

Catalyst-free dehydrative S_N1-type reaction of indolyl alcohols with diverse nucleophiles “on water”

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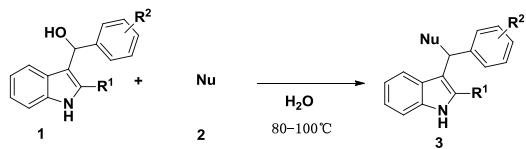
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General Information

Reagents were purchased from chemical companies. All the reactions were performed in sealed tube and monitored by TLC (0.2 mm silica gel-coated HSGF 254 plates). The products were purified by flash column chromatography (200-300 mesh silica gel) eluted with the gradient of petroleum ether and ethyl acetate. Proton nuclear magnetic resonance spectra (¹H NMR) were recorded on a Bruker 500 MHz NMR spectrometer (CDCl₃ or DMSO-d₆ solvent). The chemical shifts were reported in parts per million (ppm), downfield from SiMe₄ (δ 0.0) and relative to the signal of chloroform-d (δ 7.26, singlet) or dimethyl sulfoxide-d₆ (δ 2.54, singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublets of doublet) or m (multiplets). The number of protons for a given resonance is indicated by nH. Coupling constants are reported as a J value in Hz. Carbon nuclear magnetic resonance spectra (¹³C NMR) were reported in ppm using solvent CDCl₃ (δ (ppm) = 77.16 ppm) as an internal standard. HRMS analyses were performed on a Waters XEVO QTOF mass spectrometer.

General Procedure



A 15 mL sealed tube was charged with **1** (0.2 mmol) and **2** (0.3 mmol). Then H₂O (2 mL) was added and the resulting mixture was stirred at 80–100°C temperature. The reaction was monitored by TLC until starting material disappeared. The mixture was extracted with ethyl acetate (3×5 mL) and the extract dried with MgSO₄. The product **3** was purified by flash chromatography.

Characterization of Products

1-methyl-3-(phenyl(2-phenyl-1H-indol-3-yl)methyl)-1H-indole (3a).

white solid; yield 79%; **¹H NMR** (500 MHz, CDCl₃) δ 7.91 (s, 1H), 7.42 (d, *J* = 6.7 Hz, 2H), 7.33-7.22 (m, 8H), 7.17-7.13 (m, 4H), 7.11 (d, *J* = 7.1 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.85 (t, *J* = 7.5 Hz, 1H), 6.67 (s, 1H), 6.02 (s, 1H), 3.55 (s, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 144.2, 137.3, 136.3, 135.0, 133.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.0, 127.9, 127.8, 125.9, 121.9, 121.5, 121.4, 120.0, 119.5, 118.8, 117.4, 115.7, 110.9, 109.2, 39.3, 32.7; **HRMS (ESI)**: calcd for C₃₀H₂₃N₂ [M-H]⁻ 411.1861, found 411.1862.

1,2-dimethyl-3-(phenyl(2-phenyl-1H-indol-3-yl)methyl)-1H-indole (3b).

white solid; yield 94%; **¹H NMR** (500 MHz, CDCl₃) δ 7.84 (s, 1H), 7.30-7.27 (m, 7H), 7.21-7.14 (m, 5H), 7.11 (d, *J* = 8.0 Hz, 1H), 7.05-6.99 (m, 2H), 6.78 (dd, *J* = 13.7, 6.9 Hz, 2H), 6.68 (d, *J* = 7.9 Hz, 1H), 6.02 (s, 1H), 3.41 (s, 3H), 1.81 (s, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 144.4, 136.5, 136.2, 135.3, 134.2, 133.2, 129.2, 128.8, 128.6, 128.5, 128.3, 127.8, 127.7, 126.0, 121.9, 121.6, 119.9, 119.8, 119.5, 118.7, 115.2, 113.4, 110.8, 108.4, 40.0, 29.3, 10.6; **HRMS (ESI)**: calcd for C₃₁H₂₅N₂ [M-H]⁻ 425.2018, found 425.2017.

1-methyl-2-phenyl-3-(phenyl(2-phenyl-1H-indol-3-yl)methyl)-1H-indole (3c).

white solid; yield 90%; **¹H NMR** (500 MHz, CDCl₃) δ 7.81 (s, 1H), 7.30-7.25 (m, 3H), 7.23-7.10 (m, 9H), 7.06-7.00(m, 6H), 6.90-6.83(m, 4H), 6.76 (t, *J* = 7.5 Hz, 1H), 5.92 (s, 1H), 3.41 (s, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 145.0, 139.1, 137.1, 136.0, 135.2, 133.0, 131.9, 130.4, 129.3, 129.0, 128.4, 128.3, 128.2, 127.8, 127.7, 127.5, 127.3, 126.0, 121.9, 121.6, 121.3, 121.0, 119.4, 119.2, 115.7, 115.2, 110.5, 109.2, 40.2, 30.8; **HRMS (ESI)**: calcd for C₃₆H₂₇N₂ [M-H]⁻ 487.2174, found 487.2174.

5-methoxy-1-methyl-3-(phenyl(2-phenyl-1H-indol-3-yl)methyl)-1H-indole (3d).

white solid; yield 95%; **¹H NMR** (500 MHz, CDCl₃) δ 8.00 (s, 1H), 7.44-7.42 (m, 2H), 7.33-7.27 (m, 6H), 7.24 (d, *J* = 8.1 Hz, 1H), 7.19-7.16 (m, 2H), 7.13-7.08(m, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.86(t, *J* = 7.5 Hz, 1H), 6.81 (dd, *J* = 8.8, 2.0 Hz, 1H), 6.67 (s, 1H), 6.58 (s, 1H), 5.97 (s, 1H), 3.57 (s, 3H), 3.54 (s, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 153.5, 144.1, 136.4, 135.0, 133.1, 132.7, 129.1, 128.9, 128.8, 128.6, 128.5, 128.2, 128.1, 127.9, 125.9, 121.9, 121.6, 119.5, 117.0, 115.7, 111.6, 110.9, 109.9, 101.6, 55.8, 39.2, 32.9; **HRMS (ESI)**: calcd for C₃₁H₂₅N₂O [M-H]⁻ 441.1967, found 441.1965.

1,4-dimethyl-3-(phenyl(2-phenyl-1H-indol-3-yl)methyl)-1H-indole (3e).

white solid; yield 71%; **¹H NMR** (500 MHz, CDCl₃) δ 8.10 (s, 1H), 7.56 (d, *J* = 7.1 Hz, 2H), 7.42-7.36 (m, 4H), 7.22-7.14 (m, 9H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 6.8 Hz, 1H), 6.80 (s, 1H), 6.36 (s, 1H), 3.65 (s, 3H), 2.32 (s, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 145.8, 137.8, 136.3, 134.6, 133.1, 131.7, 129.5, 128.9, 128.8, 128.7, 128.4, 128.0, 127.9, 126.6, 125.7, 122.0, 121.6, 120.8, 119.6, 117.9, 117.0, 110.9, 107.2, 40.4, 32.9, 20.1; **HRMS (ESI)**: calcd for C₃₁H₂₅N₂ [M-H]⁻ 425.2018, found 425.2017.

4-bromo-1-methyl-3-(phenyl(2-phenyl-1H-indol-3-yl)methyl)-1H-indole (3f).

white solid; yield 65%; **¹H NMR** (500 MHz, CDCl₃) δ 8.16 (s, 1H), 7.57-7.55 (m, 2H), 7.43-7.40 (m, 3H), 7.38-7.35 (m, 1H), 7.30-7.28 (m, 2H), 7.22-7.15 (m, 7H), 7.09 (t, *J* = 7.9 Hz, 1H), 6.95-6.92 (m, 1H), 6.90 (s, 1H), 6.80 (s, 1H), 3.68 (s, 3H); **¹³C NMR** (125MHz, CDCl₃) δ 145.8, 138.5, 136.3, 134.9, 133.0, 131.0, 129.0, 128.8, 128.7, 128.3, 127.9, 127.8, 125.8, 125.6, 123.8, 122.4, 121.9, 121.5, 119.6, 118.0, 116.7, 114.9, 110.9, 108.6, 39.0, 33.1;

HRMS (ESI): calcd for C₃₀H₂₂BrN₂ [M-H]⁻ 489.0966, found 489.0963.

5-bromo-1-methyl-3-(phenyl(2-phenyl-1H-indol-3-yl)methyl)-1H-indole (3g).

white solid; yield 66%; **¹H NMR** (500 MHz, DMSO-d₆) δ 11.36 (s, 1H), 7.54-7.47 (m, 4H), 7.45-7.32 (m, 3H), 7.31-7.11 (m, 7H), 7.03-6.96 (m, 2H), 6.82 (s, 1H), 6.77 (t, J = 7.0 Hz, 1H), 5.88 (s, 1H), 3.69 (s, 3H); **¹³C NMR** (125 MHz, DMSO-d₆) δ 143.3, 137.6, 136.8, 133.0, 130.6, 128.6, 127.9, 127.5, 127.4, 127.2, 124.9, 124.0, 122.1, 121.7, 120.1, 120.0, 119.5, 118.9, 118.8, 116.9, 111.2, 109.3, 39.6, 32.8; **HRMS (ESI):** calcd for C₃₀H₂₂BrN₂ [M-H]⁻ 489.0966, found 489.0979.

6-chloro-1-methyl-3-(phenyl(2-phenyl-1H-indol-3-yl)methyl)-1H-indole (3h).

white solid; yield 67%; **¹H NMR** (500 MHz, CDCl₃) δ 7.97 (s, 1H), 7.42-7.40 (m, 2H), 7.35-7.31 (m, 3H), 7.27 (d, J = 8.1 Hz, 1H), 7.25-7.22(m, 4H), 7.17 (t, J = 7.4 Hz, 2H), 7.12 (t, J = 7.1 Hz, 1H), 7.07 (t, J = 7.5 Hz, 1H), 7.02 (d, J = 8.4 Hz, 1H), 6.88-6.84 (m, 2H), 6.63 (s, 1H), 5.96 (s, 1H), 3.52 (s, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 143.9, 137.8, 136.3, 135.1, 132.9, 129.3, 128.9, 128.8, 128.5, 128.4, 128.2, 128.0, 127.6, 126.4, 126.0, 122.0, 121.3, 120.8, 119.6, 119.5, 117.9, 115.3, 110.9, 109.3, 39.3, 32.8; **HRMS (ESI):** calcd for C₃₀H₂₂ClN₂ [M-H]⁻ 445.1462, found 445.1468.

6-fluoro-1-methyl-3-(phenyl(2-phenyl-1H-indol-3-yl)methyl)-1H-indole (3i).

white solid; yield 90%; **¹H NMR** (500 MHz, CDCl₃) δ 7.91 (s, 1H), 7.41-7.39 (m, 2H), 7.33-7.27 (m, 3H), 7.26-7.22(m, 4H), 7.16 (t, J = 7.4 Hz, 2H), 7.13-7.10(m, 1H), 7.05 (t, J=7.5Hz, 1H), 7.02-6.99 (m, 1H), 6.90-6.80 (m, 2H), 6.68-6.62 (m, 1H), 6.59 (s, 1H), 5.96 (s, 1H), 3.47 (s, 3H); **¹³C NMR** (125MHz, CDCl₃) δ160.8, 159.0 144.1, 137.4, 136.3, 135.1, 132.9, 128.9, 128.8, 128.6, 128.1, 127.9, 126.0, 124.4, 122.0, 121.3, 120.7, 119.6, 117.9, 115.3, 111.0, 107.5, 107.4, 107.3, 95.7, 95.5, 39.4, 32.6; **HRMS (ESI):** calcd for C₃₀H₂₂FN₂ [M-H]⁻ 429.1767, found 429.1762.

1-benzyl-3-(phenyl(2-phenyl-1H-indol-3-yl)methyl)-1H-indole (3j).

white solid; yield 88%; **¹H NMR** (500 MHz, CDCl₃) δ 8.04 (s, 1H), 7.50-7.48 (m, 2H), 7.41 -7.37 (m, 2H), 7.36-7.34 (m, 1H), 7.33-7.28 (m, 4H), 7.24-7.12 (m, 8H), 7.10-7.06 (m, 2H), 7.01-6.99 (m, 2H), 6.93-6.88 (m, 1H), 6.86-6.82 (m, 1H), 6.80 (s, 1H), 6.04 (s, 1H), 5.22-5.14 (m, 2H); **¹³C NMR** (125 MHz, CDCl₃) δ 144.2, 138.1, 137.0, 136.3, 135.1, 133.1, 129.0, 128.9, 128.8, 128.6, 128.5, 128.3, 128.2, 128.0, 127.4, 126.4, 126.0, 122.0, 121.8, 121.6, 120.1, 119.5, 119.1, 118.5, 115.4, 110.9, 109.8, 50.0, 39.5; **HRMS (ESI):** calcd for C₃₆H₂₇N₂ [M-H]⁻ 487.2174, found 487.2185.

3-((1H-indol-3-yl)(phenyl)methyl)-2-phenyl-1H-indole(3k)^[1]

white solid; yield 69%; **¹H NMR** (500 MHz, CDCl₃) δ 7.82 (s, 1H), 7.66 (s, 1H), 7.41-7.38 (m, 2H), 7.32-7.21 (m, 8H), 7.17-7.07 (m, 6H), 6.93 (t, J = 7.5 Hz, 1H), 6.86 (t, J = 7.5 Hz, 1H), 6.64 (s, 1H), 5.97 (s, 1H); **¹³C NMR** (125 MHz, CDCl₃) δ 144.1, 136.6, 136.4, 135.1, 133.1, 128.9, 128.9, 128.6, 128.1, 128.0, 127.5, 125.9, 124.2, 122.0, 121.6, 119.9, 119.5, 119.4, 119.1, 115.7, 111.1, 110.9, 39.4; **HRMS (ESI):** calcd for C₂₉H₂₁N₂ [M-H]⁻ 397.1705, found 397.1707.

1-methyl-3-((1-methyl-1H-indol-3-yl)(phenyl)methyl)-2-phenyl-1H-indole (3l).

white solid; yield 85%; **¹H NMR** (500 MHz, CDCl₃) δ 7.52-7.50(m, 4H), 7.43-7.36 (m, 3H), 7.39-7.36 (m, 3H), 7.31-7.28 (m, 4H), 7.25-7.22(m, 2H), 7.07-7.02 (m, 2H), 6.81 (s, 1H), 5.89 (s, 1H), 3.74 (s, 3H), 3.72 (s, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 144.7, 138.2, 137.6, 137.3, 132.0, 130.8, 128.8, 128.7, 128.4, 128.2, 128.0, 127.9, 127.2, 125.7, 121.4, 121.3,

121.2, 120.1, 119.1, 118.6, 117.8, 115.8, 109.4, 109.0, 39.7, 32.7, 31.0

3-((1H-indol-3-yl)(phenyl)methyl)-1-methyl-1H-indole (3m).^[2]

yield 92%; **¹H NMR** (500 MHz, CDCl₃) δ 7.84 (s, 1H), 7.39-7.31 (m, 5H), 7.29-7.13 (m, 6H), 7.01-6.97 (m, 2H), 6.64 (s, 1H), 6.50 (s, 1H), 5.87 (s, 1H), 3.65 (s, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 144.4, 137.6, 136.8, 128.8, 128.3, 127.6, 127.2, 126.2, 123.8, 122.0, 121.6, 120.2, 120.1, 120.0, 119.3, 118.8, 118.3, 111.1, 109.2, 40.3, 32.8.

1-methyl-3-(phenyl(1-tosyl-1H-indol-3-yl)methyl)-1H-indole (3n).

white solid; yield 85%; **¹H NMR** (500 MHz, CDCl₃) δ 7.98 (d, *J* = 8.1 Hz, 1H), 7.62-7.57 (m, 2H), 7.31-7.19 (m, 10H), 7.18-7.16 (m, 2H), 7.09-7.02 (m, 2H), 6.97 (t, *J* = 6.8 Hz, 1H), 6.37 (s, 1H), 5.71 (s, 1H), 3.64 (s, 3H), 2.33 (s, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 144.7, 142.3, 137.6, 136.0, 135.1, 130.8, 129.8, 128.7, 128.6, 128.3, 127.2, 126.9, 126.8, 126.6, 125.7, 124.7, 123.3, 121.8, 120.5, 119.7, 118.9, 116.6, 114.0, 109.5, 40.1, 32.8, 21.7; **HRMS (ESI)**: calcd for C₃₁H₂₅N₂O₂S [M-H]⁻ 489.1637, found 489.1630.

3-((1H-indol-3-yl)(p-tolyl)methyl)-1-methyl-1H-indole (3o).^[2]

yield 94%; **¹H NMR** (500 MHz, CDCl₃) δ 7.86 (s, 1H), 7.40-7.36 (m, 2H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.28-7.13 (m, 5H), 7.07 (d, *J* = 7.3 Hz, 2H), 7.01-6.97 (m, 2H), 6.66 (s, 1H), 6.51 (s, 1H), 5.84 (s, 1H), 3.66 (s, 3H), 2.31 (s, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 141.3, 137.6, 136.8, 135.6, 129.0, 128.7, 128.3, 127.6, 127.3, 123.7, 122.6, 122.0, 121.5, 120.2, 120.1, 119.3, 118.7, 118.5, 111.1, 109.2, 39.9, 32.8.

3-((2,4-dichlorophenyl)(1H-indol-3-yl)methyl)-1-methyl-1H-indole (3p).

white solid; yield 71%; **¹H NMR** (500 MHz, CDCl₃) δ 7.78 (s, 1H), 7.54 (d, *J* = 1.9 Hz, 1H), 7.50-7.44 (m, 2H), 7.39-7.22 (m, 5H), 7.16-7.10 (m, 3H), 6.60 (s, 1H), 6.55 (s, 1H), 6.38 (s, 1H), 3.69 (s, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 140.4, 137.6, 136.8, 134.7, 132.5, 131.3, 129.4, 128.5, 127.4, 127.1, 126.9, 123.9, 122.3, 121.8, 120.0, 119.8, 119.6, 119.0, 118.0, 116.3, 111.3, 109.4, 36.4, 32.8; **HRMS (ESI)**: calcd for C₂₄H₁₇Cl₂N₂ [M-H]⁻ 403.0769, found 403.0763.

3-((2-bromophenyl)(1H-indol-3-yl)methyl)-1-methyl-1H-indole (3q).^[3]

yield 74%; **¹H NMR** (500 MHz, CDCl₃) δ 7.86 (s, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.25-7.10 (m, 4H), 7.08-7.05 (m, 1H), 7.03-6.98 (m, 2H), 6.60 (s, 1H), 6.46 (s, 1H), 6.30 (s, 1H), 3.65 (s, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 143.3, 137.6, 136.8, 133.0, 130.6, 128.6, 127.9, 127.5, 127.4, 127.2, 124.9, 124.0, 122.1, 121.7, 120.1, 120.0, 119.5, 118.9, 118.8, 116.9, 111.2, 109.3, 39.6, 32.8.

3-((1H-indol-3-yl)(2-nitrophenyl)methyl)-1-methyl-1H-indole (3r).^[4]

yield 70%; **¹H NMR** (500 MHz, CDCl₃) δ 7.93 (s, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.45-7.29 (m, 7H), 7.25-7.16 (m, 2H), 7.05-7.00 (m, 2H), 6.68 (s, 1H), 6.65 (s, 1H), 6.53 (s, 1H), 3.67 (s, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 149.8, 146.4, 138.3, 137.5, 136.7, 132.3, 131.2, 128.5, 127.2, 126.8, 124.4, 123.9, 122.2, 121.8, 119.9, 119.8, 119.6, 119.0, 117.9, 116.1, 111.2, 109.3, 34.8, 32.8.

3-((1H-indol-3-yl)(thiophen-2-yl)methyl)-1-methyl-1H-indole (3s)

white solid; yield 75%; **¹H NMR** (500 MHz, CDCl₃) δ 7.70 (s, 1H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.28-7.09 (m, 5H), 7.01-6.97 (m, 2H), 6.90-6.85 (m, 2H), 6.72 (s, 1H), 6.65 (s, 1H), 6.13 (s, 1H), 3.60 (s, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 149.1, 137.4, 136.7, 127.9, 127.3, 126.9, 126.5, 125.2, 123.7, 123.3, 122.1, 121.7, 120.0, 119.9, 119.8, 119.4, 118.9, 118.2, 111.2, 109.3, 35.4, 32.8.

3-(1-(1H-indol-3-yl)propyl)-1-methyl-1H-indole (3t)^[5]

yield 87%; **¹H NMR** (500 MHz, CDCl₃) δ 7.6-7.54 (m, 3H), 7.24-7.06 (m, 4H), 7.05-6.97 (m, 2H), 6.82 (s, 1H), 6.76 (s, 1H), 4.34 (t, *J* = 6.4 Hz, 1H), 3.58 (s, 3H), 2.25-2.15 (m, 2H), 0.98 (t, *J* = 5.4 Hz, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 137.4, 136.7, 127.8, 127.3, 126.4, 121.8, 121.5, 121.4, 120.5, 119.9, 119.8, 119.0, 119.0, 118.5, 111.2, 109.2, 35.9, 32.6, 29.1, 13.2.

4-(phenyl(2-phenyl-1H-indol-3-yl)methyl)phenol (5a).

white solid; yield 30%; **¹H NMR** (500 MHz, CDCl₃) δ 8.10 (s, 1H), 7.46-7.33 (m, 6H), 7.27-7.16 (m, 5H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.06-7.04 (m, 3H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.69 (d, *J* = 8.2 Hz, 2H), 5.75 (s, 1H), 4.75 (s, 1H); **¹³C NMR** (125 MHz, CDCl₃) δ 153.8, 144.5, 136.6, 136.3, 135.7, 133.1, 130.5, 129.3, 128.9, 128.7, 128.5, 128.3, 128.1, 126.1, 122.1, 121.7, 119.8, 115.5, 115.1, 110.9, 47.0; **HRMS (ESI)**: calcd for C₂₇H₂₀NO [M-H]⁺ C₂₇H₂₀NO 374.1545, found 374.1546.

2-phenyl-3-(phenyl(2,4,6-trimethoxyphenyl)methyl)-1H-indole (5b).

white solid; yield 29%; **¹H NMR** (500 MHz, CDCl₃) δ 7.97 (s, 1H), 7.38-7.30 (m, 6H), 7.19-7.11 (m, 6H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.87 (t, *J* = 7.6 Hz, 1H), 6.27 (s, 1H), 6.08 (s, 2H), 3.79 (s, 3H), 3.38 (s, 6H); **¹³C NMR** (125 MHz, CDCl₃) δ 159.8, 159.2, 144.3, 136.3, 135.9, 134.1, 129.4, 129.1, 128.4, 128.2, 127.7, 127.5, 125.2, 123.3, 121.3, 118.9, 115.7, 113.5, 110.3, 91.1, 55.4, 55.3, 37.3; **HRMS (ESI)**: calcd for C₃₀H₂₇NO₃Na [M+Na]⁺ 472.1889, found 472.1889.

2-phenyl-3-(phenyl(1H-pyrrol-2-yl)methyl)-1H-indole(5c)

white solid; yield 57%; **¹H NMR** (500 MHz, CDCl₃) δ 8.11 (s, 1H), 7.93 (s, 1H), 7.46-7.35 (m, 6H), 7.28-7.23 (m, 4H), 7.21-7.12 (m, 2H), 7.07 (d, *J* = 8.0 Hz, 1H), 6.97-6.92 (m, 1H), 6.62 (dd, *J* = 4.0, 2.5 Hz, 1H), 6.14 (dd, *J* = 5.9, 2.8 Hz, 1H), 5.87-5.84 (m, 1H), 5.76 (s, 1H); **¹³C NMR** (125 MHz, CDCl₃) δ 143.7, 136.3, 135.9, 134.1, 132.7, 129.0, 128.7, 128.6, 128.4, 128.3, 126.5, 122.4, 121.1, 120.3, 116.9, 113.9, 111.0, 108.2, 107.5, 41.5; **HRMS (ESI)**: calcd for C₂₅H₁₉N₂ [M-H]⁺ 347.1543, found 347.1534.

3-((5-methylfuran-2-yl)(phenyl)methyl)-2-phenyl-1H-indole(5d)

white solid; yield 68%; **¹H NMR** (500 MHz, CDCl₃) δ 8.03 (s, 1H), 7.47-7.43 (m, 2H), 7.41-7.38 (m, 2H), 7.36-7.29 (m, 3H), 7.23-7.21 (m, 4H), 7.18-7.10 (m, 2H), 6.95 (t, *J* = 7.7 Hz, 1H), 5.85 (d, *J* = 2.5 Hz, 1H), 5.83 (d, *J* = 3.0 Hz, 1H), 5.74 (s, 1H), 2.18 (s, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 155.2, 151.2, 142.6, 136.2, 135.7, 132.9, 128.9, 128.7, 128.6, 128.4, 128.3, 128.1, 126.4, 122.1, 121.5, 119.8, 113.1, 110.9, 108.9, 106.0, 42.1, 13.8; **HRMS (ESI)**: calcd for C₂₆H₂₀NO [M-H]⁺ 362.1539, found 362.1535.

3-(phenyl(2-phenyl-1H-indol-3-yl)methyl)pentane-2,4-dione (7a).^[6]

yield 90%; **¹H NMR** (500 MHz, CDCl₃) δ 8.26 (brs, 1H), 7.89 (d, *J* = 5.1 Hz, 1H), 7.50-7.44 (m, 5H), 7.32-7.26 (m, 3H), 7.22-7.09 (m, 5H), 5.23-5.16 (m, 2H), 1.98 (s, 3H), 1.80 (s, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 204.0, 203.2, 142.4, 136.2, 136.1, 132.7, 129.1, 128.9, 128.80, 128.5, 127.8, 127.0, 126.7, 122.3, 120.5, 120.3, 111.9, 111.5, 73.1, 43.1, 30.1, 29.4.

1-phenyl-2-(phenyl(2-phenyl-1H-indol-3-yl)methyl)butane-1,3-dione (7b).

white solid; yield 96%; **¹H NMR** (500 MHz, CDCl₃) δ 8.19 (s, 1H), 7.99-7.97 (m, 3H), 7.59-7.50 (m, 5H), 7.50-7.43 (m, 3H), 7.39-7.36 (m, 3H), 7.27-7.22 (m, 2H), 7.17 (t, *J* = 7.6 Hz, 2H), 7.09 (t, *J* = 7.3 Hz, 1H), 5.98 (d, *J* = 11.8 Hz, 1H), 5.61 (d, *J* = 11.8 Hz, 1H), 1.81 (s, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 202.6, 194.9, 142.7, 137.1, 136.2, 136.1, 133.7, 132.8, 129.1, 129.0, 128.9, 128.8, 128.6, 128.5, 128.1, 127.7, 126.5, 122.5, 120.8, 120.4, 112.2, 111.4, 68.0,

42.8, 27.5; **HRMS (ESI)**: calcd for $C_{31}H_{25}NO_2Na$ [M+Na]⁺ 466.1783, found 466.1784.

1,3-diphenyl-2-(phenyl(2-phenyl-1H-indol-3-yl)methyl)propane-1,3-dione (7c).

yellow solid; yield 86%; **¹H NMR** (500 MHz, CDCl₃) δ 7.91 (s, 1H), 7.89-7.85 (m, 2H), 7.79-7.74 (m, 1H), 7.58-7.54 (m, 2H), 7.4-7.39 (m, 3H), 7.37-7.28 (m, 7H), 7.24-7.20 (m, 1H), 7.13-7.07 (m, 3H), 7.07-6.98 (m, 5H), 6.69 (d, *J* = 11.4 Hz, 1H), 5.78 (d, *J* = 11.4 Hz, 1H); **¹³C NMR** (125MHz, CDCl₃) δ 194.8, 194.1, 142.7, 137.0, 136.3, 136.1, 136.1, 133.3, 132.7, 132.6, 128.9, 128.8, 128.7, 128.5, 128.3, 128.2, 128.1, 128.0, 127.8, 126.3, 122.0, 120.6, 119.8, 112.3, 111.3, 60.9, 43.3; **HRMS (ESI)**: calcd for $C_{36}H_{27}NO_2Na$ [M+Na]⁺ 528.1939, found 528.1937.

