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Supporting Information

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Indole Synthesis by Rhodium(III)-Catalyzed Hydrazine-Directed C–H Activation: Redox-Neutral and Traceless by N–N Bond Cleavage**

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Supporting Information

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1 General information

Unless otherwise noted, all reactions were carried out under an atmosphere of argon in flame-dried glassware. Reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated. The solvents used were purified by distillation over the drying agents indicated in parentheses and were transferred under argon.

Commercially available chemicals were obtained from Acros Organics, Aldrich Chemical Co., Strem Chemicals, Alfa Aesar, ABCR and TCI Europe and used as received unless otherwise stated.

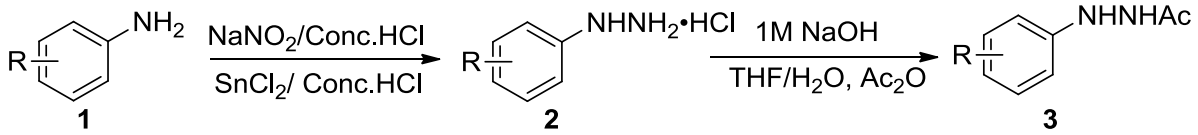
Analytical thin layer chromatography was performed on Polygram SIL G/UV_{254} plates. Flash chromatography was either performed on Merck silica gel (40-63 mesh) by standard technique eluting with solvents as indicated.

GC-MS Spectra were recorded on an Agilent Technologies 7890A GC-system with an Agilent 5975C VL MSD or an Agilent 5975 inert Mass Selective Detector (EI) and a HP-5MS column (0.25 mm × 30 m, Film: 0.25 μm). The major signals are quoted in m/z with the relative intensity in parentheses.

^{1}H and ^{13}C-NMR spectra were recorded on a Bruker AV 300 or AV 400, Varian 500 MHz INOVA or Varian Unity plus 600 in solvents as indicate. Chemical shifts (δ) are given in ppm relative to TMS. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm). ESI mass spectra were recorded on a Bruker Daltonics MicroTof. No attempts were made to optimize yields for substrate synthesis.

2 Synthesis of 2-acetyl-1-arylhydrazines and diaryl substituted alkynes

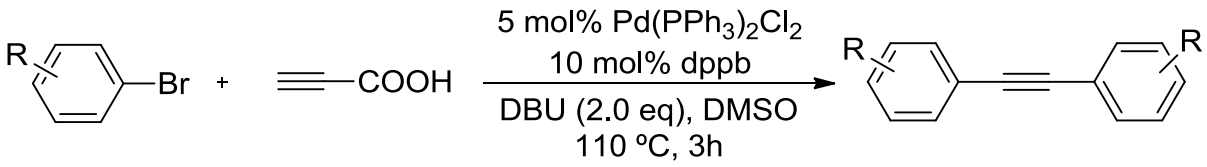
2.1 General procedure for the synthesis of 2-acetyl-1-arylhydrazines [1]



Following a literature procedure,[1] to a suspension of aryl amine **1** (20 mmol) in water (65 mL) and conc. HCl (25 mL) cooled down to 0-5 °C, sodium nitrite (1.55 g, 22 mmol) in water (15 mL) was added dropwise. It was kept under stirring at the same temperature for 45 minutes and, subsequently, a solution of $SnCl_2$ (40 mmol) in conc. HCl (10 mL) was added. Once the addition was performed, the temperature was allowed to slowly increase until achieving room temperature, and the suspension was filtered. The remaining solid was washed with saturated brine and diethyl ether and, subsequently, it was suspended in diethyl ether with stirring during a few minutes. It was filtered and dried resulting in a crude brown solid **2**, which was used directly in the following synthesis step.

The arylhydrazine hydrochloride salt **2** (13 mmol) was dissolved in 1*N* NaOH (25 mL) and THF (6 mL). With stirring, acetic anhydride (1.3 g, 13 mmol) was added dropwise, and after stirring for 30 min the mixture was extracted with EtOAc (3x20 mL). The combined organic solvent was evaporated to afford a solid residue. Recrystallization from a mixture of pentane and dichloromethane (1:1) gave 2-acetyl-1-arylhydrazine **3**.

2.2 General procedure for the synthesis of diaryl substituted alkynes [2]

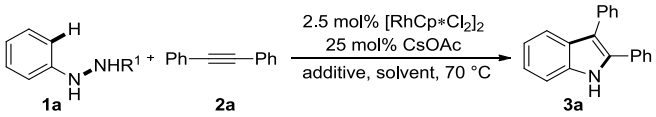


Following a literature procedure,[2] $Pd(PPh_3)_2Cl_2$ (105 mg, 0.15 mmol), 1,4-bis(diphenylphosphino)butane (128 mg, 0.30 mmol), aryl halides (6.00 mmol), and propiolic acid (212 mg, 3.0 mmol) were combined with DBU (913 mg, 6.0 mmol) in a small round-bottomed flask. DMSO (15.0 mL) was added, and the flask was sealed with a septum. The resulting mixture was placed in an oil bath at 80 °C for 3 h. The reaction was poured into 25 mL of saturated aqueous ammonium chloride and extracted with EtOAc (4x20 mL). The combined EtOAc extracts were washed with brine (90 mL), dried over $MgSO_4$, and filtered. The solvent was removed under vacuum, and the resulting crude product was purified by flash chromatography on silica gel. The product was eluted with 5% ethyl acetate in hexane.

3 Rh(III)-catalyzed hydrazine-directed redox-neutral C-H annulation to diverse indoles

3.1 Optimization of the Rh(III)-catalyzed hydrazine-directed redox-neutral C−H annulation to indole

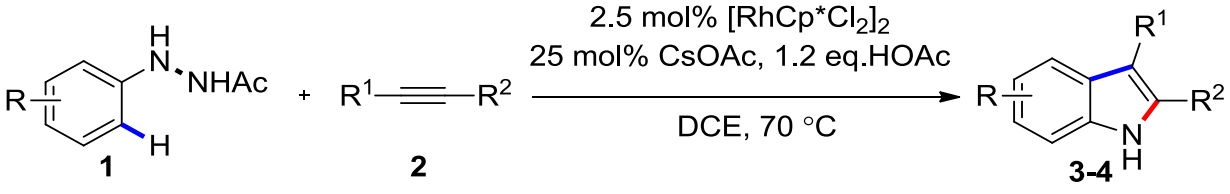
Table S1. Optimization of the Rh(III)-catalyzed hydrazine-directed redox-neutral C−H annulation to indole.[a]



Entry	R^1	Additive	Solvent	Yield [%][b]
1	H	---	DCE	n.r
2	Ac	---	DCE	12
3	Piv	---	DCE	n.r
4[c]	Ac	---	DCE	n.r
5	**Ac**	**HOAc**	**DCE**	**88**
6	Ac	TfOH	DCE	trace
7	Ac	TFA	DCE	41
8	Ac	HOAc	dioxane	n.r
9	Ac	HOAc	methanol	56
10	Ac	HOAc	$CHCl_3$	58
11	Ac	HOAc	toluene	n.r
12[d]	Ac	HOAc	DCE	73
13[e]	Ac	HOAc	DCE	62
14[f]	Ac	---	DCE	89
15[g]	Ac	HOAc	DCE	77
16[h]	Ac	HOAc	DCE	28

[a] Reactions were carried out by using $[RhCp^*Cl_2]_2$ (2.5 mol%), CsOAc (25 mol%), additive (0-1.2 equiv.), hydrazines (0.2 mmol), and diphenylacetylene (0.22 mmol) in solvent (1 mL) for 16 h at 70 °C under an argon atmosphere. [b] Isolated yield. [c] N'-methyl-N'-phenylacetohydrazide was used as the substrate. [d] NaOAc (25 mol%) was used as the base; [e] CsOPiv (25 mol%) was used as the base; [f] $RhCp^*(OAc)_2$ (5 mol%) was used as the catalyst; [g] 12 h; [h] room temperature. n.r = no reaction.

3.2 General procedure for the Rh(III)-catalyzed hydrazine-directed redox-neutral C-H annulation



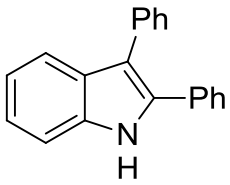
To a 50 mL screw-capped vial equipped with a 10 x 5 mm spinvane-shaped Teflon stirrer bar were charged with 2-acetyl-1-arylhydrazine (0.2 mmol), alkyne **2** (0.22 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol%), CsOAc (25 mol%), acetic acid (1.2 equiv.), and 1,2-dichloroethane (1.5 mL) under the Argon atmosphere. The resulting mixture was sealed with a Teflon-lined cap and

stirred at 70 °C for 16 h in an oil bath. The reaction was cooled to room temperature, filtered through a plug of celite and washed with dichloromethane (15 mL). The desired product was obtained by column chromatography using an appropriate eluent.

3.3 Procedure for the gram scale preparation of 2,3-Diphenyl-1H-indole (3a)

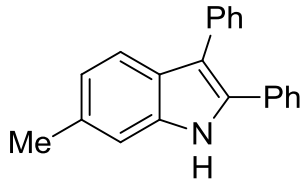
To a 150 mL screw-capped vial equipped with a 10 x 5 mm spinvane-shaped Teflon stirrer bar were charged with 2-acetyl-1-phenylhydrazine (1.5 g, 10 mmol), alkyne **2** (1.96 g, 11 mmol), $[Cp^*RhCl_2]_2$ (155 mg, 0.25 mmol), CsOAc (480 mg, 2.5 mmol), acetic acid (720 µL, 12 mmol), and 1,2-dichloroethane (50 mL) under the Argon atmosphere. The resulting mixture was sealed with a Teflon-lined cap and stirred at 70 °C for 16 h in an oil bath. The reaction was cooled to room temperature, filtered through a plug of celite and washed with dichloromethane (25 mL). The desired product was obtained by column chromatography (pentane/ethyl acetate10:1). 2,3-Diphenyl-1H-indole **(3a)** was formed in 86% yield (2.32 g).

2,3-Diphenyl-1H-indole (3a)



Following the general procedure, the C-H activation/cyclization reaction was carried out with 2-acetyl-1-phenylhydrazine (30 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), diphenylacetylene (39.15 mg, 0.22 mmol), CsOAc (9.6 mg, 0.05 mmol), HOAc (14.4 µL, 0.24 mmol) and 1,2-dichloroethane (1 mL) at 70 ºC for 16 h. 2,3-Diphenyl-1H-indole **(3a)** was formed in 88% yield. **R_f** (pentane/ethyl acetate 10:1): 0.25; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.24 (s, 1H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.54 – 7.21 (m, 12H), 7.17 (t, *J* = 7.5 Hz, 1H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 136.01, 135.17, 134.21, 132.83, 132.80, 130.29, 128.88, 128.83, 128.66, 128.30, 127.84, 126.37, 122.85, 120.57, 119.84, 111.01. **HRMS**: m/z (ESI) calcd for $[C_{20}H_{16}N]^+$: 270.1283, found: 270.1277.

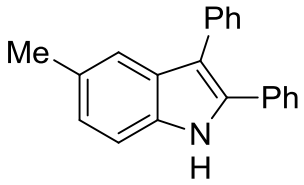
6-Methyl-2,3-diphenyl-1*H*-indole (3b)



Following the general procedure, the C-H activation/cyclization reaction was carried out with 2-acetyl-1-(3-methylphenyl)hydrazine (32.8 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), diphenylacetylene (39.15 mg, 0.22 mmol), CsOAc (9.6 mg, 0.05 mmol), HOAc (14.4 µL, 0.24 mmol) and 1,2-dichloroethane (1 mL) at 70 ºC for 16 h. 6-Methyl-2,3-diphenyl-1*H*-indole (**3b**) was formed in 93% yield. R_f (pentane/ethyl acetate = 10:1): 0.30; **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 8.09 (s, 1H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.52 –

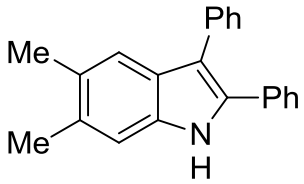
7.27 (m, 10H), 7.22 (s, 1H), 7.02 (dd, *J* = 8.2, 0.9 Hz, 1H), 2.52 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 136.35, 135.26, 133.38, 132.88, 132.60, 130.09, 128.62, 128.46, 128.04, 127.46, 126.69, 126.12, 122.18, 119.36, 114.94, 110.80, 21.72. **HRMS**: m/z (ESI) calcd for $C_{21}H_{17}NNa$ $(M + Na)^+$ 306.1259, found 306.1253.

5-Methyl-2,3-diphenyl-1H-indole (3c)



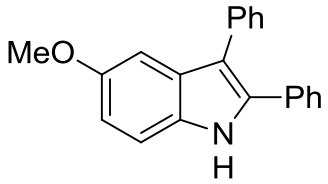
Following the general procedure, the C-H activation/cyclization reaction was carried out with 2-acetyl-1-(4-methylphenyl)hydrazine (32.8 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), diphenylacetylene (39.15 mg, 0.22 mmol), CsOAc (9.6 mg, 0.05 mmol), HOAc (14.4 μL, 0.24 mmol) and 1,2-dichloroethane (1 mL) at 70 ºC for 16 h. 5-Methyl-2,3-diphenyl-1H-indole (**3c**) was formed in 91% yield. **R_f** (pentane/ethyl acetate 10:1): 0.25; **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 8.14 (s, 1H), 7.56 – 7.23 (m, 12H), 7.09 (d, *J* = 8.2 Hz, 1H), 2.46 (s, 3H); **^{13}C NMR (75 MHz, $CDCl_3$):**δ 135.37, 134.33, 132.94, 130.32, 129.87, 129.13, 128.78, 128.64, 128.22, 127.70, 126.29, 124.43, 119.36, 114.77, 110.69, 21.70. **HRMS**: m/z (ESI) calcd for $[C_{21}H_{17}N + Na]^+$: 306.1259, found: 306.1253.

5,6-Dimethyl-2,3-diphenyl-1*H*-indole (3d)



Following the general procedure, the C-H activation/cyclization reaction was carried out with 2-acetyl-1-(3,4-dimethylphenyl)hydrazine (35.6 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), diphenylacetylene (39.15 mg, 0.22 mmol), CsOAc (9.6 mg, 0.05 mmol), HOAc (14.4 μL, 0.24 mmol) and 1,2-dichloroethane (1 mL) at 70 ºC for 16 h. 5,6-Dimethyl-2,3-diphenyl-1*H*-indole (**3d**) was formed in 90% yield. **R_f** (pentane/ethyl acetate = 10:1): 0.30; **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 8.08 (s, 1H), 7.58 – 7.32 (m, 11H), 7.26 (s, 1H), 2.47 (s, 3H), 2.42 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 135.48, 134.91, 133.24, 133.00, 131.84, 130.15, 129.12, 128.58, 128.45, 127.98, 127.34, 127.23, 126.05, 119.64, 114.58, 111.25, 20.44, 20.10. **HRMS:** m/z (ESI) calcd for $C_{21}H_{17}NONa$ $(M + Na)^+$ 322.1208, found 322.1202.

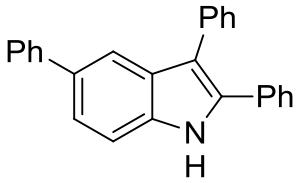
5-Methoxy-2,3-diphenyl-1*H*-indole (3e)



Following the general procedure, the C-H activation/cyclization reaction was carried out with 2-acetyl-1-(4-

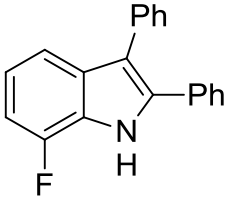
methoxyphenyl)hydrazine (36 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), diphenylacetylene (39.15 mg, 0.22 mmol), CsOAc (9.6 mg, 0.05 mmol), HOAc (14.4 μL, 0.24 mmol) and 1,2-dichloroethane (1 mL) at 70 ºC for 16 h. 5-Methoxy-2,3-diphenyl-1*H*-indole (**3e**) was formed in 92% yield. $\mathbf{R_f}$ (pentane/ethyl acetate = 10:1): 0.30; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.15 (s, 1H), 7.48 – 7.37 (m, 6H), 7.36 – 7.28 (m, 5H), 7.13 (d, *J* = 2.4 Hz, 1H), 6.92 (dd, *J* = 8.7, 2.4 Hz, 1H), 3.83 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 154.76, 135.18, 134.92, 132.70, 131.02, 130.06, 129.14, 128.63, 128.58, 128.04, 127.59, 126.16, 114.91, 112.99, 111.67, 101.18, 55.91. **HRMS**: m/z (ESI) calcd for $C_{21}H_{17}NONa$ $(M + Na)^+$ 322.1208, found 322.1202.

2,3,5-Triphenyl-1H-indole (3f)



Following the general procedure, the C-H activation/cyclization reaction was carried out with 2-acetyl-1-(4-phenylphenyl)hydrazine (45.2 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), diphenylacetylene (39.15 mg, 0.22 mmol), CsOAc (9.6 mg, 0.05 mmol), HOAc (14.4 μL, 0.24 mmol) and 1,2-dichloroethane (1 mL) at 70 ºC for 16 h. 2,3,5-Triphenyl-1H-indole **(3f)** was formed in 86% yield. $\mathbf{R_f}$ (pentane/ethyl acetate 8:1): 0.25; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.16 (s, 1H), 7.79 (s, 1H), 7.55 (dt, *J* = 8.3, 1.8 Hz, 2H), 7.48 – 7.17 (m, 15H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 142.65, 135.58, 135.10, 134.93, 134.28, 132.76, 130.37, 129.46, 128.85, 128.75, 128.28, 127.91, 127.56, 126.53, 126.49, 122.74, 118.34, 115.61, 111.26. **HRMS**: m/z (ESI) calcd for $[C_{26}H_{19}N + Na]^+$: 368.1415, found 368.1405.

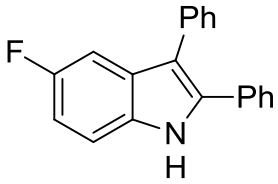
7-Fluoro-2,3-diphenyl-1H-indole (3g)



Following the general procedure, the C-H activation/cyclization reaction was carried out with 2-acetyl-1-(2-fluorophenyl)hydrazine (33.6 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), diphenylacetylene (39.15 mg, 0.22 mmol), CsOAc (9.6 mg, 0.05 mmol), HOAc (14.4 μL, 0.24 mmol) and 1,2-dichloroethane (1 mL) at 70 ºC for 16 h. 7-Fluoro-2,3-diphenyl-1H-indole **(3g)** was formed in 83% yield. $\mathbf{R_f}$ (pentane/ethyl acetate 10:1): 0.30; **^{1}H NMR (300 MHz, $CDCl_3$):** 8.40 (s, 1H), 7.57 – 7.27 (m, 11H), 7.08 (td, *J* = 7.9, 4.9 Hz, 1H), 6.98 (ddd, *J* = 10.9, 7.9, 0.9 Hz, 1H); **^{13}C NMR (75 MHz, $CDCl_3$):** 151.14, 147.91, 135.01, 134.72, 132.49, 132.43, 132.29, 130.21, 128.90, 128.73, 128.34, 128.18, 126.64, 124.41, 124.23,

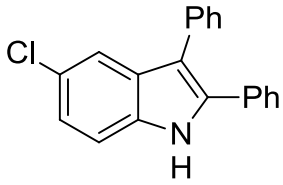
120.75, 120.66, 115.80, 115.76, 115.61, 115.57, 107.69, 107.48. **^{19}F NMR (282.3 MHz, $CDCl_3$):** δ 135.6. **HRMS:** m/z (ESI) calcd for [$C_{20}H_{14}FN$]: 287.1110, found 287.1105.

5-Fluoro-2,3-diphenyl-1*H*-indole (3h)



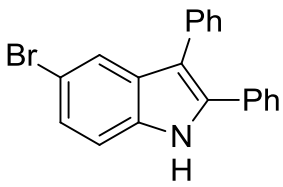
Following the general procedure, the C-H activation/cyclization reaction was carried out with 2-acetyl-1-(4-fluorophenyl)hydrazine (33.6 mg, 0.2 mmol), [Cp*$RhCl_2$]$_2$ (3.1 mg, 0.005 mmol), diphenylacetylene (39.15 mg, 0.22 mmol), CsOAc (9.6 mg, 0.05 mmol), HOAc (14.4 μL, 0.24 mmol) and 1,2-dichloroethane (1 mL) at 70 ºC for 16 h. 5-Fluoro-2,3-diphenyl-1H-indole (**3h**) was formed in 64% yield. **R_f** (pentane/ethyl acetate = 10:1): 0.30; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.22 (s, 1H), 7.54 – 7.28 (m, 12H), 7.00 (td, J = 9.0, 2.5 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 158.46 (d, J_{1F} = 236.34 Hz), 135.84, 134.57, 132.34, 129.91, 129.20 (d, J_{3F} = 9.09 Hz), 128.68 (d, J_{3F} = 11.11 Hz), 128.11, 127.94, 126.41, 115.20, 115.53 (d, J_{4F} = 4.04 Hz), 110.00 (d, J_{2F} = 27.27 Hz), 104.57 (d, J_{2F} = 24.24 Hz). **^{19}F NMR (282.3 MHz, $CDCl_3$):** δ 123.55. **HRMS:** m/z (ESI) calcd for $C_{20}H_{14}NFNa$ (M + Na)$^+$ 310.1108, found 310.1102.

5-Chloro-2,3-diphenyl-1*H*-indole (3i)



Following the general procedure, the C-H activation/cyclization reaction was carried out with 2-acetyl-1-(4-chlorophenyl)hydrazine (36.8 mg, 0.2 mmol), [Cp*$RhCl_2$]$_2$ (3.1 mg, 0.005 mmol), diphenylacetylene (39.15 mg, 0.22 mmol), CsOAc (9.6 mg, 0.05 mmol), HOAc (14.4 μL, 0.24 mmol) and 1,2-dichloroethane (1 mL) at 70 ºC for 16 h. 5-Chloro-2,3-diphenyl-1H-indole (**3i**) was formed in 78% yield. **R_f** (pentane/ethyl acetate = 10:1): 0.30; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.25 (s, 1H), 7.65 (d, J = 2.0 Hz, 1H), 7.49 – 7.28 (m, 11H), 7.20 (dd, J = 8.6, 2.0 Hz, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 135.40, 134.37, 134.20, 132.17, 130.02, 129.92, 128.73, 128.65, 128.10, 128.00, 126.54, 126.16, 122.91, 119.10, 114.78, 111.88. **HRMS:** m/z (ESI) calcd for $C_{20}H_{14}NClNa$ (M + Na)$^+$ 326.0712, found 326.0708.

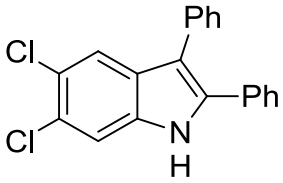
5-Bromo-2,3-diphenyl-1H-indole (3j)



Following the general procedure, the C-H activation/cyclization reaction was carried out with 2-acetyl-1-(4-bromophenyl)hydrazine

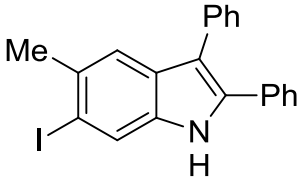
(45.8 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), diphenylacetylene (39.15 mg, 0.22 mmol), CsOAc (9.6 mg, 0.05 mmol), HOAc (14.4 μL, 0.24 mmol) and 1,2-dichloroethane (1 mL) at 70 ºC for 16 h. 5-Bromo-2,3-diphenyl-1H-indole (**3g**) was formed in 92% yield. $\mathbf{R_f}$ (pentane/ethyl acetate 10:1): 0.30; **^{1}H NMR(300 MHz, $CDCl_3$):** δ 8.25 (s, 1H), 7.80 (d, *J* = 1.7 Hz, 1H), 7.46 – 7.37 (m, 6H), 7.37 – 7.27 (m, 6H); **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 135.33, 134.56, 134.43, 132.21, 130.64, 130.16, 128.89, 128.81, 128.24, 128.17, 126.70, 125.59, 122.29, 114.76, 113.82, 112.47, 77.58, 77.16, 76.74. **HRMS**: m/z (ESI) calcd for $[C_{20}H_{14}BrN+Na]^+$: 370.0207, found 370.0197.

5,6-Dichloro-2,3-diphenyl-1*H*-indole (3k)



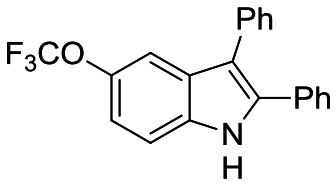
Following the general procedure, the C-H activation/cyclization reaction was carried out with 2-acetyl-1-(3,4-dichlorophenyl)hydrazine (43.6 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), diphenylacetylene (39.15 mg, 0.22 mmol), CsOAc (9.6 mg, 0.05 mmol), HOAc (14.4 μL, 0.24 mmol) and 1,2-dichloroethane (1 mL) at 70 ºC for 16 h. 5,6-Dichloro-2,3-diphenyl-1*H*-indole (**3k**) was formed in 60% yield. R_f (pentane/ethyl acetate = 10:1): 0.30; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.24 (s, 1H), 7.71 (s, 1H), 7.51 (s, 1H), 7.47 – 7.28 (m, 11H). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 135.87, 134.58, 133.92, 131.80, 129.95, 128.82, 128.75, 128.68, 128.26, 128.07, 126.78, 126.28, 124.56, 120.66, 114.69, 112.31. **HRMS**: m/z (ESI) calcd for $C_{20}H_{13}NCl_2Na$ $(M + Na)^+$ 360.0323, found 360.0317.

6-Iodo-5-methyl-2,3-diphenyl-1H-indole (3l)



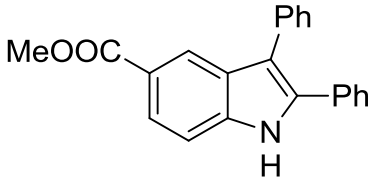
Following the general procedure, the C-H activation/cyclization reaction was carried out with 2-acetyl-1-(4-iodo-3-methylphenyl)hydrazine (58 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), diphenylacetylene (39.15 mg, 0.22 mmol), CsOAc (9.6 mg, 0.05 mmol), HOAc (14.4 μL, 0.24 mmol) and 1,2-dichloroethane (1 mL) at 70 ºC for 16 h. 6-Iodo-5-methyl-2,3-diphenyl-1H-indole (**3l**) was formed in 81% yield. $\mathbf{R_f}$ (pentane/ethyl acetate 8:1): 0.30; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.09 (s, 1H), 7.91 (s, 1H), 7.53 (s, 1H), 7.49 – 7.27 (m, 10H), 2.51 (s, 3H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 135.72, 134.81, 132.45, 132.26, 130.25, 129.55, 128.87, 128.75, 128.23, 128.04, 126.59, 121.01, 119.71, 114.80, 93.84, 28.30. **HRMS**: m/z (ESI) calcd for $[C_{21}H_{16}IN+Na]^+$: 432.0225, found 432.0215.

2,3-Diphenyl-5-(trifluoromethoxy)-1H-indole (3m)



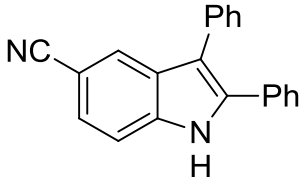
Following the general procedure, the C-H activation/cyclization reaction was carried out with 2-acetyl-1-(3-trifluoromethoxy phenyl)hydrazine (46.8 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), diphenylacetylene (39.15 mg, 0.22 mmol), CsOAc (9.6 mg, 0.05 mmol), HOAc (14.4 μL, 0.24 mmol) and 1,2-dichloroethane (1 mL) at 70 ºC for 16 h. 2,3-Diphenyl-5-(trifluoromethoxy)-1H-indole (**3m**) was formed in 92% yield. $\mathbf{R_f}$ (pentane/ethyl acetate 8:1): 0.25; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.30 (s, 1H), 7.65 (d, *J* = 8.7 Hz, 1H), 7.50 – 7.27 (m, 11H), 7.06 (ddq, *J* = 8.7, 1.9, 0.9 Hz, 1H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 145.59, 145.56, 135.58, 135.52, 134.57, 132.34, 130.21, 128.93, 128.80, 128.23, 128.17, 127.70, 126.73, 122.64, 120.59, 119.25, 115.22, 114.60, 104.04; **^{19}F NMR (282.3 MHz, $CDCl_3$):** δ 57.89. **HRMS**: m/z (ESI) calcd for $[C_{21}H_{14}F_3NO + Na]^+$: 376.0925, found 376.0920.

Methyl 2,3-diphenyl-1H-indole-5-carboxylate (3n)



Following the general procedure, the C-H activation/cyclization reaction was carried out with 2-acetyl-1-(methyl-4-phenyl carboxylate)hydrazine (41.6 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), diphenylacetylene (39.15 mg, 0.22 mmol), CsOAc (9.6 mg, 0.05 mmol), HOAc (14.4 μL, 0.24 mmol) and 1,2-dichloroethane (1 mL) at 70 ºC for 16 h. 5-Methyl 2,3-diphenyl-1H-indole-5-carboxylate (**3n**) was formed in 82% yield. $\mathbf{R_f}$ (pentane/ethyl acetate 5:1): 0.30; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.50 (s, 1H), 8.46 – 8.37 (m, 1H), 7.96 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.51 – 7.27 (m, 11H), 3.91 (s, 3H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 168.23, 138.55, 135.39, 134.36, 132.21, 130.30, 128.94, 128.85, 128.61, 128.26, 128.22, 126.79, 124.27, 122.84, 122.66, 116.29, 110.72, 52.03. **HRMS**: m/z (ESI) calcd for $[C_{22}H_{17}NO_2 + Na]^+$: 350.1157, found 350.1159.

