

## Supporting Information

# Radical heteroarylation of unactivated remote C(sp<sup>3</sup>)–H bonds via intramolecular heteroaryl migration

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## 1. General experimental details

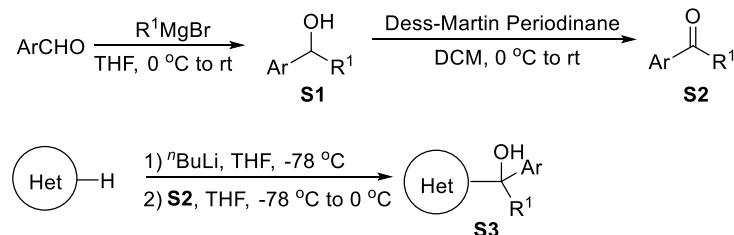
Commercially available reagents were used without further purification. THF was distilled from sodium. Infrared (FT-IR) spectra were recorded on a BRUKER VERTEX 70,  $\nu_{\text{max}}$  in  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  spectra were recorded on a BRUKER AVANCE III HD (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as internal standard ( $\text{CDCl}_3$ :  $\delta$  7.26). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, q = quadruplet, br = broad, m = multiplet), coupling constants (Hz) and integration.  $^{13}\text{C-NMR}$  spectra were recorded on a BRUKER AVANCE III HD (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ( $\text{CDCl}_3$ :  $\delta$  77.00).  $^{19}\text{F-NMR}$  spectra were recorded on a BRUKER AVANCE III HD (376 MHz) spectrometer. Mass spectra were measured with an Agilent Technologies 6120 Quadrupole LC/MS. High resolution mass spectrometry (HRMS) were measured with a GCT Premier<sup>TM</sup> and BRUKER micrOTF-Q III. Melting points were measured using INESA WRR and values are uncorrected.

## 2. General procedures for synthesis of starting materials

The starting materials **1a-1v**, **1z-1ai** were prepared according to **General Procedure A**.

The starting materials **1w-1y** were prepared according to **General Procedure B**.

### General Procedure A

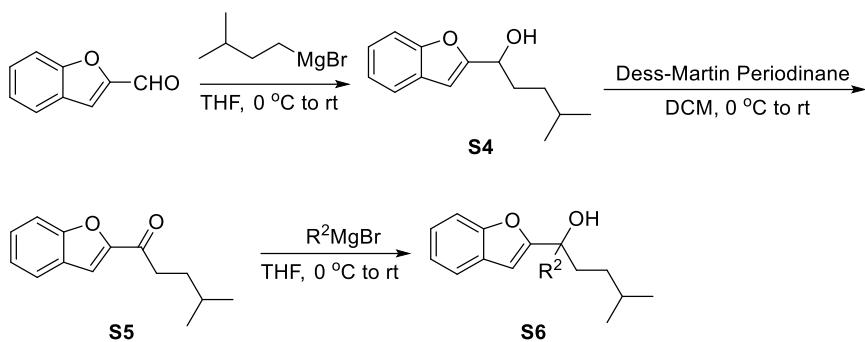


To a solution of freshly prepared Grignard reagent (1.2 equiv.) in THF was added a solution of aryl formaldehyde (1.0 equiv.) in THF dropwise at 0 °C under  $\text{N}_2$ . After ambient temperature was reached, the reaction mixture was stirred for 2 h, and quenched with saturated  $\text{NH}_4\text{Cl}$  solution. The resulting mixture was extracted with EtOAc. The combined organic extracts were washed by brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, concentrate, and purified by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether) to give **S1**.

Dess-Martin periodinane (1.4 equiv.) was added to a solution of **S1** (1.0 equiv.) in DCM at 0 °C. The reaction was stirred in ice bath overnight, during which time the reaction was warmed up to room temperature. The reaction was quenched with saturated  $\text{NaHCO}_3$  solution and filtered with celite. The resulting mixture was extracted with DCM. The combined organic extracts were washed by brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, concentrated, and purified by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether) to give **S2**.

To a solution of heteroaryls (1.2 equiv.) in THF was slowly added  $^n\text{BuLi}$  (1.2 equiv., 2.5 M in THF) at -78 °C under  $\text{N}_2$ , then the mixture was stirred for 1 h. A solution of **S2** (1.0 equiv) in THF was added to the mixture dropwise at -78 °C. The mixture was gradually warmed to 0 °C. After the reaction was complete, the mixture was quenched with saturated  $\text{NH}_4\text{Cl}$  solution. The resulting mixture was extracted with EtOAc. The combined organic extracts were washed by brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, concentrated, and purified by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether) to give **S3**.

### General Procedure B



To a solution of freshly prepared Grignard reagent (1.2 equiv.) in THF was added a solution of 2-benzofurancarboxaldehyde (1.0 equiv.) in THF dropwise at 0 °C under  $\text{N}_2$ . After ambient temperature was reached, the reaction mixture was stirred for 2 h, and quenched with saturated  $\text{NH}_4\text{Cl}$  solution. The resulting mixture was extracted with EtOAc. The combined organic extracts were washed by brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, concentrate, and purified by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether) to give **S4**.

Dess-Martin periodinane (1.4 equiv.) was added to a solution of **S4** (1.0 equiv.) in DCM at 0 °C. The reaction was stirred in the ice bath overnight, during which time the reaction warmed up to room temperature. The reaction was quenched with saturated  $\text{NaHCO}_3$  solution and filtered with celite. The resulting mixture was extracted with DCM. The combined organic extracts were washed by brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, concentrated, and purified by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether) to give **S5**.

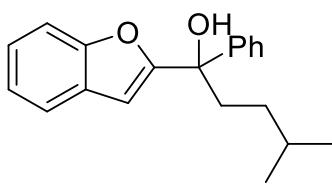
To a solution of **S5** (1.0 equiv.) in THF was added a solution of Grignard reagent (1.5 equiv.) in THF dropwise at 0 °C under  $\text{N}_2$ . After ambient temperature was reached, the reaction mixture was stirred for 2 h, and quenched with saturated  $\text{NH}_4\text{Cl}$  solution. The resulting mixture was extracted with EtOAc. The combined organic extracts were washed by brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, concentrated, and purified by flash column chromatography on silica gel (eluent: EtOAc/Petroleum ether) to give **S6**.

### 3. General procedures for synthesis of 2

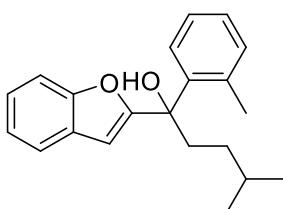
PIDA (iodobenzene diacetate) (0.8 mmol, 4.0 equiv.) and NaN<sub>3</sub> (0.8 mmol, 4.0 equiv.) were loaded in a reaction vial which was subjected to evacuation/ flushing with N<sub>2</sub> three times and was added to a solution of tertiary alcohol **1** (0.2 mmol, 1.0 equiv.) in MeCN (2.5 mL). The reaction was stirred at 80 °C for 12 h. Afterwards the reaction was quenched with saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution and extracted with EtOAc. The combined organic extracts were washed by brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, concentrated, and purified by flash column chromatography on silica gel to give the product. (PIDA (1.2 mmol, 6.0 equiv.) and NaN<sub>3</sub> (1.2 mmol, 6.0 equiv.) were used for **2g**).

## 4. Characterization of starting materials and products

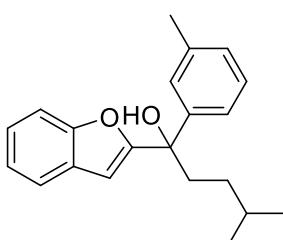
### a. New starting materials



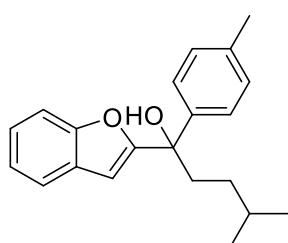
**1a:** yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.54-7.50 (m, 1H), 7.49-7.45 (m, 2H), 7.42-7.39 (m, 1H), 7.36-7.30 (m, 2H), 7.29-7.17 (m, 3H), 6.63 (d, *J* = 0.8 Hz, 1H), 2.53 (br, 1H), 2.39-2.30 (m, 1H), 2.26-2.17 (m, 1H), 1.60-1.48 (m, 1H), 1.33-1.23 (m, 1H), 1.21-1.10 (m, 1H), 0.87 (d, *J* = 6.8 Hz, 3H), 0.86 (d, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 161.4, 154.7, 144.0, 128.1, 128.1, 127.3, 125.6, 124.0, 122.8, 121.0, 111.3, 103.0, 75.9, 38.8, 32.3, 28.2, 22.5, 22.5. FT-IR: ν (cm<sup>-1</sup>) δ 3353, 2972, 2945, 2160, 1976, 1683, 1580, 1471, 1357, 1272, 1165. HRMS [ESI] calcd for C<sub>20</sub>H<sub>22</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup> 317.1512, found 317.1519.



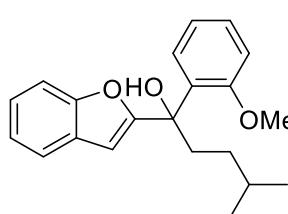
**1b:** yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.60-7.56 (m, 1H), 7.56-7.52 (m, 1H), 7.45-7.40 (m, 1H), 7.29-7.19 (m, 4H), 7.17-7.12 (m, 1H), 6.60 (d, *J* = 0.8 Hz, 1H), 2.48-2.34 (m, 2H), 2.22 (s, 3H), 1.63-1.51 (m, 1H), 1.39-1.29 (m, 1H), 1.15-1.05 (m, 1H), 0.91 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 161.4, 154.5, 141.0, 135.9, 132.2, 128.1, 127.6, 126.9, 125.6, 124.1, 122.8, 121.1, 111.4, 103.2, 76.0, 36.6, 32.3, 28.3, 22.6, 22.5, 21.3. FT-IR: ν (cm<sup>-1</sup>) δ 2954, 1577, 1384, 1338, 1250, 1173, 1067, 1033, 1006. HRMS [ESI] calcd for C<sub>21</sub>H<sub>24</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup> 331.1669, found 331.1678.



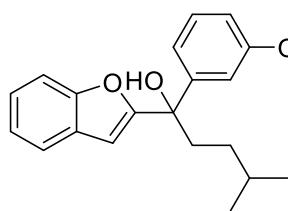
**1c:** yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.56-7.52 (m, 1H), 7.46-7.40 (m, 1H), 7.32 (s, 1H), 7.29-7.18 (m, 4H), 7.12-7.07 (m, 1H), 6.65 (d, *J* = 0.8 Hz, 1H), 2.54 (s, 1H), 2.40-2.31 (m, 1H), 2.36 (s, 3H), 2.26-2.17 (m, 1H), 1.62-1.50 (m, 1H), 1.35-1.13 (m, 2H), 0.90 (d, *J* = 6.4 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 161.5, 154.7, 143.9, 137.7, 128.1, 128.1, 128.0, 126.2, 124.0, 122.7, 121.0, 111.3, 102.9, 75.9, 38.8, 32.3, 28.2, 22.5, 21.6. FT-IR: ν (cm<sup>-1</sup>) δ 3676, 2955, 1772, 1684, 1608, 1576, 1489, 1436, 1386, 1251, 1067. HRMS [ESI] calcd for C<sub>21</sub>H<sub>24</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup> 331.1669, found 331.1670.



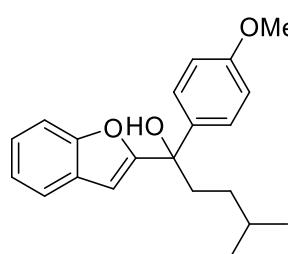
**1d:** yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55-7.51 (m, 1H), 7.44-7.40 (m, 1H), 7.38-7.34 (m, 2H), 7.25-7.18 (m, 2H), 7.18-7.13 (m, 2H), 6.63 (s, 1H), 2.51 (s, 1H), 2.39-2.29 (m, 1H), 2.34 (s, 3H), 2.26-2.16 (m, 1H), 1.61-1.50 (m, 1H), 1.34-1.13 (m, 2H), 0.89 (d,  $J = 6.0$  Hz, 3H), 0.87 (d,  $J = 6.4$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.6, 154.7, 141.1, 136.9, 128.8, 128.1, 125.5, 124.0, 122.7, 121.0, 111.3, 102.9, 75.8, 38.8, 32.3, 28.3, 22.6, 22.5, 21.0. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  3649, 2955, 2363, 1749, 1684, 1636, 1569, 1508, 1473, 1396, 1250, 1114. HRMS [ESI] calcd for  $\text{C}_{21}\text{H}_{24}\text{NaO}_2$  [ $\text{M}+\text{Na}]^+$  331.1669, found 331.1672.



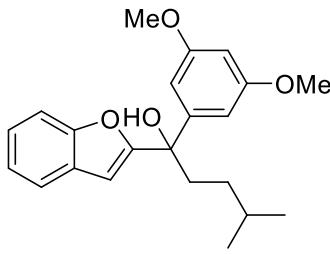
**1e:** white solid, m.p. 80-81 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53-7.49 (m, 1H), 7.42 (d,  $J = 7.6$  Hz, 1H), 7.32-7.23 (m, 2H), 7.23-7.14 (m, 2H), 6.99-6.94 (m, 1H), 6.89 (d,  $J = 8.4$  Hz, 1H), 6.58 (s, 1H), 4.87 (s, 1H), 3.74 (s, 3H), 2.45-2.30 (m, 2H), 1.63-1.52 (m, 1H), 1.45-1.34 (m, 1H), 1.33-1.22 (m, 1H), 0.90 (d,  $J = 6.0$  Hz, 3H), 0.89 (d,  $J = 6.0$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.7, 157.1, 154.6, 131.6, 128.8, 128.4, 127.6, 123.5, 122.5, 121.0, 120.8, 111.8, 111.2, 102.5, 76.1, 55.5, 36.8, 32.5, 28.3, 22.6, 22.5. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  3395, 2931, 2160, 1976, 1581, 1433, 1371, 1257, 1174, 1092. HRMS [ESI] calcd for  $\text{C}_{21}\text{H}_{24}\text{NaO}_3$  [ $\text{M}+\text{Na}]^+$  347.1618, found 347.1619.



**1f:** yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 (d,  $J = 7.6$  Hz, 1H), 7.41 (d,  $J = 8.0$  Hz, 1H), 7.26-7.16 (m, 3H), 7.10 (s, 1H), 7.06-7.02 (m, 1H), 6.80 (dd,  $J = 8.0, 2.0$  Hz, 1H), 6.63 (s, 1H), 3.78 (s, 3H), 2.67 (br, 1H), 2.39-2.29 (m, 1H), 2.25-2.16 (m, 1H), 1.60-1.49 (m, 1H), 1.35-1.25 (m, 1H), 1.23-1.12 (m, 1H), 0.88 (d,  $J = 6.8$  Hz, 3H), 0.87 (d,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.3, 159.5, 154.7, 145.7, 129.1, 128.1, 124.0, 122.7, 121.0, 118.1, 112.4, 111.7, 111.3, 102.9, 75.8, 55.2, 38.8, 32.2, 28.2, 22.5, 22.5. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  3432, 2954, 2159, 1600, 1486, 1432, 1367, 1289, 1164, 1049. HRMS [ESI] calcd for  $\text{C}_{21}\text{H}_{24}\text{NaO}_3$  [ $\text{M}+\text{Na}]^+$  347.1618, found 347.1611.

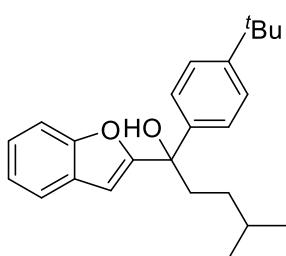


**1g:** yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49-7.45 (m, 1H), 7.38-7.32 (m, 3H), 7.21-7.12 (m, 2H), 6.84-6.78 (m, 2H), 6.56 (s, 1H), 3.71 (s, 3H), 2.68 (s, 1H), 2.34-2.24 (m, 1H), 2.21-2.11 (m, 1H), 1.56-1.44 (m, 1H), 1.28-1.09 (m, 2H), 0.84 (d,  $J = 5.6$  Hz, 3H), 0.83 (d,  $J = 6.0$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.7, 158.7, 154.7, 136.2, 128.1, 126.8, 123.9, 122.7, 120.9, 113.4, 111.2, 102.8, 75.6, 55.1, 38.8, 32.3, 28.2, 22.5, 22.5. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  2954, 2360, 1610, 1510, 1455, 1367, 1303, 1249, 1175, 1068. HRMS [ESI] calcd for  $\text{C}_{21}\text{H}_{24}\text{NaO}_3$  [ $\text{M}+\text{Na}]^+$  347.1618, found 347.1617.



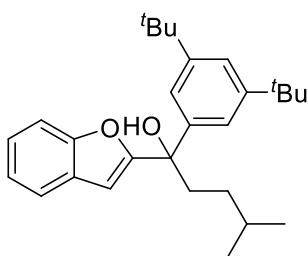
**1h:** yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57-7.53 (m, 1H), 7.44 (d,  $J = 8.0$  Hz, 1H), 7.29-7.20 (m, 2H), 6.73-6.70 (m, 2H), 6.67 (s, 1H), 6.43-6.40 (m, 1H), 3.79 (s, 6H), 2.76 (s, 1H), 2.41-2.31 (m, 1H), 2.28-2.18 (m, 1H), 1.63-1.52 (m, 1H), 1.40-1.29 (m, 1H), 1.27-1.16 (m, 1H), 0.92 (d,  $J = 6.8$  Hz, 3H), 0.90 (d,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.2, 160.6, 154.7, 146.6, 128.1, 124.0, 122.7, 121.0, 111.2, 104.1, 102.9, 98.9, 75.9, 55.2, 38.8, 32.2, 28.2, 22.5, 22.5. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )

$\delta$  3458, 2954, 2159, 1977, 1595, 1454, 1384, 1291, 1055. HRMS [ESI] calcd for  $\text{C}_{22}\text{H}_{26}\text{NaO}_4$  [ $\text{M}+\text{Na}]^+$  377.1723, found 377.1716.



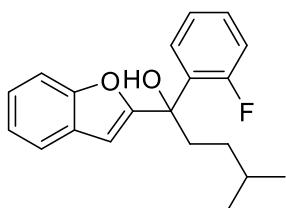
**1i:** yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57-7.53 (m, 1H), 7.46-7.35 (m, 5H), 7.28-7.19 (m, 2H), 6.66 (s, 1H), 2.58 (s, 1H), 2.42-2.32 (m, 1H), 2.28-2.18 (m, 1H), 1.64-1.52 (m, 1H), 1.33 (s, 9H), 1.31-1.23 (m, 2H), 0.91 (d,  $J = 6.8$  Hz, 3H), 0.90 (d,  $J = 6.4$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.6, 154.8, 150.2, 141.2, 128.2, 125.3, 125.1, 123.9, 122.7, 121.0, 111.3, 102.9, 75.9, 38.8, 34.4, 32.4, 31.3, 28.3, 22.5. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  3546, 2955, 1780, 1668, 1510,

1403, 1305, 1215, 1133, 1068. HRMS [ESI] calcd for  $\text{C}_{24}\text{H}_{30}\text{NaO}_2$  [ $\text{M}+\text{Na}]^+$  373.2138, found 373.2142.

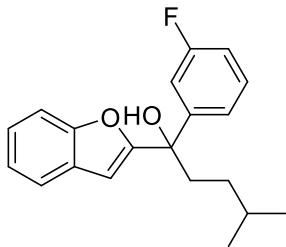


**1j:** yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56-7.51 (m, 1H), 7.44 (d,  $J = 7.6$  Hz, 1H), 7.37 (s, 3H), 7.27-7.18 (m, 2H), 6.61 (s, 1H), 2.61 (s, 1H), 2.42-2.33 (m, 1H), 2.29-2.19 (m, 1H), 1.62-1.51 (m, 1H), 1.36-1.21 (m, 2H), 1.32 (s, 18H), 0.90 (d,  $J = 6.8$  Hz, 3H), 0.88 (d,  $J = 6.4$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.7, 154.8, 150.4, 143.1, 128.2, 123.9, 122.6, 121.2, 121.0, 119.9, 111.2, 103.0, 76.5, 39.0, 34.9, 32.6, 31.5, 28.2, 22.6, 22.5. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )

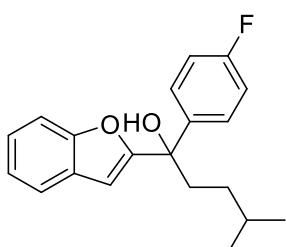
$\delta$  3355, 2954, 2160, 1712, 1598, 1469, 1384, 1252, 1152, 1092. HRMS [ESI] calcd for  $\text{C}_{28}\text{H}_{38}\text{NaO}_2$  [ $\text{M}+\text{Na}]^+$  429.2764, found 429.2755.



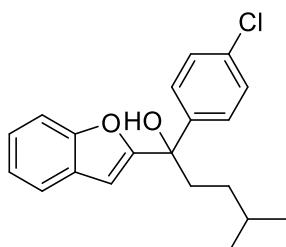
**1k:** yellow solid, m.p. 75-76 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66-7.60 (m, 1H), 7.51-7.47 (m, 1H), 7.38 (d,  $J = 8.0$  Hz, 1H), 7.27-7.10 (m, 4H), 6.97 (dd,  $J = 11.6, 8.0$  Hz, 1H), 6.58 (s, 1H), 2.89 (s, 1H), 2.54-2.44 (m, 1H), 2.43-2.33 (m, 1H), 1.60-1.49 (m, 1H), 1.41-1.30 (m, 1H), 1.14-1.02 (m, 1H), 0.88 (d,  $J = 6.8$  Hz, 3H), 0.86 (d,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.3, 159.7 (d,  $J_{\text{C}-\text{F}} = 245.3$  Hz), 154.5, 130.5 (d,  $J_{\text{C}-\text{F}} = 10.9$  Hz), 129.4 (d,  $J_{\text{C}-\text{F}} = 8.5$  Hz), 128.2 (d,  $J_{\text{C}-\text{F}} = 3.3$  Hz), 128.1, 124.1, 123.9 (d,  $J_{\text{C}-\text{F}} = 3.2$  Hz), 122.7, 121.1, 116.0 (d,  $J_{\text{C}-\text{F}} = 23.1$  Hz), 111.2, 102.7 (d,  $J_{\text{C}-\text{F}} = 2.1$  Hz), 74.1 (d,  $J_{\text{C}-\text{F}} = 2.5$  Hz), 36.5 (d,  $J_{\text{C}-\text{F}} = 3.5$  Hz), 32.2, 28.2, 22.6, 22.4.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -112.2 (s). FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  3341, 2965, 2026, 1976, 1612, 1580, 1453, 1319, 1217, 1177. HRMS [ESI] calcd for  $\text{C}_{20}\text{H}_{21}\text{FNaO}_2$  [ $\text{M}+\text{Na}]^+$  335.1418, found 335.1423.



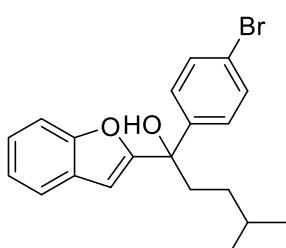
**1l:** yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53-7.48 (m, 1H), 7.39 (d,  $J = 8.0$  Hz, 1H), 7.29-7.15 (m, 5H), 6.96-6.89 (m, 1H), 6.62 (s, 1H), 2.61 (s, 1H), 2.35-2.26 (m, 1H), 2.21-2.12 (m, 1H), 1.57-1.46 (m, 1H), 1.32-1.22 (m, 1H), 1.15-1.05 (m, 1H), 0.86 (d,  $J = 7.2$  Hz, 3H), 0.84 (d,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.8 (d,  $J_{\text{C}-\text{F}} = 244.0$  Hz), 160.8, 154.7, 146.7 (d,  $J_{\text{C}-\text{F}} = 6.5$  Hz), 129.6 (d,  $J_{\text{C}-\text{F}} = 8.1$  Hz), 128.0, 124.3, 122.9, 121.3 (d,  $J_{\text{C}-\text{F}} = 2.8$  Hz), 121.1, 114.2 (d,  $J_{\text{C}-\text{F}} = 21.0$  Hz), 113.0 (d,  $J_{\text{C}-\text{F}} = 22.8$  Hz), 111.3, 103.1, 75.6 (d,  $J_{\text{C}-\text{F}} = 1.5$  Hz), 38.8, 32.1, 28.2, 22.5, 22.4.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -112.8 (s). FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  3398, 2956, 2158, 1614, 1589, 1485, 1328, 1249, 1142, 1050. HRMS [ESI] calcd for  $\text{C}_{20}\text{H}_{21}\text{FNaO}_2$  [ $\text{M}+\text{Na}]^+$  335.1418, found 335.1425.



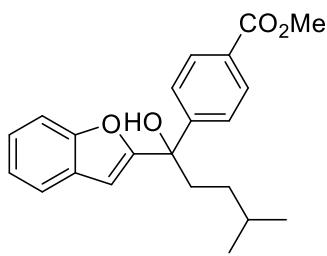
**1m:** yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56-7.52 (m, 1H), 7.48-7.40 (m, 3H), 7.29-7.19 (m, 2H), 7.06-6.98 (m, 2H), 6.63 (d,  $J = 0.8$  Hz, 1H), 2.57 (s, 1H), 2.38-2.29 (m, 1H), 2.24-2.15 (m, 1H), 1.61-1.49 (m, 1H), 1.33-1.23 (m, 1H), 1.20-1.09 (m, 1H), 0.89 (d,  $J = 6.8$  Hz, 3H), 0.87 (d,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.0 (d,  $J_{\text{C}-\text{F}} = 244.4$  Hz), 161.1, 154.7, 139.7 (d,  $J_{\text{C}-\text{F}} = 3.0$  Hz), 128.0, 127.4 (d,  $J_{\text{C}-\text{F}} = 8.1$  Hz), 124.2, 122.9, 121.1, 114.9 (d,  $J_{\text{C}-\text{F}} = 21.2$  Hz), 111.3, 103.0, 75.6, 38.9, 32.2, 28.2, 22.5, 22.5.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -115.6 (s). FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  3457, 2955, 2870, 2216, 1603, 1507, 1468, 1408, 1225, 1131. HRMS [ESI] calcd for  $\text{C}_{20}\text{H}_{21}\text{FNaO}_2$  [ $\text{M}+\text{Na}]^+$  335.1418, found 335.1415.



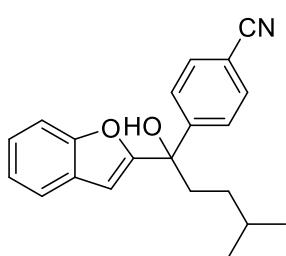
**1n:** yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57-7.52 (m, 1H), 7.46-7.40 (m, 3H), 7.34-7.28 (m, 2H), 7.28-7.20 (m, 2H), 6.64 (s, 1H), 2.55 (s, 1H), 2.38-2.29 (m, 1H), 2.24-2.15 (m, 1H), 1.61-1.49 (m, 1H), 1.35-1.24 (m, 1H), 1.19-1.07 (m, 1H), 0.89 (d,  $J = 6.8$  Hz, 3H), 0.88 (d,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.9, 154.8, 142.4, 133.2, 128.3, 128.0, 127.2, 124.3, 122.9, 121.1, 111.3, 103.1, 75.6, 38.8, 32.2, 28.2, 22.6, 22.5. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  3373, 2956, 1489, 1400, 1346, 1252, 1172, 1092, 1013. HRMS [ESI] calcd for  $\text{C}_{20}\text{H}_{21}\text{ClNaO}_2$  [ $\text{M}+\text{Na}]^+$  351.1122, found 351.1129.



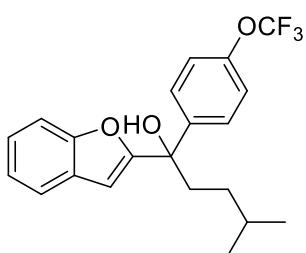
**1o:** yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 (d,  $J = 7.2$  Hz, 1H), 7.50-7.45 (m, 2H), 7.43 (d,  $J = 8.0$  Hz, 1H), 7.40-7.34 (m, 2H), 7.30-7.20 (m, 2H), 6.64 (s, 1H), 2.56 (s, 1H), 2.38-2.28 (m, 1H), 2.25-2.14 (m, 1H), 1.61-1.50 (m, 1H), 1.35-1.24 (m, 1H), 1.18-1.07 (m, 1H), 0.90 (d,  $J = 6.8$  Hz, 3H), 0.88 (d,  $J = 7.6$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.8, 154.7, 143.0, 131.2, 127.9, 127.5, 124.3, 122.9, 121.3, 121.1, 111.3, 103.1, 75.6, 38.7, 32.1, 28.2, 22.5, 22.4. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  3402, 2955, 2159, 1620, 1581, 1411, 1368, 1222, 1162, 1068. HRMS [ESI] calcd for  $\text{C}_{20}\text{H}_{21}\text{BrNaO}_2$  [ $\text{M}+\text{Na}]^+$  395.0617, found 395.0616.



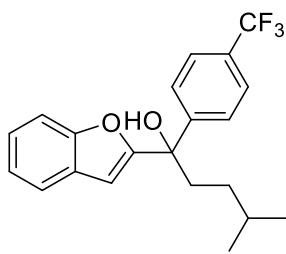
**1p:** yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02-7.97 (m, 2H), 7.59-7.54 (m, 2H), 7.54-7.50 (m, 1H), 7.40 (d,  $J = 8.0$  Hz, 1H), 7.27-7.17 (m, 2H), 6.64 (s, 1H), 3.88 (s, 3H), 2.80 (s, 1H), 2.40-2.30 (m, 1H), 2.27-2.17 (m, 1H), 1.59-1.48 (m, 1H), 1.36-1.25 (m, 1H), 1.14-1.03 (m, 1H), 0.87 (d,  $J = 6.8$  Hz, 3H), 0.85 (d,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.9, 160.7, 154.7, 148.9, 129.5, 129.1, 127.9, 125.7, 124.3, 122.9, 121.1, 111.3, 103.2, 75.8, 52.0, 38.8, 32.1, 28.2, 22.5, 22.4. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  3474, 2972, 2160, 1977, 1692, 1576, 1438, 1368, 1280, 1177. HRMS [ESI] calcd for  $\text{C}_{22}\text{H}_{24}\text{NaO}_4$  [ $\text{M}+\text{Na}]^+$  375.1567, found 375.1570.



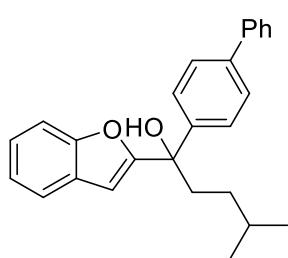
**1q:** yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65-7.61 (m, 4H), 7.57-7.54 (m, 1H), 7.42 (d,  $J = 8.0$  Hz, 1H), 7.31-7.20 (m, 2H), 6.69 (s, 1H), 2.66 (s, 1H), 2.39-2.30 (m, 1H), 2.25-2.16 (m, 1H), 1.60-1.49 (m, 1H), 1.37-1.25 (m, 1H), 1.11-1.01 (m, 1H), 0.89 (d,  $J = 6.4$  Hz, 3H), 0.87 (d,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.0, 154.7, 149.2, 132.0, 127.8, 126.5, 124.5, 123.0, 121.2, 118.7, 111.3, 111.0, 103.3, 75.6, 38.7, 32.0, 28.1, 22.5, 22.4. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  3470, 2952, 2929, 2231, 1608, 1500, 1454, 1385, 1250, 1218. HRMS [ESI] calcd for  $\text{C}_{21}\text{H}_{21}\text{NNaO}_2$  [ $\text{M}+\text{Na}]^+$  342.1465, found 342.1459.



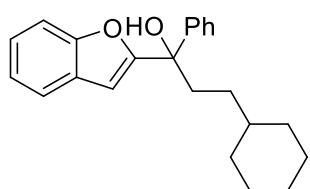
**1r:** yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58-7.50 (m, 3H), 7.46-7.41 (m, 1H), 7.30-7.22 (m, 2H), 7.22-7.16 (m, 2H), 6.66 (d,  $J = 0.8$  Hz, 1H), 2.58 (s, 1H), 2.40-2.30 (m, 1H), 2.25-2.16 (m, 1H), 1.62-1.51 (m, 1H), 1.35-1.24 (m, 1H), 1.20-1.11 (m, 1H), 0.90 (d,  $J = 6.8$  Hz, 3H), 0.88 (d,  $J = 6.4$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.8, 154.8, 148.4 (q,  $J_{\text{C-F}} = 1.8$  Hz), 142.7, 128.0, 127.2, 124.3, 123.0, 121.1, 120.5, 120.5 (q,  $J_{\text{C-F}} = 255.4$  Hz), 111.3, 103.2, 75.6, 38.9, 32.2, 28.2, 22.5, 22.4.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -57.7 (s). FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  3676, 2957, 2361, 1772, 1699, 1636, 1576, 1521, 1507, 1489, 1374, 1221, 1019. HRMS [ESI] calcd for  $\text{C}_{21}\text{H}_{21}\text{F}_3\text{NaO}_3$  [ $\text{M}+\text{Na}]^+$  401.1335, found 401.1336.



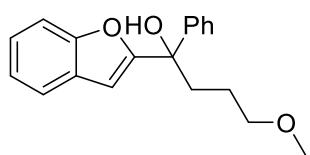
**1s:** yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64-7.55 (m, 4H), 7.53 (d,  $J = 7.2$  Hz, 1H), 7.40 (d,  $J = 7.6$  Hz, 1H), 7.26-7.17 (m, 2H), 6.64 (s, 1H), 2.77 (s, 1H), 2.40-2.30 (m, 1H), 2.26-2.17 (m, 1H), 1.60-1.48 (m, 1H), 1.36-1.25 (m, 1H), 1.14-1.03 (m, 1H), 0.88 (d,  $J = 6.8$  Hz, 3H), 0.86 (d,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.5, 154.8, 147.9, 129.5 (q,  $J_{\text{C-F}} = 32.1$  Hz), 127.9, 126.1, 125.1 (q,  $J_{\text{C-F}} = 3.8$  Hz), 124.4, 124.2 (q,  $J_{\text{C-F}} = 270.4$  Hz), 123.0, 121.2, 111.3, 103.3, 75.7, 38.8, 32.1, 28.2, 22.5, 22.4.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.3 (s). FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  3394, 2956, 2159, 1976, 1620, 1581, 1411, 1369, 1324, 1068. HRMS [ESI] calcd for  $\text{C}_{21}\text{H}_{21}\text{F}_3\text{NaO}_2$  [ $\text{M}+\text{Na}]^+$  385.1386, found 385.1385.



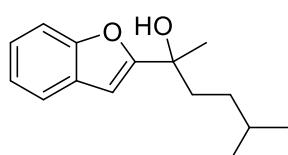
**1t:** yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62-7.54 (m, 7H), 7.47-7.41 (m, 3H), 7.37-7.32 (m, 1H), 7.29-7.20 (m, 2H), 6.69 (s, 1H), 2.59 (s, 1H), 2.45-2.35 (m, 1H), 2.32-2.22 (m, 1H), 1.64-1.56 (m, 1H), 1.39-1.17 (m, 2H), 0.91 (d,  $J = 6.4$  Hz, 3H), 0.90 (d,  $J = 6.4$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.3, 154.8, 143.0, 140.6, 140.1, 128.7, 128.1, 127.2, 127.0, 126.9, 126.1, 124.1, 122.8, 121.1, 111.3, 103.1, 75.8, 38.8, 32.3, 28.3, 22.6, 22.5. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  3394, 2924, 2160, 1975, 1574, 1453, 1366, 1247, 1170, 1075. HRMS [ESI] calcd for  $\text{C}_{26}\text{H}_{26}\text{NaO}_2$  [ $\text{M}+\text{Na}]^+$  393.1825, found 393.1829.



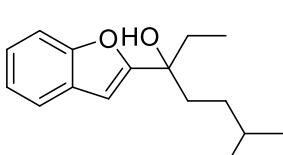
**1u:** yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54-7.50 (m, 1H), 7.50-7.45 (m, 2H), 7.43-7.39 (m, 1H), 7.36-7.30 (m, 2H), 7.29-7.25 (m, 1H), 7.24-7.17 (m, 2H), 6.62 (s, 1H), 2.58 (s, 1H), 2.41-2.32 (m, 1H), 2.28-2.18 (m, 1H), 1.75-1.58 (m, 5H), 1.34-1.07 (m, 6H), 0.93-0.79 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.4, 154.7, 144.0, 128.1, 128.1, 127.3, 125.6, 124.0, 122.8, 121.0, 111.3, 103.0, 76.0, 38.4, 37.9, 33.3, 33.2, 30.8, 26.6, 26.3. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  3413, 2921, 2159, 1970, 1600, 1582, 1452, 1379, 1251, 1092. HRMS [ESI] calcd for  $\text{C}_{23}\text{H}_{26}\text{NaO}_2$  [ $\text{M}+\text{Na}]^+$  357.1825, found 357.1824.



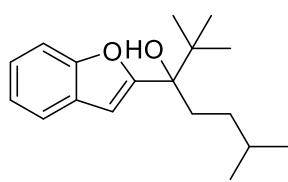
**1v:** yellow solid, m.p. 85-86 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56-7.49 (m, 3H), 7.41 (d,  $J = 7.6$  Hz, 1H), 7.35-7.30 (m, 2H), 7.26-7.15 (m, 3H), 6.65 (s, 1H), 4.33 (s, 1H), 3.40 (t,  $J = 6.0$  Hz, 2H), 3.32 (s, 3H), 2.59-2.50 (m, 1H), 2.39-2.30 (m, 1H), 1.74-1.54 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.8, 154.8, 144.3, 128.2, 128.1, 127.2, 125.7, 123.8, 122.6, 121.0, 111.2, 103.0, 75.2, 72.9, 58.5, 38.7, 24.1. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  3367, 1677, 1581, 1454, 1386, 1303, 1254, 1154, 1115, 1066. HRMS [ESI] calcd for  $\text{C}_{19}\text{H}_{20}\text{NaO}_3$  [ $\text{M}+\text{Na}]^+$  319.1305, found 319.1311.



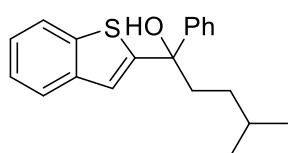
**1w:** yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 (d,  $J = 7.2$  Hz, 1H), 7.45 (d,  $J = 8.0$  Hz, 1H), 7.26-7.17 (m, 2H), 6.57 (s, 1H), 2.39 (s, 1H), 1.95-1.89 (m, 2H), 1.61 (s, 3H), 1.56-1.44 (m, 1H), 1.21-1.12 (m, 2H), 0.86 (d,  $J = 6.8$  Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.5, 154.6, 128.3, 123.7, 122.6, 120.8, 111.1, 101.2, 72.0, 39.3, 32.9, 28.2, 26.7, 22.5. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  3383, 2955, 2159, 1584, 1454, 1384, 1328, 1251, 1142, 1069. HRMS [ESI] calcd for  $\text{C}_{15}\text{H}_{20}\text{NaO}_2$  [ $\text{M}+\text{Na}]^+$  255.1356, found 255.1354.



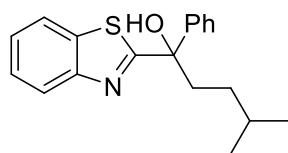
**1x:** yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55-7.51 (m, 1H), 7.45 (d,  $J = 7.6$  Hz, 1H), 7.26-7.18 (m, 2H), 6.60 (s, 1H), 2.08 (s, 1H), 2.02-1.80 (m, 4H), 1.56-1.44 (m, 1H), 1.29-1.18 (m, 1H), 1.13-1.03 (m, 1H), 0.89-0.83 (m, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.7, 154.7, 128.4, 123.5, 122.6, 120.7, 111.1, 102.4, 75.1, 37.3, 32.6, 32.3, 28.3, 22.5, 22.5, 7.8. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  3676, 2956, 1772, 1699, 1576, 1498, 1396, 1339, 1256, 1162, 1056. HRMS [ESI] calcd for  $\text{C}_{16}\text{H}_{22}\text{NaO}_2$  [ $\text{M}+\text{Na}]^+$  269.1512, found 269.1510.



**1y:** yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57-7.53 (m, 1H), 7.48-7.44 (m, 1H), 7.27-7.19 (m, 2H), 6.62 (s, 1H), 2.20-2.11 (m, 2H), 1.87-1.77 (m, 1H), 1.58-1.47 (m, 1H), 1.29-1.18 (m, 1H), 1.03 (s, 9H), 0.87 (d,  $J = 6.4$  Hz, 3H), 0.85 (d,  $J = 6.4$  Hz, 3H), 0.83-0.73 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.3, 154.4, 128.3, 123.3, 122.6, 120.6, 111.0, 104.1, 79.8, 38.7, 32.8, 31.5, 28.4, 25.6, 22.7, 22.4. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  2957, 1466, 1396, 1305, 1214, 1177, 1132, 1072, 1037. HRMS [ESI] calcd for  $\text{C}_{18}\text{H}_{26}\text{NaO}_2$  [ $\text{M}+\text{Na}^+$ ] 297.1825, found 297.1822.



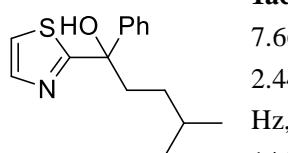
**1z:** yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (d,  $J = 8.0$ , 1H), 7.69-7.65 (m, 1H), 7.55-7.50 (m, 2H), 7.37-7.30 (m, 2H), 7.29-7.23 (m, 3H), 7.14 (s, 1H), 2.55-2.28 (m, 3H), 1.63-1.51 (m, 1H), 1.41-1.29 (m, 1H), 1.22-1.10 (m, 1H), 0.89 (d,  $J = 6.8$  Hz, 3H), 0.88 (d,  $J = 6.4$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  153.7, 145.4, 139.6, 139.6, 128.2, 127.2, 125.6, 124.2, 124.1, 123.5, 122.3, 120.2, 77.5, 41.1, 32.6, 28.3, 22.6, 22.5. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  3059, 2953, 1601, 1458, 1384, 1304, 1216, 1156, 1130, 1032. HRMS [ESI] calcd for  $\text{C}_{20}\text{H}_{22}\text{NaOS}$  [ $\text{M}+\text{Na}^+$ ] 333.1284, found 333.1287.



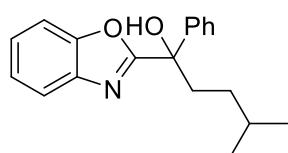
**1aa:**<sup>1</sup> yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03-7.99 (m, 1H), 7.85-7.81 (m, 1H), 7.72-7.68 (m, 2H), 7.49-7.43 (m, 1H), 7.40-7.32 (m, 3H), 7.31-7.26 (m, 1H), 3.93 (s, 1H), 2.51-2.44 (m, 2H), 1.66-1.54 (m, 1H), 1.37-1.21 (m, 2H), 0.90 (d,  $J = 6.4$  Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  178.4, 152.6, 144.0, 135.7, 128.4, 127.5, 125.9, 125.6, 124.9, 123.1, 121.7, 78.9, 40.5, 32.3, 28.2, 22.6, 22.5.



**1ab:**<sup>1</sup> yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 (d,  $J = 8.8$  Hz, 1H), 7.69-7.64 (m, 2H), 7.39-7.33 (m, 2H), 7.29-7.24 (m, 2H), 7.05 (dd,  $J = 8.8, 2.4$  Hz, 1H), 3.85 (s, 3H), 3.83 (s, 1H), 2.47-2.40 (m, 2H), 1.64-1.53 (m, 1H), 1.31-1.22 (m, 2H), 0.89 (d,  $J = 6.8$  Hz, 3H), 0.89 (d,  $J = 6.4$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  175.7, 157.5, 147.0, 144.2, 137.0, 128.3, 127.4, 125.5, 123.5, 115.2, 104.2, 78.8, 55.8, 40.5, 32.3, 28.2, 22.6, 22.5.



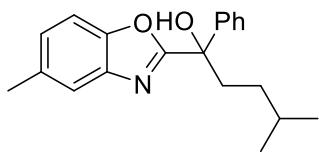
**1ac:**<sup>1</sup> yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71 (d,  $J = 3.2$  Hz, 1H), 7.66-7.62 (m, 2H), 7.40-7.34 (m, 2H), 7.31-7.26 (m, 2H), 3.75 (s, 1H), 2.44-2.38 (m, 2H), 1.63-1.52 (m, 1H), 1.27-1.19 (m, 2H), 0.90 (d,  $J = 6.4$  Hz, 3H), 0.89 (d,  $J = 6.4$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  178.0, 144.5, 141.9, 128.3, 127.3, 125.4, 119.4, 78.7, 40.9, 32.3, 28.2, 22.6, 22.4.



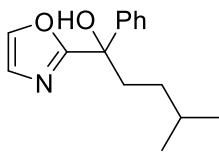
**1ad:** yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73-7.67 (m, 1H), 7.62 (d,  $J = 7.6$  Hz, 2H), 7.52-7.46 (m, 1H), 7.37-7.23 (m, 5H), 3.93 (s, 1H), 2.48-2.38 (m, 1H), 2.38-2.28 (m, 1H), 1.60-1.51 (m, 1H), 1.36-1.25 (m, 1H), 1.21-1.10 (m, 1H), 0.90-0.82 (m, 6H);  $^{13}\text{C}$  NMR

<sup>1</sup> X. Wu, M. Wang, L. Huan, D. Wang, J. Wang and C. Zhu, *Angew. Chem. Int. Ed.*, 2018, **57**, 1640.

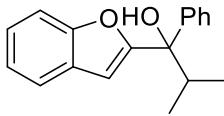
(100 MHz, CDCl<sub>3</sub>) δ 169.2, 151.2, 142.8, 140.3, 128.4, 127.7, 125.3, 125.1, 124.5, 120.1, 110.9, 76.1, 39.0, 32.2, 28.1, 22.5, 22.4. FT-IR: ν (cm<sup>-1</sup>) δ 3359, 2966, 1562, 1456, 1351, 1272, 1198, 1104, 1004. HRMS [ESI] calcd for C<sub>19</sub>H<sub>21</sub>NNaO<sub>2</sub> [M+Na]<sup>+</sup> 318.1465, found 318.1462.



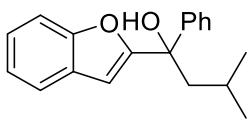
**1ae:** yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.65-7.60 (m, 2H), 7.50-7.47 (m, 1H), 7.40-7.33 (m, 3H), 7.30-7.25 (m, 1H), 7.15-7.11 (m, 1H), 3.87 (br, 1H), 2.49-2.39 (m, 1H), 2.46 (s, 3H), 2.36-2.28 (m, 1H), 1.62-1.51 (m, 1H), 1.38-1.27 (m, 1H), 1.20-1.10 (m, 1H), 0.88 (d, J = 6.4 Hz, 3H), 0.87 (d, J = 6.4 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 169.2, 149.5, 143.0, 140.5, 134.4, 128.4, 127.7, 126.1, 125.3, 120.0, 110.2, 76.1, 39.0, 32.3, 28.1, 22.5, 22.4, 21.4. FT-IR: ν (cm<sup>-1</sup>) δ 3028, 1601, 1483, 1384, 1261, 1176, 1142, 1088, 1032. HRMS [ESI] calcd for C<sub>20</sub>H<sub>23</sub>NNaO<sub>2</sub> [M+Na]<sup>+</sup> 332.1621, found 332.1628.



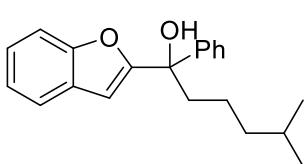
**1af:** yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.60 (d, J = 0.8 Hz, 1H), 7.52-7.48 (m, 2H), 7.36-7.30 (m, 2H), 7.28-7.23 (m, 1H), 7.02 (d, J = 0.8 Hz, 1H), 4.07 (br, 1H), 2.35-2.16 (m, 2H), 1.58-1.46 (m, 1H), 1.31-1.21 (m, 1H), 1.13-1.03 (m, 1H), 0.86 (d, J = 6.4 Hz, 3H), 0.85 (d, J = 6.8 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 167.4, 143.5, 139.1, 128.2, 127.5, 126.5, 125.2, 75.9, 39.4, 32.3, 28.1, 22.5, 22.4. FT-IR: ν (cm<sup>-1</sup>) δ 2956, 1599, 1492, 1357, 1289, 1222, 1170, 1078. HRMS [ESI] calcd for C<sub>15</sub>H<sub>19</sub>NNaO<sub>2</sub> [M+Na]<sup>+</sup> 268.1308, found 268.1301.



**1ag:** yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.62-7.58 (m, 2H), 7.54-7.50 (m, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.36-7.31 (m, 2H), 7.25-7.17 (m, 3H), 6.72 (s, 1H), 2.86-2.75 (m, 1H), 2.49 (s, 1H), 1.00 (d, J = 6.8 Hz, 3H), 0.84 (d, J = 6.8 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 161.5, 154.7, 143.3, 128.2, 128.0, 127.1, 125.6, 123.8, 122.7, 120.9, 111.2, 102.7, 78.7, 36.2, 17.3, 16.7. FT-IR: ν (cm<sup>-1</sup>) δ 3420, 2974, 2159, 2019, 1599, 1490, 1386, 1281, 1164, 1050. HRMS [ESI] calcd for C<sub>18</sub>H<sub>18</sub>NNaO<sub>2</sub> [M+Na]<sup>+</sup> 289.1199, found 289.1194.

