Supporting Information

Brønsted acid catalyzed multicomponent synthesis of *N*-arylindole and *N*-arylbenzo[e]indole

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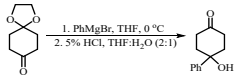
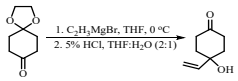
1. General information

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. The reactions were monitored by TLC with Haiyang GF-254 silica gel plates (Qingdao Haiyang chemical industry Co. Ltd, Qingdao, China) using UV light or $KMnO_4$ as visualizing agents as needed. Flash column chromatography was performed using 200-300 mesh silica gel at increased pressure. ^1H NMR spectra and ^{13}C NMR spectra were respectively recorded on Brüker AV-400 spectrometers. Chemical shifts (δ) were expressed in ppm relative to Me_4Si in $CDCl_3$ or DMSO-d_6, and coupling constants (J) were reported in Hz. High-resolution mass spectra (HRMS) were obtained on Brüker Compass Data Analysis 4.0. Melting points were determined on a microscopic melting point apparatus and are uncorrected. IR spectra were recorded on a Bruker FT-IR (EQUINOX 55) using KBr pellets or neat liquid technology.

2. The synthesis of substituted 4-hydroxycyclohexanones[1]

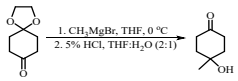


To a solution of 1,4-cyclohexanedione monoethylene acetal (500 mg, 3.2 mmol) in THF (10 ml) at 0 °C was added phenylmagnesium bromide (1.2 ml, 3.4M solution in tetrahydrofuran, 4.16 mmol) and the reaction mixture was stirred at room temperature for 1h. After reaction progress was confirmed by TLC, saturated ammonium chloride solution (15 ml) was added carefully prior to addition of ethyl acetate (20 ml). Workup was done with ethyl acetate (3 × 15 ml), organic portion was washed with water and brine. Sodium sulphate (2 g) was added to remove the remaining traces of water followed by removal of solvent under reduced pressure. Crude product obtained was re-dissolved in THF-H_2O (2:1 v/v, 15 ml), cooled to 0 ºC and 5% HCl (10 ml) was added and reaction mixture was stirred for 4h at room temperature. After completion, the reaction mixture was carefully neutralized with saturated sodium bicarbonate (20 ml), extracted with ethyl acetate (3 × 15 ml) and combined organic layer was washed with brine (40 ml), dried over sodium sulphate and solvent removed under reduced pressure. Crude product was purified with column chromatography using ethyl acetate/hexanes as eluent (40:60). The product was obtained as a colorless liquid in 88% yield (505 mg, over 2-steps).

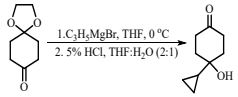


To a solution of 1,4-cyclohexanedione monoethylene acetal (500 mg, 3.2 mmol) in THF (10 ml) at 0 °C was added vinylmagnesium bromide (1.2 ml, 3.4M solution in tetrahydrofuran, 4.16 mmol) and the reaction mixture was stirred at room temperature for 1h. After reaction progress was confirmed by TLC, saturated ammonium chloride solution (15 ml) was added carefully prior to addition of ethyl acetate (20 ml). Workup was done with ethyl acetate (3 × 15 ml), organic portion was washed with water and brine. Sodium sulphate (2 g) was added to remove the remaining traces of water followed by removal of solvent under reduced pressure. Crude product obtained was re-dissolved in THF-H_2O (2:1 v/v, 15 ml), cooled to 0 ºC and 5% HCl (10 ml) was added and reaction mixture was stirred for 4h at room temperature. After completion, the reaction mixture was carefully neutralized with saturated sodium bicarbonate (20 ml), extracted with ethyl acetate (3 × 15 ml) and combined organic layer was washed with brine (40 ml), dried over sodium sulphate and solvent removed under reduced pressure. Crude product was purified with column chromatography using

ethyl acetate/hexanes as eluent (40:60). The product was obtained as a colorless liquid in 75% yield (336 mg, over 2-steps).



To a solution of 1,4-cyclohexanedione monoethylene acetal (500 mg, 3.2 mmol) in THF (10 ml) at 0 °C was added methylmagnesium bromide (1.2 ml, 3.4M solution in tetrahydrofuran, 4.16 mmol) and the reaction mixture was stirred at room temperature for 1h. After reaction progress was confirmed by TLC, saturated ammonium chloride solution (15 ml) was added carefully prior to addition of ethyl acetate (20 ml). Workup was done with ethyl acetate (3 × 15 ml), organic portion was washed with water and brine. Sodium sulphate (2 g) was added to remove the remaining traces of water followed by removal of solvent under reduced pressure. Crude product obtained was re-dissolved in THF-H_2O (2:1 v/v, 15 ml), cooled to 0 ºC and 5% HCl (10 ml) was added and reaction mixture was stirred for 4h at room temperature. After completion, the reaction mixture was carefully neutralized with saturated sodium bicarbonate (20 ml), extracted with ethyl acetate (3 × 15 ml) and combined organic layer was washed with brine (40 ml), dried over sodium sulphate and solvent removed under reduced pressure. Crude product was purified with column chromatography using ethyl acetate/hexanes as eluent (40:60). The product was obtained as a colorless liquid in 86% yield (352 mg, over 2-steps).



To a solution of 1,4-cyclohexanedione monoethylene acetal (500 mg, 3.2 mmol) in THF (10 ml) at 0 °C was added cyclopropylmagnesium bromide (1.2 ml, 3.4M solution in tetrahydrofuran, 4.16 mmol) and the reaction mixture was stirred at room temperature for 1h. After reaction progress was confirmed by TLC, saturated ammonium chloride solution (15 ml) was added carefully prior to addition of ethyl acetate (20 ml). Workup was done with ethyl acetate (3 × 15 ml), organic portion was washed with water and brine. Sodium sulphate (2 g) was added to remove the remaining traces of water followed by removal of solvent under reduced pressure. Crude product obtained was re-dissolved in THF-H_2O (2:1 v/v, 15 ml), cooled to 0 ºC and 5% HCl (10 ml) was added and reaction mixture was stirred for 4h at room temperature. After completion, the reaction mixture was carefully neutralized with saturated sodium bicarbonate (20 ml), extracted with ethyl acetate (3 × 15 ml) and combined organic layer was washed with brine (40 ml), dried over sodium sulphate and solvent removed under reduced pressure. Crude product was purified with column chromatography using ethyl acetate/hexanes as eluent (40:60). The product was obtained as a colorless liquid in 81% yield (399 mg, over 2-steps).

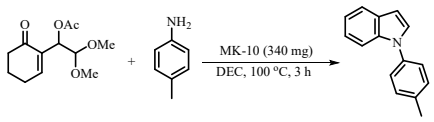
3. General procedure for synthesis of *N*-arylindole

The reaction was conducted in a 10 mL of V-type flask equipped with triangle magnetic stirring in oil bath. The aromatic amine **1** (0.3 mmol), 4-hydroxycyclohexanone **2** (0.2 mmol), 2,2-dimethoxyacetaldehyde **3a** (0.3 mmol) and PTSA (15 mol%) in EtOH (1.0 mL). The mixture was then stirred at 80 °C for 12 h. After the completion of the reaction, the mixture cooled to room temperature and then subjected to an isolation with preparative TLC by using a mixture of petroleum ether and ethyl acetate as eluting solution (EA/PE = 10/1 v/v). Tests for substrate scope were all performed with an analogous procedure.

4. The EcoScale values for reported literature methods toward 4a (Table S1)

Green metrics	Present work	*Green Chem.*, 2023, **25**, 946	*Green Chem.*, 2018, **20**, 1634	*Green Chem.*, 2018, **20**, 5346	*RSC Adv.*, 2021, **11**, 22278	*J. Am. Chem. Soc.*, 2002, **124**, 11684
EcoScale	67.5	63.5	63.0	64.0	63.0	66.0

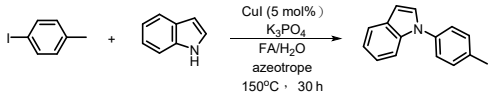
(a) *Green Chem.*, 2023, **25**, 946



Parameter	Penalty points
1. Yield (100-%yield)/2 = (100-79)/2	10.5
2. Price of reaction components	
(To obtain 10 mmol of end product)	
a. 1a = 2.42 g = $ 14.53 (estimated)	
b. *p*-Toluidine = 1.07 g = $0.12	
c. MK-10 = 0.34 g = $0.15	
d. DEC = 18ml = $1.62	
Total price (USD) = $16.42	
Thus, Expensive (> $10 and < $50)	3
3. Safety	
Solvent: DEC	
Toxic (T)	5
Highly flammable (F)	5
4. Technical Setup	
Common setup	0
5. Temperature and time	
Heating, > 1 h	3
6. Workup and purification	
Removal of solvent with bp < 150°C	0
Classical Chromatography	10
Total Penalty Points	36.5

EcoScale = 100 – 36.5 = 63.5 (an acceptable synthesis)

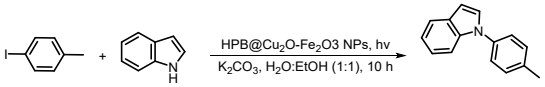
(b) *Green Chem.*, 2018, **20**, 1634



Parameter	Penalty points
1. Yield (100-%yield)/2 = (100-80)/2	10
2. Price of reaction components	
(To obtain 10 mmol of end product)	
a. indole = 1.17 g = $3.27	
b. 4-iodotoluene = 2.03 g = $10.72	
c. FA/H_2O azeotrope = 20.50 g = $0.821	
d. CuI = 0.09 g = $0.36	
e. K_3PO_4 = 4.24 g = $1.02	
f. EtOAc = 7.14 G = $0.39	
Total price (USD) = $16.58	
Thus, Expensive (> $10 and < $50)	3
3. Safety	
Solvent: FA/H_2O azeotrope	0
Toxic (T)	5
Highly flammable (F)	5
4. Technical Setup	
Common setup	1
5. Temperature and time	
Heating, > 1 h	3
6. Workup and purification	
Removal of solvent with bp < 150°C	0
Classical Chromatography	10
Total Penalty Points	37.0

EcoScale = 100 – 37.0 = 63.0 (an acceptable synthesis)

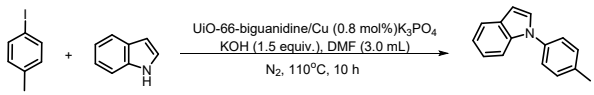
(c) *Green Chem.*, 2018, **20**, 5346



Parameter	Penalty points
1. Yield (100-%yield)/2 = (100-80)/2	10
2. Price of reaction components	
(To obtain 10 mmol of end product)	
a. indole = 5.85 g = $11.24	
b. 4-iodotoluene = 2.18 g = $10.72	
c. Reactant 3 = $34.55	
d. K_2CO_3 = 3.45 g = $1.77	
f. H_2O = 4.99 g = $0.22	
g. EtOH = 3.95 g = $0.66	
Total price (USD) = $59.16	
Thus, very expensive (>50)	5
3. Safety	
Solvent: H_2O:EtOH(1:1)	
Highly flammable (F)	5
4. Technical Setup	
Common setup	0
5. Temperature and time	
Heating, > 1 h	3
6. Workup and purification	
Liquid-liquid extraction	3
Classical Chromatography	10
Total Penalty Points	36

EcoScale = 100 – 36.0 = 64.0 (an acceptable synthesis)

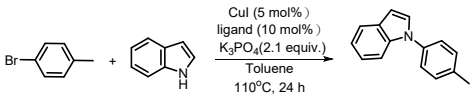
(d) *RSC Adv.*, 2021, **11**, 22278



Parameter	Penalty points
1. Yield (100-%yield)/2 = (100-90)/2	5
2. Price of reaction components	
(To obtain 10 mmol of end product)	
a. 1a = 1.17 g = $3.27	
b. 4-iodotoluene = 2.18 g = $10.72	
c. Reactant 3 = $2.11	
d. KOH = 0.084 g = $0.10	
f. DMF = 2.832 g = $0.53	
Total price (USD) = $16.72	
Thus, Expensive (> $10 and < $50)	3
3. Safety	
Solvent: DMF	3
Toxic (T)	5
Highly flammable (F)	5
4. Technical Setup	
Common setup	0
5. Temperature and time	
Heating, > 1 h	3
6. Workup and purification	
Liquid-liquid extraction	3
Classical Chromatography	10
Total Penalty Points	37.0

EcoScale = 100 – 37.0 = 63.0 (an acceptable synthesis)

(e) *J. Am. Chem. Soc.,* 2002, **124**, 11684



Parameter	Penalty points
1. Yield (100-%yield)/2 = (100-96)/2	2
2. Price of reaction components	
(To obtain 10 mmol of end product)	
a. 1a = 1.17 g = $3.27	
b. 1-bromo-4-methylbenzene = 2.03 g = $24.89	
c. Ligand = 0.07 g = $20.58	
d. CuI = 0.02 g = $0.08	
e. K_3PO_4 = 4.46 g = $1.07	
f. Toluene = 8.72 g = $0.05	
Total price (USD) = $51.94	
Thus, very expensive (> $50)	5
3. Safety	
Solvent: Toluene	3
Toxic (T)	5
Highly flammable (F)	5
4. Technical Setup	
Common setup	1
5. Temperature and time	
Heating, > 1 h	3
6. Workup and purification	
Removal of solvent with bp < 150°C	0
Classical Chromatography	10
Total Penalty Points	34.0

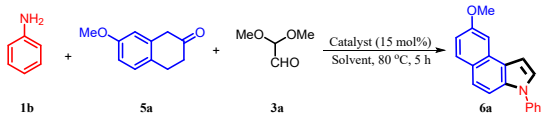
EcoScale = 100 – 33.0 = 66.0 (an acceptable synthesis)

5. General procedure for optimization and synthesis of *N*-arylbenzo[e]indole

The reaction was conducted in a 10 mL of V-type flask equipped with triangle magnetic stirring oil bath. The aromatic amine **1** (0.3 mmol), 2-tetralone **5** (0.2 mmol), 2,2-dimethoxyacetaldehyde **3a** (0.3 mmol) and TFA (15 mol%) in CPME (1.0 mL). The mixture was then stirred at 80 °C for 5 h. After the completion of the reaction, the mixture cooled to room temperature and then subjected to an isolation with preparative TLC by using a mixture of petroleum ether and ethyl acetate as eluting solution (EA/PE = 20/1 v/v). Tests for optimization and substrate scope were all performed with an analogous procedure.

6. The optimization table for MCRs synthesis of *N*-arylbenzo[e]indole (Table S2)

Table S1 Optimization of the reaction conditions.[a]



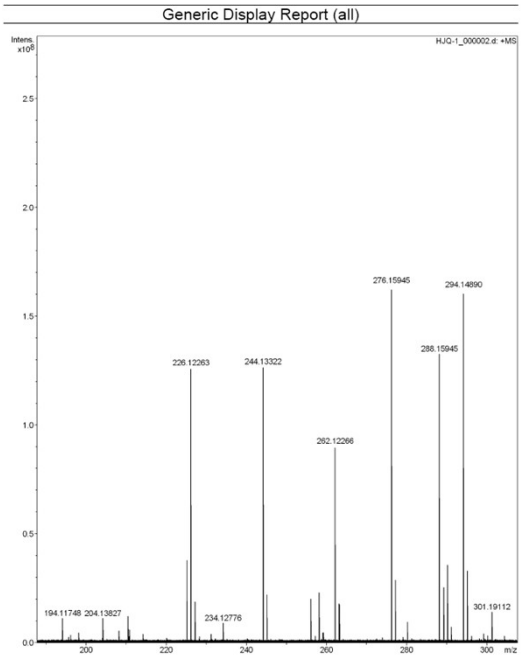
1b 5a 3a 6a

Entry	Catalyst	Solvent	Yield (%)[b]
1	PTSA	EtOH	44
2	TFA	EtOH	48
3	TFA	CPME	60
4	TFA	DMC	12
5	TFA	H_2O	trace

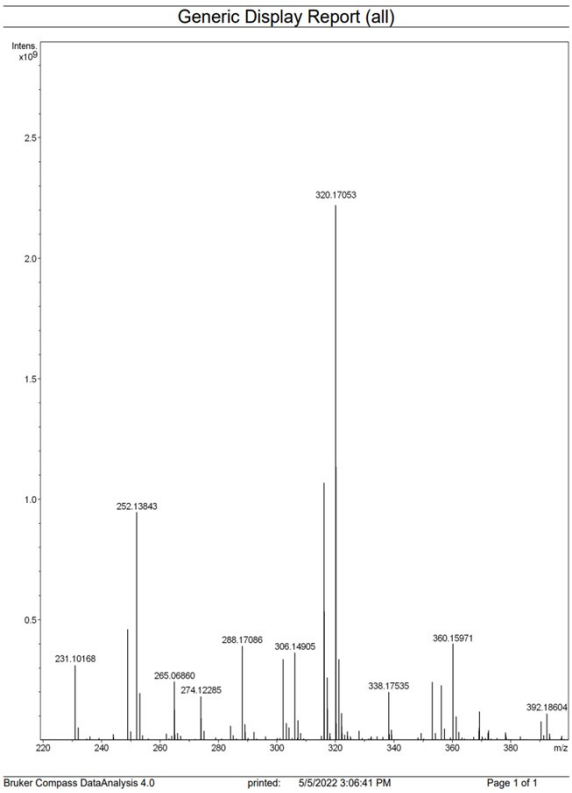
[a]Reaction condition: **1b** (0.3 mmol), **5a** (0.2 mmol), **3a** (0.30 mmol), catalyst (15 mol %), solvent (1.0 mL), 80 °C, 5 h. Isolated yield.

7. The reports of ESI-TOF HRMS analysis

(1) The report of HRMS of the reaction mixture of *p*-toluidine, 4-hydroxycyclohexanone, and 2,2-dimethoxyacetaldehyde

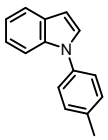


(2) The report of HRMS of the reaction mixture of aniline, 7-methoxy-2-tetralone, and 2,2-dimethoxyacetaldehyde



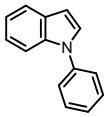
8. Characterization data of synthesized compounds

1-(*p*-tolyl)-1*H*-indole[1] (4a)



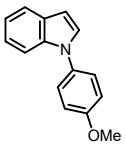
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.7 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.18 (m, 3H), 7.14 – 7.05 (m, 2H), 6.57 (d, *J* = 3.3 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 136.3, 136.0, 130.1, 129.21, 128.1, 124.3, 122.2, 121.0, 120.2, 110.5, 103.2, 21.1.

1-phenyl-1*H*-indole[2] (4b)



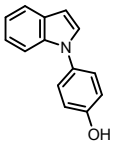
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.7 Hz, 1H), 7.53 – 7.40 (m, 5H), 7.33 – 7.25 (m, 2H), 7.18 – 7.08 (m, 2H), 6.61 (d, *J* = 3.2 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 139.8, 135.8, 129.6, 129.3, 127.9, 126.4, 124.3, 122.3, 121.1, 120.3, 110.4, 103.5.

1-(4-methoxyphenyl)-1*H*-indole[3] (4c)



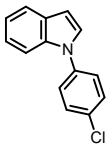
^{1}H NMR (400 MHz, DMSO) δ 7.64 (d, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 3.2 Hz, 1H), 7.51 – 7.41 (m, 3H), 7.21 – 7.06 (m, 4H), 6.66 (d, *J* = 3.2 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 158.2, 135.9, 132.5, 129.2, 129.1, 125.9, 122.5, 121.2, 120.3, 115.3, 110.5, 103.2, 55.9.

4-(1*H*-indol-1-yl)phenol[4] (4d)



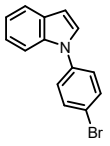
^{1}H NMR (400 MHz, DMSO) δ 9.72 (s, 1H), 7.63 (d, J = 7.8 Hz, 1H), 7.52 (d, J = 3.2 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.95 (d, *J* = 8.3 Hz, 2H), 6.63 (d, *J* = 3.2 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 136.3, 133.0, 128.9, 128.2, 126.2, 122.1, 121.0, 120.1, 116.2, 110.3, 102.9.

1-(4-chlorophenyl)-1*H*-indole[1] (4e)



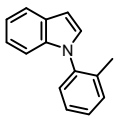
^{1}H NMR (400 MHz, DMSO) δ 7.65 (d, *J* = 13.0 Hz, 7H), 7.59 – 7.53 (m, 1H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.15 (t, *J* = 7.3 Hz, 1H), 6.73 (d, *J* = 3.1 Hz, 1H).^{13}C NMR (100 MHz, DMSO-d_6) δ 135.9, 135.7, 129.3, 129.1, 126.5, 126.4, 122.8, 121.3, 120.7, 117.1, 116.9, 110.5, 103.8. HRMS (ESI): m/z calcd for $C_{14}H_{11}ClN$, $[M + H]^+$: 228.0575, found: 228.0572.

1-(4-bromophenyl)-1*H*-indole[5] (4f)



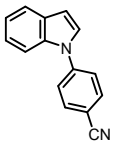
^{1}H NMR (400 MHz, DMSO-d6) δ 7.30 (d, *J* = 8.7 Hz, 2H), 7.24 – 7.18 (m, 2H), 7.12 (d, *J* = 8.8 Hz, 3H), 6.76 (t, *J* = 7.4 Hz, 1H), 6.69 (t, *J* = 7.3 Hz, 1H), 6.27 (d, *J* = 3.1 Hz, 1H), 2.92 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 158.2, 135.9, 132.5, 129.2, 129.1, 125.9, 122.5, 121.2, 120.3, 115.3, 110.5, 103.2, 55.9.

1-(*o*-tolyl)-1*H*-indole[1] (4g)



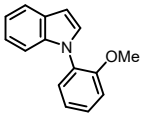
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 1H), 7.31 – 7.18 (m, 4H), 7.11 – 7.03 (m, 3H), 6.99 – 6.92 (m, 1H), 6.58 (d, *J* = 3.2 Hz, 1H), 1.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 137.0, 135.8, 131.2, 128.7, 128.3, 128.2, 128.1, 126.8, 122.0, 120.8, 119.9, 110.5, 102.5, 17.7.

4-(1*H*-indol-1-yl)benzonitrile[1] (4h)



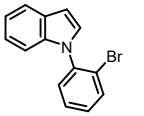
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.7 Hz, 1H), 7.55 (t, *J* = 8.7 Hz, 3H), 7.27 (d, *J* = 3.4 Hz, 1H), 7.24 – 7.12 (m, 2H), 6.68 (d, *J* = 3.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 135.2, 133.8, 129.9, 127.0, 123.8, 123.2, 121.6, 121.3, 118.4, 110.3, 109.3, 105.7.

1-(2-methoxyphenyl)-1*H*-indole[3] (4i)



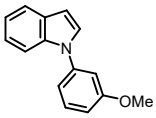
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.5 Hz, 1H), 7.36 (ddt, *J* = 9.7, 7.8, 3.2 Hz, 2H), 7.27 (d, *J* = 3.2 Hz, 1H), 7.16, 7.05 (t, *J* = 7.8 Hz, 2H), 6.65 (d, *J* = 3.2 Hz, 1H), 3.73 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 136.8, 129.3, 128.6, 128.5, 128.2, 128.1, 121.9, 120.9, 120.8, 119.9, 112.5, 110.9, 102.5, 55.7.

1-(2-bromophenyl)-1*H*-indole[6] (4j)



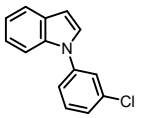
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.73 – 7.65 (m, 1H), 7.44 (q, *J* = 5.2, 4.6 Hz, 2H), 7.33 (ddd, *J* = 8.6, 6.1, 3.0 Hz, 1H), 7.26 – 7.22 (m, 1H), 7.21 – 7.14 (m, 2H), 7.14 – 7.07 (m, 1H), 6.70 (d, *J* = 3.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 136.7, 133.9, 129.7, 129.5, 128.7, 128.4, 128.3, 122.2, 122.0, 120.9, 120.3, 110.6, 103.1.

1-(3-methoxyphenyl)-1*H*-indole[1] (4k)



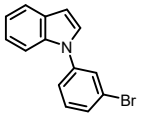
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.7 Hz, 1H), 7.53 (d, *J* = 8.2 Hz, 1H), 7.34 (t, *J* = 8.1 Hz, 1H), 7.27 (d, *J* = 3.3 Hz, 1H), 6.82 (dd, *J* = 8.4, 2.5 Hz, 1H), 6.60 (d, *J* = 3.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 140.9, 135.8, 130.34, 129.3, 127.9, 122.3, 121.1, 120.3, 116.5, 112.0, 110.6, 110.2, 103.5, 55.5.

1-(3-chlorophenyl)-1*H*-indole[1] (4l)



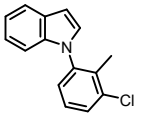
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.7 Hz, 1H), 7.48 (d, *J* = 8.2 Hz, 1H), 7.43 (d, *J* = 2.1 Hz, 1H), 7.39 – 7.27 (m, 2H), 7.27 – 7.20 (m, 2H), 7.19 – 7.07 (m, 2H), 6.61 (d, *J* = 3.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 135.6, 135.2, 130.6, 129.4, 127.6, 126.4, 124.3, 122.7, 122.3, 121.3, 120.7, 110.3, 104.3.

1-(3-bromophenyl)-1*H*-indole[6] (4m)



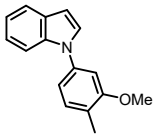
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.8 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 1H), 7.44 – 7.34 (m, 2H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 3.3 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.61 (d, *J* = 3.3 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 135.6, 130.8, 129.4, 129.4, 127.6, 127.2, 123.1, 122.7, 122.7, 121.3, 120.7, 110.3, 104.3.

1-(3-chloro-2-methylphenyl)-1*H*-indole (4n)



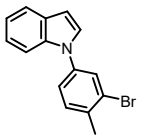
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 6.9 Hz, 1H), 7.40 (dd, *J* = 6.4, 2.9 Hz, 1H), 7.16 (q, *J* = 5.1, 4.6 Hz, 2H), 7.08 (d, *J* = 10.7, 7.9, 2.6 Hz, 3H), 6.94 (d, *J* = 8.9 Hz, 1H), 6.62 – 6.58 (m, 1H), 1.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 137.0, 135.8, 134.6, 129.1, 128.5, 128.3, 127.0, 126.7, 122.3, 120.9, 120.1, 110.4, 103.0, 15.3. IR: *v* = 3053, 2923, 2853, 1574, 1512, 1478, 1451, 1331, 1216, 1108, 1017, 960, 883, 791, 743, 711, 604, 427 cm^{-1}. HRMS (ESI): m/z calcd for $C_{15}H_{13}ClN$, $[M + H]^+$: 242.0731, found: 242.0730.

1-(3-methoxy-4-methylphenyl)-1*H*-indole (4o)



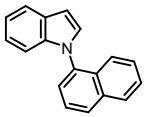
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.7 Hz, 1H), 7.48 (d, *J* = 8.1 Hz, 1H), 7.25 (d, *J* = 3.2 Hz, 1H), 7.20 – 7.05 (m, 3H), 6.94 – 6.85 (m, 2H), 6.59 (d, *J* = 3.2 Hz, 1H), 3.78 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 138.6, 136.0, 131.0, 129.1, 128.1, 125.1, 122.2, 121.1, 120.2, 116.2, 110.5, 106.8, 103.1, 55.5, 15.9. IR: *v* = 3000, 2958, 2924, 2837, 1680, 1592, 1515, 1461, 1414, 1336, 1312, 1252, 1217, 1128, 1038, 855, 811, 742, 718, 644, 599, 427 cm^{-1}. HRMS (ESI): m/z calcd for $C_{16}H_{16}NO$, $[M + H]^+$: 238.1226, found: 238.1225.

1-(3-bromo-4-methylphenyl)-1*H*-indole (4p)



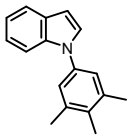
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 9.7 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.29 – 7.24 (m, 2H), 7.22 – 7.05 (m, 3H), 6.59 (d, *J* = 3.4 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 136.1, 135.8, 131.4, 129.3, 128.0, 127.7, 125.2, 123.1, 122.5, 121.2, 120.5, 110.3, 103.9, 22.5. IR: *v* = 3054, 3030, 2921, 2854, 1602, 1499, 1455, 1334, 1233, 1233, 1211, 1133, 1036, 882, 817, 763, 741, 693, 603, 586, 427 cm^{-1}. HRMS (ESI): m/z calcd for $C_{15}H_{13}BrN$, $[M + H]^+$: 286.0226, found: 286.0225.

1-(naphthalen-1-yl)-1*H*-indole[7] (4q)



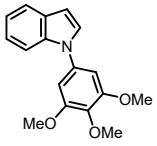
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.70 – 7.63 (m, 1H), 7.45 7.37 (d, *J* = 8.4 Hz, 1H), 7.29, 7.07 (dq, *J* = 21.3, 7.9, 7.1 Hz, 2H), 6.94 (d, *J* = 8.1 Hz, 1H), 6.68 (d, *J* = 3.4 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 136.0, 134.5, 130.6, 129.8, 128.5, 128.2, 126.9, 126.6, 126.6, 125.5, 125.1, 123.4, 122.1, 120.9, 120.1, 110.8, 102.9.

1-(3,4,5-trimethylphenyl)-1*H*-indole[7] (4r)



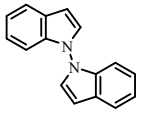
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.7 Hz, 1H), 7.46 (d, *J* = 8.1 Hz, 1H), 7.21 (d, *J* = 3.4 Hz, 1H), 7.15 – 7.03 (m, 4H), 6.55 (d, *J* = 3.4 Hz, 1H), 2.27 (s, 6H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 136.9, 136.0, 133.5, 129.1, 128.1, 123.5, 122.0, 121.0, 120.0, 110.7, 102.9, 20.8, 15.2.

1-(3,4,5-trimethoxyphenyl)-1*H*-indole (4s)



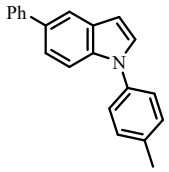
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.30 (d, *J* = 3.3 Hz, 1H), 7.26 – 7.20 (m, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 6.70 (s, 2H), 6.66 (d, *J* = 3.3 Hz, 1H), 3.91 (s, 3H), 3.88 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 136.7, 136.0, 135.6, 129.1, 128.1, 122.4, 121.2, 120.3, 110.5, 103.3, 102.2, 61.0, 56.3. IR: *v* = 3100, 3055, 2964, 2939, 2830, 1596, 1510, 1461, 1421, 1281, 1232, 1128, 1010, 828, 763, 744, 646, 525, 428 cm^{-1}. HRMS (ESI): m/z calcd for $C_{17}H_{18}NO_3$, $[M + H]^+$: 284.1281, found: 284.1283.

1,1'-biindole[8] (4t)



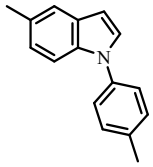
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.65 (d, *J* = 8.0 Hz,2H), 7.32 (d, *J* = 3.4 Hz, 2H), 7.19 (pd, *J* = 7.1, 1.3 Hz, 4H), 6.89 (d, *J* = 7.8 Hz, 2H), 6.67 (d, *J* = 3.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 127.9, 126.2, 123.2, 121.3, 121.2, 108.9, 102.2.

5-phenyl-1-(*p*-tolyl)-1*H*-indole (4u)



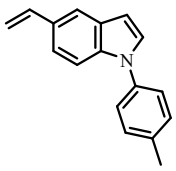
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.69 – 7.64 (m, 2H), 7.59 (d, *J* = 8.6 Hz, 1H), 7.49 – 7.39 (m, 5H), 7.37 – 7.29 (m, 4H), 6.72 (d, *J* = 3.2 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 136.1, 135.3, 134.4, 132.7, 129.1, 128.6, 127.6, 127.6, 126.3, 125.3, 123.2, 121.0, 118.5, 109.7, 102.5, 20.0. IR: *v* = 3033, 2921, 2851, 1609, 1518, 1468, 1336, 1229, 1182, 1093, 821, 755, 722, 698 cm^{-1}. HRMS (ESI): m/z calcd for $C_{21}H_{18}N$, $[M + H]^+$: 284.1434, found: 284.1430.

5-methyl-1-(*p*-tolyl)-1*H*-indole (4v)



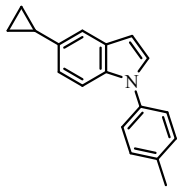
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.42 (d, *J* = 8.5 Hz, 1H), 7.38 (d, *J* = 1.9 Hz, 1H), 7.36 (s, 1H), 7.30 (s, 1H), 7.27 (t, *J* = 4.0 H, 2H), 7.03 (dd, *J* = 8.4, 1.7 Hz, 1H), 6.57 (d, *J* = 3.2 Hz, 1H), 2.46 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.4, 135.0, 133.2, 129.0, 128.4, 128.4, 126.9, 123.0, 122.7, 119.6, 109.1, 101.6, 20.3, 19.9. IR: *v* = 3033, 2919, 2858, 1519, 1477, 1372, 1334, 1221, 1158, 822, 794, 716 cm^{-1}. HRMS (ESI): m/z calcd for $C_{16}H_{16}N$, $[M + H]^+$: 222.1277, found: 222.1275.