2-(phenyl(2-phenyl-1H-indol-3-yl)methyl)malononitrile (7d).

pale yellow solid; yield 84%; **¹H NMR** (500 MHz, CDCl₃) δ 8.31 (s, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.50-7.41 (m, 7H), 7.37-7.34 (m, 3H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 4.98 (d, *J* = 10.7 Hz, 1H), 4.71 (d, *J* = 10.7 Hz, 1H); **¹³C NMR** (125 MHz, CDCl₃) δ 138.1, 137.8, 136.2, 131.7, 129.3, 129.2, 128.4, 127.9, 126.1, 123.0, 120.9, 119.6, 112.7, 112.4, 112.0, 108.5, 44.8, 28.5; **HRMS (ESI)**: calcd for $C_{24}H_{16}N_3$ [M-H]⁻ 346.1344, found 346.1339.

3-(2-nitro-1-phenylethyl)-2-phenyl-1H-indole (7e).^[7]

yield 20%; **¹H NMR** (500 MHz, CDCl₃) δ 8.18 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.50-7.43 (m, 5H), 7.40 (d, *J* = 8.1 Hz, 1H), 7.37-7.28 (m, 4H), 7.25-7.20 (m, 2H), 7.12 (t, *J* = 7.5 Hz, 1H), 5.33 (t, *J* = 7.9 Hz, 1H), 5.20 (dd, *J* = 12.5, 7.3 Hz, 1H), 5.14 (dd, *J* = 12.5, 8.6 Hz, 1H); **¹³C NMR** (125 MHz, CDCl₃) δ 140.0, 137.1, 136.2, 132.3, 129.1, 129.0, 128.9, 128.8, 127.6, 127.3, 127.2, 122.6, 120.4, 120.1, 111.5, 109.7, 79.2, 40.9.

N-(phenyl(2-phenyl-1H-indol-3-yl)methyl)aniline (9a)

white solid; yield 82%; **¹H NMR** (500 MHz, CDCl₃) δ 8.06 (s, 1H), 7.52-7.35 (m, 8H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.26-7.21 (m, 2H), 7.20-7.12 (m, 2H), 7.07 (t, *J* = 7.8 Hz, 2H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.65 (t, *J* = 7.3 Hz, 1H), 6.47 (d, *J* = 7.9 Hz, 2H), 5.91 (s, 1H), 4.52 (s, 1H); **¹³C NMR** (125 MHz, CDCl₃) δ 147.7, 142.8, 136.2, 136.0, 132.6, 129.3, 129.1, 128.7, 128.5, 128.4, 127.3, 127.1, 126.8, 122.6, 120.6, 120.2, 117.3, 114.5, 113.3, 111.1, 54.8; **HRMS (ESI)**: calcd for $C_{27}H_{21}N_2$ [M-H]⁻ 373.1699, found 373.1695.

4-methoxy-N-(phenyl(2-phenyl-1H-indol-3-yl)methyl)aniline (9b)

white solid; yield 68%; **¹H NMR** (500 MHz, CDCl₃) δ 8.13 (s, 1H), 7.53-7.48 (m, 2H), 7.46-7.35 (m, 7H), 7.27-7.24 (m, 2H), 7.21-7.12 (m, 2H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.68-6.66 (m, 2H), 6.44-6.42 (m, 2H), 5.84 (s, 1H), 3.70 (s, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 152.0, 143.1, 142.1, 136.3, 135.9, 132.7, 129.1, 128.7, 128.5, 128.4, 127.4, 127.1, 126.8, 122.6, 120.8, 120.2, 114.9, 114.7, 114.5, 111.0, 55.9, 55.7.

4-methyl-N-(phenyl(2-phenyl-1H-indol-3-yl)methyl)benzenesulfonamide(9c)

white solid; yield 81%; **¹H NMR** (500 MHz, DMSO) δ 11.19 (s, 1H), 8.47 (d, *J* = 7.3 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.46-7.40 (m, 3H), 7.34-7.30 (m, 2H), 7.29-7.21 (m, 7H), 7.19-7.15 (m, 1H), 7.04-6.98 (m, 3H), 6.83 (t, *J* = 7.8 Hz, 1H), 5.85 (d, *J* = 7.3 Hz, 1H), 2.26 (s, 3H); **¹³C NMR** (125 MHz, DMSO) δ 141.7, 141.6, 137.9, 136.2, 135.7, 132.1, 128.7, 128.5, 128.3, 128.0, 127.9, 126.9, 126.7, 126.0, 125.9, 121.3, 120.6, 118.6, 111.0, 110.6, 53.5, 20.9; **HRMS (ESI)**: calcd for $C_{28}H_{23}N_2O_2S$ [M-H]⁻ 451.1475, found 451.1471.

3-((tert-butylthio)(phenyl)methyl)-2-phenyl-1H-indole (9d).

white solid; yield 85%; **¹H NMR** (500 MHz, CDCl₃) δ 8.04 (s, 1H), 8.01 (d, *J* = 8.1 Hz, 1H),

7.64 (d, $J = 7.7$ Hz, 2H), 7.51-7.39 (m, 5H), 7.37 (d, $J = 8.1$ Hz, 1H), 7.29 (t, $J = 7.5$ Hz, 2H), 7.24-7.19 (m, 2H), 7.14 (t, $J = 7.5$ Hz, 1H), 5.64 (s, 1H), 1.08 (s, 9H); ^{13}C NMR (125 MHz, CDCl₃) δ 143.0, 136.4, 134.6, 132.9, 129.0, 128.7, 128.6, 128.4, 128.3, 128.2, 126.6, 122.8, 122.5, 119.7, 114.6, 111.0, 44.5, 43.9, 31.1; HRMS (ESI): calcd for C₂₅H₂₆NS [M+H]⁺ 372.1786, found 372.1775.

2-phenyl-3-(phenyl(p-tolylthio)methyl)-1H-indole (9e).

white solid; yield 93%; ^1H NMR (500 MHz, CDCl₃) δ 7.94 (s, 1H), 7.86 (d, $J = 8.0$ Hz, 1H), 7.58 (d, $J = 7.7$ Hz, 2H), 7.35-7.31 (m, 4H), 7.28-7.16 (m, 6H), 7.08 (t, $J = 7.5$ Hz, 1H), 6.93 (d, $J = 7.9$ Hz, 2H), 6.83 (d, $J = 7.7$ Hz, 2H), 5.89 (s, 1H), 2.21 (s, 3H); ^{13}C NMR (125 MHz, CDCl₃) δ 141.0, 136.7, 136.5, 136.3, 132.6, 132.4, 132.1, 129.3, 128.8, 128.7, 128.6, 128.4, 128.3, 127.6, 127.0, 122.5, 122.3, 119.8, 112.1, 111.0, 50.5, 21.2; HRMS (ESI): calcd for C₂₈H₂₄NS [M+H]⁺ 406.1629, found 406.1620.

10-(phenyl(2-phenyl-1H-indol-3-yl)methyl)anthracen-9(10H)-one (11).

yellow solid; yield 94%; ^1H NMR (500 MHz, CDCl₃) δ 8.00-7.97 (m, 2H), 7.85 (d, $J = 7.6$ Hz, 1H), 7.41-7.37 (m, 2H), 7.32-7.13 (m, 11H), 7.03-6.97 (m, 2H), 7.96-6.90 (m, 2H), 6.87 (d, $J = 7.6$ Hz, 1H), 6.73 (d, $J = 7.3$ Hz, 2H), 5.25 (d, $J = 7.0$ Hz, 1H), 4.66 (d, $J = 6.9$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl₃) δ 184.9, 144.3, 143.7, 142.3, 138.1, 135.9, 133.6, 133.0, 132.3, 131.5, 131.3, 129.1, 129.0, 128.7, 128.5, 128.4, 128.3, 128.0, 127.9, 127.3, 127.1, 126.8, 126.7, 126.5, 122.0, 121.7, 119.8, 111.2, 109.9, 55.9, 48.8; HRMS (ESI): calcd for C₃₅H₂₅NONa [M+Na]⁺ 498.1834, found 498.1833.

1,3-diphenyl-3-(2-phenyl-1H-indol-3-yl)propan-1-one (13).^[8]

yield 45%; ^1H NMR (500 MHz, CDCl₃) δ 8.10 (s, 1H), 7.87-7.82 (m, 2H), 7.64 (d, $J = 8.0$ Hz, 1H), 7.56-7.48 (m, 3H), 7.47-7.34 (m, 8H), 7.28 (dd, $J = 8.7, 6.5$ Hz, 2H), 7.23-7.18 (m, 2H), 7.11 (t, $J = 7.5$ Hz, 1H), 5.35 (t, $J = 6.9$ Hz, 1H), 4.01 (dd, 16.9, 7.0 Hz, 2H), 3.93 (dd, 16.9, 7.0 Hz, 2H); ^{13}C NMR (125 MHz, CDCl₃) δ 198.8, 144.6, 137.0, 136.3, 135.6, 133.1, 133.0, 128.9, 128.8, 128.5, 128.4, 128.2, 128.1, 127.9, 127.7, 126.1, 122.1, 120.7, 119.8, 114.8, 111.2, 44.6, 36.9.

2-phenyl-2-(2-phenyl-1H-indol-3-yl)acetonitrile(14)

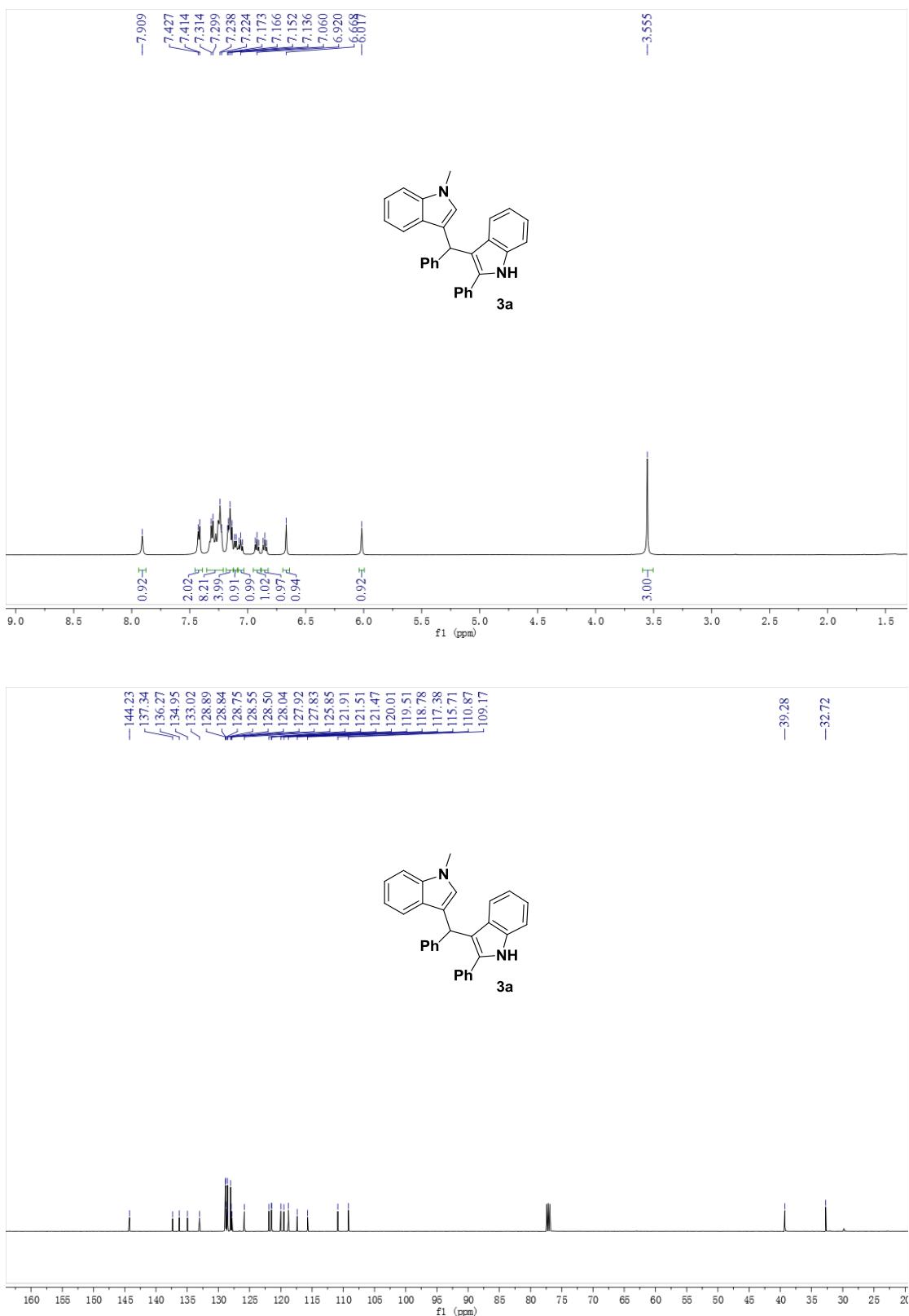
white solid; yield 75%; ^1H NMR (500 MHz, CDCl₃) δ 8.27 (s, 1H), 7.42-7.31 (m, 9H), 7.27-7.20 (m, 3H), 7.16-7.13 (m, 1H), 7.02-6.98 (m, 1H), 5.52 (s, 1H); ^{13}C NMR (125 MHz, CDCl₃) δ 137.0, 136.1, 135.5, 131.6, 129.4, 129.1, 128.6, 128.0, 127.3, 126.8, 123.2, 120.8, 120.0, 119.7, 111.3, 106.1, 33.5; HRMS (ESI): calcd for C₂₂H₁₅N₂ [M-H]⁻ 307.1230, found 307.1228.

References

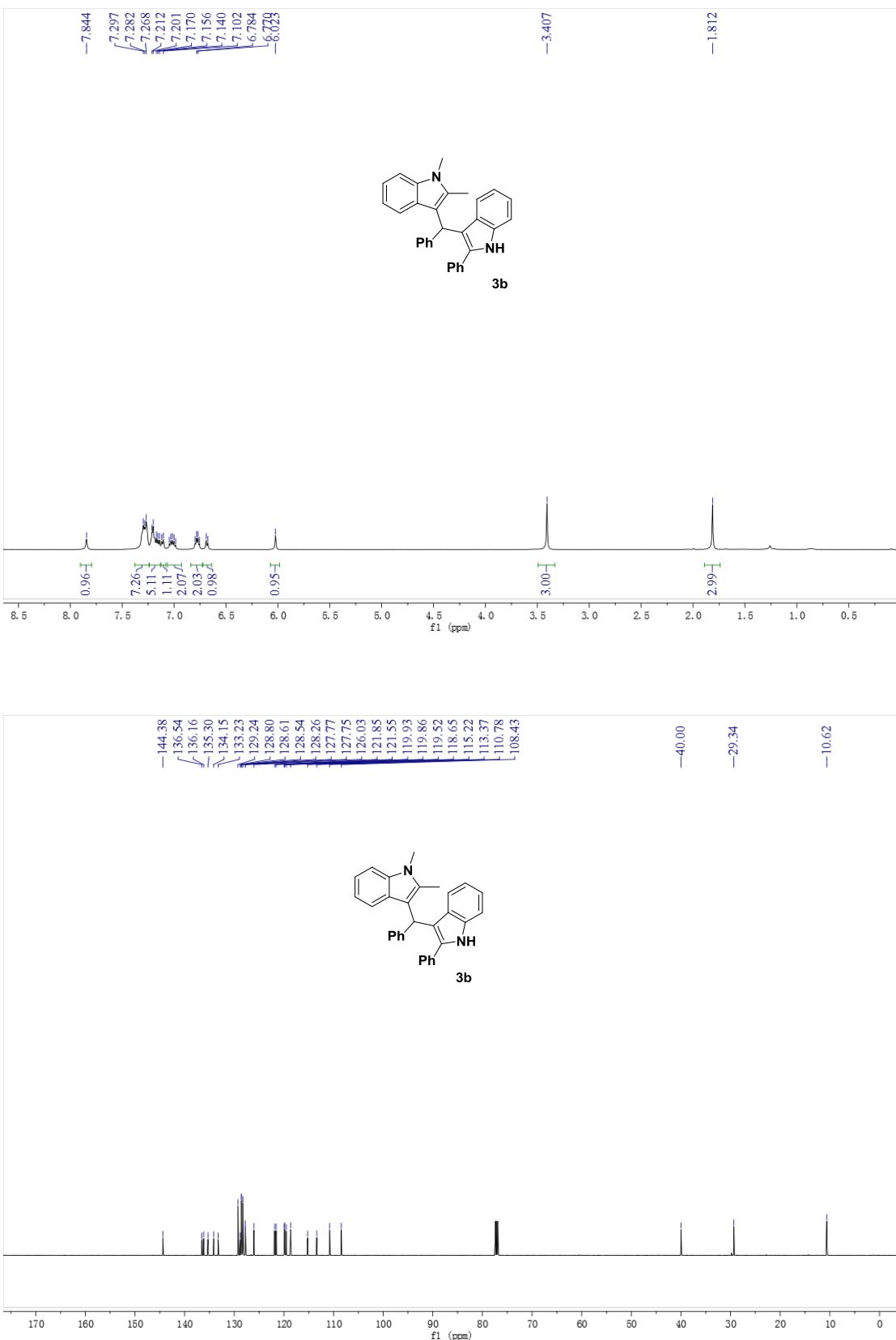
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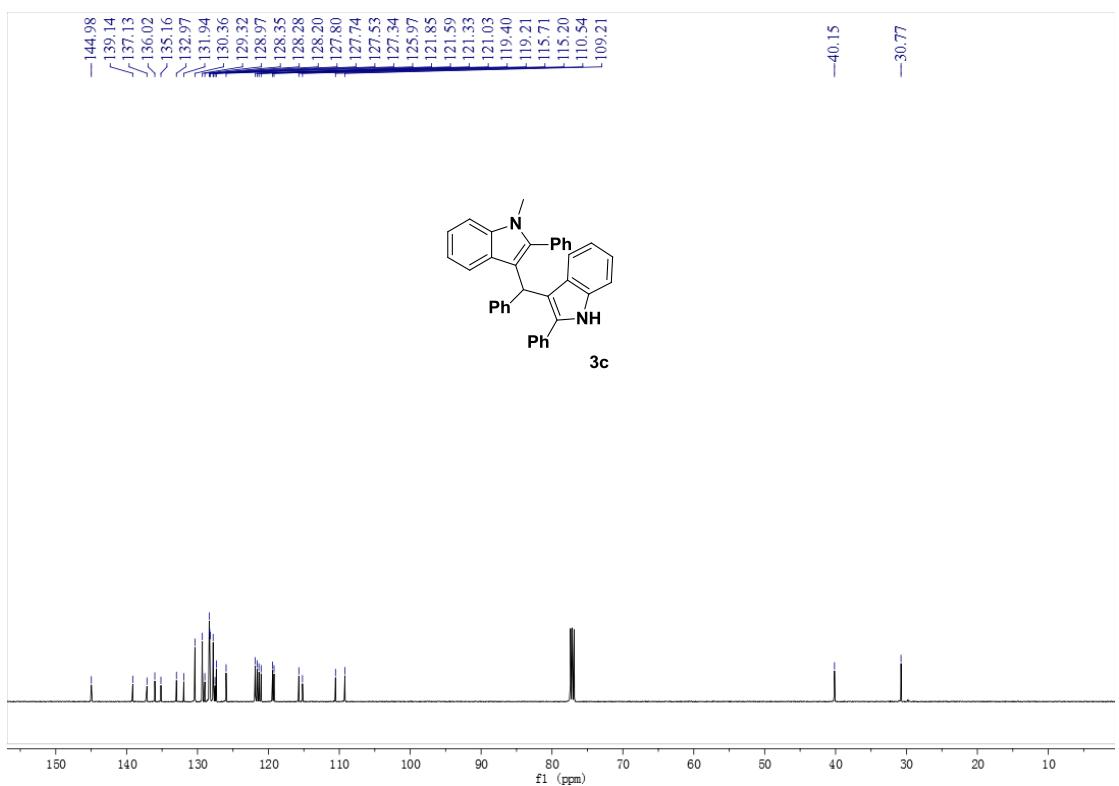
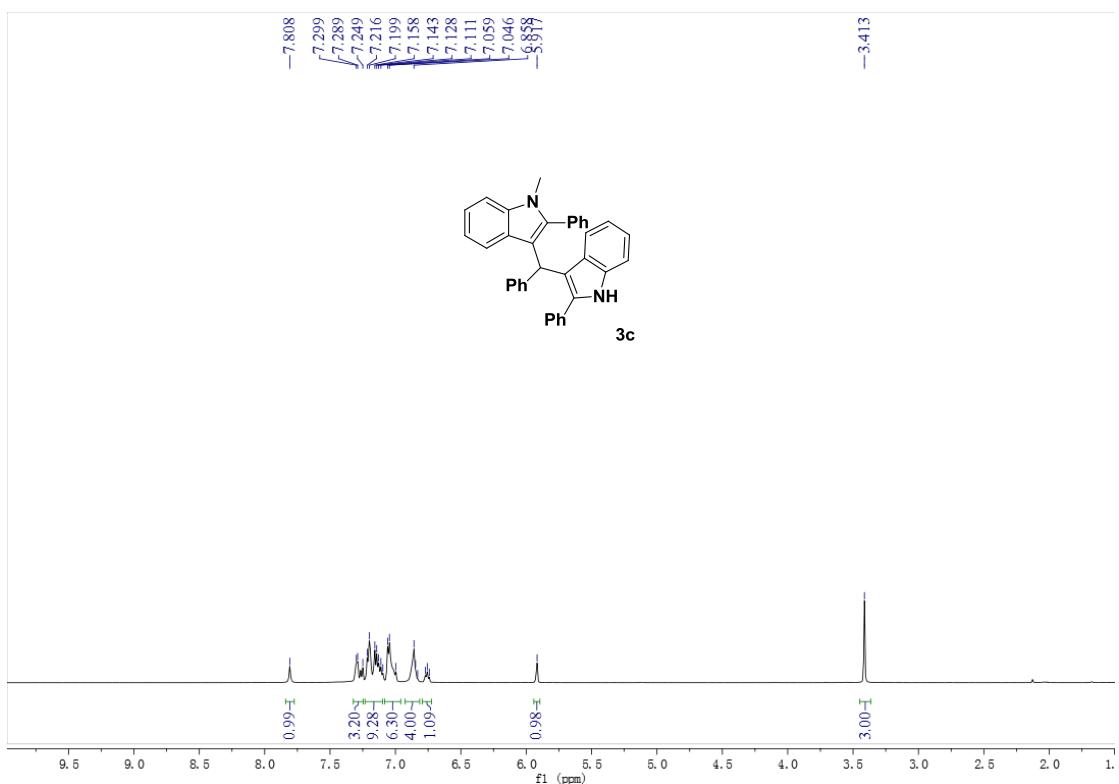
¹H and ¹³C Spectra
1-methyl-3-(phenyl(2-phenyl-1H-indol-3-yl)methyl)-1H-indole 3a



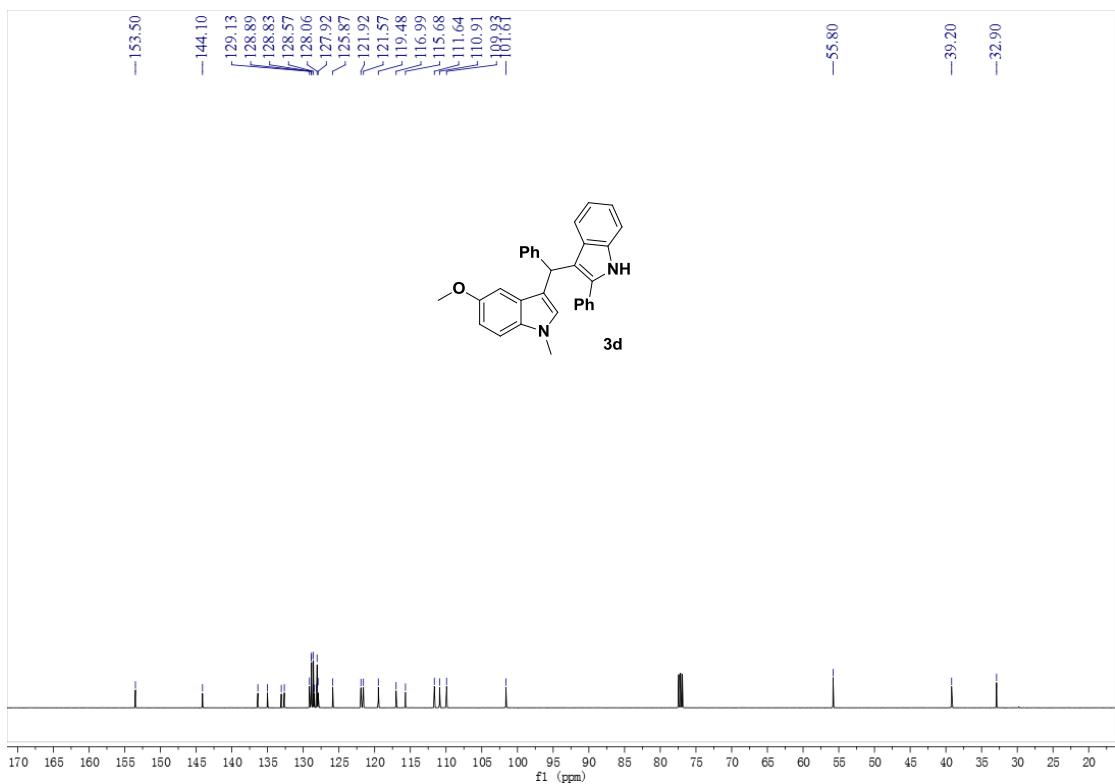
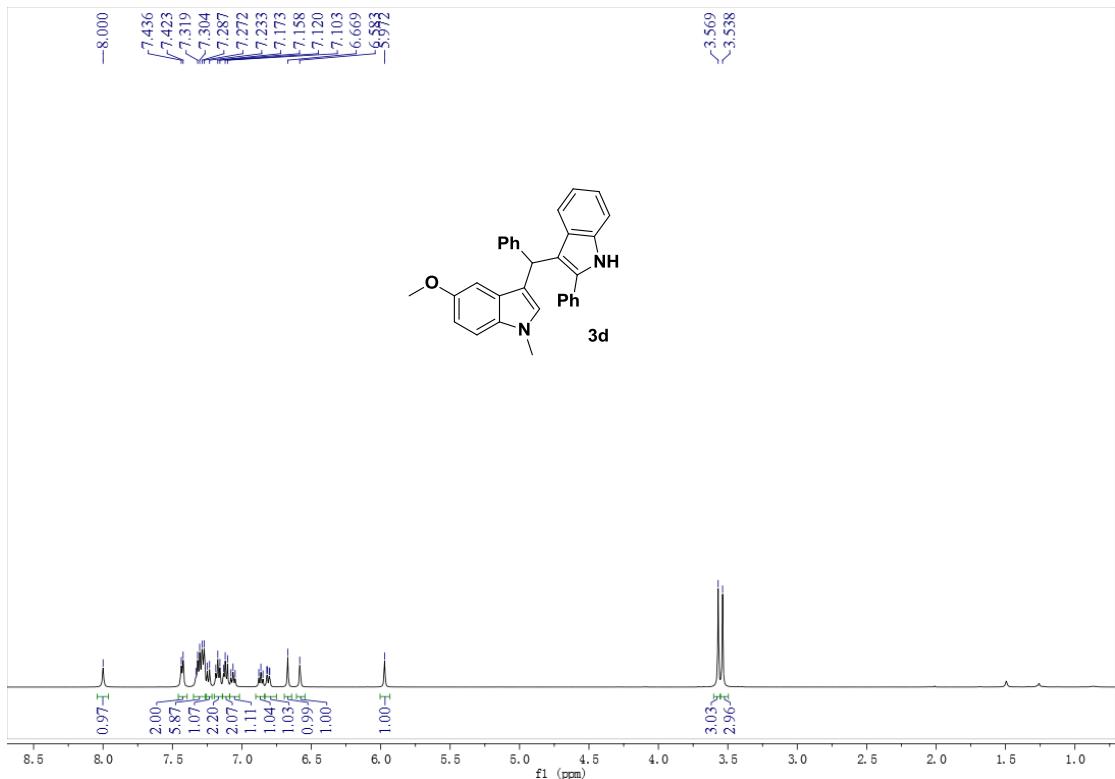
1,2-dimethyl-3-(phenyl(2-phenyl-1H-indol-3-yl)methyl)-1H-indole **3b**



