SUPPORTING INFORMATION

Synthesis of spiro-4*H*-pyrazole-oxindoles and fused 1*H*-pyrazoles *via* divergent, thermally induced tandem cyclization/migration of alkyne-tethered diazo compounds

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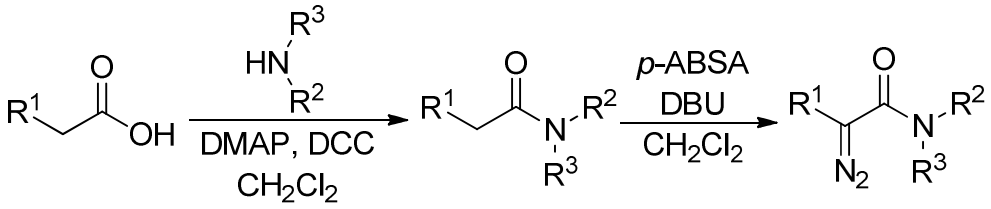
Table of Contents

General Information

DMF (*N,N*-dimethylformamide) and other solvents were dried by standard methods over CaH_2. Flash column chromatography was performed using silica gel (300-400 mesh). Analytical thin-layer chromatography was performed using glass plates pre-coated with 200-300 mesh silica gel impregnated with a fluorescent indicator (254 nm). ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$/DMSO-d_6 on a 400 MHz spectrometer. Chemical shifts are reported in ppm with the solvent signals as reference, and coupling constants (*J*) are given in Hertz. The peak information is described as: s = singlet, br = broad, d = doublet, t = triplet, q = quartet, m = multiplet, comp = composite. High-resolution mass spectra (HRMS) were recorded on a commercial apparatus (CI+ Source).

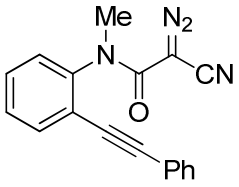
General Procedure for the Preparation of Diazoamides 1a-1h, 1j and 3a-3j.



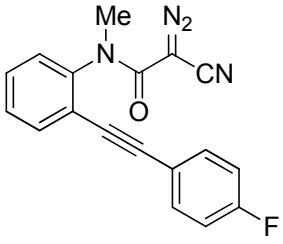
Synthesis of **S2**: To a solution of secondary amine (2.0 mmol), **S1** (2.2 mmol) and 4-dimethylaminopyridine (DMAP, 24.5 mg, 0.2 mmol) in CH_2Cl_2 (10.0 mL), dicyclohexylcarbodiimide (DCC, 494.8 mg, 2.4 mmol) was added within 5 min at 0 ℃. The reaction mixture was stirred overnight and the reaction temperature was slowly warmed to room temperature. After filtering through Celite and the filtrate was washed with saturated aqueous $NaHCO_3$ (10.0 mL) and brine (10.0 mL) in sequence, and dried over anhydrous Na_2SO_4. Then the solvent was evaporated under vacuum after filtration, the obtained product **S2** was directly used for the next step without further purification.

Synthesis of **1:** The above obtained **S2** and *p*-ABSA (4-acetamidobenzenesulfonyl azide, 576.6 mg, 2.4 mmol) was dissolved in DCM (10.0 mL), and DBU

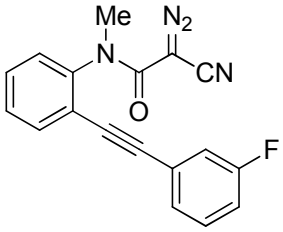
(1,8-Diazabicyclo[5.4.0]undec-7-ene, 456.7 mg, 3.0 mmol) in DCM (5.0 mL) was added slowly at 0 ℃. The reaction mixture was stirred at 0℃ for 0.5 h. Upon completion (monitored by TLC), the solvent was evaporated under vacuum after filtering through Celite, and the resulting residues was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 3:1) to give the pure diazoamides **1** (40% – 80% yields based on secondary amine).



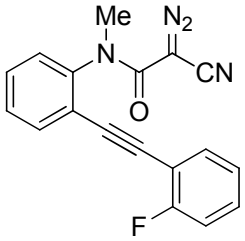
2-Cyano-2-diazo-*N*-methyl-N-(2-(phenylethynyl)phenyl)acetamide (**1a**). 366.4 mg, 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.66 – 7.62 (m, 1H), 7.54 – 7.50 (comp, 2H), 7.48 – 7.41 (comp, 2H), 7.38 – 7.32 (comp, 4H), 3.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 159.9, 142.5, 133.3, 131.8, 130.0, 129.8, 129.1, 129.0, 128.6, 123.5, 122.4, 107.4, 95.5, 84.6, 38.4. HRMS (TOF MS CI$^+$) calculated for $C_{18}H_{13}N_4O^+$ $[M+H]^+$: 301.1089, found 301.1084.



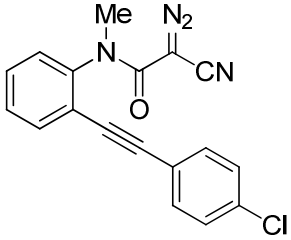
2-Cyano-2-diazo-*N*-(2-((4-fluorophenyl)ethynyl)phenyl)-*N*-methylacetamide (**1b**). 439.2 mg, 69% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.64 – 7.56 (m, 1H), 7.52 – 7.39 (m, 4H), 7.35 – 7.28 (m, 1H), 7.08 – 7.00 (m, 2H), 3.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 162.8 (d, J = 250.8 Hz), 159.8, 142.3, 133.6 (d, J = 8.5 Hz), 133.0, 130.0, 129.6, 128.8, 123.1, 118.3 (d, J = 3.5 Hz), 115.8 (d, J = 22.2 Hz), 107.2, 94.2, 84.3 (d, J = 1.4 Hz), 38.2. HRMS (TOF MS CI$^+$) calculated for $C_{18}H_{12}FN_4O^+$ $[M+H]^+$: 319.0995, found 319.0986.



2-Cyano-2-diazo-*N*-(2-((3-fluorophenyl)ethynyl)phenyl)-*N*-methylacetamide (**1c**). 496.6 mg, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.56 (d, *J* = 7.5 Hz, 1H), 7.69 – 7.61 (m, 1H), 7.51 – 7.45 (comp, 2H), 7.38 – 7.27 (comp, 3H), 7.26 – 7.19 (m, 1H), 7.13 – 7.05 (m, 1H), 3.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 162.4 (d, *J* = 247.2 Hz), 159.9, 142.6, 133.4, 130.4, 130.2 (d, *J* = 8.6 Hz), 129.8, 129.0, 127.7 (d, *J* = 3.1 Hz), 124.1 (d, *J* = 9.5 Hz), 122.9, 118.4 (d, *J* = 23.0 Hz), 116.4 (d, *J* = 21.2 Hz), 107.3, 94.0 (d, *J* = 3.4 Hz), 85.4, 38.3. HRMS (TOF MS CI$^+$) calculated for $C_{18}H_{12}FN_4O^+$ $[M+H]^+$: 319.0995, found 319.0998.

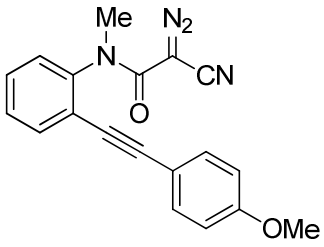


2-Cyano-2-diazo-*N*-(2-((2-fluorophenyl)ethynyl)phenyl)-*N*-methylacetamide (**1d**). 362.9 mg, 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.70 – 7.64 (m, 1H), 7.52 – 7.43 (comp, 3H), 7.38 – 7.31 (comp, 2H), 7.17 – 7.08 (comp, 2H), 3.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 162.8 (d, *J* = 252.6 Hz), 159.6, 142.6, 133.6, 131.0, 130.9, 130.4, 129.9, 129.1, 124.3 (d, *J* = 3.7 Hz), 123.2, 115.8 (d, *J* = 20.7 Hz), 111.2 (d, *J* = 15.6 Hz), 107.5, 89.6 (d, *J* = 3.3 Hz), 88.7, 46.4. HRMS (TOF MS CI$^+$) calculated for $C_{18}H_{12}FN_4O^+$ $[M+H]^+$: 319.0995, found 319.0998.

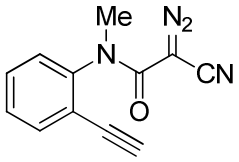


***N*-(2-((4-Chlorophenyl)ethynyl)phenyl)-2-cyano-2-diazo-*N*-**

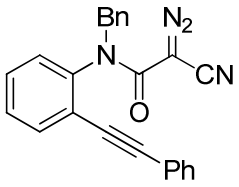
methylacetamide (**1e**). 488.8 mg, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.65 – 7.58 (m, 1H), 7.49 – 7.40 (comp, 4H), 7.38 – 7.28 (comp, 3H), 3.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 159.9, 142.5, 135.1, 133.2, 132.9, 130.2, 129.7, 129.0, 128.9, 123.0, 120.8, 107.3, 94.2, 85.5, 38.3. HRMS (TOF MS CI$^+$) calculated for $C_{18}H_{12}ClN_4O^+$ $[M+H]^+$: 335.06700, found 335.0698.



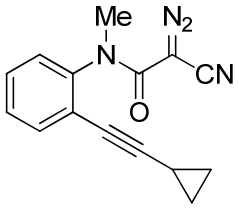
2-Cyano-2-diazo-*N*-(2-((4-methoxyphenyl)ethynyl) phenyl)-*N*-methylacetamide (**1f**). 284.1 mg, 43% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.63 – 7.56 (m, 1H), 7.50 – 7.36 (comp, 4H), 7.34 – 7.27 (m, 1H), 6.92 – 6.85 (comp, 2H), 3.83 (s, 3H), 3.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 160.3, 160.0, 142.3, 133.4, 133.0, 129.8, 129.6, 129.0, 123.9, 114.5, 114.3, 107.5, 95.8, 83.6, 55.5, 38.4. HRMS (TOF MS CI$^+$) calculated for $C_{19}H_{15}N_4O_2^+$ $[M+H]^+$: 331.1195, found 331.1198.



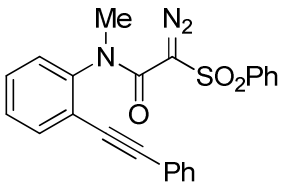
2-Cyano-2-diazo-*N*-(2-ethynylphenyl)-*N*-methylacetamide (**1g**). 242.1 mg, 54% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.61 – 7.57 (m, 1H), 7.46 – 7.42 (comp, 2H), 7.31 – 7.28 (m, 1H), 3.35 (s, 4H), 1.02 (t, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 159.4, 142.9, 134.1, 130.5, 129.7, 128.9, 122.2, 107.1, 83.2, 78.8, 38.1. HRMS (TOF MS CI$^+$) calculated for $C_{12}H_9N_4O^+$ $[M+H]^+$: 225.0776, found 225.0778.



***N*-Benzyl-2-cyano-2-diazo-*N*-(2-(phenylethynyl)phenyl)acetamide** (**1h**). 308.7 mg, 41% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.64 – 7.56 (m, 1H), 7.54 – 7.46 (comp, 2H), 7.45 – 7.35 (comp, 4H), 7.31 – 7.22 (comp, 6H), 7.02 – 6.95 (m, 1H), 5.02 (dd, J = 307.8, 14.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 160.0, 140.6, 136.0, 133.3, 131.8, 130.1, 129.8, 129.5, 129.5, 129.1, 128.6, 128.5, 128.0, 124.0, 122.4, 107.3, 95.6, 85.0, 54.2. HRMS (TOF MS CI$^+$) calculated for $C_{24}H_{17}N_4O^+$ $[M+H]^+$: 377.1402, found 377.1398.

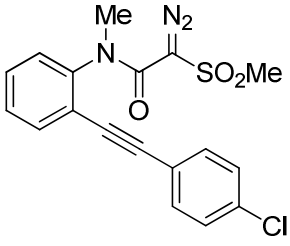


2-Cyano-*N*-(2-(cyclopropylethynyl)phenyl)-2-diazo-*N*-methylacetamide (**1j**). 354.1 mg, 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.45 – 7.38 (m, 1H), 7.36 – 7.27 (m, 2H), 7.23 – 7.17 (m, 1H), 3.26 (s, 3H), 1.46 – 1.34 (m, 1H), 0.94 – 0.82 (m, 2H), 0.81 – 0.68 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 159.5, 142.3, 133.1, 129.4, 128.9, 128.5, 123.8, 107.2, 100.0, 70.9, 37.9, 9.1, 8.8, 0.2. HRMS (TOF MS CI$^+$) calculated for $C_{15}H_{13}N_4O^+$ $[M+H]^+$: 265.1089, found 265.1084.

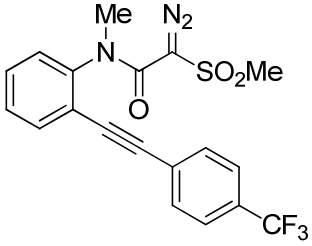


2-Diazo-*N*-methyl-*N*-(2-(phenylethynyl)phenyl)-2-(phenylsulfonyl)acetamide (**3a**). 407.2 mg, 49% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.08 – 7.98 (comp, 2H), 7.62 – 7.58 (m, 1H), 7.50 – 7.47 (m, 1H), 7.45 – 7.37 (comp, 6H), 7.35 – 7.27 (comp, 4H), 3.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 158.6, 143.0, 142.2, 133.6, 133.6, 131.9, 130.2, 129.6, 129.1, 128.9, 128.8, 128.5,

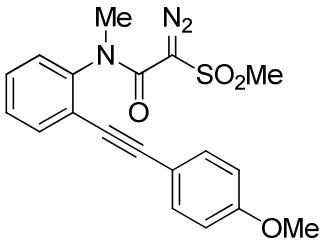
128.3, 123.2, 122.2, 96.2, 84.1, 37.5. HRMS (TOF MS CI$^+$) calculated for $C_{23}H_{18}N_3O_3S^+$ $[M+H]^+$: 416.1063, found 416.1069.



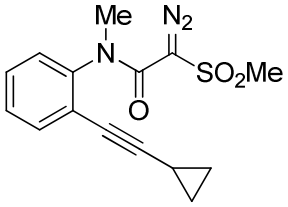
***N*-(2-((4-chlorophenyl)ethynyl)phenyl)-2-diazo-*N*-methyl-2-(methylsulfonyl)acetamide** (**3b**). 395.6 mg, 51% yield. ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm) 7.74 – 7.69 (m, 1H), 7.61 – 7.54 (comp, 4H), 7.53 – 7.46 (comp, 3H), 3.39 (s, 3H), 3.29 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm) 158.5, 142.7, 134.1, 133.3, 133.1, 130.9, 129.5, 128.9, 128.8, 121.4, 120.5, 93.7, 85.4, 73.3(C(N_2)), 44.7, 37.15. HRMS (TOF MS CI$^+$) calculated for $C_{18}H_{15}ClN_3O_3S^+$ $[M+H]^+$: 388.0523, found 388.0525.



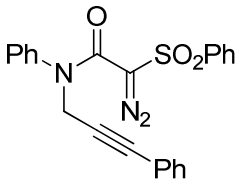
2-Diazo-*N*-methyl-2-(methylsulfonyl)-*N*-(2-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)acetamide (**3c**). 539.4 mg, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.99 – 7.70 (m, 1H), 7.67 – 7.59 (comp, 4H), 7.49 – 7.41 (comp, 2H), 7.39 – 7.32 (m, 1H), 3.39 (s, 3H), 3.33 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 159.4, 143.1, 133.8, 132.2, 130.9, 130.2, 129.6, 128.6, 126.0, 125.5 (q, J = 3.7 Hz), 123.8 (q, J = 179.2, 93.2 Hz), 122.4, 94.4, 86.2, 45.4, 37.7. HRMS (TOF MS CI$^+$) calculated for $C_{19}H_{15}F_3N_3O_3S$+ $[M+H]^+$: 422.0786, found 422.0781.



2-Diazo-*N*-(2-((4-methoxyphenyl)ethynyl)phenyl)-*N*-methyl-2-(methylsulfonyl)acetamide (**3d**). 306.7 mg, 40% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.65 – 7.56 (m, 1H), 7.55 – 7.47 (comp, 2H), 7.45 – 7.38 (comp, 2H), 7.37 – 7.32 (m, 1H), 6.95 – 6.86 (comp, 2H), 3.81 (s, 3H), 3.41 (s, 3H), 3.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 160.1, 159.0, 142.2, 133.2, 132.9, 129.6, 129.3, 128.4, 123.1, 114.0, 113.9, 96.0, 82.9, 55.1, 44.9, 37.2. HRMS (TOF MS CI$^+$) calculated for $C_{19}H_{18}N_3O_4S^+$ $[M+H]^+$: 384.1018, found 384.1013.

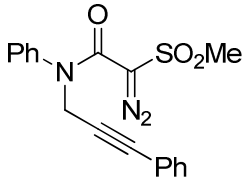


***N*-(2-(Cyclopropylethynyl)phenyl)-2-diazo-*N*-methyl-2-(methylsulfonyl)acetamide** (**3e**). 285.6 mg, 45% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.50 – 7.44 (m, 1H), 7.40 – 7.33 (comp, 2H), 7.32 – 7.26 (m, 1H), 3.39 (s, 3H), 3.31 (s, 3H), 1.54 – 1.41 (m, 1H), 0.97 – 0.81 (comp, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 158.7, 142.5, 133.2, 129.1, 129.0, 128.2, 123.4, 100.7, 70.4, 44.9, 36.7, 8.7, 0.1. HRMS (TOF MS CI$^+$) calculated for $C_{15}H_{16}N_3O_3S^+$ $[M+H]^+$: 318.0912, found 318.0907.

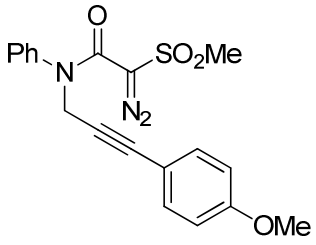


2-Diazo-2-(methylsulfonyl)-*N*-phenyl-*N*-(3-phenylprop-2-yn-1-yl)acetamide (**3f**). 506.8 mg, 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.12 – 8.04 (comp, 2H), 7.67 – 7.62 (m, 1H), 7.59 – 7.54 (comp, 2H), 7.49 – 7.45 (comp,

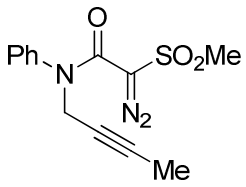
3H), 7.39 – 7.34 (comp, 2H), 7.32 – 7.25 (comp, 5H), 4.68 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 158.0, 142.2, 139.8, 133.9, 131.8, 130.4, 129.7, 129.0, 128.6, 128.4, 128.4, 128.3, 122.5, 85.1, 83.5, 40.2. HRMS (TOF MS CI$^+$) calculated for $C_{23}H_{18}N_3O_3S^+$ $[M+H]^+$: 416.1069, found 416.1068.



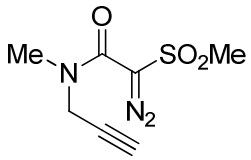
2-Diazo-2-(methylsulfonyl)-*N*-phenyl-*N*-(3-phenylprop-2-yn-1-yl)acetamide (**3g**). 450.0 mg, 58% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.54 – 7.41 (comp, 5H), 7.40 – 7.34 (comp, 2H), 7.33 – 7.26 (comp, 3H), 4.78 (s, 2H), 3.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 158.4, 139.5, 131.7, 130.3, 129.8, 128.6, 128.4, 128.3, 122.3, 85.0, 83.4, 45.3, 40.1. HRMS (TOF MS CI$^+$) calculated for $C_{18}H_{16}N_3O_3S^+$ $[M+H]^+$: 354.0912, found 354.0902.



2-Diazo-*N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-2-(methylsulfonyl)-*N*-phenylacetamide (**3h**). 306.4 mg, 47% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.50 – 7.42 (comp, 5H), 7.32 – 7.26 (comp, 2H), 6.87 – 6.78 (comp, 2H), 4.76 (s, 2H), 3.80 (s, 3H), 3.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 159.8, 158.5, 139.7, 133.2, 130.3, 129.8, 128.6, 114.5, 114.0, 85.0, 82.0, 55.3, 45.4, 40.2.. HRMS (TOF MS CI$^+$) calculated for $C_{19}H_{18}N_3O_4S^+$ $[M+H]^+$: 384.1018, found 384.1010.

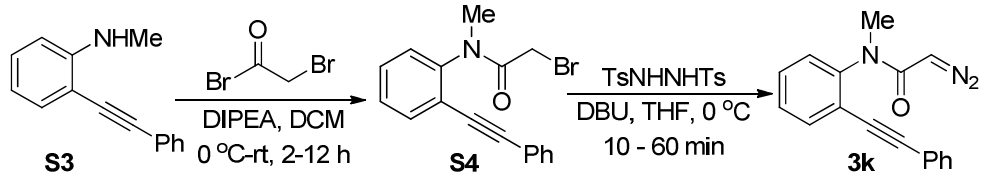


***N*-(but-2-yn-1-yl)-2-diazo-2-(methylsulfonyl)-*N*-phenylacetamide** (**3i**). 413.3 mg, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.46 – 7.40 (comp, 3H), 7.35 (comp , 2H), 4.51 – 4.47 (m, 2H), 3.34 (s, 3H), 2.26 (t, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 158.4, 139.5, 130.3, 129.7, 128.1, 78.0, 73.2, 45.3, 39.4. HRMS (TOF MS CI$^+$) calculated for $C_{13}H_{14}N_3O_3S^+$ $[M+H]^+$: 292.0756, found 292.0750.



2-Diazo-*N*-methyl-2-(methylsulfonyl)-*N*-(prop-2-yn-1-yl)acetamide (**3j**). 357.3 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 4.15 (s, 2H), 3.38 (s, 3H), 3.07 (s, 3H), 2.32 (t, J = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 159.4, 76.8, 73.6, 45.4, 38.5, 35.2. HRMS (TOF MS CI$^+$) calculated for $C_7H_{10}N_3O_3S^+$ $[M+H]^+$: 216.0443, found 216.0440.

Procedure for the Preparation of Diazoamide 3k.



Synthesis of **3k** **:** To a 50-mL oven-dried flask with a magnetic stirring bar, *N*-methyl-2-(phenylethynyl)aniline (**S3**, 788.0 mg, 3.8 mmol) and DIPEA (*N*,*N*-Diisopropylethylamine, 0.66 mL, 3.8 mmol) were dissolved in dry DCM (20.0 mL), bromoacetyl bromide (0.34 mL, 3.8 mmol) was added slowly at 0 °C, then the mixture was stirred at room temperature for 12 h. After the reaction was completed, the reaction was quenched by saturated brine (30.0 mL), and the reaction mixture was

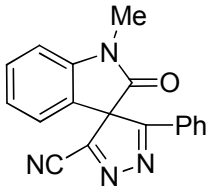
extracted with DCM (20.0 mL × 3). The combined organic phase was dried with anhydrous Na_2SO_4. Then the solvent was evaporated under vacuum, and the obtained product **S4** was directly used for the next step without further purification.

To a 50-mL oven-dried flask with a magnetic stirring bar, the above obtained **S4** and *N,N′*-ditosylhydrazine (3.2 g，9.5 mmol) were dissolved in THF (20.0 mL), DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene, 2.7 mL, 18.0 mmol) was added slowly over 5 min at 0 ℃, and the reaction mixture was stirred for 60 minutes until no more gas was generated from the reaction mixture. The reaction was quenched by saturated $NaHCO_3$ solution (30.0 mL), and the reaction mixture was extracted with ethyl acetate (20.0 mL × 3), The combined organic phase was dried with anhydrous Na_2SO_4. The crude product was purified by column chromatography (silica gel, petroleum ether : ethyl acetate = 10:1 to 2:1) to give the 2-Diazo-*N*-methyl-*N*-(2-(phenylethynyl) phenyl)acetamide **3k**. 554.5 mg, 53% yield (based on **S3**). ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.62 – 7.58 (m, 1H), 7.53 – 7.48 (comp, 2H), 7.39 – 7.32 (comp, 5H), 7.25 – 7.22 (m, 1H), 4.41 (s, 1H), 3.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 166.0, 144.1, 133.2, 131.8, 129.7, 128.9, 128.7, 128.5, 128.4, 123.0, 122.5, 95.2, 85.0, 47.4, 36.3. HRMS (TOF MS CI$^+$) calculated for $C_{17}H_{14}N_3O^+$ $[M+H]^+$: 276.1137, found 276.1133.

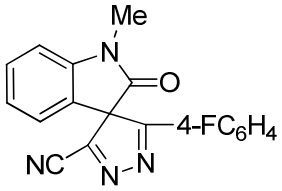
Thermally Induced Reaction for the Preparation of 2 and 4:

To a 10-mL oven-dried vial with a magnetic stirring bar, diazo compound **1** or **3** (0.2 mmol) was dissolved in *N*, *N*-dimethylformamide (DMF, 2.0 mL). After the reaction mixture stirred at 80 ℃ overnight, the reaction was quenched with water (10 mL) and extracted with CH_2Cl_2 (5.0 mL × 3). The combined organic phase was washed with saturated brine (10 mL), and dried over anhydrous sodium sulfate. Then the solvent was removed under vacuo to give a white solid. The solid product was further purified by recrystallization (solvents: petroleum ether/ethyl acetate /CH_2Cl_2 = 1: 2: 5,) to give the pure products **2** or **4** in high yields (**2i** was purified by column chromatography;

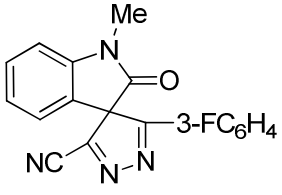
and the yields of **4g** and **4j** were given without recrystallization).



1-Methyl-2-oxo-5'-phenylspiro[indoline-3,4'-pyrazole]-3'-carbonitrile (**2a**). White solid; m.p. 221.0 – 224.0 ℃. 52.9 mg, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.57 – 7.53 (comp, 3H), 7.48 – 7.45 (m, 1H), 7.35 – 7.31 (comp, 2H), 7.16 – 7.11 (comp, 2H), 6.87 (d, *J* = 7.5 Hz, 1H), 3.43 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$) (δ, ppm) 173.1, 164.4, 150.3, 144.3, 133.5, 131.9, 129.5, 128.7, 127.3, 125.0, 124.5, 119.2, 110.7, 110.1, 28.1. HRMS (TOF MS CI$^+$) calculated for $C_{24}H_{17}N_2O_2^+$ $[M+H]^+$: 301.1089, found 301.1084.

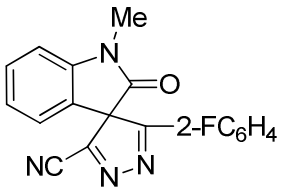


5'-(4-Fluorophenyl)-1-methyl-2-oxospiro[indoline-3,4'-pyrazole]-3'-carbonitrile (**2b**). White solid; m.p. 218.0 – 221.0 ℃. 57.3 mg, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.61 – 7.52 (comp, 3H), 7.19 – 7.12 (comp, 2H), 7.07 – 6.99 (comp, 2H), 6.91 – 6.86 (m, 1H), 3.43 (s, 3H); ^{13}C NMR (150MHz, $CDCl_3$) (δ, ppm) 172.0, 165.9 (d, *J* = 257.2 Hz), 164.3, 150.2, 144.3, 132.1, 131.1 (d, *J* = 9.2 Hz), 125.1, 124.6, 123.8 (d, *J* = 3.1 Hz), 119.1, 117.0 (d, *J* = 22.3 Hz), 110.7, 110.1, 28.2. ^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -103.2. HRMS (TOF MS CI$^+$) calculated for $C_{18}H_{12}FN_4O^+$ $[M+H]^+$: 319.0995, found 319.0986.