1-(*p*-tolyl)-5-vinyl-1*H*-indole (4w)



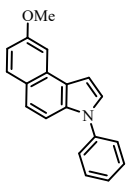
^{1}H NMR (400 MHz, DMSO) δ 7.65 (d, *J* = 13.0 Hz, 7H), 7.59 – 7.53 (m, 1H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.15 (t, *J* = 7.3 Hz, 1H), 6.73 (d, *J* = 3.1 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6, 136.1, 135.3, 134.7, 129.1, 128.3, 127.5, 123.1, 119.3, 118.3, 110.1, 109.5, 102.4, 20.0. IR: *v* = 3035, 2921, 2855, 1609, 1519, 1474, 1335, 1220, 989, 884, 822, 808, 725 cm^{-1}. HRMS (ESI): m/z calcd for $C_{17}H_{16}N$, $[M + H]^+$: 234.1277, found: 234.1275.

5-cyclopropyl-1-(*p*-tolyl)-1*H*-indole (4x)



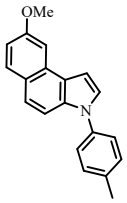
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 4H), 7.23 – 7.17 (m, 3H), 6.90 (dd, *J* = 8.6, 1.8 Hz, 1H), 6.49 (d, *J* = 3.2 Hz, 1H), 2.34 (s, 3H), 1.94 (m, 1H), 0.89 – 0.82 (m, 2H), 0.67 – 0.61 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 136.1, 135.5, 134.5, 130.1, 129.4, 128.2, 124.1, 121.1, 117.7, 110.3, 102.8, 29.7, 21.0, 15.4, 8.6. IR: *v* = 3002, 2923, 2855, 1519, 1477, 1332, 1222, 1018, 821, 800, 718 cm^{-1}. HRMS (ESI): m/z calcd for $C_{18}H_{18}N$, $[M + H]^+$: 248.1434, found: 248.1430.

8-methoxy-3-phenyl-3*H*-benzo[*e*]indole (6a).



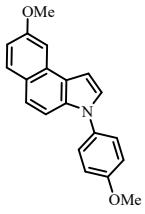
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.8 Hz, 1H), 7.54 – 7.41 (m, 7H), 7.36 – 7.27 (m, 2H), 7.08 (d, *J* = 3.2 Hz, 1H), 7.02 (dd, *J* = 8.9, 2.5 Hz, 1H), 3.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 139.7, 132.9, 130.0, 129.6, 129.4, 126.8, 125.9, 124.7, 124.3, 123.7, 123.0, 115.0, 109.7, 102.7, 102.3, 55.4. IR: *v* = 2941, 2850, 1631, 1600, 1565, 1469, 1415, 1327, 1138, 1101, 1076, 891, 696, 597, 536 cm^{-1}. HRMS (ESI): m/z calcd for $C_{19}H_{16}NO$, $[M + H]^+$: 274.1226, found: 274.1225

8-methoxy-3-(*p*-tolyl)-3*H*-benzo[*e*]indole (6b).



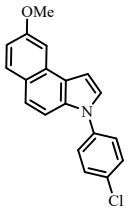
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.8 Hz, 1H), 7.58 (d, J = 2.6 Hz, 1H), 7.50 (q, J = 8.9 Hz, 2H), 7.42 (d, J = 7.9 Hz, 2H), 7.33 (d, J = 7.9 Hz, 3H), 7.16 – 7.05 (m, 2H), 4.00 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 137.2, 136.7, 133.0, 130.1, 130.0, 129.4, 126.0, 124.7, 124.2, 123.5, 122.9, 114.9, 109.7, 102.8, 102.0, 55.4, 21.0. IR: *v* = 2931, 2832, 1627, 1595, 1501, 1224, 1180, 1031, 828, 726 cm^{-1}. HRMS (ESI): m/z calcd for $C_{20}H_{18}NO$, $[M + H]^+$: 288.1383, found: 288.1381.

8-methoxy-3-(4-methoxyphenyl)-3*H*-benzo[*e*]indole (6c).



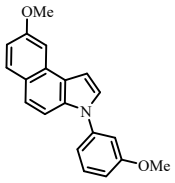
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.8 Hz, 1H), 7.59 (d, *J* = 2.6 Hz, 1H), 7.53 (d, *J* = 8.9 Hz, 1H), 7.44 (t, *J* = 9.2 Hz, 3H), 7.32 (d, *J* = 3.2 Hz, 1H), 7.15 – 7.02 (m, 4H), 4.01 (s, 3H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 158.0, 133.3, 132.7, 130.0, 129.4, 126.3, 126.2, 124.2, 123.3, 122.8, 114.9, 114.7, 109.6, 102.7, 101.8, 55.6, 55.4. IR: *v* = 2959, 2918, 2849, 2834, 1625, 1514, 1514, 1249, 1222, 1178, 1032, 827, 722, 608 cm^{-1}. HRMS (ESI): m/z calcd for $C_{20}H_{18}NO_2$, $[M + H]^+$: 304.1332, found: 304.1335.

3-(4-chlorophenyl)-8-methoxy-3*H*-benzo[*e*]indole (6d).



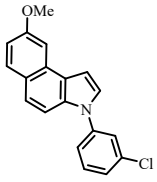
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.8 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.53 (s, 1H), 7.46 (dd, *J* = 10.8, 7.3 Hz, 5H), 7.30 (d, *J* = 3.2 Hz, 1H), 7.16 – 7.12 (m, 1H), 7.09 (dd, *J* = 8.9, 2.5 Hz, 1H), 3.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 138.3, 132.8, 132.4, 130.0, 129.8, 129.4, 125.9, 125.7, 124.3, 123.8, 123.3, 115.2, 109.3, 102.8, 102.8, 55.4. IR: *v* = 2961, 2932, 1626, 1502, 1381, 1224, 1093, 1030, 827, 721, 561, 516 cm^{-1}. HRMS (ESI): m/z calcd for $C_{19}H_{15}ClNO$, $[M + H]^+$: 308.0837, found: 308.0836.

8-methoxy-3-(3-methoxyphenyl)-3*H*-benzo[*e*]indole (6e).



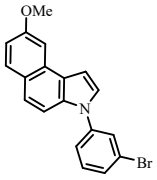
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.9 Hz, 1H), 7.50 (d, *J* = 2.6 Hz, 1H), 7.47 – 7.44 (m, 2H), 7.35 (t, *J* = 8.1 Hz, 1H), 7.29 (d, *J* = 3.2 Hz, 1H), 7.05 (d, *J* = 4.0 Hz, 2H), 7.02-6.99 (m, 2H), 6.85 (dd, *J* = 8.3, 2.5 Hz, 1H), 3.92 (s, 3H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 158.1, 140.9, 132.8, 130.3, 130.0, 129.4, 125.9, 124.3, 123.8, 123.0, 116.9, 115.1, 112.3, 110.6, 109.8, 102.8, 102.4, 55.5, 55.4. IR: *v* = 2957, 2936, 2834, 1625, 1605, 1500, 1467, 1381, 1218, 1034, 841, 826, 723, 698 cm^{-1}. HRMS (ESI): m/z calcd for $C_{20}H_{18}NO_2$, $[M + H]^+$: 304.1332, found: 304.1335.

3-(3-chlorophenyl)-8-methoxy-3*H*-benzo[*e*]indole (6f).



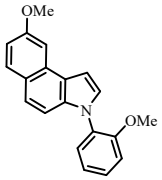
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.8 Hz, 1H), 7.47 (dd, *J* = 6.3, 3.3 Hz, 3H), 7.41 (d, *J* = 9.0 Hz, 1H), 7.36 (d, *J* = 6.0 Hz, 2H), 7.30 – 7.22 (m, 2H), 7.07 (d, *J* = 3.2 Hz, 1H), 7.02 (dd, *J* = 8.9, 2.5 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 140.9, 135.2, 132.7, 130.6, 130.0, 129.4, 126.8, 125.6, 124.8, 124.4, 123.9, 123.4, 122.7, 115.3, 109.3, 103.1, 102.8, 55.4. IR: v = 2961, 2932, 1627, 1594, 1500, 1381, 1224, 828, 724 cm^{-1}. HRMS (ESI): m/z calcd for $C_{19}H_{15}ClNO$, $[M + H]^+$: 308.0837, found: 308.0836.

3-(3-bromophenyl)-8-methoxy-3*H*-benzo[*e*]indole (6g).



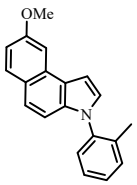
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.8 Hz, 1H), 7.62 (d, *J* = 2.1 Hz, 1H), 7.49 – 7.45 (m, 2H), 7.43 – 7.36 (m, 3H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 3.2 Hz, 1H), 7.06 (d, *J* = 3.2 Hz, 1H), 7.01 (dd, *J* = 8.9, 2.5 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 141.0, 132.7, 130.9, 130.1, 129.8, 129.4, 127.7, 125.6, 124.4, 123.9, 123.4, 123.2, 123.1, 115.3, 109.3, 103.1, 102.8, 55.4. IR: *v* = 2956, 2934, 1626, 1591, 1500, 1381, 1224, 1179, 1031, 828, 719 cm^{-1}. HRMS (ESI): m/z calcd for $C_{19}H_{14}BrNONa$, $[M + Na]^+$: 374.0151, found: 374.0152.

8-methoxy-3-(2-methoxyphenyl)-3*H*-benzo[*e*]indole (6h).



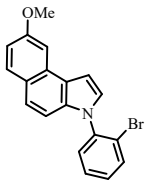
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.8 Hz, 1H), 7.59 (d, *J* = 2.5 Hz, 1H), 7.48 (d, *J* = 8.9 Hz, 1H), 7.40 (t, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 3.1 Hz, 1H), 7.18 (d, *J* = 8.9 Hz, 1H), 7.15 – 7.04 (m, 4H), 3.99 (s, 3H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 154.6, 133.9, 129.9, 129.4, 128.9, 128.4, 128.2, 127.1, 124.2, 122.8, 122.5, 120.9, 114.8, 112.5, 110.2, 102.8, 101.5, 55.8, 55.4. IR: *v* = 3004, 2936, 2835, 1625, 1510, 1464, 1381, 1222, 1179, 1028, 827, 755, 724 cm^{-1}. HRMS (ESI): m/z calcd for $C_{20}H_{18}NO_2$, $[M + H]^+$: 304.1332, found: 304.1334.

8-methoxy-3-(o-tolyl)-3*H*-benzo[*e*]indole (6i).



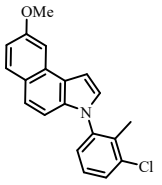
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.8 Hz, 1H), 7.53 (d, *J* = 2.6 Hz, 1H), 7.41 (d, *J* = 8.8 Hz, 1H), 7.31 (dd, *J* = 4.0, 2.0 Hz, 2H), 7.28 (t, *J* = 3.7 Hz, 2H), 7.13 (d, *J* = 3.1 Hz, 1H), 7.06 (d, *J* = 3.1 Hz, 1H), 7.01 (d, *J* = 2.6 Hz, 1H), 6.99 (d, *J* = 2.5 Hz, 1H), 6.94 (d, *J* = 8.8 Hz, 1H), 3.93 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 137.2, 134.9, 133.0, 130.1, 129.0, 128.4, 127.3, 127.1, 125.7, 125.4, 123.1, 121.8, 121.6, 113.8, 108.7, 101.7, 100.4, 54.4, 16.5. IR: *v* = 2930, 2832, 1625, 1499, 1224, 1030, 827, 762, 720 cm^{-1}. HRMS (ESI): m/z calcd for $C_{20}H_{18}NO$, $[M + H]^+$: 288.1383, found: 288.1383.

3-(2-bromophenyl)-8-methoxy-3*H*-benzo[*e*]indole (6j).



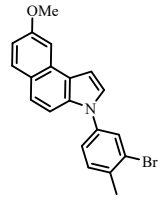
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 8.4, 4.2 Hz, 2H), 7.60 (d, *J* = 2.6 Hz, 1H), 7.52 (d, *J* = 8.8 Hz, 1H), 7.50 – 7.46 ((d, *J* = 4.0 Hz, 2H), 7.36 (dt, *J* = 8.0, 4.6 Hz, 1H), 7.27 (d, *J* = 3.2 Hz, 1H), 7.17 (d, *J* = 3.1 Hz, 1H), 7.11 – 7.05 (m, 2H), 4.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 138.5, 133.9, 133.8, 130.1, 129.9, 129.7, 129.3, 128.3, 126.5, 124.3, 123.0, 122.8, 122.2, 115.1, 109.7, 102.7, 102.0, 55.4. IR: *v* = 2958, 2932, 1626, 1501, 1381, 1224, 1031, 827, 722 cm^{-1}. HRMS (ESI): m/z calcd for $C_{19}H_{14}BrNONa$, $[M + Na]^+$: 374.0151, found: 374.0153.

3-(3-chloro-2-methylphenyl)-8-methoxy-3*H*-benzo[*e*]indole (6k).



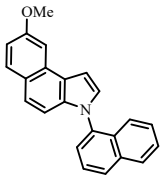
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.9 Hz, 1H), 7.60 (d, *J* = 2.5 Hz, 1H), 7.53 – 7.48 (m, 2H), 7.32 – 7.23 (m, 2H), 7.21 – 7.13 (m, 2H), 7.09 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.99 (d, *J* = 8.8 Hz, 1H), 4.01 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 139.6, 135.8, 134.8, 134.1, 130.1, 129.4, 129.3, 127.0, 126.8, 126.4, 124.2, 123.1, 122.7, 115.0, 109.5, 102.7, 102.0, 55.4, 15.3. IR: *v* = 2956, 2831, 1626, 1467, 1381, 1225, 1178, 1032, 828, 724 cm^{-1}. HRMS (ESI): m/z calcd for $C_{20}H_{16}ClNONa$, $[M + Na]^+$: 344.08131, found: 344.0814.

3-(3-bromo-4-methylphenyl)-8-methoxy-3*H*-benzo[*e*]indole (6l).



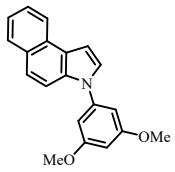
^{1}H NMR (400 MHz, CDCl3) δ 7.80 (d, J = 8.8 Hz, 1H), 7.73 (s, 1H), 7.59 – 7.51 (m, 2H), 7.46 (d, J = 8.9 Hz, 1H), 7.41 – 7.33 (m, 2H), 7.30 (d, J = 3.2 Hz, 1H), 7.17 – 7.04 (m, 2H), 3.99 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 138.5, 136.5, 132.8, 131.4, 130.0, 129.4, 128.4, 125.7, 125.2, 124.3, 123.7, 123.5, 123.3, 115.2, 109.4, 102.7, 102.7, 55.4, 22.5. IR: *v* = 2930, 2832, 1626, 1502, 1224, 1034, 830, 722 cm^{-1}. HRMS (ESI): m/z calcd for $C_{20}H_{16}BrNONa$, $[M + Na]^+$: 388.0307, found: 388.0309.

8-methoxy-3-(naphthalen-1-yl)-3*H*-benzo[*e*]indole (6m).



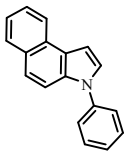
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.86 (m, 2H), 7.72 (d, *J* = 8.9 Hz, 1H), 7.58 (d, *J* = 2.6 Hz, 1H), 7.54 – 7.51 (m, 2H), 7.46 (t, *J* = 4.1 Hz, 1H), 7.39 – 7.28 (m, 4H), 7.15 (s, 1H), 7.02 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.91 (d, *J* = 8.9 Hz, 1H), 3.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 136.0, 135.0, 134.4, 130.7, 130.1, 129.4, 128.7, 128.2, 127.7, 127.1, 126.7, 125.5, 125.2, 124.2, 123.3, 122.9, 122.8, 115.0, 110.0, 102.8, 101.8, 55.4. IR: *v* = 2957, 2910, 1625, 1515, 1418, 1225, 1029, 827, 774, 724 cm^{-1}. HRMS (ESI): m/z calcd for $C_{23}H_{18}NO$, $[M + H]^+$: 324.1383, found: 324.1385.

3-(3,5-dimethoxyphenyl)-3*H*-benzo[*e*]indole (6n).



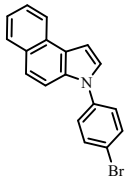
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 – 8.24 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 9.0 Hz, 1H), 7.63 – 7.53 (m, 2H), 7.47 – 7.39 (m, 2H), 7.19 (d, *J* = 3.2 Hz, 1H), 6.71 (d, *J* = 2.3 Hz, 2H), 6.50 (t, *J* = 2.3 Hz, 1H), 3.86 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 141.3, 132.3, 129.3, 128.4, 128.2, 126.1, 125.9, 124.3, 123.6, 123.2, 123.0, 112.3, 103.2, 102.4, 98.8, 55.6. IR: *v* = 2960, 2930, 2848, 1609, 1498, 1476, 1228, 1157, 802, 747, 727 cm^{-1}. HRMS (ESI): m/z calcd for $C_{20}H_{18}NO_2$, $[M + H]^+$: 304.1332, found: 304.1334.

3-phenyl-3*H*-benzo[*e*]indole (6o).



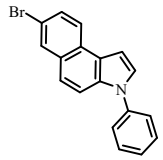
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.1 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.56 (d, *J* = 9.0 Hz, 1H), 7.51 (s, 1H), 7.50 – 7.47 (d, *J* = 4.0 Hz 1H), 7.46 – 7.39 (m, 4H), 7.37 – 7.26 (m, 3H), 7.11 (d, *J* = 3.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.60, 131.36, 128.57, 128.31, 127.42, 127.23, 125.79, 125.15, 124.85, 123.70, 123.22, 122.58, 122.14, 121.95, 111.03, 101.45. IR: v = 3054, 2922, 1596, 1503, 1389, 1188, 924, 801, 746, 700 cm^{-1}. HRMS (ESI): m/z calcd for $C_{15}H_{14}N$, $[M + H]^+$: 244.1121, found: 244.1119.

3-(4-bromophenyl)-3*H*-benzo[*e*]indole (6p).



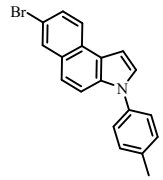
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.59 – 7.53 (m, 2H), 7.53 – 7.46 (m, 3H), 7.39 – 7.28 (m, 3H), 7.24 (d, *J* = 3.2 Hz, 1H), 7.12 (d, *J* = 3.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 132.8, 132.3, 129.4, 128.5, 128.2, 126.2, 126.1, 125.9, 124.4, 123.8, 123.5, 123.0, 120.3, 111.7, 103.0. IR: *v* = 3055, 2920, 1587, 1501, 1389, 1187, 1010, 922, 830, 800, 746, 725 cm^{-1}. HRMS (ESI): m/z calcd for $C_{18}H_{12}BrNNa$, $[M + Na]^+$: 344.0045, found: 344.0043.

7-bromo-3-phenyl-3*H*-benzo[*e*]indole (6q).



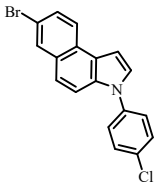
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.7 Hz, 1H), 8.03 (d, *J* = 2.1 Hz, 1H), 7.66 – 7.59 (m, 2H), 7.56 – 7.43 (m, 5H), 7.39 (m, 2.4 Hz, 2H), 7.14 (d, *J* = 3.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 132.5, 130.7, 130.5, 129.7, 128.9, 127.1, 126.8, 126.7, 124.8, 124.1, 122.1, 117.1, 113.2, 102.4. IR: *v* = 3063, 2918, 1597, 1582, 1503, 1366, 1183, 1087, 922, 884, 818, 756, 724 cm^{-1}. HRMS (ESI): m/z calcd for $C_{18}H_{12}BrNNa$, $[M + Na]^+$: 344.0045, found: 344.0048.

7-bromo-3-(p-tolyl)-3*H*-benzo[*e*]indole (6r).



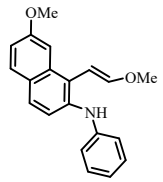
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.7 Hz, 1H), 8.04 (d, *J* = 2.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 9.0 Hz, 1H), 7.42 – 7.36 (m, 3H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 3.1 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 136.8, 132.6, 130.6, 130.4, 130.2, 128.9, 126.8, 126.8, 124.8, 124.7, 123.9, 122.0, 116.9, 113.2, 21.1. IR: *v* = 2918, 2851, 1517, 1367, 1181, 1088, 819, 725, 499 cm^{-1}. HRMS (ESI): m/z calcd for $C_{19}H_{14}BrNNa$, $[M + Na]^+$: 358.0202, found: 358.0205.

7-bromo-3-(4-chlorophenyl)-3*H*-benzo[*e*]indole (6s).



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.7 Hz, 1H), 8.05 (d, *J* = 2.1 Hz, 1H), 7.65 – 7.57 (m, 2H), 7.54 – 7.48 (m, 3H), 7.45 (d, *J* = 8.8 Hz, 2H), 7.35 (d, *J* = 3.2 Hz, 1H), 7.16 (d, *J* = 3.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 132.7, 132.4, 130.7, 130.5, 129.9, 129.1, 126.7, 126.5, 125.9, 124.8, 124.2, 122.4, 117.2, 112.8, 102.8. IR: *v* = 2917, 2850, 1499, 1366, 1279, 1182, 1095, 818, 795, 774, 725 cm^{-1}. HRMS (ESI): m/z calcd for $C_{18}H_{11}BrClNNa$, $[M + Na]^+$: 377.9656, found: 377.9658.

(*E*)-7-methoxy-1-(2-methoxyvinyl)-*N*-phenylnaphthalen-2-amine (IV-typed intermediate).



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 9.0 Hz, 2H), 7.41 (s, 1H), 7.25 (t, *J* = 7.6 Hz, 2H), 7.07 (d, *J* = 7.9 Hz, 2H), 6.95 – 6.80 (m, 4H), 5.86 (d, *J* = 12.7 Hz, 1H), 5.59 (s, 1H), 3.79 (s, 3H), 3.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 150.78, 143.3, 140.0, 134.5, 129.4, 128.7, 125.9, 125.5, 124.9, 121.3, 118.8, 116.4, 111.1, 104.5, 100.5, 99.9, 56.7, 55.2. IR: *v* = 3376, 2972, 2838, 1647, 1593, 1459, 1407, 1197, 1105, 1079, 826, 763, 513 cm^{-1}. HRMS (ESI): m/z calcd for $C_{20}H_{20}NO_2$, $[M + H]^+$: 306.1489, found: 306.1489.

9. References

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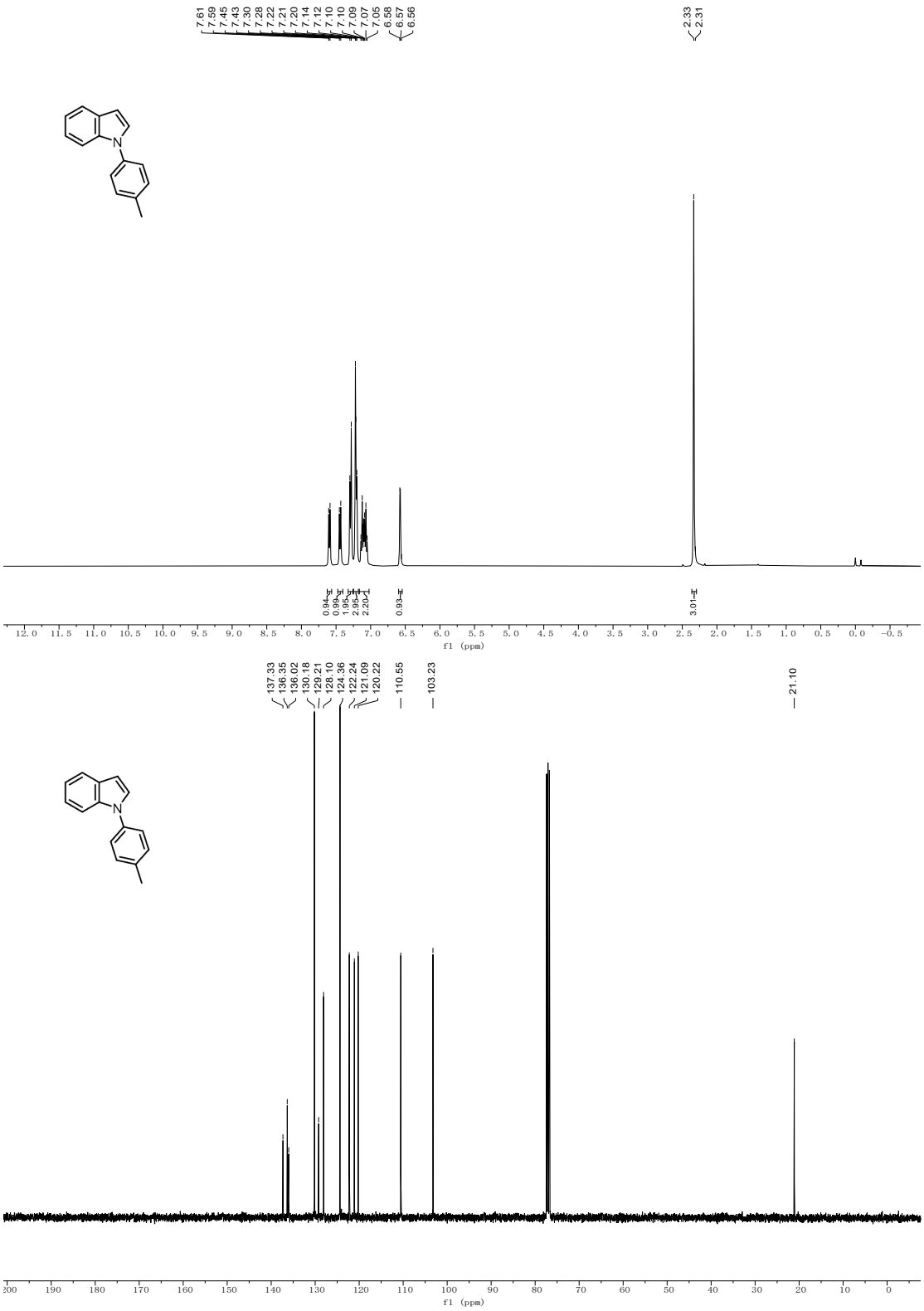
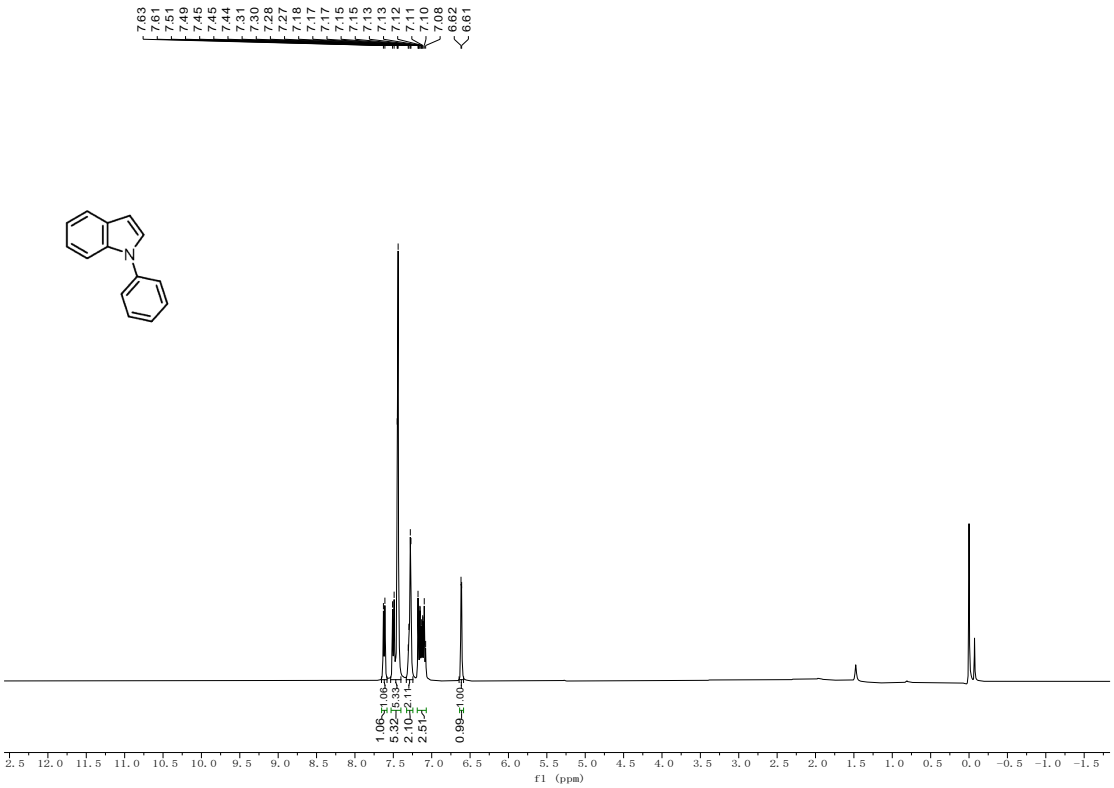
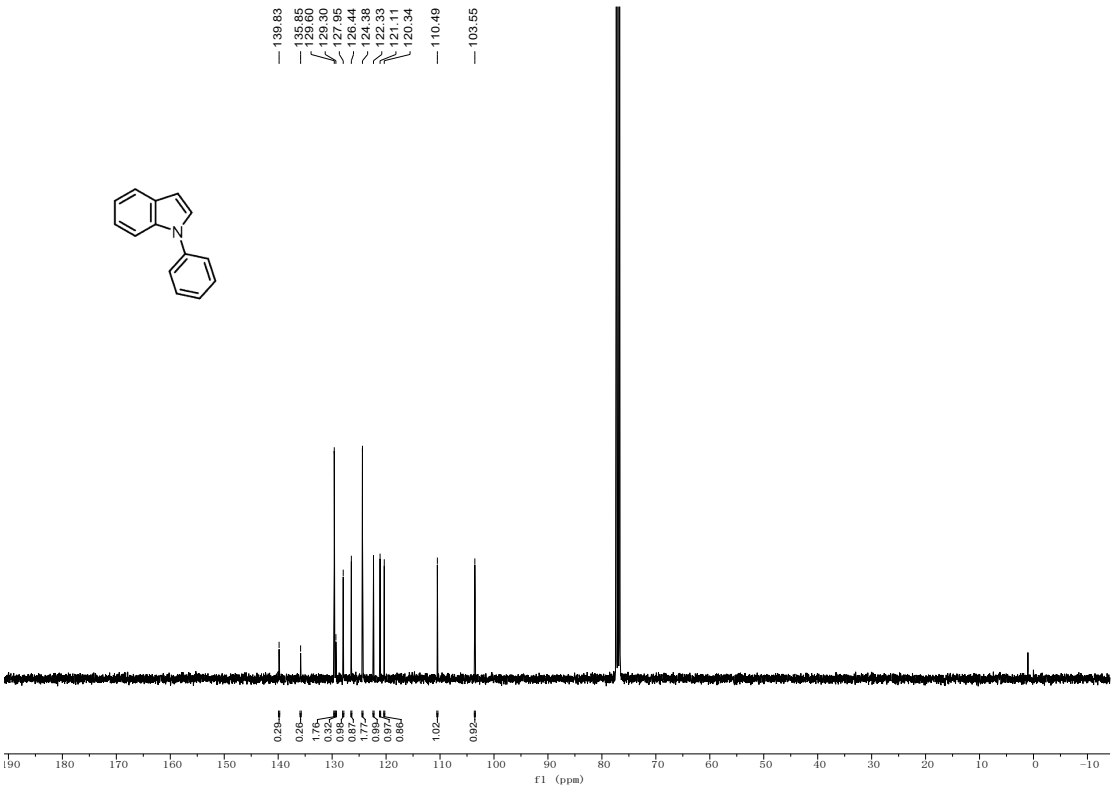
10. ^{1}H NMR and ^{13}C NMR spectra of synthesized compounds

1-(*p*-tolyl)-1*H*-indole (4a)

