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Electronic Supplementary Information

Rh(III)-Catalyzed C-7 Arylation of Indolines with Arylsilanes

Haiqing Luo,* Qi Xie, Kai Sun, Jianbo Deng, Lin Xu, Kejun Wang, Xuzhong Luo*
Department of Chemistry & Chemical Engineering, Gannan Normal University, Ganzhou 341000, China.

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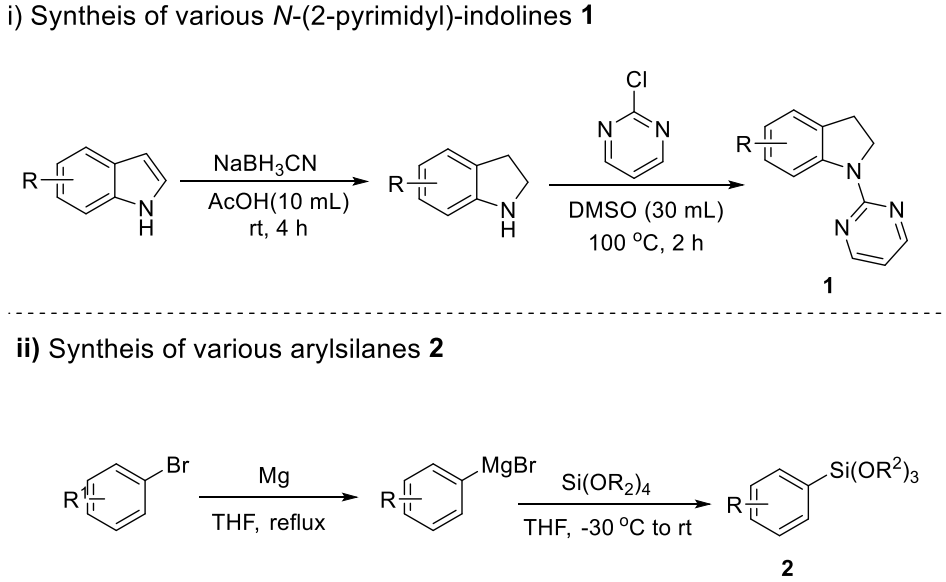
I. General Informations

Analytical methods: Proton nuclear magnetic resonance (^{1}H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectroscopy were performed on a Bruker Advance 300, 400 and 500 NMR spectrometers. Chemical shifts ^{1}H NMR spectra are reported as in units of parts per million (ppm) downfield from $SiMe_4$ (0.0) and relative to the signal of chloroform-*d* (*J* = 7.264, singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); ddd (doublet of doublets of doublets); dddd (doublet of doublets of doublets of doublets); dt (doublet of triplets); m (multiplets) and etc. The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as d in units of parts per million (ppm) downfield from $SiMe_4$ (0.0) and relative to the signal of chloroform-*d* (*J* = 77.03, triplet). High resolution mass spectral analysis (HRMS) was performed on Water XVEO G2 Q-TOF (Waters Corporation). Infrared spectra were recorded on a Nicolet IS50 Fourier transform spectrometer (FT-IR) and are reported in wave numbers (cm^{-1}).

Materials: All commercial available reagents were used without further purification unless otherwise noted. It must be point out that tetrahydrofuran was dried by sodium and distilled until the diphenylmethanone turned blue. All substituted indoline,[1-2] arylsilanes[3] were prepared according to the known methods (Scheme 1). In addition, column chromatography was performed using 200-300 mesh silica gels.



Scheme 1

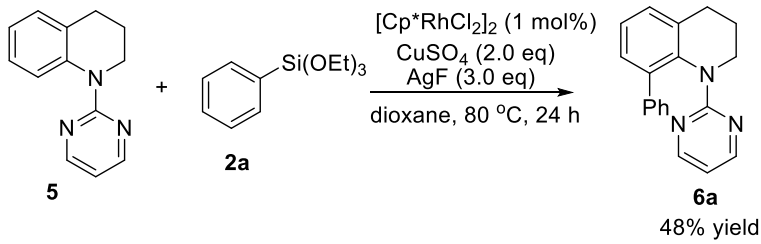
II. Experimental Procedures

1. General procedure for Rh(III)-catalyzed C-7 arylation of indoline with arylsilanes

To a septum capped 15 mL of dried sealed tube with a magnetic stirring bar were added 1-(pyrimidin-2-yl)indoline (**1f**, 0.3 mmol), $[Cp^*RhCl_2]_2$ (1.9 mg 1 mol%), $CuSO_4$ (95.8 mg, 0.6 mmol), AgF (114.2 mg, 0.9 mmol) and 2 mL Dioxane, followed by addition of triethoxy(phenyl)silane (**2a,** 217.2 μL, 0.9 mmol) by microsyringe. The sealed tube was screw capped and heated to 80 °C for 24 h (oil bath). After completed, the reaction was cooled to room temperature, and then the mixture was diluted with 10 mL water. The aqueous layer was extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified with silica gel chromatography (petroleum ether/ethyl acetate) to provide pure product **3fa.**

2. Rh(III)-catalyzed the direct C-8 arylation of *N*-(2-pyrimidyl)-tetrahydroquinoline with phenyltriethoxysilane

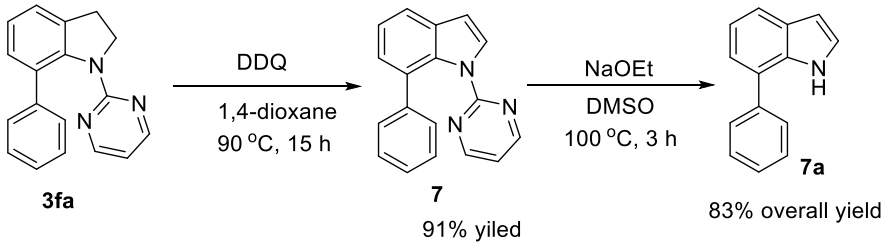
To a septum capped 15 mL of dried sealed tube with a magnetic stirring bar were added *N*-(2-pyrimidyl)-tetrahydroquinoline (**5**, 63.4 mg, 0.3 mmol), $[Cp^*RhCl_2]_2$ (1.9 mg 1 mol%), $CuSO_4$ (95.8 mg, 0.6 mmol), AgF (114.2 mg, 0.9 mmol) and 2 mL Dioxane, followed by addition of triethoxy(phenyl)silane (**2a**, 217.2 μL, 0.9 mmol) by microsyringe. The sealed tube was screw capped and heated to 80 °C for 24 h (oil bath). After completed, the reaction was cooled to room temperature, and then the mixture was diluted with 10 mL water. The aqueous layer was extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified with silica gel chromatography (petroleum ether/ethyl acetate) to provide pure product **6** (41.4 mg, 48 %).



3. Transformation of C-7-arylated indoline 3fa to the corresponding indole[4]

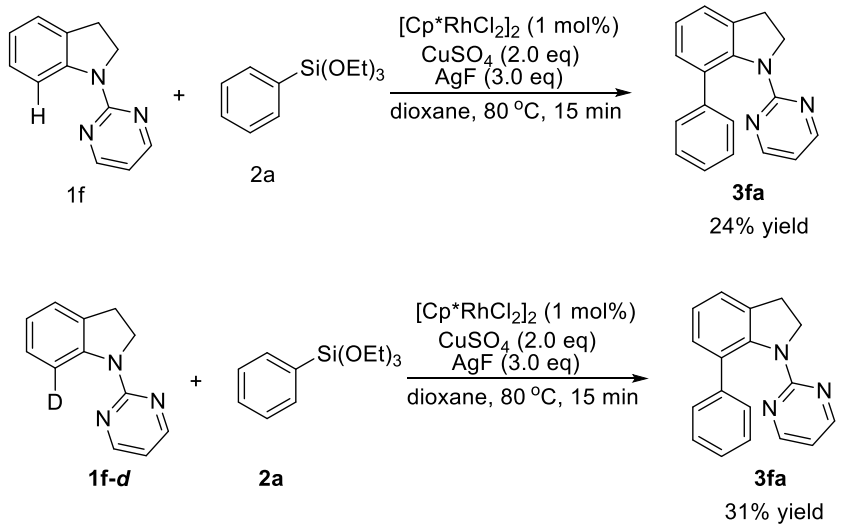
To a stirred solution of 7-phenyl-1-(pyrimidin-2-yl)indoline **3fa** (0.1 mmol) in 1,4-dioxane, DDQ (0.2 mmol) was added at room temperature. The resultant solution was further stirred at 90 °C for 15 h. After completion, as indicated by TLC, the reaction mixture was cooled to room temperature and diluted with ethyl acetate (1 x 20 mL). The mixture was successively washed with brine (2 x 10 mL) and water (10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using n-hexane and ethyl acetate as an eluent to afford 7-phenyl-1-(pyrimidin-2-yl)-1H-indole **7** as a yellowish liquid. Next, indole **7** was dissolved

in DMSO (2 mL) and NaOEt (5 equiv.) in EtOH (0.5 mL) was added to the mixture. The mixture was stirred at 100 °C for 3 h. After completion, the reaction mixture was cooled to room temperature and diluted with ethyl acetate (1 x 15 mL). The mixture was then washed with 2 N HCl (1 x 10 mL), brine (2 x 10 mL) and water (10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using n-hexane and ethyl acetate as an eluent to afford 7-phenyl-1H-indole **7a** as a brown liquid.



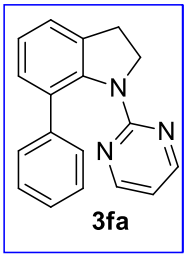
4. Parallel kinetic Isotope experiment[4]

In a set of two experiments: in first set, Phenyl-triethoxysilane **2a** (0.6 mmol) was reacted with 1-(pyrimidin-2-yl)indoline **1f** (0.2 mmol) for 15 min under standard reaction condition. Whereas in another set, 1-(pyrimidin-2-yl)indoline-7-*d* **1f-*d*** (0.2 mmol, 97% D) was used instead of **1f** in the reaction with Phenyl-triethoxysilane **2a** (0.6 mmol) under the standard reaction conditions. The two reactions were allowed to stir at 80 °C for 15 min. For the both cases, The aqueous layer was extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified with silica gel chromatography (petroleum ether/ethyl acetate) to provide pure product **3fa**. The yield of **3fa** was obtained as 24% (13.1 mg) and 31% yields (16.9 mg), respectively. The KIE value of 0.80 was determined by the ratio of obtained yield of **3fa** (KIE = 24%/31%/97% = 0.80).



III. Spectroscopic Data for Arylated Products

7-phenyl-1-(pyrimidin-2-yl)indoline (3fa)



3fa

The product **3fa** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 8:1, Rf = 0.35) to give product as a yellowish solid (80.4 mg, 98% yield).

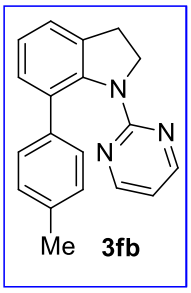
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 4.8 Hz, 2H), 7.34 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.30 – 7.20 (m, 2H), 7.19 – 7.04 (m, 4H), 6.36 (t, *J* = 4.8 Hz, 1H), 4.45 (t, *J* = 7.9 Hz, 2H), 3.18 (t, *J* = 7.9 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.13, 156.43, 142.21, 141.01, 134.90, 130.30, 128.89, 127.83, 126.62, 125.97, 123.69, 123.57, 111.72, 52.13, 29.51.

IR (KBr disk): 3028, 2957, 2848, 1687, 1576, 1551, 1456, 1421, 1128 cm^{-1}.

This compound is known. [4]

1-(pyrimidin-2-yl)-7-(p-tolyl)indoline (3fb)



3fb

The product **3fb** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 10:1, Rf = 0.45) to give product as a yellowish solid (81.7 mg, 95% yield).

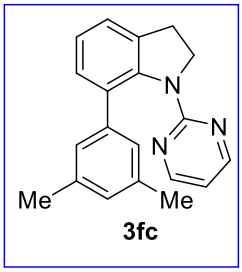
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 4.8 Hz, 2H), 7.31 – 7.16 (m, 4H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 7.9 Hz, 2H), 6.36 (t, *J* = 4.8 Hz, 1H), 4.44 (t, *J* = 7.9 Hz, 2H), 3.16 (t, *J* = 7.9 Hz, 2H), 2.25 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.20, 156.41, 140.95, 139.18, 135.55, 134.84, 130.30, 128.82, 128.48, 126.39, 123.68, 123.29, 111.69, 52.14, 29.52, 21.02.

IR (KBr disk): 3023, 2994, 2847, 1607, 1517, 1451, 1379, 1273, 1216 cm^{-1}.

HRMS (ESI) calcd for $C_{19}H_{18}N_3^+$ [M + H]$^+$ 288.1495, found: 288.1498.

7-(3,5-dimethylphenyl)-1-(pyrimidin-2-yl)indoline (3fc)



3fc

The product **3fc** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 9:1, Rf = 0.30) to give product as a yellowish solid (81.4 mg, 90% yield).

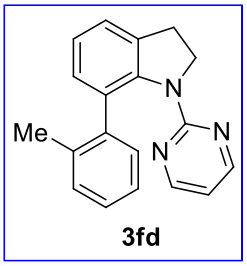
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 4.8 Hz, 2H), 7.26 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.19 (dd, *J* = 7.3, 1.1 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.95 (s, 2H), 6.72 (s, 1H), 6.35 (t, *J* = 4.8 Hz, 1H), 4.43 (t, *J* = 7.9 Hz, 2H), 3.15 (t, *J* = 7.9 Hz, 2H), 2.15 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.02, 156.16, 141.75, 140.81, 137.09, 134.62, 129.81, 128.71, 127.40, 124.39, 123.36, 123.28, 111.51, 52.04, 29.39, 20.98.

IR (KBr disk): 3025, 2964, 2914, 2878, 2839, 1573, 1465, 1414, 1277 cm^{-1}.

HRMS (ESI) calcd for $C_{20}H_{20}N_3^+$ $[M + H]^+$302.1652, found: 302.1656.

1-(pyrimidin-2-yl)-7-(o-tolyl)indoline (3fd)



3fd

The product **3fd** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 7:1, Rf = 0.50) to give product as a yellow liquid (28.4 mg, 33% yield).

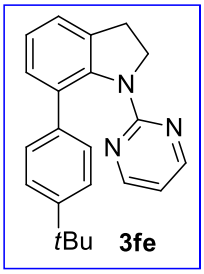
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 4.8 Hz, 2H), 7.25 – 7.21 (m, 1H), 7.16 – 7.10 (m, 2H), 7.06 (t, *J* = 7.4 Hz, 1H), 7.04 – 6.97 (m, 3H), 6.34 (t, *J* = 4.8 Hz, 1H), 4.37 (t, *J* = 7.9 Hz, 2H), 3.17 (t, *J* = 7.9 Hz, 2H), 2.18 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.85, 156.17, 141.93, 141.48, 134.72, 134.41, 129.85, 129.74, 129.45, 128.66, 126.20, 125.12, 123.40, 122.87, 111.56, 51.77, 29.39, 19.67.

IR (KBr disk): 3021, 2963, 2921, 2878, 1575, 1550, 1457, 1382, 1283, 1081 cm^{-1}.

This compound is known.[4]

7-(4-(tert-butyl)phenyl)-1-(pyrimidin-2-yl)indoline (3fe)



The product **3fe** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 7:1, Rf = 0.40) to give product as a yellow solid (89.1 mg, 90% yield).

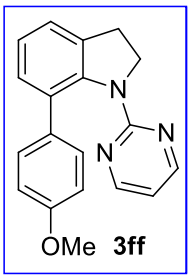
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 4.8 Hz, 2H), 7.28 (d, *J* = 7.7 Hz, 1H), 7.25 – 7.19 (m, 3H), 7.18 – 7.12 (dt, J=8.52,1.96Hz, 2H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.31 (t, *J* = 4.8 Hz, 1H), 4.43 (t, *J* = 7.9 Hz, 2H), 3.17 (t, *J* = 7.9 Hz, 2H), 1.25 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.91, 156.19, 149.11, 141.08, 139.18, 134.75, 129.82, 128.68, 126.27, 124.58, 123.50, 123.36, 111.37, 52.08, 34.33, 31.38, 29.49.

IR (KBr disk): 3029, 2954, 2900, 2865, 1576, 1455, 1433, 1266, 1194, 1109 cm^{-1}.

HRMS (ESI) calcd for $C_{22}H_{24}N_3^+$ $[M + H]^+$ 330.1965, found: 330.1966.

7-(4-methoxyphenyl)-1-(pyrimidin-2-yl)indoline (3ff)



The product **3ff** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate =7:1, Rf = 0.40) to give product as a yellow solid (78.3 mg, 86 % yield).

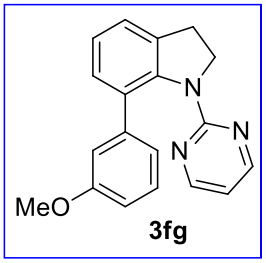
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 4.8 Hz, 2H), 7.30 – 7.22 (m, 3H), 7.20 (dd, *J* = 7.3, 1.1 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 1H), 6.74 – 6.60 (m, 2H), 6.39 (t, *J* = 4.8 Hz, 1H), 4.44 (t, *J* = 7.9 Hz, 2H), 3.73 (s, 3H), 3.16 (t, *J* = 7.9 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.16, 158.00, 156.44, 140.92, 134.89, 134.73, 130.00, 128.69, 127.62, 123.72, 123.12, 113.24, 111.73, 55.17, 52.20, 29.53.

IR (KBr disk):3030, 2992, 2974, 2933, 2846, 1578, 1451, 1431, 1279, 1238, 1175 cm^{-1}.

HRMS (ESI) calcd for $C_{19}H_{18}N_3O^+$ $[M + H]^+$304.1445, found: 304.1449.

7-(3-methoxyphenyl)-1-(pyrimidin-2-yl)indoline (3fg)



The product **3fg** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate

= 9:1, Rf = 0.30) to give product as a yellow solid (87.0 mg, 96 % yield).

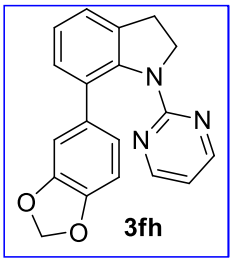
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 4.8 Hz, 2H), 7.28 (d, *J* = 7.7 Hz, 1H), 7.25 – 7.19 (m, 1H), 7.06 (dt, *J* = 15.4, 7.7 Hz, 2H), 6.94 (dt, *J* = 7.6, 1.1 Hz, 1H), 6.92 – 6.90 (m, 1H), 6.65 (ddd, *J* = 8.2, 2.6, 0.9 Hz, 1H), 6.37 (t, *J* = 4.8 Hz, 1H), 4.44 (t, *J* = 8.0 Hz, 2H), 3.65 (s, 3H), 3.15 (t, *J* = 7.9 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.25, 159.08, 156.31, 143.36, 140.78, 134.77, 129.74, 128.69, 128.65, 123.57, 123.53, 119.18, 112.22, 111.72, 111.35, 55.01, 52.03, 29.34.

IR (KBr disk): 3000, 2955, 2882, 1575, 1548, 1472, 1429, 1292, 1225, 1171 cm^{-1}.

This compound is known. [4]

7-(benzo[d][1,3]dioxol-5-yl)-1-(pyrimidin-2-yl)indoline (3fh)



3fh

The product **3fh** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 10:1, Rf = 0.25) to give product as a yellowish solid (78.3 mg, 82% yield).

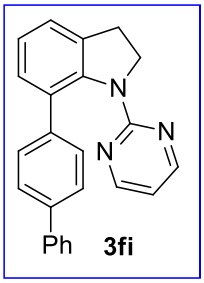
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 4.8 Hz, 2H), 7.20 (t, *J* = 6.7 Hz, 2H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 1.6 Hz, 1H), 6.82 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 1H), 6.43 (t, *J* = 4.8 Hz, 1H), 5.83 (s, 2H), 4.43 (t, *J* = 7.9 Hz, 2H), 3.14 (t, *J* = 7.9 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.21, 156.42, 147.21, 145.65, 140.83, 136.23, 134.89, 129.98, 128.61, 123.65, 123.27, 119.99, 111.78, 107.72, 107.27, 100.51, 52.06, 29.44.

IR (KBr disk): 3027, 2958, 2894, 1575, 1552, 1467, 1423, 1252, 1226, 1036 cm^{-1}.

HRMS (ESI) calcd for $C_{19}H_{16}N_3O_2^+$ [M + H]$^+$318.1237, found: 318.1238.

7-([1,1'-biphenyl]-4-yl)-1-(pyrimidin-2-yl)indoline (3fi)



3fi

The product **3fi** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 7:1, Rf = 0.50) to give product as a yellowish solid (82.0 mg, 78 % yield).

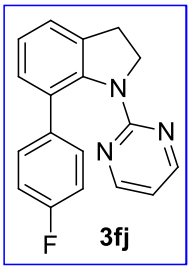
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 4.8 Hz, 2H), 7.52 (dt, *J* = 8.1, 1.8 Hz, 2H), 7.40 (d, *J* = 6.0 Hz, 6H), 7.30 (tdd, *J* = 7.3, 5.2, 2.5 Hz, 2H), 7.26 – 7.18 (m, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.31 (t, *J* = 4.8 Hz, 1H), 4.46 (t, *J* = 7.9 Hz, 2H), 3.16 (t, *J* = 7.9 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.05, 156.35, 141.20, 140.99, 140.78, 138.63, 134.87, 129.64, 128.66, 128.59, 126.96, 126.91, 126.73, 126.43, 123.63, 123.60, 111.76, 52.06, 29.42.

IR (KBr disk): 3034, 2959, 2913, 2842, 1574, 1548, 1454, 1436, 1329, 1285, 1184, 1042 cm^{-1}.

HRMS (ESI) calcd for $C_{24}H_{20}N_3^+$ $[M + H]^+$350.1652, found: 350.1657.

7-(4-fluorophenyl)-1-(pyrimidin-2-yl)indoline (3fj)



3fj

The product **3fj** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 8:1, Rf = 0.30) to give product as a yellowish solid (84.6 mg, 97% yield).

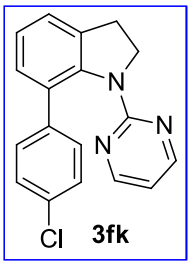
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 4.8 Hz, 2H), 7.30 (ddd, *J* = 8.4, 5.3, 2.6 Hz, 2H), 7.26 – 7.19 (m, 2H), 7.16 – 7.05 (m, 1H), 6.92 – 6.78 (m, 2H), 6.41 (t, *J* = 4.8 Hz, 1H), 4.44 (t, *J* = 7.9 Hz, 2H), 3.16 (t, *J* = 7.9 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ161.37 (d, J_{C-F} = 244.9 Hz), 159.12, 156.52, 140.99, 138.23 (d, J_{C-F} = 3.4 Hz), 135.02, 129.37, 128.70, 128.11 (d, J_{C-F} = 7.9 Hz), 123.77, 123.66, 114.64 (d, J_{C-F} = 21.2 Hz), 111.94, 52.17, 29.47.

IR (KBr disk): 3049, 2959, 2885, 1575, 1549, 1509, 1454, 1428, 1212, 1154 cm^{-1}.

This compound is known. [4]

7-(4-chlorophenyl)-1-(pyrimidin-2-yl)indoline (3fk)



3fk

The product **3fk** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 7:1, Rf = 0.45) to give product as a yellow solid (90.5 mg, 98% yield).

