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SUPPORTING INFORMATION

An unexpected rearrangement of pyrazolium halides based on N-N bond cleavage

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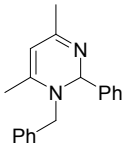
Contents

1. General information

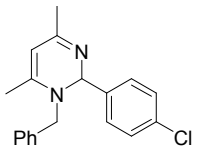
^{1}H and ^{13}C NMR data was acquired on a Bruker AV-400 MHz spectrometer. HRMS were obtained from Agilent 6520 Q-TOF LC/MS. Commercial reagents were purchased and used without further purification. THF and toluene were distilled over benzophenone ketyl under nitrogen. DMF and MeOH was distilled over CaH_2 under nitrogen. Dioxane was distilled over $LiAlH_4$ under nitrogen. Pyrazolium halides were prepared according to provious procedure [1].

2. General procedure for the rearrangement of pyrazolium salts:

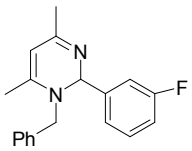
A reaction tube was charged with pyrazolium salt (0.20 mmol), potassium carbonate (0.30 mmol). To the reaction tube was added toluene (2.0 mL). The mixture was stirred at 70 °C for several hours. The mixture was cooled to room temperature and directly purified through silica gel column chromatography or preparative TLC to give the product.



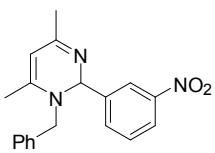
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, J = 4.8 Hz, 2H), 7.35 – 7.32 (m, 4H), 7.30 – 7.26 (m, 2H), 7.20 (d, J = 4.8 Hz, 2H), 5.91 (s, 1H), 4.92 (s, 1H), 4.71 (d, J = 11.2 Hz, 1H), 4.17 (d, J = 11.2 Hz, 1H), 1.98 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 149.5, 140.6, 136.6, 127.8, 127.2, 126.8, 126.3, 125.6, 125.3, 96.0, 76.8, 50.7, 23.0, 18.3. HRMS-ESI(*m/z*): Calcd for $C_{19}H_{21}N_2$ $[M+H]^+$: 277.1699, Found: 277.1701.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 4H), 7.28 – 7.26 (m, 3H), 7.19 (d, J = 7.2 Hz, 2H), 5.87 (s, 1H), 4.94 (s, 1H), 4.70 (d, J = 16.8 Hz, 1H), 4.16 (d, J = 16.8 Hz, 1H), 1.97 (s, 3H), 1.95 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 150.4, 140.2, 137.5, 133.5, 129.0, 128.9, 128.4, 128.0, 127.5, 126.4, 97.5, 77.2, 51.9, 24.0, 19.3. HRMS-ESI(*m/z*): Calcd for $C_{19}H_{20}ClN_2$ $[M+H]^+$: 311.1310, Found: 311.1308.

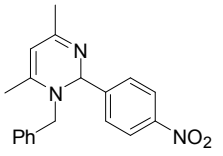


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.32 (m, 2H), 7.28 – 7.24 (m, 2H), 7.21 – 7.17 (m, 3H), 7.13 (d, J = 9.6 Hz, 1H), 6.96 (td, J = 8.3, 2.0 Hz, 1H), 5.91 (s, 1H), 4.94 (s, 1H), 4.73 (d, J = 16.8 Hz, 1H), 4.17 (d, J = 16.8 Hz, 1H), 1.98 (s, 3H), 1.96 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 162.1, 150.4, 144.6 (d, J = 5.8 Hz), 137.5, 129.7 (d, J = 8.0 Hz), 128.9, 127.5, 126.4, 122.1 (d, J = 2.7 Hz), 114.6 (d, J = 21.3 Hz), 113.5 (d, J = 21.9 Hz), 97.5, 77.3， 52.0, 24.0, 19.3. HRMS-ESI(*m/z*): Calcd for $C_{19}H_{20}FN_2$ $[M+H]^+$: 295.1605, Found: 295.1605.

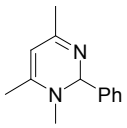


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 1.8 Hz, 1H), 8.12 (dd, J = 8.1 and 1.3 Hz, 1H), 7.76 (d, J = 7.7 Hz, 1H), 7.47 (t, J = 7.9 Hz, 1H), 7.34 (t, J = 7.3 Hz, 2H), 7.27 (t, J = 7.3 Hz, 1H), 7.20 (d, J = 7.2 Hz, 2H), 6.00 (s, 1H), 5.01 (s, 1H), 4.79 (d, J = 16.8 Hz, 1H), 4.24 (d, J = 16.8 Hz, 1H), 2.03 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 150.4, 148.2, 143.9, 137.1, 133.0, 129.2, 129.0, 127.7, 126.5, 122.8, 121.3,

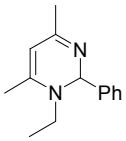
98.6, 76.8, 52.5, 23.9, 19.4. HRMS-ESI(*m/z*): Calcd for $C_{19}H_{20}N_3O_2$ $[M+H]^+$: 322.1550, Found: 322.1556.



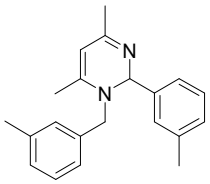
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.34 – 7.32 (m, 2H), 7.26 (d, *J* = 7.2 Hz, 1H), 7.19 (d, *J* = 7.2 Hz, 2H), 6.00 (s, 1H), 4.99 (s, 1H), 4.77 (d, *J* = 16.8 Hz, 1H), 4.22 (d, *J* = 16.8 Hz, 1H), 2.01 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 150.5, 148.9, 147.5, 137.0, 129.0, 127.7, 127.4, 126.5, 123.5, 98.6, 77.0, 52.5, 23.9, 19.3. HRMS-ESI(*m/z*): Calcd for $C_{19}H_{20}N_3O_2$ $[M+H]^+$:322.1550, Found: 322.1550.



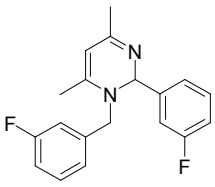
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.2 Hz, 2H), 7.35 – 7.28 (m, 3H), 5.83 (s, 1H), 4.83 (s, 1H), 2.90 (s, 3H), 1.97 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.3, 150.4, 140.2, 127.3, 126.8, 125.5, 94.2, 78.5, 34.6, 22.9, 18.3. HRMS-ESI(*m/z*): Calcd for $C_{13}H_{17}N_2$ $[M+H]^+$: 201.1386, Found: 201.1387.



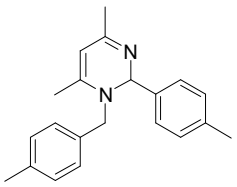
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 6.8 Hz, 2H), 7.33 – 7.28 (m, 3H), 5.89 (s, 1H), 4.86 (s, 1H), 3.44 (dq, *J* = 14.4, 7.2 Hz, 1H), 3.17 (dq, *J* = 14.4, 7.2 Hz, 1H), 2.01 (s, 3H), 1.92 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 150.1, 142.2, 128.1, 127.6, 126.4, 97.1, 58.4, 43.5, 23.8, 18.9, 15.3. HRMS-ESI(*m/z*): Calcd for $C_{14}H_{19}N_2$ $[M+H]^+$: 215.1543, Found: 215.1550.



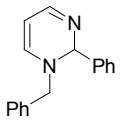
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.18 (m, 4H), 7.10 – 7.00 (m, 4H), 5.87 (s, 1H), 4.89 (s, 1H), 4.64 (d, *J* = 16.8 Hz, 1H), 4.11 (d, *J* = 16.8 Hz, 1H), 2.331 (s, 3H), 2.326 (s, 3H), 1.97 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 150.6, 141.8, 138.5, 137.9, 137.7, 128.7, 128.6, 128.2, 128.1, 127.4, 127.1, 123.6, 123.5, 96.7, 78.0, 51.6, 24.1, 21.6, 21.5, 19.4. HRMS-ESI(*m/z*): Calcd for $C_{21}H_{25}N_2$ $[M+H]^+$: 305.2012, Found: 305.2013.



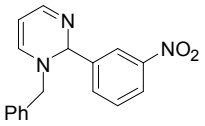
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.12 (d, *J* = 9.6 Hz, 1H), 6.99 – 6.95 (m, 3H), 6.90 (d, *J* = 9.6 Hz, 1H), 5.88 (s, 1H), 4.98 (s, 1H), 4.70 (d, *J* = 17.2 Hz, 1H), 4.17 (d, *J* = 17.2 Hz, 1H), 1.99 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 164.0, 163.7, 162.5, 162.1, 150.2, 144.2 (d, *J* = 5.8 Hz), 140.3 (d, *J* = 6.6 Hz), 130.5 (d, *J* = 8.2 Hz), 129.8 (d, *J* = 8.0 Hz), 122.1 (d, *J* = 2.8 Hz), 121.9 (d, *J* = 2.8 Hz), 114.8 (d, *J* = 21.3 Hz), 114.5 (d, *J* = 21.2 Hz), 113.4 (dd, *J* = 28.0, 22.0 Hz), 98.0, 51.6, 24.0, 19.2. HRMS-ESI(*m/z*): Calcd for $C_{19}H_{19}F_2N_2$ $[M+H]^+$: 313.1511, Found: 313.1513.



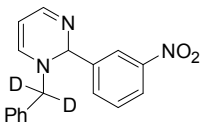
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.0 Hz, 2H), 7.14 – 7.08 (m, 6H), 5.88 (s, 1H), 4.89 (s, 1H), 4.65 (d, *J* = 16.8 Hz, 1H), 4.12 (d, *J* = 16.8 Hz, 1H), 2.33 (s, 6H), 1.96 (s, 3H), 1.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 150.4, 138.9, 137.4, 136.9, 134.7, 129.5, 129.0, 126.5, 126.4, 96.9, 77.6, 51.5, 24.1, 21.2, 21.1, 19.3. HRMS-ESI(*m/z*): Calcd for $C_{21}H_{25}N_2$ $[M+H]^+$: 305.2012, Found: 305.2021. HRMS-ESI(*m/z*): Calcd for $C_{19}H_{21}N_2$ $[M+H]^+$: 277.1699, Found: 277.1693.



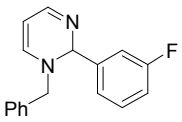
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 3.0 Hz, 1H), 7.48 (dd, *J* = 7.6, 1.2 Hz, 2H), 7.38 – 7.27 (m, 6H), 7.22 (d, *J* = 6.8 Hz, 2H), 6.67 (d, *J* = 6.8 Hz, 1H), 5.96 (s, 1H), 4.96 (dd, *J* = 6.8 and 3.4 Hz, 1H), 4.27 (d, *J* = 15.2 Hz, 1H), 4.19 (d, *J* = 15.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 143.8, 140.6, 136.5, 128.9, 128.5, 128.3, 127.9, 127.6, 126.8, 93.7, 75.7, 56.7. HRMS-ESI(*m/z*): Calcd for $C_{17}H_{17}N_2$ $[M+H]^+$: 249.1386, Found: 249.1385.



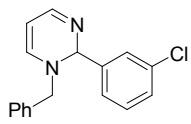
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.15 (dd, *J* = 8.0 and 1.6 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 3.2 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.37 – 7.26 (m, 3H), 7.21 (d, *J* = 6.8 Hz, 2H), 6.78 (dd, *J* = 6.8, 1.6 Hz, 1H), 6.09 (s, 1H), 5.06 (dd, *J* = 6.8 and 3.2 Hz, 1H), 4.40 (d, *J* = 15.6 Hz, 1H), 4.27 (d, *J* = 15.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 148.2, 143.6, 142.7, 136.0, 133.1, 129.4, 129.0, 128.2, 127.5, 123.1, 121.6, 95.1, 74.7, 57.5. HRMS-ESI(*m/z*): Calcd for $C_{17}H_{16}N_3O_2$ $[M+H]^+$: 294.1237, Found: 294.1237.



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.16 (d, *J* = 7.4 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.59 (s, 1H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.40 – 7.28 (m, 3H), 7.21 (d, *J* = 7.2 Hz, 2H), 6.78 (d, *J* = 6.9 Hz, 1H), 6.09 (s, 1H), 5.06 (dd, *J* = 6.8 and 3.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 148.2, 143.5, 142.7, 135.9, 133.0, 129.4, 129.0, 128.3, 127.6, 123.1, 121.6, 95.1, 74.7. HRMS-ESI(*m/z*): Calcd for $C_{17}H_{14}D_2N_3O_2$ $[M+H]^+$: 296.1361, Found: 296.1363.

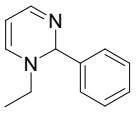


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.57 (m, 1H), 7.37 – 7.28 (m, 4H), 7.24 – 7.18 (m, 4H), 7.03 - 6.98 (m, 1H), 6.69 (d, *J* = 6.8 Hz, 1H), 5.97 (s, 1H), 4.98 (dd, *J* = 6.8, 3.6 Hz, 1H), 4.31 (d, *J* = 15.6, 1H), 4.20 (d, *J* = 15.6, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 162.2, 156.1, 143.7, 136.2, 130.0 (d, *J* = 7.9 Hz), 128.9, 128.1, 127.6, 122.3, 115.1 (d, *J* = 21.2 Hz), 113.8 (d, *J* = 21.9 Hz), 94.1, 75.1, 56.9. HRMS-ESI(*m/z*): Calcd for $C_{17}H_{16}FN_2$ $[M+H]^+$: 267.1292, Found: 267.1300.

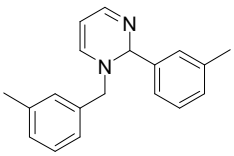


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 3.6 Hz, 1H), 7.45 (s, 1H), 7.37 – 7.26 (m, 6H), 7.22 - 7.20 (m, 2H), 6.69 (d, *J* = 7.2 Hz, 1H), 5.95 (s, 1H), 4.99 (dd, *J* = 6.8, 3.6 Hz, 1H), 4.31 (d, *J* = 15.6 Hz, 1H), 4.19 (d, *J* = 15.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1,

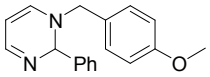
143.7, 142.6, 136.2, 134.4, 129.8, 128.9, 128.4, 128.1, 127.6, 127.0, 124.9, 94.2, 75.1, 57.0. HRMS-ESI(*m/z*): Calcd for $C_{17}H_{16}ClN_2$ $[M+H]^+$: 283.0097, Found: 283.0095.



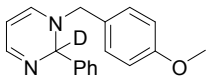
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.49 (m, 3H), 7.37 – 7.30 (m, 3H), 6.67 (dt, *J* = 6.8, 1.3 Hz, 1H), 5.99 (s, 1H), 4.94 (dd, *J* = 6.8 and 3.6 Hz, 1H), 3.14 (dq, *J* = 7.2 and 2.4 Hz, 2H), 1.16 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 142.8, 141.2, 128.3, 128.0, 126.6, 93.8, 75.6, 47.9, 14.7. HRMS-ESI(*m/z*): Calcd for $C_{12}H_{15}N_2$ $[M+H]^+$: 187.1230, Found: 187.1226.



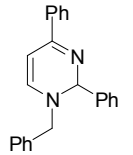
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 3.6 Hz, 1H), 7.28 – 7.21 (m, 4H), 7.15 – 7.10 (m, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.73 (d, *J* = 6.8 Hz, 1H), 5.95 (s, 1H), 4.96 (dd, *J* = 6.8 and 3.6 Hz, 1H), 4.25 (d, *J* = 15.2 Hz, 1H), 4.16 (d, *J* = 15.6 Hz, 1H), 2.35 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 144.5, 140.2, 138.6, 138.2, 136.1, 129.2, 128.8, 128.4, 128.4, 127.5, 124.8, 123.8, 93.3, 75.3, 56.8, 21.6, 21.5. HRMS-ESI(*m/z*): Calcd for $C_{19}H_{21}N_2$ $[M+H]^+$: 277.1699, Found: 277.1693.



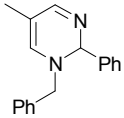
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 3.2 Hz, 1H), 7.48 (d, *J* = 6.8 Hz, 2H), 7.37 – 7.24 (m, 3H), 7.12 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.65 (d, *J* = 6.8 Hz, 1H), 5.95 (s, 1H), 4.93 (dd, *J* = 6.8, 3.2 Hz, 1H), 4.20 (d, *J* = 14.8 Hz, 1H), 4.12 (d, *J* = 14.8 Hz, 1H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 154.8, 142.6, 139.6, 128.0, 127.4, 125.7, 113.2, 92.4, 74.4, 55.1, 54.3. HRMS-ESI(*m/z*): Calcd for $C_{18}H_{19}N_2O$ $[M+H]^+$: 279.1492, Found: 279.1496.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 2.8 Hz, 1H), 7.48 (d, *J* = 6.8 Hz, 2H), 7.36 – 7.26 (m, 3H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.66 (d, *J* = 6.8 Hz, 1H), 4.92 (dd, *J* = 6.8, 3.2 Hz, 1H), 4.20 (d, *J* = 14.8 Hz, 1H), 4.12 (d, *J* = 14.8 Hz, 1H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 155.8, 143.6, 140.6, 129.0, 128.4, 126.7, 114.2, 93.5, 56.2, 55.3. HRMS-ESI(*m/z*): Calcd for $C_{18}H_{18}DN_2O$ $[M+H]^+$: 280.1554, Found: 280.1404.

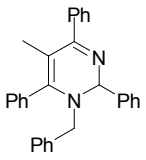


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 3.2 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.53 – -7.51 (m, 2H), 7.44 – 7.27 (m, 7H), 7.25 – 7.20 (m, 2H), 7.12 (d, *J* = 6.8 Hz, 2H), 6.15 (s, 1H), 5.45 (d, *J* = 3.2 Hz, 1H), 4.61 (d, *J* = 15.6 Hz, 1H), 4.17 (d, *J* = 15.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 153.2, 141.3, 138.3, 135.4, 129.9, 128.8, 128.6, 128.5, 128.1, 127.8, 127.5, 126.5, 102.7, 75.6, 55.0. HRMS-ESI(*m/z*): Calcd for $C_{23}H_{21}N_2$ $[M+H]^+$: 325.1699, Found: 325.1812.

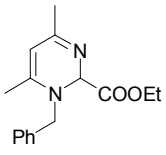


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.48 – 7.42 (m, 2H), 7.36 - 7.27 (m, 6H), 7.20 (d, *J* = 6.8 Hz, 2H), 6.40 (s, 1H), 5.87 (s, 1H), 4.23 (d, *J* = 15.2 Hz, 1H), 4.16 (d, *J* = 15.6 Hz, 1H), 1.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 140.8, 140.2, 137.3, 128.8, 128.3, 128.0, 127.7, 127.5, 126.9,

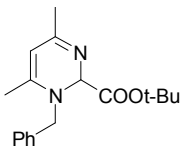
102.6, 75.5, 56.4, 14.7. HRMS-ESI(*m/z*): Calcd for $C_{18}H_{19}N_2$ $[M+H]^+$: 263.1543, Found: 263.1541.



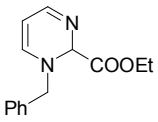
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.6 Hz, 2H), 7.57 – 7.55 (m, 2H), 7.42 – 7.34 (m, 10H), 7.31 – 7.21 (m, 4H), 7.13 (d, *J* = 7.2 Hz, 2H), 6.26 (s, 1H), 4.32 (d, *J* = 15.6 Hz, 1H), 4.12 (d, *J* = 15.2 Hz, 1H), 1.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 142.0, 138.6, 134.8, 130.2, 129.1, 128.7, 128.5, 128.4, 128.08, 128.06, 127.9, 127.4, 127.3, 126.7, 110.9, 74.9, 55.4, 15.6. HRMS-ESI(*m/z*): Calcd for $C_{30}H_{27}N_2$ $[M+H]^+$: 415.2169, Found: 415.2175



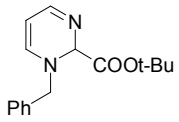
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.2 Hz, 2H), 7.28 – 7.22 (m, 3H), 5.37 (s, 1H), 5.02 (s, 1H), 4.78 (d, *J* = 16.8 Hz, 1H), 4.32 (d, *J* = 16.4 Hz, 1H), 4.24 – 4.13 (m, 2H), 2.02 (s, 3H), 1.95 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 166.3, 151.5, 137.2, 128.9, 127.6, 126.7, 98.0, 75.4, 61.2, 52.5, 23.7, 19.0, 14.3. HRMS-ESI(*m/z*): Calcd for $C_{16}H_{21}N_2O_2$ $[M+H]^+$: 273.1598, Found: 273.1590.



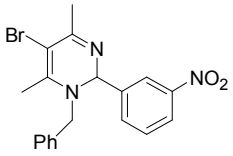
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.6 Hz, 2H), 7.28 – 7.20 (m, 3H), 5.25 (s, 1H), 4.99 (s, 1H), 4.73 (d, *J* = 16.4 Hz, 1H), 4.32 (d, *J* = 16.4 Hz, 1H), 2.01 (s, 3H), 1.93 (s, 3H), 1.45 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 165.9, 151.0, 137.3, 128.8, 127.5, 126.7, 97.8, 81.7, 75.8, 52.5, 28.1, 23.7, 19.0. HRMS-ESI(*m/z*): Calcd for $C_{18}H_{25}N_2O_2$ $[M+H]^+$: 301.1911, Found: 301.1902.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 3.2 Hz, 1H), 7.40 – 7.24 (m, 5H), 6.67 (d, *J* = 6.8 Hz, 1H), 5.51 (s, 1H), 5.09 (dd, *J* = 6.8, 3.6 Hz, 1H), 4.48 (d, *J* = 15.2 Hz, 1H), 4.43 (d, *J* = 14.8 Hz, 1H), 4.26 – 4.18 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 158.1, 143.6, 135.8, 128.9, 128.2, 127.9, 95.2, 72.8, 61.5, 57.5, 14.3. HRMS-ESI(*m/z*): Calcd for $C_{14}H_{17}N_2O_2$ $[M+H]^+$: 245.1285, Found: 245.1280.

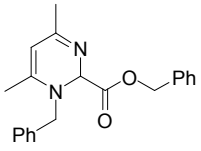


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 3.2 Hz, 1H), 7.31 – 7.17 (m, 5H), 6.64 (d, *J* = 6.8 Hz, 1H), 5.38 (s, 1H), 4.98 (dd, *J* = 6.8, 3.6 Hz, 1H), 4.44 (d, *J* = 15.2 Hz, 1H), 4.40 (d, *J* = 15.2 Hz, 1H), 1.47 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 156.7, 142.3, 134.8, 127.9, 127.1, 126.9, 93.9, 81.2, 72.3, 56.4, 27.0. HRMS-ESI(*m/z*): Calcd for $C_{16}H_{21}N_2O_2$ $[M+H]^+$: 273.1598, Found: 273.1601.