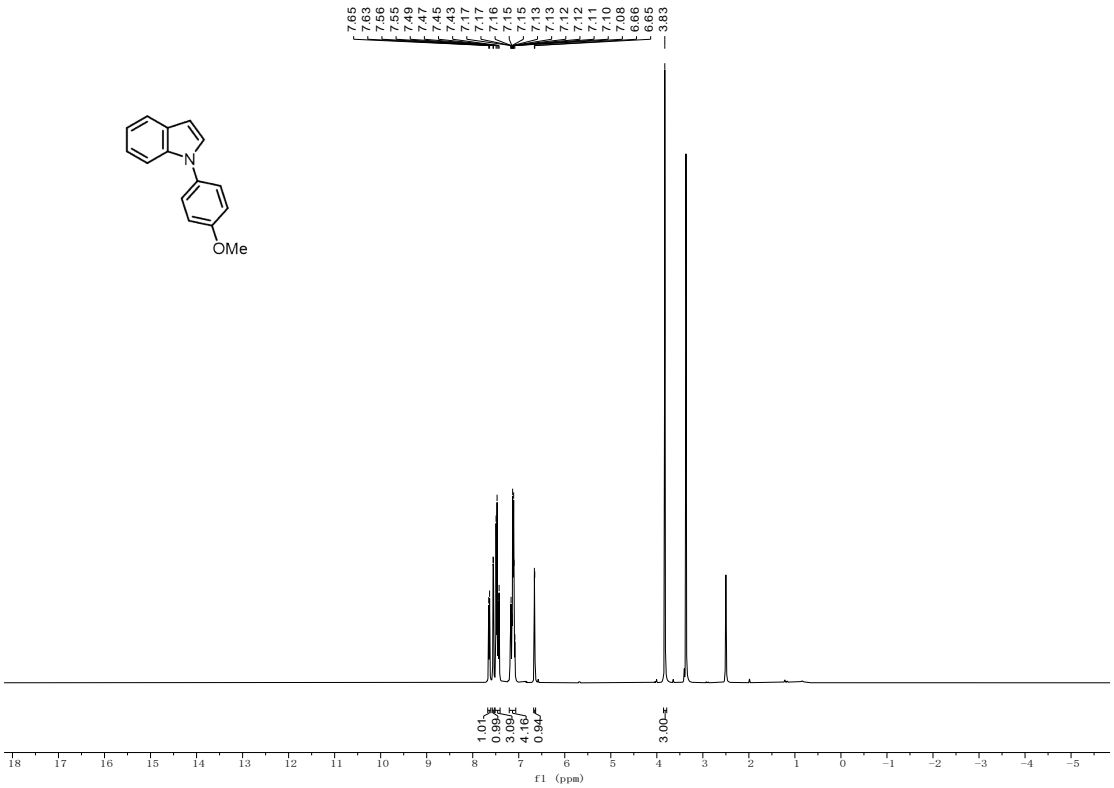


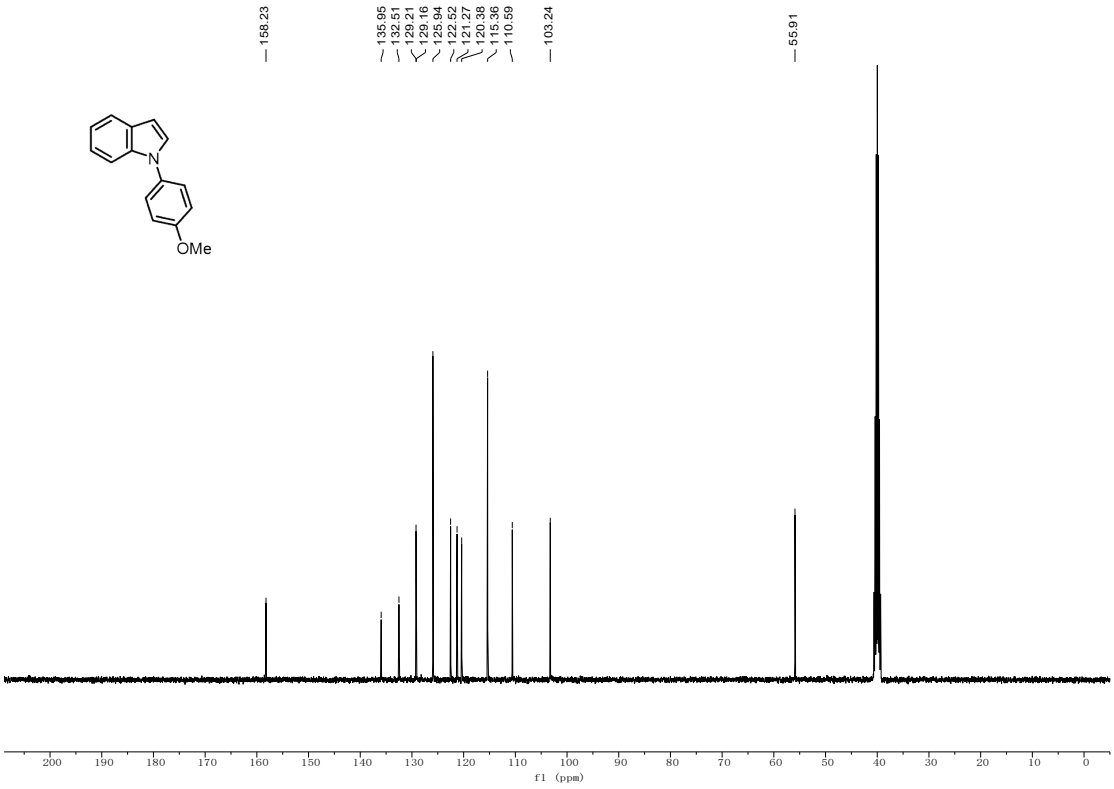
1-phenyl-1*H*-indole (4b)



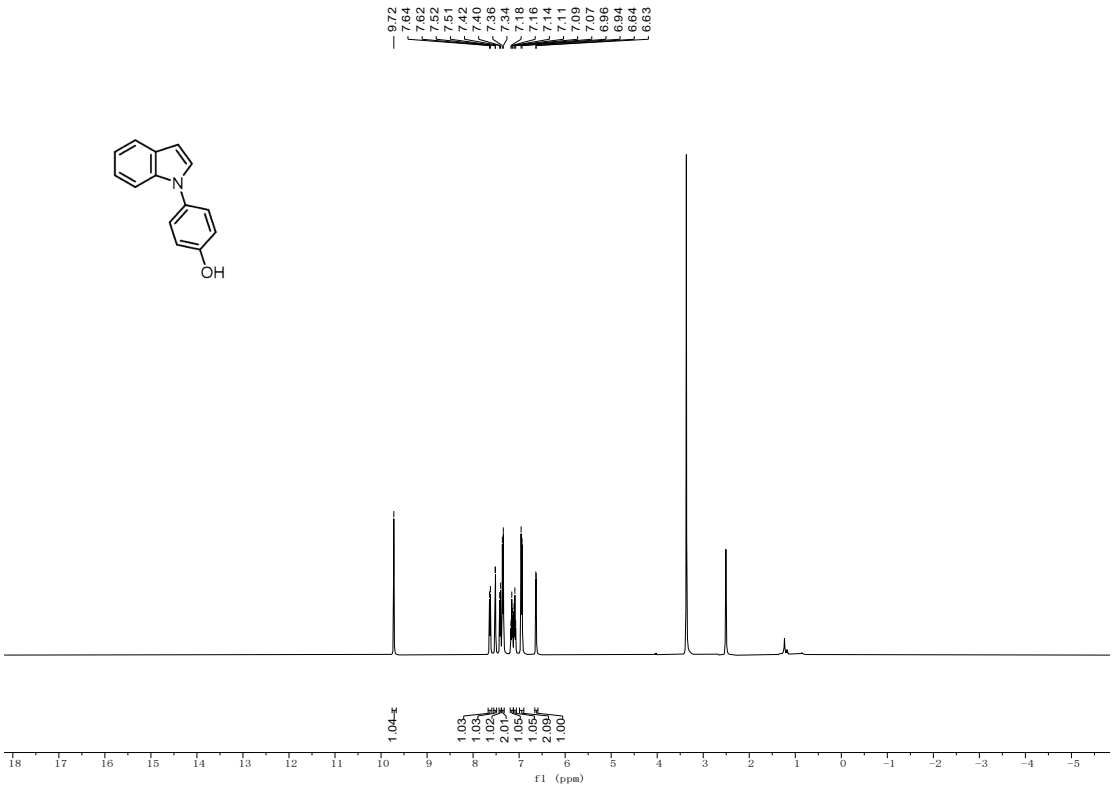


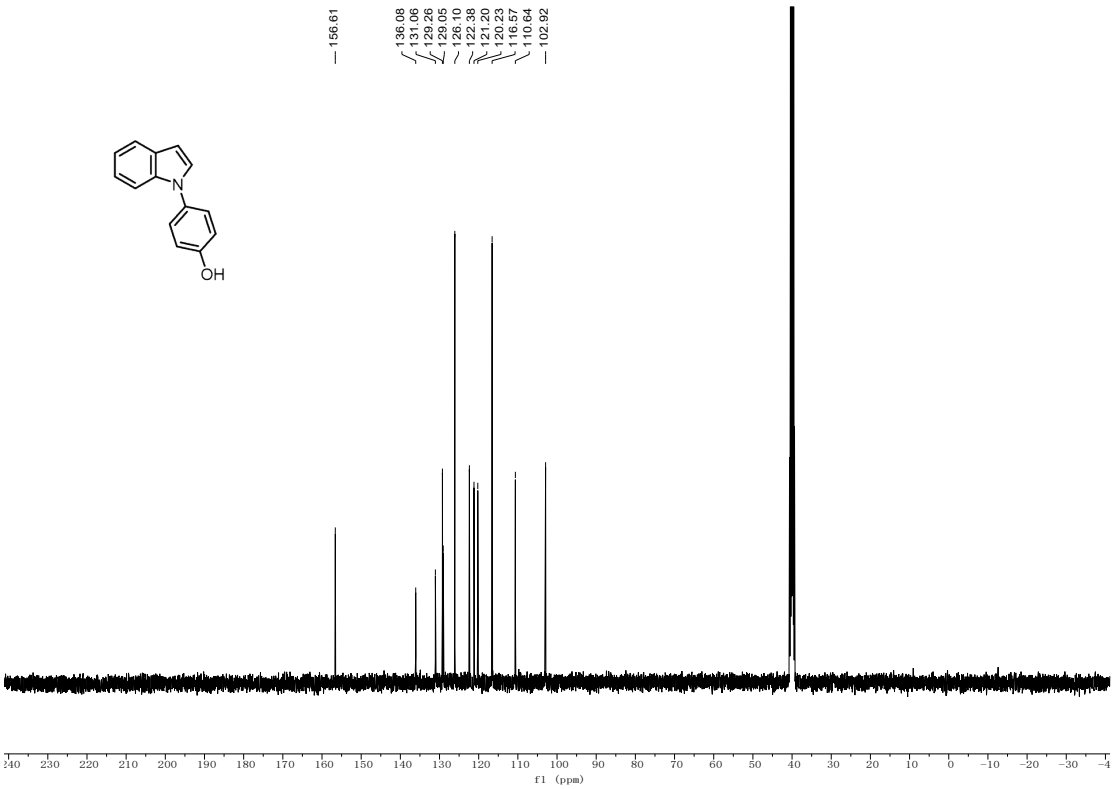
1-(4-methoxyphenyl)-1*H*-indole (4c)



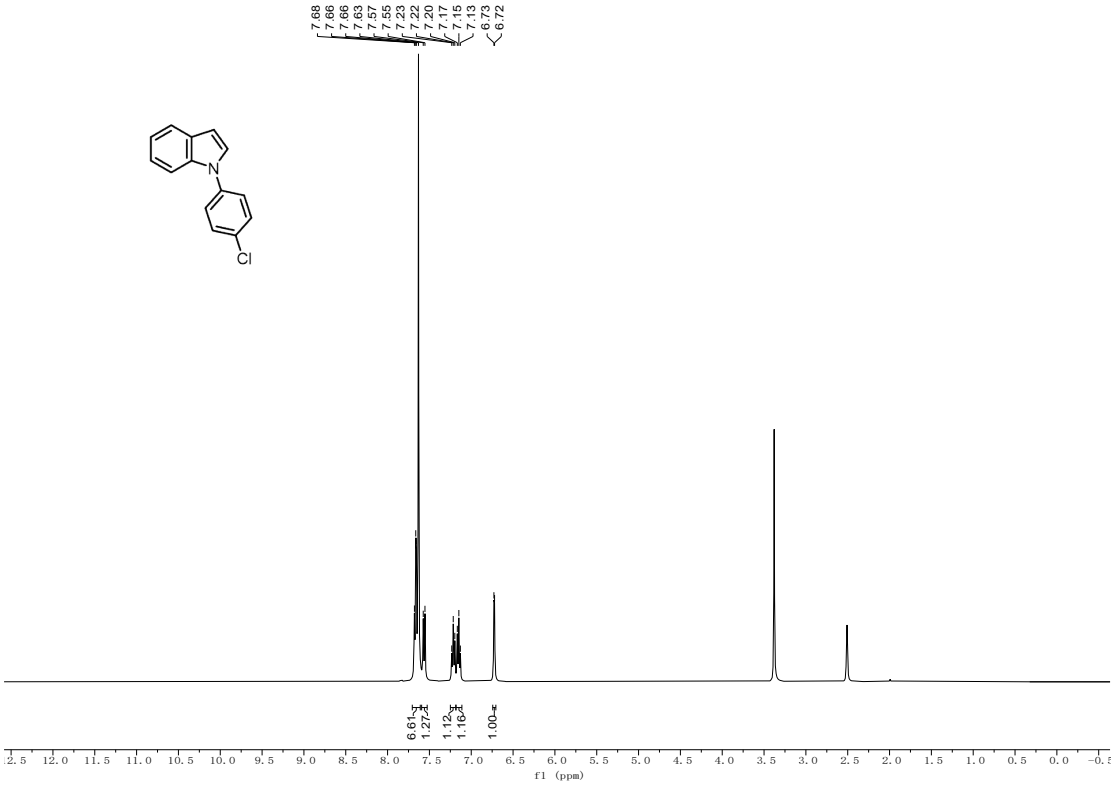


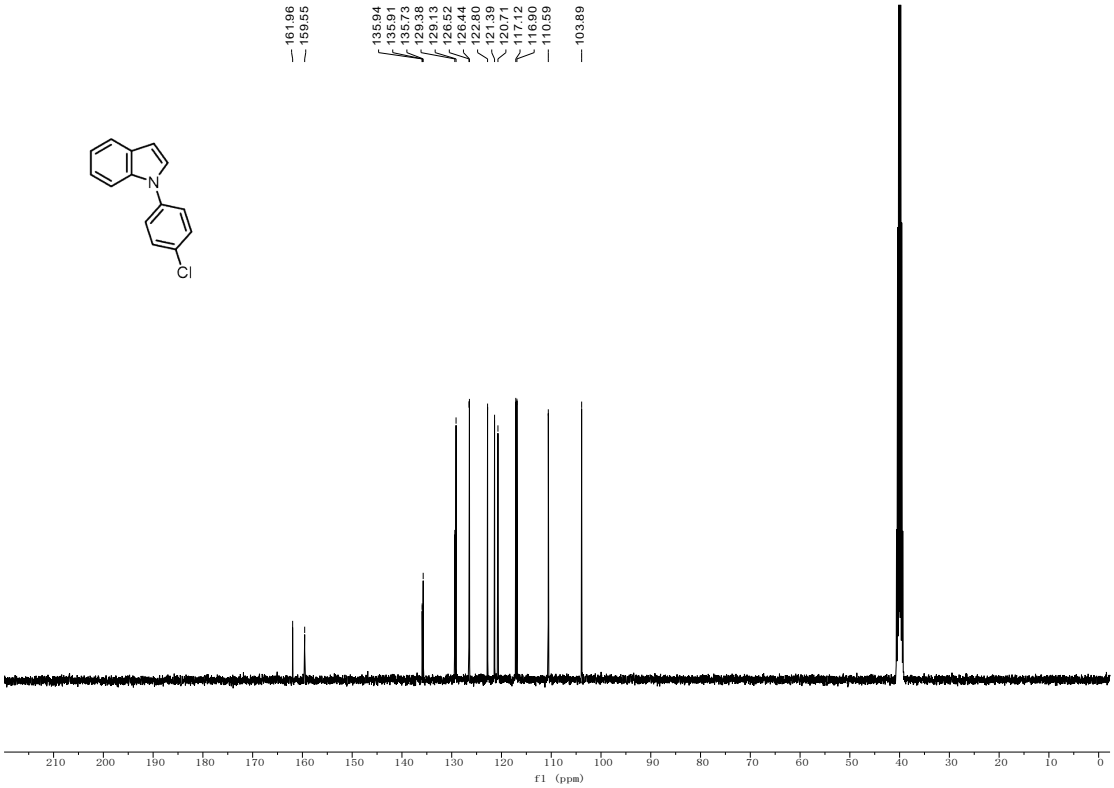
4-(1*H*-indol-1-yl)phenol (4d)



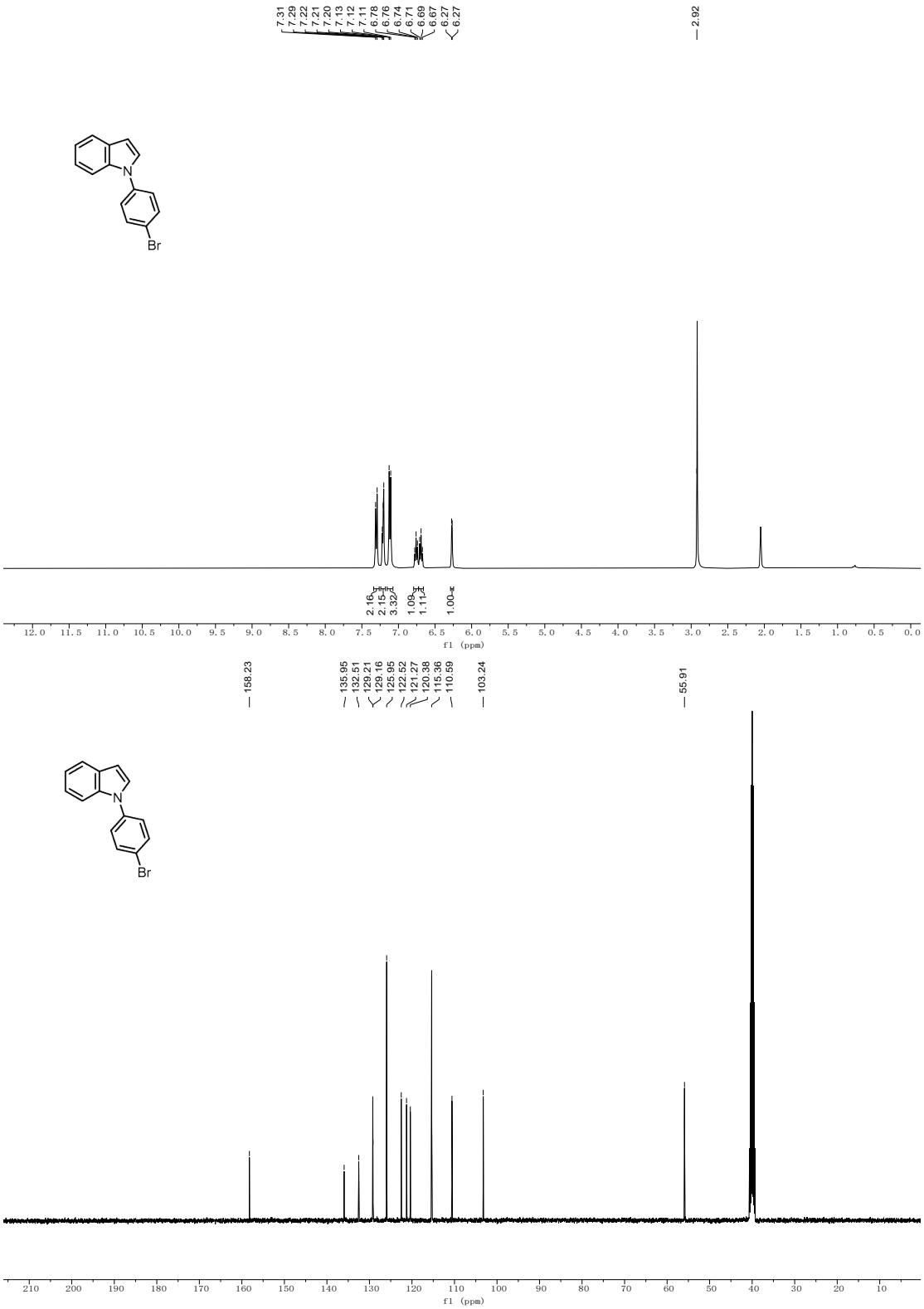


1-(4-chlorophenyl)-1*H*-indole (4e)

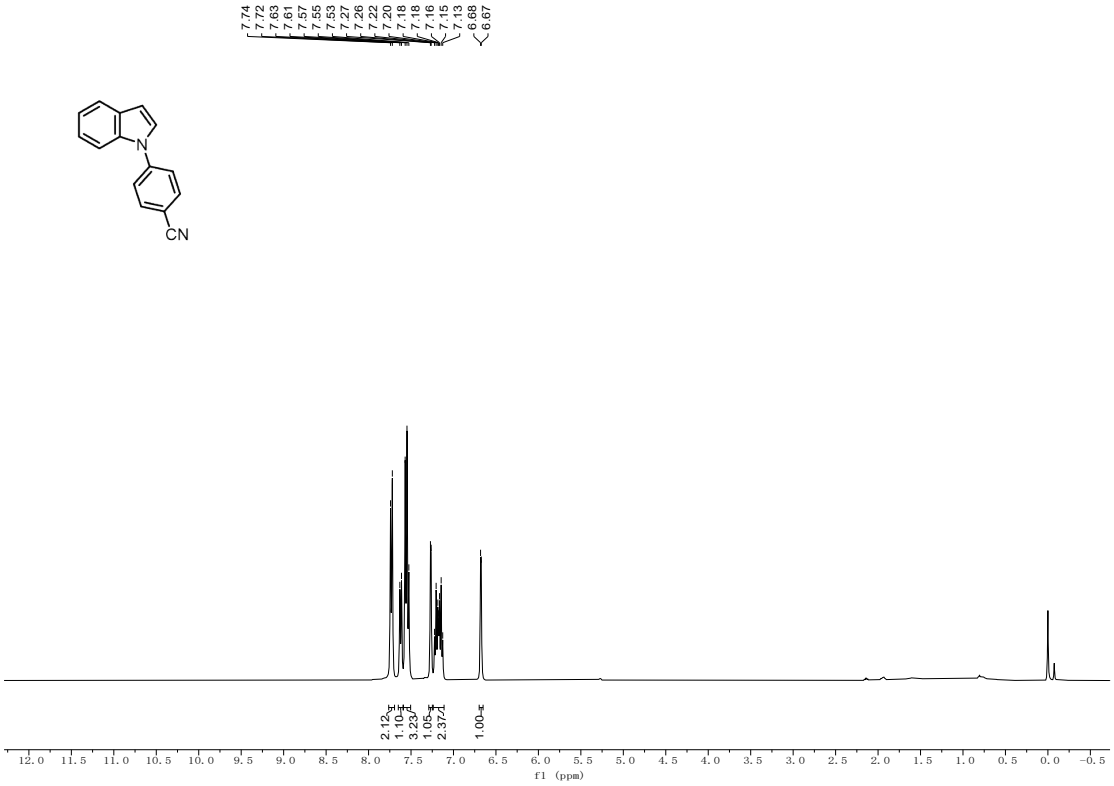


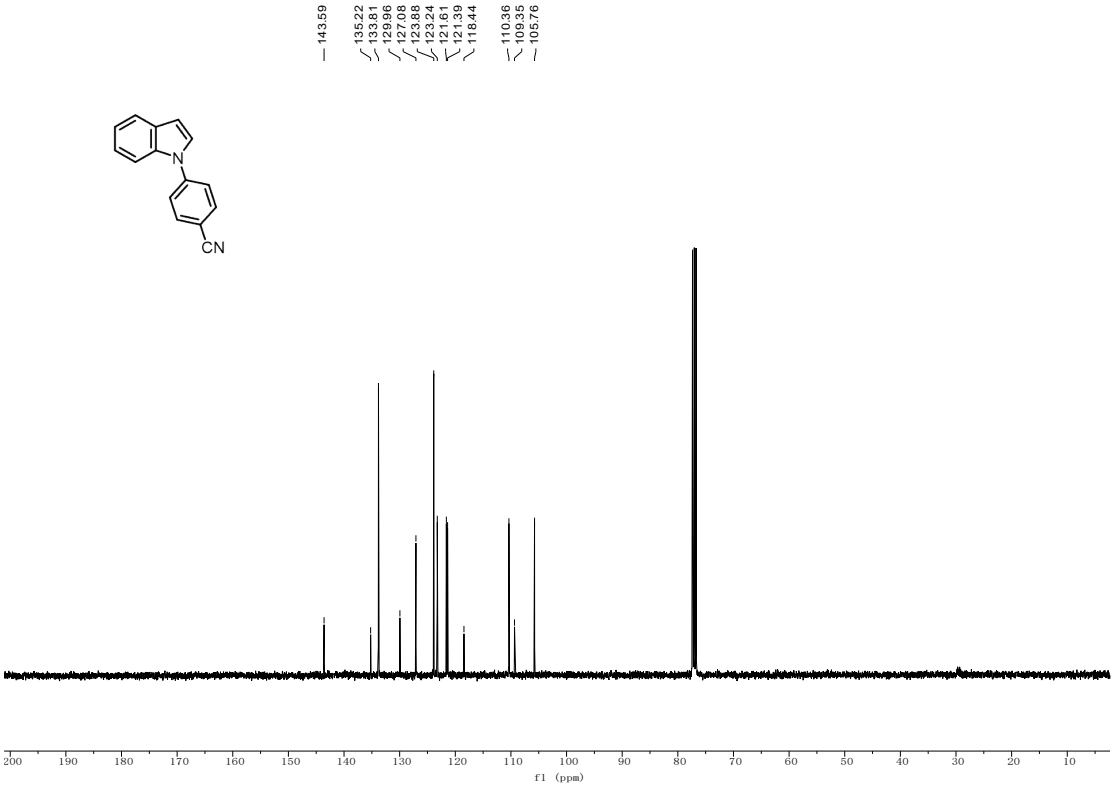


1-(4-bromophenyl)-1*H*-indole (4f)

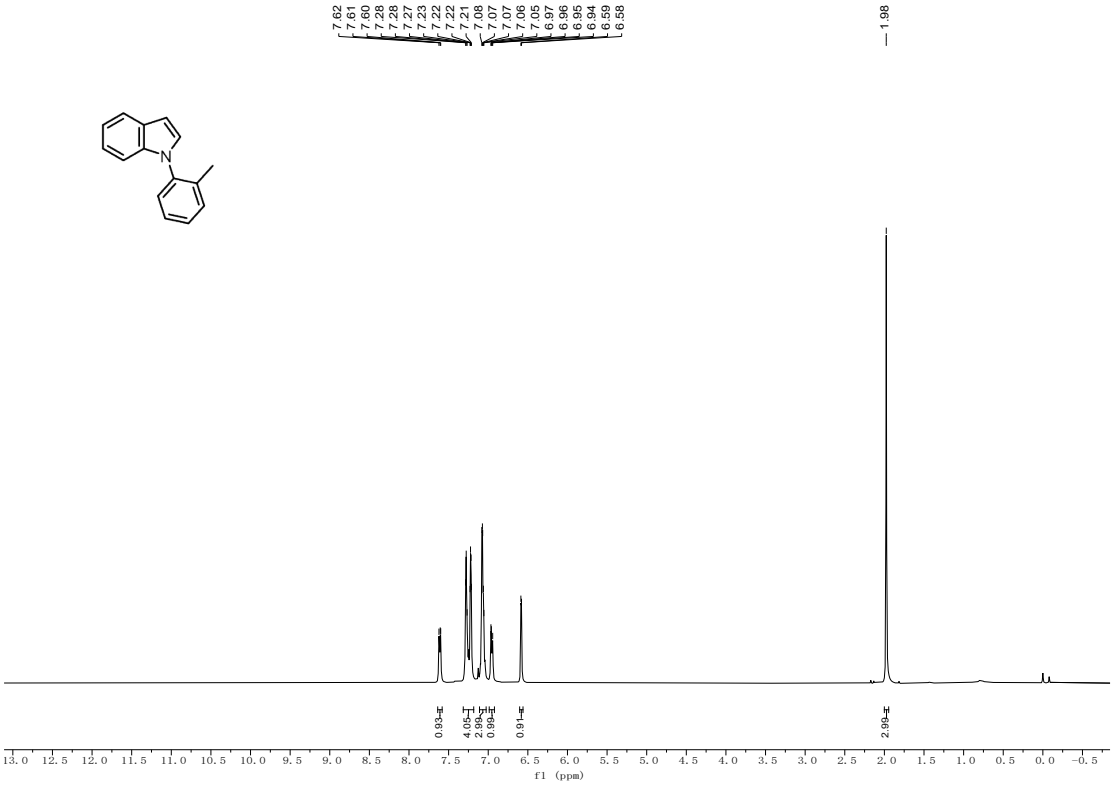


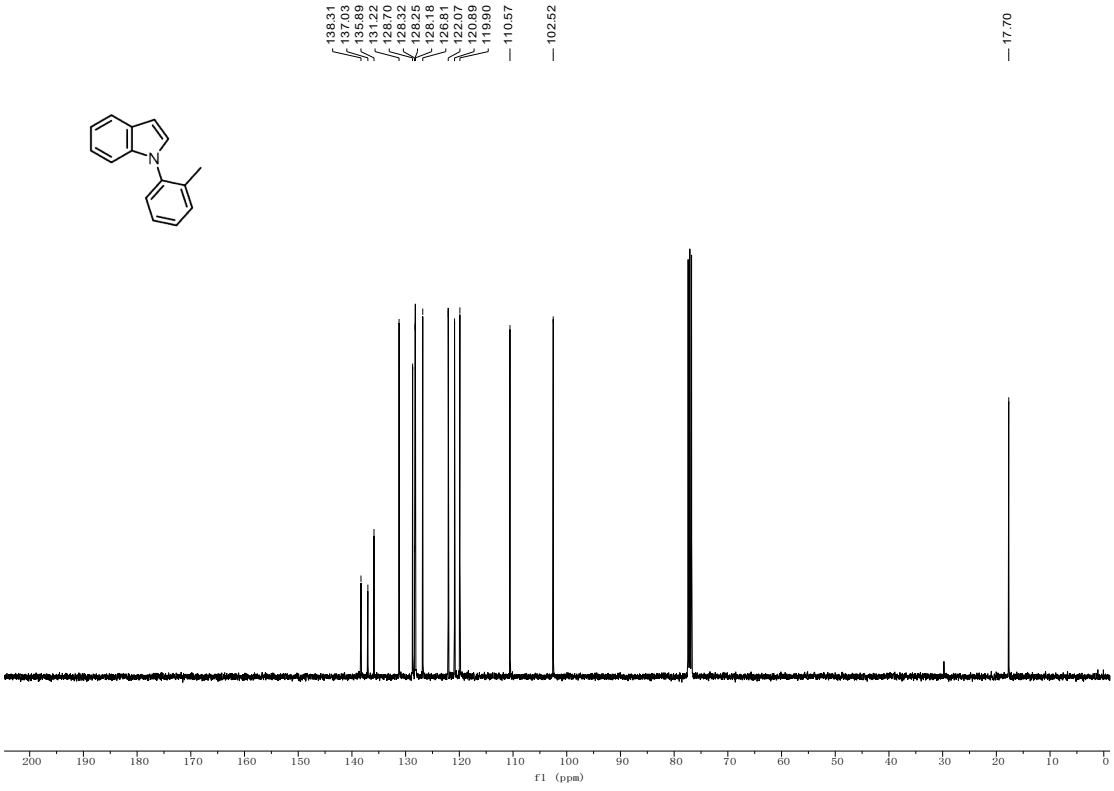
4-(1*H*-indol-1-yl)benzonitrile (4g)



