Supporting Information

Solvent Incorporated Sequential [3+2] Annulation/Substitution Reaction of Azomethine Imines and Propargyl Sulfur Ylide

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Supporting Material

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A. General Information

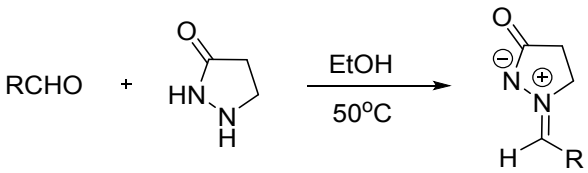
General Procedures. All anhydrous reactions were run under a positive pressure of argon or nitrogen. All syringes, needles, and reaction flasks required for anhydrous reactions were dried in an oven and cooled under an N_2 atmosphere or in a desiccator.

Analysis and Purification. Analytical thin layer chromatography (TLC) was performed on percolated glass backed plates (silica gel 60 F254; 0.25 mm thickness). The TLC plates were visualized by UV illumination and by staining. Solvents for chromatography are listed as volume: volume ratios. Flash column chromatography was carried out on silica gel (40-63 μm). Melting points were recorded using an electrothermal melting point apparatus and are uncorrected.

Identity. Proton (^{1}H NMR) and carbon (^{13}C NMR) nuclear magnetic resonance spectra were recorded on *Bruker UltraShield-600* (600 MHz) and 150 MHz respectively. The chemical shifts are given in parts per million (ppm) on the delta (δ) scale. Coupling constants are reported in hertz (Hz). The spectra were recorded in solutions of deuterated chloroform ($CDCl_3$), with residual chloroform (7.26 ppm for ^{1}H NMR, δ 77.0 ppm for ^{13}C NMR) or tetramethylsilane (0.00 for ^{1}H NMR, 0.00 for ^{13}C NMR) as the internal reference. Data are reported as follows: (s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; dd = doublet of doublets; dt = doublet of triplets; td = triplet of doublets; tt = triplet of triplets; qd = quartet of doublets; ddd = doublet of doublet of doublets; br s = broad singlet). Infrared (IR) spectra were obtained as thin films on KBr plates by dissolving the compound in CH_2Cl_2 followed by evaporation.

B. General Procedure for the Synthesis of Azomethine Imines (reported

procedure)[1]



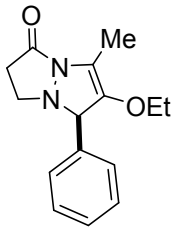
The aldehyde (5.0 mmol) was added to the solution of pyrazolidin-3-one (5.0 mmol) in EtOH (1 mL). The resulting mixture was stirred for 1 h–24 h (depending on TLC monitor) at 50 °C and then diluted with Et_2O (20 mL). The precipitate was collected by filtration, washed with Et_2O, and dried under vacuum to afford the corresponding azomethine imine as a solid in 40–90% yield.

C. **General Procedures for the Synthesis of pyrazolone 2**

Propargyl sulfur ylide was prepared through a known procedure.[2]

To a flame-dried two-neck bottom equipped with a stir bar was added azomethine imine **2** from *general procedure B* (0.5 mmol, 1.0 equiv), and propargyl sulfur ylide (0.75 mmol, 1.5 equiv). After the vial was evacuated and backfilled twice with N_2, EtOH (1 mL) and Na_2CO_3 (1 mmol, 2.0 equiv) were added at 0 °C. The mixture was warmed up to 22 °C and stirred for several hours (monitored by TLC until the azomethine imine was fully consumed). The reaction mixture was concentration *in vacuo*, the residue was subsequently purified through column chromatography (hexanes/EtOAc: from 10:1 to 2:1) to afford the desired products.

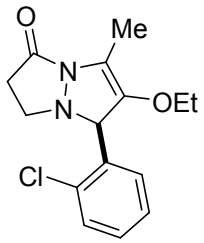
D. Characterization Data for the [3 + 2] Annulation Products



3a

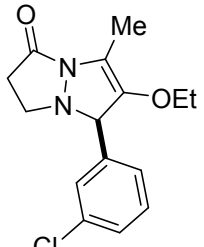
5-(4-chlorophenyl)-6-ethoxy-7-methyl-2,3-dihydro-1H,5H-pyrazolo[1,2-a]pyrazol-1-one (3a): ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.46–7.39 (m, 5H), 6.05 (s, 1H),

4.33 (t, 2H, J = 6.0 Hz), 4.09 (dd, 2H, J = 18, 6.0 Hz), 2.85 (t, 2H, J = 6.0 Hz), 2.29 (s, 3H), 1.20 (t, 3H, J = 6.0 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 171.1, 148.3, 144.7, 131.0, 129.0, 128.9, 128.6, 106.1, 60.8, 44.7, 35.0, 14.2, 13.7. FT-IR (KBr pellet, cm^{-1}): 3134, 2925, 1759, 1451, 773. HRMS: calcd. for $C_{15}H_{19}N_2O_2^+$, $[M+H]^+$ 259.1441, found 259.1443.



3b

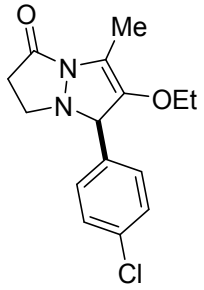
5-(2-chlorophenyl)-6-ethoxy-7-methyl-2,3-dihydro-1H,5H-pyrazolo[1,2-a]pyrazol-1-one (3b): ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.40–7.27 (m, 4H), 6.04 (s, 1H), 4.14 (t, 2H, J = 7.2 Hz), 4.07 (q, 2H, J = 7.2 Hz), 2.84 (t, 2H, J = 7.2 Hz), 2.32 (s, 3H), 1.20 (t, 3H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 170.9, 148.0, 140.8, 134.1, 132.0, 130.3, 129.9, 129.8, 126.7, 106.7, 60.5, 44.4, 34.5, 14.0, 13.6. FT-IR (KBr pellet, cm^{-1}): 3105, 1898, 1679, 1380, 762. HRMS: calcd. for $C_{15}H_{18}ClN_2O_2^+$, $[M+H]^+$ 293.1051, found 293.1053.



3c

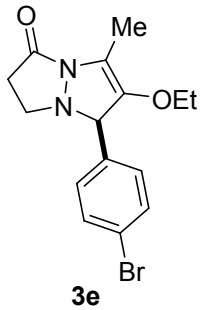
5-(3-chlorophenyl)-6-ethoxy-7-methyl-2,3-dihydro-1H,5H-pyrazolo[1,2-a]pyrazol-1-one (3c): ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.43–7.27 (m, 4H), 6.06 (d, 1H, J = 10.2 Hz), 4.32–4.29 (m, 2H), 4.09 (dd, 2H, J = 7.2, 3.0 Hz), 2.88–2.85 (m, 2H), 2.29 (s, 3H), 1.21 (t, 3H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 170.8, 148.2, 143.3, 143.0, 134.5, 132.4, 130.0, 129.9, 129.1, 128.9, 128.8, 128.5, 126.8, 106.2, 106.1, 60.6, 44.5, 44.4, 34.6, 14.0, 13.5. FT-IR (KBr pellet, cm^{-1}): 3105, 1769, 1629,

1401, 783. HRMS: calcd. for $C_{15}H_{18}ClN_2O_2^+$, $[M+H]^+$ 293.1051, found 293.1050.



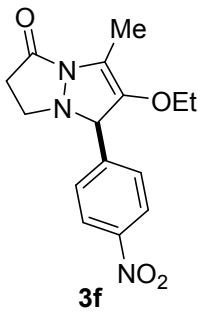
3d

5-(4-chlorophenyl)-6-ethoxy-7-methyl-2,3-dihydro-1H,5H-pyrazolo[1,2-a]pyrazol-1-one (3d): ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.43 (d, 2H, *J* = 8.4 Hz), 7.37 (d, 2H, *J* = 8.4 Hz), 6.06 (s, 1H), 4.31 (t, 2H, *J* = 7.2 Hz), 4.10 (d, 2H, *J* = 7.2 Hz), 2.88 (t, 2H, *J* = 7.2 Hz), 2.30 (s, 3H), 1.22 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 170.8, 148.2, 143.3, 134.5, 130.0, 129.1, 128.9, 106.1, 60.6, 44.4, 34.6, 14.0, 13.5. FT-IR (KBr pellet, cm^{-1}): 3125, 2984, 1709, 1490, 812. HRMS: calcd. for $C_{15}H_{18}ClN_2O_2^+$, $[M+H]^+$ 293.1051, found 293.1048.



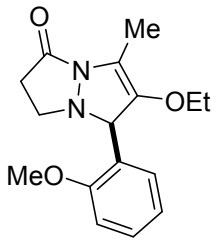
3e

5-(4-bromophenyl)-6-ethoxy-7-methyl-2,3-dihydro-1H,5H-pyrazolo[1,2-a]pyrazol-1-one (3e): ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.57 (d, 2H, *J* = 6.0 Hz), 7.27 (t, 2H, *J* = 6.0 Hz), 6.04 (s, 1H), 4.29 (t, 2H, *J* = 6.0 Hz), 4.08 (q, 2H, *J* = 6.0 Hz), 2.86 (t, 2H, *J* = 6.0 Hz), 2.28 (s, 3H), 1.20 (t, 3H, *J* = 6.0 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 170.9, 148.3, 143.4, 131.9, 130.4, 129.7, 122.8, 106.1, 60.7, 44.5, 34.7, 14.1, 13.5. FT-IR (KBr pellet, cm^{-1}): 3100, 2940, 1710, 1490, 793. HRMS: calcd. for $C_{15}H_{17}BrN_2O_2Na^+$, $[M+H]^+$ 359.0366, found 359.0364.



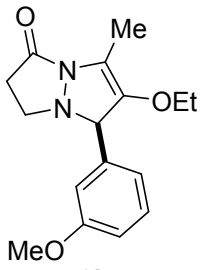
3f

6-ethoxy-7-methyl-5-(4-nitrophenyl)-2,3-dihydro-1H,5H-pyrazolo[1,2-a]pyrazol-1-one (3f): ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.31(d, 2H, *J* = 8.4 Hz) 7.62 (d, 2H, *J* = 8.4 Hz), 6.15 (s, 1H), 4.33 (t, 2H, *J* = 7.2 Hz), 4.09 (d, 2H, *J* = 8.4 Hz), 2.92 (t, 2H, *J* = 7.2 Hz), 2.30 (s, 3H), 1.20 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 170.8, 148.7, 142.4, 137.1, 129.5, 124.0, 107.0, 60.7, 44.7, 34.3, 14.0, 13.5. FT-IR (KBr pellet, cm^{-1}): 3105, 2975, 1709, 1520, 892. HRMS: calcd. for $C_{15}H_{17}N_3O_4Na^+$, $[M+H]^+$ 326.1111, found 326.1110.



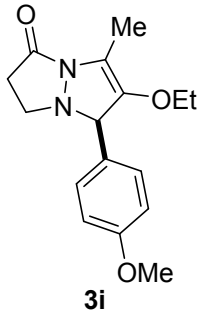
3g

6-ethoxy-5-(2-methoxyphenyl)-7-methyl-2,3-dihydro-1H,5H-pyrazolo[1,2-a]pyrazol-1-one (3g): ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.17 (s, 1H), 6.90–6.85 (m, 3H), 4.26 (t, 2H, *J* = 6.0 Hz), 4.00 (t, 2H, *J* = 6.0 Hz), 3.76 (s, 3H), 2.78 (t, 2H, *J* = 6.0Hz), 2.21 (s, 3H), 1.12 (t, 3H, *J* = 6.0 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 170.9, 156.5, 147.7, 140.5, 131.5, 130.2, 120.4, 119.4, 110.7, 106.0, 60.2, 55.1, 44.6, 34.6, 13.8, 13.4. FT-IR (KBr pellet, cm^{-1}): 3310, 1800, 1620, 1501, 803. HRMS: calcd. for $C_{16}H_{21}N_2O_3^+$, $[M+H]^+$ 289.1547, found 289.1550.



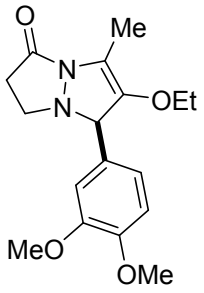
3h

6-ethoxy-5-(3-methoxyphenyl)-7-methyl-2,3-dihydro-1H,5H-pyrazolo[1,2-a]pyrazol-1-one (3h): ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.37 (t, 1H, *J* = 7.2 Hz), 6.98 (d, 1H, *J* = 7.8 Hz), 6.97–6.95 (m, 2H), 6.07 (s,1H), 4.36 (t, 2H, *J* = 6.0 Hz) , 4.11 (q, 2H, *J* = 6.0 Hz), 3.86 (s, 3H) , 2.87 (t, 2H, *J* = 6.0 Hz), 2.30 (s, 3H) , 1.22 (t, 3H, *J* = 6.0 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 170.9, 159.6, 148.2, 144.3, 131.9, 129.7, 114.4, 113.9, 105.9, 60.6, 55.2, 44.5, 34.8, 14.0,13.5. FT-IR (KBr pellet, cm^{-1}): 3155, 1729, 1629, 1530, 1390. HRMS: calcd. for $C_{16}H_{21}N_2O_3^+$, $[M+H]^+$ 289.1547, found 289.1545.



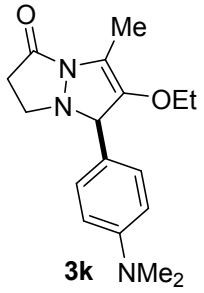
3i

6-ethoxy-5-(4-methoxyphenyl)-7-methyl-2,3-dihydro-1H,5H-pyrazolo[1,2-a]pyrazol-1-one (3i): ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.32 (d, 2H, *J* = 8.4 Hz), 6.97 (d, 2H, *J* = 8.4 Hz), 6.01 (s, 1H), 4.31 (t, 2H, *J* = 7.8 Hz), 4.10 (q, 2H, *J* = 7.2 Hz), 3.86 (s, 3H), 2.85 (t, 3H, *J* = 7.2 Hz), 2.29 (s, 3H), 1.21 (t, 3H, *J* =7.2 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 170.9, 159.6, 148.0, 144.2, 130.0, 123.0, 114.0, 105.6, 60.6, 55.3, 44.4, 34.8, 14.0, 13.5. FT-IR (KBr pellet, cm^{-1}): 3055, 1720, 1620, 1510, 842. HRMS: calcd. for $C_{16}H_{21}N_2O_3^+$, $[M+H]^+$ 289.1547, found 289.1546.



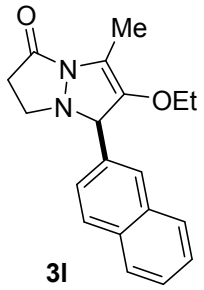
3j

5-(3,4-dimethoxyphenyl)-6-ethoxy-7-methyl-2,3-dihydro-1H,5H-pyrazolo[1,2-a]pyrazol-1-one (3j): ^{1}H NMR ($CDCl_3$, 600 MHz): δ, 6.94–6.93 (m, 3H), 6.02 (s, 1H), 4.32 (t, 2H, *J* = 6.0 Hz), 4.10 (q, 2H, *J* = 6.0 Hz), 3.91 (s, 6H), 2.86 (t, 2H, *J* = 6.0 Hz), 2.28 (s, 1H), 1.20 (t, 3H, *J* = 6.0 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 170.8, 149.0, 148.7, 147.8, 144.2, 123.1, 121.1, 111.8, 110.9, 105.5, 60.4, 55.7, 44.2, 34.5, 13.8, 13.3. FT-IR (KBr pellet, cm^{-1}): 3100, 1750, 1680, 1430, 896. HRMS: calcd. for $C_{17}H_{23}N_2O_4^+$, $[M+H]^+$ 319.1652, found 319.1650.



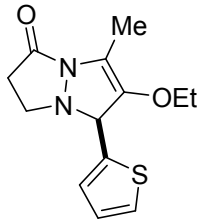
3k

5-(4-(dimethylamino)phenyl)-6-ethoxy-7-methyl-2,3-dihydro-1H,5H-pyrazolo[1,2-a]pyrazol-1-one (3k): ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.26 (t, 2H, *J* = 12.0 Hz), 6.75 (d, 2H, *J* = 12.0 Hz), 5.97 (s, 1H), 4.31 (dd, 2H, *J* = 18.0, 6.0 Hz), 4.10 (dd, 2H, *J* = 18.0, 6.0 Hz), 3.00 (s, 6H), 2.83 (t, 2H, *J* = 12.0 Hz), 2.27 (s, 3H), 1.21 (t, 3H, *J* = 6.0 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 170.9, 149.2, 148.9, 148.0, 144.4, 123.3, 121.3, 112.1, 111.1, 105.7, 60.0, 55.9, 44.4, 34.7, 14.0, 13.5. FT-IR (KBr pellet, cm^{-1}): 2925, 1670, 1460, 1380, 852. HRMS: calcd. for $C_{17}H_{24}N_3O_2^+$, $[M+H]^+$ 302.1863, found 302.1860.



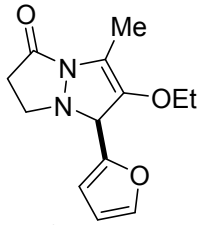
3l

6-ethoxy-7-methyl-5-(naphthalen-2-yl)-2,3-dihydro-1H,5H-pyrazolo[1,2-a]pyrazol-1-one (3l): ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.65–7.27 (m, 7H), 6.15 (d, 1H, *J* = 3.0 Hz), 4.11 (s, 2H), 3.98 (t, 2H, *J* = 3.6 Hz), 2.74 (s, 2H), 2.73 (s, 3H), 1.13 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 170.7, 148.1, 141.9, 133.5, 132.2, 139.3, 128.3, 128.2, 126.8, 125.3, 125.1, 107.5, 60.5, 44.6, 34.9, 13.9, 13.6. FT-IR (KBr pellet, cm^{-1}): 3174, 1749, 1640, 1390, 822. HRMS: calcd. for $C_{19}H_{20}N_2O_2Na^+$, $[M+H]^+$ 331.1417, found 331.1416.



