Rhodium(III)-Catalyzed Selective mono Arylation of β or γ C(sp^3)-H Bonds Assisted by a Trimethylpyrazole Group

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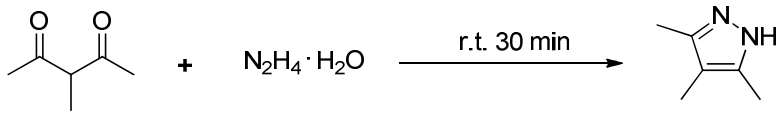
1. **Reagents:** Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. Column chromatography purifications were performed using 200–300 mesh silica gel.

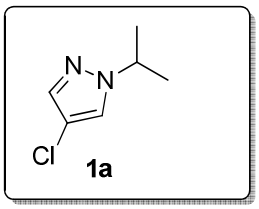
2. **2. Instruments:** NMR spectra were recorded on Varian Inova–400 MHz, Inova–300 MHz, Bruker DRX–400 or Bruker DRX–500 instruments and calibrated using residual solvent peaks as internal reference. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, br = broad singlet, m = multiplet. HRMS analysis were carried out using a Bruker micrOTOF–Q instrument or a TOF–MS instrument.

3. **General procedures for the preparation of 3, 4, 5-trimethyl-1H-pyrazole.**

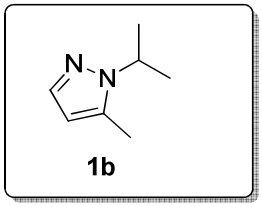


A round-bottom flask was changed with 3-methylpentane-2, 4-dione, excess hydrazine hydrate was added dropwise. When the reaction was completed, the mixture was washed with petroleum ether to give the product 3, 4, 5-trimethyl-1H-pyrazole as a white solid.

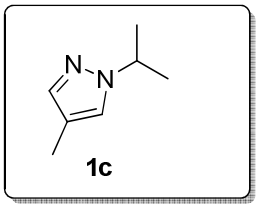
4. **General procedures for the preparation of 1-isopropyl-3,4,5-trimethyl-1H-pyrazole and its derivatives were according to articles [1].**



Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 4.8 Hz, 2H), 4.47-4.41 (M, 1H), 1.48 (d, *J* = 6.7 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 137.13, 124.66, 54.69, 22.90. HRMS Calcd for $C_6H_{10}N_2Cl$ [M+H$^+$]: 145.0533; Found: 145.0537.

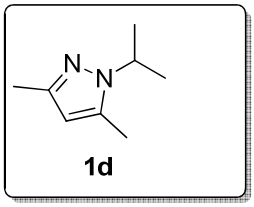


Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 0.5H), 7.29 (d, *J* = 2.0 Hz, 0.5H), 6.04 – 5.92 (m, 1H), 4.52 – 4.27 (m, 1H), 2.28 (s, 3H), 1.47 (dd, *J* = 6.7, 2.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.79, 138.03, 136.81, 126.82, 104.92, 104.45, 53.32, 49.49, 23.05, 22.51, 13.65, 11.04. HRMS Calcd for $C_7H_{13}N_2$ [M+H$^+$]: 125.1079; Found: 125.1080.



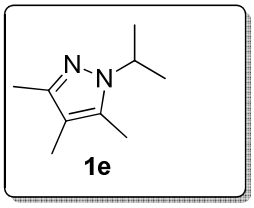
1c

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 4.9 Hz, 1H), 7.17 (s, 1H), 4.46-4.43 (m, 1H), 2.05 (s, 3H), 1.45 (d, *J* = 6.7 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 138.49, 124.85, 114.96, 53.00, 22.58, 8.52. HRMS Calcd for $C_7H_{13}N_2$ [M+H$^+$]: 125.1079; Found: 125.1082.



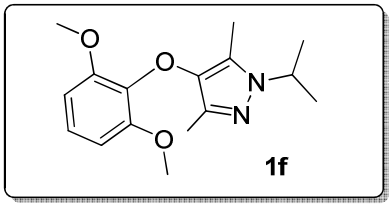
1d

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78 (s, 1H), 4.31-4.41 (m, *J* = 13.3, 6.7 Hz, 1H), 2.26 (d, *J* = 6.6 Hz, 6H), 1.47 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.40, 137.07, 104.13, 48.65, 21.96, 13.09, 10.47. HRMS Calcd for $C_8H_{15}N_2$ [M+H$^+$]: 139.1235; Found: 139.1238.



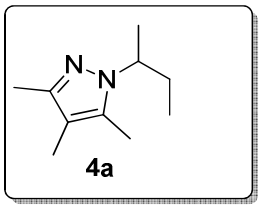
1e

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.29-4.36 (m, *J* = 13.3, 6.7 Hz, 1H), 2.17 (s, 3H), 2.13 (s, 3H), 1.88 (s, 3H), 1.43 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.74, 134.60, 110.93, 49.32, 22.58, 12.03, 9.57, 8.10. HRMS Calcd for $C_9H_{17}N_2$ [M+H$^+$]: 153.1392; Found: 153.1396.



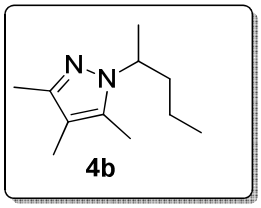
1f

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (t, *J* = 8.4 Hz, 1H), 6.55 (d, *J* = 8.4 Hz, 2H), 4.30-4.20 (m, 1H), 3.75 (s, 6H), 2.13 (s, 3H), 2.01 (s, 3H), 1.39 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.91, 138.46, 137.16, 136.32, 126.97, 123.93, 105.48, 56.19, 49.57, 22.22, 10.87, 8.30. HRMS Calcd for $C_{16}H_{23}N_2O_3$ [M+H$^+$]: 291.1709; Found: 291.1715.



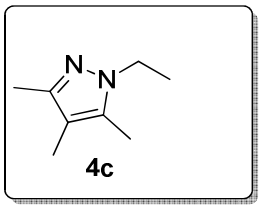
4a

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.97-4.05 (m, *J* = 8.6, 6.6 Hz, 1H), 2.16 (s, 3H), 2.11 (s, 3H), 1.96 – 1.90 (m, 1H), 1.88 (s, 3H), 1.77 – 1.64 (m, 1H), 1.40 (d, *J* = 6.7 Hz, 3H), 0.75 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.84, 135.25, 110.38, 55.26, 29.89, 20.91, 12.05, 11.15, 9.69, 8.13. HRMS Calcd for $C_{10}H_{19}N_2$ [M+H$^+$]: 167.1548; Found: 167.1556.



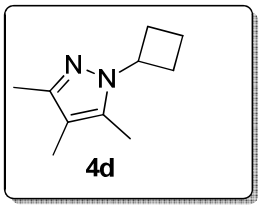
4b

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.06-4.14 (m, 1H), 2.15 (s, 3H), 2.10 (s, 3H), 1.97 – 1.88 (m, 1H), 1.87 (s, 3H), 1.68-1.59 (m, 1H), 1.39 (d, *J* = 6.7 Hz, 3H), 1.26 – 1.02 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.83, 135.09, 110.41, 53.49, 38.97, 21.19, 19.81, 13.93, 12.07, 9.70, 8.15. HRMS Calcd for $C_{11}H_{21}N_2$ [M+H$^+$]: 181.1705; Found: 181.1710.



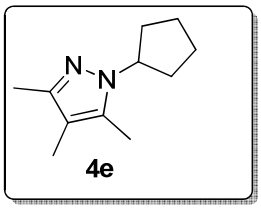
4c

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.97 (q, *J* = 7.2 Hz, 2H), 2.13 (s, 3H), 2.11 (s, 3H), 1.86 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.76, 134.96, 111.20, 43.59, 15.69, 11.79, 9.42, 8.08. HRMS Calcd for $C_8H_{15}N_2$ [M+H$^+$]: 139.1235; Found: 139.1239.



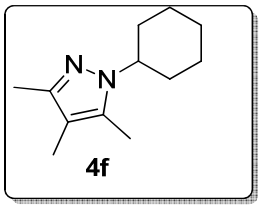
4d

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.66 – 4.48 (m, 1H), 2.70-2.60 (m, 2H), 2.29-2.36 (m, 2H), 2.18 (s, 3H), 2.09 (s, 3H), 1.87 (s, 3H), 1.86 – 1.69 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.03, 135.06, 111.27, 51.84, 30.10, 14.83, 11.97, 9.48, 7.99. HRMS Calcd for $C_{10}H_{17}N_2$ [M+H$^+$]: 165.1392; Found: 165.1398.

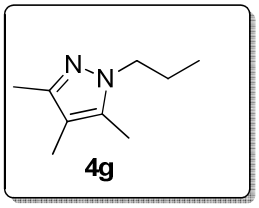


4e

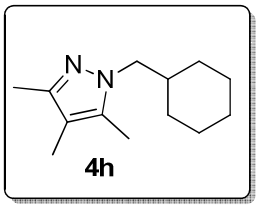
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.48-4.40 (m, 1H), 2.17 (s, 3H), 2.15 (s, 3H), 2.09 – 1.90 (m, 6H), 1.89 (s, 3H), 1.71 – 1.53 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.69, 135.46, 111.09, 58.89, 32.30, 24.39, 12.10, 9.79, 8.17. HRMS Calcd for $C_{11}H_{19}N_2$ [M+H$^+$]: 179.1548; Found: 179.1556.



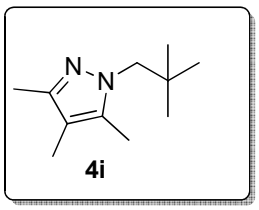
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.90-3.82 (m, 1H), 2.17 (s, 3H), 2.13 (s, 3H), 1.97 – 1.81 (m, 9H), 1.73 – 1.64 (m, 1H), 1.40 – 1.30 (m, 2H), 1.30 – 1.20 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.66, 134.69, 110.81, 57.37, 33.02, 26.02, 25.39, 12.05, 9.66, 8.14. HRMS Calcd for $C_{12}H_{21}N_2$ [M+H$^+$]: 193.1705; Found: 193.1712.



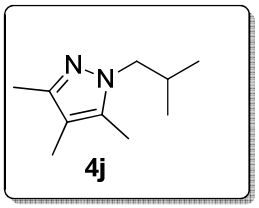
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.99 – 3.73 (m, 2H), 2.11 (d, J = 1.3 Hz, 3H), 2.08 (d, J = 1.1 Hz, 3H), 1.84 (s, 3H), 1.80 – 1.66 (m, 2H), 0.88-0.84 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.61, 135.25, 110.86, 50.31, 23.81, 11.73, 11.16, 9.48, 8.03. HRMS Calcd for $C_9H_{16}N_2$ [M+H$^+$]: 152.1313; Found: 152.1321.



Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.77 – 3.64 (m, 2H), 2.11 (d, J = 14.9 Hz, 6H), 1.87 (s, 3H), 1.75 – 1.50 (m, 6H), 1.26 – 1.04 (m, 3H), 0.96-0.88 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.55, 135.73, 110.59, 54.82, 38.99, 30.74, 26.36, 25.76, 11.70, 9.71, 8.05. HRMS Calcd for $C_{13}H_{22}N_2$ [M+H$^+$]: 206.1783; Found: 206.1790.



Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.72 (s, 2H), 2.14 (s, 3H), 2.11 (s, 3H), 1.88 (s, 3H), 0.95 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.49, 136.21, 110.80, 59.49, 33.87, 28.17, 11.92, 10.54, 8.33. HRMS Calcd for $C_{11}H_{21}N_2$ [M+H$^+$]: 181.1705; Found: 181.1713.

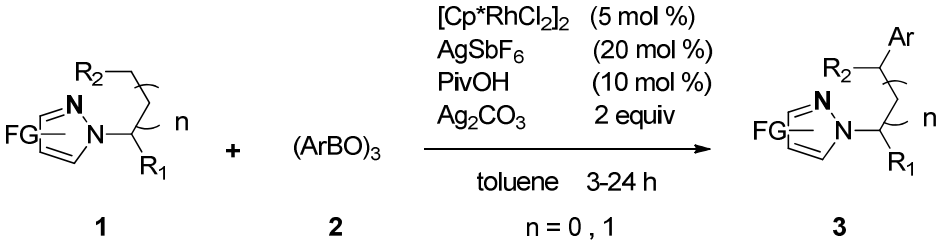


4j

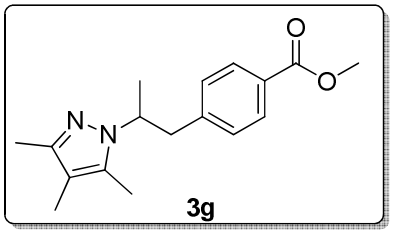
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.71 (d, *J* = 7.5 Hz, 1H), 2.19-2.16 (m, 2H), 2.13 (s, 3H), 2.10 (s, 3H), 1.87 (s, 3H), 0.86 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.78, 135.76, 110.82, 56.05, 29.84, 20.08, 11.85, 9.83, 8.20. HRMS Calcd for $C_{10}H_{19}N_2$ [M+H$^+$]: 167.1548; Found: 167.1554.

5. **General procedures for the preparation of 2,4,6-triphenyl-1,3,5,2,4,6-trioxatriborinane and its derivatives was according to an article [2].**

6. **Rhodium(III)-catalyzed β, γ- C(sp^3)-H bonds.**

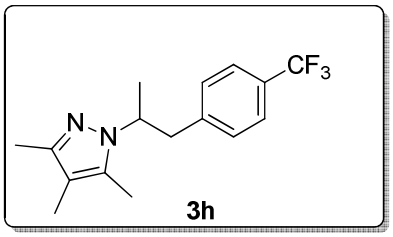


A mixture of **1**(0.2 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (6 mg, 0.05 equiv), $AgSbF_6$ (13.6 mg, 0.2 equiv), PivOH (2 mg, 0.1 equiv), Ag_2CO_3 (110 mg, 2 equiv) and toluene (1-2 mL) in a 15 mL glass vial sealed was heated at 130 ^{o}C for 3-24 hours. The reaction mixture was cooled to room temperature and concentrated *in vacuo*. The resulting residue was purified by column chromatography (PE:EA / 20:1) on silica gel to give the product **3g-v**, **5a-f** and **6a-c**.



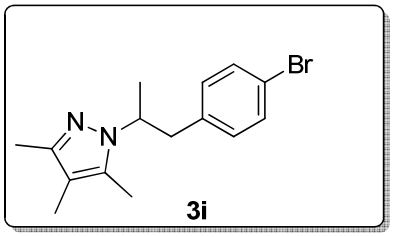
3g

Yellow oil. Isolated yield: 48.6 mg 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.2 Hz, 2H), 7.01 (d, *J* = 8.2 Hz, 2H), 4.41 – 4.20 (m, 1H), 3.94 (s, 3H), 3.32 (dd, *J* = 13.3, 9.1 Hz, 1H), 3.03 (dd, *J* = 13.3, 5.3 Hz, 1H), 2.25 (s, 3H), 1.86 (s, 3H), 1.74 (s, 3H), 1.58 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.62, 145.71, 144.08, 135.18, 129.03, 128.64, 127.77, 109.91, 54.56, 51.53, 42.91, 20.56, 11.50, 8.61, 7.47. HRMS Calcd for $C_{17}H_{23}N_2O_2$ [M+H$^+$]: 287.1760; Found: 287.1764.

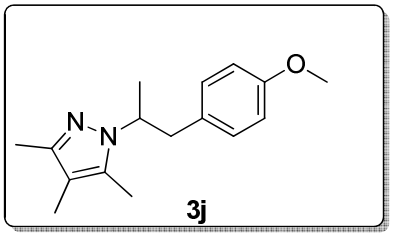


3h

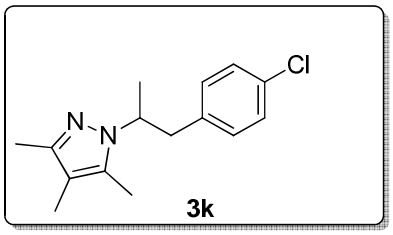
Yellow oil. Isolated yield: 44.9 mg 76%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 8.0 Hz, 2H), 4.25-4.31 (m, 1H), 3.31 (dd, J = 13.4, 9.1 Hz, 1H), 3.01 (dd, J = 13.4, 5.3 Hz, 1H), 2.23 (s, 3H), 1.84 (s, 3H), 1.73 (s, 3H), 1.55 (d, J = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.39, 143.33 (d, $J_{C\text{-}F}$ = 1 Hz), 135.78, 129.53, 125.21 (q, $J_{C\text{-}F}$ = 4 Hz), 110.64, 55.14, 43.23, 21.16, 12.12, 9.19, 8.07. HRMS Calcd for $C_{16}H_{19}N_2F_3$ [M+H$^+$]: 297.1579; Found: 297.1587.



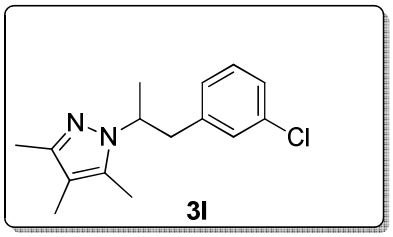
Yellow oil. Isolated yield: 44.0 mg 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 8.4 Hz, 2H), 4.27 – 4.10 (m, 1H), 3.17 (dd, J = 13.4, 9.0 Hz, 1H), 2.89 (dd, J = 13.5, 5.4 Hz, 1H), 2.20 (s, 3H), 1.83 (s, 3H), 1.73 (s, 3H), 1.51 (d, J = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.25, 137.68, 135.80, 132.24, 130.56, 128.41, 110.50, 55.33, 42.86, 21.03, 12.14, 9.26, 8.10. HRMS Calcd for $C_{15}H_{20}N_2F$ [M+H$^+$]: 307.0810; Found: 307.0804.



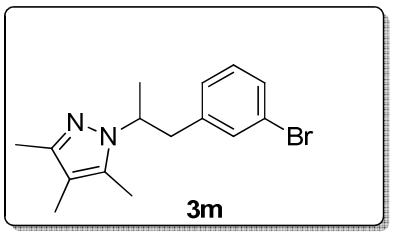
Yellow oil. Isolated yield: 32.5 mg 63%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (d, J = 8.6 Hz, 2H), 6.74 (d, J = 8.7 Hz, 2H), 4.25 – 4.12 (m, 1H), 3.76 (s, 3H), 3.10 (dd, J = 13.5, 8.5 Hz, 1H), 2.88 (dd, J = 13.5, 5.9 Hz, 1H), 2.21 (s, 3H), 1.83 (s, 3H), 1.75 (s, 3H), 1.50 (d, J = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.27, 146.08, 135.88, 131.35, 130.19, 116.26, 114.94, 113.73, 110.40, 55.72, 55.36, 42.79 , 20.74, 12.13, 9.29 , 8.12. HRMS Calcd for $C_{16}H_{22}N_2O$ [M+H$^+$]: 259.1810; Found: 259.1824.



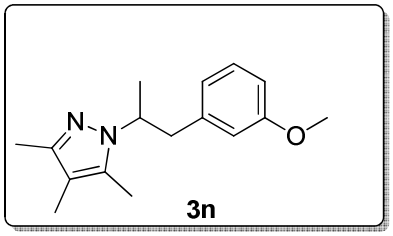
Yellow oil. Isolated yield: 48.2 mg 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, J = 8.3 Hz, 2H), 6.86 (d, J = 8.3 Hz, 2H), 4.41 – 4.16 (m, 1H), 3.22 (dd, J = 13.4, 9.0 Hz, 1H), 2.93 (dd, J = 13.5, 5.4 Hz, 1H), 2.25 (s, 3H), 1.87 (s, 3H), 1.77 (s, 3H), 1.55 (d, J = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.63, 137.06, 135.21, 131.63, 129.94, 127.80, 109.89, 54.72, 42.24, 20.41, 11.51, 8.64, 7.48. HRMS Calcd for $C_{15}H_{20}N_2Cl$ [M+H$^+$]: 263.1315; Found: 263.1327.



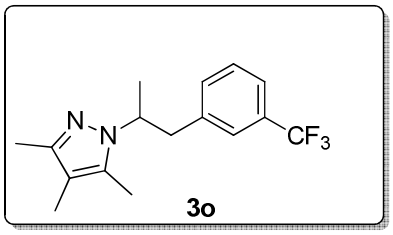
Yellow oil. Isolated yield: 37.7 mg 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.08 (m, 2H), 6.83 (d, *J* = 1.8 Hz, 1H), 6.78 (d, *J* = 7.2 Hz, 1H), 4.29 – 4.13 (m, 1H), 3.16 (dd, *J* = 13.4, 8.9 Hz, 1H), 2.90 (dd, *J* = 13.4, 5.6 Hz, 1H), 2.21 (s, 3H), 1.83 (s, 3H), 1.72 (s, 3H), 1.52 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.77, 140.55, 135.35, 133.43, 128.91, 128.70, 126.80, 126.01, 110.04, 54.59, 42.67, 20.28, 11.50, 8.60, 7.44. HRMS Calcd for $C_{15}H_{20}N_2Cl$ [M+H$^+$]: 263.1315; Found: 263.1330.



Yellow oil. Isolated yield: 38.5 mg 63%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.04 (t, *J* = 7.8 Hz, 1H), 6.96 (s, 1H), 6.81 (s, 1H), 4.26 – 4.13 (m, 1H), 3.15 (dd, *J* = 13.3, 9.0 Hz, 1H), 2.88 (dd, *J* = 13.4, 5.4 Hz, 1H), 2.21 (s, 3H), 1.83 (s, 3H), 1.70 (s, 3H), 1.53 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.33, 141.41, 135.97, 132.20, 129.76, 129.49, 127.81, 122.26, 110.60, 55.15, 43.26, 20.85, 12.08, 9.15, 8.03. HRMS Calcd for $C_{15}H_{20}N_2Br$ [M+H$^+$]: 307.0810; Found: 307.0804.

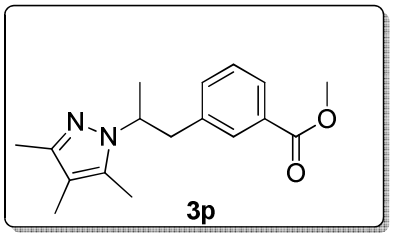


Yellow oil. Isolated yield: 28.3 mg 55%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (t, *J* = 7.8 Hz, 1H), 6.71 (dd, *J* = 7.9, 2.2 Hz, 1H), 6.59 (d, *J* = 7.4 Hz, 1H), 6.33 (s, 1H), 4.30 – 4.19 (m, 1H), 3.67 (s, 3H), 3.17 – 3.07 (m, 1H), 2.90 (dd, *J* = 13.3, 5.7 Hz, 1H), 2.21 (s, 3H), 1.83 (s, 3H), 1.72 (s, 3H), 1.52 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.52, 146.11, 140.75, 136.08, 129.25, 121.52, 114.23, 112.51, 110.36, 55.46, 55.07, 43.73, 20.92, 12.14, 9.22, 8.10. HRMS Calcd for $C_{16}H_{22}N_2O$ [M+H$^+$]: 259.1810; Found: 259.1820.

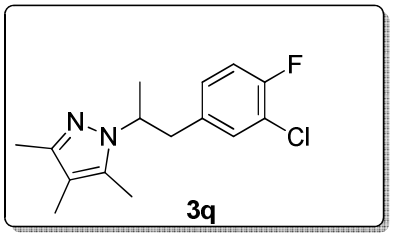


Yellow oil. Isolated yield: 48.5 mg 82%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 1H), 6.96 (s, 1H), 4.29 – 4.13 (m, 1H), 3.26 (dd, *J* =

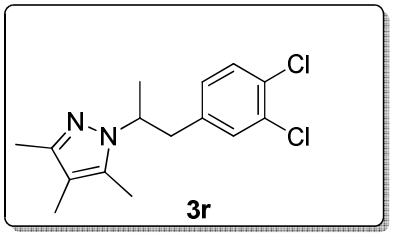
13.4, 9.7 Hz, 1H), 2.96 (dd, J = 13.4, 4.8 Hz, 1H), 2.21 (s, 3H), 1.79 (s, 3H), 1.60 (s, 3H), 1.57 (d, J = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.51, 140.00, 136.09, 132.56, 130.54 (q, J_{C-F} = 35 Hz), 128.59, 126.02, 123.28, 110.67, 55.17, 43.39, 21.07, 12.07, 9.02, 7.90. HRMS Calcd for $C_{16}H_{19}N_2F_3$ [M+H$^+$]: 297.1579; Found: 297.1587.



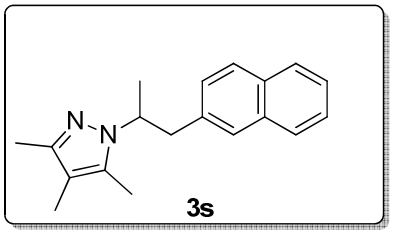
Yellow oil. Isolated yield: 32.6 mg 57%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.76 (m, 1H), 7.62 (t, J = 1.5 Hz, 1H), 7.24 (t, J = 7.7 Hz, 1H), 7.01 (d, J = 7.6 Hz, 1H), 4.37 – 4.18 (m, 1H), 3.90 (s, 3H), 3.24 (dd, J = 13.4, 9.0 Hz, 1H), 2.98 (dd, J = 13.4, 5.5 Hz, 1H), 2.22 (s, 3H), 1.80 (s, 3H), 1.68 (s, 3H), 1.54 (d, J = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.63, 145.73, 138.87, 135.30, 133.37, 129.67, 129.51, 127.73, 127.16, 109.95, 54.64, 51.58, 42.71, 20.31, 11.51, 8.60, 7.43. HRMS Calcd for $C_{17}H_{23}N_2O_2$ [M+H$^+$]: 287.1760; Found: 287.1764.



Yellow oil. Isolated yield: 39.7 mg 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (t, J = 8.7 Hz, 1H), 6.82 (dd, J = 7.1, 2.2 Hz, 1H), 6.69-6.73 (m, J = 8.4, 4.6, 2.2 Hz, 1H), 4.24 – 4.12 (m, 1H), 3.15 (dd, J = 13.5, 9.4 Hz, 1H), 2.85 (dd, J = 13.5, 5.1 Hz, 1H), 2.20 (s, 3H), 1.82 (s, 3H), 1.71 (s, 3H), 1.52 (d, J = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.32(d, J_{C-F} = 245 Hz), 145.84, 135.54 (d, J_{C-F} = 4.0 Hz), 135.37, 130.58, 128.19 (d, J_{C-F} = 7.0 Hz), 119.85 (d, J_{C-F}= 17.6 Hz), 115.60 (d, J_{C-F}= 20.8 Hz), 110.10, 54.58, 41.90, 20.36, 11.49, 8.62, 7.42. HRMS Calcd for $C_{15}H_{19}N_2FCl$ [M+H$^+$]: 281.1221; Found: 281.1233.

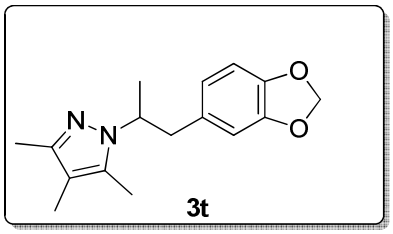


Yellow oil. Isolated yield: 47.9 mg 81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 8.2 Hz, 1H), 6.89 (d, J = 2.0 Hz, 1H), 6.70 (dd, J = 8.2, 2.0 Hz, 1H), 4.29 – 4.09 (m, 1H), 3.17 (dd, J = 13.5, 9.4 Hz, 1H), 2.85 (dd, J = 13.5, 5.1 Hz, 1H), 2.20 (s, 3H), 1.83 (s, 3H), 1.73 (s, 3H), 1.52 (d, J = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.87, 138.78, 135.30, 131.50, 130.54, 129.79, 129.53, 128.02, 110.15, 54.39, 41.96, 20.45, 11.51, 8.68, 7.45. HRMS Calcd for $C_{15}H_{19}N_2Cl_2$ [M+H$^+$]: 297.0925; Found: 297.0939.



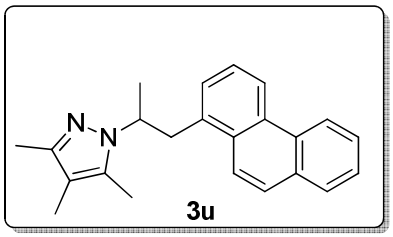
3s

Yellow solid. Isolated yield: 34.4 mg 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 5.8, 3.4 Hz, 1H), 7.69 (dd, *J* = 10.2, 5.4 Hz, 2H), 7.40-7.45 (m, 2H), 7.38 (s, 1H), 7.04 (dd, *J* = 8.4, 1.6 Hz, 1H), 4.33-4.38 (m, 1H), 3.33 (dd, *J* = 13.4, 8.4 Hz, 1H), 3.10 (dd, *J* = 13.4, 6.0 Hz, 1H), 2.23 (s, 3H), 1.80 (s, 3H), 1.70 (s, 3H), 1.54 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.21, 136.72, 135,85, 133.58, 132.30, 127.86, 127.76, 127.71, 127.69, 127.65, 125.98, 125.46, 110.57, 55.46, 43.77, 20.91, 12.17, 9.33, 8.09. HRMS Calcd for $C_{19}H_{23}N_2$ [M+H$^+$]: 279.1861; Found: 279.1772.



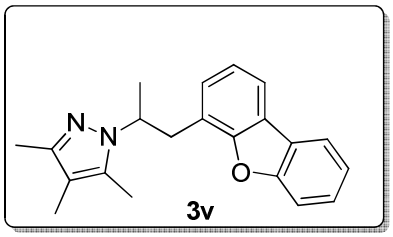
3t

Yellow oil. Isolated yield: 39.7 mg 73%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.65 (d, *J* = 7.7 Hz, 1H), 6.43 – 6.37 (m, 2H), 5.89 (s, 2H), 4.29 – 4.10 (m, 1H), 3.08 (dd, *J* = 13.5, 8.4 Hz, 1H), 2.85 (dd, *J* = 13.5, 6.0 Hz, 1H), 2.20 (s, 3H), 1.84 (s, 3H), 1.81 (s, 3H), 1.49 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.87, 145.52, 145.45, 135.15, 132.39, 121.57, 109.86, 108.99, 107.55, 100.25, 55.00, 42.67, 20.13, 11.52, 8.74, 7.50. HRMS Calcd for $C_{16}H_{21}N_2O_2$ [M+H$^+$]: 273.1603; Found: 273.1609.



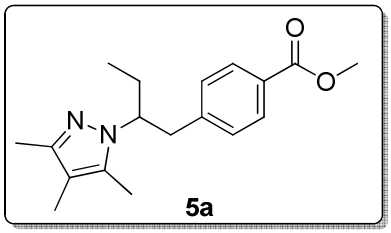
3u

Yellow solid. Isolated yield: 39.3 mg 60%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 – 8.70 (m, 1H), 8.64 (d, *J* = 8.1 Hz, 1H), 8.05 – 7.94 (m, 1H), 7.74 – 7.69 (m, 1H), 7.68 – 7.50 (m, 4H), 7.30 (s, 1H), 4.54 (dd, *J* = 13.8, 6.7 Hz, 1H), 3.64 – 3.52 (m, 2H), 2.26 (s, 3H), 1.72 (s, 3H), 1.61 (d, *J* = 6.7 Hz, 3H), 1.54 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.37, 135.89, 133.18, 131.78, 131.22, 130.74, 129.87, 128.33, 128.32, 126.74, 126.73, 126.34, 126.29, 124.13, 123.48, 122.52, 110.55, 53.95, 41.01, 21.14, 12.20, 9.20, 8.00. HRMS Calcd for $C_{23}H_{25}N_2$ [M+H$^+$]: 329.2018; Found: 329.2022.



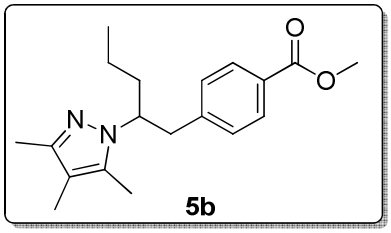
3v

Yellow solid. Isolated yield: 27.3 mg 43%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.6 Hz, 1H), 7.79 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.53 – 7.43 (m, 1H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.2 Hz, 1H), 4.77 – 4.51 (m, 1H), 3.41 (d, *J* = 7.2 Hz, 2H), 2.22 (s, 3H), 1.79 (s, 3H), 1.75 (s, 3H), 1.58 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.11, 154.92, 146.17, 135.71, 128.63, 127.14, 124.61, 123.82, 123.13, 122.85, 122.82, 120.86, 119.05, 111.77, 110.51, 53.54, 38.11, 20.68, 12.19, 9.14, 8.08. HRMS Calcd for $C_{21}H_{23}N_2O$ [M+H$^+$]: 319.1810; Found: 319.1814.



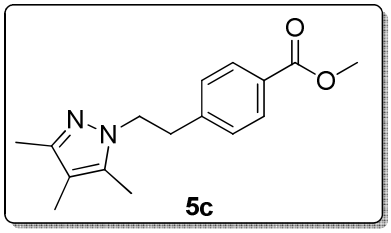
5a

Yellow oil. Isolated yield: 42.6 mg 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.3 Hz, 2H), 6.93 (d, *J* = 8.3 Hz, 2H), 3.90-3.98 (m, 1H), 3.88 (s, 3H), 3.27 (dd, *J* = 13.2, 9.8 Hz, 1H), 2.99 (dd, *J* = 13.3, 4.4 Hz, 1H), 2.20 (s, 3H), 2.09-2.17 (m, 1H), 1.88 – 1.81 (m, 1H), 1.80 (s, 3H), 1.63 (s, 3H), 0.74 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.25, 146.41, 144.92, 136.72, 129.56, 129.21, 128.25, 109.96, 61.61, 52.09, 42.21, 28.52, 12.17, 11.08, 9.23, 8.12. HRMS Calcd for $C_{18}H_{25}N_2O_2$ [M+H$^+$]: 301.1916 Found: 301.1922.



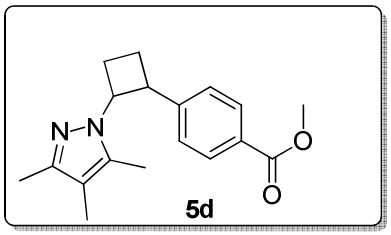
5b

Yellow oil. Isolated yield: 42.7 mg 68%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.2 Hz, 2H), 6.92 (d, *J* = 8.2 Hz, 2H), 4.10 – 3.97 (m, 1H), 3.88 (s, 3H), 3.27 (dd, *J* = 13.2, 9.9 Hz, 1H), 2.97 (dd, *J* = 13.2, 4.4 Hz, 1H), 2.20 (s, 3H), 2.18 – 2.08 (m, 1H), 1.79 (s, 3H), 1.77 – 1.68 (m, 1H), 1.61 (s, 3H), 1.21 – 1.03 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.26, 146.35, 144.92, 136.55, 129.56, 129.22, 128.26, 109.97, 59.76, 52.10, 42.41, 37.47, 19.69, 13.86, 12.18, 9.21, 8.13. HRMS Calcd for $C_{19}H_{27}N_2O_2$ [M+H$^+$]: 315.2073; Found: 315.2084.



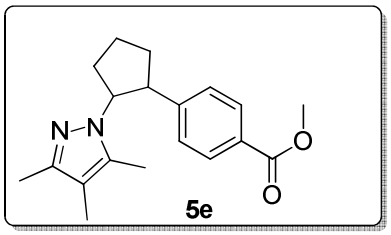
5c

Yellow oil. Isolated yield: 42.4 mg 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.11 (d, *J* = 8.3 Hz, 2H), 4.15 (t, *J* = 7.2 Hz, 2H), 3.90 (s, 3H), 3.11 (t, *J* = 7.2 Hz, 2H), 2.18 (s, 3H), 1.85 (s, 3H), 1.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.15, 146.55, 144.23, 136.02, 129.92, 129.10, 128.63, 111.18, 52.20, 49.81, 37.24, 11.97, 9.34, 8.19. HRMS Calcd for $C_{16}H_{21}N_2O$ [M+H$^+$]: 273.1603; Found: 273.1614.



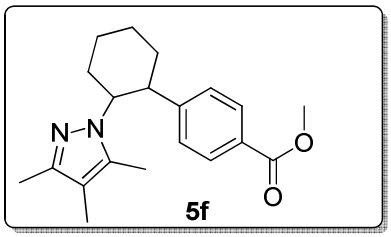
5d

Yellow oil. Isolated yield: 39.9 mg 67%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.00 (d, *J* = 8.3 Hz, 2H), 5.10 – 4.87 (m, 1H), 3.92 (dd, *J* = 15.5, 7.8 Hz, 1H), 3.86 (s, 3H), 3.29 – 3.00 (m, 1H), 2.80 – 2.50 (m, 2H), 2.45 – 2.28 (m, 1H), 2.07 (s, 3H), 1.76 (s, 3H), 1.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.34, 145.56, 145.10, 135.88, 129.09, 128.15, 111.83, 56.89, 52.06, 46.62, 24.30, 24.11, 11.91, 9.49, 8.02, 1.15. HRMS Calcd for $C_{18}H_{23}N_2O_2$ [M+H$^+$]: 299.1760; Found: 299.1764.



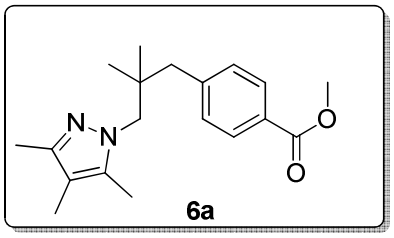
5e

Yellow oil. Isolated yield: 31.8 mg 51%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 2H), 4.67-4.59 (m, 1H), 3.90 (s, 3H), 3.32-3.14 (m, 1H), 2.45 – 2.21 (m, 4H), 2.19 (s, 3H), 2.17 (s, 3H), 2.14 – 1.97 (m, 2H), 1.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.29, 150.30, 146.14, 135.51, 129.84, 128.19, 127.37, 111.36, 58.31, 52.13, 44.50, 40.46, 32.52, 31.46, 12.16, 9.80, 8.19. HRMS Calcd for $C_{19}H_{25}N_2O_2$ [M+H$^+$]: 313.1916; Found: 313.1921.