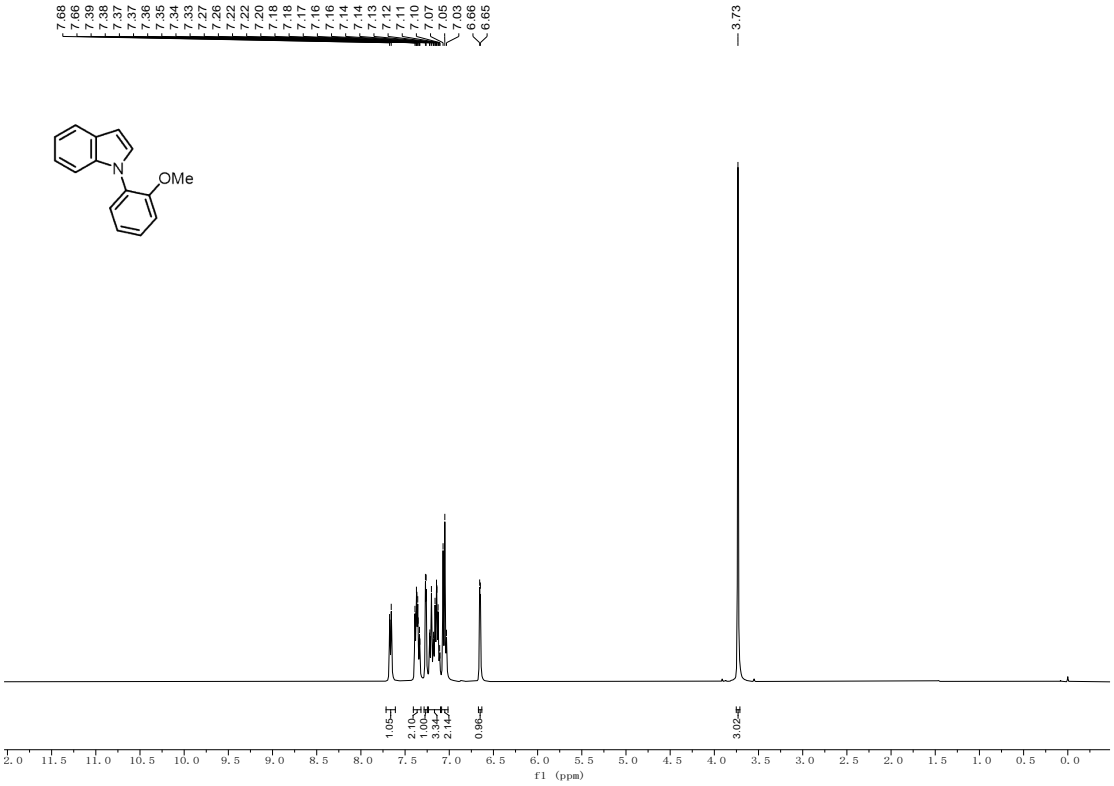


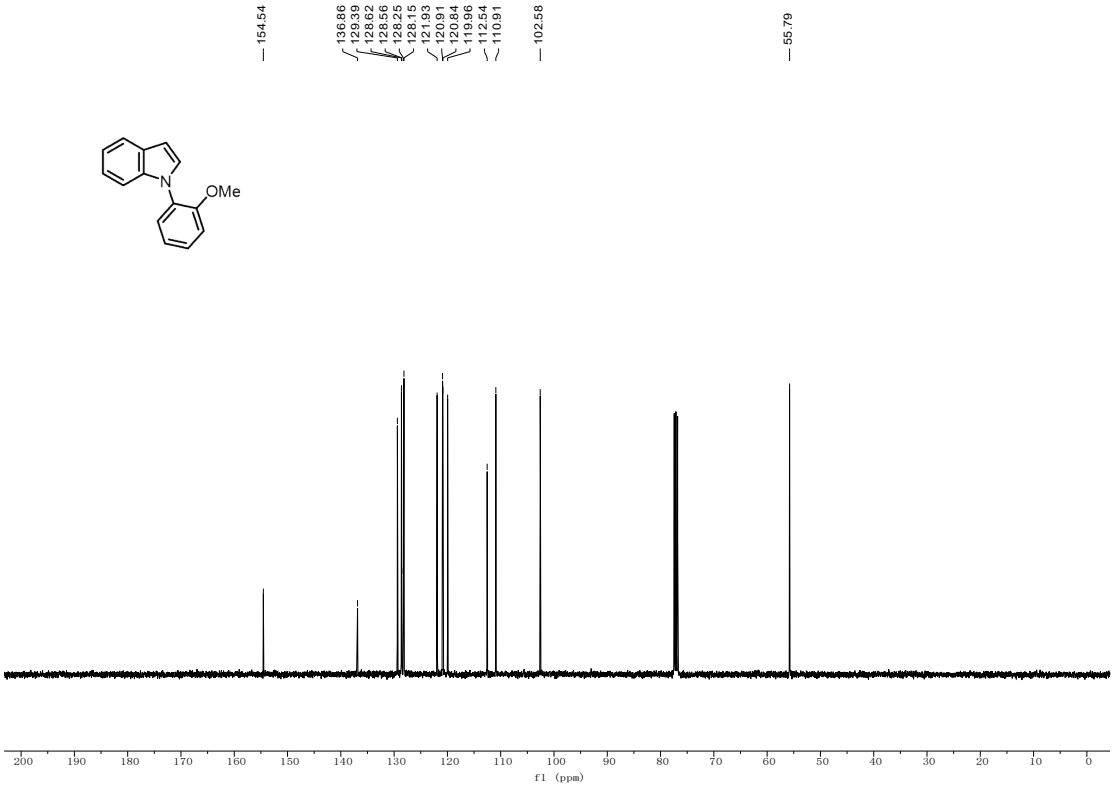
1-(*o*-tolyl)-1*H*-indole (4h)



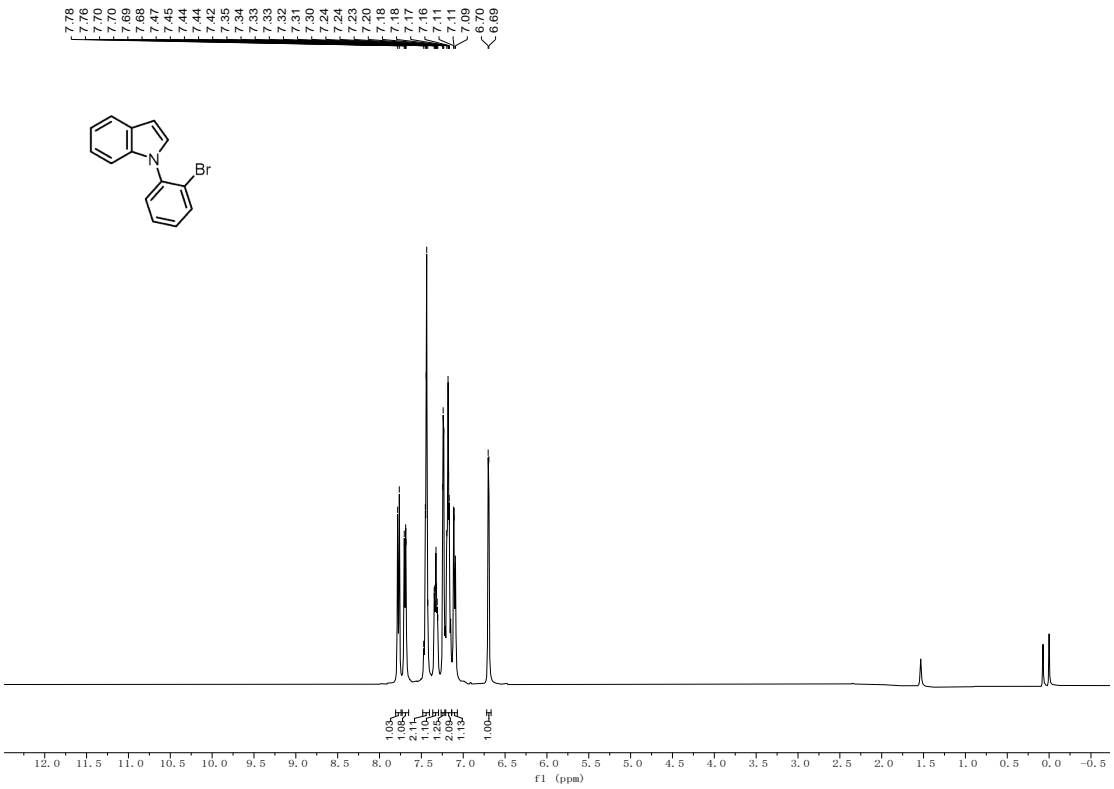


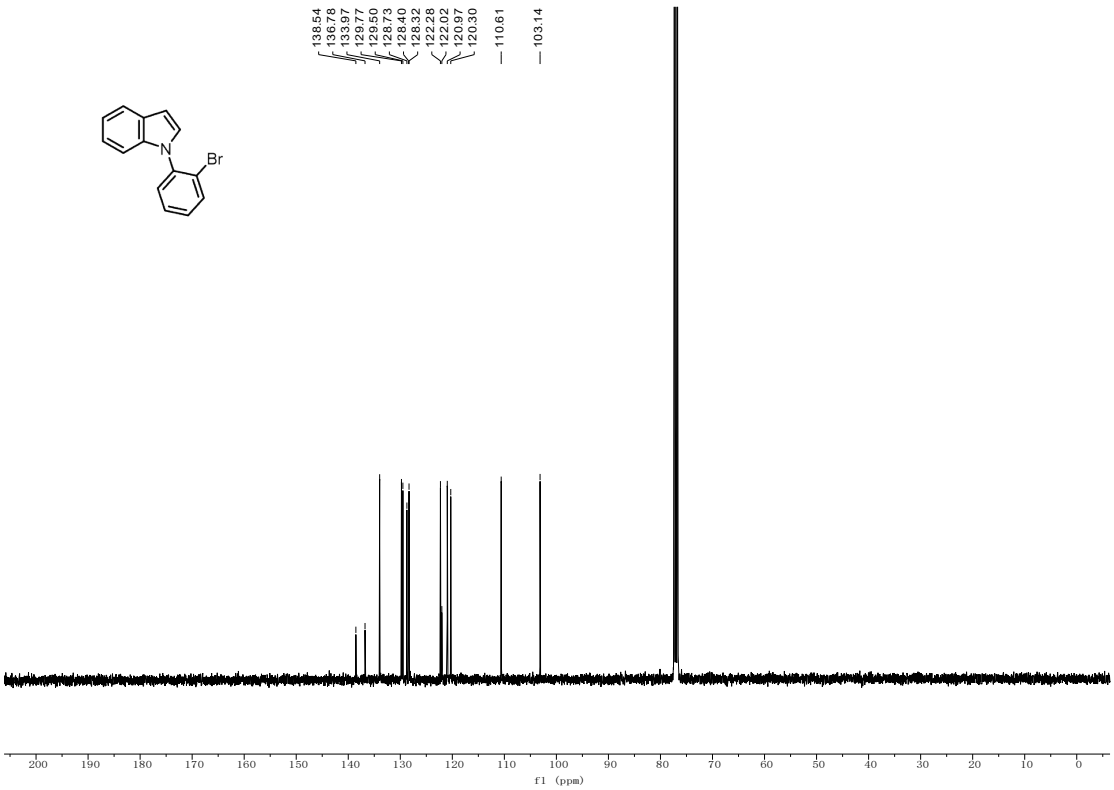
1-(2-methoxyphenyl)-1*H*-indole (4i)



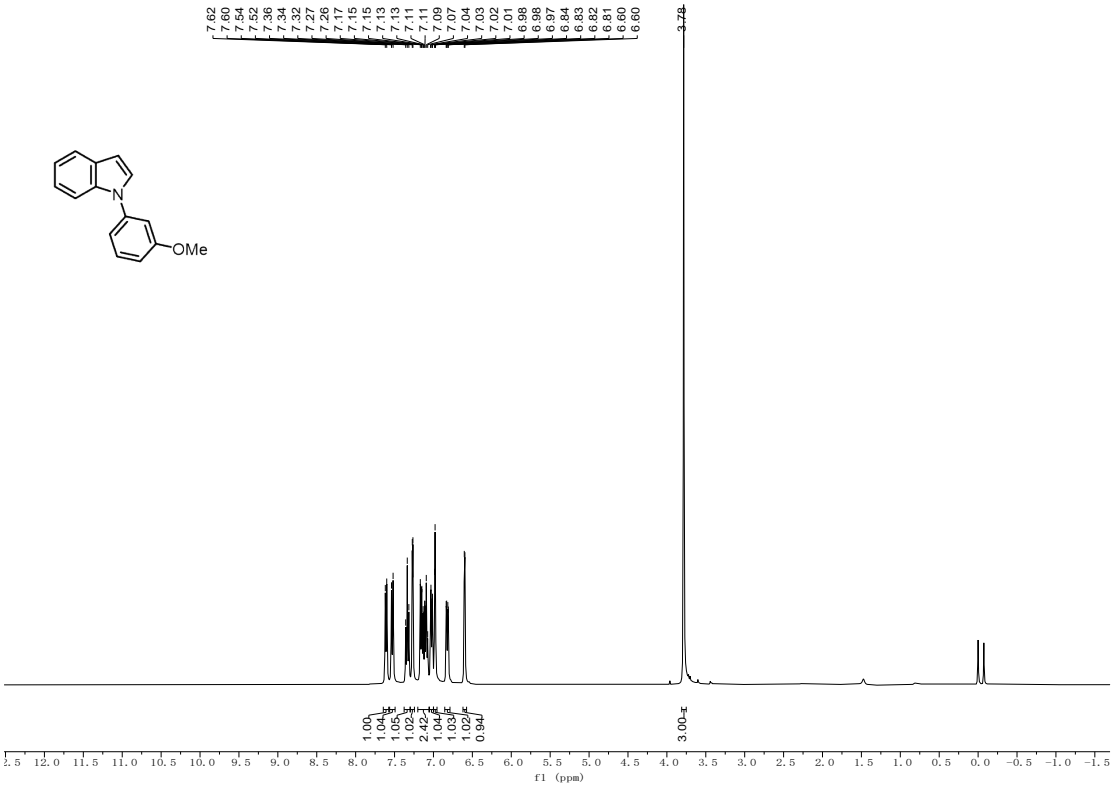


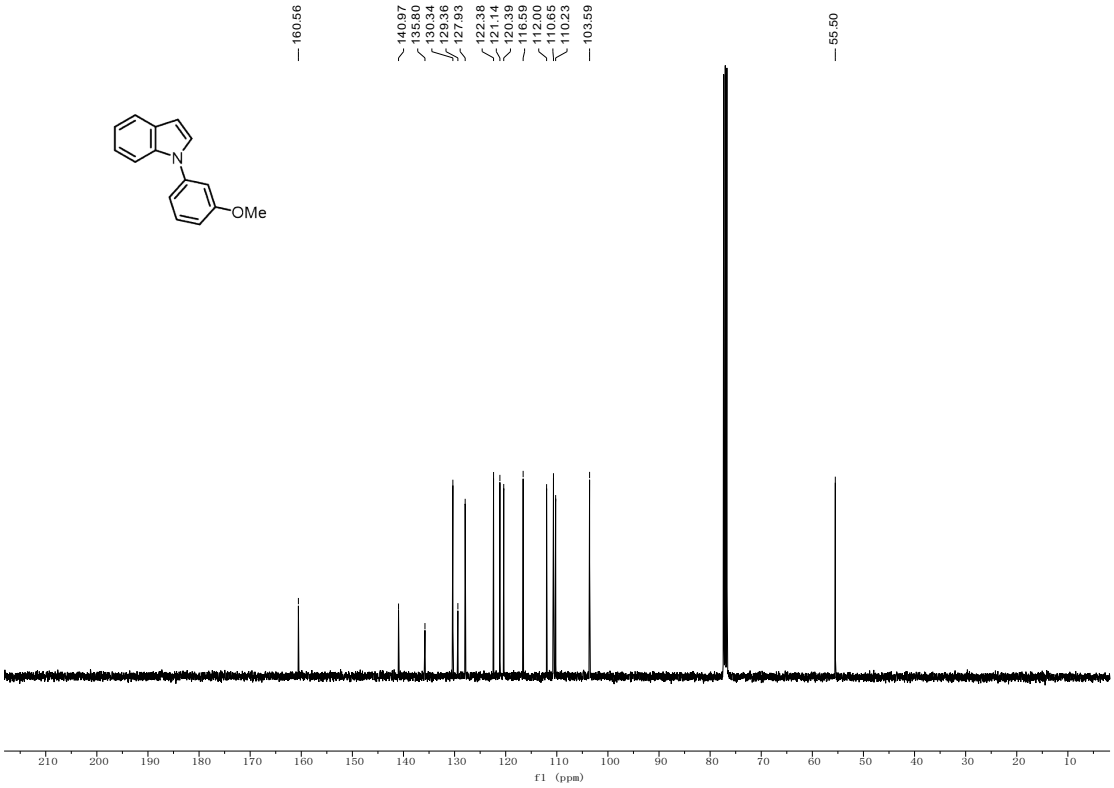
1-(2-bromophenyl)-1*H*-indole (4j)



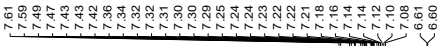


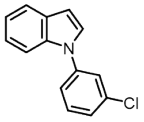
1-(3-methoxyphenyl)-1*H*-indole (4k)

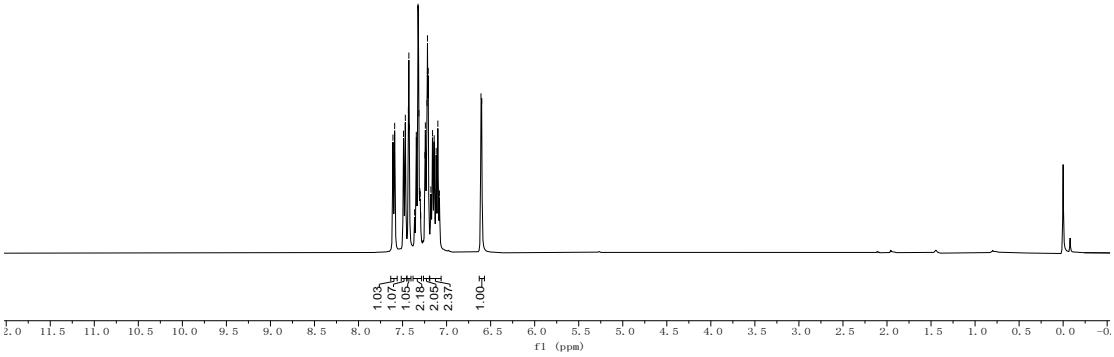


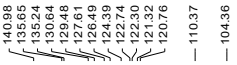


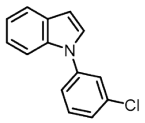
1-(3-chlorophenyl)-1*H*-indole (4l)

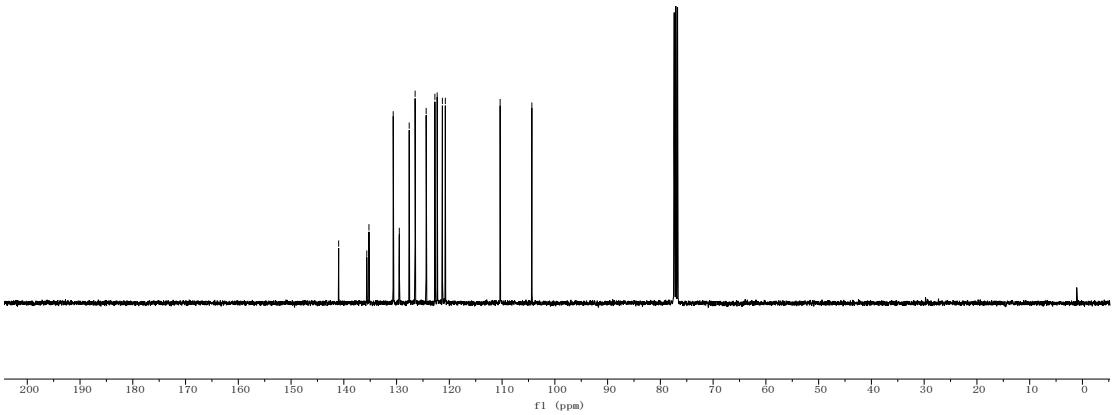




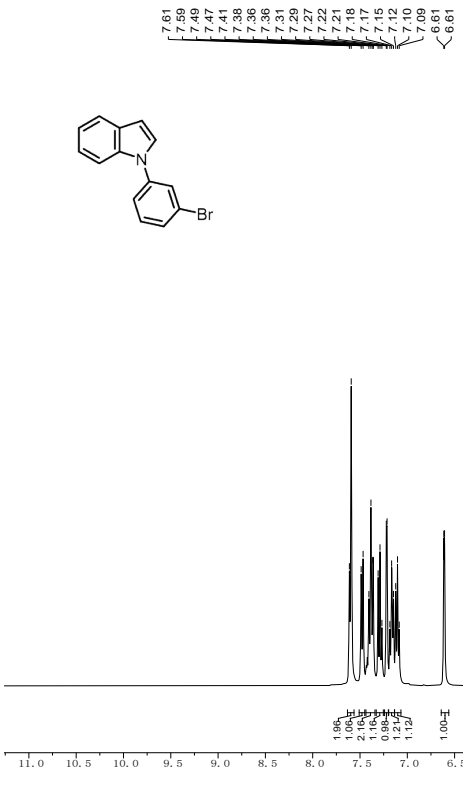


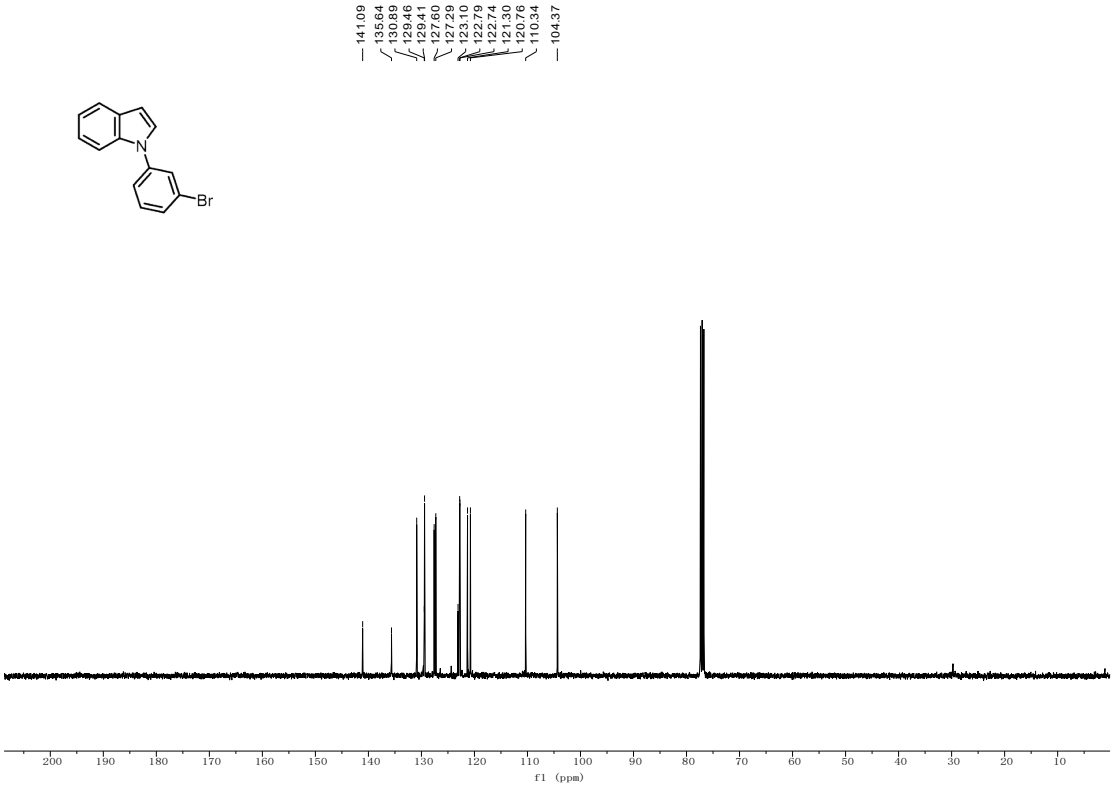




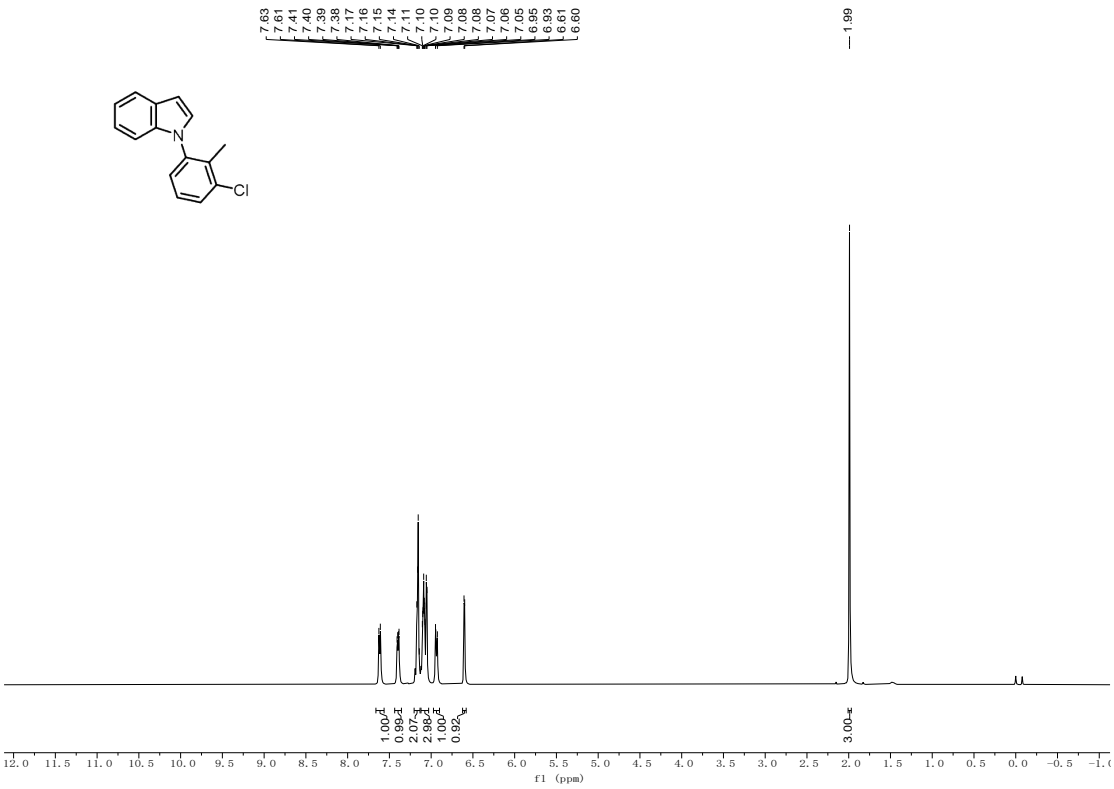


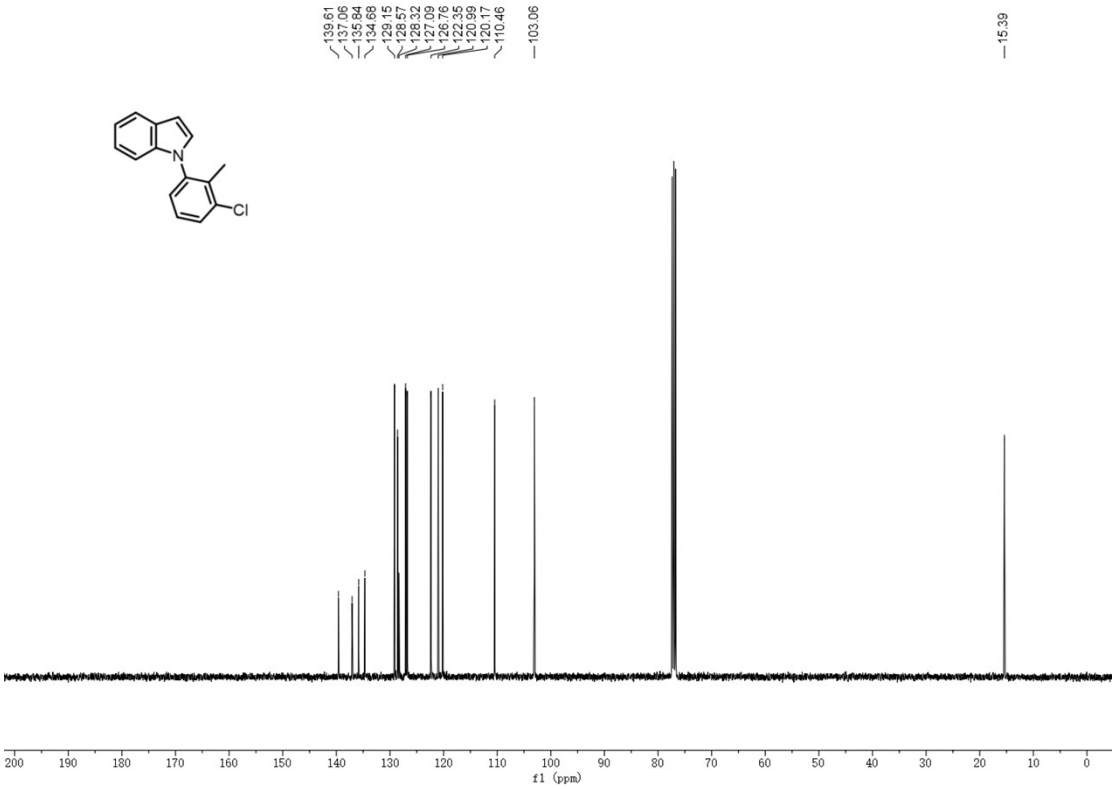
1-(3-bromophenyl)-1*H*-indole (4m)



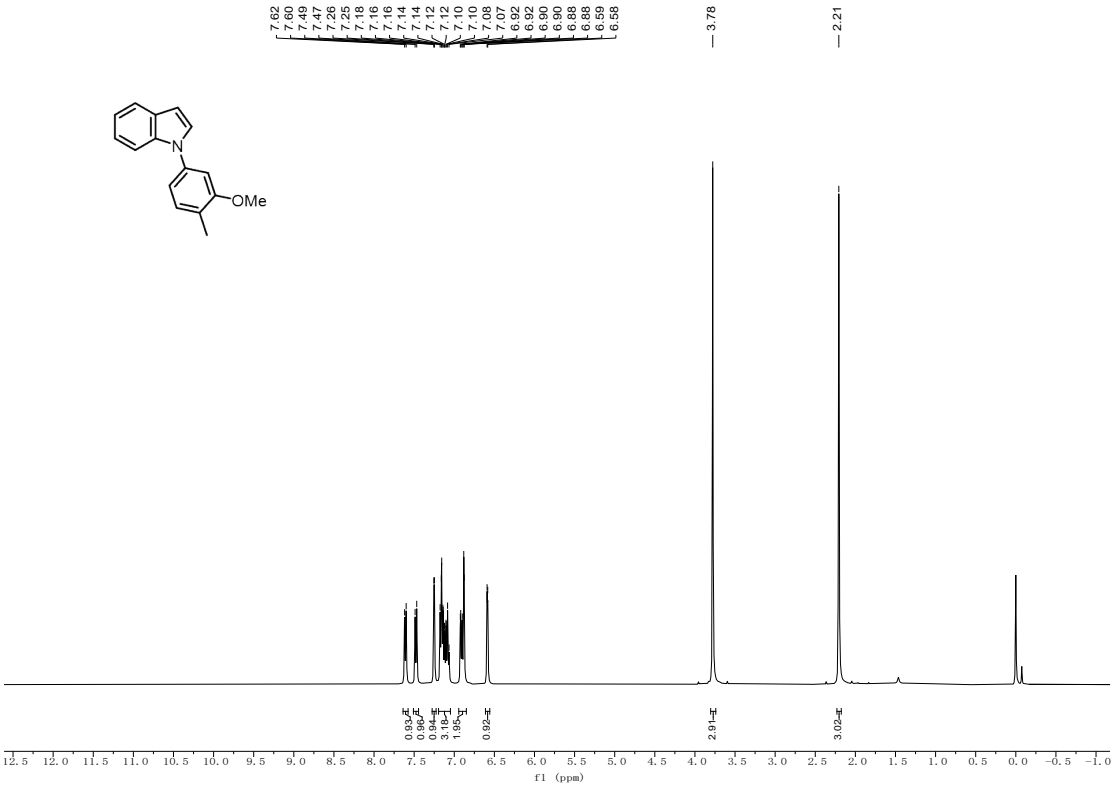


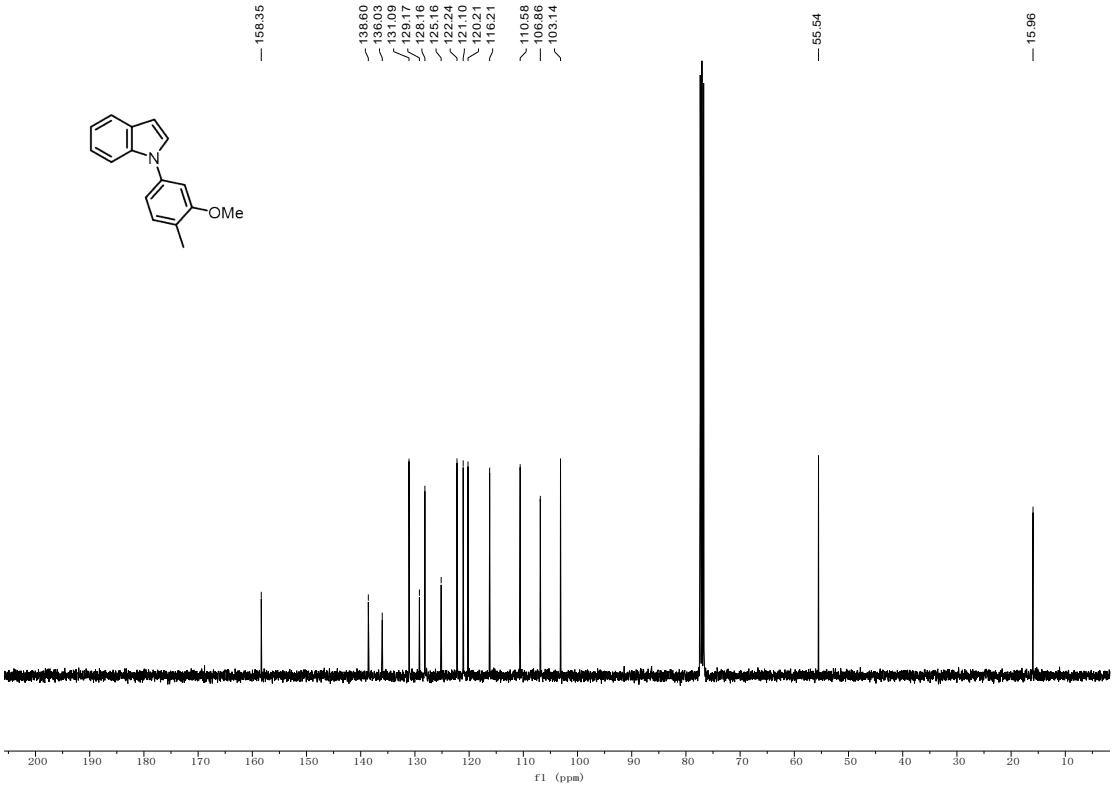
1-(3-chloro-2-methylphenyl)-1*H*-indole (4n)



