Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Molybdenum-Silver Co-catalyzed Cycloaddition of Alkynes with *N*-Isocyanoiminotriphenylphosphorane (NIITP): an Efficient Strategy for the Synthesis of Monosubstituted Pyrazoles

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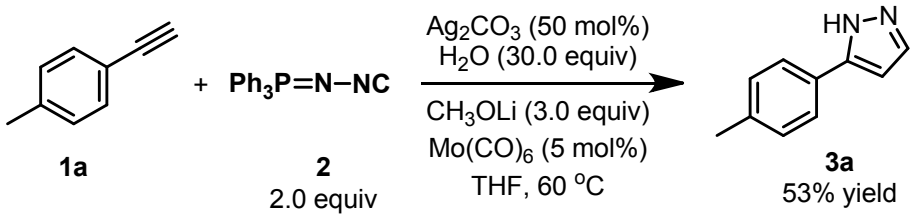
Contents

I. General information

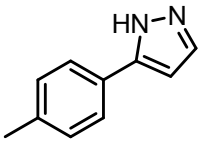
All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel. ^{1}H-NMR and ^{13}C-NMR spectra were recorded at 25 ºC on a Varian 500 MHz and 125 MHz, and BRUKER 600 MHz and 150 MHz respectively, and TMS was used as internal standard. Mass spectra were recorded on BRUKER AutoflexIII Smartbeam MS-spectrometer. High resolution mass spectra (HRMS) were recorded on Bruck microTof by using ESI method. High Performance Liquid Chromatography were recorded on Agilent Technologies Inc.1220.

II Synthesis and spectra data of 3a-3u

Typical synthetic procedure:

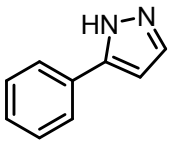


The mixture of 2 (181 mg, 0.6 mmol), CH_3OLi (34.2 mg, 0.9 mmol), $Mo(CO)_6$ (4 mg, 0.015 mmol) and Ag_2CO_3 (41.4 mg, 0.15 mmol) were added in a Schlenk tube. After evacuated and refilled with nitrogen 3 times, tetrahydrofuran (2.5 ml), 1b (34.8 mg, 0.3 mmol) and H_2O (162 μl, 9 mmol) was added in one portion to the tube by syringe, follow stirred for 12 h at 60 °C. After completed, the reaction mixture was cooled to room temperature and quenched with water. The organic layer was extracted with 2M HCl (20 ml × 3), then use NaOH to adjust the aqueous layer's pH to 12-13, then the aqueous layer was extracted with CH_2Cl_2 (100 ml × 3). The combined organic layers were dried over $MgSO_4$ and filtered, evacuated under vacuum. The residue was purified by column chromatography (PE：EA = 2：1) to give 3a 36.1 mg (76%).



(3a) 5(3)-4-Tolyl-1H-pyrazole [1]

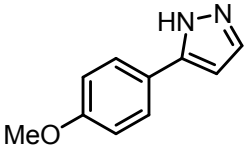
White Solid (36.1 mg, 76%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 11.95 (s, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.59 (s, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.56 (s, 1H), 2.37 (s, 3H).; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 148.6, 138.1, 133.6, 129.5, 128.7, 125.8, 102.4, 21.2; **HRMS** (ESI) *m/z* calculated $C_{10}H_{11}N_2$ $[M+H]^+$ 159.0937, found 159.0917.



(3b) 5(3)-Phenyl-1H-pyrazole [1]

The mixture of 2 (181 mg, 0.6 mmol), CH_3OLi (34.2 mg, 0.9 mmol), $Mo(CO)_6$ (4 mg, 0.015 mmol) and Ag_2CO_3 (41.4 mg, 0.15 mmol) were added in a Schlenk tube. After evacuated and refilled with nitrogen 3 times, tetrahydrofuran (2.5 ml), 1b (31.6 mg, 0.3 mmol) and H_2O (162 μl, 9 mmol) was added in one portion to the tube by syringe, follow stirred for 12 h at 60 °C. After completed, the reaction mixture was cooled to room temperature and quenched with water. The organic layer was extracted with 2M HCl (20 ml × 3), then use NaOH to adjust the aqueous layer's pH to 12-13, then the aqueous layer was extracted with CH_2Cl_2 (100 ml × 3). The combined organic layers were dried over $MgSO_4$ and filtered, evacuated under vacuum. The residue was purified by column chromatography (PE：EA = 2：1) to give 3b 27.6 mg (64%).

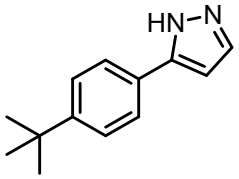
White Solid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 11.63 (s, 1H), 7.75 (d, *J* = 7.2 Hz, 2H), 7.60 (d, *J* = 2.4 Hz, 1H), 7.39 (t, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 6.60 (d, *J* = 2.4 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 149.2, 133.5, 132.2, 128.7, 128.0, 125.9, 102.6; **HRMS** (ESI) *m/z* calculated $C_9H_9N_2$ $[M+H]^+$ 145.0760, found 145.0760.



(3c) 5(3)-(4-Methoxyphenyl)-1H-pyrazole [1]

The mixture of 1c (39.6 mg, 0.3 mmol), 2 (181 mg, 0.6 mmol), CH_3OLi (34.2 mg, 0.9 mmol), $Mo(CO)_6$ (4 mg, 0.015 mmol) and Ag_2CO_3 (41.4 mg, 0.15 mmol) were added in a Schlenk tube. After evacuated and refilled with nitrogen 3 times, tetrahydrofuran (2.5 ml) and H_2O (162 μl, 9 mmol) was added in one portion to the tube by syringe, follow stirred for 12 h at 60 °C. After completed, the reaction mixture was cooled to room temperature and quenched with water. The organic layer was extracted with 2M HCl (20 ml × 3), then use NaOH to adjust the aqueous layer's pH to 12-13, then the aqueous layer was extracted with CH_2Cl_2 (100 ml × 3). The combined organic layers were dried over $MgSO_4$ and filtered, evacuated under vacuum. The residue was purified by column chromatography (PE：EA = 2：1) to give 3c 40.2 mg (77%).

White Solid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 12.23 (s, 1H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 2.2 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.51 (d, *J* = 2.2 Hz, 1H), 3.82 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.5, 148.4, 133.6, 127.1, 124.8, 114.1, 102.0, 55.3; **HRMS** (ESI) *m/z* calculated $C_{10}H_{11}N_2O$ $[M+H]^+$ 175.0873, found 175.0866.

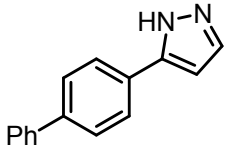


(3d) 5(3)-(4-(tert-butyl)phenyl)-1H-pyrazole

The mixture of 2 (181 mg, 0.6 mmol), CH_3OLi (34.2 mg, 0.9 mmol), $Mo(CO)_6$ (4 mg, 0.015 mmol) and Ag_2CO_3 (41.4 mg, 0.15 mmol) were added in a Schlenk tube. After evacuated and

refilled with nitrogen 3 times, tetrahydrofuran (2.5 ml), 1d (47.5 mg, 0.3 mmol) and H_2O (162 μl, 9 mmol) was added in one portion to the tube by syringe, follow stirred for 12 h at 60 °C. After completed, the reaction mixture was cooled to room temperature and quenched with water. Then the aqueous layer was extracted with CH_2Cl_2 (100 ml × 3). The combined organic layers were dried over $MgSO_4$ and filtered, evacuated under vacuum. The residue was purified by column chromatography (PE：EA = 5：1) to give 3d 31.8 mg (53%).

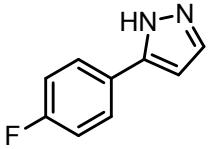
Light Yellow Solid; mp: 53-55°C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.85 (s, 1H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 1.2 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 2H), 6.57 (d, *J* = 1.2 Hz, 1H), 1.34 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 151.1, 148.5, 133.8, 129.1, 125.7, 125.5, 102.4, 34.6, 31.3; **HRMS** (ESI) *m/z* calculated $C_{13}H_{17}N_2$ $[M+H]^+$ 201.1395, found 201.1386.



(3e) 5(3)-(4-[1,1'-biphenyl]-4-yl)-1H-pyrazole

The mixture of 1e (53.5 mg, 0.3 mmol), 2 (181 mg, 0.6 mmol), CH_3OLi (34.2 mg, 0.9 mmol), $Mo(CO)_6$ (4 mg, 0.015 mmol) and Ag_2CO_3 (41.4 mg, 0.15 mmol) were added in a Schlenk tube. After evacuated and refilled with nitrogen 3 times, tetrahydrofuran (2.5 ml) and H_2O (162 μl, 9 mmol) was added in one portion to the tube by syringe, follow stirred for 12 h at 60 °C. After completed, the reaction mixture was cooled to room temperature and quenched with water. Then the aqueous layer was extracted with CH_2Cl_2 (100 ml × 3). The combined organic layers were dried over $MgSO_4$ and filtered, evacuated under vacuum. The residue was purified by column chromatography (PE：EA = 5：1) to give 3e 40.3 mg (61%).

White Solid; mp: 151-153 °C; **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 11.63 (s, 1H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.64 – 7.59 (m, 5H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 1H), 6.65 (s, 1H); **^{13}C-NMR** (150 MHz, $CDCl_3$) δ 148.8, 140.7, 140.5, 133.3, 131.0, 128.8, 127.4, 127.4, 126.9, 126.2, 102.7, 77.2, 77.0, 76.8.; **HRMS** (ESI) *m/z* calculated $C_{15}H_{13}N_2$ $[M+H]^+$ 221.1081, found 221.1073.

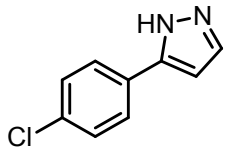


(3f) 5(3)-(4-fluorophenyl)-1H-pyrazole [1]

The mixture of 2 (181 mg, 0.6 mmol), CH_3OLi (34.2 mg, 0.9 mmol), $Mo(CO)_6$ (4 mg, 0.015 mmol) and Ag_2CO_3 (41.4 mg, 0.15 mmol) were added in a Schlenk tube. After evacuated and refilled with nitrogen 3 times, tetrahydrofuran (2.5 ml), 1f (36.0 mg, 0.3 mmol) and H_2O (162 μl, 9 mmol) was added in one portion to the tube by syringe, follow stirred for 12 h at 60 °C. After completed, the reaction mixture was cooled to room temperature and quenched with water. The organic layer was extracted with 2M HCl (20 ml × 3), then use NaOH to adjust the aqueous layer's pH to 12-13, then the aqueous layer was extracted with CH_2Cl_2 (100 ml × 3). The combined organic layers were dried over $MgSO_4$ and filtered, evacuated under vacuum. The residue was purified by column chromatography (PE：EA = 2：1) to give 3f 36.0 mg (74%).

White Solid; **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 12.09 (s, 1H), 7.72 – 7.65 (m, 2H), 7.55 (d, *J* = 2.2 Hz, 1H), 7.09 – 7.00 (m, 2H), 6.54 (d, *J* = 2.2 Hz, 1H); **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 162.6 (d, *J* = 245

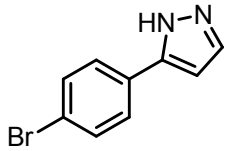
Hz), 149.1, 132.3, 128.7, 127.5 (d, *J* = 8.75 Hz), 115.7 (d, *J* = 22.5 Hz), 102.6; **HRMS** (ESI) *m/z* calculated $C_9H_8FN_2$ $[M+H]^+$ 163.0670, found 163.0666.



(3g) 5(3)-(4-chlorophenyl)-1H-pyrazole [1]

The mixture of 1g (40.8 mg, 0.3 mmol), 2 (181 mg, 0.6 mmol), CH_3OLi (34.2 mg, 0.9 mmol), $Mo(CO)_6$ (4 mg, 0.015 mmol) and Ag_2CO_3 (41.4 mg, 0.15 mmol) were added in a Schlenk tube. After evacuated and refilled with nitrogen 3 times, tetrahydrofuran (2.5 ml) and H_2O (162 μl, 9 mmol) was added in one portion to the tube by syringe, follow stirred for 12 h at 60 °C. After completed, the reaction mixture was cooled to room temperature and quenched with water. The organic layer was extracted with 2M HCl (20 ml × 3), then use NaOH to adjust the aqueous layer's pH to 12-13, then the aqueous layer was extracted with CH_2Cl_2 (100 ml × 3). The combined organic layers were dried over $MgSO_4$ and filtered, evacuated under vacuum. The residue was purified by column chromatography (PE：EA = 2：1) to give 3g 44.4 mg (83%).

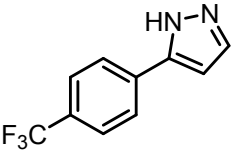
White Solid; **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 11.21 (s, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 2.4 Hz, 1H), 7.39 – 7.35 (m, 2H), 6.60 (d, *J* = 1.8 Hz, 1H); **^{13}C-NMR** (150 MHz, $CDCl_3$) δ 148.8, 133.8, 132.5, 130.9, 128.9, 127.1, 102.7; **HRMS** (ESI) *m/z* calculated $C_9H_8ClN_2$ $[M+H]^+$ 179.0373, found 179.0371.



(3h) 5(3)-(4-bromophenyl)-1H-pyrazole [1]

The mixture of 1h (55.4 mg, 0.3 mmol), 2 (181 mg, 0.6 mmol), CH_3OLi (34.2 mg, 0.9 mmol), $Mo(CO)_6$ (4 mg, 0.015 mmol) and Ag_2CO_3 (41.4 mg, 0.15 mmol) were added in a Schlenk tube. After evacuated and refilled with nitrogen 3 times, tetrahydrofuran (2.5 ml) and H_2O (162 μl, 9 mmol) was added in one portion to the tube by syringe, follow stirred for 12 h at 60 °C. After completed, the reaction mixture was cooled to room temperature and quenched with water. The organic layer was extracted with 4M HCl (20 ml × 3), then use NaOH to adjust the aqueous layer's pH to 12-13, then the aqueous layer was extracted with CH_2Cl_2 (100 ml × 3). The combined organic layers were dried over $MgSO_4$ and filtered, evacuated under vacuum. The residue was purified by column chromatography (PE：EA = 2：1) to give 3h 48.2 mg (72%).

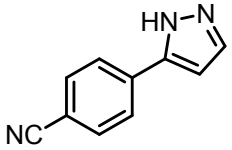
White Solid; **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 12.52 (s, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 2.2 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 6.57 (d, *J* = 2.2 Hz, 1H); **^{13}C-NMR** (150 MHz, $CDCl_3$) δ 148.8, 132.3, 131.8, 131.3, 127.4, 121.9, 102.7; **HRMS** (ESI) *m/z* calculated $C_9H_8BrN_2$ $[M+H]^+$ 222.9872, found 222.9865.



(3i) 5(3)-(4-trifluoromethylphenyl)-1H-pyrazole

The mixture of 2 (181 mg, 0.6 mmol), CH_3OLi (34.2 mg, 0.9 mmol), $Mo(CO)_6$ (4 mg, 0.015 mmol) and Ag_2CO_3 (41.4 mg, 0.15 mmol) were added in a Schlenk tube. After evacuated and refilled with nitrogen 3 times, tetrahydrofuran (2.5 ml), 1i (52.1 mg, 0.3 mmol) and H_2O (162 μl, 9 mmol) was added in one portion to the tube by syringe, follow stirred for 12 h at 60 °C. After completed, the reaction mixture was cooled to room temperature and quenched with water. The organic layer was extracted with 6M HCl (20 ml × 3), then use NaOH to adjust the aqueous layer's pH to 12-13, then the aqueous layer was extracted with CH_2Cl_2 (100 ml × 3). The combined organic layers were dried over $MgSO_4$ and filtered, evacuated under vacuum. The residue was purified by column chromatography (PE：EA = 2：1) to give 3i 48.3 mg (76%).

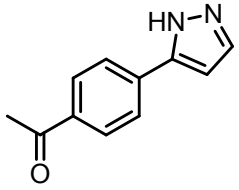
White Solid; mp: 106-108 °C; **^{1}H-NMR** (600 MHz, $CDCl_3$) ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.60 (s, 1H), 7.88 (d, *J* = 7.8 Hz, 2H), 7.66 – 7.63 (m, 3H), 6.68 (d, *J* = 2.4 Hz, 1H); **^{13}C-NMR** (150 MHz, $CDCl_3$) δ 149.1, 135.9, 131.9, 129.9 (q, *J* = 18.0 Hz), 126.0, 125.7 (q, *J* = 3.0 Hz), 124.1 (q, *J* = 270.0 Hz), 103.3; **HRMS** (ESI) *m/z* calculated $C_{10}H_8F_3N_2$ $[M+H]^+$ 213.0642, found 213.0634.



(3j) 5(3)-(4-cyanogroupphenyl)-1H-pyrazole [2]

The mixture of 2 (181 mg, 0.6 mmol), CH_3OLi (34.2 mg, 0.9 mmol), $Mo(CO)_6$ (4 mg, 0.015 mmol) and Ag_2CO_3 (41.4 mg, 0.15 mmol) were added in a Schlenk tube. After evacuated and refilled with nitrogen 3 times, tetrahydrofuran (2.5 ml), 1j (39.3 mg, 0.3 mmol) and H_2O (162 μl, 9 mmol) was added in one portion to the tube by syringe, follow stirred for 12 h at 60 °C. After completed, the reaction mixture was cooled to room temperature and quenched with water. The organic layer was extracted with 2M HCl (20 ml × 3), then use NaOH to adjust the aqueous layer's pH to 12-13, then the aqueous layer was extracted with CH_2Cl_2 (100 ml × 3). The combined organic layers were dried over $MgSO_4$ and filtered, evacuated under vacuum. The residue was purified by column chromatography (PE：EA = 2：1) to give 3j 34.5 mg (68%).

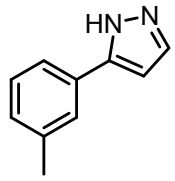
White Solid; **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 11.10 (s, 1H), 7.91 (d, *J* = 7.8 Hz, 2H), 7.69 (d, *J* = 7.8 Hz, 2H), 7.66 (d, *J* = 2.4 Hz, 1H), 6.71 (d, *J* = 1.8 Hz, 1H); **^{13}C-NMR** (150 MHz, $CDCl_3$) δ 149.1, 137.2, 132.6, 131.3, 126.1, 118.9, 111.1, 103.5; **HRMS** (ESI) *m/z* calculated $C_{10}H_8N_3$ $[M+H]^+$ 170.0719, found 170.0713.



(3k) 5(3)-(4-ethanoylphenyl)-1H-pyrazole

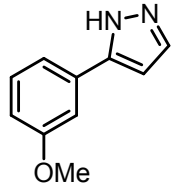
The mixture of 1k (43.3 mg, 0.3 mmol), 2 (181 mg, 0.6 mmol), CH_3OLi (34.2 mg, 0.9 mmol), $Mo(CO)_6$ (4 mg, 0.015 mmol) and Ag_2CO_3 (41.4 mg, 0.15 mmol) were added in a Schlenk tube. After evacuated and refilled with nitrogen 3 times, tetrahydrofuran (2.5 ml) and H_2O (162 μl, 9 mmol) was added in one portion to the tube by syringe, follow stirred for 12 h at 60 °C. After completed, the reaction mixture was cooled to room temperature and quenched with water. The organic layer was extracted with 4M HCl (20 ml × 3), then use NaOH to adjust the aqueous layer's pH to 12-13, then the aqueous layer was extracted with CH_2Cl_2 (100 ml × 3). The

combined organic layers were dried over $MgSO_4$ and filtered, evacuated under vacuum. The residue was purified by column chromatography (PE：EA = 2：1) to give 3k 41.9 mg (75%).
White Solid; mp: 136-138 °C; **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 10.37 (s, 1H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.90 (d, *J* = 7.8 Hz, 2H), 7.66 (d, *J* = 2.4 Hz, 1H), 6.73 (d, *J* = 2.4 Hz, 1H), 2.64 (s, 3H); **^{13}C-NMR** (150 MHz, $CDCl_3$) δ 197.7, 149.1, 137.0, 136.3, 131.9, 128.9, 125.7, 103.4, 26.6.; **HRMS** (ESI) *m/z* calculated $C_{11}H_{11}N_2O$ $[M+H]^+$ 187.0869, found 187.0866.



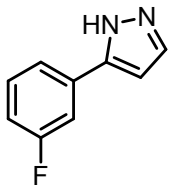
(3l) 5(3)-3-Tolyl-1H-pyrazole

The mixture of 2 (181 mg, 0.6 mmol), CH_3OLi (34.2 mg, 0.9 mmol), $Mo(CO)_6$ (4 mg, 0.015 mmol) and Ag_2CO_3 (41.4 mg, 0.15 mmol) were added in a Schlenk tube. After evacuated and refilled with nitrogen 3 times, tetrahydrofuran (2.5 ml), 1l (34.8 mg, 0.3 mmol) and H_2O (162 μl, 9 mmol) was added in one portion to the tube by syringe, follow stirred for 12 h at 60 °C. After completed, the reaction mixture was cooled to room temperature and quenched with water. The organic layer was extracted with 2M HCl (20 ml × 3), then use NaOH to adjust the aqueous layer's pH to 12-13, then the aqueous layer was extracted with CH_2Cl_2 (100 ml × 3). The combined organic layers were dried over $MgSO_4$ and filtered, evacuated under vacuum. The residue was purified by column chromatography (PE：EA = 2：1) to give 3l 26.6 mg (56%).
Light Yellow Oil; **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 12.15 (s, 1H), 7.57 (d, *J* = 2.2 Hz, 2H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.26 (t, *J* = 7.2 Hz, 1H), 7.13 (d, *J* = 6.6 Hz, 1H), 6.58 (d, *J* = 2.2 Hz, 1H), 2.35 (s, 3H); **^{13}C-NMR** (150 MHz, $CDCl_3$) δ 149.1, 138.4, 134.2, 132.0, 128.7, 128.7, 126.5, 123.0, 102.5, 21.4; **HRMS** (ESI) *m/z* calculated $C_{10}H_{11}N_2$ $[M+H]^+$ 159.0912, found 159.0917.



(3m) 5(3)-(3-Methoxyphenyl)-1H-pyrazole [1]

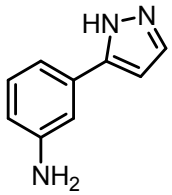
The mixture of 2 (181 mg, 0.6 mmol), CH_3OLi (34.2 mg, 0.9 mmol), $Mo(CO)_6$ (4 mg, 0.015 mmol) and Ag_2CO_3 (41.4 mg, 0.15 mmol) were added in a Schlenk tube. After evacuated and refilled with nitrogen 3 times, tetrahydrofuran (2.5 ml), 1m (39.6 mg, 0.3 mmol) and H_2O (162 μl, 9 mmol) was added in one portion to the tube by syringe, follow stirred for 12 h at 60 °C. After completed, the reaction mixture was cooled to room temperature and quenched with water. The organic layer was extracted with 2M HCl (20 ml × 3), then use NaOH to adjust the aqueous layer's pH to 12-13, then the aqueous layer was extracted with CH_2Cl_2 (100 ml × 3). The combined organic layers were dried over $MgSO_4$ and filtered, evacuated under vacuum. The residue was purified by column chromatography (PE：EA = 2：1) to give 3m 34.0 mg (65%).
White Solid; **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 12.53 (s, 1H), 7.57 (d, *J* = 1.8 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.29 (t, *J* = 7.8 Hz, 1H), 6.86 (ddd, *J* = 7.8, 2.4, 1.2 Hz, 1H), 6.58 (d, *J* = 2.4 Hz, 1H), 3.78 (d, *J* = 1.2 Hz, 3H); **^{13}C-NMR** (150 MHz, $CDCl_3$) δ 159.9, 149.2, 133.5, 133.1, 129.8, 118.4, 113.8, 111.1, 102.7, 55.2; **HRMS** (ESI) *m/z* calculated $C_{10}H_{11}N_2O$ $[M+H]^+$ 175.0852, found 175.0866.



