

Organocatalytic Asymmetric [3+2] Cyclization: Enantioselective Synthesis of α -Indolyl Pyrrolo[1,2-a]indole Scaffolds

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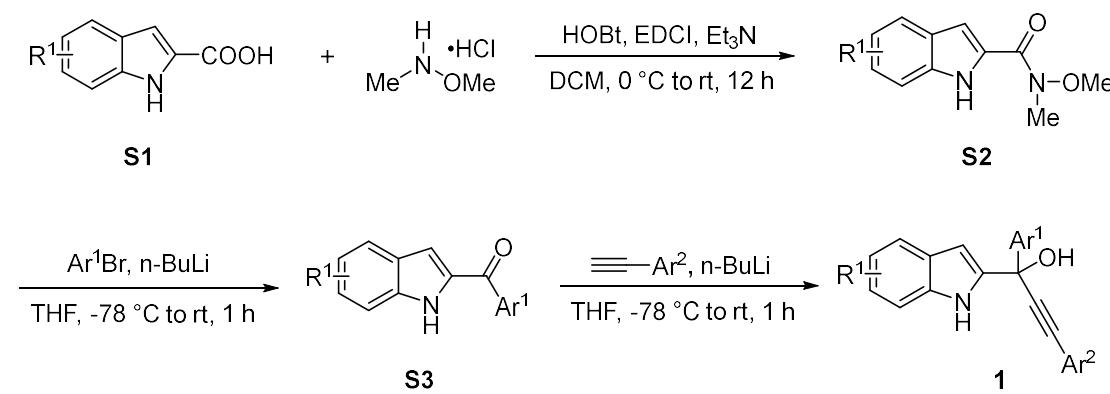
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1. Methods of synthesizing substrates α -indolyl propargylic alcohol 1

Caution! Extreme care should be taken both in the handling of the cryogen liquid nitrogen and its use in the Schlenk line trap to avoid the condensation of oxygen from air.

1,1-Dichloro-1-fluoroethane (CAS 1717-00-6) is a Category 1 ozone depleting agent with a low boiling point (32 °C), high toxicity, and high flammability. Every effort should be made to contain and collect it, as with a cold finger trap, and then it should be disposed of appropriately.



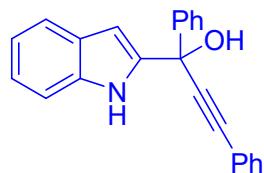
Substrates **S2** and **S3** were prepared according to the general procedure reported by Huang and coworkers.¹¹

Under N₂ at 0 °C, to a round-bottom flask charged with indole-2-carboxylic acid **S1** (25 mmol, 1.0 equiv), 1-hydroxybenzotriazole (HOBr, 336 mg, 2.5 mmol, 0.1 equiv), N,O-dimethylhydroxylamine (2.42 g, 25 mmol, 1.0 equiv), Et₃N (7.0 mL, 50 mmol, 2.0 equiv) and DCM (50 mL) was added a solution of 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDCI, 5.27 g, 27.5 mmol, 1.2 equiv) in DCM (20 mL) dropwise. The mixture was allowed to stir at room temperature for 12 h before it was quenched with water (50 mL), dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography to afford the desired Weinreb amide **S2**.

Under N₂ at -78 °C, to a round-bottom flask charged with the aryl bromide (20 mmol, 2.0 equiv) and THF (20 mL) was added with a solution of n-BuLi in n-hexane (2.5 M, 8 mL,

20.0 mmol, 2.0 equiv) dropwise. The mixture was allowed to stir at -78 °C for 30 min before it was added slowly to a cold solution (-78 °C) of the above Weinreb amide **S2** (10 mmol, 1.0 equiv) in THF (20 mL) via syringe. The resulting mixture was next warm up to room temperature and kept stirring for 1 h before it was quenched with aqueous NH₄Cl solution (20 mL) and extracted with ethyl acetate (30 mL × 3). The combined organic layers were washed with water (30 mL × 2), dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography to afford the desired ketone derivatives **S3**.

Substrates **1** were prepared according to the general procedure reported by Sun and coworkers.⁹ At -78 °C, to a stirred solution of the terminal alkyne (6 mmol, 3.0 equiv) in THF (10 mL) was slowly added n-BuLi (2.5 M in hexane, 2.4 mL, 6 mmol, 3.0 equiv). The resulting mixture was kept stirring at -78 °C for 30 min. Next, a solution of the ketone **S3** (2 mmol, 1.0 equiv) in THF (10 mL) was added. The mixture was slowly warmed to room temperature and then kept stirring overnight. A saturated aqueous solution of NH₄Cl (10 mL) was added to quench the reaction. The reaction mixture was extracted with EtOAc (2 × 10 mL). The combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated. The residue was purified by silica gel flash chromatography to afford the desired substrates **1**.



1-(1H-indol-2-yl)-1,3-diphenylprop-2-yn-1-ol (1a)

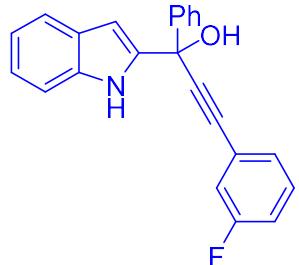
The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 20:1-8:1, v/v) to afford **1a** as a yellow solid, 0.59 g (92% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.35 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.58 – 7.50 (m, 2H), 7.37 (ddt, *J* = 18.5, 12.5, 7.5 Hz, 7H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.62 (s, 1H), 3.11 (s, 1H).

$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) δ 142.9, 141.1, 136.3, 132.0, 129.1, 128.6, 128.5, 127.9, 126.2, 122.6, 122.1, 121.1, 120.2, 111.3, 101.5, 90.0, 87.0, 71.1.

HRMS (ESI-TOF) m/z: $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{23}\text{H}_{18}\text{NO}$ 324.1383; Found: 324.1382.

IR (KBr, cm^{-1}) 3426, 3059, 2229, 1598, 1489, 1455, 1288, 792, 755, 692.



3-(3-fluorophenyl)-1-(1H-indol-2-yl)-1-phenylprop-2-yn-1-ol (1b)

The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 20:1-8:1, v/v) to afford **1b** as a brown solid, 0.60 g (88% yield).

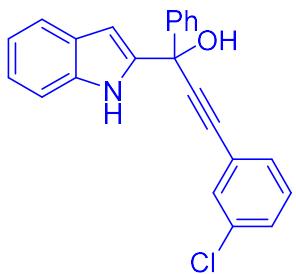
^1H NMR (400 MHz, CDCl_3) δ 8.27 (s, 1H), 7.67 (d, $J = 7.5$ Hz, 2H), 7.55 (d, $J = 7.8$ Hz, 1H), 7.41 – 7.28 (m, 4H), 7.23 – 7.11 (m, 3H), 7.05 (dd, $J = 13.1, 6.6$ Hz, 3H), 6.55 (s, 1H), 3.08 (s, 1H) ppm.

$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) δ 162.4 (d, $J = 247.0$ Hz), 142.6, 140.8, 136.4, 130.2 (d, $J = 8.6$ Hz), 128.7, 127.9, 126.1, 123.9 (d, $J = 9.5$ Hz), 122.7, 121.1, 120.2, 118.8 (d, $J = 23.0$ Hz), 116.5 (d, $J = 21.1$ Hz), 111.3, 101.6, 90.9, 85.7, 71.0.

$^{19}\text{F}\{\text{H}\}$ NMR (376 MHz, CDCl_3) δ 112.15.

HRMS (ESI-TOF) m/z: $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{23}\text{H}_{17}\text{FNO}$ 342.1289; Found: 342.1288.

IR (KBr, cm^{-1}) 3423, 3062, 2230, 1607, 1581, 1486, 1288, 964, 872, 786.



3-(3-chlorophenyl)-1-(1H-indol-2-yl)-1-phenylprop-2-yn-1-ol (1c)

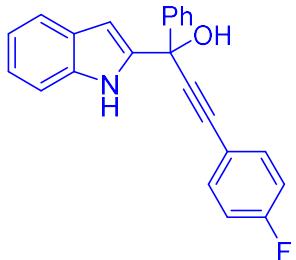
The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 20:1-8:1, v/v) to afford **1c** as a brown solid, 0.64 g (89% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.31 (s, 1H), 7.72 (d, *J* = 7.7 Hz, 2H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.52 (s, 1H), 7.35 (ddd, *J* = 34.4, 14.4, 7.2 Hz, 7H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.60 (s, 1H), 3.10 (s, 1H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 142.6, 140.8, 136.4, 134.4, 131.8, 130.1, 129.8, 129.4, 128.7, 127.9, 126.1, 123.8, 122.7, 121.1, 120.2, 111.3, 101.6, 91.2, 85.5, 71.0.

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₃H₁₇ClNO 358.0993; Found: 358.0978.

IR (KBr, cm⁻¹) 3432, 3062, 2229, 1592, 1561, 1288, 878, 846, 786, 752.



3-(4-fluorophenyl)-1-(1H-indol-2-yl)-1-phenylprop-2-yn-1-ol (1d)

The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 20:1-8:1, v/v) to afford **1d** as a yellow solid, 0.59 g (87% yield).

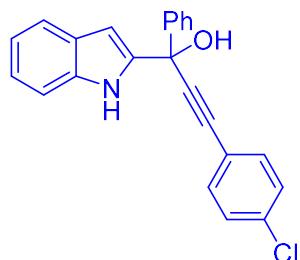
¹H NMR (400 MHz, CDCl₃) δ 8.34 (s, 1H), 7.73 (d, *J* = 7.7 Hz, 2H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.54 – 7.47 (m, 2H), 7.39 (dt, *J* = 11.8, 7.0 Hz, 3H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.05 (t, *J* = 7.9 Hz, 2H), 6.60 (s, 1H), 3.14 (s, 1H).

$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) δ 163.0 (d, $J = 250.4$ Hz), 142.8, 141.0, 136.4, 134.0 (d, $J = 8.5$ Hz), 128.6, 128.6, 127.9, 126.1, 122.7, 121.1, 120.2, 118.2, 115.9 (d, $J = 22.1$ Hz), 111.3, 101.5, 89.8, 85.9, 71.1.

$^{19}\text{F}\{\text{H}\}$ NMR (376 MHz, CDCl_3) δ 109.73.

HRMS (ESI-TOF) m/z: $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{23}\text{H}_{17}\text{FNO}$ 342.1289; Found: 342.1286.

IR (KBr, cm^{-1}) 3420, 3059, 2229, 1601, 1506, 1455, 1288, 1231, 697, 531.



3-(4-chlorophenyl)-1-(1H-indol-2-yl)-1-phenylprop-2-yn-1-ol (1e)

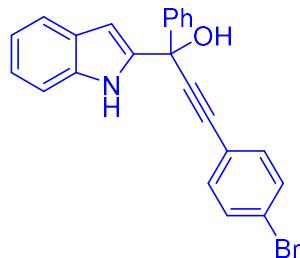
The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 20:1-8:1, v/v) to afford **1e** as a brown solid, 0.57 g (80% yield).

^1H NMR (400 MHz, CDCl_3) δ 8.33 (s, 1H), 7.72 (d, $J = 7.4$ Hz, 2H), 7.60 (d, $J = 7.7$ Hz, 1H), 7.41 (dt, $J = 17.5, 9.1$ Hz, 5H), 7.33 (d, $J = 8.2$ Hz, 3H), 7.20 (t, $J = 7.4$ Hz, 1H), 7.12 (t, $J = 7.4$ Hz, 1H), 6.60 (s, 1H), 3.14 (s, 1H).

$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) δ 142.7, 140.9, 136.4, 135.2, 133.2, 128.9, 128.6, 128.6, 127.9, 126.1, 122.7, 121.1, 120.5, 120.2, 111.3, 101.6, 91.0, 85.8, 71.1.

HRMS (ESI-TOF) m/z: $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{23}\text{H}_{17}\text{ClNO}$ 358.0993; Found: 358.0974.

IR (KBr, cm^{-1}) 3432, 3059, 2229, 1592, 1489, 1452, 1291, 829, 795, 746.



3-(4-bromophenyl)-1-(1H-indol-2-yl)-1-phenylprop-2-yn-1-ol (1f)

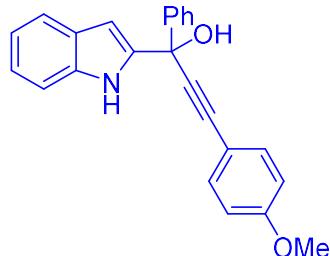
In the third step of the synthesis reaction ($S3 \rightarrow 1$), LDA is used instead of n-BuLi. The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 20:1-8:1, v/v) to afford **1f** as a white solid, 0.75 g (93% yield).

^1H NMR (400 MHz, CDCl₃) δ 8.31 (s, 1H), 7.72 (d, *J* = 7.9 Hz, 2H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 7.9 Hz, 2H), 7.44 – 7.34 (m, 5H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.60 (s, 1H), 3.10 (s, 1H).

$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl₃) δ 142.6, 140.8, 136.4, 133.4, 131.8, 128.6, 127.9, 126.1, 123.4, 122.7, 121.1, 121.0, 120.2, 111.3, 101.6, 91.2, 85.9, 71.1.

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₃H₁₇BrNO 404.0468; Found: 404.0470.

IR (KBr, cm⁻¹) 3426, 3059, 2229, 1486, 1452, 1288, 1070, 1010, 792, 743.



1-(1H-indol-2-yl)-3-(4-methoxyphenyl)-1-phenylprop-2-yn-1-ol (1g)

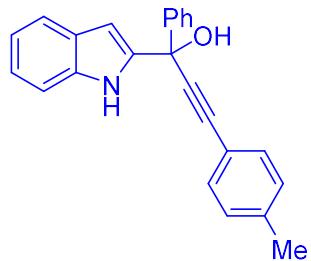
The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 20:1-4:1, v/v) to afford **1g** as a white solid, 0.54 g (76% yield).

^1H NMR (400 MHz, DMSO-d₆) δ 11.03 (s, 1H), 7.70 (d, *J* = 8.1 Hz, 2H), 7.48 (t, *J* = 8.3 Hz, 3H), 7.32 (ddd, *J* = 29.7, 14.6, 7.2 Hz, 4H), 7.08 – 6.90 (m, 5H), 6.40 (s, 1H), 3.78 (s, 3H).

$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, DMSO-d₆) δ 159.6, 144.9, 143.3, 136.6, 133.0, 128.0, 127.4, 127.2, 125.9, 121.1, 120.1, 118.9, 114.4, 114.0, 111.5, 98.9, 90.9, 84.8, 69.7, 55.3.

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₄H₂₀NO₂ 354.1489; Found: 354.1510.

IR (KBr, cm⁻¹) 3423, 3059, 2227, 1604, 1509, 1455, 1291, 1245, 752, 697.



1-(1H-indol-2-yl)-1-phenyl-3-(p-tolyl)prop-2-yn-1-ol (1h)

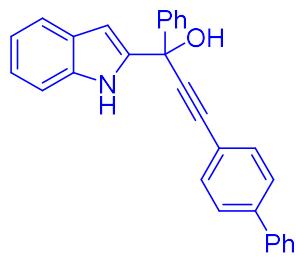
The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 20:1-8:1, v/v) to afford **1h** as a white solid, 0.58 g (86% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.35 (s, 1H), 7.75 (d, *J* = 7.6 Hz, 2H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.38 (ddd, *J* = 30.3, 15.8, 7.8 Hz, 6H), 7.15 (tt, *J* = 14.8, 7.3 Hz, 4H), 6.60 (s, 1H), 3.09 (s, 1H), 2.38 (s, 3H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 143.0, 141.3, 139.3, 136.3, 131.9, 129.3, 128.6, 128.5, 128.0, 126.2, 122.6, 121.1, 120.1, 119.0, 111.3, 101.4, 89.4, 87.2, 71.1, 21.7.

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₄H₂₀NO 338.1539; Found: 338.1540.

IR (KBr, cm⁻¹) 3423, 3059, 2924, 2224, 1509, 1449, 1277, 818, 749, 697.



3-([1,1'-biphenyl]-4-yl)-1-(1H-indol-2-yl)-1-phenylprop-2-yn-1-ol (1i)

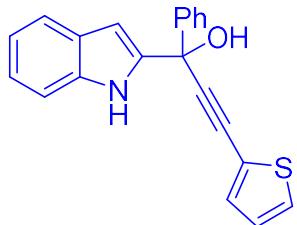
The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 20:1-8:1, v/v) to afford **1i** as a yellow solid, 0.68 g (85% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.36 (s, 1H), 7.77 (d, *J* = 7.2 Hz, 2H), 7.61 (d, *J* = 7.7 Hz, 7H), 7.41 (ddt, *J* = 31.2, 18.2, 7.8 Hz, 7H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.13 (t, *J* = 7.2 Hz, 1H), 6.63 (s, 1H), 3.11 (s, 1H).

$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) δ 142.9, 141.8, 141.1, 140.3, 136.4, 132.4, 129.0, 128.6, 128.5, 127.9, 127.2, 126.2, 122.6, 121.1, 120.9, 120.2, 111.3, 101.5, 90.7, 86.9, 71.2.

HRMS (ESI-TOF) m/z: $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{29}\text{H}_{22}\text{NO}$ 400.1696; Found: 400.1715.

IR (KBr, cm^{-1}) 3423, 3059, 2227, 1486, 1340, 1291, 1019, 795, 763, 697.



1-(1H-indol-2-yl)-1-phenyl-3-(thiophen-2-yl)prop-2-yn-1-ol (1j)

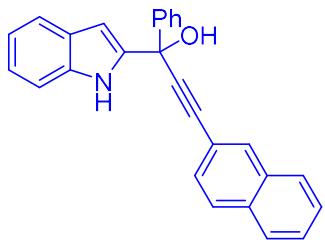
The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 20:1-8:1, v/v) to afford **1j** as a brown solid, 0.55 g (83% yield).

^1H NMR (400 MHz, CDCl_3) δ 8.34 (s, 1H), 7.74 (d, $J = 7.9$ Hz, 2H), 7.60 (d, $J = 7.8$ Hz, 1H), 7.57 – 7.49 (m, 1H), 7.40 (td, $J = 11.2, 9.4, 4.5$ Hz, 3H), 7.33 – 7.26 (m, 2H), 7.19 (d, $J = 5.1$ Hz, 2H), 7.12 (t, $J = 7.4$ Hz, 1H), 6.59 (s, 1H), 3.11 (s, 1H).

$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) δ 142.8, 141.1, 136.3, 130.0, 129.9, 128.6, 128.5, 127.9, 126.2, 125.7, 122.6, 121.1, 120.2, 111.3, 101.5, 89.7, 82.2, 71.1.

HRMS (ESI-TOF) m/z: $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{16}\text{NOS}$ 330.0947; Found: 330.0943.

IR (KBr, cm^{-1}) 3426, 3108, 3059, 2227, 1489, 1455, 1288, 964, 869, 7752



1-(1H-indol-2-yl)-3-(naphthalen-2-yl)-1-phenylprop-2-yn-1-ol (1k)

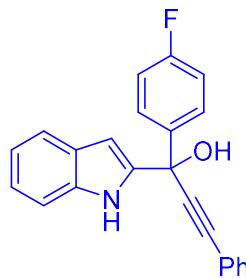
The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 20:1-8:1, v/v) to afford **1k** as a yellow solid, 0.60 g (80% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.38 (s, 1H), 8.06 (s, 1H), 7.86 – 7.75 (m, 5H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.56 (dd, *J* = 8.5, 1.3 Hz, 1H), 7.52 (dd, *J* = 6.2, 3.2 Hz, 2H), 7.39 (dq, *J* = 22.9, 8.2, 7.6 Hz, 4H), 7.23 – 7.17 (m, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.65 (d, *J* = 1.2 Hz, 1H), 3.14 (s, 1H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 142.9, 141.2, 136.4, 133.2, 133.0, 132.2, 128.6, 128.5, 128.4, 128.2, 128.0, 127.1, 126.8, 126.2, 122.6, 121.1, 120.2, 119.3, 111.3, 101.5, 90.3, 87.3, 71.2.

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₇H₂₀NO 374.1539; Found: 374.1547.

IR (KBr, cm⁻¹) 3423, 3056, 2224, 1595, 1455, 1288, 1019, 861, 798, 749.



1-(4-fluorophenyl)-1-(1H-indol-2-yl)-3-phenylprop-2-yn-1-ol (1l)

The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 20:1-8:1, v/v) to afford **1l** as a white solid, 0.60 g (88% yield).

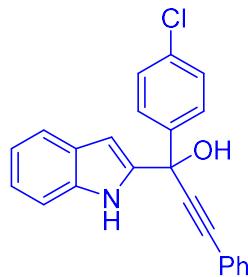
¹H NMR (400 MHz, CDCl₃) δ 8.33 (s, 1H), 7.74 – 7.64 (m, 2H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.52 – 7.47 (m, 2H), 7.37 – 7.29 (m, 4H), 7.21 – 7.16 (m, 1H), 7.11 (d, *J* = 7.9 Hz, 1H), 7.08 – 7.02 (m, 2H), 6.56 (d, *J* = 2.1 Hz, 1H), 3.15 (s, 1H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 162.8 (d, *J* = 247.2 Hz), 141.0, 138.8 (d, *J* = 3.2 Hz), 136.4, 132.0, 129.2, 128.6, 128.1 (d, *J* = 8.3 Hz), 127.9, 122.8, 121.9, 121.1, 120.3, 115.4 (d, *J* = 21.6 Hz), 111.3, 101.6, 89.8, 87.2, 70.7.

¹⁹F{¹H} NMR (376 MHz, CDCl₃) δ 113.83.

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₃H₁₇FNO 342.1289; Found: 342.1244.

IR (KBr, cm⁻¹) 3423, 3059, 2227, 1601, 1506, 1492, 1455, 1288, 755, 692.



1-(4-chlorophenyl)-1-(1H-indol-2-yl)-3-phenylprop-2-yn-1-ol (1m)

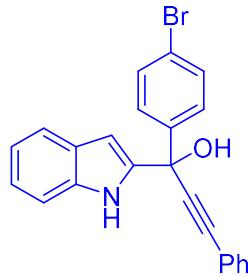
The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 20:1-8:1, v/v) to afford **1m** as a white solid, 0.62 g (87% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.32 (s, 1H), 7.71 – 7.63 (m, 2H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.52 (dd, *J* = 7.6, 1.8 Hz, 2H), 7.41 – 7.30 (m, 6H), 7.23 – 7.17 (m, 1H), 7.15 – 7.09 (m, 1H), 6.64 – 6.53 (m, 1H), 3.09 (s, 1H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 141.5, 140.7, 136.4, 134.4, 132.0, 129.3, 128.7, 128.6, 127.9, 127.7, 122.9, 121.8, 121.2, 120.3, 111.3, 101.7, 89.6, 87.3, 70.6.

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₃H₁₇ClNO 358.0993; Found: 358.0969.

IR (KBr, cm⁻¹) 3432, 3059, 2227, 1489, 1455, 1288, 1016, 792, 755, 689.



1-(4-bromophenyl)-1-(1H-indol-2-yl)-3-phenylprop-2-yn-1-ol (1n)

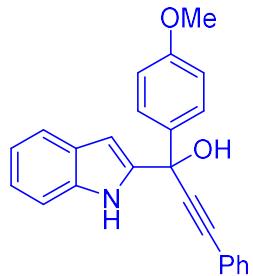
The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 20:1-8:1, v/v) to afford **1n** as a yellow solid, 0.68 g (85% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.33 (s, 1H), 7.64 – 7.57 (m, 3H), 7.55 – 7.48 (m, 4H), 7.36 (dt, *J* = 13.6, 6.9 Hz, 4H), 7.23 – 7.18 (m, 1H), 7.15 – 7.09 (m, 1H), 6.62 – 6.56 (m, 1H), 3.14 (s, 1H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 142.0, 140.6, 136.4, 132.0, 131.6, 129.3, 128.6, 128.0, 127.8, 122.8, 122.6, 121.8, 121.1, 120.3, 111.3, 101.7, 89.5, 87.3, 70.7.

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₃H₁₇BrNO 404.0468; Found: 404.0472.

IR (KBr, cm⁻¹) 3432, 3056, 2229, 1483, 1288, 1073, 1010, 826, 792, 755.



1-(1H-indol-2-yl)-1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-ol (**1o**)

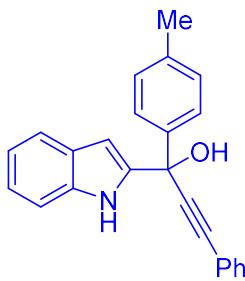
The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 20:1-8:1, v/v) to afford **1o** as a white solid, 0.60 g (85% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.35 (s, 1H), 7.65 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.56 – 7.47 (m, 2H), 7.34 (dd, *J* = 10.5, 7.1 Hz, 4H), 7.19 (t, *J* = 7.3 Hz, 1H), 7.12 (d, *J* = 7.3 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.63 – 6.54 (m, 1H), 3.82 (s, 3H), 3.09 (s, 1H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 159.7, 141.4, 136.3, 135.2, 132.0, 129.0, 128.5, 128.0, 127.6, 122.5, 122.1, 121.1, 120.1, 113.8, 111.3, 101.3, 90.2, 86.9, 70.8, 55.5.

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₄H₂₀NO₂ 354.1489; Found: 354.1522.

IR (KBr, cm⁻¹) 3423, 3056, 2930, 2227, 1607, 1509, 1455, 1248, 752, 692.



1-(1H-indol-2-yl)-3-phenyl-1-(p-tolyl)prop-2-yn-1-ol (1p)

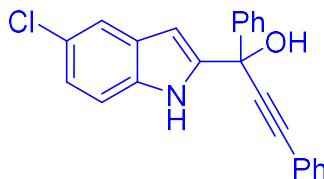
The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 20:1-8:1, v/v) to afford **1p** as a pale yellow solid, 0.59 g (87% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.34 (s, 1H), 7.64 – 7.57 (m, 3H), 7.54 – 7.51 (m, 2H), 7.37 – 7.31 (m, 4H), 7.22 – 7.16 (m, 3H), 7.10 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 6.60 (dd, *J* = 2.1, 1.0 Hz, 1H), 3.08 (s, 1H), 2.38 (s, 3H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 141.3, 140.1, 138.4, 136.3, 132.0, 129.3, 129.0, 128.5, 128.0, 126.1, 122.6, 122.2, 121.1, 120.1, 111.2, 101.3, 90.2, 86.8, 71.0, 21.3.

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₄H₂₀NO 338.1539; Found: 338.1542.

IR (KBr, cm⁻¹) 3423, 2927, 2227, 1509, 1489, 1455, 1340, 1021, 798, 752.



1-(5-chloro-1H-indol-2-yl)-1,3-diphenylprop-2-yn-1-ol (1q)

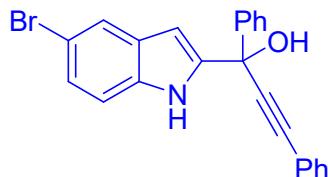
The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 20:1-8:1, v/v) to afford **1q** as a white solid, 0.61 g (85% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.39 (s, 1H), 7.79 – 7.69 (m, 2H), 7.57 – 7.48 (m, 3H), 7.44 – 7.32 (m, 6H), 7.22 (d, *J* = 8.6 Hz, 1H), 7.13 (dd, *J* = 8.7, 2.0 Hz, 1H), 6.53 (dd, *J* = 2.1, 0.9 Hz, 1H), 3.13 (s, 1H).

$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) δ 142.7, 142.6, 134.6, 132.0, 129.2, 129.1, 128.7, 128.6, 126.1, 125.7, 122.9, 121.9, 120.4, 112.3, 101.0, 89.7, 87.3, 71.0.

HRMS (ESI-TOF) m/z: $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{23}\text{H}_{17}\text{ClNO}$ 358.0993; Found: 358.0981.

IR (KBr, cm^{-1}) 3423, 3059, 2227, 1489, 1461, 1446, 1062, 1013, 795, 758.



1-(5-bromo-1H-indol-2-yl)-1,3-diphenylprop-2-yn-1-ol (1r)

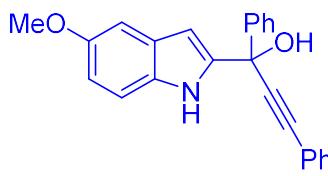
The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 20:1-8:1, v/v) to afford **1r** as a white solid, 0.66 g (82% yield).

^1H NMR (400 MHz, CDCl_3) δ 8.40 (s, 1H), 7.72 (ddd, $J = 8.9, 7.2, 1.8$ Hz, 3H), 7.56 – 7.48 (m, 2H), 7.45 – 7.31 (m, 6H), 7.27 – 7.24 (m, 1H), 7.18 (d, $J = 8.6$ Hz, 1H), 6.56 – 6.49 (m, 1H), 3.13 (s, 1H).

$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) δ 142.7, 142.4, 134.9, 132.0, 129.7, 129.2, 128.7, 128.6, 126.1, 125.5, 123.5, 121.9, 113.3, 112.7, 100.9, 89.7, 87.3, 71.0.

HRMS (ESI-TOF) m/z: $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{23}\text{H}_{17}\text{BrNO}$ 404.0468; Found: 404.0460.

IR (KBr, cm^{-1}) 3426, 3059, 2227, 1598, 1572, 1489, 1446, 1053, 869, 795.



1-(5-methoxy-1H-indol-2-yl)-1,3-diphenylprop-2-yn-1-ol (1s)

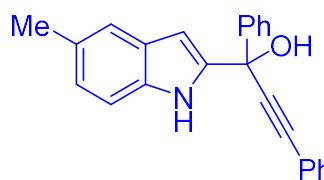
The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 20:1-8:1, v/v) to afford **1s** as a white solid, 0.60 g (85% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.25 (s, 1H), 7.79 – 7.70 (m, 2H), 7.53 (dd, *J* = 7.3, 2.4 Hz, 2H), 7.44 – 7.30 (m, 6H), 7.20 (d, *J* = 8.8 Hz, 1H), 7.05 (d, *J* = 2.5 Hz, 1H), 6.85 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.53 (d, *J* = 2.5 Hz, 1H), 3.83 (s, 3H), 3.17 (s, 1H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 154.4, 143.0, 141.9, 132.0, 131.5, 129.1, 128.6, 128.5, 128.5, 128.4, 126.2, 122.1, 112.9, 112.0, 102.8, 101.3, 90.2, 86.9, 71.1, 56.0.

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₄H₂₀NO₂ 354.1489; Found: 354.1510.

IR (KBr, cm⁻¹) 3432, 3059, 2935, 2227, 1627, 1587, 1489, 1449, 786, 740.



1-(5-methyl-1H-indol-2-yl)-1,3-diphenylprop-2-yn-1-ol (1t)

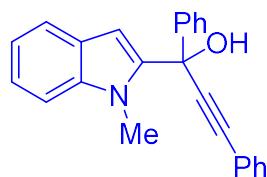
The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 20:1-8:1, v/v) to afford **1t** as a white solid, 0.59 g (87% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.24 (s, 1H), 7.78 – 7.71 (m, 2H), 7.58 – 7.50 (m, 2H), 7.39 (dt, *J* = 11.8, 6.6 Hz, 7H), 7.21 (d, *J* = 8.2 Hz, 1H), 7.02 (dd, *J* = 8.2, 1.6 Hz, 1H), 6.54 (d, *J* = 2.1 Hz, 1H), 3.10 (s, 1H), 2.45 (s, 3H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 143.1, 141.2, 134.7, 132.0, 129.4, 129.0, 128.6, 128.5, 128.5, 128.3, 126.2, 124.3, 122.2, 120.7, 110.9, 101.1, 90.2, 86.9, 71.2, 21.6.

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₄H₂₀NO 338.1539; Found: 338.1539.

IR (KBr, cm⁻¹) 3432, 3024, 2921, 2227, 1489, 1449, 1159, 872, 798, 755.



1-(1-methyl-1H-indol-2-yl)-1,3-diphenylprop-2-yn-1-ol (9)

The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc = 20:1-8:1, v/v) to afford **9** as a yellow solid, 0.57 g (85% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.67 – 7.61 (m, 2H), 7.60 – 7.55 (m, 1H), 7.48 – 7.42 (m, 2H), 7.38 – 7.26 (m, 6H), 7.25 – 7.18 (m, 2H), 7.08 (ddd, *J* = 7.9, 6.6, 1.5 Hz, 1H), 6.60 (s, 1H), 3.62 (s, 3H), 3.10 (s, 1H).

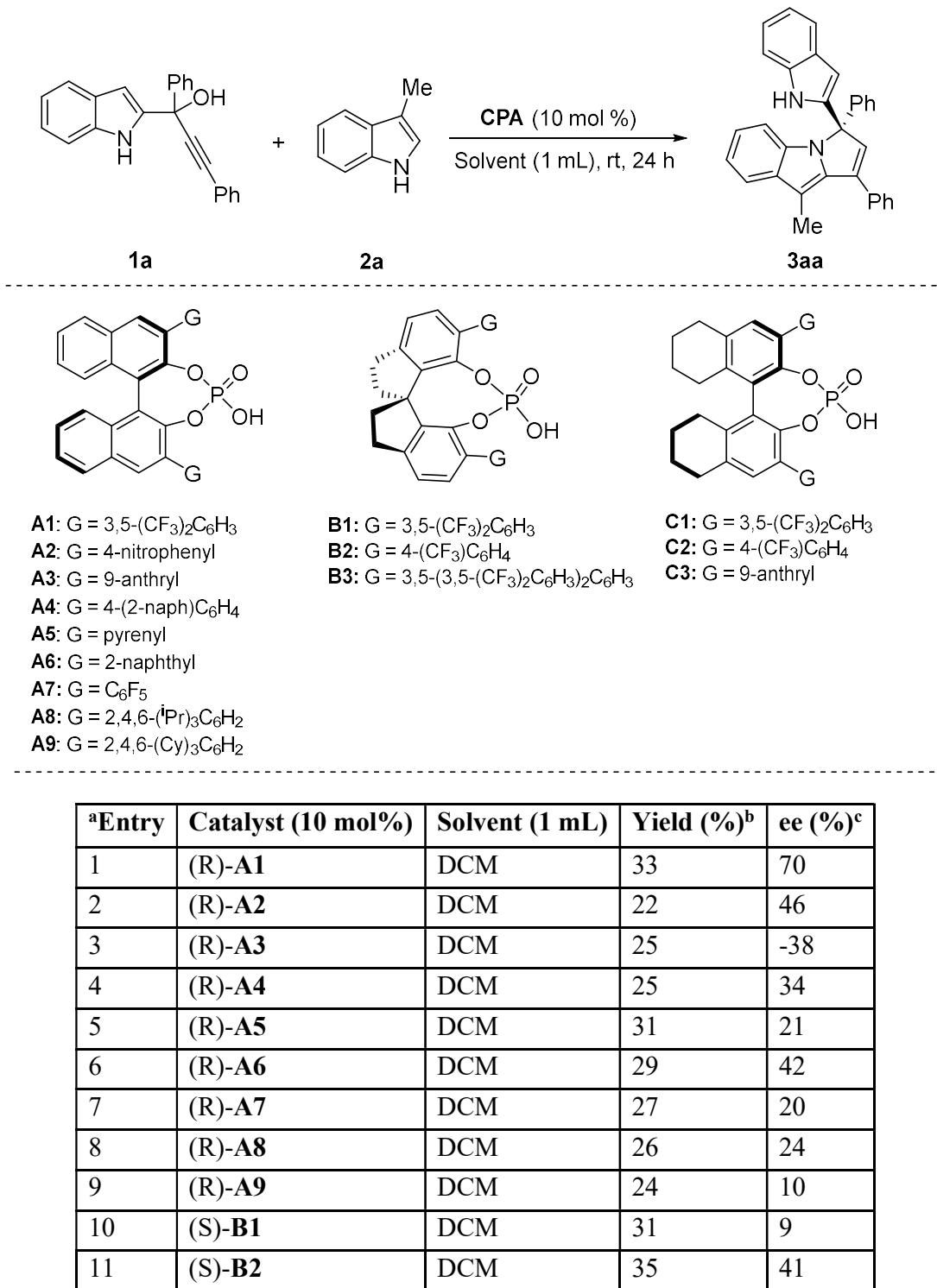
¹³C{¹H} NMR (101 MHz, CDCl₃) δ 142.7, 141.3, 139.0, 131.8, 128.9, 128.5, 128.5, 128.4, 126.6, 122.3, 121.2, 119.8, 109.3, 102.7, 90.3, 87.3, 71.2, 31.4.

HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₄H₂₀NO 338.1539; Found: 338.1537.

IR (KBr, cm⁻¹) 3506, 3056, 2926, 2224, 1489, 1469, 1449, 981, 786, 740.

2. Optimization of reaction conditions

Table S1. Optimization of the reaction conditions

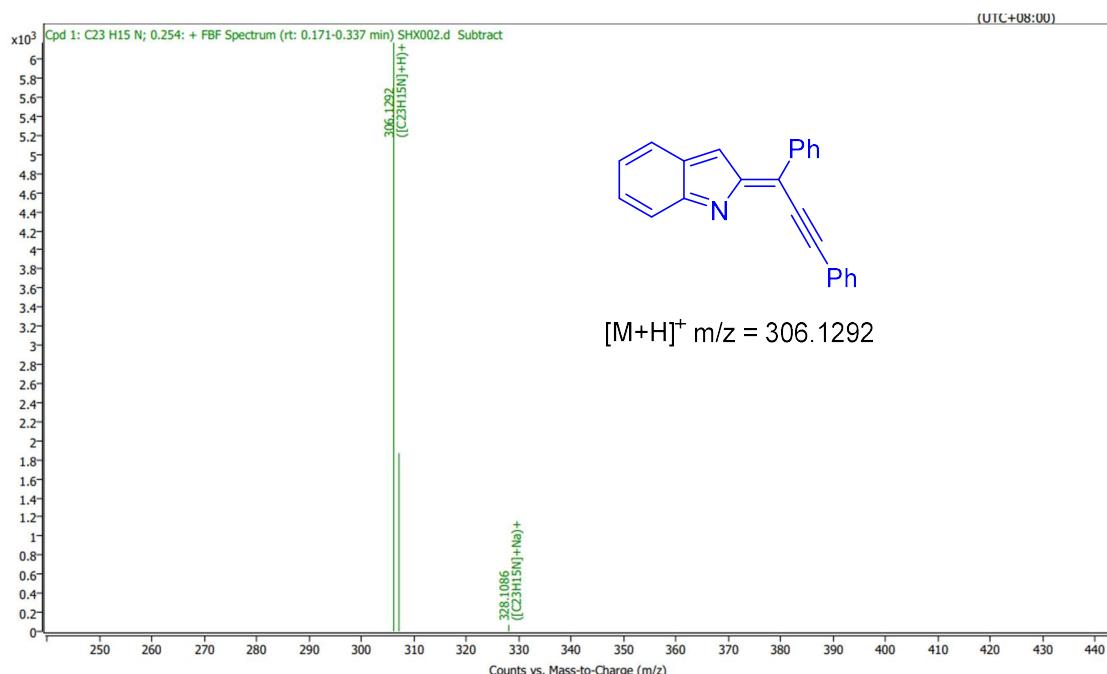


12	(S)- B3	DCM	29	11
13	(R)- C1	DCM	21	55
14	(R)- C2	DCM	28	54
15	(R)- C3	DCM	26	-30
16	(R)- A1	DCE	38	82
17	(R)- A1	Toluene	NR	-
18	(R)- A1	CHCl ₃	45	78
19	(R)- A1	CH ₃ CN	15	74
20	(R)- A1	PhCl	39	77
21	(R)- A1	CH ₃ CFCl ₂	78	77
22 ^d	(R)- A1	DCE	40	82
23 ^e	(R)- A1	DCE	33	84
24 ^f	(R)- A1	DCE	41	84
25 ^g	(R)- A1	DCE	25	90
26 ^{fg}	(R)- A1	DCE	30	92
27 ^f	(R)- A1	CH ₃ CFCl ₂	80	87
28 ^{fg}	(R)- A1	CH ₃ CFCl ₂	77/70 ⁱ	96
29 ^{fh}	(R)- A1	CH ₃ CFCl ₂	35	95

^aUnless noted, the reaction was carried out with **1a** (0.05 mmol), **2a** (0.05 mmol), and catalyst (10 mol %) in 1.0 mL of solvent at room temperature for 24 h. ^bDetermined by ¹H NMR with 1,3,5-trimethoxybenzene as internal standard. ^cThe ee was determined by HPLC analysis on a chiral stationary phase. ^dAdditive Na₂SO₄ (10 mg). ^eAdditive 4 Å MS (50 mg). ^fAdditive 3 Å MS (50 mg). ^gTemperature at -10 °C. ^hTemperature at -20 °C. ⁱIsolated yield. NR= No reaction.

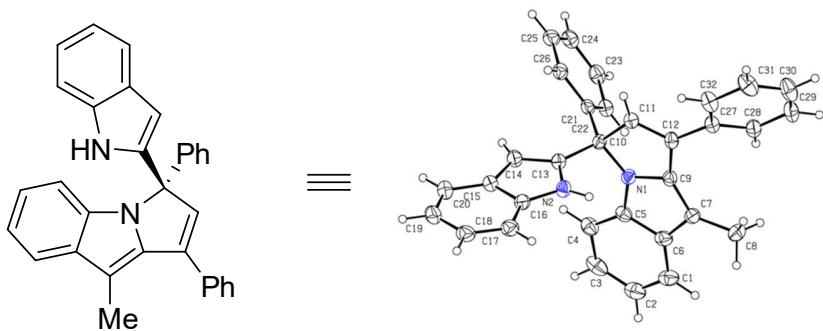
3. HR MS copies of intermediates

To get a mechanistic insight into reaction mechanism, we performed the following control experiment. To gain insight into the mechanism of this cascade reaction, we monitored the reaction of α -indolyl propargylic alcohol **1a** with (R)-**A1** and tried to isolated some intermediate products. Disappointingly, we failed to obtain intermediate product. Therefore, we tried to detect the signals of some possible intermediates via HRMS. After stirring the reaction for 3 hours, we detect a useful signal via HRMS. The signal at [M+H]⁺ m/z 306.1292 was possibly due to 2-(1,3-diphenylprop-2-yn-1-ylidene)-2H-indole.



4. X-Ray Structure and Crystal Data of 3aa

Single crystal of **3aa** was obtained from the mixed solution of dichloromethane, isopropyl alcohol and petroleum ether (10:1:10) maintained at room temperature for a week. The absolute structure of product **3aa** was determined by X-ray diffraction analysis of a single crystal (Bruker APEX-II CCD' diffractometer). The X-ray data have been deposited at the Cambridge Crystallographic Data Center (CCDC 2324844). The stereochemistry of other products was assumed by analogy.



240109_shx096_0m (**3aa**)

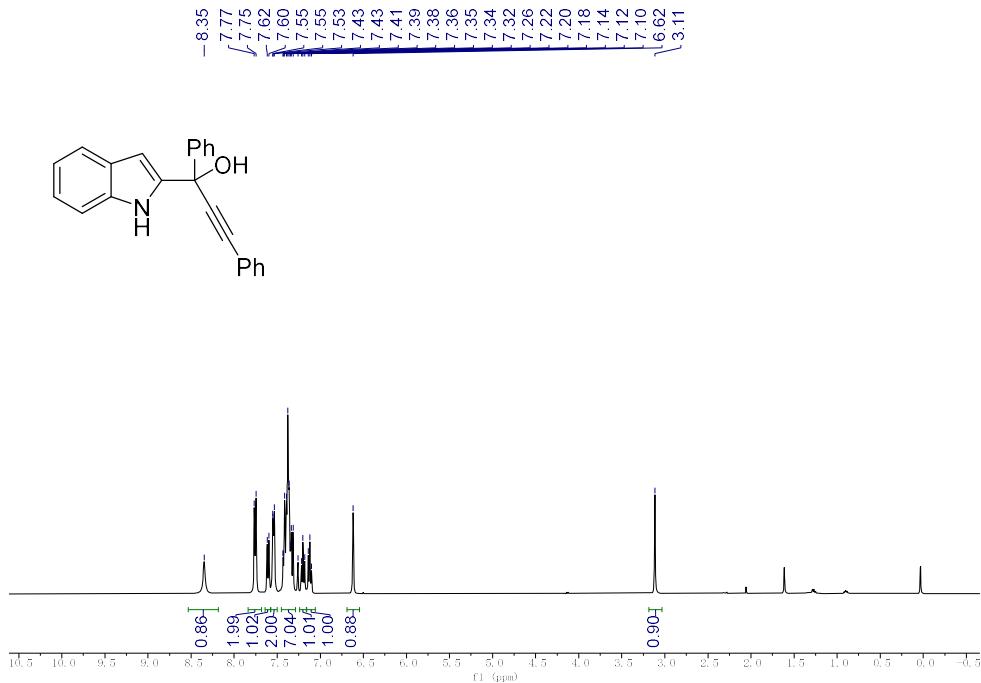
Table 1 Crystal data and structure refinement for 240109_shx096_0m.

Identification code	240109_shx096_0m
Empirical formula	C ₃₂ H ₂₄ N ₂
Formula weight	436.53
Temperature/K	170.00
Crystal system	monoclinic
Space group	P2 ₁
a/Å	10.7294(7)
b/Å	41.364(3)
c/Å	11.0861(7)
α/°	90
β/°	105.551(4)
γ/°	90
Volume/Å ³	4740.0(5)
Z	8
ρ _{calc} g/cm ³	1.223
μ/mm ⁻¹	0.348
F(000)	1840.0
Crystal size/mm ³	0.12 × 0.02 × 0.02
Radiation	GaKα ($\lambda = 1.34139$)
2Θ range for data collection/°	7.2 to 114.454
Index ranges	-13 ≤ h ≤ 13, -50 ≤ k ≤ 51, -13 ≤ l ≤ 13
Reflections collected	210462
Independent reflections	19458 [R _{int} = 0.1150, R _{sigma} = 0.0578]

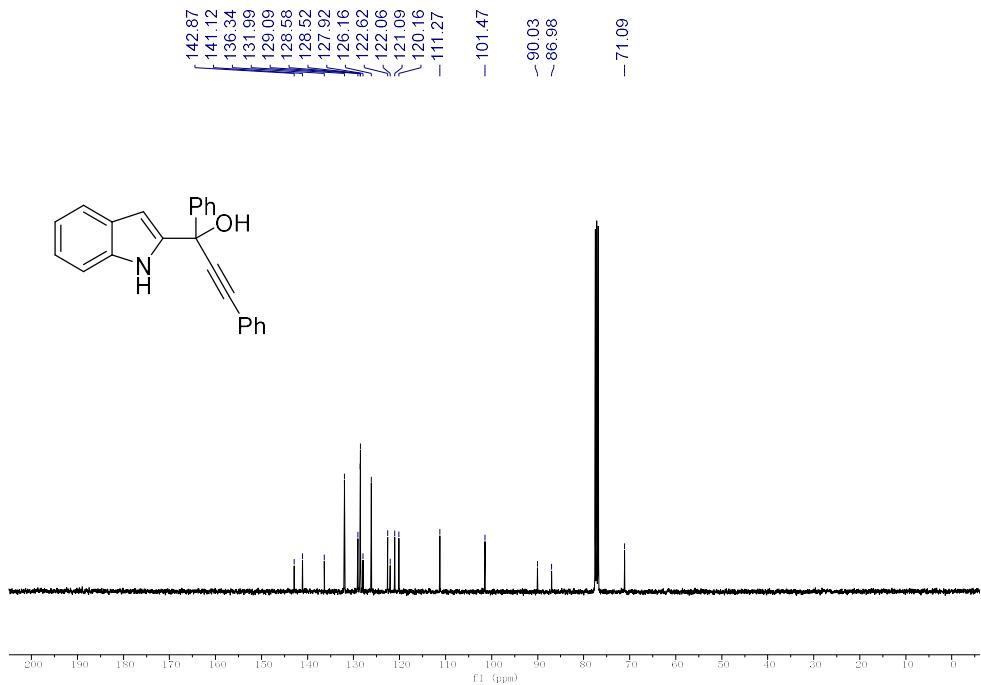
Data/restraints/parameters 19458/1/1229
Goodness-of-fit on F^2 1.067
Final R indexes [$I \geq 2\sigma(I)$] $R_1 = 0.0524$, $wR_2 = 0.1135$
Final R indexes [all data] $R_1 = 0.0741$, $wR_2 = 0.1243$
Largest diff. peak/hole / e Å⁻³ 0.17/-0.31
Flack parameter 0.0(2)

5. Copies of NMR spectra

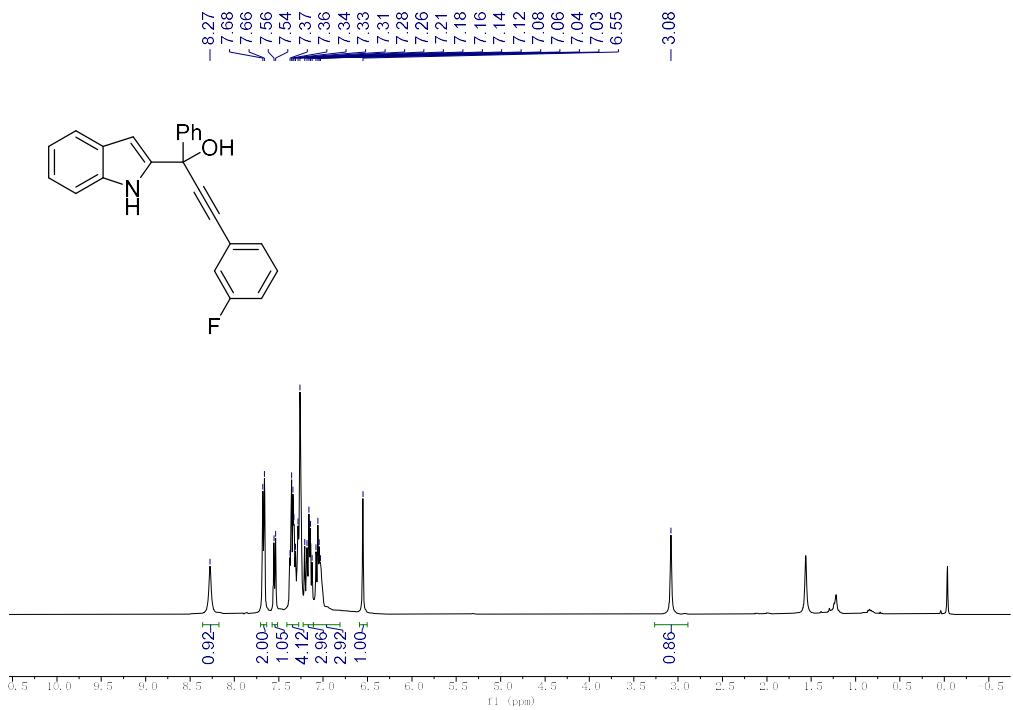
^1H NMR (400 MHz, CDCl_3) of **1a**



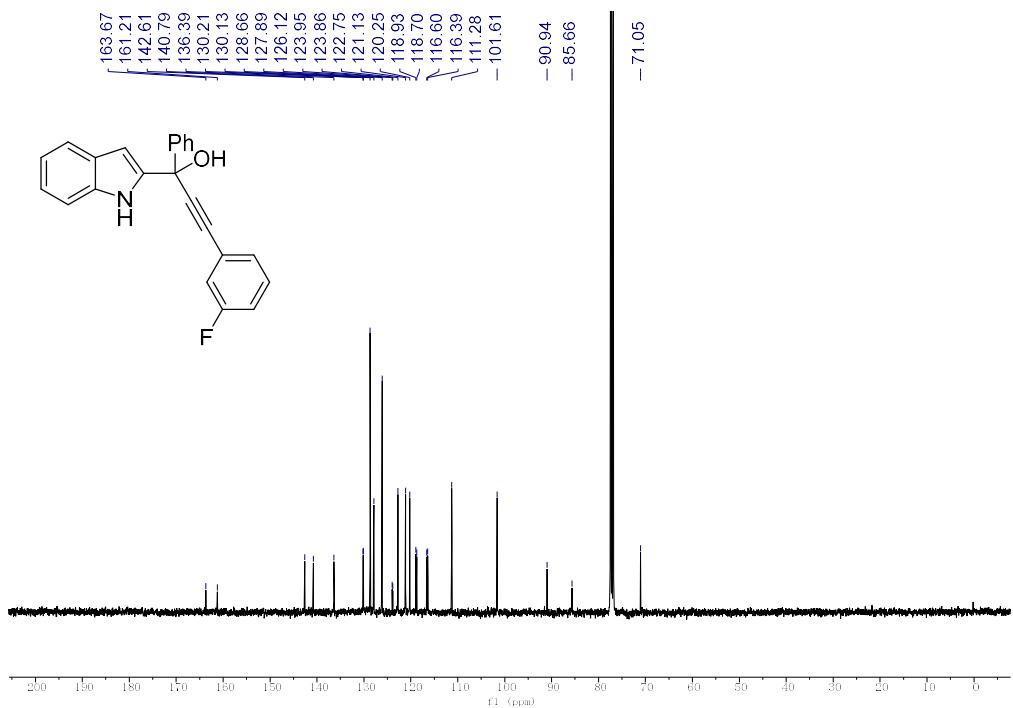
$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) of **1a**



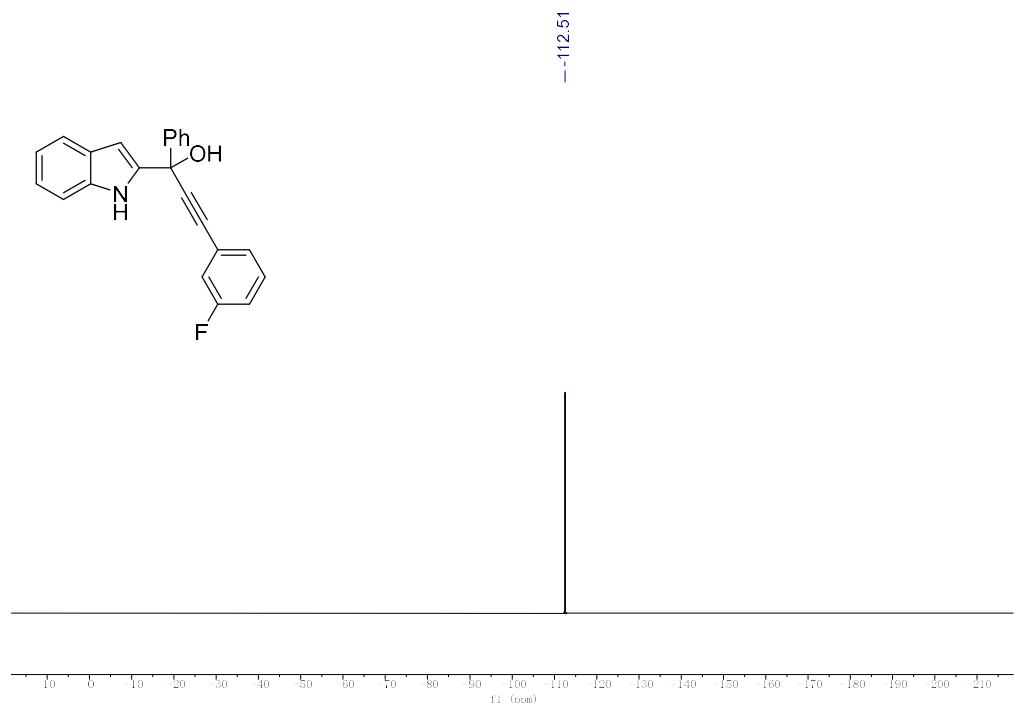
¹H NMR (400 MHz, CDCl₃) of **1b**



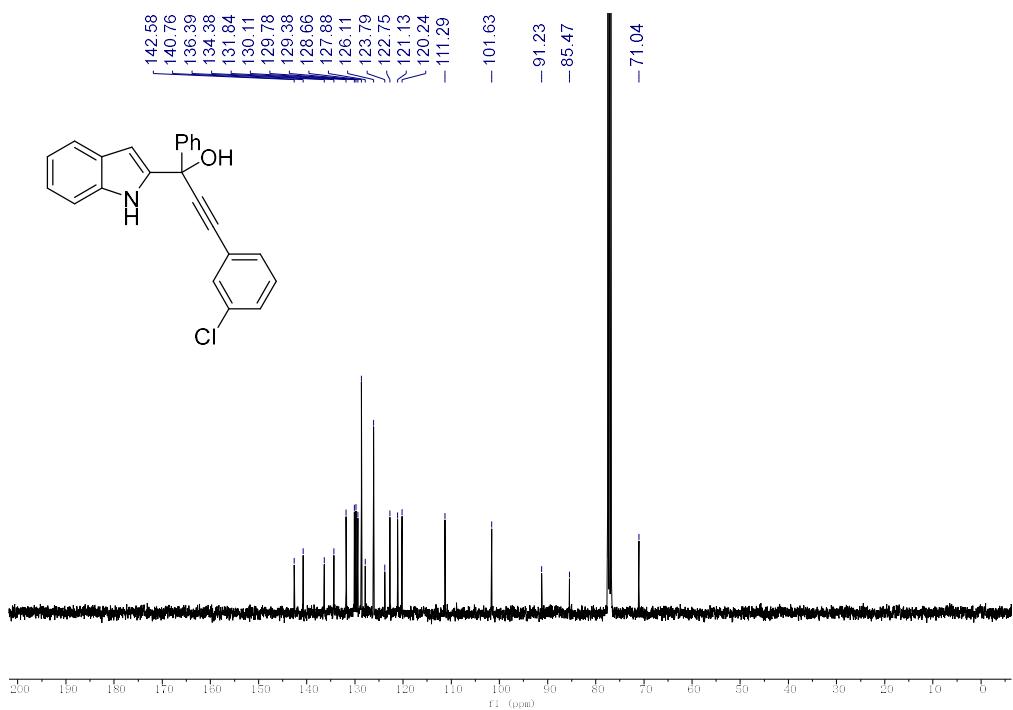
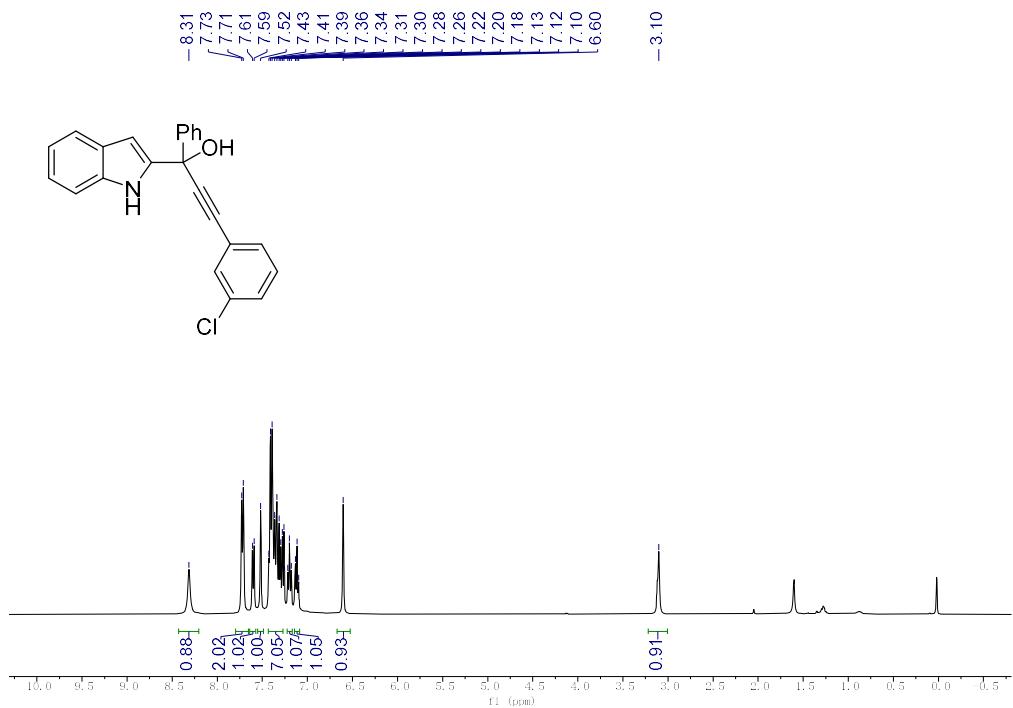
¹³C{¹H} NMR (101 MHz, CDCl₃) of **1b**