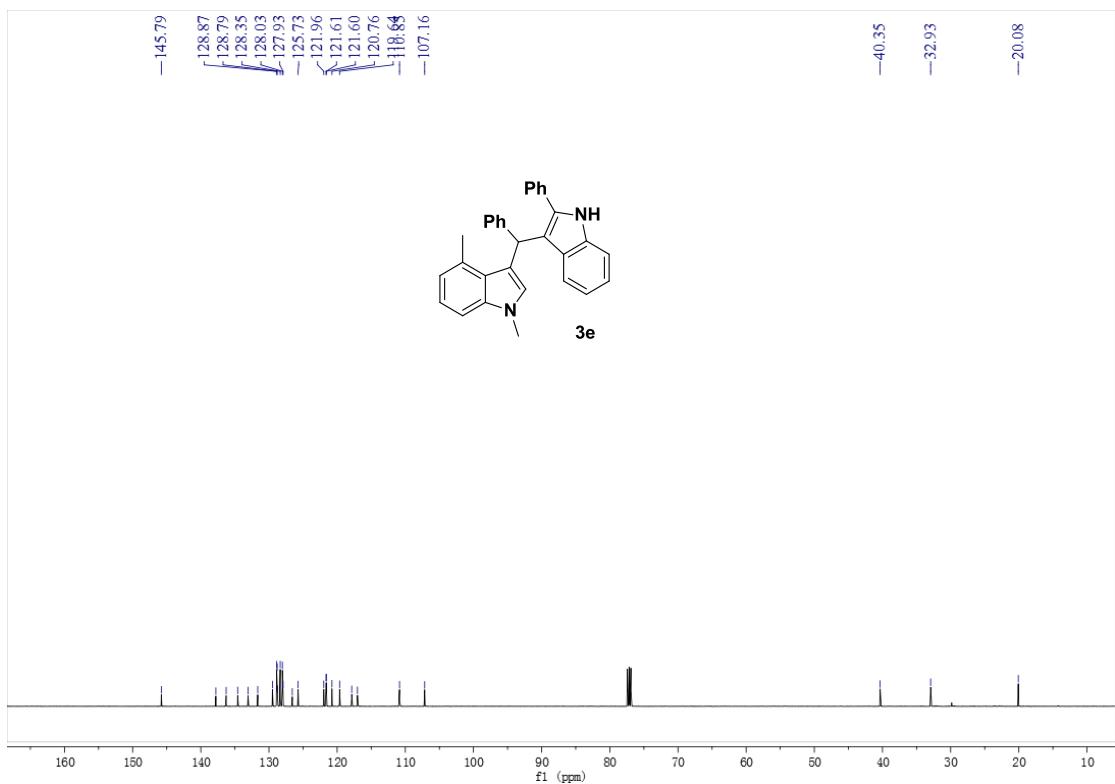
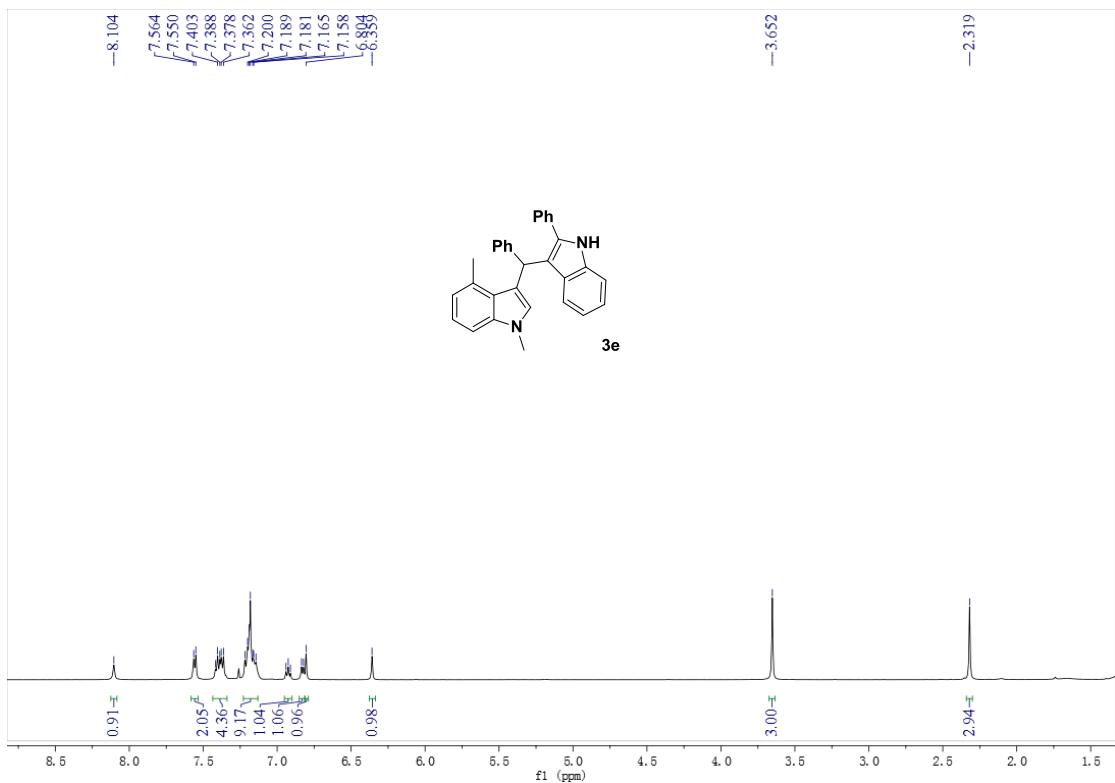
1-methyl-2-phenyl-3-(phenyl(2-phenyl-1H-indol-3-yl)methyl)-1H-indole **3c**



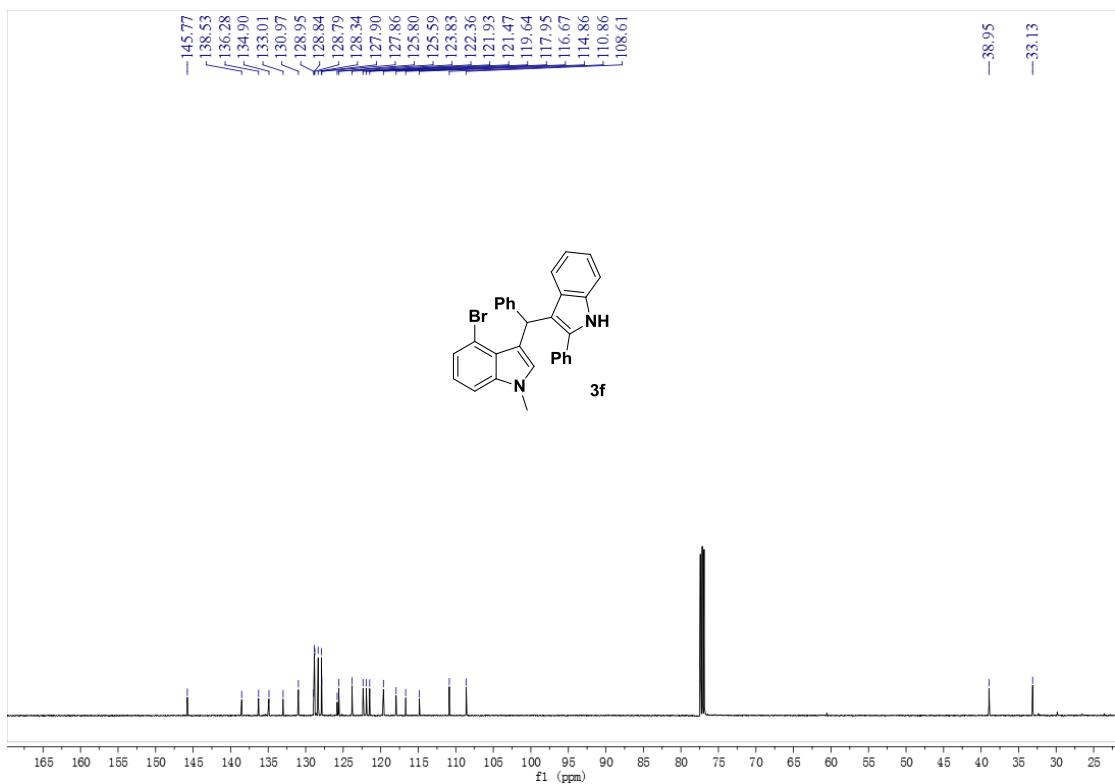
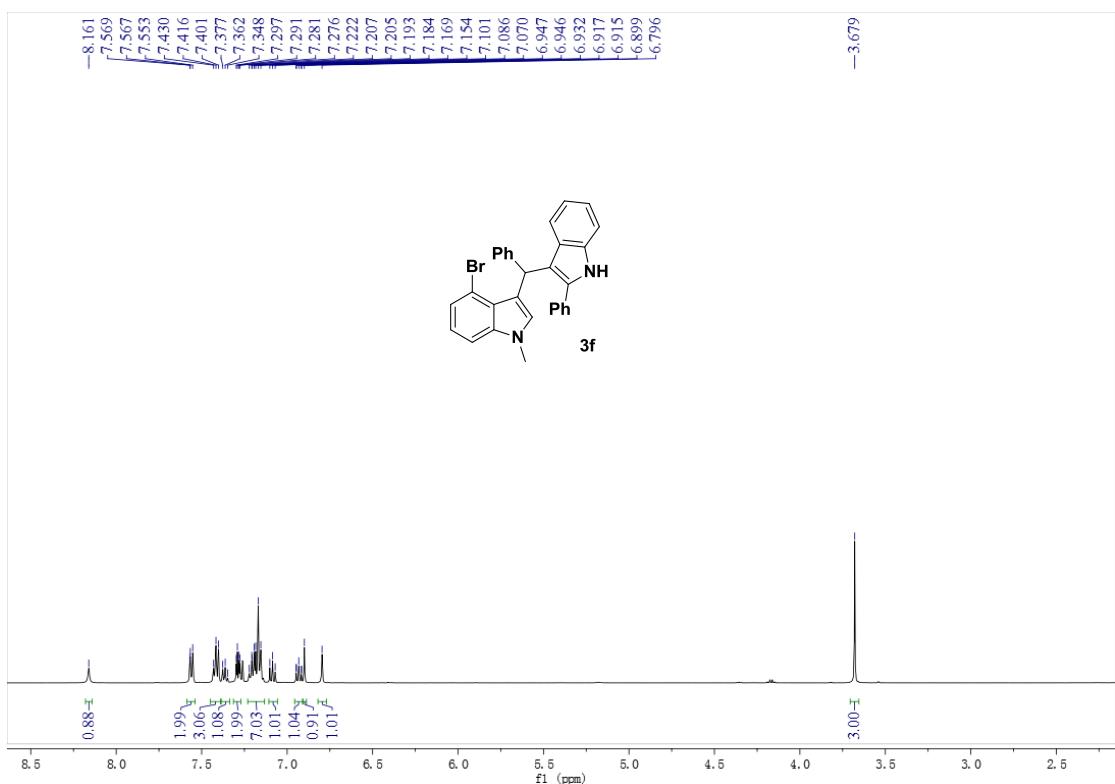
5-methoxy-1-methyl-3-(phenyl(2-phenyl-1H-indol-3-yl)methyl)-1H-indole **3d**



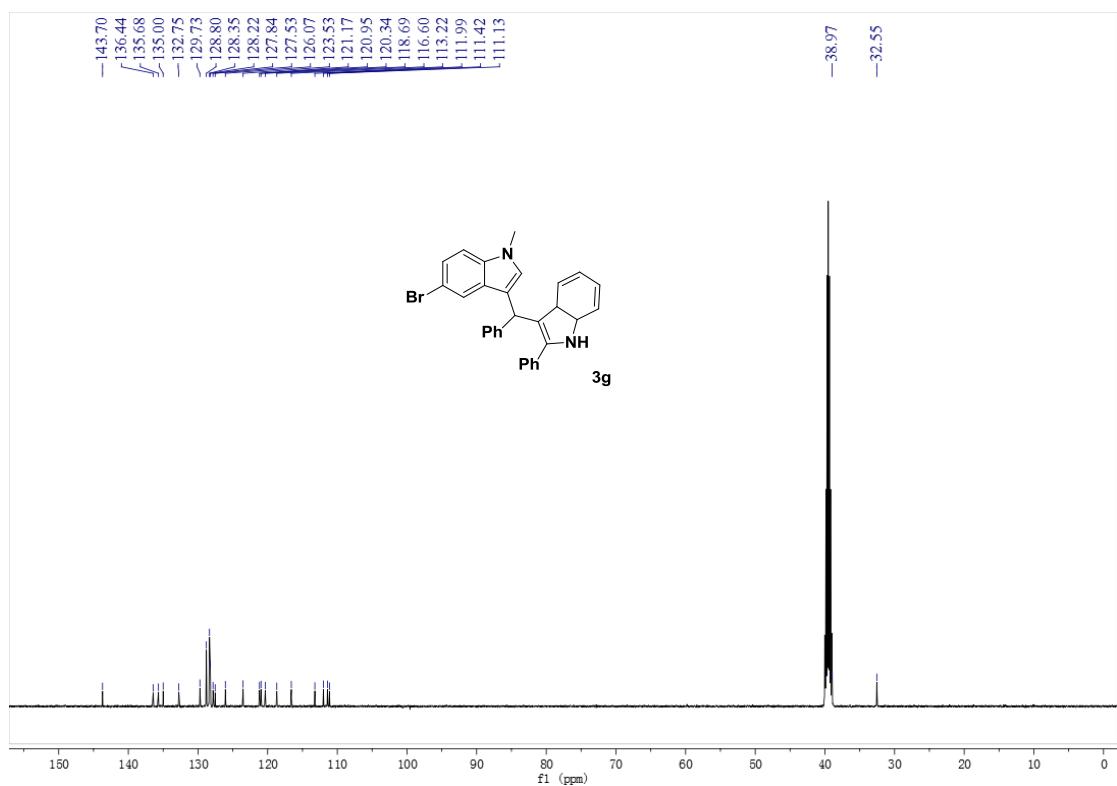
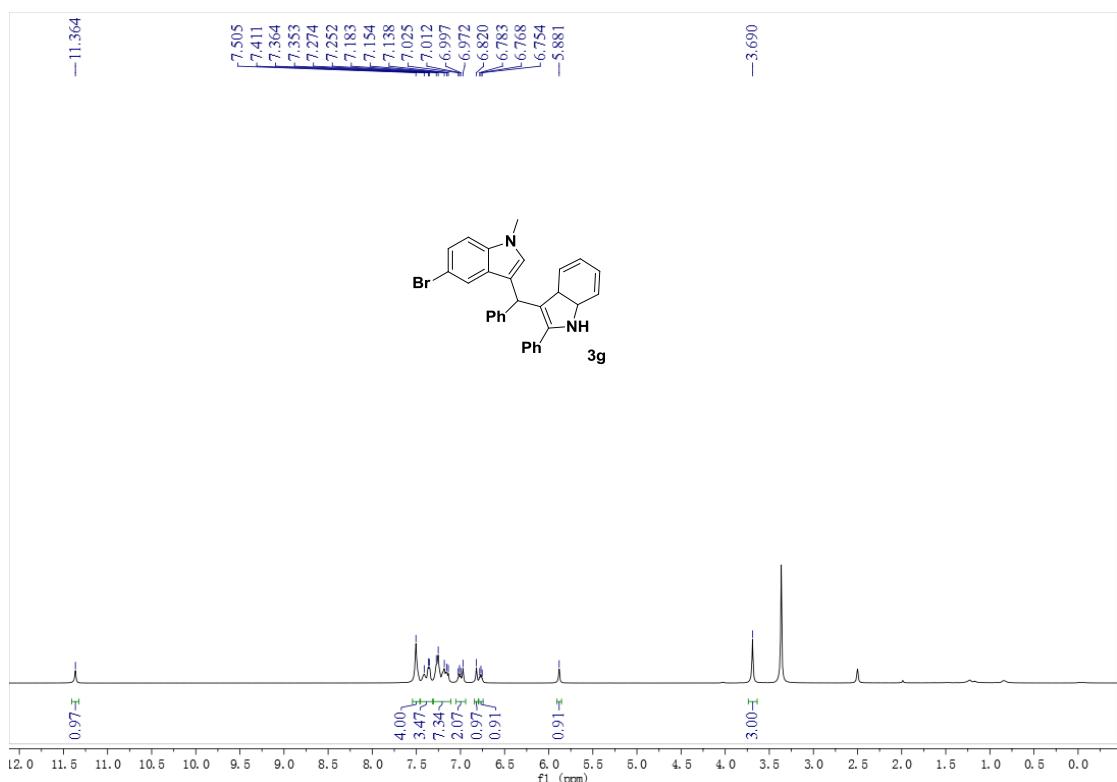
1,4-dimethyl-3-(phenyl(2-phenyl-1H-indol-3-yl)methyl)-1H-indole **3e**



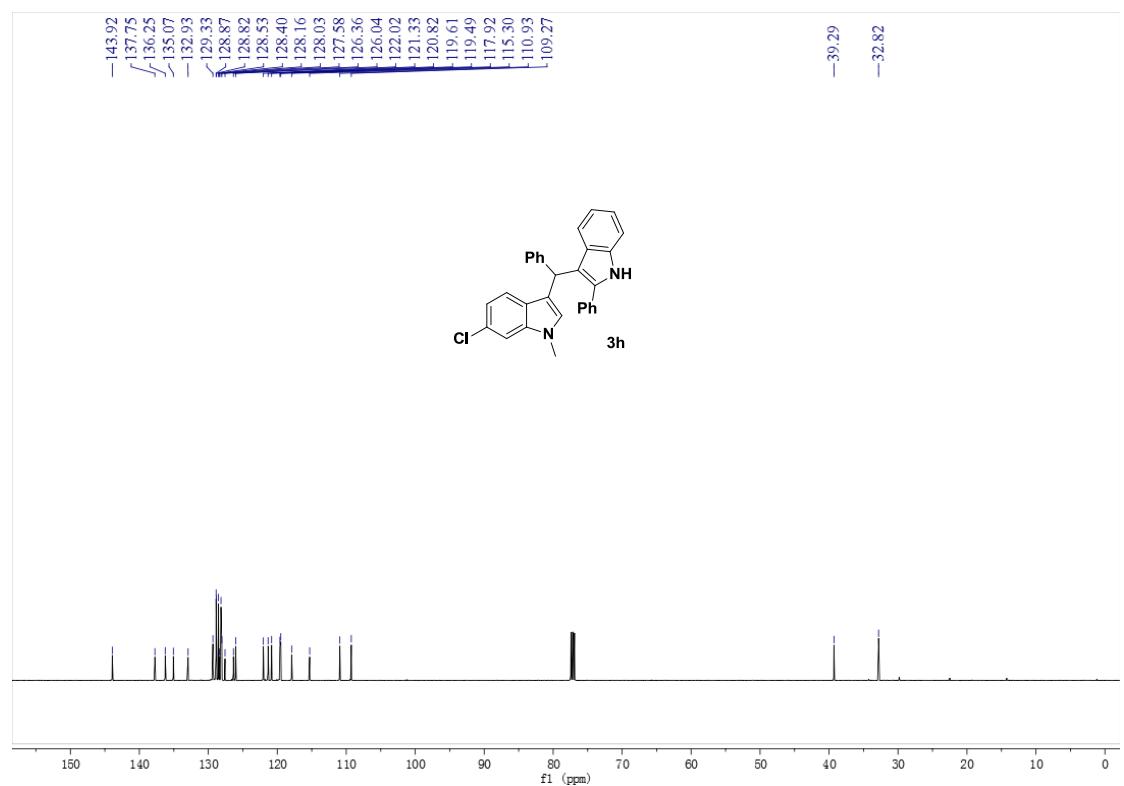
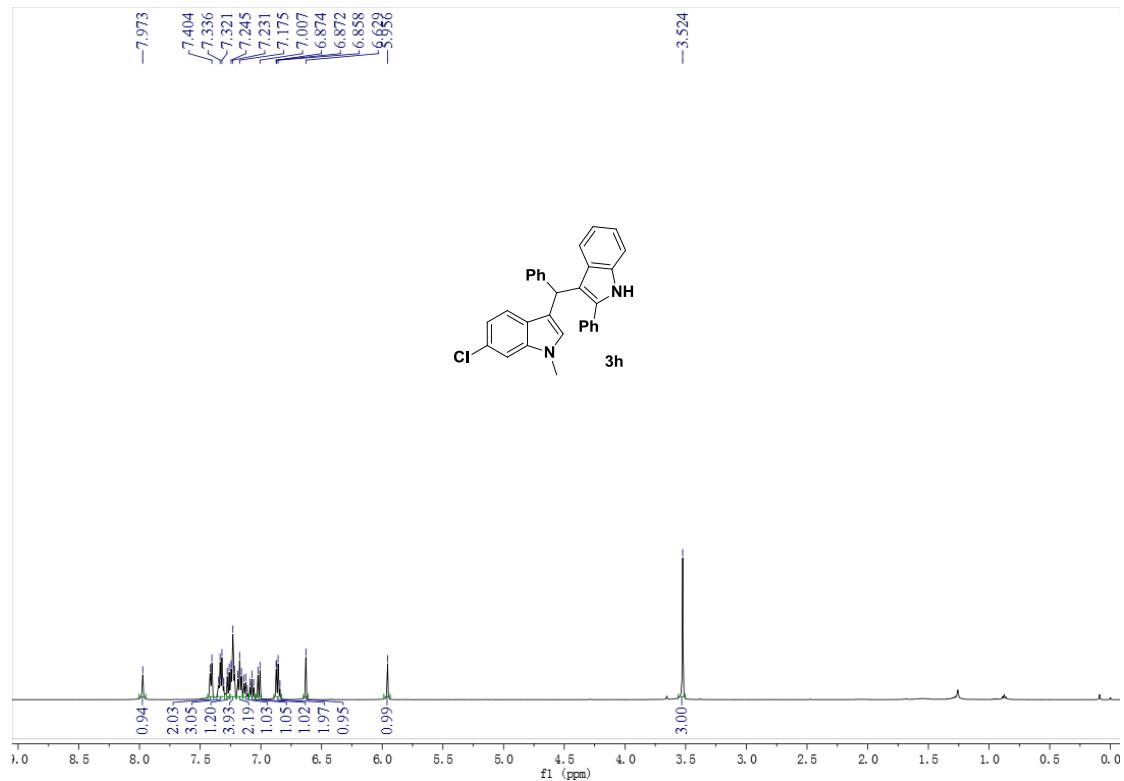
4-bromo-1-methyl-3-(phenyl(2-phenyl-1H-indol-3-yl)methyl)-1H-indole **3f**



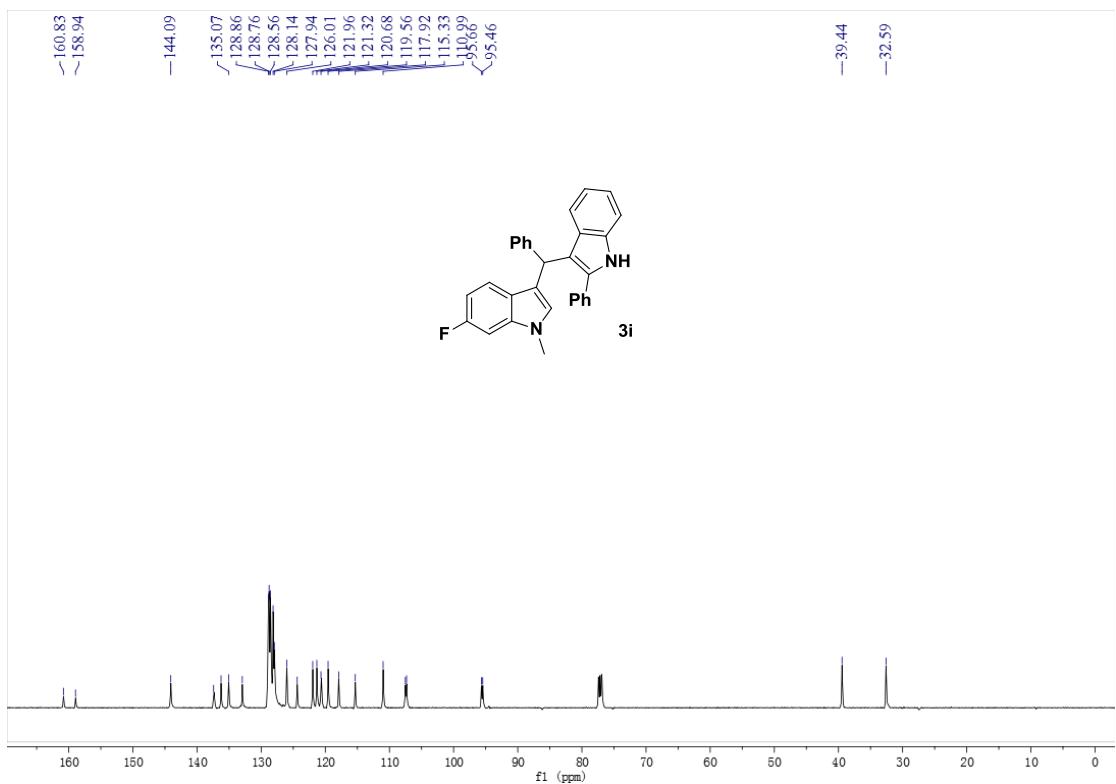
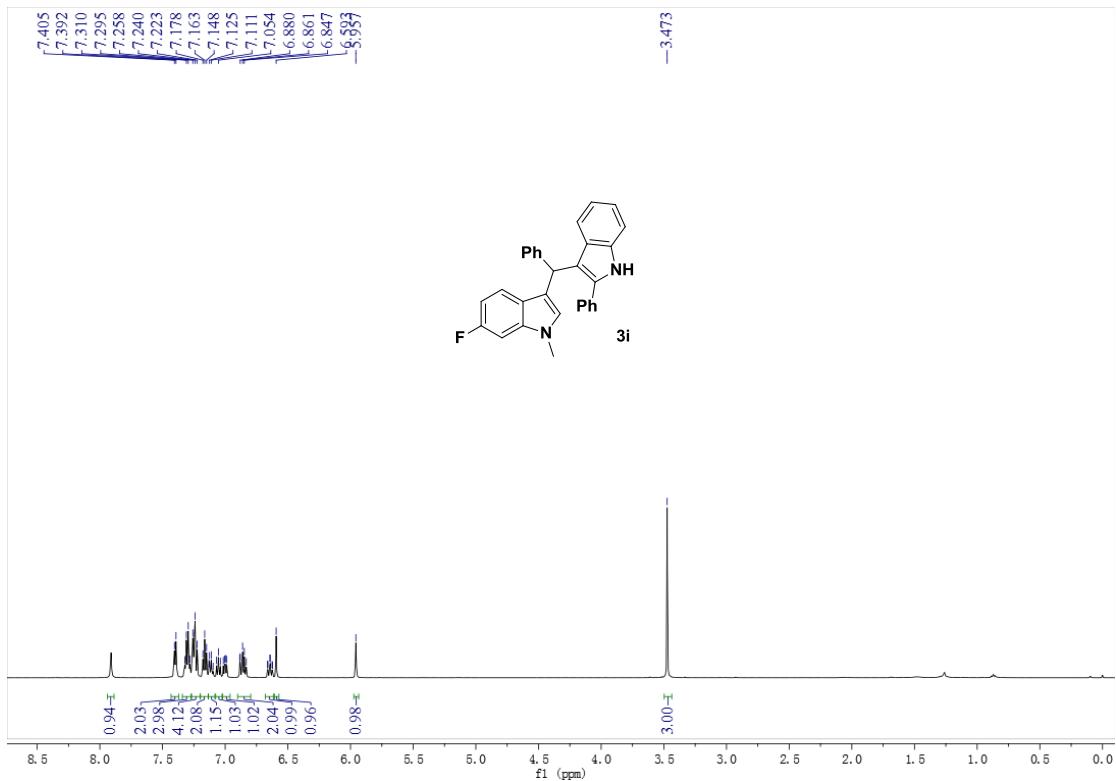
5-bromo-1-methyl-3-(phenyl(2-phenyl-1H-indol-3-yl)methyl)-1H-indole **3g**