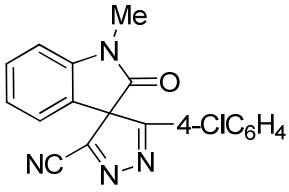


5'-(3-Fluorophenyl)-1-methyl-2-oxospiro[indoline-3,4'-pyrazole]-3'-carbonitrile (**2c**). White solid; m.p. 223.0 – 226.0 ℃. 56.7 mg, 89% yield. ^{1}H

NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.56 (t, *J* = 7.8 Hz, 1H), 7.35 – 7.28 (comp, 2H), 7.25 – 7.14 (comp, 4H), 6.88 (d, *J* = 7.6 Hz, 1H), 3.43 (s, 3H); ^{13}C NMR (150MHz, $CDCl_3$) (δ, ppm) 172.0 (d, *J* = 2.8 Hz), 164.0, 162.9 (d, *J* = 248.9 Hz), 150.7, 144.3, 132.2, 131.3 (d, *J* = 8.1 Hz), 129.2 (d, *J* = 8.1 Hz), 125.1, 124.5, 124.4 (d, *J* = 2.8 Hz), 120.6 (d, J = 21.4 Hz), 118.7, 115.4 (d, J = 23.7 Hz), 110.8, 109.9, 28.2. ^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -110.1. HRMS (TOF MS CI^+) calculated for $C_{18}H_{12}FN_4O^+$ $[M+H]^+$: 319.0995, found 319.0998.

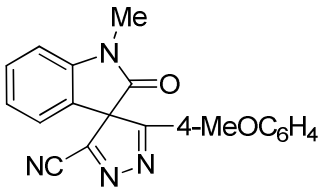


5'-(2-Fluorophenyl)-1-methyl-2-oxospiro[indoline-3,4'-pyrazole]-3'-carbonitrile (**2d**). White solid; m.p. 185.0 – 189.0 ℃. 57.9 mg, 91% yield. ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.39 – 8.28 (m, 1H), 7.57 – 7.44 (comp, 2H), 7.31 – 7.22 (m, 1H), 7.11 – 7.03 (comp, 2H), 7.01 – 6.93 (m, 1H), 6.76 (d, *J* = 7.6 Hz, 1H), 3.40 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$) (δ, ppm) 170.1 (d, *J* = 4.1 Hz), 164.0 (d, *J* = 2.7 Hz), 161.2 (d, *J* = 256.0 Hz), 150.8, 145.6, 135.5 (d, *J* = 9.3 Hz), 131.6, 131.2 (d, *J* = 2.4 Hz), 125.4 (d, *J* = 3.2 Hz), 124.1 (d, *J* = 68.4 Hz), 117.2 (d, *J* = 1.8 Hz), 116.8 (d, *J* = 22.5 Hz), 115.7 (d, *J* = 12.2 Hz), 110.1, 109.9, 53.6, 28.0. ^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -111.4. HRMS (TOF MS CI^+) calculated for $C_{18}H_{12}FN_4O^+$ $[M+H]^+$: 319.0995, found 319.0998.

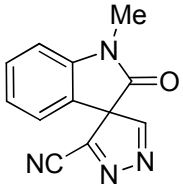


3'-(4-Chlorophenyl)-1-methyl-2-oxospiro[indoline-3,4'-pyrazole]-5'-carbonitrile (**2e**). White solid; m.p. 159.0 – 162.0 ℃. 58.2 mg, 87% yield. ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm) 7.66 – 7.59 (m, 1H), 7.59 – 7.43 (comp, 5H), 7.27 – 7.13 (comp, 2H), 3.42 (s, 3H); ^{13}C NMR (100MHz, DMSO-d_6) (δ, ppm) 172.0, 163.5, 150.1, 144.1, 138.8, 132.1, 130.2, 129.9, 125.3, 125.0, 124.8, 118.0, 111.8,

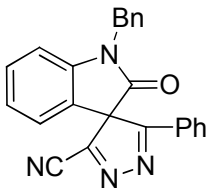
110.2, 77.0, 28.2. HRMS (TOF MS CI$^+$) calculated for $C_{18}H_{12}ClN_4O^+$ $[M+H]^+$: 335.0700, found 335.0698.



3'-(4-Chlorophenyl)-1-methyl-2-oxospiro[indoline-3,4'-pyrazole]-5'-carbonitrile (**2f**). White solid; m.p. 268.0 – 271.0 ℃. 56.2 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.56 – 7.47 (comp, 3H), 7.16 – 7.10 (comp, 2H), 6.90 – 6.79 (comp, 3H), 3.80 (s, 3H), 3.43 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$) (δ, ppm) 172.6, 164.9, 164.0, 149.1, 144.3, 131.8, 130.9, 124.9, 124.6, 120.1, 120.0, 115.0, 110.5, 110.4, 55.7, 28.1. HRMS (TOF MS CI$^+$) calculated for $C_{19}H_{15}N_4O_2^+$ $[M+H]^+$: 331.1195, found 331.1190.

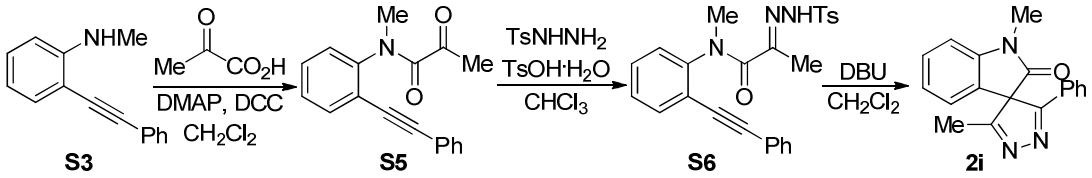


1-Methyl-2-oxospiro[indoline-3,4'-pyrazole]-3'-carbonitrile (**2g**). White solid; m.p. 234.0 – 237.0 ℃. 42.6 mg, 95% yield. ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm) 7.92 (d, J = 7.6 Hz, 1H), 7.83 – 7.72 (m, 1H), 7.57 (d, J = 8.5 Hz, 1H), 7.38 – 7.30 (m, 1H), 6.85 (s, 1H), 3.59 (s, 3H); ^{13}C NMR (100MHz, DMSO-d_6) (δ, ppm) 158.7, 147.6, 139.6, 134.1, 124.8, 122.7, 116.0, 115.4, 115.1, 92.7, 38.9, 29.7. HRMS (TOF MS CI$^+$) calculated for $C_{12}H_9N_4O^+$ $[M+H]^+$: 225.0776, found 225.0787.



1-Benzyl-2-oxo-5'-phenylspiro[indoline-3,4'-pyrazole]-3'-carbonitrile (**2h**). White solid; m.p. 196.0 – 199.0 ℃. 49.6 mg, 66% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.52 – 7.48 (comp, 2H), 7.47 – 7.40 (comp, 2H), 7.40 – 7.34

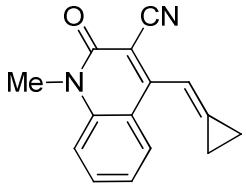
(comp, 5H), 7.26 – 7.20 (comp, 2H), 7.11 – 7.06 (comp, 2H), 6.87 (d, J = 7.5 Hz, 1H), 5.06 (dd, J = 87.9, 15.3 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) (δ, ppm) 173.2, 164.6, 150.3, 143.5, 134.3, 133.5, 131.8, 129.4, 129.3, 128.9, 128.7, 128.0, 127.2, 124.9, 124.6, 119.4, 111.7, 110.3, 45.6. HRMS (TOF MS CI$^+$) calculated for $C_{24}H_{17}N_4O^+$ $[M+H]^+$: 337.1402, found 337.1390.



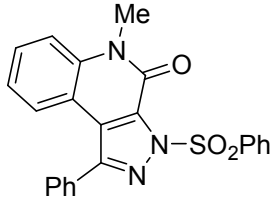
Synthesis of **2i**: To a solution of *N*-methyl-2-(phenylethynyl)aniline (**S3**, 83.0 mg, 0.4 mmol), 2-oxopropanoic acid (43.0 mg, 0.48 mmol) and 4-dimethylaminopyridine (DMAP, 5.0 mg, 0.04 mmol) in CH_2Cl_2 (4.0 mL), dicyclohexylcarbodiimide (DCC, 98.0 mg, 0.48 mmol) was added within 5 min at 0 ℃ under argon atmosphere. The reaction mixture was stirred overnight and the reaction temperature was slowly warmed to room temperature. After filtering through Celite and the filtrate was washed with saturated aqueous $NaHCO_3$ (10.0 mL) and brine (10.0 mL) in sequence, and dried over anhydrous Na_2SO_4. The solvent was evaporated under vacuum after filtration, and the obtained product **S5** was directly used for the next step without further purification.

To a solution of above obtained **S5** in $CHCl_3$ (5.0 mL） was added $TsNHNH_2$ (111.8 mg, 0.6 mmol) and $TsOH{\cdot}H_2O$ (3.8 mg, 0.02 mmol). The reaction mixture was refluxed for 5 h. After cooling to room temperature, the solvent was evaporated under reduced pressure and the resulting crude product **S6** was dissolved in DCM (30 mL). Then DBU (92.0 mg, 0.6 mmol) was added and the reaction mixture was stirred at room temperature for 2 h. After consumption of the material **S6**, the reaction mixture was washed with saturated aqueous ammonium chloride (10.0 mL), saturated aqueous sodium bicarbonate (10.0 mL), and brines (10.0 mL) in sequence. The organic layer was dried with anhydrous Na_2SO_4, and the solvent was removed under reduced

pressure after filtration. The crude reaction mixture was purified by flash column chromatography on silica gel (EtOAc/petroleum ether = 1:5) to afford 1,3'-Dimethyl-5'-phenylspiro [indoline-3,4'-pyrazol]-2-one (**2i**). White solid; m.p. 208.0 – 211.0 ℃. 55.5 mg, 48% yield (based on **S3**). ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.49 – 7.41 (comp, 3H), 7.38 – 7.32 (m, 1H), 7.27 – 7.25 (comp, 2H), 7.10 – 7.05 (comp, 2H), 6.85 (d, *J* = 7.2 Hz, 1H), 3.40 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (150MHz, $CDCl_3$) (δ, ppm) 172.7, 171.5, 168.1, 144.2, 131.5, 130.5, 129.2, 129.1, 127.5, 124.4, 124.0, 123.2, 109.8, 27.6, 12.6. HRMS (TOF MS CI$^+$) calculated for $C_{18}H_{16}N_3O^+$ $[M+H]^+$: 290.1293, found 290.1297.

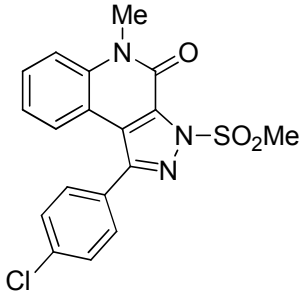


4-(Cyclopropylidenemethyl)-1-methyl-2-oxo-1,2-dihydroquinoline-3-carbonitrile (**2j**). White solid; m.p. 184.0 – 187.0 ℃. 40.2 mg, 85% yield. ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm) 8.13 (d, *J* = 8.2 Hz, 1H), 7.84 – 7.77 (m, 1H), 7.63 (d, *J* = 8.6 Hz, 1H), 7.42 – 7.34 (m, 1H), 6.92 (s, 1H), 3.64 (s, 3H), 3.26 – 3.17 (m, 2H), 2.76 – 2.68 (m, 2H); ^{13}C NMR (100MHz, DMSO-d_6) (δ, ppm) 158.3, 150.4, 144.7, 140.5, 139.6, 134.1, 128.0, 123.1, 117.1, 115.9, 115.9, 102.1, 40.15, 33.4, 30.0, 28.5. HRMS (TOF MS CI$^+$) calculated for $C_{15}H_{13}N_2O^+$ $[M+H]^+$: 237.1028, found 237.1033.

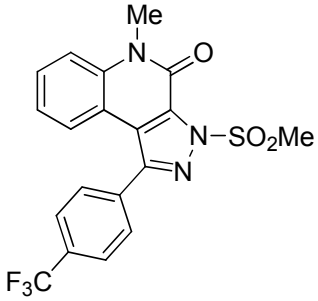


5-Methyl-1-phenyl-3-(phenylsulfonyl)-3*H*-pyrazolo[3,4-*c*]quinolin-4(5*H*)-one (**4a**). White solid; m.p. 254.0 – 257.0 ℃. 74.8 mg, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.39 – 8.31 (comp, 2H), 7.77 – 7.73 (m, 1H), 7.69 – 7.62 (comp, 3H), 7.60 – 7.53 (comp, 5H), 7.50 – 7.45 (m, 1H), 7.39 (d, *J* = 8.4 Hz,

1H), 7.08 (t, J = 7.5 Hz, 1H), 3.77 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) (δ, ppm) 152.7, 150.1, 138.1, 134.5, 132.2, 131.7, 129.9, 129.8, 129.6, 129.3, 129.2, 129.0, 124.4, 124.3, 122.8, 115.4, 115.3, 30.2. HRMS (TOF MS CI$^+$) calculated for $C_{23}H_{18}N_3O_3S^+$ $[M+H]^+$: 416.1063, found 416.1069.

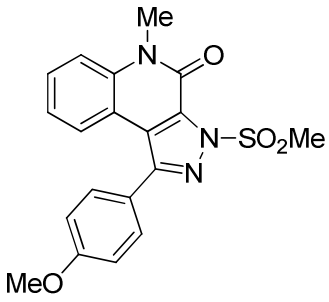


1-(4-Chlorophenyl)-5-methyl-3-(methylsulfonyl)-3*H*-pyrazolo[3,4-*c*]quinolin-4(5*H*)-one (**4b**). White solid; m.p. 293.0 – 296.0 ℃. 71.2 mg, 92% yield. ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm) 7.75 – 7.69 (comp, 5H), 7.65 – 7.60 (comp, 2H), 7.28 – 7.24 (m, 1H), 4.05 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) (δ, ppm) 152.2, 147.2, 137.5, 134.6, 131.4, 130.9, 130.7, 129.5, 129.1, 123.2, 123.0, 116.4, 114.4, 42.5, 29.9. HRMS (TOF MS CI$^+$) calculated for $C_{18}H_{15}ClN_3O_3S^+$ $[M+H]^+$: 388.0523, found 388.0535.

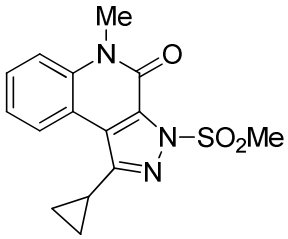


5-Methyl-3-(methylsulfonyl)-1-(4-(trifluoromethyl)phenyl)-3*H*-pyrazolo[3,4-*c*]quinolin-4(5*H*)-one (**4c**). White solid; m.p. 296.0 – 299.0 ℃. 76.7 mg, 91% yield. ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm) 8.02 – 7.94 (comp, 4H), 7.74 – 7.71 (m, 1H), 7.65 – 7.61 (comp, 2H), 7.31 – 7.24 (m, 1H), 4.07 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) (δ, ppm) 152.2, 146.9, 137.6, 136.8, 136.1, 131.1, 130.5, 130.1, 129.6, 126.0 (q, J = 7.2 Hz), 123.2 (q, J = 8.4 Hz), 122.3 (q, J = 583.6 Hz), 116.4, 114.3, 42.5, 30.0. ^{19}F NMR (376 MHz, DMSO-d_6) (δ, ppm) -61.1.

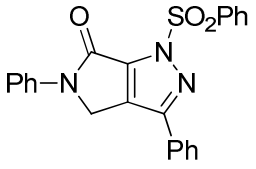
HRMS (TOF MS CI$^+$) calculated for $C_{19}H_{15}F_3N_3O_3S^+$ [M+H]$^+$: 422.0786, found 422.0780.



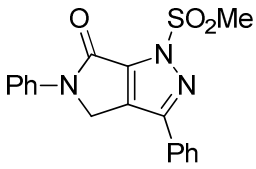
1-(4-Methoxyphenyl)-5-methyl-3-(methylsulfonyl)-3*H*-pyrazolo[3,4-*c*]quinolin-4(5*H*)-one (**4d**). White solid; m.p. 256.0 – 259.0 ℃. 68.2 mg, 89% yield. ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm) 7.77 – 7.67 (comp, 2H), 7.66 – 7.53 (comp, 3H), 7.28 – 7.21 (m, 1H), 7.21 – 7.09 (comp, 2H), 4.04 (s, 3H), 3.88 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) (δ, ppm) 160.2, 152.3, 148.2, 137.5, 130.8, 130.6, 129.4, 123.8, 123.2, 123.1, 122.9, 116.3, 114.7, 114.4, 55.3, 42.5, 29.9. HRMS (TOF MS CI$^+$) calculated for $C_{19}H_{18}N_3O_4S^+$ [M+H]$^+$: 384.1018, found 384.1010.



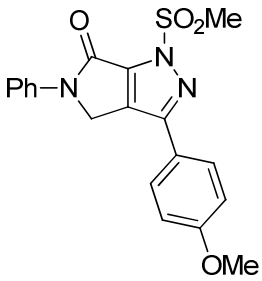
1-Cyclopropyl-5-methyl-3-(methylsulfonyl)-3*H*-pyrazolo[3,4-*c*]quinolin-4(5*H*)-one (**4e**). White solid; m.p. 248.0 – 251.0 ℃. 59.0 mg, 93% yield. ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm) 8.32 – 8.24 (m, 1H), 7.59 – 7.52 (m, 1H), 7.52 – 7.45 (m, 1H), 7.38 – 7.31 (m, 1H), 3.67 (s, 3H), 2.48 (s, 3H), 2.35 – 2.27 (m, 1H), 1.12 – 0.99 (m, 2H), 0.94 – 0.82 (m, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) (δ, ppm) 154.5, 146.4, 136.6, 133.4, 127.1, 123.6, 122.7, 118.1, 117.2, 115.7, 34.5, 29.1, 8.7, 6.7. HRMS (TOF MS CI$^+$) calculated for $C_{15}H_{16}N_3O_3S^+$ [M+H]$^+$: 318.0912, found 318.0910.



3,5-Diphenyl-1-(phenylsulfonyl)-4,5-dihydropyrrolo[3,4-*c*]pyrazol-6(1*H*)-one (**4f**). White solid; m.p. 235.0 – 238.0 ℃. 78.1 mg, 94% yield. ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm) 8.23 – 8.12 (comp, 2H), 7.93 – 7.76 (comp, 5H), 7.75 – 7.66 (comp, 2H), 7.61 – 7.40 (comp, 5H), 7.23 (t, J = 7.4 Hz, 1H), 5.19 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm) 154.7, 147.9, 142.7, 139.5, 136.4, 135.6, 132.7, 130.2, 130.1, 129.5, 129.3, 129.0, 127.9, 126.6, 124.9, 119.9, 45.5. HRMS (TOF MS CI$^+$) calculated for $C_{23}H_{18}N_3O_3S^+$ [M+H]$^+$: 416.1069, found 416.1063.

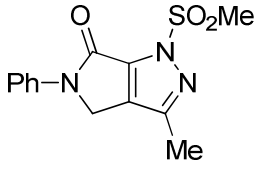


1-(Methylsulfonyl)-3,5-diphenyl-4,5-dihydropyrrolo[3,4-*c*]pyrazol-6(1*H*)-one (**4g**). White solid; m.p. 256.0 – 259.0 ℃. 67.9 mg, >95% yield (without recrystallization). ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm) 7.92 – 7.84 (comp, 3H), 7.69 – 7.30 (comp, 6H), 7.29 – 7.18 (m, 1H), 5.26 (s, 2H), 3.81 (s, 3H); ^{13}C NMR (100MHz, DMSO-d_6) (δ, ppm) 155.2, 146.6, 142.4, 139.5, 131.3, 129.9, 129.8, 129.2, 129.0, 126.5, 124.9, 119.9, 45.7, 41.8. HRMS (TOF MS CI$^+$) calculated for $C_{18}H_{16}N_3O_3S^+$ [M+H]$^+$: 354.0912, found 354.0907.

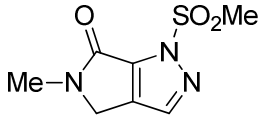


3-(4-Methoxyphenyl)-1-(methylsulfonyl)-5-phenyl-4,5-dihydropyrrolo[3,4-*c*]pyrazol-6(1*H*)-one (**4h**). White solid; m.p. 245.0 – 248.0 ℃. 72.1 mg, 94% yield. ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm) 7.88 – 7.80 (comp, 4H),

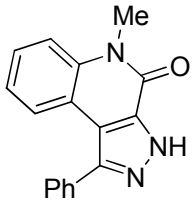
7.50 – 7.44 (comp, 2H), 7.23 (t, J = 7.4 Hz, 1H), 7.13 – 7.08 (comp, 2H), 5.22 (s, 2H), 3.84 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (150MHz, DMSO-d_6) (δ, ppm) 160.5, 155.2, 146.7, 142.3, 139.5, 131.0, 129.0, 128.1, 124.8, 122.3, 119.9, 114.6, 55.4, 45.7, 41.8. HRMS (TOF MS CI$^+$) calculated for $C_{19}H_{18}N_3O_4S^+$ $[M+H]^+$: 384.1018, found 384.1013.



3-Methyl-1-(methylsulfonyl)-5-phenyl-4,5-dihydropyrrolo[3,4-*c*]pyrazol-6(1*H*)-one (**4i**). White solid; m.p. 214.0 – 217.0 ℃. 51.3 mg, 88% yield. ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm) 7.81 – 7.78 (comp, 2H), 7.42 – 7.38 (comp, 2H), 7.16 – 7.11 (m, 1H), 4.76 (s, 2H), 2.47 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm) 161.7, 149.4, 140.4, 133.6, 128.9, 124.0, 121.3, 119.3, 45.0, 39.7, 10.0. HRMS (TOF MS CI$^+$) calculated for $C_{13}H_{14}N_3O_3S^+$ $[M+H]^+$: 292.0756, found 292.0755.

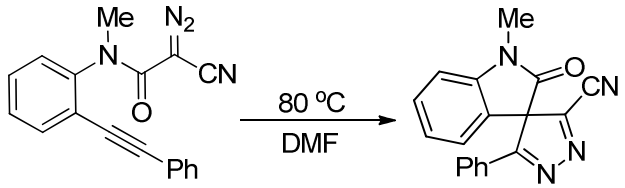


5-Methyl-1-(methylsulfonyl)-4,5-dihydropyrrolo[3,4-*c*]pyrazol-6(1*H*)-one (4j) . White gum, 41.8 mg, >95% yield (without recrystallization). ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.67 (s, 1H), 4.24 (s, 2H), 3.52 (s, 3H), 3.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 157.0, 142.1, 136.0, 133.6, 46.2, 42.1, 30.7. HRMS (TOF MS CI$^+$) calculated for $C_7H_{10}N_3O_3S^+$ $[M+H]^+$: 216.0443, found 216.0444.



5-Methyl-1-phenyl-3*H*-pyrazolo[3,4-*c*]quinolin-4(5*H*)-one (**4k**). White solid; m.p. 287.0 – 291.0 ℃. 45.7 mg, 83% yield. ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm) 14.47 (s, 1H), 7.82 – 7.71 (m, 1H), 7.70 – 7.63 (comp, 2H), 7.63 – 7.50 (comp, 4H), 7.49 – 7.40 (m, 1H), 7.23 – 7.04 (m, 1H), 3.72 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) (δ, ppm) 153.6, 147.0, 136.7, 134.0, 131.8, 129.3, 128.7, 128.6, 127.6, 122.5, 122.4, 117.0, 116.4, 116.2, 29.2. HRMS (TOF MS CI+) calculated for $C_{17}H_{14}N_3O^+$ $[M+H]^+$: 276.1137, found 276.1130.

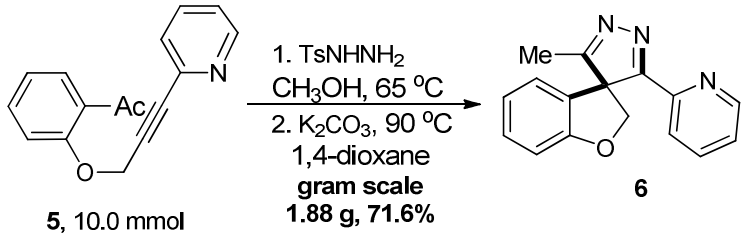
Scale Up:



1a, 4.0 mmol **2a**, 81% yield

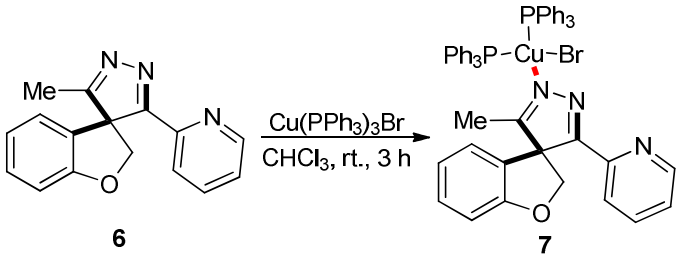
To a 100-mL oven-dried round-bottom flask with a magnetic stirring bar, diazo compound **1a** (4.0 mmol, 1.2 g) was dissolved in *N*,*N*-dimethylformamide (DMF, 40.0 mL). After stirring overnight at 80 ℃, the reaction was quenched with water (100 mL) and the aqueous phase extracted with CH_2Cl_2 (50.0 mL × 3). The combined organic phase was washed with saturated brine (100 mL × 2), and the organic phase was dried over anhydrous Na_2SO_4. Then the solvent was removed in vacuo after filtration to give a white solid. The solid product was further purified by recrystallization (solvents: petroleum ether/ethyl acetate /CH_2Cl_2 = 1: 2: 5,) to give 0.972 g pure product **2a** in 81% yield.

Procedure for the Preparation of Copper Complex 7.



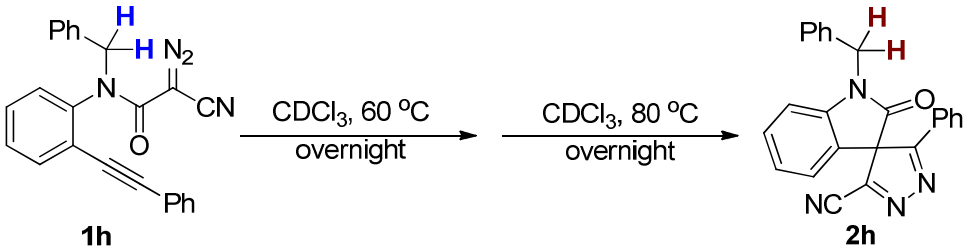
To a 100-mL oven-dried flask containing a magnetic stirring bar, was added **5** (10.0 mmol, 2.51 g), sulfonyl hydrazide (11 mmol, 2.05 g) and methanol (20.0 mL) in sequence, and the reaction mixture was stirred at 60~65 ^{o}C for 12 h. Then the solvent was evaporated under vacuum, and the crude product was directly used for the next step without further purification.

To a 100-mL oven-dried flask containing a magnetic stirring bar, the above obtained product, K_2CO_3 (20 mmol, 2.0 equiv, 2.76 g), and 1,4-dioxane (20 mL) were added in sequence under atmosphere of argon, and the reaction mixture was stirred at 90 ^{o}C for 10 h. After the reaction was completed (monitored by TLC), the reaction mixture was quenched with saturated brine (20 mL) and extracted with EtOAc (3×20 mL). The combined organic phase was dried over Na_2SO_4, and the solvent was evaporated under vacuum after filtration. The crude reaction mixture was purified by flash column chromatography on silica gel (Hexanes:EtOAc = 5:1 to 2:1) to give pure **6** as a yellow solid (1.88 g, 71.6% yield). mp: 159-160 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.45 (d, *J* = 4.8 Hz, 1H), 8.27 (d, *J* = 8.0 Hz, 1H), 7. 74-7.70 (m, 1H), 7.24-7.17 (m, 2H), 6.98 (d, *J* = 8.1 Hz, 1H), 6.74 (t, *J* = 7.5 Hz, 1H), 6.60 – 6.49 (m, 1H), 5.39 (d, *J* = 9.0 Hz, 1H), 4.64 (d, *J* = 9.0 Hz, 1H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 179.3, 175.1, 161.7, 149.6, 149.2, 136.6, 130.1, 125.0, 124.9, 123.1, 122.7, 121.1, 110.7, 74.2, 73.5, 12.6. HRMS (TOF MS ESI^{+}) calculated for $C_{16}H_{14}N_3O^{+}$ $[M+H]^{+}$: 264.1137, found 264.1346.