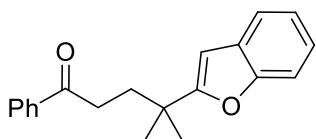


**1ah:** yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.57-7.51 (m, 3H), 7.44 (d, J = 7.6 Hz, 1H), 7.39-7.33 (m, 2H), 7.31-7.19 (m, 3H), 6.65 (s, 1H), 2.56 (s, 1H), 2.35-2.28 (m, 1H), 2.24-2.18 (m, 1H), 1.84-1.73 (m, 1H), 0.95 (d, J = 6.8 Hz, 3H), 0.86 (d, J = 6.8 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 161.8, 154.7, 144.2, 128.1, 127.3, 125.6, 124.0, 122.8, 121.0, 111.3, 102.7, 76.4, 49.2, 24.5, 24.2, 24.2. FT-IR: ν (cm<sup>-1</sup>) δ 2954, 1558, 1468, 1365, 1252, 1173, 1128, 1058. HRMS [ESI] calcd for C<sub>19</sub>H<sub>20</sub>NNaO<sub>2</sub> [M+Na]<sup>+</sup> 303.1356, found 303.1355.

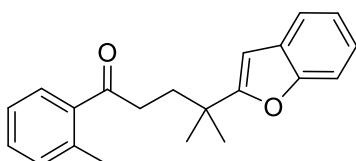


**1ai:** yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.55-7.51 (m, 1H), 7.50-7.45 (m, 2H), 7.41 (d, J = 8.0 Hz, 1H), 7.36-7.30 (m, 2H), 7.29-7.17 (m, 3H), 6.63 (s, 1H), 2.60 (br, 1H), 2.37-2.28 (m, 1H), 2.23-2.14 (m, 1H), 1.56-1.46 (m, 1H), 1.46-1.35 (m, 1H), 1.32-1.23 (m, 1H), 1.23-1.13 (m, 2H), 0.82 (d, J = 6.4 Hz, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 161.4, 154.7, 143.9, 128.1, 128.1, 127.3, 125.6, 124.1, 122.8, 121.0, 111.3, 103.0, 75.9, 41.1, 39.1, 27.7, 22.6, 22.5, 21.2. FT-IR: ν (cm<sup>-1</sup>) δ 3676, 2953, 1717, 1653, 1521, 1508, 1473, 1386, 1252, 1066. HRMS [ESI] calcd for C<sub>21</sub>H<sub>24</sub>NNaO<sub>2</sub> [M+Na]<sup>+</sup> 331.1669, found 331.1675.

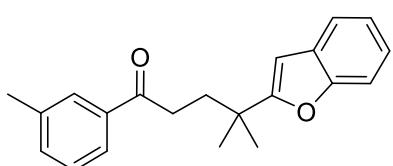
**b. Products**



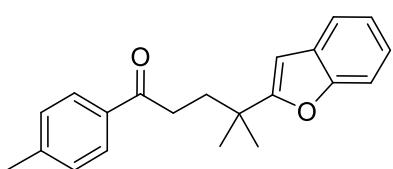
**2a:** 40.6 mg, 70% yield, yellow solid, m.p. 50-51 °C. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/100-1/50). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.85 (d, *J* = 7.6 Hz, 2H), 7.55-7.47 (m, 2H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.42-7.35 (m, 2H), 7.27-7.18 (m, 2H), 6.46 (s, 1H), 2.90-2.82 (m, 2H), 2.23-2.15 (m, 2H), 1.45 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.0, 164.9, 154.6, 136.7, 132.8, 128.6, 128.4, 127.9, 123.3, 122.4, 120.4, 110.8, 101.0, 35.8, 35.6, 34.3, 26.7. FT-IR:  $\nu$  (cm<sup>-1</sup>) δ 2972, 2160, 1976, 1683, 1471, 1357, 1255, 1213, 1165, 1080. HRMS [ESI] calcd for C<sub>20</sub>H<sub>20</sub>O<sub>2</sub>Na [M+Na]<sup>+</sup> 315.1356, found 315.1364.



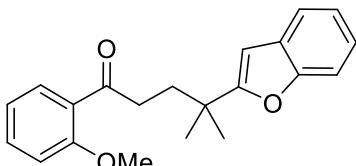
**2b:** 25.8 mg, 42% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/100-1/50). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.52-7.46 (m, 2H), 7.44-7.40 (m, 1H), 7.35-7.29 (m, 1H), 7.25-7.14 (m, 4H), 6.42 (d, *J* = 0.8 Hz, 1H), 2.80-2.74 (m, 2H), 2.43 (s, 3H), 2.17-2.11 (m, 2H), 1.41 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 204.2, 165.1, 154.6, 138.0, 137.9, 131.8, 131.1, 128.6, 128.3, 125.6, 123.3, 122.4, 120.4, 110.9, 101.0, 37.4, 35.9, 35.7, 26.8, 21.2. FT-IR:  $\nu$  (cm<sup>-1</sup>) δ 2966, 1683, 1580, 1454, 1300, 1214, 1082, 1006. HRMS [ESI] calcd for C<sub>21</sub>H<sub>22</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup> 329.1512, found 329.1504.



**2c:** 28.9 mg, 47% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/100-1/50). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.64-7.60 (m, 2H), 7.52-7.48 (m, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.33-7.16 (m, 4H), 6.44 (s, 1H), 2.85-2.78 (m, 2H), 2.34 (s, 3H), 2.18-2.13 (m, 2H), 1.42 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.4, 165.1, 154.7, 138.3, 136.8, 133.6, 128.7, 128.5, 128.3, 125.3, 123.3, 122.4, 120.4, 110.9, 101.0, 35.9, 35.8, 34.5, 26.8, 21.3. FT-IR:  $\nu$  (cm<sup>-1</sup>) δ 2965, 1682, 1583, 1470, 1301, 1254, 1110, 1006. HRMS [ESI] calcd for C<sub>21</sub>H<sub>22</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup> 329.1512, found 329.1504.

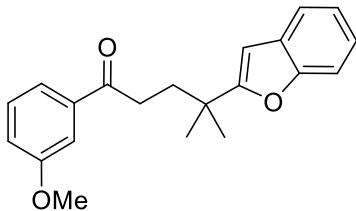


**2d:** 31.4 mg, 51% yield, yellow solid, m.p. 81-82 °C. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/100-1/50). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.77-7.73 (m, 2H), 7.54-7.50 (m, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.26-7.17 (m, 4H), 6.45 (s, 1H), 2.85-2.79 (m, 2H), 2.39 (s, 3H), 2.20-2.14 (m, 2H), 1.43 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 199.8, 165.1, 154.6, 143.6, 134.3, 129.1, 128.6, 128.1, 123.3, 122.4, 120.4, 110.9, 101.0, 35.9, 35.8, 34.3, 26.8, 21.5. FT-IR:  $\nu$  (cm<sup>-1</sup>) δ 2975, 1749, 1653, 1607, 1558, 1489, 1418, 1388, 1303, 1221, 1082, 1008. HRMS [ESI] calcd for C<sub>21</sub>H<sub>22</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup> 329.1512, found 329.1509.

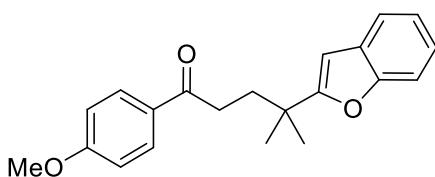


**2e:** 42.7 mg, 66% yield, yellow oil. Purification by flash column chromatography (eluent: Acetone/Petroleum ether = 1/100-1/50). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.58 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.52-7.48 (m, 1H), 7.44-7.38 (m, 2H), 7.25-7.16 (m, 2H), 6.98-6.93 (m, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 6.42 (s,

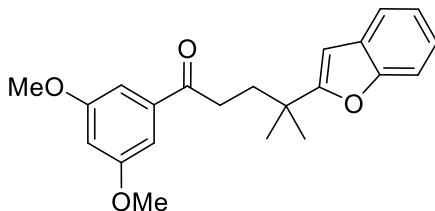
1H), 3.70 (s, 3H), 2.91-2.85 (m, 2H), 2.15-2.09 (m, 2H), 1.41 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  202.9, 165.4, 158.2, 154.6, 133.1, 130.1, 128.7, 128.6, 123.1, 122.3, 120.5, 120.3, 111.4, 110.8, 100.7, 55.2, 39.5, 35.9, 35.9, 26.7. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  2968, 1672, 1579, 1455, 1387, 1283, 1165, 1082, 1024. HRMS [ESI] calcd for  $\text{C}_{21}\text{H}_{22}\text{NaO}_3$  [ $\text{M}+\text{Na}]^+$  345.1461, found 345.1468.



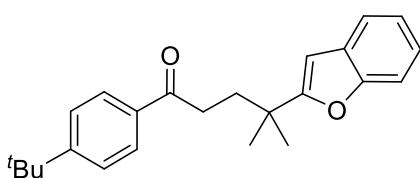
**2f:** 35.5 mg, 55% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/100-1/50).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53-7.49 (m, 1H), 7.45-7.38 (m, 3H), 7.32-7.16 (m, 3H), 7.09-7.04 (m, 1H), 6.44 (s, 1H), 3.81 (s, 3H), 2.86-2.80 (m, 2H), 2.20-2.14 (m, 2H), 1.43 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  200.0, 165.0, 159.7, 154.6, 138.2, 129.4, 128.6, 123.3, 122.4, 120.7, 120.4, 119.3, 112.3, 110.9, 101.0, 55.4, 35.9, 35.8, 34.6, 26.8. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  2967, 2360, 1684, 1582, 1522, 1487, 1388, 1255, 1196, 1110, 1010. HRMS [ESI] calcd for  $\text{C}_{21}\text{H}_{22}\text{NaO}_3$  [ $\text{M}+\text{Na}]^+$  345.1461, found 345.1464.



**2g:** 41.0 mg, 64% yield, yellow solid, m.p. 47-48 °C. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/100-1/50).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84-7.79 (m, 2H), 7.53-7.49 (m, 1H), 7.43 (d,  $J$  = 8.0 Hz, 1H), 7.26-7.16 (m, 2H), 6.88-6.83 (m, 2H), 6.44 (s, 1H), 3.84 (s, 3H), 2.81-2.75 (m, 2H), 2.18-2.12 (m, 2H), 1.42 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  198.8, 165.1, 163.3, 154.6, 130.3, 129.8, 128.6, 123.3, 122.4, 120.4, 113.6, 110.9, 101.0, 55.4, 36.0, 36.0, 34.1, 26.8. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  2967, 1679, 1577, 1510, 1419, 1307, 1216, 1170, 1095, 1031. HRMS [ESI] calcd for  $\text{C}_{21}\text{H}_{22}\text{NaO}_3$  [ $\text{M}+\text{Na}]^+$  345.1461, found 345.1464.

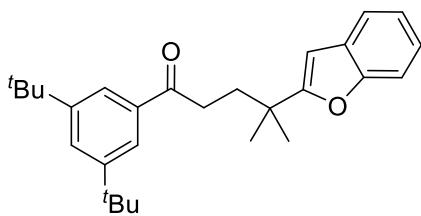


**2h:** 30.1 mg, 43% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/80-1/40).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52-7.48 (m, 1H), 7.42 (d,  $J$  = 7.6 Hz, 1H), 7.25-7.16 (m, 2H), 7.00-6.97 (m, 2H), 6.62-6.59 (m, 1H), 6.44 (s, 1H), 3.78 (s, 6H), 2.83-2.77 (m, 2H), 2.18-2.13 (m, 2H), 1.42 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  199.8, 164.9, 160.8, 154.6, 138.8, 128.6, 123.3, 122.4, 120.4, 110.9, 105.9, 105.0, 101.0, 55.5, 35.9, 35.9, 34.6, 26.8. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  2921, 2360, 1684, 1593, 1455, 1387, 1255, 1205, 1110, 1064, 1013. HRMS [ESI] calcd for  $\text{C}_{22}\text{H}_{24}\text{NaO}_4$  [ $\text{M}+\text{Na}]^+$  375.1567, found 375.1568.

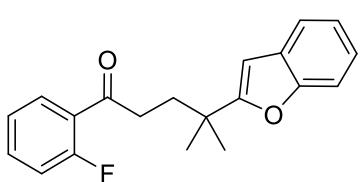


**2i:** 45.3 mg, 65% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/100-1/50).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81-7.76 (m, 2H), 7.54-7.50 (m, 1H), 7.45-7.38 (m, 3H), 7.26-7.17 (m, 2H), 6.45 (s, 1H), 2.86-2.80 (m, 2H), 2.20-2.14 (m, 2H), 1.43 (s, 6H), 1.33 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  199.9, 165.1, 156.5, 154.6, 134.2, 128.6, 128.0, 125.4, 123.3, 122.4, 120.4, 110.9, 101.0, 36.0, 35.8, 35.0, 34.4, 31.0, 26.8. FT-IR:  $\nu$

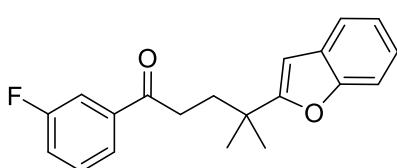
(cm<sup>-1</sup>) δ 2966, 2360, 1682, 1606, 1559, 1471, 1388, 1300, 1255, 1192, 1083. HRMS [ESI] calcd for C<sub>24</sub>H<sub>28</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup> 371.1982, found 371.1985.



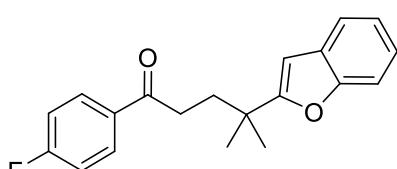
**2j:** 53.8 mg, 67% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/100-1/50). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.73 (d, *J* = 1.6 Hz, 2H), 7.64-7.62 (m, 1H), 7.54-7.50 (m, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.26-7.17 (m, 2H), 6.47 (s, 1H), 2.91-2.85 (m, 2H), 2.22-2.15 (m, 2H), 1.46 (s, 6H), 1.34 (s, 18H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 201.1, 165.1, 154.7, 151.1, 136.5, 128.6, 127.1, 123.3, 122.4, 122.3, 120.4, 110.9, 100.9, 36.5, 36.0, 34.9, 34.6, 31.3, 26.8. FT-IR: ν (cm<sup>-1</sup>) δ 2965, 2361, 1683, 1596, 1473, 1364, 1204, 1168, 1083. HRMS [ESI] calcd for C<sub>28</sub>H<sub>36</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup> 427.2608, found 427.2611.



**2k:** 37.8 mg, 61% yield, yellow solid, m.p. 57-58 °C. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/100-1/50). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.78-7.72 (m, 1H), 7.52-7.39 (m, 3H), 7.25-7.14 (m, 3H), 7.11-7.04 (m, 1H), 6.43 (s, 1H), 2.92-2.86 (m, 2H), 2.20-2.14 (m, 2H), 1.43 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 198.5 (d, *J*<sub>C-F</sub> = 3.9 Hz), 165.0, 161.7 (d, *J*<sub>C-F</sub> = 252.8 Hz), 154.6, 134.2 (d, *J*<sub>C-F</sub> = 9.0 Hz), 130.5 (d, *J*<sub>C-F</sub> = 2.7 Hz), 128.6, 125.8 (d, *J*<sub>C-F</sub> = 13.0 Hz), 124.3 (d, *J*<sub>C-F</sub> = 3.2 Hz), 123.2, 122.3, 120.4, 116.5 (d, *J*<sub>C-F</sub> = 23.5 Hz), 110.9, 100.9, 39.4 (d, *J*<sub>C-F</sub> = 7.1 Hz), 35.7, 35.3 (d, *J*<sub>C-F</sub> = 1.3 Hz), 26.7; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -109.6 (s). FT-IR: ν (cm<sup>-1</sup>) δ 2930, 1683, 1582, 1479, 1404, 1388, 1255, 1165, 1111, 1004. HRMS [ESI] calcd for C<sub>20</sub>H<sub>19</sub>FNaO<sub>2</sub> [M+Na]<sup>+</sup> 333.1261, found 333.1269.

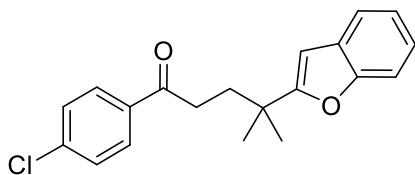


**2l:** 29.1 mg, 47% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/100-1/50). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.62-7.58 (m, 1H), 7.57-7.49 (m, 2H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.39-7.32 (m, 1H), 7.26-7.17 (m, 3H), 6.45 (s, 1H), 2.84-2.79 (m, 2H), 2.20-2.14 (m, 2H), 1.43 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 198.8 (d, *J*<sub>C-F</sub> = 2.0 Hz), 164.8, 162.8 (d, *J*<sub>C-F</sub> = 246.3 Hz), 154.6, 138.9 (d, *J*<sub>C-F</sub> = 6.2 Hz), 130.1 (d, *J*<sub>C-F</sub> = 7.7 Hz), 128.6, 123.8 (d, *J*<sub>C-F</sub> = 2.9 Hz), 123.4, 122.5, 120.4, 119.9 (d, *J*<sub>C-F</sub> = 21.5 Hz), 114.8 (d, *J*<sub>C-F</sub> = 22.0 Hz), 110.9, 101.2, 35.9, 35.7, 34.6, 26.8; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -111.9 (s). FT-IR: ν (cm<sup>-1</sup>) δ 2968, 2362, 1734, 1653, 1541, 1487, 1444, 1367, 1255, 1200, 1110, 1006. HRMS [ESI] calcd for C<sub>20</sub>H<sub>19</sub>FNaO<sub>2</sub> [M+Na]<sup>+</sup> 333.1261, found 333.1253.

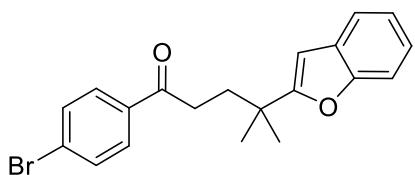


**2m:** 38.8 mg, 63% yield, yellow solid, m.p. 87-88 °C. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/100-1/50). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.88-7.82 (m, 2H), 7.54-7.49 (m, 1H), 7.45-7.40 (m, 1H), 7.26-7.17 (m, 2H), 7.08-7.02 (m, 2H), 6.45 (d, *J* = 0.8 Hz, 1H), 2.84-2.78 (m, 2H), 2.19-2.13 (m, 2H), 1.43 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ

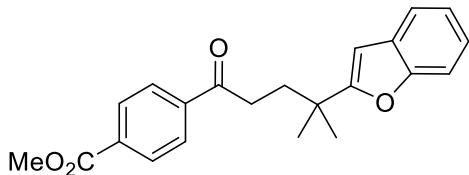
198.5, 165.6 (d,  $J_{C-F} = 252.8$  Hz), 164.9, 154.6, 133.2 (d,  $J_{C-F} = 3.0$  Hz), 130.6 (d,  $J_{C-F} = 9.1$  Hz), 128.6, 123.4, 122.5, 120.4, 115.5 (d,  $J_{C-F} = 21.6$  Hz), 110.9, 101.1, 35.9, 35.8, 34.4, 26.8;  $^{19}F$  NMR (376 MHz,  $CDCl_3$ )  $\delta$  -105.6 (s). FT-IR:  $\nu$  ( $cm^{-1}$ )  $\delta$  2967, 1684, 1506, 1455, 1368, 1255, 1167, 1083, 1012. HRMS [ESI] calcd for  $C_{20}H_{19}FNaO_2$  [ $M+Na$ ]<sup>+</sup> 333.1261, found 333.1262.



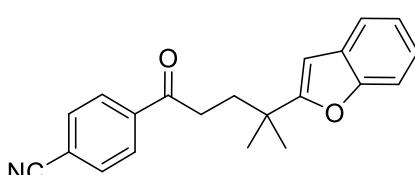
**2n:** 36.4 mg, 56% yield, yellow solid, m.p. 71-72 °C. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/100-1/50).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.78-7.74 (m, 2H), 7.53-7.49 (m, 1H), 7.42 (d,  $J = 8.0$  Hz, 1H), 7.37-7.33 (m, 2H), 7.25-7.17 (m, 2H), 6.45 (s, 1H), 2.83-2.77 (m, 2H), 2.19-2.12 (m, 2H), 1.43 (s, 6H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  198.9, 164.8, 154.6, 139.3, 135.0, 129.4, 128.7, 128.6, 123.4, 122.5, 120.4, 110.9, 101.2, 35.9, 35.7, 34.4, 26.8. FT-IR:  $\nu$  ( $cm^{-1}$ )  $\delta$  2975, 1682, 1585, 1464, 1371, 1255, 1214, 1111, 1067. HRMS [ESI] calcd for  $C_{20}H_{19}ClNaO_2$  [ $M+Na$ ]<sup>+</sup> 349.0966, found 349.0967.



**2o:** 39.7 mg, 54% yield, yellow solid, m.p. 55-56 °C. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/100-1/50).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.70-7.65 (m, 2H), 7.53-7.49 (m, 3H), 7.41 (d,  $J = 8.0$  Hz, 1H), 7.26-7.17 (m, 2H), 6.44 (s, 1H), 2.82-2.76 (m, 2H), 2.18-2.12 (m, 2H), 1.42 (s, 6H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  199.1, 164.8, 154.6, 135.4, 131.7, 129.6, 128.6, 128.0, 123.4, 122.5, 120.4, 110.9, 101.2, 35.9, 35.7, 34.4, 26.8. FT-IR:  $\nu$  ( $cm^{-1}$ )  $\delta$  2957, 1682, 1558, 1452, 1396, 1255, 1206, 1179, 1064, 1009. HRMS [ESI] calcd for  $C_{20}H_{19}BrNaO_2$  [ $M+Na$ ]<sup>+</sup> 393.0461, found 393.0465.

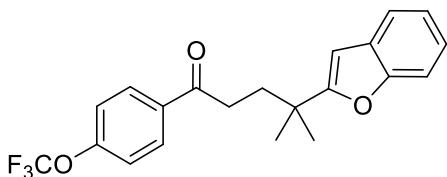


**2p:** 32.2 mg, 46% yield, yellow solid, m.p. 117-118 °C. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/100-1/50).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.04 (d,  $J = 8.4$  Hz, 2H), 7.87 (d,  $J = 8.0$  Hz, 2H), 7.51 (d,  $J = 7.2$  Hz, 1H), 7.42 (d,  $J = 8.0$  Hz, 1H), 7.26-7.17 (m, 2H), 6.45 (s, 1H), 3.93 (s, 3H), 2.89-2.83 (m, 2H), 2.20-2.14 (m, 2H), 1.43 (s, 6H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  199.6, 166.2, 164.8, 154.6, 140.0, 133.7, 129.7, 128.6, 127.9, 123.4, 122.5, 120.4, 110.9, 101.2, 52.4, 35.9, 35.6, 34.8, 26.8. FT-IR:  $\nu$  ( $cm^{-1}$ )  $\delta$  3419, 2975, 2160, 1977, 1715, 1642, 1504, 1456, 1370, 1193. HRMS [ESI] calcd for  $C_{22}H_{22}NaO_4$  [ $M+Na$ ]<sup>+</sup> 373.1410, found 373.1407.

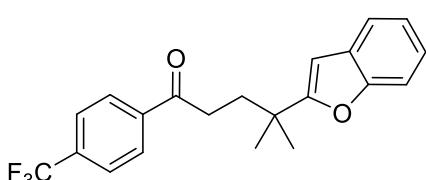


**2q:** 25.9 mg, 41% yield, yellow solid, m.p. 73-74 °C. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/80-1/40).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.89-7.85 (m, 2H), 7.68-7.65 (m, 2H), 7.52-7.48 (m, 1H), 7.40 (d,  $J = 7.6$  Hz, 1H), 7.26-7.17 (m, 2H), 6.44 (s, 1H), 2.87-2.81 (m, 2H), 2.19-2.14 (m, 2H), 1.43 (s, 6H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  198.6, 164.5, 154.6, 139.6, 132.3, 128.5, 128.4, 123.5, 122.6, 120.5, 117.9, 116.1, 110.8, 101.3, 35.9,

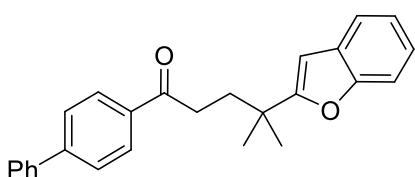
35.5, 34.8, 26.8. FT-IR:  $\nu$  (cm<sup>-1</sup>)  $\delta$  2965, 1688, 1607, 1508, 1455, 1387, 1294, 1164, 1079, 1002. HRMS [ESI] calcd for C<sub>21</sub>H<sub>19</sub>NNaO<sub>2</sub> [M+Na]<sup>+</sup> 340.1308, found 340.1301.



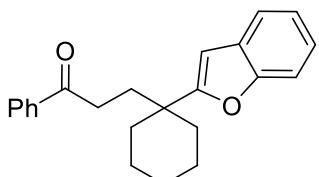
**2r:** 31.7 mg, 42% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/100-1/50). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.89-7.84 (m, 2H), 7.53-7.49 (m, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.26-7.23 (m, 1H), 7.23-7.17 (m, 3H), 6.45 (d, *J* = 0.8 Hz, 1H), 2.85-2.79 (m, 2H), 2.20-2.14 (m, 2H), 1.43 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  198.5, 164.8, 154.6, 152.4 (q, *J*<sub>C-F</sub> = 1.7 Hz), 135.0, 130.0, 128.6, 123.4, 122.5, 120.4, 120.2, 120.2 (q, *J*<sub>C-F</sub> = 257.1 Hz), 110.9, 101.2, 35.9, 35.7, 34.5, 26.8. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -57.6 (s). FT-IR:  $\nu$  (cm<sup>-1</sup>)  $\delta$  2971, 2358, 1688, 1541, 1471, 1389, 1302, 1211, 1083. HRMS [ESI] calcd for C<sub>21</sub>H<sub>19</sub>F<sub>3</sub>NaO<sub>3</sub> [M+Na]<sup>+</sup> 399.1179, found 399.1176.



**2s:** 34.9 mg, 48% yield, yellow solid, m.p. 49-50 °C. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/100-1/50). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.91 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.53-7.49 (m, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.26-7.17 (m, 2H), 6.45 (s, 1H), 2.89-2.83 (m, 2H), 2.21-2.15 (m, 2H), 1.44 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  199.1, 164.7, 154.6, 139.4, 134.2 (q, *J*<sub>C-F</sub> = 32.4 Hz), 128.6, 128.3, 125.5 (q, *J*<sub>C-F</sub> = 3.6 Hz), 123.6 (q, *J*<sub>C-F</sub> = 271.0 Hz), 123.5, 122.5, 120.5, 110.9, 101.3, 35.9, 35.6, 34.8, 26.8. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -63.1 (s). FT-IR:  $\nu$  (cm<sup>-1</sup>)  $\delta$  2976, 1687, 1541, 1470, 1390, 1320, 1253, 1166, 1109, 1066, 1016. HRMS [ESI] calcd for C<sub>21</sub>H<sub>19</sub>F<sub>3</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup> 383.1229, found 383.1228.

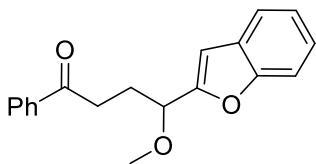


**2t:** 44.1 mg, 60% yield, white solid, m.p. 129-130 °C. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/100-1/50). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.94-7.90 (m, 2H), 7.64-7.59 (m, 4H), 7.55-7.52 (m, 1H), 7.50-7.44 (m, 3H), 7.43-7.37 (m, 1H), 7.28-7.19 (m, 2H), 6.48 (s, 1H), 2.92-2.85 (m, 2H), 2.25-2.18 (m, 2H), 1.46 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  199.7, 165.0, 154.7, 145.5, 139.9, 135.5, 128.9, 128.6, 128.6, 128.1, 127.2, 127.1, 123.4, 122.5, 120.4, 110.9, 101.1, 36.0, 35.8, 34.5, 26.8. FT-IR:  $\nu$  (cm<sup>-1</sup>)  $\delta$  2959, 2925, 2217, 1977, 1675, 1604, 1576, 1453, 1301, 1255. HRMS [ESI] calcd for C<sub>26</sub>H<sub>24</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup> 391.1669, found 391.1668.

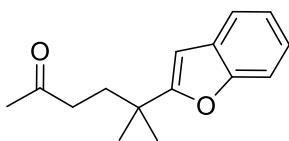


**2u:** 28.5 mg, 43% yield, yellow solid, m.p. 60-61 °C. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/100-1/50). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.78-7.73 (m, 2H), 7.54-7.46 (m, 2H), 7.45-7.41 (m, 1H), 7.38-7.31 (m, 2H), 7.26-7.17 (m, 2H), 6.50 (s, 1H), 2.80-2.74 (m, 2H), 2.24-2.15 (m, 2H), 2.14-2.07 (m, 2H), 1.66-1.35 (m, 8H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  200.4, 163.3, 154.4, 136.8, 132.8, 128.7, 128.4, 128.0, 123.2, 122.4, 120.3, 110.9, 103.1, 39.9, 35.0, 33.5, 26.2, 22.4. FT-IR:  $\nu$

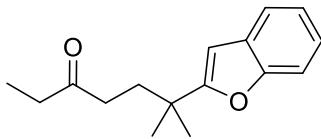
(cm<sup>-1</sup>) δ 2932, 2104, 1679, 1580, 1451, 1307, 1256, 1202, 1171, 1090. HRMS [ESI] calcd for C<sub>23</sub>H<sub>24</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup> 355.1669, found 355.1673.



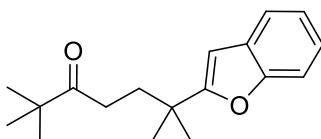
**2v:** 18.2 mg, 31% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/100-1/50). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.97-7.93 (m, 2H), 7.58-7.52 (m, 2H), 7.50-7.42 (m, 3H), 7.31-7.20 (m, 2H), 6.69 (s, 1H), 4.48 (dd, *J* = 7.6, 6.0 Hz, 1H), 3.35 (s, 3H), 3.20-3.05 (m, 2H), 2.48-2.31 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 199.5, 156.5, 155.0, 136.9, 133.0, 128.5, 128.0, 127.9, 124.2, 122.8, 121.0, 111.4, 104.8, 76.1, 56.9, 34.1, 28.5. FT-IR: ν (cm<sup>-1</sup>) δ 2933, 1678, 1581, 1454, 1353, 1279, 1199, 1097, 1022. HRMS [ESI] calcd for C<sub>19</sub>H<sub>18</sub>NaO<sub>3</sub> [M+Na]<sup>+</sup> 317.1148, found 317.1156.



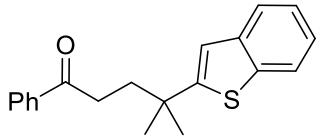
**2w:** 16.2 mg, 35% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/100-1/50). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.52-7.48 (m, 1H), 7.44-7.40 (m, 1H), 7.25-7.16 (m, 2H), 6.39 (s, 1H), 2.34-2.28 (m, 2H), 2.07 (s, 3H), 2.02-1.96 (m, 2H), 1.36 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 208.6, 165.0, 154.6, 128.6, 123.3, 122.4, 120.4, 110.9, 100.9, 39.5, 35.6, 34.9, 29.9, 26.7. FT-IR: ν (cm<sup>-1</sup>) δ 2968, 2361, 1716, 1653, 1541, 1471, 1387, 1301, 1204, 1166, 1083. HRMS [ESI] calcd for C<sub>15</sub>H<sub>19</sub>O<sub>2</sub> [M+H]<sup>+</sup> 231.1380, found 231.1382.



**2x:** 17.6 mg, 36% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/100-1/50). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.49 (d, *J* = 7.2 Hz, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.25-7.15 (m, 2H), 6.39 (s, 1H), 2.38-2.31 (m, 2H), 2.31-2.24 (m, 2H), 2.03-1.96 (m, 2H), 1.36 (s, 6H), 0.99 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 211.3, 165.1, 154.6, 128.6, 123.3, 122.4, 120.3, 110.9, 100.8, 38.1, 35.9, 35.7, 35.0, 26.7, 7.8. FT-IR: ν (cm<sup>-1</sup>) δ 2969, 1714, 1580, 1454, 1388, 1254, 1167, 1111, 1008. HRMS [ESI] calcd for C<sub>16</sub>H<sub>20</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup> 267.1356, found 267.1362.

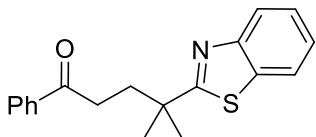


**2y:** 25.5 mg, 47% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/100-1/50). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.52-7.48 (m, 1H), 7.44-7.40 (m, 1H), 7.25-7.16 (m, 2H), 6.40 (d, *J* = 0.8 Hz, 1H), 2.39-2.34 (m, 2H), 2.01-1.96 (m, 2H), 1.37 (s, 6H), 1.07 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 215.7, 165.3, 154.6, 128.6, 123.2, 122.3, 120.3, 110.8, 100.7, 44.3, 35.8, 35.4, 32.1, 26.8, 26.4. FT-IR: ν (cm<sup>-1</sup>) δ 2966, 1704, 1581, 1470, 1388, 1300, 1204, 1111, 1081, 1049. HRMS [ESI] calcd for C<sub>18</sub>H<sub>24</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup> 295.1669, found 295.1673.

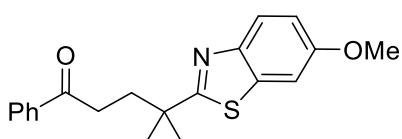


**2z:** 19.7 mg, 32% yield, yellow solid, m.p. 52-53 °C. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/100-1/50). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.88-7.84 (m, 2H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.54-7.48 (m, 1H), 7.42-7.36 (m, 2H), 7.35-7.24 (m, 2H), 7.07 (s, 1H), 2.91-2.86 (m, 2H), 2.20-2.14 (m, 2H), 1.51 (s,

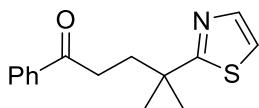
6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  200.1, 155.5, 139.9, 139.1, 136.8, 132.9, 128.5, 128.0, 124.1, 123.6, 123.0, 122.2, 119.2, 38.9, 37.7, 34.5, 29.9. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  2962, 1678, 1579, 1412, 1319, 1298, 1179, 1074. HRMS [ESI] calcd for  $\text{C}_{20}\text{H}_{20}\text{NaOS} [\text{M}+\text{Na}]^+$  331.1127, found 331.1132.



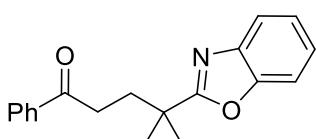
**2aa:** 31.2 mg, 50% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/100-1/50).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 (d,  $J$  = 8.0 Hz, 1H), 7.91-7.88 (m, 2H), 7.88-7.85 (m, 1H), 7.54-7.48 (m, 1H), 7.48-7.43 (m, 1H), 7.43-7.37 (m, 2H), 7.37-7.33 (m, 1H), 2.99-2.93 (m, 2H), 2.32-2.27 (m, 2H), 1.58 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  199.8, 179.9, 153.1, 136.8, 135.0, 132.9, 128.5, 128.1, 125.8, 124.7, 122.8, 121.5, 41.1, 37.9, 34.3, 28.8. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  2927, 2329, 1680, 1578, 1490, 1388, 1276, 1181, 1083, 1013. HRMS [ESI] calcd for  $\text{C}_{19}\text{H}_{20}\text{NOS} [\text{M}+\text{H}]^+$  310.1260, found 310.1265.



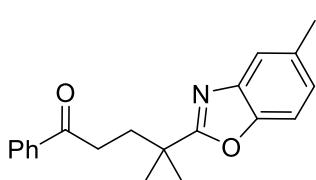
**2ab:** 30.6 mg, 45% yield, yellow solid, m.p. 50-51 °C. Purification by flash column chromatography (eluent: Acetone/Petroleum ether = 1/100-1/50).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91-7.84 (m, 3H), 7.54-7.48 (m, 1H), 7.43-7.37 (m, 2H), 7.32 (d,  $J$  = 2.4 Hz, 1H), 7.05 (dd,  $J$  = 8.8, 2.4 Hz, 1H), 3.87 (s, 3H), 2.98-2.92 (m, 2H), 2.28-2.23 (m, 2H), 1.55 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  199.9, 177.3, 157.3, 147.5, 136.8, 136.3, 132.9, 128.5, 128.1, 123.2, 115.0, 104.2, 55.8, 40.9, 37.9, 34.3, 28.7. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  2923, 1682, 1579, 1447, 1386, 1293, 1217, 1156, 1032. HRMS [ESI] calcd for  $\text{C}_{20}\text{H}_{21}\text{NNaO}_2\text{S} [\text{M}+\text{Na}]^+$  362.1185, found 362.1181.



**2ac:** 27.5 mg, 53% yield, yellow solid, m.p. 55-56 °C. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/100-1/50).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90-7.86 (m, 2H), 7.70 (d,  $J$  = 3.6 Hz, 1H), 7.55-7.49 (m, 1H), 7.44-7.38 (m, 2H), 7.23 (d,  $J$  = 3.2 Hz, 1H), 2.92-2.87 (m, 2H), 2.22-2.17 (m, 2H), 1.51 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  199.9, 179.4, 142.0, 136.8, 132.9, 128.5, 128.0, 118.0, 40.2, 38.1, 34.2, 28.9. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  2962, 1733, 1677, 1580, 1541, 1472, 1413, 1370, 1255, 1210, 1155, 1040. HRMS [ESI] calcd for  $\text{C}_{15}\text{H}_{17}\text{NNaOS} [\text{M}+\text{Na}]^+$  282.0923, found 282.0930.

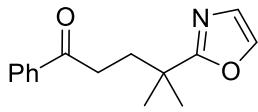


**2ad:** 35.1 mg, 60% yield, yellow solid, m.p. 61-62 °C. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/100-1/50).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (d,  $J$  = 7.6 Hz, 2H), 7.73-7.67 (m, 1H), 7.54-7.46 (m, 2H), 7.43-7.37 (m, 2H), 7.34-7.27 (m, 2H), 2.98-2.91 (m, 2H), 2.32-2.24 (m, 2H), 1.55 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  199.5, 171.9, 150.8, 141.1, 136.7, 133.0, 128.5, 128.0, 124.6, 124.1, 119.8, 110.4, 37.1, 35.6, 34.2, 26.5. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  2935, 1679, 1596, 1456, 1394, 1283, 1212, 1182, 1137, 1027, 1002. HRMS [ESI] calcd for  $\text{C}_{19}\text{H}_{19}\text{NNaO}_2 [\text{M}+\text{Na}]^+$  316.1308, found 316.1306.

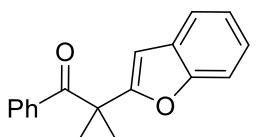


**2ae:** 19.5 mg, 32% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/100-1/50).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89-7.86 (m, 2H), 7.54-7.47 (m, 2H),

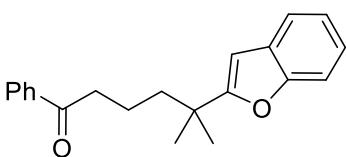
7.43-7.33 (m, 3H), 7.13-7.09 (m, 1H), 2.96-2.90 (m, 2H), 2.46 (s, 3H), 2.29-2.23 (m, 2H), 1.54 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  199.6, 172.0, 149.0, 141.3, 136.8, 133.9, 133.0, 128.5, 128.0, 125.6, 119.7, 109.8, 37.1, 35.7, 34.3, 26.5, 21.4. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  2970, 1683, 1565, 1474, 1371, 1307, 1277, 1208, 1156, 1021. HRMS [ESI] calcd for  $\text{C}_{20}\text{H}_{21}\text{NNaO}_2$  [ $\text{M}+\text{Na}$ ] $^+$  330.1465, found 330.1462.



**2af:** 16.9 mg, 35% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/100-1/50).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91-7.87 (m, 2H), 7.58 (d,  $J$  = 0.8 Hz, 1H), 7.56-7.50 (m, 1H), 7.45-7.40 (m, 2H), 7.02 (d,  $J$  = 0.4 Hz, 1H), 2.90-2.84 (m, 2H), 2.17-2.12 (m, 2H), 1.44 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  199.7, 169.8, 138.3, 136.8, 132.9, 128.5, 128.0, 126.6, 36.6, 35.9, 34.2, 26.5. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  2968, 1676, 1562, 1413, 1392, 1262, 1181, 1029. HRMS [ESI] calcd for  $\text{C}_{15}\text{H}_{17}\text{NNaO}_2$  [ $\text{M}+\text{Na}$ ] $^+$  266.1151, found 266.1156.



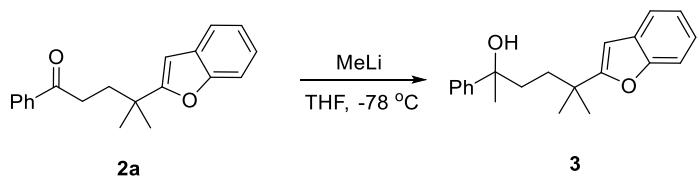
**2ag:** 10.6 mg, 20% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/100-1/50).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64-7.60 (m, 2H), 7.57-7.53 (m, 1H), 7.41-7.35 (m, 2H), 7.26-7.20 (m, 4H), 6.65 (s, 1H), 1.71 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  200.9, 161.6, 154.7, 136.5, 131.9, 128.7, 128.4, 128.2, 123.9, 122.8, 120.8, 111.3, 101.7, 48.4, 25.7. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  2928, 1717, 1654, 1558, 1508, 1464, 1364, 1251, 1168, 1110, 1003. HRMS [ESI] calcd for  $\text{C}_{18}\text{H}_{16}\text{NaO}_2$  [ $\text{M}+\text{Na}$ ] $^+$  287.1043, found 287.1040.



**2ai:** 15.4 mg, 25% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/100-1/50).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90-7.85 (m, 2H), 7.55-7.46 (m, 2H), 7.44-7.38 (m, 3H), 7.23-7.14 (m, 2H), 6.40 (d,  $J$  = 0.8 Hz, 1H), 2.90 (t,  $J$  = 7.2 Hz, 2H), 1.82-1.76 (m, 2H), 1.70-1.62 (m, 2H), 1.39 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  200.1, 165.8, 154.6, 137.0, 132.8, 128.8, 128.5, 127.9, 123.1, 122.3, 120.3, 110.8, 100.6, 41.1, 38.8, 36.2, 26.7, 19.5. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  2965, 1684, 1580, 1408, 1363, 1254, 1208, 1110, 1002. HRMS [ESI] calcd for  $\text{C}_{21}\text{H}_{22}\text{NaO}_2$  [ $\text{M}+\text{Na}$ ] $^+$  329.1512, found 329.1513.

## 5. Synthetic applications

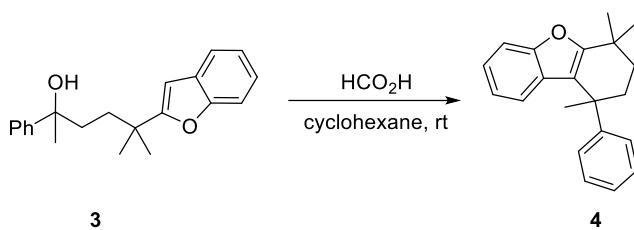
### a. construction of ring-fused heterocycle



To a stirred solution of **2a** (0.5 mmol, 1.0 equiv.) at -78 °C in dry THF (5.0 mL), MeLi (1.3 M, 0.55 mmol, 1.1 equiv.) was added dropwise. The mixture was stirred for an additional 1 h at -78 °C. The flask was moved to the ice bath overnight, during which time the reaction warmed up to room temperature. After workup with water, the crude material was extracted with EtOAc. The

combined organic extracts were washed by brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, concentrated, and purified by flash column chromatography on silica gel to afford the product as yellow oil.

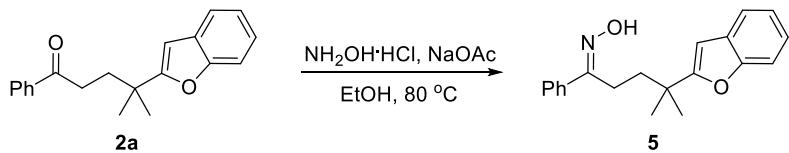
**3:** 136.2 mg, 88% yield, yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.48-7.44 (m, 1H), 7.39-7.35 (m, 1H), 7.34-7.25 (m, 4H), 7.24-7.13 (m, 3H), 6.30 (d, *J* = 0.8 Hz, 1H), 1.72-1.62 (m, 4H), 1.47 (s, 3H), 1.29 (s, 3H), 1.27 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.6, 154.5, 147.5, 128.7, 128.1, 126.5, 124.7, 123.1, 122.3, 120.3, 110.8, 100.7, 74.5, 38.8, 35.8, 35.5, 30.5, 26.8, 26.6. FT-IR: ν (cm<sup>-1</sup>) δ 2968, 1580, 1470, 1295, 1167, 1066, 1028, 1008. HRMS [ESI] calcd for C<sub>21</sub>H<sub>24</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup> 331.1669, found 331.1666.



Alcohol **3** (123.2 mg, 0.4 mmol) was dissolved in cyclohexane (1.5 mL), and formic acid (98%) (0.1 mL) was added. The mixture was stirred vigorously for 3 h at room temperature under inert atmosphere. Ice water was added, the aqueous layer was extracted with ether. The combined extracts were washed with 5% NaHCO<sub>3</sub> solution and brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, concentrated, and purified by flash column chromatography on silica gel to afford the product as a yellow oil.

**4:** 110.3 mg, 95% yield, yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.51-7.47 (m, 1H), 7.32-7.26 (m, 4H), 7.25-7.19 (m, 2H), 7.12-7.04 (m, 2H), 2.15-2.07 (m, 1H), 2.06-1.97 (m, 1H), 1.84 (s, 3H), 1.77-1.69 (m, 1H), 1.67-1.59 (m, 1H), 1.44 (s, 3H), 1.42 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 160.7, 154.5, 148.2, 128.1, 127.7, 126.7, 125.8, 122.8, 121.9, 120.8, 117.4, 111.0, 40.5, 39.0, 35.7, 32.4, 27.8, 27.3, 27.2. FT-IR: ν (cm<sup>-1</sup>) δ 2964, 1609, 1452, 1361, 1242, 1170, 1123, 1108, 1026. HRMS [EI] calcd for C<sub>21</sub>H<sub>22</sub>O [M]<sup>+</sup> 290.1671, found 290.1672.

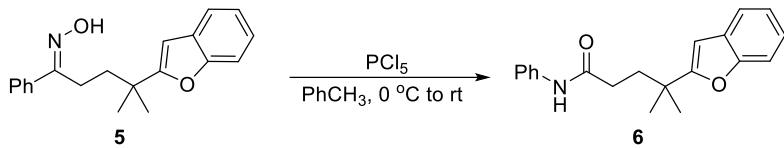
### b. Beckmann rearrangement



To a mixture of hydroxylamine hydrochloride (0.4 mmol, 2.0 equiv.), NaOAc (0.8 mmol, 4.0 equiv.), EtOH (2.0 mL) was added **2a** (0.2 mmol, 1.0 equiv.), and the mixture was stirred at 80 °C for 3 h. The reaction mixture was cooled down to room temperature, and then EtOH was removed under reduced pressure. The resulting mixture was extracted with EtOAc. The combined organic extracts were washed by brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, concentrated, and purified by flash column chromatography on silica gel to afford the product as a white solid.