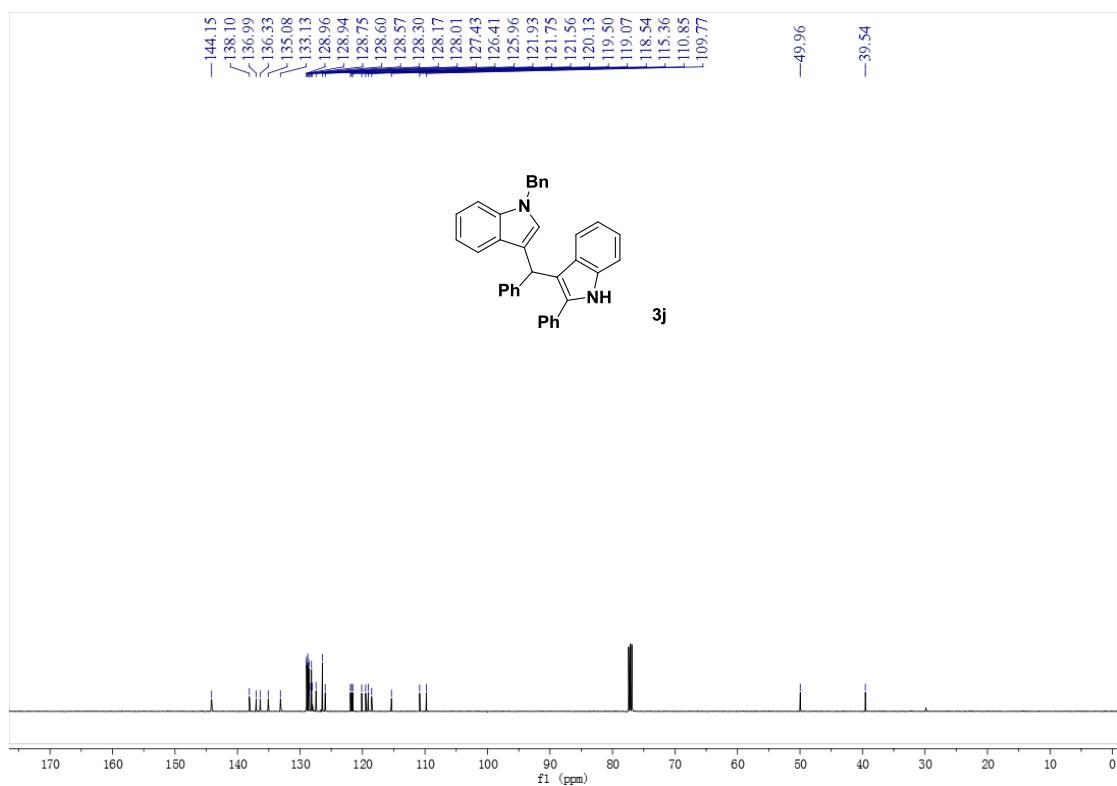
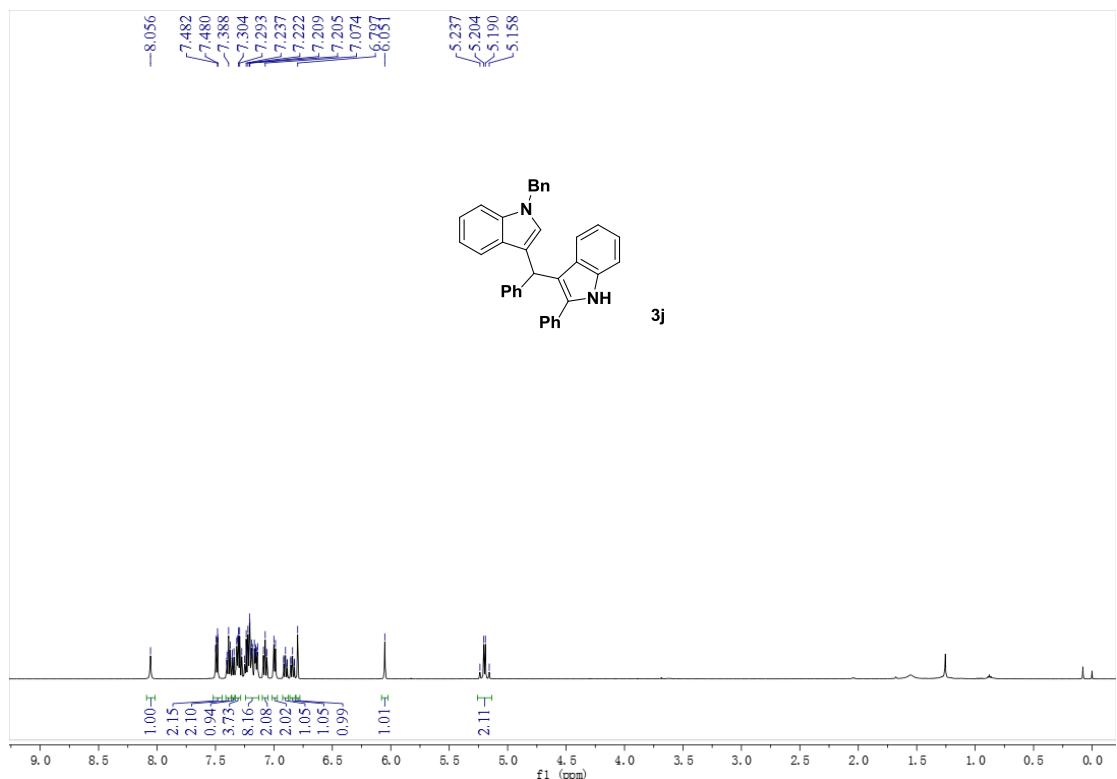
6-chloro-1-methyl-3-(phenyl(2-phenyl-1H-indol-3-yl)methyl)-1H-indole **3h**



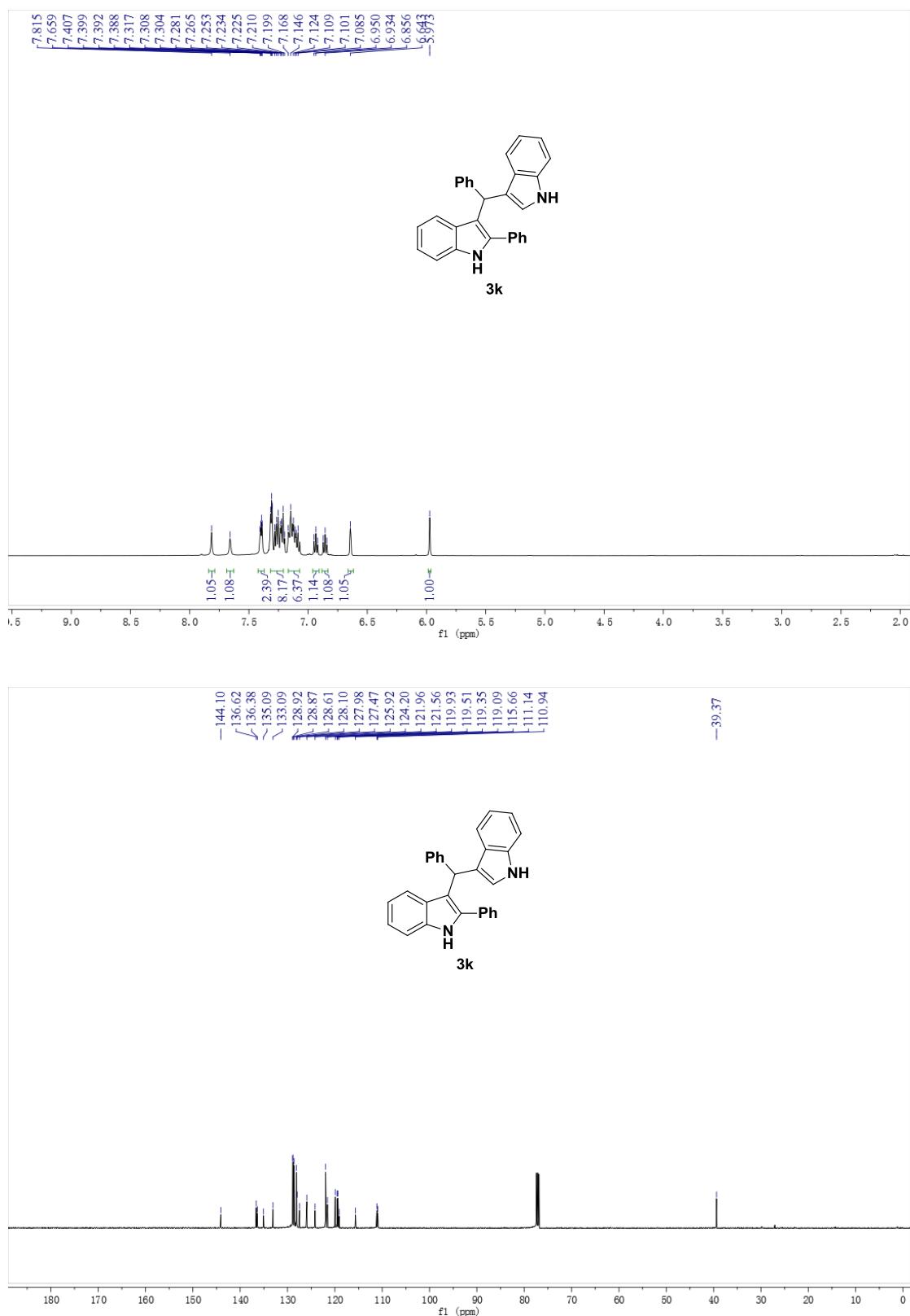
6-fluoro-1-methyl-3-(phenyl(2-phenyl-1H-indol-3-yl)methyl)-1H-indole **3i**



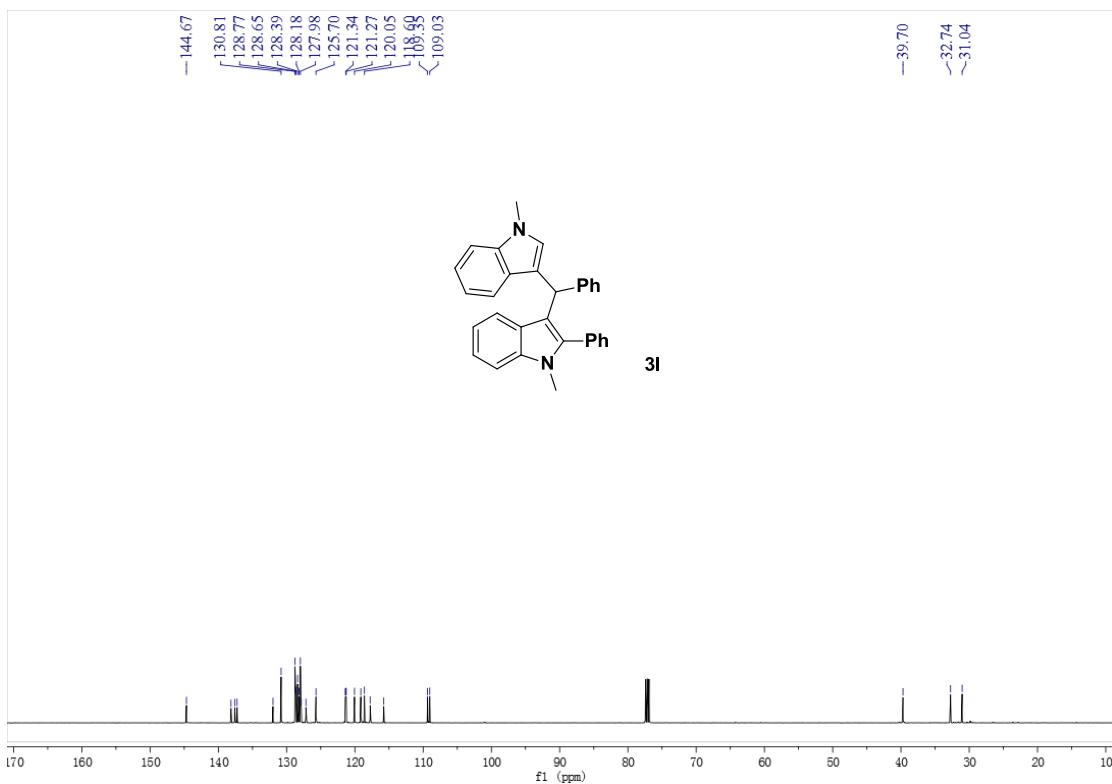
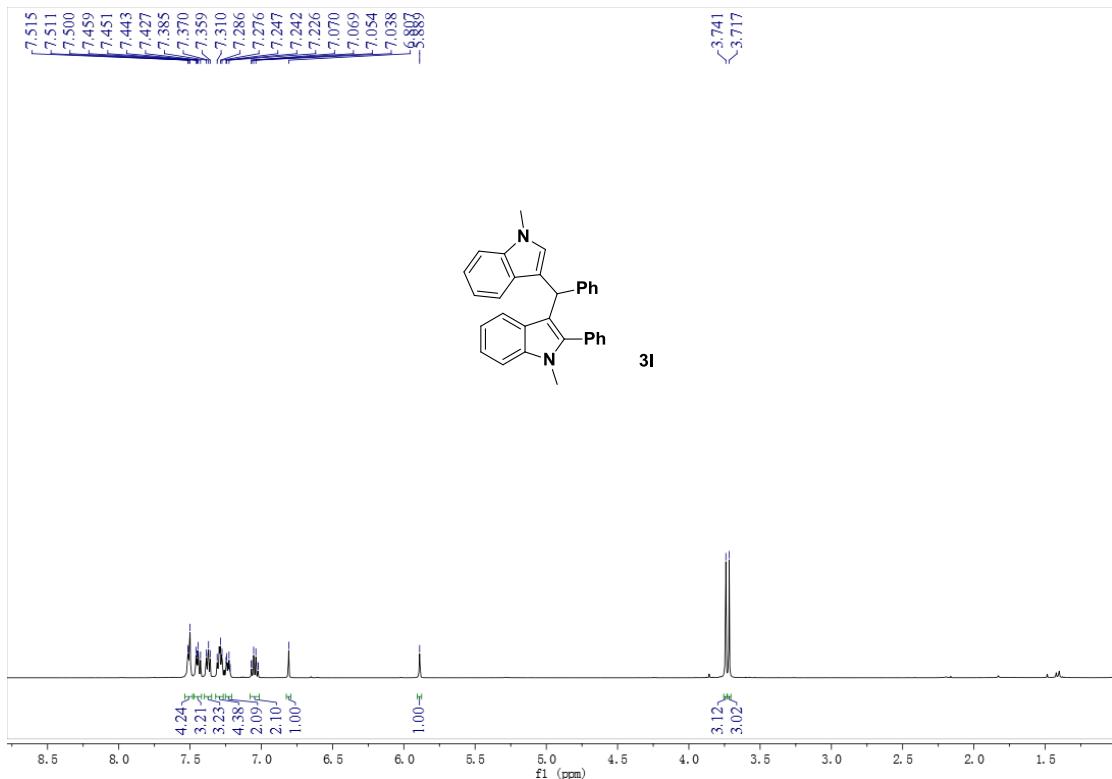
1-benzyl-3-(phenyl(2-phenyl-1H-indol-3-yl)methyl)-1H-indole **3j**



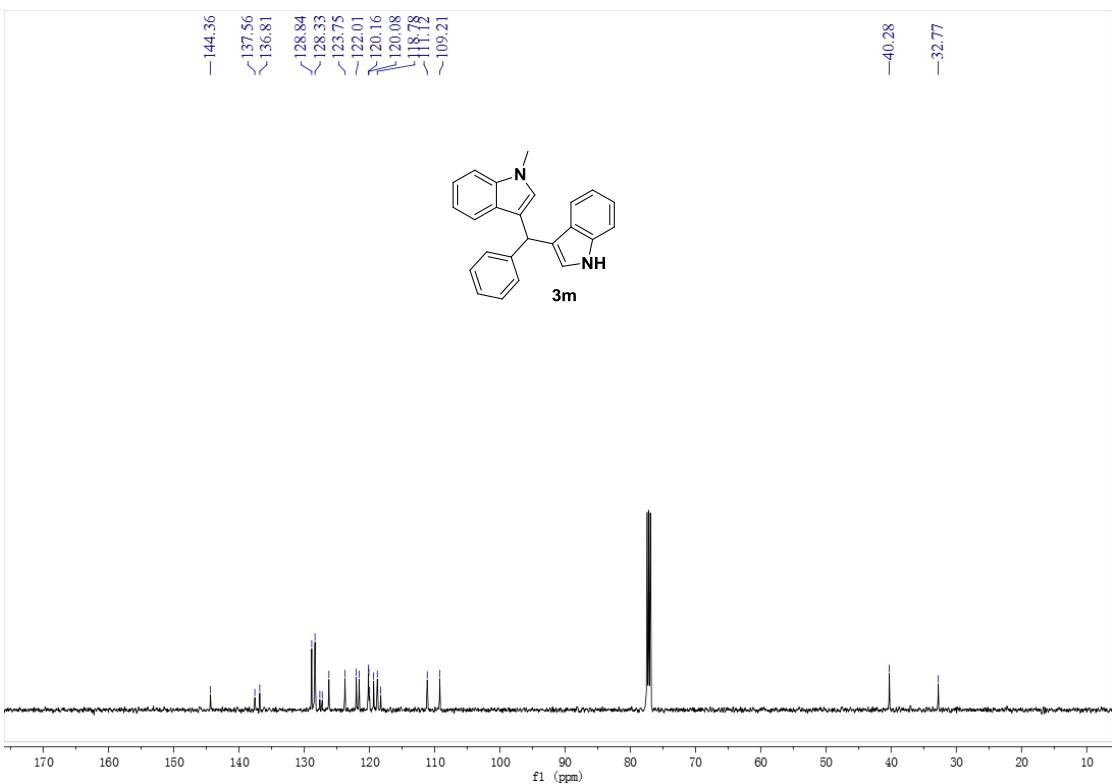
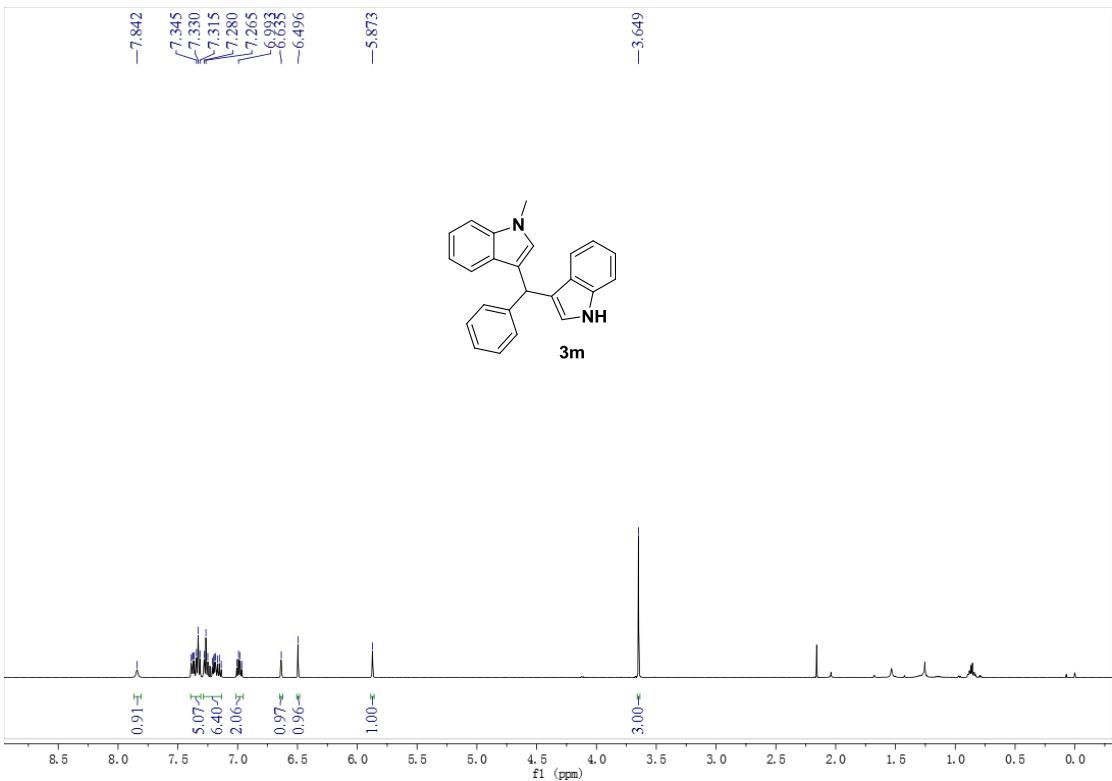
3-((1H-indol-3-yl)(phenyl)methyl)-2-phenyl-1H-indole **3k**



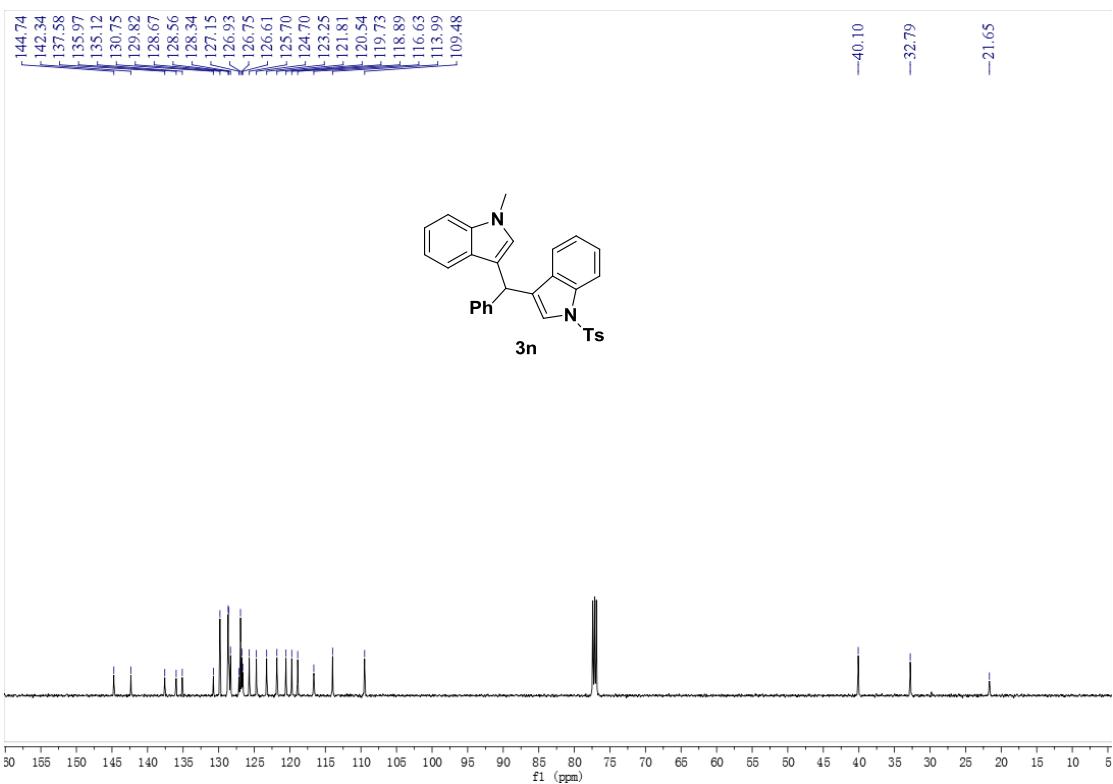
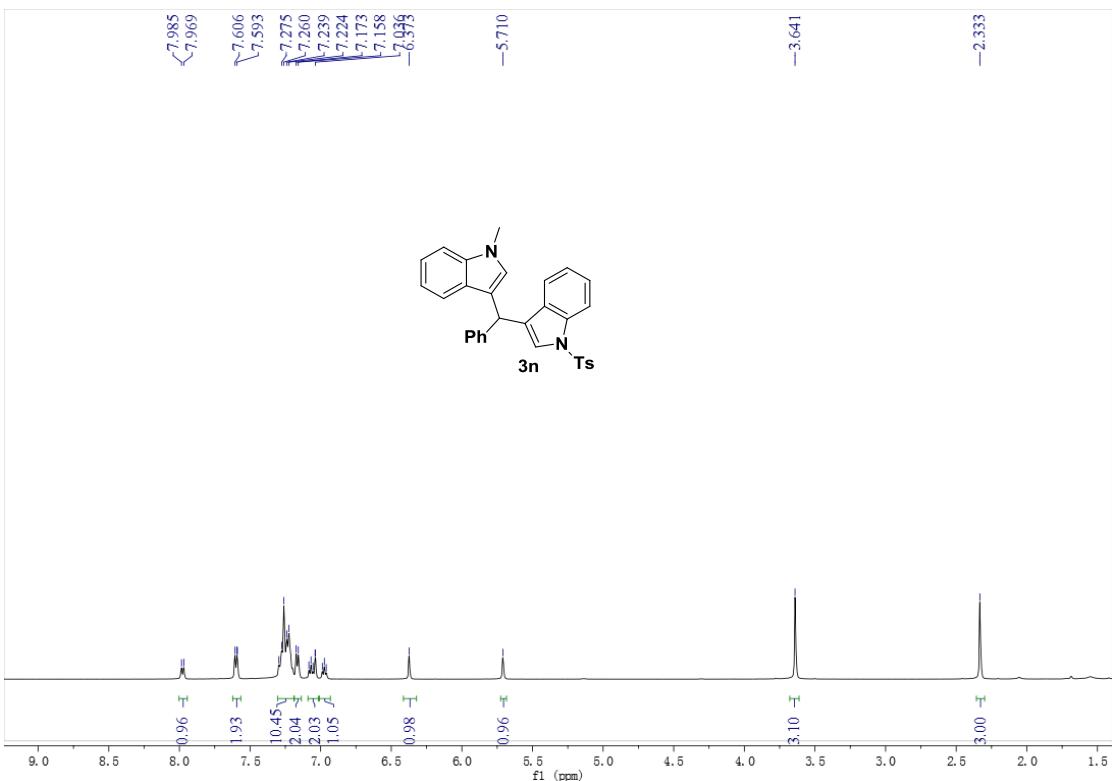
1-methyl-3-((1-methyl-1H-indol-3-yl)(phenyl)methyl)-2-phenyl-1H-indole **3l**