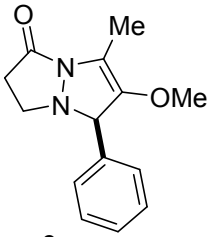
3m

6-ethoxy-7-methyl-5-(thiophen-2-yl)-2,3-dihydro-1H,5H-pyrazolo[1,2-a]pyrazol-1-one (3m): ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.51 (d, 1H, *J* = 1.2 Hz), 6.58 (d, 1H, *J* = 3.6 Hz), 6.51 (q, 1H, *J* = 1.8 Hz), 6.24 (s, 1H), 4.58 (t, 2H, *J* = 7.2 Hz), 4.15 (q, 2H, *J* = 7.2 Hz), 2.91 (t, 2H, *J* = 7.2 Hz), 2.28 (s, 3H), 1.24 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 170.6, 136.8, 130.8, 127.4, 126.8, 126.3, 106.6, 60.4, 44.6, 34.6, 13.9, 13.2. FT-IR (KBr pellet, cm^{-1}): 1780, 1705, 1680, 1620, 1380. HRMS: calcd. for $C_{13}H_{17}N_2O_2S^+$, $[M+H]^+$ 265.1005, found 265.1008.



3n

6-ethoxy-5-(furan-2-yl)-7-methyl-2,3-dihydro-1H,5H-pyrazolo[1,2-a]pyrazol-1-one (3n): ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.50 (t, 1H, *J* = 6.0 Hz), 6.56 (s, 1H), 6.50 (q, 1H, *J* = 6.0 Hz), 6.22 (s, 1H), 4.56 (t, 2H, *J* = 12 Hz), 4.13 (q, 2H, *J* = 6.0 Hz), 2.89 (t, 2H, *J* = 6.0 Hz), 2.26 (s, 3H), 1.23 (t, 3H, *J* = 6.0 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 170.9, 148.1, 144.6, 142.5, 134.2, 108.48, 104.8, 60.6, 45.9, 34.9, 14.0, 13.3. FT-IR (KBr pellet, cm^{-1}): 2870, 2850, 1750, 1720, 680. HRMS: calcd. for $C_{13}H_{17}N_2O_2^+$, $[M+H]^+$ 249.1234, found 249.1235.

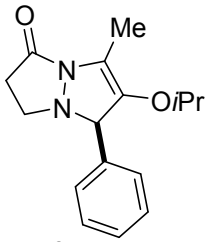


3o

To a flame-dried two-neck bottom equipped with a stir bar was added azomethine imine **2** from *general procedure B* (0.5 mmol, 1.0 equiv), and propargyl sulfur ylide (0.73 mmol, 1.5 equiv). After the vial was evacuated and backfilled twice with N_2, MeOH (1 mL) and Na_2CO_3 (1.5 mmol, 3.0 equiv) were added at 0 °C. The mixture was warmed up to 22 °C and stirred for several hours (monitored by TLC until the azomethine imine was fully consumed). The reaction mixture was concentration *in vacuo*, the residue was subsequently purified through column chromatography (hexanes/EtOAc: from 10:1 to 2:1) to afford the desired products **3o** as colorless oil (99 mg, 82% yield).

6-methoxy-7-methyl-5-phenyl-2,3-dihydro-1H,5H-pyrazolo[1,2-a]pyrazol-1-one (3o): ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.43–7.26 (m, 5H), 6.05 (s, 1H), 4.33 (t, 2H, *J* = 7.2 Hz), 3.62 (s, 3H), 2.89–2.86 (m, 2H), 2.29 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ

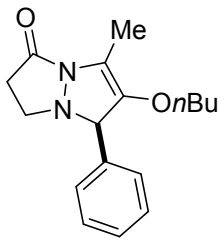
171.3, 148.2, 144.5, 130.7, 128.8, 128.7, 128.4, 105.9, 51.7, 44.4, 34.5, 13.5. FT-IR (KBr pellet, cm^{-1}): 3134, 2925, 1759, 1451, 773. HRMS: calcd. for $C_{14}H_{17}N_2O_2^+$, $[M+H]^+$ 245.1285, found 245.1288.



3p

To a flame-dried two-neck bottom equipped with a stir bar was added azomethine imine **2** from *general procedure B* (0.5 mmol, 1.0 equiv), and propargyl sulfur ylide (0.75 mmol, 1.5 equiv). After the vial was evacuated and backfilled twice with N_2, iso-propanol (1 mL) and Na_2CO_3 (1.5 mmol, 3.0 equiv) were added at 0 °C. The mixture was warmed up to 22 °C and stirred for several hours (monitored by TLC until the azomethine imine was fully consumed). The reaction mixture was concentration *in vacuo*, the residue was subsequently purified through column chromatography (hexanes/EtOAc from 10:1 to 2:1) to afford the desired products **3p** as colorless oil (97 mg, 71% yield).

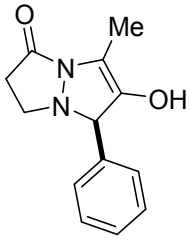
6-isopropoxy-7-methyl-5-phenyl-2,3-dihydro-1H,5H-pyrazolo[1,2-a]pyrazol-1-one (3p): ^1H NMR ($CDCl_3$, 600 MHz): δ 7.44–7.39 (m, 5H), 6.05 (s, 1H), 4.96 (t, 1H, J = 6.0 Hz), 4.32 (t, 2H, J = 6.0 Hz), 2.82 (t, 2H, J = 6.0 Hz), 2.29 (s, 3H), 1.25 (s, 3H), 1.17 (d, 3H, J = 6.0 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 170.4, 148.0, 144.4, 130.8, 128.8, 128.6, 128.4, 105.9, 68.0, 44.6, 35.1, 29.6, 21.7, 13.5. FT-IR (KBr pellet, cm^{-1}): 3200, 2920, 1670, 1370, 860. HRMS: calcd. for $C_{16}H_{21}N_2O_2^+$, $[M+H]^+$ 273.1598, found 273.1599.



3q

The reaction was carried out in 0.3 mmol scale by following the synthesis of **3o**. The product **3q** was isolated through column chromatography (hexanes/EtOAc: from 15:1 to 2:1:) as colorless oil (65 mg, 76% yield).

6-butoxy-7-methyl-5-phenyl-2,3-dihydro-1H,5H-pyrazolo[1,2-a]pyrazol-1-one (3q): ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.43–7.39 (m, 5H), 6.05 (s, 1H), 4.33 (t, 2H, *J* = 6.0 Hz), 4.03 (t, 2H, *J* = 6.0 Hz), 2.86 (t, 2H, *J* = 6.0 Hz), 2.29 (s, 3H), 1.25 (s, 3H), 0.91 (t, 3H, *J* = 6.0 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 170.9, 148.2, 128.8, 128.7, 128.4, 105.9, 64.5, 44.5, 30.5, 29.6, 19.0, 13.6, 13.5. FT-IR (KBr pellet, cm^{-1}): 3020, 3000, 1750, 1640, 840. HRMS: calcd. for $C_{17}H_{23}N_2O_2^+$, $[M+H]^+$ 287.1754, found 287.1756.

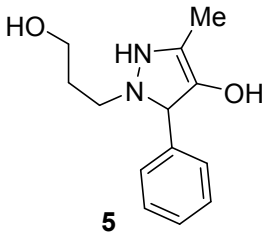


4

A solution of compound **3a** (26 mg, 0.1 mmol) in 2 mL of THF was added 0.5 mL of 1N HCl at room temperature. And the mixture was stirred for about 2h. The reaction was monitored by TLC until **3a** was fully consumed. The reaction mixture was extracted with 10 mL of EtOAc. And the organic layer washed successively with $NaHCO_3$, water and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash column chromatography (petroleum ether/EtOAc = 3：1) to give compound **4** as colorless oil (23 mg, 87% yield).

6-hydroxy-7-methyl-5-phenyl-2,3-dihydro-1H,5H-pyrazolo[1,2-a]pyrazol-1-one (4): ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.45 (m, 3H), 7.36 (m, 2H), 6.09 (s, 1H), 4.33 (t, 2H, *J* = 7.2 Hz), 2.90 (t, 2H, *J* = 6.0 Hz), 2.31 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ

173.7, 148.1, 144.9, 139.8, 128.9, 128.8, 106.1, 60.6, 44.0, 35.7, 13.1. FT-IR (KBr pellet, cm^{-1}): 3010, 2890, 2860, 1700, 750. HRMS: calcd. for $C_{13}H_{15}N_2O_2^+$, $[M+H]^+$ 231.1128, found 231.1130.



5

A solution of **3a** (30 mg, 0.11 mmol) in ethanol was added sodium borohydride (12 mg, 0.33 mmol). The mixture was stirred for about 1h at 0 ℃. The reaction was monitored by TLC until **3a** was fully consumed. The residue was purified by flash column chromatography (petroleum ether/EtOAc = 3：1) to give compound **5** as colorless oil (26 mg, 81% yield).

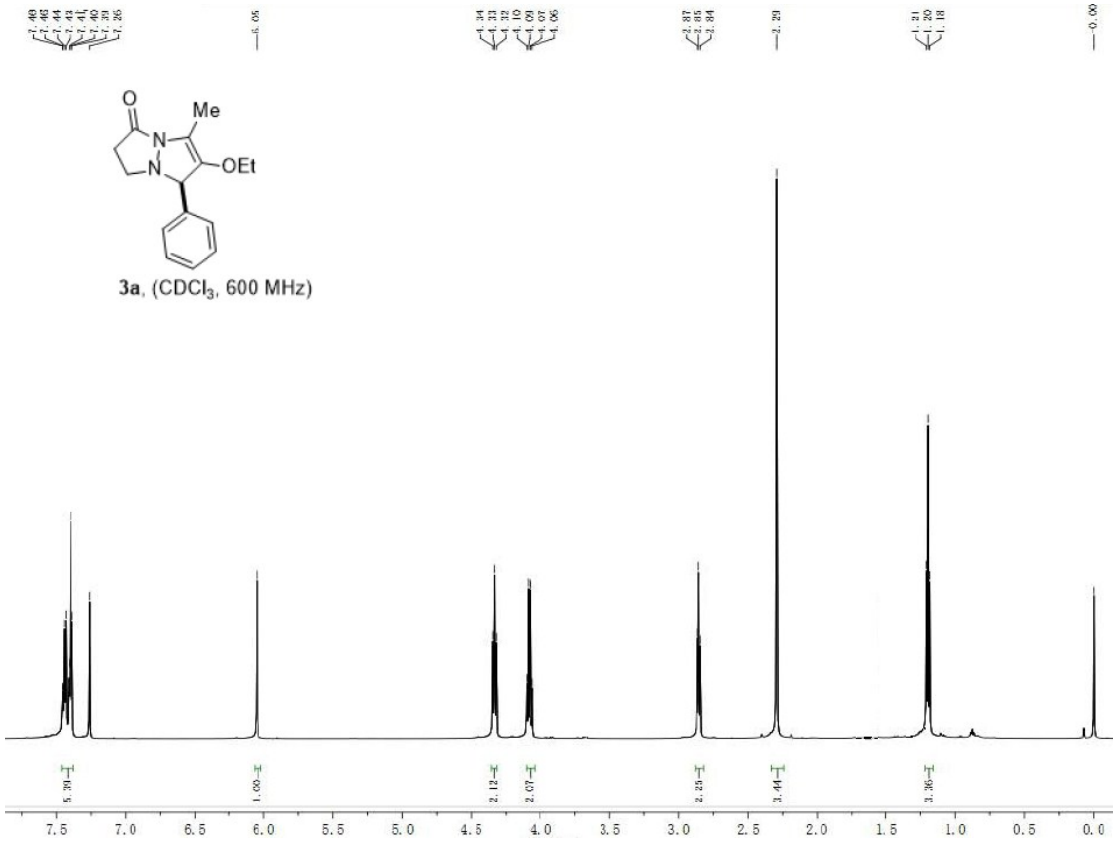
2-(3-hydroxypropyl)-5-methyl-3-phenyl-2,3-dihydro-1H-pyrazol-4-ol (5): ^1H NMR ($CDCl_3$, 600 MHz): δ 7.46–7.37 (m, 5H), 6.07 (s, 1H), 4.21 (t, 2H, *J* = 6.0 Hz), 3.65 (t, 2H, *J* = 6.0 Hz), 2.29 (s, 3H), 1.94 (t, 3H, *J* = 6.0 Hz), 1.25 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ147.8, 144.6, 130.7, 128.6, 128.4, 105.7, 60.1, 46.6, 32.7, 29.5, 13.3. FT-IR (KBr pellet, cm^{-1}) 3030, 2850, 1730, 1680, 841. HRMS: calcd. for $C_{13}H_{19}N_2O_2^+$, $[M+H]^+$ 235.1441, found 235.1441.

E. References:

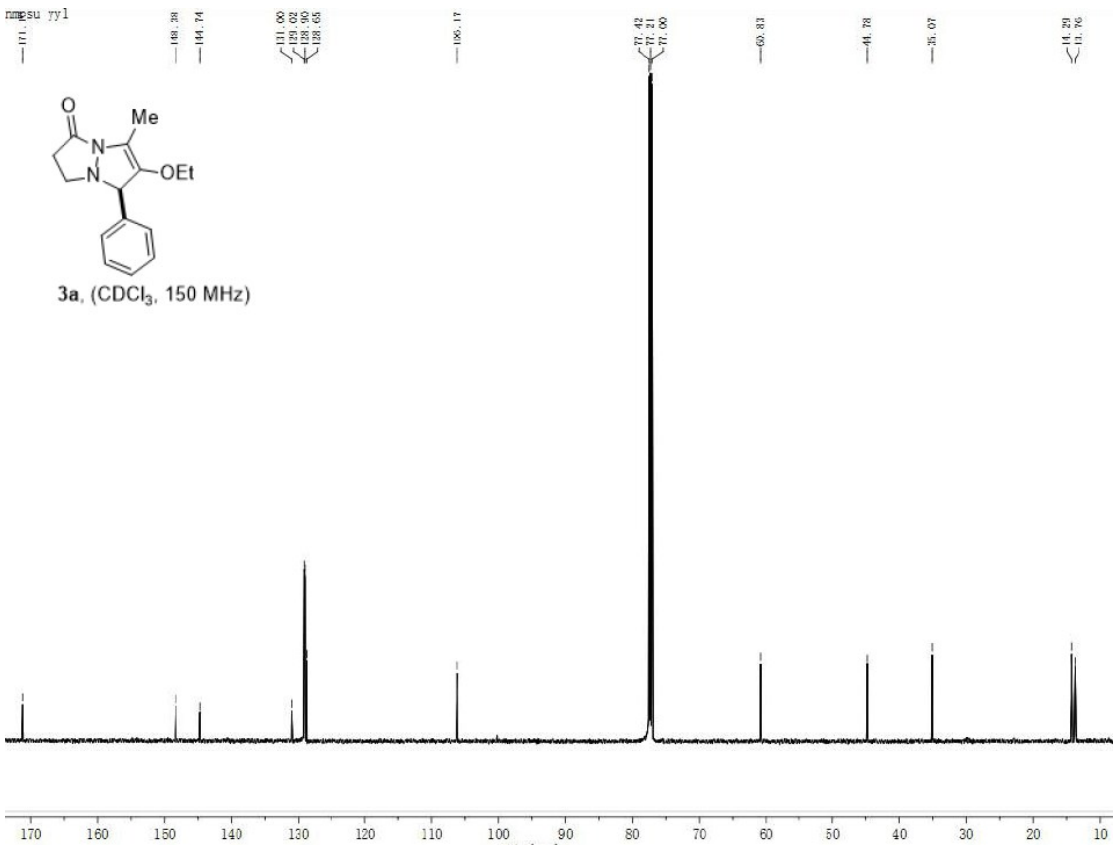
[1] H. Guo, H. Liu, F.-L. Zhu, R. Na, H. Jiang, Y. Wu, L. Zhang, Z. Li, H. Yu, B. Wang, Y. Xiao, X.-P. Hu and M. Wang, *Angew. Chem. Int. Ed.* 2013, ***52***, 12641–12645.

[2] N. Kern, A. Blanc, J.-M. Weibel and P. Pale, *Chem. Commun.* 2011, **47**, 6665–6667.

