

FeCl₃-Mediated Radical Tandem Reactions of 3-Benzyl-2-Oxindoles with Styrene Derivatives for the Stereoselective Synthesis of Spirocyclohexene Oxindoles

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1. General Method

All the ¹H and ¹³C NMR were recorded on Bruker-AV 300 or Bruker-AV 400 spectrometer and chemical shifts reported in CDCl₃ with tetramethylsilane as an internal standard. IR spectra were recorded on a NICOLET 6000 infrared spectrometer. Melting points were measured on

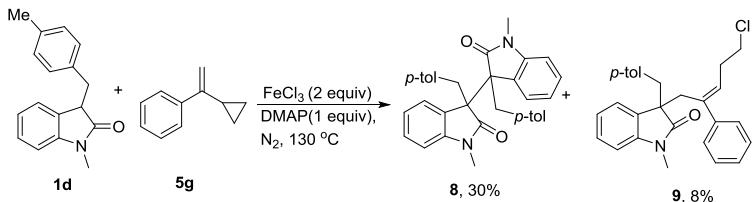
Beijing-Tiker X-4 apparatus without correction. HRMS spectra were recorded on Thermo Fish Scientific-Exactivemass spectrometer. X-ray structure was determined on a Bruker Smart-1000 X-ray Diffraction meter. Common reagents were purchased from commercial sources and were used without further purification. 3-Benzyl- 2-Oxindoles were prepared according to original or modified literature procedures.¹ Column chromatography was performed using silica gel (200-300mesh) eluting with ethyl acetate and petroleum ether. TLC was performed on glass-backed silica plates.

(1) Cheng, L.; Liu, L.; Wang, D.; Chen, Y. *J. Org. Lett.* **2009**, *11*, 3874.

2. Experimental Procedures

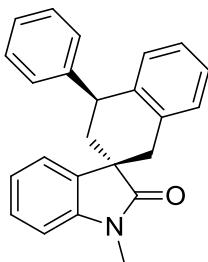
General procedure radical tandem reaction of 3-benzyl- 2-oxindoles with aryl ethylene for direct synthesis of spirocyclohexene oxindoles: A mixture of 3-benzyl- 2-oxindoles (0.2 mmol) and aryl ethylene (1.0 mmol) in the presence of FeCl_3 (0.4 mmol) and DMAP (0.2 mmol) at 130 °C in PhCl (8 mL) under N_2 atmosphere were stirred for 7 h. The mixture was cooled to room temperature, and the PhCl was removed under reduced pressure. The residue was purified by flash column chromatography eluted with ethyl acetate/petroleum ether (6:1) to afford the desired product.

3 The reaction of oxindole **1d** with 1-phenylvinylcyclopane (**5g**)



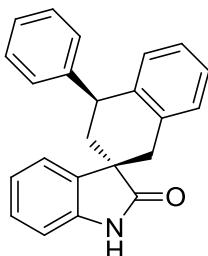
A mixture of 3-(4-methylbenzyl)-2-oxindole (**1d**) with 1-phenylvinylcyclopane (**5g**) (**1d/5g** = 1 : 3) in the presence of FeCl_3 (0.4 mmol) and DMAP (0.2 mmol) at 130 °C in PhCl (8 mL) under N_2 atmosphere were stirred for 7 h. The mixture was cooled to room temperature, and the PhCl was removed under reduced pressure. The residue was purified by flash column chromatography eluted with ethyl acetate/petroleum ether (6:1) to afford the desired product.

4 Product Characterization



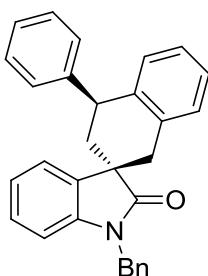
1-methyl-4'-phenyl-3',4'-dihydro-1'H-spiro[indoline-3,2'-naphthalen]-2-one (3a)