To a 25-mL oven-dried vial containing a magnetic stirring bar, $Cu(PPh_3)_3Br$ (93.0 mg, 0.1 mmol) was dissolved in 5 mL of chloroform at room temperature. **5** (26.3 mg, 0.1 mmol) was then added to reaction mixture. The colorless solution immediately turned orange. The contents of the flask were allowed to stir at room temperature for 25 min and the solvent was removed in vacuo. The resulting orange solid was dissolved in 4 mL of DCM and layered with 8 mL of ether. The precipitate was collected and recrystallized with DCM, ether and hexane to give **6** as an orange solid (83.8 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.44 (d, J = 4.8 Hz, 1H), 8.01 (bs, 1H), 7.76 (bs, 1H), 7.35-7.19 (comp, 33H), 7.00 (d, J = 8.1 Hz, 1H), 6.75 (td, J = 7.5, 1.0 Hz, 1H), 6.46 (bs, 1H), 4.62 (d, J = 9.0 Hz, 1H), 2.18 (s, 3H).

Mechanism Studies



To a dry NMR tube, diazo compound **1h** (0.05 mmol, 18.8 mg) was dissolved in $CDCl_3$ (0.5 mL). After warming to 60 ℃ in a oil bath for 12 h, the most of the staring material **1h** transferred into the desired pyrazole **2h** and there was no obvious other signal (Fig. S1, the middle spectrum). After another 12 h at 80 °C, all the material transferred to product **2h** (Fig. S1, the bottom spectrum).

Comments: no proton NMR signal of corresponding 3H-pyrazole intermediate was observed.

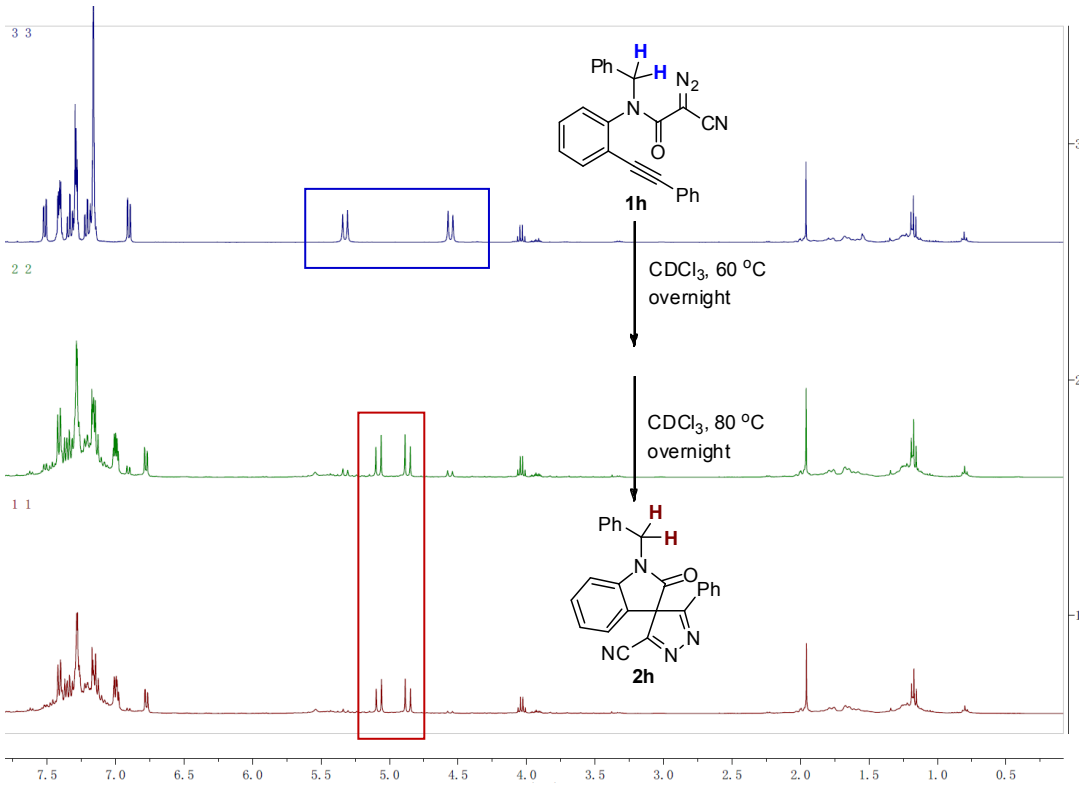
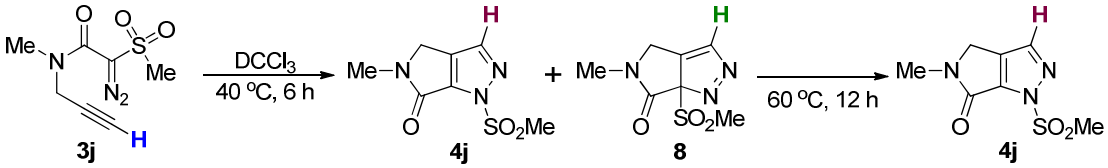
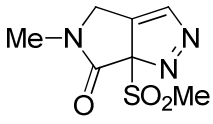


Fig. S1 Proton NMR observation of reaction with **1h**.



To a dry NMR tube, diazo compound **3j** (0.05 mmol, 10.8 mg) was dissolved in $CDCl_3$ (0.5 mL). After warming to 40 ℃ in a oil bath for 6 h, all the material is consumed, and the desired pyrazole **4j** was formed as the major product combined with other product, which most probably account for the proton signals of 3*H*-pyrazole **8** (Fig. S2, the middle spectrum). After another 12 h at 60 °C, compound **8** transferred to product **4j** (Fig. S2, the bottom spectrum).

Comments: Proton signals, which most probably account for the corresponding 3H-pyrazole intermediate 8 was observed.



5-Methyl-6a-(methylsulfonyl)-4,6a-dihydropyrrolo[3,4-*c*]pyrazol-6(5*H*)-one (8). ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 6.30 (s, 1H), 4.11 (s, 2H), 3.15 (s, 3H), 2.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 165.5, 152.6, 119.7, 51.8, 49.5, 42.6, 29.1.

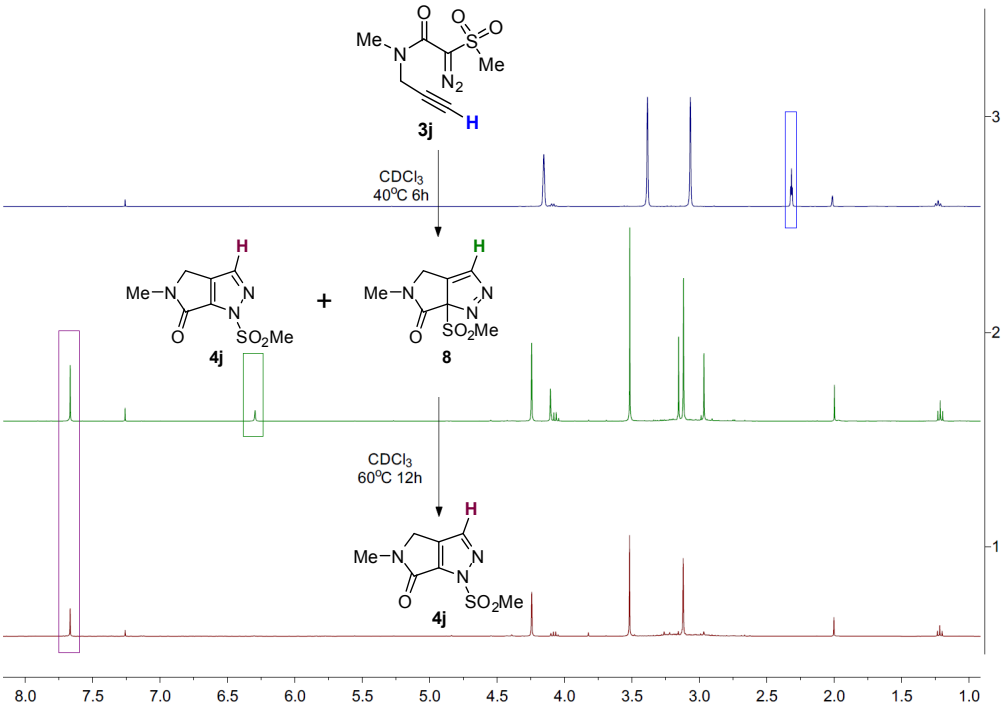
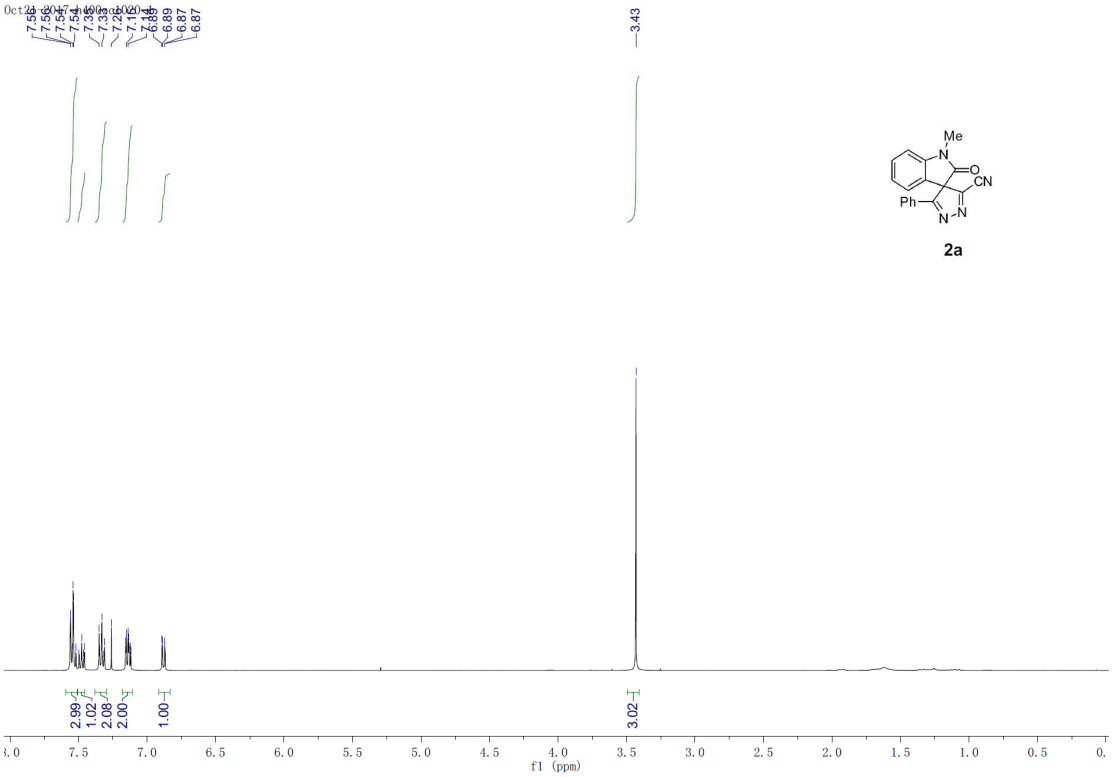


Fig. S2 Proton NMR observation of 3*H*-pyrazole intermediate **8**.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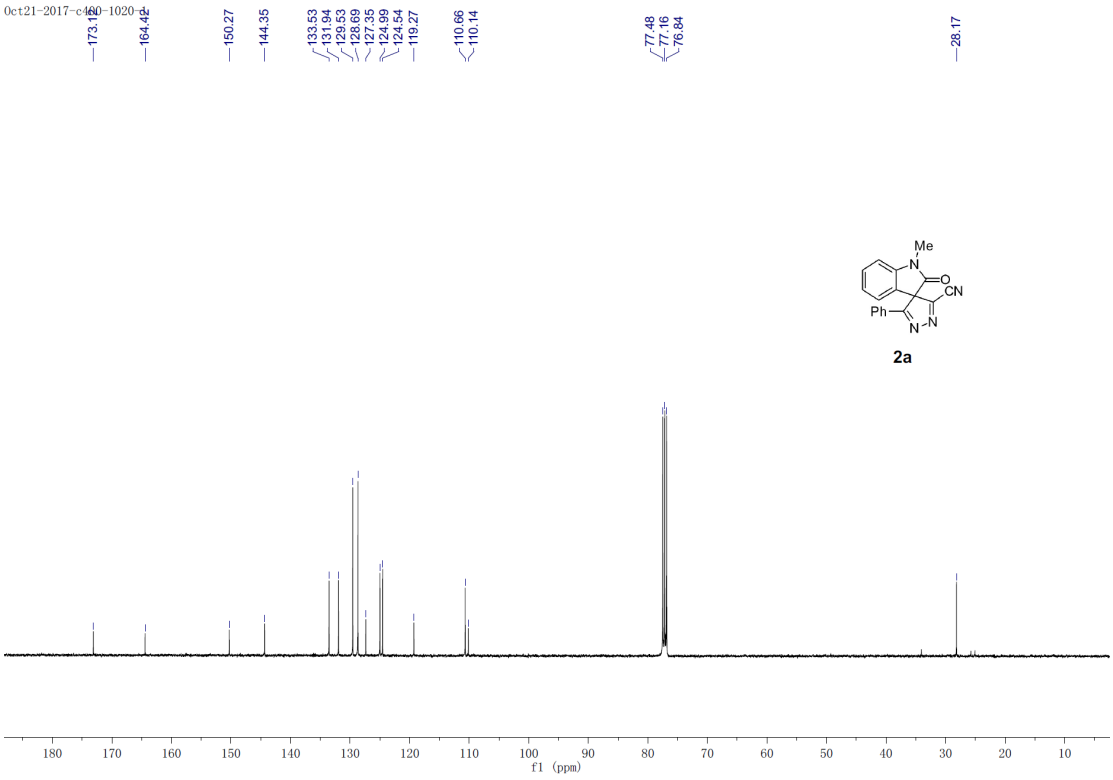
7.56
7.54
7.54
7.38
7.26
7.15
6.89
6.87
6.87
3.43
Me
N
O
CN
Ph
N
N
2a
2.99
1.02
2.08
2.00
1.00
3.02
f1 (ppm)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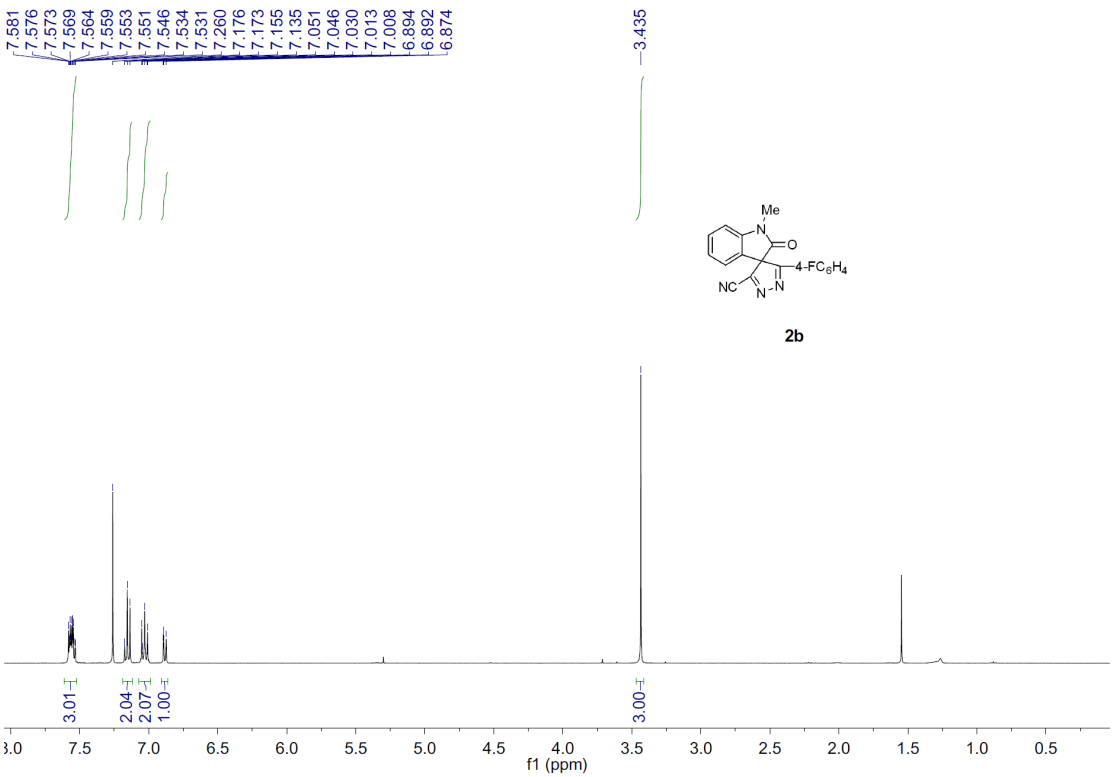
164.42
150.27
144.35
133.53
131.94
129.53
128.69
127.35
124.99
124.54
119.27
110.66
110.14
77.48
77.16
76.84
28.17
Me
N
O
CN
Ph
N
N
2a
f1 (ppm)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7.576
7.573
7.569
7.564
7.559
7.553
7.551
7.546
7.534
7.531
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7.176
7.173
7.155
7.135
7.051
7.046
7.030
7.013
7.008
6.894
6.892
6.874
3.435
Me
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O
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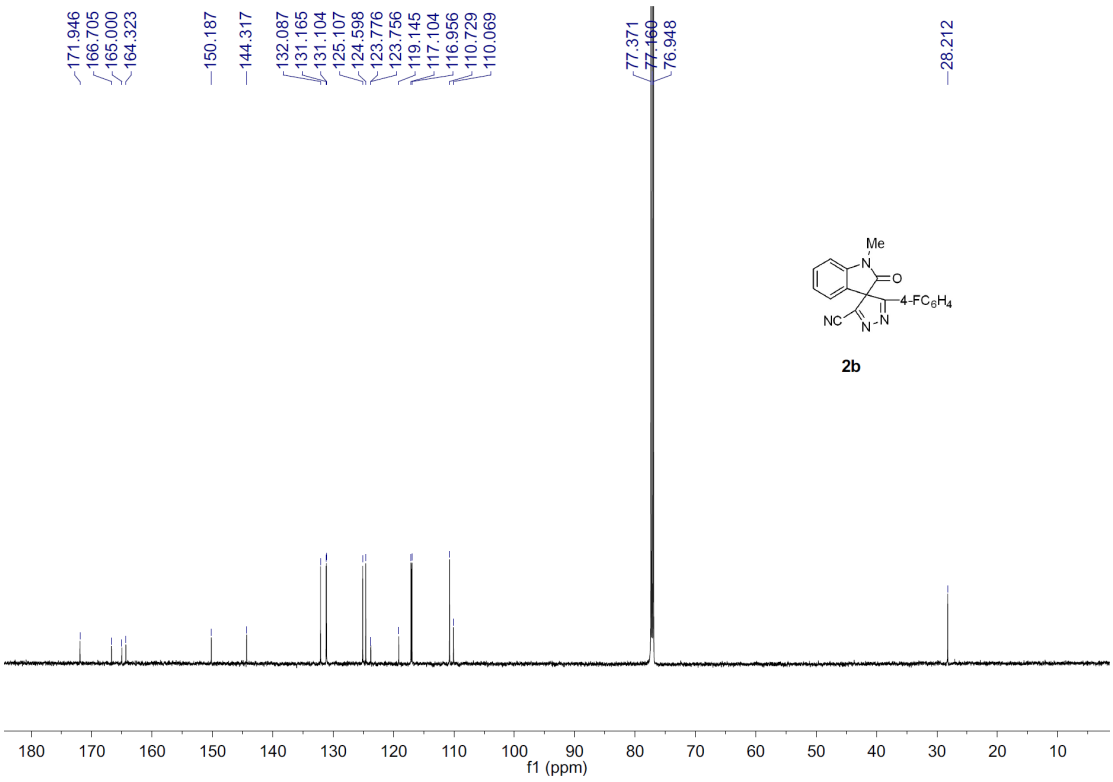
NC
N
N
2b
3.01
2.04
2.07
1.00
3.00
f1 (ppm)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165.000
164.323
150.187
144.317
132.087
131.165
131.104
125.107
124.598
123.776
123.756
119.145
117.104
116.956
110.729
110.069
77.371
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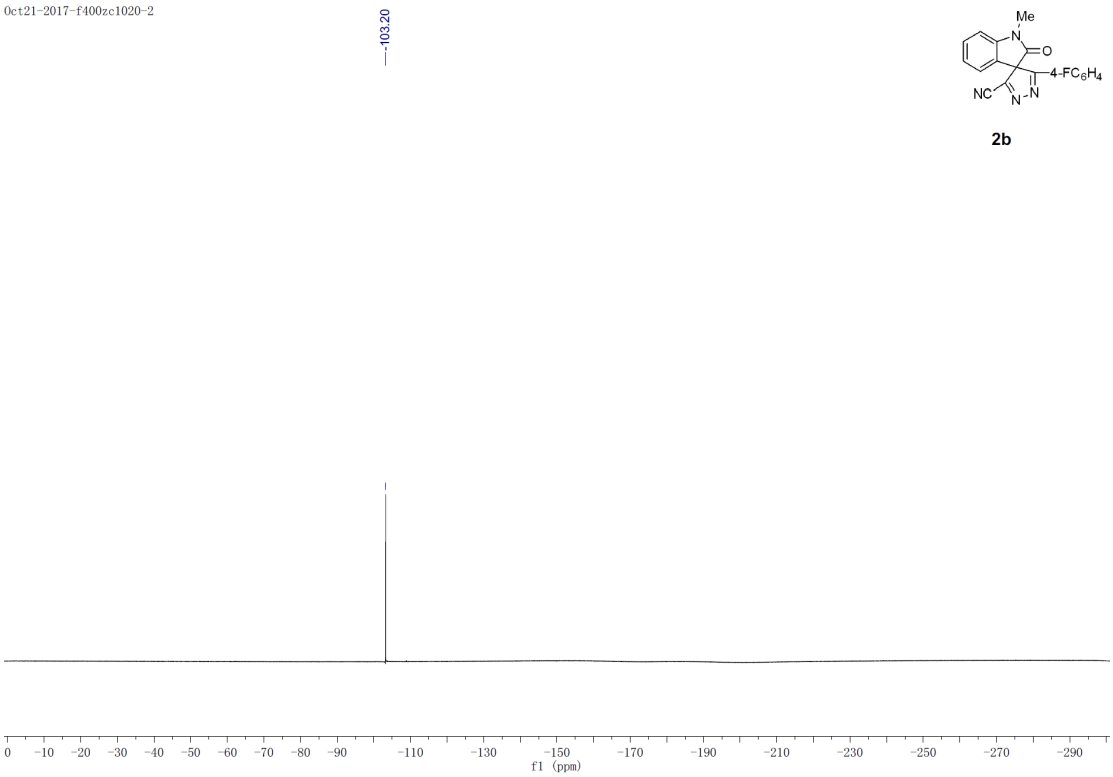
76.948
28.212
Me
N
O
4-FC6H4
NC
N
N
2b
f1 (ppm)


0ct21-2017-f400zc1020-2
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O
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NC
N
N
2b
0
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-30
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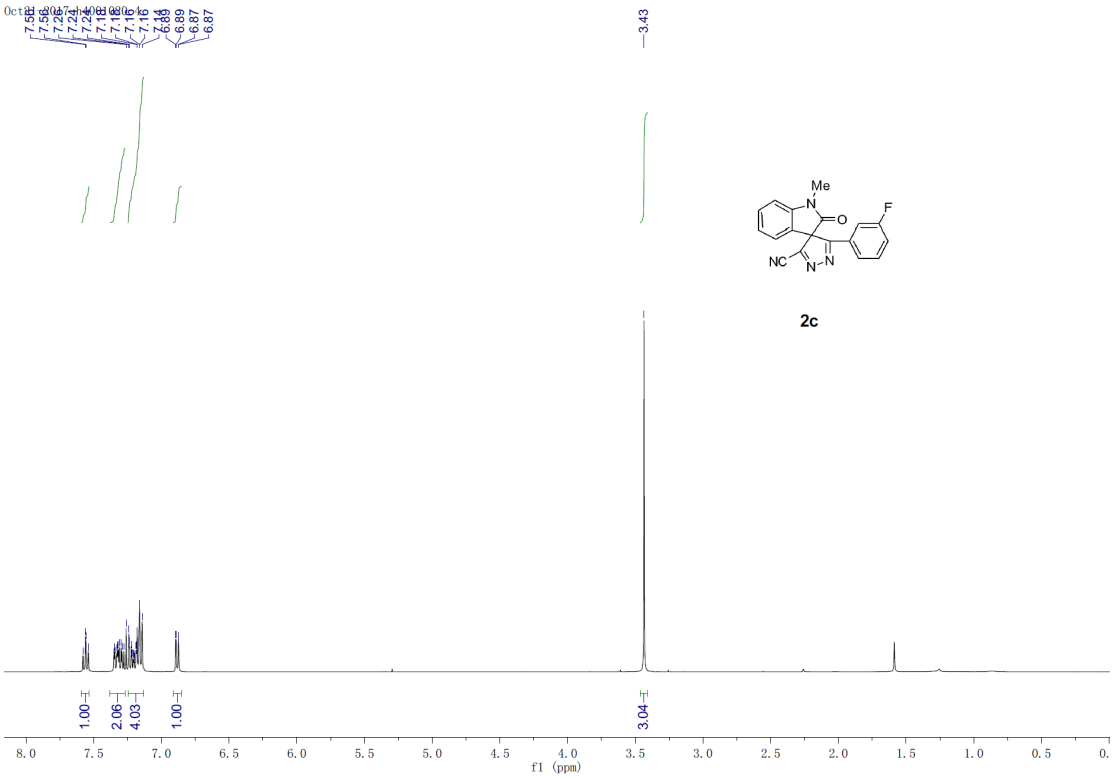
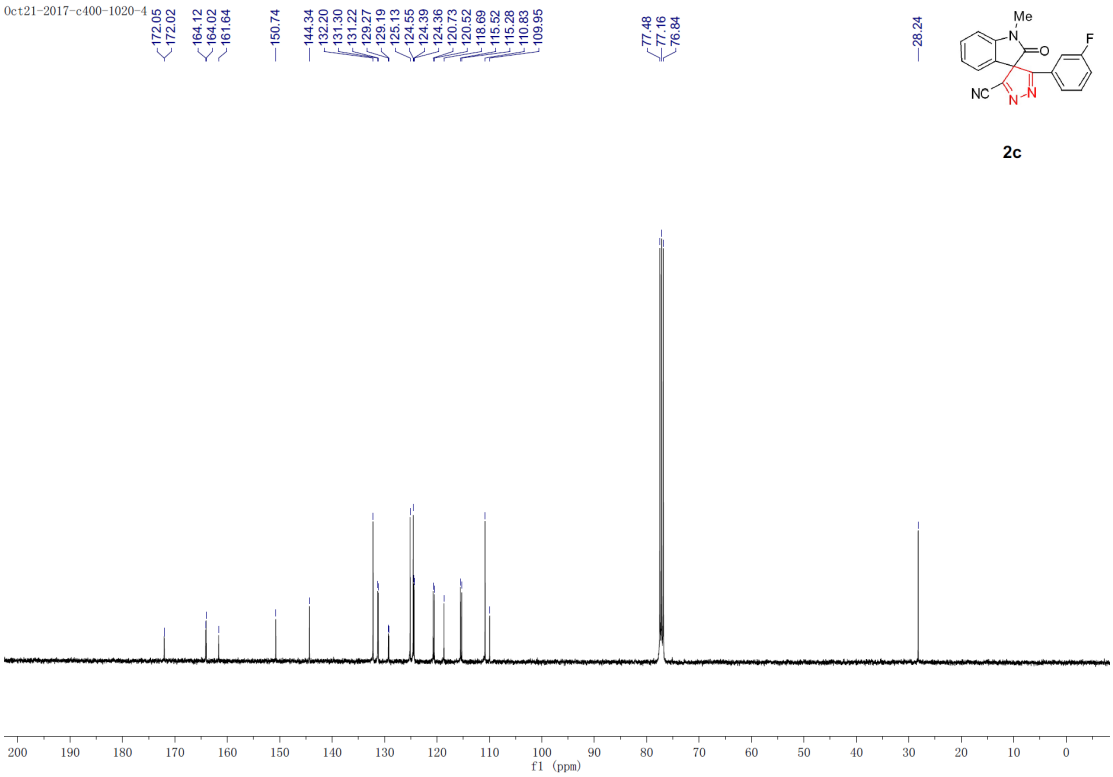
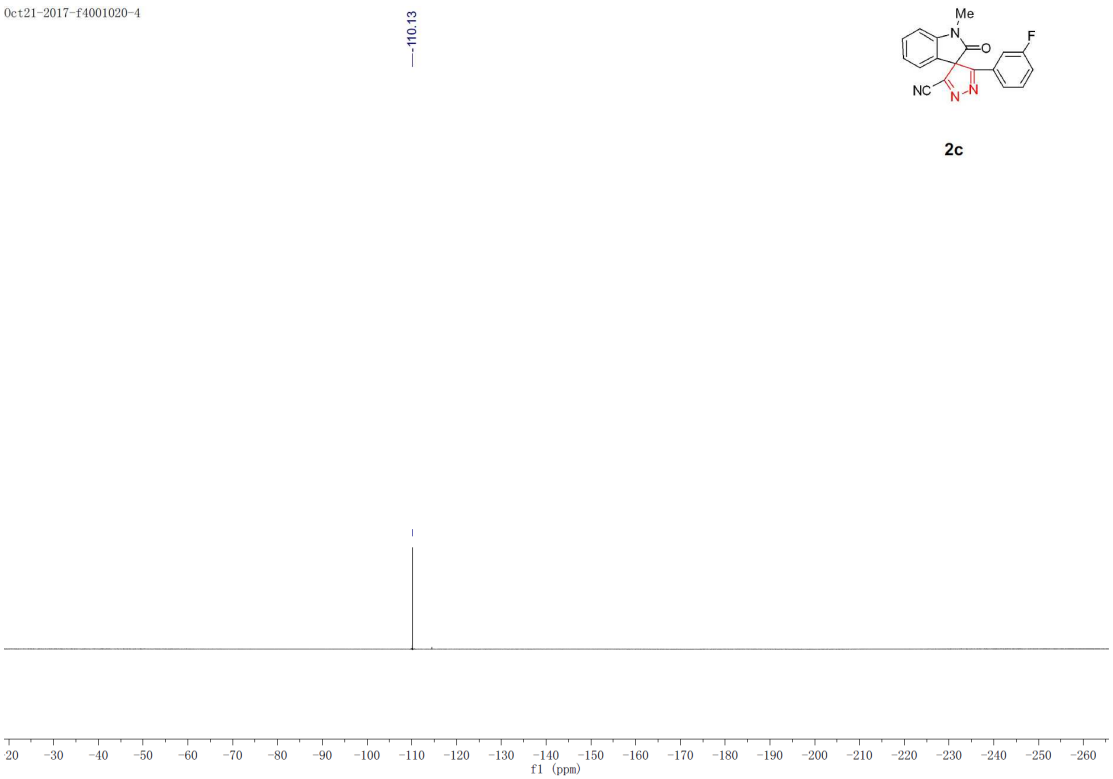
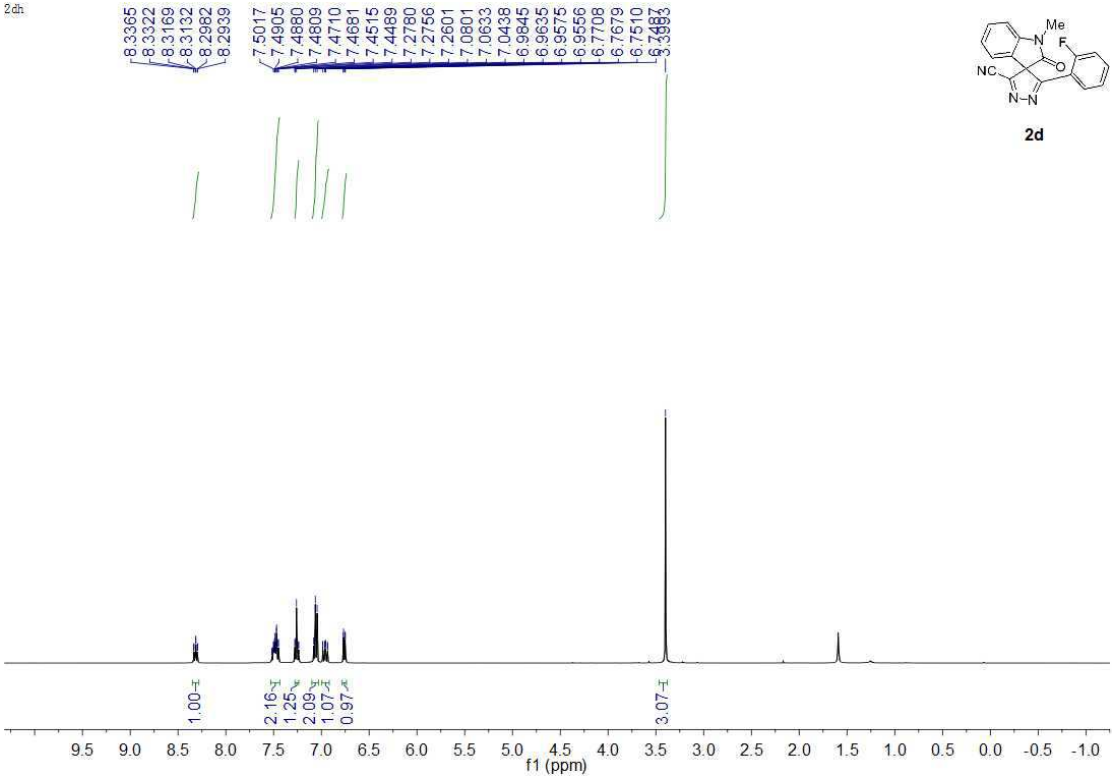
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
-290
f1 (ppm)


