

## Supporting Information

# Remote C(sp<sup>3</sup>)-H vinylation via radical-mediated consecutive fission of C-H and C-C bonds

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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, 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 ( $\text{CDCl}_3$ :  $\delta$  77.16).  $^{19}\text{F}$ -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 procedure for the C(sp<sup>3</sup>)-H vinylation reaction

Propargylic alcohol **1** (0.2 mmol), potassium phthalimide or potassium fluoride (0.12 mmol), TBPB or TBPA (0.4 mmol) were loaded in a sealed tube, and MeCN (5 mL) was added to the mixture via syringe. Then the reaction was stirred at 130 °C until the starting material had been consumed as monitored by TLC. The mixture was quenched with aq.  $\text{NaHCO}_3$  solution. The aqueous layer was extracted with EtOAc (3 x 10 mL). The organic layer was combined, washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , concentrated in vacuo, and purified by flash column chromatography on silica gel (eluent: ethyl acetate/ petroleum ether) to give the corresponding products **3**.

## 3. Synthesis of starting materials

### (1) General procedure for the preparation of ketones

Alkyl magnesium bromide (2.0 equiv.) was added dropwise to aldehyde (1 equiv.) in anhydrous THF at 0 °C, and the reaction was stirred for 1-2 h. After quenching with sat.  $\text{NH}_4\text{Cl}$  solution, the reaction mixture was extracted with EtOAc, and the organic layers were dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated in vacuo. The resultant crude secondary alcohol was directly subjected to the oxidation by PCC (2.0 equiv.) or Dess-Martin periodinane (1.5 equiv.) in DCM. After reaction completion, the crude reaction mixture was filtered and concentrated in vacuo. Purification by flash column chromatography on silica gel afforded the corresponding ketone.

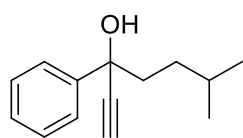
### (2) General procedure for the preparation of propargyl alcohols

Ethynylmagnesium bromide (2.0 equiv, 0.5 M in THF) or alkynyl lithium (2.0 equiv.) was added to the ketones (1.0 equiv.) in anhydrous THF at 0 °C, and the reaction was stirred for 1-2 h. After quenching with sat.  $\text{NH}_4\text{Cl}$  solution, the reaction mixture was extracted with EtOAc, and the organic layers were dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated in vacuo. Purification by flash column chromatography on silica gel afforded the corresponding propargylic alcohol **1**.

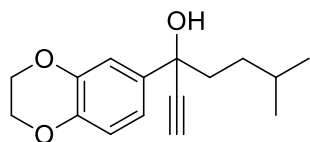
## 4. Characterization of starting materials and products

### a. starting materials

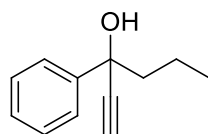
The starting materials **1q** and **1x** are new compounds; other starting materials **1a-1p**, **1r-1w** are known compounds, which have been reported in our previous papers.<sup>1</sup>



**1a**: 1.64 g, 81% yield, yellow solid, m.p. 53-54 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.66-7.61 (m, 2H), 7.40-7.34 (m, 2H), 7.33-7.28 (m, 1H), 2.69 (s, 1H), 2.38 (br, 1H), 2.00-1.85 (m, 2H), 1.57-1.46 (m, 1H), 1.43-1.33 (m, 1H), 1.28-1.19 (m, 1H), 0.86 (t, *J* = 6.8 Hz, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 144.3, 128.2, 127.8, 125.4, 86.3, 74.1, 73.3, 43.2, 33.4, 28.0, 22.6, 22.5. FT-IR: ν (cm<sup>-1</sup>) 3321, 3260, 2957, 2935, 2867, 2850, 1493, 1469, 1445, 1367, 1306, 1249. HRMS [ESI] calcd for C<sub>14</sub>H<sub>18</sub>ONa [M+Na]<sup>+</sup> 225.1250, found 225.1266.

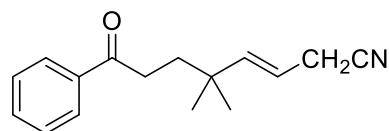


**1q**: 1.6 g, 62% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/50-1/10). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.16-7.13 (m, 1H), 7.11-7.06 (m, 2H), 6.83 (d, *J* = 8.4 Hz, 1H), 4.25 (s, 4H), 2.66 (s, 1H), 2.46 (s, 1H), 1.97-1.79 (m, 2H), 1.55-1.45 (m, 1H), 1.41-1.31 (m, 1H), 1.27-1.16 (m, 1H), 0.86 (t, *J* = 6.8 Hz, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 143.1, 143.0, 137.8, 118.5, 116.9, 114.7, 100.0, 86.4, 74.0, 72.9, 64.4, 43.0, 33.5, 28.0, 22.6, 22.5. FT-IR: ν (cm<sup>-1</sup>) δ 3465, 2954, 1590, 1503, 1384, 1283, 1256, 1068. HRMS [ESI] calcd for C<sub>16</sub>H<sub>20</sub>O<sub>3</sub>Na [M+Na]<sup>+</sup> 283.1305, found 283.1309.



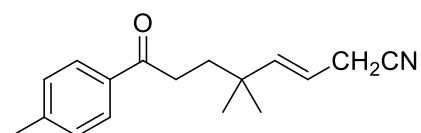
**1x**: 0.68 g, 68% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/50-1/20). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.67-7.63 (m, 2H), 7.41-7.35 (m, 2H), 7.34-7.28 (m, 1H), 2.80 (s, 1H), 2.70 (s, 1H), 2.02-1.83 (m, 2H), 1.59-1.47 (m, 1H), 1.45-1.31 (m, 1H), 0.92 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 144.3, 128.2, 127.8, 125.5, 86.5, 74.2, 73.3, 47.4, 18.0, 14.0. FT-IR: ν (cm<sup>-1</sup>) δ 3735, 3297, 2960, 2362, 1466, 1378, 1200, 1110, 1065. HRMS [ESI] calcd for C<sub>12</sub>H<sub>14</sub>ONa [M+Na]<sup>+</sup> 197.0937, found 197.0928.

### b. Products

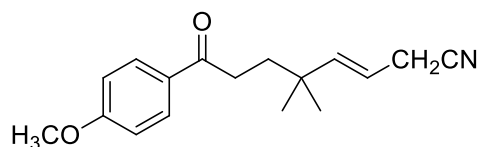


**3a**: 33.8 mg, 70% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/50-1/10). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95-7.91 (m, 2H), 7.58-7.53 (m, 1H), 7.49-7.43 (m, 2H), 5.79 (dt, *J* = 15.6, 1.6 Hz, 1H), 5.31 (dt, *J* = 15.6, 5.6 Hz, 1H), 3.08 (dd, *J* = 5.6, 1.6 Hz, 2H), 2.89-2.84 (m, 2H), 1.80-1.74 (m, 2H), 1.07 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.3, 144.9, 136.9, 133.0, 128.6, 128.0, 117.8, 114.7, 36.4, 36.0, 34.1, 26.9, 20.6. FT-IR: ν (cm<sup>-1</sup>) δ 3853, 2953, 2361, 1682, 1491, 1366, 1180. HRMS [ESI] calcd for C<sub>16</sub>H<sub>20</sub>NO [M+H]<sup>+</sup> 242.1539, found 242.1547.

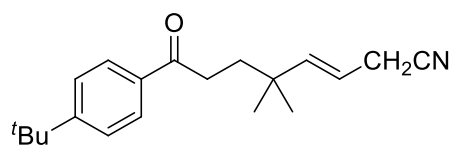
1. (a) S. Wu, X. Wu, D. Wang and C. Zhu, *Angew. Chem. Int. Ed.*, 2019, **58**, 1499; (b) S. Wu, X. Wu, Z. Wu and C. Zhu, *Sci. China Chem.*, 2019, **62**, 1507; (c) S. Yang, X. Wu, S. Wu and C. Zhu, *Org. Lett.*, 2019, **21**, 4837.



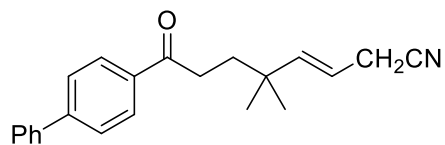
**3b**: 32.2 mg, 63% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/50-1/10).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85-7.81 (m, 2H), 7.27-7.23 (m, 2H), 5.79 (dt,  $J = 15.6, 1.6$  Hz, 1H), 5.31 (dt,  $J = 15.6, 5.6$  Hz, 1H), 3.08 (dd,  $J = 5.6, 1.6$  Hz, 2H), 2.86-2.80 (m, 2H), 2.40 (s, 3H), 1.79-1.73 (m, 2H), 1.07 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  200.0, 145.0, 143.8, 134.5, 129.3, 128.2, 117.9, 114.7, 36.6, 36.0, 34.0, 26.9, 21.6, 20.6. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  3735, 2960, 2250, 1678, 1573, 1387, 1282, 1180. HRMS [ESI] calcd for  $\text{C}_{17}\text{H}_{21}\text{NONa}$  [ $\text{M}+\text{Na}$ ] $^+$  278.1515, found 278.1521.



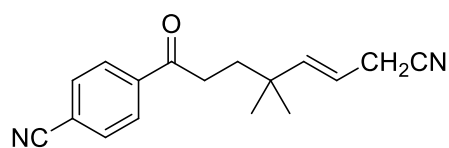
**3c**: 30.7 mg, 57% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/50-1/10).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94-7.89 (m, 2H), 6.96-6.91 (m, 2H), 5.79 (dt,  $J = 15.6, 1.6$  Hz, 1H), 5.31 (dt,  $J = 15.6, 5.6$  Hz, 1H), 3.87 (s, 3H), 3.08 (dd,  $J = 5.6, 1.6$  Hz, 2H), 2.84-2.78 (m, 2H), 1.79-1.72 (m, 2H), 1.07 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  198.9, 163.4, 145.0, 130.3, 130.0, 117.9, 114.6, 113.8, 55.5, 36.7, 36.1, 33.7, 26.9, 20.6. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  3735, 2925, 2250, 1672, 1575, 1462, 1256. HRMS [ESI] calcd for  $\text{C}_{17}\text{H}_{21}\text{NO}_2\text{Na}$  [ $\text{M}+\text{Na}$ ] $^+$  294.1465, found 294.1464.



**3d**: 39.1 mg, 66% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/50-1/10).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89-7.85 (m, 2H), 7.49-7.45 (m, 2H), 5.79 (dt,  $J = 15.6, 1.6$  Hz, 1H), 5.31 (dt,  $J = 15.6, 5.6$  Hz, 1H), 3.08 (dd,  $J = 5.6, 1.6$  Hz, 2H), 2.87-2.81 (m, 2H), 1.79-1.73 (m, 2H), 1.34 (s, 9H), 1.07 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  200.0, 156.7, 145.0, 134.4, 128.0, 125.6, 117.9, 114.7, 36.6, 36.1, 35.1, 34.0, 31.1, 26.9, 20.6. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  3735, 2961, 2251, 1678, 1605, 1387, 1269, 1107. HRMS [ESI] calcd for  $\text{C}_{20}\text{H}_{27}\text{NONa}$  [ $\text{M}+\text{Na}$ ] $^+$  320.1985, found 320.1989.

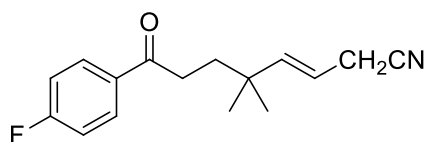


**3e**: 38.3 mg, 60% yield, yellow solid, m.p. 72-73  $^{\circ}\text{C}$ . Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/50-1/10).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03-7.99 (m, 2H), 7.71-7.66 (m, 2H), 7.65-7.60 (m, 2H), 7.50-7.44 (m, 2H), 7.43-7.37 (m, 1H), 5.81 (dt,  $J = 15.6, 1.6$  Hz, 1H), 5.33 (dt,  $J = 15.6, 5.6$  Hz, 1H), 3.10 (dd,  $J = 5.6, 1.6$  Hz, 2H), 2.93-2.86 (m, 2H), 1.83-1.77 (m, 2H), 1.09 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  199.9, 145.7, 144.9, 139.9, 135.6, 129.0, 128.7, 128.2, 127.3, 117.9, 117.8, 114.7, 36.5, 36.1, 34.1, 26.9, 20.6. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  3802, 2955, 2248, 1770, 1578, 1442, 1366, 1022. HRMS [ESI] calcd for  $\text{C}_{22}\text{H}_{23}\text{NONa}$  [ $\text{M}+\text{Na}$ ] $^+$  340.1672, found 340.1671.

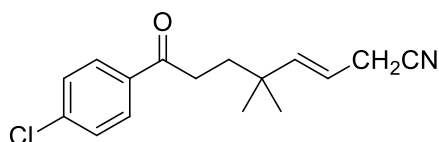


**3f**: 26.4 mg, 50% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/50-1/10).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02-7.98 (m, 2H), 7.78-7.73 (m, 2H), 5.77 (dt,  $J = 15.6,$

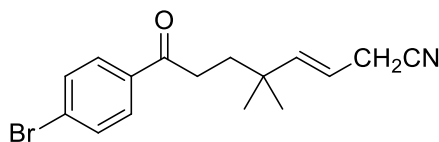
1.6 Hz, 1H), 5.31 (dt,  $J = 15.6, 5.6$  Hz, 1H), 3.09 (dd,  $J = 5.6, 1.6$  Hz, 2H), 2.90-2.83 (m, 2H), 1.79-1.72 (m, 2H), 1.06 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  198.8, 144.6, 139.8, 134.3, 132.6, 128.4, 123.6, 117.9, 117.8, 116.3, 115.0, 36.1, 35.9, 34.4, 26.8, 20.5. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  3735, 2961, 2250, 1774, 1688, 1404, 1243, 1109. HRMS [ESI] calcd for  $\text{C}_{17}\text{H}_{18}\text{N}_2\text{ONa}$   $[\text{M}+\text{Na}]^+$  289.1311, found 289.1322.



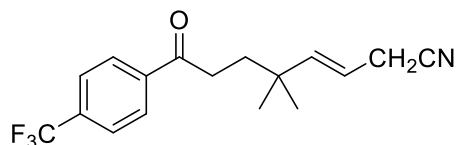
**3g**: 33.1 mg, 64% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/50-1/10).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98-7.93 (m, 2H), 7.16-7.09 (m, 2H), 5.78 (dt,  $J = 15.6, 1.6$  Hz, 1H), 5.31 (dt,  $J = 15.6, 5.6$  Hz, 1H), 3.09 (dd,  $J = 5.6, 1.6$  Hz, 2H), 2.86-2.80 (m, 2H), 1.79-1.73 (m, 2H), 1.07 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  198.6, 165.7 (d,  $J_{\text{C-F}} = 253.2$  Hz), 144.8, 133.3 (d,  $J_{\text{C-F}} = 2.9$  Hz), 130.7 (d,  $J_{\text{C-F}} = 9.3$  Hz), 117.8, 115.7 (d,  $J_{\text{C-F}} = 21.7$  Hz), 114.8, 36.4, 36.0, 34.0, 26.9, 20.6;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -105.4 (s). FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  3690, 3587, 2920, 2123, 1976, 1772, 1596, 1387, 1156. HRMS [ESI] calcd for  $\text{C}_{16}\text{H}_{18}\text{FNONa}$   $[\text{M}+\text{Na}]^+$  282.1265, found 282.1277.



**3h**: 28.4 mg, 52% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/50-1/10).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89-7.85 (m, 2H), 7.45-7.41 (m, 2H), 5.78 (dt,  $J = 15.6, 1.6$  Hz, 1H), 5.31 (dt,  $J = 15.6, 5.6$  Hz, 1H), 3.09 (dd,  $J = 5.6, 1.6$  Hz, 2H), 2.86-2.80 (m, 2H), 1.79-1.72 (m, 2H), 1.07 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  199.0, 144.8, 139.5, 135.2, 129.5, 129.0, 117.8, 114.8, 36.3, 36.0, 34.1, 26.9, 20.6. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  3735, 2961, 2250, 1283, 1572, 1414, 1292, 1176, 1092, 1000. HRMS [ESI] calcd for  $\text{C}_{16}\text{H}_{18}\text{ClNONa}$   $[\text{M}+\text{Na}]^+$  298.0969, found 298.0966.

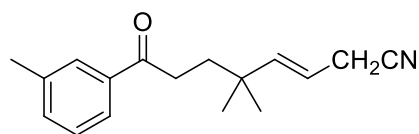


**3i**: 33.6 mg, 53% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/50-1/10).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82-7.77 (m, 2H), 7.63-7.58 (m, 2H), 5.78 (dt,  $J = 15.6, 1.6$  Hz, 1H), 5.31 (dt,  $J = 15.6, 5.6$  Hz, 1H), 3.09 (dd,  $J = 5.6, 1.6$  Hz, 2H), 2.85-2.79 (m, 2H), 1.79-1.72 (m, 2H), 1.07 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  199.2, 144.8, 135.6, 132.0, 129.6, 128.2, 117.8, 114.8, 36.3, 36.0, 34.0, 26.9, 20.6. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  2960, 2260, 1683, 1585, 1414, 1290, 1207, 1070. HRMS [ESI] calcd for  $\text{C}_{16}\text{H}_{18}\text{BrNONa}$   $[\text{M}+\text{Na}]^+$  342.0464, found 342.0462.

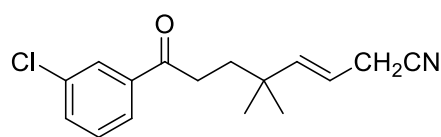


**3j**: 36.3 mg, 59% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/50-1/10).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 (d,  $J = 8.4$  Hz, 2H), 7.72 (d,  $J = 8.0$  Hz, 2H), 5.79 (dt,  $J = 15.6, 1.6$  Hz, 1H), 5.32 (dt,  $J = 15.6, 5.6$  Hz, 1H), 3.09 (dd,  $J = 5.6, 1.6$  Hz, 2H), 2.91-2.85 (m, 2H), 1.81-1.75 (m, 2H), 1.08 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  199.2, 144.7, 139.6, 134.3 (q,  $J_{\text{C-F}} = 32.6$  Hz), 128.4, 125.7 (q,  $J_{\text{C-F}} = 3.4$  Hz), 123.6 (q,  $J_{\text{C-F}} = 270.8$  Hz), 117.8, 114.9, 36.2, 36.0, 34.4, 26.8, 20.6;  $^{19}\text{F}$  NMR (376

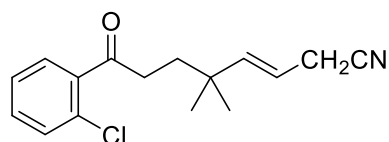
MHz, CDCl<sub>3</sub>)  $\delta$  -63.1 (s). FT-IR:  $\nu$  (cm<sup>-1</sup>)  $\delta$  2962, 2251, 1689, 1389, 1324, 1109, 1066. HRMS [ESI] calcd for C<sub>17</sub>H<sub>18</sub>F<sub>3</sub>NONa [M+Na]<sup>+</sup> 332.1233, found 332.1238.



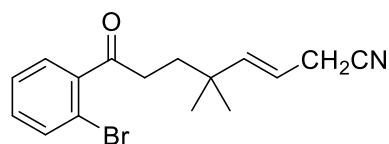
**3k**: 30.8 mg, 60% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/50-1/10). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.75-7.70 (m, 2H), 7.39-7.31 (m, 2H), 5.79 (dt,  $J$  = 15.6, 1.6 Hz, 1H), 5.31 (dt,  $J$  = 15.6, 5.6 Hz, 1H), 3.08 (dd,  $J$  = 5.6, 1.6 Hz, 2H), 2.88-2.82 (m, 2H), 2.41 (s, 3H), 1.79-1.73 (m, 2H), 1.07 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  200.6, 144.9, 138.4, 137.0, 133.8, 128.5, 128.5, 125.3, 117.8, 114.7, 36.5, 36.0, 34.1, 26.9, 21.4, 20.6. FT-IR:  $\nu$  (cm<sup>-1</sup>)  $\delta$  3732, 2960, 2250, 1681, 1586, 1366, 1256, 1090. HRMS [ESI] calcd for C<sub>17</sub>H<sub>21</sub>NONa [M+Na]<sup>+</sup> 278.1515, found 278.1519.



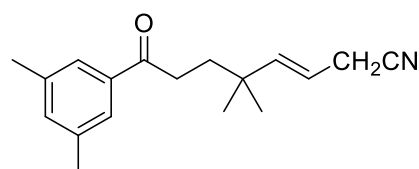
**3l**: 31.8 mg, 58% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/50-1/10). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.90-7.88 (m, 1H), 7.82-7.78 (m, 1H), 7.55-7.50 (m, 1H), 7.43-7.38 (m, 1H), 5.78 (dt,  $J$  = 15.6, 1.6 Hz, 1H), 5.32 (dt,  $J$  = 15.6, 5.6 Hz, 1H), 3.09 (dd,  $J$  = 5.6, 1.6 Hz, 2H), 2.86-2.80 (m, 2H), 1.80-1.72 (m, 2H), 1.07 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  198.9, 144.8, 138.5, 135.0, 133.0, 130.0, 128.1, 126.1, 117.8, 114.8, 36.2, 36.0, 34.2, 26.9, 20.6. FT-IR:  $\nu$  (cm<sup>-1</sup>)  $\delta$  3735, 2961, 2251, 1686, 1571, 1417, 1296, 1203. HRMS [ESI] calcd for C<sub>16</sub>H<sub>18</sub>ClNONa [M+Na]<sup>+</sup> 298.0969, found 298.0968.



**3m**: 33.1 mg, 60% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/50-1/10). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.43-7.35 (m, 3H), 7.34-7.29 (m, 1H), 5.75 (dt,  $J$  = 15.6, 1.6 Hz, 1H), 5.28 (dt,  $J$  = 15.6, 5.6 Hz, 1H), 3.08 (dd,  $J$  = 5.6, 1.6 Hz, 2H), 2.86-2.80 (m, 2H), 1.77-1.71 (m, 2H), 1.04 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  203.6, 144.7, 139.7, 131.6, 130.7, 130.5, 128.8, 127.0, 117.8, 114.7, 38.6, 36.1, 35.9, 26.8, 20.6. FT-IR:  $\nu$  (cm<sup>-1</sup>)  $\delta$  2960, 2250, 1698, 1433, 1296, 1162, 1075. HRMS [ESI] calcd for C<sub>16</sub>H<sub>18</sub>ClNONa [M+Na]<sup>+</sup> 298.0969, found 298.0977.

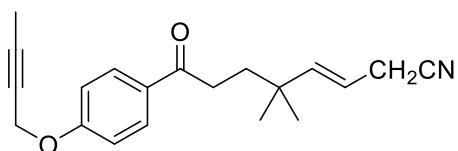


**3n**: 33.2 mg, 52% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/50-1/10). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.60 (d,  $J$  = 8.0 Hz, 1H), 7.40-7.32 (m, 2H), 7.31-7.25 (m, 1H), 5.76 (dt,  $J$  = 15.6, 1.6 Hz, 1H), 5.28 (dt,  $J$  = 15.6, 5.6 Hz, 1H), 3.08 (dd,  $J$  = 5.6, 1.6 Hz, 2H), 2.84-2.78 (m, 2H), 1.79-1.72 (m, 2H), 1.05 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  204.4, 144.7, 142.0, 133.6, 131.5, 128.3, 127.5, 118.6, 117.8, 114.7, 38.4, 36.0, 35.9, 26.8, 20.6. FT-IR:  $\nu$  (cm<sup>-1</sup>)  $\delta$  3735, 2961, 2250, 1698, 1563, 1387, 1295, 1121. HRMS [ESI] calcd for C<sub>16</sub>H<sub>18</sub>BrNONa [M+Na]<sup>+</sup> 342.0464, found 342.0464.

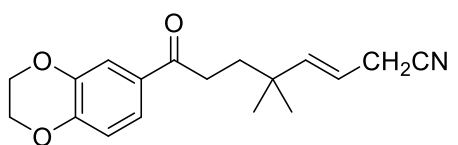


**3o**: 28.3 mg, 53% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether =

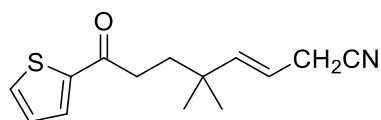
1/50-1/10). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.52 (s, 2H), 7.19 (s, 1H), 5.79 (dt, *J* = 15.6, 1.6 Hz, 1H), 5.30 (dt, *J* = 15.6, 5.6 Hz, 1H), 3.09 (dd, *J* = 5.6, 1.6 Hz, 2H), 2.86-2.80 (m, 2H), 2.37 (s, 6H), 1.78-1.72 (m, 2H), 1.07 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.8, 145.0, 138.3, 137.1, 134.6, 125.8, 117.9, 114.6, 36.5, 36.0, 34.1, 26.9, 21.3, 20.6. FT-IR: ν (cm<sup>-1</sup>) δ 3870, 3675, 2961, 2250, 1680, 1558, 1417, 1308. HRMS [ESI] calcd for C<sub>18</sub>H<sub>23</sub>NONa [M+Na]<sup>+</sup> 292.1672, found 292.1678..



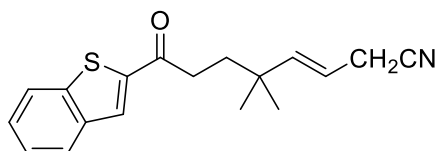
**3p:** 19.6 mg, 32% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/50-1/10). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95-7.89 (m, 2H), 7.02-6.97 (m, 2H), 5.79 (dt, *J* = 15.6, 1.6 Hz, 1H), 5.31 (dt, *J* = 15.6, 5.6 Hz, 1H), 4.72-4.70 (m, 2H), 3.08 (dd, *J* = 5.6, 1.6 Hz, 2H), 2.84-2.78 (m, 2H), 1.86 (t, *J* = 2.4 Hz, 3H), 1.79-1.72 (m, 2H), 1.07 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 198.9, 161.6, 145.0, 130.4, 130.2, 123.6, 117.9, 114.6, 84.5, 73.3, 56.5, 36.6, 36.0, 33.7, 26.9, 20.6, 3.7. FT-IR: ν (cm<sup>-1</sup>) δ 3839, 3587, 2959, 2360, 1673, 1576, 1316, 1219. HRMS [ESI] calcd for C<sub>20</sub>H<sub>23</sub>NO<sub>2</sub>Na [M+Na]<sup>+</sup> 332.1621, found 332.1624.



**3q:** 32.7 mg, 55% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/50-1/10). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.49-7.44 (m, 2H), 6.93-6.88 (m, 1H), 5.77 (dt, *J* = 15.6, 1.6 Hz, 1H), 5.29 (dt, *J* = 15.6, 5.6 Hz, 1H), 4.33-4.24 (m, 4H), 3.08 (dd, *J* = 5.6, 1.6 Hz, 2H), 2.80-2.74 (m, 2H), 1.77-1.70 (m, 2H), 1.06 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 198.8, 147.9, 145.0, 143.3, 130.8, 122.1, 117.8, 117.6, 117.2, 114.6, 64.7, 64.1, 36.6, 36.0, 33.8, 26.8, 20.6. FT-IR: ν (cm<sup>-1</sup>) δ 3334, 2873, 2251, 1731, 1581, 1428, 1285, 1131, 1065. HRMS [ESI] calcd for C<sub>18</sub>H<sub>22</sub>NO<sub>3</sub> [M+H]<sup>+</sup> 300.1594, found 300.1596.

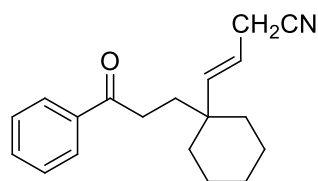


**3r:** 16.3 mg, 33% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/50-1/10). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.72-7.68 (m, 1H), 7.64-7.60 (m, 1H), 7.14-7.11 (m, 1H), 5.78 (dt, *J* = 15.6, 1.6 Hz, 1H), 5.30 (dt, *J* = 15.6, 5.6 Hz, 1H), 3.08 (dd, *J* = 5.6, 1.6 Hz, 2H), 2.82-2.76 (m, 2H), 1.81-1.75 (m, 2H), 1.07 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 193.2, 144.8, 144.2, 133.5, 131.7, 128.1, 117.8, 114.8, 36.8, 36.1, 35.0, 26.8, 20.6. FT-IR: ν (cm<sup>-1</sup>) δ 3853, 3649, 2598, 2363, 1656, 1414, 1237. HRMS [ESI] calcd for C<sub>14</sub>H<sub>18</sub>NOS [M+H]<sup>+</sup> 248.1104, found 248.1105.

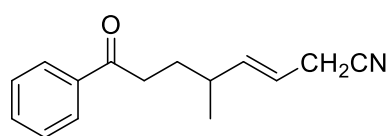


**3s:** 21.2 mg, 36% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/50-1/10). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.94 (s, 1H), 7.92-7.84 (m, 2H), 7.49-7.38 (m, 2H), 5.81 (dt, *J* = 15.6, 1.6 Hz, 1H), 5.34 (dt, *J* = 15.6, 5.6 Hz, 1H), 3.10 (dd, *J* = 5.6, 1.6 Hz, 2H), 2.94-2.87 (m, 2H), 1.86-1.79 (m, 2H), 1.09 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 194.7, 144.8, 143.6, 142.5, 139.1, 128.9, 127.4, 126.0, 125.0, 123.0, 117.9, 114.9, 36.8, 36.1, 34.9, 26.9, 20.6. FT-IR: ν (cm<sup>-1</sup>) δ

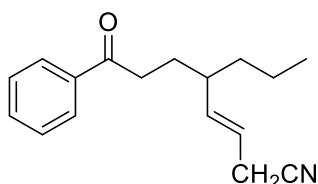
2960, 2250, 1734, 1594, 1416, 1294, 1158. HRMS [ESI] calcd for C<sub>18</sub>H<sub>19</sub>NOSNa [M+Na]<sup>+</sup> 320.1080, found 320.1086.



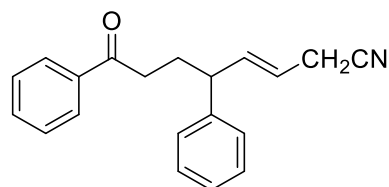
**3t**: 32.6 mg, 58% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/50-1/10). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.96-7.89(m, 2H), 7.58-7.52 (m, 1H), 7.49-7.42 (m, 2H), 5.66 (dt, *J* = 15.6, 1.6 Hz, 1H), 5.32 (dt, *J* = 15.6, 5.6 Hz, 1H), 3.11 (dd, *J* = 5.6, 1.6 Hz, 2H), 2.87-2.80 (m, 2H), 1.81-1.74 (m, 2H), 1.65-1.56 (m, 2H), 1.55-1.30 (m, 8H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.6, 143.5, 137.0, 133.0, 128.6, 128.0, 117.9, 116.6, 39.1, 35.7, 34.9, 33.0, 26.3, 22.0, 20.8. FT-IR: ν (cm<sup>-1</sup>) δ 3567, 2967, 2250, 1682, 1371, 1448, 1292, 1180, 1021. HRMS [ESI] calcd for C<sub>19</sub>H<sub>23</sub>NONa [M+Na]<sup>+</sup> 304.1672, found 304.1674.



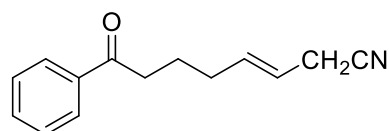
**3u**: 20.7 mg, 46% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/50-1/10). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.97-7.91 (m, 2H), 7.58-7.53 (m, 1H), 7.49-7.43 (m, 2H), 5.75-5.67 (m, 1H), 5.39-5.30 (m, 1H), 3.07-3.03 (m, 2H), 2.94 (t, *J* = 7.6 Hz, 2H), 2.32-2.23 (m, 1H), 1.85-1.68 (m, 2H), 1.06 (d, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.1, 141.1, 137.0, 133.0, 128.6, 128.0, 117.8, 116.7, 36.3, 36.1, 30.7, 20.4, 20.4. FT-IR: ν (cm<sup>-1</sup>) δ 3567, 2959, 2250, 1682, 1449, 1320, 1208, 1002. HRMS [ESI] calcd for C<sub>15</sub>H<sub>17</sub>NONa [M+Na]<sup>+</sup> 250.1202, found 250.1211.



**3v**: 19.2 mg, 38% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/50-1/10). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.96-7.91 (m, 2H), 7.58-7.53 (m, 1H), 7.49-7.43 (m, 2H), 5.62-5.54 (m, 1H), 5.33 (dt, *J* = 15.6, 5.6 Hz, 1H), 3.06 (dd, *J* = 5.6, 1.6 Hz, 2H), 2.95-2.89 (m, 2H), 2.16-2.06 (m, 1H), 1.96-1.85 (m, 1H), 1.70-1.60 (m, 1H), 1.47-1.37 (m, 1H), 1.37-1.18 (m, 3H), 0.88 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.2, 140.0, 137.0, 133.0, 128.6, 128.0, 117.9, 117.7, 42.2, 37.3, 36.1, 29.2, 20.4, 20.3, 14.1. FT-IR: ν (cm<sup>-1</sup>) δ 3060, 2871, 2250, 1682, 1580, 1449, 1281, 1204, 1001. HRMS [ESI] calcd for C<sub>17</sub>H<sub>21</sub>NONa [M+Na]<sup>+</sup> 278.1515, found 278.1515.