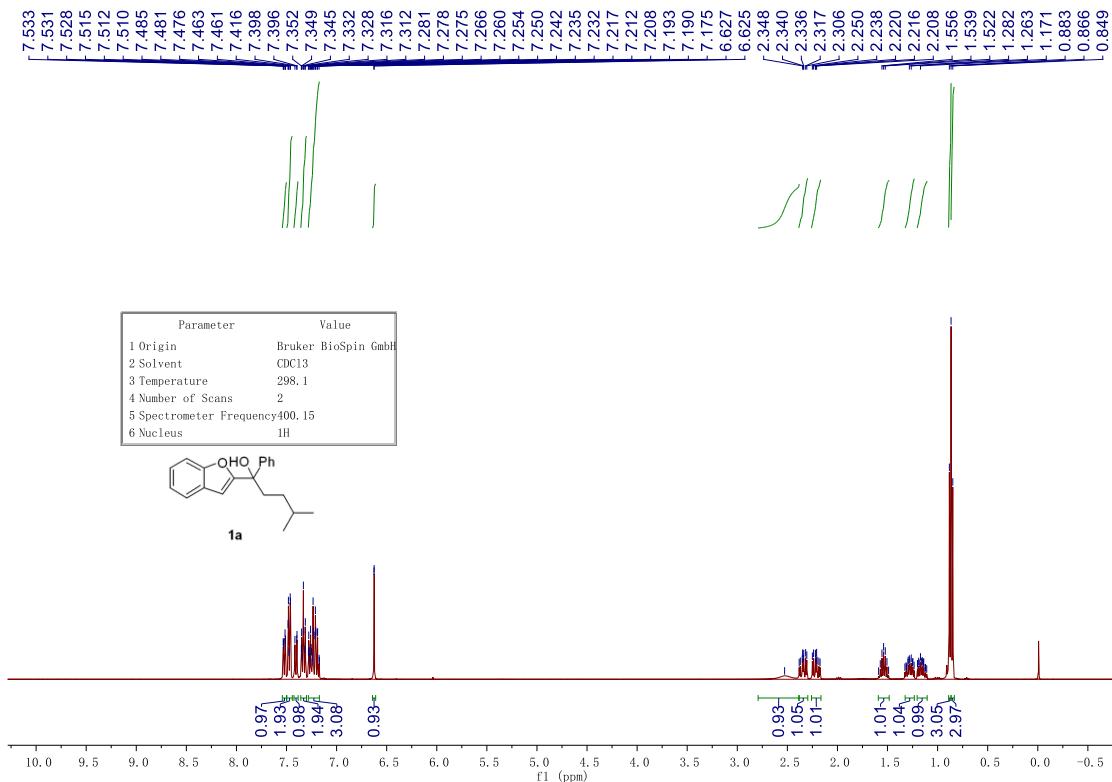
**5:** 56.7 mg, 92% yield, white solid, m.p. 115-116 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.97 (br, 1H), 7.51-7.47 (m, 1H), 7.47-7.40 (m, 3H), 7.34-7.23 (m, 3H), 7.23-7.15 (m, 2H), 6.44 (d, *J* = 0.4 Hz, 1H), 2.69-2.63 (m, 2H), 1.99-1.93 (m, 2H), 1.41 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.1, 159.5, 154.6, 135.3, 129.2, 128.7, 128.5, 126.1, 123.3, 122.4, 120.4, 110.8, 101.2, 37.3, 36.5, 26.5,

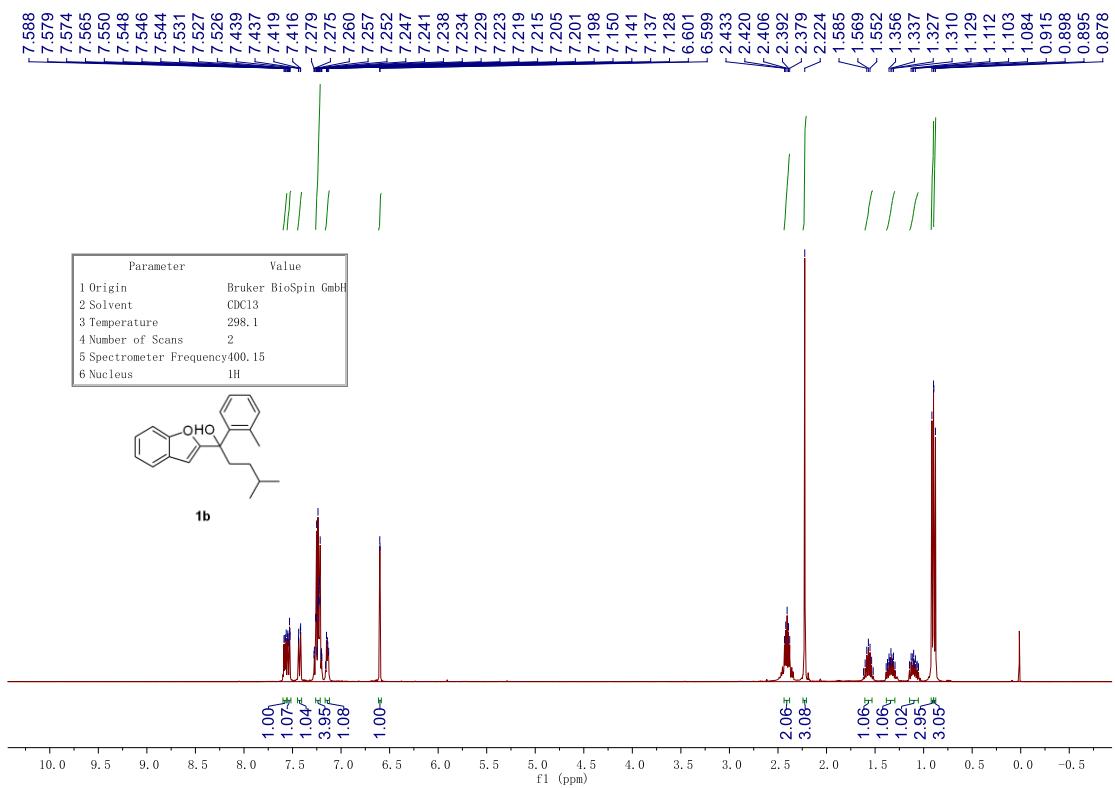
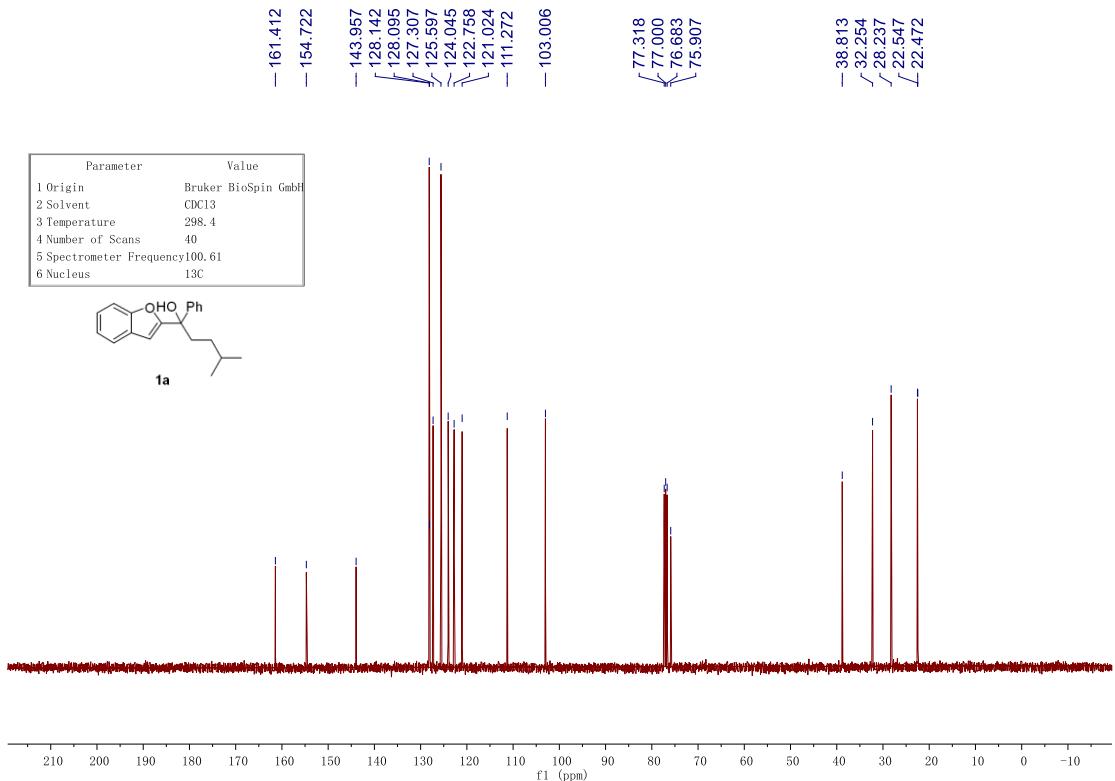
22.0. FT-IR:  $\nu$  (cm<sup>-1</sup>)  $\delta$  2925, 1454, 1324, 1304, 1252, 1166, 1081. HRMS [ESI] calcd for C<sub>20</sub>H<sub>22</sub>NO<sub>2</sub> [M+H]<sup>+</sup> 308.1645, found 308.1643.

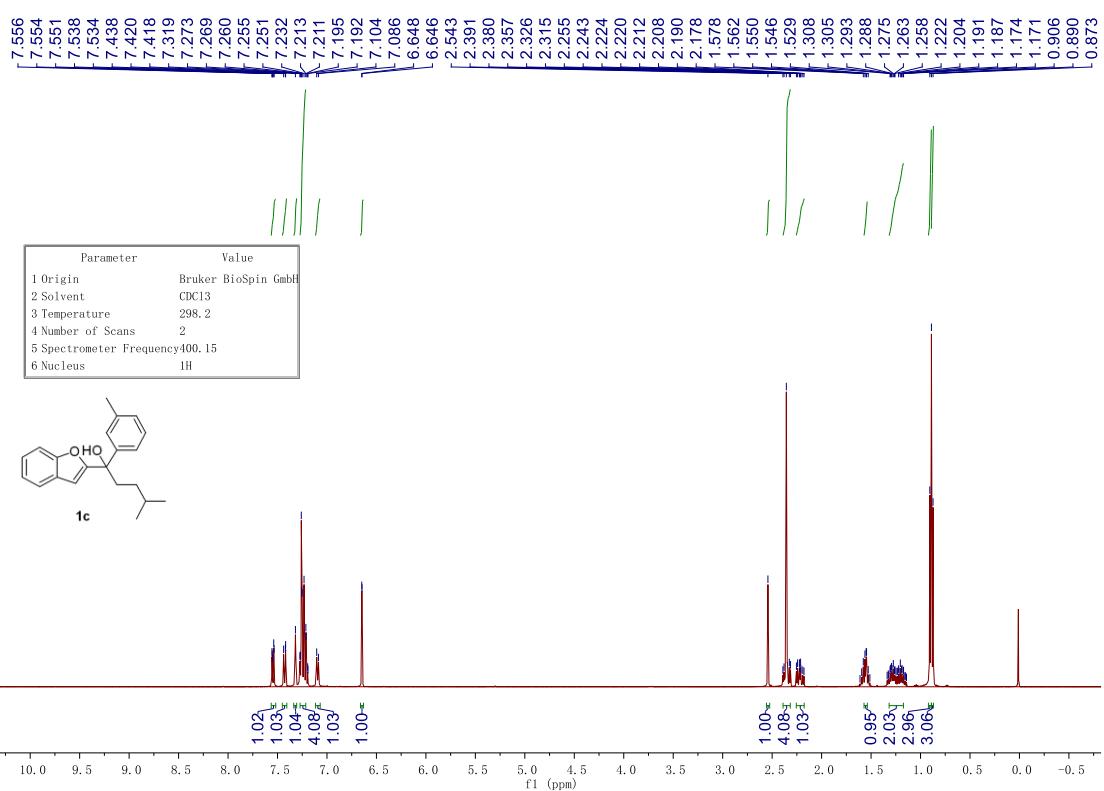
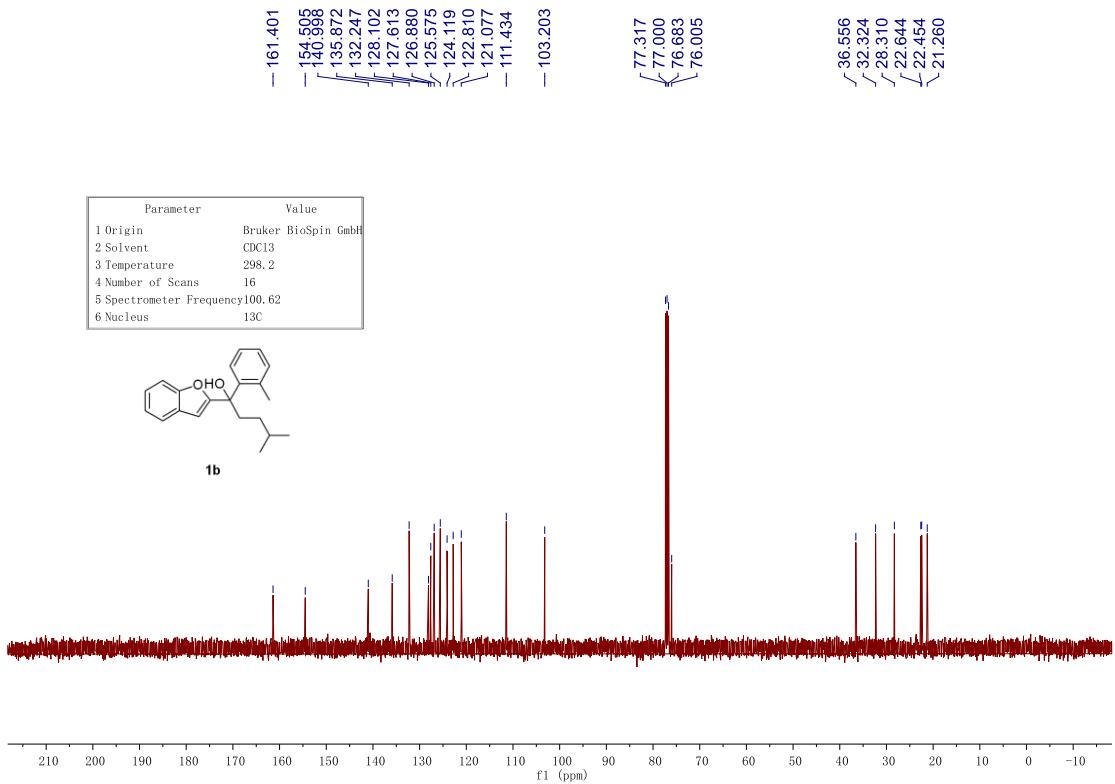


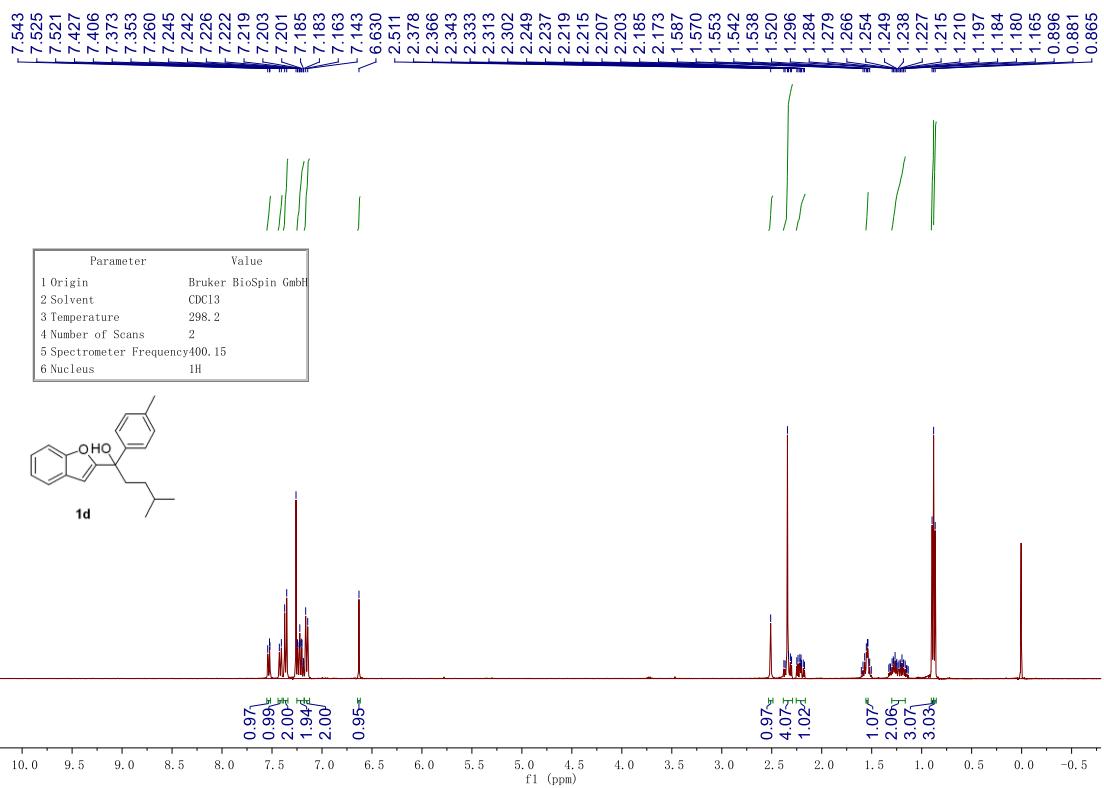
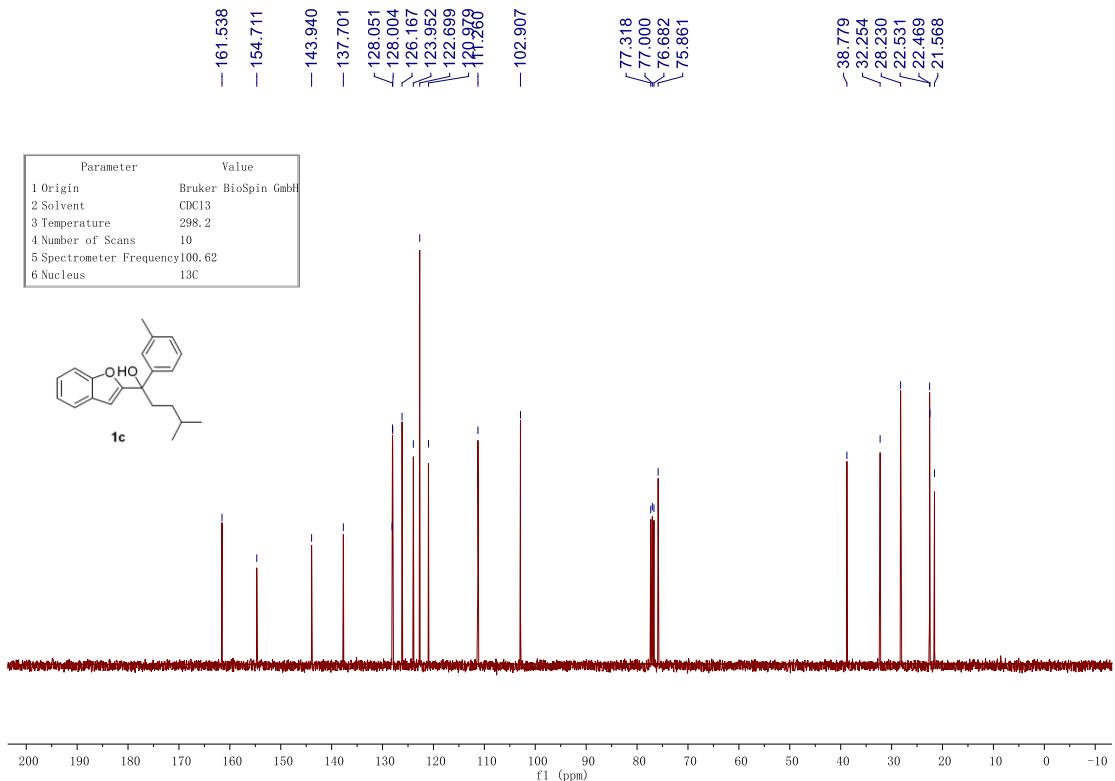
To a solution of **5** (0.2 mmol, 1.0 equiv.) in toluene (2.0 mL) was added PCl<sub>5</sub> (0.4 mmol, 2.0 equiv.) at 0 °C. After ambient temperature was reached, the reaction mixture was stirred for 4 h, diluted with water and extracted with DCM. Organic layers were washed with 1 M KHSO<sub>4</sub> solution, saturated NaHCO<sub>3</sub> solution, brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, concentrated, and purified by flash column chromatography on silica gel to afford the product as a yellow solid.  
**6:** 31.3 mg, 51% yield, yellow solid, m.p. 116-117 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.52-7.48 (m, 1H), 7.45-7.40 (m, 3H), 7.30-7.24 (m, 2H), 7.23-7.16 (m, 2H), 7.10-7.04 (m, 2H), 6.42 (s, 1H), 2.22-2.11 (m, 4H), 1.40 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  171.0, 164.9, 154.6, 137.8, 128.9, 128.6, 124.1, 123.4, 122.5, 120.4, 119.6, 111.0, 101.1, 36.8, 35.9, 33.5, 26.7. FT-IR:  $\nu$  (cm<sup>-1</sup>)  $\delta$  2922, 1680, 1598, 1488, 1387, 1304, 1208, 1139, 1081. HRMS [ESI] calcd for C<sub>20</sub>H<sub>21</sub>NNaO<sub>2</sub> [M+Na]<sup>+</sup> 330.1465, found 330.1455.

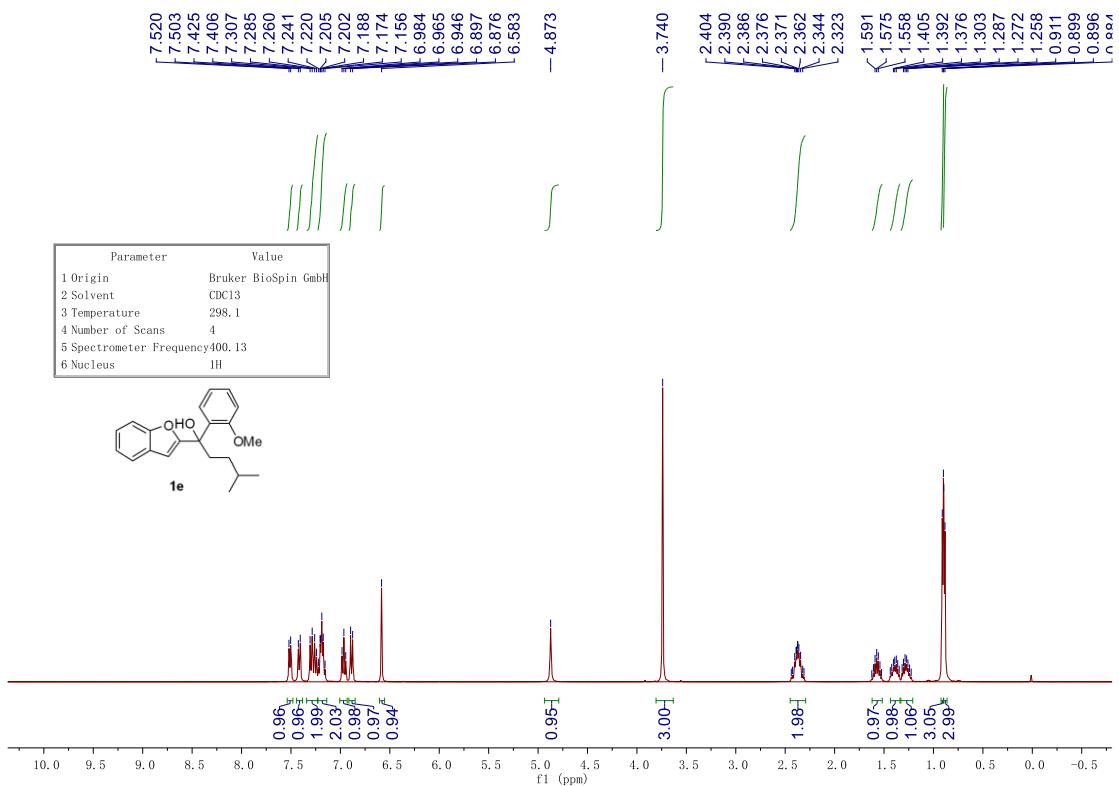
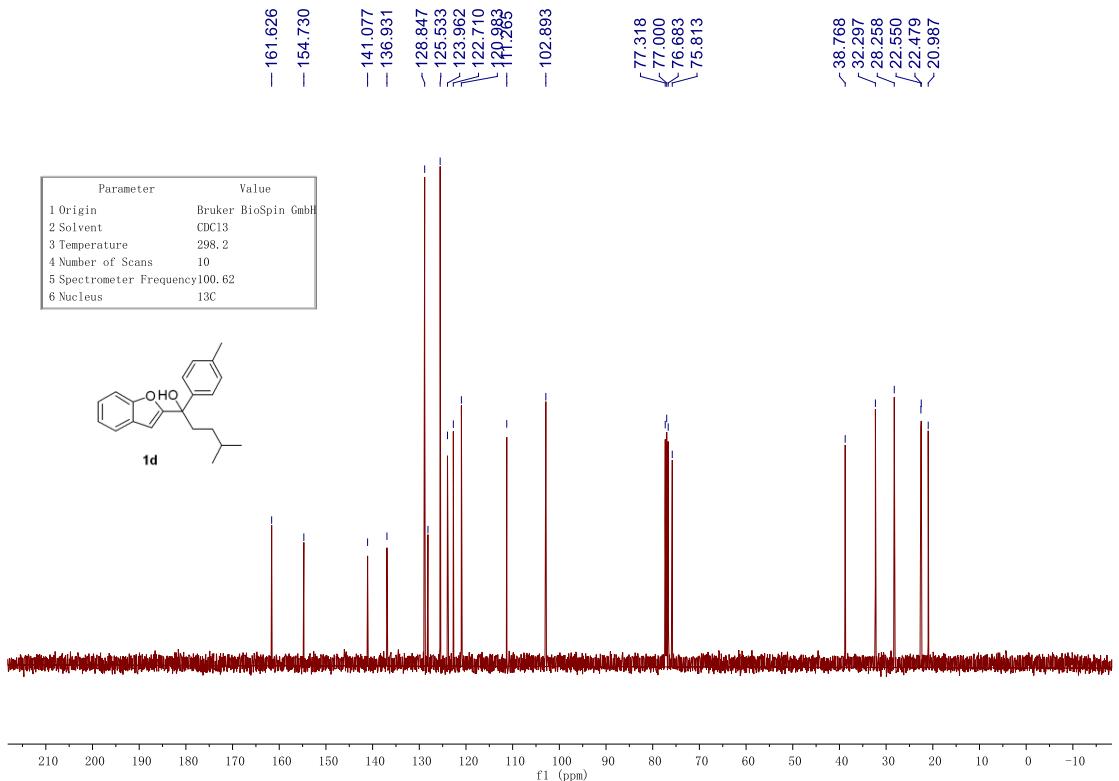
## 6. <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR spectra

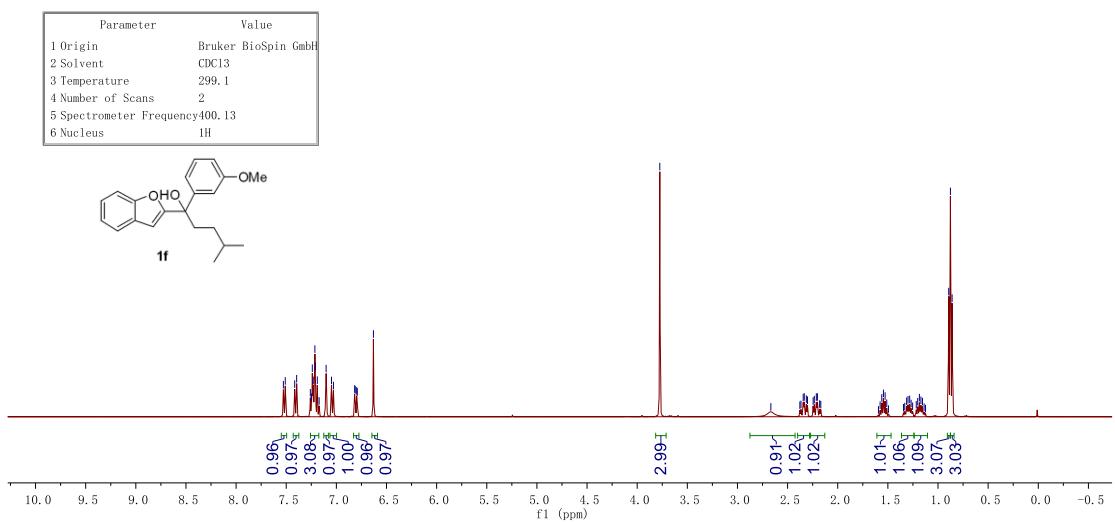
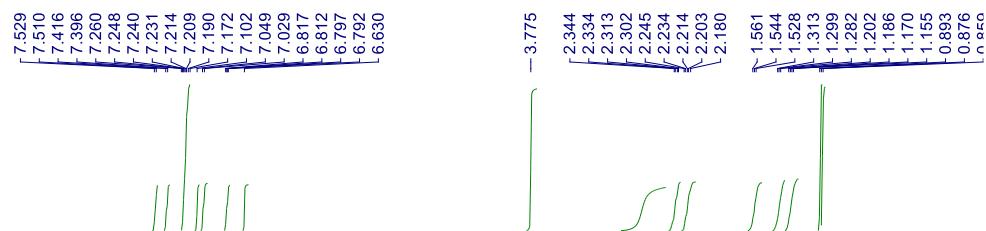
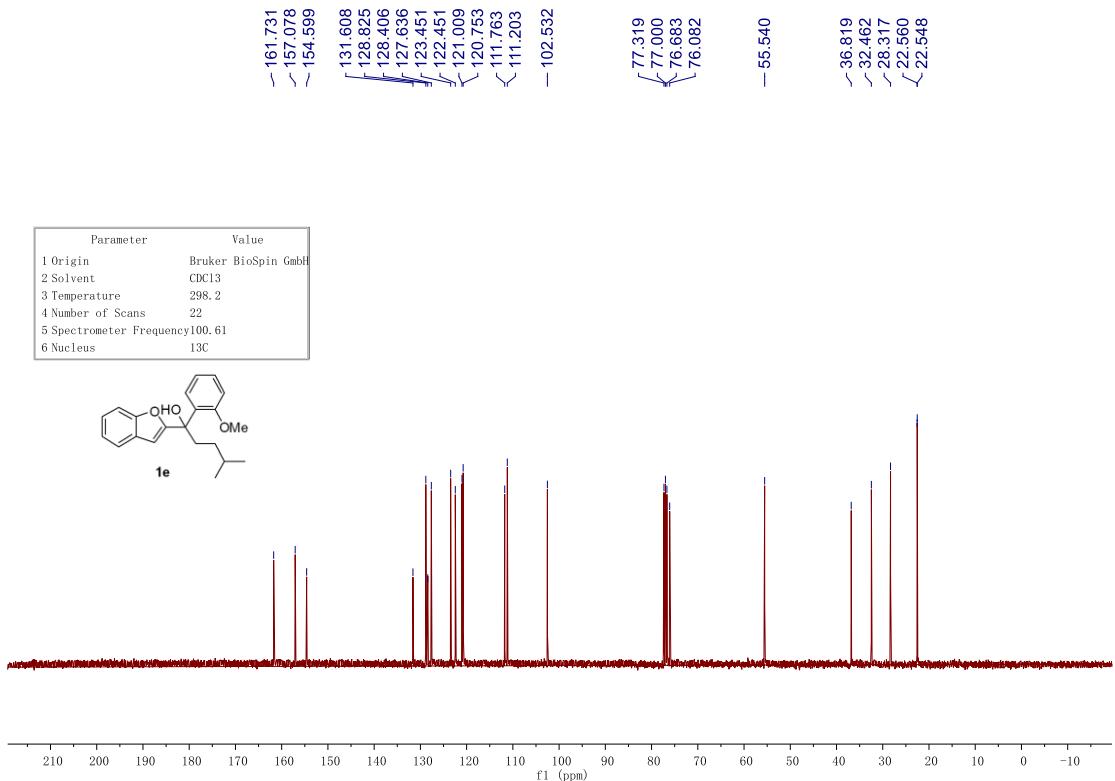


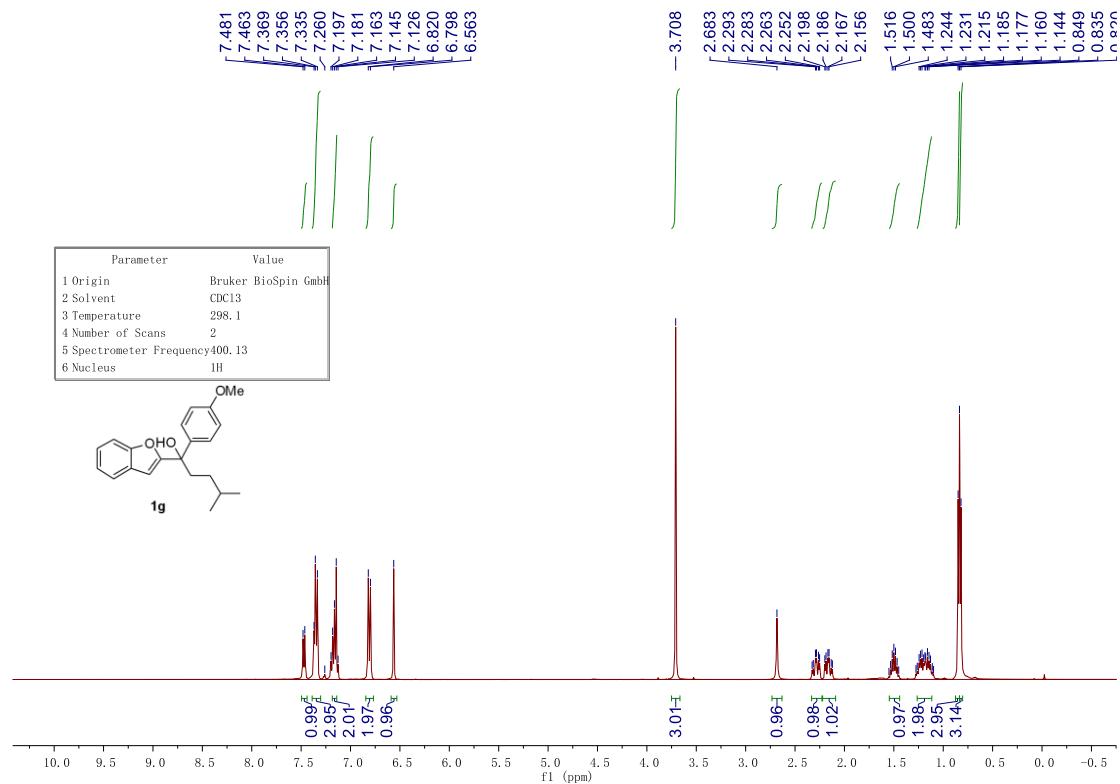
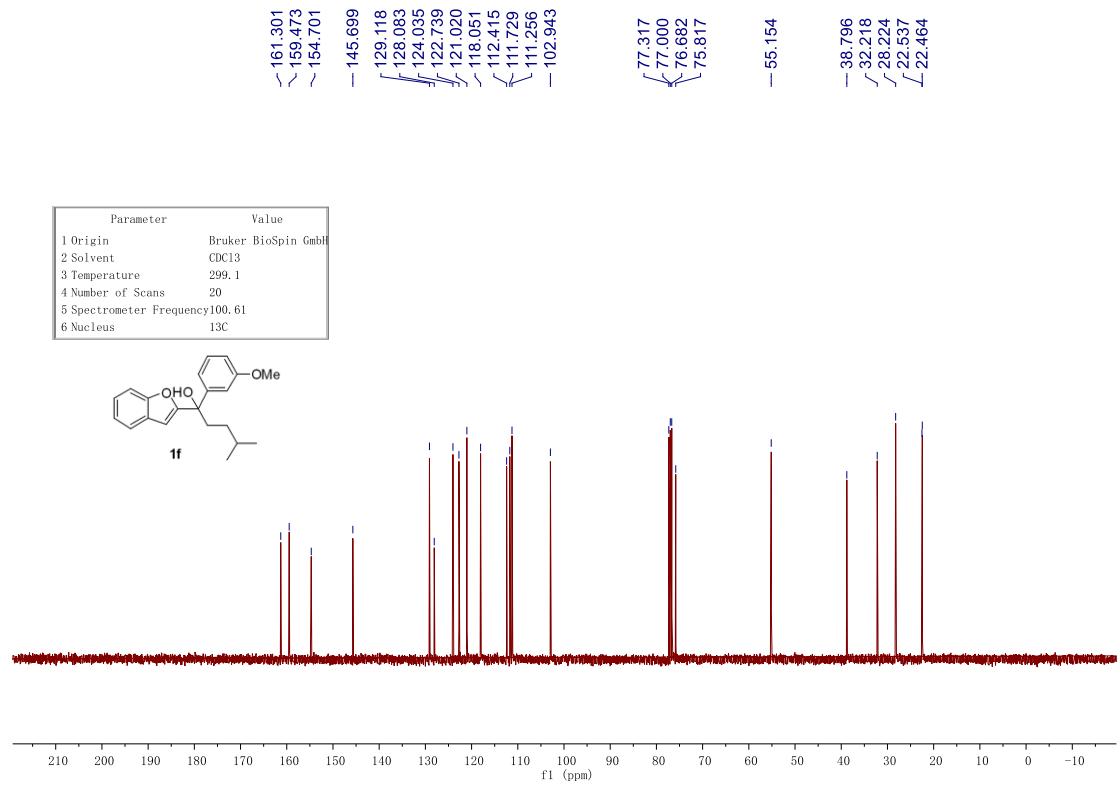


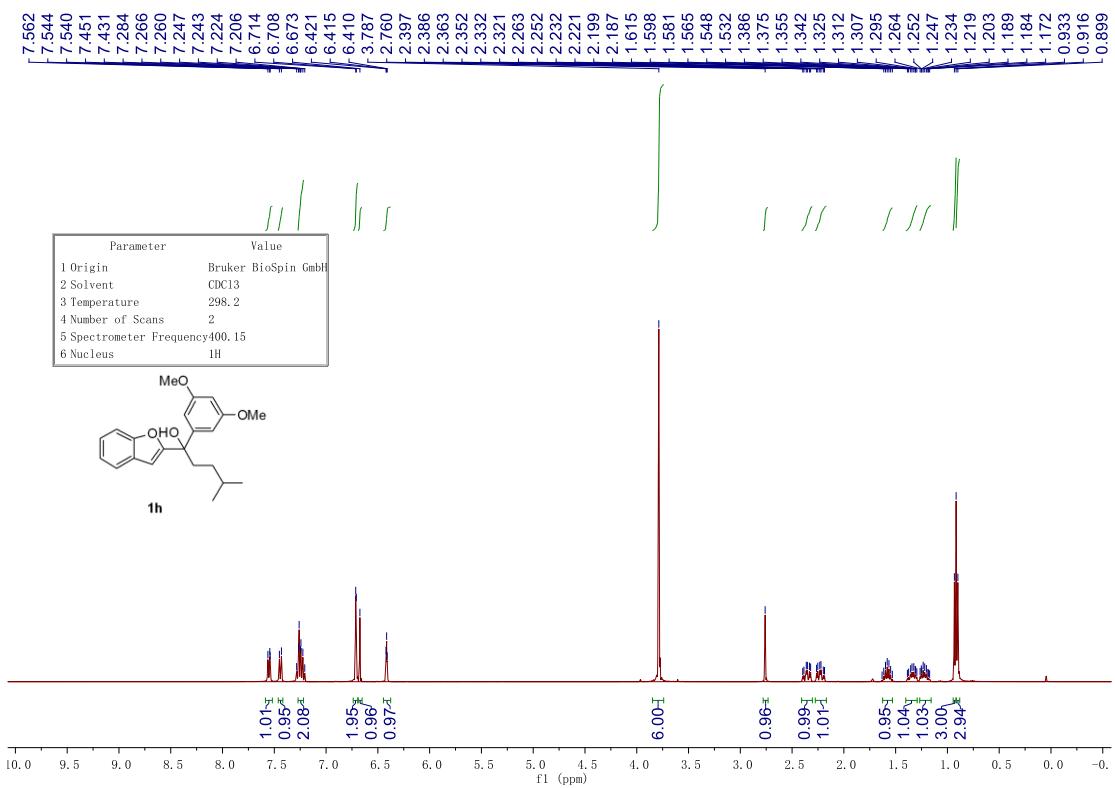
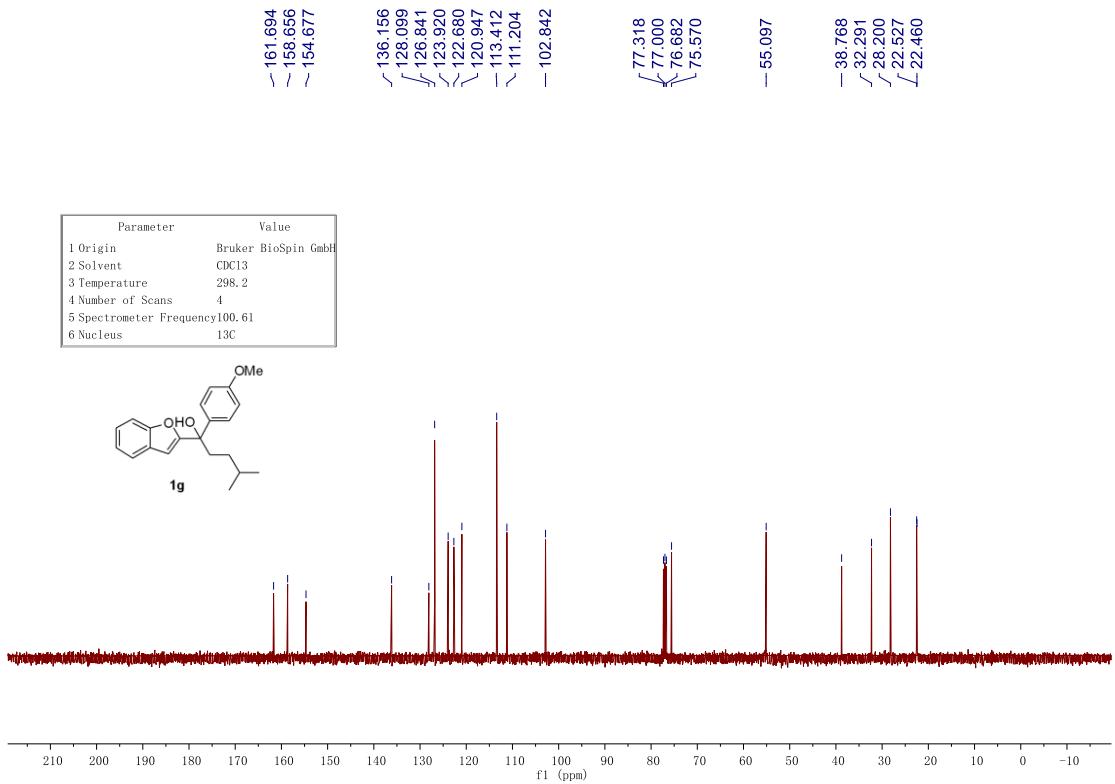


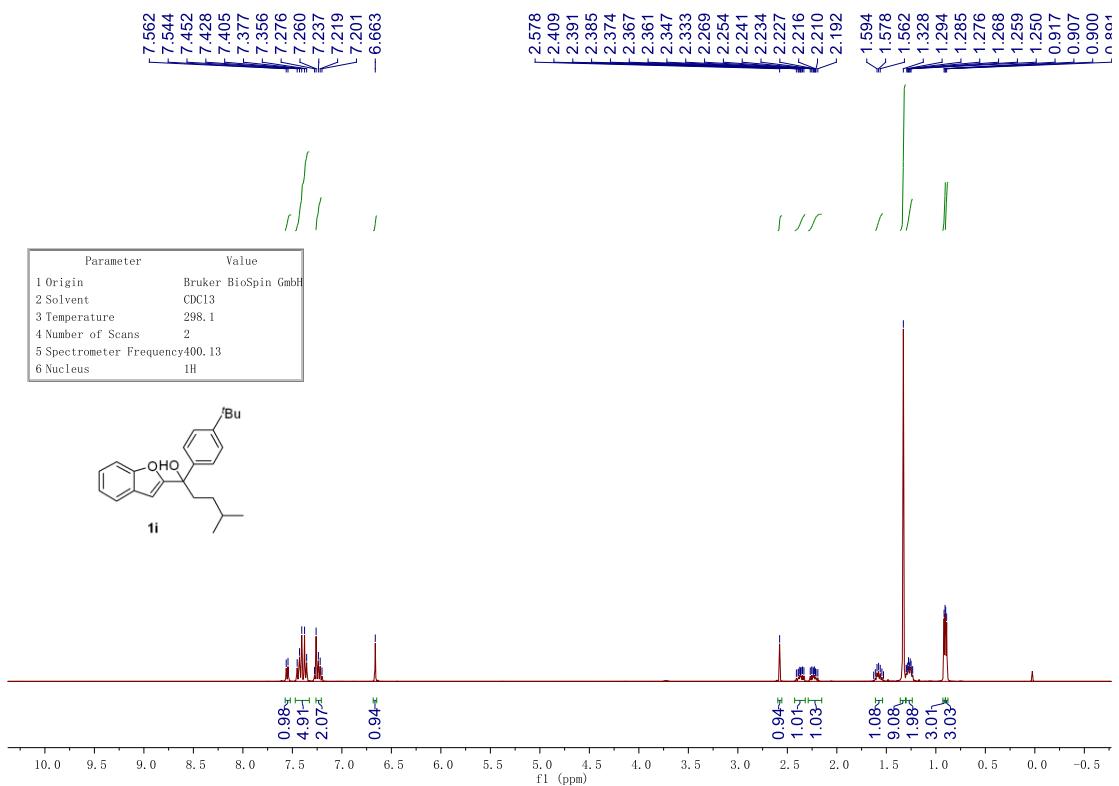
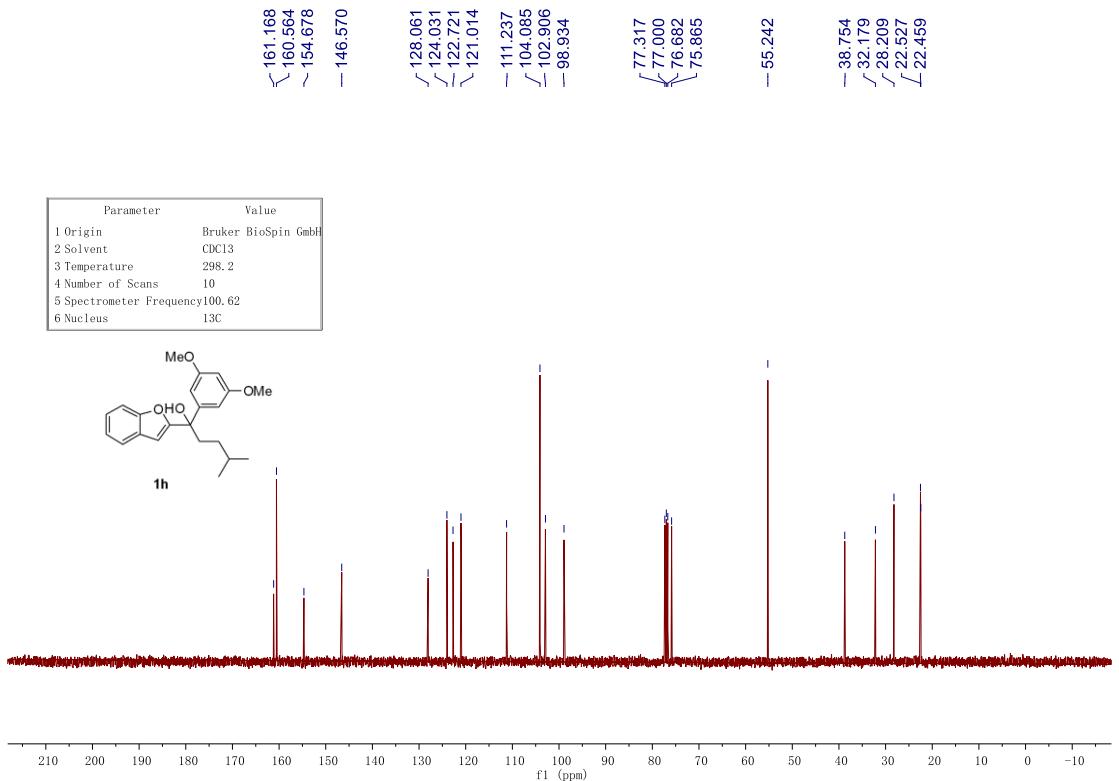


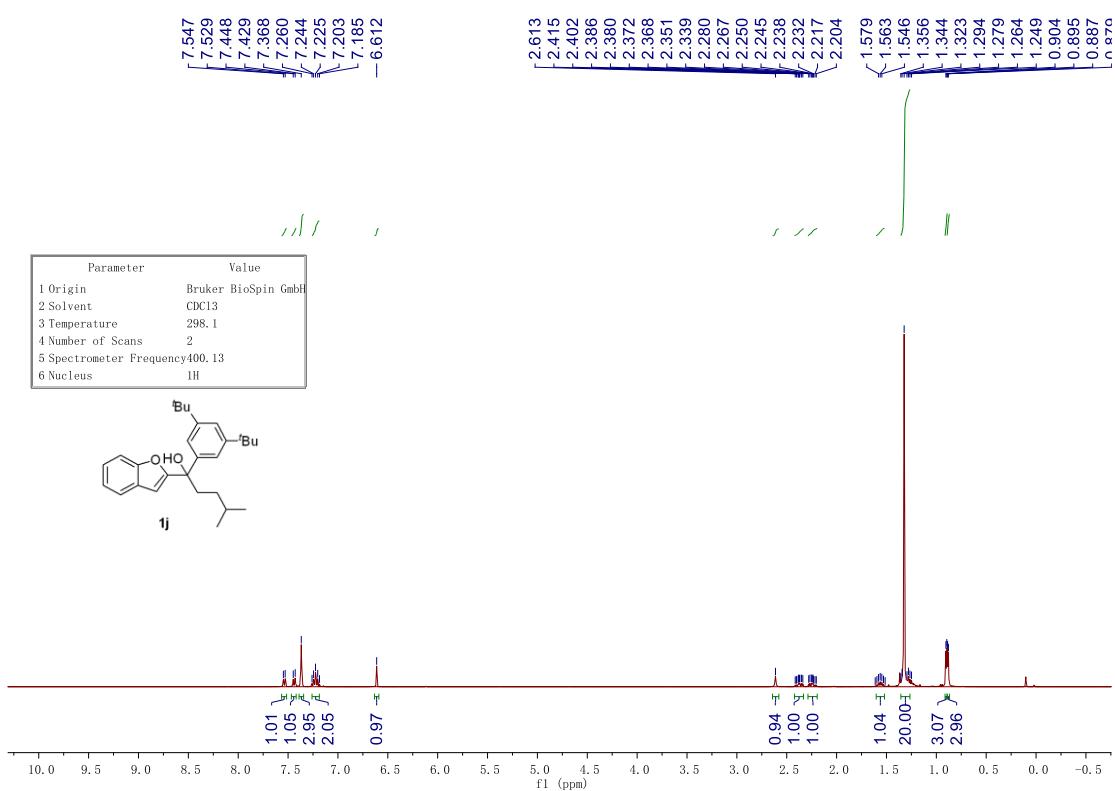
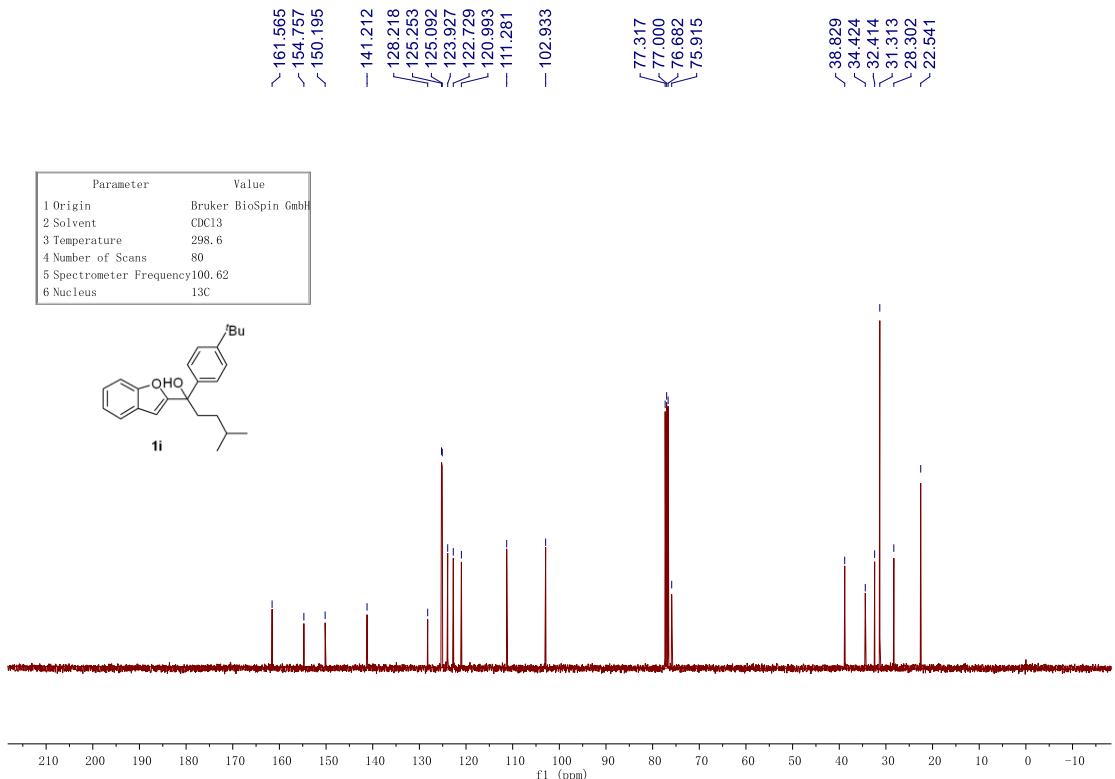


