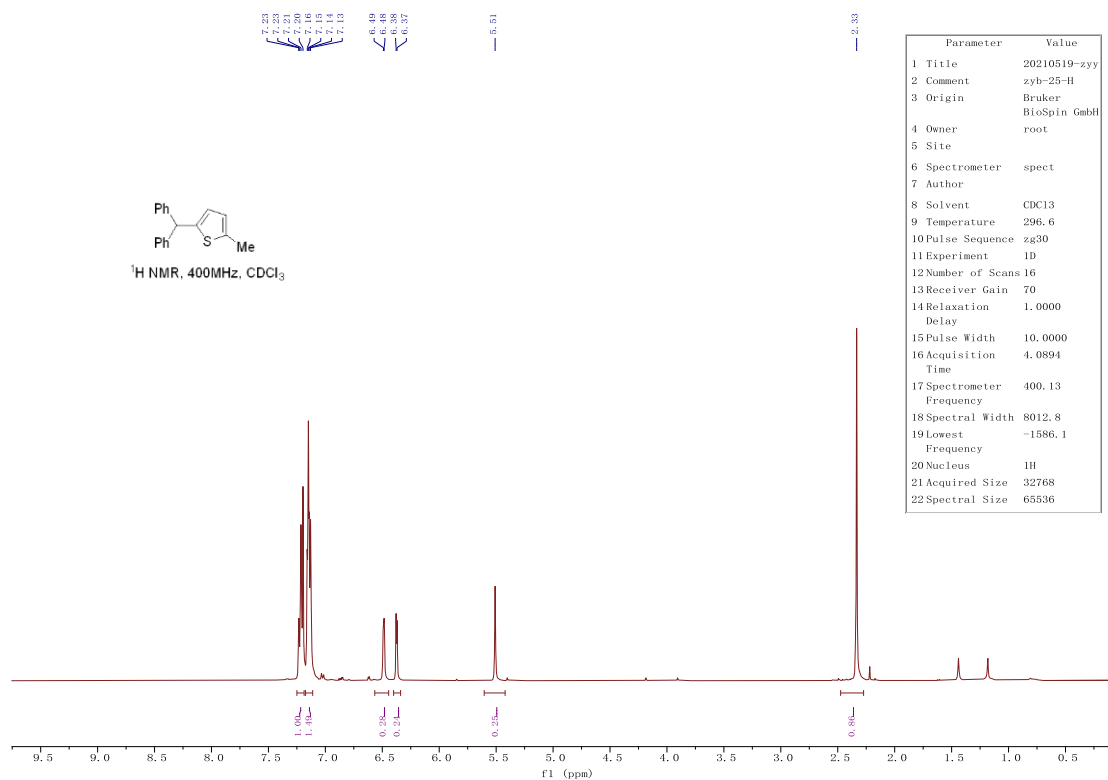


## 2-benzhydrylthiophene (4d):

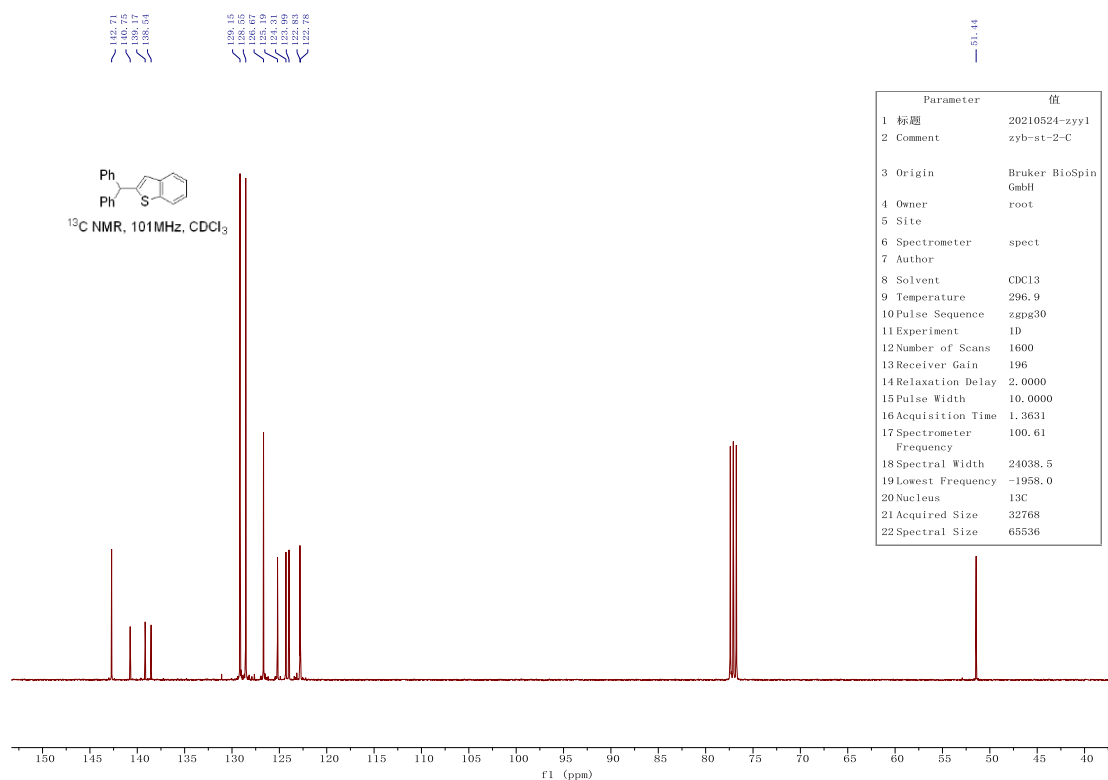
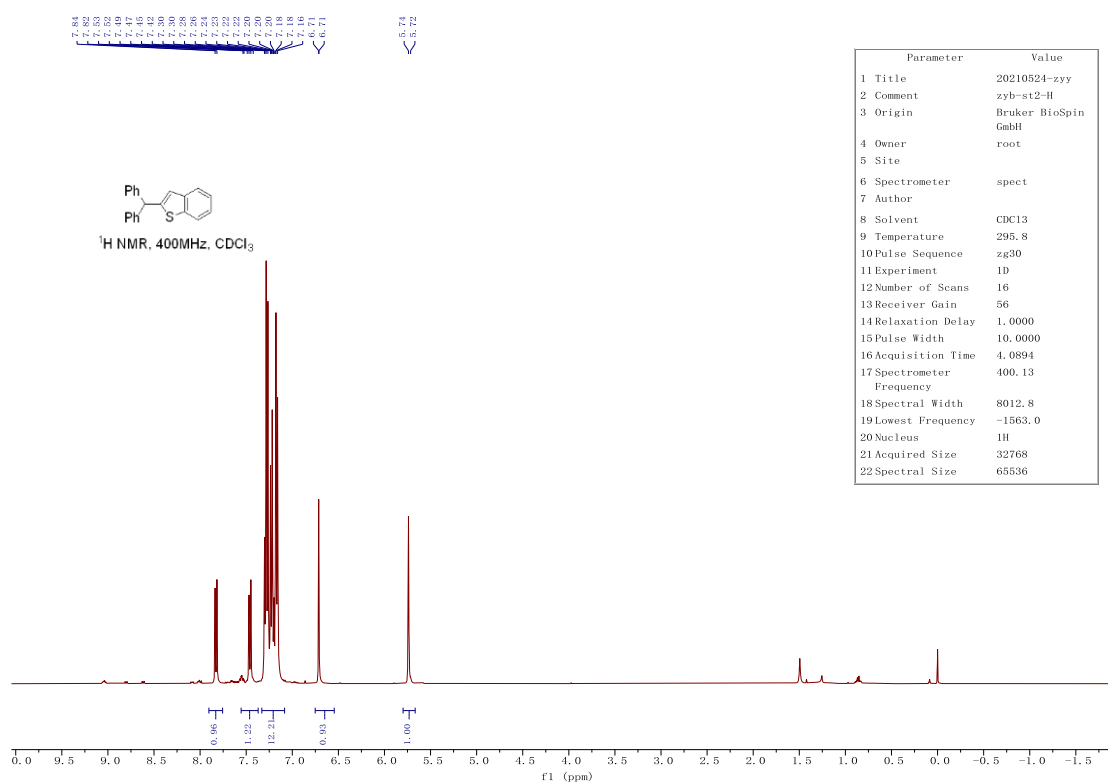