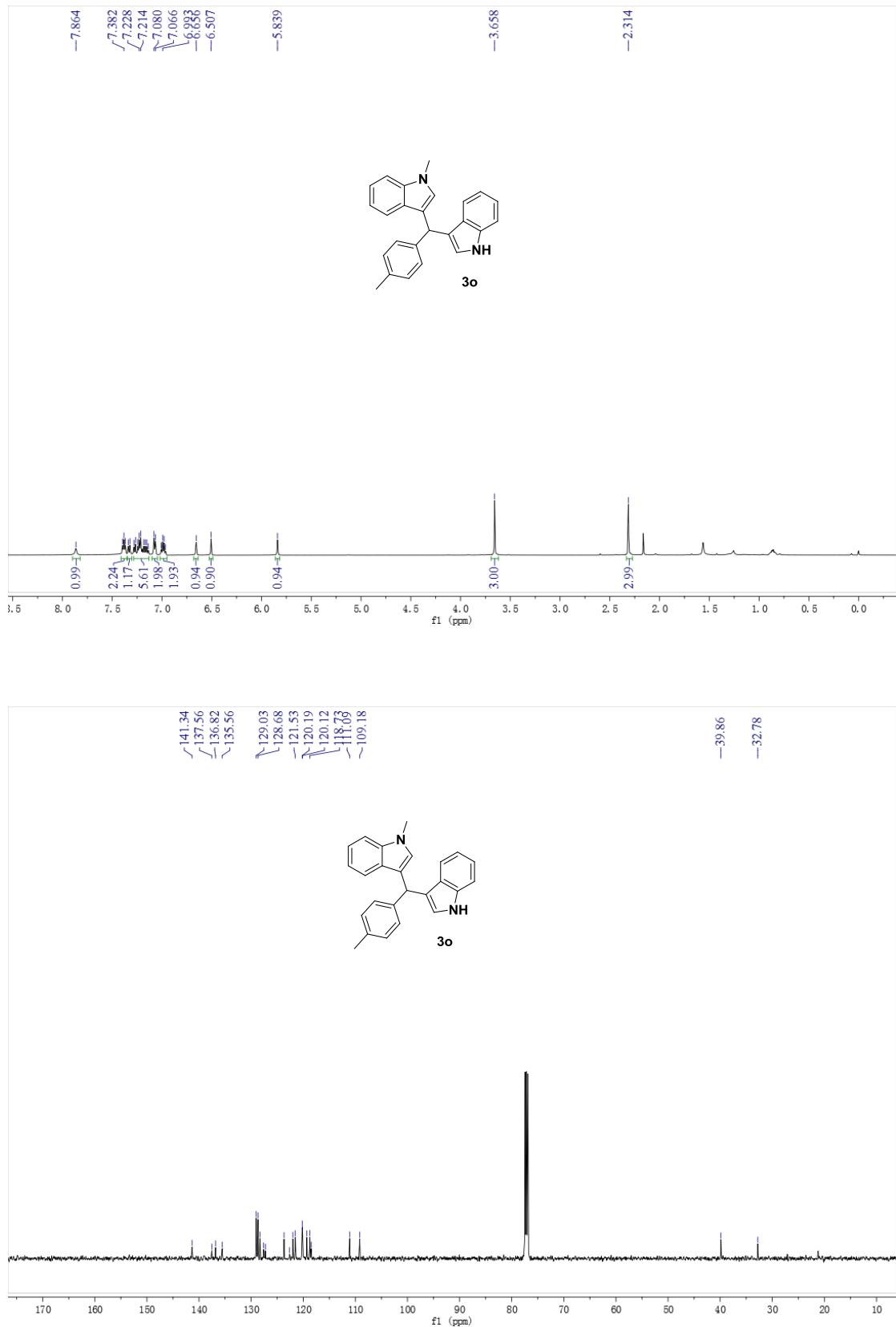
3-((1H-indol-3-yl)(phenyl)methyl)-1-methyl-1H-indole **3m**



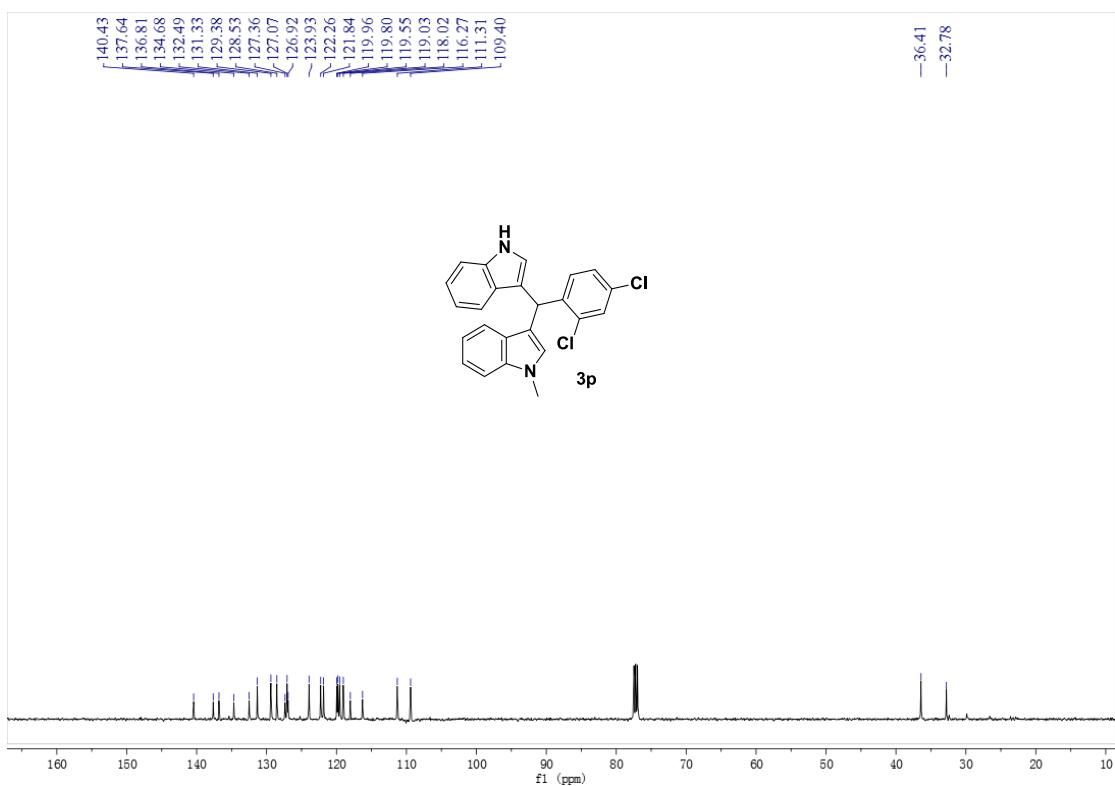
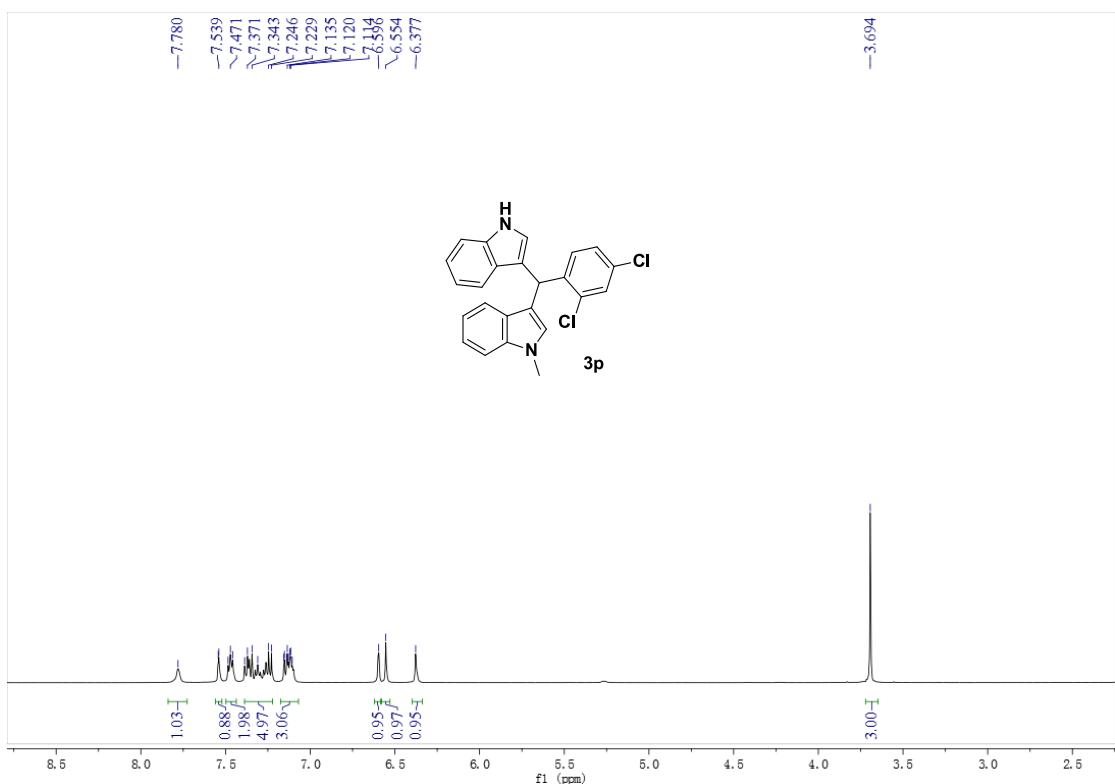
1-methyl-3-(phenyl(1-tosyl-1H-indol-3-yl)methyl)-1H-indole **3n**



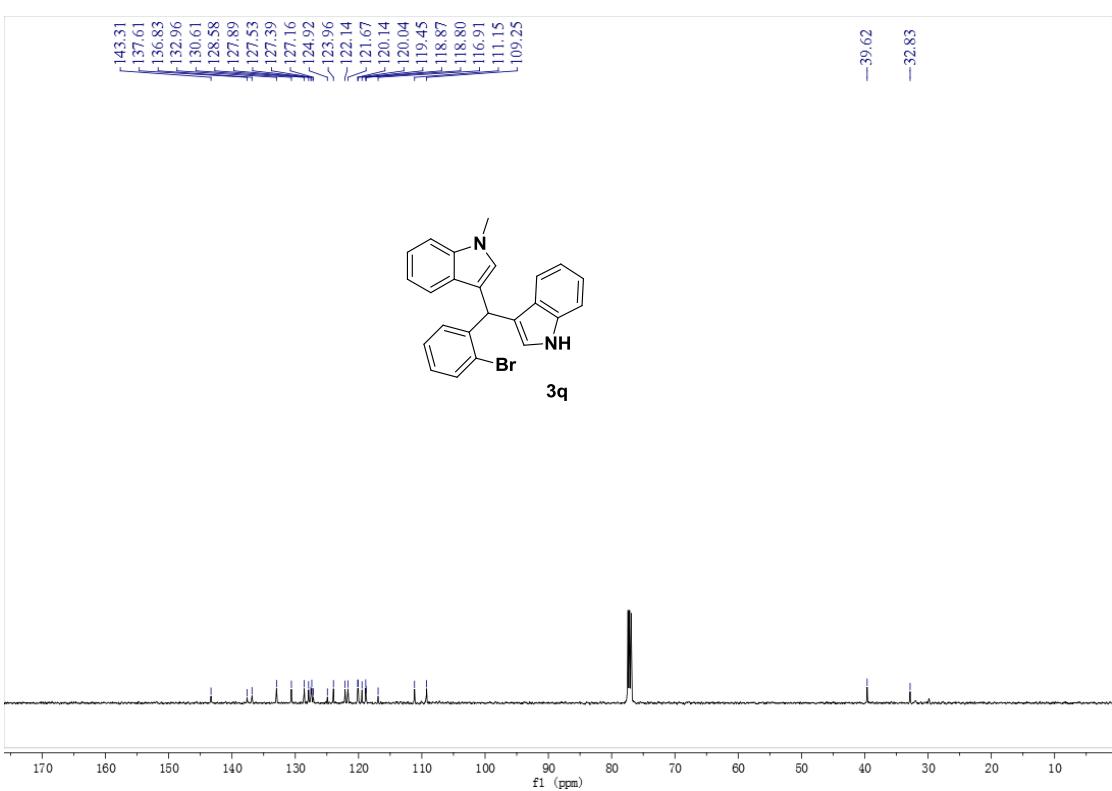
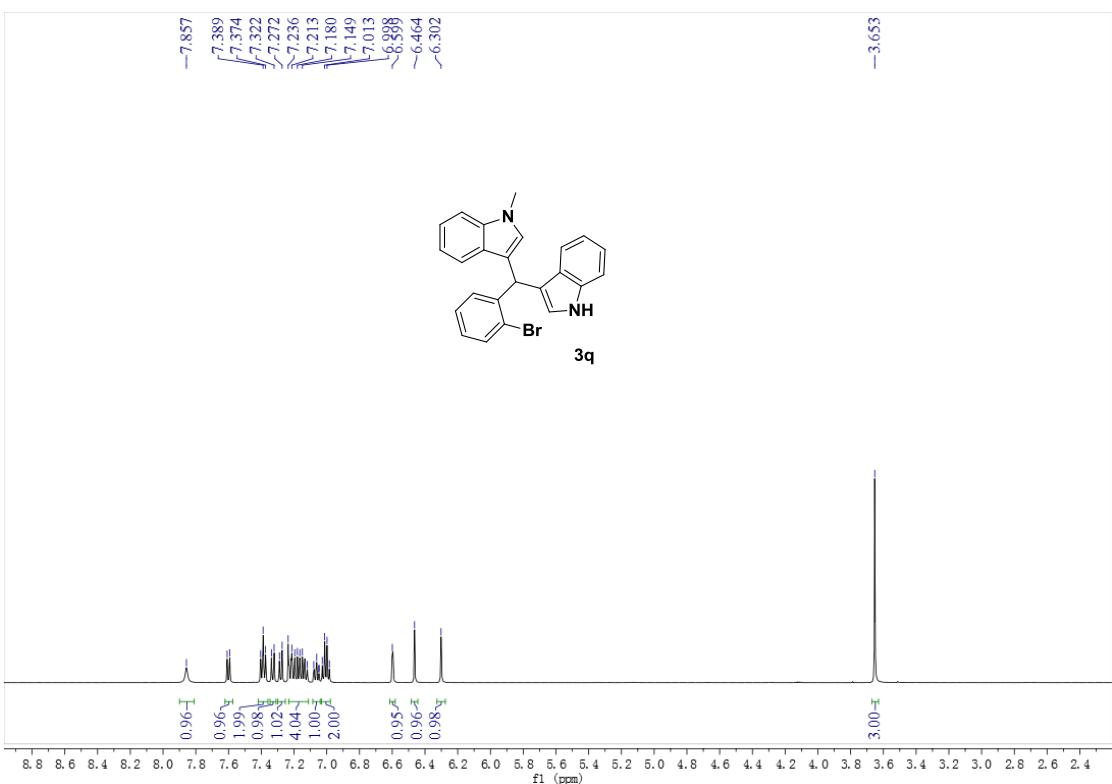
3-((1H-indol-3-yl)(p-tolyl)methyl)-1-methyl-1H-indole **3o**



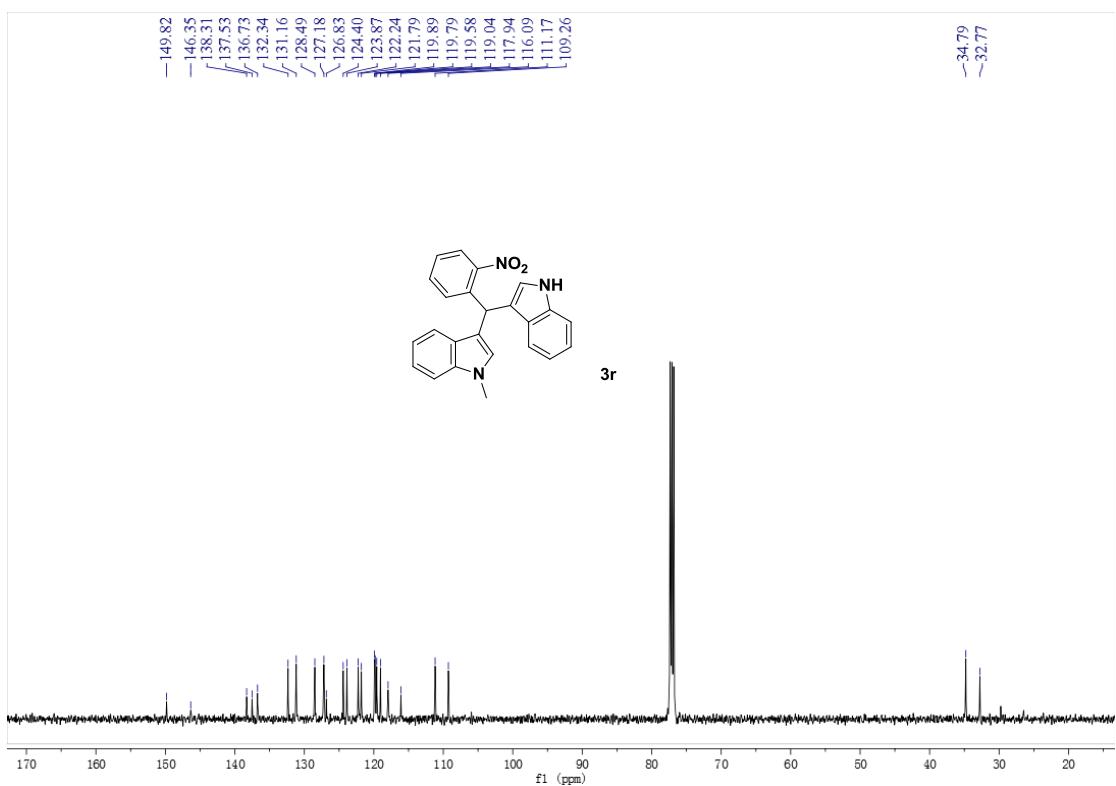
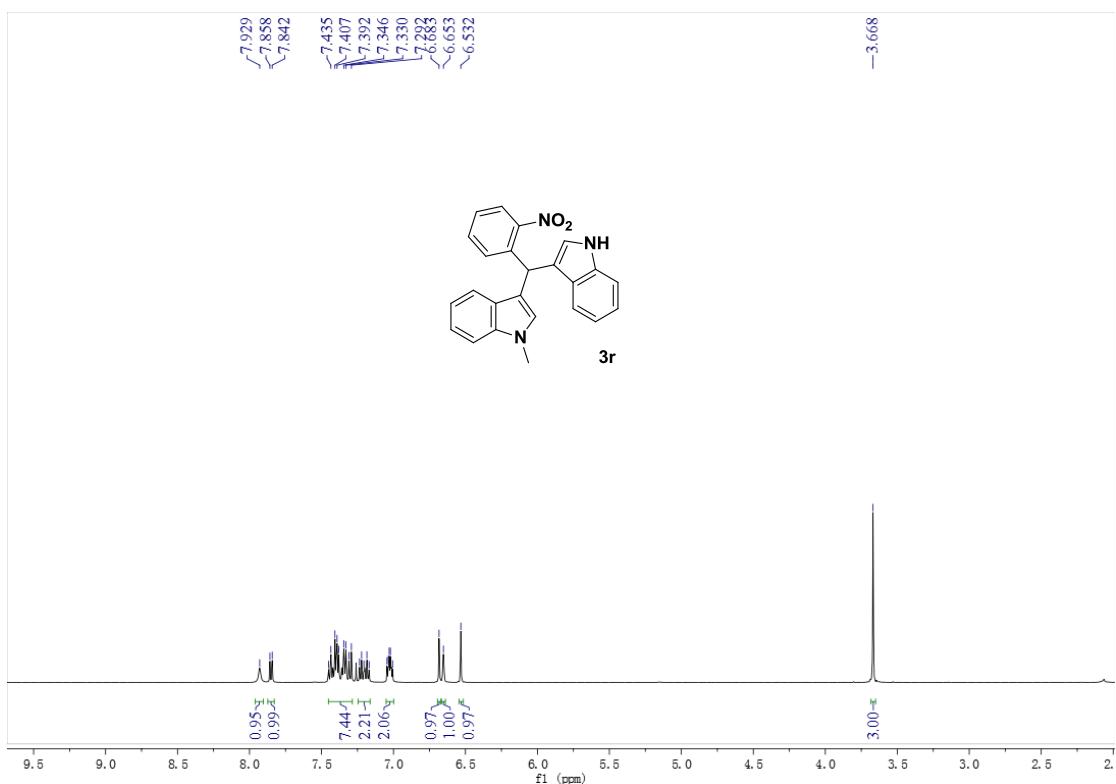
3-((2,4-dichlorophenyl)(1H-indol-3-yl)methyl)-1-methyl-1H-indole **3p**



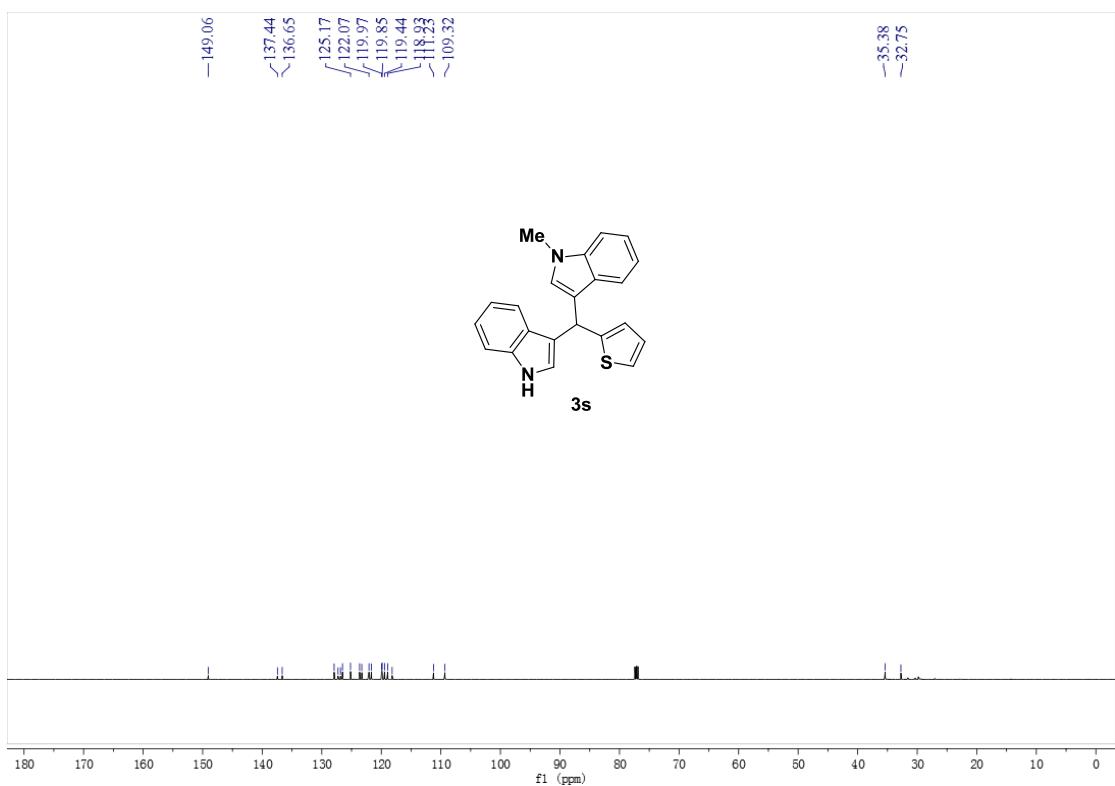
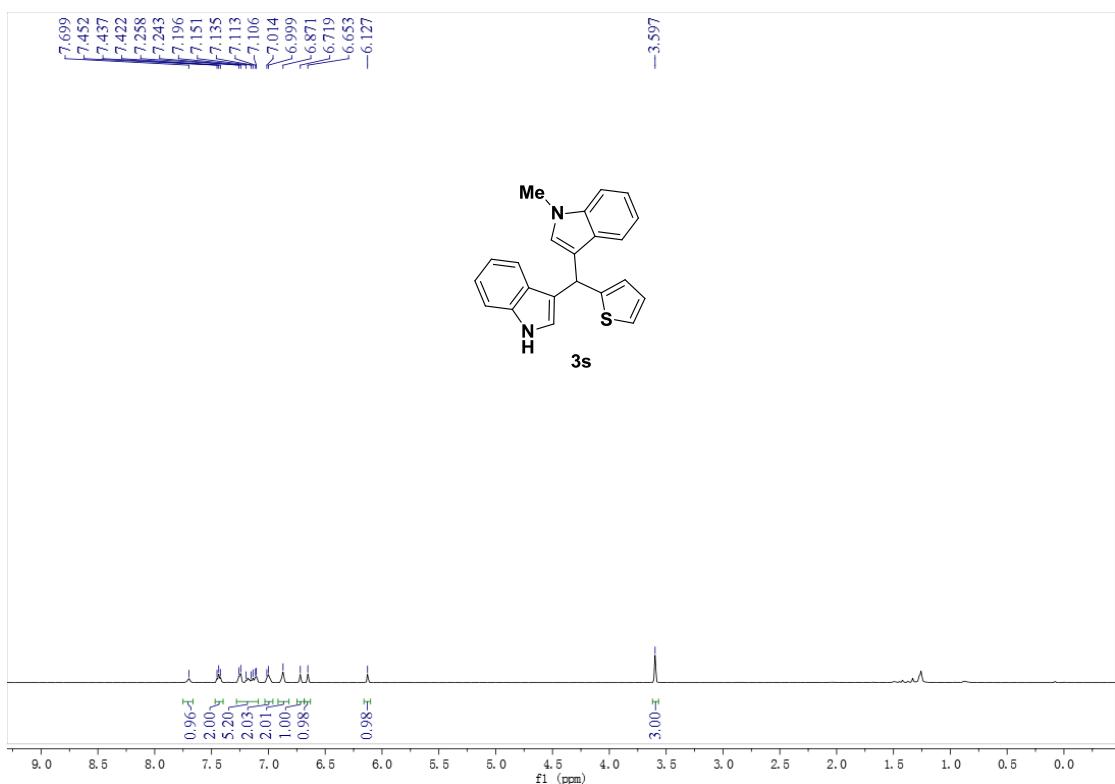
3-((2-bromophenyl)(1H-indol-3-yl)methyl)-1-methyl-1H-indole **3q**



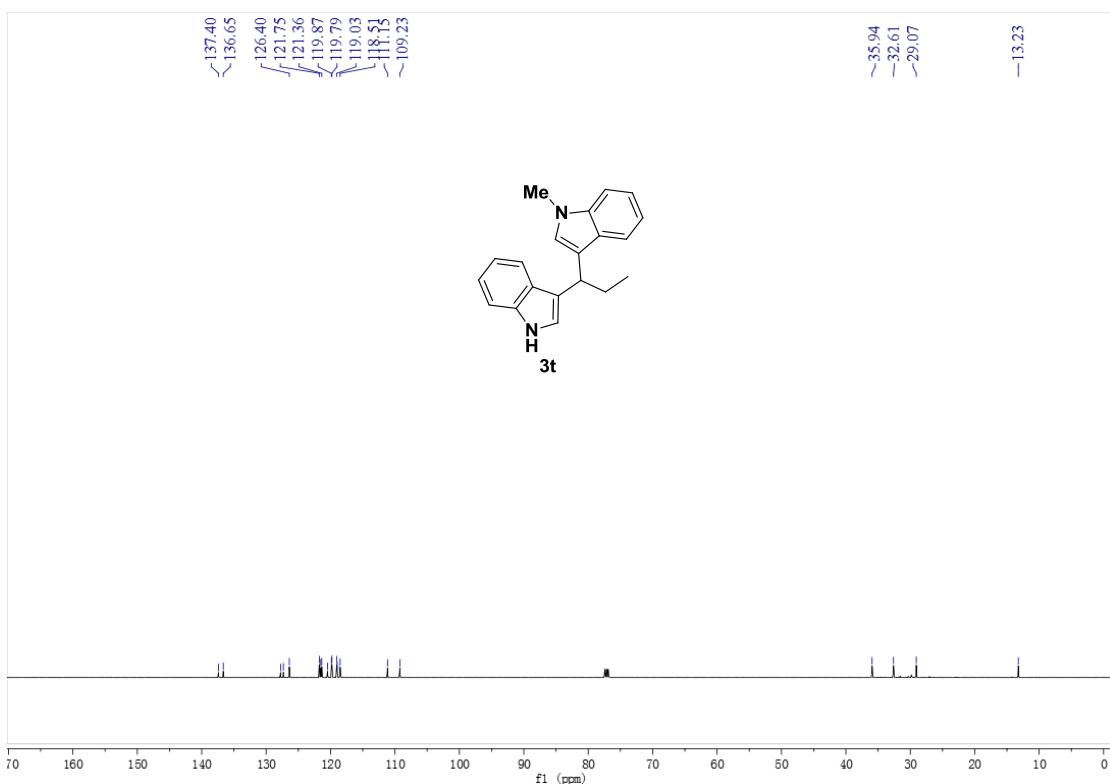
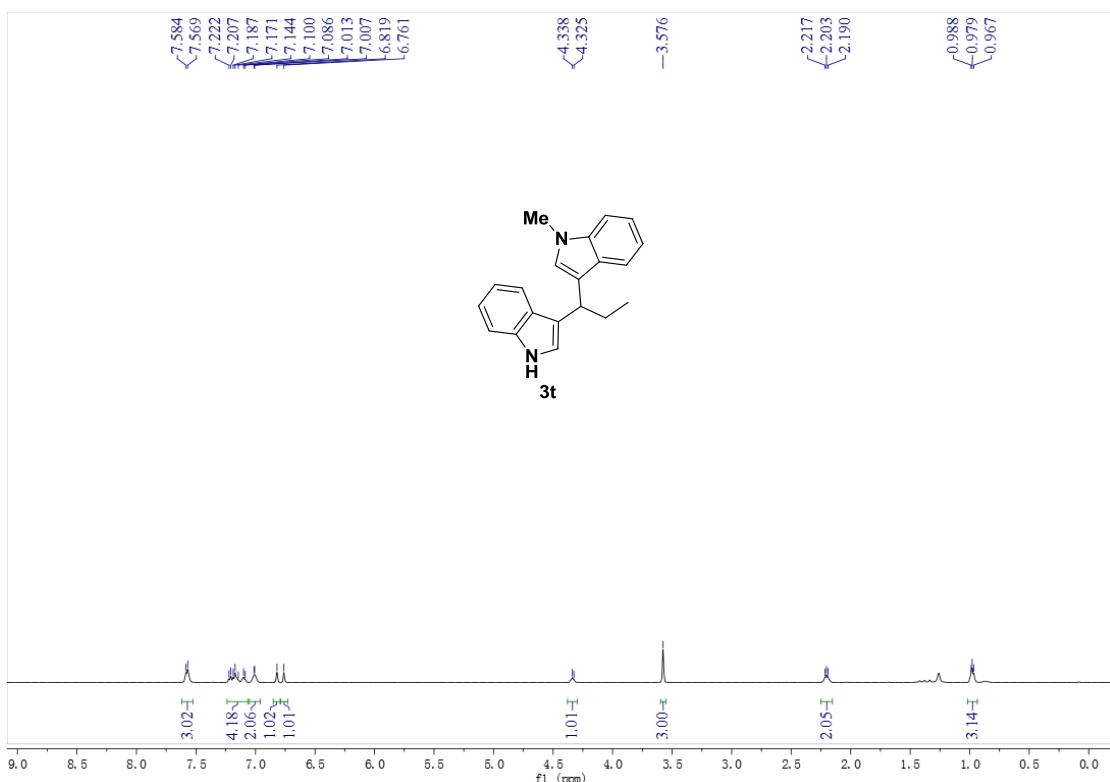
3-((1H-indol-3-yl)(2-nitrophenyl)methyl)-1-methyl-1H-indole **3r**