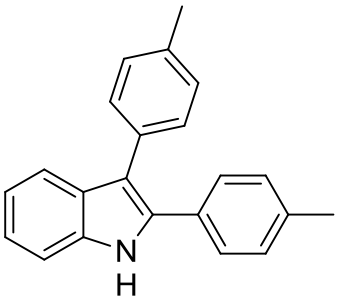
2,3-Diphenyl-1*H*-indole-5-carbonitrile (3o)



Following the general procedure, the C-H activation/cyclization reaction was carried out with 2-acetyl-1-(4-cyanophenyl

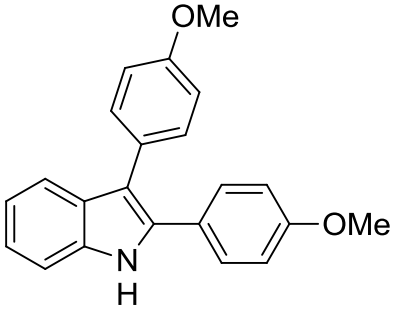
carboxylate)hydrazine (35 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), diphenylacetylene (39.15 mg, 0.22 mmol), CsOAc (9.6 mg, 0.05 mmol), HOAc (14.4 μL, 0.24 mmol) and 1,2-dichloroethane (1 mL) at 70 ºC for 16 h. 2,3-Diphenyl-1*H*-indole-5-carbonitrile (**3o**) was formed in 41% yield. $\mathbf{R_f}$ (pentane/ethyl acetate = 3:1): 0.30; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.60 (s, 1H), 8.00 (s, 1H), 7.53 – 7.30 (m, 12H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 137.58, 136.21, 133.67, 131.65, 130.10, 129.05, 128.99, 128.85, 128.62, 128.31, 127.16, 125.66, 125.57, 120.81, 115.65, 111.89, 103.67. **HRMS**: m/z (ESI) calcd for $C_{21}H_{14}N_2Na$ $(M + Na)^+$ 317.1055, found 326.0707.

2,3-Di-*p*-tolyl-1H-indole (4a)



Following the general procedure, the C-H activation/cyclization reaction was carried out with 2-acetyl-1-phenylhydrazine (30 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), 1,2-di-p-tolylethyne (45.32 mg, 0.22 mmol), CsOAc (9.6 mg, 0.05 mmol), HOAc (14.4 μL, 0.24 mmol) and 1,2-dichloroethane (1 mL) at 70 ºC for 16 h. 2,3-Di-*p*-tolyl-1H-indole (**4a**) was formed in 93% yield. $\mathbf{R_f}$ (pentane/ethyl acetate 10:1): 0.25; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.16 (s, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.45 – 7.28 (m, 5H), 7.27 – 7.07 (m, 6H), 2.39 (s, 3H), 2.35 (s, 3H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 137.60, 135.91, 135.80, 134.14, 132.25, 130.09, 130.02, 129.50, 129.38, 129.01, 128.11, 122.56, 120.37, 119.75, 114.62, 110.92, 21.40. **HRMS:** m/z (ESI) calcd for $[C_{22}H_{19}N]$: 297.1517, found 297.1512.

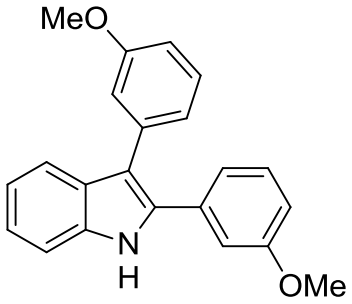
2,3-Bis(4-methoxyphenyl)-1H-indole (4b)



Following the general procedure, the C-H activation/cyclization reaction was carried out with 2-acetyl-1-phenylhydrazine (30 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), 1,2-bis(4-methoxyphenyl)ethyne (52.36 mg, 0.22 mmol), CsOAc (9.6 mg, 0.05 mmol), HOAc (14.4 μL, 0.24 mmol) and 1,2-dichloroethane (1 mL) at 70 ºC for 16 h. 2,3-Bis(4-methoxyphenyl)-1H-indole (**4b**) was formed in 91% yield. $\mathbf{R_f}$ (pentane/ethyl acetate 7:1): 0.25; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.24 (s, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.47 – 7.31 (m, 5H), 7.18 (dt, *J* = 14.9, 7.3 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H), 3.82 (s, 3H); **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 159.17, 158.11, 135.82, 133.86, 131.26, 129.44, 129.08, 127.69, 125.42, 122.37, 120.29, 119.51, 114.22, 114.12, 113.80,

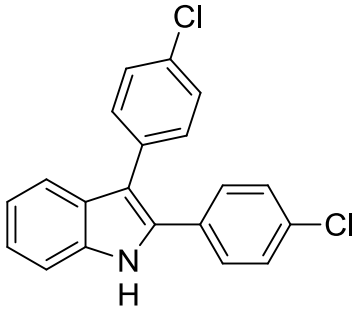
110.87, 55.36, 55.34. **HRMS**: m/z (ESI) calcd for $[C_{22}H_{19}NO_2+Na]^+$: 352.1313, found: 352.1296.

2,3-Bis(3-methoxyphenyl)-1H-indole (4c)



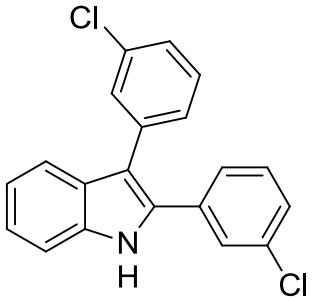
Following the general procedure, the C-H activation/cyclization reaction was carried out with 2-acetyl-1-phenylhydrazine (30 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), 1,2-bis(3-methoxyphenyl)ethyne (52.36 mg, 0.22 mmol), CsOAc (9.6 mg, 0.05 mmol), HOAc (14.4 μL, 0.24 mmol) and 1,2-dichloroethane (1 mL) at 70 ºC for 16 h. 2,3-Bis(3-methoxyphenyl)-1H-indole (**4b**) was formed in 70% yield. $\mathbf{R_f}$ (pentane/ethyl acetate 7:1): 0.25; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.24 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.30 – 7.17 (m, 3H), 7.12 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 7.03 – 6.97 (m, 3H), 6.96 – 6.91 (m, 1H), 6.85 – 6.76 (m, 2H), 3.72 (s, 3H), 3.63 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 159.77, 159.68, 136.54, 135.88, 134.07, 133.97, 129.83, 129.60, 128.80, 122.90, 120.58, 120.49, 119.86, 115.54, 115.20, 113.85, 113.55, 112.29, 111.03, 55.32, 55.25. **HRMS**: m/z (ESI) calcd for $[C_{22}H_{19}NO_2+Na]^+$: 352.1313, found: 352.1308.

2,3-Bis(4-chlorophenyl)-1H-indole (4d)



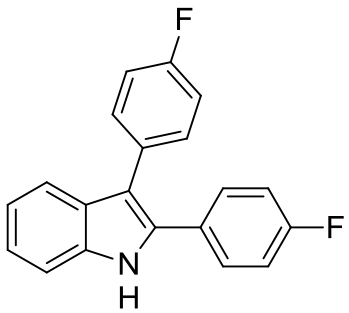
Following the general procedure, the C-H activation/cyclization reaction was carried out with 2-acetyl-1-phenylhydrazine (30 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), 1,2-bis(4-chlorophenyl)ethyne (54.34 mg, 0.22 mmol), CsOAc (9.6 mg, 0.05 mmol), HOAc (14.4 μL, 0.24 mmol) and 1,2-dichloroethane (1 mL) at 100 ºC for 16 h. 2,3-Bis(4-chlorophenyl)-1H-indole (**4d**) was formed in 58% yield. $\mathbf{R_f}$ (pentane/ethyl acetate 9:1): 0.25; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.18 (s, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.36 – 7.17 (m, 9H), 7.18 – 7.06 (m, 1H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 136.05, 134.00, 133.35, 133.20, 132.80, 132.38, 131.43, 130.95, 129.51, 129.23, 129.04, 128.51, 123.31, 120.94, 119.60, 114.38, 111.18. **HRMS**: m/z (ESI) calcd for $[C_{20}H_{13}Cl_2N+Na]^+$: 360.0323, found: 360.0317.

2,3-Bis(3-chlorophenyl)-1H-indole (4e)



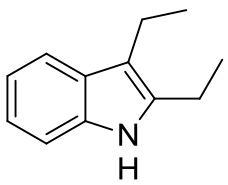
Following the general procedure, the C-H activation/cyclization reaction was carried out with 2-acetyl-1-phenylhydrazine (30 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), 1,2-bis(3-chlorophenyl)ethyne (54.34 mg, 0.22 mmol), CsOAc (9.6 mg, 0.05 mmol), HOAc (14.4 μL, 0.24 mmol) and 1,2-dichloroethane (1 mL) at 70 ºC for 16 h. 2,3-Bis(3-chlorophenyl)-1H-indole (**4e**) was formed in 72% yield. $\mathbf{R_f}$ (pentane/ethyl acetate 8:1): 0.25; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.19 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.46 – 7.34 (m, 3H), 7.31 – 7.10 (m, 8H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 136.64, 136.04, 134.83, 134.51, 134.16, 133.00, 130.17, 130.03, 129.98, 128.45, 128.40, 128.12, 127.92, 126.79, 126.70, 123.48, 121.04, 119.70, 114.59, 111.23. **HRMS**: m/z (ESI) calcd for $[C_{20}H_{13}Cl_2N+Na]^+$: 360.0323, found: 360.0322.

2,3-Bis(4-fluorophenyl)-1H-indole (4f)



Following the general procedure, the C-H activation/cyclization reaction was carried out with 2-acetyl-1-phenylhydrazine (30 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), 1,2-bis(4-fluorophenyl)ethyne (47.08 mg, 0.22 mmol), CsOAc (9.6 mg, 0.05 mmol), HOAc (14.4 μL, 0.24 mmol) and 1,2-dichloroethane (1 mL) at 70 ºC for 16 h. 2,3-Bis(4-fluorophenyl)-1H-indole (**4f**) was formed in 91% yield. $\mathbf{R_f}$ (pentane/ethyl acetate 10:1): 0.25; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.19 (s, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.42 – 7.33 (m, 4H), 7.31 – 7.24 (m, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.15 – 6.98 (m, 4H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 163.71, 162.96, 161.24, 160.53, 135.89, 133.33, 131.72, 131.64, 130.86, 130.83, 130.07, 129.99, 128.76, 128.72, 128.71, 123.03, 120.77, 119.56, 116.11, 115.90, 115.83, 115.62, 114.13, 111.08, 77.48, 77.16, 76.84. **^{19}F NMR (282.3 MHz, $CDCl_3$):** δ 118.3, 116.2. **HRMS**: m/z (ESI) calcd for $[C_{14}H_{20}N]^+$: 202.1596, found: 202.1576.

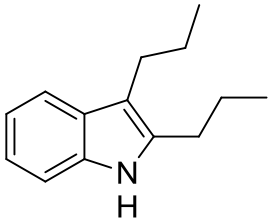
2,3-Diethyl-1H-indole (4g)



Following the general procedure, the C-H activation/cyclization reaction was carried out with 2-acetyl-1-phenylhydrazine (30 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), hex-3-yne (18 mg, 0.22 mmol), CsOAc (9.6 mg, 0.05 mmol), HOAc (14.4 μL, 0.24 mmol) and 1,2-dichloroethane (1 mL) at 100 ºC for 16 h. 2,3-Diethyl-1H-indole (**4g**) was formed in 68% yield. $\mathbf{R_f}$ (pentane/ethyl acetate 12:1): 0.25; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.70 (s, 1H), 7.59

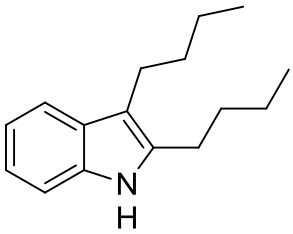
– 7.53 (m, 1H), 7.32 – 7.27 (m, 1H), 7.18 – 7.06 (m, 2H), 2.76 (dq, *J* = 10.4, 7.6 Hz, 4H), 1.28 (dt, *J* = 15.3, 7.6 Hz, 6H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 136.15, 135.35, 128.59, 120.95, 119.07, 118.35, 113.26, 110.40, 77.48, 77.16, 76.84, 19.46, 17.44, 15.92, 14.60. **HRMS**: m/z (ESI) calcd for $[C_{12}H_{16}N]^+$: 174.1283, found: 4174.1251.

2,3-Dipropyl-1H-indole (4h)



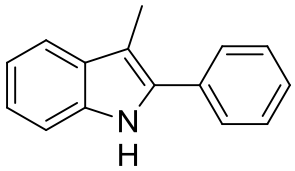
Following the general procedure, the C-H activation/cyclization reaction was carried out with 2-acetyl-1-phenylhydrazine (30 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), oct-4-yne (24.2 mg, 0.22 mmol), CsOAc (9.6 mg, 0.05 mmol), HOAc (14.4 μL, 0.24 mmol) and 1,2-dichloroethane (1 mL) at 100 ºC for 16 h. 2,3-Dipropyl-1H-indole (**4h**) was formed in 86% yield. **R_f** (pentane/ethyl acetate 12:1): 0.25; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.63 (s, 1H), 7.48 – 7.40 (m, 1H), 7.22 – 7.16 (m, 1H), 7.08 – 6.91 (m, 2H), 2.71 – 2.51 (m, 4H), 1.59 (hept, *J* = 7.4 Hz, 4H), 0.90 (q, *J* = 7.4 Hz, 6H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 135.38, 135.33, 128.92, 120.85, 118.95, 118.46, 112.28, 110.31, 33.39, 32.20, 25.97, 24.04, 22.93, 22.66, 14.21, 14.06. HRMS m/z (ESI) calcd for $[C_{14}H_{19}N]$: 201.1517, found: 201.1513.

2,3-Dibutyl-1H-indole (4i)



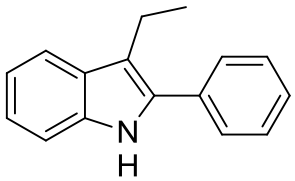
Following the general procedure, the C-H activation/cyclization reaction was carried out with 2-acetyl-1-phenylhydrazine (30 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), dec-5-yne (30.4 mg, 0.22 mmol), CsOAc (9.6 mg, 0.05 mmol), HOAc (14.4 μL, 0.24 mmol) and 1,2-dichloroethane (1 mL) at 100 ºC for 16 h. 2,3-Dibutyl-1H-indole (**4i**) was formed in 80% yield. **R_f** (pentane/ethyl acetate 12:1): 0.25; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.70 (s, 1H), 7.60 – 7.54 (m, 1H), 7.32 – 7.27 (m, 1H), 7.13 (pd, *J* = 7.1, 1.4 Hz, 2H), 2.81 – 2.65 (m, 4H), 1.65 (ddd, *J* = 12.5, 9.2, 6.3 Hz, 4H), 1.44 (dq, *J* = 14.4, 7.4 Hz, 4H), 0.99 (td, *J* = 7.3, 3.4 Hz, 6H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 135.38, 135.33, 128.92, 120.85, 118.95, 118.46, 112.28, 110.31, 33.39, 32.20, 25.97, 24.04, 22.93, 22.66, 14.21, 14.06. HRMS m/z (ESI) calcd for $[C_{16}H_{24}N]^+$: 230.1909, found: 230.1856.

3-Methyl-2-phenyl-1H-indole (4j)[3]



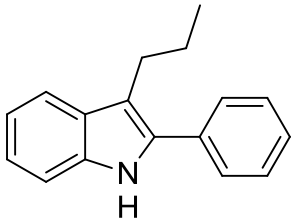
Following the general procedure, the C-H activation/cyclization reaction was carried out with 2-acetyl-1-phenylhydrazine (30 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), prop-1-yn-1-ylbenzene (25.5 mg, 0.22 mmol), CsOAc (9.6 mg, 0.05 mmol), HOAc (14.4 μL, 0.24 mmol) and 1,2-dichloroethane (1 mL) at 100 ºC for 16 h. 3-Methyl-2-phenyl-1H-indole (**4j**) was formed in 49% yield. $\mathbf{R_f}$ (pentane/ethyl acetate 12:1): 0.25; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.03 (s, 1H), 7.64 – 7.57 (m, 3H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.40 – 7.33 (m, 2H), 7.22 (td, *J* = 8.1, 7.6, 1.3 Hz, 1H), 7.15 (td, *J* = 7.5, 7.1, 1.1 Hz, 1H), 2.48 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 135.94, 134.14, 133.47, 130.14, 128.95, 127.86, 127.45, 122.45, 119.65, 119.11, 110.78, 108.84, 9.80. HRMS m/z (ESI) calcd for $[C_{15}H_{14}N]^+$: 208.1126, found: 208.1076.

3-Ethyl-2-phenyl-1H-indole (4k)



Following the general procedure, the C-H activation/cyclization reaction was carried out with 2-acetyl-1-phenylhydrazine (30 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), but-1-yn-1-ylbenzene (28.6 mg, 0.22 mmol), CsOAc (9.6 mg, 0.05 mmol), HOAc (14.4 μL, 0.24 mmol) and 1,2-dichloroethane (1 mL) at 100 ºC for 16 h. 3-Ethyl-2-phenyl-1H-indole (**4k**) was formed in 58% yield. $\mathbf{R_f}$ (pentane/ethyl acetate 12:1): 0.25; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.99 (s, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.57 (dt, *J* = 8.0, 1.7 Hz, 2H), 7.49 (td, *J* = 6.8, 6.3, 1.7 Hz, 2H), 7.38 (tt, *J* = 6.8, 1.4 Hz, 2H), 7.19 (dtd, *J* = 19.3, 7.1, 1.2 Hz, 2H), 2.94 (q, *J* = 7.5 Hz, 2H), 1.37 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 136.08, 133.82, 133.50, 129.14, 128.96, 127.99, 127.61, 122.34, 119.59, 119.33, 115.56, 110.93, 17.93, 15.77. HRMS m/z (ESI) calcd for $[C_{16}H_{16}N]^+$: 222.1283, found: 222.1255.

2-Phenyl-3-propyl-1H-indole (4l)

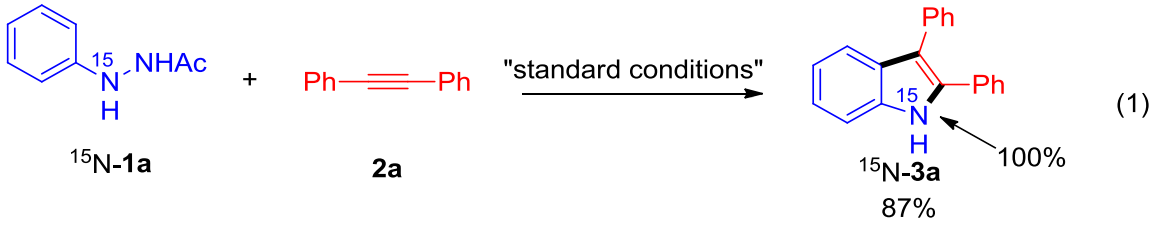


Following the general procedure, the C-H activation/cyclization reaction was carried out with 2-acetyl-1-phenylhydrazine (30 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), pent-1-yn-1-ylbenzene (31.7 mg, 0.22 mmol), CsOAc (9.6 mg, 0.05 mmol), HOAc (14.4 μL, 0.24 mmol) and 1,2-dichloroethane (1 mL) at 100 ºC for 16 h. 2-Phenyl-3-propyl-1H-indole (**4l**) was formed in 77% yield. $\mathbf{R_f}$ (pentane/ethyl acetate 12:1): 0.25; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.99 (s, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.60 – 7.55 (m,

2H), 7.49 (td, *J* = 7.0, 1.7 Hz, 2H), 7.38 (dddd, *J* = 8.7, 4.0, 2.9, 1.3 Hz, 2H), 7.22 (ddd, *J* = 8.1, 7.1, 1.3 Hz, 1H), 7.16 (ddd, *J* = 8.0, 7.1, 1.1 Hz, 1H), 2.94 – 2.85 (m, 2H), 1.78 (dq, *J* = 15.0, 7.4 Hz, 2H), 1.02 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 136.01, 134.24, 133.62, 129.48, 128.93, 128.08, 127.59, 122.28, 119.56, 119.49, 114.11, 110.86, 26.85, 24.39, 14.58. **HRMS**: m/z (ESI) calcd for [$C_{17}H_{17}N$]: 235.1361, found: 235.1356.

4 Mechanistic Experiments

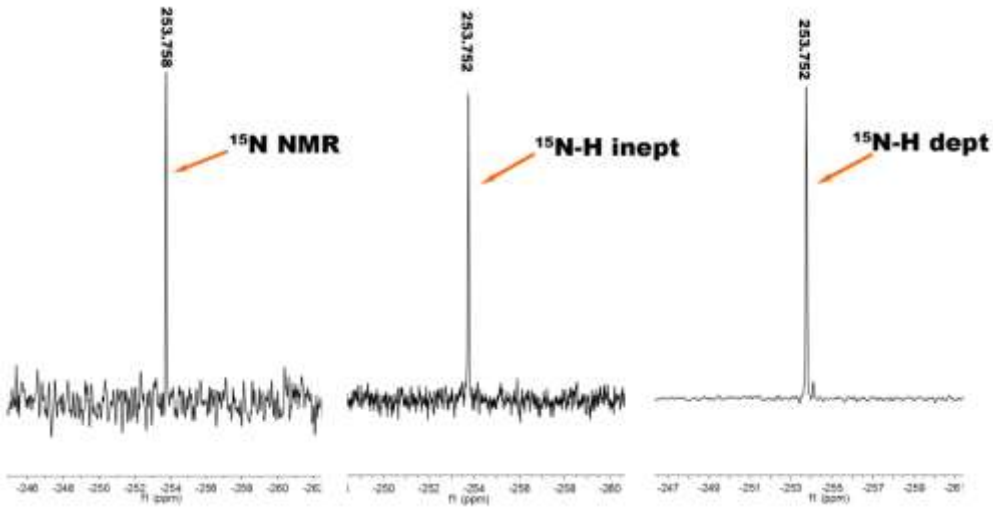
4.1 Isotope-labeled experiments



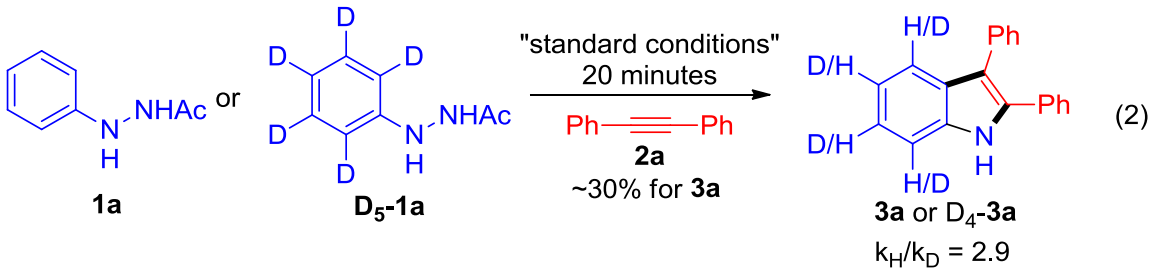
^{15}N-**1a** **2a** ^{15}N-**3a** 87% (1)

To a 10 mL Schlenk tube was added [$Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), CsOAc (9.6 mg, 25.0 mol %), ^{15}N-**1a** (30.2 mg, 0.20 mmol), **2a** (40.0 mg, 0.22 mmol) and the tube was purged with Ar for three times, followed by addition of AcOH (14.4 μL, 1.2 equiv), DCE (1.0 mL). The formed mixture was stirred at 70 ºC under Ar for 16 h as monitored by TLC. The solution was then cooled to rt, and the solvent was removed under vaccum directly. The crude product was purified by column chromatography on silica gel (eluent: pentane/ethyl acetate = 10:1) to afford 47.0 mg (87%) of ^{15}N-**3a**. The ratio of **3a** and ^{15}N-**3a** was determined by ^{15}N NMR and HRMS. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.08 (d, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.40 – 7.11 (m, 12H), 7.11 – 7.01 (m, 1H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 135.97, 135.77, 135.07, 134.14, 133.95, 132.71, 130.15, 128.65, 128.49, 128.16, 127.66, 126.21, 122.70, 122.67, 120.41, 119.69, 115.04, 110.87. **^{15}N NMR:** δ -253.70. **HRMS:** m/z (ESI) calcd for $C_{20}H_{15}{}^{15}NNa$ $(M + Na)^+$ 293.1073, found 293.1067.

Product	m/z	Res	S/N	I	FWHM
3a+Na	292.1097	-	-	-	-
^{15}N-**3a**+Na	293.1067	7522	96.1	5341	0.0390



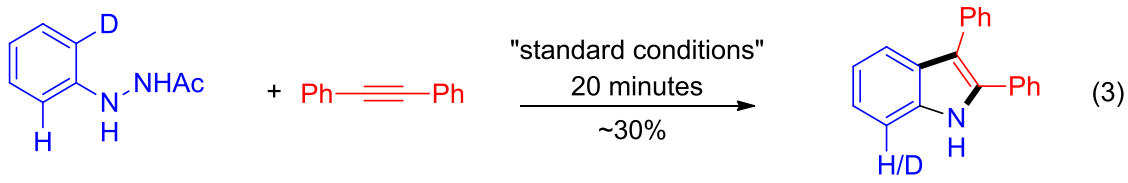
4.2 Deuteration experiments



(2)

$[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), CsOAc (9.6 mg, 25.0 mol %), AcOH (14.4 μL, 1.2 equiv), **1a** (30.0 mg, 0.20 mmol) or D5-**1a** (31.0 mg, 0.20 mmol), **2a** (40.0 mg, 0.22 mmol) and DCE (1.0 mL) were added in two separated Schlenk tubes. They were stirred at 70 ºC under Ar for 30 minutes, then immediately quenched with EtOAc at the same time. Then two reaction mixtures were combined and the volatiles were removed under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: pentane/ethyl acetate = 10:1) to afford 24.0 mg of **3a** and **D4-3a**. The ratio of **3a** and **D4-3a** was determined by HRMS to be 2.9 : 1.

Product	m/z	Res	S/N	I	FWHM
3a+Na	292.1103	7897	433.8	23914	0.0370
D4-**3a**+Na	296.1331	7607	149.5	8410	0.0389



D_1-1a **2a** **3a & D_1-3a**

k_H/k_D = 2.3

$[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), CsOAc (9.6 mg, 25.0 mol %), AcOH (14.4 μL, 1.2 equiv), D1-**1a** (30.2 mg, 0.20 mmol), **2a** (40.0 mg, 0.22 mmol) and DCE (1.0 mL) were added in a Schlenk tube. It was stirred at 70 ºC under Ar for 30 minutes, then immediately quenched with EtOAc. Then the crude product was purified by column chromatography on silica gel (eluent: pentane/ethyl acetate = 10:1) to afford 16.0 mg of **3a** and **D1-3a**. The ratio of **3a** and **D4-3a** was determined by HRMS to be 2.3 : 1.