7.52
7.56
7.25
7.24
7.23
7.18
7.16
7.15
7.14
6.89
6.87
6.87
-3.43
Me
N
O
F
NC
N
N
2c
1.00
2.06
4.03
1.00
3.04
8.0
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
0.
f1 (ppm)

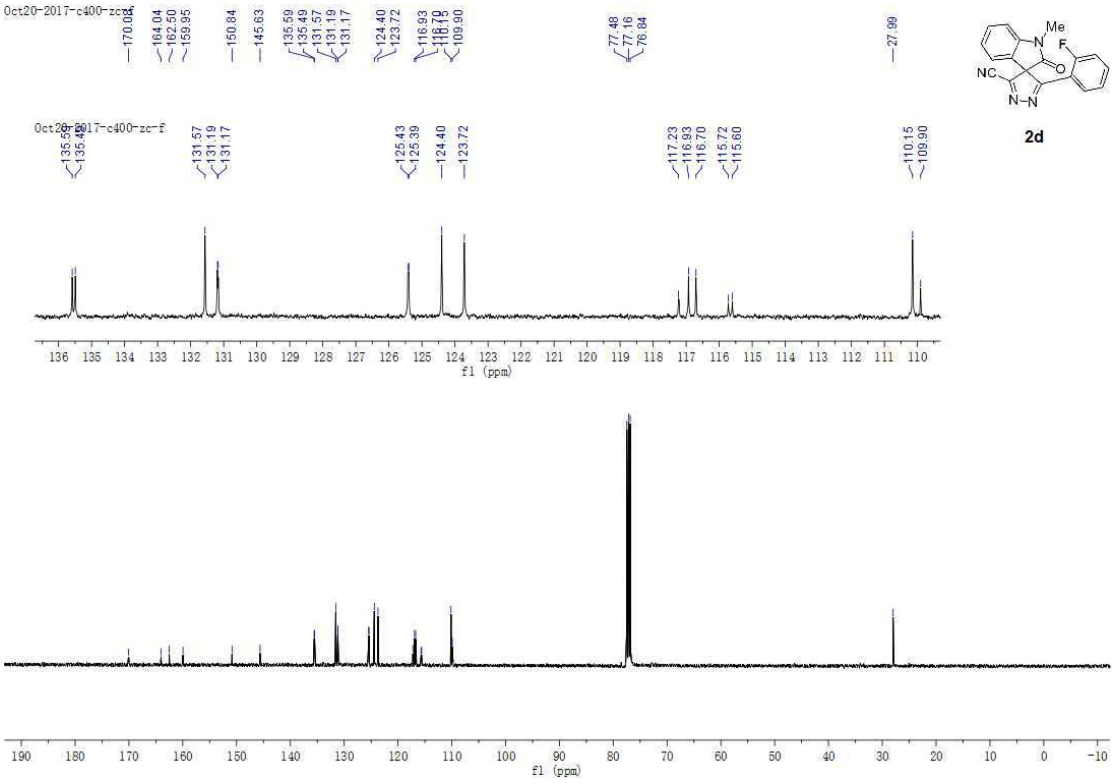

0ct21-2017-c400-1020-4
172.05
172.02
164.12
164.02
161.64
150.74
144.34
132.20
131.30
131.22
129.27
129.19
125.13
124.55
124.39
124.36
120.73
120.52
118.69
115.52
115.28
110.83
109.95
77.48
77.16
76.84
28.24
Me
N
O
F
NC
N
N
2c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


0ct21-2017-f4001020-4
110.13
Me
N
O
F
NC
N
N
2c
20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
-250
-260
f1 (ppm)


2dh
8.3365
8.3322
8.3169
8.3132
8.2982
8.2939
7.5017
7.4905
7.4880
7.4809
7.4710
7.4681
7.4515
7.4489
7.2780
7.2756
7.2601
7.0801
7.0633
7.0438
6.9845
6.9635
6.9575
6.9556
6.7708
6.7679
6.7510
3.3993
1.00
2.16
1.25
2.09
1.07
0.97
3.07
f1 (ppm)

Me
F
NC
O
N-N

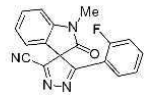
2d


0oct20-2017-c400-zcxd
170.08
164.04
162.50
159.95
150.84
145.63
135.59
135.49
131.57
131.19
131.17
124.40
123.72
116.93
116.70
116.19
109.90
77.48
77.16
76.84
27.99
0oct20-2017-c400-zc-f
135.59
135.49
131.57
131.19
131.17
125.43
125.39
124.40
123.72
117.23
116.93
116.70
115.72
115.60
110.15
109.90
f1 (ppm)

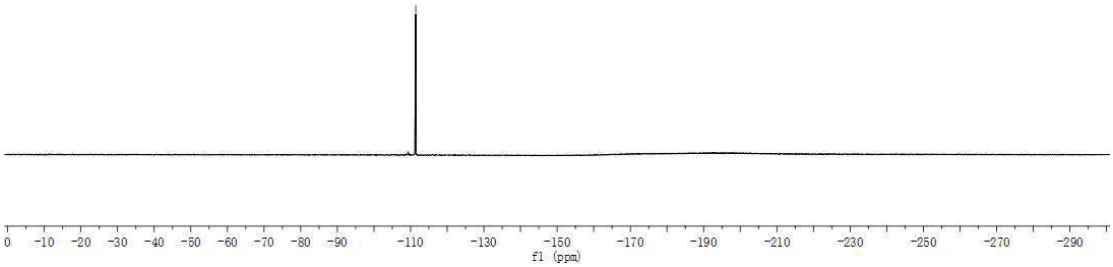
Me
F
NC
O
N-N

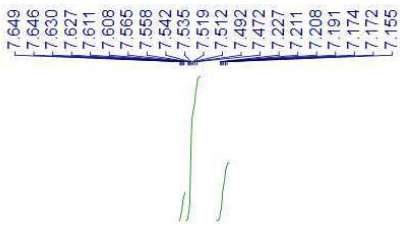
2d

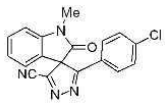
Oct24-2017-f400-zc-f



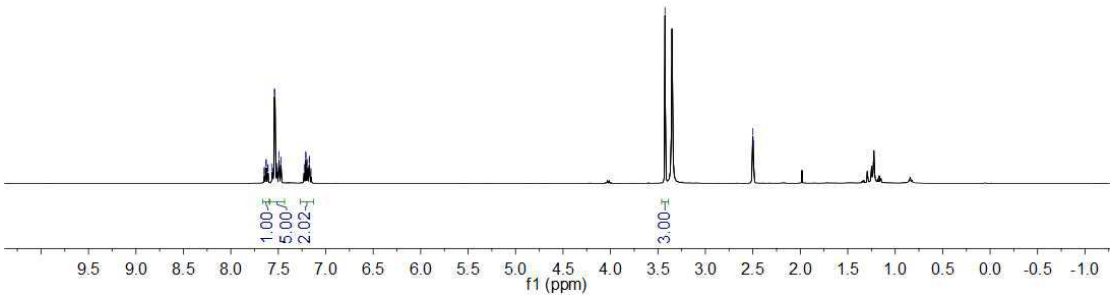
2d

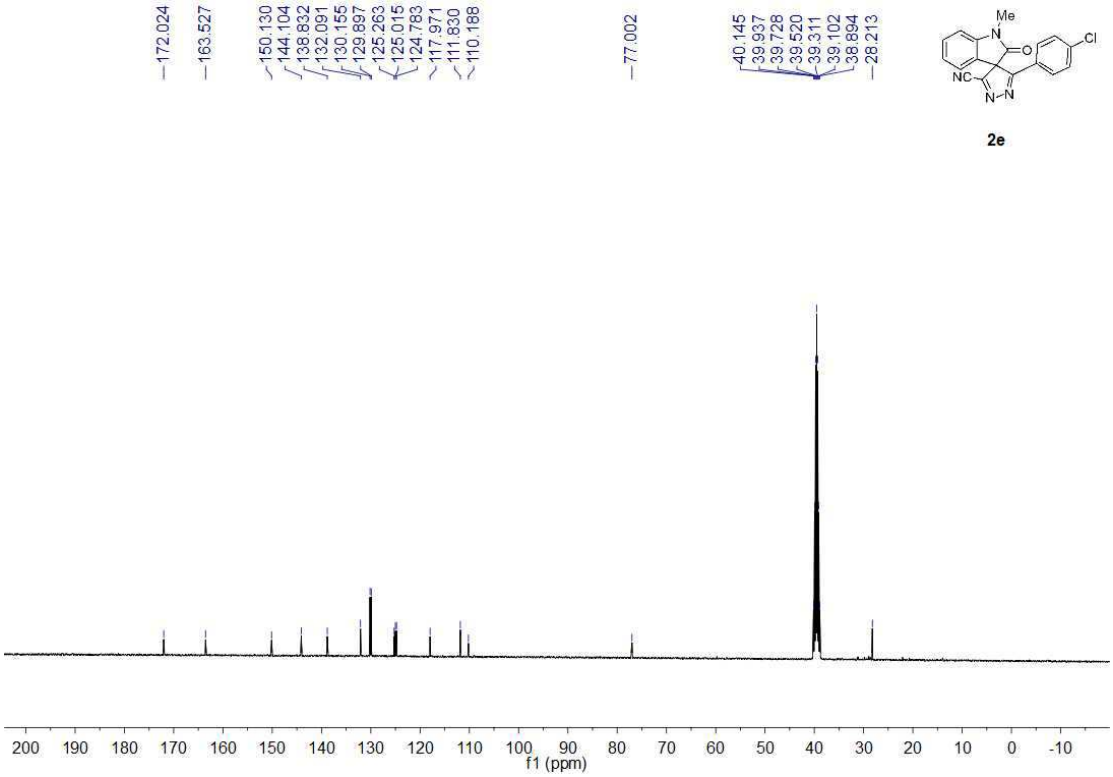


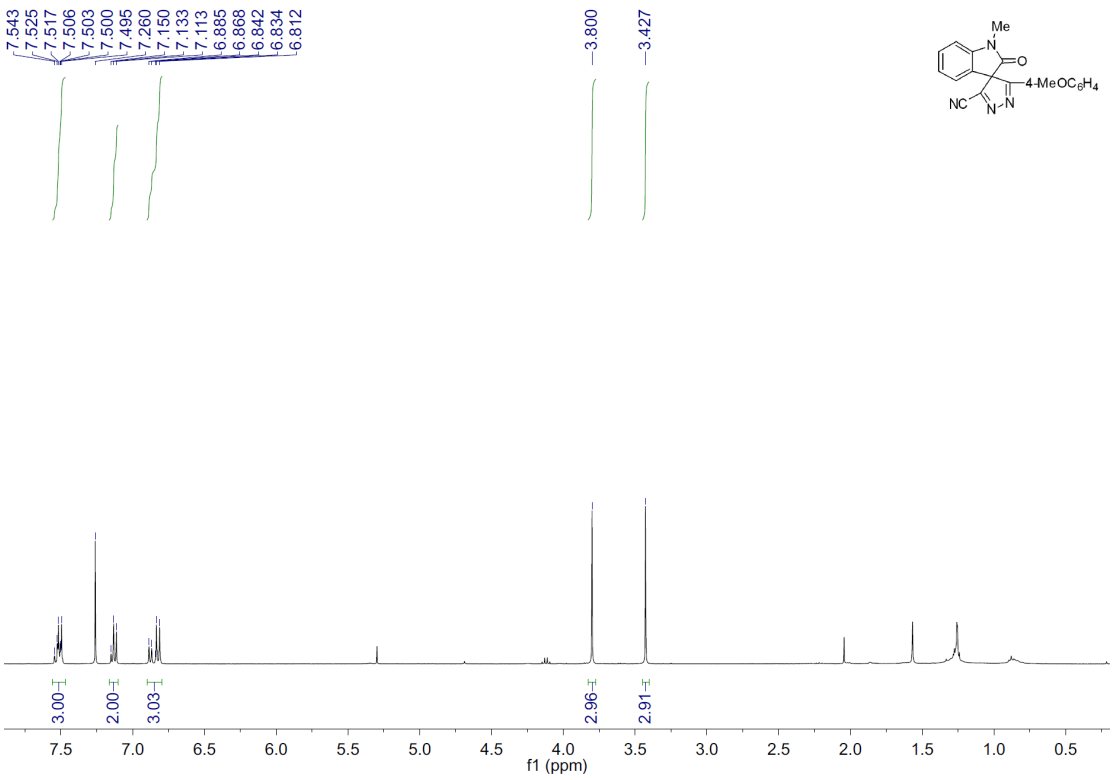


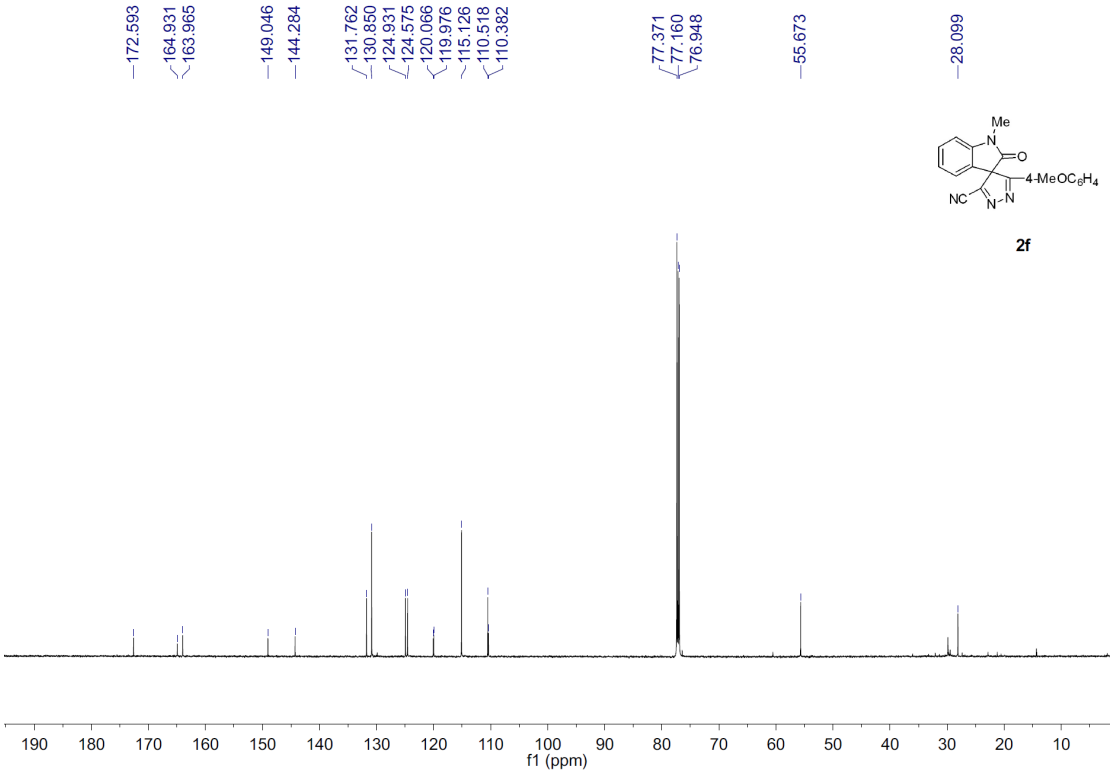


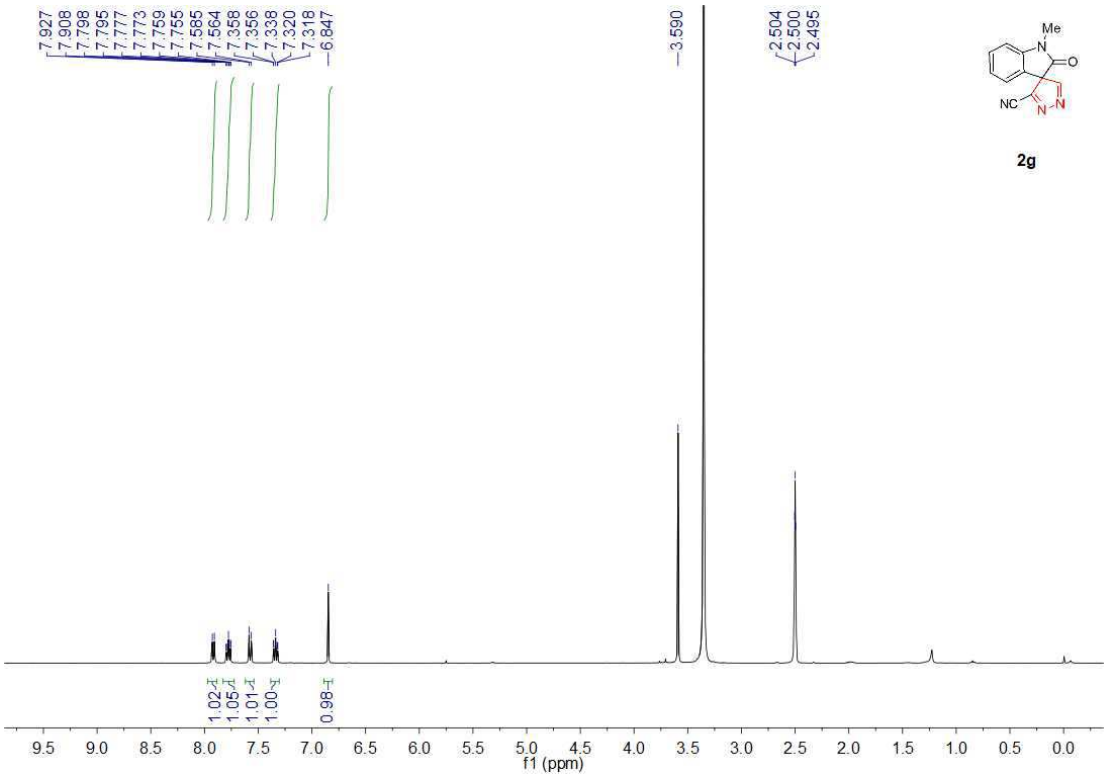
2e

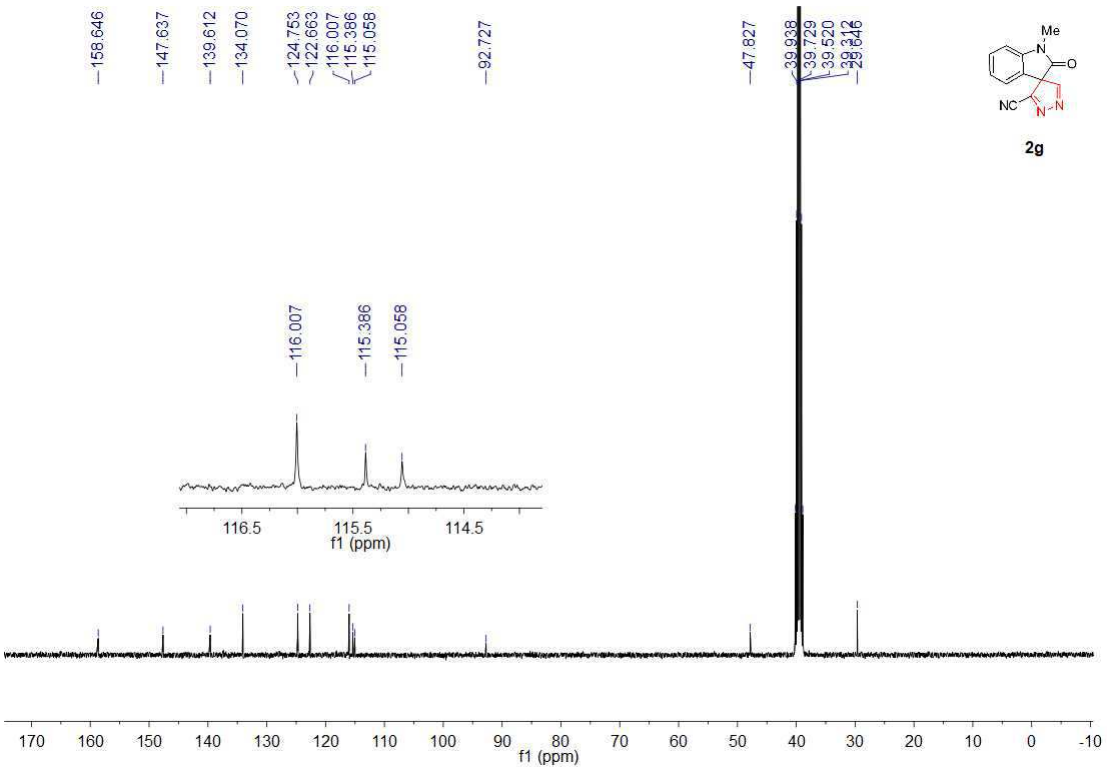


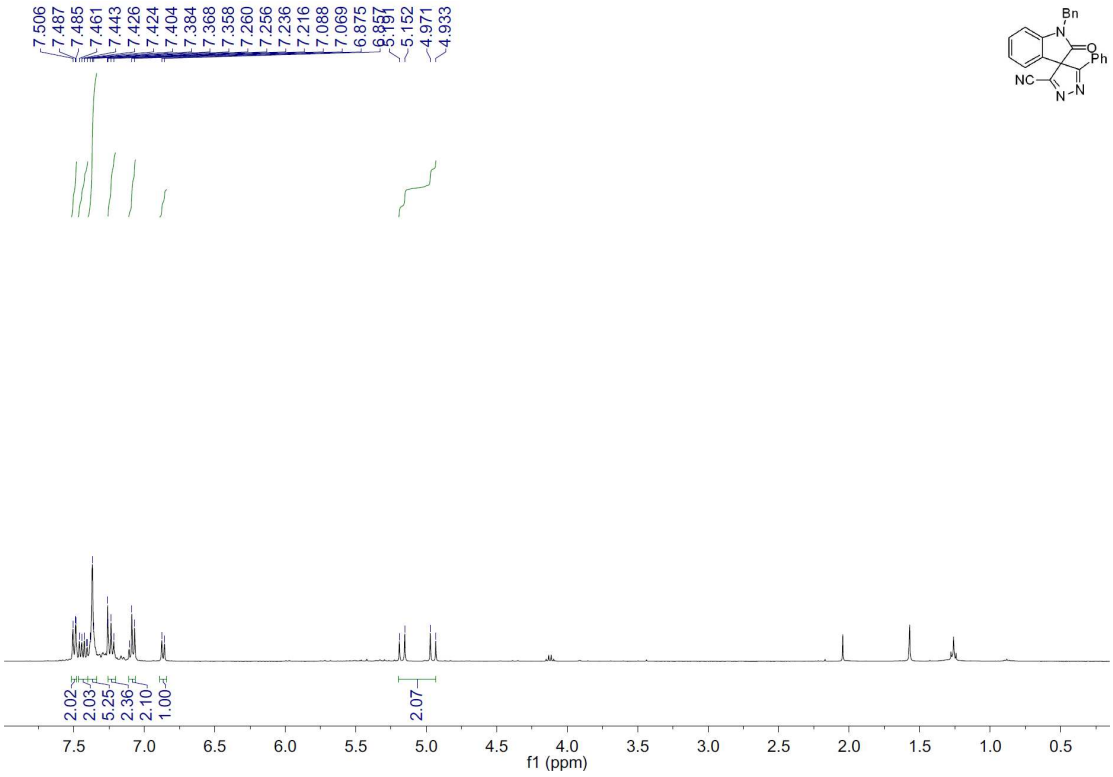

172.024
163.527
150.130
144.104
138.832
132.091
130.155
129.897
125.263
125.015
124.783
117.971
111.830
110.188
77.002
40.145
39.937
39.728
39.520
39.311
39.102
38.894
28.213
Me
N
O
Cl
NC
N-N
2e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