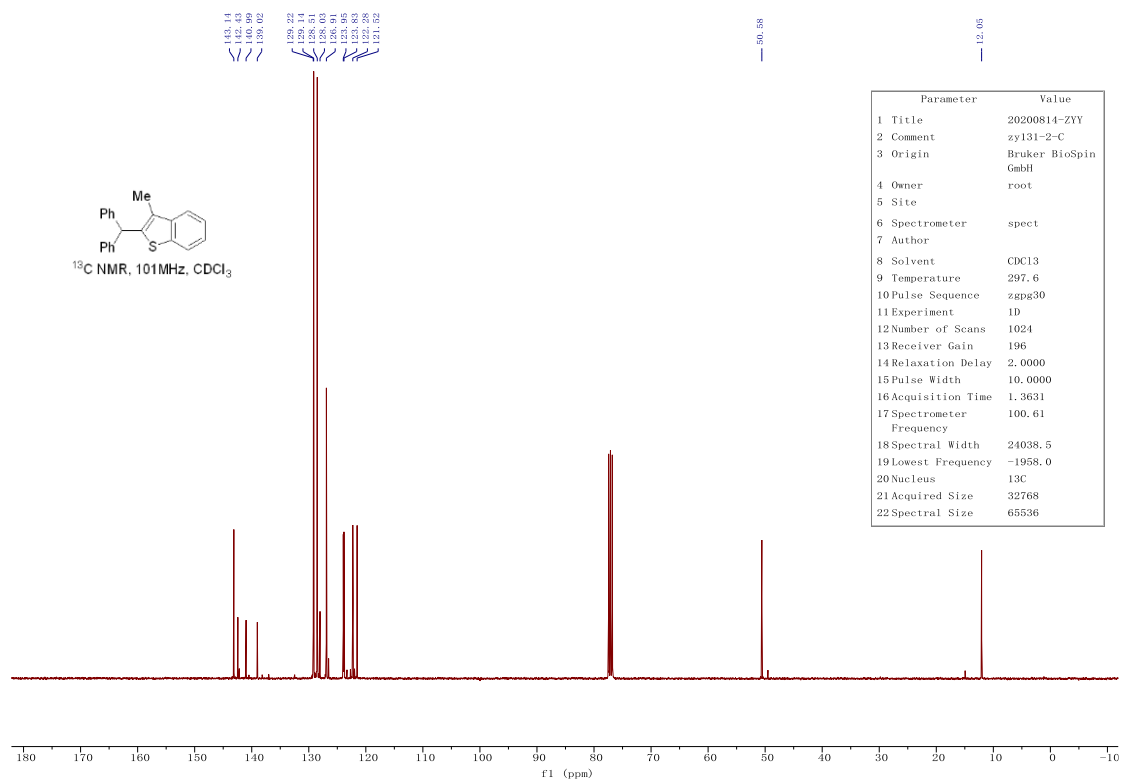
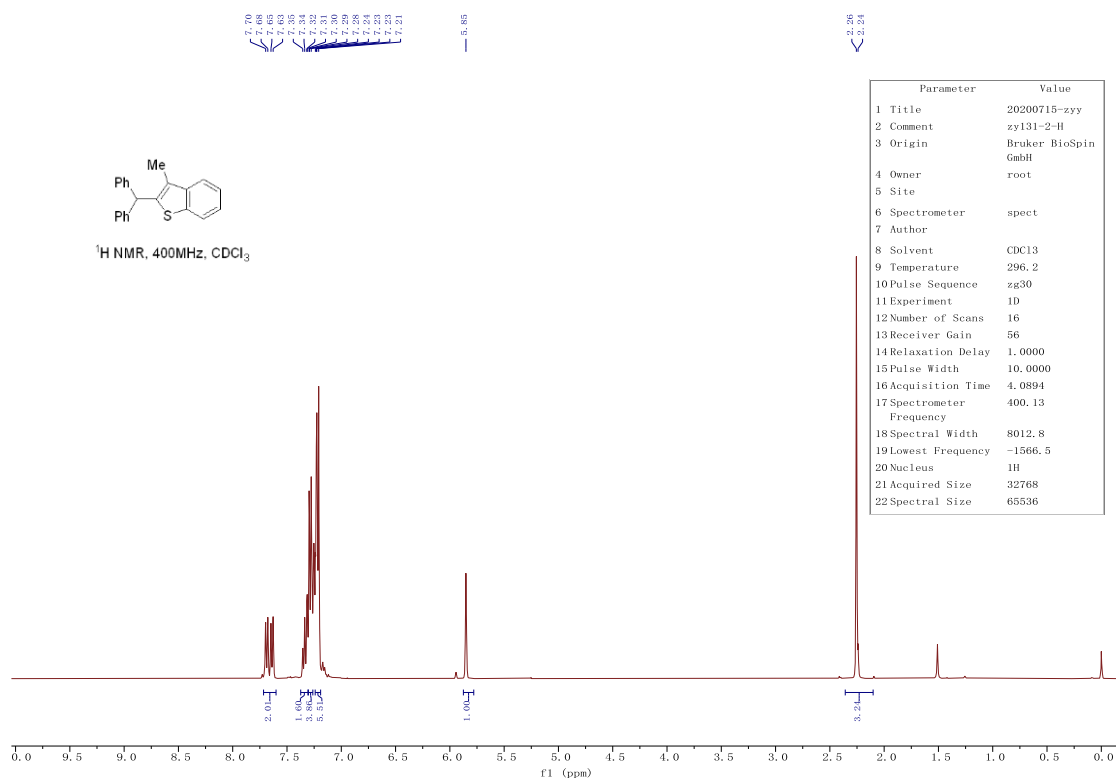
## 2-(diphenylmethyl)-5-methylthiophene (4e):