5f

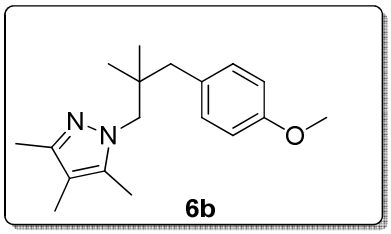
Yellow oil. Isolated yield: 21.5 mg 33%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 4.11-4.03 (m, 1H), 3.89 (s, 3H), 2.85 – 2.70 (m, 1H), 2.22 (dd, *J* = 12.4, 6.4 Hz, 1H), 2.17 (s, 3H), 2.16 (s, 3H), 2.10 – 1.90 (m, 5H), 1.89 (s, 3H), 1.64 – 1.46 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.21, 151.43, 146.00, 134.76, 129.91, 128.25, 127.07, 111.04, 57.05, 52.10, 44.16, 39.65, 33.18, 32.26, 25.67, 12.06, 9.68, 8.13. HRMS Calcd for $C_{20}H_{27}N_2O_2$ [M+H$^+$]: 327.2073; Found: 327.2082.



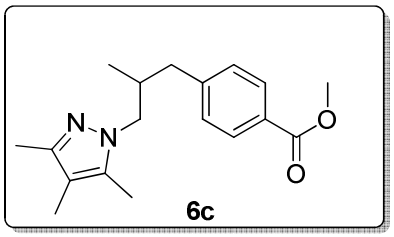
6a

Yellow oil. Isolated yield: 44.5 mg 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.28 – 7.23 (m, 2H), 3.90 (s, 3H), 3.82 (s, 2H), 2.71 (s, 3H), 2.17 (s, 3H), 2.10 (s, 3H), 1.90 (s, 1H), 0.88 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.36 145.92, 144.27, 136.50, 130.95, 129.20,

128.17, 111.06, 58.61, 52.15, 46.77, 37.59, 25.30, 12.03, 10.61, 8.39. HRMS Calcd for $C_{19}H_{27}N_2O_2$ [M+H$^+$]: 315.2073; Found: 315.2084.

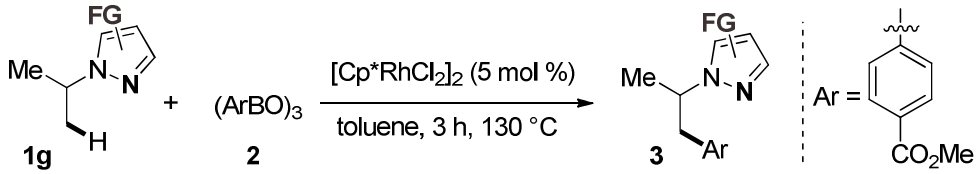


Yellow oil. Isolated yield: 34.8 mg 61%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 3.80 (s, 2H), 3.79 (s, 3H), 2.58 (s, 2H), 2.17 (s, 3H), 2.09 (s, 3H), 1.90 (s, 3H), 0.88 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.10, 145.68, 136.46, 132.10, 131.77, 130.52, 113.31, 110.88, 58.60, 55.32, 46.11, 37.46, 25.24, 11.99, 10.60, 8.37. HRMS Calcd for $C_{18}H_{27}N_2O$ [M+H$^+$]: 287.2123; Found: 287.2132.



Yellow oil. Isolated yield: 34.8 mg 58%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 3.90 (s, 3H), 3.86 (d, *J* = 6.5 Hz, 1H), 3.80 (d, *J* = 7.5 Hz, 1H), 2.72 (dd, *J* = 12.0, 3.9 Hz, 1H), 2.47 – 2.33 (m, 1H), 2.15 (s, 3H), 2.09 (s, 3H), 1.88 (s, 3H), 0.80 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.26, 146.15, 145.93, 135.82, 129.72, 129.25, 128.13, 111.16, 54.53, 52.14, 40.93, 36.47, 17.24, 11.98, 9.89, 8.26. HRMS Calcd for $C_{18}H_{25}N_2O_2$ [M+H$^+$]: 301.1916; Found: 301.1915.

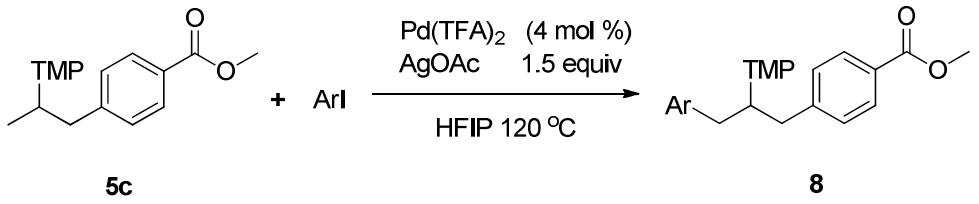
7. **Table S1: Rhodium-catalyzed arylation of C(sp^3)-H bonds.**



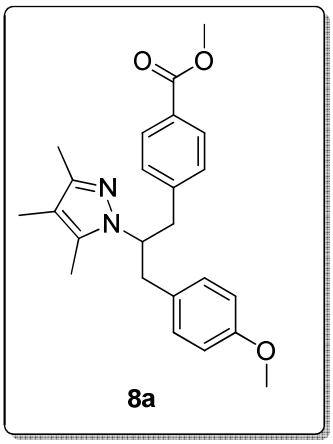
	Oxidants (2 equiv)	Additive (0.2 equiv)	Additive (0.1 equiv)	Yield of **4a** (%)
1	Ag_2CO_3	$AgSbF_6$	no	56
2	Ag_2CO_3	$AgSbF_6$	NaOAc	66
3	Ag_2CO_3	$AgSbF_6$	PivOH	86
4	Ag_2CO_3	$AgSbF_6$	1-Ad-OH	81
5	Ag_2CO_3	$AgSbF_6$	$(n\text{-}BuO)_2PO_2H$	78
6	Ag_2O	$AgSbF_6$	PivOH	56
7	AgOAc	$AgSbF_6$	PivOH	56
8	$Cu(OAc)_2$	$AgSbF_6$	PivOH	5
9	$K_2S_2O_8$	$AgSbF_6$	PivOH	trace
10	O_2	$AgSbF_6$	PivOH	trace
11	Ag_2CO_3	no	PivOH	65
12	Ag_2CO_3	$KSbF_6$	PivOH	15
13	Ag_2CO_3	KBF_4	PivOH	8
14[a]	Ag_2CO_3	$AgSbF_6$	PivOH	6
15[b]	Ag_2CO_3	$AgSbF_6$	PivOH	17
16[c]	Ag_2CO_3	$AgSbF_6$	PivOH	-

a, phenylboronic acid was used instead of **2**; b, 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolanphenylboronic acide was used instead of **2;** c,$[Cp^*RhCl_2]_2$ was not added in the reaction.

8. **General procedures for Palladium-Catalyzed C(sp^3)-H bonds arylation.**

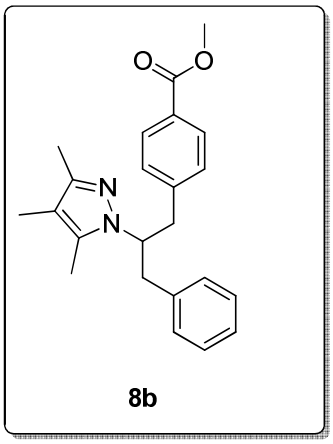


A mixture of **4a** (0.2 mmol , 1.0 equiv), Aryl iodide (1.2 equiv), $Pd(TFA)_2$ (2.6 mg, 0.04equiv), AgOAc (49.6mg, 1.5 equiv) and HFIP (0.5 ml) in a 15 ml glass vial sealed was heated at 120 ^oC for 12 hours. The reaction mixture was cooled to room temperature and concentrated *in vacuo*. The resulting residue was purified by column chromatography (PE:EA / 5:1) on silica gel to give the product **8a-b** as a yellow oil.



8a

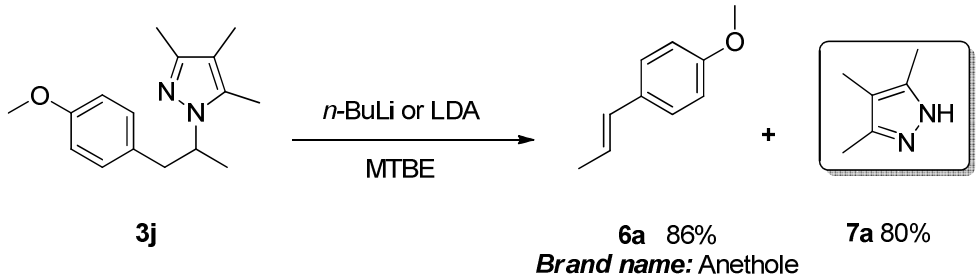
Yellow oil. Isolated yield: 64.2 mg 82%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.3 Hz, 2H), 6.94 (d, *J* = 8.3 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 6.75 – 6.68 (m, 2H), 4.11-4.16 (m, 4.8 Hz, 1H), 3.87 (s, 3H), 3.75 (s, 3H), 3.41 (dd, *J* = 13.3, 10.0 Hz, 1H), 3.27 (dd, *J* = 13.6, 9.1 Hz, 1H), 2.99-3.09 (m, 2H), 2.23 (s, 3H), 1.73 (s, 3H), 1.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.26, 158.30, 146.42, 144.77, 136.99, 130.91, 130.13, 129.61, 129.20, 128.30, 113.79, 109.99, 62.07, 55.33, 52.13, 41.40, 41.14, 12.19, 8.84, 8.07. HRMS Calcd for $C_{24}H_{29}N_2O_3$ [M+H$^+$]: 393.2178; Found: 393.2186.



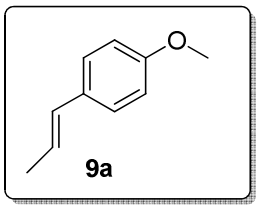
8b

Yellow oil. Isolated yield: 61.5 mg 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.21-7.19 (m, 3H), 7.00 – 6.90 (m, 4H), 4.25-4.17 (m, 1H), 3.90 (s, 3H), 3.49-3.33 (m, 2H), 3.13-3.07 (m, 2H), 2.26 (s, 3H), 1.75 (s, 3H), 1.67 (s, 3H), 1.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.63, 145.86, 144.07, 138.23, 136.33, 129.01, 128.57, 127.80, 125.94, 125.94, 109.40, 61.27, 51.51, 41.43, 40.85, 11.59, 8.14, 7.44. HRMS Calcd for $C_{23}H_{27}N_2O_3$ [M+H$^+$]: 363.2073; Found: 363.2080.

9. General procedures for the removal and transformation of directing group.



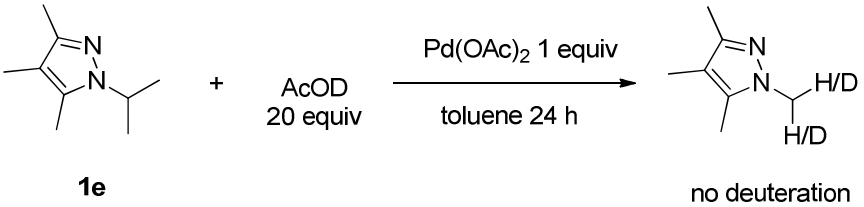
To a stirred solution of **4h** (0.2mmol, 1equiv) in MTBE (1 ml) under argon was added dropwise n-butylithium (3M in hexane, 0.5 ml) or LDA (3M in hexane, 0.5 ml) at room temperature for 24 hours. Then the reaction mixture was concentrated *in vacuo*. The resulting residue was purified by column chromatography (PE:EA / 40:1) on silica gel to give the product **9a** as a colourless liquid and **10a** (PE:EA / 3:1, Isolated yield: 17.6 mg 80%.) as a white solid.



Colorless oil. Isolated yield: 25.4 mg 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 8.7 Hz, 2H), 6.93 (d, J = 8.7 Hz, 2H), 6.45 (d, J = 15.7 Hz, 2H), 6.26 – 6.04 (m, 2H), 3.86 (s, 3H), 1.96 (dd, J = 6.5, 1.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.67, 130.85, 130.47, 126.94, 123.41, 113.94, 55.19, 18.45. HRMS Calcd for $C_{10}H_{13}O$ [M+H$^+$]: 149.0966; Found: 149.0970.

10. Mechanistic study.

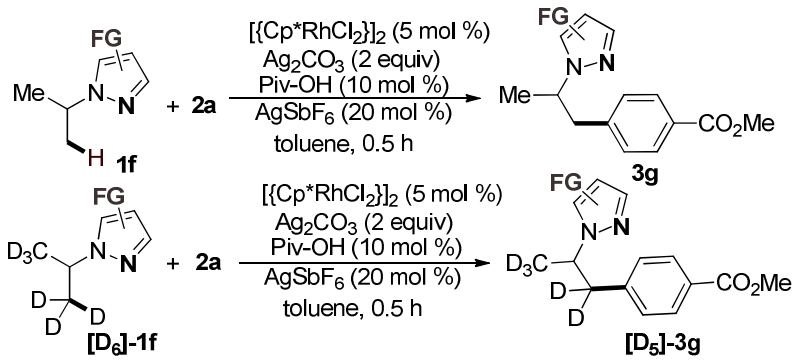
a) Hydrogen-deuterium exchange experiment.



Scheme S1. Hydrogen-deuterium exchange experiment.

A sealed tube with a magnetic stir bar was charged with $Pd(OAc)_2$ (44.8 mg, 0.2 mmol), **1f** (30.4 mg, 0.2 mmol), and AcOD (122 mg, 4 mmol) under an Ar atmosphere at 130 ^{o}C for 24 hours. According to the TLC analysis showed that no deuteration was observed.

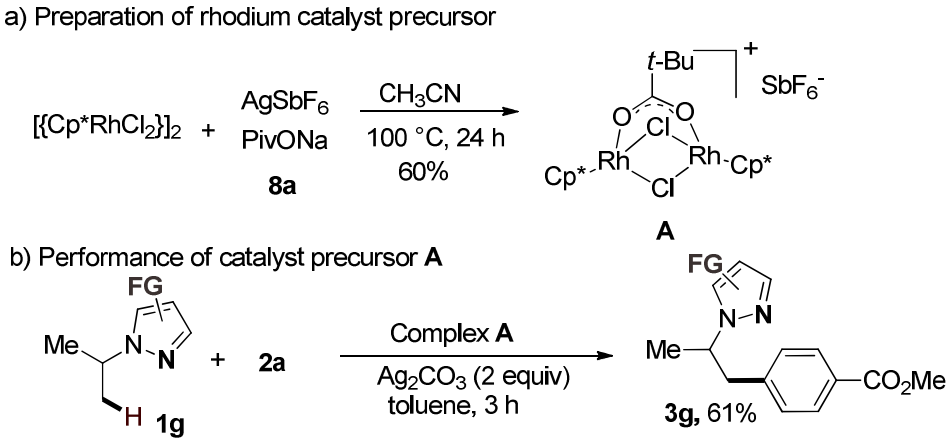
b) Kinetic isotope effect.



Scheme S2. Kinetic isotope effect.

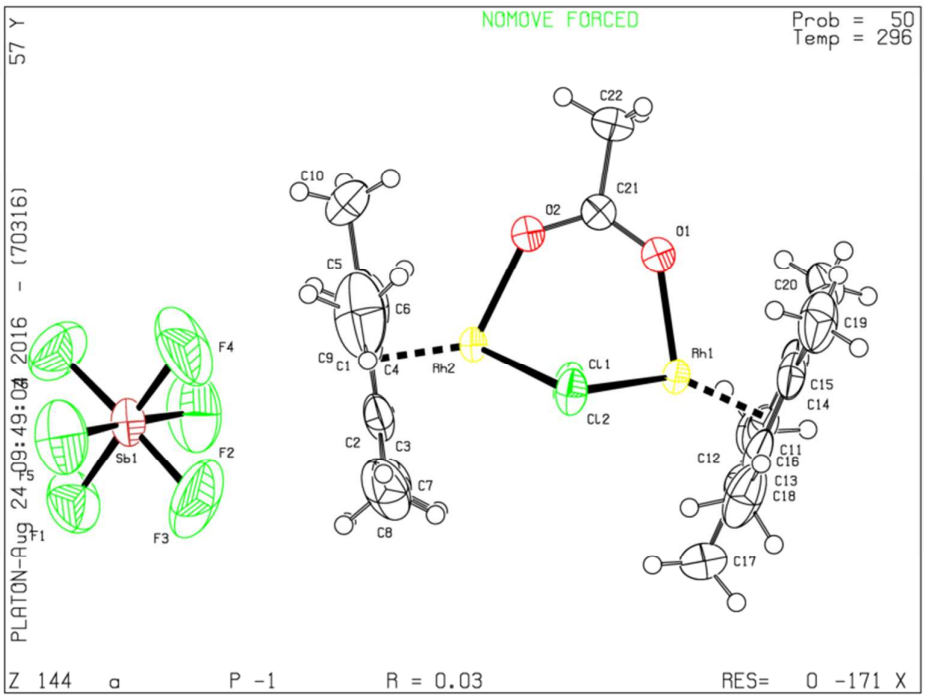
A sealed tube with a magnetic stir bar was charged with $[\{Cp^*RhCl_2\}]_2$ (6, 0.01 mmol), Ag_2CO_3 (110 mg, 0.4 mmol), PivOH (2 mg, 0.02 mmol), **1f** (30.4 mg, 0.2 mmol), 1**g** (31.6 mg, 0.2 mmol), **2a** (192 mg, 0.4 mmol) and toluene (1 mL) under an Ar atmosphere. The resulting mixture was stirred at 130 °C for 0.5 h. The reaction was detected by GC, the conversation of **1f** was 27% and the conversation of **[D6]-1g** was 12% (KIE = 2.3).

11. Synthesis of complex A.



Scheme S3. Synthesis of complex A.

$[Cp^*RhCl_2]_2$ (90 mg, 0.15 mmol), $AgSbF_6$ (102 mg, 0.3 mmol), 4g (54 mg, 0.3 mmol), and NaOAc (40.8 mg, 0.3 mmol) were add to MeCN (2 mL). The reaction was stirred in a sealed tube under Ar atmosphere at 100 °C for 24 h, and then the purified product was collected by filtration, washed with hexane (0.5 mL). Orange crystals were obtained from the concentrated MeCN solution at room temperature in one day (76 mg, 61 %). The structure was verified by X–ray crystallography.



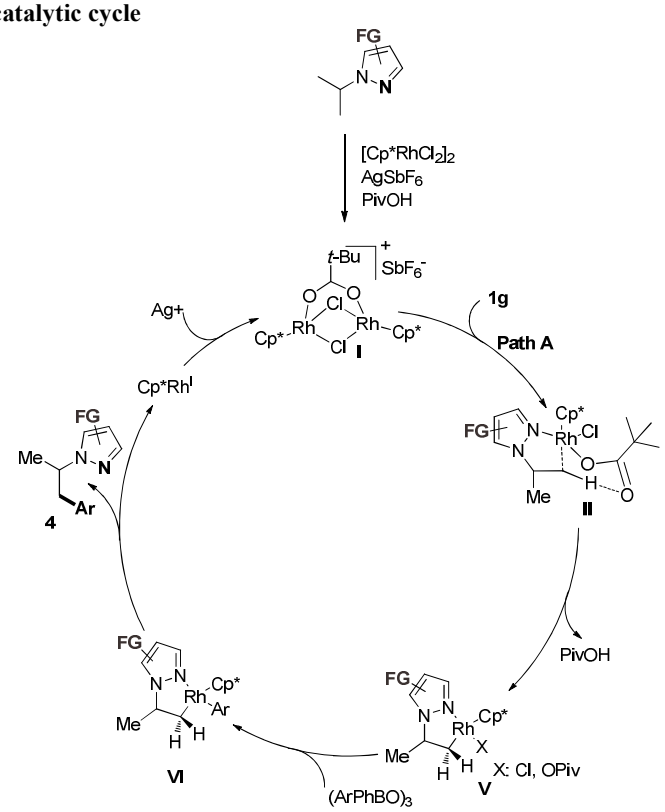
X–Ray Data for Complex A: Intensity data were collected with a Rigaku Mercury CCD area detector in ω scan mode using Mo Kαradiation (λ = 0.71070 Å). The diffracted intensities were corrected for Lorentz polarization effects and empirical absorption corrections. Details of the intensity data collection and crystal data are given in Table 2. The structures were solved by direct methods and refined by fullmatrix least–squares procedures based on |F|2 . All the non–hydrogen atoms were refined anisotropically. All the H atoms were held stationaryand included in the structure factor calculation in the final stage of full–matrix least–squares refinement. The structures were solved and refinedusing OLEX-2 programs.

Table S2. Crystal data and structure refinement for complex A.

Empirical formula	C22 H33 Cl2 O2 Rh2, F6 Sb
Formula weight	841.97
Temperature	298(2) K
Wavelength	0.71073 A
Crystal system, space group	triclinic, P -1
Unit cell dimensions	a = 7.9410(7) A alpha = 69.361(1) deg
	b = 7.9410(7) A beta = 88.954(2) deg
	c = 7.9410(7) A gamma = 80.282(2) deg
Volume	1448.1(2) A^3
Z, Calculated density	2, 1.9308 Mg/m^3
Absorption coefficient	2.293 mm^-1
F(000)	815.3050
Crystal size	0.44 x 0.40 x 0.20 mm
Thata range for data collection	2.57 to 25.02 deg
Limiting indices	–9<=h<=9, –15<=k<=16, 0<=l<=16
Reflections collected / unique	9474 / 5032
Completeness to theta = 25.00	99.7 %
Absorption correction	Semi–empirical from equivalents
Max. and min. transmission	0.700 and 0.485
Refinement method	Full–matrix least–squares on F^2

Data / restraints / parameters	5032 / 0 / 327
Goodness–of–fit on F^2	1.0495
Final R indices [I>2sigma(I)]	R1 = 0.0827, wR2 = 0.1936
R indices (all data)	R2 = 0.0975, wR2 = 0.2098
Largest diff. peak and hole	4.1781 and -7.3271 e.A^-3

12. The plausible catalytic cycle

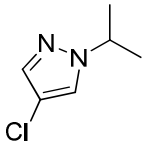


13. References.

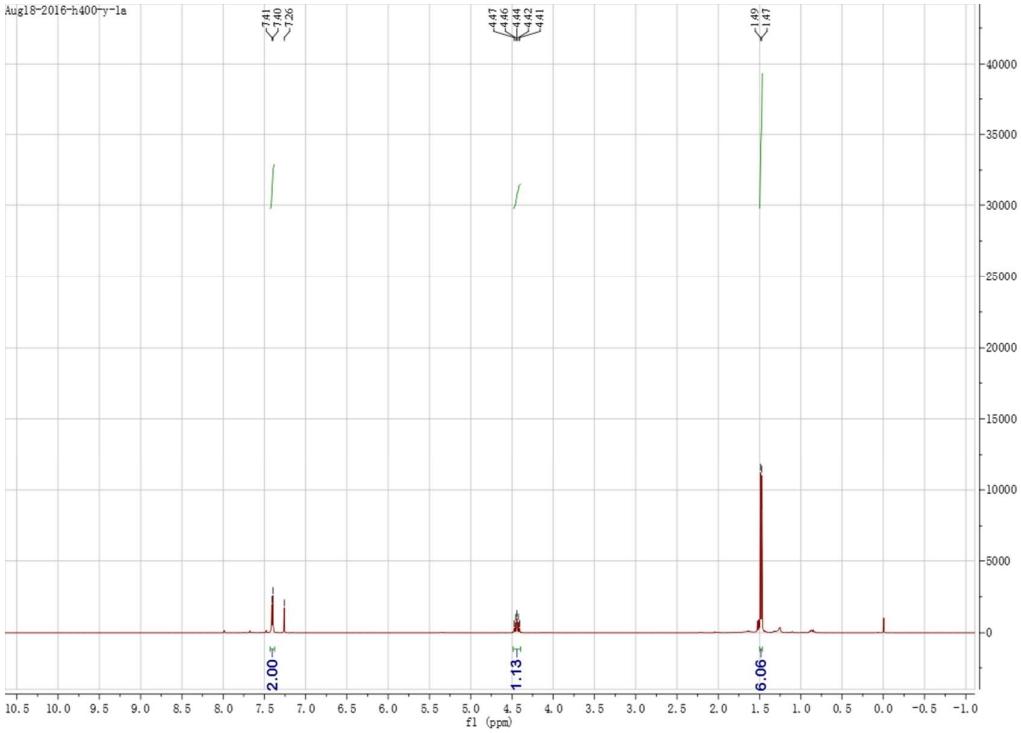
[1] (a) L. Papernaya, A. Shatrova, E. Levanova, A. Albanov, L. Klyba, E. Rudyakova, G. Levkovskaya, *Heteaoat. Chem.* **2015**, *26*, 5-11. b) V. Zarubaev, E. Golod, P. Anfimov, A. Shtro, V. Saraev, A. Gavrilov, A. Logvinov, O. Kiselev, *Bioorg. Med. Chem.* **2010**, *18*, 839-848; c) I. Beria, D. Ballinari, R. Ferguson, *J. Med. Chem*. **2010**, *53*, 3532-3551. d) Jason D. Katz, James P. Jewell, *J. Med. Chem*. **2011**, *54*, 4092–4108; e) Yuya Oguro, Naoki Miyamoto a, Terufumi Takagi, *Bioorg. Med. Chem.* **2010**, *18*, 7150–7163.

[2] Y.-H. Huang, Hayashi, *J. Am. Chem. Soc.*, **2015**, *137(24)*, 7556-7559.

NMR spectra



1a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4.41
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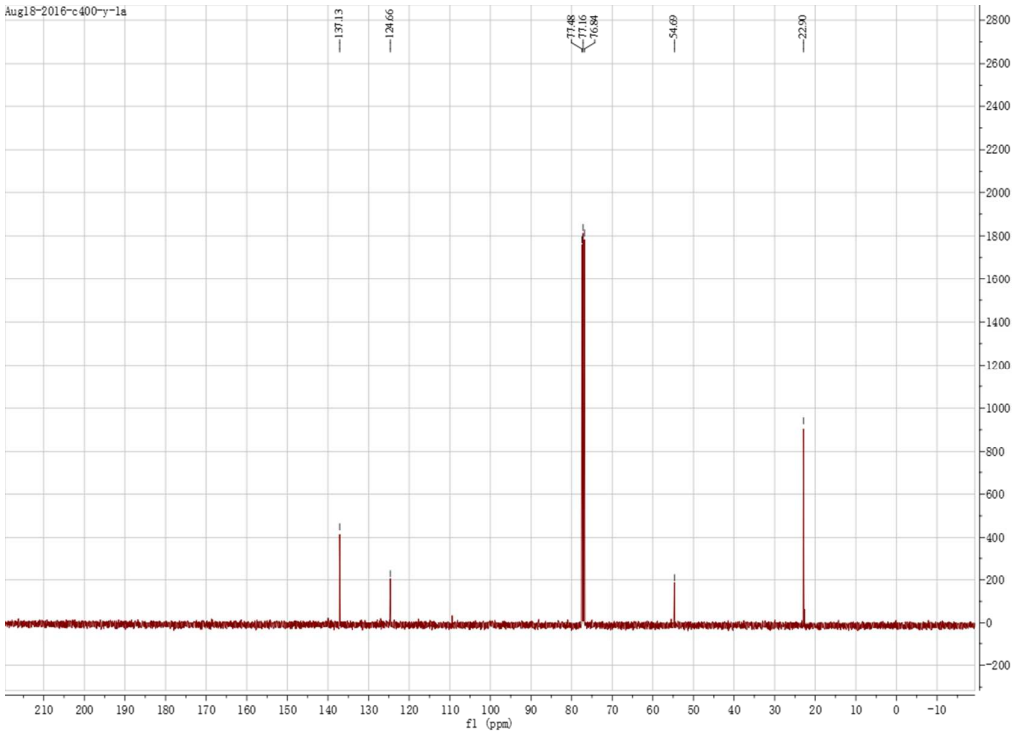
6.06
f1 (ppm)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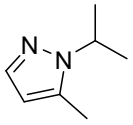
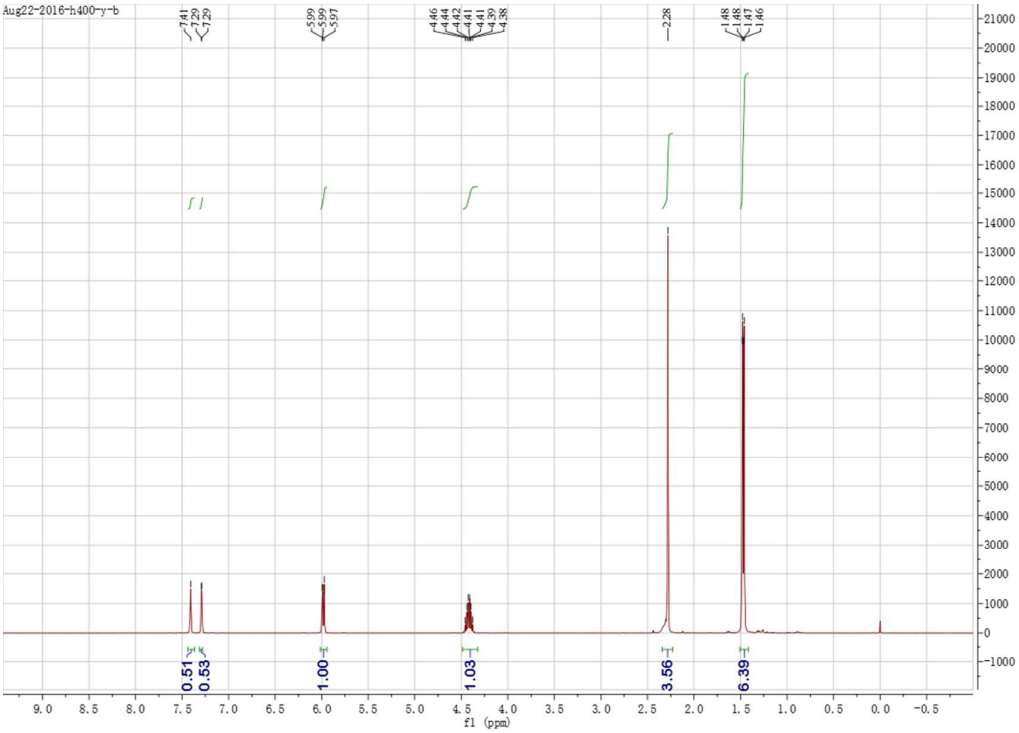
f1 (ppm)



1b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4.39
4.38
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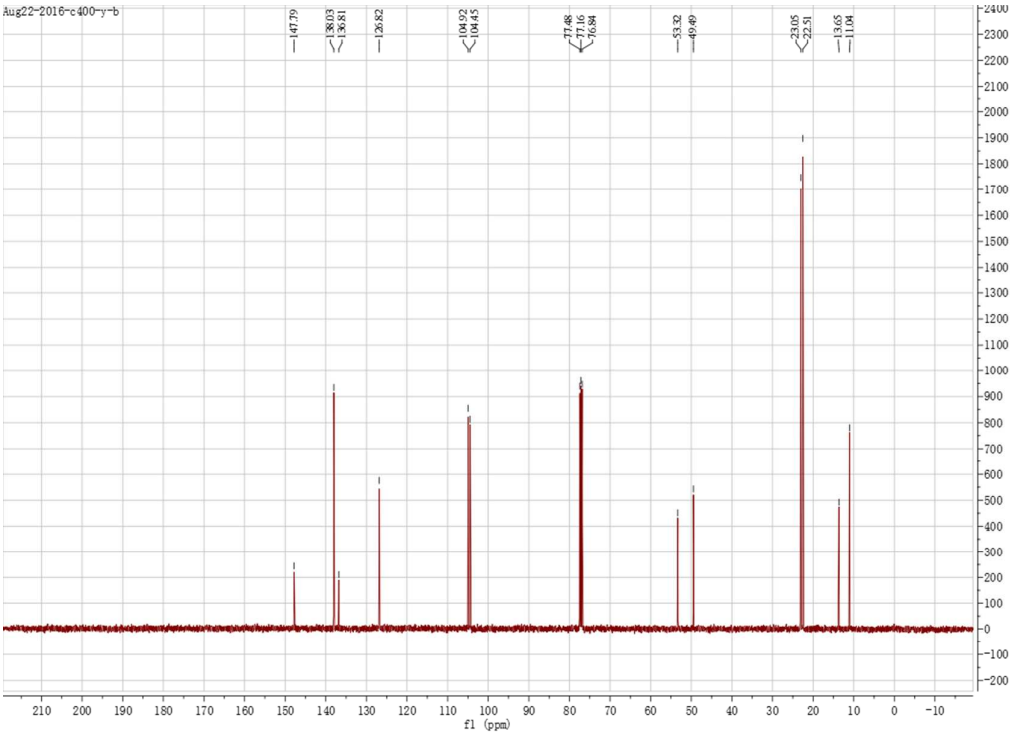
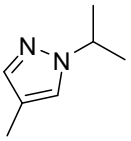
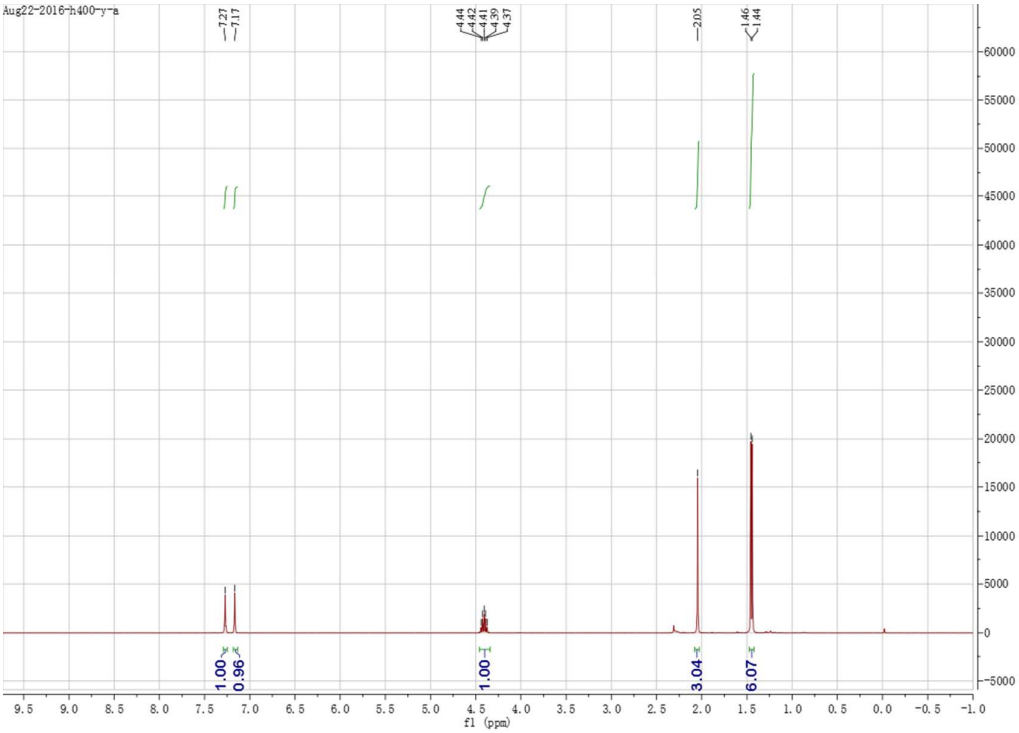
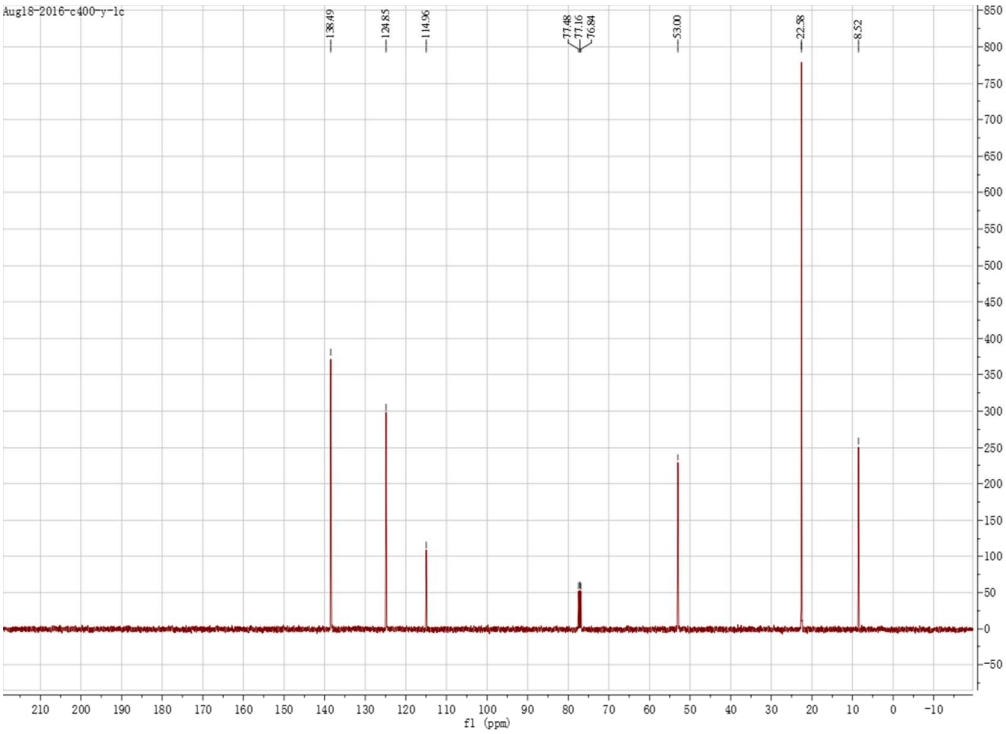
1.48
1.48
1.47
1.46
0.51
0.53
1.00
1.03
3.56
6.39
f1 (ppm)

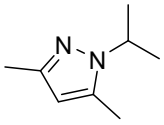

Aug22-2016-c400-y-b
147.79
138.03
136.81
126.82
104.92
104.45
77.48
77.16
76.84
53.32
49.49
23.05
22.51
13.65
11.04
f1 (ppm)