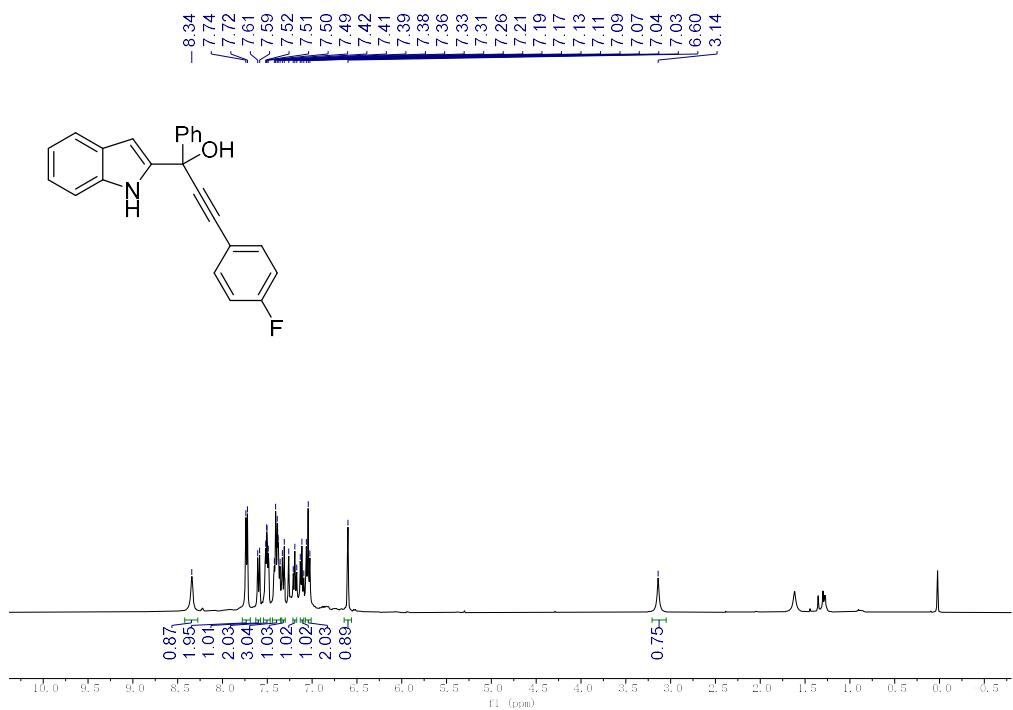
$^{19}\text{F}\{\text{H}\}$ NMR (376 MHz, CDCl_3) of **1b**



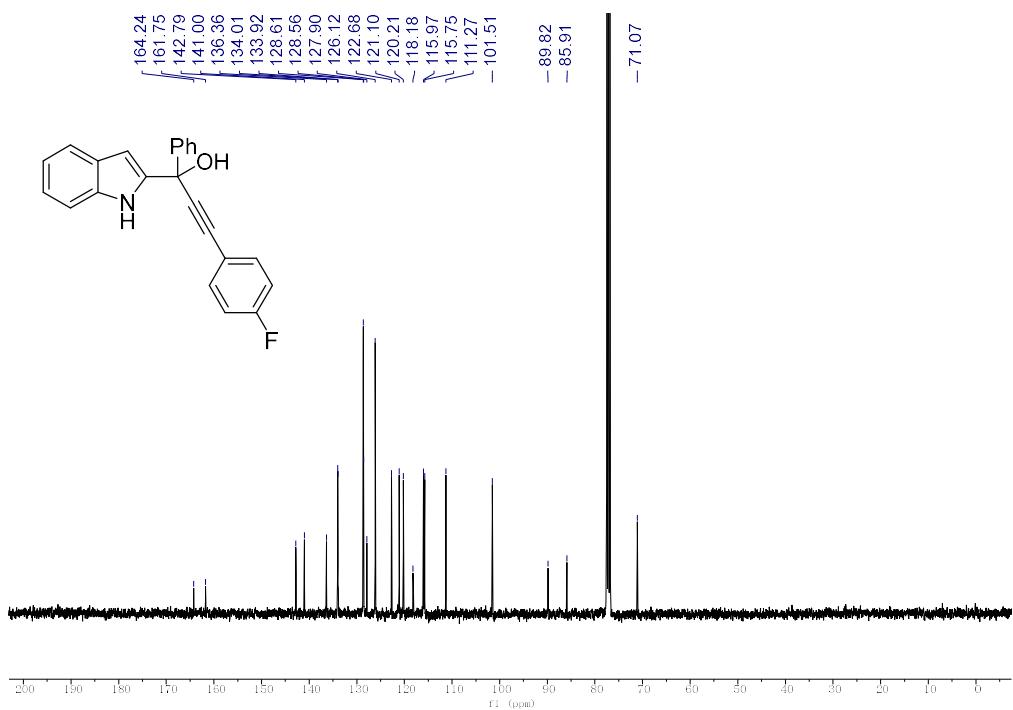
¹H NMR (400 MHz, CDCl₃) of **1c**



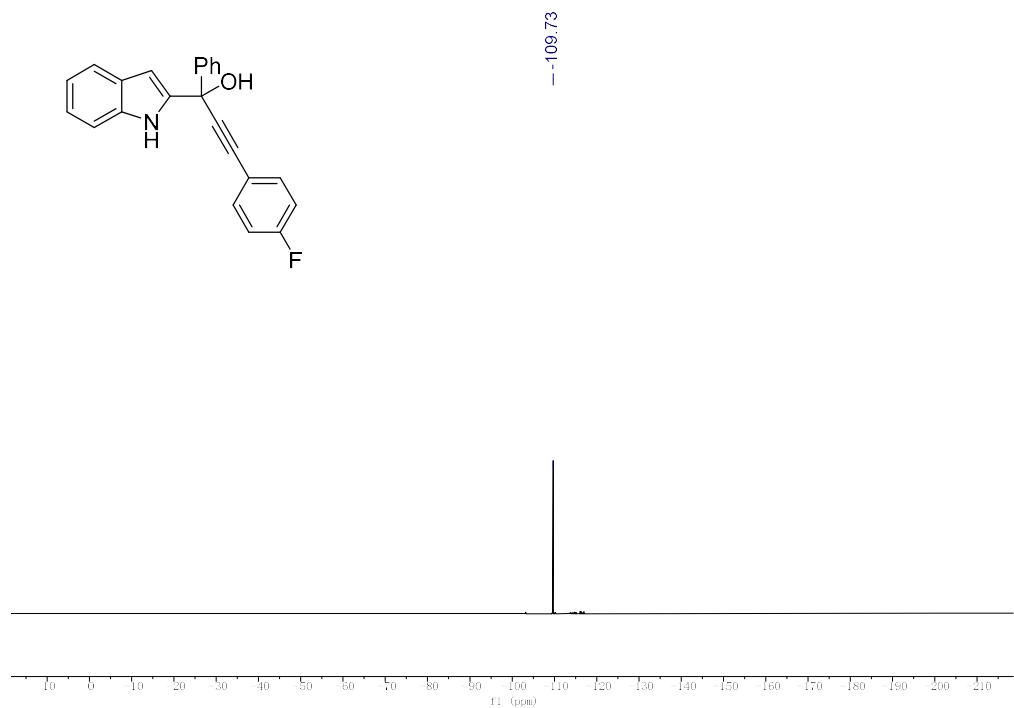
¹H NMR (400 MHz, CDCl₃) of **1d**



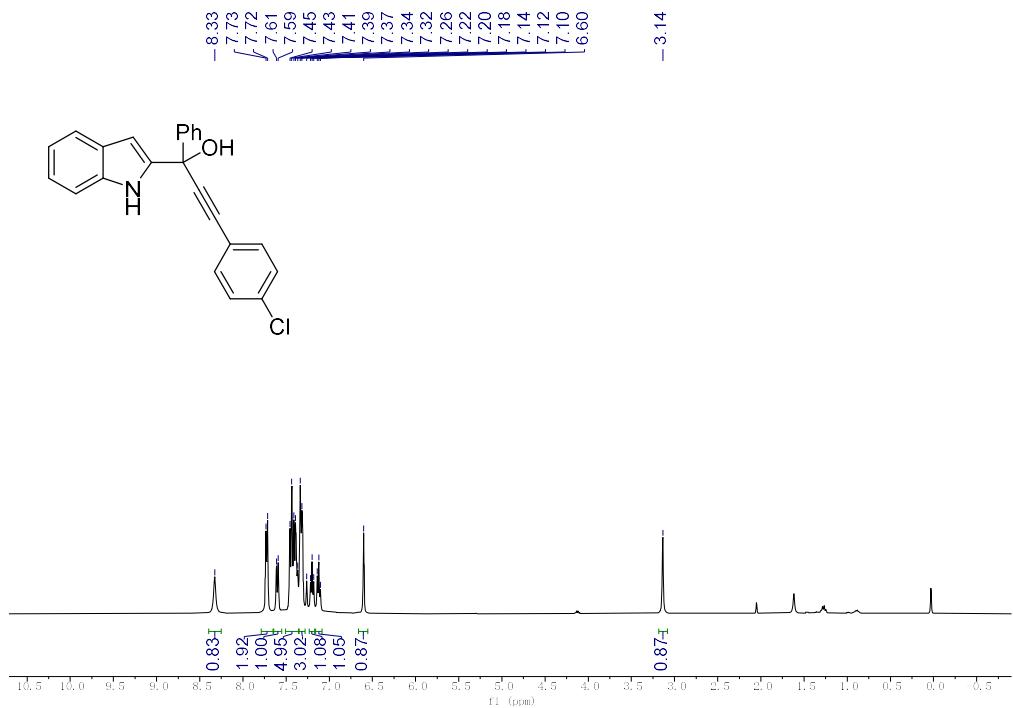
¹³C{¹H} NMR (101 MHz, CDCl₃) of **1d**



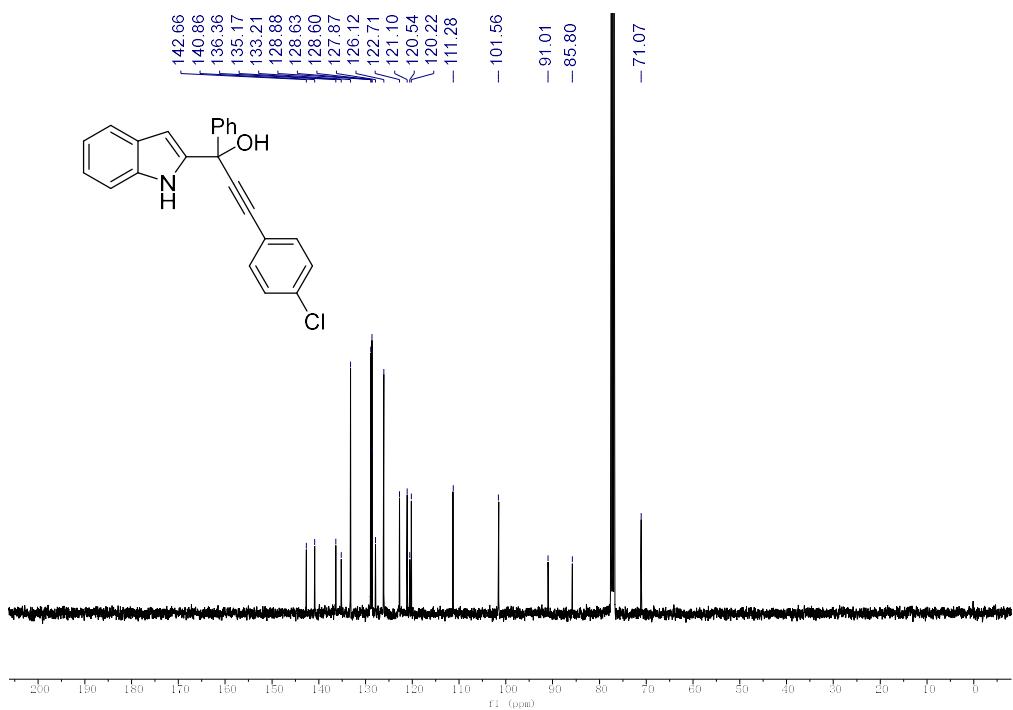
$^{19}\text{F}\{\text{H}\}$ NMR (376 MHz, CDCl_3) of **1d**



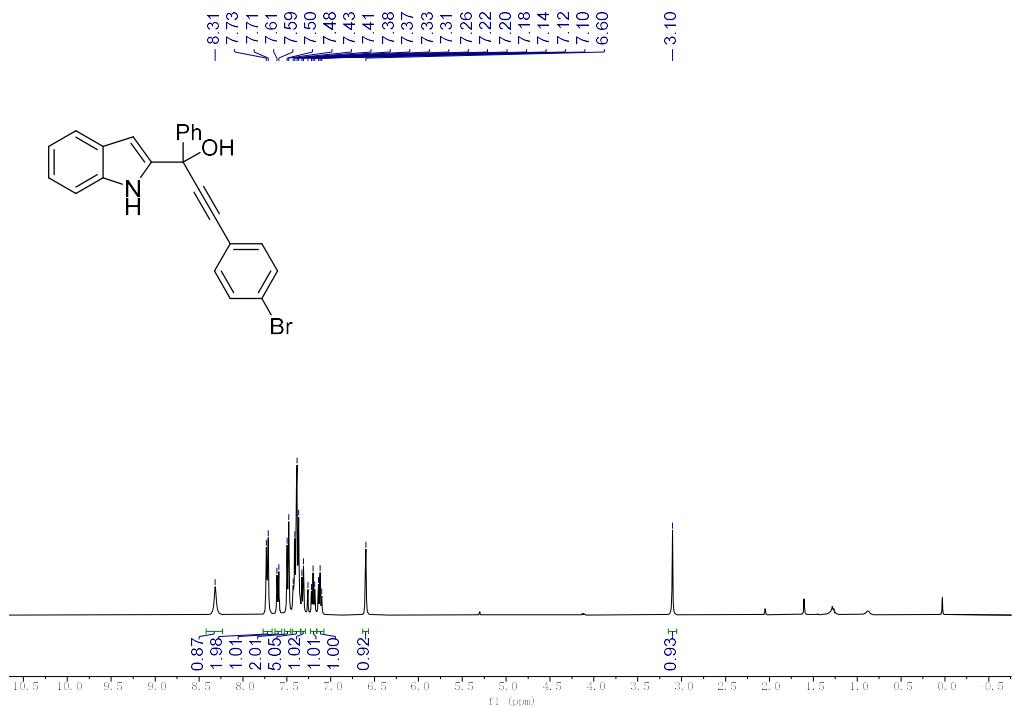
¹H NMR (400 MHz, CDCl₃) of **1e**



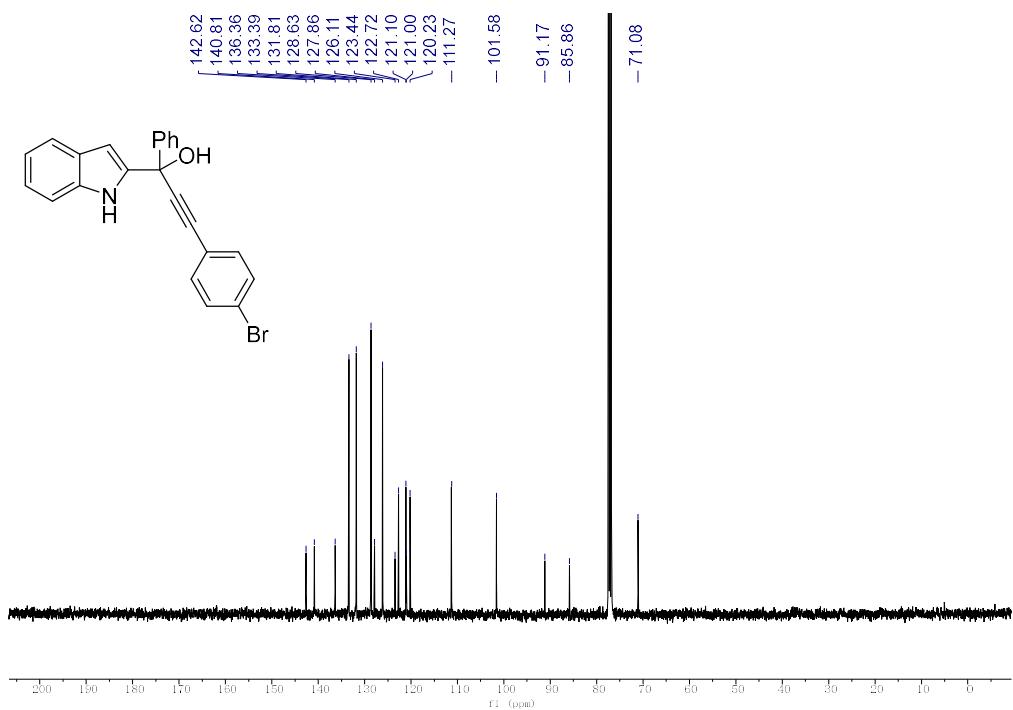
¹³C{¹H} NMR (101 MHz, CDCl₃) of **1e**



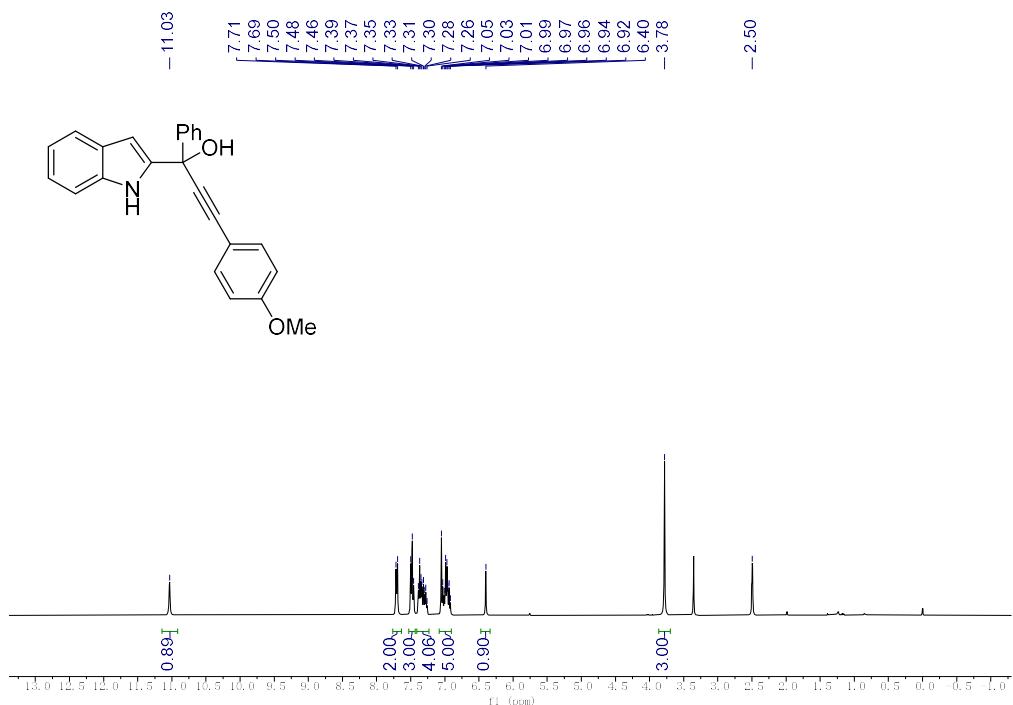
¹H NMR (400 MHz, CDCl₃) of **1f**



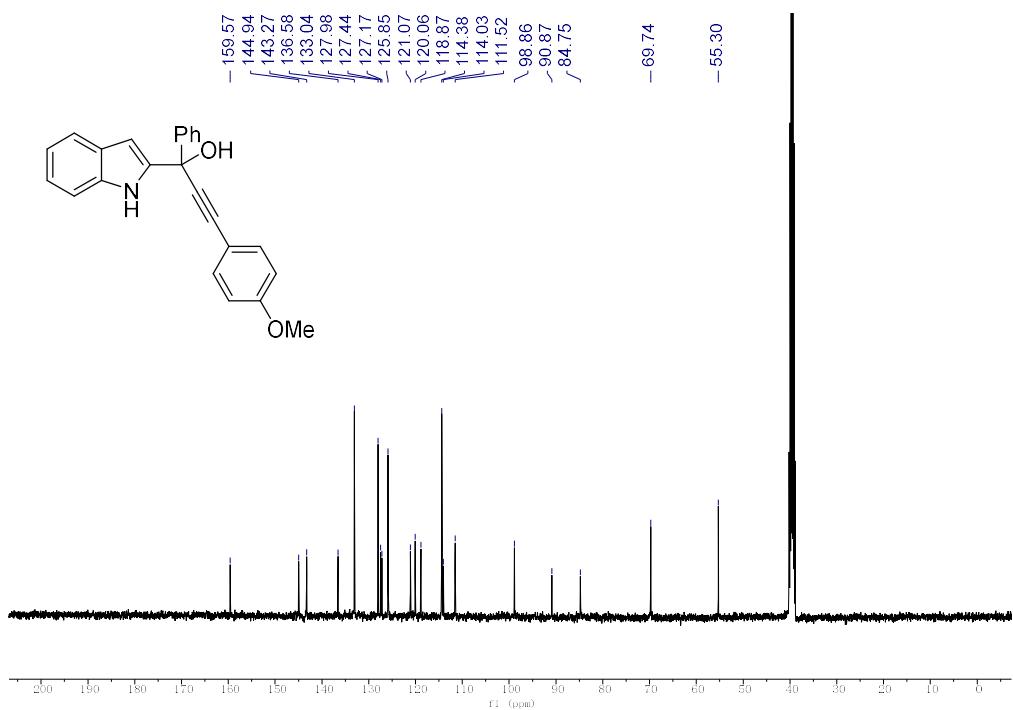
¹³C{¹H} NMR (101 MHz, CDCl₃) of **1f**



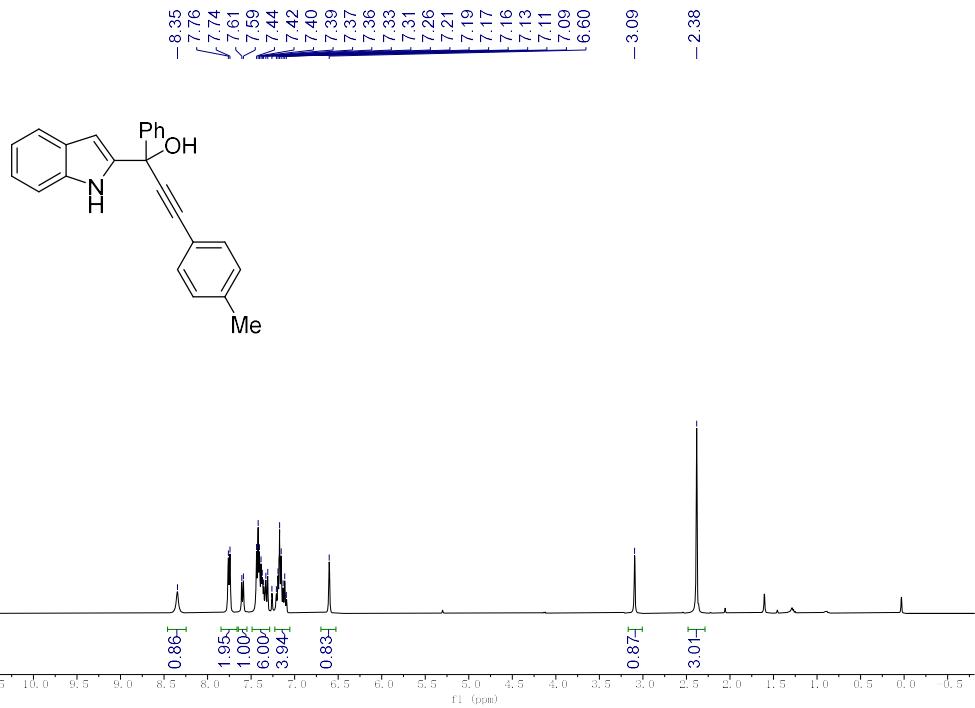
¹H NMR (400 MHz, DMSO-d₆) of **1g**



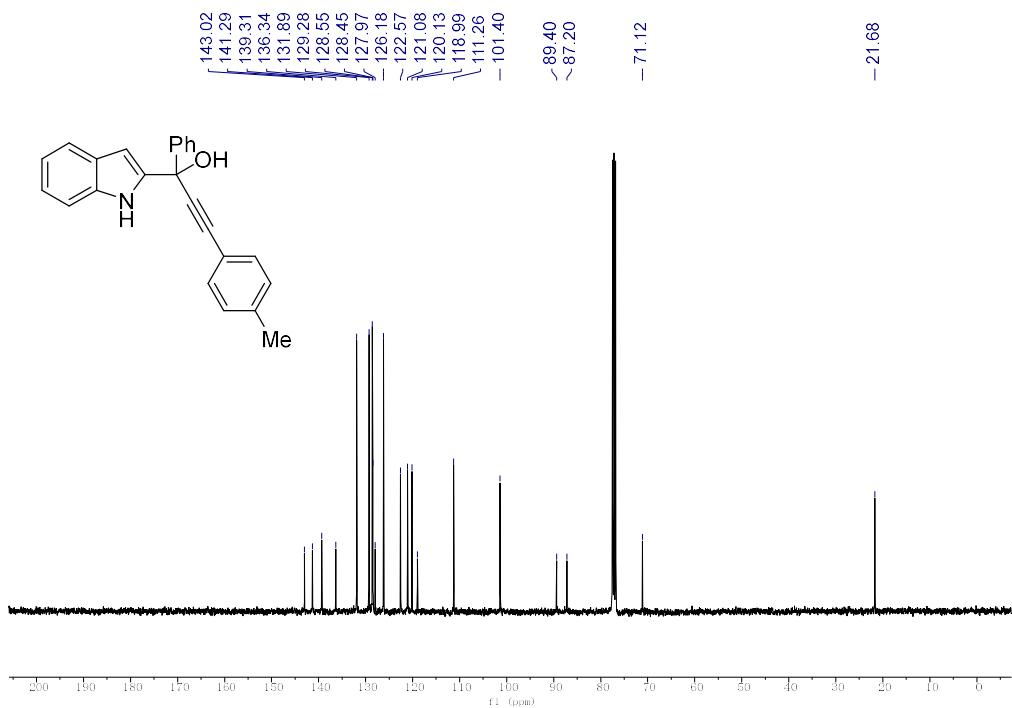
¹³C{¹H} NMR (101 MHz, DMSO-d₆) of **1g**



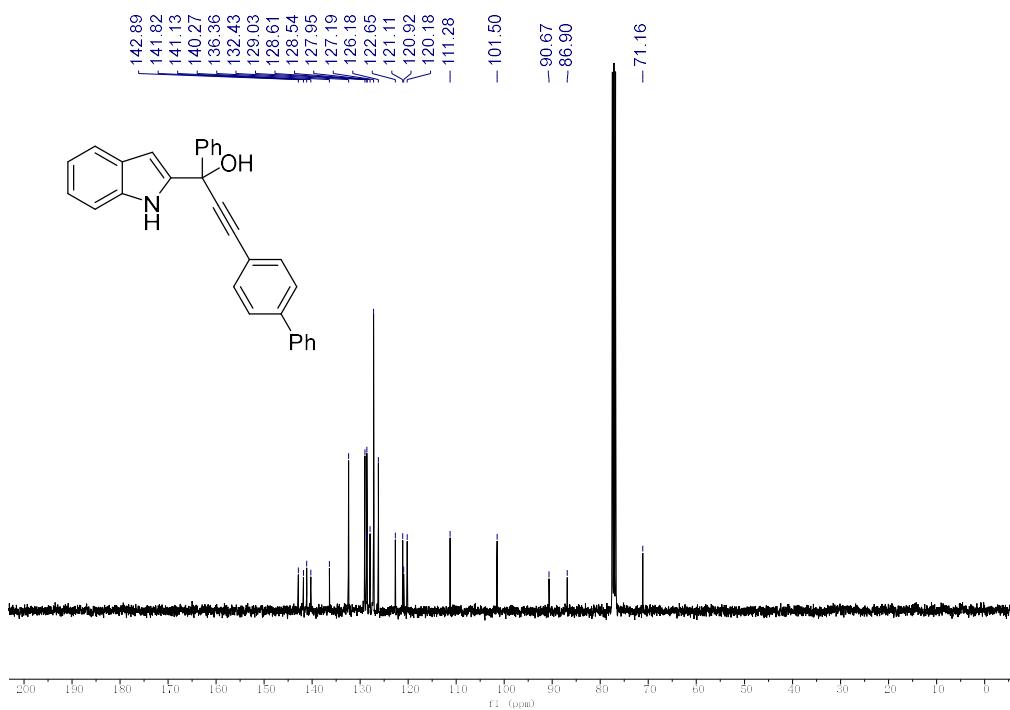
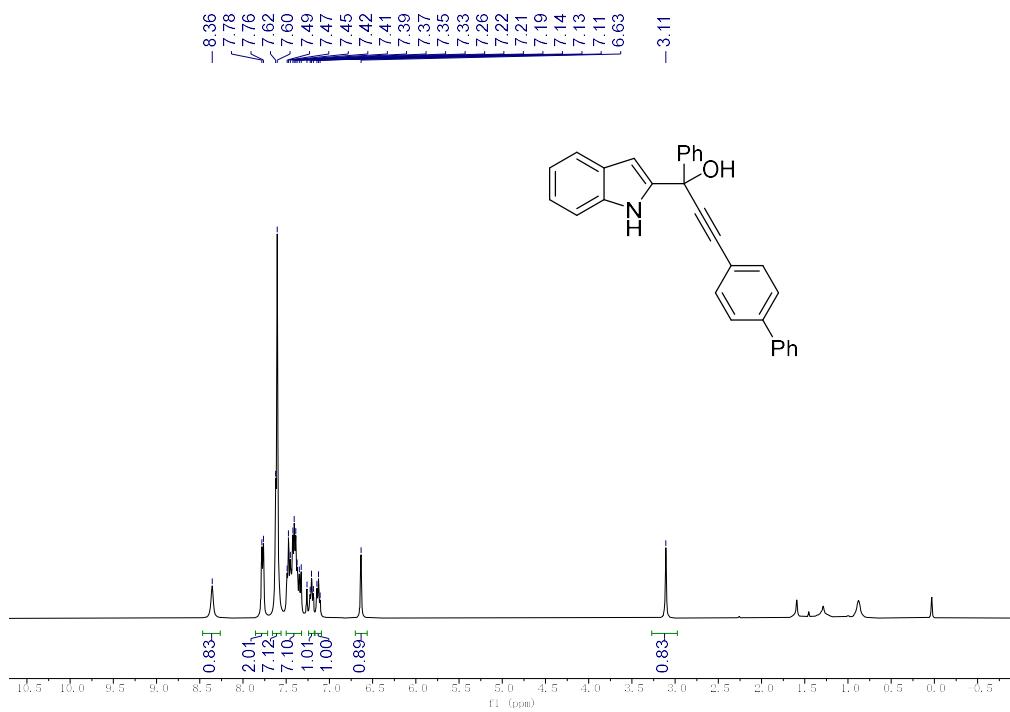
¹H NMR (400 MHz, CDCl₃) of **1h**



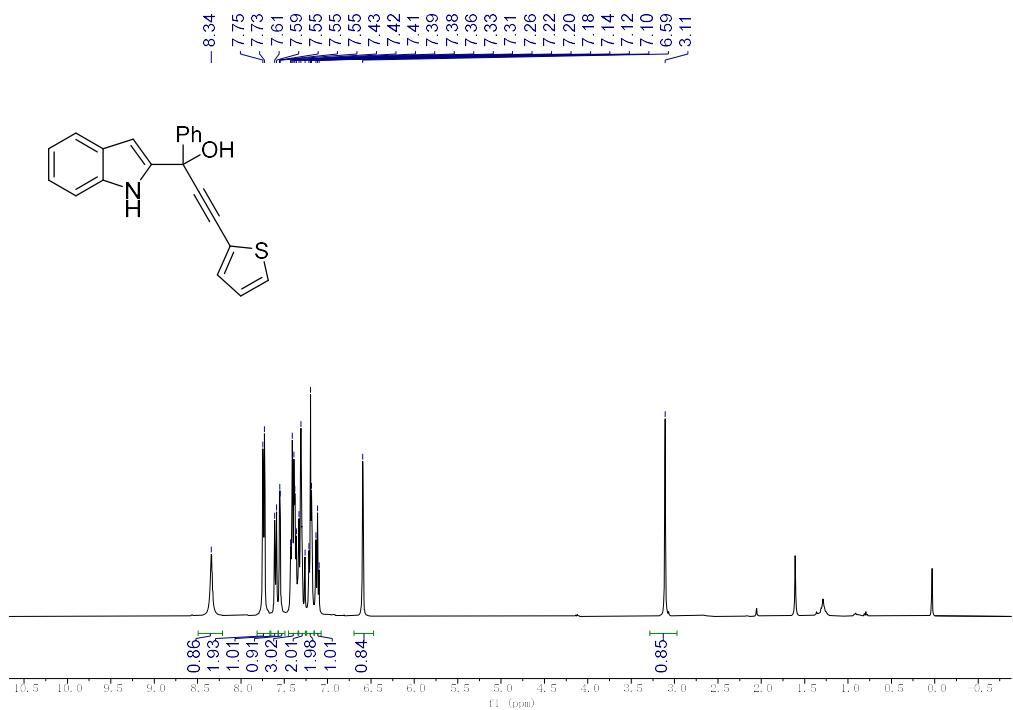
$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) of **1h**



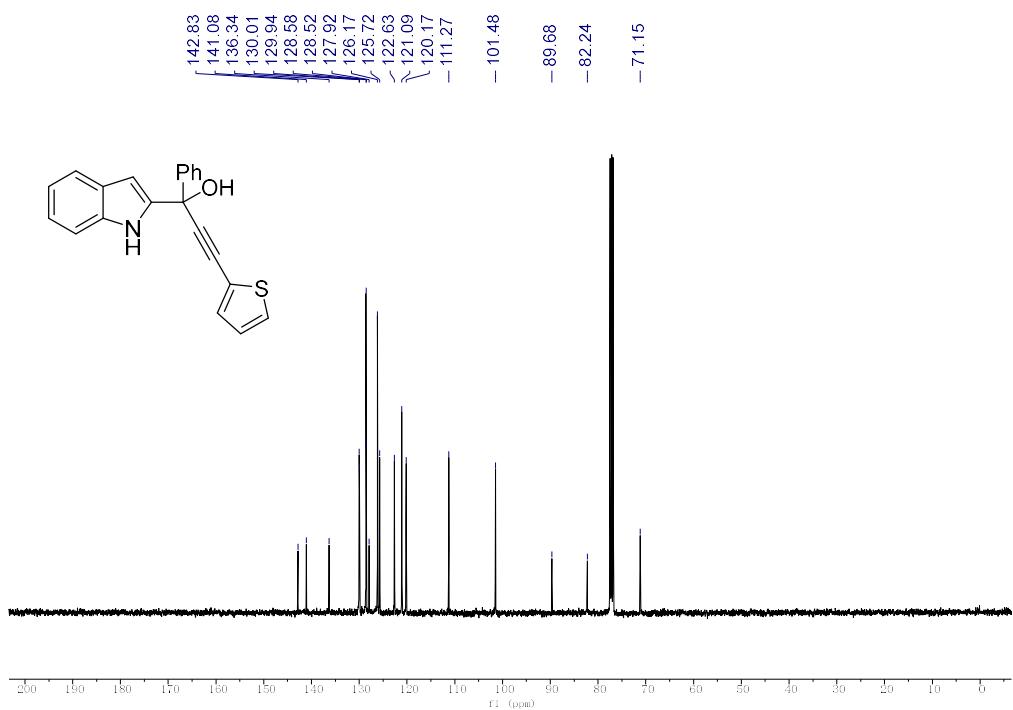
¹H NMR (400 MHz, CDCl₃) of **1i**



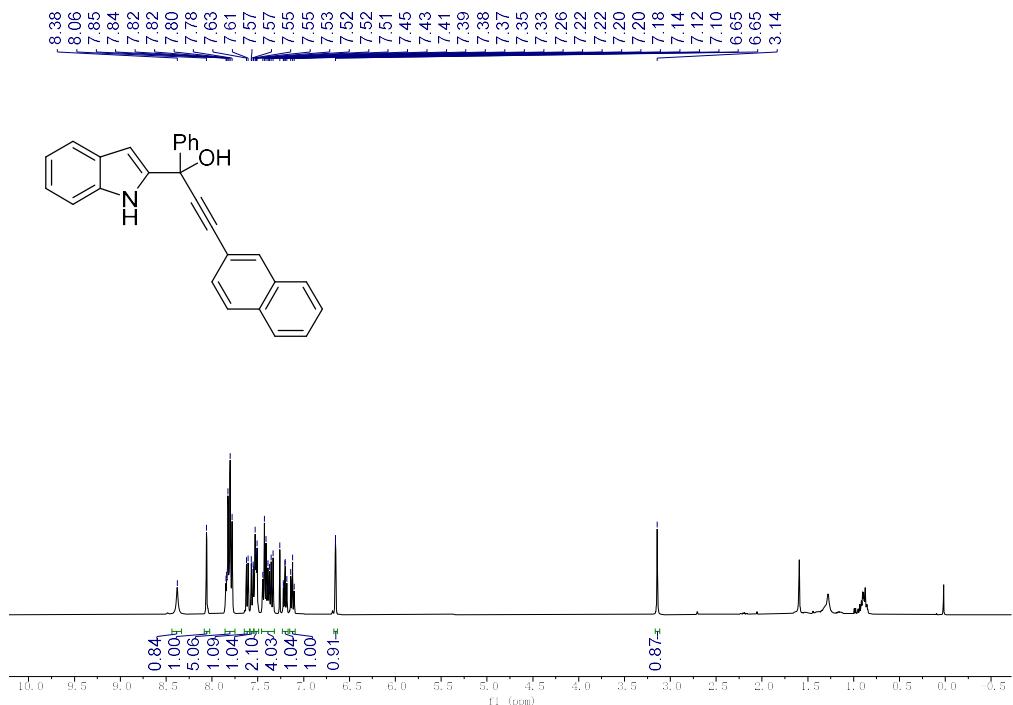
¹H NMR (400 MHz, CDCl₃) of **1j**



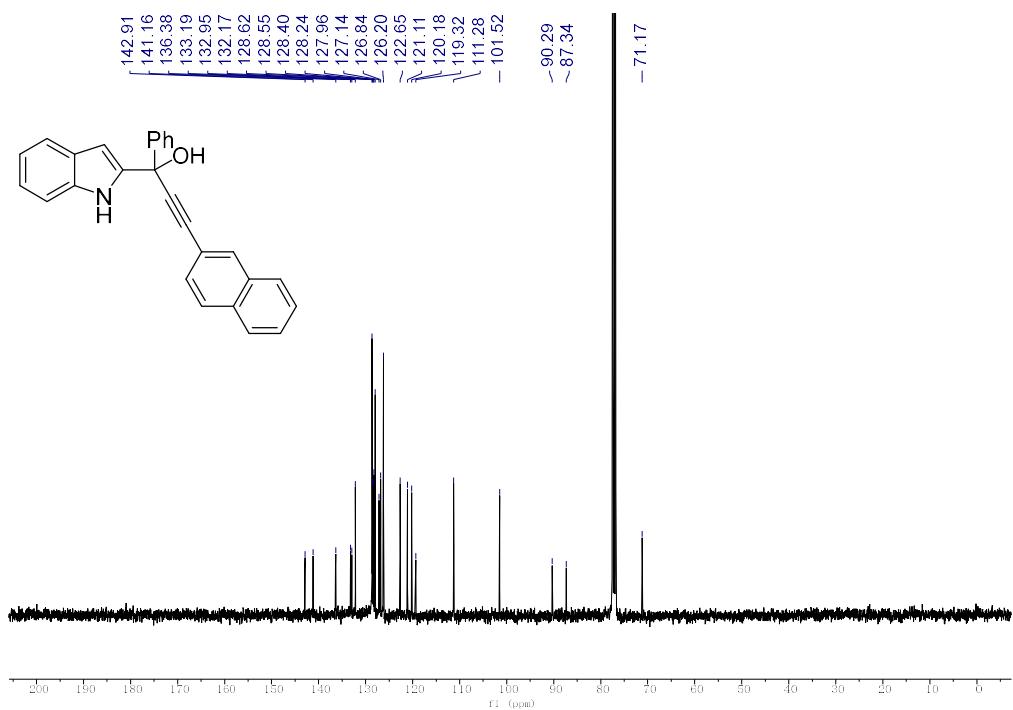
¹³C{¹H} NMR (101 MHz, CDCl₃) of **1j**



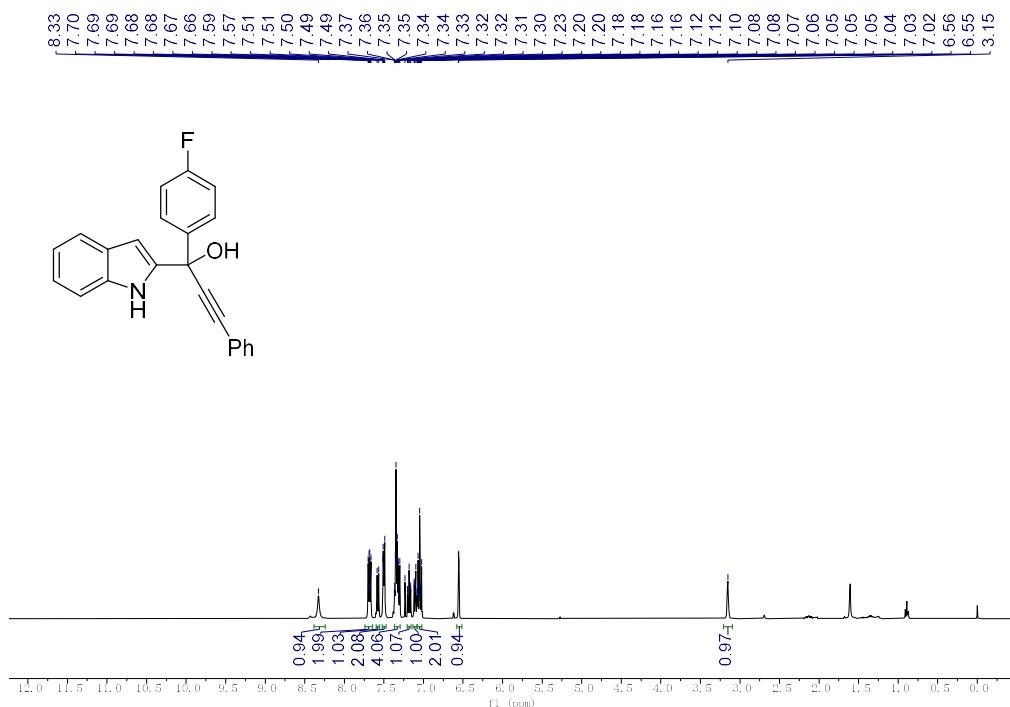
¹H NMR (400 MHz, CDCl₃) of **1k**



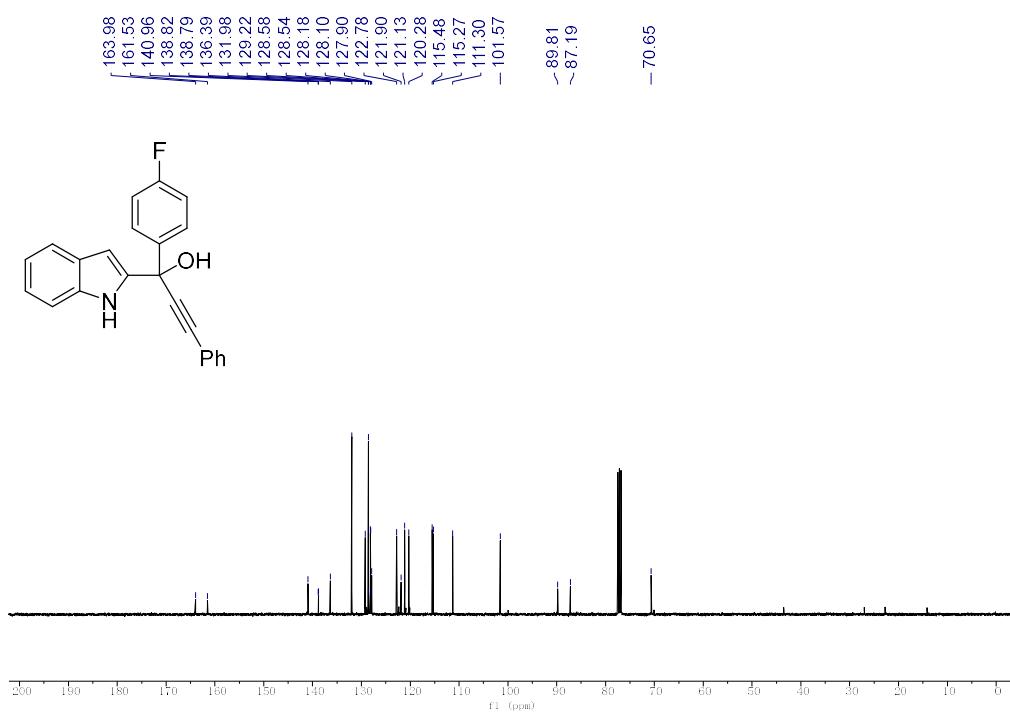
¹³C{¹H} NMR (101 MHz, CDCl₃) of **1k**



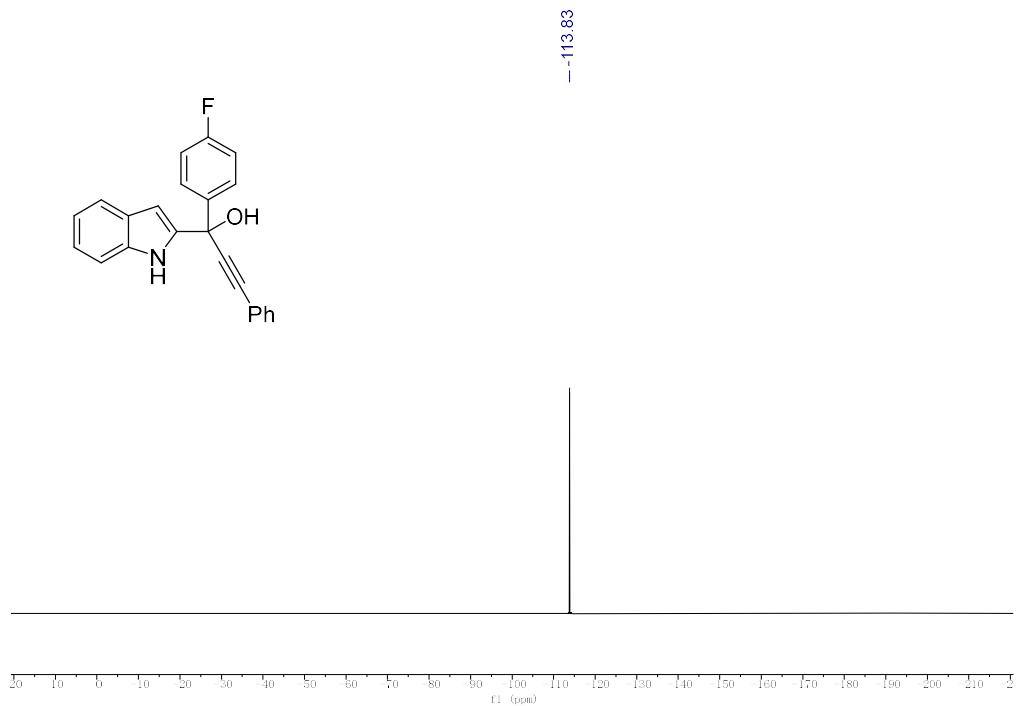
¹H NMR (400 MHz, CDCl₃) of **1I**



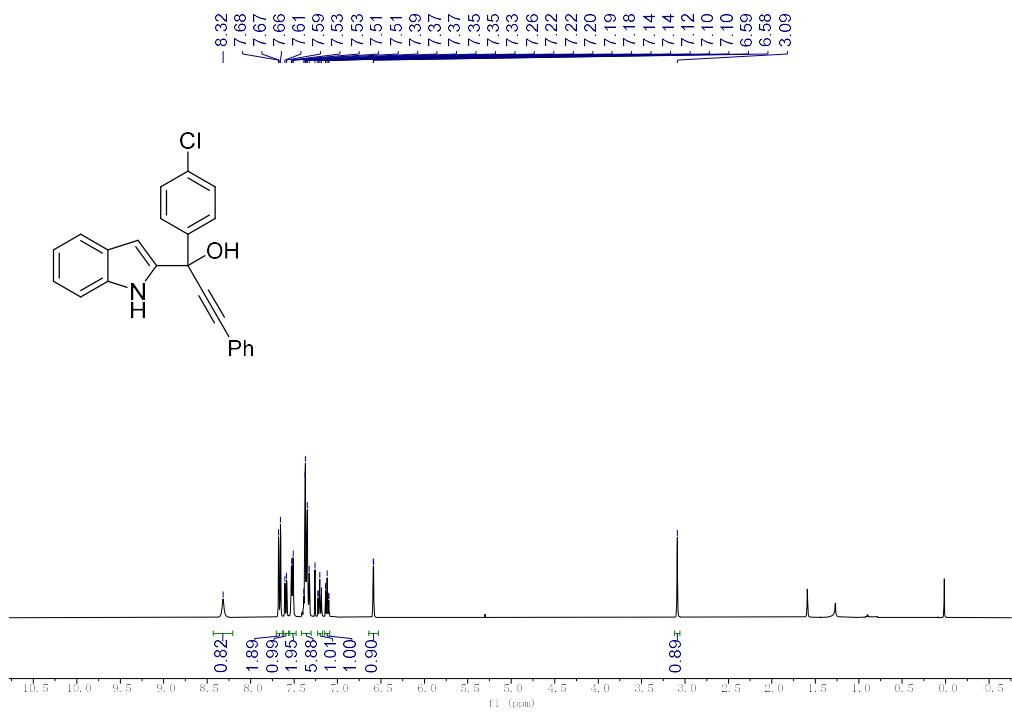
¹³C{¹H} NMR (101 MHz, CDCl₃) of **1I**



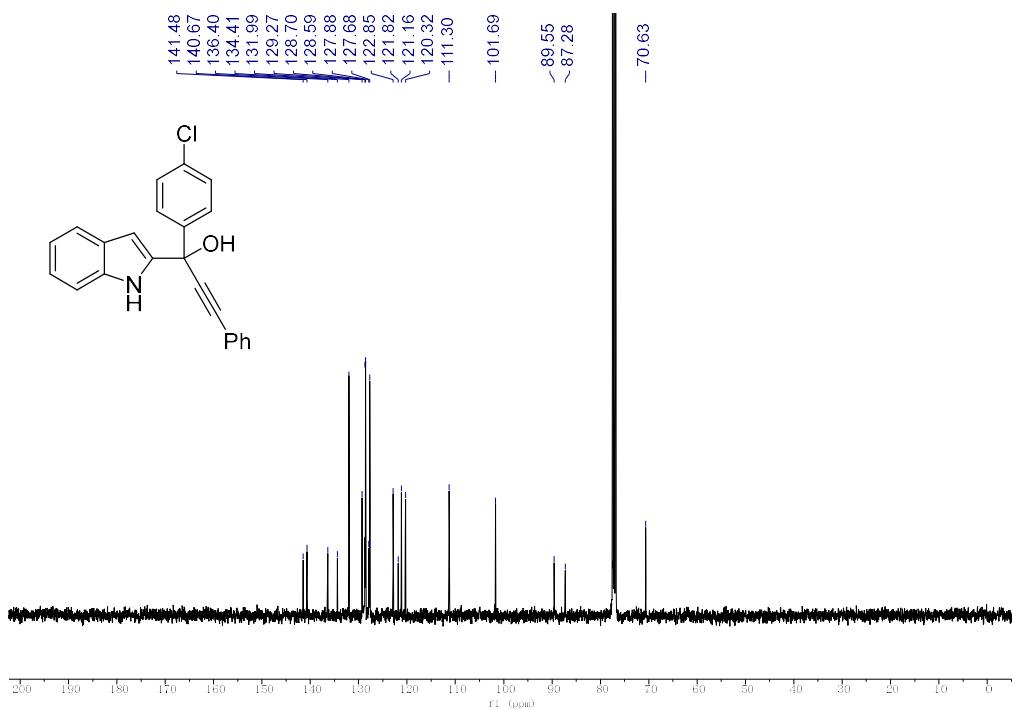
$^{19}\text{F}\{\text{H}\}$ NMR (376 MHz, CDCl_3) of **1l**



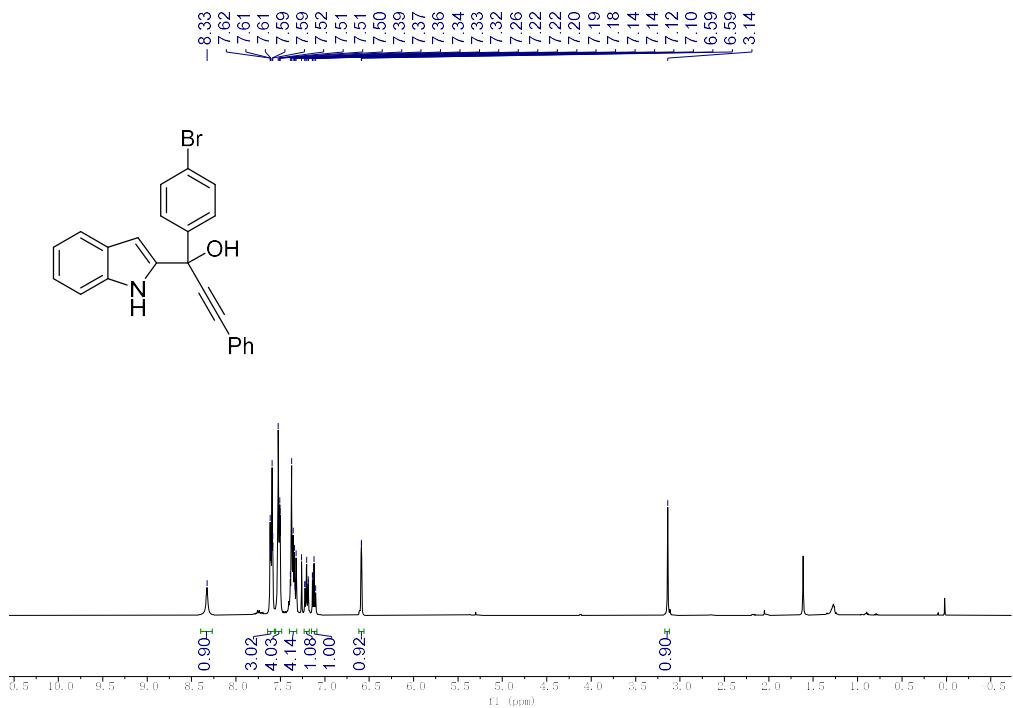
¹H NMR (400 MHz, CDCl₃) of **1m**



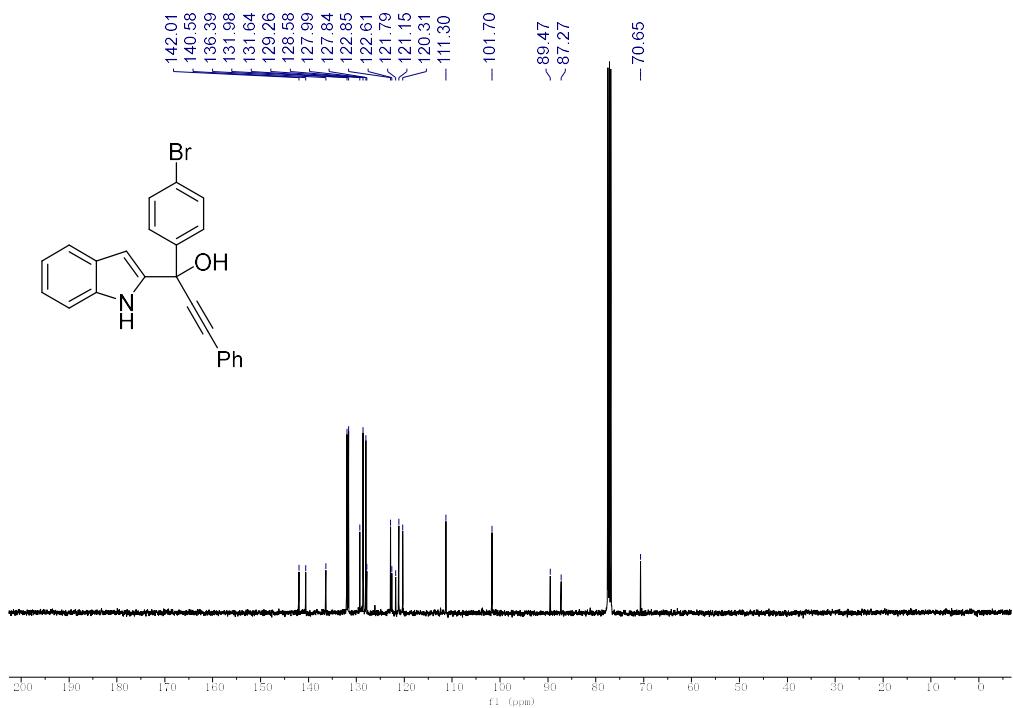
¹³C{¹H} NMR (101 MHz, CDCl₃) of **1m**



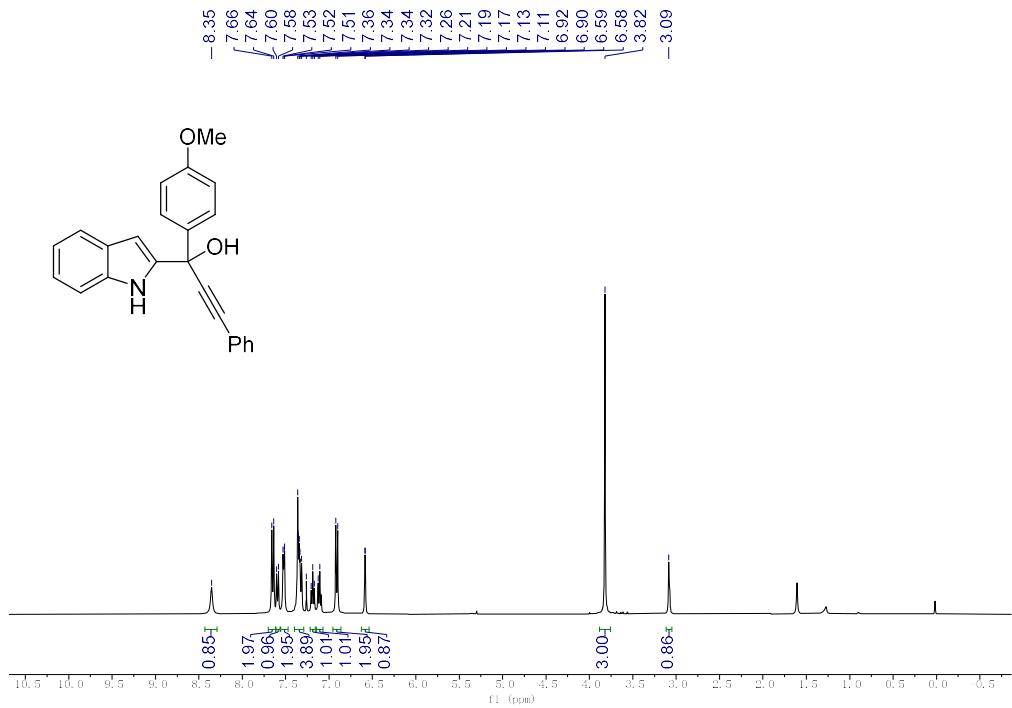
¹H NMR (400 MHz, CDCl₃) of **1n**



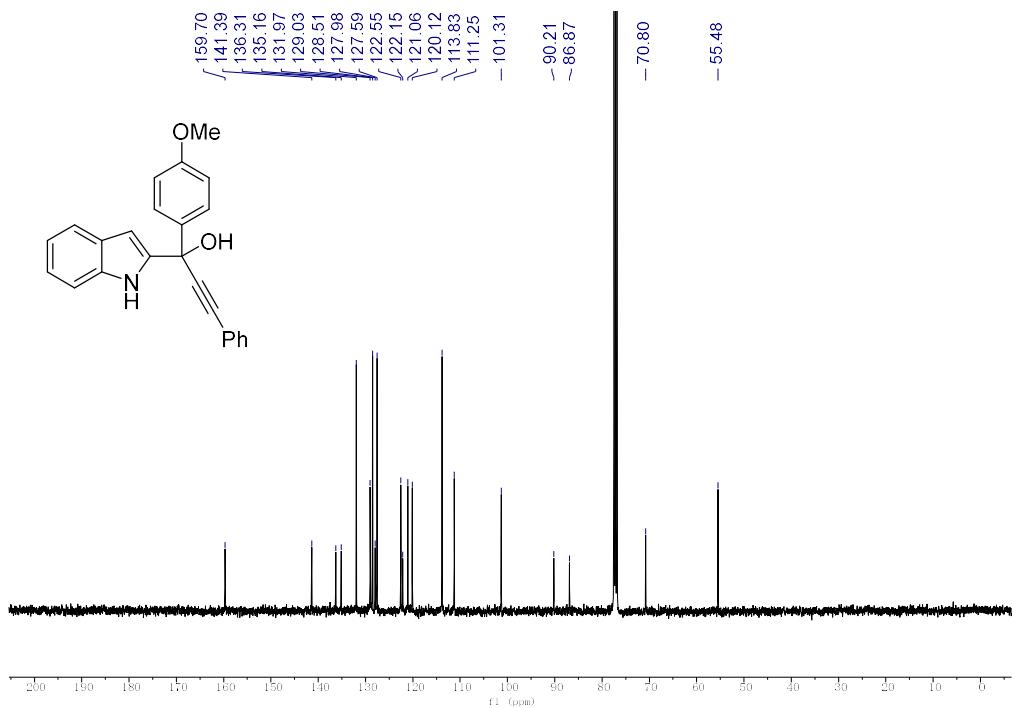
¹³C{¹H} NMR (101 MHz, CDCl₃) of **1n**



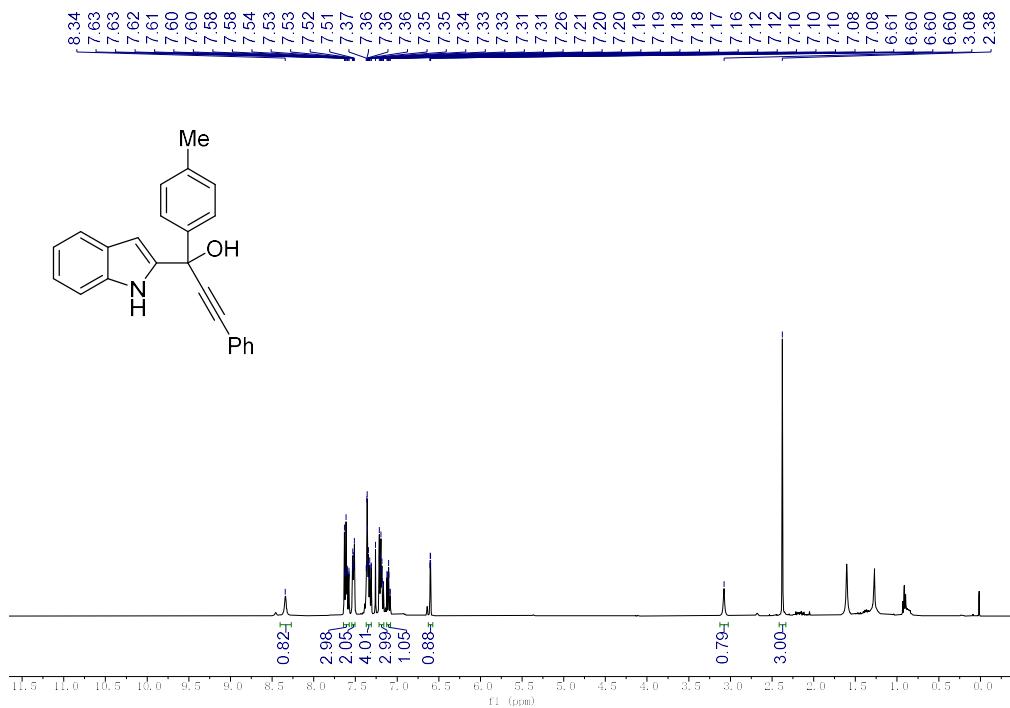
¹H NMR (400 MHz, CDCl₃) of **1o**



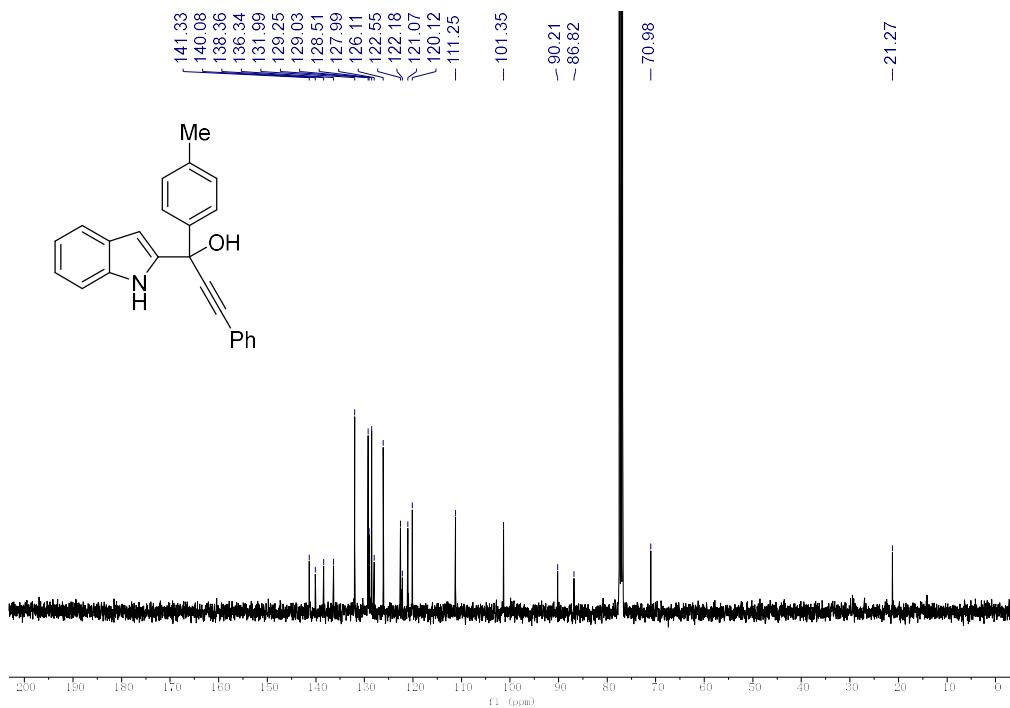
$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) of **1o**