(3n) 5(3)-(3-fluorophenyl)-1H-pyrazole

The mixture of 2 (181 mg, 0.6 mmol), CH_3OLi (34.2 mg, 0.9 mmol), $Mo(CO)_6$ (4 mg, 0.015 mmol) and Ag_2CO_3 (41.4 mg, 0.15 mmol) were added in a Schlenk tube. After evacuated and refilled with nitrogen 3 times, tetrahydrofuran (2.5 ml), 1n (36.0 mg, 0.3 mmol) and H_2O (162 μl, 9 mmol) was added in one portion to the tube by syringe, follow stirred for 12 h at 60 °C. After completed, the reaction mixture was cooled to room temperature and quenched with water. The organic layer was extracted with 2M HCl (20 ml × 3), then use NaOH to adjust the aqueous layer's pH to 12-13, then the aqueous layer was extracted with CH_2Cl_2 (100 ml × 3). The combined organic layers were dried over $MgSO_4$ and filtered, evacuated under vacuum. The residue was purified by column chromatography (PE：EA = 2：1) to give 3n 34.5 mg (71%).

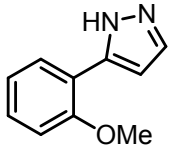
White Solid; mp: 62-64 °C; **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 12.26 (s, 1H), 7.59 (d, *J* = 2.4 Hz, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 10.2 Hz, 1H), 7.37 – 7.30 (m, 1H), 7.01 (td, *J* = 8.4, 1.8 Hz, 1H), 6.60 (d, *J* = 2.4 Hz, 1H); **^{13}C-NMR** (150 MHz, $CDCl_3$) δ 163.1 (d, *J* = 203 Hz), 149.1, 134.7, 132.7, 130.3 (d, *J* = 7.5 Hz), 121.5 (d, *J* = 2.5 Hz), 114.7 (d, *J* = 17.5 Hz), 112.7 (d, *J* = 18.75 Hz), 102.9; **HRMS** (ESI) *m/z* calculated $C_9H_7FN_2$ $[M+H]^+$ 163.0627, found 163.0752.



(3o) 5(3)-(3-aminophenyl)-1H-pyrazole

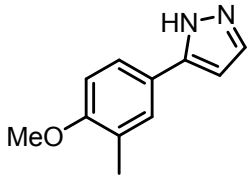
The mixture of 2 (181 mg, 0.6 mmol), CH_3OLi (34.2 mg, 0.9 mmol), $Mo(CO)_6$ (4 mg, 0.015 mmol) and Ag_2CO_3 (41.4 mg, 0.15 mmol) were added in a Schlenk tube. After evacuated and refilled with nitrogen 3 times, tetrahydrofuran (2.5 ml), 1o (35.9 mg, 0.3 mmol) and H_2O (162 μl, 9 mmol) was added in one portion to the tube by syringe, follow stirred for 12 h at 60 °C. After completed, the reaction mixture was cooled to room temperature and quenched with water. The organic layer was extracted with 2M HCl (20 ml × 3), then use NaOH to adjust the aqueous layer's pH to 12-13, then the aqueous layer was extracted with CH_2Cl_2 (100 ml × 6). The combined organic layers were dried over $MgSO_4$ and filtered, evacuated under vacuum. The residue was purified by column chromatography (PE：EA = 1：1) to give 3o 24.4 mg (51%).

Light yellow Solid; mp: 115-117 °C; **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 7.56 (d, *J* = 2.4 Hz, 1H), 7.16 (t, *J* = 7.8 Hz, 1H), 7.12 (d, *J* = 7.8 Hz, 1H), 7.06 (s, 1H), 6.62 (dd, *J* = 7.8, 1.2 Hz, 1H), 6.53 (d, *J* = 2.4 Hz, 1H); **^{13}C-NMR** (150 MHz, $CDCl_3$) δ 148.5, 146.8, 133.8, 132.8, 129.7, 116.3, 114.9, 112.3, 102.6; **HRMS** (ESI) *m/z* calculated $C_9H_{10}N_3$ $[M+H]^+$ 160.0862, found 160.0869.



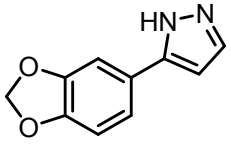
(3p) 5(3)-(2-Methoxyphenyl)-1H-pyrazole[3]

The mixture of 2 (181 mg, 0.6 mmol), CH_3OLi (34.2 mg, 0.9 mmol), $Mo(CO)_6$ (4 mg, 0.015 mmol) and Ag_2CO_3 (41.4 mg, 0.15 mmol) were added in a Schlenk tube. After evacuated and refilled with nitrogen 3 times, tetrahydrofuran (2.5 ml), 1p (39.6 mg, 0.3 mmol) and H_2O (162 μl, 9 mmol) was added in one portion to the tube by syringe, follow stirred for 12 h at 60 °C. After completed, the reaction mixture was cooled to room temperature and quenched with water. The organic layer was extracted with 2M HCl (20 ml × 3), then use NaOH to adjust the aqueous layer's pH to 12-13, then the aqueous layer was extracted with CH_2Cl_2 (100 ml × 3). The combined organic layers were dried over $MgSO_4$ and filtered, evacuated under vacuum. The residue was purified by column chromatography (PE：EA = 2：1) to give 3p 33.9 mg (65%).
White Solid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 11.43 (s, 1H), 7.69 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.61 (d, *J* = 1.8 Hz, 1H), 7.33 – 7.28 (m, 1H), 7.06 – 7.00 (m, 2H), 6.65 (d, *J* = 1.8 Hz, 1H), 3.97 (s, 3H); **^{13}C-NMR** (150 MHz, $CDCl_3$) δ 155.8, 141.2, 139.1, 129.1, 128.0, 121.3, 118.1, 111.5, 102.8, 55.7; **HRMS** (ESI) *m/z* calculated $C_{10}H_{11}N_2O$ $[M+H]^+$ 175.0865, found 175.0866.



(3q) 5(3)-(4-methoxy-3-methylphenyl)-1H-pyrazole

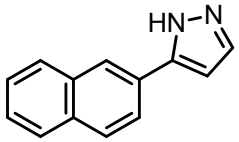
The mixture of 2 (181 mg, 0.6 mmol), CH_3OLi (34.2 mg, 0.9 mmol), $Mo(CO)_6$ (4 mg, 0.015 mmol) and Ag_2CO_3 (41.4 mg, 0.15 mmol) were added in a Schlenk tube. After evacuated and refilled with nitrogen 3 times, tetrahydrofuran (2.5 ml), 1q (43.8 mg, 0.3 mmol) and H_2O (162 μl, 9 mmol) was added in one portion to the tube by syringe, follow stirred for 12 h at 60 °C. After completed, the reaction mixture was cooled to room temperature and quenched with water. The organic layer was extracted with 2M HCl (20 ml × 3), then use NaOH to adjust the aqueous layer's pH to 12-13, then the aqueous layer was extracted with CH_2Cl_2 (100 ml × 3). The combined organic layers were dried over $MgSO_4$ and filtered, evacuated under vacuum. The residue was purified by column chromatography (PE：EA = 2：1) to give 3q 32.2 mg (57%).
Light Yellow Solid; mp: 101-103 °C; **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 10.71 (s, 1H), 7.57 (d, *J* = 2.4 Hz, 1H), 7.51 (s, 2H), 6.80 (d, *J* = 9.0 Hz, 1H), 6.50 (d, *J* = 2.4 Hz, 1H), 3.83 (s, 3H), 2.22 (s, 3H); **^{13}C-NMR** (150 MHz, $CDCl_3$) δ 157.7, 148.3, 134.0, 128.3, 126.9, 124.4, 124.1, 110.0, 101.9, 55.3, 16.2; **HRMS** (ESI) *m/z* calculated $C_{11}H_{13}N_2O$ $[M+H]^+$ 189.1027, found 189.1022.



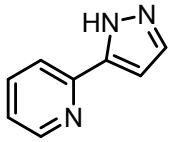
(3r) 5(3)-(1,3-benzodioxol-5-yl)-1H-pyrazole

The mixture of 2 (181 mg, 0.6 mmol), CH_3OLi (34.2 mg, 0.9 mmol), $Mo(CO)_6$ (4 mg, 0.015 mmol) and Ag_2CO_3 (41.4 mg, 0.15 mmol) were added in a Schlenk tube. After evacuated and refilled with nitrogen 3 times, tetrahydrofuran (2.5 ml), 1r (43.8 mg, 0.3 mmol) and H_2O (162 μl, 9 mmol) was added in one portion to the tube by syringe, follow stirred for 12 h at 60 °C. After completed, the reaction mixture was cooled to room temperature and quenched with water. The organic layer was extracted with 2M HCl (20 ml × 3), then use NaOH to adjust the aqueous layer's pH to 12-13, then the aqueous layer was extracted with CH_2Cl_2 (100 ml × 3). The

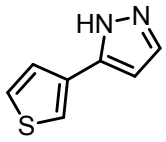
combined organic layers were dried over $MgSO_4$ and filtered, evacuated under vacuum. The residue was purified by column chromatography (PE：EA = 2：1) to give 3r 35.6 mg (63%).
White Solid; mp: 105-107 °C; **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 11.91 (s, 1H), 7.55 (d, *J* = 2.4 Hz, 1H), 7.22 – 7.18 (m, 2H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.48 (d, *J* = 1.8 Hz, 1H), 5.97 (s, 2H); **^{13}C-NMR** (150 MHz, $CDCl_3$) δ 149.3, 148.0, 147.4, 133.8, 126.6, 119.6, 108.5, 106.5, 102.2, 101.1; **HRMS** (ESI) *m/z* calculated $C_{10}H_9N_2O_2$ $[M+H]^+$ 189.0664, found 189.0659.



(3s) 5(3)-(2-naphthalen)-1H-pyrazole [5]
The mixture of 1s (45.6 mg, 0.3 mmol), 2 (181 mg, 0.6 mmol), CH_3OLi (34.2 mg, 0.9 mmol), $Mo(CO)_6$ (4 mg, 0.015 mmol) and Ag_2CO_3 (41.4 mg, 0.15 mmol) were added in a Schlenk tube. After evacuated and refilled with nitrogen 3 times, tetrahydrofuran (2.5 ml) and H_2O (162 μl, 9 mmol) was added in one portion to the tube by syringe, follow stirred for 12 h at 60 °C. After completed, the reaction mixture was cooled to room temperature and quenched with water. The organic layer was extracted with 4M HCl (20 ml × 3), then use NaOH to adjust the aqueous layer's pH to 12-13, then the aqueous layer was extracted with CH_2Cl_2 (100 ml × 3). The combined organic layers were dried over $MgSO_4$ and filtered, evacuated under vacuum. The residue was purified by column chromatography (PE：EA = 2：1) to give 3s 33.2 mg (57%).
White Solid; **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 11.00 (s, 1H), 8.21 (s, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.88 – 7.82 (m, 3H), 7.67 (d, *J* = 2.4 Hz, 1H), 7.50 – 7.45 (m, 2H), 6.75 (d, *J* = 1.8 Hz, 1H); **^{13}C-NMR** (150 MHz, $CDCl_3$) δ 149.5, 133.5, 133.1, 133.0, 129.6, 128.5, 128.1, 127.7, 126.4, 126.1, 124.4, 124.0, 103.0; **HRMS** (ESI) *m/z* calculated $C_{13}H_{11}N_2$ $[M+H]^+$ 195.0918, found 195.0917.



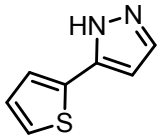
(3t) 5(3)-(2- pyridine)-1H-pyrazole [4]
The mixture of 2 (181 mg, 0.6 mmol), CH_3OLi (34.2 mg, 0.9 mmol), $Mo(CO)_6$ (4 mg, 0.015 mmol) and Ag_2CO_3 (41.4 mg, 0.15 mmol) were added in a Schlenk tube. After evacuated and refilled with nitrogen 3 times, tetrahydrofuran (2.5 ml), 1t (30.9 mg, 0.3 mmol) and H_2O (162 μl, 9 mmol) was added in one portion to the tube by syringe, follow stirred for 12 h at 60 °C. After completed, the reaction mixture was cooled to room temperature and quenched with water. The organic layer was extracted with 2M HCl (20 ml × 3), then use NaOH to adjust the aqueous layer's pH to 12-13, then the aqueous layer was extracted with CH_2Cl_2 (100 ml × 3). The combined organic layers were dried over $MgSO_4$ and filtered, evacuated under vacuum. The residue was purified by column chromatography (PE：EA = 2：1) to give 3t 26.1 mg (60%).
White Solid; **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 12.11 (s, 1H), 8.68 (d, *J* = 4.8 Hz, 1H), 7.80 – 7.71 (m, 2H), 7.67 (d, *J* = 1.8 Hz, 1H), 7.24 (dd, *J* = 8.4, 4.8 Hz, 1H), 6.81 (s, 1H); **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 149.4, 144.5, 137.5, 137.0, 122.8, 120.2, 103.4; **HRMS** (ESI) *m/z* calculated $C_8H_8N_3$ $[M+H]^+$ 146.0719, found 146.0713.



(3u) 5(3)-(Thien-3-yl)-1H-pyrazole

The mixture of 2 (181 mg, 0.6 mmol), CH_3OLi (34.2 mg, 0.9 mmol), $Mo(CO)_6$ (4 mg, 0.015 mmol) and Ag_2CO_3 (41.4 mg, 0.15 mmol) were added in a Schlenk tube. After evacuated and refilled with nitrogen 3 times, tetrahydrofuran (2.5 ml), 1u (32.4 mg, 0.3 mmol) and H_2O (162 μl, 9 mmol) was added in one portion to the tube by syringe, follow stirred for 12 h at 60 °C. After completed, the reaction mixture was cooled to room temperature and quenched with water. The organic layer was extracted with 2M HCl (20 ml × 3), then use NaOH to adjust the aqueous layer's pH to 12-13, then the aqueous layer was extracted with CH_2Cl_2 (100 ml × 3). The combined organic layers were dried over $MgSO_4$ and filtered, evacuated under vacuum. The residue was purified by column chromatography (PE：EA = 2：1) to give 3u 32.4 mg (72%).

White Solid; mp: 102-104 °C; **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 12.46 (s, 1H), 7.55 (d, *J* = 1.8 Hz, 1H), 7.52 (dd, *J* = 3.0, 1.2 Hz, 1H), 7.41 (dd, *J* = 5.4, 1.2 Hz, 1H), 7.33 (dd, *J* = 4.8, 3.0 Hz, 1H), 6.48 (d, *J* = 2.4 Hz, 1H); **^{13}C-NMR** ($CDCl_3$, 150 MHz) δ 145.1, 133.6, 133.0, 126.2, 126.0, 120.9, 102.8; **HRMS** (ESI) *m/z* calculated $C_7H_7N_2S$ $[M+H]^+$ 151.0318, found 151.0324.

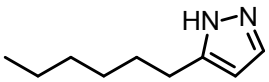


(3v) 5(3)-(Thien-2-yl)-1H-pyrazole[1]

The mixture of 2 (181 mg, 0.6 mmol), CH_3OLi (34.2 mg, 0.9 mmol), $Mo(CO)_6$ (4 mg, 0.015 mmol) and Ag_2CO_3 (41.4 mg, 0.15 mmol) were added in a Schlenk tube. After evacuated and refilled with nitrogen 3 times, tetrahydrofuran (2.5 ml), 1v (32.4 mg, 0.3 mmol) and H_2O (162 μl, 9 mmol) was added in one portion to the tube by syringe, follow stirred for 12 h at 60 °C. After completed, the reaction mixture was cooled to room temperature and quenched with water. The organic layer was extracted with 2M HCl (20 ml × 3), then use NaOH to adjust the aqueous layer's pH to 12-13, then the aqueous layer was extracted with CH_2Cl_2 (100 ml × 3). The combined organic layers were dried over $MgSO_4$ and filtered, evacuated under vacuum. The residue was purified by column chromatography (PE：EA = 2：1) to give 3v 22.1 mg (49%).

White Solid; **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 12.20 (s, 1H), 7.61 (d, *J* = 2.4 Hz, 1H), 7.33 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.26 (dd, *J* = 5.4, 1.2 Hz, 1H), 7.06 (dd, *J* = 4.8, 3.6 Hz, 1H), 6.53 (d, *J* = 1.8 Hz, 1H); **^{13}C-NMR** (150 MHz, $CDCl_3$) δ 145.6, 135.8, 131.4, 127.6, 124.6, 124.1, 102.6; **HRMS** (ESI) *m/z* calculated $C_7H_7N_2S$ $[M+H]^+$ 151.0326, found 151.0324.

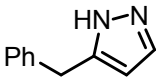
III. Synthesis and spectra data of 5a-5k



(5a) 5(3)-heptyl-1H-pyrazole

The mixture of 2 (136 mg, 0.45 mmol), CH_3OLi (34.2 mg, 0.9 mmol), $Mo(CO)_6$ (4 mg, 0.015 mmol) and Ag_2CO_3 (41.4 mg, 0.15 mmol) were added in a Schlenk tube. After evacuated and refilled with nitrogen 3 times, tetrahydrofuran (2.5 ml), 4a (33.1 mg, 0.3 mmol) and H_2O (162 μl, 9 mmol) was added in one portion to the tube by syringe, follow stirred for 12 h at 60 °C. After completed, the reaction mixture was cooled to room temperature and quenched with water. The organic layer was extracted with 2M HCl (20 ml × 3), then use NaOH to adjust the aqueous layer's pH to 12-13, then the aqueous layer was extracted with CH_2Cl_2 (100 ml × 3). The combined organic layers were dried over $MgSO_4$ and filtered, evacuated under vacuum. The residue was purified by column chromatography (PE：EA = 1：1) to give 5a 23.7 mg (52%).

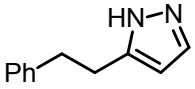
Light Yellow Oil; **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 11.23 (s, 1H), 7.49 (d, *J* = 1.8 Hz, 1H), 6.09 (d, *J* = 1.8 Hz, 1H), 2.70 – 2.66 (m, 2H), 1.69 – 1.63 (m, 2H), 1.39 – 1.33 (m, 2H), 1.33 – 1.28 (m, 4H), 0.88 (t, *J* =7.2 Hz, 3H); **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 148.0, 135.2, 103.3, 31.6, 29.4, 29.0, 26.7, 22.5, 14.0; **HRMS** (ESI) *m/z* calculated $C_9H_{17}N_2$ $[M+H]^+$ 153.1393, found 153.1386.



(5b) 5(3)-phenmethyl-1H-pyrazole

The mixture of 2 (136 mg, 0.45 mmol), CH_3OLi (34.2 mg, 0.9 mmol), $Mo(CO)_6$ (4 mg, 0.015 mmol) and Ag_2CO_3 (41.4 mg, 0.15 mmol) were added in a Schlenk tube. After evacuated and refilled with nitrogen 3 times, tetrahydrofuran (2.5 ml), 4b (34.8 mg, 0.3 mmol) and H_2O (162 μl, 9 mmol) was added in one portion to the tube by syringe, follow stirred for 12 h at 60 °C. After completed, the reaction mixture was cooled to room temperature and quenched with water. The organic layer was extracted with 2M HCl (20 ml × 3), then use NaOH to adjust the aqueous layer's pH to 12-13, then the aqueous layer was extracted with CH_2Cl_2 (100 ml × 3). The combined organic layers were dried over $MgSO_4$ and filtered, evacuated under vacuum. The residue was purified by column chromatography (PE：EA = 1：1) to give 5b 24.2 mg (51%).

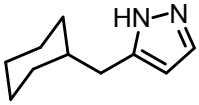
Light Yellow Oil; **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 11.15 (s, 1H), 7.41 (d, *J* = 1.8 Hz, 1H), 7.30 – 7.26 (m, 2H), 7.21 (d, *J* = 7.2 Hz, 3H), 6.06 (d, *J* = 2.4 Hz, 1H), 4.01 (s, 2H); **^{13}C-NMR** (150 MHz, $CDCl_3$) δ 147.8, 139.1, 134.1, 128.7, 128.5, 126.4, 104.3, 33.5.; **HRMS** (ESI) *m/z* calculated $C_{10}H_{11}N_2$ $[M+H]^+$ 159.0911, found 159.0917.



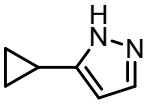
(5c) 5(3)-phenethyl-1H-pyrazole

The mixture of 2 (136 mg, 0.45 mmol), CH_3OLi (34.2 mg, 0.9 mmol), $Mo(CO)_6$ (4 mg, 0.015 mmol) and Ag_2CO_3 (41.4 mg, 0.15 mmol) were added in a Schlenk tube. After evacuated and refilled with nitrogen 3 times, tetrahydrofuran (2.5 ml), 4c (39.1 mg, 0.3 mmol) and H_2O (162 μl, 9 mmol) was added in one portion to the tube by syringe, follow stirred for 12 h at 60 °C. After completed, the reaction mixture was cooled to room temperature and quenched with water. The

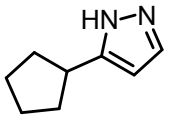
organic layer was extracted with 2M HCl (20 ml × 3), then use NaOH to adjust the aqueous layer's pH to 12-13, then the aqueous layer was extracted with CH_2Cl_2 (100 ml × 3). The combined organic layers were dried over $MgSO_4$ and filtered, evacuated under vacuum. The residue was purified by column chromatography (PE：EA = 1：1) to give 5c 29.4 mg (57%).
Light Yellow Oil; **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 9.41 (s, 1H), 7.47 (d, *J* = 1.8 Hz, 1H), 7.27 (t, *J* = 7.2 Hz, 2H), 7.21 – 7.15 (m, 3H), 6.07 (d, *J* = 1.8 Hz, 1H), 3.01 – 2.95 (m, 4H); **^{13}C-NMR** (150 MHz, $CDCl_3$) δ 147.6, 141.2, 134.2, 128.4, 128.3, 126.1, 103.6, 35.6, 28.7; **HRMS** (ESI) *m/z* calculated $C_{11}H_{13}N_2$ $[M+H]^+$ 173.1078, found 173.1073.