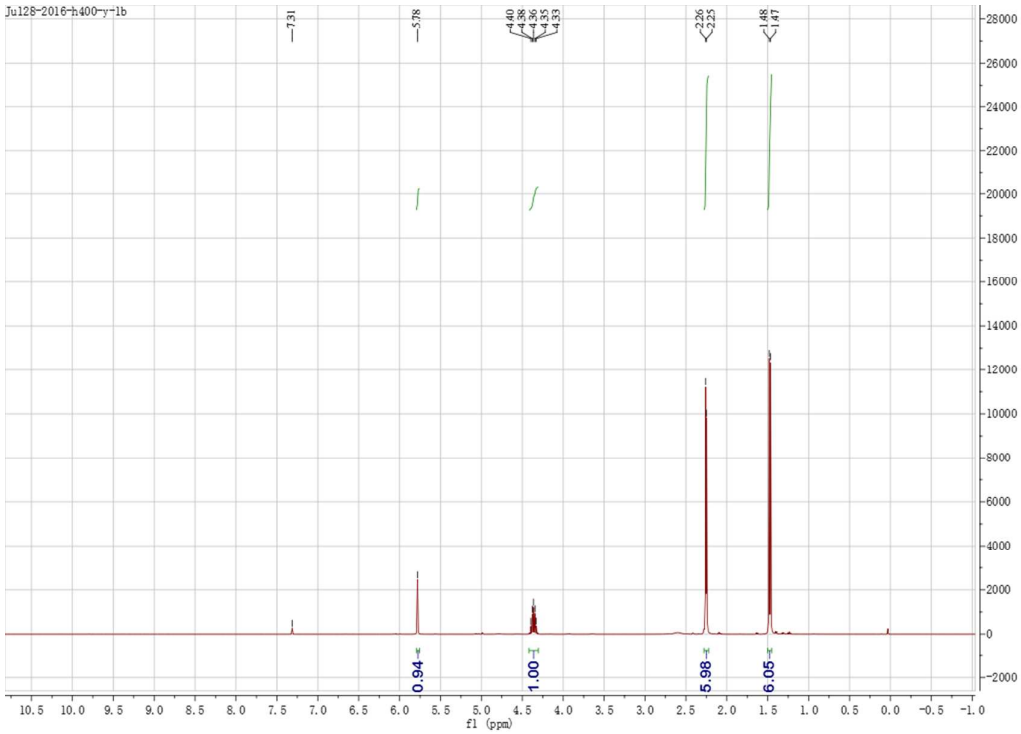
1c

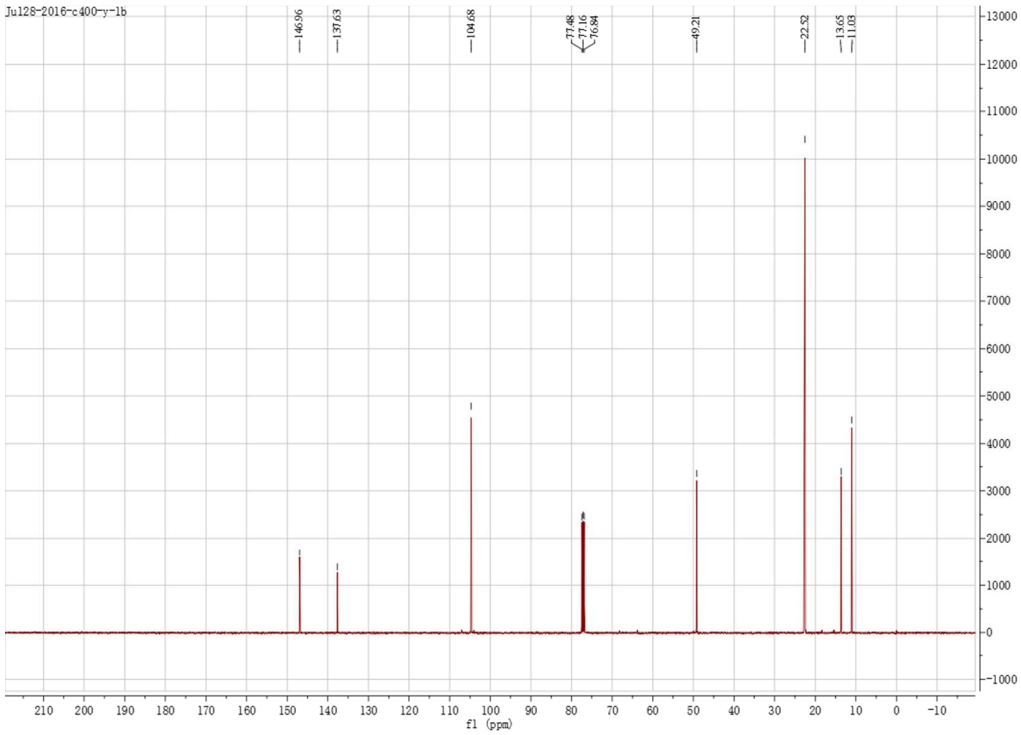

Aug22-2016-h400-y-a
7.27
7.17
4.44
4.42
4.41
4.39
4.37
2.05
1.46
1.44
1.00
0.96
1.00
3.04
6.07
f1 (ppm)

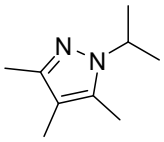

Aug18-2016-c400-y-1c
138.49
124.85
114.96
77.48
77.16
76.84
53.00
22.58
8.52
f1 (ppm)



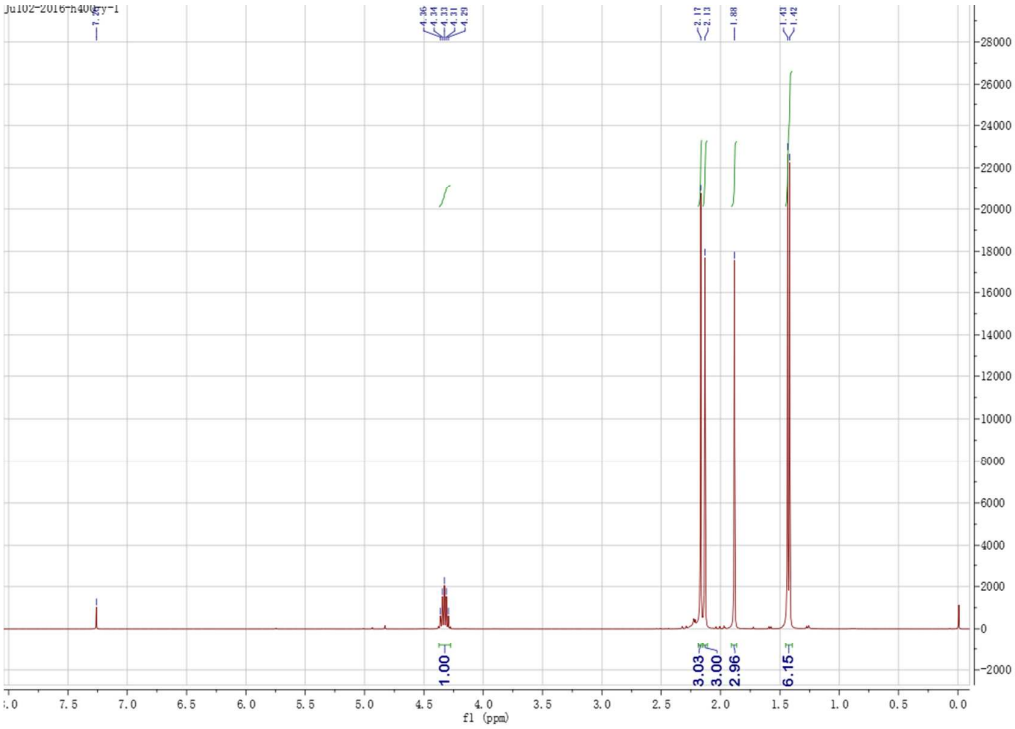
1d

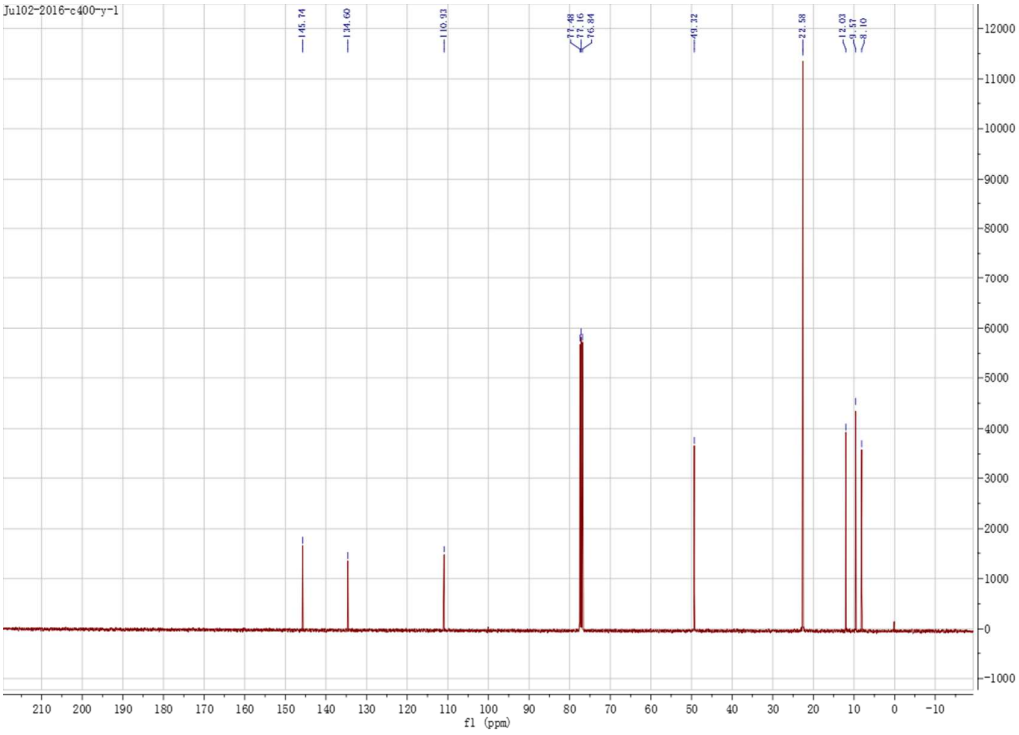

Ju128-2016-h400-y-1b
7.31
5.78
4.40
4.38
4.36
4.35
4.33
2.26
2.25
1.48
1.47
0.94
1.00
5.98
6.05
f1 (ppm)

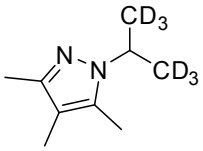

Ju128-2016-c400-y-1b
146.96
137.63
104.68
77.48
77.16
76.84
49.21
22.52
13.65
11.03
f1 (ppm)

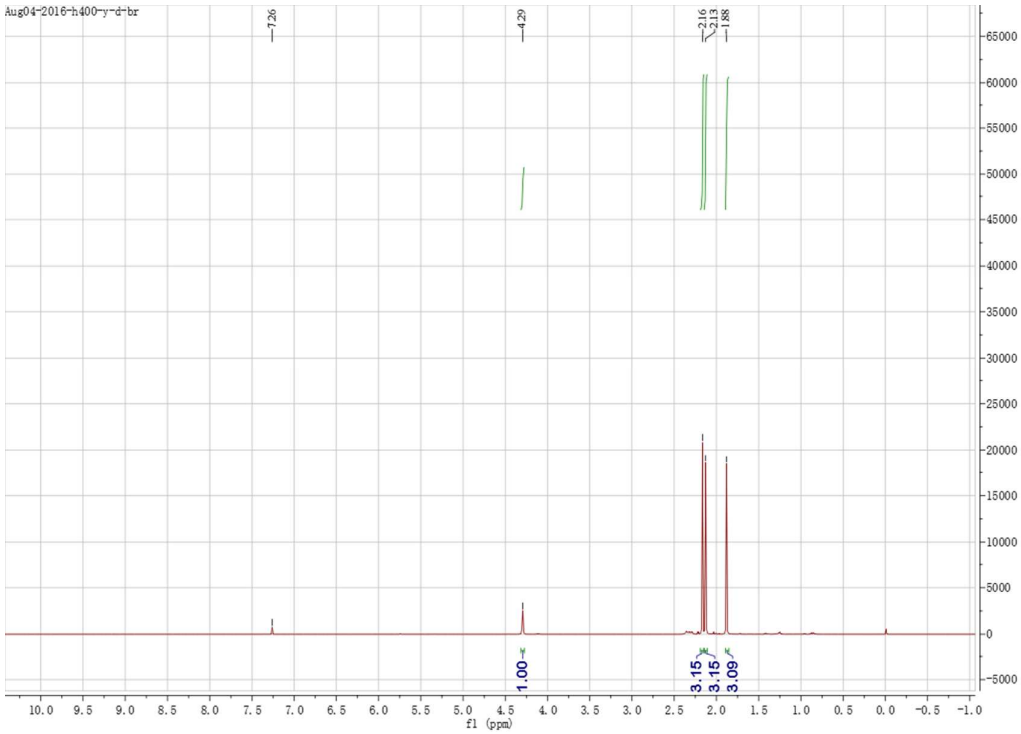


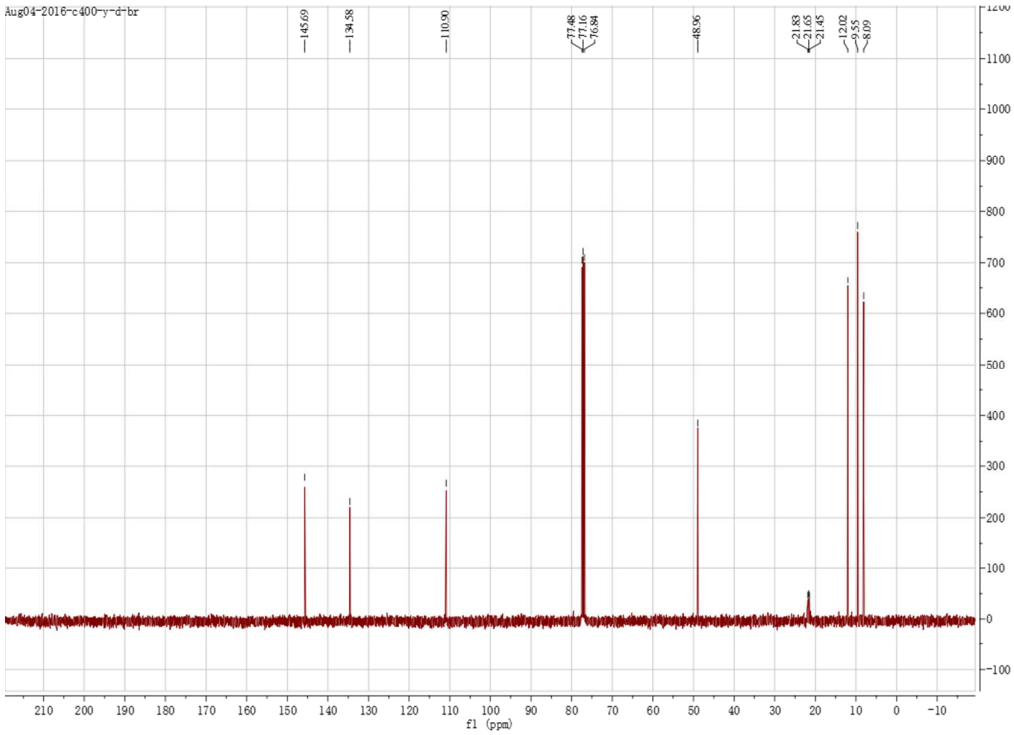
1e

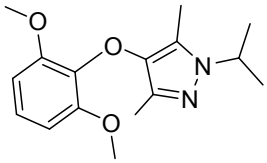

Ju102-2016-h400-y-1
4.36
4.34
4.33
4.31
4.29
2.17
2.13
1.88
1.43
1.42
1.00
3.03
3.00
2.96
6.15
f1 (ppm)


Ju102-2016-c400-y-1
145.74
134.60
110.93
77.48
77.16
76.84
49.32
22.58
12.03
10.57
8.10
f1 (ppm)

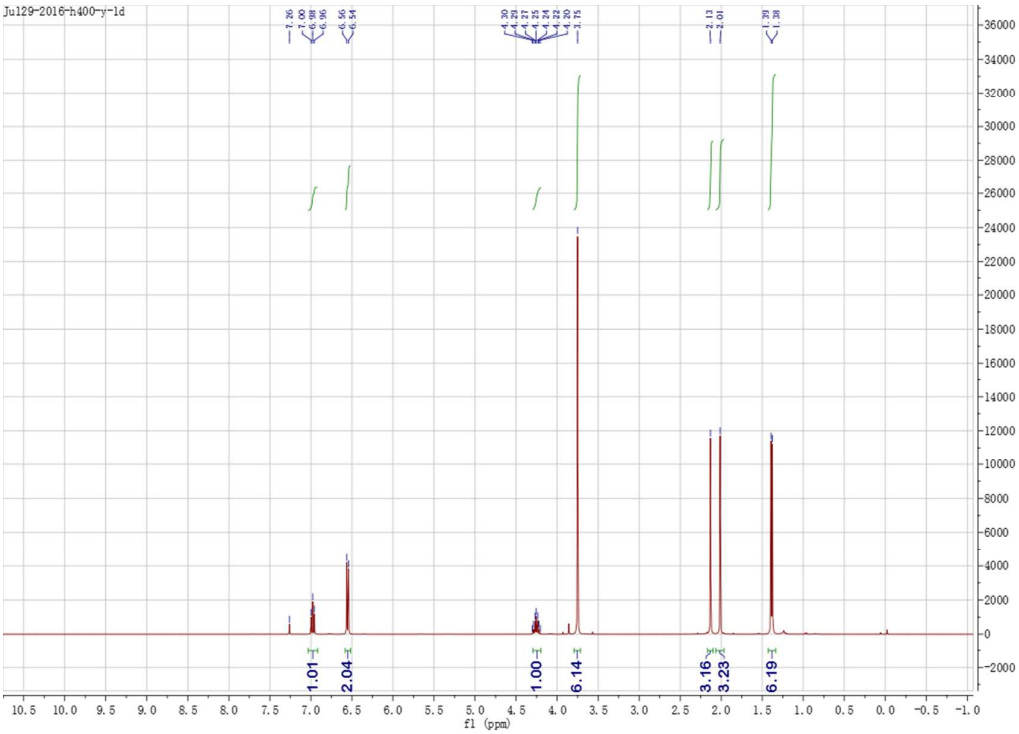

CD3
N
N
CD3

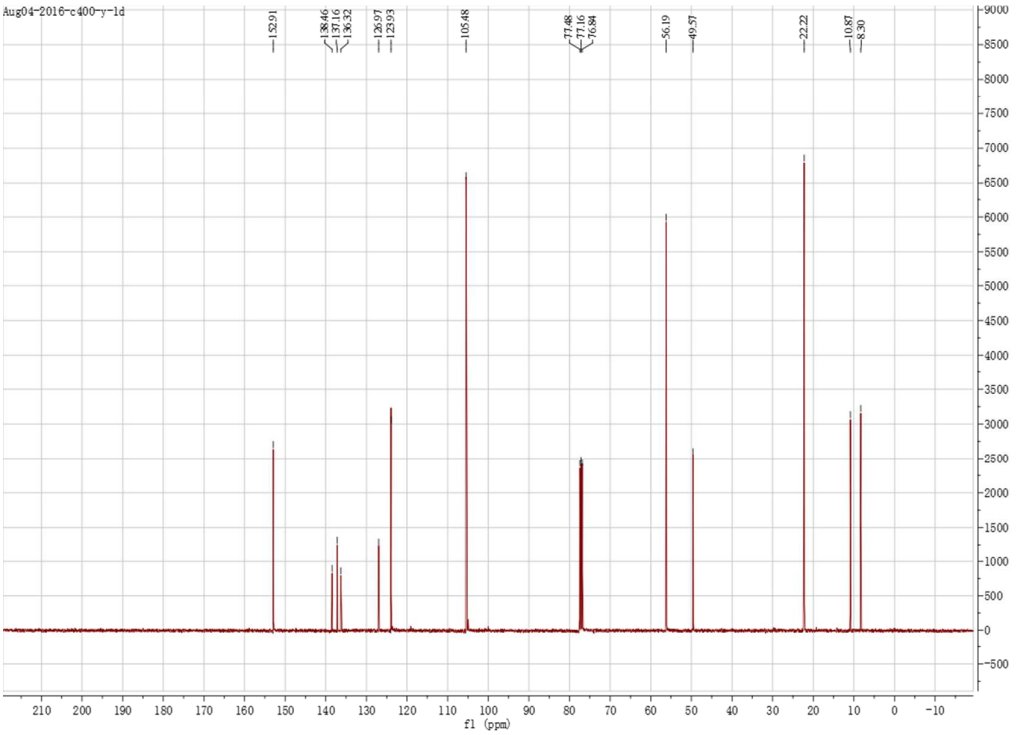

Aug04-2016-h400-y-d-br
7.26
4.29
2.16
2.13
1.88
1.00
3.15
3.15
3.09
f1 (ppm)

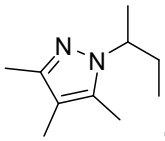

Aug04-2016-c400-y-d-br
145.69
134.58
110.90
77.48
77.16
76.84
48.96
21.83
21.65
21.45
12.02
9.55
8.09
f1 (ppm)



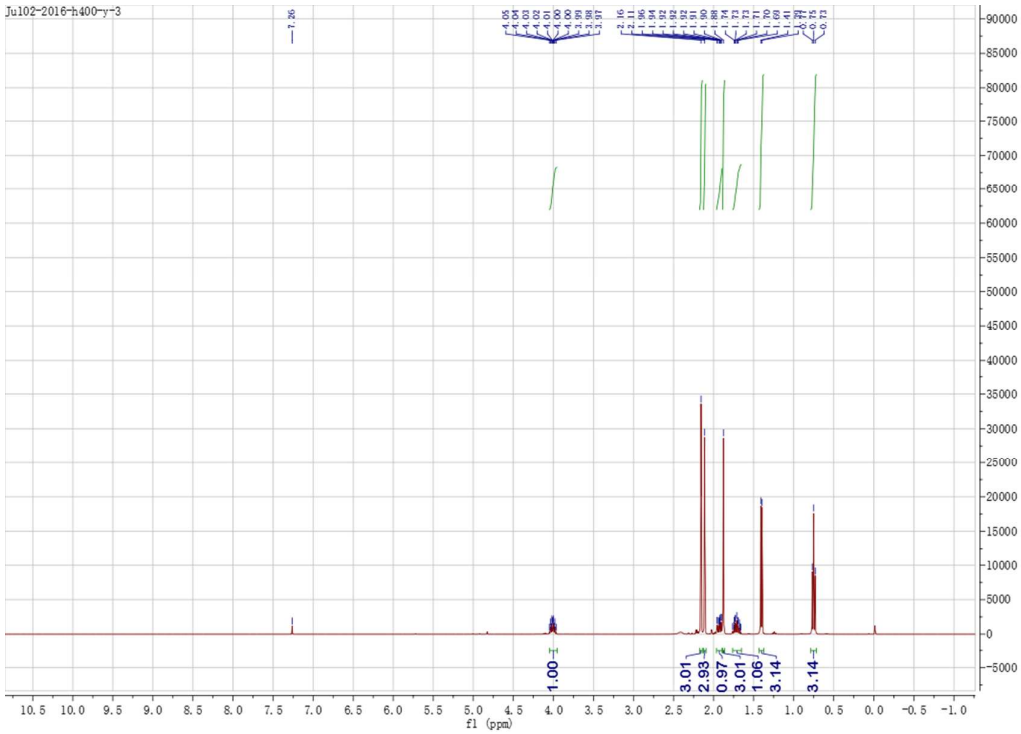
1f

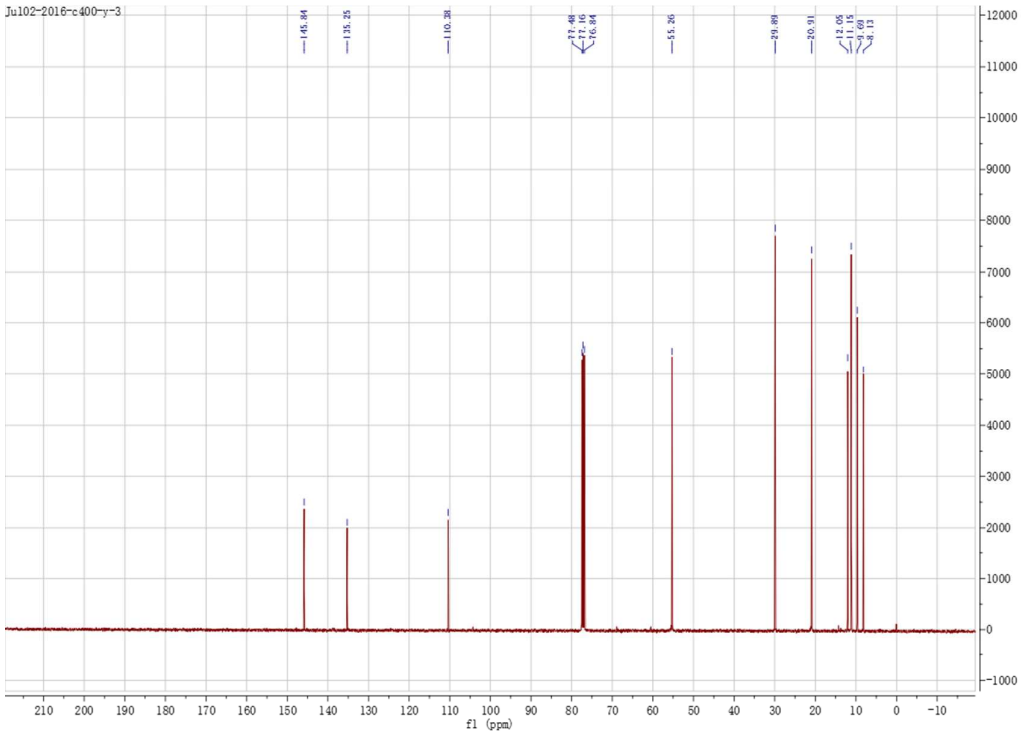

Jul29-2016-h400-y-1d
7.26
7.00
6.98
6.96
6.56
6.54
4.30
4.29
4.27
4.25
4.24
4.22
4.20
3.75
2.13
2.01
1.39
1.38
1.01
2.04
1.00
6.14
3.16
3.23
6.19
f1 (ppm)

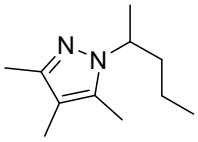

Aug04-2016-c400-y-1d
152.91
138.46
137.16
136.32
126.97
123.93
105.48
77.48
77.16
76.84
56.19
49.57
22.22
10.87
8.30
f1 (ppm)



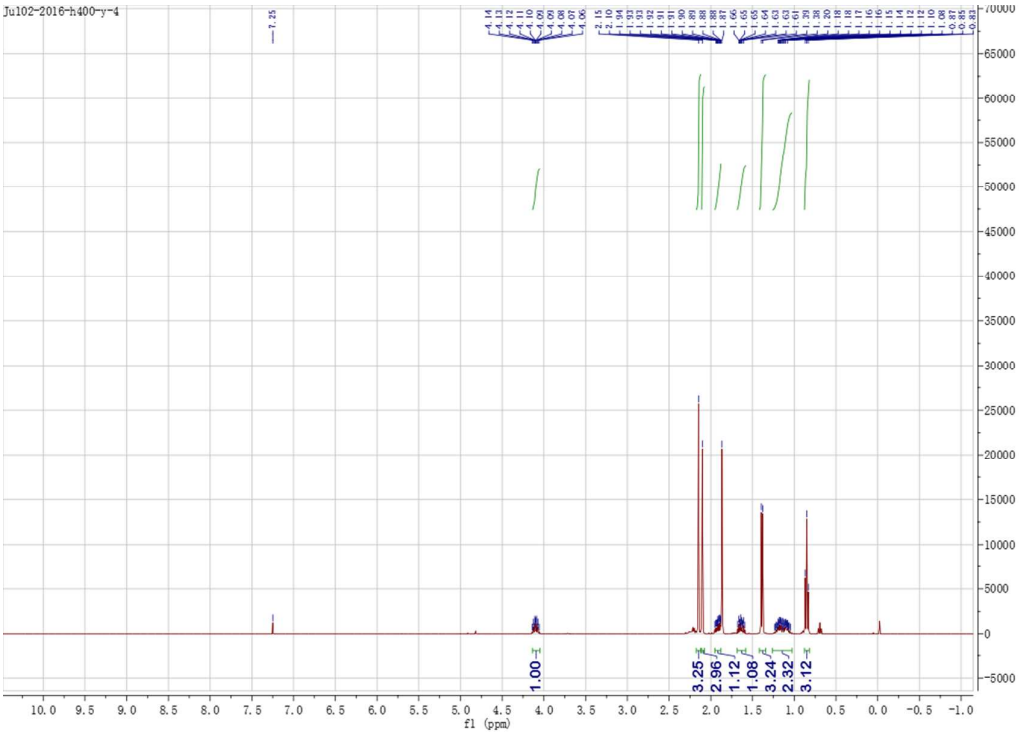
4a

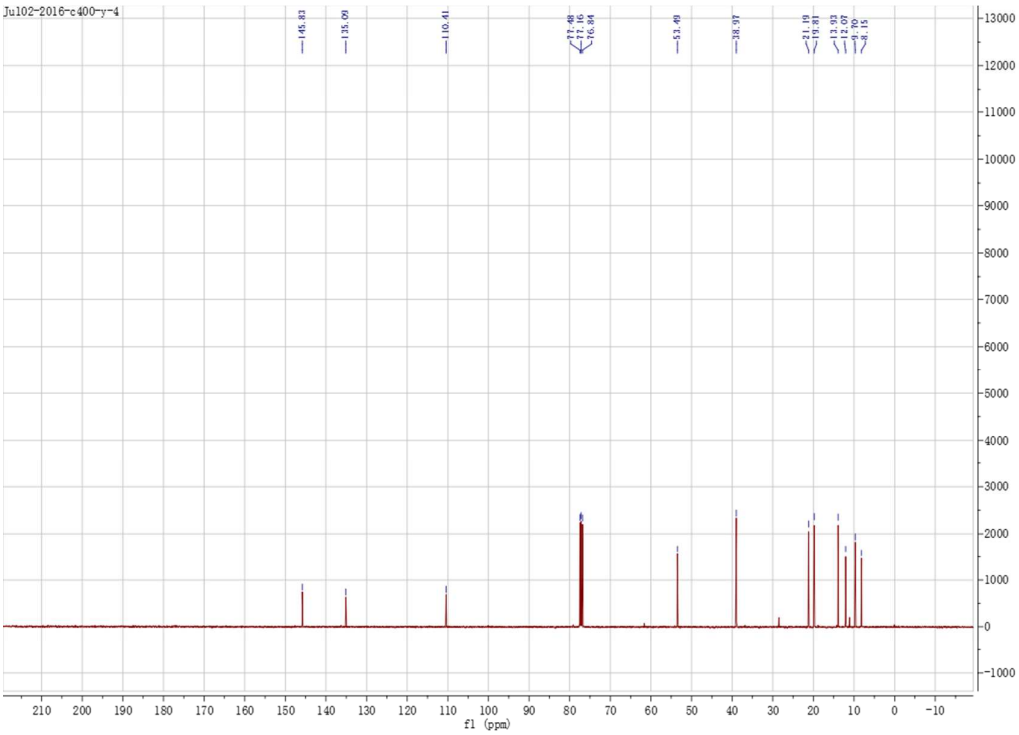

Ju102-2016-h400-y-3
7.26
1.00
3.01
2.93
0.97
3.01
1.06
3.14
3.14
f1 (ppm)

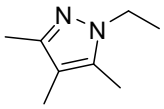

Ju102-2016-c400-y-3
145.84
135.25
110.38
77.48
77.16
76.84
55.26
29.89
20.91
12.05
11.15
9.69
8.13
f1 (ppm)



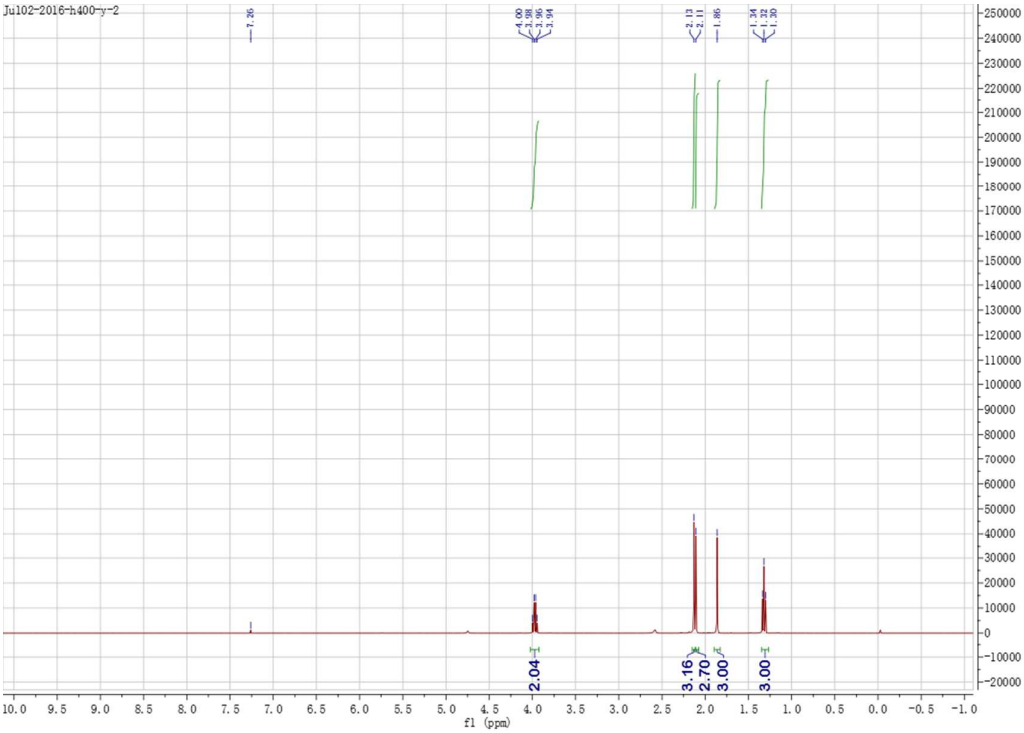
4b

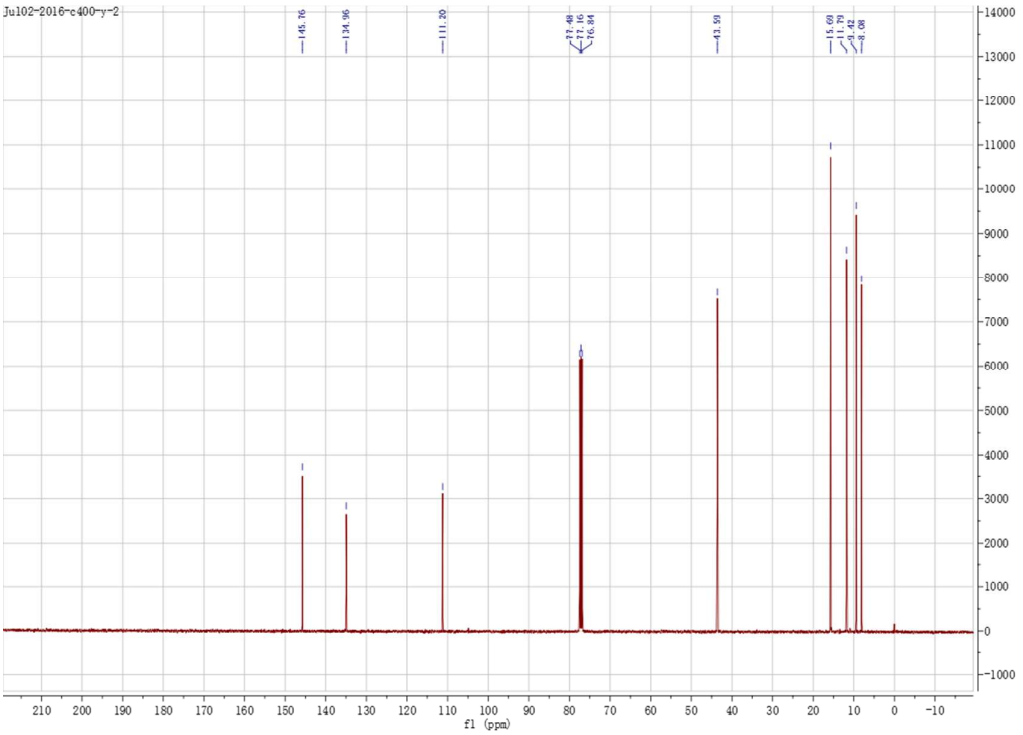

Ju102-2016-h400-y-4
7.25
1.00
3.25
2.96
1.12
1.08
3.24
2.32
3.12
f1 (ppm)

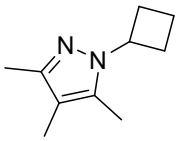

Ju102-2016-c400-y-4
145.83
135.09
110.41
77.48
77.16
76.84
53.49
38.97
21.19
19.81
13.93
12.07
11.90
8.15
f1 (ppm)



