Supporting Information

A Concise Protocol for the Synthesis of 2-Alkenylindoles through [4+1] Annulation of Aminobenzyl Phosphonium Salts with Acrylaldehydes

Jia-Cheng Yang,[a,†] Mao-Lin Liao,[a,†] Ping-Gui Li*,[b] and Liang-Hua Zou*,[a,c]

[a] Key Laboratory of Carbohydrate Chemistry and Biotechnology, Ministry of Education; School of Life Science and Health Engineering, Jiangnan University, Wuxi 214122, P.R. China

[b] School of Environmental Engineering, Wuxi University, Wuxi 214105, P.R. China

[c] School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang 453007, P.R. China

* Correspondence: lipg@cwxu.edu.cn; zoulianghua@jiangnan.edu.cn

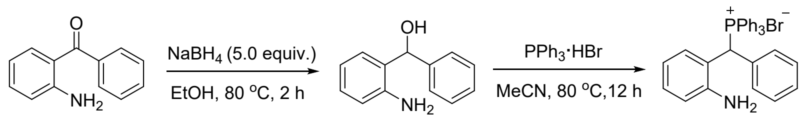
† These authors contributed equally to this work.

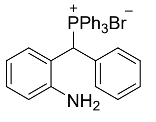
Contents

1. General Information

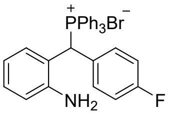
All solvents were dried over molecular sieves. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Aminobenzyl phosphonium salts **1a-1g** were synthesized according to the reference.[1] The products were isolated by column chromatography on silica gel (200-300 mesh) by using petroleum ether (PE, 30-60 °C) and ethyl acetate (EA) as eluents. Silica gel for column chromatography was purchased from AnhuiLiangchen Chemical Co, Lt. All yields described herein are the isolated yields after column chromatography. Reaction progress and product mixtures were routinely monitored by TLC using TLC SiO_2 sheets, and compounds were visualized under ultraviolet light. ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker AVANCE III 400 spectrometer. The spectra were recorded using $CDCl_3$ or DMSO-d_6 as a solvent. ^1H NMR chemical shifts are referenced to tetramethylsilane (TMS, 0 ppm). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). High-Resolution Mass Spectra (HRMS) were recorded on Agilent 6540 or FTICR-MS bruker7 T. Melting points were measured with a melting point instrument (Shanghai Yidian Physical Optical Instrument Co., Ltd., SGW, X-4A) and were uncorrected.

2. Synthesis of Staring Materials 1a-1g

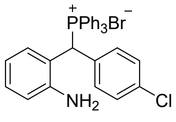




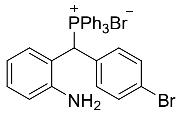
1a, 88%



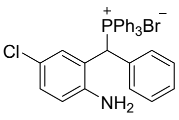
1b, 85%



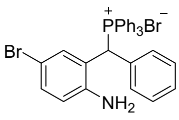
1c, 82%



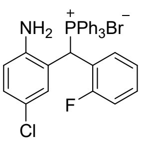
1d, 86%



1e, 88%



1f, 81%



1g, 89%

Take the synthesis of **1a** as one example. (2-aminophenyl)(phenyl)methanone (3.9 g, 20 mmol) was added in a round bottomed flask (250 mL) with a stirring bar, and dissolved in the solution of EtOH (60 mL). Next, $NaBH_4$ (3.8 g, 100 mmol) was added slowly at 0 ºC and refluxed at 80 ºC for 2 h. After the reaction was completed, the reaction was quenched by H_2O, extracted with EA (50 mL×5), and dried *via* anhydrous sodium sulfate. Then, the product was refluxed with triphenylphosphonium bromide (7.2 g, 20 mmol) in dry acetonitrile (50 mL) for 12 h. After cooling, the resulting precipitates were filtered and washed with ether, affording product **1a** as a white powder (8.2 g, 78% yield).[1]

Aminobenzyl phosphonium salt 1a

Compound **1a** was synthesized in accordance with the typical procedure as white powder (8.2 g, 78% yield) (m.p. 188.5-190.5 °C).

^1H NMR (400 MHz, DMSO-d_6) δ 7.92-7.87 (m, 3H), 7.73 (td, J = 7.9, 3.7 Hz, 7H), 7.64 (dd, J = 12.0, 7.5 Hz, 6H), 7.40-7.22 (m, 6H), 7.06 (t, J = 7.6 Hz, 1H), 6.79 (d, J = 8.2 Hz, 1H), 6.67-6.56 (m, 2H), 6.41-6.35 (m, 1H). HRMS m/z (ESI) calcd for $C_{31}H_{27}NP$ $(M)^+$ 444.1876, found

444.1886.

Aminobenzyl phosphonium salt 1b

Compound **1b** was synthesized in accordance with the typical procedure as a white powder (8.0 g, 74% yield) (m.p. 185.5-187.5 °C).

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.94-7.88 (m, 3H), 7.74 (td, *J* = 7.8, 3.7 Hz, 6H), 7.69-7.59 (m, 6H), 7.39 (dd, *J* = 4.3, 2.3 Hz, 1H), 7.23 (ddt, *J* = 7.6, 5.5, 2.2 Hz, 3H), 7.14 (t, *J* = 8.7 Hz, 2H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 8.2 Hz, 1H), 6.65-6.49 (m, 2H), 6.43-6.33 (m, 1H). HRMS m/z (ESI) calcd for $C_{31}H_{26}FNP$ $(M)^+$ 462.1781, found 462.1772.

Aminobenzyl phosphonium salt 1c

Compound **1c** was synthesized in accordance with the typical procedure as a white powder (8.8 g, 79% yield) (m.p. 209.5-211.5 °C).

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.94-7.89 (m, 3H), 7.74 (td, *J* = 7.9, 3.7 Hz, 6H), 7.64 (dd, *J* = 11.6, 7.6 Hz, 6H), 7.40-7.19 (m, 5H), 7.07 (t, *J* = 7.7 Hz, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 6.63-6.50 (m, 2H), 6.40-6.35 (m, 1H). HRMS m/z (ESI) calcd for $C_{31}H_{26}ClNP$ $(M)^+$ 478.1486, found 478.1482.

Aminobenzyl phosphonium salt 1d

Compound **1d** was synthesized in accordance with the typical procedure as a white powder (8.8 g, 73% yield) (m.p. 205.5-207.5 °C).

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.91 (td, *J* = 7.4, 1.8 Hz, 3H), 7.74 (td, *J* = 7.9, 3.7 Hz, 6H), 7.69-7.61 (m, 6H), 7.51-7.39 (m, 3H), 7.25-7.21 (m, 1H), 7.18-7.03 (m, 3H), 6.77 (d, *J* = 8.1 Hz, 1H), 6.62-6.48 (m, 2H), 6.40-6.33 (m, 1H). HRMS m/z (ESI) calcd for $C_{31}H_{26}BrNP$ $(M)^+$ 522.0981, found 522.0988.

Aminobenzyl phosphonium salt 1e

Compound **1e** was synthesized in accordance with the typical procedure as a white powder (8.6 g, 77% yield) (m.p. 201.5-203.5 °C).

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.93 (td, *J* = 7.3, 1.7 Hz, 3H), 7.76 (td, *J* = 7.9, 3.8 Hz, 6H), 7.68 (dd, *J* = 12.1, 7.5 Hz, 6H), 7.41-7.21 (m, 6H), 7.10 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.79 (dd, *J* = 8.8, 1.3 Hz, 1H), 6.60 (d, *J* = 22.5 Hz, 1H), 6.40 (dd, *J* = 2.6, 1.1 Hz, 1H). HRMS m/z (ESI) calcd for $C_{31}H_{26}ClNP$ $(M)^+$ 478.1486, found 478.1483.

Aminobenzyl phosphonium salt 1f

Compound **1f** was synthesized in accordance with the typical procedure as a white powder (8.5 g, 71% yield) (m.p. 203.5-205.5 °C).

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.92 (t, *J* = 7.8 Hz, 3H), 7.80-7.66 (m, 13H), 7.42-7.23 (m, 6H), 7.19 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.77-6.62 (m, 2H), 6.53 (d, *J* = 2.3 Hz, 1H). HRMS m/z (ESI) calcd for $C_{31}H_{26}BrNP$ $(M)^+$ 522.0981, found 522.0991.

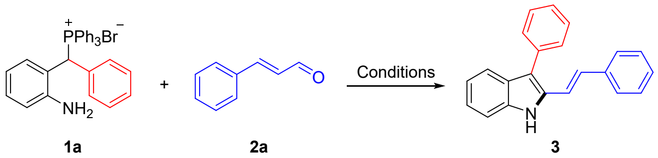
Aminobenzyl phosphonium salt 1g

Compound **1g** was synthesized in accordance with the typical procedure as a white powder (8.0 g, 70% yield) (m.p. 205.5-207.5 °C).

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.91 (ddd, *J* = 8.8, 5.2, 1.6 Hz, 3H), 7.76-7.70 (m, 12H), 7.43-7.37 (m, 2H), 7.24-7.15 (m, 4H), 7.10 (ddd, *J* = 8.7, 2.4, 1.0 Hz, 1H), 6.86-6.78 (m, 2H), 6.57 (t, *J* = 1.5 Hz, 1H). HRMS m/z (ESI) calcd for $C_{31}H_{25}ClFNP$ $(M)^+$ 496.1392, found 496.1383.

3. Optimization Studies

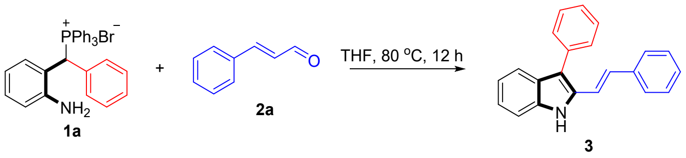
Table S1. Optimization of the Reaction Conditions[a]



Entry	Ligand	Acid	Base	Solvent	Additive	Temp. (°C)	Time (h)	Yield (%)
1	/	/	/	DCM	/	110	6	68
2	/	/	/	EtOH	/	110	6	45
3	/	/	/	DCE	/	110	6	47
4	/	/	/	DMF	/	110	6	43
5	/	/	/	DMSO	/	110	6	0
6	/	/	/	THF	/	110	6	72
7	/	/	/	2-MeTHF	/	110	6	65
8	/	/	/	HFIP	/	110	6	0
9	/	/	/	1,4-dioxane	/	110	6	39
10	/	/	/	EA	/	110	6	63
11	/	/	/	PhMe	/	110	6	61
12	CuBr	/	/	THF	/	110	6	72
13	AgOTf	/	/	THF	/	110	6	67
14	PdCl	/	/	THF	/	110	6	60
15	$CoCO_3$	/	/	THF	/	110	6	58
16	/	MAS	/	/	/	110	6	41
17	/	HAc	/	/	/	110	6	43
18	/	TFA	/	/	/	110	6	25
19	/	H_3PO_4	/	/	/	110	6	Trace
20	/	/	Cs_2CO_3	THF	/	110	6	Trace
21	/	/	t-BuOK	THF	/	110	6	Trace
22	/	/	NaH	THF	/	110	6	Trace
23	/	/	K_2CO_3	THF	/	110	6	Trace
24	/	/	/	THF	KI	110	6	68
25	/	/	/	THF	KCl	110	6	65
26	/	/	/	THF	K_3PO_4	110	6	61
27	/	/	/	THF	/	100	6	75
28	/	/	/	THF	/	90	6	82
29	/	/	/	THF	/	80	6	87
30	/	/	/	THF	/	70	6	79
31	/	/	/	THF	/	80	12	92
32	/	/	/	THF	/	80	18	92
33	/	/	/	THF	/	80	24	90

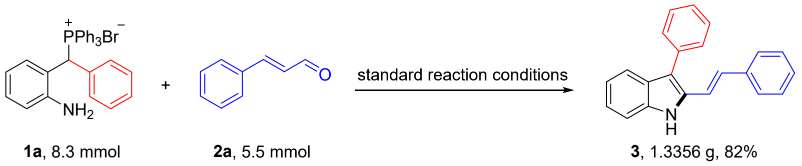
[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.2 mmol), solvent (1 mL), 80 °C, 12 h.

4. General Procedure for the Synthesis of Products 3-51



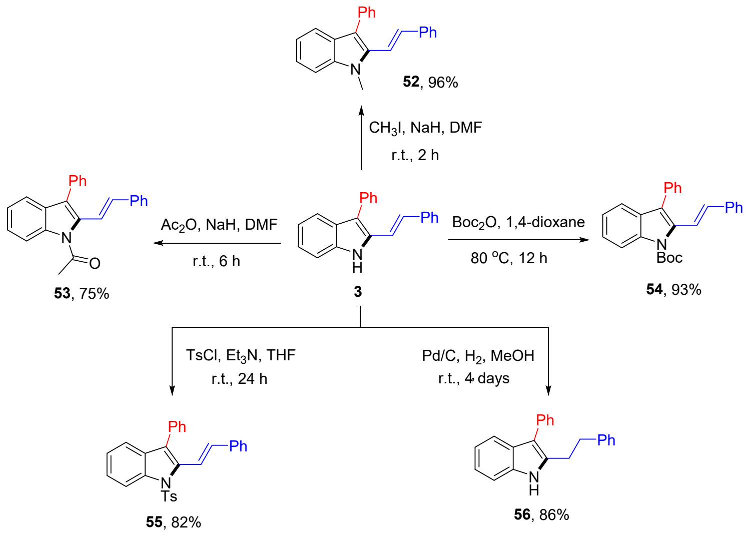
General procedure for the synthesis of products **3-51** (take the synthesis of **3** as one example): A mixture of **1a** (0.3 mmol, 1.5 equiv), **2a** (0.2 mmol, 1.0 equiv) were added in a Schlenk tube equipped with a stirring bar. Dry THF (1 mL) was added and the mixture was stirred at 80 °C for 12 h. Then, the mixture was cooled to room temperature and concentrated in vacuo, and the resulting residue was purified by flash column chromatography on silica gel with PE:EA = 10:1, affording product **3** as a yellow solid in 92% yield (54.4 mg).

5. Gram-scale Reaction



A mixture of **1a** (5.5 mmol, 1.0 equiv) and **2a** (8.3 mmol, 1.5 equiv) were added in a round bottomed flask (500 mL) with a stirring bar. Dry THF (50 mL) was added and the mixture was stirred at 80 °C in a pre-heated oil bath for 12 h. Then, the mixture was cooled to room temperature and concentrated in vacuo, and the resulting residue was purified by flash column chromatography on silica gel with PE/EA, affording product **3** as a yellow solid in 82% yield (1.3356 g).

6. Product Derivatization for the Synthesis of Compounds 52-56



Procedure for the synthesis of compound **52**: To a solution of **3** (0.2 mmol, 1.0 equiv) in DMF (2.0 mL) was added NaH (0.3 mmol, 1.5 equiv) at 0 °C. After 10 min, CH_3I was added and the mixture was stirred at r.t. for 2 h. After that, the reaction was quenched by NH_4Cl solution, extracted with EA (2×30 mL) and dried ($MgSO_4$). The combined extracts were concentrated under vacuum and purified by flash column chromatography on silica gel with PE/EA=10:1, affording product **52** as a yellow solid in 96% yield (59.3 mg).

Procedure for the synthesis of compound **53**: To a solution of **3** (0.2 mmol, 1.0 equiv) in DMF (2.0 mL) was added NaH (0.3 mmol, 1.5 equiv) at 0 °C. After 10 min, Ac_2O was added and the mixture was stirred at r.t. for 6 h. After that, the reaction was quenched by NH_4Cl solution, extracted with EA (2×30 mL) and dried ($MgSO_4$). The combined extracts were concentrated under vacuum and purified by flash column chromatography on silica gel with PE/EA=10:1, affording product **53** as a yellow solid in 75% yield (50.6 mg).

Procedure for the synthesis of compound **54**: A mixture of **3** (0.2 mmol, 1.0 equiv) and Boc_2O (1 mmol, 5.0 equiv) were added in a Schlenk tube with a stirring bar. Dry 1,4-dioxane (2 mL) was added and the mixture was stirred at 80 °C for 12 h. Then, the mixture was cooled to room temperature and concentrated in vacuo, and the resulting residue was purified by flash column chromatography on silica gel with PE/EA=10:1, affording product **54** as a yellow solid in 93% yield (73.5 mg).

Procedure for the synthesis of compound **55**: A mixture of **3** (0.2 mmol, 1.0 equiv) and TsCl (0.24 mmol, 1.2 equiv) with Et_3N (0.3 mmol, 1.5 equiv) were added in a Schlenk tube with a stirring bar. Dry THF (2 mL) was added and the mixture was stirred at r.t. for 24 h. Then, the mixture was concentrated in vacuo, and the resulting residue was purified by flash column chromatography on silica gel with PE/EA=10:1, affording product **55** as a yellow solid in 82% yield (67.3 mg).

Procedure for the synthesis of compound **56**: A mixture of **3** (0.2 mmol, 1.0 equiv) and Pd/C (0.02 mmol, 0.1 equiv) were added in a Schlenk tube with a stirring bar. MeOH (2 mL) was added and the mixture was stirred at r.t. for 4 days under H_2 atmosphere. Then, the mixture was filtered by diatomite and concentrated in vacuo. After that, the resulting residue was purified by flash column chromatography on silica gel with PE/EA=10:1, affording product **56** as a yellow oil in 86% yield (51.1 mg).

7. Control Reactions

A mixture of **1a** (0.3 mmol, 1.5 equiv.), **2a** (0.2 mmol, 1.0 equiv.), and BHT (0.2 mmol, 1.0 equiv) were added in a Schlenk tube equipped with a stirring bar. Dry THF (1 mL) was added and the mixture was stirred at 80 °C for 12 h. Then, the mixture was cooled to room temperature and concentrated in vacuo, and the resulting residue was purified by flash column chromatography on silica gel with PE/EA, affording product **3** as a yellow solid in 90% yield (53.2 mg).

A mixture of **1a** (0.3 mmol, 1.5 equiv.), **2a** (0.2 mmol, 1.0 equiv.), and TEMPO (0.2 mmol, 1.0 equiv) were added in a Schlenk tube equipped with a stirring bar. Dry THF (1 mL) was added and the mixture was stirred at 80 °C for 12 h. Then, the mixture was cooled to room temperature and concentrated in vacuo, and the resulting residue was purified by flash column chromatography on silica gel with PE/EA, affording product **3** as a yellow solid in 87% yield (51.4 mg).

8. Analytical Data of the Products

(*E*)-3-Phenyl-2-styryl-1*H*-indole (3)

Product **3** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **3** (31.5 mg, 78%) as a yellow solid (m.p. 99.5-101.5 °C).

^1H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.76 (d, J = 7.9 Hz, 1H), 7.64-7.60 (m, 2H), 7.56 (d, J = 15.3 Hz, 2H), 7.45 (dd, J = 10.4, 7.2 Hz, 3H), 7.41-7.35 (m, 3H), 7.33-7.26 (m, 3H), 7.22-

7.17 (m, 1H), 6.91 (d, *J* = 16.6 Hz, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 137.0, 136.5, 134.6, 132.6, 130.2, 128.9, 128.8, 128.3, 127.8, 127.4, 126.7, 126.5, 123.7, 120.5, 119.8, 118.9, 118.0, 110.8. The NMR spectra are consistant with the reported literature.[2]

(*E*)-3-(4-Fluorophenyl)-2-styryl-1*H*-indole (4)

Product **4** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **4** (53.2 mg, 85%) as a yellow solid (m.p. 95.5-97.5 °C).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.28 (s, 1H), 7.69 (d, *J* = 7.9 Hz, 1H), 7.56-7.51 (m, 2H), 7.49-7.45 (m, 2H), 7.40 (t, *J* = 7.6 Hz, 3H), 7.34-7.29 (m, 2H), 7.27-7.18 (m, 4H), 6.91 (d, *J* = 16.6 Hz, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 163.1, 160.7, 136.9, 136.4, 132.6, 131.7, 131.6, 130.5, 130.5, 128.9, 128.3, 127.9, 127.6, 126.5, 123.8, 120.6, 119.6, 117.8, 117.7, 115.8, 115.6, 110.8. ^{19}F NMR (376 MHz, CDCl$_3$) δ -115.7. HRMS m/z (ESI) calcd for $C_{22}H_{16}FN$ $(M+H)^+$ 314.1340, found 314.1348.

(*E*)-3-(4-Chlorophenyl)-2-styryl-1*H*-indole (5)

Product **5** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **5** (59.9 mg, 91%) as a yellow solid (m.p. 102.5-104.5 °C).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.27 (s, 1H), 7.69 (d, *J* = 7.1 Hz, 1H), 7.51 (s, 6H), 7.42-7.38 (m, 3H), 7.31 (t, *J* = 7.0 Hz, 2H), 7.22-7.17 (m, 2H), 6.90 (d, *J* = 16.5 Hz, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 136.7, 134.8, 133.9, 133.9, 130.1, 129.4, 128.9, 128.2, 128.1, 126.9, 126.6, 126.2, 123.8, 119.2, 118.3, 117.6, 111.8. HRMS m/z (ESI) calcd for $C_{22}H_{16}ClN$ $(M+H)^+$ 330.1044, found 330.1051.

(*E*)-3-(4-Bromophenyl)-2-styryl-1*H*-indole (6)

Product **6** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **6** (68.8 mg, 92%) as a yellow solid (m.p. 113.5-115.5 °C).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.29 (s, 1H), 7.71-7.62 (m, 3H), 7.49-7.42 (m, 4H), 7.41-7.37 (m, 3H), 7.31 (td, *J* = 8.1, 7.7, 1.2 Hz, 2H), 7.21-7.16 (m, 2H), 6.90 (d, *J* = 16.5 Hz, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 136.8, 136.5, 133.6, 132.7, 131.9, 131.7, 128.9, 128.0, 127.9, 126.5, 123.8, 120.7, 120.6, 119.5, 117.5, 110.9. HRMS m/z (ESI) calcd for $C_{22}H_{16}BrN$ $(M+H)^+$ 374.0539, found 374.0551.

(*E*)-5-Chloro-3-phenyl-2-styryl-1*H*-indole (7)

Product **7** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **7** (60.5 mg, 92%) as a yellow solid (m.p. 107.5-109.5 °C).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.39 (s, 1H), 7.67 (d, *J* = 2.0 Hz, 1H), 7.54 (d, *J* = 5.2 Hz, 4H), 7.46-7.41 (m, 3H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.29 (dd, *J* = 7.8, 5.4 Hz, 2H), 7.23-7.18 (m, 2H), 6.92 (d, *J* = 16.5 Hz, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 136.7, 134.8, 133.9, 133.9, 130.1, 129.3, 128.9, 128.3, 128.1, 126.9, 126.6, 126.2, 123.8, 119.1, 118.3, 117.5, 111.8. The NMR spectra are consistant with the reported literature.[2]

(*E*)-5-Chloro-3-phenyl-2-styryl-1*H*-indole (8)

Product **8** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **8** (71.8 mg, 96%) as a yellow solid (m.p. 97.5-99.5 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.81 (d, *J* = 1.8 Hz, 1H), 7.54-7.51 (m, 4H), 7.45-7.41 (m, 3H), 7.38-7.31 (m, 3H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.25-7.17 (m, 2H), 6.93 (d, *J* = 16.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.7, 135.1, 133.9, 133.7, 130.1, 130.0, 128.9, 128.4, 128.1, 126.9, 126.6, 126.3, 122.2, 118.2, 117.5, 113.7, 112.3. HRMS m/z (ESI) calcd for $C_{22}H_{16}BrN$ $(M+H)^+$ 374.0539, found 374.0534.

(*E*)-5-Chloro-3-(2-fluorophenyl)-2-styryl-1*H*-indole (9)

Product **9** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **9** (65.2 mg, 94%) as a yellow solid (m.p. 137.5-139.5 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.50 (t, *J* = 1.9 Hz, 1H), 7.48-7.37 (m, 4H), 7.36-7.25 (m, 5H), 7.24-7.18 (m, 2H), 7.05 (dd, *J* = 16.6, 1.6 Hz, 1H), 6.88 (d, *J* = 16.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5, 159.1, 136.6, 134.8, 134.7, 132.9, 132.9, 129.6, 129.2, 129.2, 128.9, 128.5, 128.2, 126.6, 126.2, 124.5, 124.4, 123.8, 121.4, 121.3, 119.4, 119.4, 117.4, 117.4, 116.4, 116.2, 111.8, 111.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.8. HRMS m/z (ESI) calcd for $C_{22}H_{15}ClFN$ $(M+H)^+$ 348.0950, found 348.0954.

(*E*)-2-(2-Methylstyryl)-3-phenyl-1*H*-indole (10)

Product **10** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **10** (55.6 mg, 90%) as a yellow solid (m.p. 91.5-93.5 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.76 (d, *J* = 9.0 Hz, 1H), 7.62 (dd, *J* = 8.1, 1.3 Hz, 2H), 7.57-7.52 (m, 3H), 7.45-7.39 (m, 2H), 7.31 (t, *J* = 7.0 Hz, 1H), 7.24-7.16 (m, 6H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.5, 136.0, 135.7, 134.6, 132.9, 130.6, 130.2, 128.8, 128.3, 127.8, 126.6, 126.4, 125.3, 125.0, 123.7, 120.5, 119.9, 119.3, 118.8, 110.8, 20.2. HRMS m/z (ESI) calcd for $C_{23}H_{19}N$ $(M+H)^+$ 310.1590, found 310.1600.

(*E*)-2-(2-Methoxystyryl)-3-phenyl-1*H*-indole (11)

Product **11** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **11** (57.9 mg, 89%) as a yellow solid (m.p. 112.5-114.5 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.62 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.56-7.51 (m, 3H), 7.44-7.32 (m, 4H), 7.30-7.25 (m, 2H), 7.19-7.14 (m, 1H), 7.00-6.92 (m, 2H), 3.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 136.5, 134.8, 133.3, 130.2, 128.9, 128.7, 128.2, 126.5, 126.2, 126.0, 123.5, 121.8, 120.9, 120.4, 119.7, 118.4, 118.2, 111.0, 110.7, 55.6. HRMS m/z (ESI) calcd for $C_{23}H_{19}NO$ $(M+H)^+$ 326.1539, found 326.1533.

(*E*)-2-(2-Chlorostyryl)-3-phenyl-1*H*-indole (12)

Product **12** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **12** (61.8 mg, 94%) as a yellow solid (m.p. 154.5-156.5 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.74 (d, *J* = 7.0 Hz, 1H), 7.63-7.52 (m, 6H), 7.45-7.39 (m, 2H), 7.33-7.26 (m, 3H), 7.23-7.09 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.7, 135.0, 134.5, 133.2, 132.4, 130.3, 130.0, 128.8, 128.7, 128.2, 127.1, 126.8, 126.3, 124.0, 122.9, 120.6, 120.4, 120.0, 119.8, 110.9. HRMS m/z (ESI) calcd for $C_{22}H_{16}ClN$ $(M+H)^+$ 330.1044, found 330.1044.

(*E*)-2-(2-Bromostyryl)-3-phenyl-1*H*-indole (13)

Product **13** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **13** (70.8 mg, 95%) as a yellow solid (m.p. 153.5-155.5 °C).

^1H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.73 (d, J = 8.9 Hz, 1H), 7.61-7.51 (m, 5H), 7.42 (dddd, J = 7.2, 5.4, 2.8, 1.2 Hz, 3H), 7.36-7.28 (m, 2H), 7.27-7.15 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.7, 134.9, 134.5, 133.2, 132.4, 130.3, 130.0, 128.8, 128.7, 128.1, 127.1, 126.8, 126.3, 124.0, 122.9, 120.6, 120.3, 119.9, 119.7, 110.9. HRMS m/z (ESI) calcd for $C_{22}H_{16}BrN$ $(M+H)^+$ 374.0539, found 374.0544.

(*E*)-2-(2-Nitrostyryl)-3-phenyl-1*H*-indole (14)

Product **14** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **14** (56.4 mg, 83%) as a yellow solid (m.p. 138.5-140.5 °C).

^1H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.98 (dd, J = 8.2, 1.3 Hz, 1H), 7.72-7.66 (m, 2H), 7.58-7.49 (m, 6H), 7.44-7.34 (m, 3H), 7.31-7.24 (m, 2H), 7.18-7.13 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 136.8, 134.3, 133.3, 132.7, 131.8, 130.3, 128.8, 128.0, 127.9, 127.8, 126.9, 125.1, 124.5, 123.1, 121.2, 120.9, 120.7, 120.1, 111.1. HRMS m/z (ESI) calcd for $C_{22}H_{16}N_2O_2$ $(M+H)^+$ 341.1285, found 341.1291.

(*E*)-2-(3-Methylstyryl)-3-phenyl-1*H*-indole (15)

Product **15** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **15** (58.7 mg, 95%) as a yellow solid (m.p. 159.5-161.5 °C).

^1H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.62 (dd, J = 8.2, 1.5 Hz, 2H), 7.56 (t, J = 7.6 Hz, 2H), 7.46-7.39 (m, 2H), 7.31-7.24 (m, 5H), 7.21-7.17 (m, 1H), 7.14-7.09 (m, 1H), 6.90 (d, J = 16.5 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 136.9, 136.5, 134.7, 132.7, 130.2, 128.8, 128.7, 128.3, 127.6, 127.1, 126.6, 123.8, 123.6, 120.5, 119.8, 118.7, 117.8, 110.8, 21.5. HRMS m/z (ESI) calcd for $C_{23}H_{19}N$ $(M+H)^+$ 310.1590, found 310.1583.

(*E*)-2-(3-Fluorostyryl)-3-phenyl-1*H*-indole (16)

Product **16** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **16** (60.1 mg, 96%) as a yellow solid (m.p. 156.5-157.5 °C).

^1H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.61-7.52 (m, 4H), 7.45-7.38 (m, 2H), 7.36-7.23 (m, 3H), 7.22-7.17 (m, 2H), 7.16-7.12 (m, 1H), 6.96 (td, J = 8.3, 7.9, 2.2 Hz, 1H), 6.85 (d, J = 16.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5, 162.1, 139.4, 139.4, 136.6, 134.4, 130.4, 130.2, 128.9, 128.2, 126.8, 126.0, 126.0, 123.9, 122.4, 122.3, 120.7, 119.9, 119.6, 119.3, 114.7, 114.4, 112.8, 112.6, 110.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.9. HRMS m/z (ESI) calcd for $C_{22}H_{16}FN$ $(M+H)^+$ 314.1340, found 314.1340.

(*E*)-2-(3-Chlorostyryl)-3-phenyl-1*H*-indole (17)

Product **17** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **17** (62.5 mg, 95%) as a yellow solid (m.p. 124.5-126.5 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.61-7.53 (m, 4H), 7.46-7.37 (m, 3H), 7.32-7.28 (m, 2H), 7.27-7.21 (m, 3H), 7.20-7.16 (m, 1H), 6.80 (d, J = 16.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.9, 136.6, 134.8, 134.4, 132.1, 130.2, 130.1, 128.9, 128.2, 127.6, 126.8, 126.2, 125.8, 124.6, 124.0, 120.7, 119.9, 119.7, 119.3, 110.9. HRMS m/z (ESI) calcd for $C_{22}H_{16}ClN$ $(M+H)^+$ 330.1044, found 330.1037.

(*E*)-3-Phenyl-2-(3-(trifluoromethyl)styryl)-1*H*-indole (18)

Product **18** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **18** (55.2 mg, 76%) as a yellow solid (m.p. 110.5-112.5 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.66 (s, 1H), 7.61-7.50 (m, 6H), 7.47-7.39 (m, 3H), 7.34-7.27 (m, 2H), 7.19 (ddd, J = 8.0, 6.9, 1.0 Hz, 1H), 6.89 (d, J = 16.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.8, 136.7, 134.4, 131.9, 131.4, 131.1, 130.2, 129.3, 129.2, 128.9, 128.2, 126.9, 125.7, 125.6, 124.2, 123.3, 122.9, 120.7, 120.05, 119.9, 119.7, 110.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.5. HRMS m/z (ESI) calcd for $C_{23}H_{16}F_3N$ $(M+Na)^+$ 386.1127, found 386.1124.

(*E*)-2-(4-Methylstyryl)-3-phenyl-1*H*-indole (19)

Product **19** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **19** (58.7 mg, 95%) as a yellow solid (m.p. 110.50-112.5 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.65-7.60 (m, 2H), 7.56 (t, J = 7.7 Hz, 2H), 7.45-7.36 (m, 4H), 7.30 (t, J = 7.0 Hz, 1H), 7.19 (td, J = 7.2, 3.9 Hz, 4H), 6.91 (d, J = 16.5 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.8, 136.5, 134.7, 134.2, 132.8, 130.2, 129.6, 128.8, 128.3, 127.5, 126.6, 126.4, 123.5, 120.5, 119.7, 118.4, 117.0, 110.8, 21.4. The NMR spectra are consistant with the reported literature.[3]

(*E*)-2-(4-Methoxystyryl)-3-phenyl-1*H*-indole (20)

Product **20** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **20** (61.7 mg, 95%) as a yellow solid (m.p. 114.5-116.5 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.62-7.59 (m, 2H), 7.54 (t, J = 7.8 Hz, 2H), 7.43-7.37 (m, 4H), 7.27 (t, J = 7.0 Hz, 1H), 7.19-7.11 (m, 2H), 6.92-6.85 (m, 3H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 136.5, 134.8, 133.0, 130.2, 129.8, 128.8, 128.4, 127.8, 127.1, 126.5, 123.4, 120.5, 119.6, 118.1, 115.9, 114.3, 110.7, 55.4. HRMS m/z (ESI) calcd for $C_{23}H_{19}NO$ $(M+H)^+$ 326.1539, found 326.1537.

(*E*)-*N*,*N*-Dimethyl-4-[2-(3-phenyl-1*H*-indol-2-yl)vinyl]aniline (21)

Product **21** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **21** (41.9 mg, 62%) as a yellow solid (m.p. 133.5-135.5 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.75 (d, J = 7.9 Hz, 1H), 7.64 (d, J = 6.7 Hz, 2H), 7.56 (t, J = 7.7 Hz, 2H), 7.44-7.36 (m, 4H), 7.27 (t, J = 7.5 Hz, 1H), 7.21-7.05 (m, 2H), 6.88 (d, J = 16.4 Hz, 1H), 6.73 (d, J = 8.5 Hz, 2H), 3.00 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 136.4, 135.0, 133.6, 130.2, 128.7, 128.4, 127.9, 127.6, 126.3, 125.4, 123.0, 120.3, 119.4, 117.1, 113.7, 112.6, 110.6, 40.5. HRMS m/z (ESI) calcd for $C_{24}H_{22}N_2$ $(M+H)^+$ 339.1856, found 339.1849.

(*E*)-2-(4-Fluorostyryl)-3-phenyl-1*H*-indole (22)

Product **22** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **22** (56.9 mg, 91%) as a yellow solid (m.p. 114.5-116.5 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.61-7.52 (m, 4H), 7.45-7.36 (m, 4H), 7.29 (d, *J* = 15.1 Hz, 1H), 7.20-7.13 (m, 2H), 7.05 (t, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 16.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7 161.2, 136.5, 134.6, 133.2, 133.2, 132.5, 130.2, 128.8, 128.3, 128.0, 127.9, 126.7, 126.2, 123.7, 120.6, 119.8, 118.9, 117.7, 115.9, 115.7, 110.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.6. HRMS m/z (ESI) calcd for $C_{22}H_{16}FN$ $(M+H)^+$ 314.1340, found 314.1331.

(*E*)-2-(4-Chlorostyryl)-3-phenyl-1*H*-indole (23)

Product **23** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **23** (57.9 mg, 88%) as a yellow solid (m.p. 130.5-132.5 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.59-7.51 (m, 4H), 7.44-7.33 (m, 4H), 7.32-7.26 (m, 3H), 7.23-7.14 (m, 2H), 6.84 (d, *J* = 16.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.6, 135.5, 134.5, 133.3, 132.3, 130.2, 129.0, 128.8, 128.2, 127.6, 126.8, 125.9, 123.9, 120.6, 119.9, 119.4, 118.6, 110.8. HRMS m/z (ESI) calcd for $C_{22}H_{16}ClN$ $(M+H)^+$ 330.1044, found 330.1041.

(*E*)-2-(4-Bromostyryl)-3-phenyl-1*H*-indole (24)

Product **24** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **24** (62.8 mg, 84%) as a yellow solid (m.p. 126.5-128.5 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.60-7.53 (m, 4H), 7.48-7.40 (m, 3H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.30 (t, *J* = 6.9 Hz, 2H), 7.25-7.15 (m, 3H), 6.77 (d, *J* = 16.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.6, 135.9, 134.5, 132.3, 131.9, 130.2, 128.8, 128.2, 127.8, 126.8, 126.0, 123.9, 121.4, 120.6, 119.9, 119.3, 118.6, 110.9. HRMS m/z (ESI) calcd for $C_{22}H_{16}BrN$ $(M+H)^+$ 374.0539, found 374.0545.

(*E*)-3-Phenyl-2-(1-phenylprop-1-en-2-yl)-1*H*-indole (25)

Product **25** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **25** (54.4 mg, 76%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.61-7.58 (m, 2H), 7.49-7.45 (m, 2H), 7.44-7.31 (m, 7H), 7.30-7.25 (m, 2H), 7.18 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 6.87 (s, 1H), 2.14 (d, *J* = 1.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.5, 137.4, 135. 7, 135.2, 130.5, 130.5, 130.1, 129.2, 128.8, 128.5, 128.4, 127.0, 126.4, 122.7, 120.4, 119.5, 115.2, 110.8, 18.2. HRMS m/z (ESI) calcd for $C_{23}H_{19}N$ $(M+H)^+$ 310.1590, found 310.1586.

(*Z*)-2-(1-Chloro-2-phenylvinyl)-3-phenyl-1*H*-indole (26)

Product **26** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **26** (57.2 mg, 87%) as a yellow oil.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.58 (s, 1H), 7.67-7.60 (m, 3H), 7.54-7.48 (m, 4H), 7.44 (dt, J = 8.1, 0.9 Hz, 1H), 7.41-7.35 (m, 3H), 7.34-7.29 (m, 2H), 7.19 (ddd, J = 8.1, 7.0, 1.0 Hz, 1H), 6.84 (s, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 135.2, 134.7, 131.3, 130.3, 129.6, 129.4, 128.9, 128.9, 128.4, 128.3, 127.0, 123.8, 122.3, 120.8, 120.1, 116.9, 111.2. HRMS m/z (ESI) calcd for $C_{22}H_{16}ClN$ (M+Na)$^+$ 352.0863, found 352.0867.

(*Z*)-2-(1-Bromo-2-phenylvinyl)-3-phenyl-1*H*-indole (27)

Product **27** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **27** (70.8 mg, 95%) as a yellow oil.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.34 (s, 1H), 7.73 (d, J = 7.9 Hz, 1H), 7.61-7.58 (m, 2H), 7.54 (t, J = 7.7 Hz, 2H), 7.48-7.45 (m, 2H), 7.43-7.34 (m, 4H), 7.29 (td, J = 4.8, 4.3, 2.2 Hz, 2H), 7.16 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 6.93 (d, J = 16.5 Hz, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 137.0, 136.6, 134.6, 132.6, 130.3, 128.9, 128.8, 128.3, 127.9, 127.4, 126.8, 126.5, 123.7, 120.6, 119.8, 118.9, 118.1, 110.8. HRMS m/z (ESI) calcd for $C_{22}H_{16}BrN$ (M+Na)$^+$ 396.0358, found 396.0360.

(*E*)-2-[2-(Furan-2-yl)vinyl]-3-phenyl-1*H*-indole (28)

Product **28** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **28** (28.5 mg, 50%) as a yellow solid (m.p. 131.5-133.5 °C).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.23 (s, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.61-7.49 (m, 4H), 7.43-7.34 (m, 3H), 7.26 (dd, J = 15.1, 1.2 Hz, 1H), 7.20-7.11 (m, 2H), 6.72 (d, J = 16.4 Hz, 1H), 6.48-6.31 (m, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 153.0, 142.5, 136.6, 134.5, 132.4, 130.2, 128.8, 128.4, 126.7, 123.7, 120.7, 119.8, 119.1, 116.4, 115.3, 111.9, 110.7, 108.8. HRMS m/z (ESI) calcd for $C_{20}H_{15}NO$ (M+H)$^+$ 286.1226, found 286.1217.

(*E*)-2-[2-(Anthracen-9-yl)vinyl]-3-phenyl-1*H*-indole (29)

Product **29** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **29** (72.7 mg, 92%) as a yellow solid (m.p. 172.5-174.5 °C).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.43 (d, J = 10.1 Hz, 2H), 8.36-8.31 (m, 2H), 8.07-8.02 (m, 2H), 7.85 (d, J = 8.0 Hz, 1H), 7.64-7.60 (m, 2H), 7.54-7.38 (m, 9H), 7.31 (dd, J = 17.5, 7.8 Hz, 2H), 7.12 (d, J = 16.7 Hz, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 136.5, 134.3, 132.3, 132.1, 131.53, 130.1, 129.7, 128.9, 128.7, 128.2, 126.9, 126.7, 126.6, 125.9, 125.8, 125.3, 123.9, 123.5, 120.7, 120.1, 118.9, 110.9. HRMS m/z (ESI) calcd for $C_{30}H_{21}N$ (M+Na)$^+$ 418.1566, found 418.1575.

(*E*)-3-Phenyl-2-(prop-1-en-1-yl)-1*H*-indole (30)

Product **30** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **30** (35.4 mg, 76%) as a yellow oil.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.17 (s, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.56 (dd, J = 8.2, 1.4 Hz, 2H), 7.53-7.48 (m, 2H), 7.39-7.34 (m, 2H), 7.26-7.21 (m, 1H), 7.13 (ddd, J = 8.1, 7.0, 1.1 Hz, 1H), 6.61 (dq, J = 16.0, 1.7 Hz, 1H), 6.09 (dq, J = 16.1, 6.7 Hz, 1H), 1.93 (dd, J = 6.7, 1.8 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 136.1, 134.9, 132.7, 130.1, 128.6, 128.3, 126.3, 125.1, 122.9, 121.1, 120.3, 119.6, 116.1, 110.6, 18.8. HRMS m/z (ESI) calcd for $C_{17}H_{15}N$ (M+H)$^+$ 256.1097, found 256.1100.

(*E*)-2-(But-1-en-1-yl)-3-phenyl-1*H*-indole (31)

Product **31** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **31** (29.6 mg, 60%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.56-7.46 (m, 4H), 7.35 (t, *J* = 6.5 Hz, 2H), 7.22 (td, *J* = 8.1, 7.6, 1.2 Hz, 1H), 7.13-7.09 (m, 1H), 6.59 (dt, *J* = 16.1, 1.7 Hz, 1H), 6.13 (ddt, *J* = 16.0, 8.3, 4.1 Hz, 1H), 2.28 (p, *J* = 7.5 Hz, 2H), 1.10 (td, *J* = 7.4, 1.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.1, 134.9, 132.7, 132.1, 130.1, 128.6, 128.3, 126.3, 122.9, 120.3, 119.6, 119.0, 116.3, 110.6, 26.4, 13.9. HRMS m/z (ESI) calcd for $C_{20}H_{21}N$ $(M+H)^+$ 248.1434, found 248.1439.

(*E*)-2-(Pent-1-en-1-yl)-3-phenyl-1*H*-indole (32)

Product **32** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **32** (26.6 mg, 51%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.59-7.47 (m, 5H), 7.39-7.35 (m, 2H), 7.25-7.21 (m, 1H), 7.15-7.11 (m, 1H), 6.60 (dt, *J* = 16.1, 1.5 Hz, 1H), 6.09 (dt, *J* = 16.1, 6.9 Hz, 1H), 2.24 (qd, *J* = 7.2, 1.5 Hz, 2H), 1.52 (q, *J* = 7.4 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.1, 134.9, 132.7, 130.4, 130.1, 128.6, 128.3, 126.3, 122.9, 120.2, 120.0, 119.5, 116.2, 110.6, 35.4, 22.7, 13.8. HRMS m/z (ESI) calcd for $C_{19}H_{19}N$ $(M+H)^+$ 262.1590, found 262.1593.

(*E*)-2-(Hex-1-en-1-yl)-3-phenyl-1*H*-indole (33)

Product **33** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **33** (24.2 mg, 44%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.69 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.57-7.54 (m, 2H), 7.53-7.49 (m, 2H), 7.39-7.34 (m, 2H), 7.23 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H), 6.60 (dt, *J* = 16.1, 1.5 Hz, 1H), 6.09 (dt, *J* = 16.1, 7.0 Hz, 1H), 2.26 (qd, *J* = 7.1, 1.5 Hz, 2H), 1.50-1.38 (m, 4H), 0.95 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.1, 134.9, 132.7, 130.7, 130.1, 128.6, 128.3, 126.3, 122.9, 120.2, 119.8, 119.5, 116.2, 110.6, 33.0, 31.7, 22.4, 14.1. HRMS m/z (ESI) calcd for $C_{20}H_{21}N$ $(M+H)^+$ 276.1747, found 276.1742.

(*E*)-2-(Hept-1-en-1-yl)-3-phenyl-1*H*-indole (34)

Product **34** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **34** (24.3 mg, 42%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.59-7.55 (m, 2H), 7.53-7.49 (m, 2H), 7.39-7.35 (m, 2H), 7.26-7.22 (m, 1H), 7.14 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 6.60 (dt, *J* = 16.1, 1.5 Hz, 1H), 6.09 (dt, *J* = 16.1, 7.0 Hz, 1H), 2.26 (qd, *J* = 7.1, 1.5 Hz, 2H), 1.50 (dt, *J* = 14.0, 7.1 Hz, 2H), 1.39-1.34 (m, 4H), 0.97-0.92 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.1, 134.9, 132.7, 130.7, 130.1, 128.6, 128.3, 126.3, 122.9, 120.2, 119.8, 119.5, 116.2, 110.6, 33.3, 31.5, 29.2, 22.6, 14.2. HRMS m/z (ESI) calcd for $C_{21}H_{23}N$ $(M+H)^+$ 290.1903, found 290.1904.

2-(2-Methylprop-1-en-1-yl)-3-phenyl-1*H*-indole (35)

Product **35** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **35** (43.5 mg, 88%) as a yellow oil.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.12 (s, 1H), 7.77 (dq, *J* = 7.9, 0.8 Hz, 1H), 7.61-7.57 (m, 2H), 7.51-7.46 (m, 2H), 7.40 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.35-7.31 (m, 1H), 7.24 (ddd, *J* = 8.1, 7.1, 1.3 Hz, 1H), 7.17 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 6.32 (p, *J* = 1.4 Hz, 1H), 1.96 (dd, *J* = 8.3, 1.3 Hz, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 137.0, 135.8, 135.6, 132.9, 129.8, 128.5, 127.5, 125.9, 122.3, 120.3, 119.4, 116.0, 115.8, 110.7, 27.1, 20.4. HRMS m/z (ESI) calcd for $C_{18}H_{17}N$ (M+H)$^+$ 248.1434, found 248.1444.

2-(Cyclohex-1-en-1-yl)-3-phenyl-1*H*-indole (36)

Product **36** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **36** (52.4 mg, 96%) as a yellow oil.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.02 (s, 1H), 7.65 (dq, *J* = 7.9, 0.8 Hz, 1H), 7.58-7.54 (m, 2H), 7.48-7.43 (m, 2H), 7.38-7.31 (m, 2H), 7.23 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.14 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 6.09 (tt, *J* = 3.8, 1.7 Hz, 1H), 2.24-2.15 (m, 4H), 1.67 (p, *J* = 3.2 Hz, 4H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 136.6, 136.0, 134.9, 131.1, 129.9, 128.8, 128.5, 128.3, 126.1, 122.2, 120.1, 119.3, 113.7, 110.6, 27.8, 25.8, 22.8, 22.1. HRMS m/z (ESI) calcd for $C_{20}H_{19}N$ (M+Na)$^+$ 296.1410, found 296.1410.