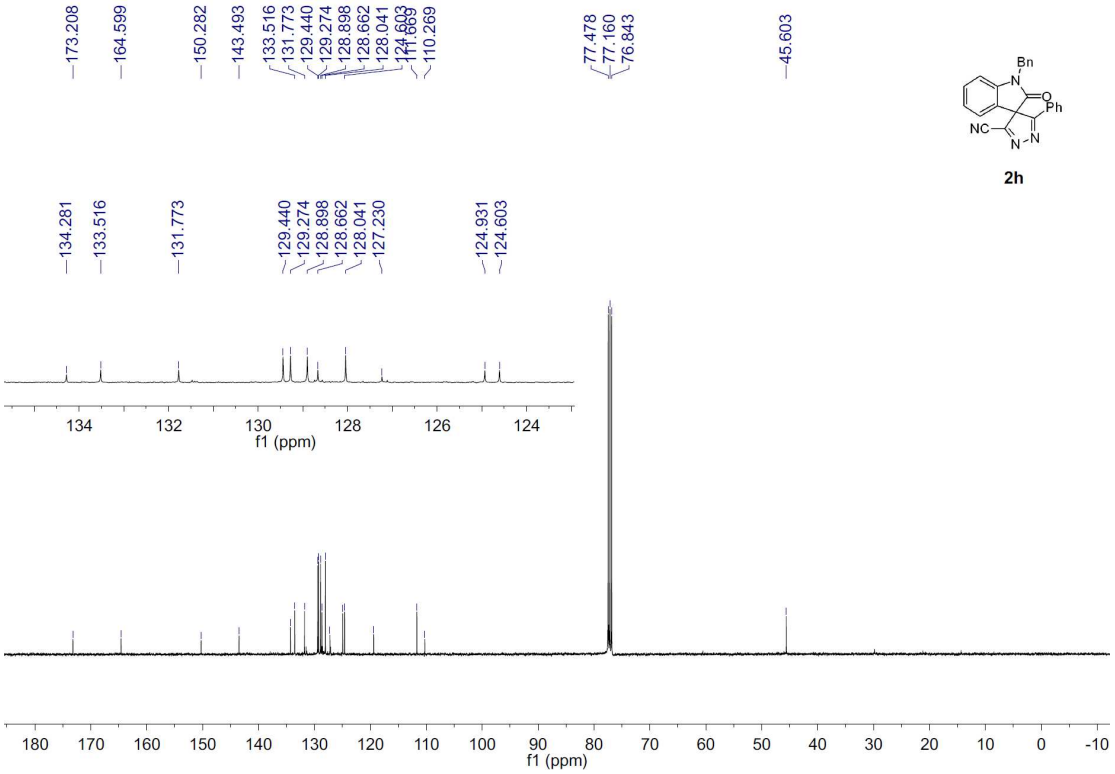

7.543
7.525
7.517
7.506
7.503
7.500
7.495
7.260
7.150
7.133
7.113
6.885
6.868
6.842
6.834
6.812
3.800
3.427
Me
N
O
4-MeOC6H4
NC
N-N
3.00
2.00
3.03
2.96
2.91
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

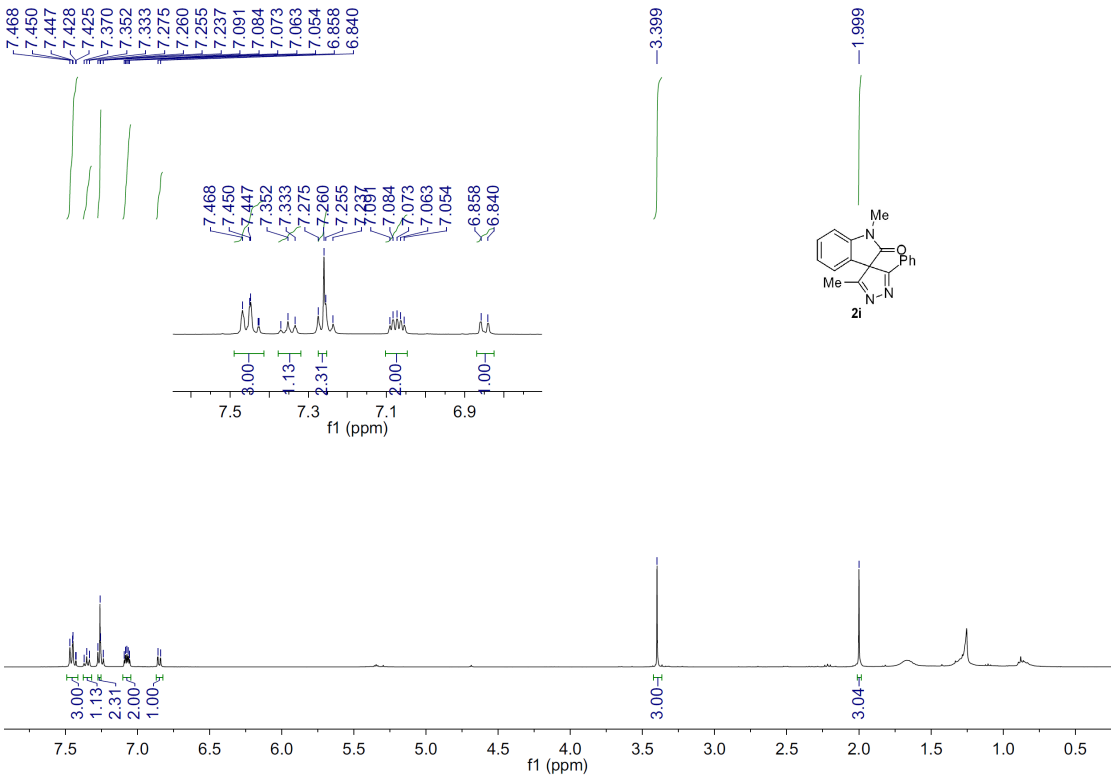

172.593
164.931
163.965
149.046
144.284
131.762
130.850
124.931
124.575
120.066
119.976
115.126
110.518
110.382
77.371
77.160
76.948
55.673
28.099
Me
N
O
4-MeOC6H4
NC
N
N
2f
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

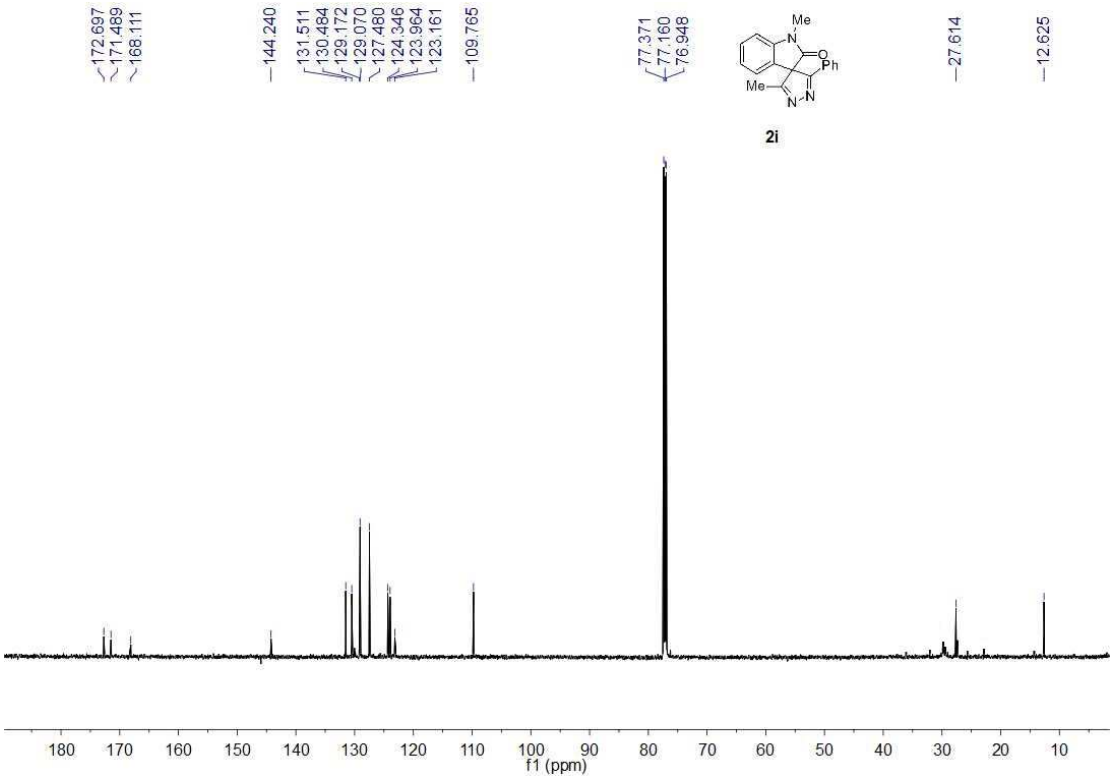

7.927
7.908
7.798
7.795
7.777
7.773
7.759
7.755
7.585
7.564
7.358
7.356
7.338
7.320
7.318
6.847
3.590
2.504
2.500
2.495
Me
N
O
NC
N
N
2g
1.02
1.05
1.01
1.00
0.98
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

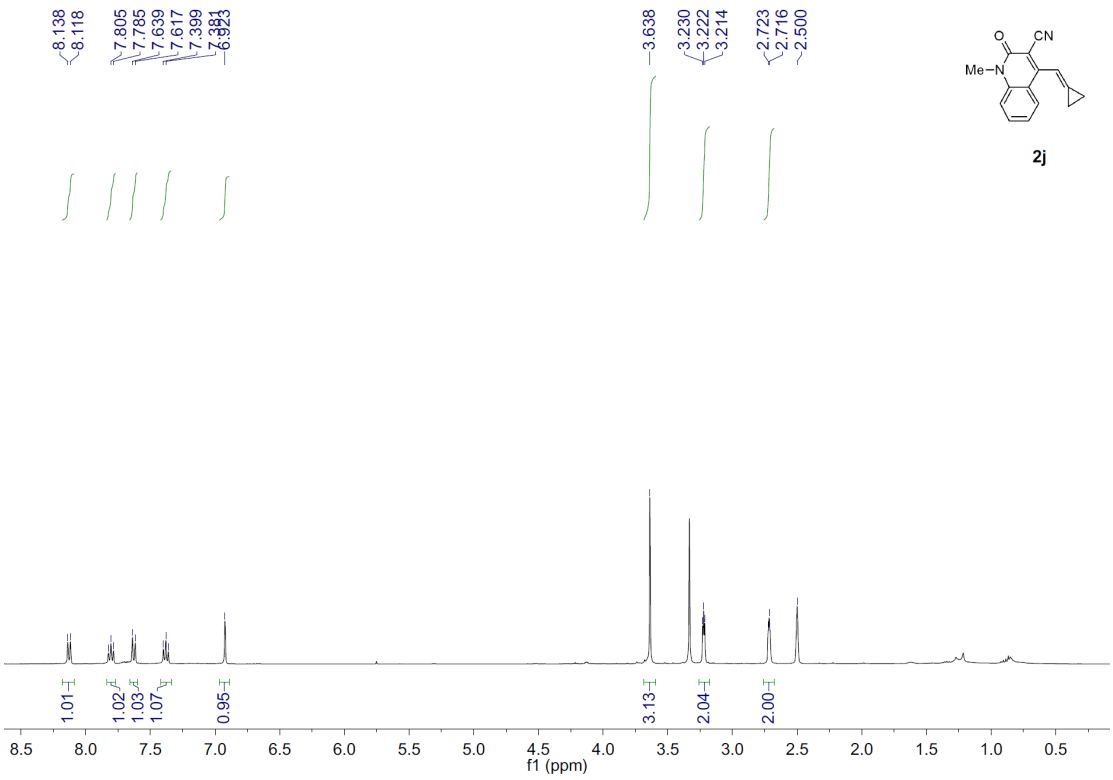

158.646
147.637
139.612
134.070
124.753
122.663
116.007
115.386
115.058
92.727
47.827
39.938
39.729
39.520
39.312
39.046
Me
O
NC
N
N
2g
116.007
115.386
115.058
116.5
115.5
114.5
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

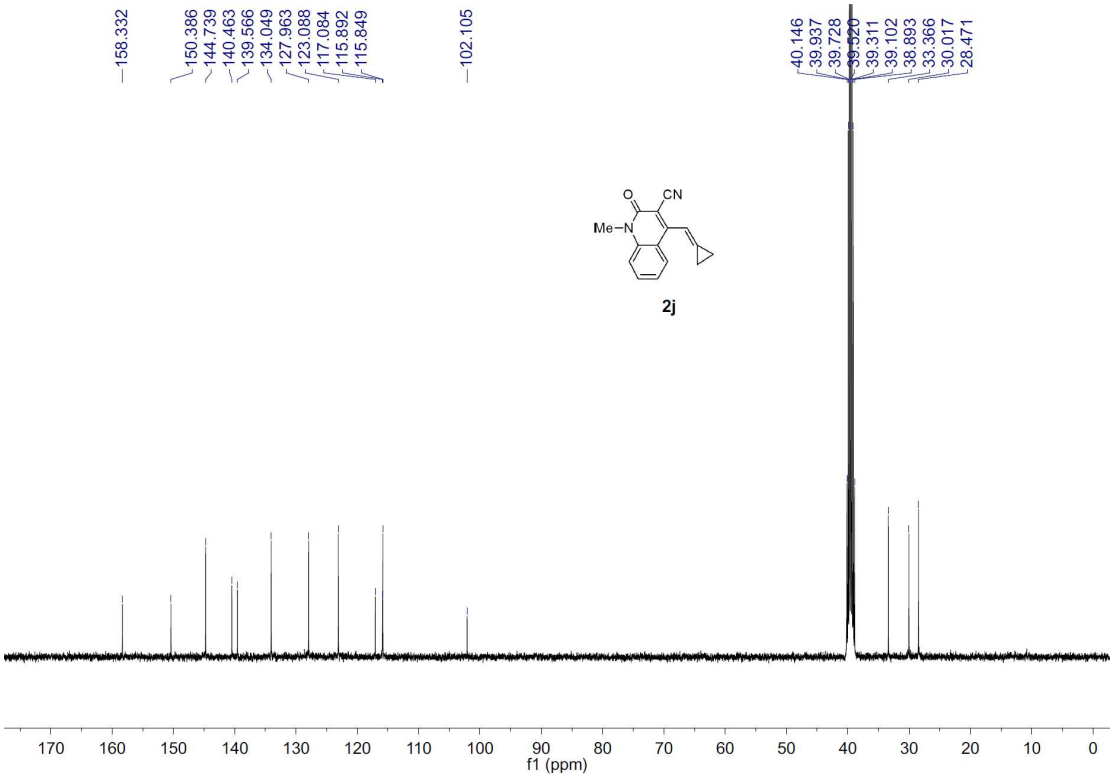

7.506
7.487
7.485
7.461
7.443
7.426
7.424
7.404
7.384
7.368
7.358
7.260
7.256
7.236
7.216
7.088
7.069
6.875
5.191
5.152
4.971
4.933
Bn
O
Ph
NC
N
N
2.02
2.03
5.25
2.36
2.10
1.00
2.07
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

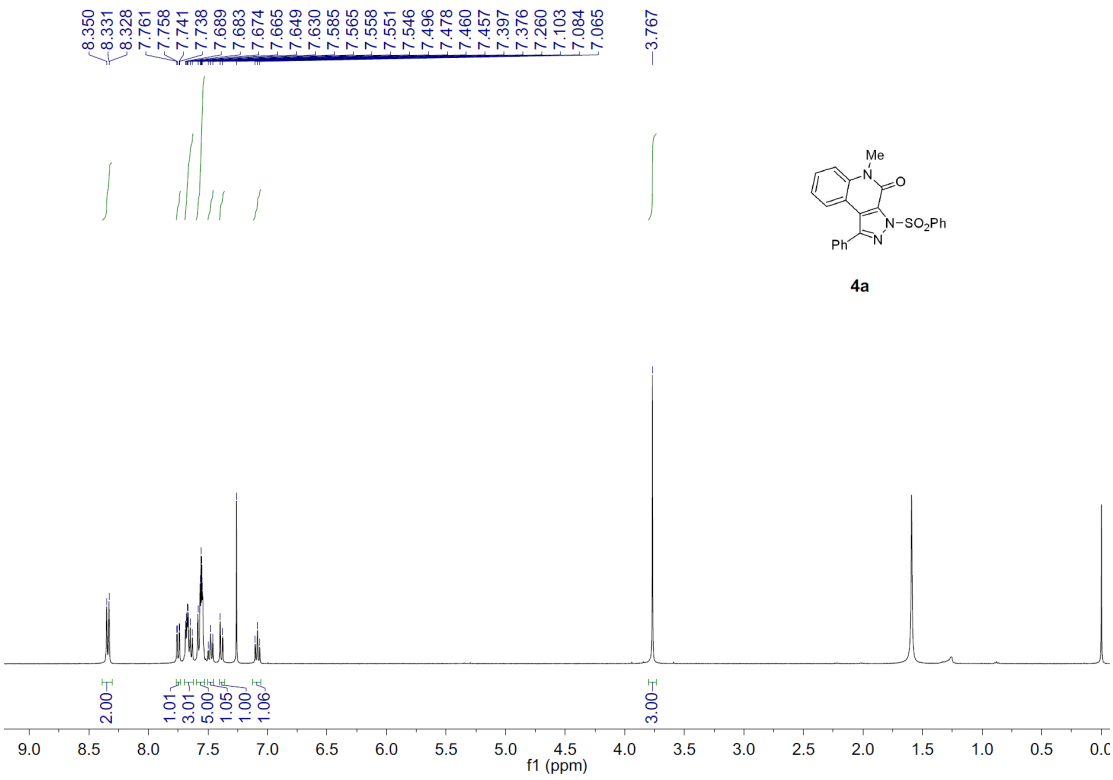

173.208
164.599
150.282
143.493
133.516
131.773
129.440
129.274
128.898
128.662
128.041
124.603
111.669
110.269
77.478
77.160
76.843
45.603
Bn
N
O
Ph
NC
N
N
2h
134.281
133.516
131.773
129.440
129.274
128.898
128.662
128.041
127.230
124.931
124.603
134
132
130
128
126
124
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

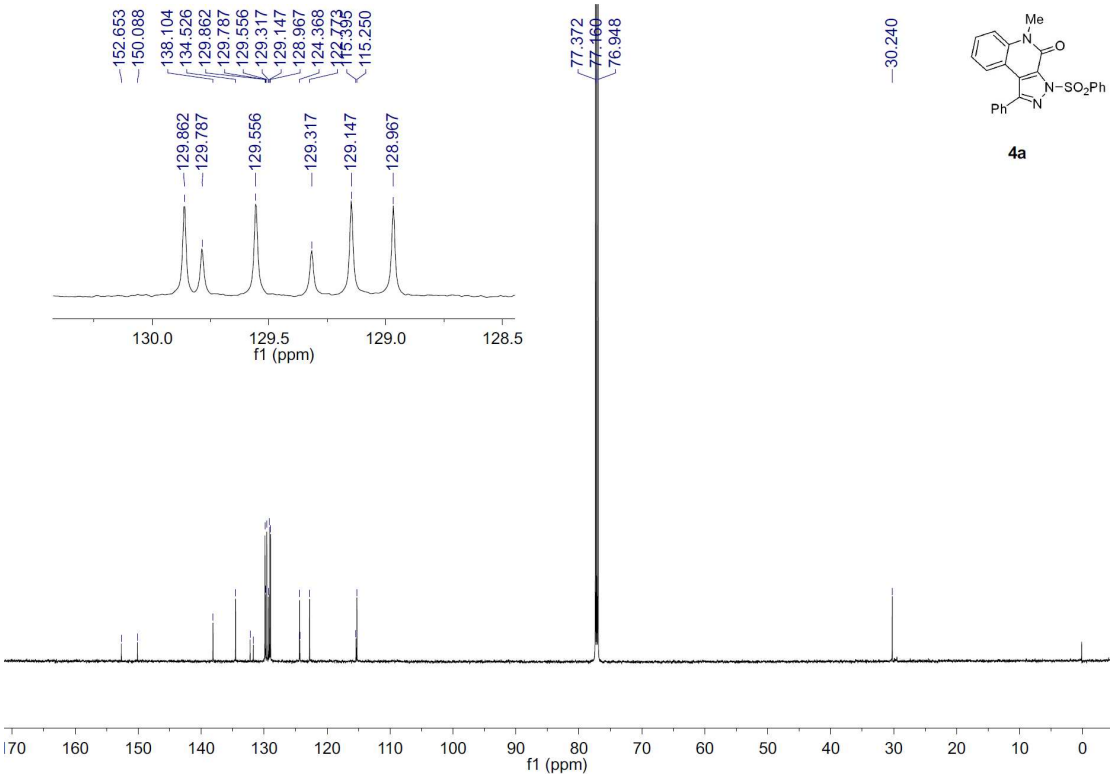

7.468
7.450
7.447
7.428
7.425
7.370
7.352
7.333
7.275
7.260
7.255
7.237
7.091
7.084
7.073
7.063
7.054
6.858
6.840
3.399
1.999
3.00
1.13
2.31
2.00
1.00
7.5
7.3
7.1
6.9
f1 (ppm)
Me
N
O
Ph
Me
N
N
2i
3.00
1.13
2.31
2.00
1.00
3.00
3.04
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

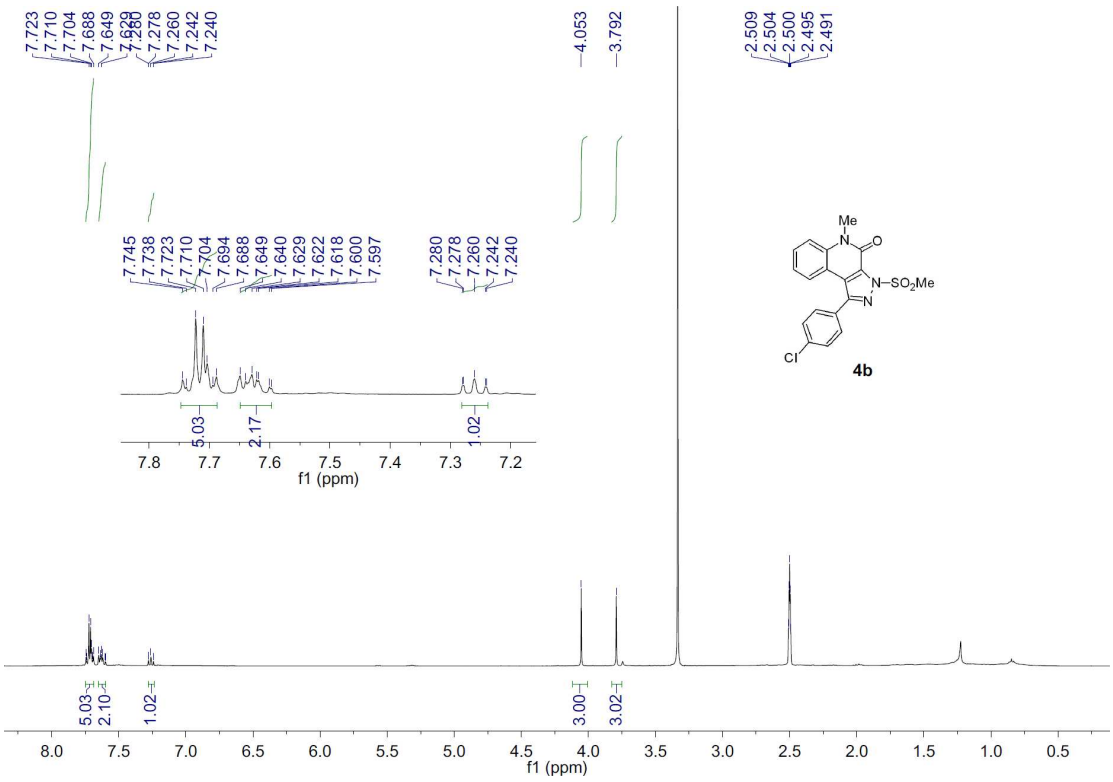

172.697
171.489
168.111
144.240
131.511
130.484
129.172
129.070
127.480
124.346
123.964
123.161
109.765
77.371
77.160
76.948
27.614
12.625
Me
N
O
Ph
Me
N
N
2i
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

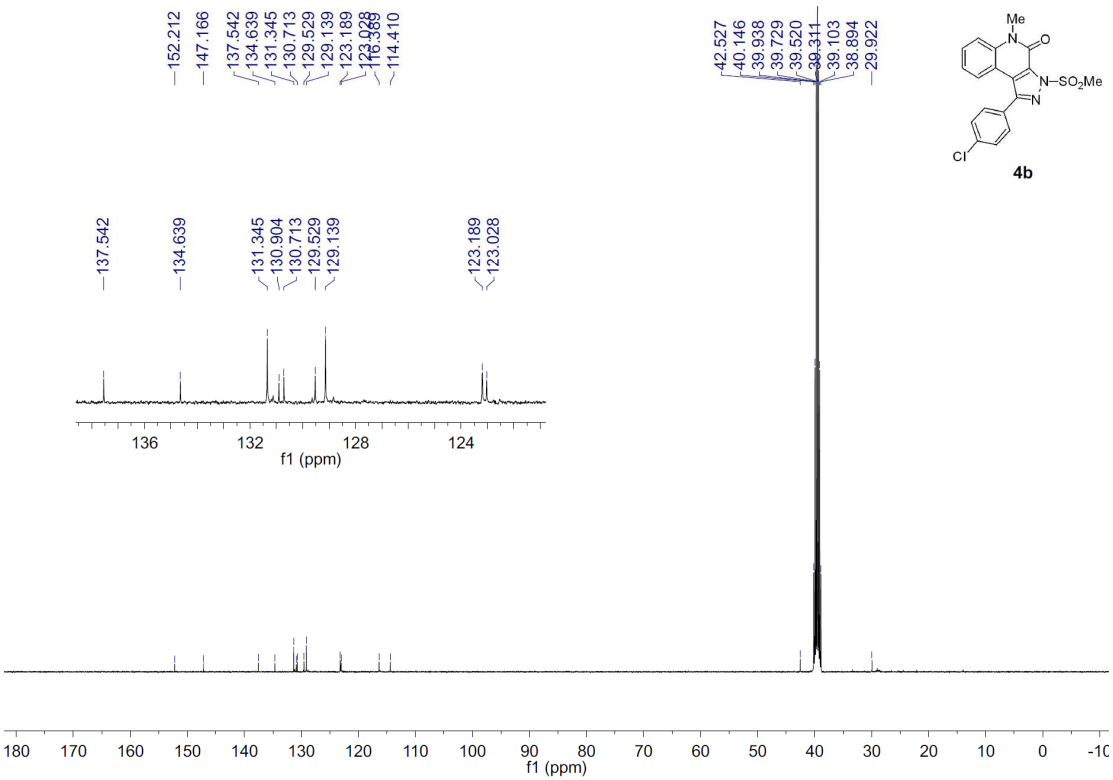

8.138
8.118
7.805
7.785
7.639
7.617
7.399
6.923
3.638
3.230
3.222
3.214
2.723
2.716
2.500
O
CN
Me
N
2j
1.01
1.02
1.03
1.07
0.95
3.13
2.04
2.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