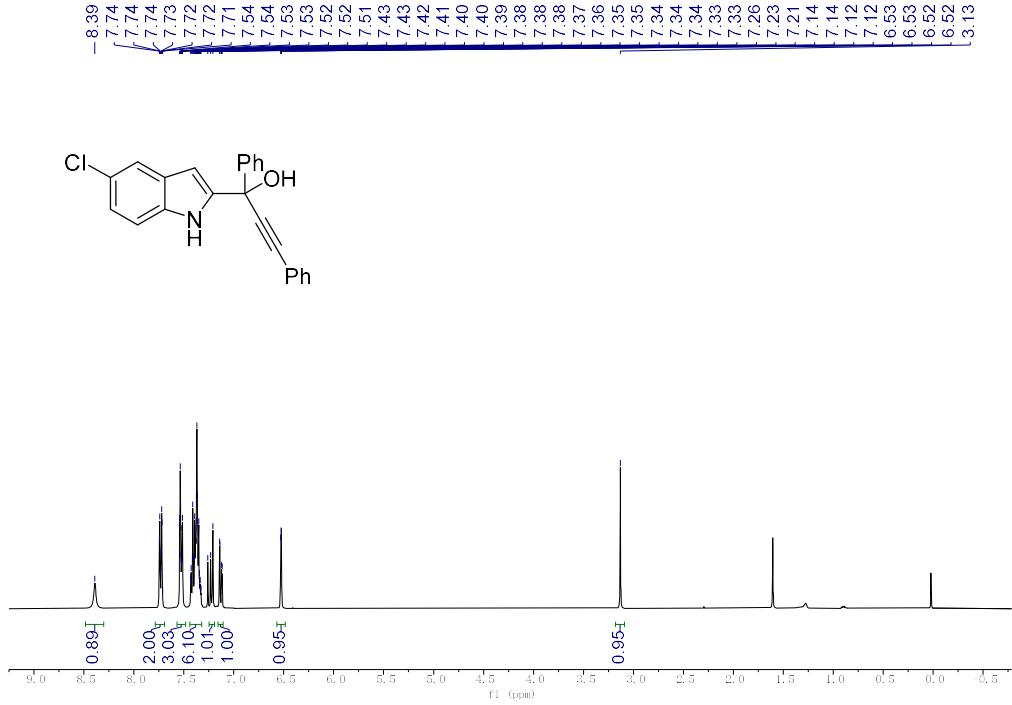
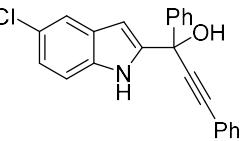
¹H NMR (400 MHz, CDCl₃) of **1p**



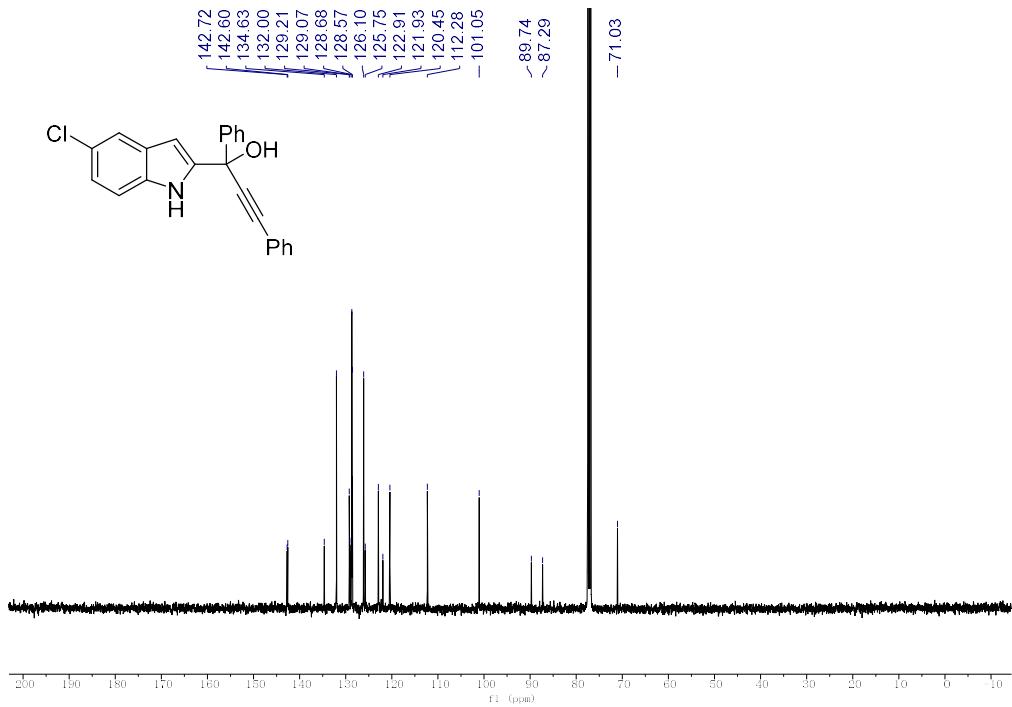
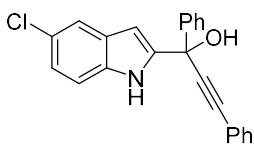
¹³C{¹H} NMR (101 MHz, CDCl₃) of **1p**



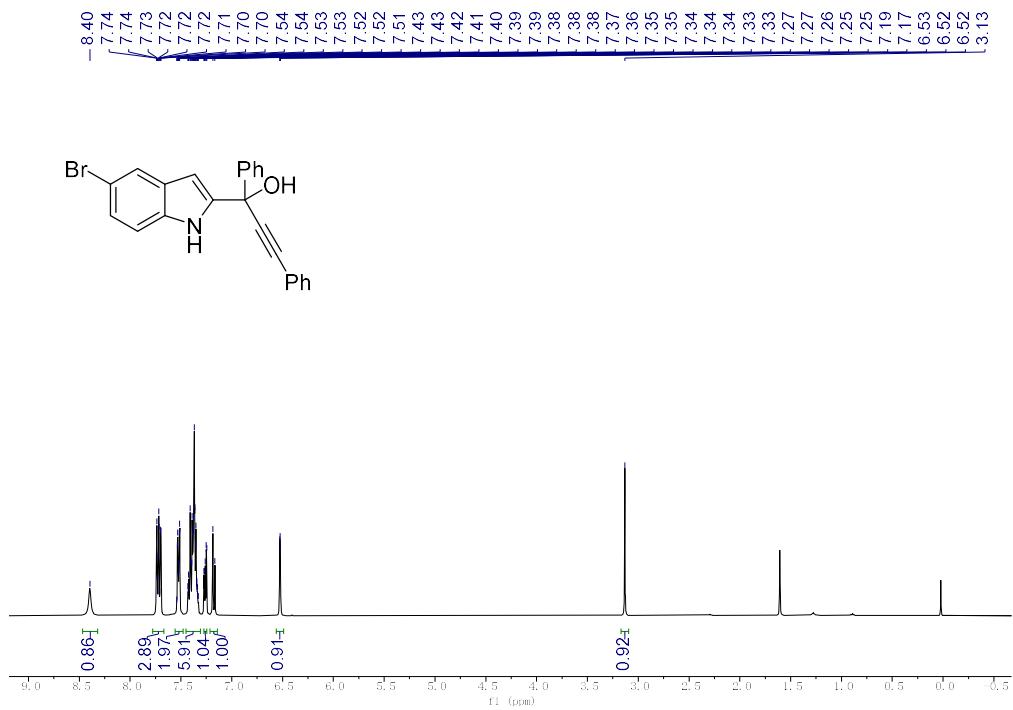
¹H NMR (400 MHz, CDCl₃) of **1q**



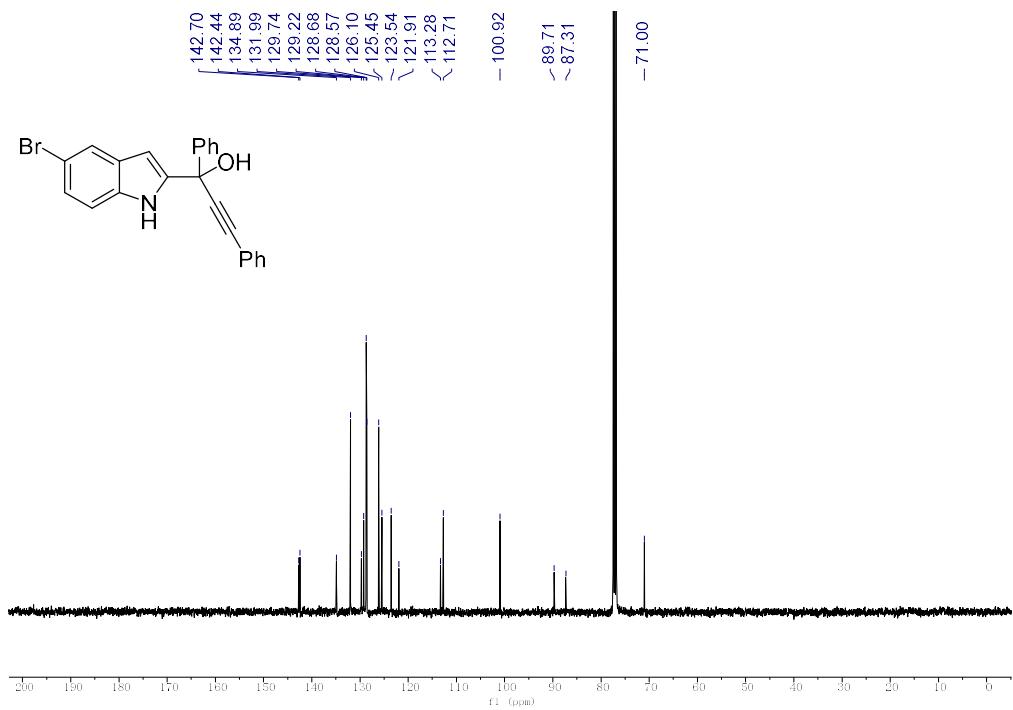
$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) of **1q**



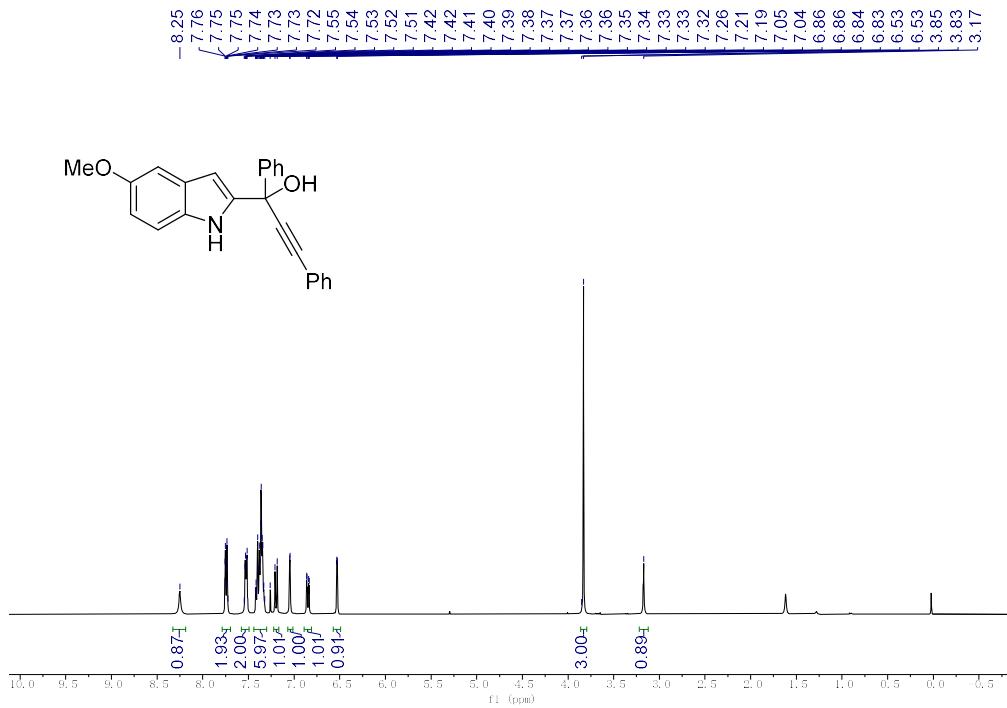
¹H NMR (400 MHz, CDCl₃) of **1r**



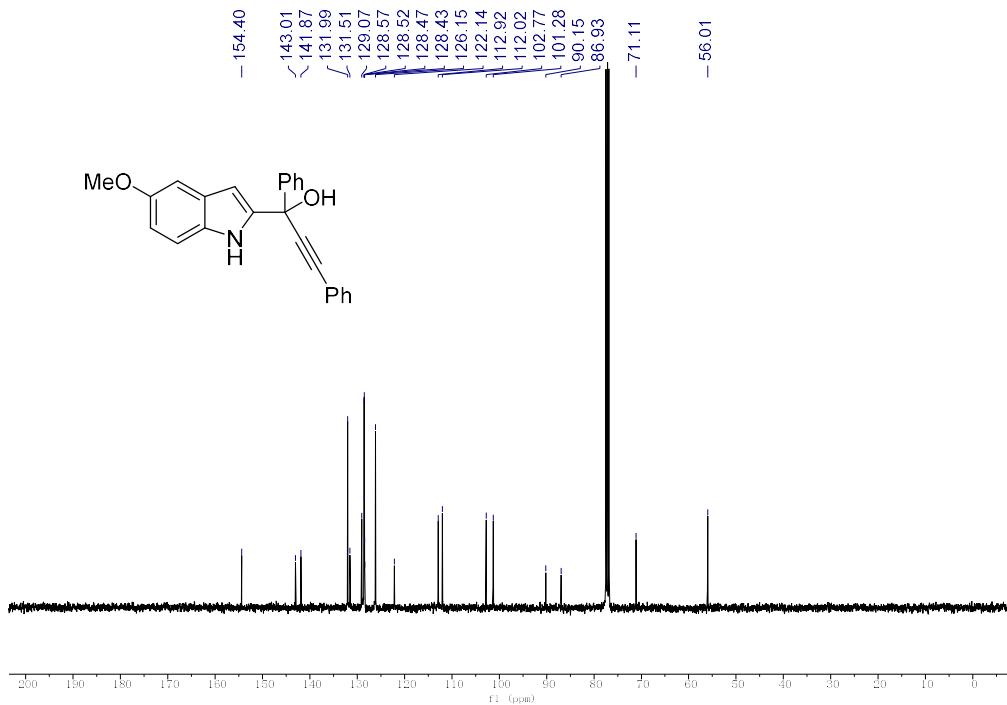
¹³C{¹H} NMR (101 MHz, CDCl₃) of **1r**



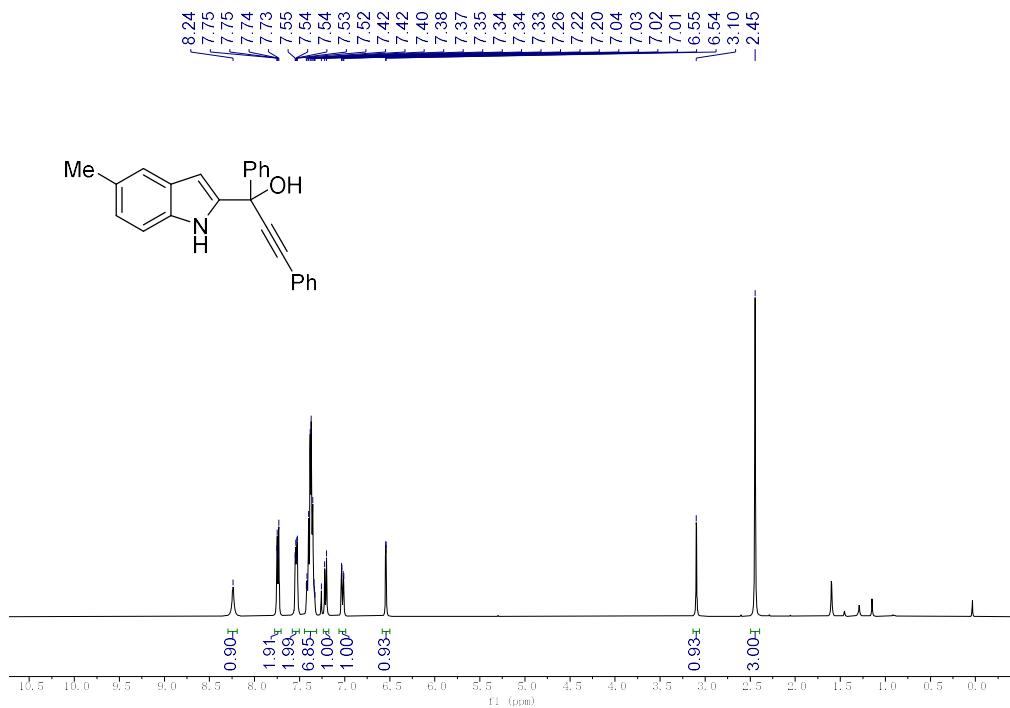
¹H NMR (400 MHz, CDCl₃) of **1s**



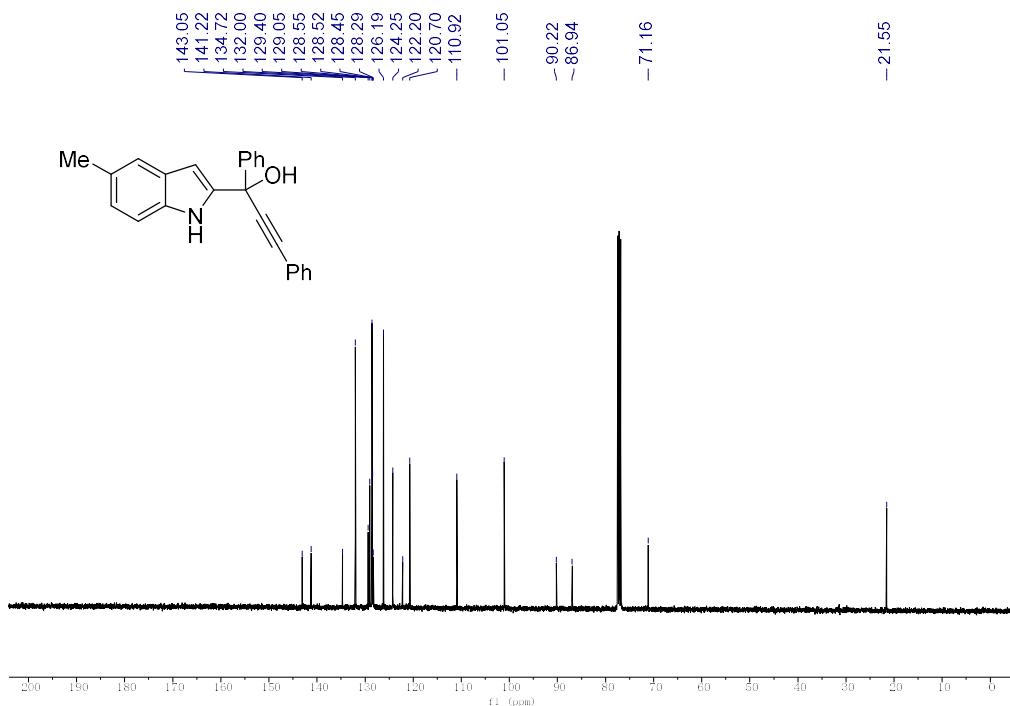
¹³C{¹H} NMR (101 MHz, CDCl₃) of **1s**



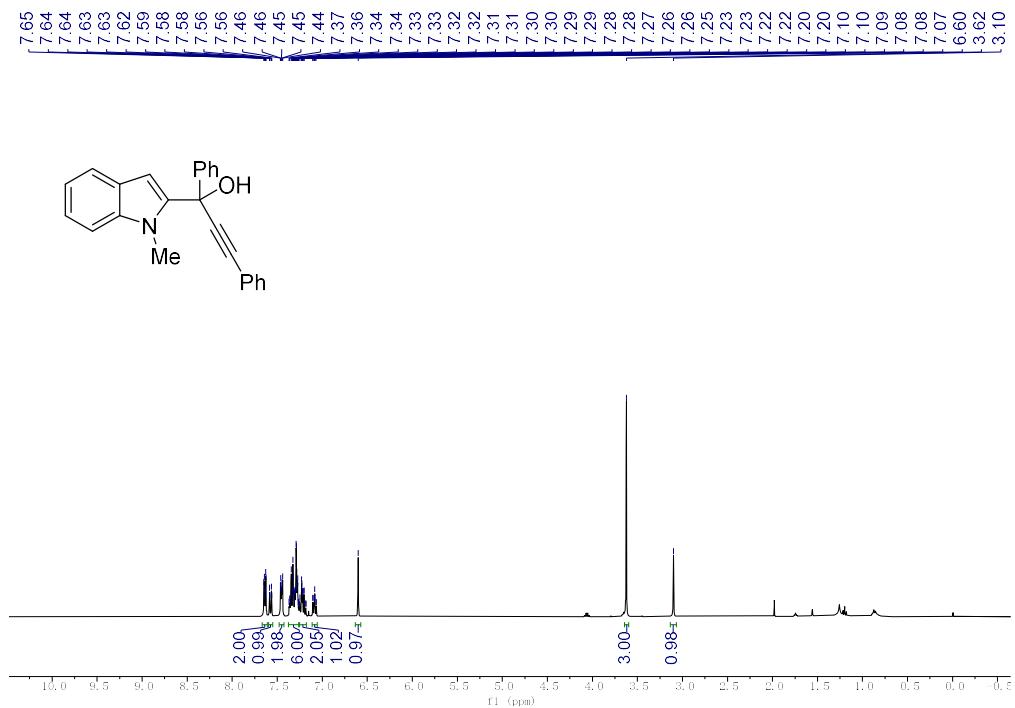
¹H NMR (400 MHz, CDCl₃) of **1t**



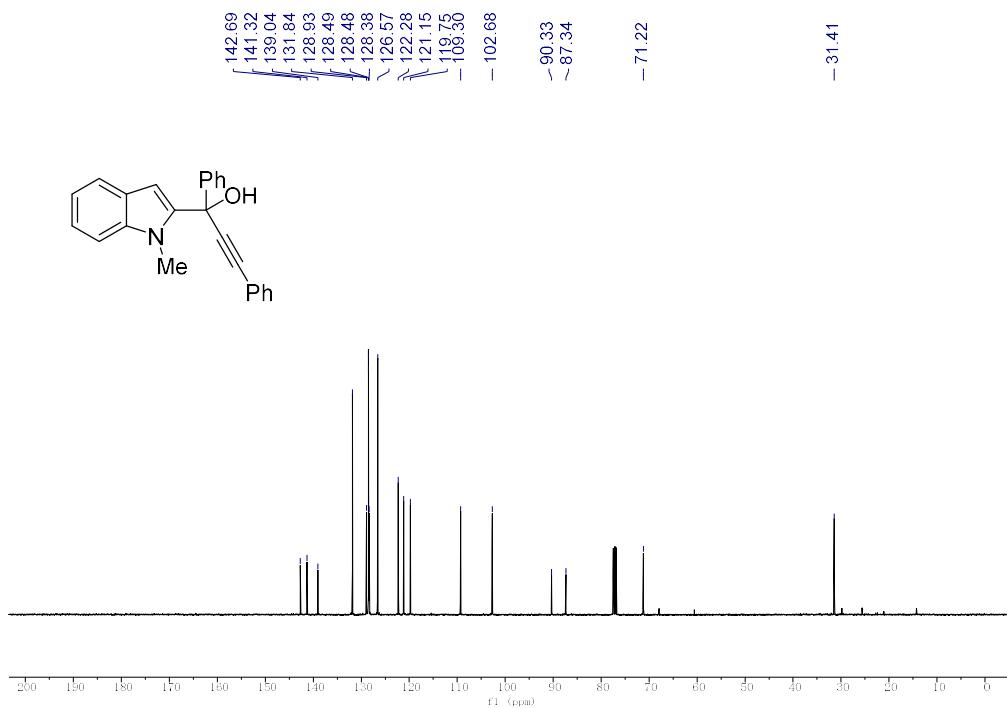
¹³C{¹H} NMR (101 MHz, CDCl₃) of **1t**



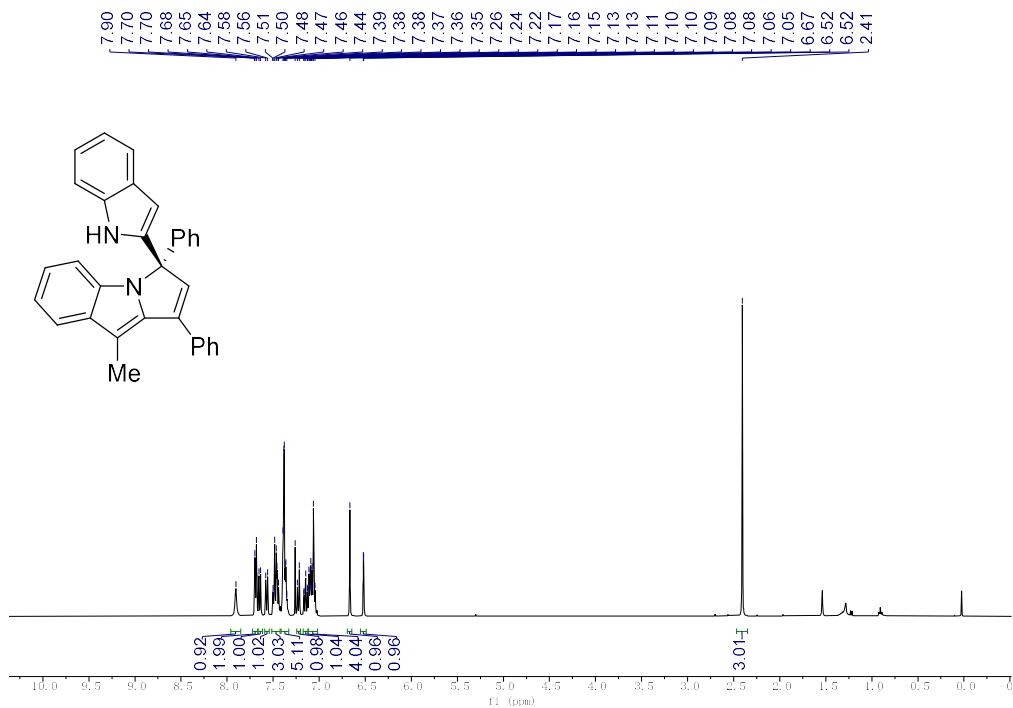
¹H NMR (400 MHz, CDCl₃) of **9**



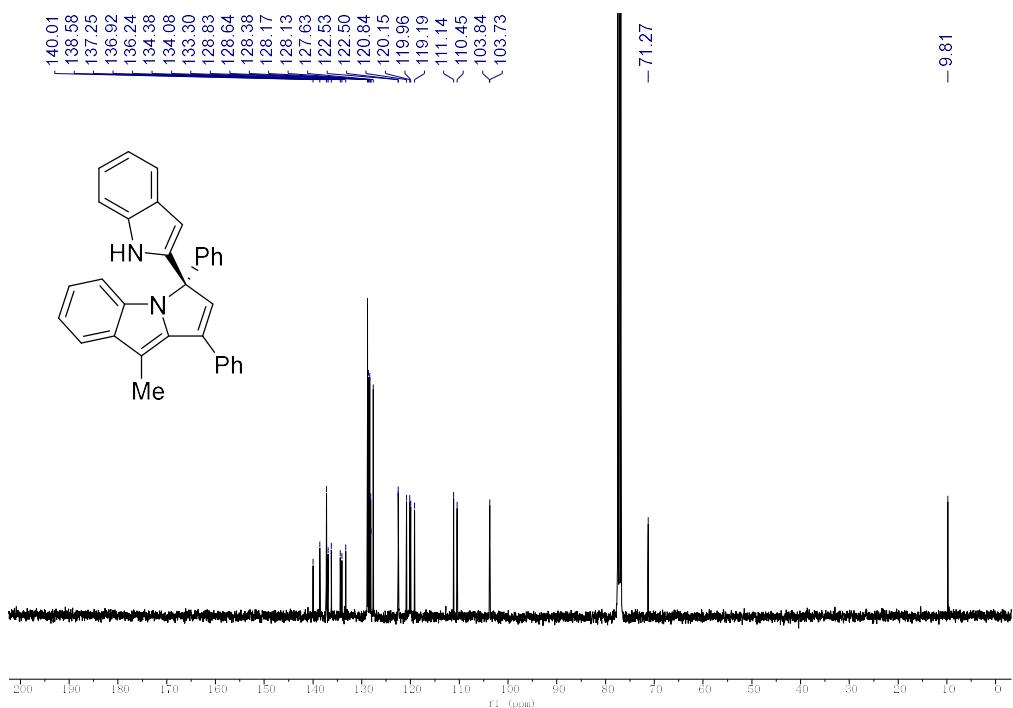
¹³C{¹H} NMR (101 MHz, CDCl₃) of **9**



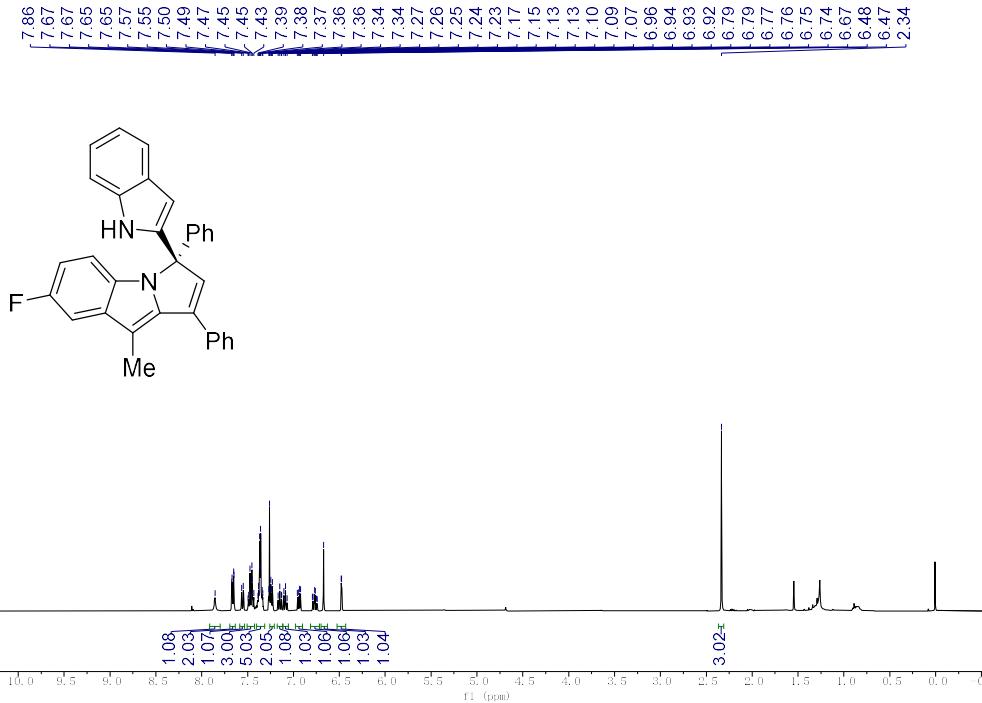
¹H NMR (400 MHz, CDCl₃) of **3aa**



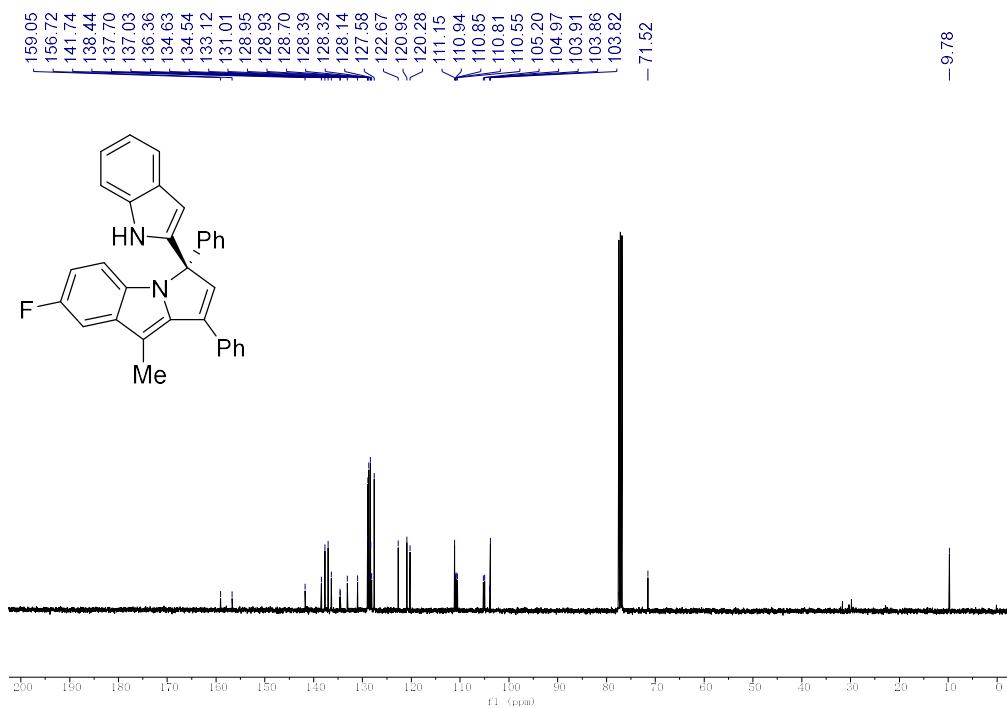
¹³C{¹H} NMR (101 MHz, CDCl₃) of **3aa**



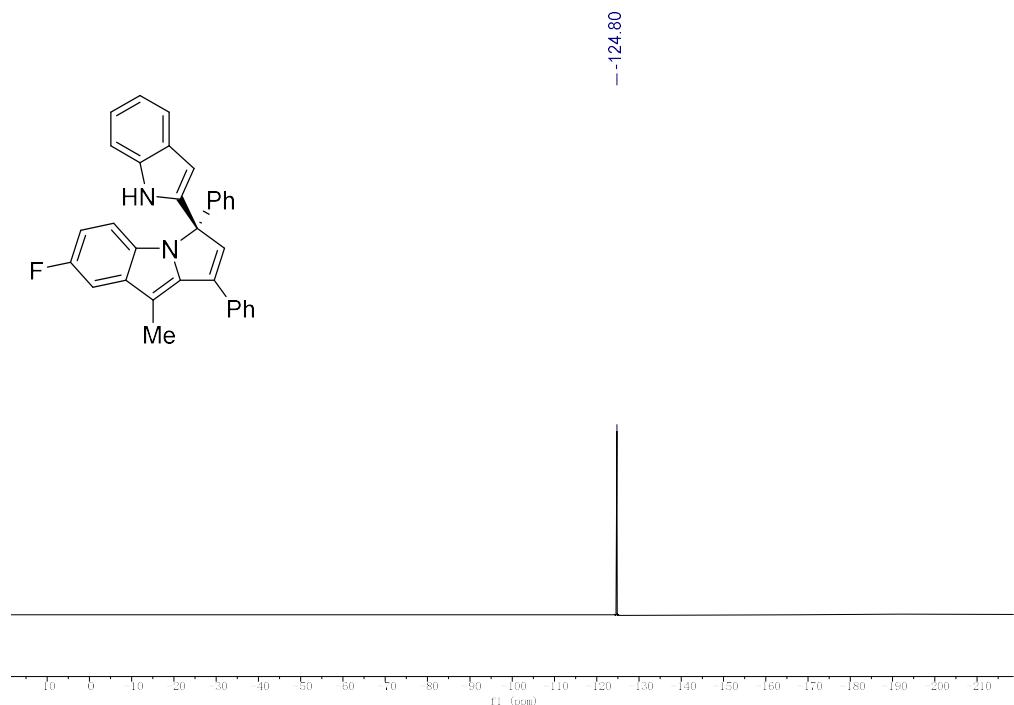
¹H NMR (400 MHz, CDCl₃) of 3ab



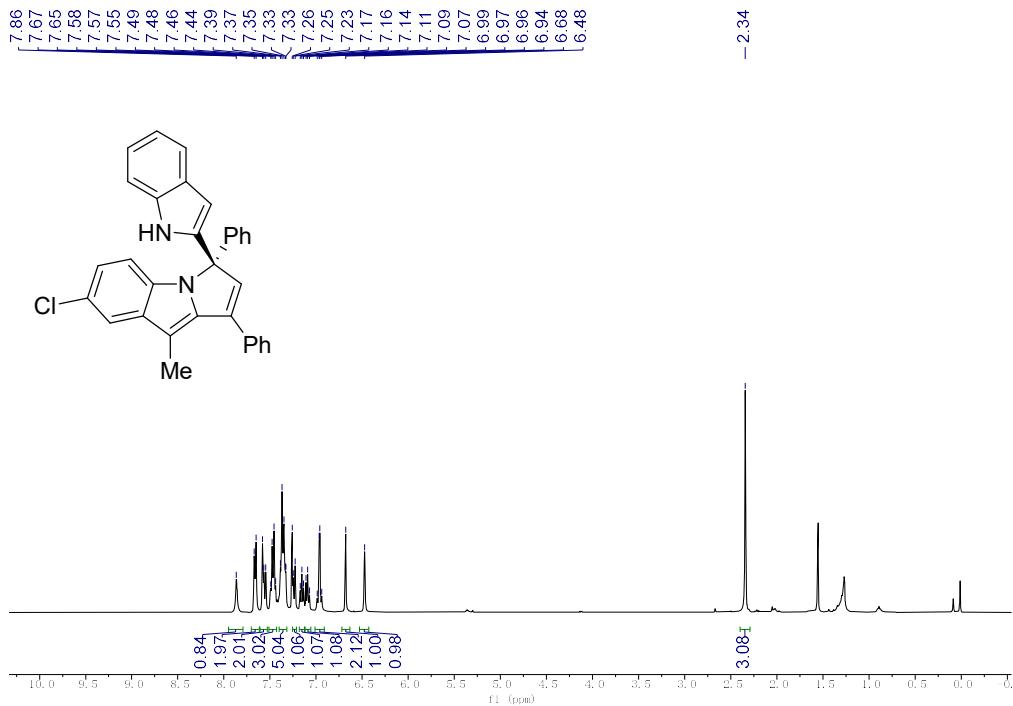
$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) of **3ab**



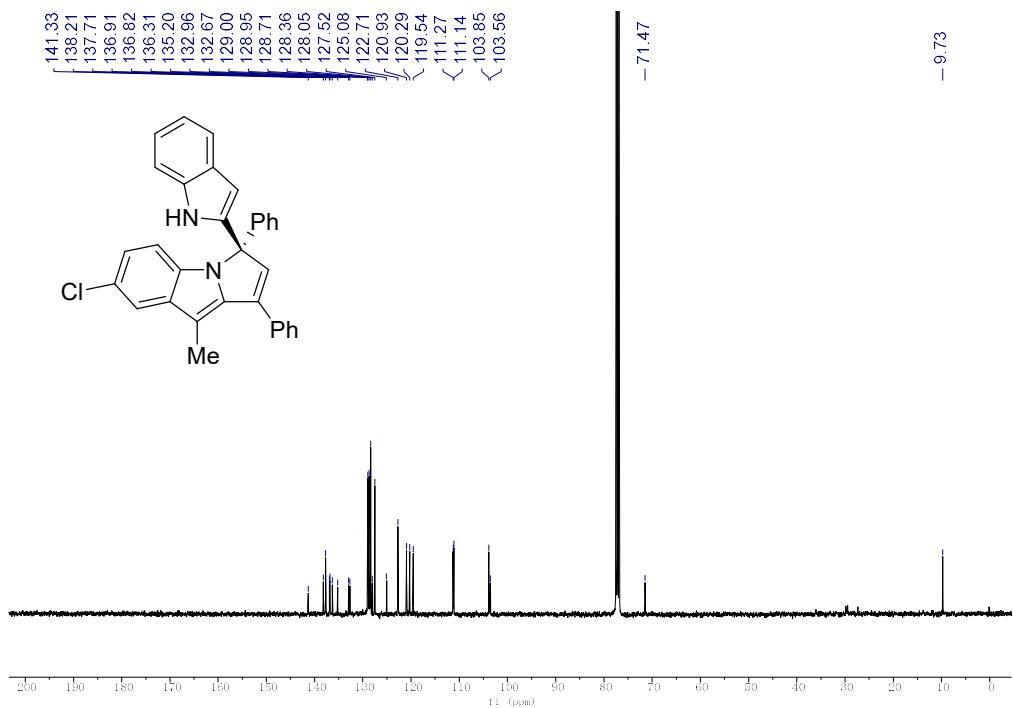
$^{19}\text{F}\{\text{H}\}$ NMR (376 MHz, CDCl_3) of **3ab**



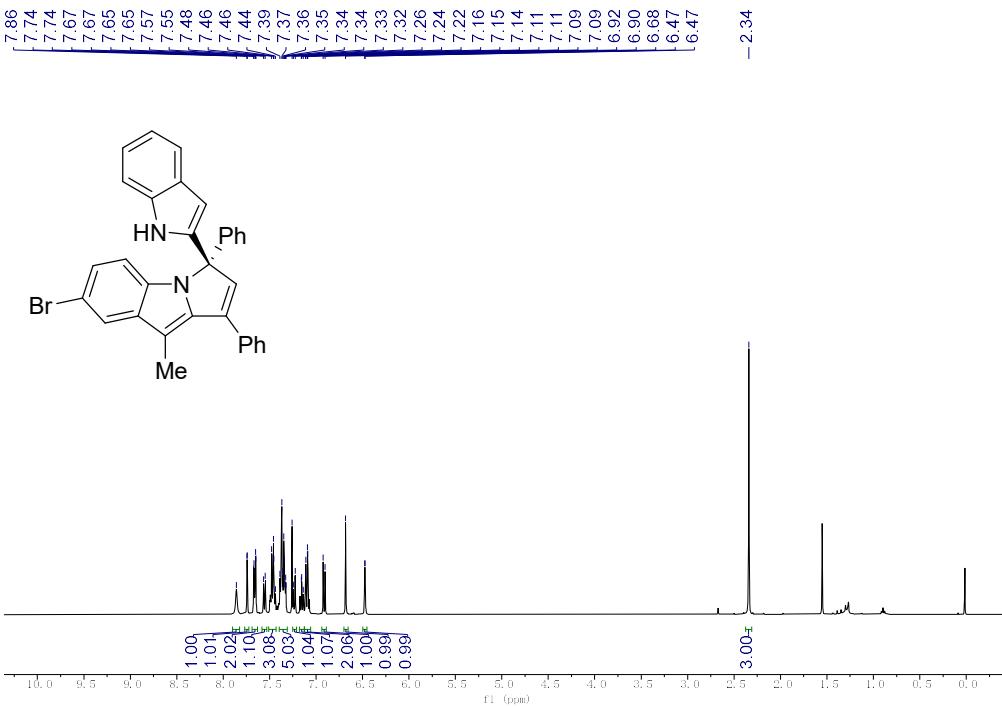
¹H NMR (400 MHz, CDCl₃) of **3ac**



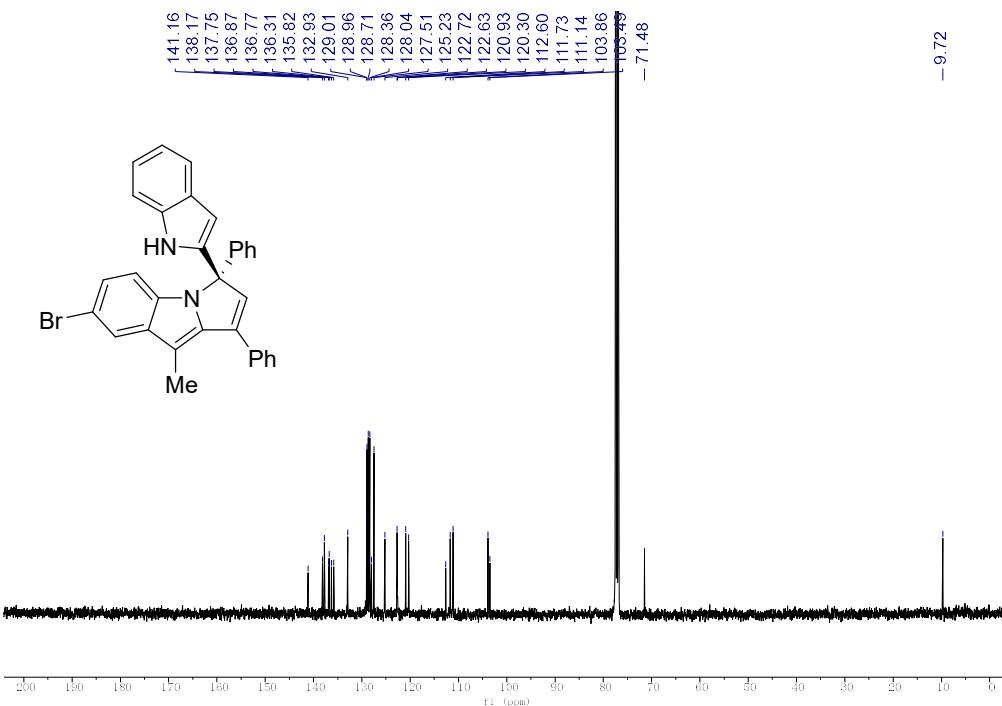
$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) of **3ac**



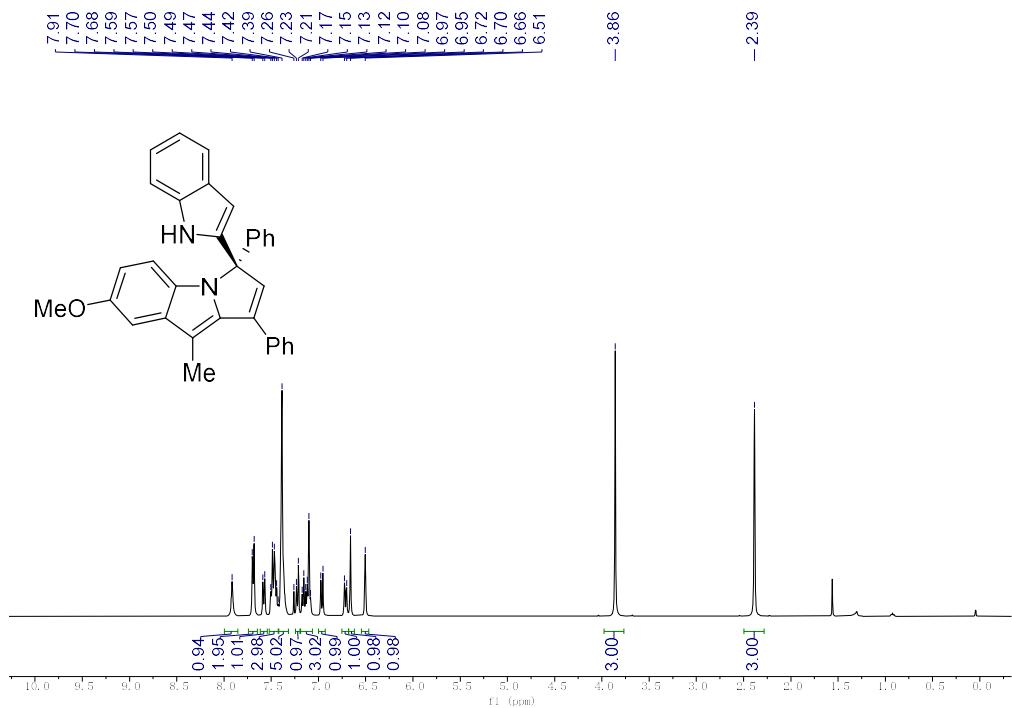
¹H NMR (400 MHz, CDCl₃) of 3ad



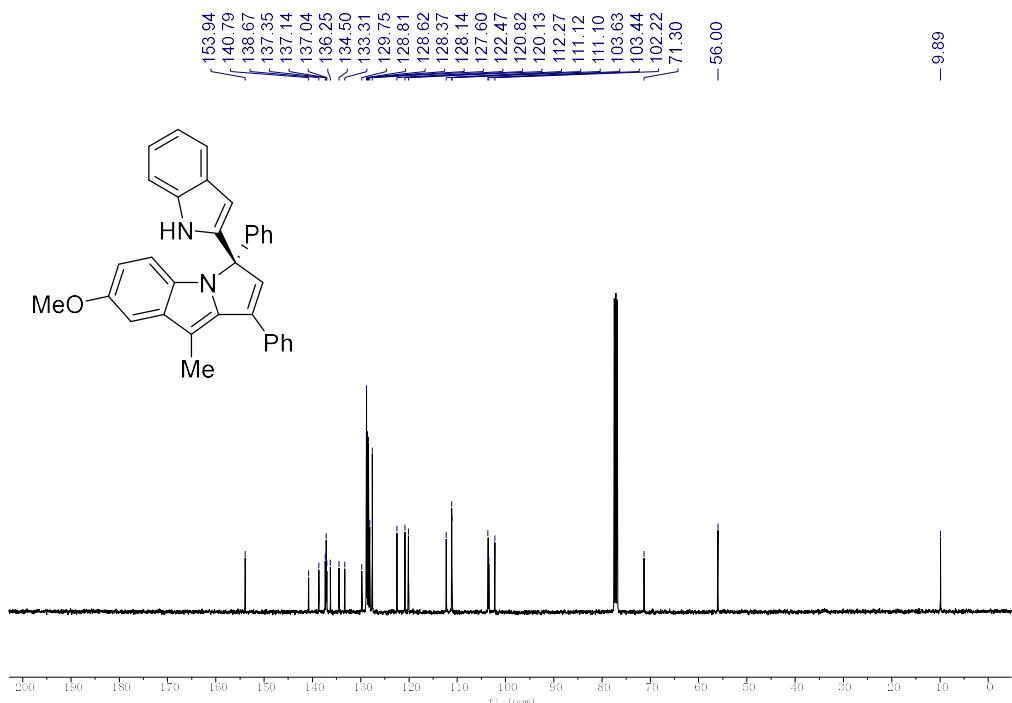
$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) of **3ad**



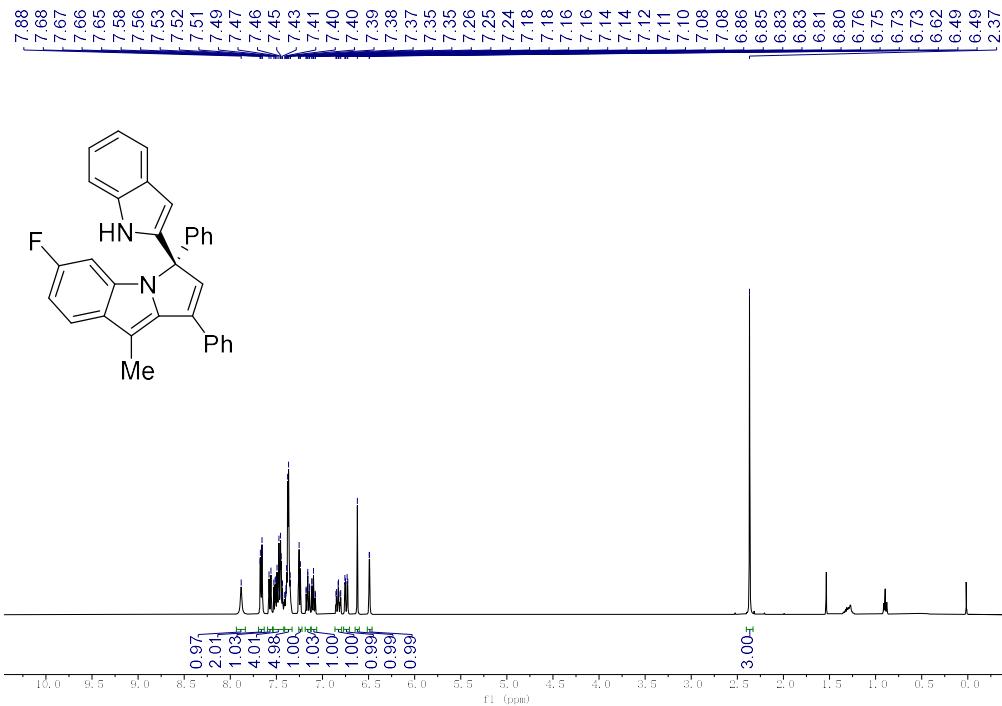
¹H NMR (400 MHz, CDCl₃) of **3ae**



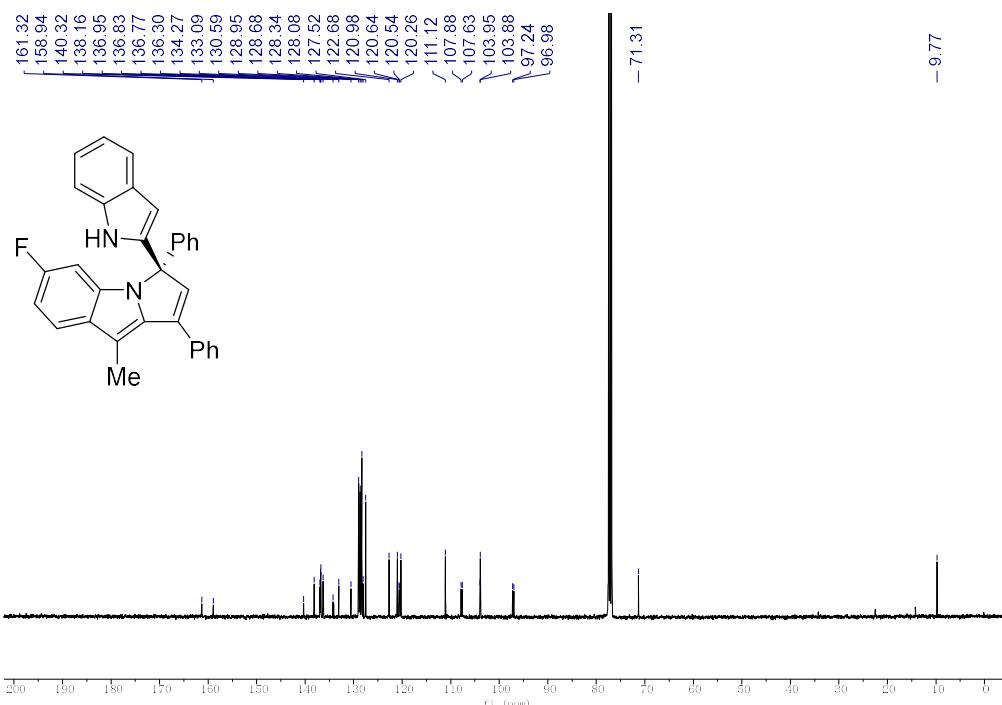
¹³C{¹H} NMR (101 MHz, CDCl₃) of **3ae**



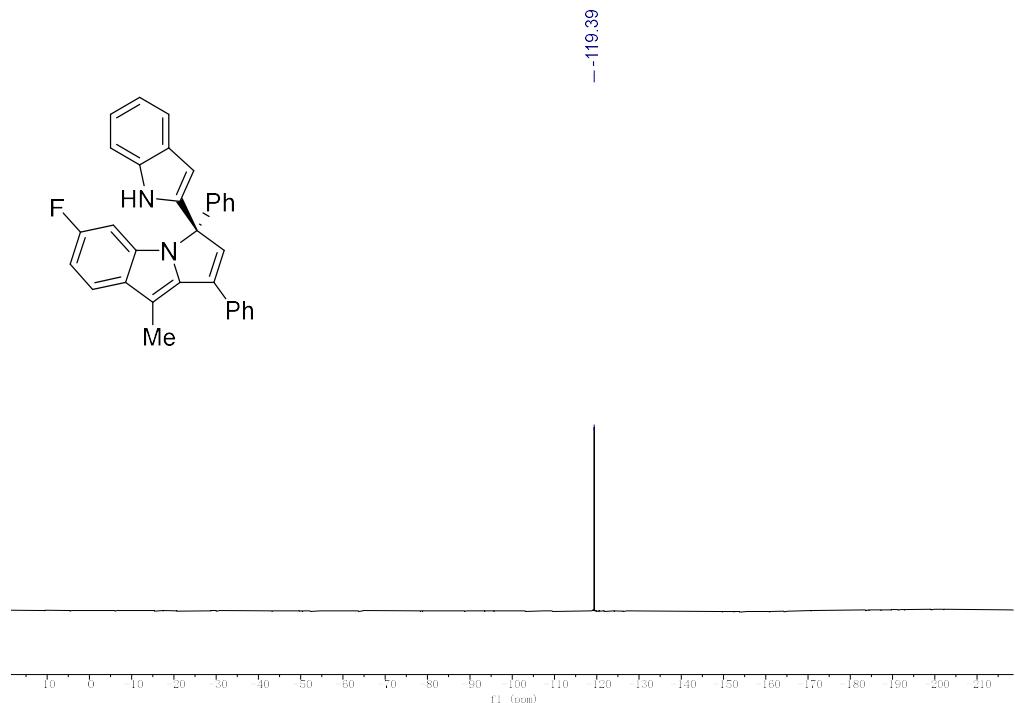
¹H NMR (400 MHz, CDCl₃) of 3af



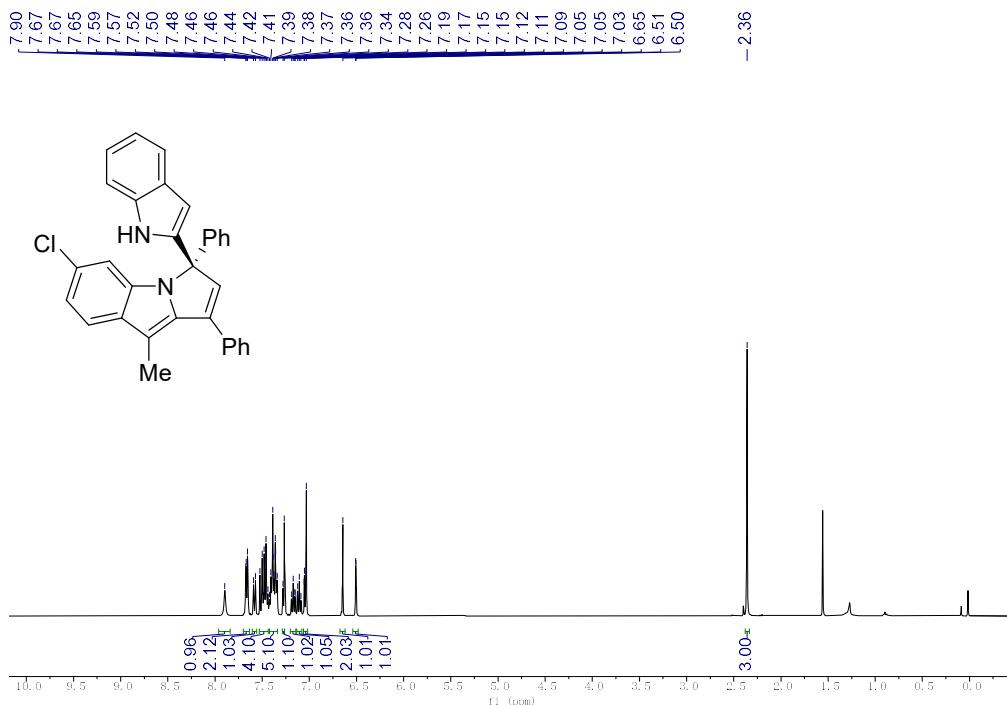
$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) of **3af**