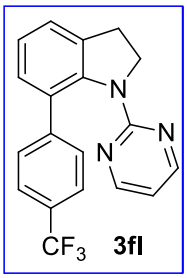
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 4.8 Hz, 2H), 7.31 – 7.26 (m, 2H), 7.26 – 7.20 (m, 2H), 7.16 – 7.07 (m, 3H), 6.43 (t, *J* = 4.8 Hz, 1H), 4.45 (t, *J* = 8.0 Hz, 2H), 3.17 (t, *J* = 7.9 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.11, 156.57, 140.95, 140.73, 135.05, 131.72, 129.16, 128.63, 127.97, 127.90, 123.89, 123.81, 112.09, 52.13, 29.43.

IR (KBr disk): 3030, 2963, 2914, 2850, 1576, 1548, 1451, 1425, 1285, 1266, 1087 cm^{-1}.

This compound is known. [4]

1-(pyrimidin-2-yl)-7-(4-(trifluoromethyl)phenyl)indoline (3fl)



3fl

The product **3fl** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 7:1, Rf = 0.40) to give product as a yellowish solid (94.2 mg, 92% yield).

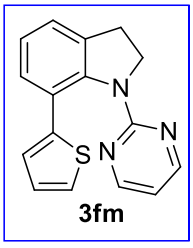
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 4.8 Hz, 2H), 7.43 (q, *J* = 8.4 Hz, 4H), 7.31 – 7.20 (m, 2H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.40 (t, *J* = 4.8 Hz, 1H), 4.46 (t, *J* = 8.0 Hz, 2H), 3.18 (t, *J* = 8.0 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.94 , 156.49 , 145.99 (d, $J_{C\text{-}F}$ = 1.6 Hz), 141.04 , 135.11 , 128.80 , 128.63 , 128.03 (q, $J_{C\text{-}F}$ = 32.2 Hz), 126.83, 124.73 (q, $J_{C\text{-}F}$ = 3.8 Hz), 124.36, 123.79, 112.07, 52.05, 29.33.

IR (KBr disk): 3047, 2956, 2899, 2848, 1616, 1578, 1553, 1463, 1435, 1328, 1287, 1156, 1110, 1067 cm^{-1}.

HRMS (ESI) calcd for $C_{19}H_{15}F_3N_3^+$ $[M + H]^+$342.1213, found: 342.1213.

1-(pyrimidin-2-yl)-7-(thiophen-2-yl)indoline (3fm)



3fm

The product **3fm** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 6:1, Rf = 0.50) to give product as a yellow solid (43.3 mg, 52% yield).

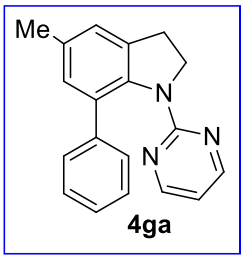
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 4.8 Hz, 2H), 7.39 – 7.33 (m, 1H), 7.21 (dd, *J* = 7.3, 1.1 Hz, 1H), 7.11 – 7.03 (m, 2H), 6.93 (dd, *J* = 3.6, 1.1 Hz, 1H), 6.78 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.49 (t, *J* = 4.8 Hz, 1H), 4.47 (t, *J* = 7.9 Hz, 2H), 3.15 (t, *J* = 7.9 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.86, 156.64, 143.57, 141.34, 135.27, 128.71, 126.54, 124.00, 123.91, 123.82, 112.12, 52.58, 29.62.

IR (KBr disk): 3030, 2967, 2887, 2841, 1573, 1552, 1447, 1414, 1351, 1280, 1228, 1183, 1045 cm^{-1}.

HRMS (ESI) calcd for $C_{16}H_{14}N_3S^+$ $[M + H]^+$280.0903, found: 280.0909.

5-methyl-7-phenyl-1-(pyrimidin-2-yl)indoline (4ga)



4ga

The product **4ga** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 7:1, Rf = 0.40) to give product as a fawn solid (84.5 mg, 98% yield).

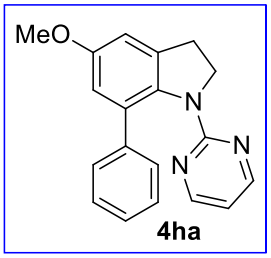
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 4.8 Hz, 2H), 7.39 (dt, *J* = 8.2, 1.8 Hz, 2H), 7.22 – 7.16 (m, 2H), 7.15 – 7.07 (m, 3H), 6.36 (t, *J* = 4.8 Hz, 1H), 4.48 (t, *J* = 7.9 Hz, 2H), 3.15 (t, *J* = 7.8 Hz, 2H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.32, 142.09, 134.99, 133.25, 130.01, 129.12, 127.68, 126.49, 125.81, 124.22, 111.36, 52.09, 29.43, 20.88.

IR (KBr disk): 3027, 2913, 2887, 2850, 1603, 1576, 1548, 1471, 1449, 1225, 1101 cm^{-1}.

This compound is known. [4]

5-methoxy-7-phenyl-1-(pyrimidin-2-yl)indoline (4ha)



4ha

The product **4ha** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 8:1, Rf = 0.30) to give product as a yellow solid (85.6 mg, 94 % yield).

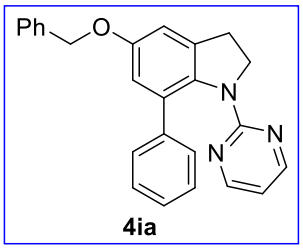
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 4.8 Hz, 2H), 7.45 – 7.31 (m, 2H), 7.19 – 7.12 (m, 2H), 7.12 – 7.06 (m, 1H), 6.83 (s, 2H), 6.31 (t, *J* = 4.8 Hz, 1H), 4.45 (t, *J* = 7.8 Hz, 2H), 3.81 (s, 3H), 3.12 (t, *J* = 7.8 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.24, 156.56, 156.40, 141.92, 136.49, 134.52, 131.05, 127.78, 126.48, 126.11, 113.21, 111.23, 110.06, 55.66, 52.20, 29.87.

IR (KBr disk): 3007, 2939, 2881, 2842, 1600, 1577, 1549, 1470, 1431, 1336, 1177 cm^{-1}.

This compound is known. [4]

5-(benzyloxy)-7-phenyl-1-(pyrimidin-2-yl)indoline (4ia)



4ia

The product **4ia** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 6:1, Rf = 0.20) to give product as a yellowish solid (98.3 mg, 86% yield).

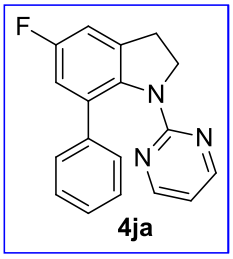
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 4.7 Hz, 2H), 7.47 (d, *J* = 7.2 Hz, 2H), 7.44 – 7.30 (m, 5H), 7.15 (dt, *J* = 26.4, 7.2 Hz, 3H), 7.00 – 6.89 (m, 2H), 6.35 (t, *J* = 4.7 Hz, 1H), 5.11 (s, 2H), 4.48 (t, *J* = 7.8 Hz, 2H), 3.14 (t, *J* = 7.8 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.27, 156.44, 155.84, 141.93, 137.16, 136.50, 134.79, 131.10, 128.48, 127.83, 127.81, 127.37, 126.53, 126.15, 114.50, 111.30, 110.91, 70.51, 52.24, 29.92.

IR (KBr disk): 3031, 2916, 2854, 1609, 1577, 1547, 1467, 1445, 1412, 1375, 1354, 1244, 1225, 1189, 1166 cm^{-1}.

This compound is known. [4]

5-fluoro-7-phenyl-1-(pyrimidin-2-yl)indoline (4ja)



4ja

The product **4ja** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 8:1, Rf = 0.25) to give product as a light brown yellow solid (75.6 mg, 86% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 4.8 Hz, 2H), 7.33 (d, *J* = 7.2 Hz, 2H), 7.15 (t, *J* = 7.3 Hz, 2H), 7.10 (dd, *J* = 8.4, 6.0 Hz, 1H), 6.97 (ddd, *J* = 18.2, 8.9, 2.3 Hz, 2H), 6.36 (t, *J* = 4.8 Hz, 1H), 4.47 (t, *J* = 7.9 Hz, 2H), 3.14 (t, *J* = 7.8 Hz, 2H).

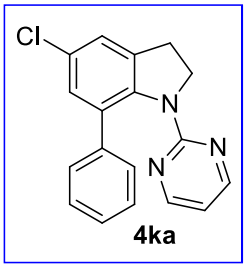
^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.59 (d, $J_{C\text{-}F}$ = 242.5 Hz), 159.09, 156.45, 141.05, 137.04 (d, $J_{C\text{-}F}$ = 2.1 Hz), 136.88 (d, $J_{C\text{-}F}$ = 8.9 Hz), 131.36 (d, $J_{C\text{-}F}$ = 8.1 Hz), 127.92, 126.47, 126.37, 114.81 (d, $J_{C\text{-}F}$ = 23.6 Hz), 111.8, 110.72 (d, $J_{C\text{-}F}$ = 23.8 Hz), 52.4, 29.70 (d, $J_{C\text{-}F}$ = 2.1 Hz).

IR (KBr disk): 3025, 2923, 2849, 1603, 1577, 1547, 1460, 1430, 1344, 1294, 1196, 1150

cm^{-1}.

This compound is known. [4]

5-chloro-7-phenyl-1-(pyrimidin-2-yl)indoline (4ka)



4ka

The product **4ka** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 7:1, Rf = 0.30) to give product as a yellow solid (78.2 mg, 85% yield).

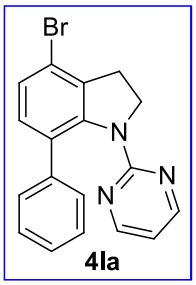
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 4.8 Hz, 2H), 7.33 – 7.27 (m, 2H), 7.25 (t, *J* = 2.1 Hz, 1H), 7.21 – 7.06 (m, 4H), 6.38 (t, *J* = 4.8 Hz, 1H), 4.45 (t, *J* = 8.0 Hz, 2H), 3.14 (t, *J* = 8.0 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.87, 156.42, 140.89, 136.75, 131.23, 128.47, 128.40, 127.92, 126.45, 126.37, 123.50, 112.01, 52.17, 29.30.

IR (KBr disk): 3027, 2929, 2858, 1576, 1547, 1443, 1427, 1287, 1225, 1195 cm^{-1}.

HRMS (ESI) calcd for $C_{18}H_{15}ClN_3^+$ $[M + H]^+$308.0949, found: 308.0955.

4-bromo-7-phenyl-1-(pyrimidin-2-yl)indoline (4la)



4la

The product **4la** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 7:1, Rf = 0.50) to give product as a brown solid (70.7 mg, 67 % yield).

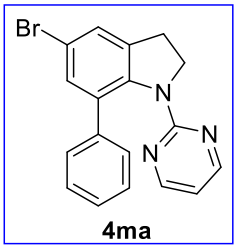
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 4.8 Hz, 2H), 7.32 – 7.26 (m, 2H), 7.23 (d, *J* = 8.3 Hz, 1H), 7.18 – 7.11 (m, 3H), 7.11 – 7.05 (m, 1H), 6.40 (t, *J* = 4.8 Hz, 1H), 4.46 (t, *J* = 8.1 Hz, 2H), 3.18 (t, *J* = 8.0 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.92, 156.43, 141.97, 141.28, 135.21, 130.52, 129.04, 127.92, 126.43, 126.32, 126.21, 118.20, 112.27, 51.40, 30.91.

IR (KBr disk): 3029, 2960, 2900, 1575, 1552, 1457, 1432, 1287, 1225, 1127 cm^{-1}.

This compound is known. [4]

5-bromo-7-phenyl-1-(pyrimidin-2-yl)indoline (4ma)



4ma

The product **4ma** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 7:1, Rf = 0.25) to give product as a yellow brown solid (66.7 mg, 63% yield).

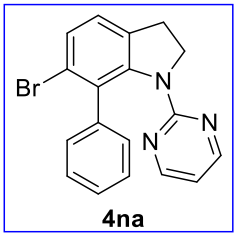
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 4.8 Hz, 2H), 7.41 (d, *J* = 2.0 Hz, 1H), 7.37 – 7.33 (m, 1H), 7.32 – 7.27 (m, 2H), 7.19 – 7.06 (m, 3H), 6.40 (t, *J* = 4.8 Hz, 1H), 4.45 (t, *J* = 8.0 Hz, 2H), 3.17 (t, *J* = 8.0 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.90, 156.49, 140.89, 140.32, 137.15, 131.75, 131.43, 127.98, 126.52, 126.45, 116.00, 112.12, 52.18, 29.28.

IR (KBr disk): 3027, 2920, 2854, 1575, 1550, 1463, 1441, 1292, 1223, 1192cm^{-1}.

This compound is known. [4]

6-bromo-7-phenyl-1-(pyrimidin-2-yl)indoline (4na)



4na

The product 4**na** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 7:1, Rf = 0.30) to give product as a yellow solid (17.6 mg, 17 % yield).

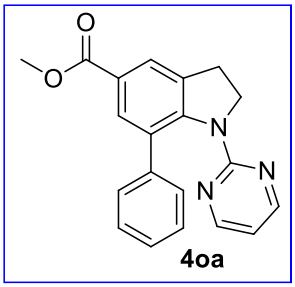
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 4.8 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.14 (t, *J* = 7.5 Hz, 2H), 7.07 (tt, *J* = 7.4, 3.8 Hz, 2H), 6.39 (t, *J* = 4.8 Hz, 1H), 4.38 (t, *J* = 7.9 Hz, 2H), 3.11 (t, *J* = 7.9 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.81, 156.46, 143.57, 139.77, 134.55, 130.32, 129.63, 127.89, 127.10, 126.68, 124.71, 122.46, 112.12, 53.04, 29.41.

IR (KBr disk): 3032, 2919, 2854, 1577, 1556, 1444, 1421, 1206, 1175 cm^{-1}.

HRMS (ESI) calcd for $C_{18}H_{15}BrN_3^+$ [M + H]$^+$352.0444, found: 352.0448.

methyl 7-phenyl-1-(pyrimidin-2-yl)indoline-5-carboxylate (4oa)



4oa

The product **4oa** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 7:1, Rf = 0.45) to give product as a yellow brown solid (65.9 mg, 66% yield).

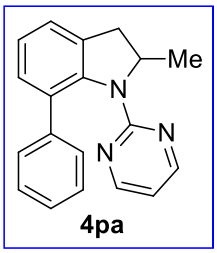
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 – 7.94 (m, 3H), 7.90 (s, 1H), 7.29 (d, *J* = 7.0 Hz, 2H), 7.13 (dt, *J* = 13.9, 7.0 Hz, 3H), 6.45 (t, *J* = 4.8 Hz, 1H), 4.48 (t, *J* = 8.1 Hz, 2H), 3.90 (s, 3H), 3.24 (t, *J* = 8.1 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.98, 158.62, 156.44, 145.25, 141.37, 134.99, 131.75, 129.08, 127.93, 126.55, 126.32, 124.90, 124.77, 112.65, 52.38, 51.92, 28.76.

IR (KBr disk): 3034, 2918, 2850, 1699, 1606, 1570, 1552, 1454, 1441, 1337, 1305, 1281, 1234, 1202, 1126 cm^{-1}.

This compound is known. [4]

2-methyl-7-phenyl-1-(pyrimidin-2-yl)indoline (4pa)



4pa

The product **4pa** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 6:1, Rf = 0.50) to give product as a yellowish solid (74.4 mg, 86% yield).

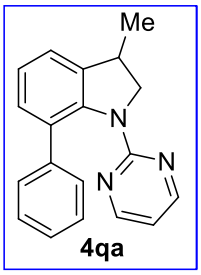
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 4.8 Hz, 2H), 7.37 – 7.30 (m, 2H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 7.7 Hz, 1H), 7.19 – 7.04 (m, 4H), 6.33 (t, *J* = 4.7 Hz, 1H), 4.91 (p, *J* = 6.7 Hz, 1H), 3.50 (dd, *J* = 15.5, 8.5 Hz, 1H), 2.63 (d, *J* = 15.5 Hz, 1H), 1.54 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.63, 156.40, 142.28, 139.45, 133.68, 130.64, 128.78, 127.81, 126.42, 125.88, 124.04, 123.70, 111.68, 59.43, 36.74, 21.09.

IR (KBr disk): 3027, 2969, 2856, 1577, 1548, 1463, 1436, 1280, 1211, 1117 cm^{-1}.

This compound is known. [4]

3-methyl-7-phenyl-1-(pyrimidin-2-yl)indoline (4qa)



The product **4qa** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 10:1, Rf = 0.40) to give product as a yellow solid (77.6 mg, 90% yield).

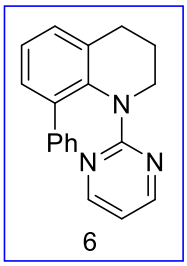
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 4.8 Hz, 2H), 7.38 – 7.32 (m, 2H), 7.30 – 7.26 (m, 1H), 7.22 – 7.18 (m, 1H), 7.17 – 7.11 (m, 3H), 7.10 – 7.05 (m, 1H), 6.35 (t, *J* = 4.8 Hz, 1H), 4.61 (dd, *J* = 10.8, 8.2 Hz, 1H), 3.98 (dd, *J* = 10.8, 7.0 Hz, 1H), 3.48 (h, *J* = 7.0 Hz, 1H), 1.35 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.16, 156.44, 142.05, 140.57, 140.02, 130.16, 128.95, 127.80, 126.59, 125.94, 123.86, 122.34, 111.64, 59.91, 36.10, 18.94.

IR (KBr disk): 3030, 2959, 2870, 1737, 1575, 1441, 1241, 1132, 1047 cm^{-1}.

This compound is known. [4]

8-phenyl-1-(pyrimidin-2-yl)-1,2,3,4-tetrahydroquinoline (6)



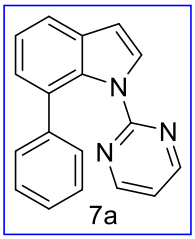
The product **6** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 15:1, Rf = 0.45) to give product as a yellow solid (41.4 mg, 48% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 3.9 Hz, 2H), 7.32 – 7.26 (m, 2H), 7.25 – 7.22 (m, 1H), 7.21 – 7.16 (m, 2H), 7.13 (t, *J* = 7.6 Hz, 2H), 7.06 – 7.00 (m, 1H), 6.24 (t, *J* = 4.8 Hz, 1H), 4.08 (s, 2H), 2.77 (t, *J* = 6.6 Hz, 2H), 2.18 – 2.04 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.22, 156.95, 141.11, 137.49, 137.26, 135.42, 128.40, 127.92, 127.69, 127.31, 126.19, 125.05, 110.92, 45.07, 27.28, 25.10.

This compound is known.[5]

7-phenyl-1-(pyrimidin-2-yl)-1H-indole (7a)



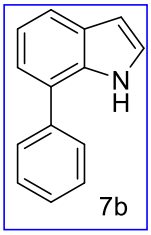
The product **7a** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 4:1, Rf = 0.45) to give product as a yellowish liquid (49.3 mg, 91% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 (d, *J* = 4.8 Hz, 2H), 7.79 (d, *J* = 3.5 Hz, 1H), 7.65 (dd, *J* = 6.7, 2.2 Hz, 1H), 7.34 – 7.27 (m, 2H), 7.21 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.08 (dd, *J* = 5.0, 1.7 Hz, 3H), 6.83 – 6.69 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.99, 156.87, 142.05, 132.73, 132.00, 129.22, 128.51, 127.71, 127.48, 125.86, 125.57, 122.09, 120.16, 116.63, 106.32.

This compound is known. [4]

7-phenyl-1H-indole (7b)



The product **7b** was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 10:1, Rf = 0.41) to give product as a brown liquid (32.1 mg, 83% overall yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.37 (s, 1H), 7.66 – 7.59 (m, 3H), 7.52 – 7.46 (m, 2H), 7.42 – 7.36 (m, 1H), 7.22 – 7.19 (m, 2H), 7.18 – 7.16 (m, 1H), 6.61 (dd, *J* = 3.2, 2.1 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.25, 133.68, 129.10, 128.24, 128.21, 127.37, 125.57, 124.31, 121.86, 120.27, 120.01, 103.03.

This compound is known. [4]

IV. References

(1) A. T. Vu, S. T. Cohn, P. Zhang, C. Y. Kim, P. E. Mahaney, J. A. Bray, G. H. Johnston, E. J. Koury, S. A. Cosmi, D. C. Deecher, V. A. Smith, J.E. Harrison, L. Leventhal, G. T. Whiteside, J. D. Kennedy,and E. J. Trybulski, *J. Med. Chem.*, 2010, **53**, 2051.

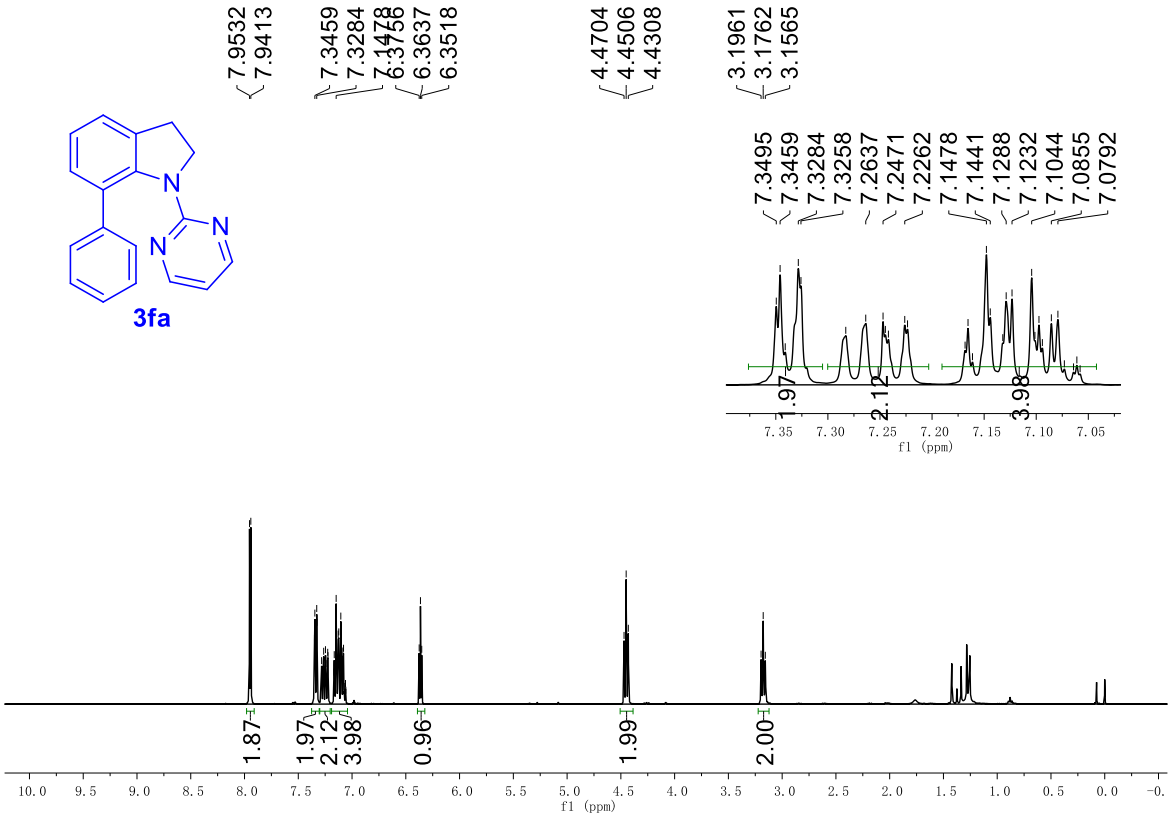
(2) Ackermann, L.; Lygin, A. V. *Org. Lett.* , 2011, **13**, 3332.