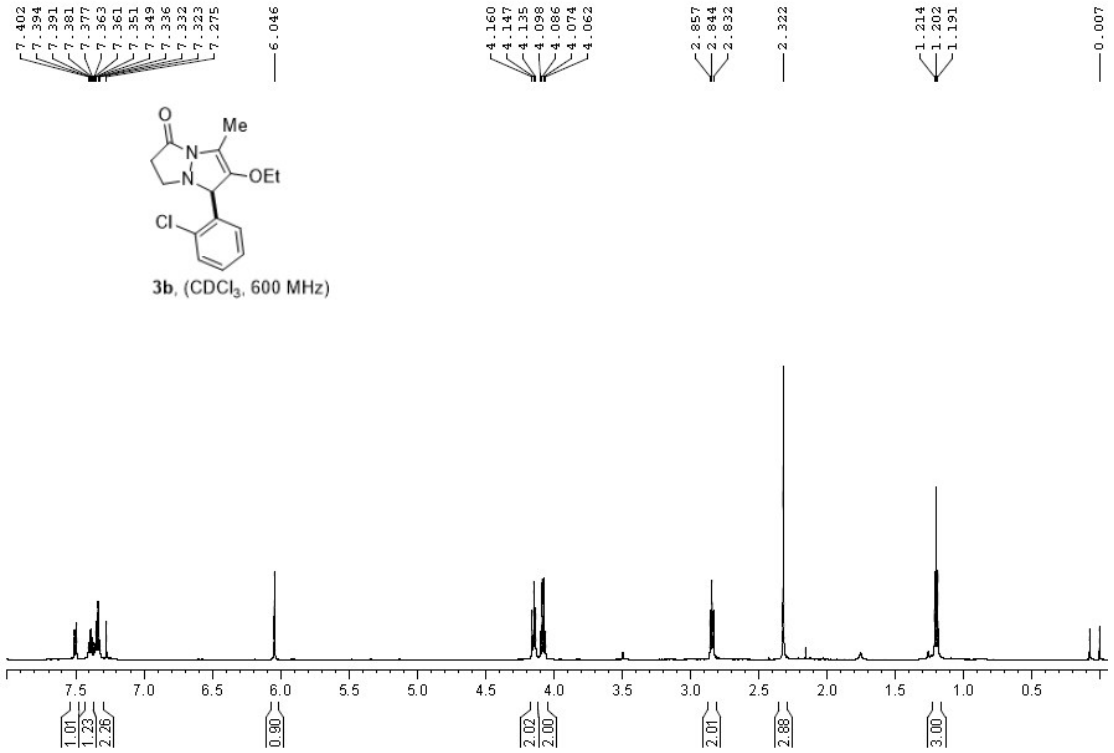
F. ^{1}H and ^{13}C NMR Spectra of Products



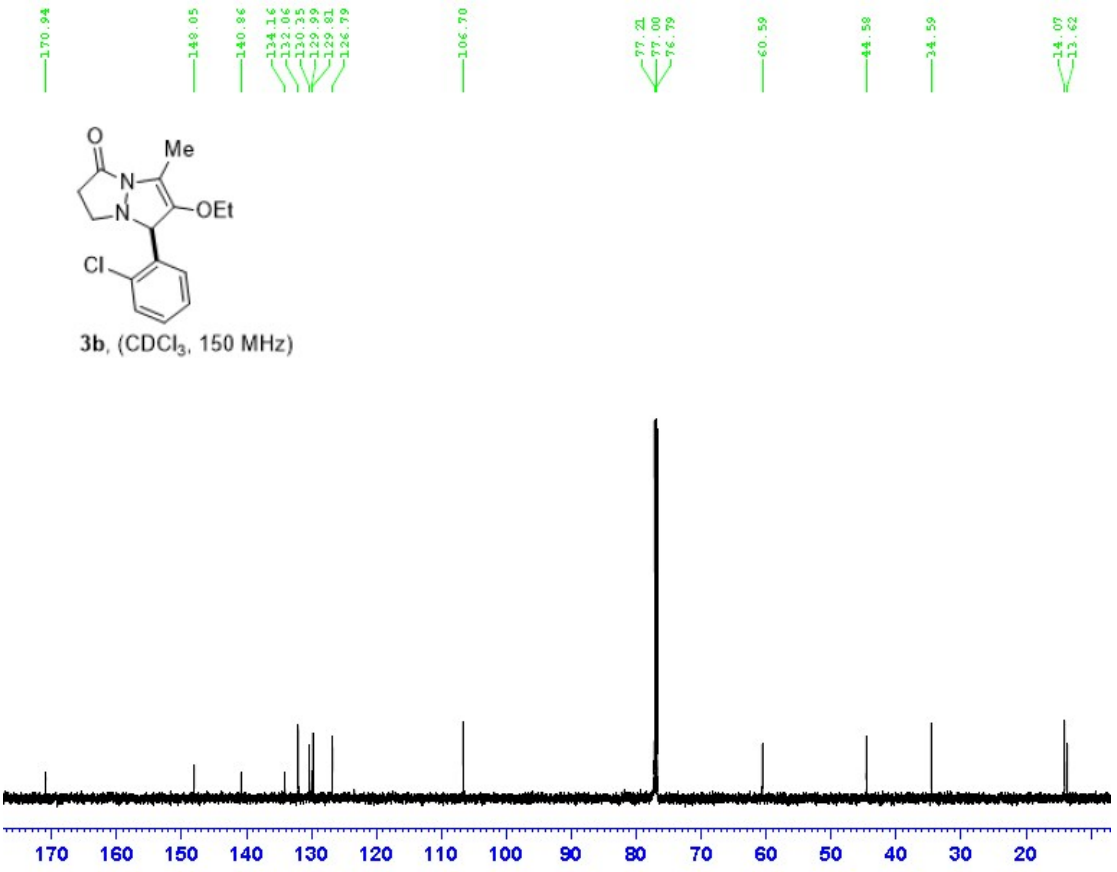
3a, ($CDCl_3$, 600 MHz)



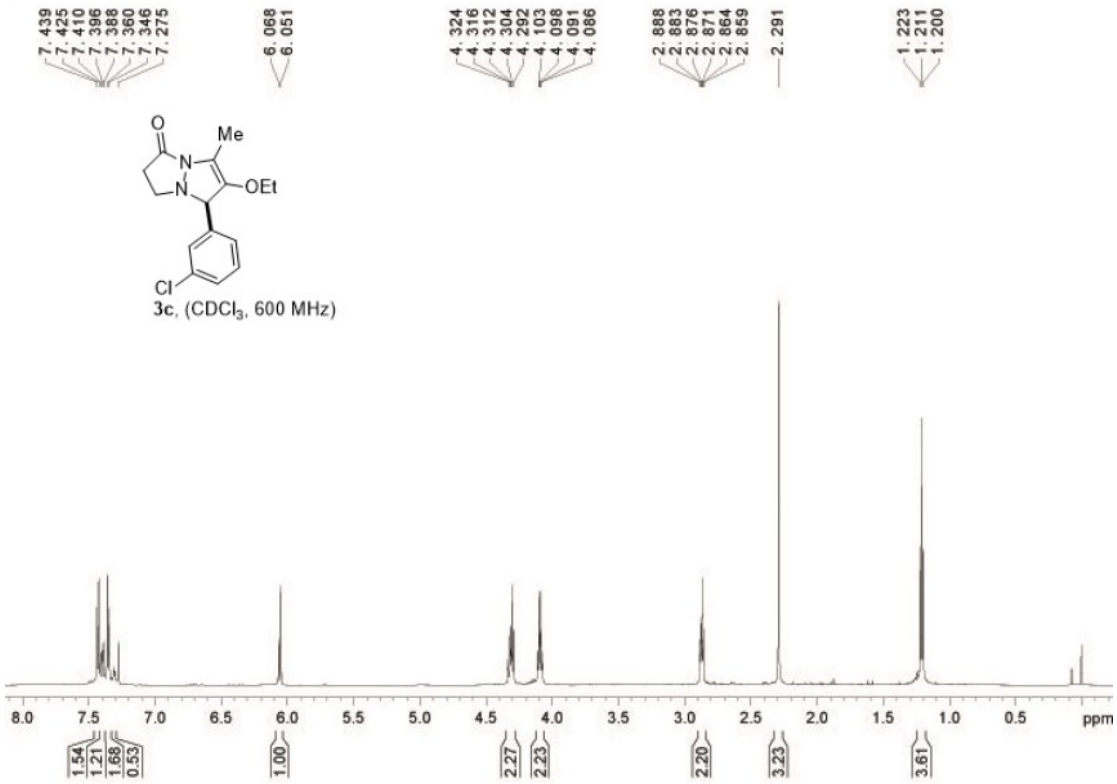
3a, ($CDCl_3$, 150 MHz)



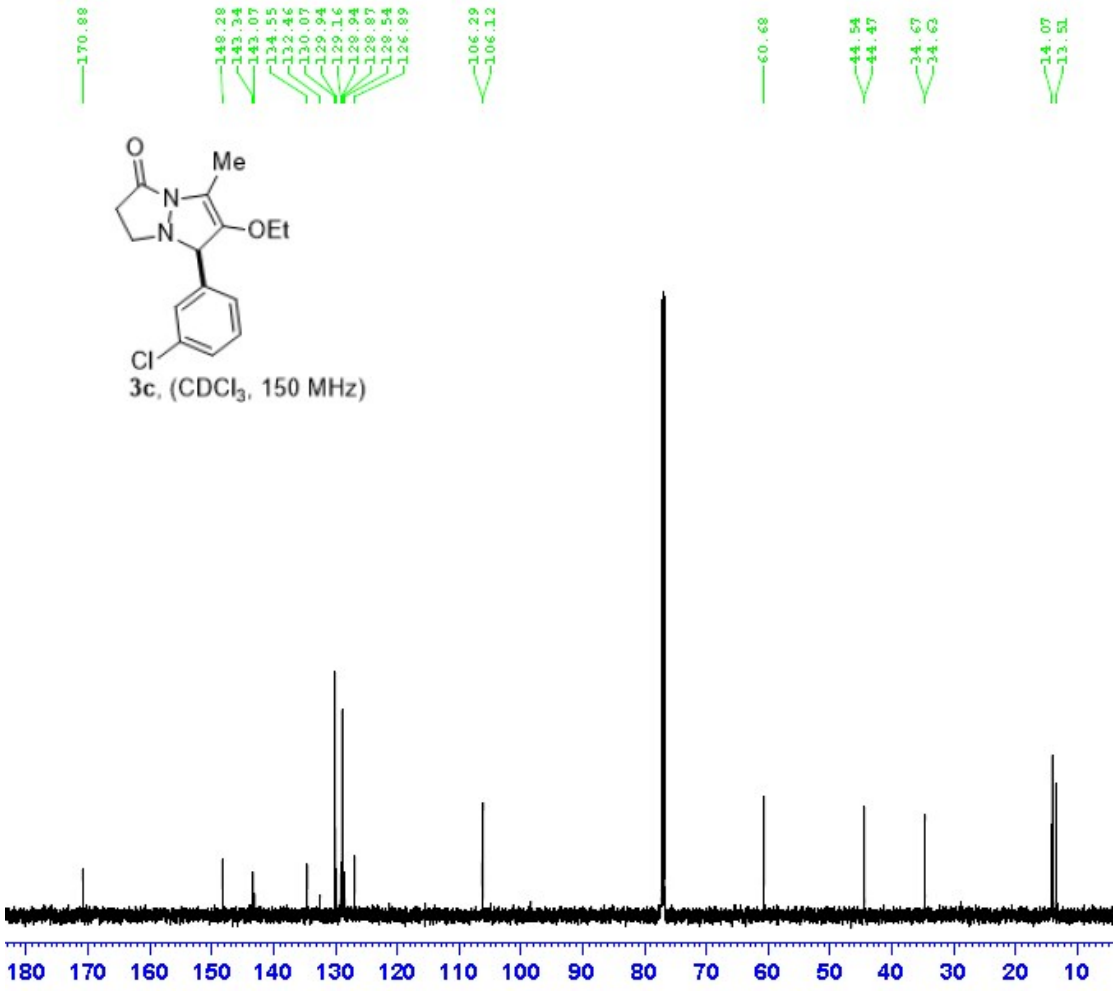
3b, ($CDCl_3$, 600 MHz)



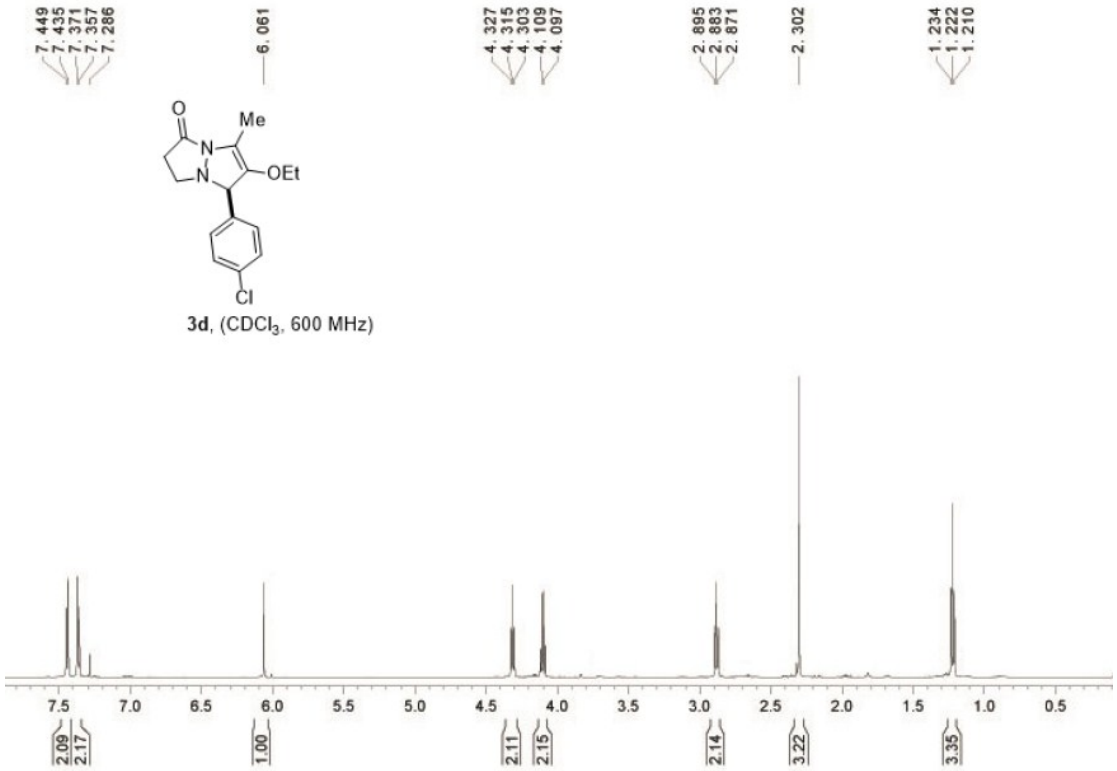
3b, ($CDCl_3$, 150 MHz)



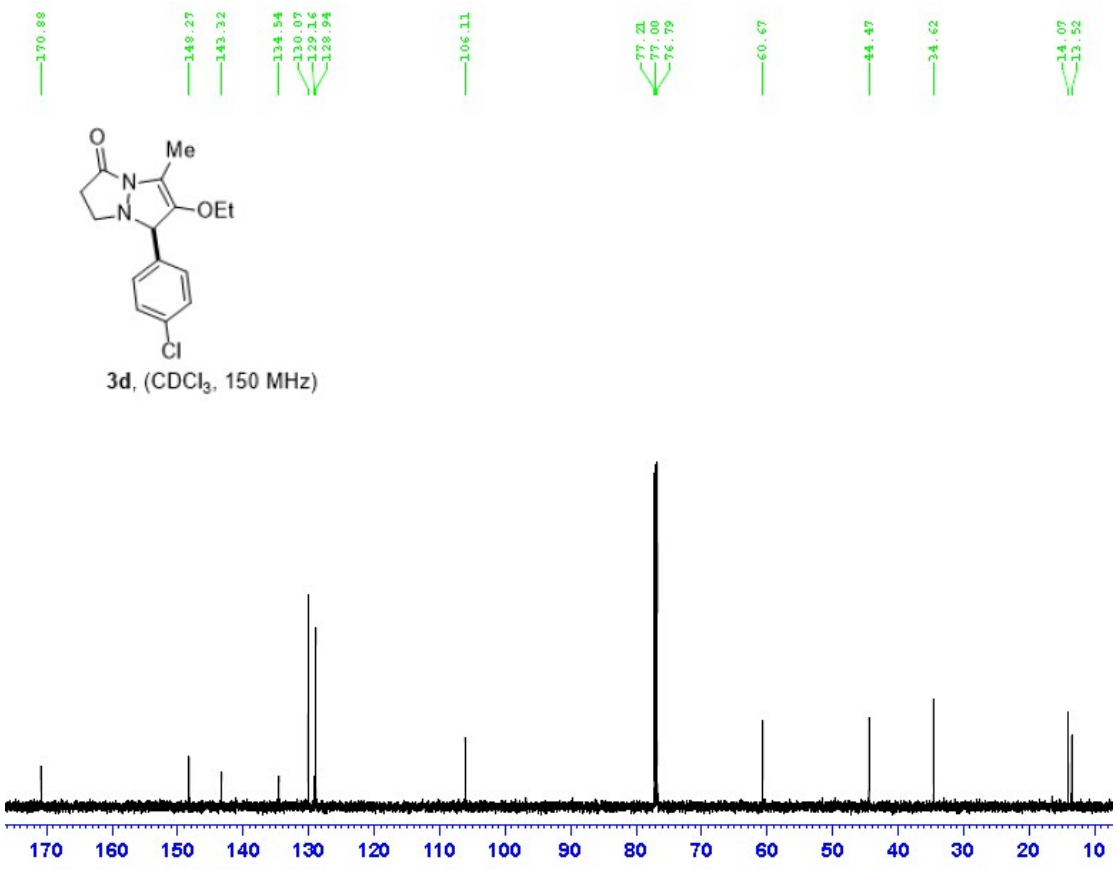
3c, ($CDCl_3$, 600 MHz)