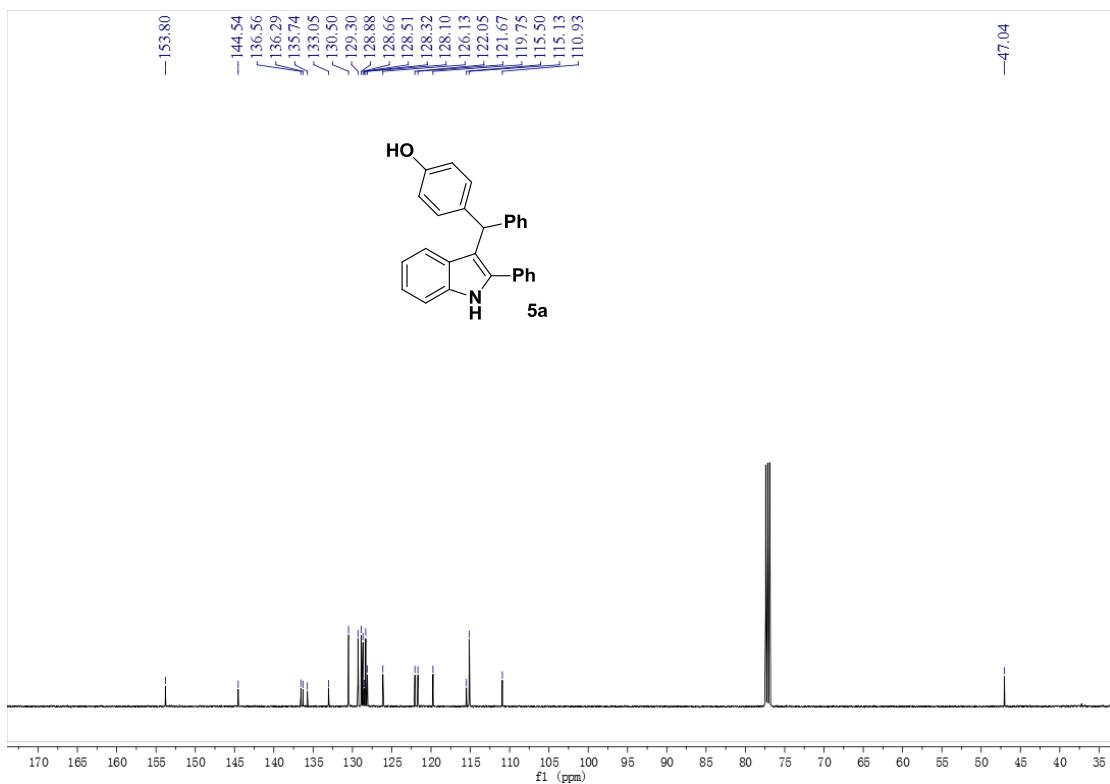
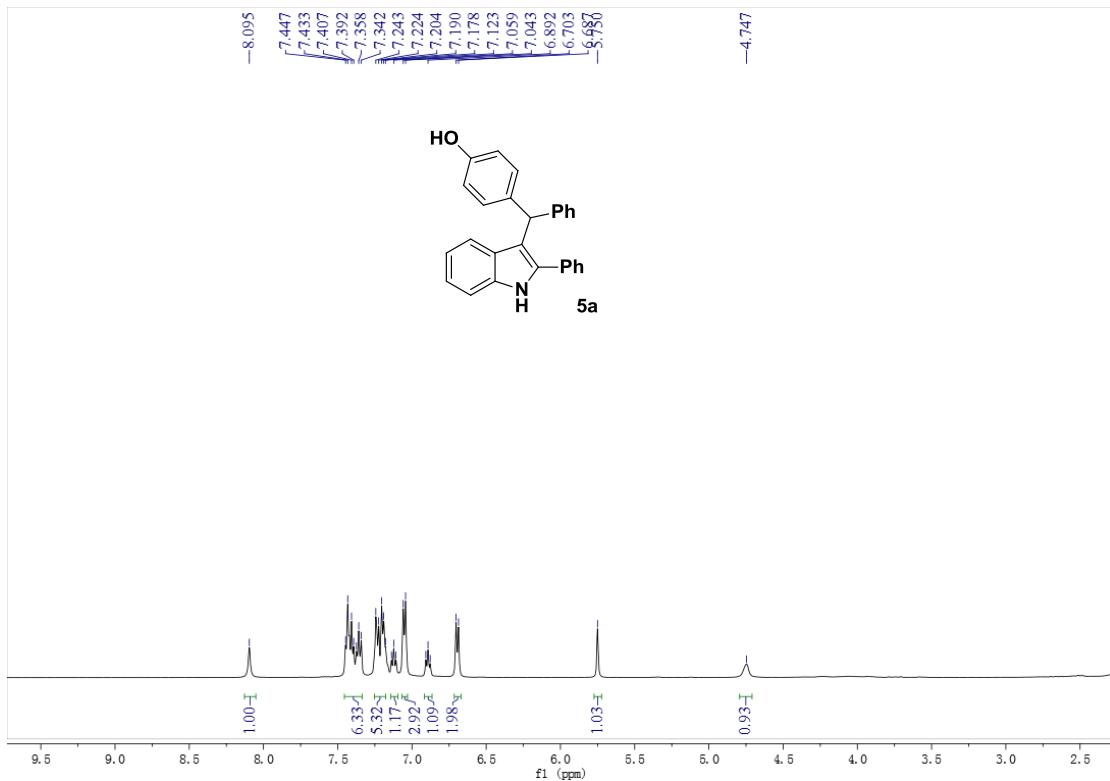
3-((1H-indol-3-yl)(thiophen-2-yl)methyl)-1-methyl-1H-indole 3s



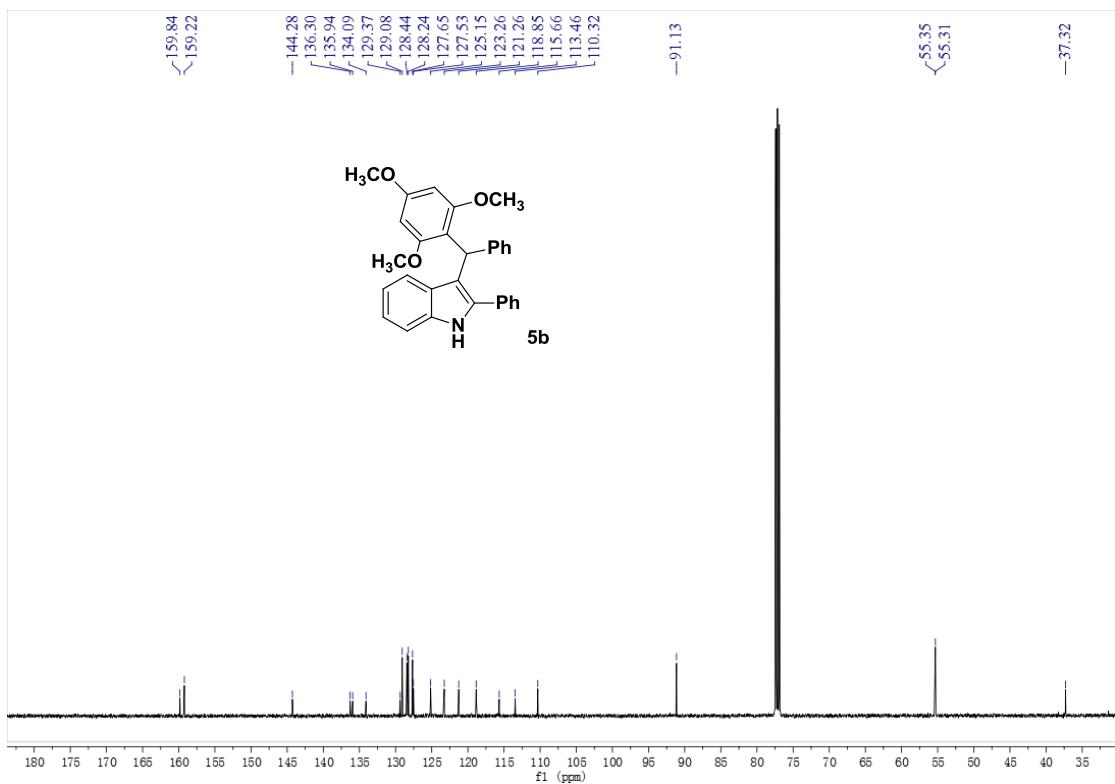
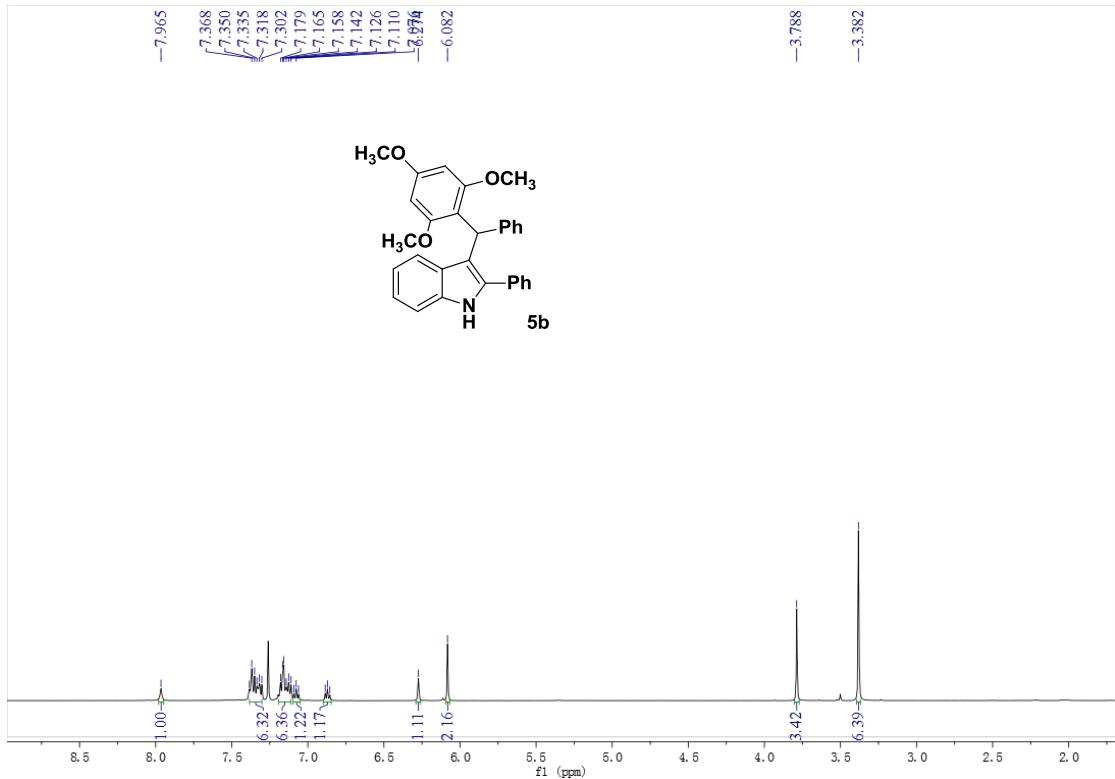
3-(1-(1H-indol-3-yl)propyl)-1-methyl-1H-indole 3t



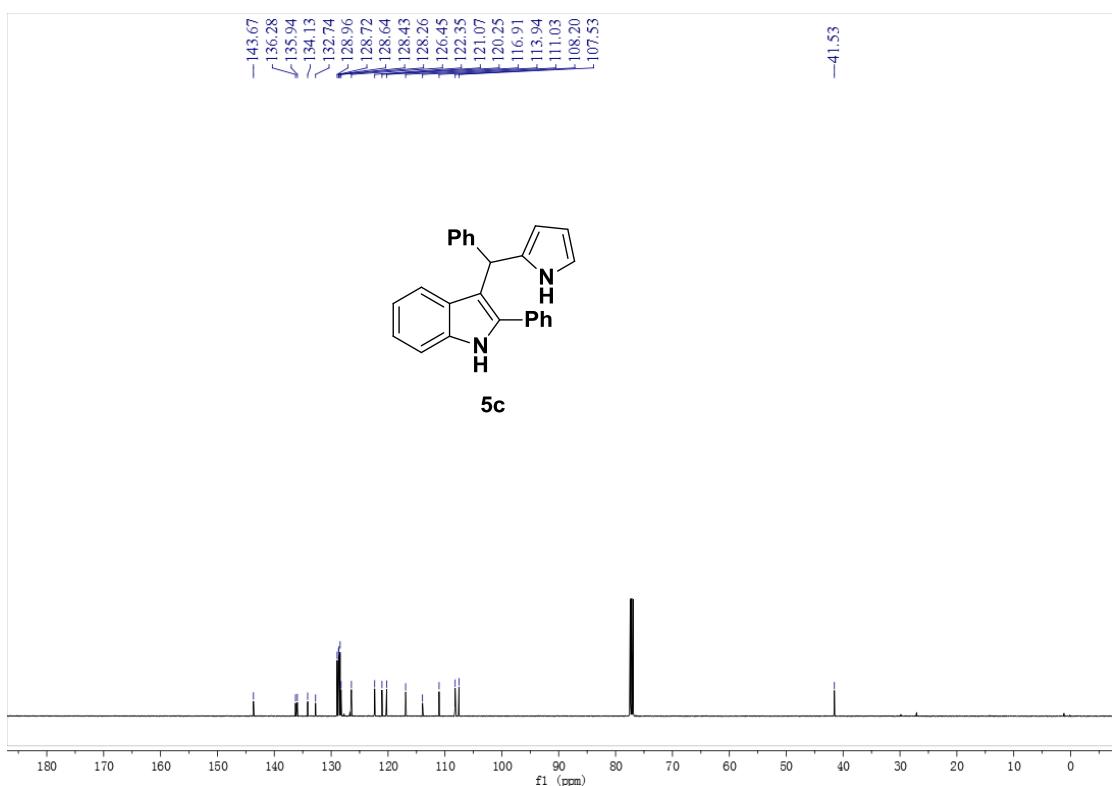
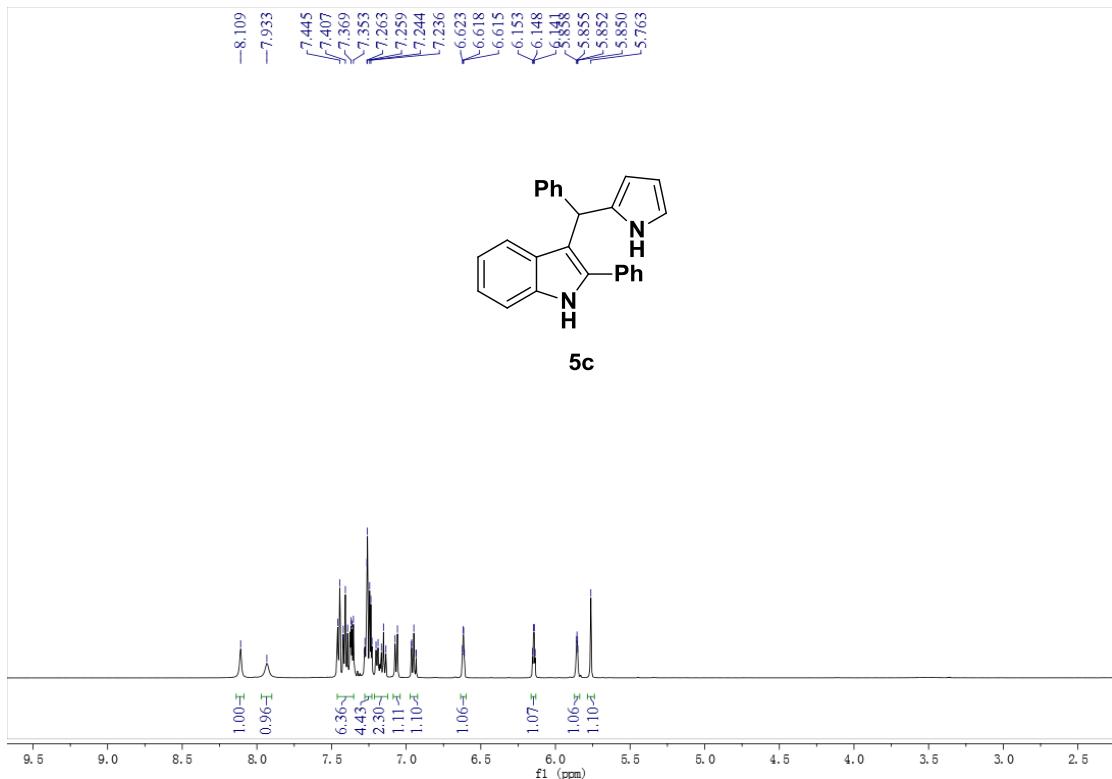
4-(phenyl(2-phenyl-1H-indol-3-yl)methyl)phenol **5a**



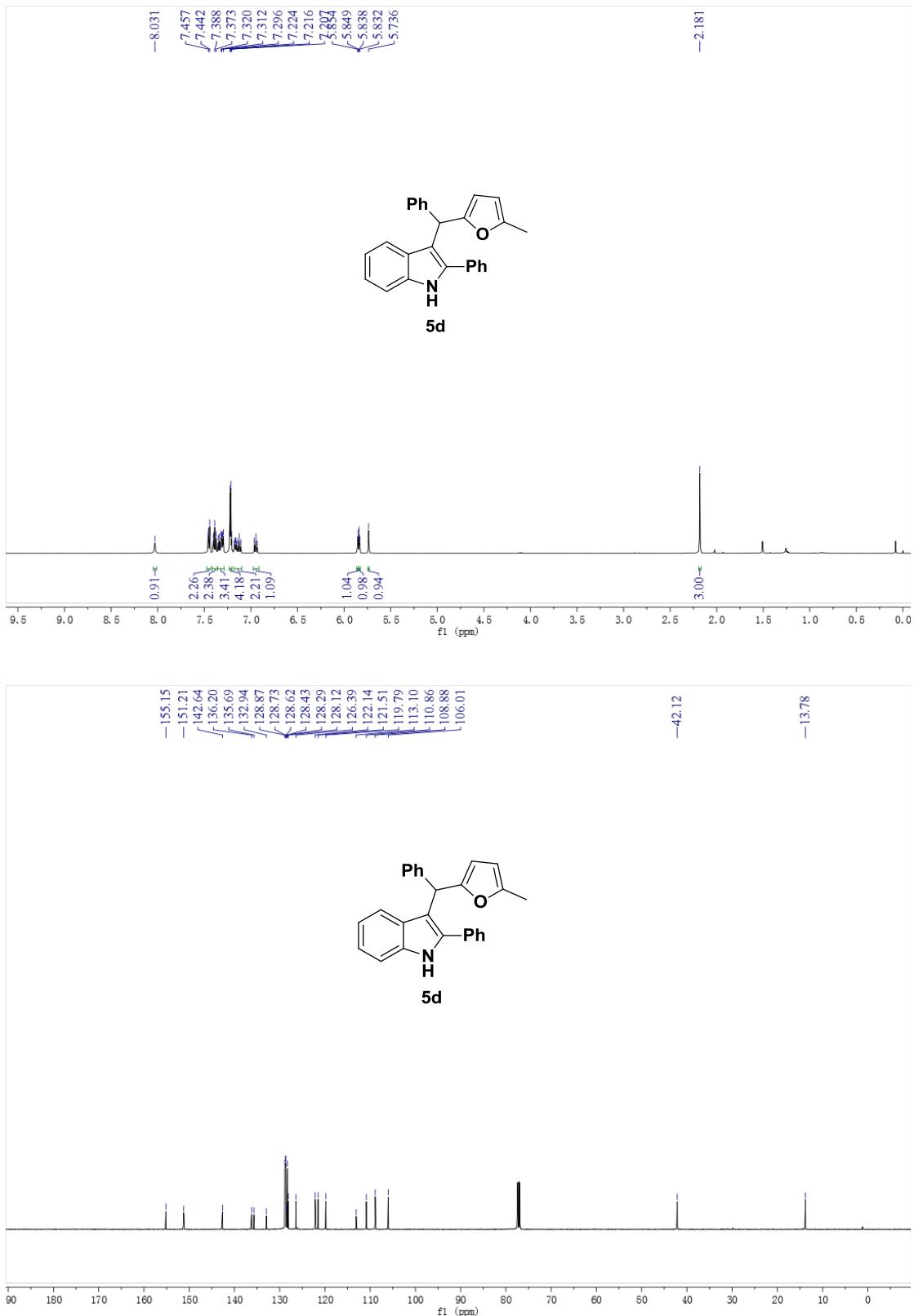
2-phenyl-3-(phenyl(2,4,6-trimethoxyphenyl)methyl)-1H-indole **5b**



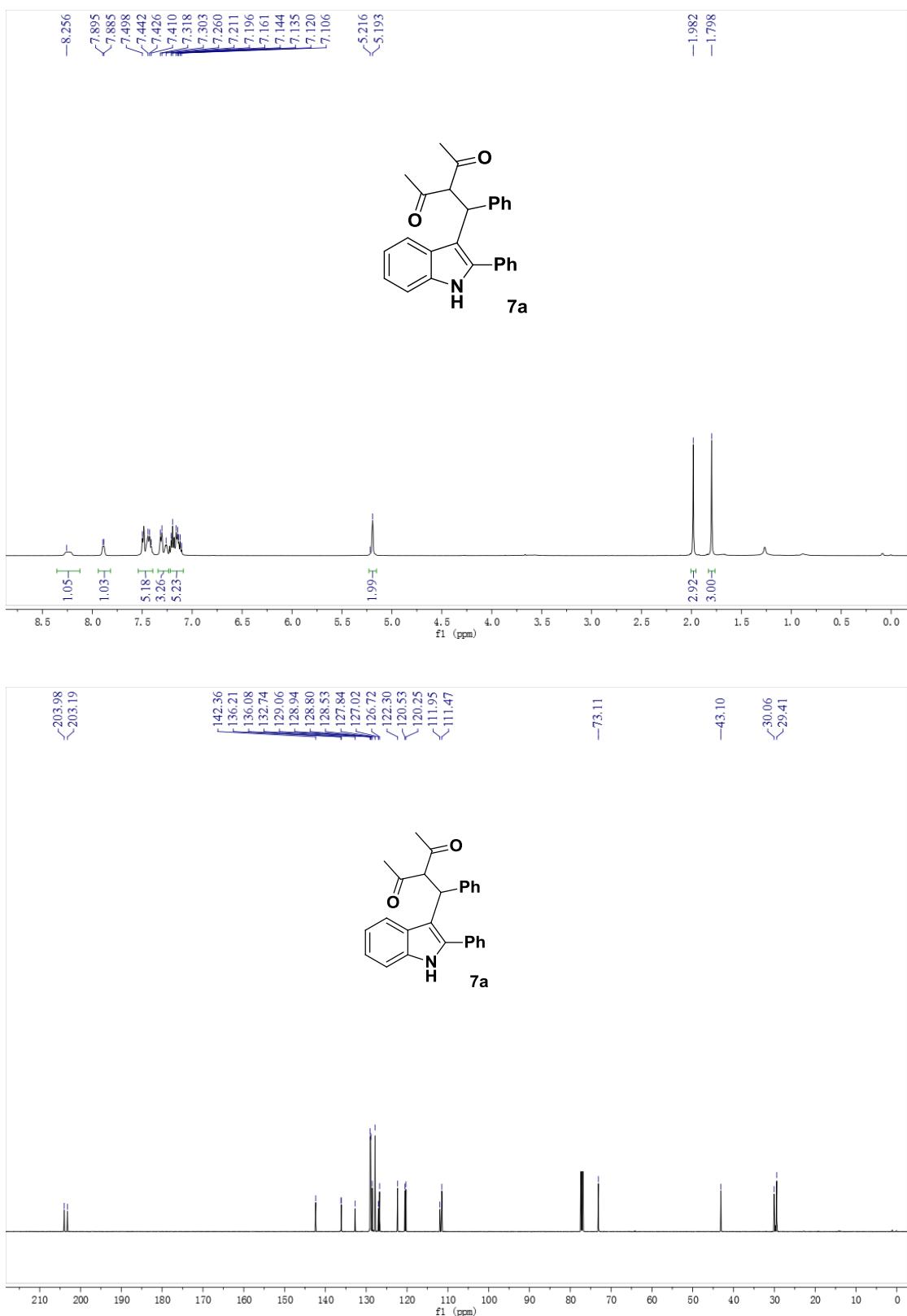
2-phenyl-3-(phenyl(1H-pyrrol-2-yl)methyl)-1H-indole **5c**