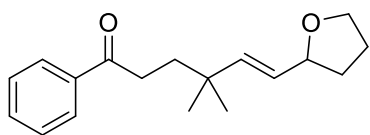
**3w**: 17.2 mg, 30% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/50-1/10). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.90-7.85 (m, 2H), 7.58-7.51 (m, 1H), 7.47-7.40 (m, 2H), 7.36-7.30 (m, 2H), 7.27-7.17 (m, 3H), 6.07-5.98 (m, 1H), 5.45-5.37 (m, 1H), 3.46-3.37 (m, 1H), 3.10-3.04 (m, 2H), 2.98-2.82 (m, 2H), 2.28-2.10 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 199.7, 142.6, 139.1, 136.9, 133.1, 128.8, 128.6, 128.0, 127.6, 126.8, 117.7, 117.5, 47.8, 36.1, 29.7, 20.4. FT-IR: ν (cm<sup>-1</sup>) δ 3028, 2251, 1682, 1449, 1263, 1075. HRMS [ESI] calcd for C<sub>20</sub>H<sub>19</sub>NONa [M+Na]<sup>+</sup> 312.1359, found 312.1358.



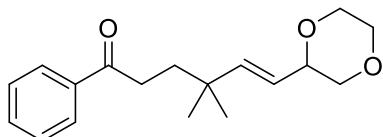
**3x**: 12.0 mg, 28% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether =



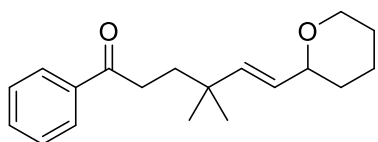
1/50-1/10). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.98-7.92 (m, 2H), 7.58-7.53 (m, 1H), 7.46-7.43 (m, 2H), 5.88-5.80 (m, 1H), 5.44-5.34 (m, 1H), 3.08-3.04 (m, 2H), 3.01-2.94 (m, 2H), 1.91-1.81 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 199.9, 136.9, 135.4, 133.1, 128.6, 128.0, 118.1, 117.7, 37.5, 31.6, 23.3, 20.4. FT-IR: ν (cm<sup>-1</sup>) δ 3649, 2925, 2250, 1682, 1580, 1414, 1200. HRMS [ESI] calcd for C<sub>14</sub>H<sub>15</sub>NONa [M+Na]<sup>+</sup> 236.1046, found 236.1052.



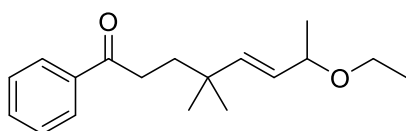
**3y:** 35.3 mg, 65% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/50-1/20). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95-7.90 (m, 2H), 7.56-7.51 (m, 1H), 7.47-7.41 (m, 2H), 5.63 (dd, *J* = 15.6, 0.8 Hz, 1H), 5.41 (dd, *J* = 15.6, 6.8 Hz, 1H), 4.28-4.21 (m, 1H), 3.94-3.86 (m, 1H), 3.80-3.73 (m, 1H), 2.90-2.84 (m, 2H), 2.06-1.97 (m, 1H), 1.96-1.84 (m, 2H), 1.76-1.70 (m, 2H), 1.62-1.52 (m, 1H), 1.06 (s, 3H), 1.05 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.8, 141.1, 137.0, 132.9, 128.6, 128.1, 127.9, 80.2, 68.0, 36.7, 35.5, 34.3, 32.5, 27.1, 25.9. FT-IR: ν (cm<sup>-1</sup>) δ 3648, 2948, 1684, 1490, 1287, 1208. HRMS [ESI] calcd for C<sub>18</sub>H<sub>24</sub>O<sub>2</sub>Na [M+Na]<sup>+</sup> 295.1669, found 295.1673.



**3z:** 29.8 mg, 52% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/50-1/10). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95-7.90 (m, 2H), 7.58-7.52 (m, 1H), 7.48-7.42 (m, 2H), 5.75 (dd, *J* = 16.0, 1.2 Hz, 1H), 5.30 (dd, *J* = 16.0, 6.4 Hz, 1H), 4.07-4.01 (m, 1H), 3.84-3.72 (m, 2H), 3.72-3.65 (m, 2H), 3.64-3.56 (m, 1H), 3.34-3.27 (m, 2H), 2.89-2.82 (m, 2H), 1.78-1.71 (m, 2H), 1.06 (s, 3H), 1.05 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 200.5, 143.4, 137.0, 132.9, 128.6, 128.0, 123.0, 76.3, 71.1, 66.6, 66.2, 36.5, 35.7, 34.2, 26.9. FT-IR: ν (cm<sup>-1</sup>) δ 3650, 3546, 2958, 2852, 1684, 1497, 1224, 1116, 1002. HRMS [ESI] calcd for C<sub>18</sub>H<sub>24</sub>O<sub>3</sub>Na [M+Na]<sup>+</sup> 311.1618, found 311.1622.

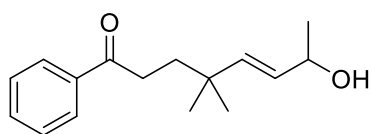


**3aa:** 28.2 mg, 49% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/50-1/10). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95-7.89 (m, 2H), 7.57-7.51 (m, 1H), 7.47-7.41 (m, 2H), 5.61 (dd, *J* = 16.0, 0.8 Hz, 1H), 5.42 (dd, *J* = 16.0, 6.0 Hz, 1H), 4.03-3.96 (m, 1H), 3.79-3.72 (m, 1H), 3.51-3.43 (m, 1H), 2.90-2.81 (m, 2H), 1.86-1.79 (m, 1H), 1.77-1.68 (m, 2H), 1.64-1.45 (m, 5H), 1.05 (s, 3H), 1.05 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.8, 140.0, 137.0, 132.9, 128.6, 128.5, 128.1, 78.4, 68.4, 36.7, 35.4, 34.3, 32.5, 27.2, 27.0, 25.9, 23.4. FT-IR: ν (cm<sup>-1</sup>) δ 3629, 3546, 2933, 2342, 1684, 1490, 1386, 1203, 1084. HRMS [ESI] calcd for C<sub>19</sub>H<sub>26</sub>O<sub>2</sub>Na [M+Na]<sup>+</sup> 309.1825, found 309.1827.

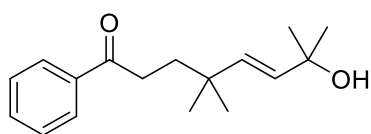


**3ab:** 16.9 mg, 31% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/50-1/40). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95-7.90 (m, 2H), 7.58-7.52 (m, 1H), 7.48-7.42 (m, 2H), 5.54 (d, *J* = 15.6 Hz, 1H), 5.30 (dd, *J* = 15.6, 7.6 Hz, 1H), 3.84-3.76 (m, 1H), 3.53-3.44 (m, 1H), 3.36-3.27 (m, 1H), 2.91-2.84 (m, 2H), 1.78-1.71 (m, 2H), 1.23 (d, *J* = 6.0 Hz, 3H), 1.16 (t, *J* = 7.2 Hz, 3H), 1.07 (s, 3H), 1.06 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.7, 141.1, 137.0, 132.9, 129.4, 128.6, 128.0, 76.6, 63.2, 36.7, 35.6, 34.3, 27.2, 27.1, 22.0, 15.4. FT-IR: ν (cm<sup>-1</sup>) δ 3649, 3543, 2931,

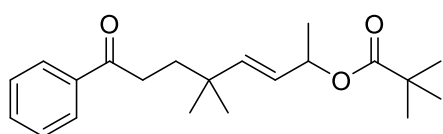
1684, 1505, 1405, 1386, 1116, 1002. HRMS [ESI] calcd for C<sub>18</sub>H<sub>26</sub>O<sub>2</sub>Na [M+Na]<sup>+</sup> 297.1825, found 297.1830.



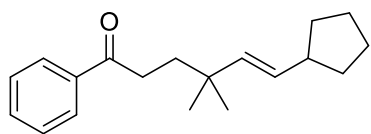
**3ac:** 23.6 mg, 48% yield, colorless oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/50-1/5). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95-7.90 (m, 2H), 7.58-7.52 (m, 1H), 7.48-7.42 (m, 2H), 5.58 (dd, *J* = 16.0, 0.8 Hz, 1H), 5.46 (dd, *J* = 16.0, 6.4 Hz, 1H), 4.31-4.23 (m, 1H), 2.89-2.83 (m, 2H), 1.77-1.71 (m, 2H), 1.70 (br, 1H), 1.25 (d, *J* = 6.4 Hz, 3H), 1.06 (s, 3H), 1.05 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.8, 139.5, 137.0, 133.0, 131.3, 128.6, 128.1, 69.1, 36.7, 35.4, 34.2, 27.1, 27.1, 23.7. FT-IR: ν (cm<sup>-1</sup>) δ 3621, 3448, 2868, 1684, 1490, 1317, 1211. HRMS [ESI] calcd for C<sub>16</sub>H<sub>22</sub>O<sub>2</sub>Na [M+Na]<sup>+</sup> 269.1512, found 269.1515.



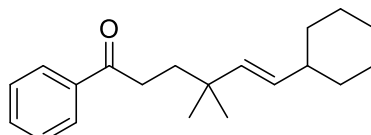
**3ad:** 21.4 mg, 41% yield, colorless oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/50-1/5). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95-7.91 (m, 2H), 7.57-7.52 (m, 1H), 7.48-7.43 (m, 2H), 5.61-5.50 (m, 2H), 2.88-2.83 (m, 2H), 1.77-1.72 (m, 2H), 1.69 (br, 1H), 1.30 (s, 6H), 1.05 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.8, 137.0, 135.7, 134.9, 133.0, 128.6, 128.0, 70.7, 36.9, 35.2, 34.2, 30.0, 27.2. FT-IR: ν (cm<sup>-1</sup>) δ 3839, 3447, 2928, 2248, 1680, 1449, 1364, 1284, 1180, 1002. HRMS [ESI] calcd for C<sub>17</sub>H<sub>24</sub>O<sub>2</sub>Na [M+Na]<sup>+</sup> 283.1669, found 283.1676.



**3ae:** 38.4 mg, 58% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/50-1/10). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.96-7.91 (m, 2H), 7.57-7.51 (m, 1H), 7.47-7.42 (m, 2H), 5.64 (dd, *J* = 15.6, 0.8 Hz, 1H), 5.39 (dd, *J* = 15.6, 6.4 Hz, 1H), 5.34-5.25 (m, 1H), 2.90-2.78 (m, 2H), 1.75-1.67 (m, 2H), 1.28 (d, *J* = 6.4 Hz, 3H), 1.16 (s, 9H), 1.04 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.7, 177.7, 141.4, 137.0, 132.9, 128.6, 128.1, 127.0, 70.8, 38.7, 36.6, 35.5, 34.2, 27.3, 27.1, 26.7, 20.5. FT-IR: ν (cm<sup>-1</sup>) δ 3567, 3503, 2961, 1684, 1617, 1497, 1282, 1158. HRMS [ESI] calcd for C<sub>21</sub>H<sub>30</sub>O<sub>3</sub>Na [M+Na]<sup>+</sup> 353.2087, found 353.2101.

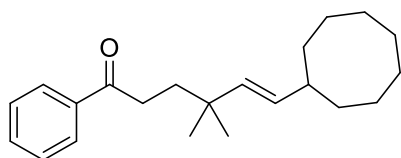


**3af:** 36.8 mg, 68% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/100). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.96-7.91 (m, 2H), 7.57-7.52 (m, 1H), 7.48-7.42 (m, 2H), 5.35-5.32 (m, 2H), 2.89-2.83 (m, 2H), 2.44-2.33 (m, 1H), 1.79-1.67 (m, 4H), 1.67-1.59 (m, 2H), 1.58-1.51 (m, 2H), 1.30-1.22 (m, 2H), 1.03 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 201.1, 137.1, 137.1, 132.8, 132.0, 128.5, 128.1, 43.5, 37.1, 35.4, 34.4, 33.4, 27.4, 25.2. FT-IR: ν (cm<sup>-1</sup>) δ 3567, 2952, 1684, 1490, 1424, 1340, 1285, 1211. HRMS [ESI] calcd for C<sub>19</sub>H<sub>26</sub>ONa [M+Na]<sup>+</sup> 293.1876, found 293.1869.

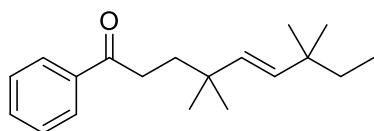


**3ag:** 34.1 mg, 60% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/100). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.98-7.91 (m, 2H),

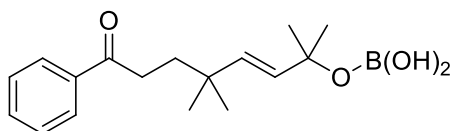
7.57-7.52 (m, 1H), 7.49-7.42 (m, 2H), 5.32-5.29 (m, 2H), 2.89-2.83 (m, 2H), 1.96-1.86 (m, 1H), 1.74-1.60 (m, 7H), 1.29-1.23 (m, 3H), 1.20-1.11 (m, 2H), 1.02 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  201.1, 137.1, 136.4, 133.4, 132.8, 128.5, 128.1, 40.8, 37.1, 35.3, 34.4, 33.5, 27.4, 26.2, 26.1. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  3568, 2919, 1684, 1490, 1363, 1179, 1208. HRMS [ESI] calcd for  $\text{C}_{20}\text{H}_{29}\text{O}$   $[\text{M}+\text{H}]^+$  285.2213, found 285.2211.



**3ah:** 41.1 mg, 66% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/100).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95-7.91 (m, 2H), 7.57-7.52 (m, 1H), 7.48-7.42 (m, 2H), 5.38-5.25 (m, 2H), 2.89-2.83 (m, 2H), 2.22-2.12 (m, 1H), 1.73-1.62 (m, 6H), 1.59-1.46 (m, 8H), 1.44-1.38 (m, 2H), 1.02 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  201.1, 137.1, 135.9, 134.3, 132.8, 128.5, 128.1, 41.0, 37.2, 35.3, 34.5, 32.4, 27.5, 26.0, 25.1. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  3528, 2918, 1684, 1497, 1316, 1284, 1179. HRMS [ESI] calcd for  $\text{C}_{22}\text{H}_{32}\text{ONa}$   $[\text{M}+\text{Na}]^+$  335.2345, found 335.2341.

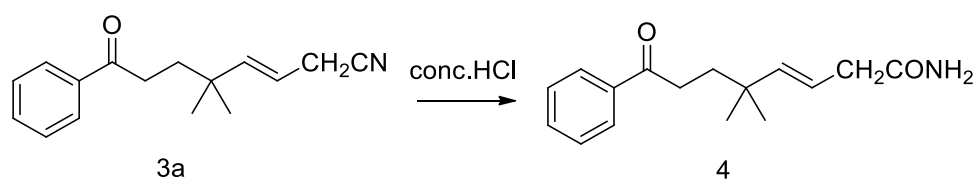


**3ai:** 27.7 mg, 51% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/100).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95-7.91 (m, 2H), 7.57-7.51 (m, 1H), 7.47-7.41 (m, 2H), 5.36-5.20 (m, 2H), 2.89-2.83 (m, 2H), 1.75-1.68 (m, 2H), 1.30 (m, 2H), 1.04 (s, 6H), 0.95 (s, 6H), 0.78 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  201.1, 137.1, 136.8, 134.9, 132.8, 128.5, 128.1, 37.2, 35.6, 35.6, 35.4, 34.5, 27.5, 27.1, 9.0. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  3712, 3629, 2960, 1684, 1534, 1448, 1385, 1284, 1179. HRMS [ESI] calcd for  $\text{C}_{19}\text{H}_{29}\text{O}$   $[\text{M}+\text{H}]^+$  273.2213, found 273.2214.



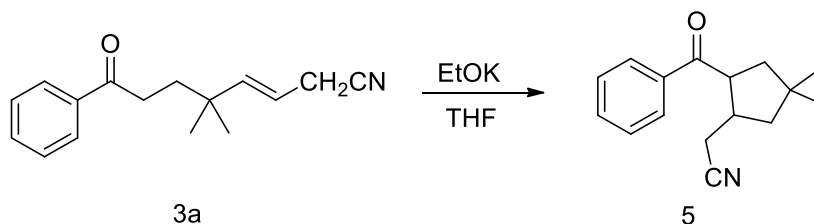
**3aj:** 27.4 mg, 45% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/100-1/10).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95-7.91 (m, 2H), 7.58-7.52 (m, 1H), 7.48-7.42 (m, 2H), 5.61-5.50 (m, 2H), 2.89-2.83 (m, 2H), 1.78-1.72 (m, 2H), 1.65 (br, 2H), 1.30 (s, 6H), 1.06 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  200.8, 137.0, 135.8, 134.9, 133.0, 128.6, 128.0, 70.8, 36.9, 35.2, 34.2, 30.0, 27.2. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  3853, 3627, 2927, 1684, 1472, 1386, 1283, 1212. HRMS [ESI] calcd for  $\text{C}_{17}\text{H}_{25}\text{BO}_4\text{Na}$   $[\text{M}+\text{Na}]^+$  327.1738, found 327.1741.

## 5. Transformations of compound 3a

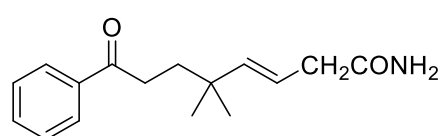


**3a** (0.2 mmol) in THF (2.0 mL) was treated with conc. HCl (1.0 mL) and stirred at rt. After the reaction was complete, the mixture was extracted with  $\text{Et}_2\text{O}$  for four times. Then the organic phase

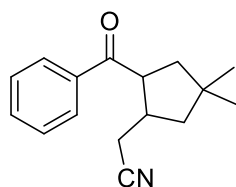
was combined and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed under vacuum and the residue was purified by flash column chromatography on silica gel to provide the product **4**.



**3a** (0.1 mmol) in THF (1.0 mL) was treated with EtOK (0.2 mmol) and stirred at  $60^\circ\text{C}$ . After the reaction was complete, the mixture was extracted with EtOAc for three times. Then the organic phase was combined and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed under vacuum and the residue was purified by flash column chromatography on silica gel to provide the product **5**.

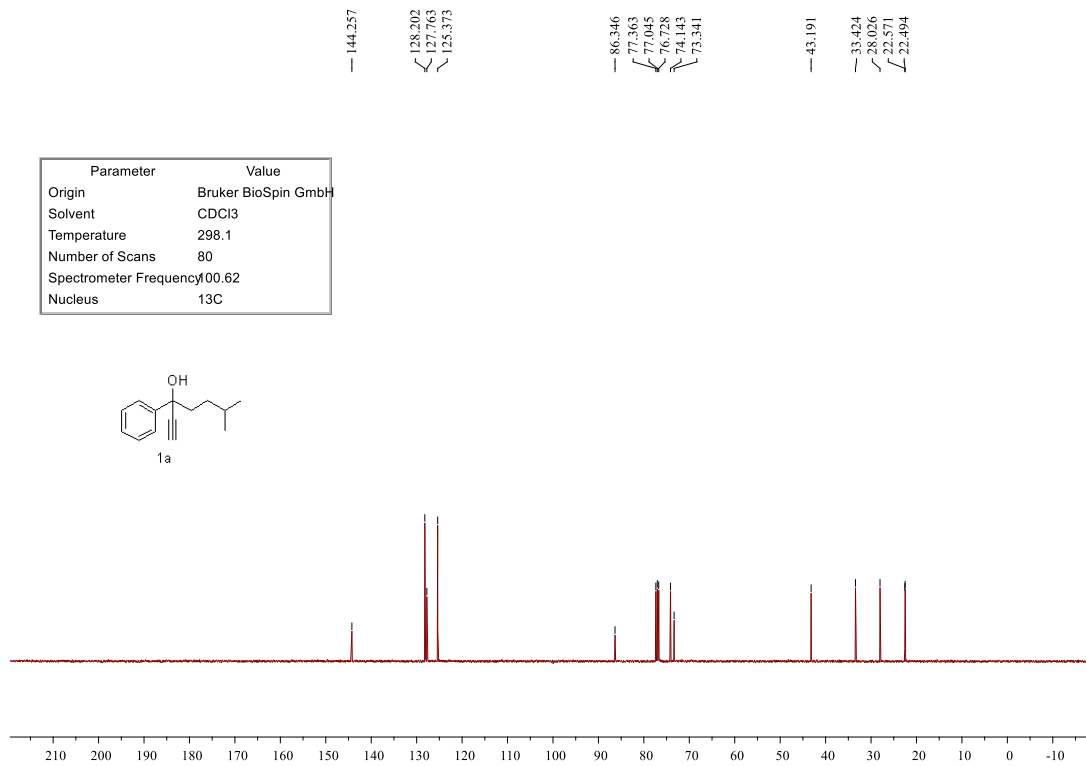
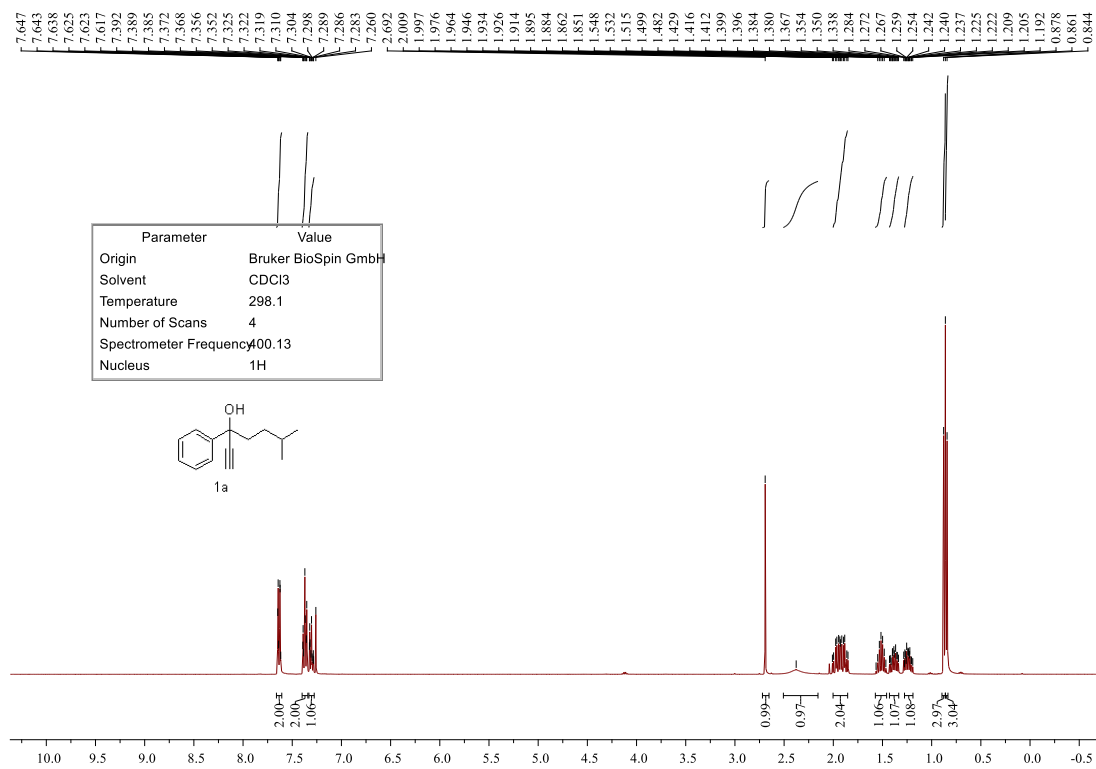


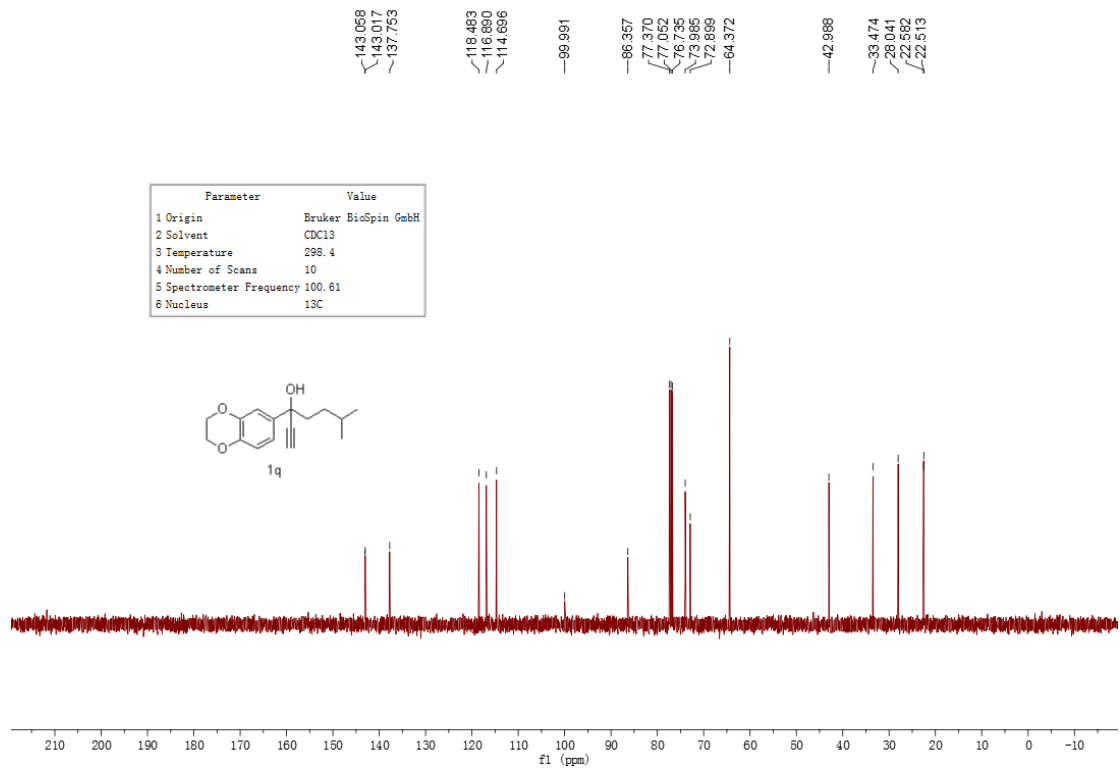
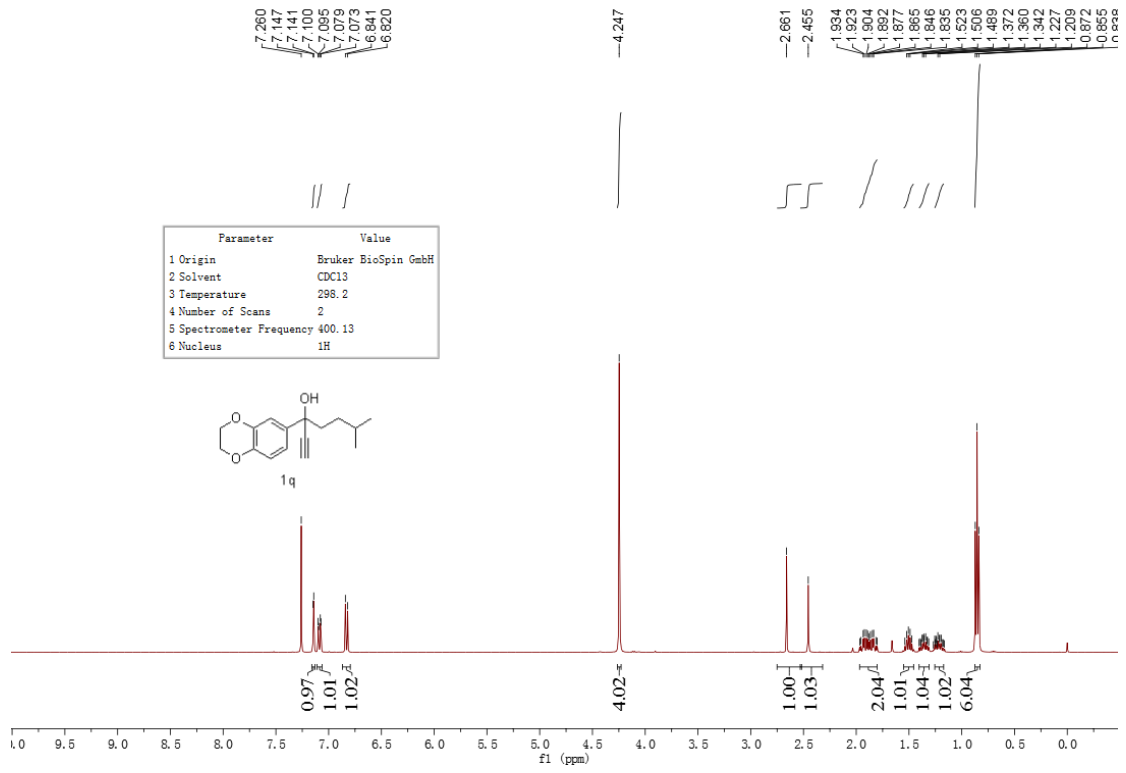
**4**: 51.3 mg, 99% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/10-1/1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94-7.90 (m, 2H), 7.57-7.51 (m, 1H), 7.47-7.41 (m, 2H), 5.90-5.60 (m, 2H), 5.56-5.45 (m, 2H), 2.95 (d,  $J = 6.4$  Hz, 2H), 2.91-2.84 (m, 2H), 1.78-1.71 (m, 2H), 1.06 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  200.8, 174.1, 144.6, 136.9, 133.0, 128.6, 128.1, 119.8, 40.1, 36.7, 36.0, 34.2, 27.1. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  3347, 3194, 2925, 2855, 1670, 1448, 1386, 1260. HRMS [ESI] calcd for  $\text{C}_{16}\text{H}_{22}\text{NO}_2$  [ $\text{M}+\text{H}$ ] $^+$  260.1645, found 260.1643.