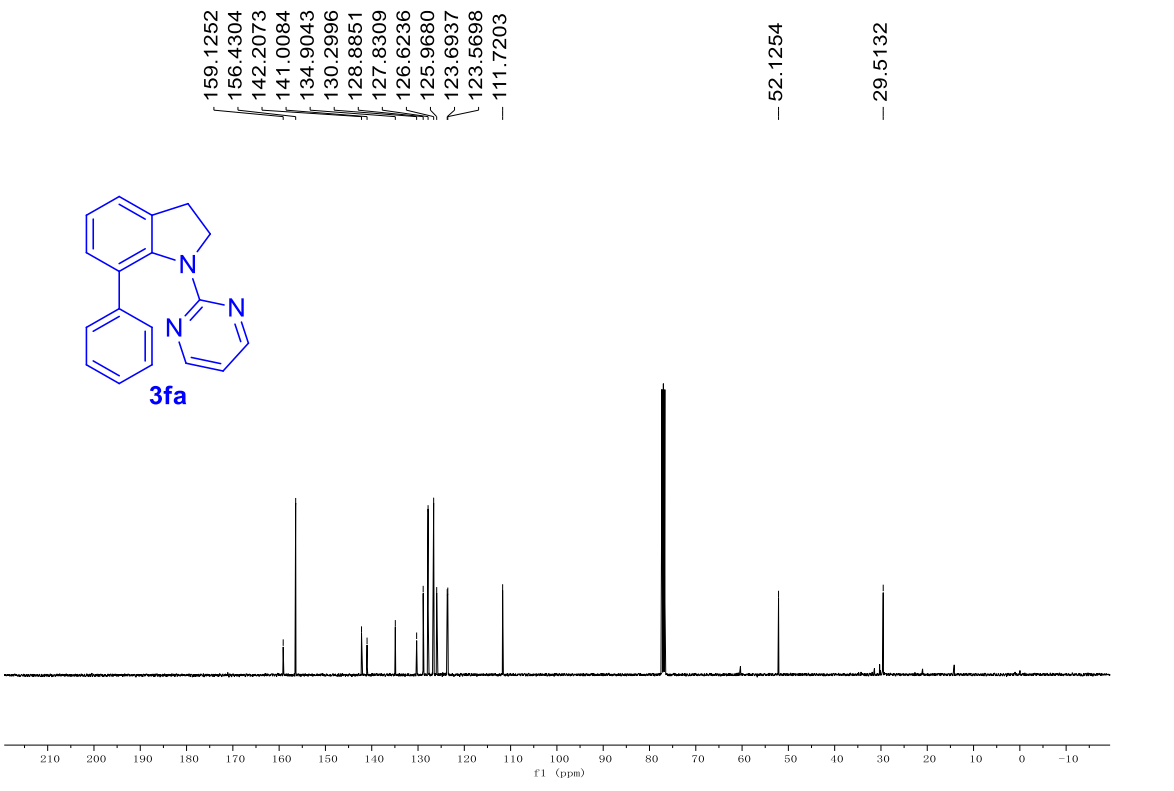
(3) A. S. Manoso, C. Ahn, A. Soheili, C. J. Handy, R. Correia, W. M. Seganish and P. DeShong, *J. Org. Chem.* 2004, **69**, 8305.

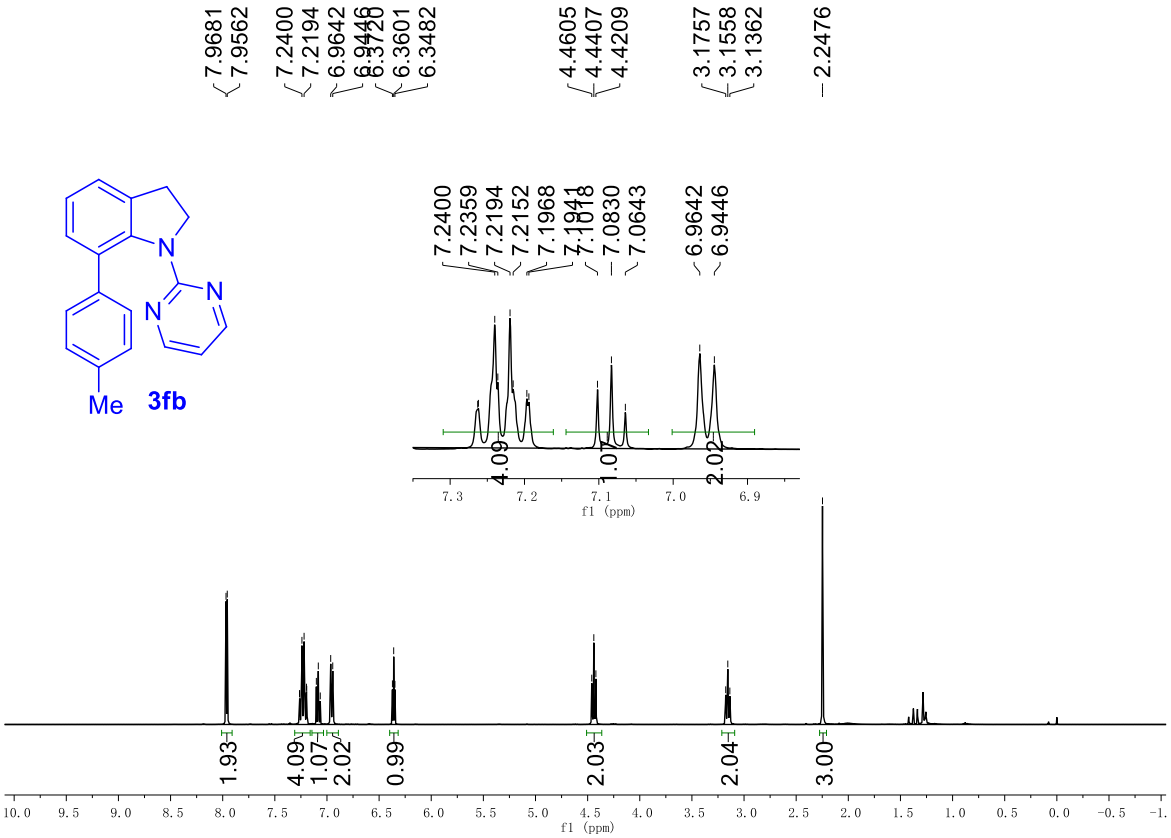
(4) P. B. De, S. Pradhan, S. Banerjee and T. Punniyamurthy, *Chem. Commun.*, 2018, **54**, 2494.

(5) C. Chen, Y. Pan, H. Zhao, X. Xu，Z. Luo，L. Cao，S. Xi，H. Li and L. Xu, *Org. Lett.*, 2018, **20**, 6799.