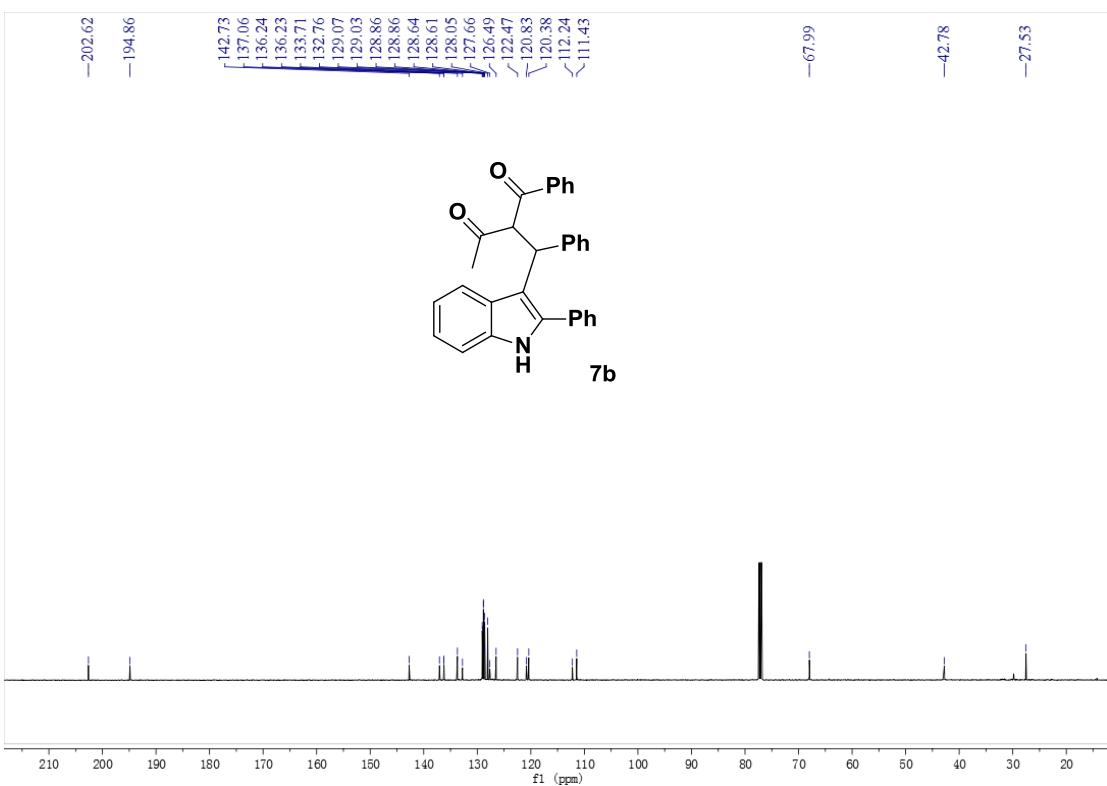
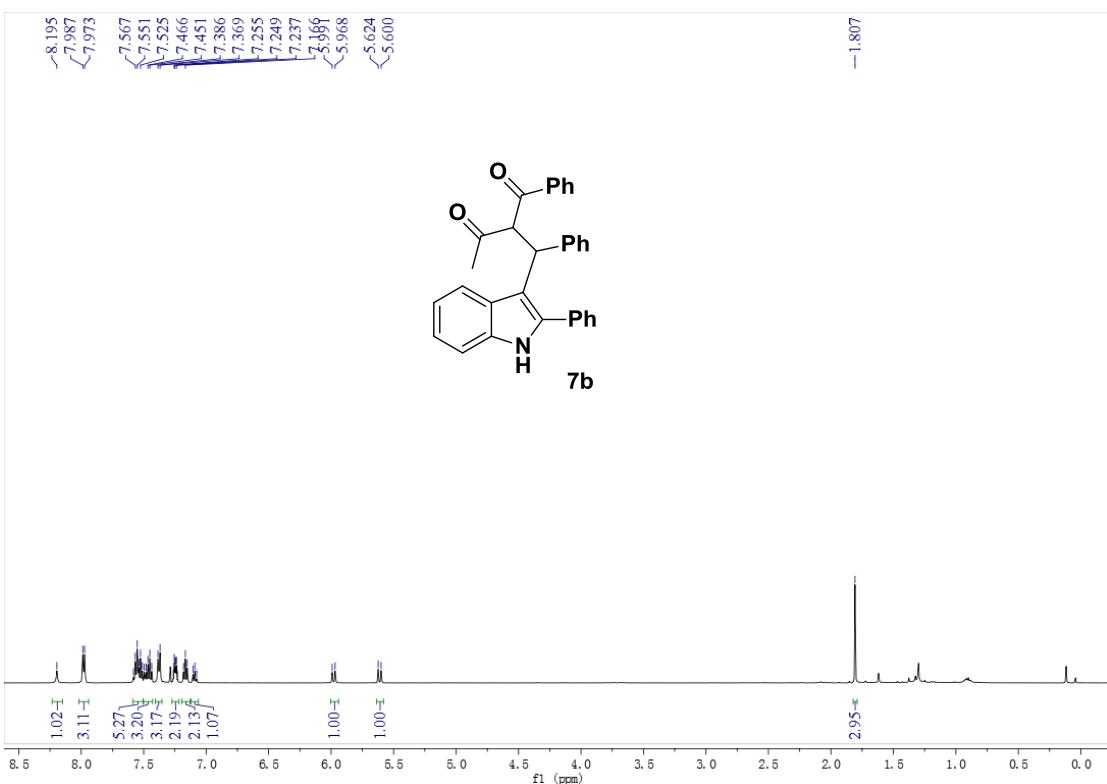
3-((5-methylfuran-2-yl)(phenyl)methyl)-2-phenyl-1H-indole **5d**



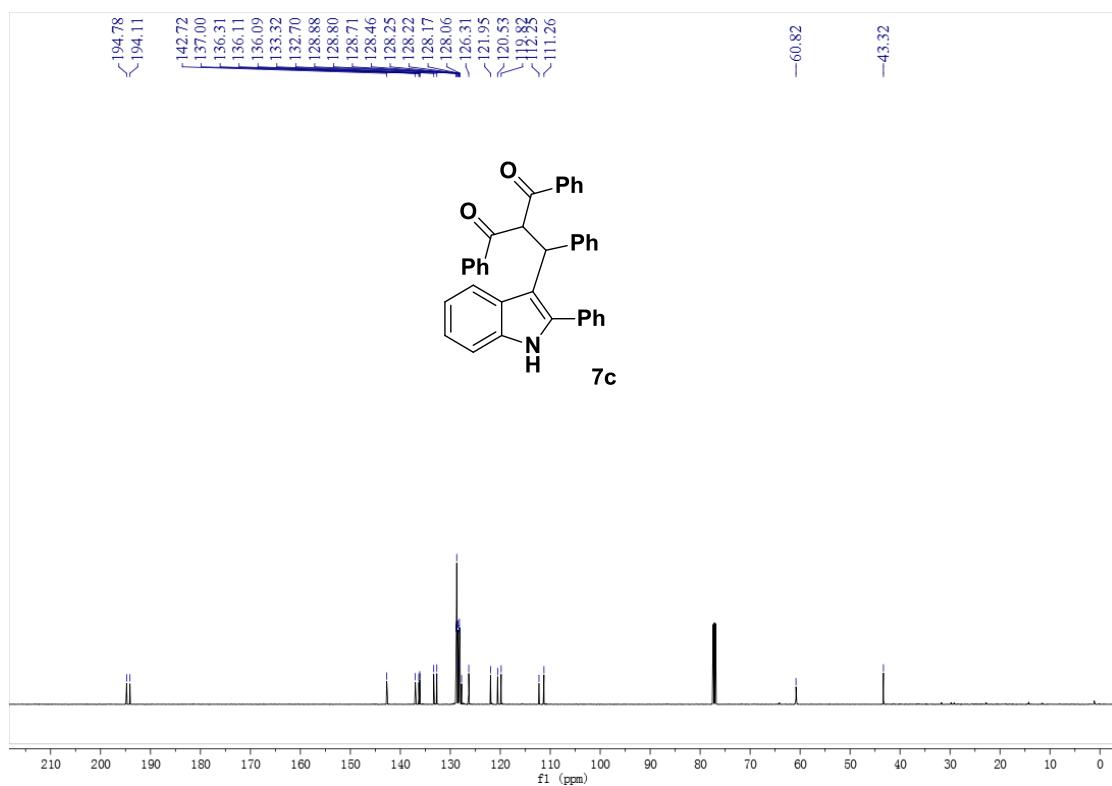
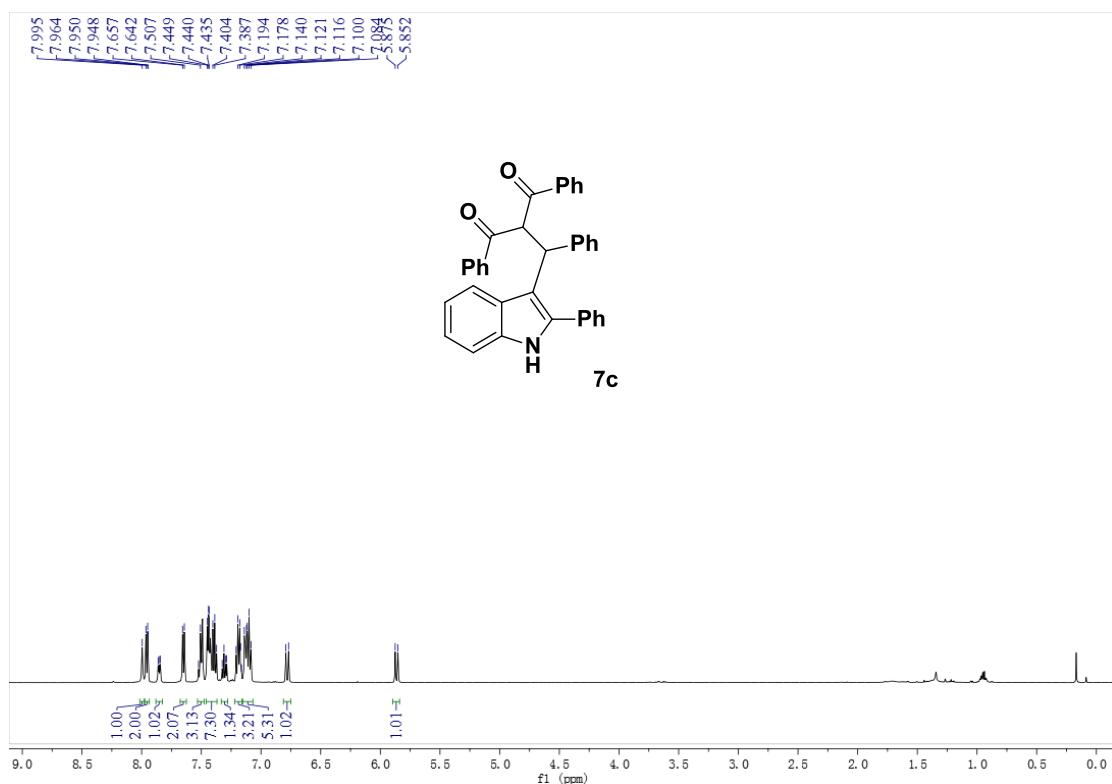
3-(phenyl(2-phenyl-1H-indol-3-yl)methyl)pentane-2,4-dione **7a**



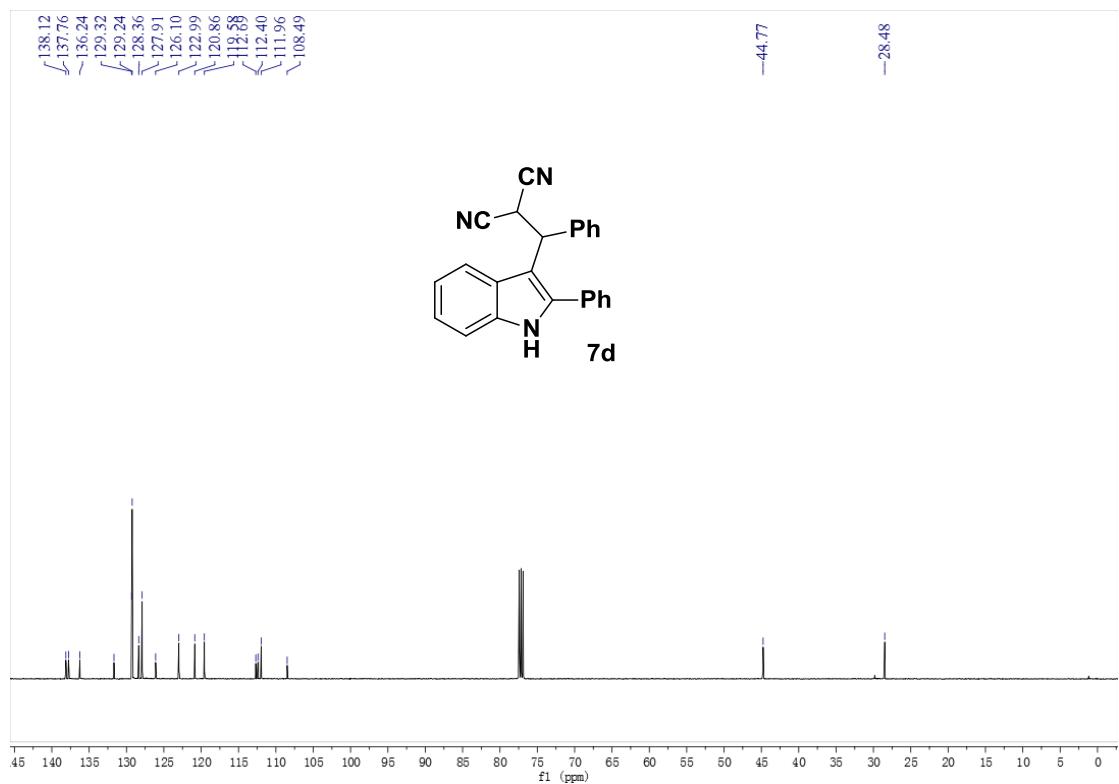
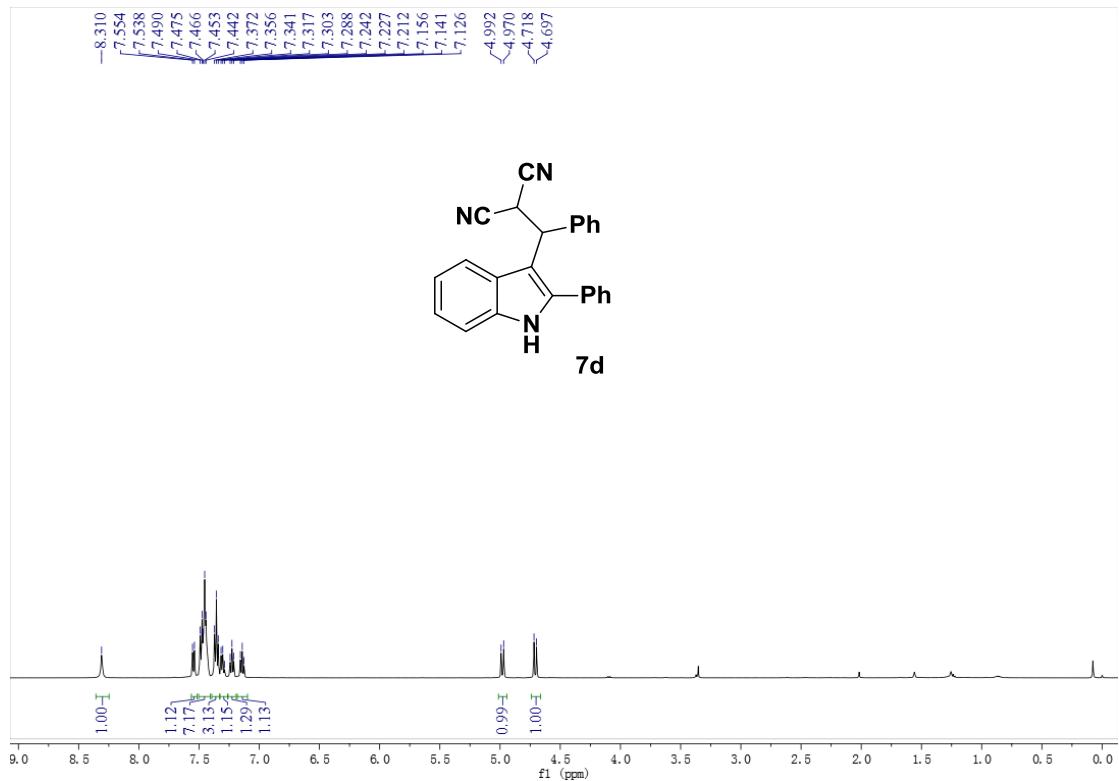
1-phenyl-2-(phenyl(2-phenyl-1H-indol-3-yl)methyl)butane-1,3-dione **7b**



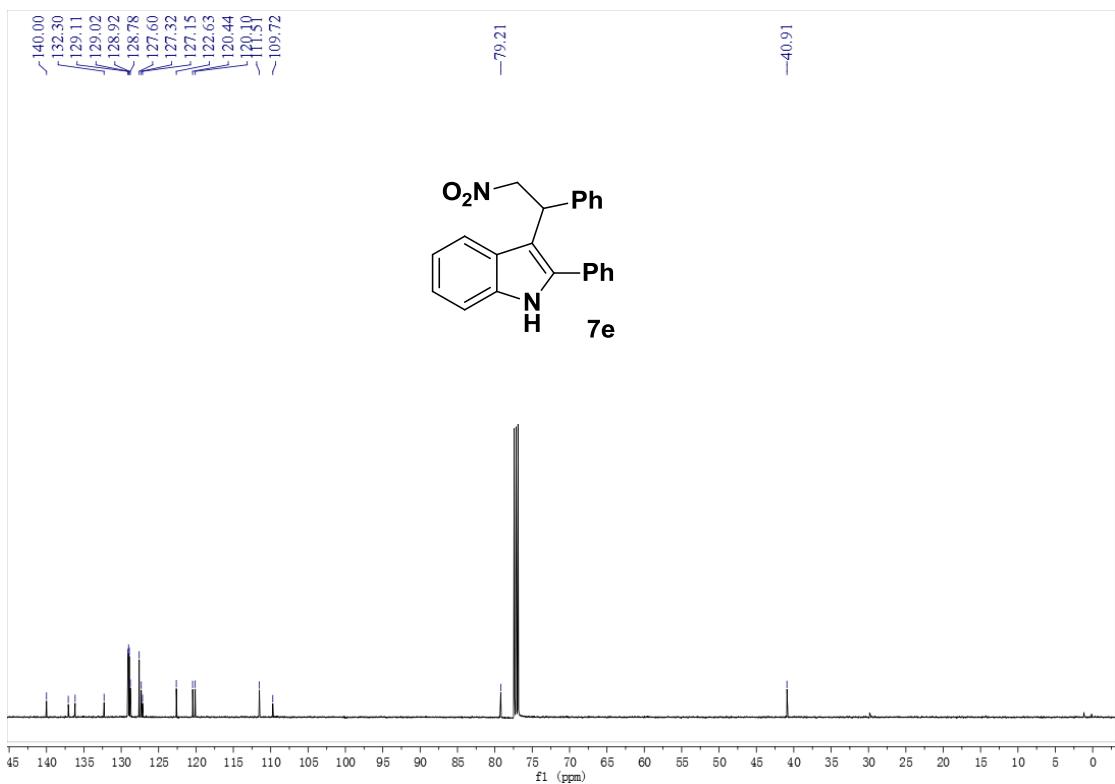
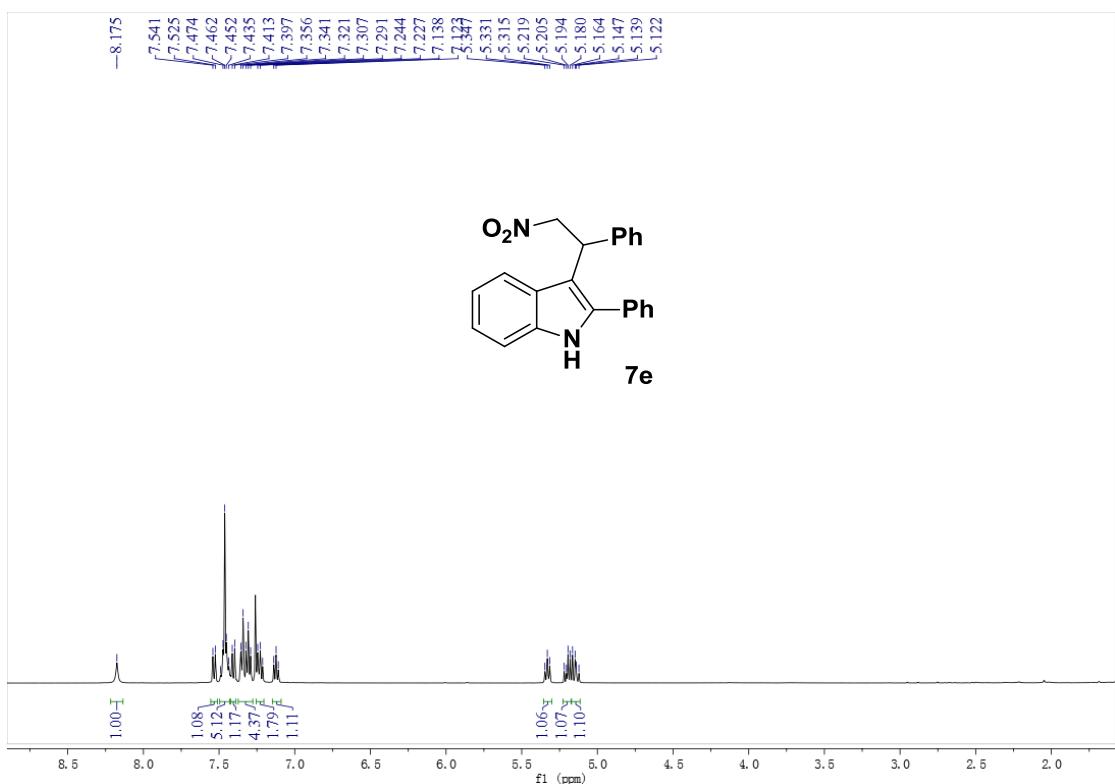
1,3-diphenyl-2-(phenyl(2-phenyl-1H-indol-3-yl)methyl)propane-1,3-dione **7c**



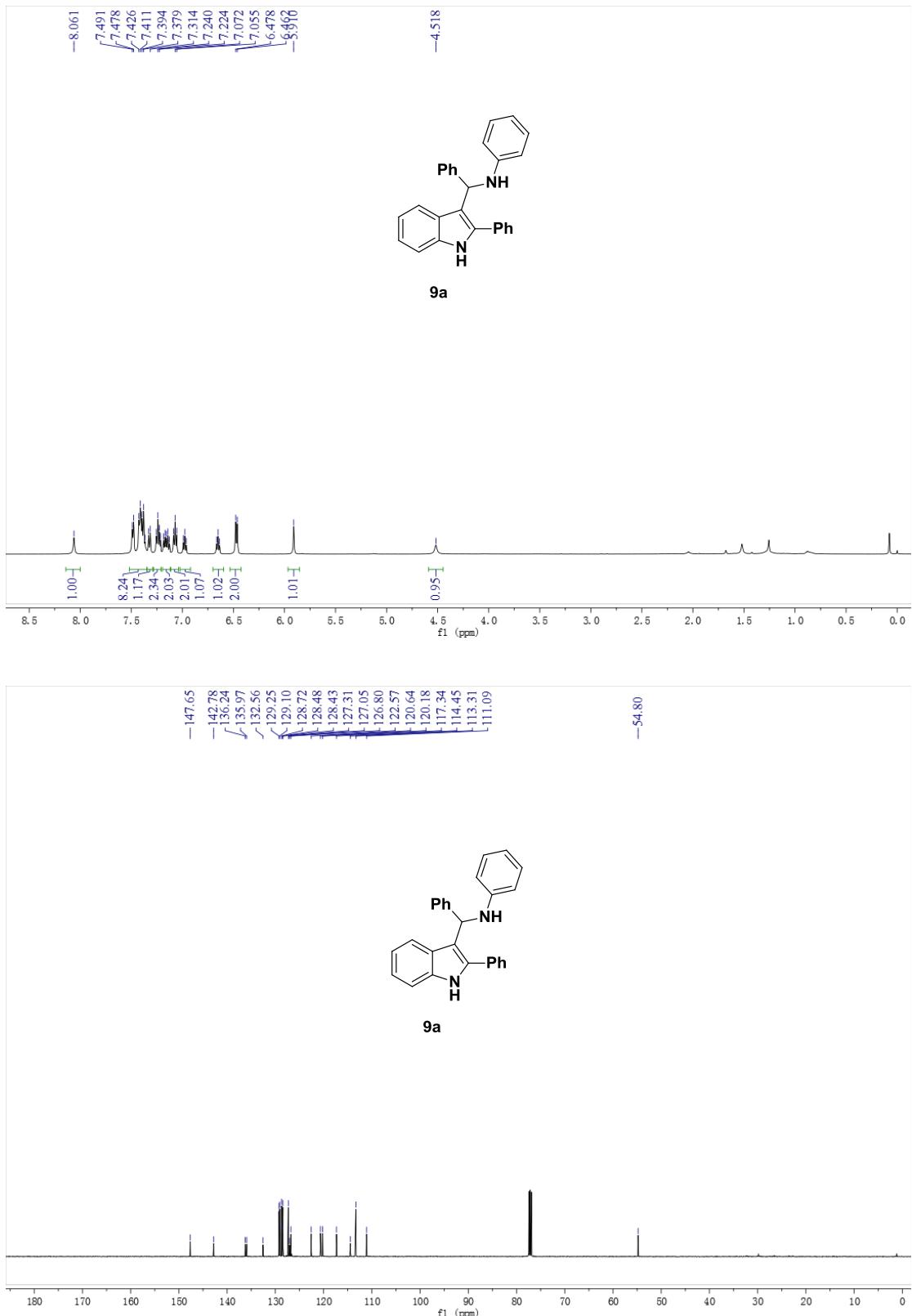
2-(phenyl(2-phenyl-1H-indol-3-yl)methyl)malononitrile **7d**



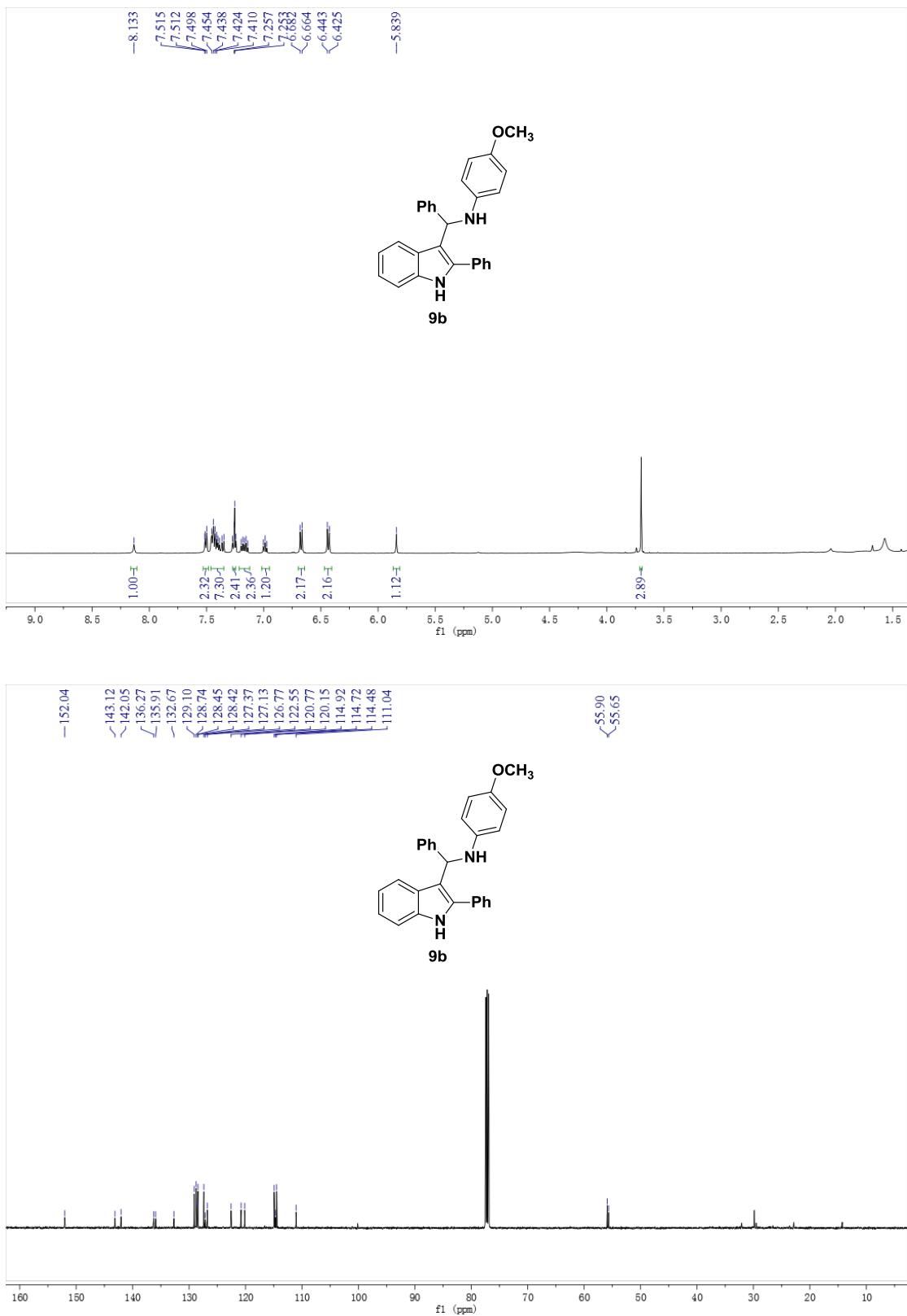
3-(2-nitro-1-phenylethyl)-2-phenyl-1H-indole **7e**