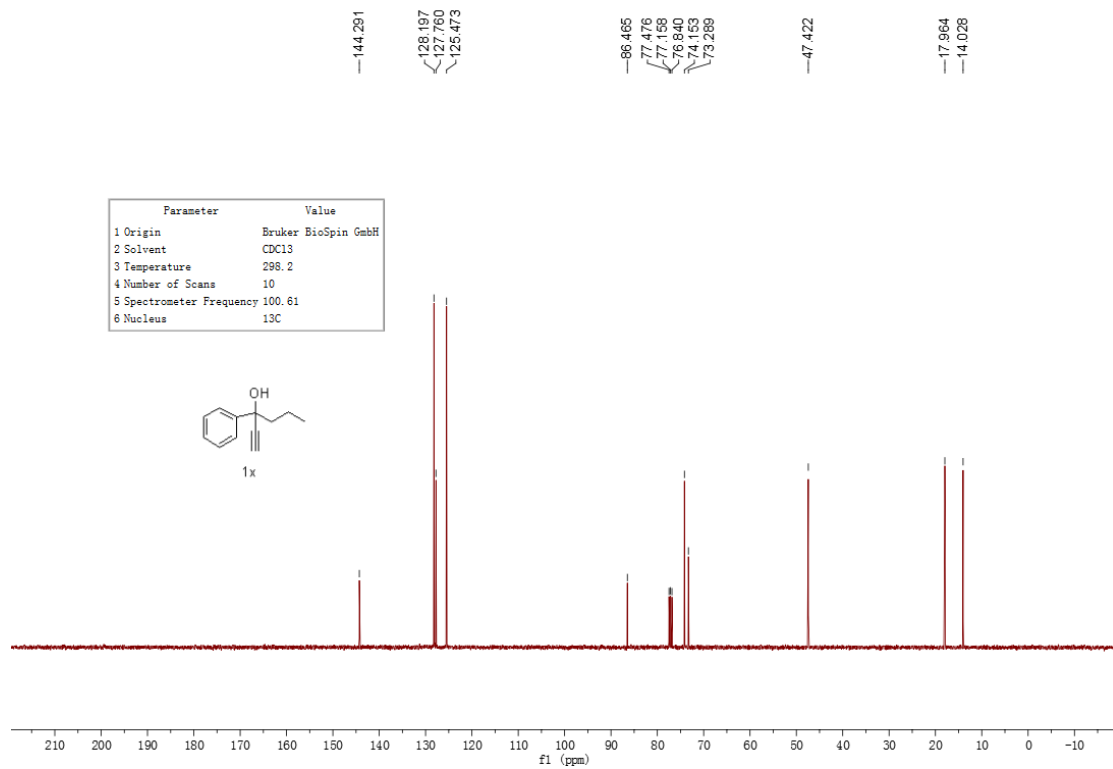
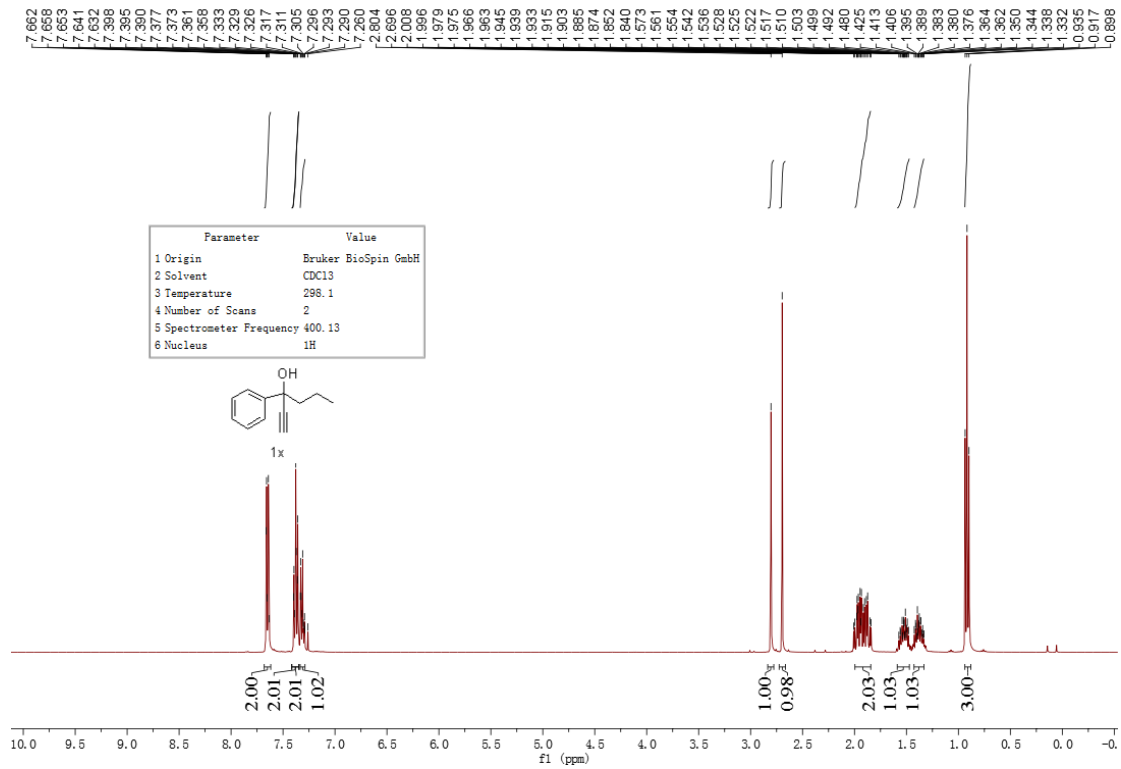


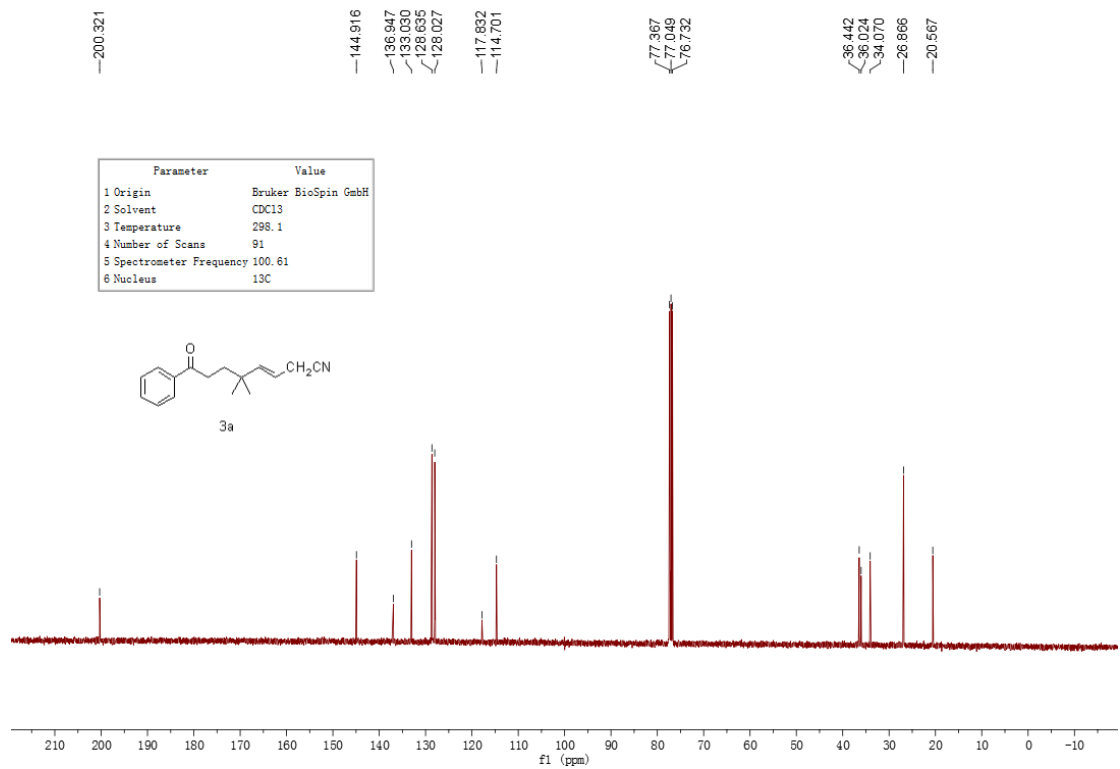
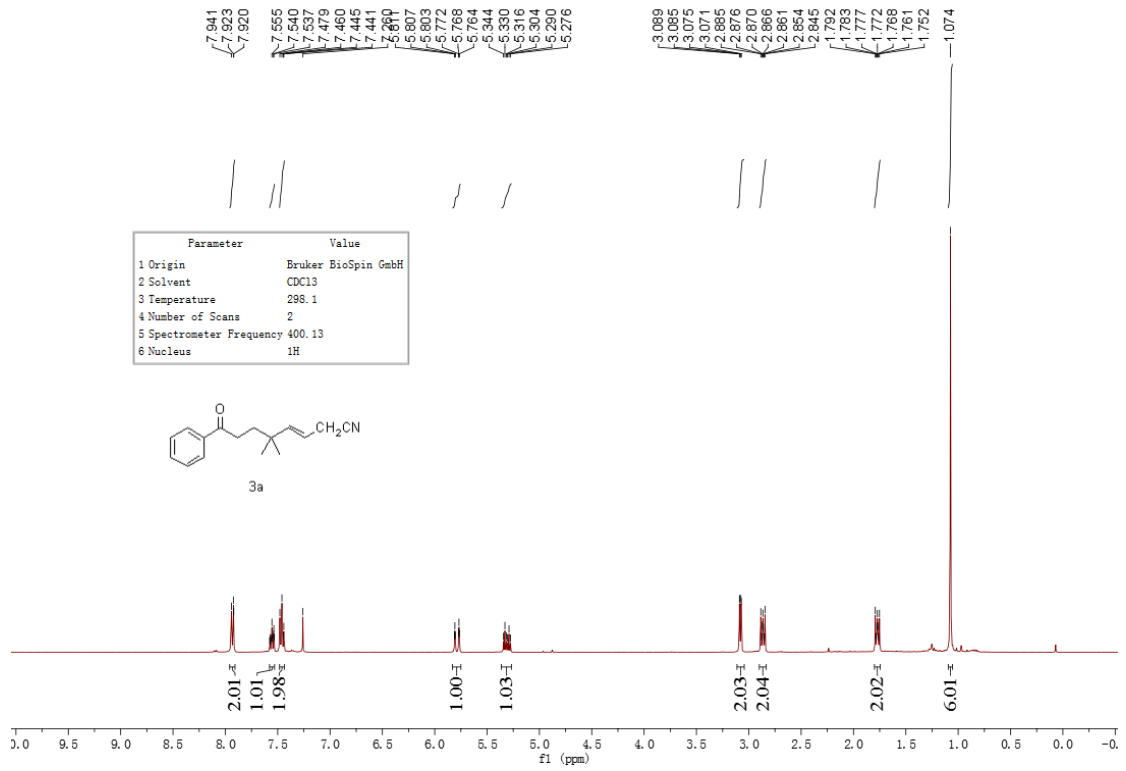
**5**: 14.9 mg, 62% yield, yellow oil. Purification by flash column chromatography (eluent: EtOAc/Petroleum ether = 1/100-1/20).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96-7.92 (m, 2H), 7.61-7.55 (m, 1H), 7.54-7.45 (m, 2H), 3.67-3.58 (m, 1H), 3.11-3.10 (m, 1H), 2.52 (dd,  $J = 16.8, 4.8$  Hz, 1H), 2.41 (dd,  $J = 16.8, 6.0$  Hz, 1H), 2.10 (dd,  $J = 12.8, 10.0$  Hz, 1H), 1.87 (dd,  $J = 12.8, 7.6$  Hz, 1H), 1.62-1.55 (m, 2H), 1.17 (s, 3H), 1.04 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  200.7, 136.4, 133.4, 128.7, 128.5, 118.5, 51.4, 46.6, 46.1, 38.6, 36.4, 30.4, 29.7, 21.3. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ )  $\delta$  3021, 2930, 2247, 1677, 1580, 1424, 1318, 1209, 1076. HRMS [ESI] calcd for  $\text{C}_{16}\text{H}_{20}\text{NO}$  [ $\text{M}+\text{H}$ ] $^+$  242.1539, found 242.1541.

## 6. $^1\text{H}$ , $^{13}\text{C}$ , $^{19}\text{F}$ NMR and HMBC spectra

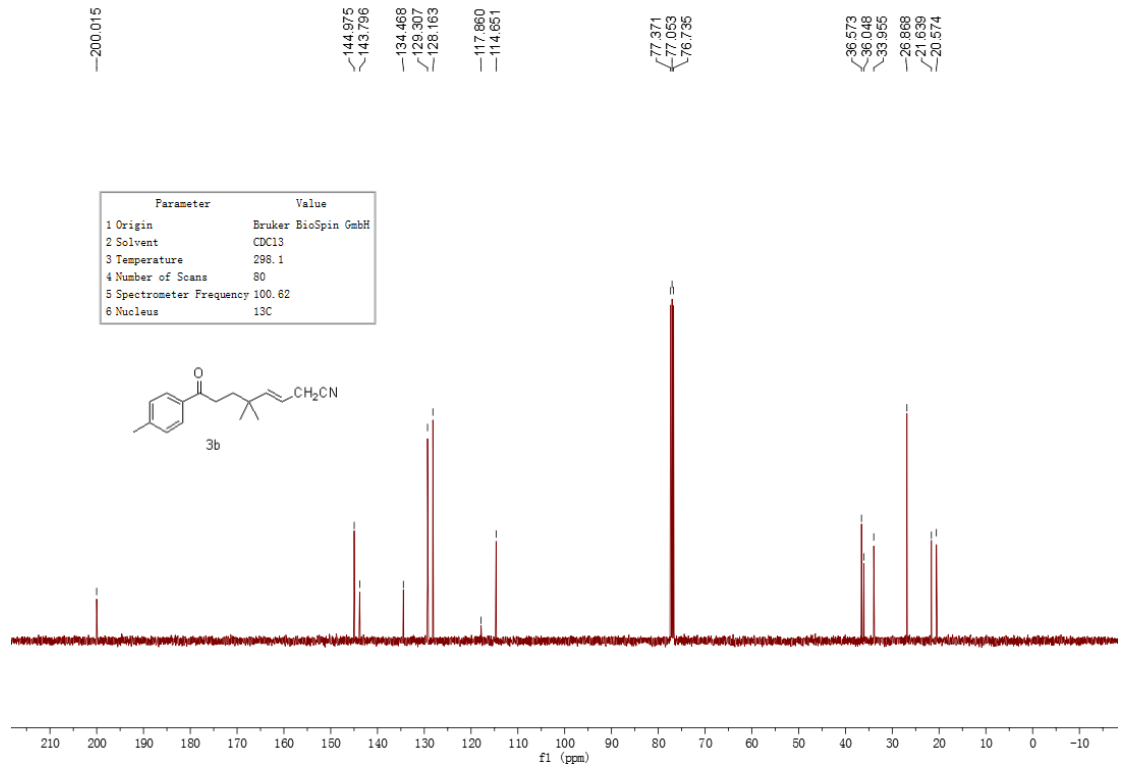
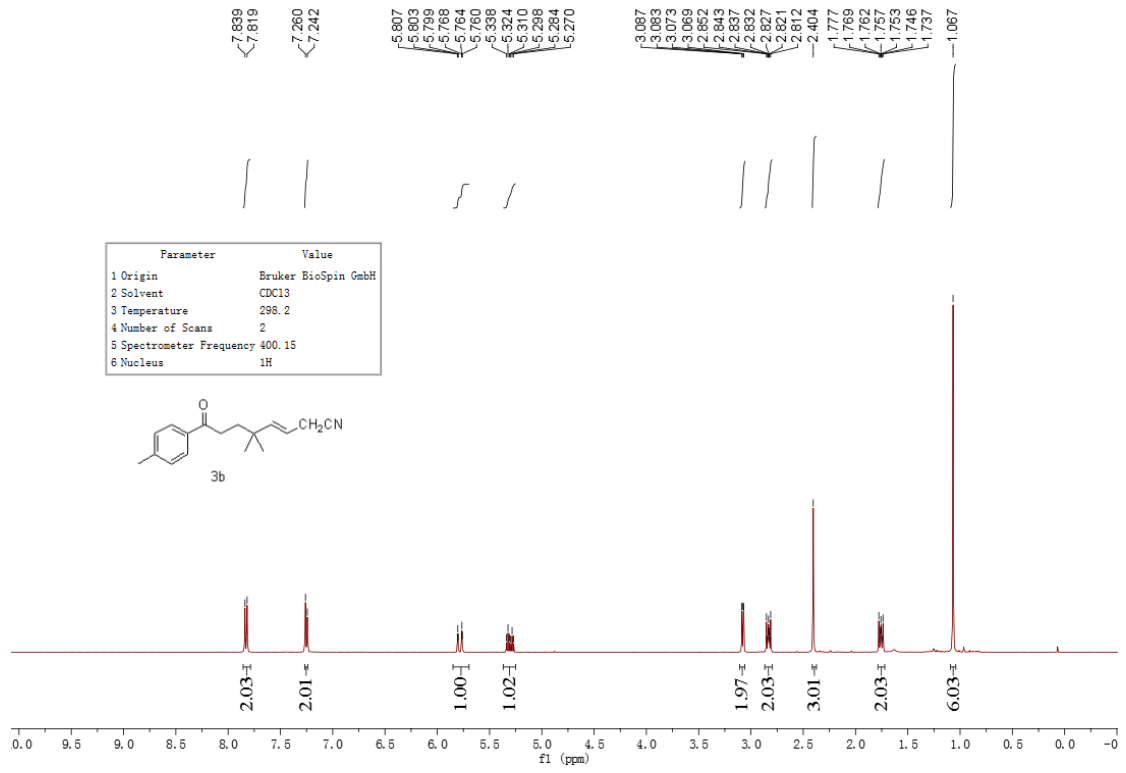


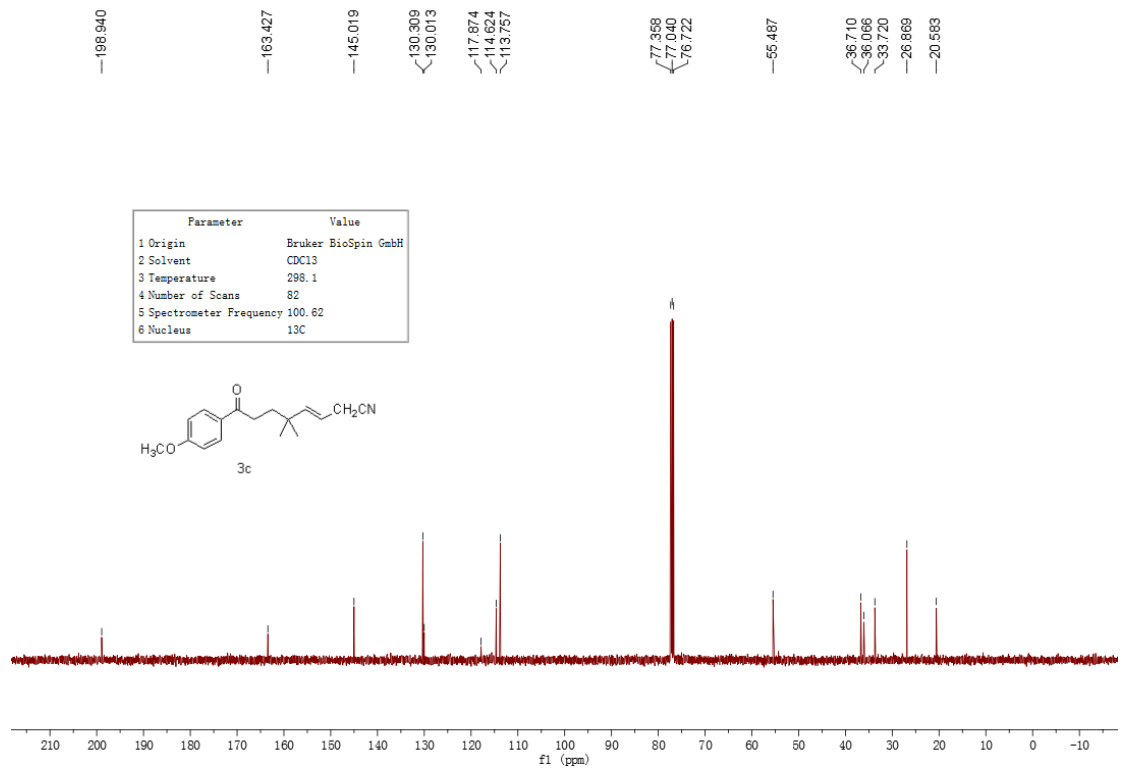
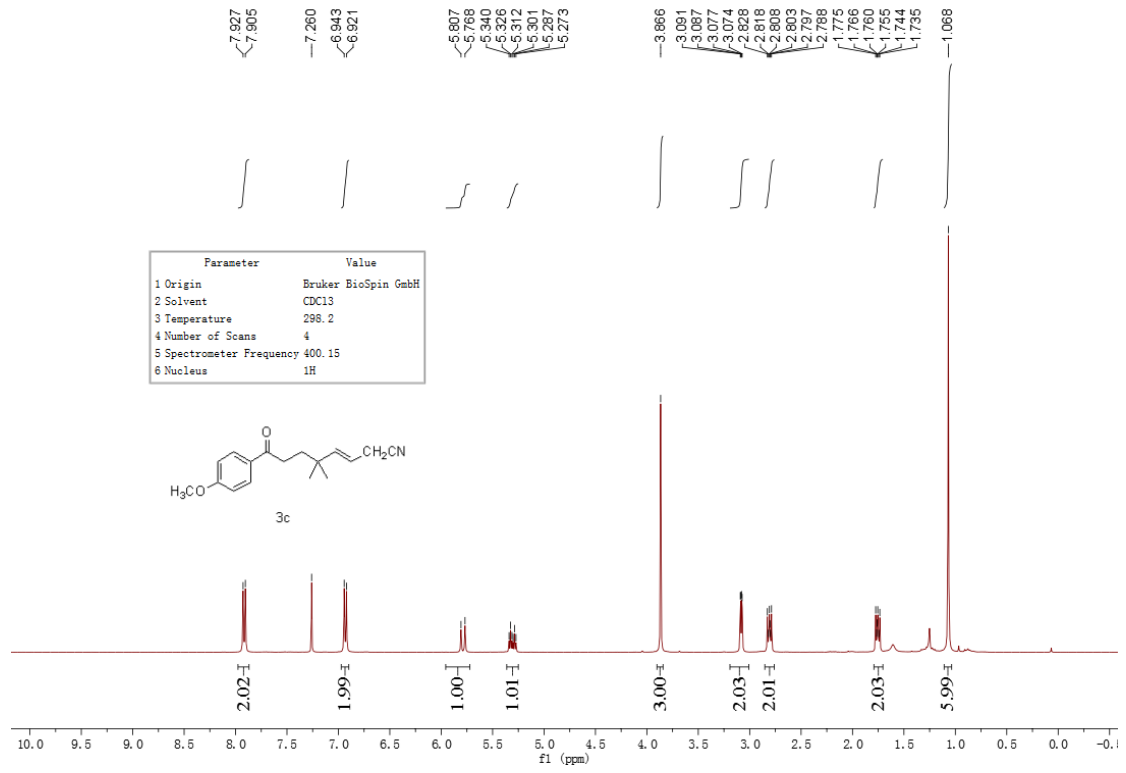


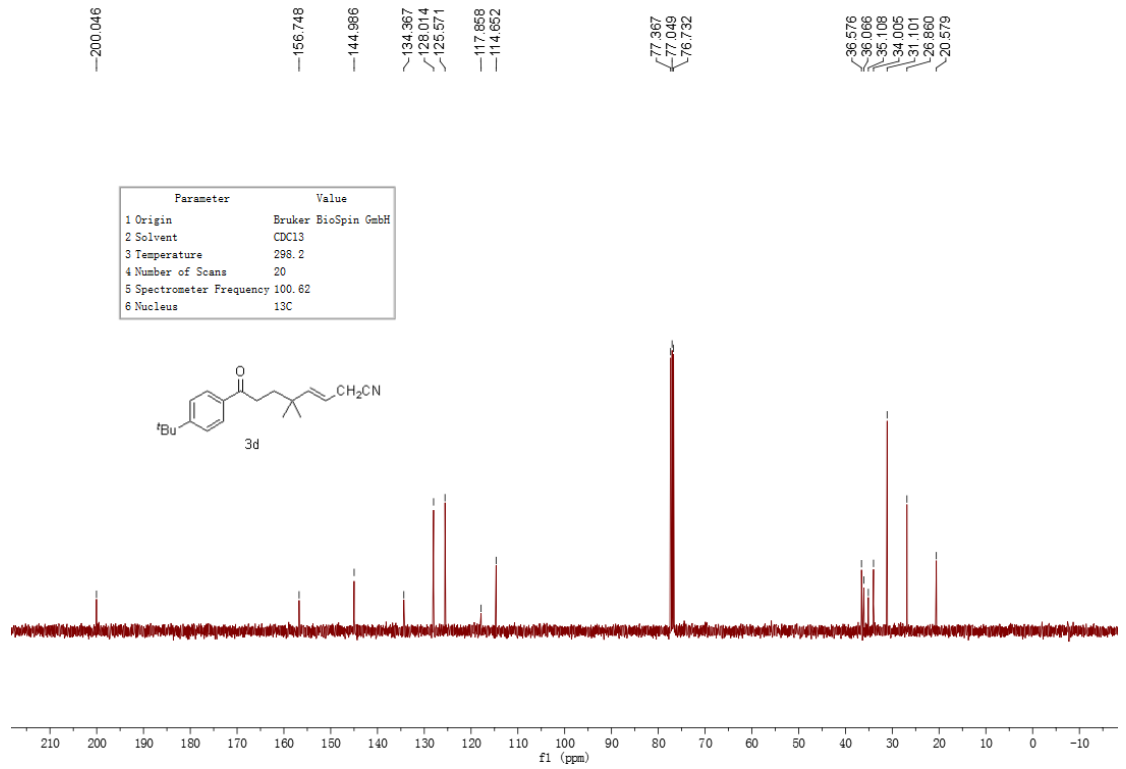
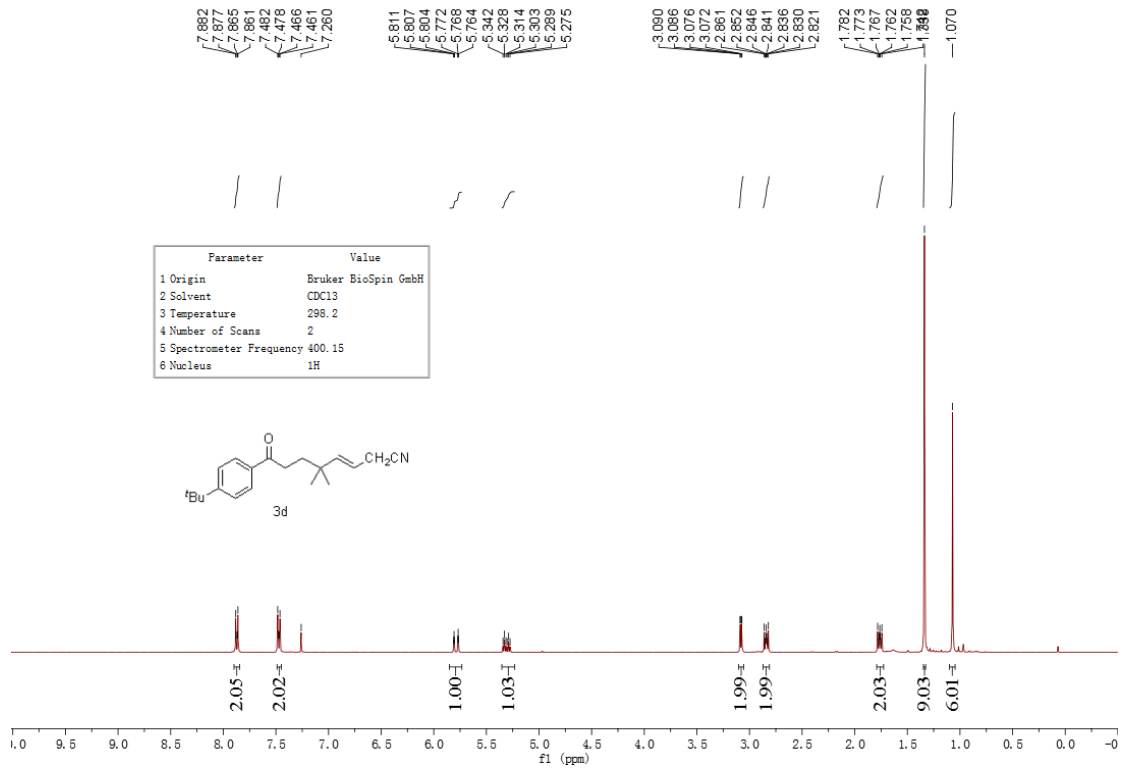


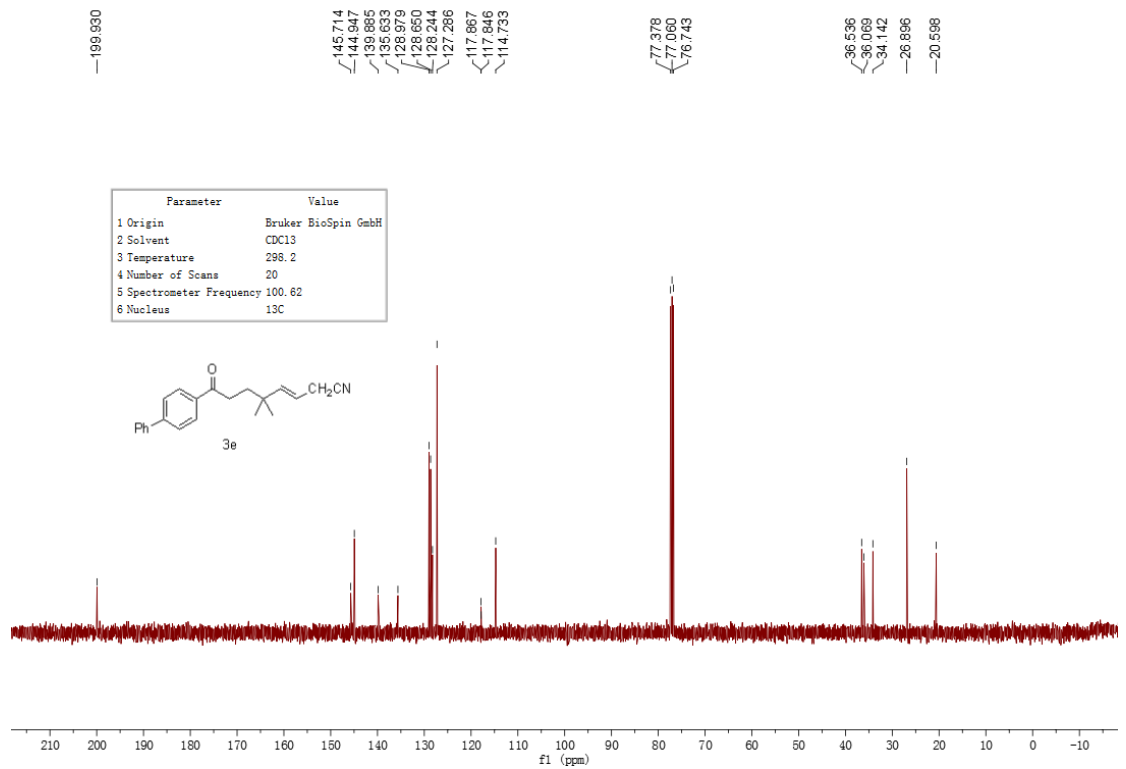
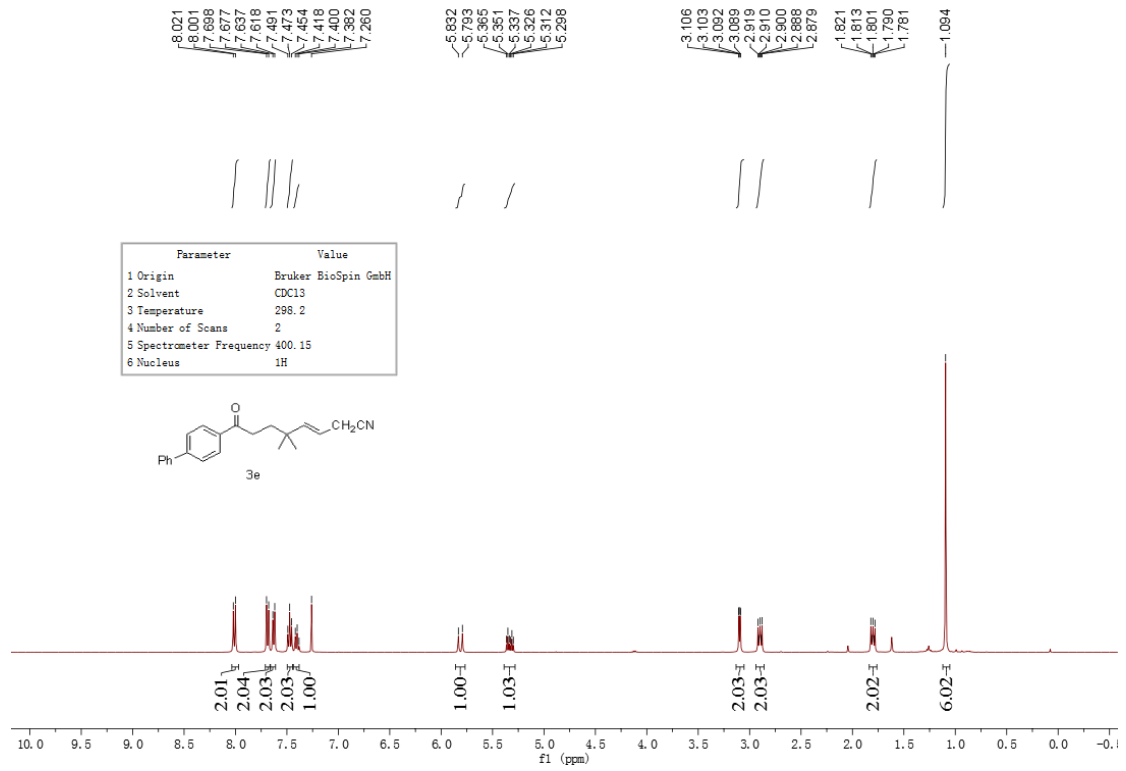






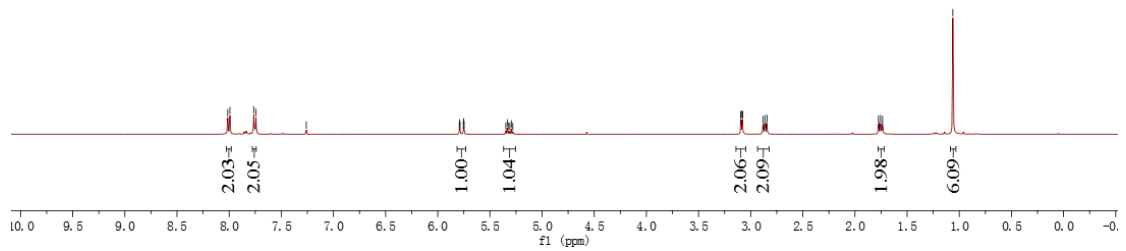
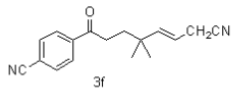






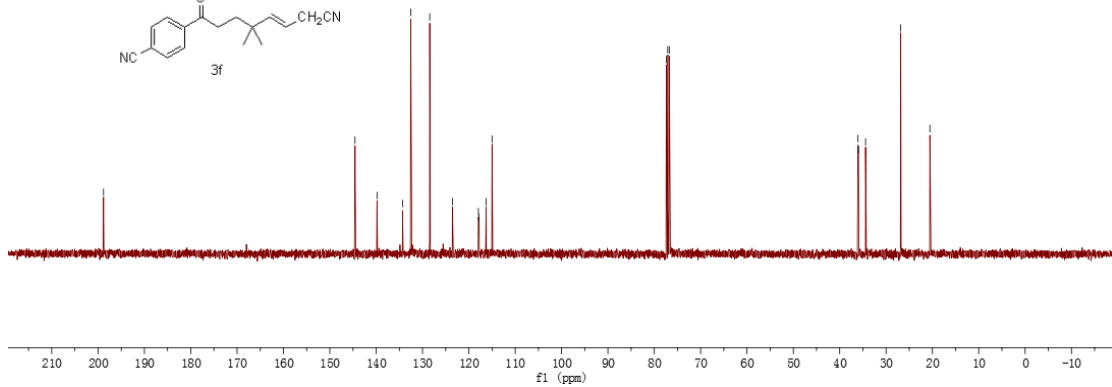
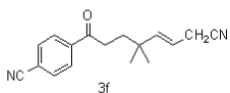
8.013  
7.982  
7.764  
7.743  
7.260  
5.793  
5.790  
5.786  
5.754  
5.751  
5.747  
5.347  
5.334  
5.320  
5.308  
5.294  
5.280  
3.095  
3.091  
3.081  
3.077  
2.883  
2.875  
2.863  
2.851  
2.843  
1.775  
1.768  
1.755  
1.743  
1.735  
1.062