Product	m/z	Res	S/N	I	FWHM
3a+Na	292.1097	7868	701.2	28195	0.0371
D1-**3a**+Na	293.1159	7599	303.1	12248	0.0386

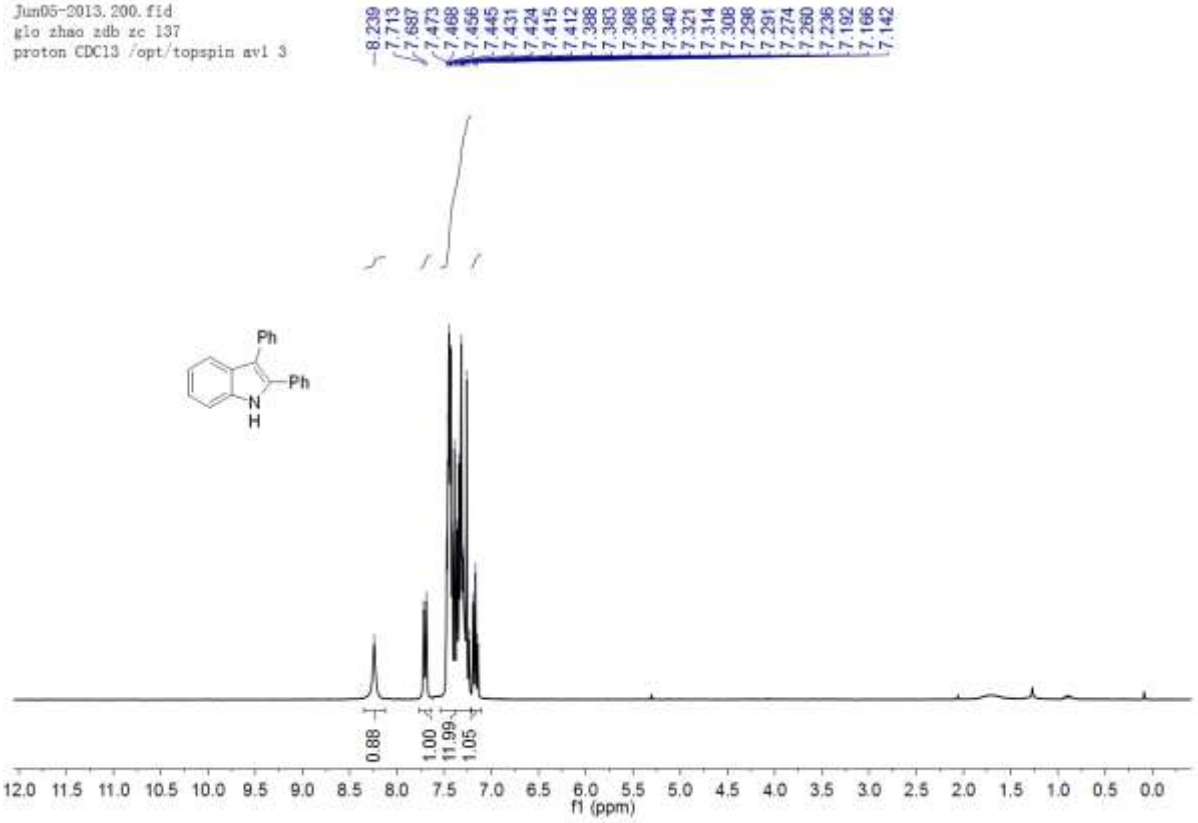
5 References

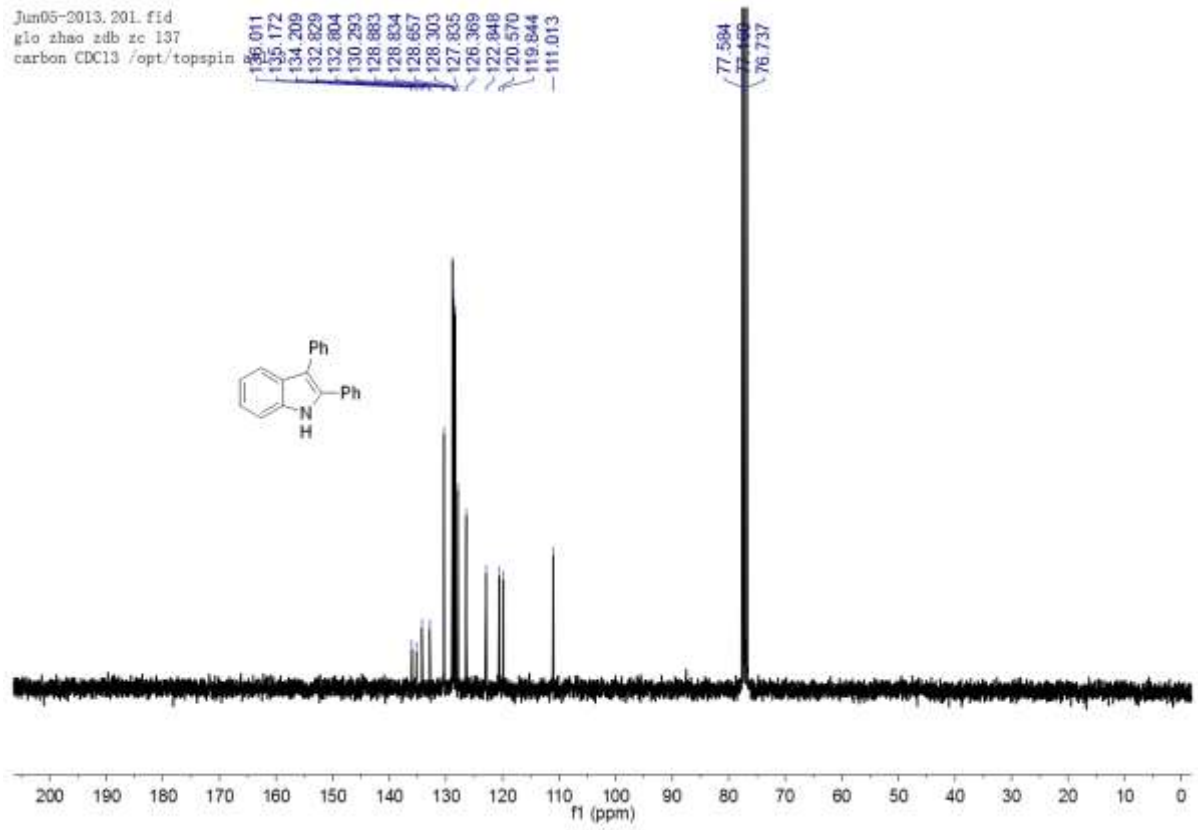
[1] a) L.-L. Jiang, Y. Tan, X.-L. Zhu, Z.-F. Wang, Y. Zuo, Q. Chen, Z. Xi, G.-F. Yang, *J. Agric. Food Chem.* **2010**, *58*, 2643; b) D. W. Brooks, A. Basha, L. Forest, B. P. Gunn, I. Lake, P. A. Bhatia, US 4970210.

[2] K. Park, G. Bae, J. Moon, J. Choe, K. H. Song, S. Lee, *J. Org. Chem.* **2010**, *75*, 6244.

[3] a) K. Sun, S. Liu, P. M. Bec, T. G. Driver, *Angew. Chem. Int. Ed.* **2011**, *50*, 1702; b) S. Gore, S. Baskaran, B. König, *Org. Lett.* **2012**, *14*, 4568; c) Q. Nguyen, T. Nguyen, T. G. Driver, *J. Am. Chem. Soc.* **2013**, *135*, 620.

6 NMR spectra





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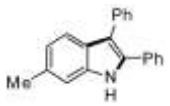

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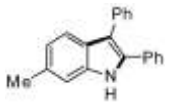

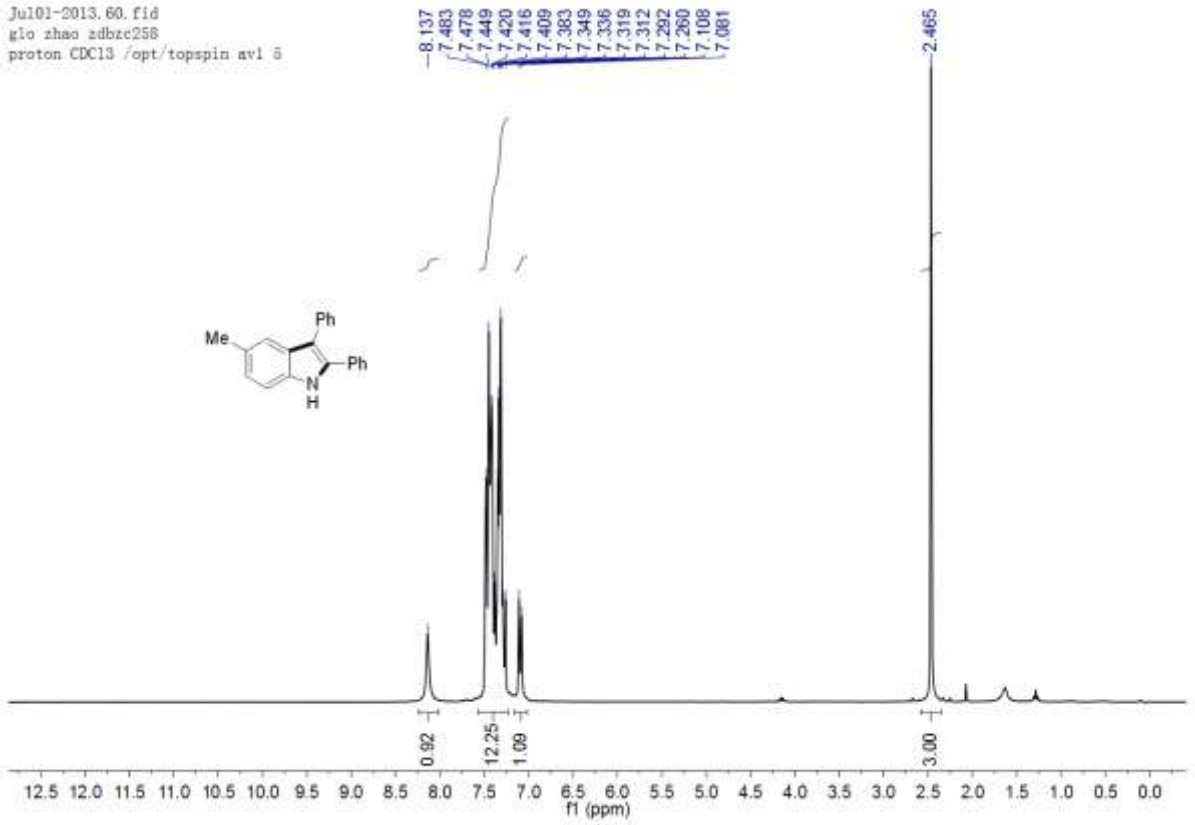
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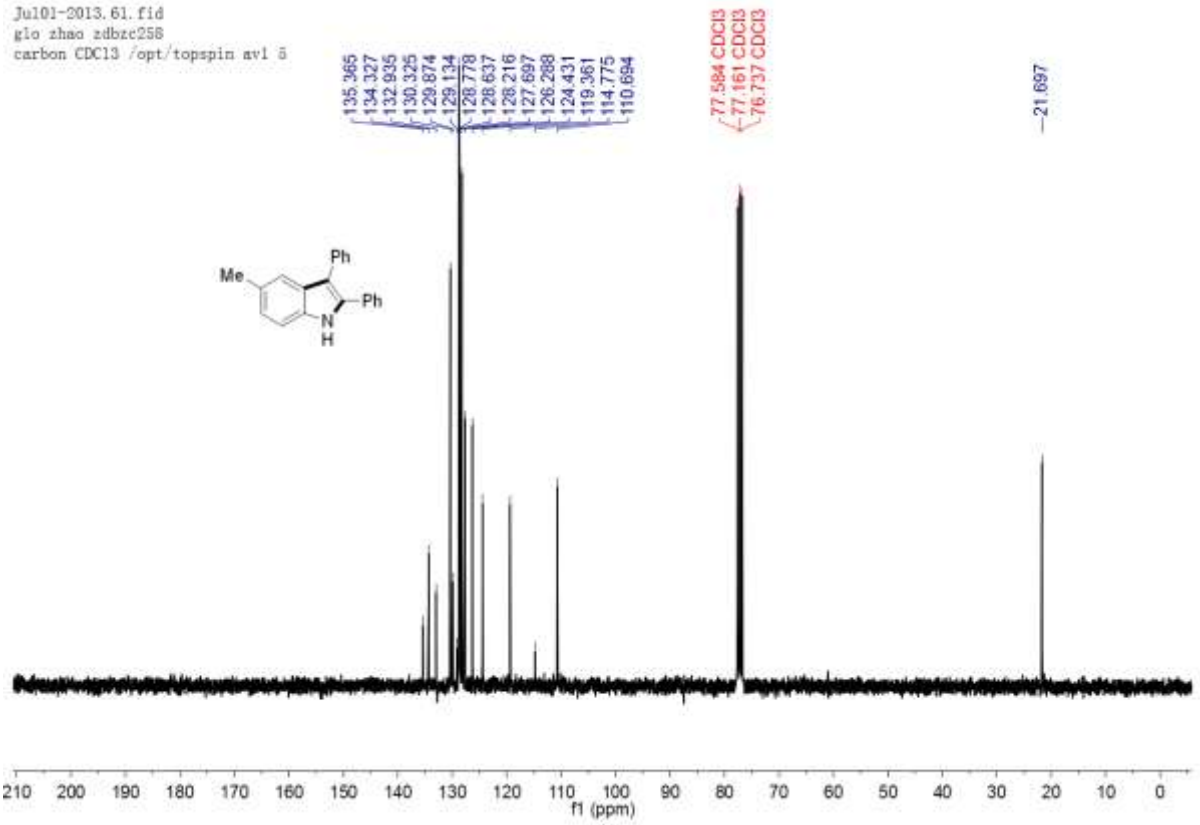
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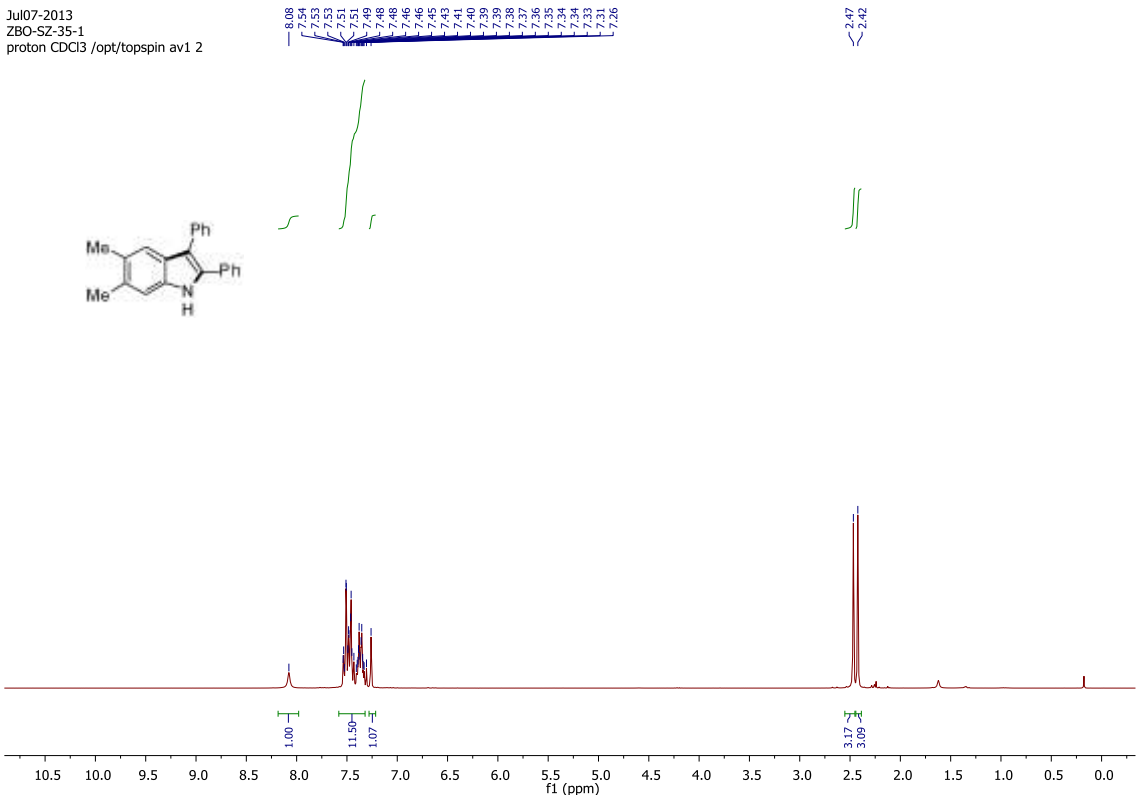
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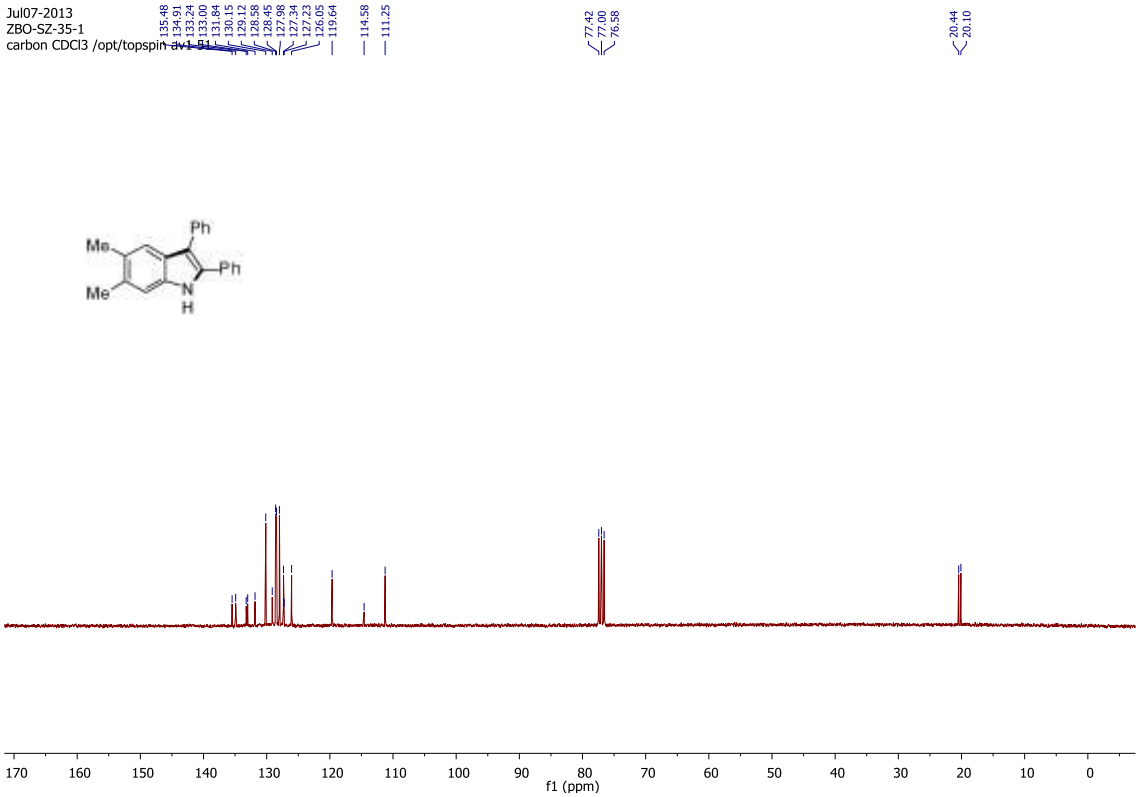
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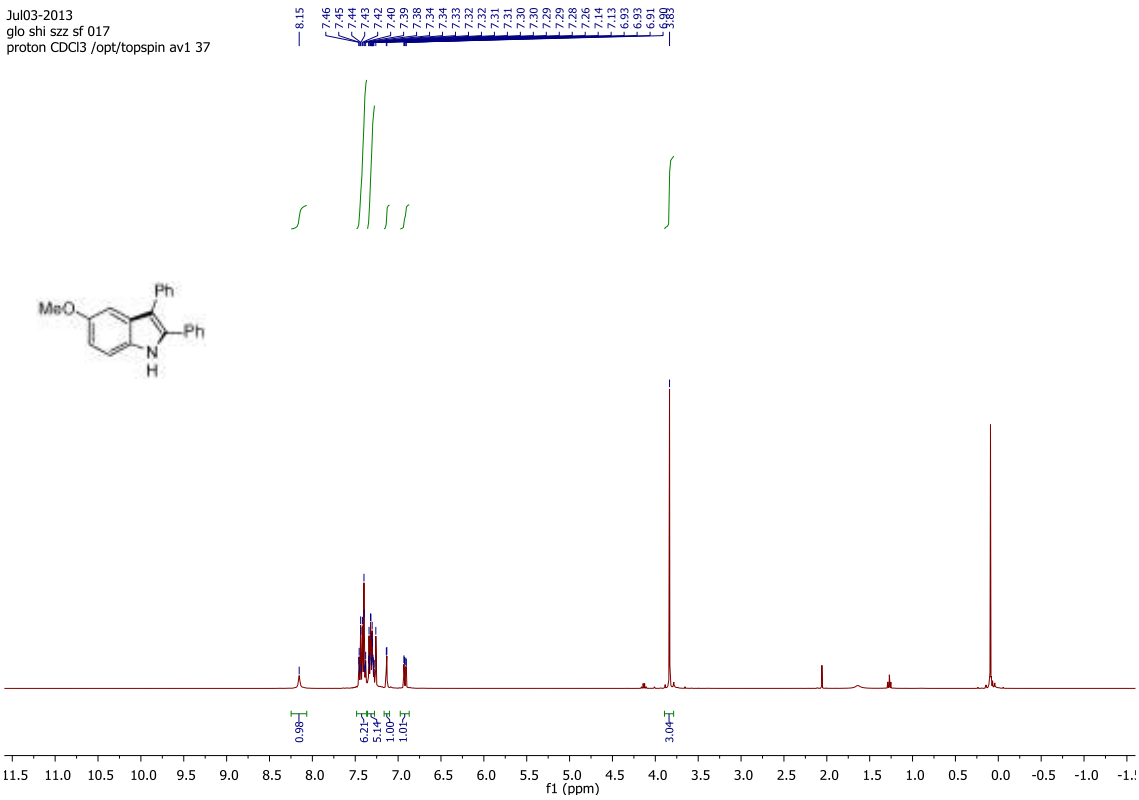
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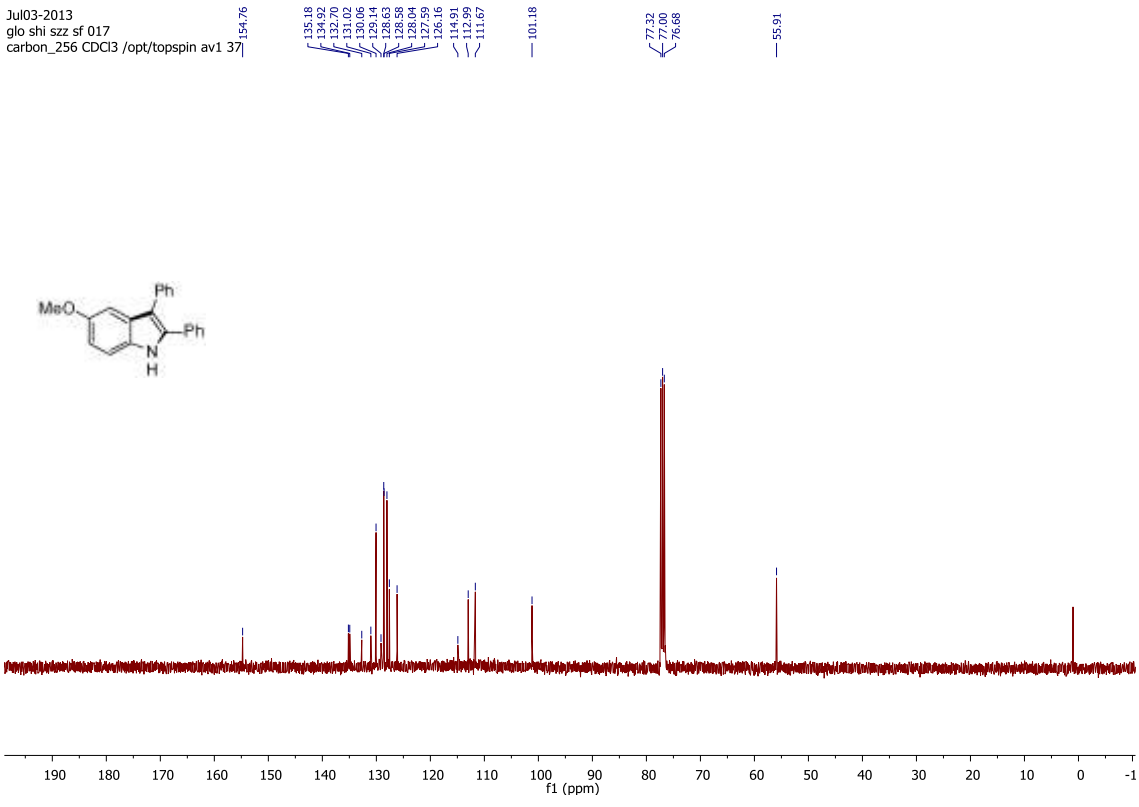
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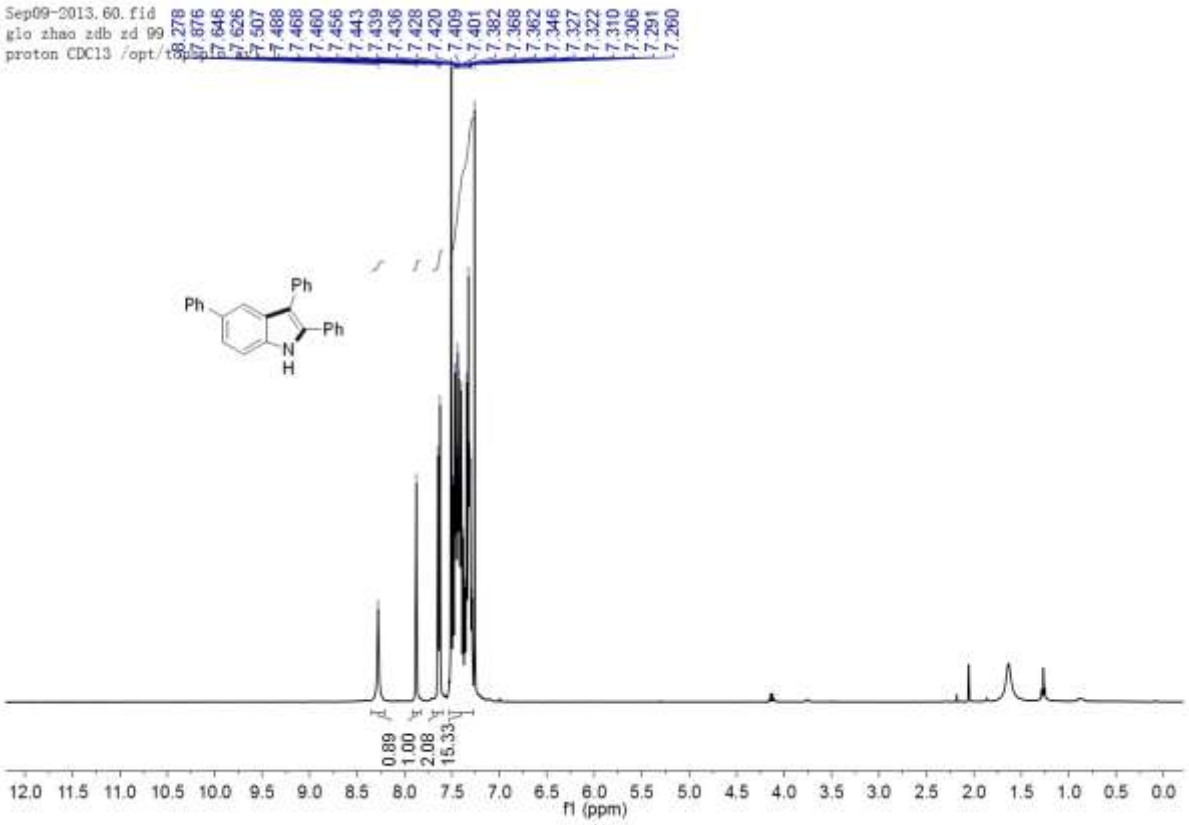
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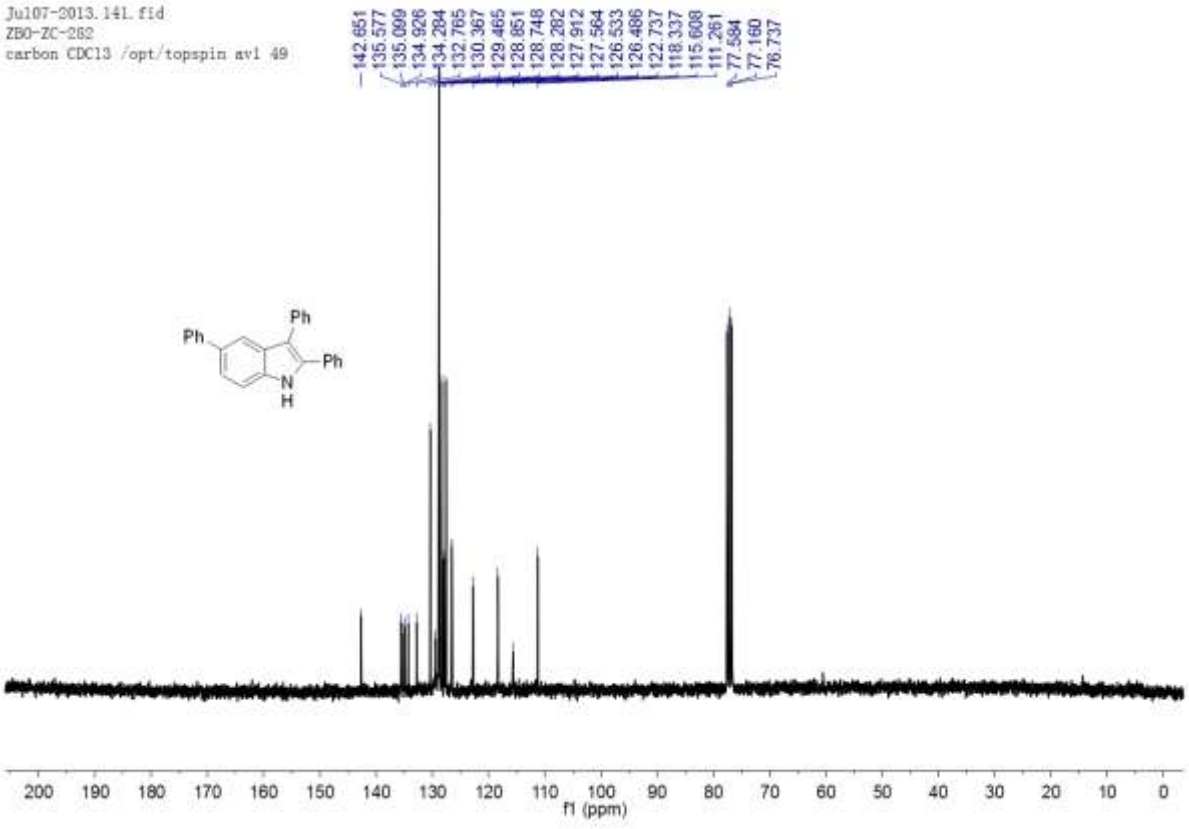
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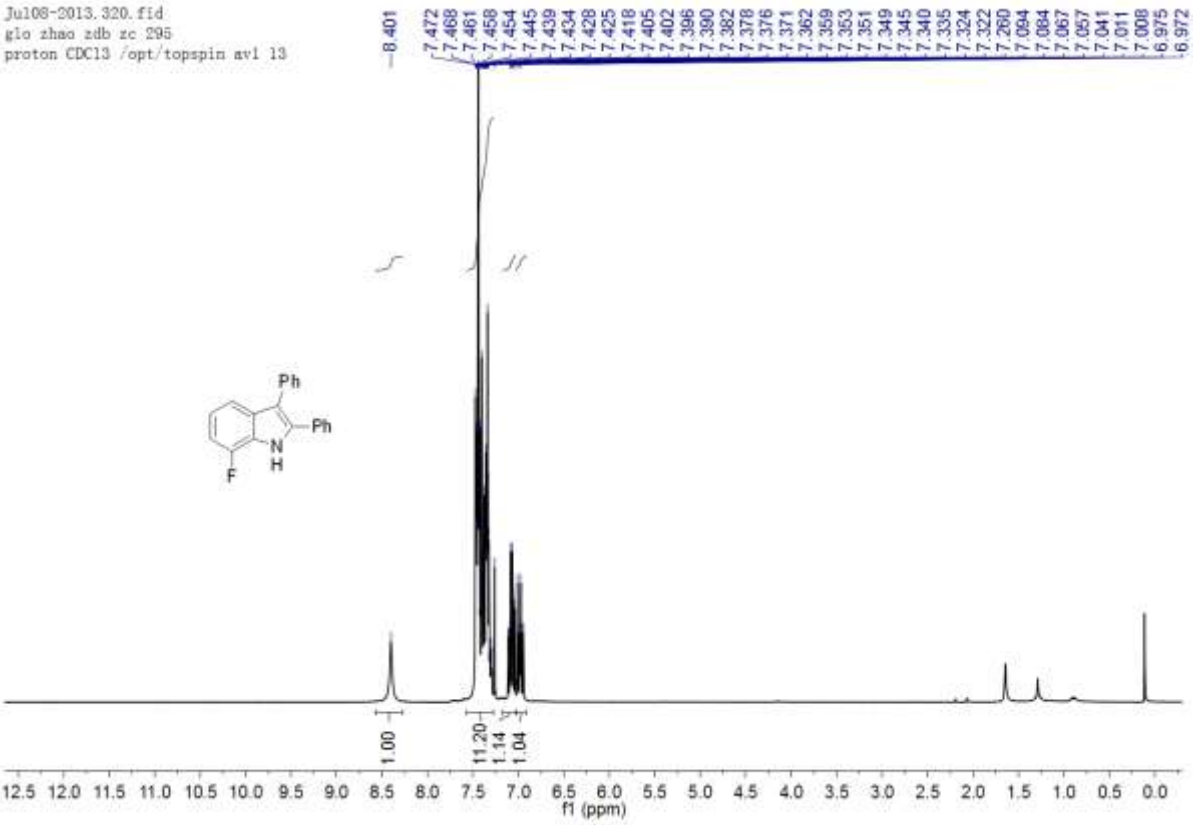
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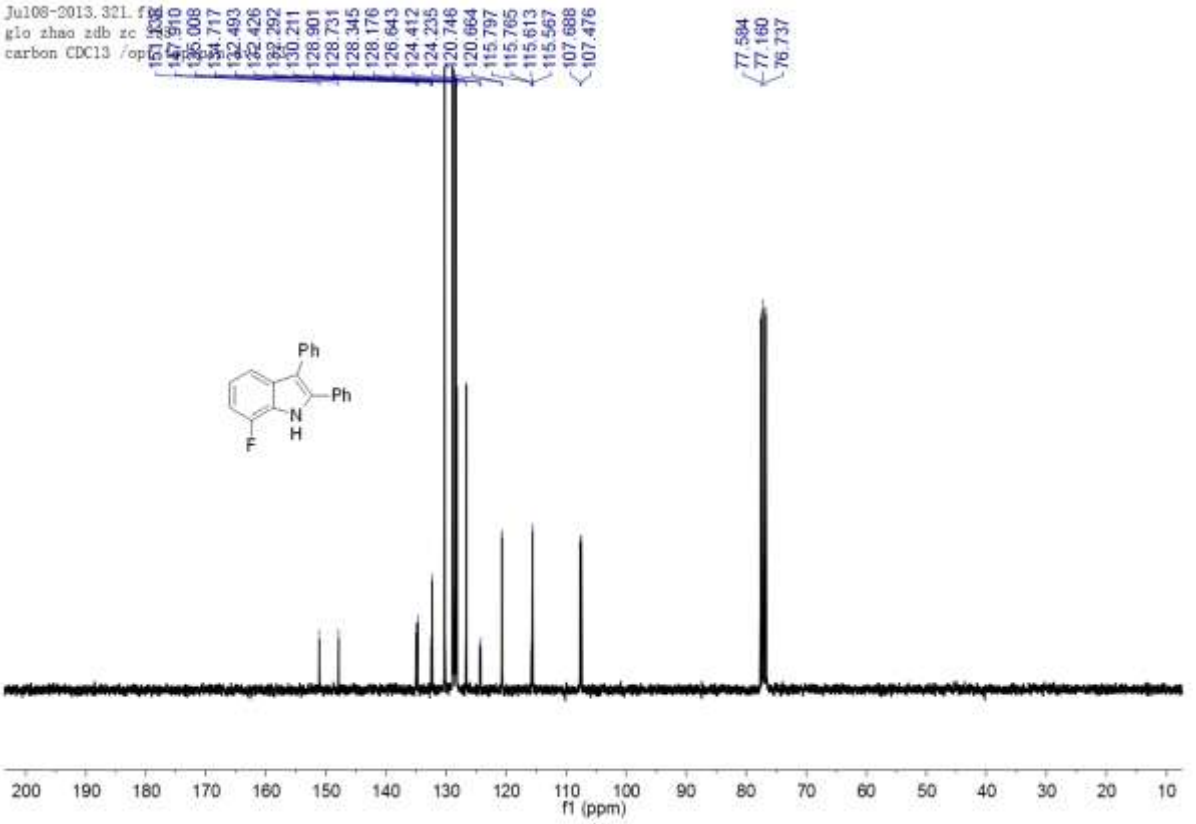
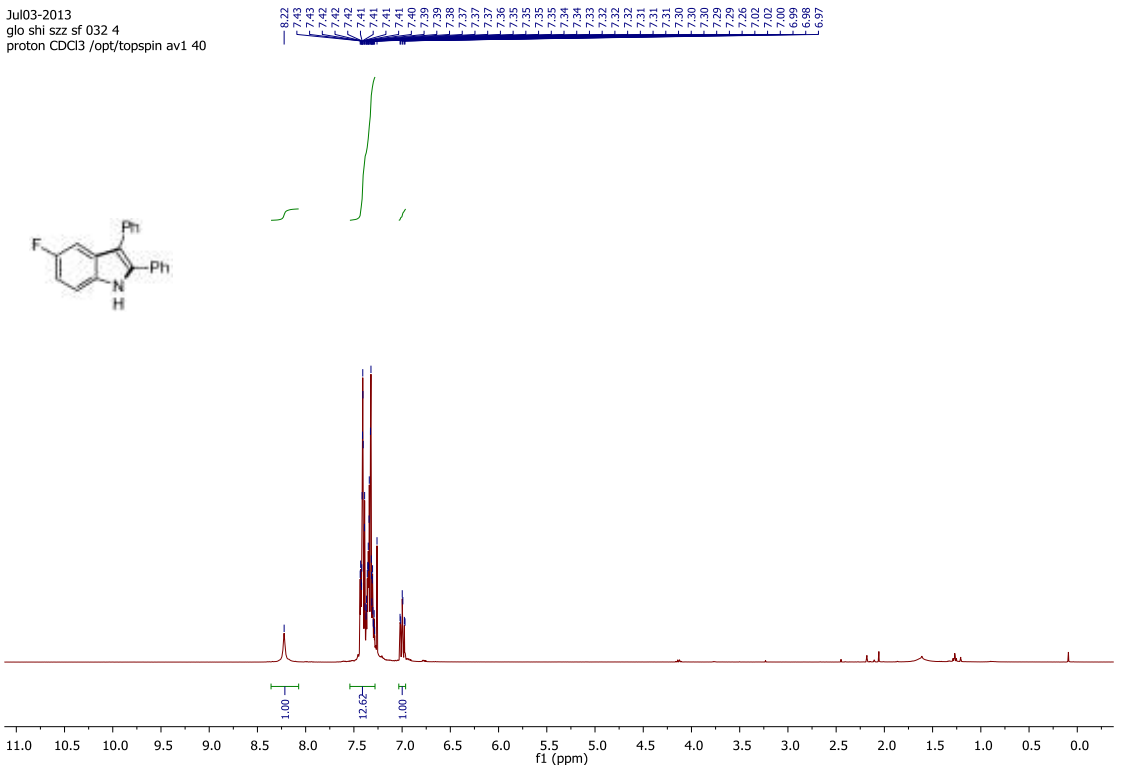
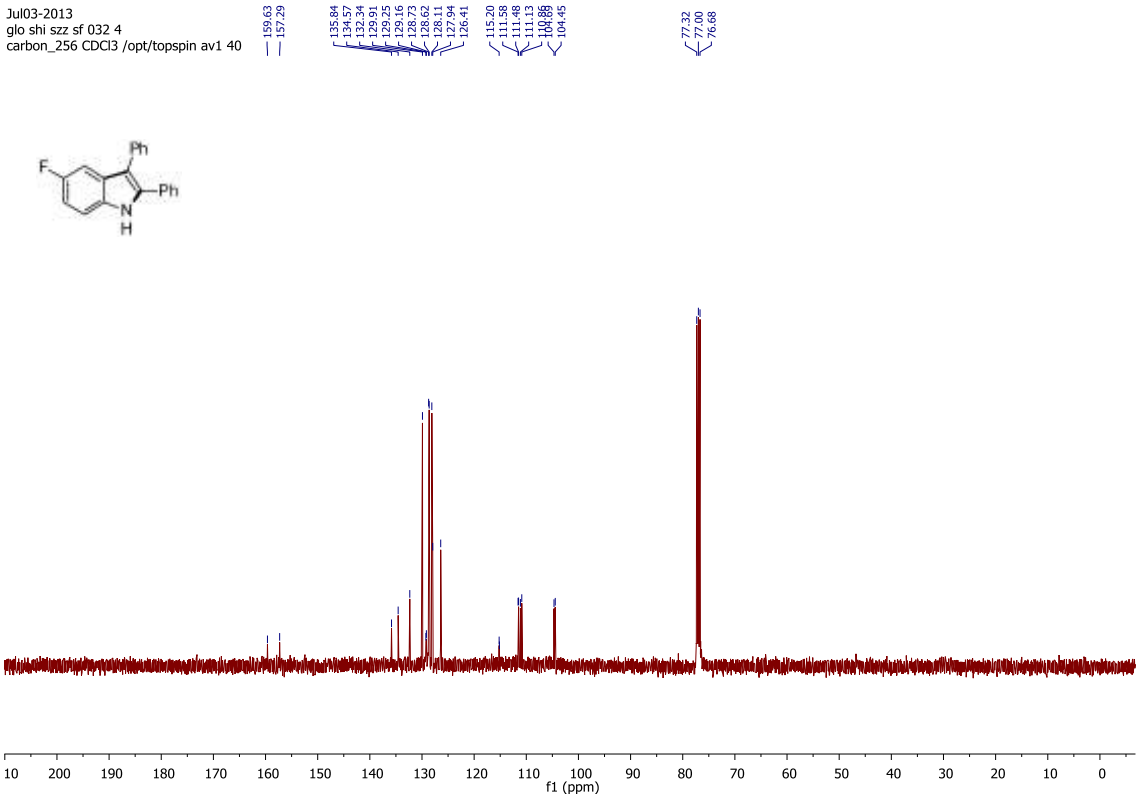
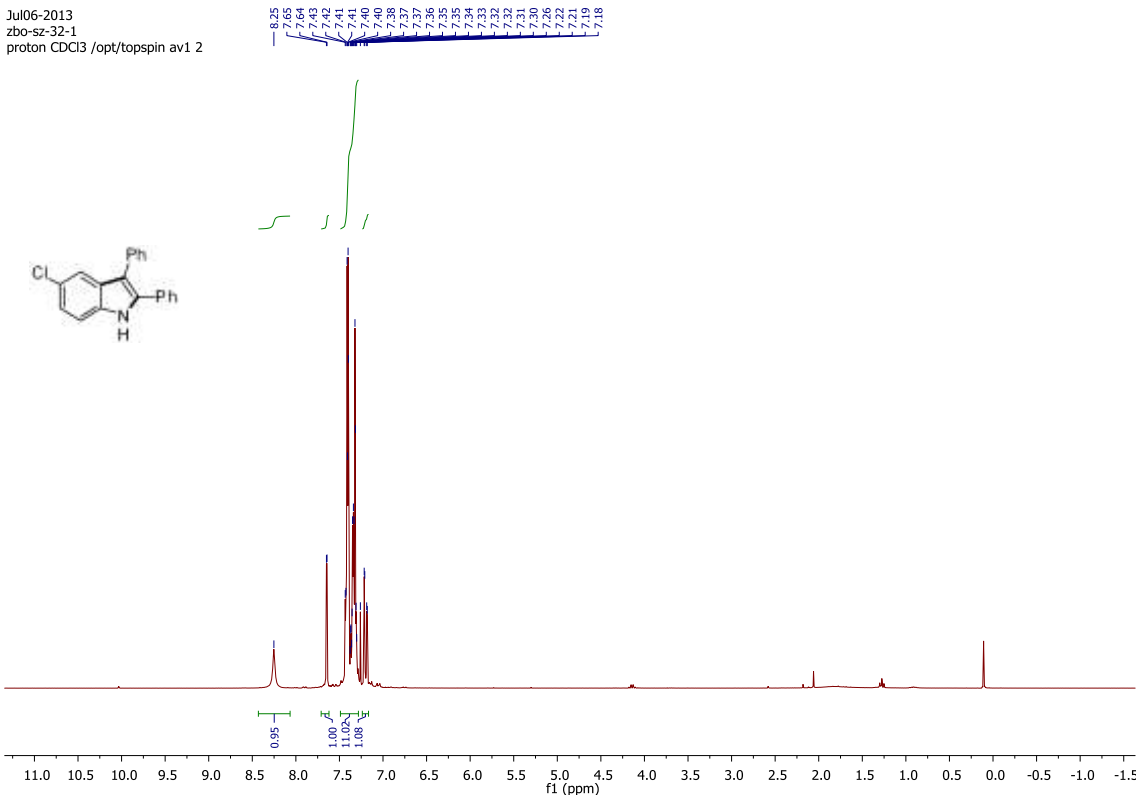
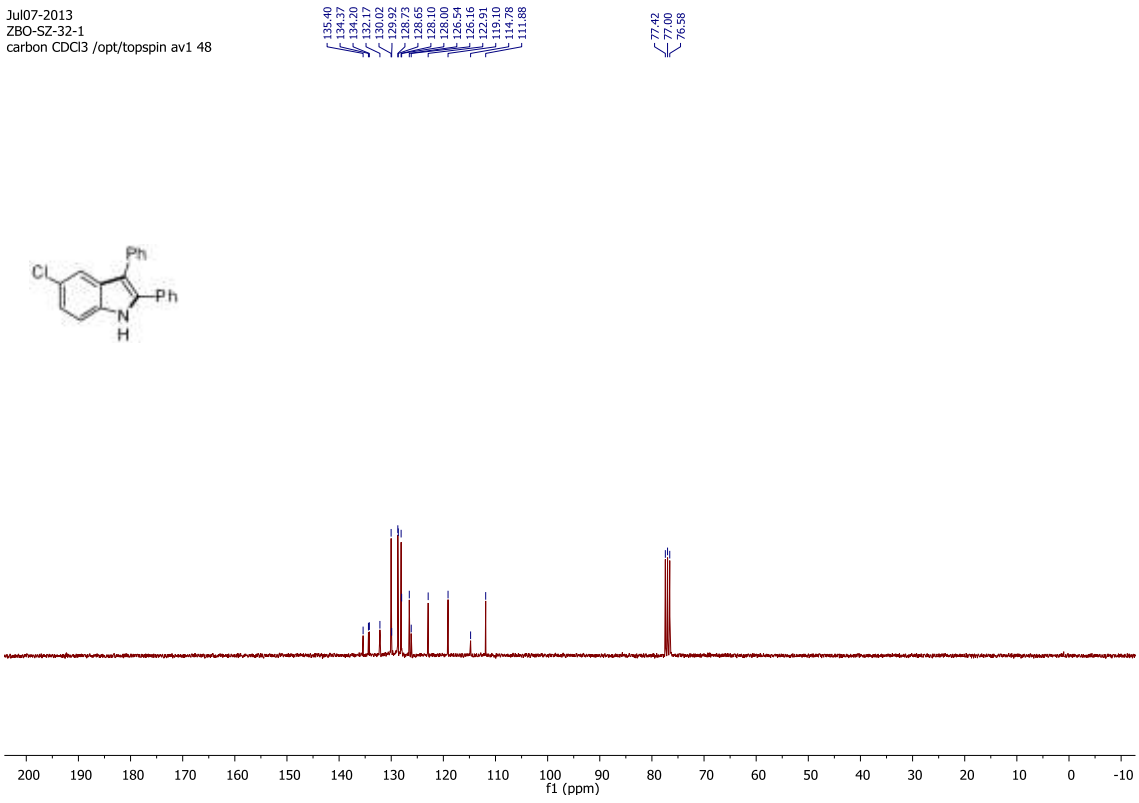
7.041
7.011
7.008
6.975
6.972
Ph
Ph
N
H
F
1.00
11.20
1.14
1.04
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