(5d) 5(3)-cyclohexylmethyl-1H-pyrazole
The mixture of 2 (136 mg, 0.45 mmol), CH_3OLi (34.2 mg, 0.9 mmol), $Mo(CO)_6$ (4 mg, 0.015 mmol) and Ag_2CO_3 (41.4 mg, 0.15 mmol) were added in a Schlenk tube. After evacuated and refilled with nitrogen 3 times, tetrahydrofuran (2.5 ml), 4d (36.7 mg, 0.3 mmol) and H_2O (162 μl, 9 mmol) was added in one portion to the tube by syringe, follow stirred for 12 h at 60 °C. After completed, the reaction mixture was cooled to room temperature and quenched with water. The organic layer was extracted with 2M HCl (20 ml × 3), then use NaOH to adjust the aqueous layer's pH to 12-13, then the aqueous layer was extracted with CH_2Cl_2 (100 ml × 3). The combined organic layers were dried over $MgSO_4$ and filtered, evacuated under vacuum. The residue was purified by column chromatography (PE：EA = 1：1) to give 5d 22.7 mg (46%).
Light Yellow Oil; **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 11.35 (s, 1H), 7.50 (d, *J* = 1.8 Hz, 1H), 6.07 (d, *J* = 1.8 Hz, 1H), 2.56 (d, *J* = 6.6 Hz, 2H), 1.70 (t, *J* = 13.2 Hz, 4H), 1.64 (d, *J* = 12.6 Hz, 1H), 1.62 – 1.55 (m, 1H), 1.25 – 1.12 (m, 3H), 1.00 – 0.92 (m, 2H); **^{13}C-NMR** (150 MHz, $CDCl_3$) δ 146.4, 135.5, 104.1, 38.4, 34.6, 33.1, 26.4, 26.1; **HRMS** (ESI) *m/z* calculated $C_{10}H_{17}N_2$ $[M+H]^+$ 165.1066, found 165.1063.



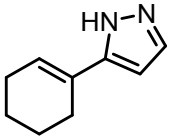
(5e) 5(3)-cyclopropyl-1H-pyrazole
The mixture of 2 (136 mg, 0.45 mmol), CH_3OLi (34.2 mg, 0.9 mmol), $Mo(CO)_6$ (4 mg, 0.015 mmol) and Ag_2CO_3 (41.4 mg, 0.15 mmol) were added in a Schlenk tube. After evacuated and refilled with nitrogen 3 times, tetrahydrofuran (2.5 ml), 4e (20.7 mg, 0.3 mmol) and H_2O (162 μl, 9 mmol) was added in one portion to the tube by syringe, follow stirred for 12 h at 60 °C. After completed, the reaction mixture was cooled to room temperature and quenched with water. The organic layer was extracted with 2M HCl (20 ml × 3), then use NaOH to adjust the aqueous layer's pH to 12-13, then the aqueous layer was extracted with CH_2Cl_2 (100 ml × 3). The combined organic layers were dried over $MgSO_4$ and filtered, evacuated under vacuum. The residue was purified by column chromatography (PE：EA = 1：1) to give 5e 15.9 mg (49%).
Light Yellow Oil; **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 10.40 (s, 1H), 7.44 (d, *J* = 1.8 Hz, 1H), 5.96 (d, *J* = 2.4 Hz, 1H), 1.95 – 1.90 (m, 1H), 0.96 – 0.91 (m, 2H), 0.76 – 0.71 (m, 2H); **^{13}C-NMR** (150 MHz, $CDCl_3$) δ 152.0, 135.9, 100.9, 8.2, 7.7; **HRMS** (ESI) *m/z* calculated $C_6H_9N_2$ $[M+H]^+$ 109.0911, found 109.0917.



(5f) 5(3)-cyclopentyl-1H-pyrazole

The mixture of 2 (136 mg, 0.45 mmol), CH_3OLi (34.2 mg, 0.9 mmol), $Mo(CO)_6$ (4 mg, 0.015 mmol) and Ag_2CO_3 (41.4 mg, 0.15 mmol) were added in a Schlenk tube. After evacuated and refilled with nitrogen 3 times, tetrahydrofuran (2.5 ml), 4f (28.2 mg, 0.3 mmol) and H_2O (162 μl, 9 mmol) was added in one portion to the tube by syringe, follow stirred for 12 h at 60 °C. After completed, the reaction mixture was cooled to room temperature and quenched with water. The organic layer was extracted with 2M HCl (20 ml × 3), then use NaOH to adjust the aqueous layer's pH to 12-13, then the aqueous layer was extracted with CH_2Cl_2 (100 ml × 3). The combined organic layers were dried over $MgSO_4$ and filtered, evacuated under vacuum. The residue was purified by column chromatography (PE：EA = 1：1) to give 5f 23.7 mg (58%).

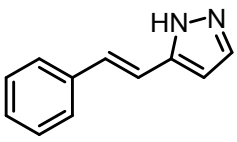
Light Yellow Oil; **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 11.02 (s, 1H), 7.41 (d, *J* = 2.4 Hz, 1H), 6.02 (d, *J* = 1.8 Hz, 1H), 3.16 – 3.09 (m, 1H), 2.10 – 2.07 (m, 2H), 1.75 – 1.65 (m, 2H), 1.64 – 1.54 (m, 4H); **^{13}C-NMR** (150 MHz, $CDCl_3$) δ 152.1, 135.7, 101.9, 37.7, 33.2, 25.2; **HRMS** (ESI) *m/z* calculated $C_8H_{13}N_2$ $[M+H]^+$ 137.1068, found 137.1073.



(5g) 5(3)-cyclohexenyl-1H-pyrazole

The mixture of 2 (136 mg, 0.45 mmol), CH_3OLi (34.2 mg, 0.9 mmol), $Mo(CO)_6$ (4 mg, 0.015 mmol) and Ag_2CO_3 (41.4 mg, 0.15 mmol) were added in a Schlenk tube. After evacuated and refilled with nitrogen 3 times, tetrahydrofuran (2.5 ml), 4g (31.9 mg, 0.3 mmol) and H_2O (162 μl, 9 mmol) was added in one portion to the tube by syringe, follow stirred for 12 h at 60 °C. After completed, the reaction mixture was cooled to room temperature and quenched with water. The organic layer was extracted with 2M HCl (20 ml × 3), then use NaOH to adjust the aqueous layer's pH to 12-13, then the aqueous layer was extracted with CH_2Cl_2 (100 ml × 3). The combined organic layers were dried over $MgSO_4$ and filtered, evacuated under vacuum. The residue was purified by column chromatography (PE：EA = 1：1) to give 5g 22.6 mg (51%).

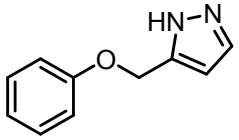
Light Yellow Oil; **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 10.04 (s, 1H), 7.50 (d, *J* = 2.4 Hz, 1H), 6.28 (d, *J* = 1.8 Hz, 1H), 6.28 – 6.25 (m, 1H), 2.43 – 2.40 (m, 2H), 2.21 – 2.17 (m, 2H), 1.78 – 1.74 (m, 2H), 1.69 – 1.64 (m, 2H); **^{13}C-NMR** (150 MHz, $CDCl_3$) δ 148.4, 135.2, 128.1, 124.9, 101.0, 26.1, 25.3, 22.5, 22.1; **HRMS** (ESI) *m/z* calculated $C_9H_{13}N_2$ $[M+H]^+$ 149.1080, found 149.1073.



(5h) 5(3)-cinnamyl-1H-pyrazole

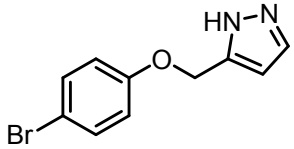
The mixture of 2 (136 mg, 0.45 mmol), CH_3OLi (34.2 mg, 0.9 mmol), $Mo(CO)_6$ (4 mg, 0.015 mmol) and Ag_2CO_3 (41.4 mg, 0.15 mmol) were added in a Schlenk tube. After evacuated and refilled with nitrogen 3 times, tetrahydrofuran (2.5 ml), 4h (38.7 mg, 0.3 mmol) and H_2O (162 μl, 9 mmol) was added in one portion to the tube by syringe, follow stirred for 12 h at 60 °C. After

completed, the reaction mixture was cooled to room temperature and quenched with water. The organic layer was extracted with 4M HCl (20 ml × 3), then use NaOH to adjust the aqueous layer's pH to 12-13, then the aqueous layer was extracted with CH_2Cl_2 (100 ml × 3). The combined organic layers were dried over $MgSO_4$ and filtered, evacuated under vacuum. The residue was purified by column chromatography (PE：EA = 2：1) to give 5h 16.9 mg (33%).
White Solid; mp: 90-92 °C; **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 9.69 (s, 1H), 7.59 (s, 1H), 7.49 – 7.45 (m, 2H), 7.32 (t, *J* = 7.2 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 1H), 7.12 (s, 2H), 6.51 (d, *J* = 2.4 Hz, 1H); **^{13}C-NMR** (150 MHz, $CDCl_3$) δ 147.1, 136.7, 133.7, 130.6, 128.7, 127.9, 126.5, 118.4, 102.8; **HRMS** (ESI) *m/z* calculated $C_{11}H_{11}N_2$ $[M+H]^+$ 171.0914, found 171.0917.



(5i) 5(3)-phenoxybut-1H-pyrazole

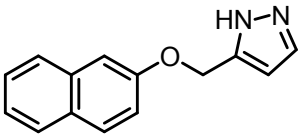
The mixture of 2 (181 mg, 0.45 mmol), CH_3OLi (34.2 mg, 0.9 mmol), $Mo(CO)_6$ (4 mg, 0.015 mmol) and Ag_2CO_3 (41.4 mg, 0.15 mmol) were added in a Schlenk tube. After evacuated and refilled with nitrogen 3 times, tetrahydrofuran (2.5 ml), 4k (63.3 mg, 0.3 mmol) and H_2O (162 μl, 9 mmol) was added in one portion to the tube by syringe, follow stirred for 12 h at 60 °C. After completed, the reaction mixture was cooled to room temperature and quenched with water. The organic layer was extracted with 2M HCl (20 ml × 3), then use NaOH to adjust the aqueous layer's pH to 12-13, then the aqueous layer was extracted with CH_2Cl_2 (100 ml × 3). The combined organic layers were dried over MgSO4 and filtered, evacuated under vacuum. The residue was purified by column chromatography (PE：EA = 1：1)to give 5k 26.1 mg (50%).
Light Yellow Oil; **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 11.27 (s, 1H), 7.53 (d, *J* = 2.4 Hz, 1H), 7.27 (t, *J* = 7.8 Hz, 2H), 7.00 – 6.90 (m, 3H), 6.38 (d, *J* = 1.8 Hz, 1H), 5.13 (s, 2H); **^{13}C-NMR** (150 MHz, $CDCl_3$) δ 158.5, 146.3, 131.7, 129.5, 121.1, 114.8, 104.6, 63.4; **HRMS** (ESI) *m/z* calculated $C_{10}H_{11}N_2O$ $[M+H]^+$ 175.0865, found 175.0866.



(5j) 5(3)-(4-bromophenoxy)but-1H-pyrazole

The mixture of 2 (181 mg, 0.45 mmol), CH_3OLi (34.2 mg, 0.9 mmol), $Mo(CO)_6$ (4 mg, 0.015 mmol) and Ag_2CO_3 (41.4 mg, 0.15 mmol) were added in a Schlenk tube. After evacuated and refilled with nitrogen 3 times, tetrahydrofuran (2.5 ml), 4j (63.3 mg, 0.3 mmol) and H_2O (162 μl, 9 mmol) was added in one portion to the tube by syringe, follow stirred for 12 h at 60 °C. After completed, the reaction mixture was cooled to room temperature and quenched with water. The organic layer was extracted with 4M HCl (20 ml × 3), then use NaOH to adjust the aqueous layer's pH to 12-13, then the aqueous layer was extracted with CH_2Cl_2 (100 ml × 3). The combined organic layers were dried over $MgSO_4$ and filtered, evacuated under vacuum. The residue was purified by column chromatography (PE：EA = 1：1) to give 5j 32.6 mg (43%).
Yellow Solid; mp: 71-73 °C； **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 10.77 (s, 1H), 7.55 (d, *J* = 2.4 Hz, 1H), 7.35 (d, *J* = 9.0 Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 6.39 (d, *J* = 2.4 Hz, 1H), 5.10 (s, 2H); **^{13}C-**

NMR (150 MHz, $CDCl_3$) δ 157.5, 146.3, 132.3, 131.4, 116.6, 113.3, 104.8, 63.7; **HRMS** (ESI) *m/z* calculated $C_{10}H_{10}BrN_2O$ $[M+H]^+$ 252.9971, found 252.9971.



(5k) 5(3)-(naphthalen-2-yloxy)but-1H-pyrazole

The mixture of 4i (54.6 mg, 0.3 mmol), 2 (181 mg, 0.45 mmol), CH_3OLi (34.2 mg, 0.9 mmol), $Mo(CO)_6$ (4 mg, 0.015 mmol) and Ag_2CO_3 (41.4 mg, 0.15 mmol) were added in a Schlenk tube. After evacuated and refilled with nitrogen 3 times, tetrahydrofuran (2.5 ml) and H_2O (162 μl, 9 mmol) was added in one portion to the tube by syringe, follow stirred for 12 h at 60 °C. After completed, the reaction mixture was cooled to room temperature and quenched with water. Then the aqueous layer was extracted with CH_2Cl_2 (100 ml × 3). The combined organic layers were dried over $MgSO_4$ and filtered, evacuated under vacuum. The residue was purified by column chromatography (PE：EA = 5：1) to give 5i 46.4 mg (69%).

White Solid; mp: 80-82 °C; **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 10.29 (s, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 9.0 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.53 (s, 1H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.22 - 7.16 (m, 2H), 6.41 (s, 1H), 5.23 (s, 2H); **^{13}C-NMR** (150 MHz, $CDCl_3$) δ 156.4, 146.2, 134.4, 131.7, 129.5, 129.1, 127.6, 126.8, 126.3, 123.8, 118.8, 107.1, 104.8, 63.4; **HRMS** (ESI) *m/z* calculated $C_{14}H_{13}N_2O$ $[M+H]^+$ 225.1027, found 225.1022.

([D]-3a) 5(3)-4-Tolyl-1H-pyrazole

White Solid (36.1 mg, 75%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.58 (s, 0.15H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.55 (s, 0.16H), 2.37 (s, 3H); **HRMS** (ESI) *m/z* calculated $C_{10}H_9D_2N_2$ $[M+H]^+$ 161.1221, found 161.1219.

Refers:

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[2] G. A. Molander and L. Jeangérard *J. Org. Chem.* 2009, **74** , 973–980.

[3] J.Catalan, F. Fabero, R. M. Claramunt, M. D. Santa Maria, M. C. Foces-Foces, F. Hernandez Cano, M. Martinez-Ripoll, J. Elguero and R. Sastre *J. Am. Chem. Soc.* 1992, **114**, 5039–5048.

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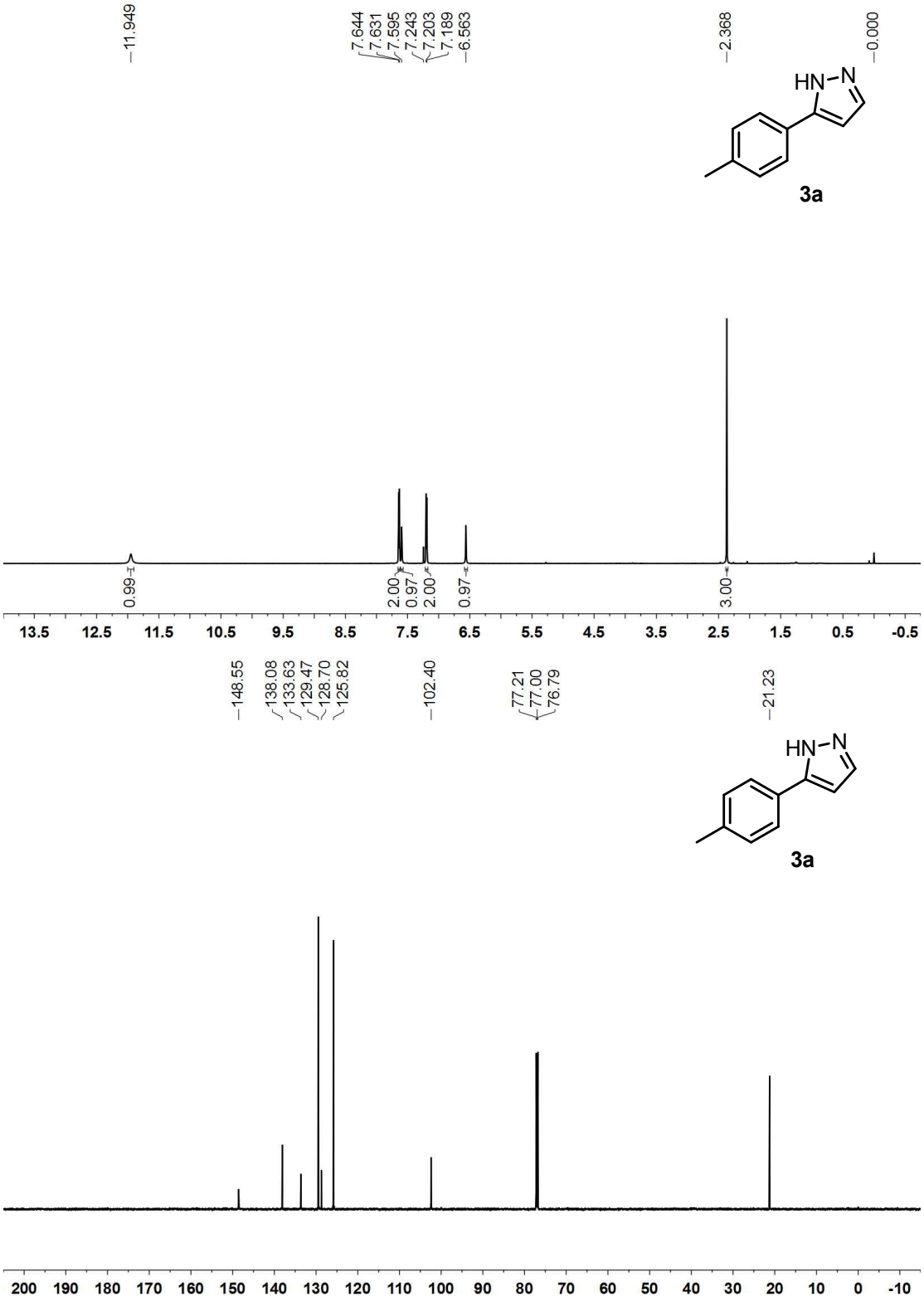
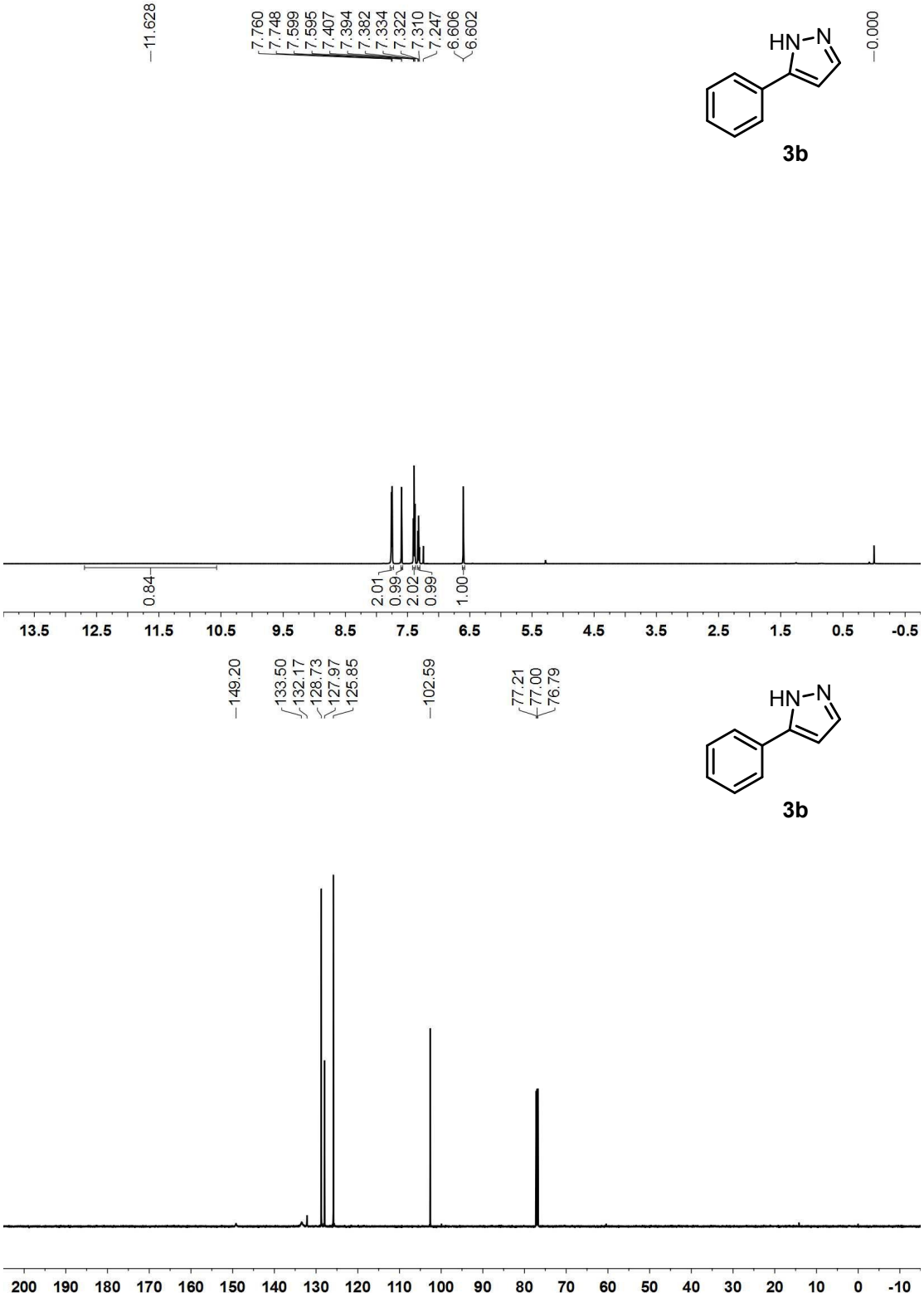
[5] E. V. Vashkevich, V. I. Potkin and N. G. Kozlov Russ. *J. Org. Chem.* 2004, **10**, 1503 –1507.