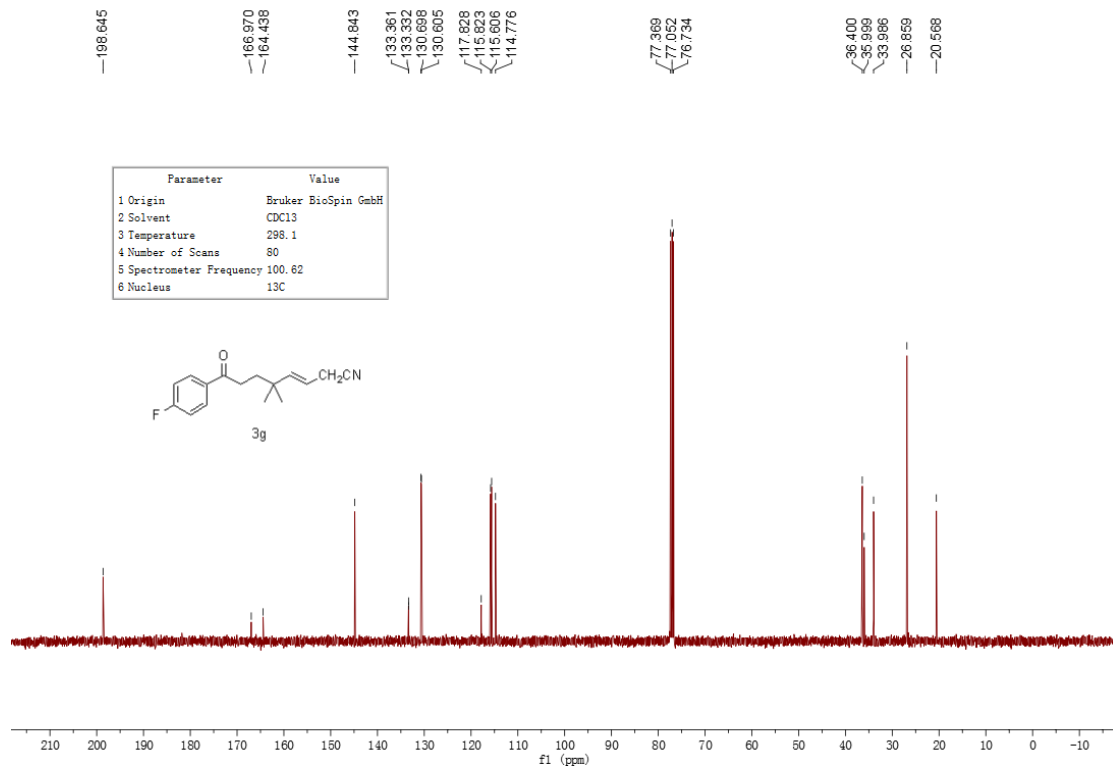
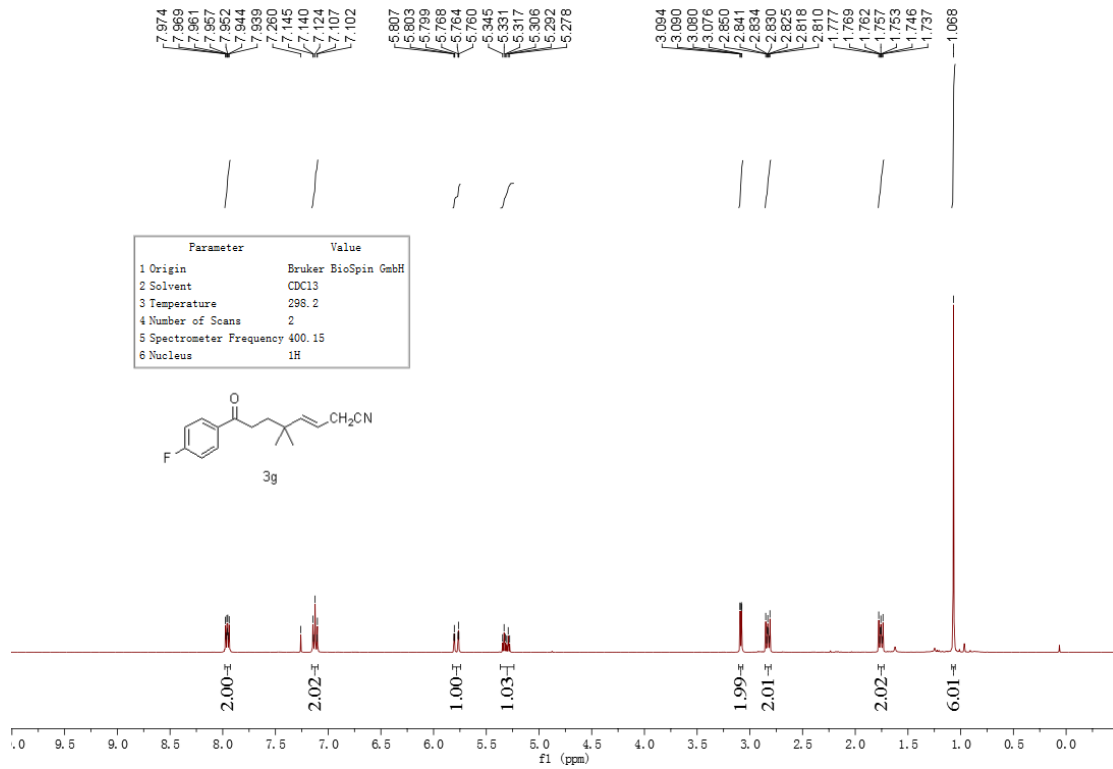
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.1
4 Number of Scans	2
5 Spectrometer Frequency	400.13
6 Nucleus	<sup>1</sup> H

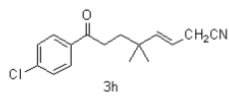
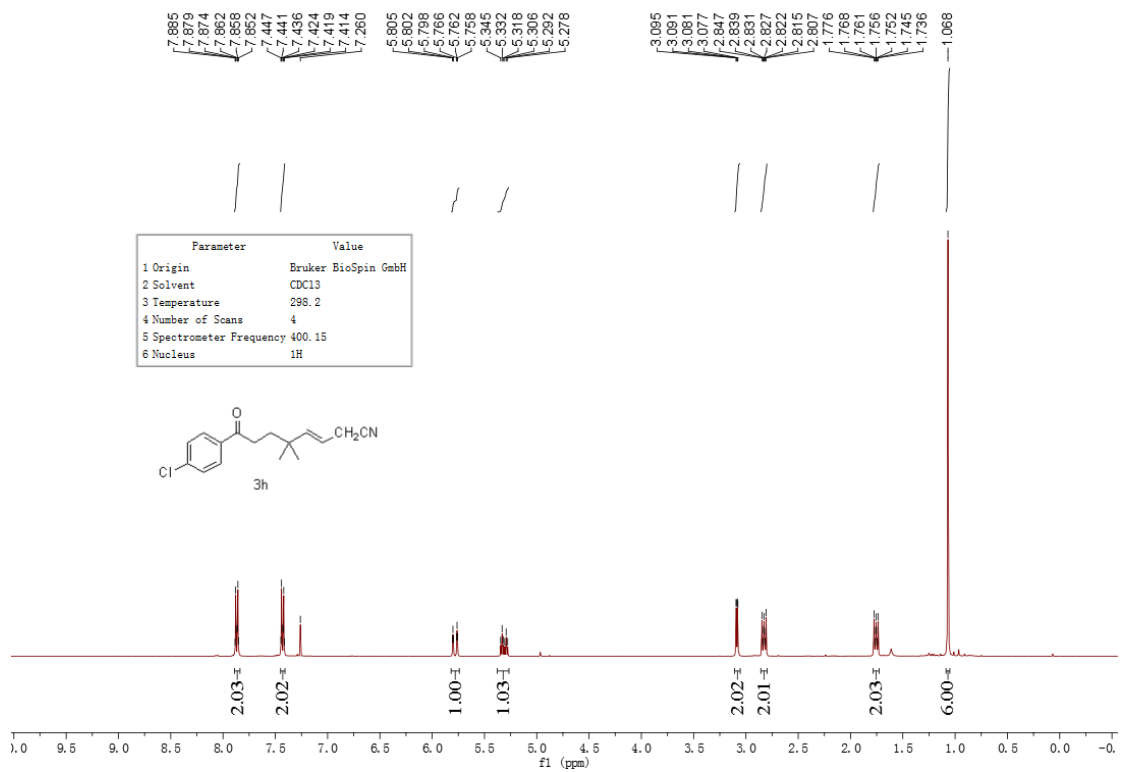
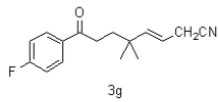
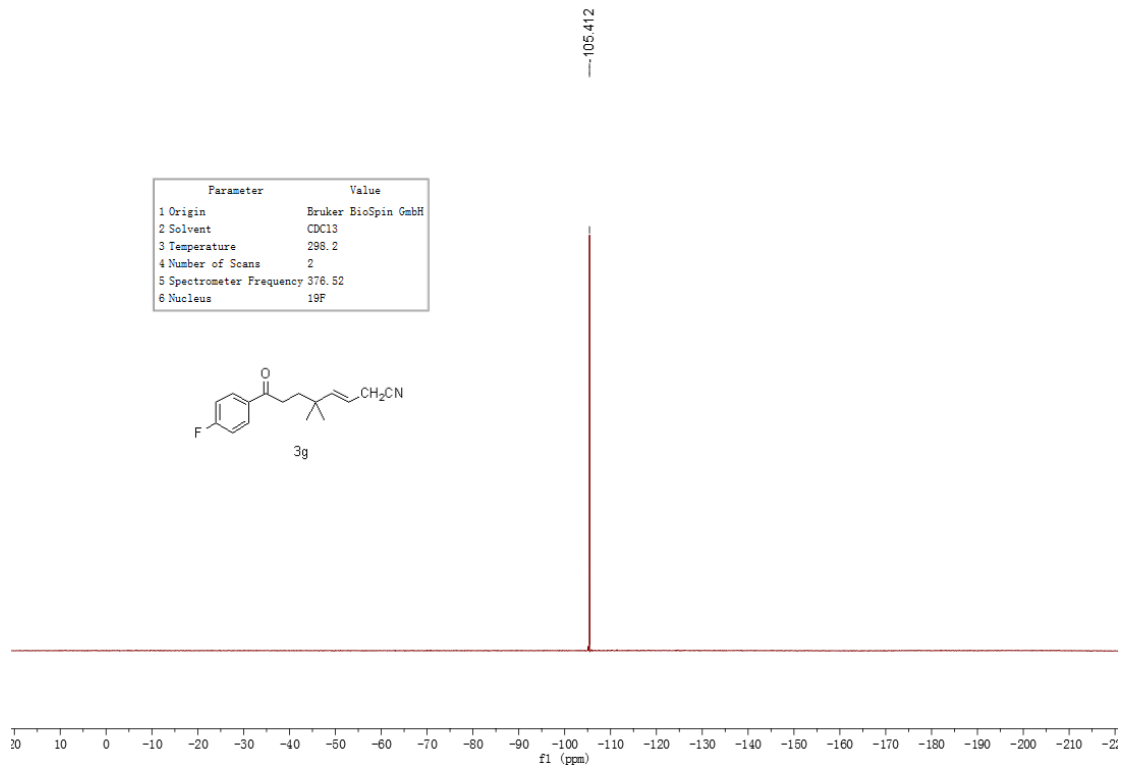


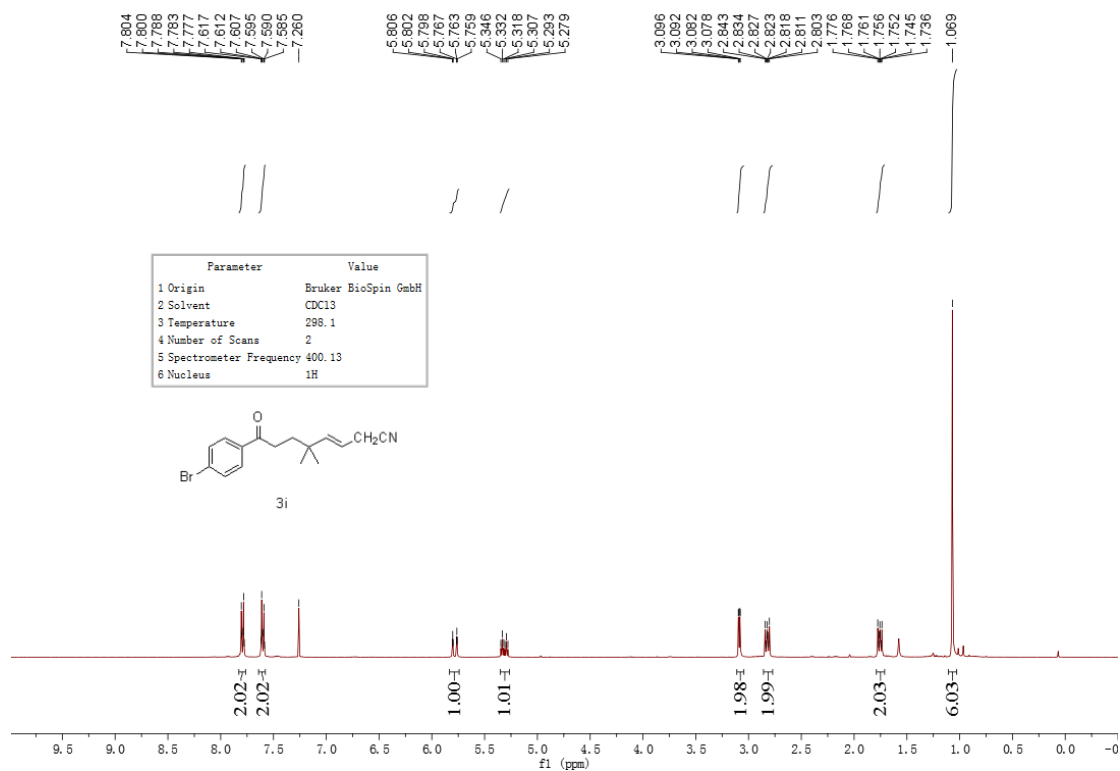
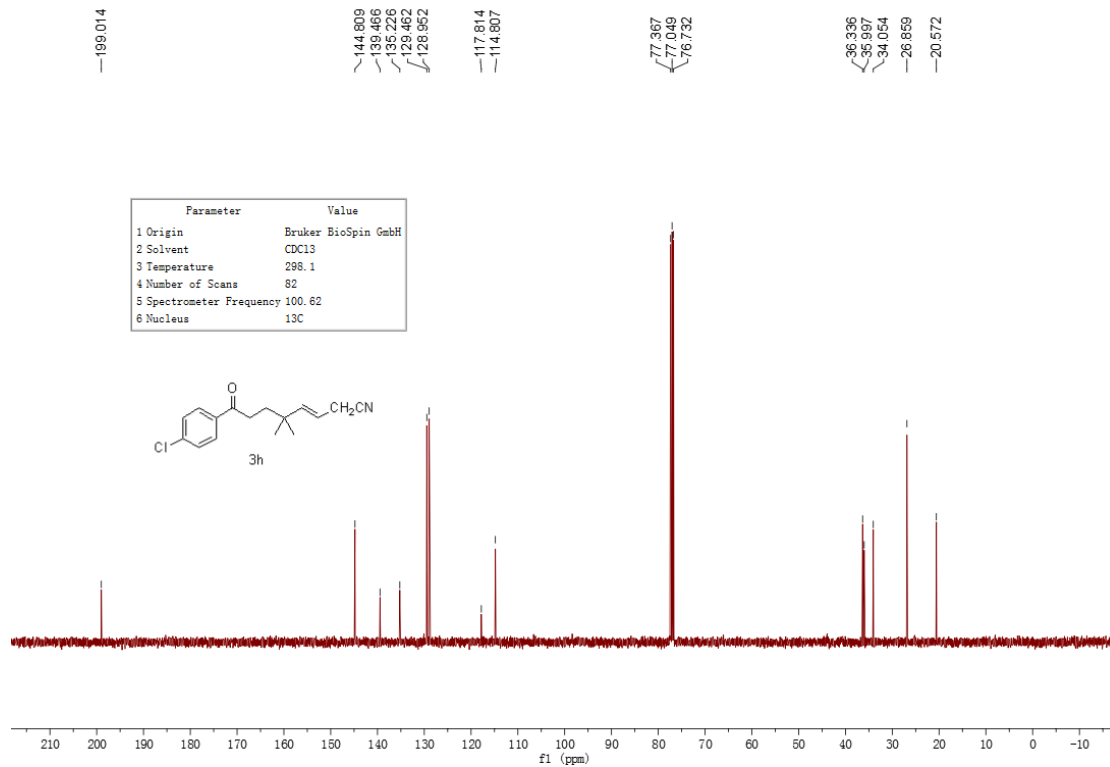
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139.816  
134.303  
132.552  
128.444  
123.555  
117.944  
117.802  
116.271  
114.989  
77.407  
77.089  
76.772  
36.058  
35.940  
34.420  
26.831  
20.545

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.1
4 Number of Scans	40
5 Spectrometer Frequency	100.62
6 Nucleus	<sup>13</sup> C

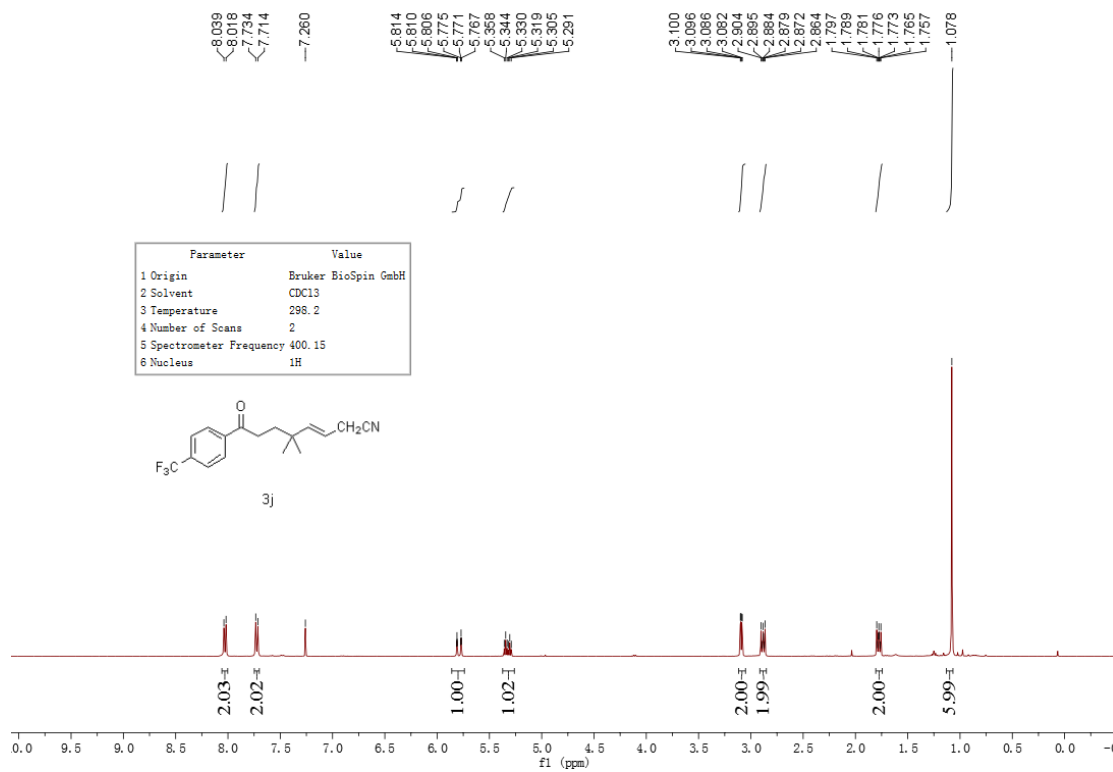
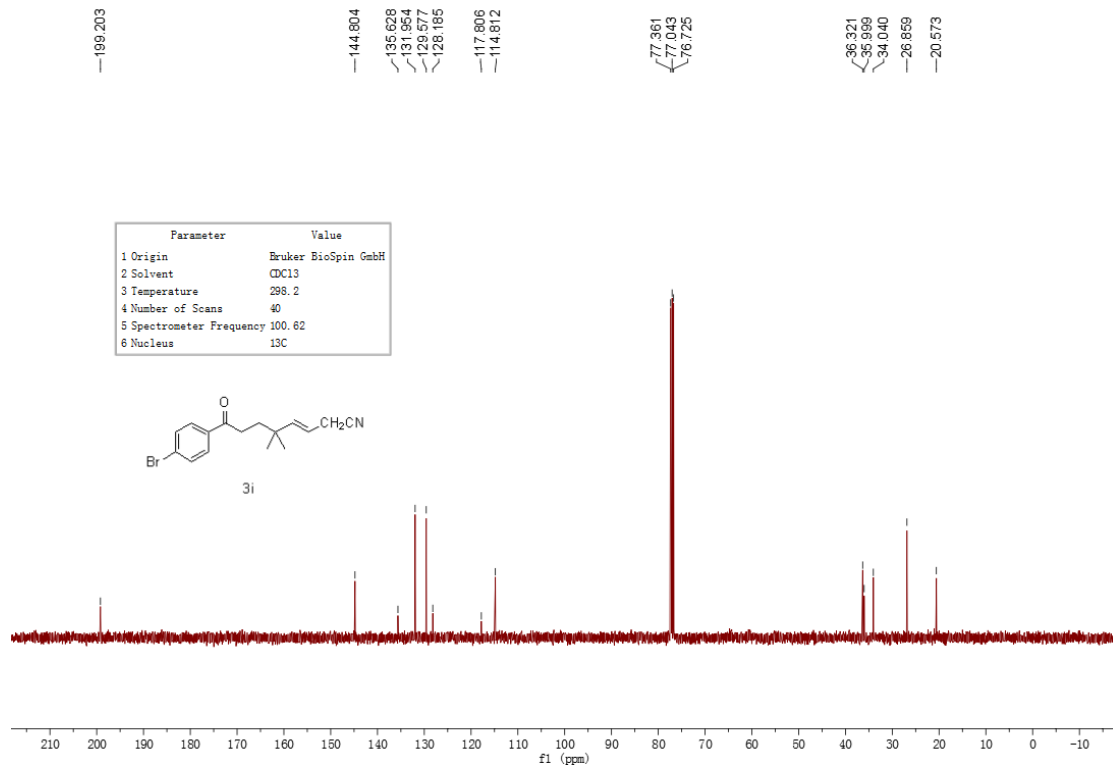


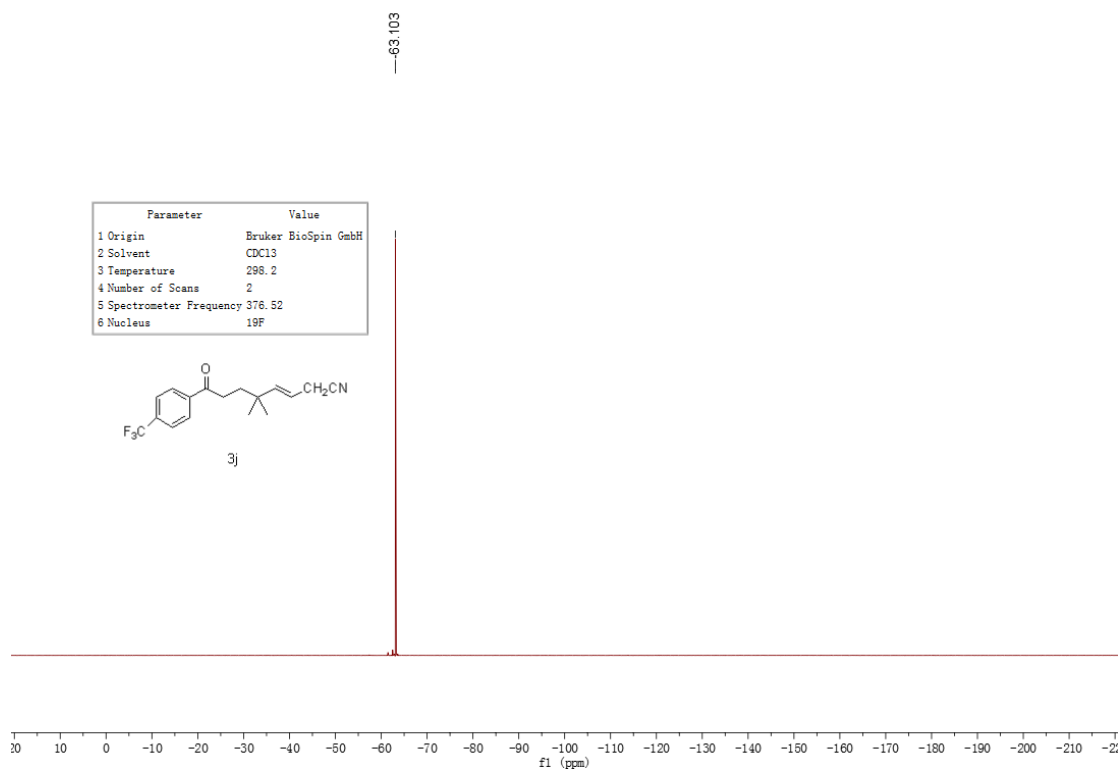
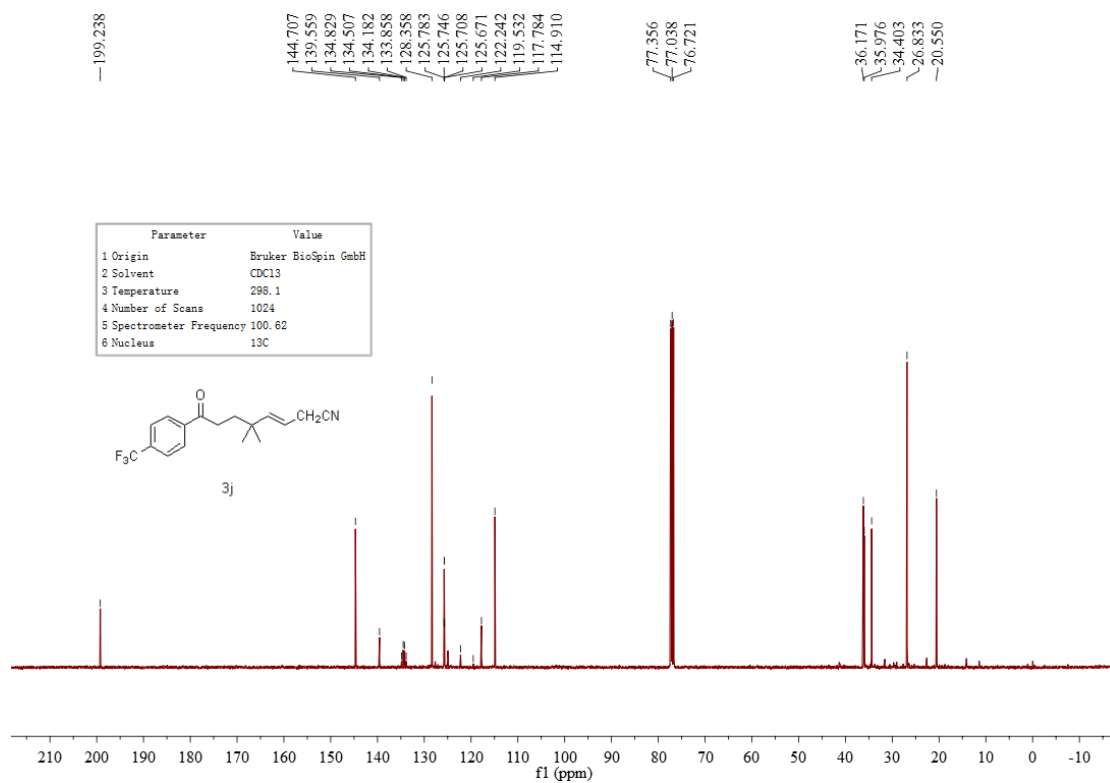


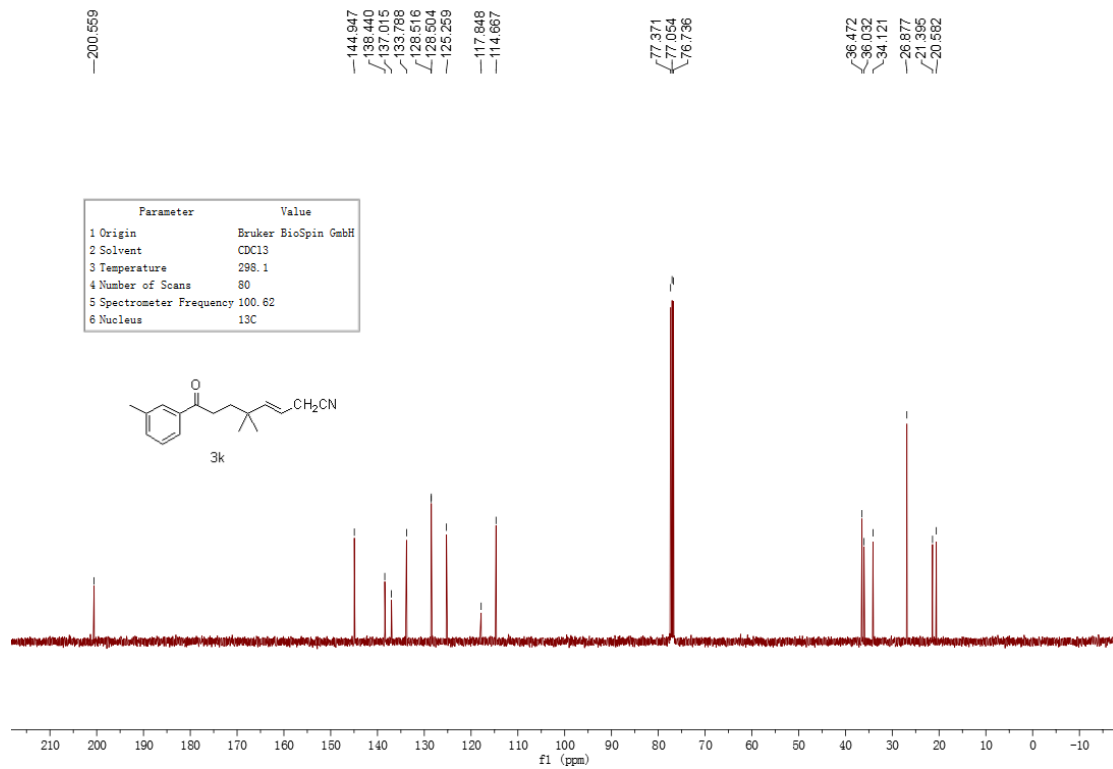
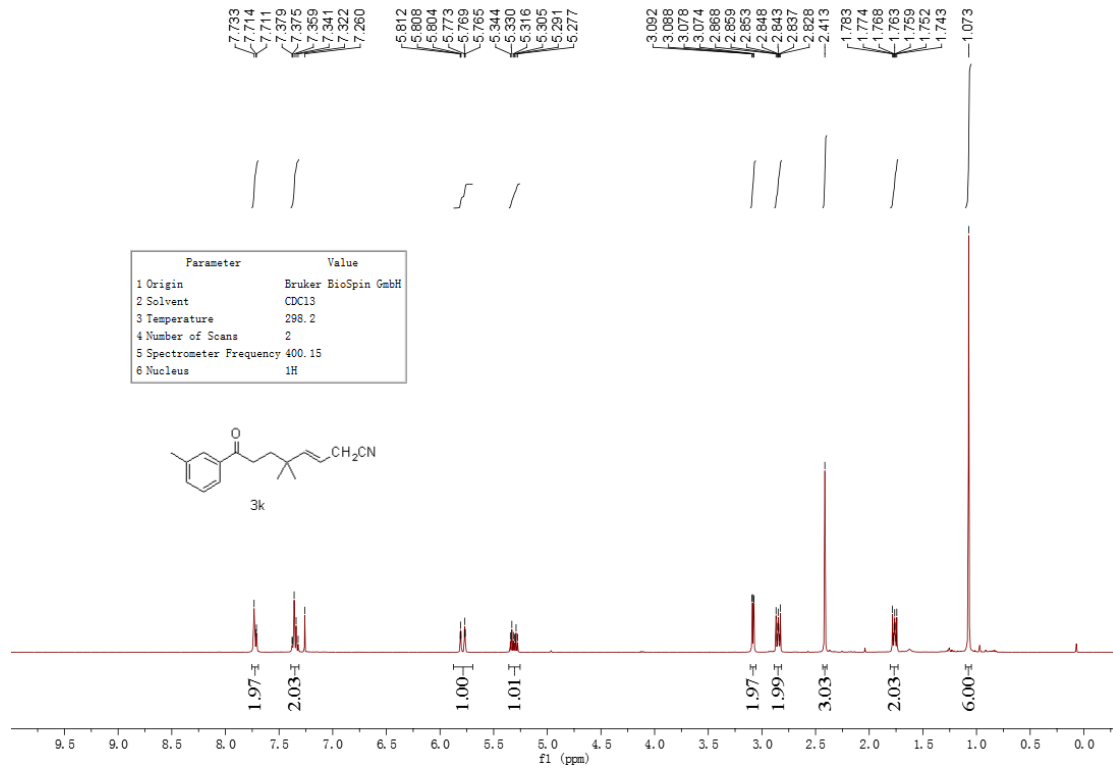