White solid. Yield: 51.0 mg (76%), m.p. 190-192°C. ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 7.22-7.36 (m, 6H), 7.07-7.16 (m, 3H), 6.98(d, *J* = 7.5 Hz, 1H), 6.80-6.85 (m, 3H), 4.61 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.22 (s, 3H), 3.13 (s, 2H), 2.33 (dd, *J* = 13.7, 6.0 Hz, 1H), 2.22 (dd, *J* = 12.0, 12.0 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ (ppm): 179.8, 144.5, 142.8, 140.5, 135.2, 134.3, 129.1, 128.5, 128.4, 128.0, 127.8, 126.5, 126.3, 126.1, 122.5, 122.4, 107.9, 46.9, 42.6, 40.8, 37.6, 26.1. HRMS (ESI): calcd for C₂₄H₂₁NONa [M+Na]⁺362.1515, found: 362.1511. IR ν_{max} (KBr, film, cm⁻¹): 3448, 1708, 1611, 1492, 1470, 1376, 1253, 1089.



4'-phenyl-3',4'-dihydro-1'H-spiro[indoline-3,2'-naphthalen]-2-one (3b)

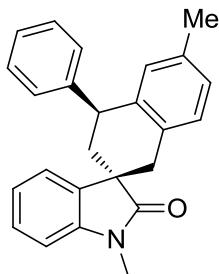
Pale yellow solid. Yield: 31.0 mg (52%), m.p. 207-210°C. ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 8.65 (s, 1H), 7.16-7.35 (m, 5H), 7.10-7.16 (m, 4H), 6.93(d, *J* = 7.5 Hz, 1H), 6.77-6.91 (m, 3H), 4.60 (dd, *J* = 12.5, 5.7 Hz, 1H), 3.17 (s, 2H), 2.37 (dd, *J* = 13.8, 6.0 Hz, 1H), 2.16-2.24 (m, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ (ppm): 182.3, 144.4, 140.5, 140.0, 135.7, 134.3, 129.1, 128.6, 128.5, 128.0, 127.8, 126.6, 126.3, 126.2, 122.7, 122.4, 109.7, 47.3, 42.6, 40.8, 37.4. HRMS (ESI): calcd for C₂₃H₂₀NO [M+H]⁺326.1539, found: 326.1533. IR ν_{max} (KBr, film, cm⁻¹): 3240, 2923, 1705, 1619, 1471, 1226, 1076.



1-benzyl-4'-phenyl-3',4'-dihydro-1'H-spiro[indoline-3,2'-naphthalen]-2-one (3c)

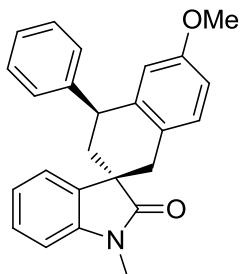
White solid. Yield: 59.0 mg (75%), m.p. 150-152°C. ¹H NMR (CDCl₃, 300 MHz) δ (ppm):

7.12-7.37 (m, 10H), 7.09-7.16 (m, 4H), 6.92(dd, $J = 7.5$, 0.9 Hz, 1H), 6.81-6.83 (m, 2H), 6.72 (d, $J = 7.8$ Hz, 1H), 4.97 (s, 2H), 4.64 (dd, $J = 12.0$, 6.0 Hz, 1H), 3.23 (d, $J = 16.0$ Hz, 1H), 3.16 (d, $J = 16.0$ Hz, 1H), 2.41 (dd, $J = 13.6$, 5.7 Hz, 1H), 2.15-2.27 (m, 1H); ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 180.0, 144.3, 141.8, 140.7, 136.2, 135.3, 134.4, 129.2, 128.8, 128.6, 128.4, 127.9, 127.8, 127.6, 127.3, 126.6, 126.4, 126.2, 122.6, 122.6, 109.0, 46.9, 43.6, 42.7, 41.0, 37.7. HRMS (ESI): calcd for $\text{C}_{30}\text{H}_{26}\text{NO} [\text{M}+\text{H}]^+$ 416.2008, found: 416.2008. IR ν_{max} (KBr, film, cm^{-1}): 3059, 2922, 1707, 1611, 1488, 1362, 1169, 1077.