V. NMR Spectra



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3.1757
3.1558
3.1362
2.2476
Me
3fb
7.2400
7.2359
7.2194
7.2152
7.1968
7.1941
7.1018
7.0830
7.0643
6.9642
6.9446
4.09
1.07
2.02
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4.09
1.07
2.02
0.99
2.03
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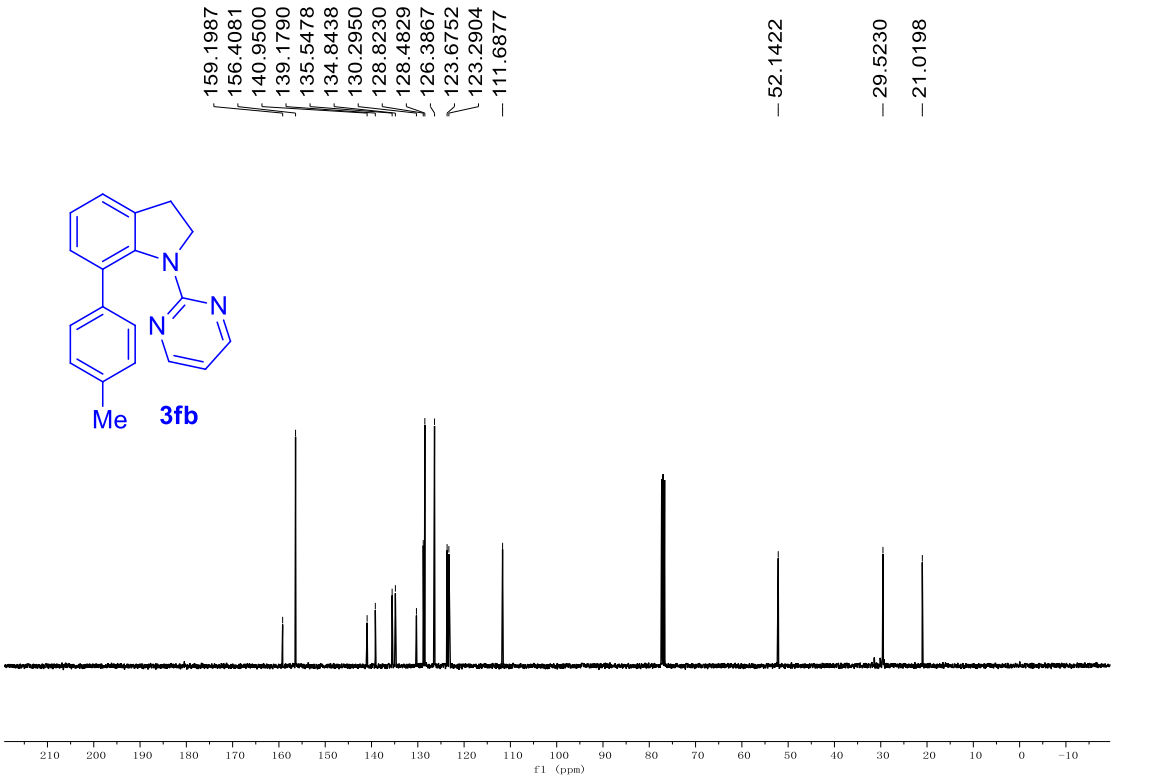
3.00
f1 (ppm)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29.5230
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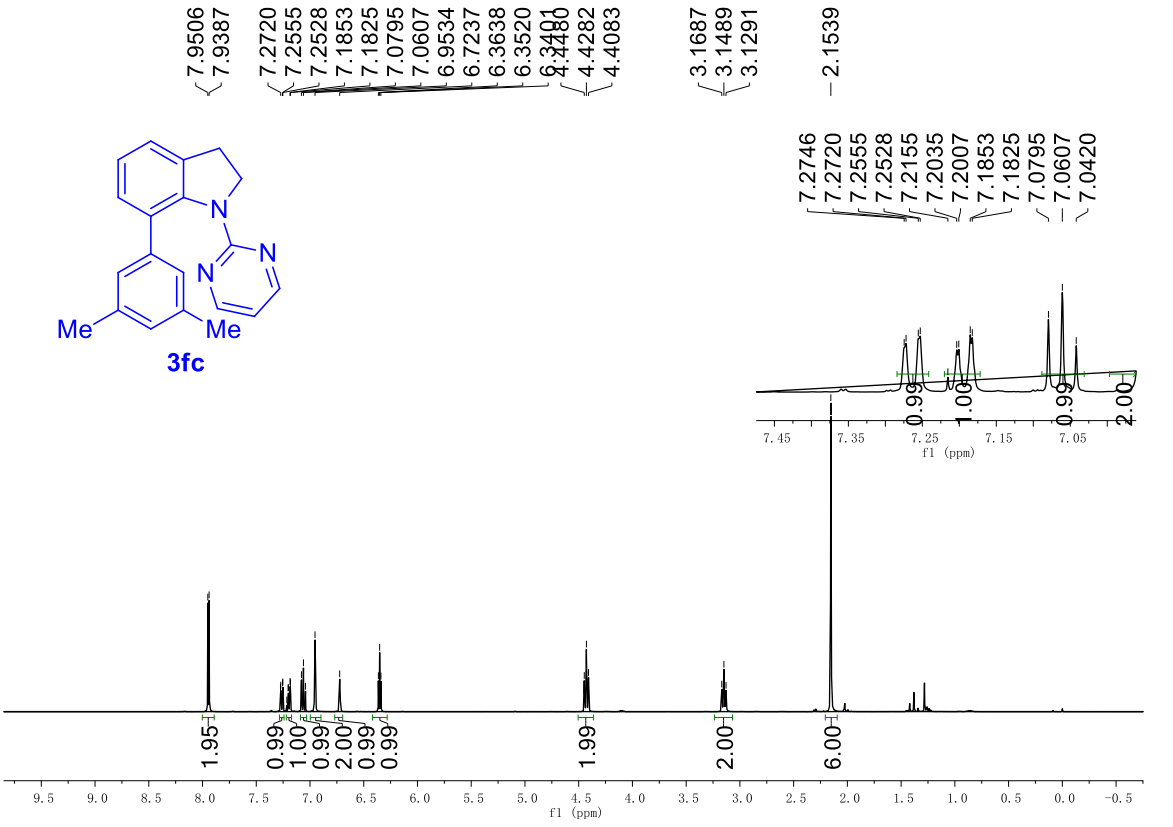
Me
3fb
f1 (ppm)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6.3638
6.3520
4.4282
4.4083
3.1687
3.1489
3.1291
2.1539
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N
N
Me
Me
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7.2746
7.2720
7.2555
7.2528
7.2155
7.2035
7.2007
7.1853
7.1825
7.0795
7.0607
7.0420
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1.00
0.99
2.00
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7.35
7.25
7.15
7.05
f1 (ppm)
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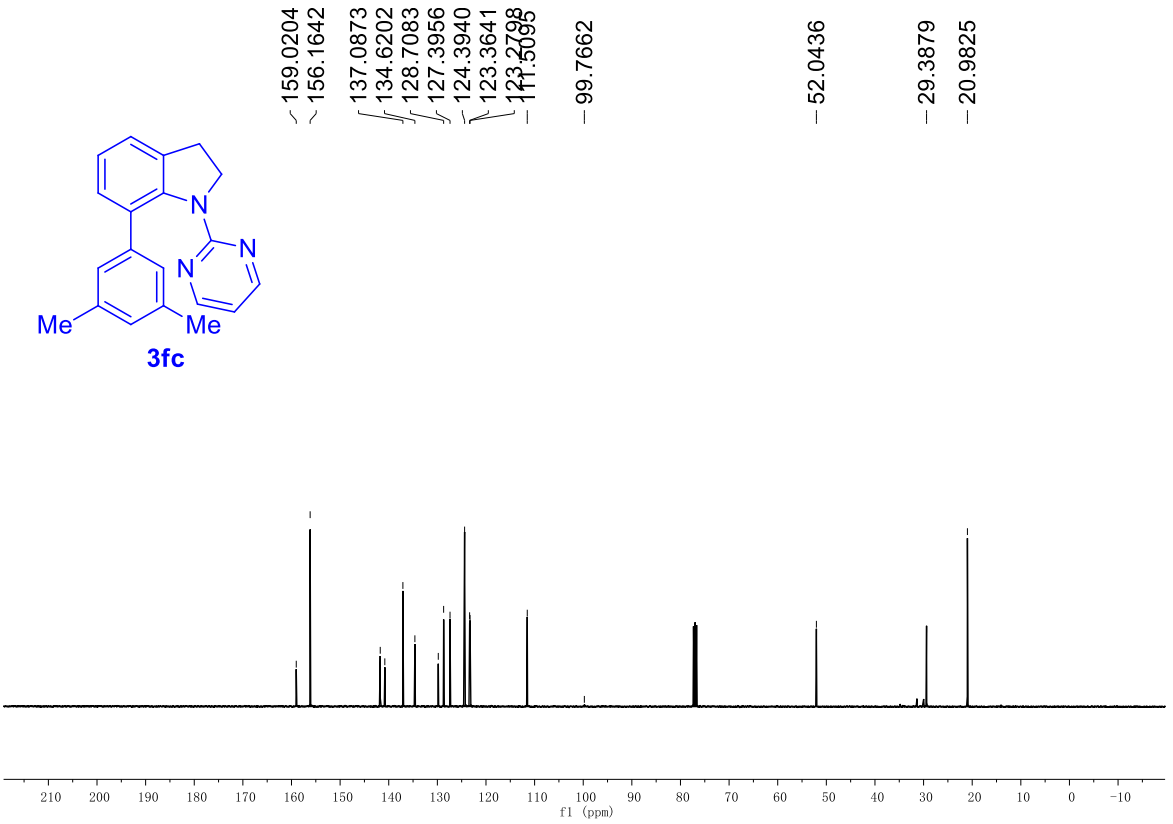
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29.3879
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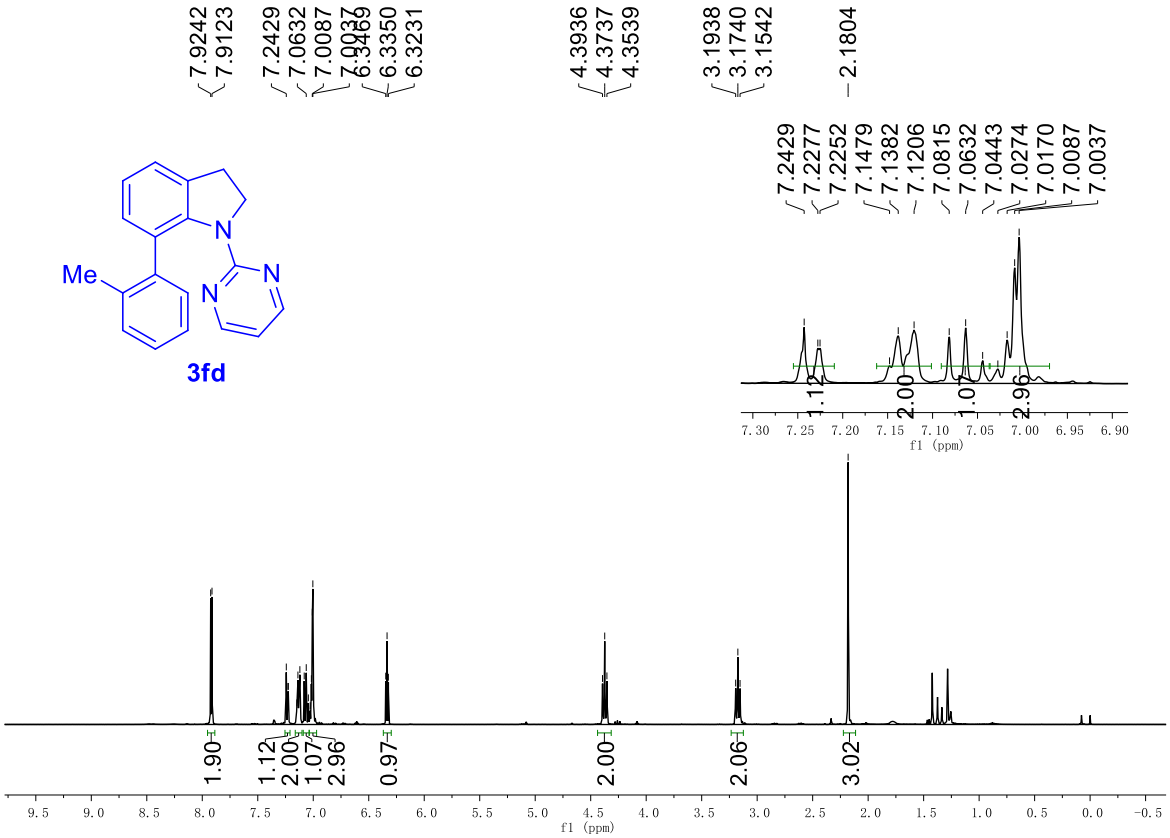
N
N
N
Me
Me
3fc
f1 (ppm)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3.1542
2.1804
Me
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N
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7.1479
7.1382
7.1206
7.0815
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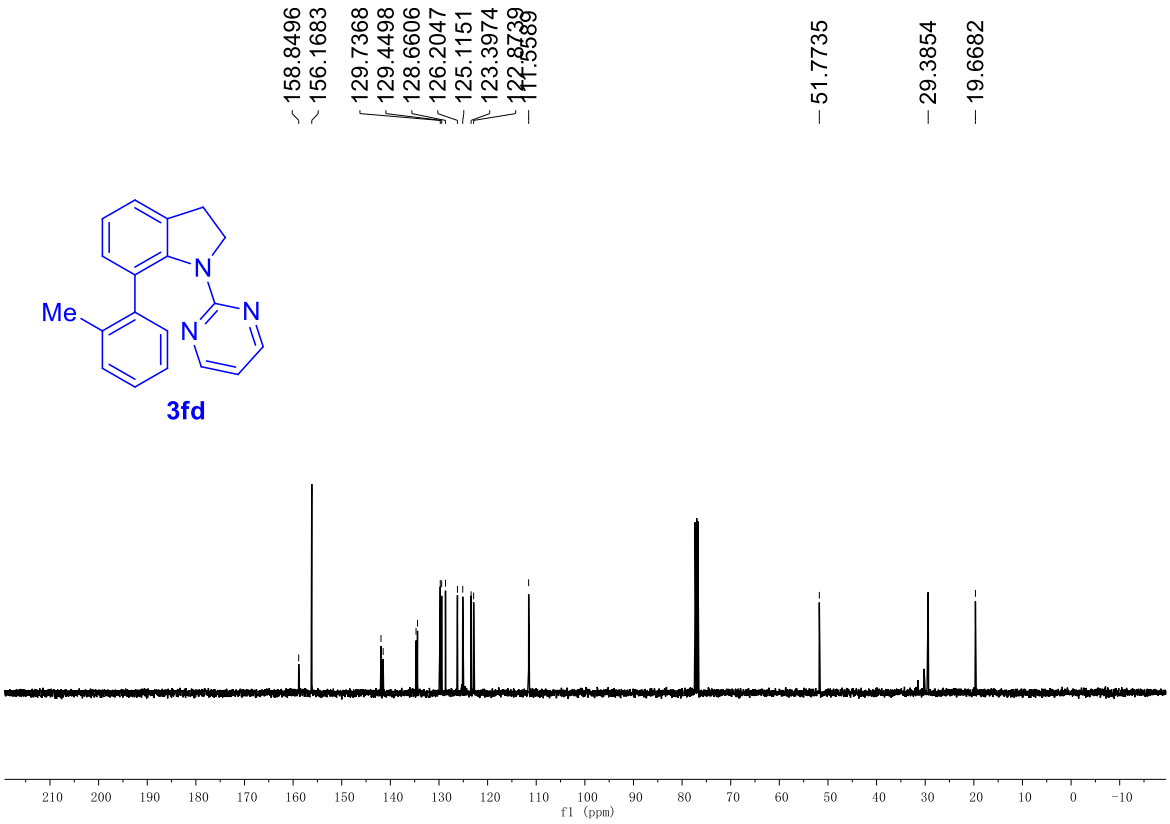
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N
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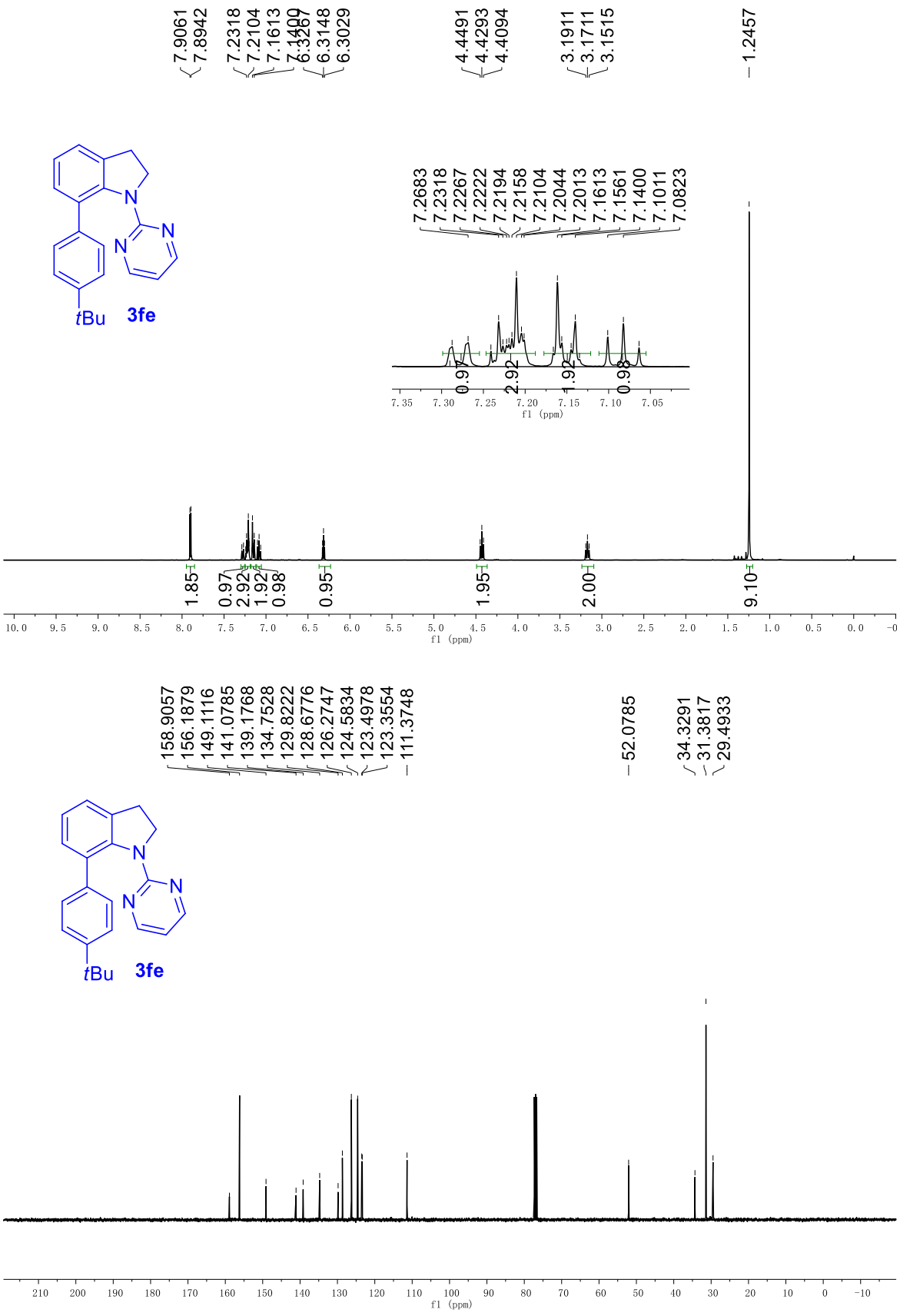
f1 (ppm)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4.4094
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3.1711
3.1515
1.2457
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7.2222
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7.2158
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7.1011
7.0823
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1.92
0.98
f1 (ppm)
1.85
0.97
2.92
1.92
0.98
0.95
1.95
2.00
9.10
f1 (ppm)
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139.1768
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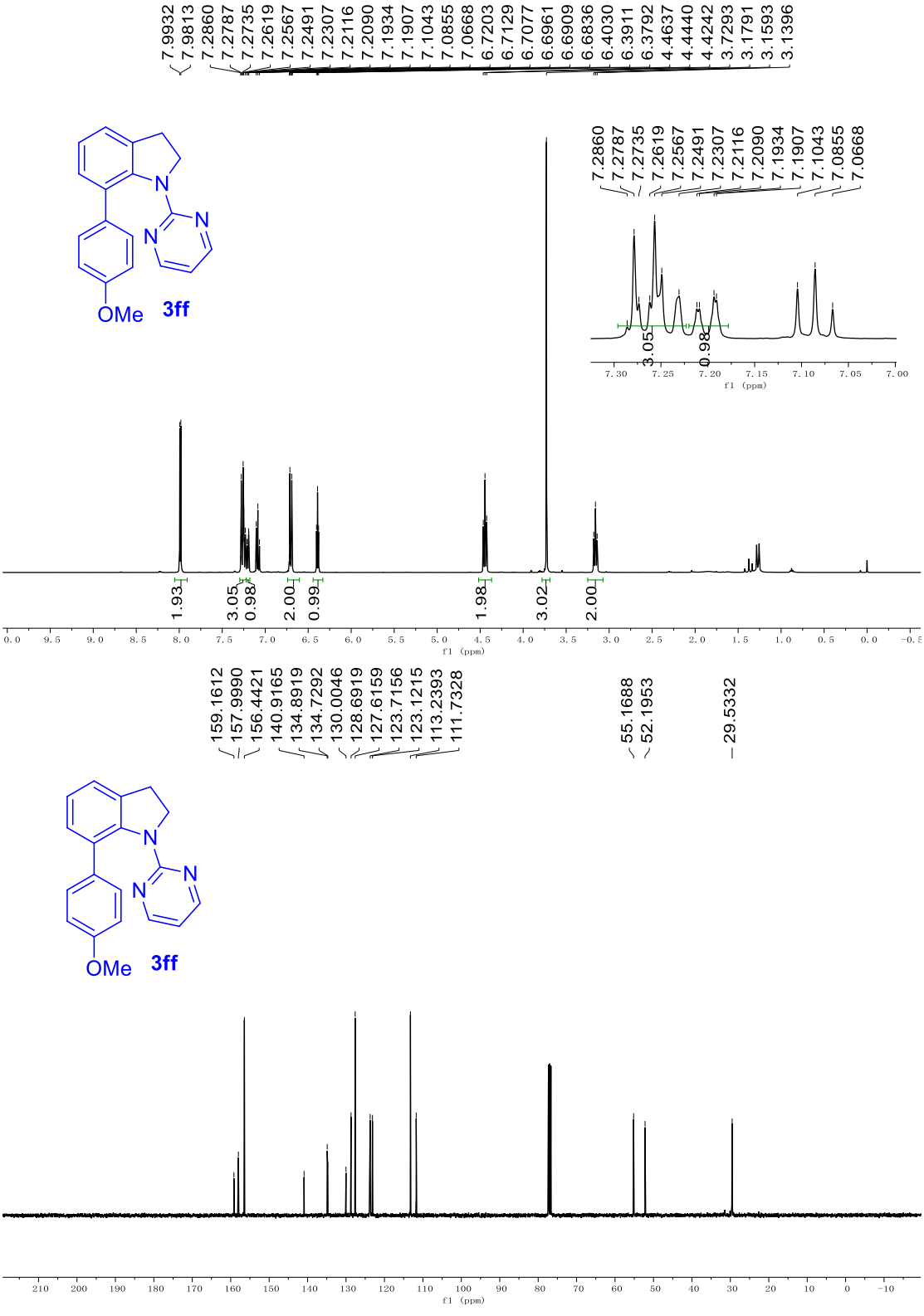
3fe
f1 (ppm)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6.7077
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4.4440
4.4242
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3ff
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2.00
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f1 (ppm)
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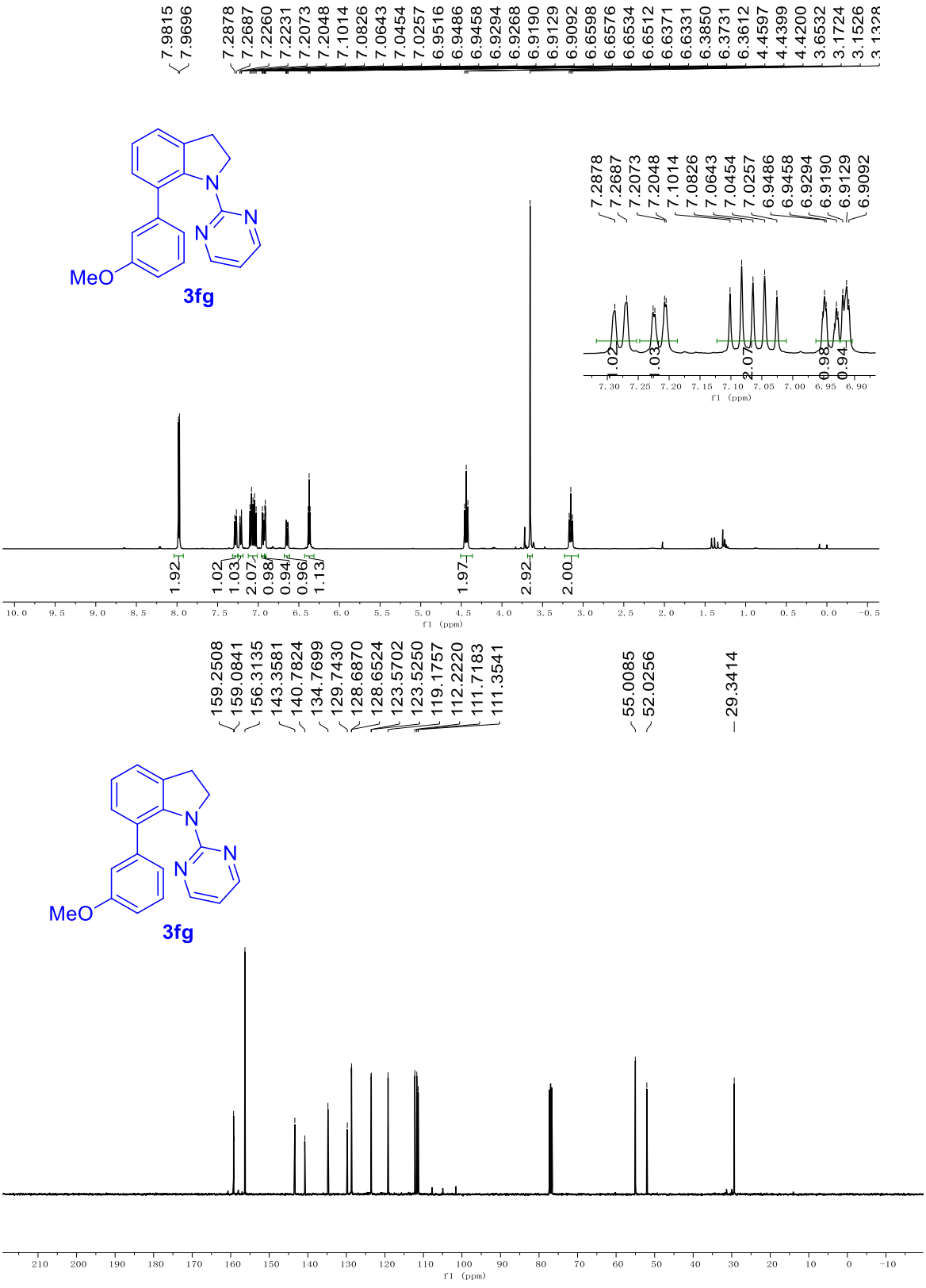
f1 (ppm)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1.03
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1.97
2.92
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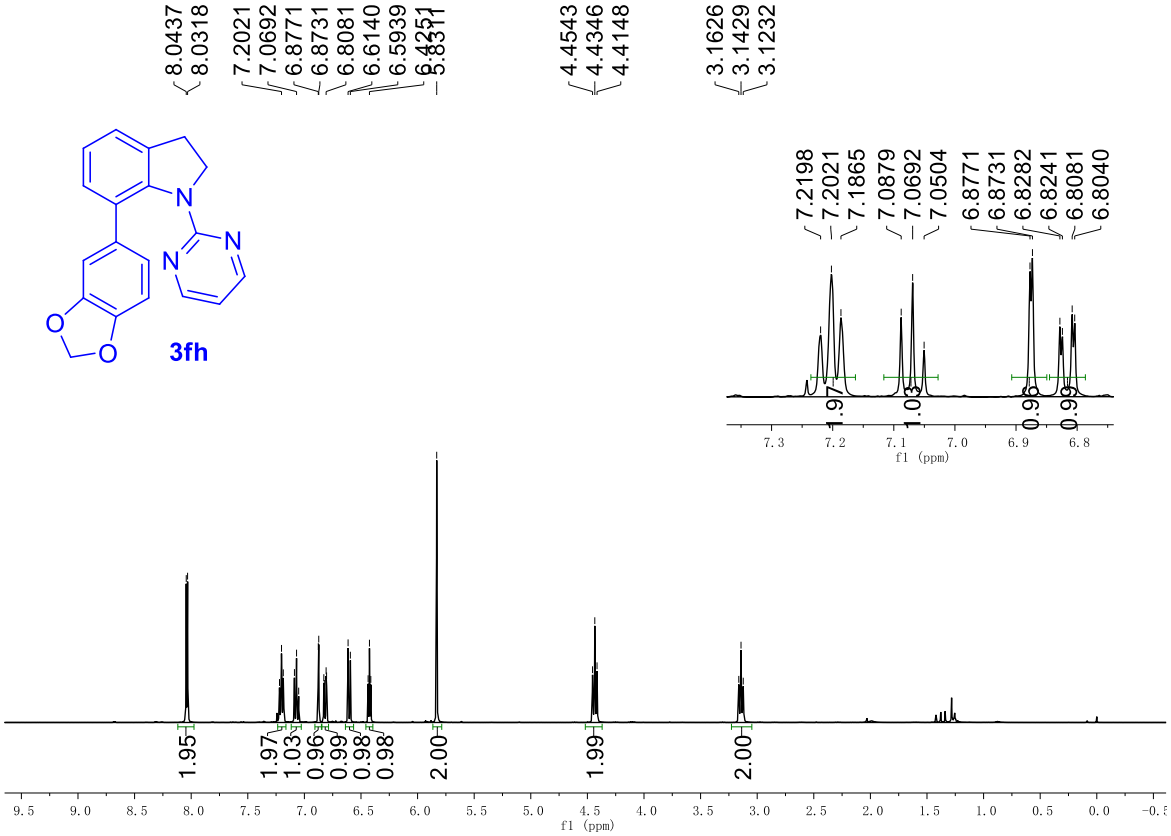
f1 (ppm)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3.1429
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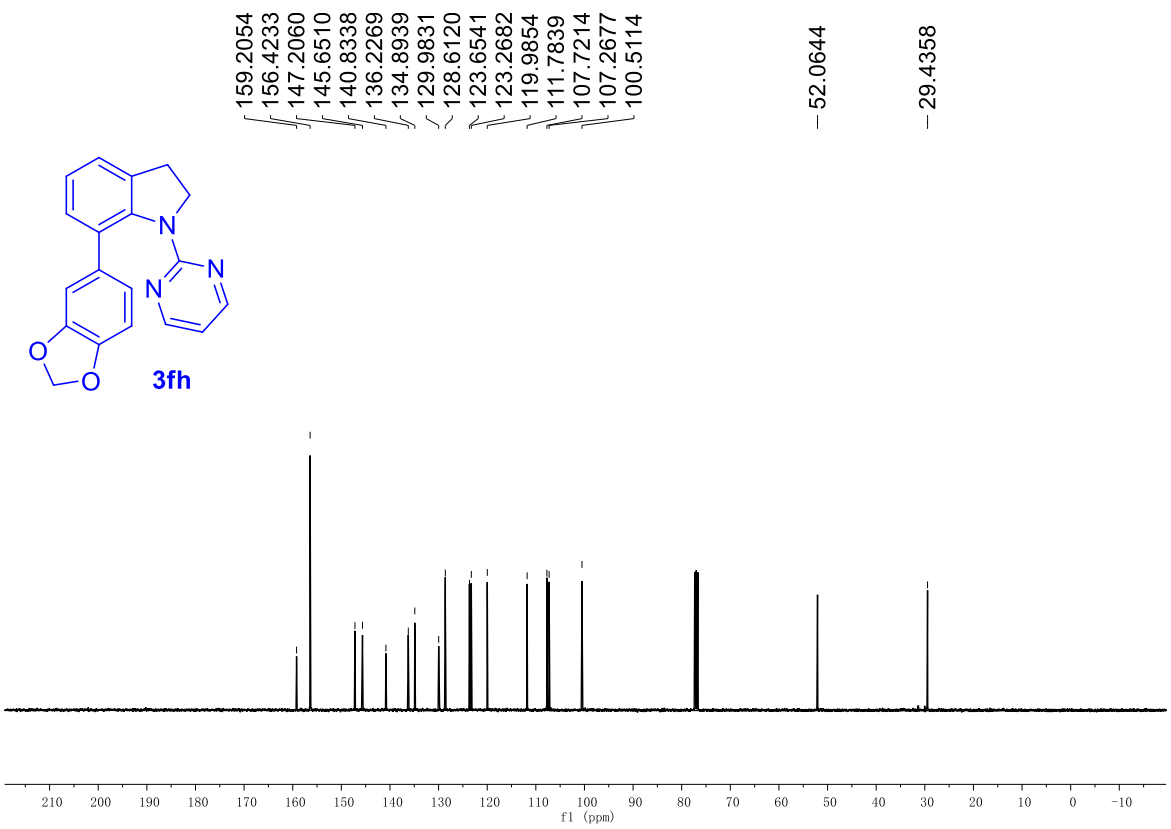
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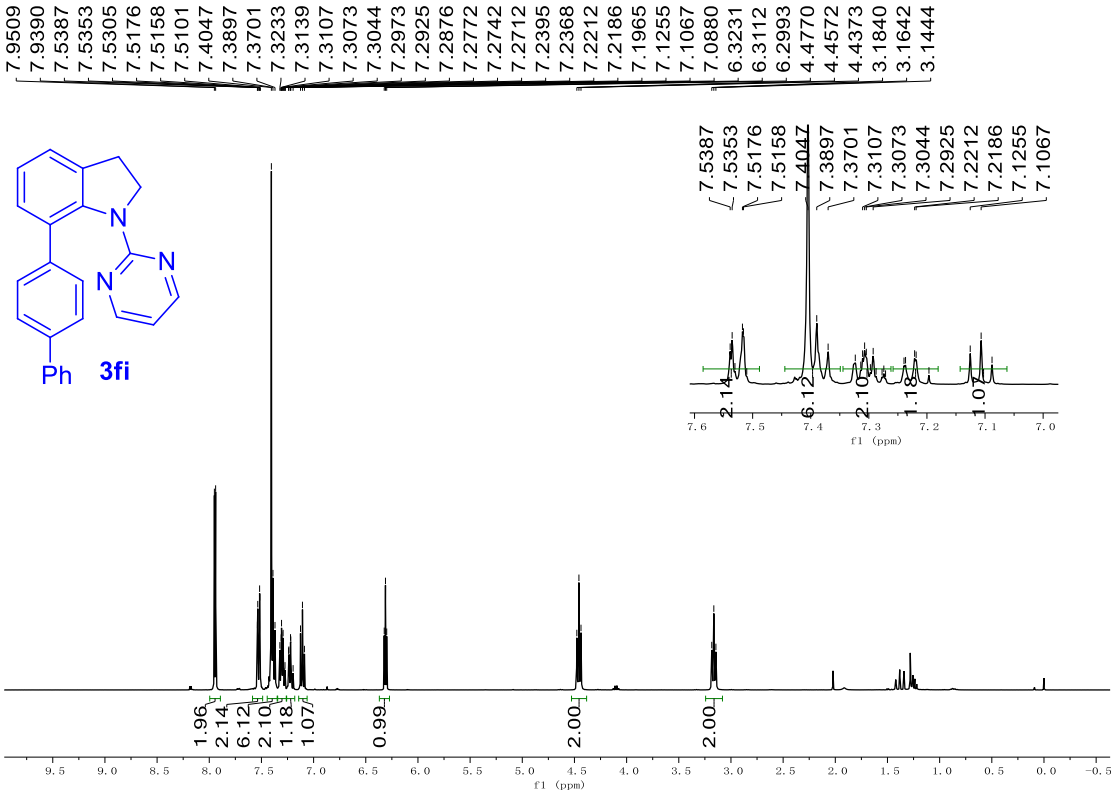
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7.3044
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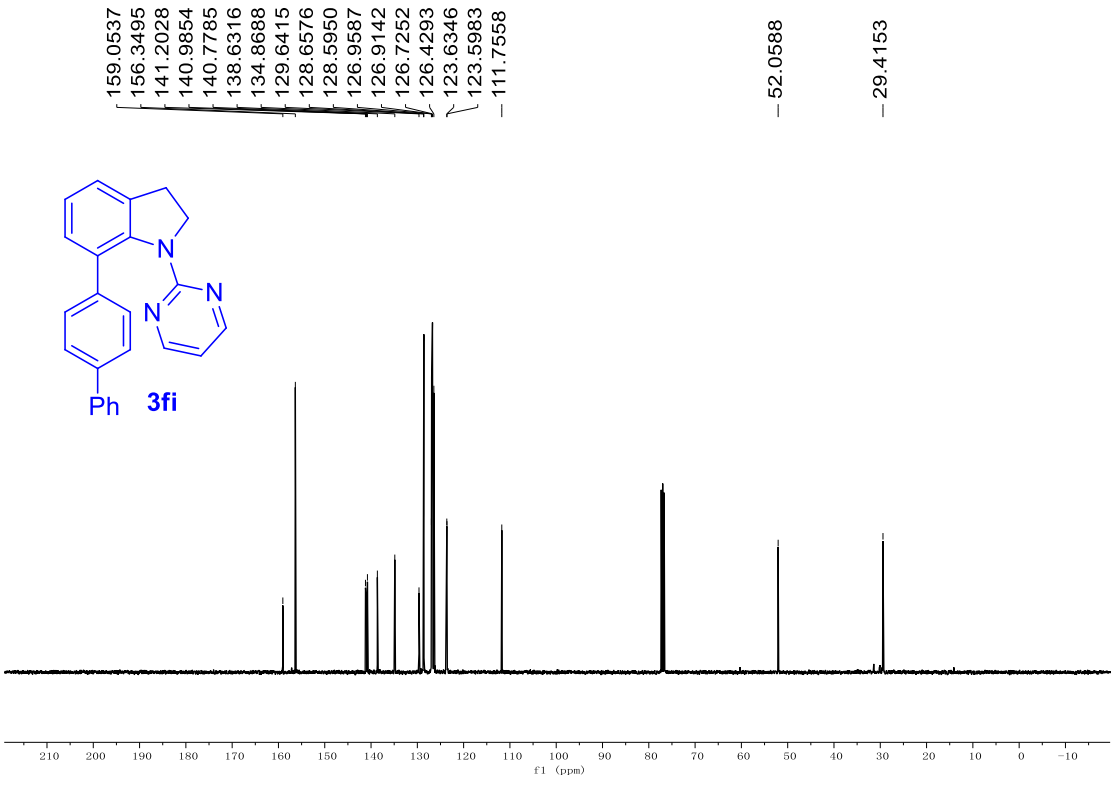
2.00
f1 (ppm)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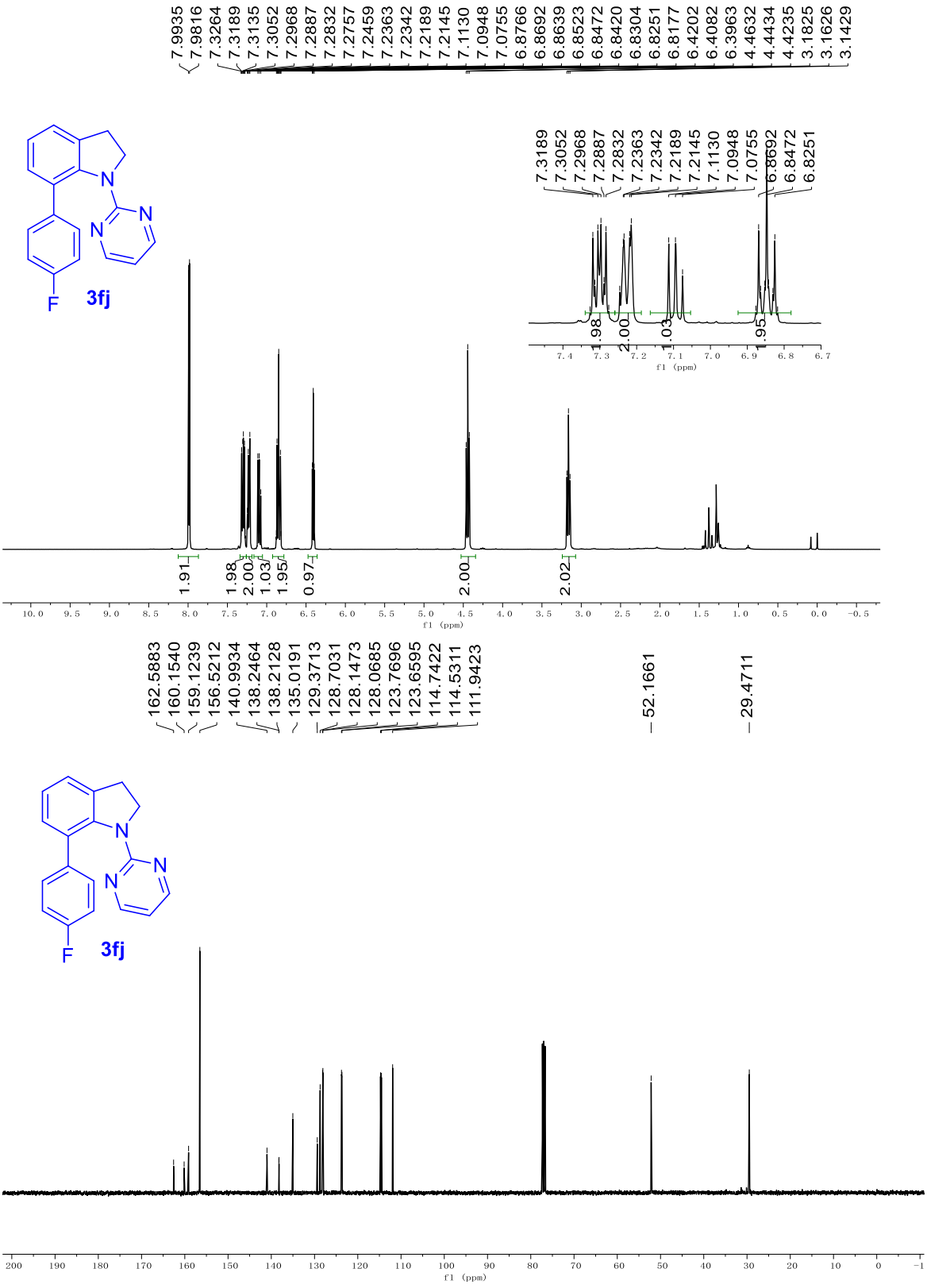
f1 (ppm)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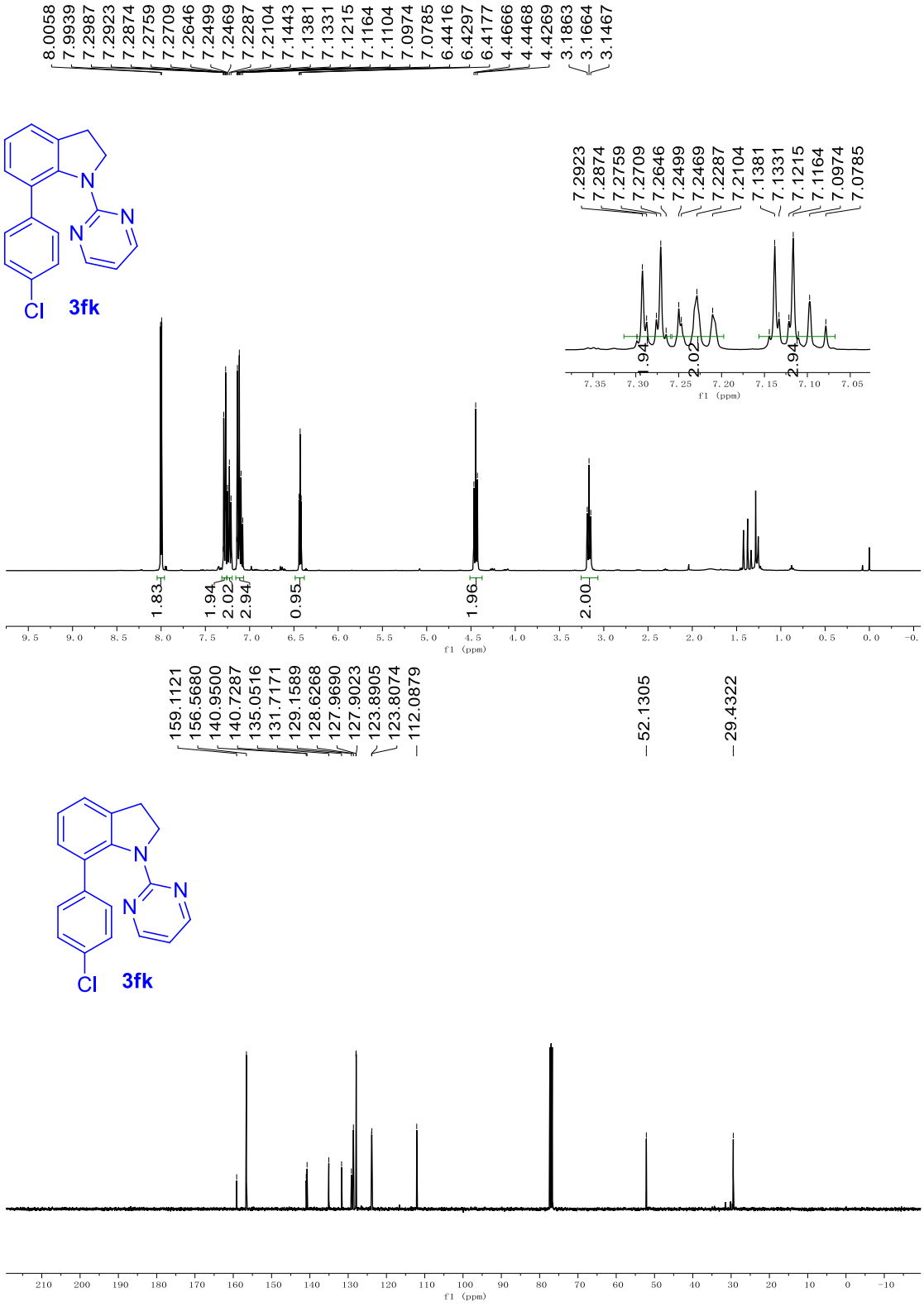
f1 (ppm)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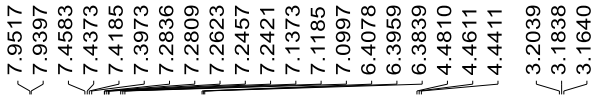
f1 (ppm)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7.1373
7.1185
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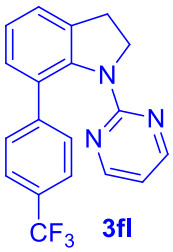
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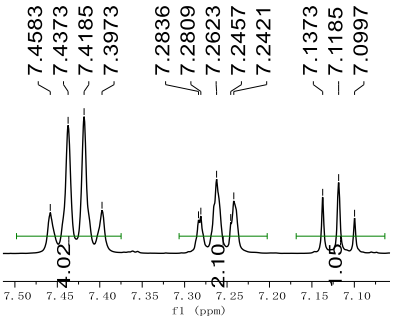
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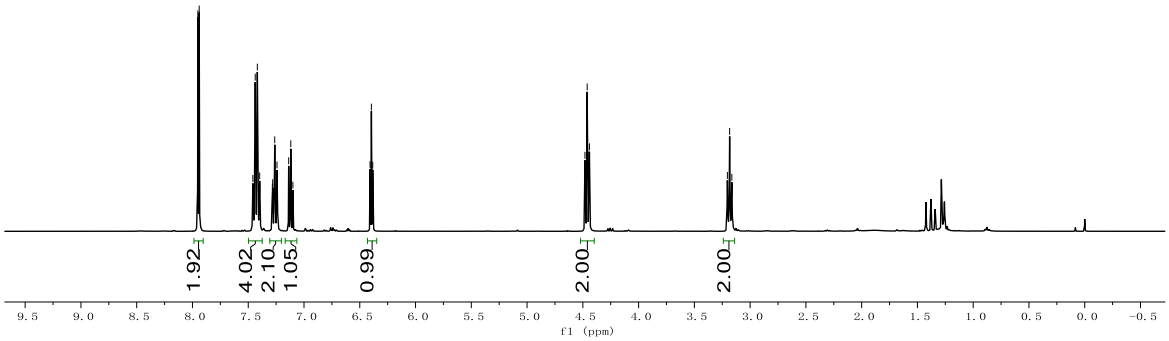
2.10
1.05
7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10
f1 (ppm)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f1 (ppm)