IV. ^{1}H- and ^{13}C-NMR spectra copies

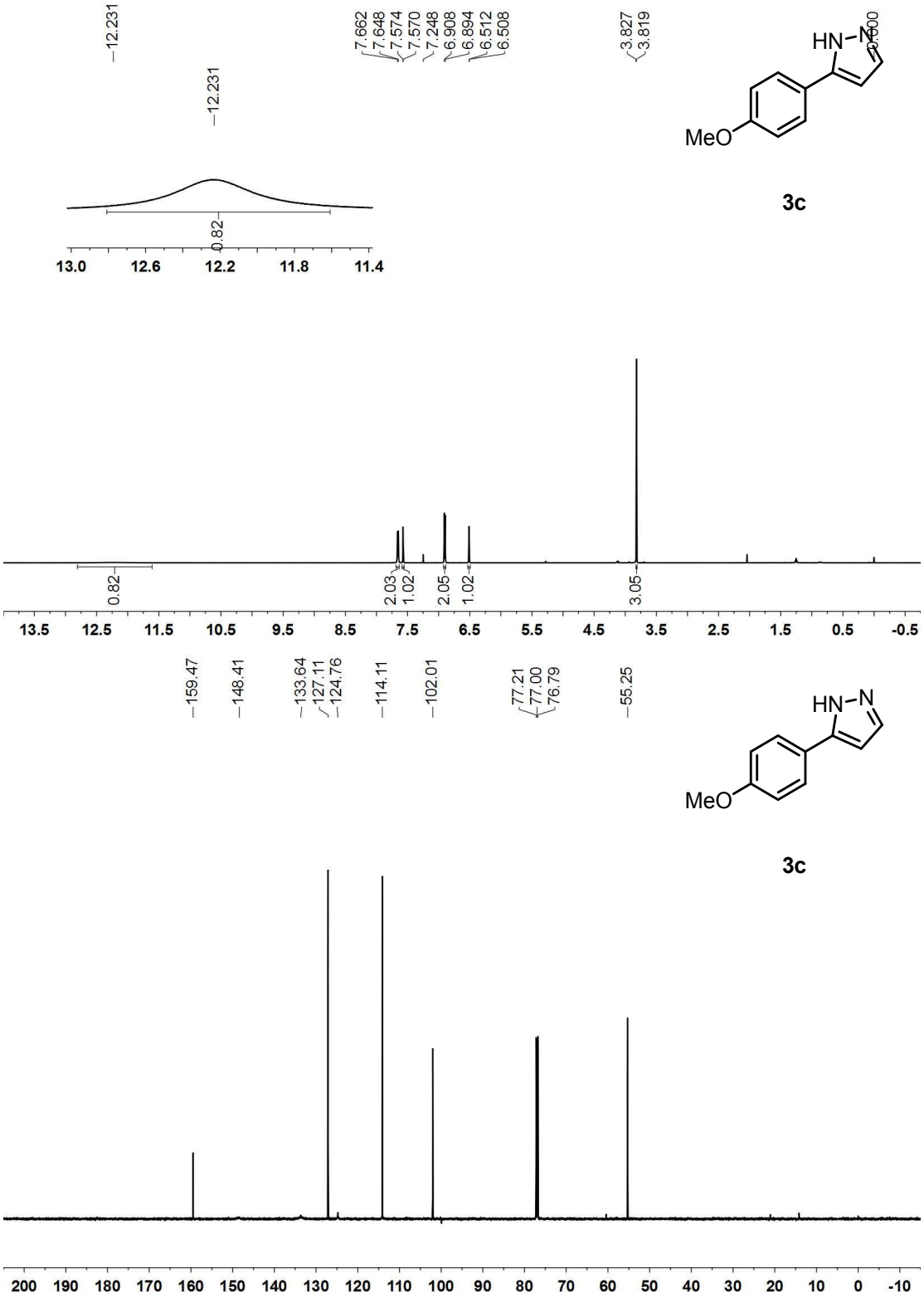
3a ^{1}**H-NMR** (600 MHz, $CDCl_3$) & ^{13}**C-NMR** ($CDCl_3$, 150 MHz)



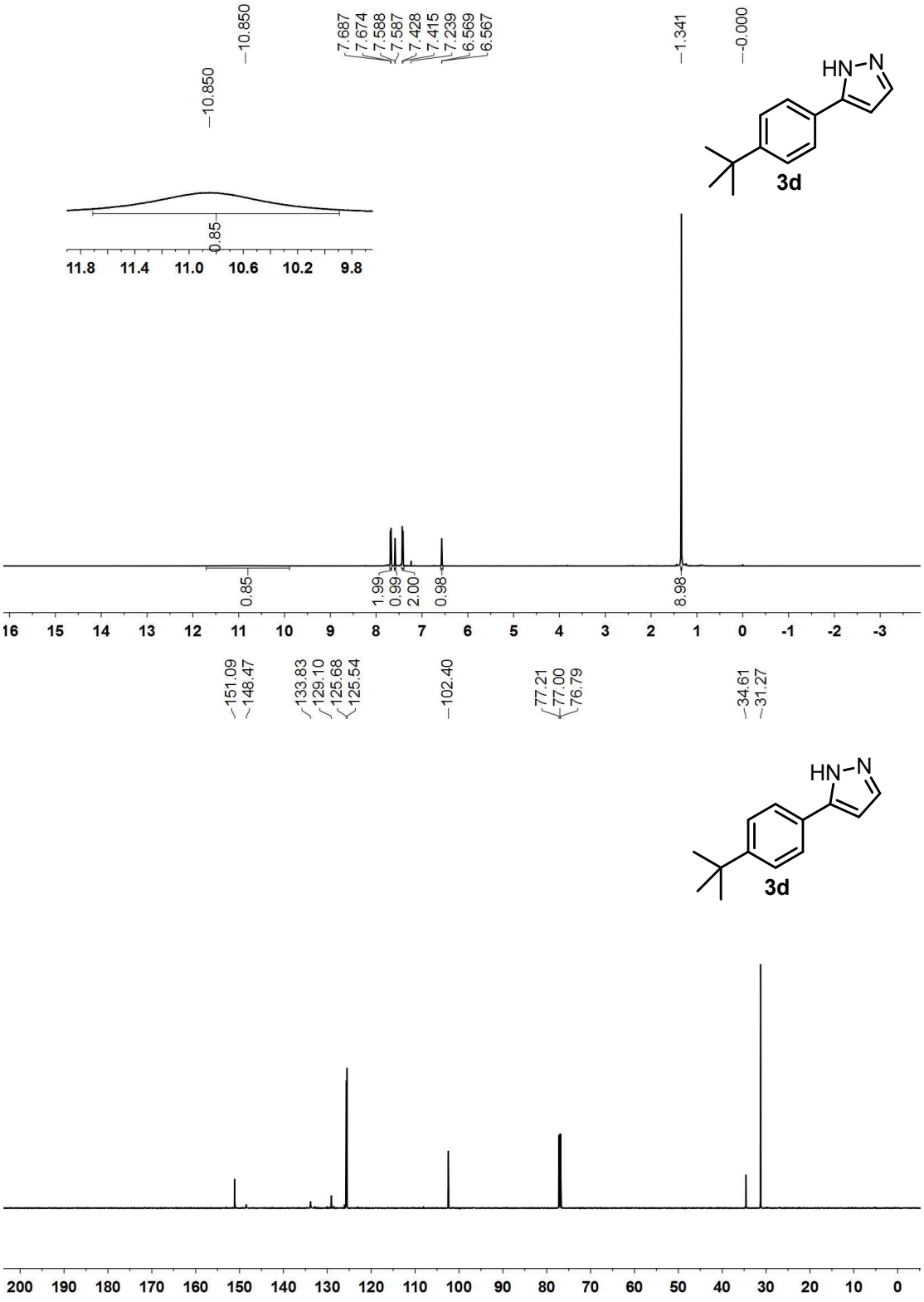
3b **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)



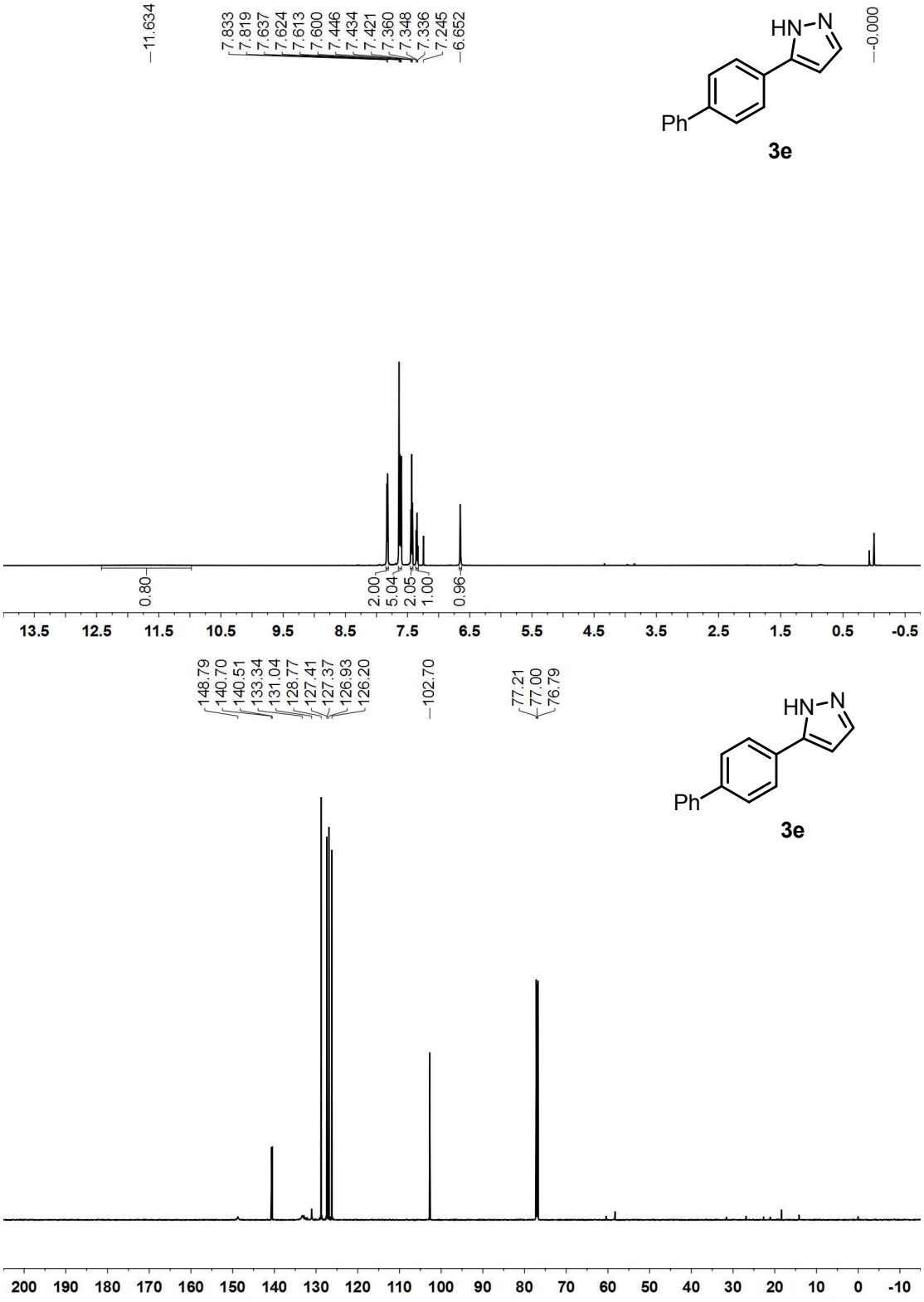
3c **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)



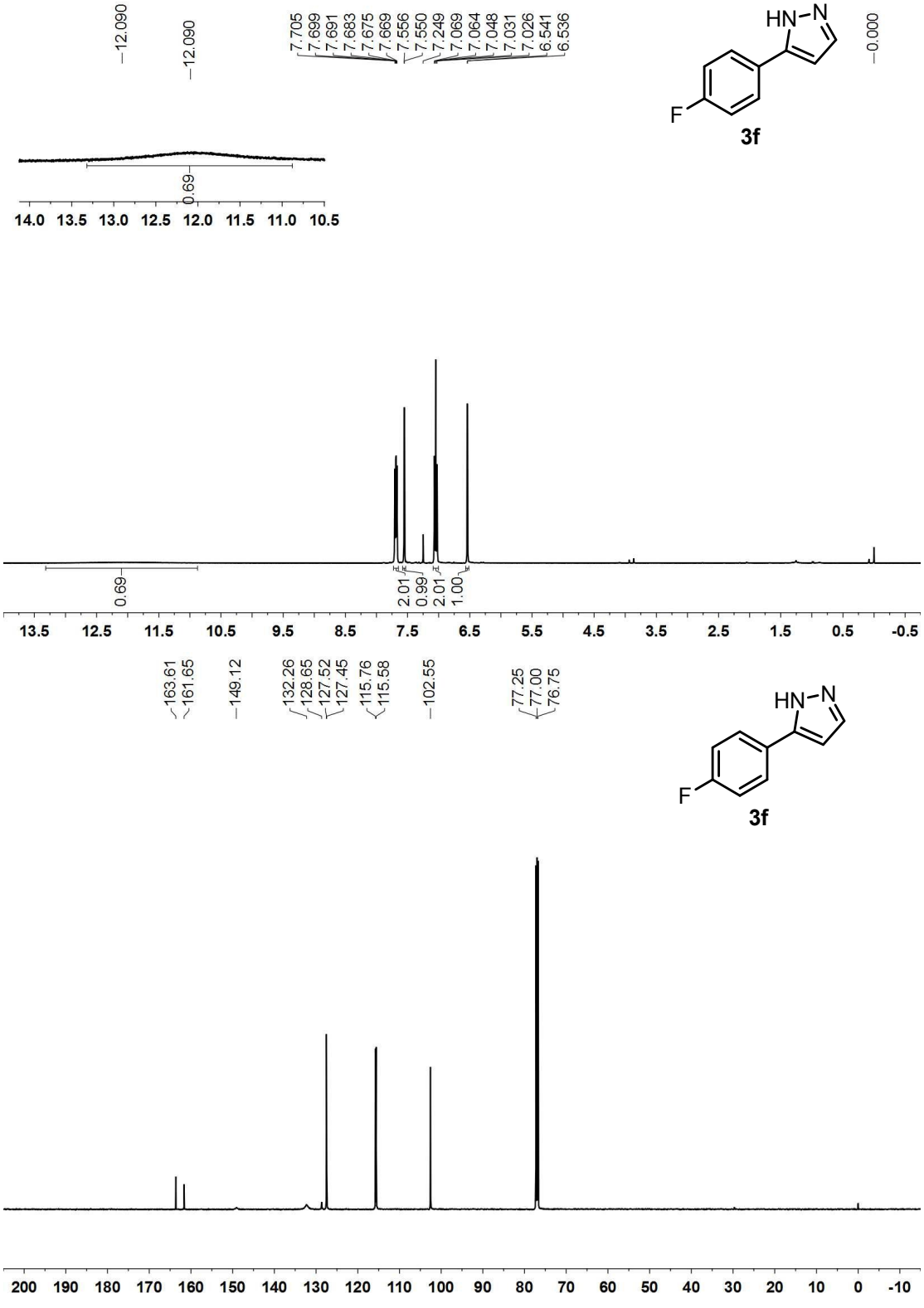
3d **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)



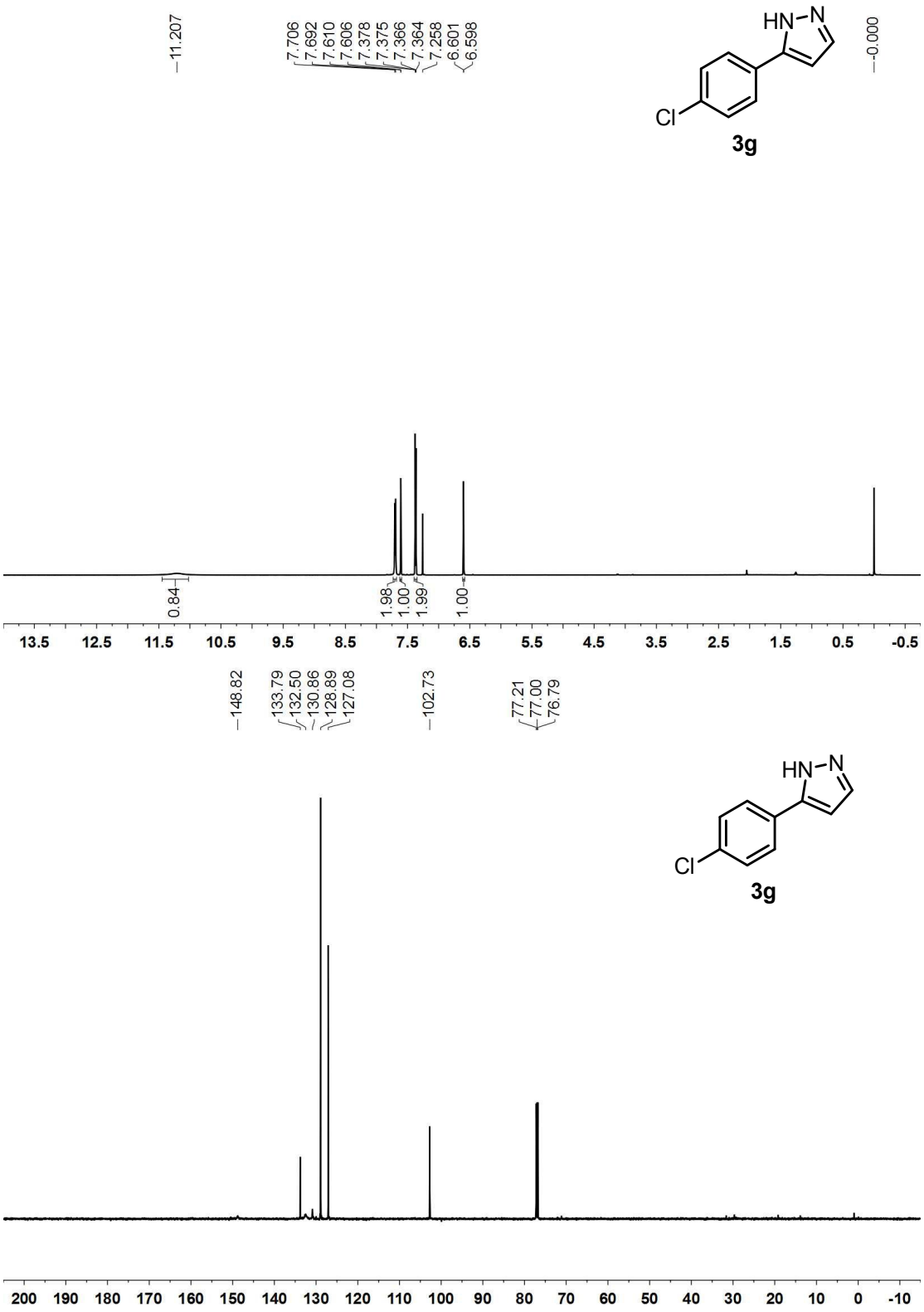
3e **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)



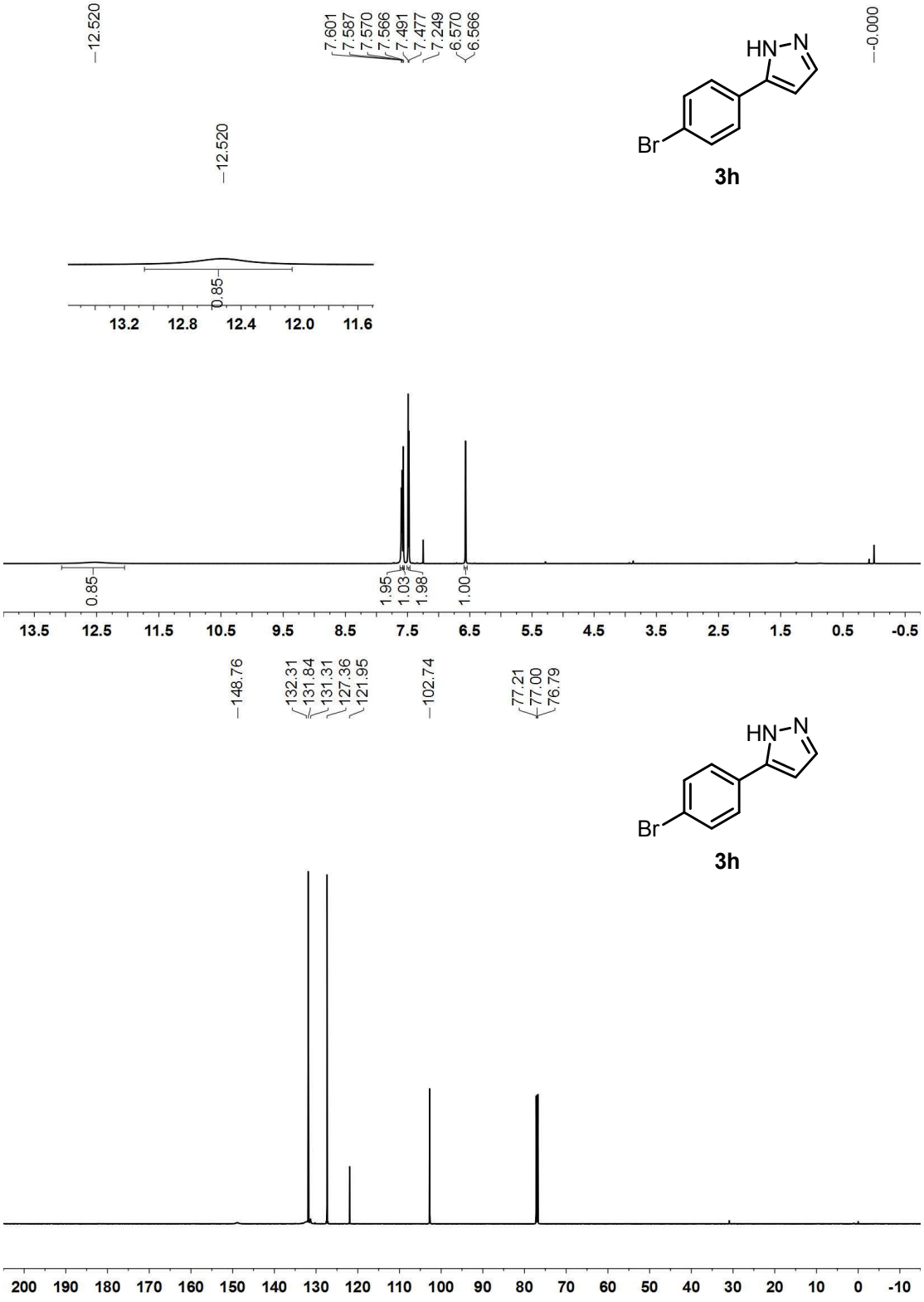
3f **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 125 MHz)