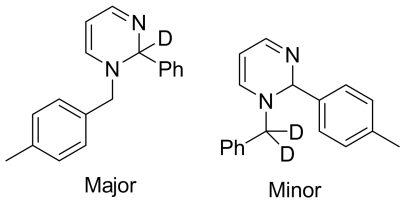


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.80 (s, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.37 – 7.28 (m, 3H), 7.17 (d, *J* = 7.6 Hz, 2H), 5.96 (s, 1H), 4.76 (d, *J* = 16.8 Hz, 1H), 4.40 (d, *J* = 16.8 Hz, 1H), 2.25 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 148.1, 142.8, 136.8, 132.9, 132.8, 129.2, 129.1, 127.9, 126.7, 123.0,

121.4, 95.1, 75.6, 54.6, 24.8, 18.6. HRMS-ESI(*m/z*): Calcd for $C_{19}H_{19}BrN_3O_2$ $[M+H]^+$: 400.0655, Found: 400.0655.



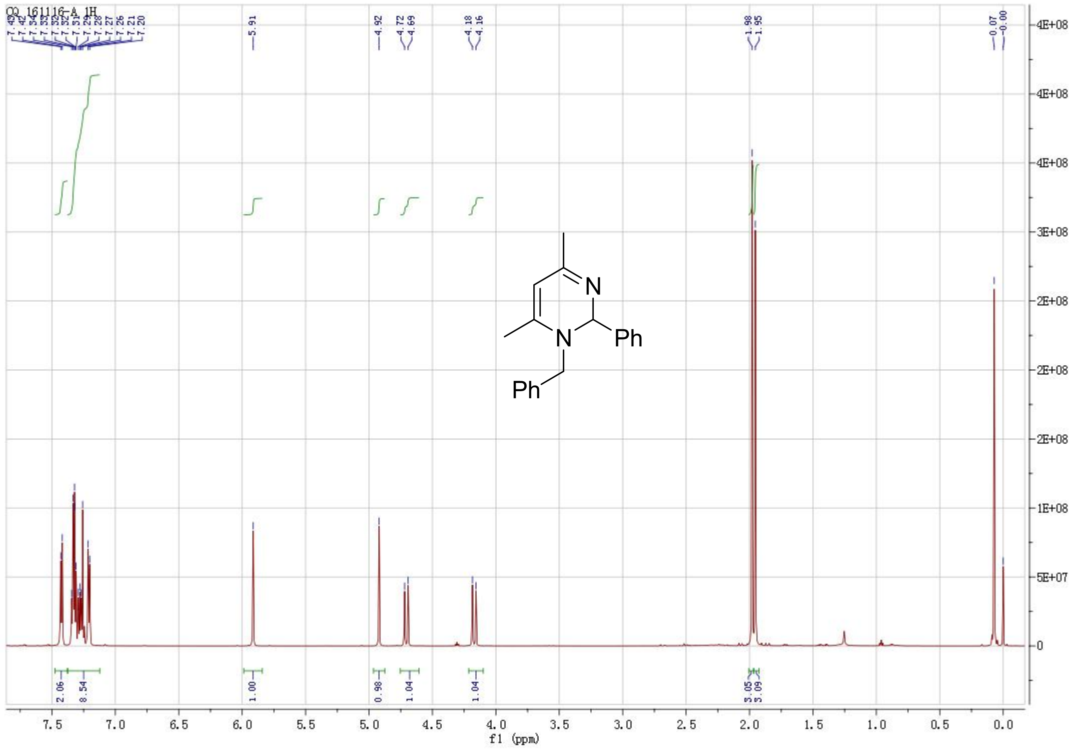
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 7H), 7.26 (d, *J* = 4.4 Hz, 1H), 7.19 (d, *J* = 7.2 Hz, 2H), 5.44 (s, 1H), 5.21 (d, *J* = 12.4 Hz, 1H), 5.14 (d, *J* = 12.4 Hz, 1H), 5.04 (s, 1H), 4.74 (d, *J* = 16.8 Hz, 1H), 4.31 (d, *J* = 16.8 Hz, 1H), 2.03 (s, 3H), 1.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 166.5, 151.5, 137.0, 136.0, 128.9, 128.5, 128.1, 127.9, 127.6, 126.7, 98.3, 75.4, 66.6, 52.6, 23.7, 19.0.



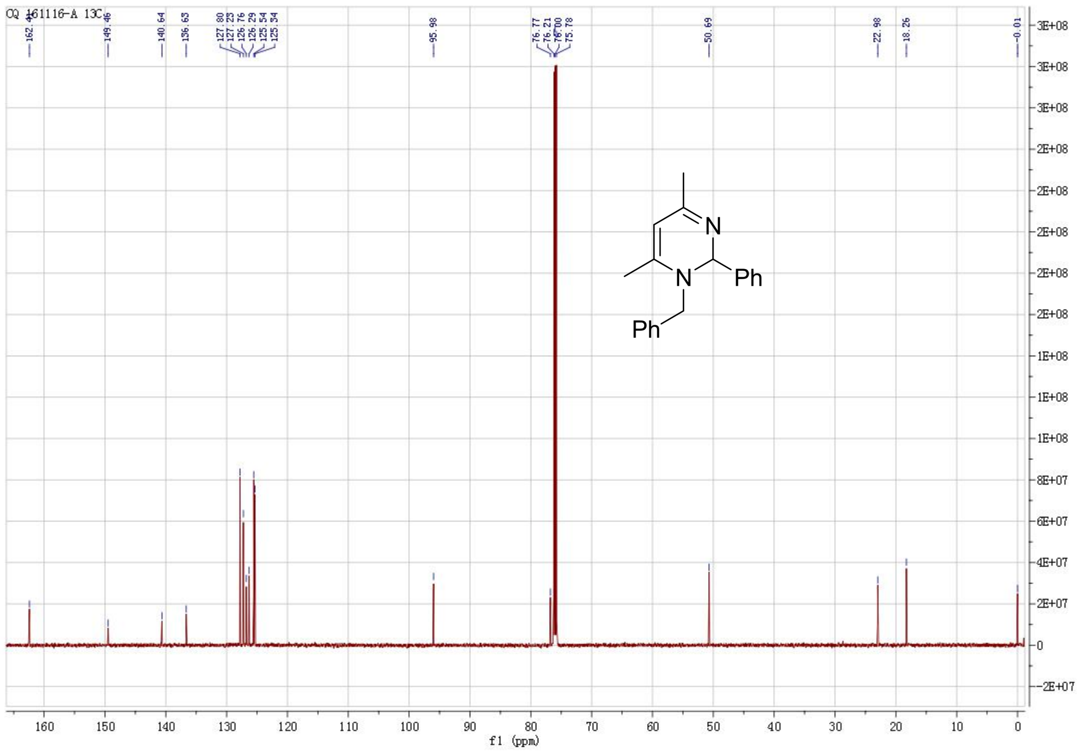
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 2.6 Hz, 1H), 7.48 (d, *J* = 6.9 Hz, 1H), 7.38 – 7.09 (m, 8H), 6.66 (d, *J* = 4.0 Hz, 0.9H), 5.92 (s, 0.29H), 4.92 (dd, *J* = 6.8, 3.2 Hz, 1H), 4.23 (d, *J* = 16.0 Hz, 0.78H), 4.15 (d, *J* = 12.0 Hz, 0.78H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.82, 155.75, 143.7， 140.6, 137.7, 133.3，129.5, 129.1，128.8, 128.5, 128.2, 127.9, 127.7, 127.6, 126.80, 126.76, 126.76, 93.5, 75.4, 56.4, 21.22, 21.15.

Reference:

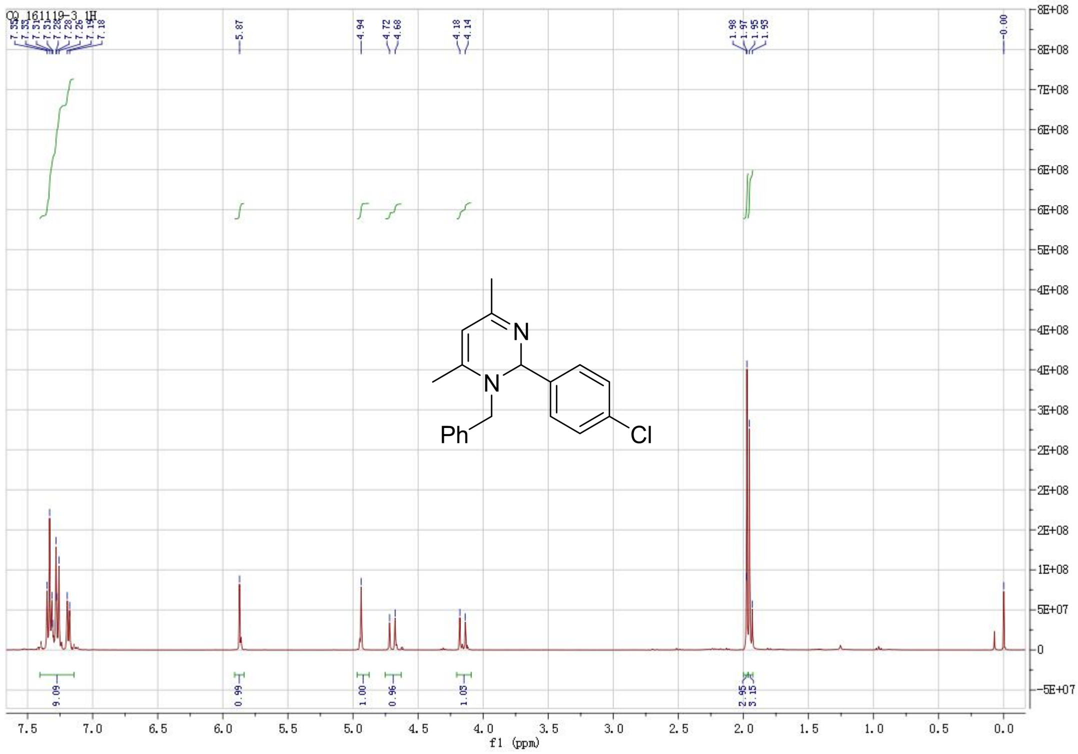
1. Han, L. J. Lee, H. V. Huynh, *Organometallics* **2009**, *28*, 2778–2786.

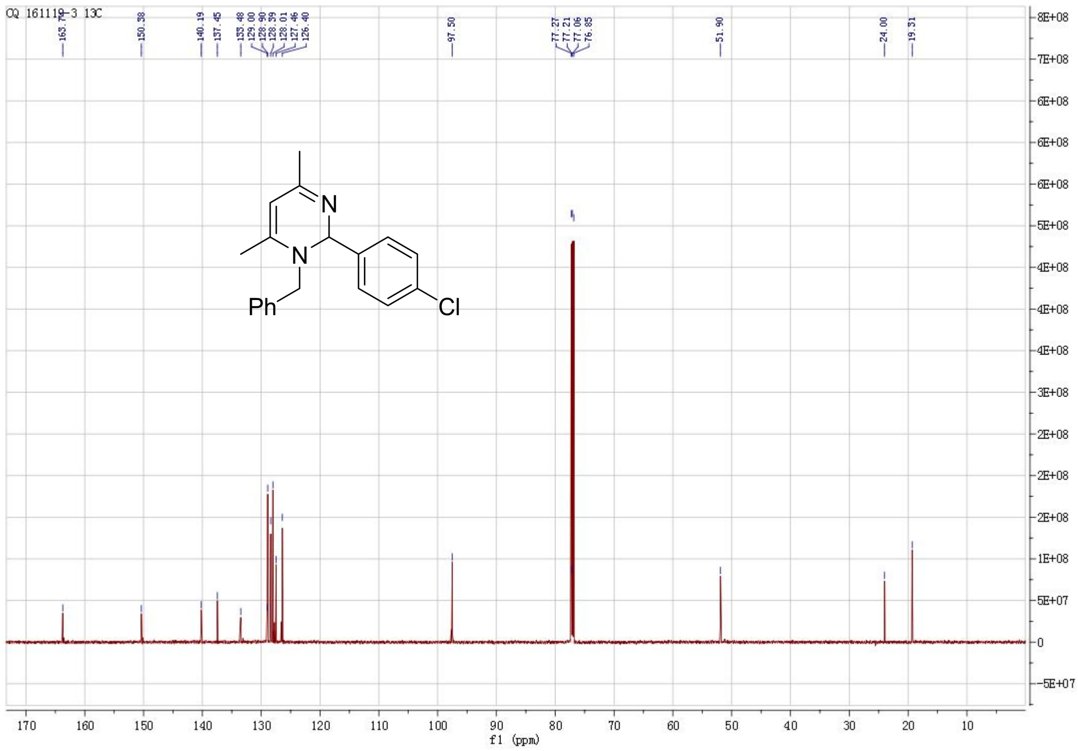


CQ 161116-A 1H
5.91
4.92
4.72
4.69
4.18
4.16
1.98
1.95
0.07
-0.00
2.06
8.54
1.00
0.98
1.04
1.04
3.05
3.09
N
Ph
N
Ph
f1 (ppm)



CQ 161116-A 13C
149.46
140.64
136.63
127.80
127.23
126.76
126.29
125.54
125.54
95.98
76.77
76.21
76.00
75.78
50.69
22.98
18.26
-0.01
N
Ph
N
Ph
f1 (ppm)


CQ 161119-3 1H
7.35 7.33 7.31 7.29 7.28 7.26 7.19 7.18
5.87
4.94 4.72 4.68
4.18 4.14
1.98 1.97 1.95 1.93
-0.00
N
N
Ph
Cl
9.09
0.99
1.00
0.96
1.03
2.95
3.15
f1 (ppm)


CQ 161119-3 13C
163.74
150.38
140.19
137.45
133.48 129.00 128.90 128.59 128.01 127.46 126.40
97.50
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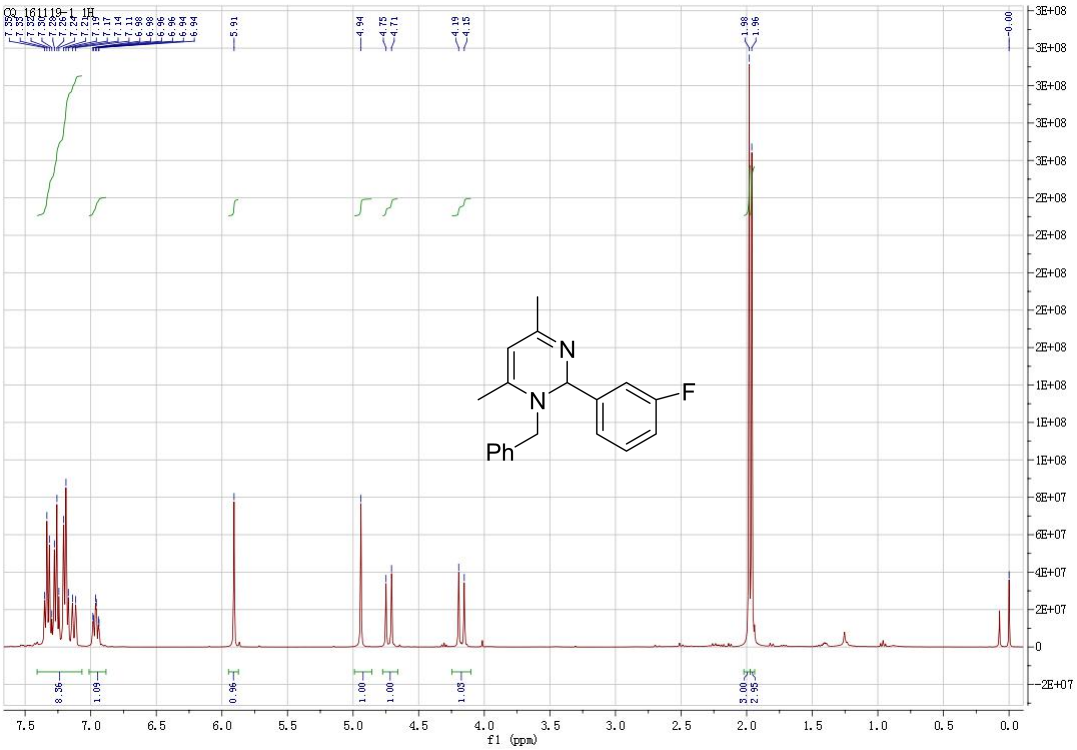
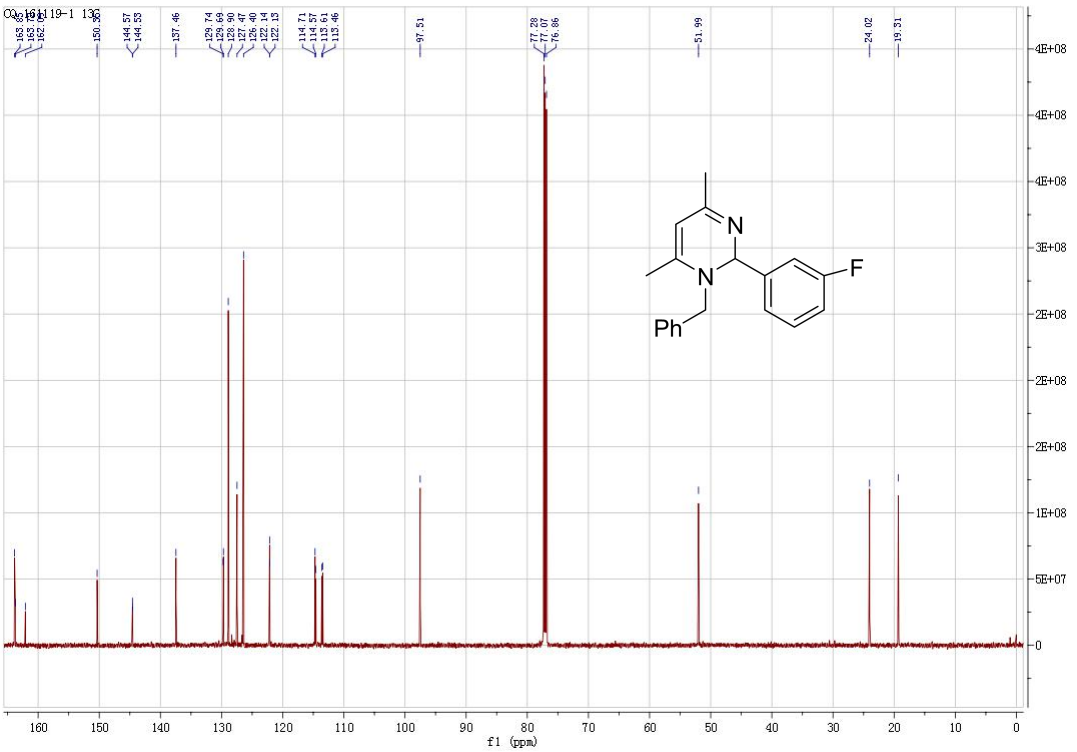
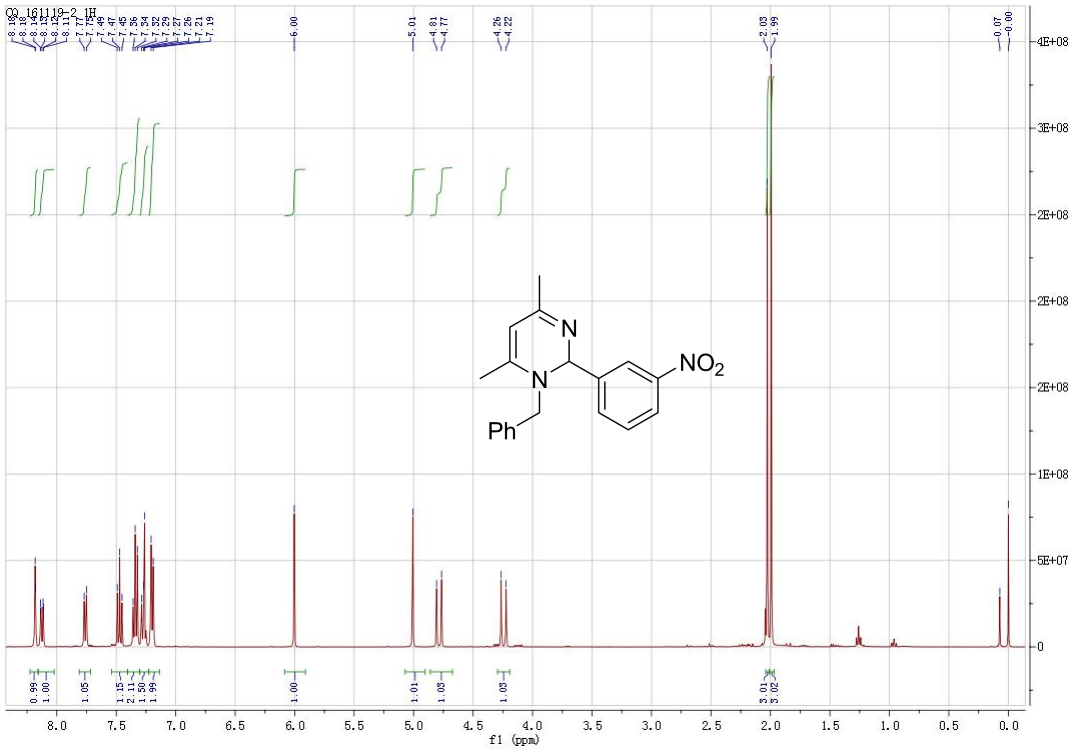
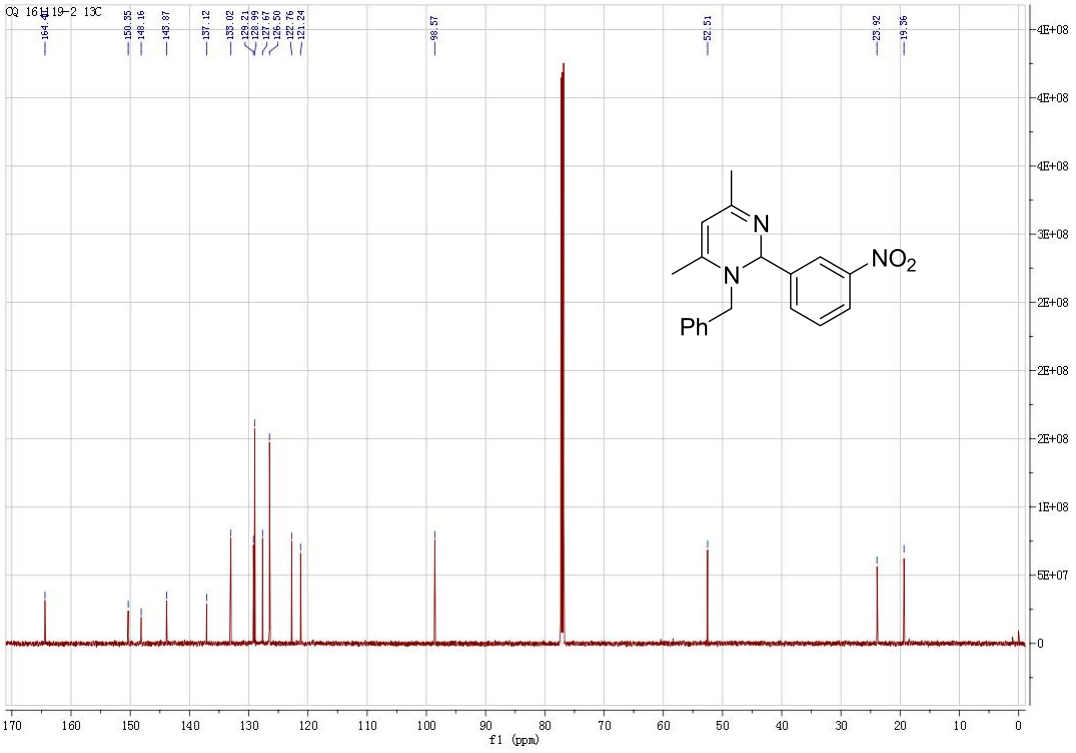
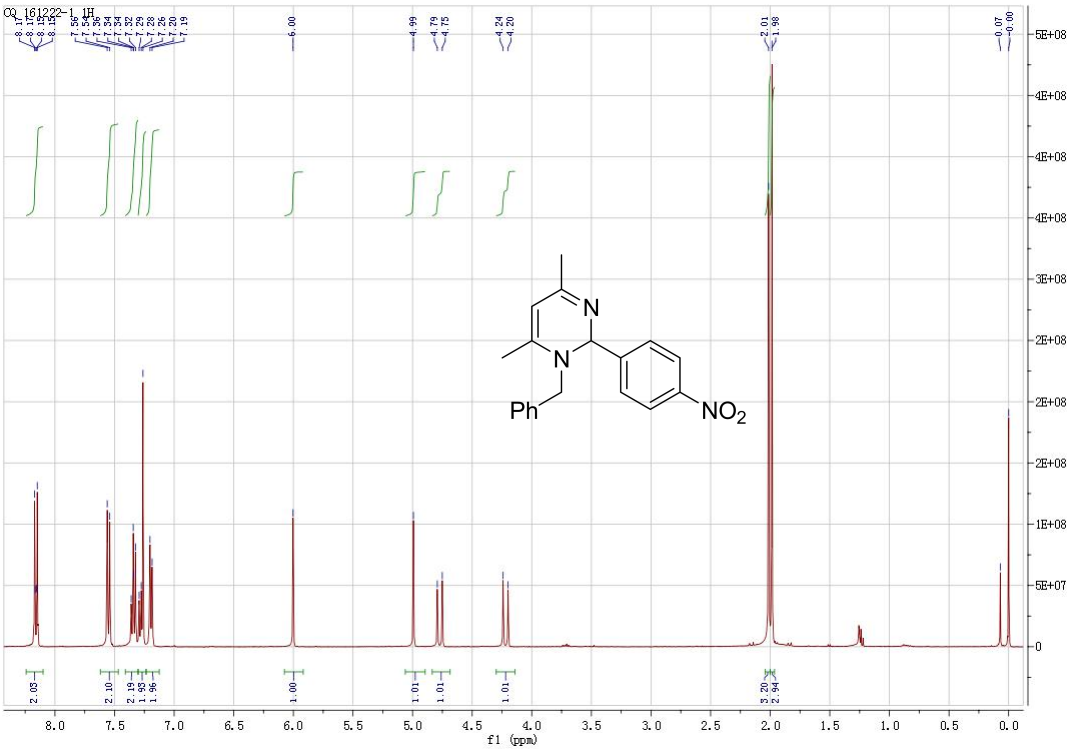
24.00
19.31
N
N
Ph
Cl
f1 (ppm)