2-(1*E*,3*E*-penta-1,3-dien-1-yl)-3-phenyl-1*H*-indole (37)

Product **37** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **37** (34.7 mg, 67%) as a yellow oil.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.23 (s, 1H), 7.66 (dq, *J* = 8.0, 0.9 Hz, 1H), 7.55-7.52 (m, 2H), 7.5-7.48 (m, 2H), 7.36-7.34 (m, 2H), 7.24-7.22 (m, 1H), 7.13-7.10 (m, 1H), 6.59 (d, *J* = 6.4 Hz, 2H), 6.26-6.17 (m, 1H), 5.85 (dq, *J* = 15.0, 6.8 Hz, 1H), 1.83 (dd, *J* = 6.8, 1.6 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 136.5, 134.8, 132.9, 131.8, 130.7, 130.2, 128.7, 128.3, 126.5, 123.3, 121.0, 120.4, 119.6, 119.1, 117.9, 110.6, 18.6. HRMS m/z (ESI) calcd for $C_{19}H_{17}N$ (M+H)$^+$ 260.1434, found 260.1403.

2-(1*E*,3*E*-hexa-1,3-dien-1-yl)-3-phenyl-1*H*-indole (38)

Product **38** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **38** (20.4 mg, 43%) as a yellow oil.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.22 (s, 1H), 7.66 (d, *J* = 6.9 Hz, 1H), 7.53 (dd, *J* = 8.3, 1.5 Hz, 2H), 7.50-7.46 (m, 2H), 7.37-7.34 (m, 2H), 7.22 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.10 (ddd, *J* = 8.0, 7.1, 1.1 Hz, 1H), 6.60 (d, *J* = 7.1 Hz, 2H), 6.24-6.16 (m, 1H), 5.89 (dt, *J* = 15.1, 6.6 Hz, 1H), 2.23-2.13 (m, 2H), 1.05 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 137.8, 136.5, 134.8, 132.9, 130.2, 129.5, 128.7, 128.5, 128.4, 126.5, 123.3, 120.4, 119.6, 119.3, 117.9, 110.6, 26.0, 13.6. HRMS m/z (ESI) calcd for $C_{20}H_{19}N$ (M+H)$^+$ 274.1590, found 274.1588.

2-(1*E*,3*E*-hepta-1,3-dien-1-yl)-3-phenyl-1*H*-indole (39)

Product **39** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **39** (21.8 mg, 38%) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.66 (d, J = 7.9 Hz, 1H), 7.55-7.46 (m, 4H), 7.38-7.32 (m, 2H), 7.22 (t, J = 7.6 Hz, 1H), 7.14-7.08 (m, 1H), 6.64-6.56 (m, 2H), 6.27-6.15 (m, 1H), 5.84 (dt, J = 14.8, 7.0 Hz, 1H), 2.18-2.09 (m, 2H), 1.46 (h, J = 7.4 Hz, 2H), 0.94 (t, J = 7.4 Hz, 3H). ^{13}C NMR (76 MHz, $CDCl_3$) δ 136.5, 136.2, 134.8, 132.9, 130.6, 130.2, 128.7, 128.5, 128.4, 126.5, 120.4, 119.6, 119.3, 117.9, 110.6, 35.1, 22.6, 13.9. HRMS m/z (ESI) calcd for $C_{20}H_{19}N$ $(M+H)^+$ 288.1747, found 288.1744.

2,3-Diphenyl-1*H*-indole (41)

Product **41** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **41** (33.4 mg, 62%) as a yellow solid (m.p. 125.5-127.5 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.48-7.43 (m, 5H), 7.39 (t, J = 7.6 Hz, 2H), 7.35-7.28 (m, 4H), 7.26 (d, J = 7.1 Hz, 1H), 7.20-7.14 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.1, 135.2, 134.2, 132.8, 130.3, 128.9, 128.8, 128.7, 128.3, 127.8, 126.4, 122.8, 120.6, 119.9, 115.2, 111.0. The NMR spectra are consistant with the reported literature.[2]

3-(4-Chlorophenyl)-2-phenyl-1*H*-indole (42)

Product **42** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **42** (32.1 mg, 53%) as a yellow solid (m.p. 136.5-138.5 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.68 (d, J = 6.7 Hz, 1H), 7.45-7.41 (m, 3H), 7.40-7.32 (m, 7H), 7.29 (ddd, J = 8.2, 7.0, 1.2 Hz, 1H), 7.21 (ddd, J = 8.0, 7.0, 1.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.9, 134.5, 133.7, 132.5, 132.1, 131.5, 130.3, 128.9, 128.5, 128.3, 128.0, 122.9, 120.7, 119.5, 113.8, 111.1. The NMR spectra are consistant with the reported literature.[2]

3-(4-Bromophenyl)-2-phenyl-1*H*-indole (43)

Product **43** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **43** (39.6 mg, 57%) as a yellow solid (m.p. 116.5-118.5 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.69 (d, J = 9.1 Hz, 1H), 7.55-7.51 (m, 2H), 7.46-7.40 (m, 3H), 7.40-7.33 (m, 4H), 7.33-7.27 (m, 2H), 7.23-7.19 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.9, 134.5, 134.2, 132.4, 131.8, 128.9, 128.5, 128.3, 128.1, 122.9, 120.8, 120.2, 119.5, 113.8, 111.1. The NMR spectra are consistant with the reported literature.[7]

3-phenyl-2-(o-tolyl)-1*H*-indole (44)

Product **44** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **44** (54.3 mg, 96%) as a yellow solid (m.p. 162.5-164.5 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.91 (d, J = 7.9 Hz, 1H), 7.46-7.38 (m, 4H), 7.36-7.22 (m, 8H), 2.05 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.7, 135.8, 135.5, 134.5, 132.7, 130.9, 130.6, 129.1, 128.7, 128.5, 127.5, 125.9, 125.8, 122.5, 120.4, 119.7, 115.9, 111.0, 20.1. HRMS m/z (ESI) calcd for $C_{21}H_{17}N$ $(M+Na)^+$ 306.1253, found 306.1253.

2-(2-Methoxyphenyl)-3-phenyl-1*H*-indole (45)

Product **45** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **45** (54.4 mg, 91%) as a yellow solid (m.p. 153.5-155.5 °C).

^{1}H NMR (400 MHz, CDCl$_3$) δ 9.04 (s, 1H), 7.81 (d, J = 7.9 Hz, 1H), 7.56-7.52 (m, 2H), 7.50-7.43 (m, 3H), 7.38-7.29 (m, 4H), 7.26-7.20 (m, 1H), 7.05 (d, J = 8.6 Hz, 1H), 6.88 (td, J = 7.5, 1.2 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 156.8, 135.9, 135.5, 132.1, 131.3, 130.2, 129.1, 128.7, 127.9, 126.1, 122.5, 121.0, 120.9, 120.0, 119.5, 115.8, 111.7, 110.9, 55.7. HRMS m/z (ESI) calcd for $C_{21}H_{17}NO$ (M+H)$^+$ 260.1434, found 260.1439.

3-Phenyl-2-(m-tolyl)-1*H*-indole (46)

Product **39** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **39** (31.7 mg, 56%) as a yellow solid (m.p. 149.5-151.5 °C).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.22 (s, 1H), 7.71 (d, J = 7.9 Hz, 1H), 7.49-7.37 (m, 5H), 7.33-7.29 (m, 1H), 7.29-7.24 (m, 2H), 7.23-7.15 (m, 3H), 7.12 (t, J = 3.7 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 138.5, 135.9, 135.2, 134.3, 132.7, 130.3, 128.9, 128.7, 128.7, 128.6, 126.3, 125.6, 122.7, 120.5, 119.8, 115.0, 110.9, 21.6. The NMR spectra are consistant with the reported literature.[4]

2-(3-Chlorophenyl)-3-phenyl-1*H*-indole (47)

Product **40** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **40** (36.9 mg, 61%) as a yellow solid (m.p. 132.5-134.5 °C).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.22 (s, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.47-7.39 (m, 6H), 7.35-7.22 (m, 5H), 7.18 (ddd, J = 8.0, 7.1, 1.1 Hz, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 136.1, 134.7, 134.6, 134.6, 132.5, 130.2, 130.0, 128.8, 127.9, 126.7, 126.6, 123.3, 120.8, 120.0, 116.1, 111.1. The NMR spectra are consistant with the reported literature.[5]

2-(3-Bromophenyl)-3-phenyl-1*H*-indole (48)

Product **41** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **41** (36.2 mg, 52%) as a yellow solid (m.p. 121.5-123.5 °C).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.23 (s, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.61 (t, J = 1.9 Hz, 1H), 7.45-7.38 (m, 6H), 7.35-7.27 (m, 3H), 7.19-7.13 (m, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 136.1, 134.9, 134.6, 132.4, 130.7, 130.7, 130.3, 130.2, 128.8, 127.1, 126.7, 123.3, 122.8, 120.8, 120.0, 116.2, 111.1. The NMR spectra are consistant with the reported literature.[6]

3-Phenyl-2-(p-tolyl)-1*H*-indole (49)

Product **49** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **49** (52.6 mg, 93%) as a yellow solid (m.p. 58-60 °C).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.17 (s, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.53 (dt, J = 8.1, 1.8 Hz, 2H), 7.46 (td, J = 7.5, 1.6 Hz, 3H), 7.39-7.34 (m, 3H), 7.33-7.29 (m, 1H), 7.23 (td, J = 7.5, 7.0, 1.1 Hz, 1H), 7.19 (d, J = 7.9 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 137.7, 135.9, 135.3, 134.4, 130.3, 129.8, 129.5, 128.9, 128.6, 128.2, 126.3, 122.6, 120.5, 119.7, 114.6, 110.9, 21.4. HRMS m/z (ESI) calcd for $C_{21}H_{17}N$ (M+Na)$^+$ 306.1253, found 306.1260.

2-(4-Methoxyphenyl)-3-phenyl-1*H*-indole (50)

Product **50** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **50** (56.8 mg, 95%) as a yellow solid (m.p. 162-164 °C).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.19 (s, 1H), 7.77 (d, J = 7.9 Hz, 1H), 7.55-7.51 (m, 2H), 7.48-7.35 (m, 6H), 7.29 (t, J = 7.5 Hz, 1H), 7.23 (t, J = 7.5 Hz, 1H), 6.92-6.87 (m, 2H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 159.3, 135.9, 135.4, 134.3, 130.3, 129.6, 128.9, 128.6, 126.2, 125.3, 122.5, 120.5, 119.6, 114.3, 110.9, 55.4. HRMS m/z (ESI) calcd for $C_{21}H_{17}NO$ (M+H)$^+$ 300.1383, found 300.1373.

3-Phenyl-2-4-(trifluoromethyl)phenyl-1*H*-indole (51)

Product **51** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **51** (30.3 mg, 45%) as a yellow solid (m.p. 123-125 °C).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.27 (s, 1H), 7.70 (d, J = 9.1 Hz, 1H), 7.60-7.50 (m, 4H), 7.47-7.41 (m, 5H), 7.39-7.34 (m, 1H), 7.31 (ddd, J = 8.2, 7.0, 1.2 Hz, 1H), 7.20 (ddd, J = 8.1, 7.0, 1.1 Hz, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 136.3, 134.6, 132.4, 130.3, 129.6, 129.3, 128.9, 128.9, 128.3, 126.9, 125.8, 125.7, 125.6, 123.6, 122.9, 120.9, 120.2, 116.8, 111.2. ^{19}F NMR (376 MHz, CDCl$_3$) δ -62.4. HRMS m/z (ESI) calcd for $C_{21}H_{14}F_3N$ (M+H)$^+$ 338.1151, found 338.1141.

3-(4-Bromophenyl)-2-phenyl-1*H*-indole (52)

Product **52** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **52** (59.3 mg, 96%) as a yellow solid (m.p. 135-137 °C).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.70 (dt, J = 7.9, 1.0 Hz, 1H), 7.60-7.57 (m, 2H), 7.50-7.43 (m, 4H), 7.39-7.33 (m, 4H), 7.32-7.27 (m, 2H), 7.23-7.14 (m, 2H), 6.89 (d, J = 16.7 Hz, 1H), 3.95 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 138.4, 137.4, 135.5, 134.3, 132.9, 130.4, 128.9, 128.7, 127.9, 127.3, 126.5, 126.3, 122.9, 120.3, 119.7, 117.9, 117.3, 109.5, 31.6. HRMS m/z (ESI) calcd for $C_{23}H_{19}N$ (M+Na)$^+$ 332.1410, found 332.1411.

3-(4-Bromophenyl)-2-phenyl-1*H*-indole (53)

Product **53** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **53** (50.6 mg, 75%) as a yellow solid (m.p. 75.5-77.5 °C).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.25 (dt, J = 8.4, 0.9 Hz, 1H), 7.52-7.45 (m, 5H), 7.41-7.37 (m, 2H), 7.34 (d, J = 4.5 Hz, 4H), 7.30-7.23 (m, 3H), 6.57 (d, J = 16.5 Hz, 1H), 2.71 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 171.6, 136.8, 136.7, 135.5, 133.8, 133.7, 130.3, 130.0, 128.9, 128.8, 128.3, 127.5, 126.7, 125.6, 124.0, 123.8, 119.9, 118.9, 115.4, 28.2. HRMS m/z (ESI) calcd for $C_{24}H_{19}NO$ (M+H)$^+$ 338.1539, found 338.1540.

***Tert*-butyl(*E*)-3-phenyl-2-styryl-1*H*-indole-1-carboxylate (54)**

Product **54** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **54** (73.5 mg, 93%) as a yellow solid (m.p. 127.5-129.5 °C).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.24 (dt, J = 8.4, 0.9 Hz, 1H), 7.57-7.52 (m, 3H), 7.51-7.46 (m, 3H), 7.39 (ddt, J = 8.4, 7.2, 1.5 Hz, 2H), 7.34-7.30 (m, 4H), 7.29-7.25 (m, 2H), 6.51 (d, J = 16.5 Hz, 1H), 1.74 (s, 9H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 150.9, 137.3, 136.2, 134.4, 134.3, 130.5, 130.2, 128.8, 128.7, 127.8, 127.2, 126.4, 124.8, 123.1, 122.2, 119.7, 119.4, 115.5, 84.2, 28.4. HRMS m/z (ESI) calcd for $C_{27}H_{25}NO_2$ (M+H)$^+$ 396.1958, found 396.1961.

(*E*)-3-Phenyl-2-styryl-1-tosyl-1*H*-indole (55)

Product **55** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **55** (67.3 mg, 75%) as a yellow solid (m.p. 146.5-148.5 °C).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.31 (d, J = 9.3 Hz, 1H), 7.66-7.61 (m, 3H), 7.43-7.27 (m, 12H), 7.25-7.21 (m, 1H), 7.12 (d, J = 7.8 Hz, 2H), 6.40 (d, J = 16.5 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 144.9, 137.1, 136.8, 136.3, 135.5, 134.7, 133.6, 131.2, 130.2, 129.7, 128.9, 128.8, 128.3, 127.5, 127.0, 126.7, 125.3, 124.2, 123.9, 117.7, 115.5, 21.7. HRMS m/z (ESI) calcd for $C_{29}H_{23}NO_2S$ (M+H)$^+$ 450.1522, found 450.1530.

2-Phenethyl-3-phenyl-1*H*-indole (56)

Product **56** was synthesized in accordance with the typical procedure. Purification using flash column chromatography on silica gel (PE:EA = 10:1) afforded product **56** (51.1 mg, 86%) as a yellow oil.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.79 (s, 1H), 7.69 (d, J = 7.9 Hz, 1H), 7.52-7.47 (m, 4H), 7.40-7.26 (m, 5H), 7.24-7.14 (m, 4H), 3.23-3.17 (m, 2H), 3.02 (t, J = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 141.1, 135.3, 135.3, 135.1, 129.7, 128.7, 128.6, 128.6, 127.9, 126.5, 126.1, 121.8, 120.0, 119.1, 114.9, 110.6, 36.2, 28.4. HRMS m/z (ESI) calcd for $C_{22}H_{19}N$ (M+H)$^+$ 298.1590, found 298.1594.

9. X-Ray Crystallographic Data of Product 41

Single crystals were grown by slow evaporation of concentrated solution in mixed solution (0.5 mL DCM and 0.5 mL PE); Compound **41** was placed in a glass vial (1 mL), which were then sealed by plugs with needles on them.

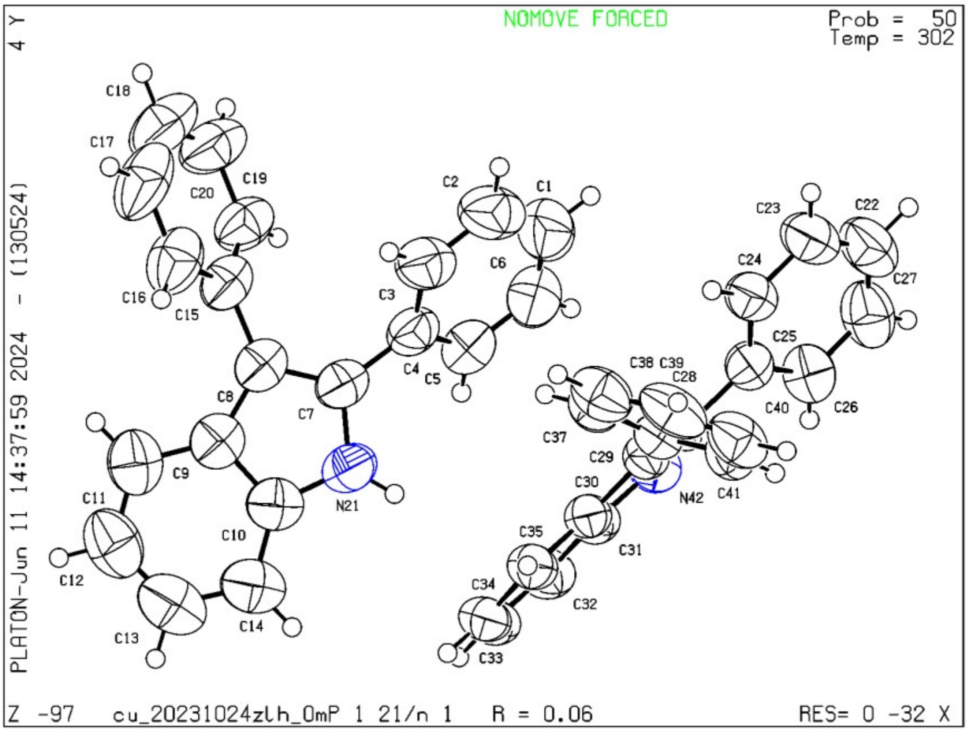


Figure S1. The crystal structure of product **41**

Table S2. Crystal data and structure refinement for product **41**.

Bond precision:	C-C = 0.0033 A	Wavelength = 1.54178	
Cell:	a = 16.0588(7)	b = 10.0682(4)	c = 18.9261(8)
	alpha = 90	beta = 103.229(2)	gamma = 90
Temperature:	302 K		
	Calculated	Reported	
Volume	2978.8(2)	2978.8(2)	
Space group	P 21/n	P 1 21/n 1	
Hall group	-P 2yn	-P 2yn	
Moiety formula	$C_{20}H_{15}N$	0.09 ($C_{20}H_{15}N$)	
Sum formula	$C_{20}H_{15}N$	C H N	
Mr	269.33	27.03	
Dx, g cm^{-3}	1.201	1.326	
z	8	88	
Mu (mm^{-1})	0.532	0.779	
F000	1136.0	1232.0	

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<tr><td>h, k, lmax</td><td>19, 12, 22</td><td>19, 12, 22</td><td></td></tr>
<tr><td>Nref</td><td>5466</td><td>5451</td><td></td></tr>
<tr><td>Tmin, Tmax</td><td>0.911, 0.940</td><td>0.591, 0.753</td><td></td></tr>
<tr><td>Tmin’</td><td>0.856</td><td></td><td></td></tr>
<tr><td colspan="4">Correction method = # Reported T Limits: Tmin = 0.591 Tmax = 0.753
AbsCorr = MULTI-SCAN</td></tr>
<tr><td colspan="2">Data completeness = 0.997</td><td colspan="2">Theta(max) = 68.438</td></tr>
<tr><td colspan="2">R (reflections) = 0.0568 (3812)</td><td colspan="2">wR2(reflections) = 0.1601 (5451)</td></tr>
<tr><td colspan="2">S = 1.031</td><td colspan="2">Npar = 379</td></tr>
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10. Reference

(1) F. Pedro, A. Carmen and S. Mónica, *Eur. J. Org. Chem.*, 1995, **1995**, 1895−1899.

(2) G. A. Kraus and H. Guo, *J. Org. Chem.* 2009, **74**, 5337−5341.

(3) P. Valentina, B. Micol, A. Giorgio. R. Silvia and R. Elisabetta, *Adv. Synth. Catal.*, 2017, **359**, 1912−1918.

(4) Y. Kang, R. Hou, X. Min, T. Wang, Y. Liang and Z. Zhang, *Synthesis*, 2022, **54**, 1621−1632.

(5) Y. Daisuke, N. Takahiro and Y. Hideki, *Chem. Commun.*, 2017, **53**, 2760−2763.

(6) R. K. Maurya, O. P. S. Patel, D. Anand and P. P. Yadav, *Org. Chem. Front.*, 2018, **5**, 1170−1175.

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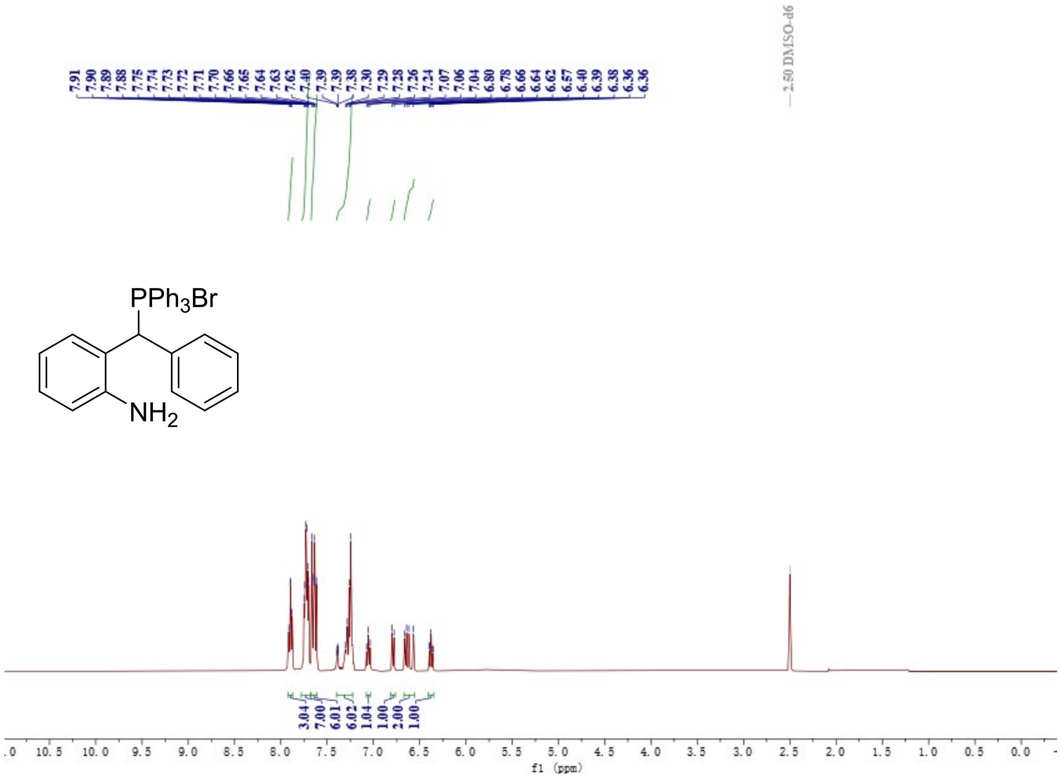
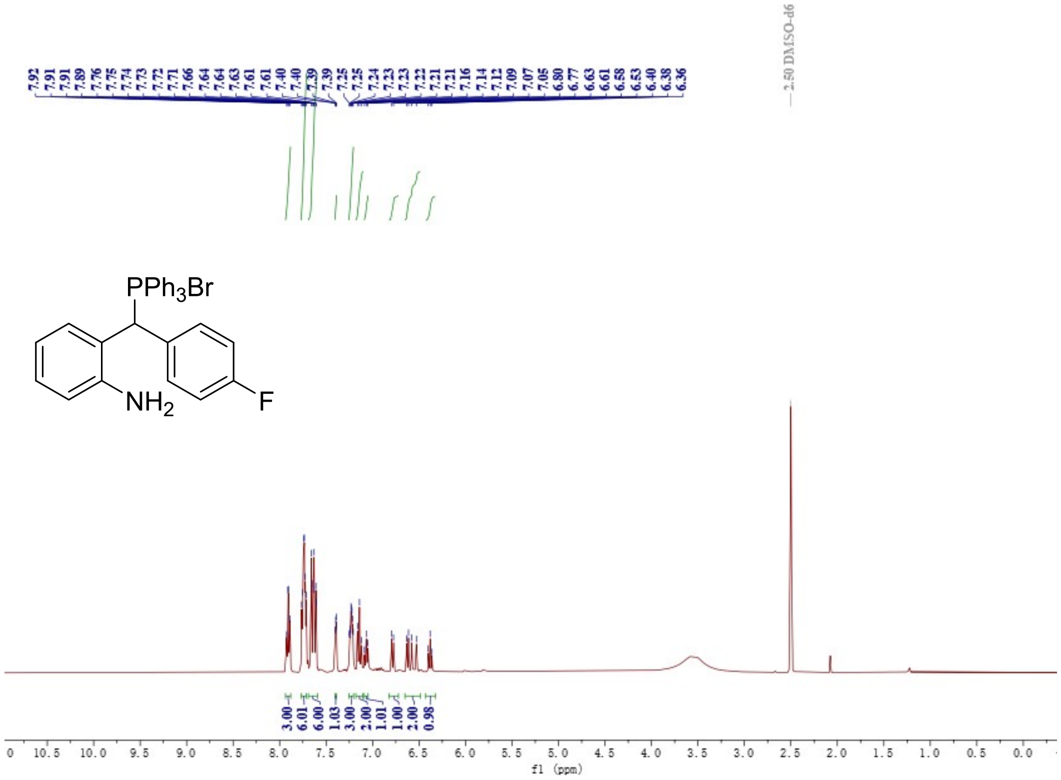
11. NMR Spectra

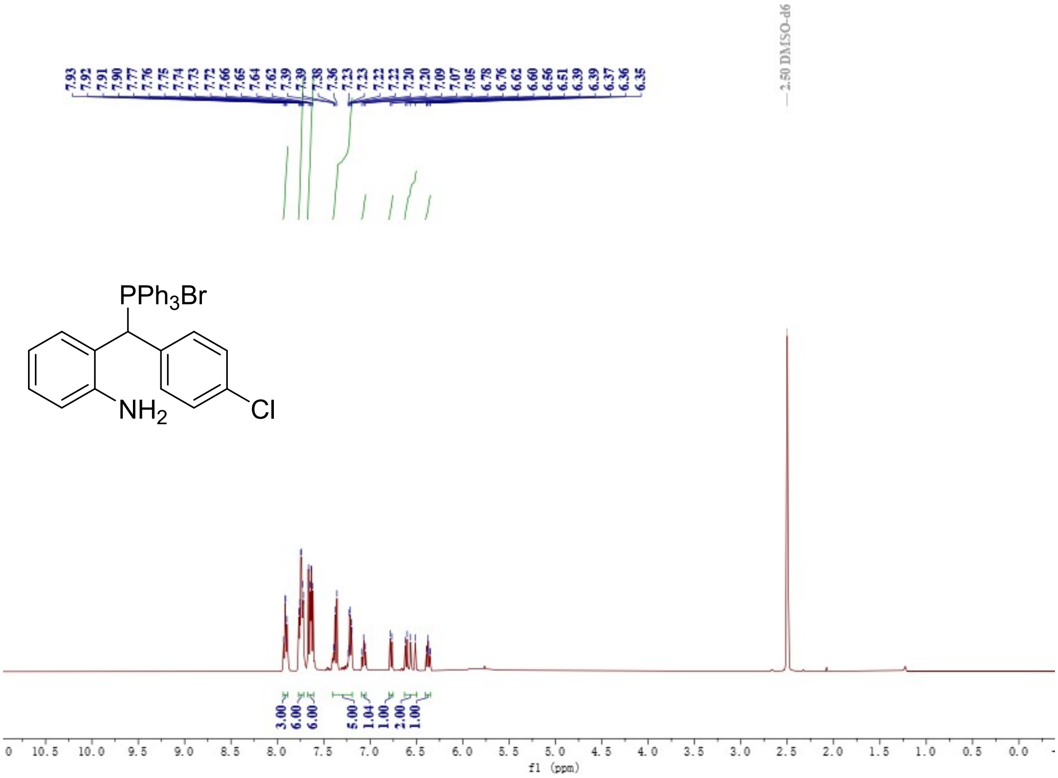
^{1}H NMR of **1a** (400 MHz, DMSO-*d*$_6$)



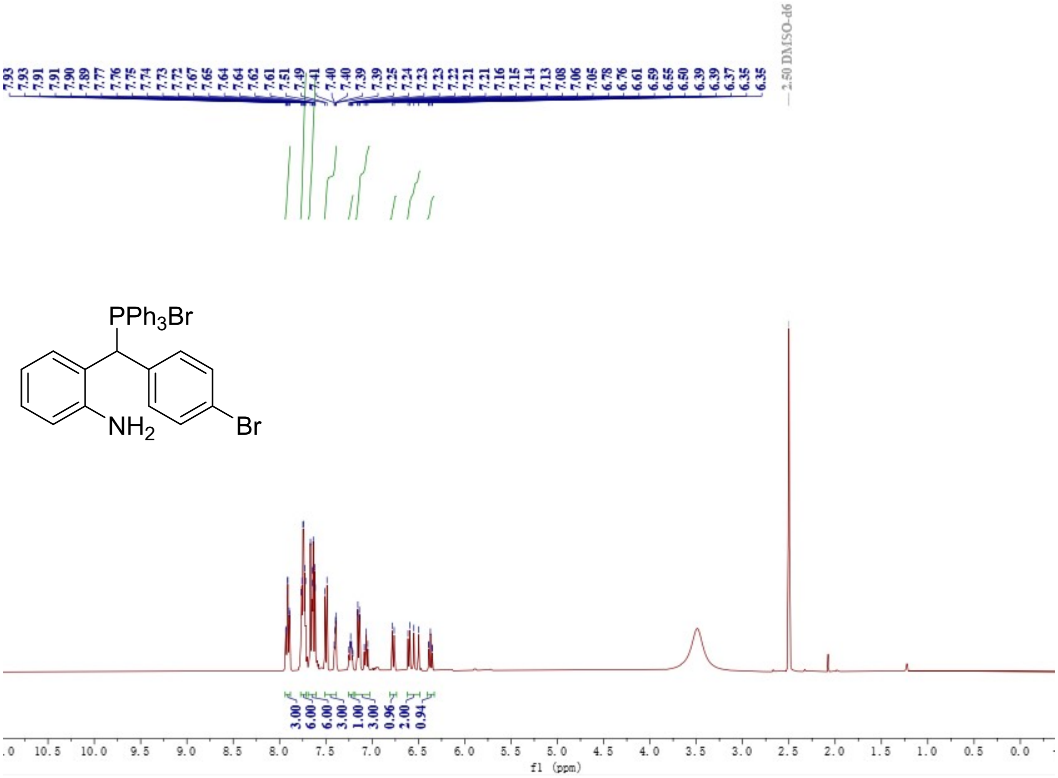
^{1}H NMR of **1b** (400 MHz, DMSO-*d*$_6$)



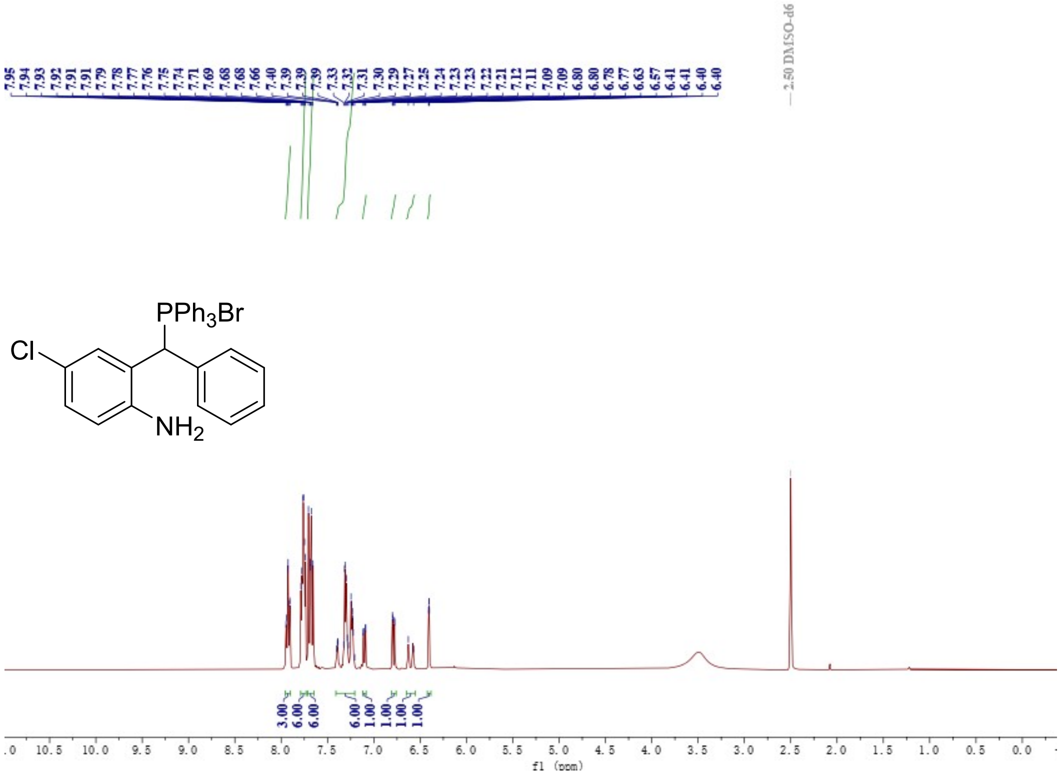
^{1}H NMR of **1c** (400 MHz, DMSO-d_6)



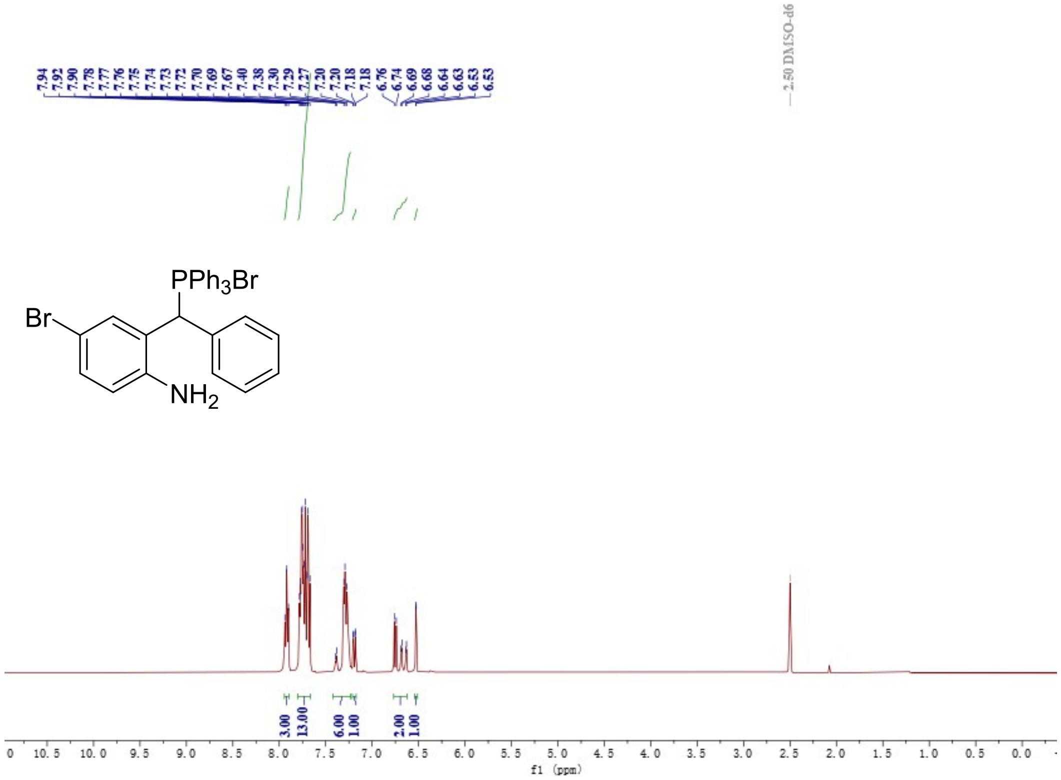
^{1}H NMR of **1d** (400 MHz, DMSO-d_6)



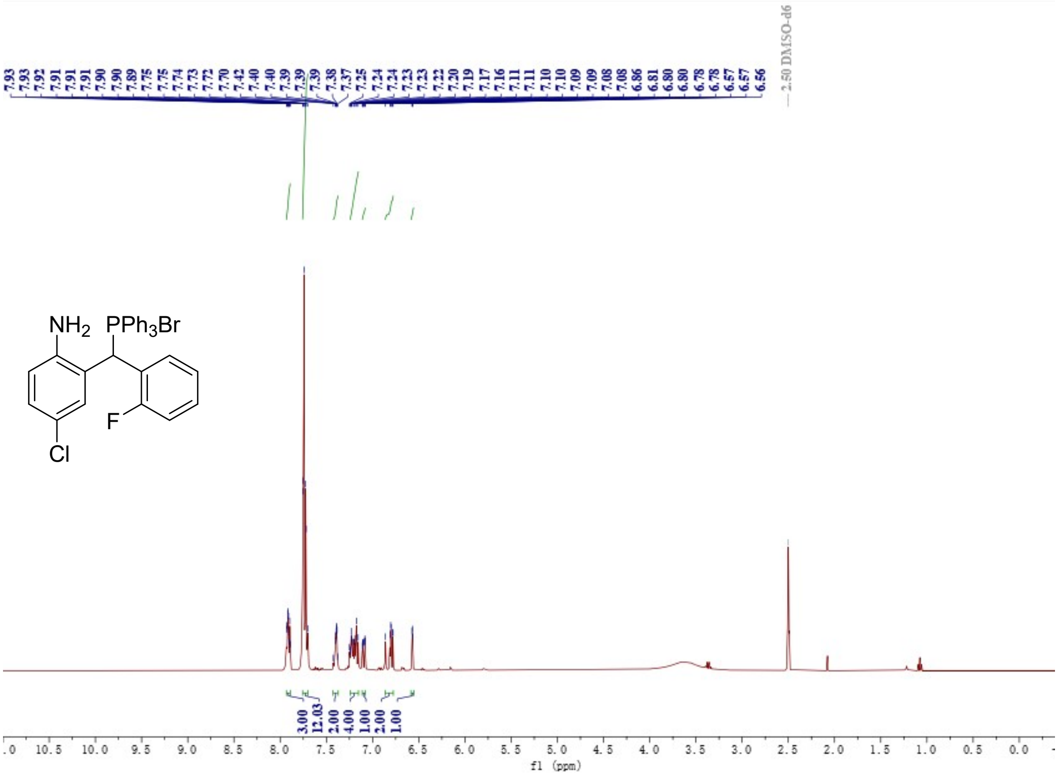
^{1}H NMR of **1e** (400 MHz, DMSO-d_6)



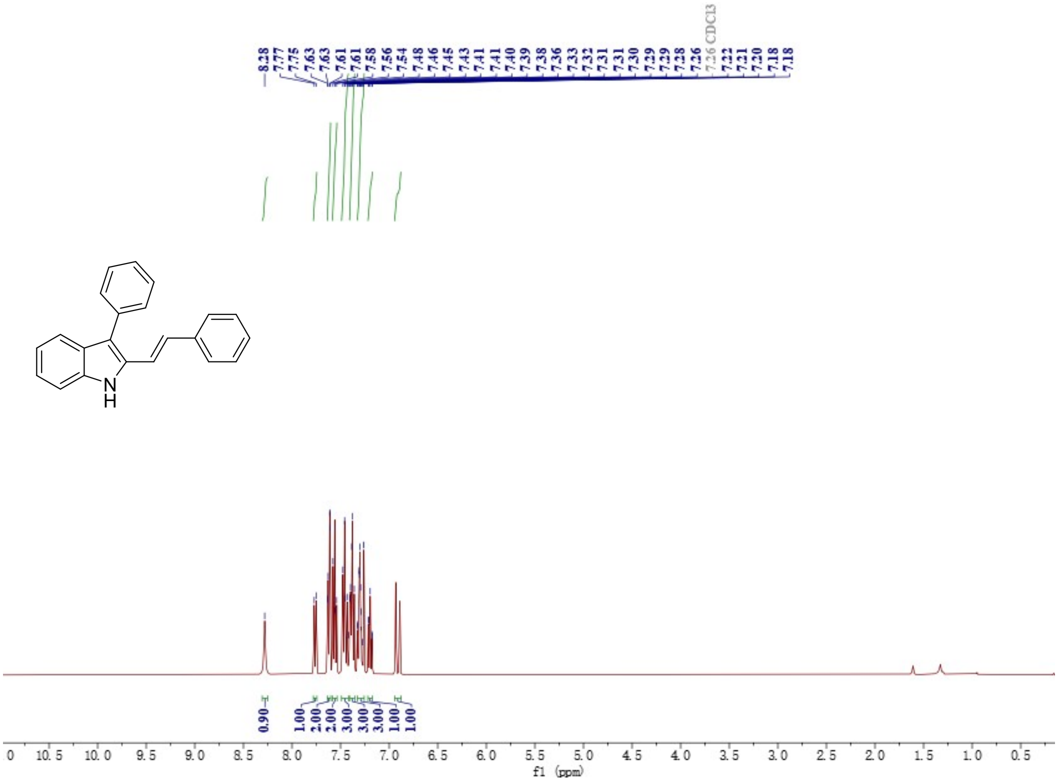
^{1}H NMR of **1f** (400 MHz, DMSO-d_6)



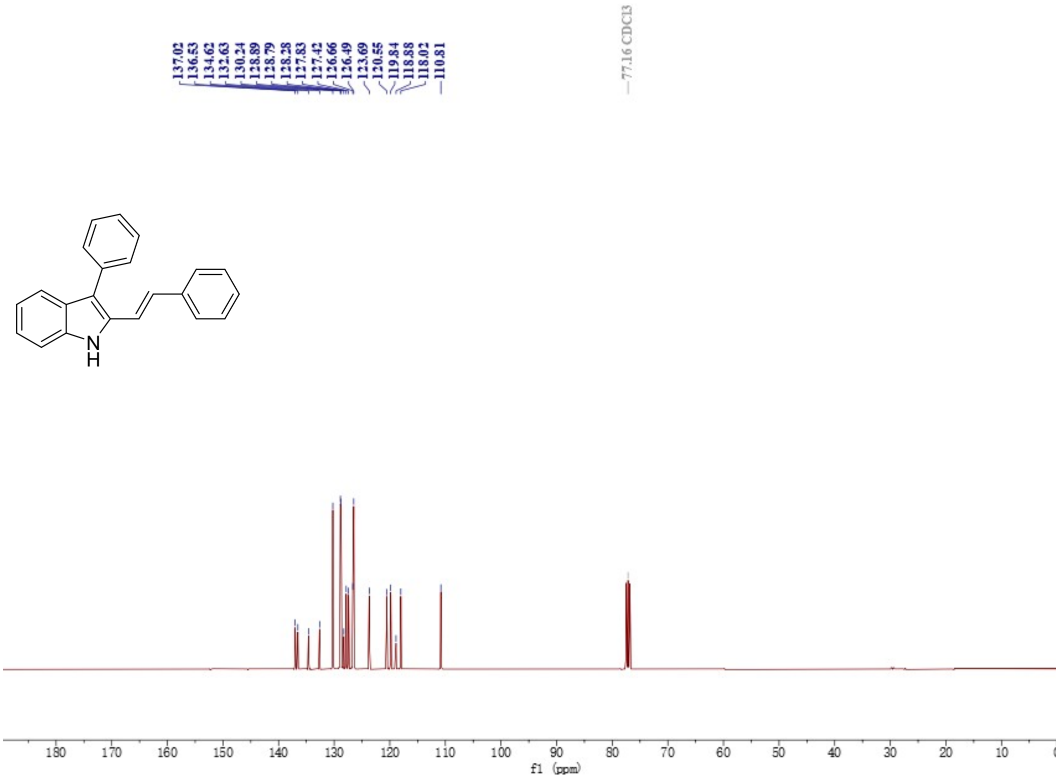
^{1}H NMR of **1g** (400 MHz, DMSO-d_6)



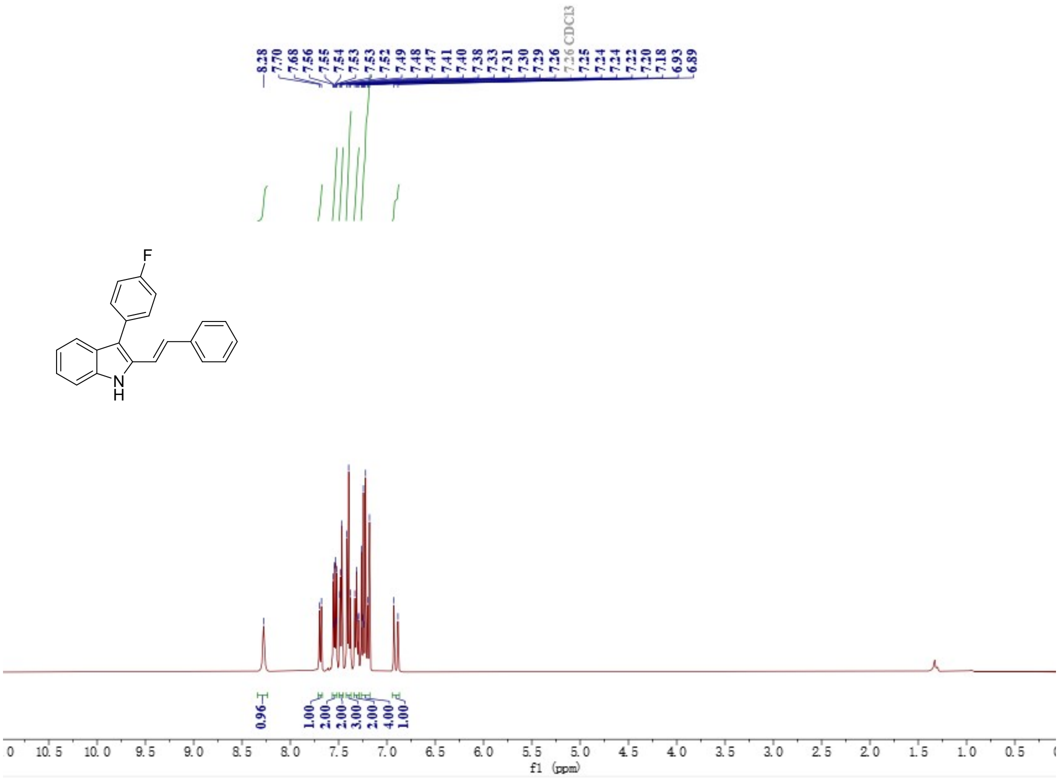
^{1}H NMR of **3** (400 MHz, CDCl$_3$)