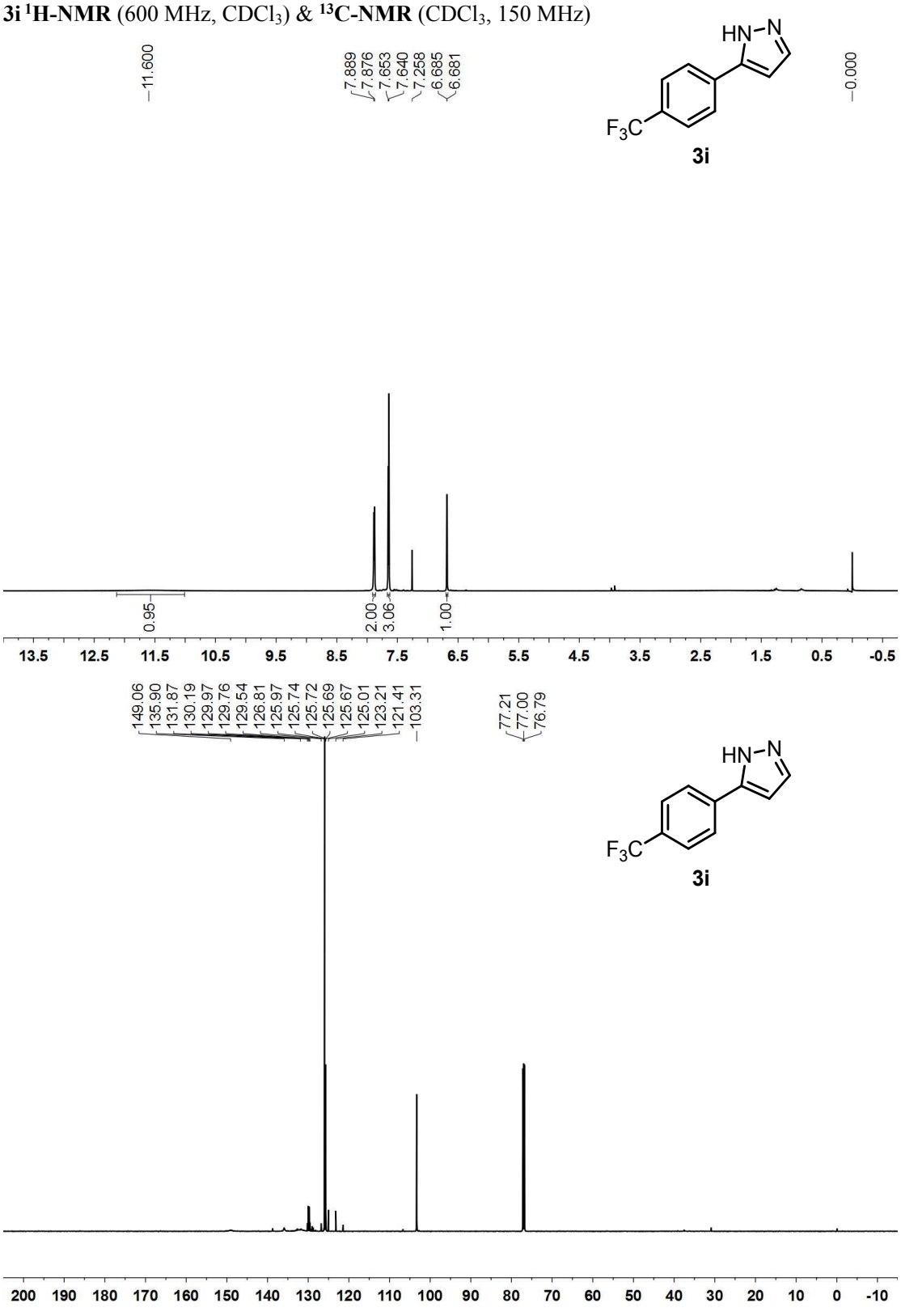
3g **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)



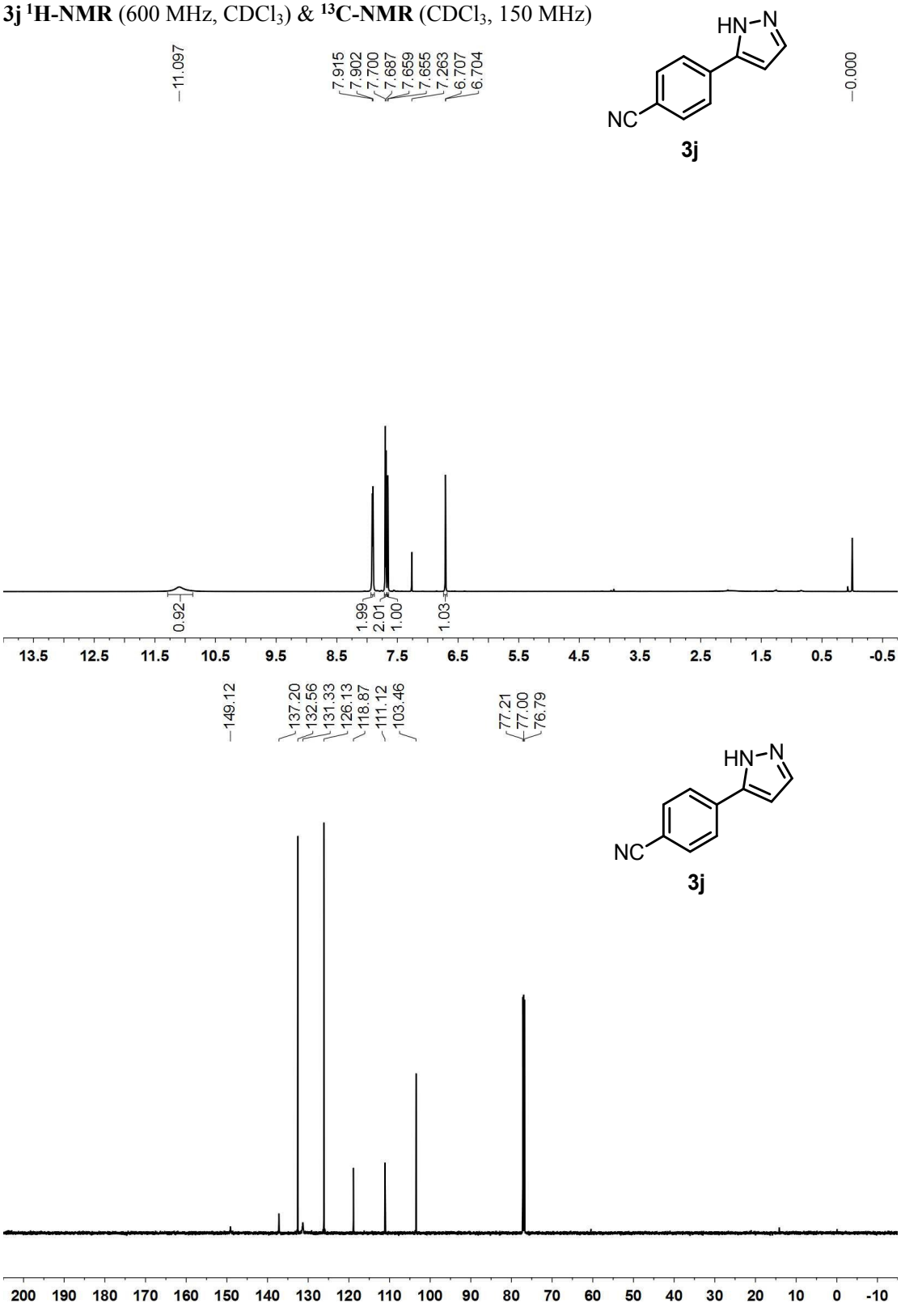
3h **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)



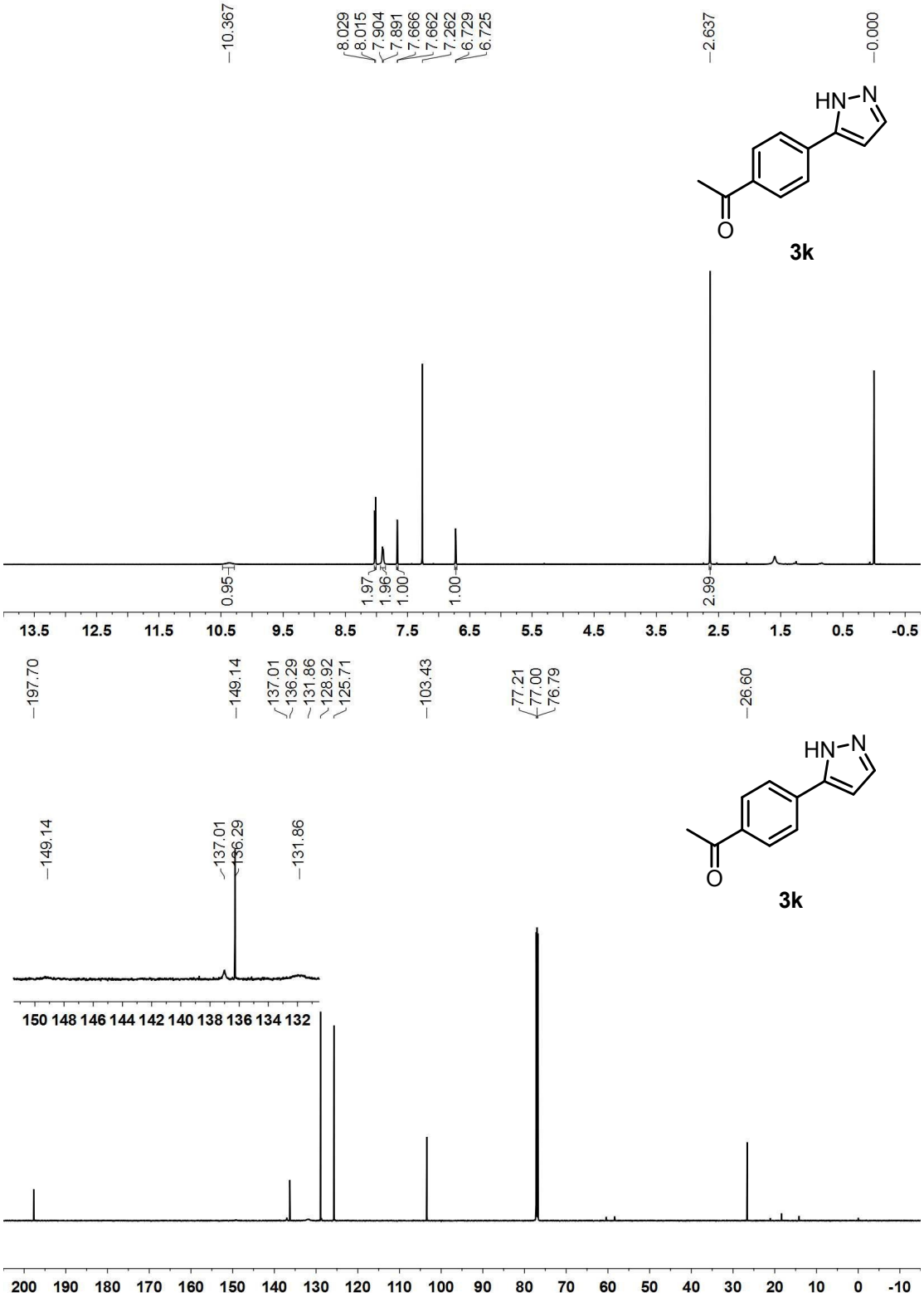
3i **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)



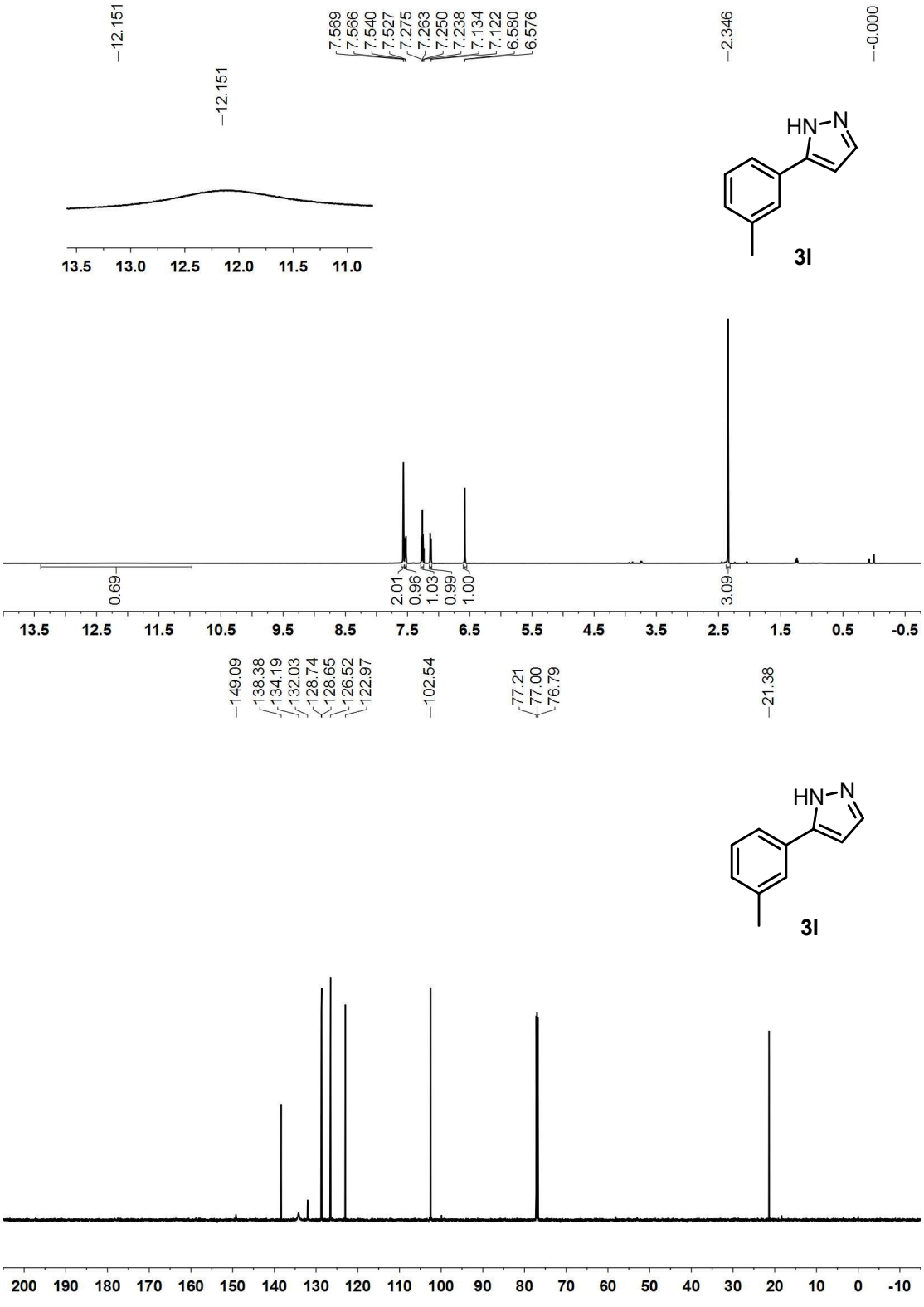
3j **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)



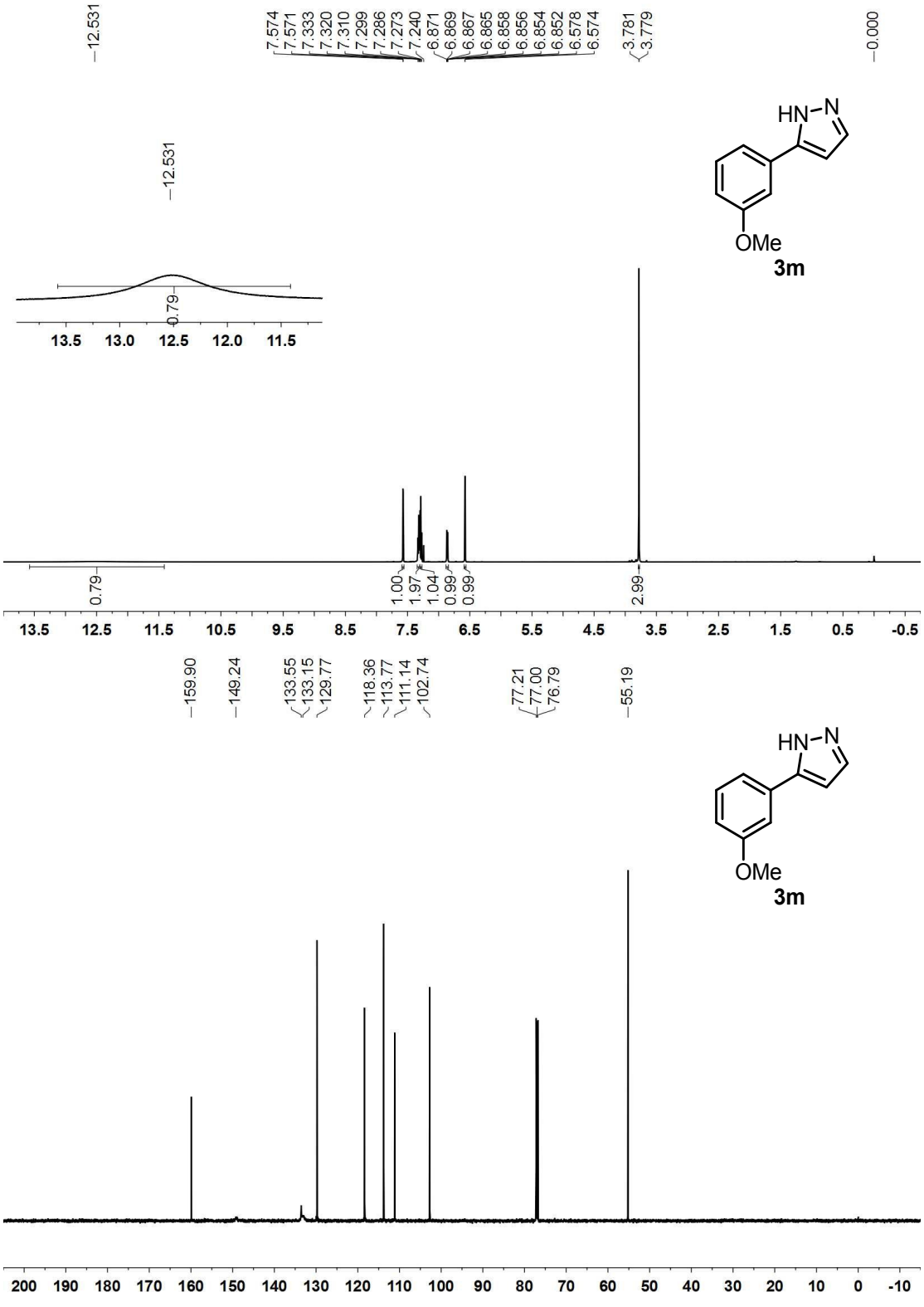
3k **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)



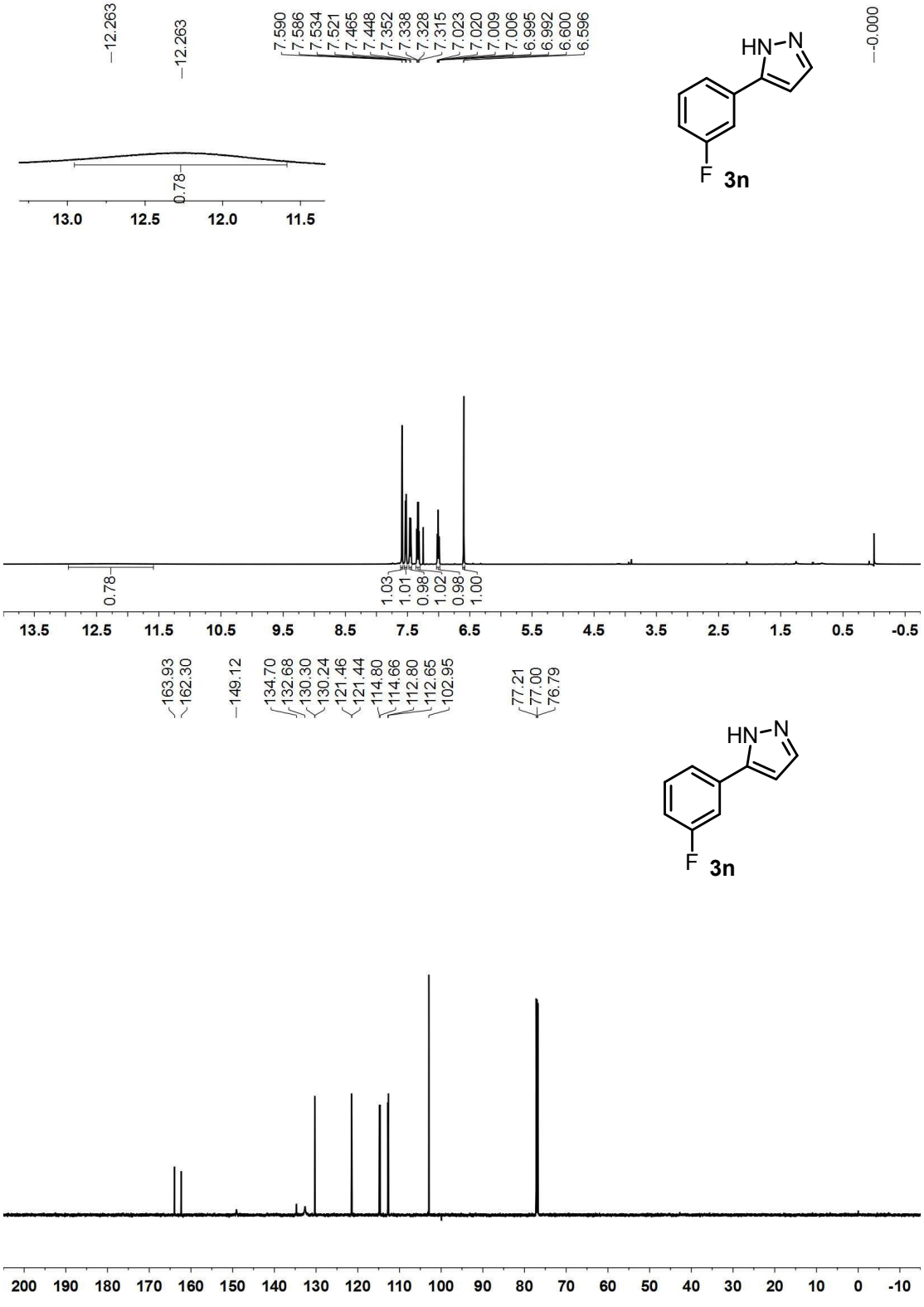
3l **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)



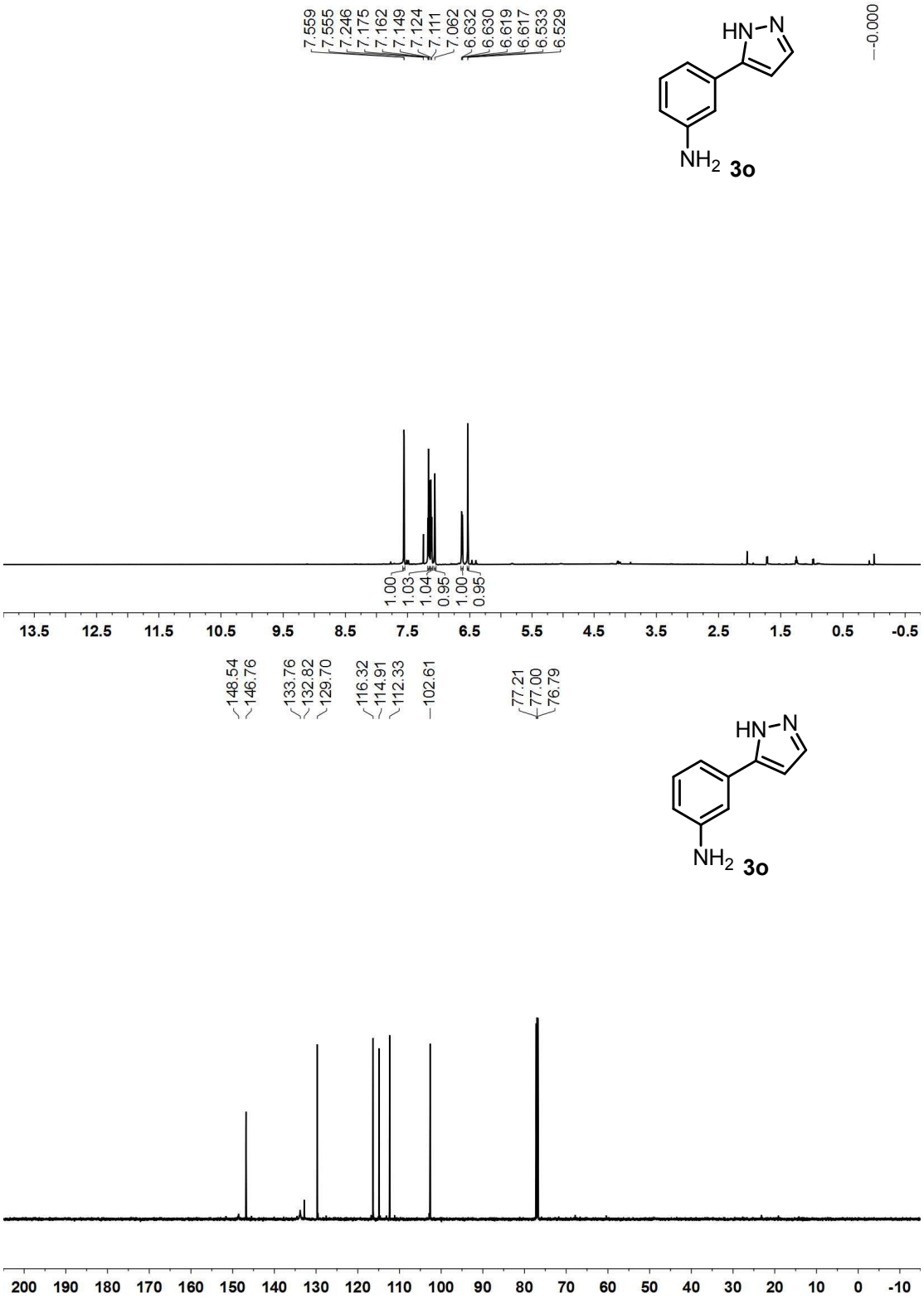
3m **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)