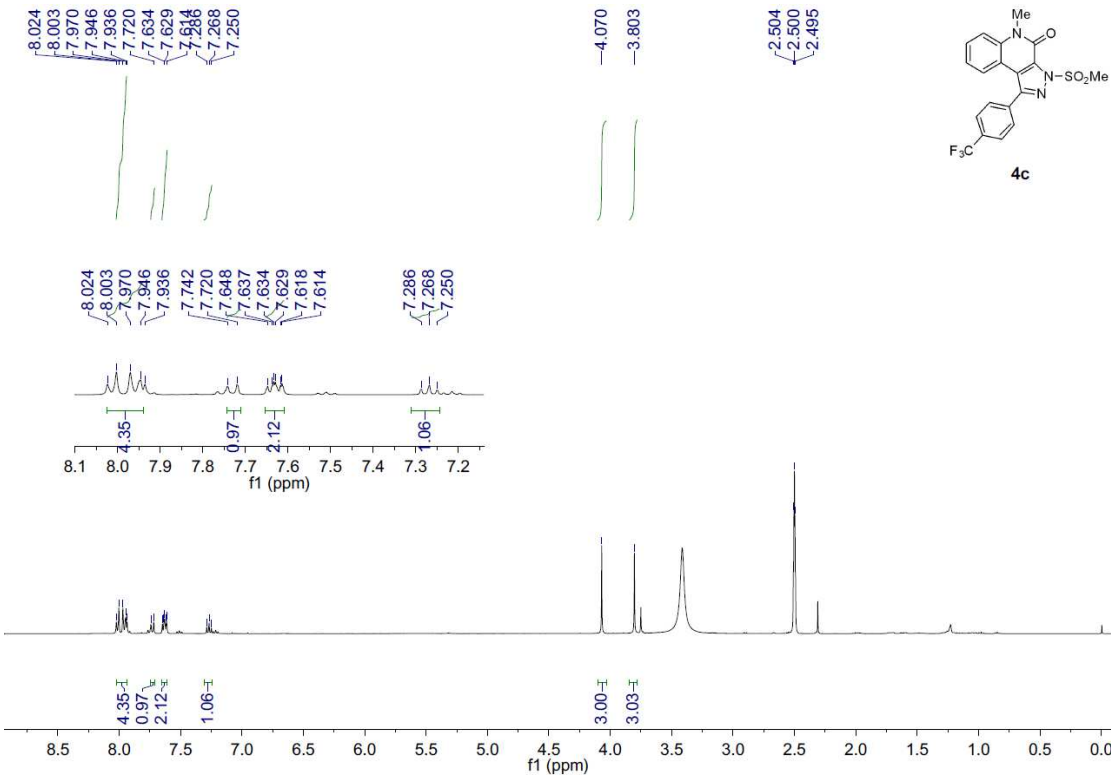

158.332
150.386
144.739
140.463
139.566
134.049
127.963
123.088
117.084
115.892
115.849
102.105
40.146
39.937
39.728
39.520
39.311
39.102
38.893
33.366
30.017
28.471
O
CN
Me–N
2j
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

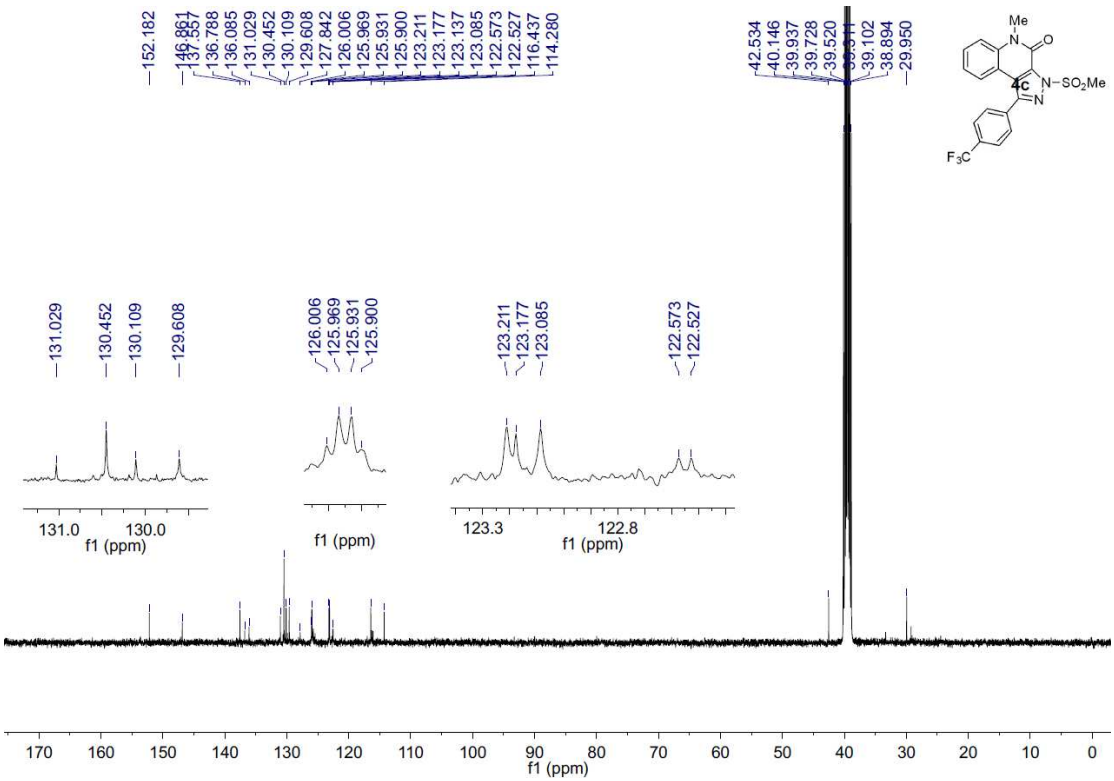

8.350
8.331
8.328
7.761
7.758
7.741
7.738
7.689
7.683
7.674
7.665
7.649
7.630
7.585
7.565
7.558
7.551
7.546
7.496
7.478
7.460
7.457
7.397
7.376
7.260
7.103
7.084
7.065
3.767
Me
N
O
N–SO2Ph
Ph
N
4a
2.00
1.01
3.01
5.00
1.05
1.00
1.06
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

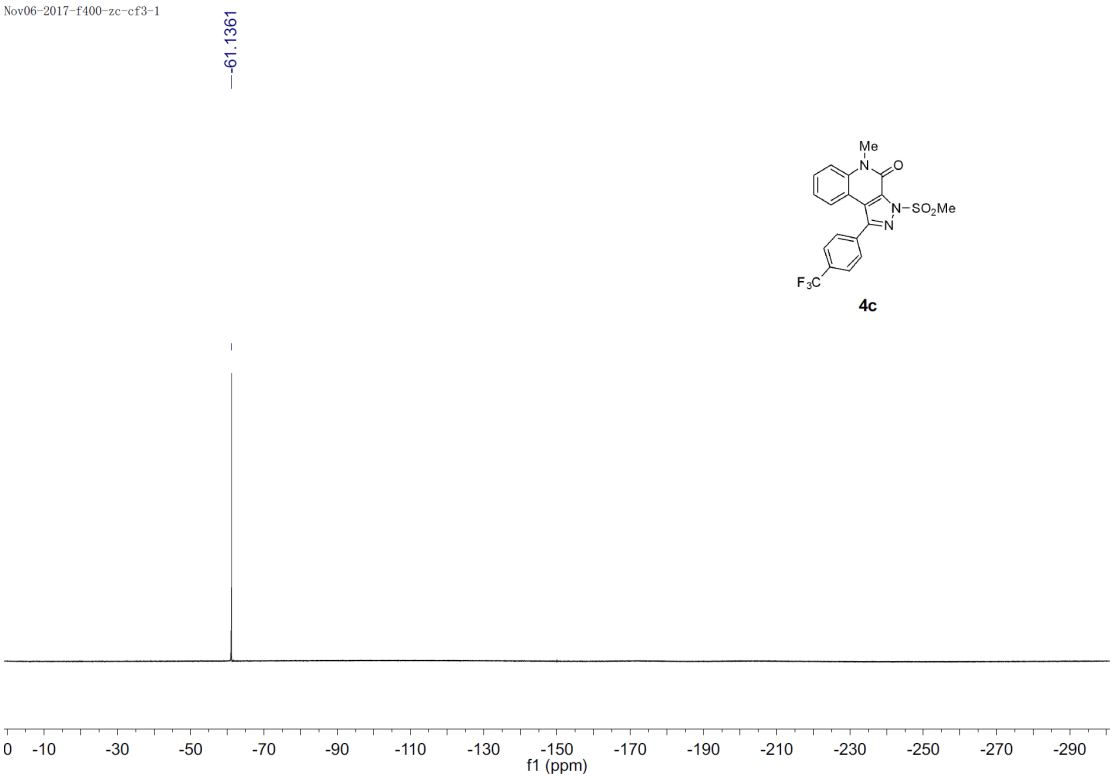

152.653
150.088
138.104
134.526
129.862
129.787
129.556
129.317
129.147
128.967
124.368
122.773
115.395
115.250
77.372
77.160
76.948
30.240
Me
N
O
N–SO2Ph
Ph
N
4a
129.862
129.787
129.556
129.317
129.147
128.967
130.0
129.5
129.0
128.5
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

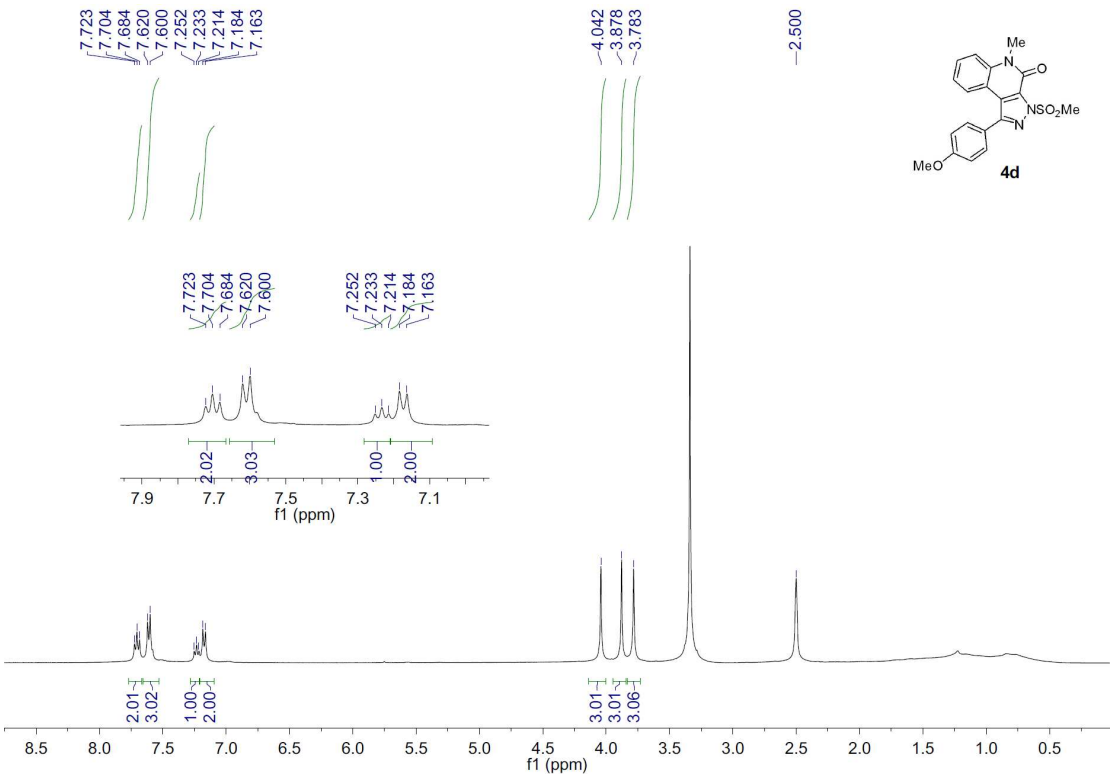

7.723
7.710
7.704
7.688
7.649
7.629
7.278
7.260
7.242
7.240
4.053
3.792
2.509
2.504
2.500
2.495
2.491
7.745
7.738
7.723
7.710
7.704
7.694
7.688
7.649
7.640
7.629
7.622
7.618
7.600
7.597
7.280
7.278
7.260
7.242
7.240
5.03
2.17
1.02
7.8
7.7
7.6
7.5
7.4
7.3
7.2
f1 (ppm)
Me
N
O
N–SO2Me
N
Cl
4b
5.03
2.10
1.02
3.00
3.02
8.0
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
f1 (ppm)

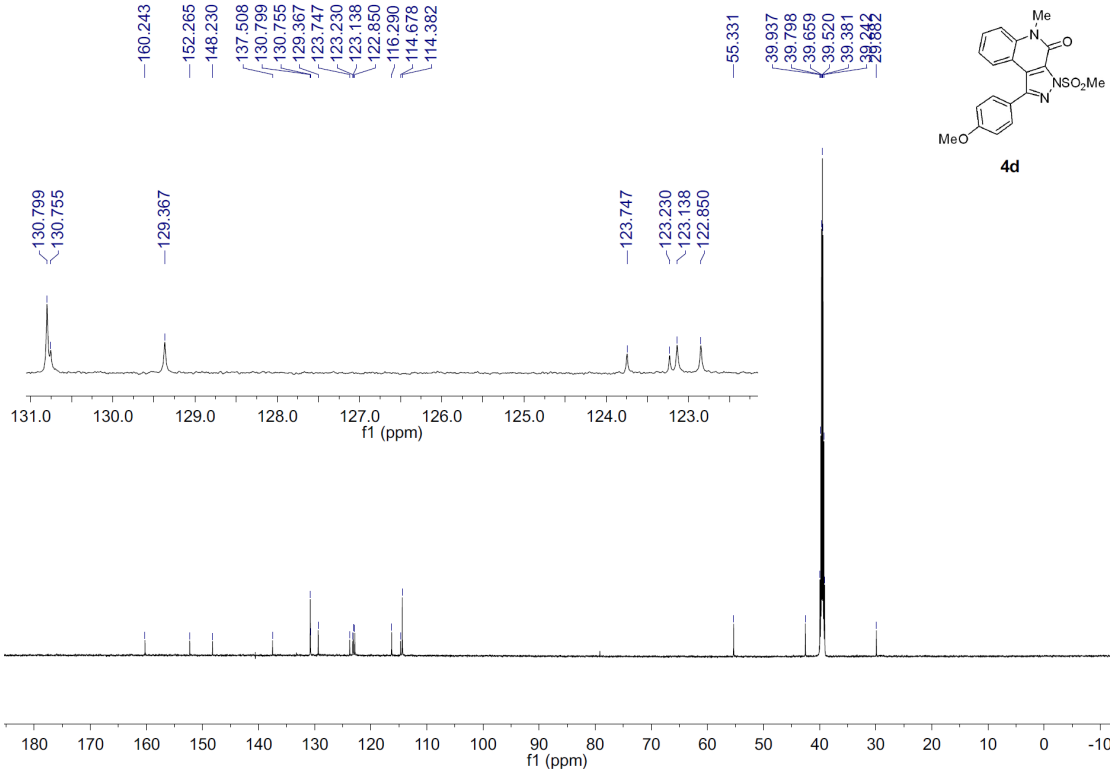

152.212
147.166
137.542
134.639
131.345
130.713
129.529
129.139
123.189
123.028
114.410
42.527
40.146
39.938
39.729
39.520
39.311
39.103
38.894
29.922
Me
N
O
N–SO2Me
N
Cl
4b
137.542
134.639
131.345
130.904
130.713
129.529
129.139
123.189
123.028
136
132
128
124
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

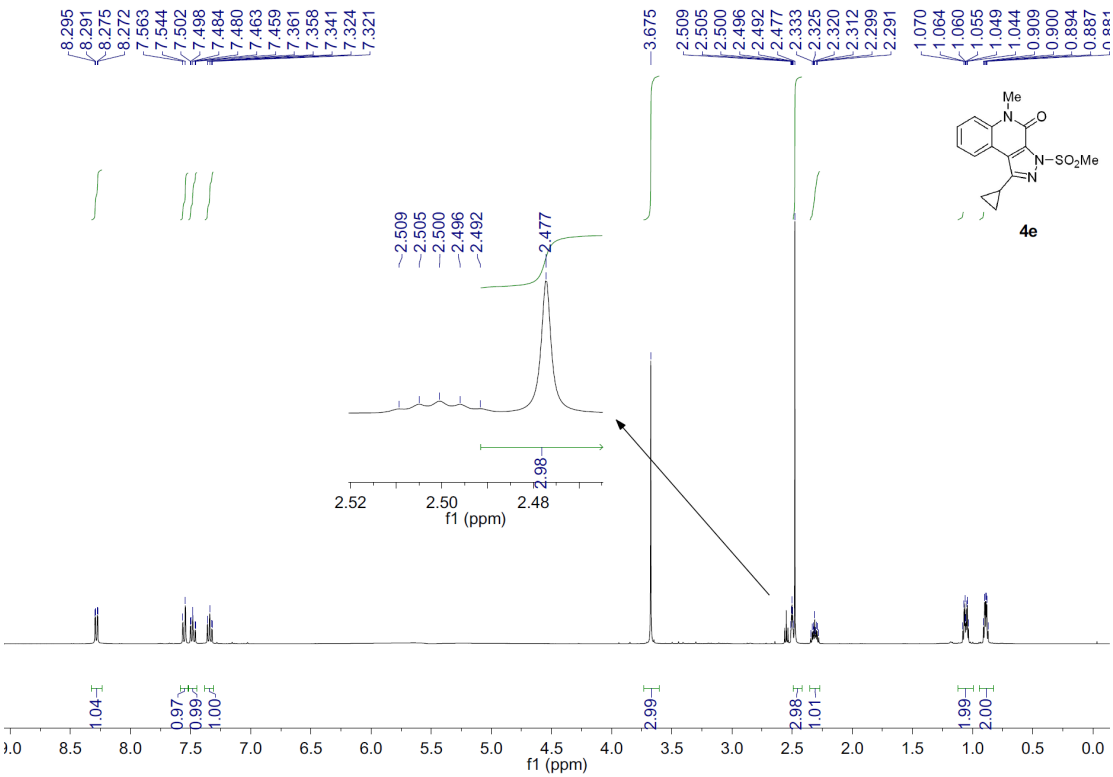

8.024
8.003
7.970
7.946
7.936
7.720
7.634
7.629
7.614
7.286
7.268
7.250
4.070
3.803
2.504
2.500
2.495
Me
N
O
N–SO2Me
N
F3C
4c
8.024
8.003
7.970
7.946
7.936
7.742
7.720
7.648
7.637
7.634
7.629
7.618
7.614
7.286
7.268
7.250
4.35
0.97
2.12
1.06
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
f1 (ppm)
4.35
0.97
2.12
1.06
3.00
3.03
8.5
8.0
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
0.0
f1 (ppm)

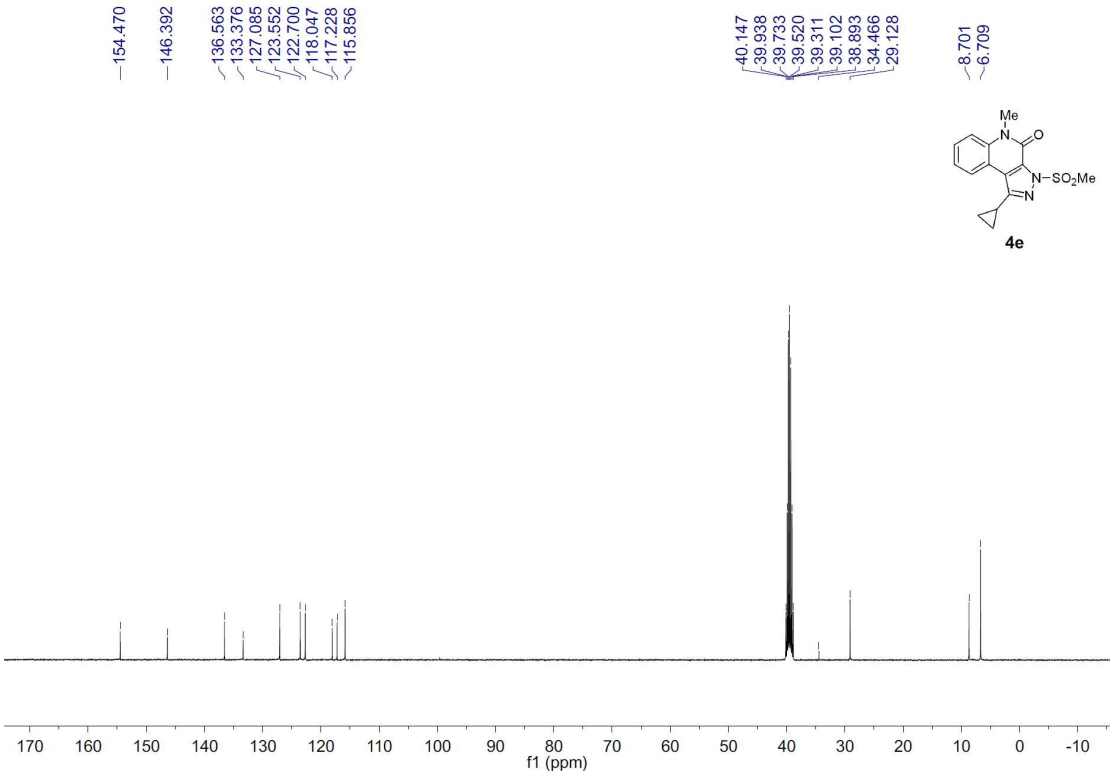

152.182
146.861
137.557
136.788
136.085
131.029
130.452
130.109
129.608
127.842
126.006
125.969
125.931
125.900
123.211
123.177
123.137
123.085
122.573
122.527
116.437
114.280
42.534
40.146
39.937
39.728
39.520
39.311
39.102
38.894
29.950
Me
N
O
N–SO2Me
N
4c
F3C
131.029
130.452
130.109
129.608
126.006
125.969
125.931
125.900
123.211
123.177
123.085
122.573
122.527
131.0
130.0
f1 (ppm)
f1 (ppm)
123.3
122.8
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

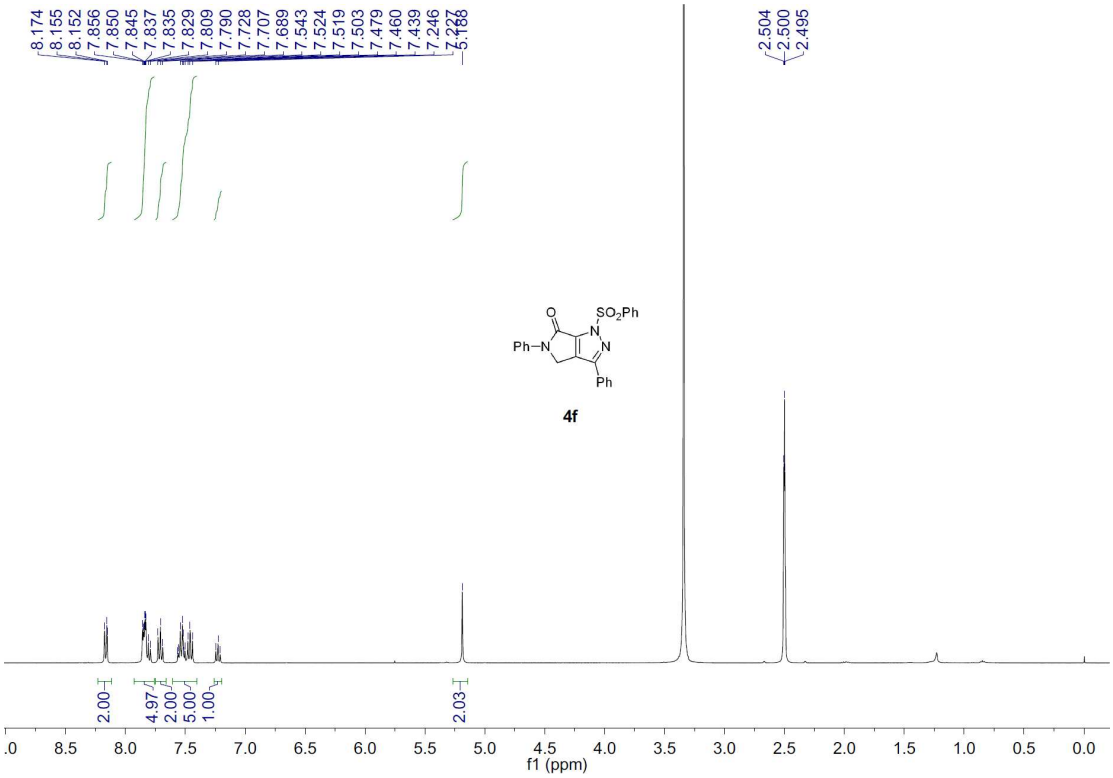

Nov06-2017-f400-zc-cf3-1
-61.1361
Me
N
O
N–SO2Me
N
F3C
4c
0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250 -270 -290
f1 (ppm)

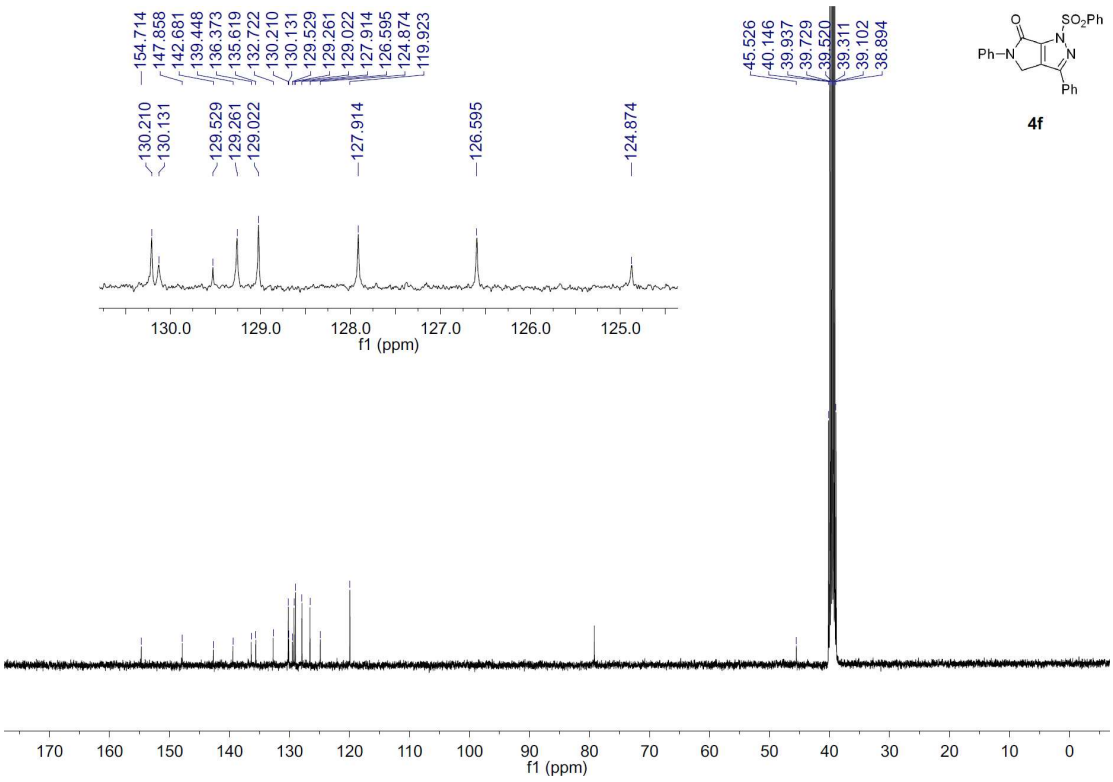

7.723
7.704
7.684
7.620
7.600
7.252
7.233
7.214
7.184
7.163
4.042
3.878
3.783
2.500
Me
N
O
NSO2Me
N
MeO
4d
2.02
3.03
1.00
2.00
f1 (ppm)
2.01
3.02
1.00
2.00
3.01
3.01
3.06
f1 (ppm)