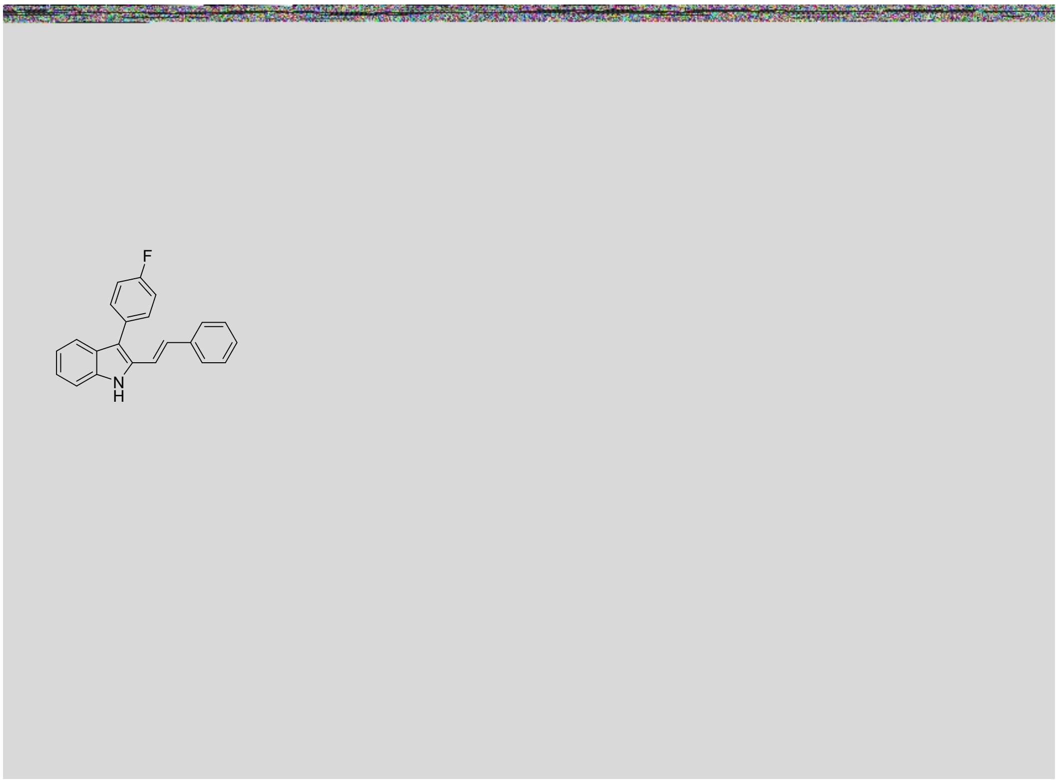
^{13}C NMR of **3** (101 MHz, $CDCl_3$)



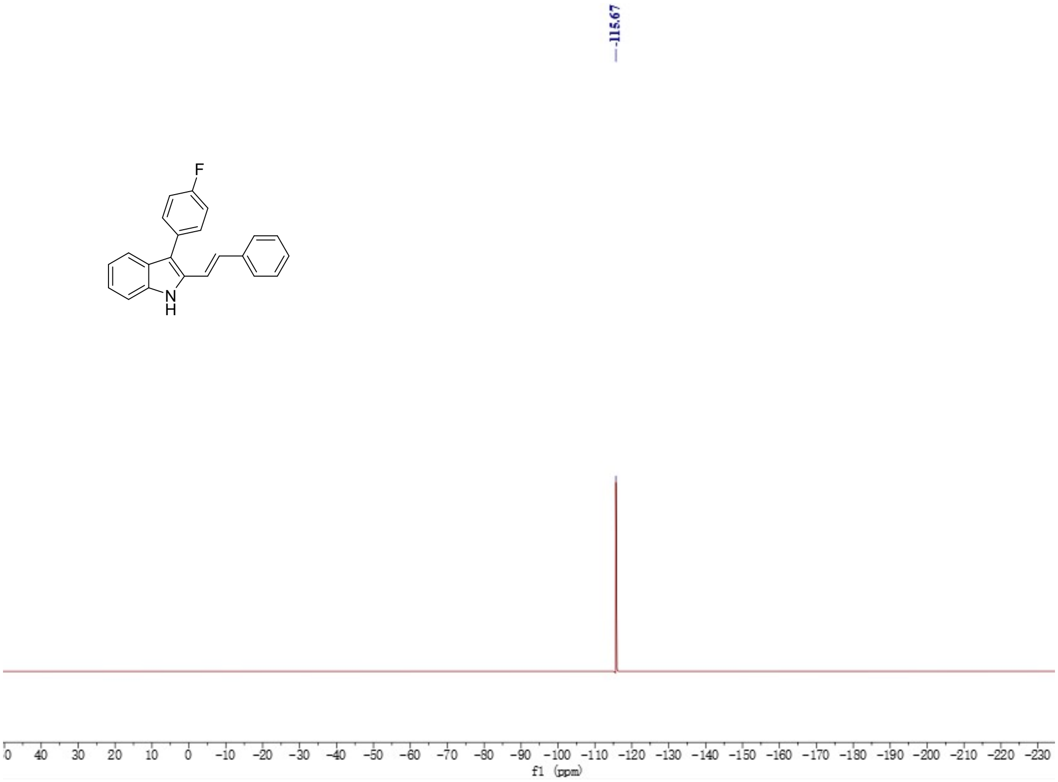
^{1}H NMR of **4** (400 MHz, $CDCl_3$)



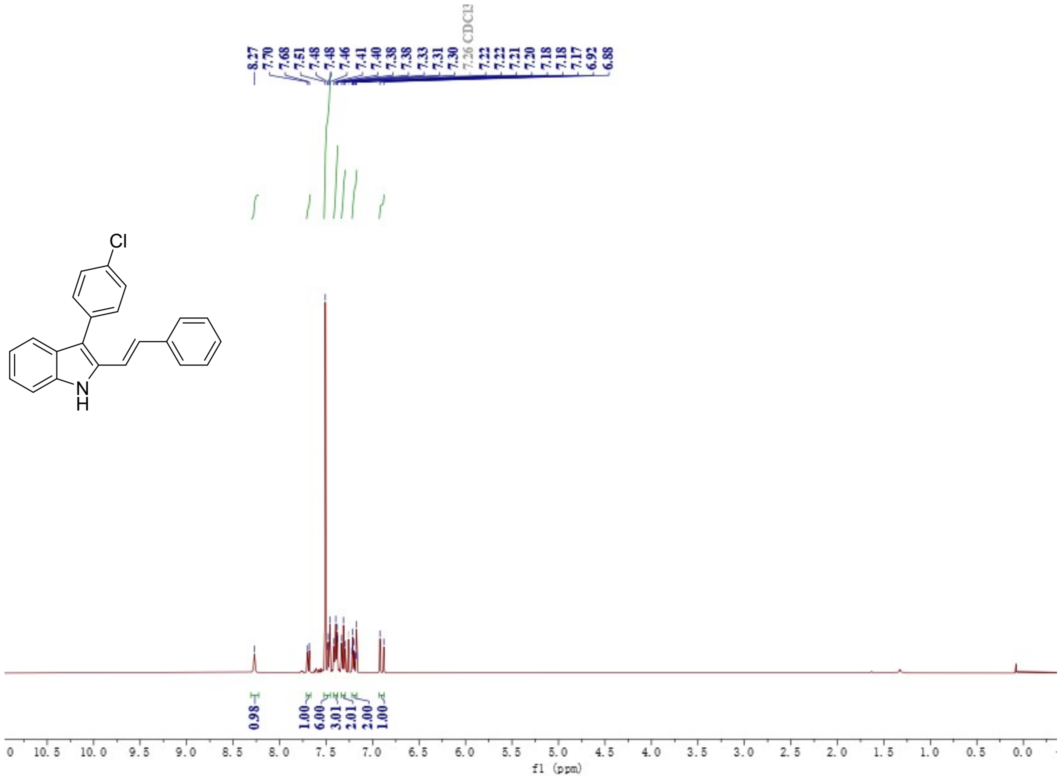
^{13}C NMR of **4** (101 MHz, CDCl$_3$)



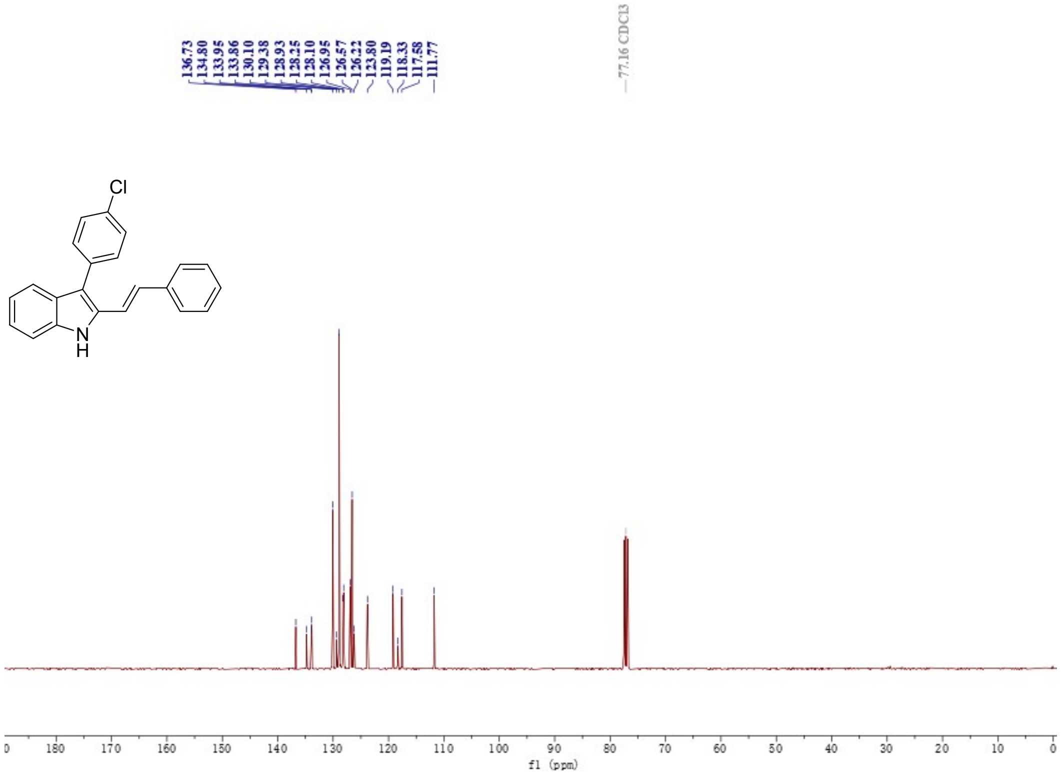
^{19}F NMR of **4** (376 MHz, CDCl$_3$)



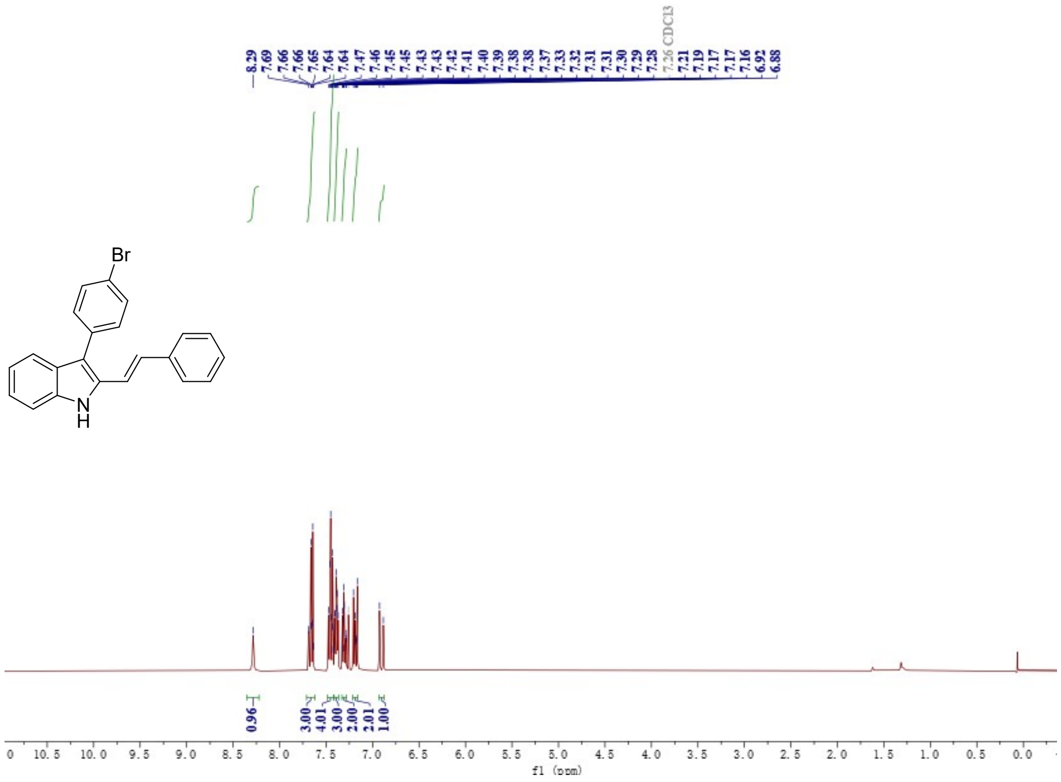
^{1}H NMR of **5** (400 MHz, CDCl$_3$)



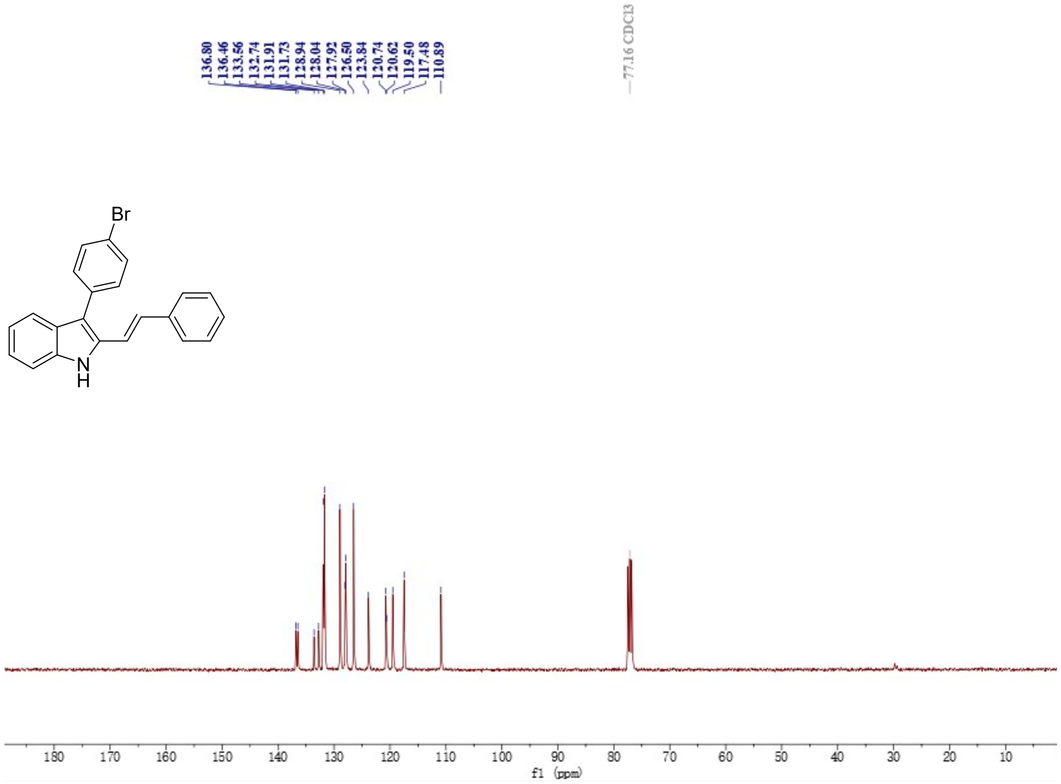
^{13}C NMR of **5** (101 MHz, CDCl$_3$)



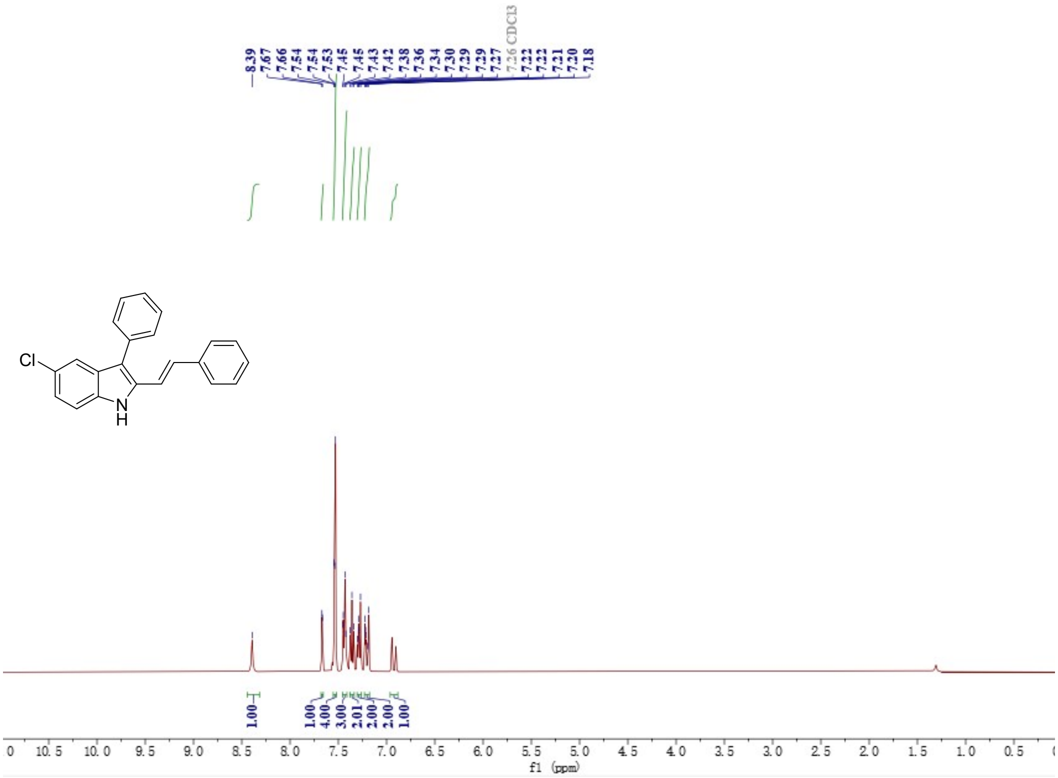
^{1}H NMR of **6** (400 MHz, CDCl$_3$)



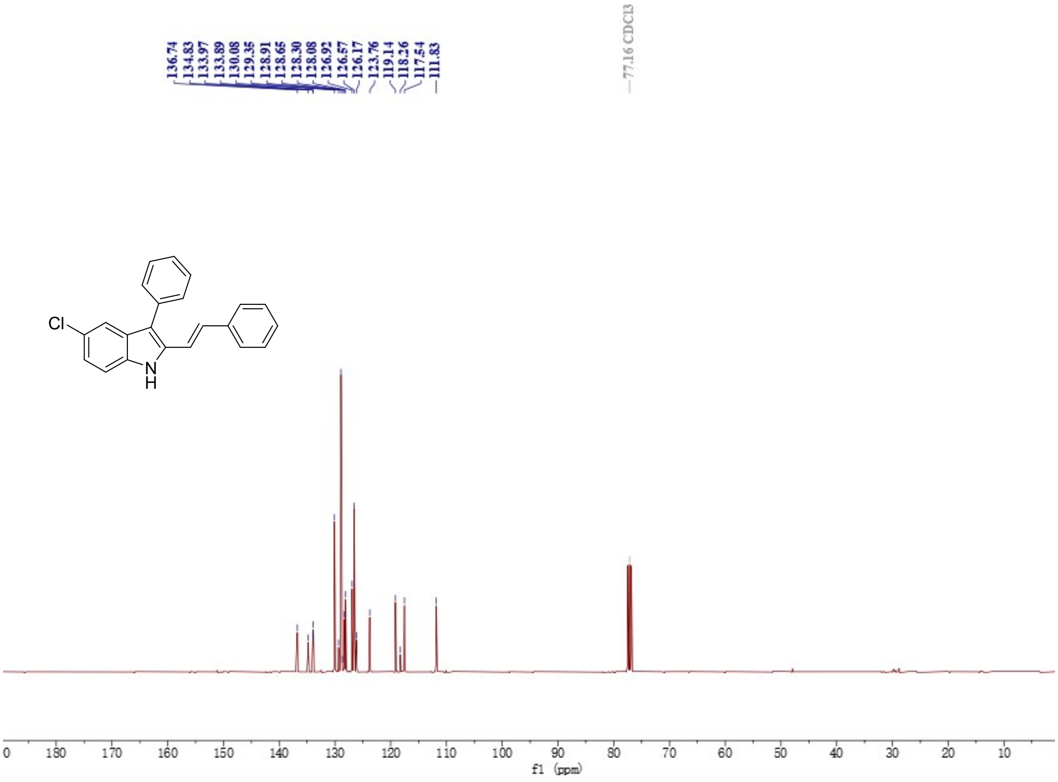
^{13}C NMR of **6** (101 MHz, CDCl$_3$)



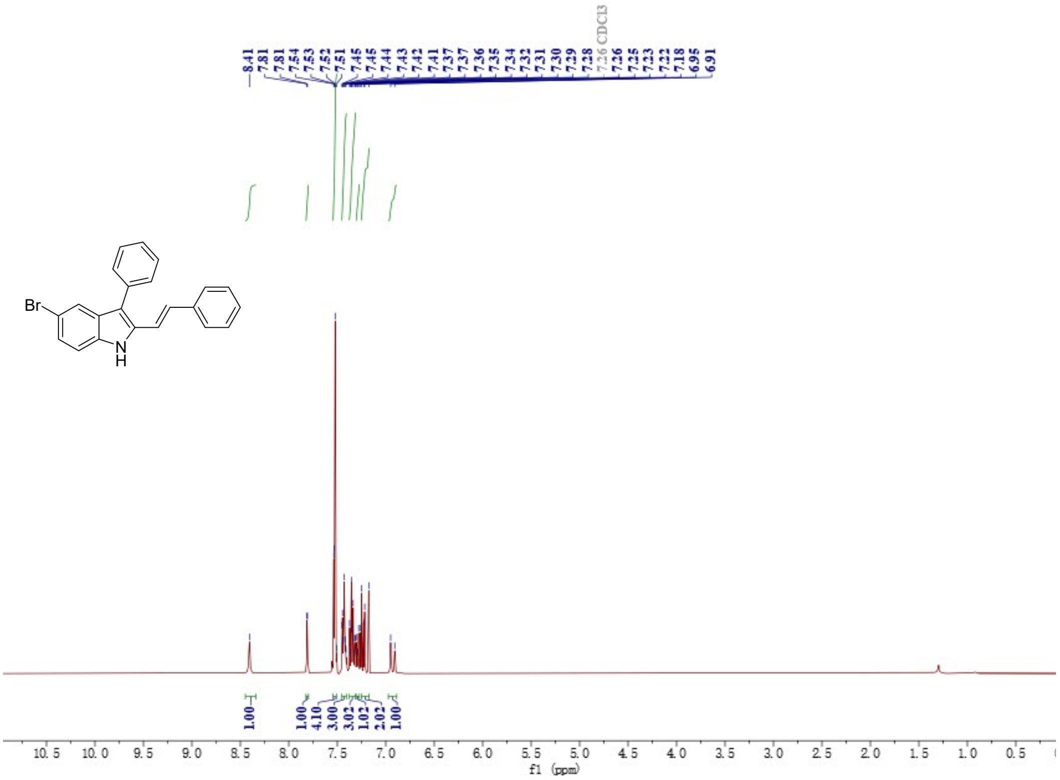
^{1}H NMR of **7** (400 MHz, $CDCl_3$)



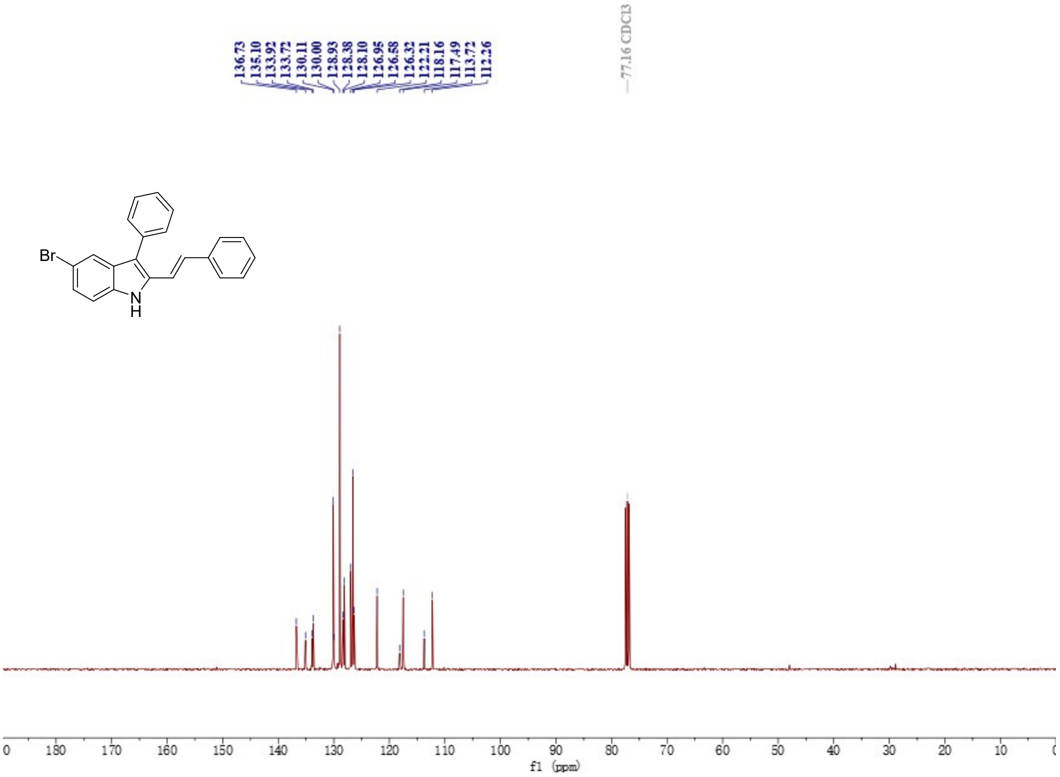
^{13}C NMR of **7** (101 MHz, $CDCl_3$)



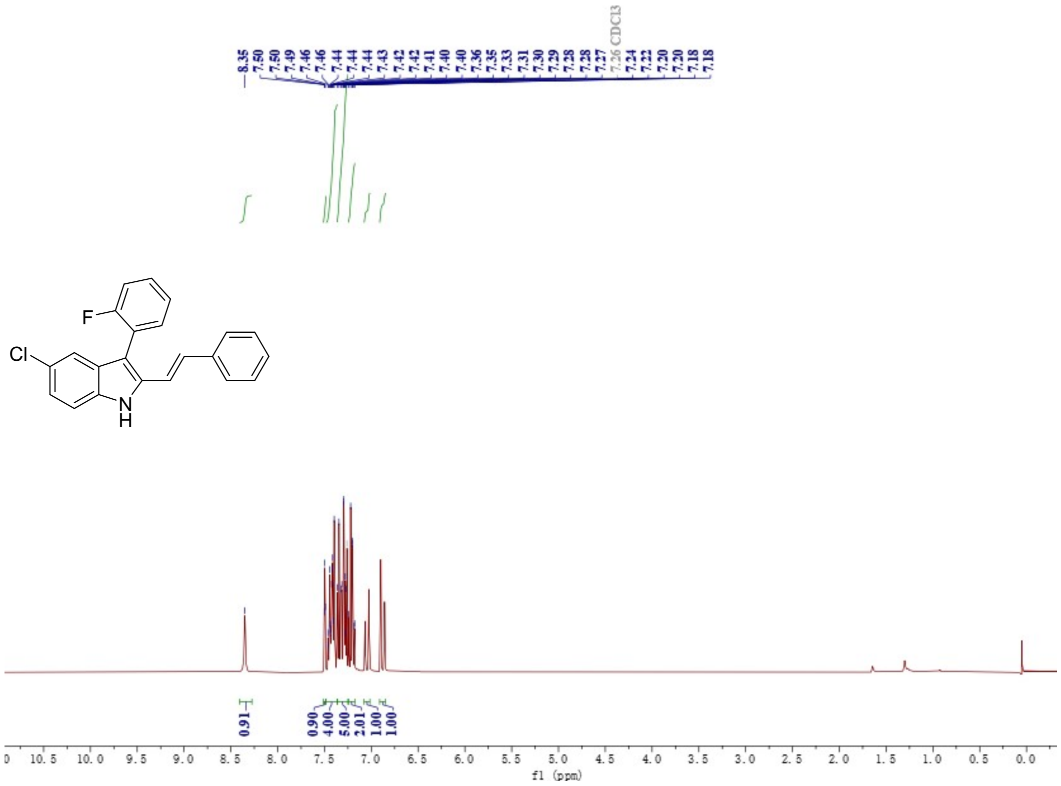
^{1}H NMR of **8** (101 MHz, CDCl$_3$)



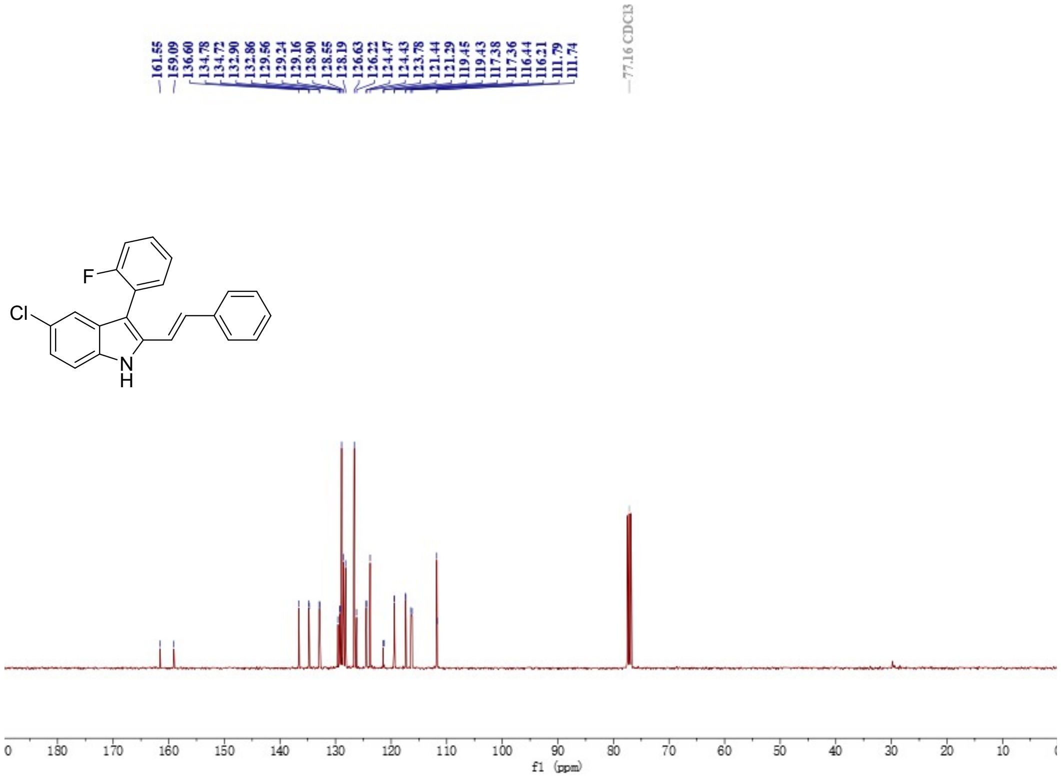
^{13}C NMR of **8** (101 MHz, CDCl$_3$)



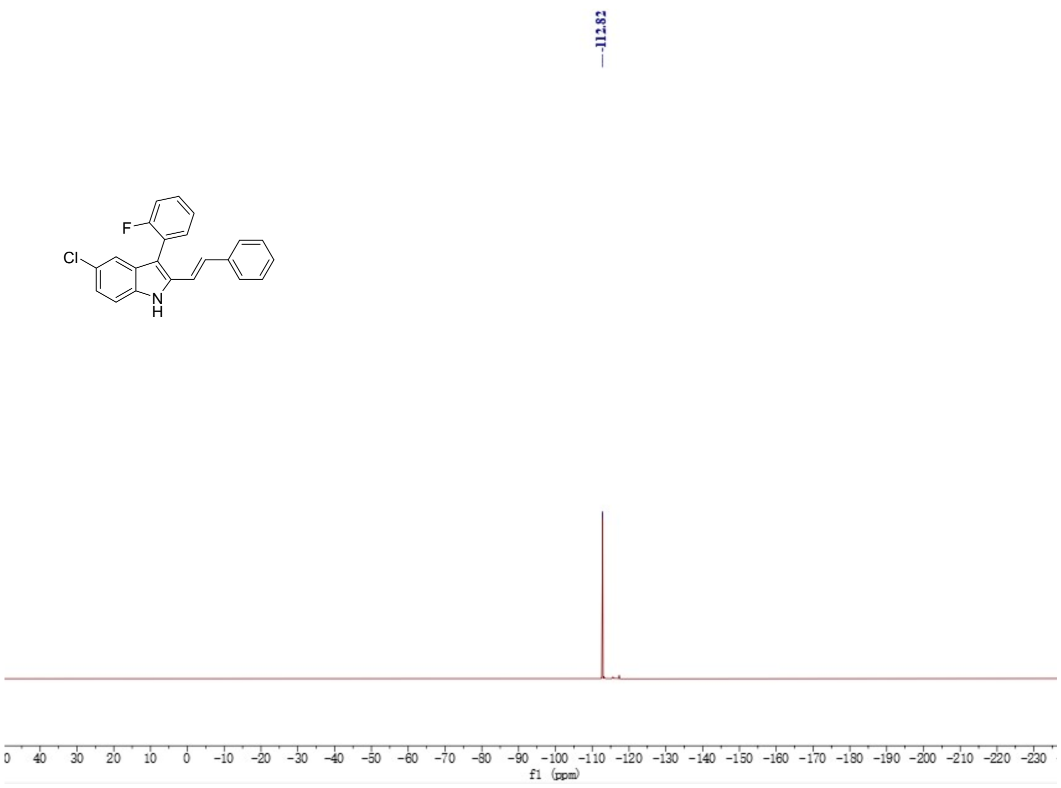
^{1}H NMR of **9** (400 MHz, CDCl$_3$)



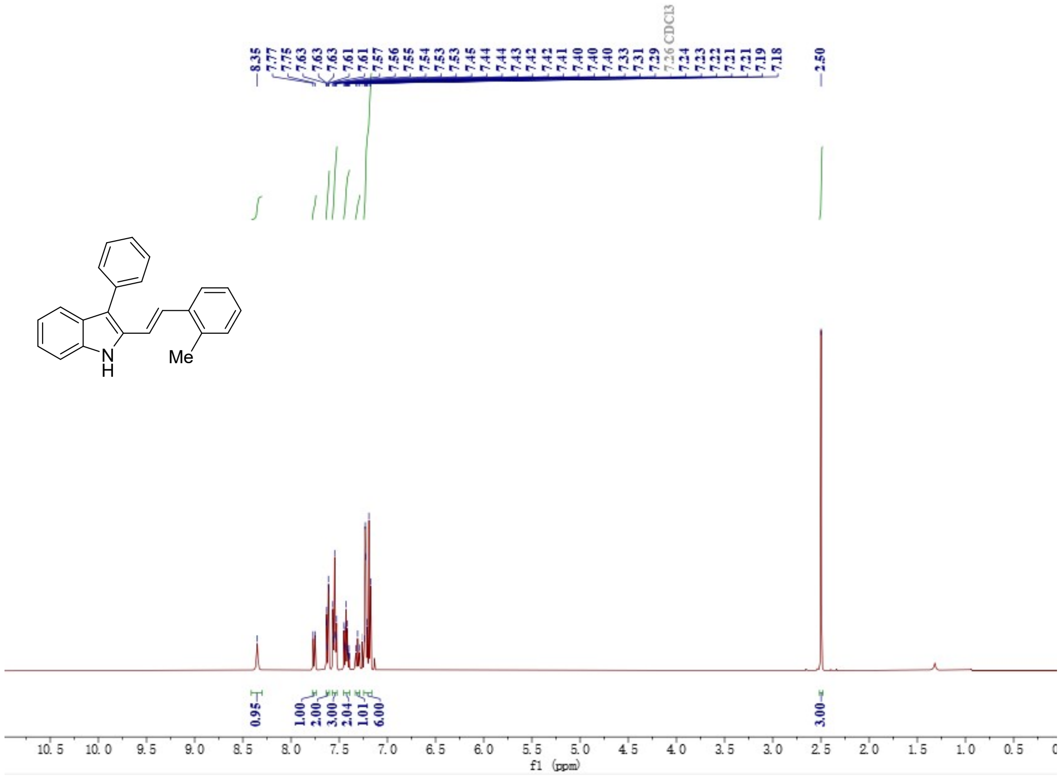
^{13}C NMR of **9** (101 MHz, CDCl$_3$)



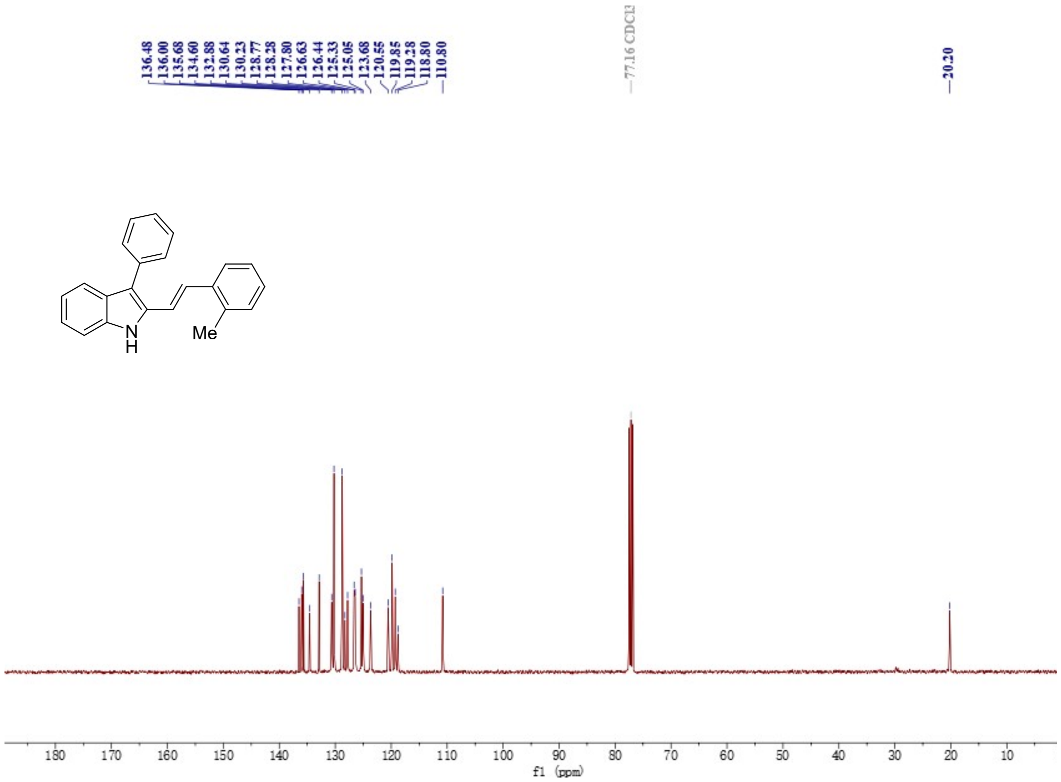
^{19}F NMR of **9** (376 MHz, CDCl$_3$)



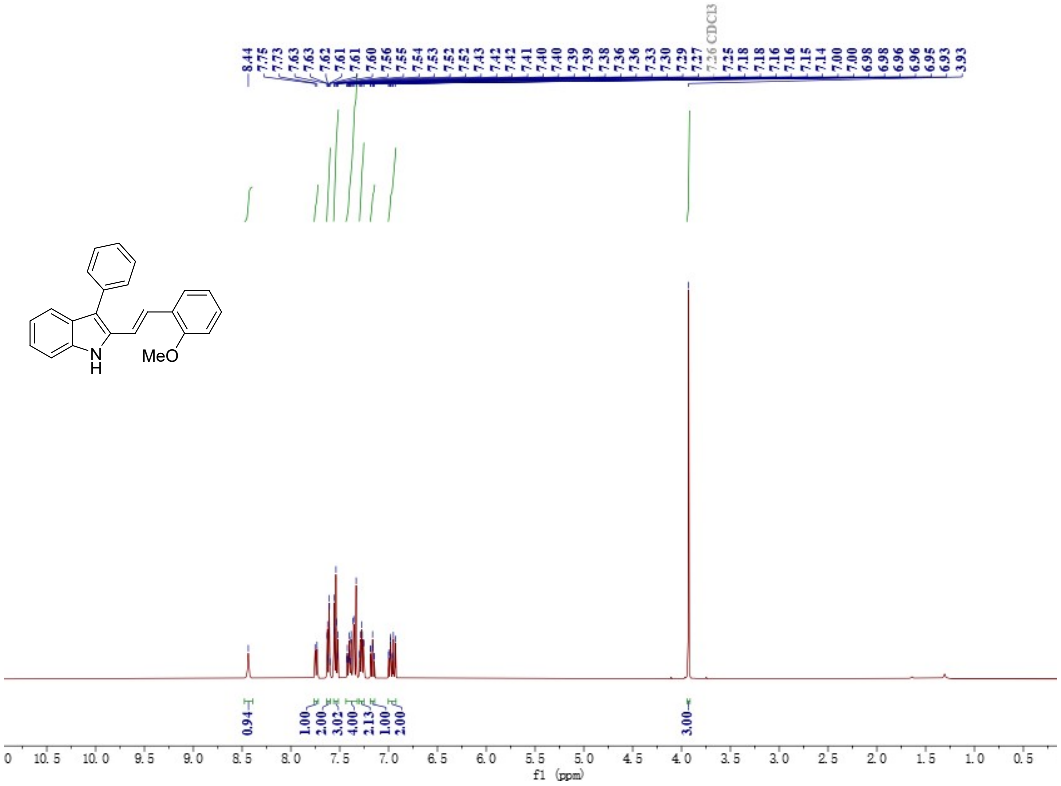
¹H NMR of **10** (400 MHz, $CDCl_3$)



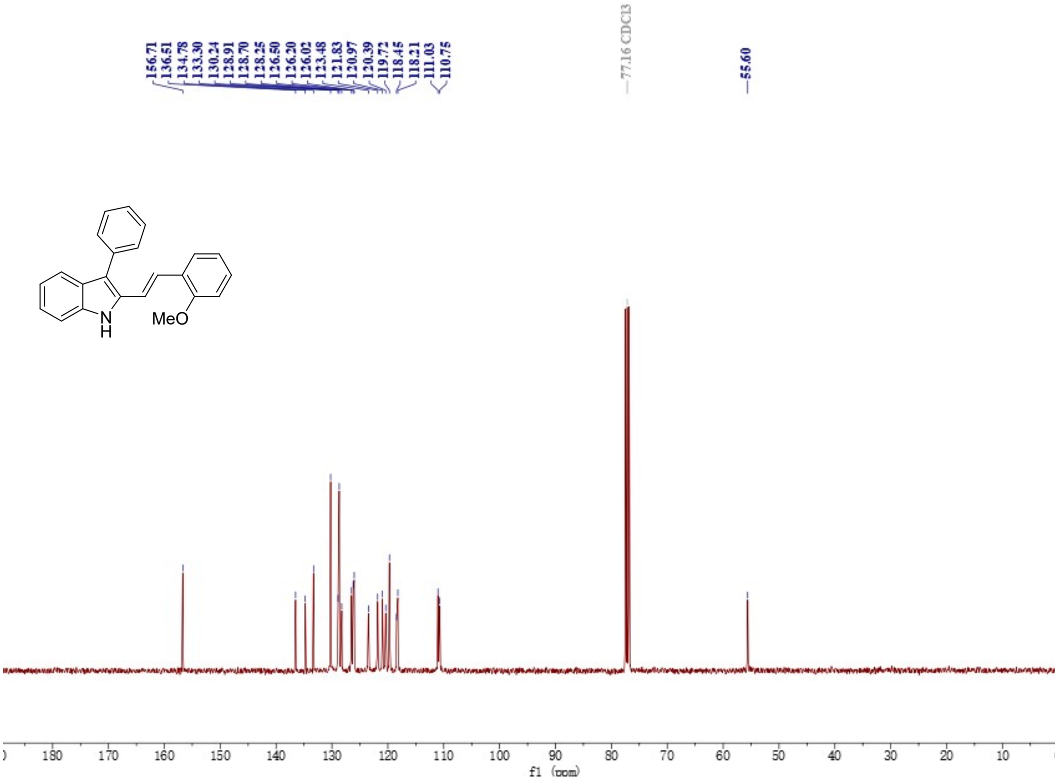
¹³C NMR of **10** (101 MHz, $CDCl_3$)



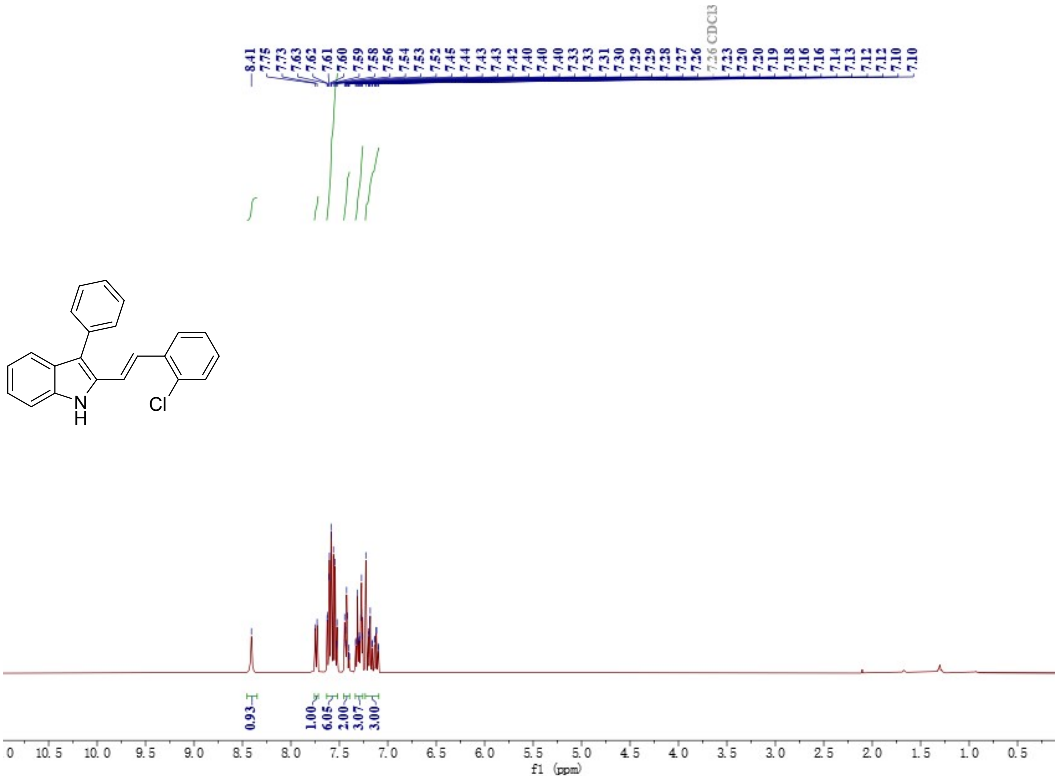
^{1}H NMR of **11** (400 MHz, CDCl$_3$)



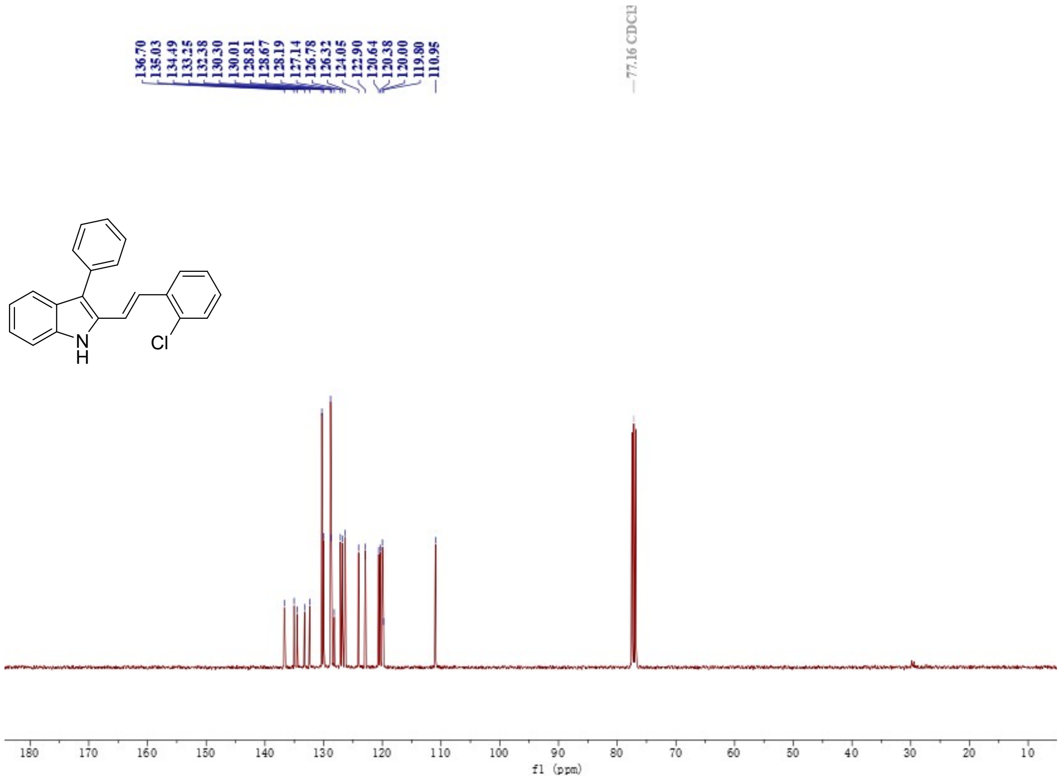
^{13}C NMR of **11** (101 MHz, CDCl$_3$)