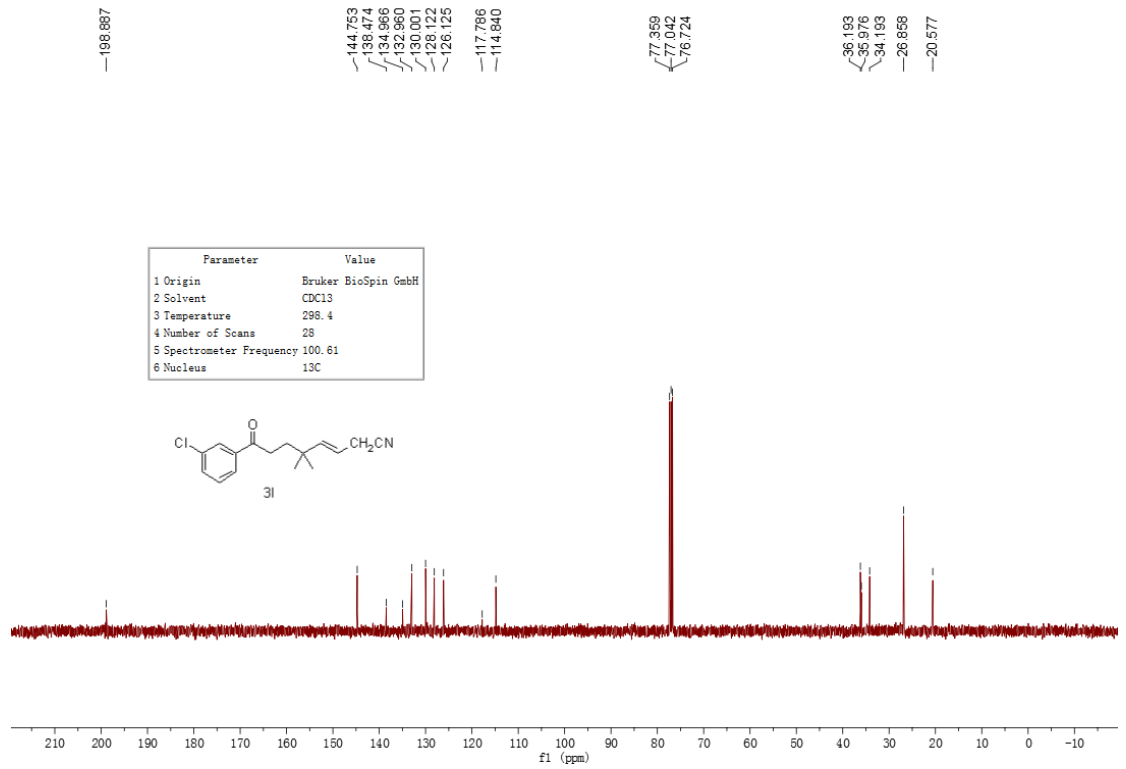
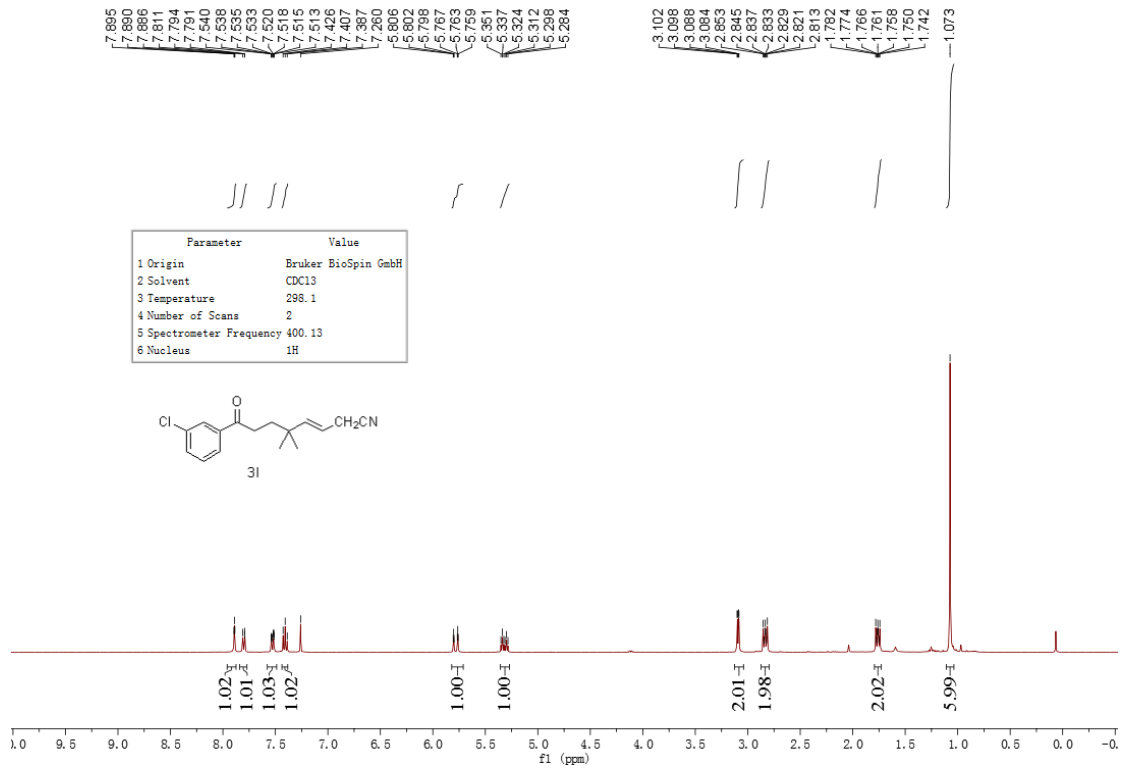


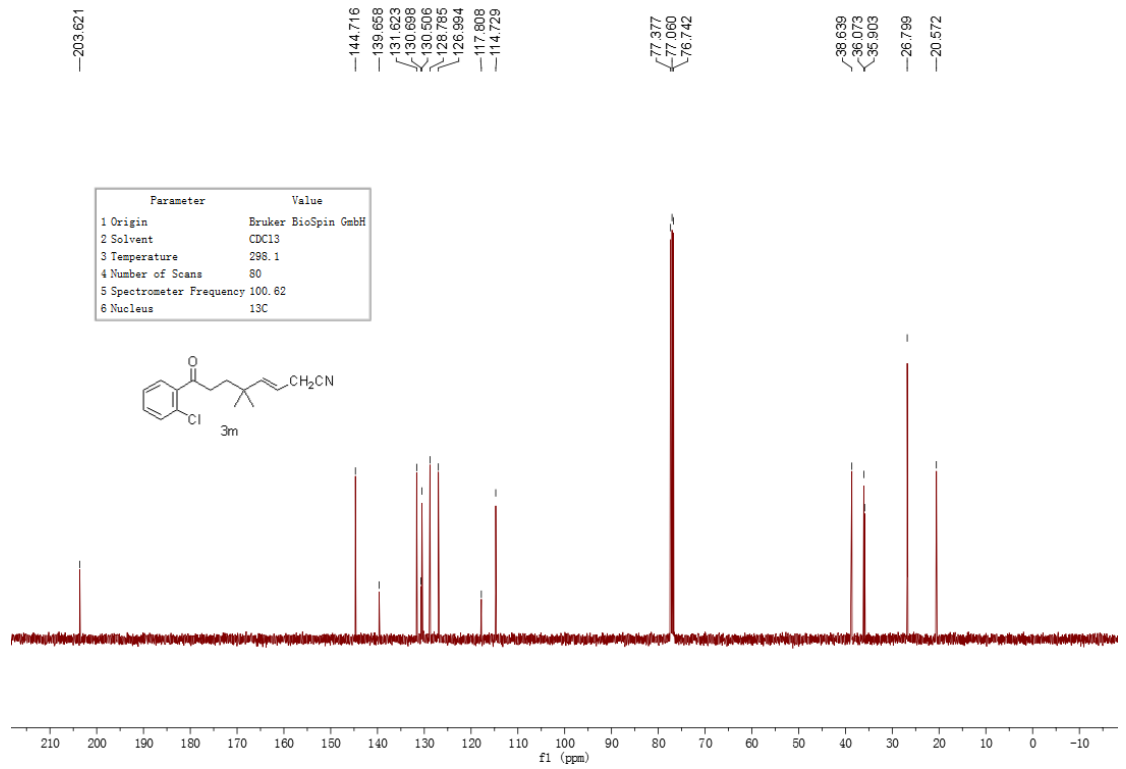
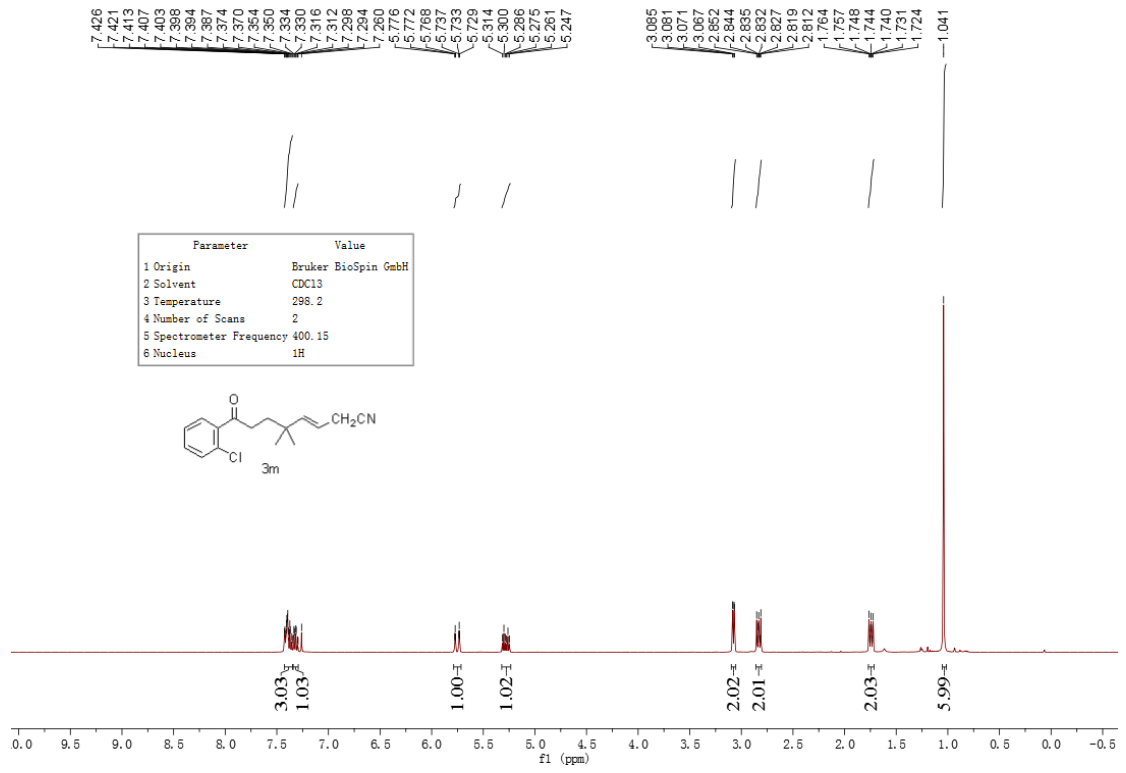


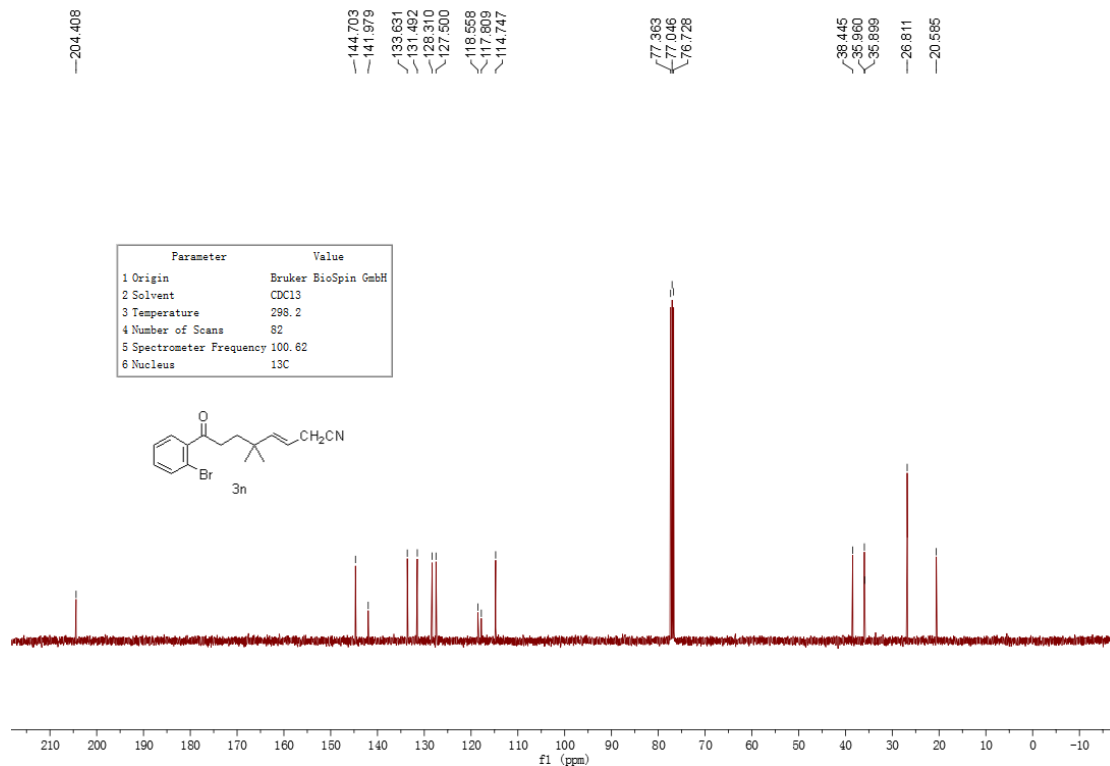
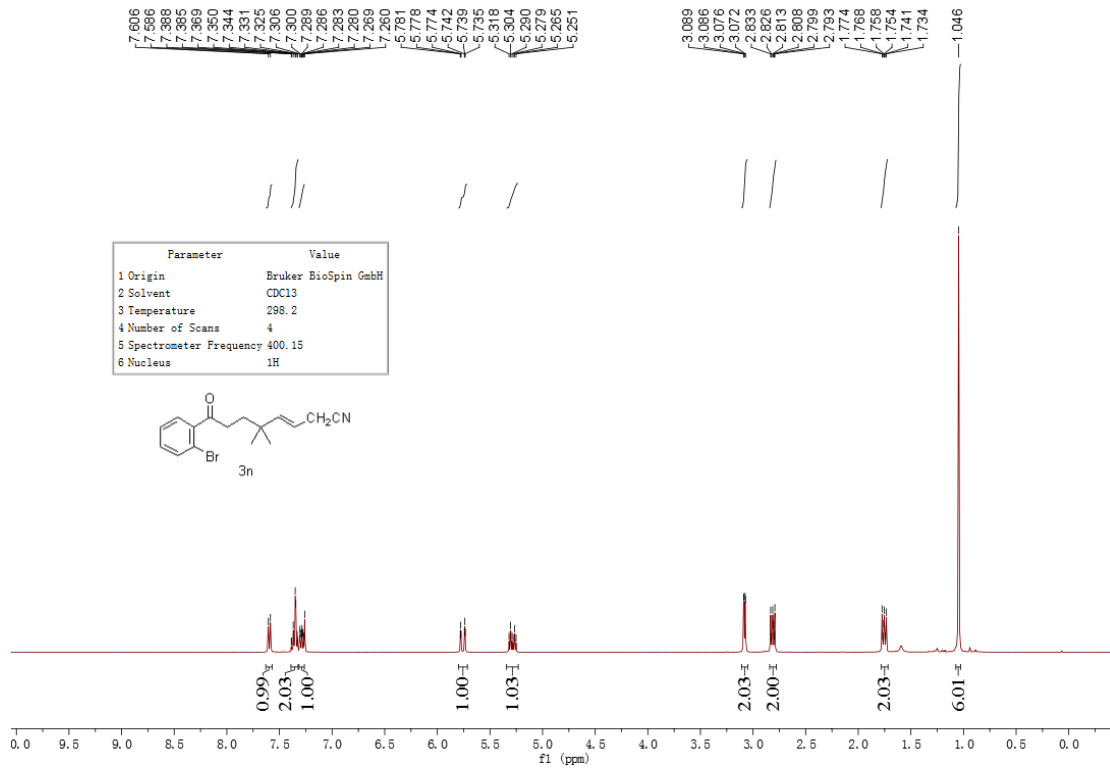


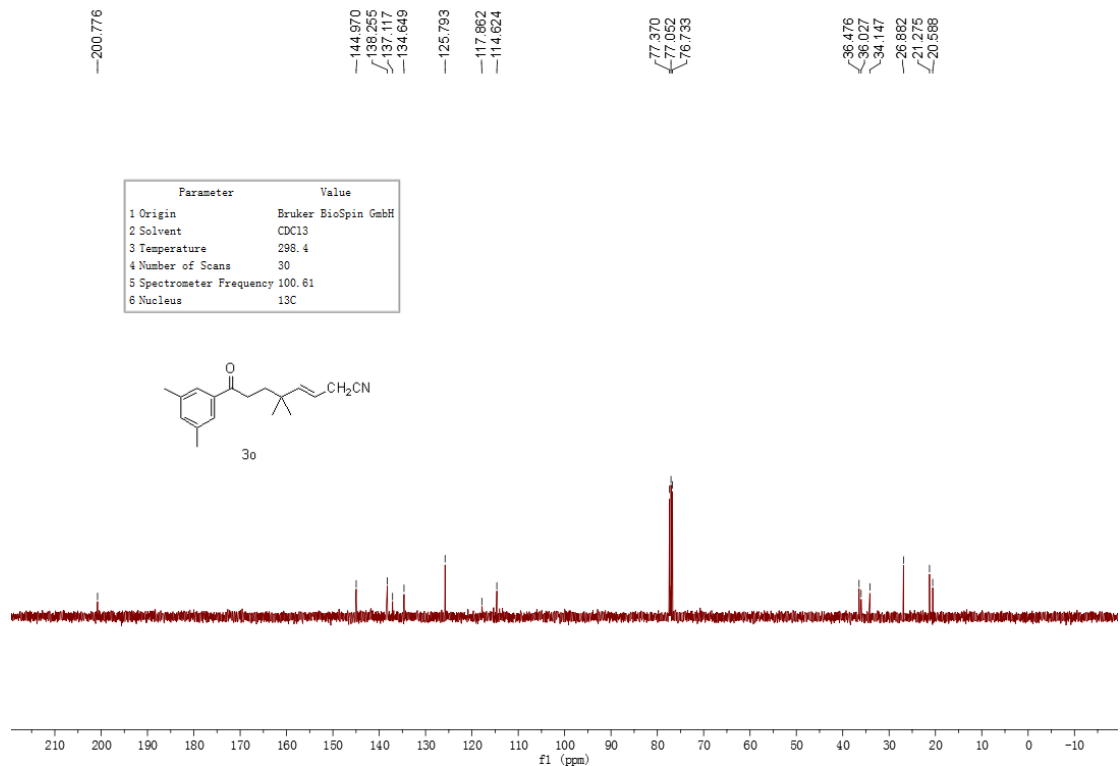
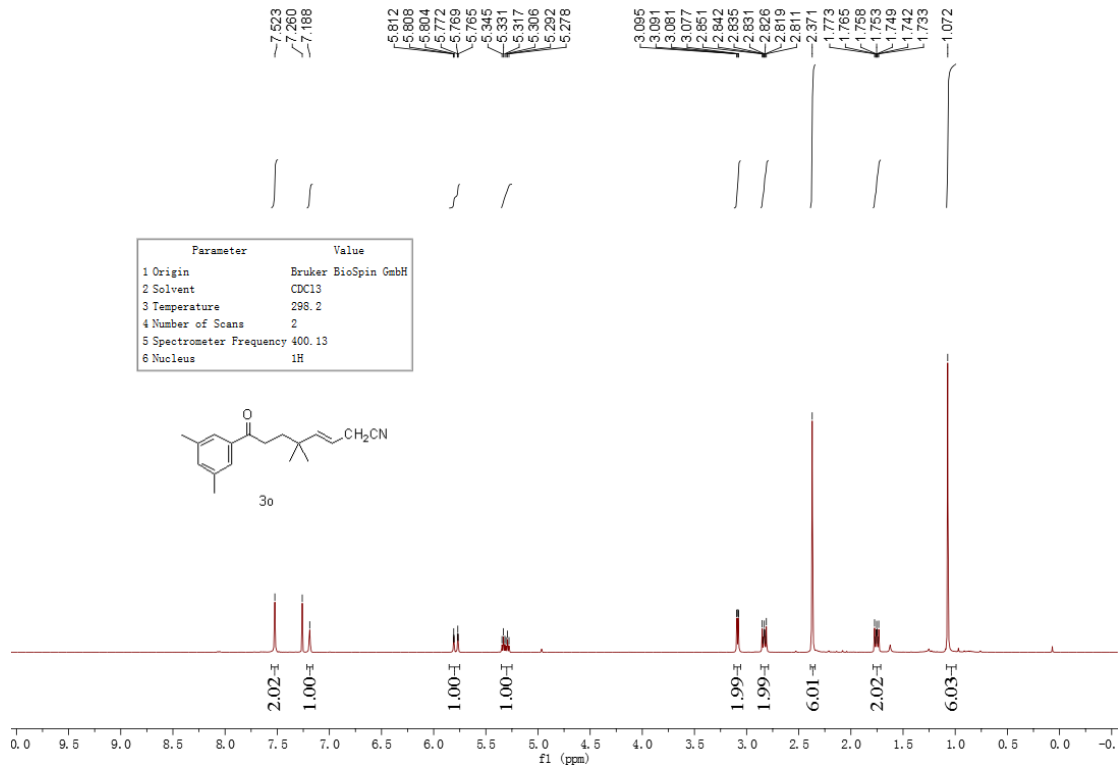


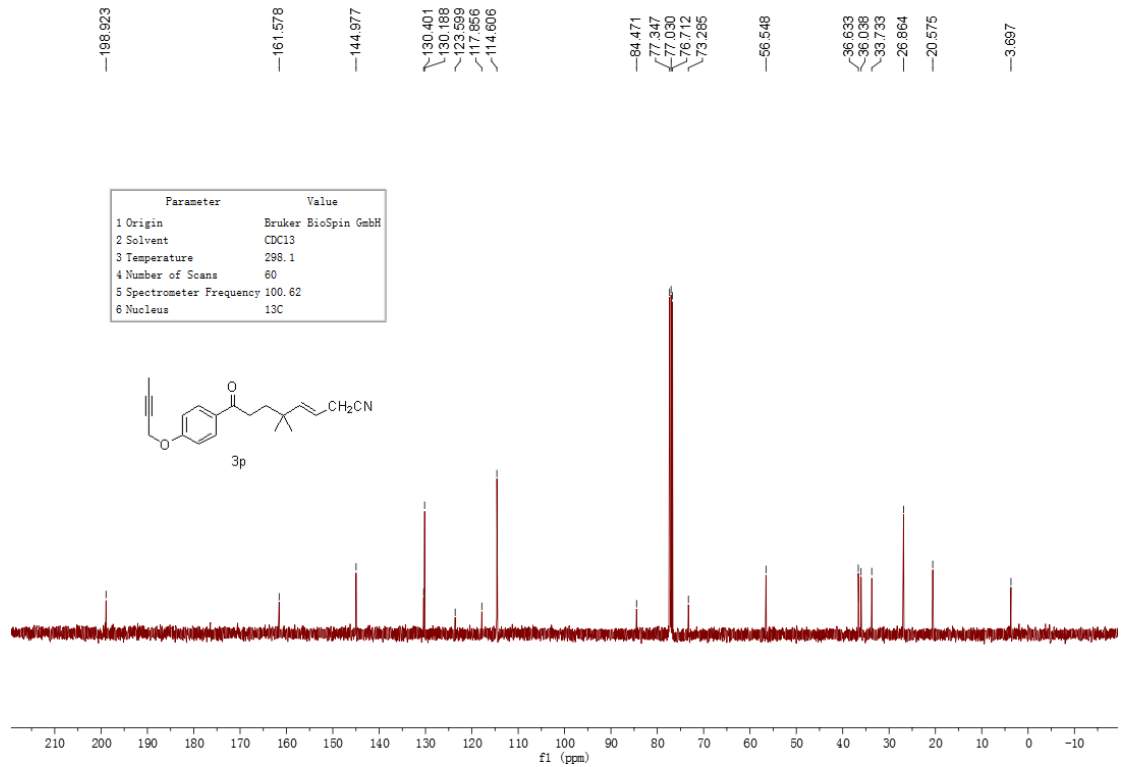
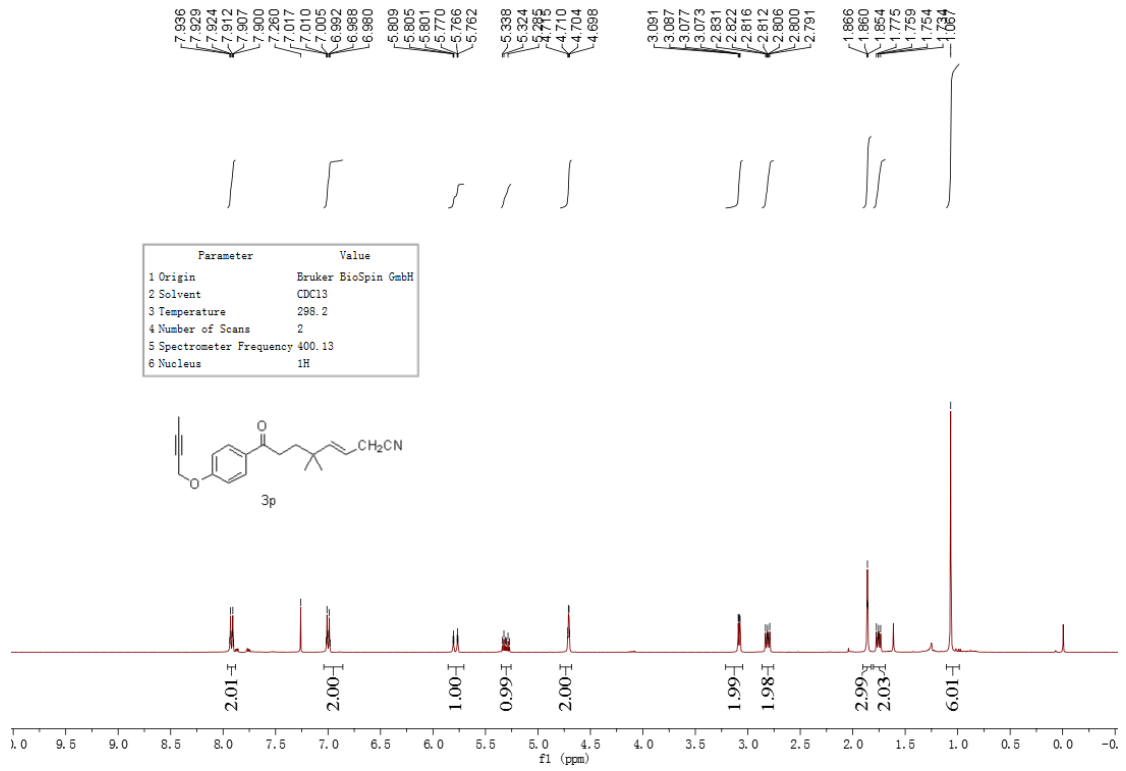




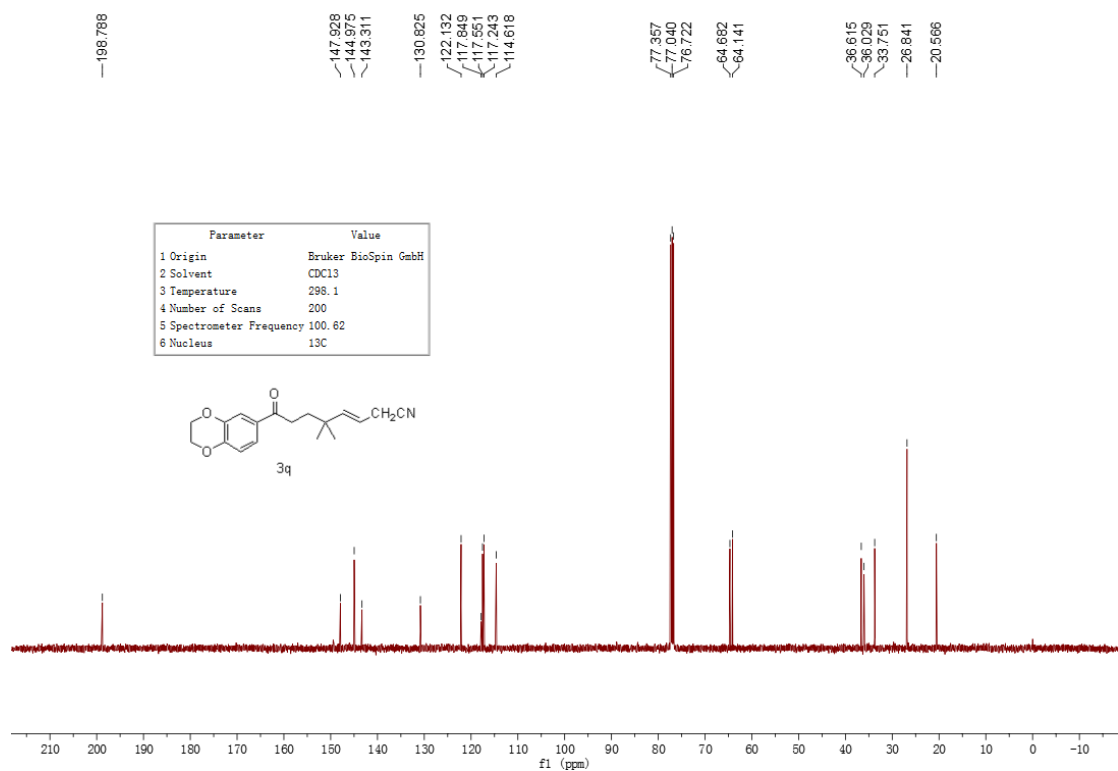
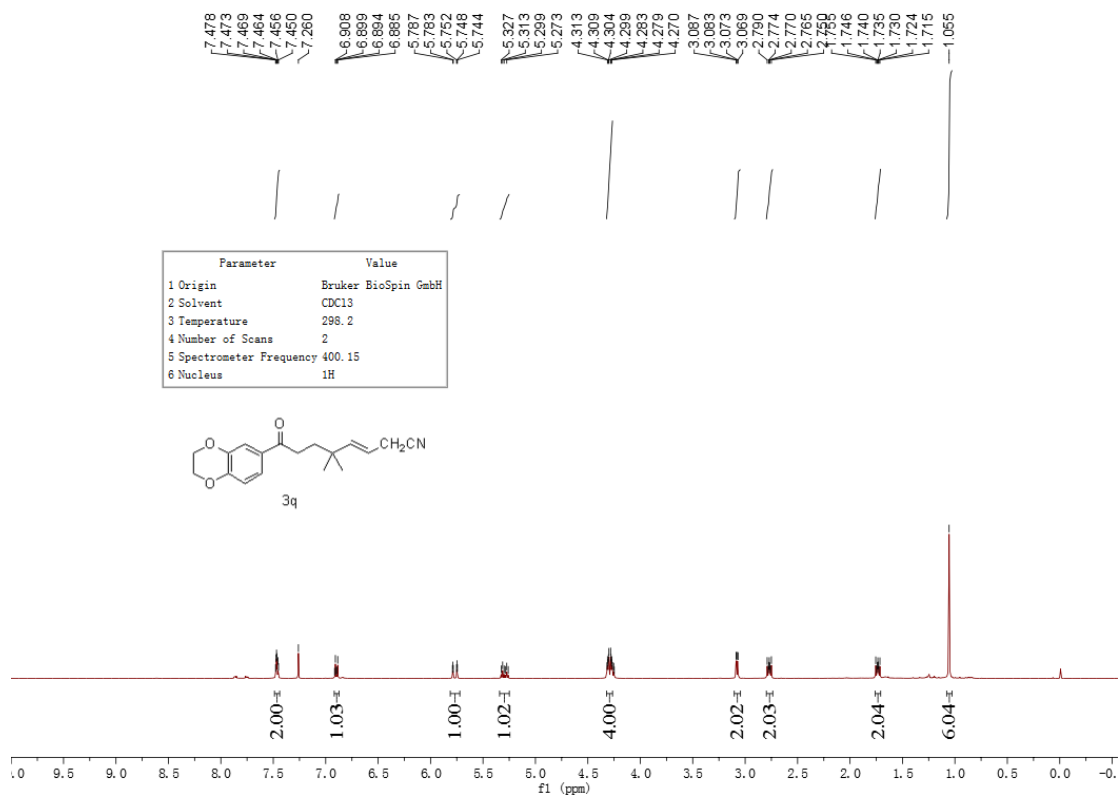