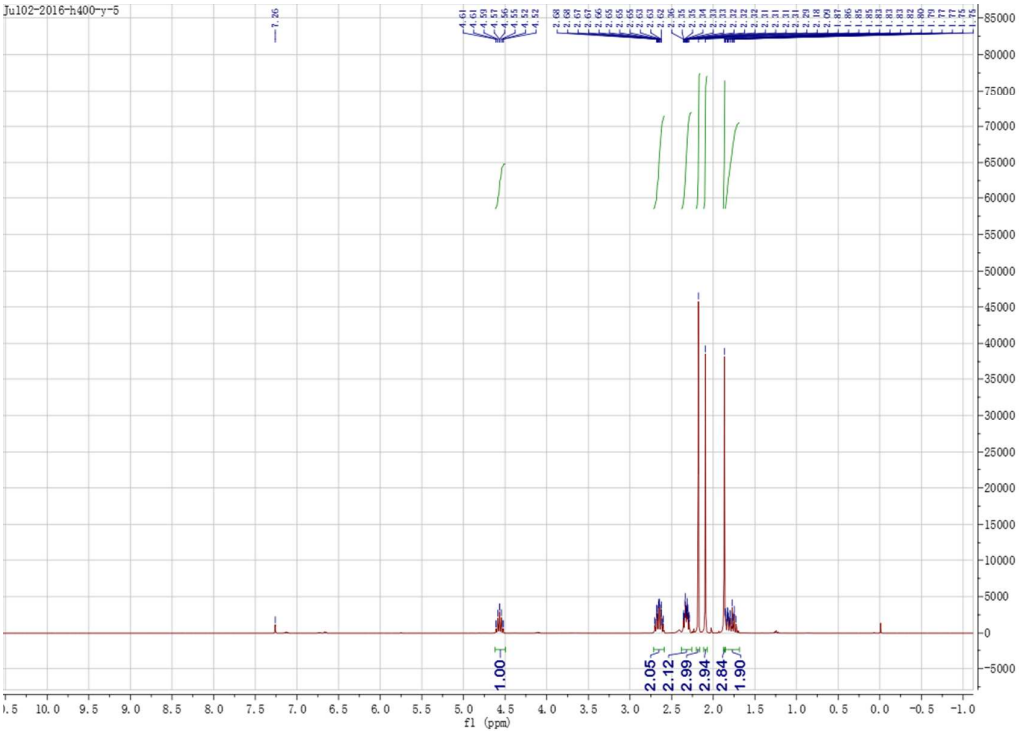
4c

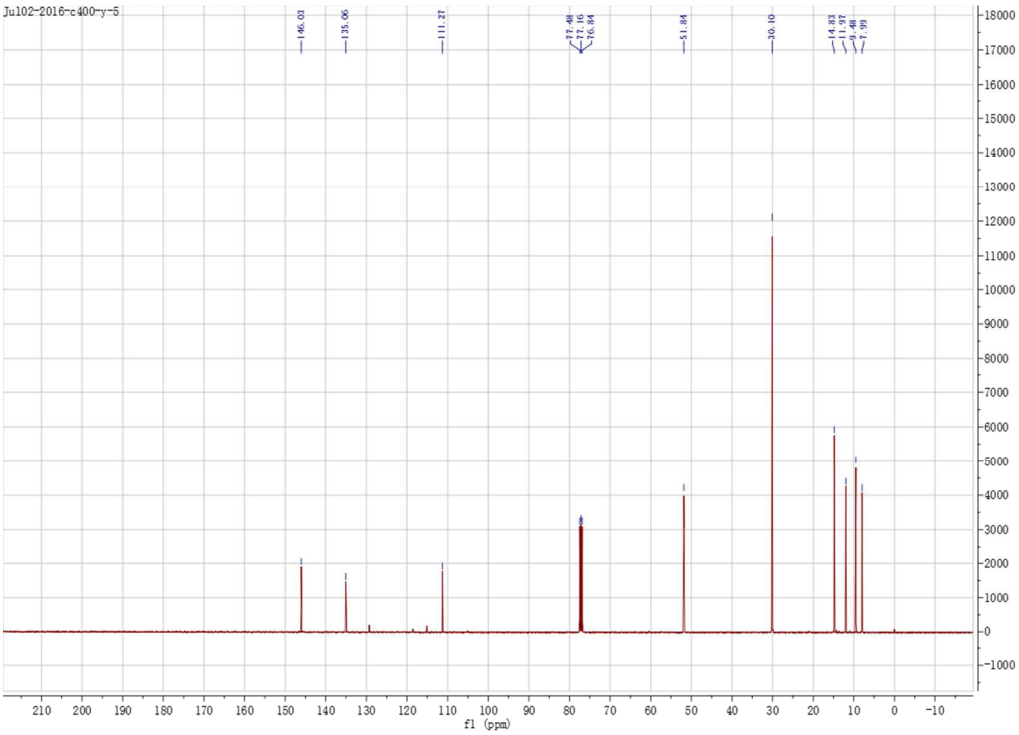

Ju102-2016-h400-y-2
7.26
4.00
3.98
3.96
3.94
2.13
2.11
1.86
1.34
1.32
1.30
2.04
3.16
2.70
3.00
3.00
f1 (ppm)

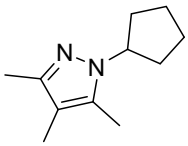

Ju102-2016-c400-y-2
145.76
134.96
111.20
77.48
77.16
76.84
43.59
15.69
11.79
9.42
8.06
f1 (ppm)



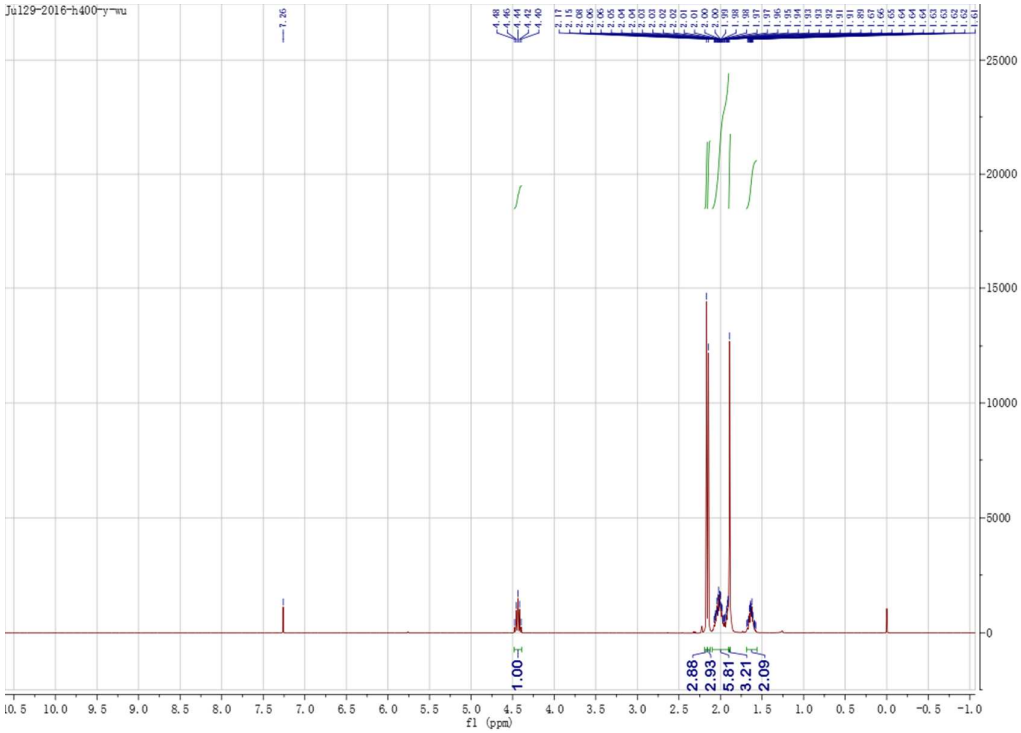
4d

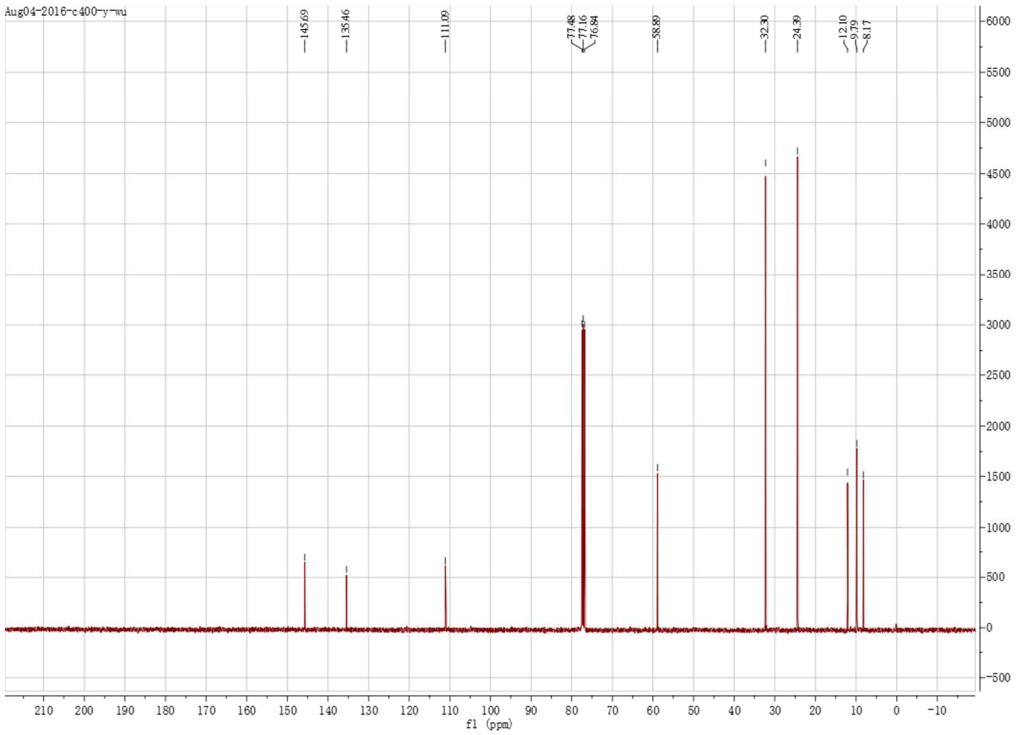

Ju102-2016-h400-y-5
7.26
1.00
2.05
2.12
2.99
2.94
2.84
1.90
f1 (ppm)

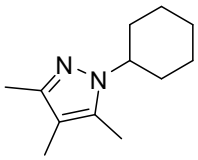

Ju102-2016-c400-y-5
146.03
135.06
111.27
77.48
77.16
76.84
51.84
30.10
14.83
11.37
10.84
7.99
f1 (ppm)



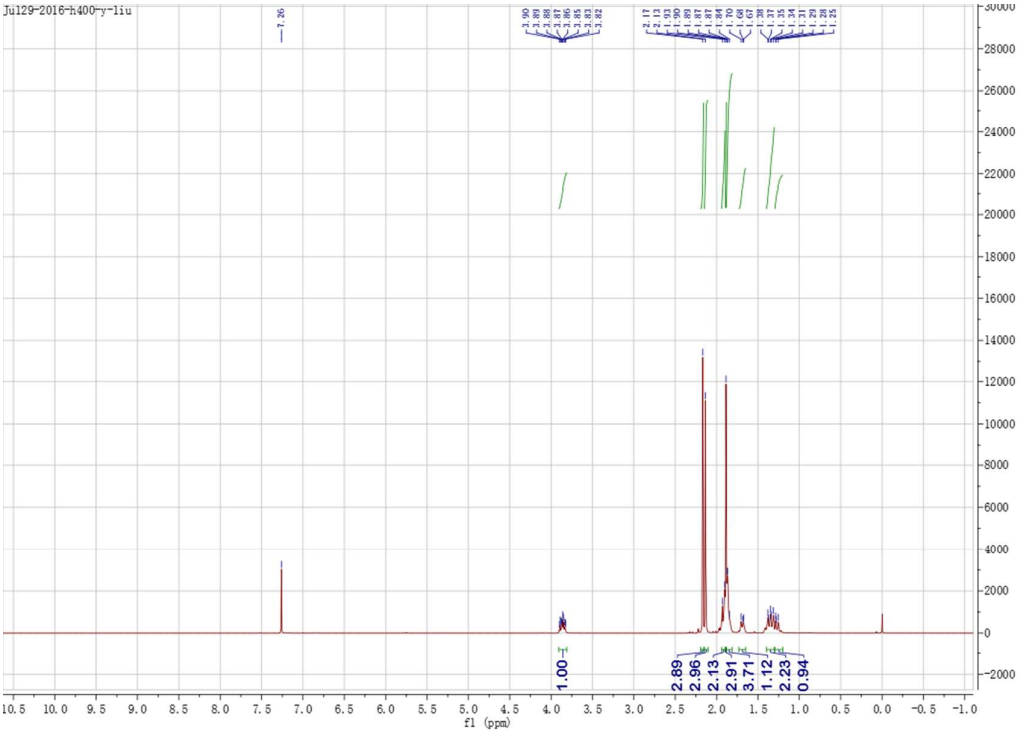
4e

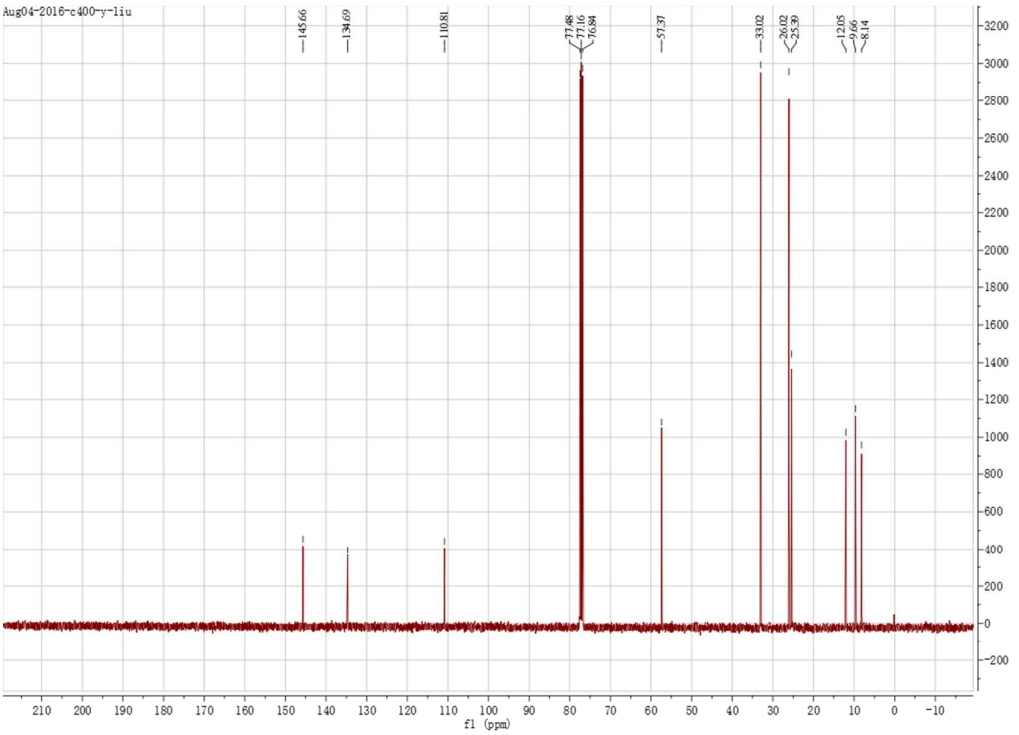

Jul29-2016-h400-y-wu
7.26
4.48
4.46
4.44
4.42
4.40
2.17
2.15
2.08
2.06
2.05
2.04
2.03
2.02
2.01
2.00
1.99
1.98
1.97
1.96
1.95
1.94
1.93
1.92
1.91
1.89
1.67
1.65
1.64
1.63
1.62
1.61
1.00
2.88
2.93
5.81
3.21
2.09
f1 (ppm)

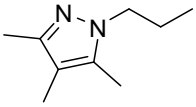

Aug04-2016-c400-y-wu
145.69
135.46
111.09
77.48
77.16
76.84
58.89
32.30
24.39
12.10
9.79
8.17
f1 (ppm)



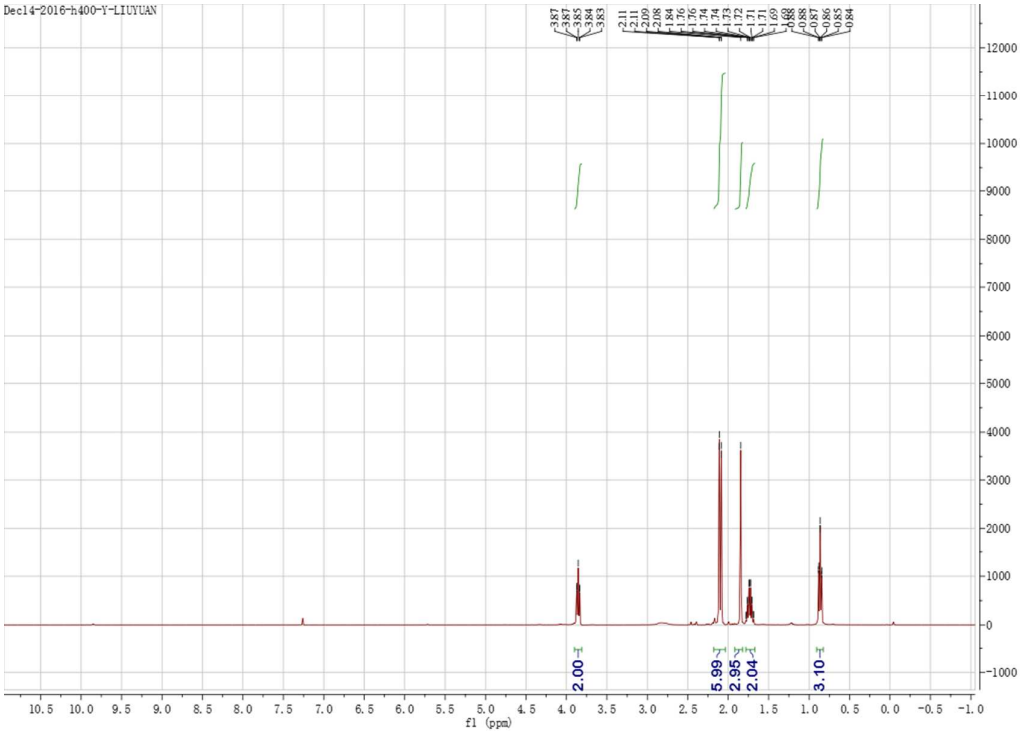
4f

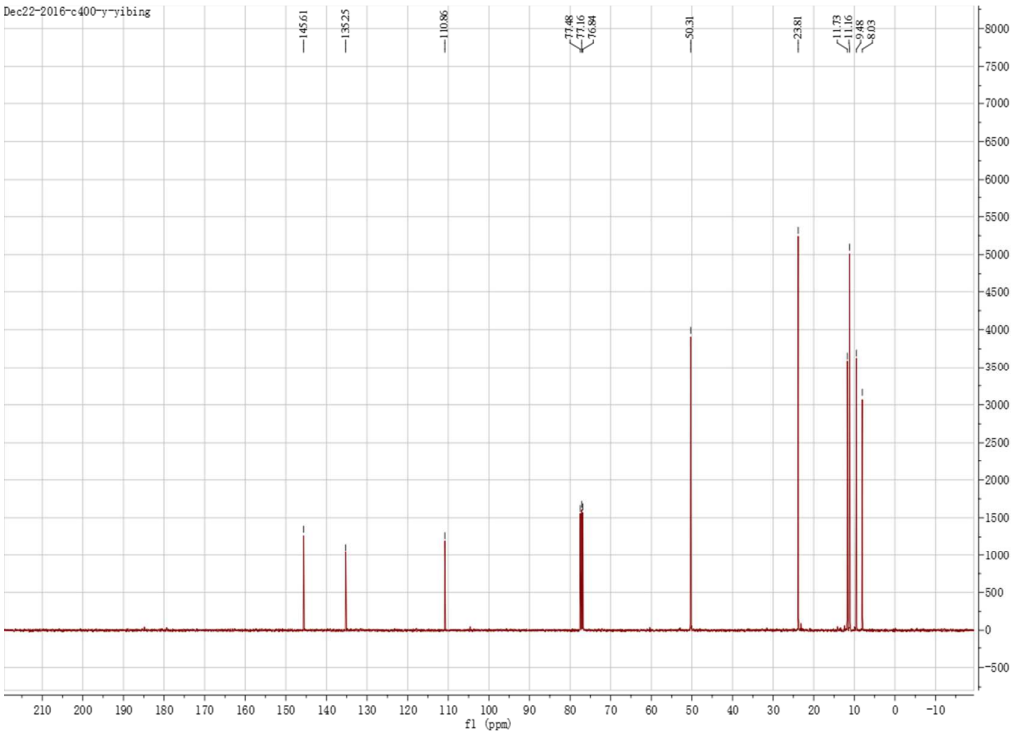

Jul29-2016-h400-y-liu
7.26
1.00
2.89
2.96
2.13
2.91
3.71
1.12
2.23
0.94
f1 (ppm)

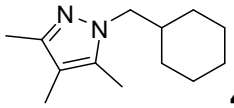

Aug04-2016-c400-y-liu
145.66
134.69
110.81
77.48
77.16
76.84
57.57
33.02
26.02
25.39
12.05
9.66
8.14
f1 (ppm)



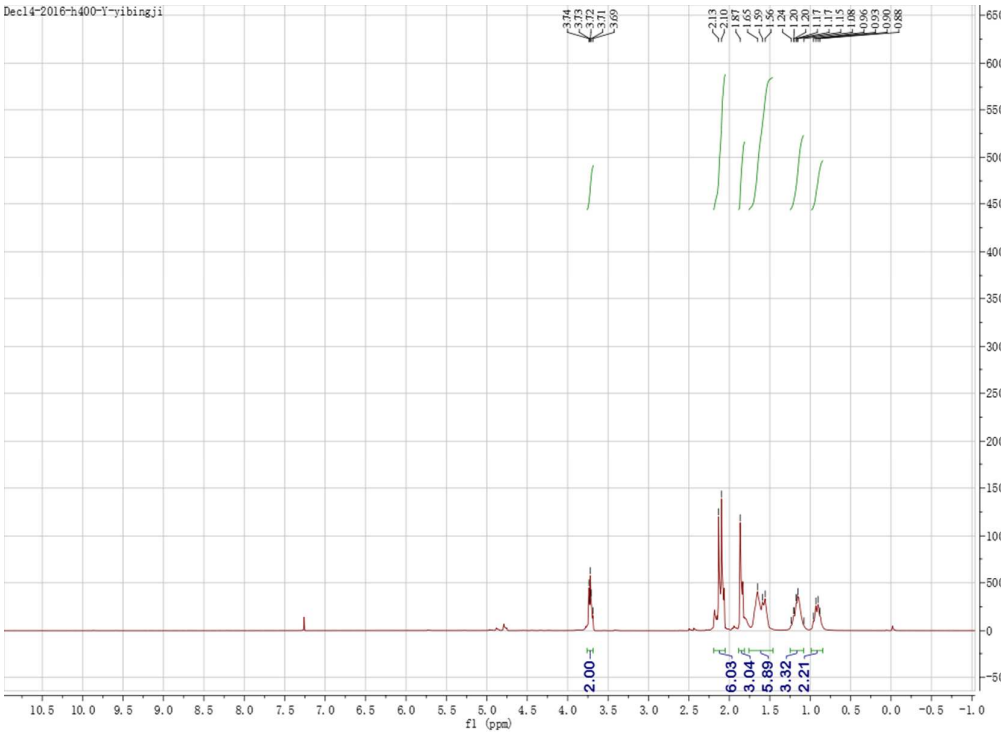
4g

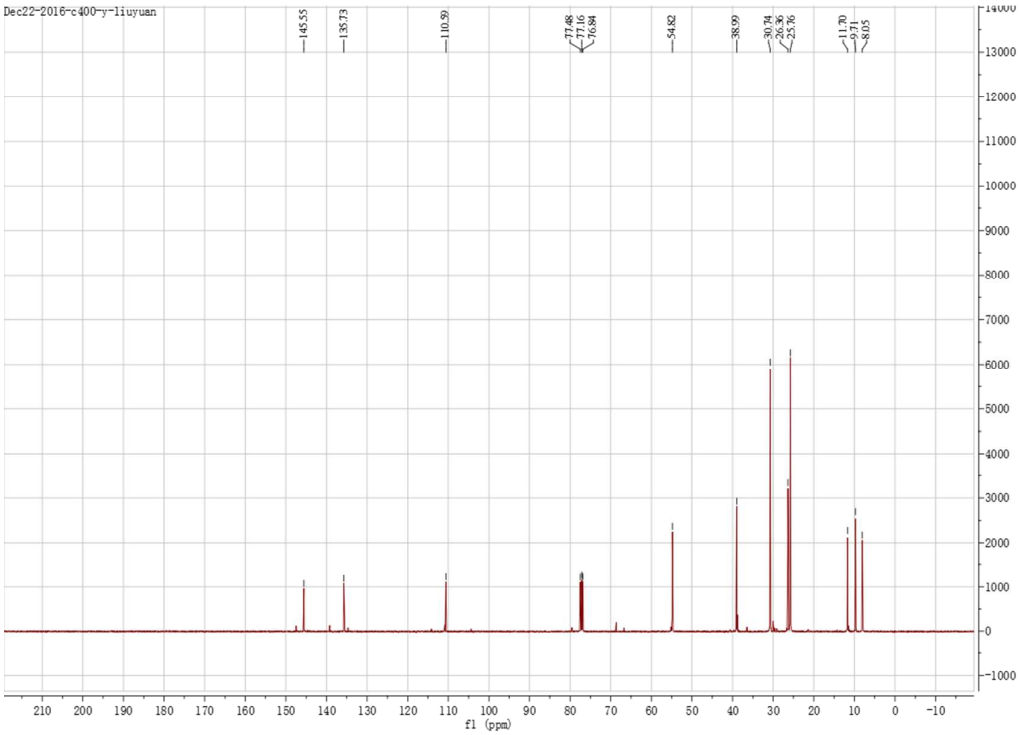

Dec14-2016-h400-Y-LIUYUAN
2.00
5.99
2.95
2.04
3.10
f1 (ppm)

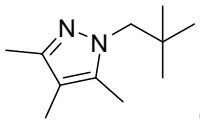

Dec22-2016-c400-y-yibing
145.61
135.25
110.86
77.48
77.16
76.84
50.31
23.81
11.73
11.16
9.48
8.03
f1 (ppm)



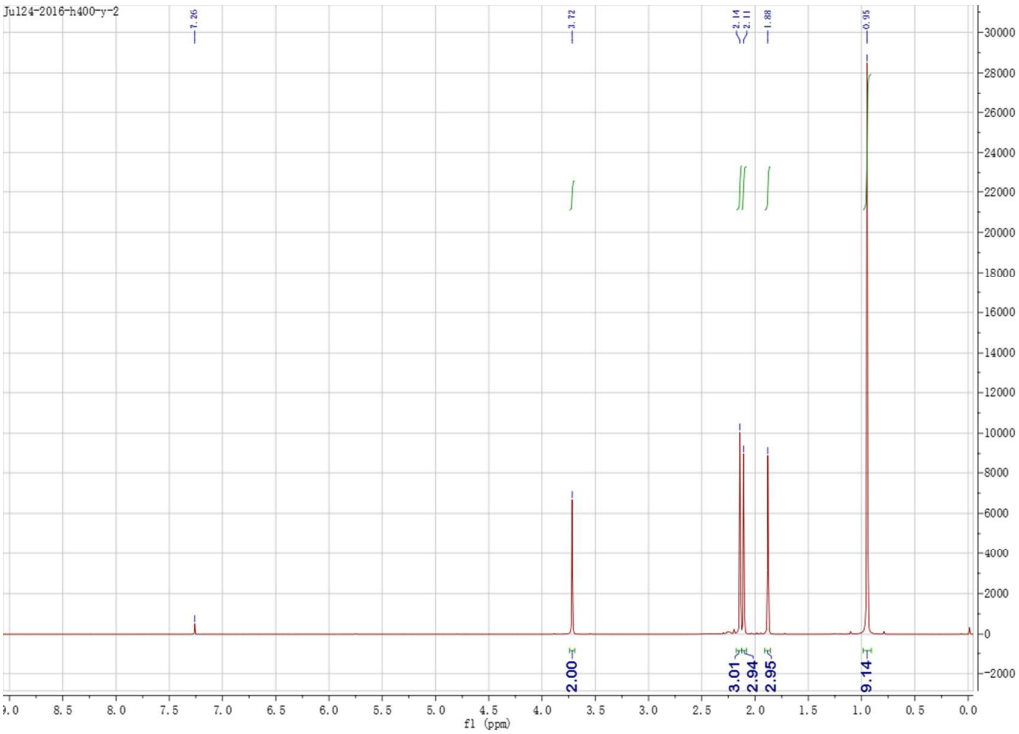
4h

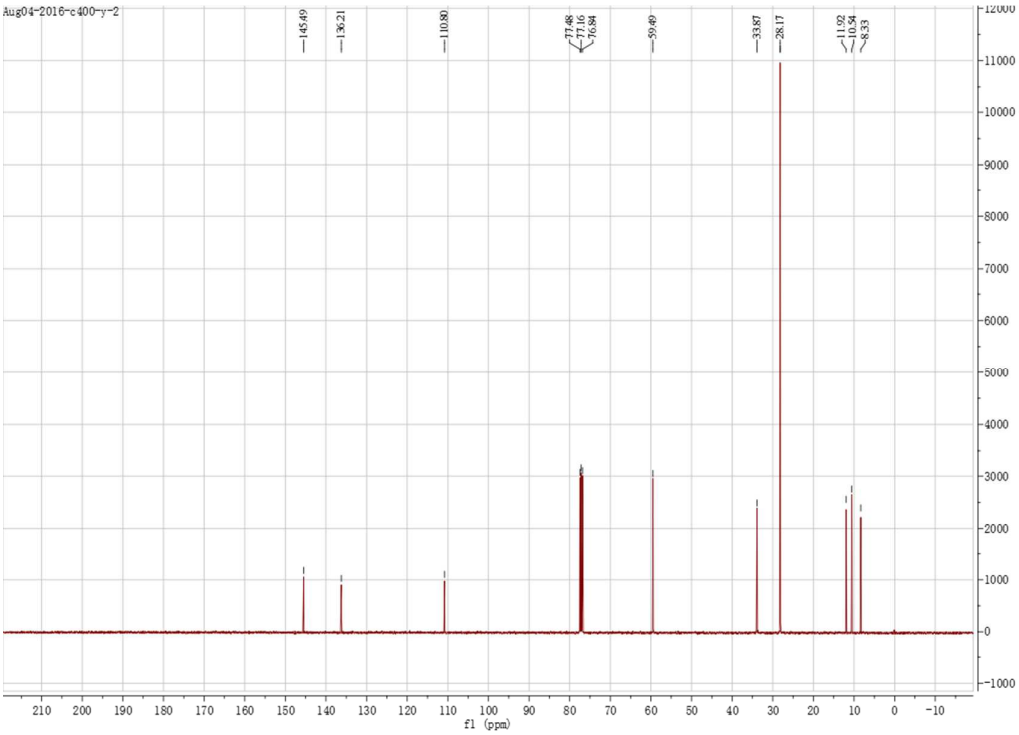

Dec14-2016-h400-Y-yibingji
3.74
3.73
3.72
3.71
3.69
2.13
2.10
1.87
1.65
1.59
1.56
1.24
1.20
1.20
1.17
1.17
1.17
1.15
1.08
0.96
0.93
0.90
0.90
0.88
2.00
6.03
3.04
5.89
3.32
2.21
f1 (ppm)

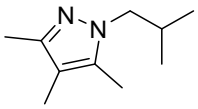

Dec22-2016-c400-y-liuyuan
145.55
135.73
110.59
77.48
77.16
76.84
54.82
38.99
30.74
26.36
25.76
11.70
9.71
8.05
f1 (ppm)



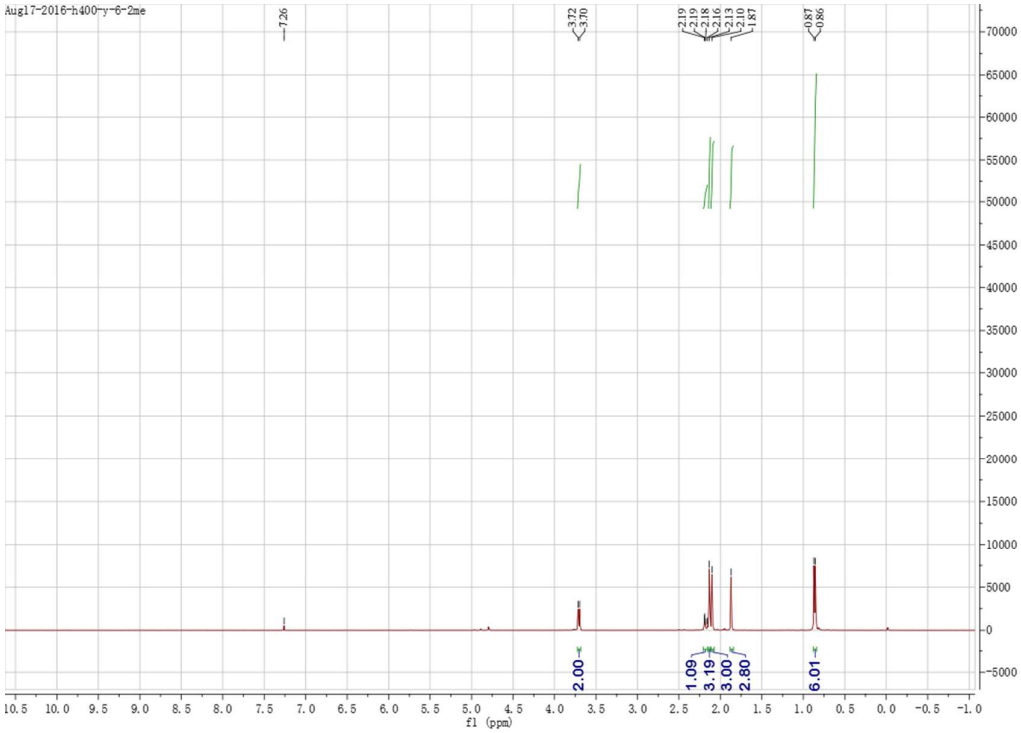
4i

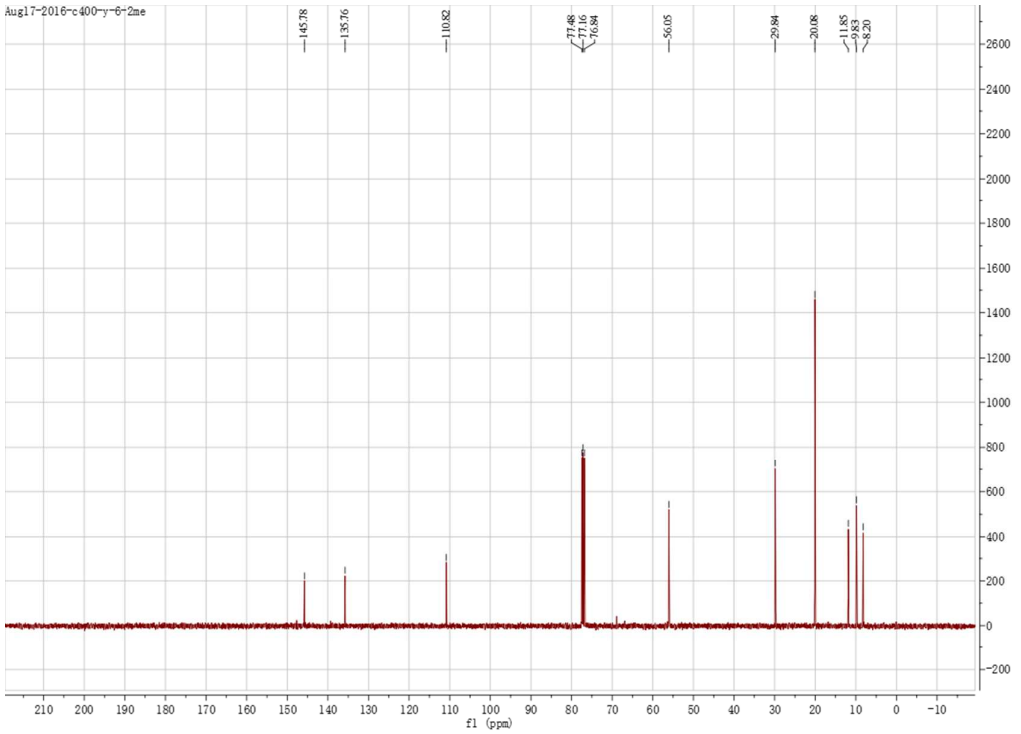

Jul24-2016-h400-y-2
7.26
3.72
2.14
2.11
1.88
0.95
2.00
3.01
2.94
2.95
9.14
f1 (ppm)

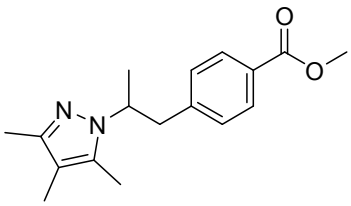

Aug04-2016-c400-y-2
145.49
136.21
110.80
77.48
77.16
76.84
59.49
33.87
28.17
11.92
10.54
8.33
f1 (ppm)