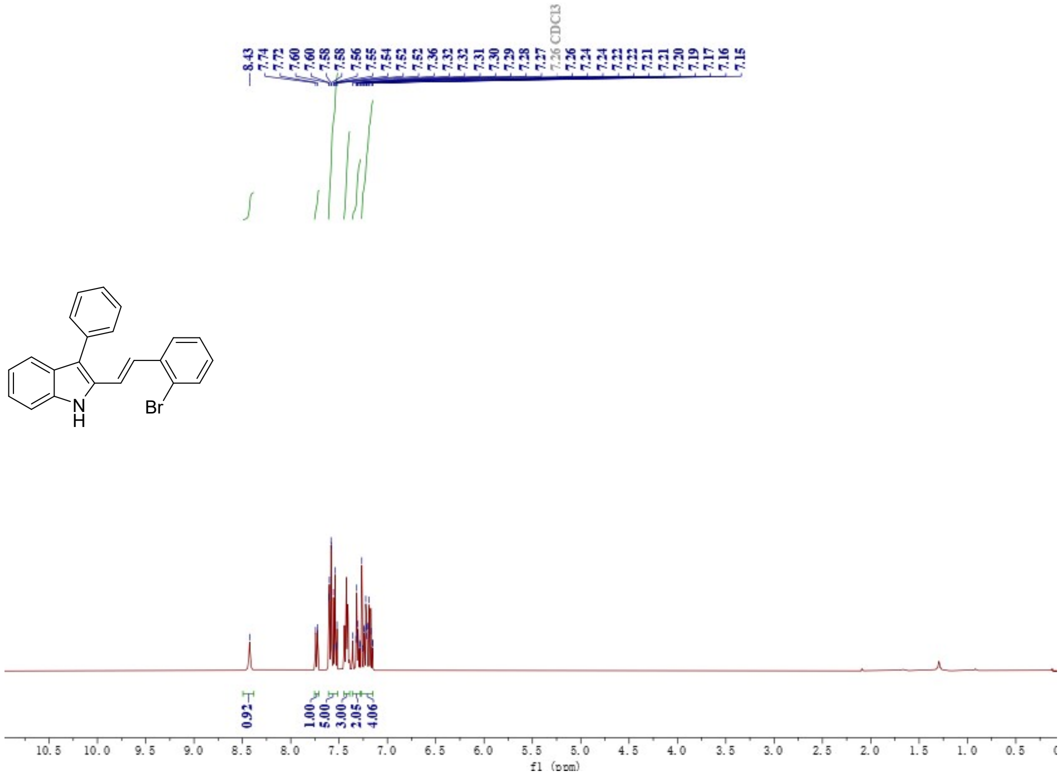
^{1}H NMR of **12** (400 MHz, CDCl$_3$)



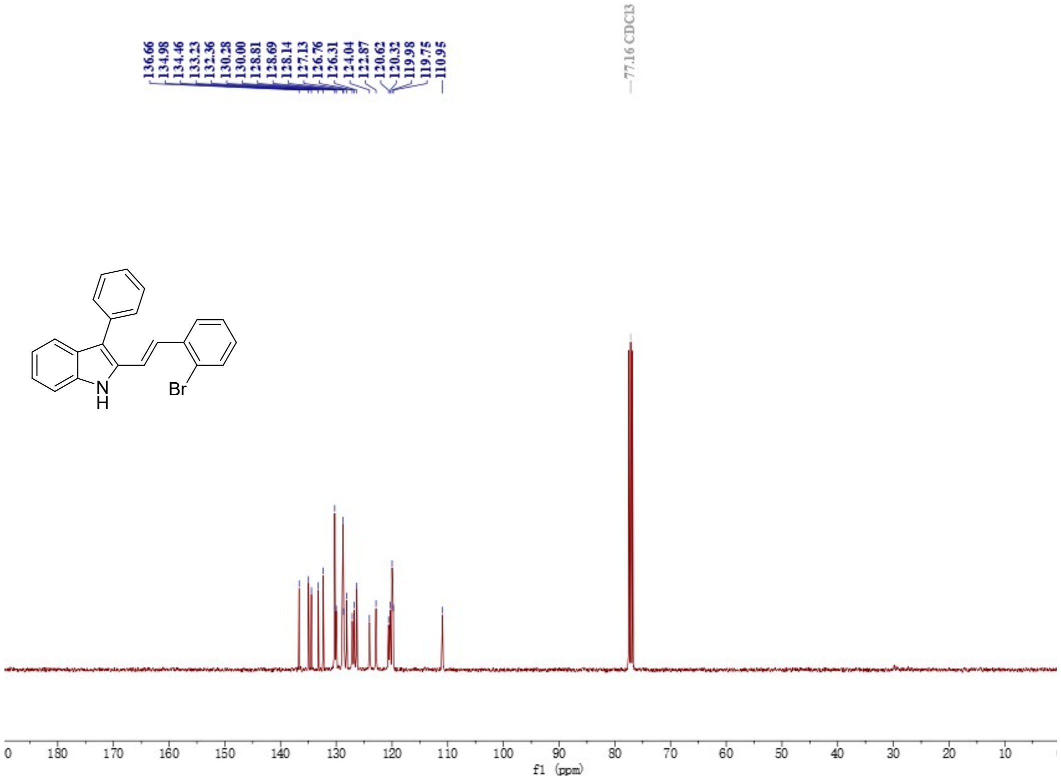
^{13}C NMR of **12** (101 MHz, CDCl$_3$)



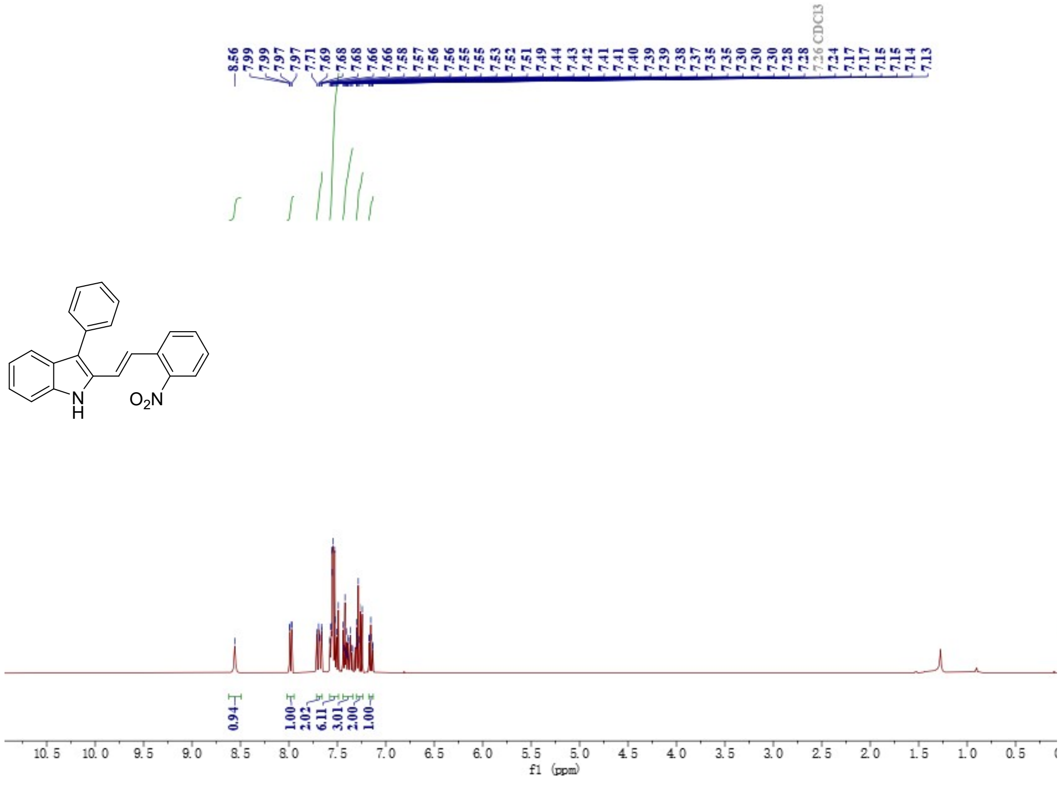
^{1}H NMR of **13** (400 MHz, CDCl$_3$)



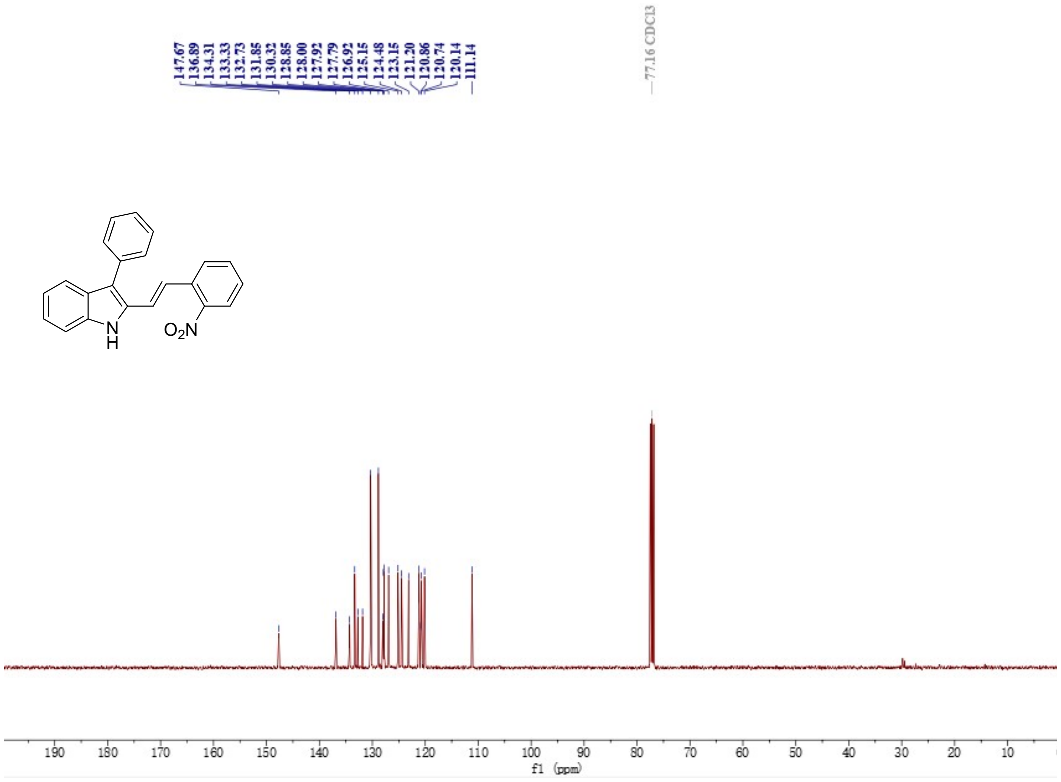
^{13}C NMR of **13** (101 MHz, CDCl$_3$)



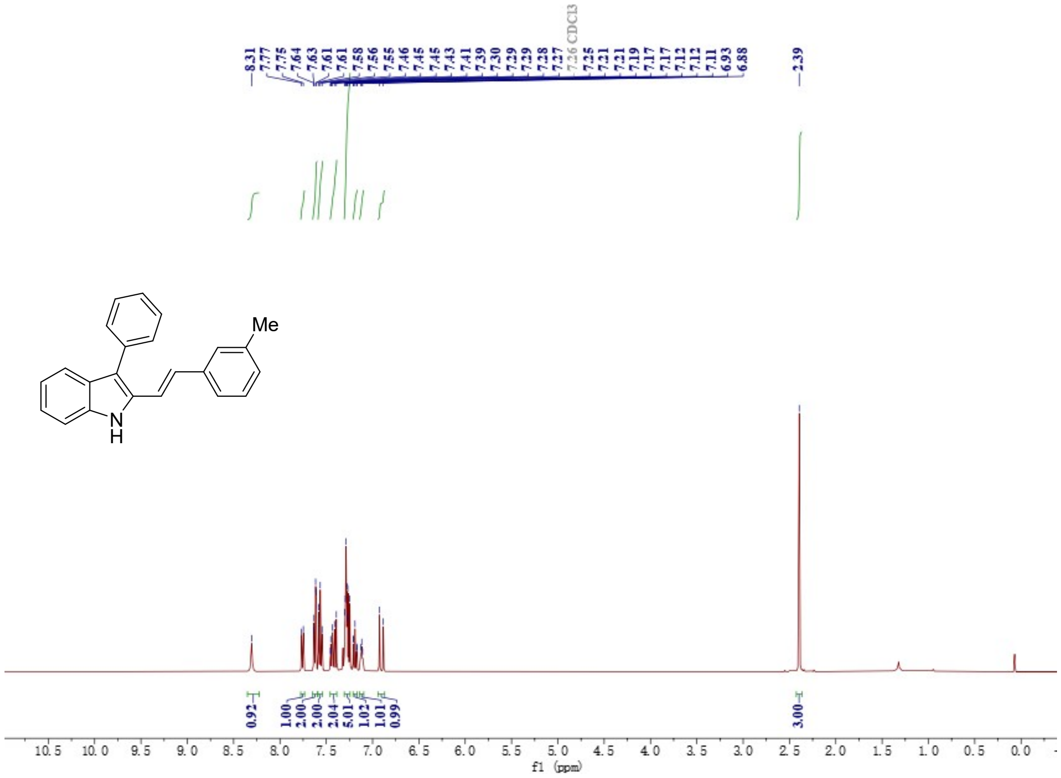
^{1}H NMR of **14** (400 MHz, CDCl$_3$)



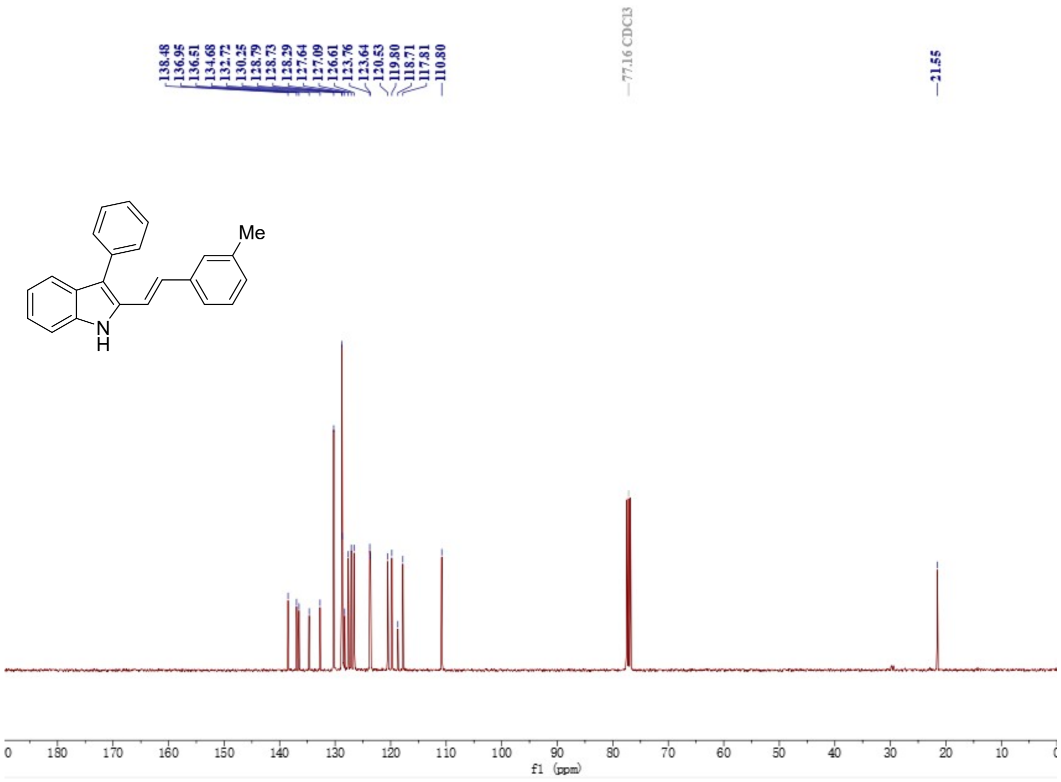
^{13}C NMR of **14** (101 MHz, CDCl$_3$)



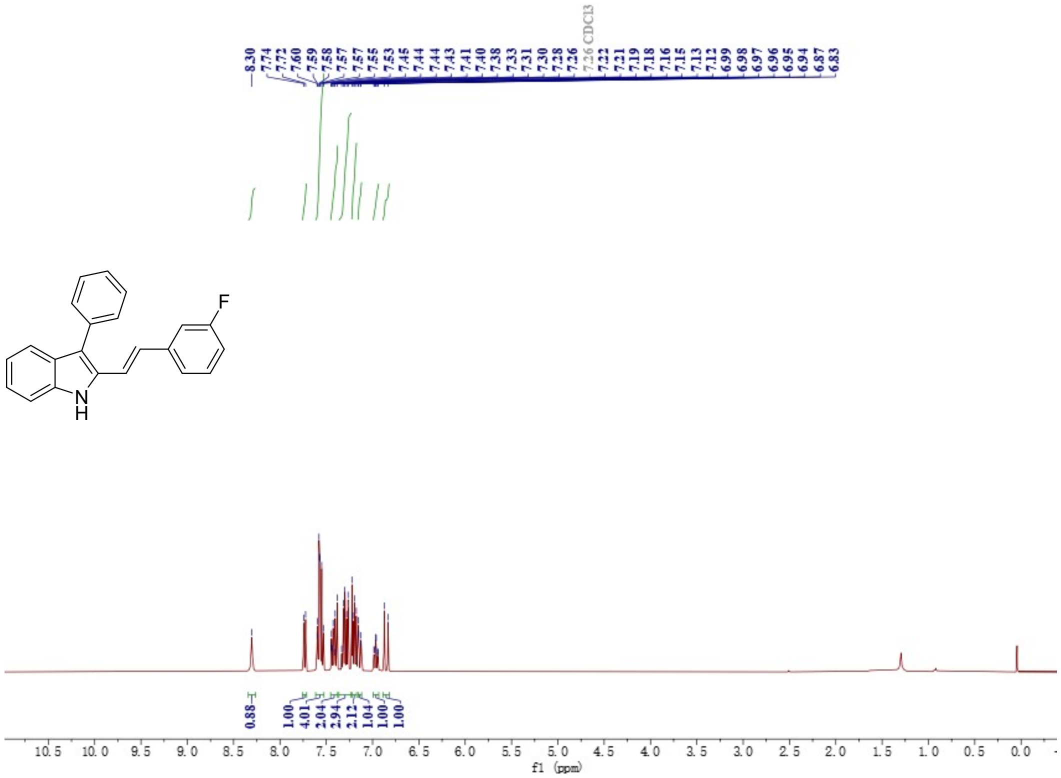
^{1}H NMR of **15** (400 MHz, CDCl$_3$)



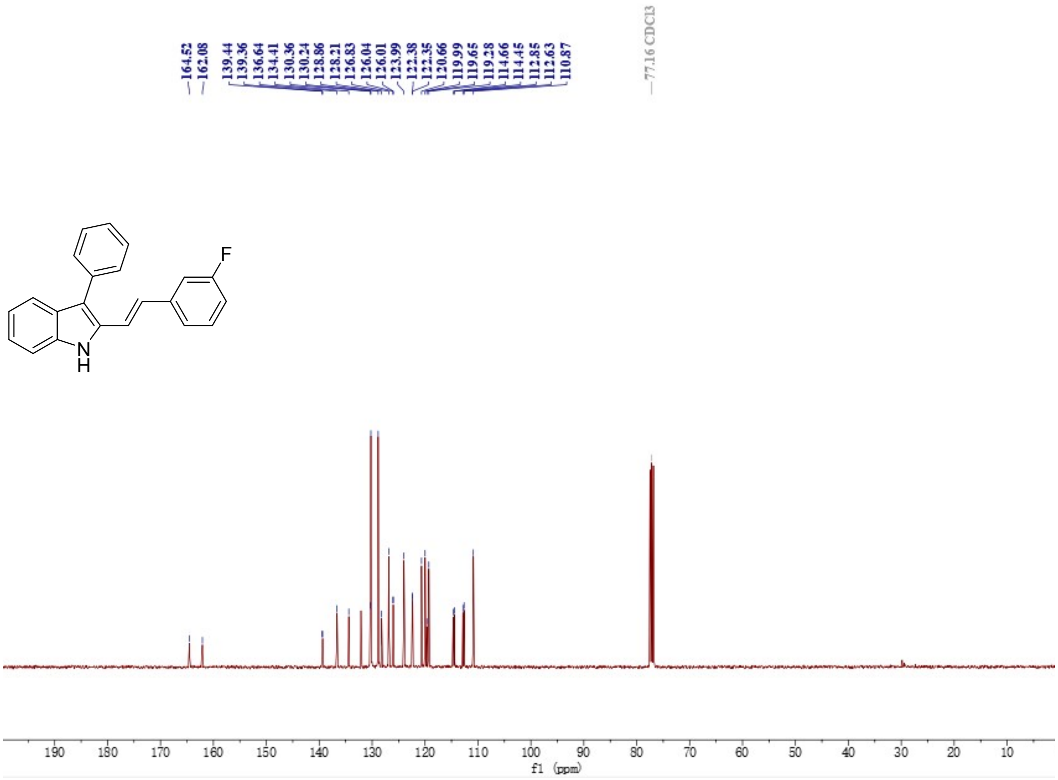
^{13}C NMR of **15** (101 MHz, CDCl$_3$)



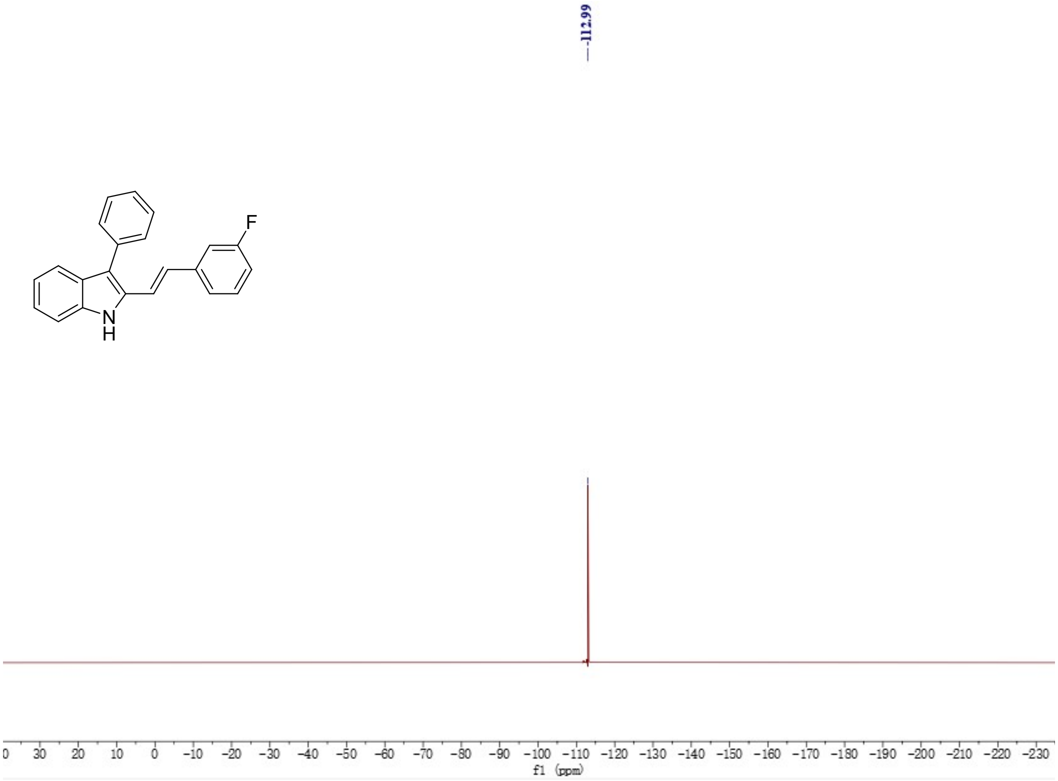
^{1}H NMR of **16** (400 MHz, CDCl$_3$)



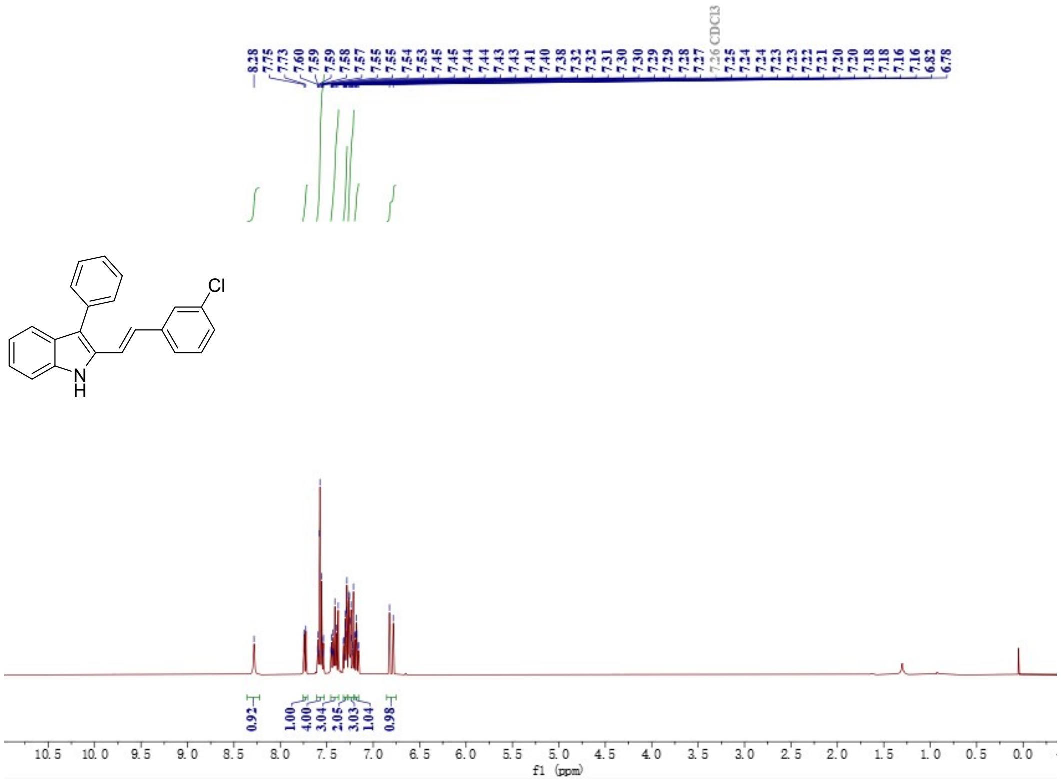
^{13}C NMR of **16** (101 MHz, CDCl$_3$)



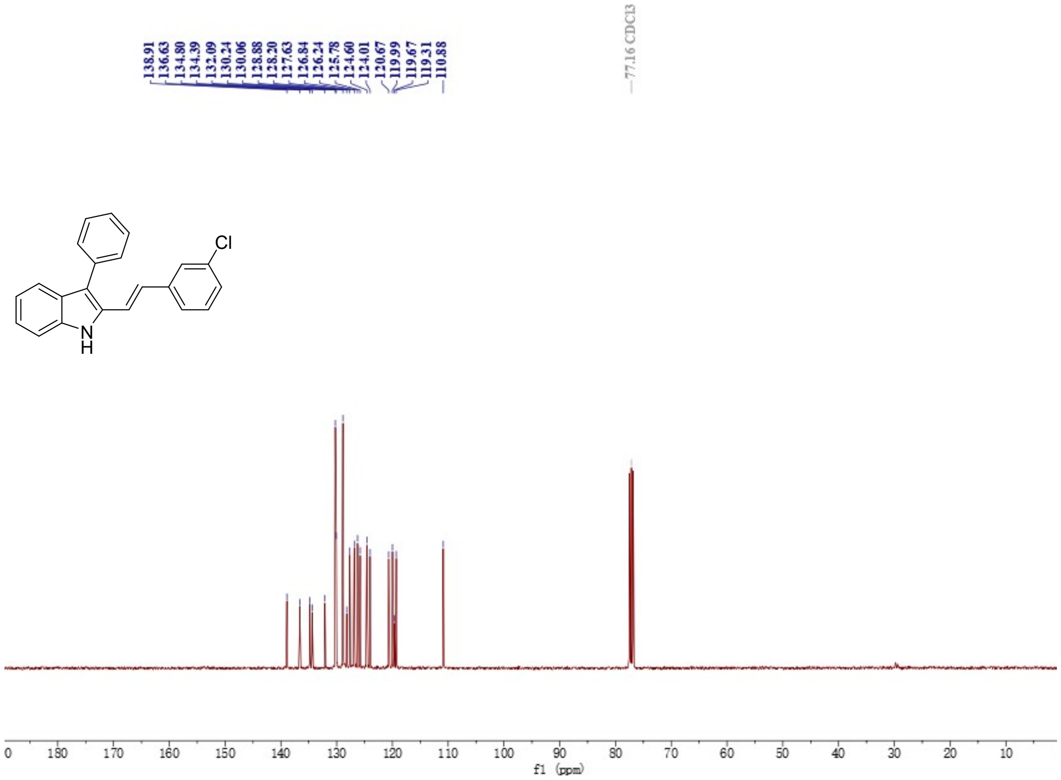
^{19}F NMR of **16** (376 MHz, $CDCl_3$)



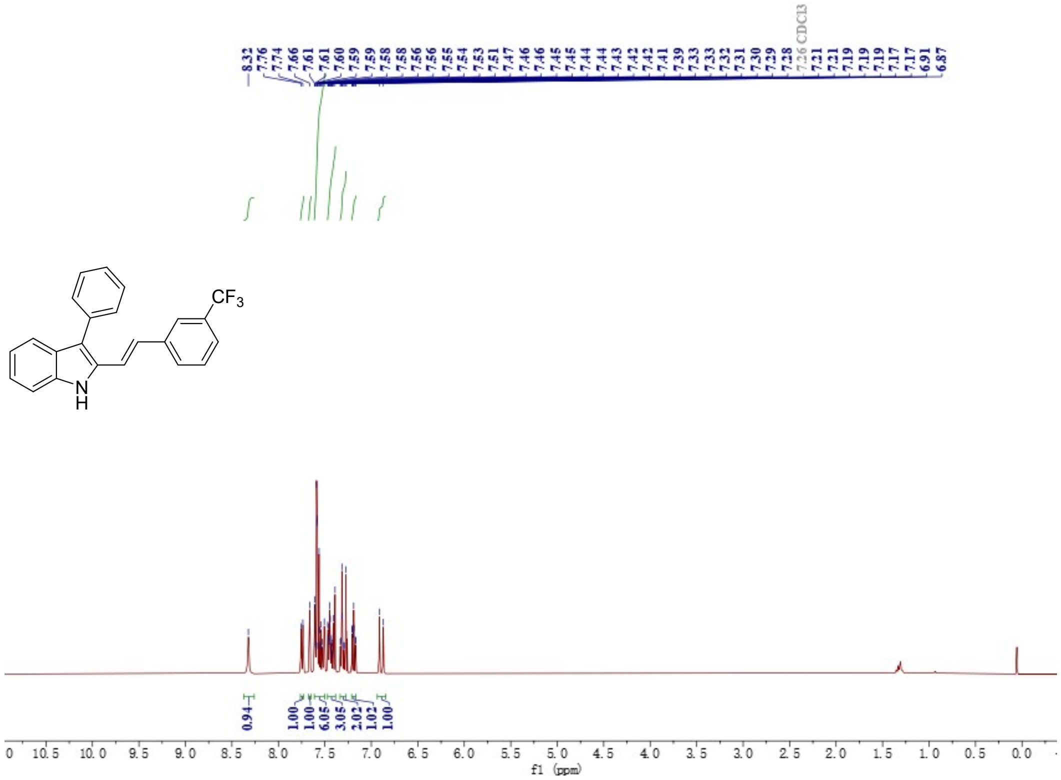
^{1}H NMR of **17** (400 MHz, $CDCl_3$)



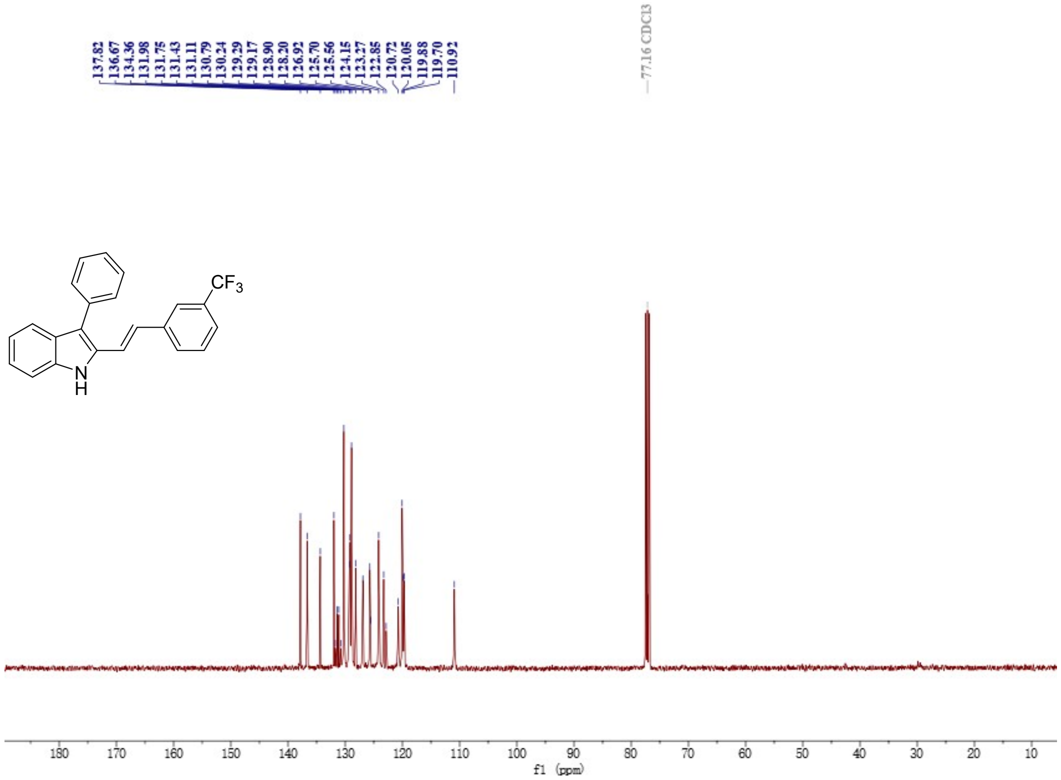
^{13}C NMR of **17** (101 MHz, CDCl$_3$)



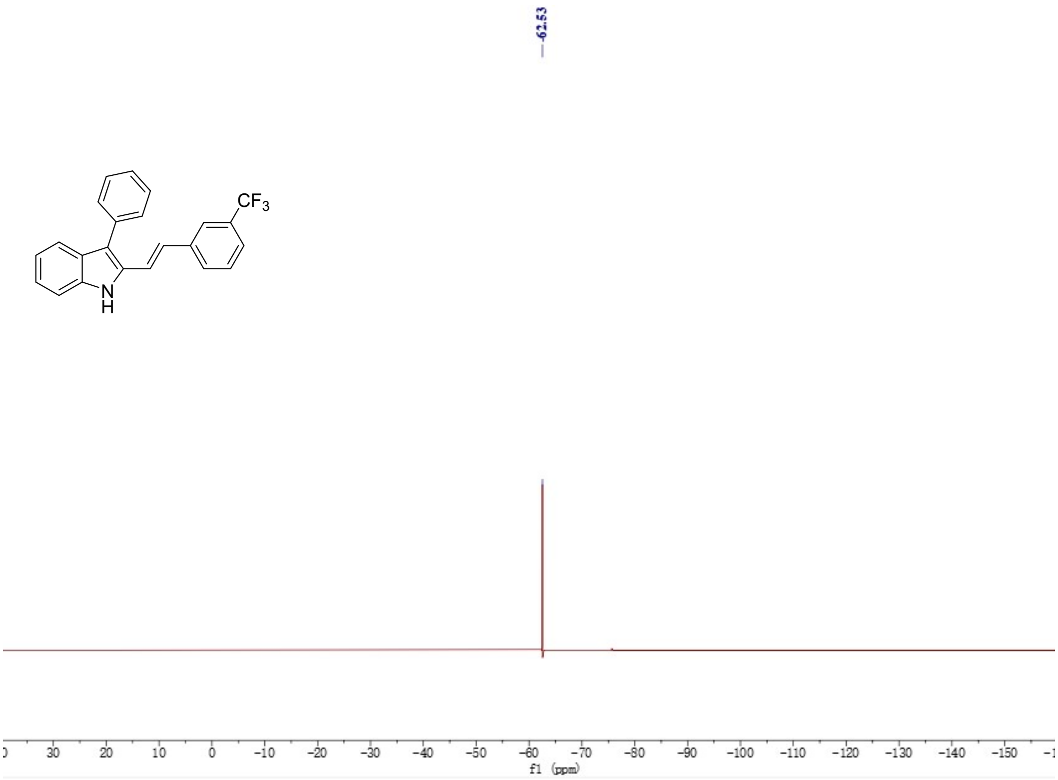
^{1}H NMR of **18** (400 MHz, CDCl$_3$)



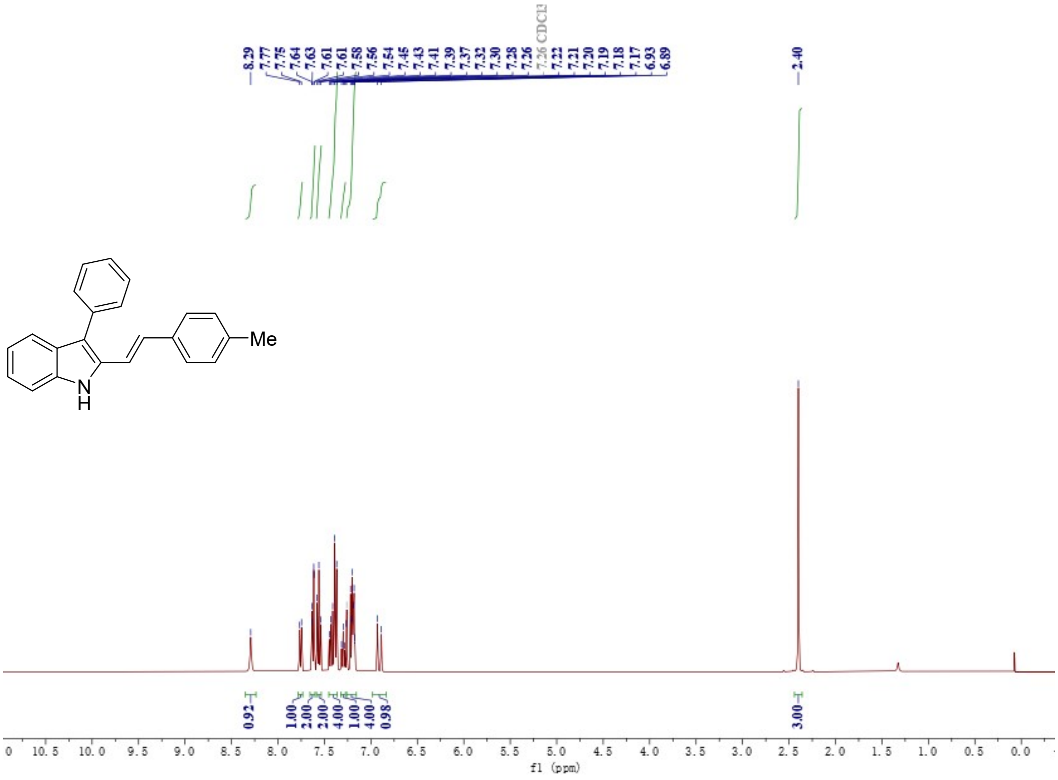
^{13}C NMR of **18** (101 MHz, $CDCl_3$)



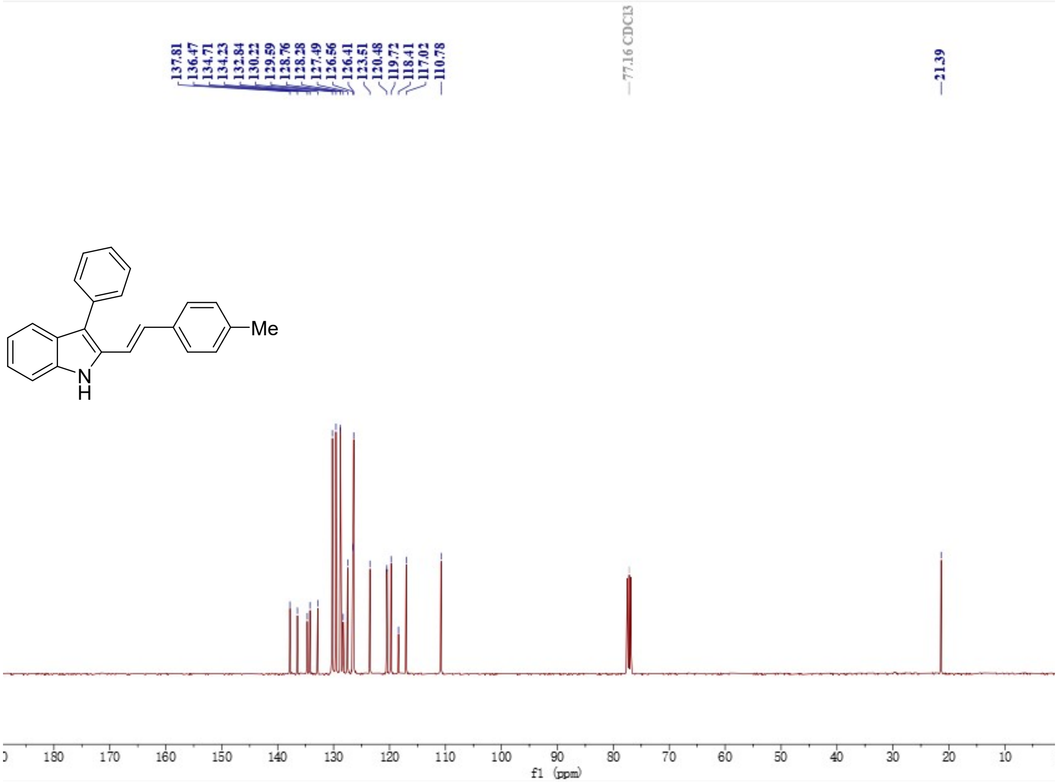
^{19}F NMR of **18** (376 MHz, $CDCl_3$)



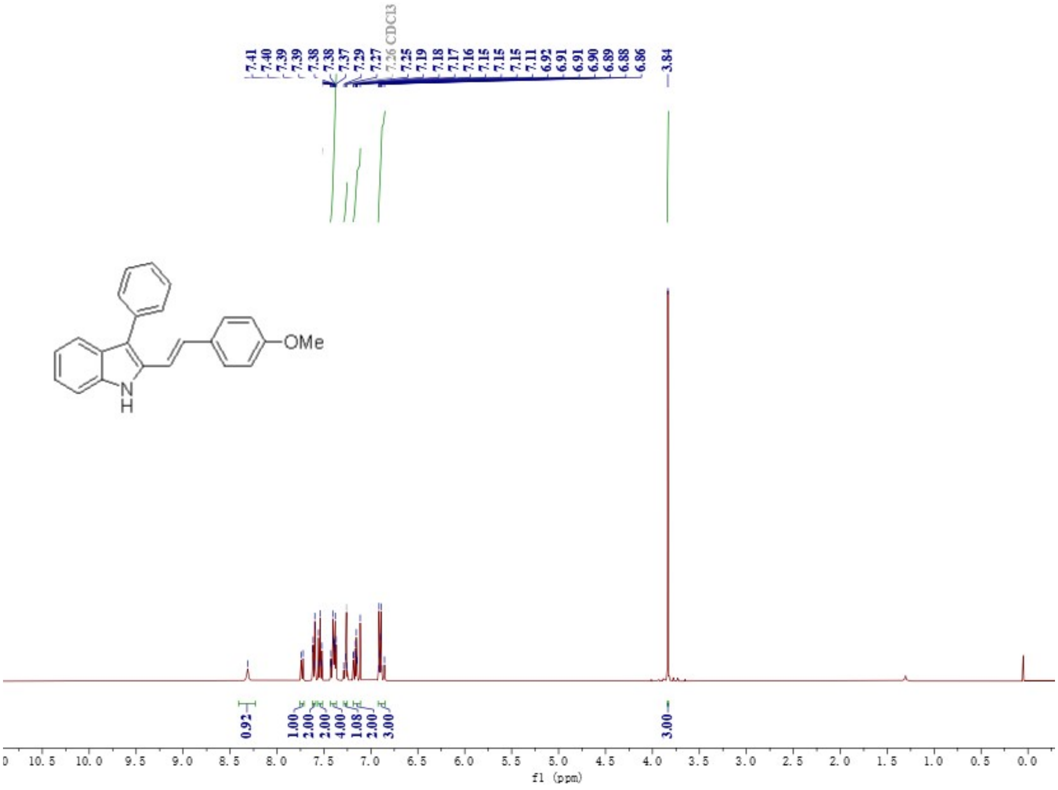
^{1}H NMR of **19** (400 MHz, CDCl$_3$)



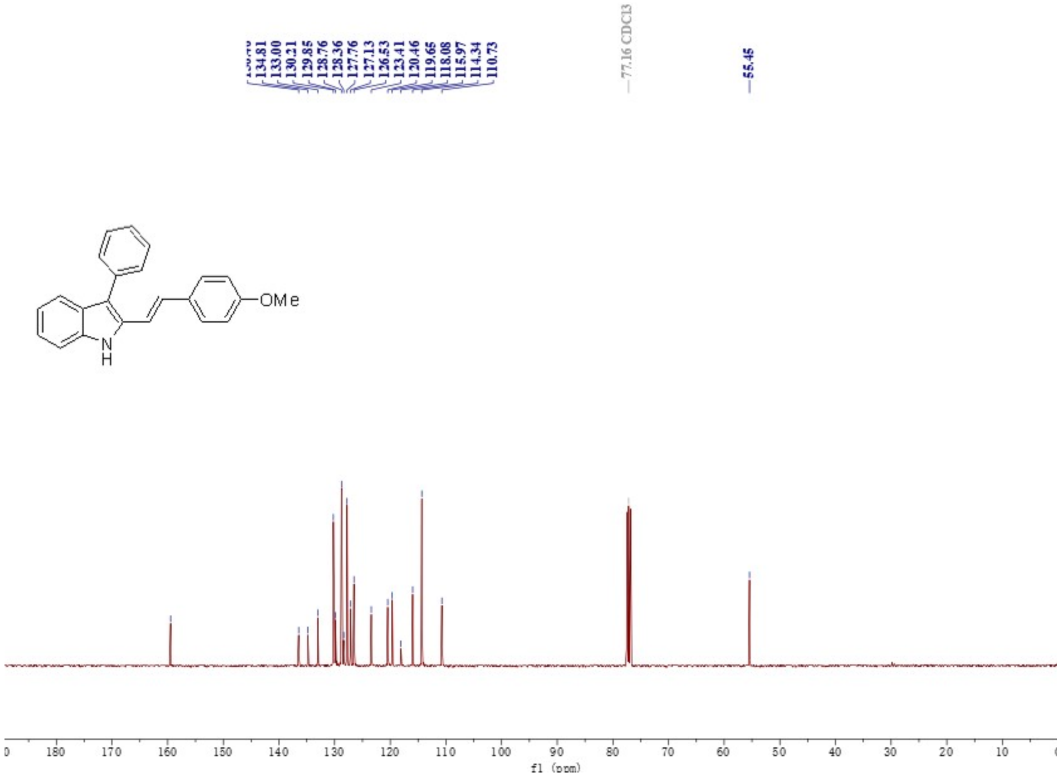
^{13}C NMR of **19** (101 MHz, CDCl$_3$)