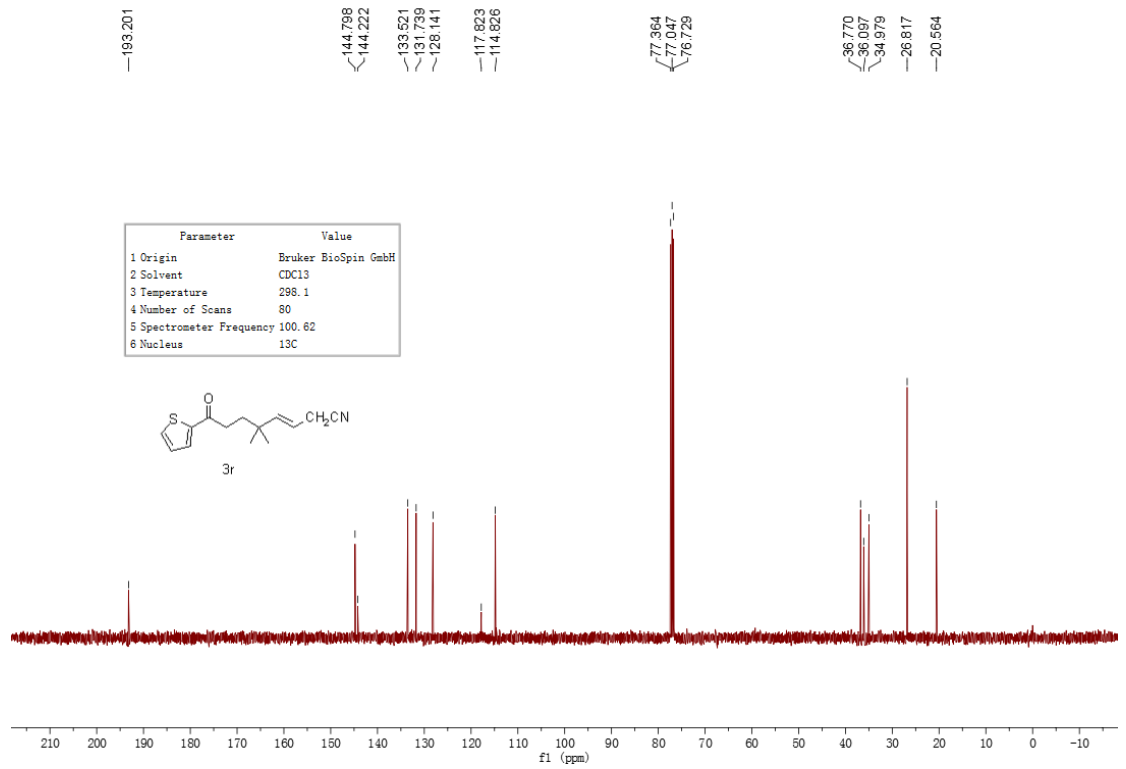
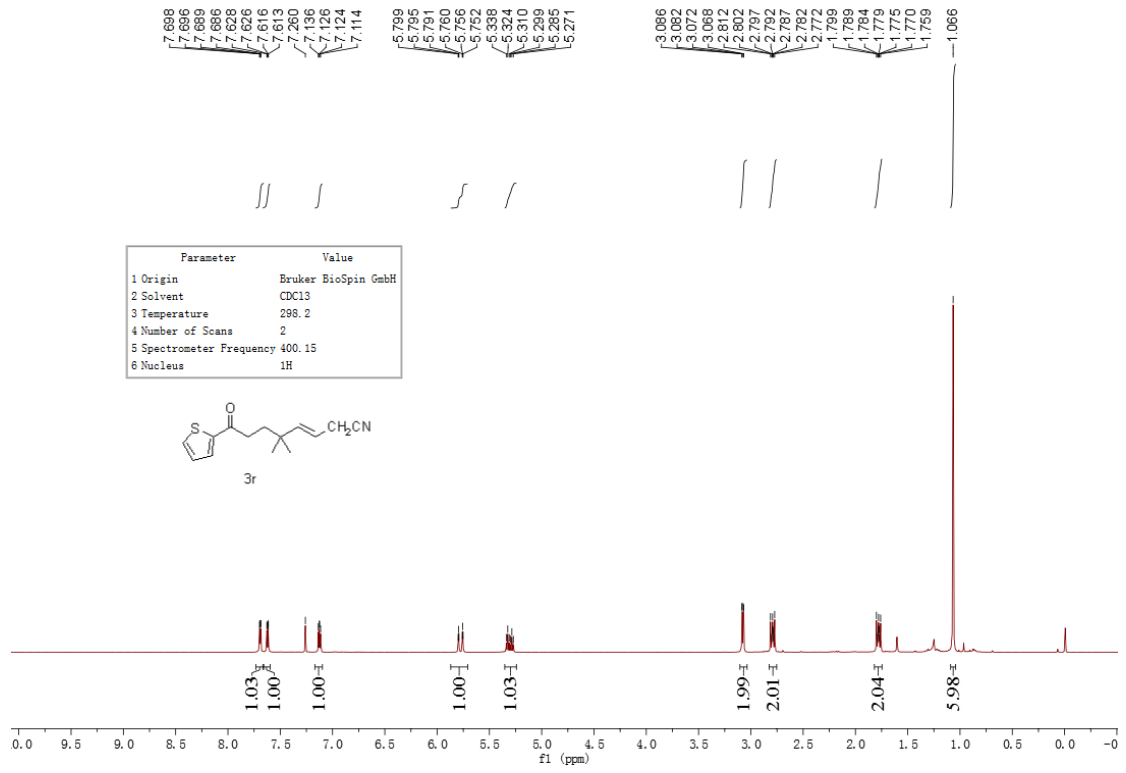




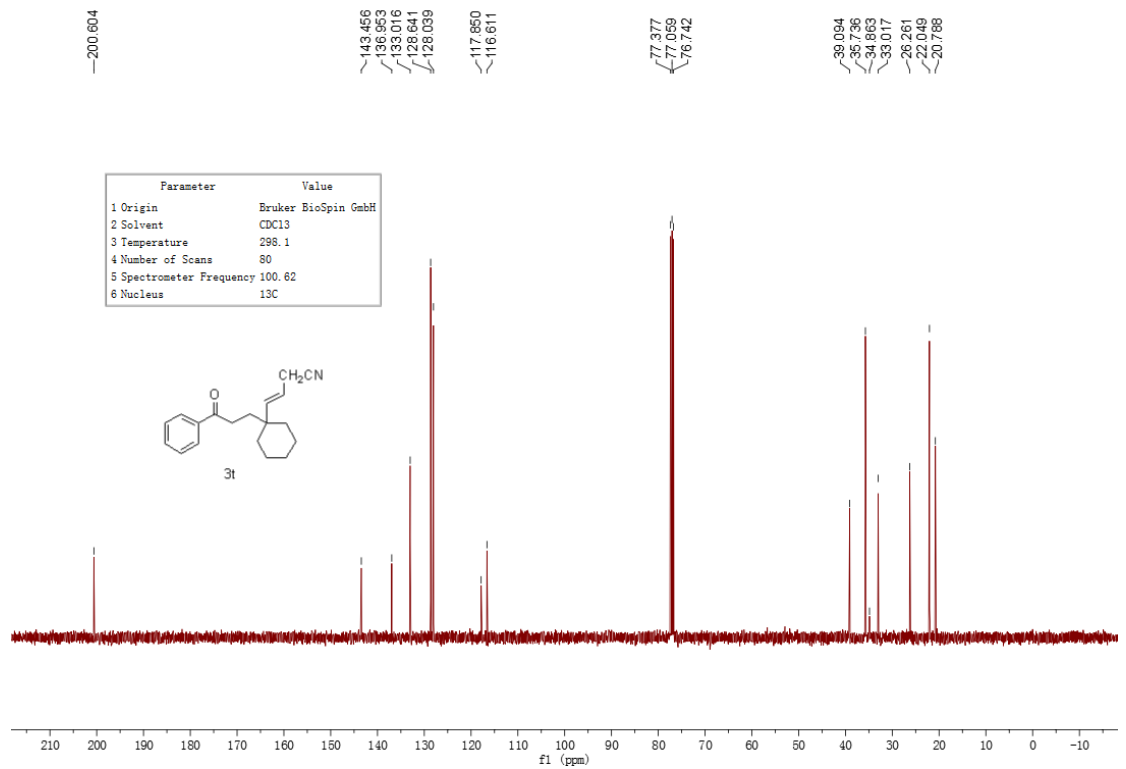
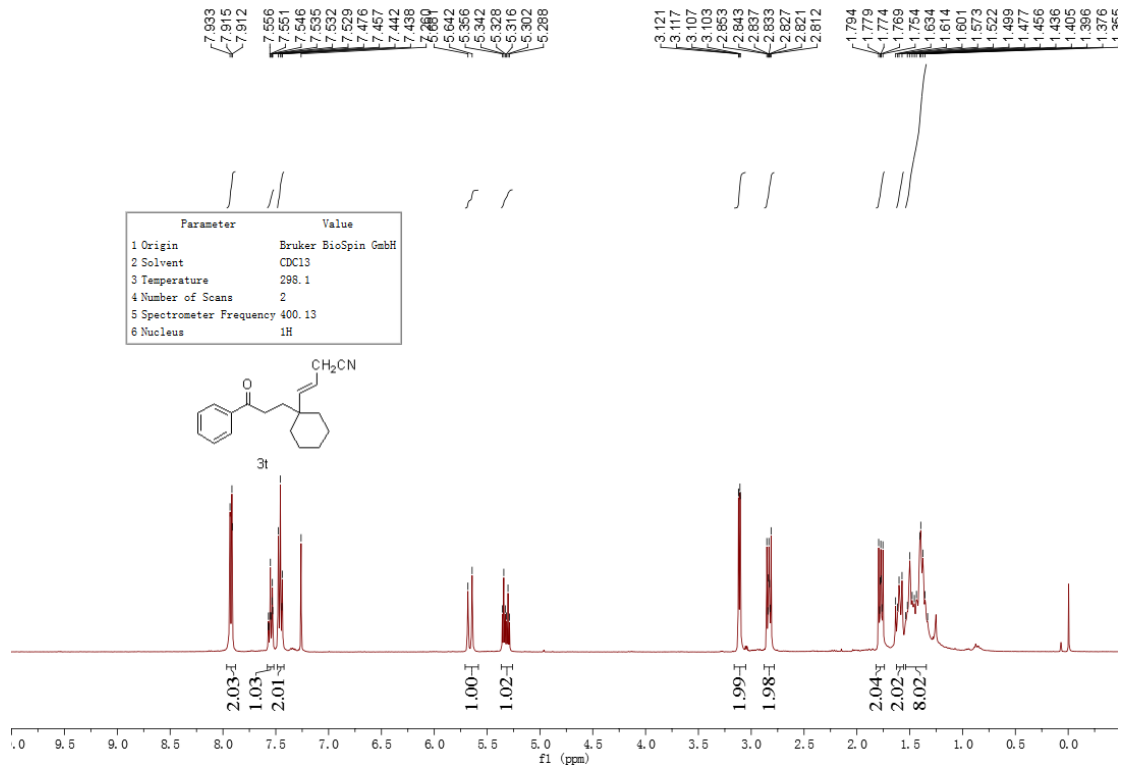


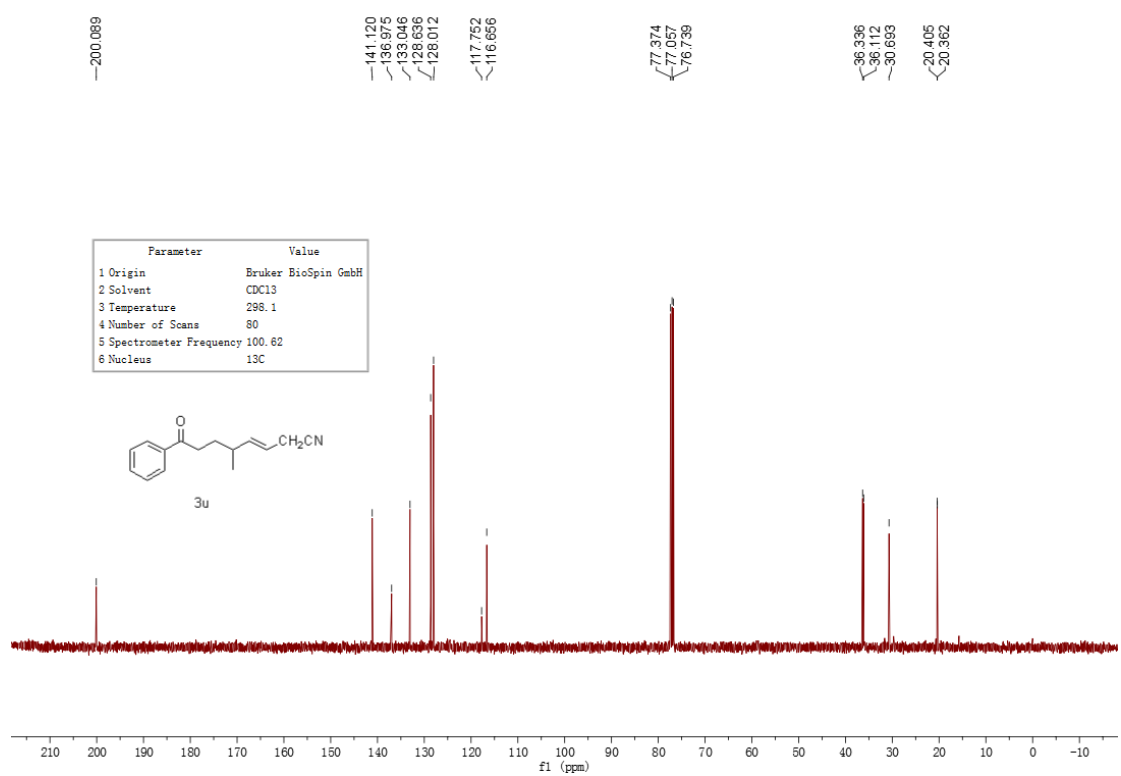
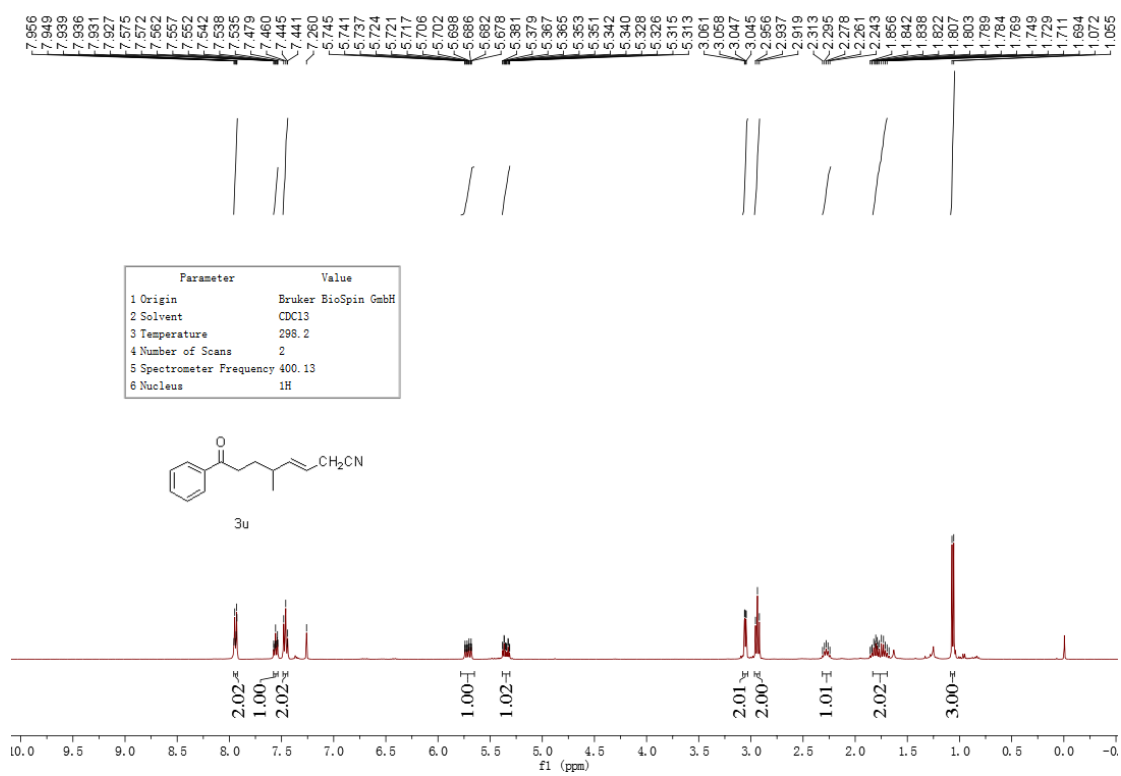


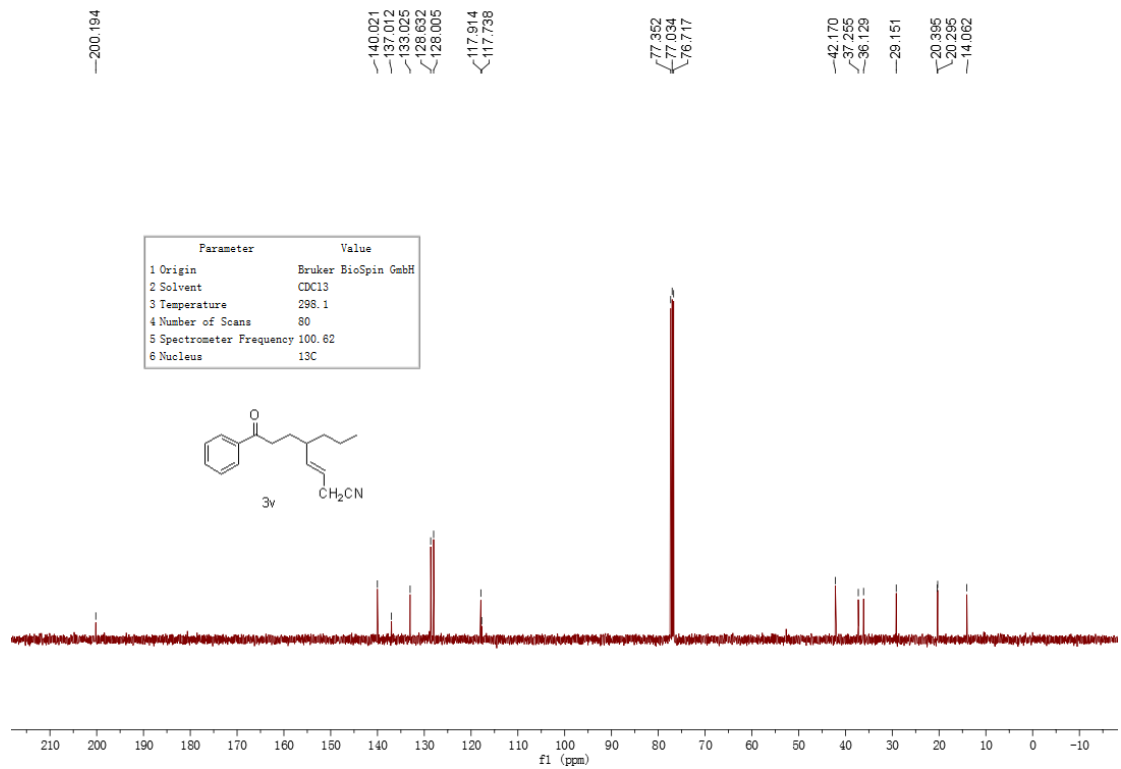
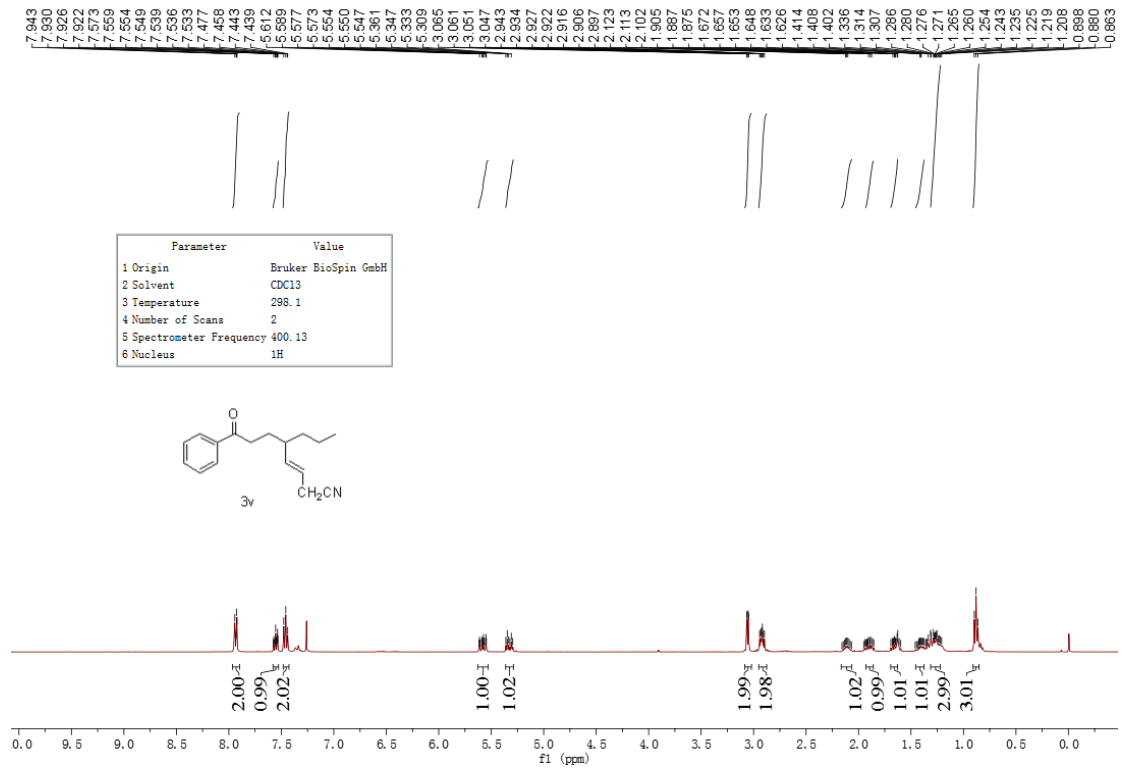


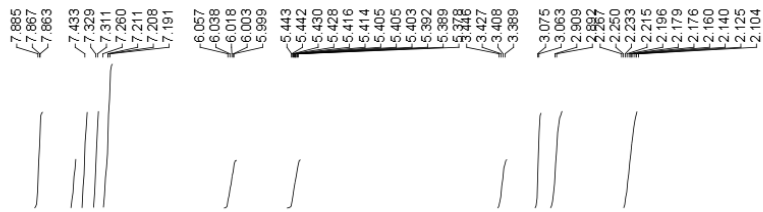




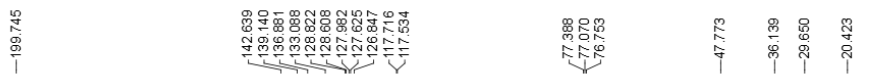
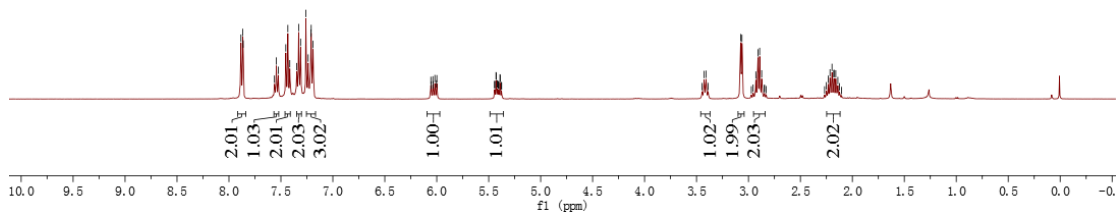
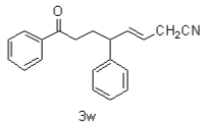




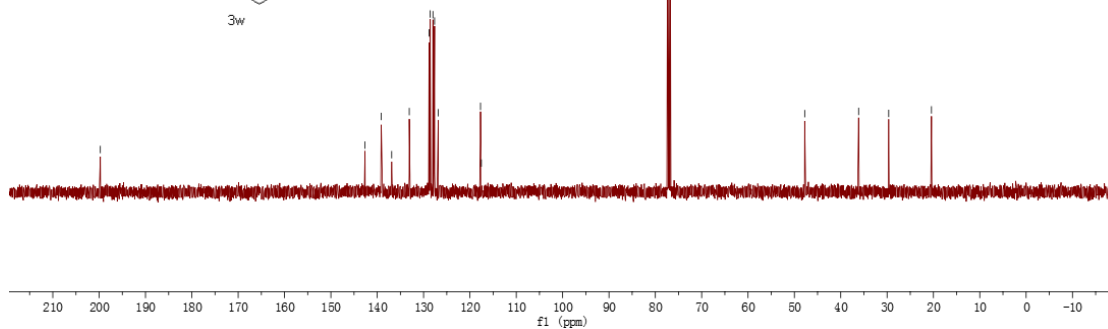
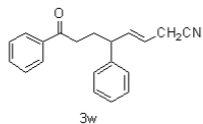




Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.1
4 Number of Scans	2
5 Spectrometer Frequency	400.13
6 Nucleus	1H

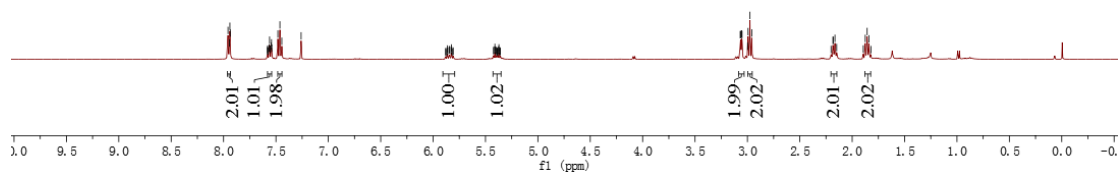
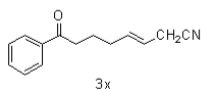


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	28
5 Spectrometer Frequency	100.61
6 Nucleus	13C





Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.1
4 Number of Scans	4
5 Spectrometer Frequency	400.13
6 Nucleus	<sup>1</sup> H



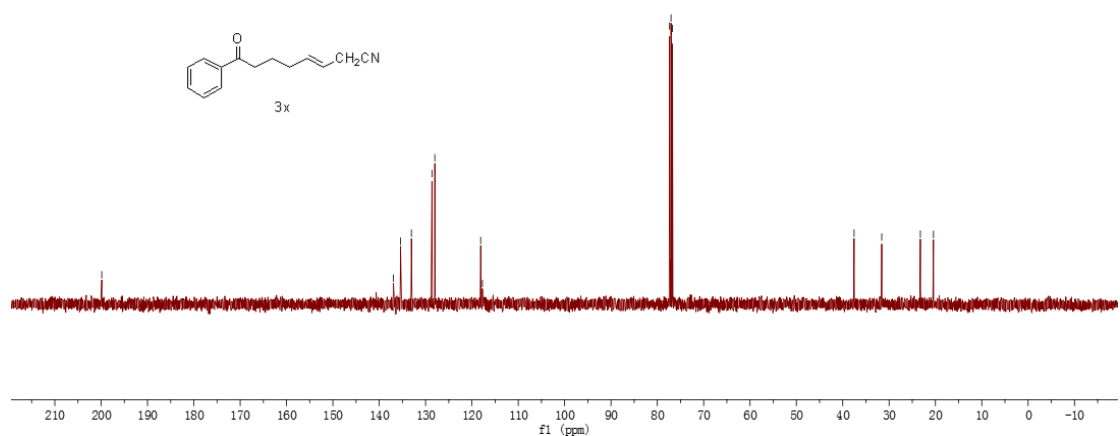
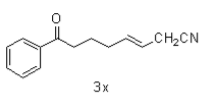
—199.867

136.942  
135.397  
133.065  
128.632  
128.010  
118.117  
117.732

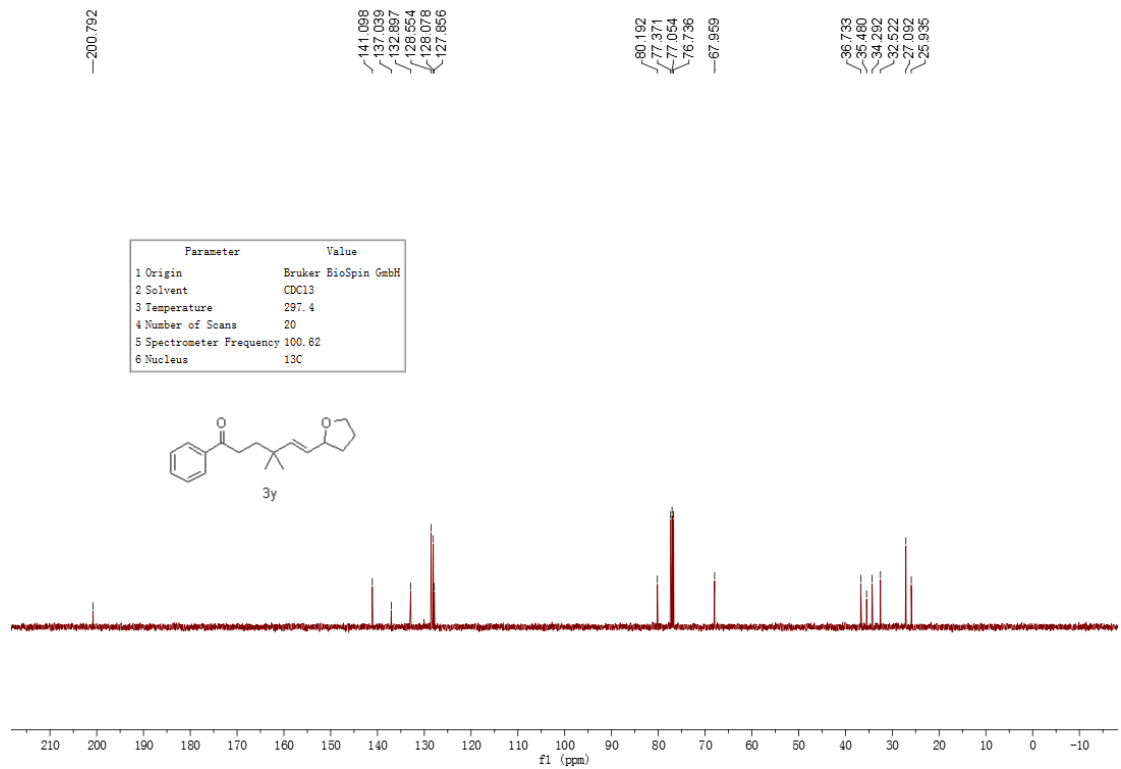
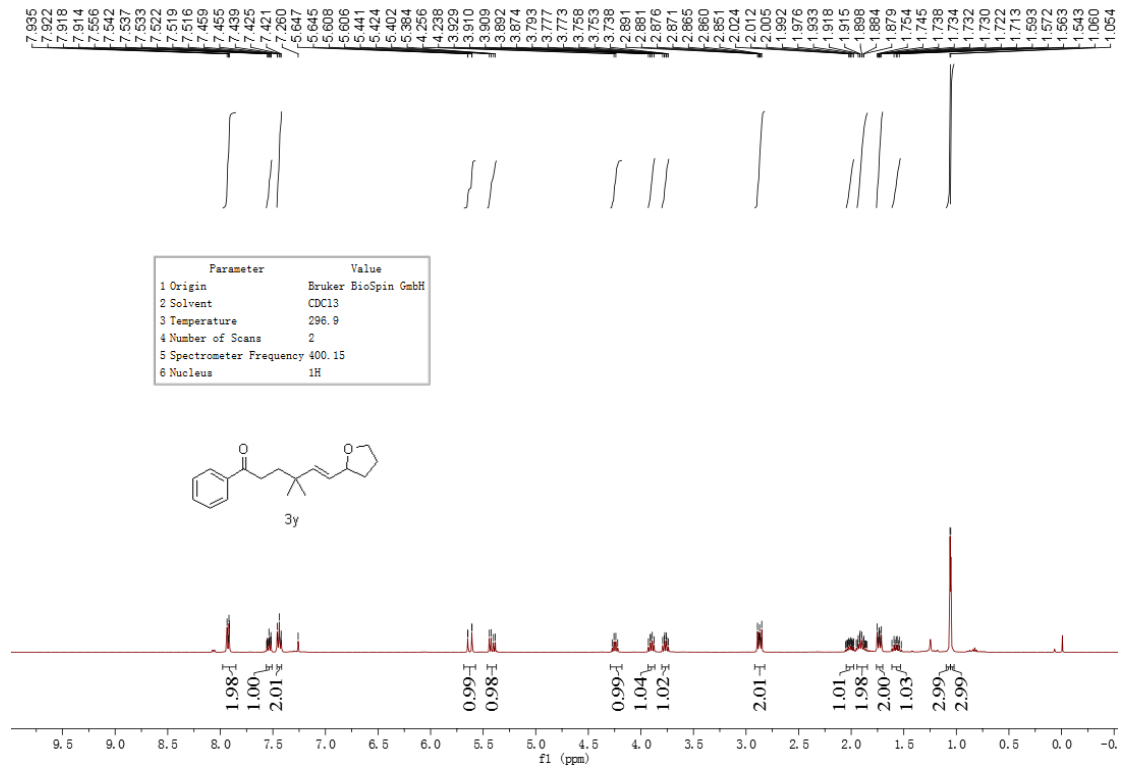
77.364  
77.045  
76.728