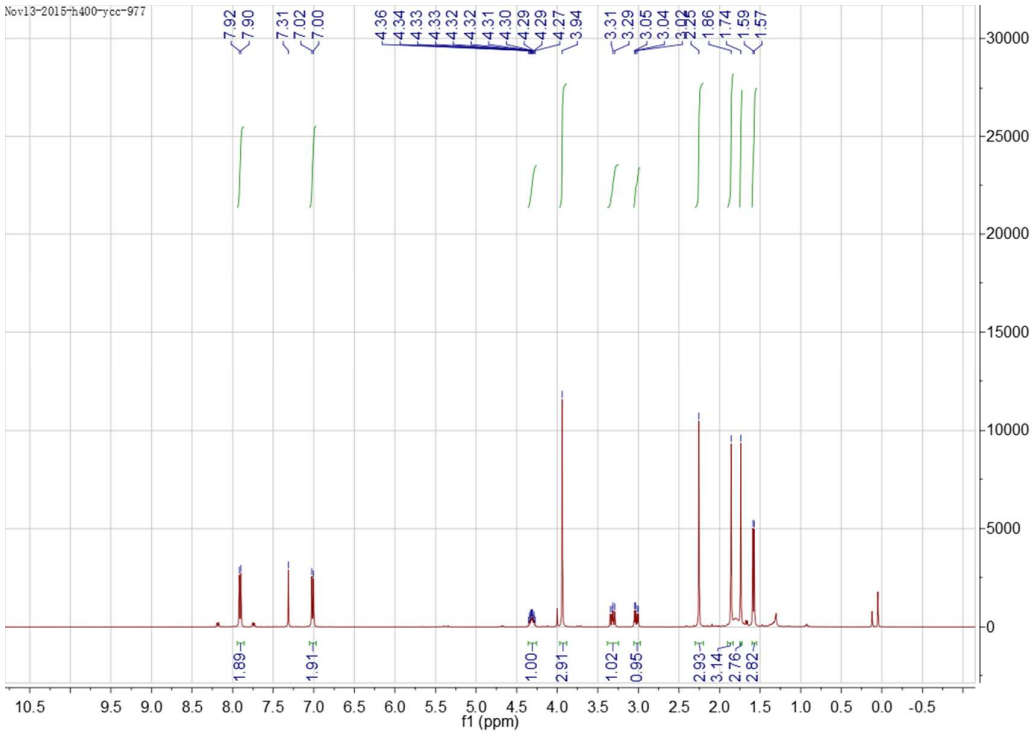
4j

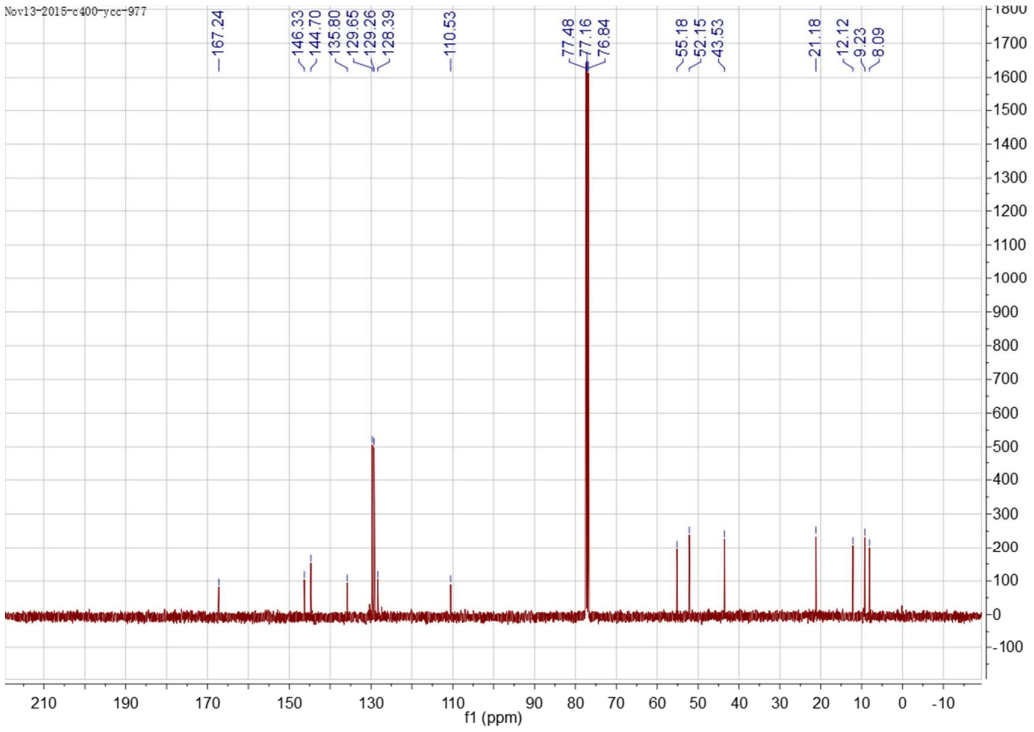

Aug17-2016-h400-y-6-2me
7.26
3.72
3.70
2.19
2.19
2.18
2.16
2.13
2.10
1.87
0.87
0.86
2.00
1.09
3.19
3.00
2.80
6.01
f1 (ppm)

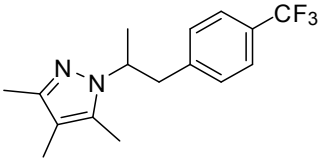

Aug17-2016-c400-y-6-2me
145.78
135.76
110.82
77.48
77.16
76.84
56.05
29.84
20.08
11.85
9.83
8.20
f1 (ppm)



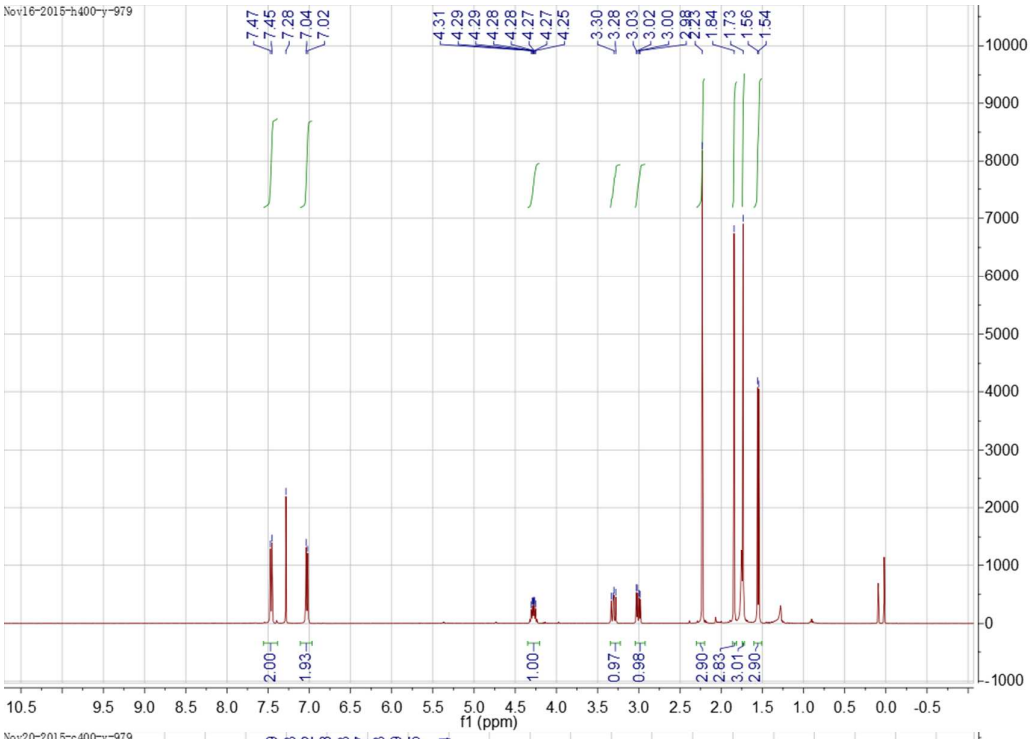
3g

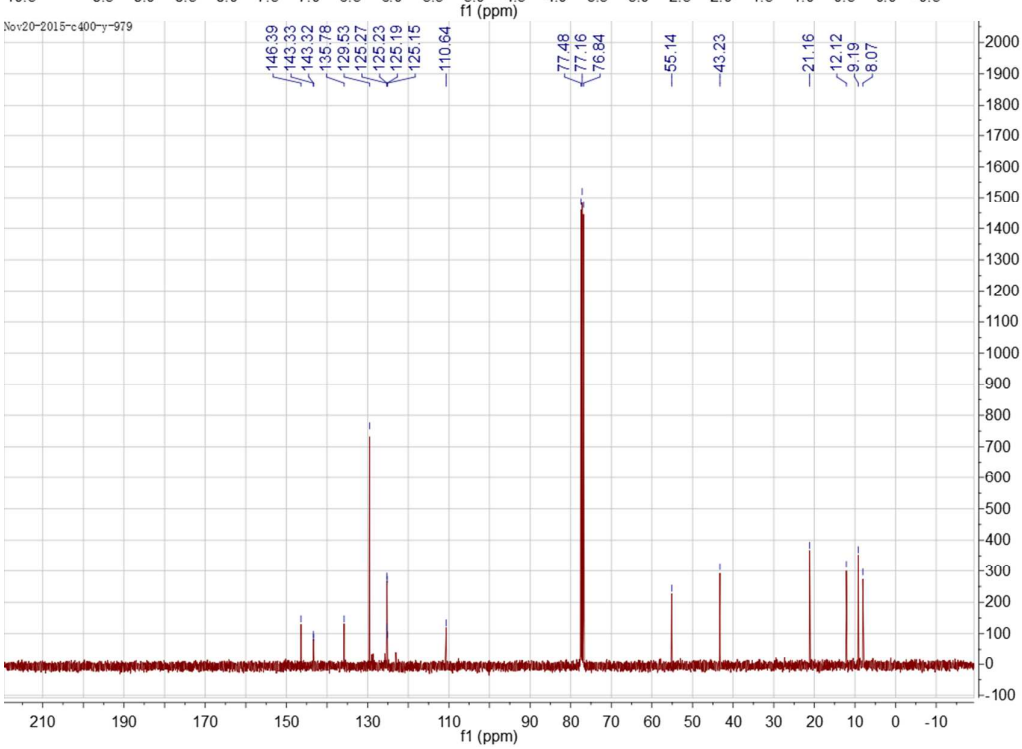

Nov13-2015-h400-ycc-977
7.92
7.90
7.31
7.02
7.00
4.36
4.34
4.33
4.33
4.32
4.32
4.31
4.30
4.29
4.29
4.27
3.94
3.31
3.29
3.05
3.04
2.25
1.86
1.74
1.59
1.57
1.89
1.91
1.00
2.91
1.02
0.95
2.93
3.14
2.76
2.82
f1 (ppm)

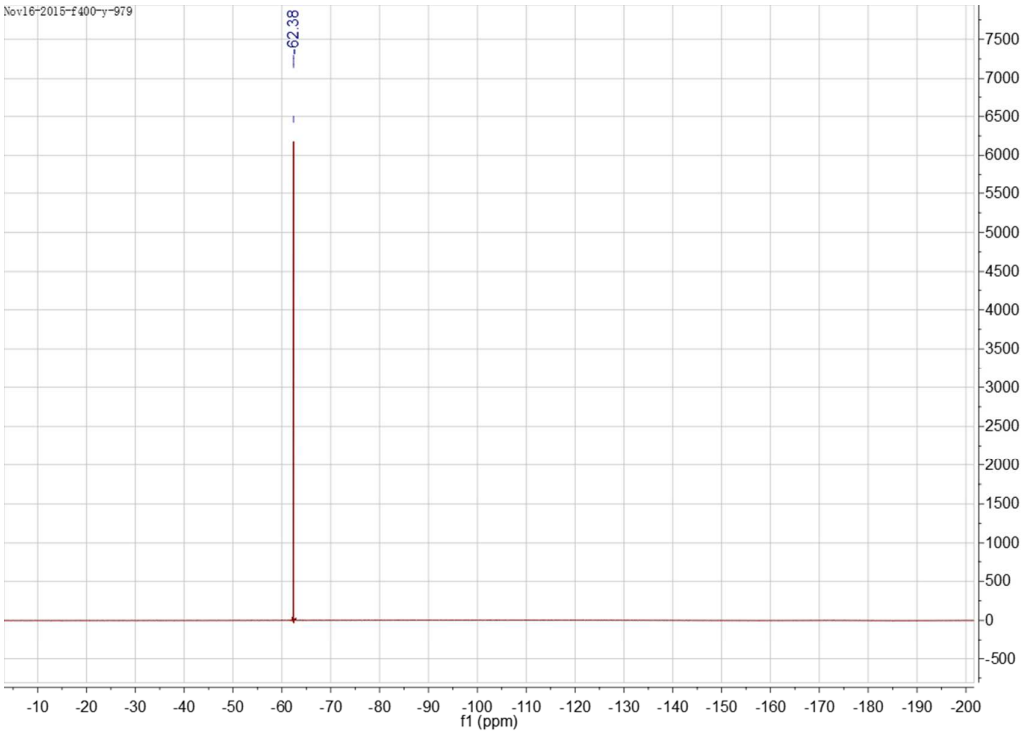

Nov13-2015-c400-ycc-977
167.24
146.33
144.70
135.80
129.65
129.26
128.39
110.53
77.48
77.16
76.84
55.18
52.15
43.53
21.18
12.12
9.23
8.09
f1 (ppm)

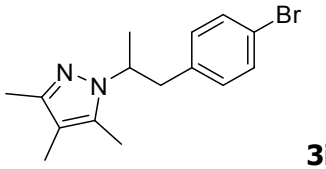

CF3
N
N

3h

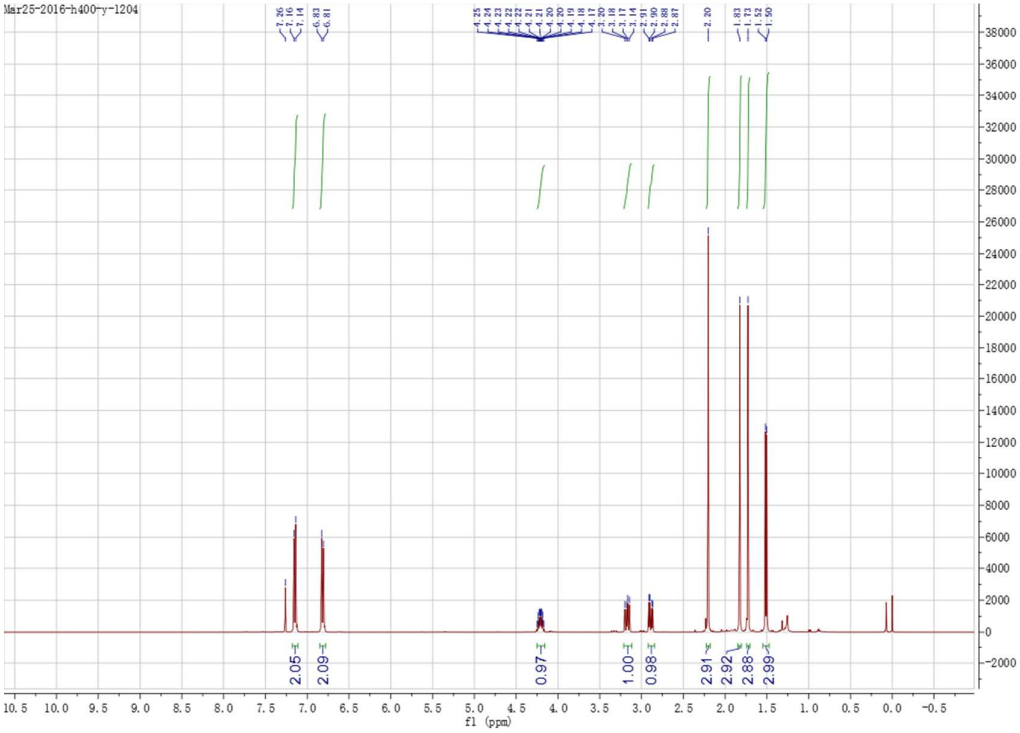

Nov16-2015-h400-y-979
7.47
7.45
7.28
7.04
7.02
4.31
4.29
4.29
4.28
4.28
4.27
4.27
4.25
3.30
3.28
3.03
3.02
3.00
2.98
2.23
1.84
1.73
1.56
1.54
2.00
1.93
1.00
0.97
0.98
2.90
2.83
3.01
2.90
f1 (ppm)

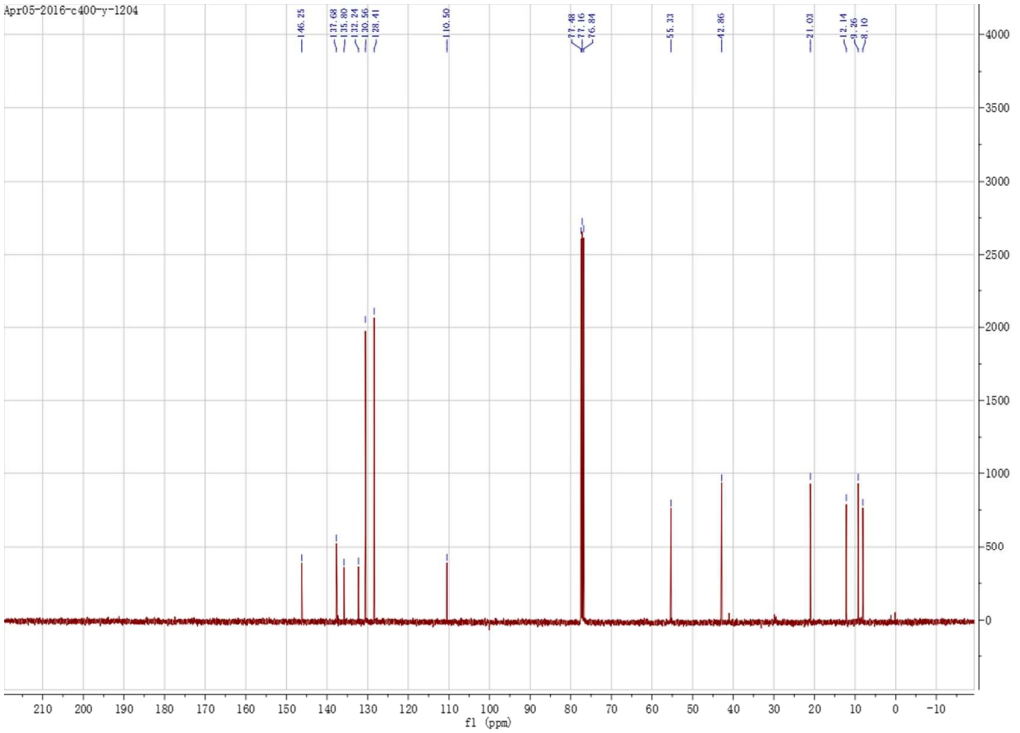

Nov20-2015-c400-y-979
146.39
143.33
143.32
135.78
129.53
125.27
125.23
125.19
125.15
110.64
77.48
77.16
76.84
55.14
43.23
21.16
12.12
9.19
8.07
f1 (ppm)

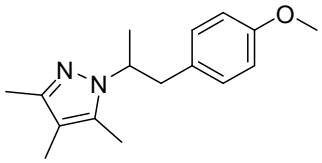

Nov16-2015-f400-y-979
-62.38
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


Br
N
N

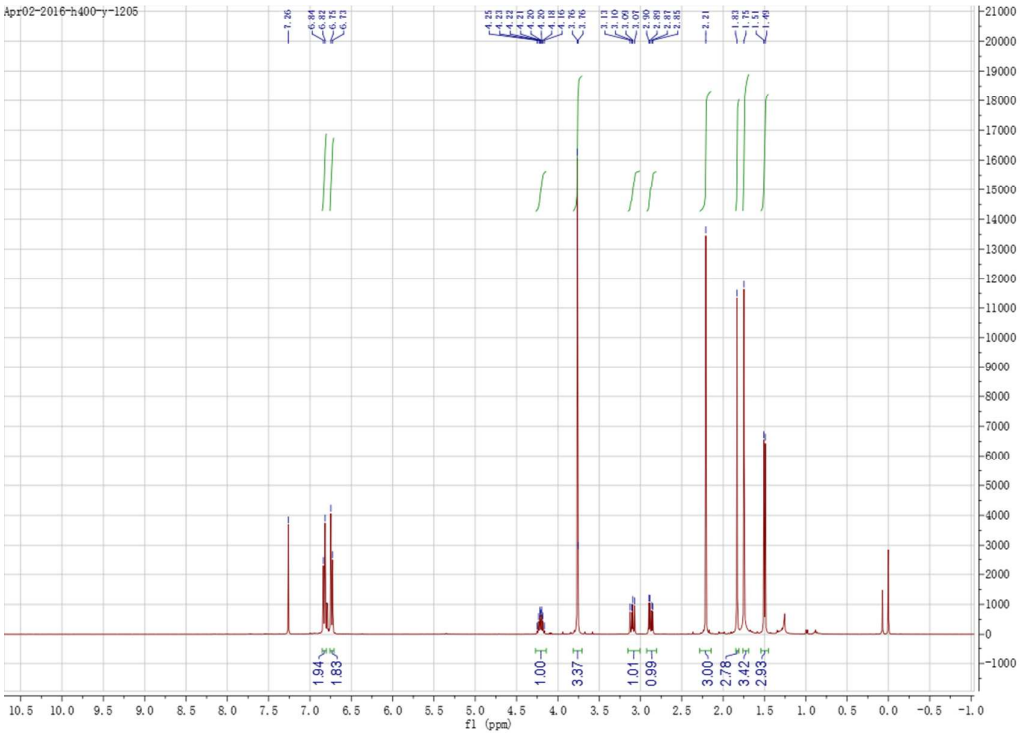
3i

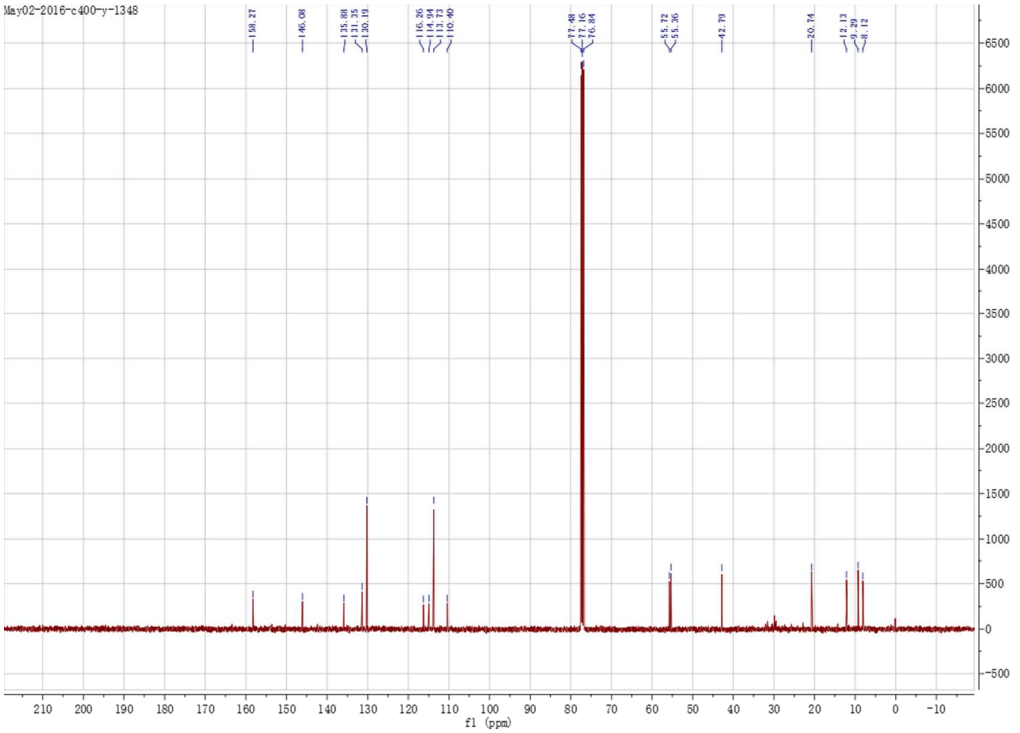

Mar25-2016-h400-y-1204
2.05
2.09
0.97
1.00
0.98
2.91
2.92
2.88
2.99
f1 (ppm)

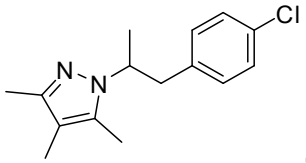

Apr05-2016-c400-y-1204
146.25
137.68
135.80
131.24
130.56
128.41
110.50
77.48
77.16
76.84
55.33
42.86
21.03
12.14
9.26
8.10
f1 (ppm)



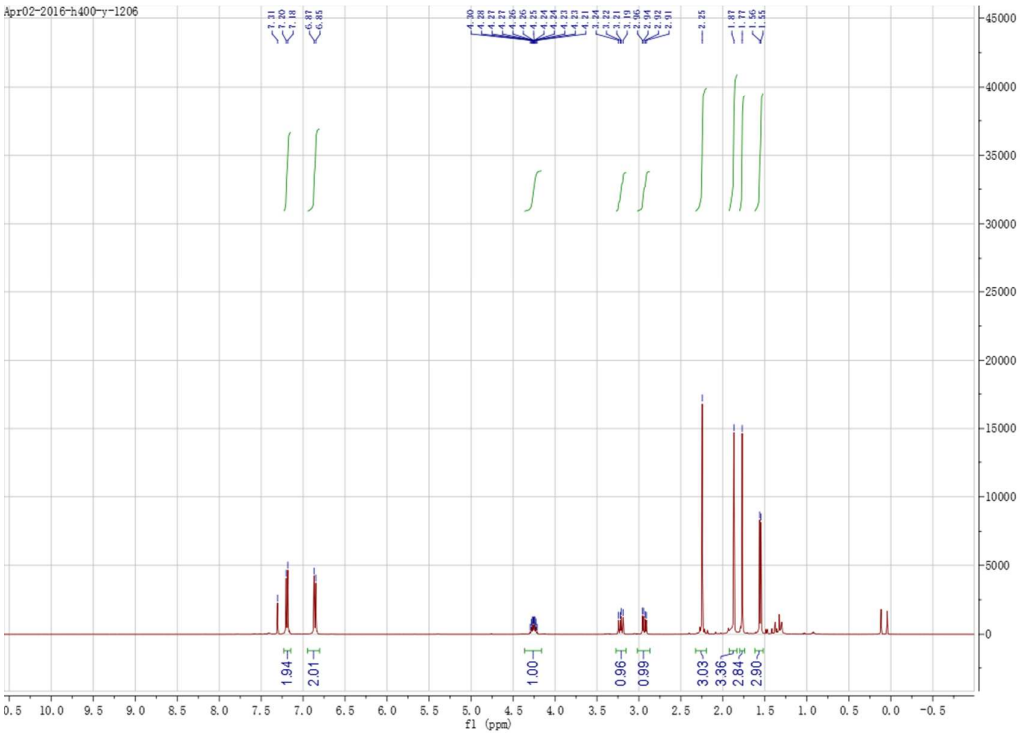
3j

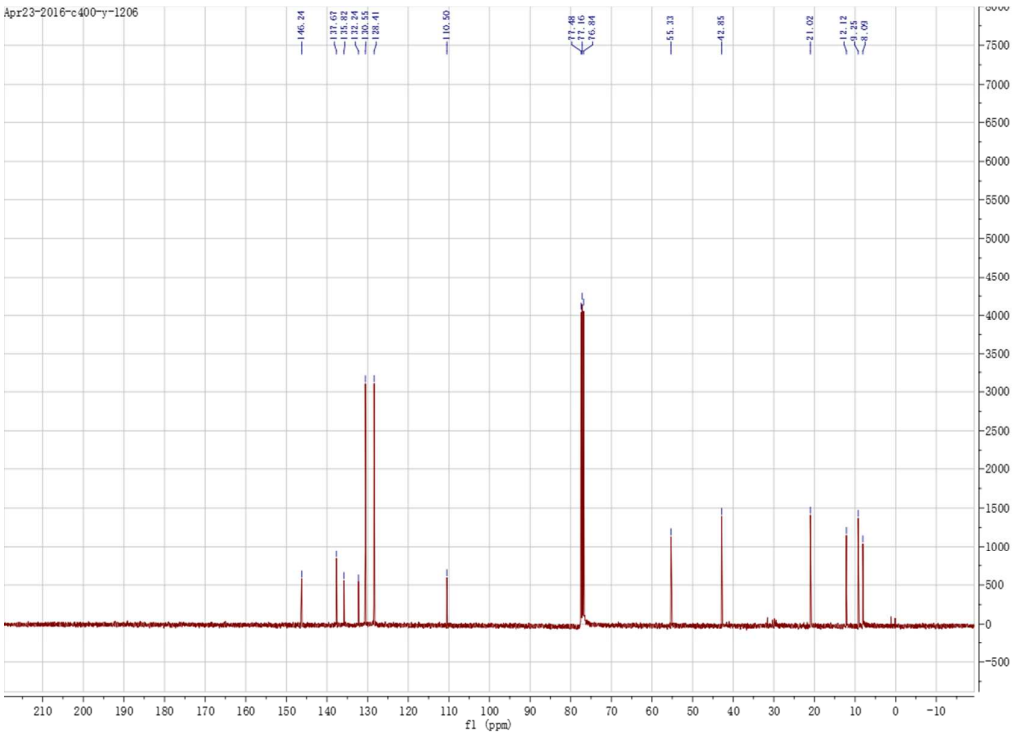


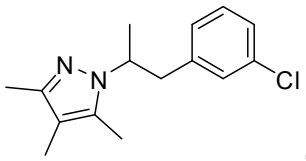




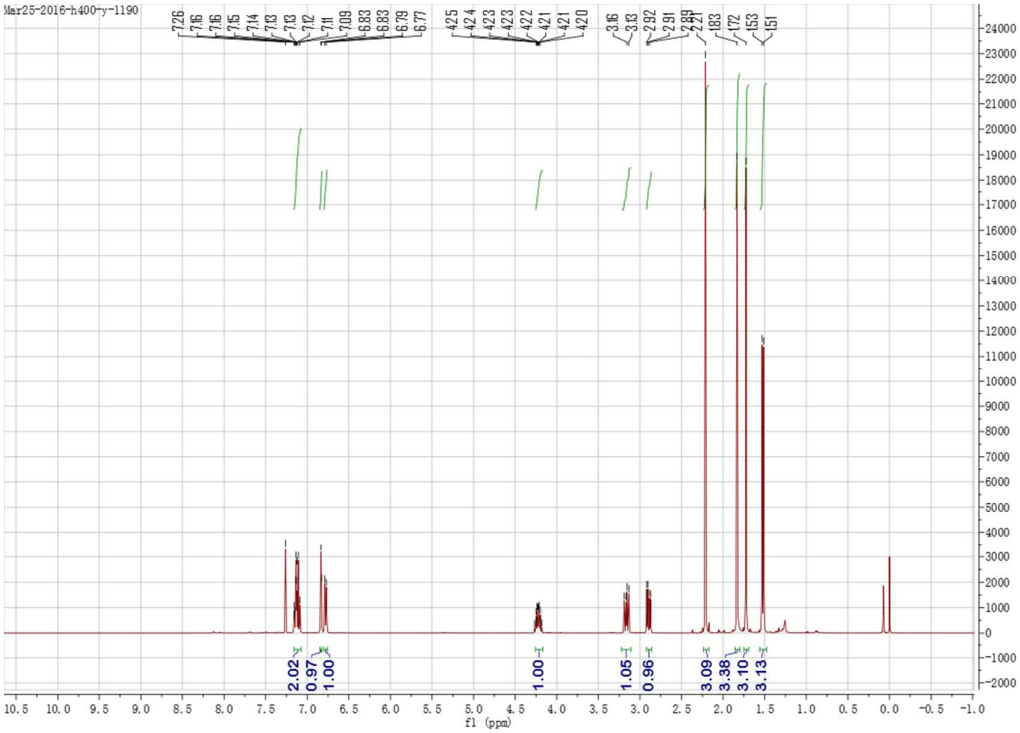
3k

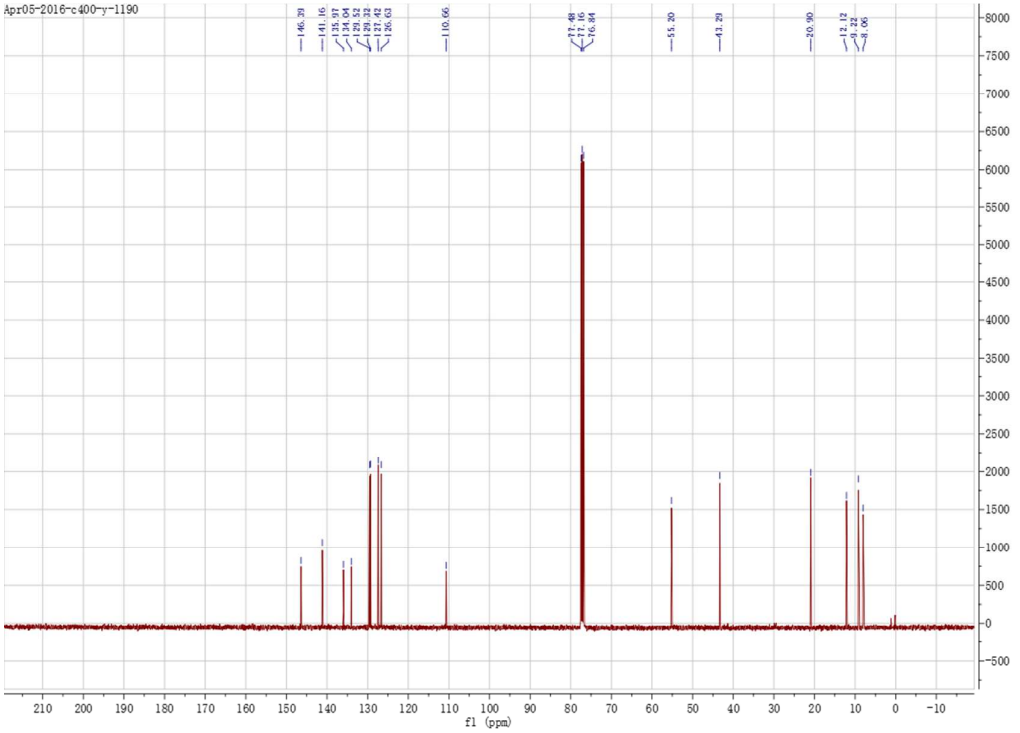


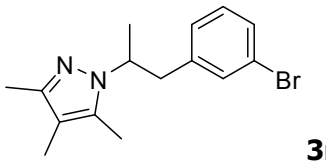




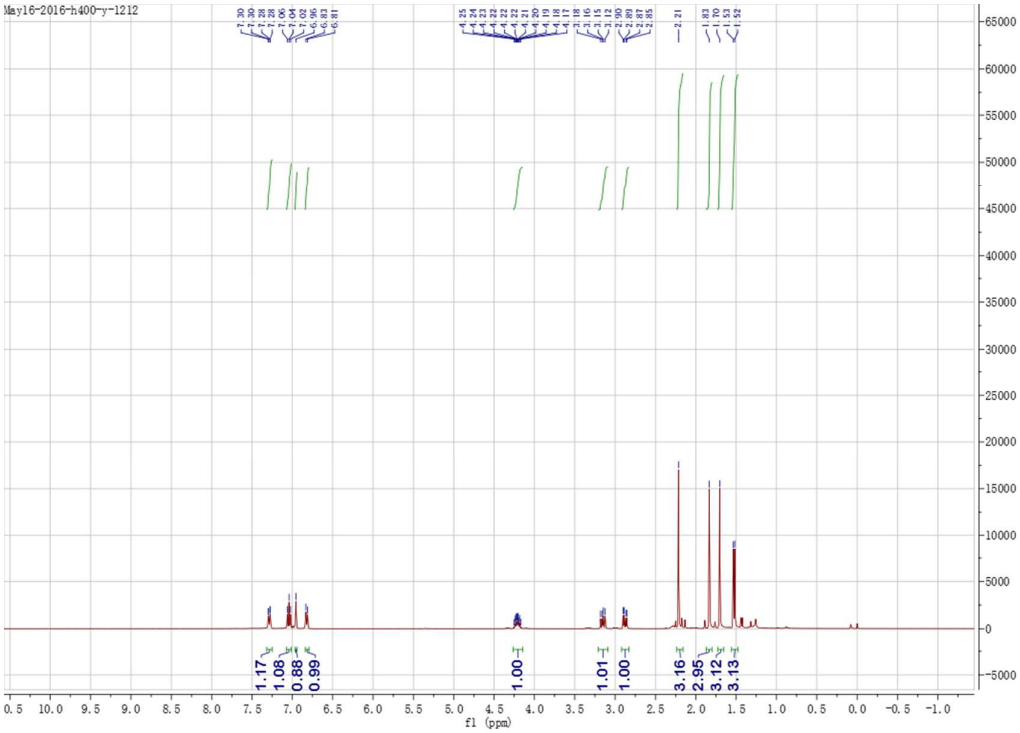
3l

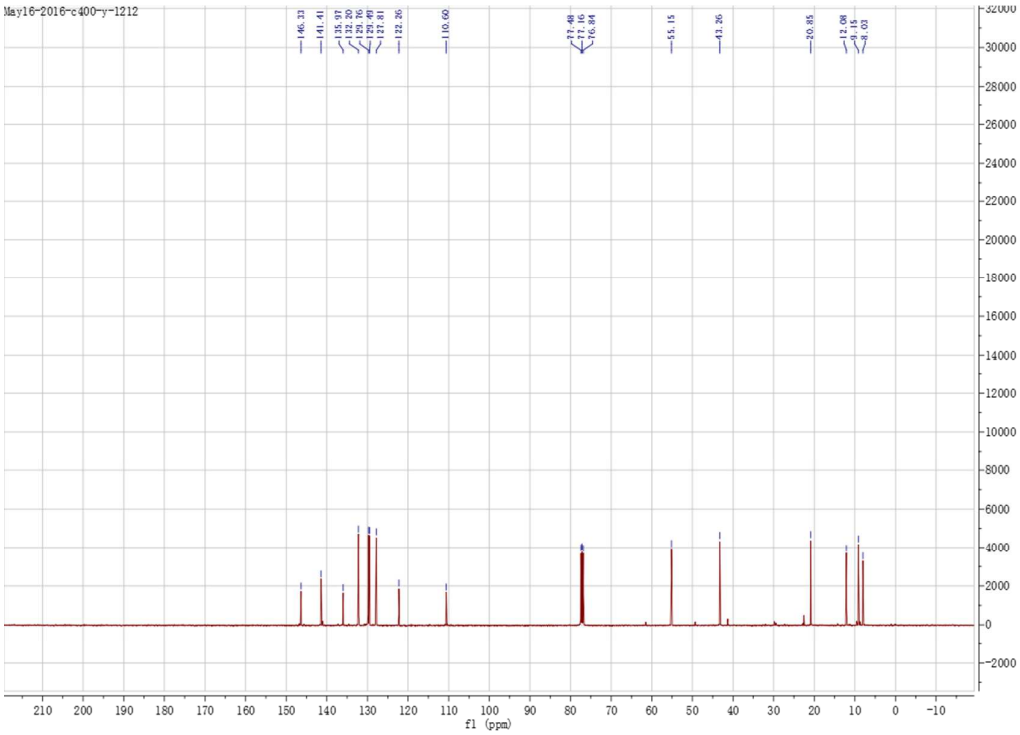


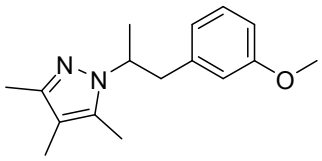




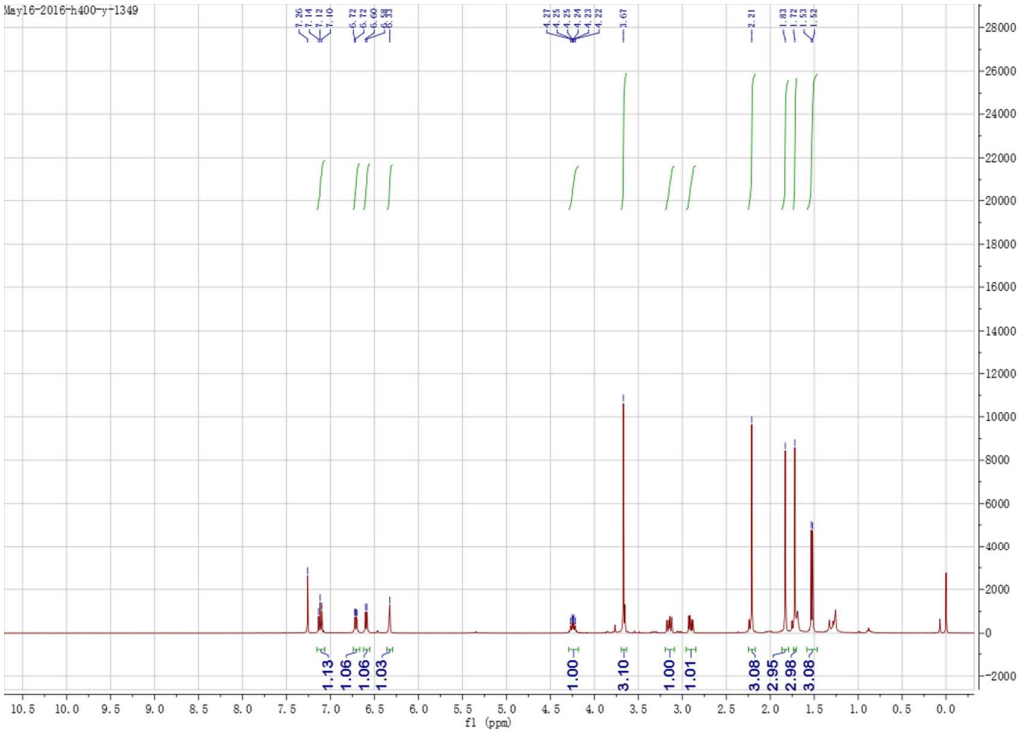
3m

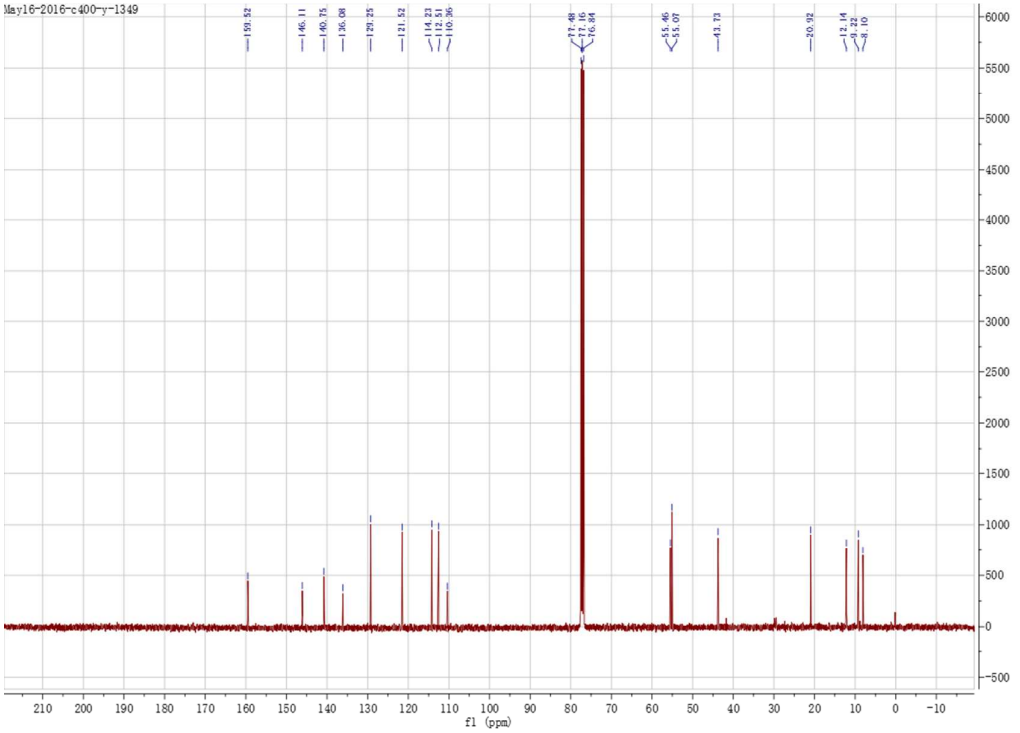

May16-2016-h400-y-1212
1.17
1.08
0.88
0.99
1.00
1.01
1.00
3.16
2.95
3.12
3.13
f1 (ppm)