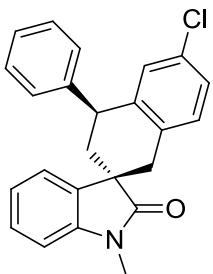
1,6'-dimethyl-4'-phenyl-3',4'-dihydro-1'H-spiro[indoline-3,2'-naphthalen]-2-one (3d)

White solid. Yield: 39.0 mg (55%). m.p. 150-152°C. ^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 7.14-7.28 (m, 5H), 6.89-6.91 (m, 3H), 6.74-6.80 (m, 2H), 6.60-6.70 (m, 1H), 6.56(s, 1H), 4.51 (dd, $J = 12.0$, 6.0 Hz, 1H), 3.14 (s, 3H), 3.05 (d, $J = 16.4$ Hz, 1H), 2.98 (d, $J = 16.4$ Hz, 1H), 2.20 (dd, $J = 14.0$, 6.4 Hz, 6.0, 1H), 2.12 (s, 3H), 2.04-2.10 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm): 179.8, 144.8, 142.8, 140.1, 135.8, 135.2, 131.2, 129.1, 128.6, 128.6, 128.3, 127.8, 127.0, 126.5, 122.5, 122.4, 107.9, 46.9, 42.7, 41.0, 37.4, 26.1, 21.2. HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{24}\text{NO} [\text{M}+\text{H}]^+$ 354.1852, found: 354.1847. IR ν_{max} (KBr, film, cm^{-1}): 3428, 1708, 1611, 1492, 1470, 1376, 1348, 1088.



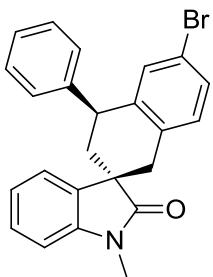
6'-methoxy-1-methyl-4'-phenyl-3',4'-dihydro-1'H-spiro[indoline-3,2'-naphthalen]-2-one (3e)

White solid. Yield: 31.0 mg (42%), m.p. 70-72°C. ^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 7.22-7.34 (m, 6H), 6.95-7.02 (m, 2H), 6.82-6.84 (m, 2H), 6.71(dd, $J = 8.2$, 2.4 Hz, 1H), 6.38(s, 1H), 4.85 (dd, $J = 12.0$, 6.0 Hz, 1H), 3.64 (s, 3H), 3.21 (s, 3H), 3.07 (s, 2H), 2.30 (dd, $J = 13.7$, 6.0 Hz, 1H), 2.07-2.20 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm): 179.8, 158.1, 144.3, 142.8, 141.8, 135.3, 129.2, 129.1, 128.6, 127.8, 126.6, 122.5, 113.7, 111.7, 107.8, 55.1, 47.0, 42.9, 40.8, 37.0, 26.1. HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{24}\text{NO}_2 [\text{M}+\text{H}]^+$ 370.1801, found: 370.1801. IR ν_{max} (KBr, film, cm^{-1}): 3447, 2926, 1708, 1611, 1492, 1470, 1348, 1257, 1108.



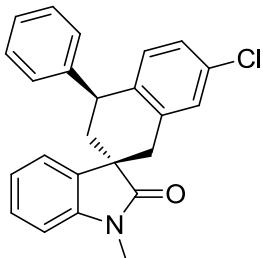
6'-chloro-1-methyl-4'-phenyl-3',4'-dihydro-1'H-spiro[indoline-3,2'-naphthalen]-2-one (3f)

White solid. Yield: 51.0 mg (65%), m.p. 176-179°C. ^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 7.32-7.36 (m, 2H), 7.23-7.28 (m, 4H), 7.12 (d, $J = 7.6$ Hz, 1H), 6.98-7.03 (m, 2H), 6.91 (d, $J = 7.2$ Hz, 1H), 6.82-6.85 (m, 2H), 4.61 (dd, $J = 12.0, 6.0$ Hz, 1H), 3.21 (s, 3H), 3.14 (d, $J = 16.0$ Hz, 1H), 3.04 (d, $J = 16.0$ Hz, 1H), 2.28 (dd, $J = 13.6, 6.0$ Hz, 1H), 2.16-2.22 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm): 179.4, 143.9, 142.8, 142.3, 134.6, 132.8, 129.7, 129.0, 128.8, 128.4, 128.2, 128.1, 126.9, 126.4, 122.6, 122.3, 108.0, 46.6, 42.6, 40.6, 37.1, 26.1. HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{21}\text{ClNO}$ $[\text{M}+\text{H}]^+$ 374.1306, found: 374.1299. IR ν_{max} (KBr, film, cm^{-1}): 3447, 3057, 2931, 1706, 1612, 1492, 1470, 1376, 1349, 1252, 1123, 1088.