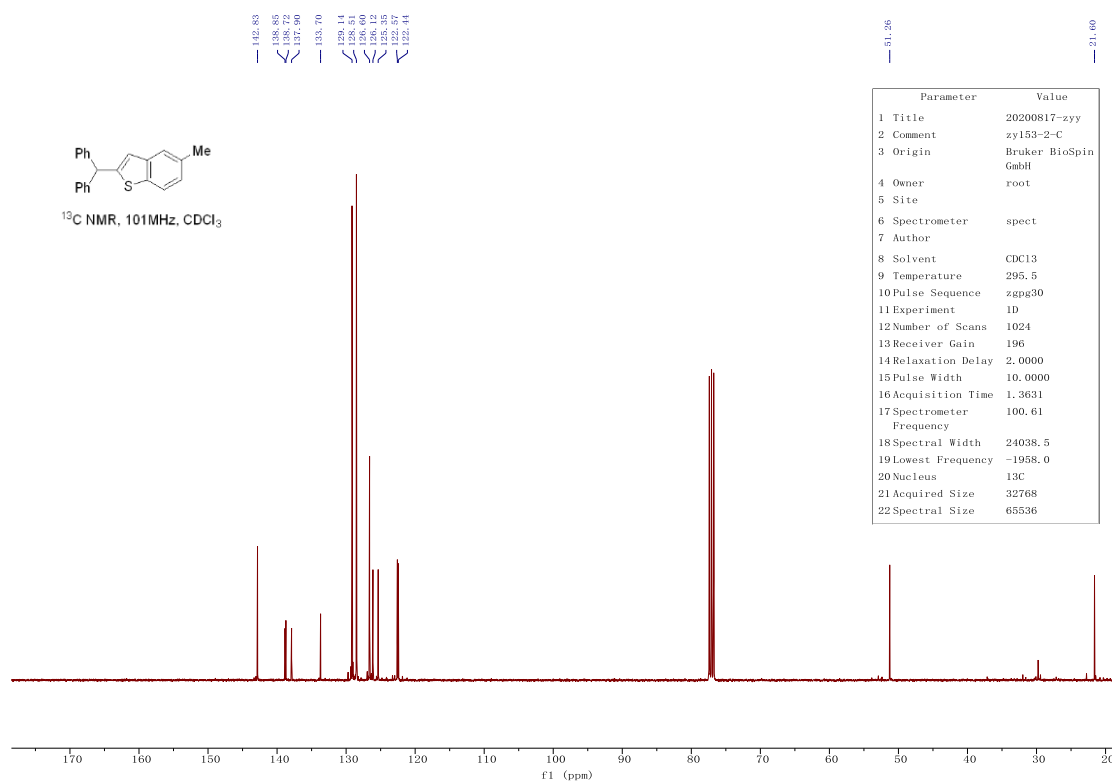
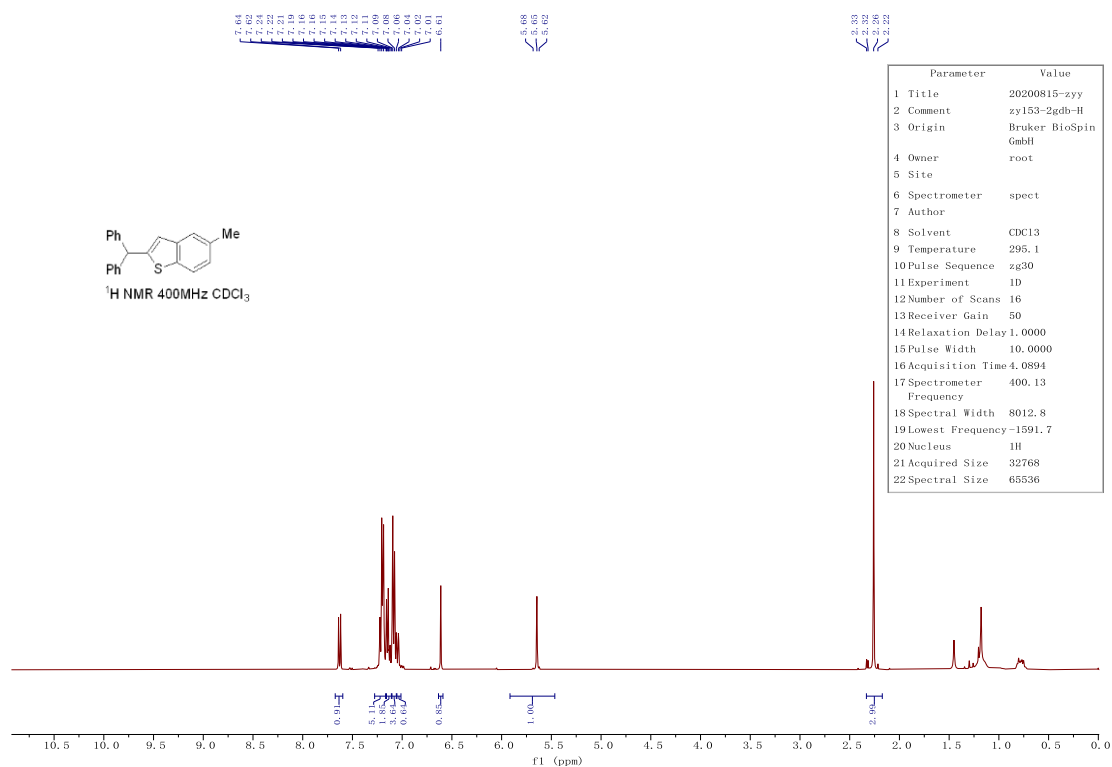
## 2-benzhydrylbenzo[b]thiophene (4f):