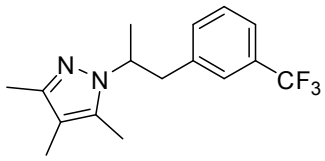

May16-2016-c400-y-1212
146.33
141.41
135.97
132.20
129.76
129.49
127.81
122.26
110.60
77.48
77.16
76.84
55.15
43.26
20.85
13.08
9.15
8.03
f1 (ppm)



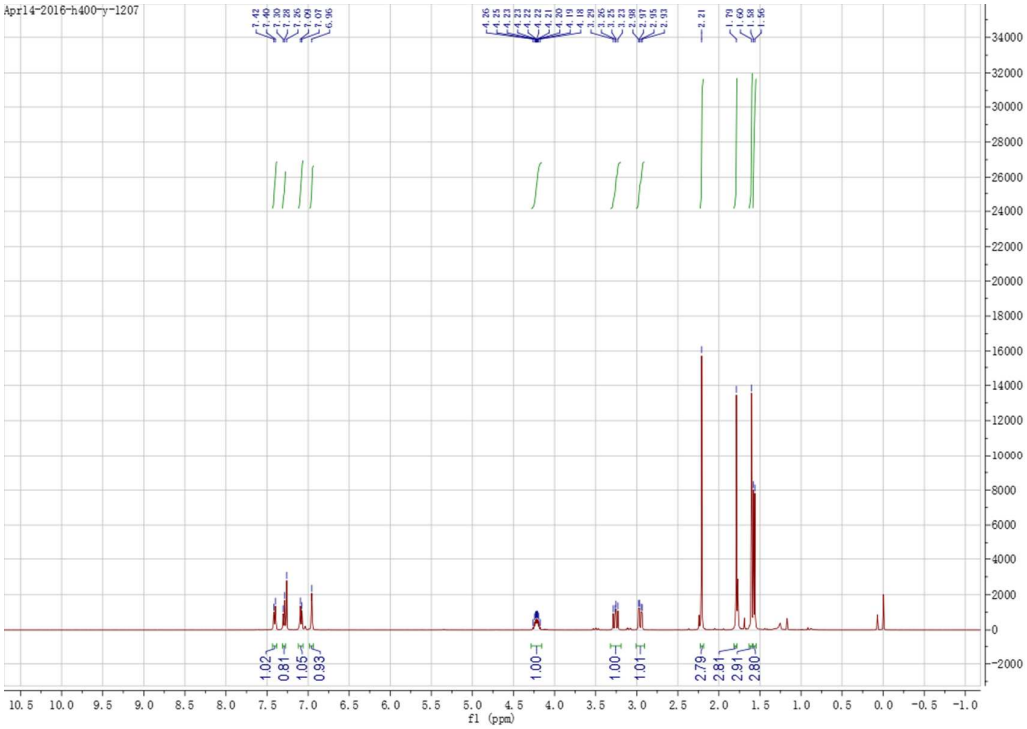
3n

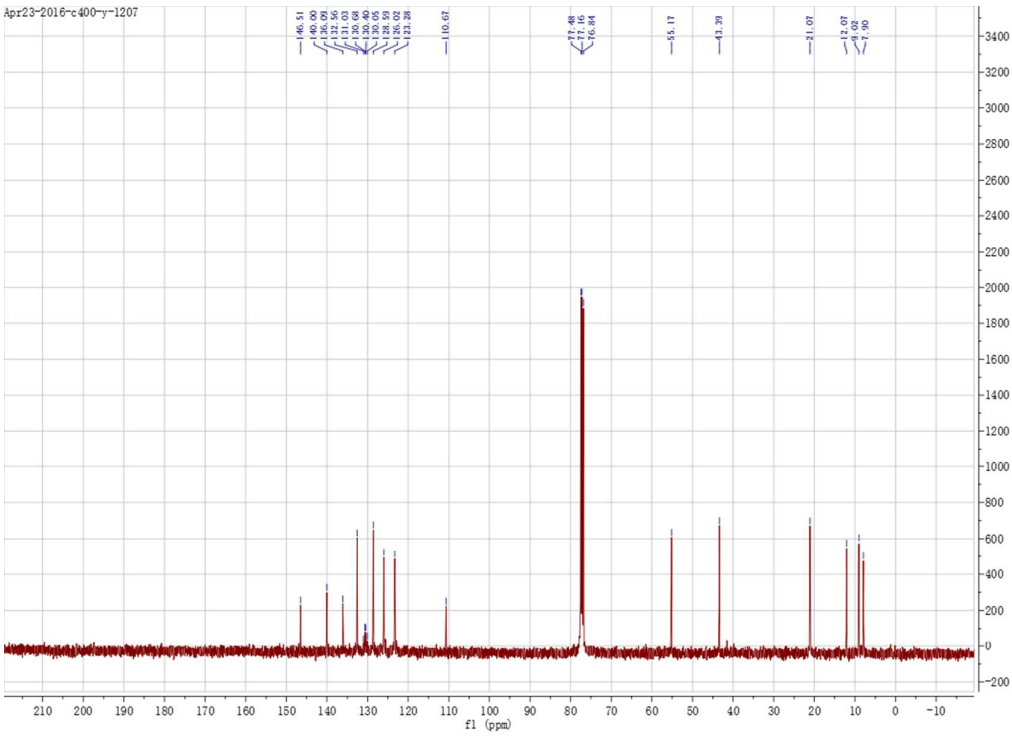

May16-2016-h400-y-1349
7.26
7.14
7.12
7.10
6.72
6.72
6.60
6.58
4.27
4.25
4.24
4.23
4.22
3.67
2.21
1.83
1.72
1.53
1.52
1.13
1.06
1.06
1.03
1.00
3.10
1.00
1.01
3.08
2.95
2.98
3.08
f1 (ppm)

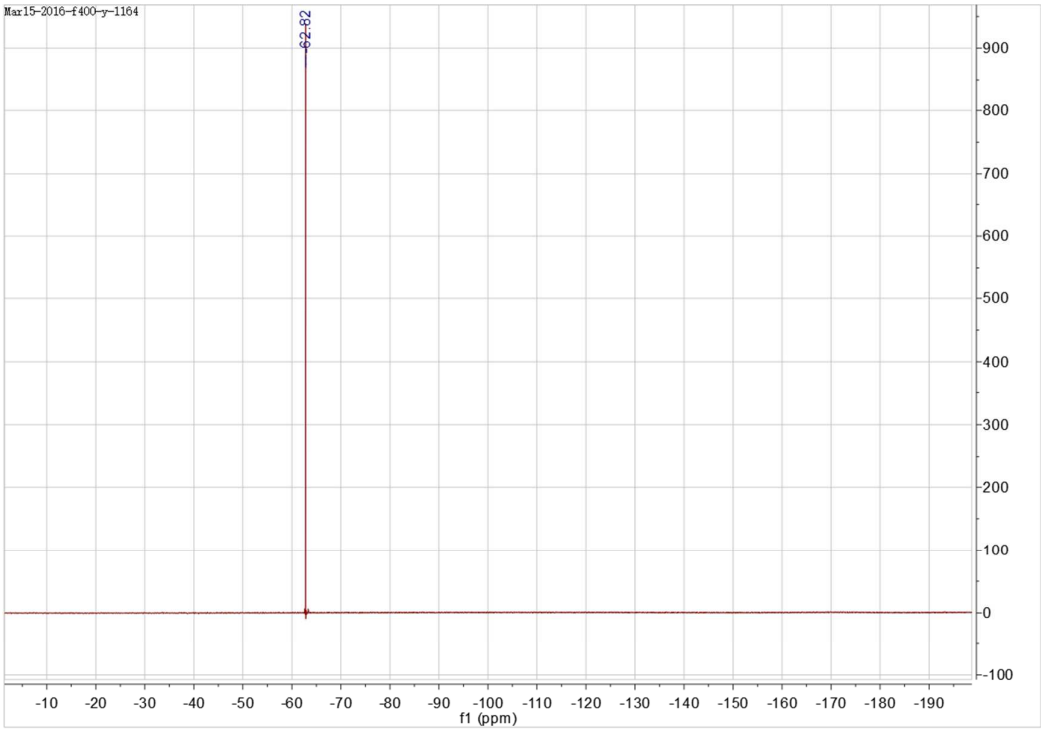

May16-2016-c400-y-1349
159.52
146.11
140.75
136.08
129.25
121.52
114.23
112.51
110.36
77.48
77.16
76.84
55.46
55.07
43.73
20.92
13.14
9.22
8.10
f1 (ppm)

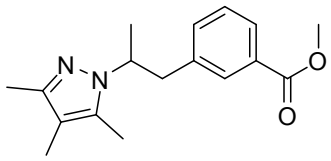


3o

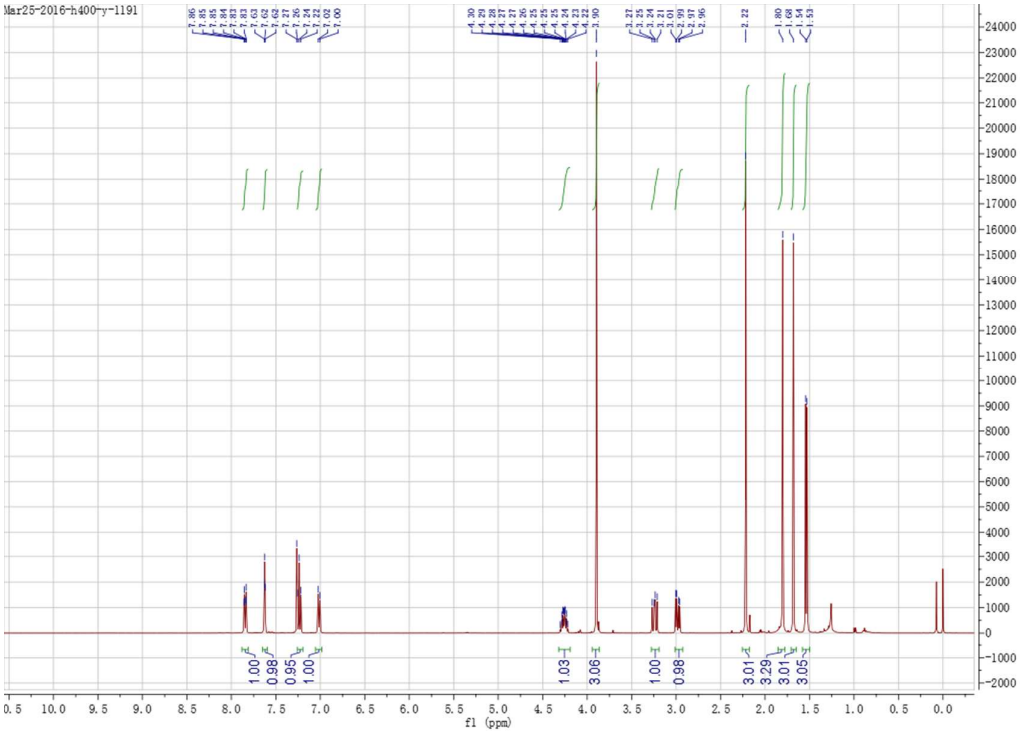


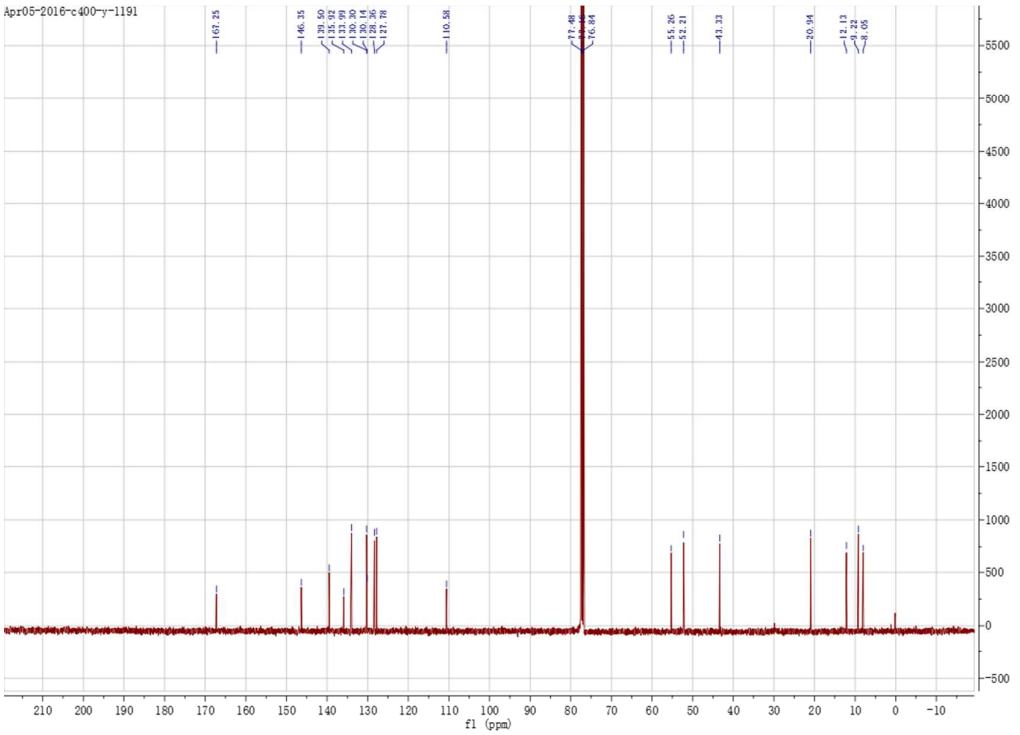


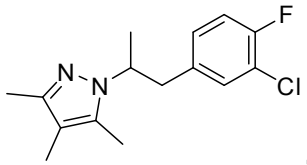

Mar15-2016-f400-y-1164
-62.82
900
800
700
600
500
400
300
200
100
0
-100
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)



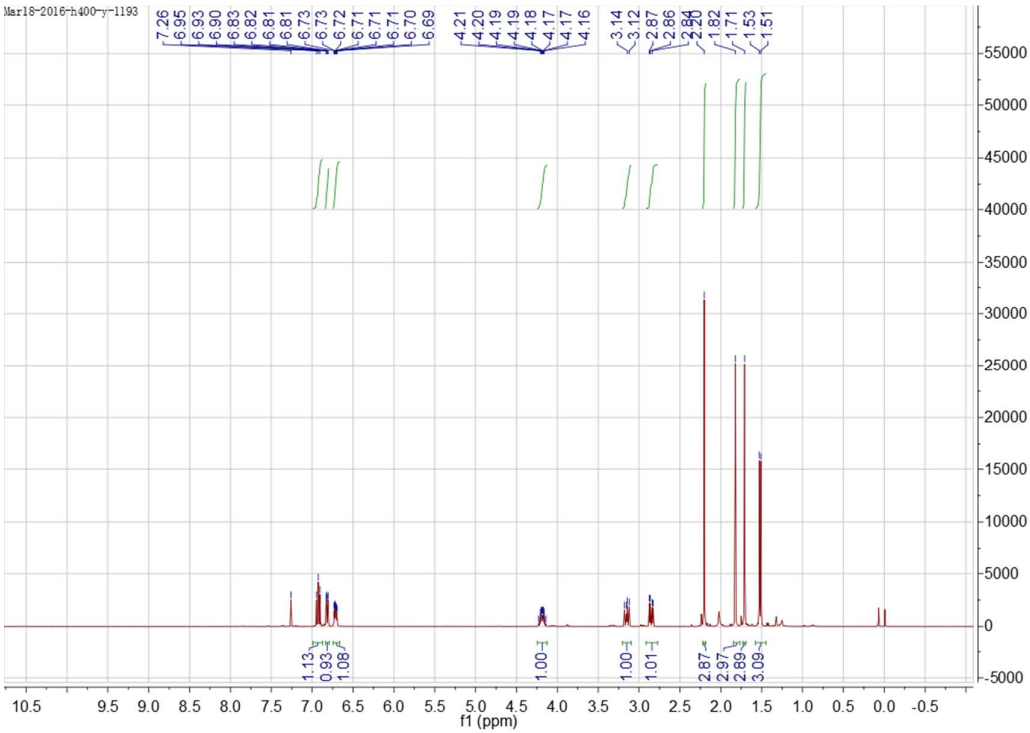
3p

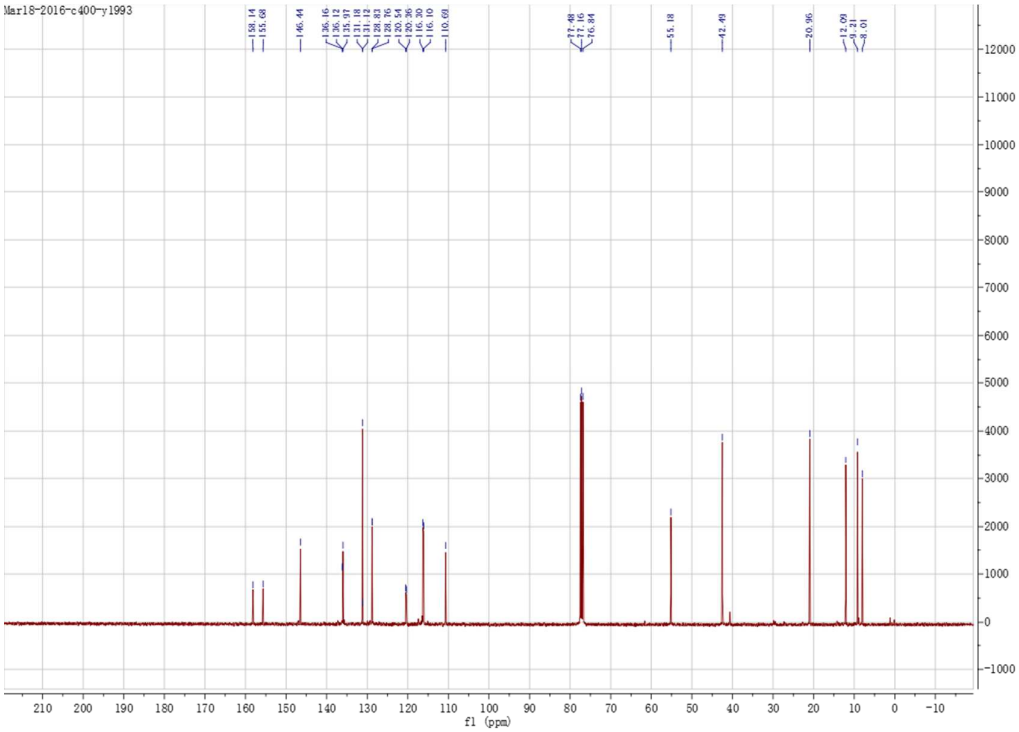


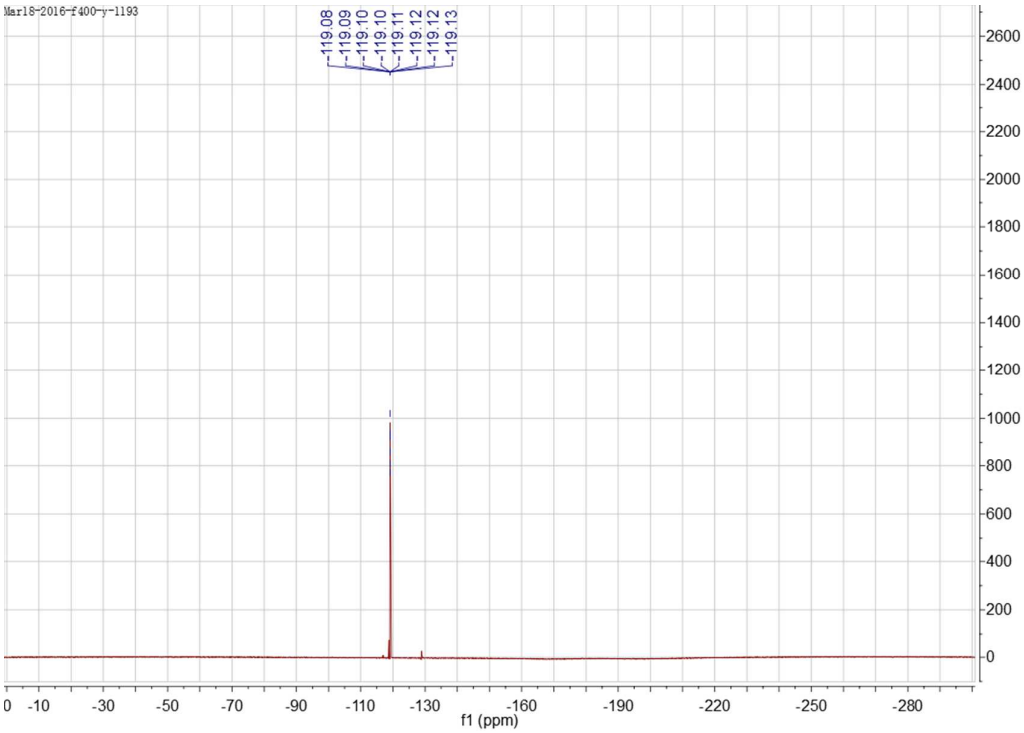


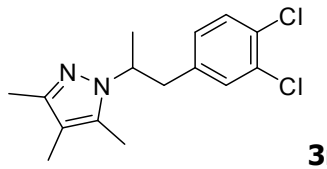


3q

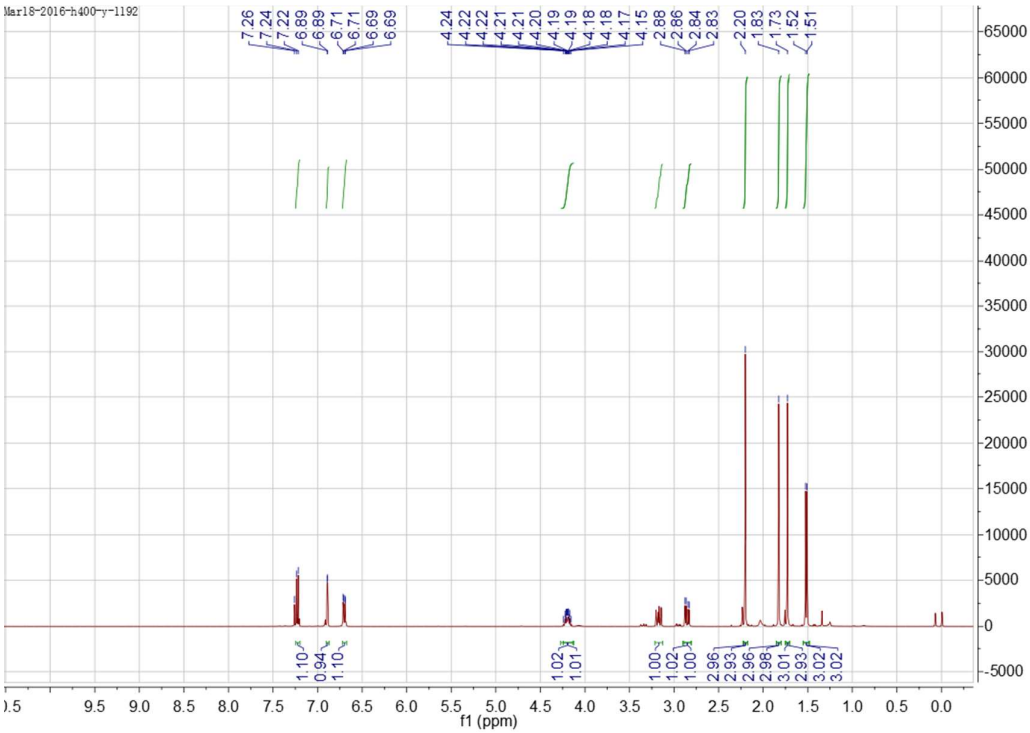


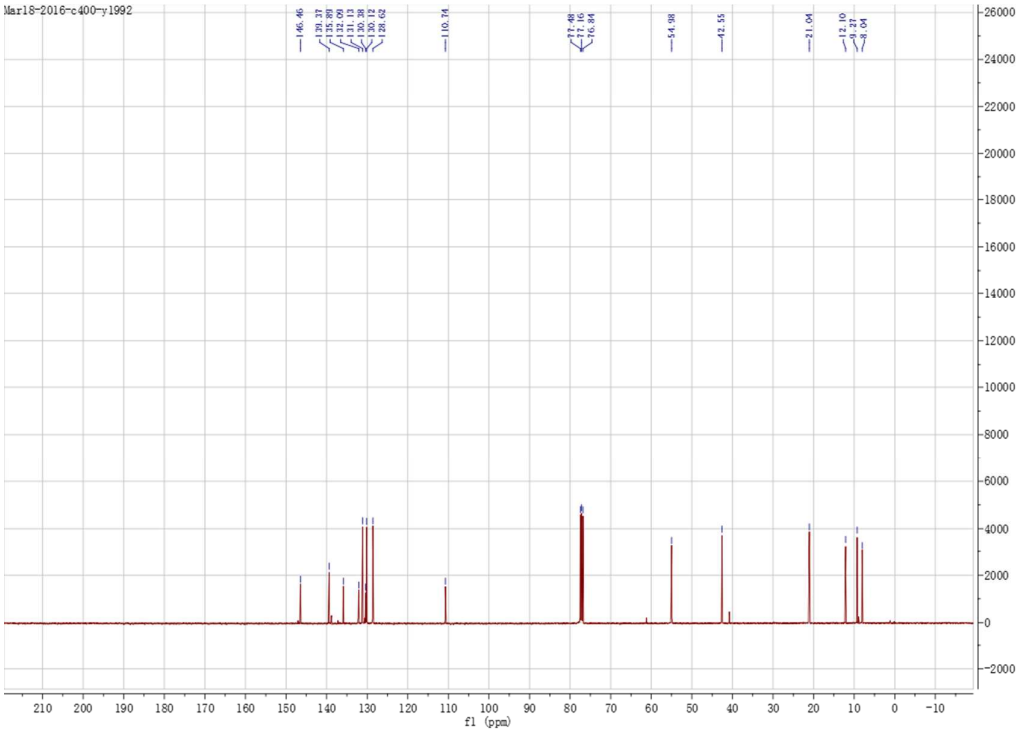


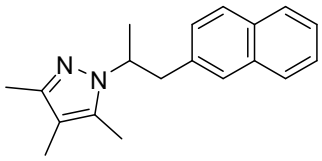

Mar18-2016-f400-y-1193
-119.08
-119.09
-119.10
-119.10
-119.11
-119.12
-119.12
-119.13
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
0
-10
-30
-50
-70
-90
-110
-130
-160
-190
-220
-250
-280
f1 (ppm)