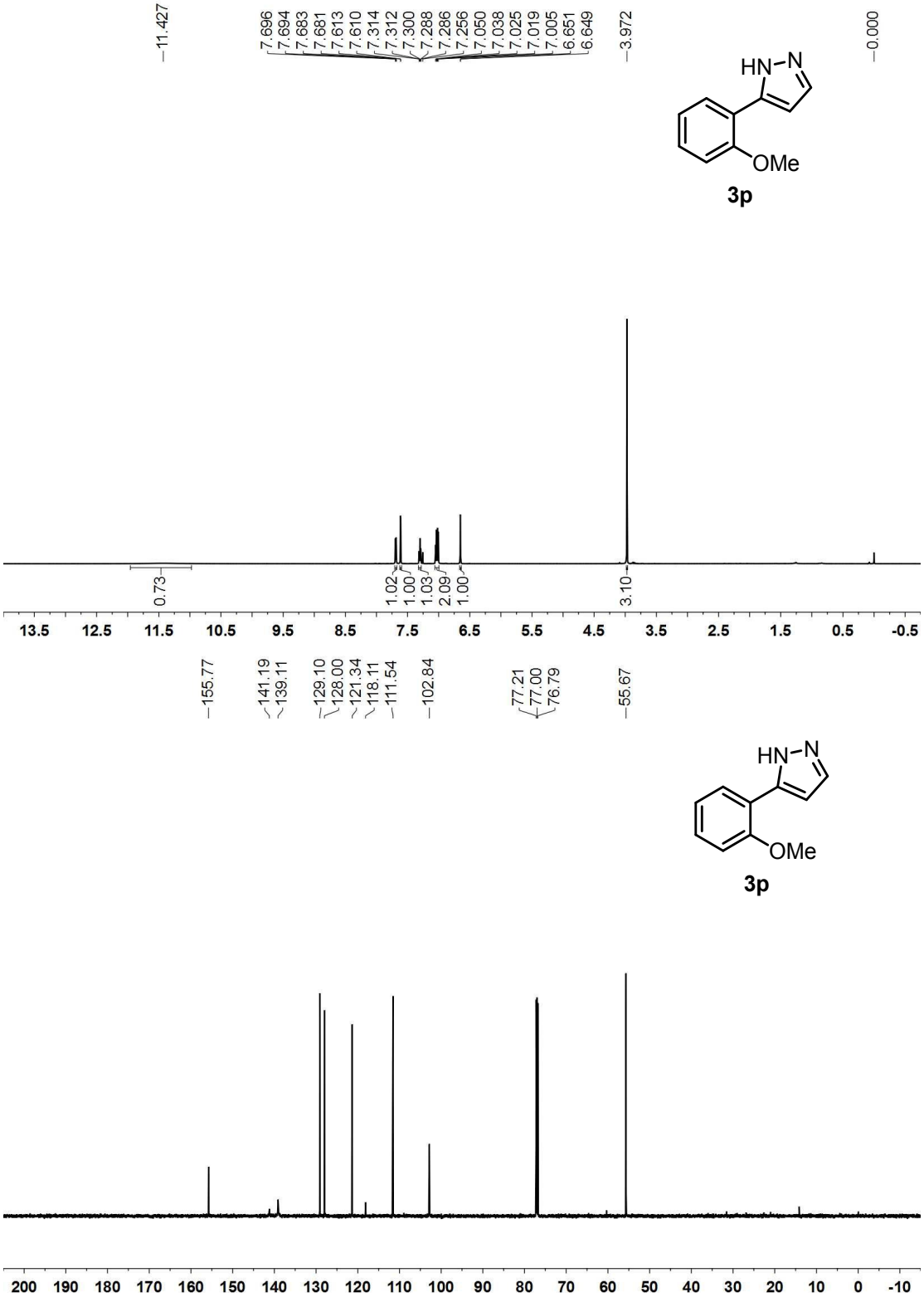
3n **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)



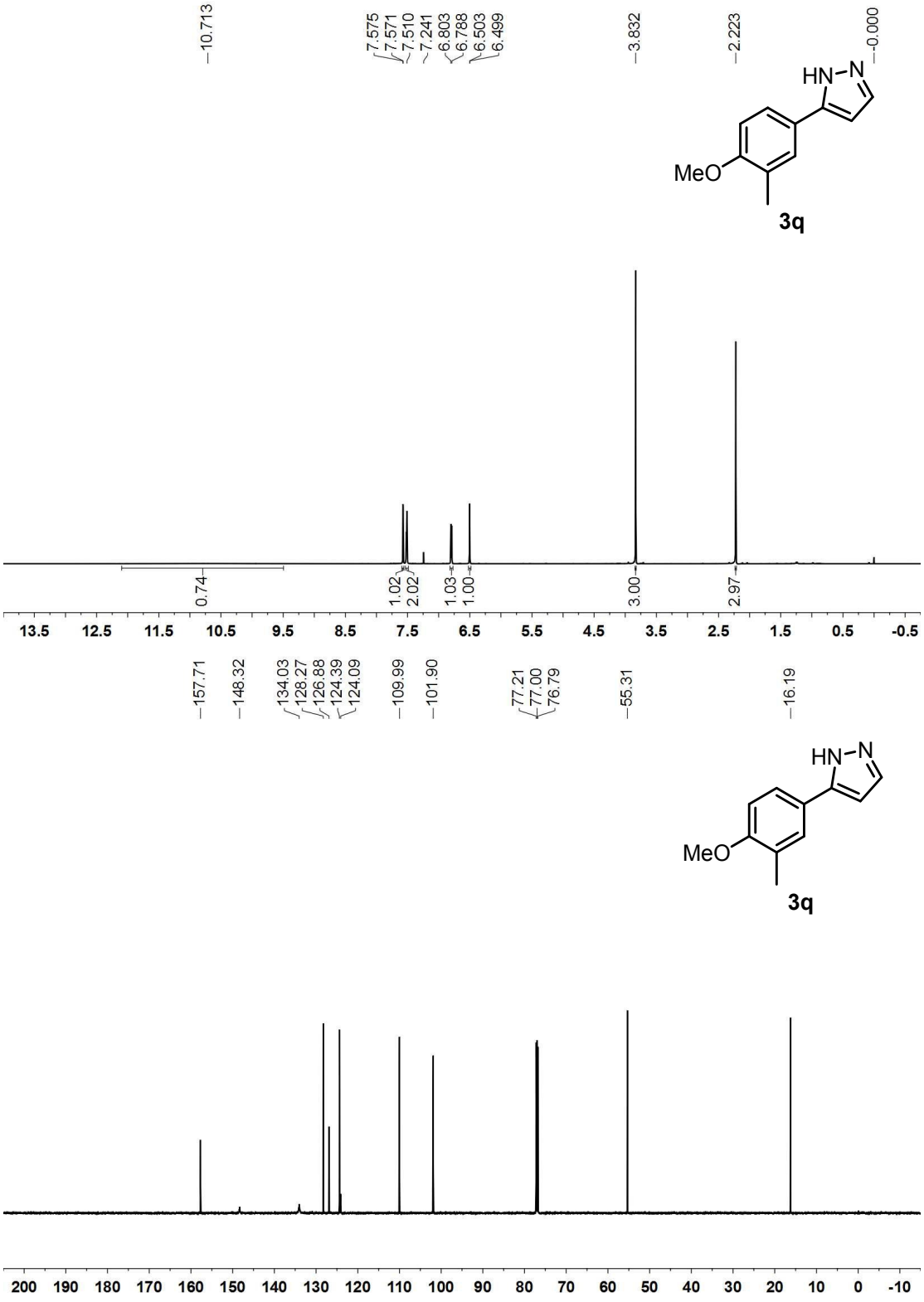
3o **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)



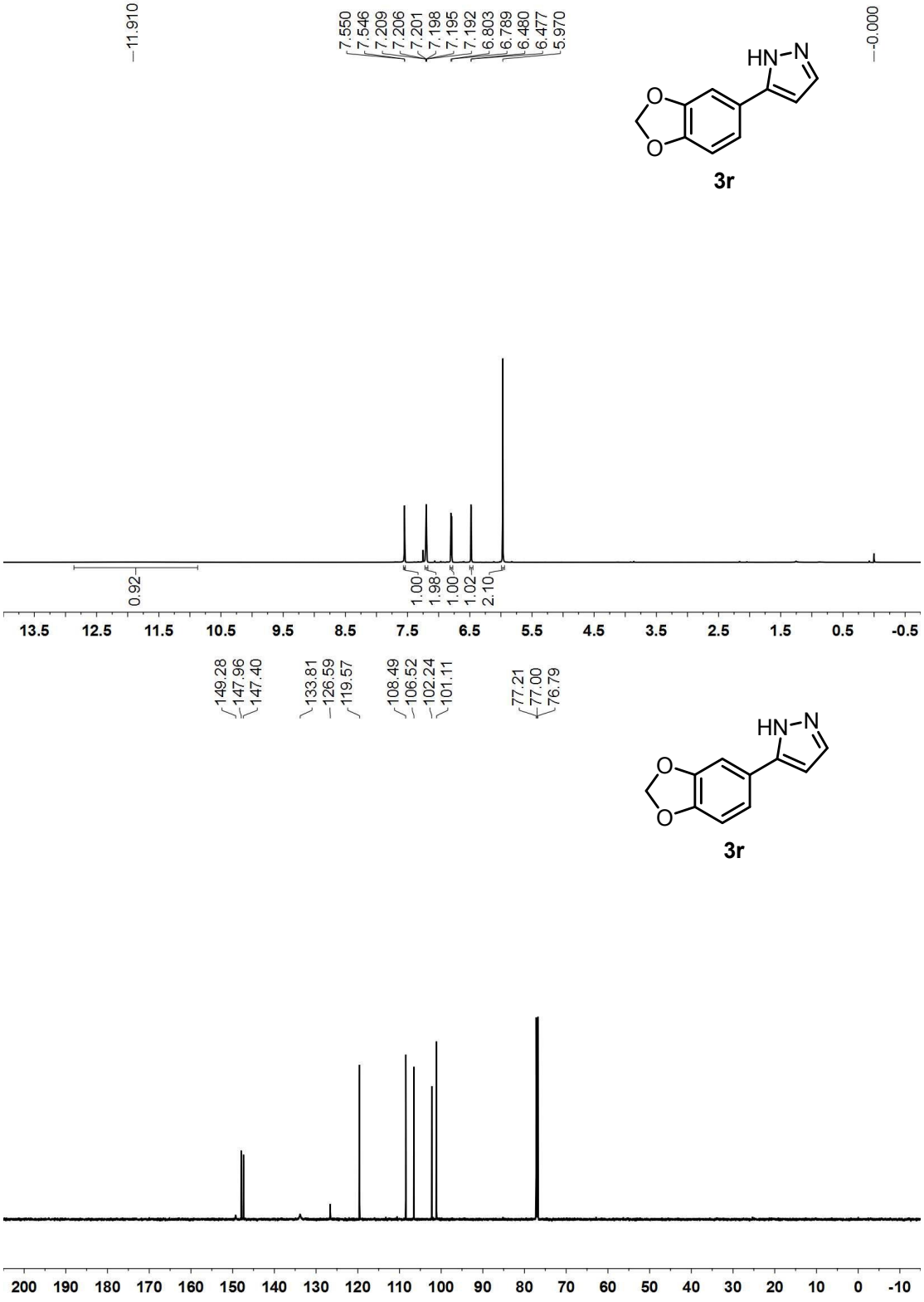
3p **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)



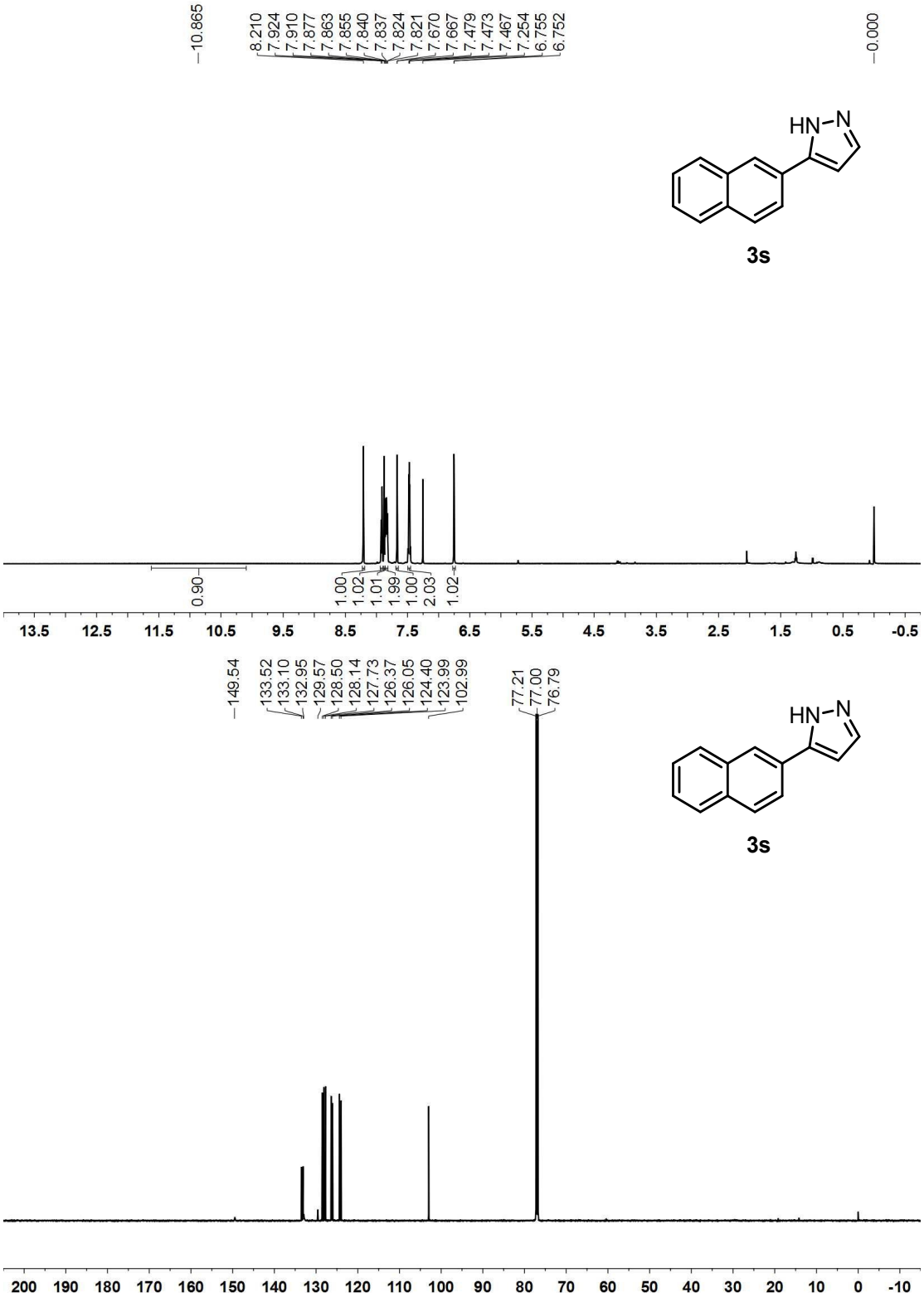
3q **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)



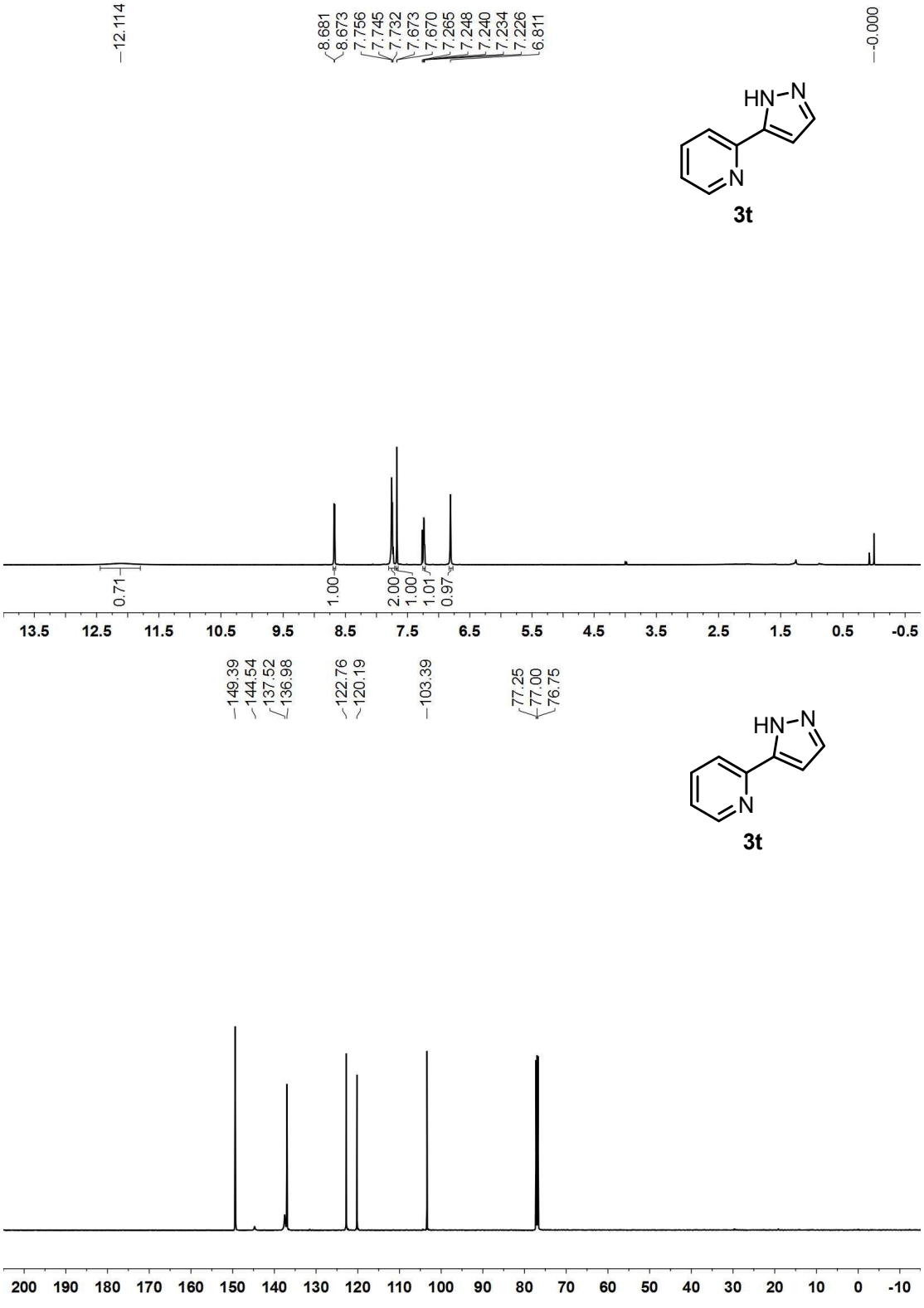
3r **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)



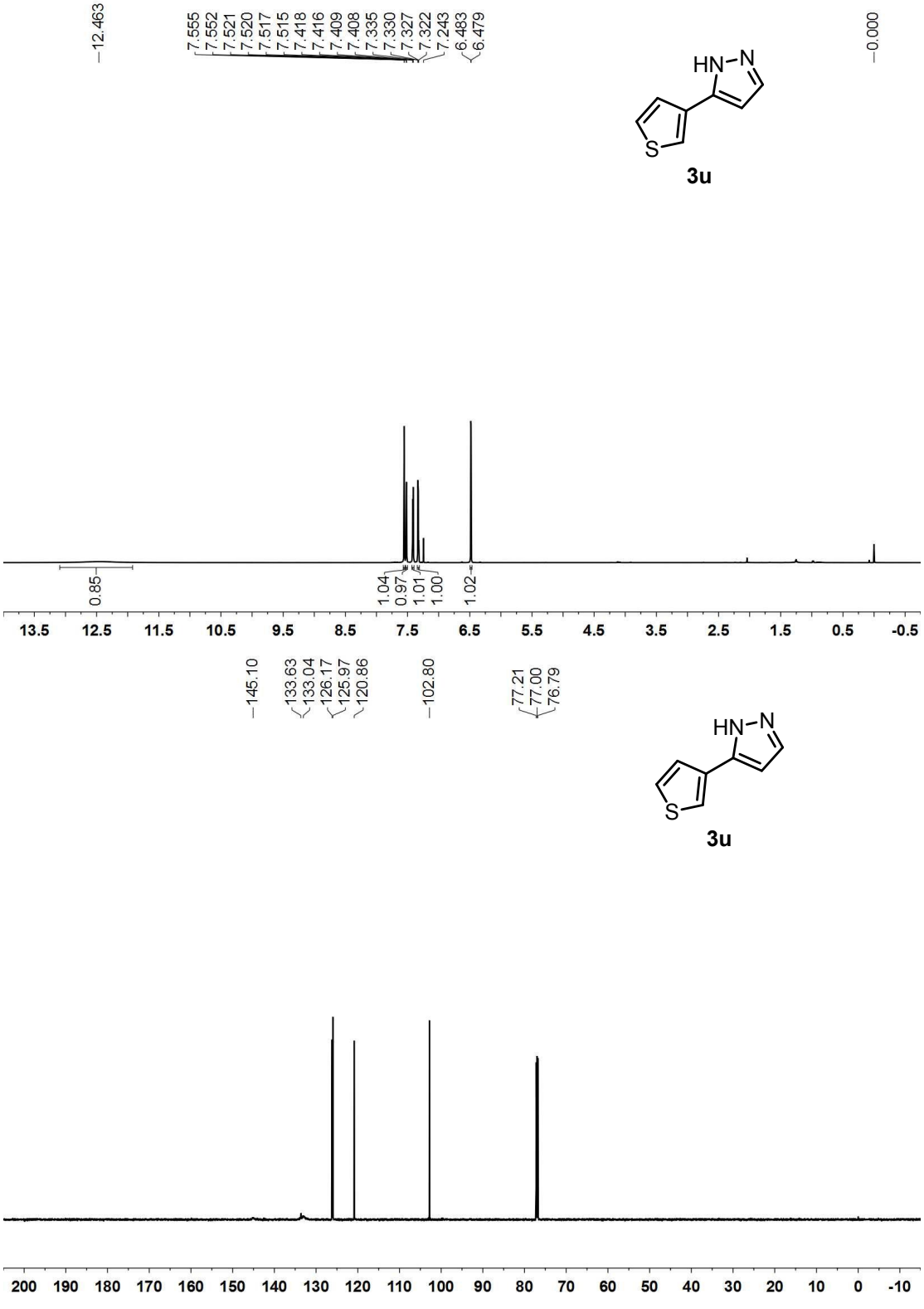
3s **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)