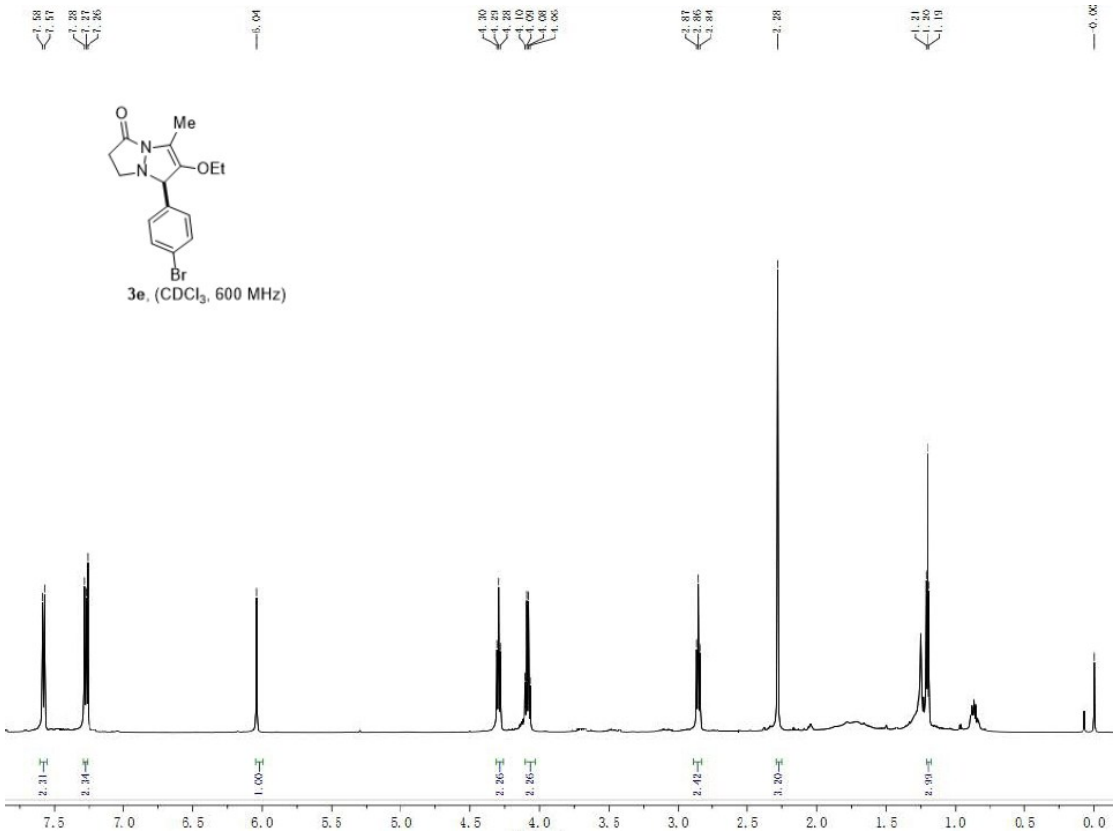
3c, ($CDCl_3$, 150 MHz)



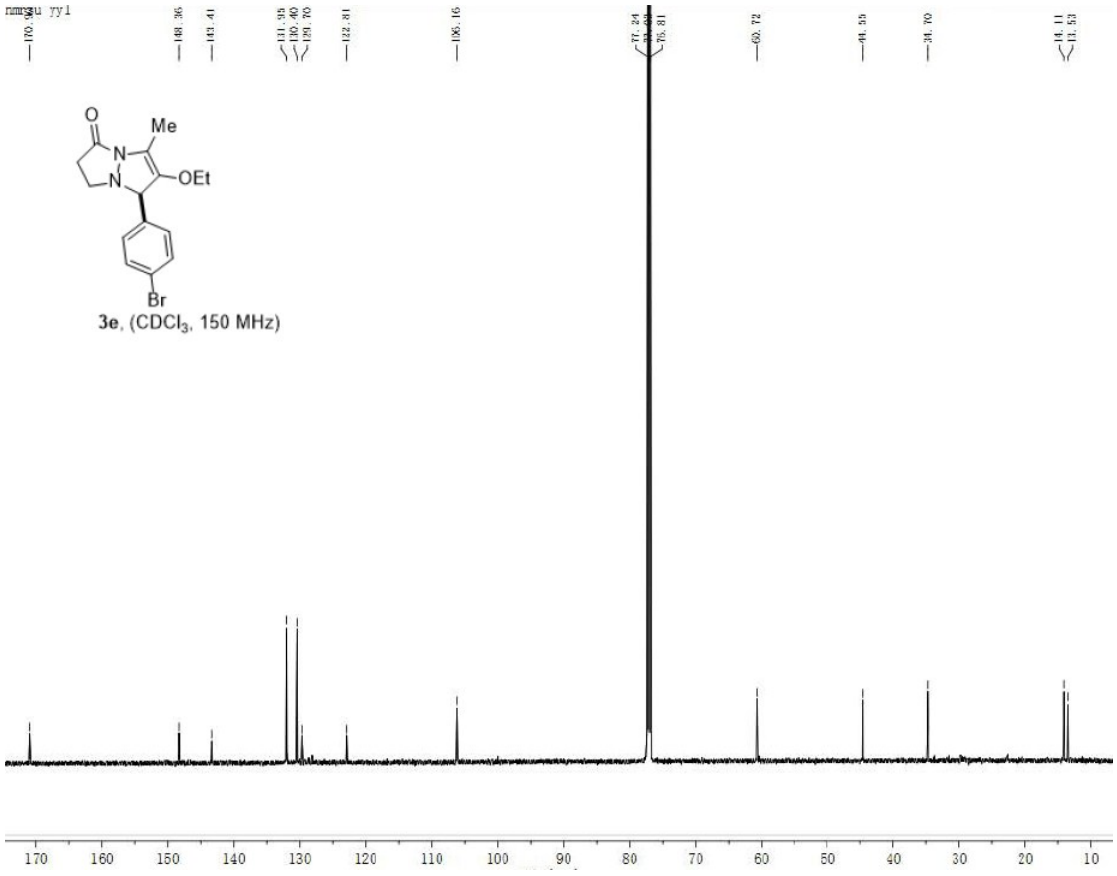
3d, ($CDCl_3$, 600 MHz)



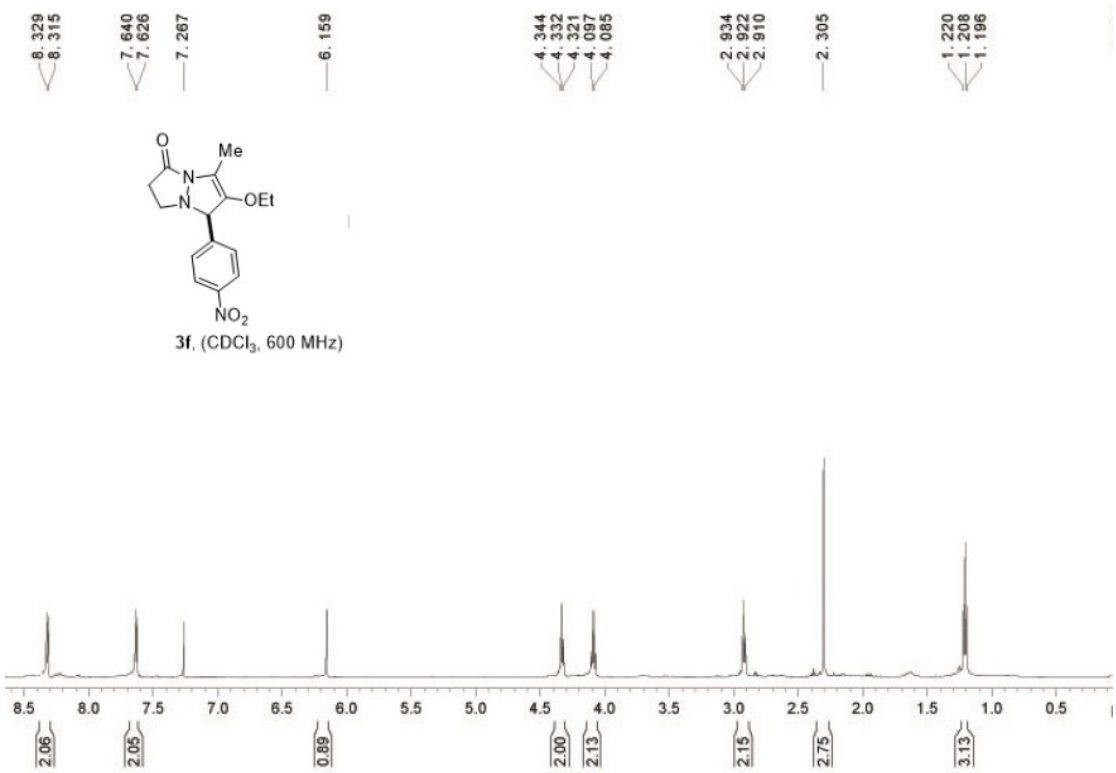
3d, ($CDCl_3$, 150 MHz)



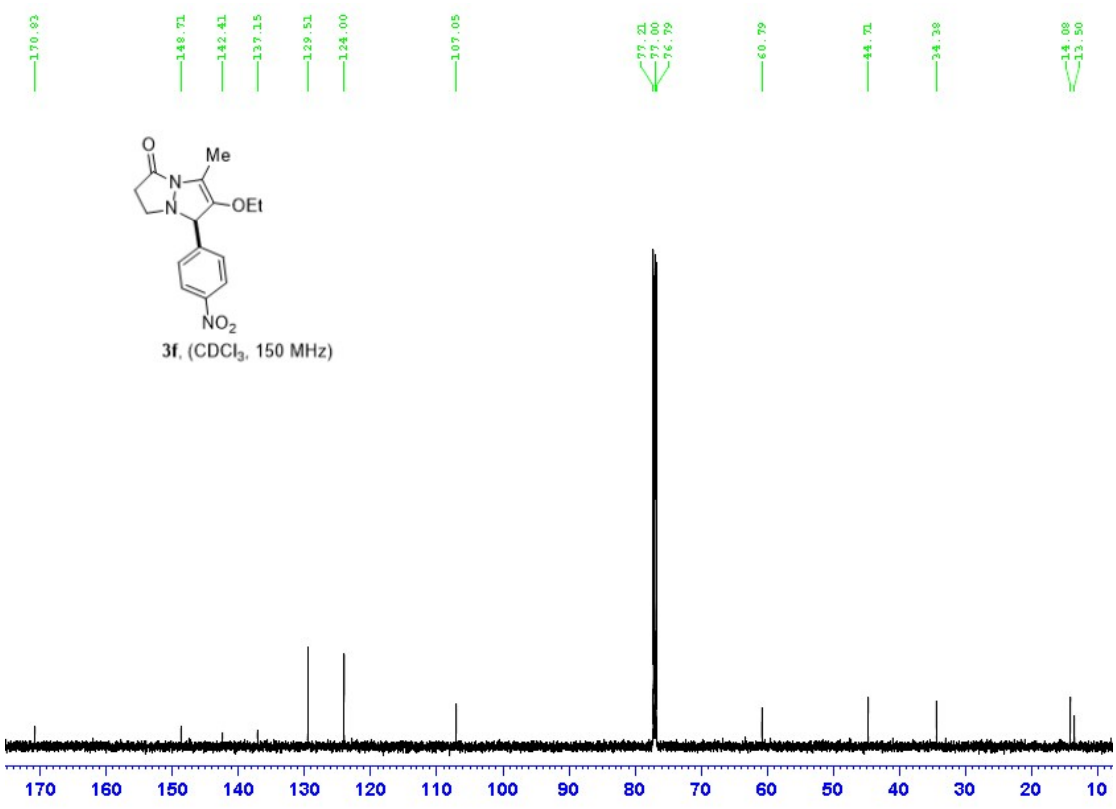
3e, ($CDCl_3$, 600 MHz)



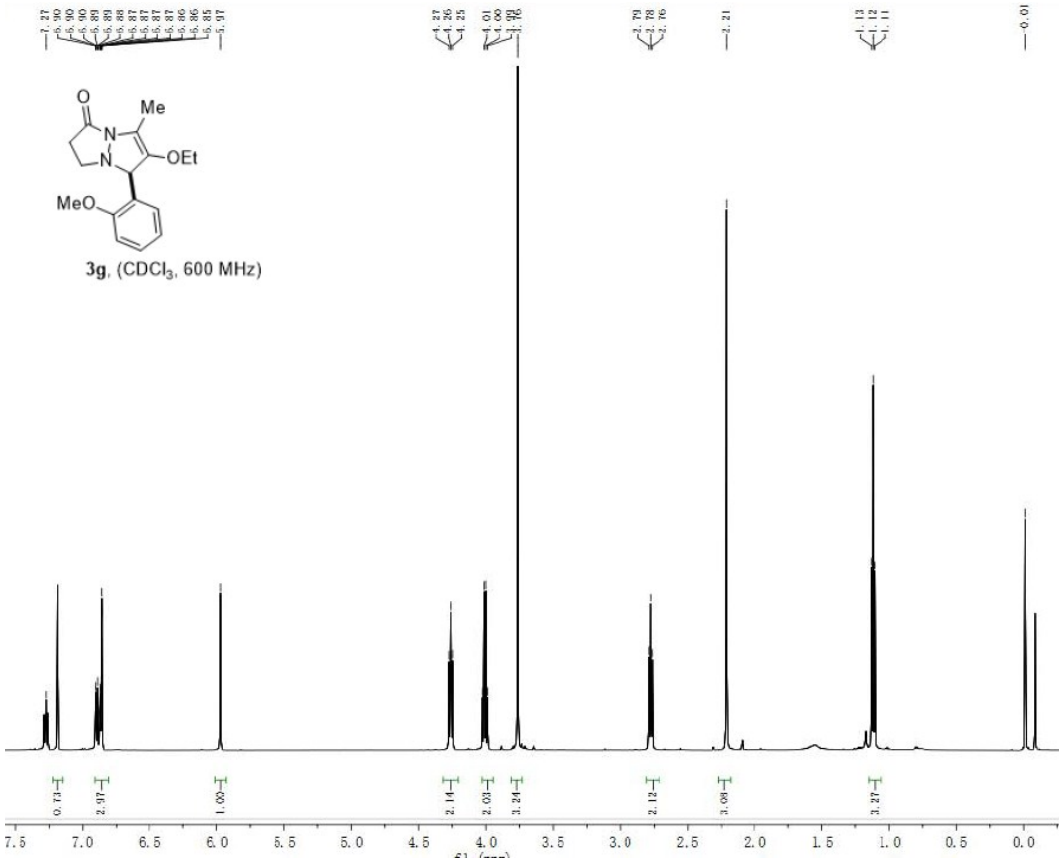
3e, ($CDCl_3$, 150 MHz)



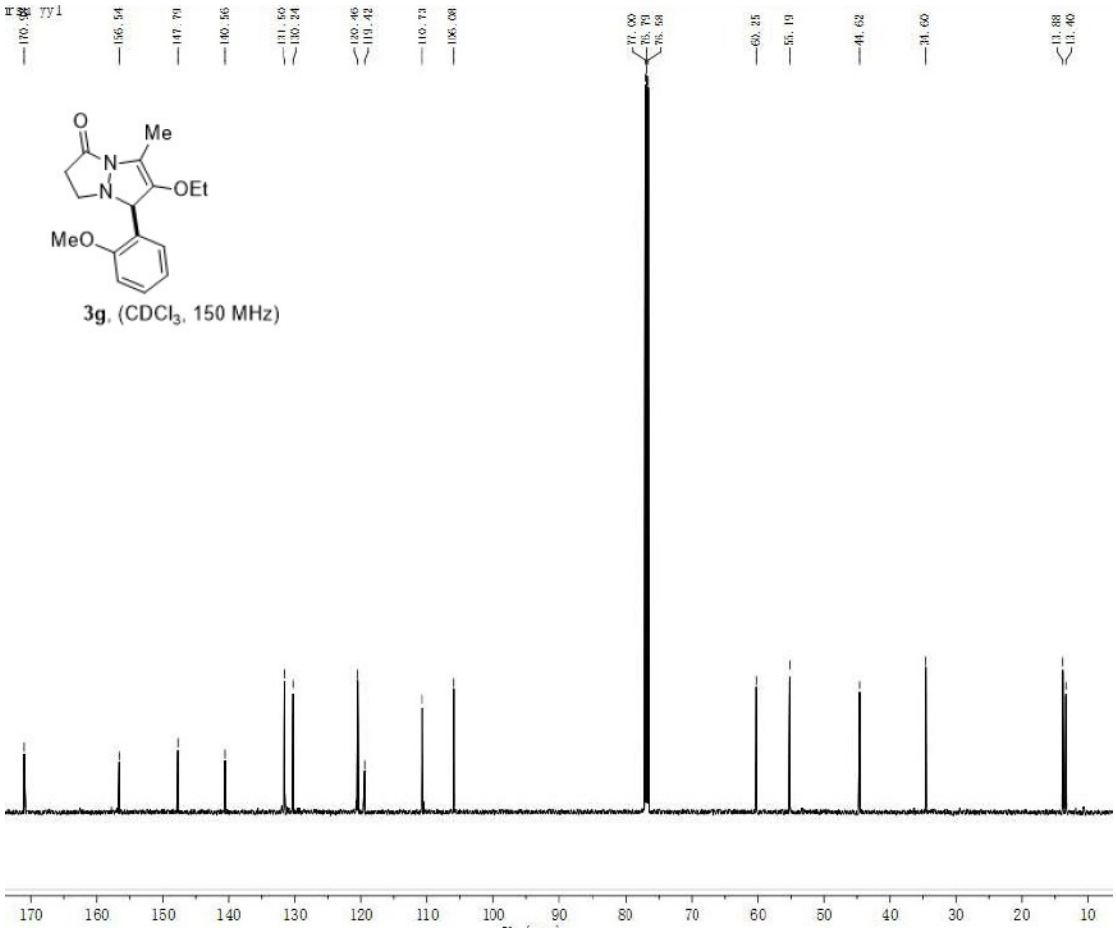
3f, ($CDCl_3$, 600 MHz)