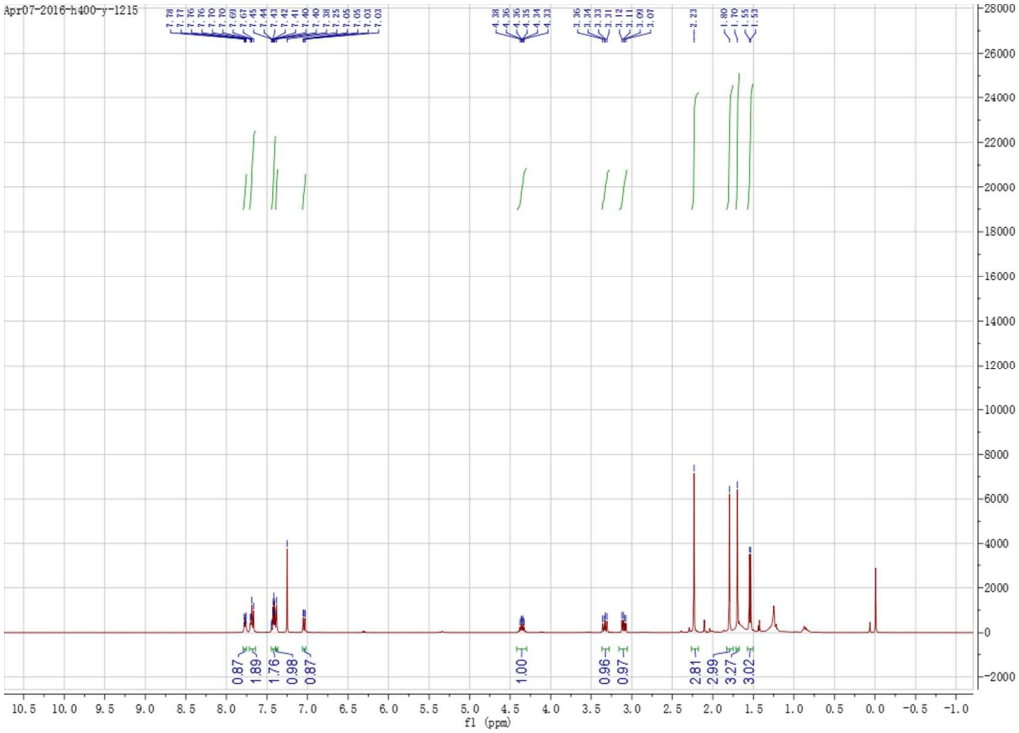
3r

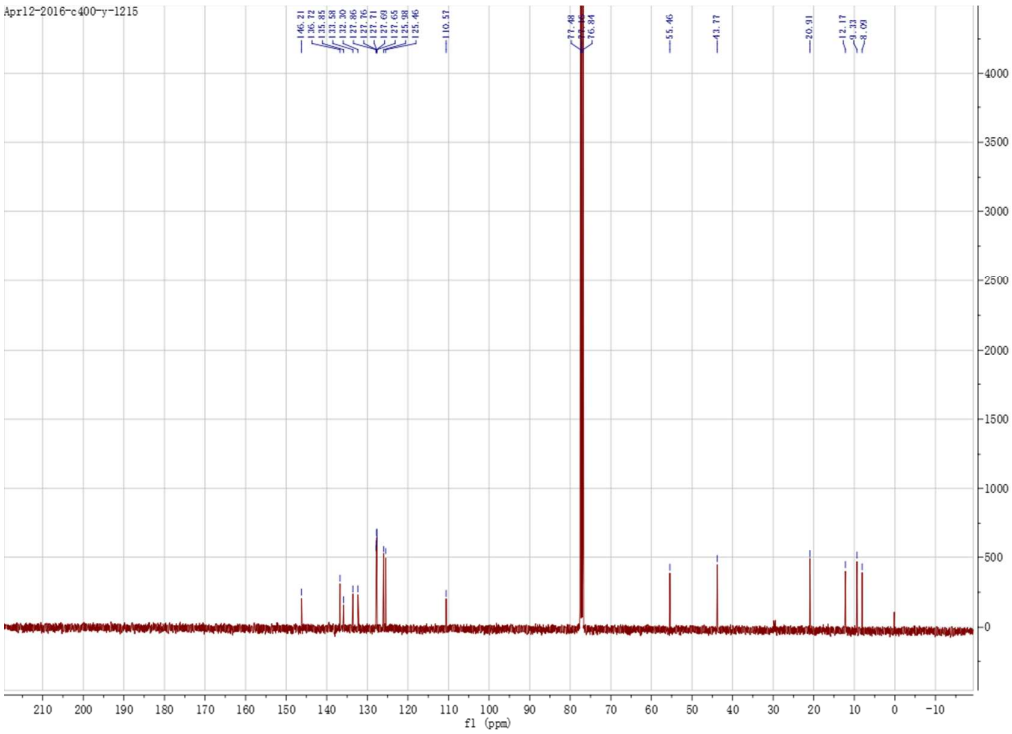


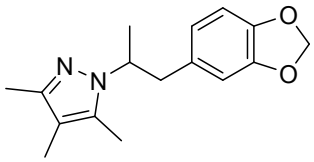




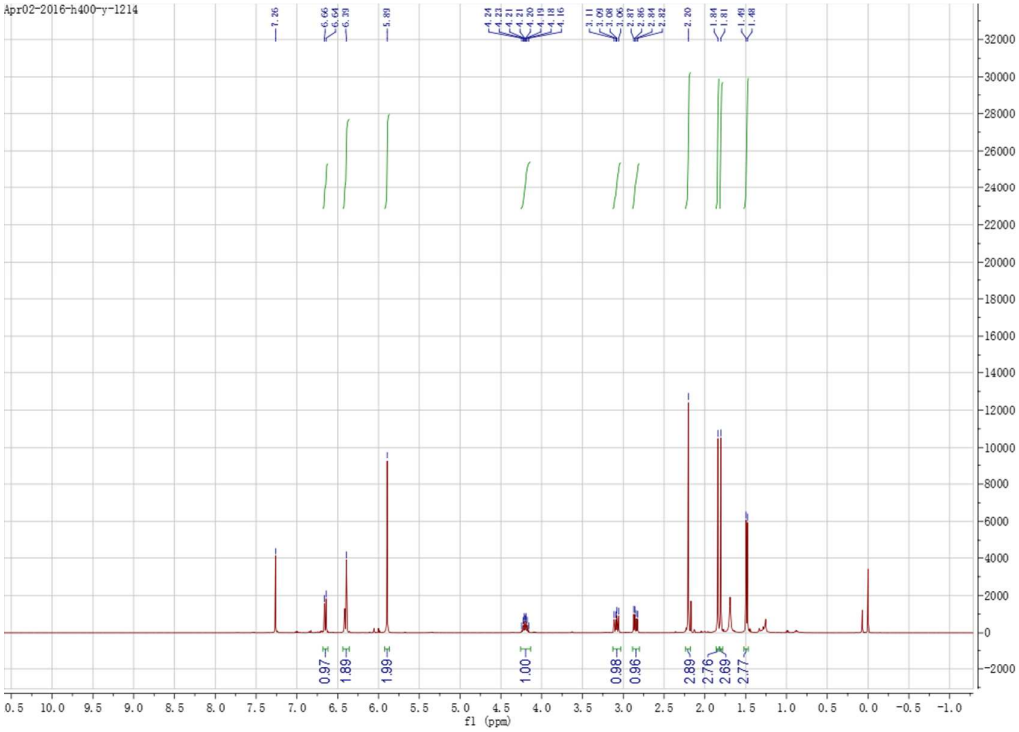
3s

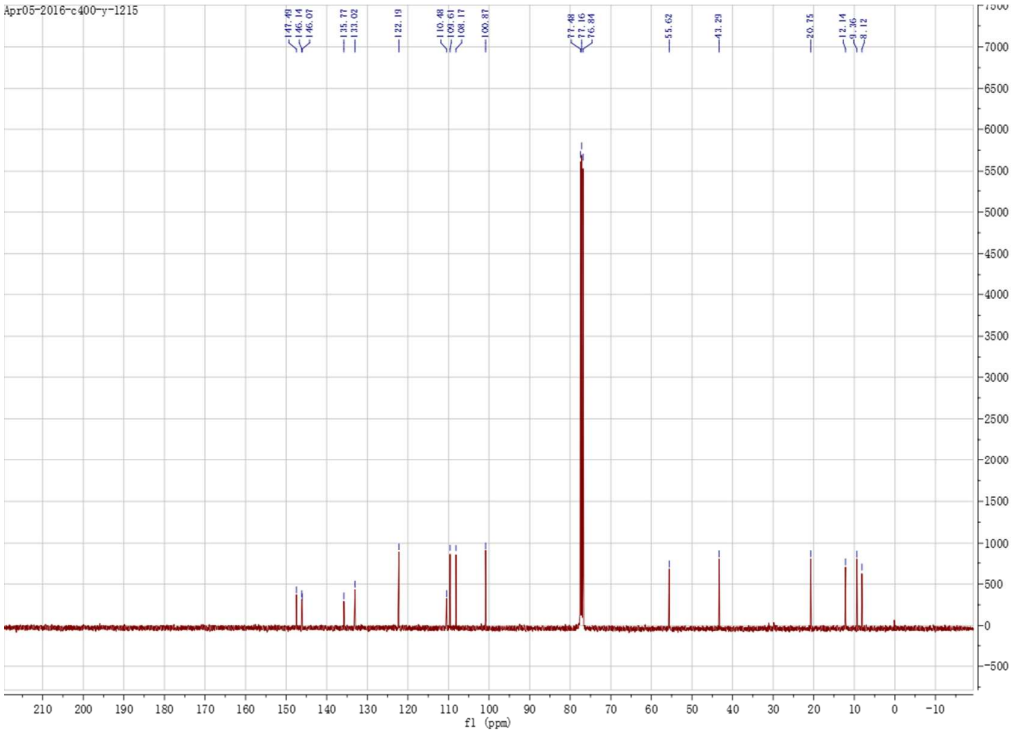


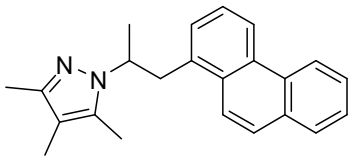




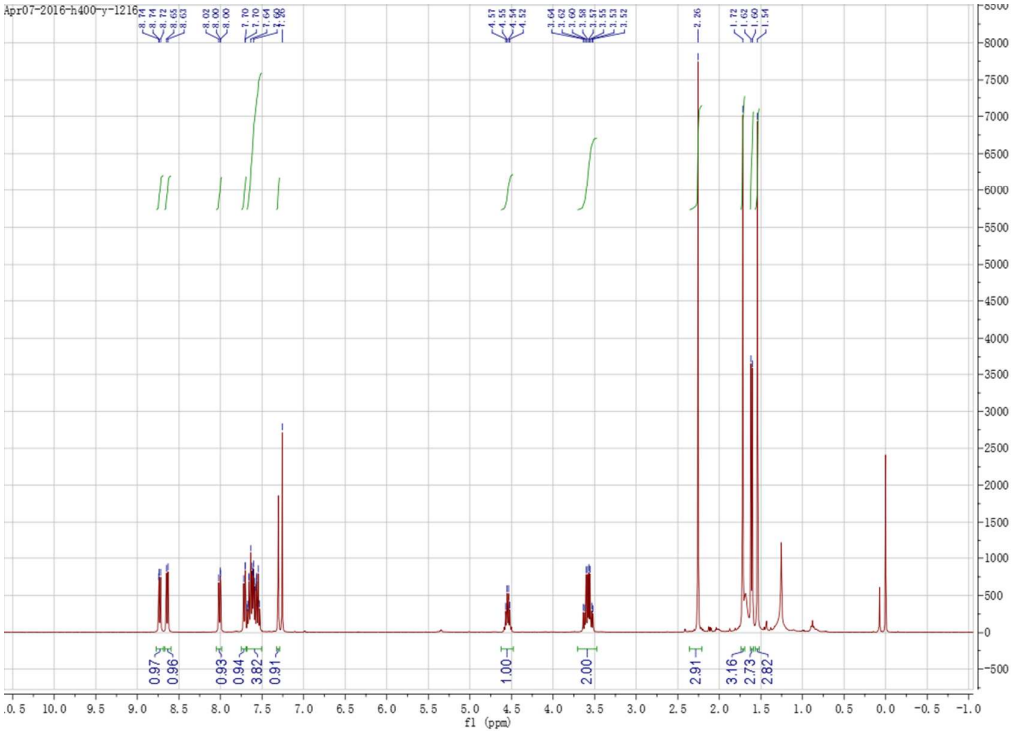
3t

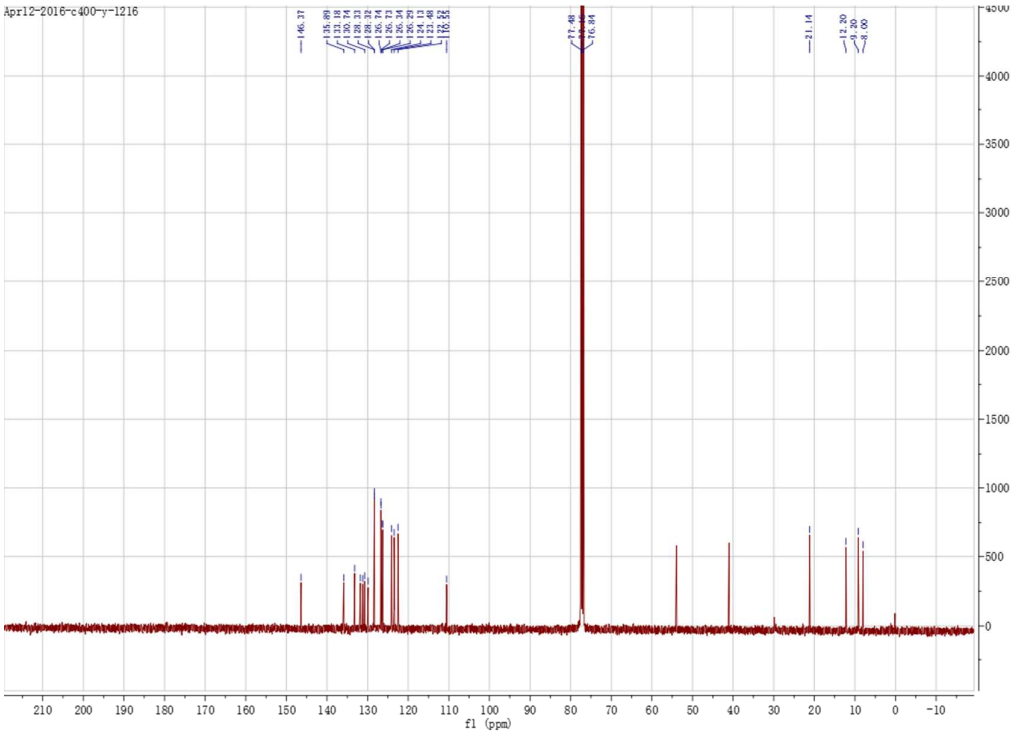


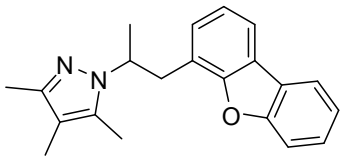




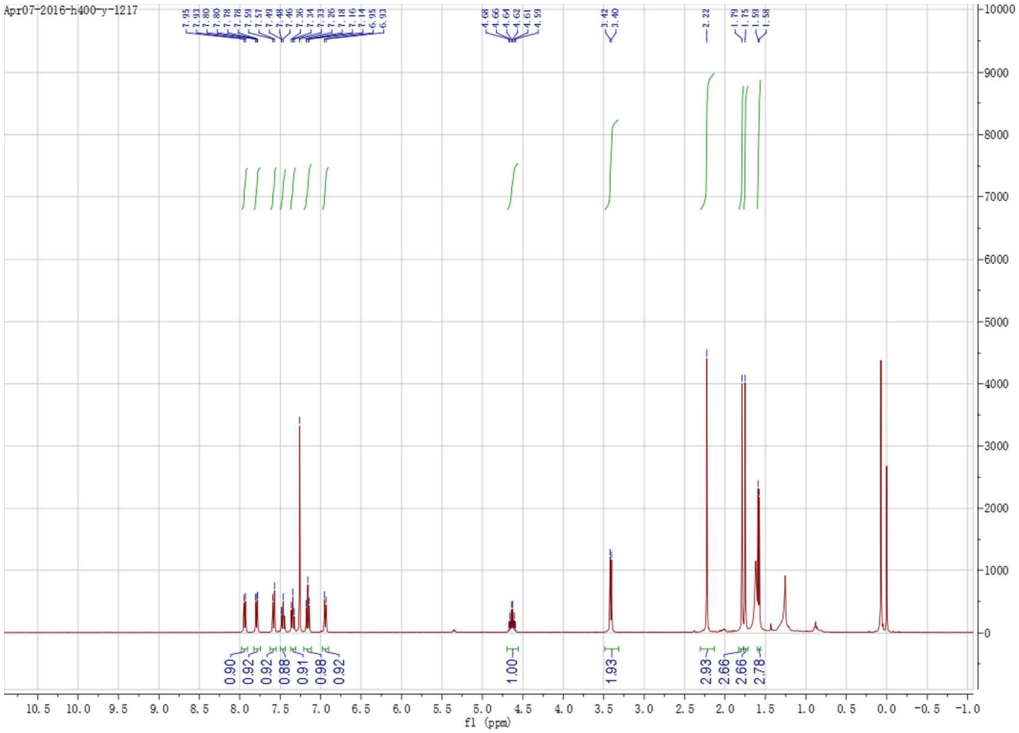
3u

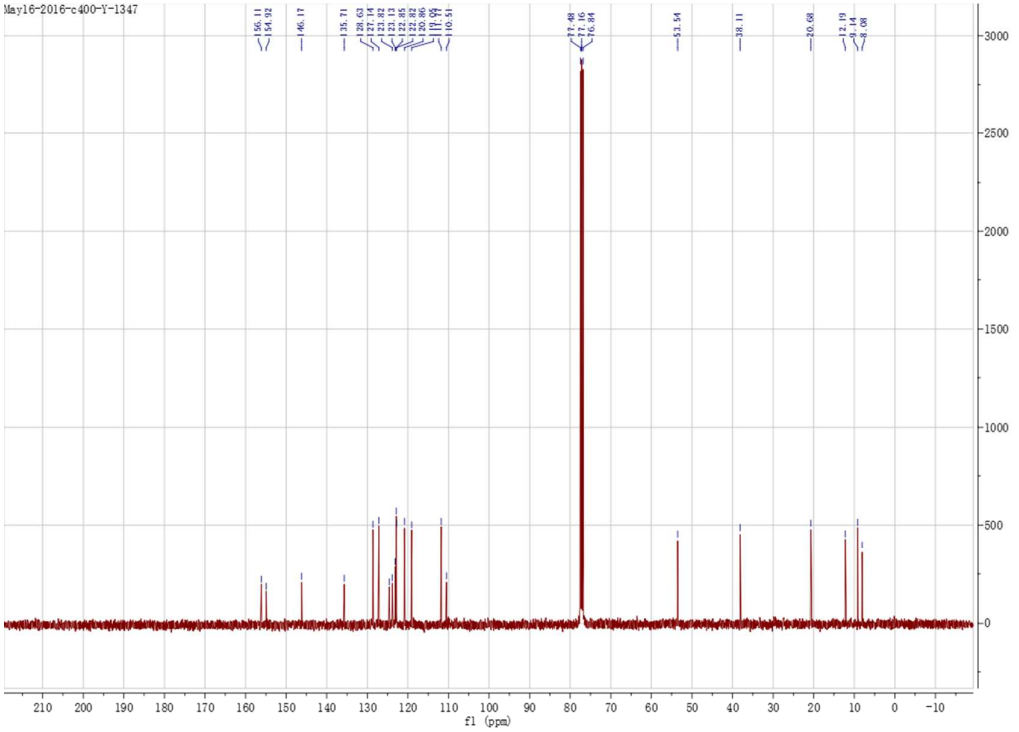


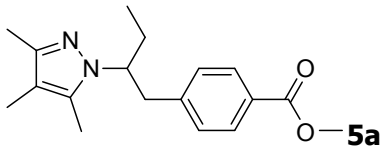




3v







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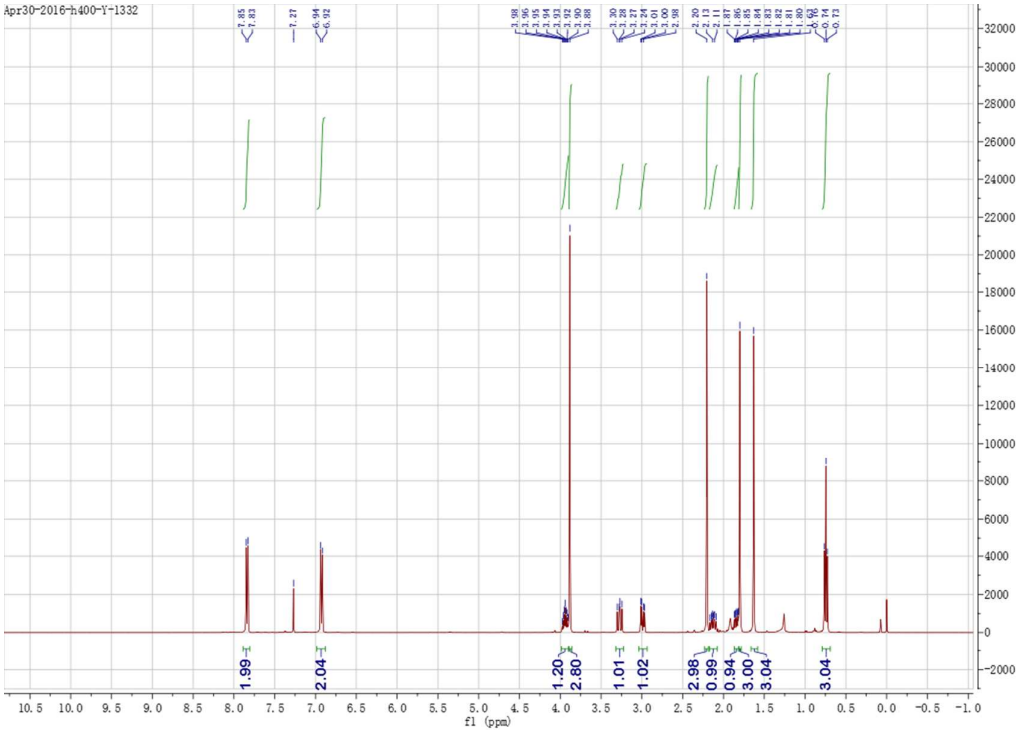
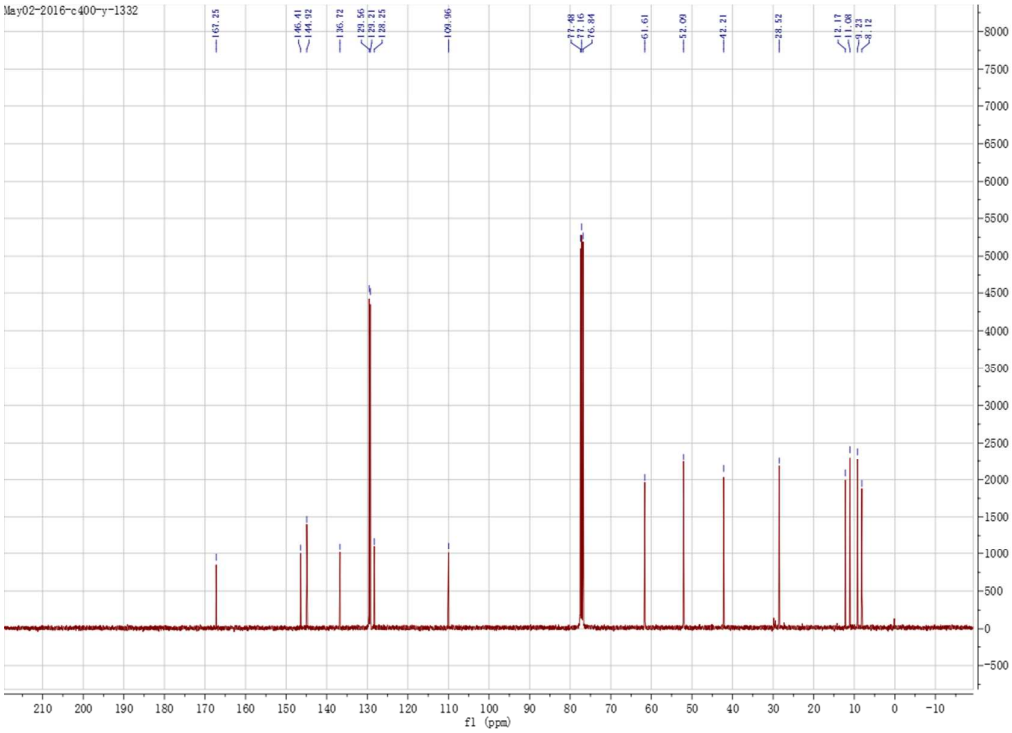
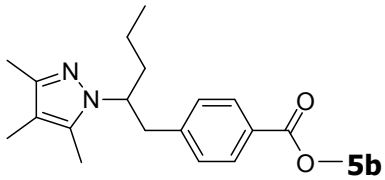
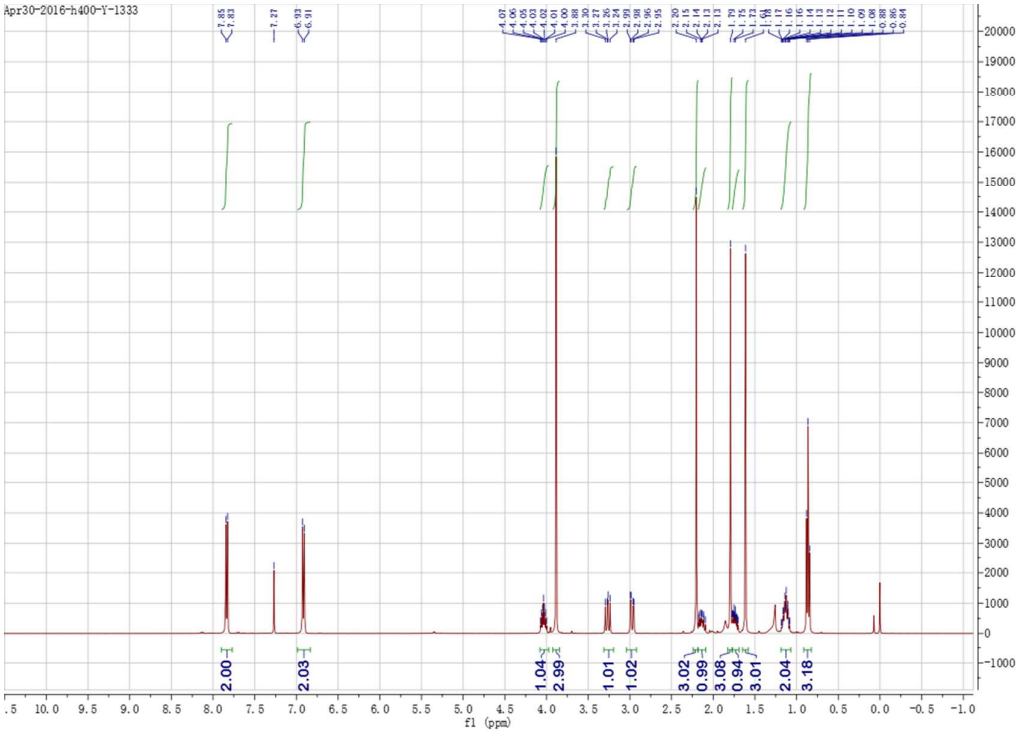
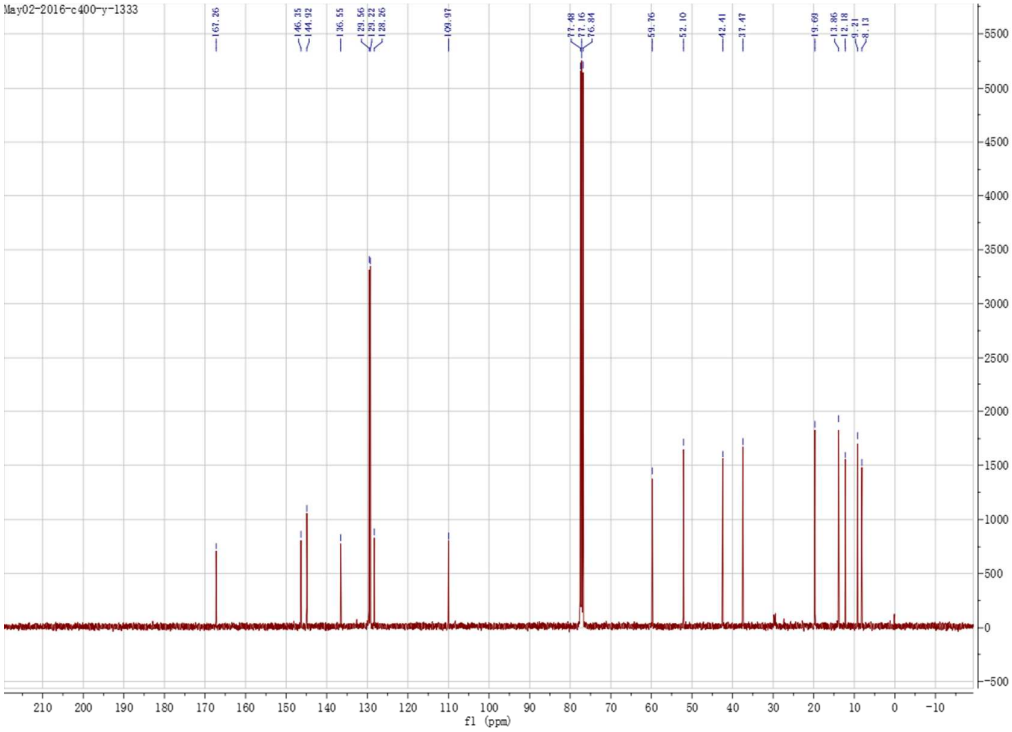


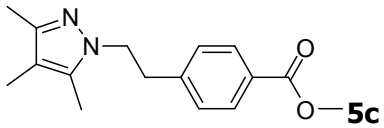




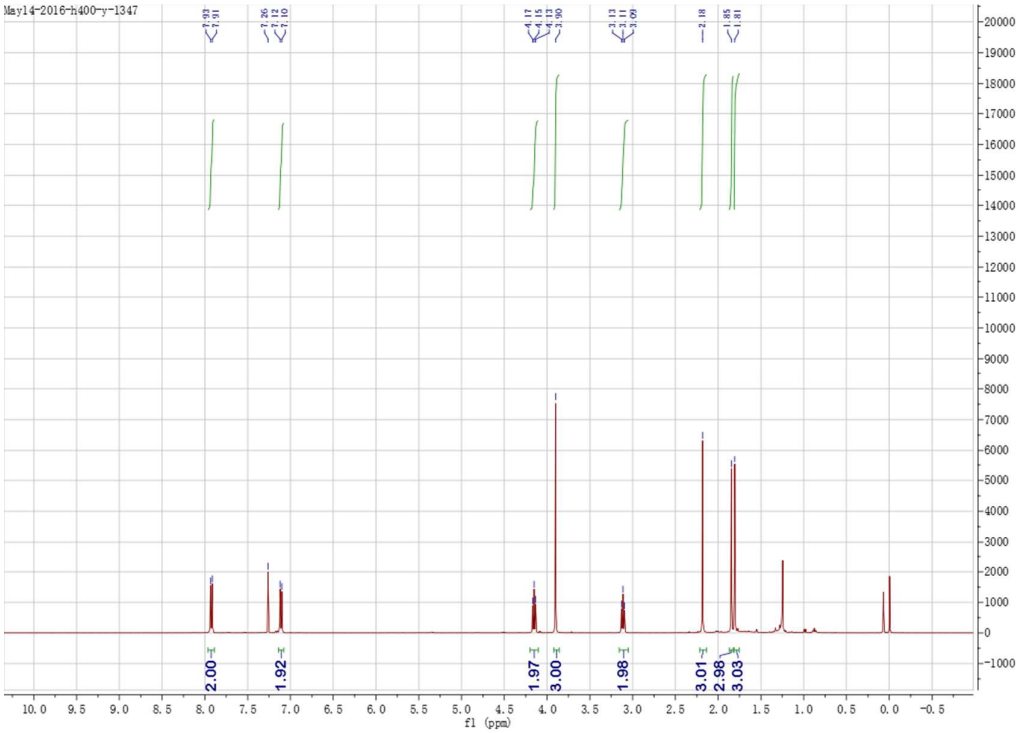
5b

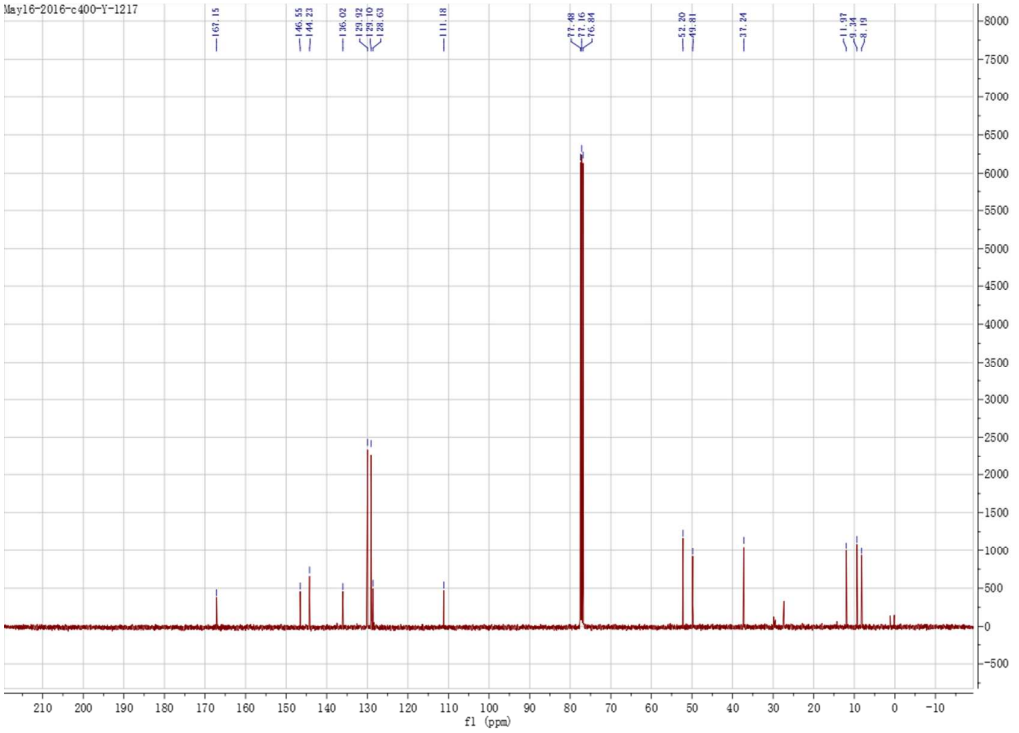


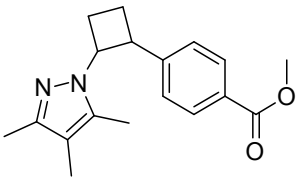




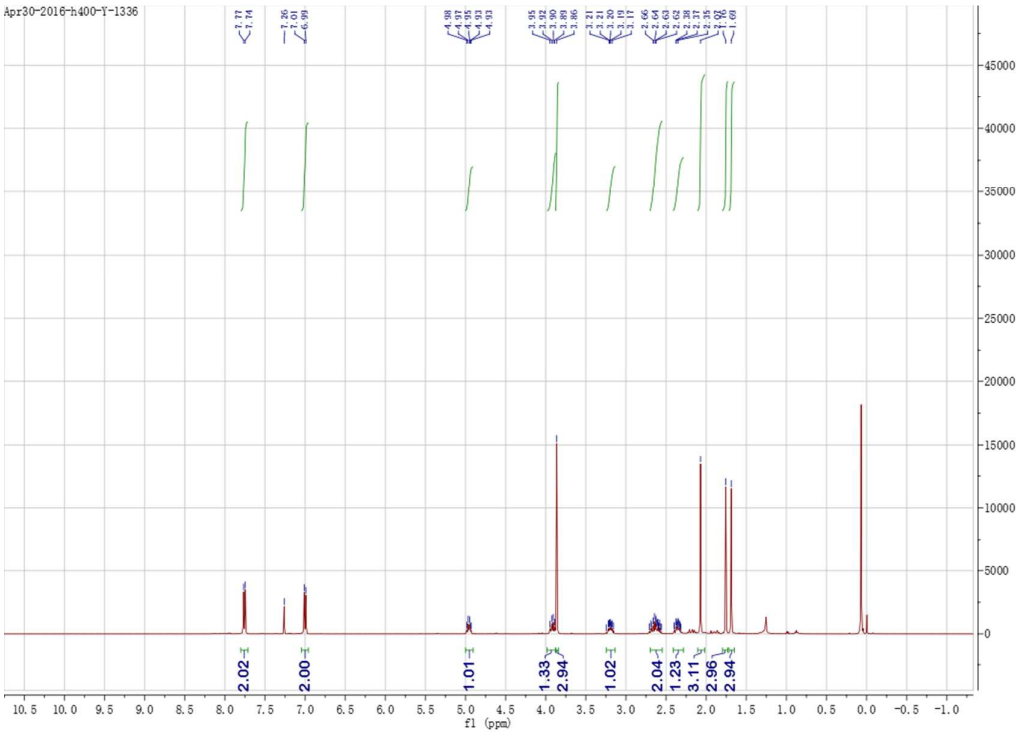
5c

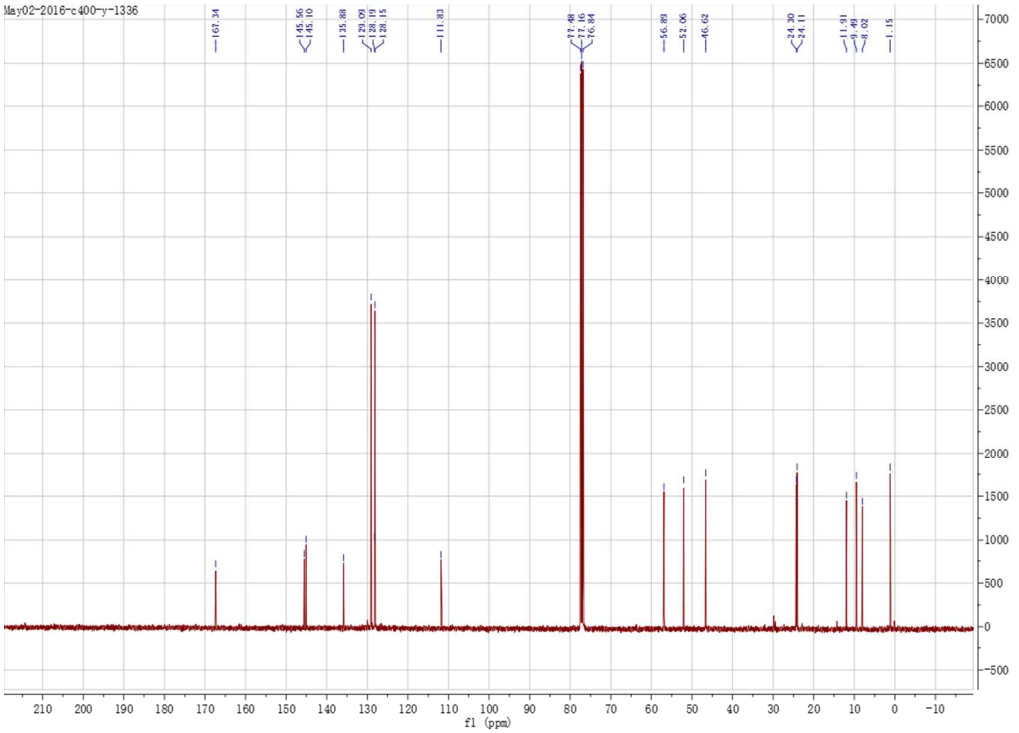

May14-2016-h400-y-1347
2.00
1.92
1.97
3.00
1.98
3.01
2.98
3.03
f1 (ppm)

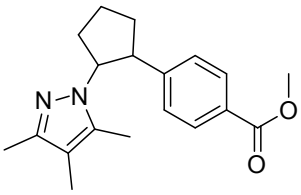

May16-2016-c400-Y-1217
167.15
146.55
144.23
135.02
129.92
129.10
128.03
111.18
77.48
77.16
76.84
52.20
49.81
37.24
11.97
9.34
8.19
f1 (ppm)



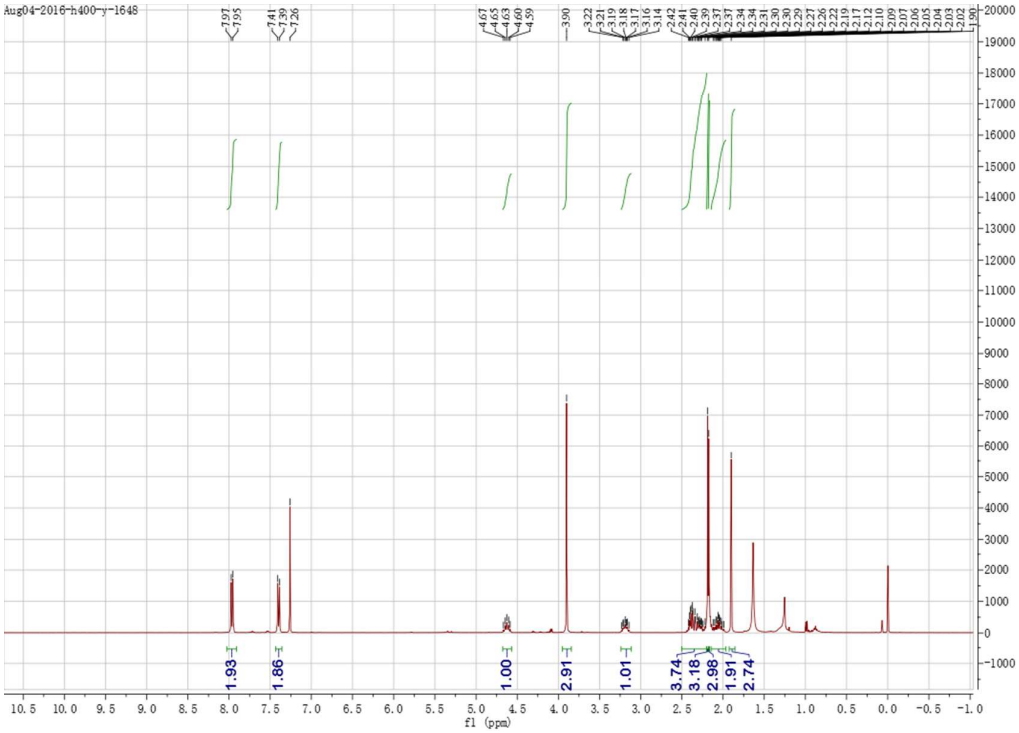
5d

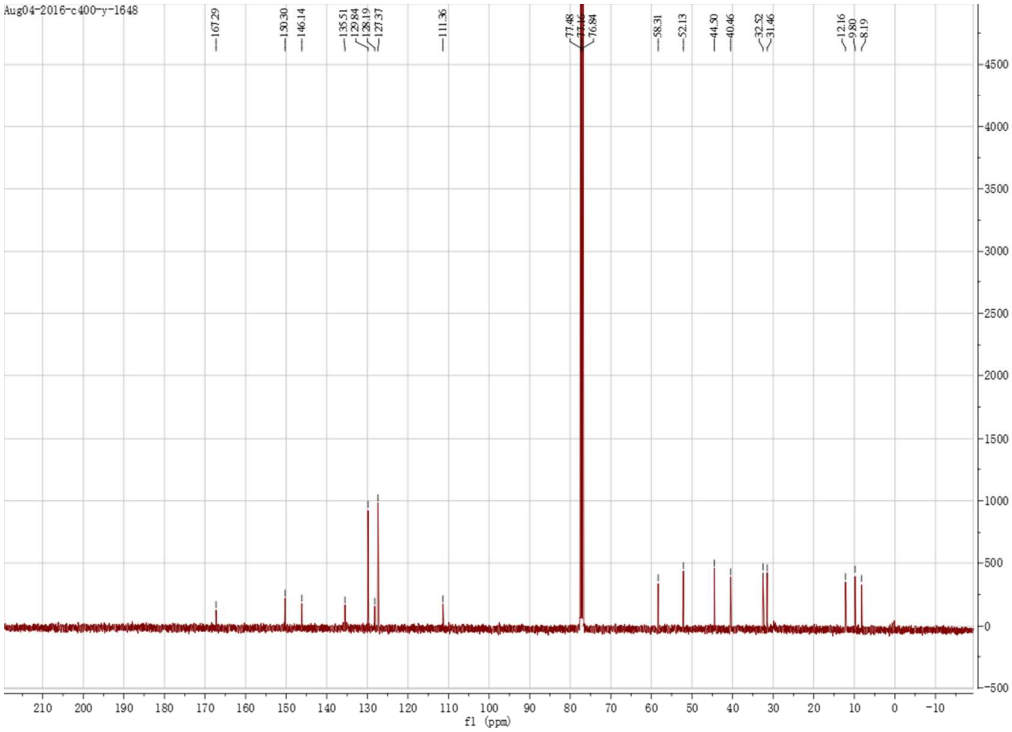

Apr30-2016-h400-Y-1336
2.02
2.00
1.01
1.33
2.94
1.02
2.04
1.23
3.11
2.96
2.94
f1 (ppm)

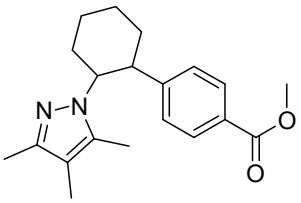

May02-2016-c400-y-1336
167.24
145.56
144.10
135.88
129.09
128.19
128.15
111.83
77.48
77.16
76.84
56.89
52.06
46.62
24.30
24.11
11.91
9.49
8.02
1.15
f1 (ppm)