6'-bromo-1-methyl-4'-phenyl-3',4'-dihydro-1'H-spiro[indoline-3,2'-naphthalen]-2-one (3g)

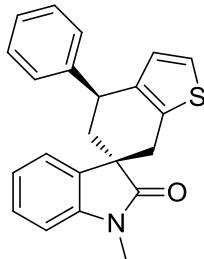
White solid. Yield: 51.0 mg (62%), m.p. 210-212°C. ^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 7.25-7.29 (m, 2H), 7.15-7.21 (m, 5H), 6.89-6.95 (m, 3H), 6.84 (d, $J = 6.8$ Hz, 1H), 6.77 (d, $J = 8.0$ Hz, 1H), 4.54 (dd, $J = 11.6, 6.0$ Hz, 1H), 3.14 (s, 3H), 3.05 (d, $J = 16.4$ Hz, 1H), 2.96 (d, $J = 16.4$ Hz, 1H), 2.21 (dd, $J = 13.7, 6.4$ Hz, 1H), 2.07-2.14 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm): 179.4, 143.8, 142.8, 142.6, 134.6, 133.3, 131.0, 130.1, 129.3, 129.0, 128.8, 128.1, 126.9, 122.6, 122.3, 120.2, 108.0, 46.6, 42.6, 40.6, 37.2, 26.1. HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{21}\text{NBrO}$ $[\text{M}+\text{H}]^+$ 418.0101, found: 418.0802. IR ν_{max} (KBr, film, cm^{-1}): 3447, 2924, 1708, 1612, 1492, 1471, 1376, 1350, 1122, 1090.



7'-chloro-1-methyl-4'-phenyl-3',4'-dihydro-1'H-spiro[indoline-3,2'-naphthalen]-2-one (3h)

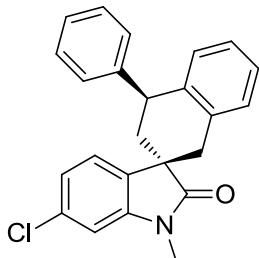
White solid. Yield: 38.0 mg (51%), m.p. 160-162°C. ^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 7.22-7.34 (m, 6H), 6.95-7.08 (m, 4H), 6.85 (d, $J = 7.6$ Hz, 1H), 6.77 (d, $J = 8.4$ Hz, 1H), 4.61 (dd,

J = 11.5, 6.4 Hz, 1H), 3.21 (s, 3H), 3.18 (d, *J* = 16.4 Hz, 1H), 2.96 (d, *J* = 16.4 Hz, 1H), 2.16-2.28 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ (ppm): 179.3, 144.5, 142.8, 138.8, 136.1, 134.4, 131.7, 129.8, 129.0, 128.7, 128.2, 128.1, 126.7, 126.5, 122.7, 122.3, 108.1, 46.5, 42.2, 40.8, 37.4, 26.1. HRMS (ESI): calcd for C₂₄H₂₁ClNO [M+H]⁺374.1306, found: 374.1306. IR ν_{max} (KBr, film, cm⁻¹): 3043, 2923, 1708, 1161, 1491, 1376, 1348, 1130, 1088.



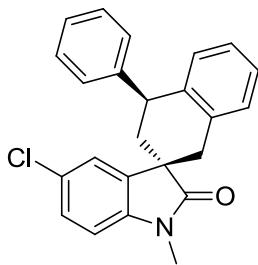
1'-methyl-4-phenyl-5,7-dihydro-4H-spiro[benzo[b]thiophene-6,3'-indolin]-2'-one (3i)

Yellow solid. Yield: 43.0 mg (62%), m.p. 190-192°C. ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 7.18-7.33 (m, 7H), 7.02-7.09 (m, 2H), 6.83(d, *J* = 7.6 Hz, 1H), 6.52 (d, *J* = 5.2 Hz, 1H), 4.60 (dd, *J* = 11.2, 5.2 Hz, 1H), 3.34 (d, *J* = 16.4 Hz, 1H), 3.21 (s, 3H), 3.05 (d, *J* = 16.4 Hz, 1H), 2.01-2.32 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ (ppm): 178.5, 145.1, 142.9, 138.2, 133.8, 132.6, 128.5, 128.3, 128.2, 127.5, 126.5, 122.6, 122.3, 122.0, 108.2, 47.0, 41.1, 40.3, 32.6, 26.1. HRMS (ESI): calcd for C₂₂H₂₀NOS [M+H]⁺346.1260, found: 346.1261. IR ν_{max} (KBr, film, cm⁻¹): 3446, 1708, 1639, 1491, 1470, 1375, 1348, 1089.