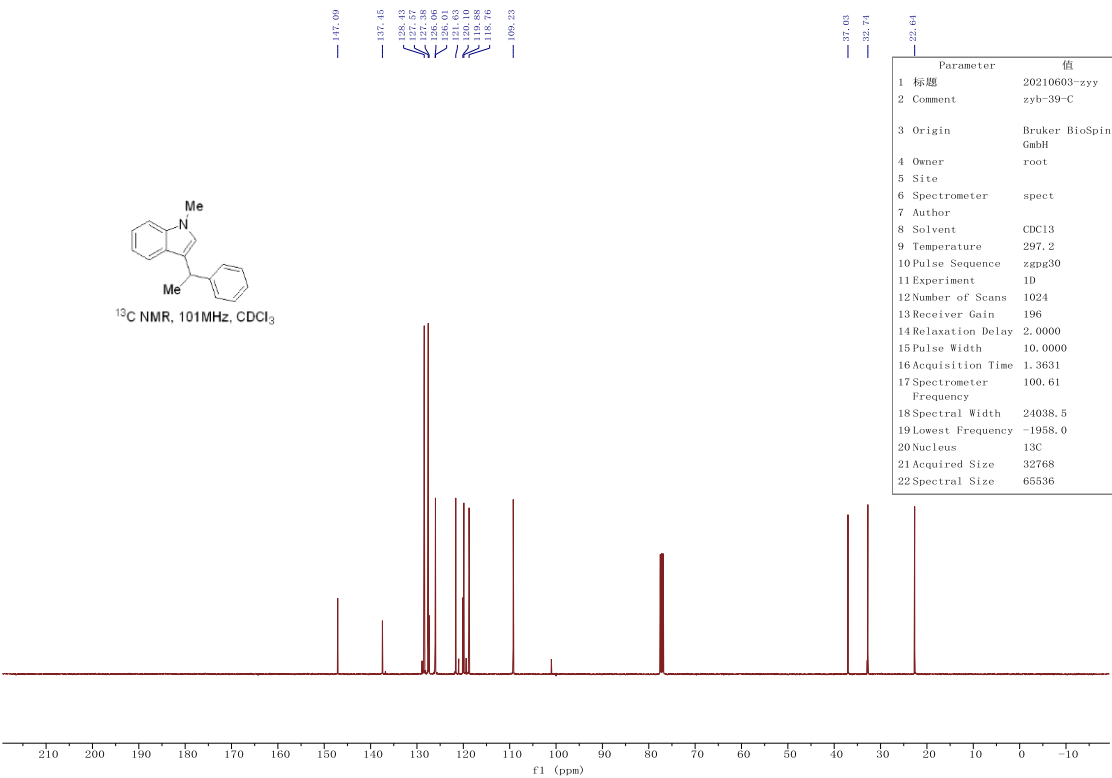
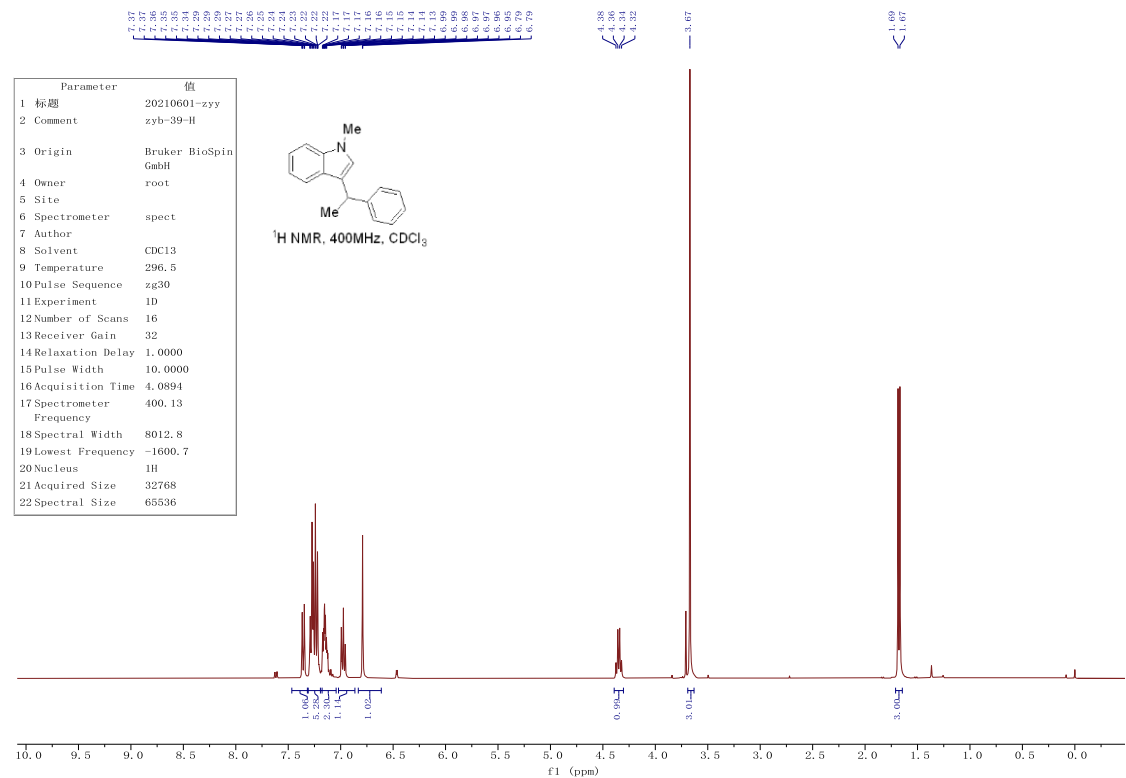
## 2-benzhydryl-3-methylbenzo[b]thiophene (4g):



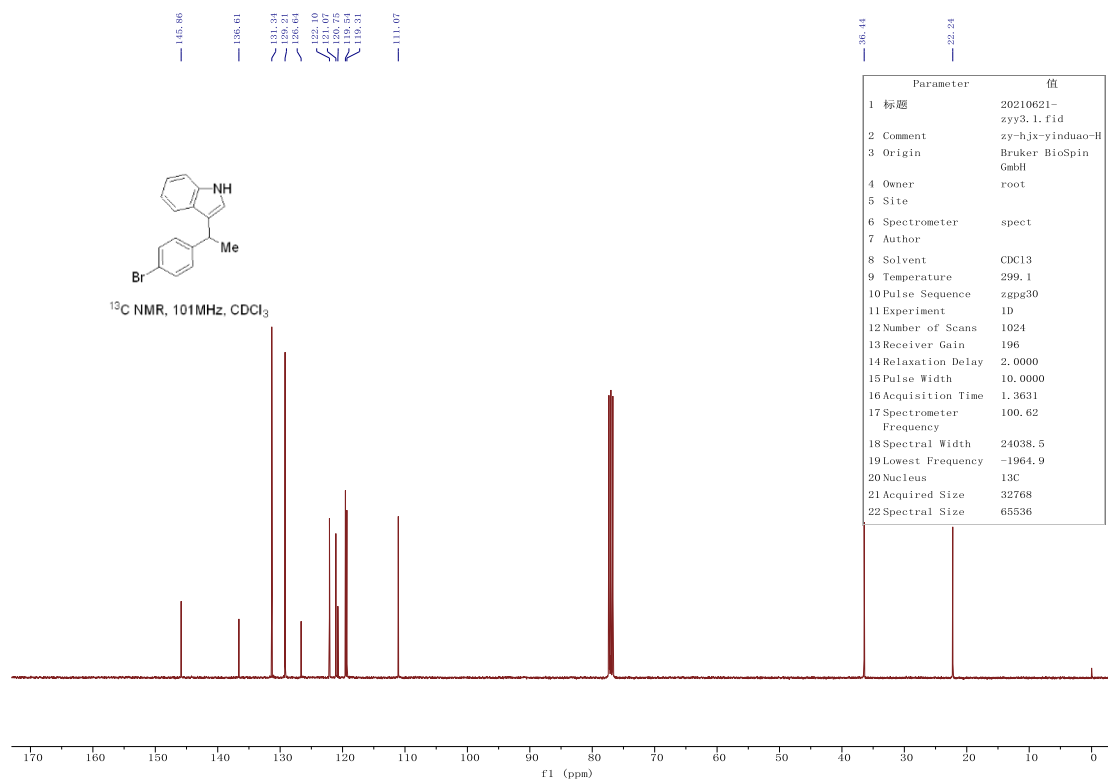
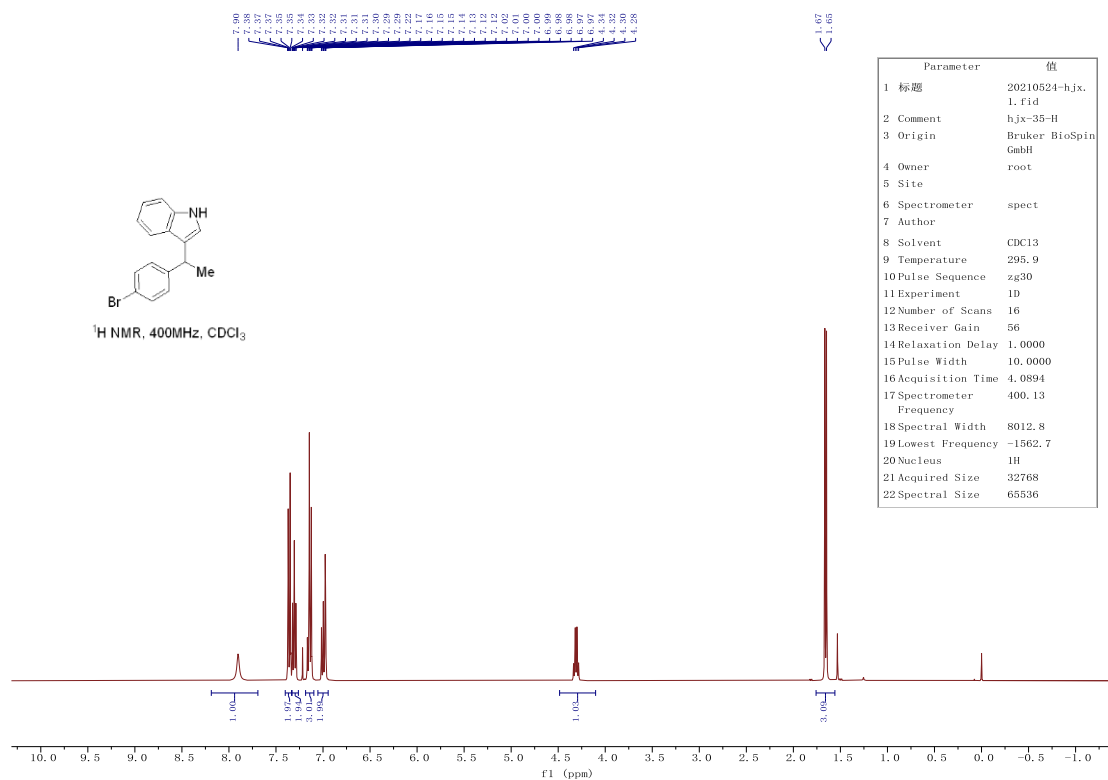
## 2-benzhydryl-5-methylbenzo[b]thiophene (4h):