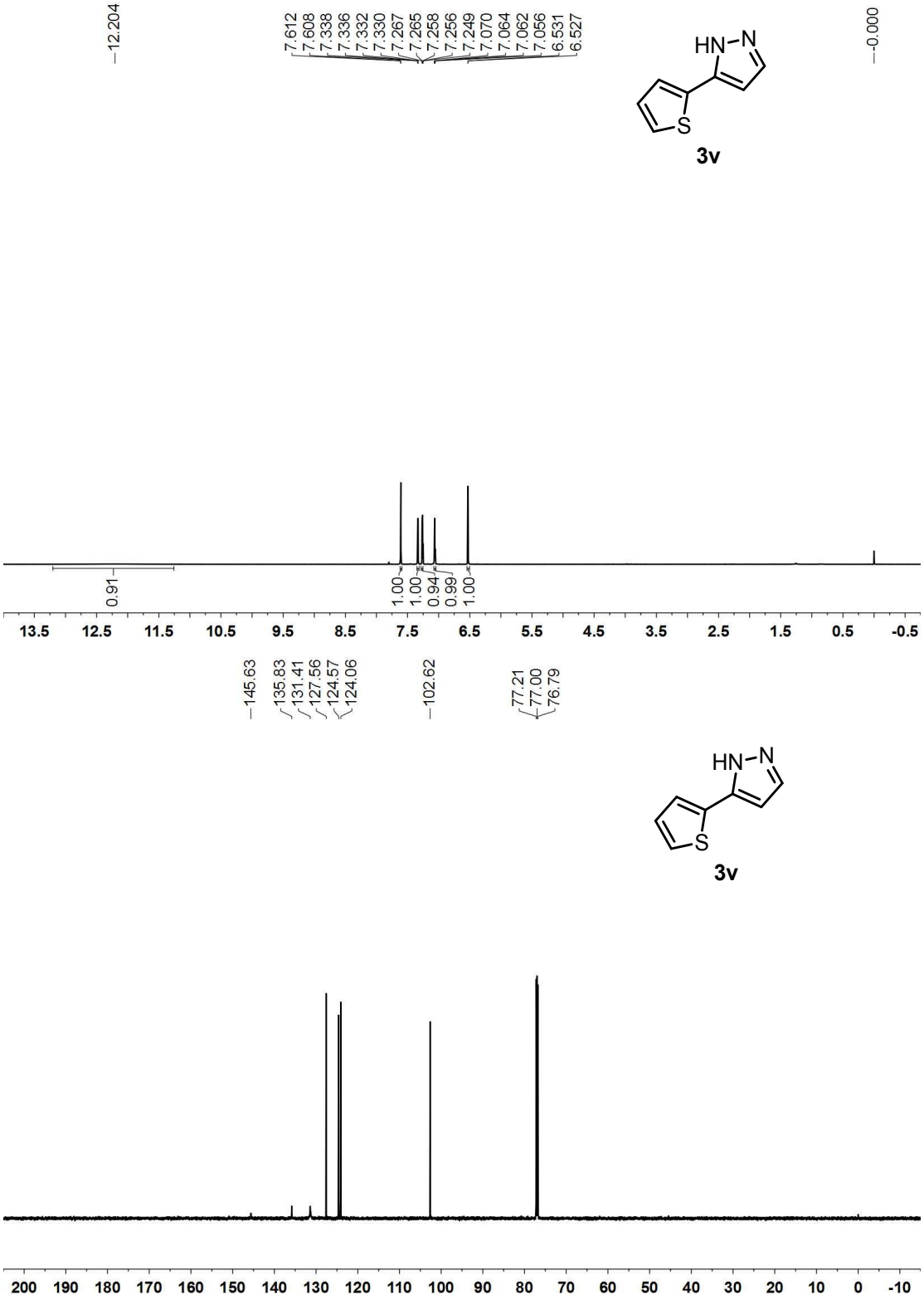
3t **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)



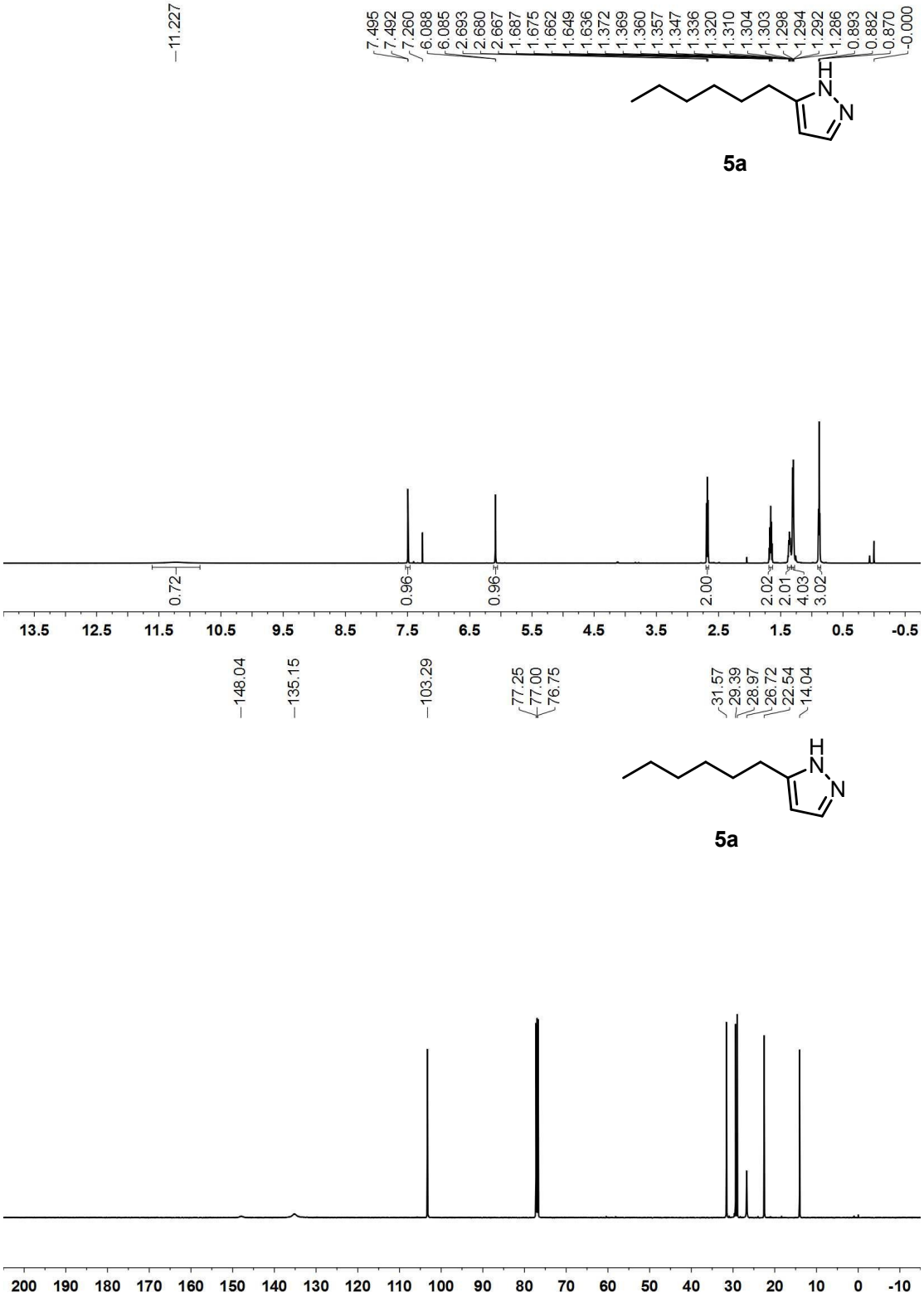
3u **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)



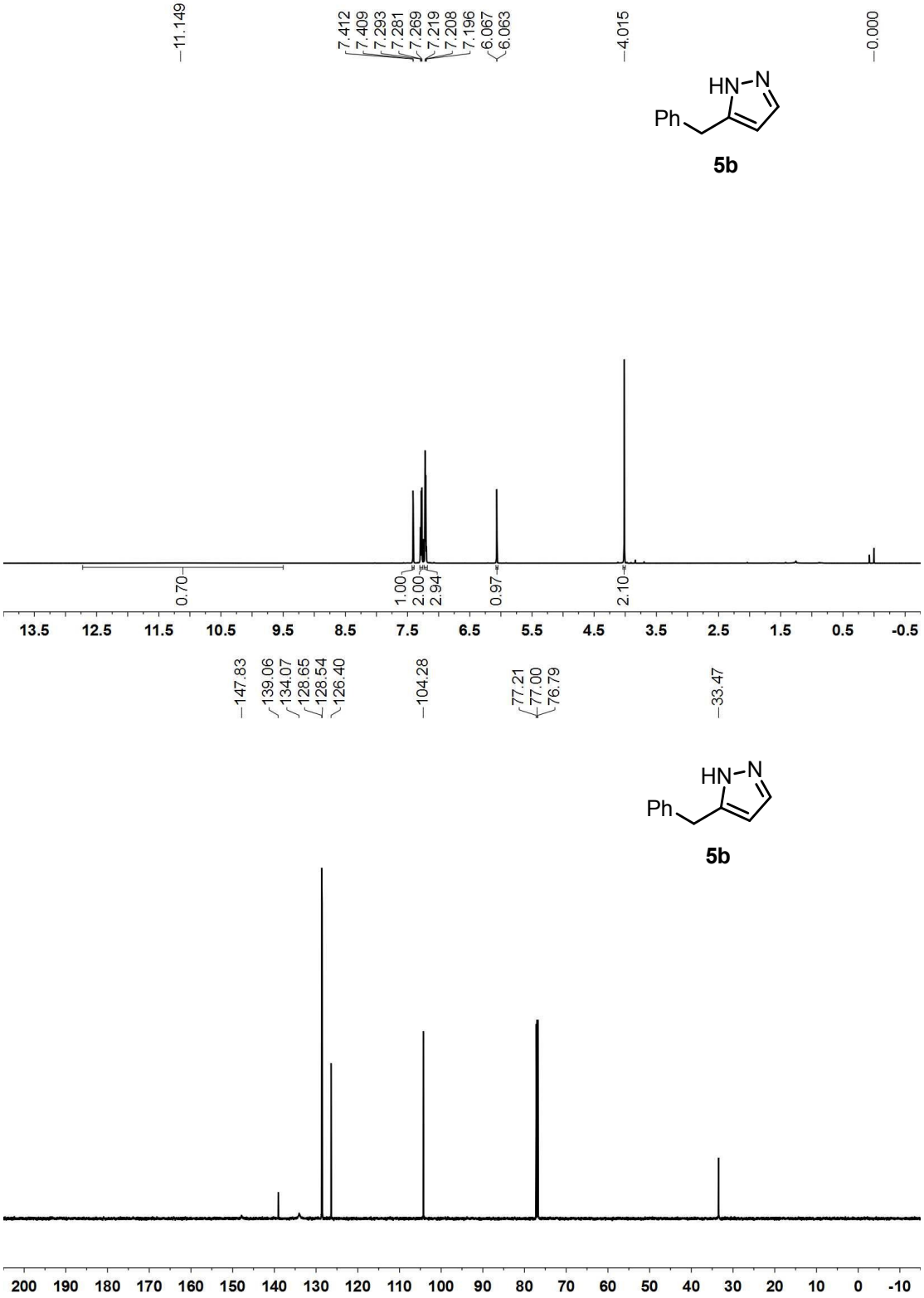
3v **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)



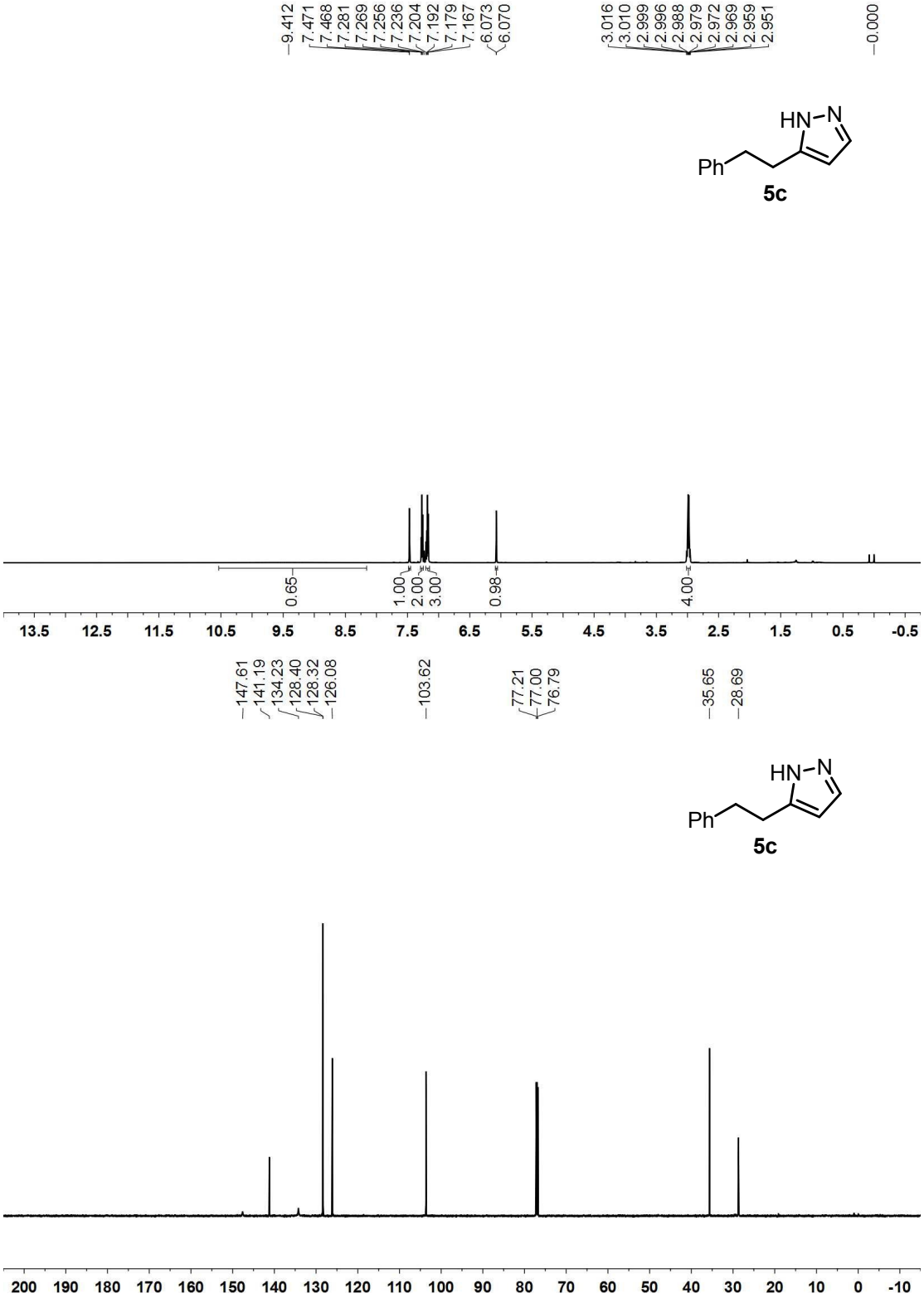
5a **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 125 MHz)



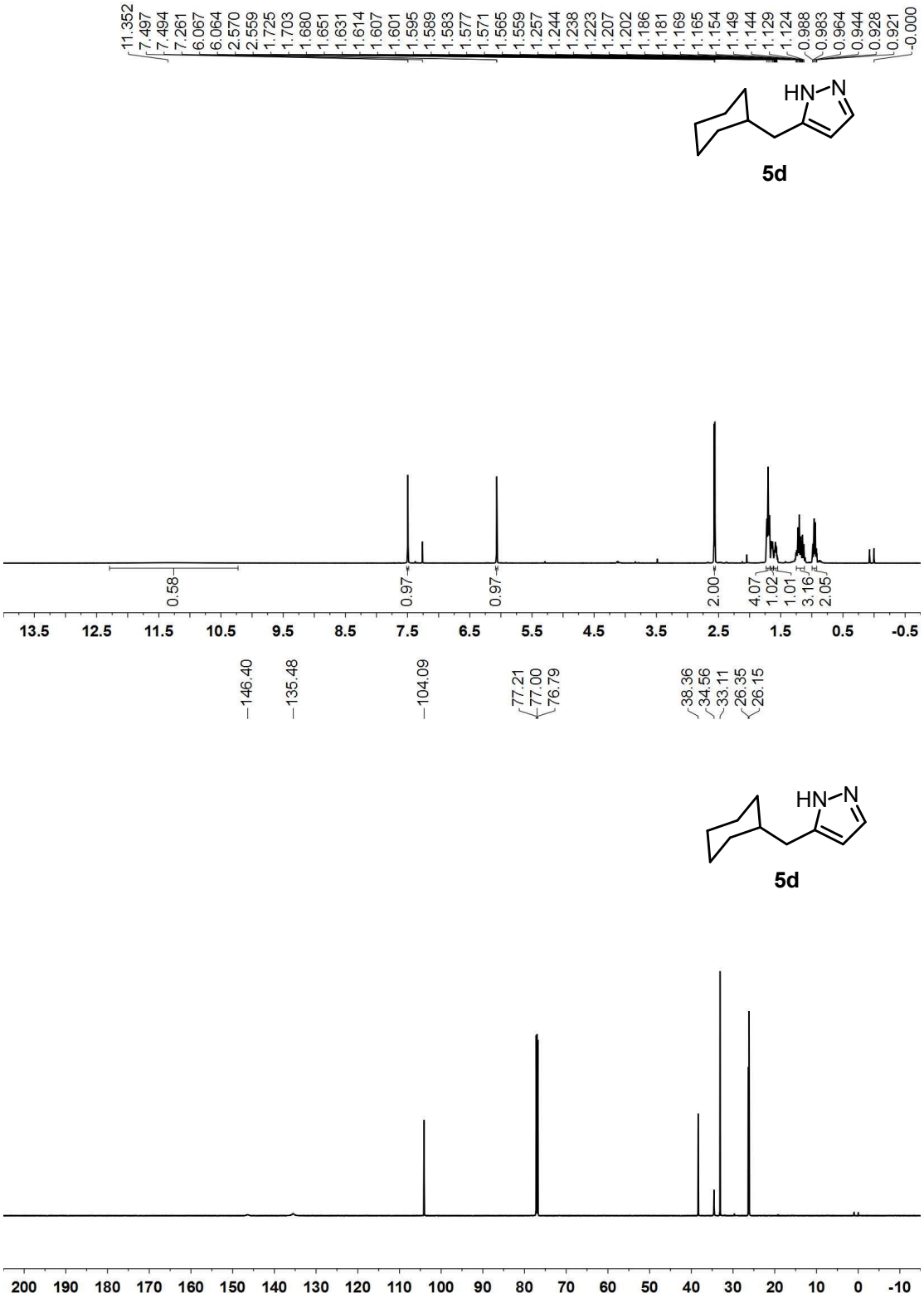
5b **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)



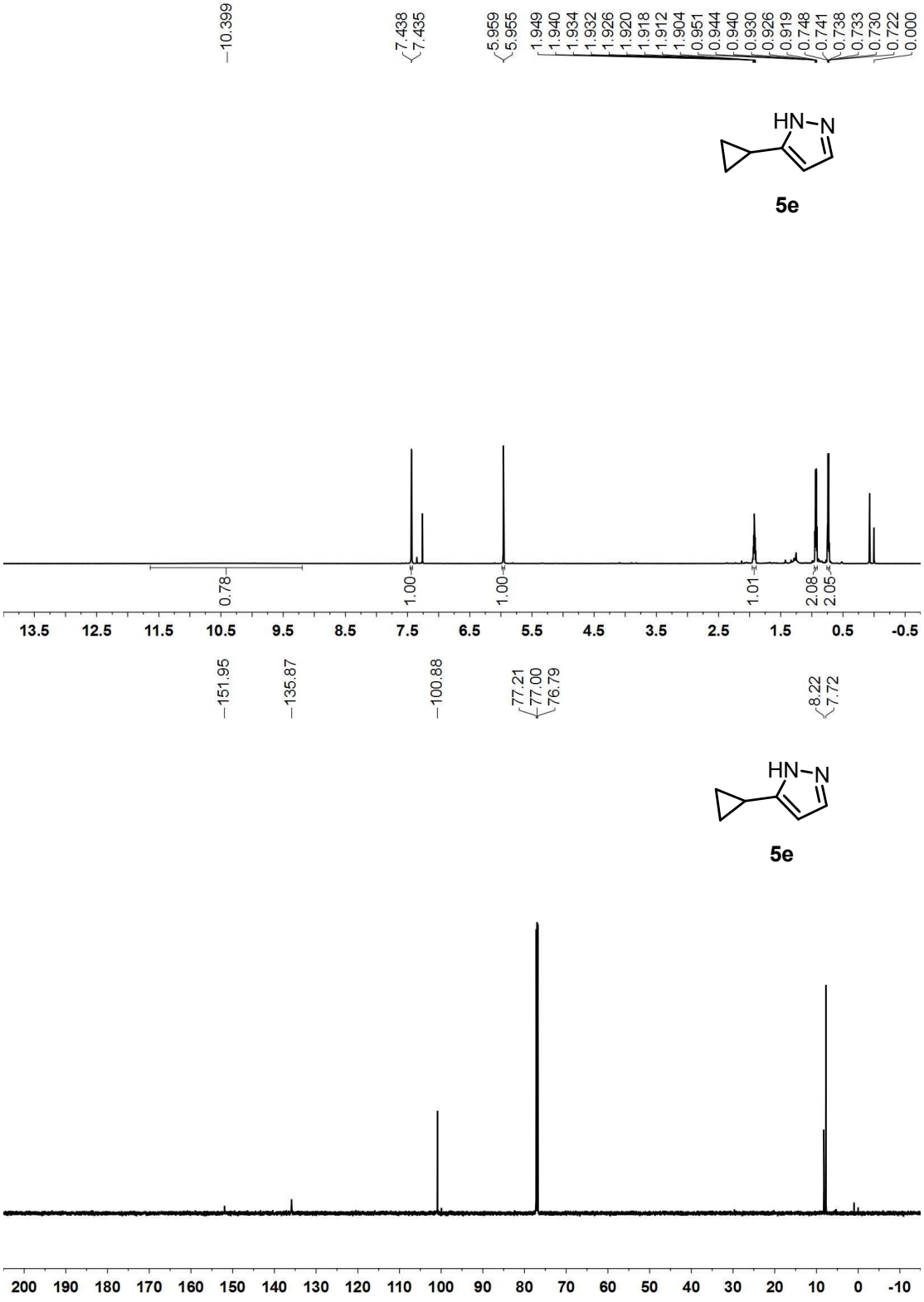
5c **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)