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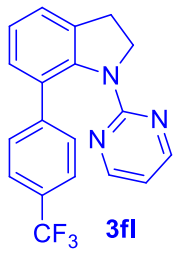
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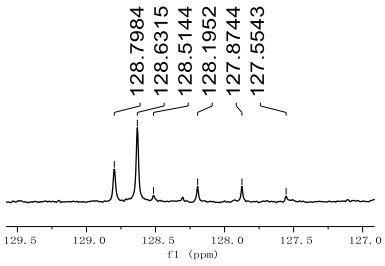
CF3
3fl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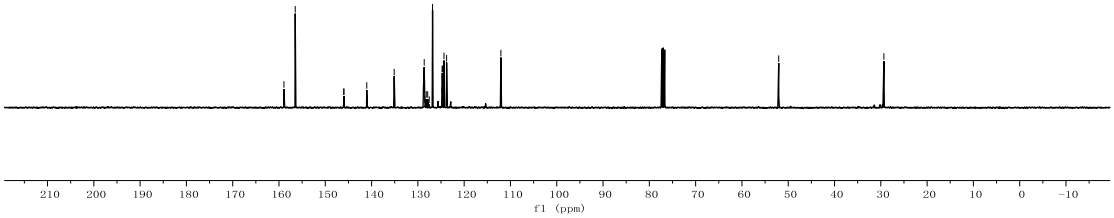
127.8744
127.5543
129.5 129.0 128.5 128.0 127.5 127.0
f1 (ppm)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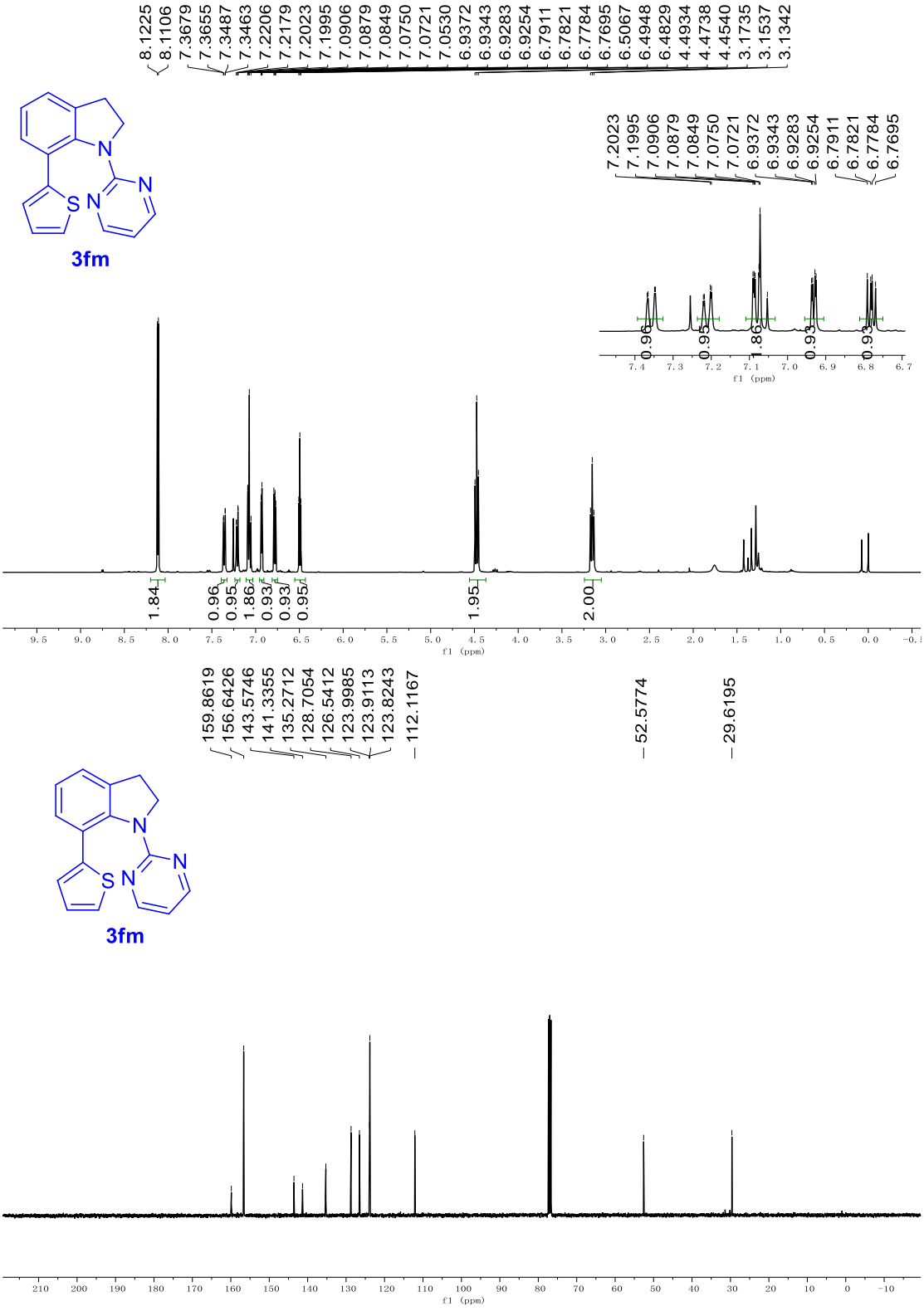
f1 (ppm)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7.3679
7.3655
7.3487
7.3463
7.2206
7.2179
7.2023
7.1995
7.0906
7.0879
7.0849
7.0750
7.0721
7.0530
6.9372
6.9343
6.9283
6.9254
6.7911
6.7821
6.7784
6.7695
6.5067
6.4948
6.4829
4.4934
4.4738
4.4540
3.1735
3.1537
3.1342
3fm
1.84
0.96
0.95
1.86
0.93
0.93
0.95
1.95
2.00
f1 (ppm)
159.8619
156.6426
143.5746
141.3355
135.2712
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123.9985
123.9113
123.8243
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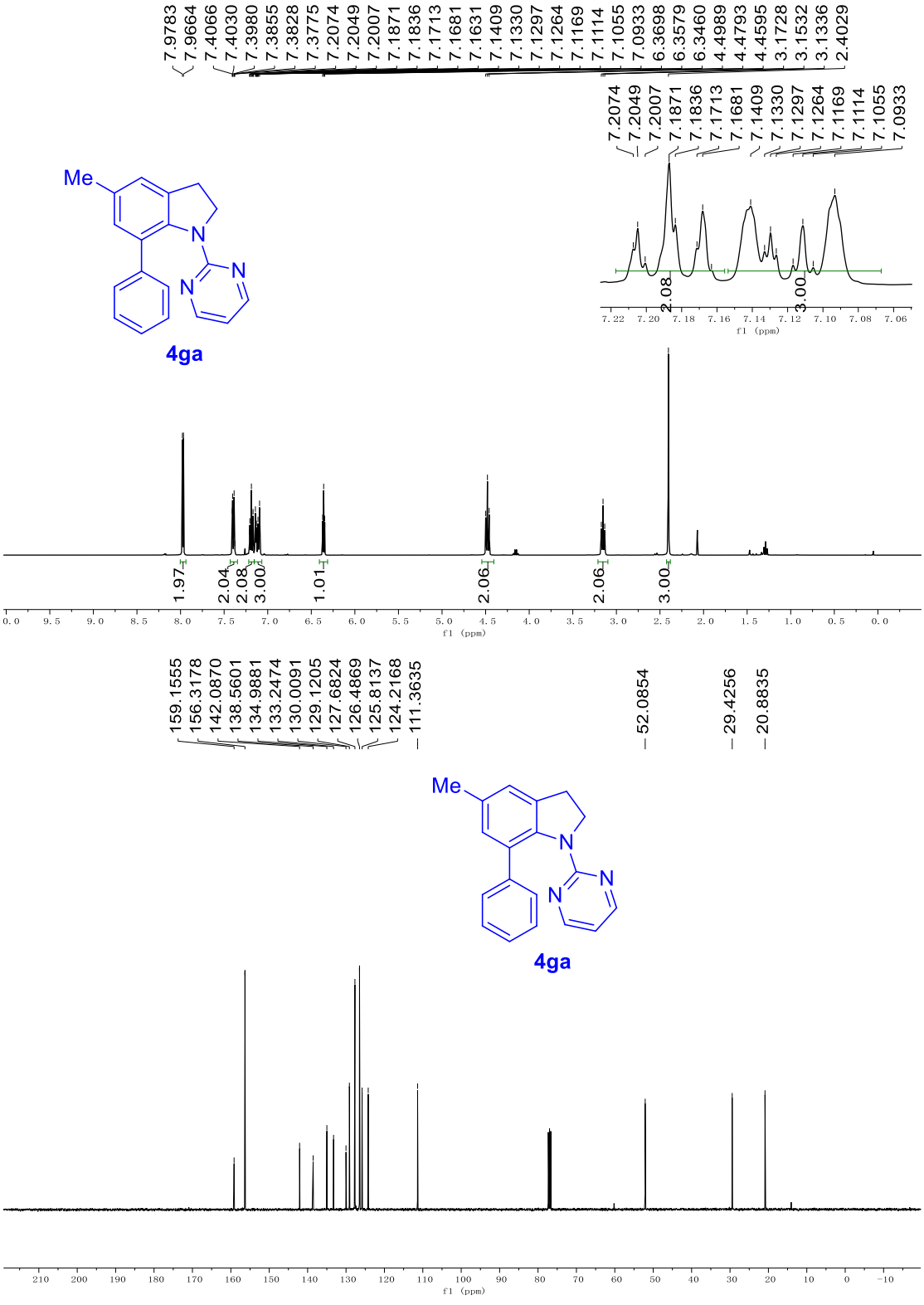
3fm
f1 (ppm)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7.3980
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7.3828
7.3775
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7.2049
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7.1871
7.1836
7.1713
7.1681
7.1631
7.1409
7.1330
7.1297
7.1264
7.1169
7.1114
7.1055
7.0933
6.3698
6.3579
6.3460
4.4989
4.4793
4.4595
3.1728
3.1532
3.1336
2.4029
Me
N
N
N
4ga
2.08
3.00
f1 (ppm)
1.97
2.04
2.08
3.00
1.01
2.06
2.06
3.00
f1 (ppm)
159.1555
156.3178
142.0870
138.5601
134.9881
133.2474
130.0091
129.1205
127.6824
126.4869
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20.8835
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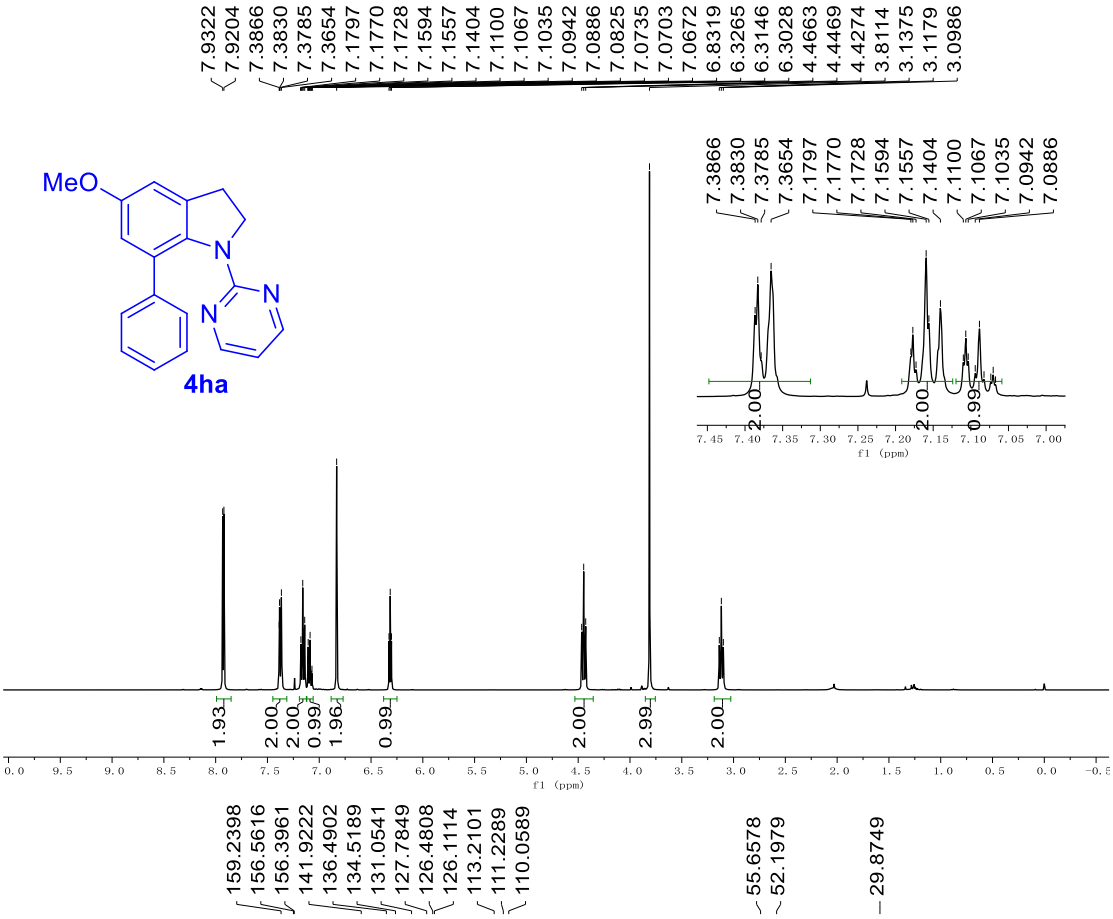
f1 (ppm)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7.3785
7.3654
7.1797
7.1770
7.1728
7.1594
7.1557
7.1404
7.1100
7.1067
7.1035
7.0942
7.0886
7.0825
7.0735
7.0703
7.0672
6.8319
6.3265
6.3146
6.3028
4.4663
4.4469
4.4274
3.8114
3.1375
3.1179
3.0986
MeO
N
N
N
4ha
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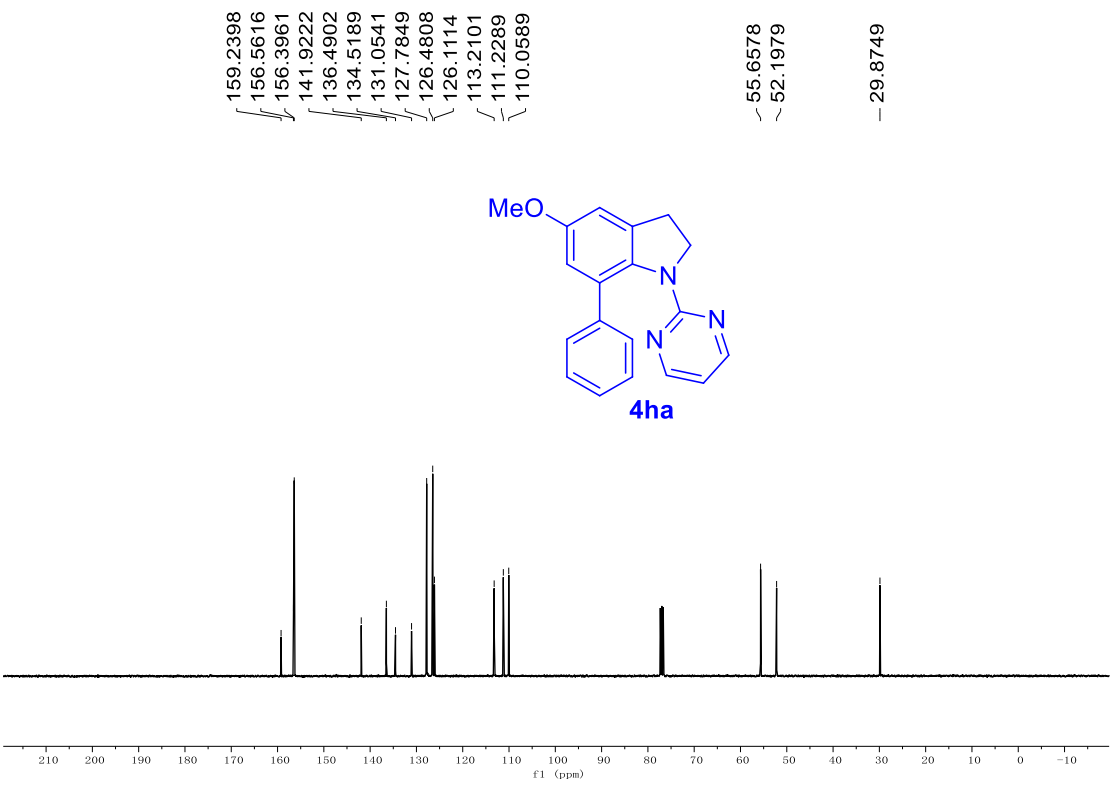
2.00
2.00
0.99
1.96
0.99
2.00
2.99
2.00
f1 (ppm)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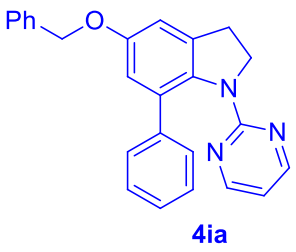
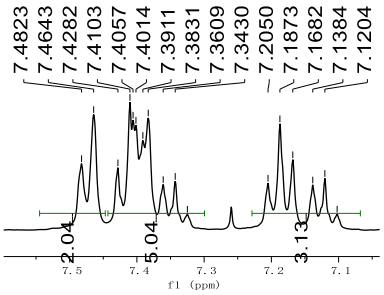
134.5189
131.0541
127.7849
126.4808
126.1114
113.2101
111.2289
110.0589
55.6578
52.1979
29.8749
MeO
N
N
N
4ha
f1 (ppm)