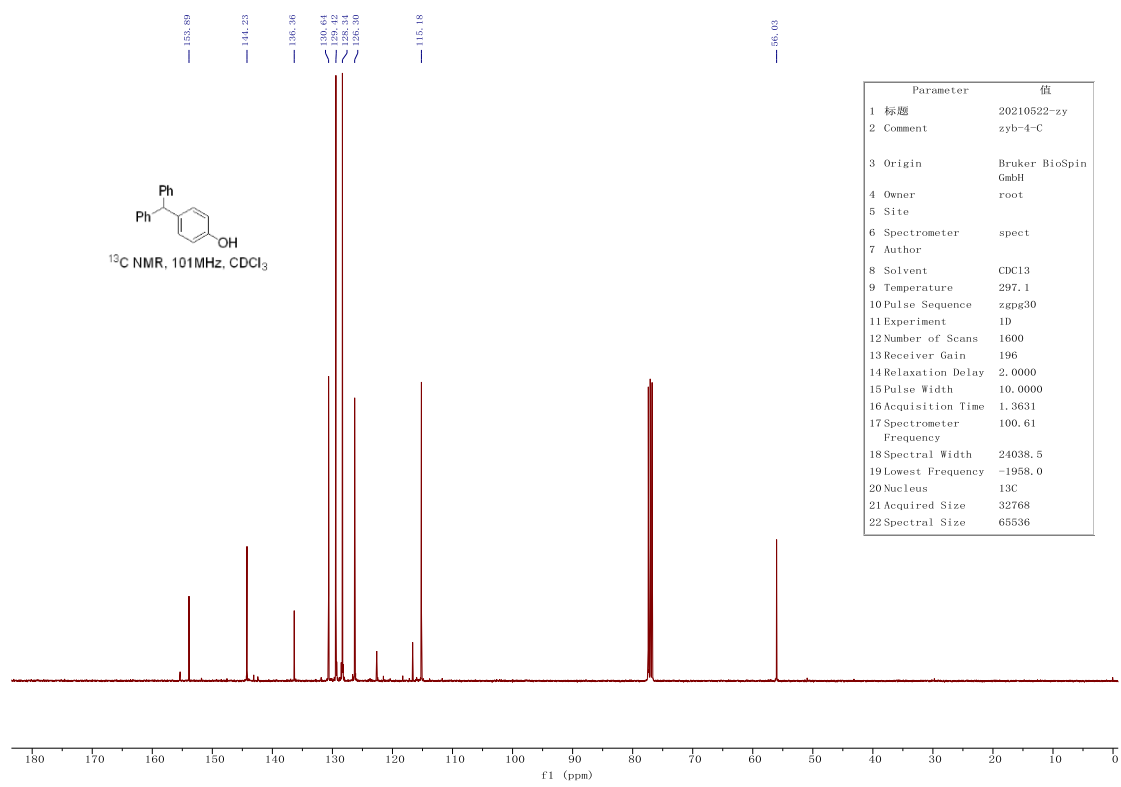
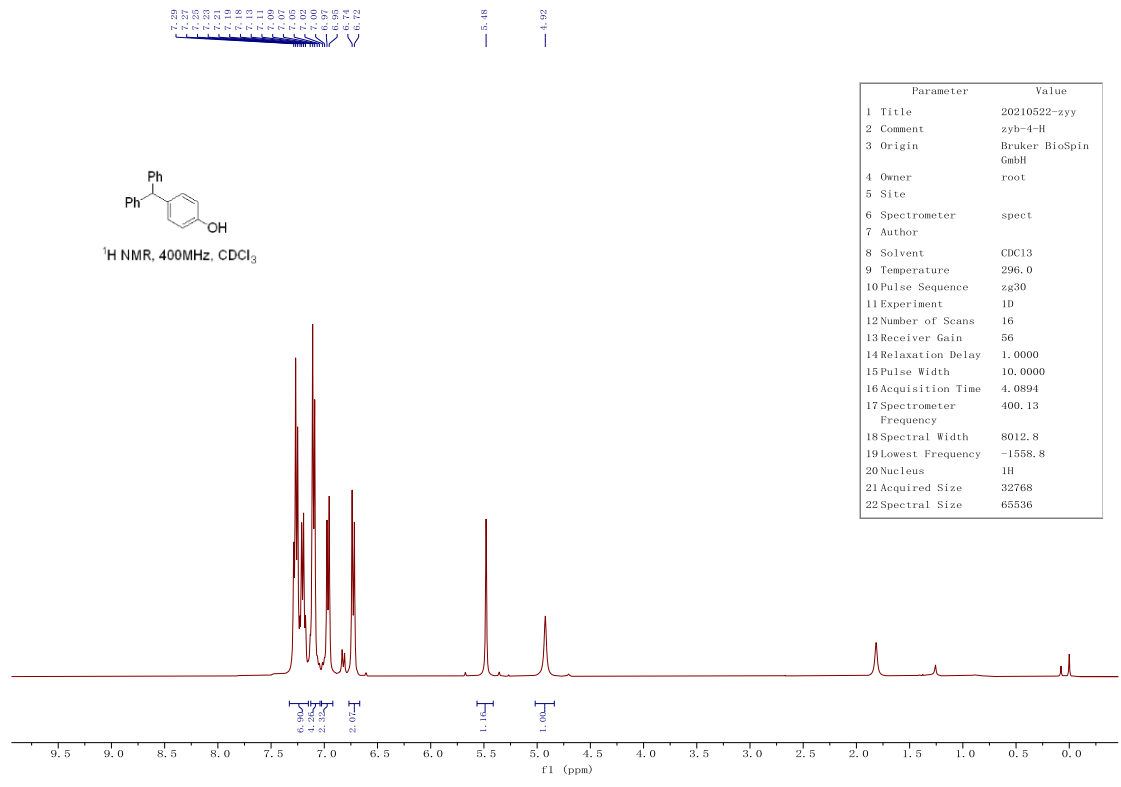
1-methyl-3-(1-phenylethyl)-1H-indole (4i):