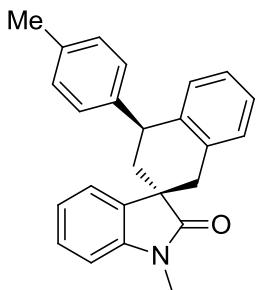
6-chloro-1-methyl-4'-phenyl-3',4'-dihydro-1'H-spiro[indoline-3,2'-naphthalen]-2-one (3j)

White solid. Yield: 50.0 mg (67%), m.p. 200-202°C. ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 7.31-7.35 (m, 2H), 7.24-7.27 (m, 3H), 7.07-7.15 (m, 3H), 6.93(dd, *J* = 8.0, 1.6 Hz, 1H), 6.80-6.84 (m, 2H), 6.70(d, *J* = 7.6 Hz, 1H), 4.57 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.19 (s, 3H), 3.10 (s, 2H), 2.31 (dd, *J* = 14.0, 6.0 Hz, 1H), 2.12-2.18 (m, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ (ppm): 179.7, 144.2, 144.0, 140.4, 134.0, 133.7, 133.5, 129.1, 128.6, 128.4, 128.0, 126.7, 126.5, 126.2, 123.4, 122.3, 108.7, 46.7, 42.6, 40.7, 37.6, 26.3. HRMS (ESI): calcd for C₂₄H₂₁ClNO [M+H]⁺374.1306, found: 374.1305. IR ν_{max} (KBr, film, cm⁻¹): 3446, 1716, 1607, 1494, 1373, 1096, 1070, 1009.



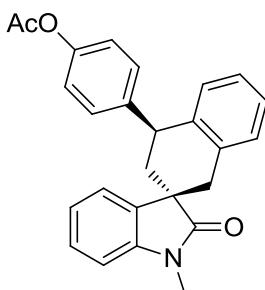
5-chloro-1-methyl-4'-phenyl-3',4'-dihydro-1'H-spiro[indoline-3,2'-naphthalen]-2-one (3k)

Yellow solid. Yield: 53.0 mg (72%), m.p. 200-202°C. ^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 7.20-7.23 (m, 2H), 7.07-6.83 (m, 7H), 6.76-6.83 (m, 2H), 6.95 (d, J = 8.4 Hz, 1H), 4.60 (dd, J = 12.0, 5.6 Hz, 1H), 3.19 (s, 3H), 3.12 (s, 2H), 2.30 (dd, J = 13.6, 6.0 Hz, 1H), 2.13-2.17 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm): 179.3, 144.3, 141.4, 140.3, 136.8, 133.8, 129.1, 128.6, 128.4, 128.1, 127.9, 127.8, 126.7, 126.5, 126.3, 123.1, 108.9, 47.1, 42.6, 40.8, 37.5, 26.3. HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{21}\text{ClNO} [\text{M}+\text{H}]^+$ 374.1306, found: 374.1306. IR ν_{max} (KBr, film, cm^{-1}): 3448, 1712, 1609, 1492, 1348, 1264, 1099.