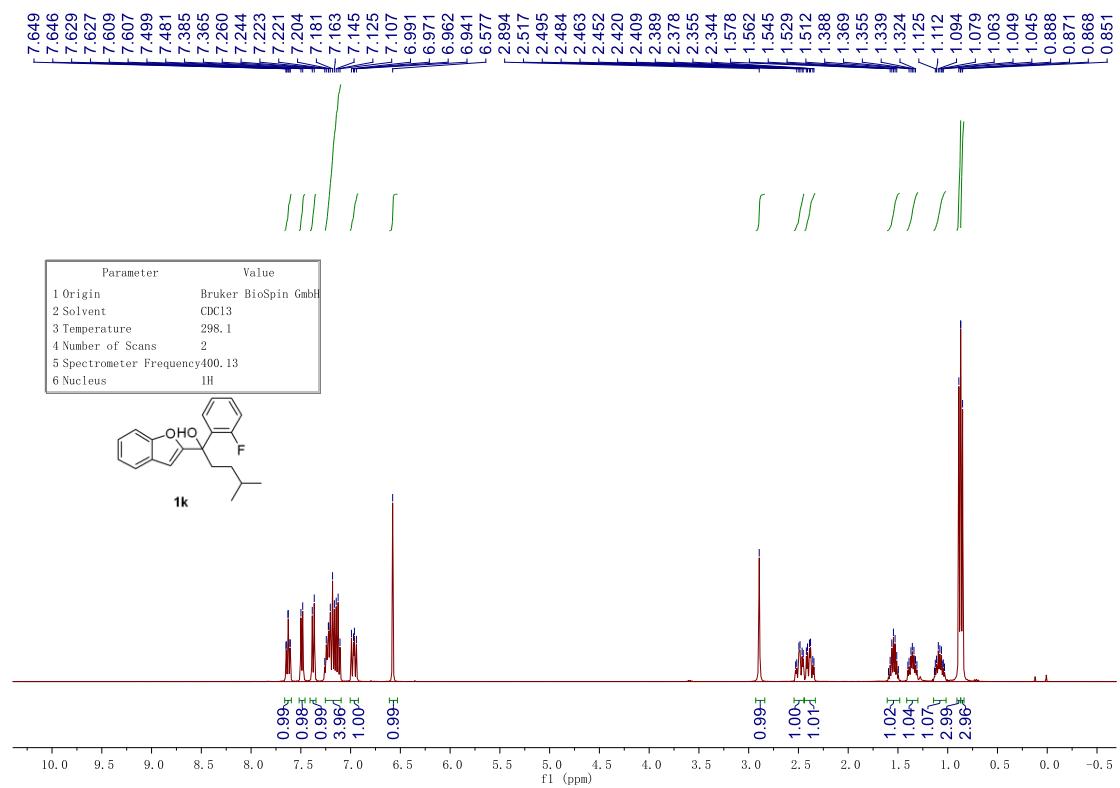
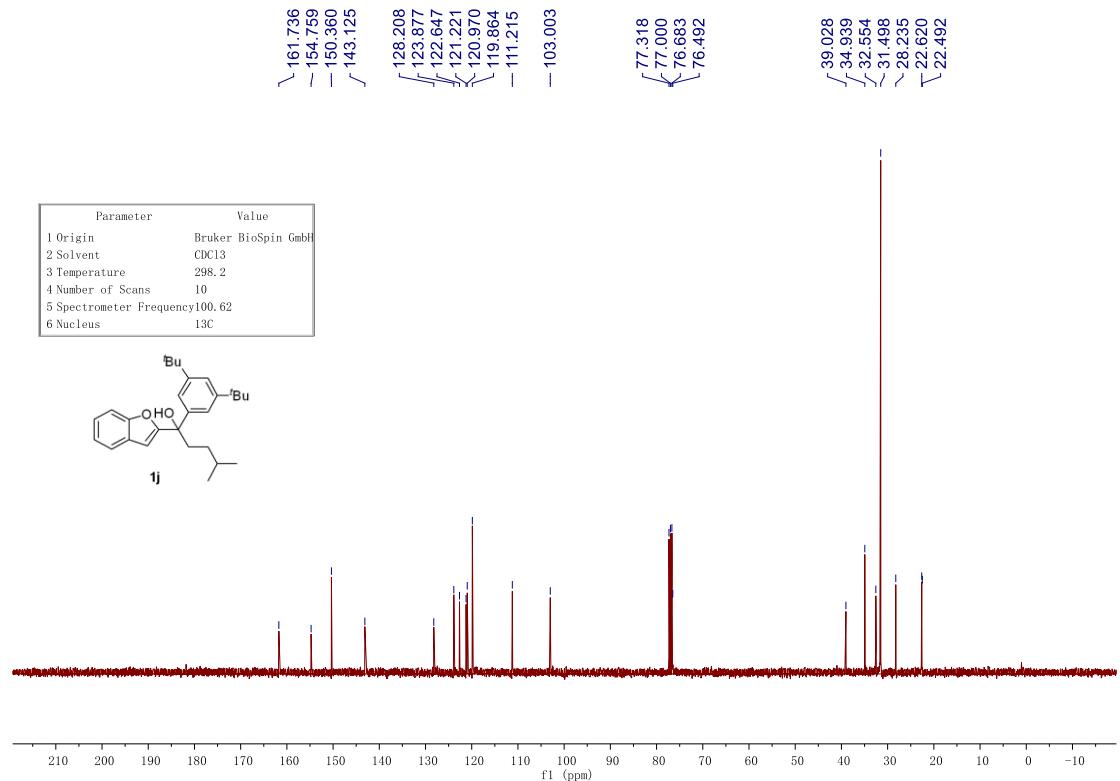


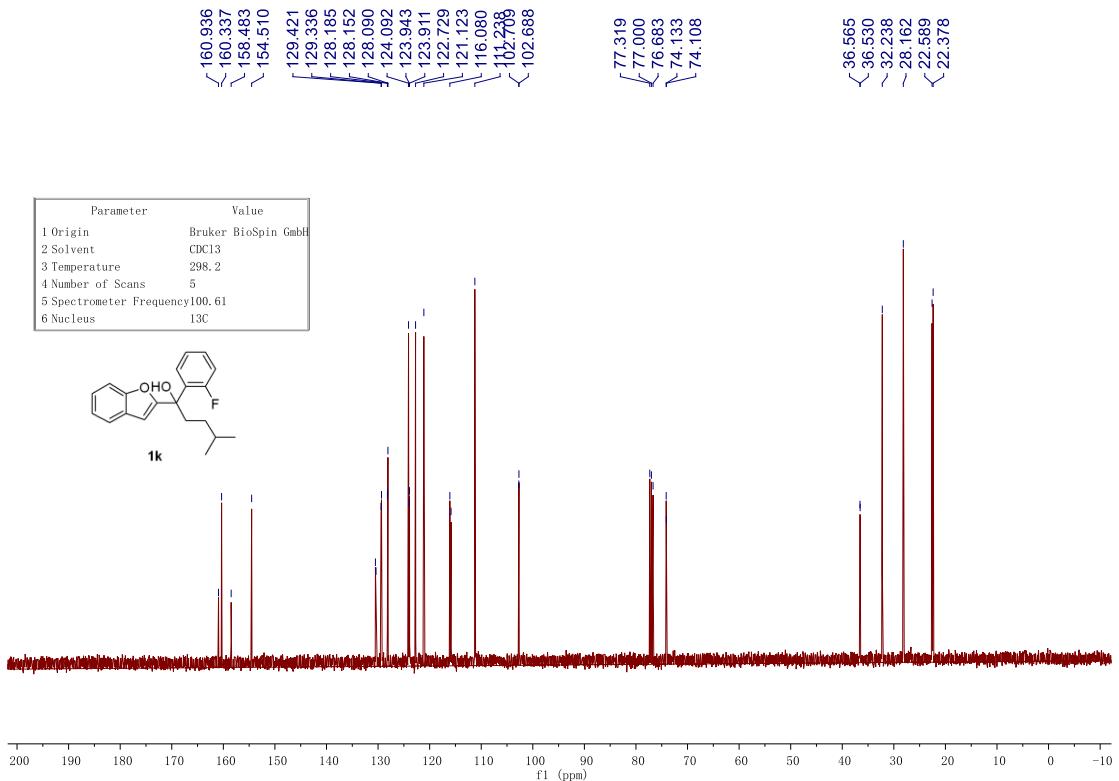




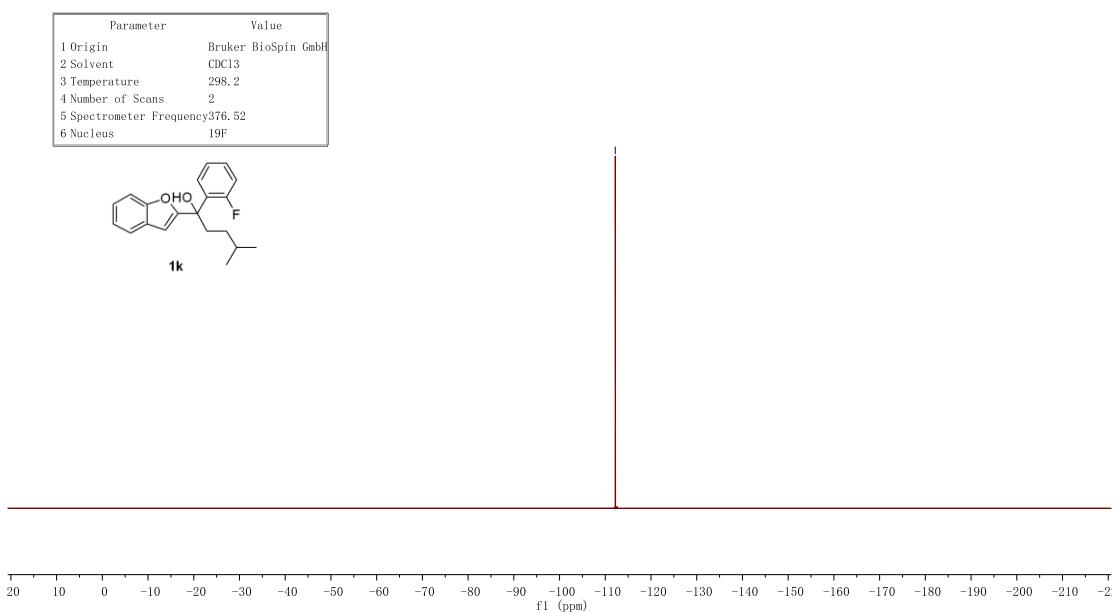


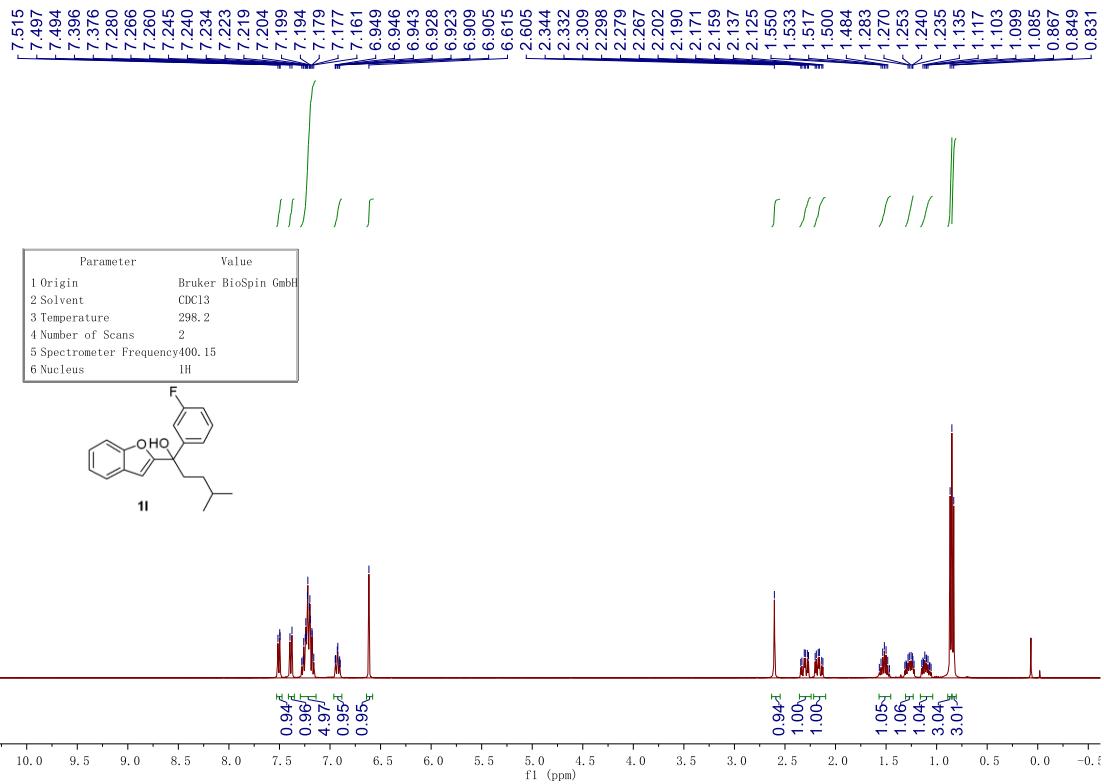






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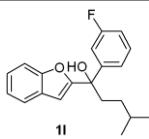




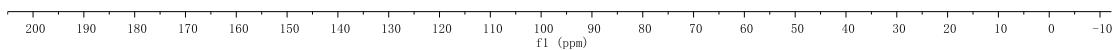
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 103.098

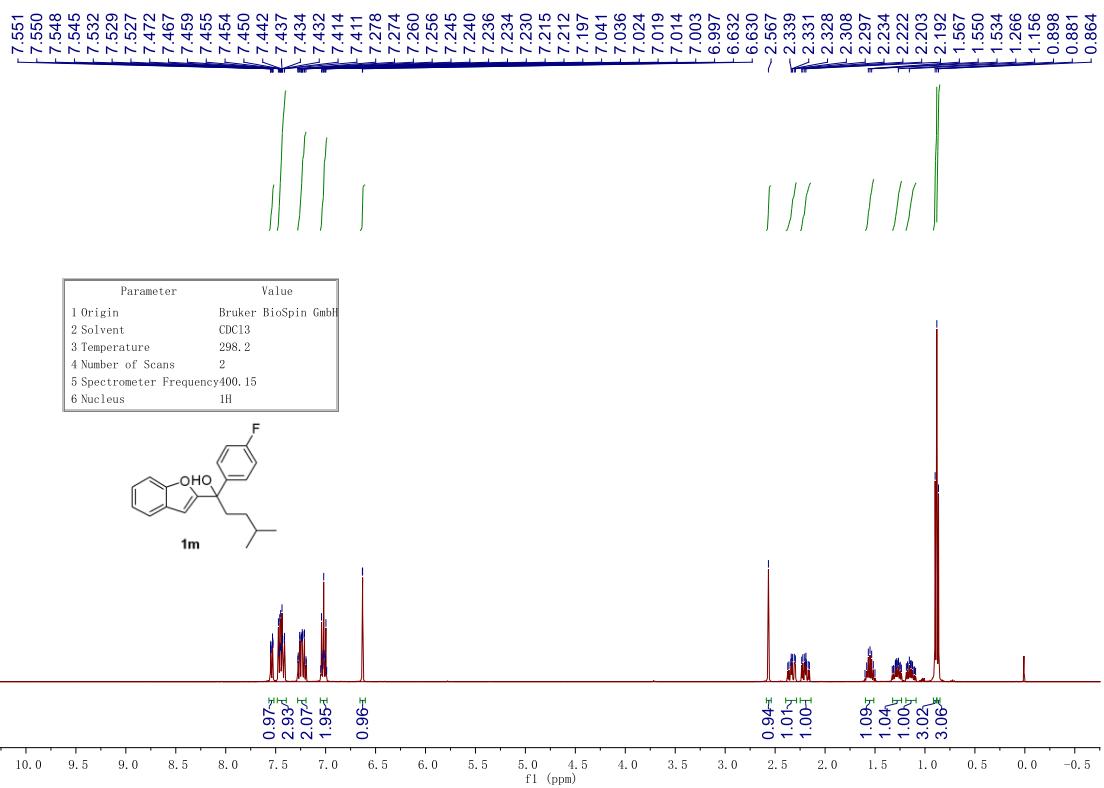
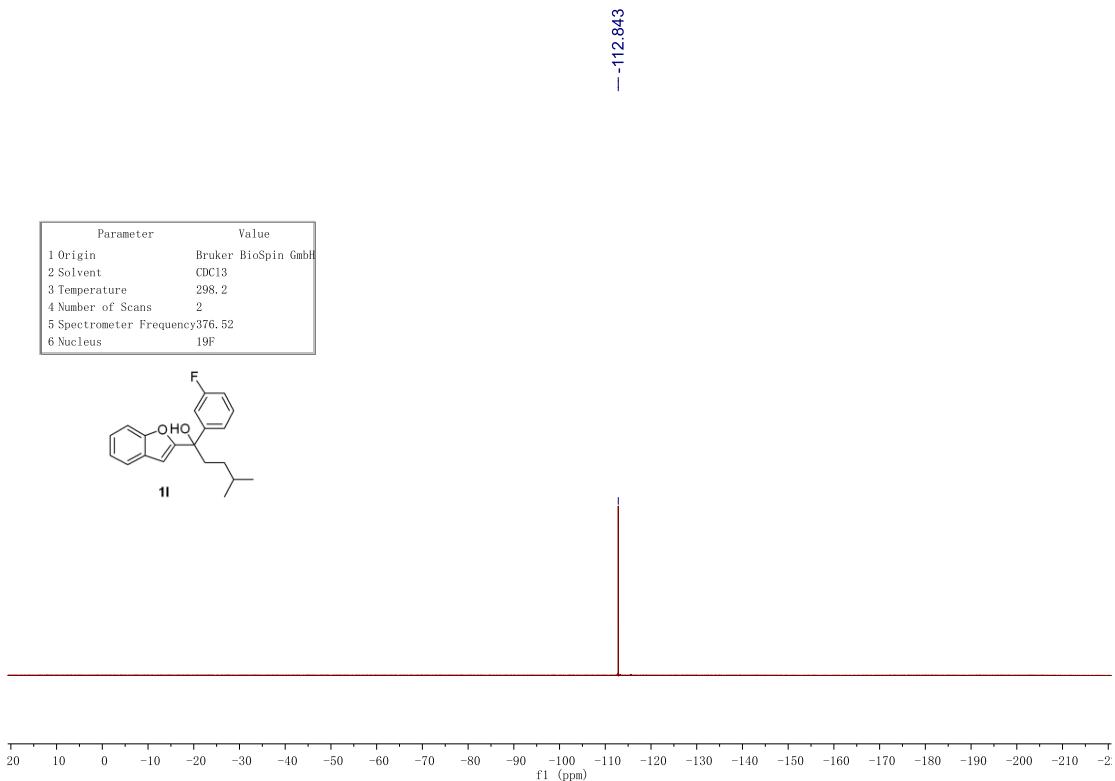
**Parameter**                  **Value**

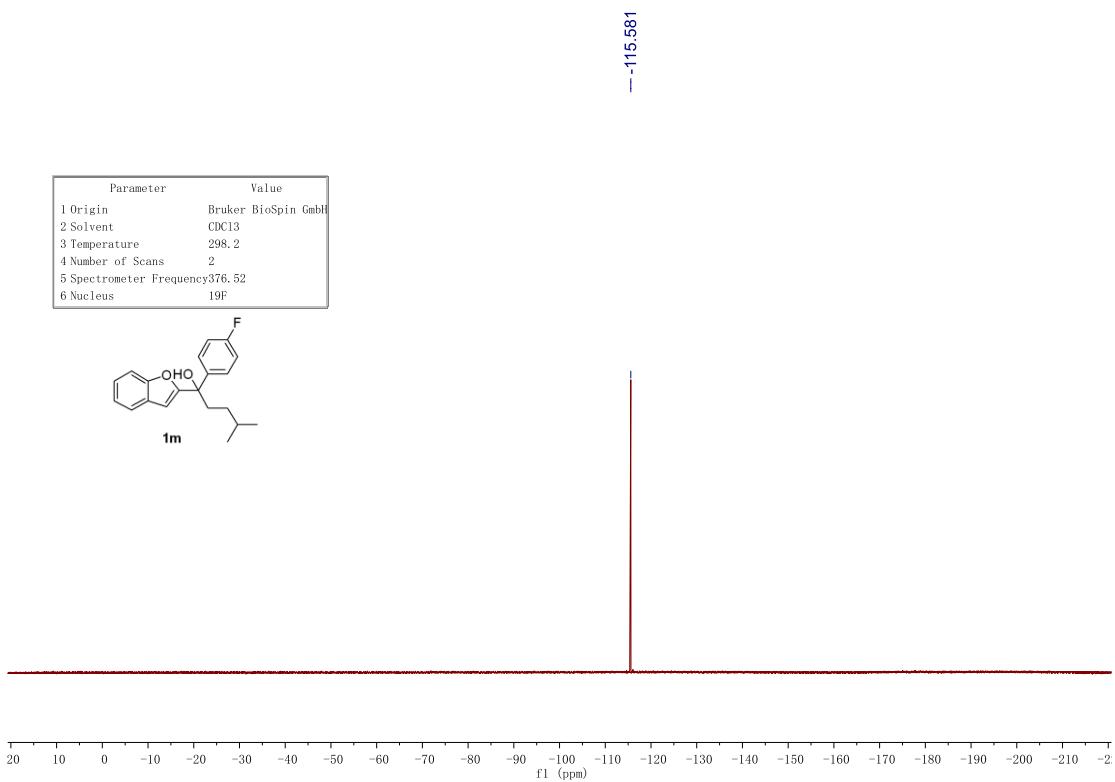
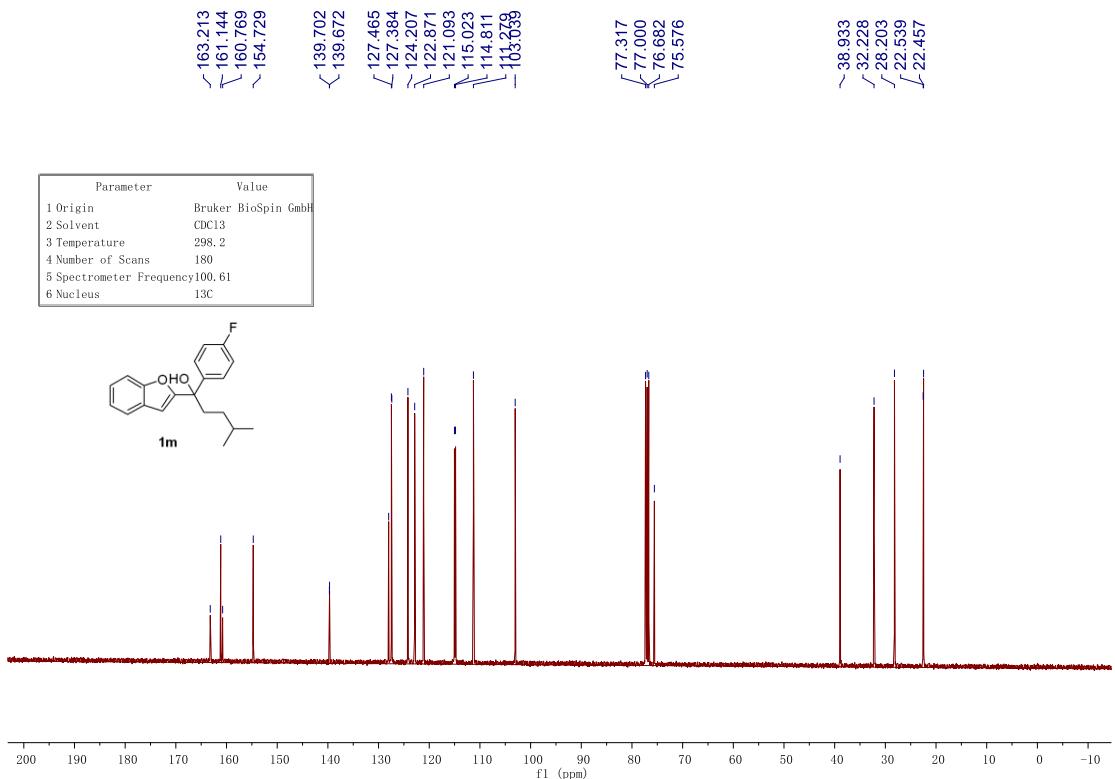
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2 Solvent	CDCl <sub>3</sub>
3 Temperature	298.2
4 Number of Scans	68
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6 Nucleus	13C

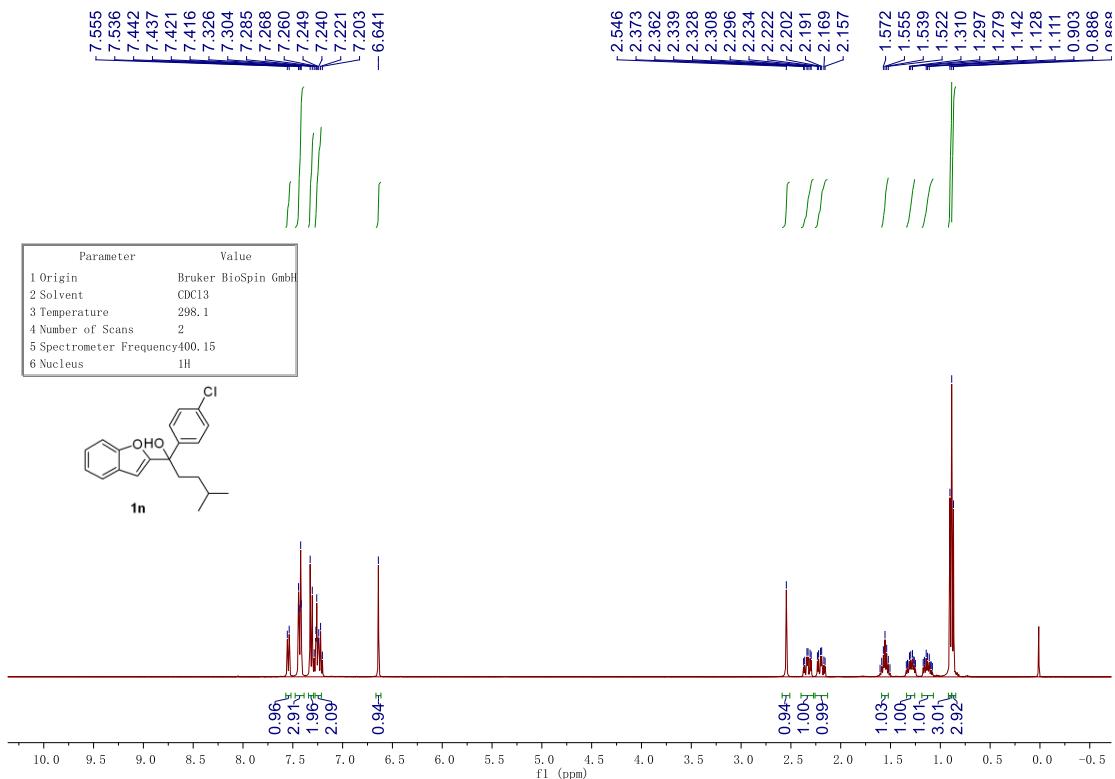


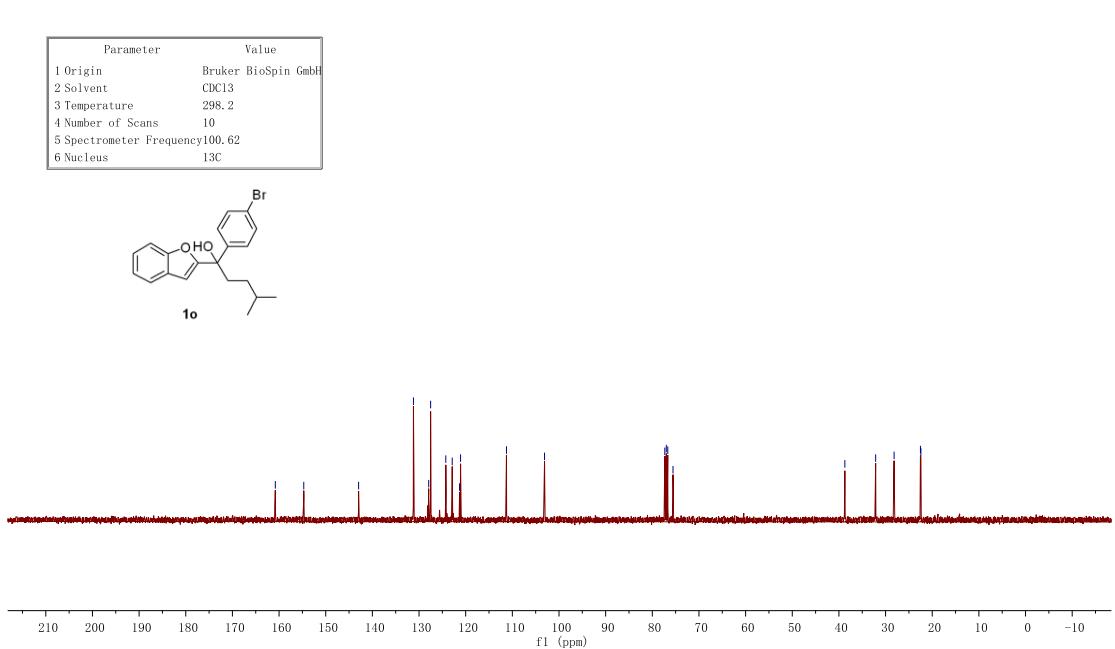
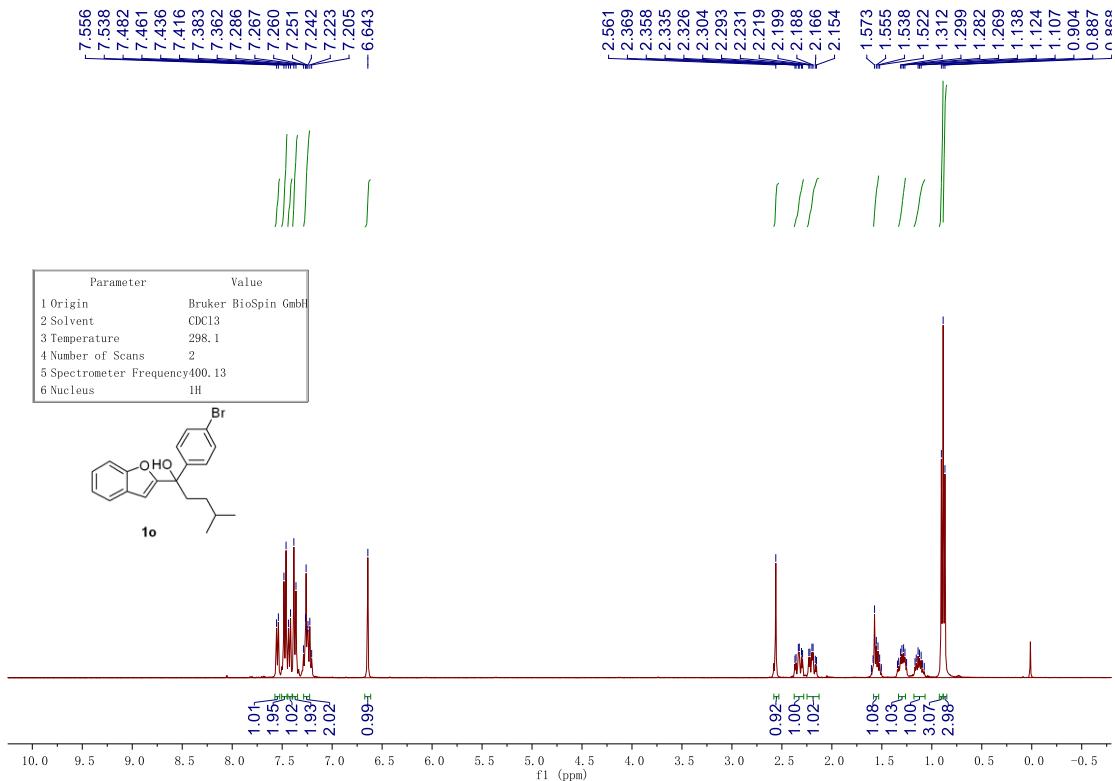
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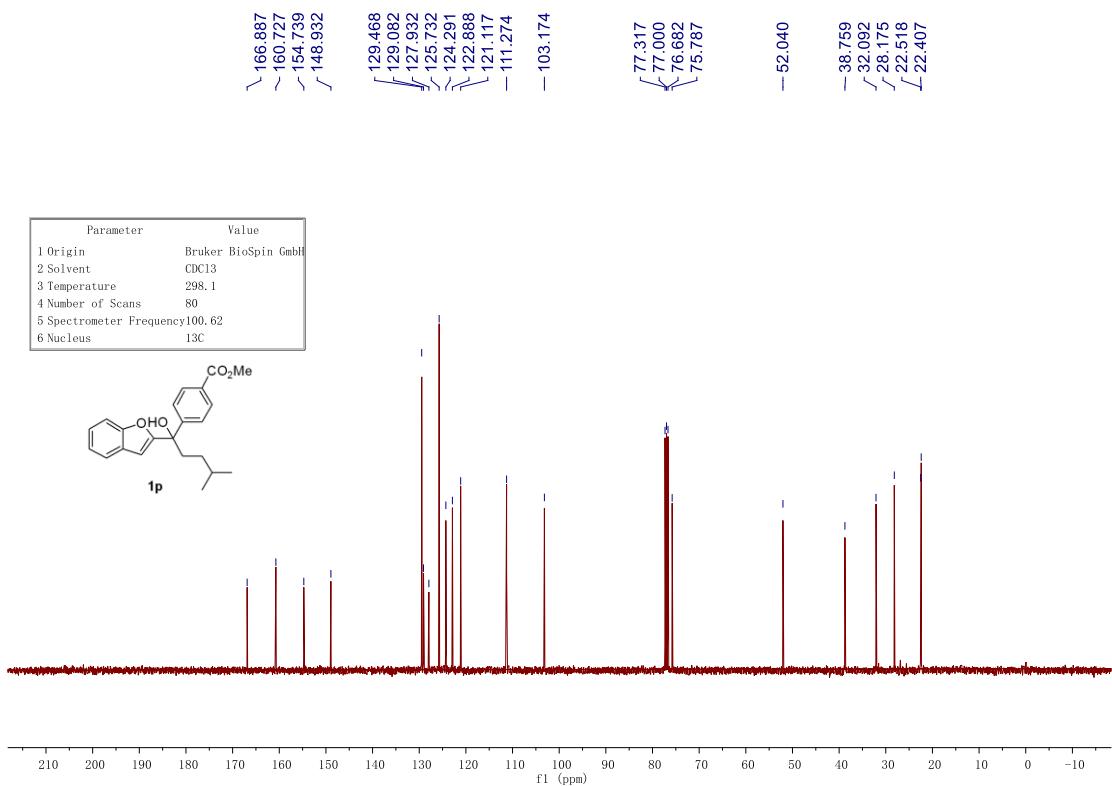
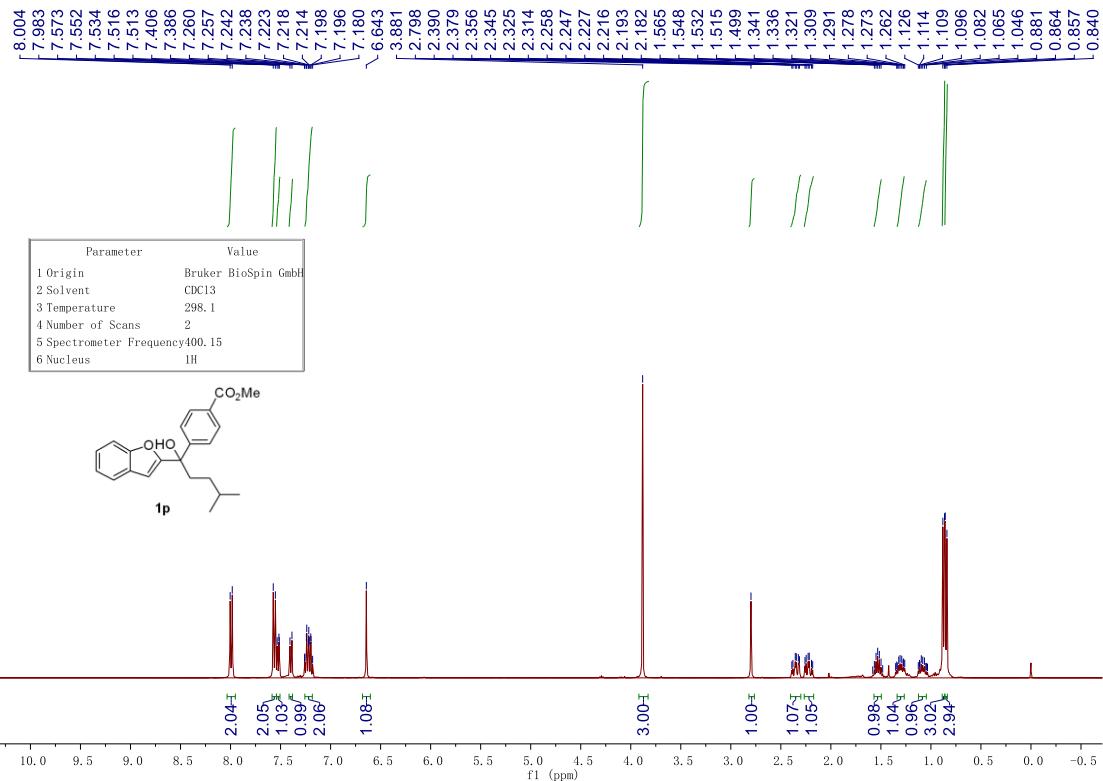


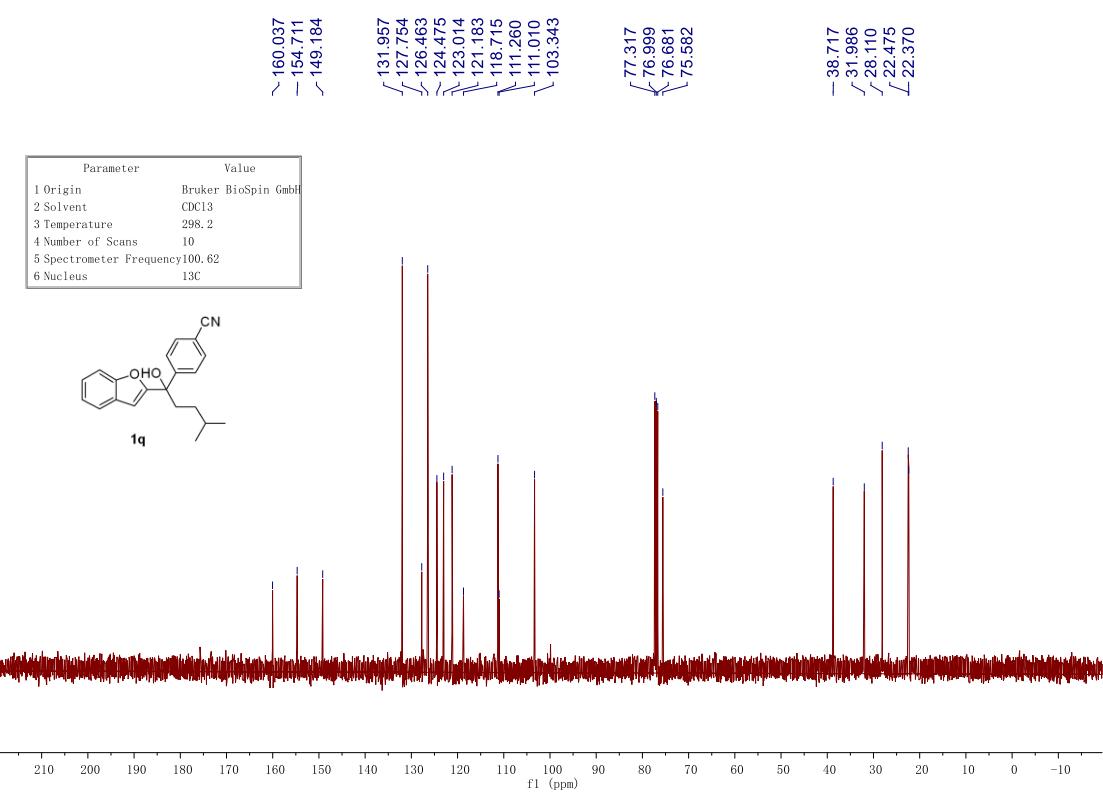
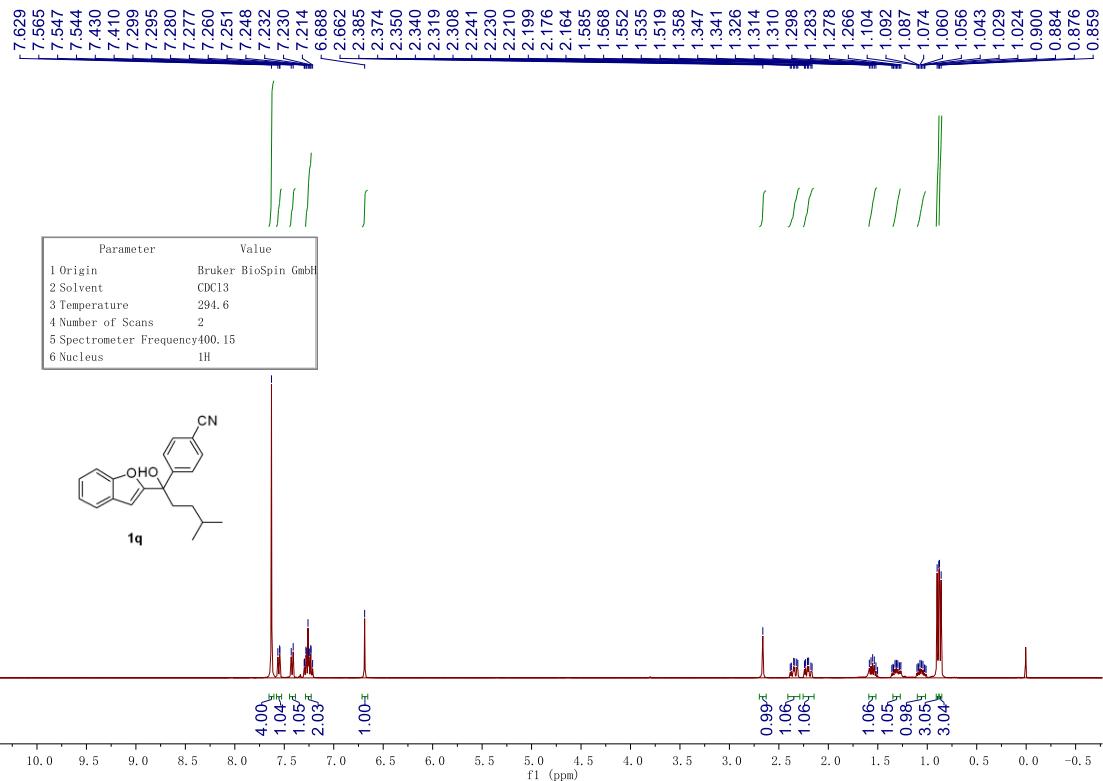