7.9646
7.9527
7.4823
7.4643
7.4282
7.4103
7.4057
7.4014
7.3911
7.3831
7.3430
7.1873
7.1682
7.1204
6.9673
6.9619
6.9318
6.3624
6.3506
6.3387
5.1065
4.4957
4.4762
4.4567


3.1624
3.1431
3.1237


Ph
O
N
N
N

4ia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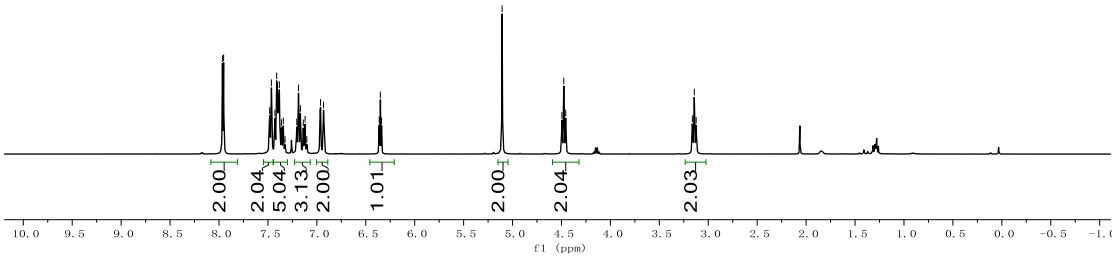
7.4057
7.4014
7.3911
7.3831
7.3609
7.3430
7.2050
7.1873
7.1682
7.1384
7.1204
2.04
5.04
3.13
7.5
7.4
7.3
7.2
7.1
f1 (ppm)


2.00
2.04
5.04
3.13
2.00
1.01
2.00
2.04
2.03
f1 (ppm)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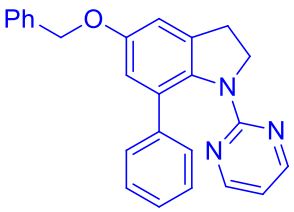
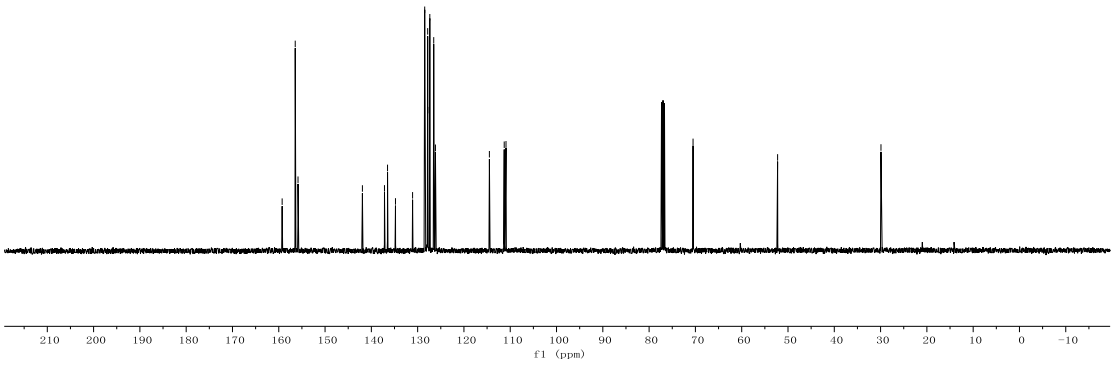
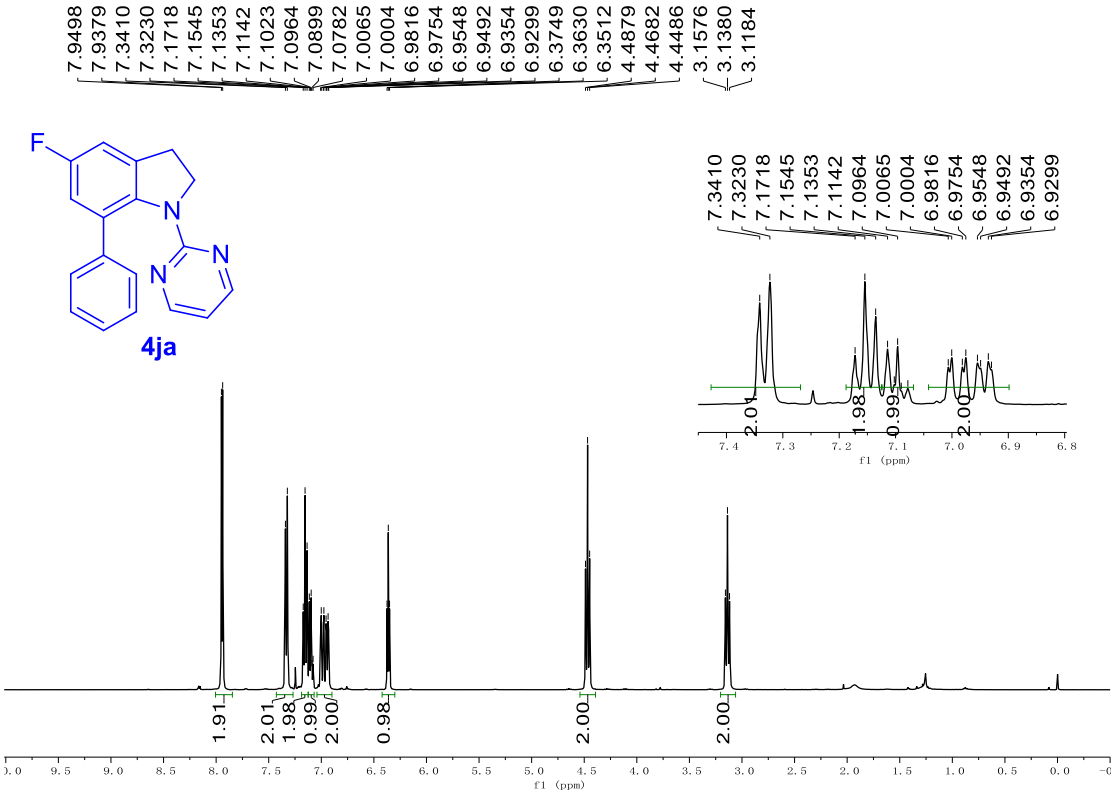
156.4425
155.8418
141.9318
137.1646
136.5036
134.7876
131.0951
128.4775
127.8318
127.8063
127.3740
126.5266
126.1545
114.5028
111.3000
110.9148


70.5095
52.2447
29.9159


Ph
O
N
N
N

4ia


f1 (ppm)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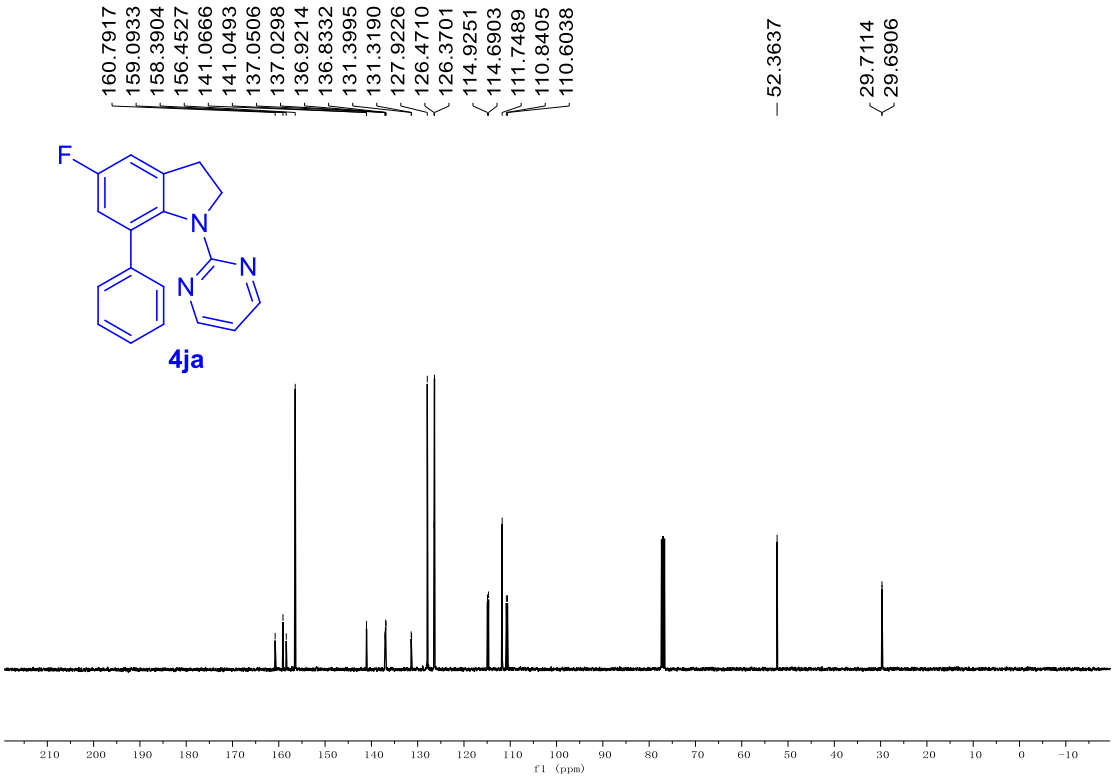
7.1545
7.1353
7.1142
7.1023
7.0964
7.0899
7.0782
7.0065
7.0004
6.9816
6.9754
6.9548
6.9492
6.9354
6.9299
6.3749
6.3630
6.3512
4.4879
4.4682
4.4486
3.1576
3.1380
3.1184
F
N
N
N
4ja
1.91
2.01
1.98
0.99
2.00
0.98
2.00
2.00
f1 (ppm)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141.0493
137.0506
137.0298
136.9214
136.8332
131.3995
131.3190
127.9226
126.4710
126.3701
114.9251
114.6903
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110.6038
52.3637
29.7114
29.6906
F
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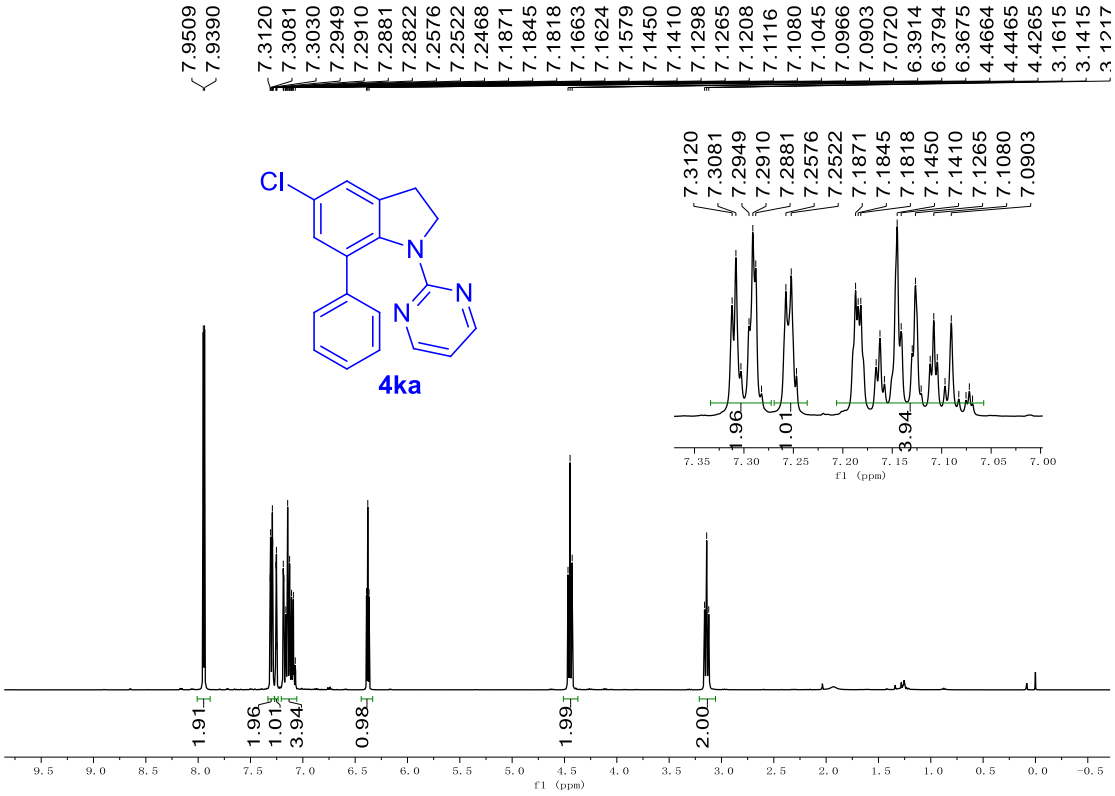
N
N
4ja
f1 (ppm)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7.2910
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7.2822
7.2576
7.2522
7.2468
7.1871
7.1845
7.1818
7.1663
7.1624
7.1579
7.1450
7.1410
7.1298
7.1265
7.1208
7.1116
7.1080
7.1045
7.0966
7.0903
7.0720
6.3914
6.3794
6.3675
4.4664
4.4465
4.4265
3.1615
3.1415
Cl
N
N
N
4ka
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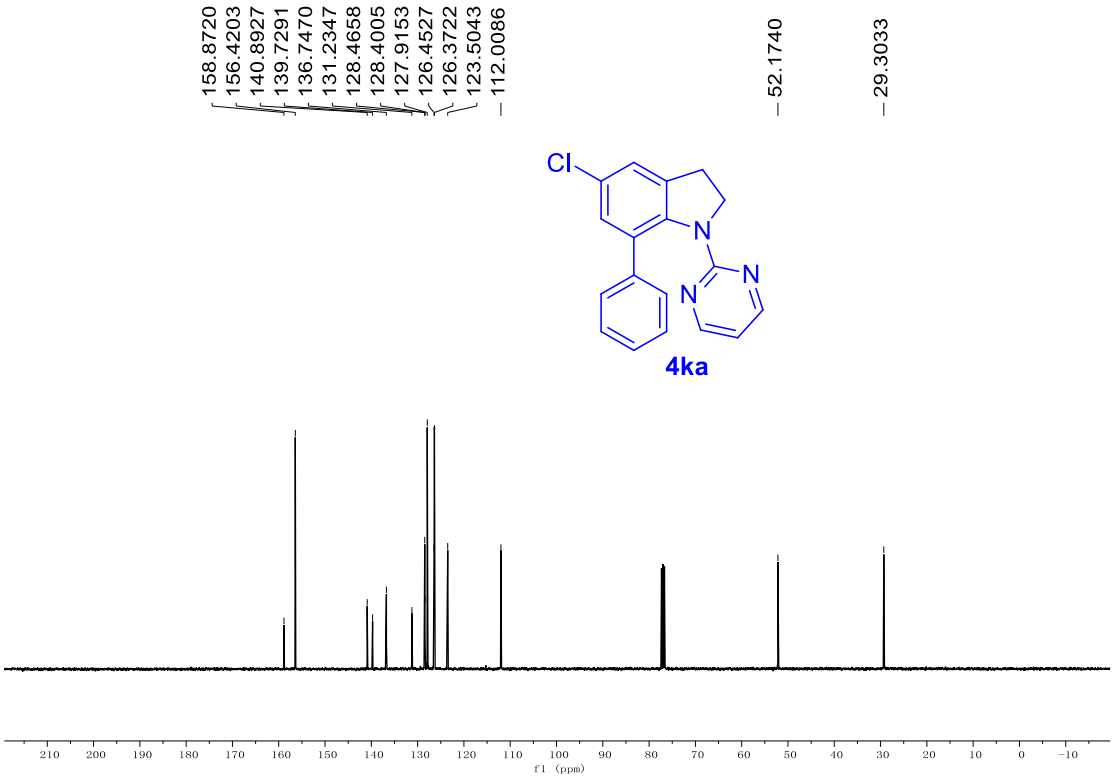
1.01
3.94
1.91
1.96
1.01
3.94
0.98
1.99
2.00
f1 (ppm)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139.7291
136.7470
131.2347
128.4658
128.4005
127.9153
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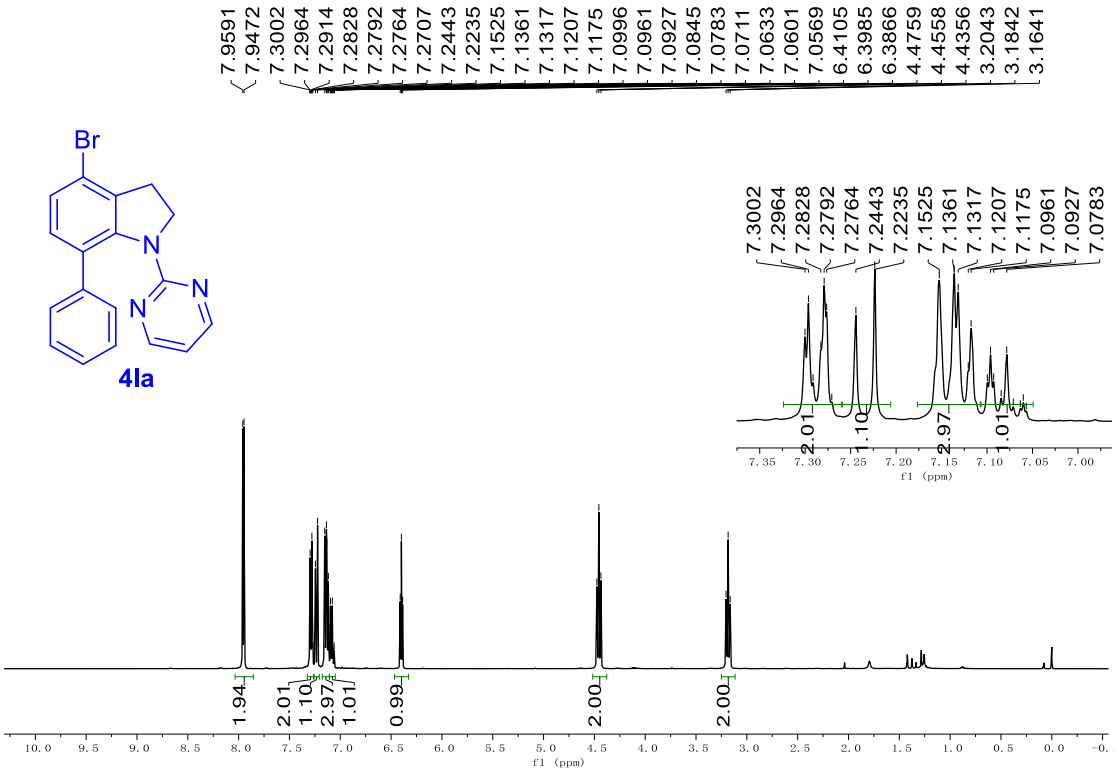
126.3722
123.5043
112.0086
52.1740
29.3033
Cl
N
N
N
4ka
f1 (ppm)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7.2792
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7.2235
7.1525
7.1361
7.1317
7.1207
7.1175
7.0996
7.0961
7.0927
7.0845
7.0783
7.0711
7.0633
7.0601
7.0569
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6.3866
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4.4356
3.2043
3.1842
3.1641
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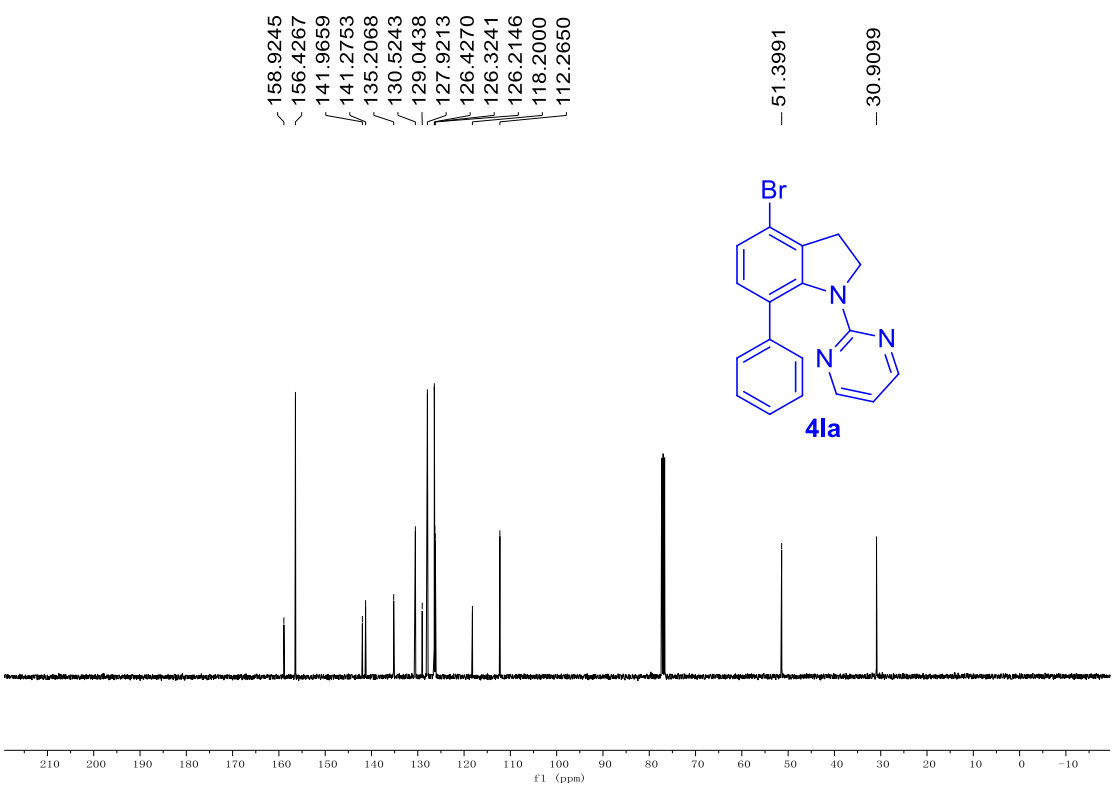
1.10
2.97
1.01
0.99
2.00
2.00
f1 (ppm)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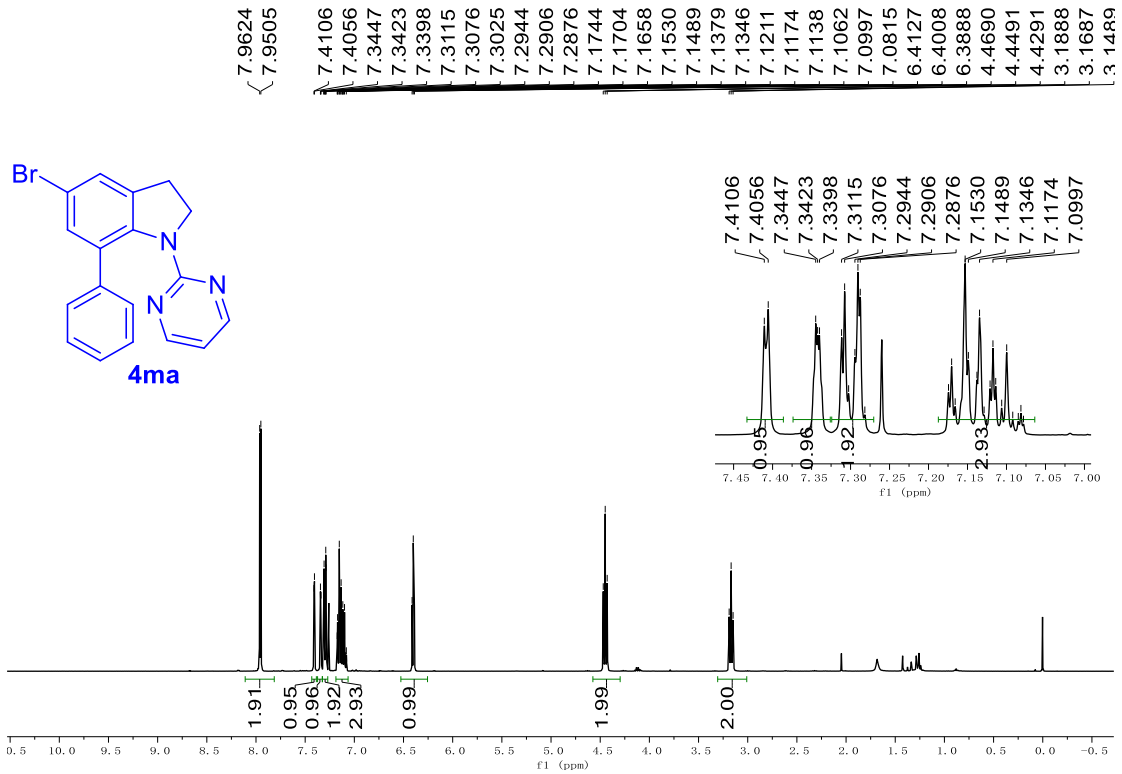
130.5243
129.0438
127.9213
126.4270
126.3241
126.2146
118.2000
112.2650
51.3991
30.9099
Br
N
N
N
4la
f1 (ppm)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7.2906
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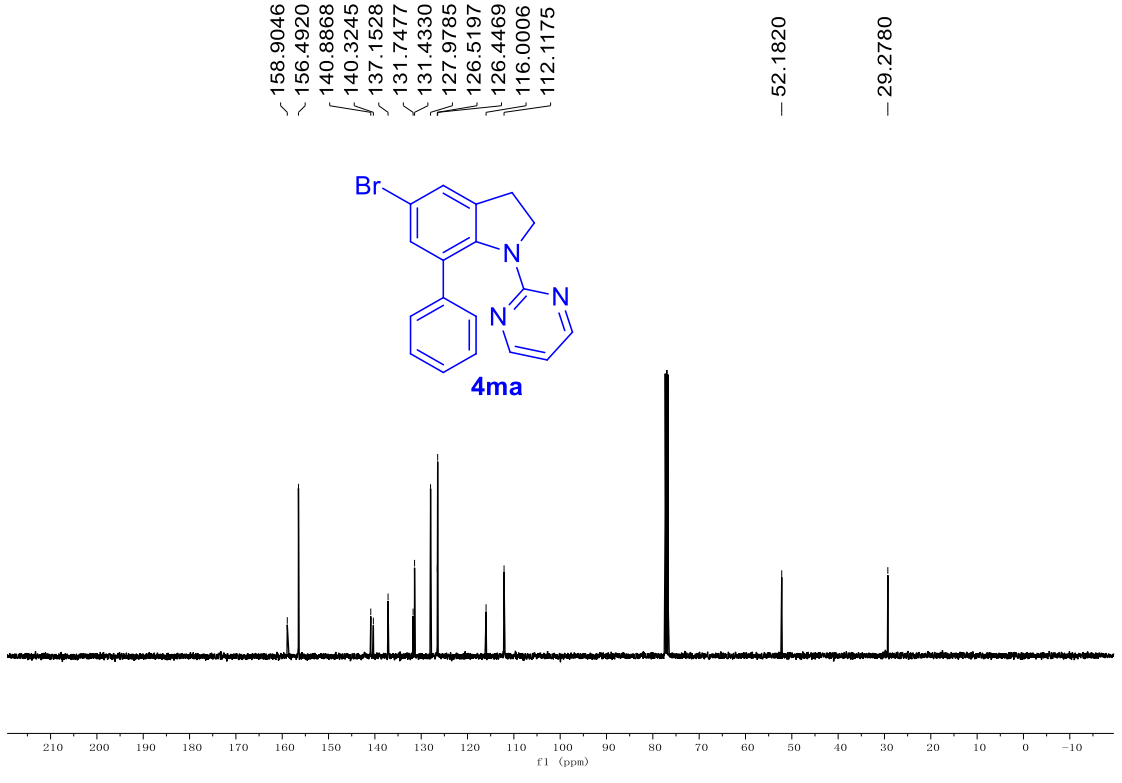
7.1744
7.1704
7.1658
7.1530
7.1489
7.1379
7.1346
7.1211
7.1174
7.1138
7.1062
7.0997
7.0815
6.4127
6.4008
6.3888
4.4690
4.4491
4.4291
3.1888
3.1687
Br
N
N
N
4ma
1.91
0.95
0.96
1.92
2.93
0.99
1.99
2.00
f1 (ppm)
0.95
0.96
1.92
2.93
f1 (ppm)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140.3245
137.1528
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131.4330
127.9785
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116.0006
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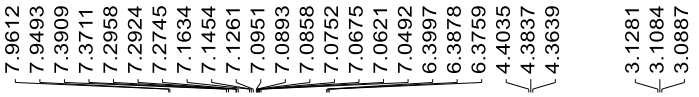
52.1820
29.2780
Br
N
N
N
4ma
f1 (ppm)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7.0951
7.0893
7.0858
7.0752
7.0675
7.0621
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6.3759
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4.3837
4.3639
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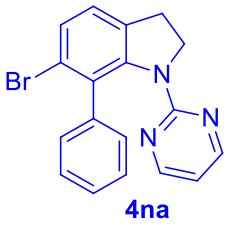
3.1084
3.0887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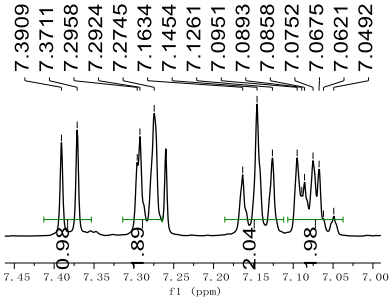
N
N
4na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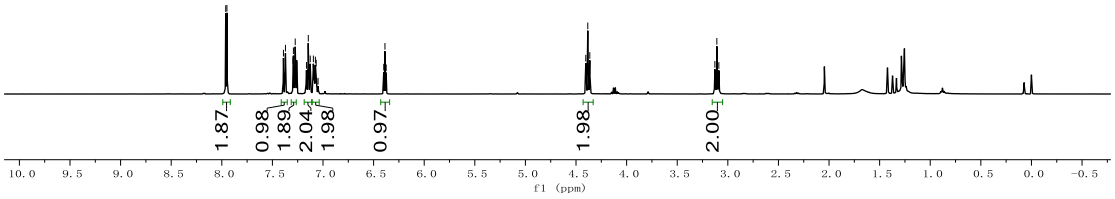
7.2924
7.2745
7.1634
7.1454
7.1261
7.0951
7.0893
7.0858
7.0752
7.0675
7.0621
7.0492
0.98
1.89
2.04
1.98
7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00
f1 (ppm)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1.89
2.04
1.98
0.97
1.98
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