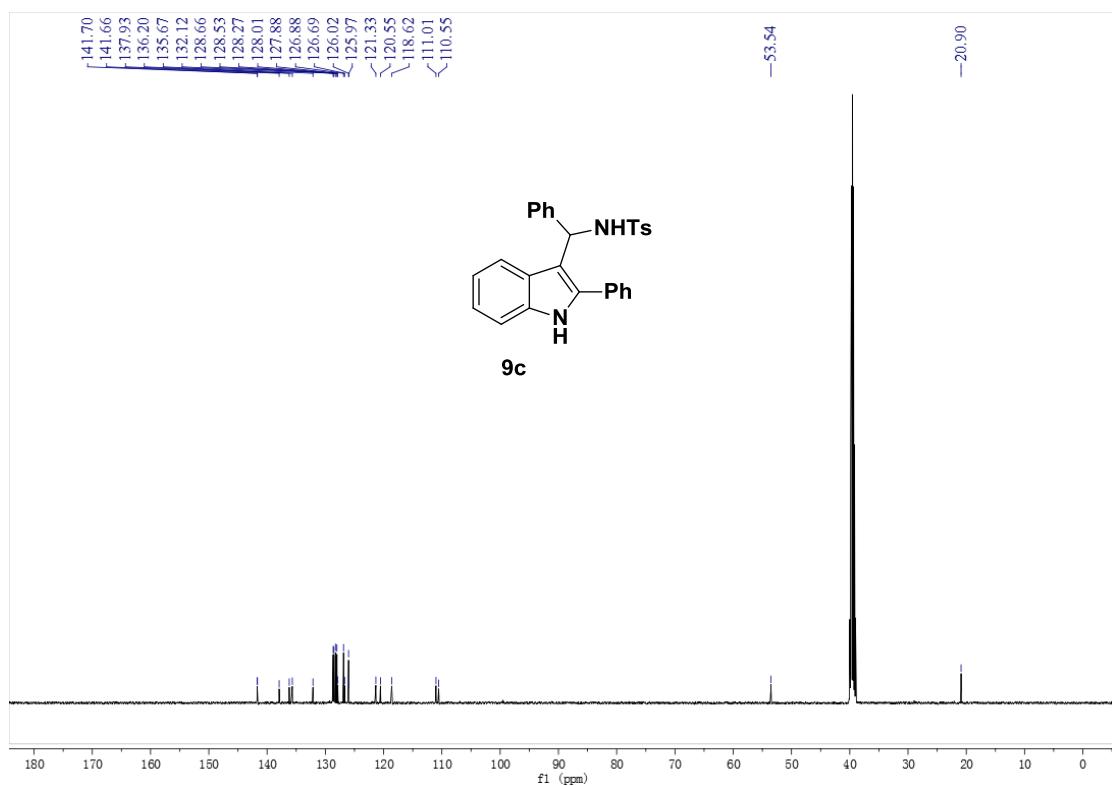
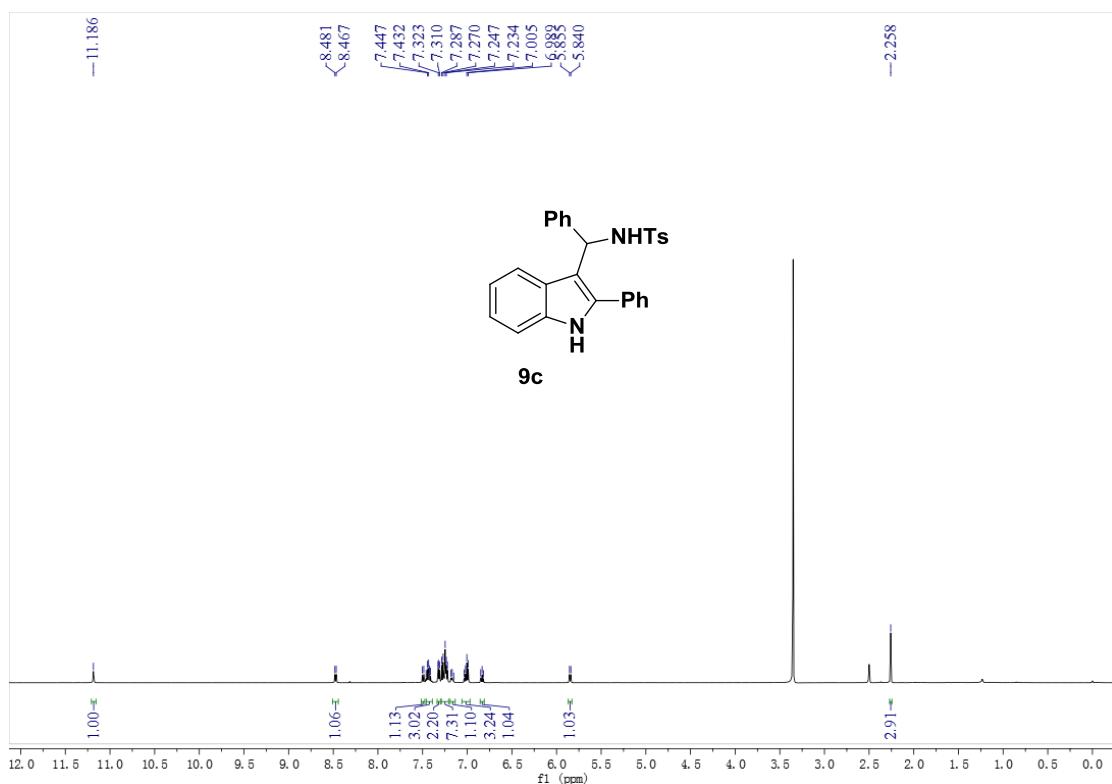
N-(phenyl(2-phenyl-1H-indol-3-yl)methyl)aniline **9a**



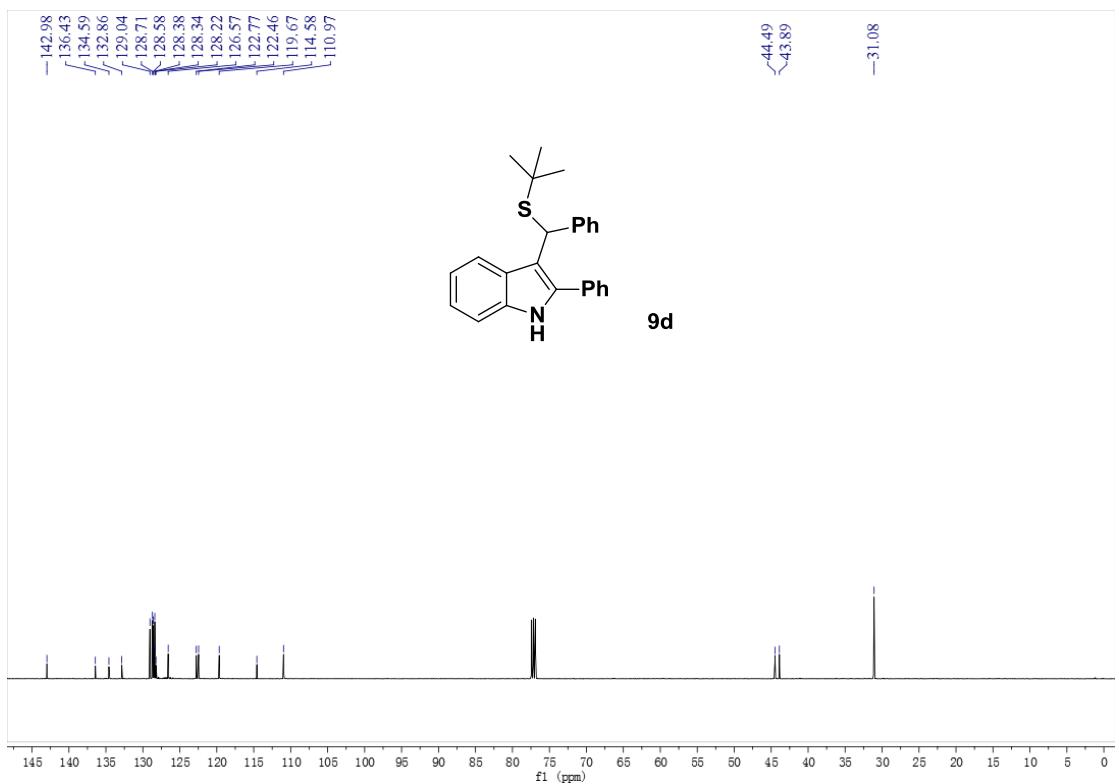
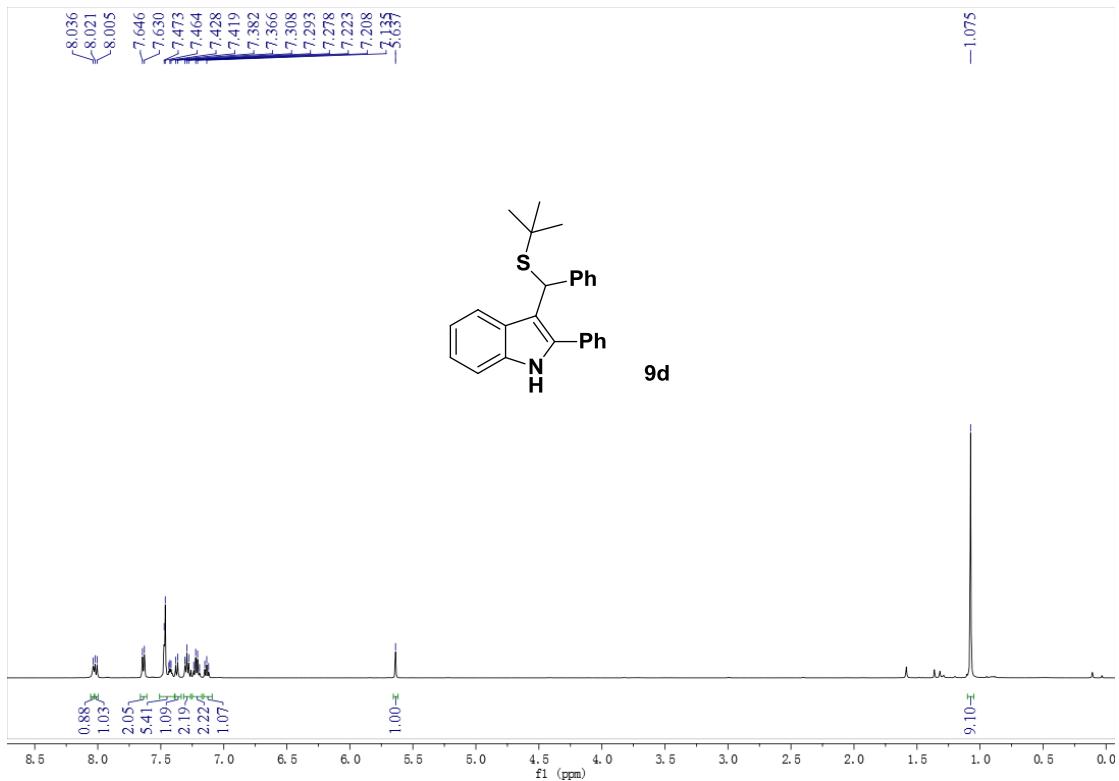
4-methoxy-N-(phenyl(2-phenyl-1H-indol-3-yl)methyl)aniline **9b**



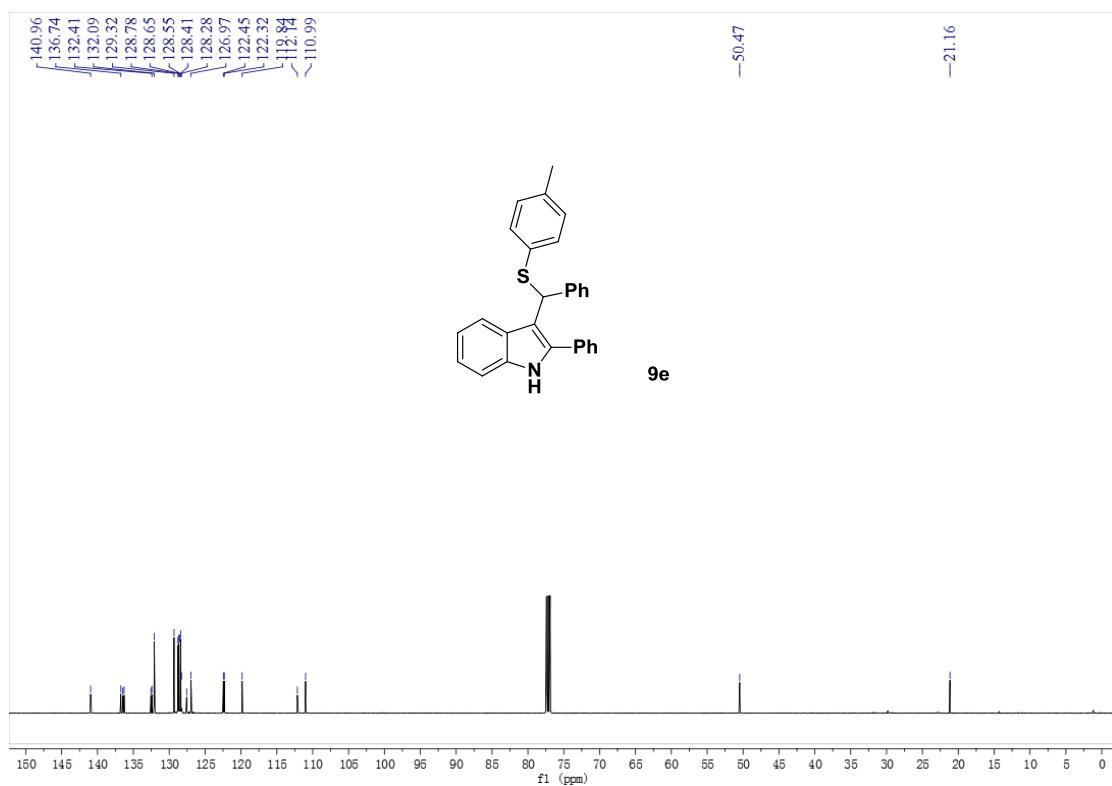
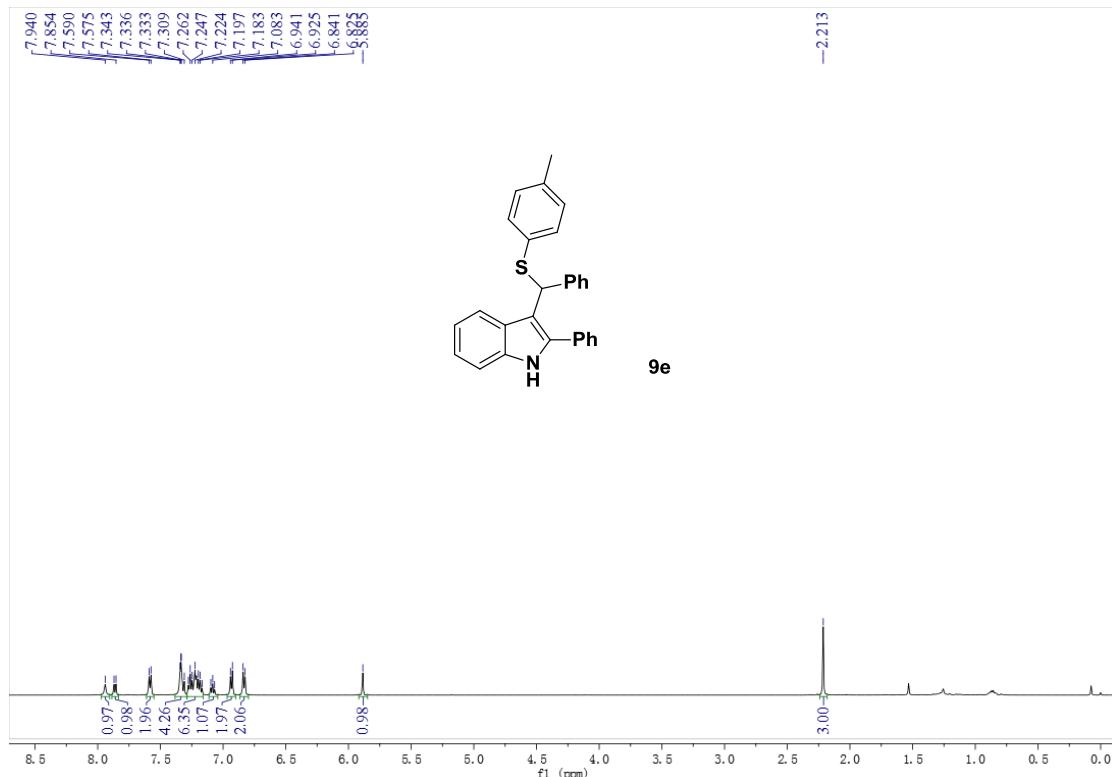
4-methyl-N-(phenyl(2-phenyl-1H-indol-3-yl)methyl)benzenesulfonamide **9c**



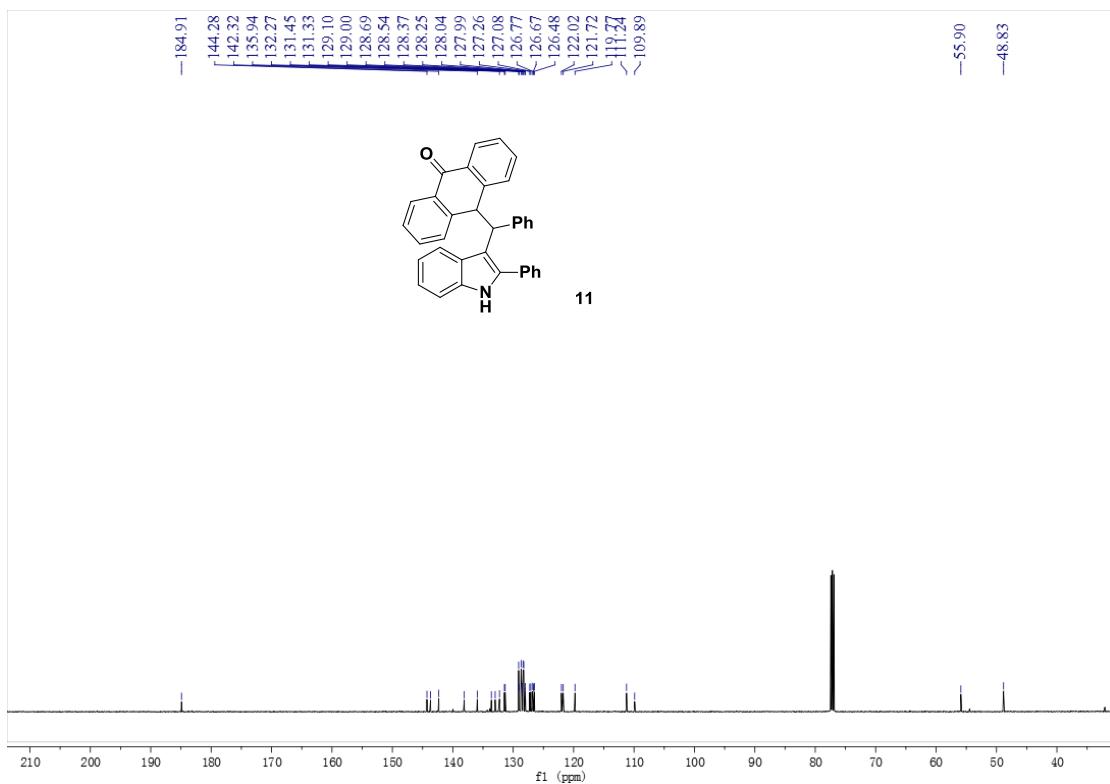
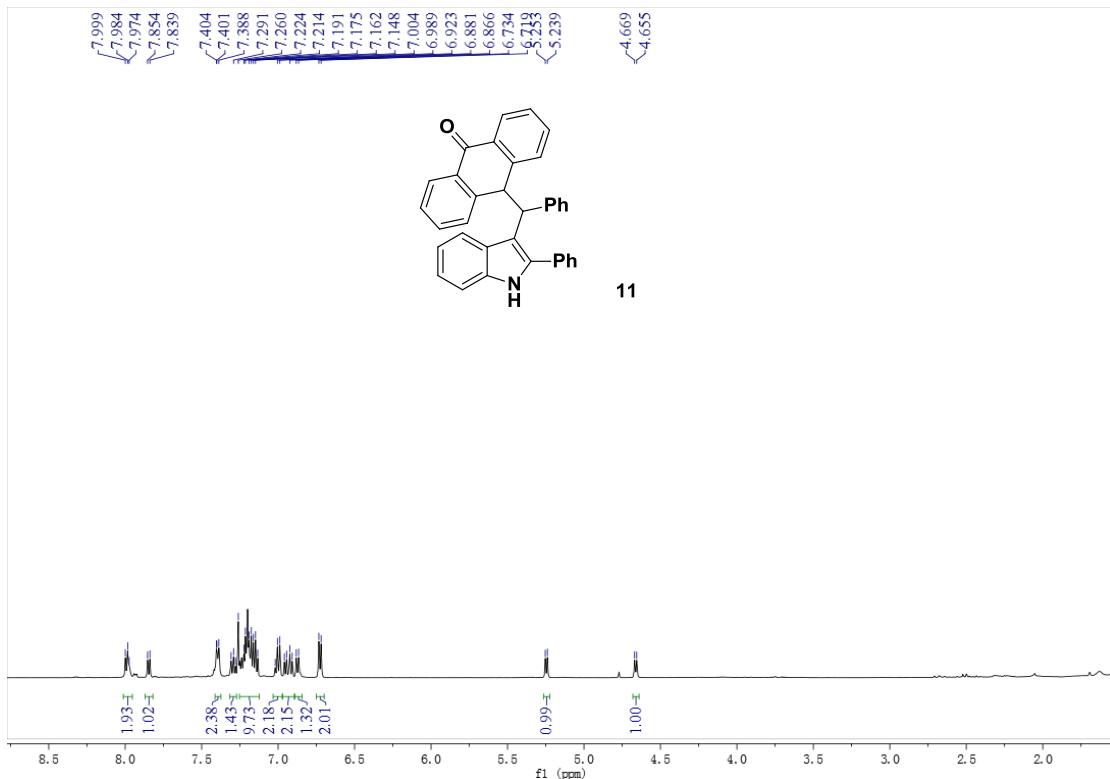
3-((tert-butylthio)(phenyl)methyl)-2-phenyl-1H-indole **9d**



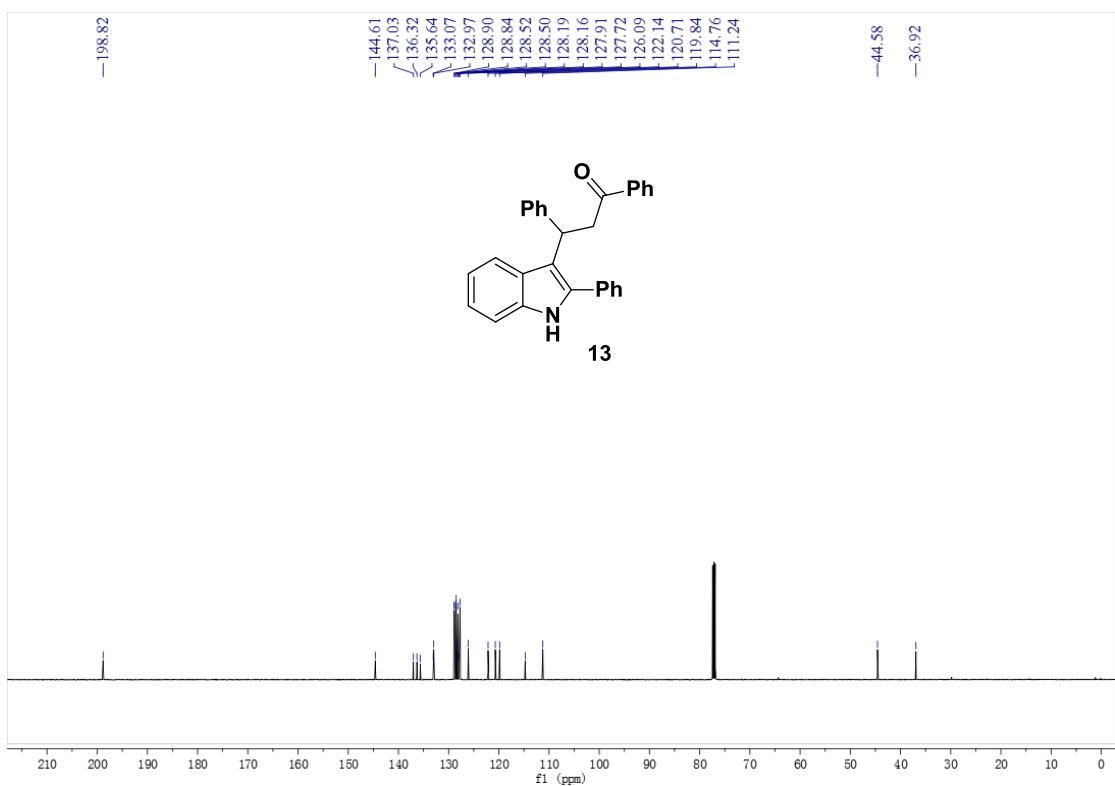
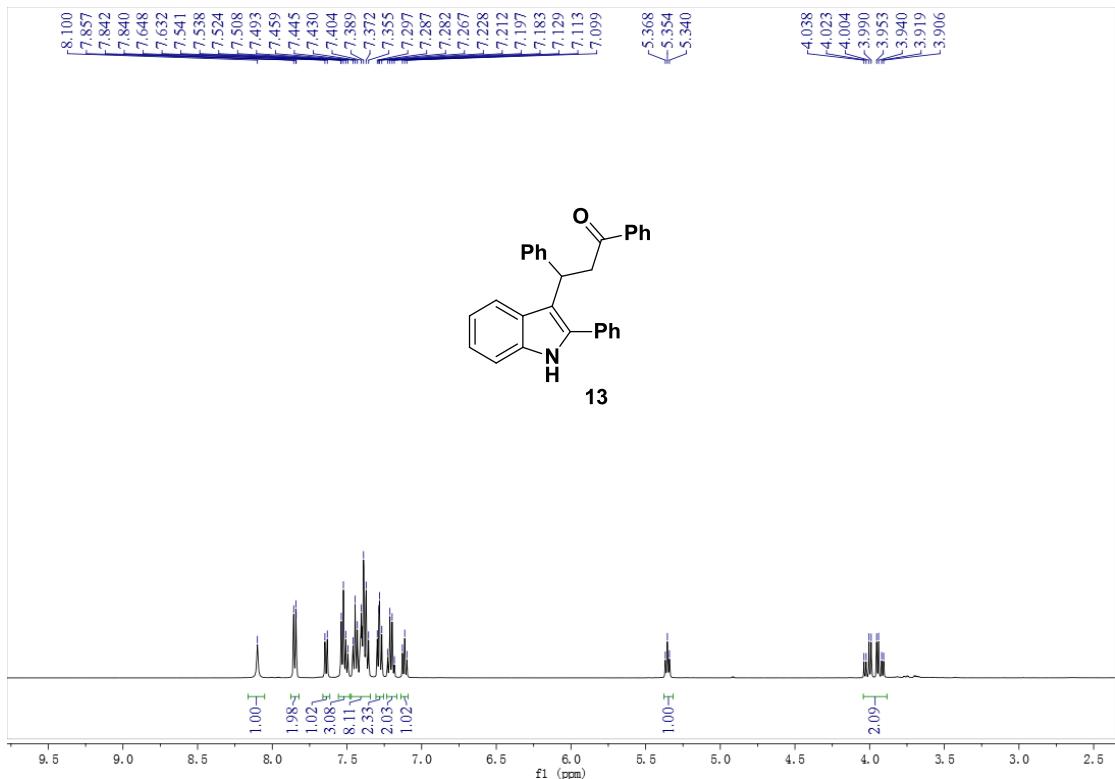
2-phenyl-3-(phenyl(p-tolylthio)methyl)-1H-indole **9e**



10-(phenyl(2-phenyl-1H-indol-3-yl)methyl)anthracen-9(10H)-one **11**



1,3-diphenyl-3-(2-phenyl-1H-indol-3-yl)propan-1-one **13**



2-phenyl-2-(2-phenyl-1H-indol-3-yl)acetonitrile **14**