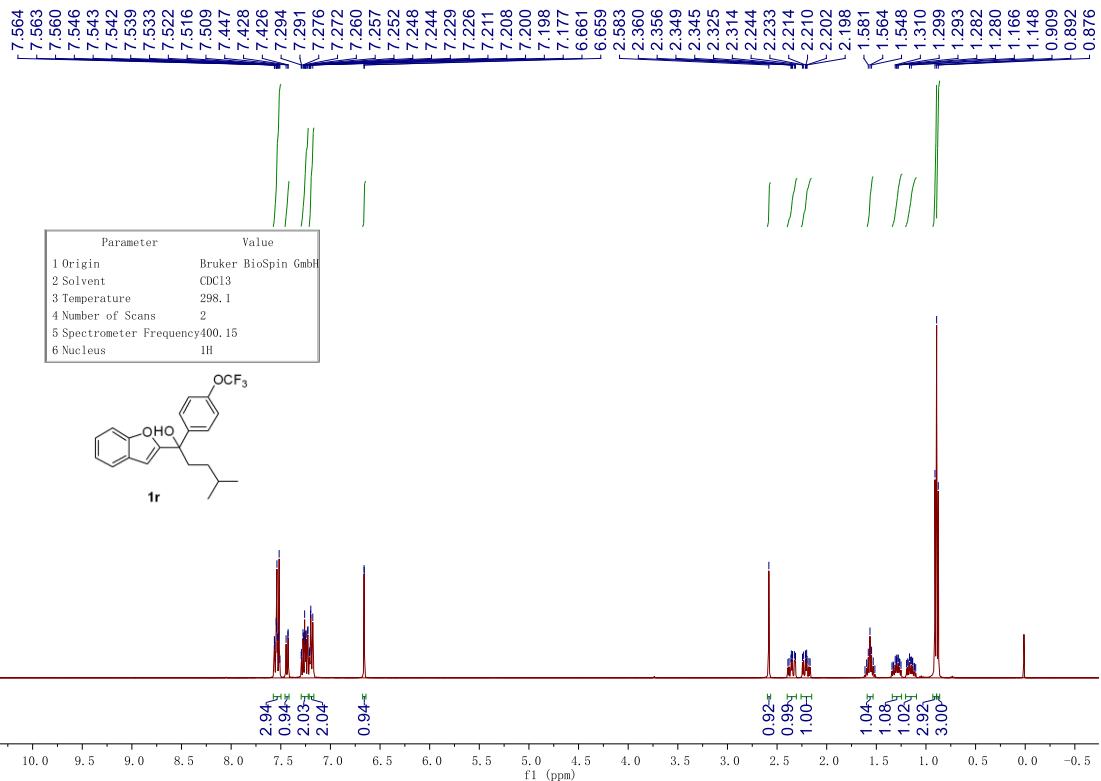


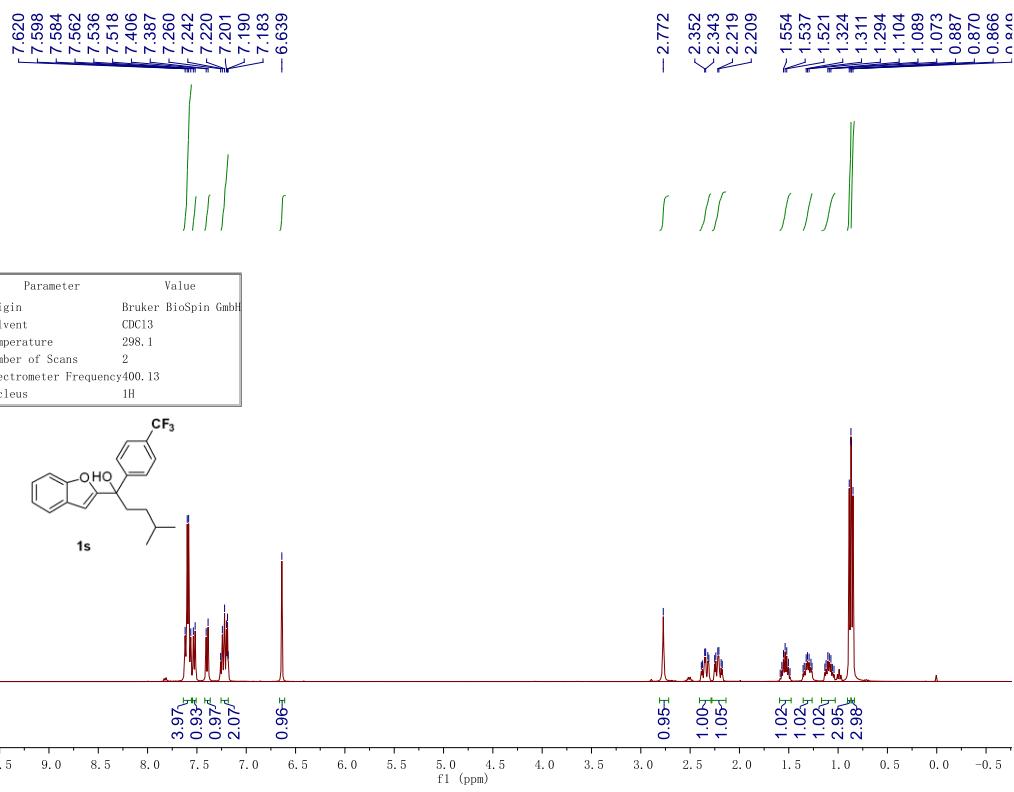
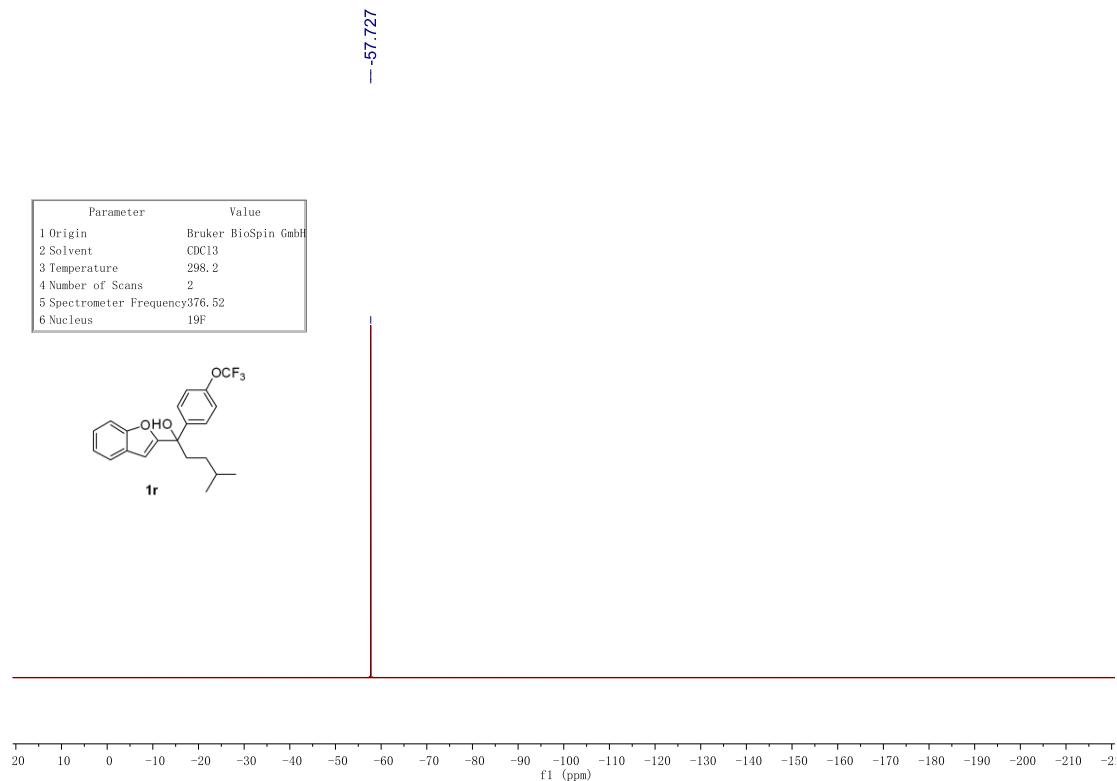


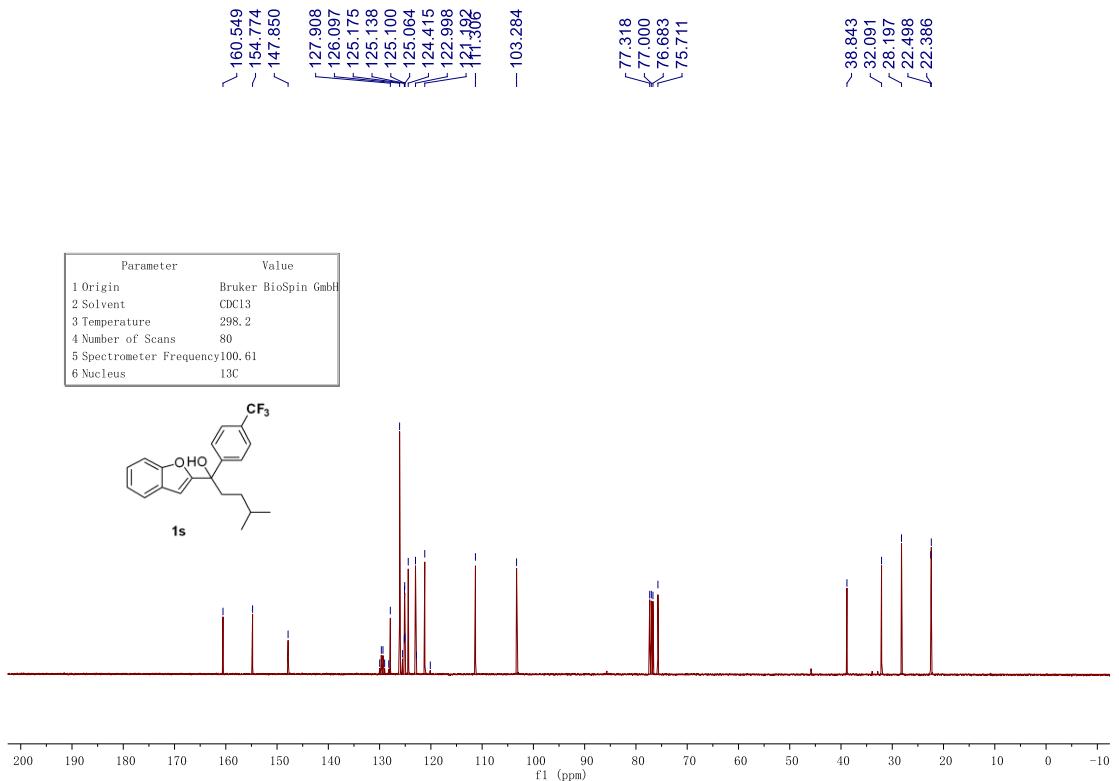




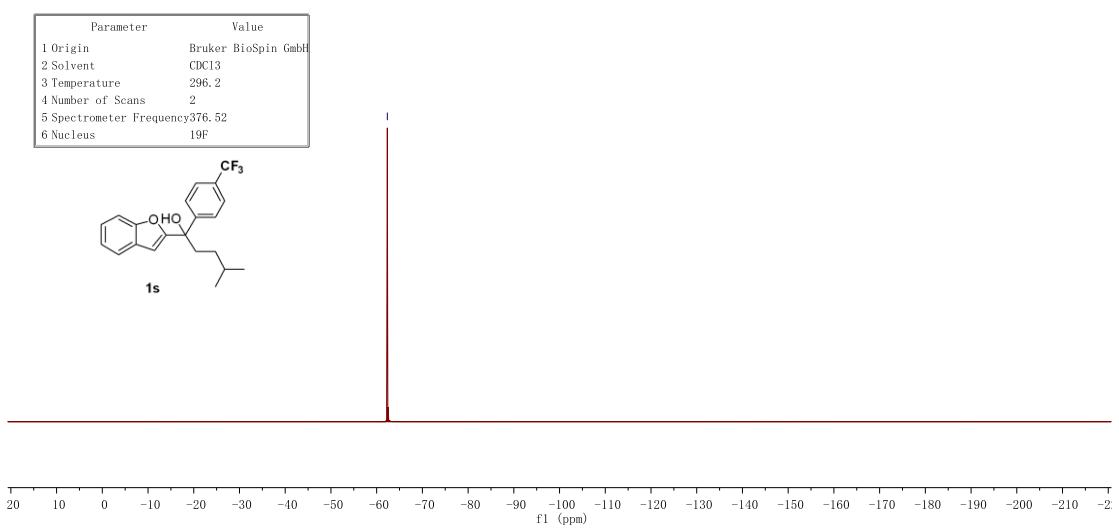


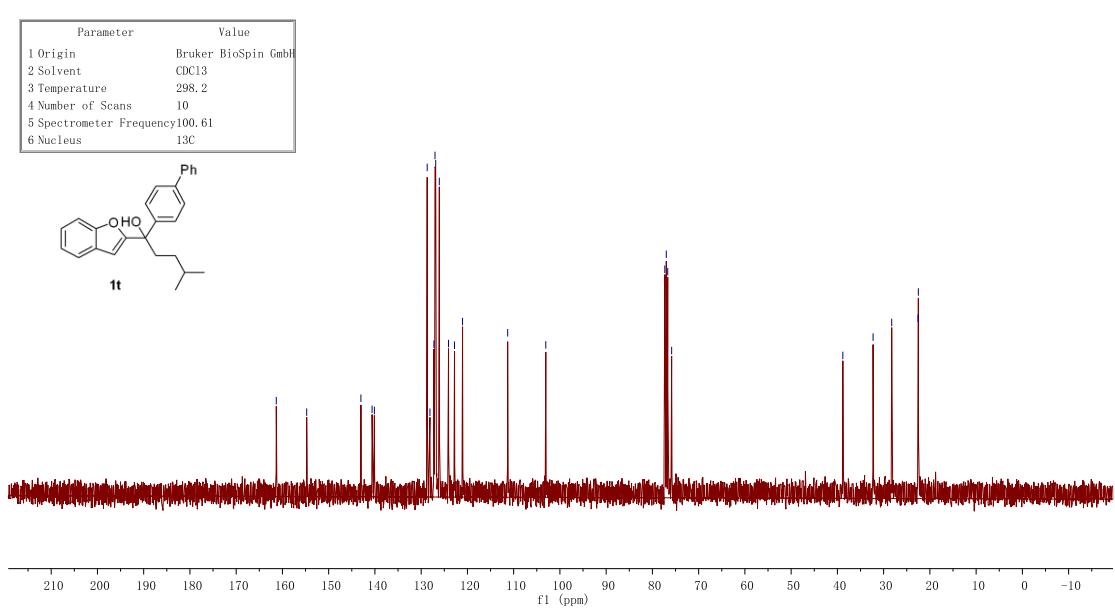
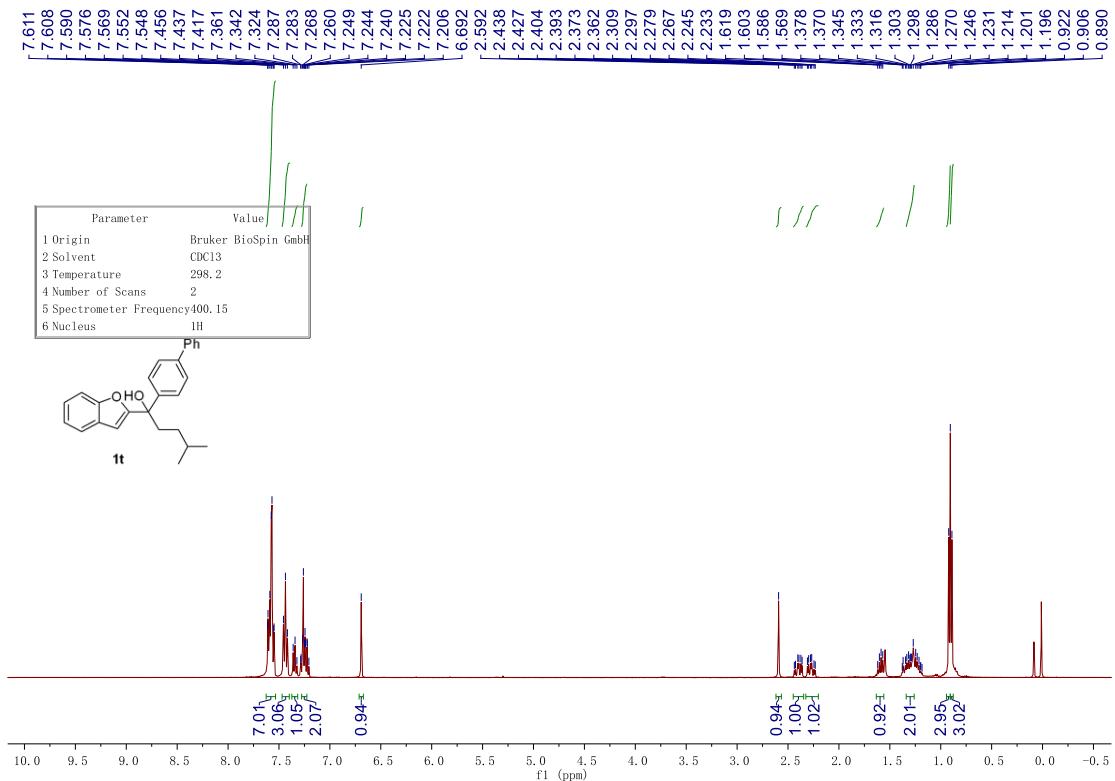


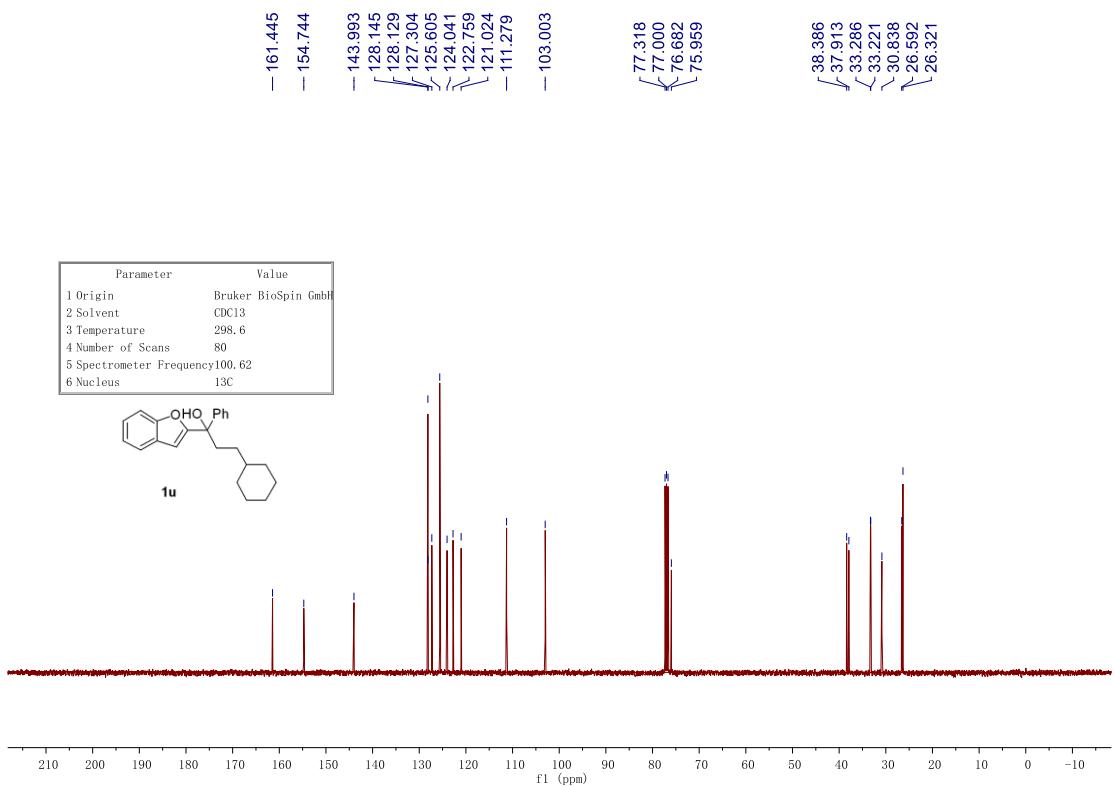
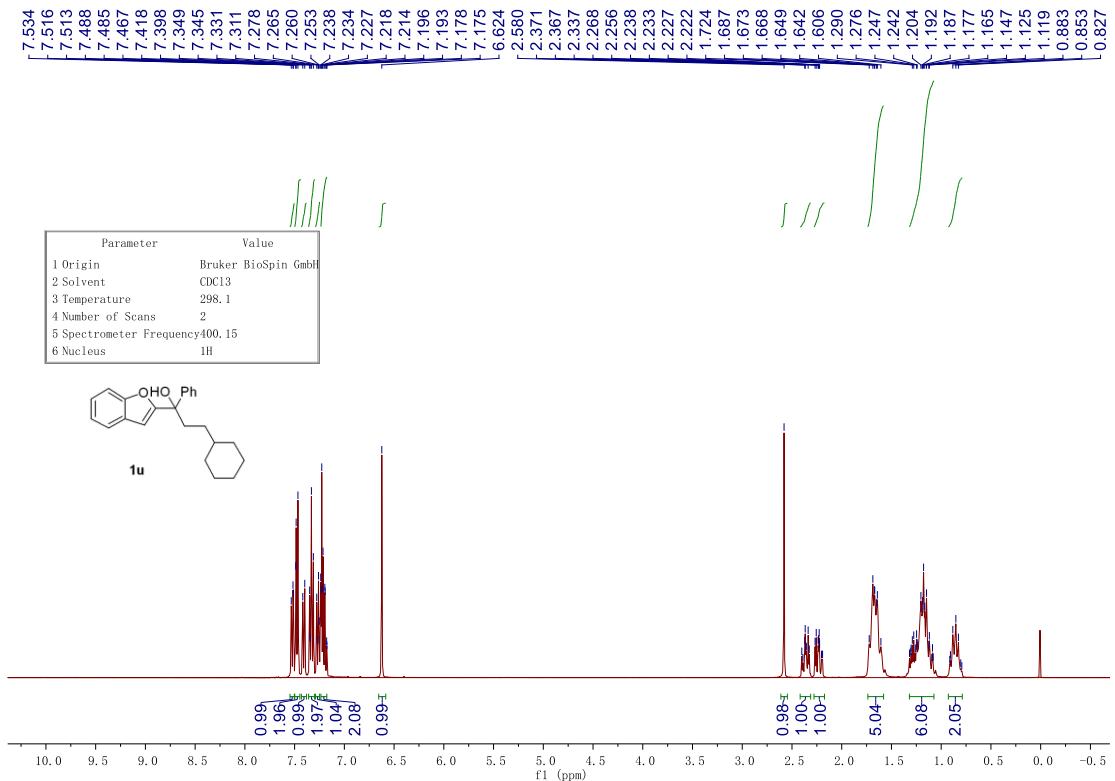


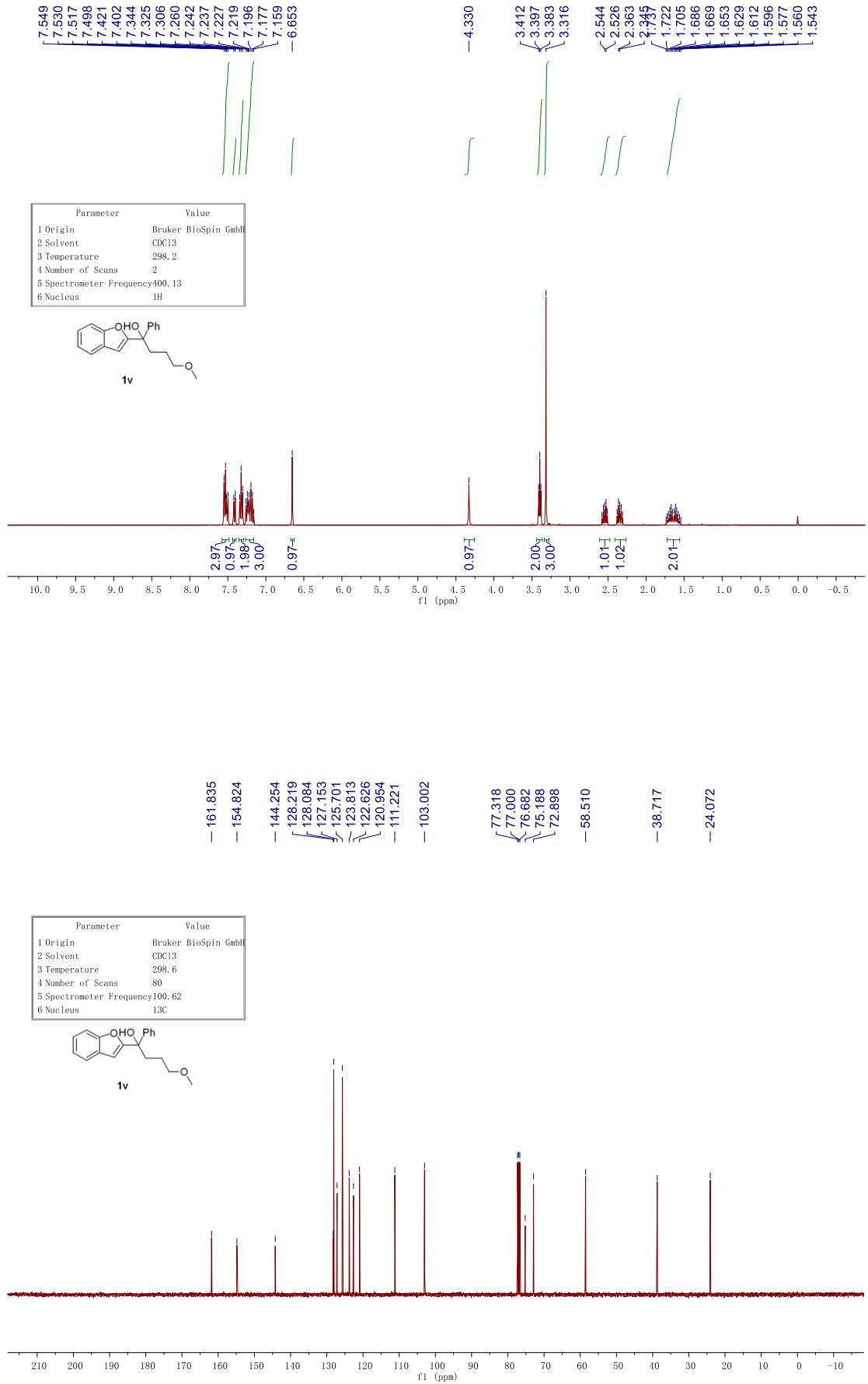


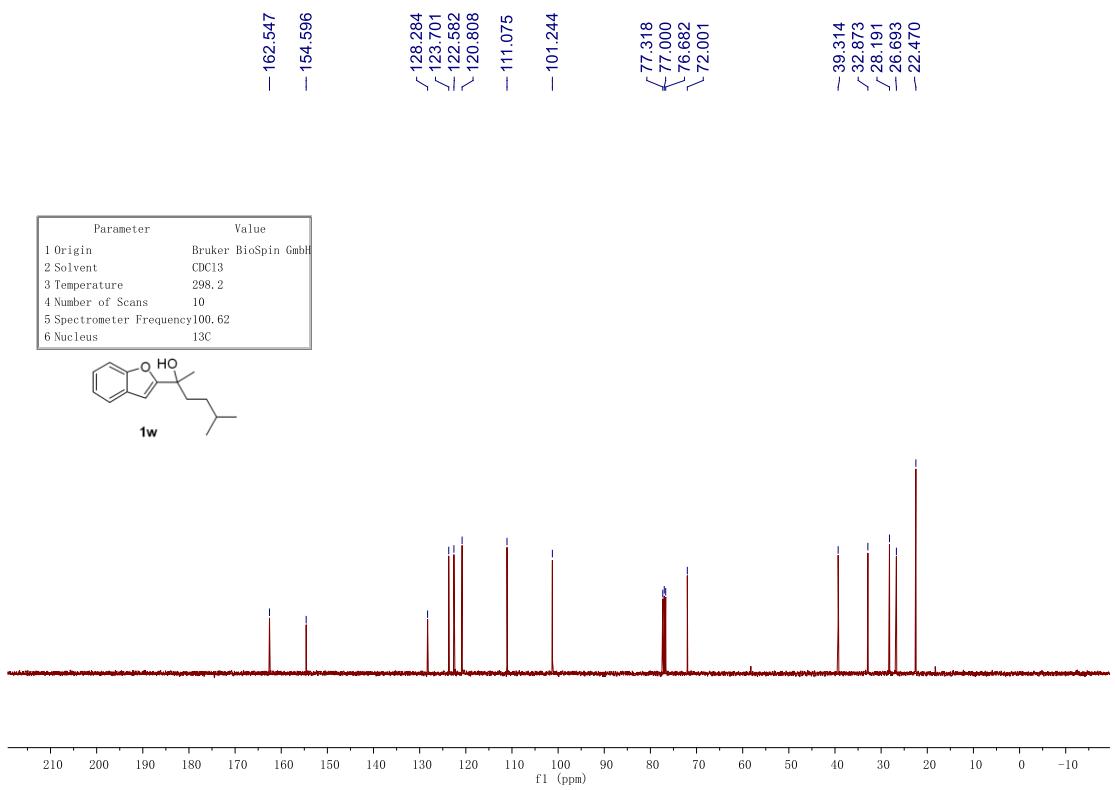
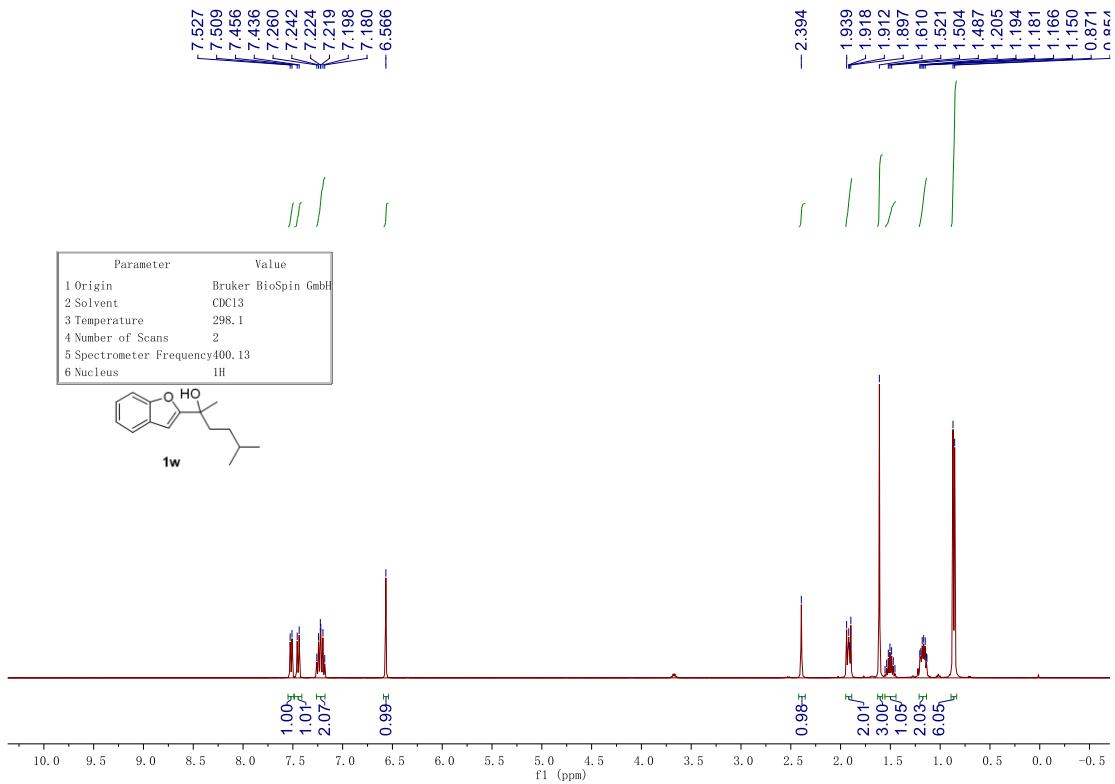
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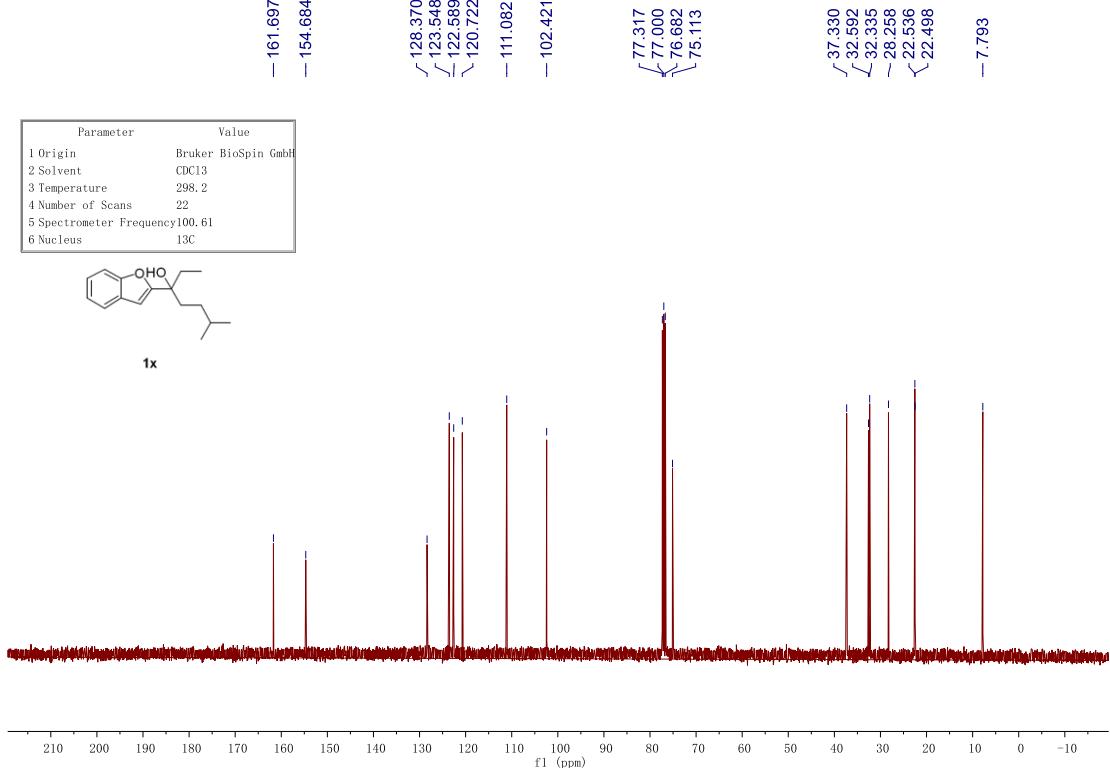
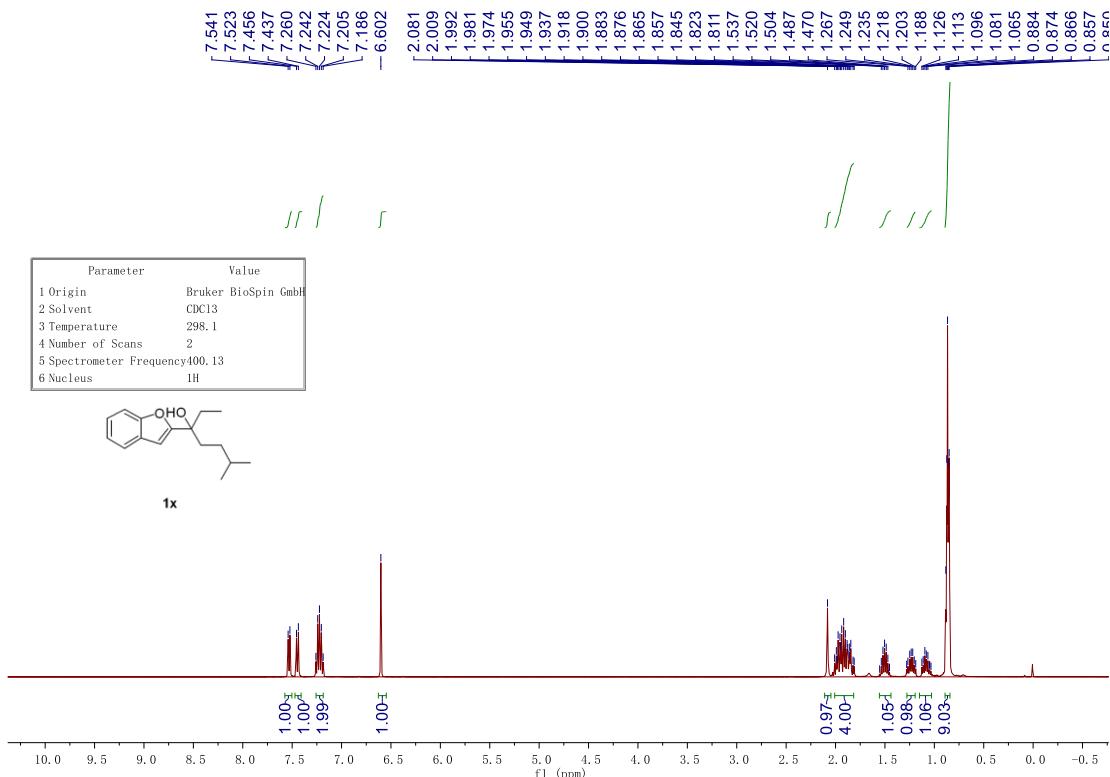


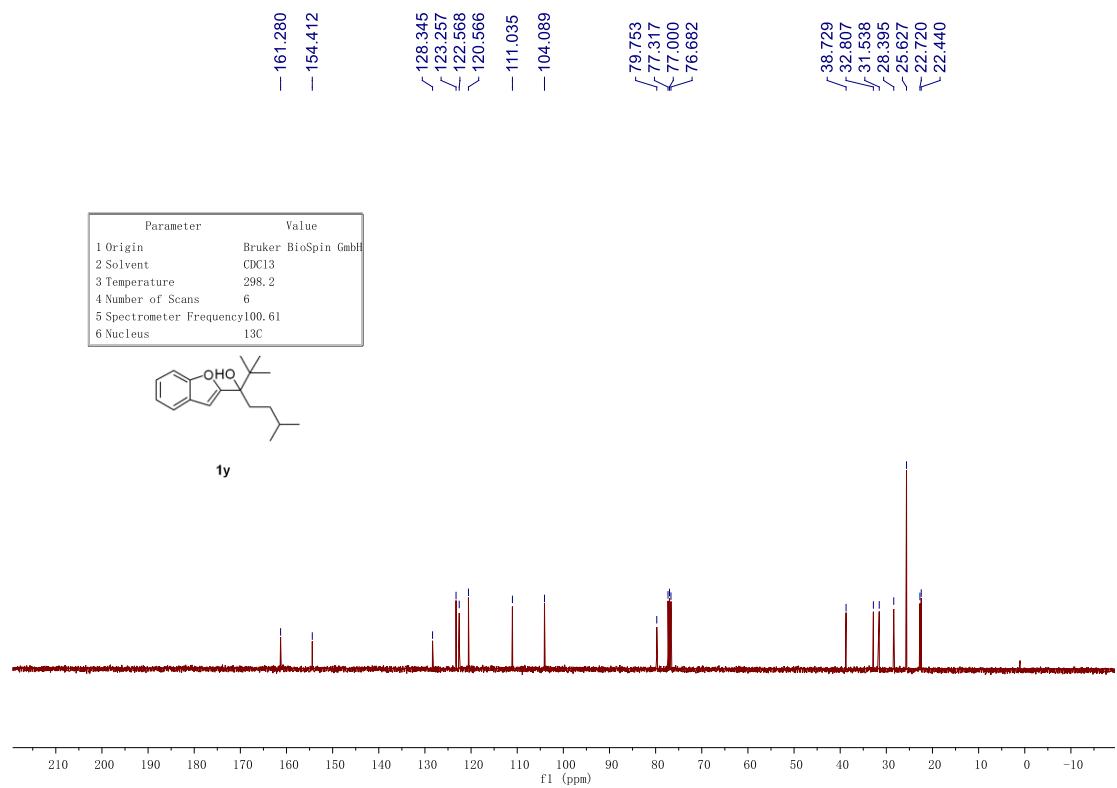
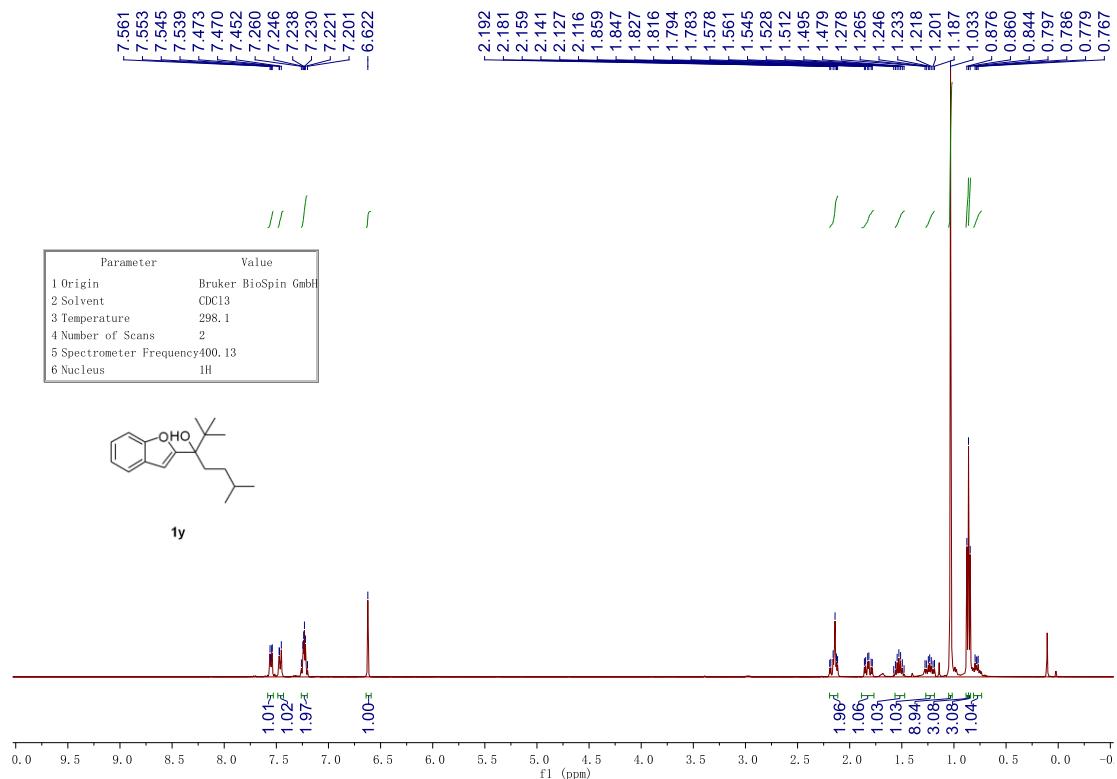