1-methyl-4'-(p-tolyl)-3',4'-dihydro-1'H-spiro[indoline-3,2'-naphthalen]-2-one (3l)

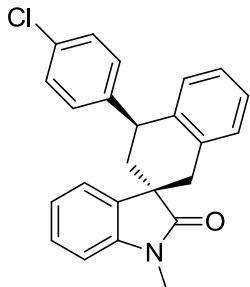
Pale yellow oil. Yield: 32.0 mg (46%). ^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 7.22-7.26 (m, 1H), 7.07-7.17 (m, 7H), 6.97 (t, J = 7.6 Hz, 1H), 6.82-6.84 (m, 3H), 4.57 (dd, J = 12.0, 6.0 Hz, 1H), 3.21 (s, 3H), 3.12 (s, 2H), 2.34 (s, 3H), 2.28-2.34 (m, 1H), 2.14-2.17 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm): 179.9, 142.8, 141.4, 140.7, 136.1, 135.3, 134.3, 129.3, 129.0, 128.4, 128.0, 127.8, 126.3, 126.1, 122.6, 122.5, 107.9, 46.9, 42.2, 40.9, 37.4, 26.1, 21.1. HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{24}\text{NO} [\text{M}+\text{H}]^+$ 354.1852, found: 354.1852. IR ν_{max} (KBr, film, cm^{-1}): 3447, 3054, 1709, 1612, 1492, 1470, 1376, 1350, 1253, 1127, 1089.



1-methyl-2-oxo-3',4'-dihydro-1'H-spiro[indoline-3,2'-naphthalen]-4'-ylphenyl acetate (3m)

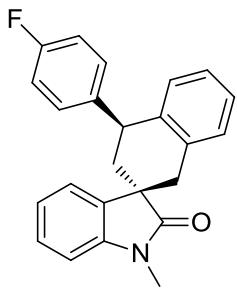
Yellow oil. Yield: 36.0 mg (46%). ^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 7.23-7.27 (m, 3H), 6.97-7.17 (m, 6H), 6.83-6.87 (m, 3H), 4.64 (dd, J = 12.0, 6.0 Hz, 1H), 3.25 (s, 3H), 3.16 (d, J =

16.0 Hz, 1H), 3.09 (d, J = 16.0 Hz, 1H), 2.28 (s, 3H), 2.26-2.28 (m, 1H), 2.13-2.16 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm): 179.7, 169.5, 149.3, 142.8, 142.2, 140.1, 135.0, 134.3, 129.1, 130.0, 128.5, 128.1, 127.9, 126.4, 126.3, 122.6, 122.4, 121.6, 108.0, 46.8, 42.1, 40.9, 37.6, 26, 21.1. HRMS (ESI): calcd for $\text{C}_{26}\text{H}_{24}\text{NO}_3$ [$\text{M}+\text{H}]^+$ 398.1570, found: 398.1570. IR ν_{max} (KBr, film, cm^{-1}): 3057, 2930, 1766, 1708, 1612, 1505, 1493, 1370, 1350, 1197, 1089, 1017.



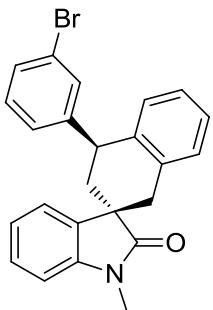
4'-(4-chlorophenyl)-1-methyl-3',4'-dihydro-1'H-spiro[indoline-3,2'-naphthalen]-2-one (3n)

Yellow solid. Yield: 56.0 mg (76%), m.p. 78-80°C. ^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 7.08-7.30 (m, 8H), 6.99 (t, J = 7.6 Hz, 1H), 6.83-6.88 (m, 2H), 6.78 (d, J = 7.2 Hz, 1H), 4.62 (dd, J = 12.0, 6.0 Hz, 1H), 3.21 (s, 3H), 3.16 (d, J = 16.0 Hz, 1H), 3.09 (d, J = 16.0 Hz, 1H), 2.27 (dd, J = 13.6, 6.0 Hz, 1H), 2.10-2.18 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm): 179.7, 143.2, 142.8, 139.9, 134.9, 134.3, 132.3, 130.5, 128.8, 128.5, 128.0, 127.9, 126.4, 126.4, 122.6, 122.4, 108.0, 46.7, 42.1, 40.8, 37.6, 26.2. HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{21}\text{ClNO}$ [$\text{M}+\text{H}]^+$ 374.1306, found: 374.1307. IR ν_{max} (KBr, film, cm^{-1}): 3446, 1706, 1612, 1491, 1470, 1376, 1350, 1089..