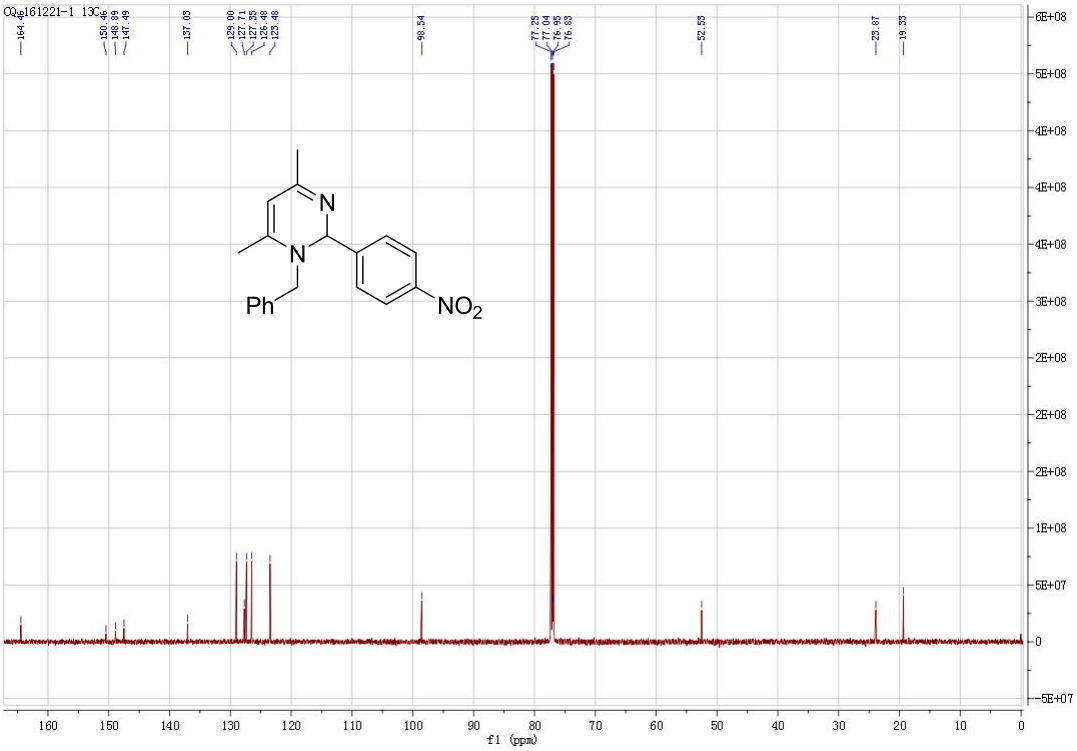

N
N
F
Ph
f1 (ppm)


N
N
F
Ph
f1 (ppm)


N
N
NO2
Ph
f1 (ppm)


N
N
NO2
Ph
f1 (ppm)


CQ_161222-1_1H
8.17
8.15
7.56
7.54
7.36
7.34
7.32
7.29
7.28
7.26
7.20
7.19
6.00
4.99
4.79
4.75
4.24
4.20
2.01
1.90
0.07
0.00
N
N
Ph
NO2
2.03
2.10
2.19
1.93
1.96
1.00
1.01
1.01
1.01
3.20
2.94
f1 (ppm)


CQ-161221-1_13C
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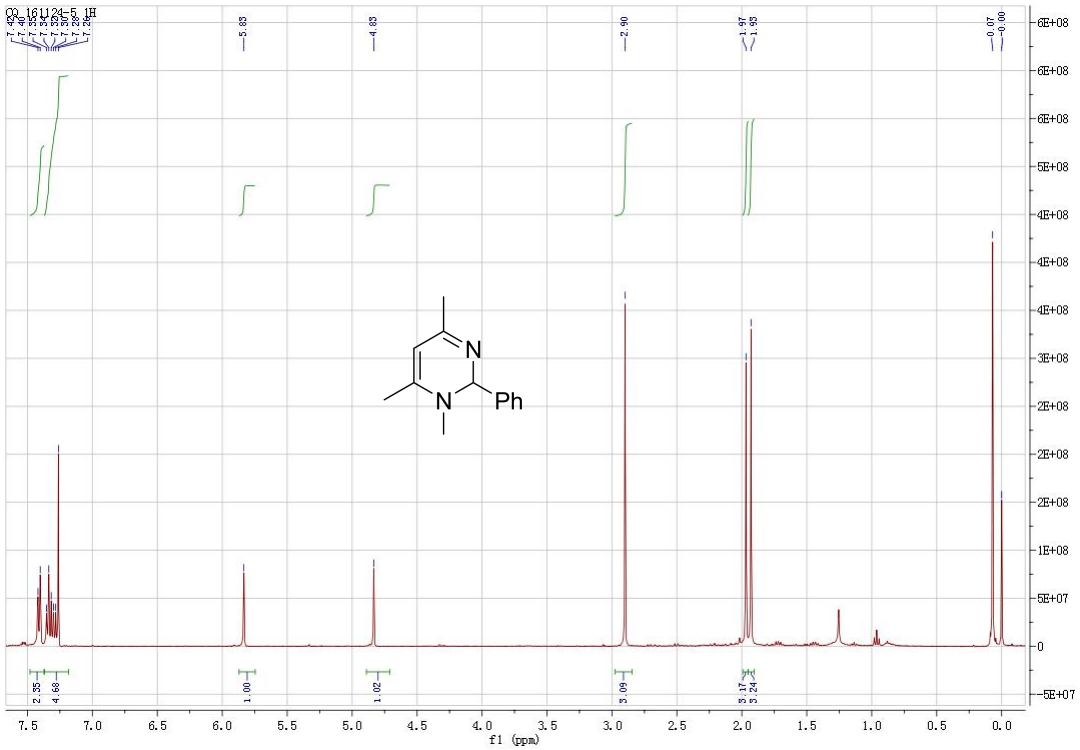
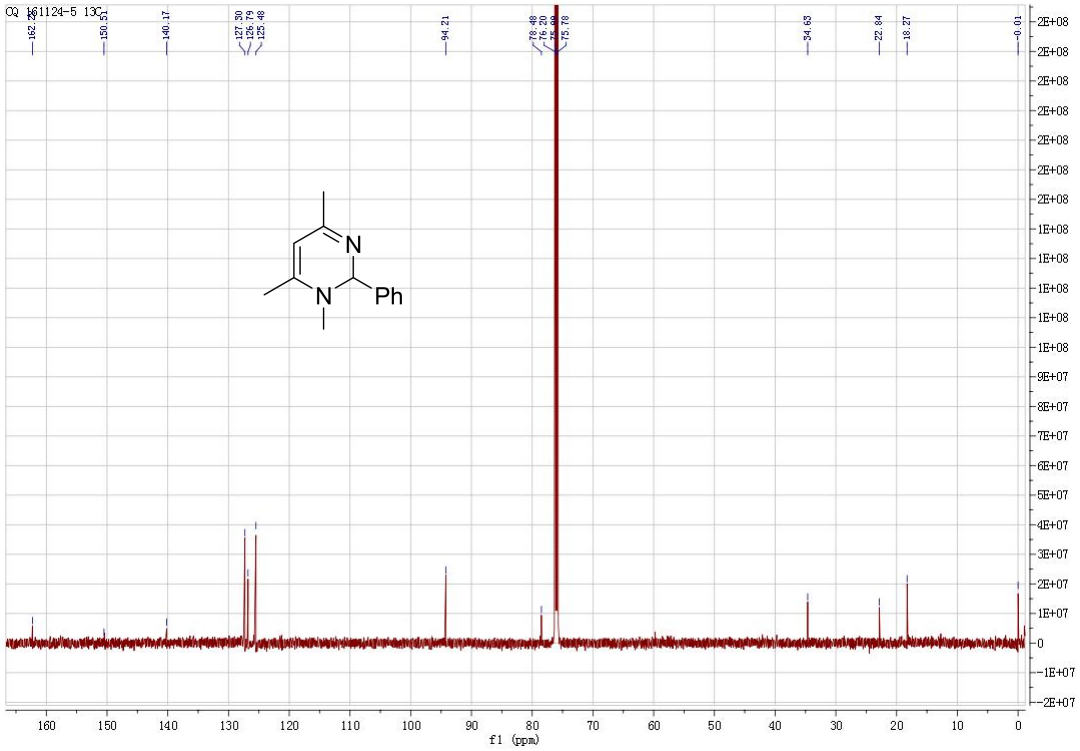
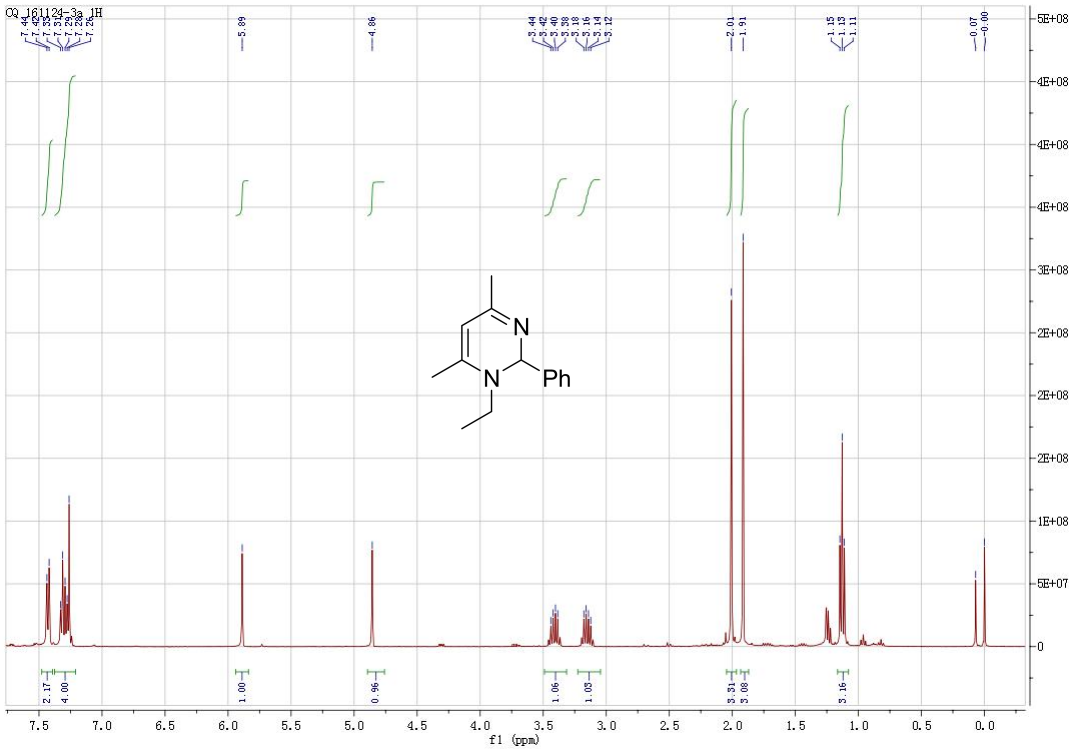
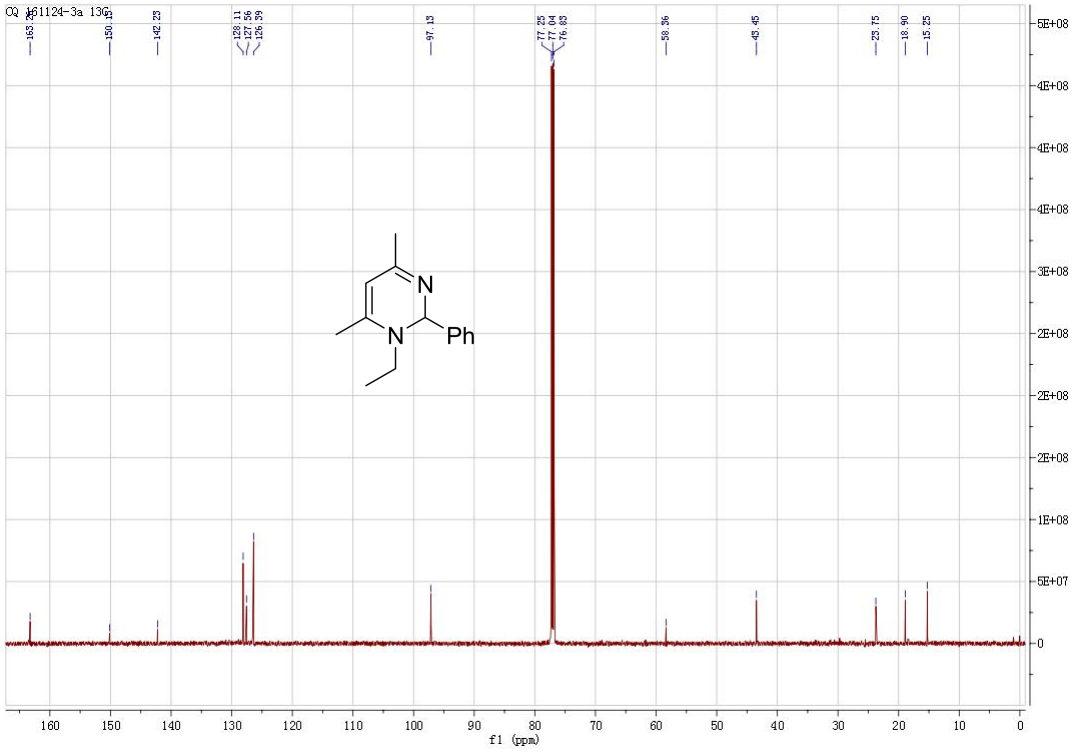
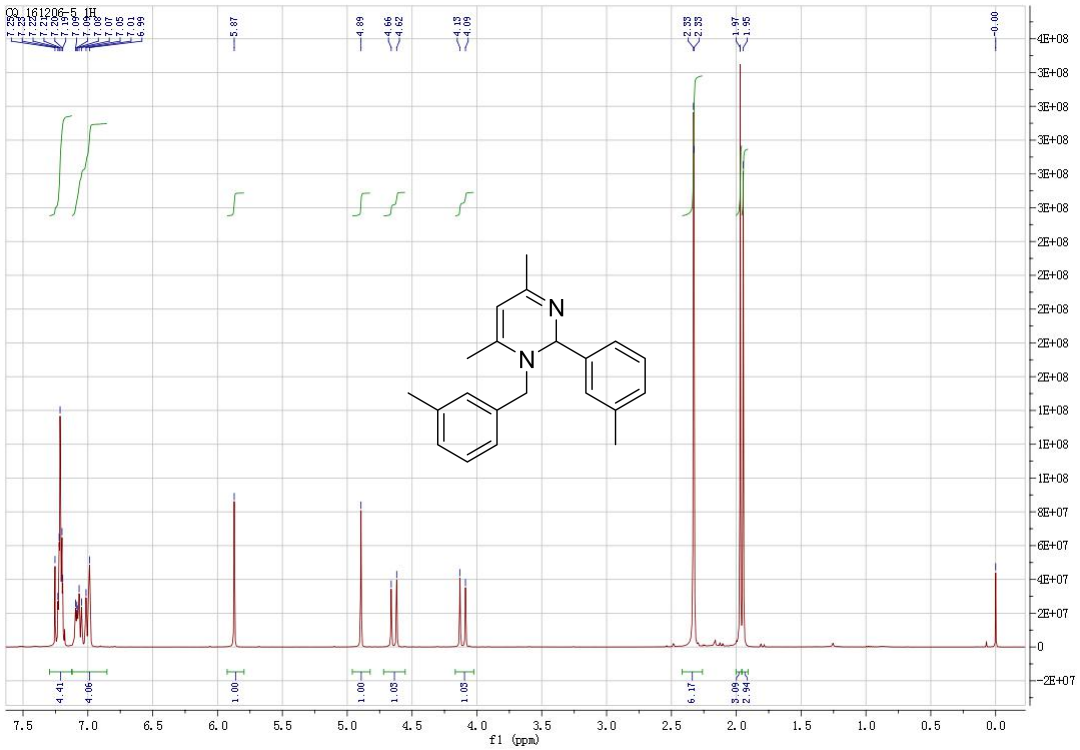
150.
148.
147.
137.
129.
127.
127.
126.
123.
98.54
77.25
77.04
76.95
76.83
52.53
23.87
19.33
N
N
Ph
NO2
f1 (ppm)

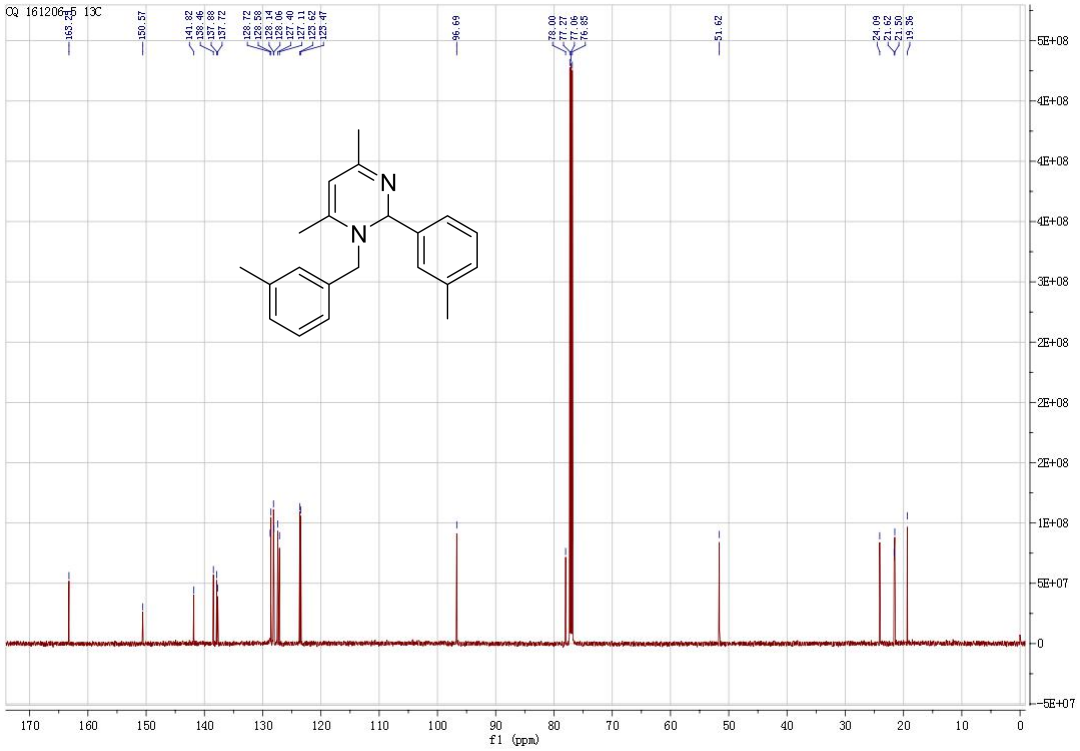

CQ_161124-5_1H
7.45
7.40
7.35
7.34
7.33
7.30
7.29
7.26
5.83
4.83
2.90
1.97
1.93
0.07
0.00
N
N
Ph
2.35
4.68
1.00
1.02
3.09
3.17
3.24
f1 (ppm)


CQ_161124-5_13C
162.
150.62
140.17
127.30
126.79
125.48
94.21
78.48
76.20
75.78
54.65
22.84
18.27
0.01
N
N
Ph
f1 (ppm)


CQ_161124-3a 1H
f1 (ppm)


CQ_161124-3a 13C
f1 (ppm)