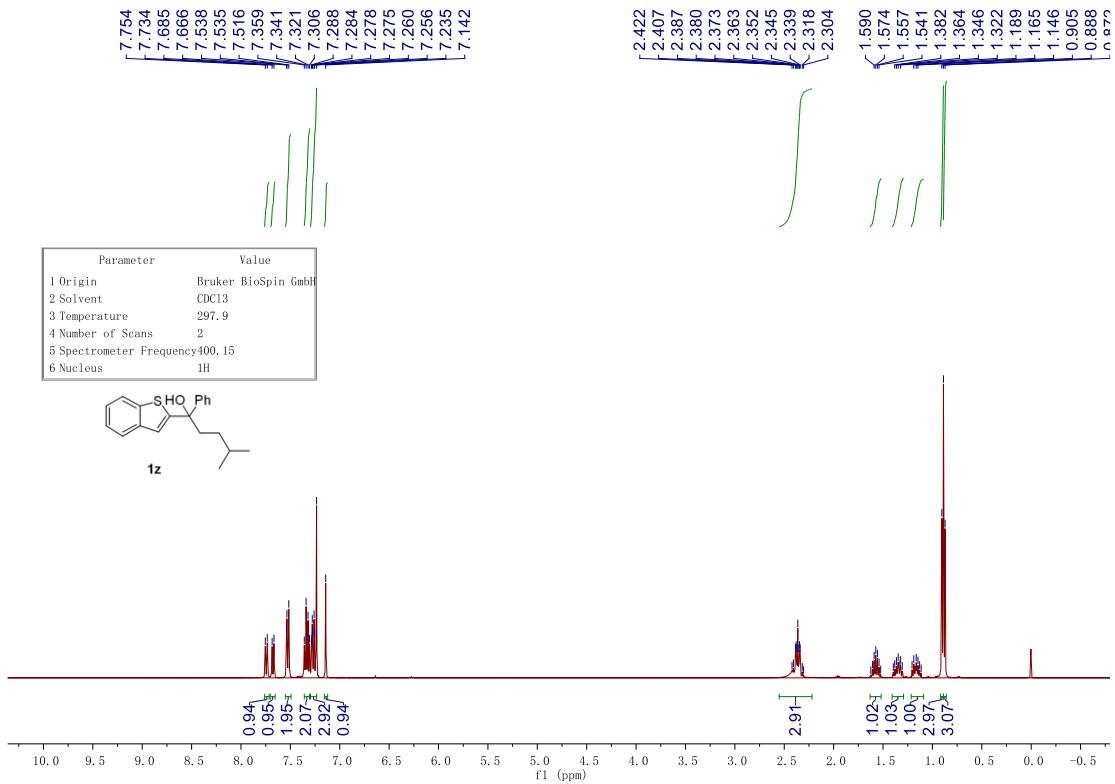




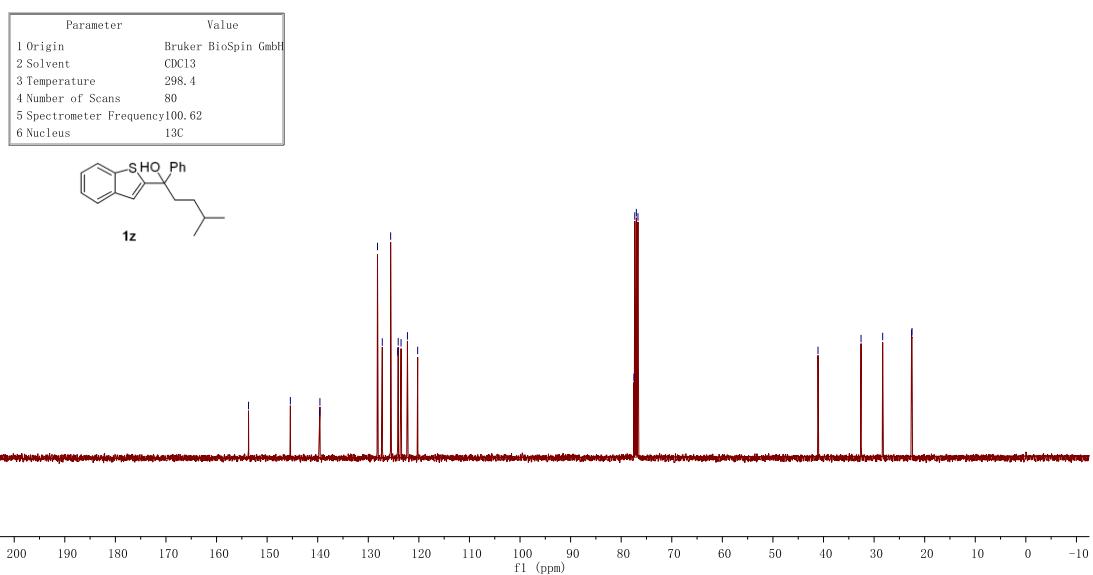


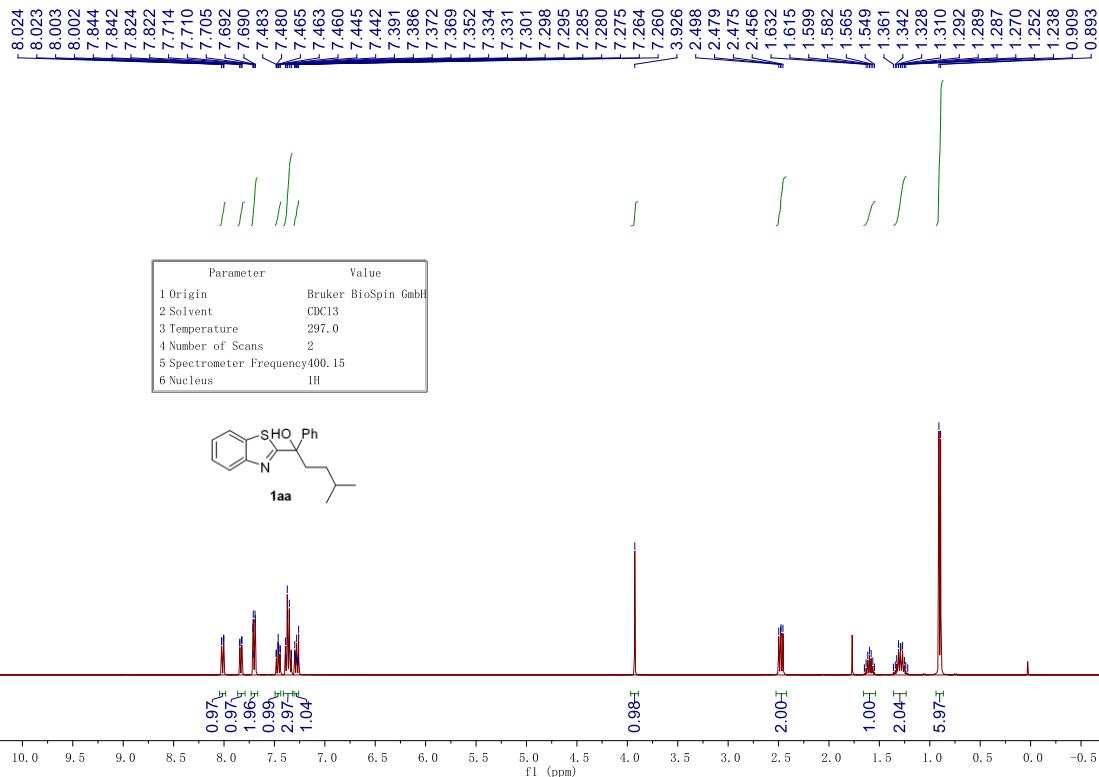






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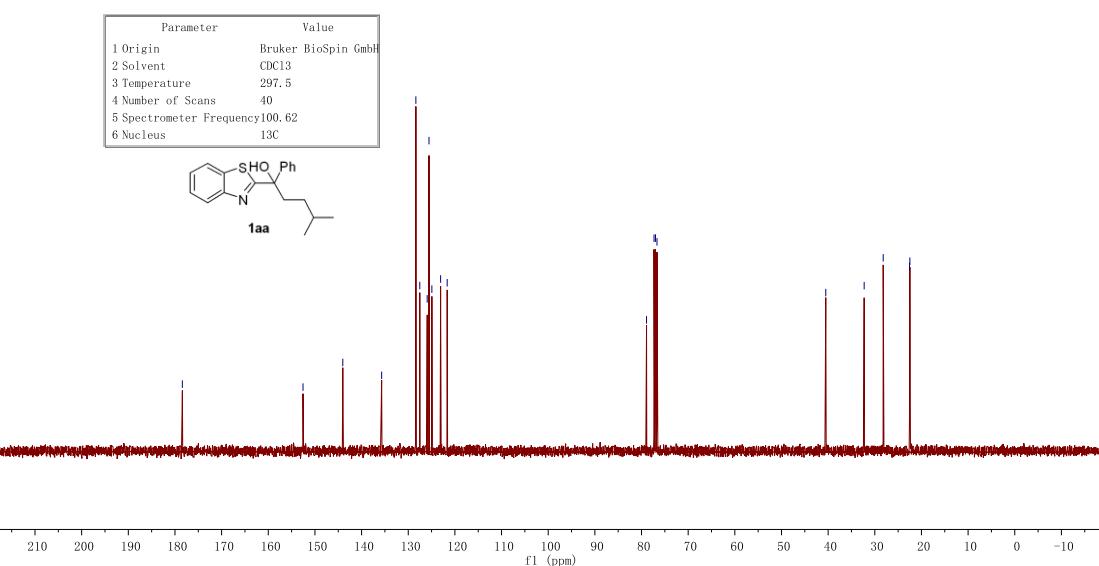
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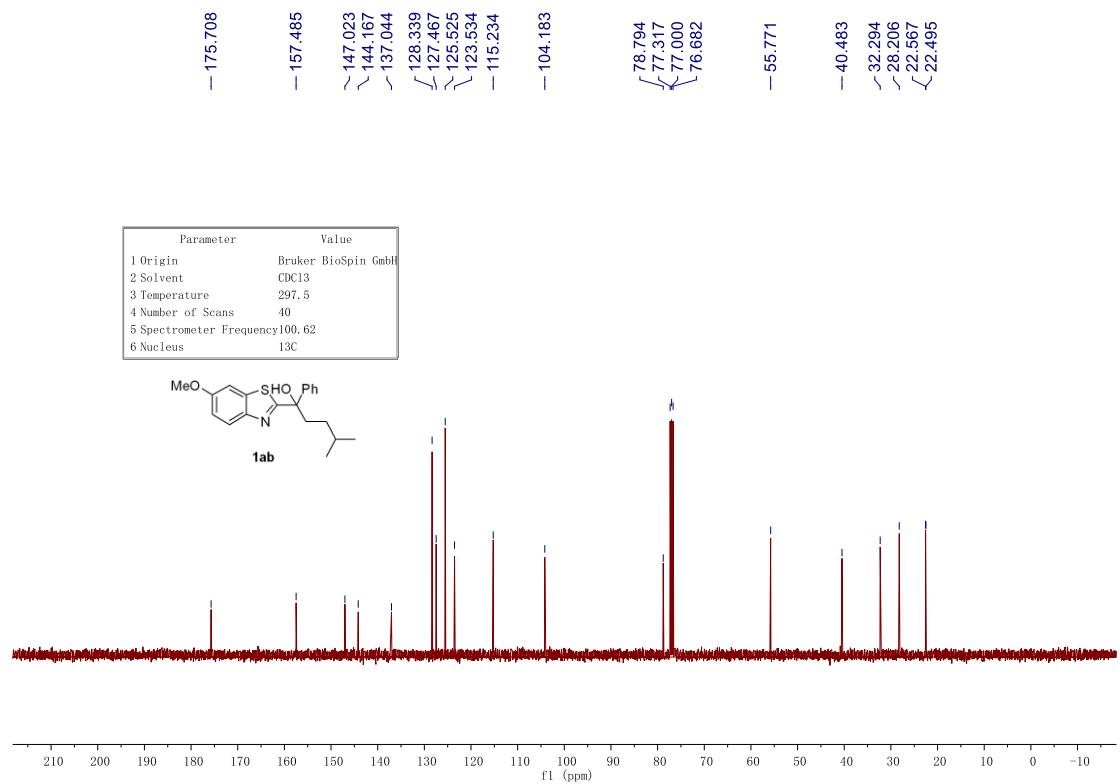
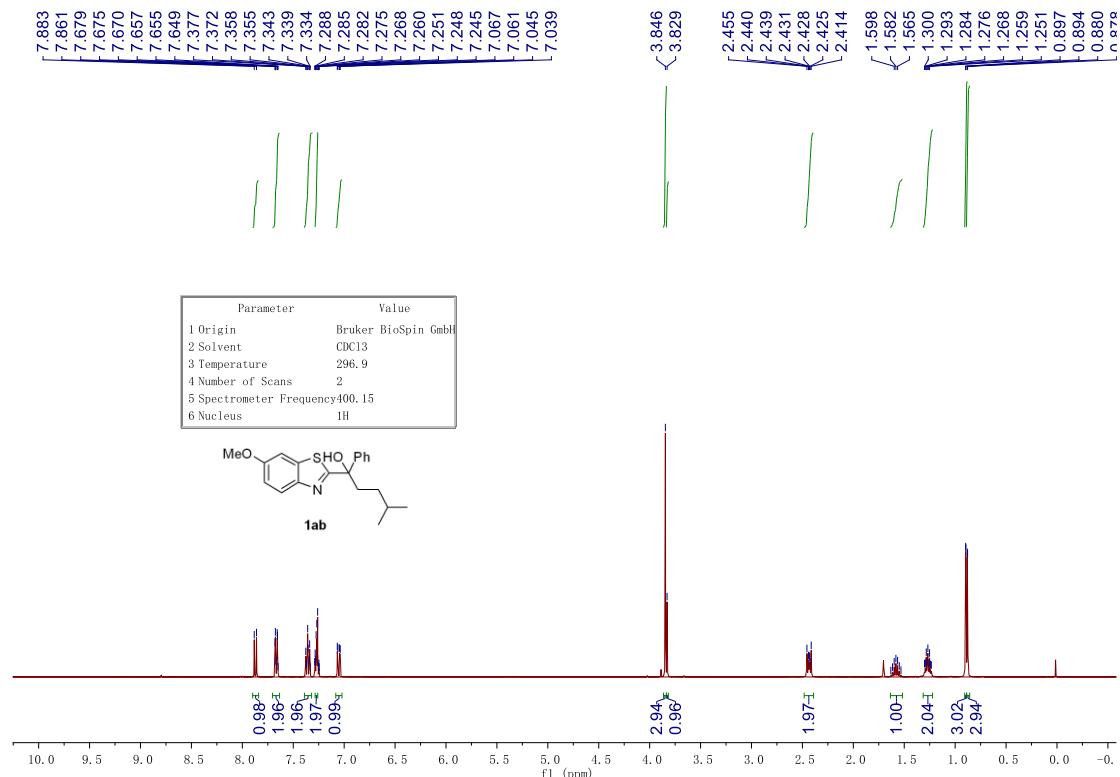
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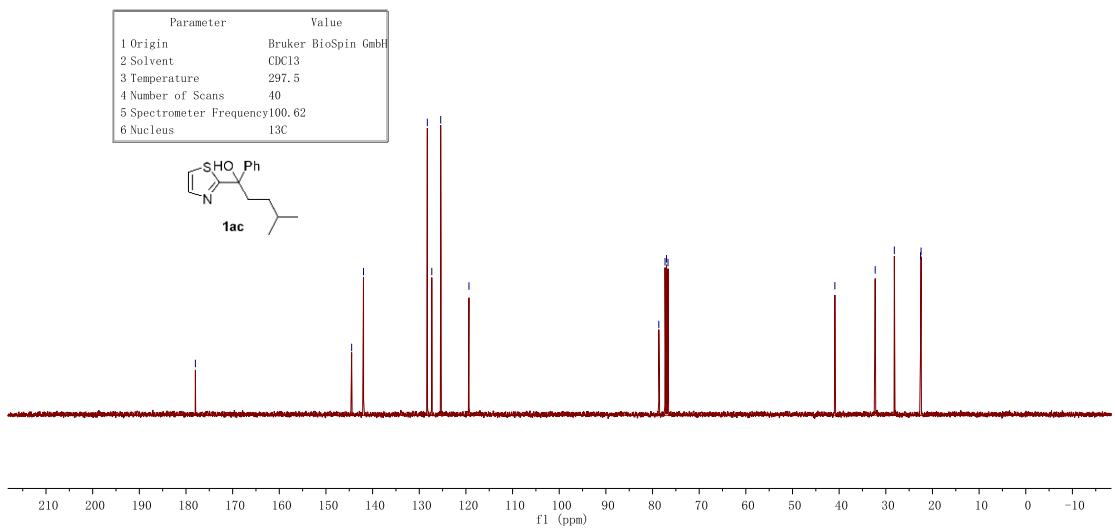
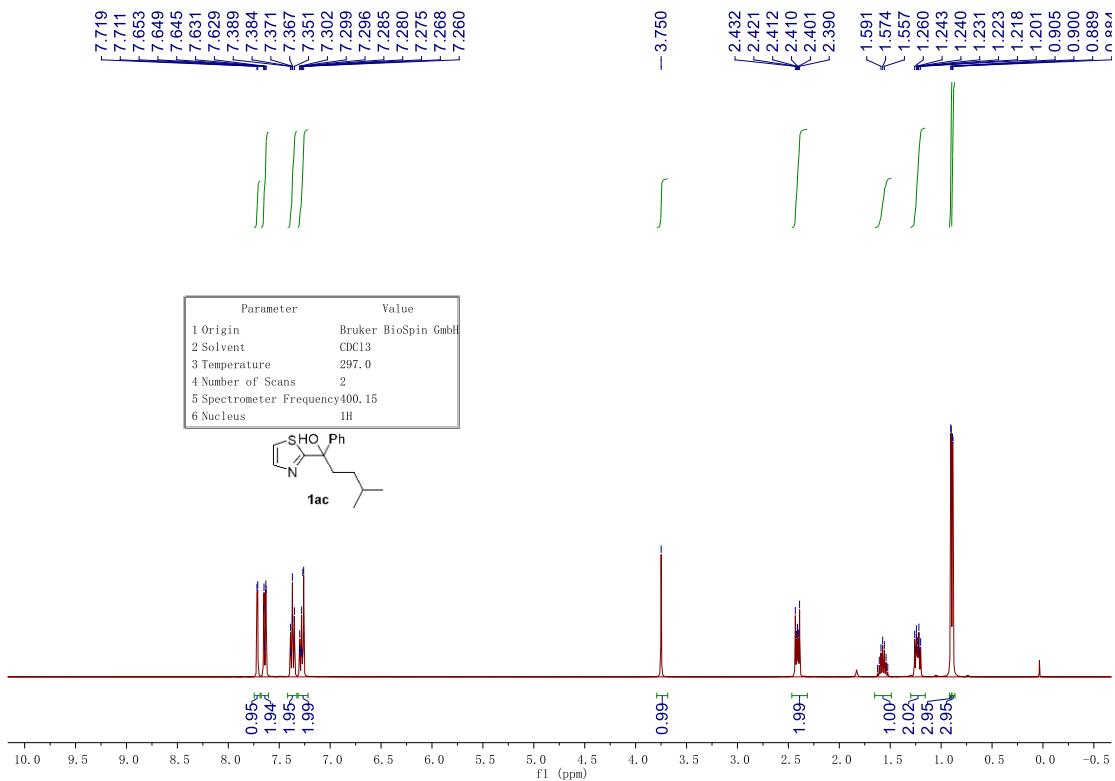
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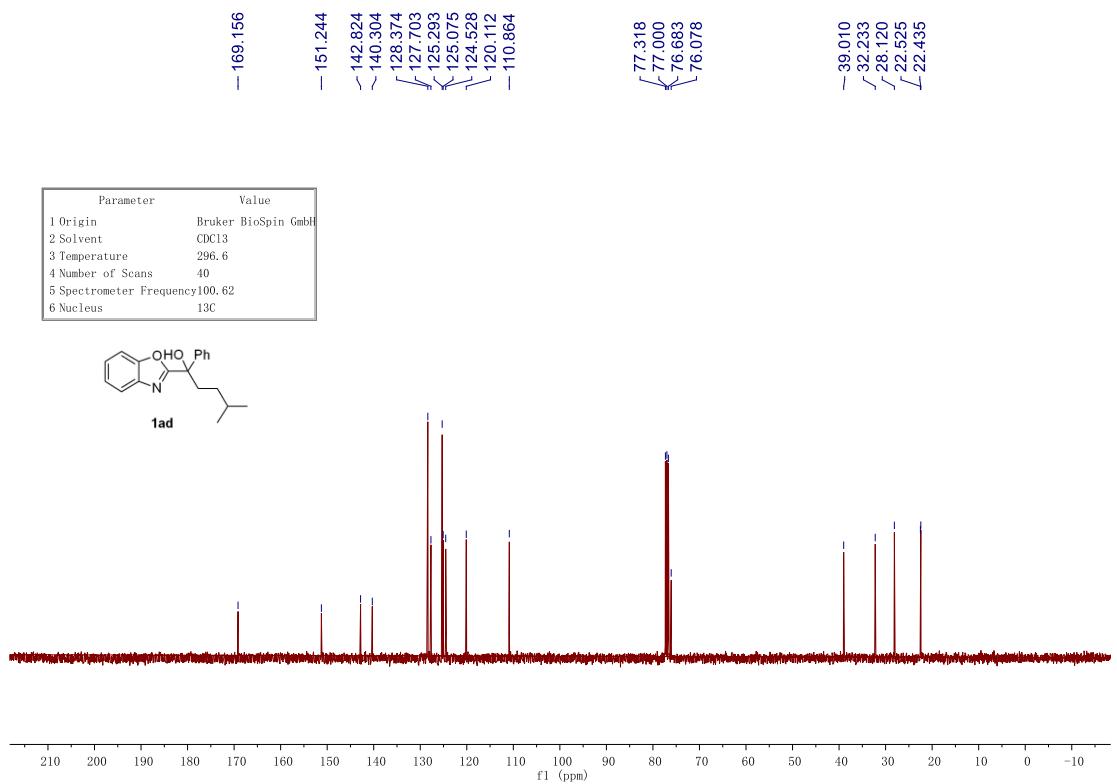
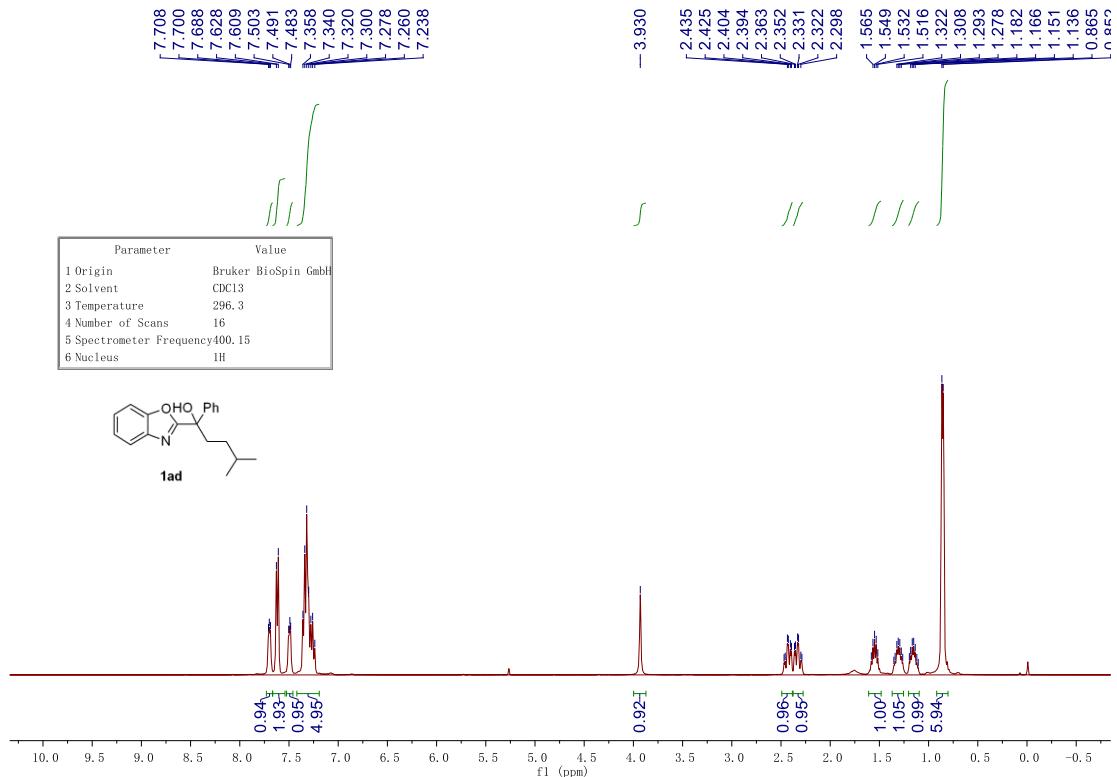
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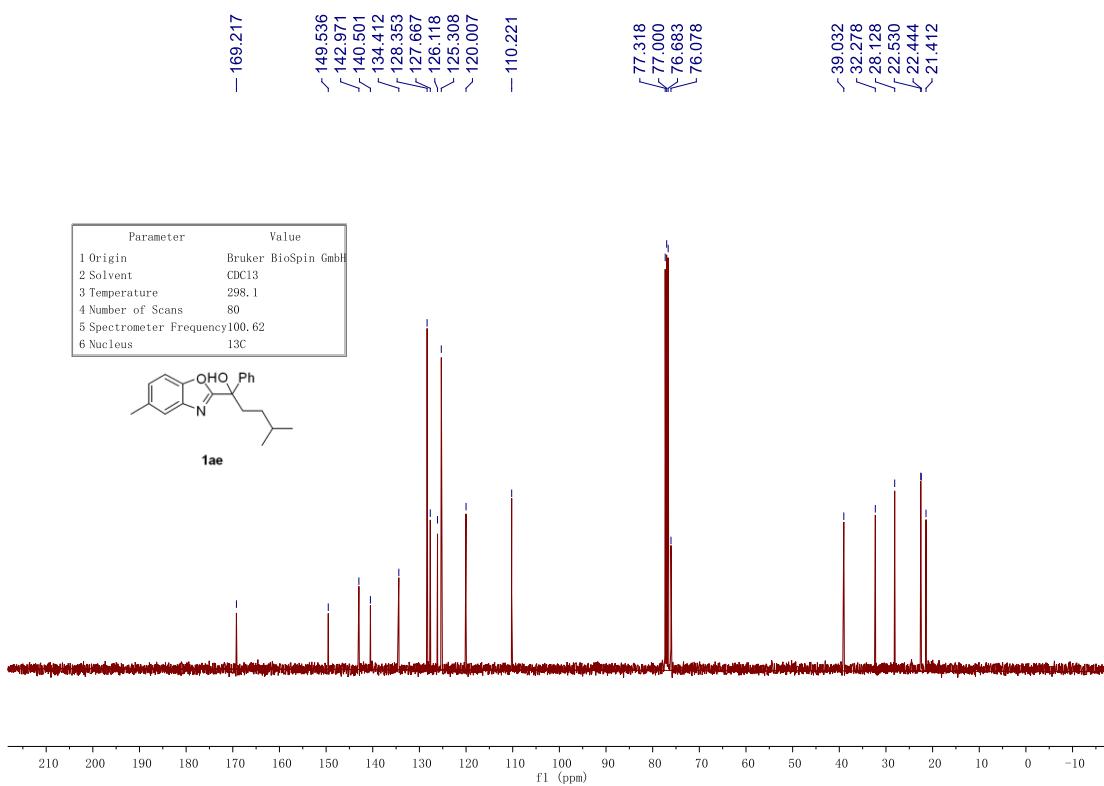
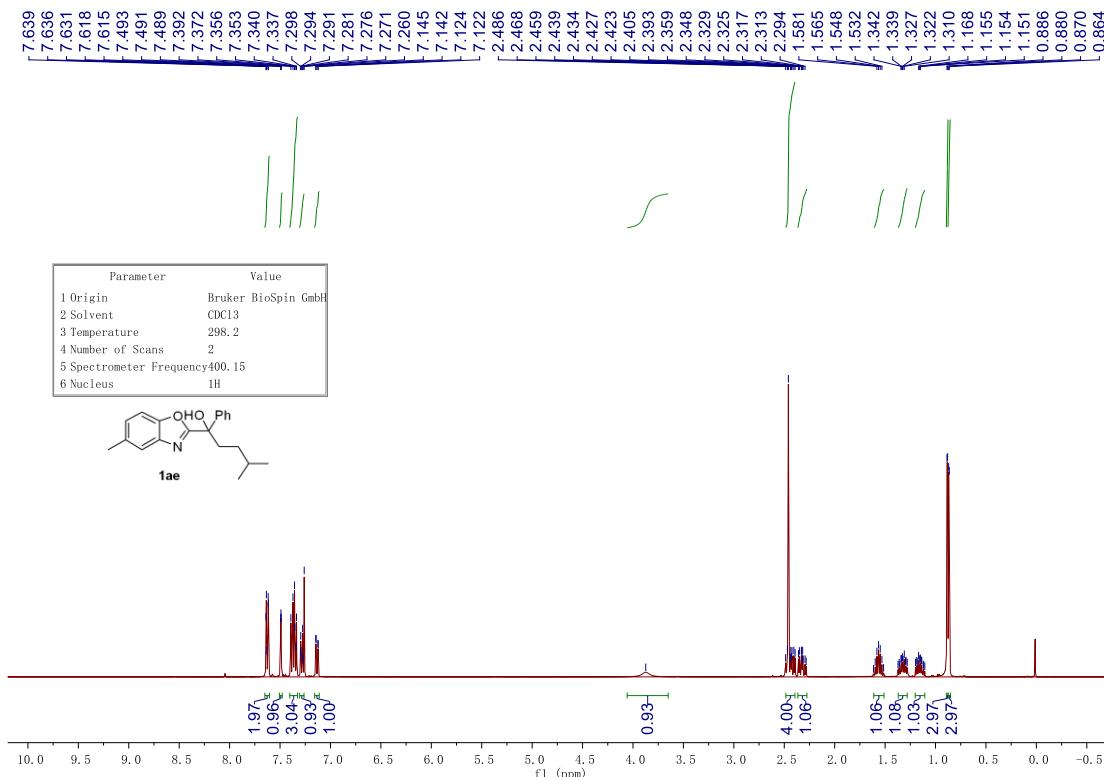
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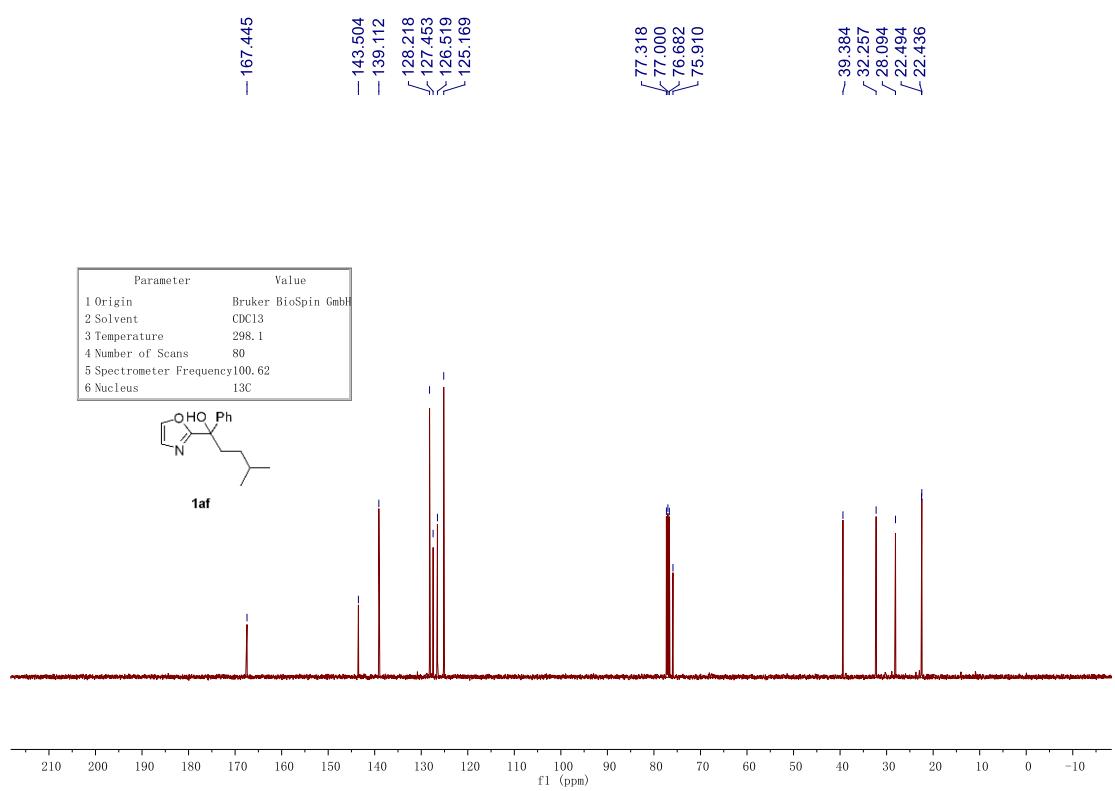
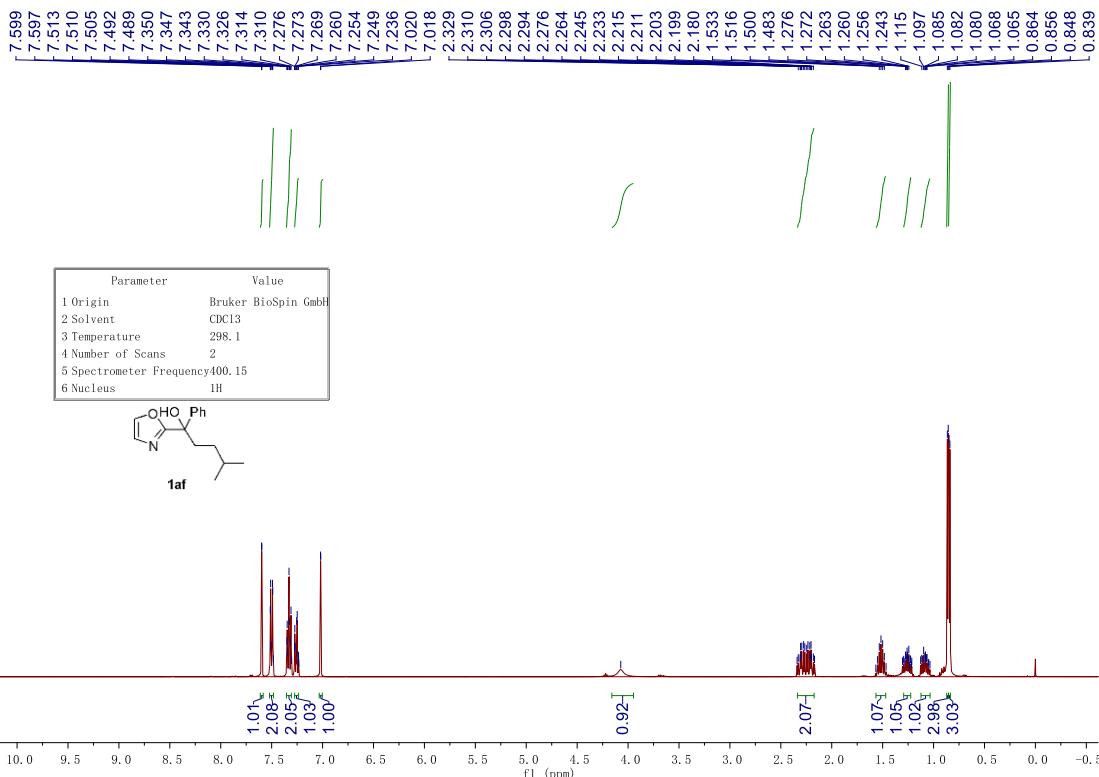


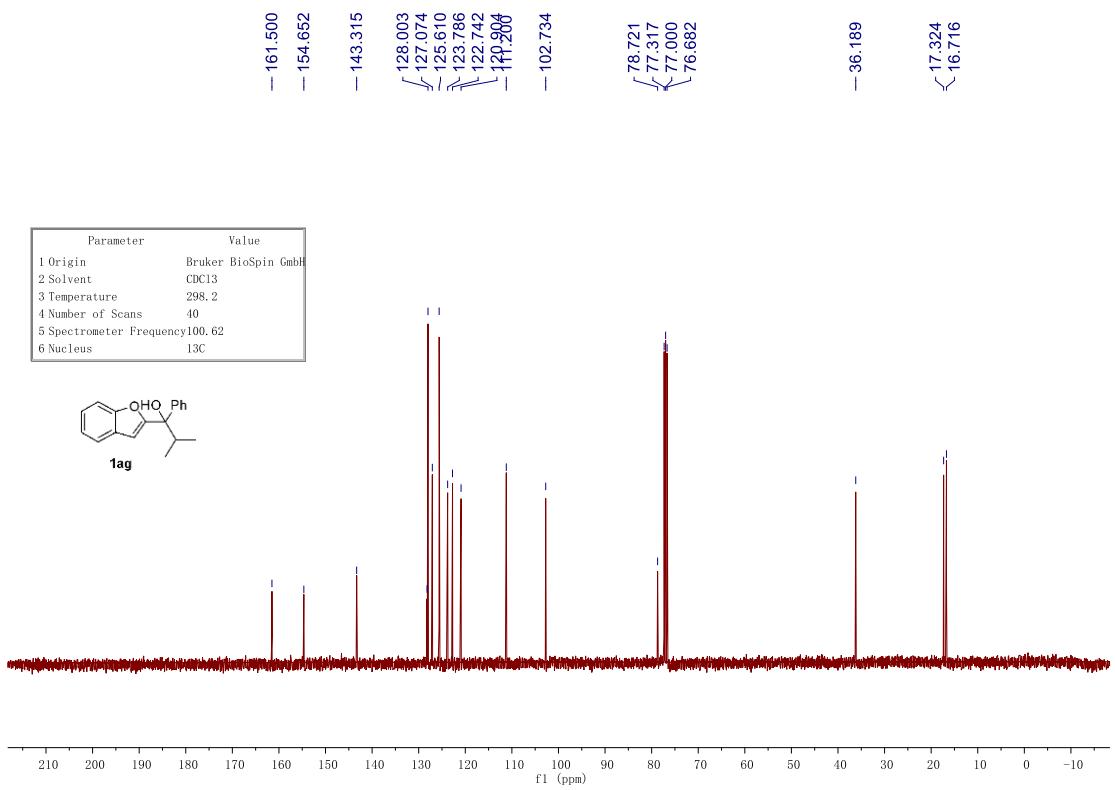
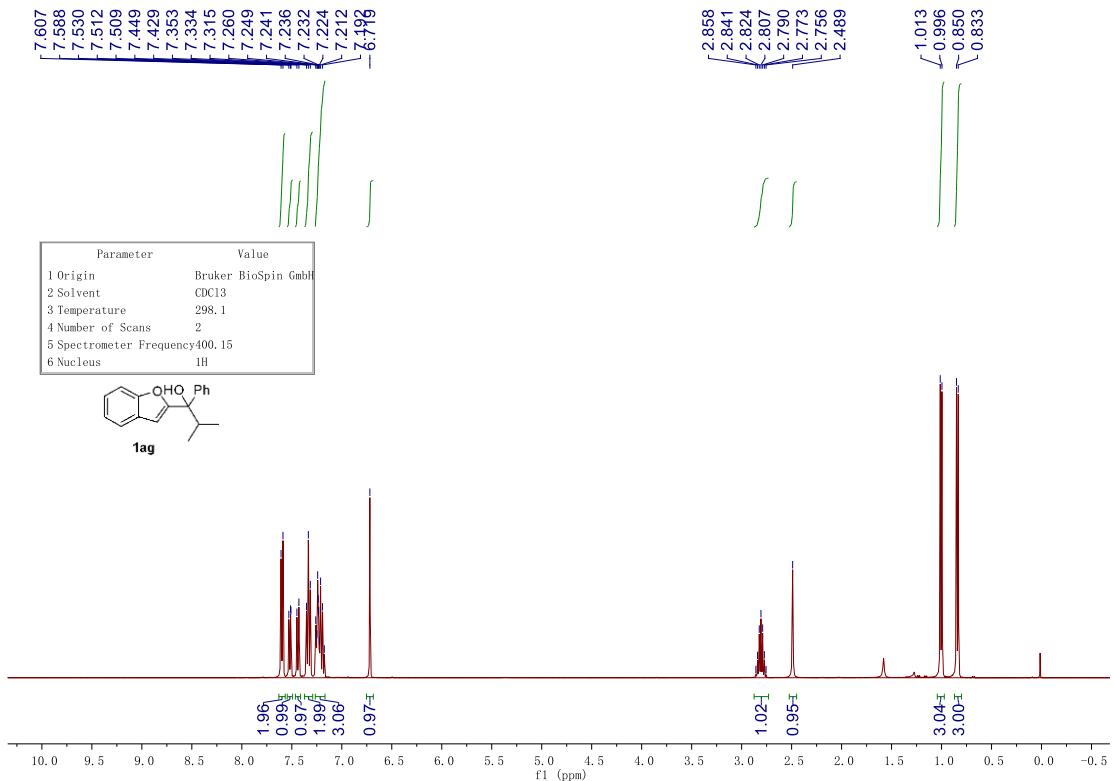


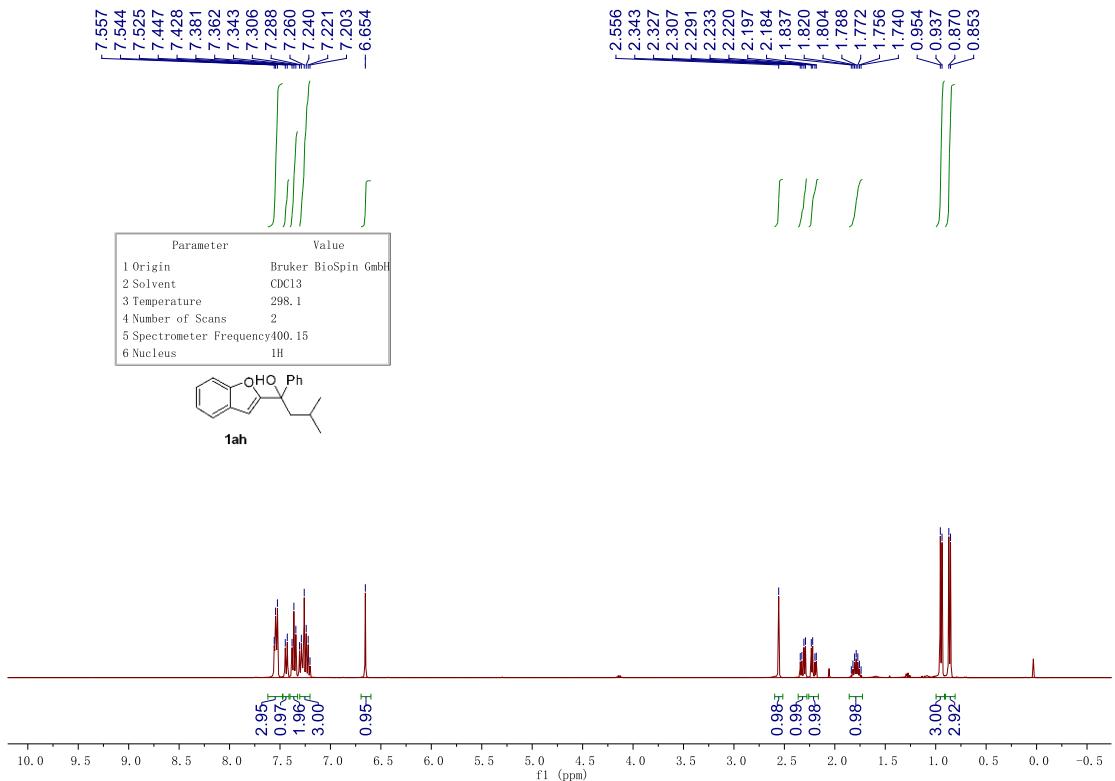


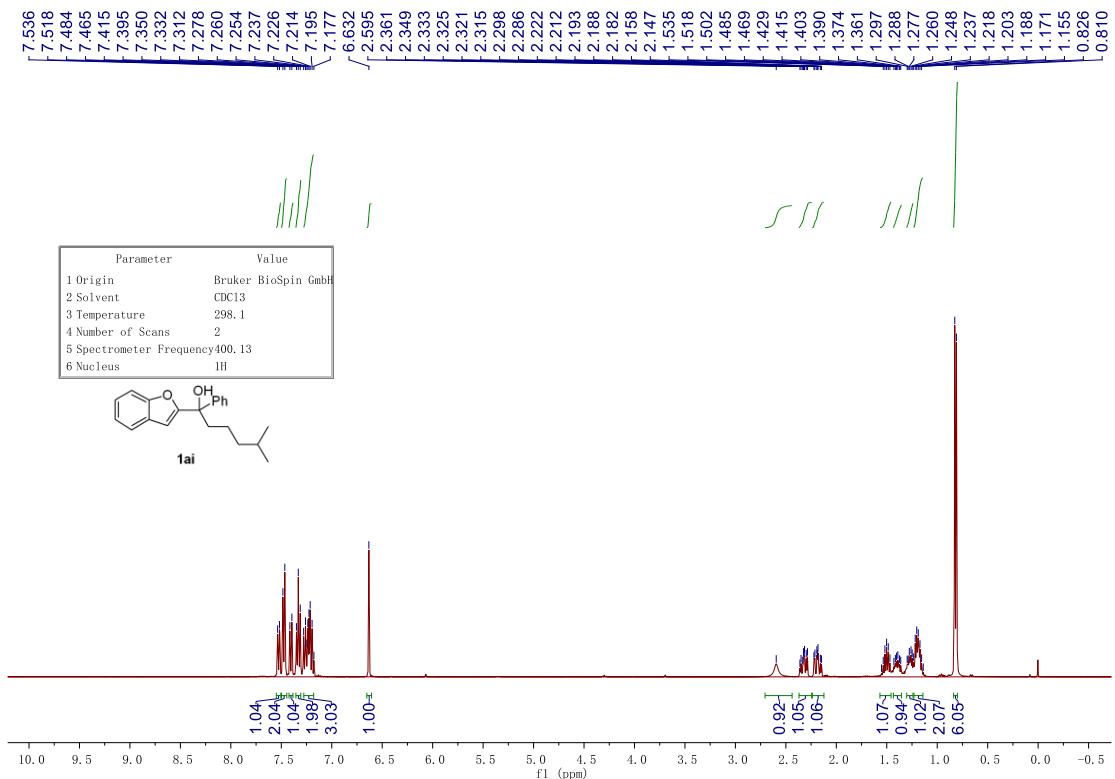






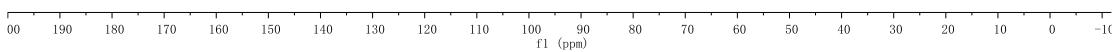
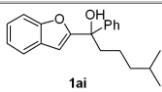


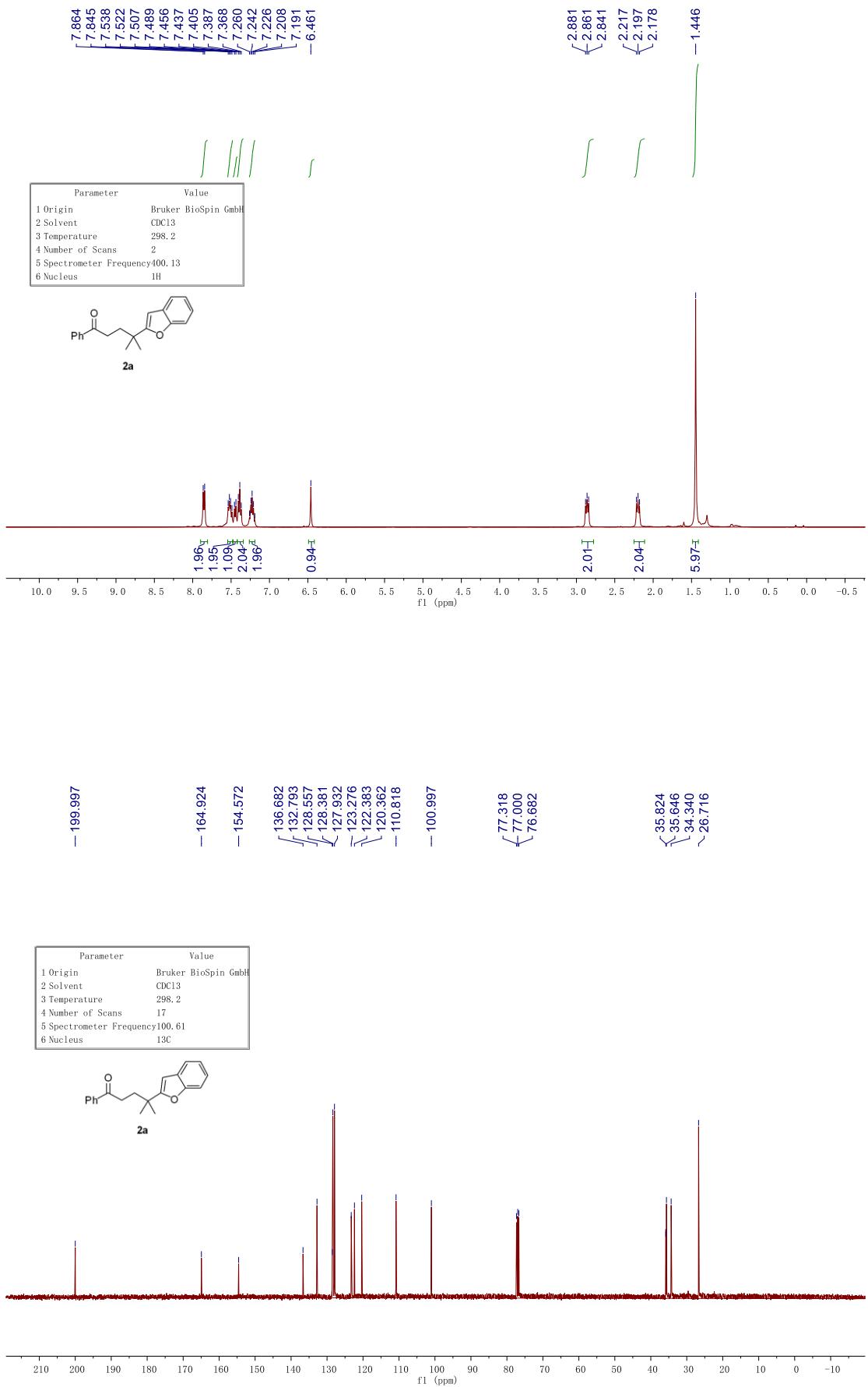


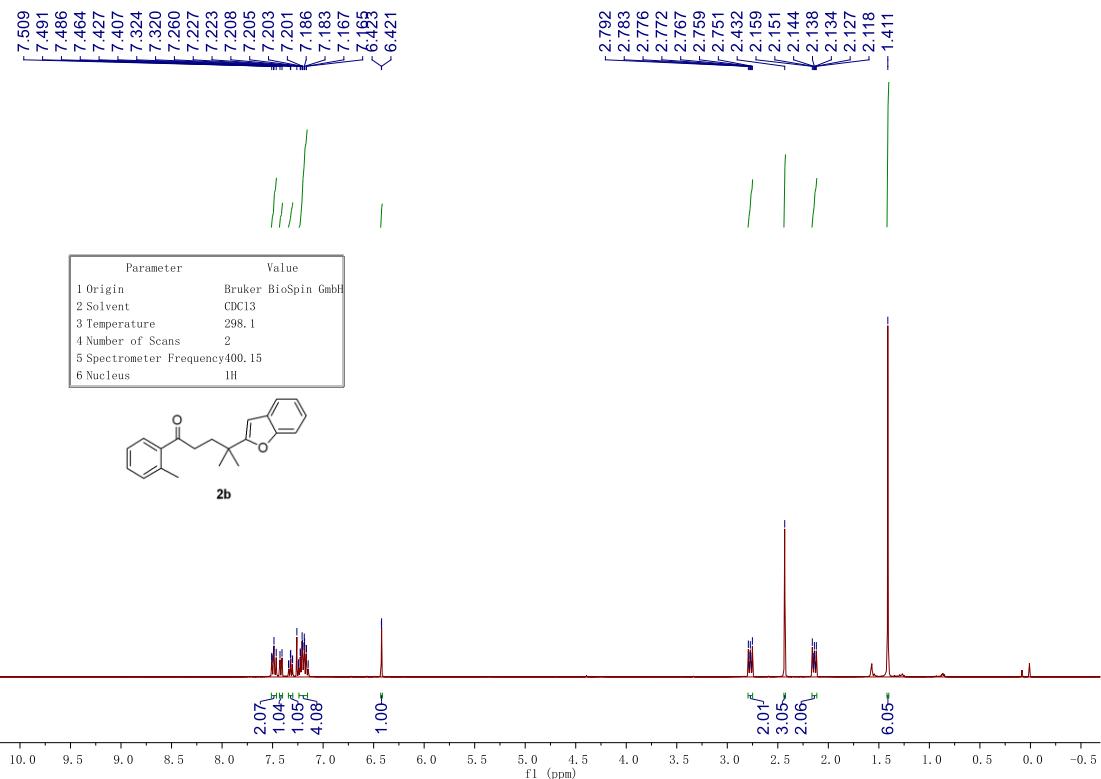


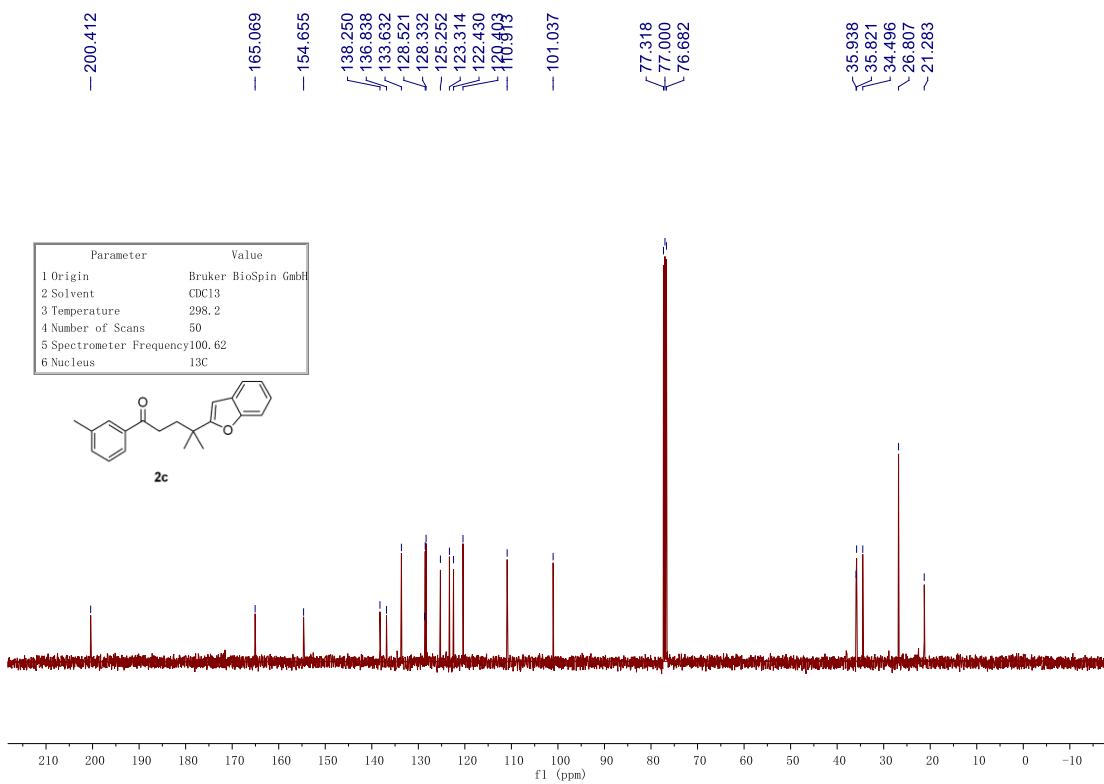
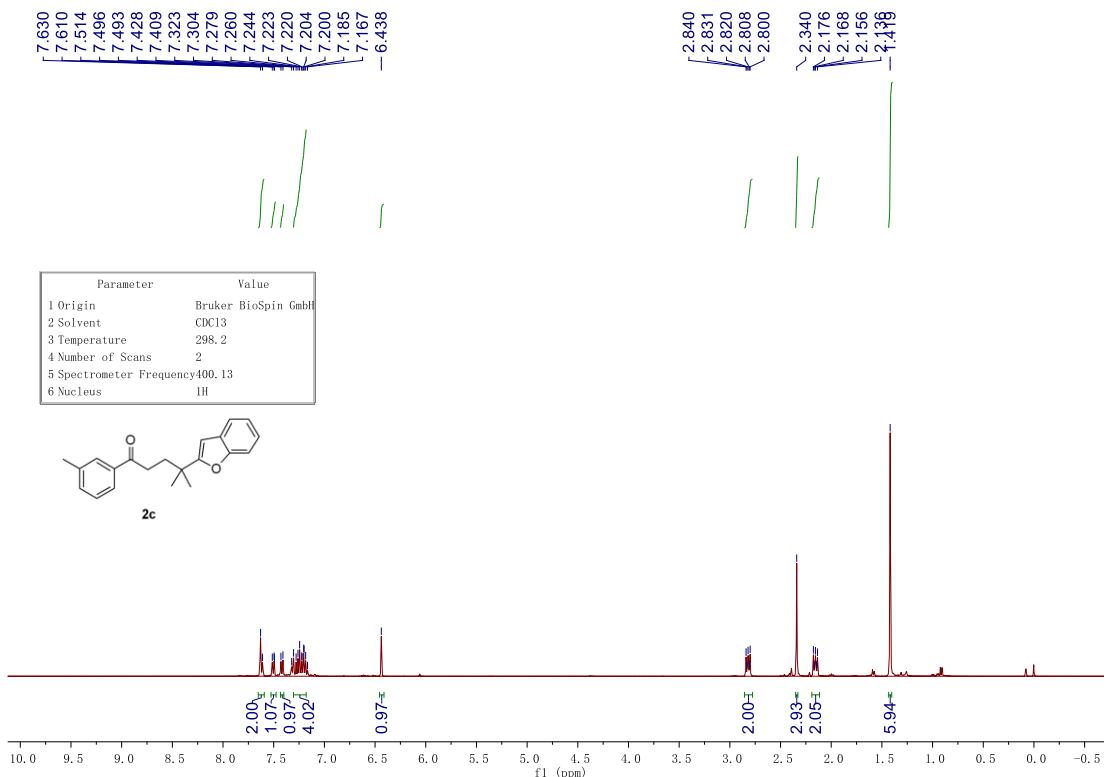
Parameter Value