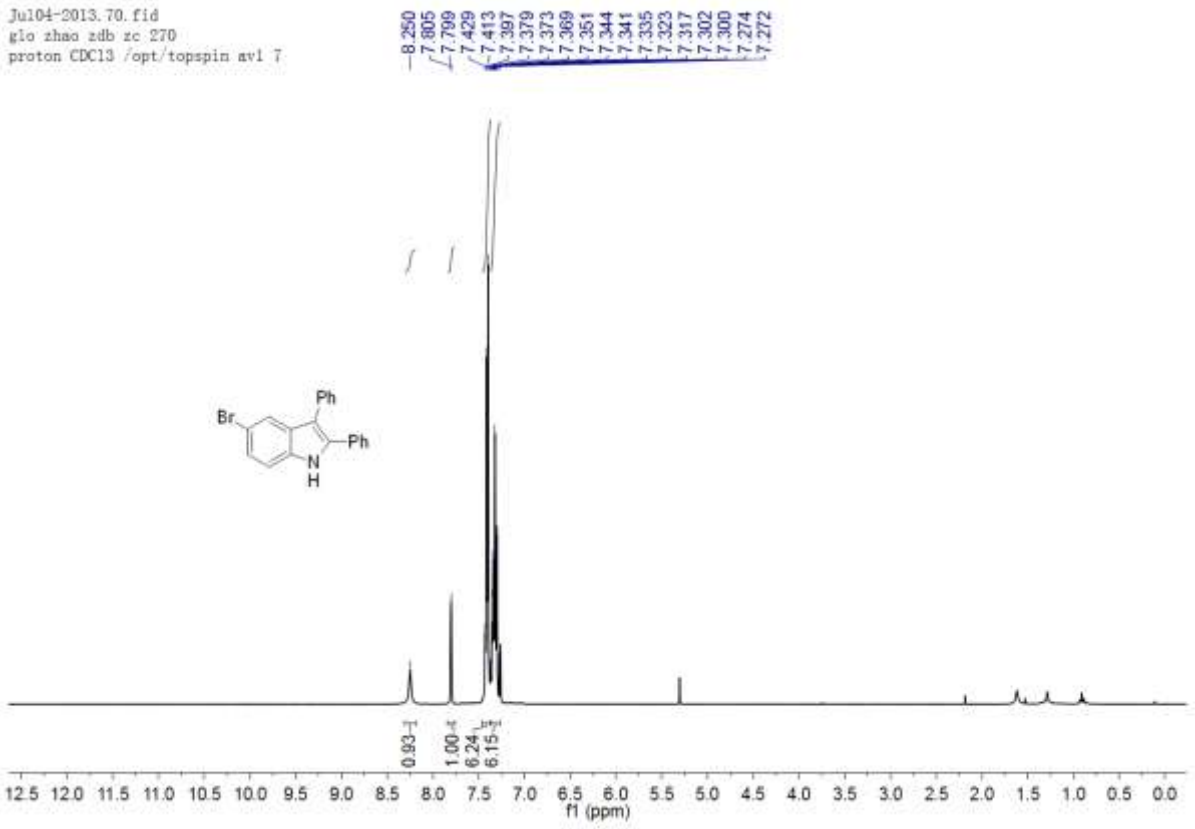

Jul08-2013.321.fi
glo zhao zdb zc
carbon CDCl3 /op
128.901
128.731
128.345
128.176
126.643
124.412
124.235
120.746
120.664
115.797
115.765
115.613
115.567
107.688
107.476
77.584
77.160
76.737
Ph
Ph
N
H
F
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

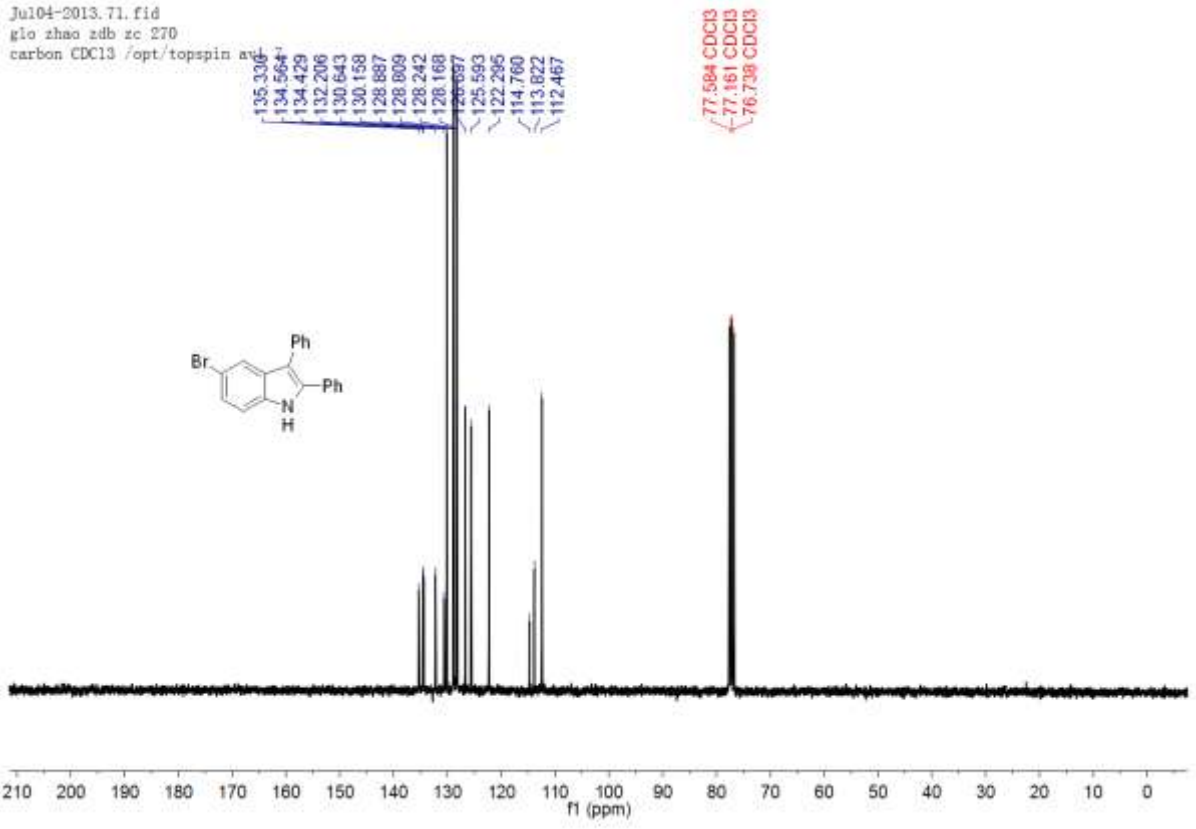

Jul03-2013
glo shi szz sf 032 4
proton CDCl3 /opt/topspin av1 40
8.22
7.43
7.43
7.42
7.42
7.42
7.41
7.41
7.41
7.40
7.39
7.39
7.38
7.37
7.37
7.37
7.36
7.35
7.35
7.35
7.34
7.34
7.33
7.32
7.32
7.32
7.31
7.31
7.31
7.30
7.30
7.30
7.29
7.29
7.26
7.02
7.02
7.00
6.99
6.98
6.97
Ph
F
Ph
N
H
1.00
12.62
1.00
11.0
10.5
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
f1 (ppm)

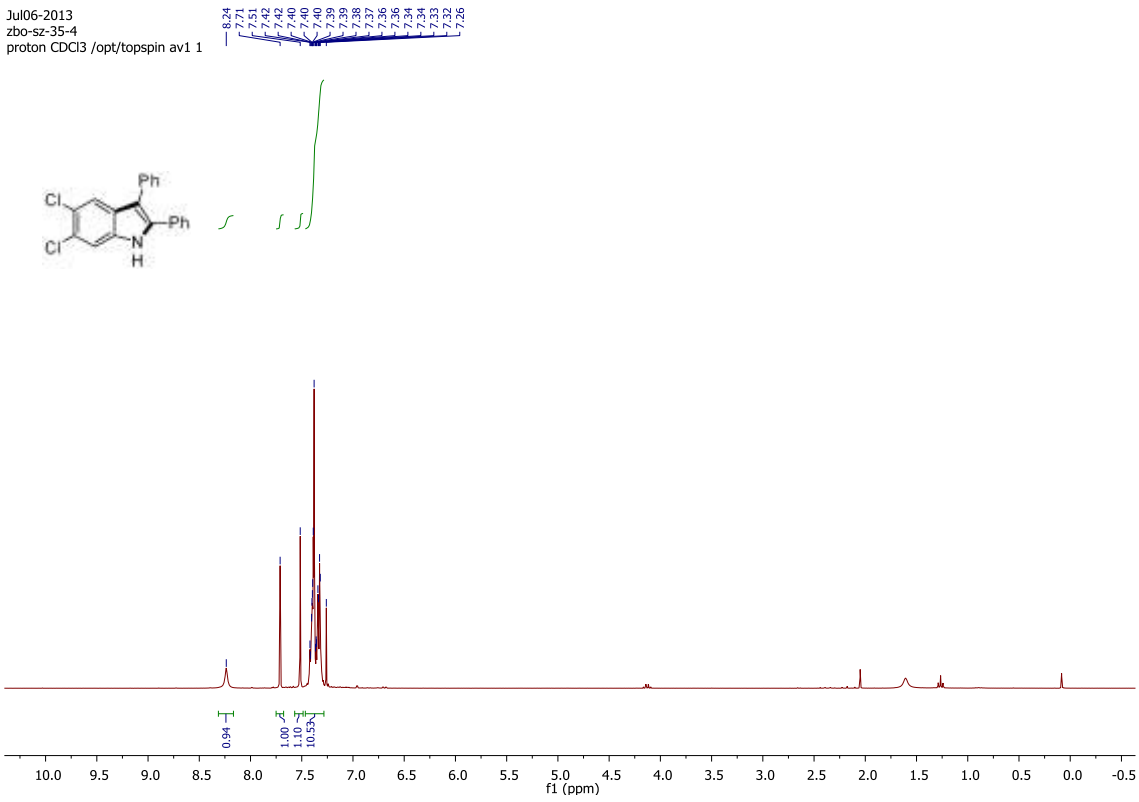

Jul03-2013
glo shi szz sf 032 4
carbon_256 CDCl3 /opt/topspin av1 40
159.63
157.29
135.84
134.57
132.34
129.91
129.25
129.16
128.73
128.62
128.11
127.94
126.41
115.20
111.58
111.48
111.13
110.89
110.86
104.45
77.32
77.00
76.68
Ph
F
Ph
N
H
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

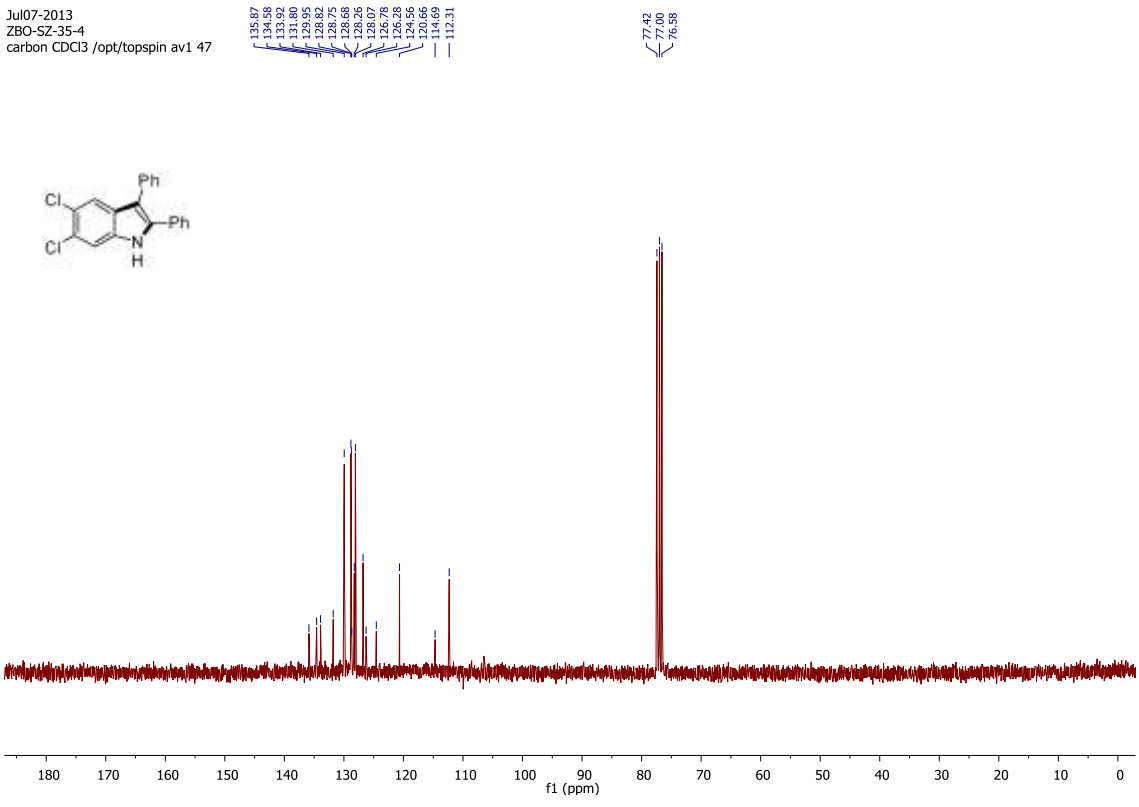

Jul06-2013
zbo-sz-32-1
proton CDCl3 /opt/topspin av1 2
8.25
7.65
7.64
7.43
7.42
7.41
7.41
7.40
7.40
7.38
7.37
7.37
7.36
7.35
7.34
7.33
7.32
7.32
7.31
7.30
7.26
7.22
7.21
7.19
7.18
Cl
Ph
Ph
N
H
0.95
1.00
11.02
1.08
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