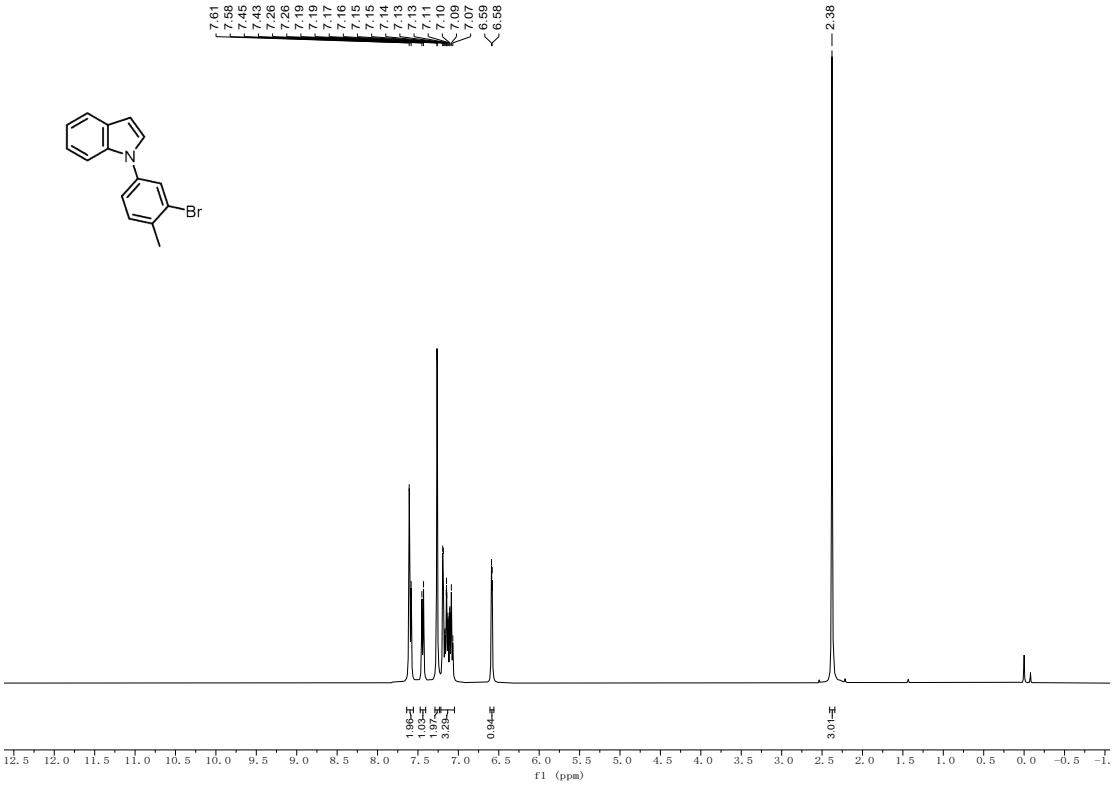


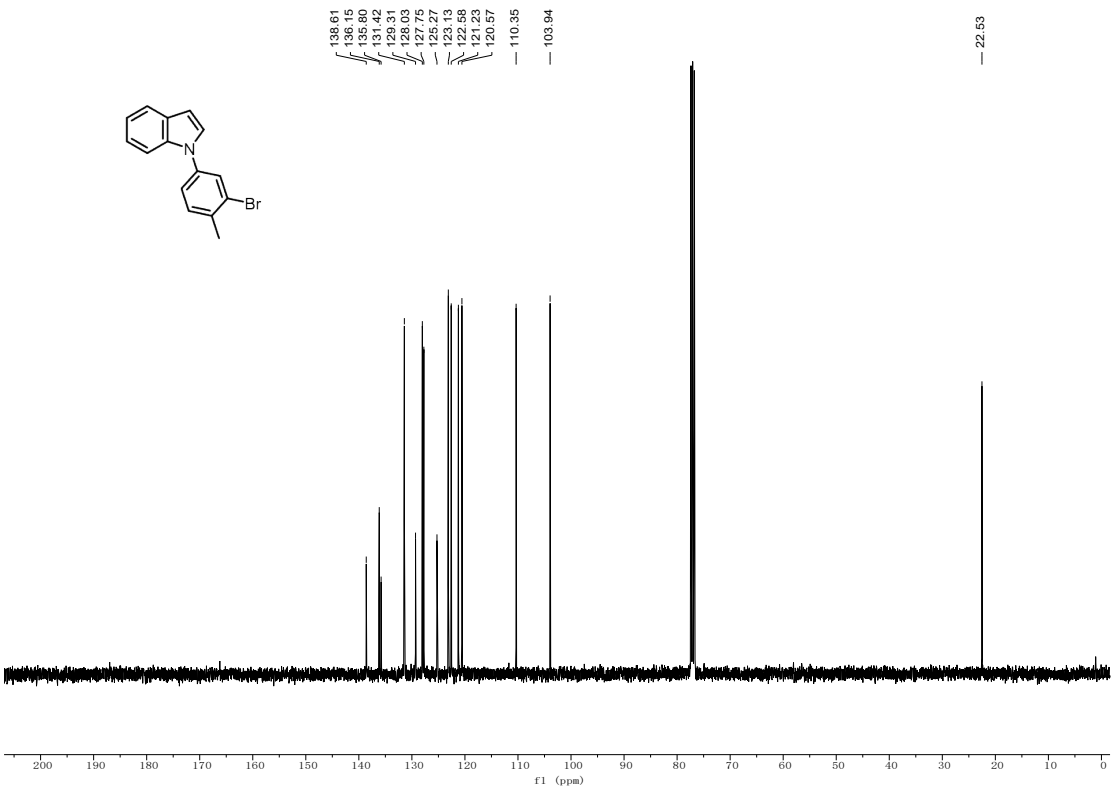
1-(3-methoxy-4-methylphenyl)-1*H*-indole (4o)



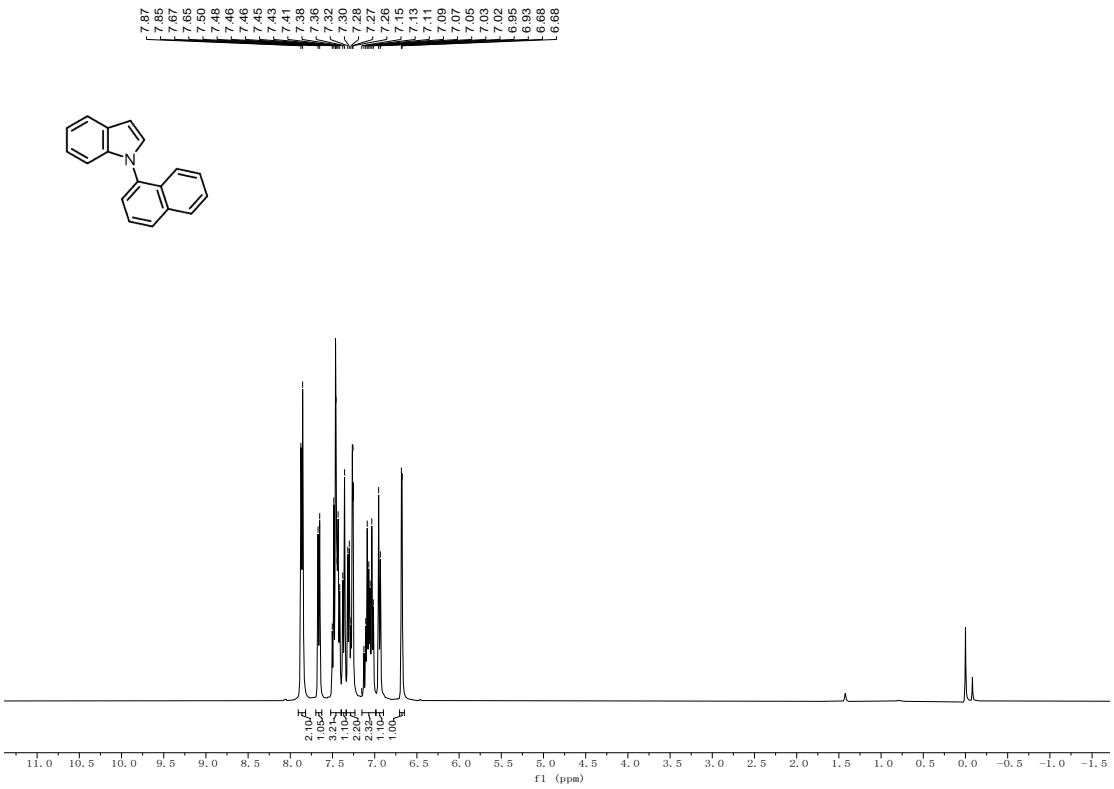


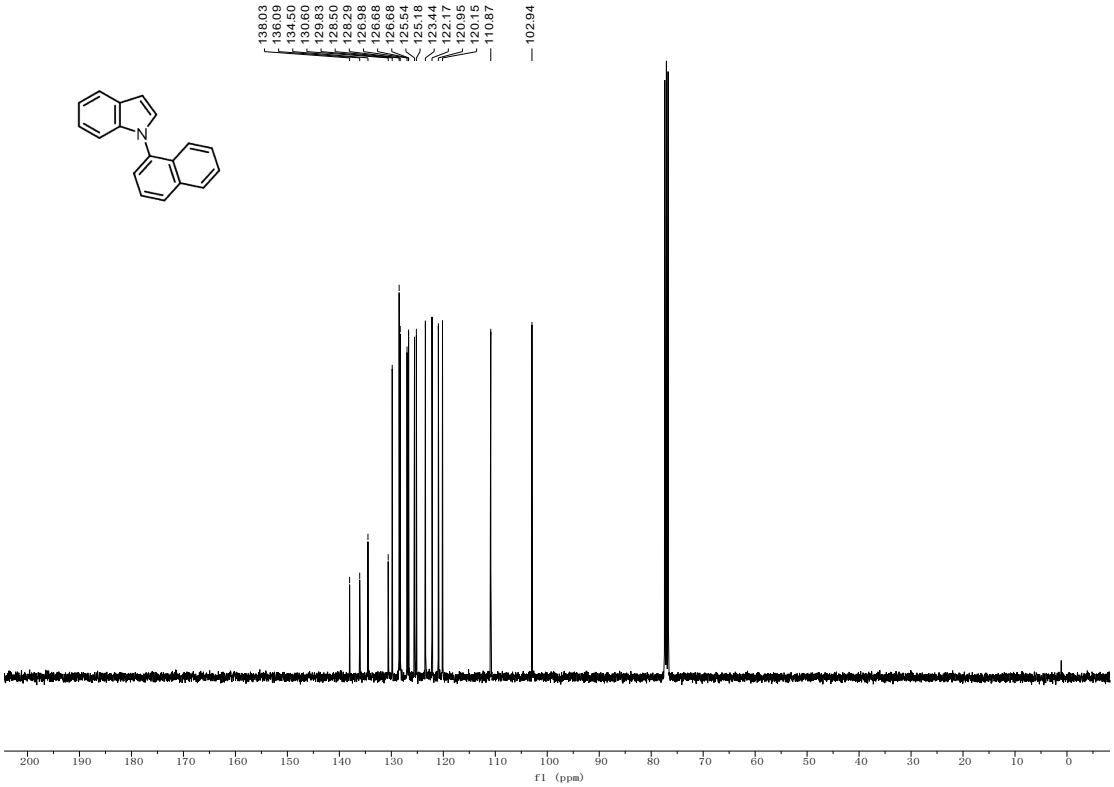
1-(3-bromo-4-methylphenyl)-1*H*-indole (4p)



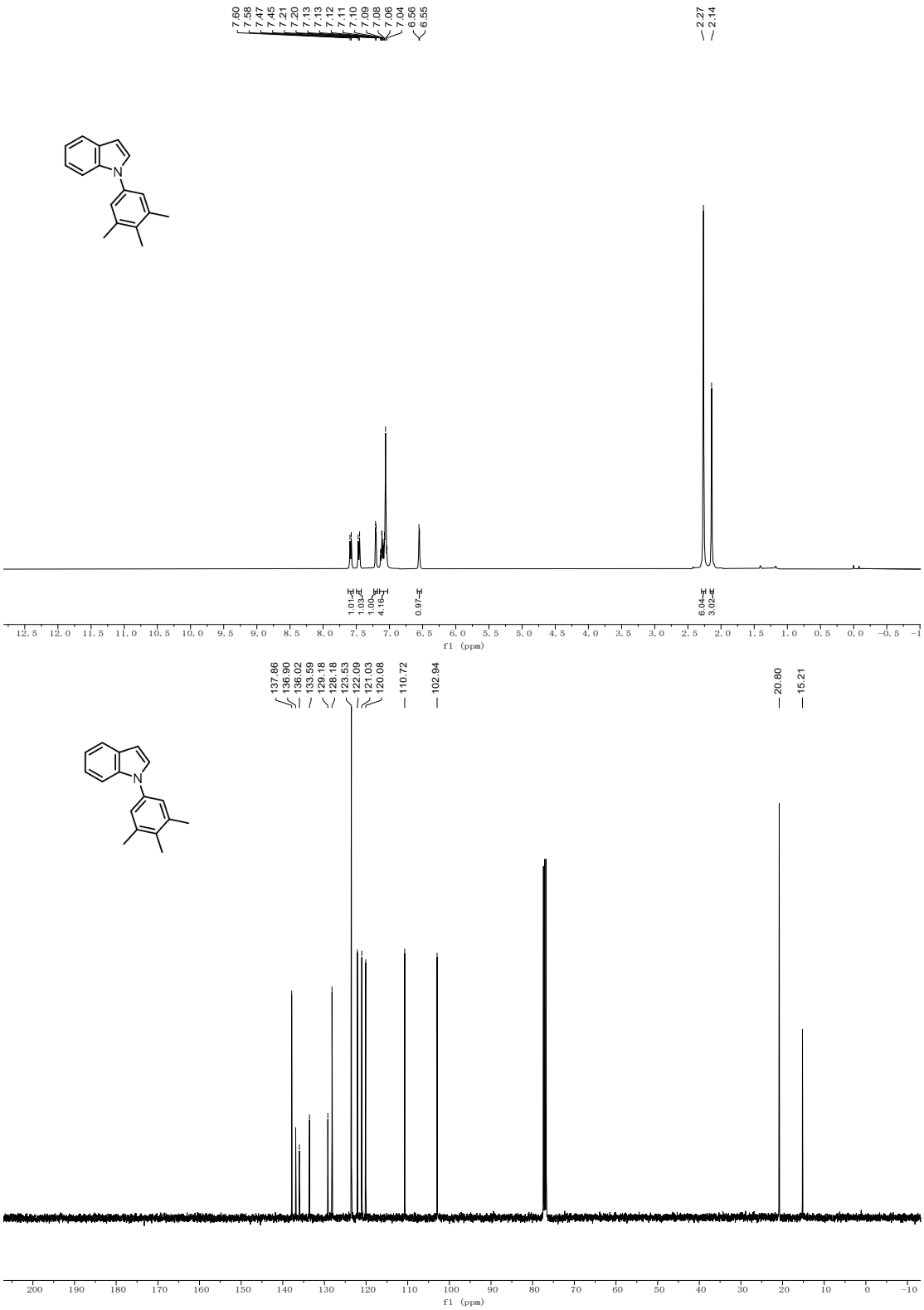


1-(naphthalen-1-yl)-1*H*-indole (4q)

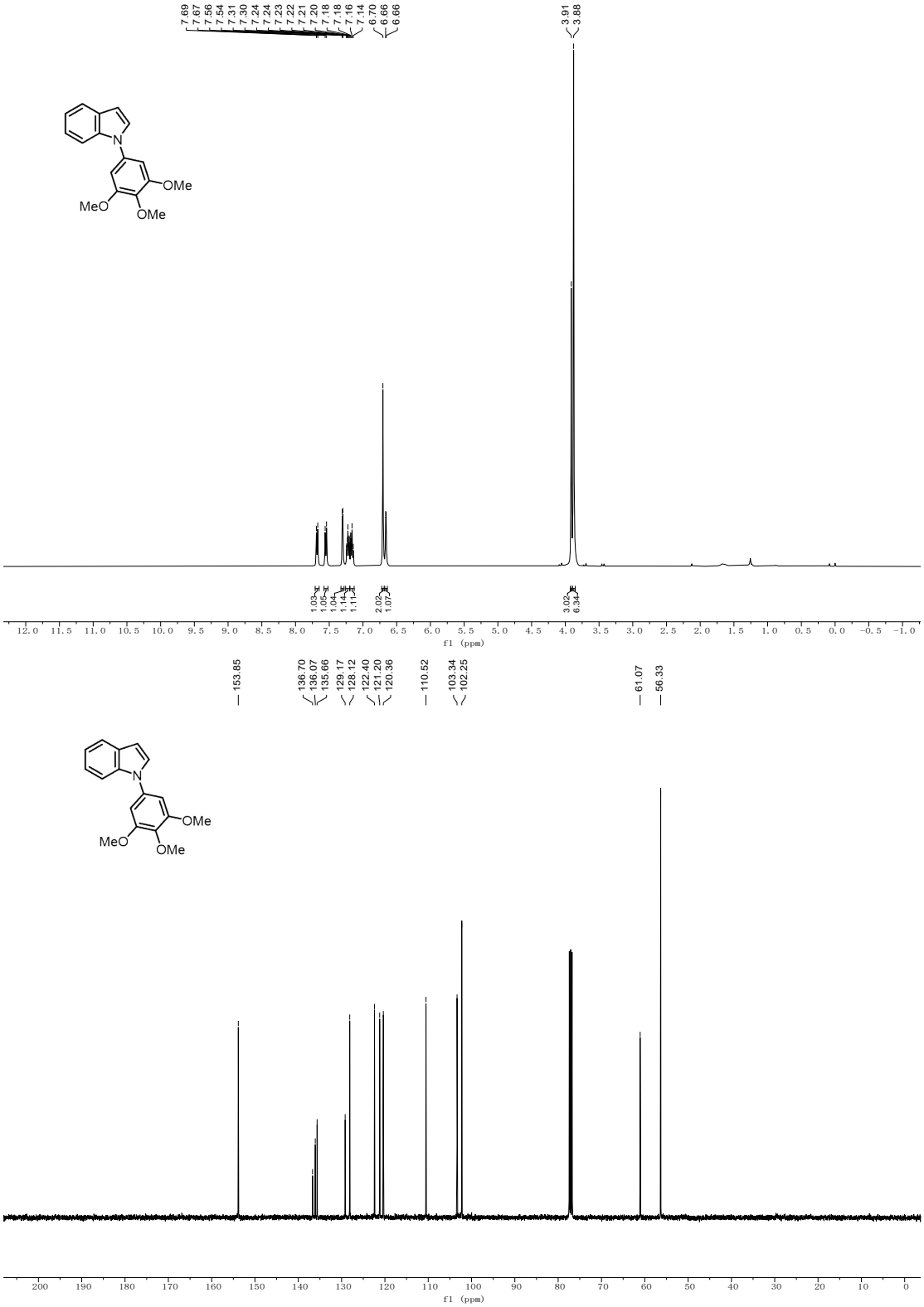




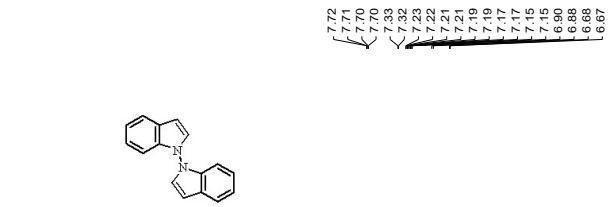
1-(3,4,5-trimethylphenyl)-1*H*-indole (4r)

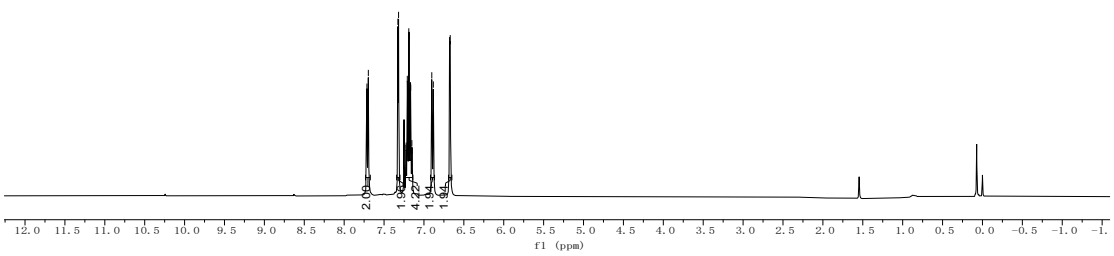


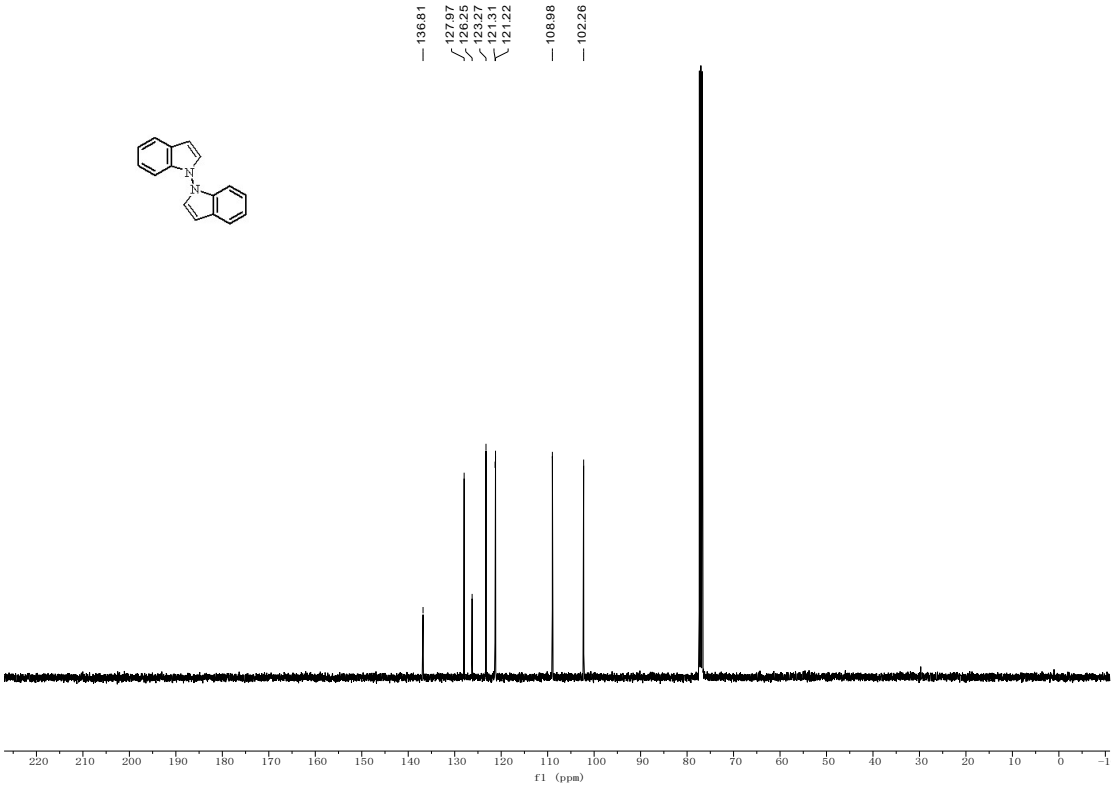
1-(3,4,5-trimethoxyphenyl)-1*H*-indole (4s)



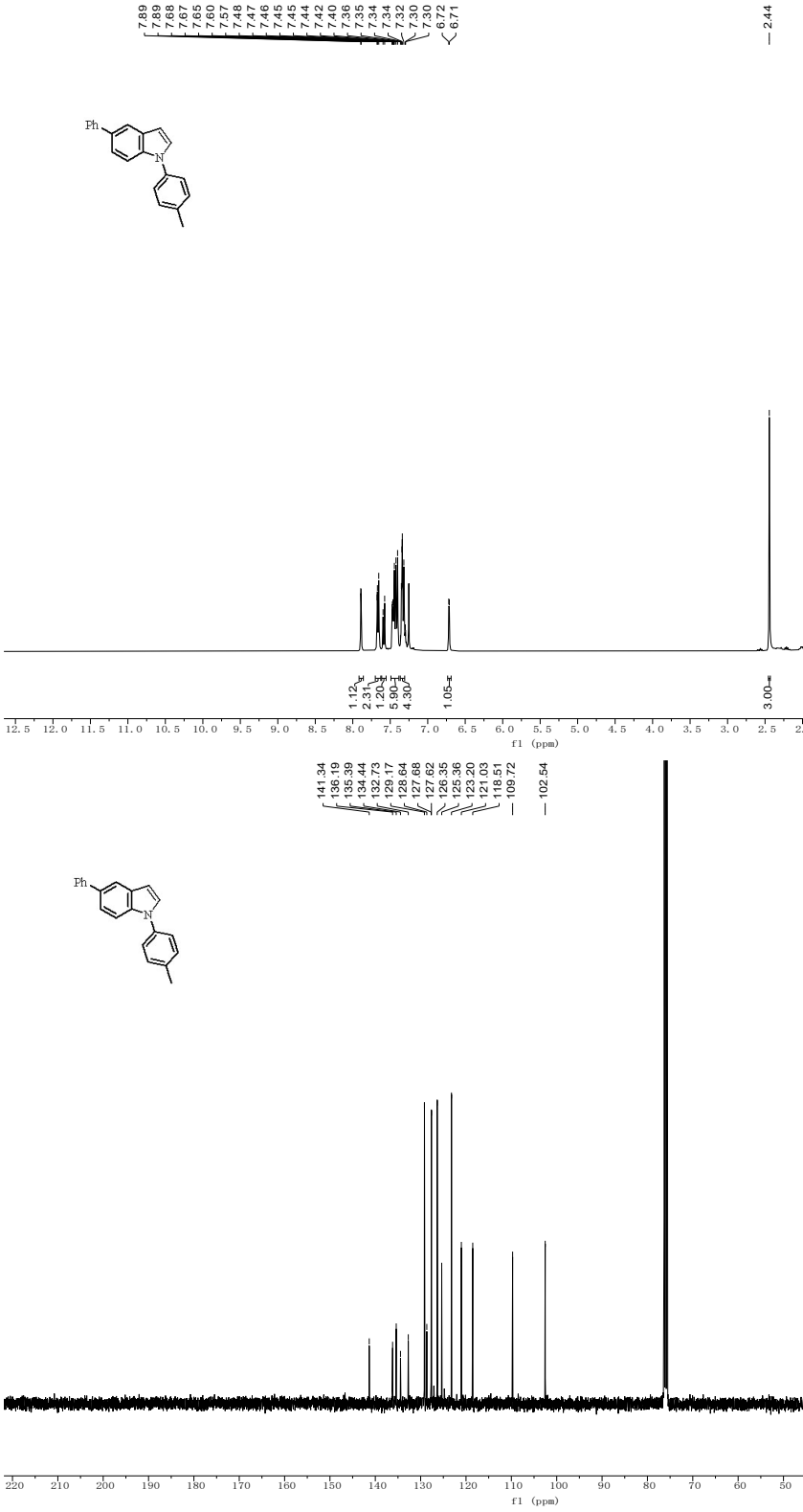
1,1'-biindole (4t)



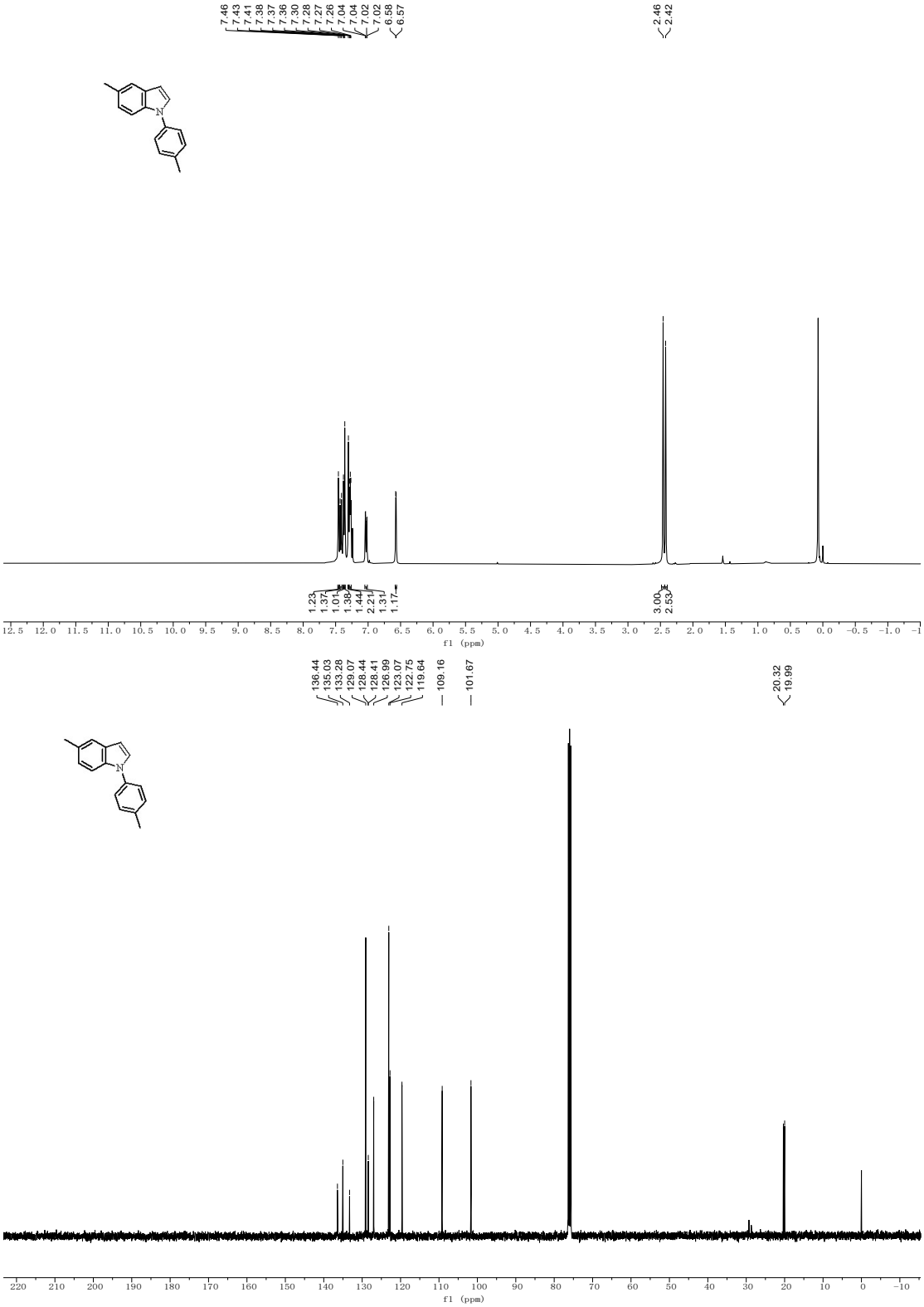




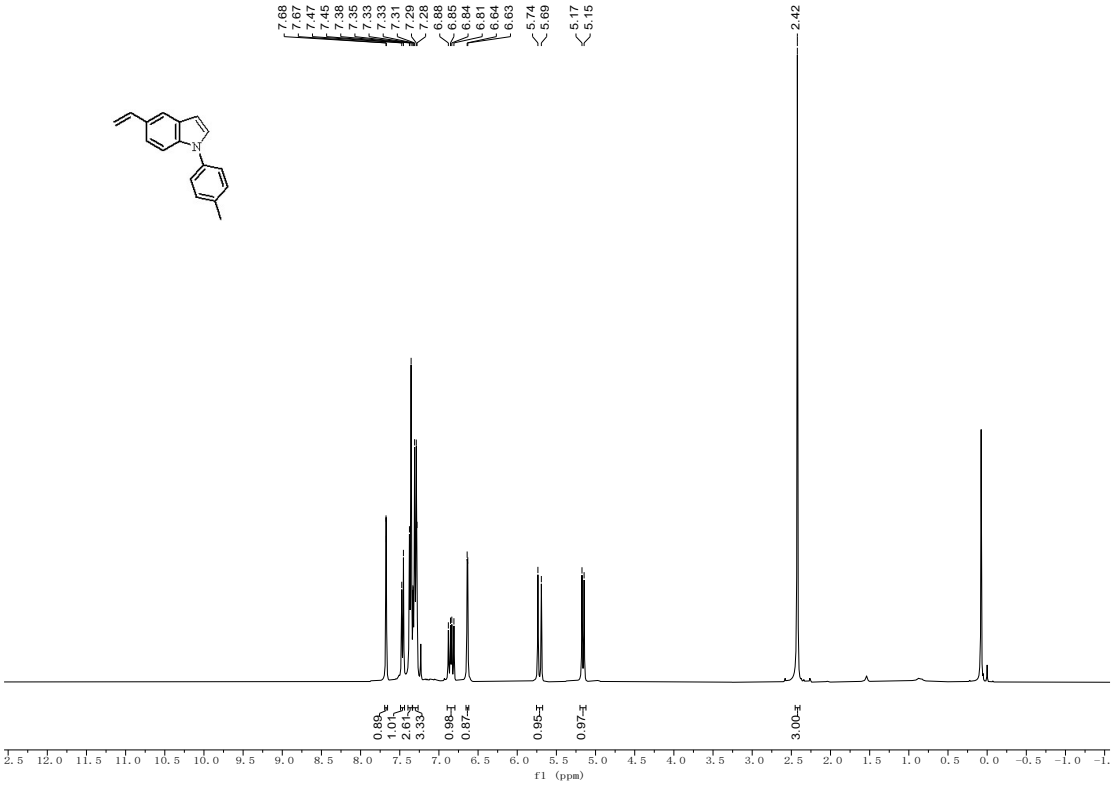
5-phenyl-1-(*p*-tolyl)-1*H*-indole (4u)