CQ_161206-5_1H
f1 (ppm)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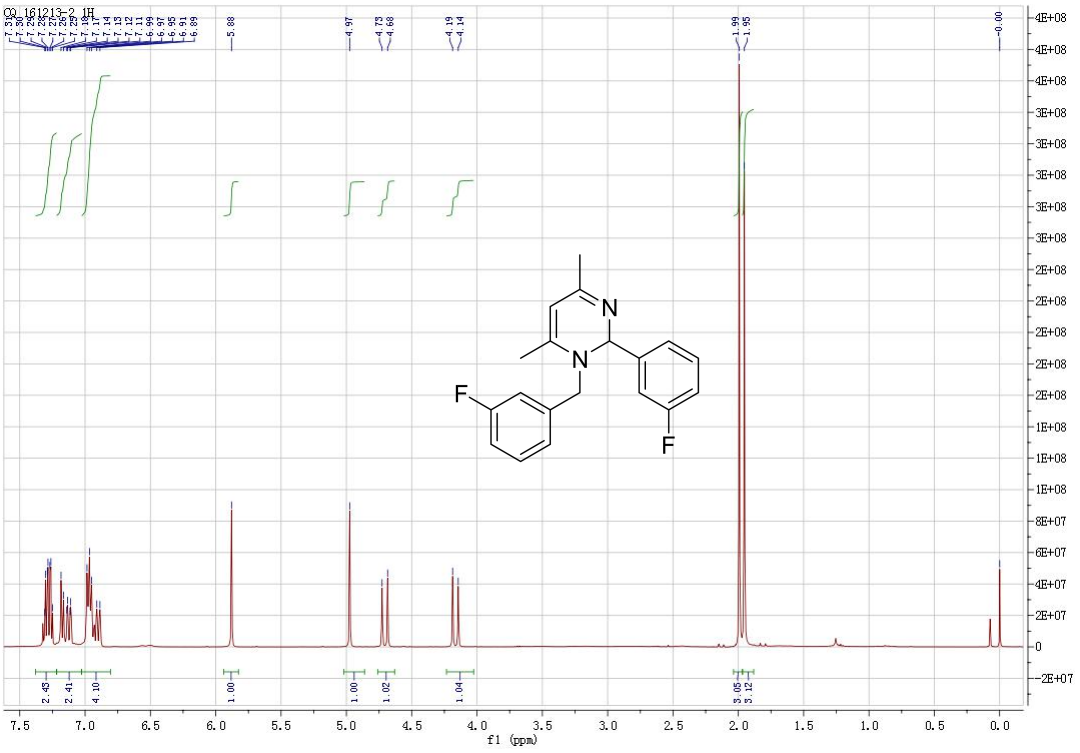
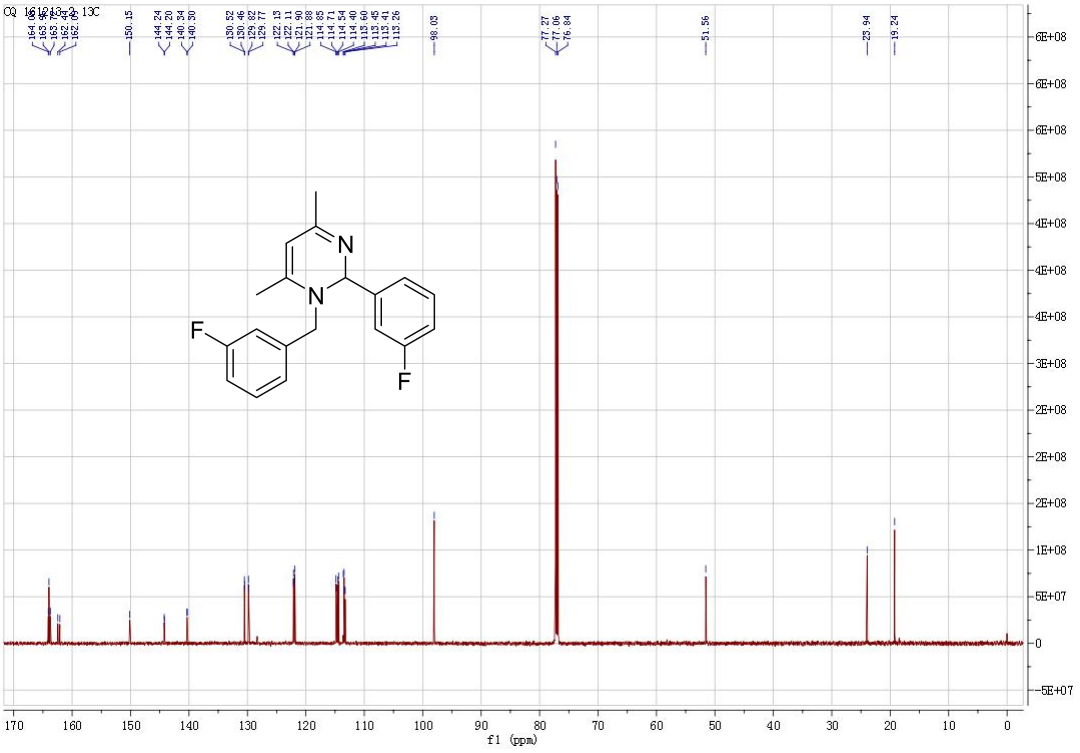
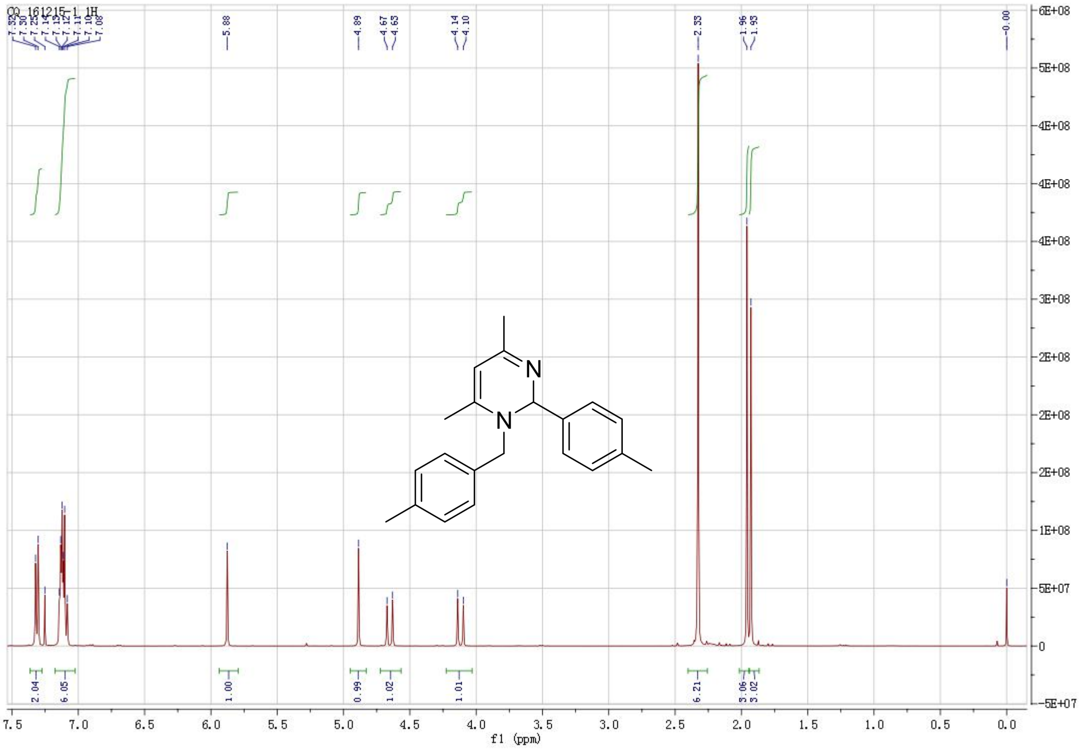
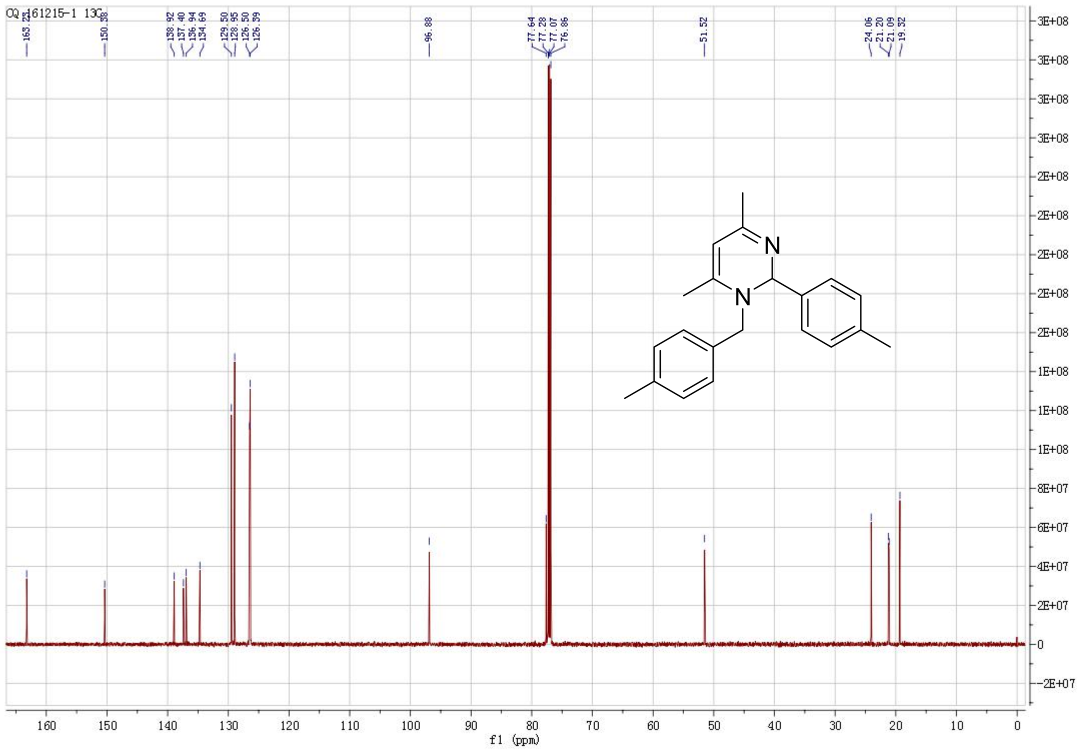
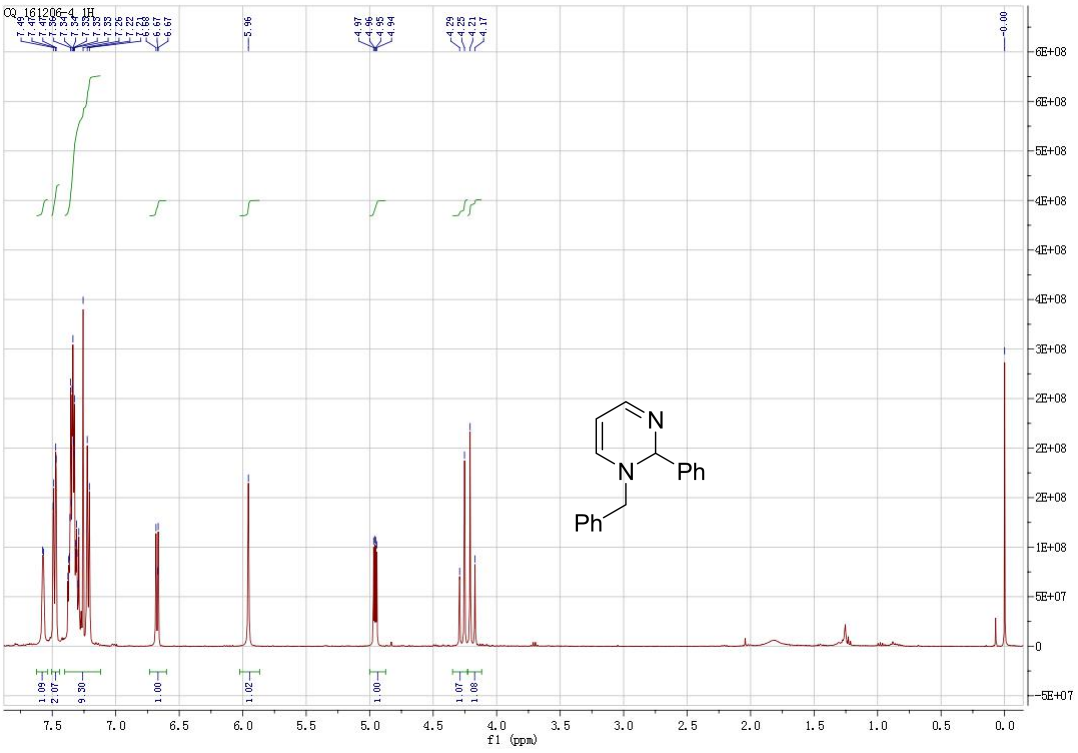
f1 (ppm)

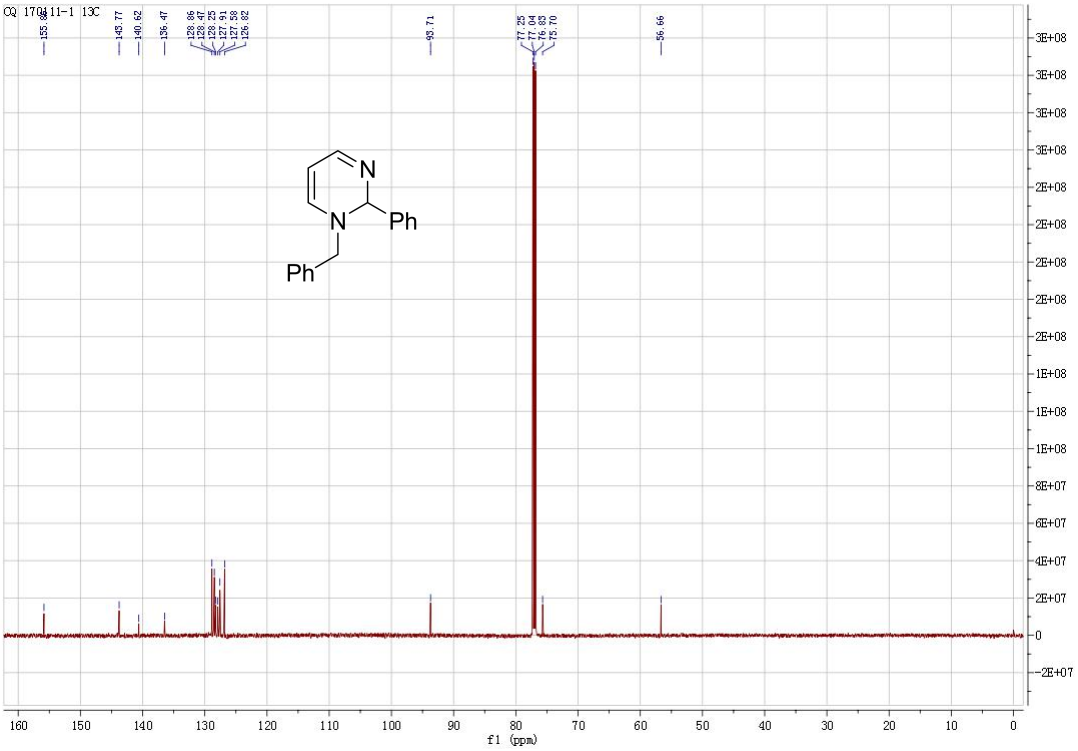

f1 (ppm)

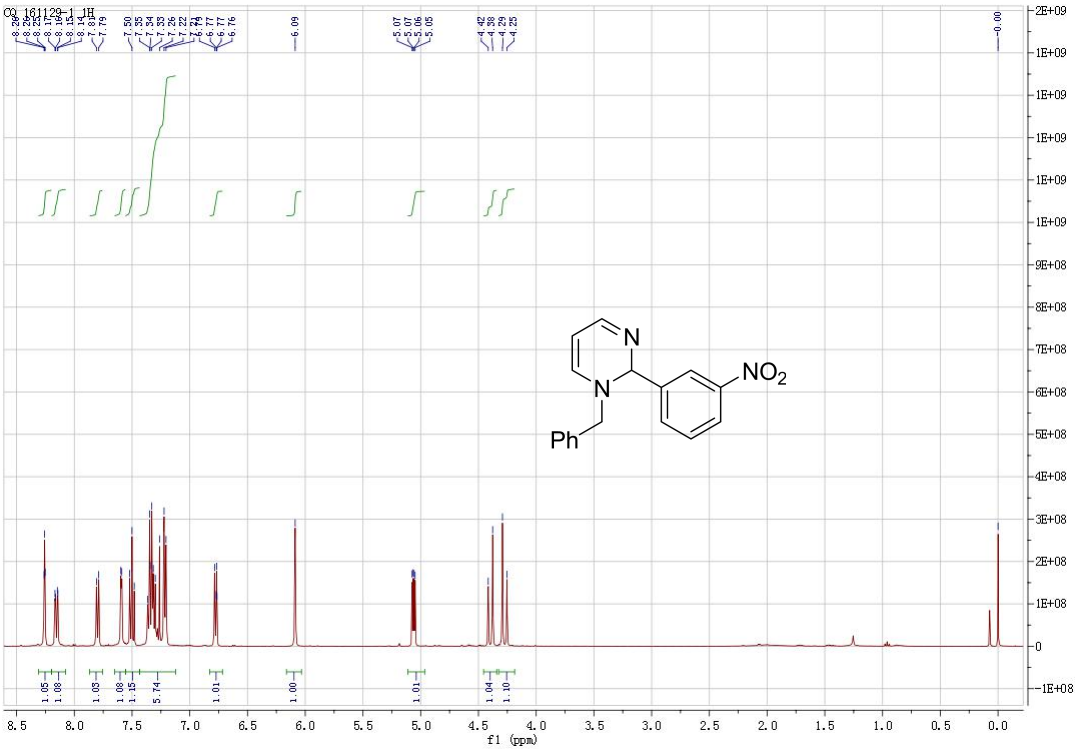

f1 (ppm)

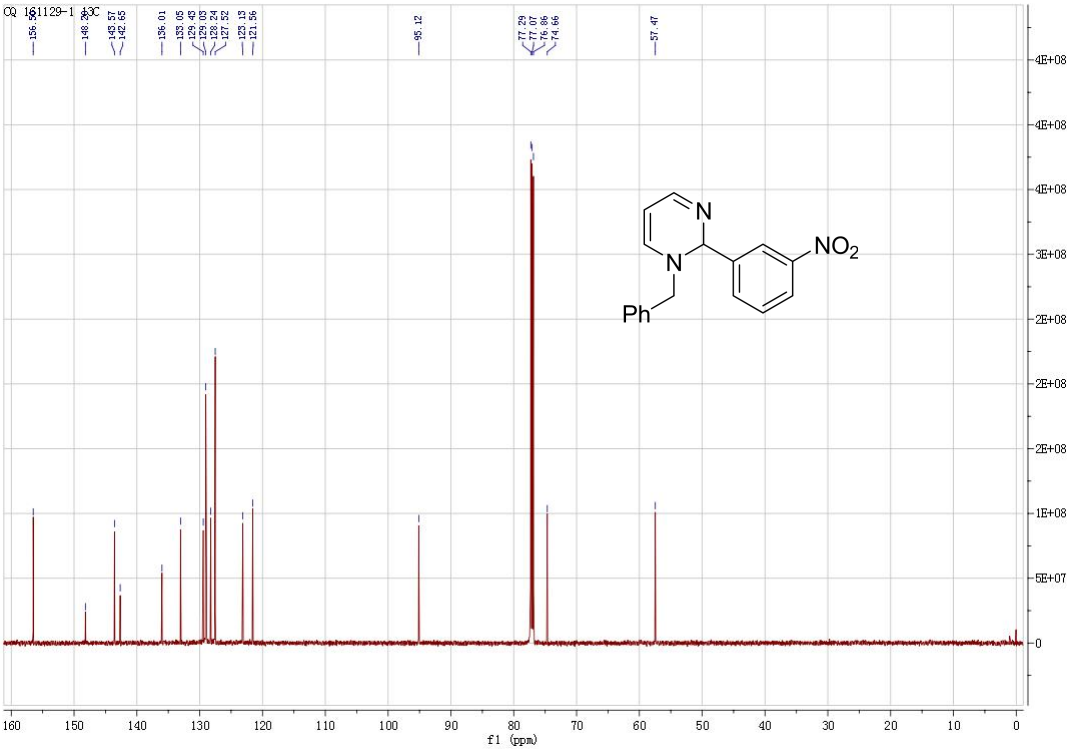

CQ 161215-1 1H
7.33
7.30
7.25
7.15
7.12
7.11
7.10
7.08
5.88
4.89
4.67
4.63
4.14
4.10
2.33
1.96
1.93
0.00
N
N
2.04
6.05
1.00
0.99
1.02
1.01
6.21
3.06
3.02
f1 (ppm)

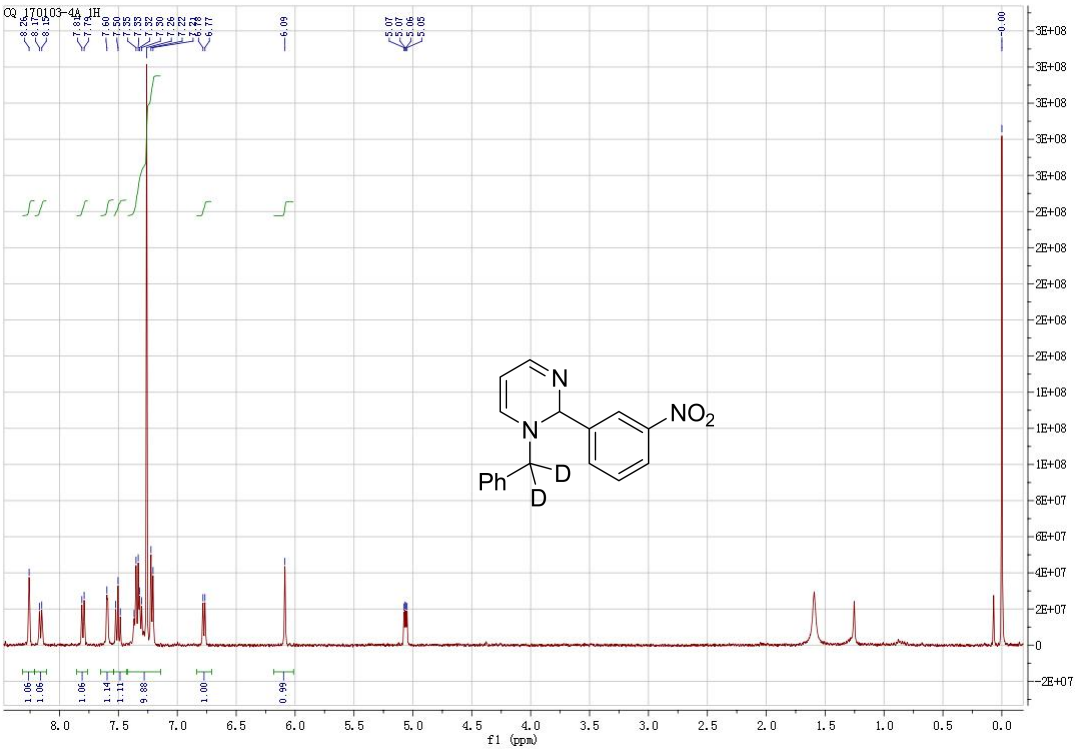

CQ 161215-1 13C
163.21
150.38
138.92
137.40
136.94
134.69
129.50
128.95
126.50
126.39
96.88
77.64
77.28
77.07
76.86
51.52
24.06
21.20
21.09
19.32
N
N
f1 (ppm)