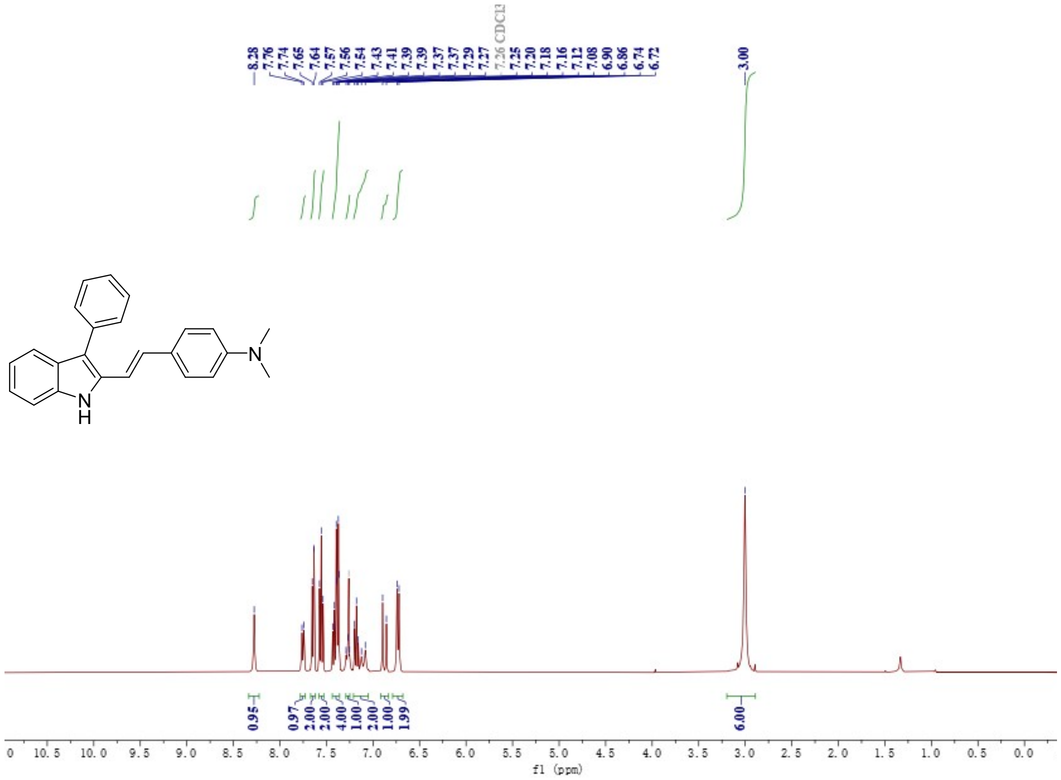
^{1}H NMR of **20** (400 MHz, CDCl$_3$)



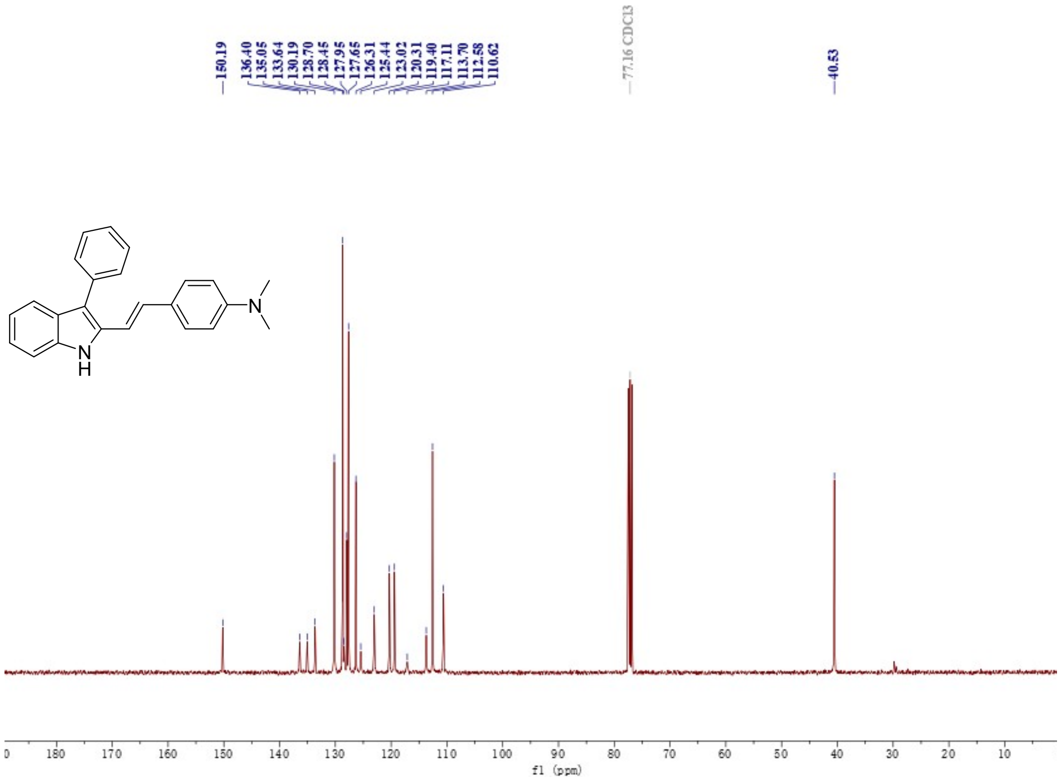
^{13}C NMR of **20** (101 MHz, CDCl$_3$)



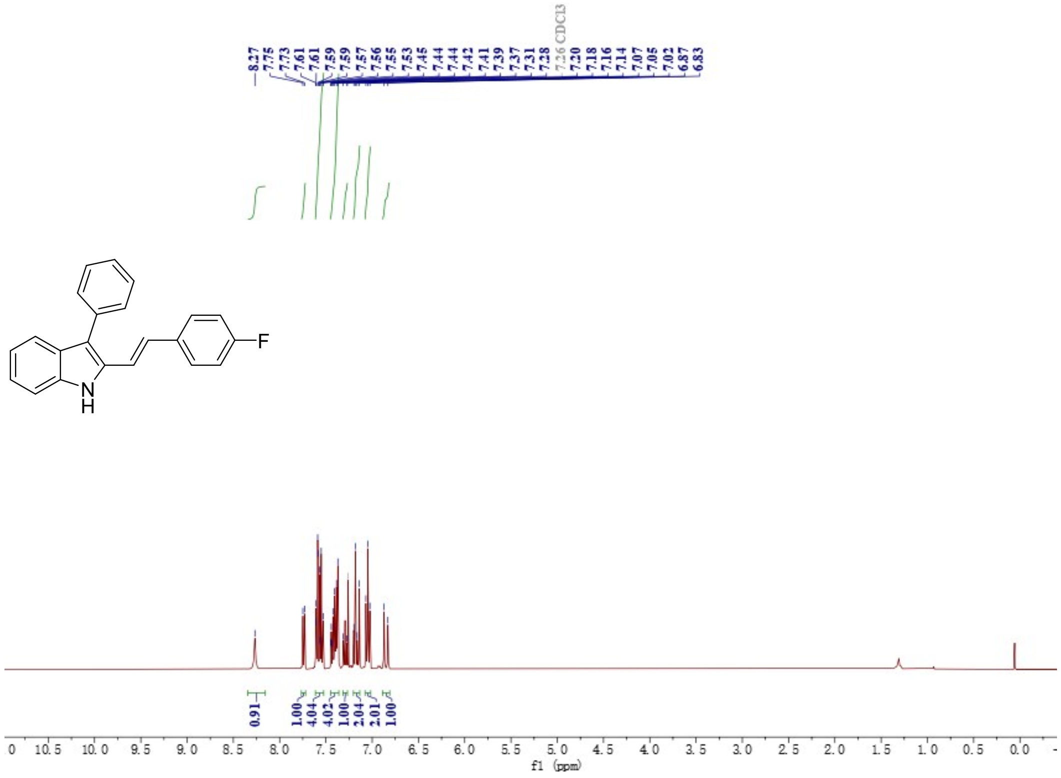
^{1}H NMR of **21** (400 MHz, CDCl$_3$)



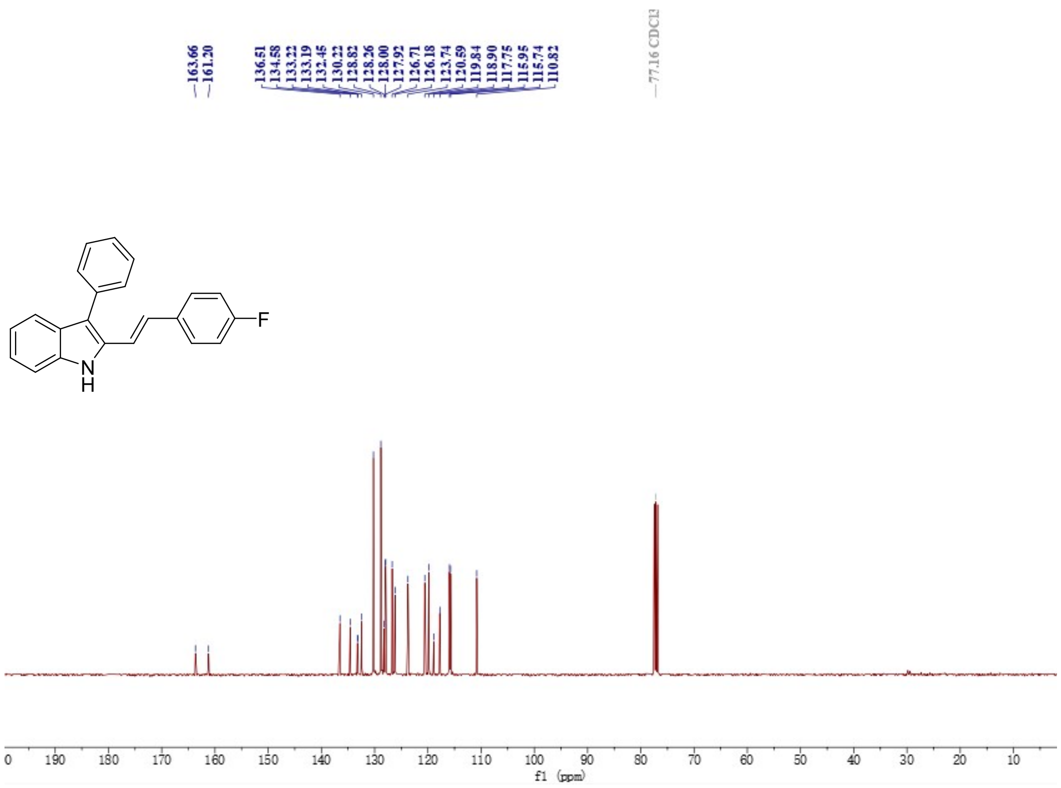
^{13}C NMR of **21** (101 MHz, CDCl$_3$)



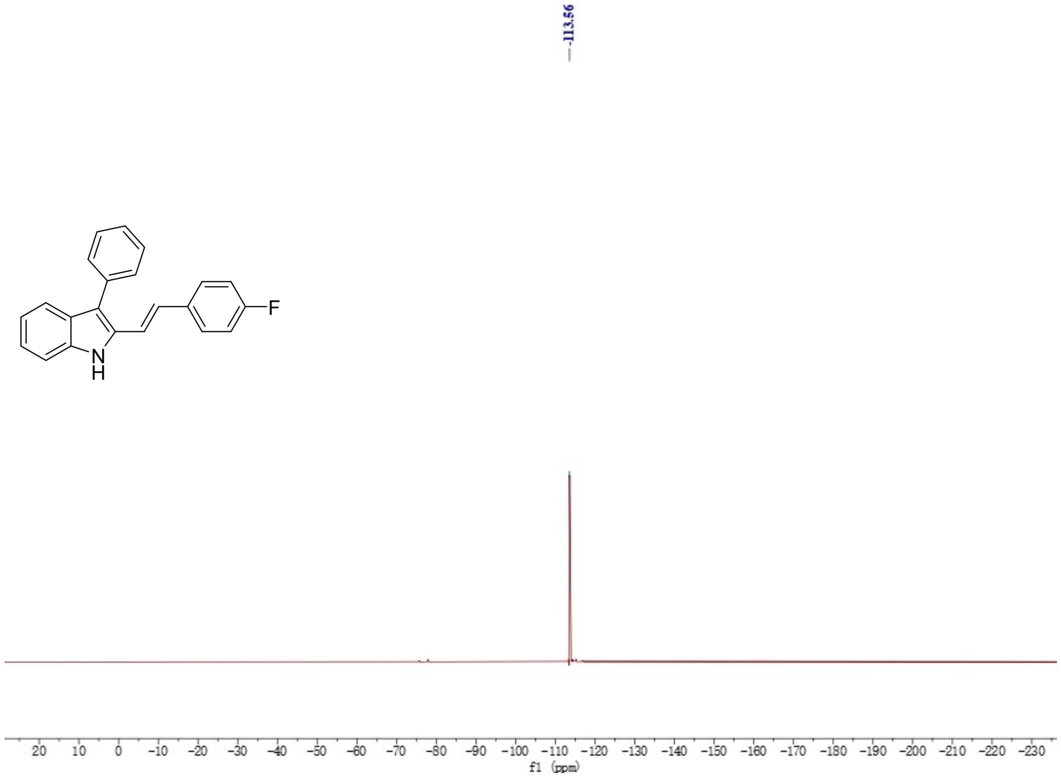
^{1}H NMR of **22** (400 MHz, CDCl$_3$)



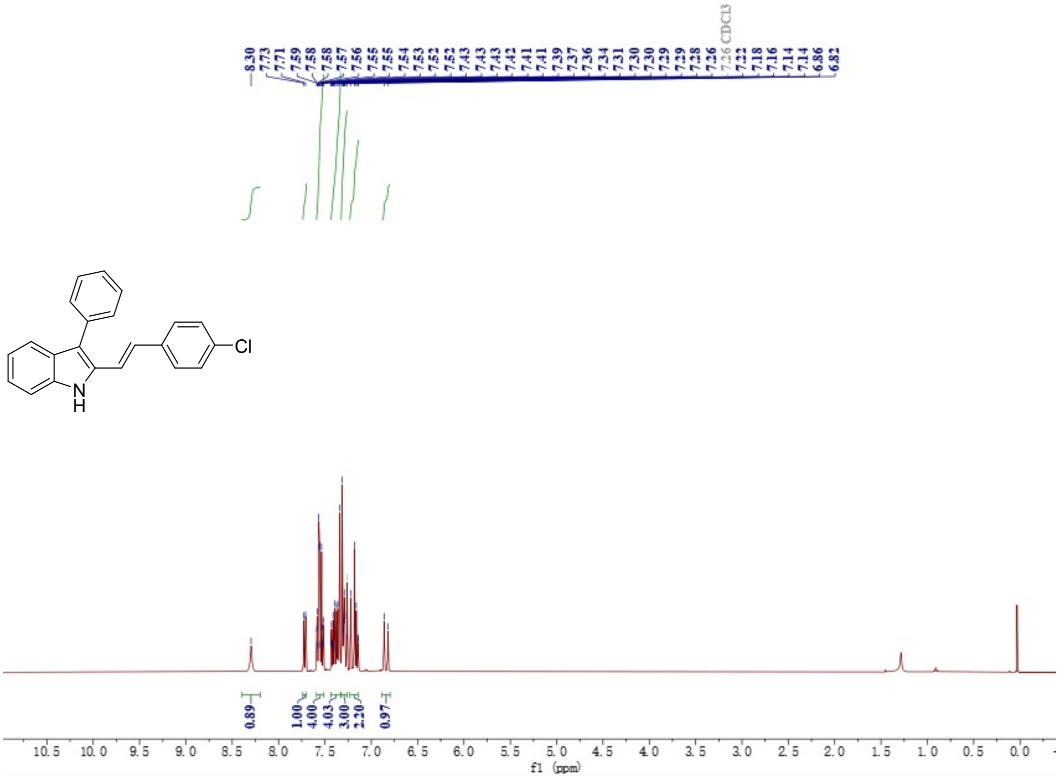
^{13}C NMR of **22** (101 MHz, CDCl$_3$)



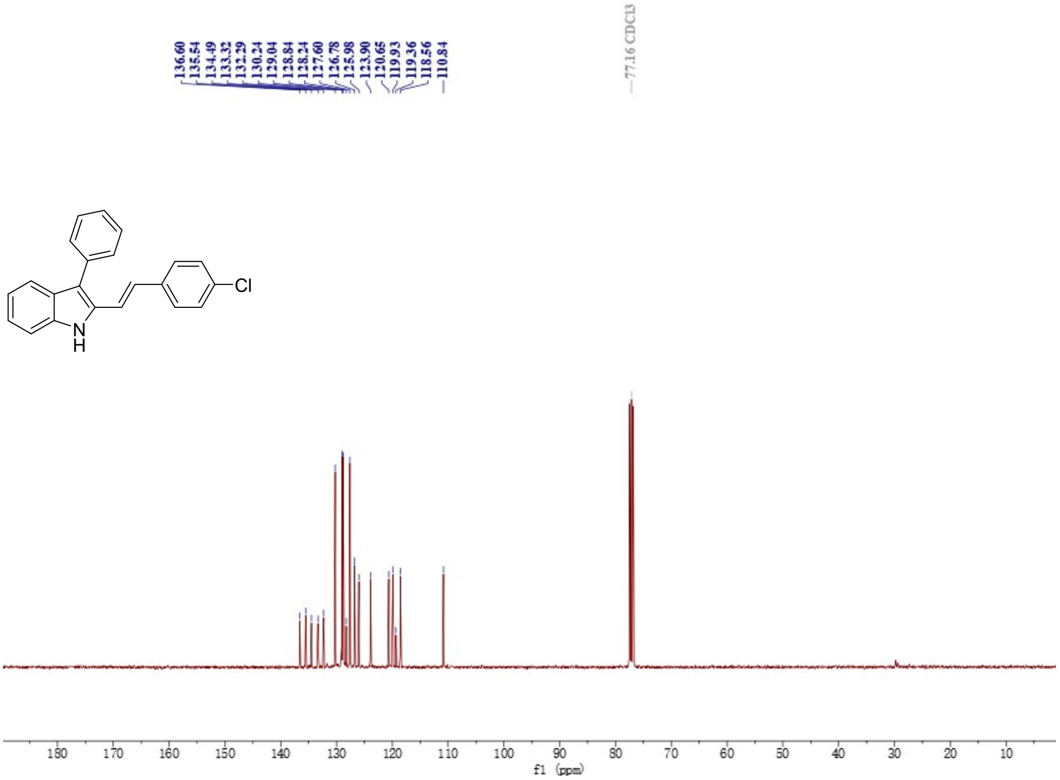
^{19}F NMR of **22** (376 MHz, $CDCl_3$)



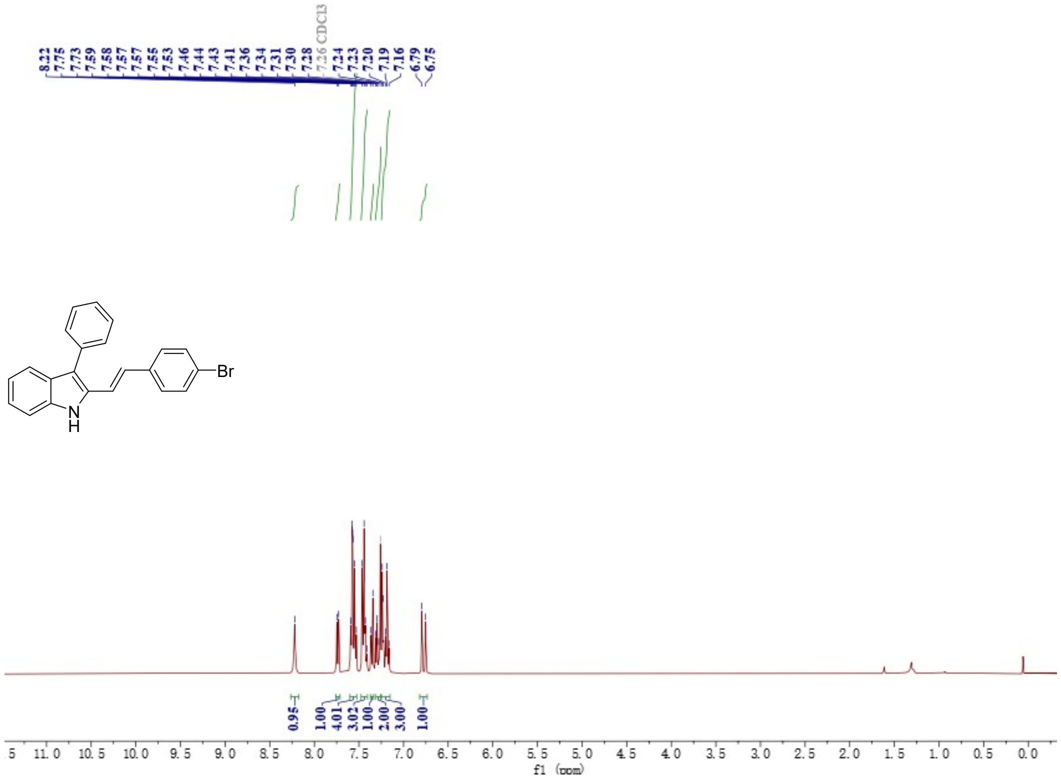
^{1}H NMR of **23** (400 MHz, $CDCl_3$)



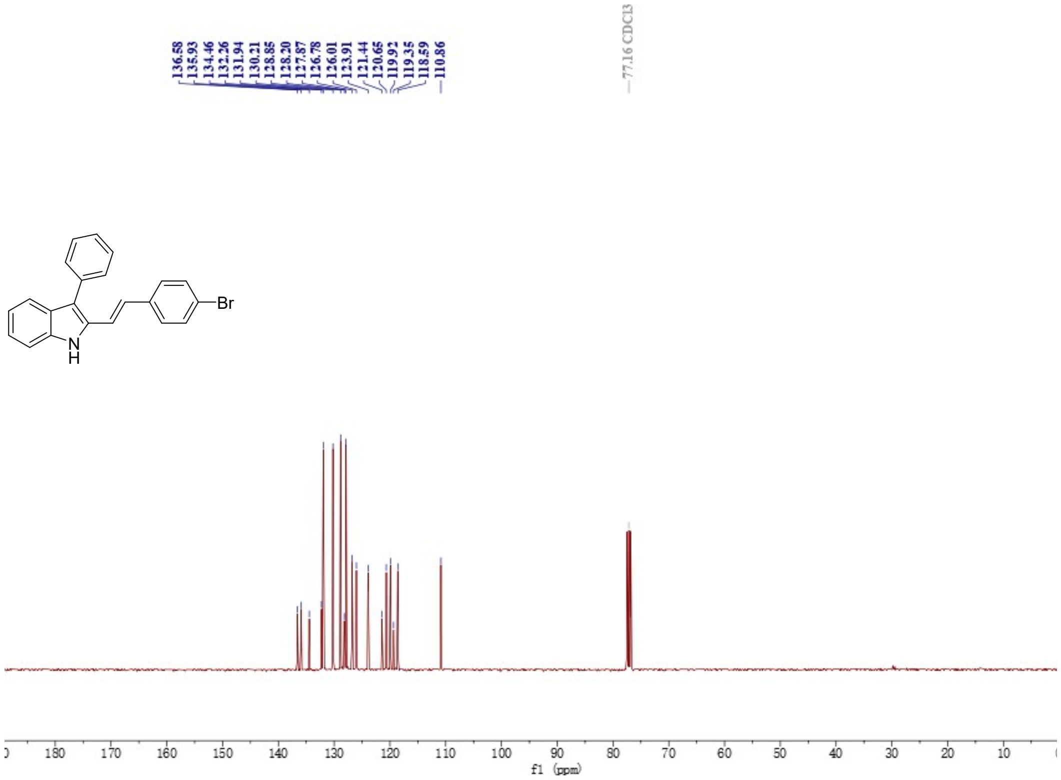
^{13}C NMR of **23** (101 MHz, CDCl$_3$)



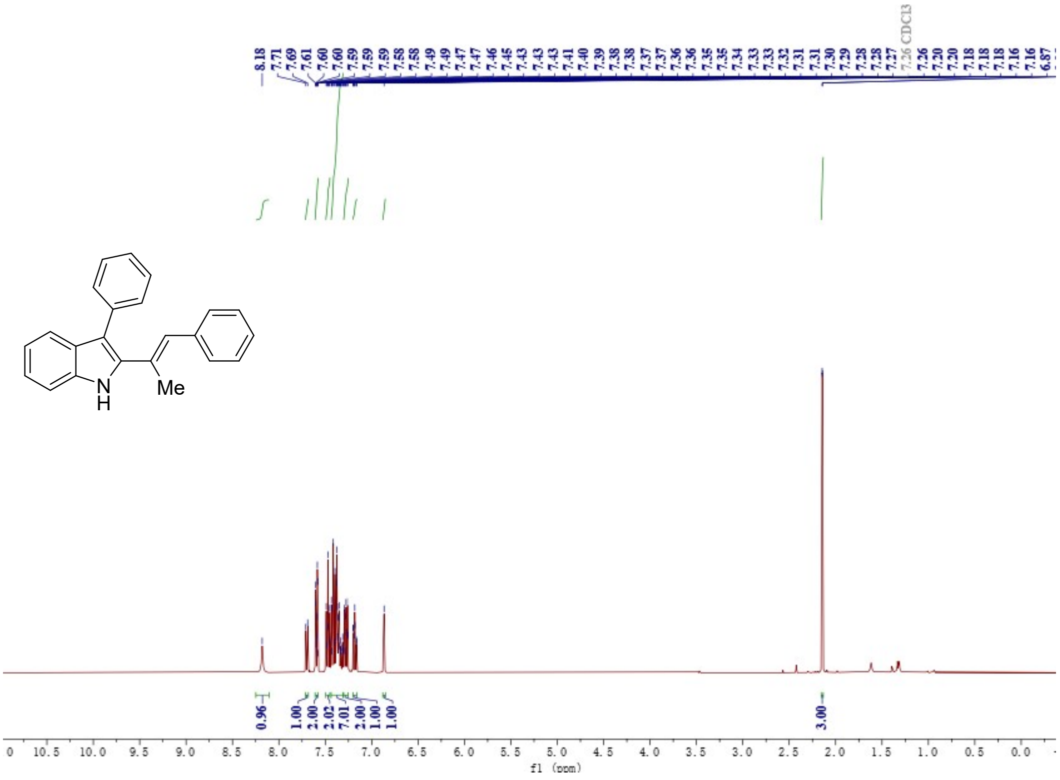
^{1}H NMR of **24** (400 MHz, CDCl$_3$)



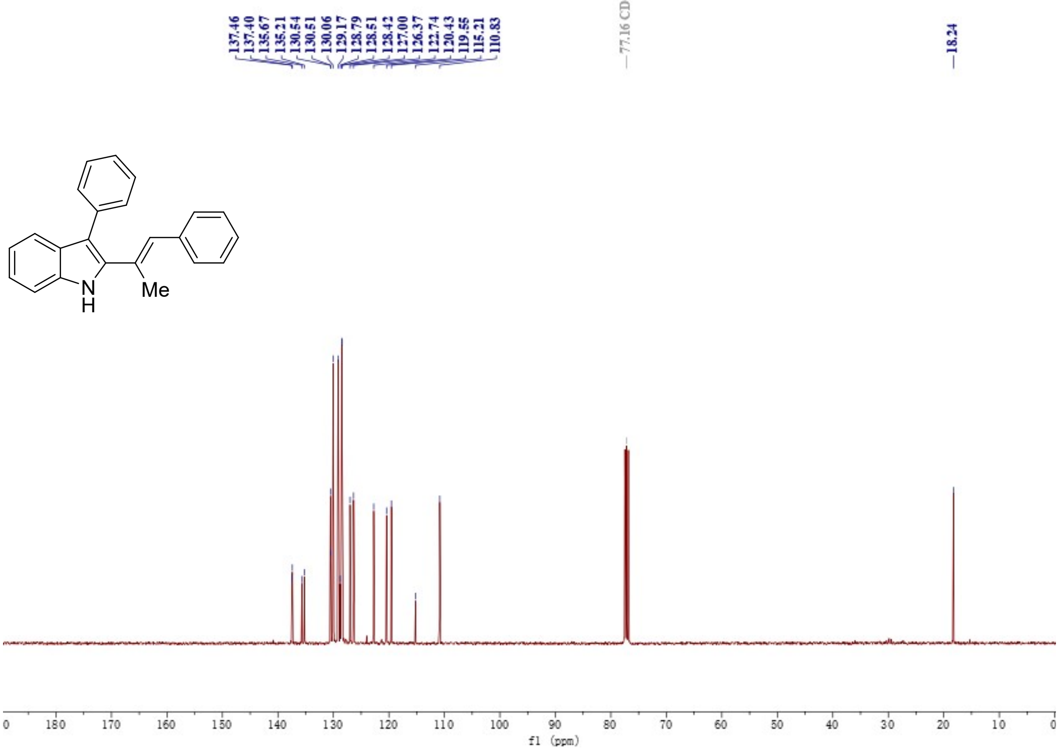
^{13}C NMR of **24** (101 MHz, $CDCl_3$)



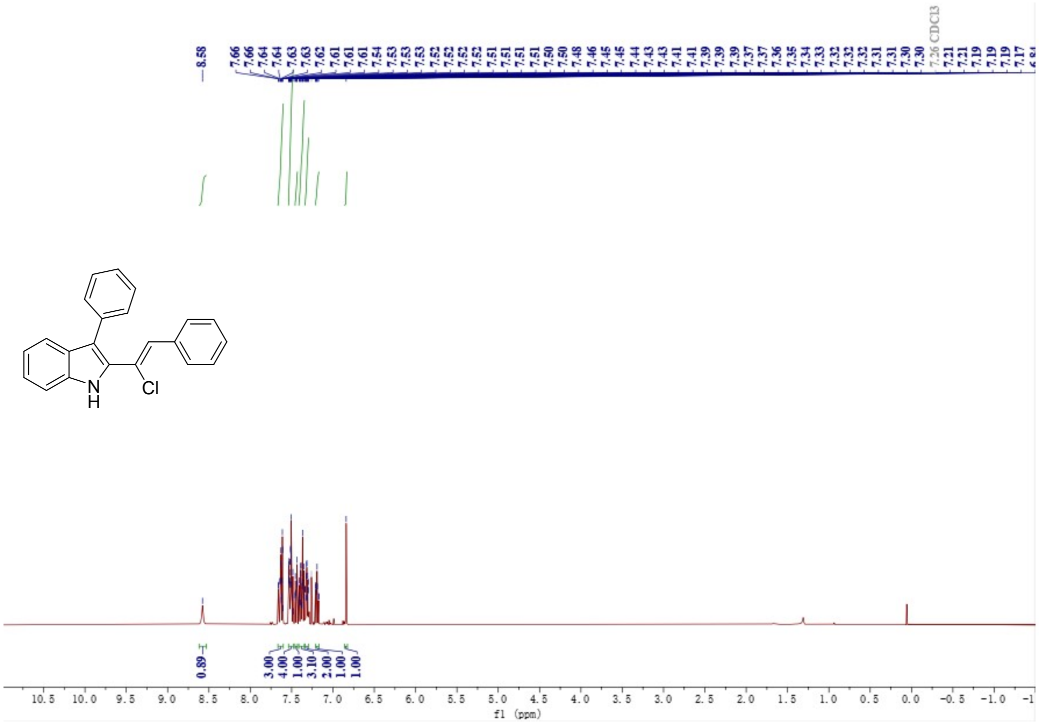
^{1}H NMR of **25** (400 MHz, $CDCl_3$)



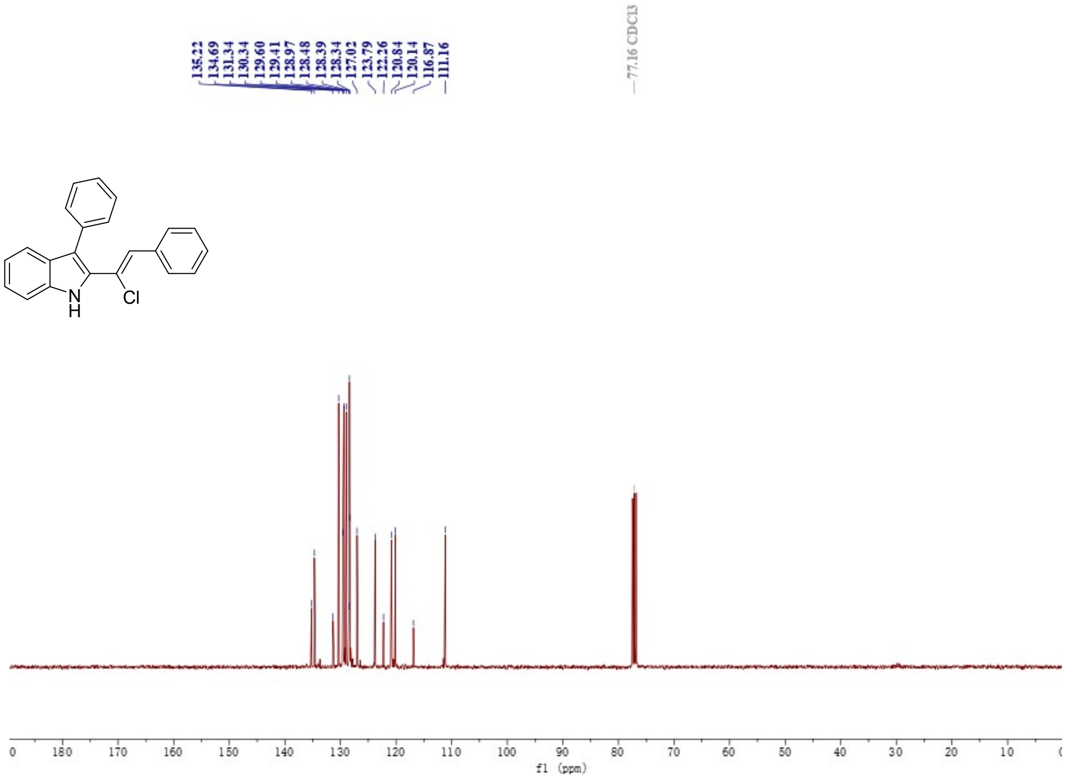
^{13}C NMR of **25** (101 MHz, $CDCl_3$)



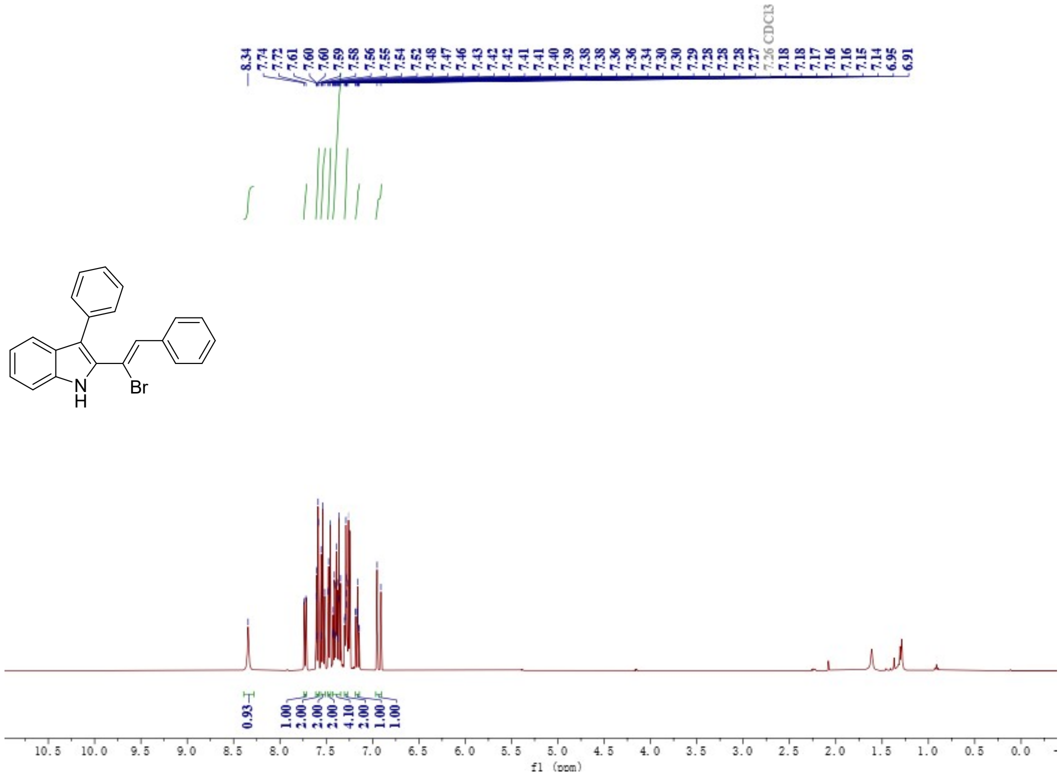
^{1}H NMR of **26** (400 MHz, $CDCl_3$)



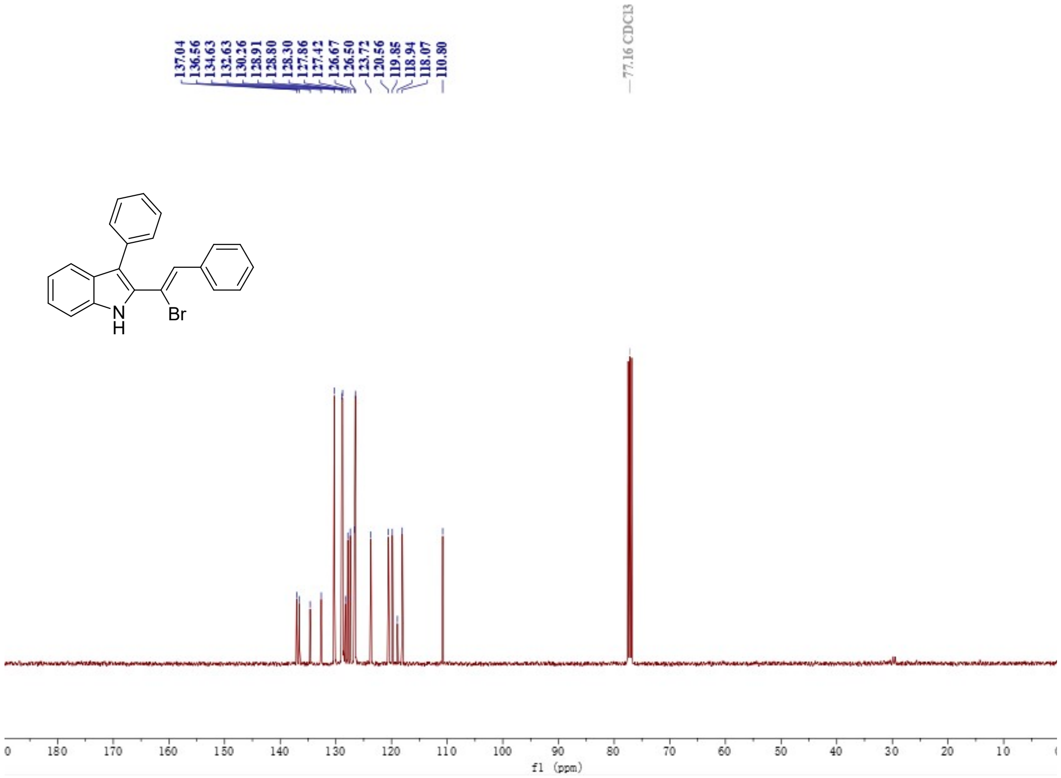
^{13}C NMR of **26** (101 MHz, $CDCl_3$)



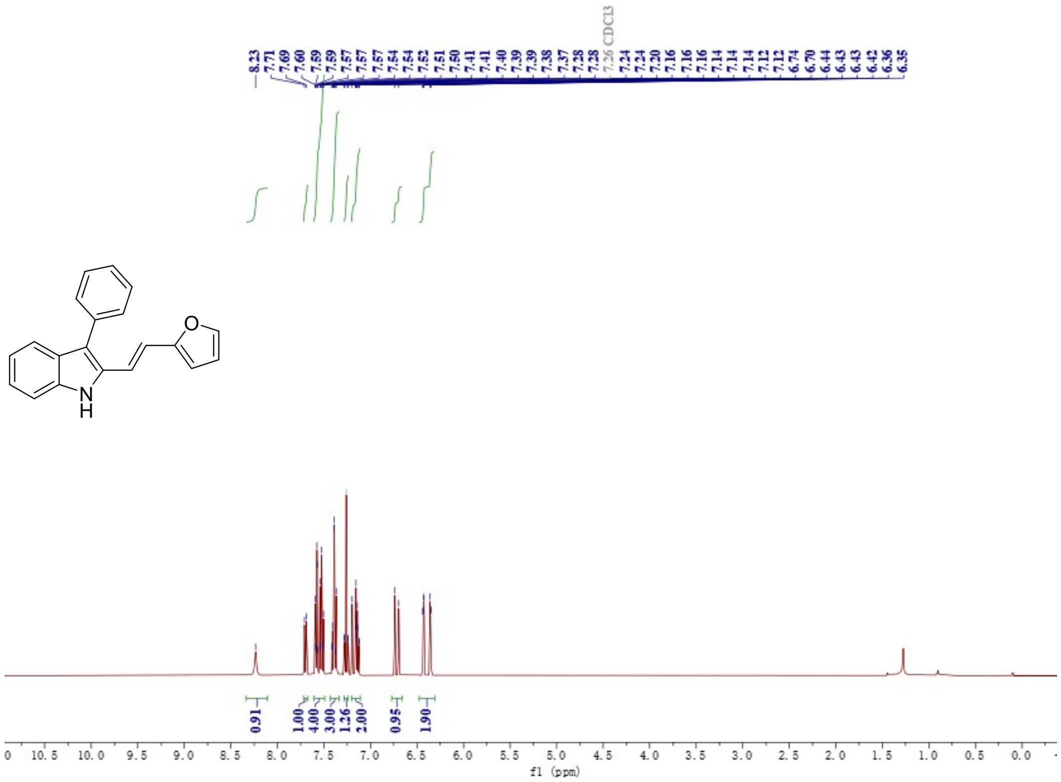
^{1}H NMR of **27** (400 MHz, $CDCl_3$)



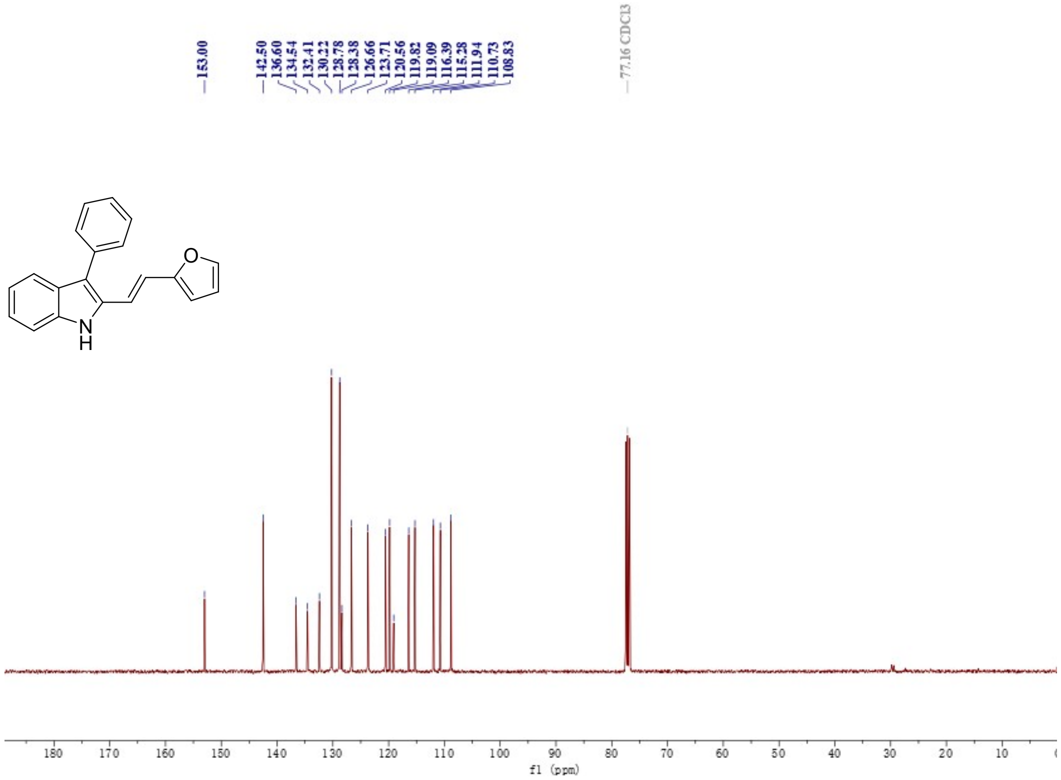
^{13}C NMR of **27** (101 MHz, $CDCl_3$)



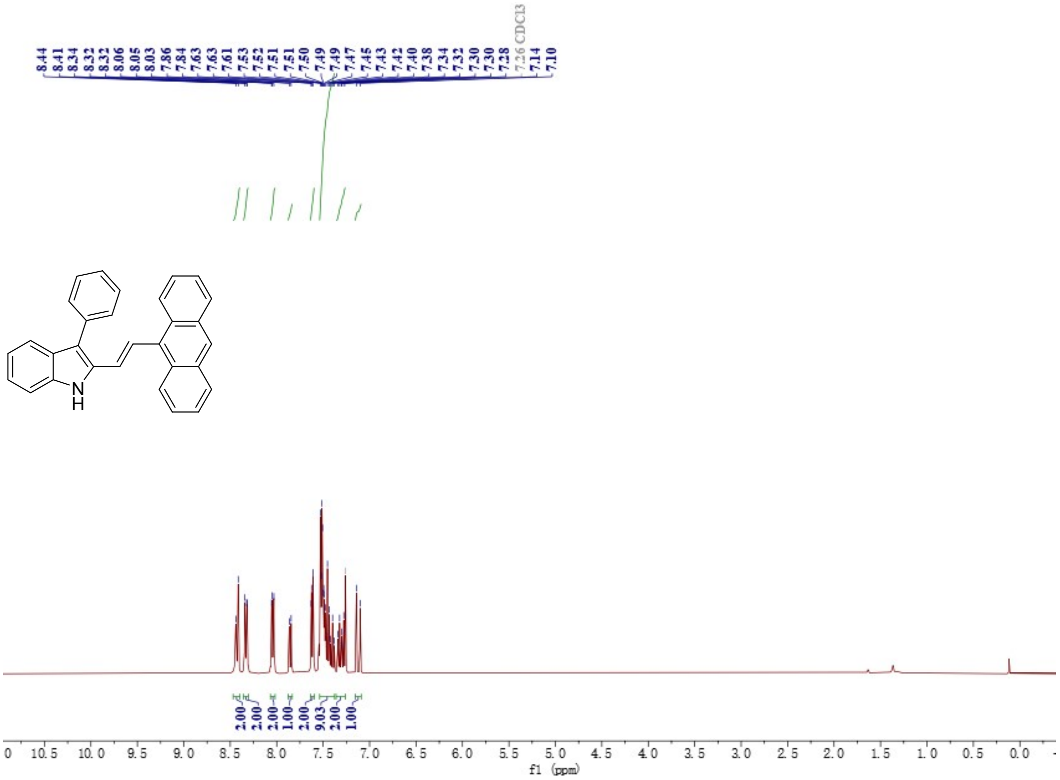
^{1}H NMR of **28** (400 MHz, $CDCl_3$)