158.8132
156.4603
143.5748
139.7653
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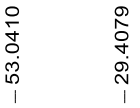
130.3247
129.6287
127.8854
127.1022
126.6757
124.7136
122.4621
112.1170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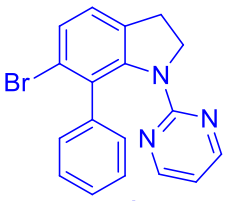
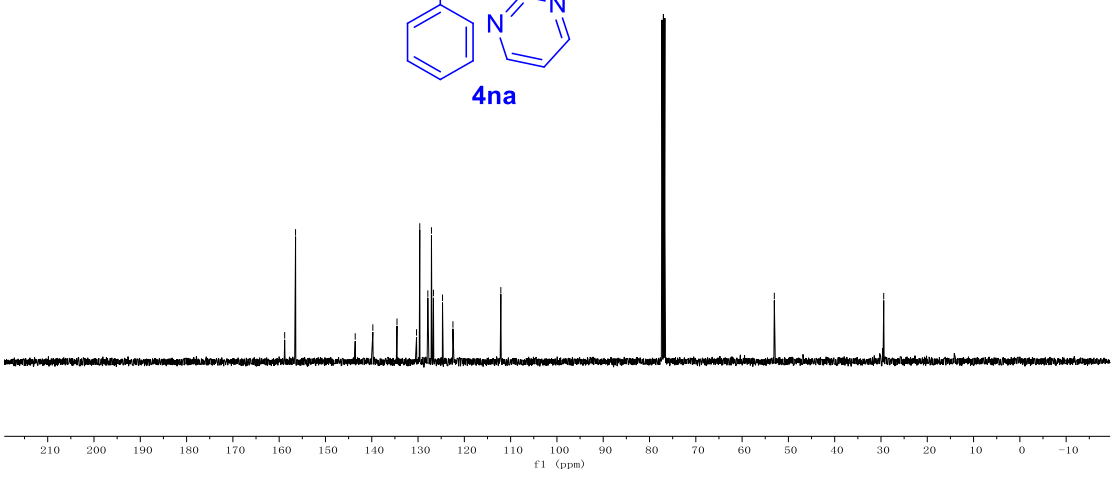
29.4079