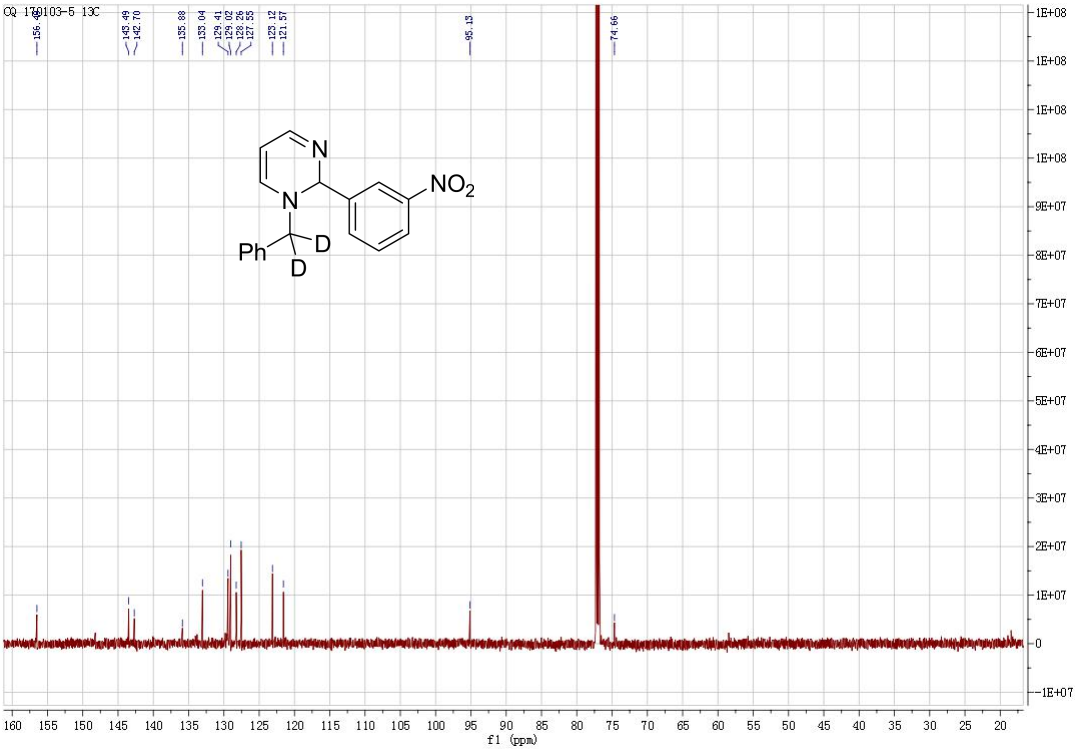

CQ_161206-4_1H
5.96
4.97
4.96
4.95
4.94
4.29
4.25
4.21
4.17
0.00
1.09
2.07
9.30
1.00
1.02
1.00
1.07
1.08
N
N
Ph
Ph
f1 (ppm)

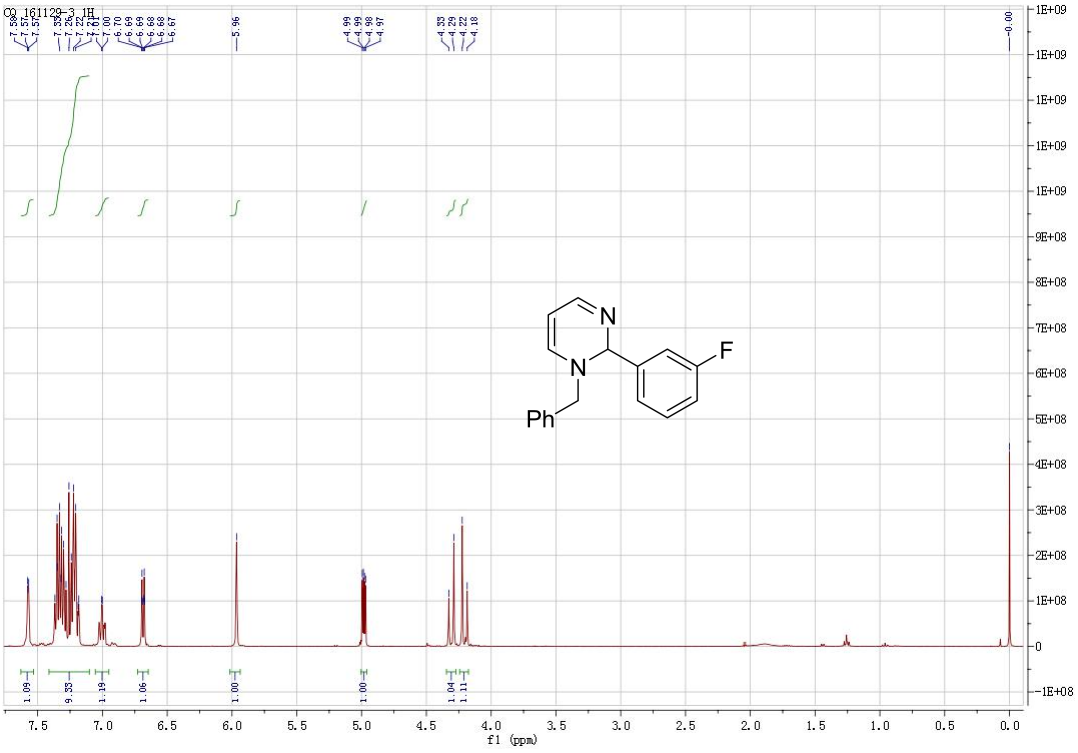

CQ 170411-1 13C
155.
148.77
140.62
136.47
128.86
128.47
128.25
127.91
127.58
126.82
93.71
77.25
77.04
76.83
75.70
56.66
N
N
Ph
Ph
f1 (ppm)

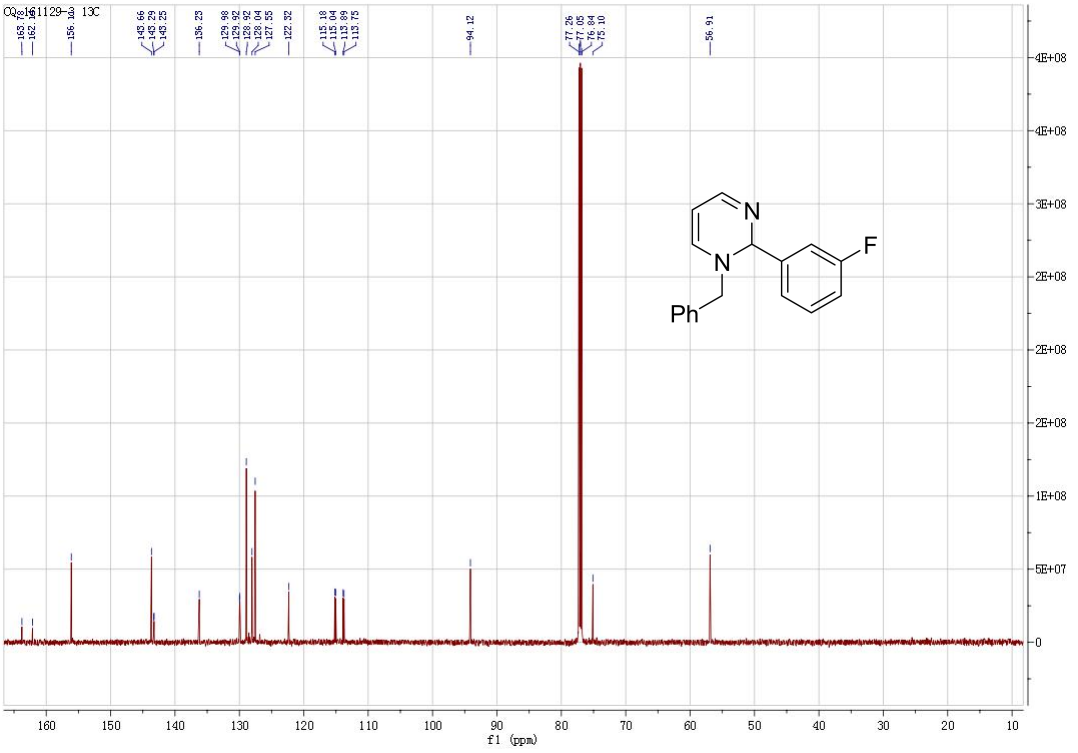

CQ 161129-1 1H
N
N
NO2
Ph
f1 (ppm)

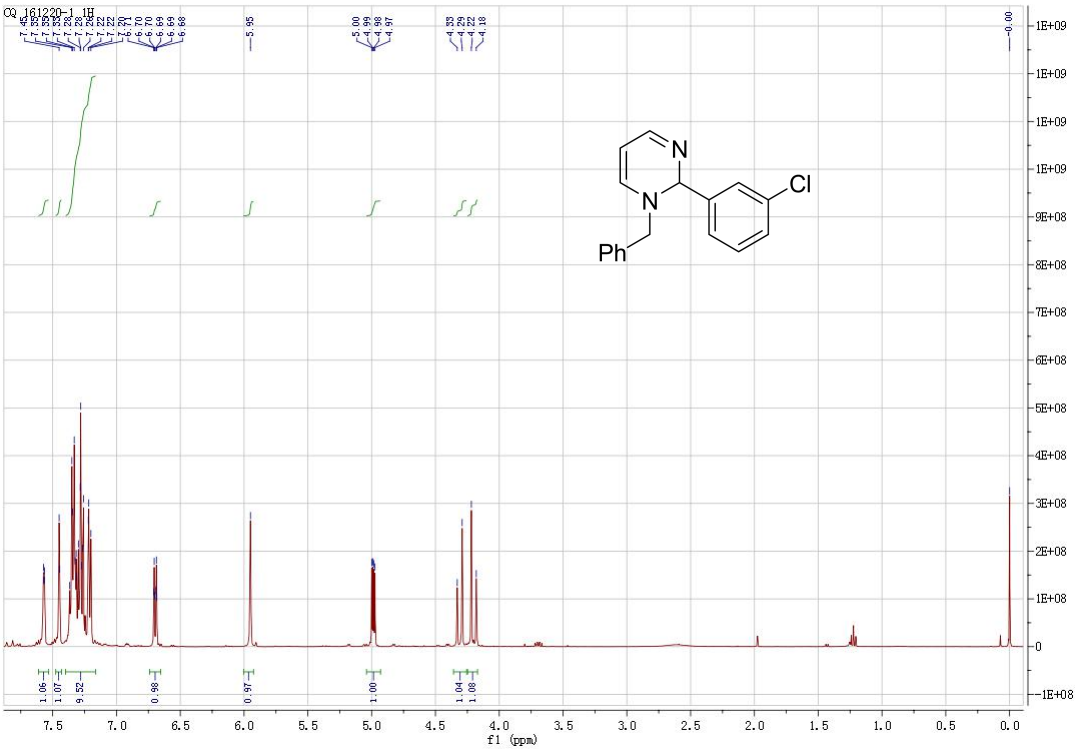

CQ 161129-1 13C
N
N
NO2
Ph
f1 (ppm)

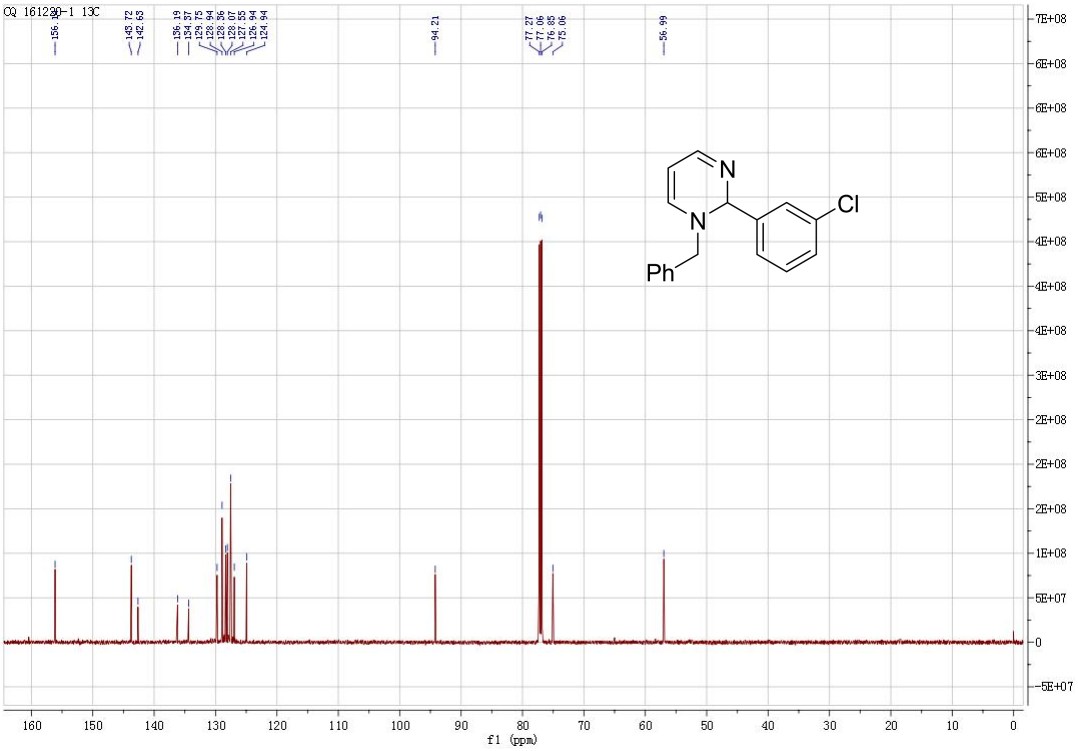

CQ 170103-4A 1H
N
N
NO2
Ph
D
D
f1 (ppm)

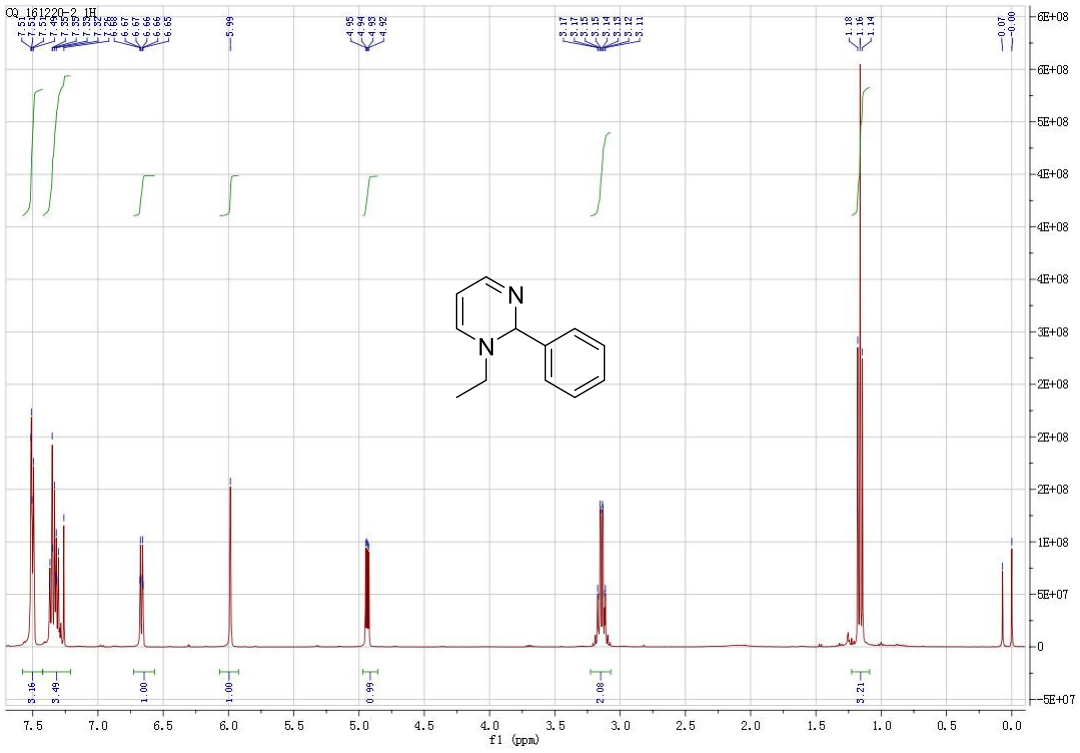

CQ 170103-5 13C
N
N
NO2
Ph
D
D
f1 (ppm)

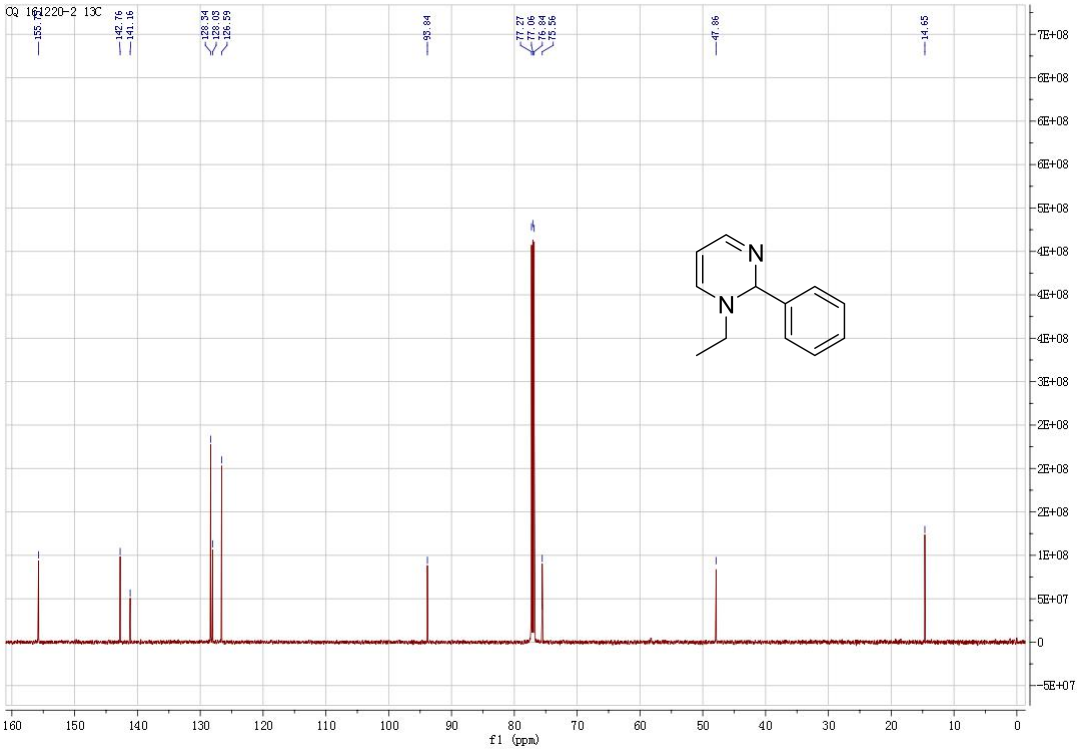

N
N
F
Ph
f1 (ppm)

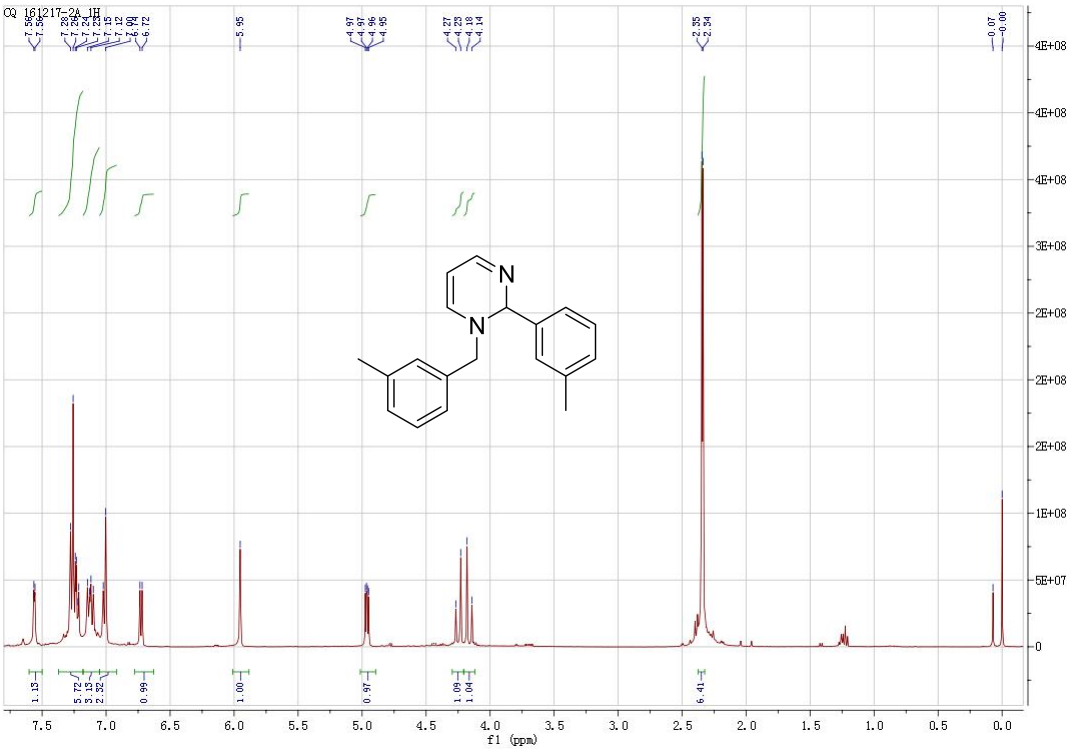

N
N
F
Ph
f1 (ppm)