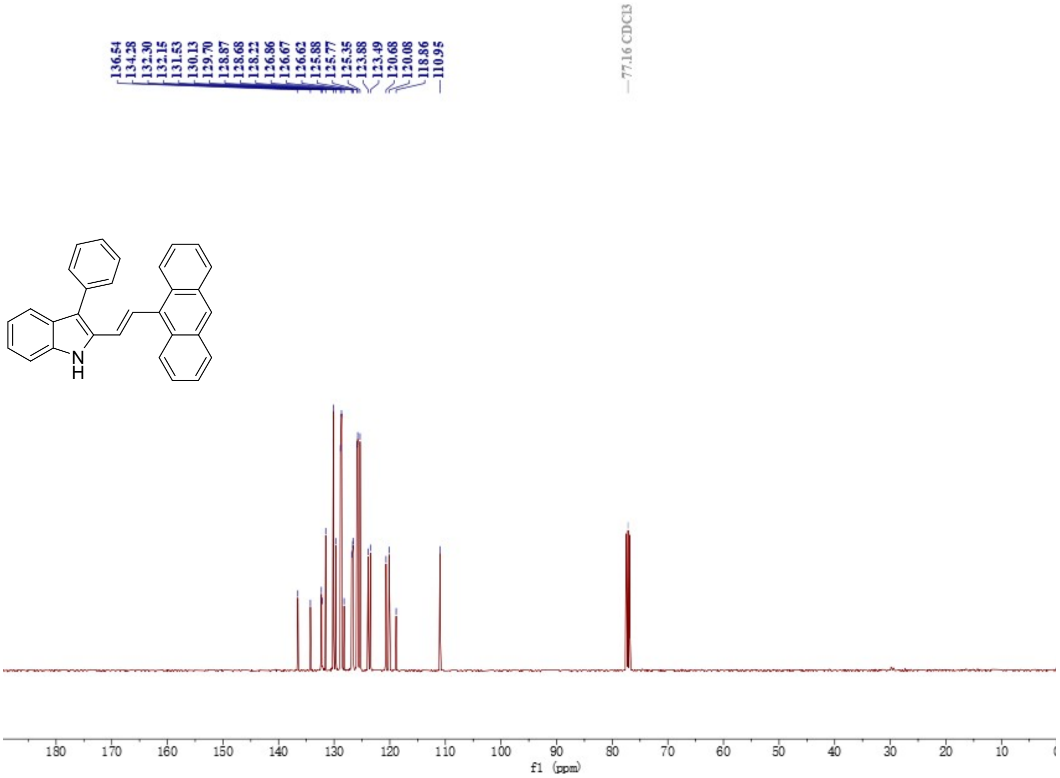
^{13}C NMR of **28** (101 MHz, CDCl$_3$)



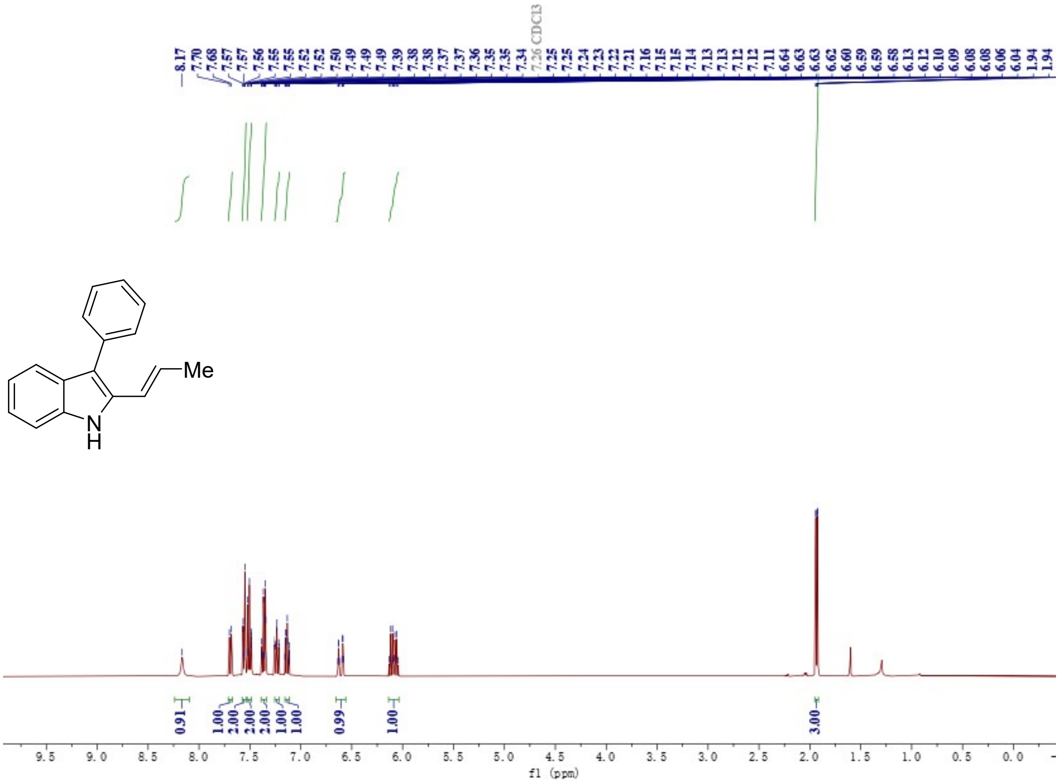
^{1}H NMR of **29** (400 MHz, CDCl$_3$)



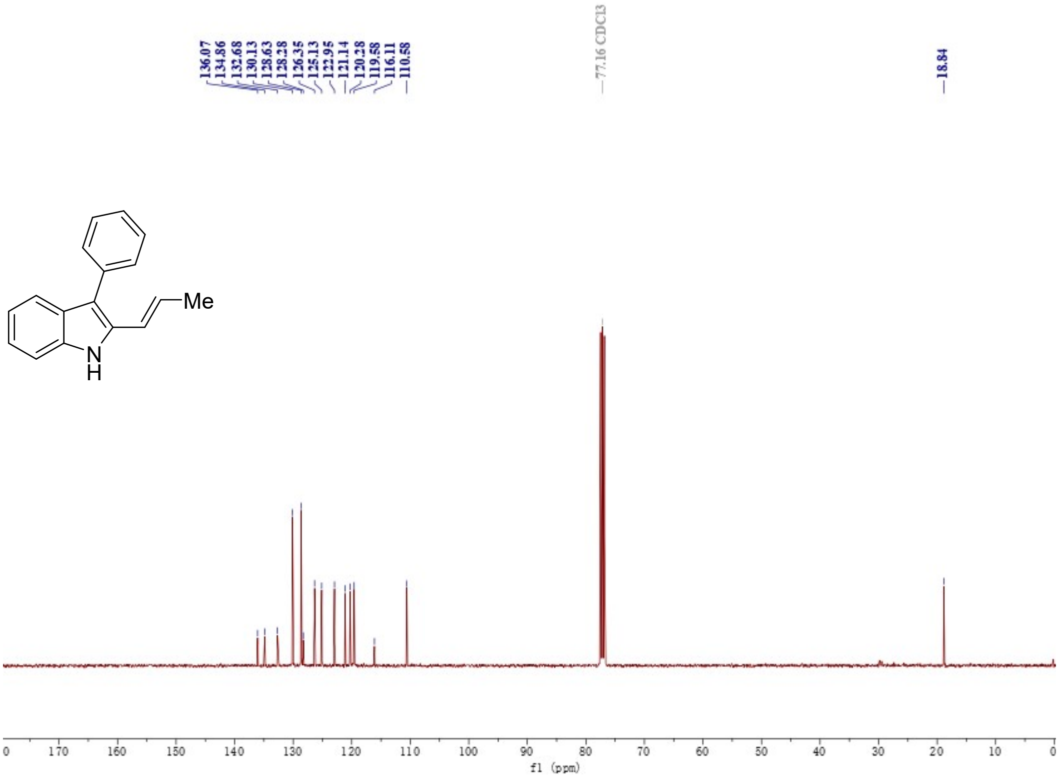
^{13}C NMR of **29** (101 MHz, CDCl$_3$)



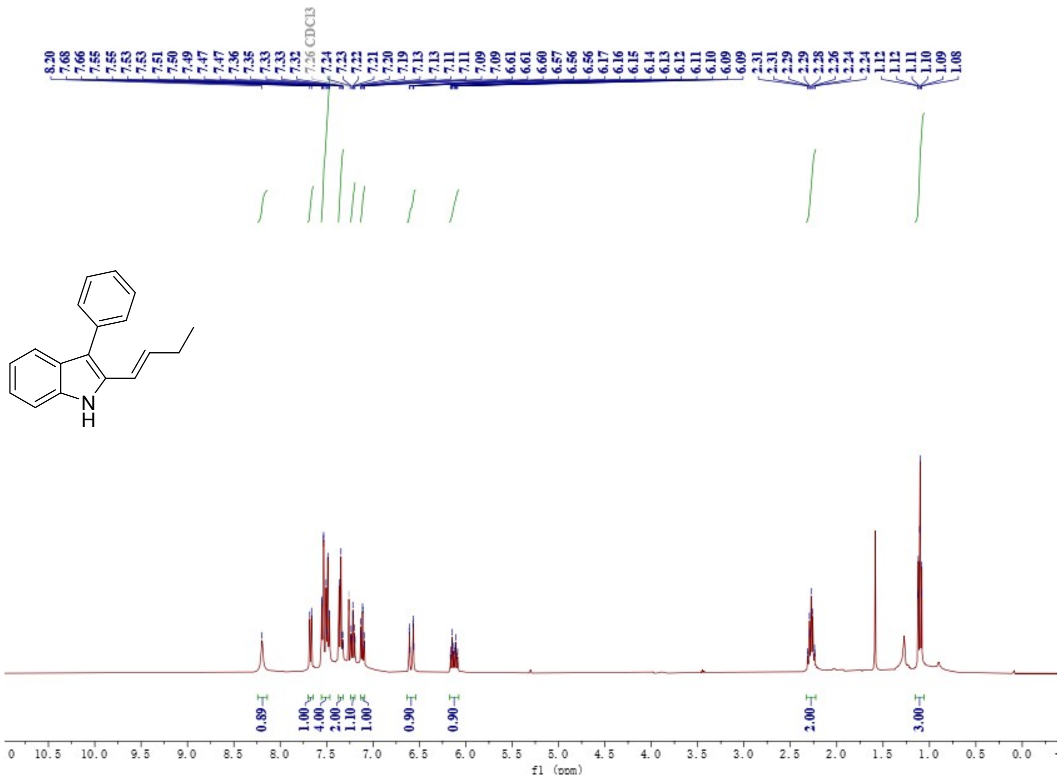
^{1}H NMR of **30** (400 MHz, CDCl$_3$)



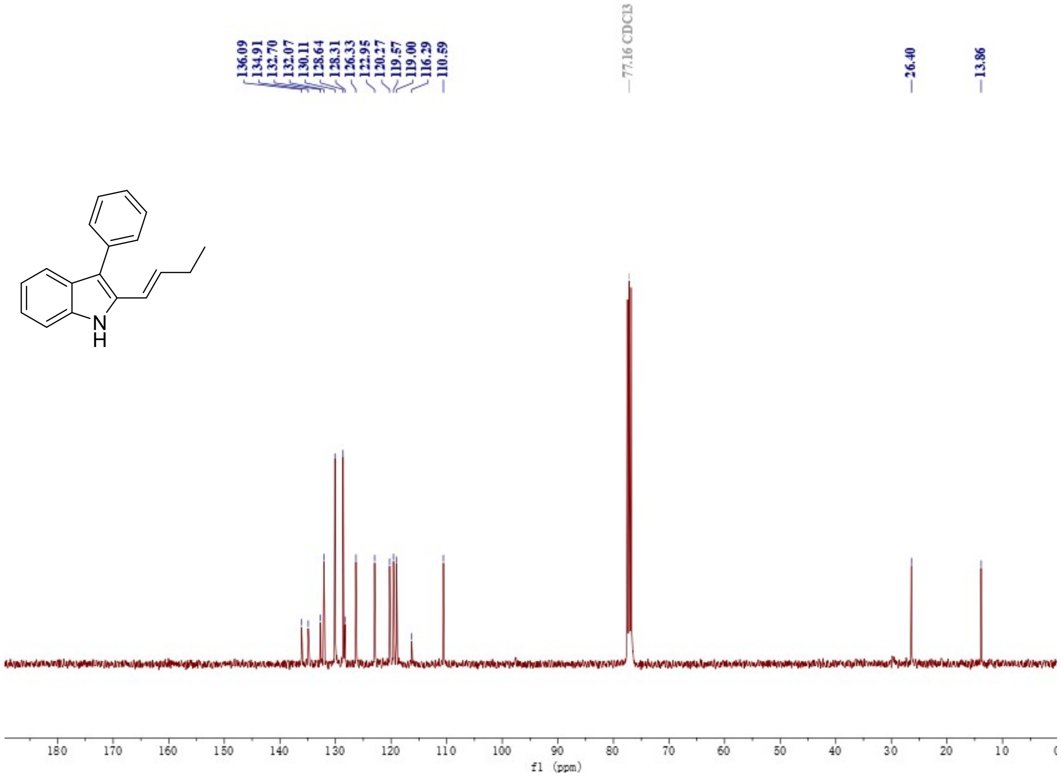
^{13}C NMR of **30** (101 MHz, CDCl$_3$)



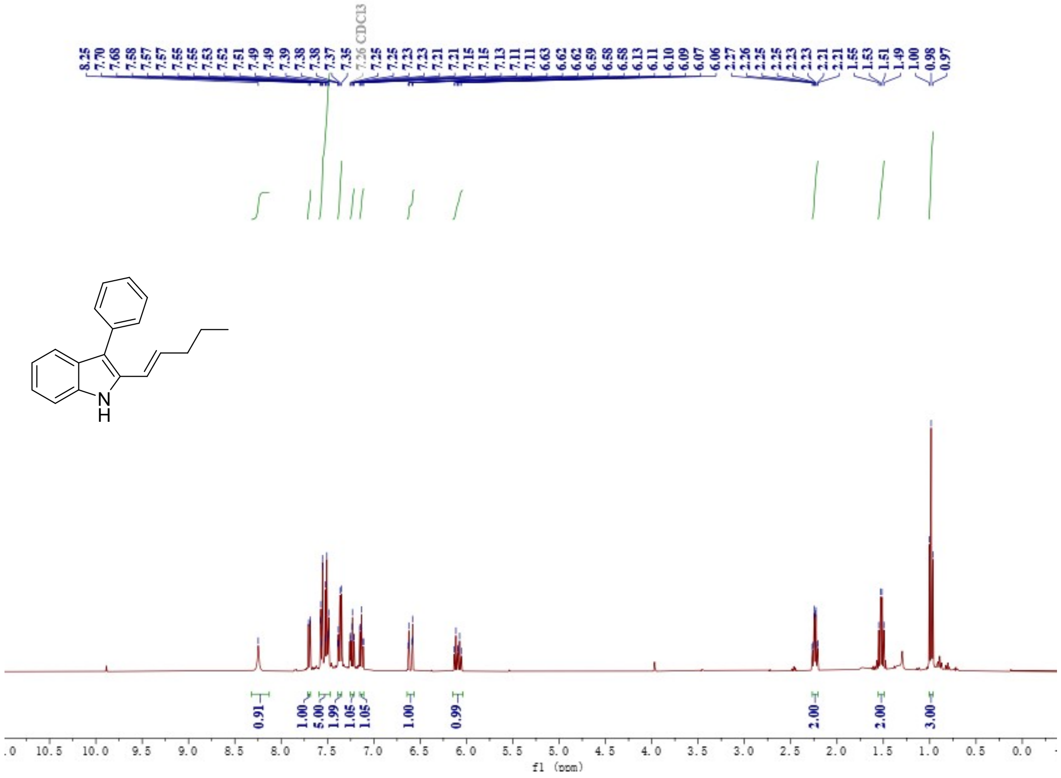
^{1}H NMR of **31** (400 MHz, CDCl$_3$)



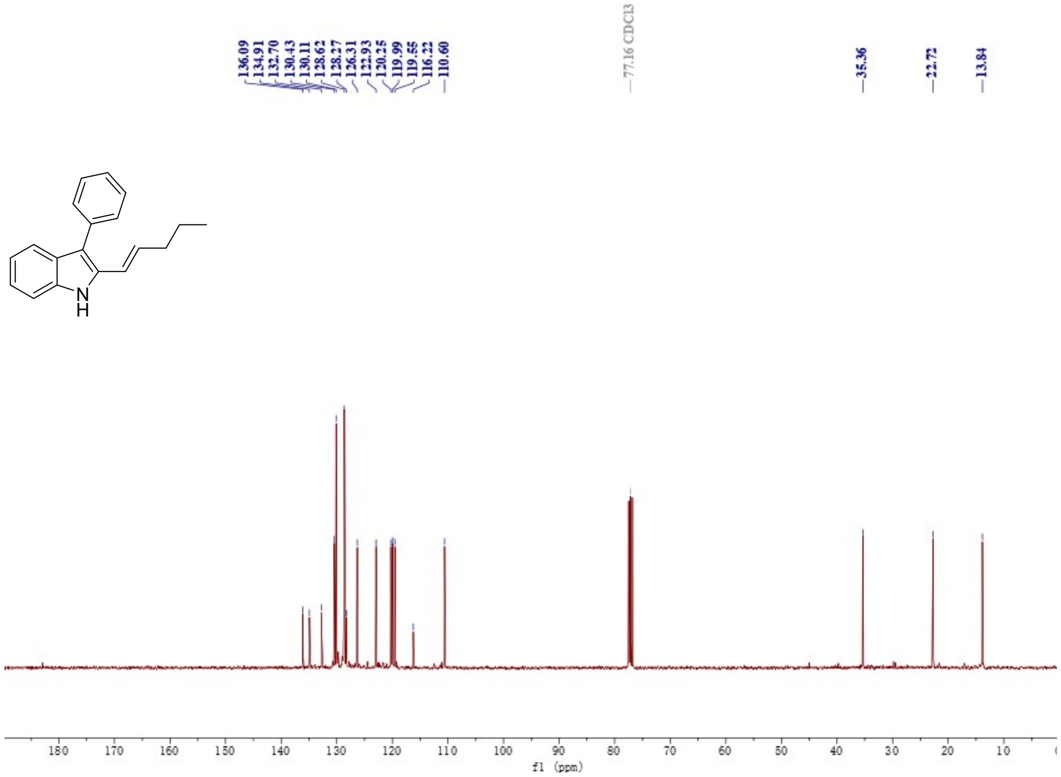
^{13}C NMR of **31** (101 MHz, CDCl$_3$)



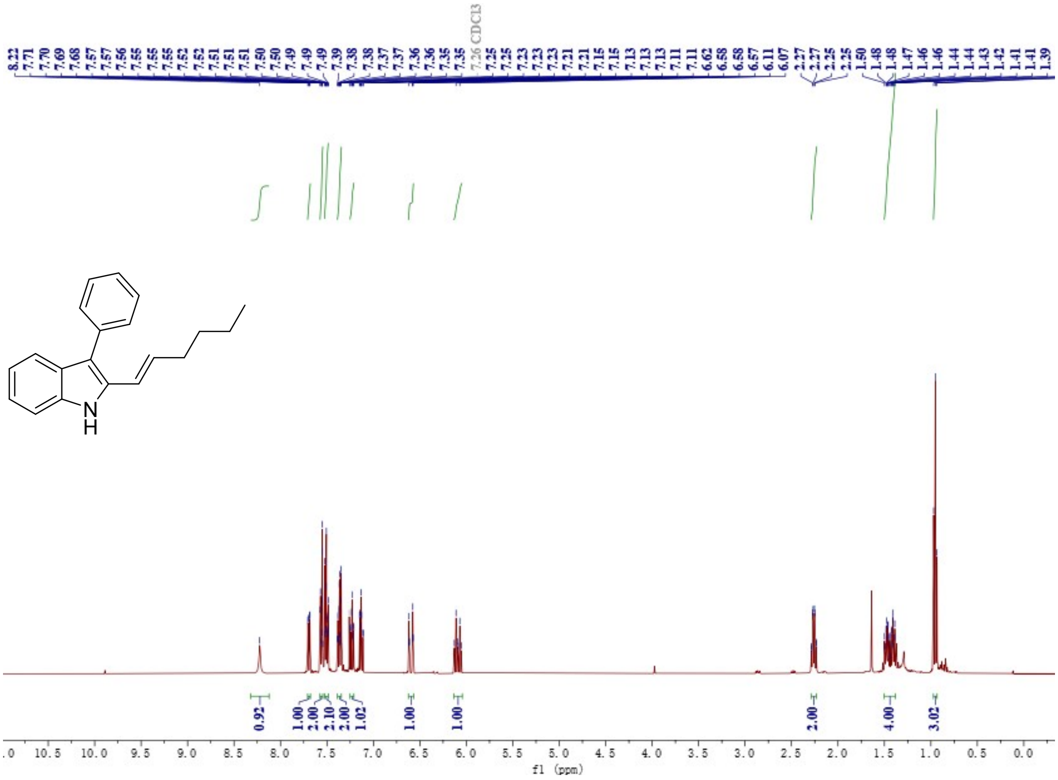
^{1}H NMR of **32** (400 MHz, CDCl$_3$)



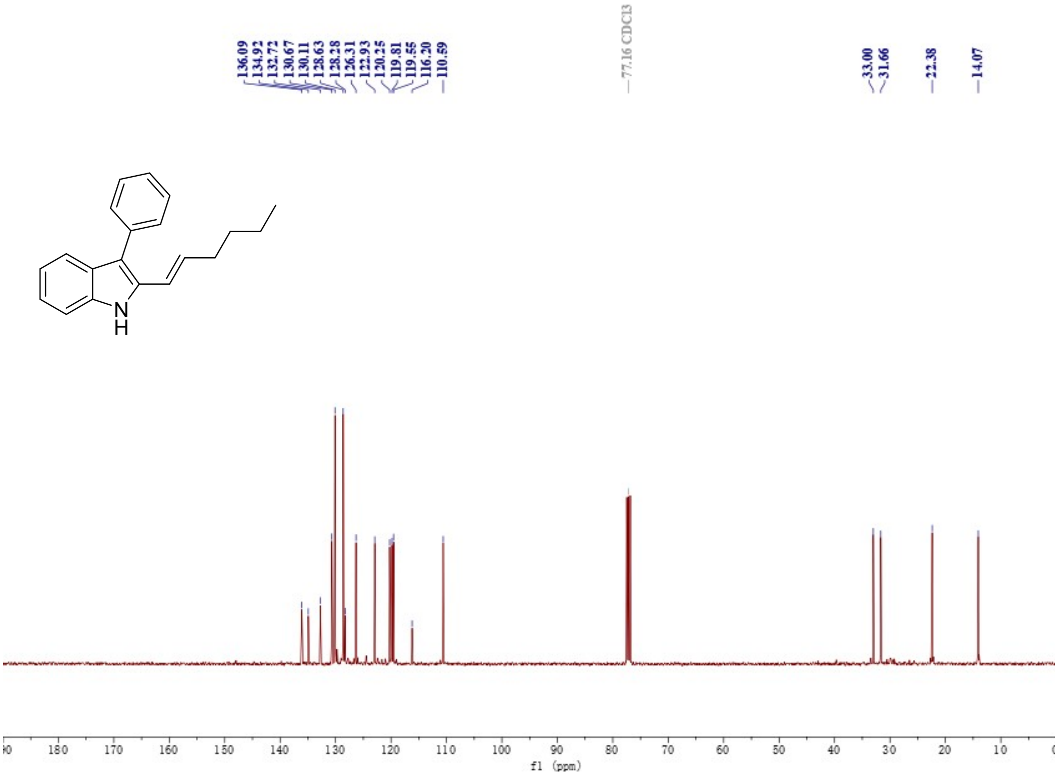
^{13}C NMR of **32** (101 MHz, CDCl$_3$)



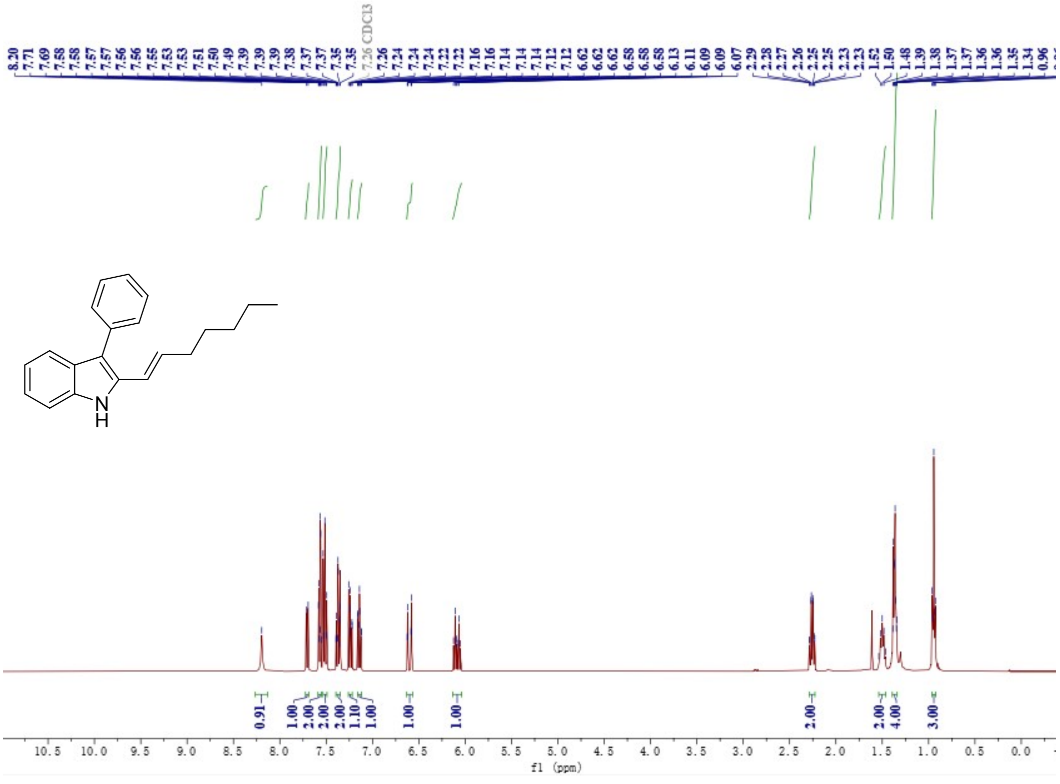
^{1}H NMR of **33** (400 MHz, CDCl$_3$)



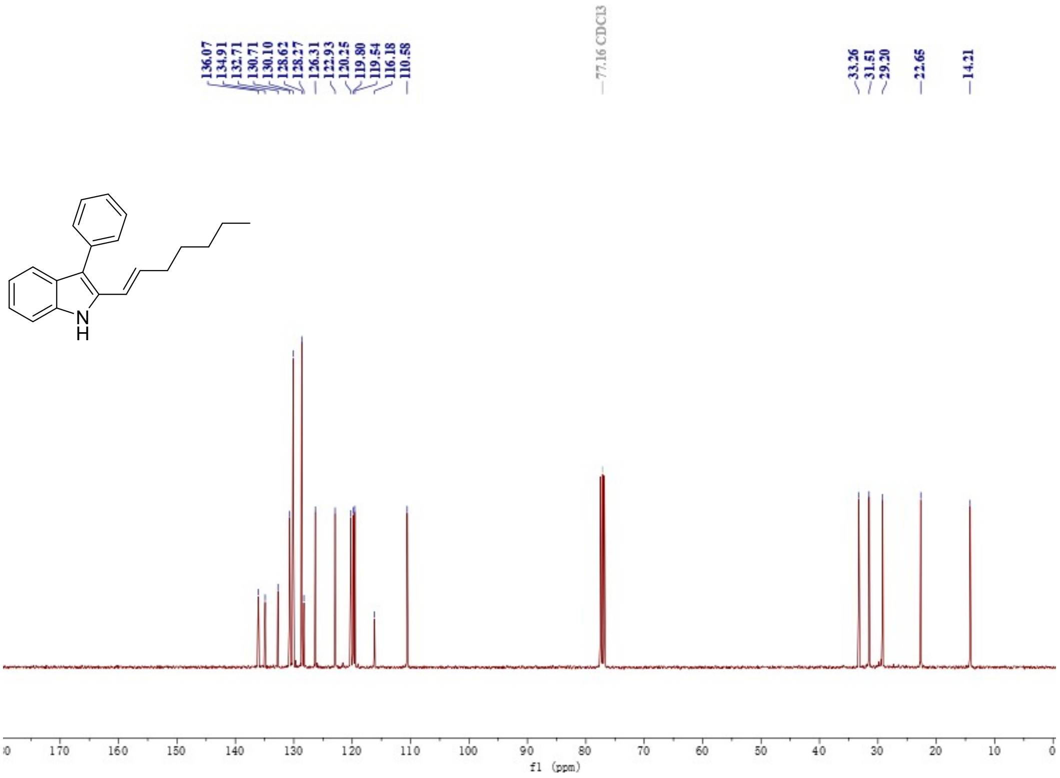
^{13}C NMR of **33** (101 MHz, CDCl$_3$)



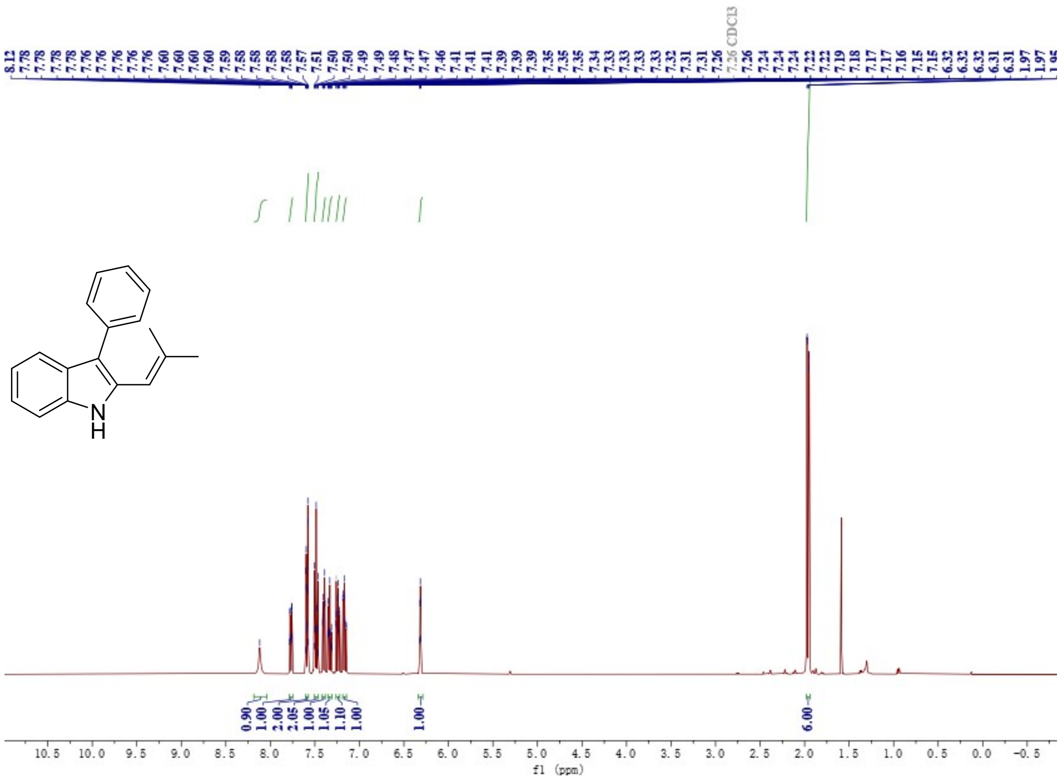
^{1}H NMR of **34** (400 MHz, CDCl$_3$)



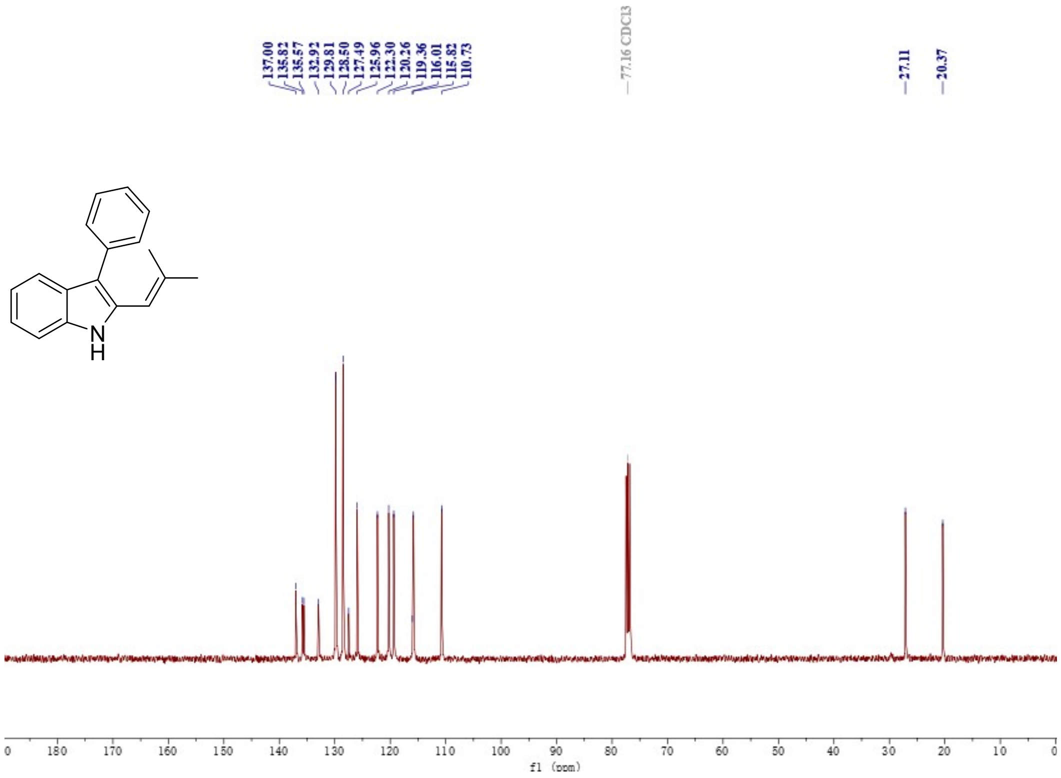
^{13}C NMR of **34** (101 MHz, $CDCl_3$)



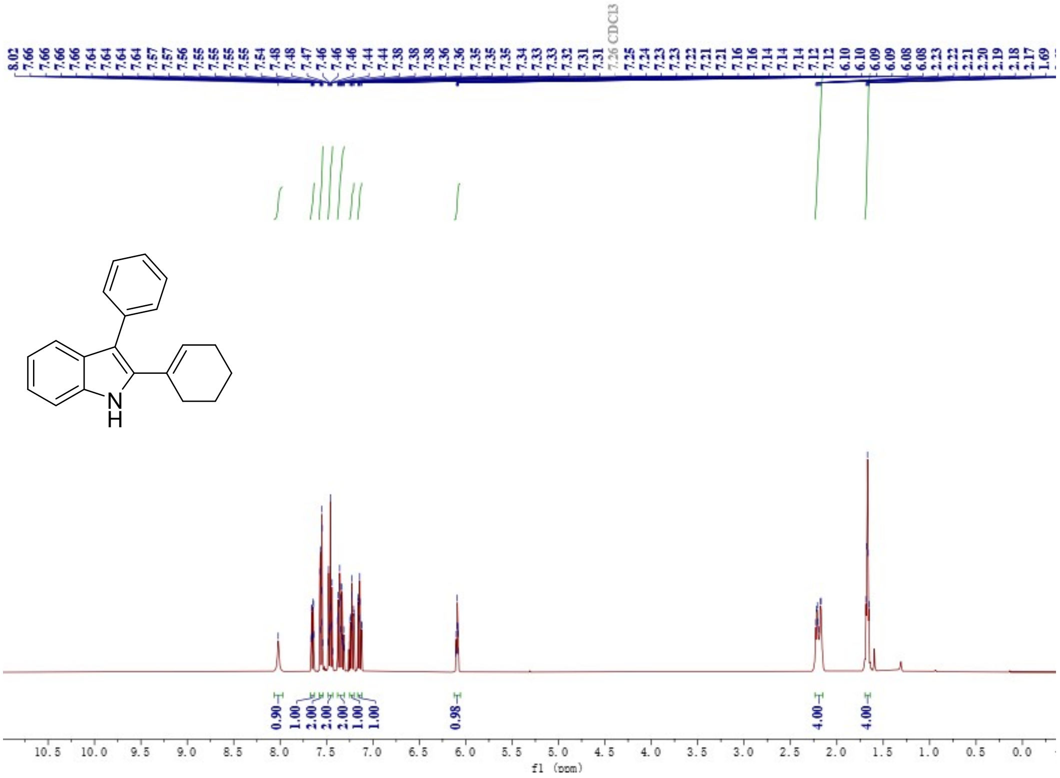
^{1}H NMR of **35** (400 MHz, $CDCl_3$)



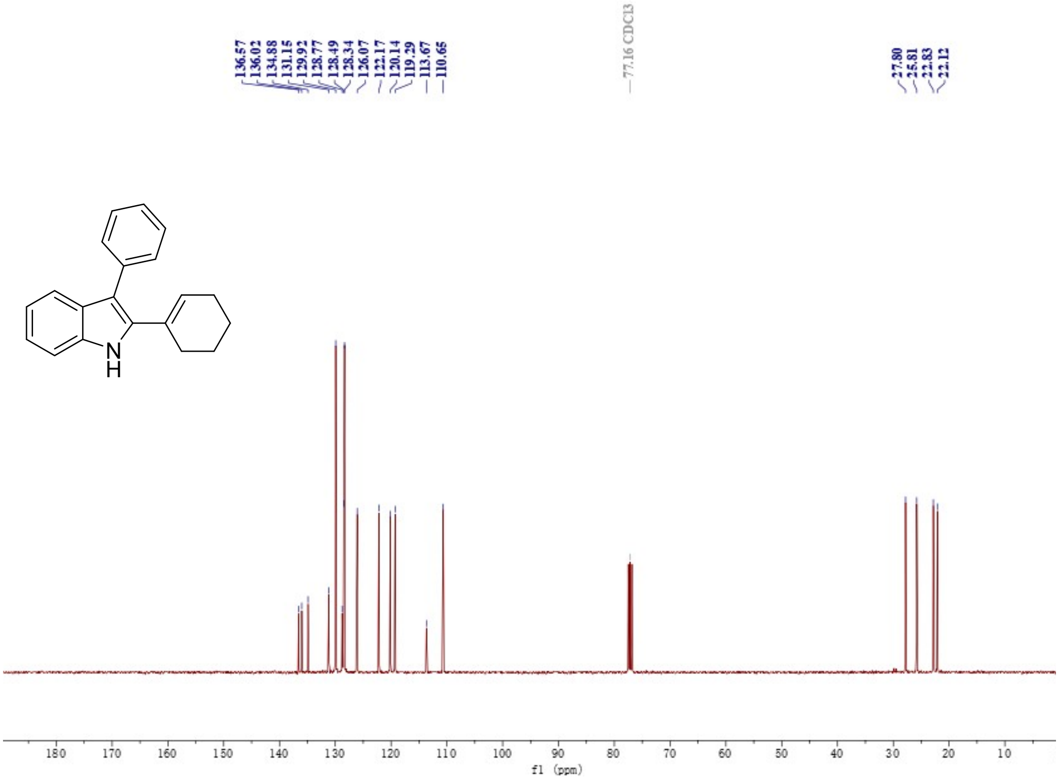
^{13}C NMR of **35** (101 MHz, $CDCl_3$)



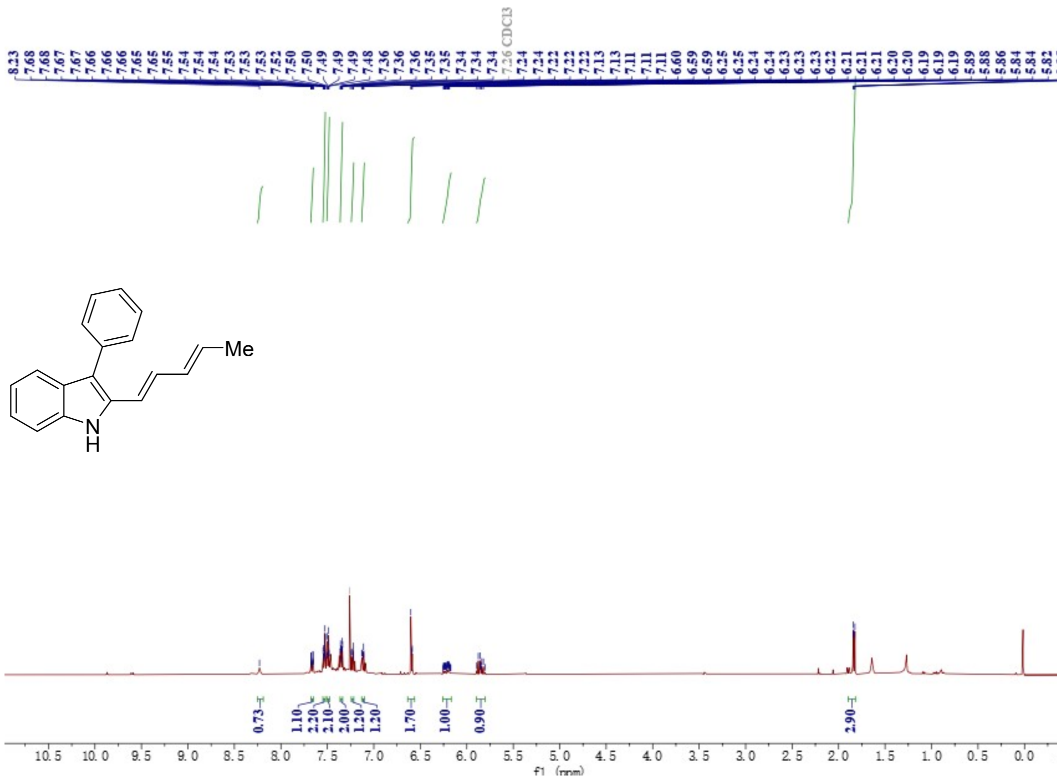
^{1}H NMR of **36** (400 MHz, $CDCl_3$)



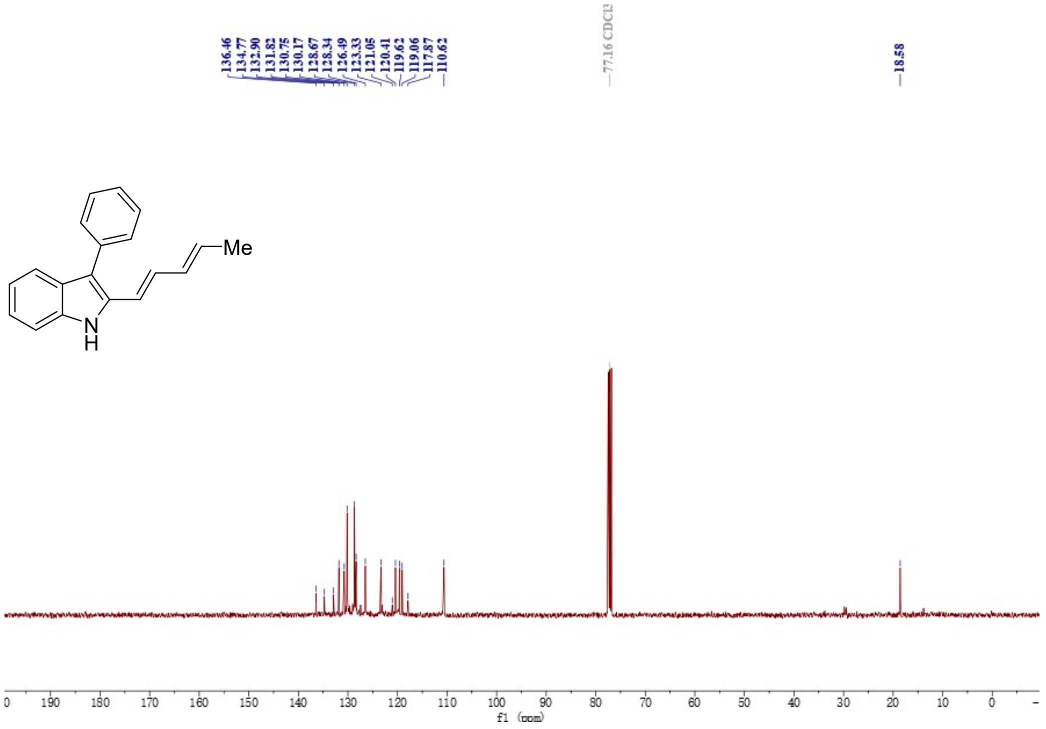
^{13}C NMR of **36** (101 MHz, CDCl$_3$)



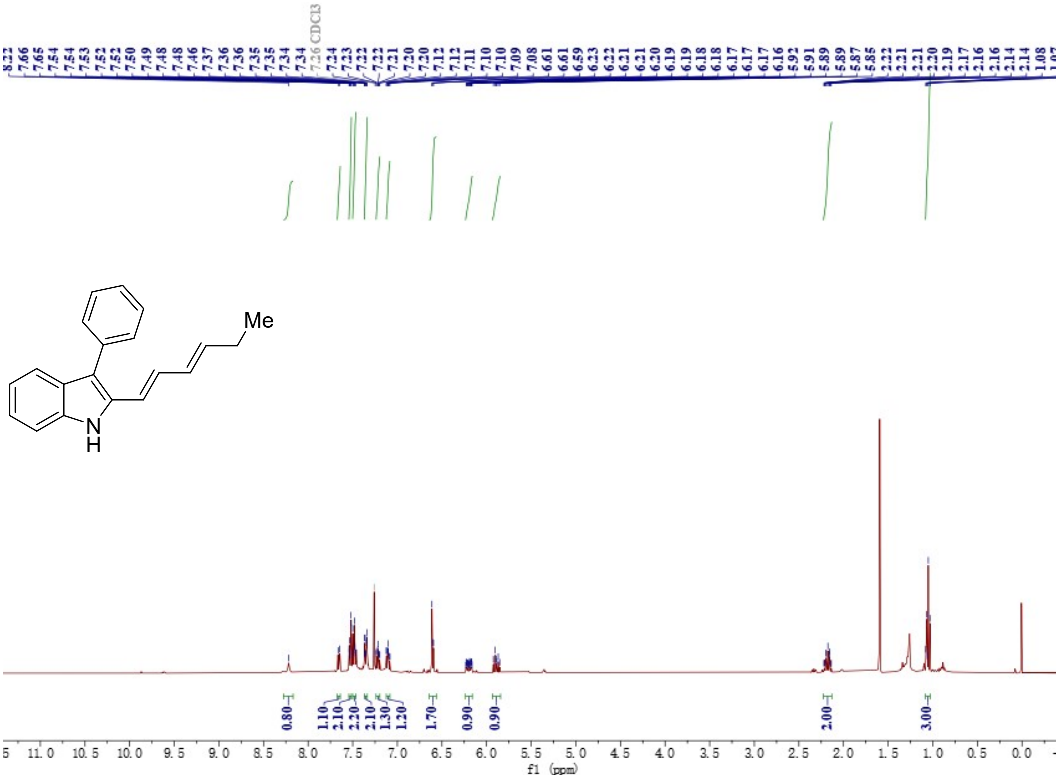
^{1}H NMR of **37** (400 MHz, CDCl$_3$)



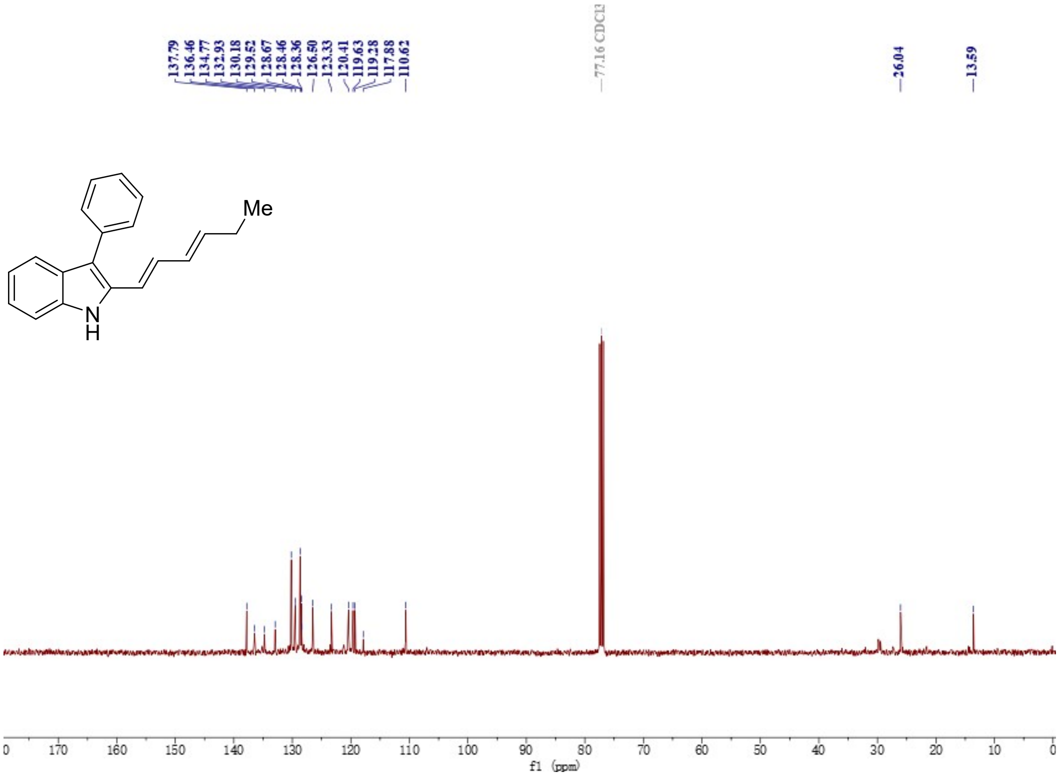
^{13}C NMR of **37** (101 MHz, CDCl$_3$)