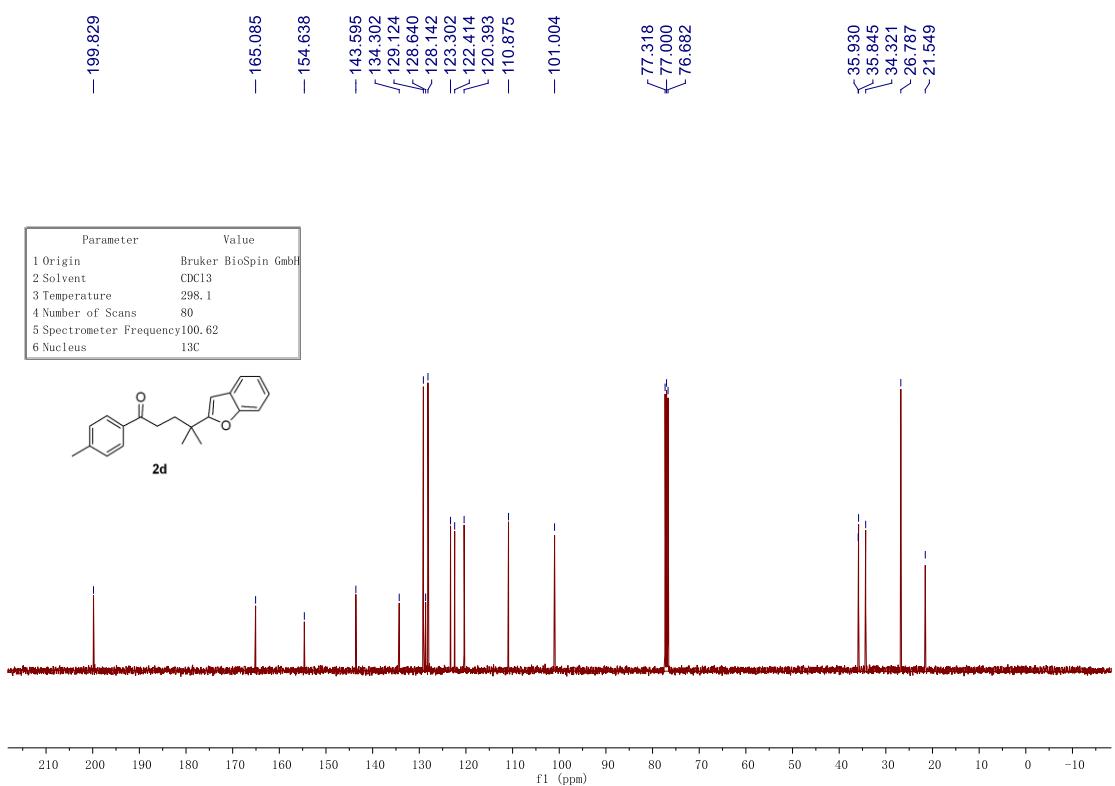
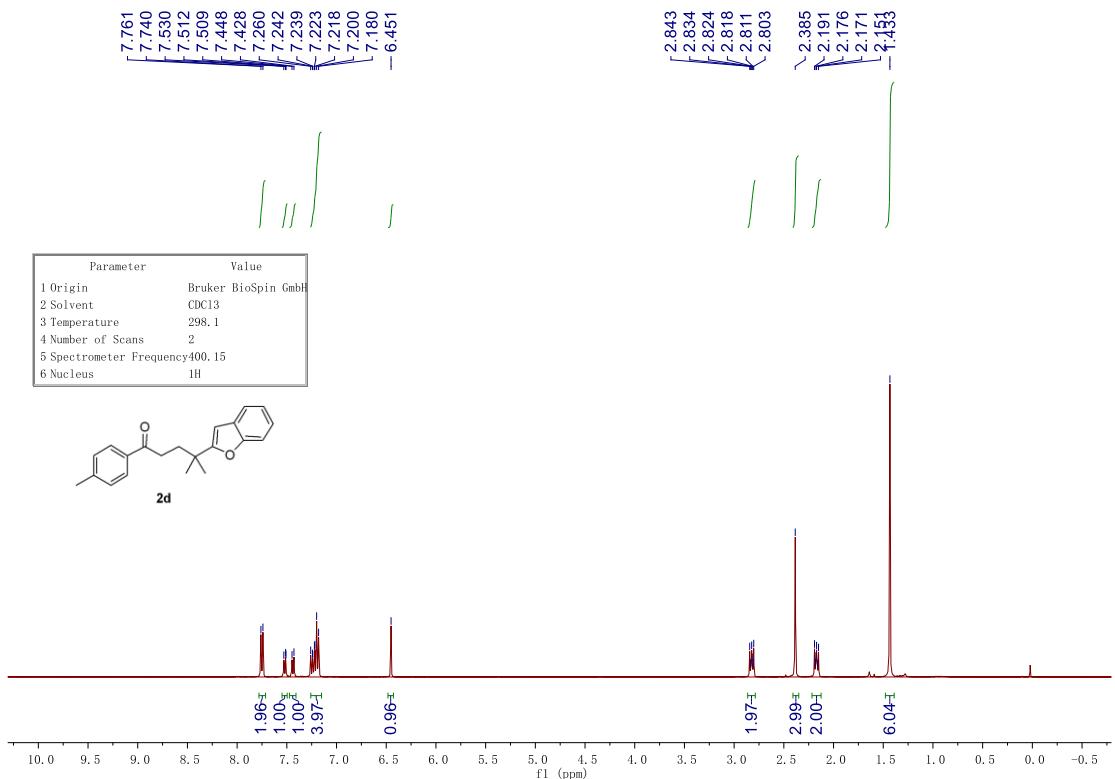
- Origin Bruker BioSpin GmbH
- Solvent CDCl<sub>3</sub>
- Temperature 298.2
- Number of Scans 50
- Spectrometer Frequency 100.62
- Nucleus <sup>13</sup>C

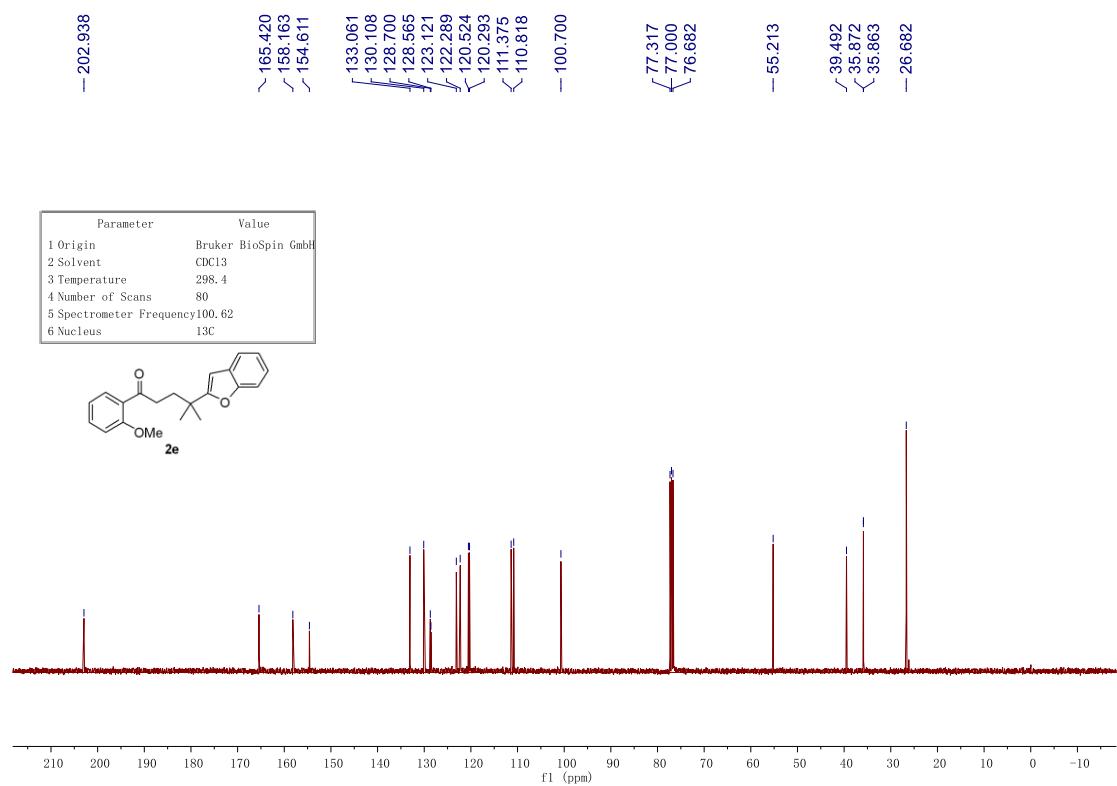
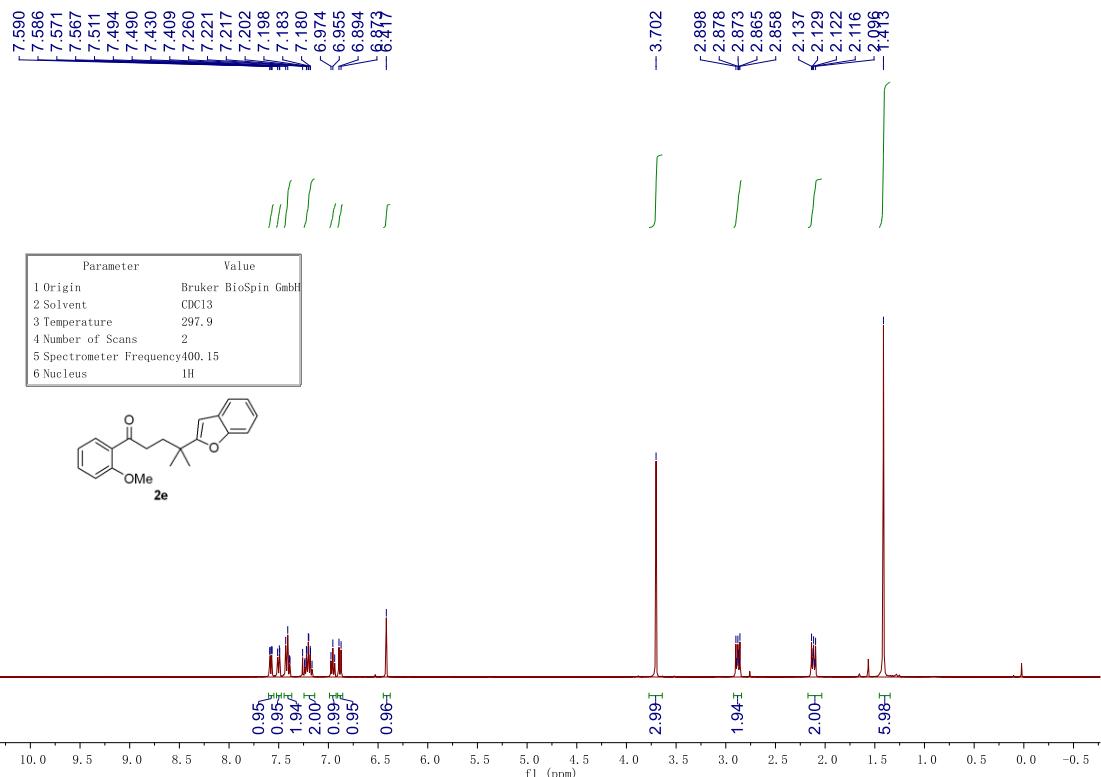


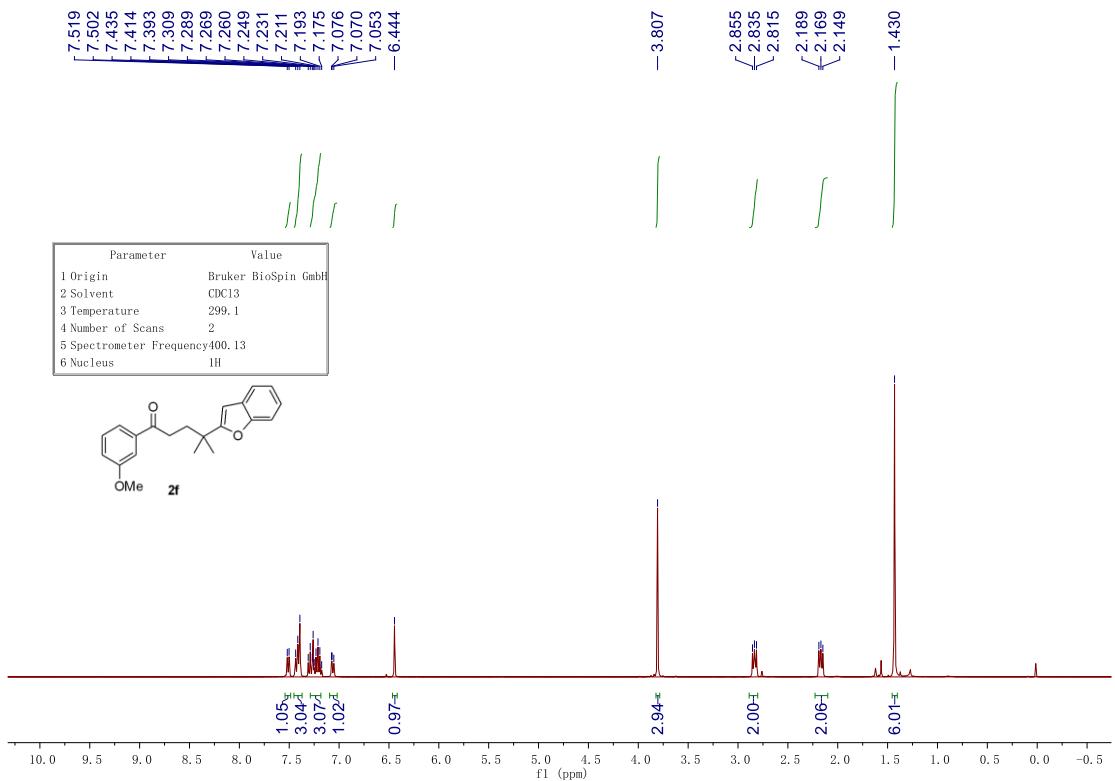


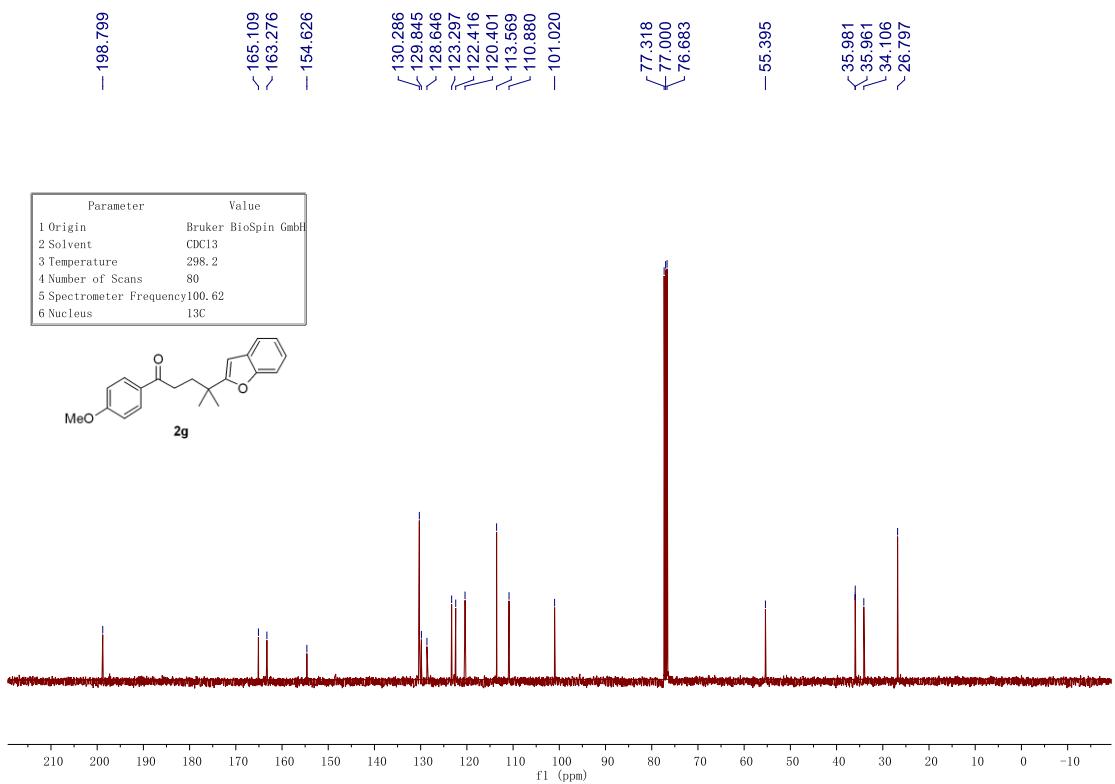
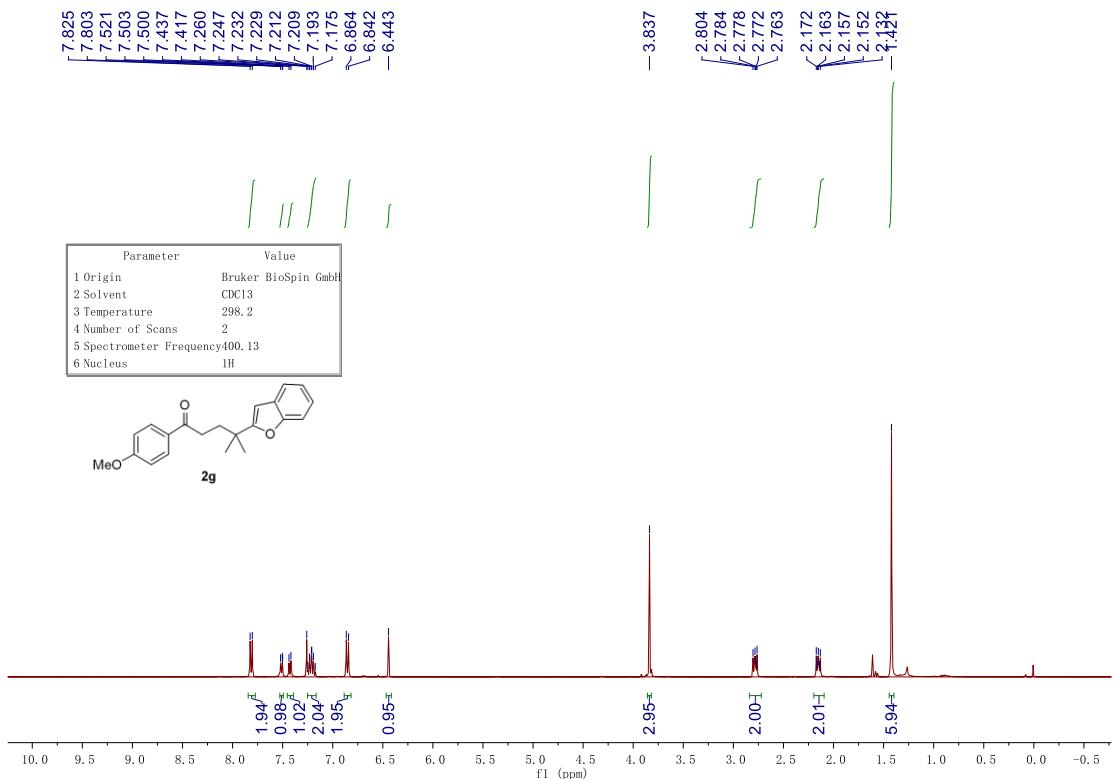


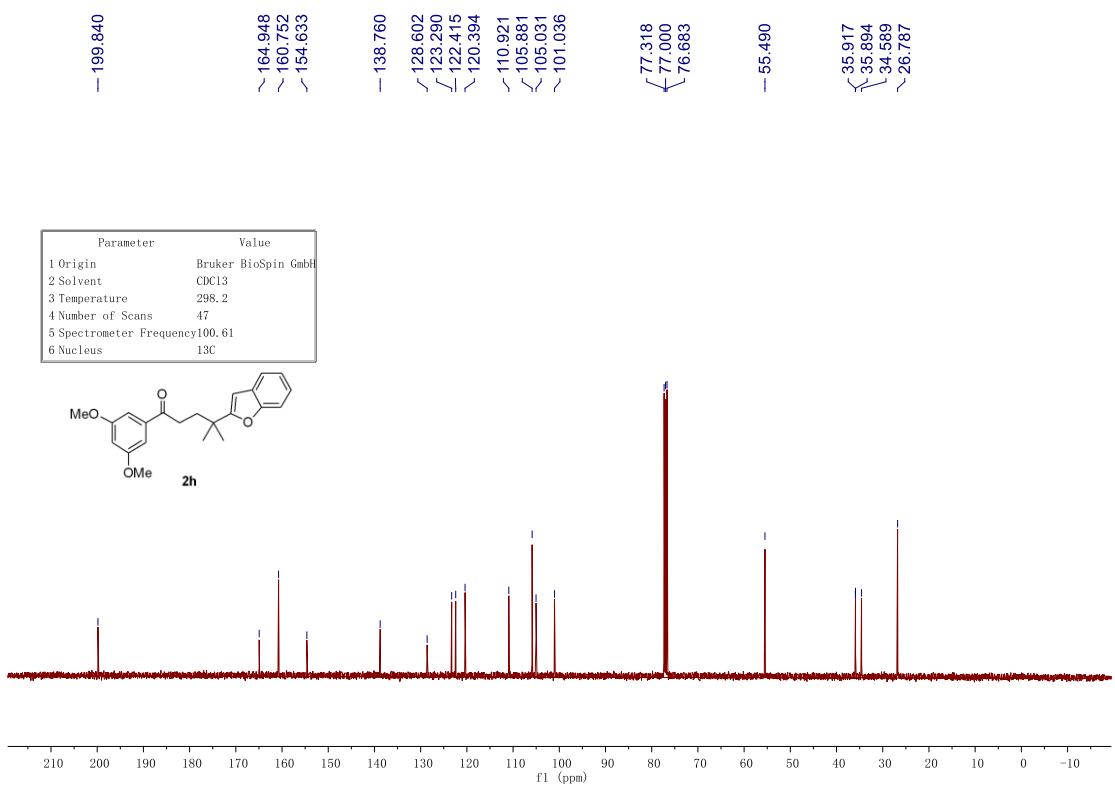
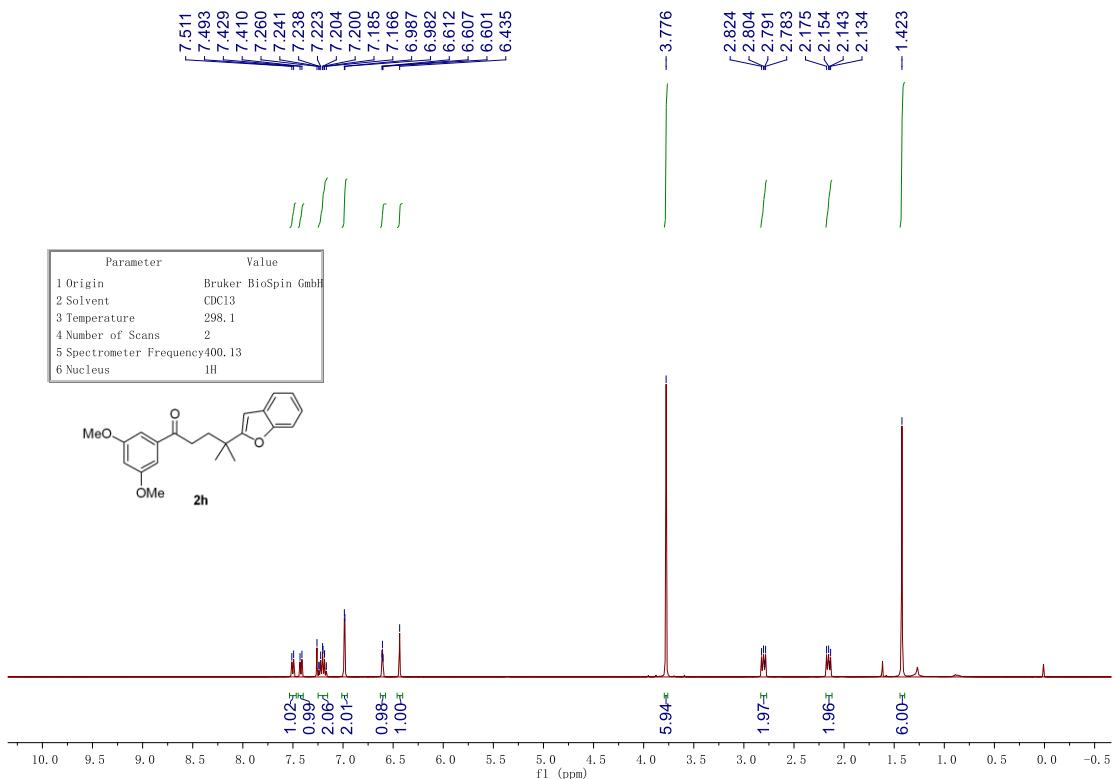


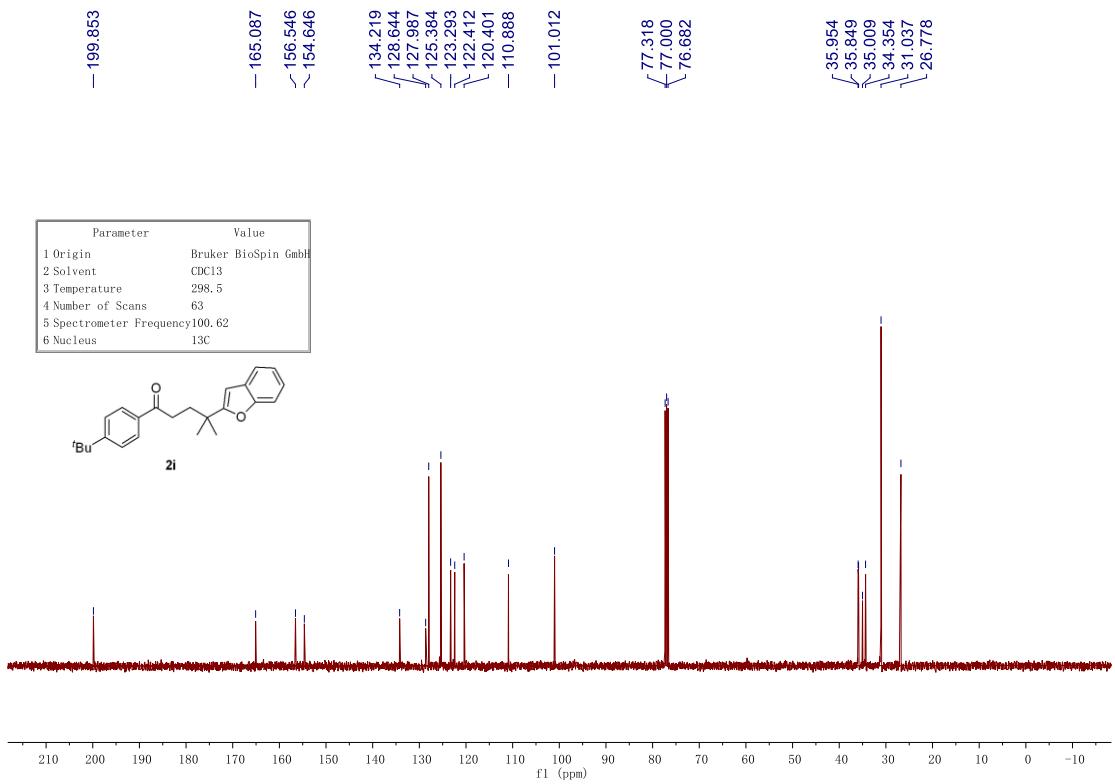
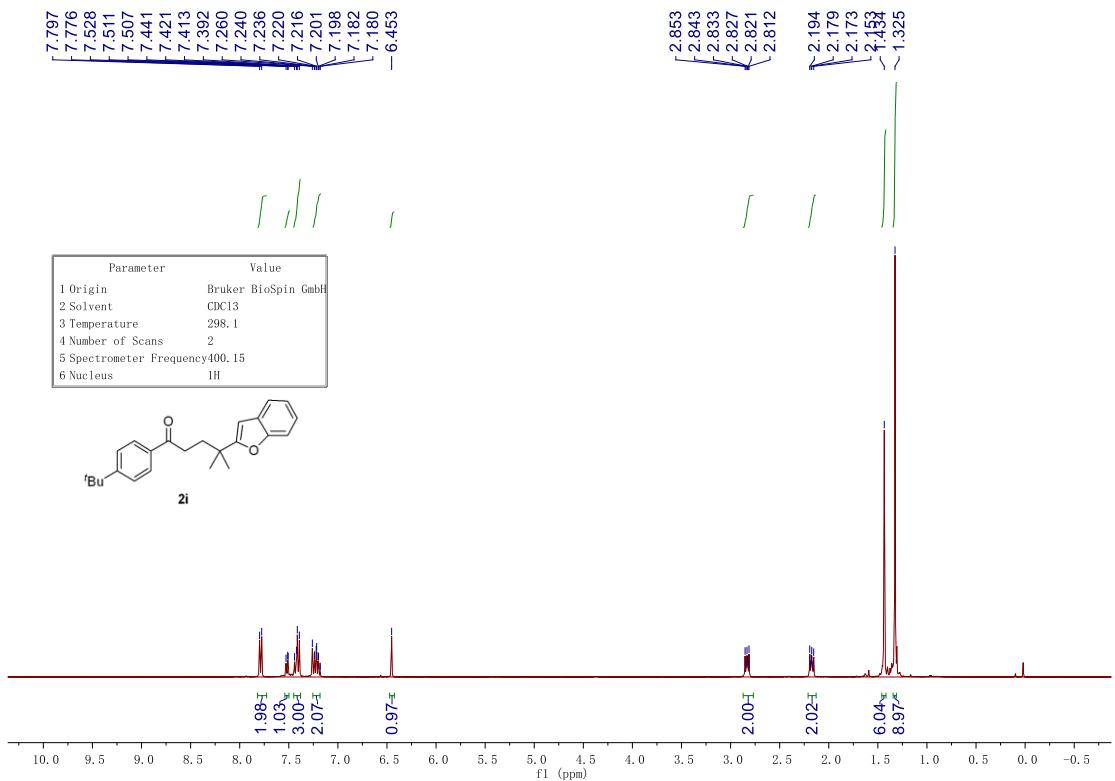


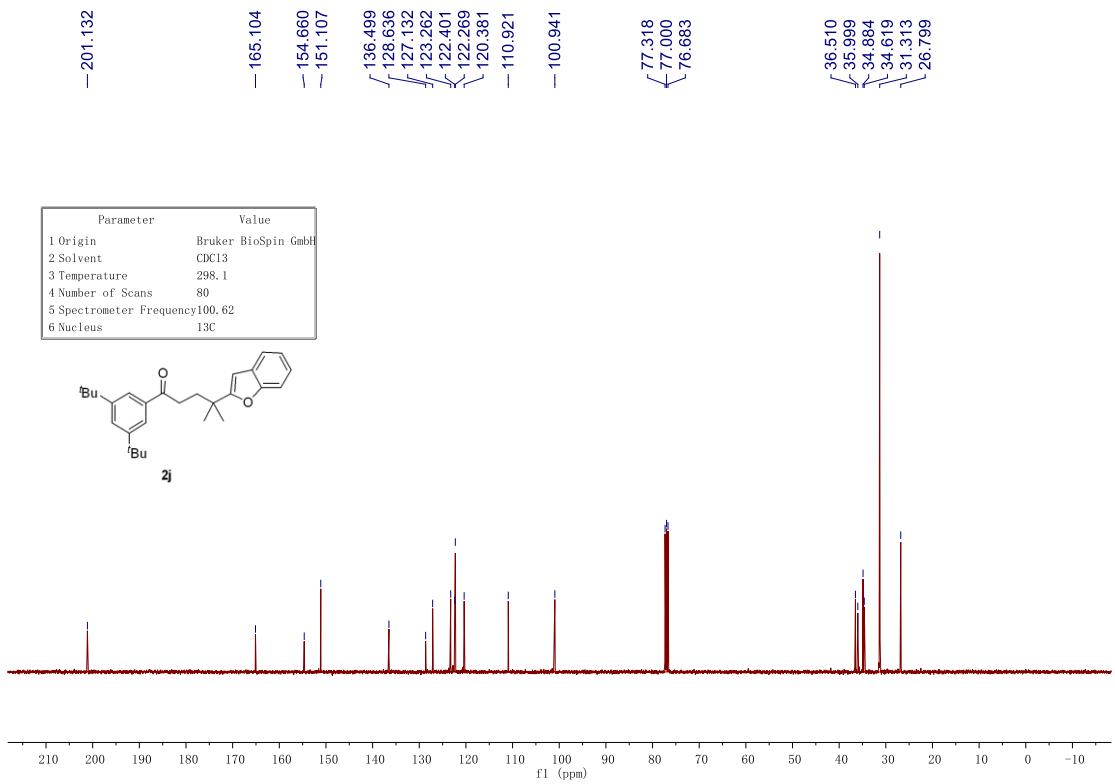
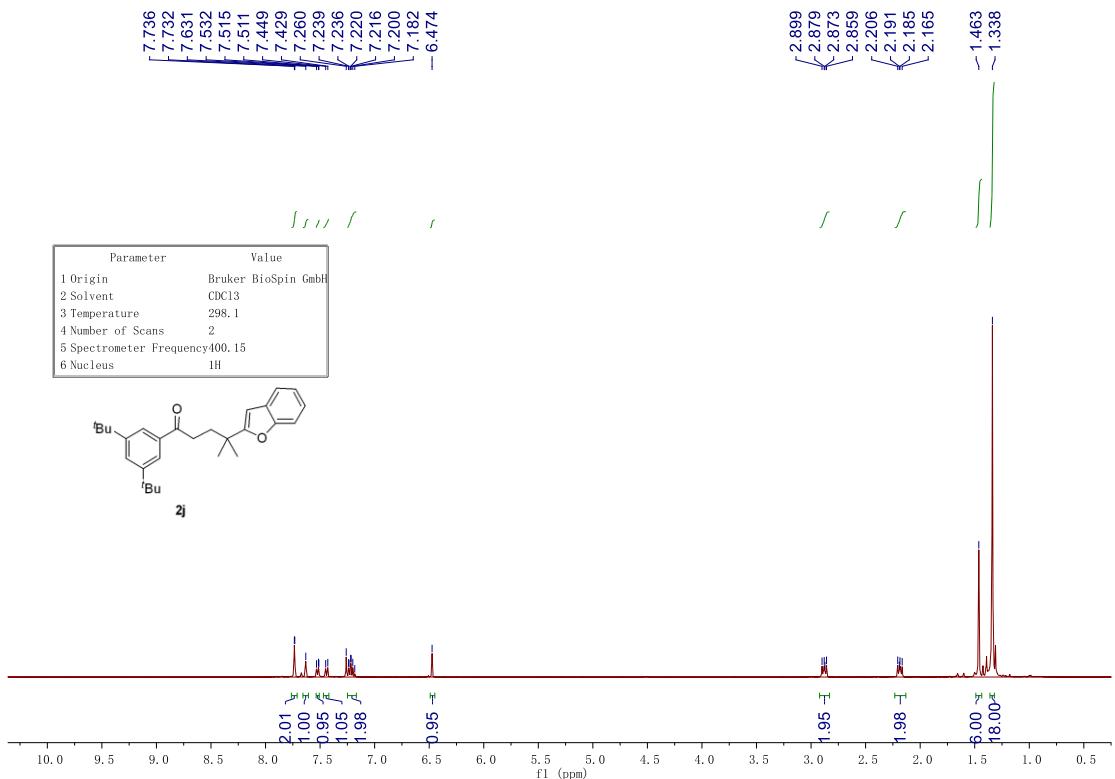


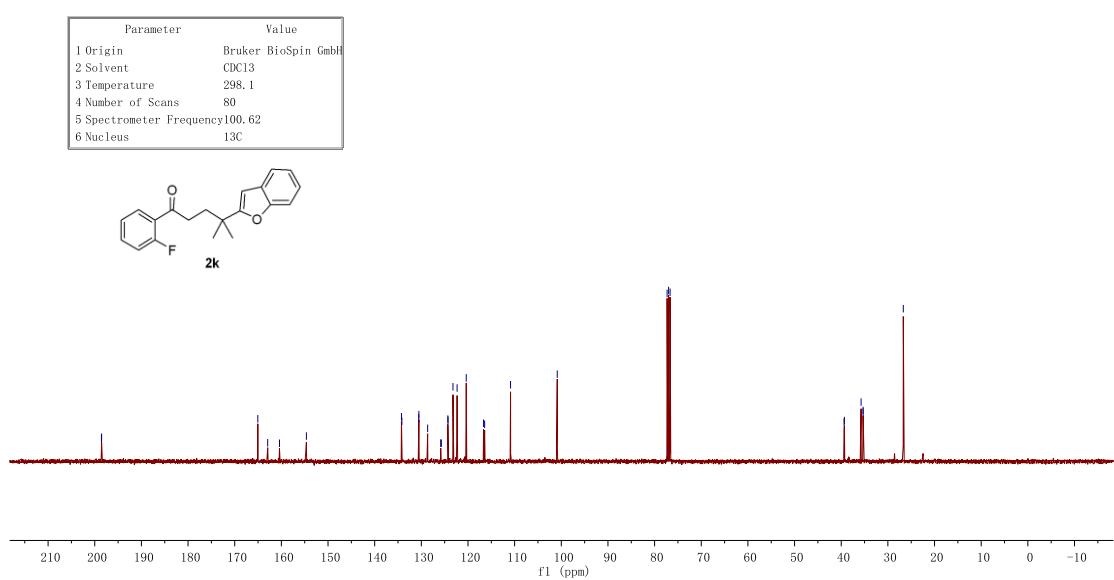
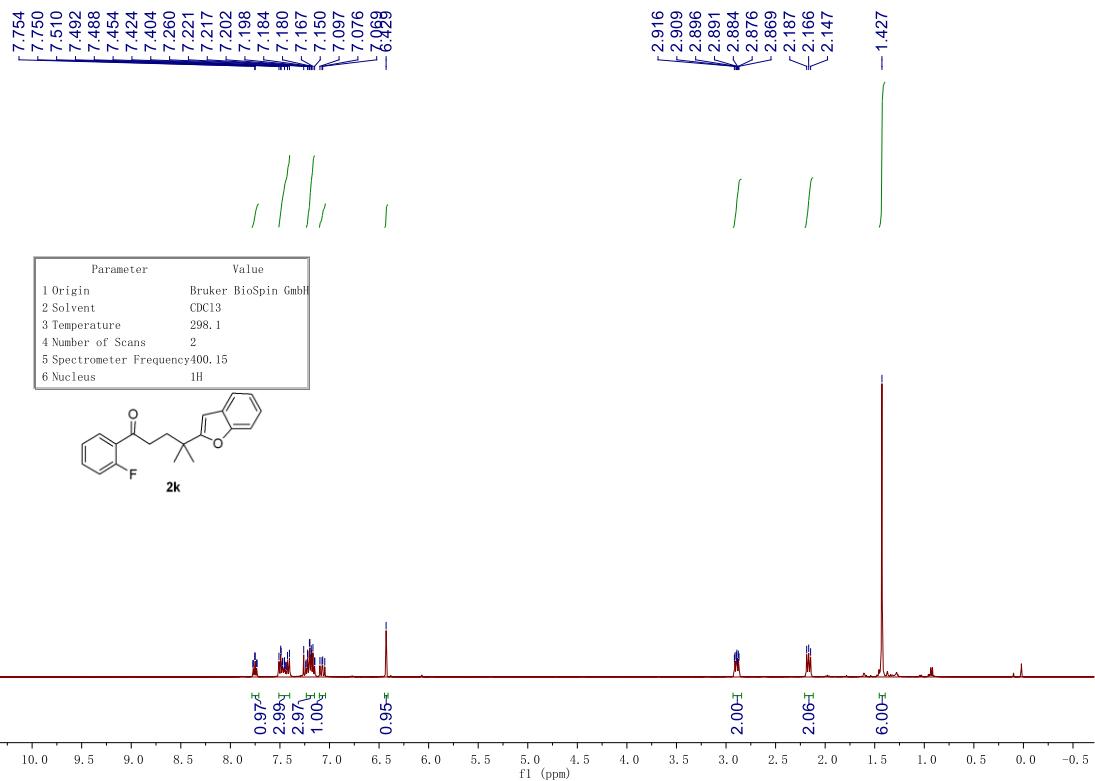


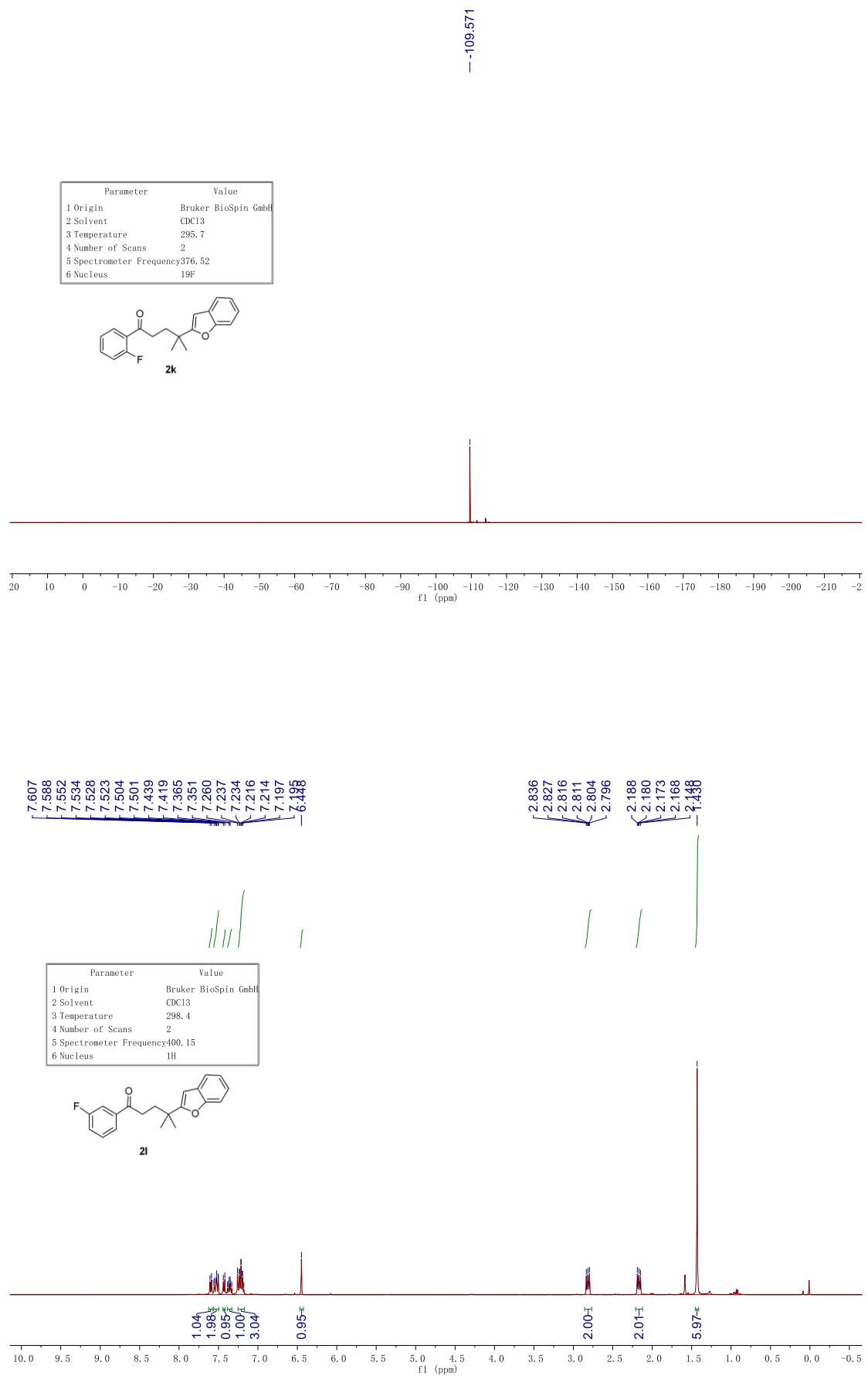


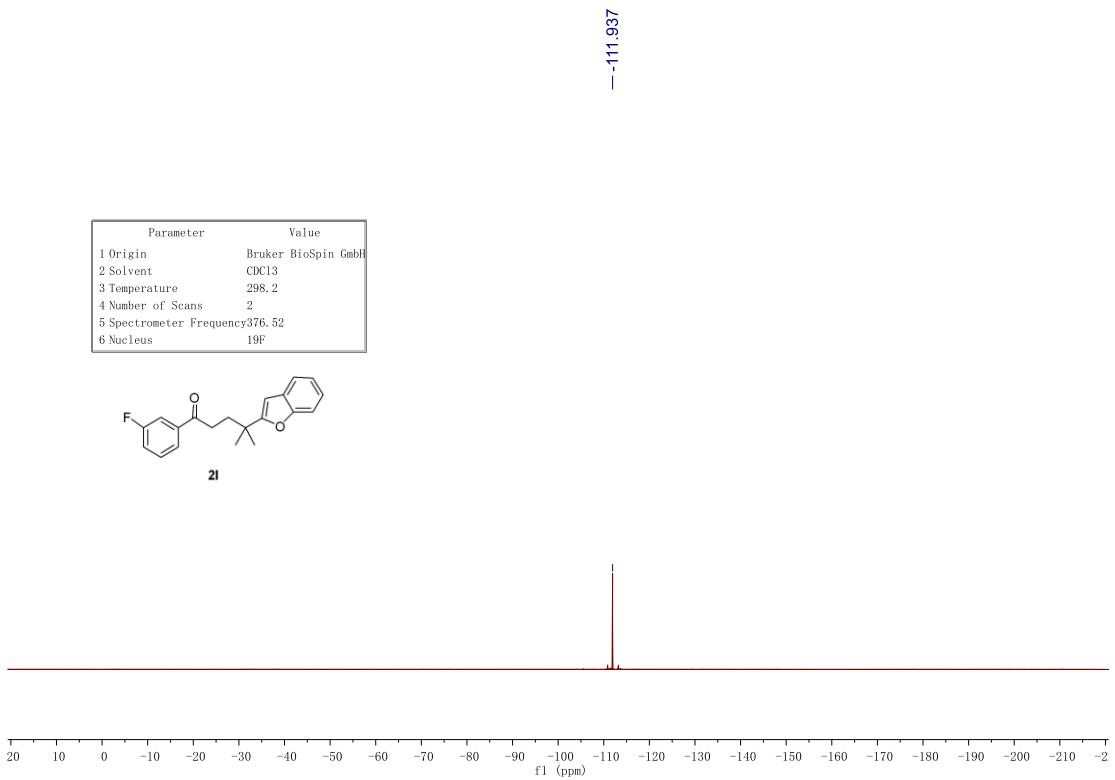
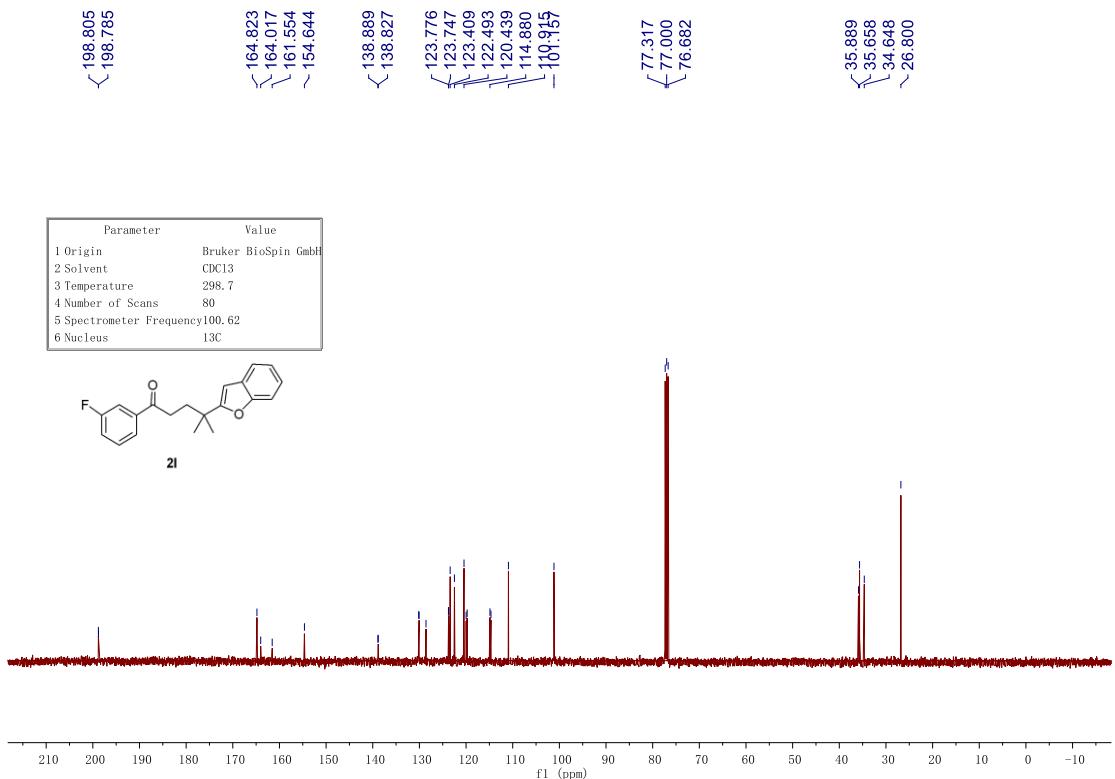