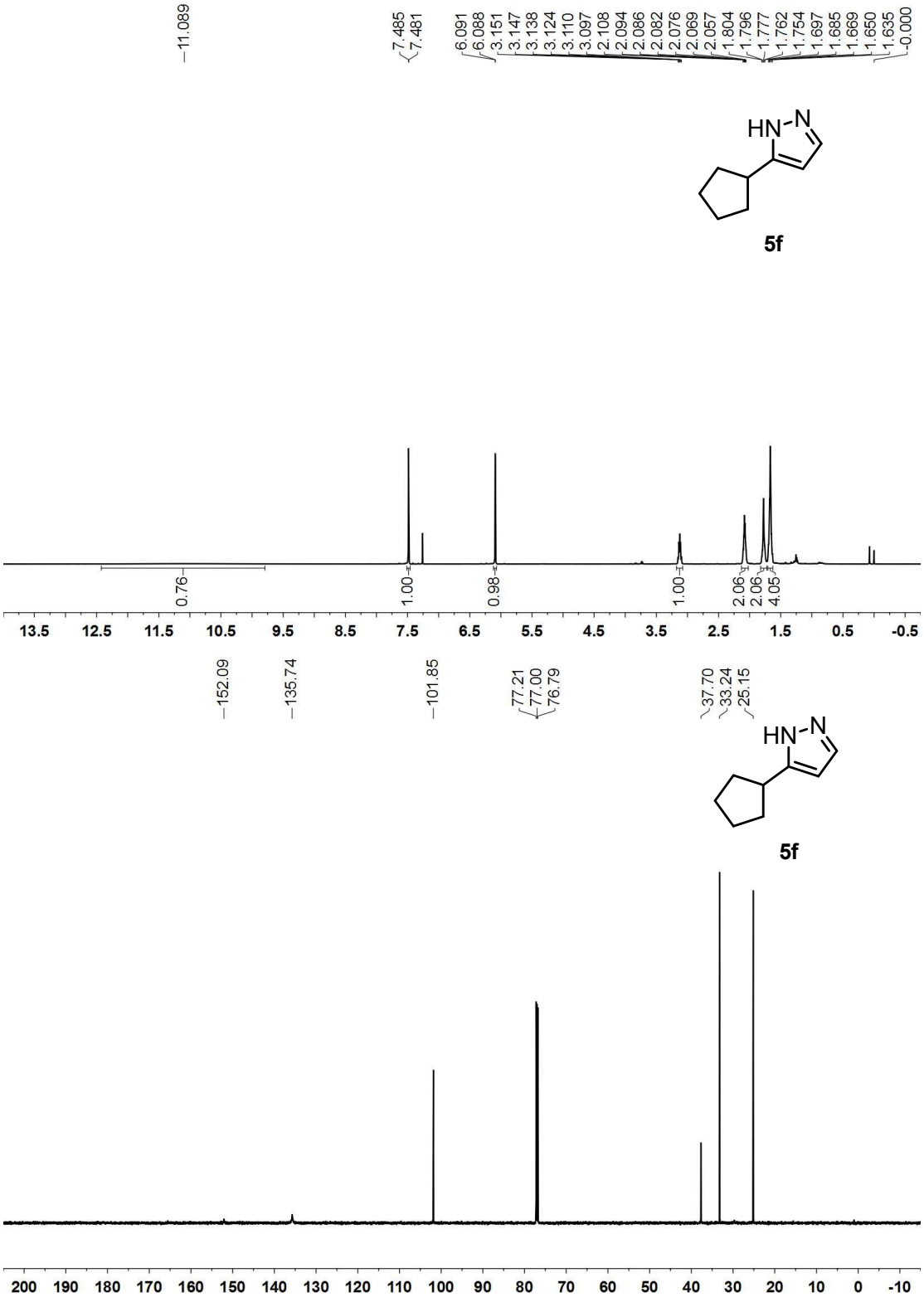
5d **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)



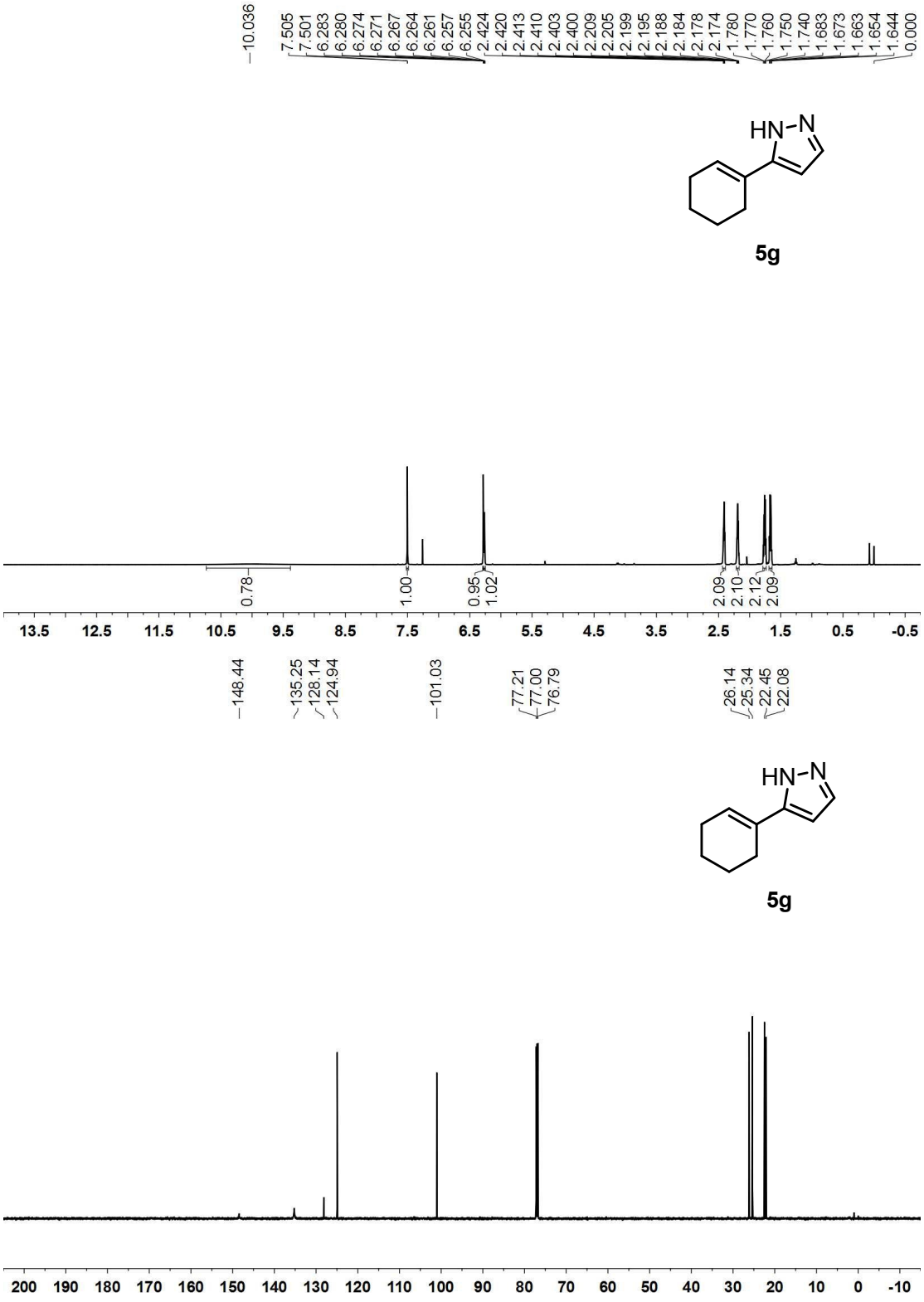
5e **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)



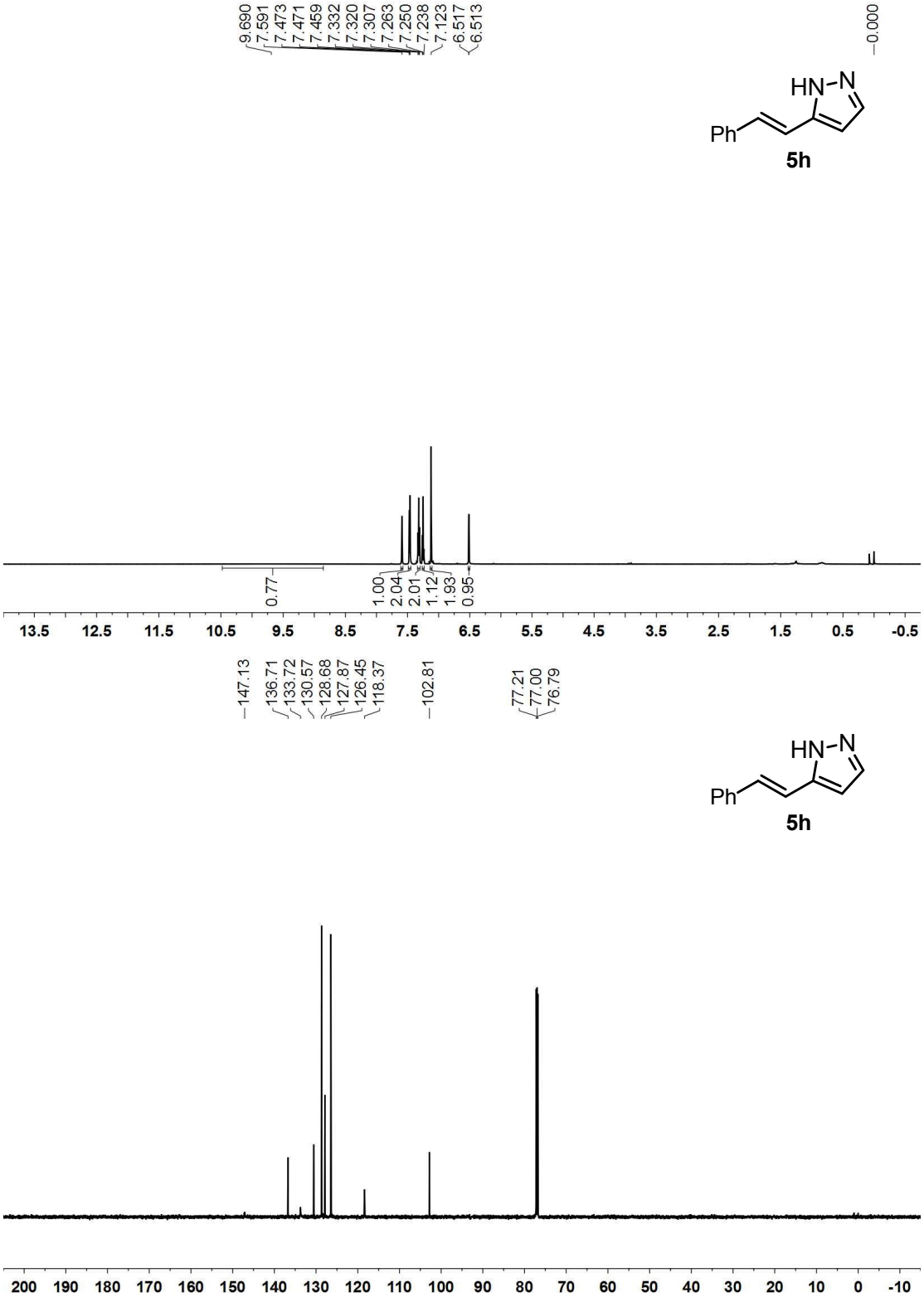
5f **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)



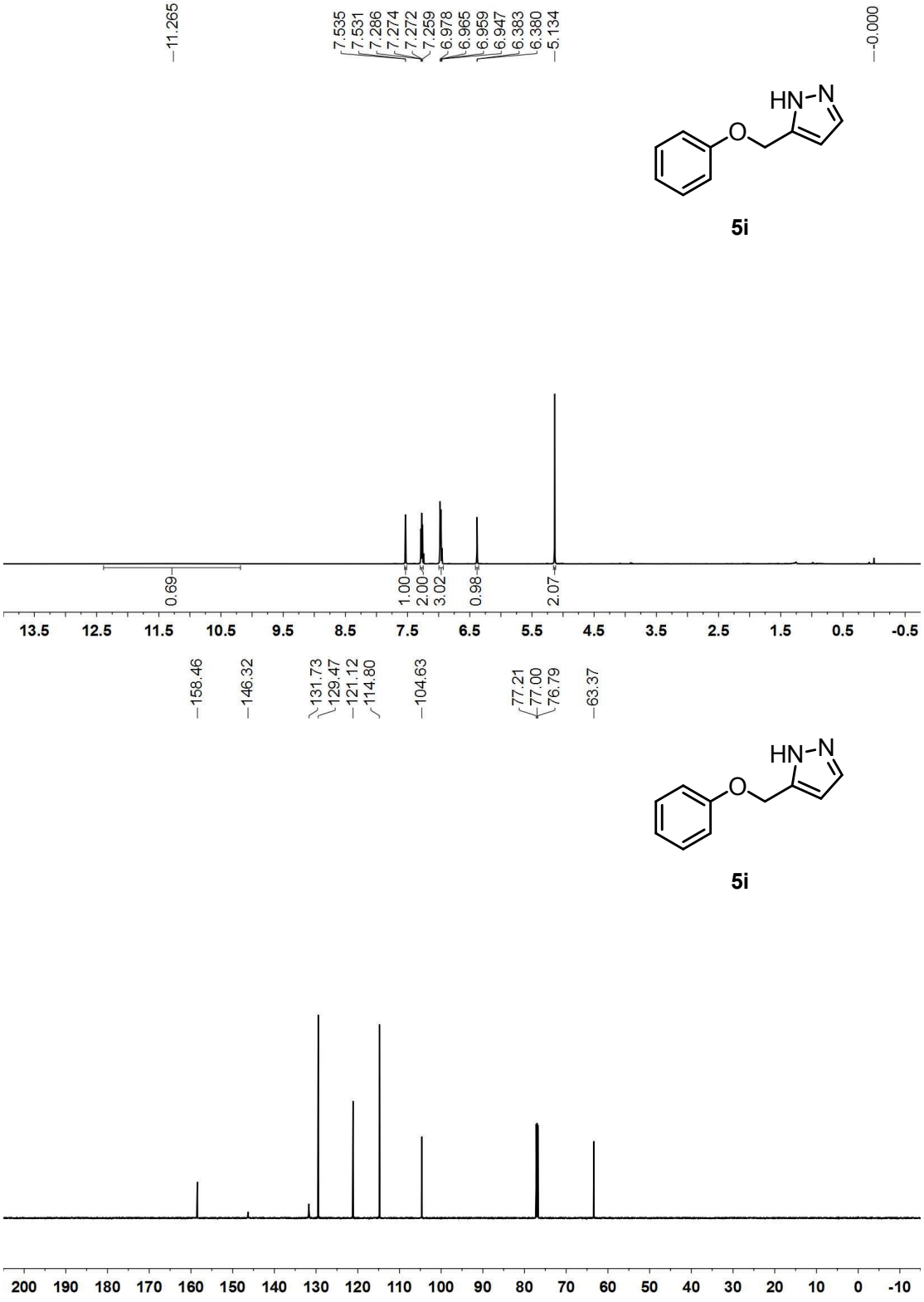
5g **^{1}H-NMR** (500 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 125 MHz)



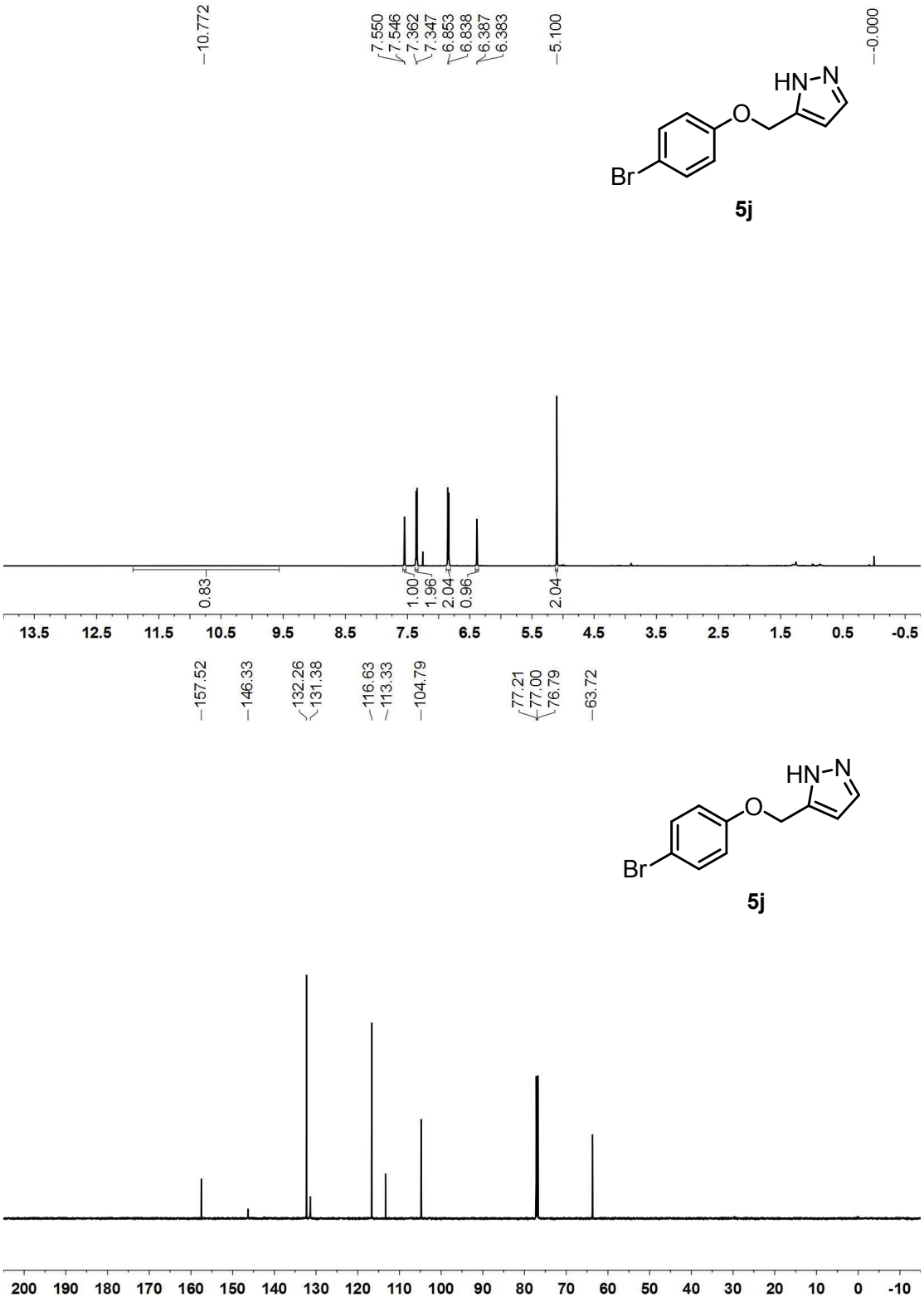
5h **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)



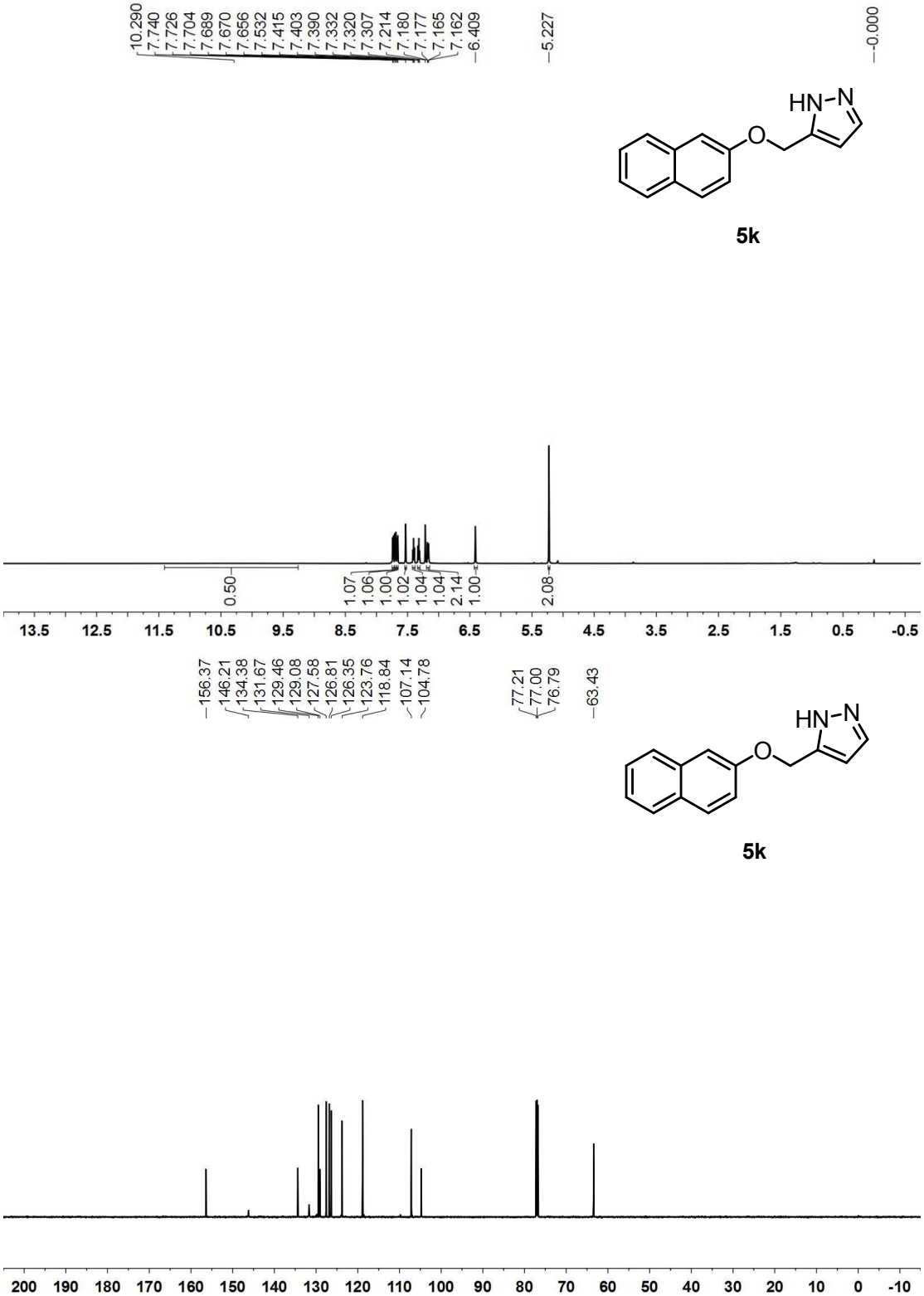
5i **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)



5j **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)



5k **^{1}H-NMR** (600 MHz, $CDCl_3$) & **^{13}C-NMR** ($CDCl_3$, 150 MHz)



[D]-3a ^{1}H-NMR (600 MHz, $CDCl_3$)