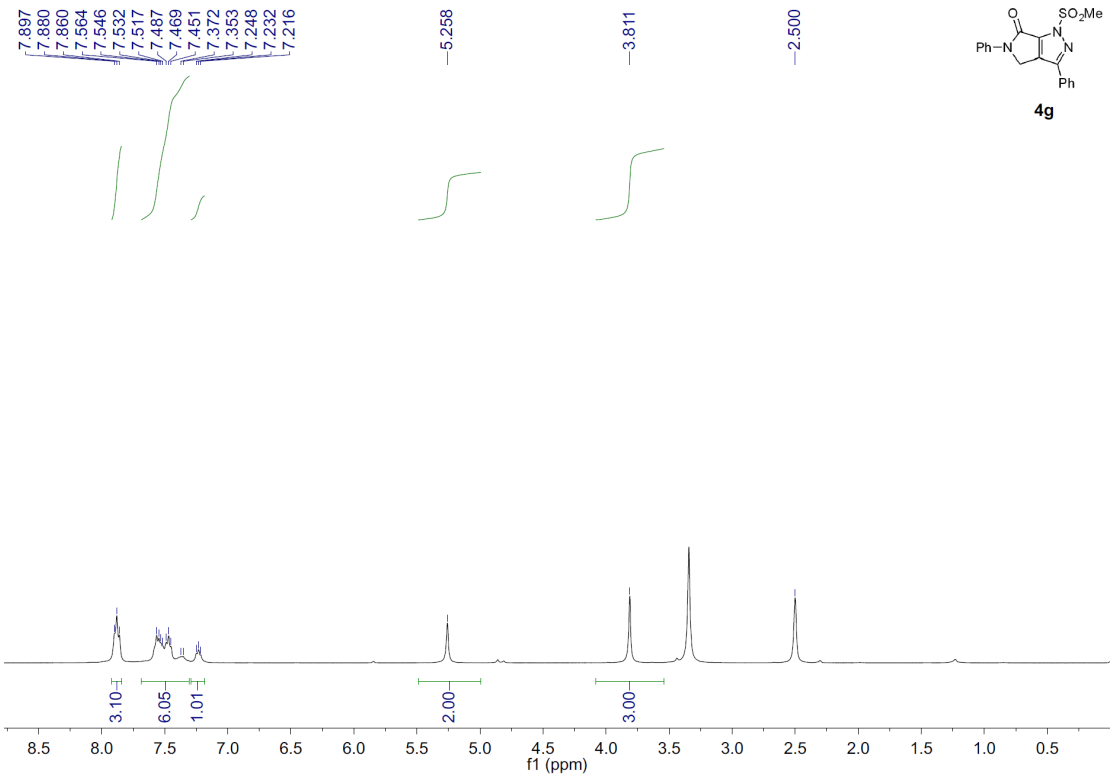

160.243
152.265
148.230
137.508
130.799
130.755
129.367
123.747
123.230
123.138
122.850
116.290
114.678
114.382
55.331
39.937
39.798
39.659
39.520
39.381
Me
N
O
NSO2Me
N
MeO
4d
130.799
130.755
129.367
123.747
123.230
123.138
122.850
f1 (ppm)
f1 (ppm)

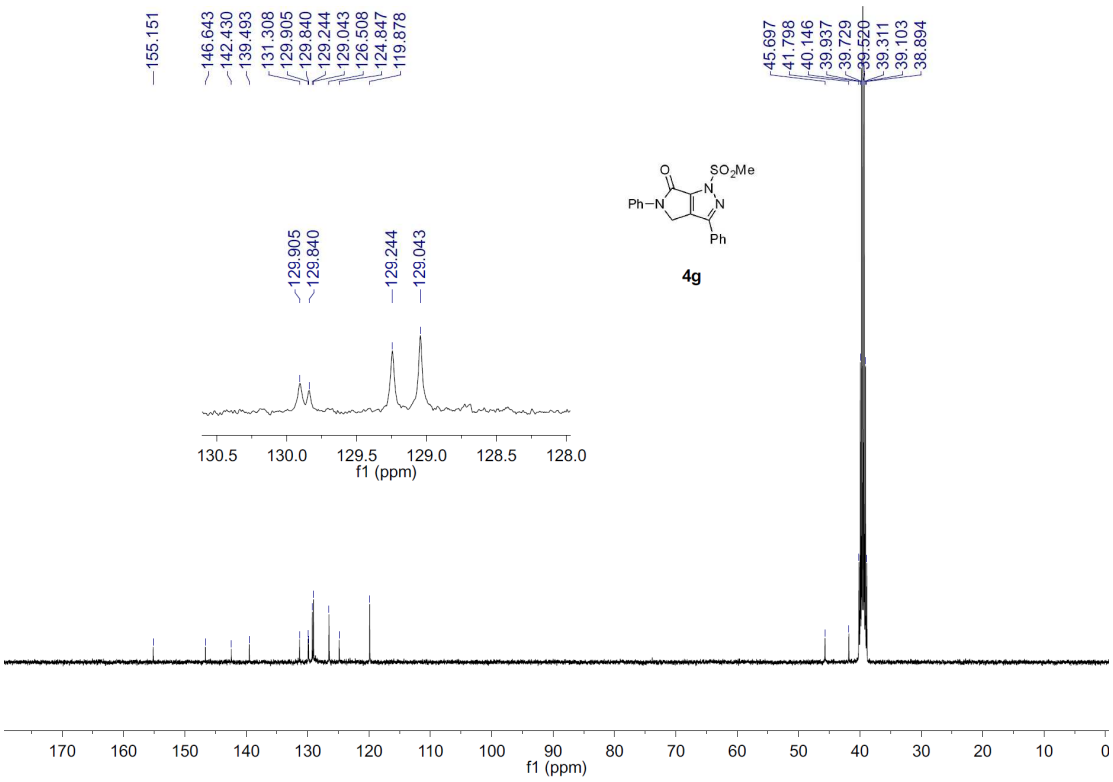

8.295
8.291
8.275
8.272
7.563
7.544
7.502
7.498
7.484
7.480
7.463
7.459
7.361
7.358
7.341
7.324
7.321
3.675
2.509
2.505
2.500
2.496
2.492
2.477
2.333
2.325
2.320
2.312
2.299
2.291
1.070
1.064
1.060
1.055
1.049
1.044
0.909
0.900
0.894
0.887
Me
N
O
N–SO2Me
N
4e
2.509
2.505
2.500
2.496
2.492
2.477
2.98
2.52
2.50
2.48
f1 (ppm)
1.04
0.97
0.99
1.00
2.99
2.98
1.01
1.99
2.00
8.5
8.0
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
0.0
f1 (ppm)

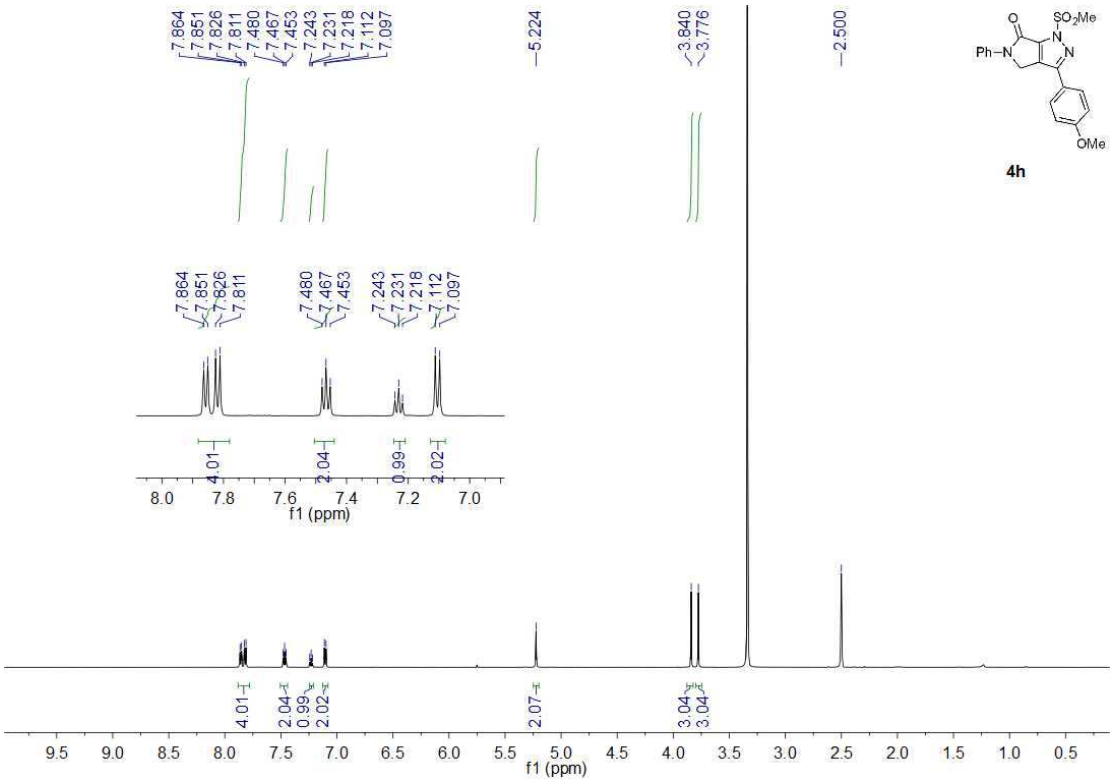

154.470
146.392
136.563
133.376
127.085
123.552
122.700
118.047
117.228
115.856
40.147
39.938
39.733
39.520
39.311
39.102
38.893
34.466
29.128
8.701
6.709
Me
N
O
N–SO2Me
N
4e
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

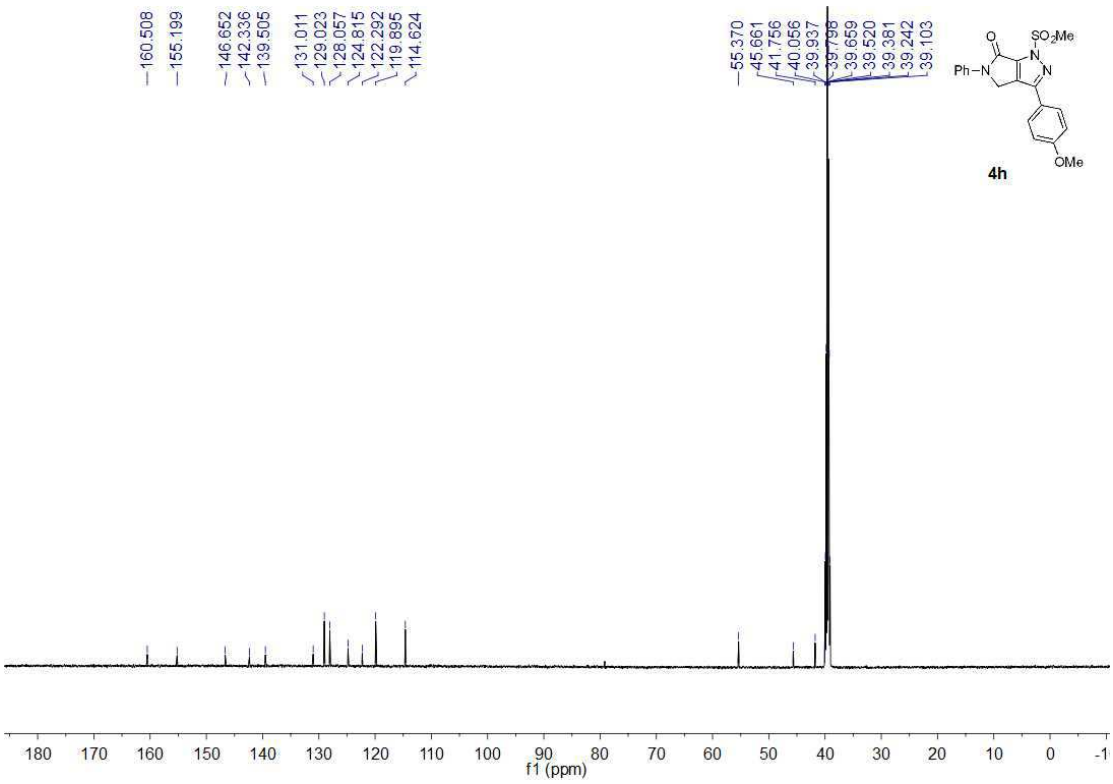

8.174
8.155
8.152
7.856
7.850
7.845
7.837
7.835
7.829
7.809
7.790
7.728
7.707
7.689
7.543
7.524
7.519
7.503
7.479
7.460
7.439
7.246
5.168
2.504
2.500
2.495
O
SO2Ph
Ph–N
N
N
Ph
4f
2.00
4.97
2.00
5.00
1.00
2.03
f1 (ppm)

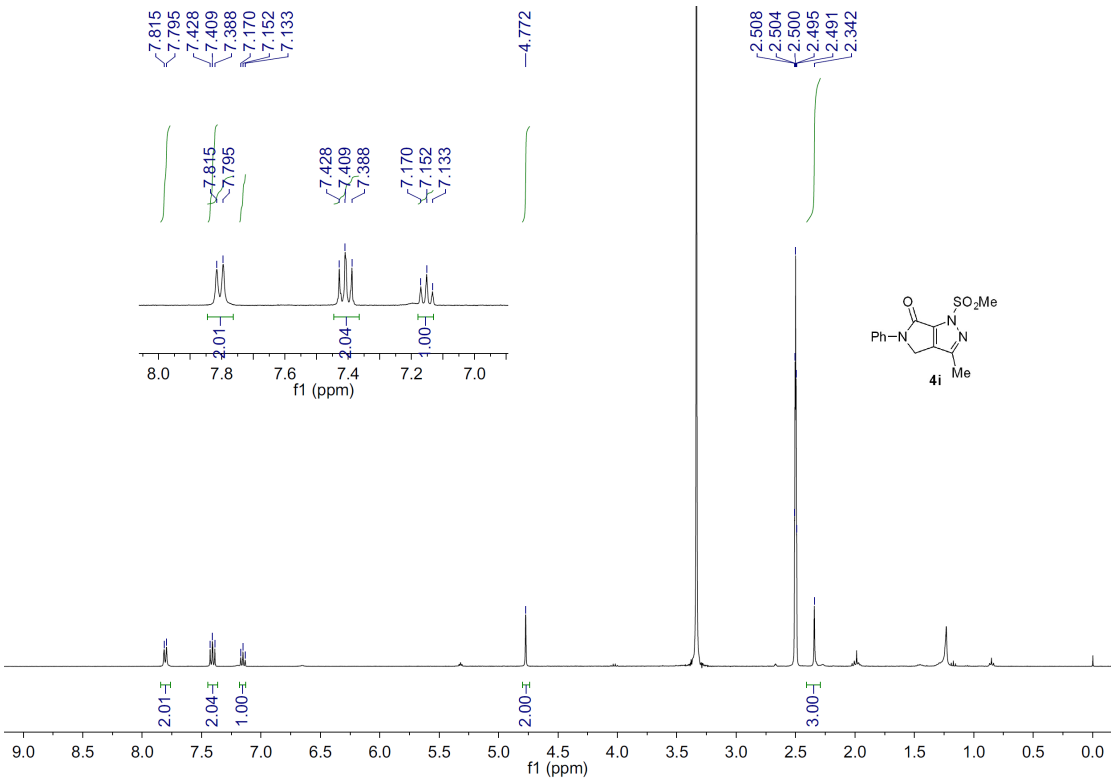

154.714
147.858
142.681
139.448
136.373
135.619
132.722
130.210
130.131
129.529
129.261
129.022
127.914
126.595
124.874
119.923
45.526
40.146
39.937
39.729
39.520
39.311
39.102
38.894
O
SO2Ph
Ph–N
N
N
Ph
4f
f1 (ppm)

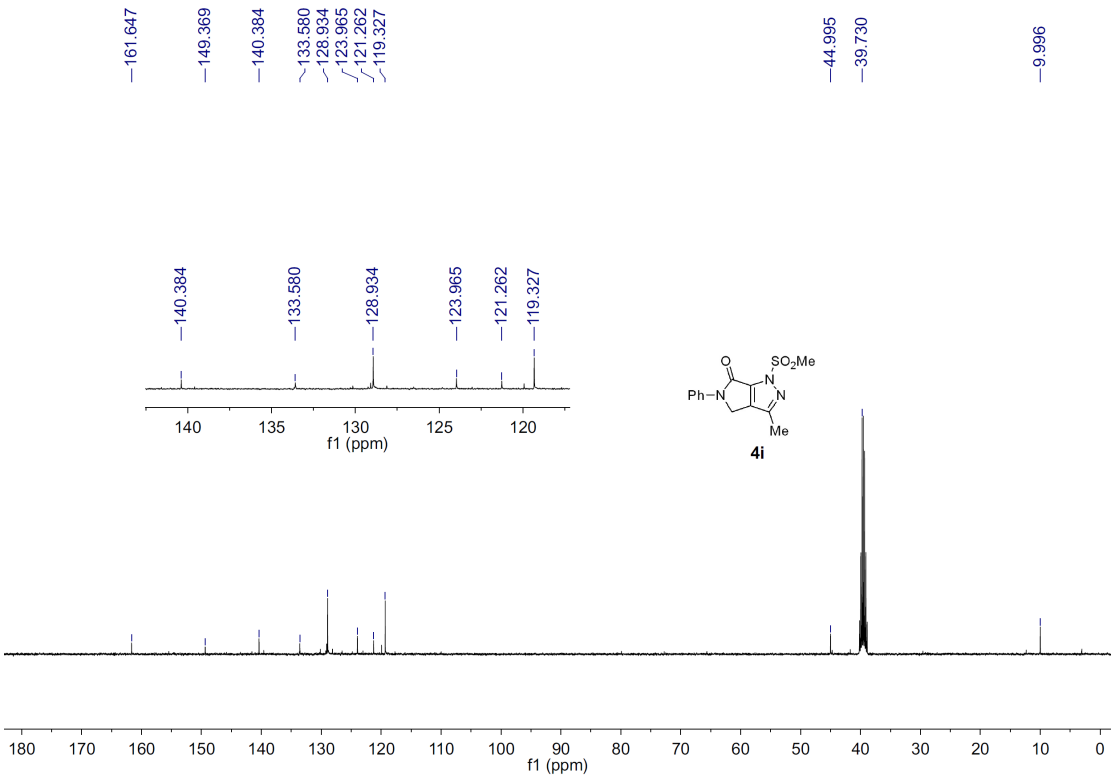

7.897
7.880
7.860
7.564
7.546
7.532
7.517
7.487
7.469
7.451
7.372
7.353
7.248
7.232
7.216
5.258
3.811
2.500
4g
3.10
6.05
1.01
2.00
3.00
f1 (ppm)

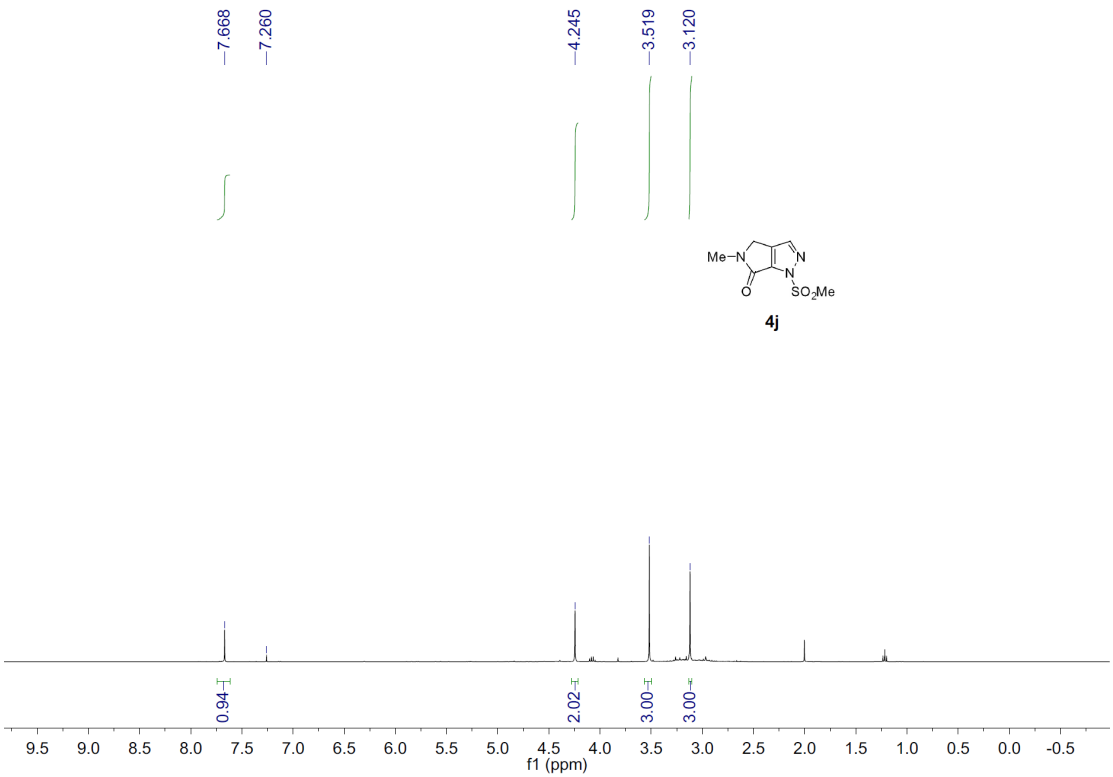

155.151
146.643
142.430
139.493
131.308
129.905
129.840
129.244
129.043
126.508
124.847
119.878
45.697
41.798
40.146
39.937
39.729
39.520
39.311
39.103
38.894
129.905
129.840
129.244
129.043
4g
f1 (ppm)
f1 (ppm)

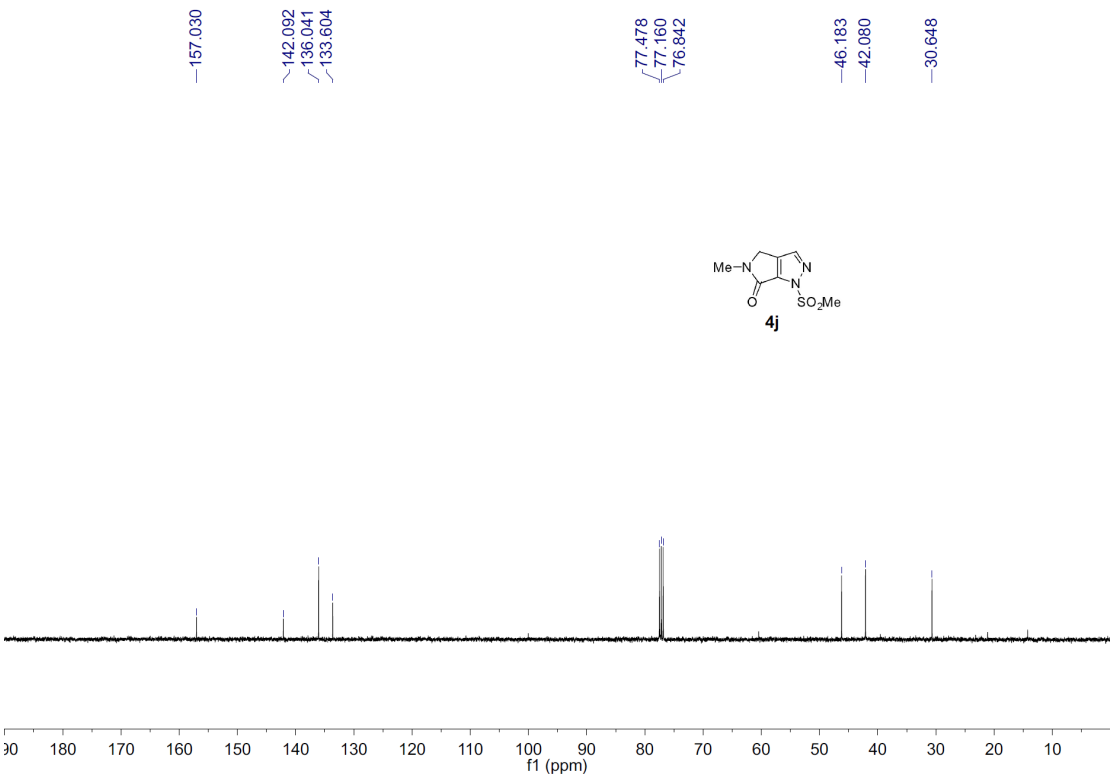

7.864
7.851
7.826
7.811
7.480
7.467
7.453
7.243
7.231
7.218
7.112
7.097
5.224
3.840
3.776
2.500
4.01
2.04
0.99
2.02
2.07
3.04
3.04
f1 (ppm)
4h

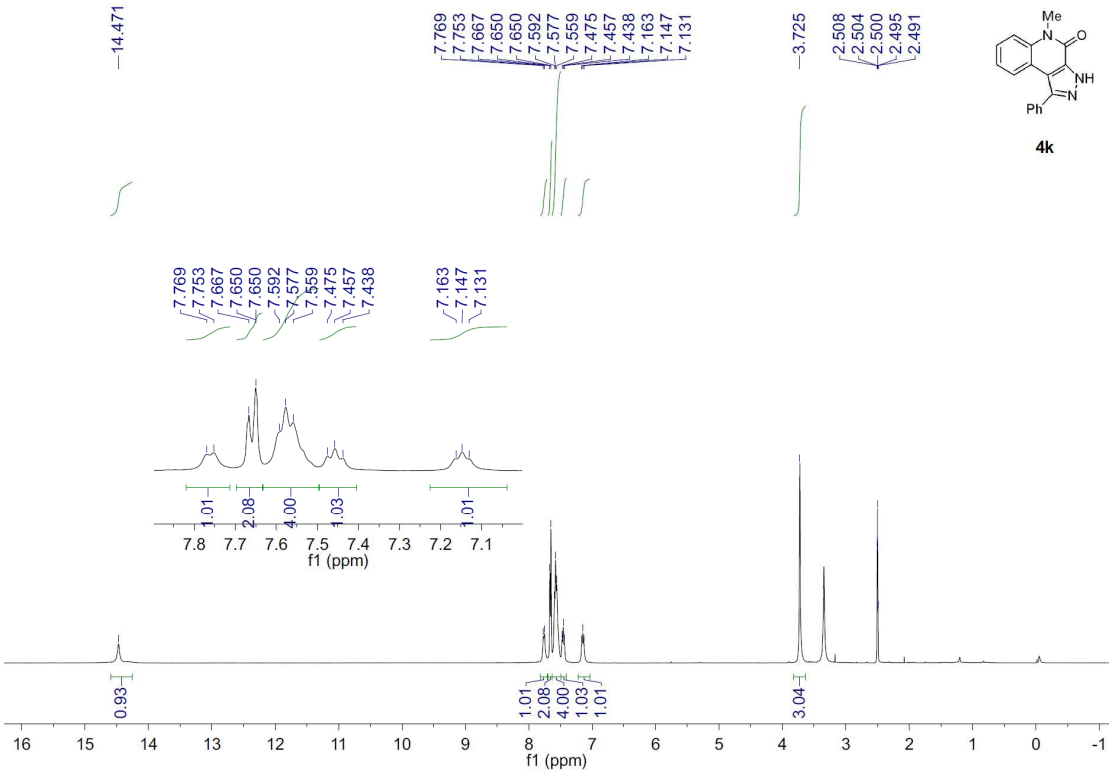

160.508
155.199
146.652
142.336
139.505
131.011
129.023
128.057
124.815
122.292
119.895
114.624
55.370
45.661
41.756
40.056
39.937
39.798
39.659
39.520
39.381
39.242
39.103
f1 (ppm)
4h