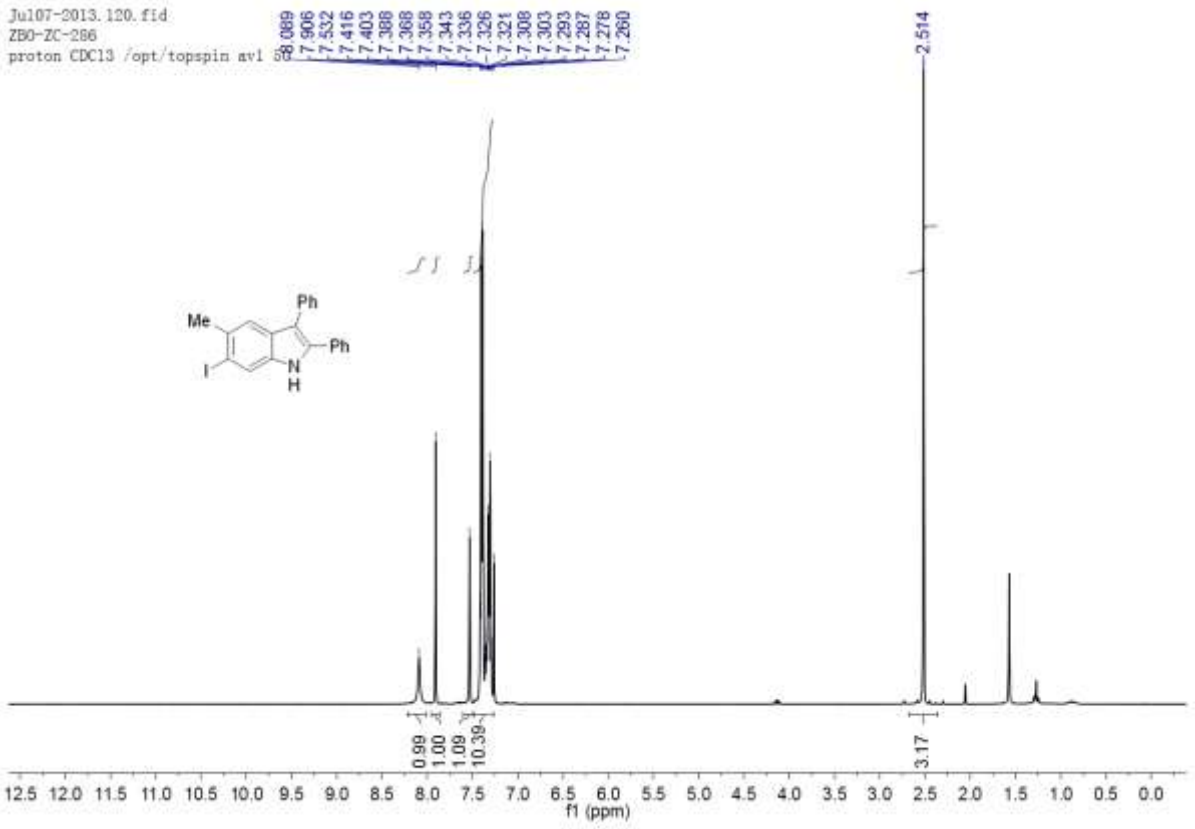

Jul07-2013
ZBO-SZ-32-1
carbon CDCl3 /opt/topspin av1 48
135.40
134.37
134.20
132.17
130.02
129.92
128.73
128.65
128.10
128.00
126.54
126.16
122.91
119.10
114.78
111.88
77.42
77.00
76.58
Cl
Ph
Ph
N
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

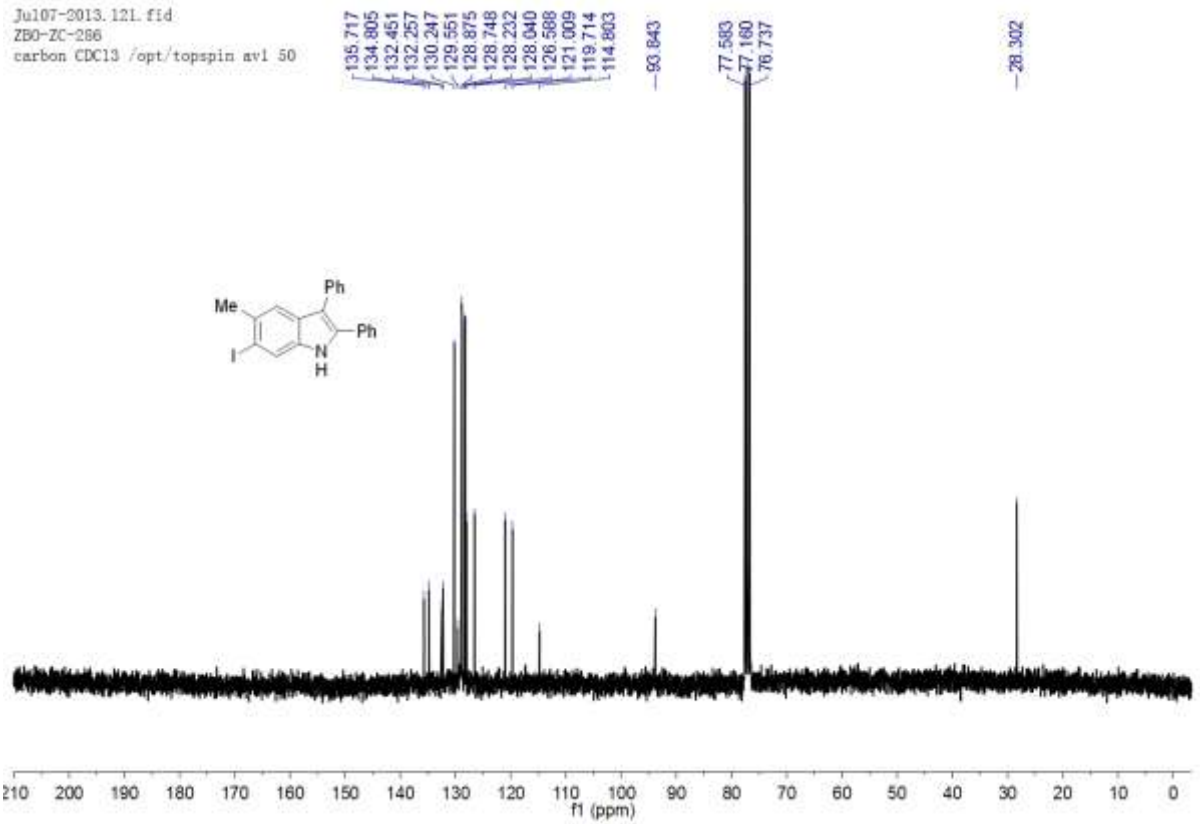

Jul04-2013.70.fid
glo zhao zdb zc 270
proton CDCl3 /opt/topspin av1 7
8.250
7.805
7.799
7.429
7.413
7.397
7.379
7.373
7.369
7.351
7.344
7.341
7.335
7.323
7.317
7.302
7.300
7.274
7.272
Br
Ph
Ph
N
H
0.93
1.00
6.24
6.15
f1 (ppm)

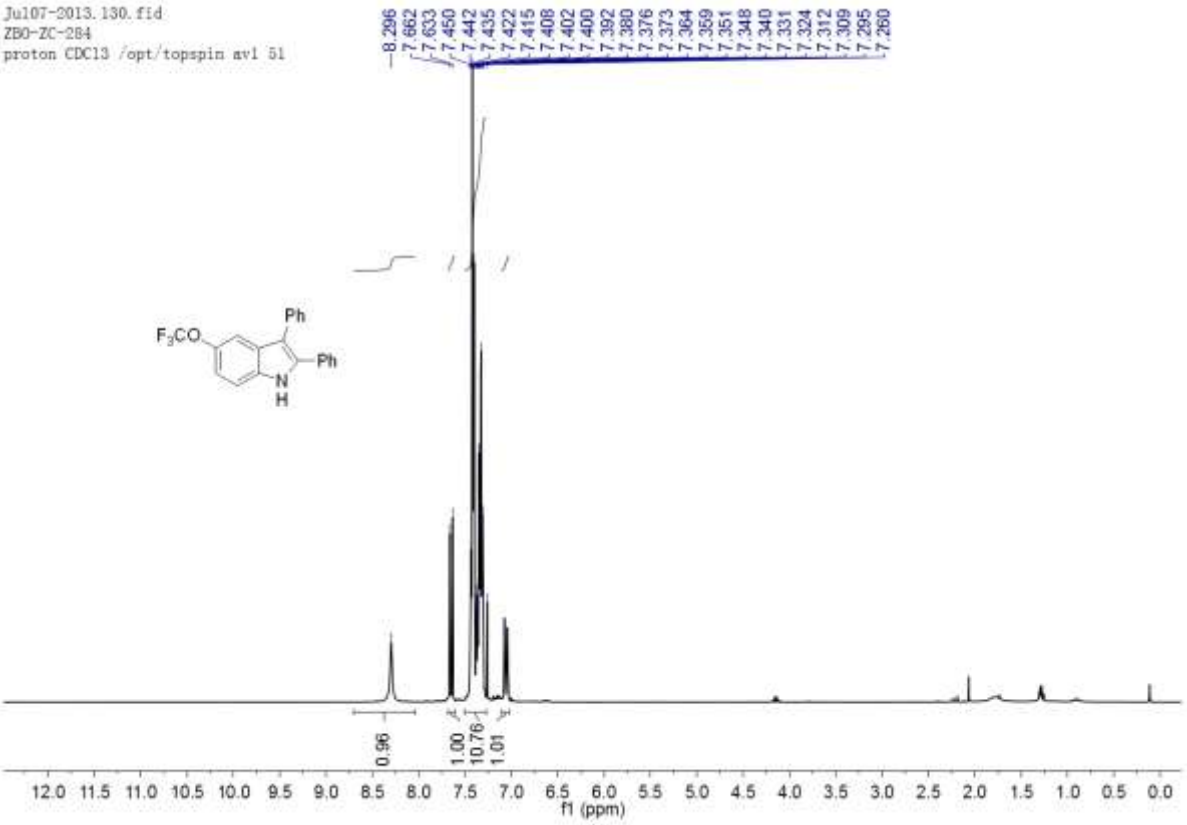

Jul04-2013.71.fid
glo zhao zdb zc 270
carbon CDCl3 /opt/topspin av
135.306
134.564
134.429
132.206
130.643
130.158
128.887
128.809
128.242
128.168
125.593
122.295
114.760
113.822
112.467
77.584 CDCl3
77.161 CDCl3
76.738 CDCl3
Br
Ph
Ph
N
H
f1 (ppm)

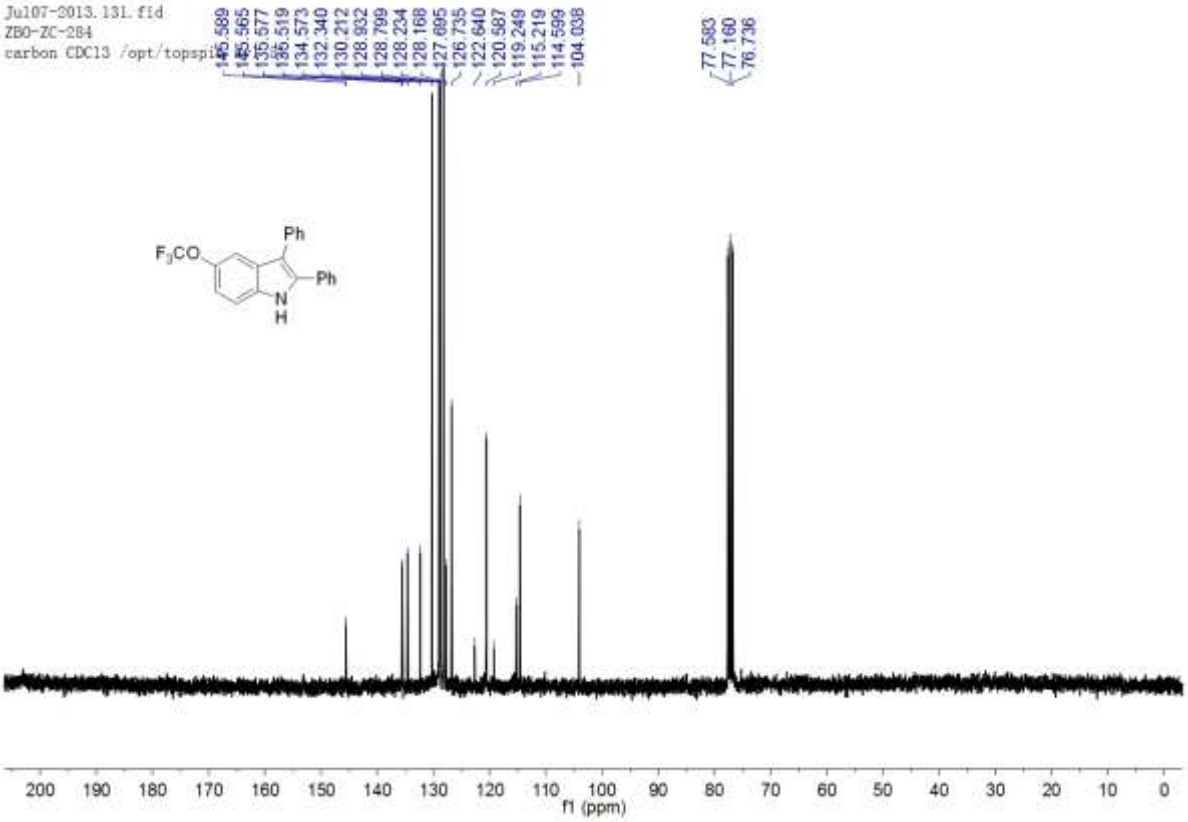

Jul06-2013
zbo-sz-35-4
proton CDCl3 /opt/topspin av1 1
8.24
7.71
7.51
7.42
7.42
7.40
7.40
7.40
7.39
7.39
7.38
7.37
7.36
7.36
7.34
7.34
7.33
7.32
7.26
Ph
Cl
Cl
Ph
N
H
0.94
1.00
1.10
10.53
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

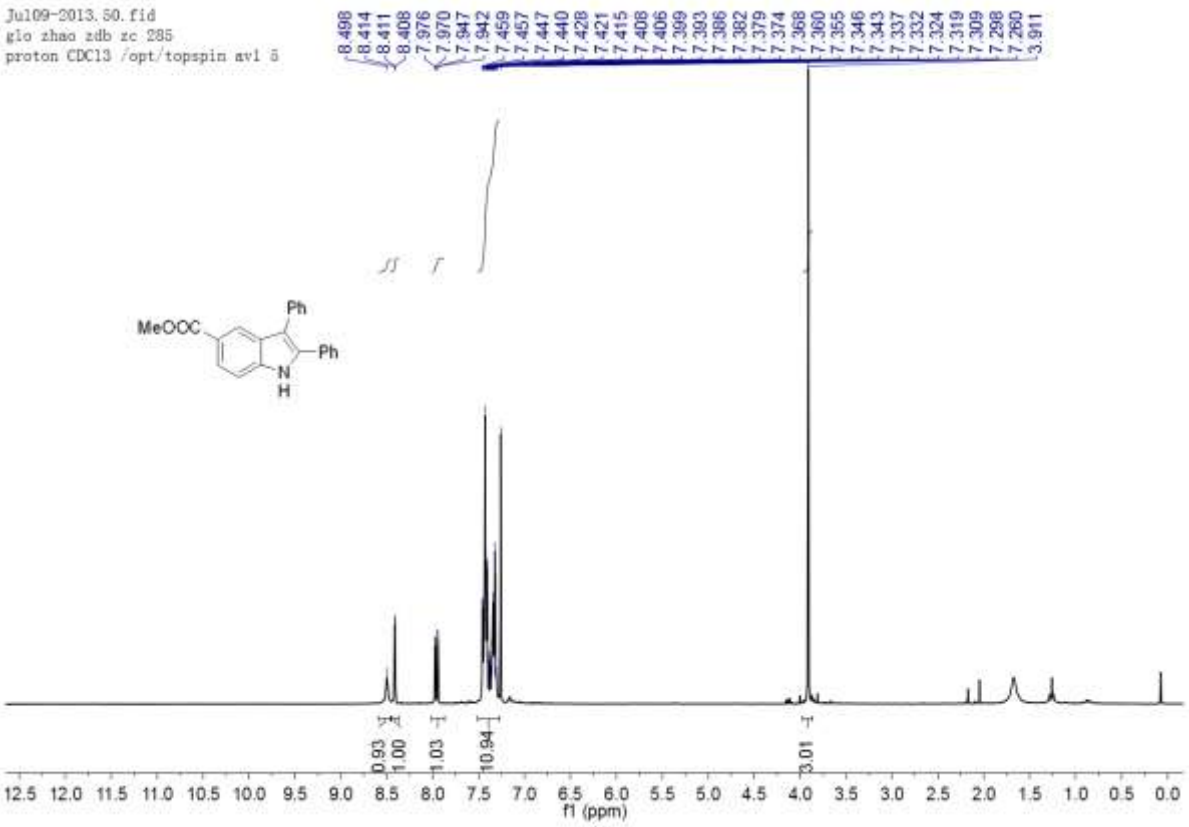

Jul07-2013
ZBO-SZ-35-4
carbon CDCl3 /opt/topspin av1 47
135.87
134.58
133.92
131.80
129.95
128.82
128.75
128.68
128.26
128.07
126.78
126.28
124.56
120.66
114.69
112.31
77.42
77.00
76.58
Ph
Cl
Cl
Ph
N
H
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

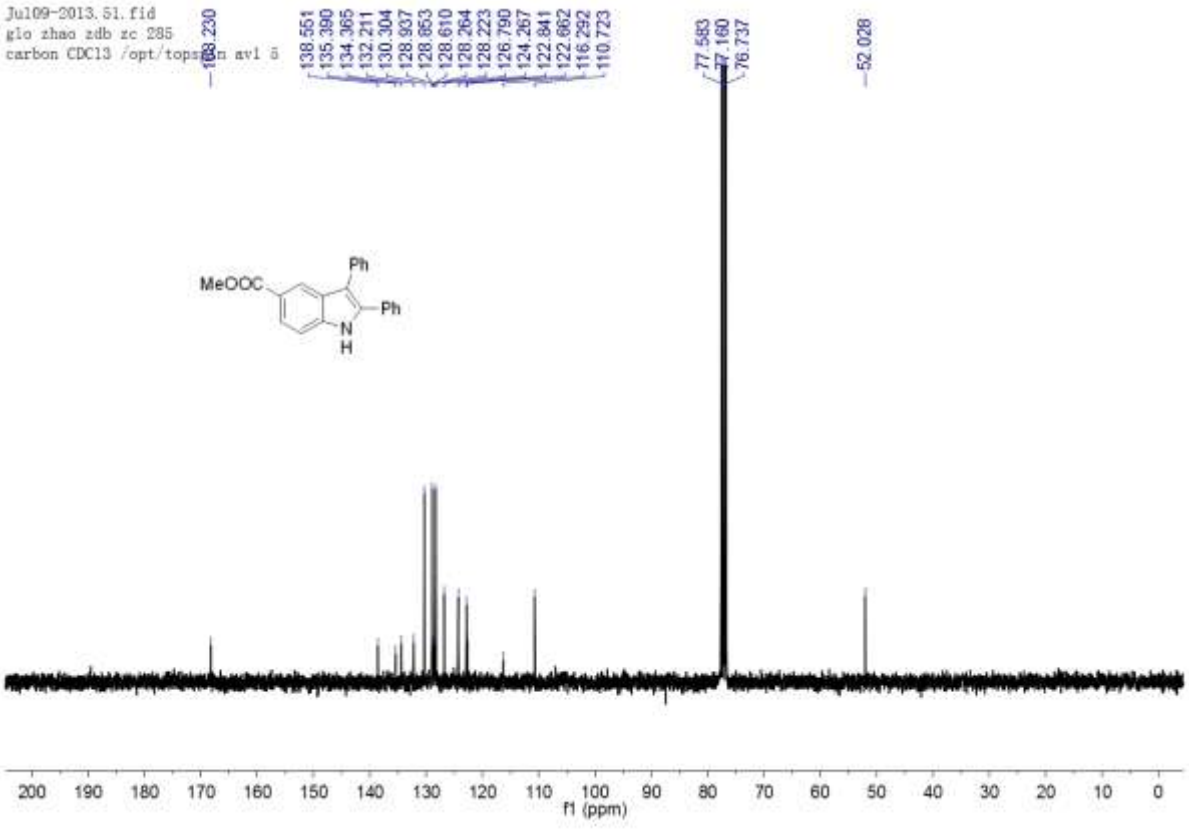

Jul07-2013.120.fid
ZBO-ZC-286
proton CDCl3 /opt/topspin av1 50
8.089
7.906
7.532
7.416
7.403
7.386
7.368
7.358
7.343
7.336
7.326
7.321
7.308
7.303
7.293
7.287
7.278
7.260
2.514
Me
Ph
Ph
I
N
H
0.99
1.00
1.09
10.39
3.17
f1 (ppm)

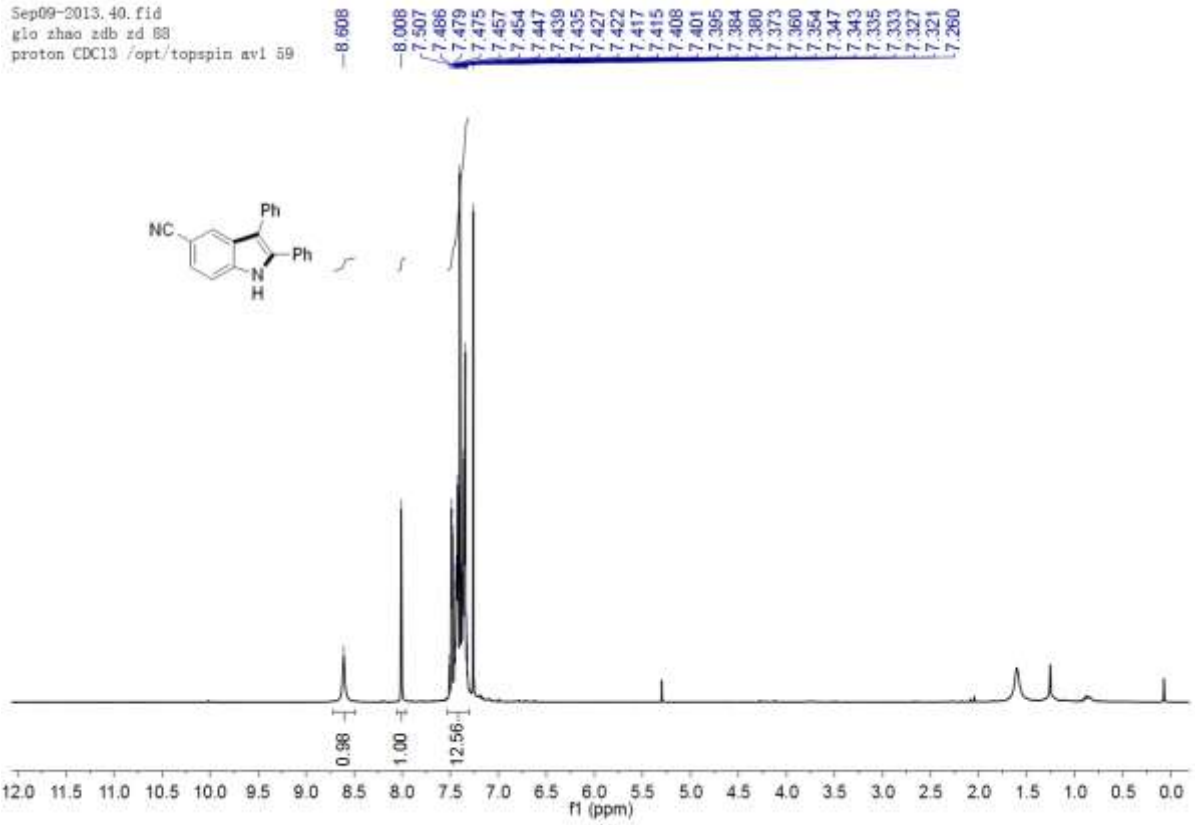

Jul07-2013.121.fid
ZBO-ZC-286
carbon CDCl3 /opt/topspin av1 50
135.717
134.805
132.451
132.257
130.247
129.551
128.875
128.748
128.232
128.040
126.588
121.009
119.714
114.803
93.843
77.583
77.160
76.737
28.302
Me
Ph
Ph
I
N
H
f1 (ppm)

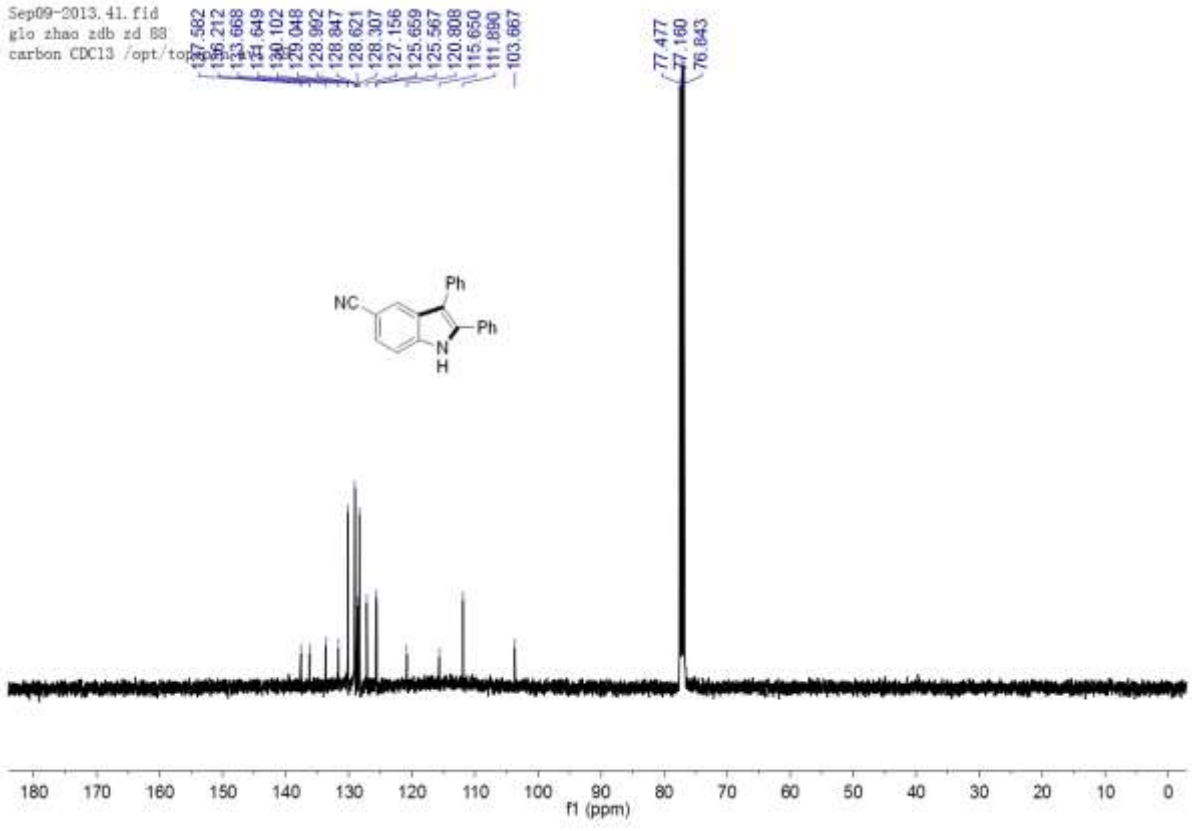

Jul07-2013.130.fid
ZBO-ZC-284
proton CDCl3 /opt/topspin av1 51
8.296
7.662
7.633
7.450
7.442
7.435
7.422
7.415
7.408
7.402
7.400
7.392
7.380
7.376
7.373
7.364
7.359
7.351
7.348
7.340
7.331
7.324
7.312
7.309
7.295
7.260
F3CO
Ph
Ph
N
H
0.96
1.00
10.76
1.01
f1 (ppm)

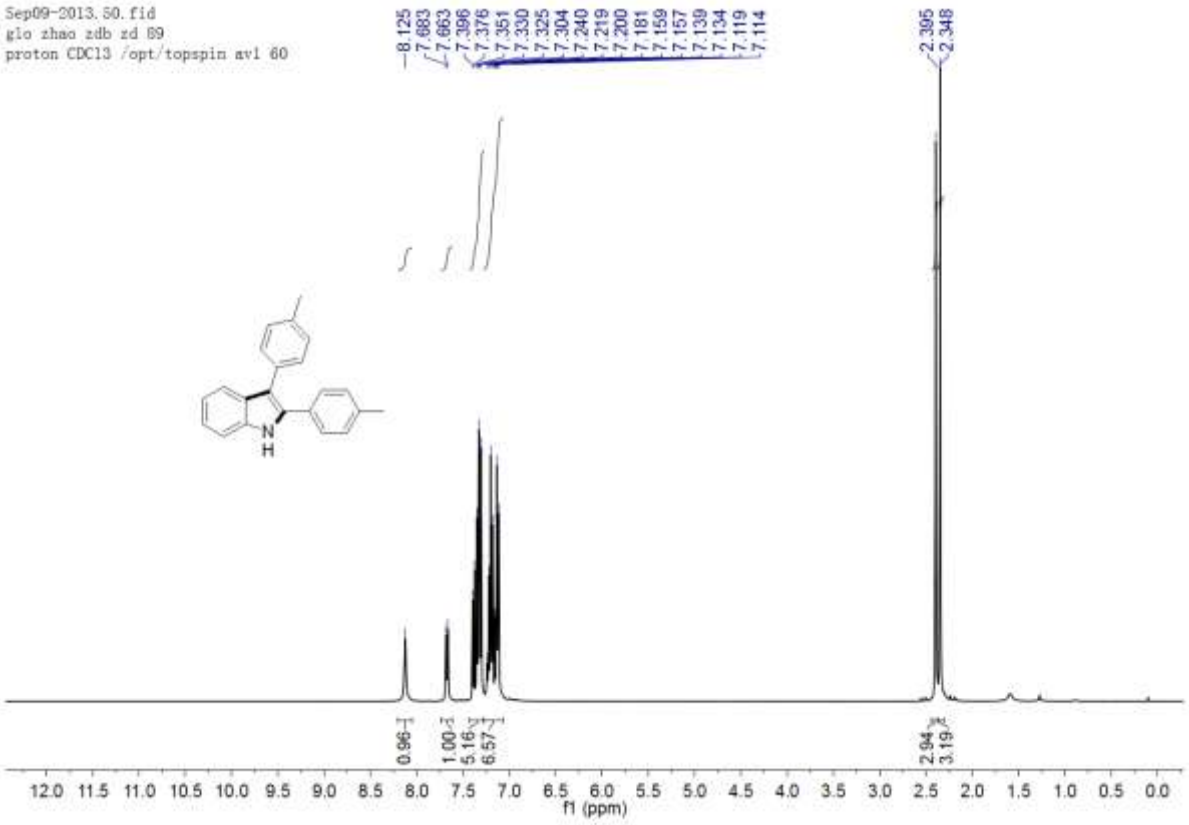

Jul07-2013.131.fid
ZBO-ZC-284
carbon CDCl3 /opt/topspin
135.577
134.573
132.340
130.212
128.932
128.799
128.234
128.168
127.695
126.735
122.640
120.587
119.249
115.219
114.599
104.038
77.583
77.160
76.736
F3CO
Ph
Ph
N
H
f1 (ppm)