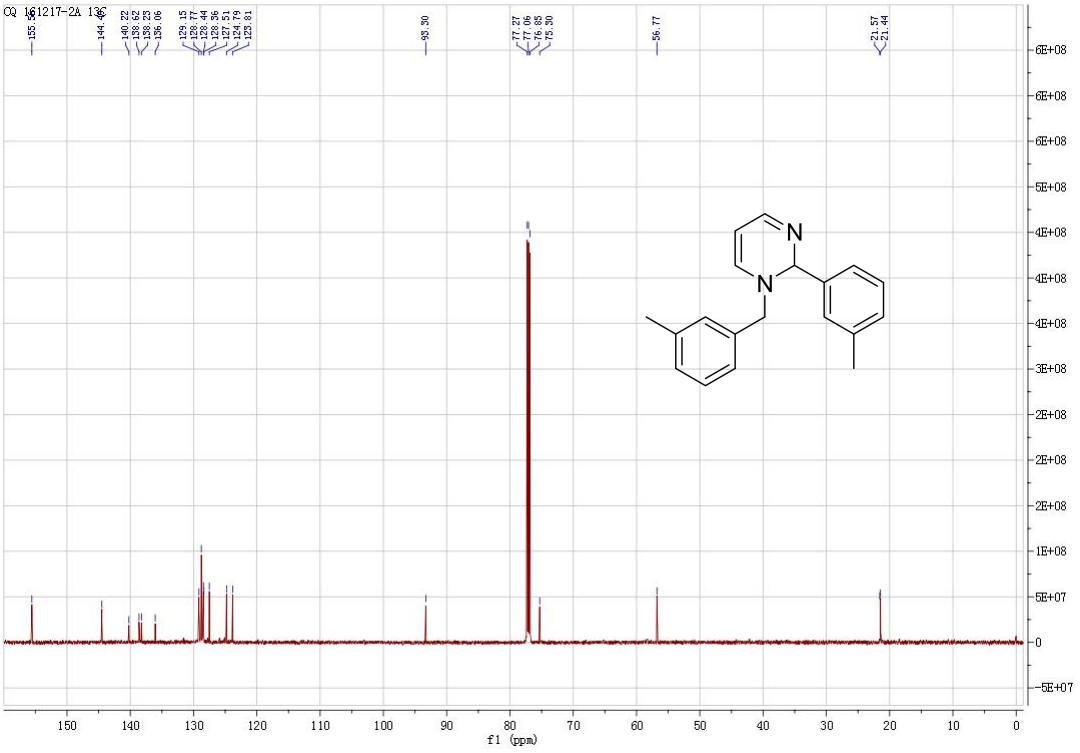

CQ 161220-1 1H
N
N
Cl
Ph
f1 (ppm)

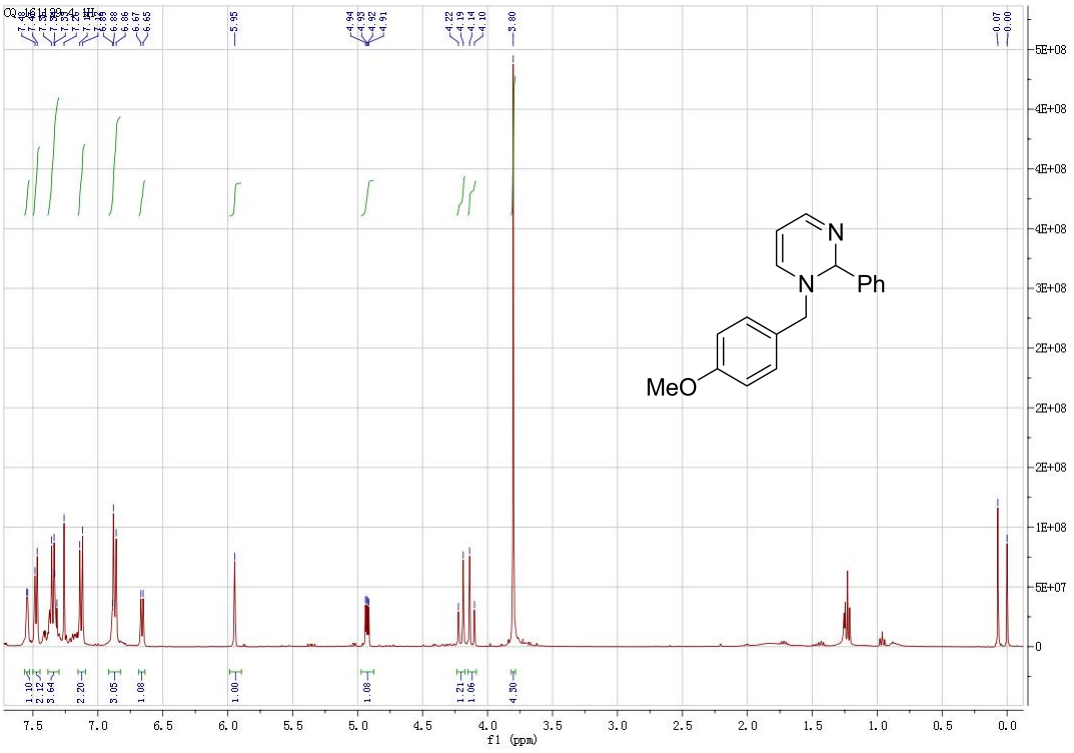

CQ 161220-1 13C
N
N
Cl
Ph
f1 (ppm)

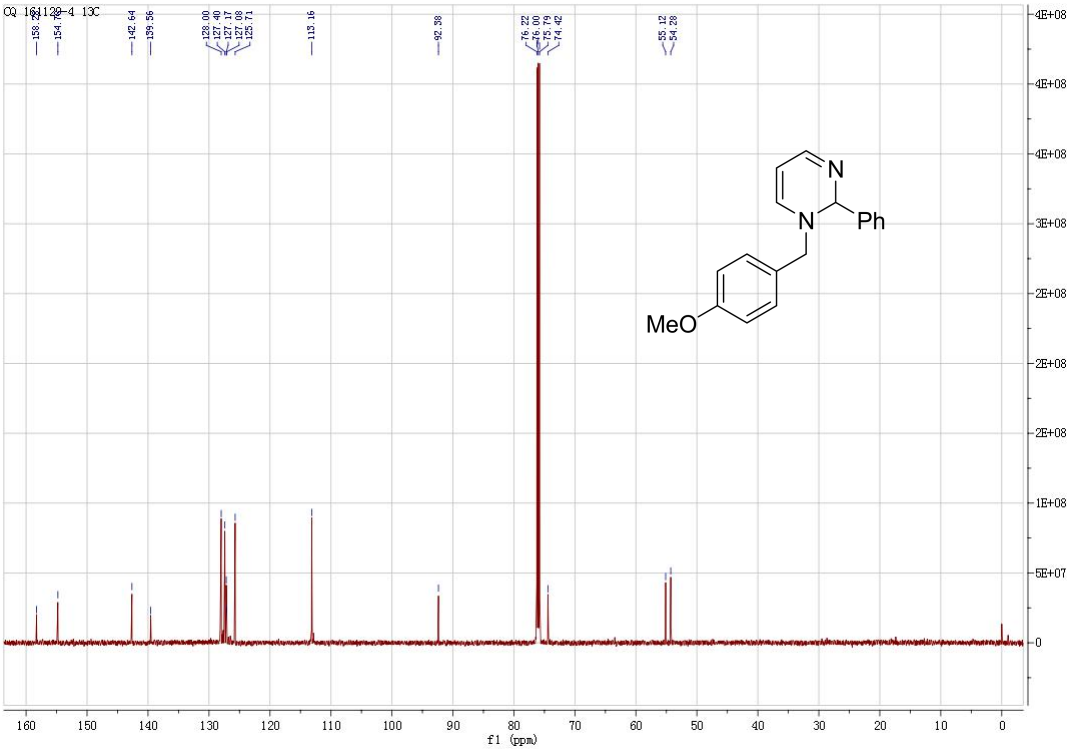

CQ_161220-2_1H
7.51
7.49
7.39
7.32
6.68
6.67
6.66
6.65
5.99
4.95
4.94
4.93
4.92
3.17
3.15
3.14
3.13
3.12
3.11
1.18
1.16
1.14
0.07
0.00
N
N
3.16
3.49
1.00
1.00
0.99
2.08
3.21
f1 (ppm)

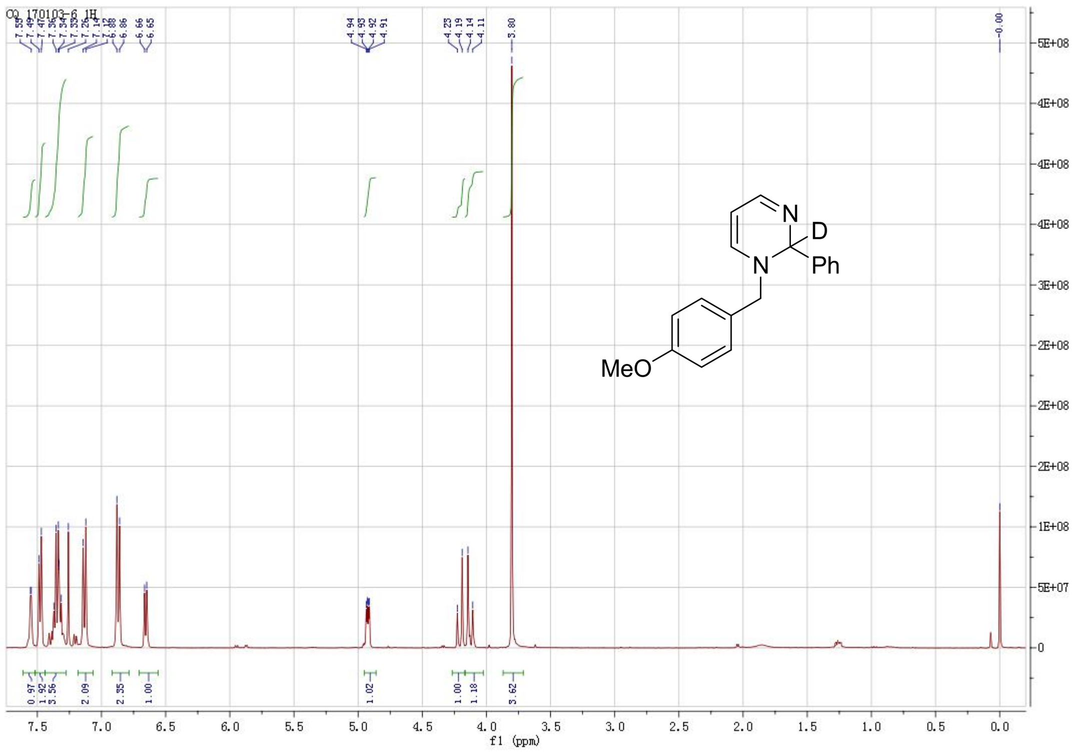

CQ_161220-2_13C
155.72
142.76
141.16
128.84
128.05
126.99
93.84
77.27
77.06
76.84
75.86
47.86
14.65
N
N
f1 (ppm)


CQ 161217-2A 1H
7.56
7.56
7.28
7.26
7.24
7.23
7.15
7.12
7.04
6.74
6.72
5.95
4.97
4.97
4.96
4.95
4.27
4.23
4.18
4.14
2.35
2.34
0.07
0.00
1.13
5.72
3.13
2.32
0.99
1.00
0.97
1.09
1.04
6.41
f1 (ppm)

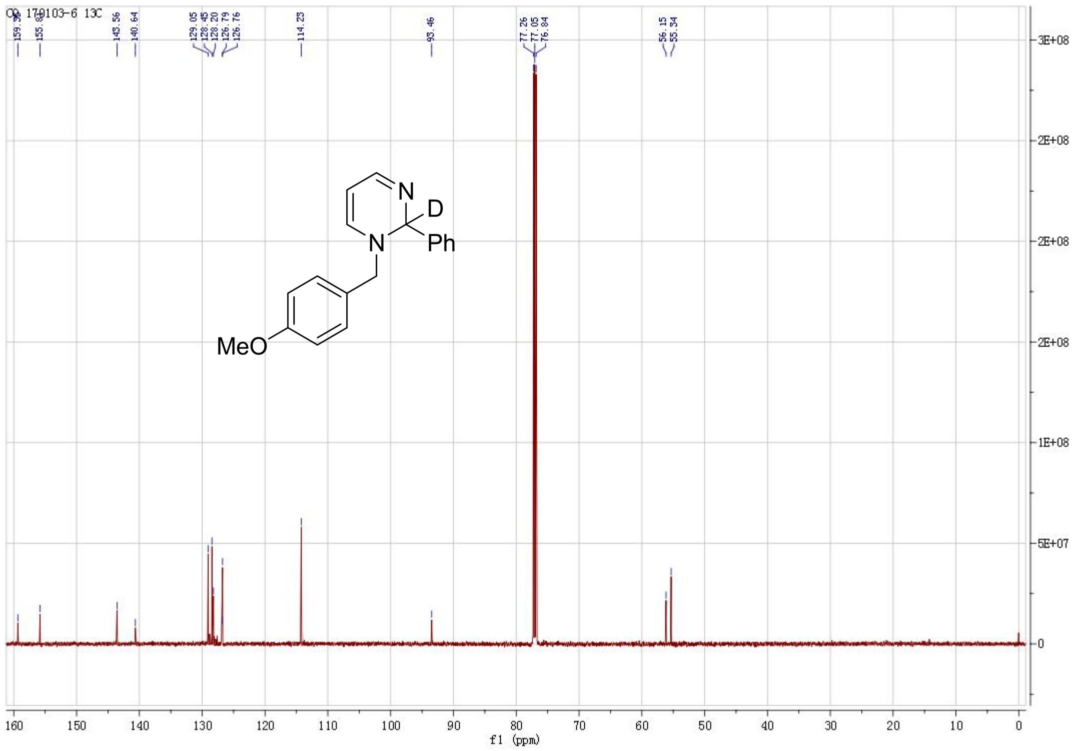

CQ 161217-2A 13C
155.
144.
140.22
138.62
138.23
136.06
129.15
128.77
128.44
128.36
127.51
124.79
123.81
93.30
77.27
77.06
76.85
75.30
56.77
21.57
21.44
f1 (ppm)


N
N
Ph
MeO
f1 (ppm)

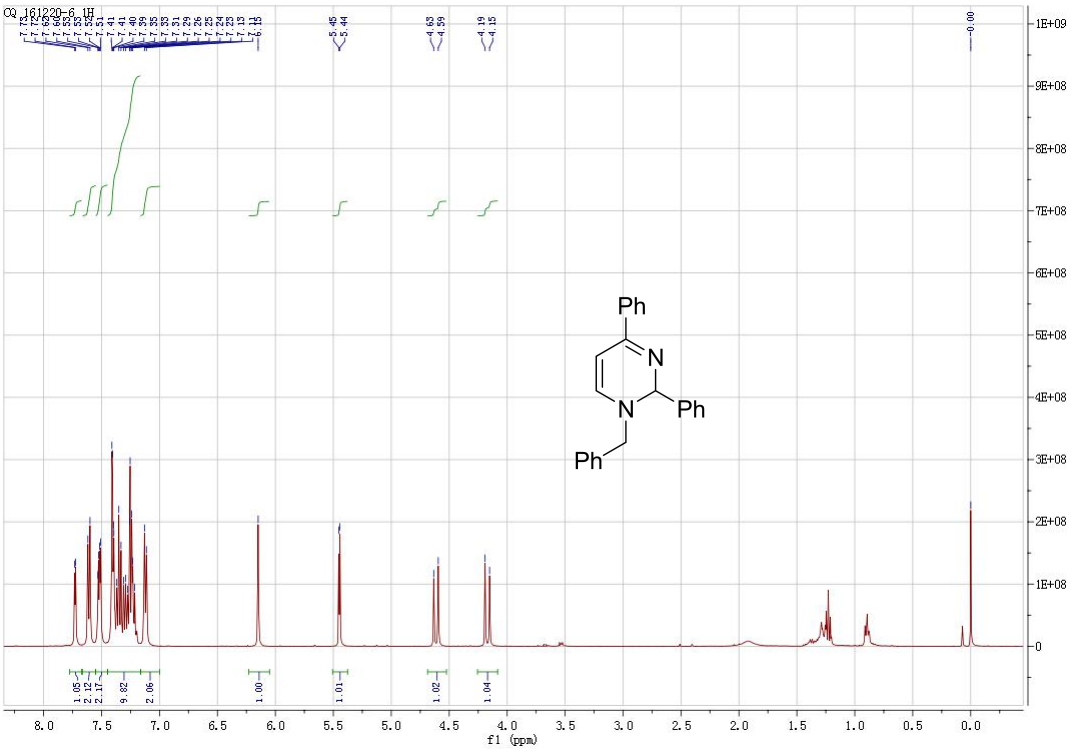

N
N
Ph
MeO
f1 (ppm)

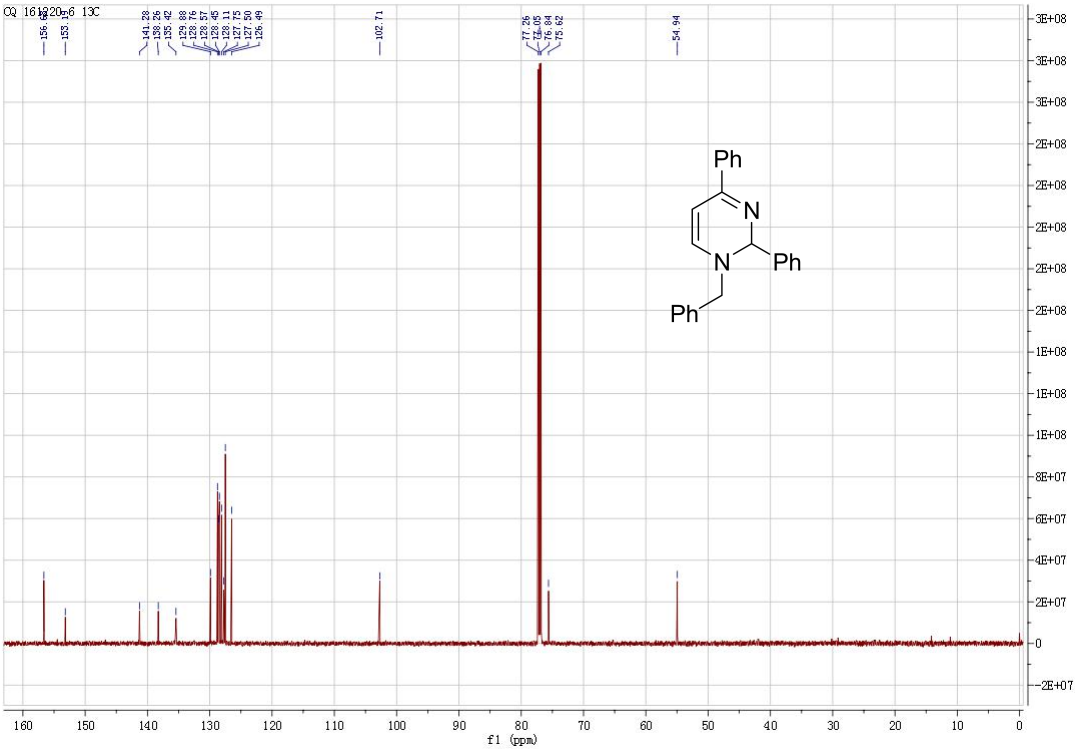


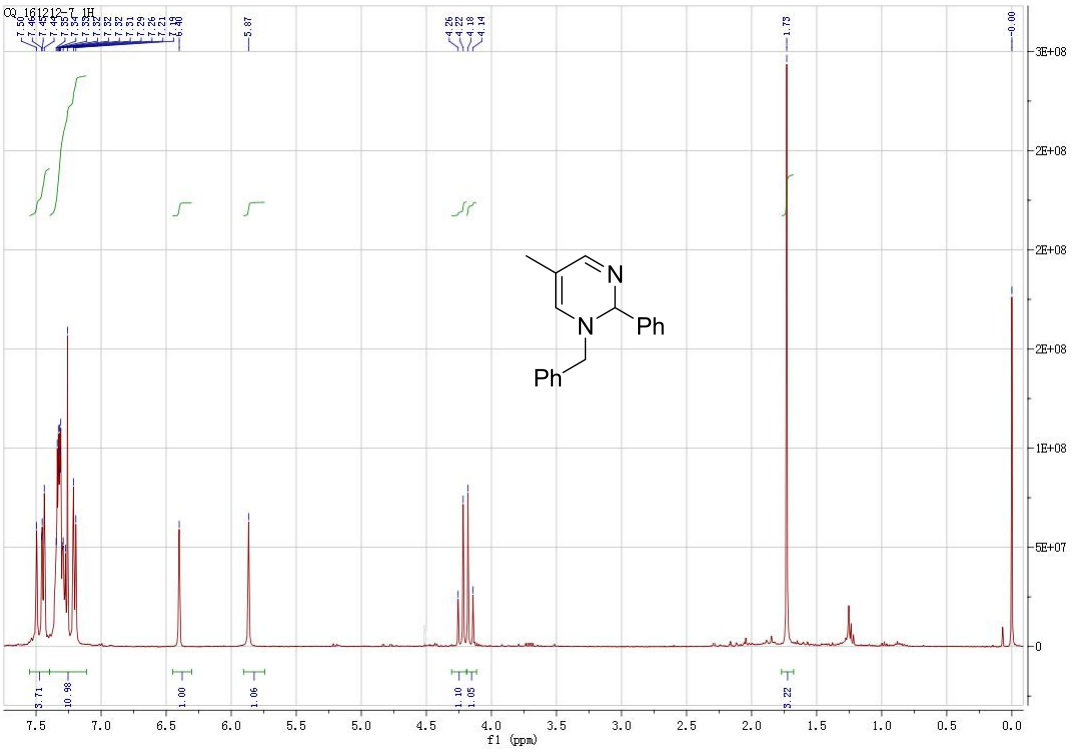
CQ 170103-6 1H
7.53
7.49
7.47
7.36
7.34
7.33
7.25
7.14
7.12
6.88
6.86
6.66
6.65
4.94
4.93
4.92
4.91
4.23
4.19
4.14
4.11
3.80
0.00
N
D
Ph
N
MeO
0.97
1.92
3.56
2.09
2.35
1.00
1.02
1.00
1.18
3.62
f1 (ppm)