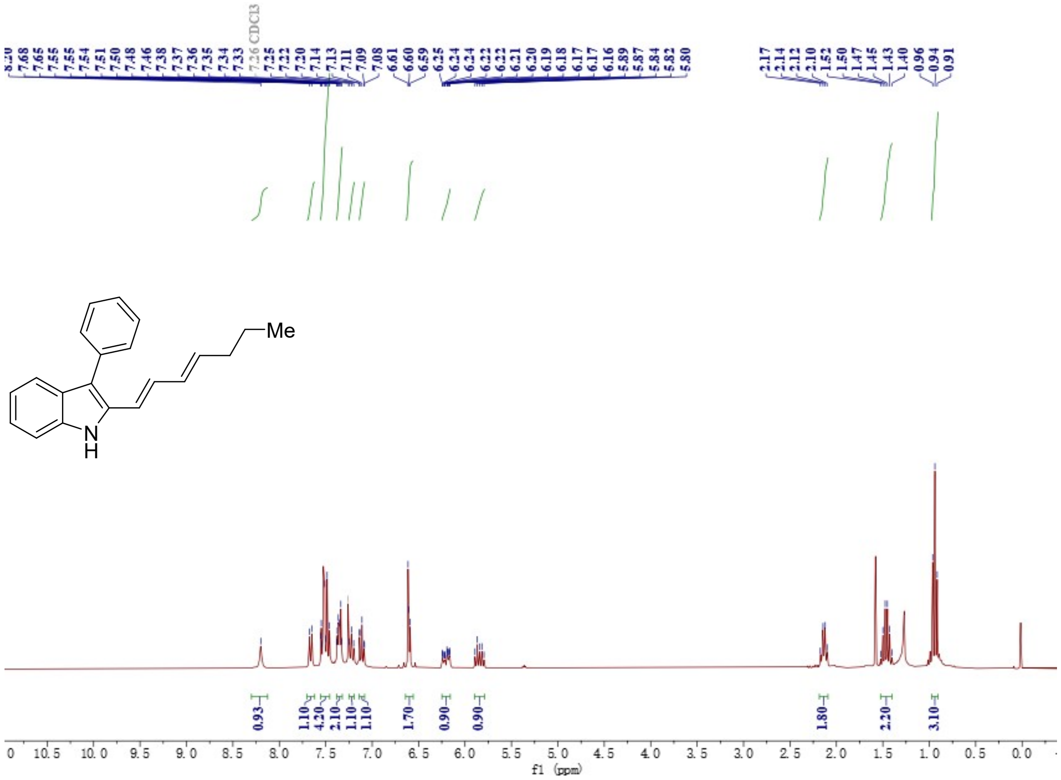
^{1}H NMR of **38** (400 MHz, CDCl$_3$)



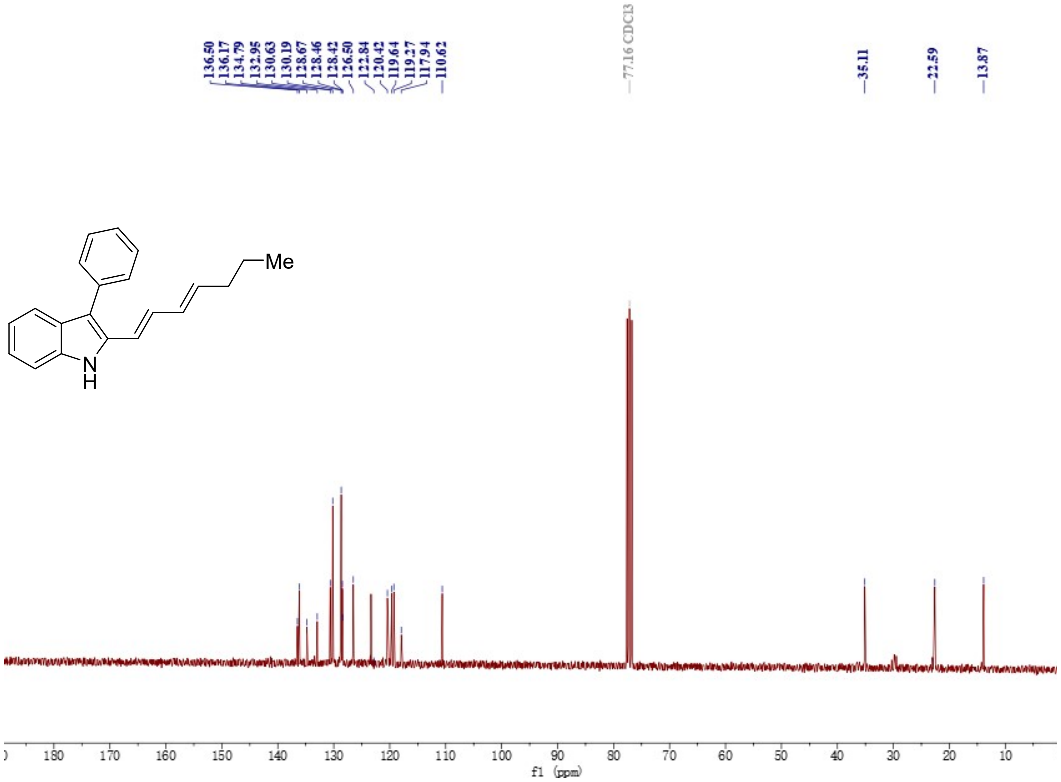
^{13}C NMR of **38** (101 MHz, CDCl$_3$)



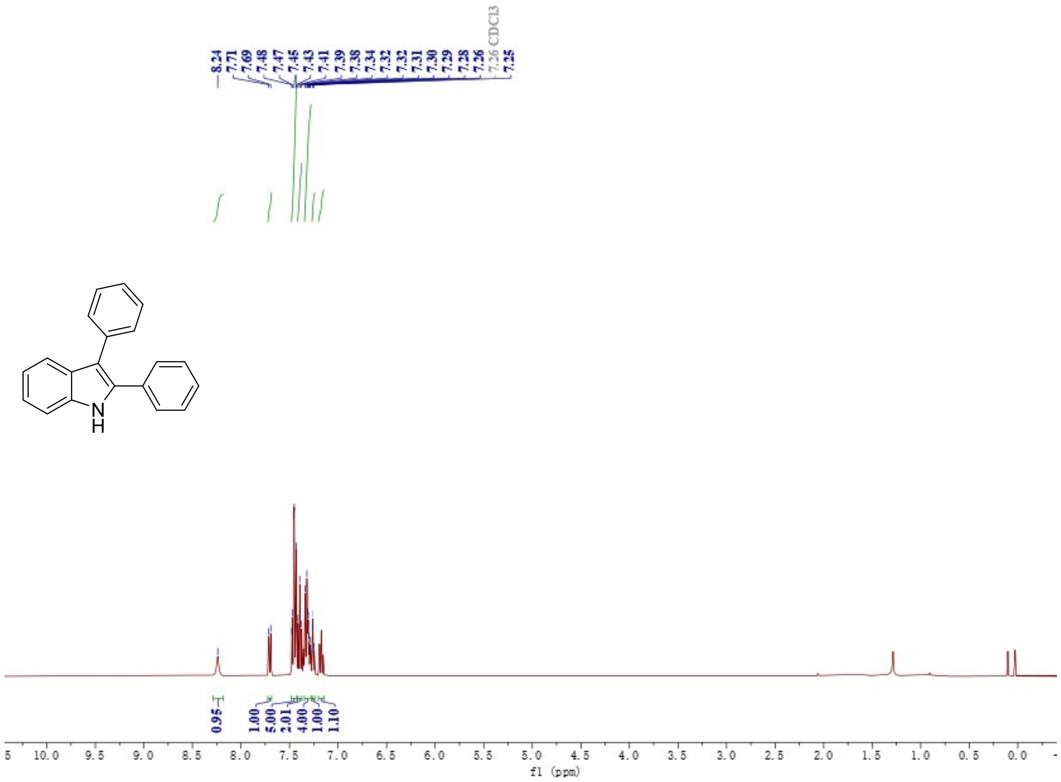
^{1}H NMR of **39** (300 MHz, CDCl$_3$)



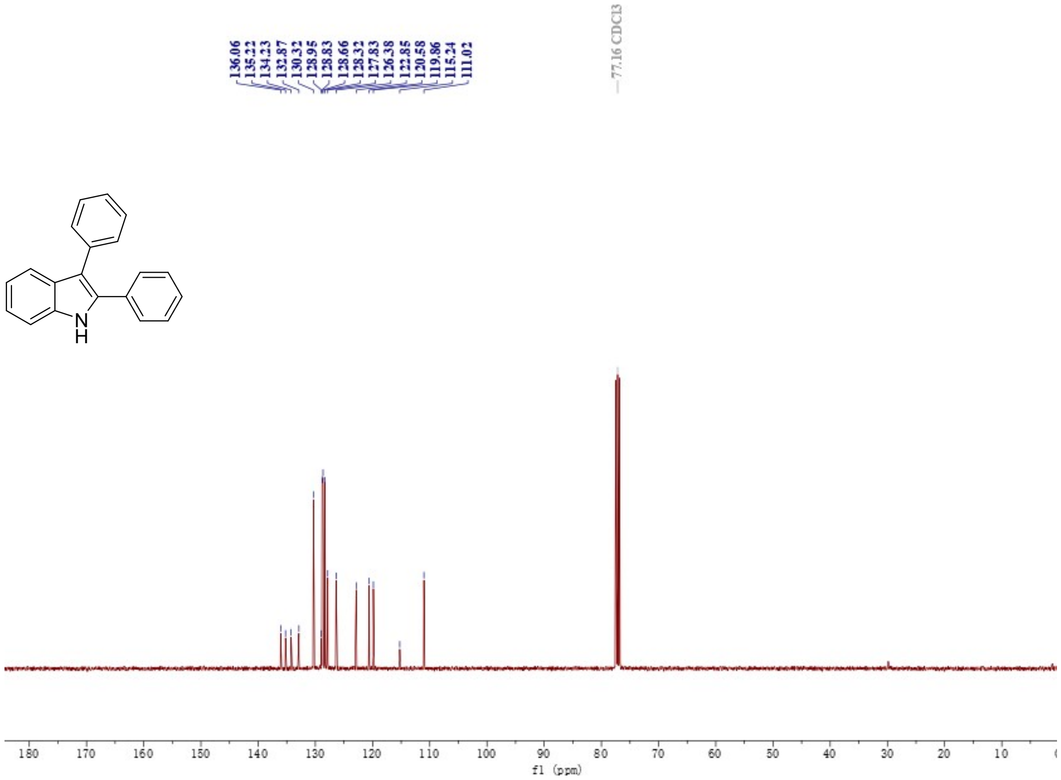
^{13}C NMR of **39** (76 MHz, CDCl$_3$)



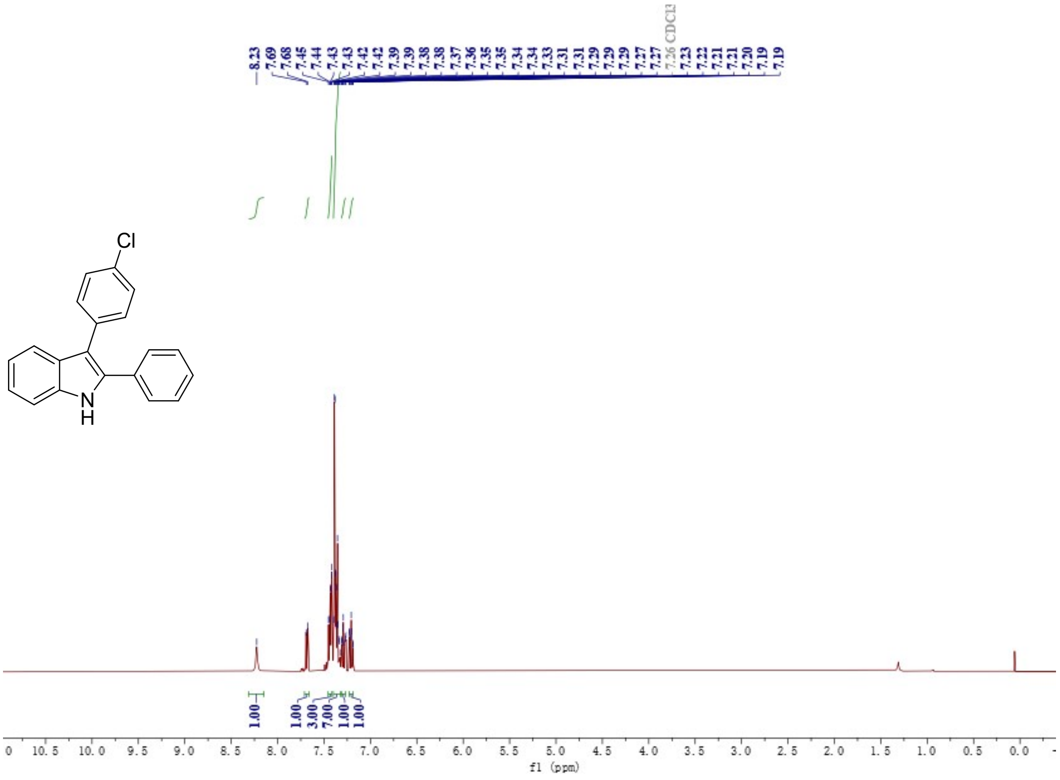
^{1}H NMR of **41** (400 MHz, CDCl$_3$)



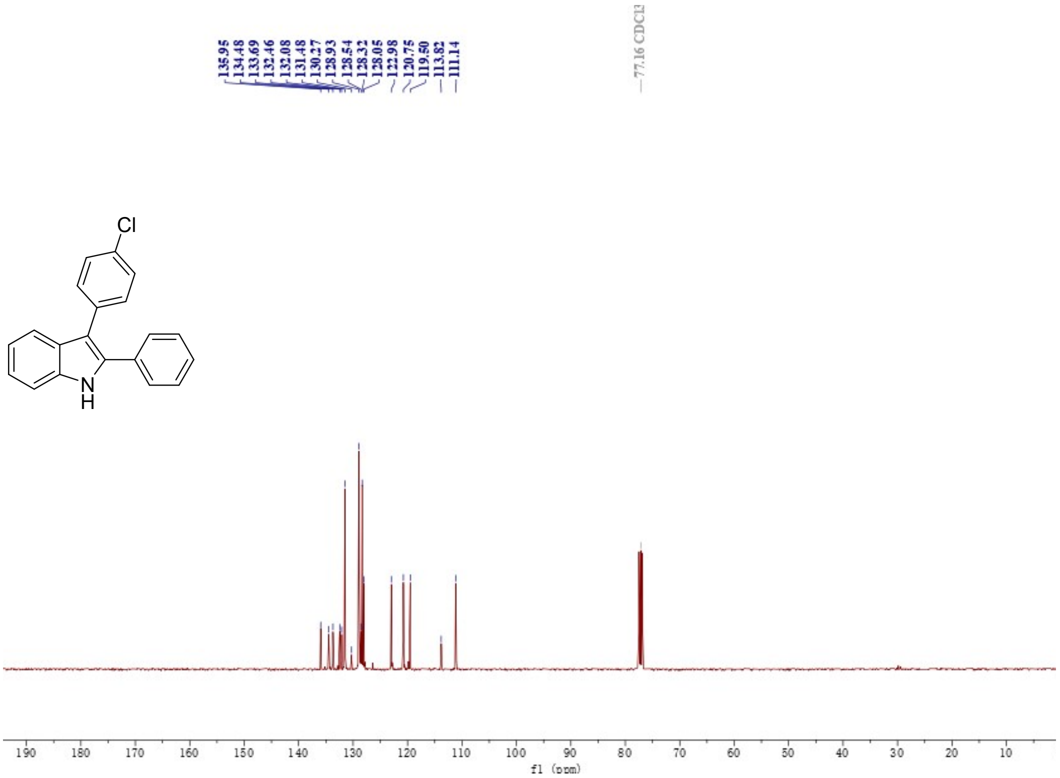
^{13}C NMR of **41** (101 MHz, CDCl$_3$)



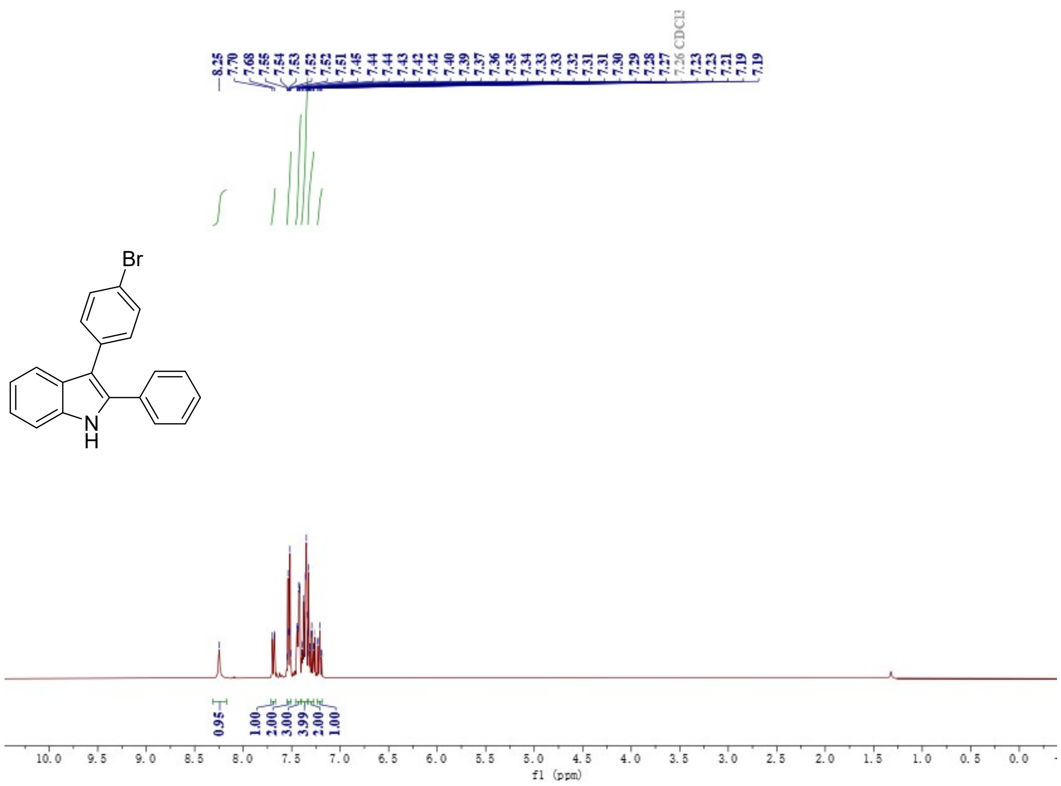
^{1}H NMR of **42** (400 MHz, CDCl$_3$)



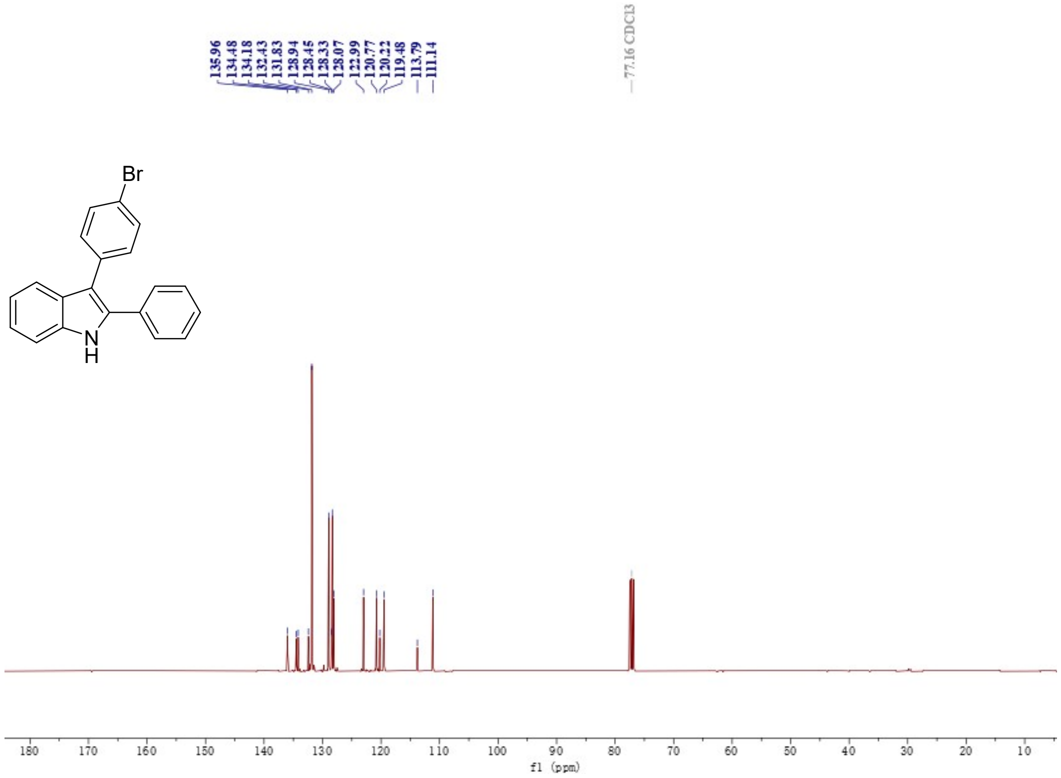
^{13}C NMR of **42** (101 MHz, CDCl$_3$)



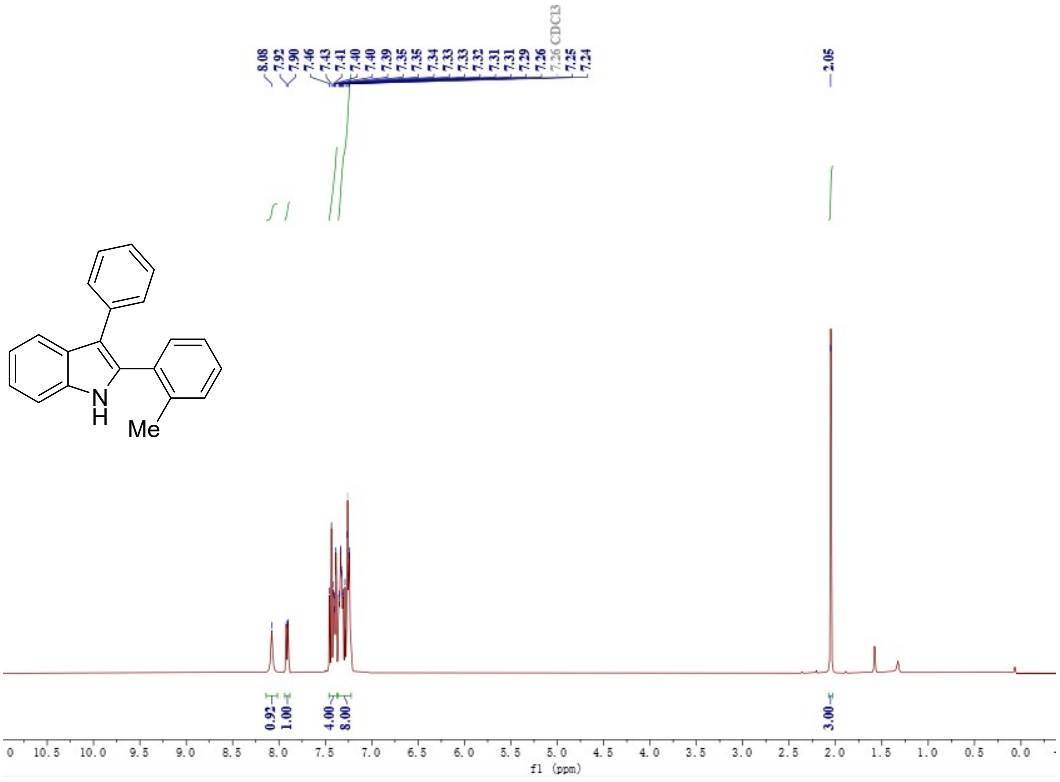
^{1}H NMR of **43** (400 MHz, CDCl$_3$)



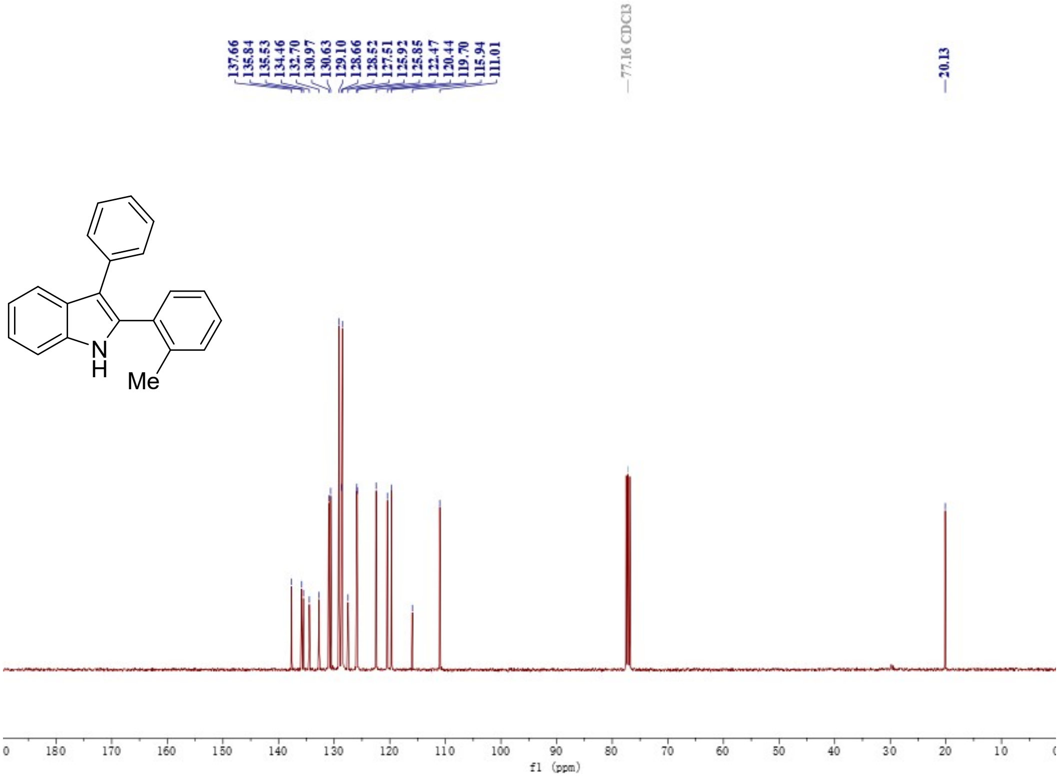
^{13}C NMR of **43** (101 MHz, $CDCl_3$)



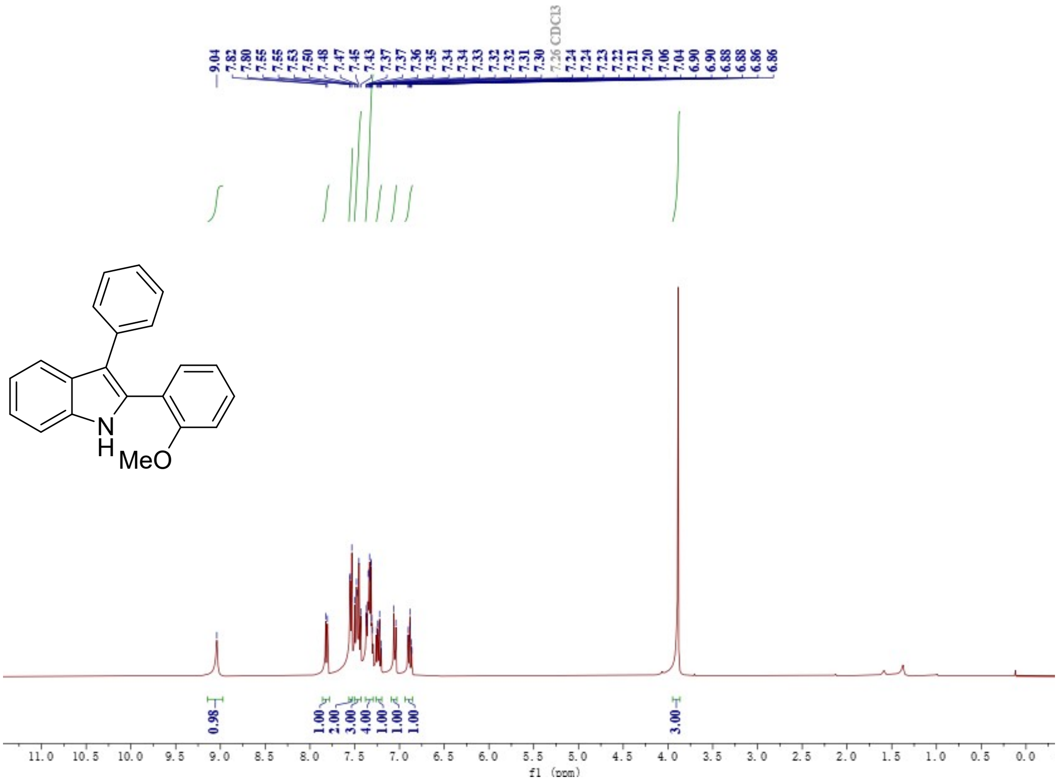
^{1}H NMR of **44** (400 MHz, $CDCl_3$)



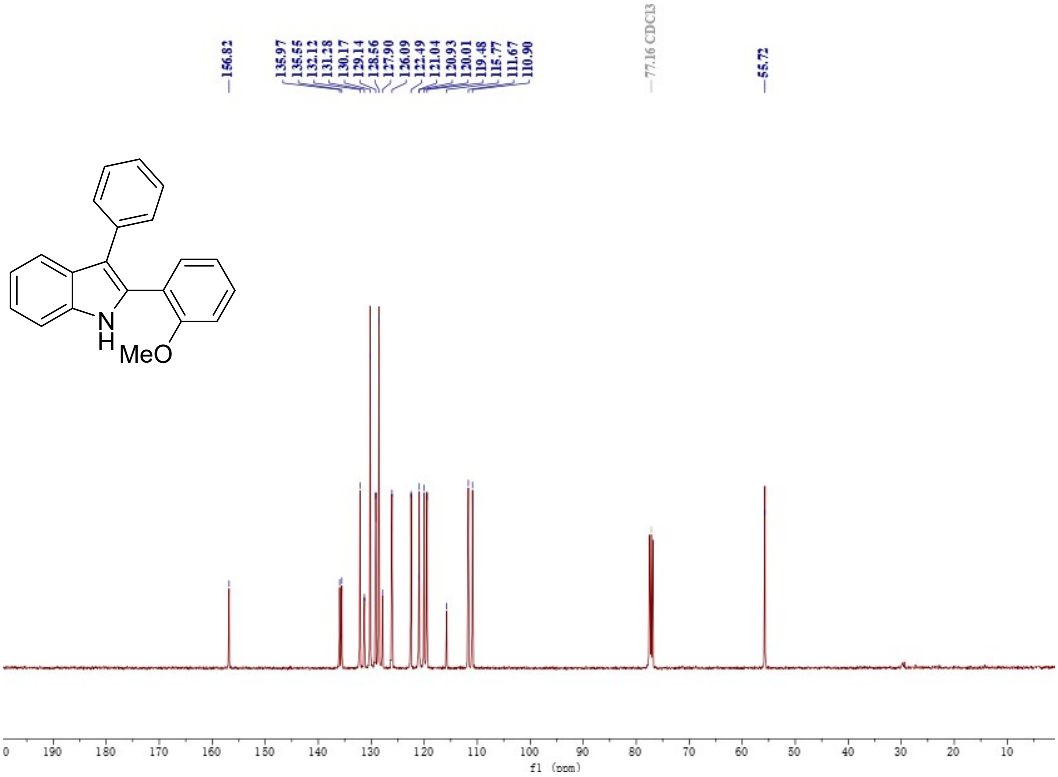
^{13}C NMR of **44** (101 MHz, CDCl$_3$)



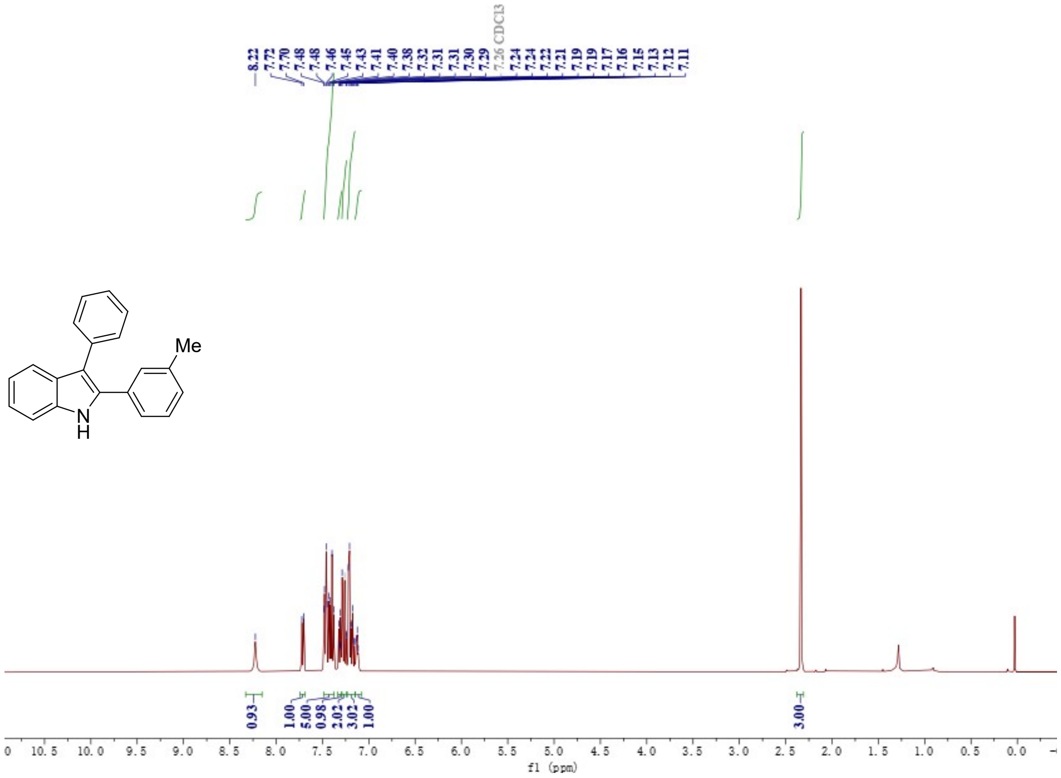
^{1}H NMR of **45** (400 MHz, CDCl$_3$)



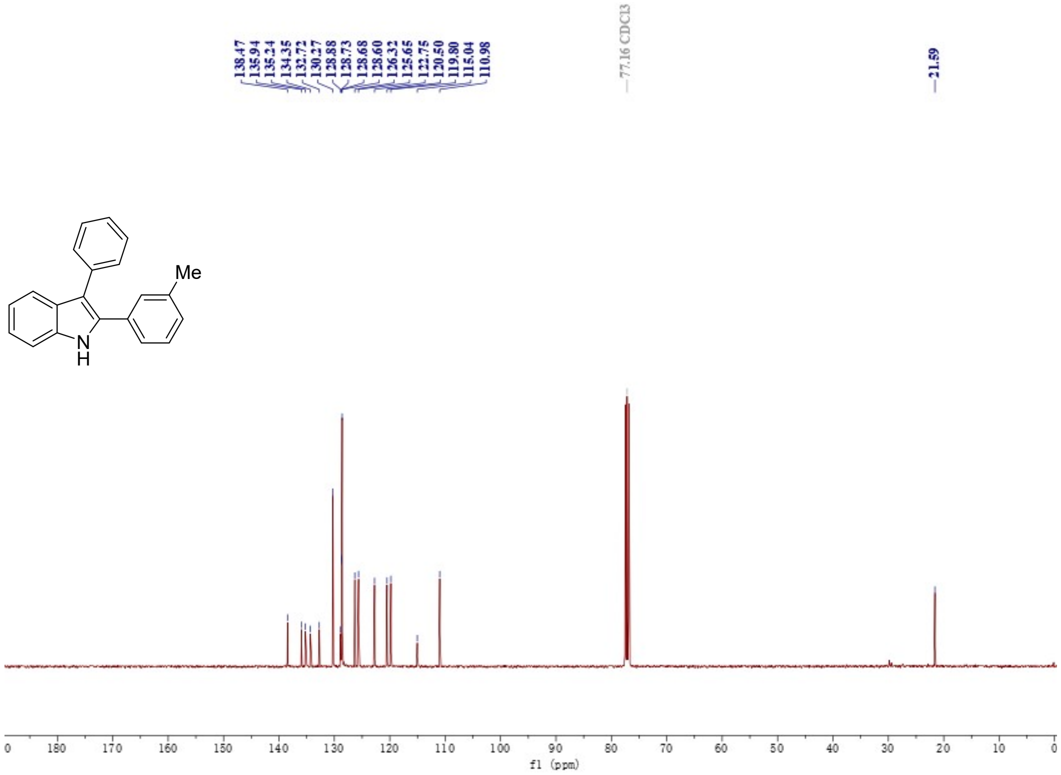
^{13}C NMR of **45** (101 MHz, $CDCl_3$)



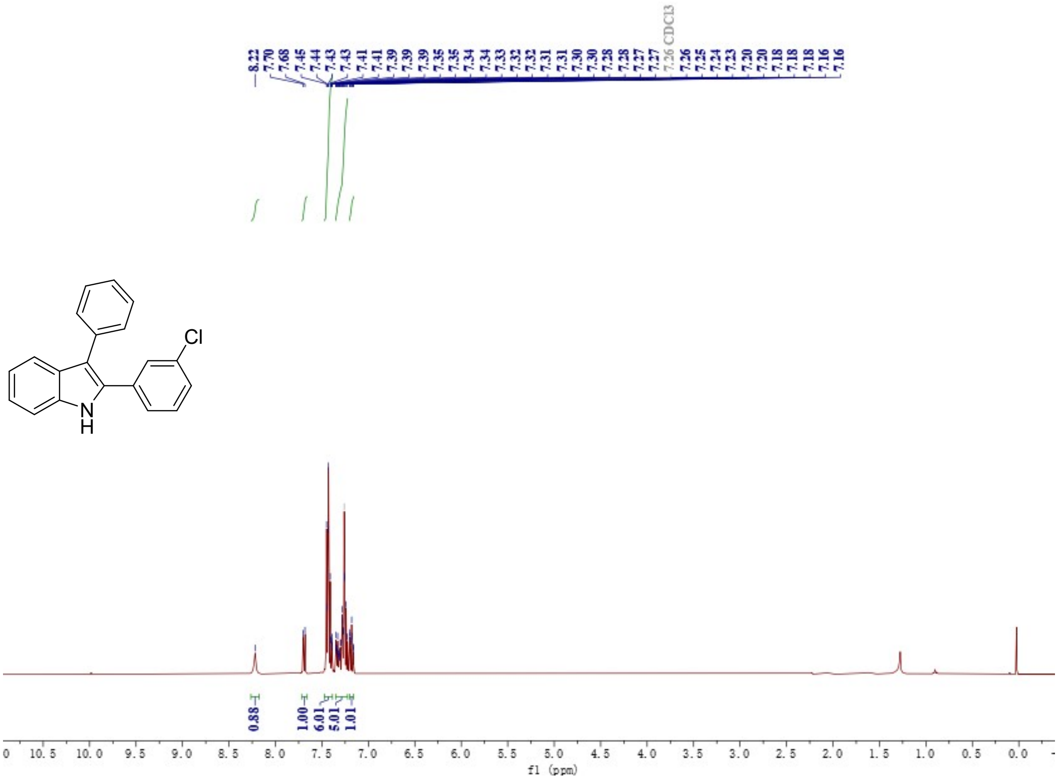
^{1}H NMR of **46** (400 MHz, $CDCl_3$)



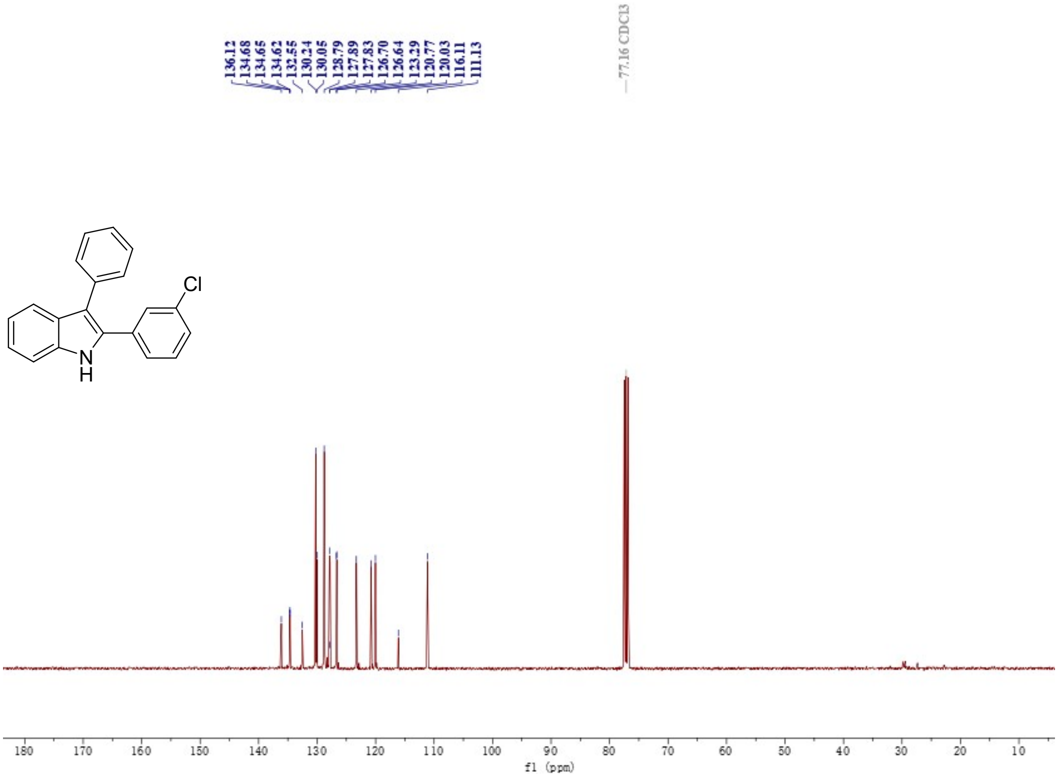
^{13}C NMR of **46** (101 MHz, CDCl$_3$)



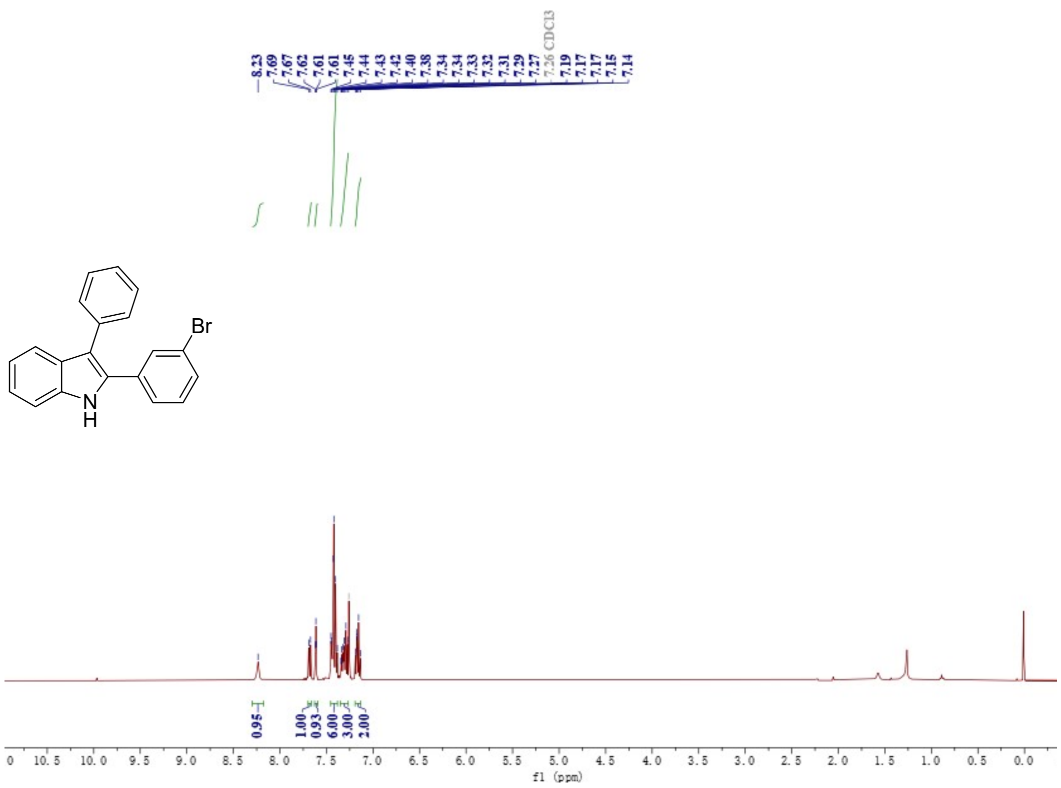
^{1}H NMR of **47** (400 MHz, $CDCl_3$)



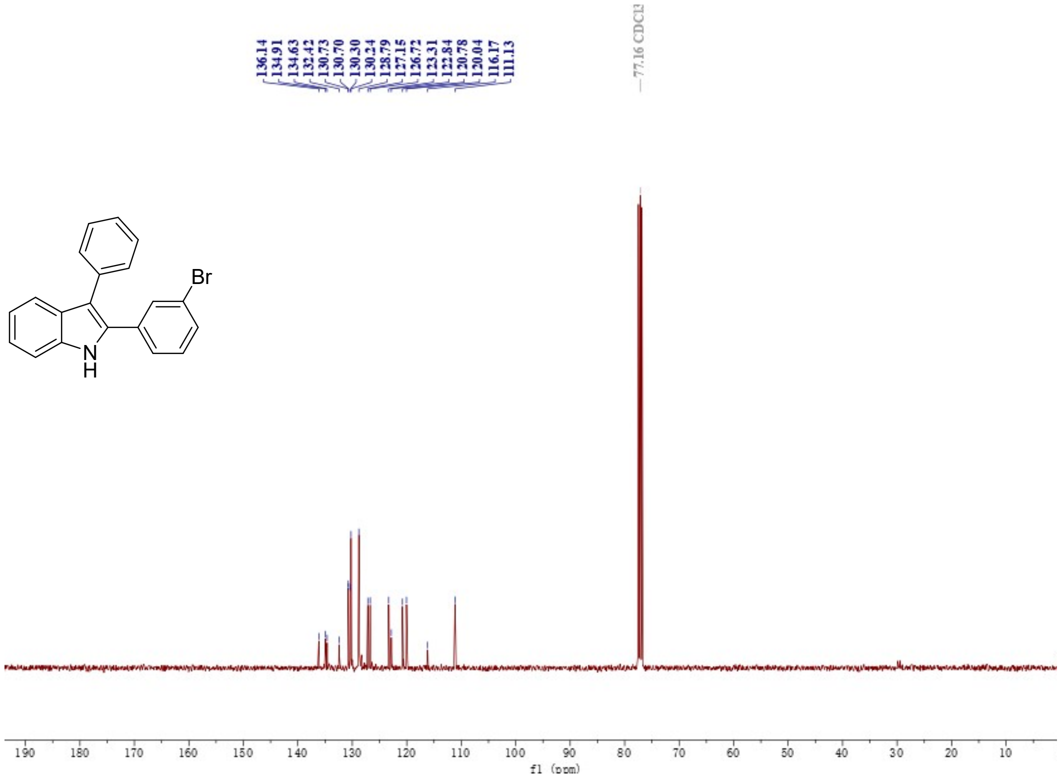
^{13}C NMR of **47** (101 MHz, $CDCl_3$)