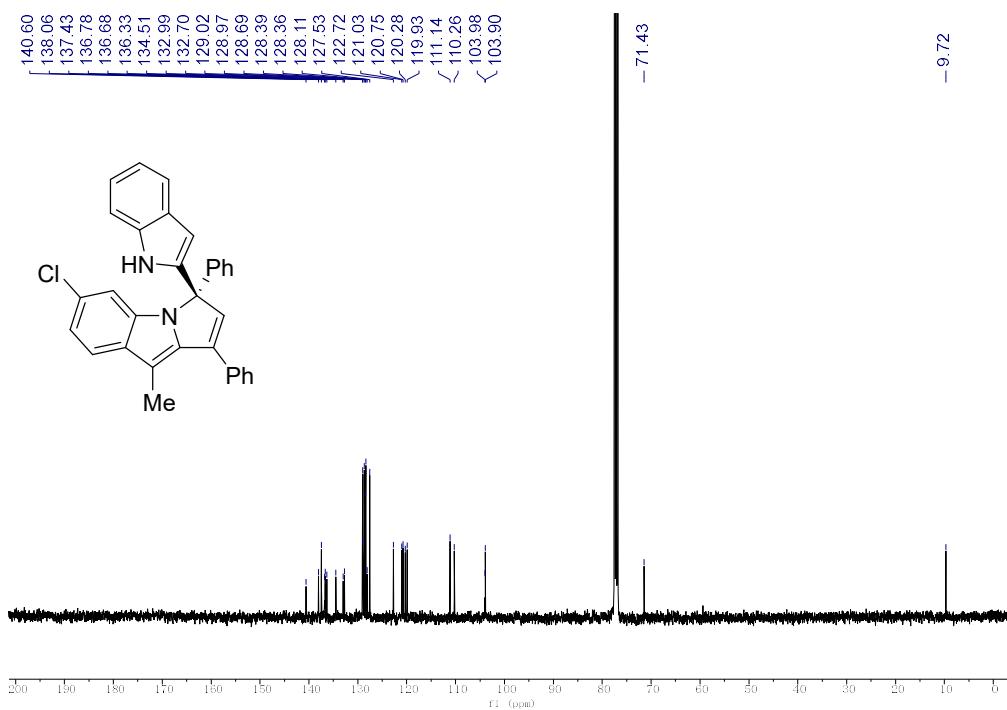
$^{19}\text{F}\{\text{H}\}$ NMR (376 MHz, CDCl_3) of **3af**



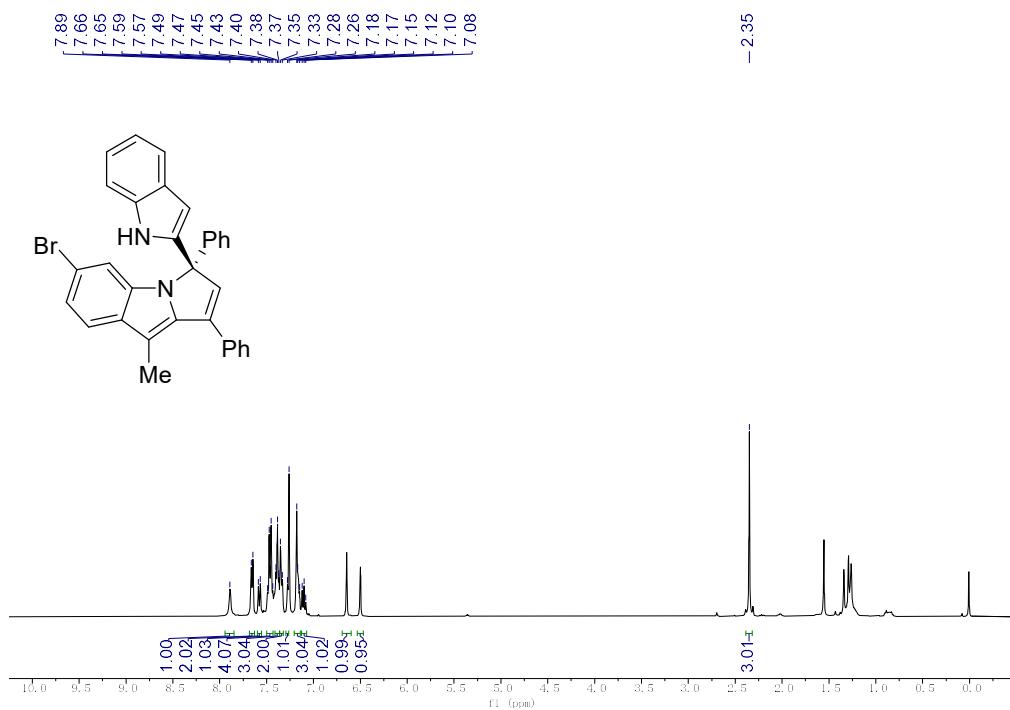
¹H NMR (400 MHz, CDCl₃) of **3ag**



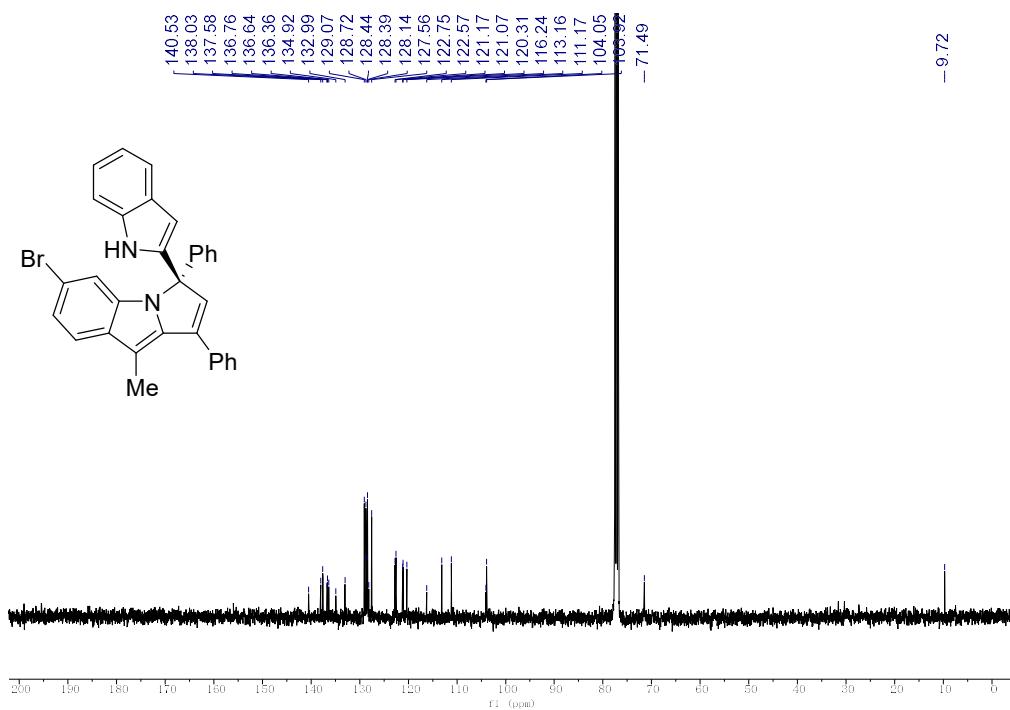
¹³C{¹H} NMR (101 MHz, CDCl₃) of **3ag**



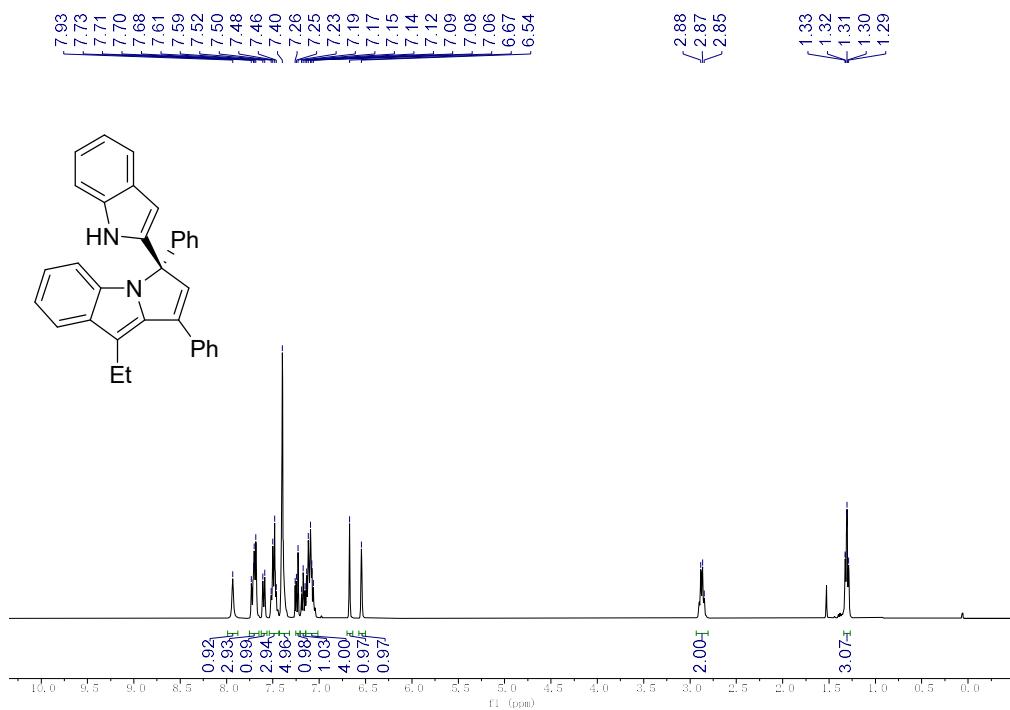
¹H NMR (400 MHz, CDCl₃) of **3ah**



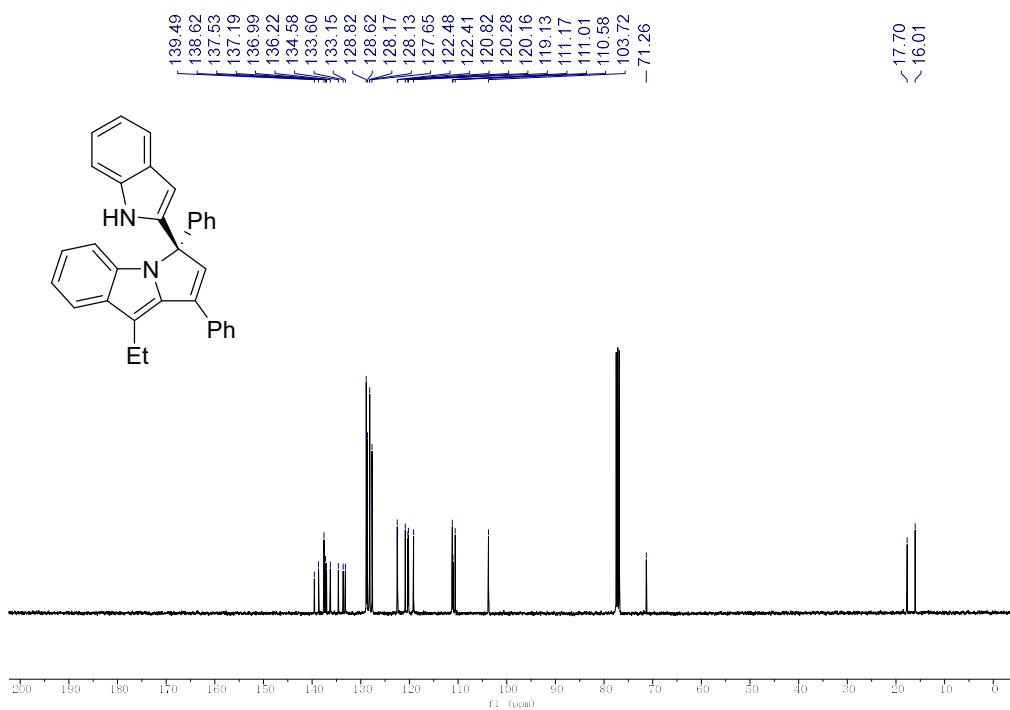
¹³C{¹H} NMR (101 MHz, CDCl₃) of **3ah**



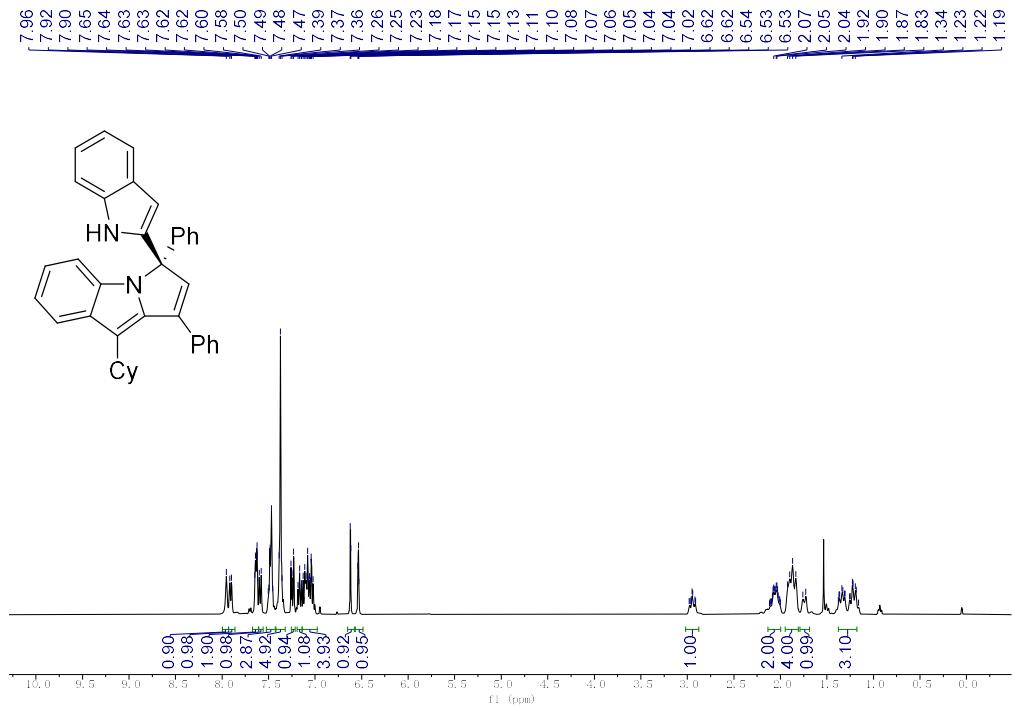
¹H NMR (400 MHz, CDCl₃) of **3ai**



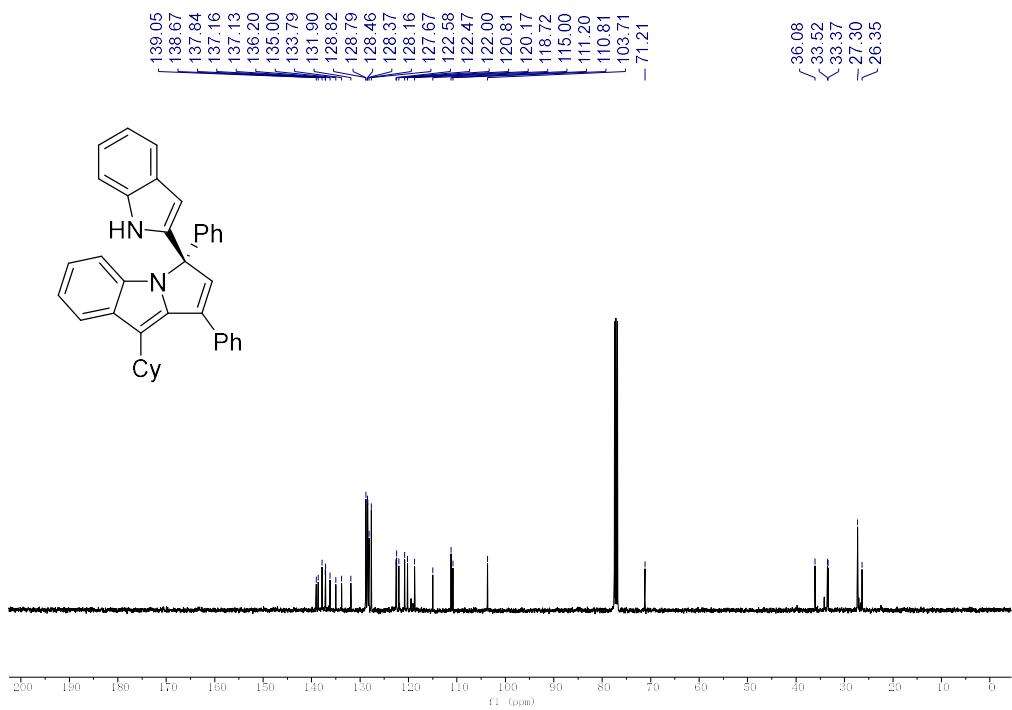
¹³C{¹H} NMR (101 MHz, CDCl₃) of **3ai**



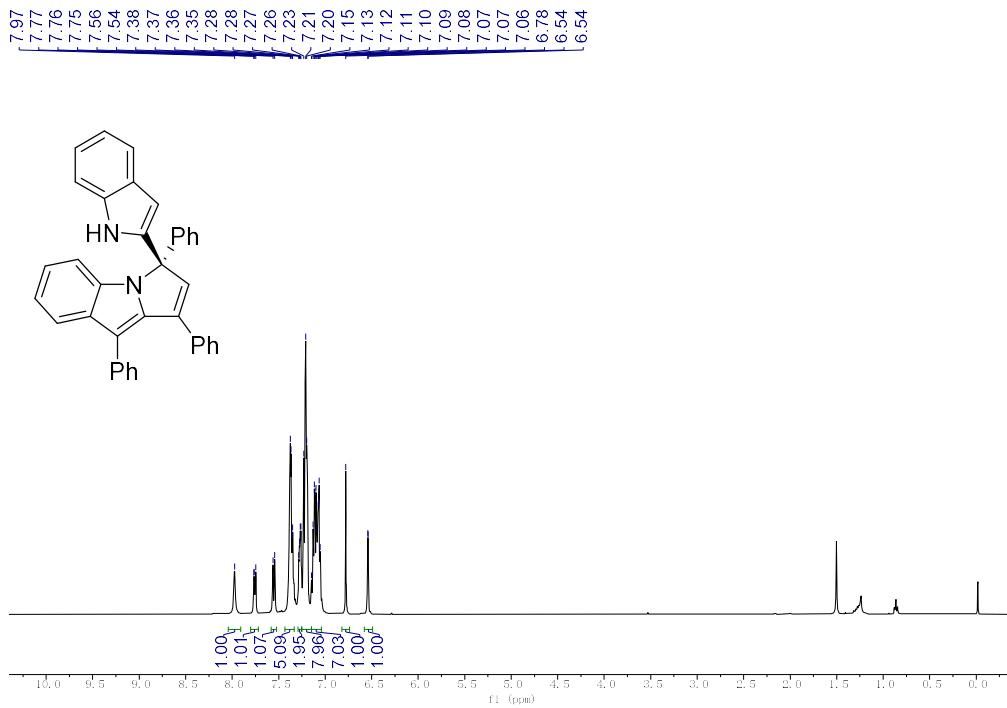
¹H NMR (400 MHz, CDCl₃) of **3aj**



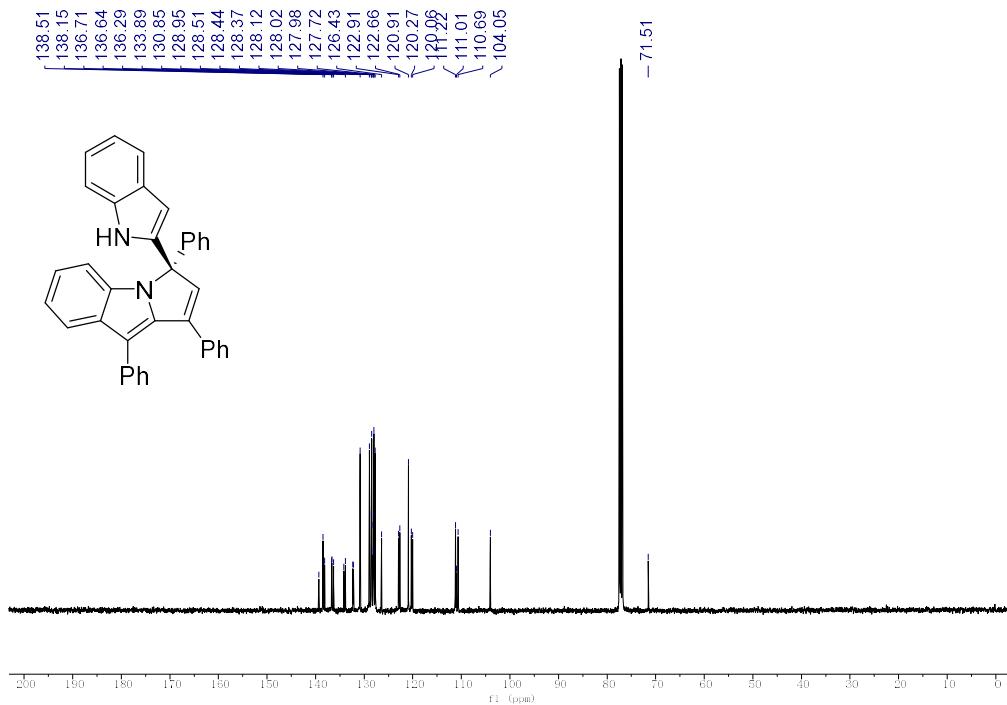
¹³C{¹H} NMR (101 MHz, CDCl₃) of **3aj**



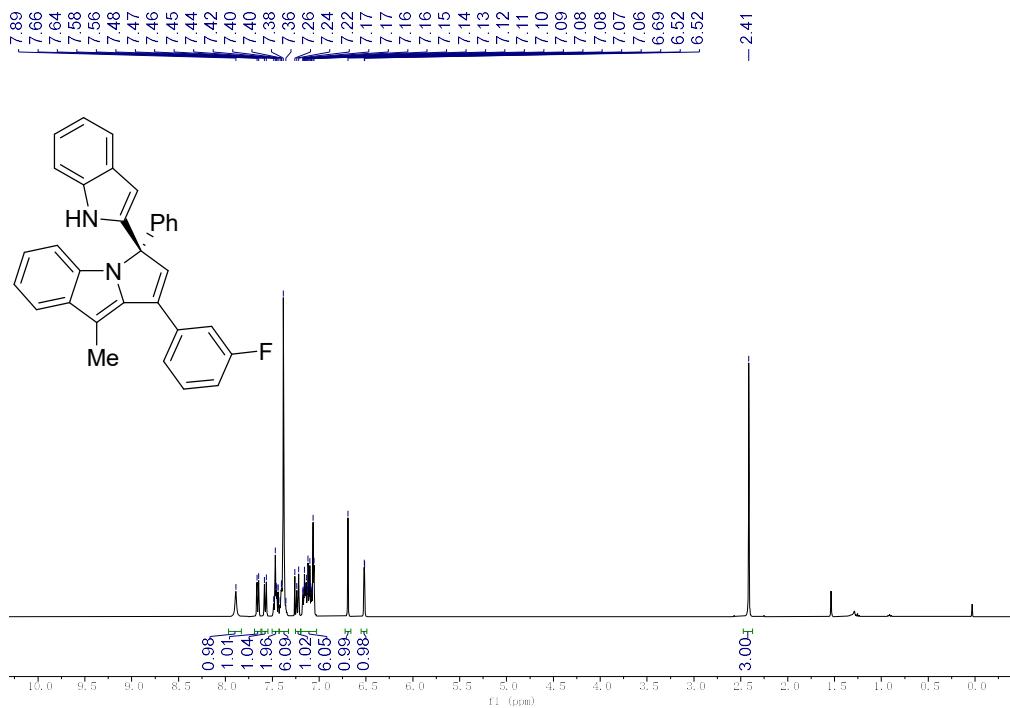
¹H NMR (400 MHz, CDCl₃) of **3ak**



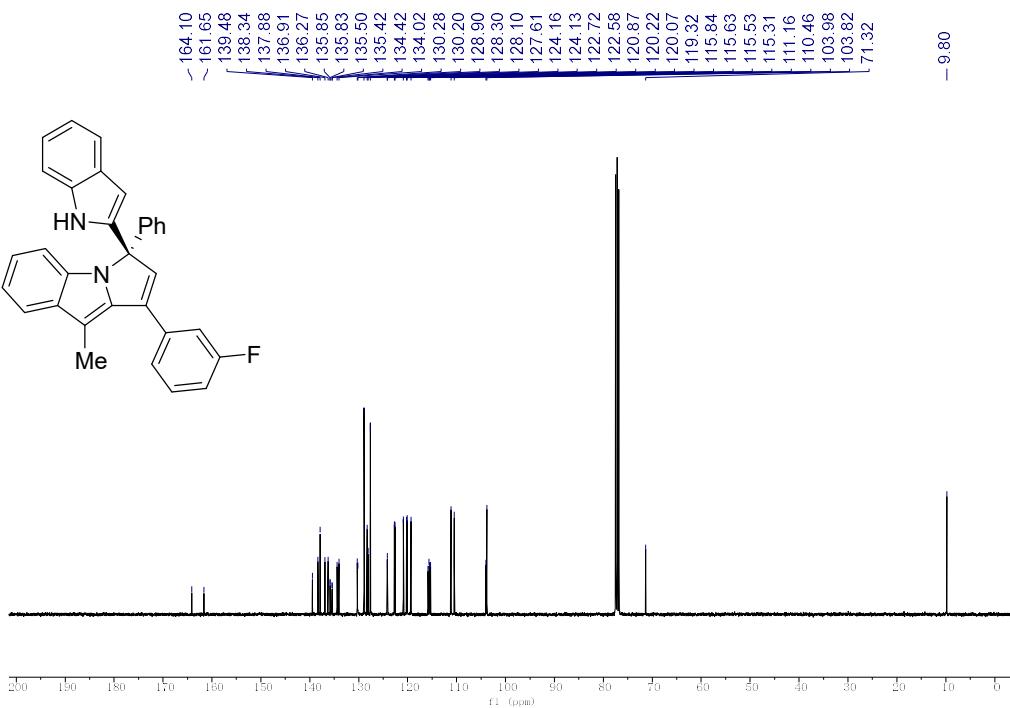
$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) of **3ak**



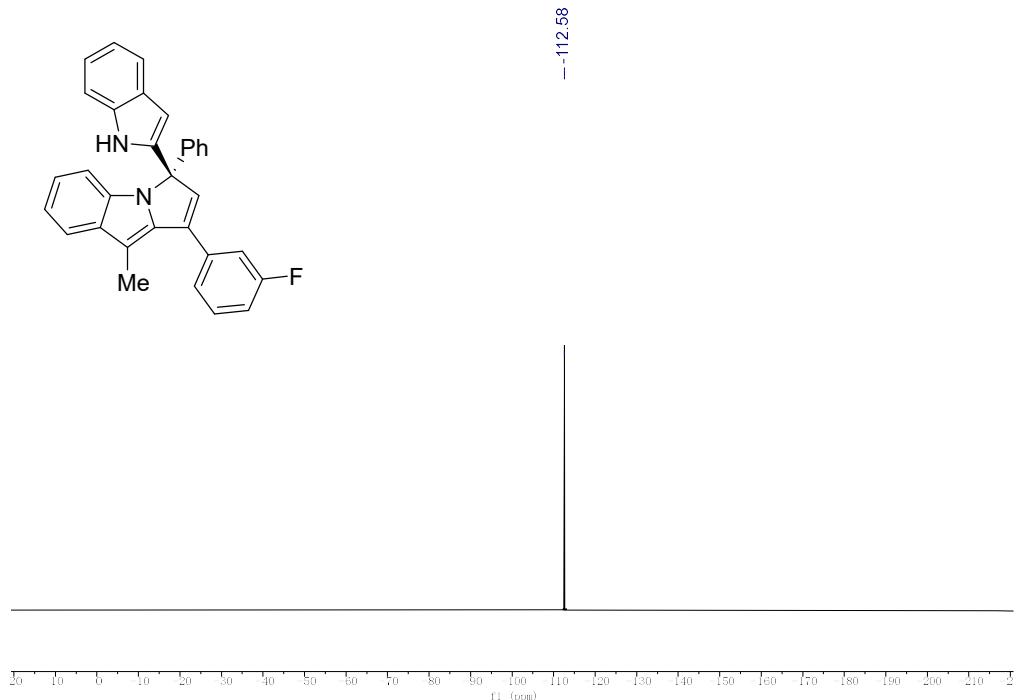
¹H NMR (400 MHz, CDCl₃) of **3ba**



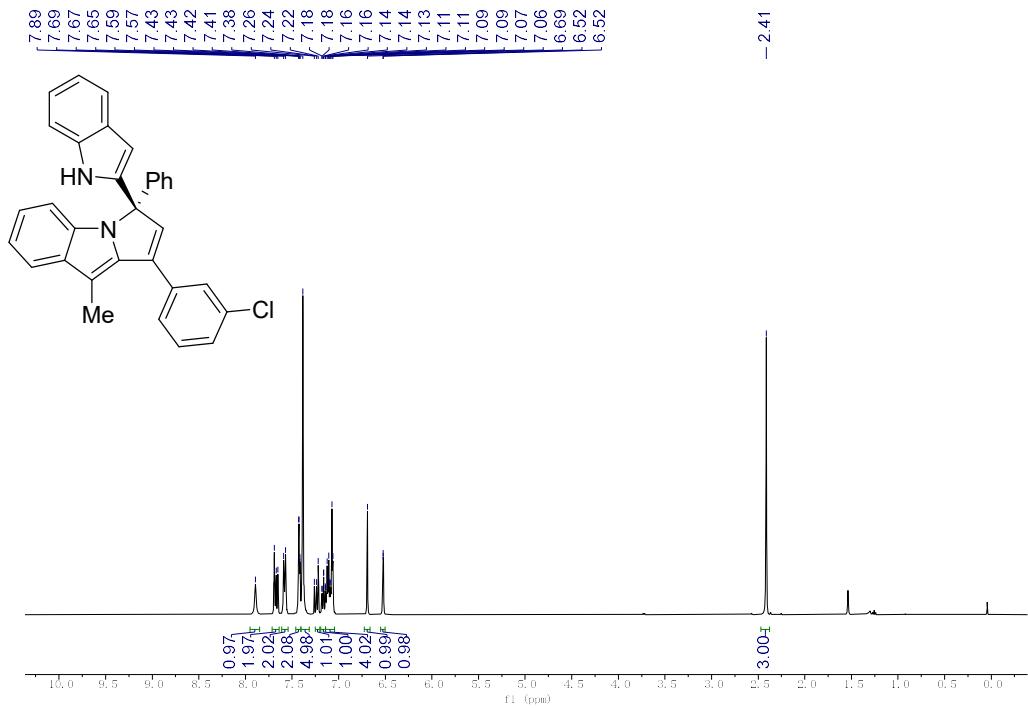
$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) of **3ba**



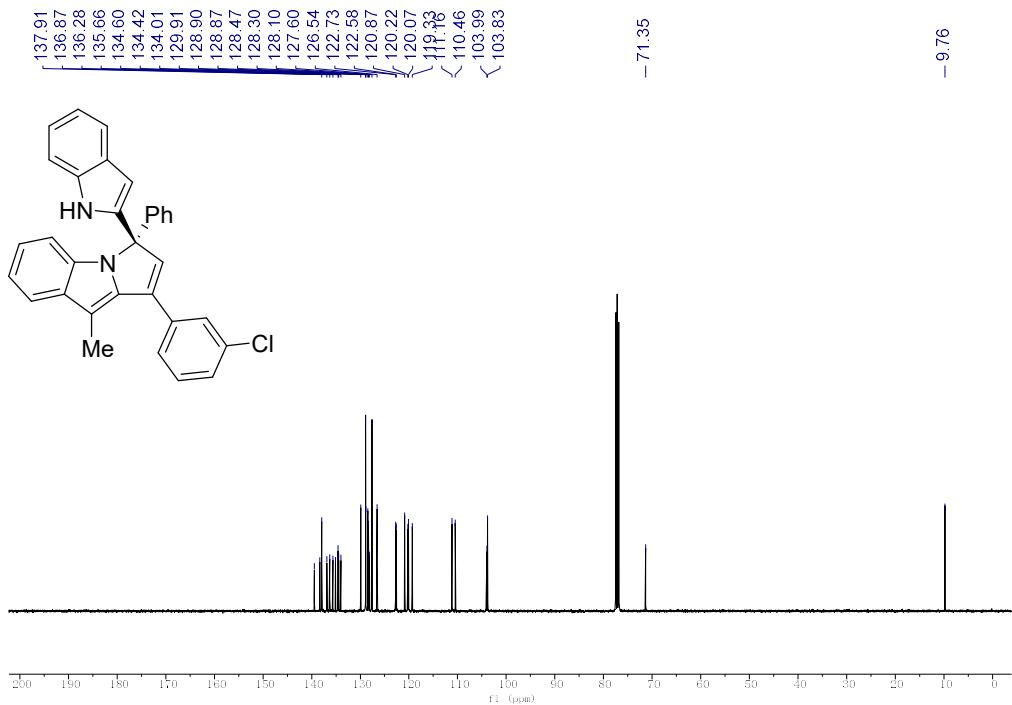
$^{19}\text{F}\{\text{H}\}$ NMR (376 MHz, CDCl_3) of **3ba**



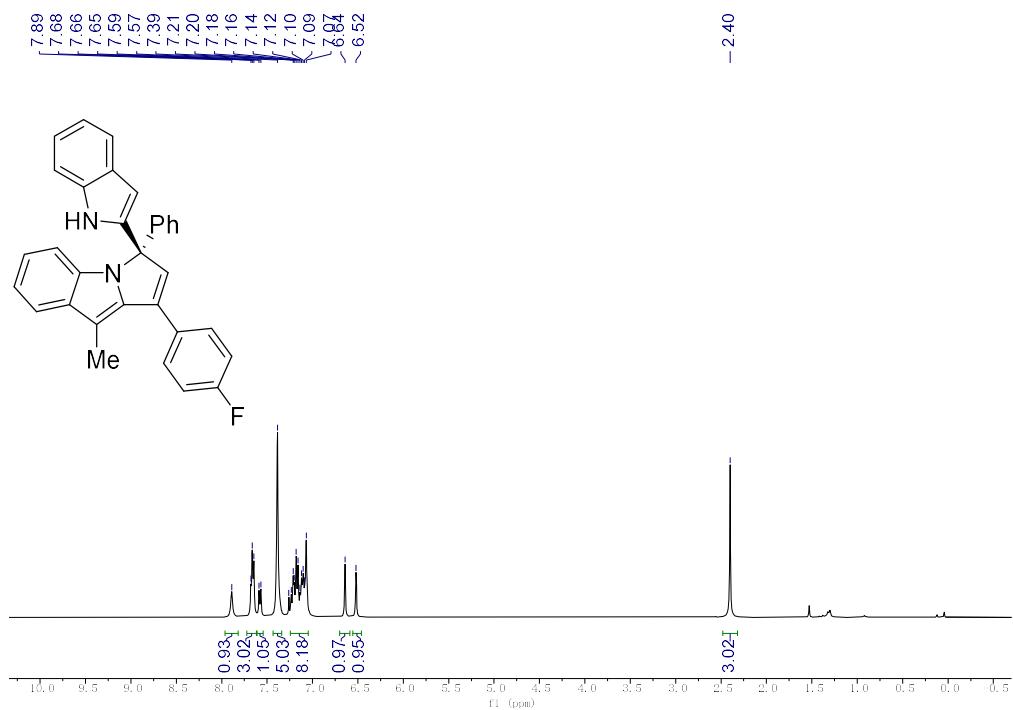
¹H NMR (400 MHz, CDCl₃) of **3ca**



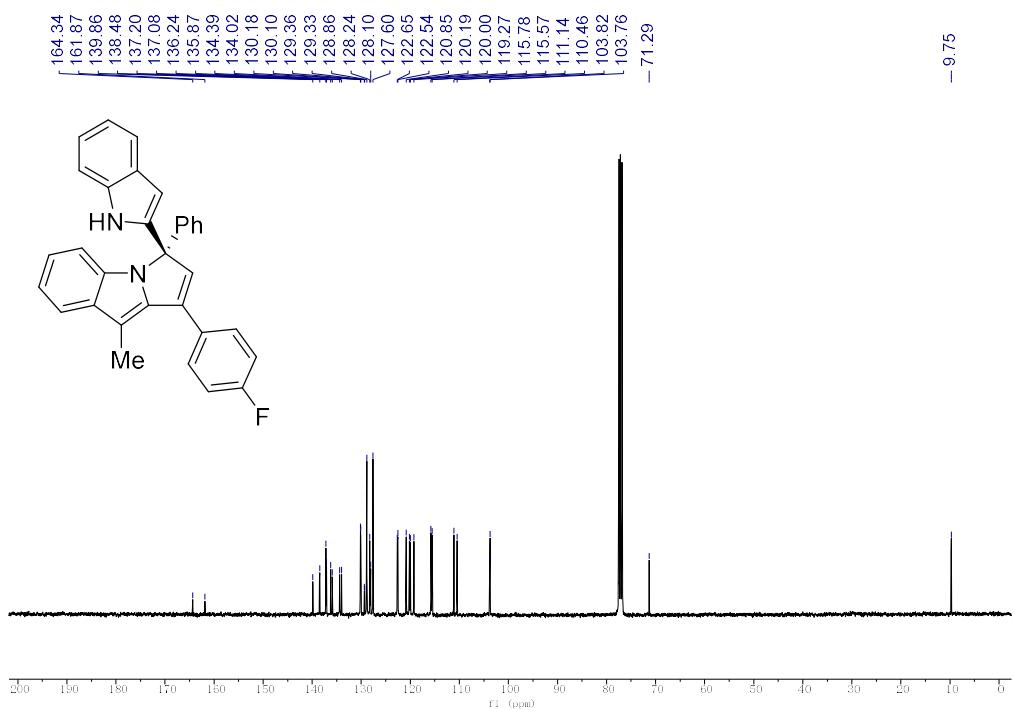
$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) of **3ca**



¹H NMR (400 MHz, CDCl₃) of **3da**



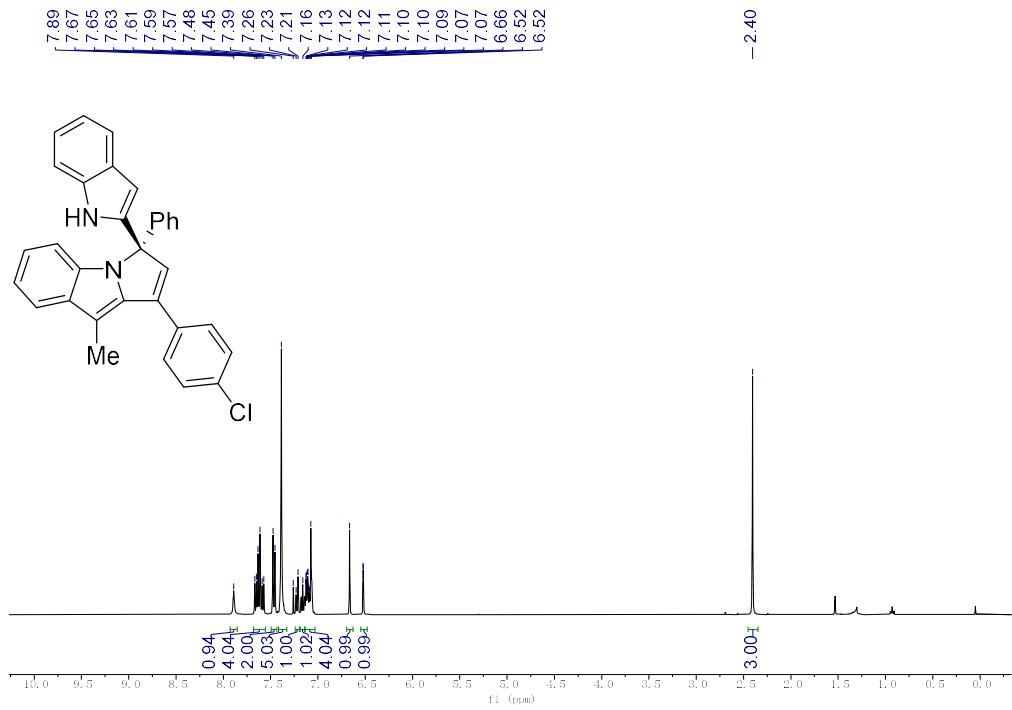
¹³C{¹H} NMR (101 MHz, CDCl₃) of **3da**



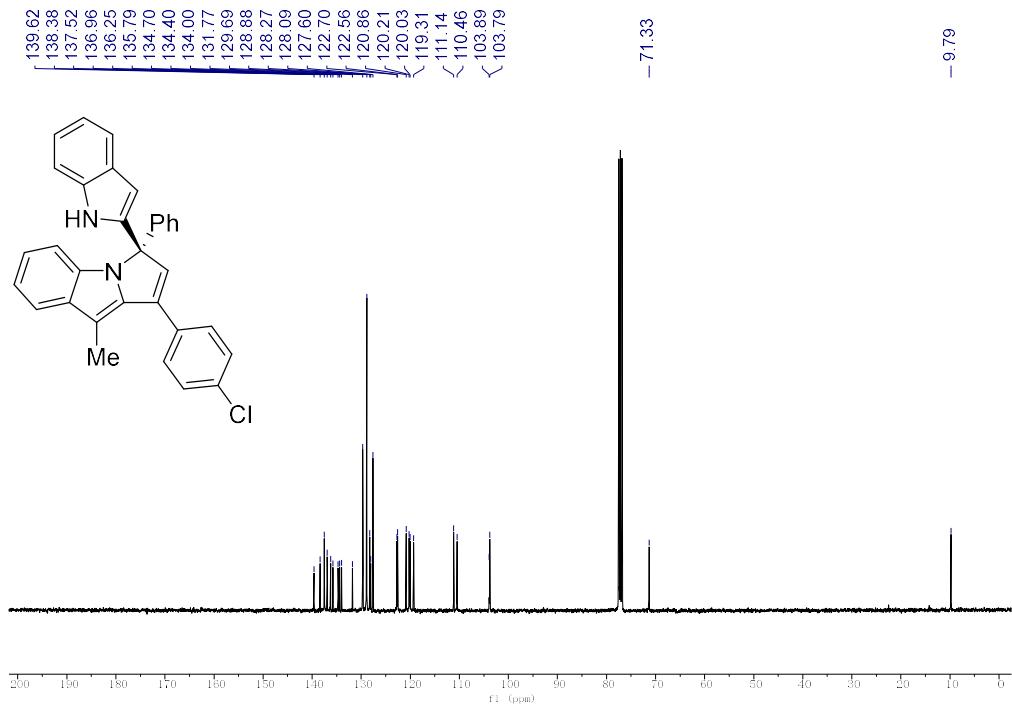
$^{19}\text{F}\{\text{H}\}$ NMR (376 MHz, CDCl_3) of **3da**



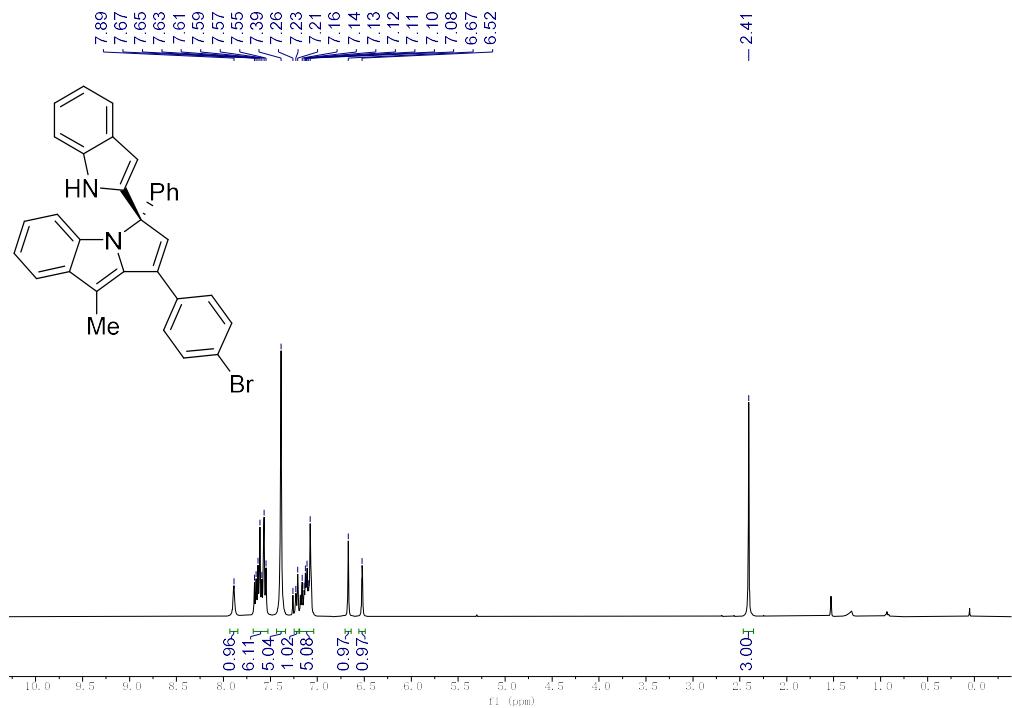
¹H NMR (400 MHz, CDCl₃) of **3ea**



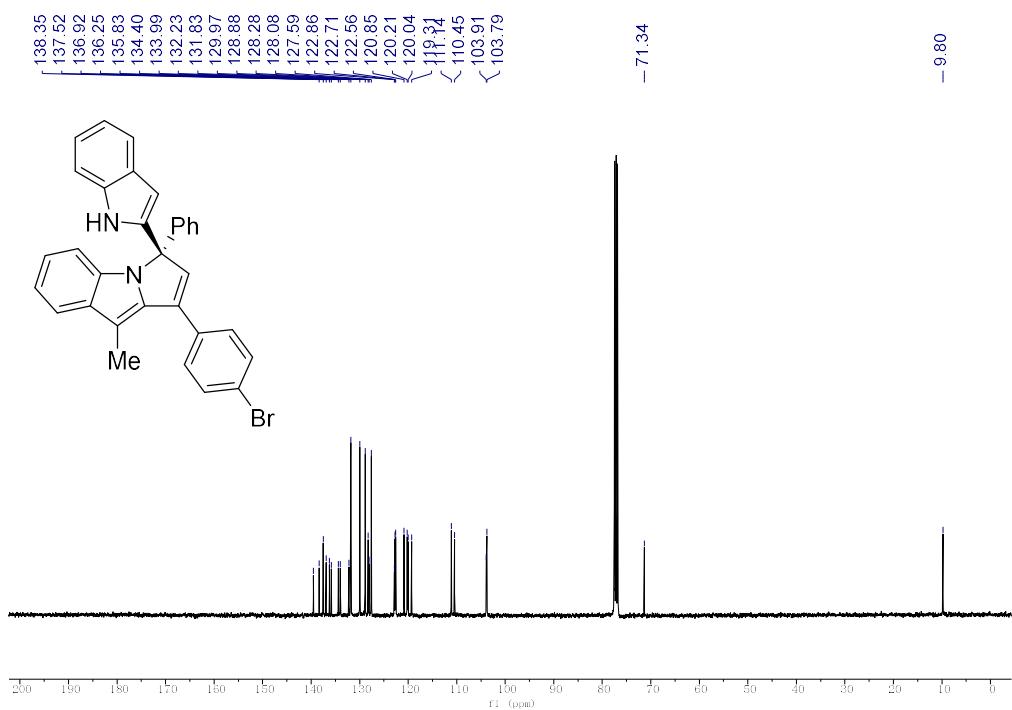
$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) of **3ea**