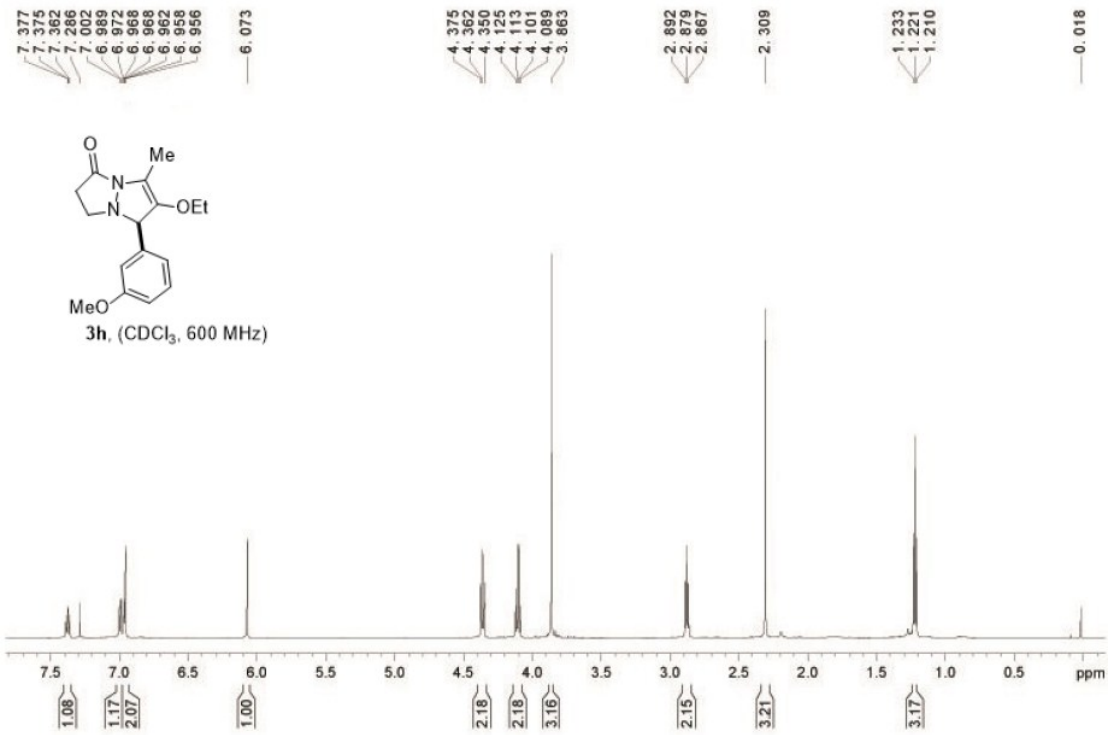
3f, ($CDCl_3$, 150 MHz)



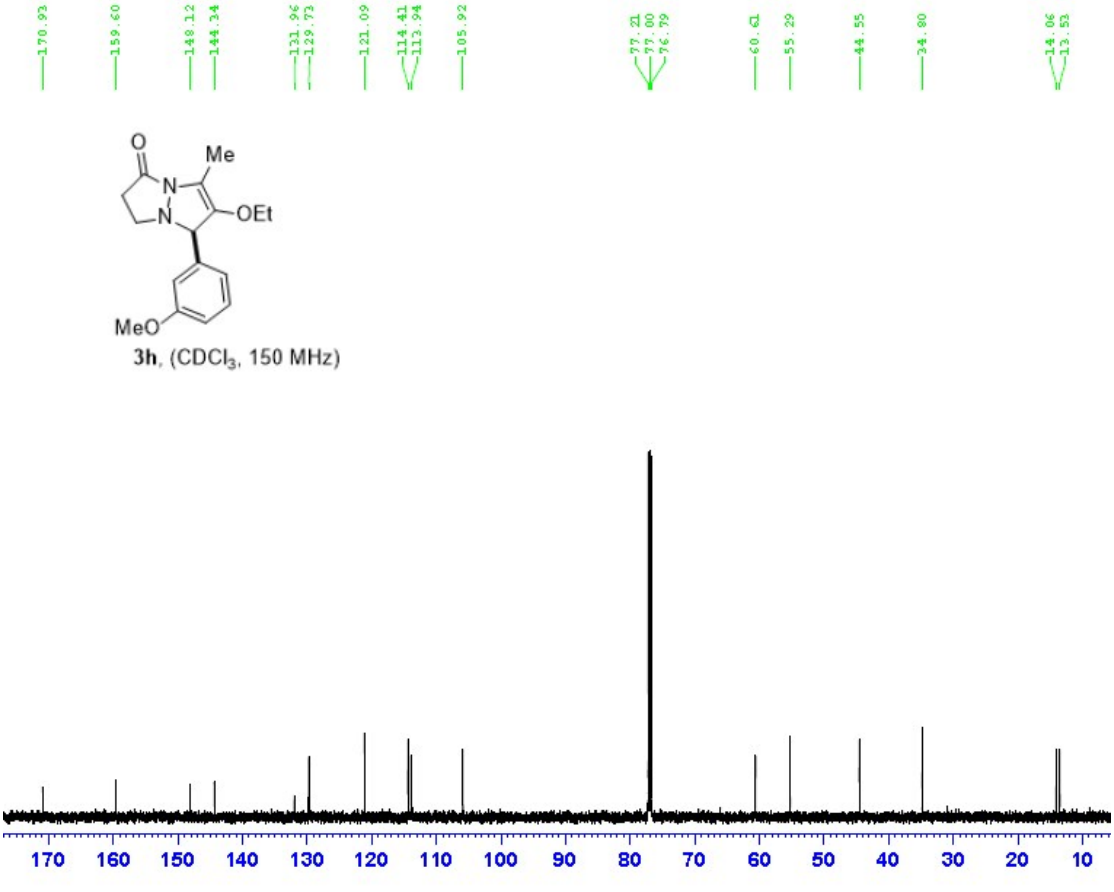
3g, ($CDCl_3$, 600 MHz)



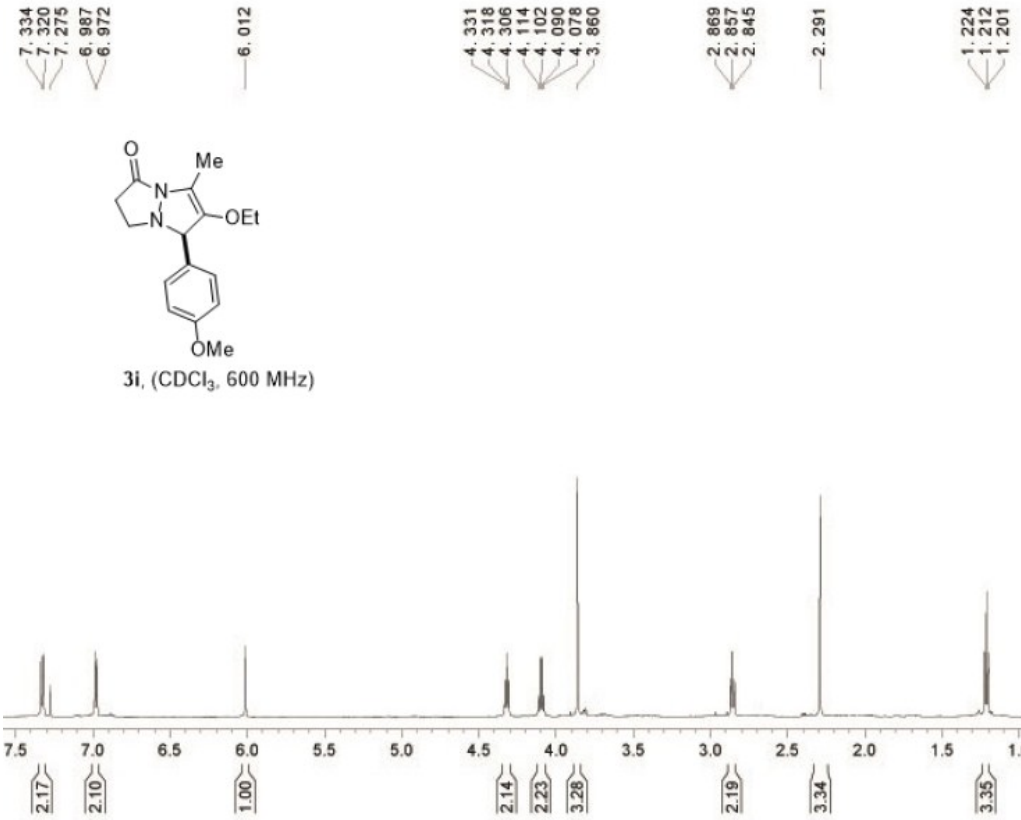
3g, ($CDCl_3$, 150 MHz)



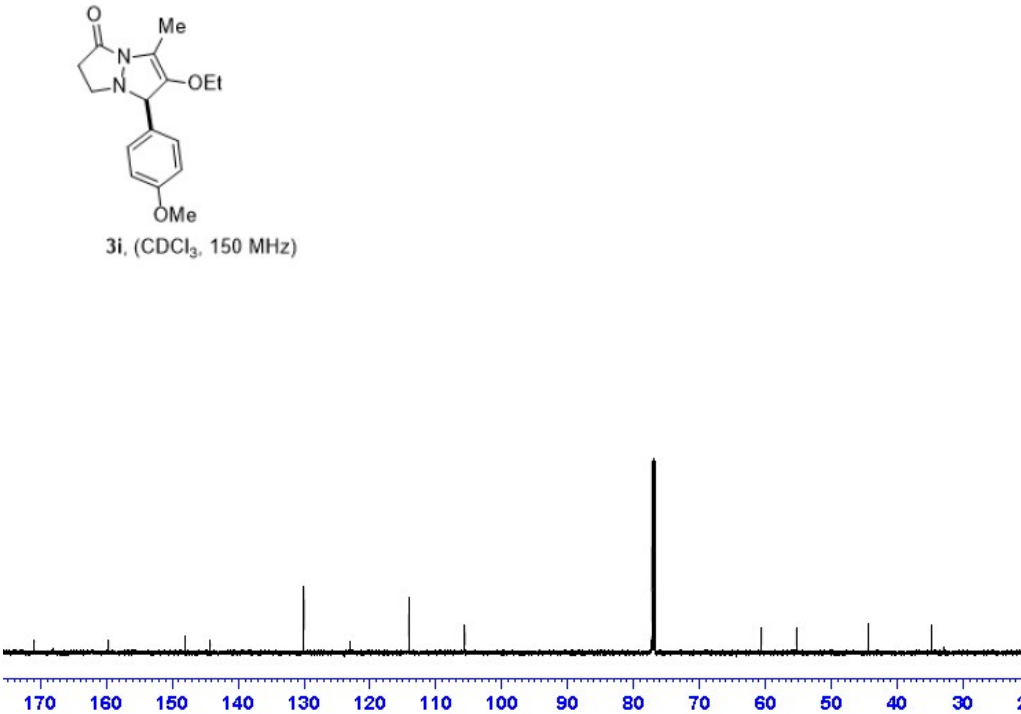
3h, ($CDCl_3$, 600 MHz)



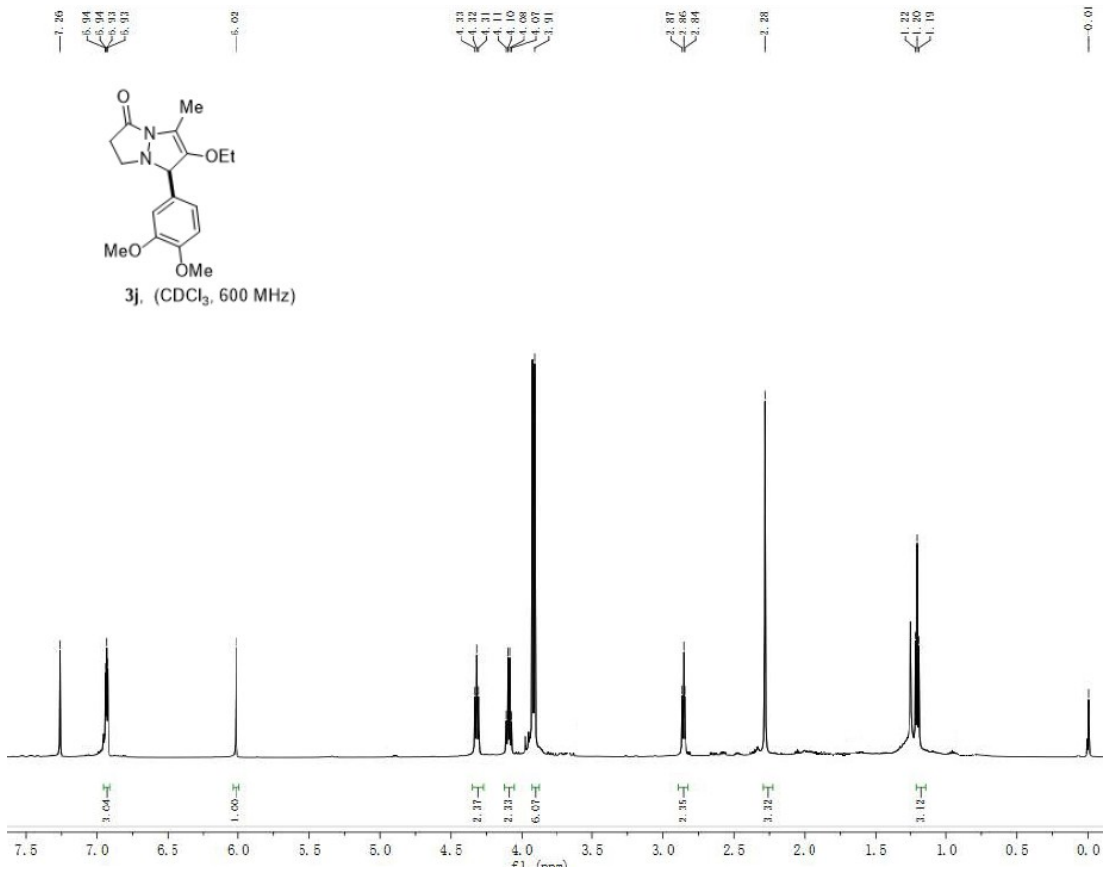
3h, ($CDCl_3$, 150 MHz)



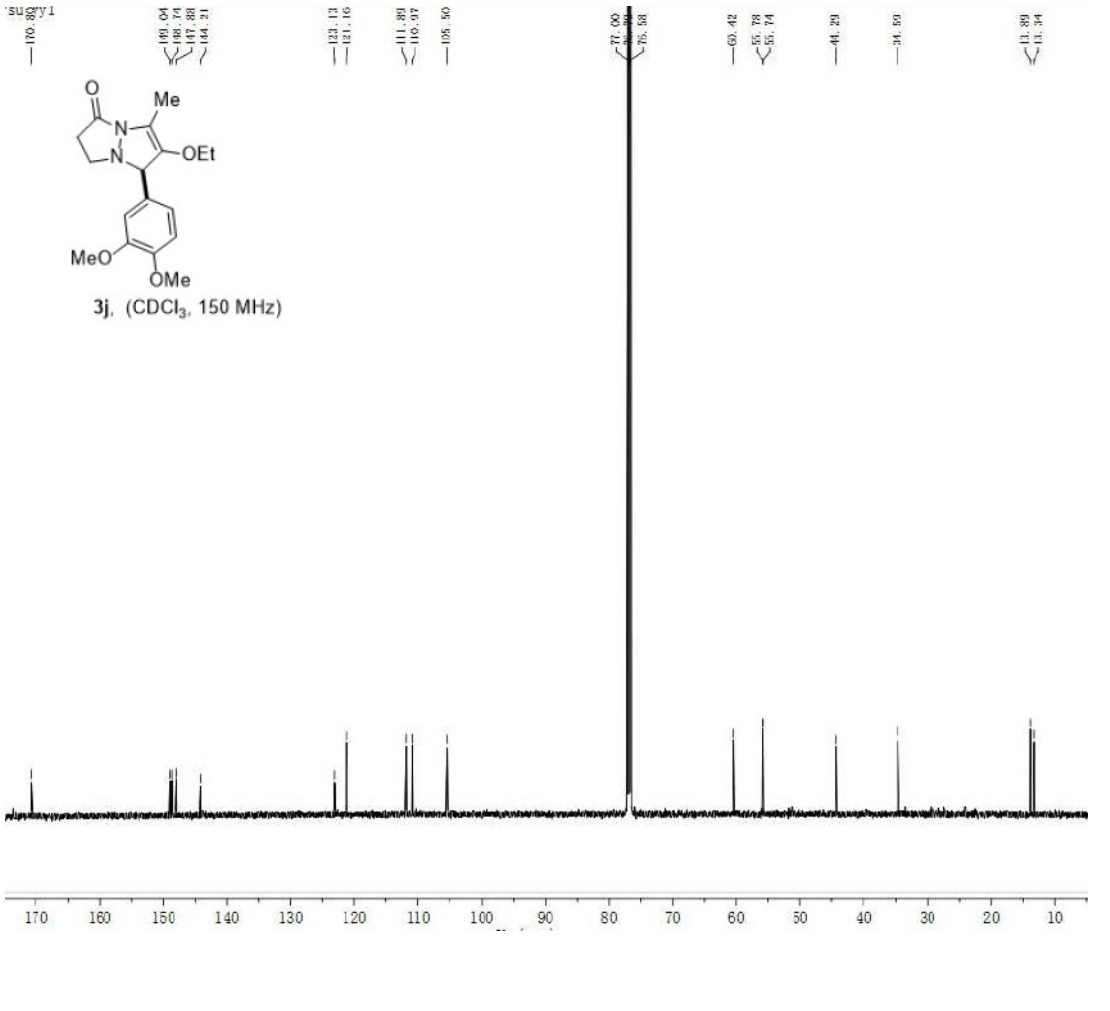
3i, ($CDCl_3$, 600 MHz)