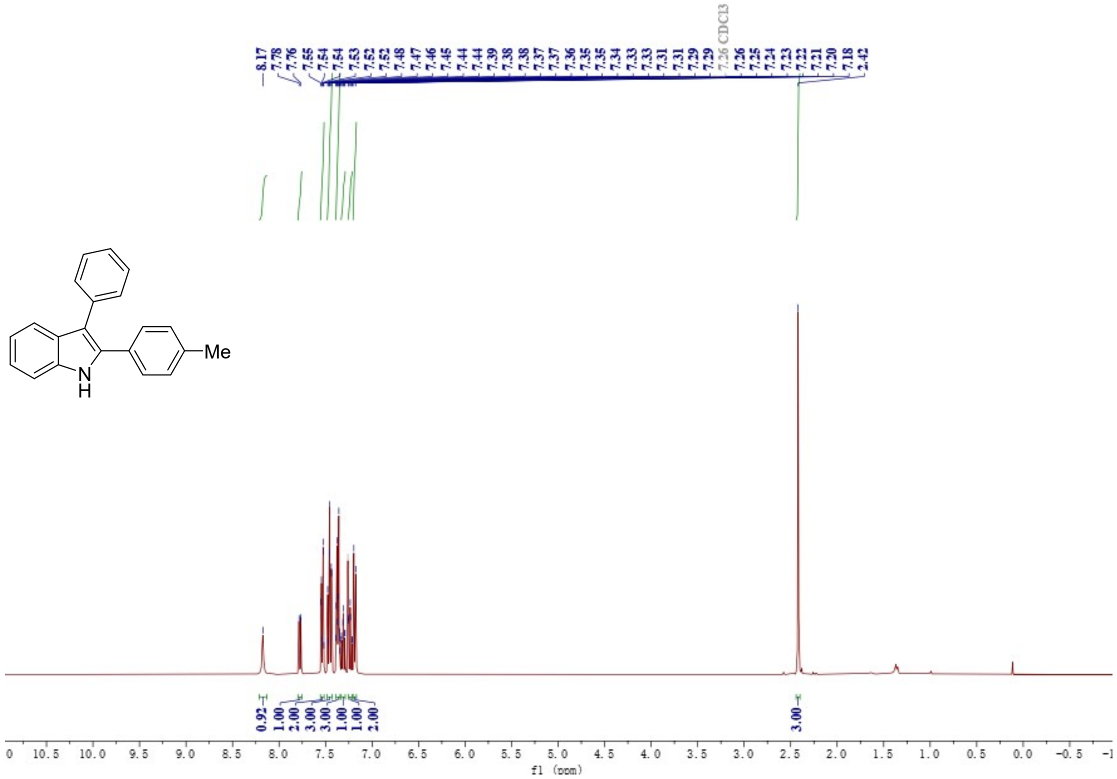
^{1}H NMR of **48** (400 MHz, $CDCl_3$)



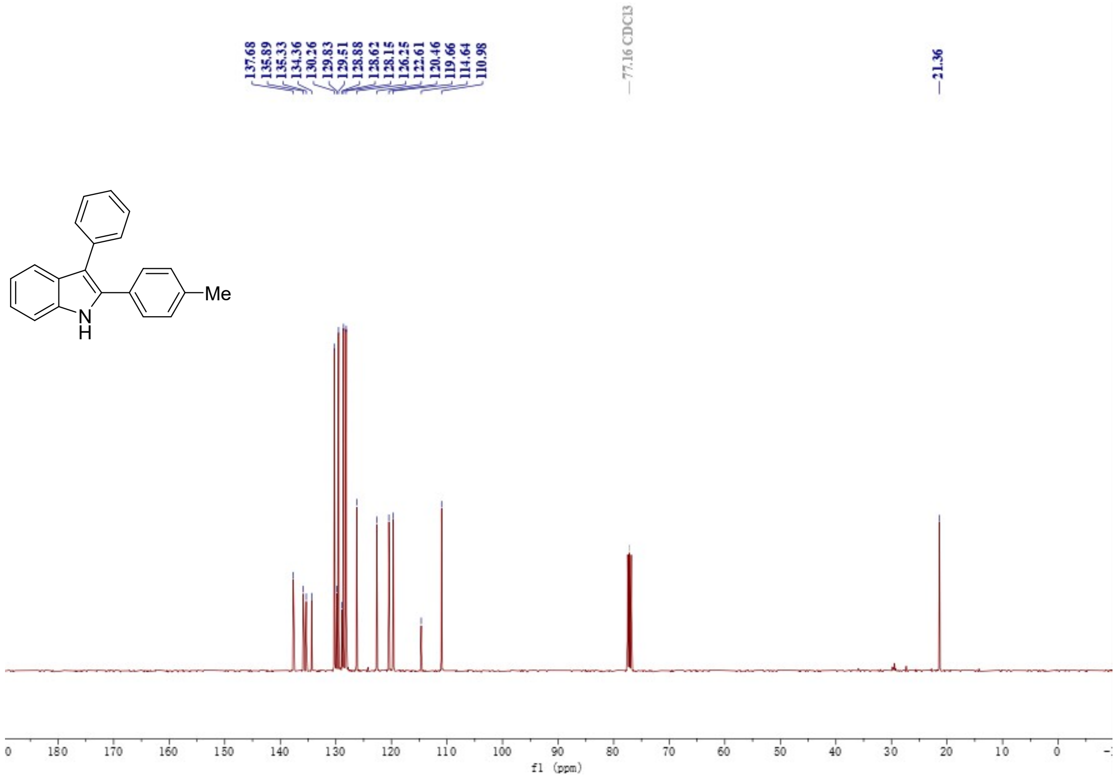
^{13}C NMR of **48** (101 MHz, CDCl$_3$)



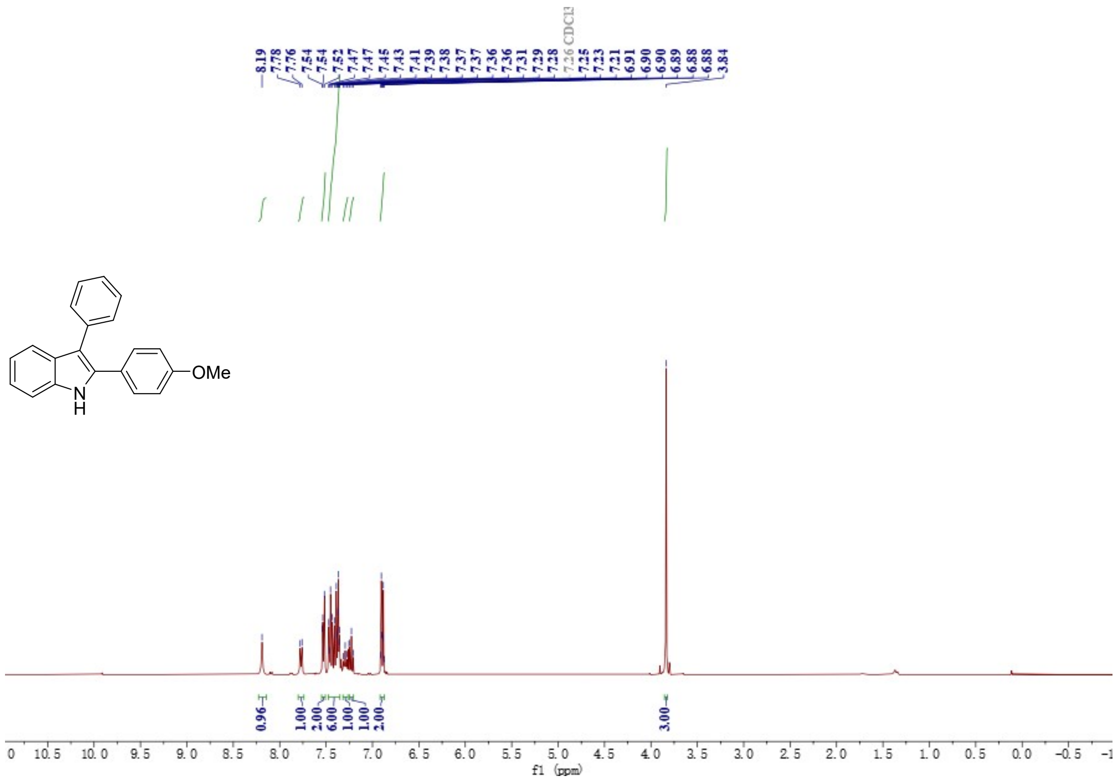
^{1}H NMR of **49** (400 MHz, CDCl$_3$)



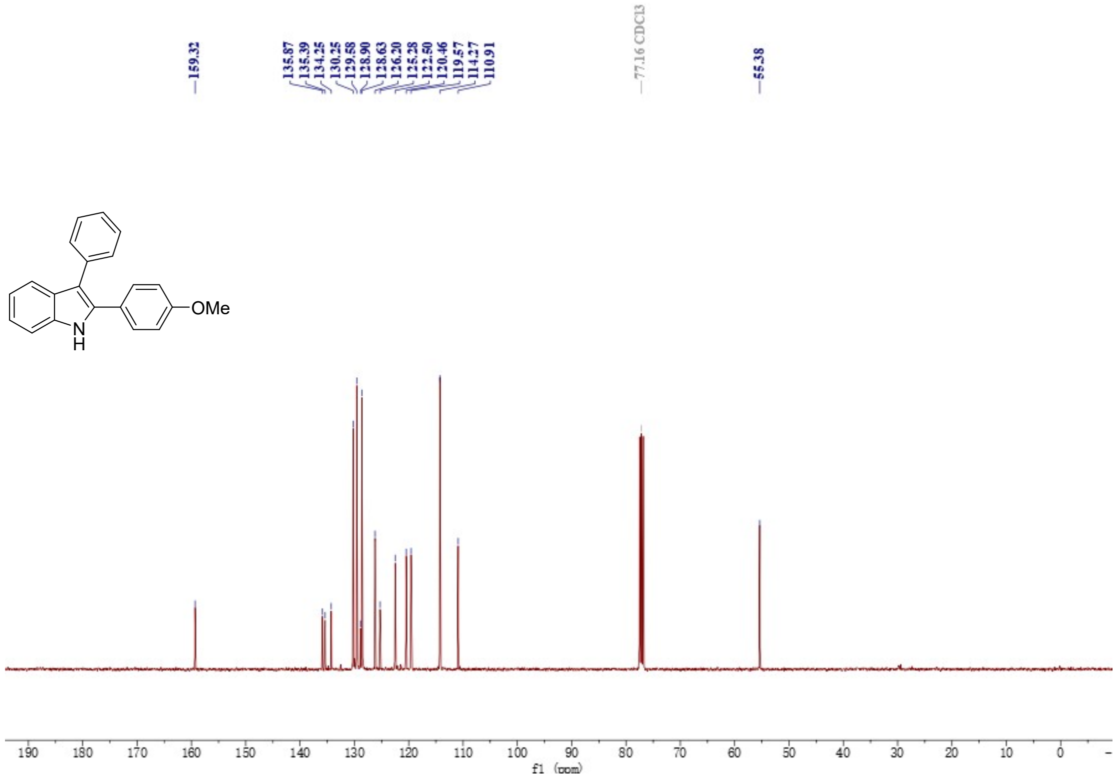
^{13}C NMR of **49** (101 MHz, $CDCl_3$)



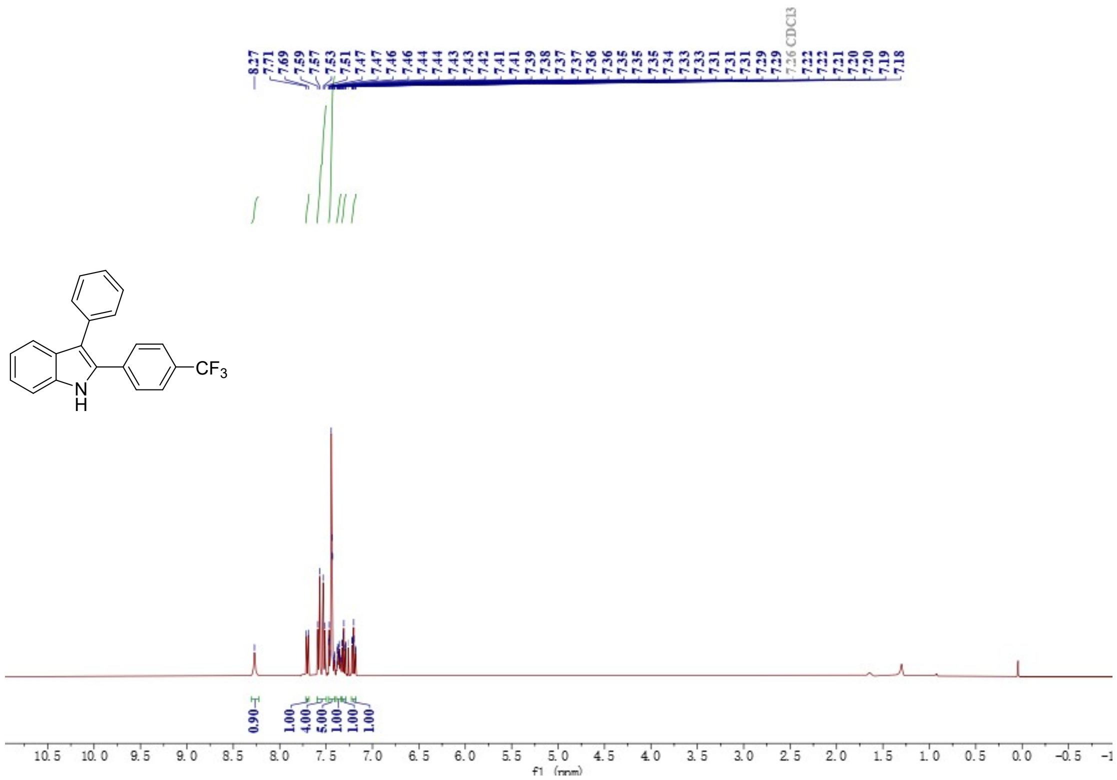
^{1}H NMR of **50** (400 MHz, $CDCl_3$)



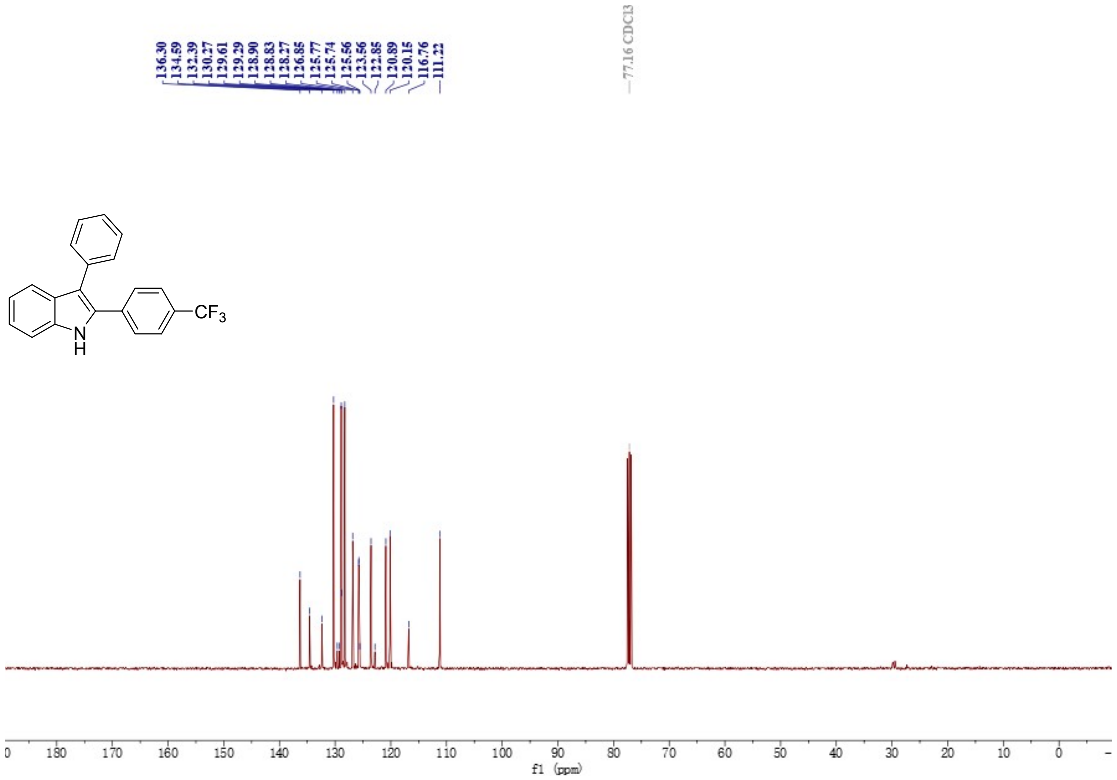
^{13}C NMR of **50** (101 MHz, CDCl$_3$)



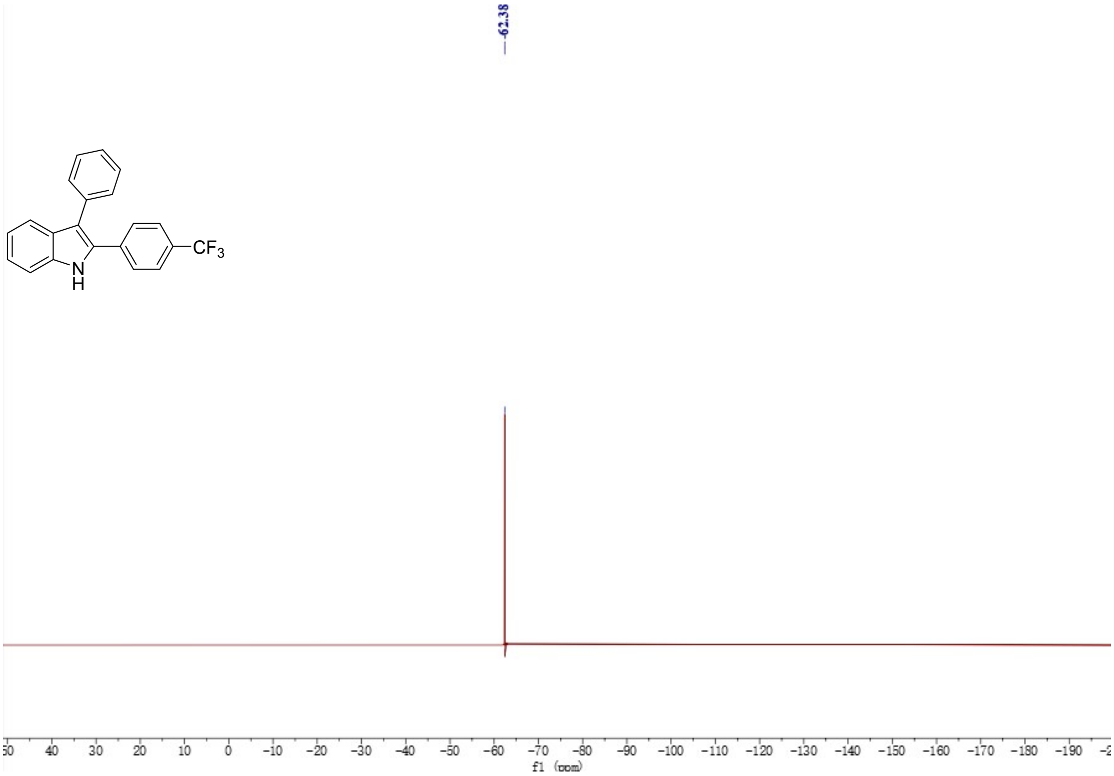
^{1}H NMR of **51** (400 MHz, CDCl$_3$)



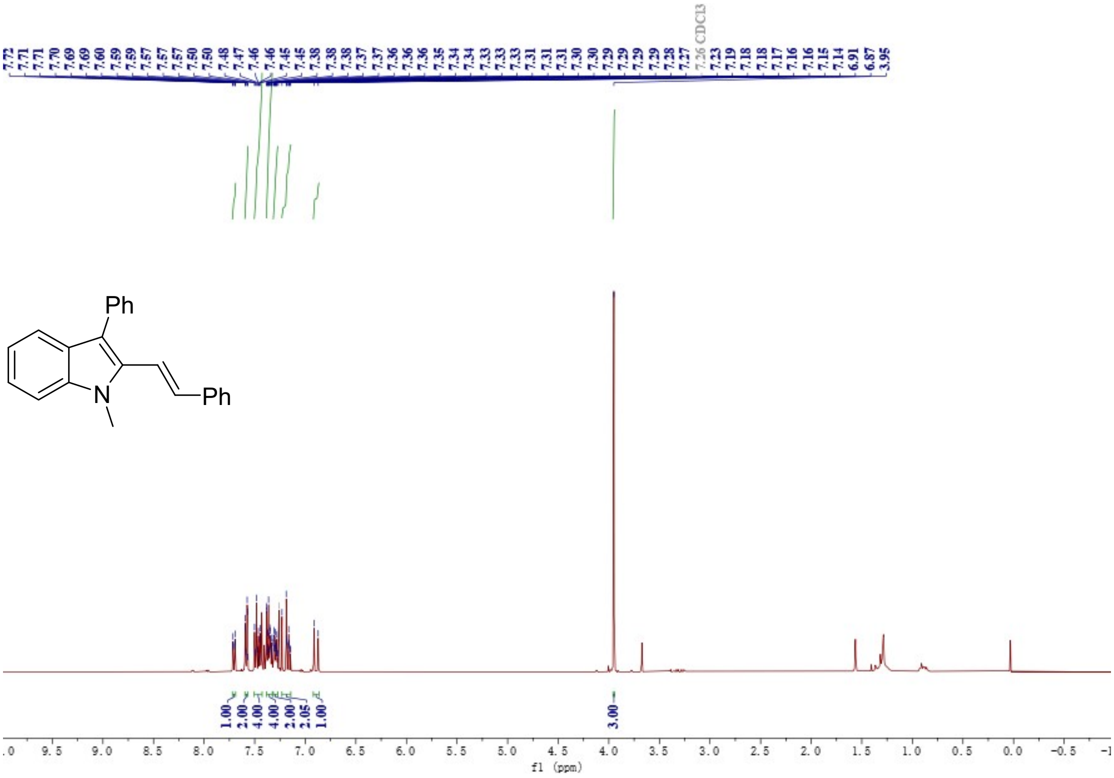
^{13}C NMR of **51** (101 MHz, CDCl$_3$)



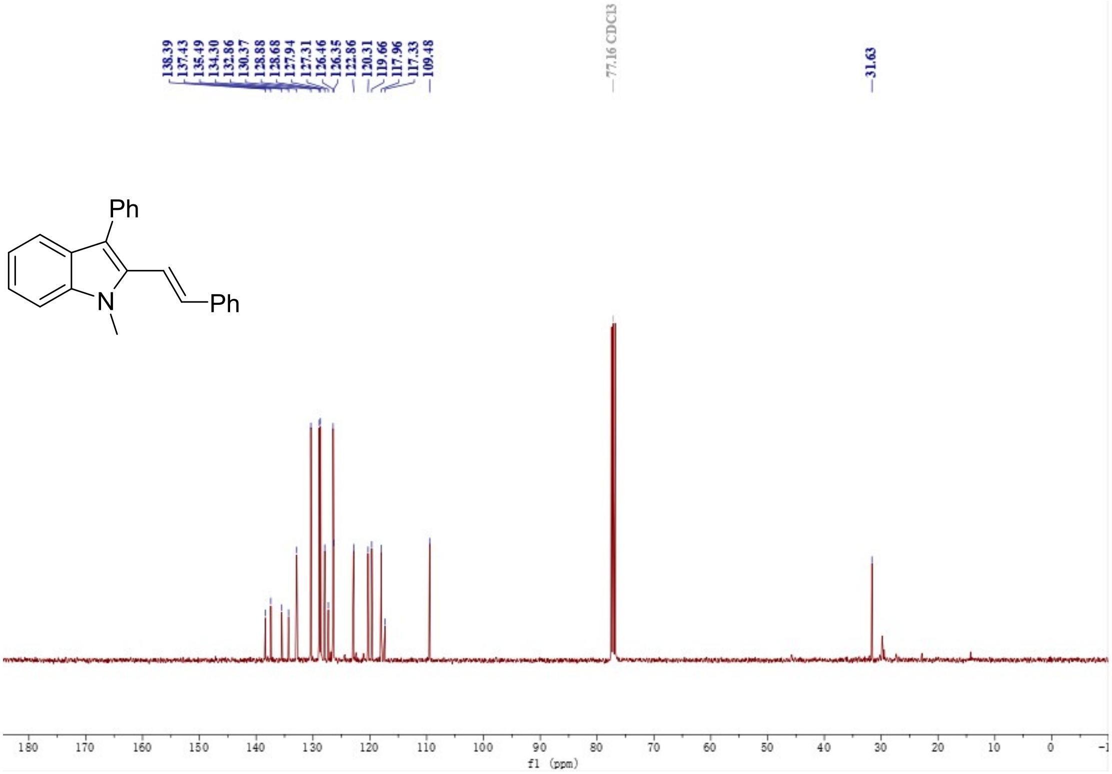
^{19}F NMR of **51** (376 MHz, CDCl$_3$)



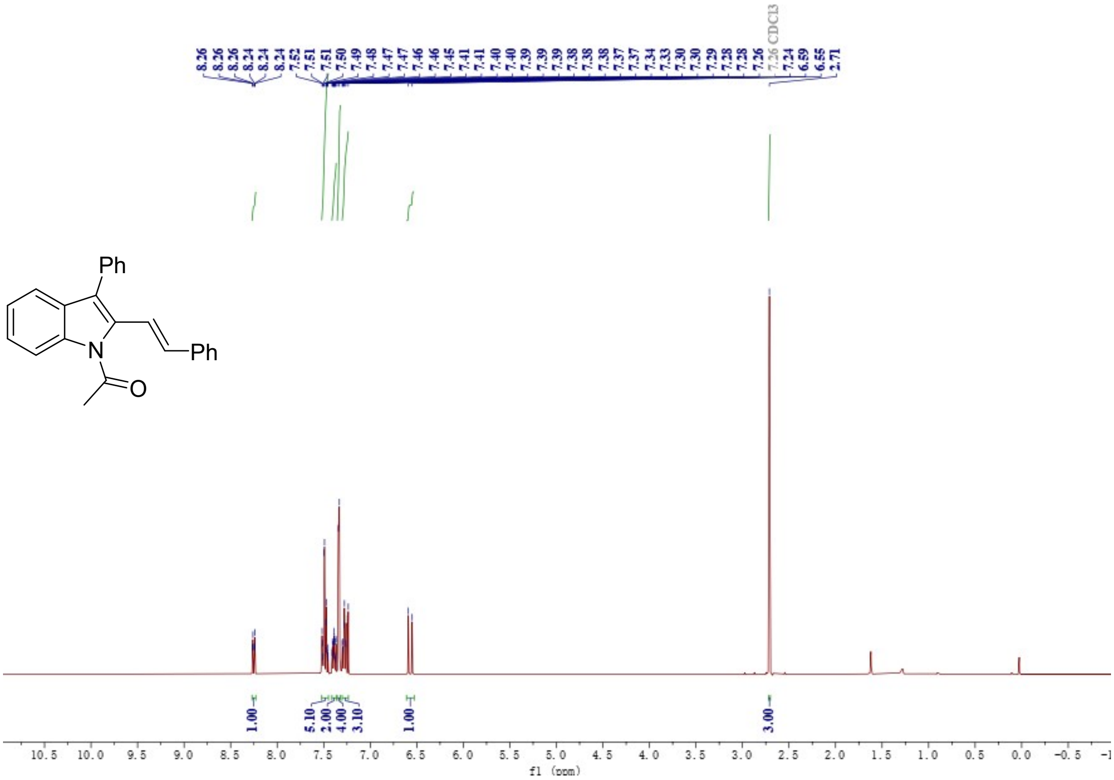
^{1}H NMR of **52** (400 MHz, $CDCl_3$)



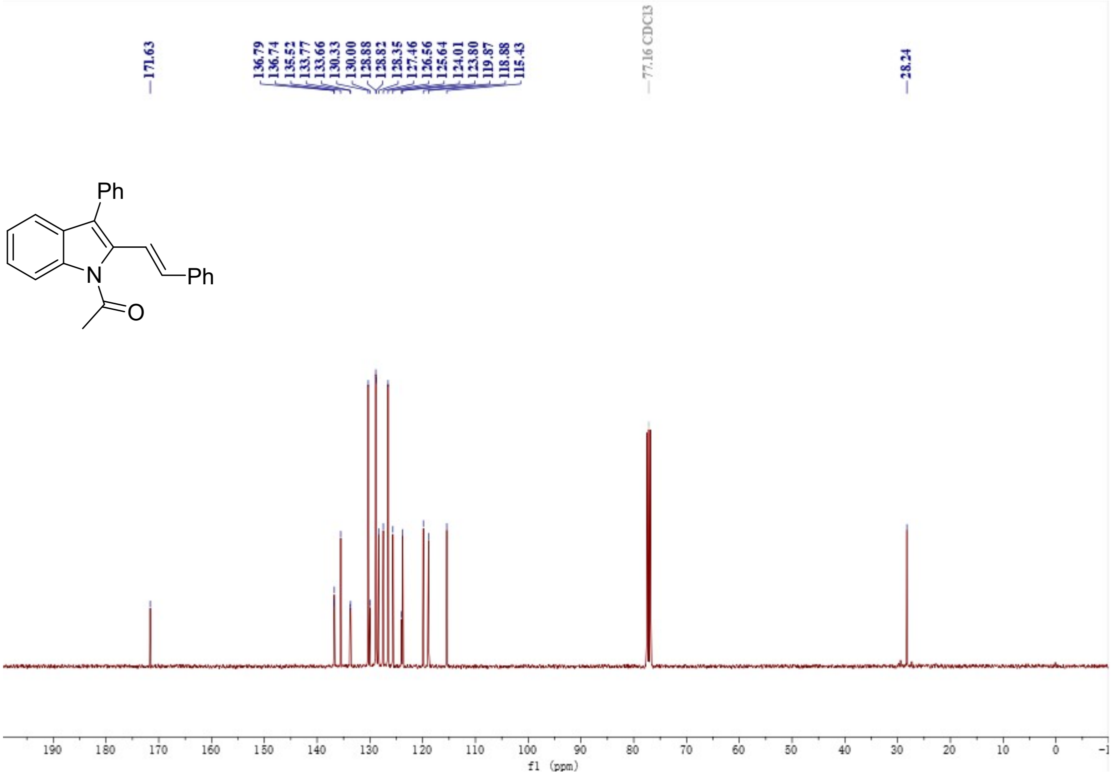
^{13}C NMR of **52** (101 MHz, $CDCl_3$)



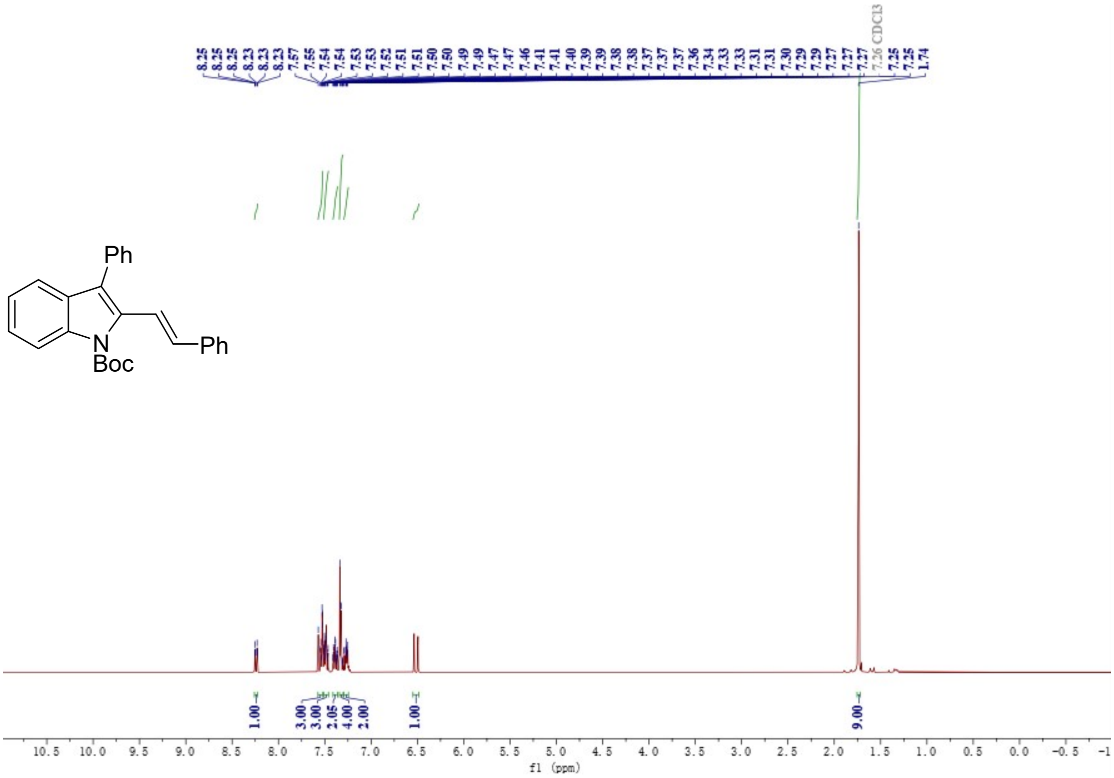
^{1}H NMR of **53** (400 MHz, $CDCl_3$)



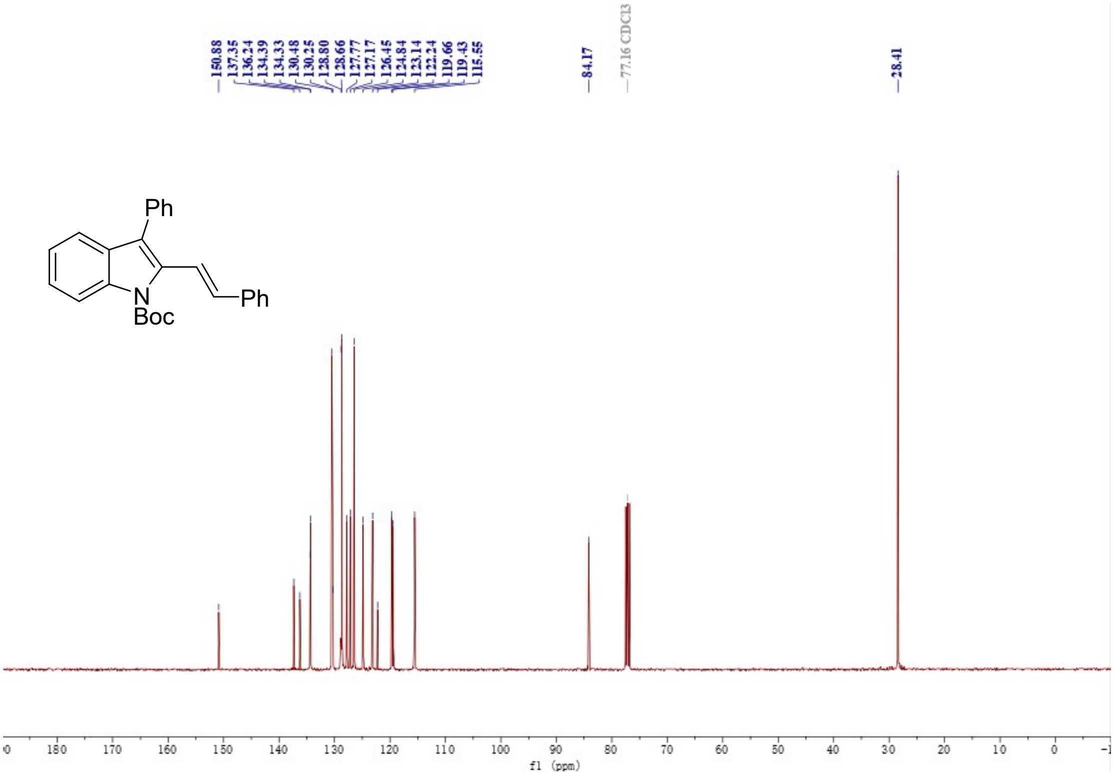
^{13}C NMR of **53** (101 MHz, $CDCl_3$)



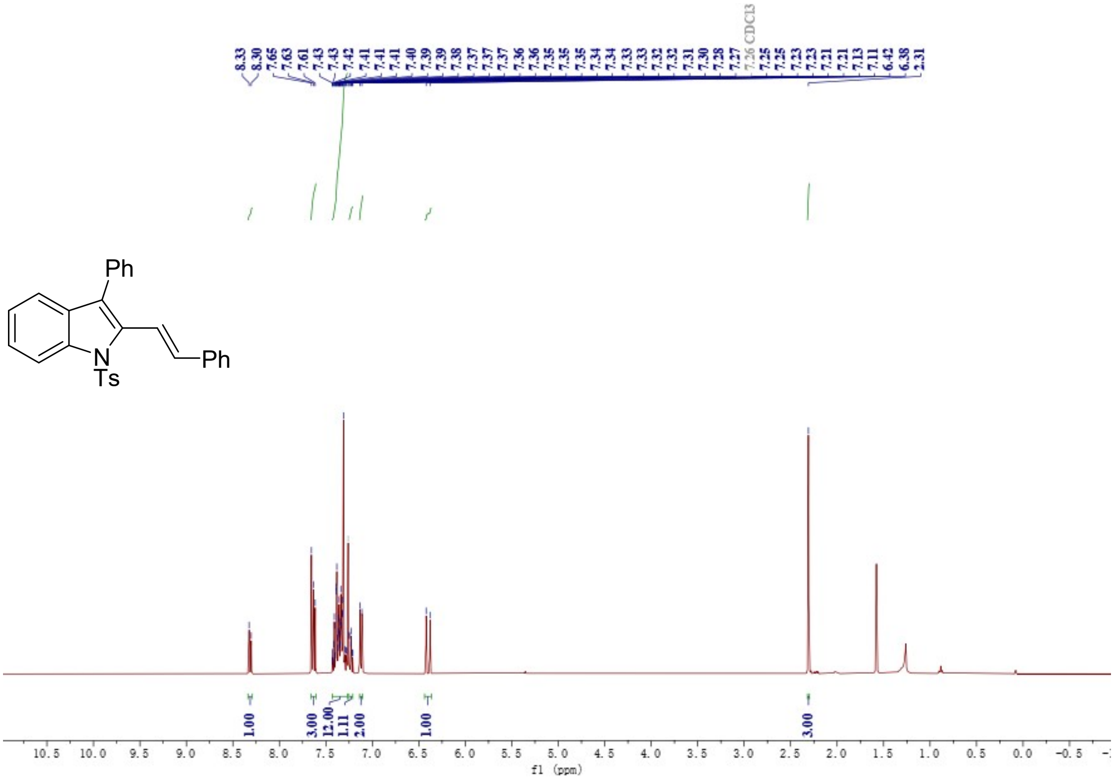
^{1}H NMR of **54** (400 MHz, $CDCl_3$)



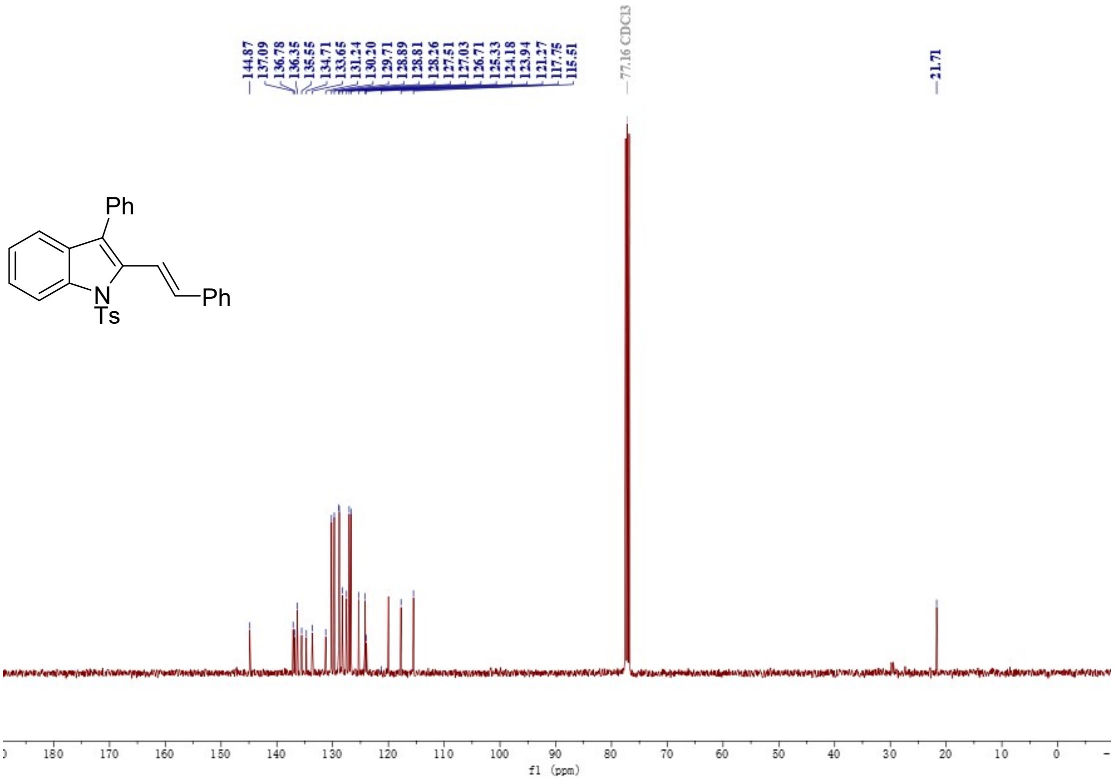
^{13}C NMR of **54** (101 MHz, $CDCl_3$)



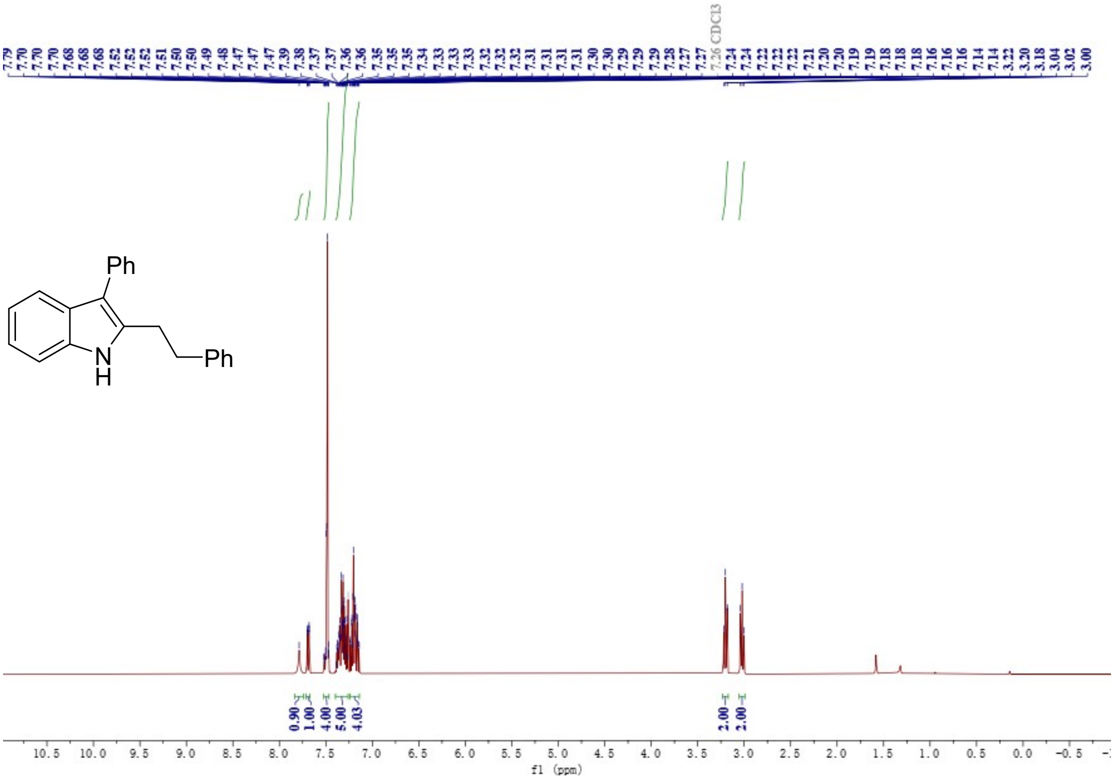
^{1}H NMR of **55** (400 MHz, CDCl$_3$)



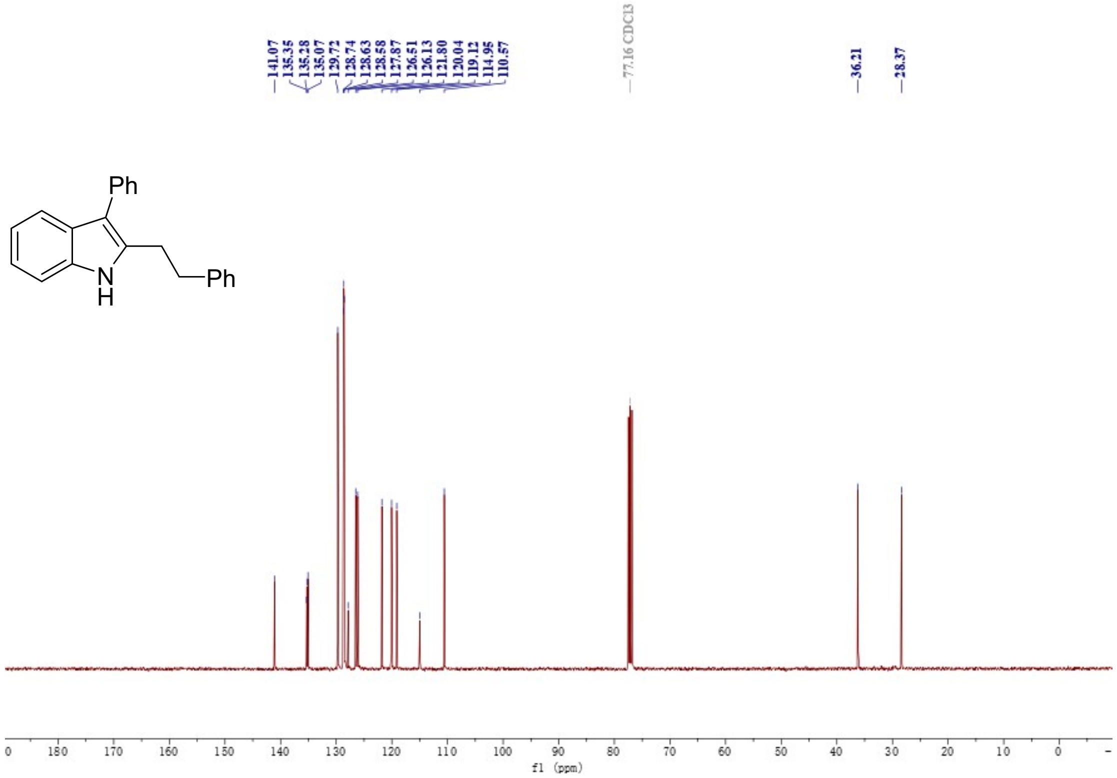
^{13}C NMR of **55** (101 MHz, CDCl$_3$)



^{1}H NMR of **56** (400 MHz, CDCl$_3$)



^{13}C NMR of **56** (101 MHz, CDCl$_3$)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135.28
135.07
129.72
128.74
128.63
128.58
127.87
126.51
126.13
121.80
120.04
119.12
114.95
110.57
77.16 CDCl3
36.21
28.37
Ph
N
H
Ph
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)