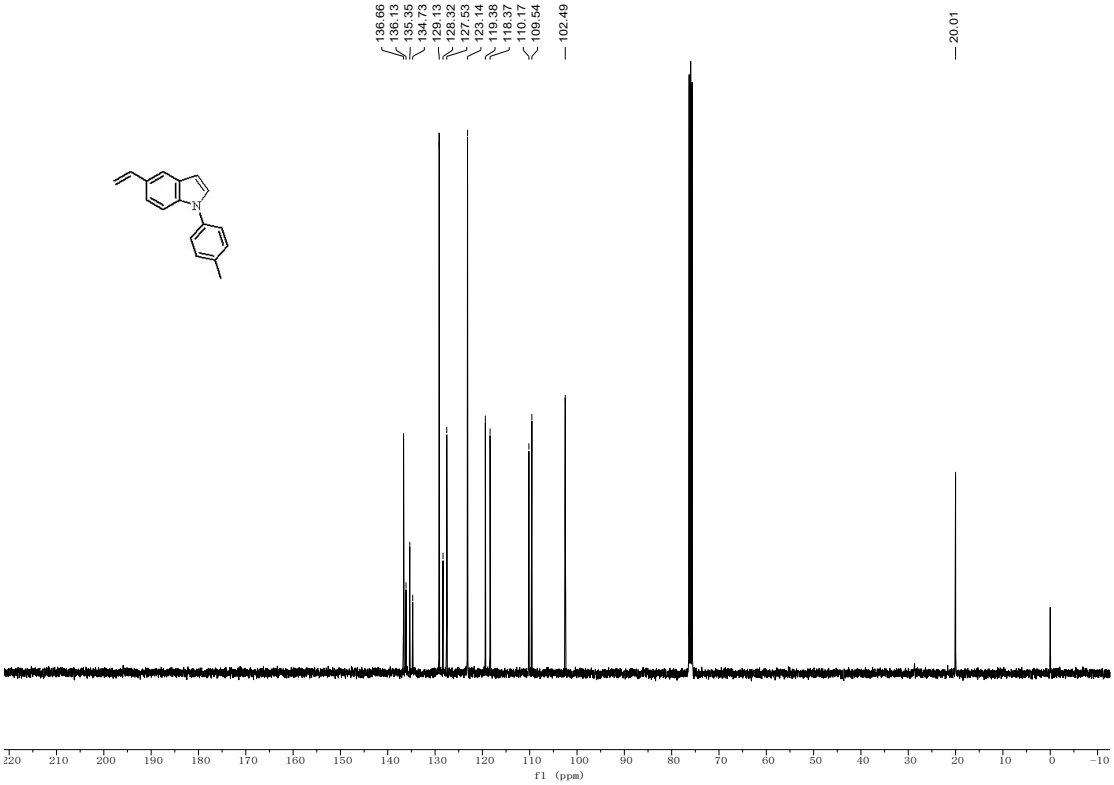


5-methyl-1-(*p*-tolyl)-1*H*-indole (4v)

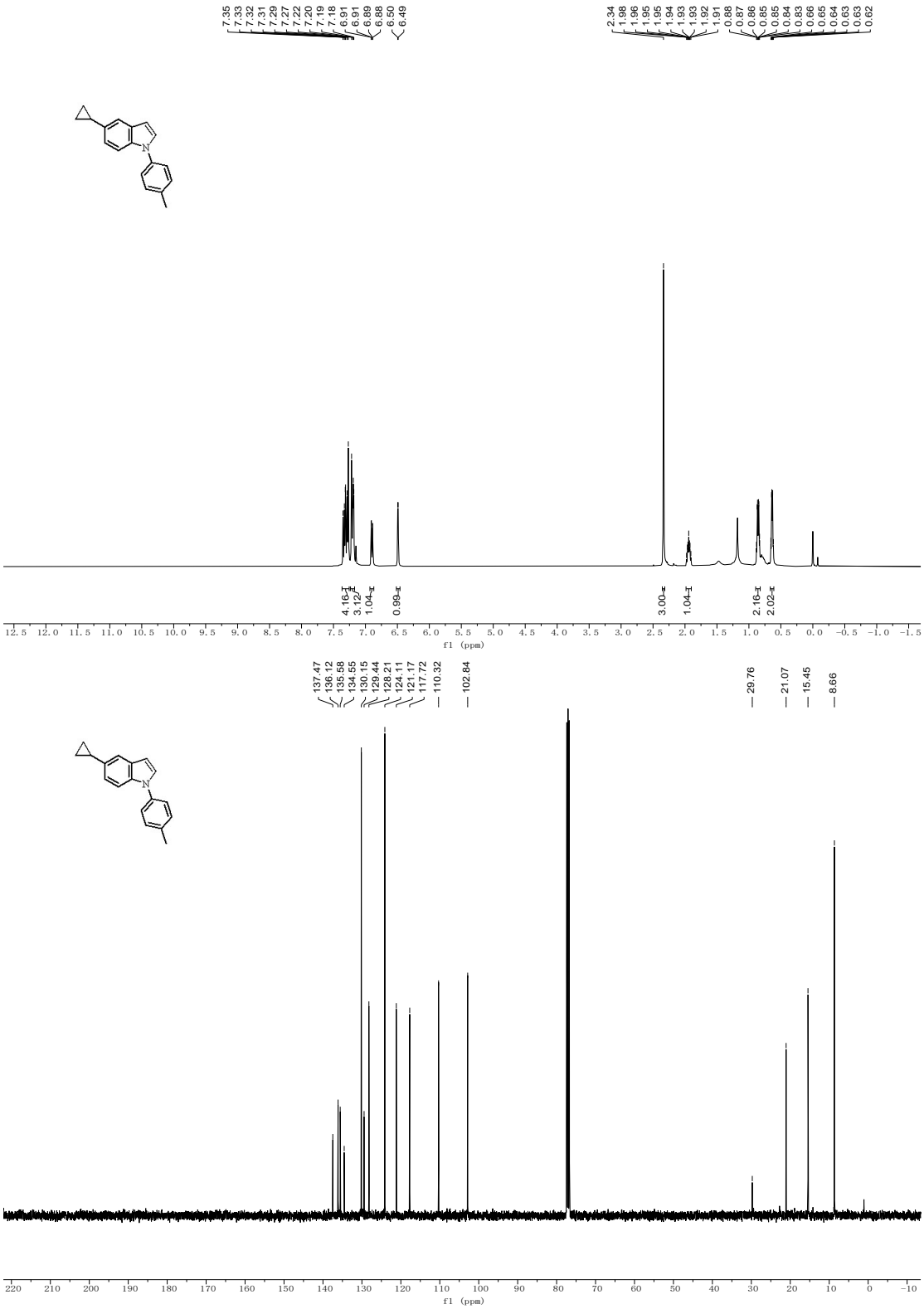


1-(*p*-tolyl)-5-vinyl-1*H*-indole (4w)

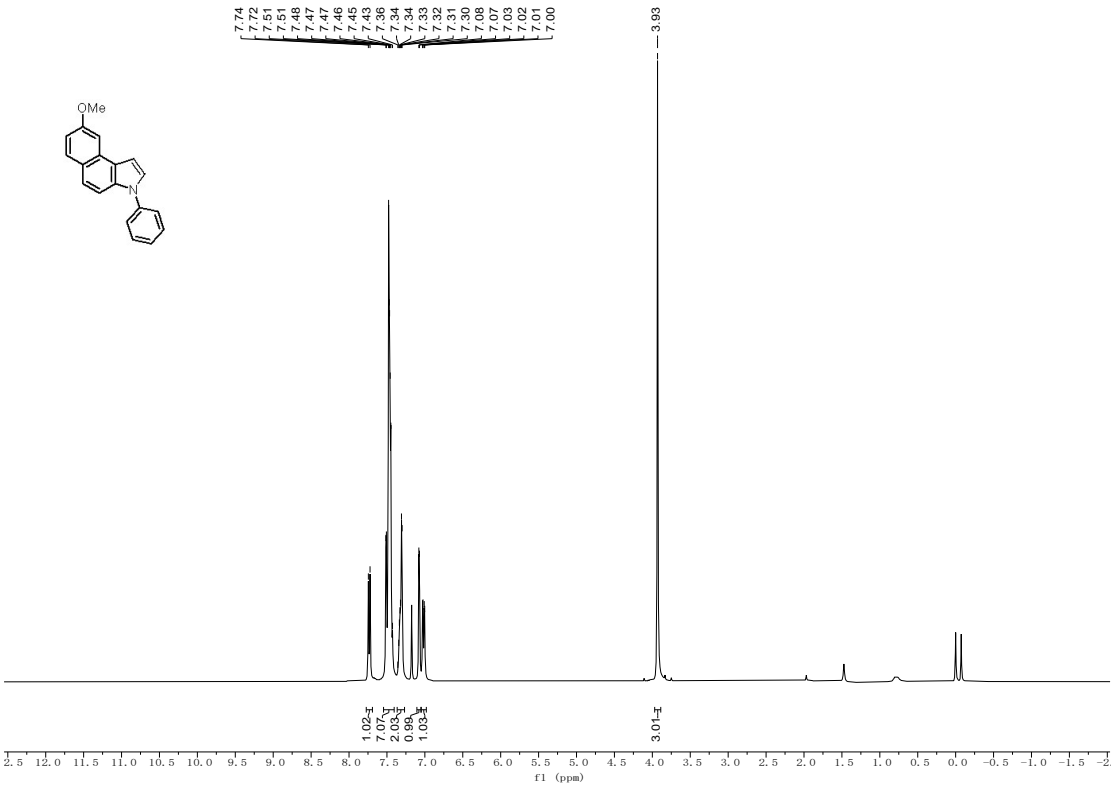


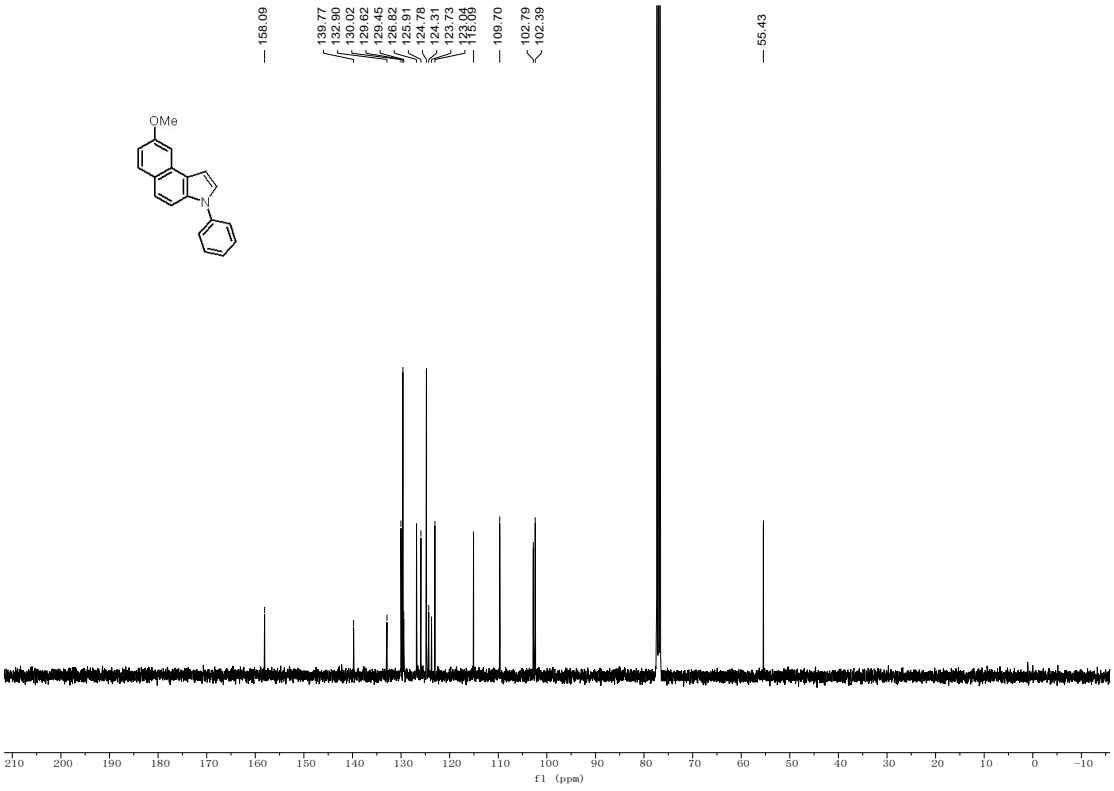


5-cyclopropyl-1-(*p*-tolyl)-1*H*-indole (4x)

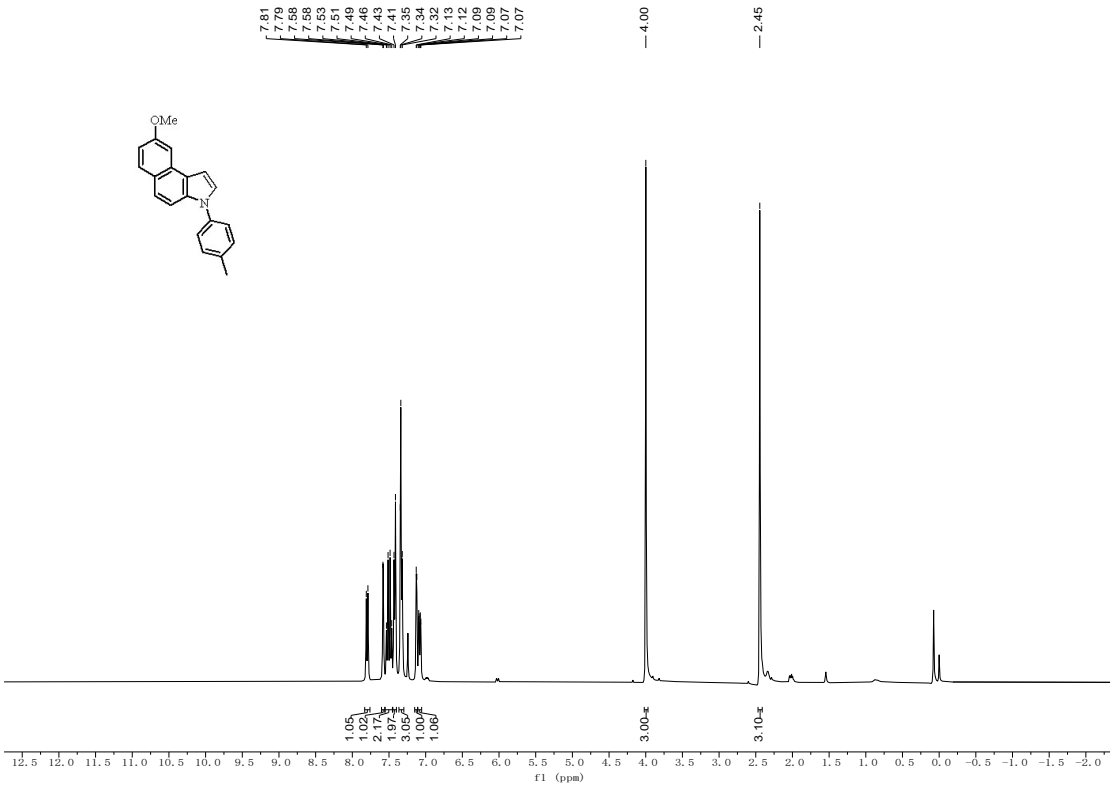


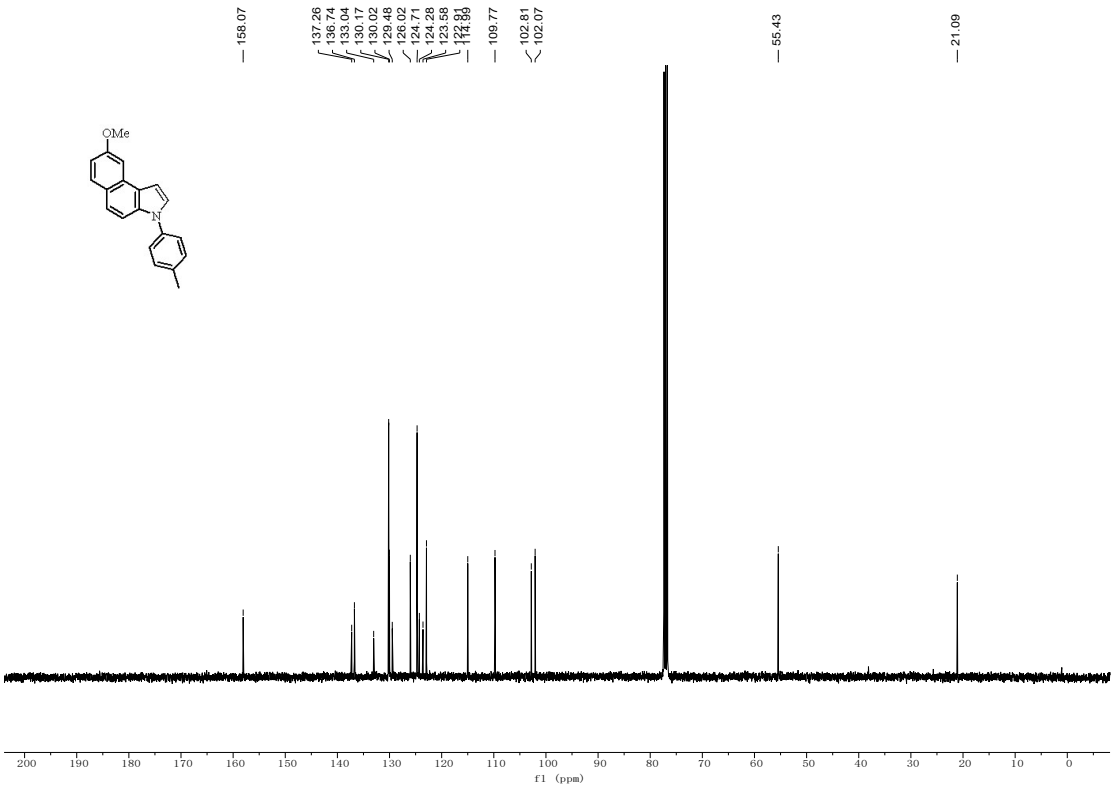
8-methoxy-3-phenyl-3*H*-benzo[*e*]indole (6a).



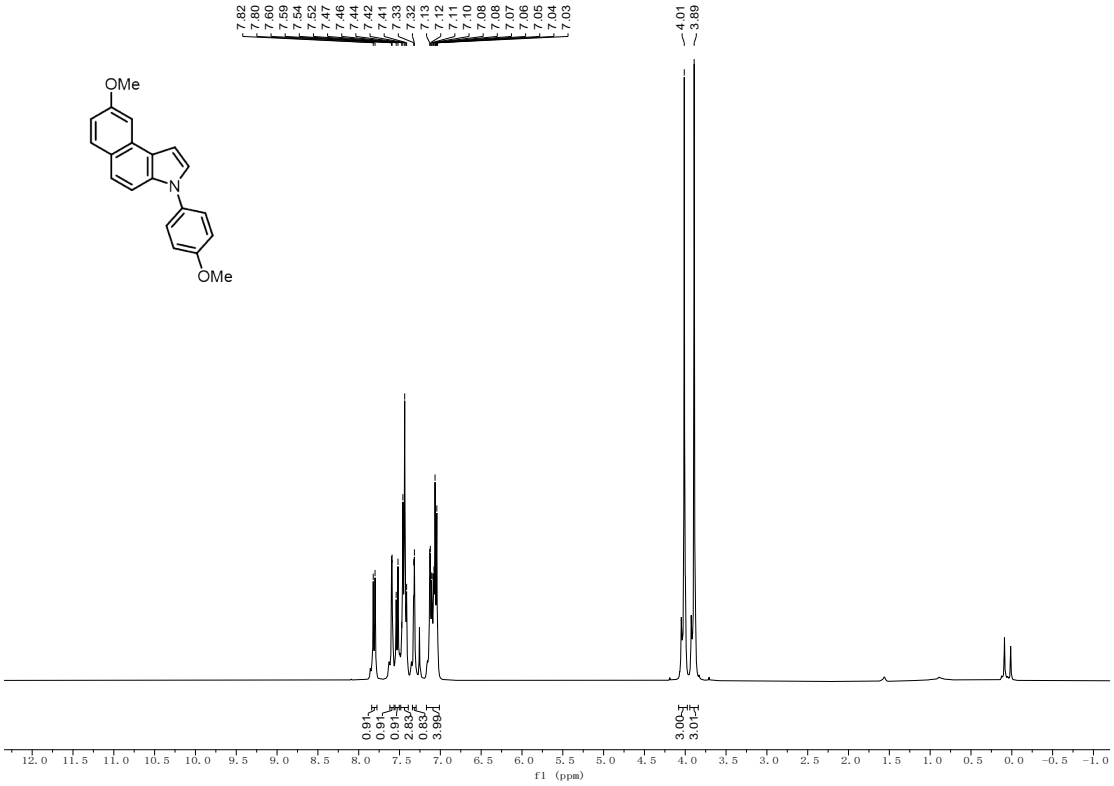


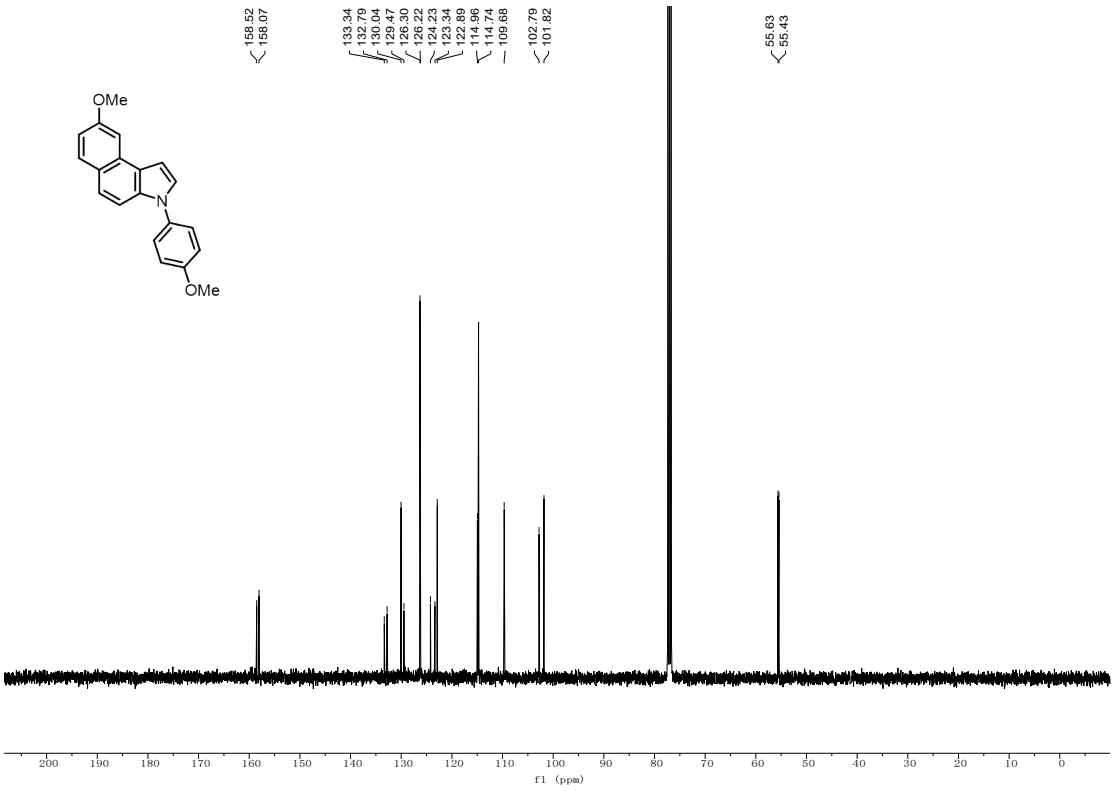
8-methoxy-3-(*p*-tolyl)-3*H*-benzo[*e*]indole (6b).



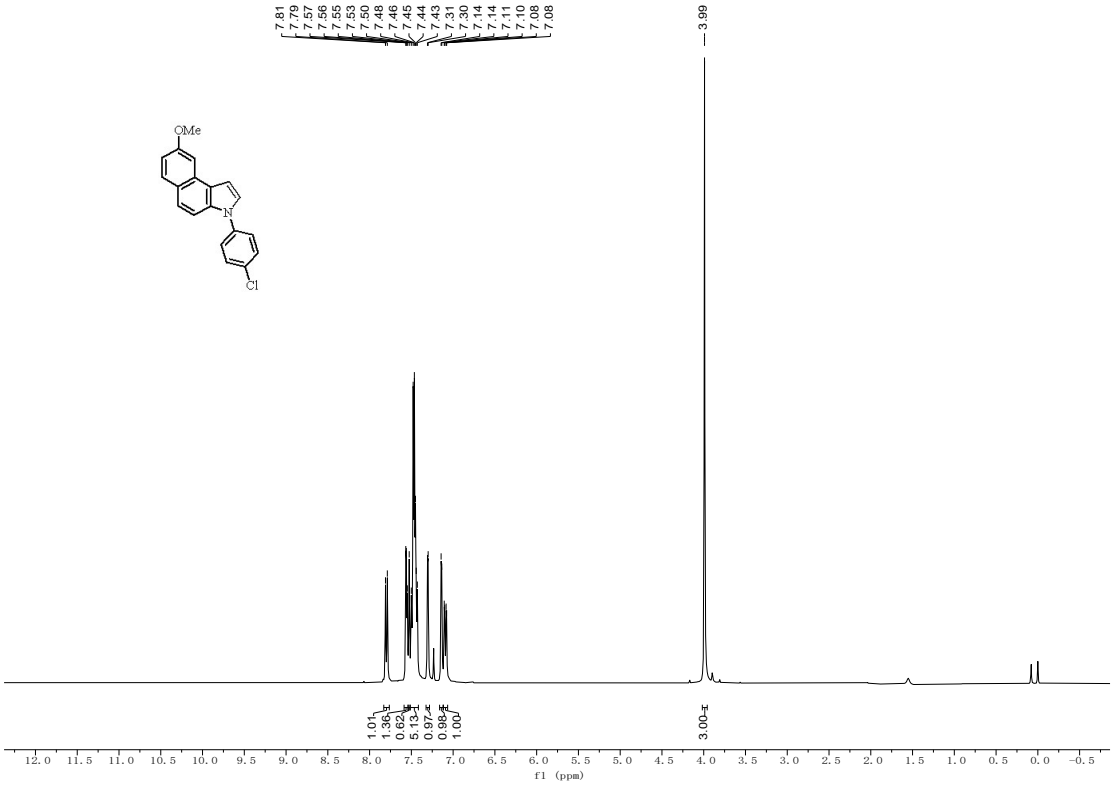


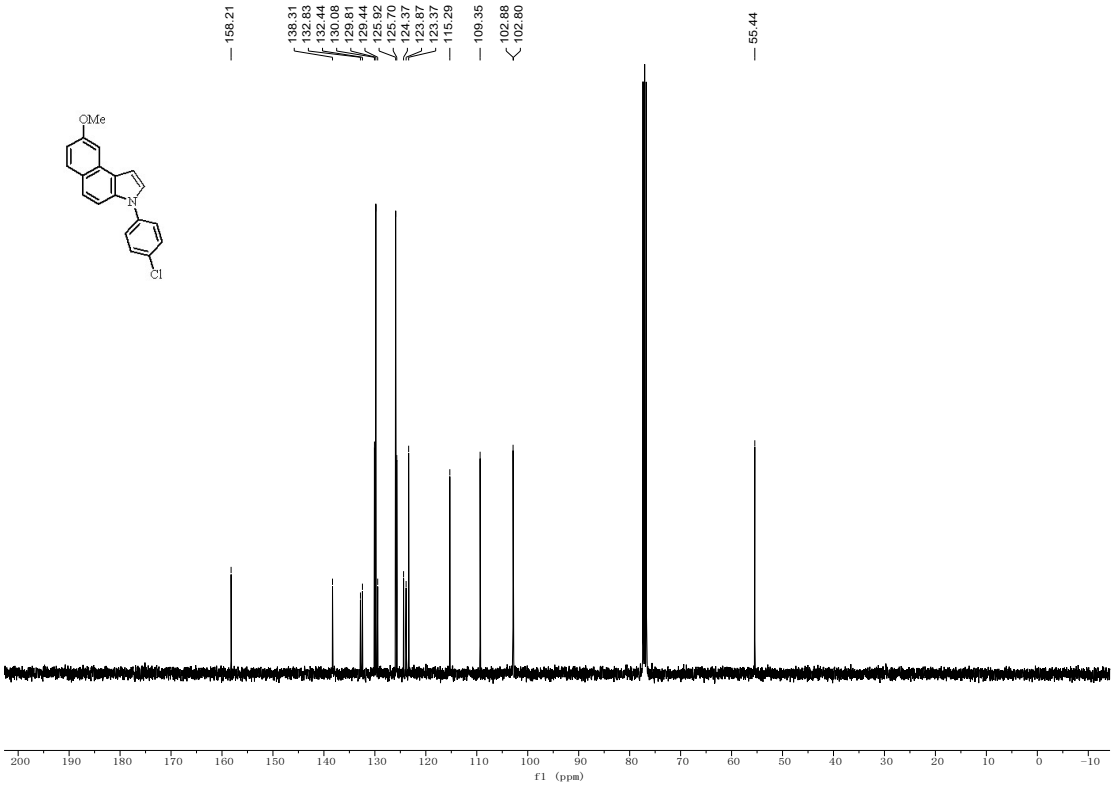
8-methoxy-3-(4-methoxyphenyl)-3*H*-benzo[*e*]indole (6c).