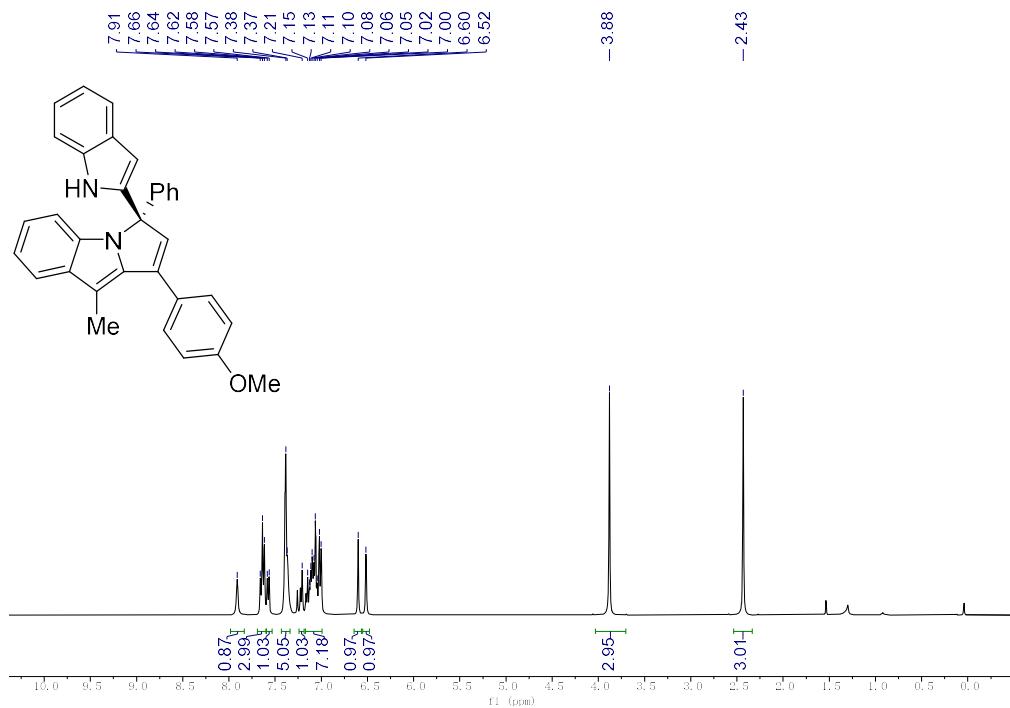
¹H NMR (400 MHz, CDCl₃) of **3fa**



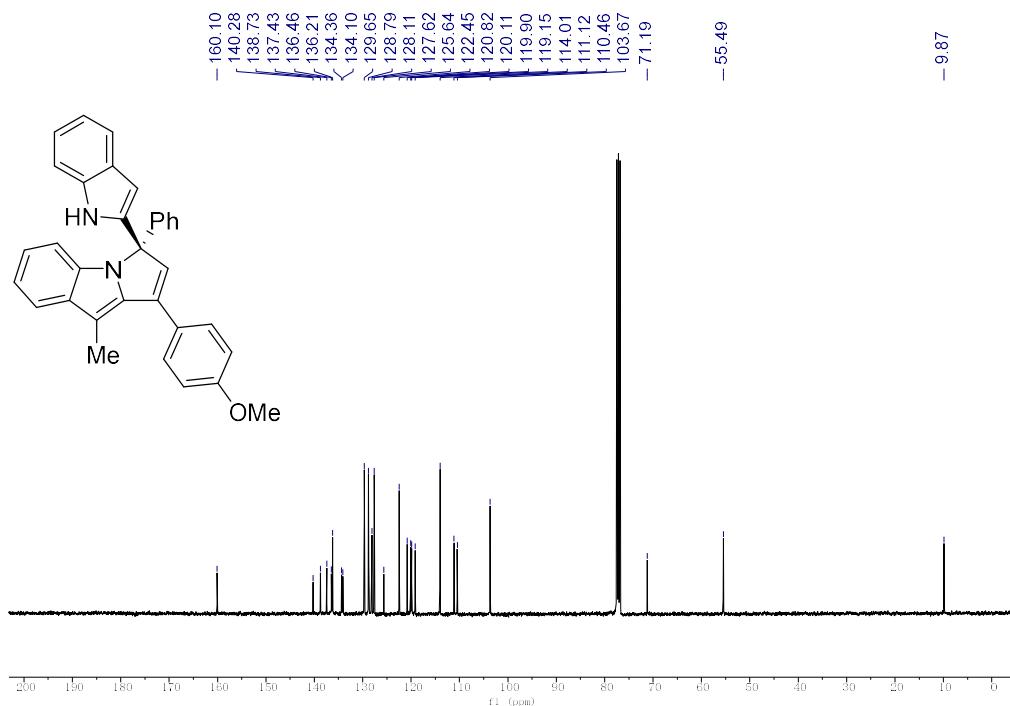
¹³C{¹H} NMR (101 MHz, CDCl₃) of **3fa**



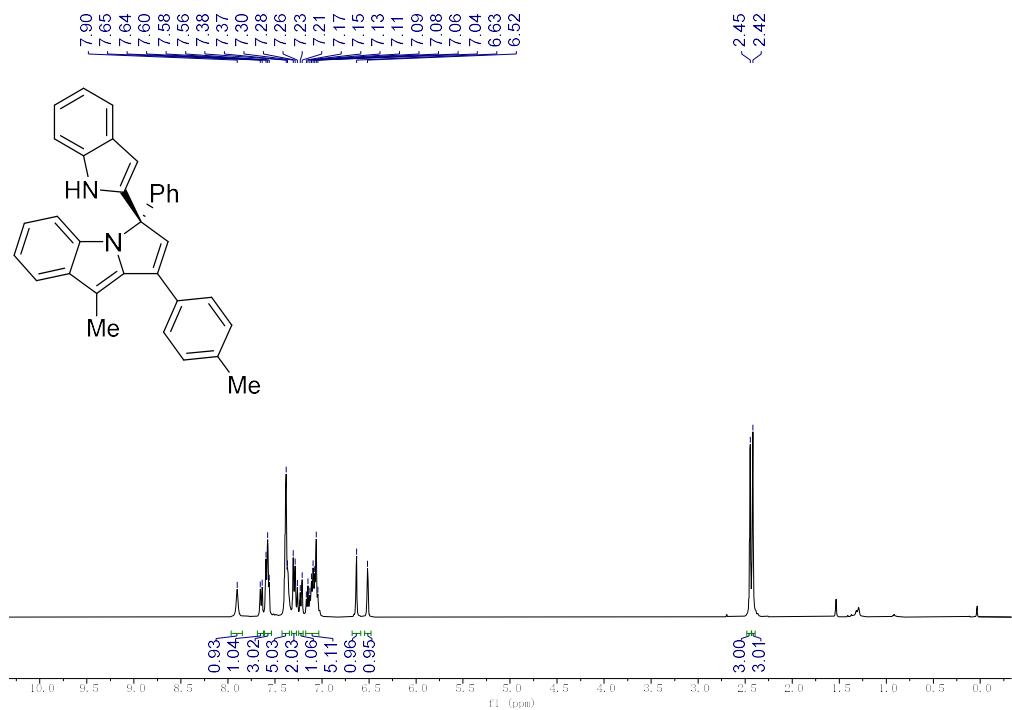
¹H NMR (400 MHz, CDCl₃) of **3ga**



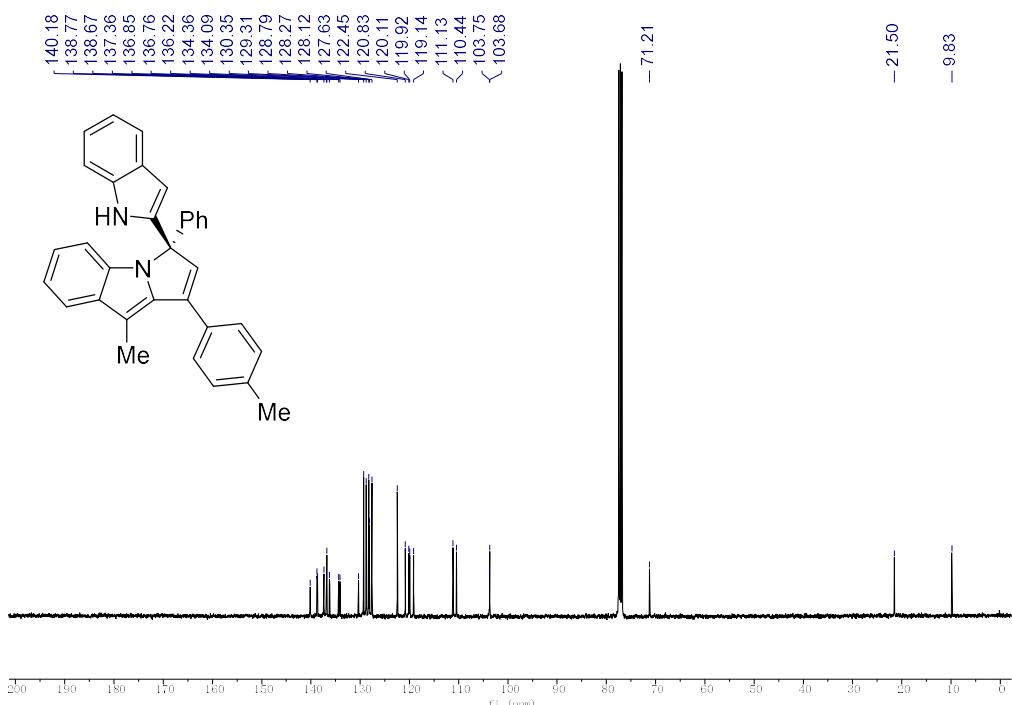
¹³C{¹H} NMR (101 MHz, CDCl₃) of **3ga**



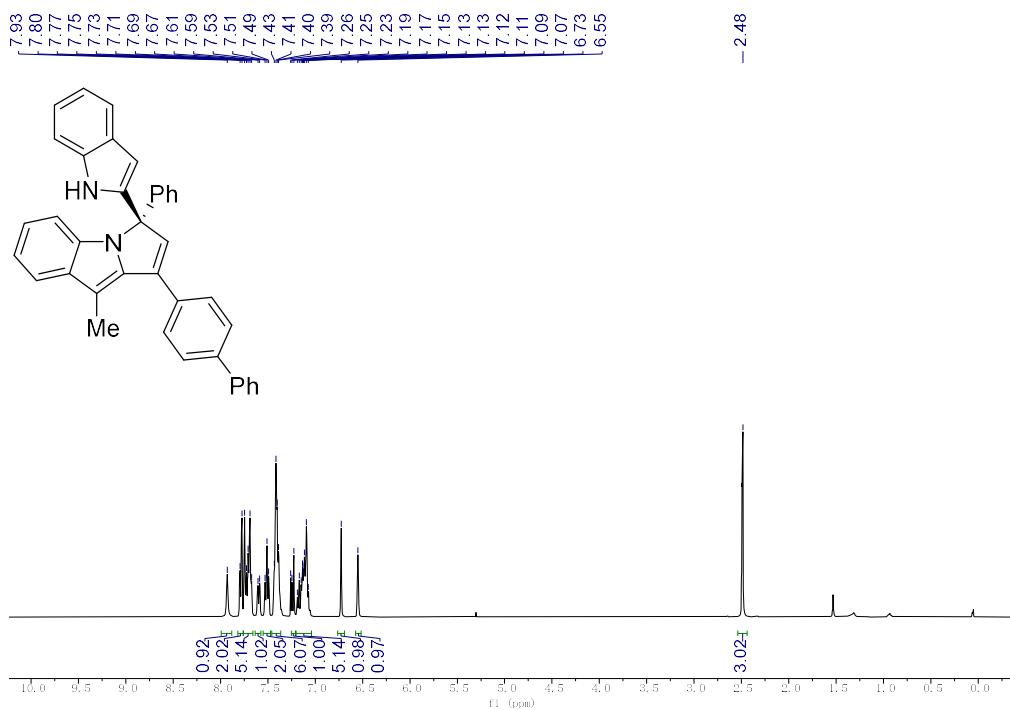
¹H NMR (400 MHz, CDCl₃) of **3ha**



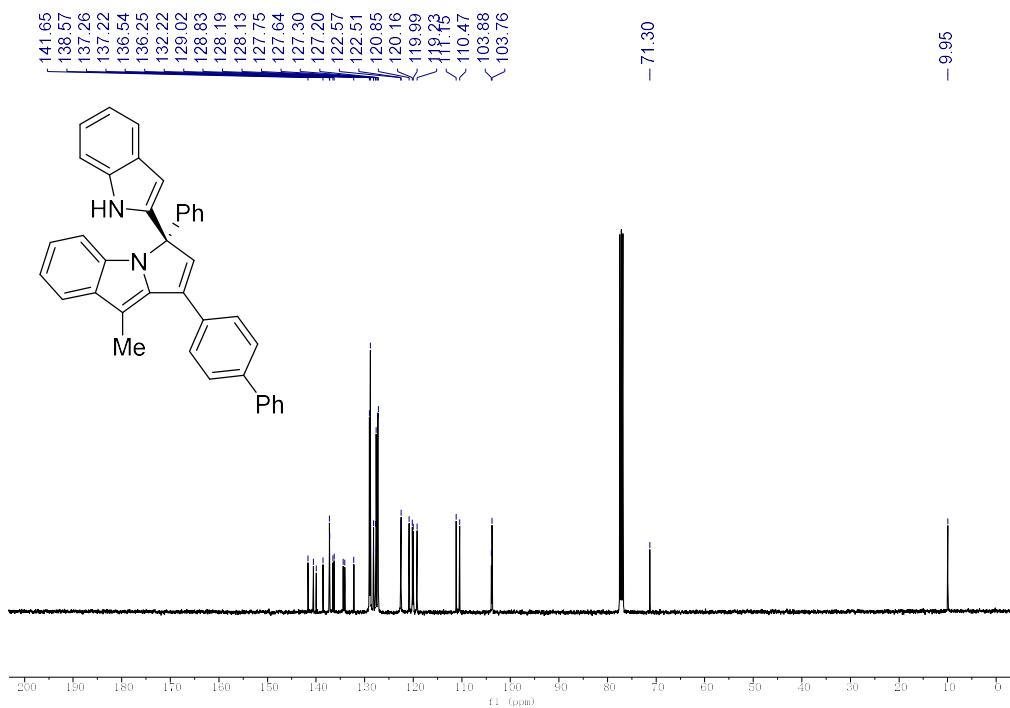
¹³C{¹H} NMR (101 MHz, CDCl₃) of **3ha**



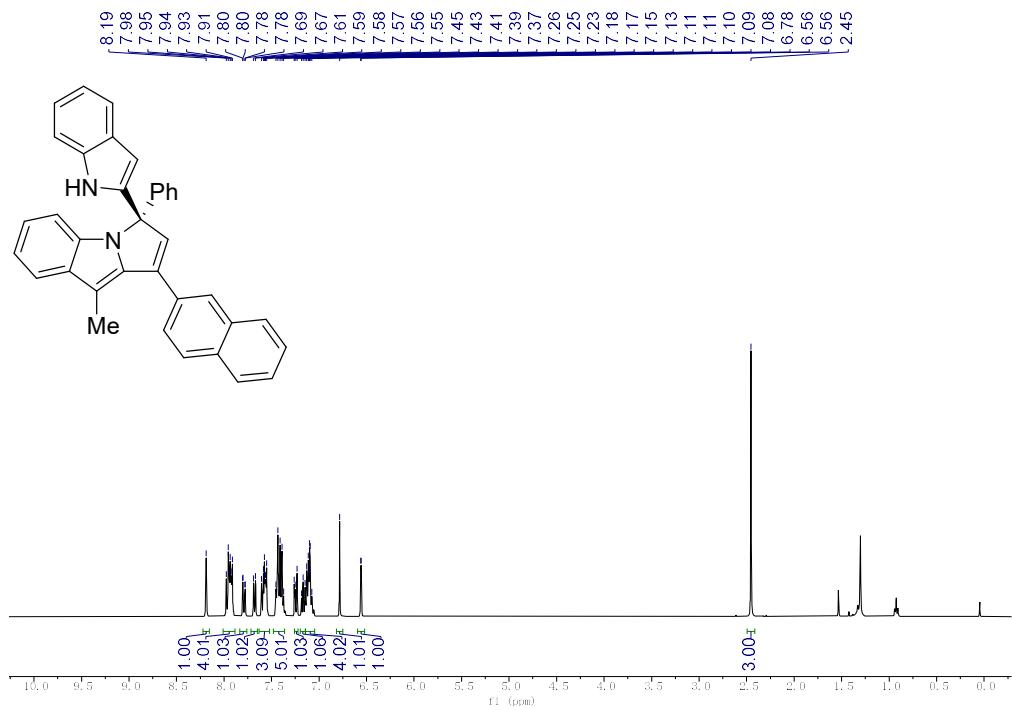
¹H NMR (400 MHz, CDCl₃) of **3ia**



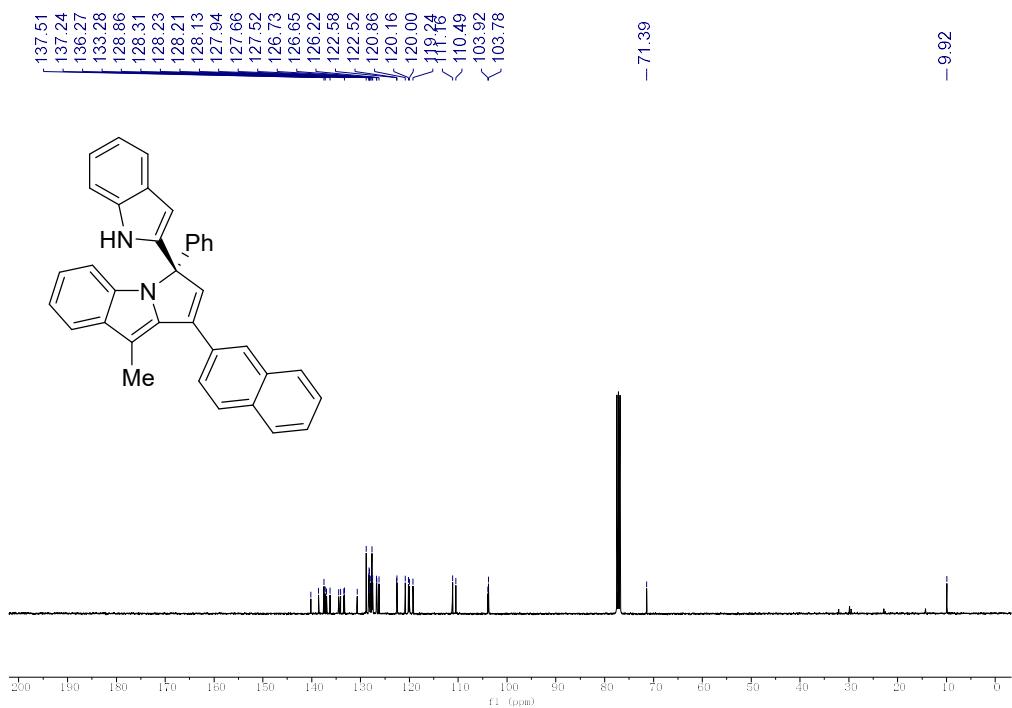
¹³C{¹H} NMR (101 MHz, CDCl₃) of **3ia**



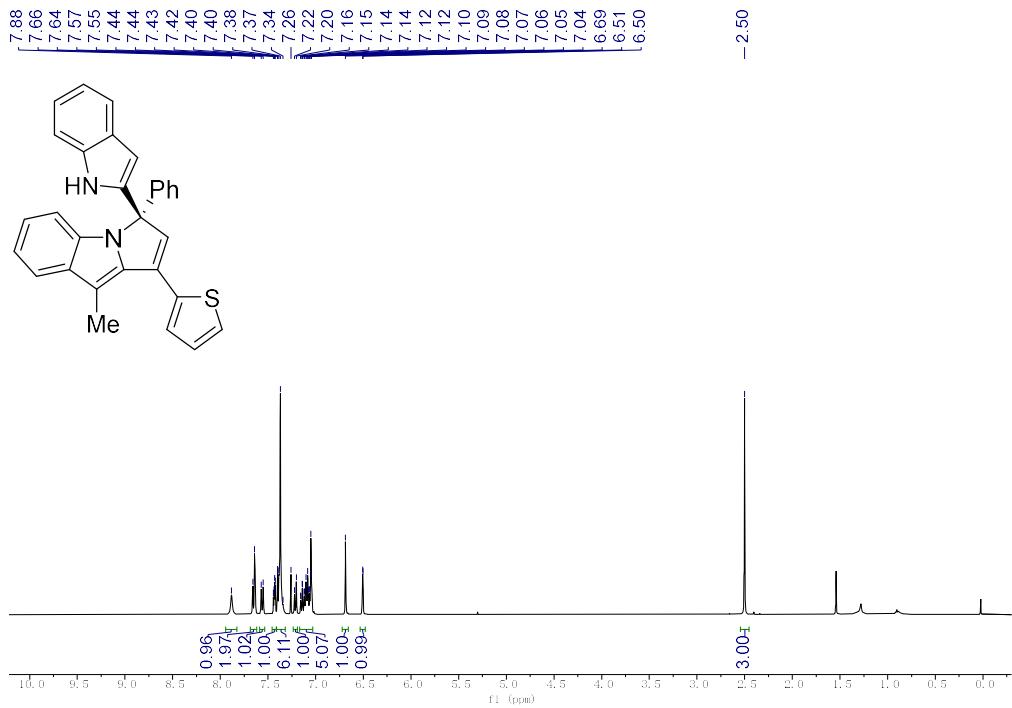
¹H NMR (400 MHz, CDCl₃) of **3ja**



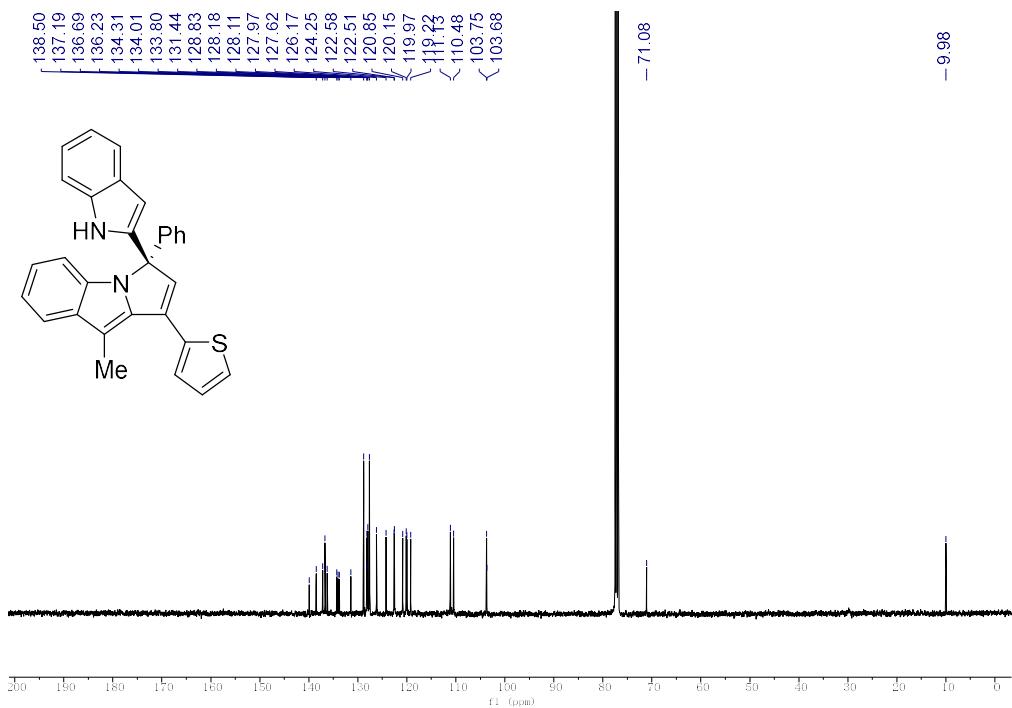
¹³C{¹H} NMR (101 MHz, CDCl₃) of **3ja**



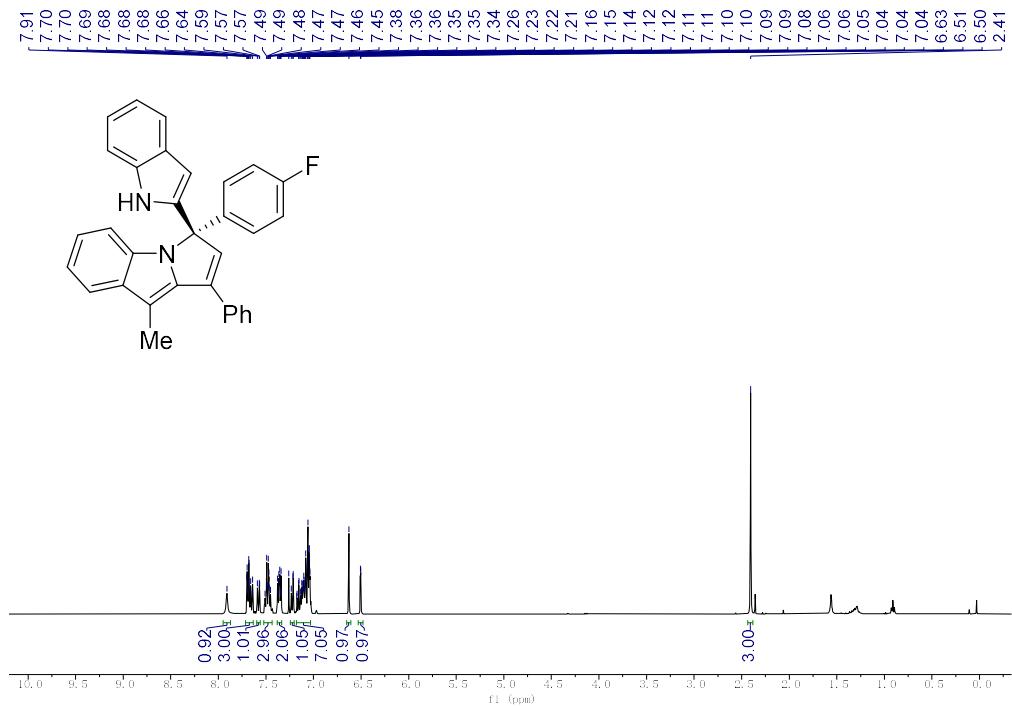
¹H NMR (400 MHz, CDCl₃) of **3ka**



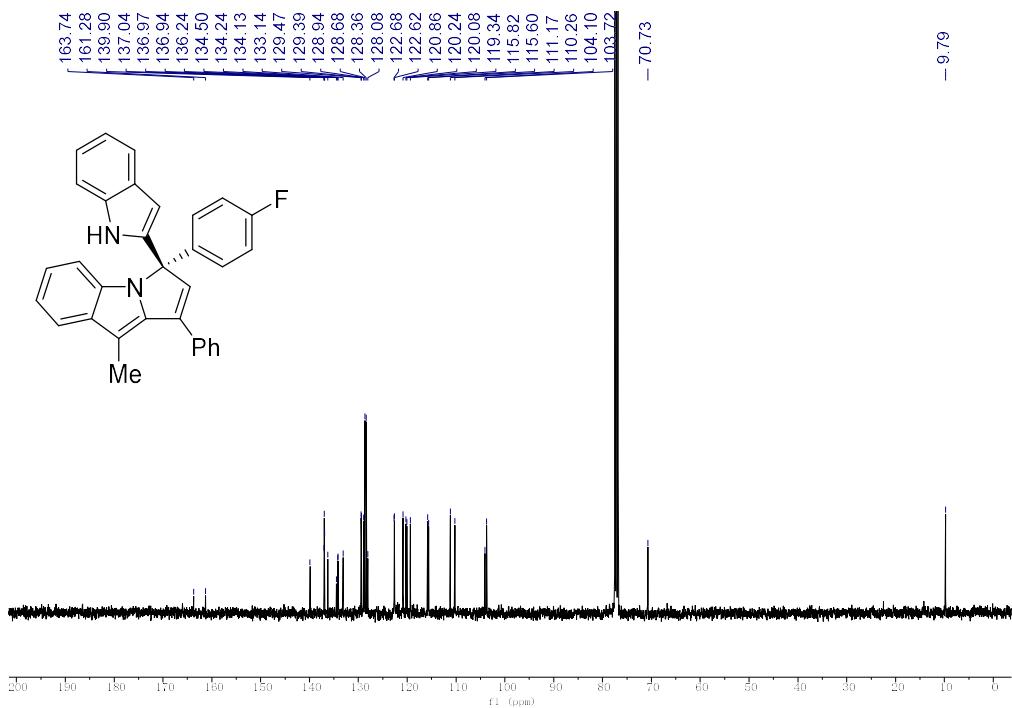
$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) of **3ka**



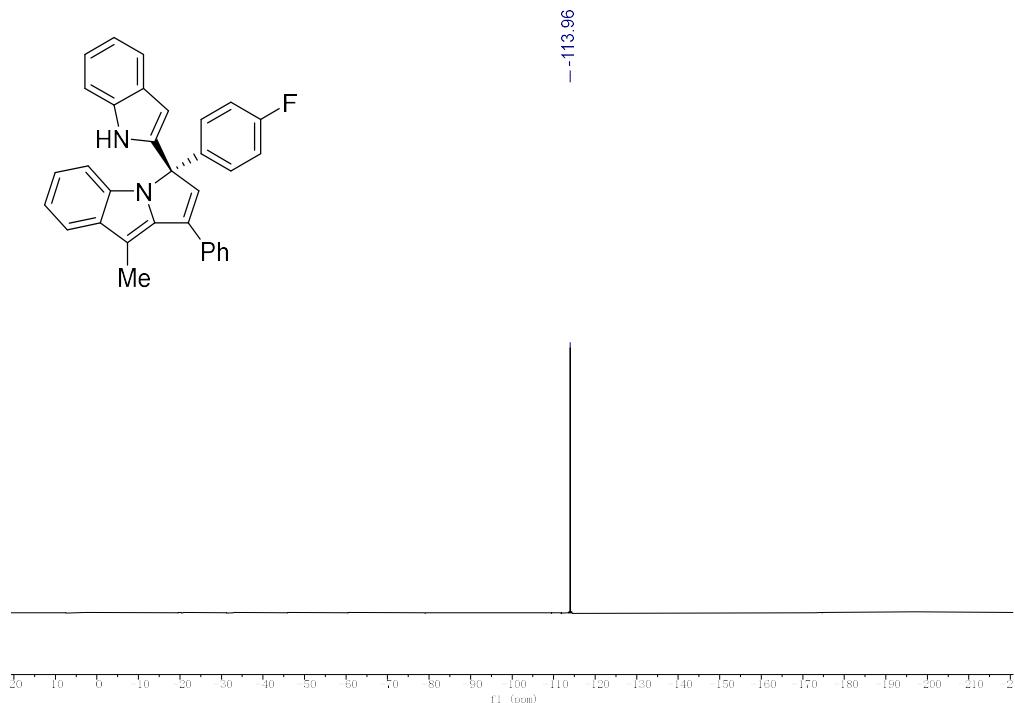
¹H NMR (400 MHz, CDCl₃) of **3la**



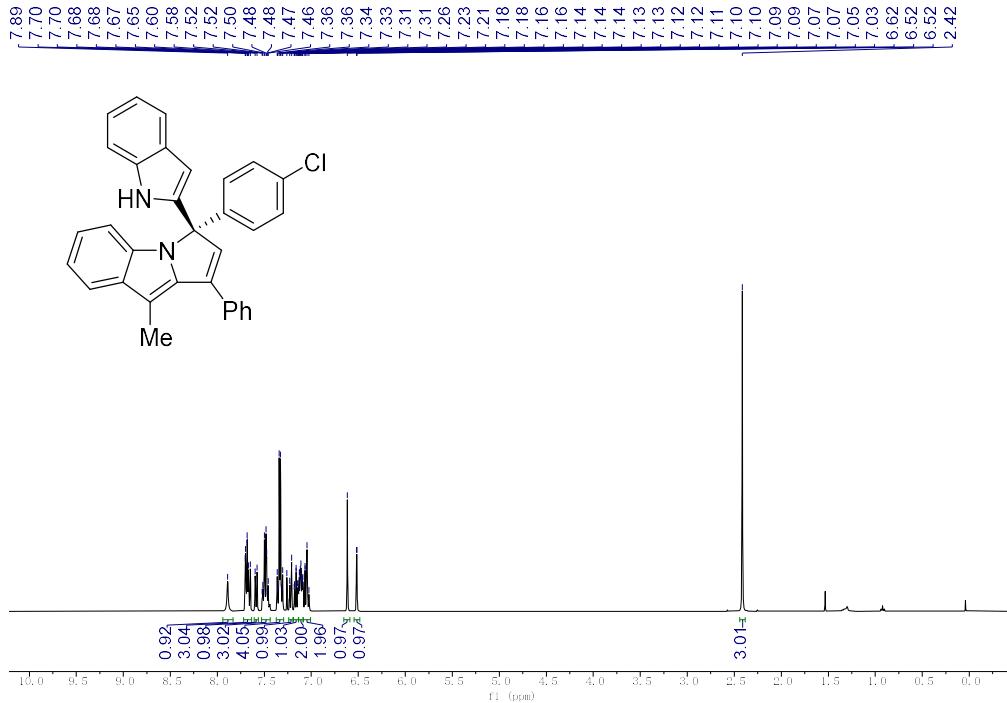
¹³C{¹H} NMR (101 MHz, CDCl₃) of **3la**



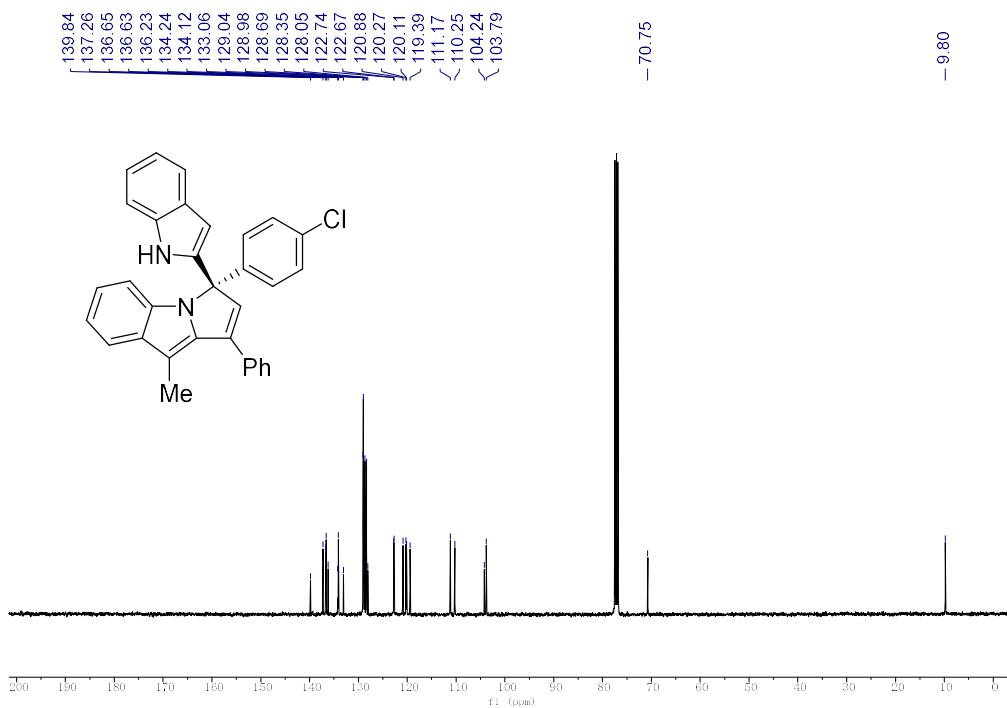
$^{19}\text{F}\{\text{H}\}$ NMR (376 MHz, CDCl_3) of **3la**



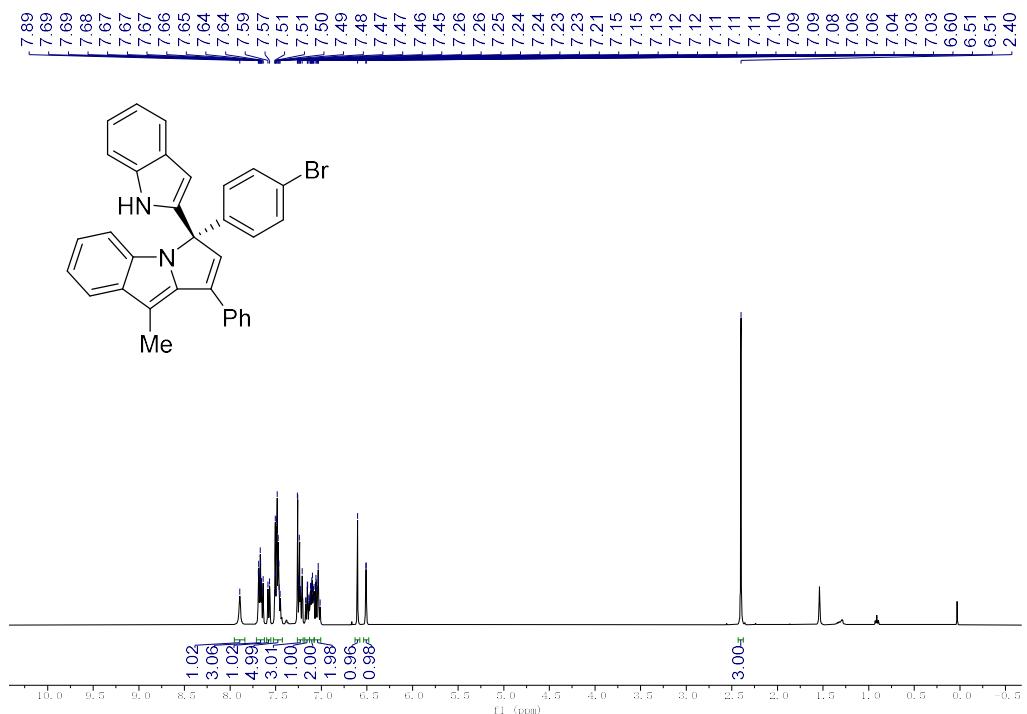
¹H NMR (400 MHz, CDCl₃) of 3ma



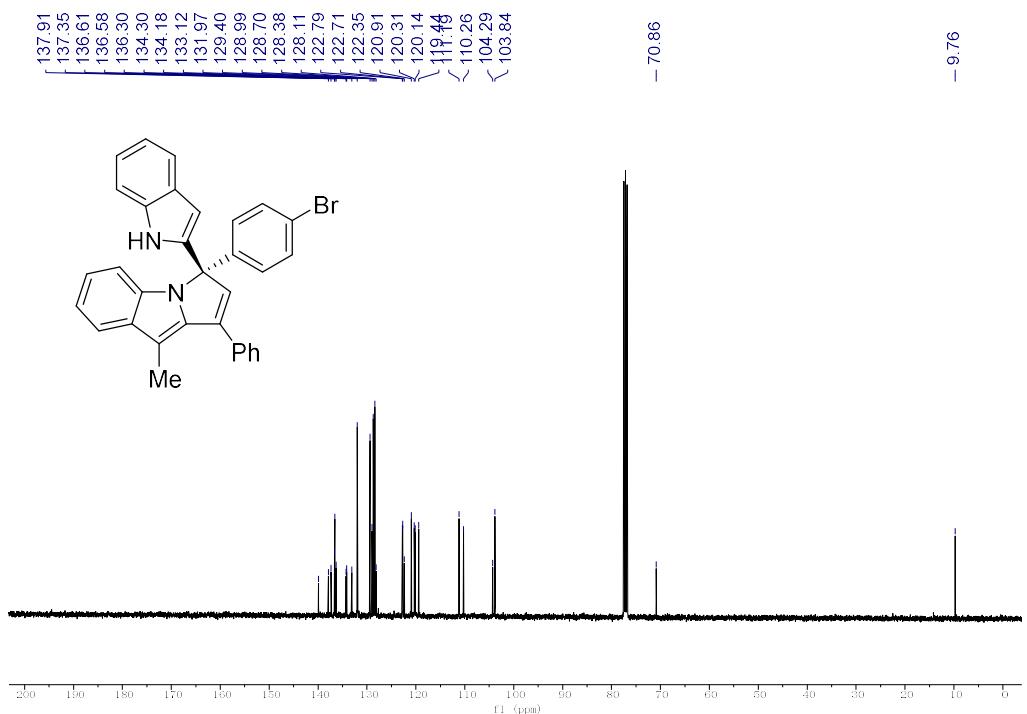
$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) of **3ma**



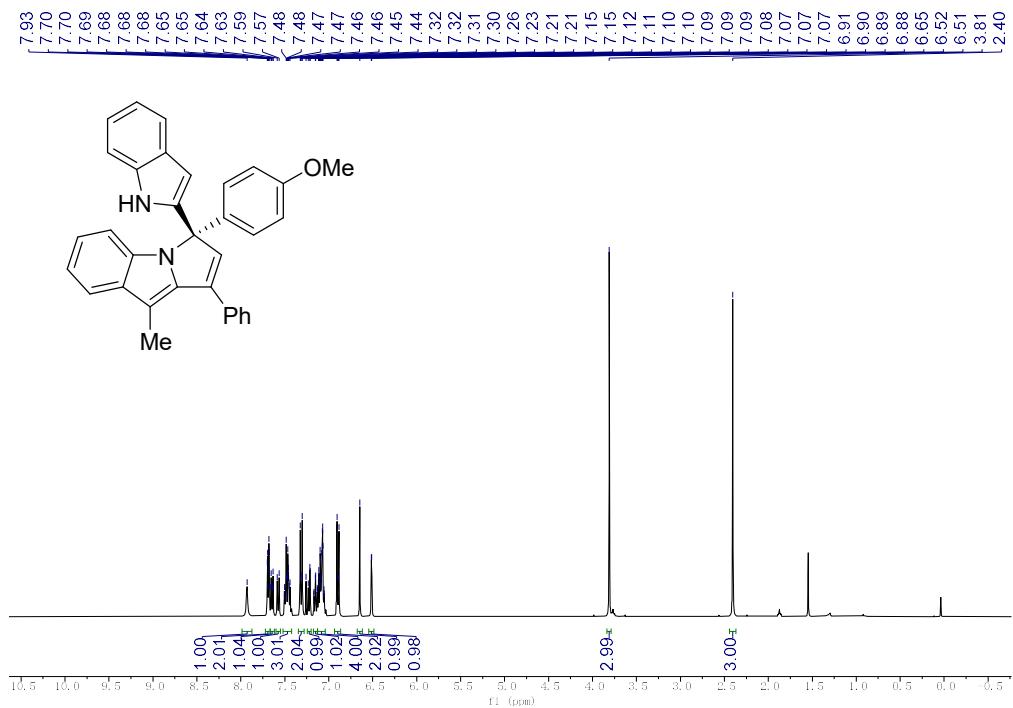
¹H NMR (400 MHz, CDCl₃) of **3na**



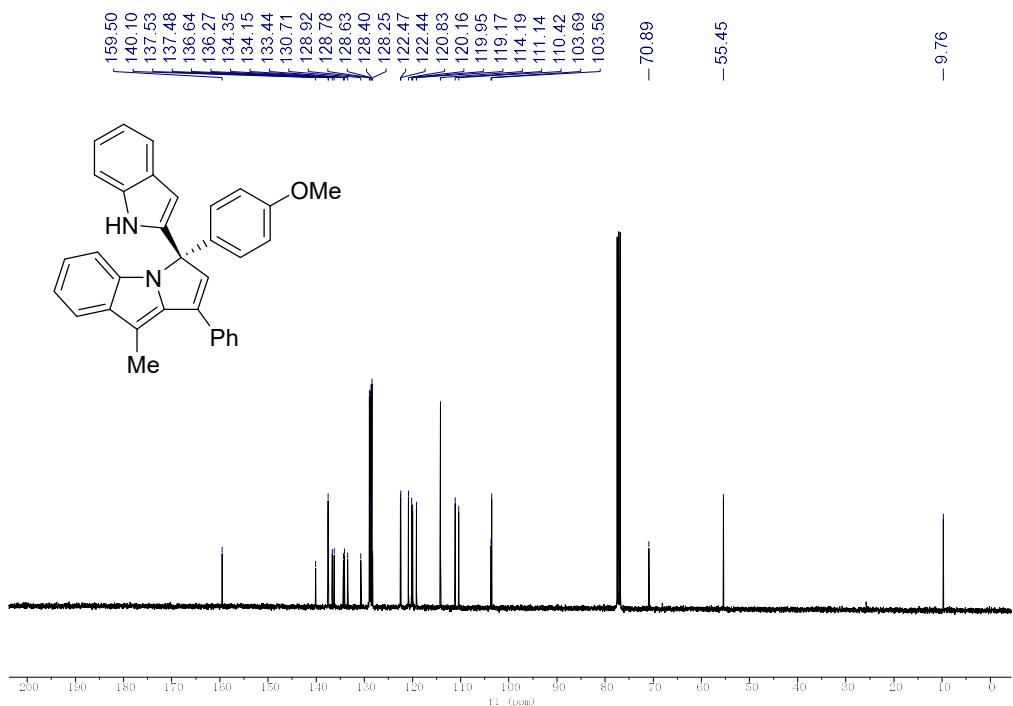
¹³C{¹H} NMR (101 MHz, CDCl₃) of **3na**



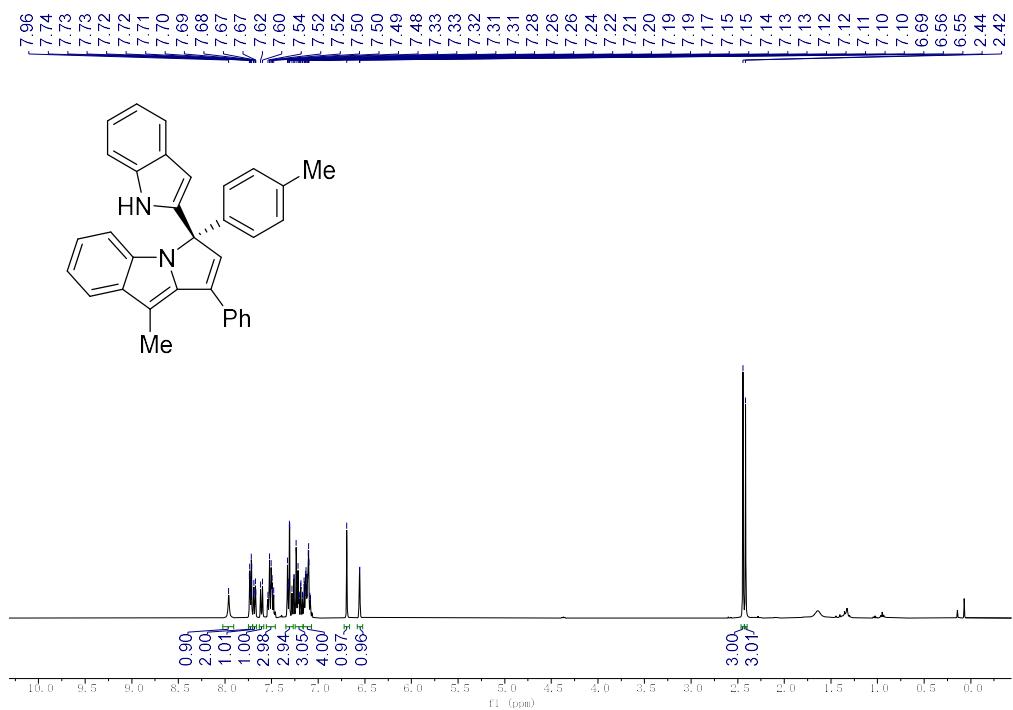
¹H NMR (400 MHz, CDCl₃) of **3oa**



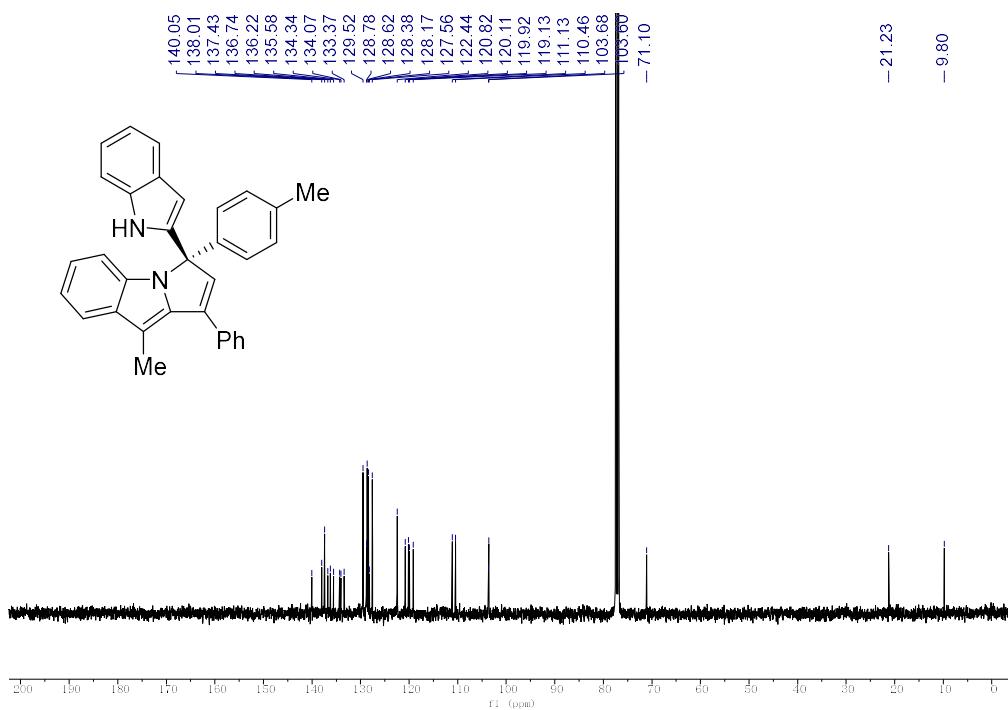
$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) of **3oa**



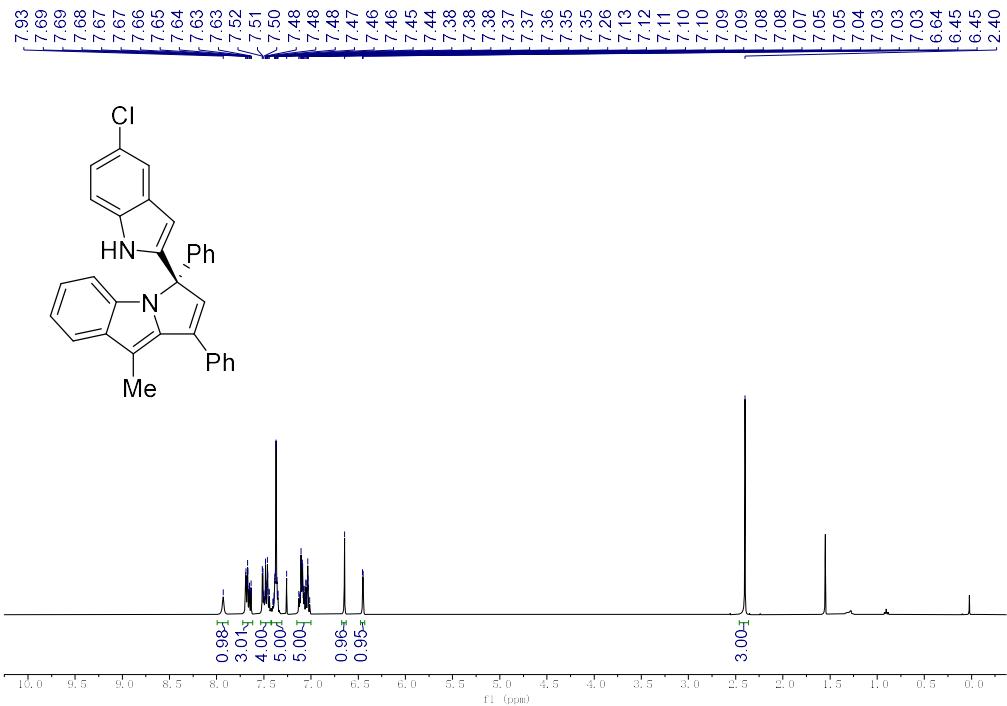
¹H NMR (400 MHz, CDCl₃) of **3pa**



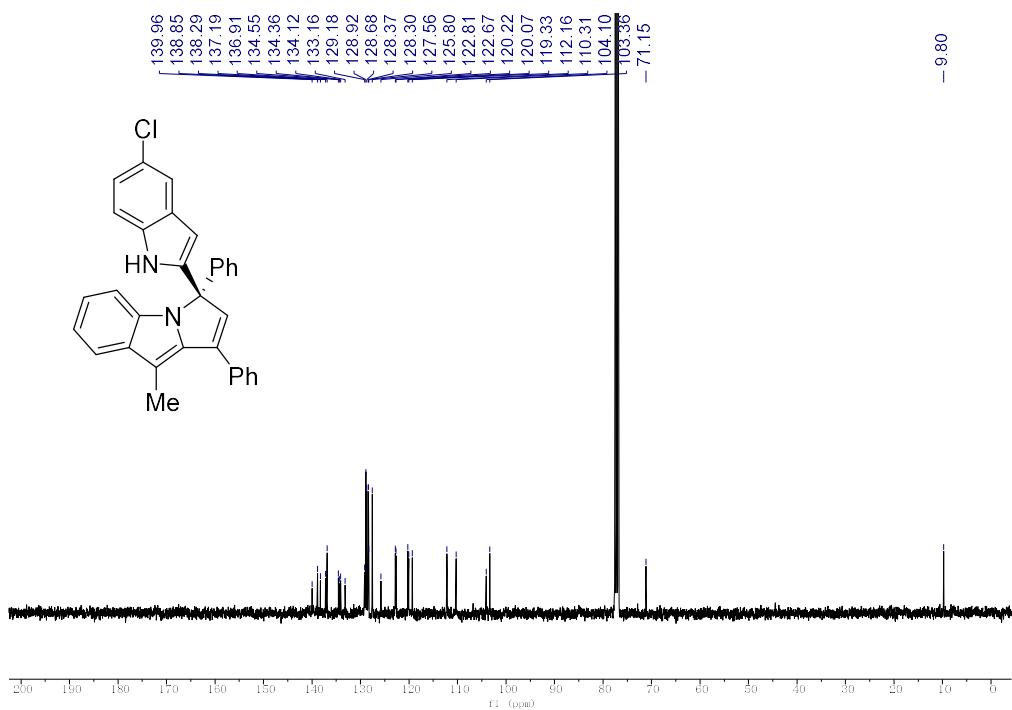
¹³C{¹H} NMR (101 MHz, CDCl₃) of **3pa**



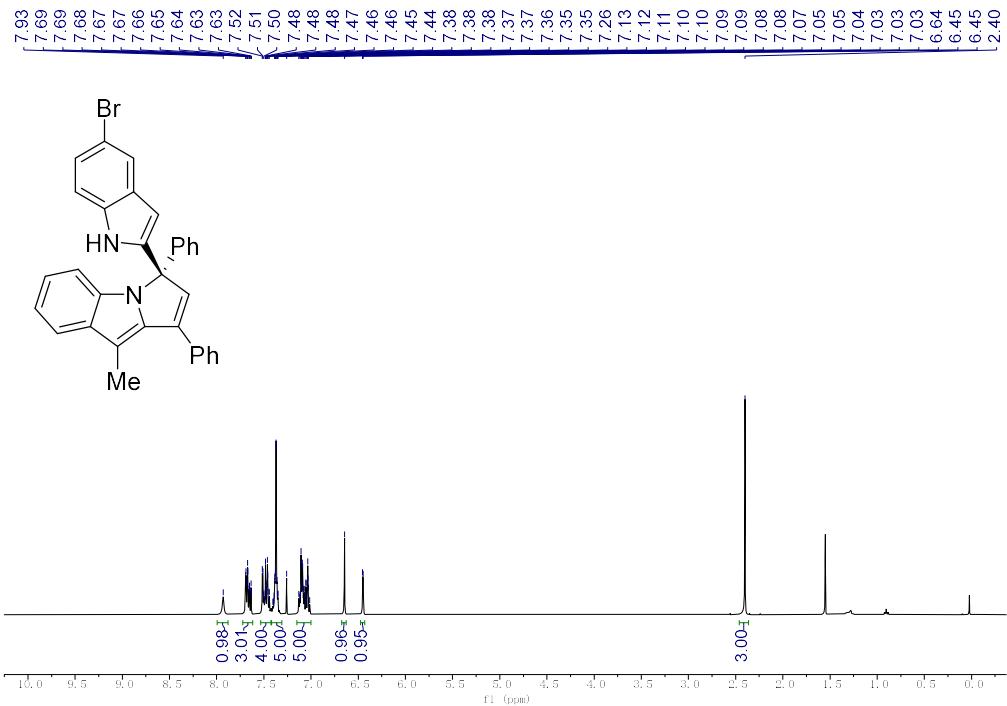
¹H NMR (400 MHz, CDCl₃) of **3qa**



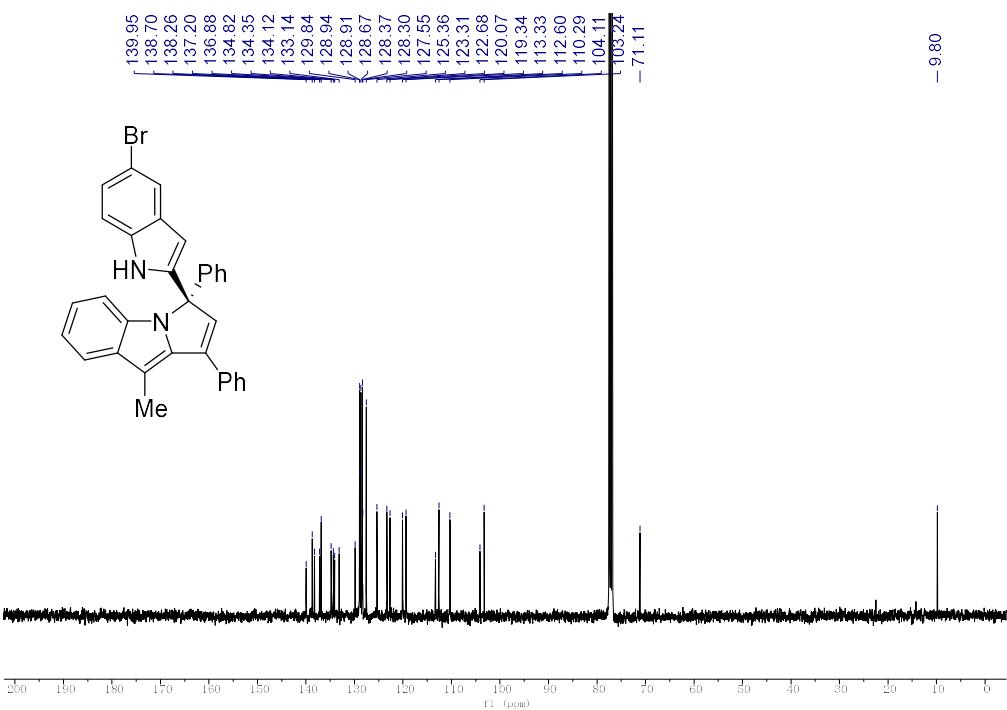
$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) of **3qa**



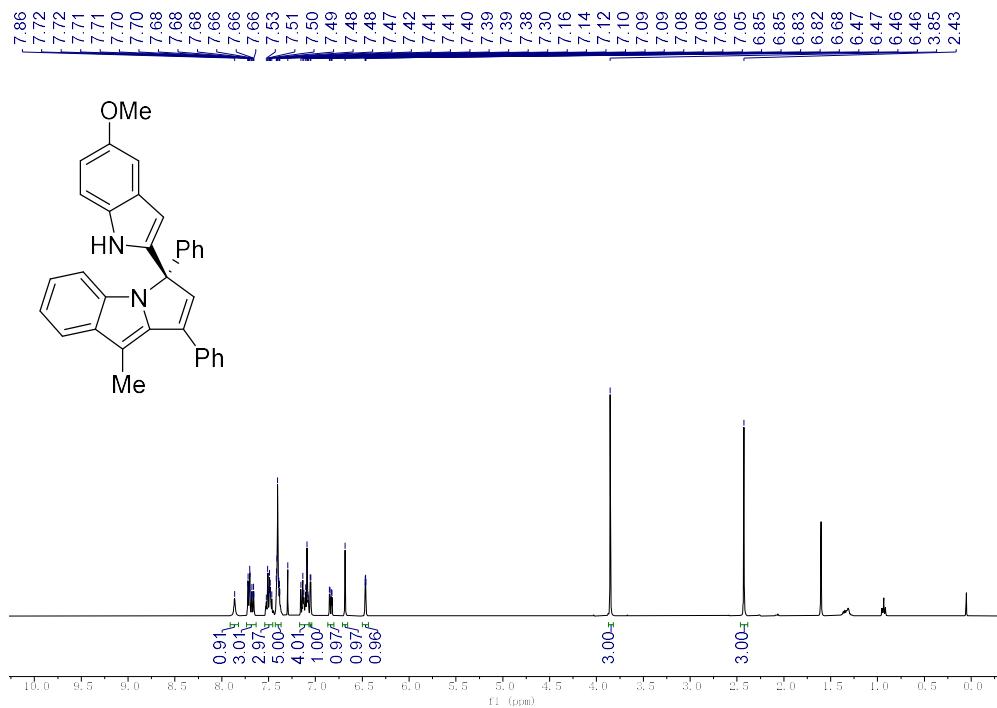
¹H NMR (400 MHz, CDCl₃) of **3ra**



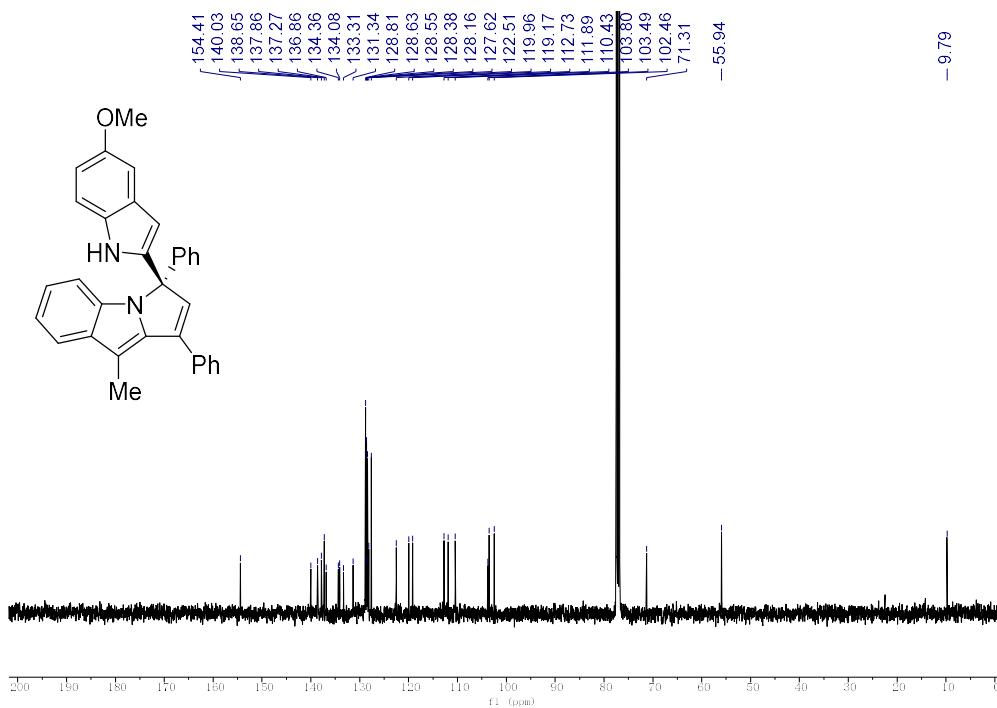
$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) of **3ra**



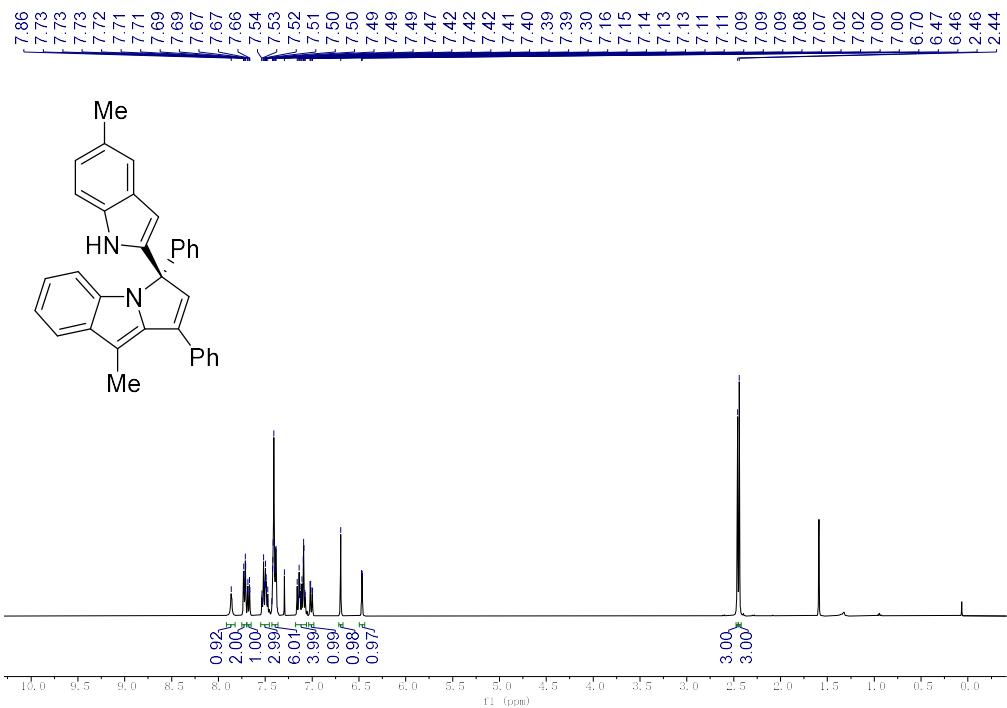
¹H NMR (400 MHz, CDCl₃) of 3sa



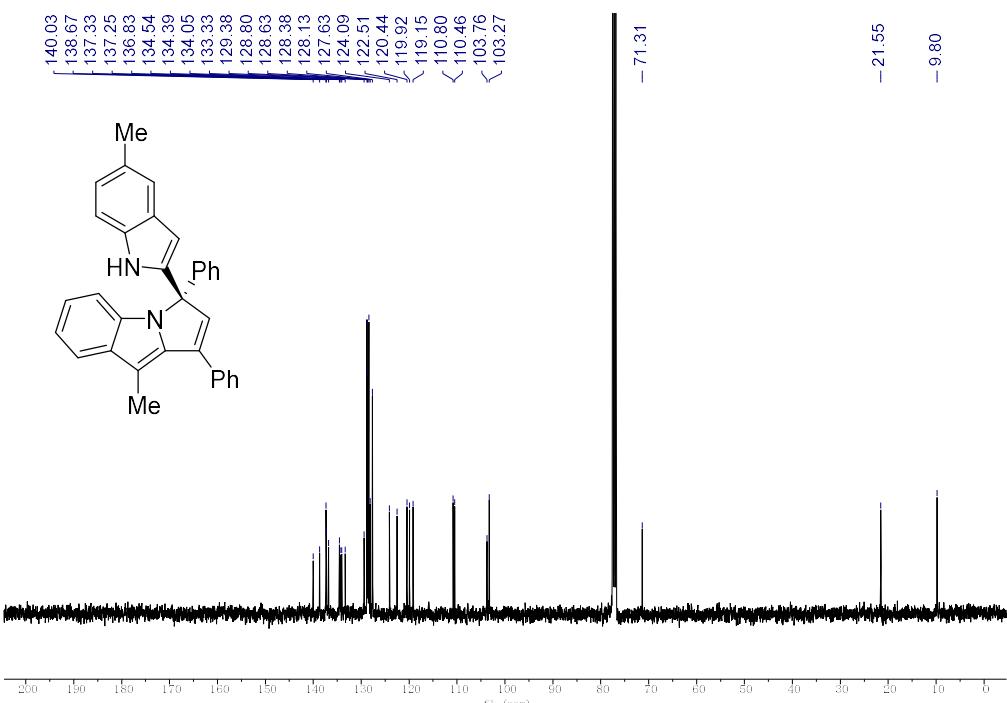
$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) of **3sa**



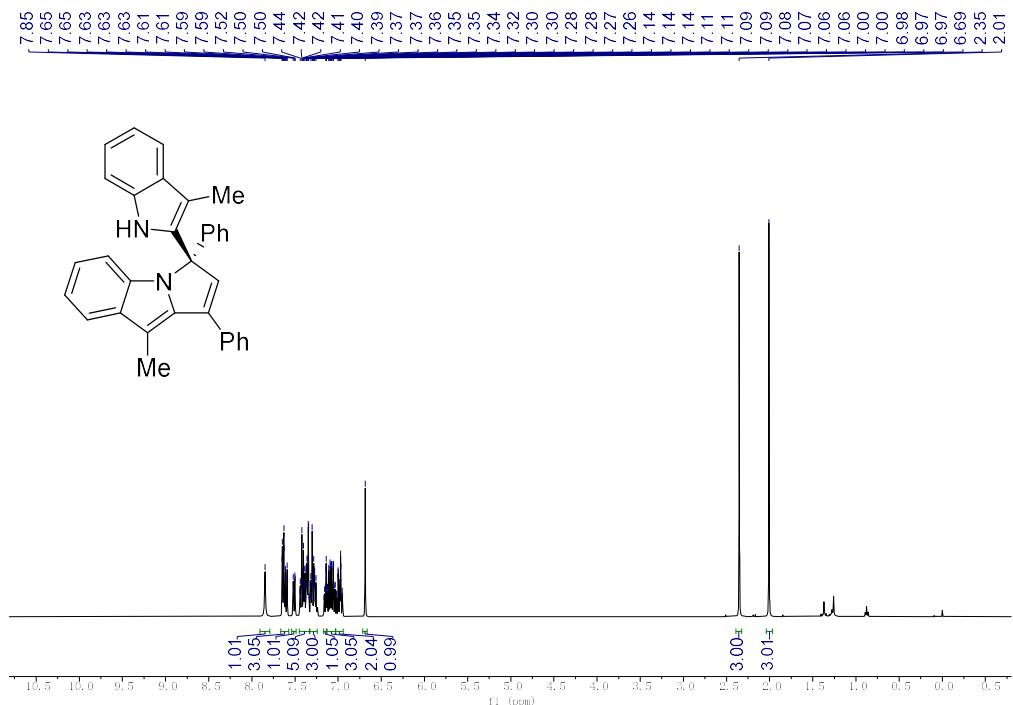
¹H NMR (400 MHz, CDCl₃) of 3ta



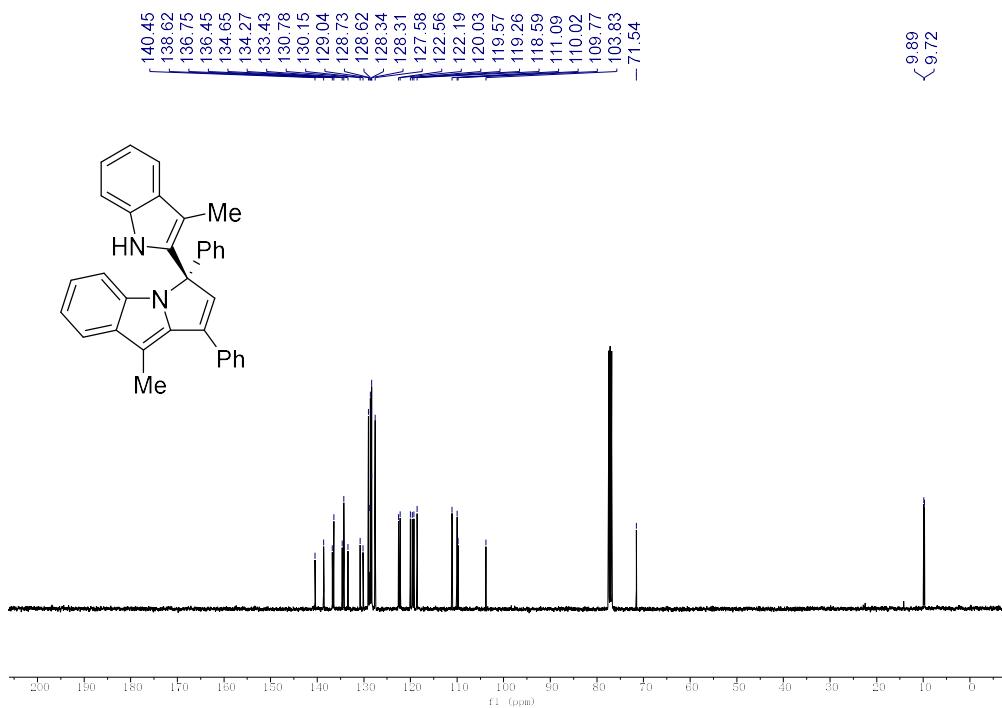
$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) of **3ta**