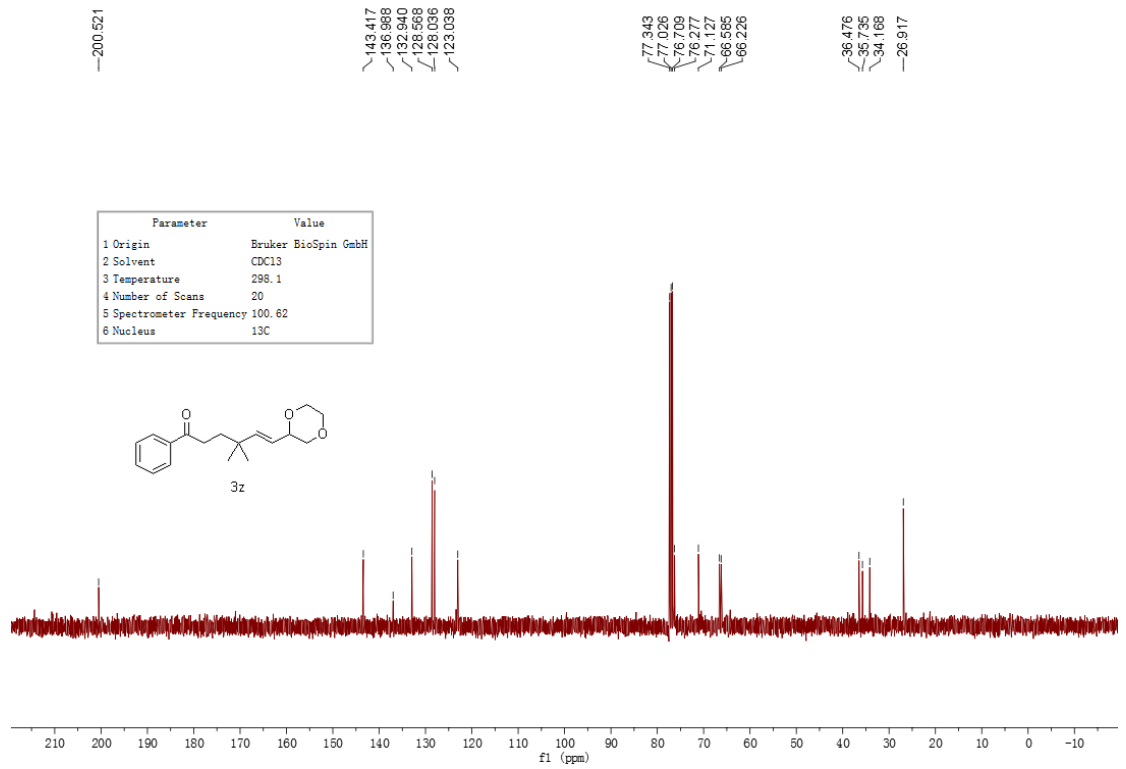
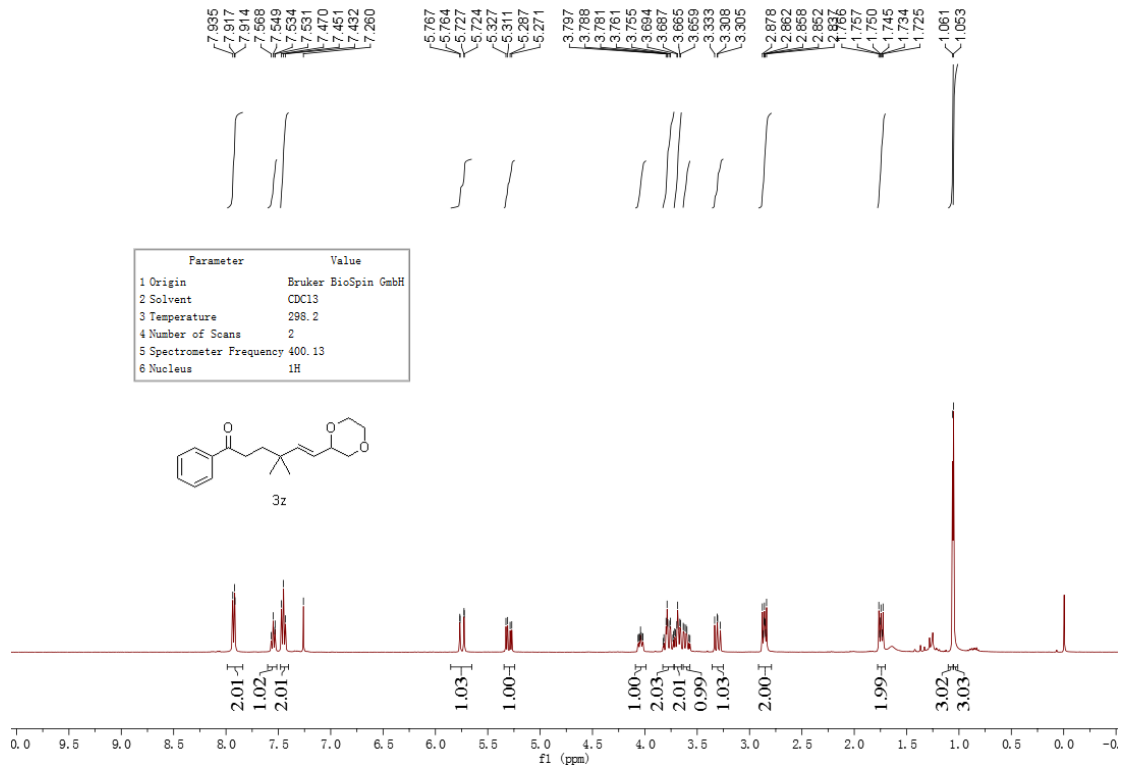
37.547  
31.582  
23.260  
20.422

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.1
4 Number of Scans	30
5 Spectrometer Frequency	100.61
6 Nucleus	<sup>13</sup> C









7.933  
7.916  
7.818  
7.457  
7.419  
7.260

5.629  
5.569  
5.567  
5.449  
5.434  
5.409  
5.394

4.016  
4.011  
3.988  
3.983  
3.978

3.739

3.435

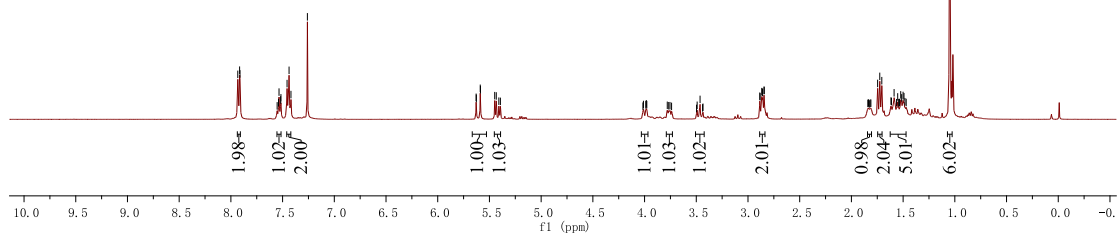
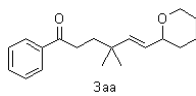
2.886

2.867  
2.862  
2.858  
2.845  
2.843

1.827  
1.746  
1.618  
1.563  
1.535  
1.500  
1.470

1.053  
1.047

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	2
5 Spectrometer Frequency	400.13
6 Nucleus	1H



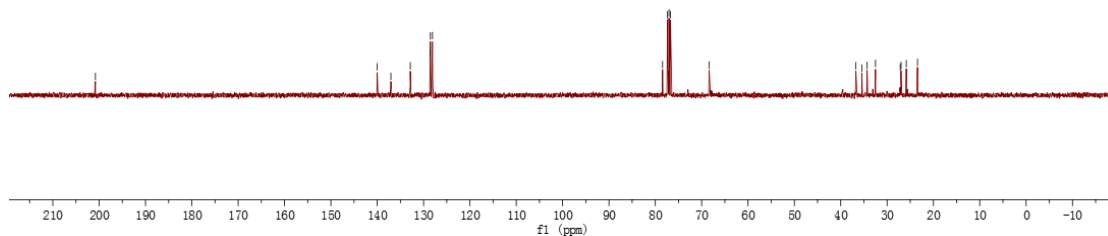
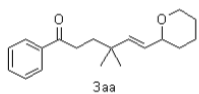
-200.800

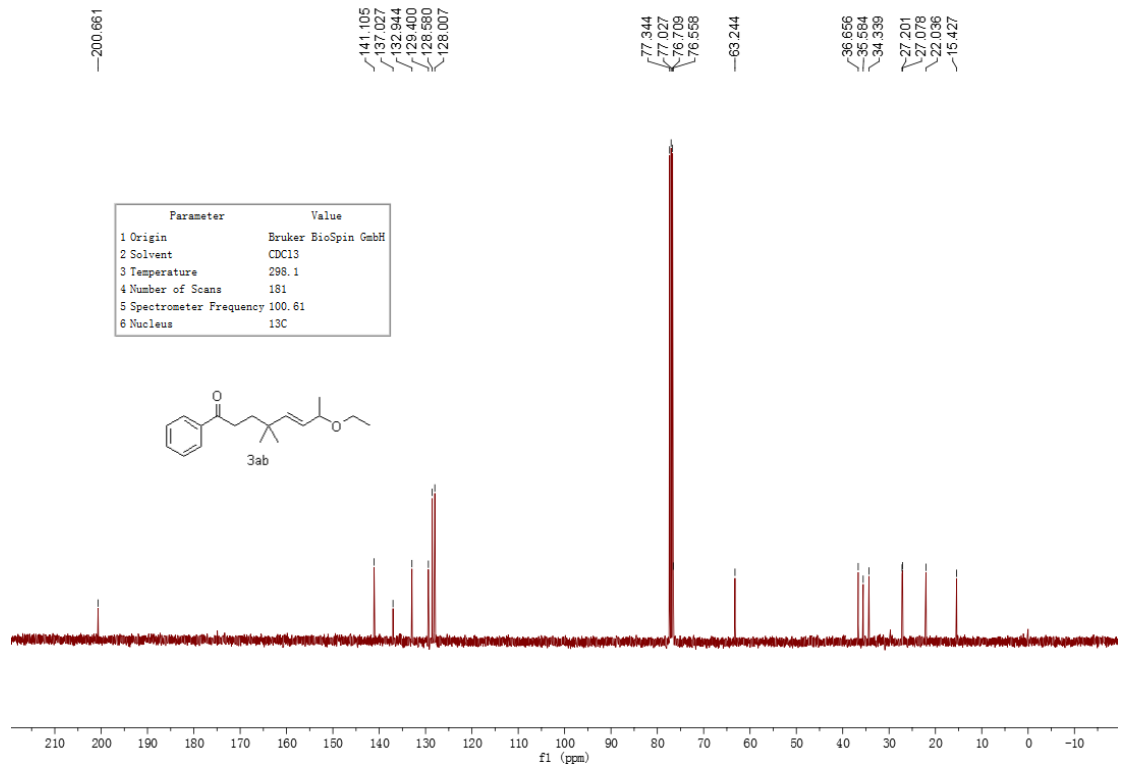
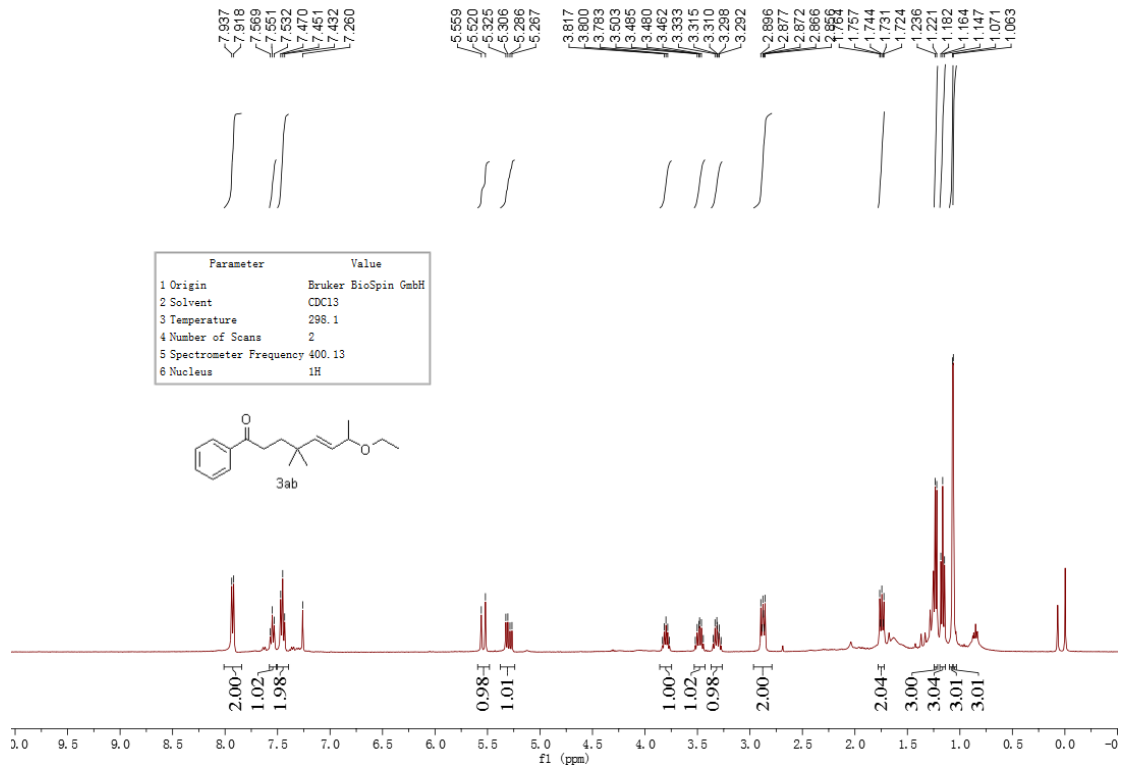
140.003  
137.049  
132.866  
128.563  
128.535  
128.079

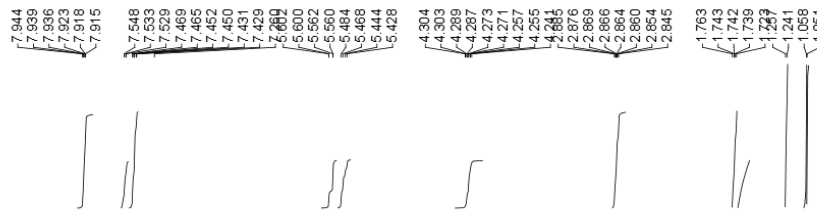
78.434  
77.373  
77.052  
76.738  
-68.379

36.727  
35.430  
34.207  
32.404  
27.154  
26.978  
25.853  
23.436

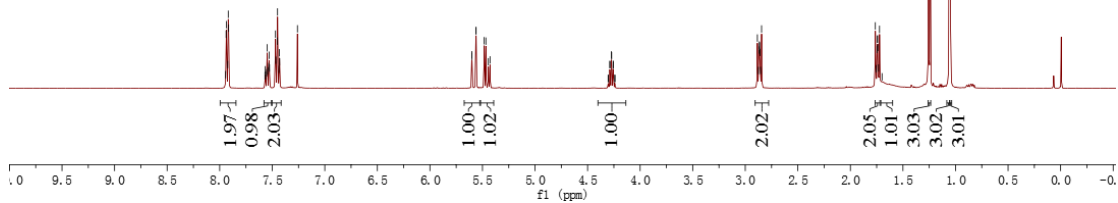
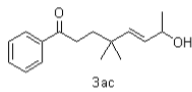
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.4
4 Number of Scans	20
5 Spectrometer Frequency	100.61
6 Nucleus	13C



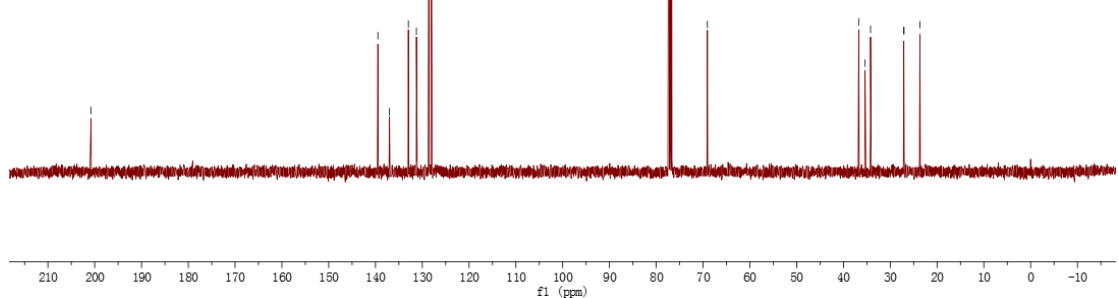
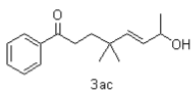


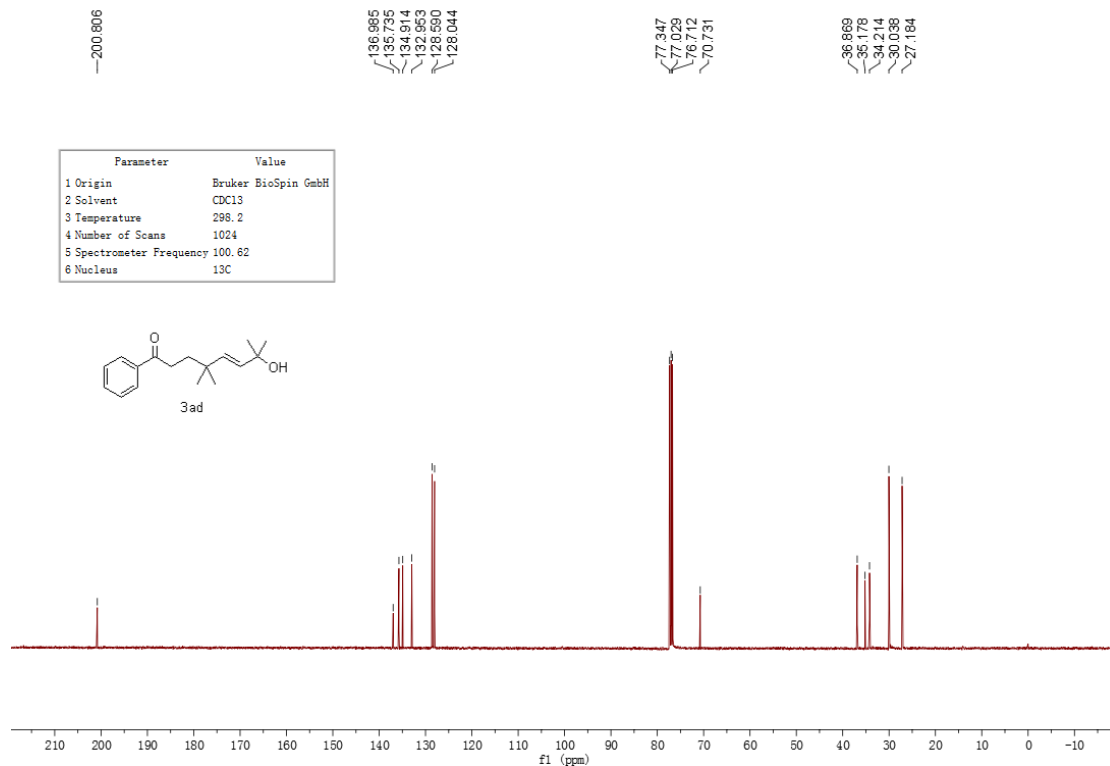
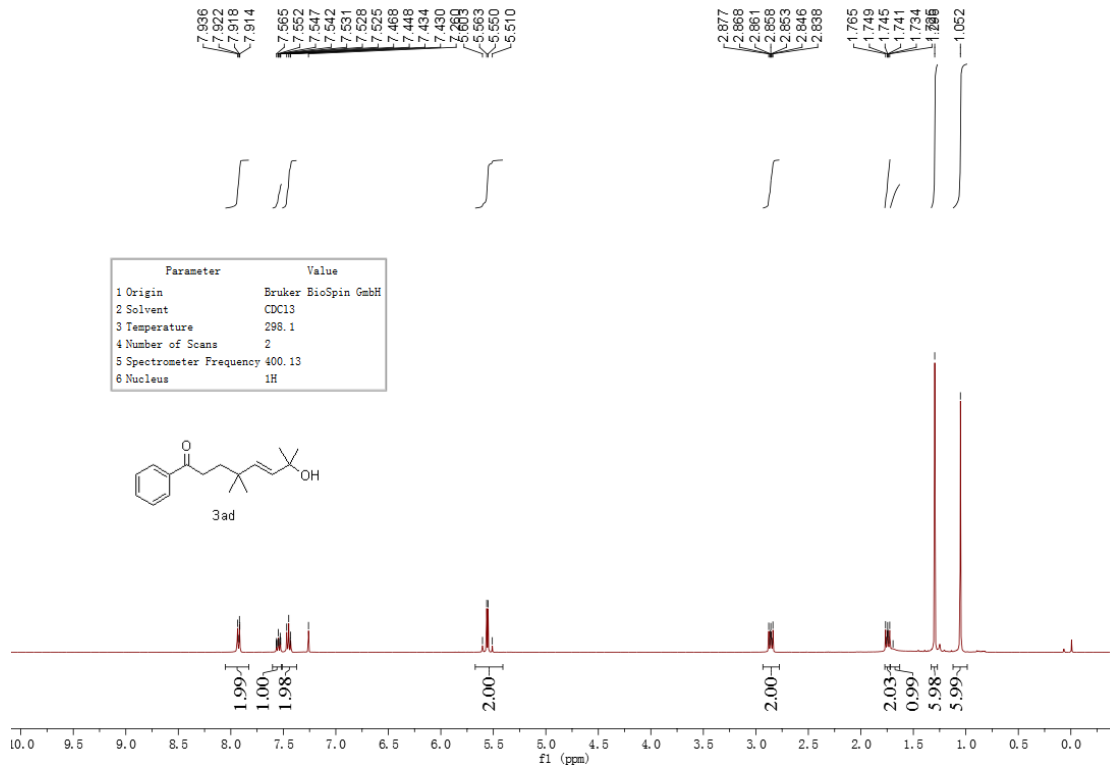


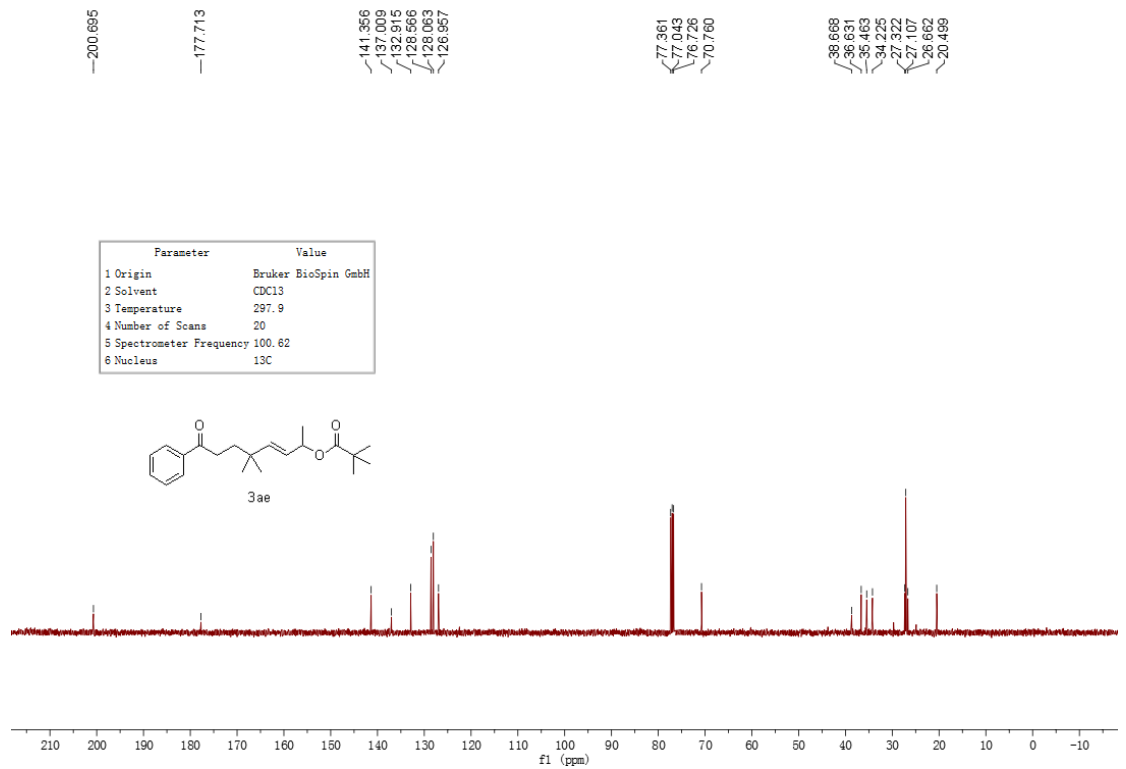
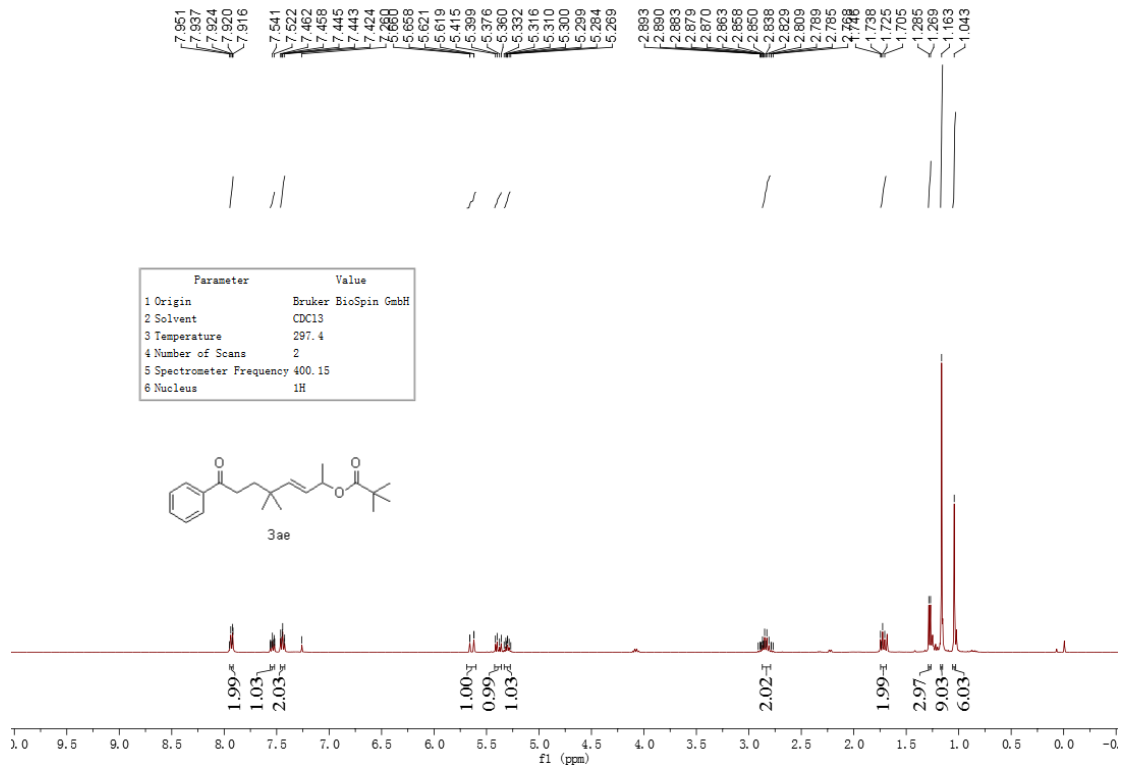
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	297.6
4 Number of Scans	2
5 Spectrometer Frequency	400.15
6 Nucleus	1H

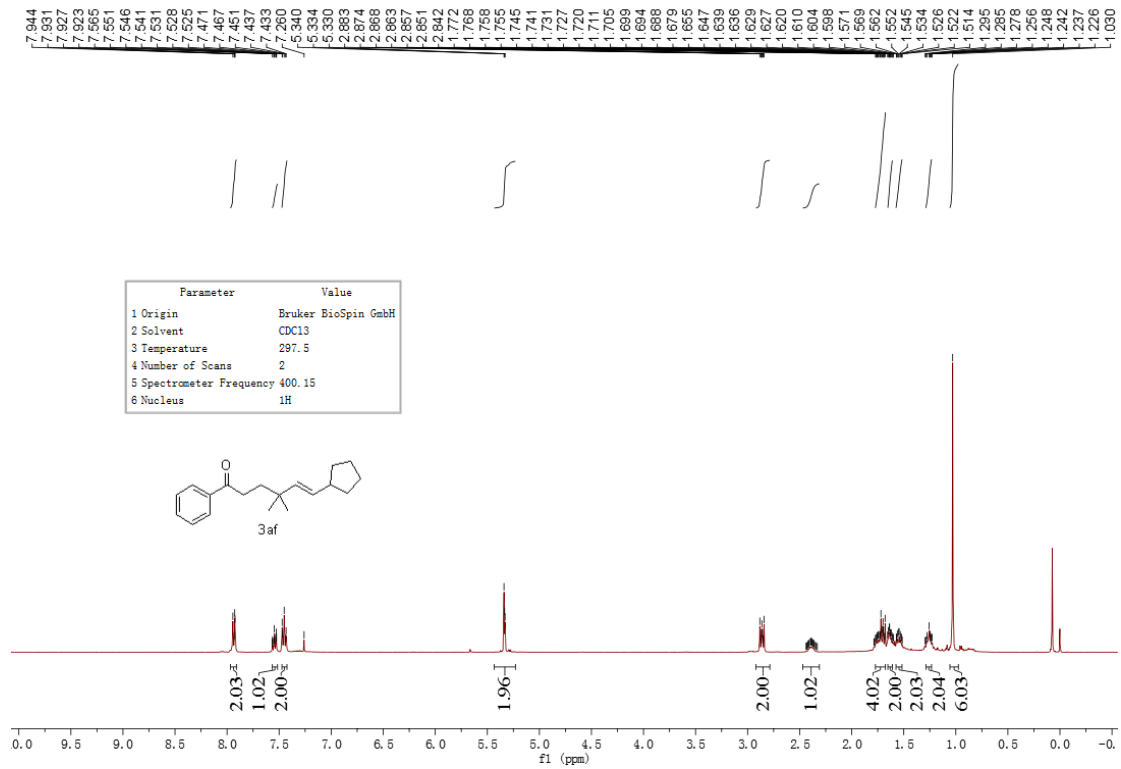


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.3
4 Number of Scans	80
5 Spectrometer Frequency	100.62
6 Nucleus	13C