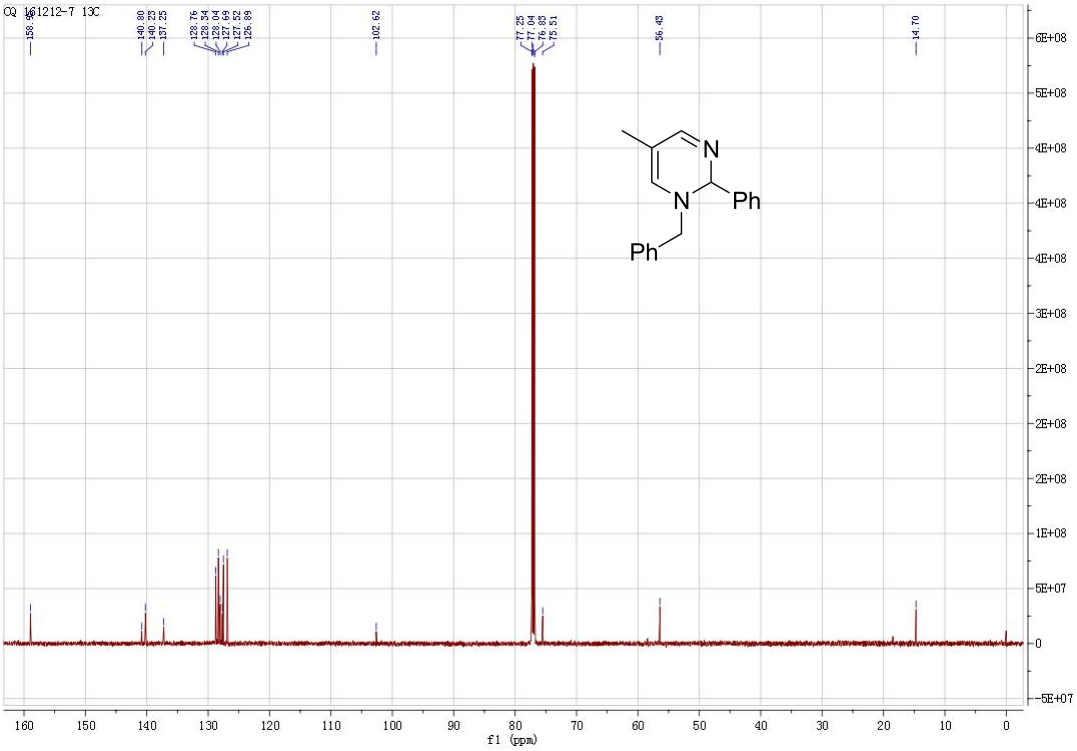


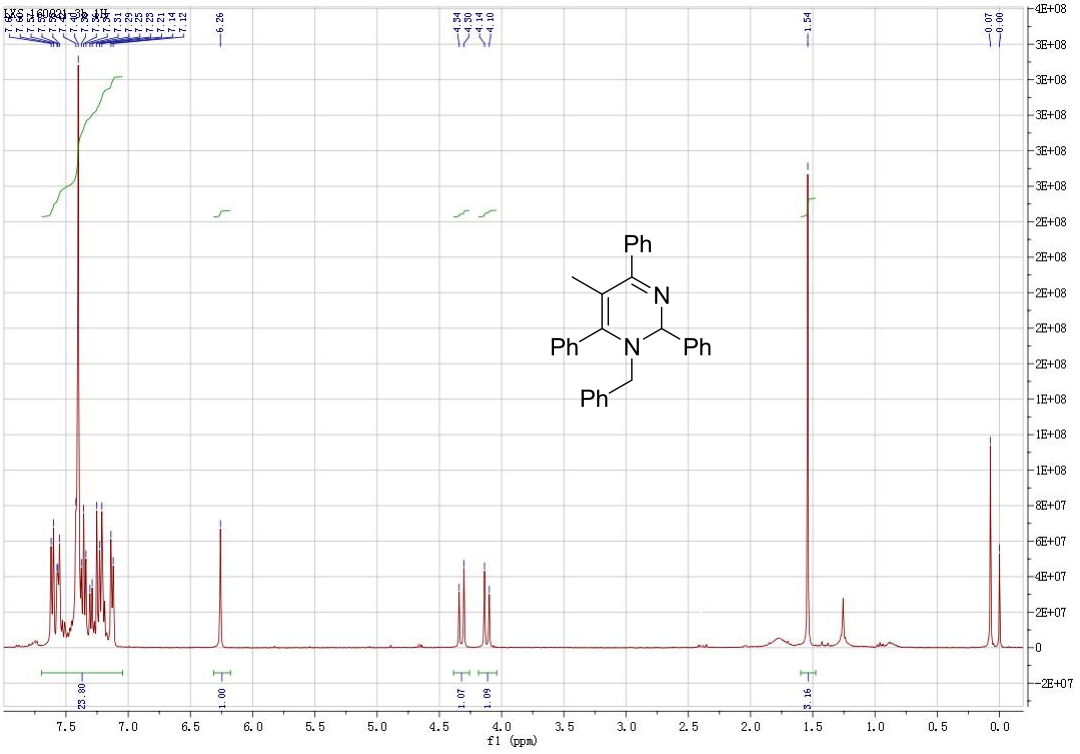
CQ 170103-6 13C
159.36
155.80
143.56
140.64
129.05
128.45
128.20
126.79
126.76
114.23
93.46
77.26
77.05
76.84
56.15
55.34
N
D
Ph
N
MeO
f1 (ppm)

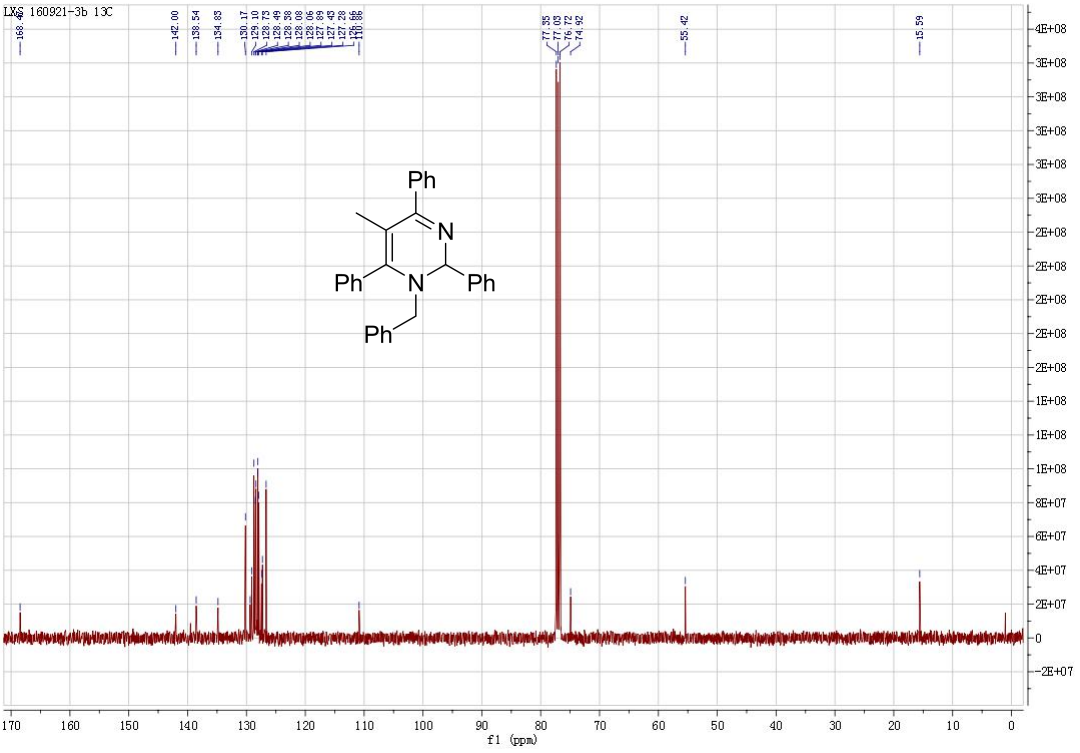

Ph
N
N
Ph
Ph
f1 (ppm)

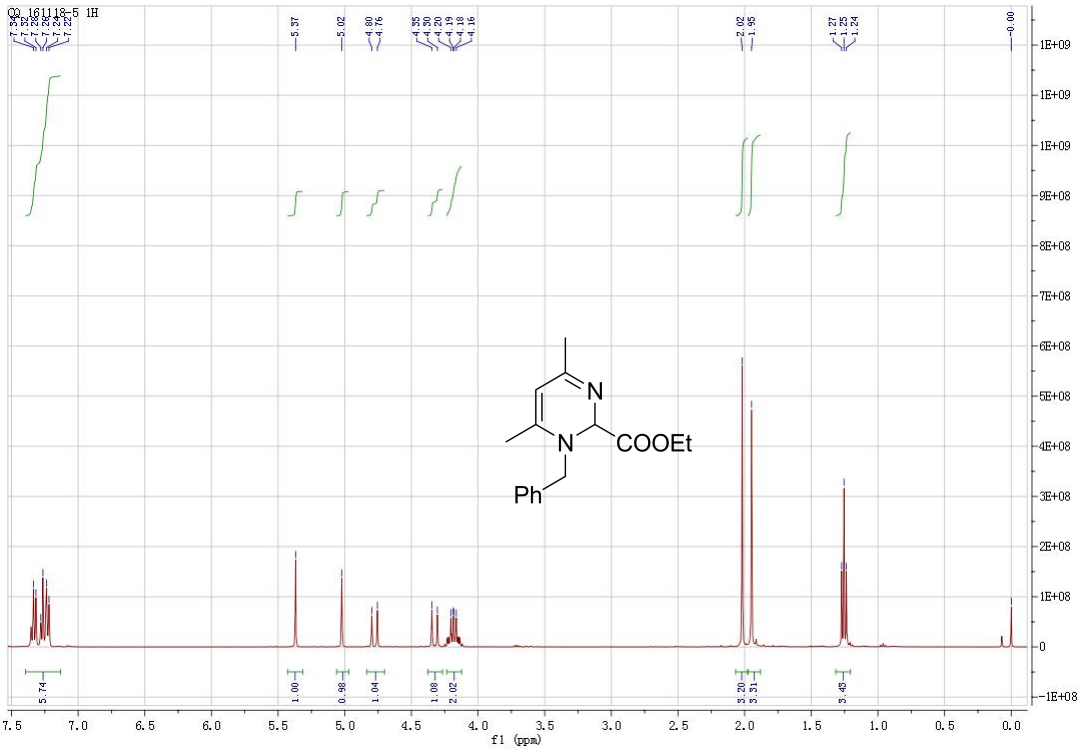

Ph
N
N
Ph
Ph
f1 (ppm)

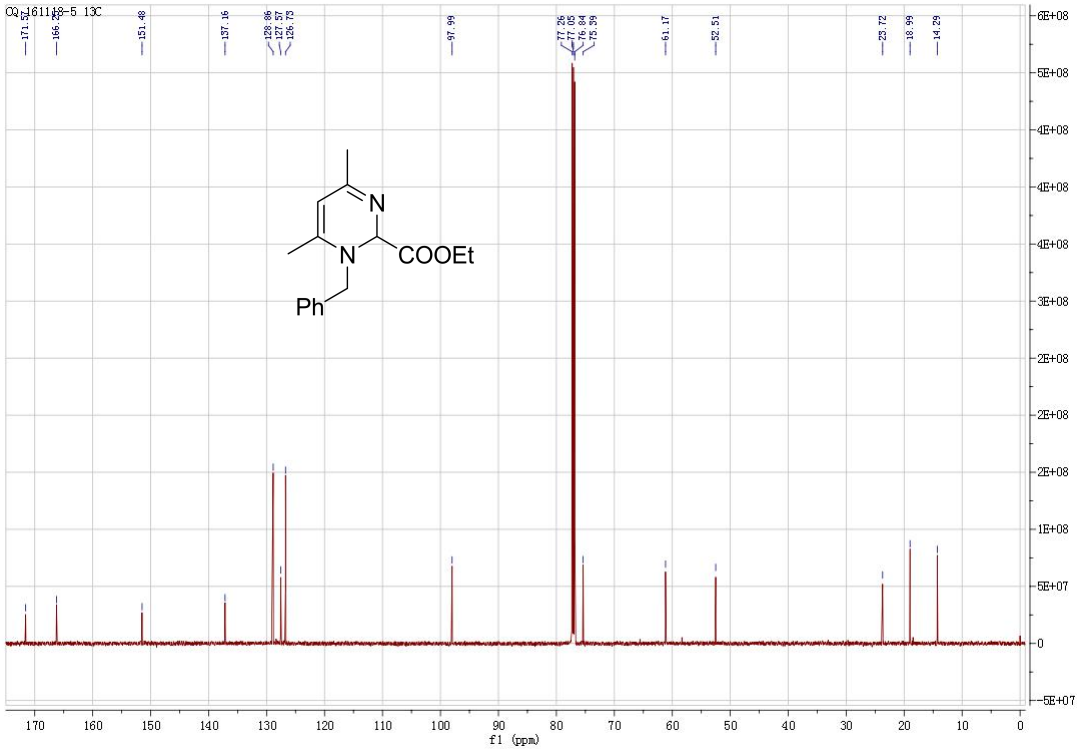

CQ_161212-7_1H
5.87
4.26
4.22
4.18
4.14
1.73
0.00
N
N
Ph
Ph
3.71
10.98
1.00
1.06
1.10
1.05
3.22
f1 (ppm)

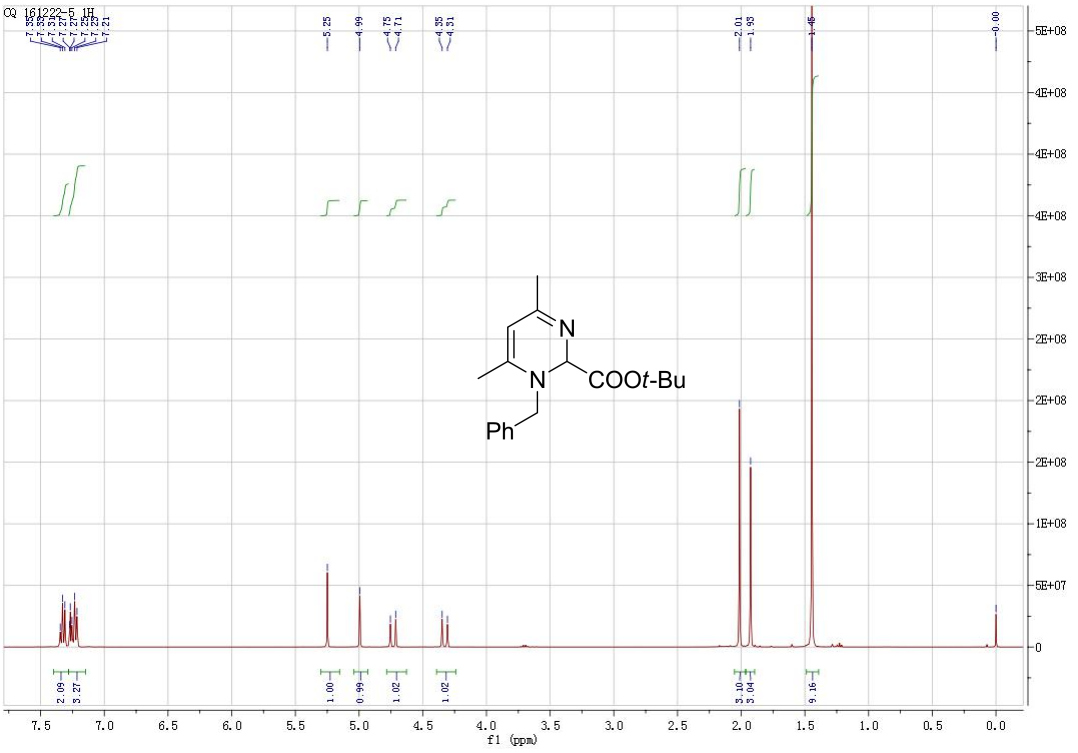

CQ_161212-7_13C
158.
140.80
140.23
137.25
128.76
128.34
128.04
127.69
127.52
126.89
102.62
77.25
77.04
76.83
75.51
56.45
14.70
N
N
Ph
Ph
f1 (ppm)

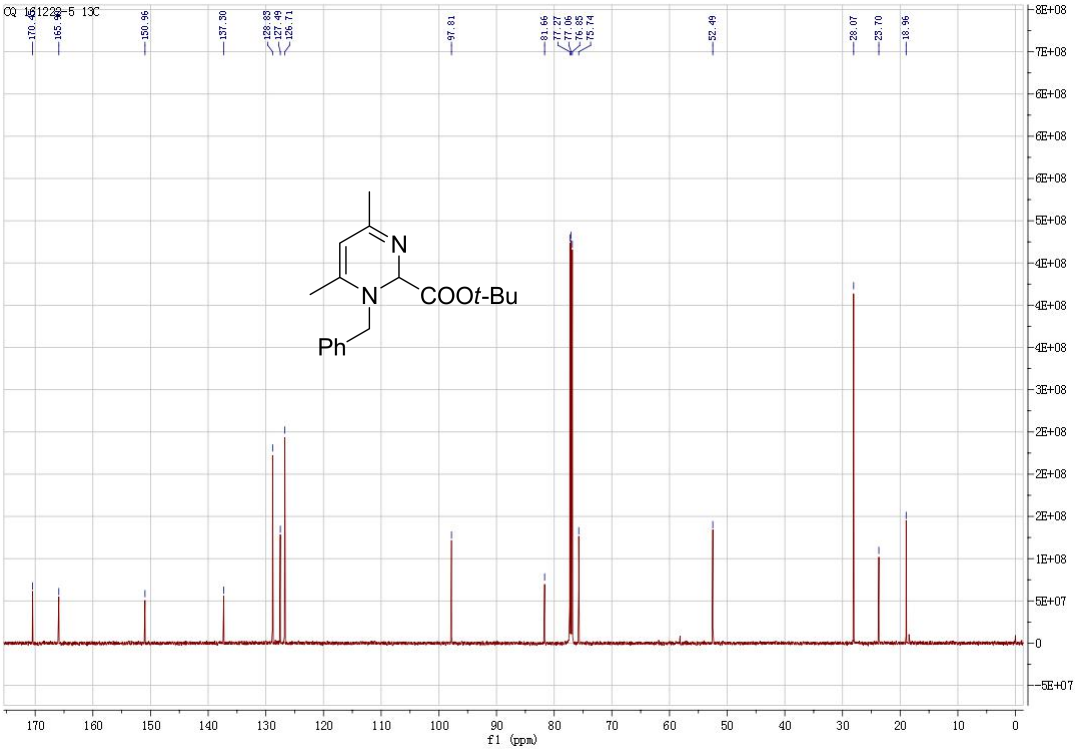

Ph
N
Ph
N
Ph
Ph
f1 (ppm)

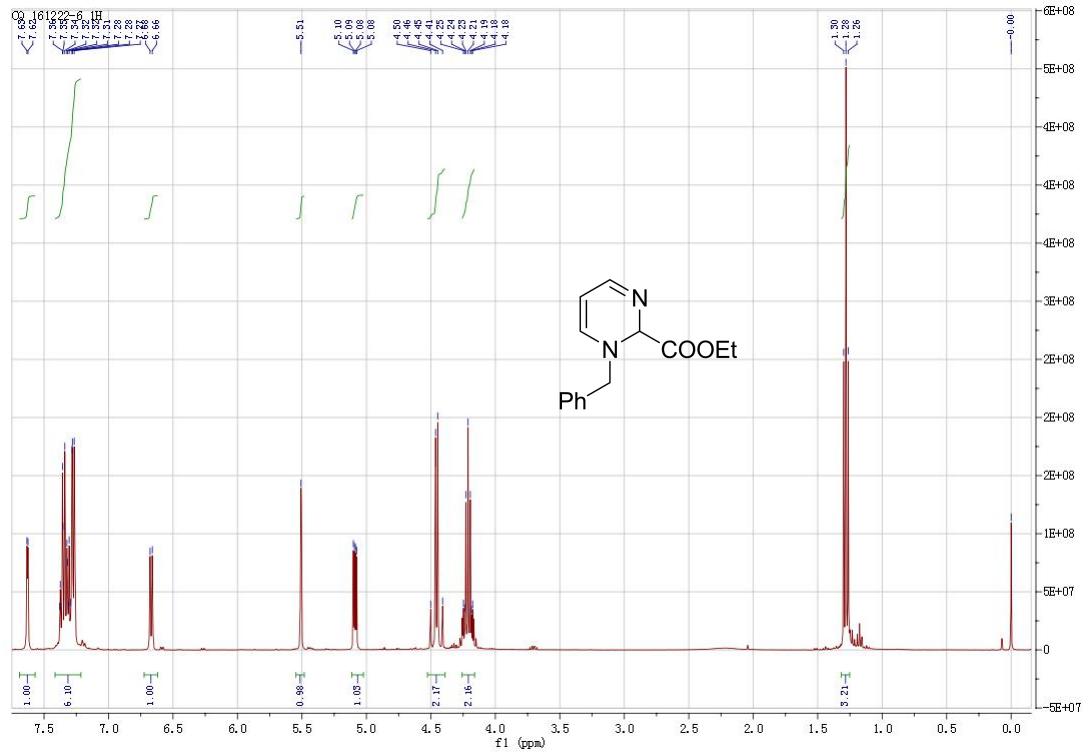

Ph
N
Ph
N
Ph
Ph
f1 (ppm)

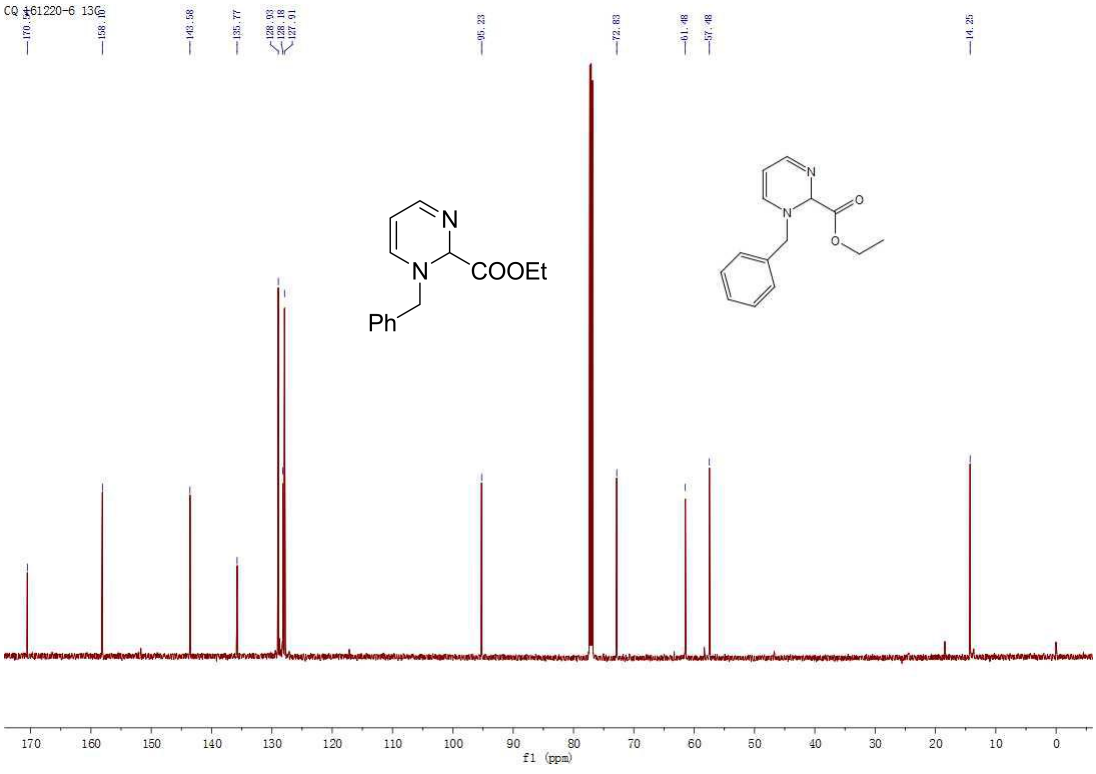

CQ_161118-5 1H
5.37
5.02
4.80
4.76
4.55
4.30
4.20
4.19
4.18
4.16
2.02
1.95
1.27
1.25
1.24
0.00
N
N
COOEt
Ph
5.74
1.00
0.98
1.04
1.09
2.02
3.20
3.31
3.45
f1 (ppm)