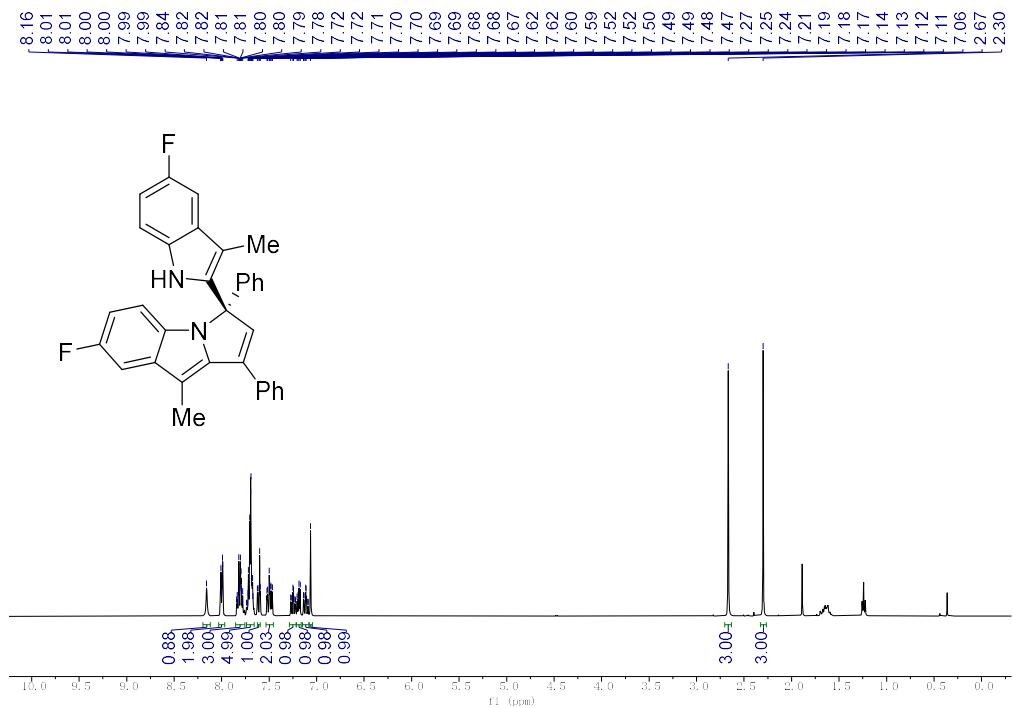
¹H NMR (400 MHz, CDCl₃) of **6aa**



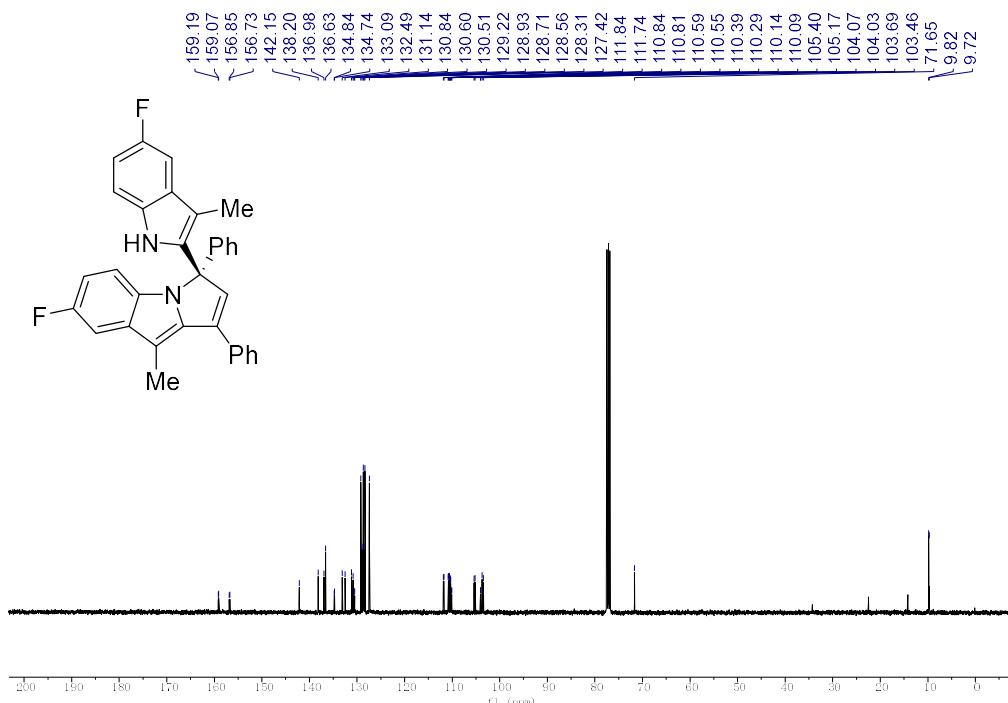
¹³C{¹H} NMR (101 MHz, CDCl₃) of **6aa**



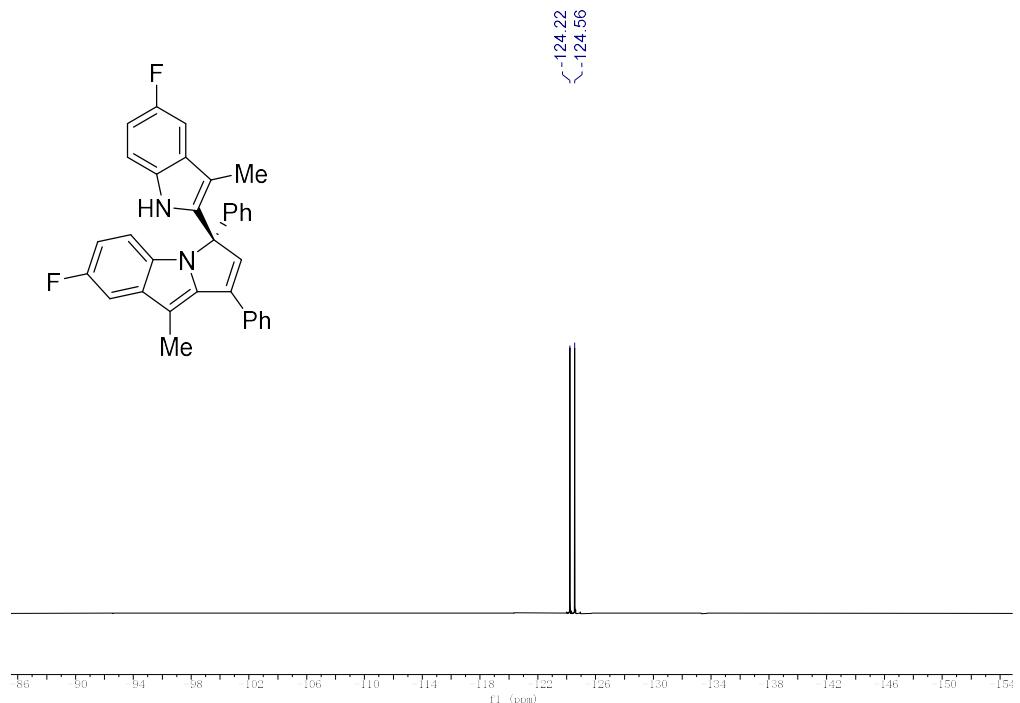
¹H NMR (400 MHz, CDCl₃) of **6bb**



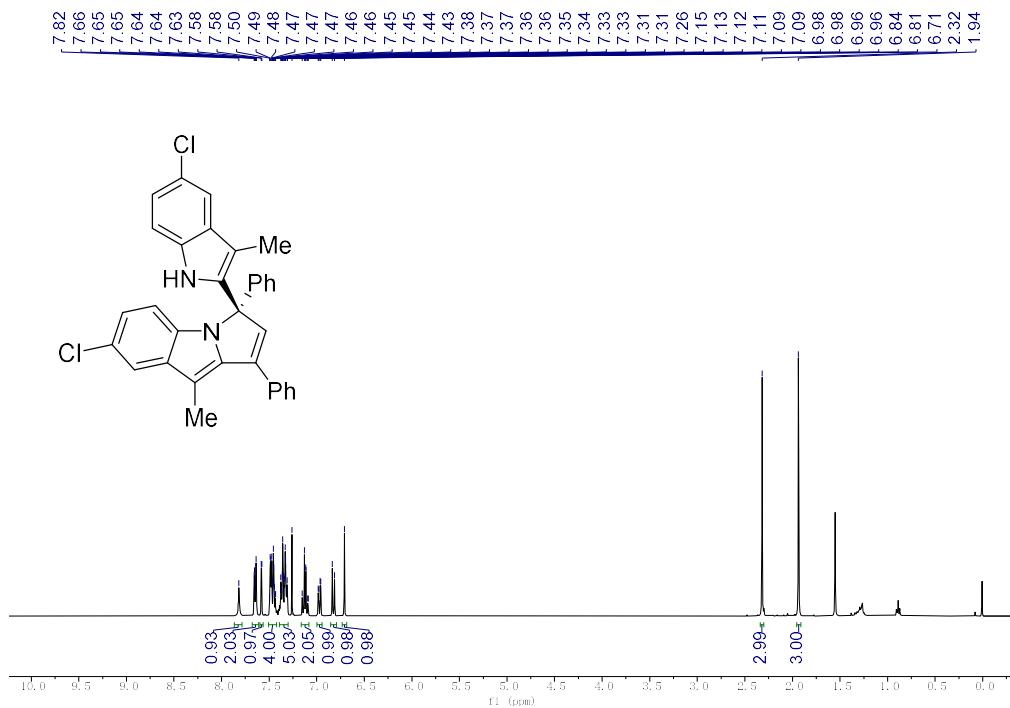
¹³C{¹H} NMR (101 MHz, CDCl₃) of **6bb**



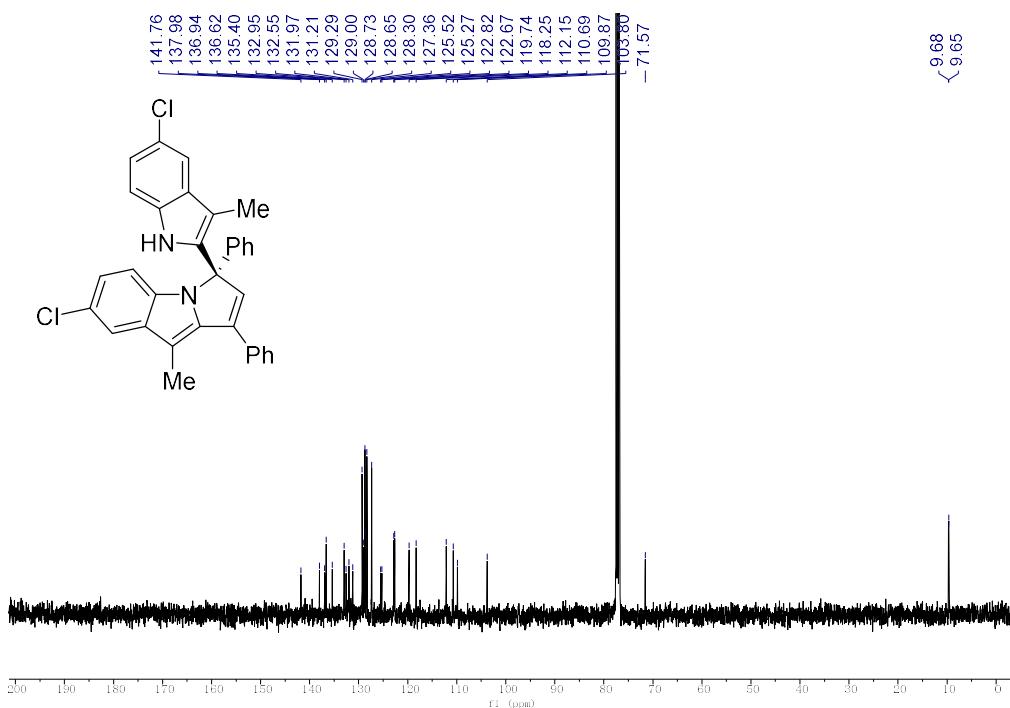
$^{19}\text{F}\{\text{H}\}$ NMR (376 MHz, CDCl_3) of **6bb**



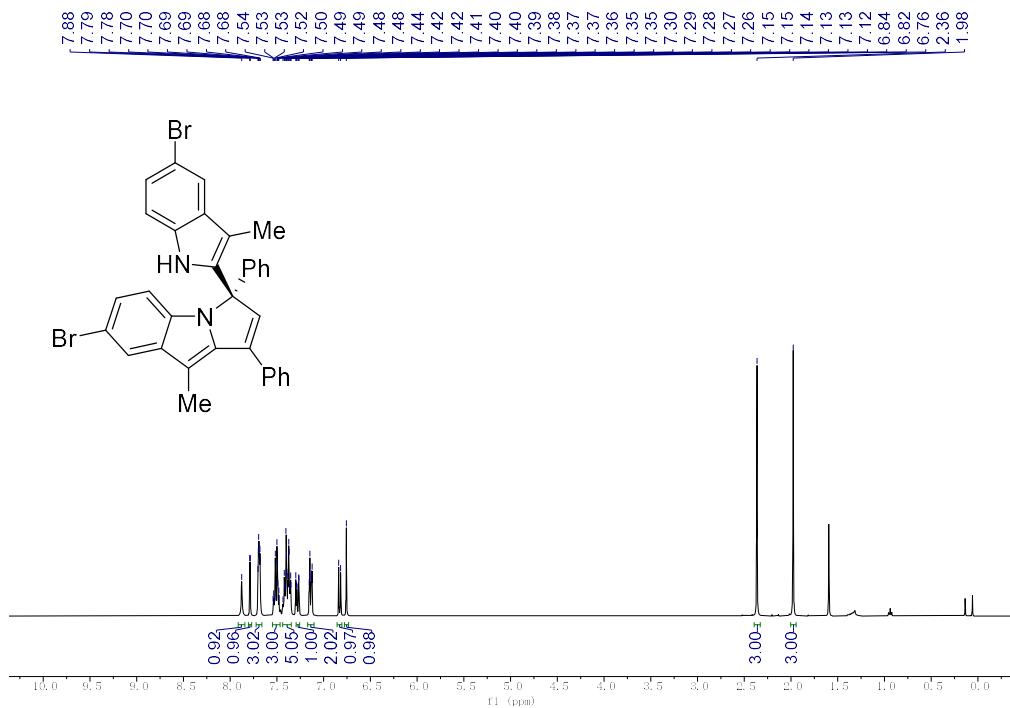
¹H NMR (400 MHz, CDCl₃) of **6cc**



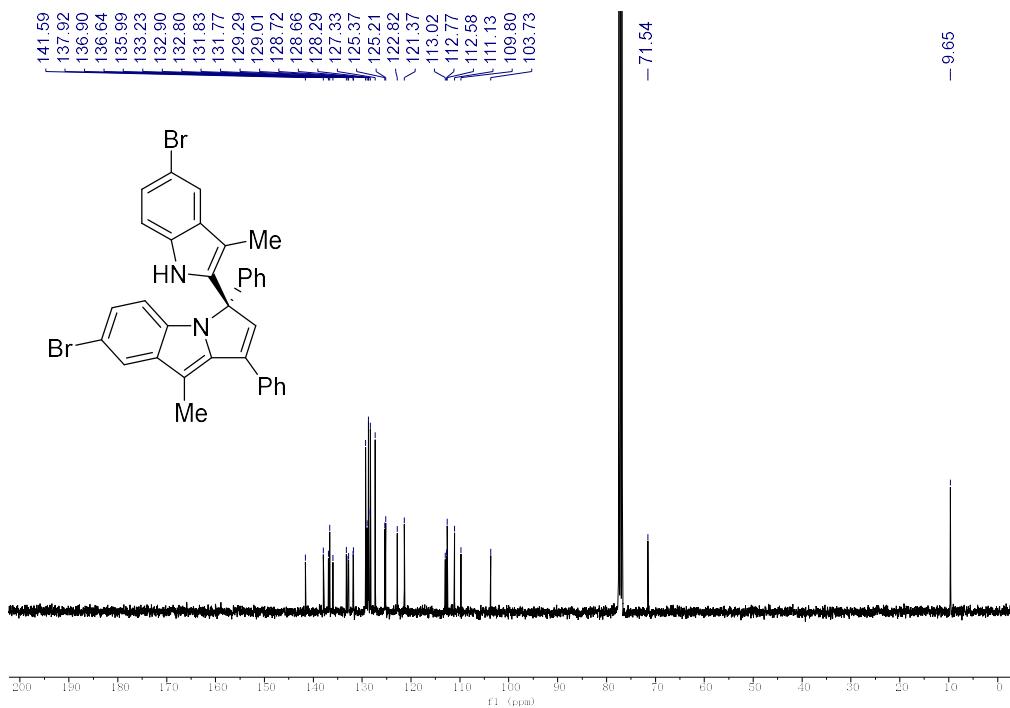
¹³C{¹H} NMR (101 MHz, CDCl₃) of **6cc**



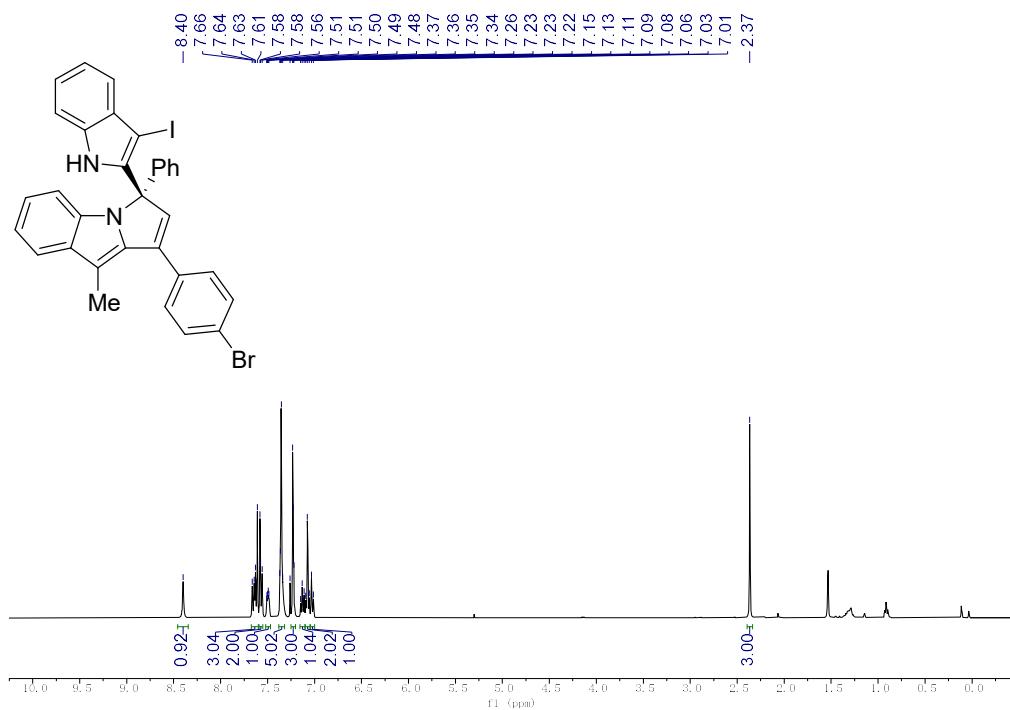
¹H NMR (400 MHz, CDCl₃) of **6dd**



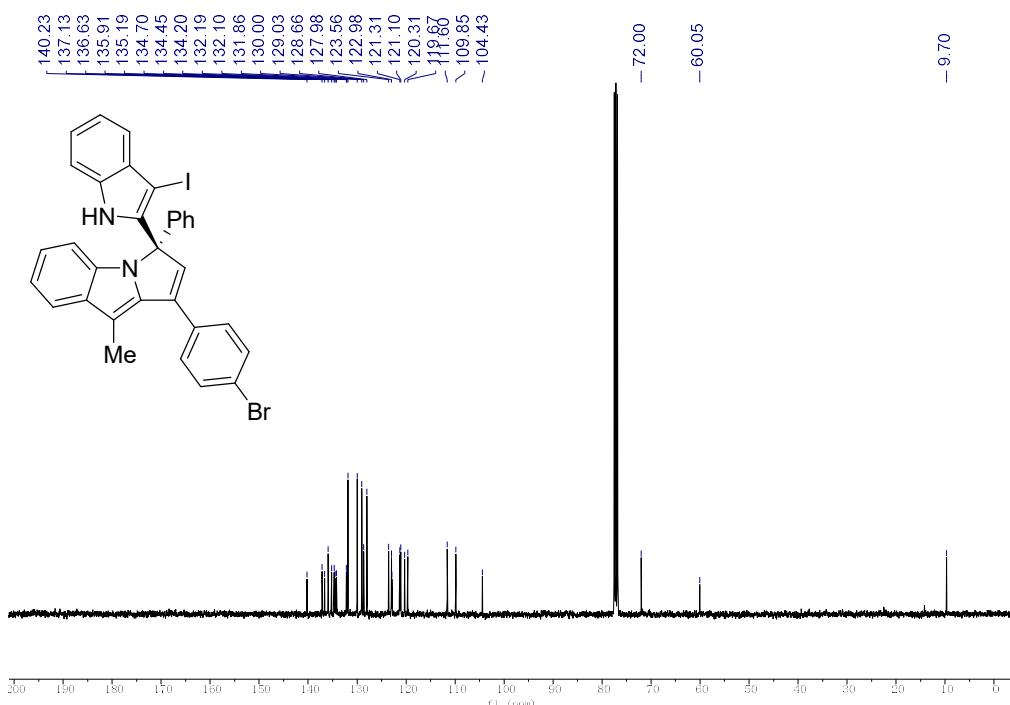
¹³C{¹H} NMR (101 MHz, CDCl₃) of **6dd**



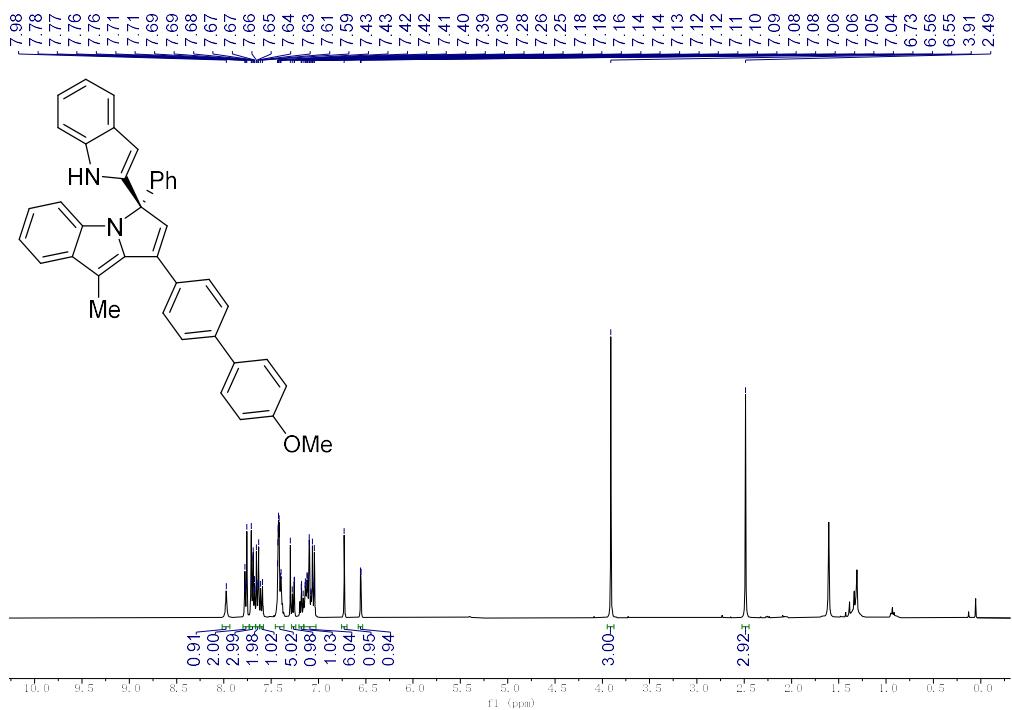
¹H NMR (400 MHz, CDCl₃) of **7**



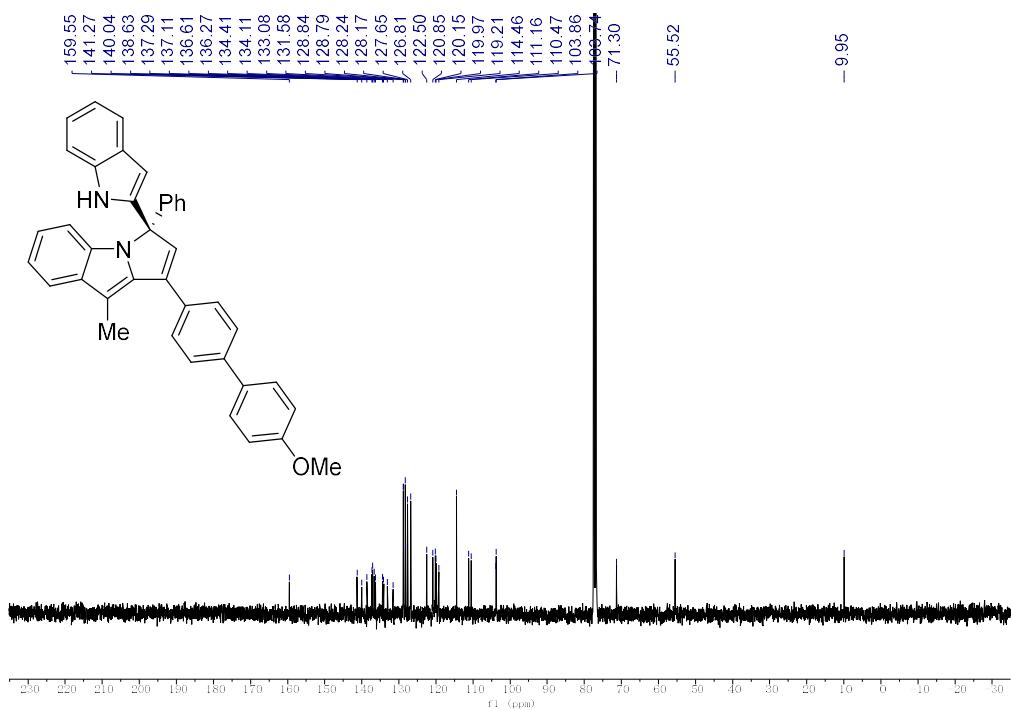
¹³C{¹H} NMR (101 MHz, CDCl₃) of **7**



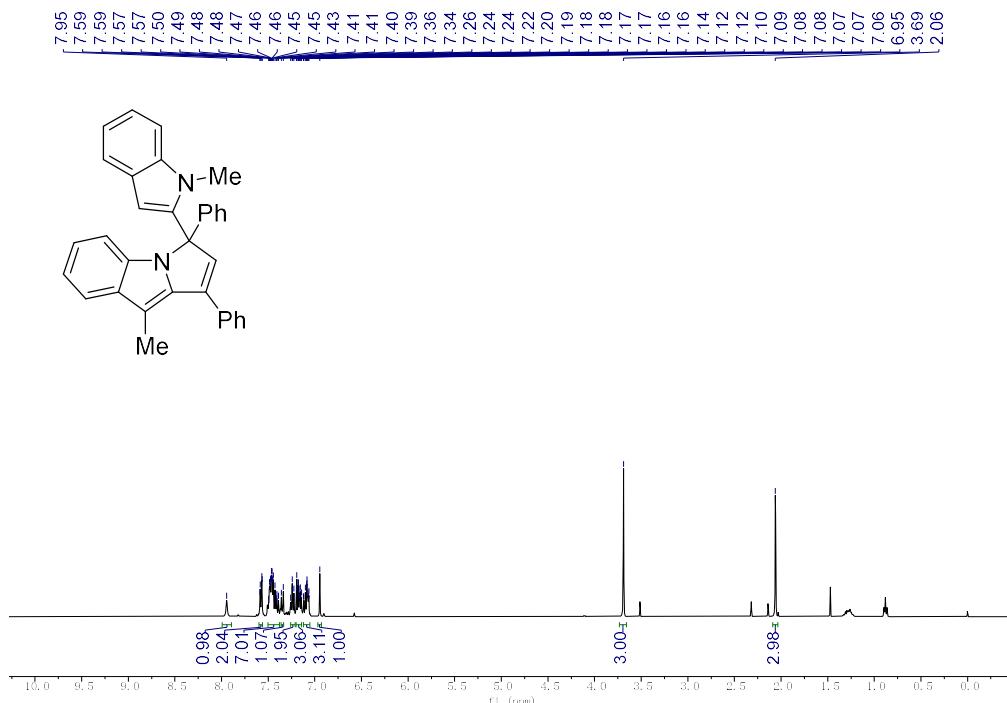
¹H NMR (400 MHz, CDCl₃) of **8**



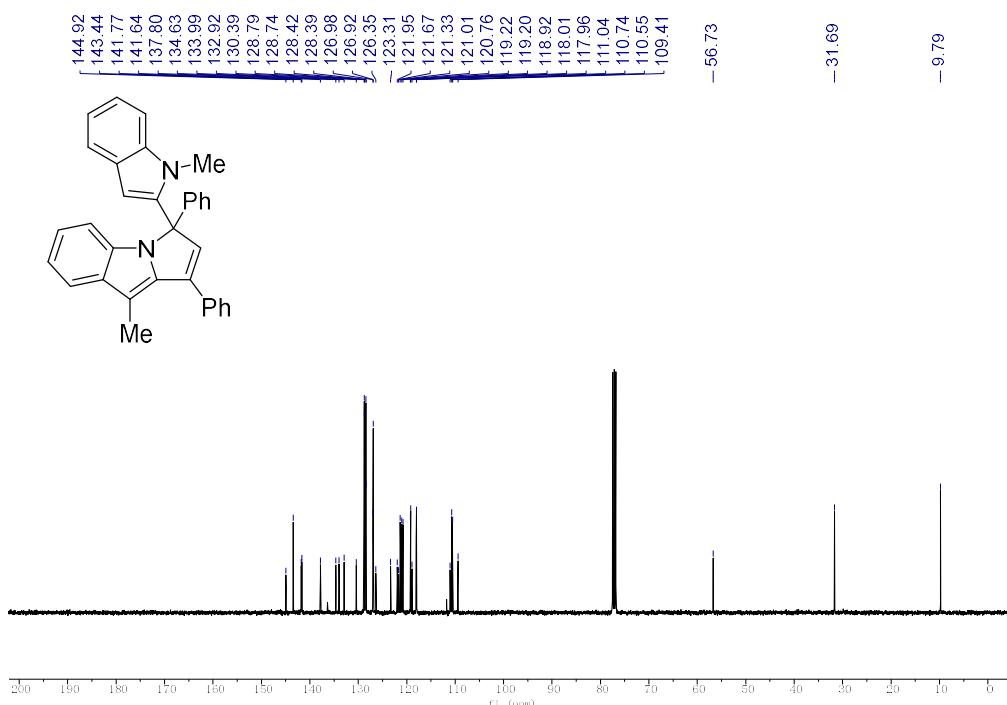
¹³C{¹H} NMR (101 MHz, CDCl₃) of **8**



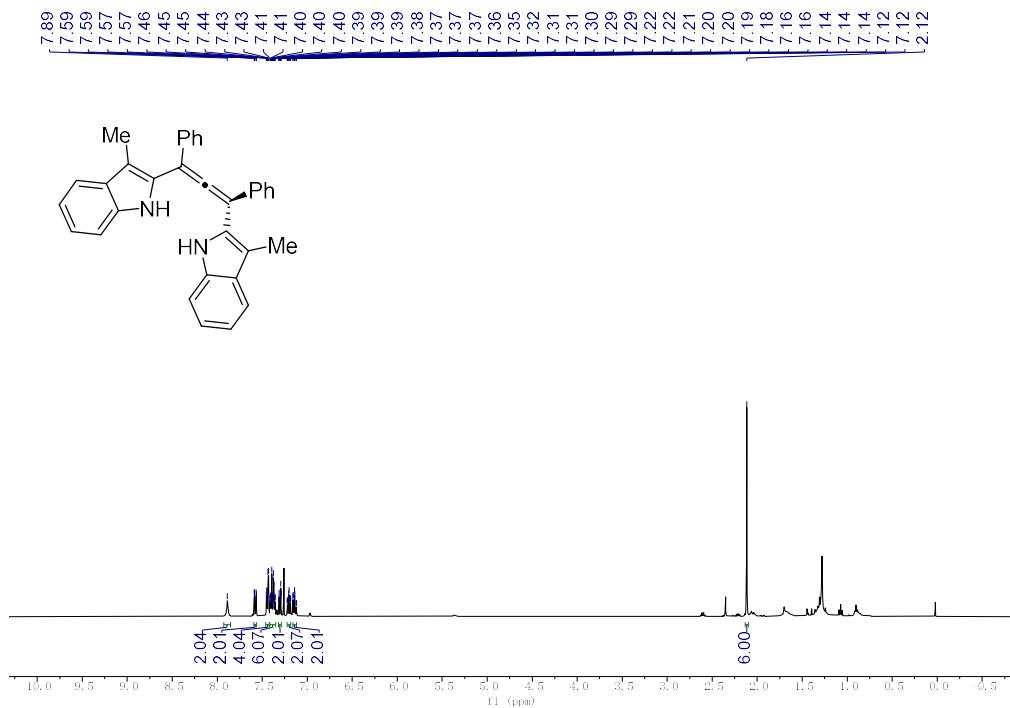
¹H NMR (400 MHz, CDCl₃) of **10**



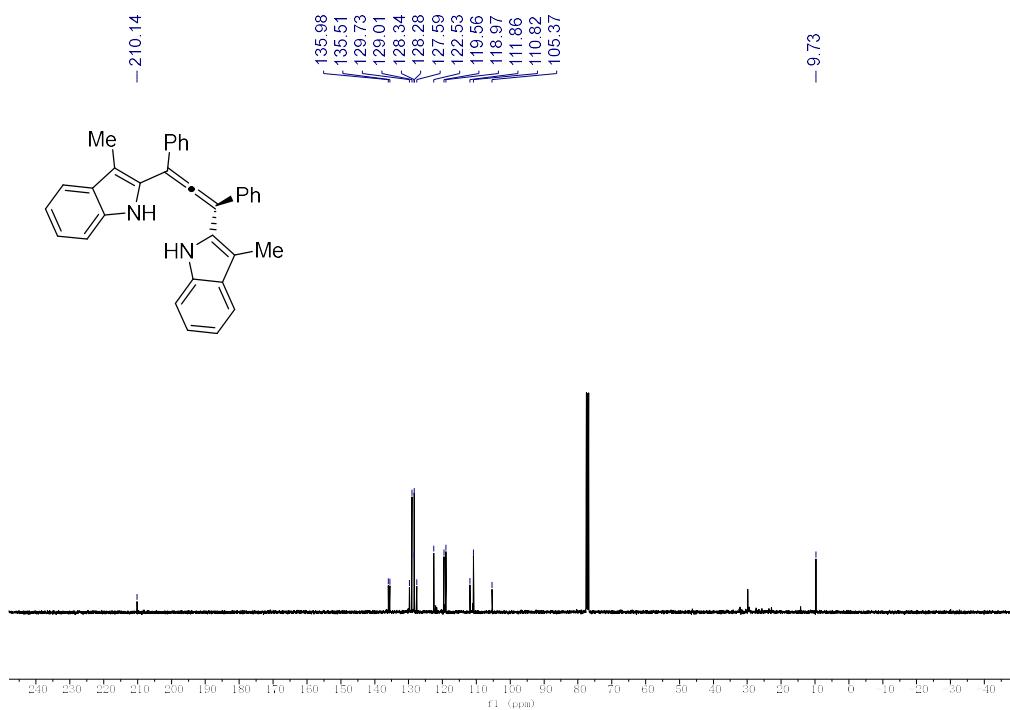
¹³C{¹H} NMR (101 MHz, CDCl₃) of **10**



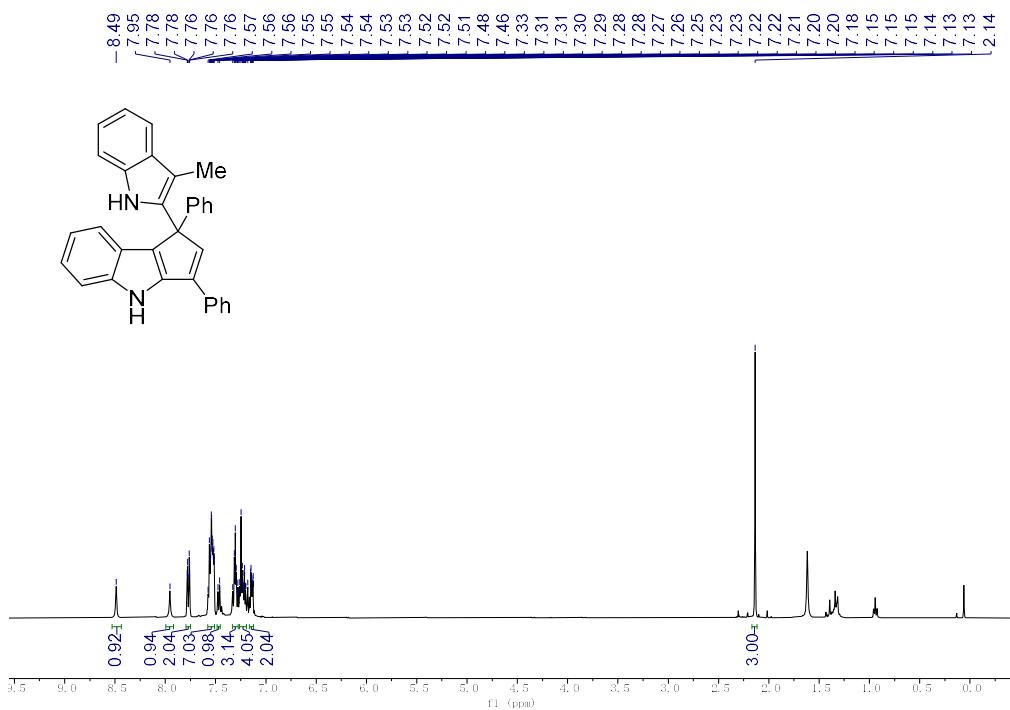
¹H NMR (400 MHz, CDCl₃) of **12**



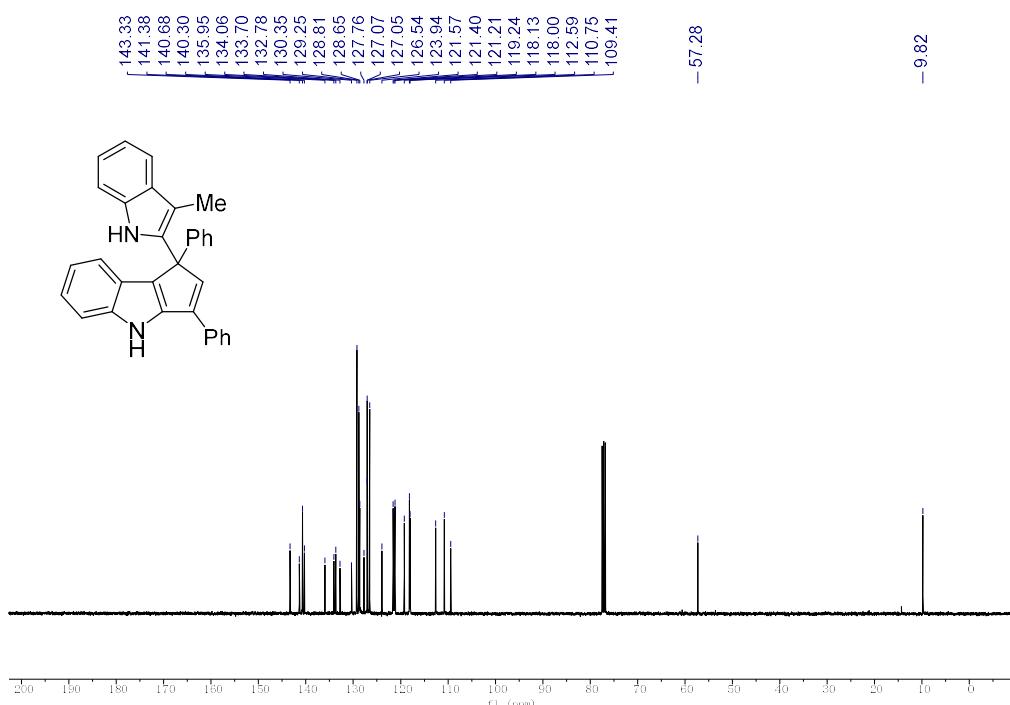
¹³C{¹H} NMR (101 MHz, CDCl₃) of **12**



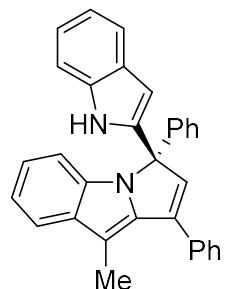
¹H NMR (400 MHz, CDCl₃) of **3aa'**



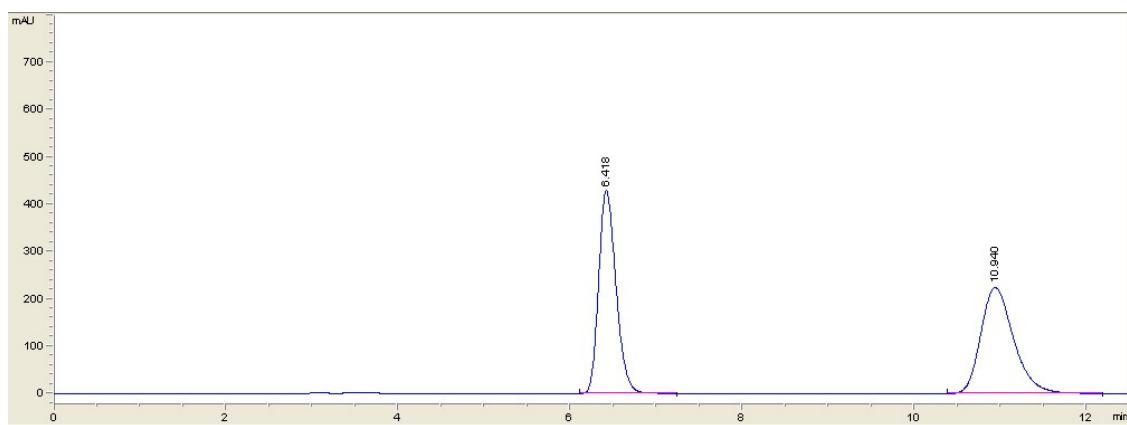
¹³C{¹H} NMR (101 MHz, CDCl₃) of **3aa'**



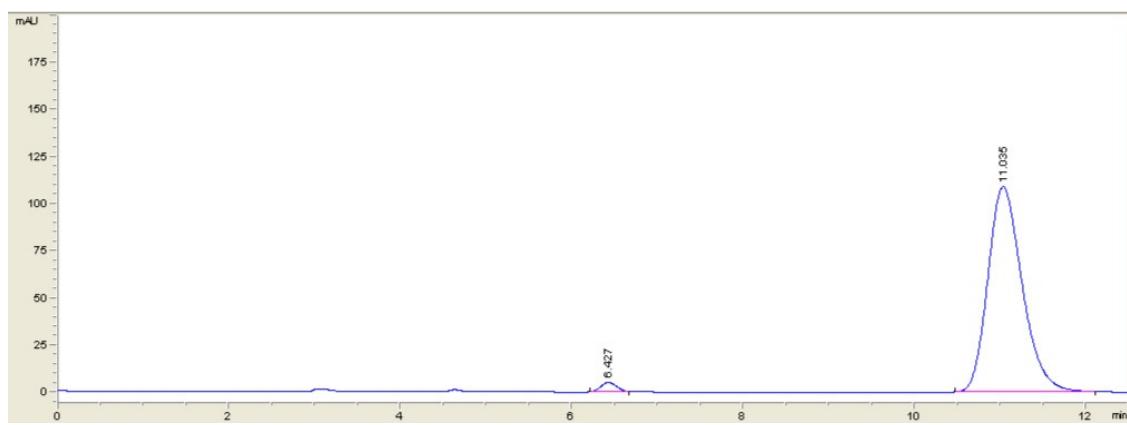
6. HPLC data



(S)-3-(1H-indol-2-yl)-9-methyl-1,3-diphenyl-3H-pyrrolo[1,2-a]indole (3aa)

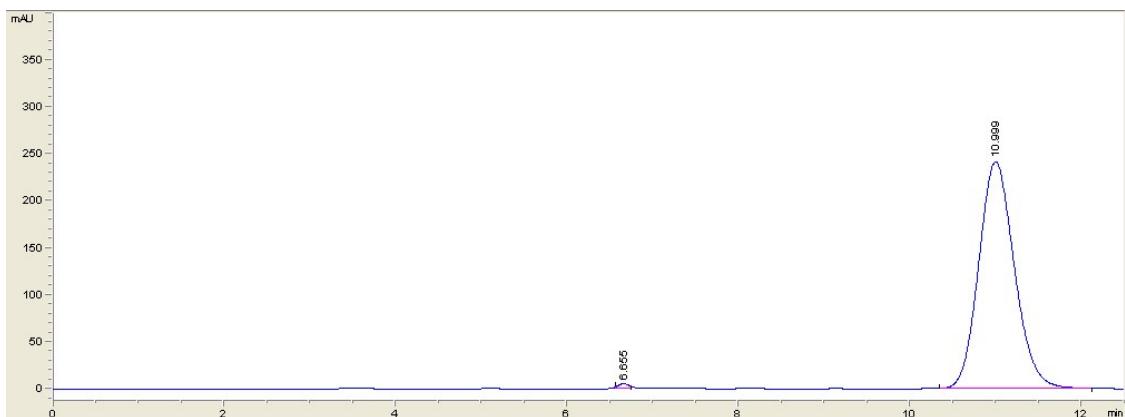


#	Time	Area	Height	Width	Area%
1	6.418	6004.1	428.8	0.2158	50.187
2	10.94	5959.5	224.3	0.409	49.813

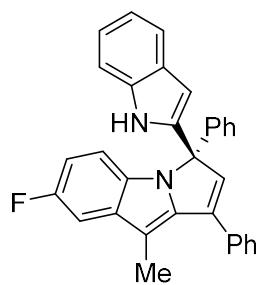


#	Time	Area	Height	Width	Area%
1	6.427	63.7	4.9	0.2144	2.051
2	11.035	3041.1	108.9	0.4305	97.949

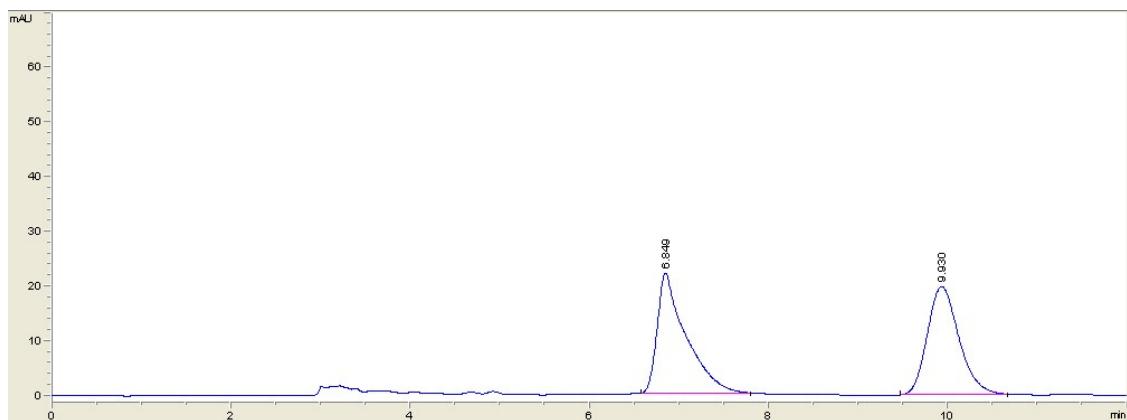
HPLC of 3aa (After recrystallization)



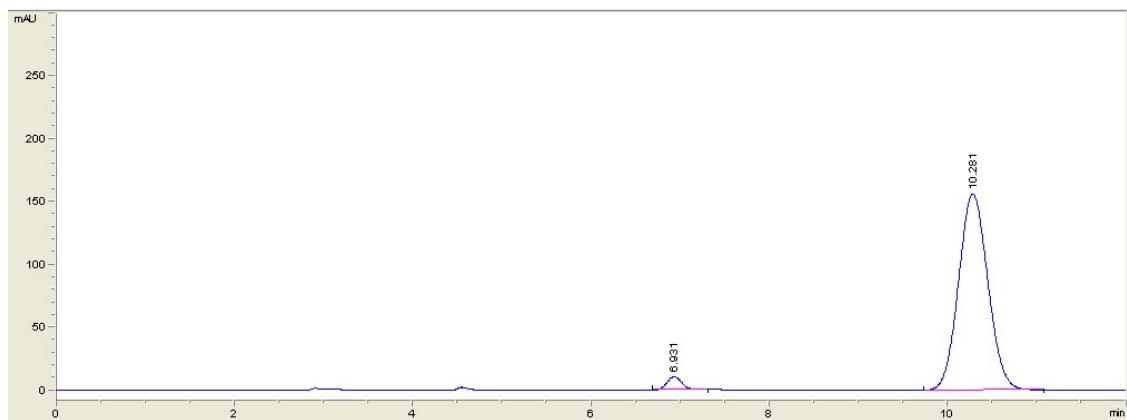
#	Time	Area	Height	Width	Area%
1	6.655	39.2	4.9	0.1322	0.558
2	10.999	6983.8	241.3	0.4484	99.442



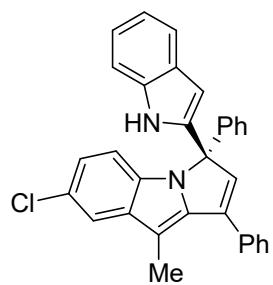
(S)-7-fluoro-3-(1H-indol-2-yl)-9-methyl-1,3-diphenyl-3H-pyrrolo[1,2-a]indole (3ab)



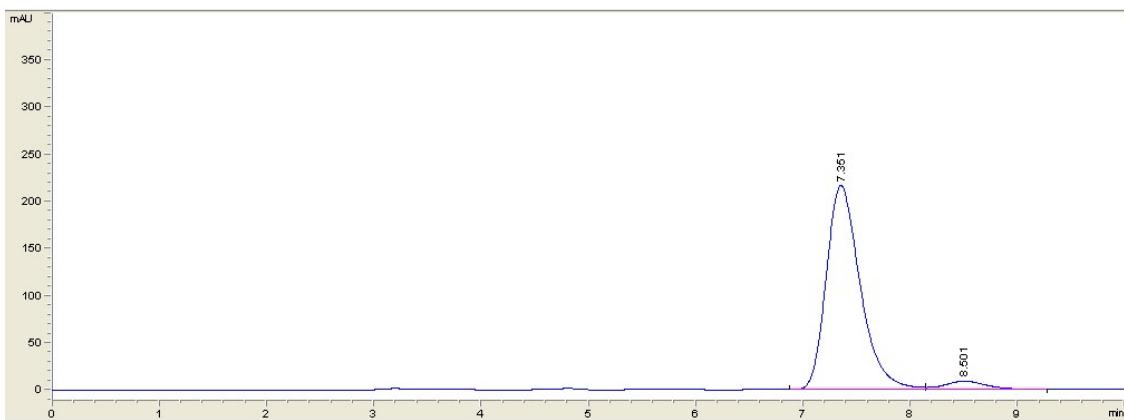
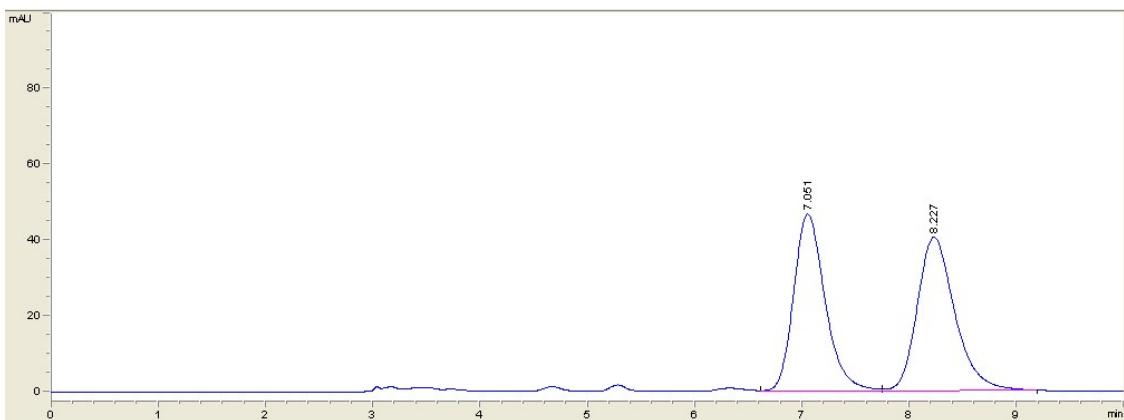
#	Time	Area	Height	Width	Area%
1	6.849	497	22.1	0.3029	50.320
2	9.93	490.7	19.8	0.3803	49.680

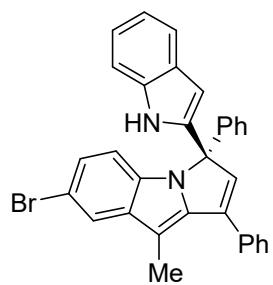


#	Time	Area	Height	Width	Area%
1	6.931	128.6	10.5	0.192	3.475
2	10.281	3572.7	156.1	0.3573	96.525

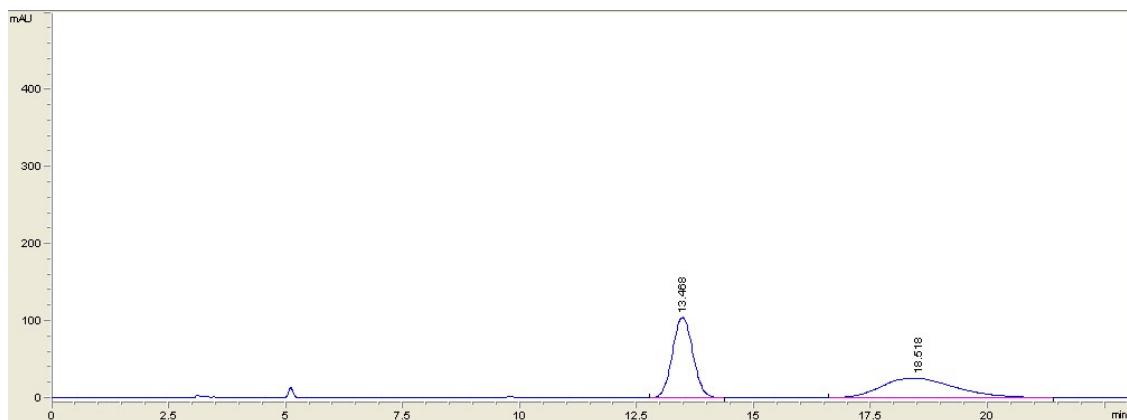


(S)-7-chloro-3-(1H-indol-2-yl)-9-methyl-1,3-diphenyl-3H-pyrrolo[1,2-a]indole (3ac)

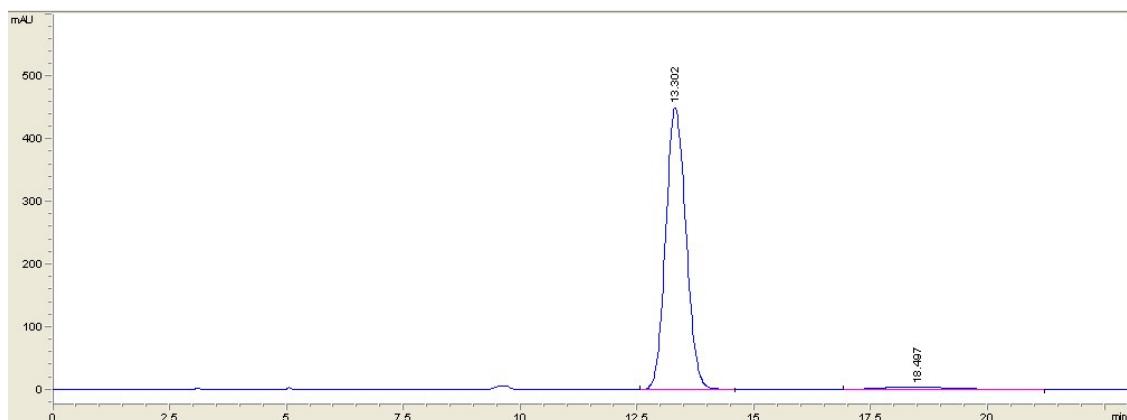




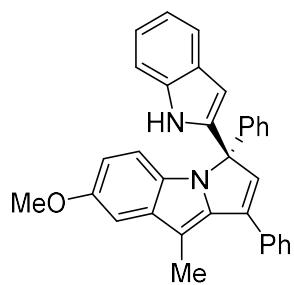
(S)-7-bromo-3-(1H-indol-2-yl)-9-methyl-1,3-diphenyl-3H-pyrrolo[1,2-a]indole (3ad)



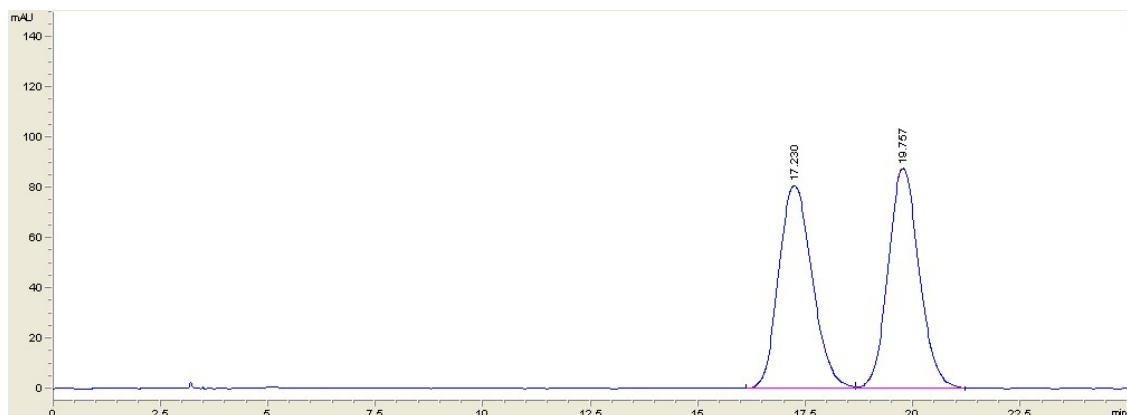
#	Time	Area	Height	Width	Area%
1	13.468	3175	104.3	0.4832	53.111
2	18.518	2803	25.3	1.4368	46.889



#	Time	Area	Height	Width	Area%
1	13.302	13587.1	449.6	0.4719	96.801
2	18.497	449	3.8	1.415	3.199



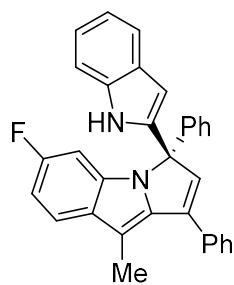
(S)-3-(1H-indol-2-yl)-7-methoxy-9-methyl-1,3-diphenyl-3H-pyrrolo[1,2-a]indole (3ae)