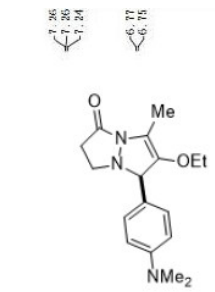
3i, ($CDCl_3$, 150 MHz)



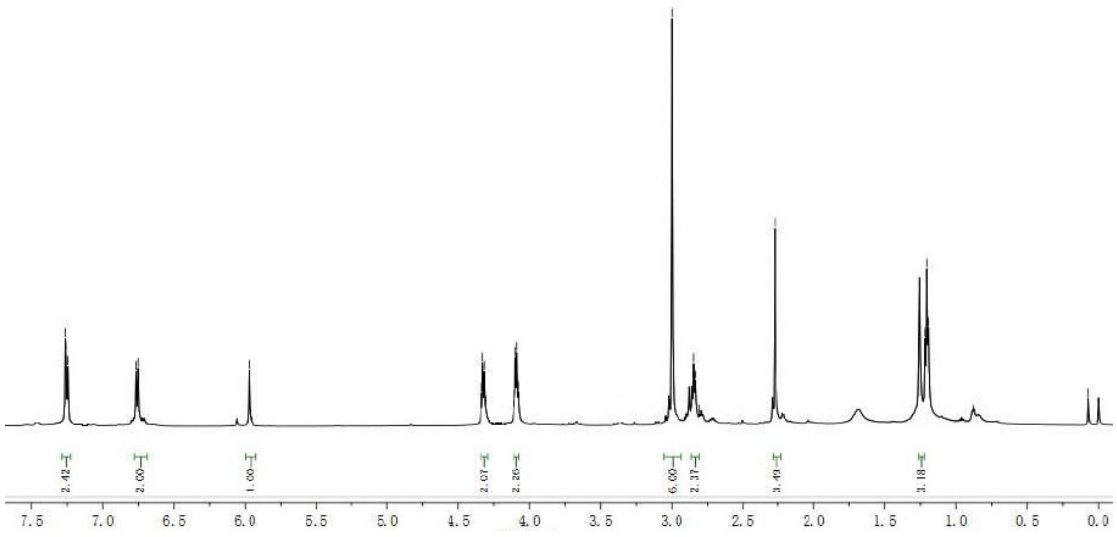
3j, ($CDCl_3$, 600 MHz)

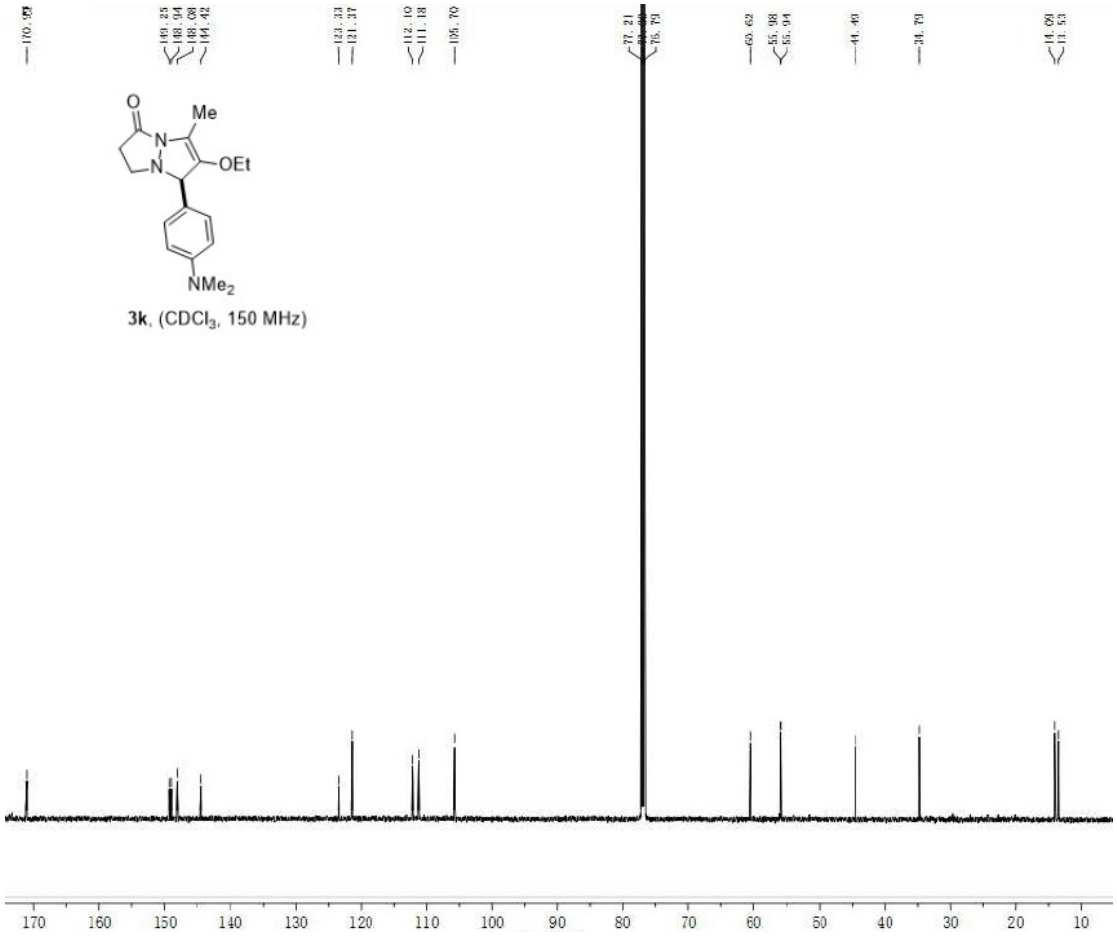


3j, ($CDCl_3$, 150 MHz)

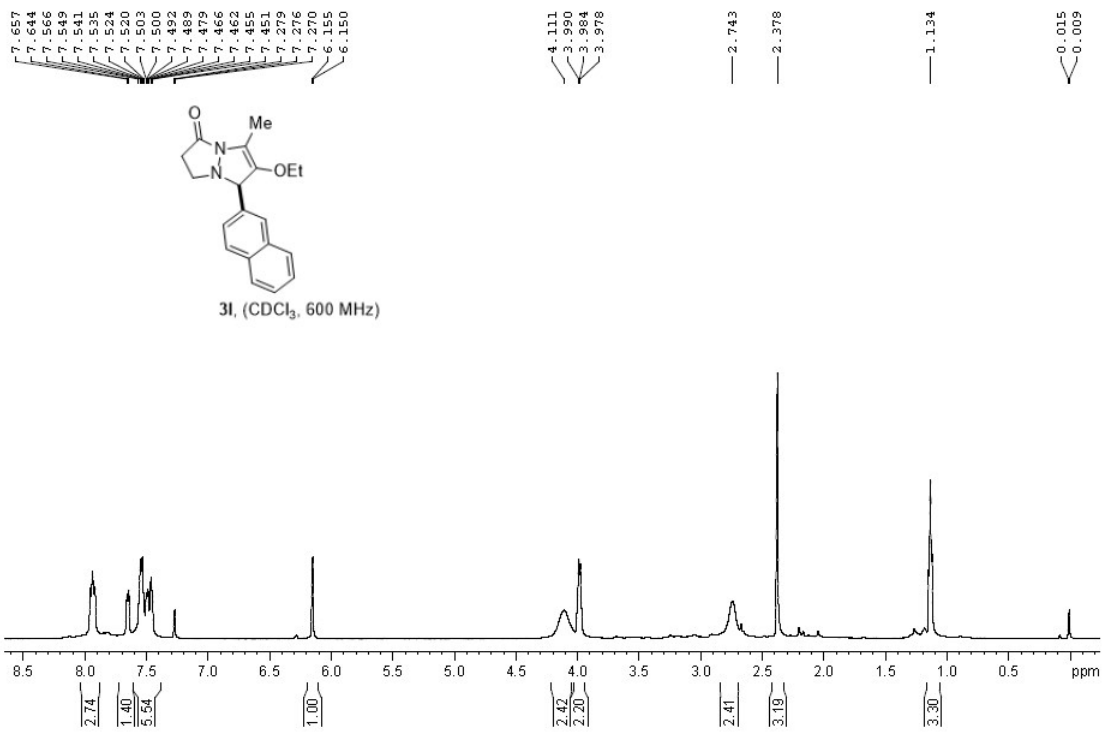


3k, ($CDCl_3$, 600 MHz)

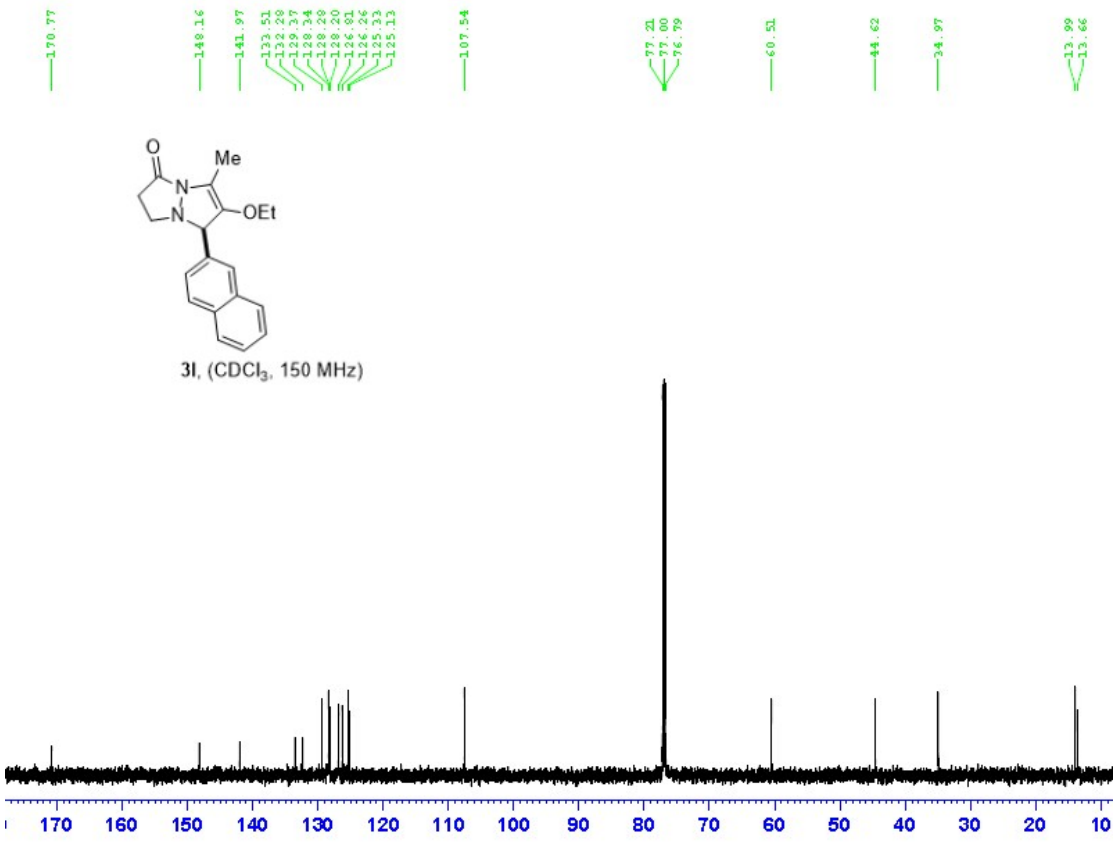




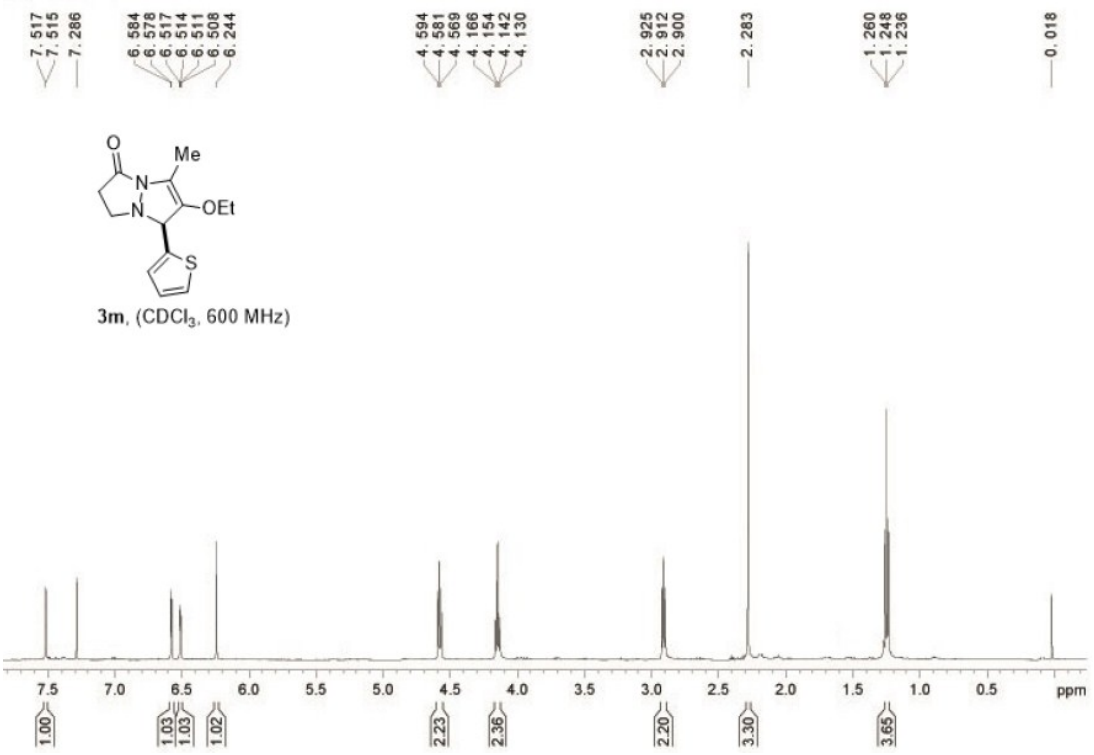
3k, ($CDCl_3$, 150 MHz)



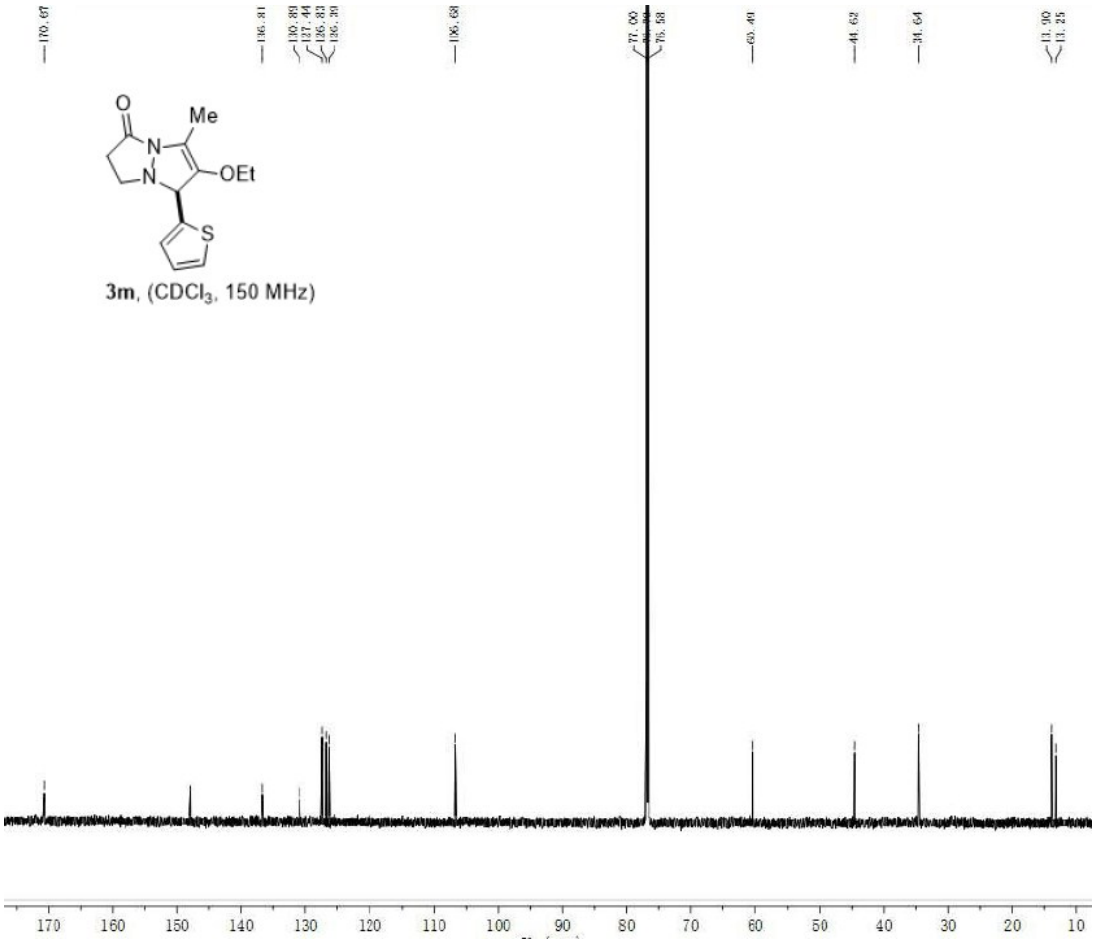
3l, ($CDCl_3$, 600 MHz)