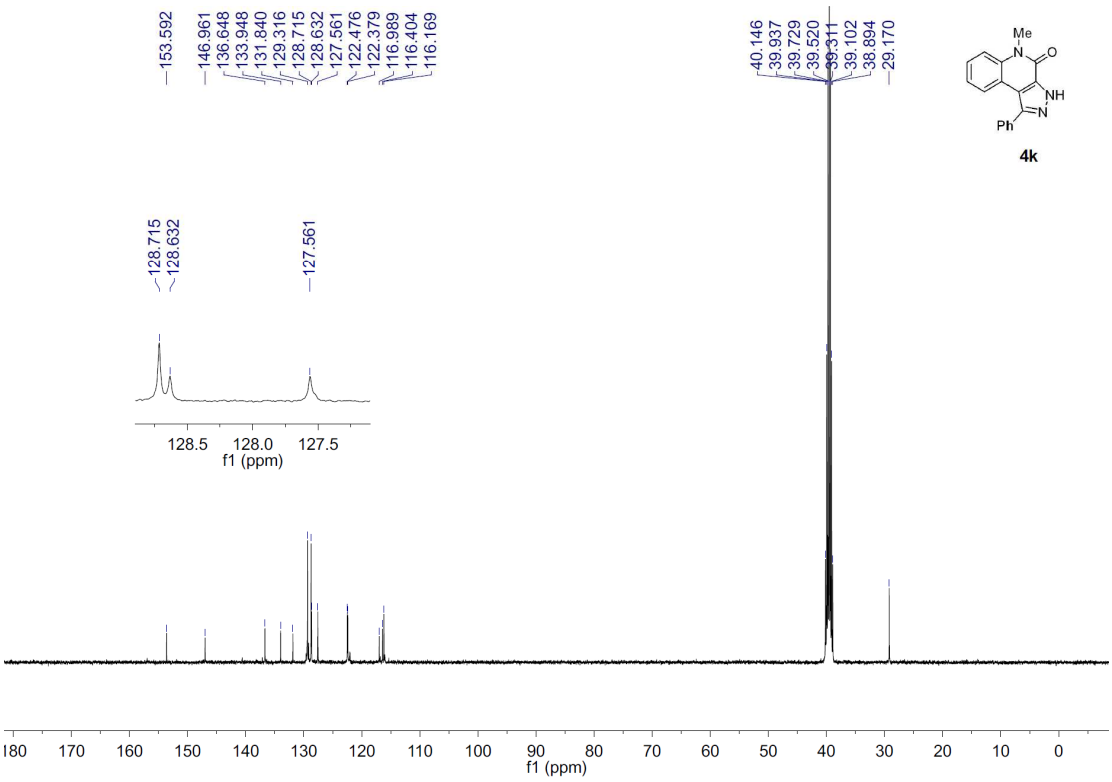

7.815
7.795
7.428
7.409
7.388
7.170
7.152
7.133
4.772
2.508
2.504
2.500
2.495
2.491
2.342
2.01
2.04
1.00
2.00
3.00
f1 (ppm)
SO2Me
Ph
N
O
Me
4i

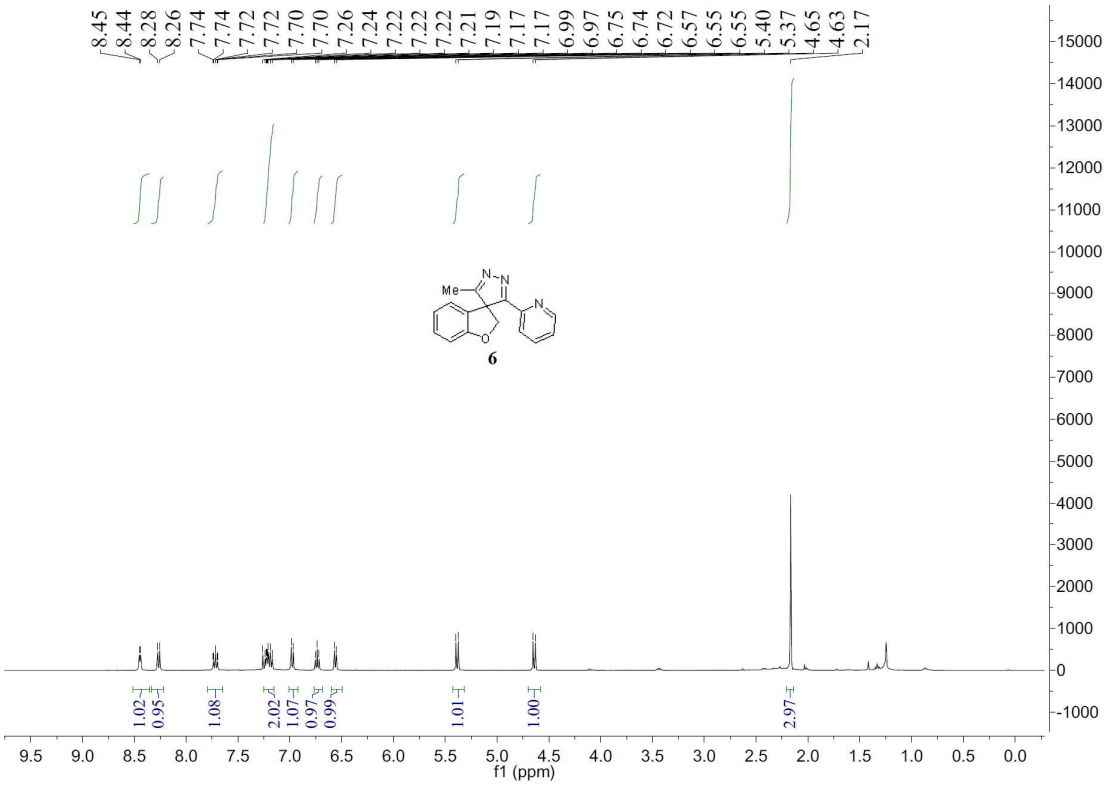

161.647
149.369
140.384
133.580
128.934
123.965
121.262
119.327
44.995
39.730
9.996
f1 (ppm)
SO2Me
Ph
N
O
Me
4i

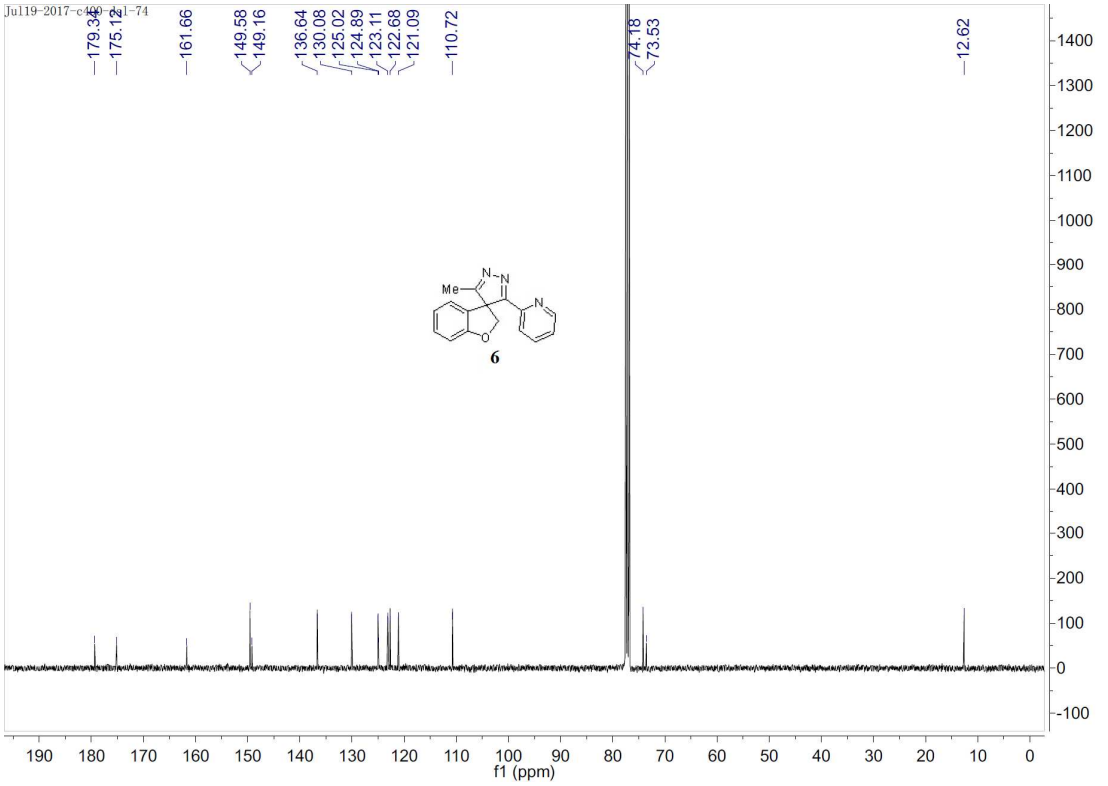

7.668
7.260
4.245
3.519
3.120
Me
N
O
N
SO2Me
4j
0.94
2.02
3.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

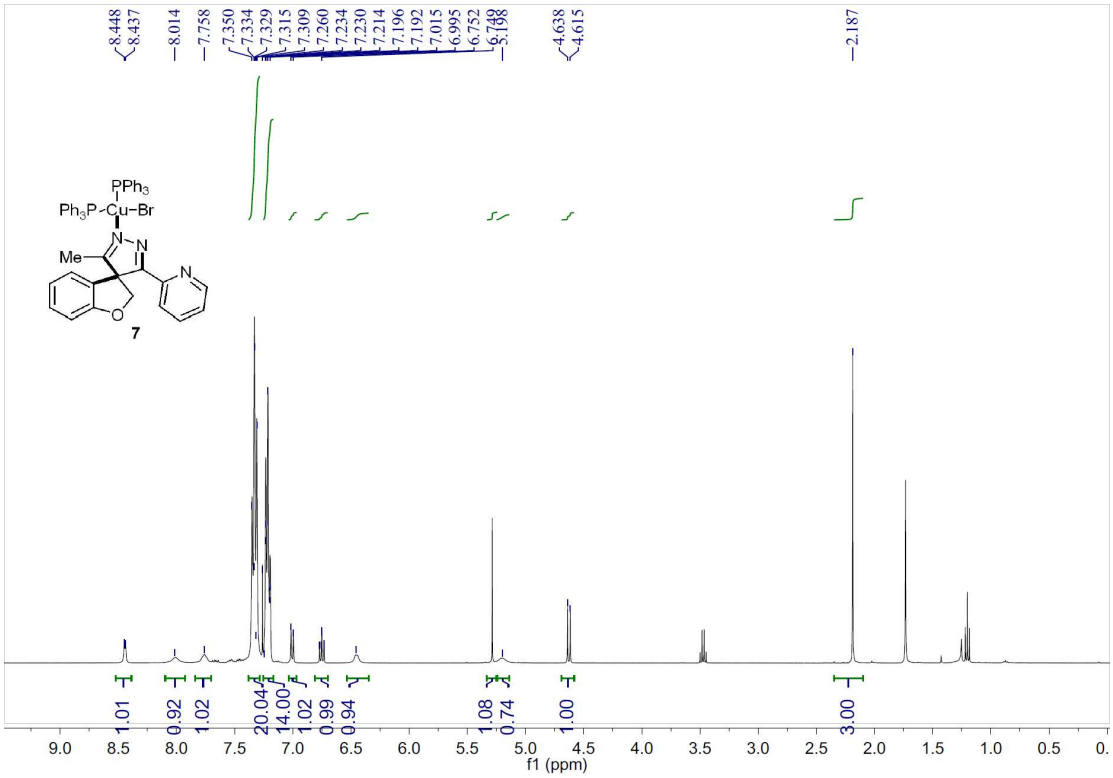

157.030
142.092
136.041
133.604
77.478
77.160
76.842
46.183
42.080
30.648
Me
N
O
N
SO2Me
4j
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

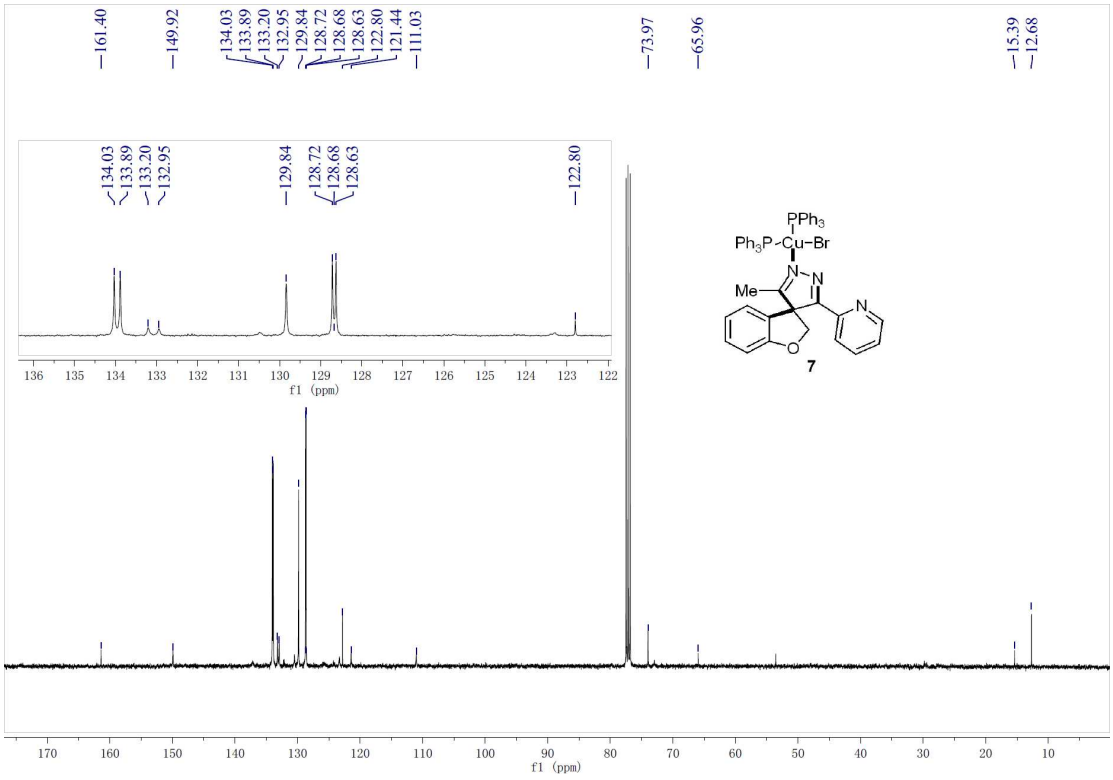

14.471
7.769
7.753
7.667
7.650
7.650
7.592
7.577
7.559
7.475
7.457
7.438
7.163
7.147
7.131
3.725
2.508
2.504
2.500
2.495
2.491
Me
N
O
NH
N
Ph
4k
1.01
2.08
4.00
1.03
1.01
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1
f1 (ppm)
0.93
1.01
2.08
4.00
1.03
1.01
3.04
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

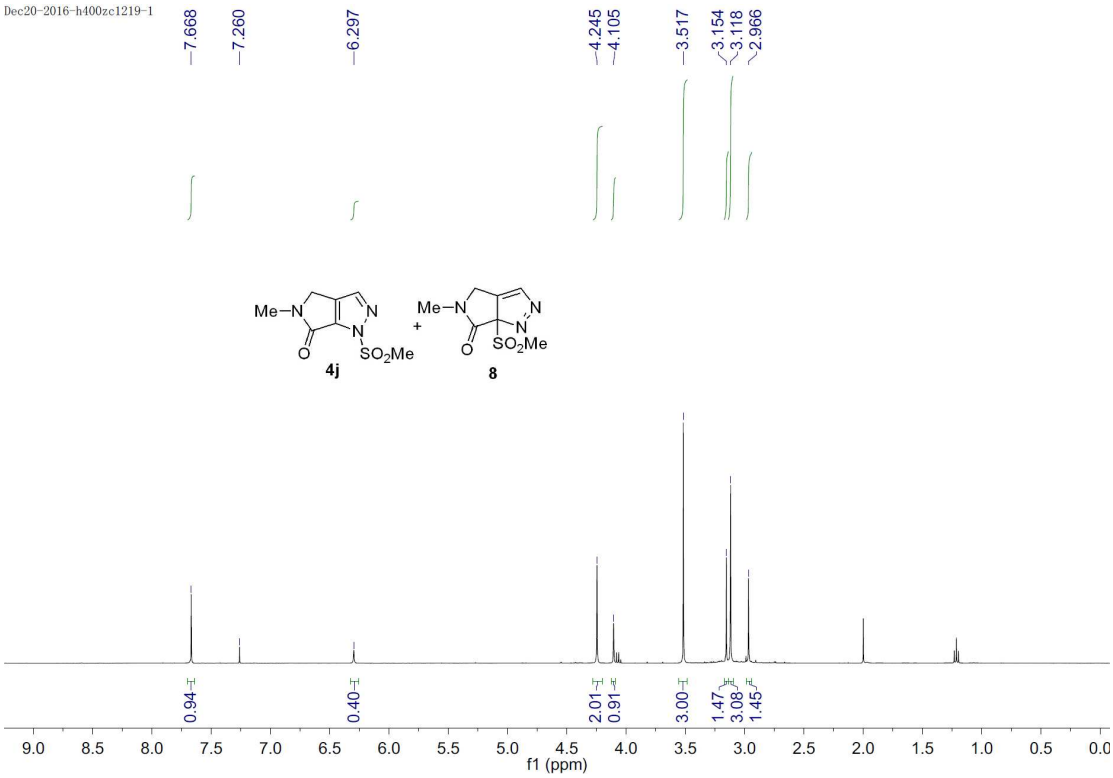

153.592
146.961
136.648
133.948
131.840
129.316
128.715
128.632
127.561
122.476
122.379
116.989
116.404
116.169
40.146
39.937
39.729
39.520
39.311
39.102
38.894
29.170
Me
N
O
NH
N
Ph
4k
128.715
128.632
127.561
128.5 128.0 127.5
f1 (ppm)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

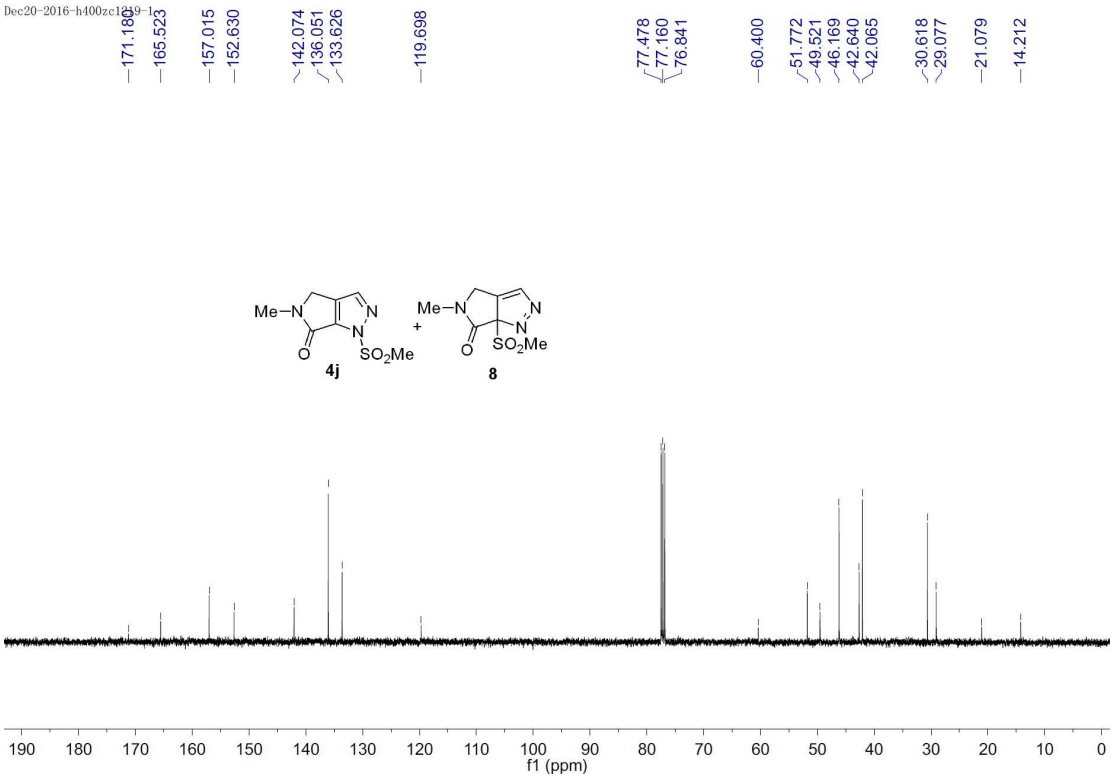

8.45
8.44
8.28
8.26
7.74
7.74
7.72
7.72
7.70
7.70
7.26
7.24
7.22
7.22
7.21
7.19
7.17
7.17
6.99
6.97
6.75
6.74
6.72
6.57
6.55
6.55
5.40
5.37
4.65
4.63
2.17
Me
N
N
O
N
6
1.02
0.95
1.08
2.02
1.07
0.97
0.99
1.01
1.00
2.97
f1 (ppm)


179.34
175.12
161.66
149.58
149.16
136.64
130.08
125.02
124.89
123.11
122.68
121.09
110.72
74.18
73.53
12.62
Me
N
N
O
N
6
f1 (ppm)

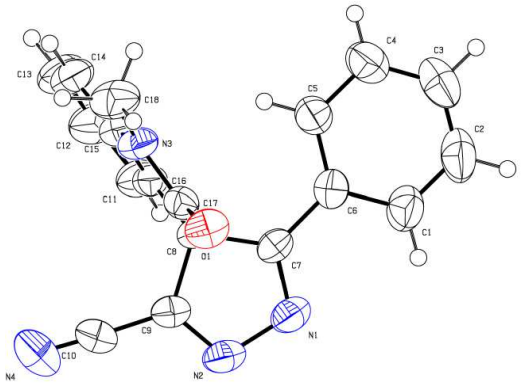

8.448
8.437
8.014
7.758
7.350
7.334
7.329
7.315
7.309
7.260
7.234
7.230
7.214
7.196
7.192
7.015
6.995
6.752
6.749
6.738
4.638
4.615
2.187
PPh3
Ph3P-Cu-Br
Me
N
O
7
1.01
0.92
1.02
20.04
14.00
1.02
0.99
0.94
1.08
0.74
1.00
3.00
f1 (ppm)


161.40
149.92
134.03
133.89
133.20
132.95
129.84
128.72
128.68
128.63
122.80
121.44
111.03
73.97
65.96
15.39
12.68
PPh3
Ph3P-Cu-Br
Me
N
O
7
f1 (ppm)


Dec20-2016-h400zc1219-1
7.668
7.260
6.297
4.245
4.105
3.517
3.154
3.118
2.966
Me–N
N
N
O
SO2Me
4j
+
8
0.94
0.40
2.01
0.91
3.00
1.47
3.08
1.45
9.0 8.5 8.0 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 0.0
f1 (ppm)


Dec20-2016-h400zc1219-1
171.186
165.523
157.015
152.630
142.074
136.051
133.626
119.698
77.478
77.160
76.841
60.400
51.772
49.521
46.169
42.640
42.065
30.618
29.077
21.079
14.212
Me–N
N
N
O
SO2Me
4j
+
8
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

X-ray crystal structure of 2a



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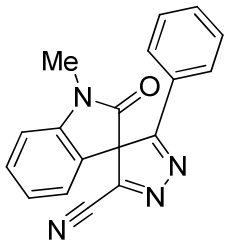


2a, CCDC:1506802

Datablock: I

Bond precision: C-C = 0.0033 A Wavelength=0.71073

Cell: a=19.3723(14) b=8.7871(5) c=19.4970(14)
alpha=90 beta=109.410(8) gamma=90
Temperature: 295 K

	Calculated	Reported
Volume	3130.3(4)	3130.3(4)
Space group	C 2/c	C 1 2/c 1
Hall group	-C 2yc	-C 2yc
Moiety formula	C18 H12 N4 O	C18 H12 N4 O
Sum formula	C18 H12 N4 O	C18 H12 N4 O
Mr	300.32	300.32
Dx,g cm-3	1.275	1.274
Z	8	8
Mu (mm-1)	0.083	0.083
F000	1248.0	1248.0
F000'	1248.46	
h,k,lmax	24,10,24	24,10,24
Nref	3193	3189
Tmin,Tmax	0.975,0.984	0.979,1.000
Tmin'	0.975	

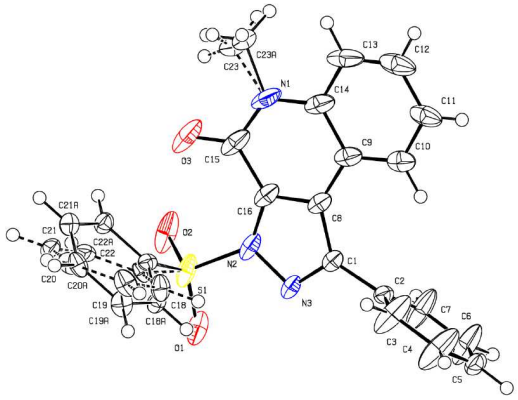
Correction method= # Reported T Limits: Tmin=0.979 Tmax=1.000
AbsCorr = MULTI-SCAN

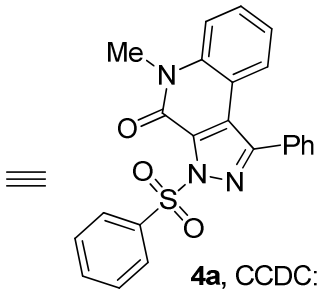
Data completeness= 0.999 Theta(max)= 26.372

R(reflections)= 0.0503(1819) wR2(reflections)= 0.1377(3189)

S = 1.010 Npar= 209

X-ray crystal structure of 4a





4a, CCDC: 1566162

Datablock: I

Bond precision: C-C = 0.0045 A Wavelength=0.71073

Cell: a=5.4320(2) b=19.9758(9) c=17.4712(8)
alpha=90 beta=97.033(2) gamma=90
Temperature: 120 K

	Calculated	Reported
Volume	1881.51(14)	1881.51(14)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C23 H17 N3 O3 S	C23 H17 N3 O3 S
Sum formula	C23 H17 N3 O3 S	C23 H17 N3 O3 S
Mr	415.46	415.45
Dx,g cm-3	1.467	1.467
Z	4	4
Mu (mm-1)	0.205	0.205
F000	864.0	864.0
F000'	864.85	
h,k,lmax	7,26,23	7,26,23
Nref	4672	4668
Tmin,Tmax	0.893,0.948	0.893,0.948
Tmin'	0.866	

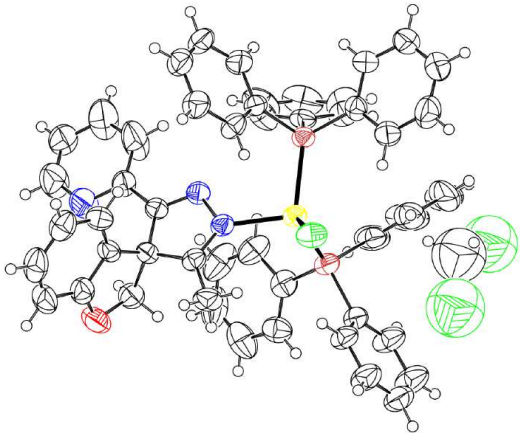
Correction method= # Reported T Limits: Tmin=0.893 Tmax=0.948
AbsCorr = MULTI-SCAN

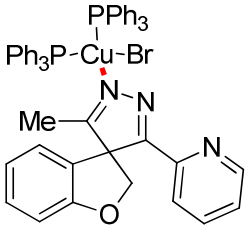
Data completeness= 0.999 Theta(max)= 28.278

R(reflections)= 0.0674(3599) wR2(reflections)= 0.1920(4668)

S = 1.159 Npar= 315

X-ray crystal structures of 7





7, CCDC: 1570779

Datablock: g170824a

Bond precision: C-C = 0.0119 A Wavelength=0.71073

Cell: a=10.2838(5) b=12.8459(10) c=20.2842(18)
alpha=101.537(7) beta=91.712(5) gamma=108.106(6)
Temperature: 293 K

	Calculated	Reported
Volume	2483.3(3)	2483.3(3)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	2(C52 H43 Br Cu N3 O P2), C H2 Cl2	C52 H43 Br Cu N3 O P2, 0.5(C H2 Cl2)
Sum formula	C105 H88 Br2 Cl2 Cu2 N6 O2 P4	C52.50 H46 Br Cl Cu N3 O P2
Mr	1947.49	975.76
Dx,g cm-3	1.302	1.305
Z	1	2
Mu (mm-1)	1.401	1.402
F000	998.0	1002.0
F000'	999.04	
h,k,lmax	12,16,25	12,16,25
Nref	10150	9961
Tmin,Tmax	0.764,0.810	0.707,1.000
Tmin'	0.496	

Correction method= # Reported T Limits: Tmin=0.707 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.981 Theta(max)= 26.370

R(reflections)= 0.0729(5126) wR2(reflections)= 0.2325(9961)

S = 1.032 Npar= 554