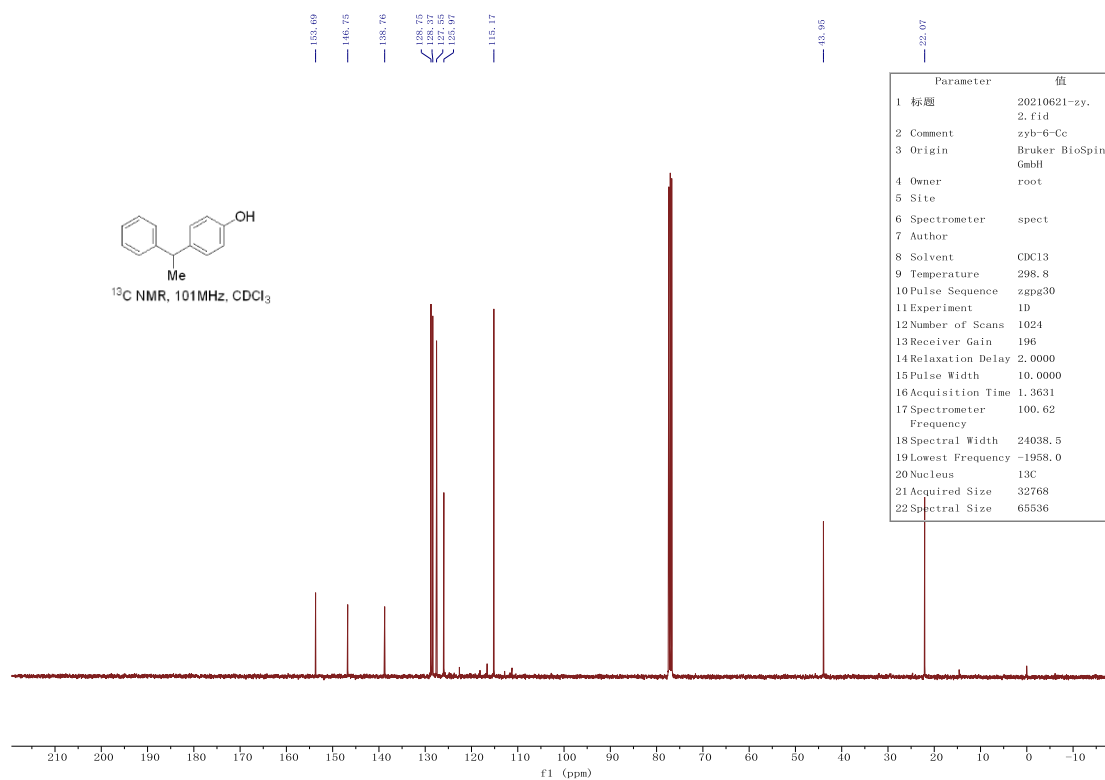
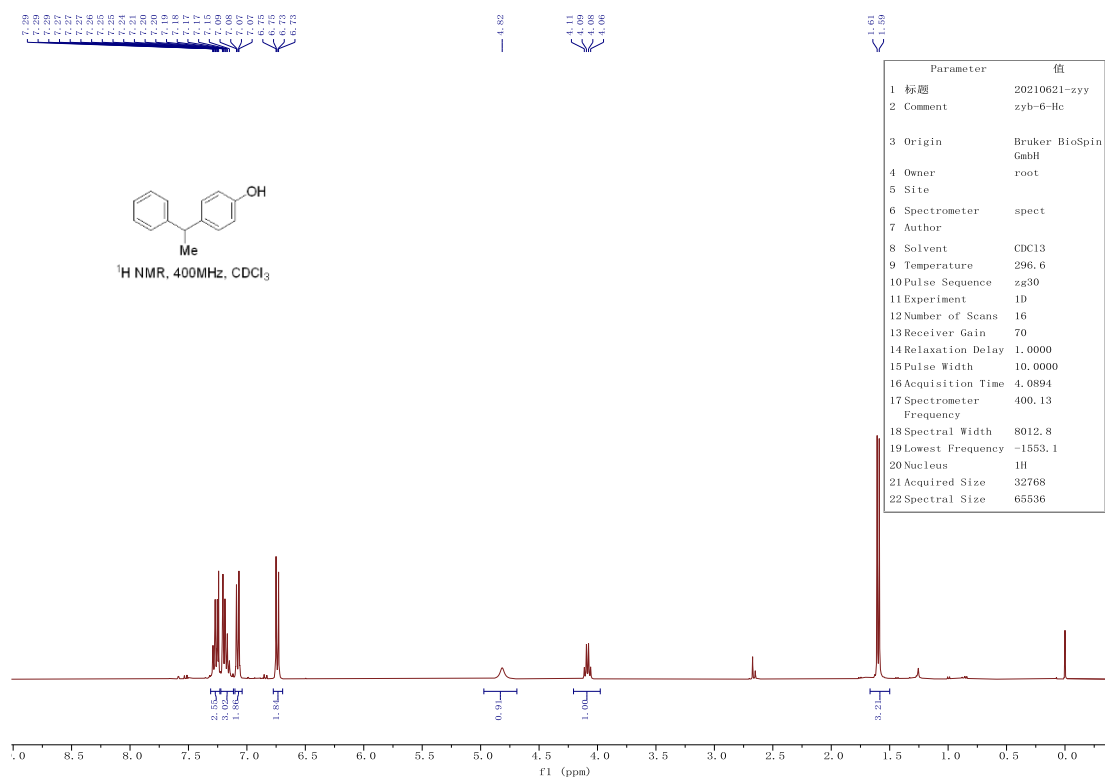
### 3-(1-(4-bromophenyl)ethyl)-1H-indole (4j):



4-benzhydrylpheno (4k):