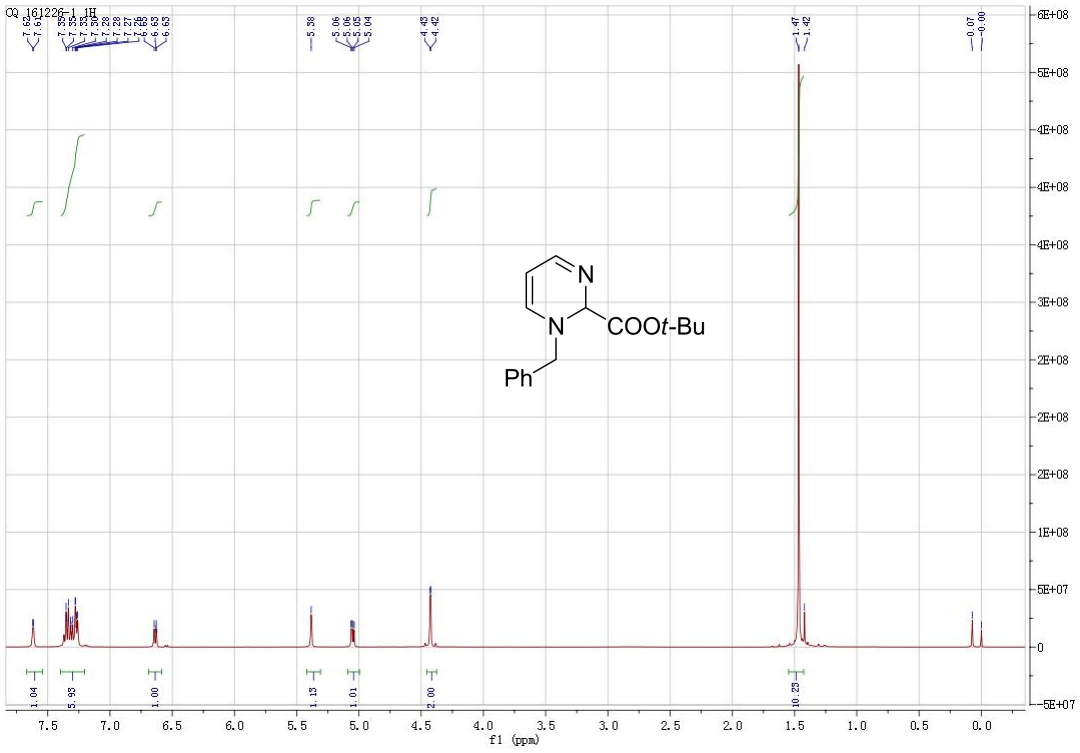

CQ_161118-5 13C
171.52
166.82
151.48
137.16
128.86
127.57
126.73
97.99
77.26
77.05
76.84
75.99
61.17
52.51
25.72
18.99
14.29
N
N
COOEt
Ph
f1 (ppm)

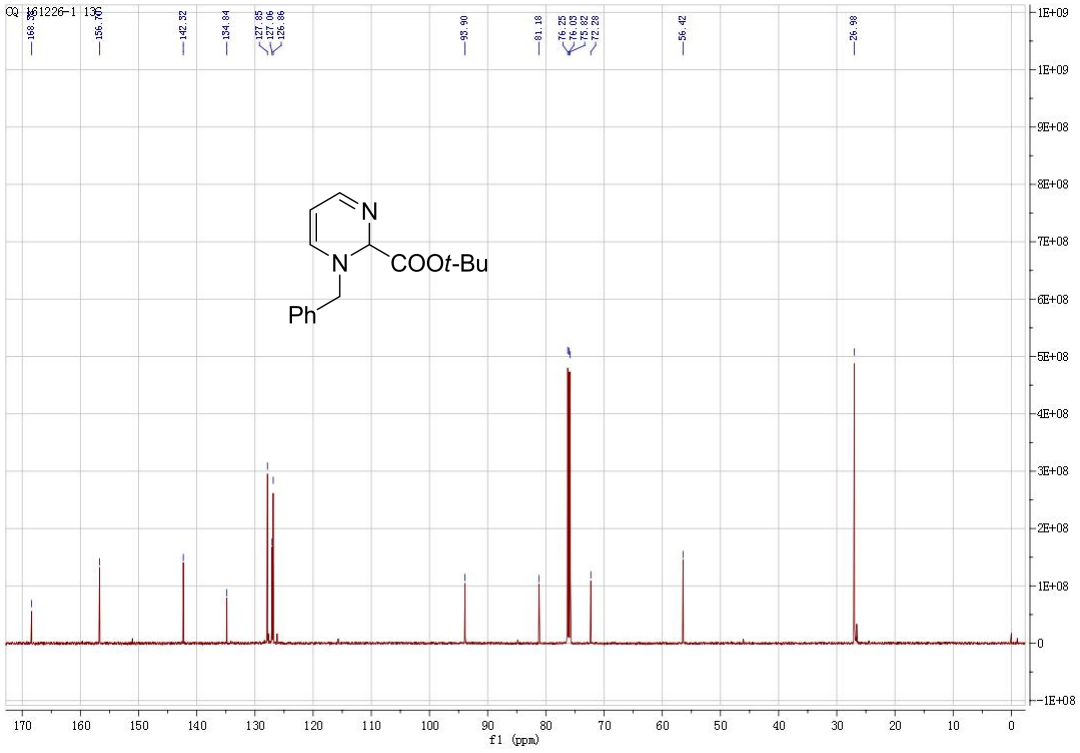

CQ 161222-5 1H
5.25
4.99
4.75
4.71
4.55
4.51
2.01
1.93
1.46
0.00
N
N
COO*t*-Bu
Ph
2.09
3.27
1.00
0.99
1.02
1.02
3.10
3.04
9.16
f1 (ppm)

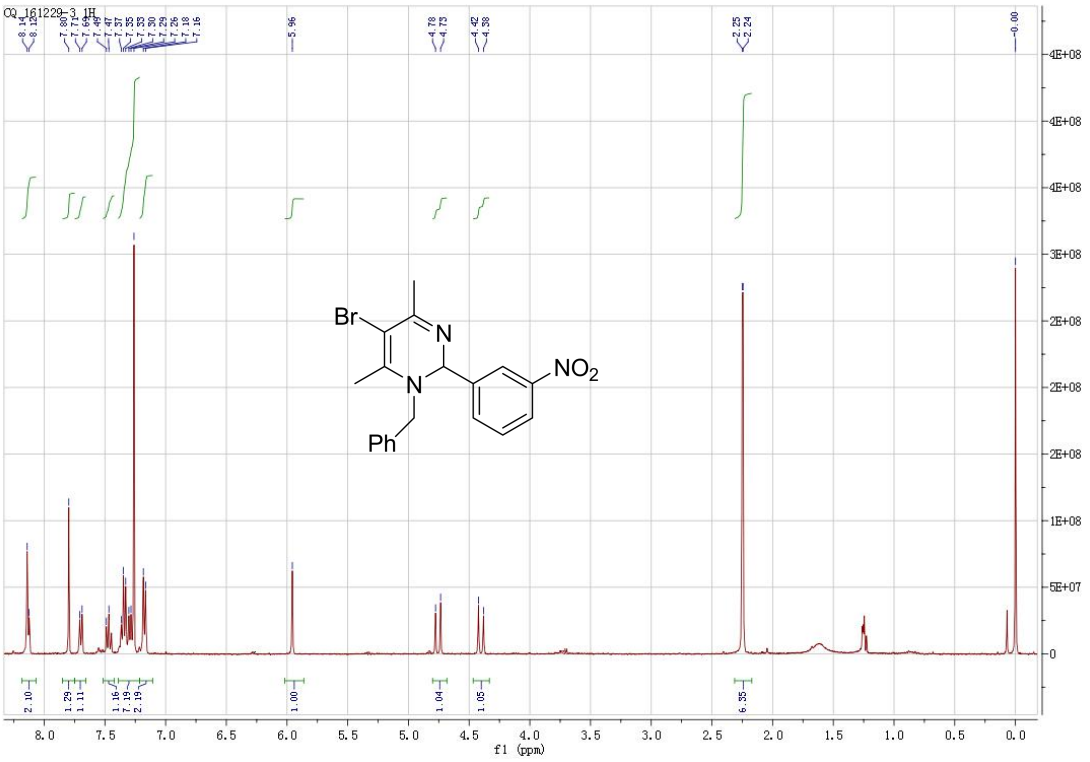

CQ 161222-5 13C
170.
165.
150.96
137.30
128.83
127.49
126.71
97.81
81.66
77.27
77.06
76.85
75.74
52.49
28.07
23.70
18.96
N
N
COO*t*-Bu
Ph
f1 (ppm)

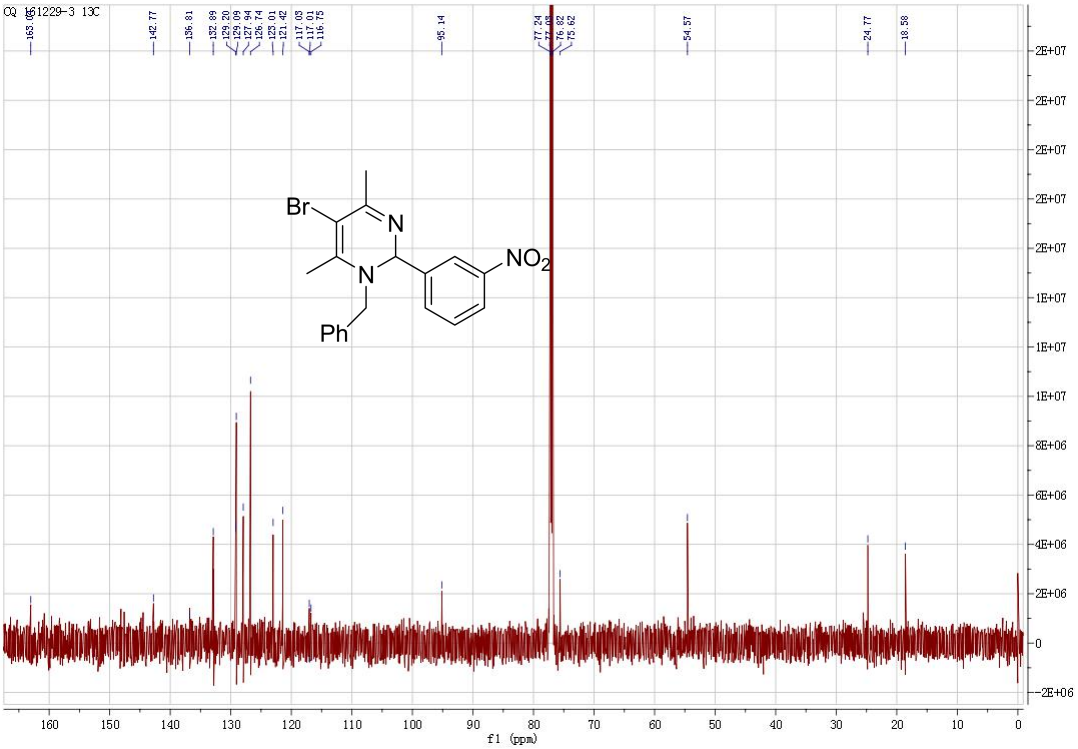

CQ_161222-6_1H
N
N
COOEt
Ph
f1 (ppm)

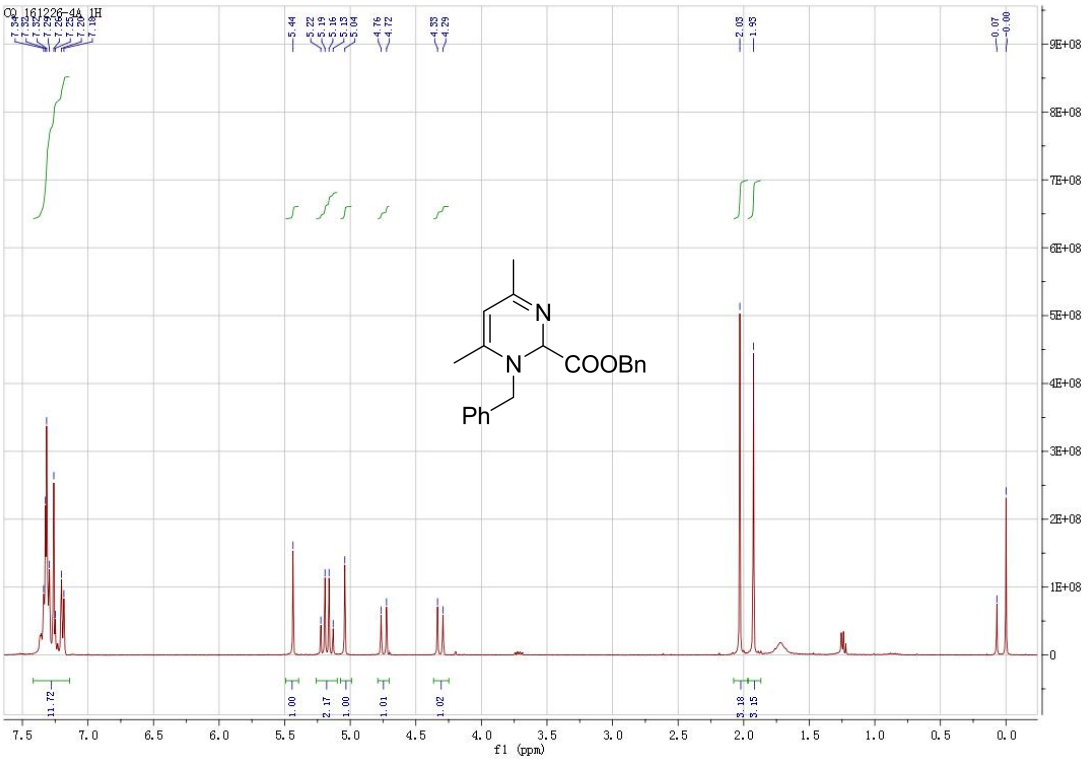

CQ_161220-6_13C
N
N
COOEt
Ph
O
O
f1 (ppm)

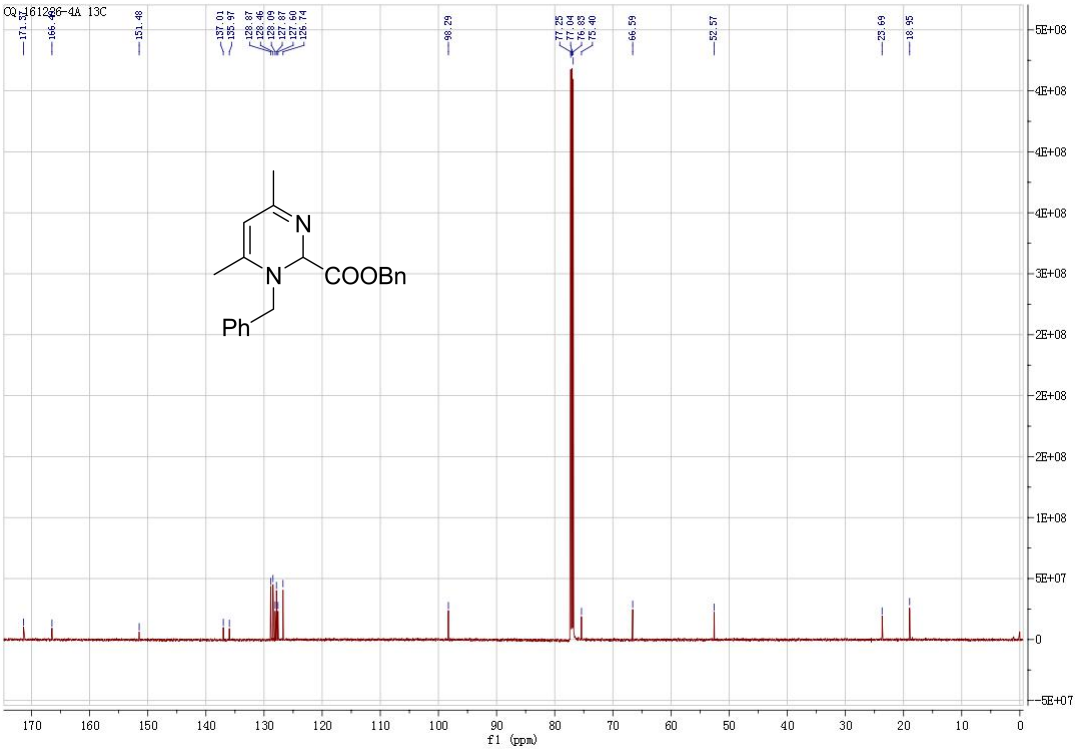

N
N
COOt-Bu
Ph
f1 (ppm)

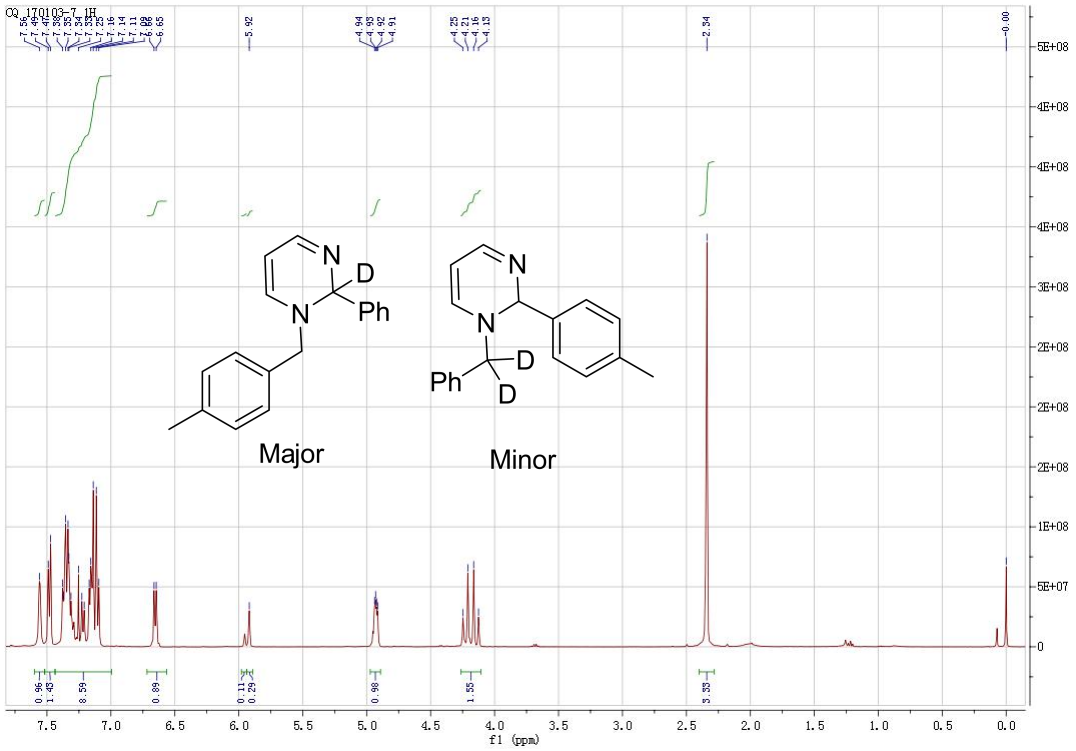

N
N
COOt-Bu
Ph
f1 (ppm)

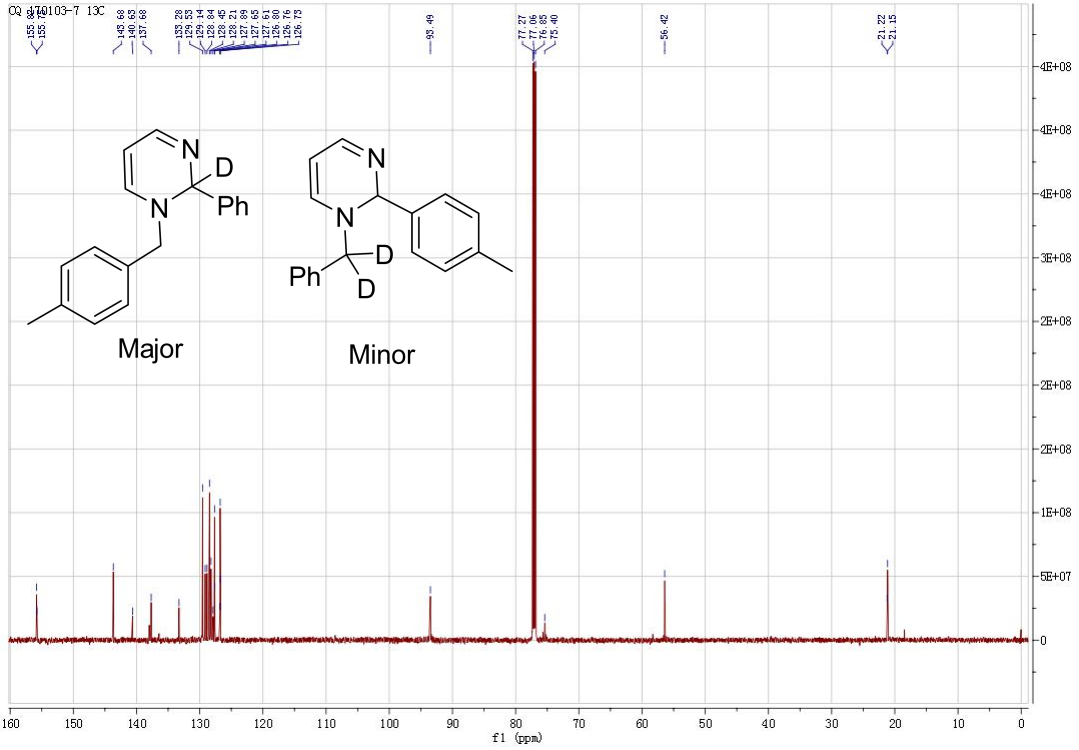

OQ_161229-3_1H
Br
N
N
NO2
Ph
f1 (ppm)


OQ_161229-3_13C
Br
N
N
NO2
Ph
f1 (ppm)


CQ-161226-4A 1H
N
N
COOBn
Ph
f1 (ppm)


CQ-161226-4A 13C
N
N
COOBn
Ph
f1 (ppm)


CQ_170103-7_1H
N
D
Ph
N
Major
N
N
D
Ph
D
Minor
f1 (ppm)


CQ_170103-7_13C
N
D
Ph
N
Major
N
N
D
Ph
D
Minor
f1 (ppm)