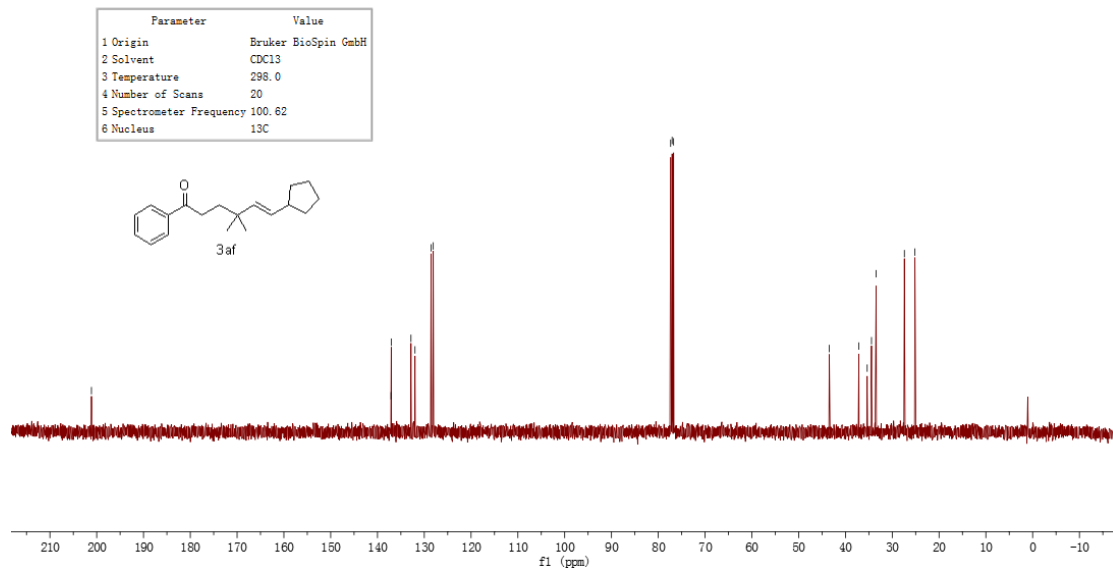


-201.124

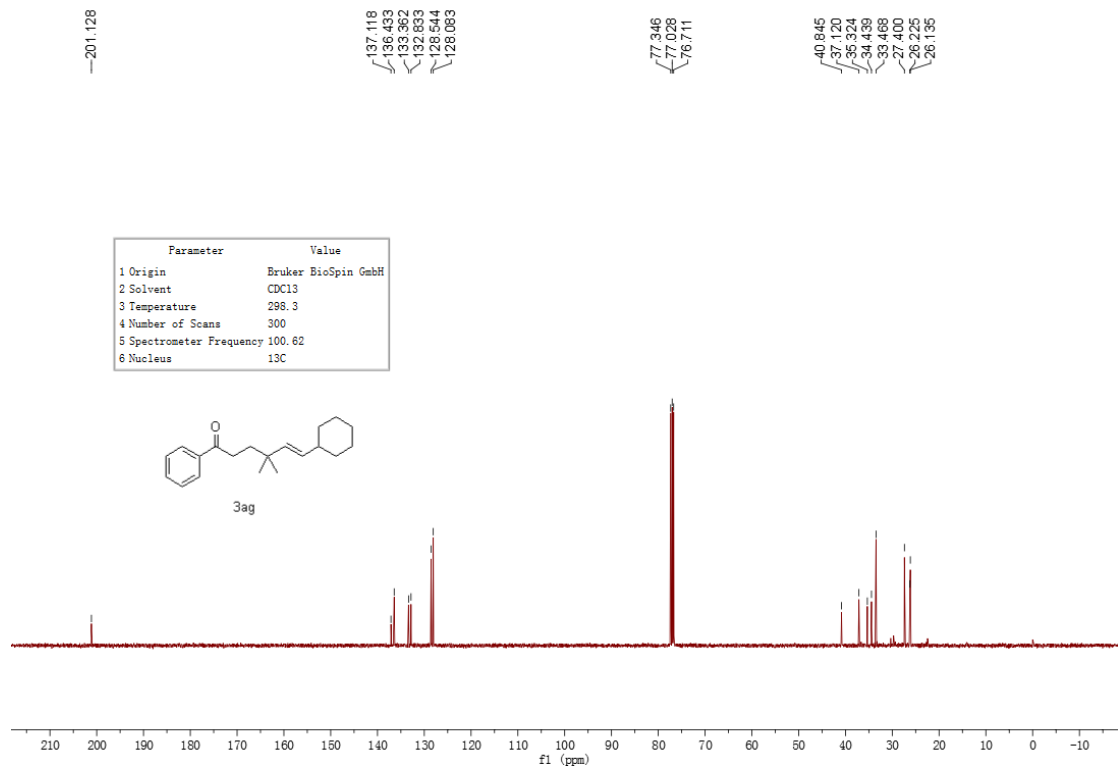
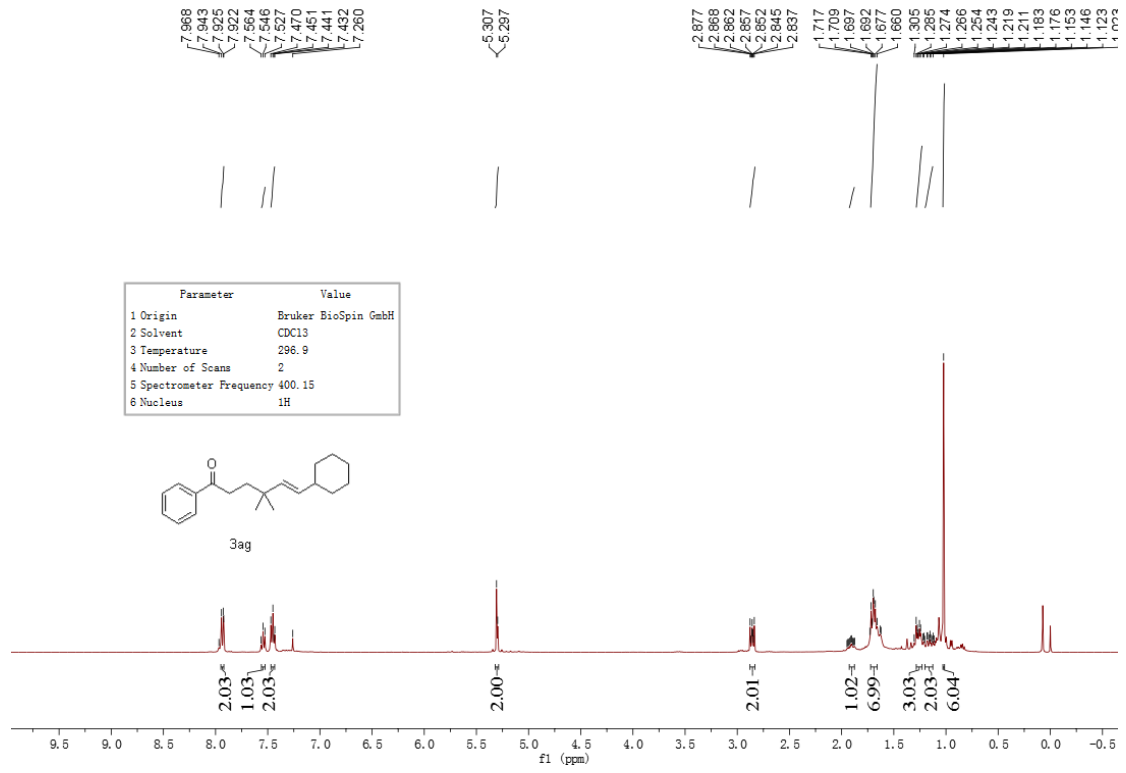
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137.061  
132.843  
131.965  
128.547  
128.064

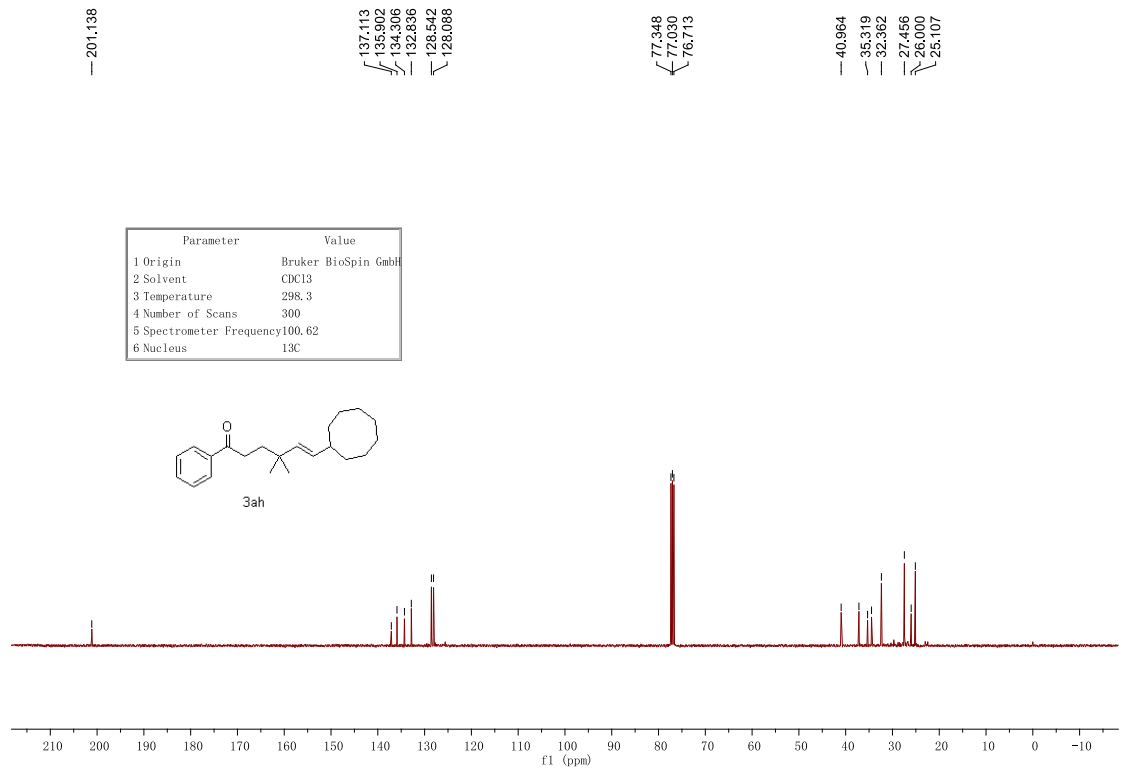
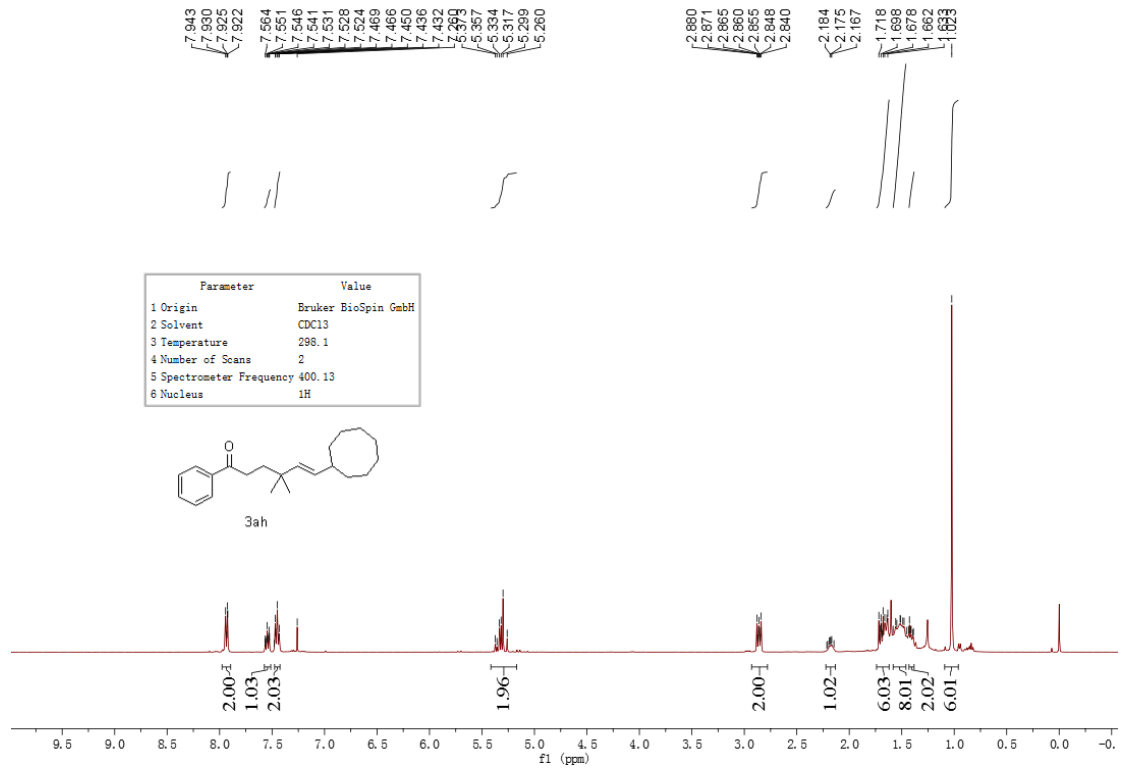
77.368  
77.040  
76.723

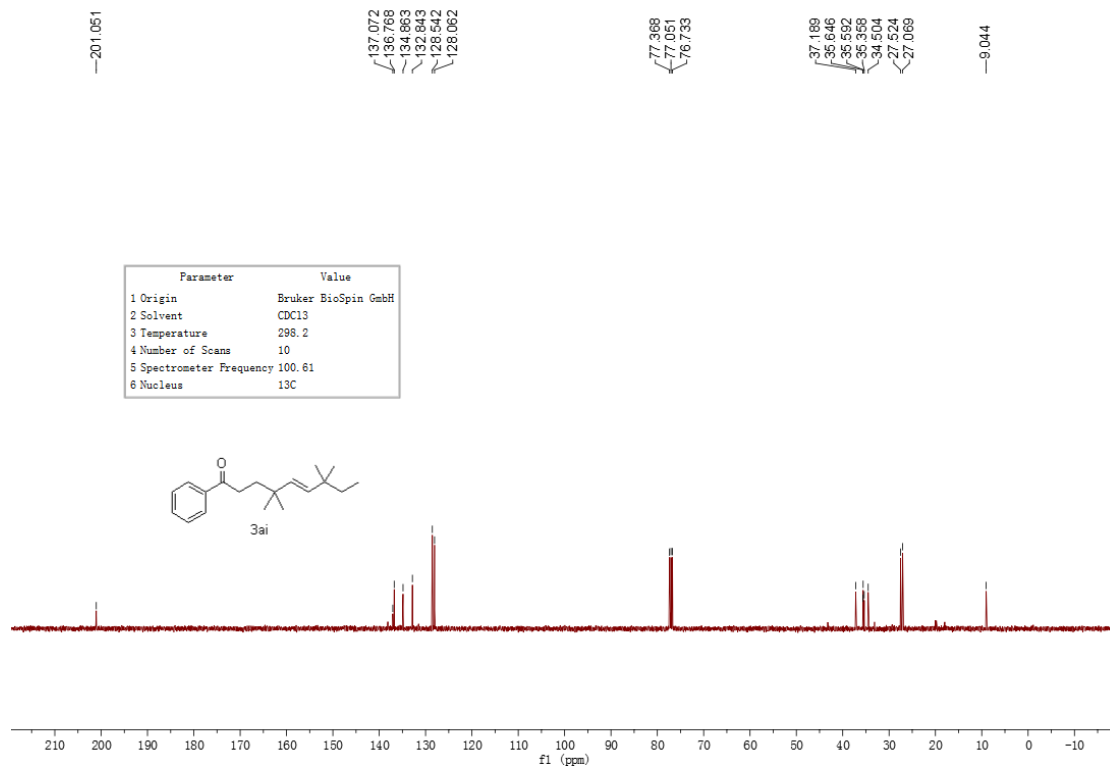
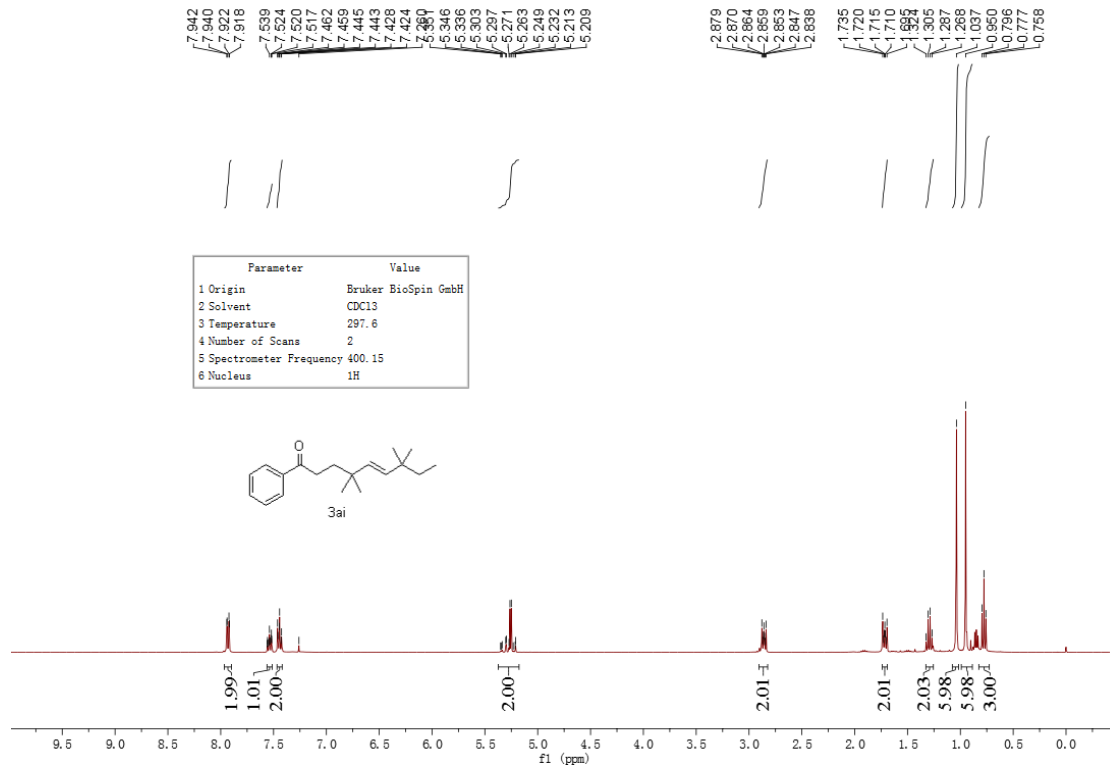
43.457  
37.135  
35.958  
34.436  
33.444  
27.410  
25.156

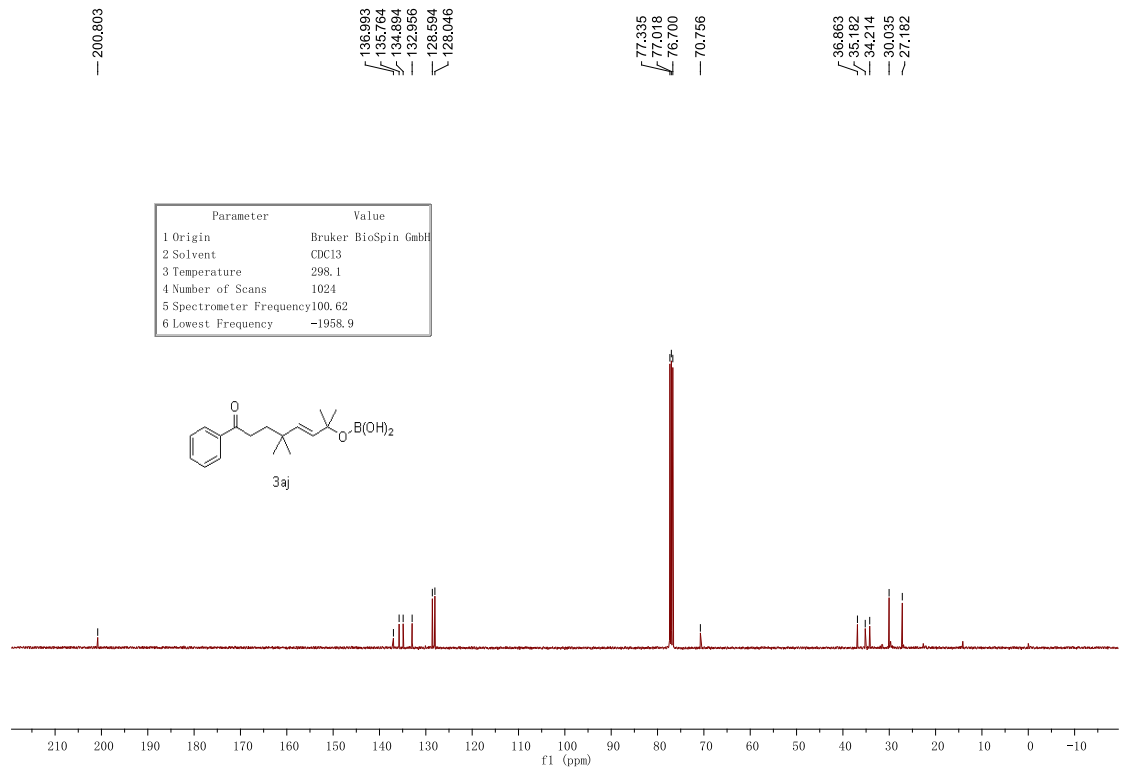
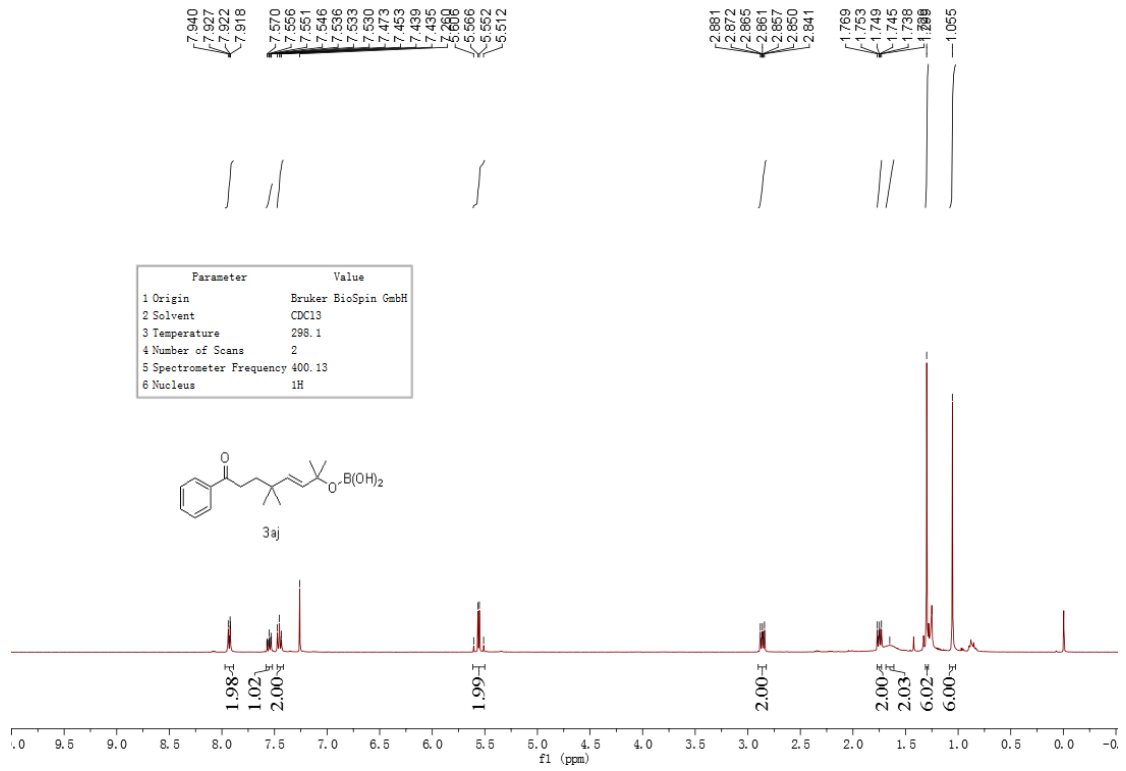


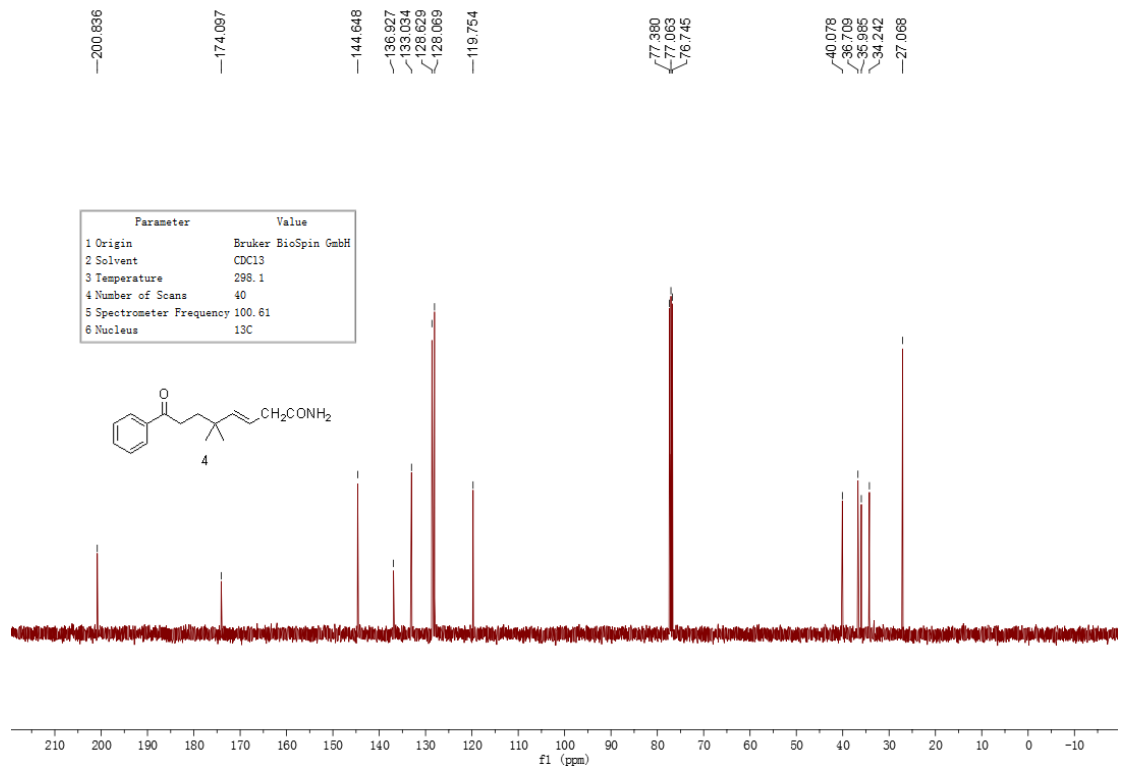
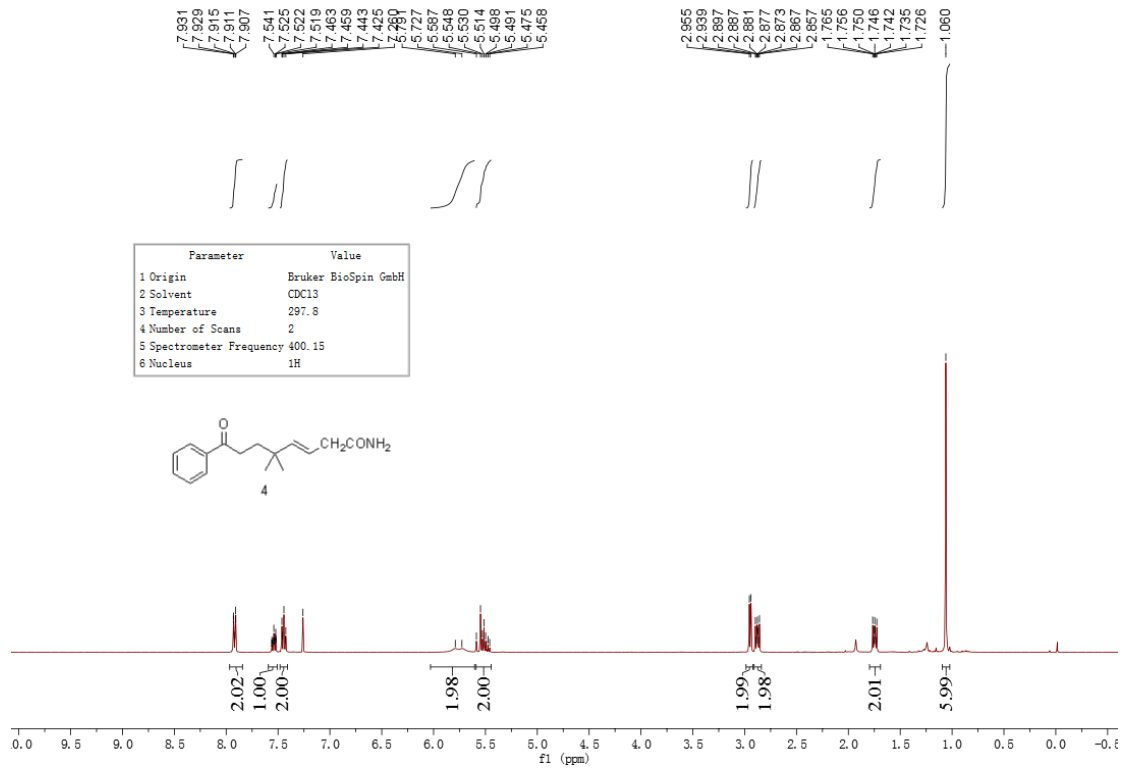


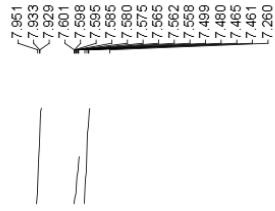




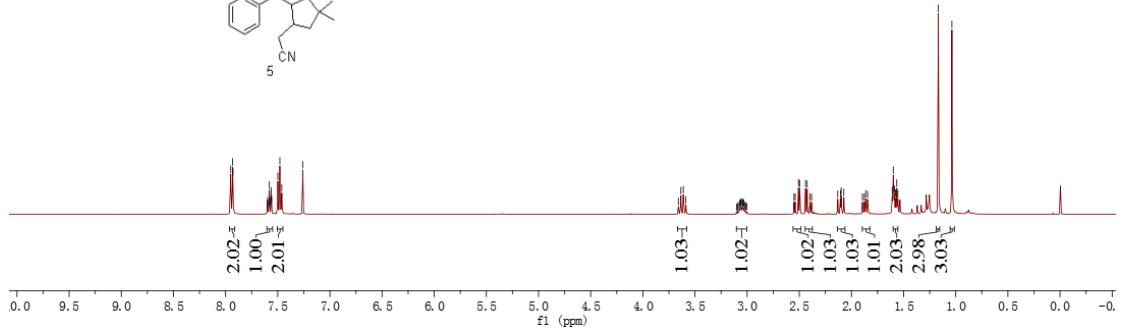
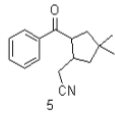






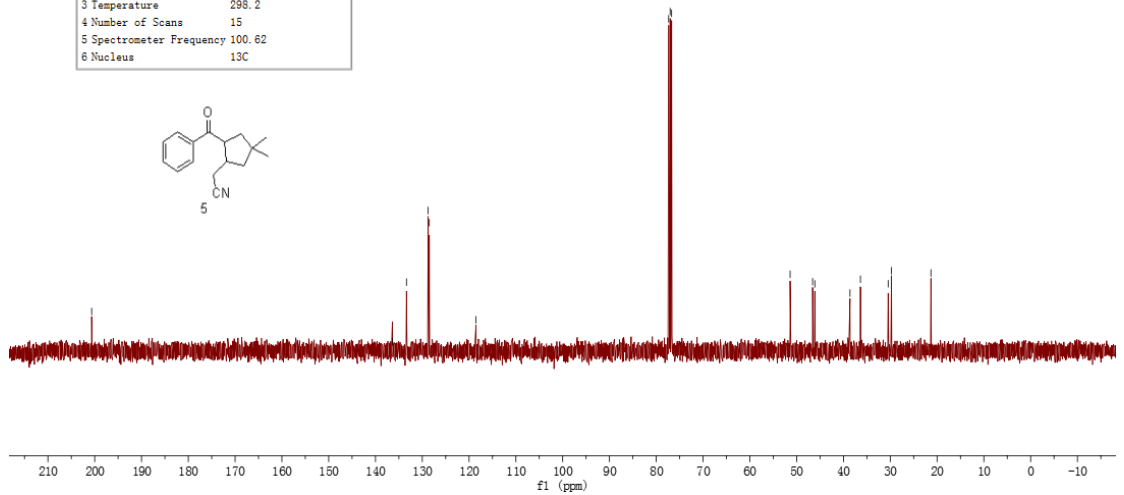
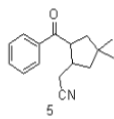


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.1
4 Number of Scans	16
5 Spectrometer Frequency	400.13
6 Nucleus	1H

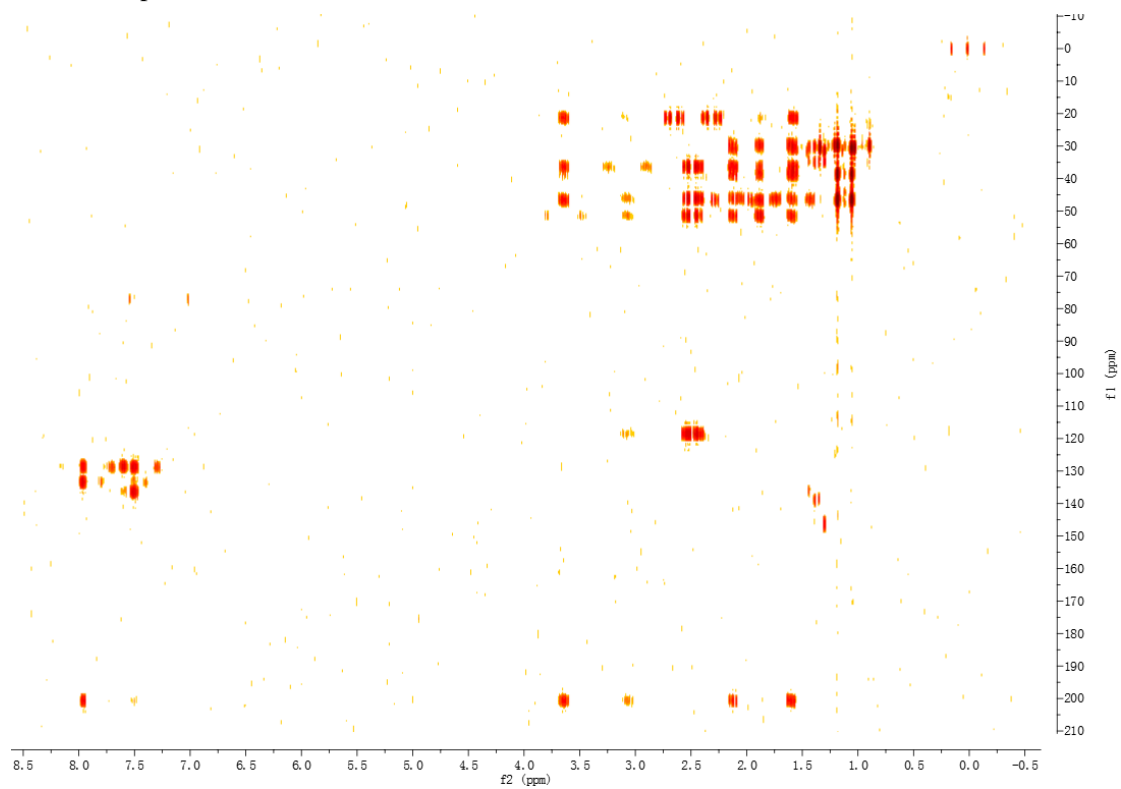


200.653  
136.365  
133.381  
128.748  
128.507  
118.523

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	15
5 Spectrometer Frequency	100.62
6 Nucleus	13C



### HMBC for product 5



### NOE for product 5