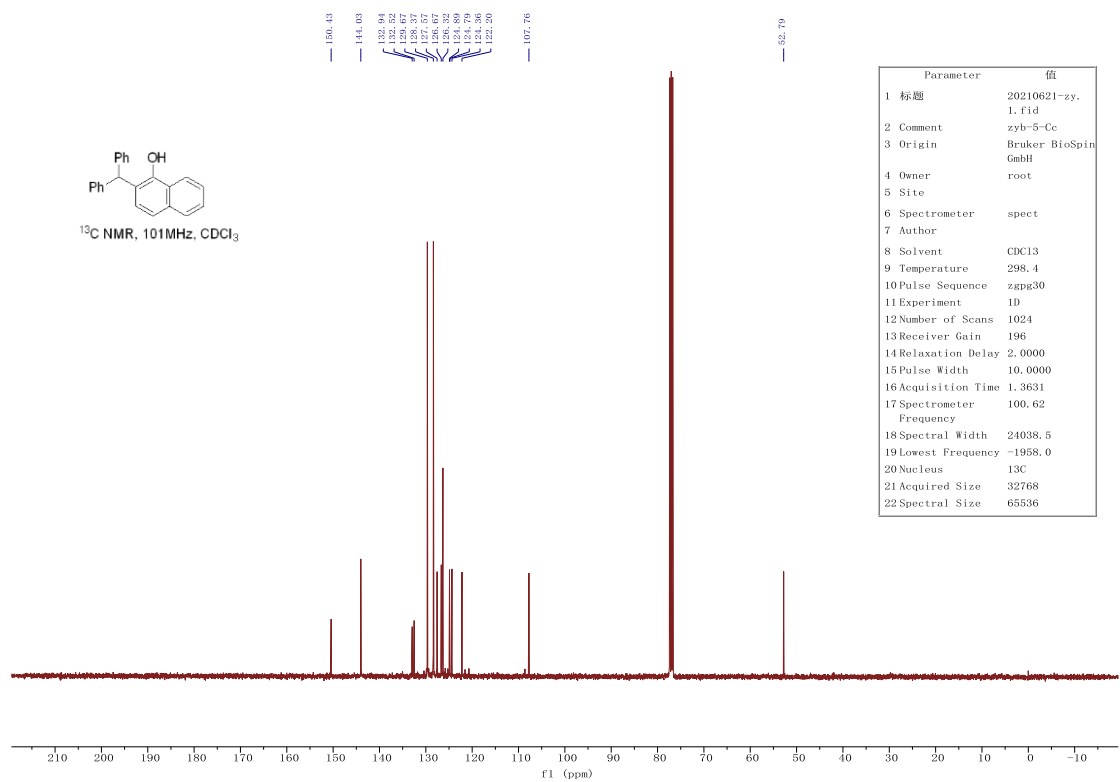
# 4-(1-phenylethyl)phenol (4I):



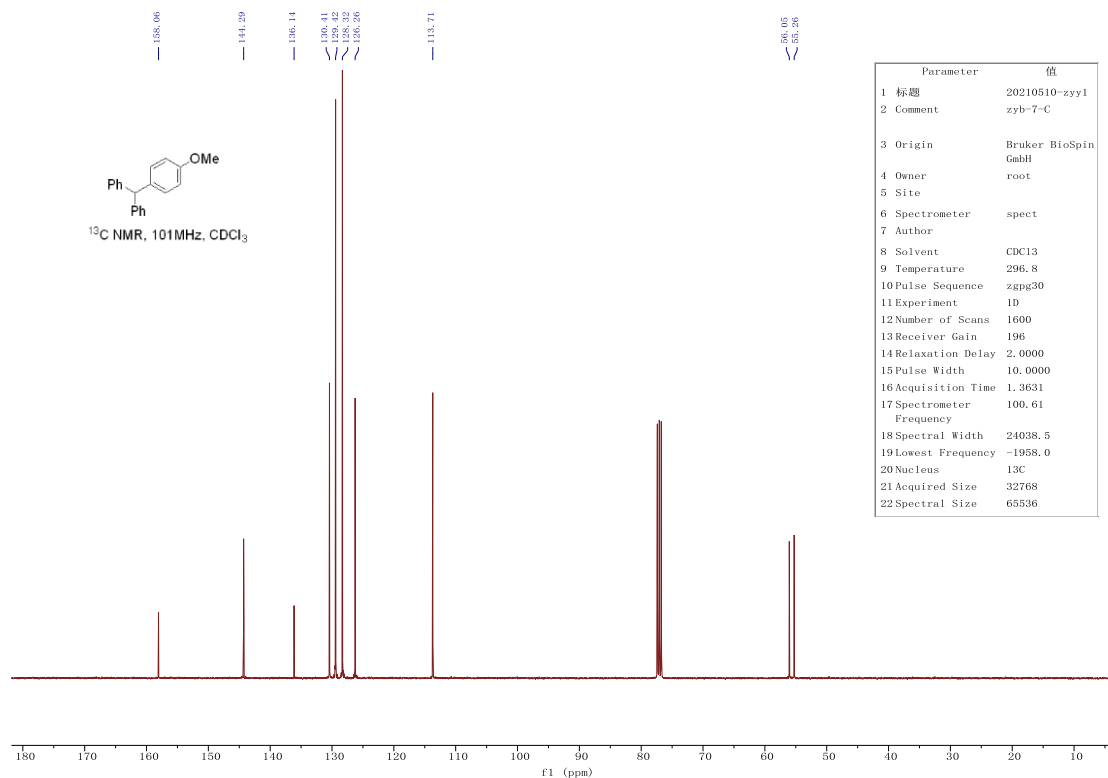
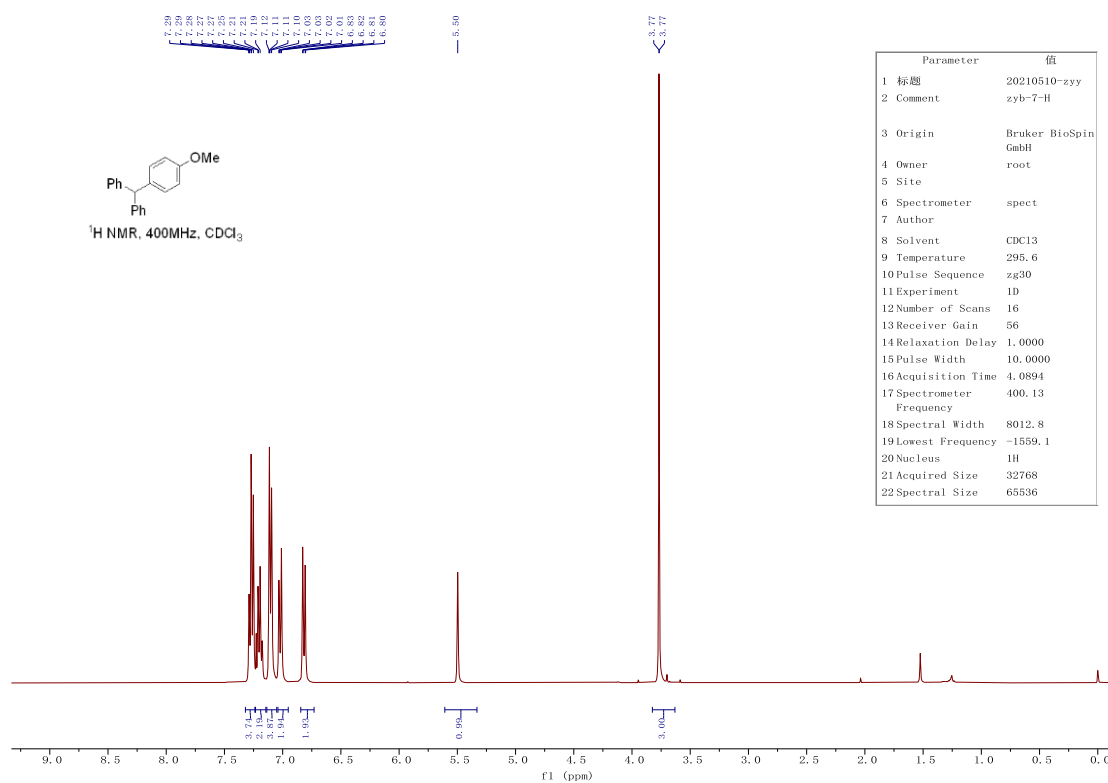


Chemical structure of 1-phenyl-2-naphthol (Ph-Naph-OH) is shown above the  $^1\text{H}$  NMR spectrum. The spectrum was recorded in  $\text{CDCl}_3$  at 400 MHz. The x-axis represents the chemical shift in ppm, ranging from -0.5 to 10.5. The spectrum displays several peaks, with integration values provided below the baseline. The integration values are: 0.88, 0.91, 2.18, 3.63, 1.87, 1.00, and 1.00. The spectrum is labeled with 'f1 (ppm)' on the x-axis.