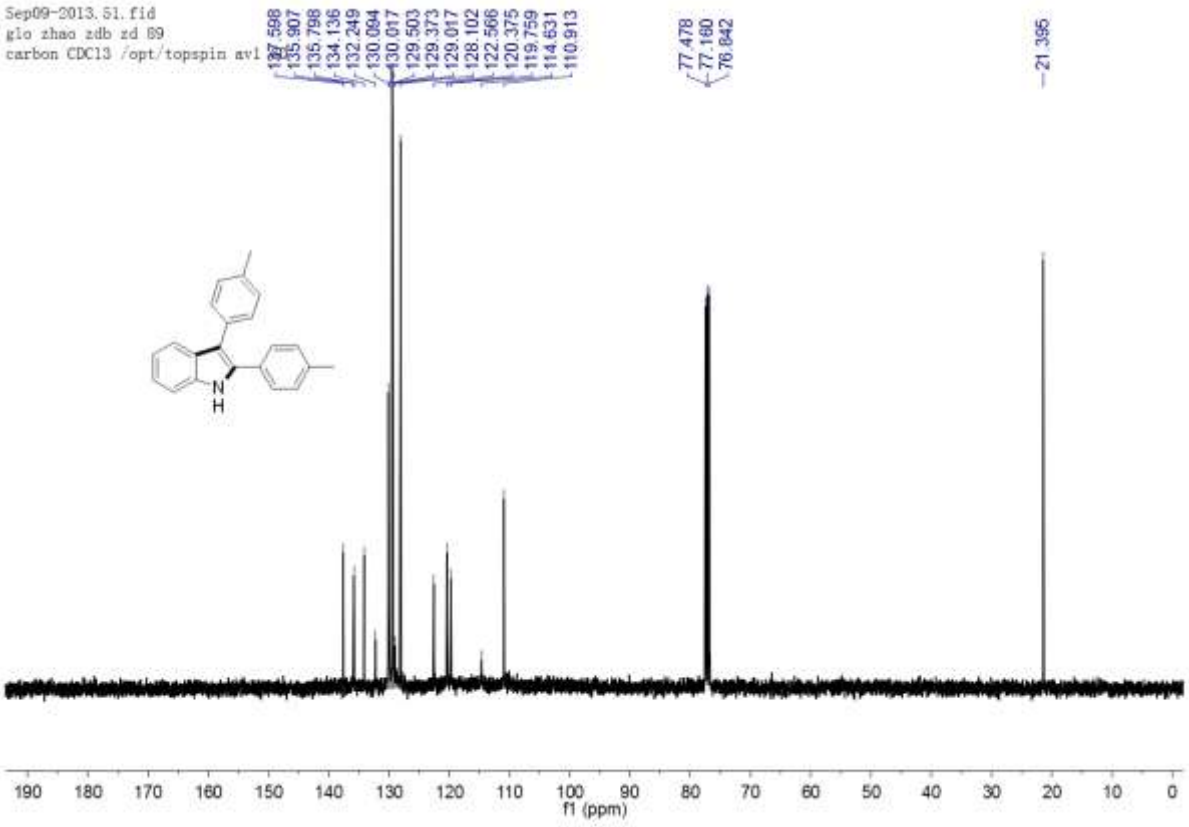

Jul09-2013.50.fid
glo zhao zdb zc 285
proton CDCl3 /opt/topspin av1 5
8.498
8.414
8.411
8.408
7.976
7.970
7.947
7.942
7.459
7.457
7.447
7.440
7.428
7.421
7.415
7.408
7.406
7.399
7.393
7.386
7.382
7.379
7.374
7.368
7.360
7.355
7.346
7.343
7.337
7.332
7.324
7.319
7.309
7.298
7.260
3.911
MeOOC
Ph
Ph
N
H
0.93
1.00
1.03
10.94
3.01
12.5 12.0 11.5 11.0 10.5 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
f1 (ppm)

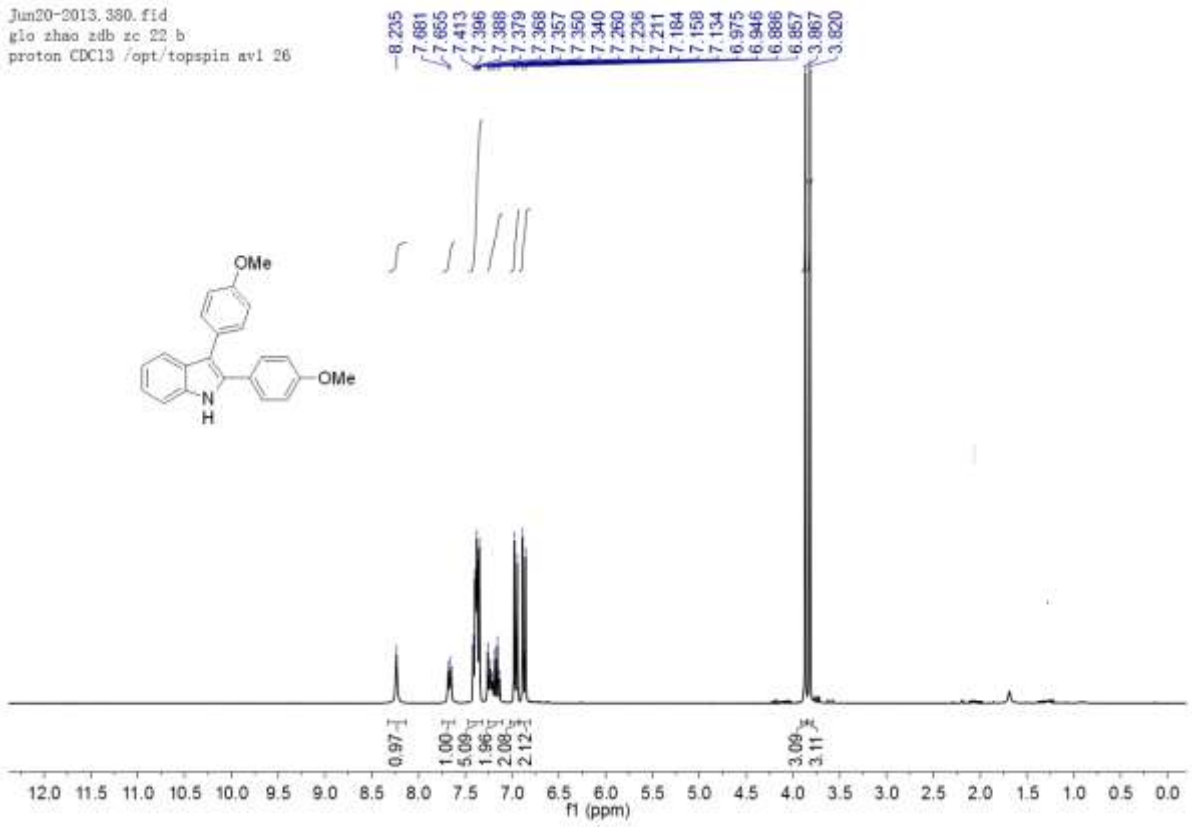

Jul09-2013.51.fid
glo zhao zdb zc 285
carbon CDCl3 /opt/topspin av1 5
168.230
138.551
135.390
134.365
132.211
130.304
128.937
128.853
128.610
128.264
128.223
126.790
124.267
122.841
122.662
116.292
110.723
77.583
77.160
76.737
52.028
MeOOC
Ph
Ph
N
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

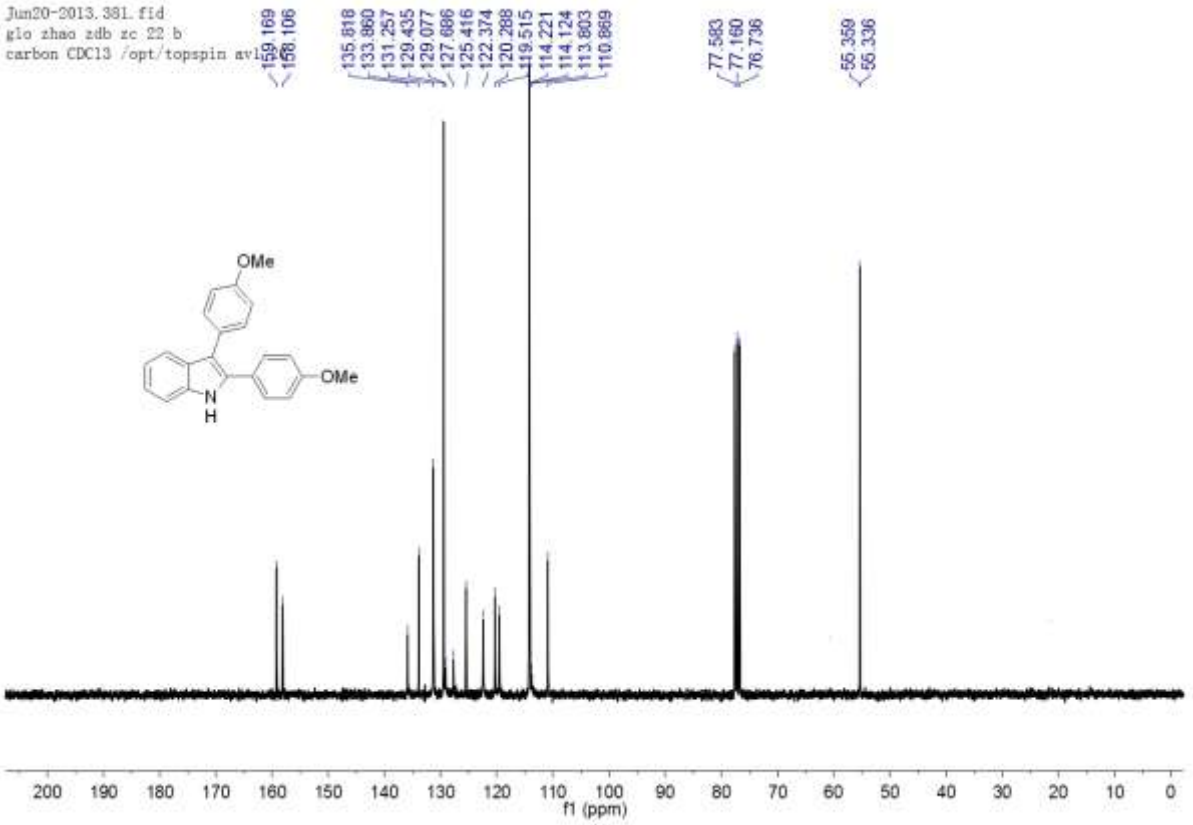

Sep09-2013.40.fid
glo zhao zdb zd 68
proton CDCl3 /opt/topspin av1 59
8.608
8.008
7.507
7.486
7.479
7.475
7.457
7.454
7.447
7.439
7.435
7.427
7.422
7.417
7.415
7.408
7.401
7.395
7.384
7.380
7.373
7.360
7.354
7.347
7.343
7.335
7.333
7.327
7.321
7.260
NC
Ph
Ph
N
H
0.98
1.00
12.56
12.0 11.5 11.0 10.5 10.0 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
f1 (ppm)

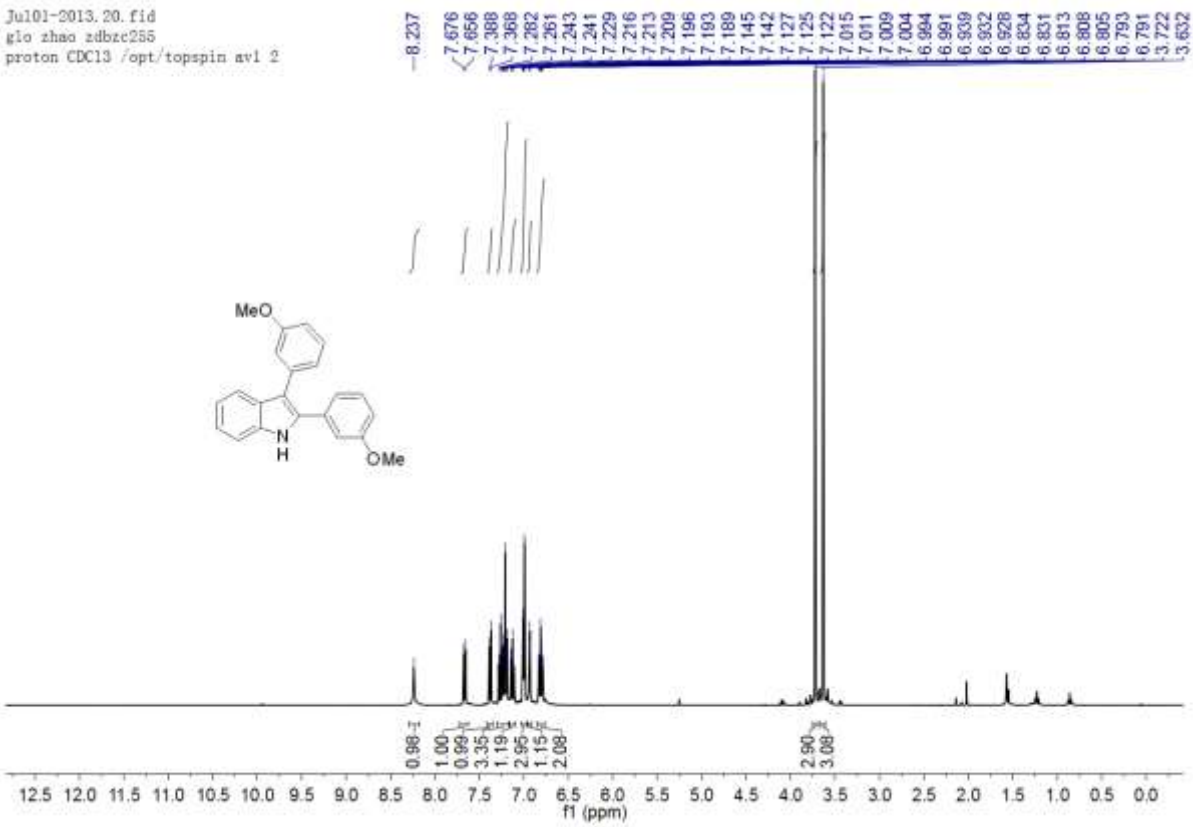

Sep09-2013.41.fid
glo zhao zdb zd 68
carbon CDCl3 /opt/top
137.582
135.212
133.668
131.649
130.102
129.048
128.992
128.847
128.621
128.307
127.156
125.659
125.567
120.808
115.650
111.890
103.667
77.477
77.160
76.843
NC
Ph
Ph
N
H
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

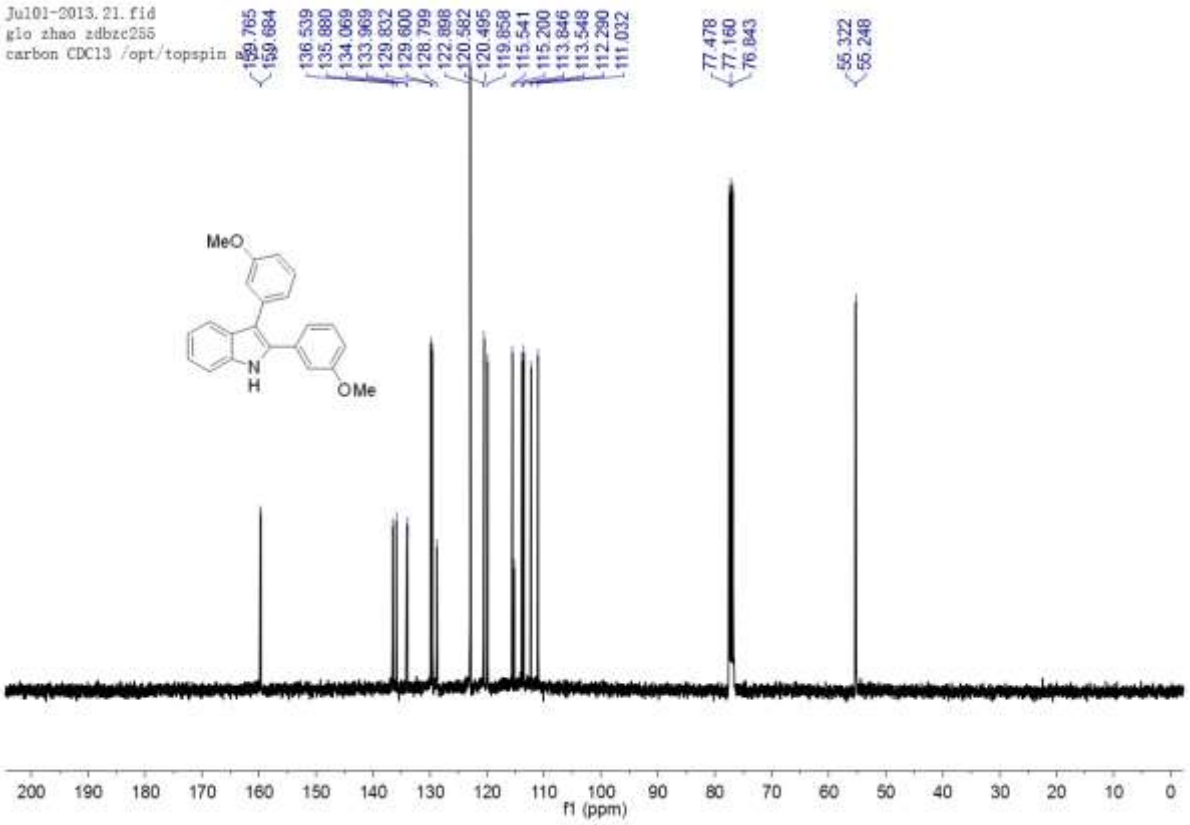

Sep09-2013.50.fid
glo zhao zdb zd 89
proton CDCl3 /opt/topspin av1 60
8.125
7.683
7.663
7.396
7.376
7.351
7.330
7.325
7.304
7.240
7.219
7.200
7.181
7.159
7.157
7.139
7.134
7.119
7.114
2.395
2.348
0.96
1.00
5.16
6.57
2.94
3.19
f1 (ppm)

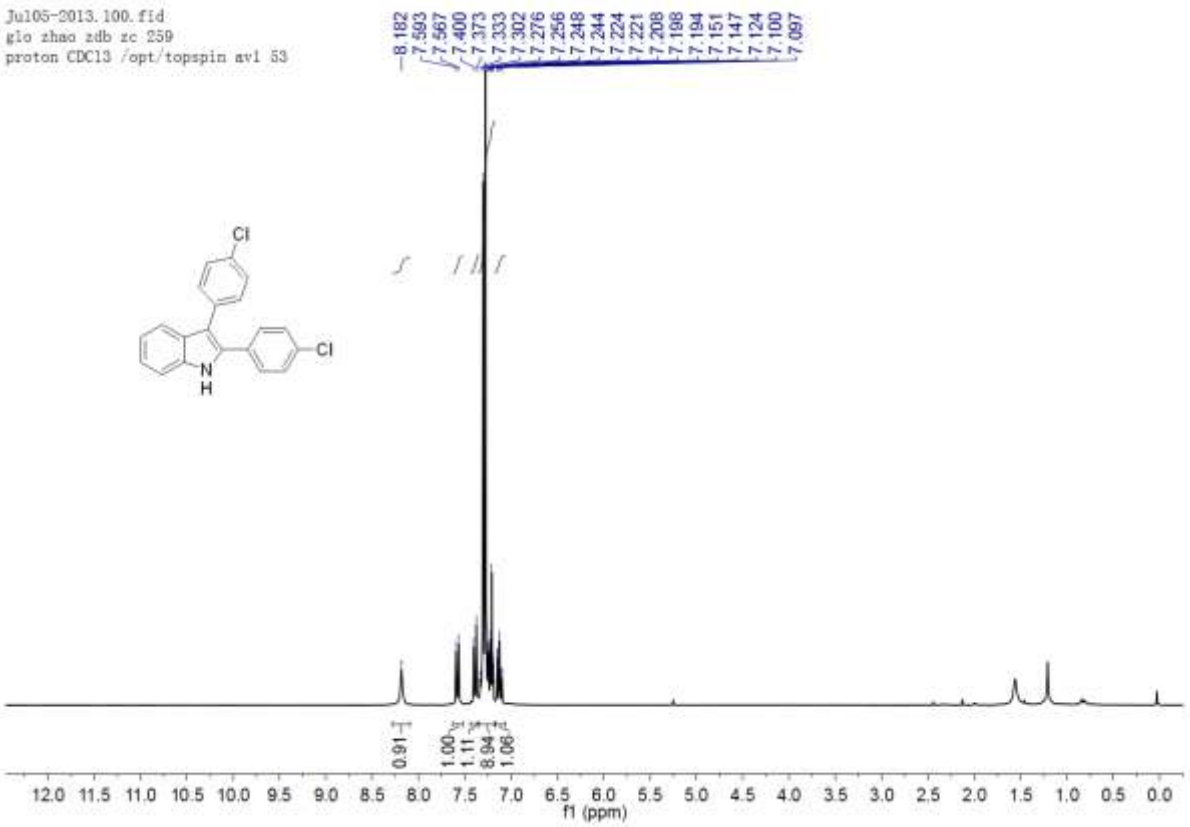

Sep09-2013.51.fid
glo zhao zdb zd 89
carbon CDCl3 /opt/topspin av1
137.598
135.907
135.798
134.136
132.249
130.094
130.017
129.503
129.373
129.017
128.102
122.566
120.375
119.759
114.631
110.913
77.478
77.160
76.842
21.395
f1 (ppm)

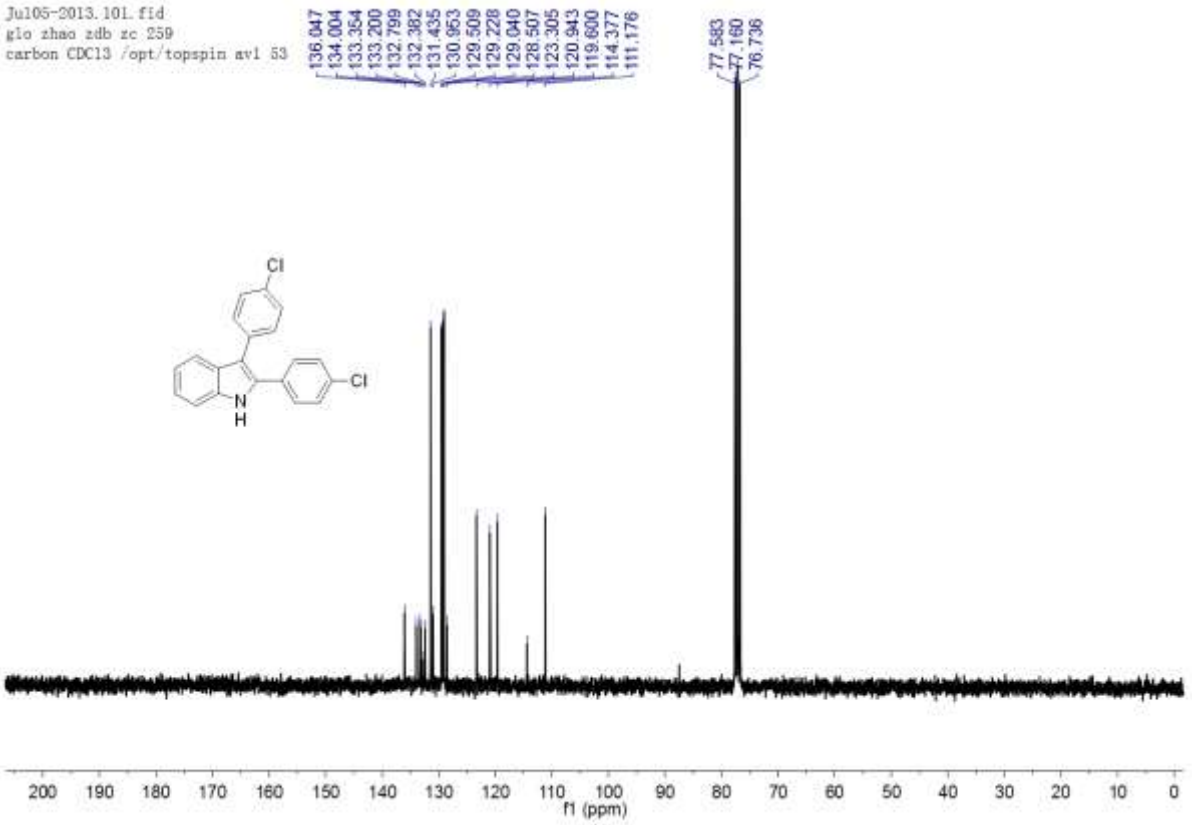

Jun20-2013.380.fid
glo zhao zdb zc 22 b
proton CDCl3 /opt/topspin av1 26
8.235
7.681
7.655
7.413
7.396
7.388
7.379
7.368
7.357
7.350
7.340
7.260
7.236
7.211
7.184
7.158
7.134
6.975
6.946
6.886
6.857
3.867
3.820
OMe
OMe
N
H
0.97
1.00
5.09
1.96
2.08
2.12
3.09
3.11
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 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
f1 (ppm)

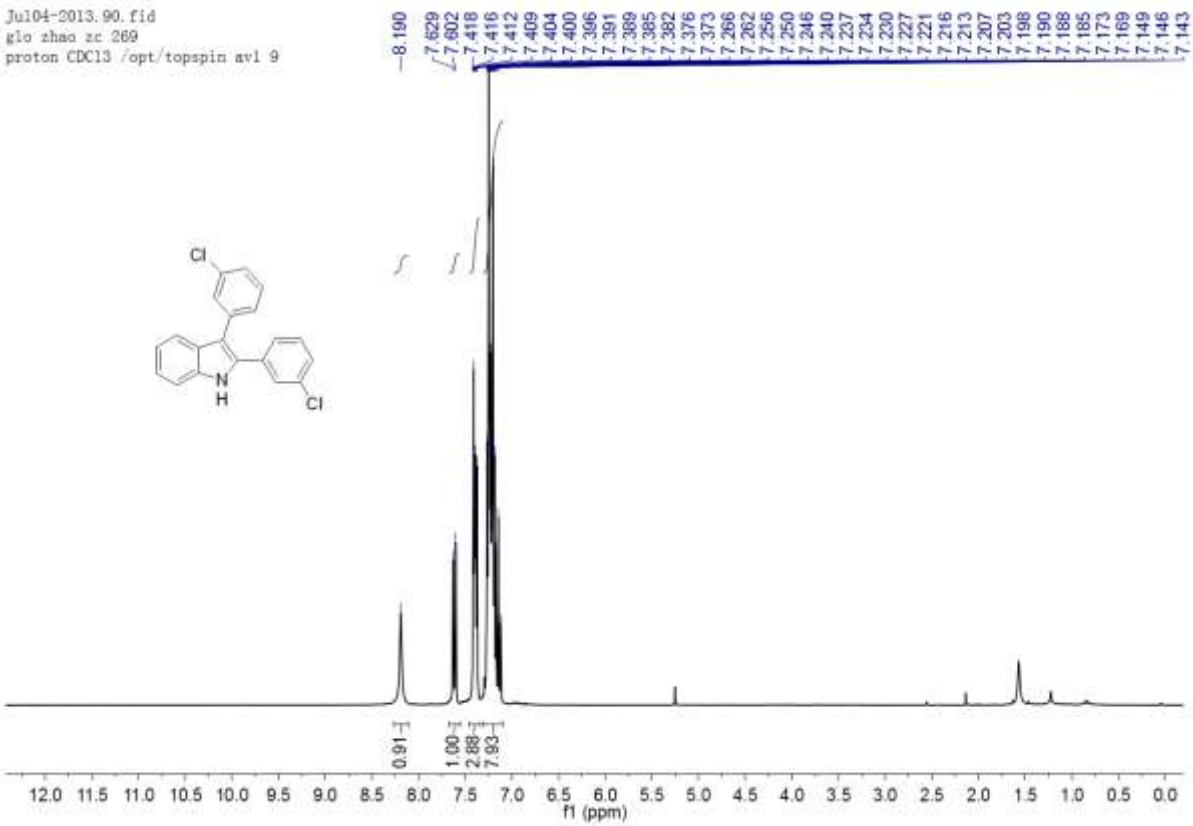

Jun20-2013.331.fid
glo zhao zdb zc 22 b
carbon CDCl3 /opt/topspin av1
159.169
158.106
135.818
133.860
131.257
129.435
129.077
127.686
125.416
122.374
120.288
119.515
114.221
114.124
113.803
110.869
77.583
77.160
76.736
55.359
55.336
OMe
OMe
N
H
f1 (ppm)