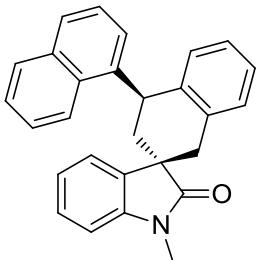
4'-(4-fluorophenyl)-1-methyl-3',4'-dihydro-1'H-spiro[indoline-3,2'-naphthalen]-2-one (3o)

Pale yellow solid. Yield: 43.0 mg (61%), m.p. 160-162°C. ^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 7.20-7.27 (m, 3H), 7.10-7.16 (m, 3H), 6.97-7.03 (m, 3H), 6.84-6.87 (m, 2H), 6.79 (d, J = 7.2 Hz, 1H), 4.62 (dd, J = 12.0, 6.0 Hz, 1H), 3.22 (s, 3H), 3.14 (d, J = 16.0 Hz, 1H), 3.11 (d, J = 16.0 Hz, 1H), 2.29 (dd, J = 14.0, 6.0 Hz, 1H), 2.12-2.18 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm): 179.8, 142.8, 140.3, 140.2, 140.2, 135.1, 134.3, 130.5, 130.4, 128.5, 128.0, 127.8, 126.4, 126.3, 122.6, 122.4, 115.5, 115.3, 108.0, 46.8, 41.9, 41.0, 37.6, 26.1. HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{21}\text{NOF}$ [$\text{M}+\text{H}]^+$ 358.1601, found: 358.1596. IR ν_{max} (KBr, film, cm^{-1}): 3449, 3057, 1708, 1612, 1508, 1493, 1376, 1350, 1222, 1157, 1088.



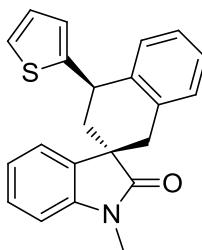
4'-(3-bromophenyl)-1-methyl-3',4'-dihydro-1'H-spiro[indoline-3,2'-naphthalen]-2-one (3p)

Pale yellow solid. Yield: 59.0 mg (71%), m.p. 180-182°C. ^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 7.36-7.41 (m, 2H), 7.26-7.28 (m, 1H), 7.09-7.20 (m, 5H), 7.00 (t, J = 7.6 Hz, 1H), 6.92 (d, J = 7.2 Hz, 1H), 6.84 (d, J = 8.0 Hz, 1H), 6.80 (d, J = 7.2 Hz, 1H), 4.60 (dd, J = 12.0, 6.0 Hz, 1H), 3.21 (s, 3H), 3.21 (d, J = 16.0 Hz, 1H), 3.08 (d, J = 16.0 Hz, 1H), 2.27 (dd, J = 13.2, 6.8 Hz, 1H), 2.13-2.20 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm): 179.6, 147.2, 142.8, 139.5, 134.8, 134.2, 132.0, 129.7, 128.6, 128.0, 128.0, 127.9, 126.5, 126.4, 122.7, 122.6, 122.4, 108.0, 46.7, 42.4, 40.7, 37.5, 26.1. HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{21}\text{NOBr} [\text{M}+\text{H}]^+$ 418.0801, found: 418.0792. IR ν_{max} (KBr, film, cm^{-1}): 3447, 3057, 2927, 1708, 1612, 1492, 1471, 1376, 1350, 1127, 1088.



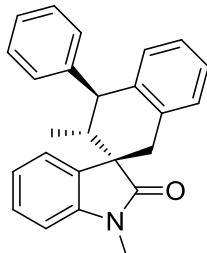
1-methyl-4'-(naphthalen-1-yl)-3',4'-dihydro-1'H-spiro[indoline-3,2'-naphthalen]-2-one (3q)