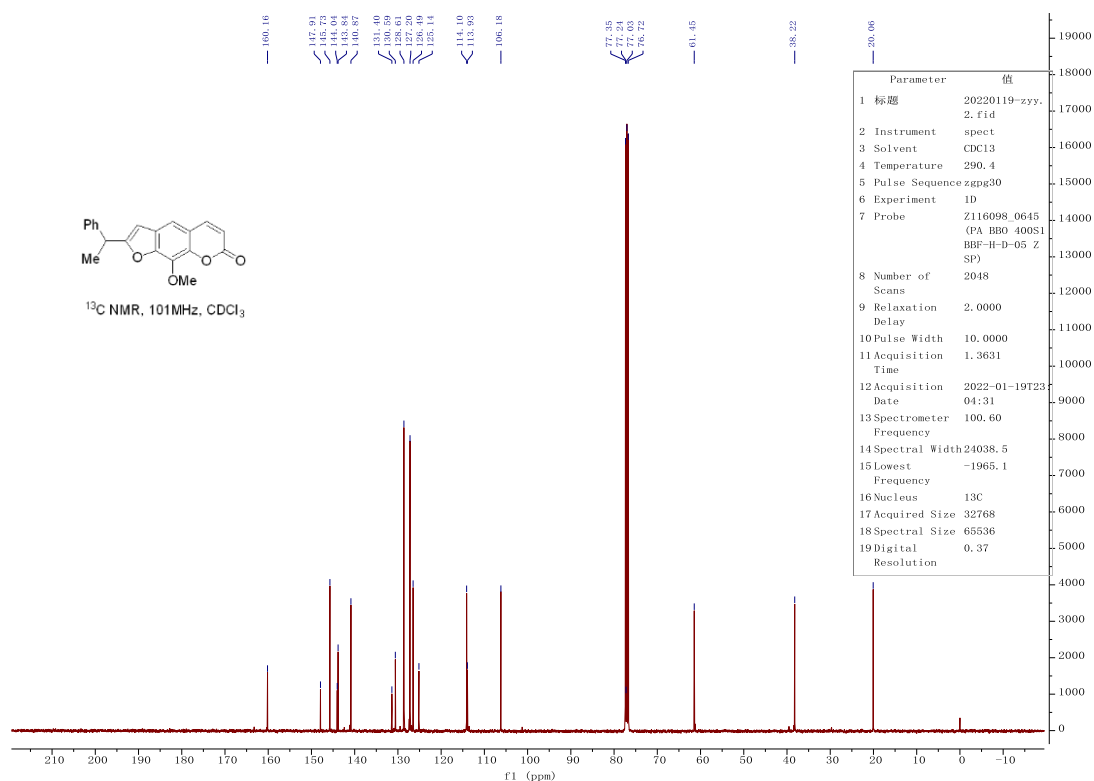
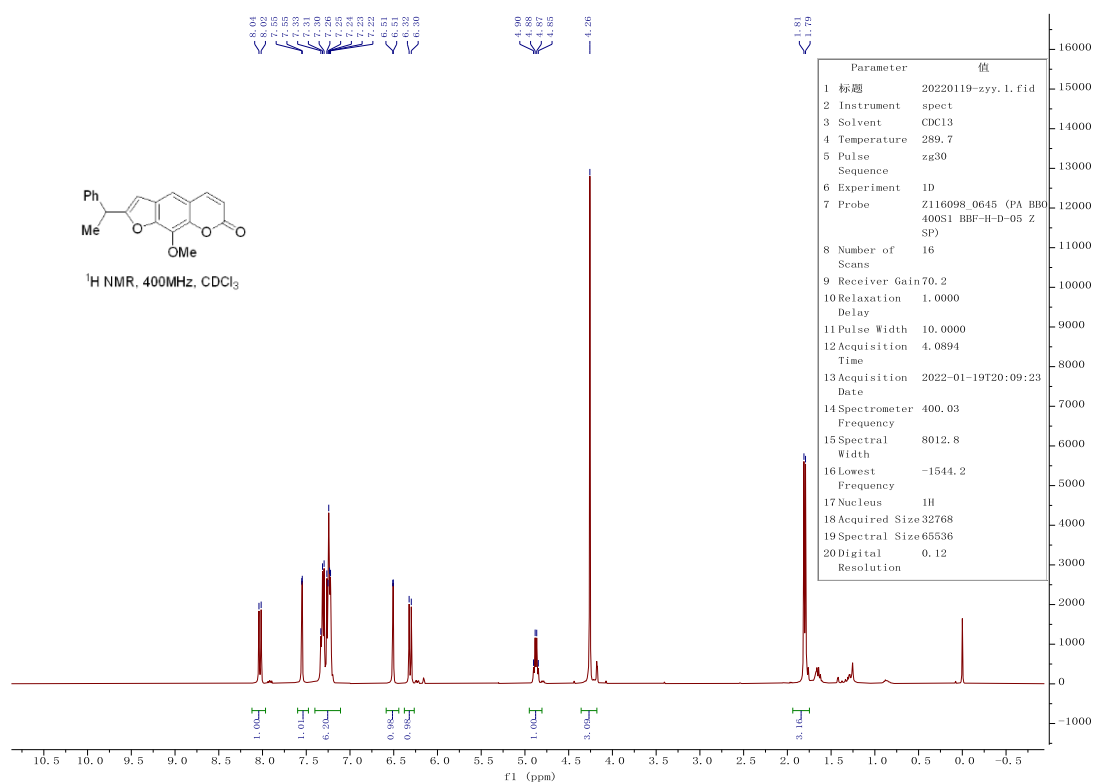
Parameter	Value
1 Title	20210621-zyy
2 Comment	zyy-5-Hc
3 Origin	Bruker BioSpin GmbH
4 Owner	root
5 Site	
6 Spectrometer	spect
7 Author	
8 Solvent	$\text{CDCl}_3$
9 Temperature	296.6
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	16
13 Receiver Gain	102
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	4.0894
17 Spectrometer Frequency	400.13
18 Spectral Width	8012.8
19 Lowest Frequency	-1552.0
20 Nucleus	$^1\text{H}$
21 Acquired Size	32768
22 Spectral Size	65536



# (4-methoxyphenyl)diphenylmethane(4n)



# 9-methoxy-2-(1-phenylethyl)-7H-furo[3,2-g]chromen-7-one (4o):



# 1-phenyl-1,2,3,4-tetrahydronaphthalene (4p)