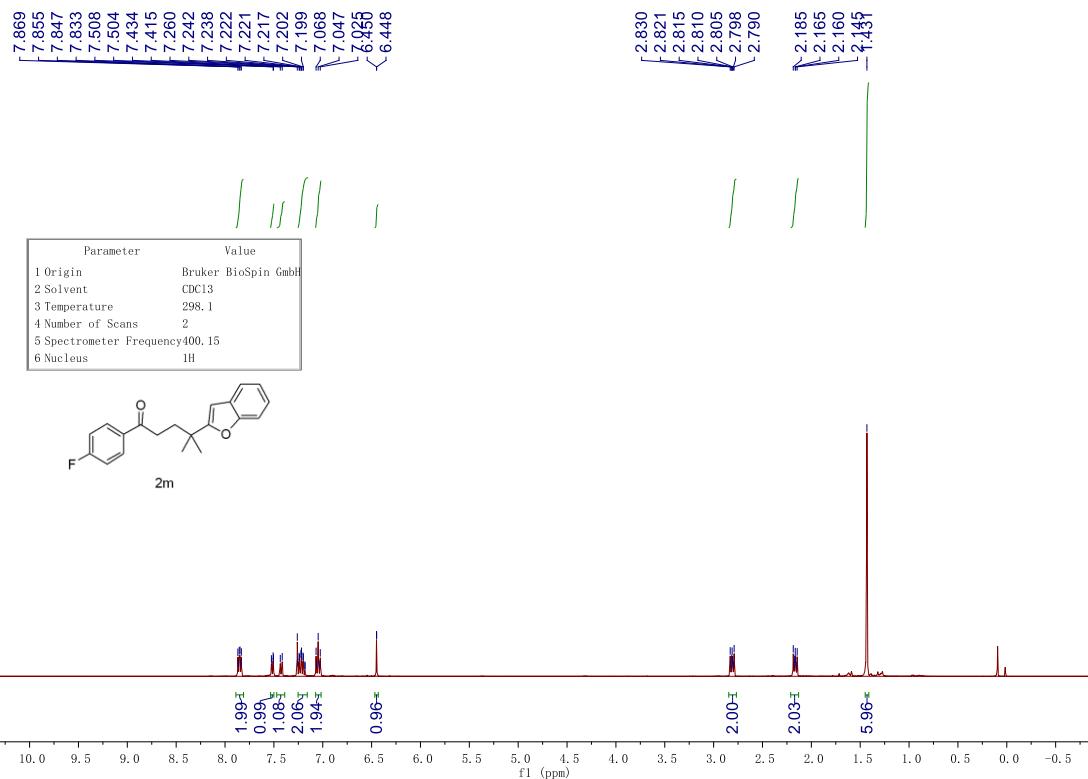










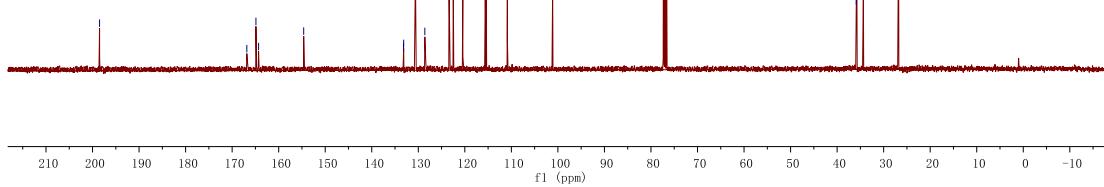
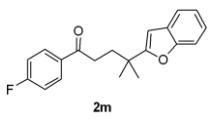


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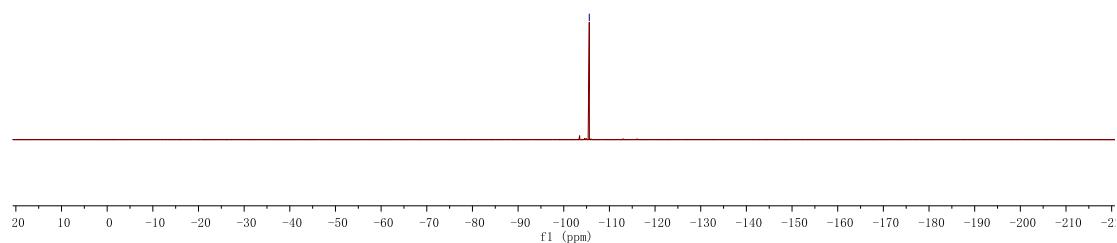
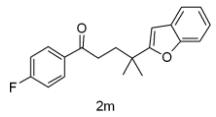
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-123.391  
-122.482  
-120.433  
-115.609  
-115.393  
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-101.130

77.317  
77.000  
76.882  
35.899  
35.753  
34.360  
26.780

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl <sub>3</sub>
3 Temperature	298.1
4 Number of Scans	82
5 Spectrometer Frequency	100.62
6 Nucleus	<sup>13</sup> C



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl <sub>3</sub>
3 Temperature	298.2
4 Number of Scans	2
5 Spectrometer Frequency	376.52
6 Nucleus	<sup>19</sup> F

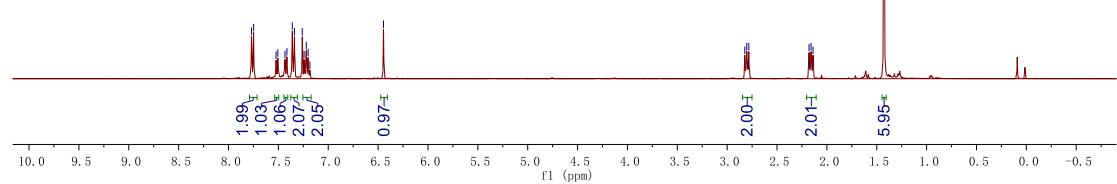
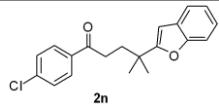


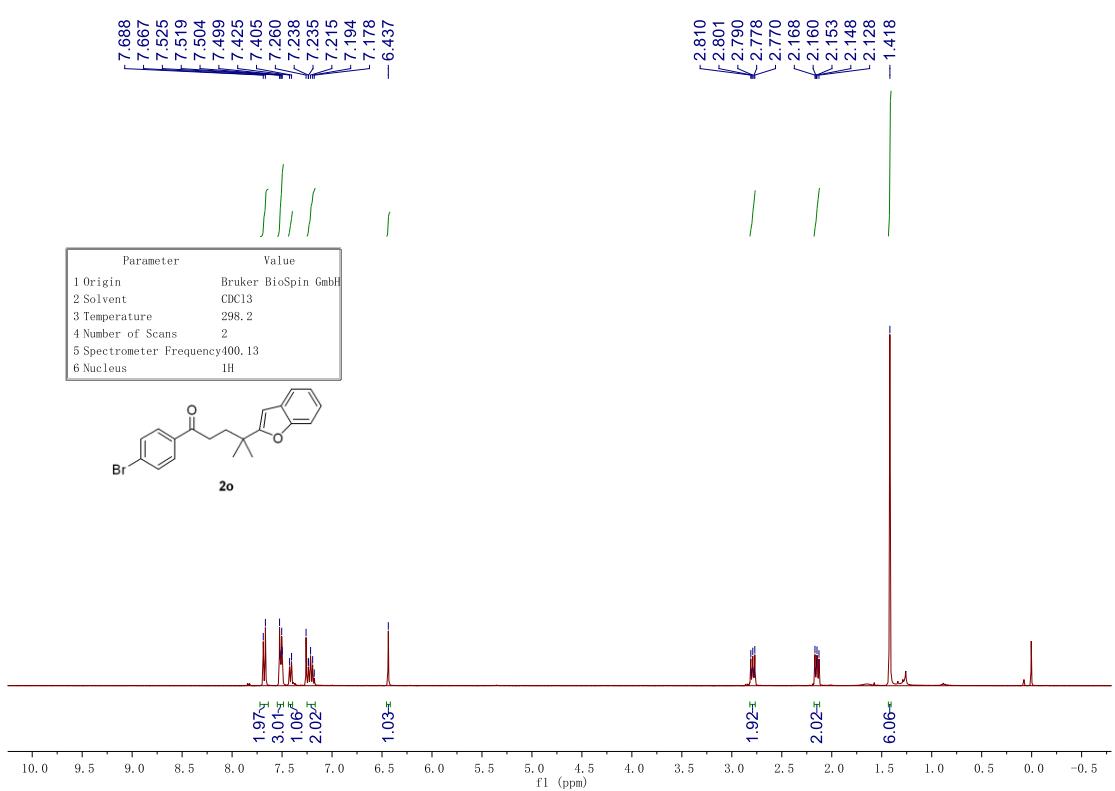
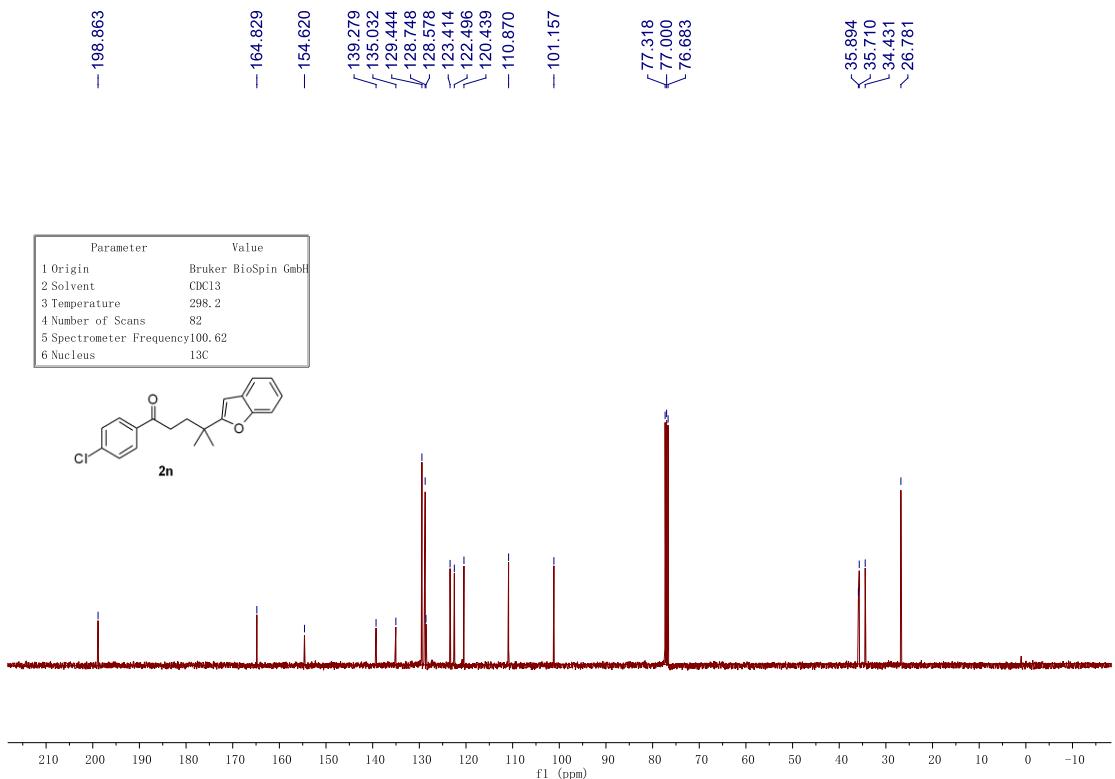
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7.523  
7.506  
7.434  
7.414  
7.360  
7.339  
7.260  
7.242  
7.220  
7.202  
7.184  
-6.446

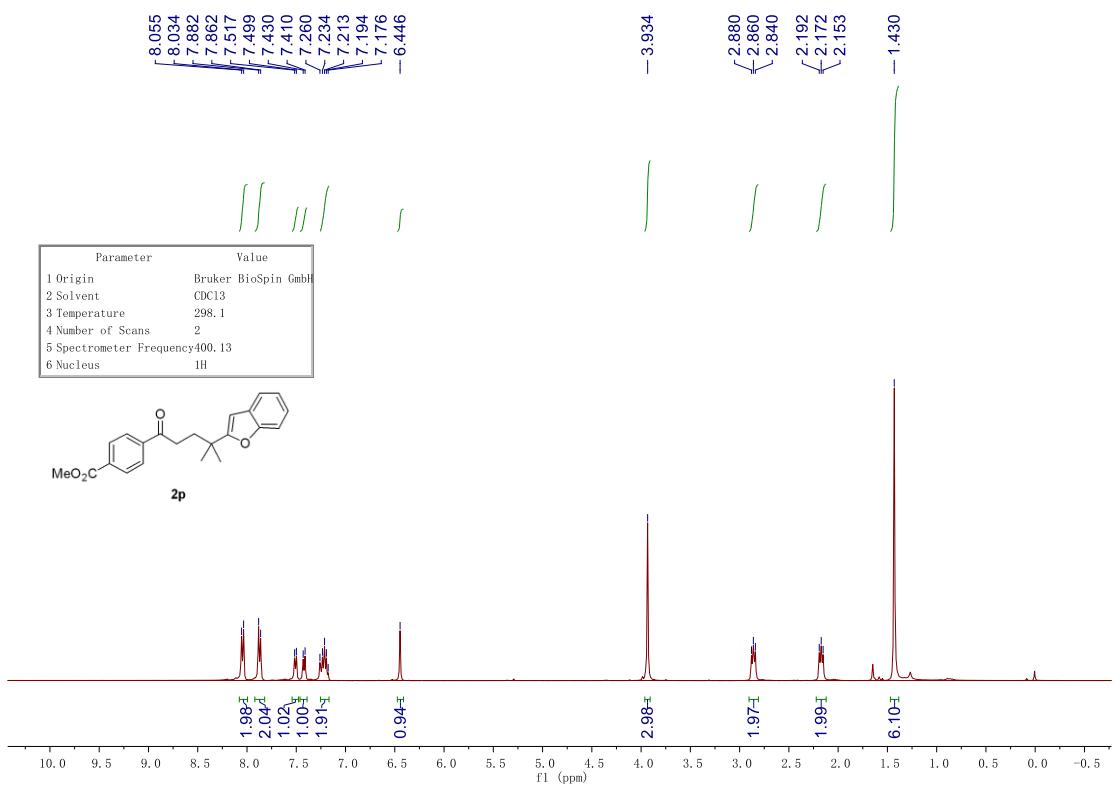
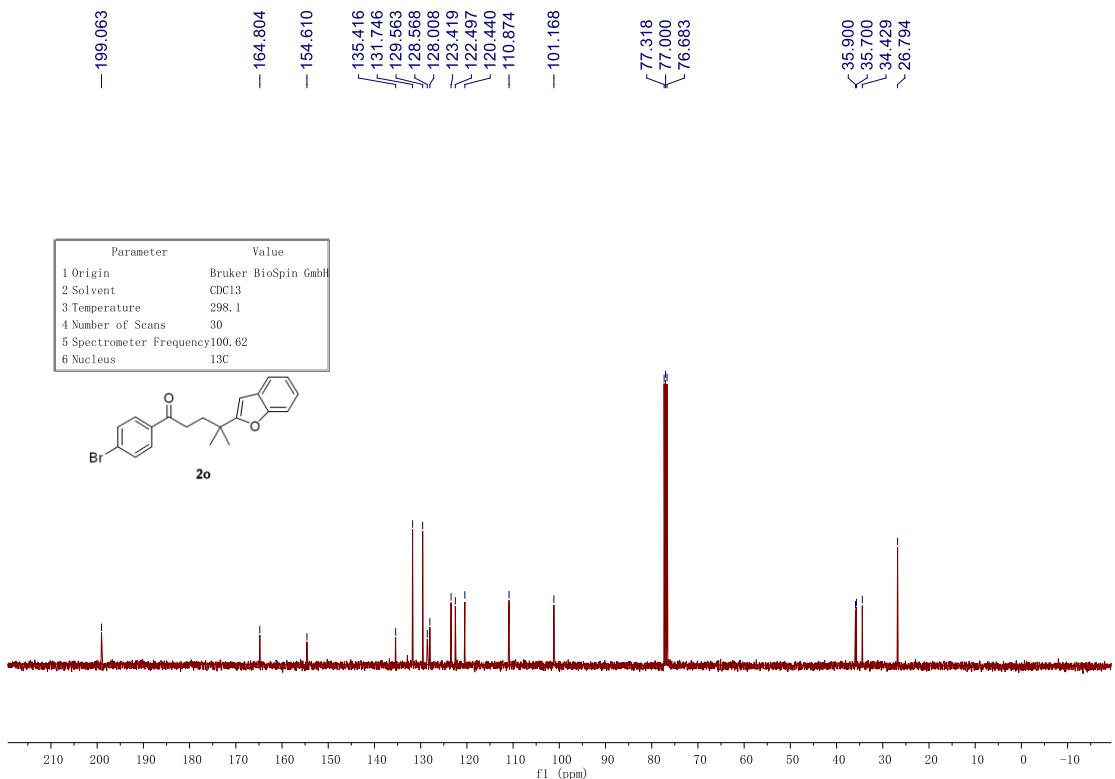
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2.803  
2.791  
2.783  
2.179  
2.170  
2.158  
2.139

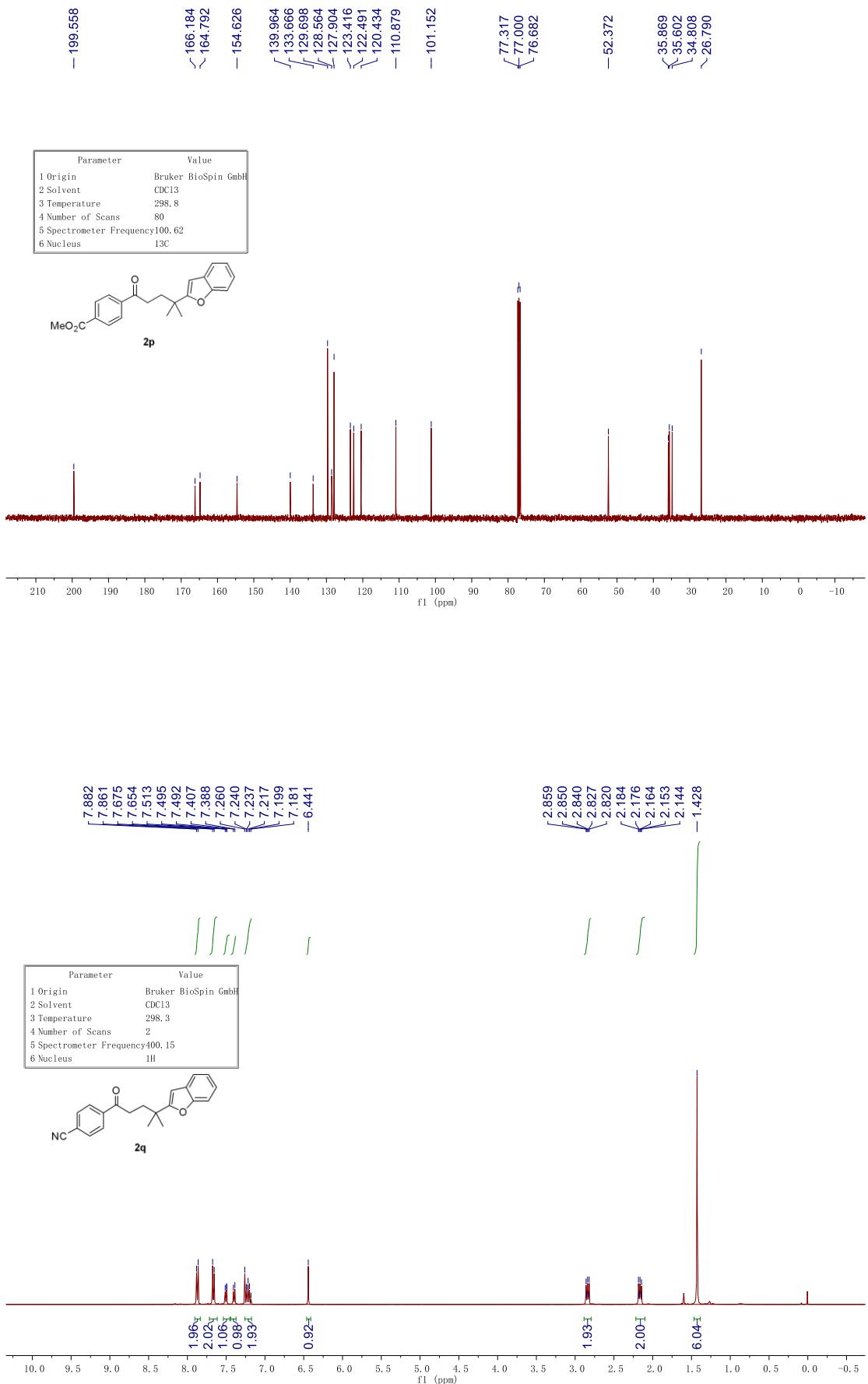
— 1.427

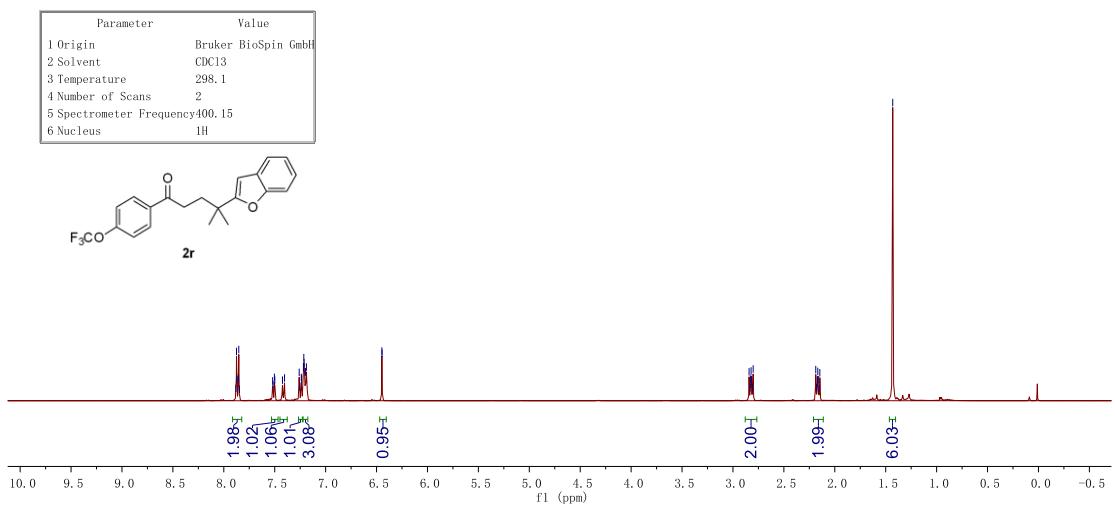
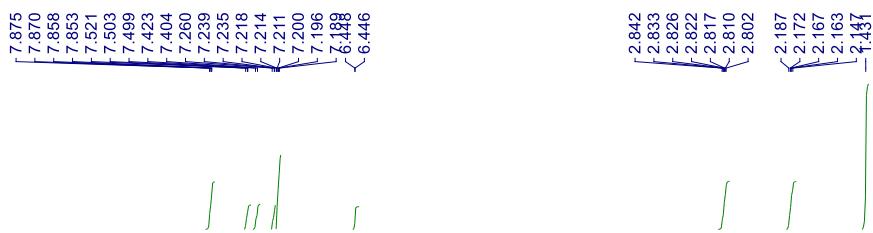
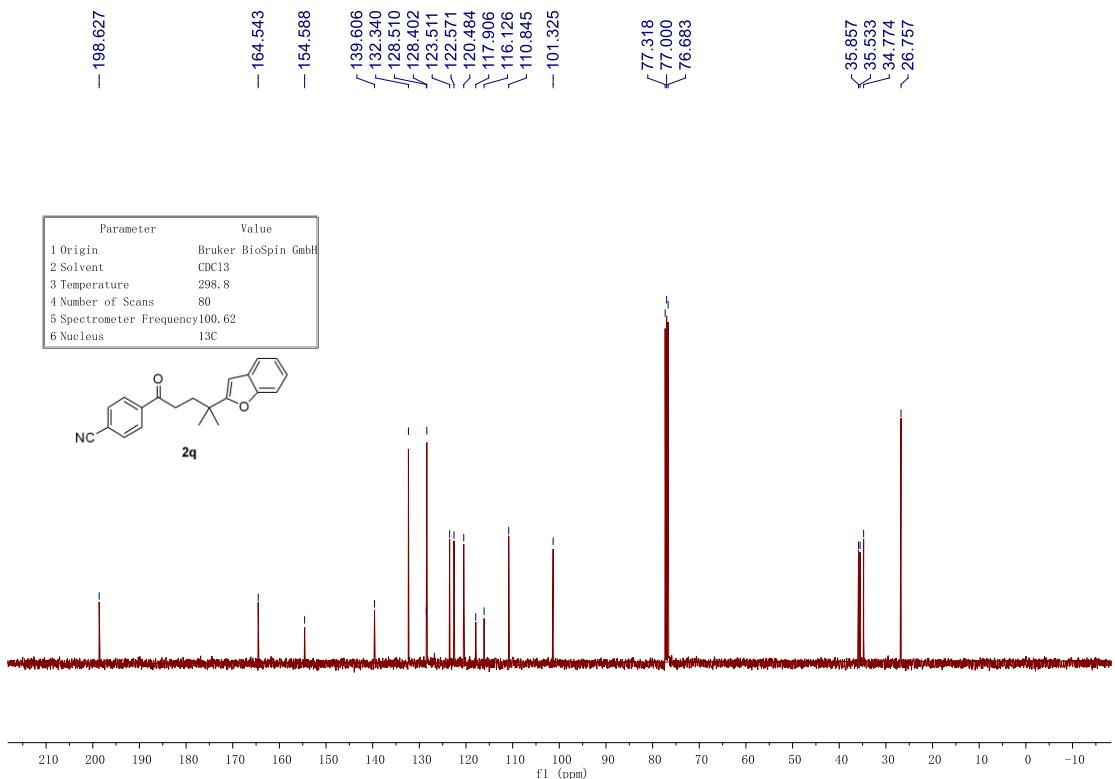
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl <sub>3</sub>
3 Temperature	298.1
4 Number of Scans	2
5 Spectrometer Frequency	400.13
6 Nucleus	<sup>1</sup> H

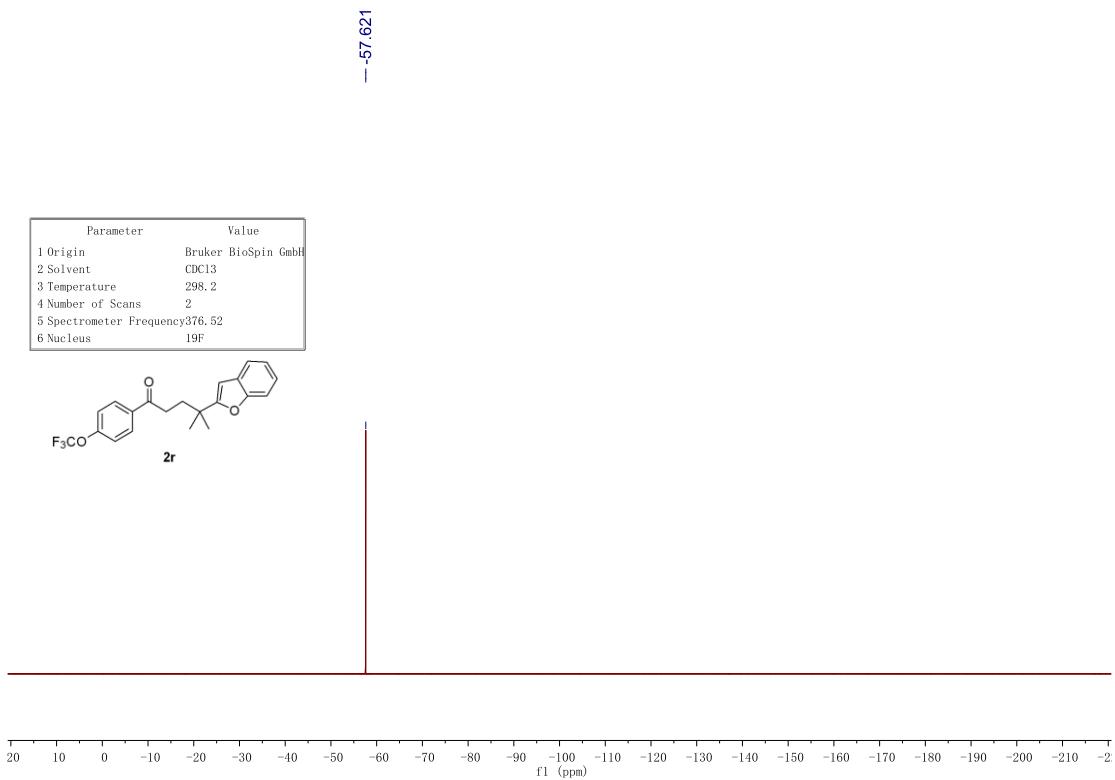
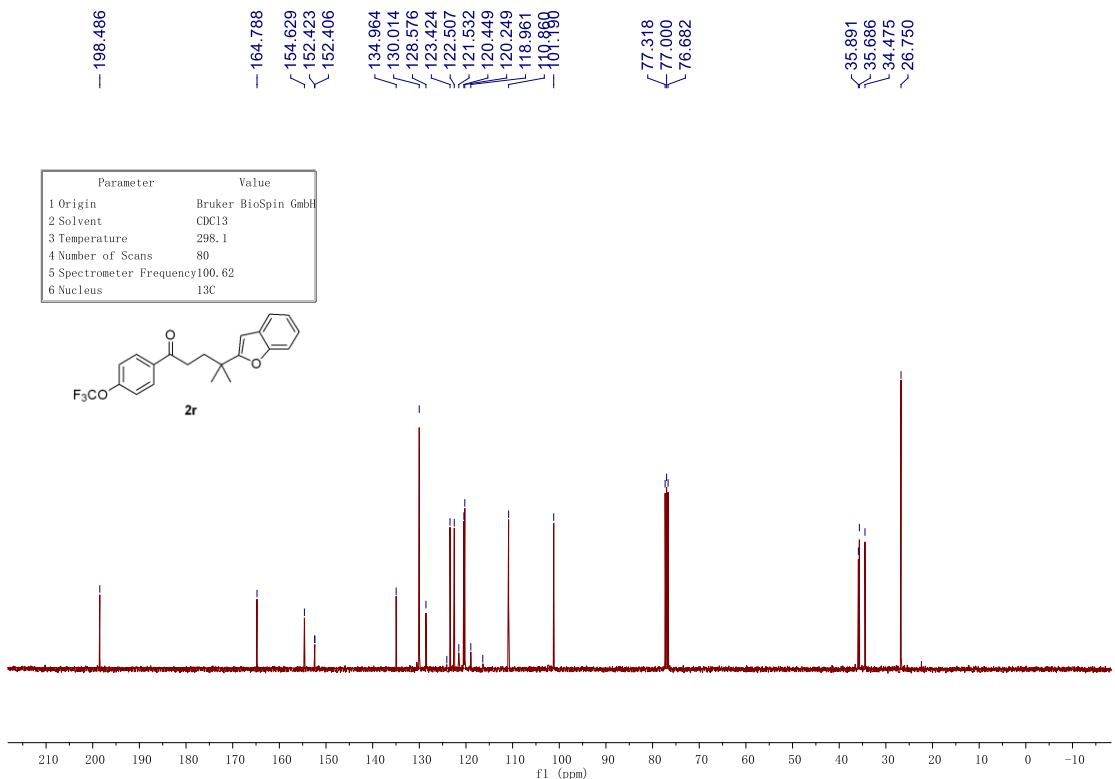


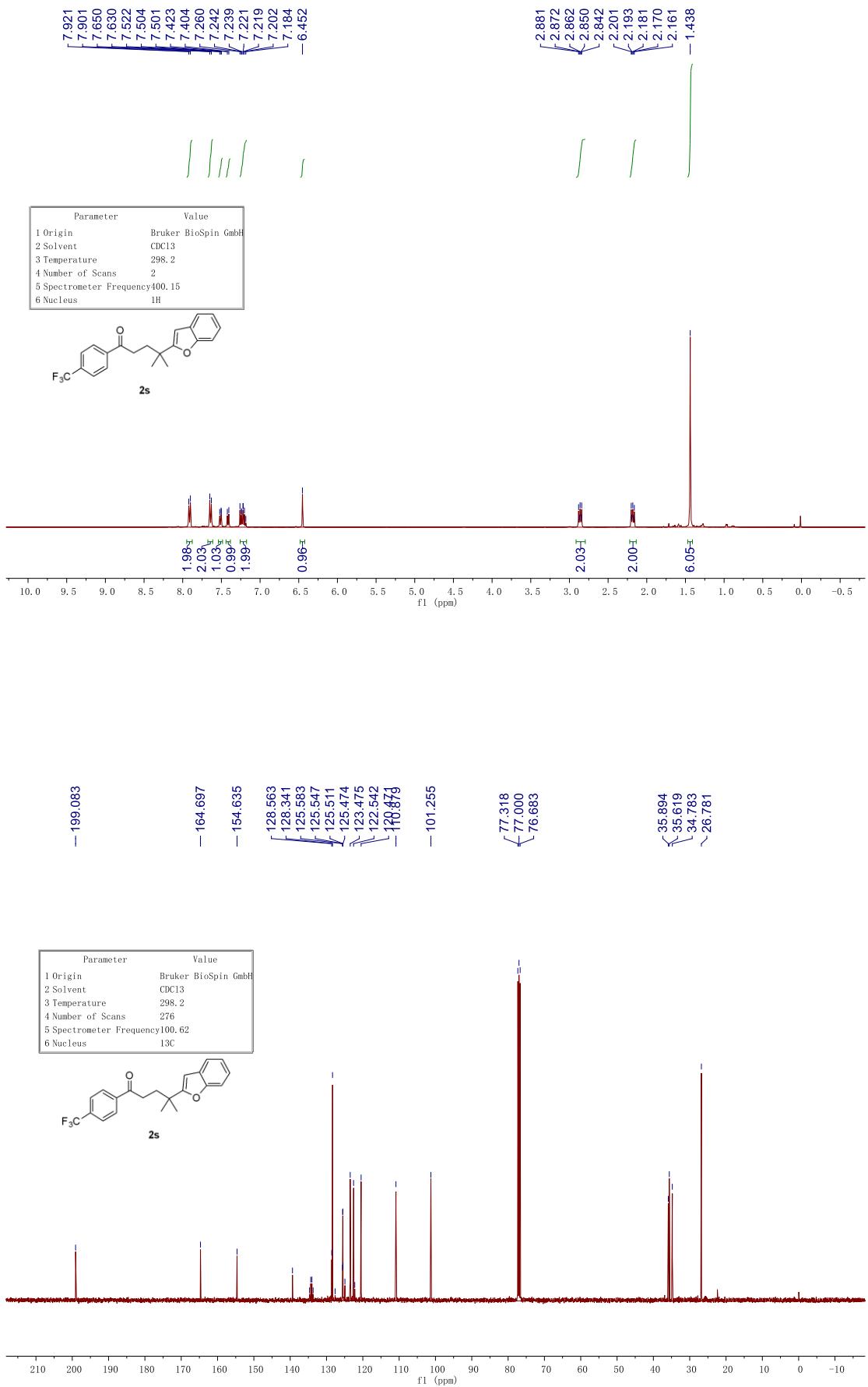


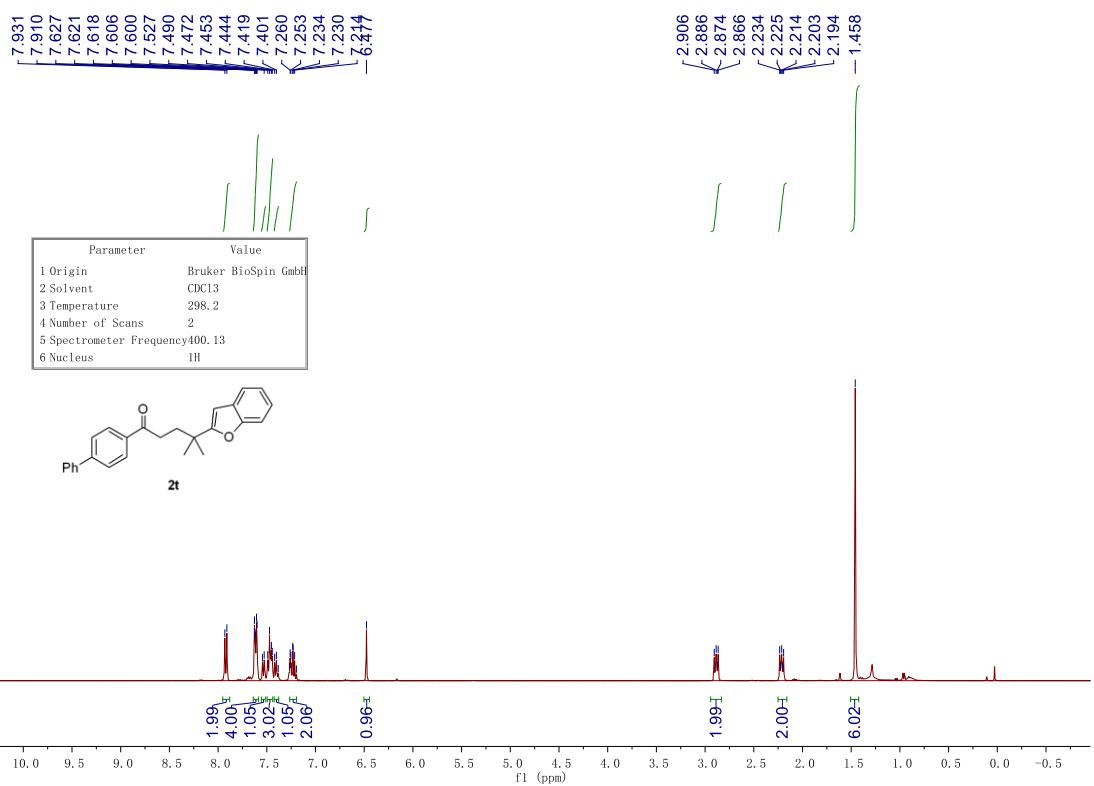
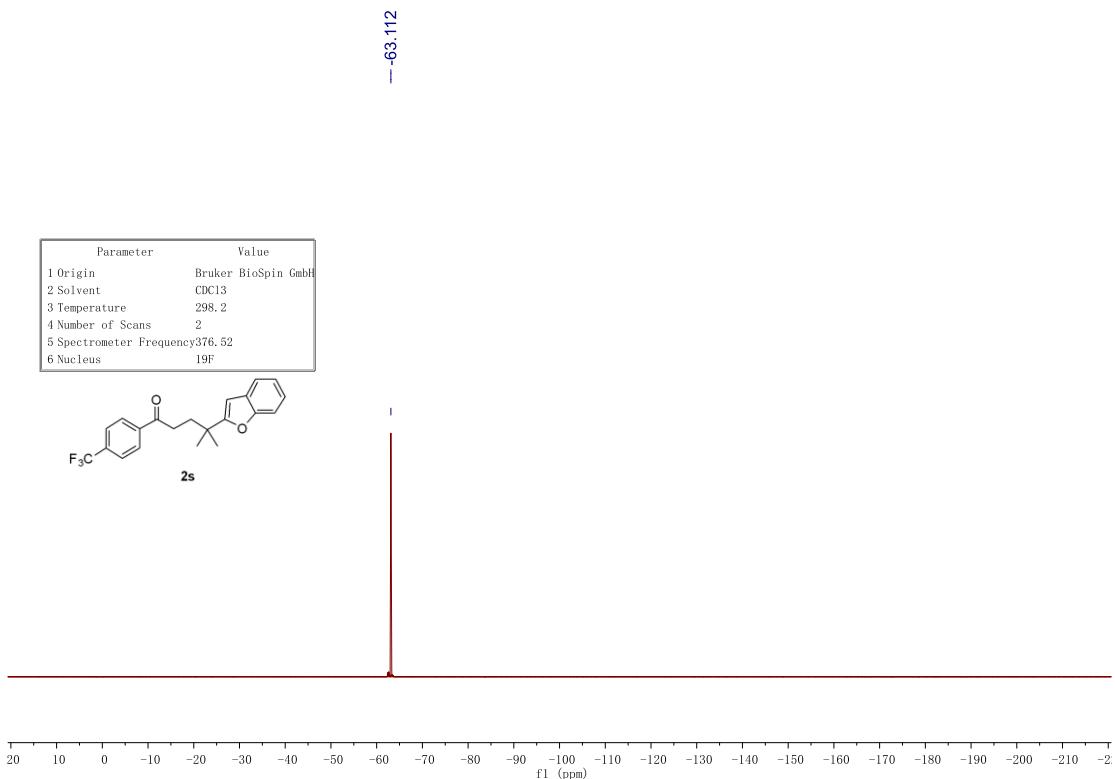


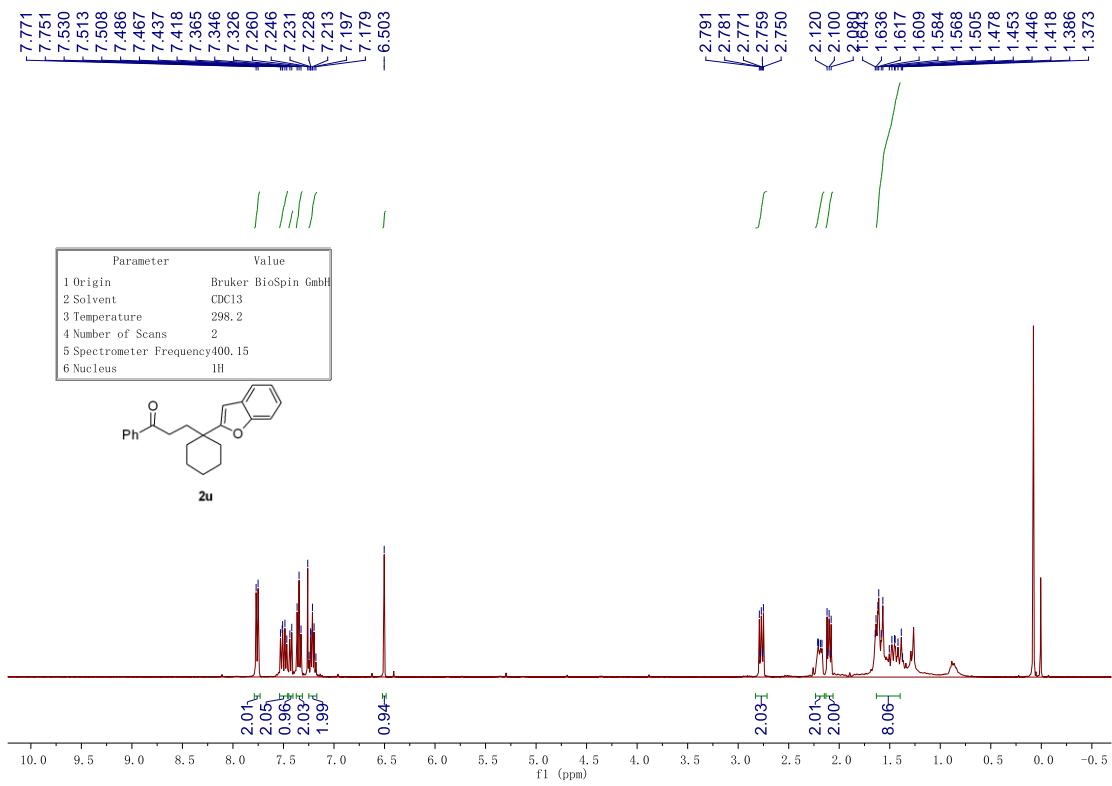
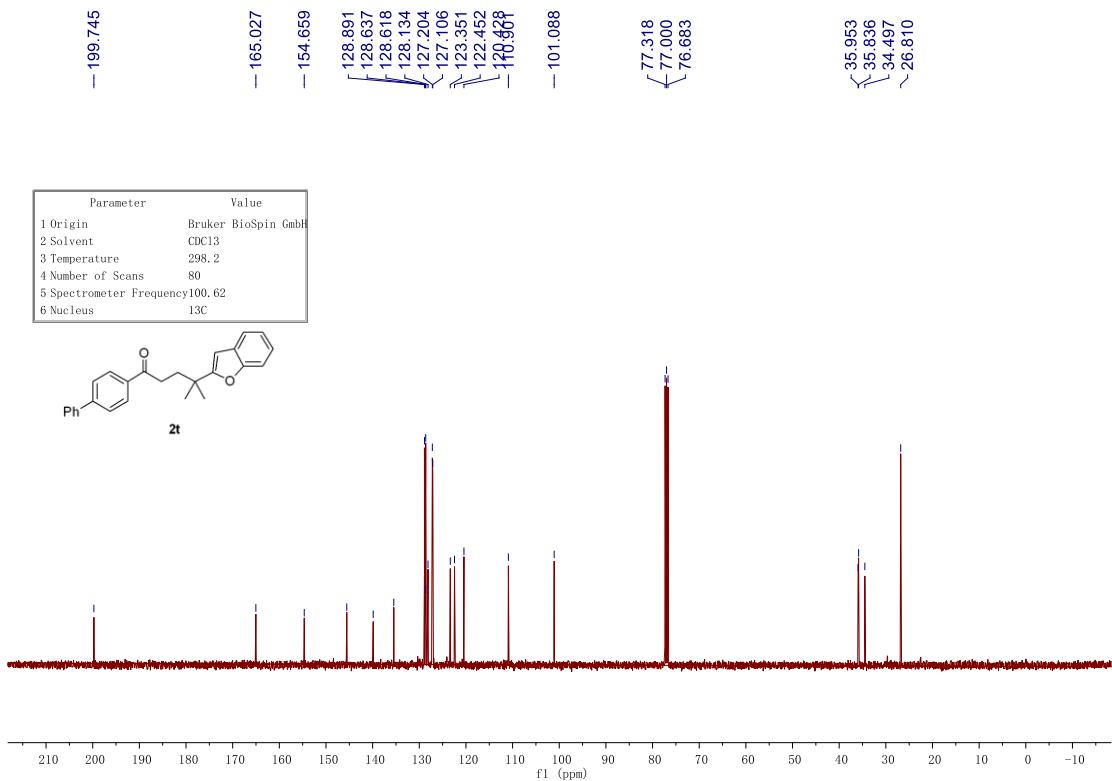


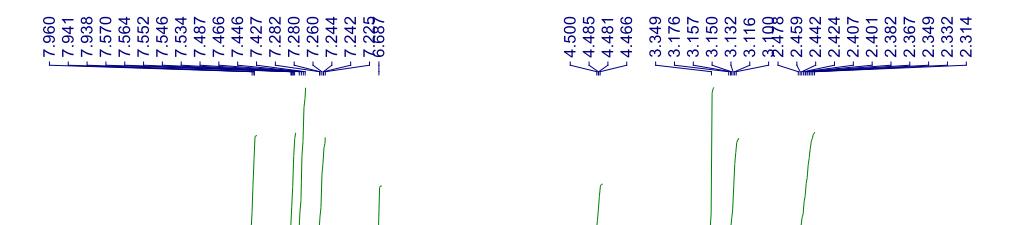
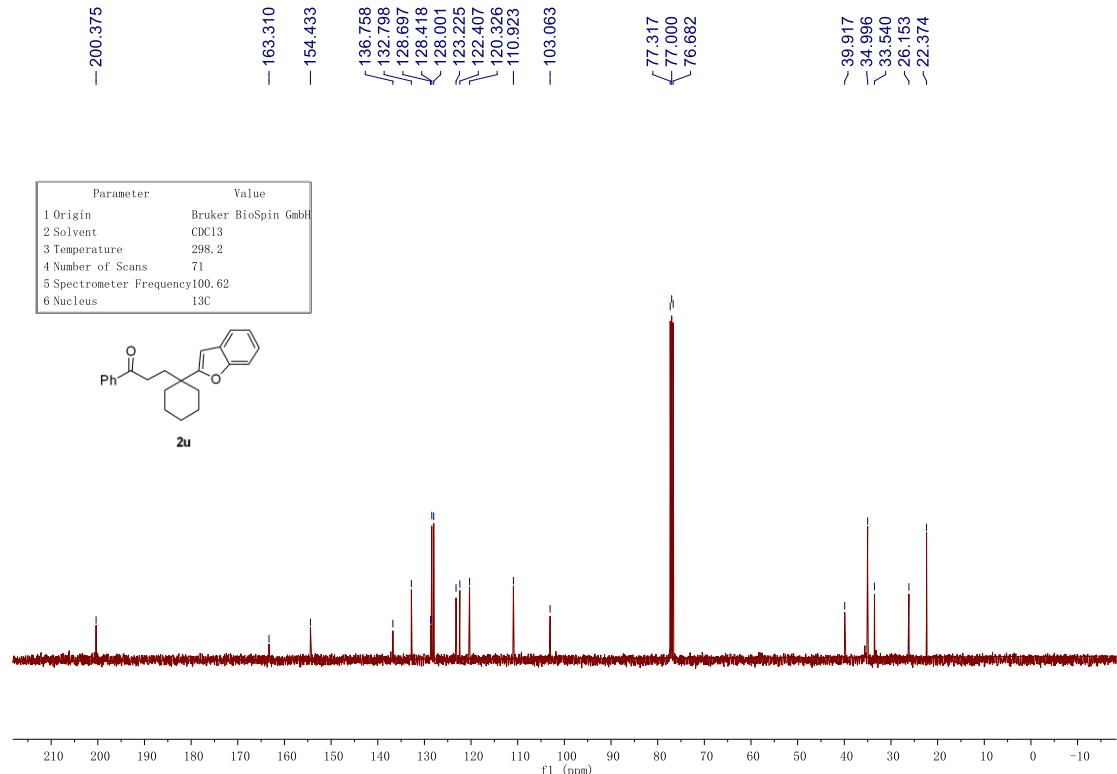












Parameter                          Value  
 1 Origin                            Bruker BioSpin GmbH  
 2 Solvent                         CDCl<sub>3</sub>  
 3 Temperature                    297.8  
 4 Number of Scans              2  
 5 Spectrometer Frequency    400.15  
 6 Nucleus                        <sup>1</sup>H