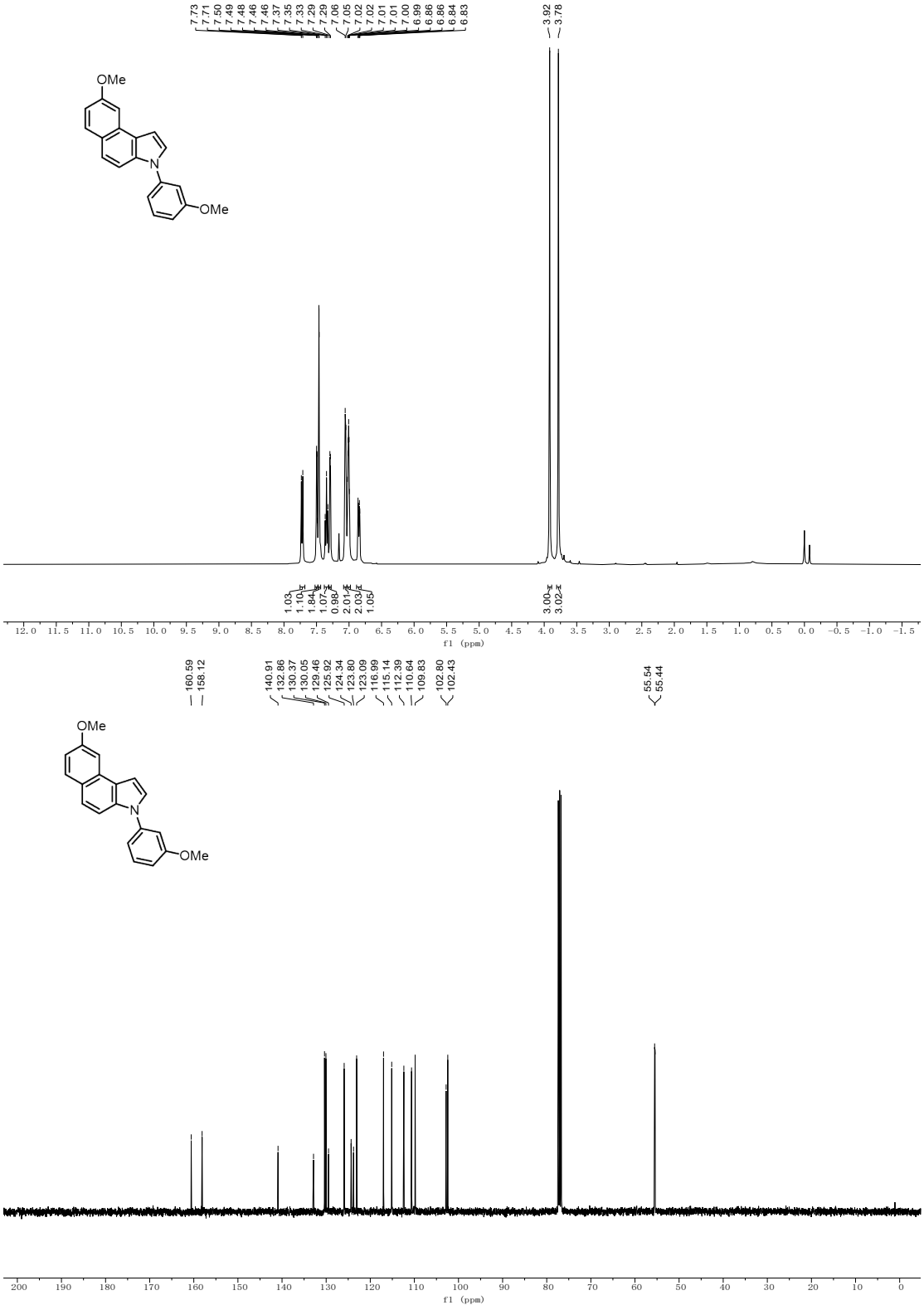


3-(4-chlorophenyl)-8-methoxy-3*H*-benzo[*e*]indole (6d).

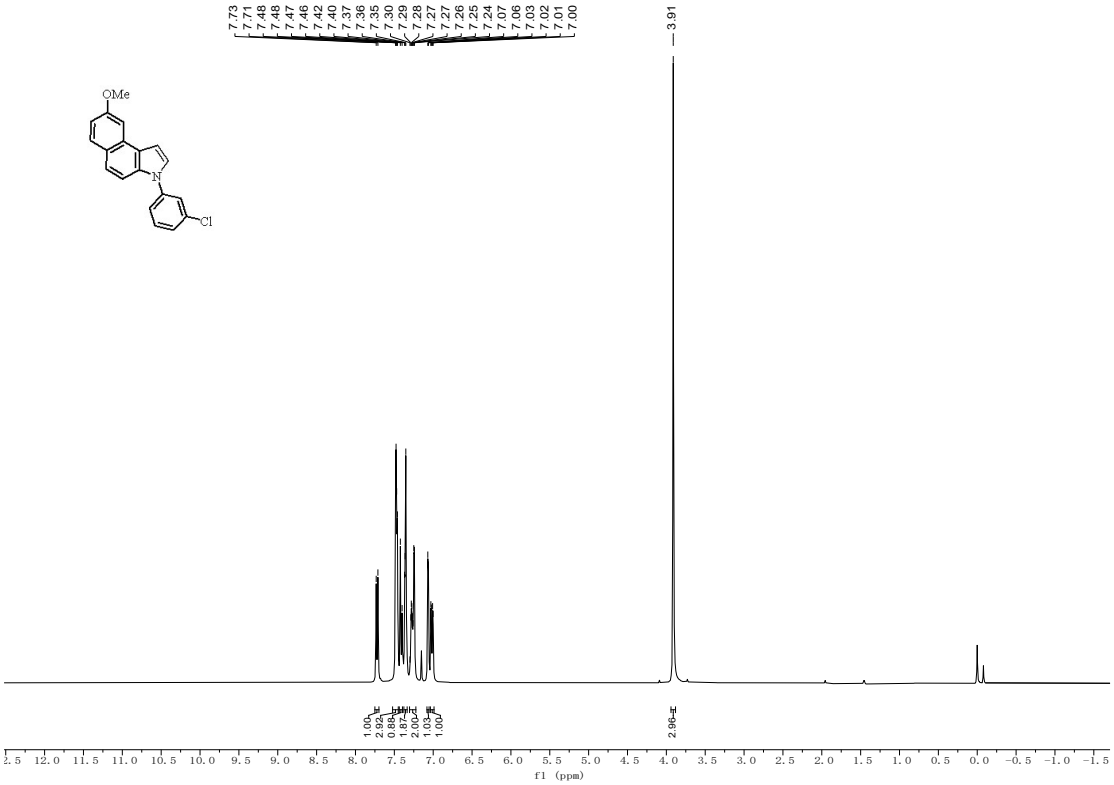


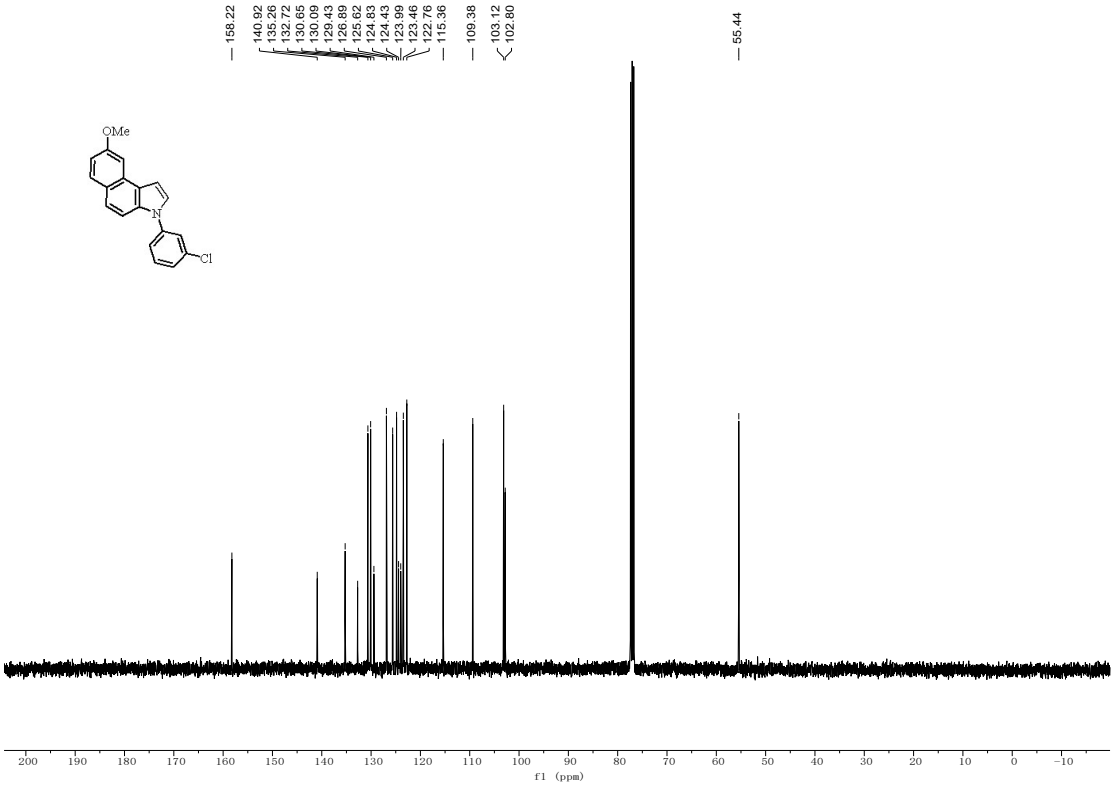


8-methoxy-3-(3-methoxyphenyl)-3*H*-benzo[*e*]indole (6e).

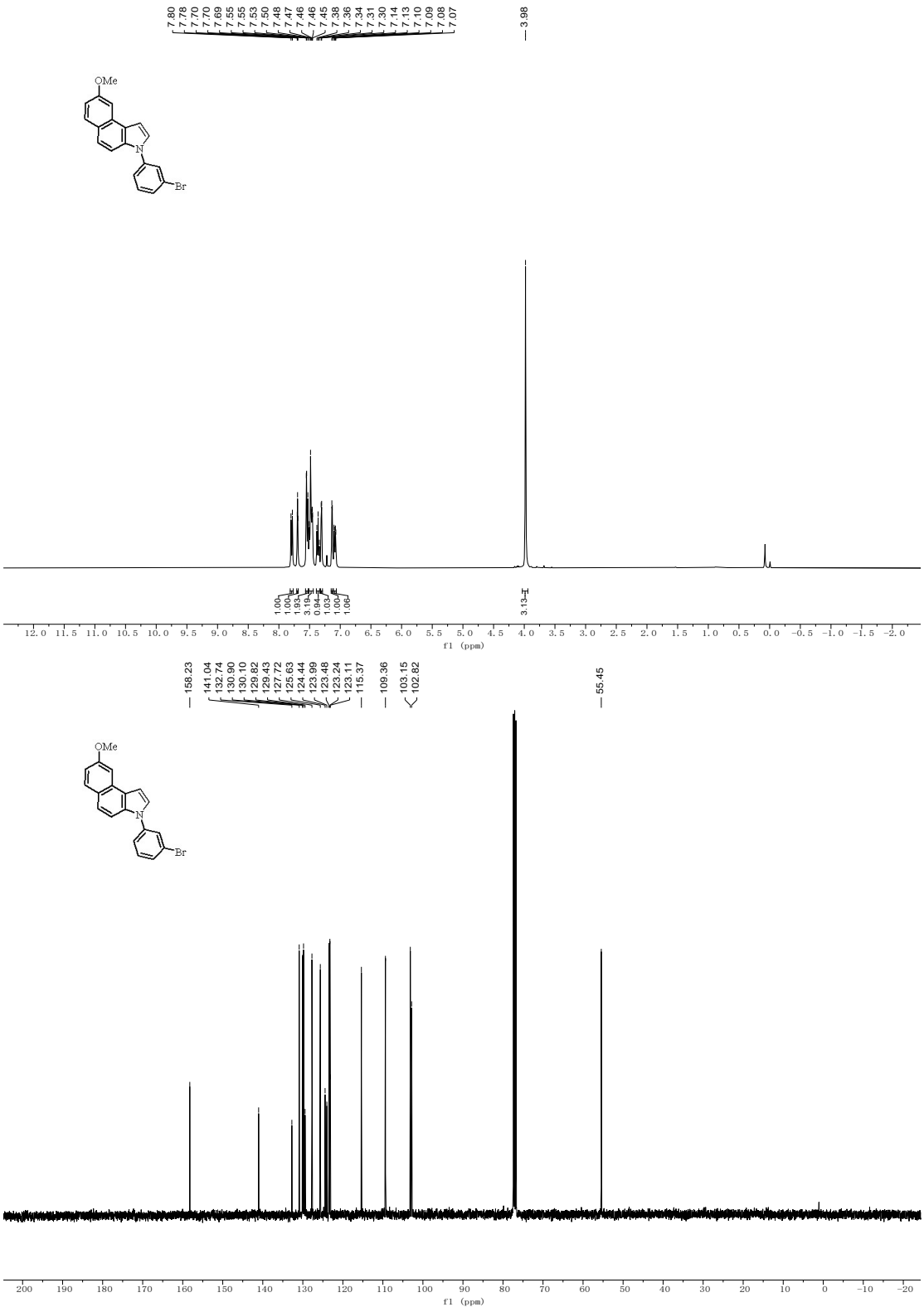


3-(3-chlorophenyl)-8-methoxy-3*H*-benzo[*e*]indole (6f).

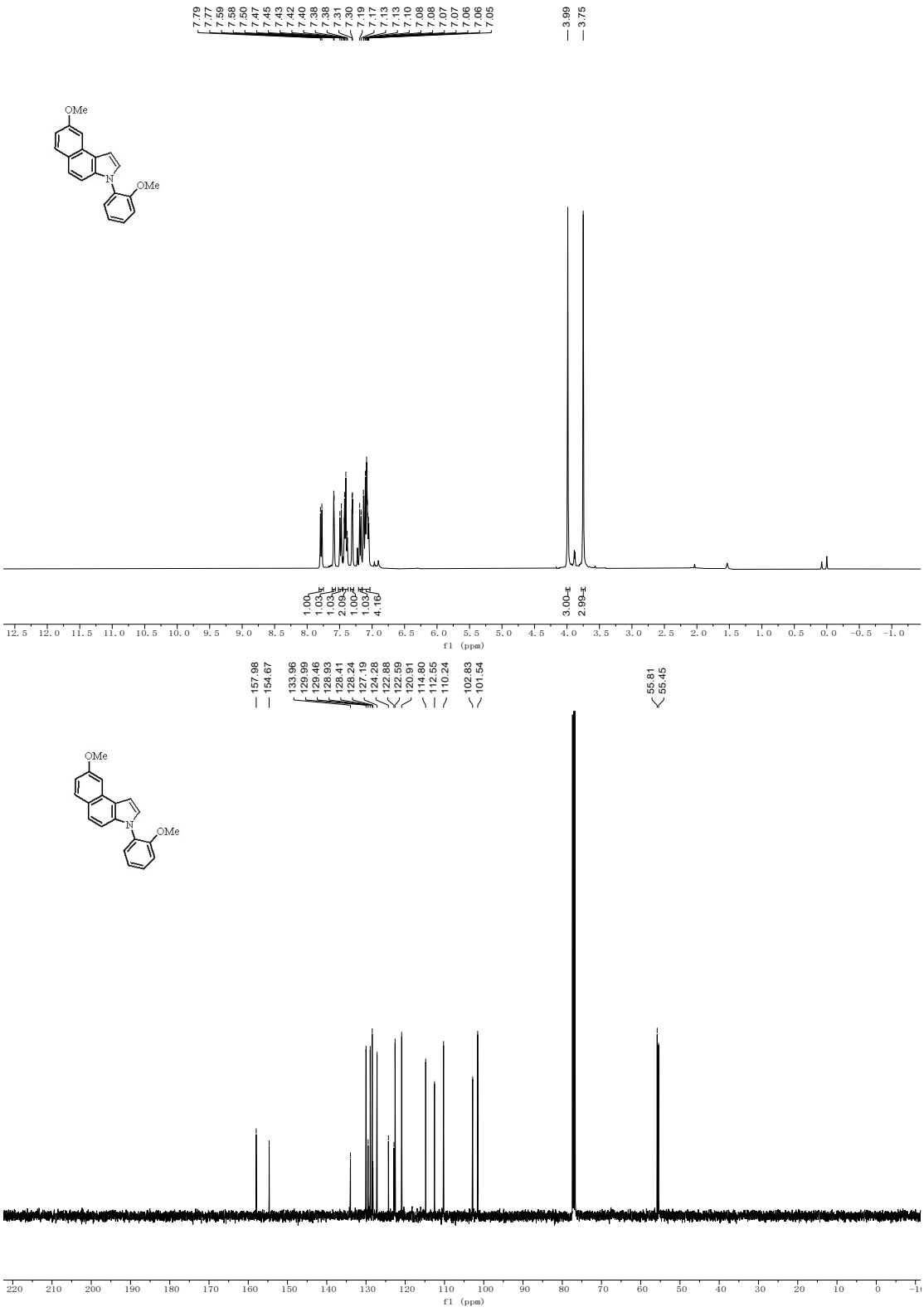




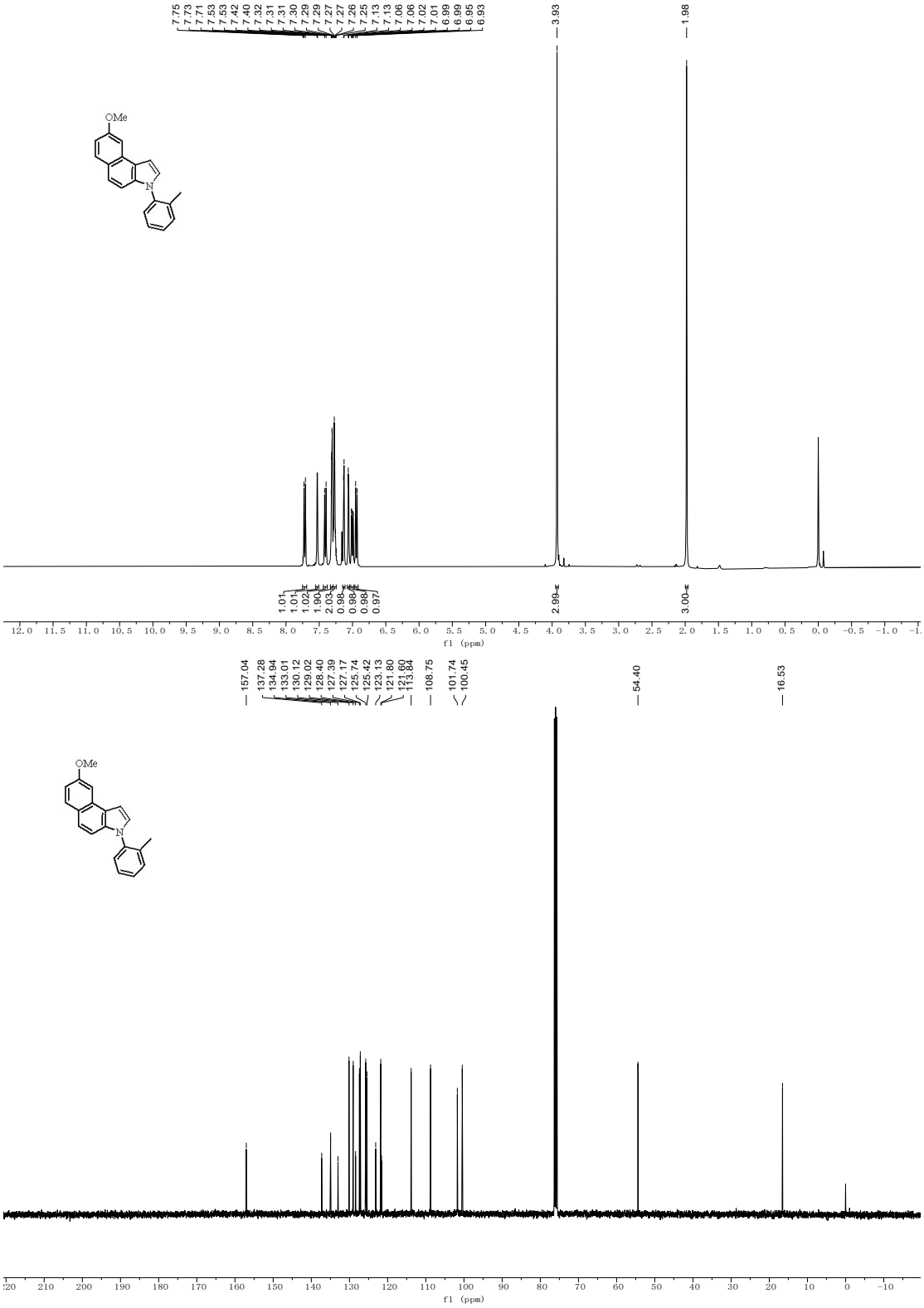
3-(3-bromophenyl)-8-methoxy-3*H*-benzo[*e*]indole (6g).



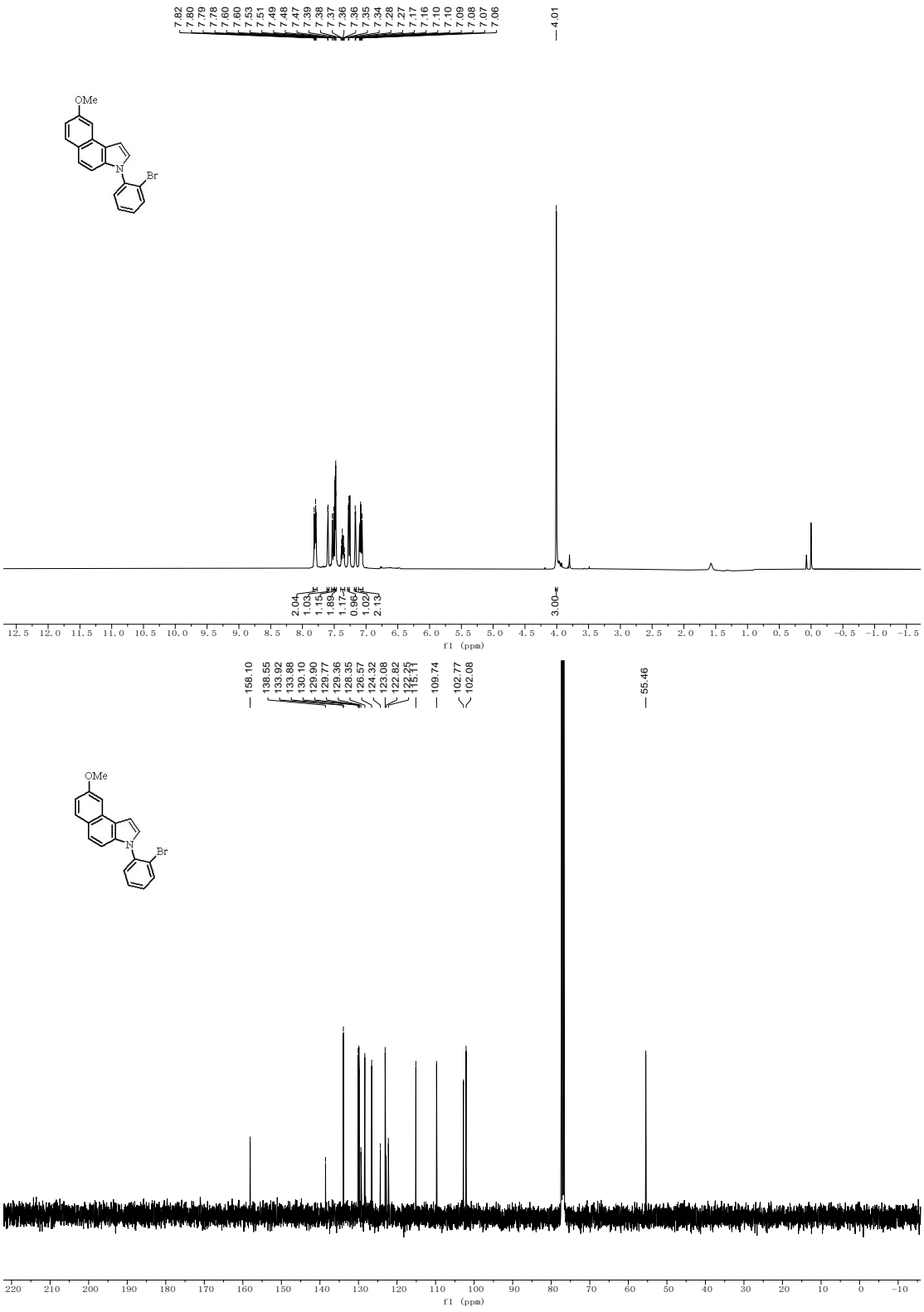
8-methoxy-3-(2-methoxyphenyl)-3*H*-benzo[*e*]indole (6h).



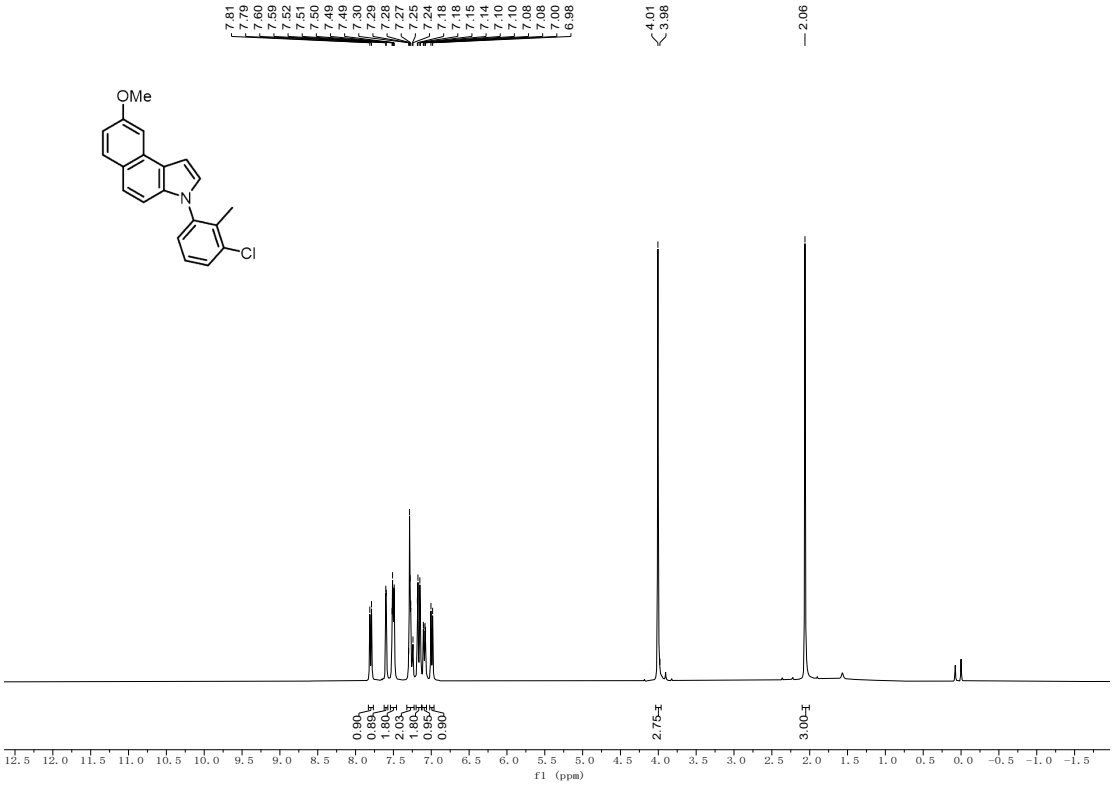
8-methoxy-3-(o-tolyl)-3*H*-benzo[*e*]indole (6i).

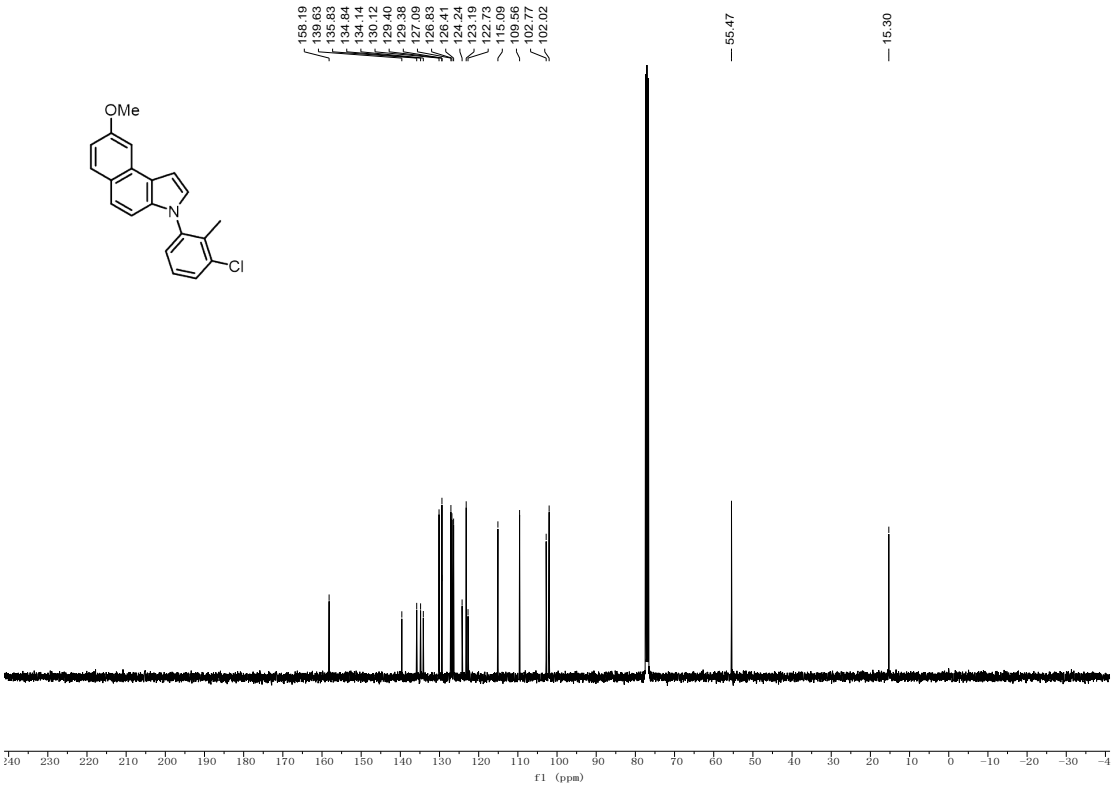


3-(2-bromophenyl)-8-methoxy-3*H*-benzo[*e*]indole (6j).