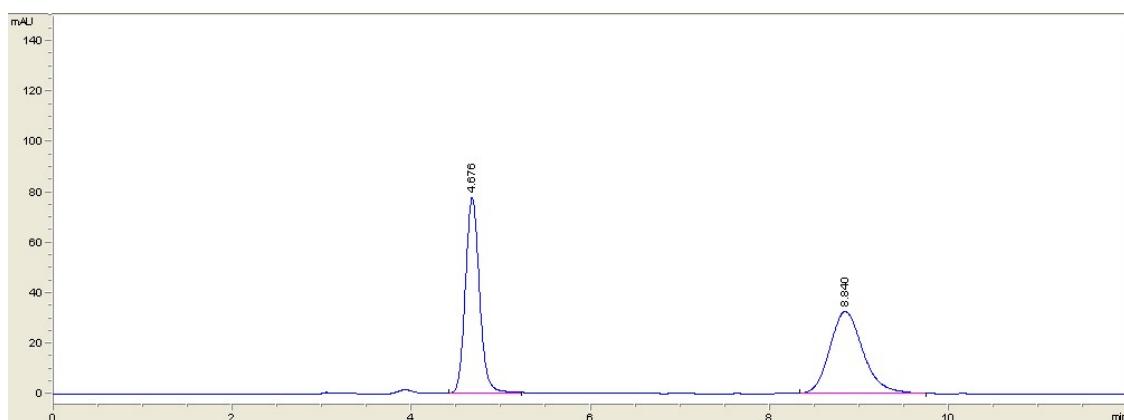
#	Time	Area	Height	Width	Area%
1	17.23	4361.9	80.6	0.8617	49.932
2	19.757	4373.8	87.5	0.7637	50.068



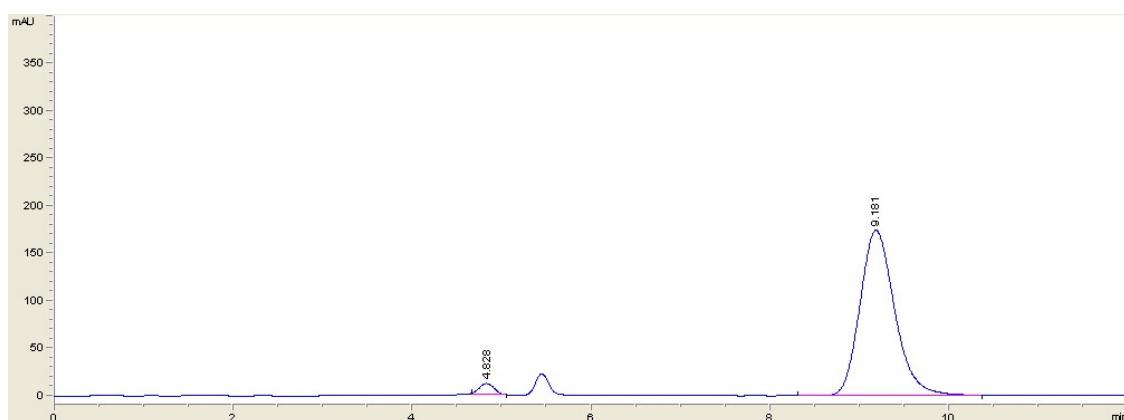
#	Time	Area	Height	Width	Area%
1	18.38	706.9	14.3	0.8245	5.042
2	20.915	13313.1	256.8	0.8204	94.958



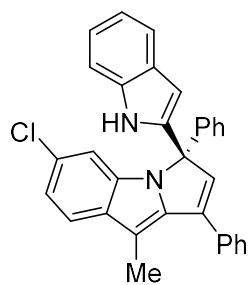
(S)-6-fluoro-3-(1H-indol-2-yl)-9-methyl-1,3-diphenyl-3H-pyrrolo[1,2-a]indole (3af)



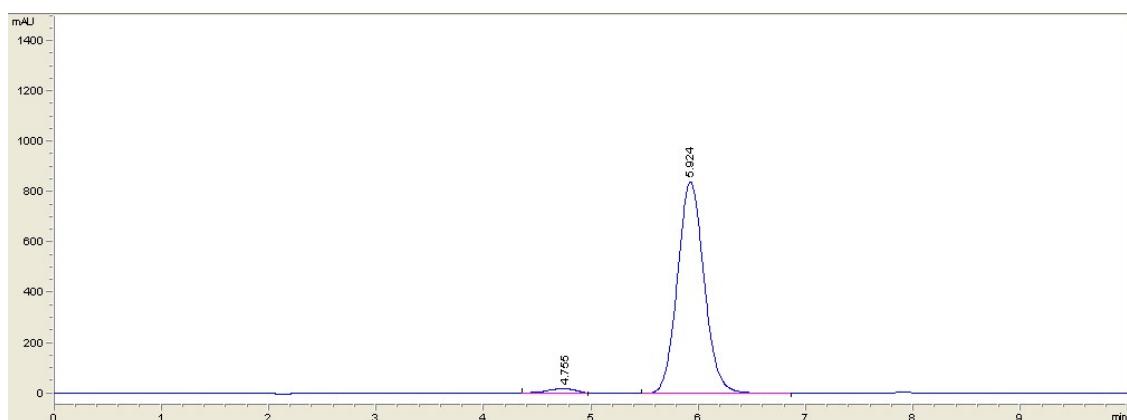
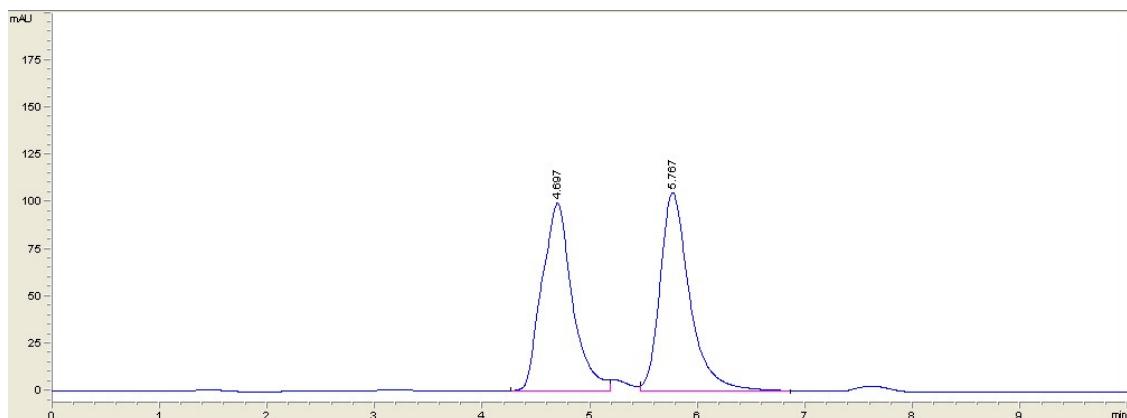
#	Time	Area	Height	Width	Area%
1	4.676	854.9	77.9	0.1689	50.312
2	8.84	844.4	32.6	0.3983	49.688

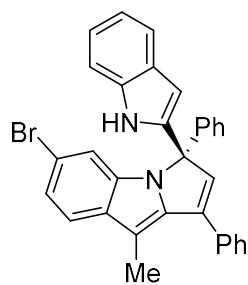


#	Time	Area	Height	Width	Area%
1	4.828	148.7	12.3	0.2019	3.051
2	9.181	4723.5	174.1	0.4155	96.949

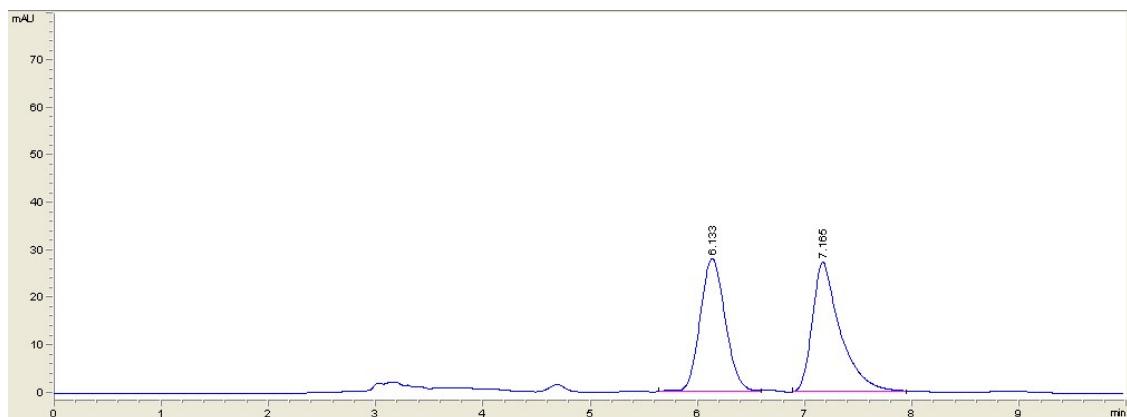


(S)-6-chloro-3-(1H-indol-2-yl)-9-methyl-1,3-diphenyl-3H-pyrrolo[1,2-a]indole (3ag)

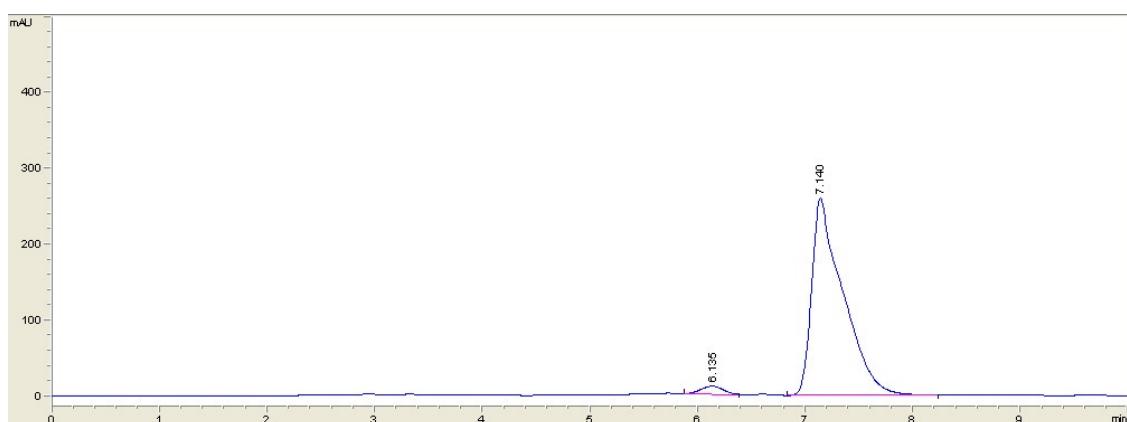




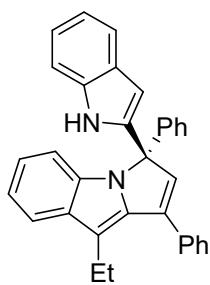
(S)-6-bromo-3-(1H-indol-2-yl)-9-methyl-1,3-diphenyl-3H-pyrrolo[1,2-a]indole (3ah)



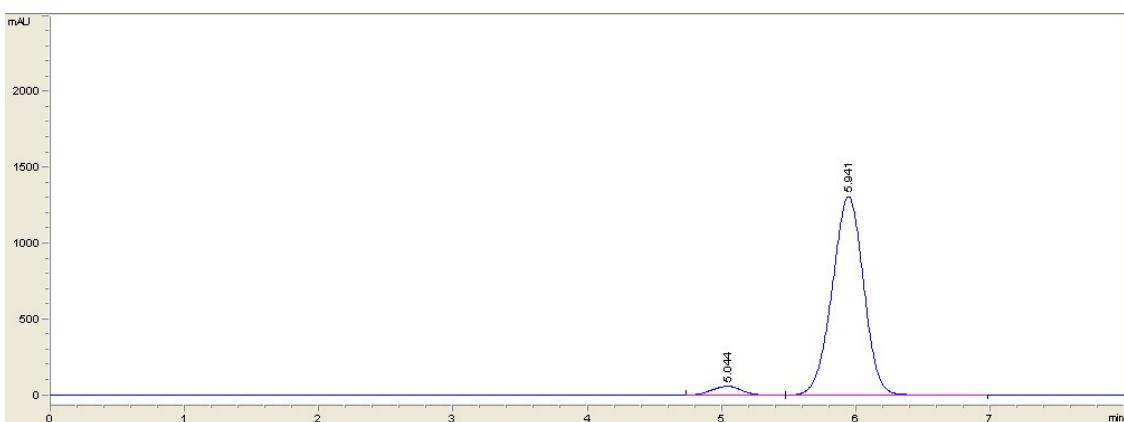
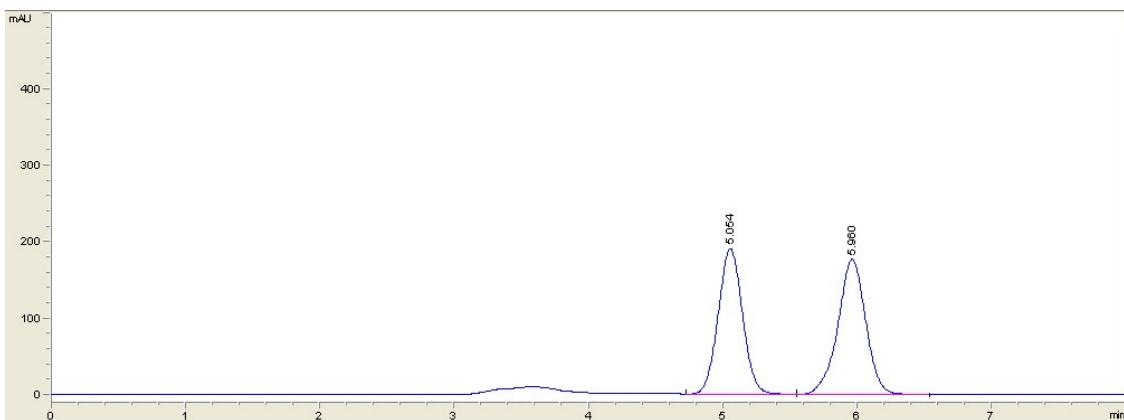
#	Time	Area	Height	Width	Area%
1	6.133	455.7	27.9	0.2543	47.912
2	7.165	495.4	27.3	0.2615	52.088

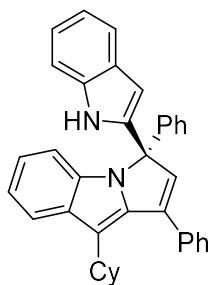


#	Time	Area	Height	Width	Area%
1	6.135	167.1	11	0.2524	3.081
2	7.14	5256.2	259.8	0.271	96.919

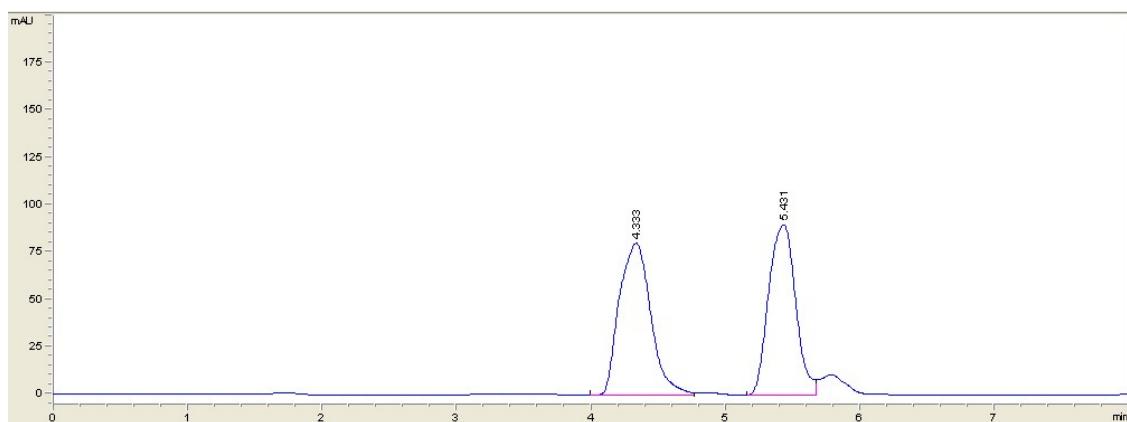


(S)-9-ethyl-3-(1H-indol-2-yl)-1,3-diphenyl-3H-pyrrolo[1,2-a]indole (3ai)

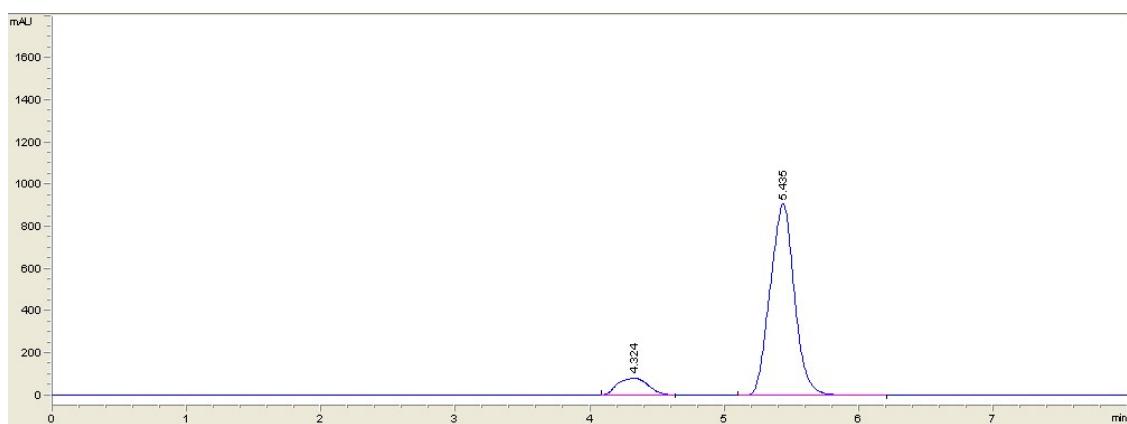




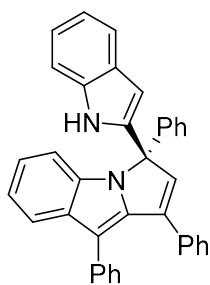
(S)-9-cyclohexyl-3-(1H-indol-2-yl)-1,3-diphenyl-3H-pyrrolo[1,2-a]indole (3aj)



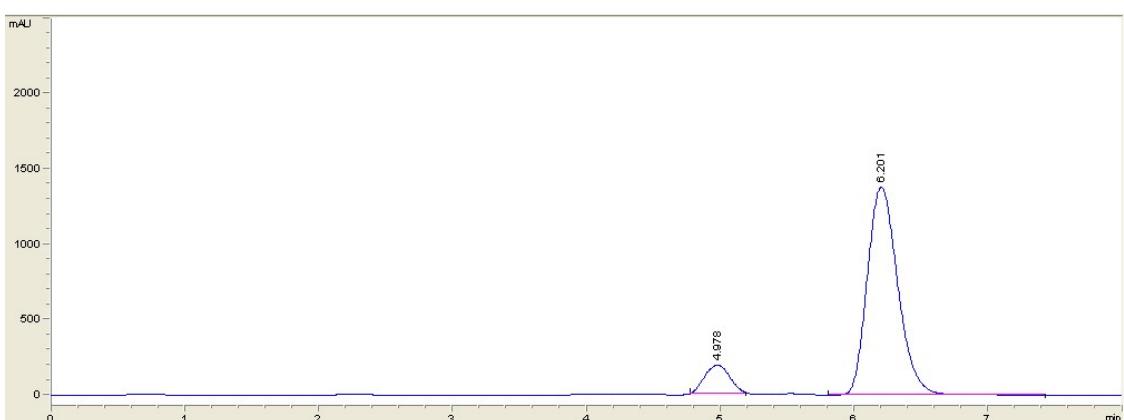
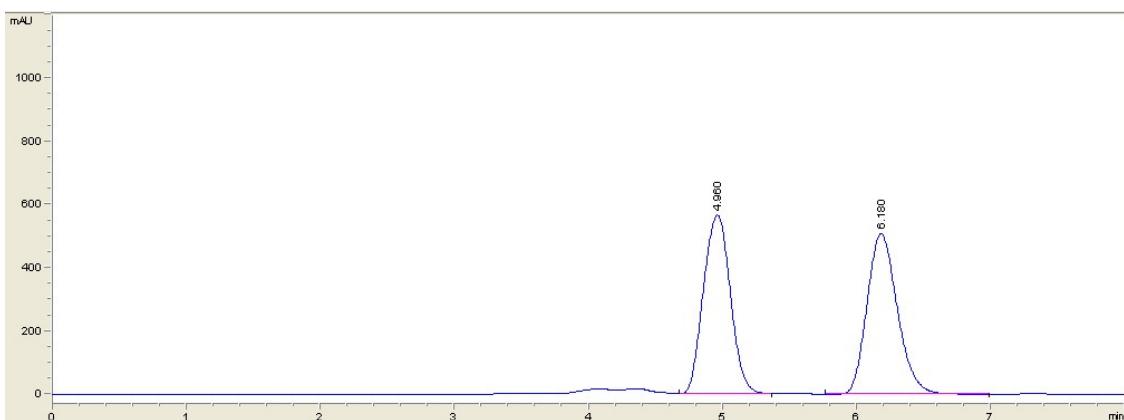
#	Time	Area	Height	Width	Area%
1	4.333	1313.5	80.3	0.271	50.802
2	5.431	1272	90.5	0.2343	49.198

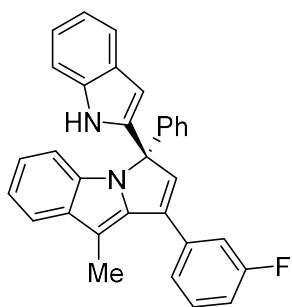


#	Time	Area	Height	Width	Area%
1	4.324	1265.4	80.3	0.2627	9.975
2	5.435	11420.1	908.6	0.2005	90.025

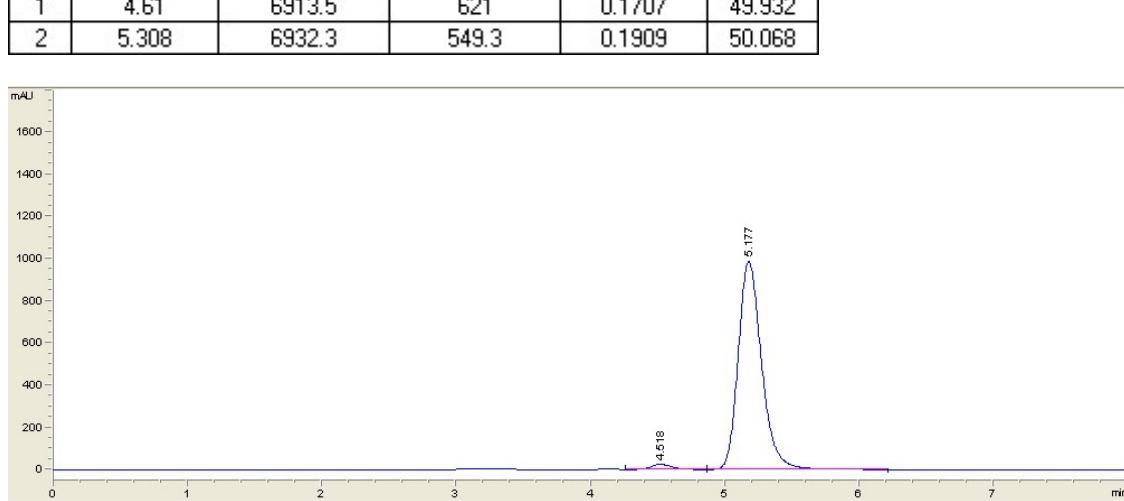
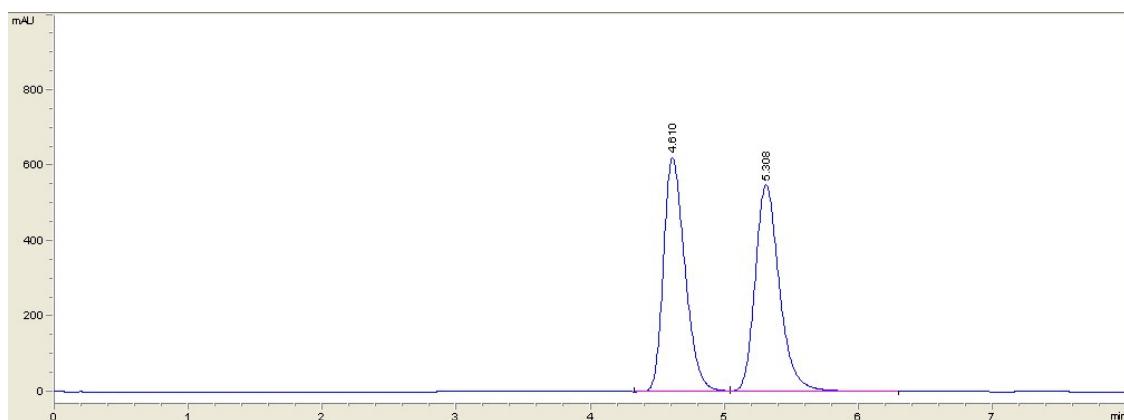


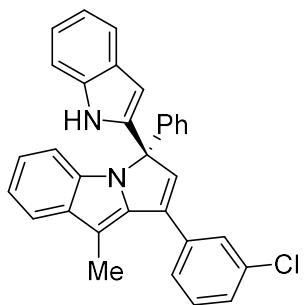
(S)-3-(1H-indol-2-yl)-1,3,9-triphenyl-3H-pyrrolo[1,2-a]indole (3ak)



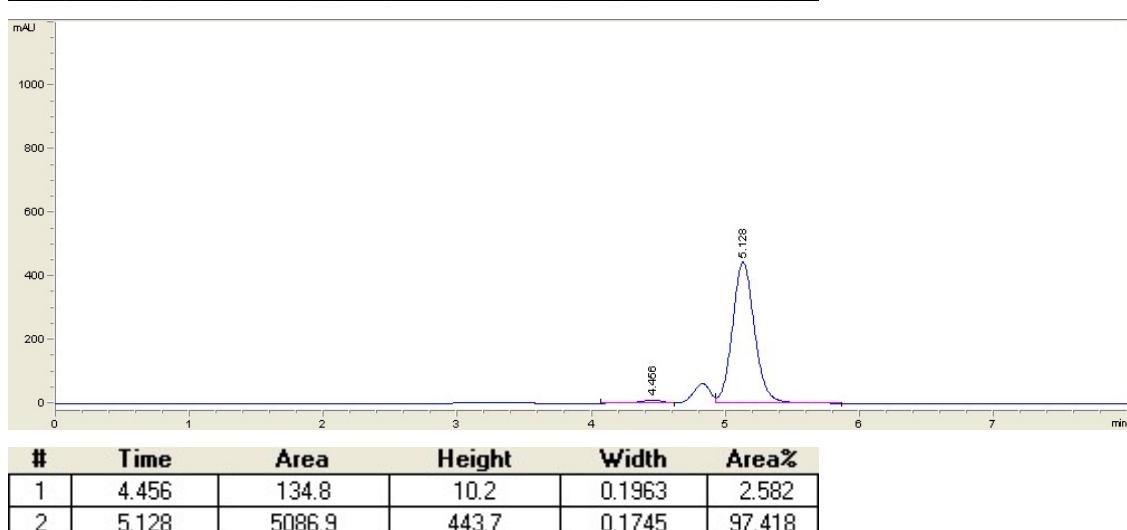
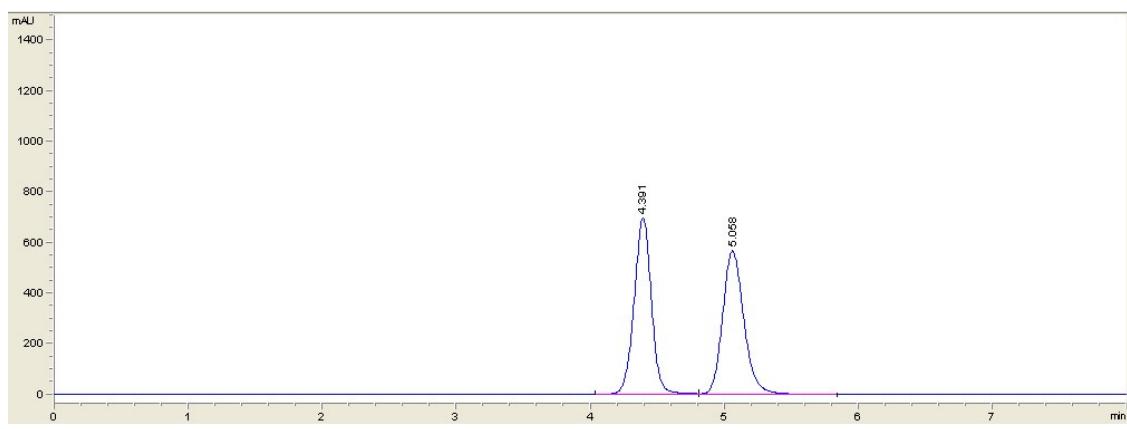


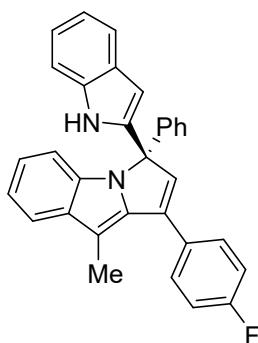
**(S)-1-(3-fluorophenyl)-3-(1H-indol-2-yl)-9-methyl-3H-pyrrolo[1,2-a]indole
(3ba)**



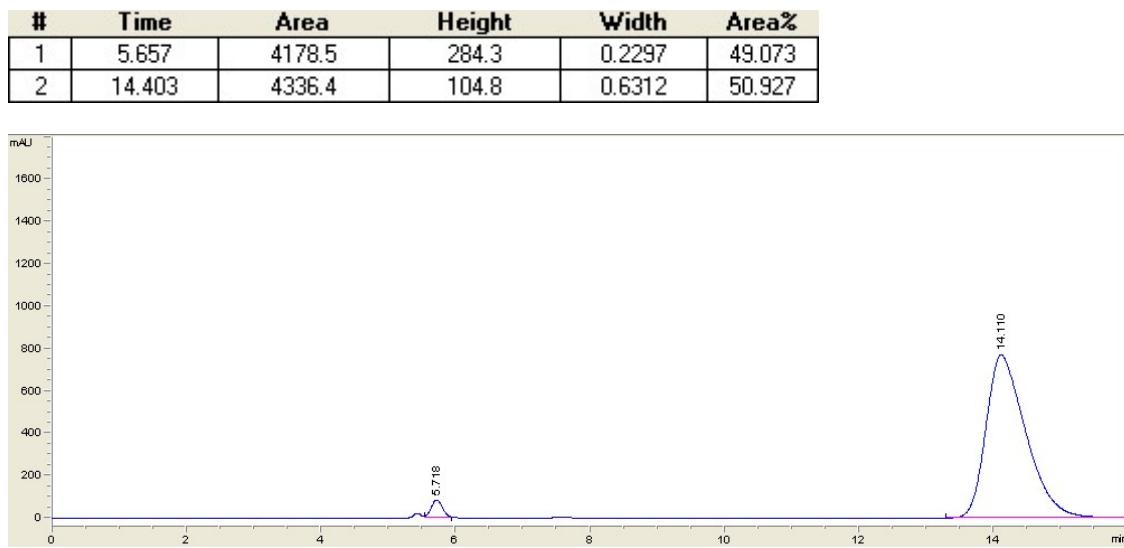
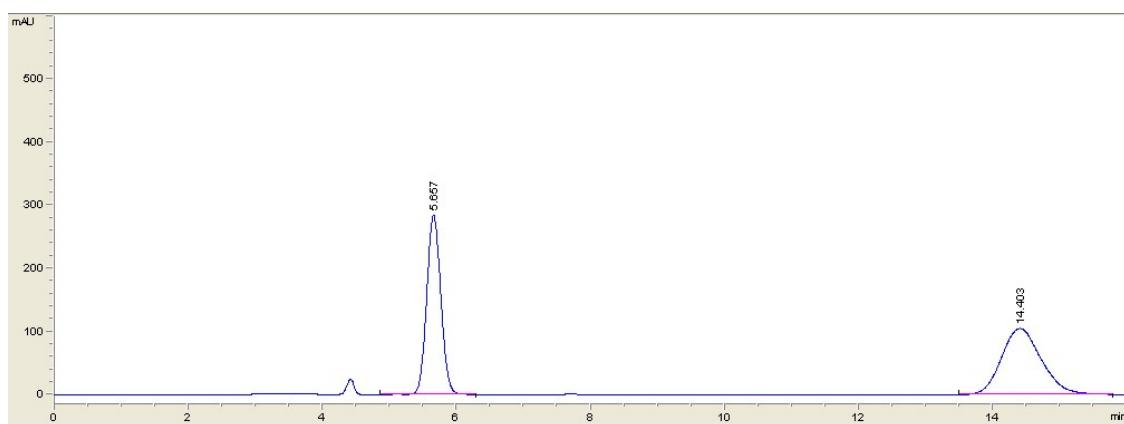


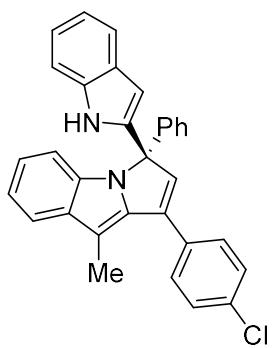
**(S)-1-(3-chlorophenyl)-3-(1H-indol-2-yl)-9-methyl-3-phenyl-3H-pyrrolo[1,2-a]indole
(3ca)**



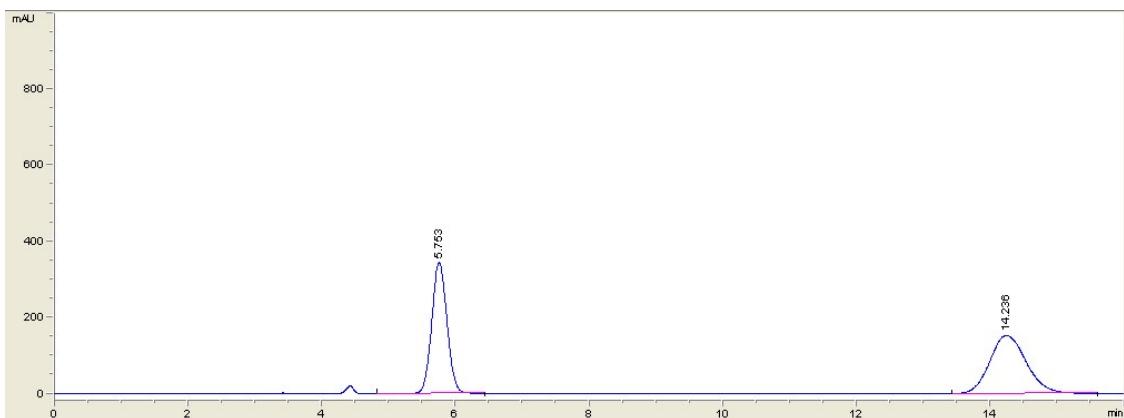


**(S)-1-(4-fluorophenyl)-3-(1H-indol-2-yl)-9-methyl-3H-pyrrolo[1,2-a]indole
(3da)**

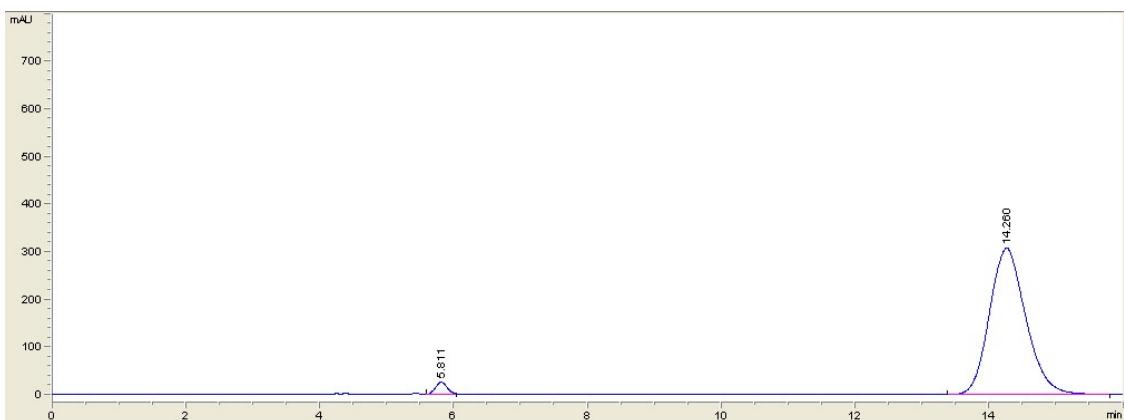




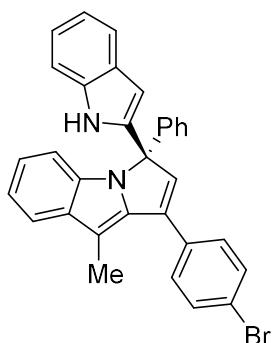
**(S)-1-(3-chlorophenyl)-3-(1H-indol-2-yl)-9-methyl-3H-pyrrolo[1,2-a]indole
(3ea)**



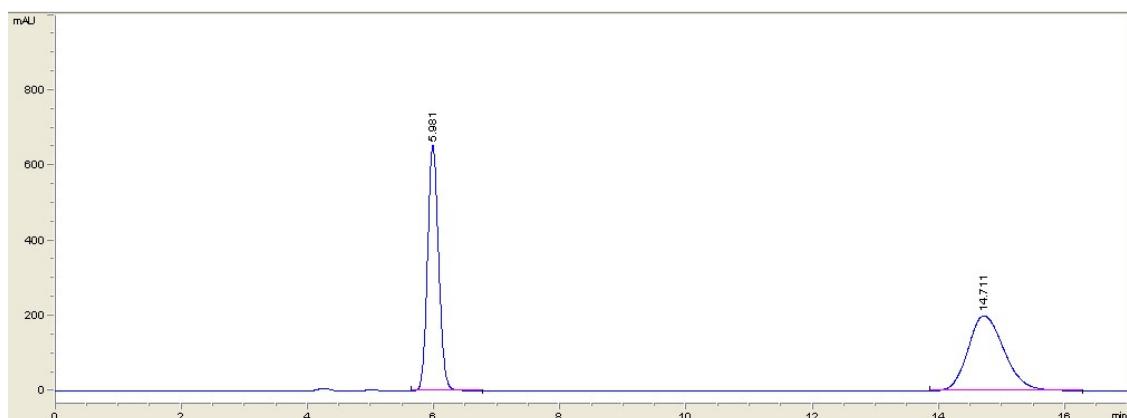
#	Time	Area	Height	Width	Area%
1	5.753	5494.7	344.1	0.2475	48.523
2	14.236	5829.3	152.5	0.5914	51.477



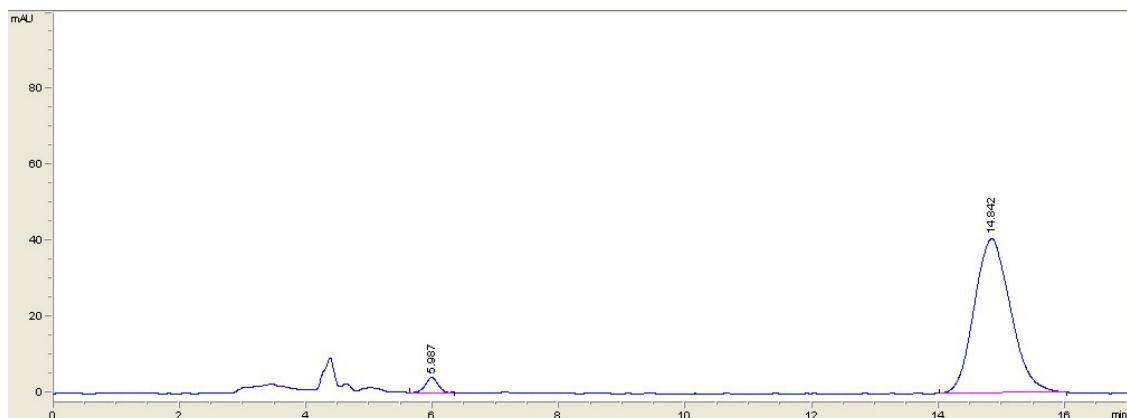
#	Time	Area	Height	Width	Area%
1	5.811	314	25.6	0.2048	2.637
2	14.26	11592.6	307.7	0.5851	97.363



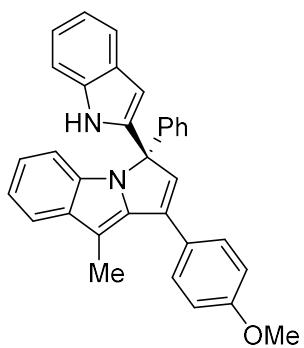
(S)-1-(4-bromophenyl)-3-(1H-indol-2-yl)-9-methyl-3-phenyl-3H-pyrrolo[1,2-a]indole (3fa)



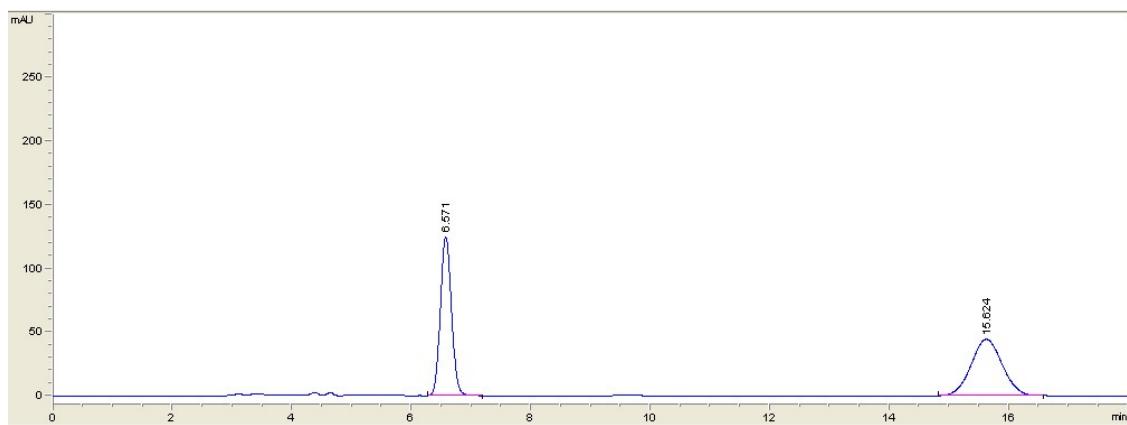
#	Time	Area	Height	Width	Area%
1	5.981	7955.7	652.3	0.1889	49.982
2	14.711	7961.3	199.4	0.6144	50.018



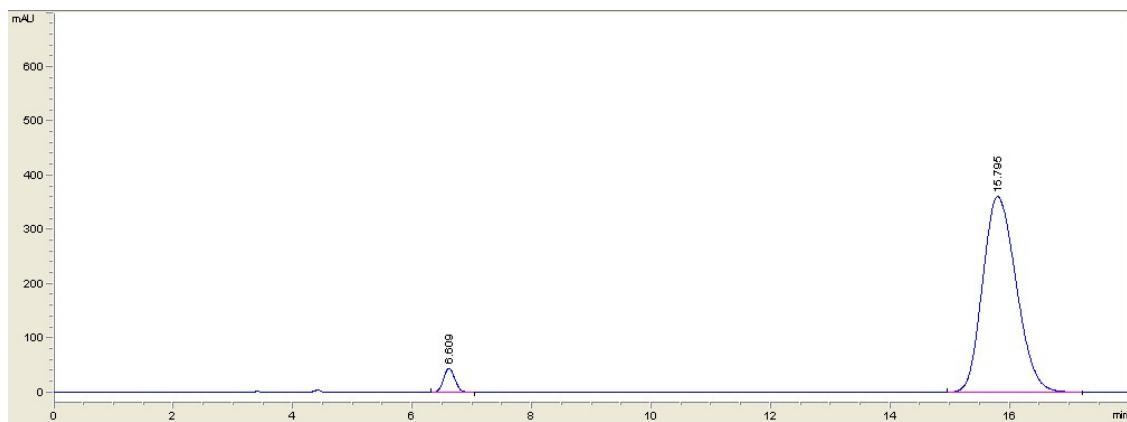
#	Time	Area	Height	Width	Area%
1	5.987	62.2	4.2	0.2213	3.680
2	14.842	1628.5	40.7	0.6269	96.320



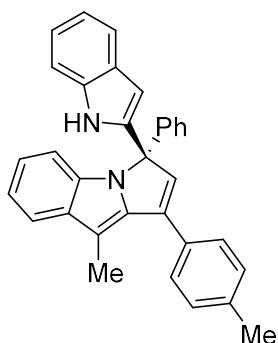
(S)-3-(1H-indol-2-yl)-1-(4-methoxyphenyl)-9-methyl-3-phenyl-3H-pyrrolo[1,2-a]indole (3ga)



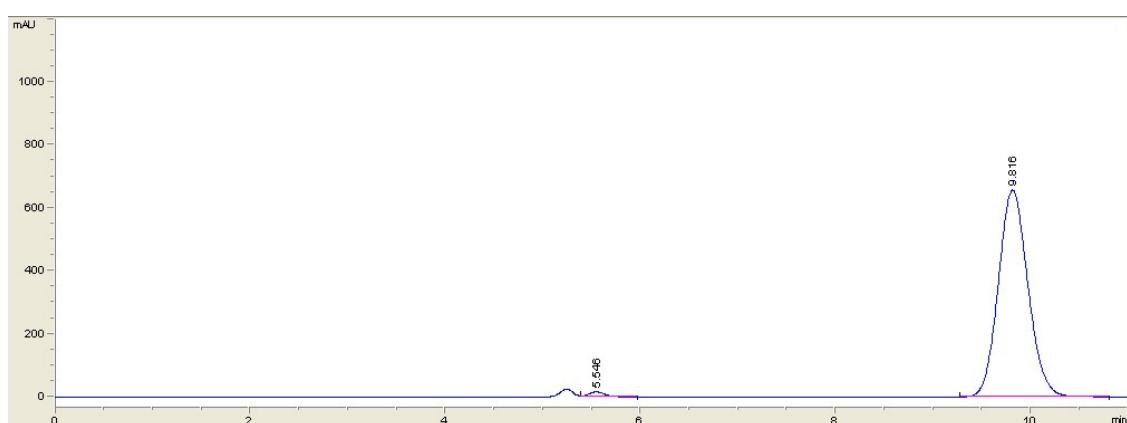
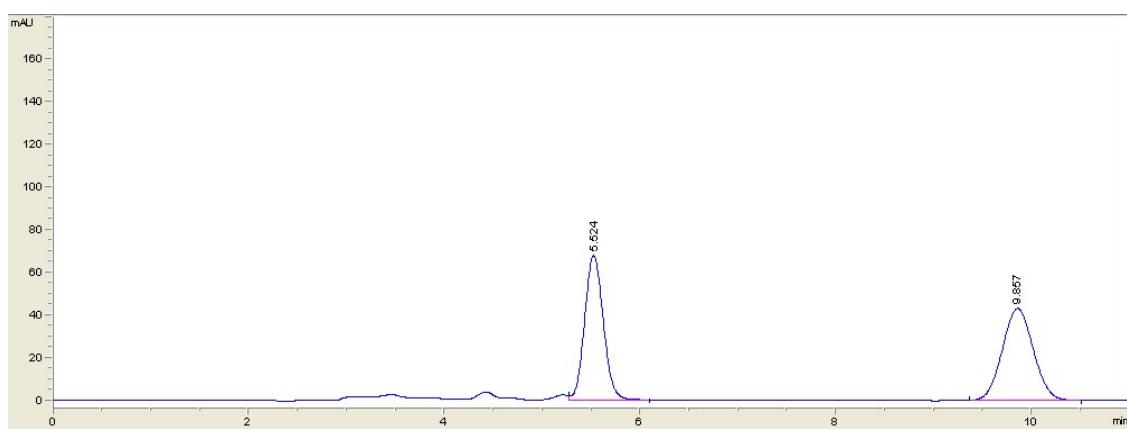
#	Time	Area	Height	Width	Area%
1	6.571	1608.8	124.9	0.1998	49.939
2	15.624	1612.8	44.4	0.5637	50.061

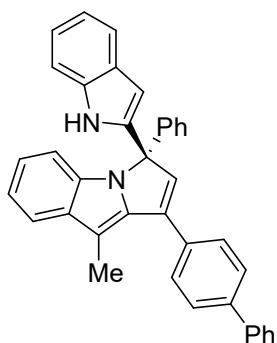


#	Time	Area	Height	Width	Area%
1	6.609	585.9	44.1	0.2059	3.986
2	15.795	14115	360.7	0.6225	96.014

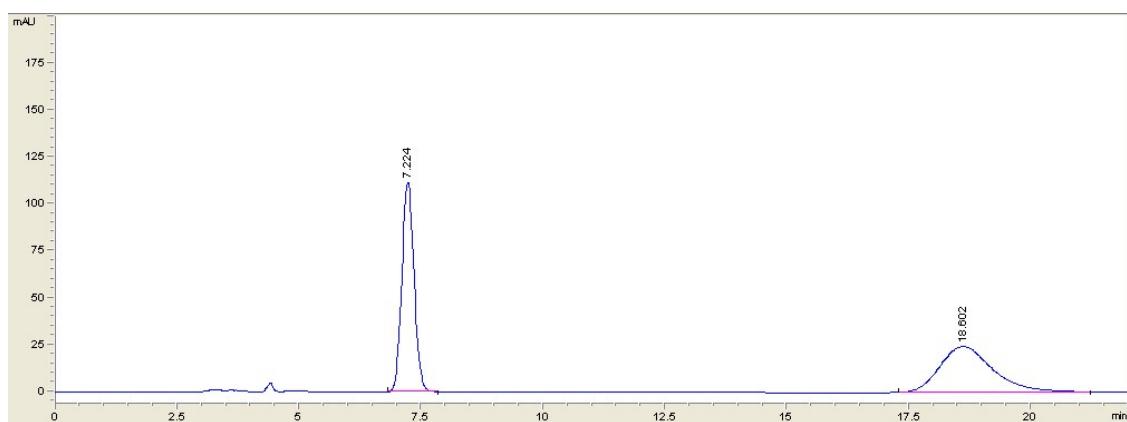


(S)-3-(1H-indol-2-yl)-9-methyl-3-phenyl-1-(p-tolyl)-3H-pyrrolo[1,2-a]indole (3ha)

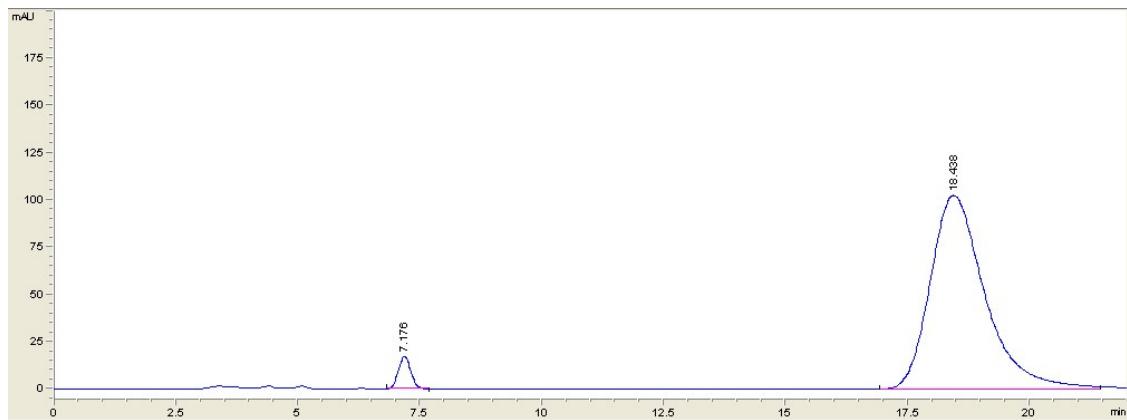




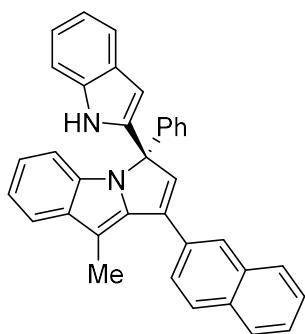
(S)-1-([1,1'-biphenyl]-4-yl)-3-(1H-indol-2-yl)-9-methyl-3-phenyl-3H-pyrrolo[1,2-a]indole (3ia)



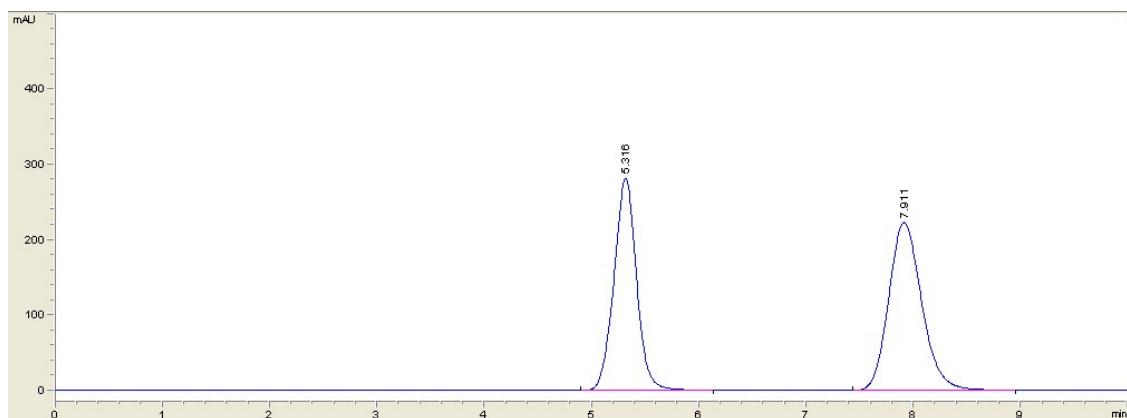
#	Time	Area	Height	Width	Area%
1	7.224	1948	111.5	0.2723	50.087
2	18.602	1941.2	24.7	1.3078	49.913



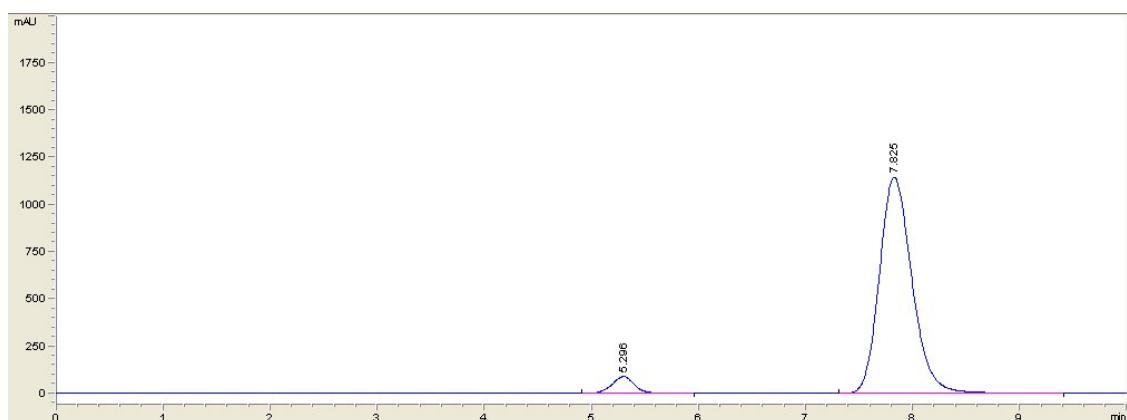
#	Time	Area	Height	Width	Area%
1	7.176	305.5	17.1	0.2808	3.635
2	18.438	8100.7	102.8	1.3128	96.365



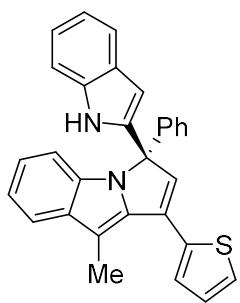
(S)-3-(1H-indol-2-yl)-9-methyl-1-(naphthalen-2-yl)-3-phenyl-3H-pyrrolo[1,2-a]indole (3ja)



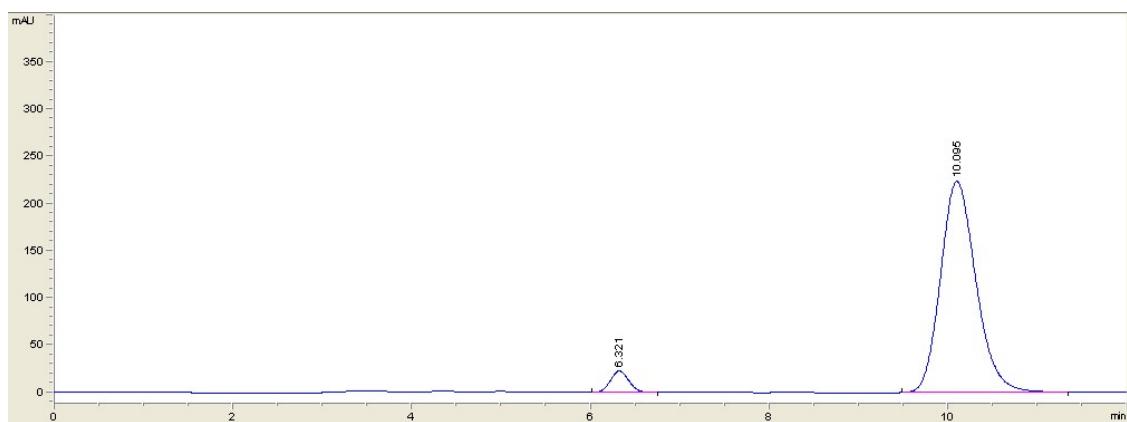
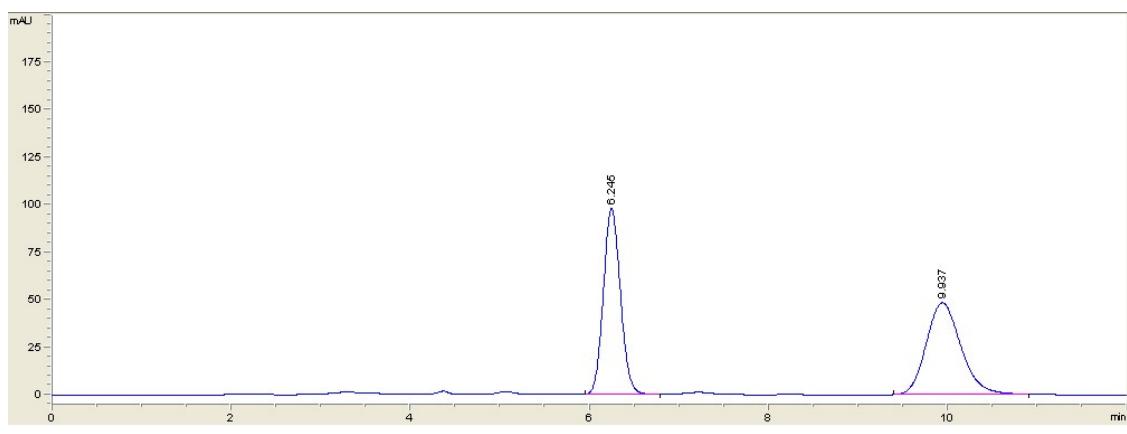
#	Time	Area	Height	Width	Area%
1	5.316	4130.2	281.4	0.2222	46.345
2	7.911	4781.6	222.9	0.3318	53.655

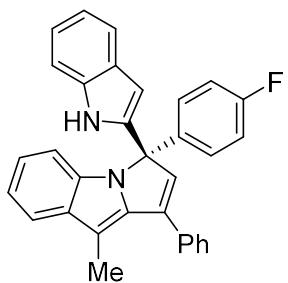


#	Time	Area	Height	Width	Area%
1	5.296	1300.2	89.5	0.2189	5.091
2	7.825	24238.9	1143.9	0.3287	94.909

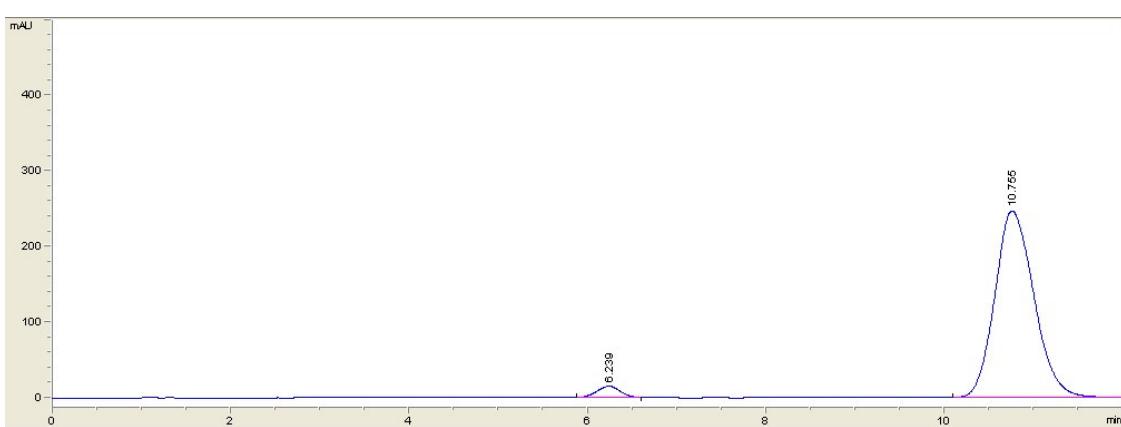
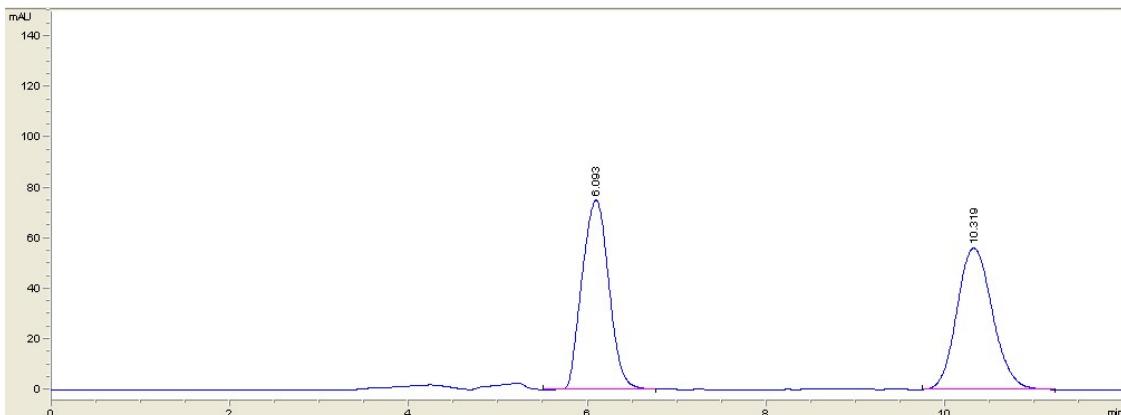