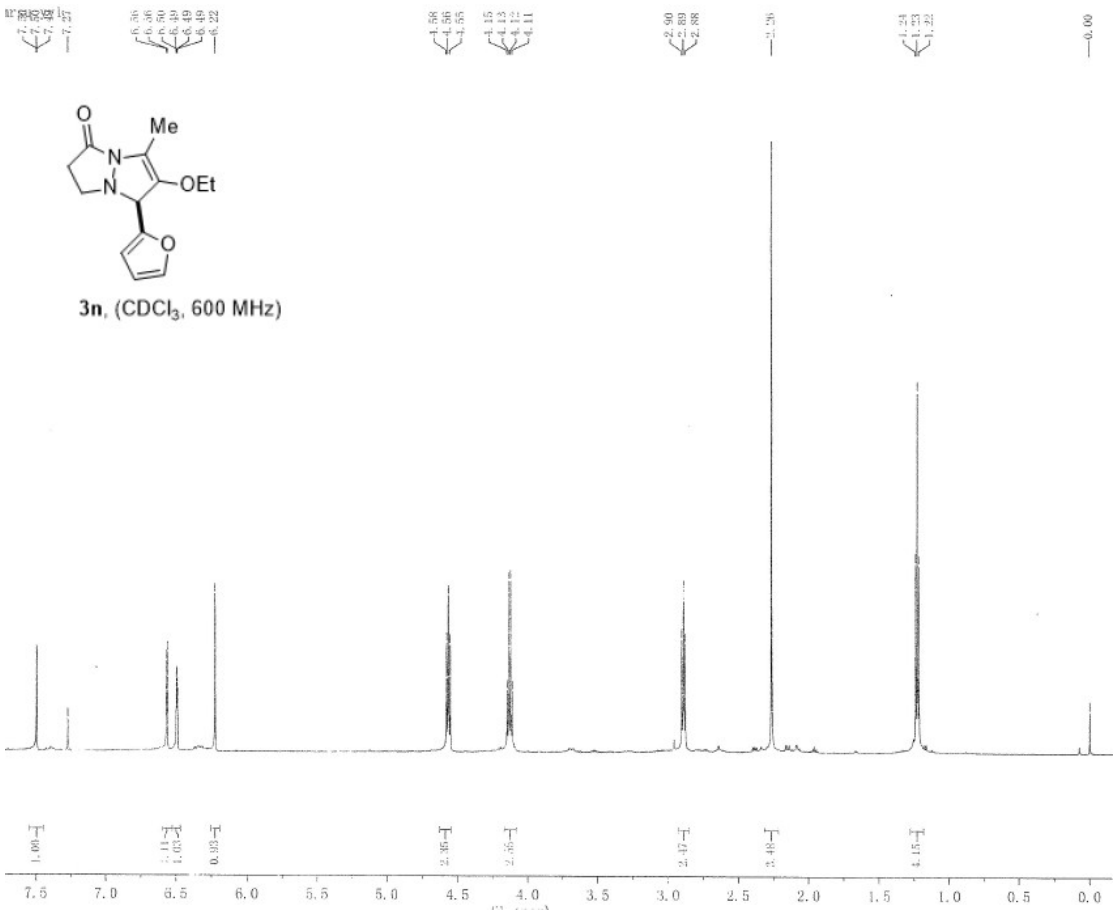
3l, ($CDCl_3$, 150 MHz)



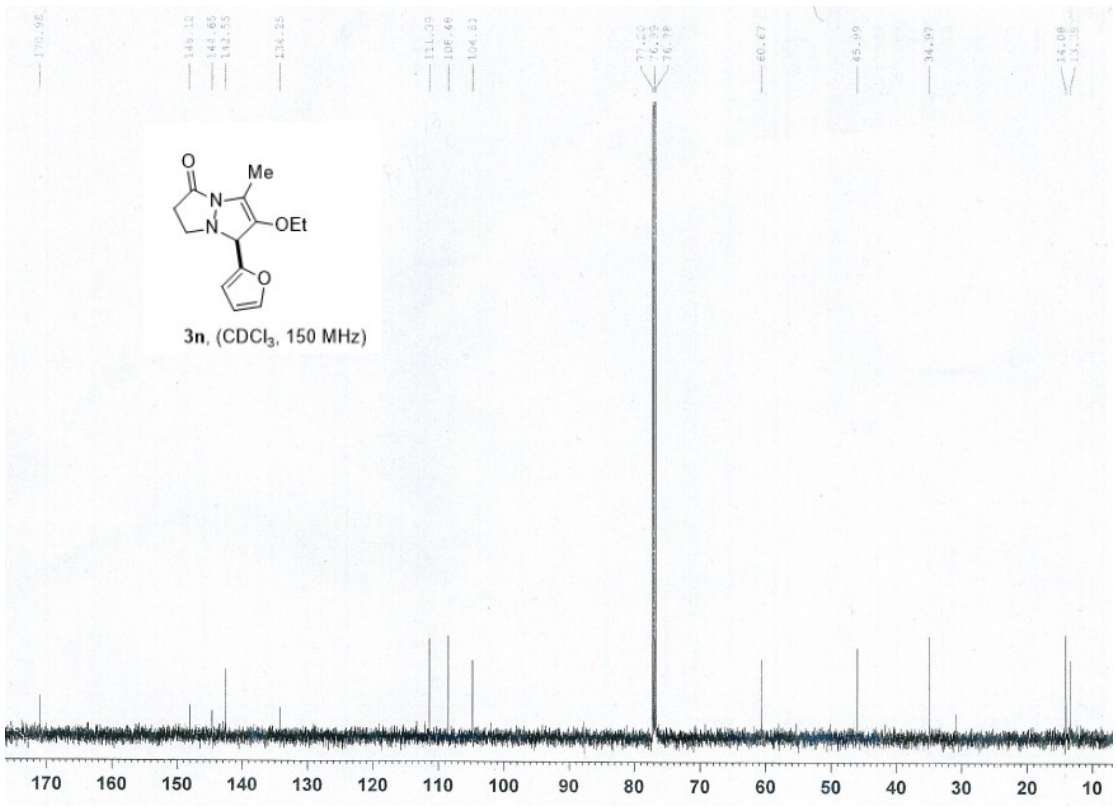
3m, ($CDCl_3$, 600 MHz)



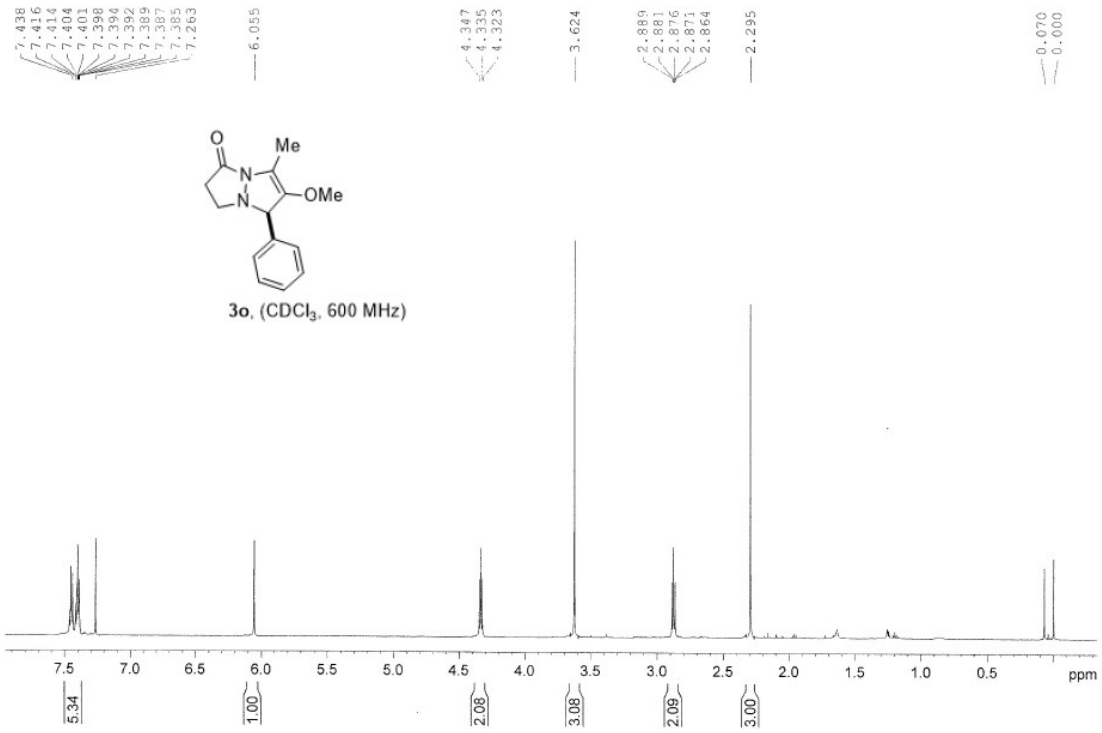
3m, ($CDCl_3$, 150 MHz)



3n, ($CDCl_3$, 600 MHz)



3n, ($CDCl_3$, 150 MHz)


7.438
7.416
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7.404
7.401
7.398
7.394
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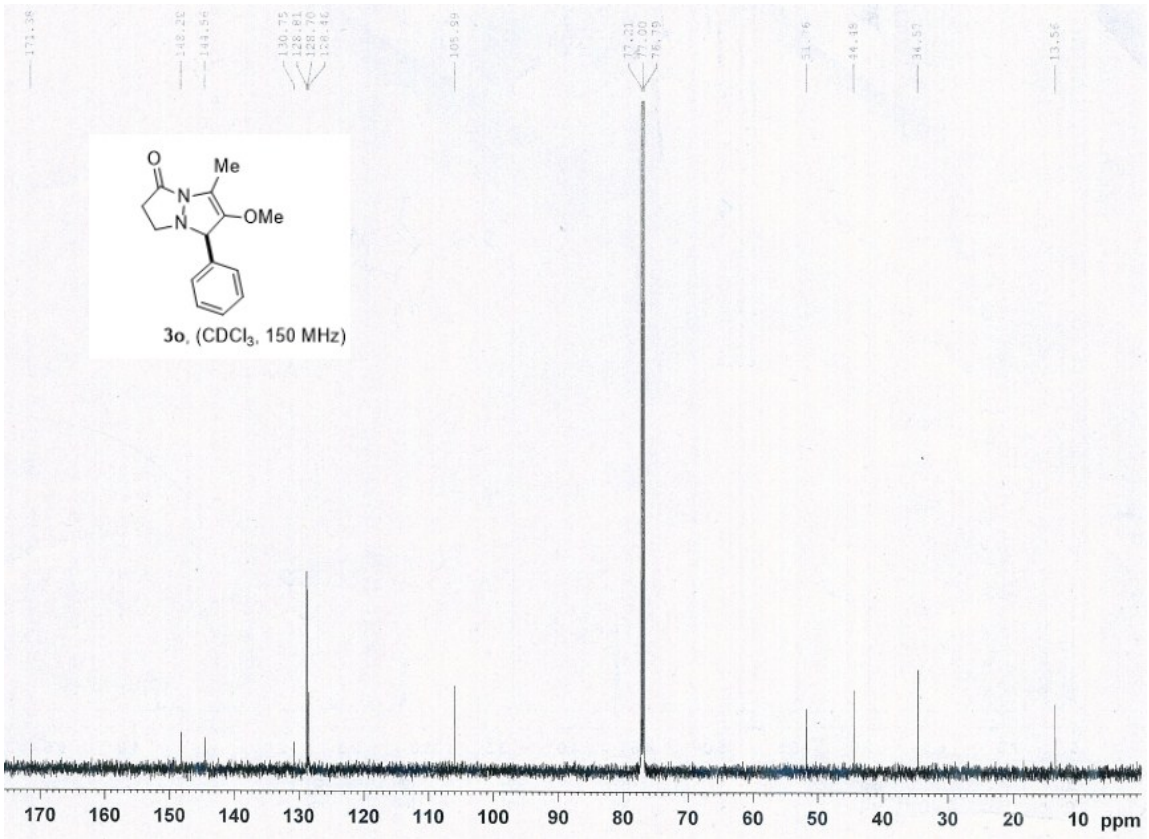
7.389
7.387
7.385
7.263
6.055
4.347
4.335
4.323
3.624
2.889
2.881
2.876
2.871
2.864
2.295
0.070
0.000
O
N
N
Me
OMe
3o, (CDCl3, 600 MHz)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
5.34
1.00
2.08
3.08
2.09
3.00