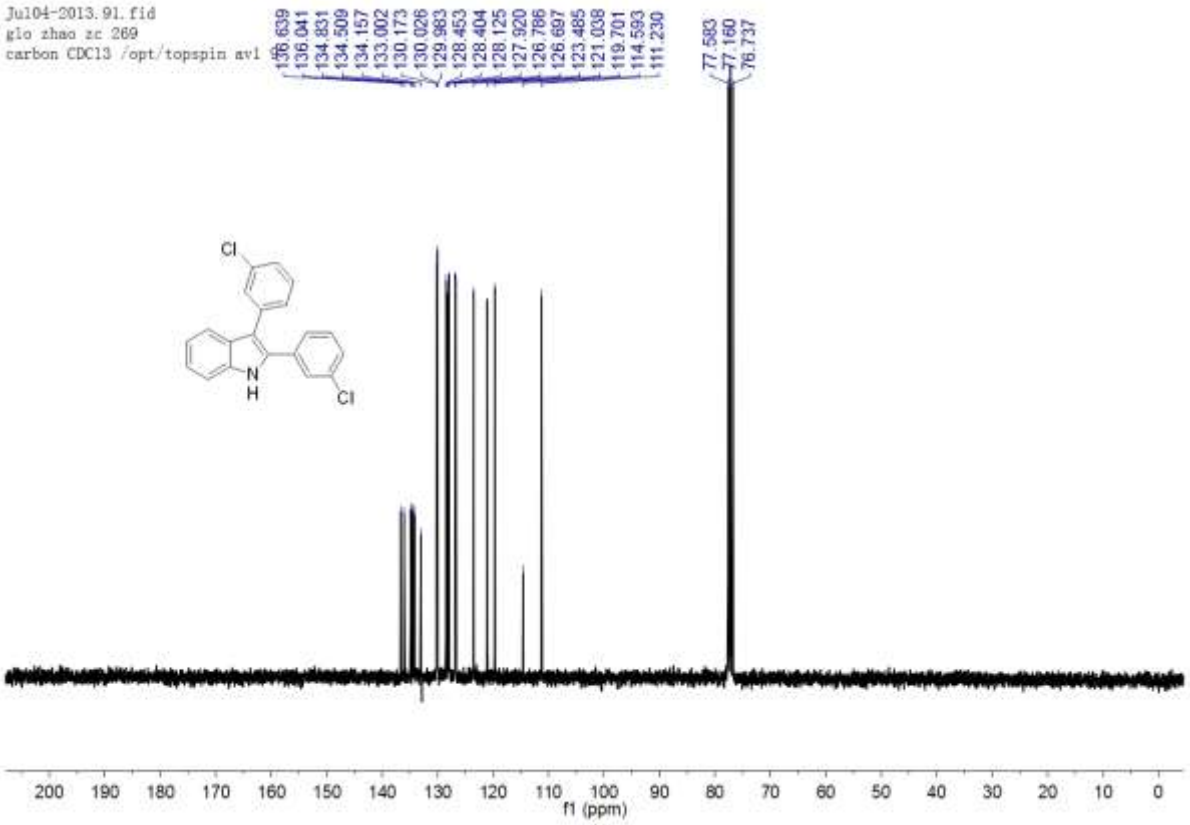

Jul01-2013.20.fid
glo zhao zdbzc255
proton CDCl3 /opt/topspin av1 2
8.237
7.676
7.656
7.388
7.368
7.282
7.261
7.243
7.241
7.229
7.216
7.213
7.209
7.196
7.193
7.189
7.145
7.142
7.127
7.125
7.122
7.015
7.011
7.009
7.004
6.994
6.991
6.939
6.932
6.928
6.834
6.831
6.813
6.808
6.805
6.793
6.791
3.722
3.632
MeO
N
H
OMe
0.98
1.00
0.99
3.35
1.19
2.95
1.15
2.08
2.90
3.08
f1 (ppm)

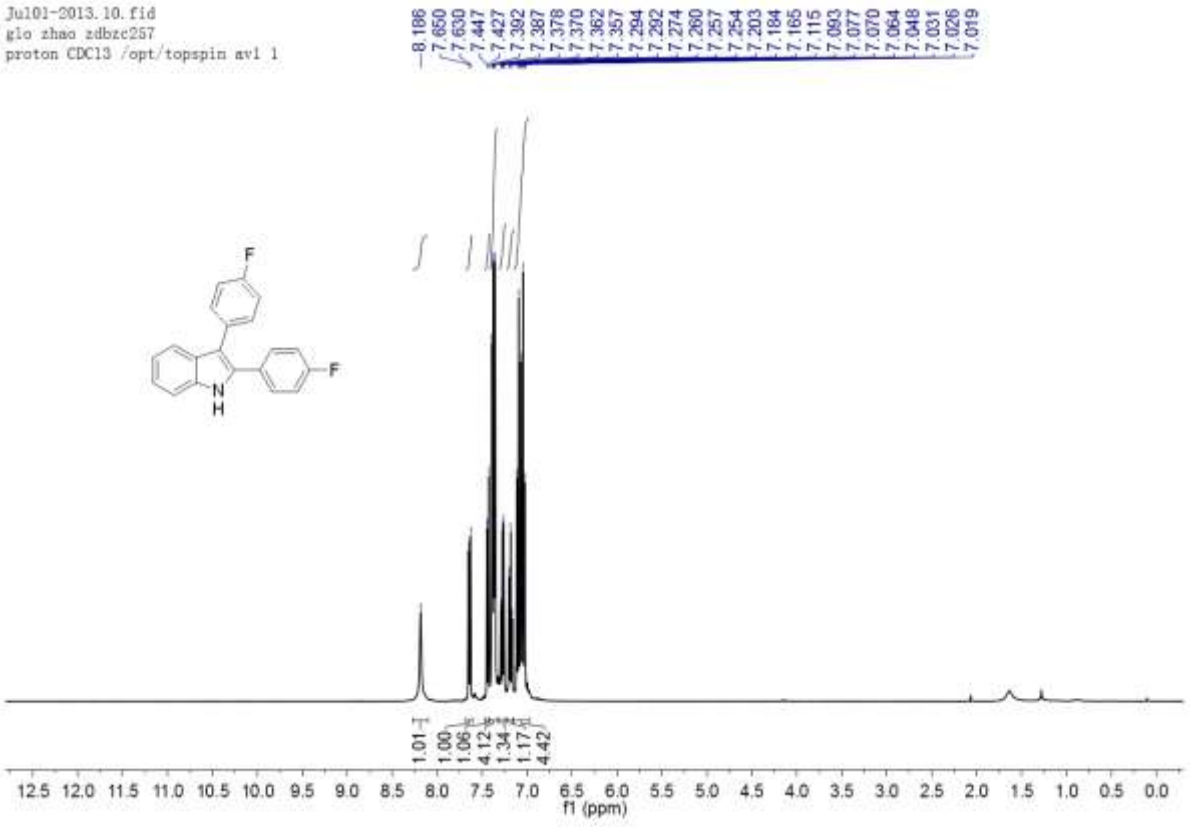

Jul01-2013.21.fid
glo zhao zdbzc255
carbon CDCl3 /opt/topspin
159.765
159.684
136.539
135.880
134.069
133.969
129.832
129.600
128.799
122.898
120.582
120.495
119.858
115.541
115.200
113.846
113.548
112.290
111.032
77.478
77.160
76.843
55.322
55.248
MeO
N
H
OMe
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

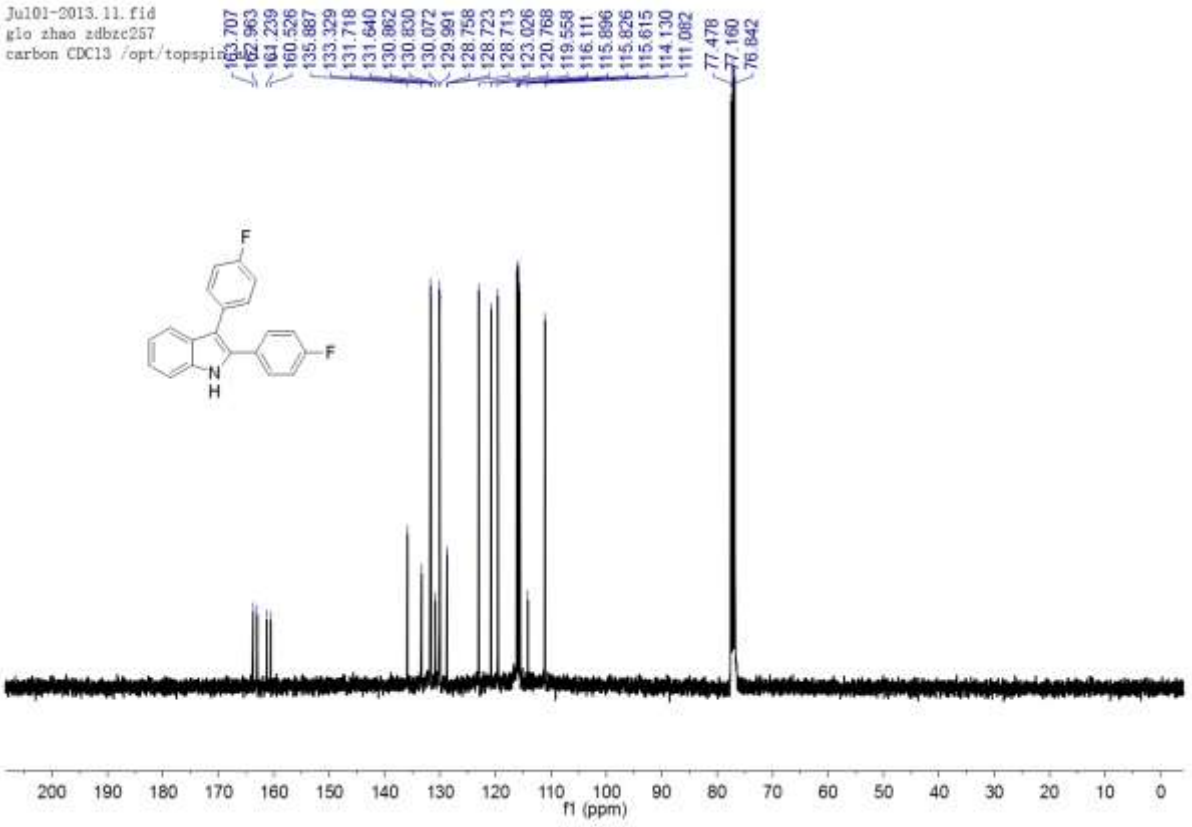

Jul05-2013.100.fid
glo zhao zdb zc 259
proton CDCl3 /opt/topspin av1 53
8.182
7.593
7.567
7.400
7.373
7.333
7.302
7.276
7.256
7.248
7.244
7.224
7.221
7.208
7.198
7.194
7.151
7.147
7.124
7.100
7.097
Cl
Cl
N
H
0.91
1.00
1.11
8.94
1.06
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

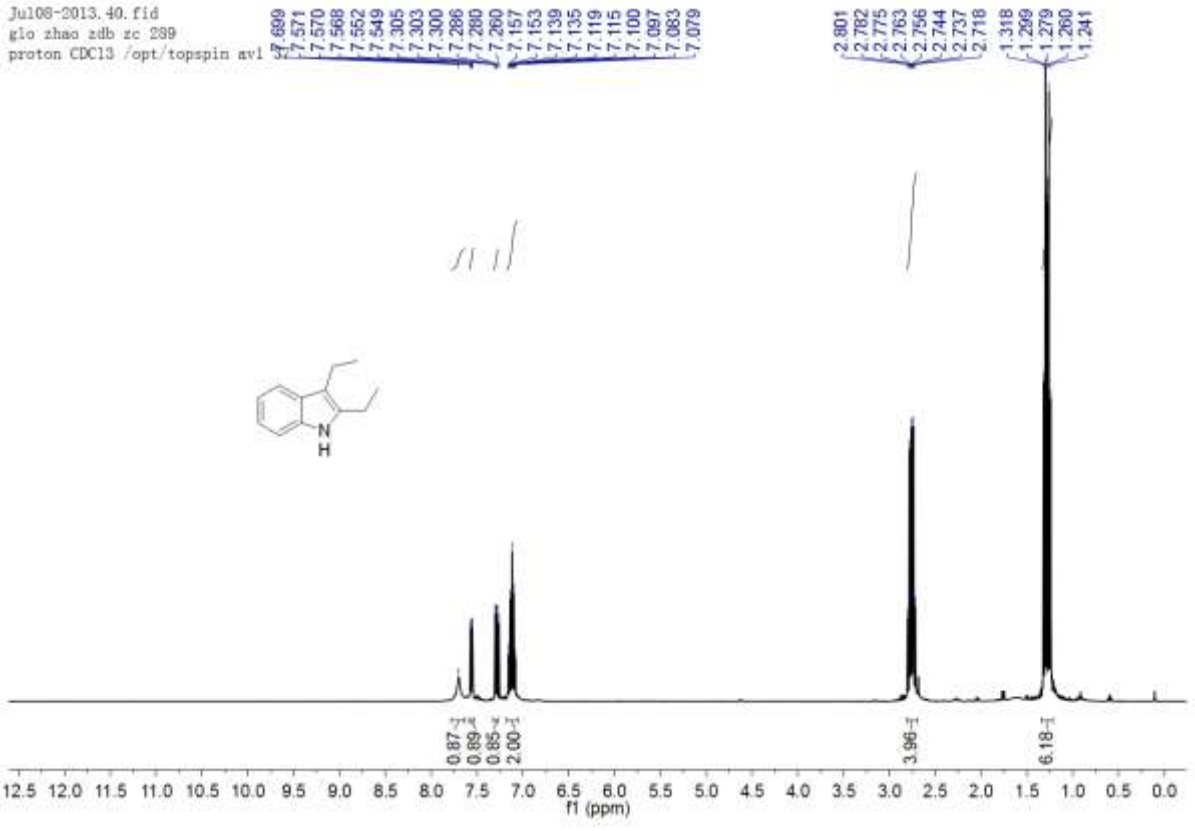

Jul05-2013.101.fid
glo zhao zdb zc 259
carbon CDCl3 /opt/topspin av1 53
136.047
134.004
133.354
133.200
132.799
132.382
131.435
130.953
129.509
129.228
129.040
128.507
123.305
120.943
119.600
114.377
111.176
77.583
77.160
76.736
Cl
Cl
N
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

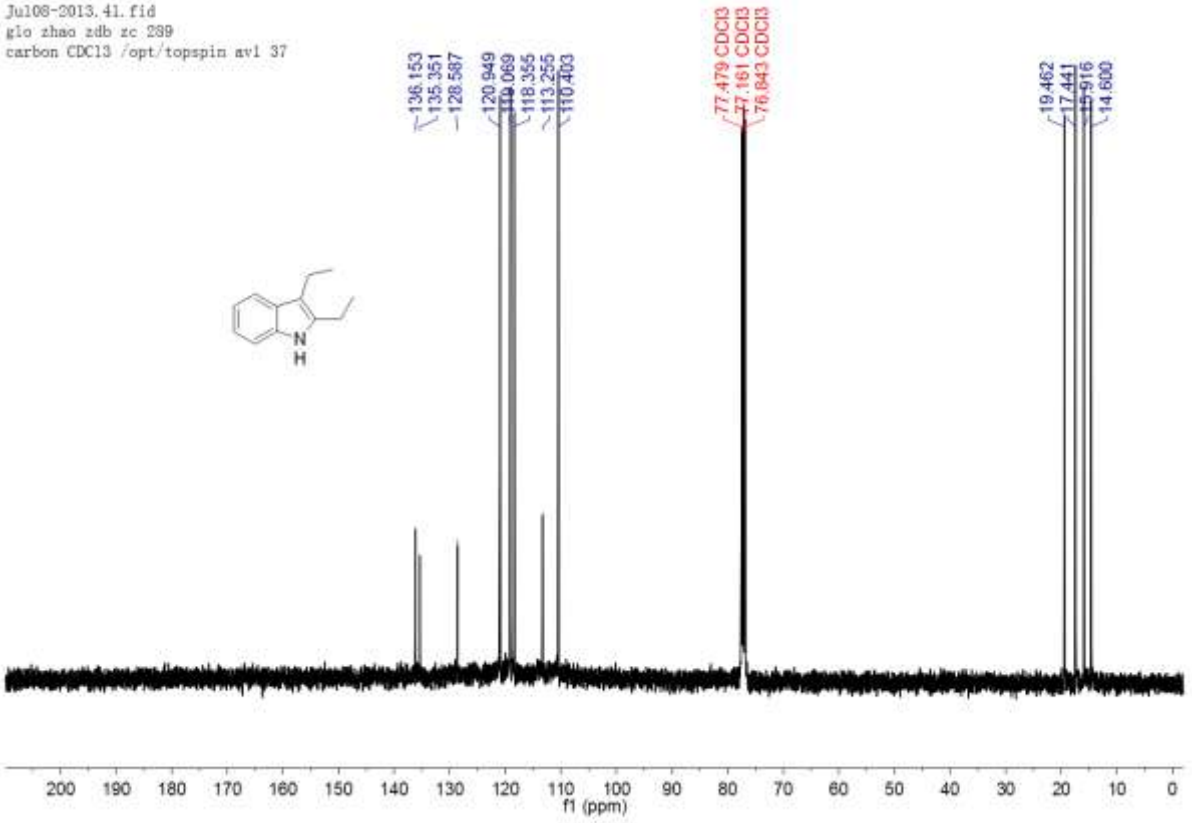

Jul04-2013.90.fid
glo zhao zc 269
proton CDCl3 /opt/topspin av1 9
8.190
7.629
7.602
7.418
7.416
7.412
7.409
7.404
7.400
7.396
7.391
7.389
7.385
7.382
7.376
7.373
7.266
7.262
7.256
7.250
7.246
7.240
7.237
7.234
7.230
7.227
7.221
7.216
7.213
7.207
7.203
7.198
7.190
7.188
7.185
7.173
7.169
7.149
7.146
7.143
Cl
Cl
N
H
0.91
1.00
2.88
7.93
12.0 11.5 11.0 10.5 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
f1 (ppm)

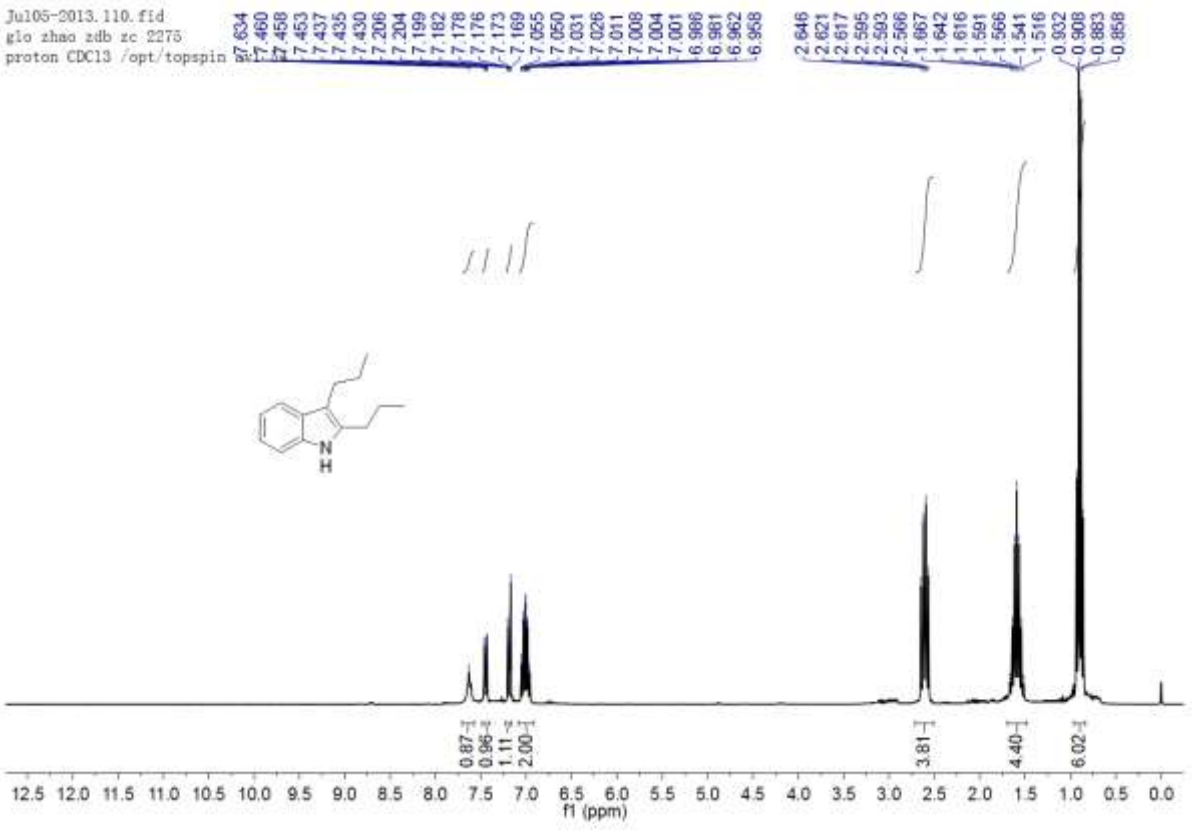

Jul04-2013.91.fid
glo zhao zc 269
carbon CDCl3 /opt/topspin av1
136.639
136.041
134.831
134.509
134.157
133.002
130.173
130.026
129.983
128.453
128.404
128.125
127.920
126.786
126.697
123.485
121.038
119.701
114.593
111.230
77.583
77.160
76.737
Cl
N
H
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

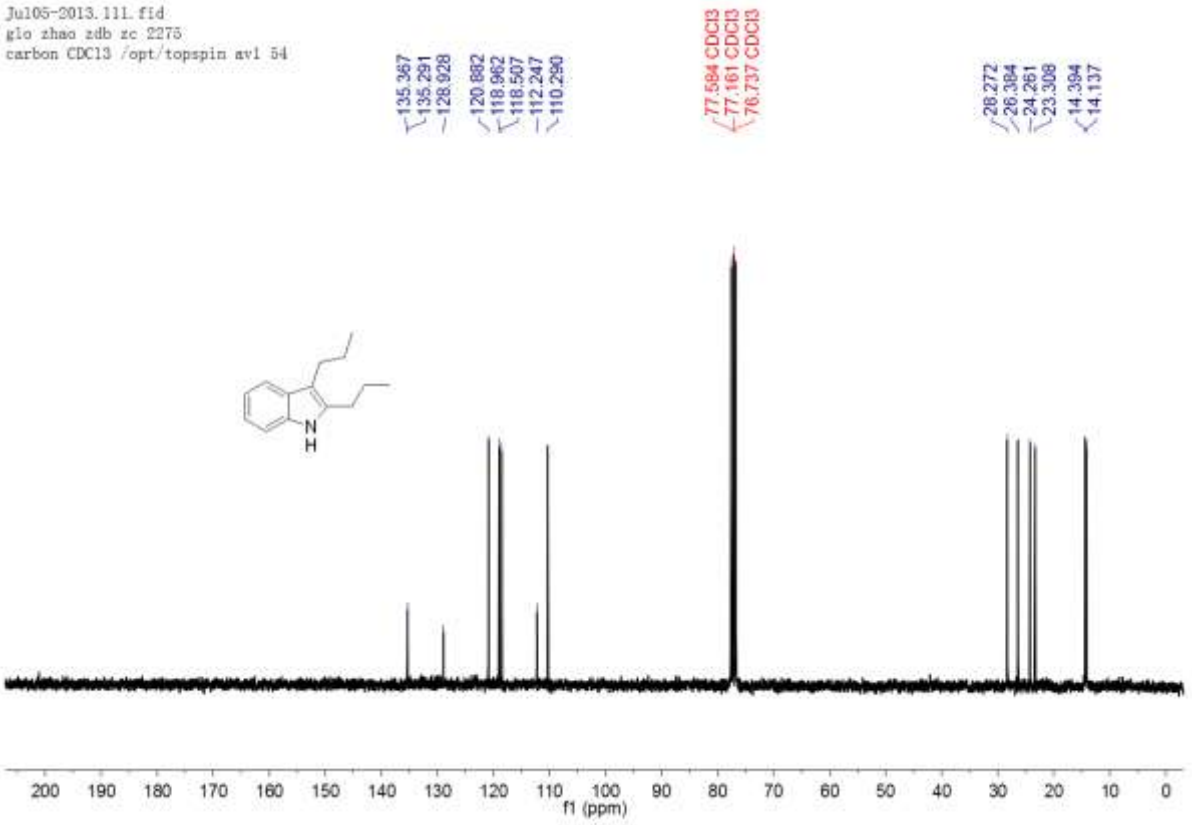

Jul01-2013.10.fid
glo zhao zdbzc257
proton CDCl3 /opt/topspin av1 1
8.186
7.650
7.630
7.447
7.427
7.392
7.387
7.378
7.370
7.362
7.357
7.294
7.292
7.274
7.260
7.257
7.254
7.203
7.184
7.165
7.115
7.093
7.077
7.070
7.064
7.048
7.031
7.026
7.019
F
N
H
F
1.01
1.00
1.06
4.12
1.34
1.17
4.42
12.5 12.0 11.5 11.0 10.5 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
f1 (ppm)

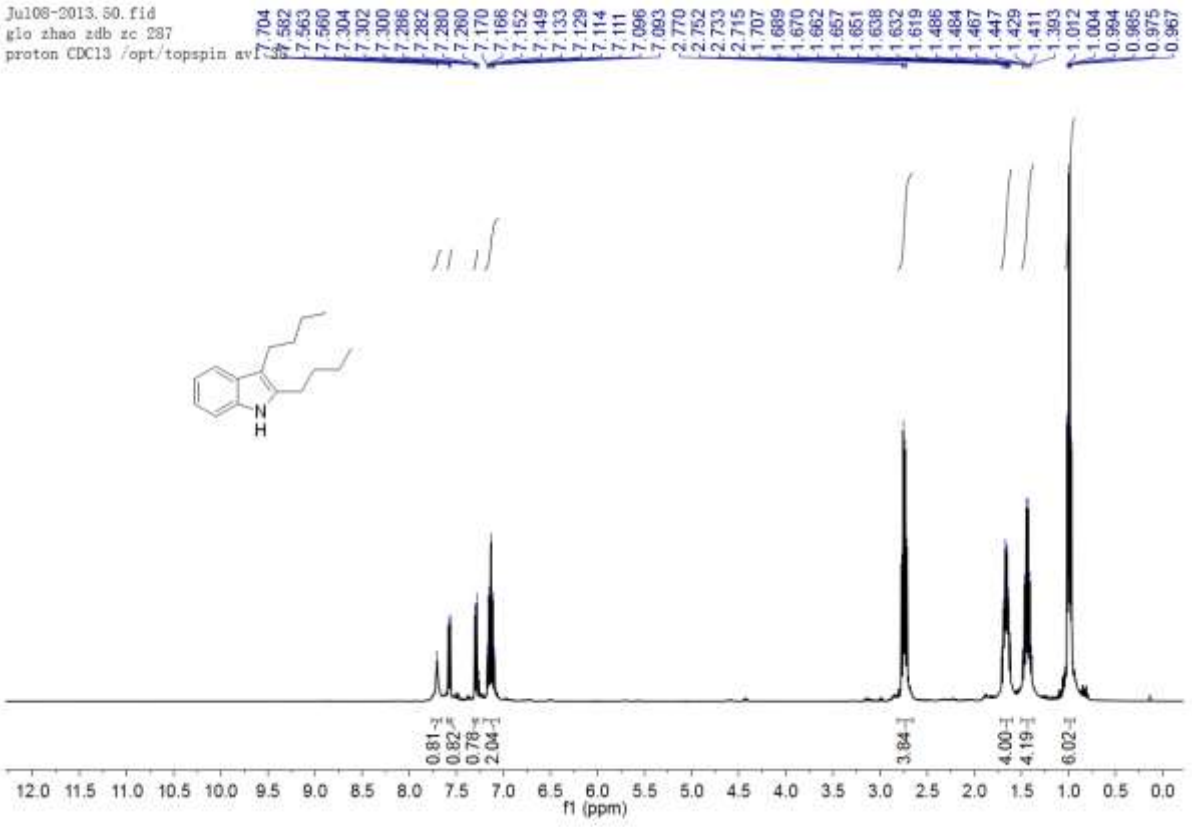

Jul01-2013.11.fid
glo zhao zdbzc257
carbon CDCl3 /opt/topspin
163.707
162.963
161.239
160.526
135.887
133.329
131.718
131.640
130.862
130.830
130.072
129.991
128.758
128.723
128.713
123.026
120.768
119.558
116.111
115.896
115.826
115.615
114.130
111.082
77.478
77.160
76.842
F
F
N
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