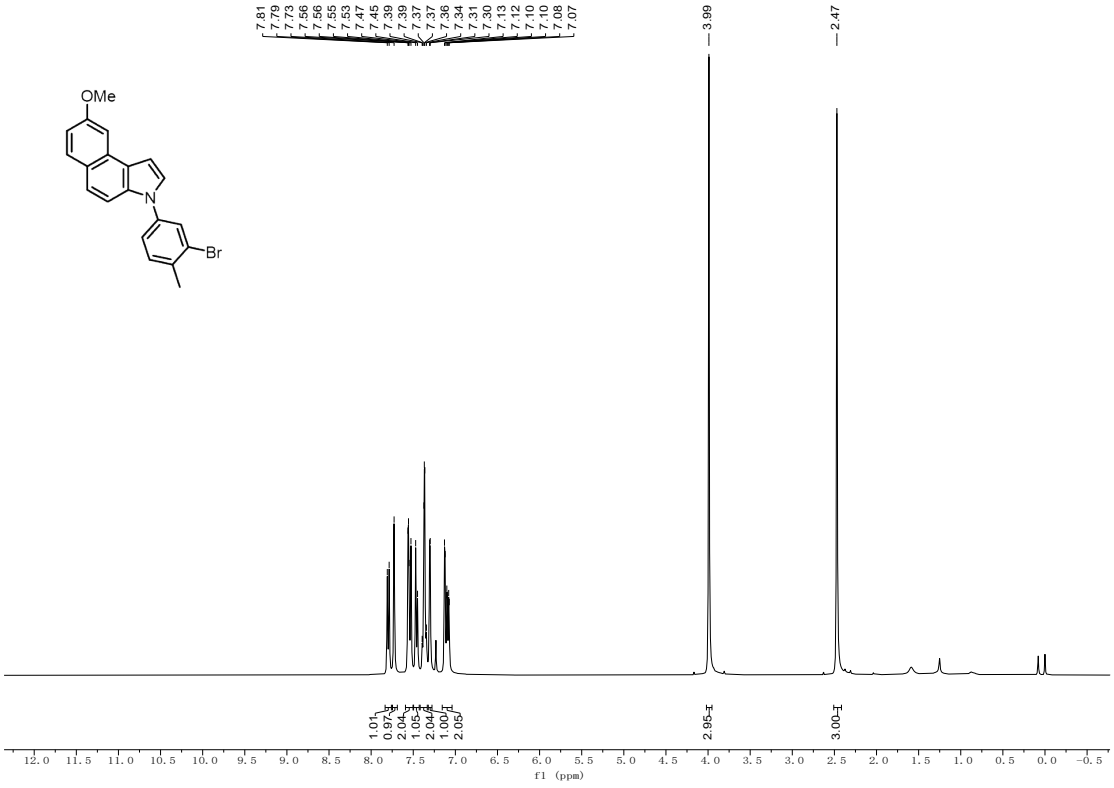


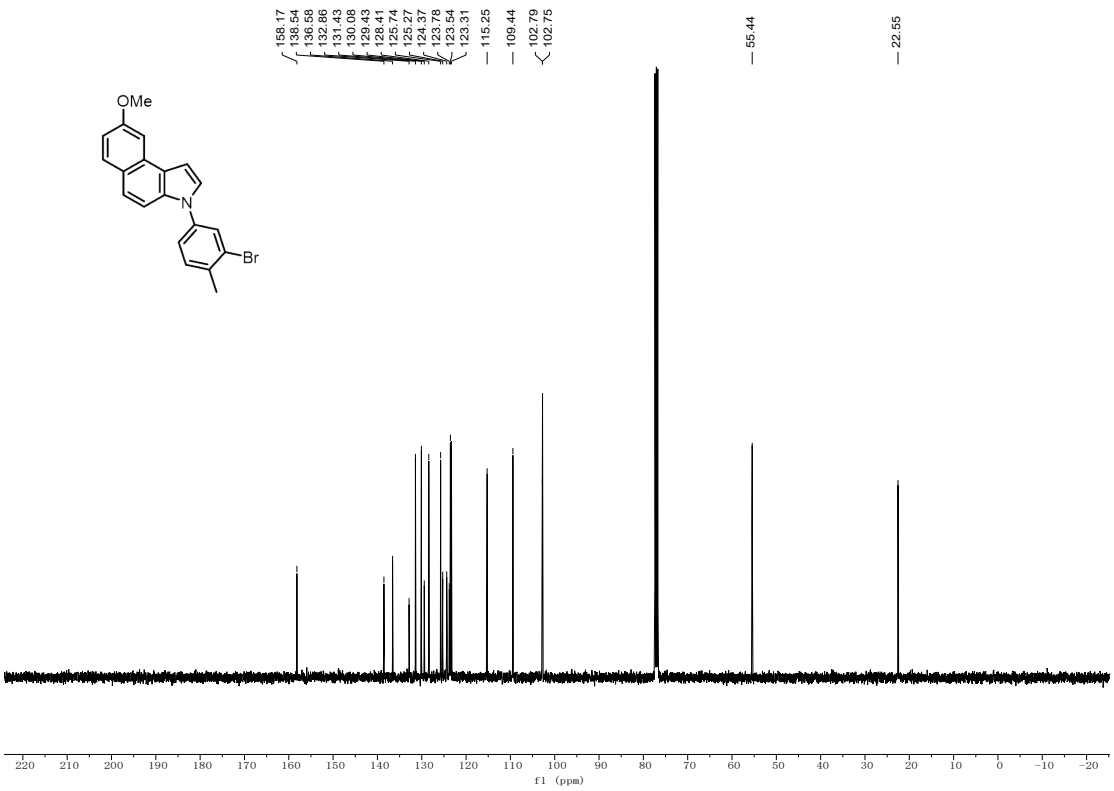
3-(3-chloro-2-methylphenyl)-8-methoxy-3*H*-benzo[*e*]indole (6k).



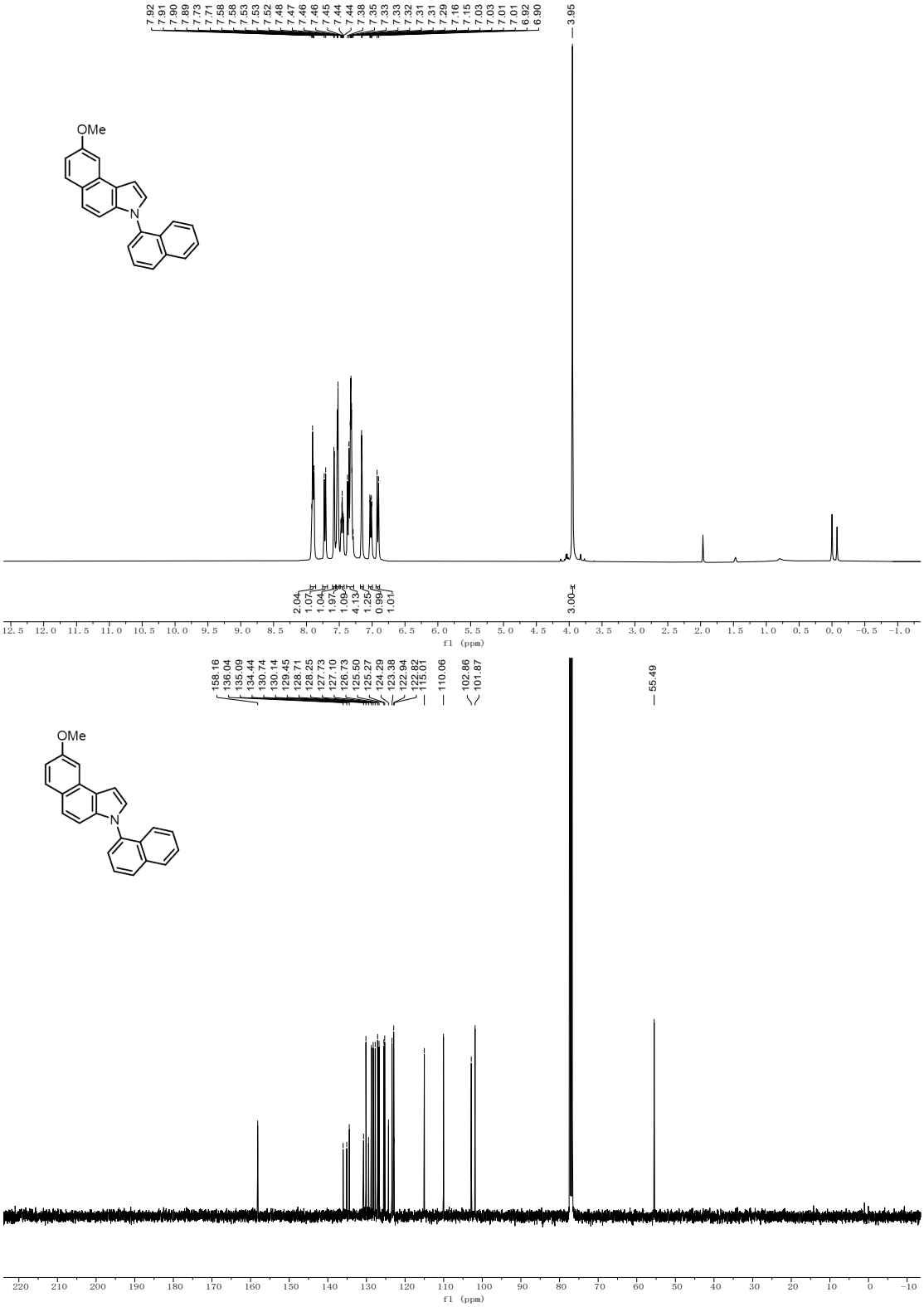


3-(3-bromo-4-methylphenyl)-8-methoxy-3*H*-benzo[*e*]indole (6l).

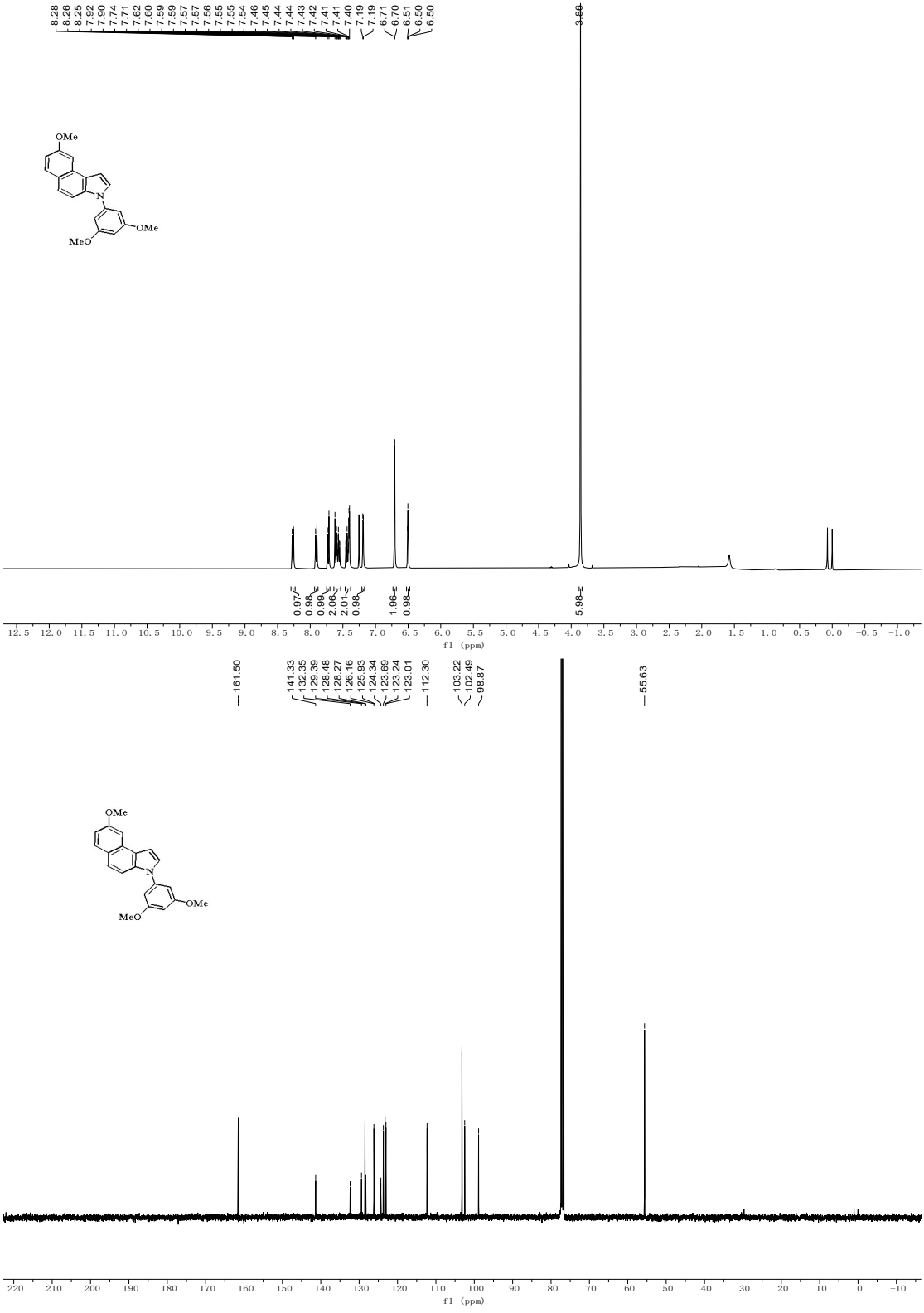




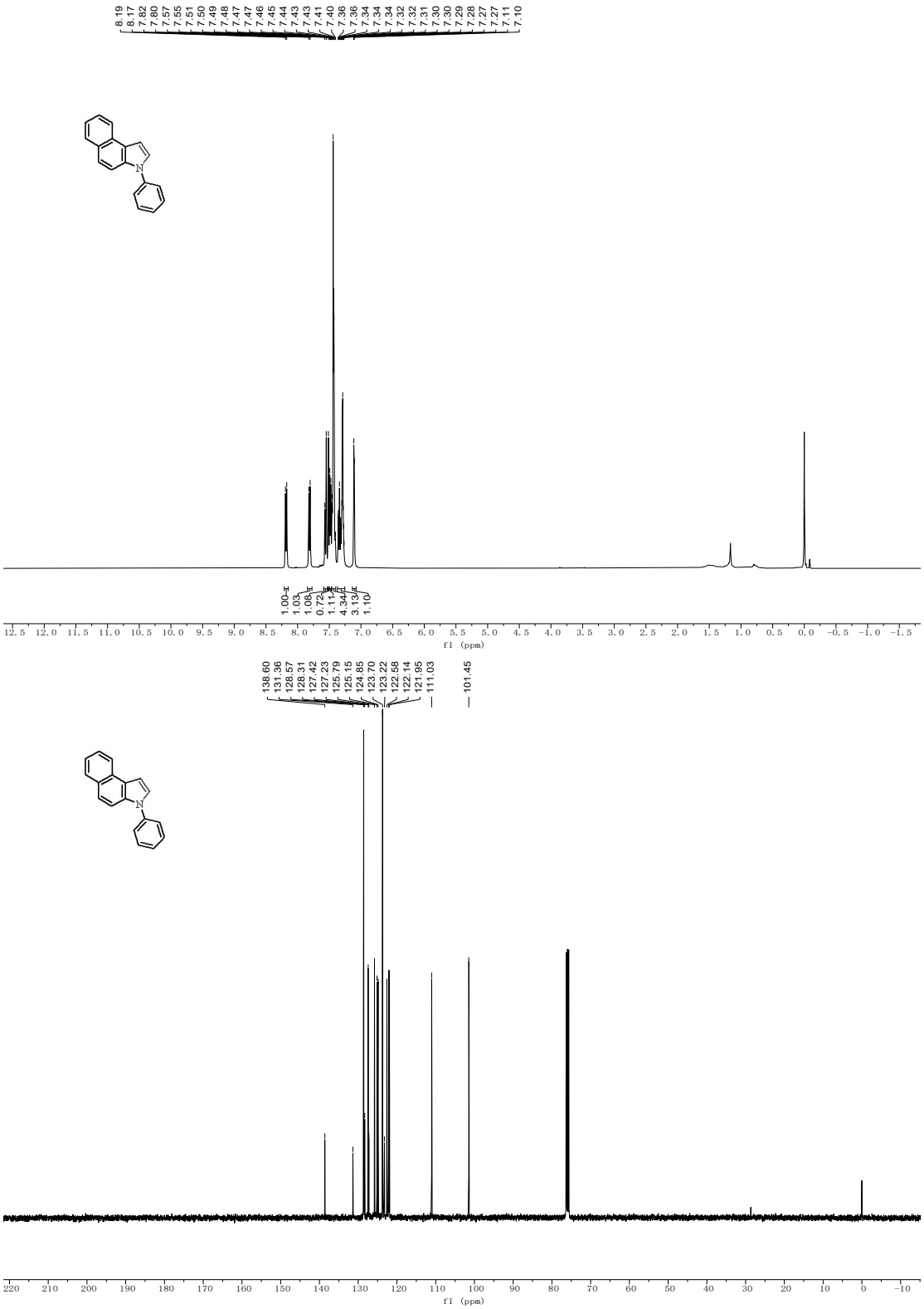
8-methoxy-3-(naphthalen-1-yl)-3*H*-benzo[*e*]indole (6m).



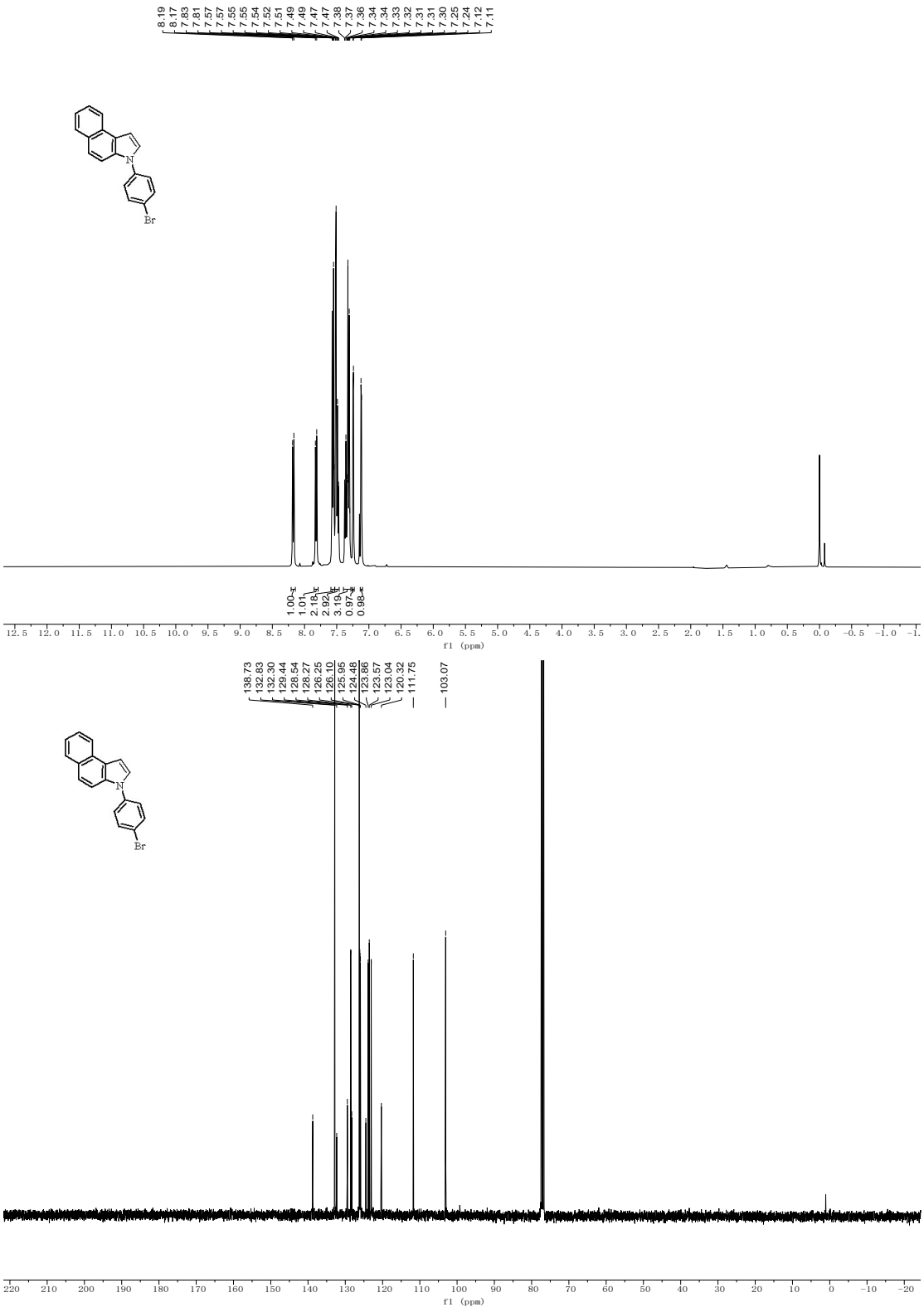
3-(3,5-dimethoxyphenyl)-3*H*-benzo[*e*]indole (6n).



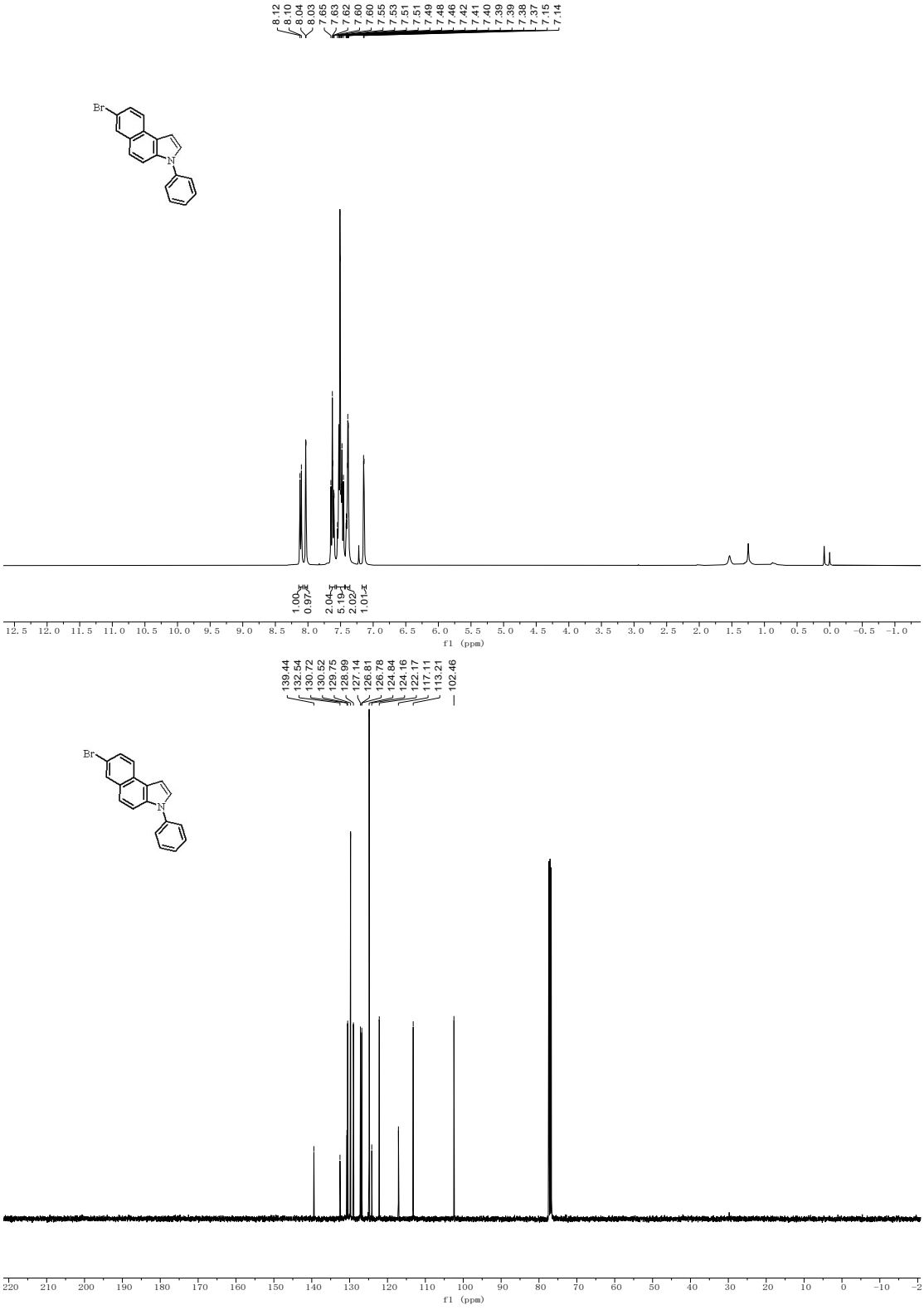
3-phenyl-3*H*-benzo[*e*]indole (6o).



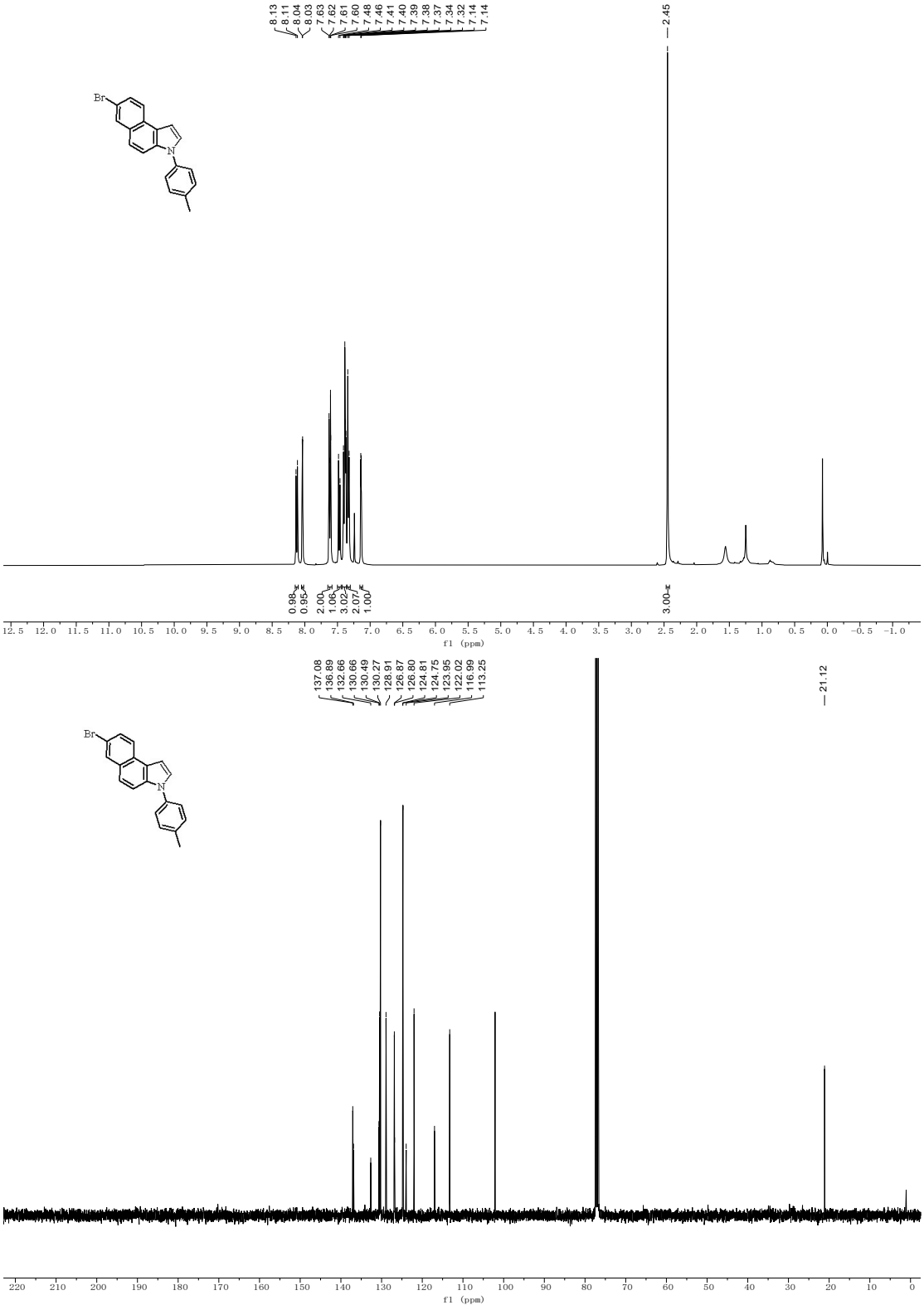
3-(4-bromophenyl)-3*H*-benzo[*e*]indole (6p).



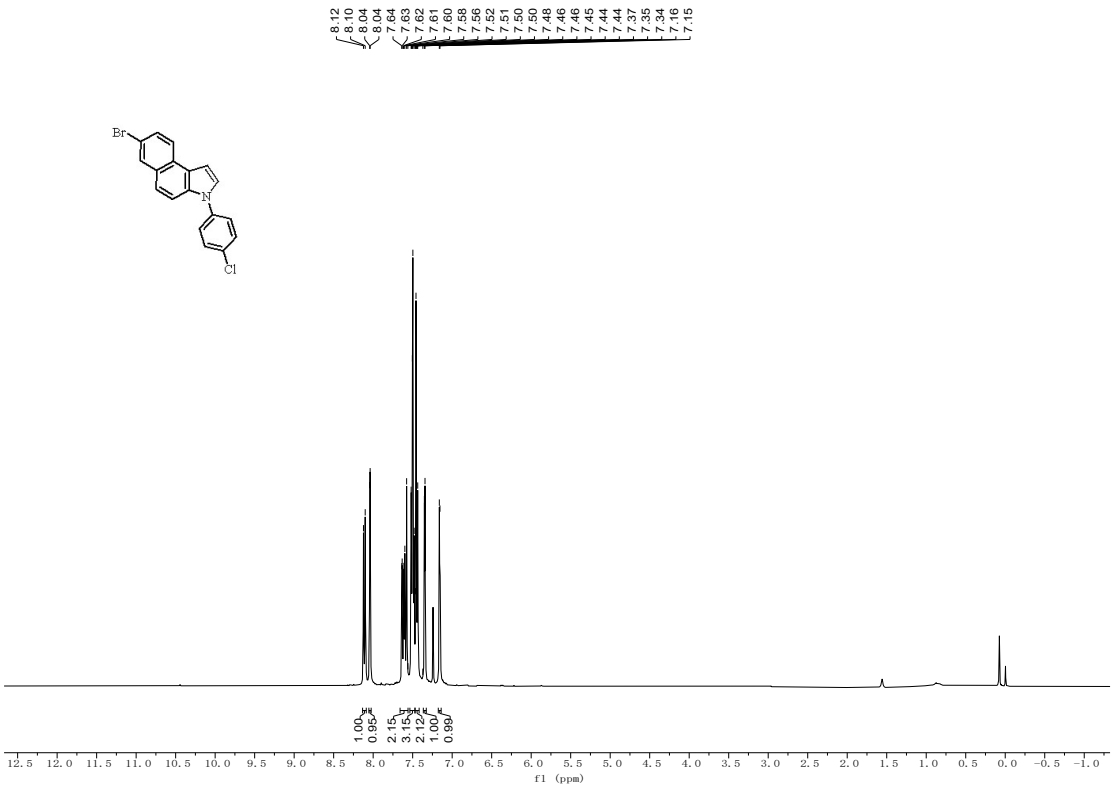
7-bromo-3-phenyl-3*H*-benzo[*e*]indole (6q).

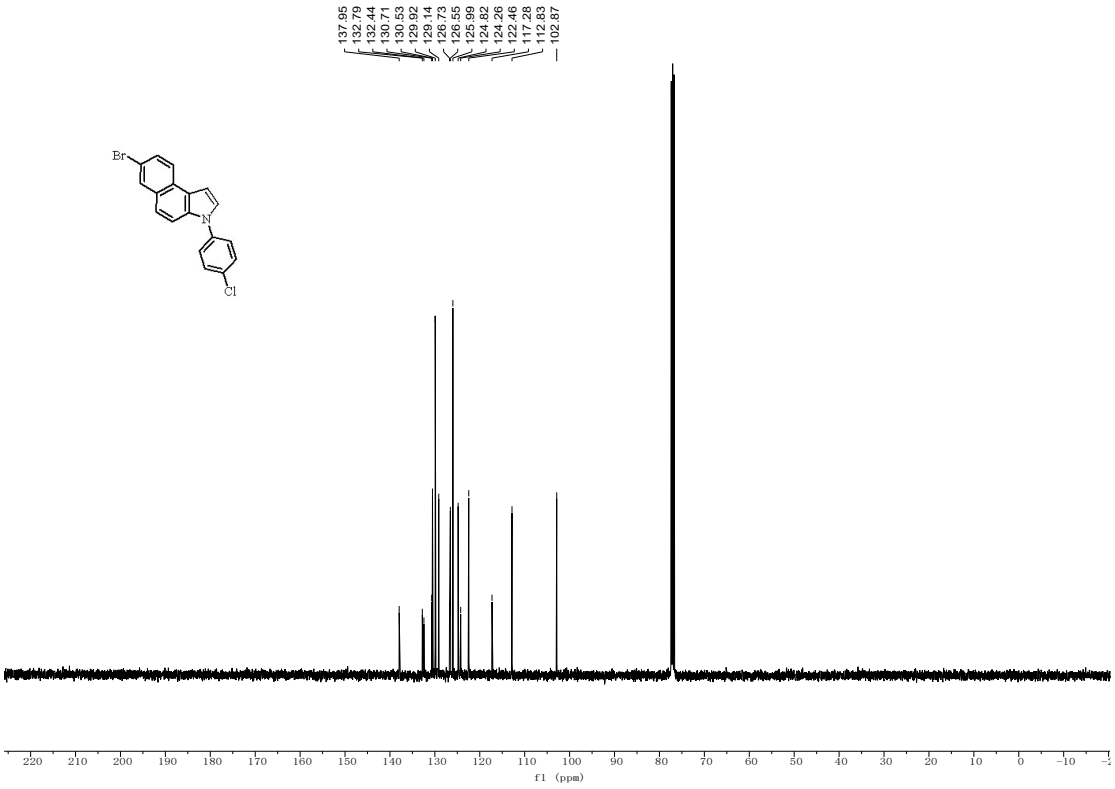


7-bromo-3-(p-tolyl)-3*H*-benzo[*e*]indole (6r).



7-bromo-3-(4-chlorophenyl)-3*H*-benzo[*e*]indole (6s).





(*E*)-7-methoxy-1-(2-methoxyvinyl)-*N*-phenylnaphthalen-2-amine (IV-typed intermediate).