Br
N
N
N
4na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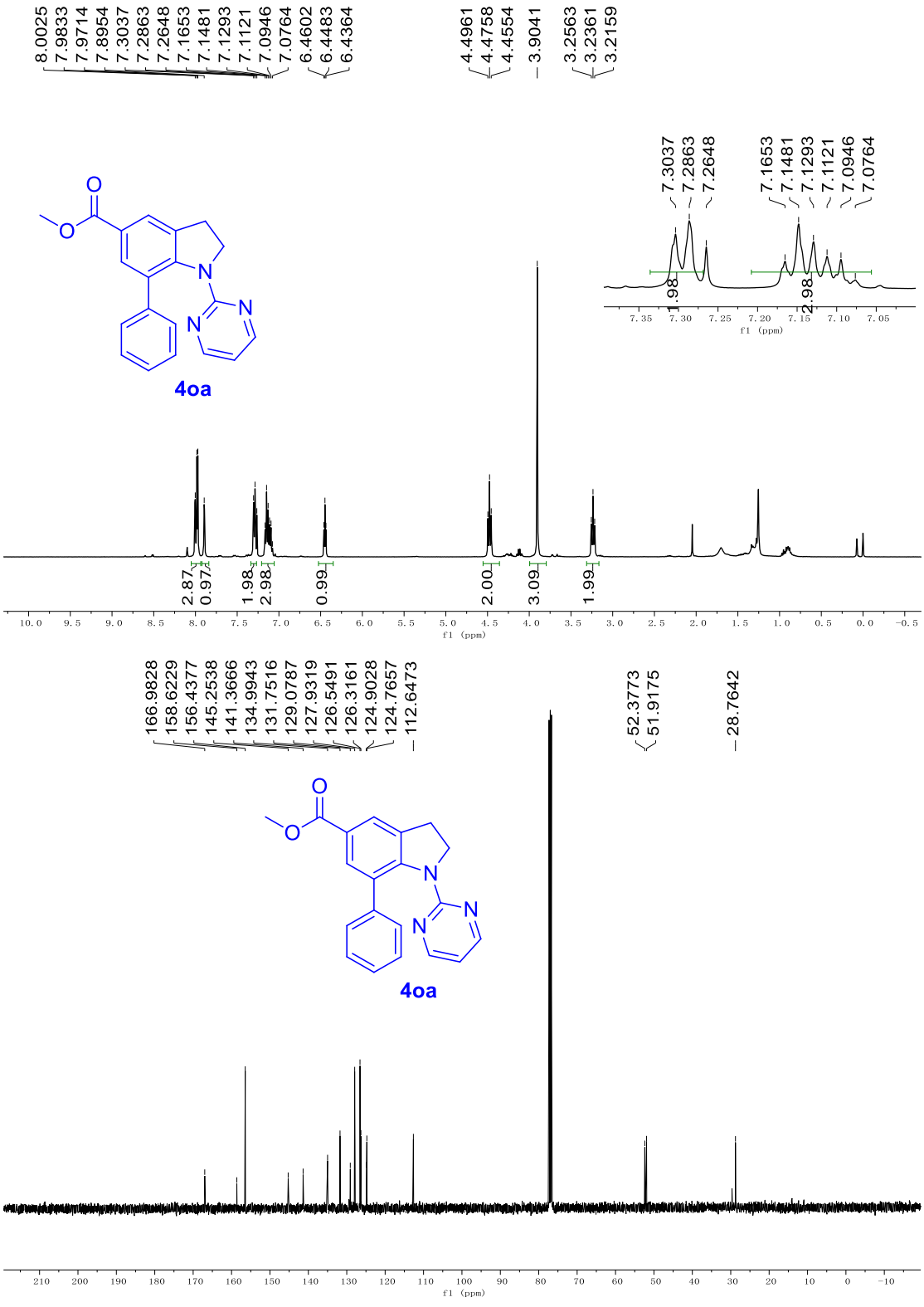
f1 (ppm)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7.1121
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7.0764
6.4602
6.4483
6.4364
4.4961
4.4758
4.4554
3.9041
3.2563
3.2361
3.2159
4oa
2.87
0.97
1.98
2.98
0.99
2.00
3.09
1.99
f1 (ppm)
166.9828
158.6229
156.4377
145.2538
141.3666
134.9943
131.7516
129.0787
127.9319
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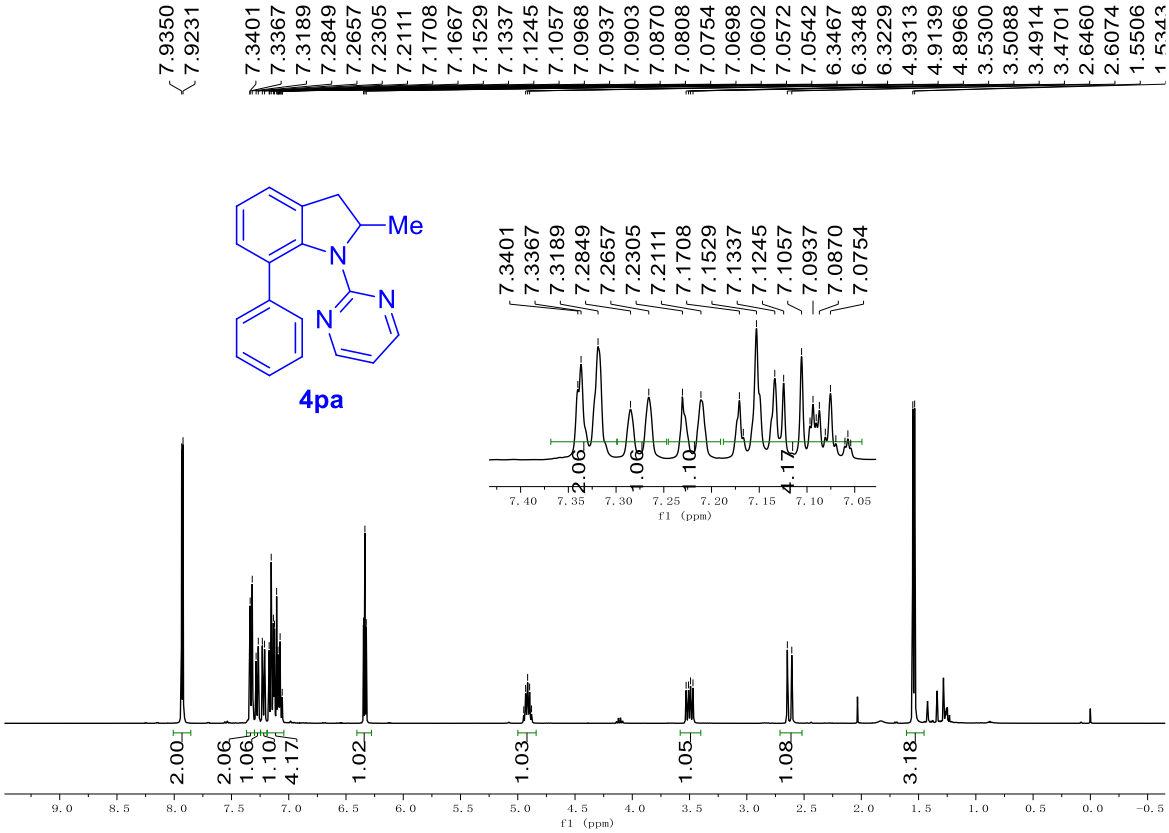
f1 (ppm)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7.1529
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7.1057
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7.0698
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7.0542
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6.3229
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Me
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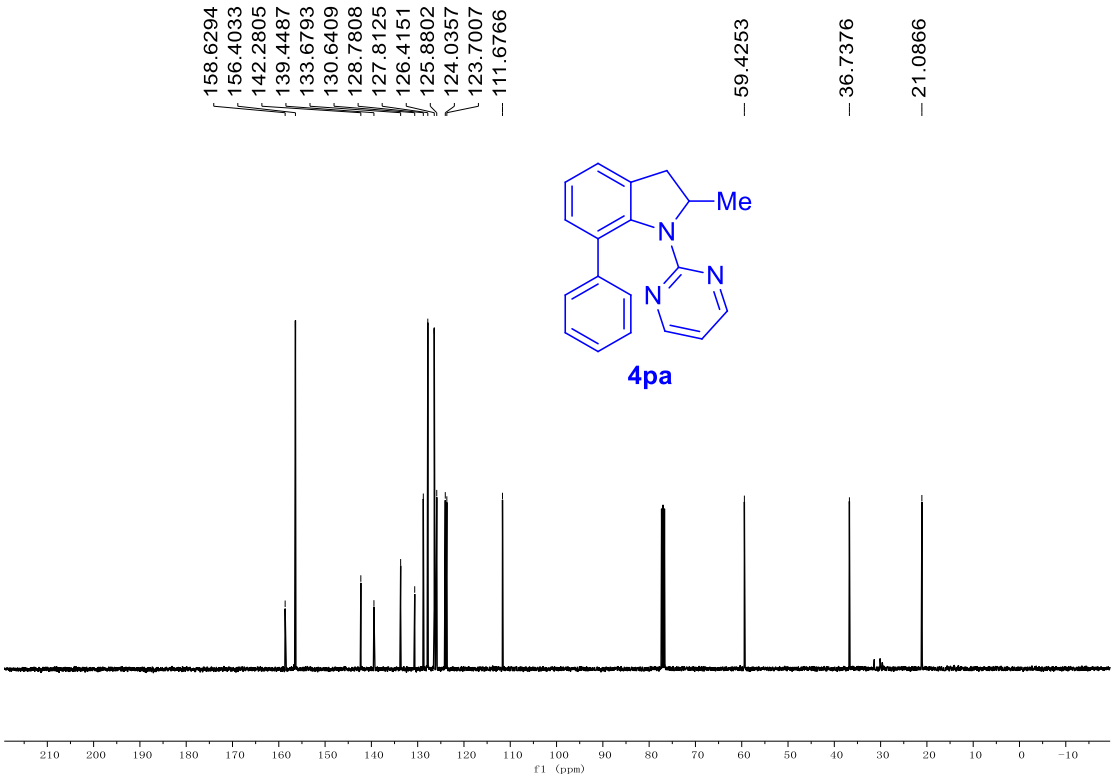
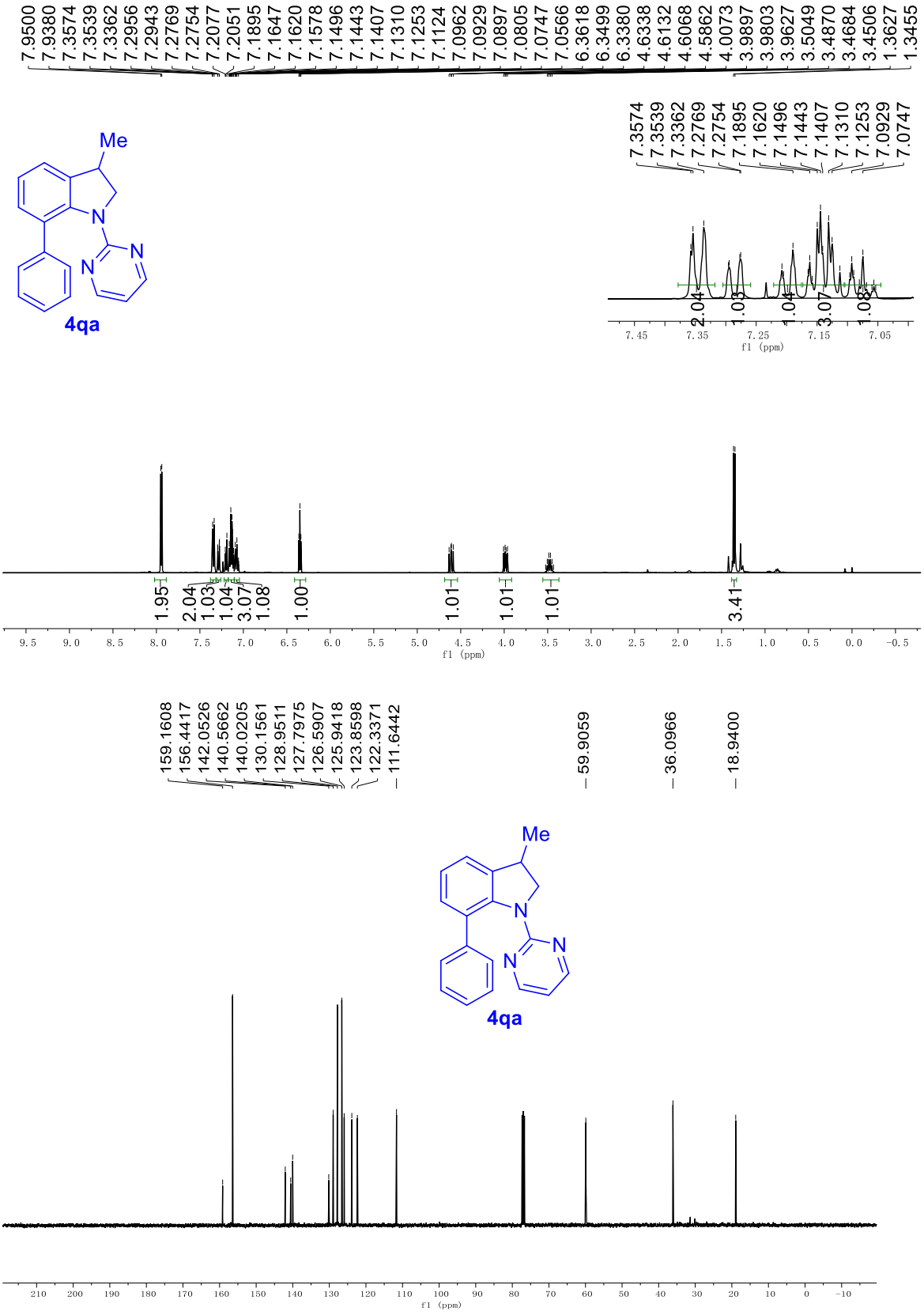
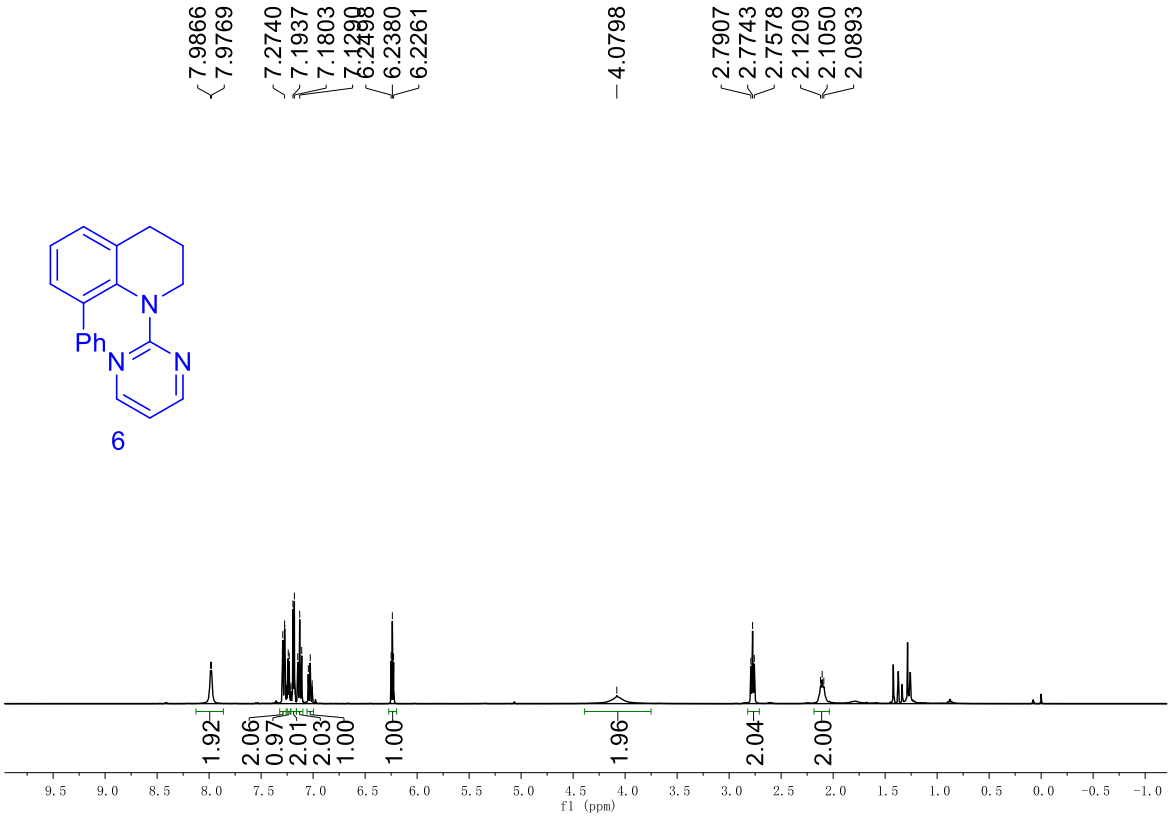
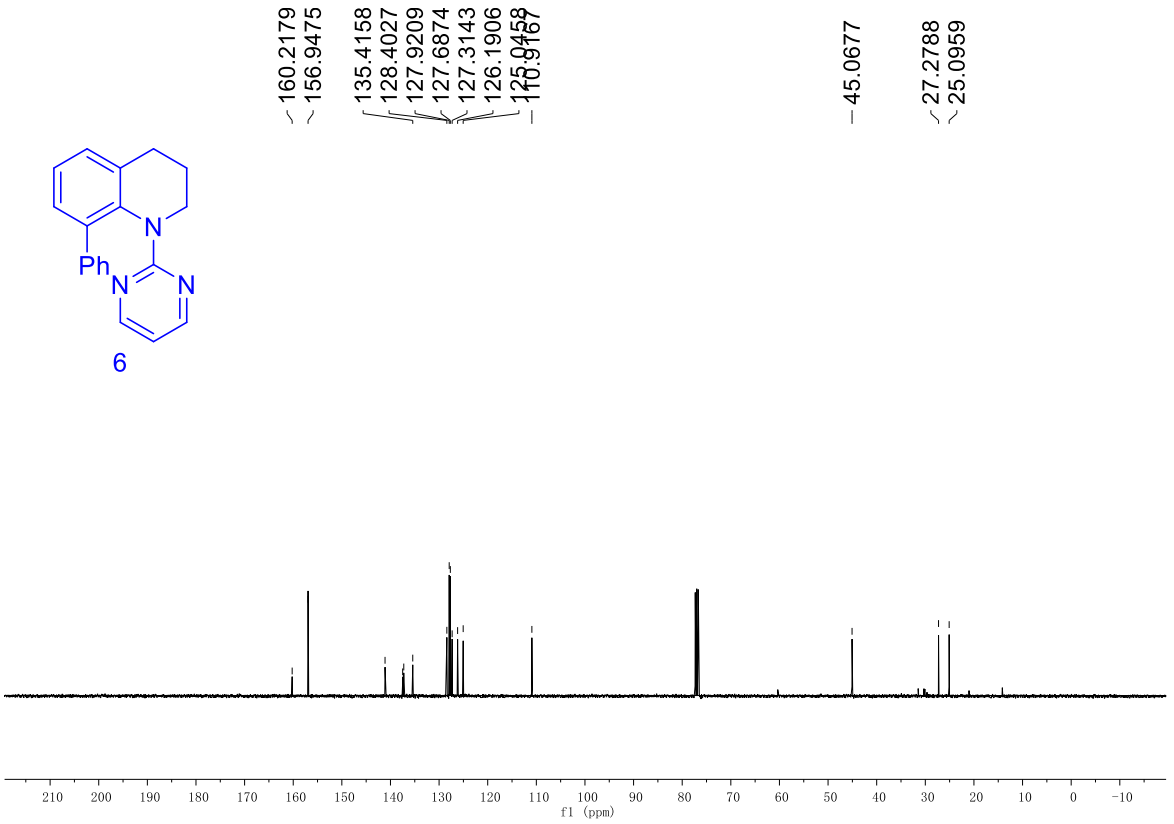
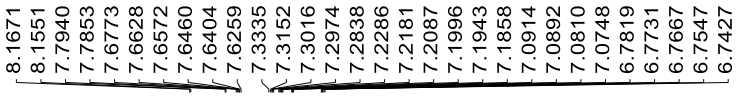
2.06
1.06
1.10
4.17
1.02
1.03
1.05
1.08
3.18
f1 (ppm)

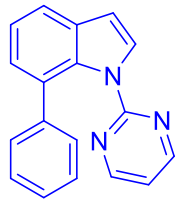

158.6294
156.4033
142.2805
139.4487
133.6793
130.6409
128.7808
127.8125
126.4151
125.8802
124.0357
123.7007
111.6766
59.4253
36.7376
21.0866
Me
N
N
N
4pa
f1 (ppm)


7.9500
7.9380
7.3574
7.3539
7.3362
7.2956
7.2943
7.2769
7.2754
7.2077
7.2051
7.1895
7.1647
7.1620
7.1578
7.1496
7.1443
7.1407
7.1310
7.1253
7.1124
7.0962
7.0929
7.0897
7.0805
7.0747
7.0566
6.3618
6.3499
6.3380
4.6338
4.6132
4.6068
4.5862
4.0073
3.9897
3.9803
3.9627
3.5049
3.4870
3.4684
3.4506
1.3627
1.3455
Me
N
N
N
4qa
7.3574
7.3539
7.3362
7.2769
7.2754
7.1895
7.1620
7.1496
7.1443
7.1407
7.1310
7.1253
7.0929
7.0747
2.04
1.03
1.04
3.07
1.08
7.45
7.35
7.25
7.15
7.05
f1 (ppm)
1.95
2.04
1.03
1.04
3.07
1.08
1.00
1.01
1.01
1.01
3.41
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)
159.1608
156.4417
142.0526
140.5662
140.0205
130.1561
128.9511
127.7975
126.5907
125.9418
123.8598
122.3371
111.6442
59.9059
36.0966
18.9400
Me
N
N
N
4qa
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

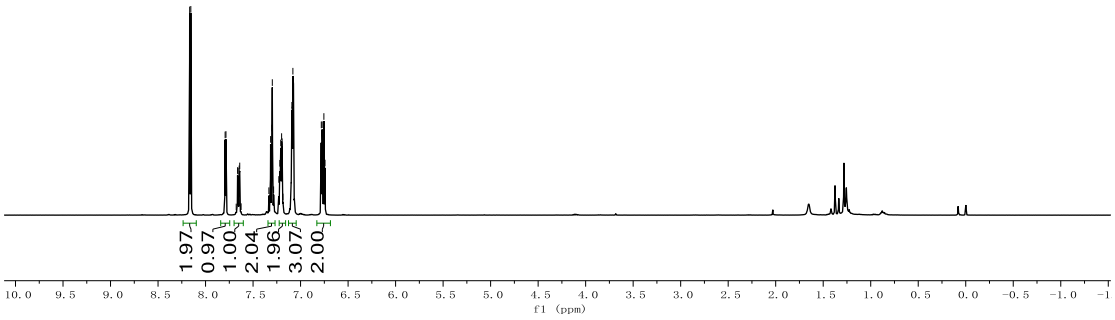

7.9866
7.9769
7.2740
7.1937
7.1803
7.1290
6.2498
6.2380
6.2261
4.0798
2.7907
2.7743
2.7578
2.1209
2.1050
2.0893
N
Ph
N
N
6
1.92
2.06
0.97
2.01
2.03
1.00
1.00
1.96
2.04
2.00
f1 (ppm)


160.2179
156.9475
135.4158
128.4027
127.9209
127.6874
127.3143
126.1906
125.0458
110.9167
45.0677
27.2788
25.0959
N
Ph
N
N
6
f1 (ppm)

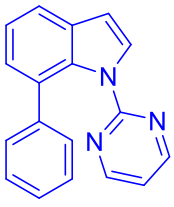

8.1671
8.1551
7.7940
7.7853
7.6773
7.6628
7.6572
7.6460
7.6404
7.6259
7.3335
7.3152
7.3016
7.2974
7.2838
7.2286
7.2181
7.2087
7.1996
7.1943
7.1858
7.0914
7.0892
7.0810
7.0748
6.7819
6.7731
6.7667
6.7547
6.7427


N
N
N

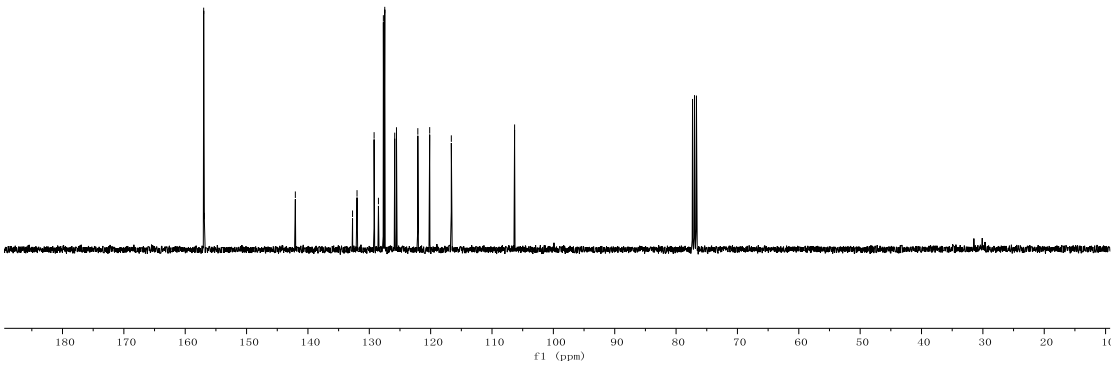
7

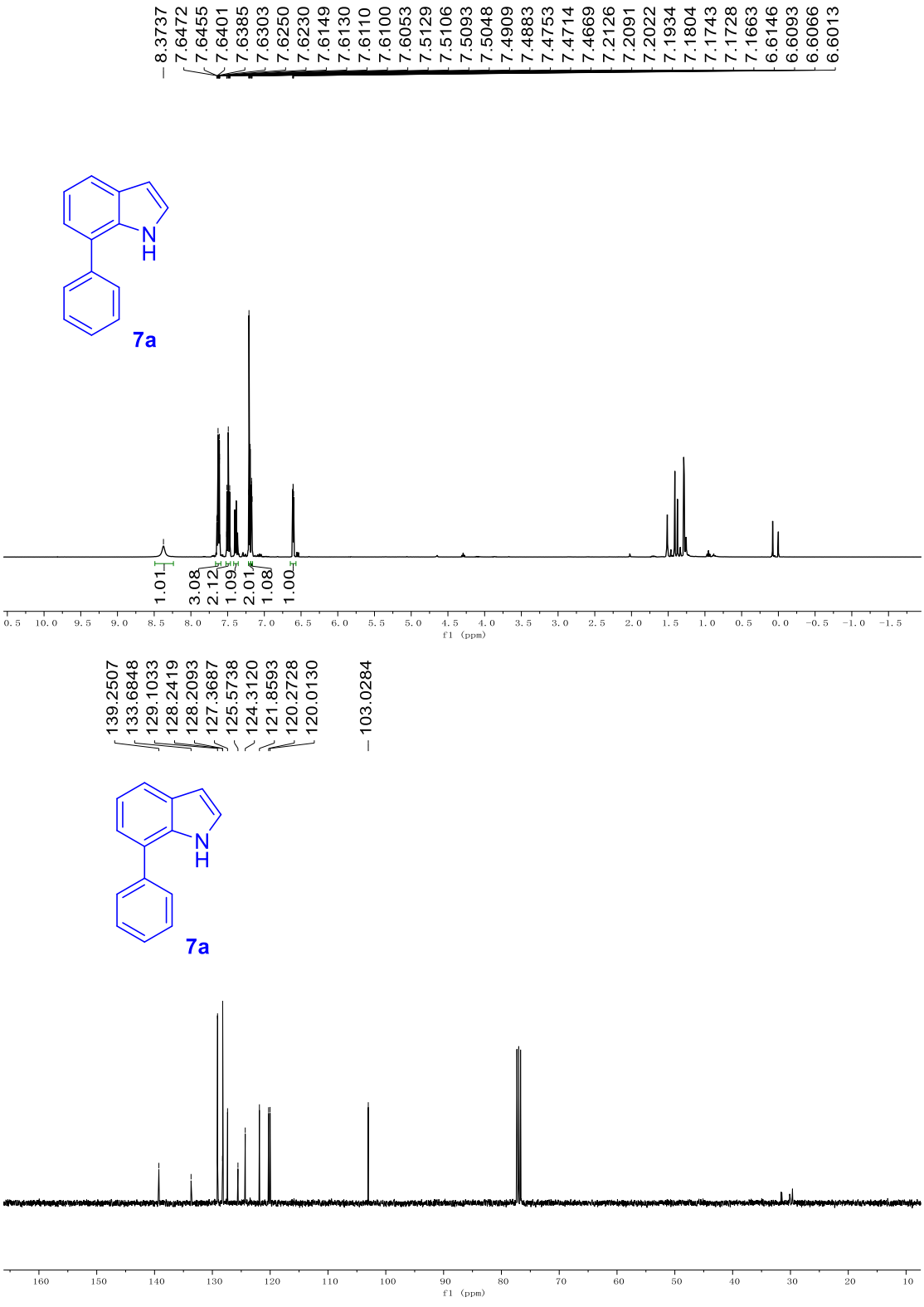

1.97
0.97
1.00
2.04
1.96
3.07
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

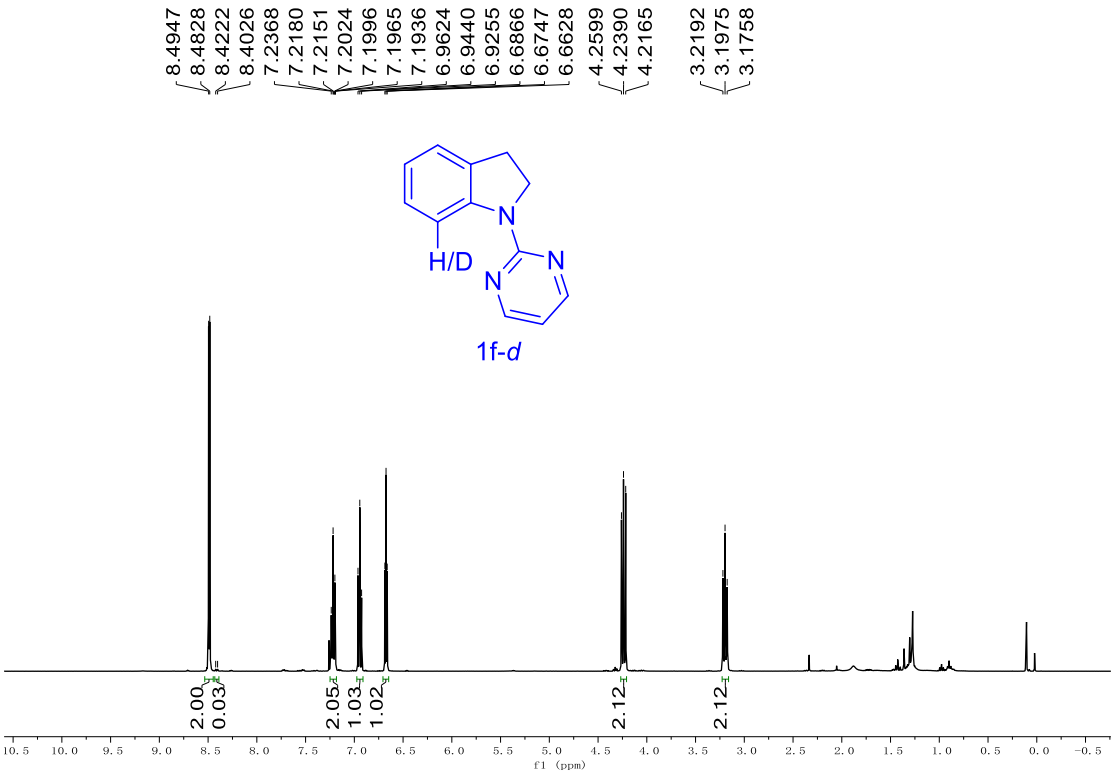

156.9907
156.8748
142.0518
132.7307
131.9976
129.2152
128.5094
127.7072
127.4784
125.8570
125.5692
122.0902
120.1579
116.6287
106.3197


N
N
N

7


180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)


8.3737
7.6472
7.6455
7.6401
7.6385
7.6303
7.6250
7.6230
7.6149
7.6130
7.6110
7.6100
7.6053
7.5129
7.5106
7.5093
7.5048
7.4909
7.4883
7.4753
7.4714
7.4669
7.2126
7.2091
7.2022
7.1934
7.1804
7.1743
7.1728
7.1663
6.6146
6.6093
6.6066
6.6013
N
H
7a
1.01
3.08
2.12
1.09
2.01
1.08
1.00
f1 (ppm)
139.2507
133.6848
129.1033
128.2419
128.2093
127.3687
125.5738
124.3120
121.8593
120.2728
120.0130
103.0284
N
H
7a
f1 (ppm)


8.4947
8.4828
8.4222
8.4026
7.2368
7.2180
7.2151
7.2024
7.1996
7.1965
7.1936
6.9624
6.9440
6.9255
6.6866
6.6747
6.6628
4.2599
4.2390
4.2165
3.2192
3.1975
3.1758
H/D
N
N
N
1f-d
2.00
0.03
2.05
1.03
1.02
2.12
2.12
f1 (ppm)