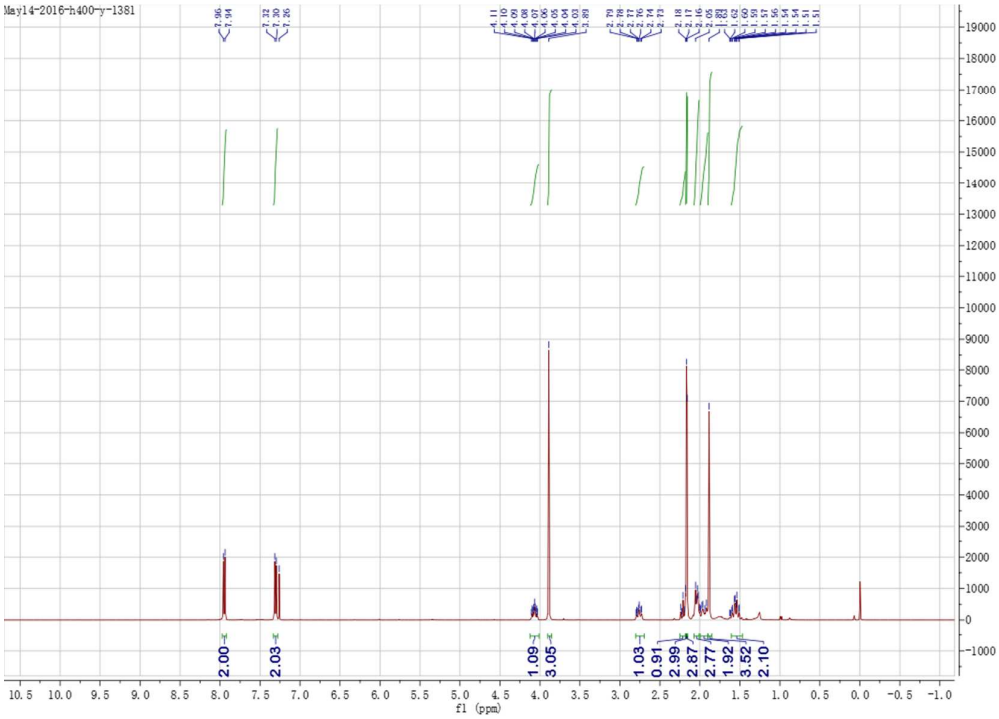
5e

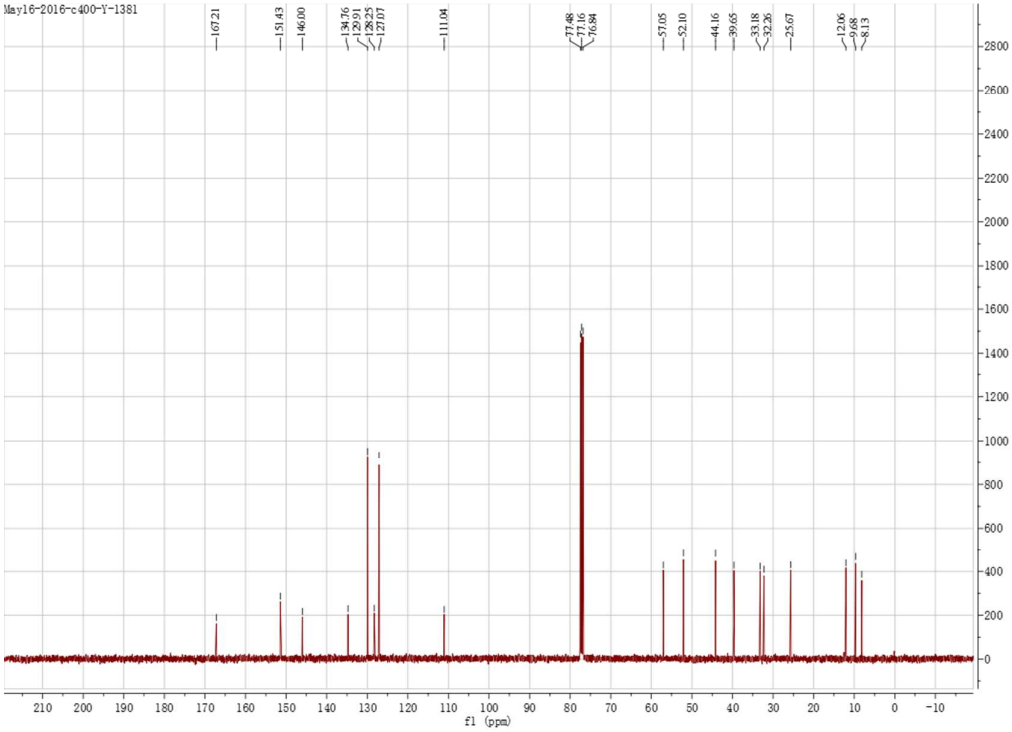

Aug04-2016-h400-y-1648
1.93
1.86
1.00
2.91
1.01
3.74
3.18
2.98
1.91
2.74
f1 (ppm)

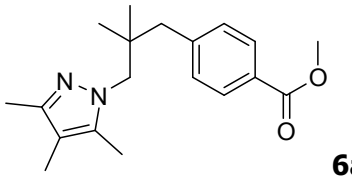

Aug04-2016-c400-y-1648
167.29
150.30
146.14
135.51
129.84
129.10
127.37
111.36
77.48
76.84
58.31
52.13
44.50
40.46
32.52
31.46
12.16
9.80
8.19
f1 (ppm)



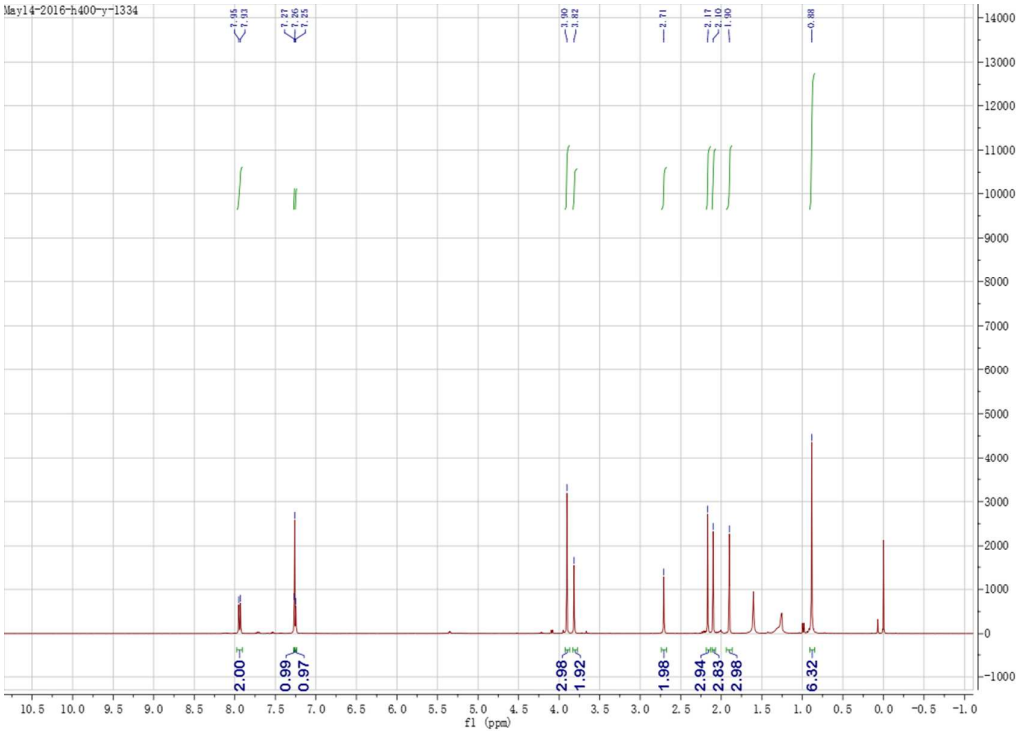
5f

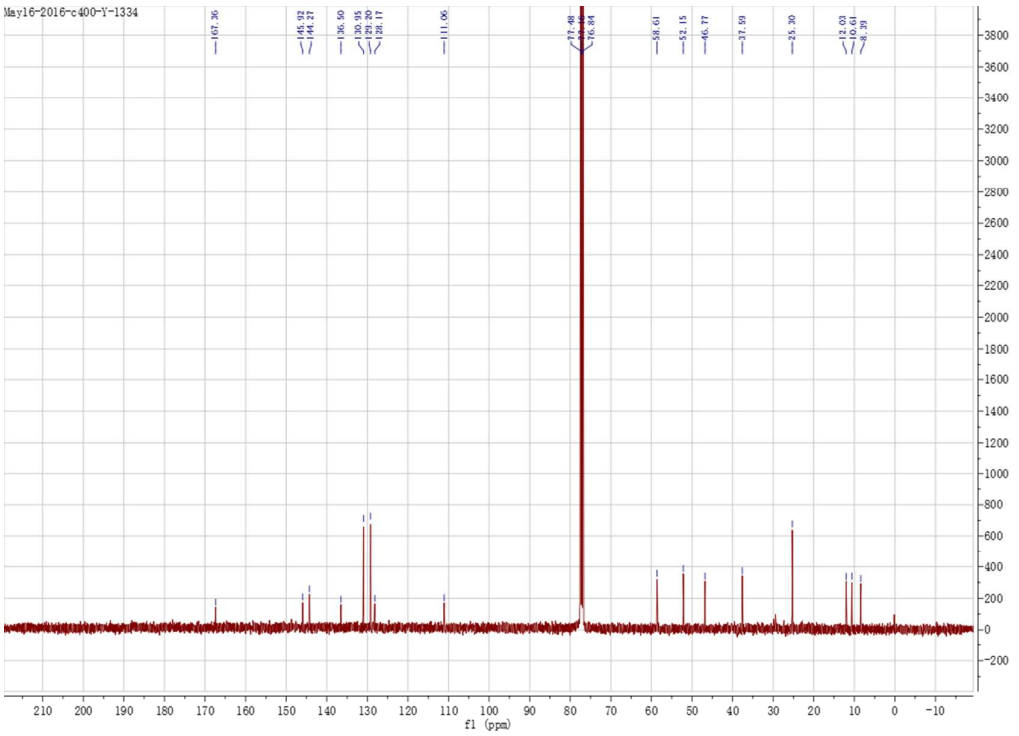

May14-2016-h400-y-1381
2.00
2.03
1.09
3.05
1.03
0.91
2.99
2.87
2.77
1.92
3.52
2.10
f1 (ppm)

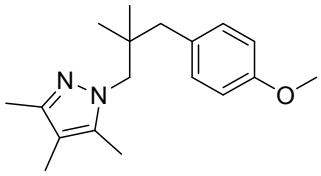

May16-2016-c400-Y-1381
167.21
151.43
146.00
134.76
129.91
128.25
127.07
111.04
77.48
77.16
76.84
57.05
52.10
44.16
39.65
33.18
32.26
25.67
12.06
9.68
8.13
f1 (ppm)



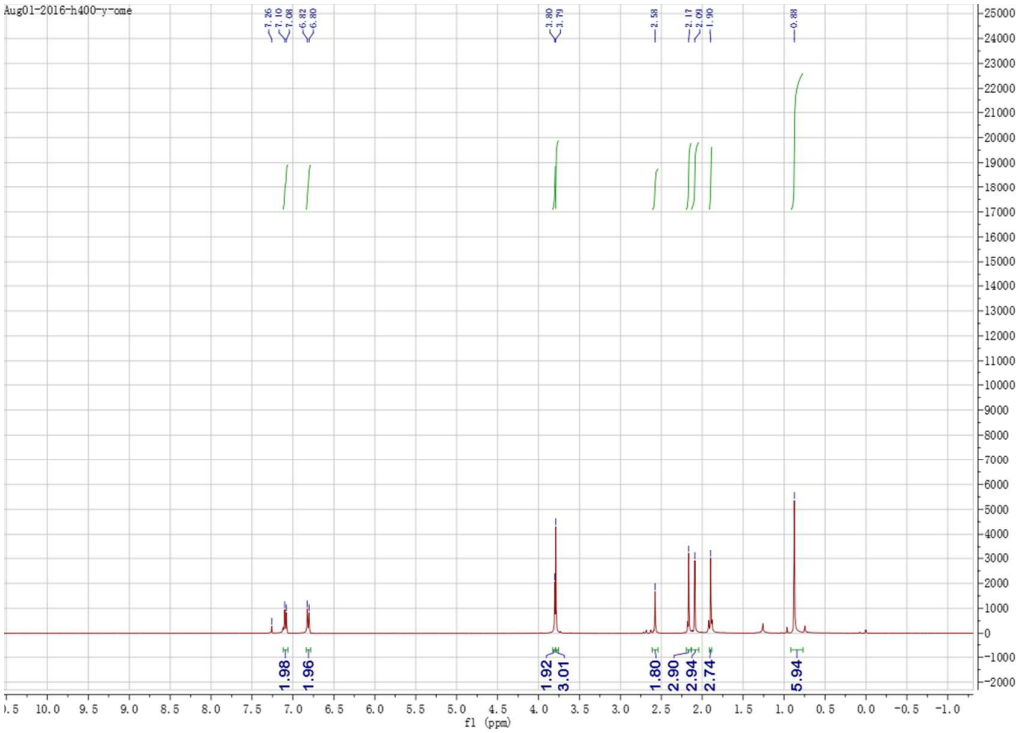
6a

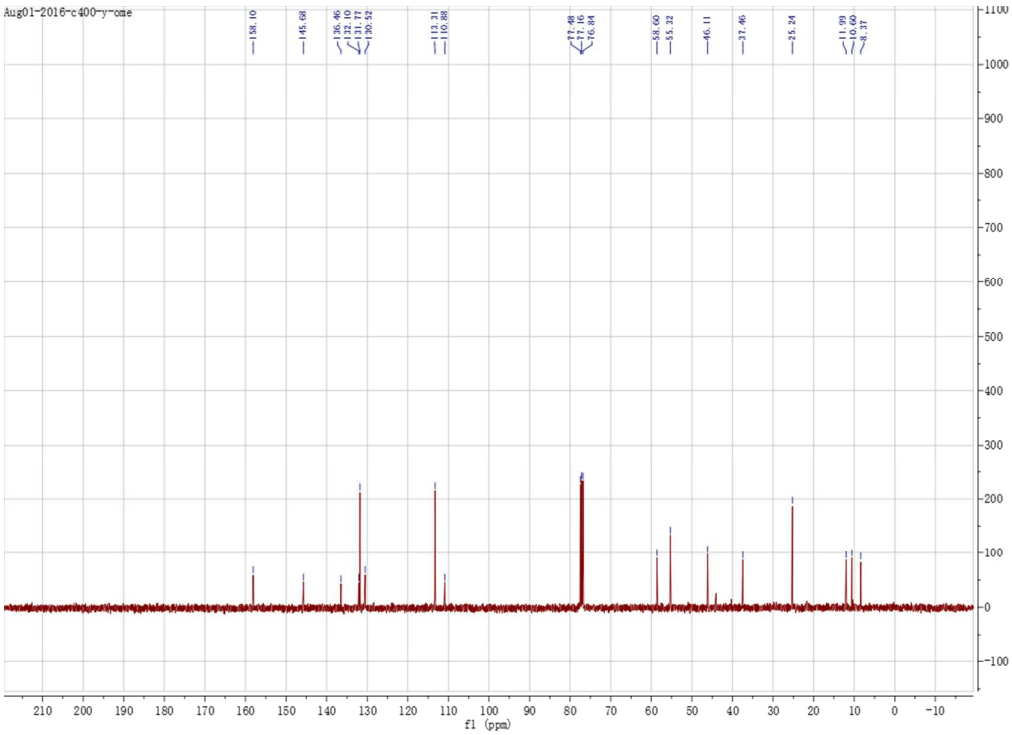

May14-2016-h400-y-1334
7.95
7.93
7.27
7.26
7.25
3.90
3.82
2.71
2.17
2.10
1.90
0.88
2.00
0.99
0.97
2.98
1.92
1.98
2.94
2.83
2.98
6.32
f1 (ppm)

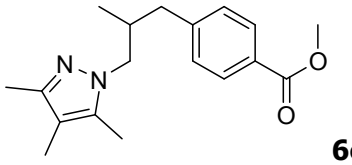

May16-2016-c400-Y-1334
167.36
145.92
144.27
136.50
130.95
129.30
128.17
111.06
77.48
76.84
76.84
58.61
52.15
46.77
37.59
25.30
12.03
10.61
8.39
f1 (ppm)



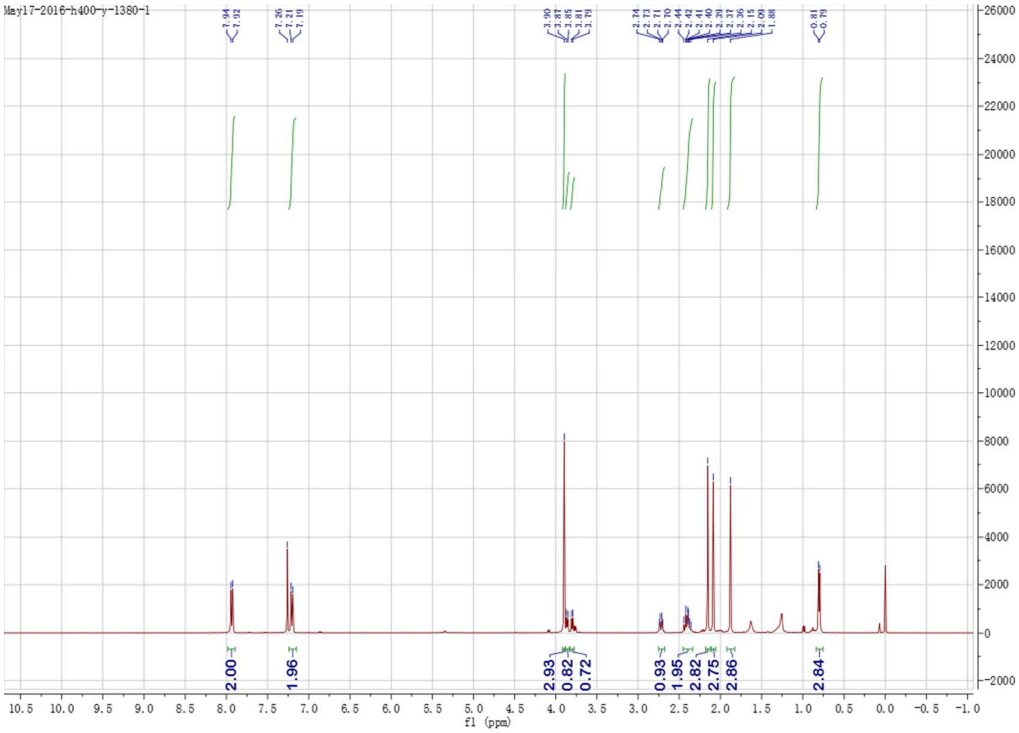
6b

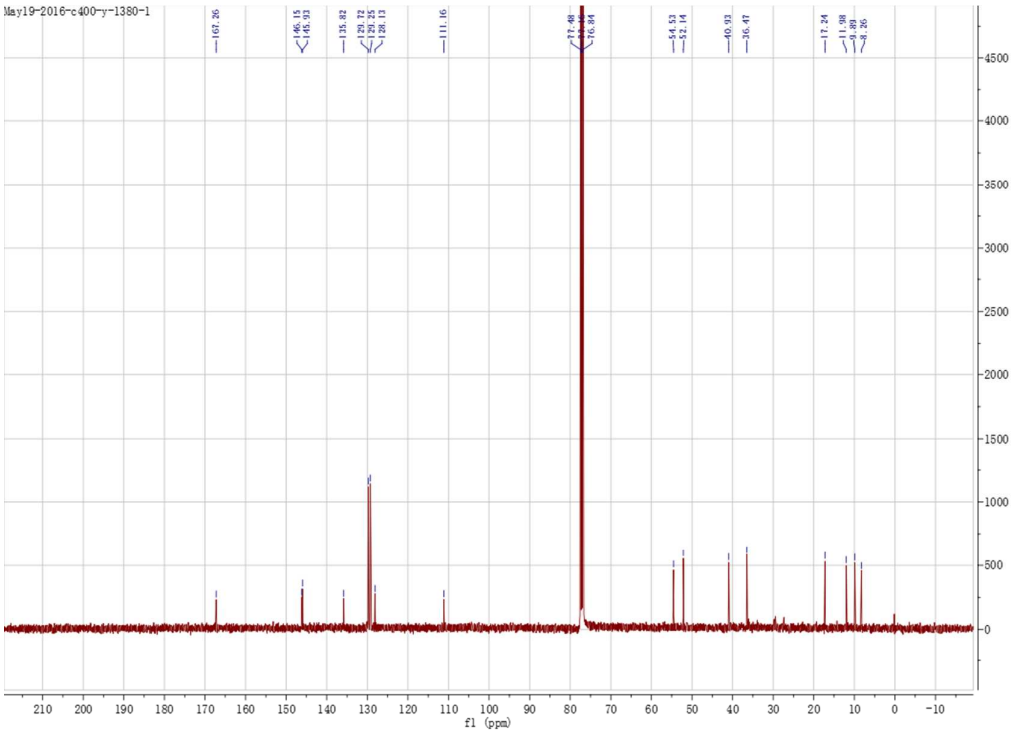

Aug01-2016-h400-y-ome
7.26
7.10
7.08
6.82
6.80
3.80
2.79
2.58
2.17
2.01
1.90
0.88
1.98
1.96
1.92
3.01
1.80
2.90
2.94
2.74
5.94
f1 (ppm)

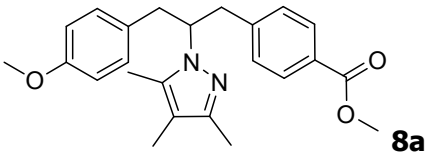

Aug01-2016-c400-y-ome
158.10
145.68
136.46
132.10
131.77
130.52
113.31
110.88
77.48
77.16
76.84
58.60
55.32
46.11
37.46
25.24
11.99
10.60
8.37
f1 (ppm)



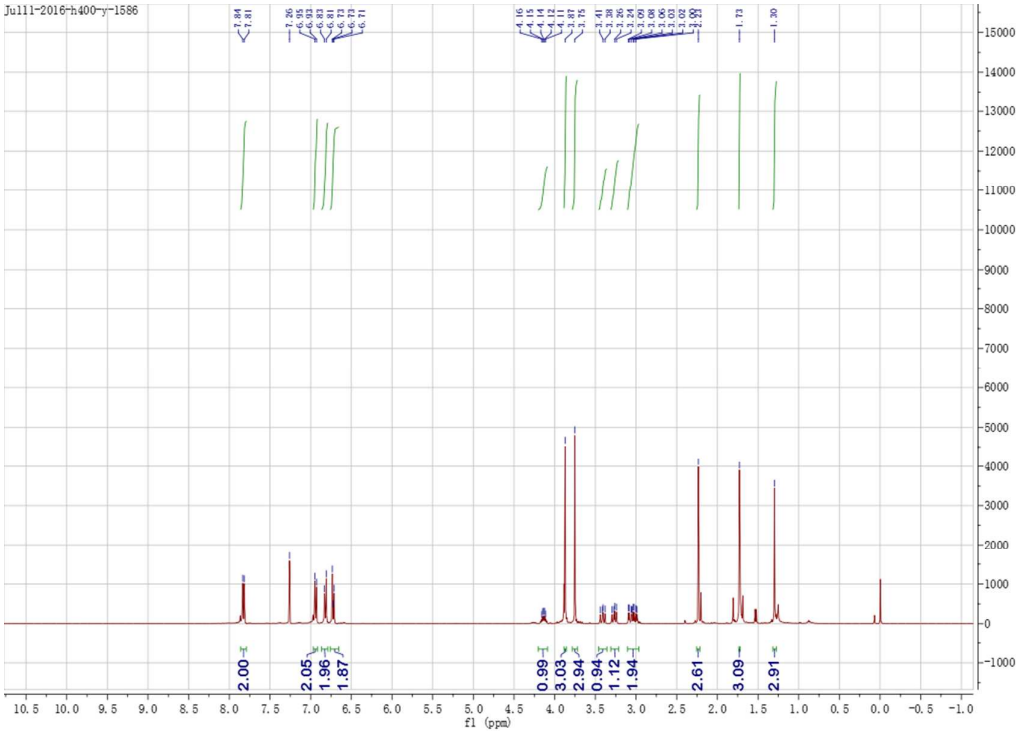
6c

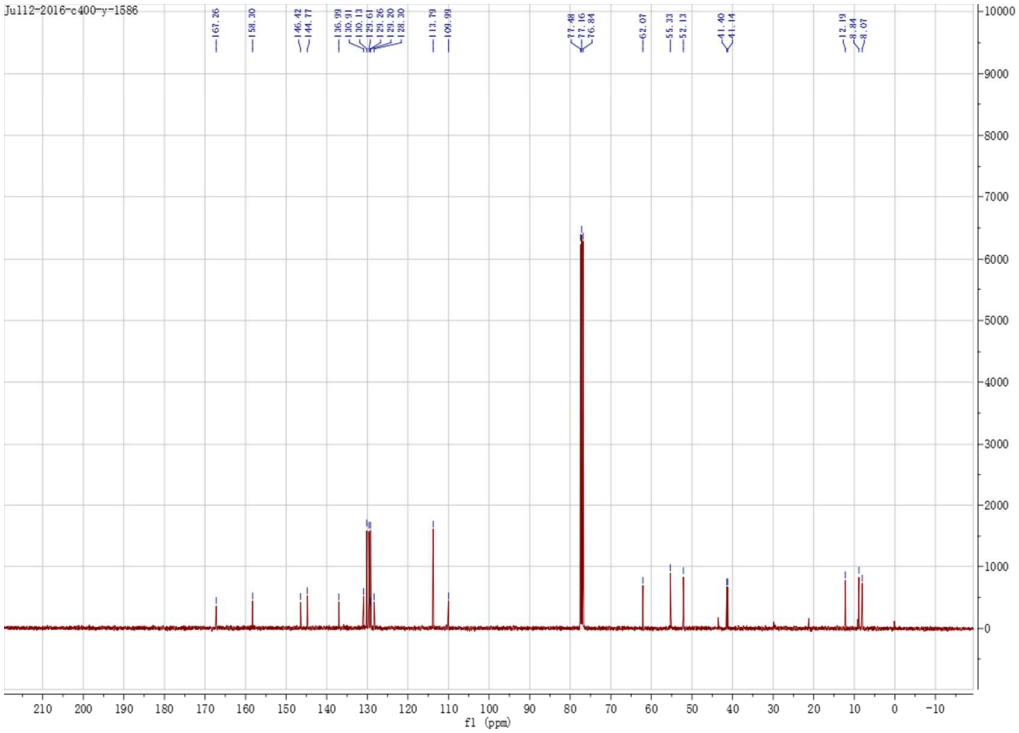

May17-2016-h400-y-1380-1
2.00
1.96
2.93
0.82
0.72
0.93
1.95
2.82
2.75
2.86
2.84
f1 (ppm)

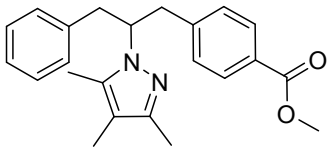

May19-2016-c400-y-1380-1
167.26
146.15
145.93
135.82
129.72
129.25
128.13
111.16
77.48
76.84
54.53
52.14
40.93
36.47
17.24
11.98
9.89
8.26
f1 (ppm)



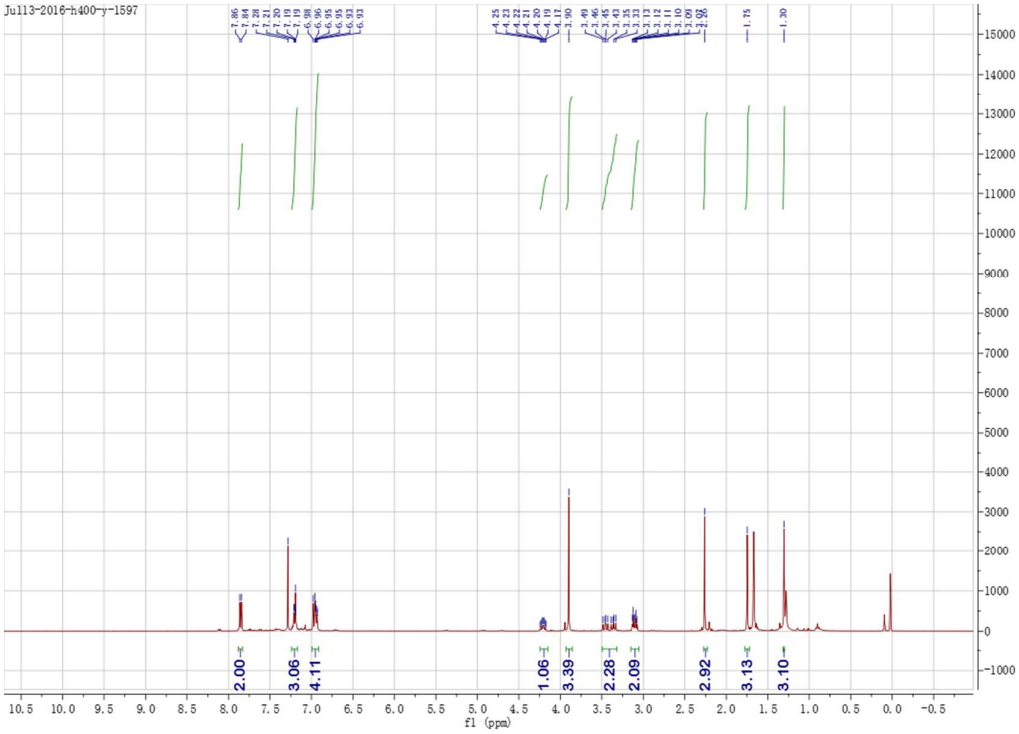
8a

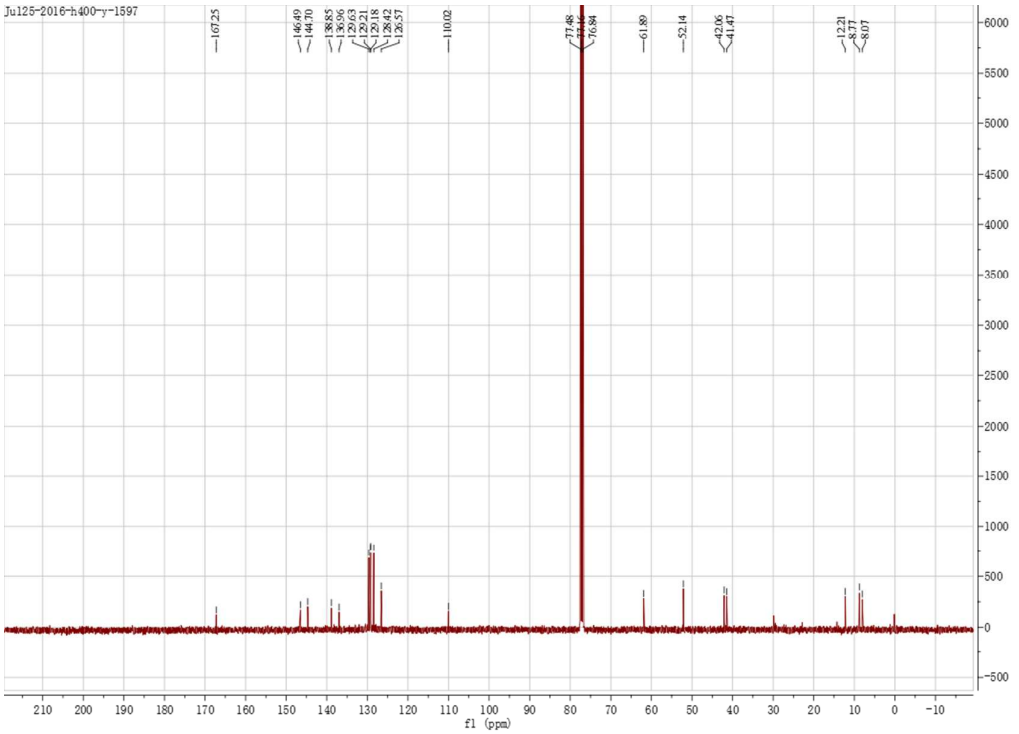


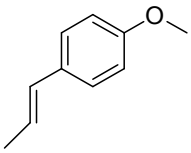




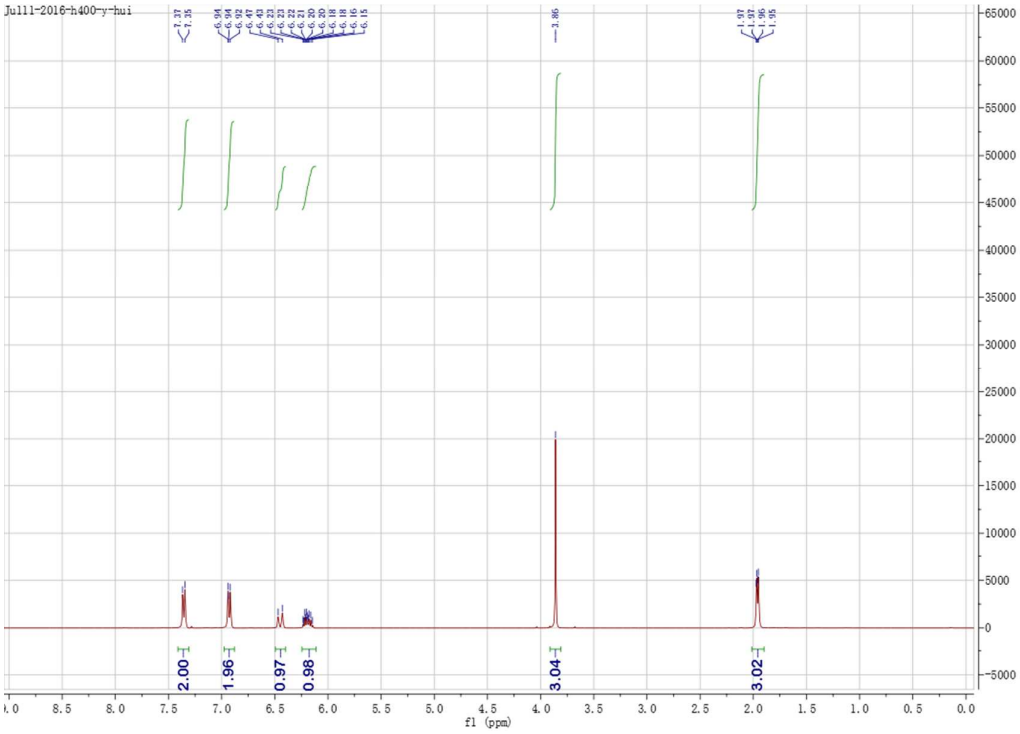
8b

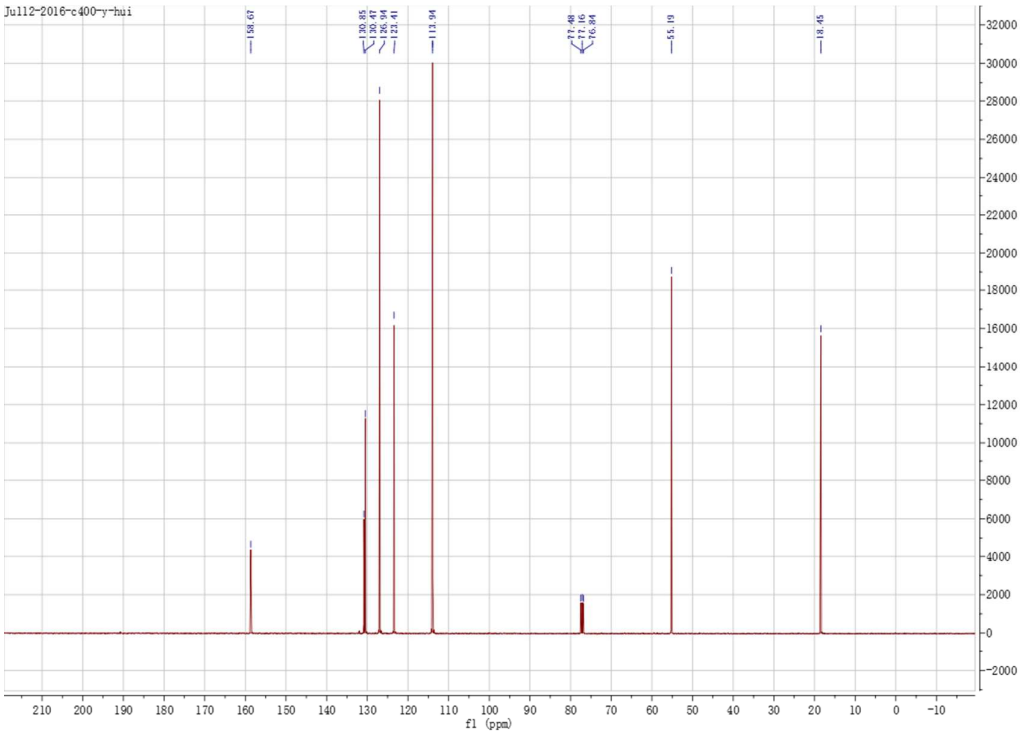

Ju113-2016-h400-y-1597
2.00
3.06
4.11
1.06
3.39
2.28
2.09
2.92
3.13
3.10
f1 (ppm)


Ju125-2016-h400-y-1597
167.25
146.49
144.70
138.85
135.66
130.55
129.21
129.18
128.42
126.57
110.02
77.48
77.16
76.84
61.89
52.14
42.06
41.47
12.21
8.77
8.07
f1 (ppm)



9a


Jul11-2016-h400-y-hui
7.37
7.35
6.94
6.94
6.92
6.47
6.43
6.23
6.22
6.21
6.20
6.18
6.16
6.15
3.86
1.97
1.97
1.96
1.95
2.00
1.96
0.97
0.98
3.04
3.02
f1 (ppm)


Jul12-2016-c400-y-hui
158.67
130.85
130.47
126.94
123.41
113.94
77.48
77.16
76.84
55.19
18.45
f1 (ppm)