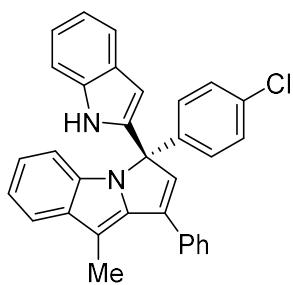
(S)-3-(1H-indol-2-yl)-9-methyl-3-phenyl-1-(thiophen-2-yl)-3H-pyrrolo[1,2-a]indole (3ka)



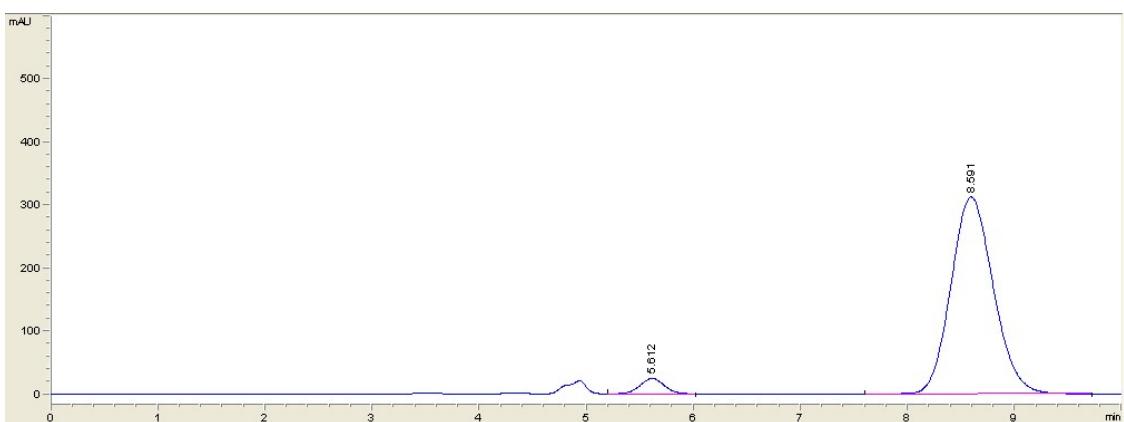
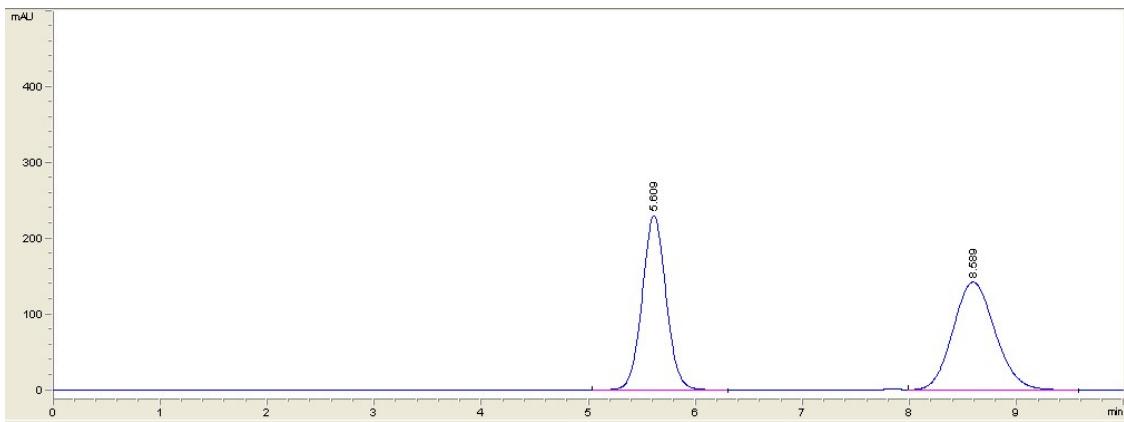


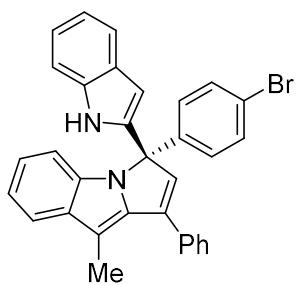
**(S)-3-(4-fluorophenyl)-3-(1H-indol-2-yl)-9-methyl-1-phenyl-3H-pyrrolo[1,2-a]indole
(3la)**



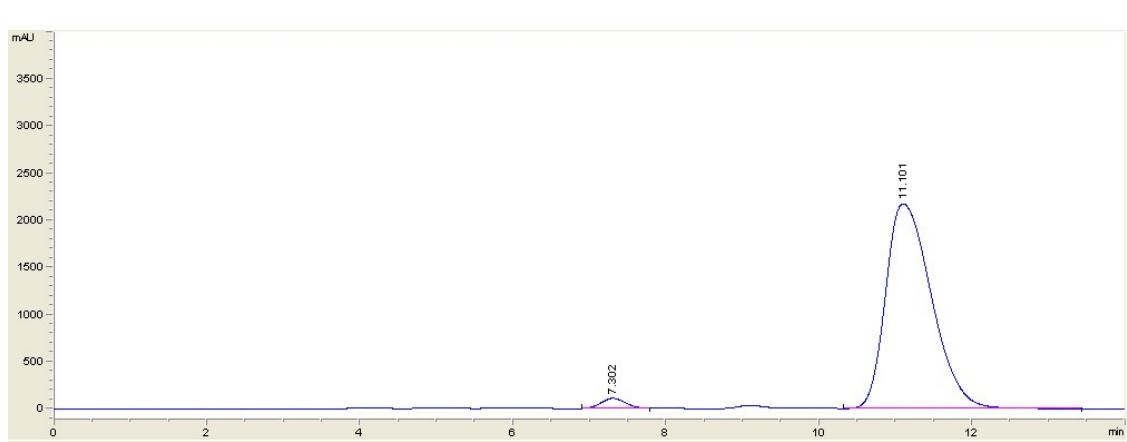
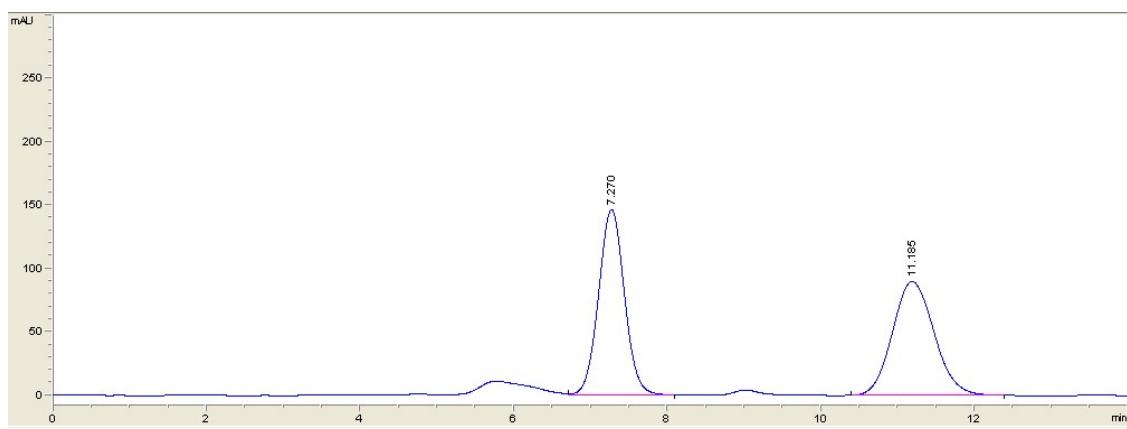


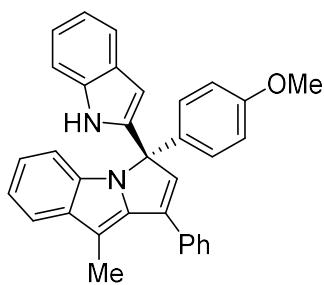
(S)-3-(4-chlorophenyl)-3-(1H-indol-2-yl)-9-methyl-1-phenyl-3H-pyrrolo[1,2-a]indole (3ma)



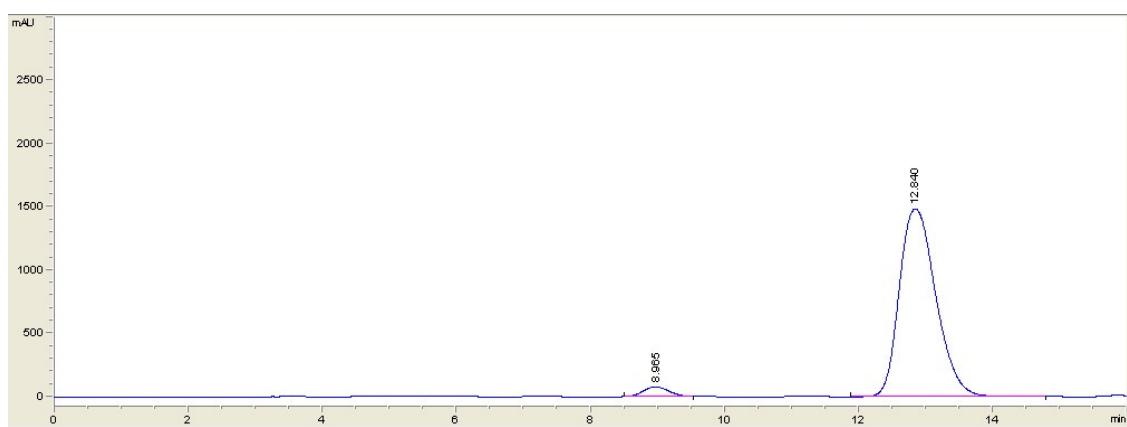
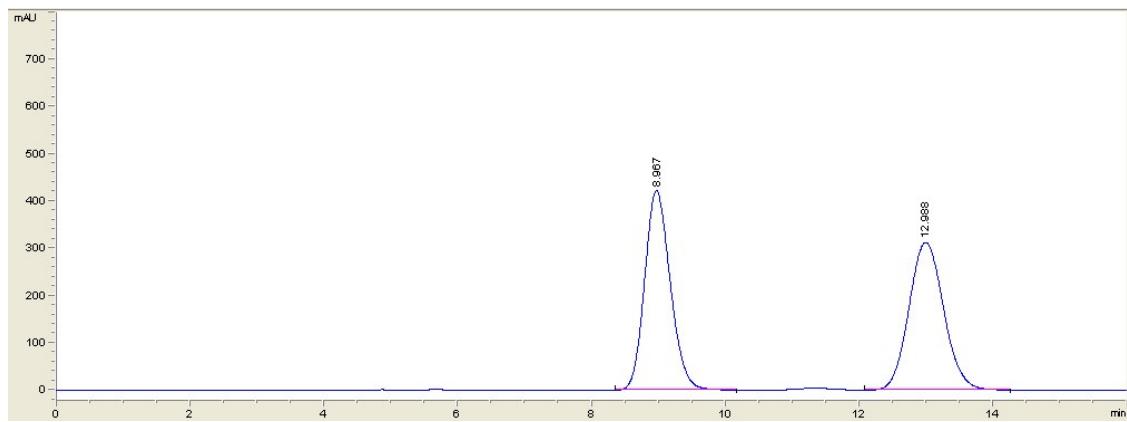


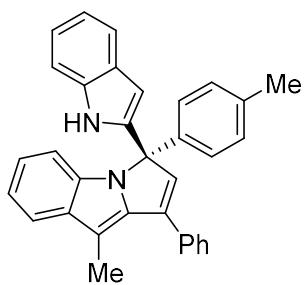
(S)-3-(4-bromophenyl)-3-(1H-indol-2-yl)-9-methyl-1-phenyl-3H-pyrrolo[1,2-a]indole (3na)



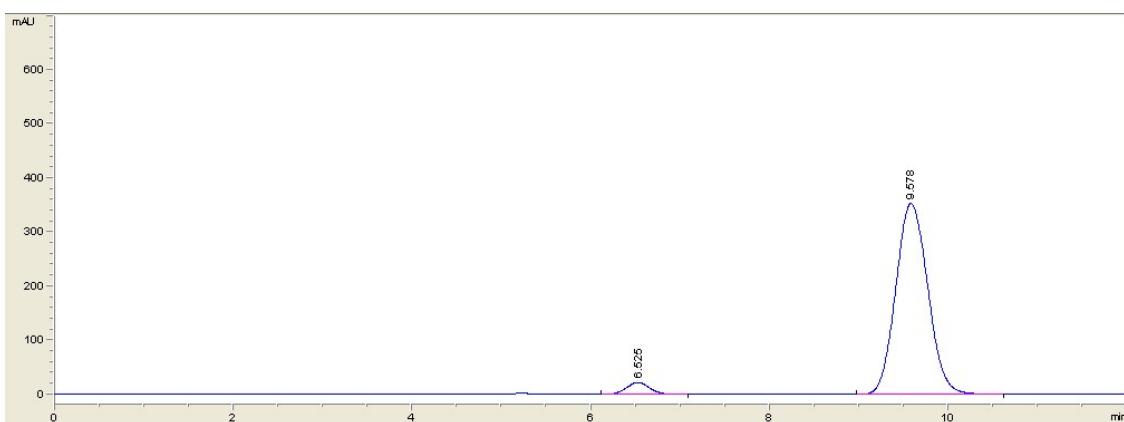
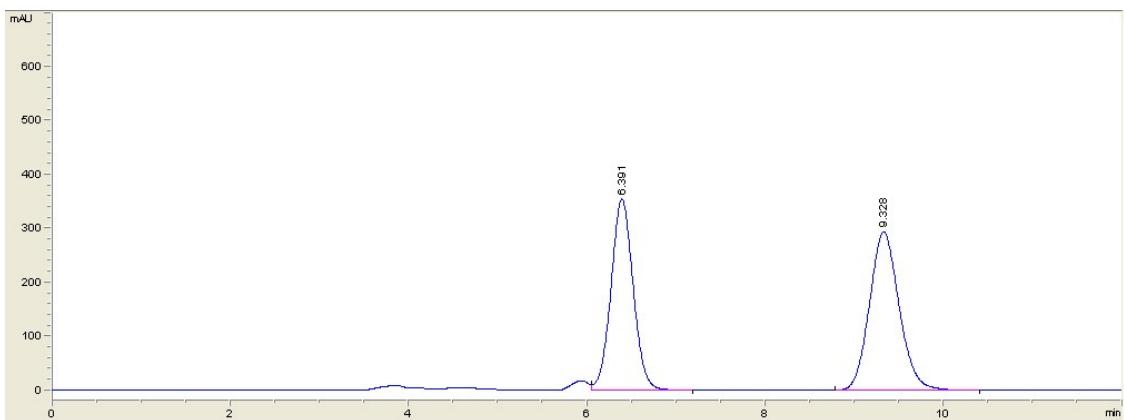


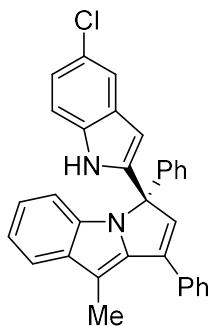
(S)-3-(1H-indol-2-yl)-3-(4-methoxyphenyl)-9-methyl-1-phenyl-3H-pyrrolo[1,2-a]indole (3oa)



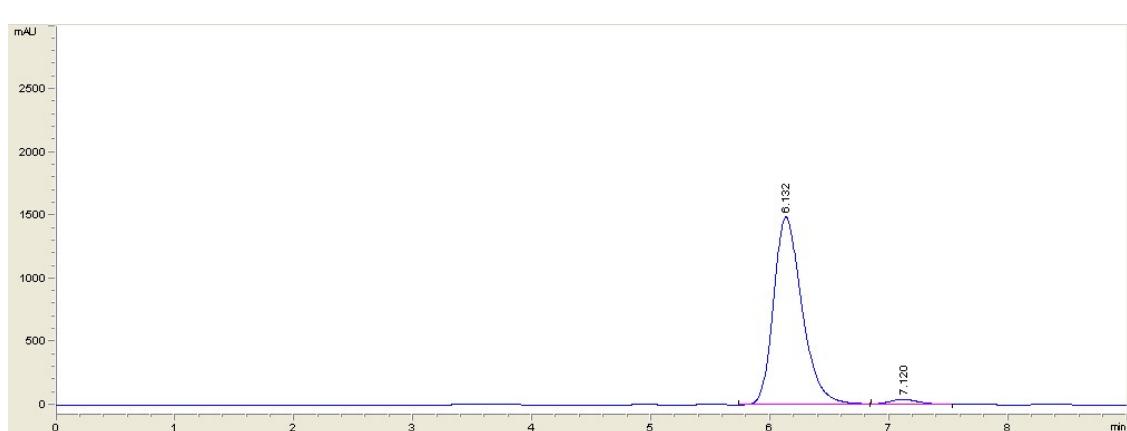
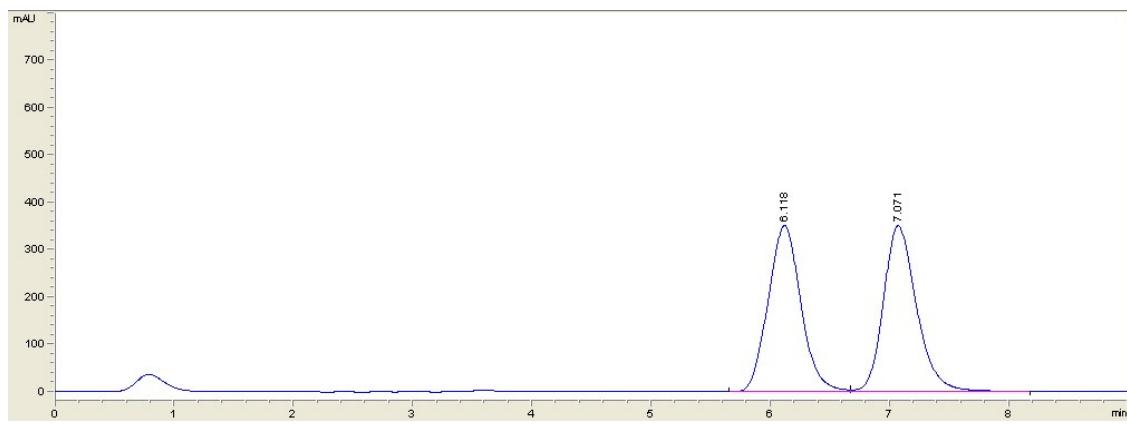


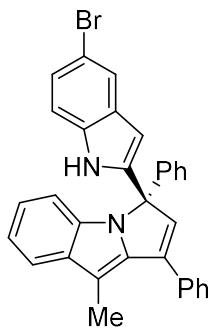
(S)-3-(1H-indol-2-yl)-9-methyl-1-phenyl-3-(p-tolyl)-3H-pyrrolo[1,2-a]indole (3pa)



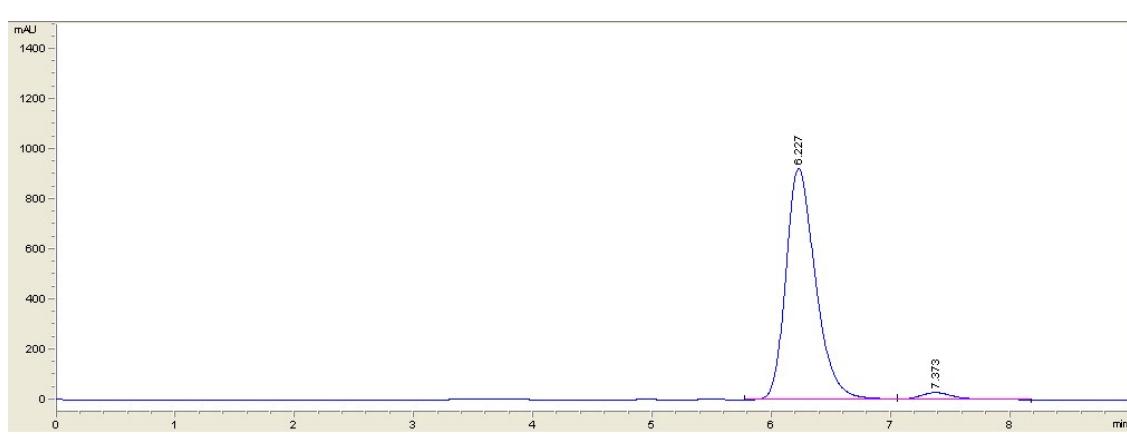
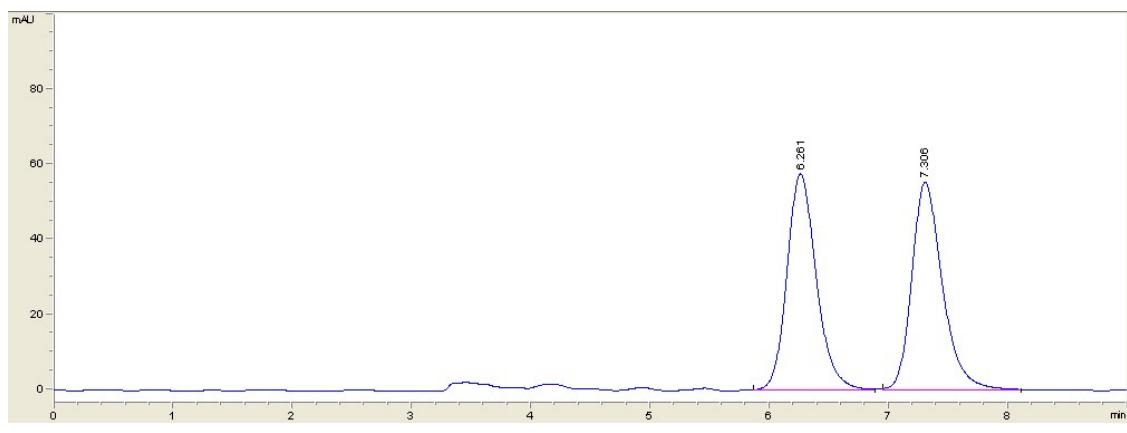


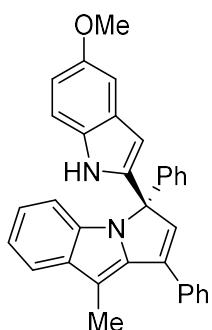
(S)-3-(5-chloro-1H-indol-2-yl)-9-methyl-1,3-diphenyl-3H-pyrrolo[1,2-a]indole (3qa)



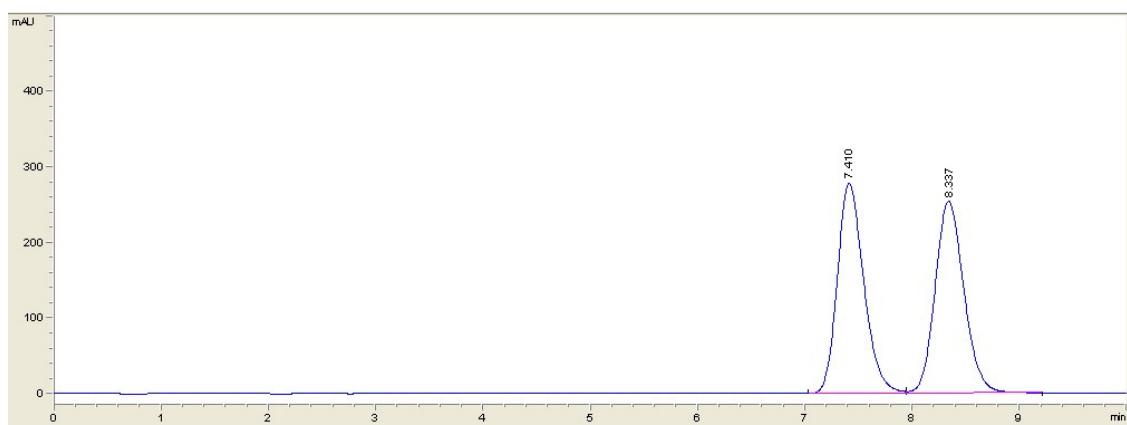


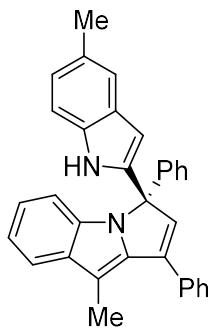
(S)-3-(5-bromo-1H-indol-2-yl)-9-methyl-1,3-diphenyl-3H-pyrrolo[1,2-a]indole (3ra)



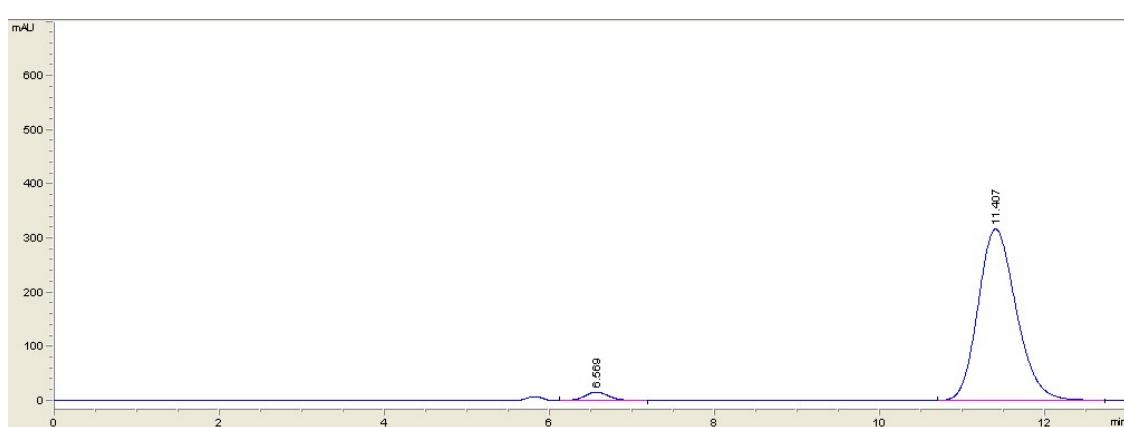
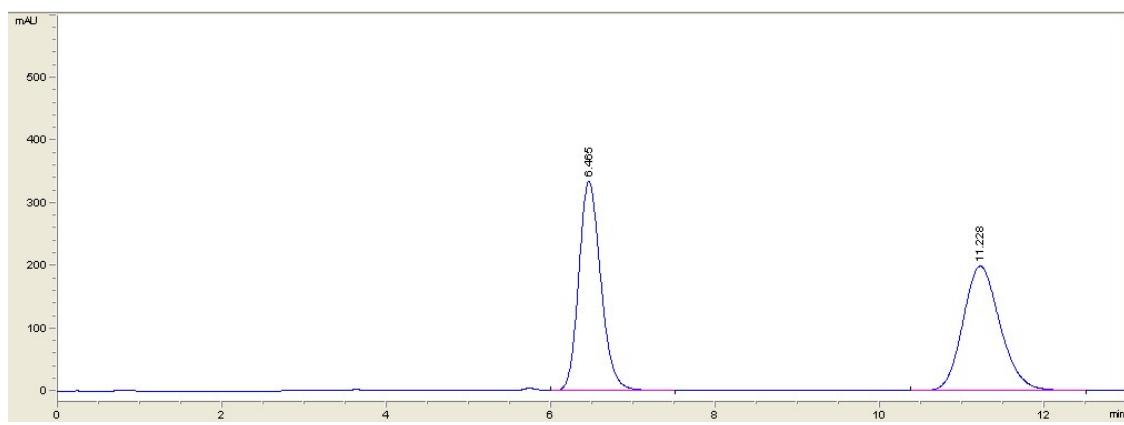


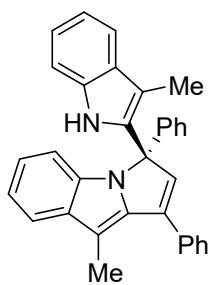
(S)-3-(5-methoxy-1H-indol-2-yl)-9-methyl-1,3-diphenyl-3H-pyrrolo[1,2-a]indole (3sa)



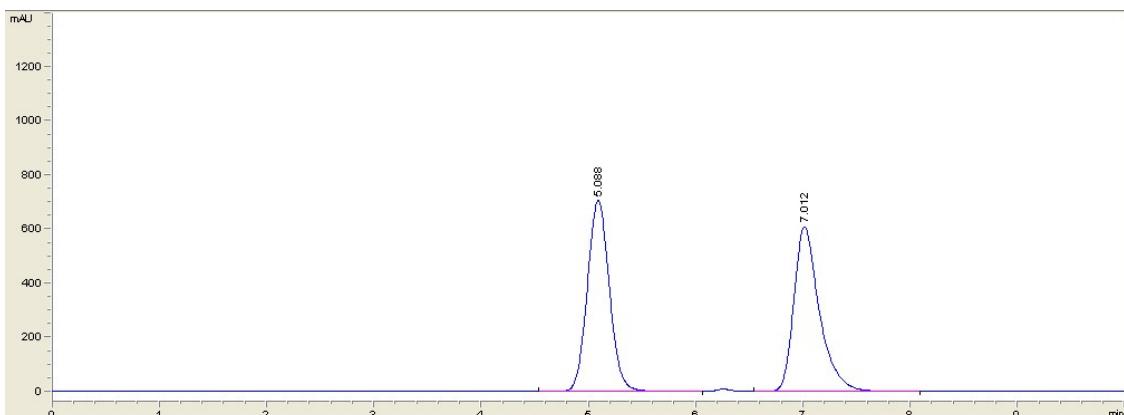


(S)-9-methyl-3-(5-methyl-1H-indol-2-yl)-1,3-diphenyl-3H-pyrrolo[1,2-a]indole (3ta)

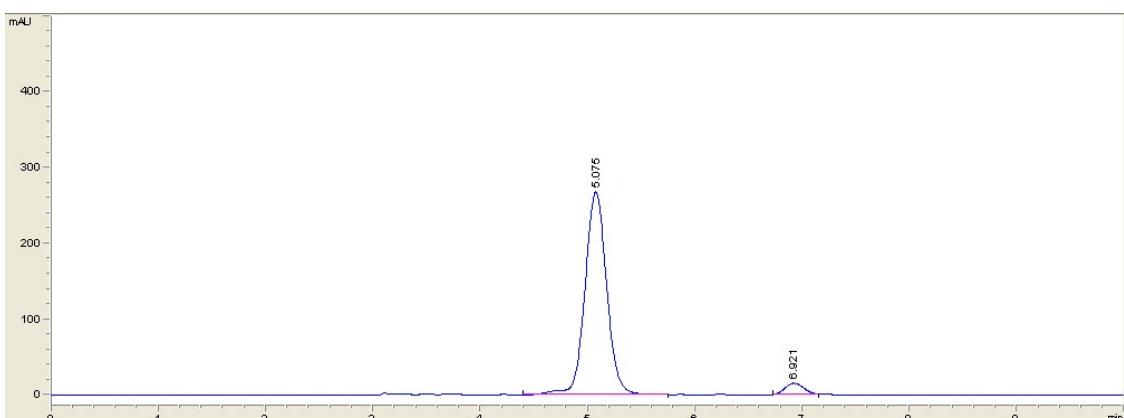




(S)-9-methyl-3-(3-methyl-1H-indol-2-yl)-1,3-diphenyl-3H-pyrrolo[1,2-a]indole (6aa)

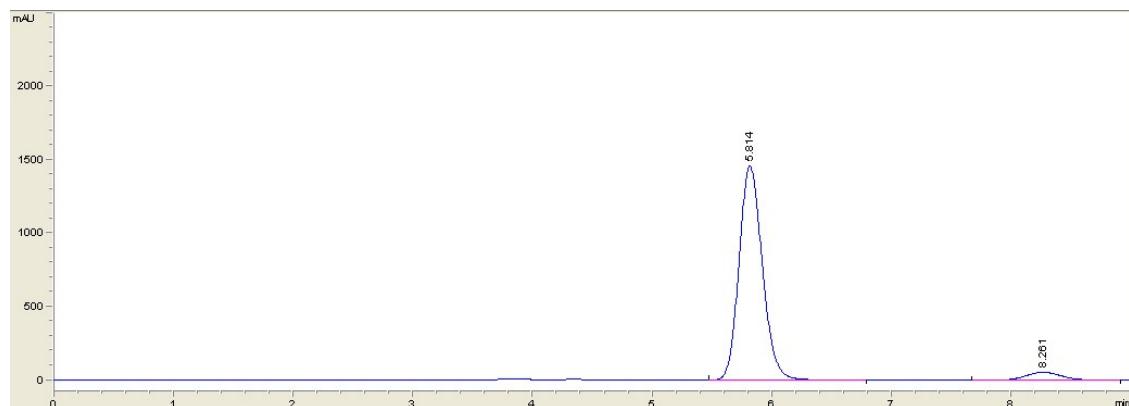


#	Time	Area	Height	Width	Area%
1	5.088	10111.8	705.4	0.224	50.095
2	7.012	10073.5	609	0.2483	49.905

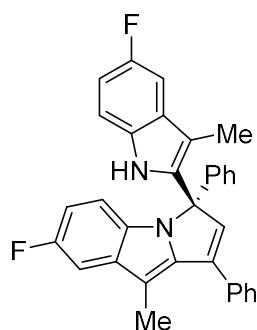


#	Time	Area	Height	Width	Area%
1	5.075	3774.6	267.3	0.2171	95.432
2	6.921	180.7	14.9	0.2024	4.568

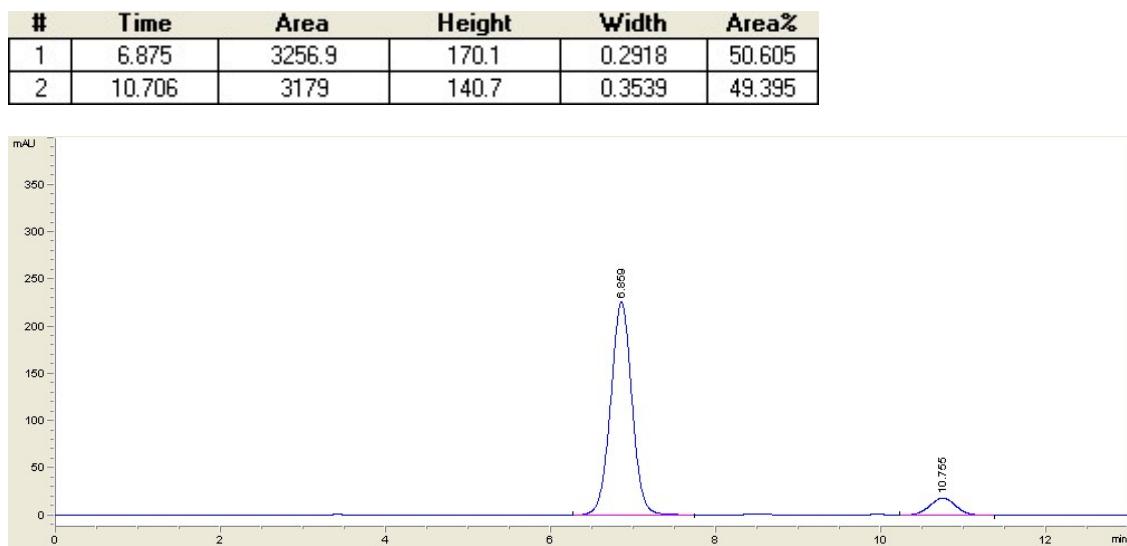
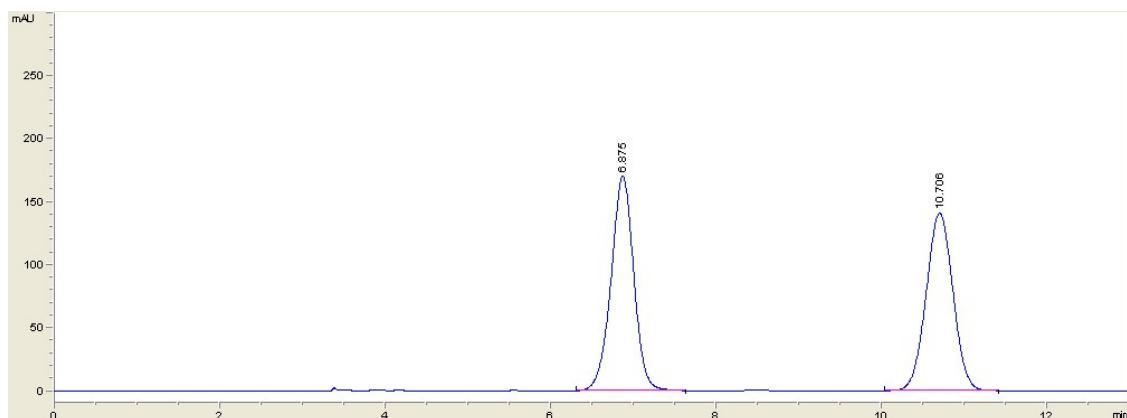
HPLC of 6aa (converted from the allene intermediate 12)

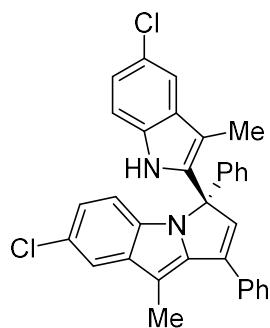


#	Time	Area	Height	Width	Area%
1	5.814	19770.5	1458	0.2092	94.719
2	8.261	1102.3	54.2	0.3189	5.281

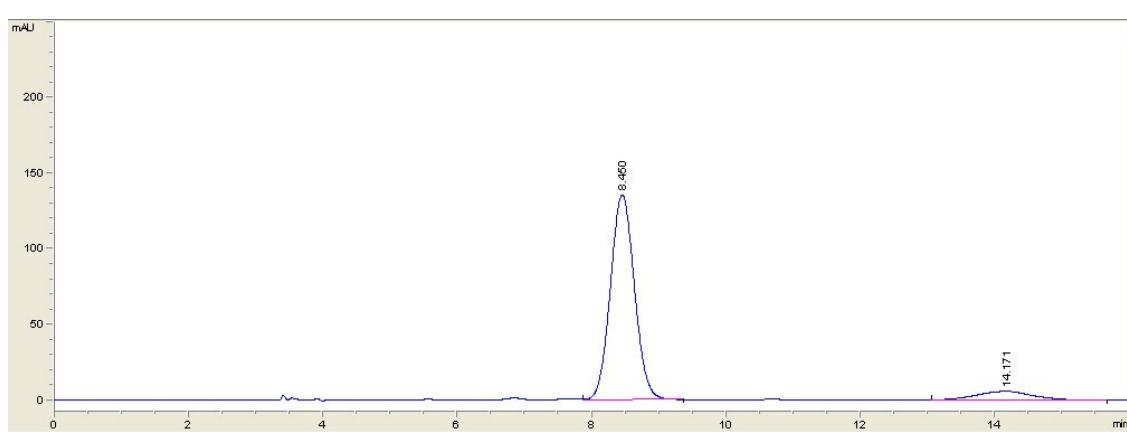
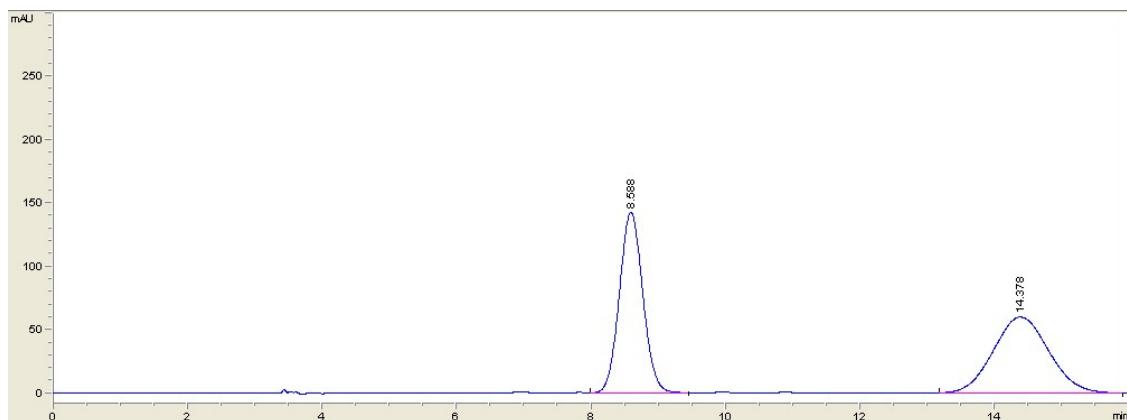


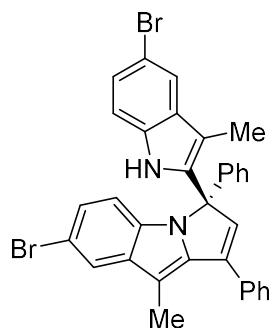
(S)-7-fluoro-3-(5-fluoro-3-methyl-1H-indol-2-yl)-9-methyl-1,3-diphenyl-3H-pyrrolo[1,2-a]indole (6bb)



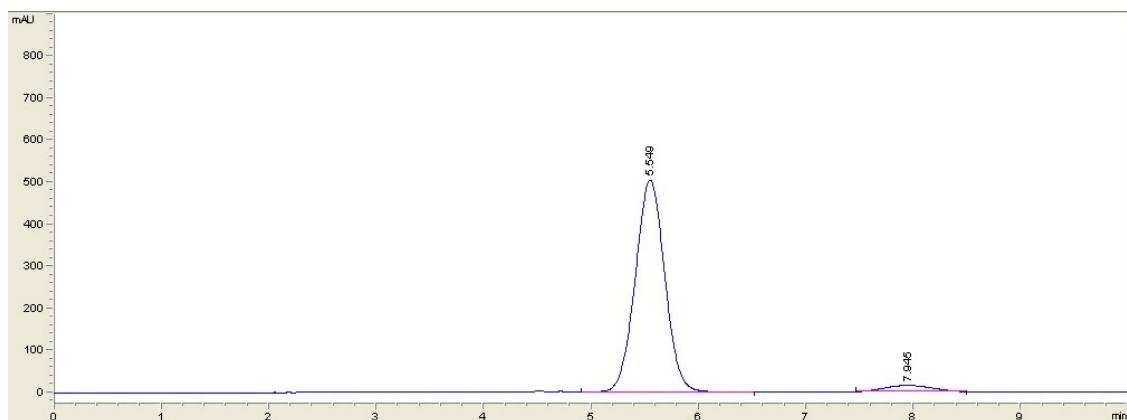
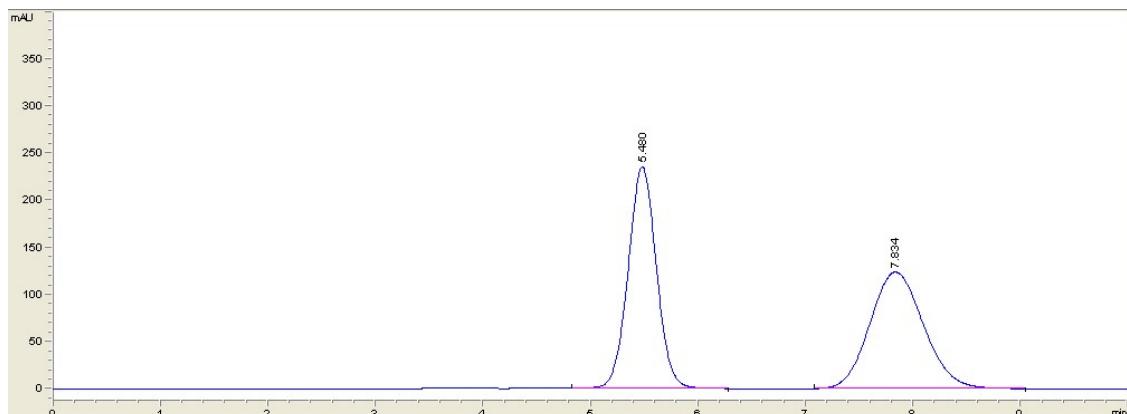


(S)-7-chloro-3-(5-chloro-3-methyl-1H-indol-2-yl)-9-methyl-1,3-diphenyl-3H-pyrrolo[1,2-a]indole (6cc)

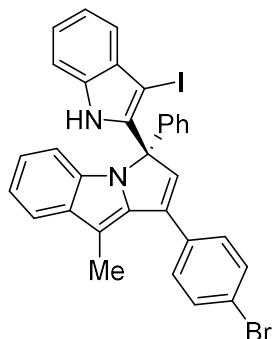




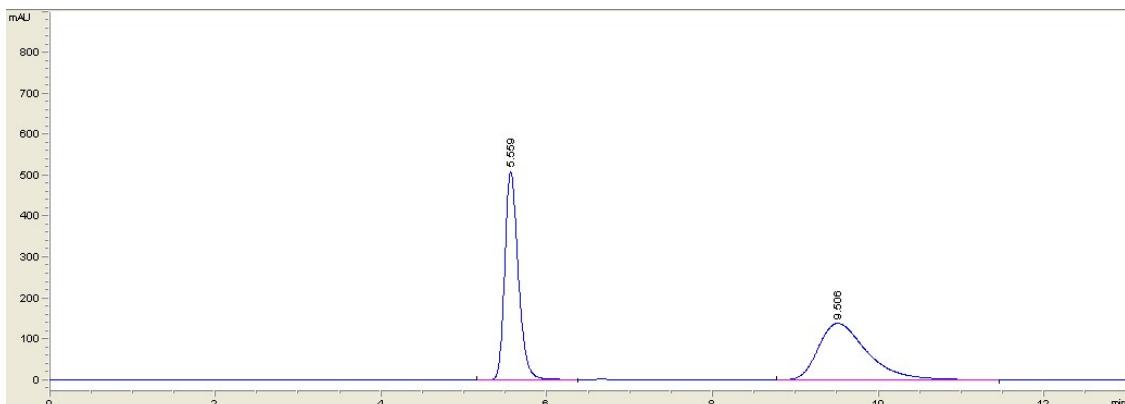
(S)-7-bromo-3-(5-bromo-3-methyl-1H-indol-2-yl)-9-methyl-1,3-diphenyl-3H-pyrrolo[1,2-a]indole (6dd)



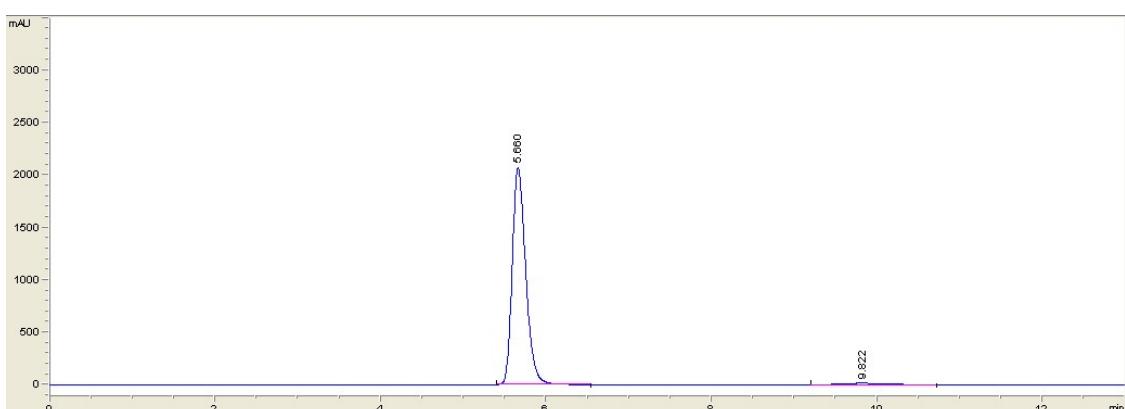
#	Time	Area	Height	Width	Area%
1	5.549	9687.4	504.4	0.2969	95.134
2	7.945	495.5	15.5	0.5331	4.866



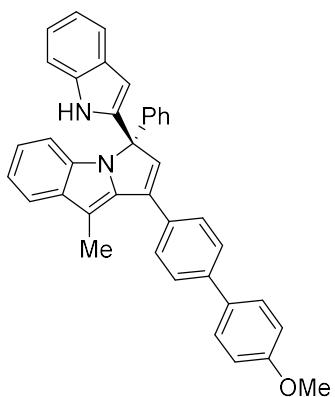
(S)-1-(4-bromophenyl)-3-(3-iodo-1H-indol-2-yl)-9-methyl-3-phenyl-3H-pyrrolo[1,2-a]indole (7)



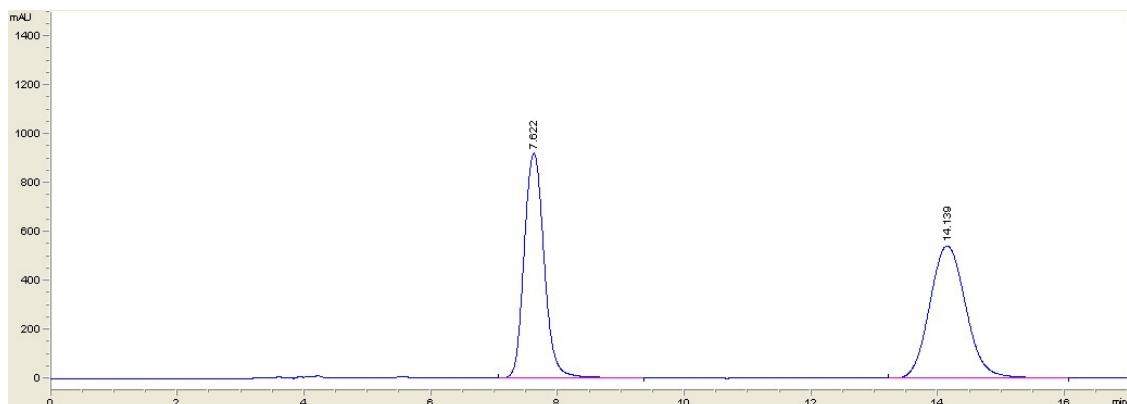
#	Time	Area	Height	Width	Area%
1	5.559	5810.2	509.2	0.1739	50.491
2	9.506	5697.2	138.5	0.6284	49.509



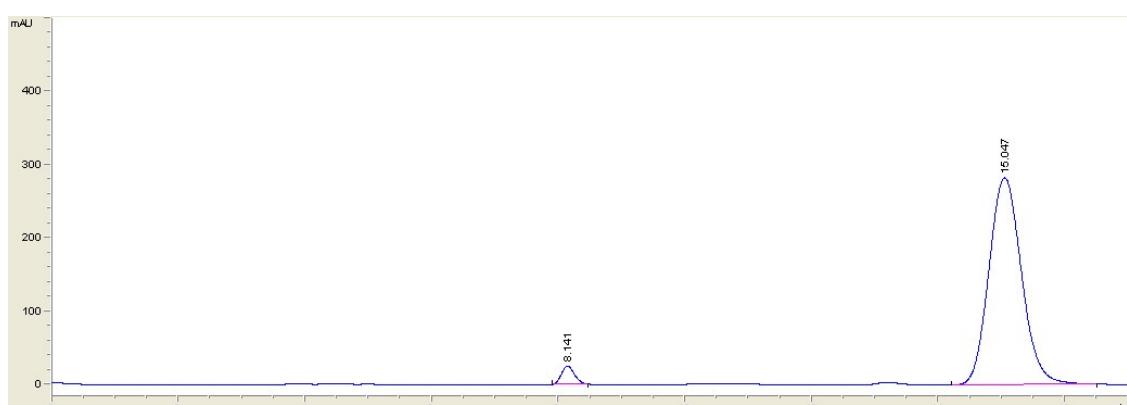
#	Time	Area	Height	Width	Area%
1	5.66	23623.9	2071.1	0.1753	96.446
2	9.822	870.6	17.9	0.8106	3.554



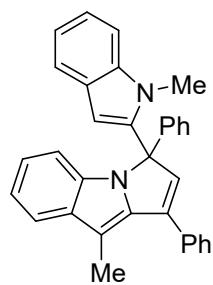
(S)-3-(1H-indol-2-yl)-1-(4'-methoxy-[1,1'-biphenyl]-4-yl)-9-methyl-3-phenyl-3H-pyrrolo[1,2-a]indole (8)



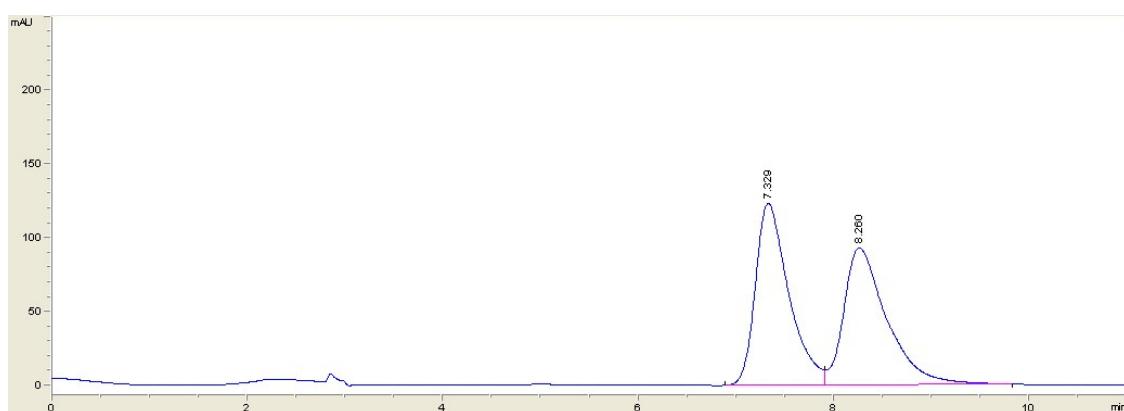
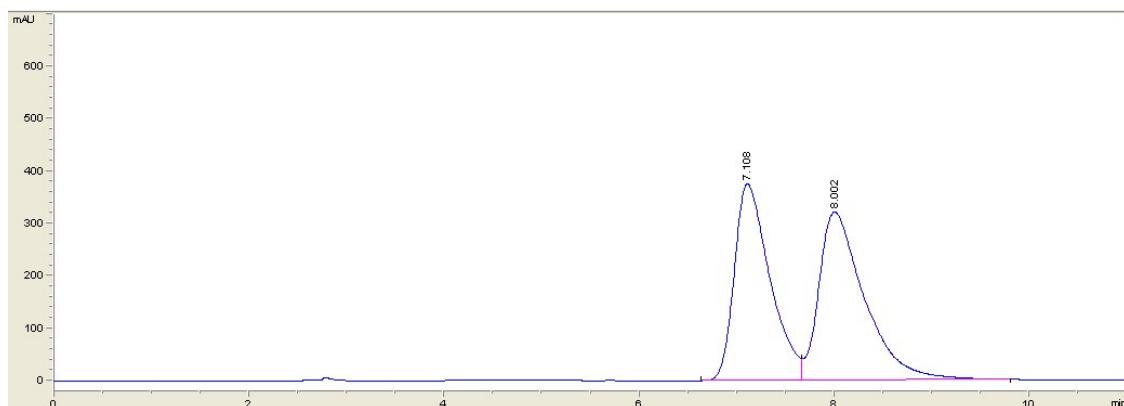
#	Time	Area	Height	Width	Area%
1	7.622	20175.1	919.8	0.3476	48.586
2	14.139	21349.2	541	0.6264	51.414

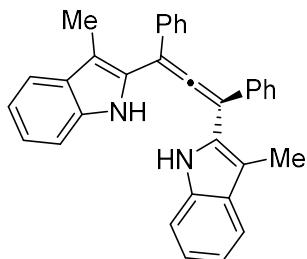


#	Time	Area	Height	Width	Area%
1	8.141	367.6	25.2	0.2431	3.508
2	15.047	10110.5	281.9	0.5611	96.492

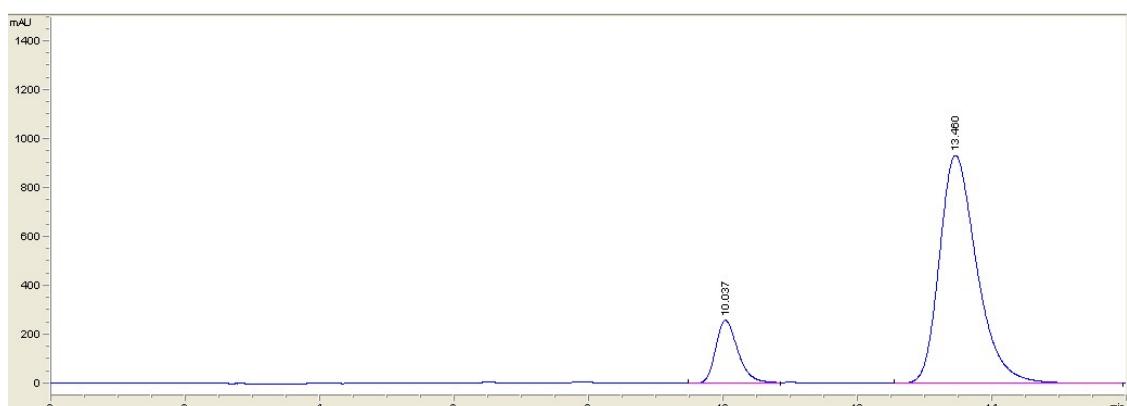
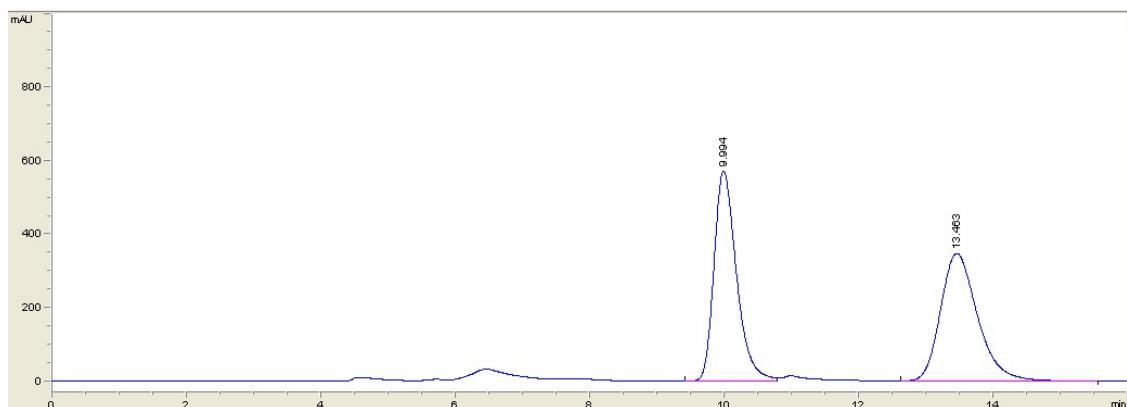


9-methyl-3-(1-methyl-1H-indol-2-yl)-1,3-diphenyl-3H-pyrrolo[1,2-a]indole (10)





(S)-1,3-Bis(3-methyl-1H-indol-2-yl)-1,3-diphenylpropa-1,2-diene (12)



7. Biological evaluation of selected products 3

Procedure for determination of PC-3 cell viability by MTT assay:

Human prostate cancer cells (PC-3) were seeded in 96-well plates at the density of 10000 cells per well with 200 μ L of complete culture medium. After adhesion for 16 hours, remove the supernatant out of the well and add 200 microliters of the sample's medium solution to each well. The whole dead cell group added 200 μ L PEI (25kD, 2 mg/ml in water) solution was the blank. The whole living cell group added 200 μ L medium was the control. The cells were then cultured for another 4 h. At the end of stimulation, the supernatant was removed, and 100 μ L MTT (0.5 mg/mL in medium) was added to each well, and the cells were cultured for another 4 h. Then, the supernatant was removed, and 100 μ L of DMSO was added to each well. The culture plates were then shaken for 2 min and the optical density (OD) values were read at a wave-length of 570 nm in a microplate reader.

$$\text{Viability} = ([\text{OD}]_{\text{experimental}} - [\text{OD}]_{\text{blank}})/([\text{OD}]_{\text{control}} - [\text{OD}]_{\text{blank}}) \times 100\%$$

Note: Viability was reported as a mean value of three determinations and analyzed by Origin.

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