O
N
N
Me
OMe
3o, (CDCl3, 150 MHz)
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150
140
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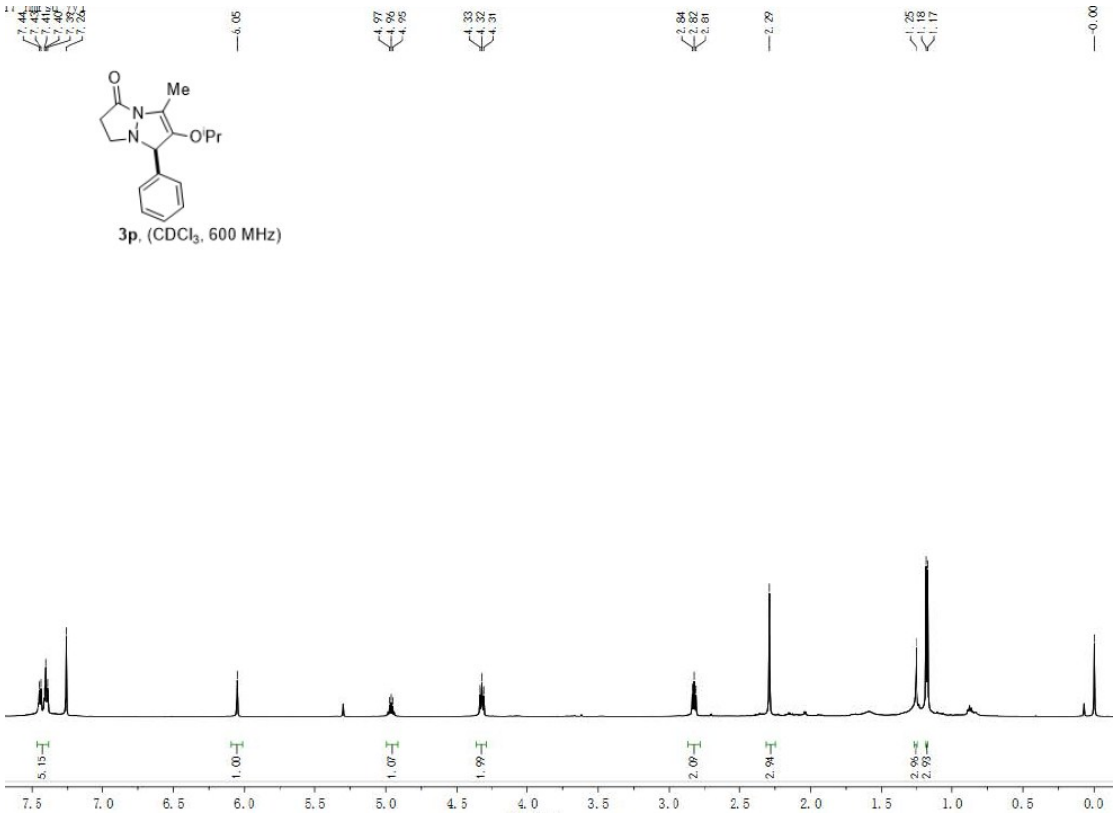
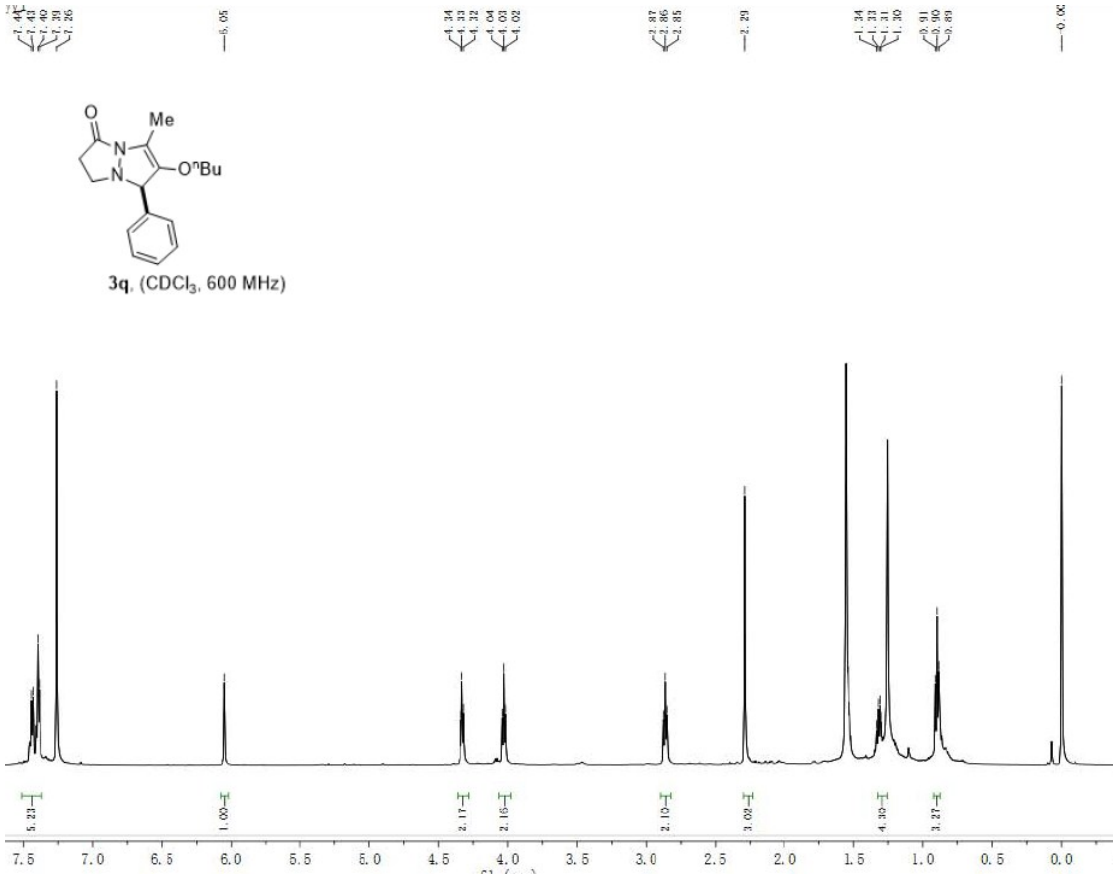
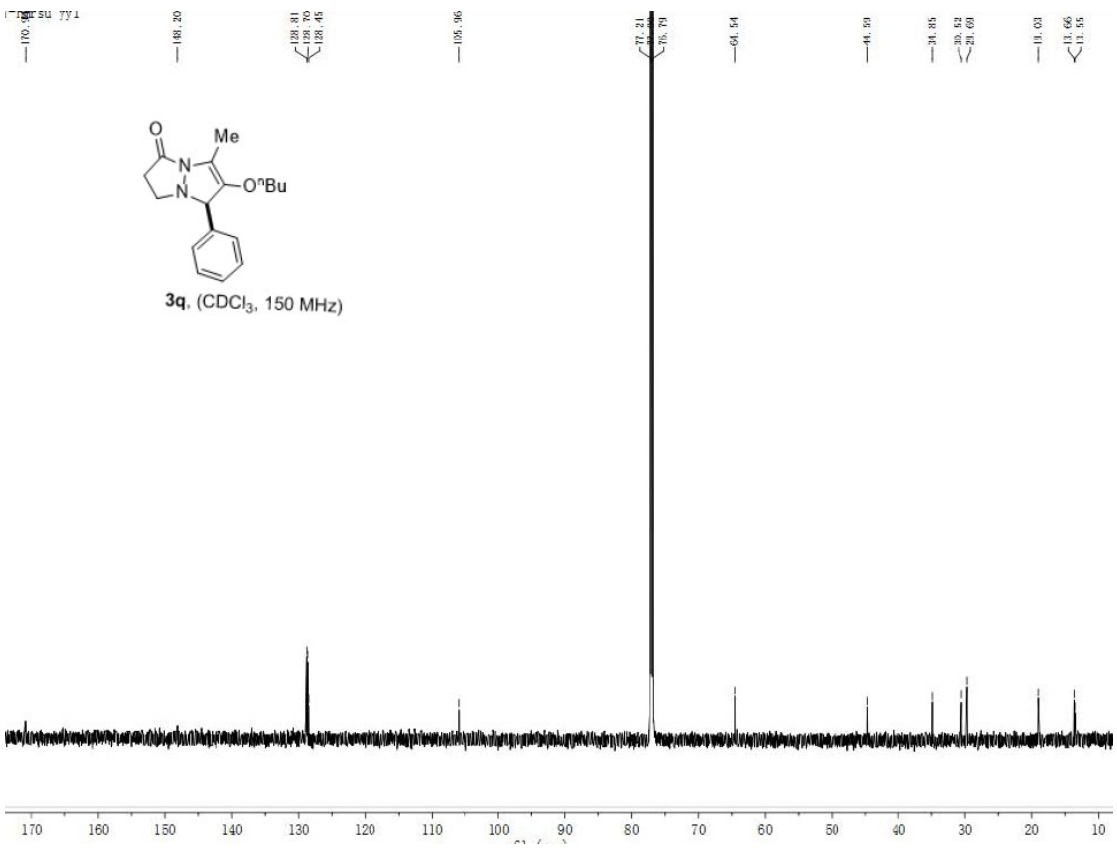
120
110
100
90
80
70
60
50
40
30
20
10
ppm

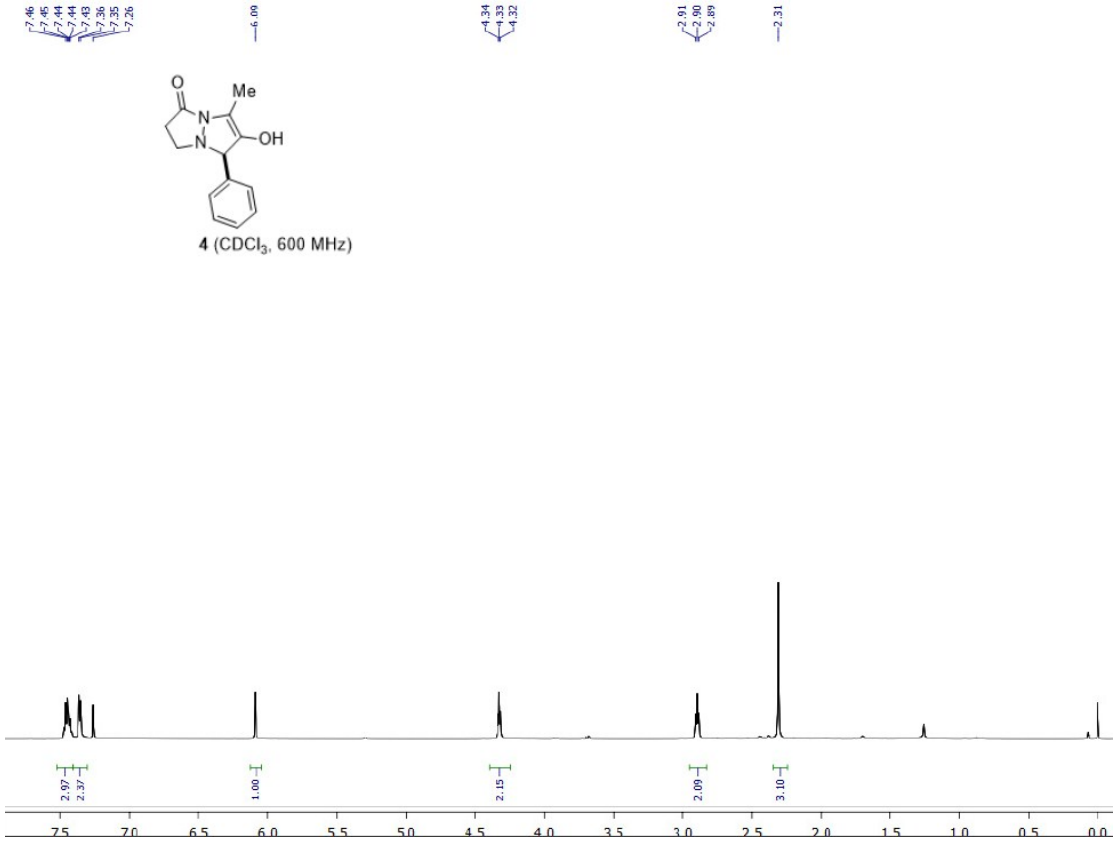


3p, ($CDCl_3$, 600 MHz)

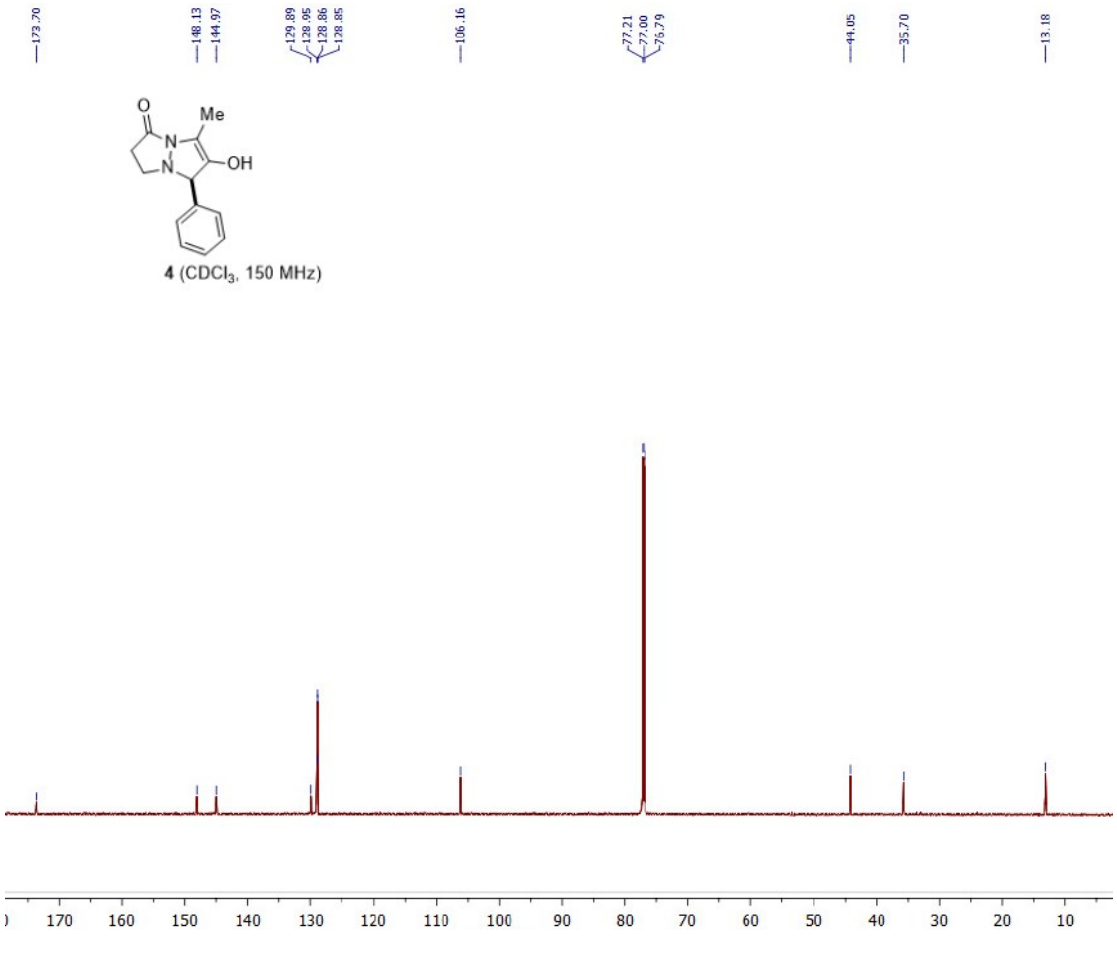
3p, ($CDCl_3$, 150 MHz)


Me
OnBu
3q, (CDCl3, 600 MHz)

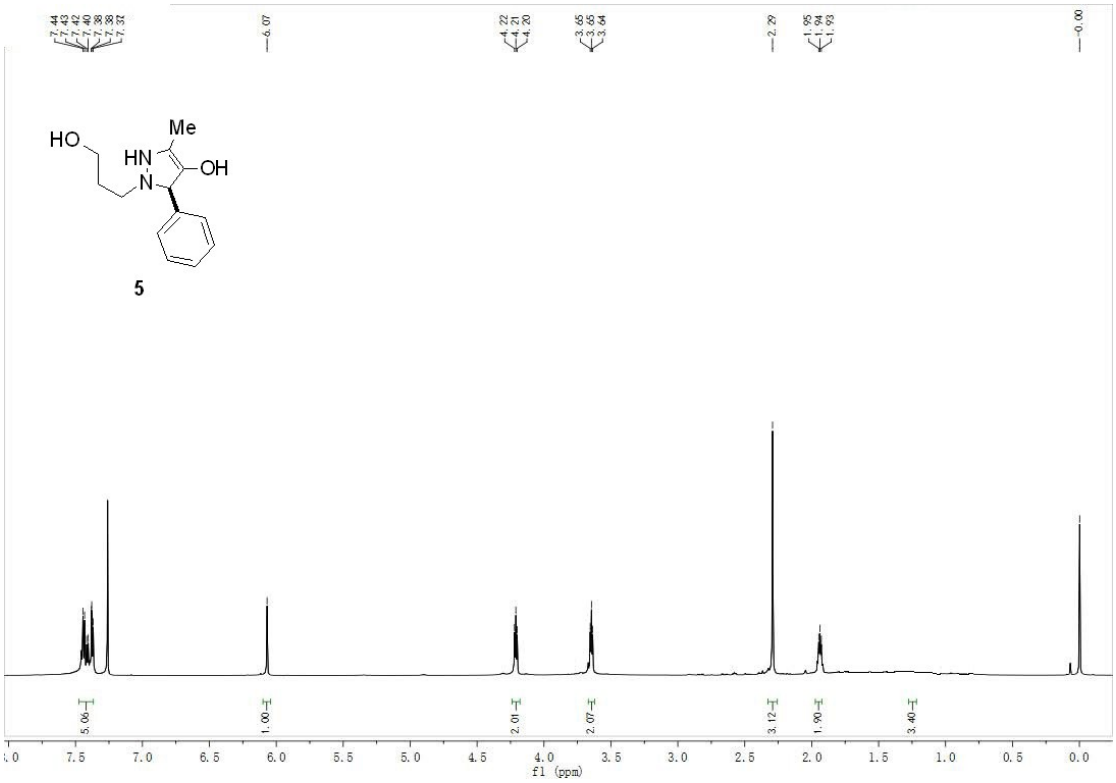

Me
OnBu
3q, (CDCl3, 150 MHz)

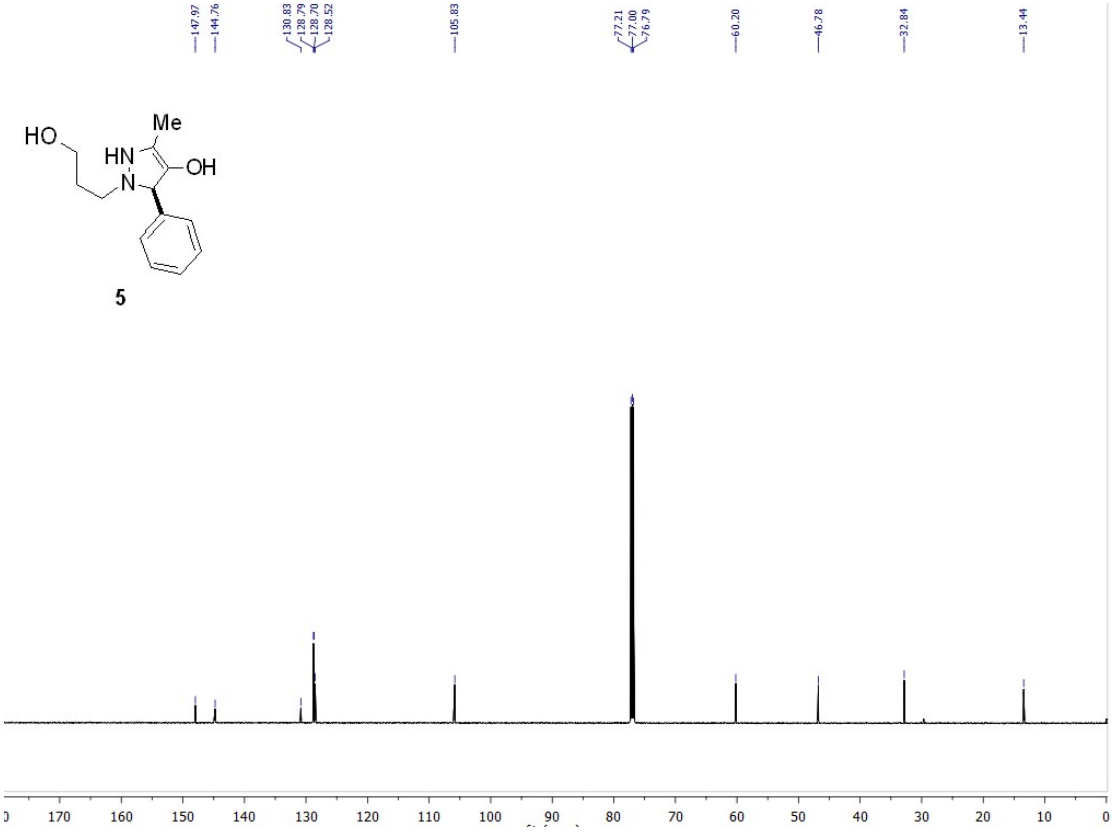


4 ($CDCl_3$, 600 MHz)



4 ($CDCl_3$, 150 MHz)


7.44
7.43
7.42
7.40
7.38
7.37
6.07
4.22
4.21
4.20
3.65
3.65
3.64
2.29
1.95
1.94
1.93
0.00
HO
Me
HN
N
OH
5
5.06
1.00
2.01
2.07
3.12
1.90
3.40
f1 (ppm)


147.97
144.76
130.83
128.79
128.70
128.52
105.83
77.21
77.00
76.79
60.20
46.78
32.84
13.44
HO
Me
HN
N
OH
5