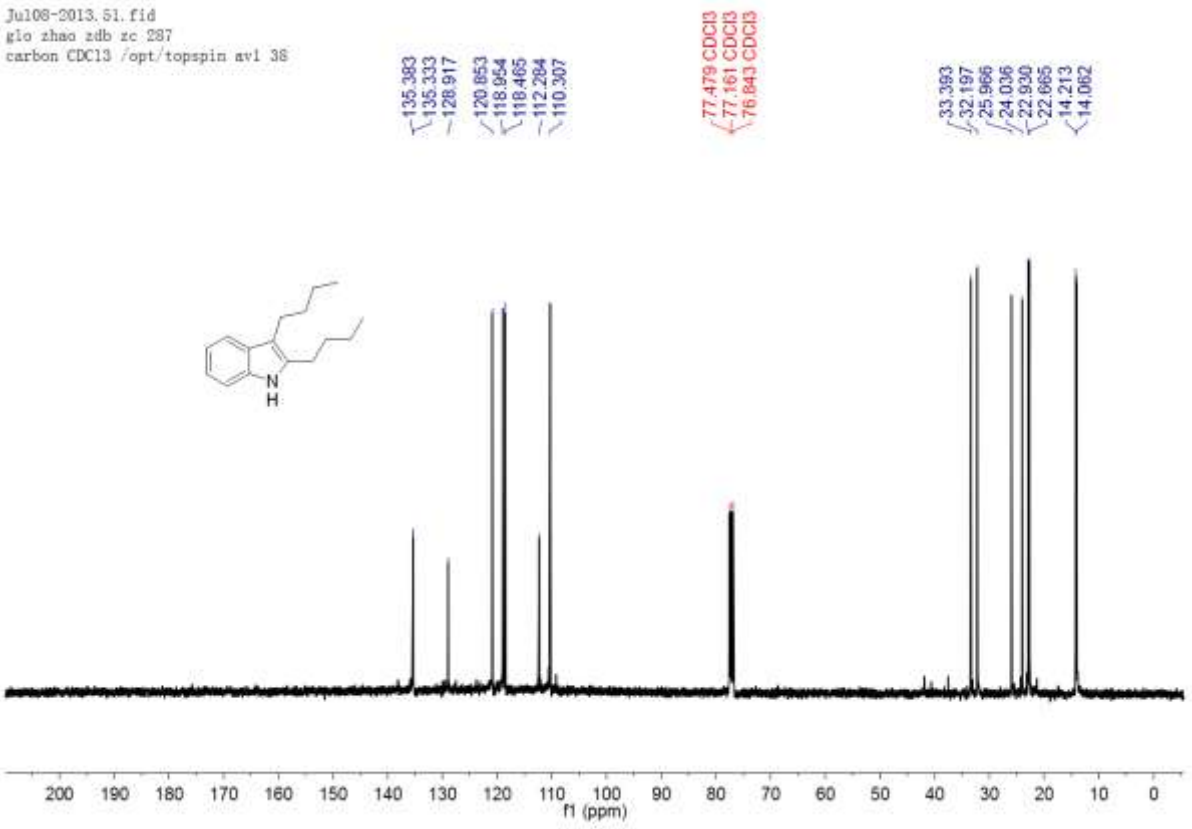

Jul08-2013.40.fid
glo zhao zdb zc 289
proton CDCl3 /opt/topspin av1
7.699
7.571
7.570
7.568
7.552
7.549
7.305
7.303
7.300
7.286
7.280
7.260
7.157
7.153
7.139
7.135
7.119
7.115
7.100
7.097
7.083
7.079
2.801
2.782
2.775
2.763
2.756
2.744
2.737
2.718
1.318
1.299
1.279
1.260
1.241
N
H
0.87
0.89
0.85
2.00
3.96
6.18
12.5 12.0 11.5 11.0 10.5 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
f1 (ppm)

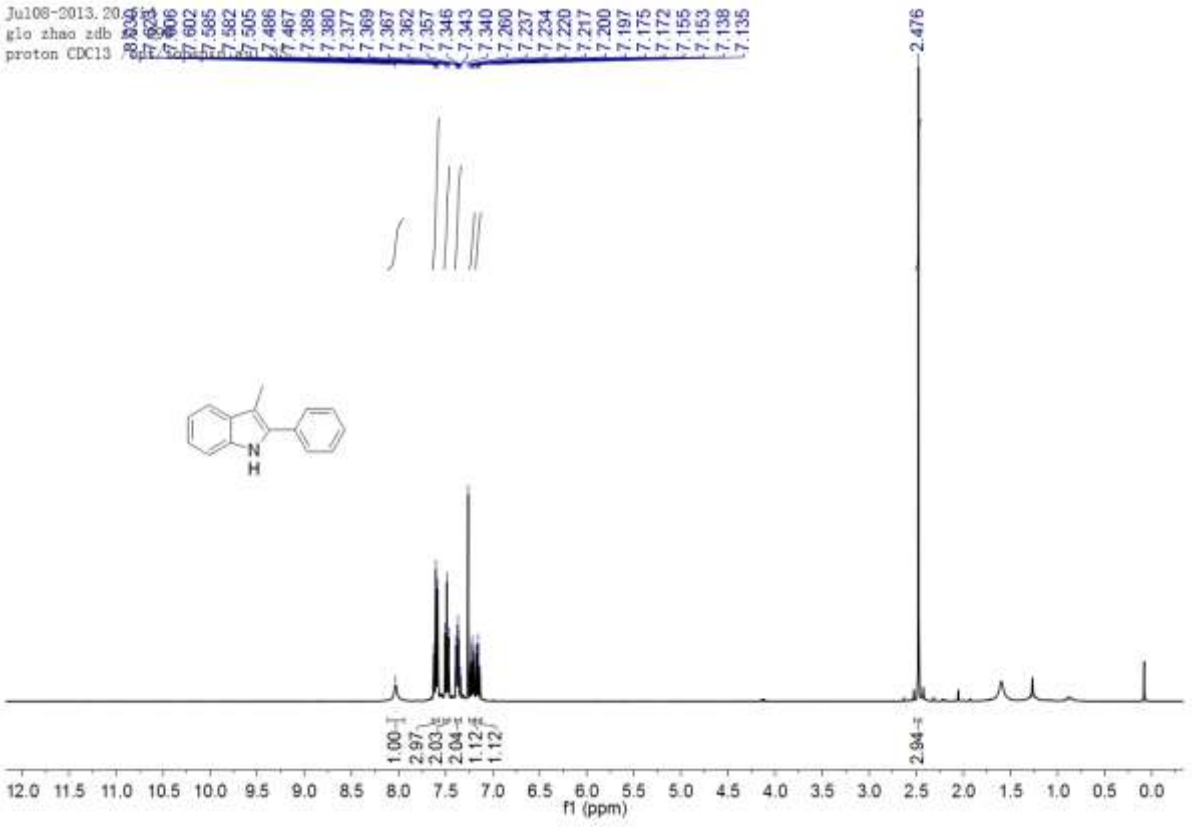

Jul08-2013.41.fid
glo zhao zdb zc 289
carbon CDCl3 /opt/topspin av1 37
136.153
135.351
128.587
120.949
119.069
118.355
113.255
110.403
77.479 CDCl3
77.161 CDCl3
76.843 CDCl3
19.462
17.441
15.916
14.600
N
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

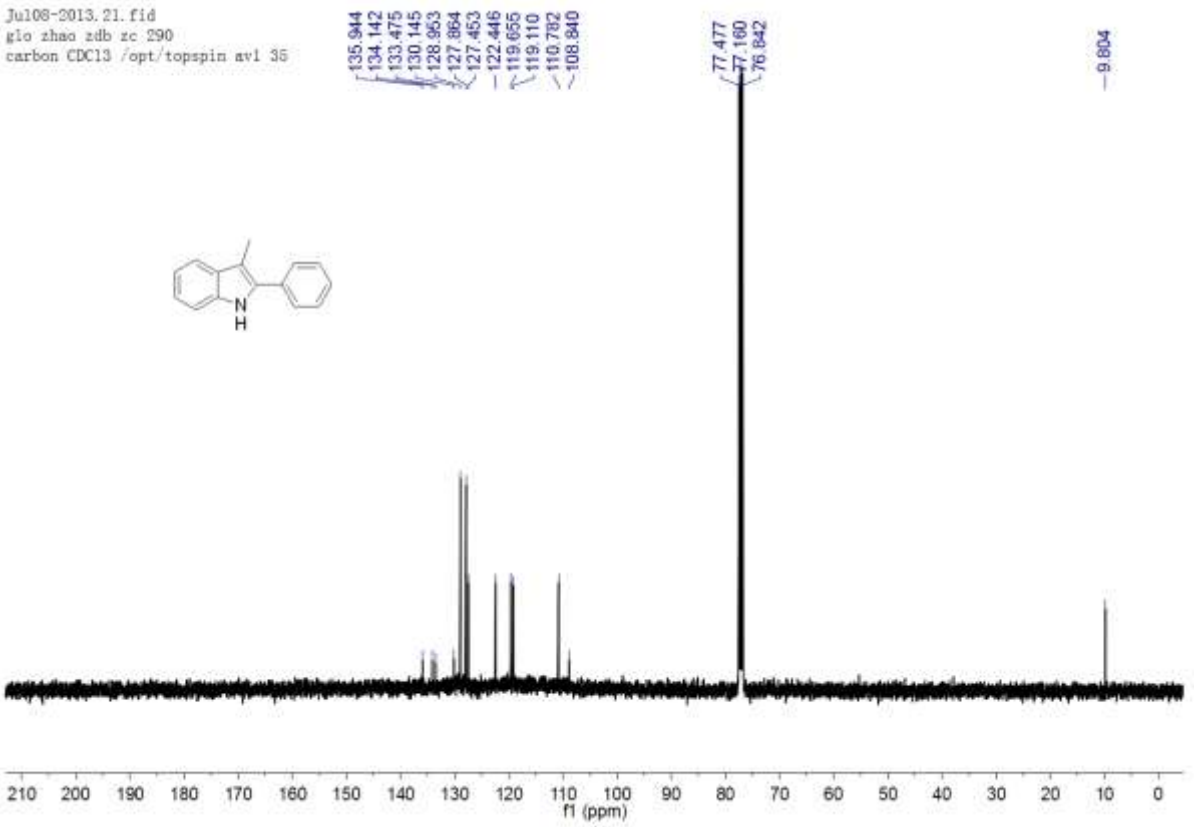

Jul05-2013.110.fid
glo zhao zdb zc 2275
proton CDCl3 /opt/topspin
7.634
7.460
7.458
7.453
7.437
7.435
7.430
7.206
7.204
7.199
7.182
7.178
7.176
7.173
7.169
7.055
7.050
7.031
7.026
7.011
7.008
7.004
7.001
6.986
6.981
6.962
6.958
2.646
2.621
2.617
2.595
2.593
2.566
1.667
1.642
1.616
1.591
1.566
1.541
1.516
0.932
0.908
0.883
0.858
N
H
0.87
0.96
1.11
2.00
3.81
4.40
6.02
12.5 12.0 11.5 11.0 10.5 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
f1 (ppm)

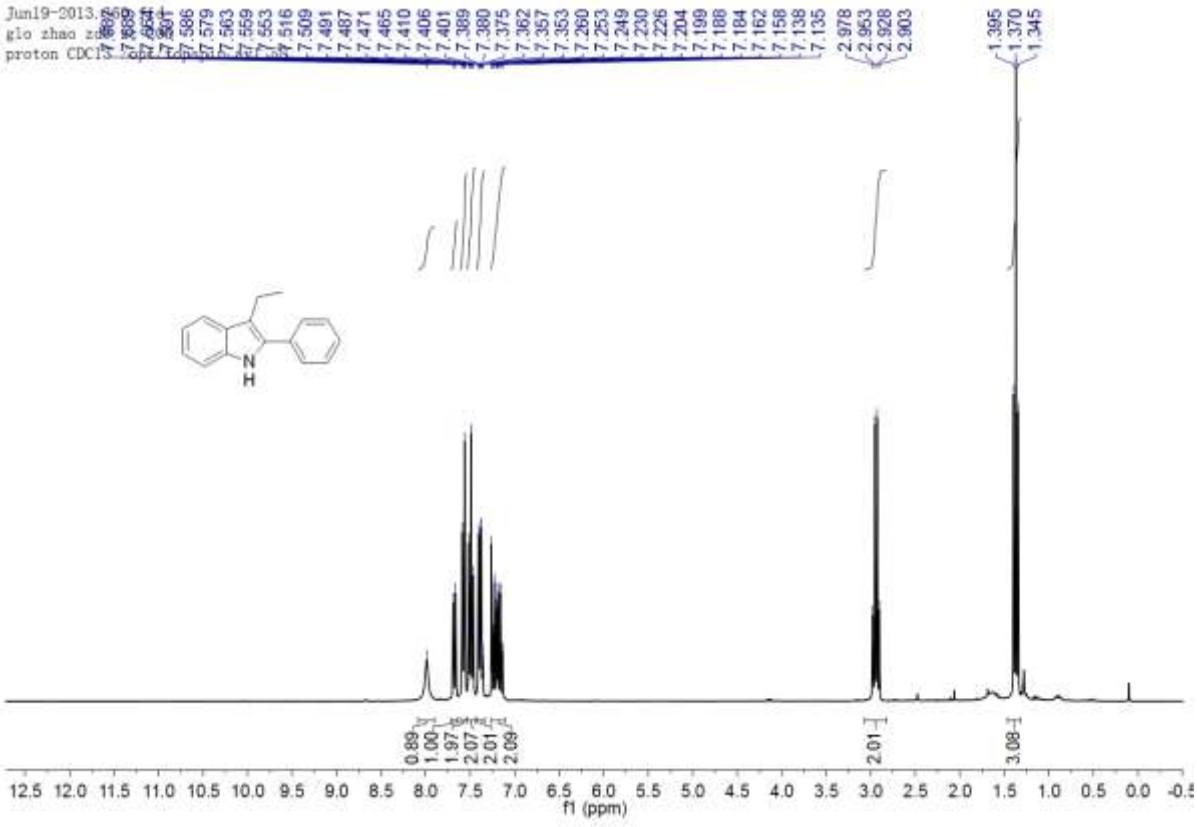

Jul05-2013.111.fid
glo zhao zdb zc 2275
carbon CDCl3 /opt/topspin av1 54
135.367
135.291
128.928
120.882
118.962
118.507
112.247
110.290
77.584 CDCl3
77.161 CDCl3
76.737 CDCl3
28.272
26.384
24.261
23.308
14.394
14.137
f1 (ppm)

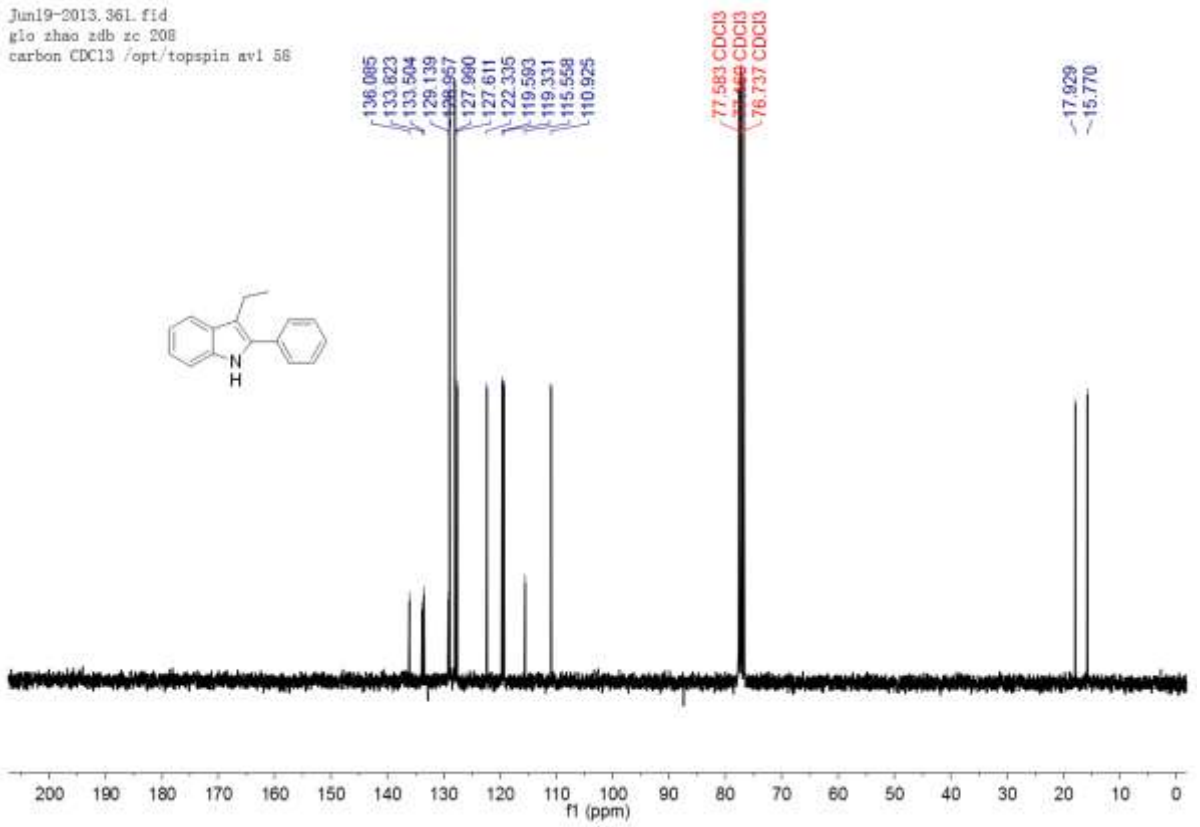

Jul08-2013.50.fid
glo zhao zdb zc 287
proton CDCl3 /opt/topspin av1
7.704
7.582
7.563
7.560
7.304
7.302
7.300
7.286
7.282
7.280
7.260
7.170
7.166
7.152
7.149
7.133
7.129
7.114
7.111
7.096
7.093
2.770
2.752
2.733
2.715
1.707
1.689
1.670
1.662
1.657
1.651
1.638
1.632
1.619
1.486
1.484
1.467
1.447
1.429
1.411
1.393
1.012
1.004
0.994
0.985
0.975
0.967
0.81
0.82
0.78
2.04
3.84
4.00
4.19
6.02
f1 (ppm)

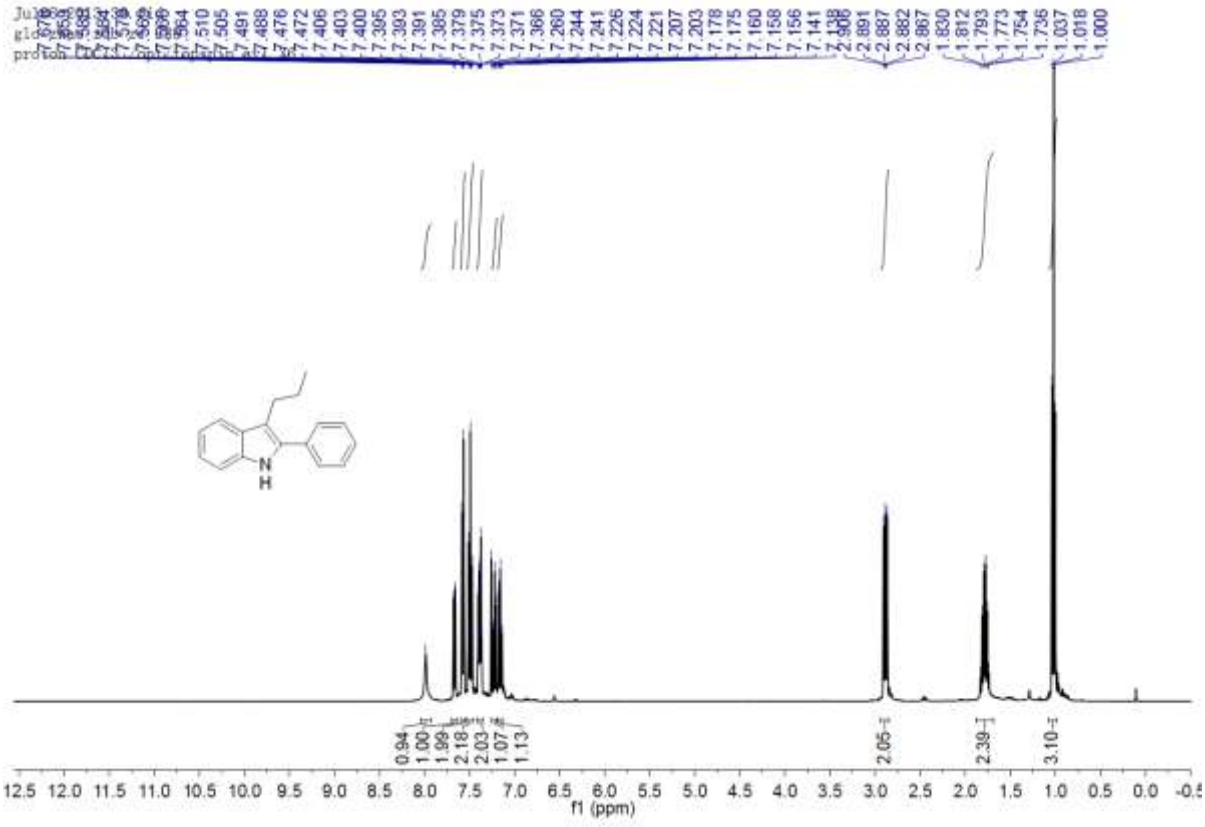

Jul08-2013.51.fid
glo zhao zdb zc 287
carbon CDCl3 /opt/topspin av1 38
135.383
135.333
128.917
120.853
118.954
118.465
112.284
110.307
77.479 CDCl3
77.161 CDCl3
76.843 CDCl3
33.393
32.197
25.966
24.036
22.930
22.665
14.213
14.062
N
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

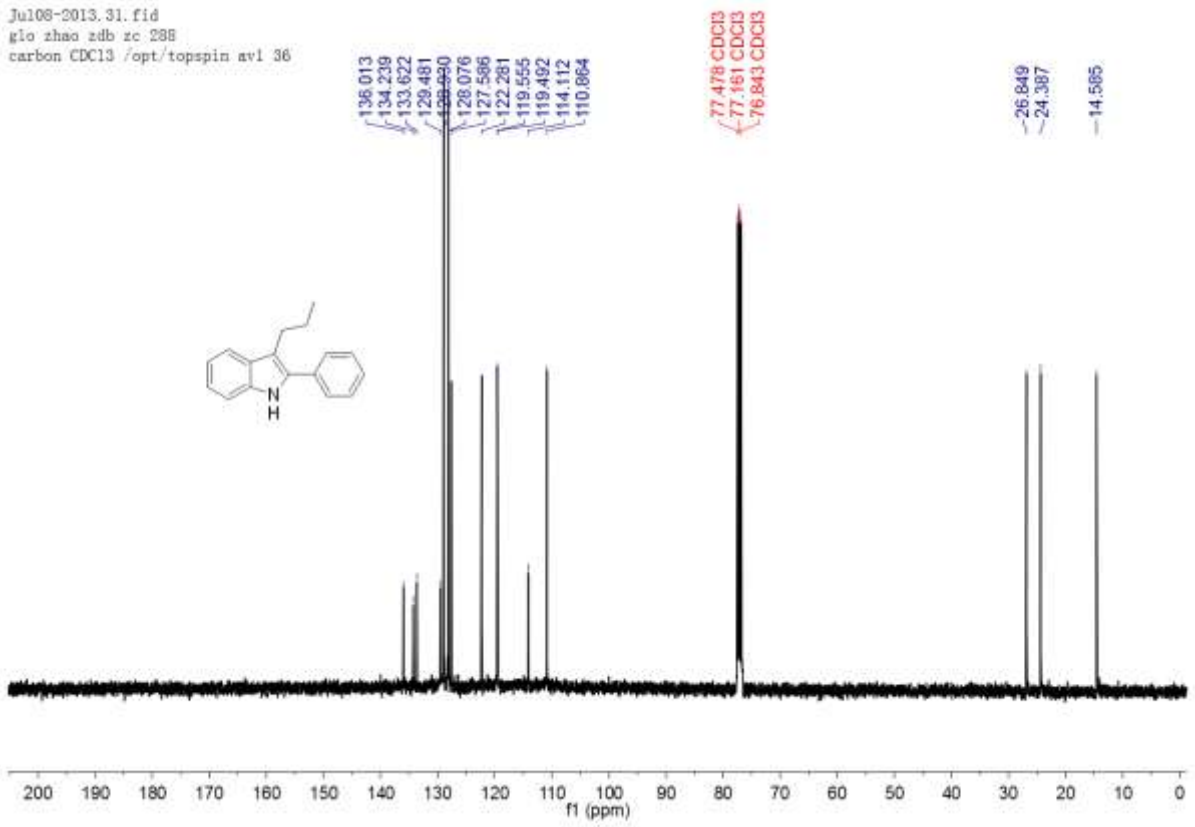

Jul08-2013.20
glo zhao zdb
proton CDCl3
7.606
7.602
7.585
7.582
7.505
7.486
7.467
7.389
7.380
7.377
7.369
7.367
7.362
7.357
7.346
7.343
7.340
7.260
7.237
7.234
7.220
7.217
7.200
7.197
7.175
7.172
7.155
7.153
7.138
7.135
2.476
N
H
1.00
2.97
2.03
2.04
1.12
1.12
2.94
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 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
f1 (ppm)

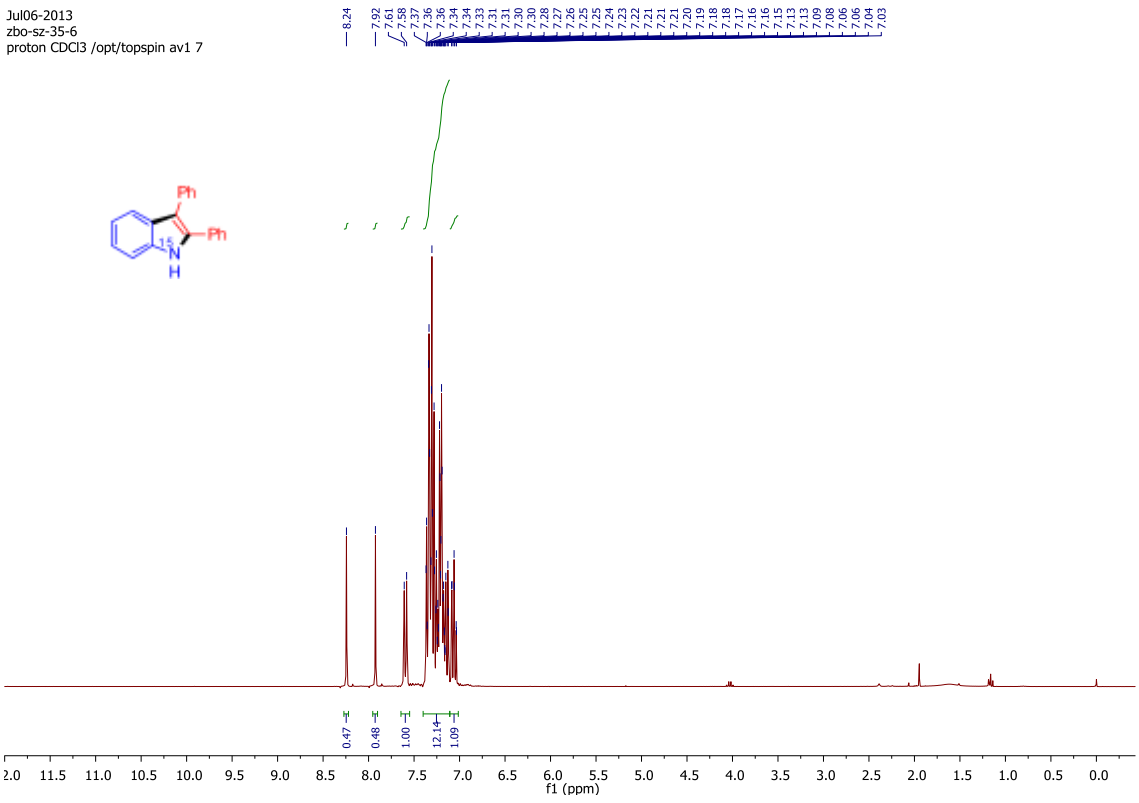

Jul08-2013.21.fid
glo zhao zdb zc 290
carbon CDCl3 /opt/topspin av1 35
135.944
134.142
133.475
130.145
128.953
127.864
127.453
122.446
119.655
119.110
110.782
108.840
77.477
77.160
76.842
9.804
N
H
f1 (ppm)


Jun19-2013.
glo zhao zd
proton CDCl3
7.586
7.579
7.563
7.559
7.553
7.516
7.509
7.491
7.487
7.471
7.465
7.410
7.406
7.401
7.389
7.380
7.375
7.362
7.357
7.353
7.260
7.253
7.249
7.230
7.226
7.204
7.199
7.188
7.184
7.162
7.158
7.138
7.135
2.978
2.953
2.928
2.903
1.395
1.370
1.345
N
H
0.89
1.00
1.97
2.07
2.01
2.09
2.01
3.08
f1 (ppm)


Jun19-2013.361.fid
glo zhao zdb zc 208
carbon CDCl3 /opt/topspin av1 58
136.085
133.823
133.504
129.139
128.957
127.980
127.611
122.335
119.593
119.331
115.558
110.925
77.583 CDCl3
77.266 CDCl3
76.737 CDCl3
17.929
15.770
f1 (ppm)


0.94
1.00
1.99
2.18
2.03
1.07
1.13
2.05
2.39
3.10
f1 (ppm)


Jul08-2013.31.fid
glo zhao zdb zc 288
carbon CDCl3 /opt/topspin av1 36
136.013
134.239
133.622
129.481
128.930
128.076
127.586
122.281
119.555
119.492
114.112
110.864
77.478 CDCl3
77.161 CDCl3
76.843 CDCl3
26.849
24.387
14.565
N
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Jul06-2013
zbo-sz-35-6
proton CDCl3 /opt/topspin av1 7
8.24
7.92
7.91
7.88
7.37
7.36
7.36
7.34
7.34
7.33
7.31
7.31
7.30
7.30
7.28
7.27
7.26
7.25
7.25
7.24
7.23
7.22
7.21
7.21
7.21
7.20
7.19
7.18
7.18
7.17
7.16
7.16
7.15
7.13
7.13
7.09
7.08
7.06
7.06
7.04
7.03
Ph
Ph
N
H
0.47
0.48
1.00
12.14
1.09
2.0 11.5 11.0 10.5 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
f1 (ppm)

Jul07-2013
ZBO-SZ-35-6
carbon CDCl3 /opt/topspin av1 51

135.97
135.77
133.07
131.14
130.95
132.71
130.15
128.65
128.49
128.16
127.66
126.21
122.70
122.67
120.41
119.69
115.04
110.87

77.42
77.00
76.58