Yellow solid. Yield: 53.0 mg (68%), m.p. 135-138°C. ^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 7.77-7.82 (m, 4H), 7.42-7.47 (m, 2H), 7.34 (dd, J = 8.4, 1.6 Hz, 1H), 7.25 (td, J = 8.0, 1.2 Hz, 1H), 7.06-7.18 (m, 3H), 6.98 (t, J = 8.4 Hz, 1H), 6.83-6.90 (m, 3H), 4.81 (dd, J = 11.6, 6.4 Hz, 1H), 3.22 (s, 3H), 3.19 (d, J = 16.4 Hz, 1H), 3.15 (d, J = 16.4 Hz, 1H), 2.21-2.36 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm): 179.8, 142.8, 141.9, 140.3, 135.2, 134.4, 133.7, 132.4, 129.1, 128.5, 128.3, 128.2, 127.9, 127.9, 127.7, 127.2, 126.4, 126.3, 126.0, 125.6, 122.6, 122.5, 108.0, 46.9, 42.8, 40.7, 37.7, 26.2. HRMS (ESI): calcd for $\text{C}_{28}\text{H}_{24}\text{NO} [\text{M}+\text{H}]^+$ 390.1852, found: 390.1846. IR ν_{max} (KBr, film, cm^{-1}): 3054, 2928, 1708, 1612, 1492, 1470, 1376, 1350, 1255, 1126, 1089.



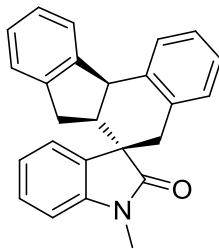
1-methyl-4'-(thiophen-2-yl)-3',4'-dihydro-1'H-spiro[indoline-3,2'-naphthalen]-2-one (3r)

White solid. Yield: 21.0 mg (30%), m.p. 170-173°C. ^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 7.21-7.28 (m, 2H), 7.15-7.17 (m, 2H), 7.07-7.09 (m, 1H), 6.96-7.01 (m, 4H), 6.81-6.86 (m, 2H), 4.97 (dd, $J = 12.0$ Hz, 6.0, 1H), 3.22 (s, 3H), 3.11 (s, 2H), 2.45 (dd, $J = 13.6$, 6.4 Hz, 1H), 2.16-2.28 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm): 179.8, 147.4, 142.8, 140.1, 135.0, 133.8, 128.3, 127.9, 127.4, 126.6, 126.5, 125.9, 124.0, 122.6, 122.5, 107.9, 46.9, 41.3, 37.8, 37.5, 26.2. HRMS (ESI): calcd for $\text{C}_{22}\text{H}_{20}\text{NOS}$ [$\text{M}+\text{H}]^+$ 346.1260, found: 346.1260. IR ν_{max} (KBr, film, cm^{-1}): 3443, 2960, 1635, 1470, 1376, 1349, 1260, 1089.



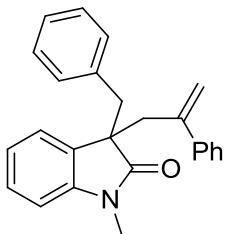
1,3'-dimethyl-4'-phenyl-3',4'-dihydro-1'H-spiro[indoline-3,2'-naphthalen]-2-one (3s)

Pale yellow solid. Yield: 36.0 mg (51%), m.p. 179-180°C. ^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 7.18-7.31 (m, 6H), 7.04-7.13 (m, 3H), 6.87-6.90 (m, 2H), 6.82 (d, $J = 6.8$ Hz, 1H), 6.72 (d, $J = 7.2$ Hz, 1H), 3.88 (d, $J = 11.2$ Hz, 1H), 3.68 (d, $J = 16.4$ Hz, 1H), 3.27 (s, 3H), 2.72 (d, $J = 16.0$ Hz, 1H), 2.57-2.63 (m, 1H), 0.44 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm): 179.4, 145.1, 143.9, 139.6, 133.8, 130.6, 129.9, 129.8, 129.1, 128.4, 128.0, 126.5, 126.5, 126.2, 124.3, 122.4, 107.8, 52.3, 51.0, 42.1, 38.1, 26.2, 14.0. HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{24}\text{NO}$ [$\text{M}+\text{H}]^+$ 354.1852, found: 354.1848. IR ν_{max} (KBr, film, cm^{-1}): 3451, 1639, 1490, 1375, 1353, 1095.



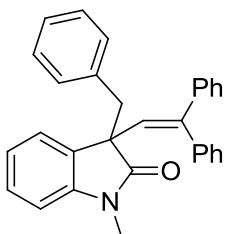
1'-methyl-5,6a,7,11b-tetrahydrospiro[benzo[c]fluorene-6,3'-indolin]-2'-one (3t)

Yellow solid. Yield: 35.0 mg (51%), m.p. 232-235°C. ^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 7.60-7.62 (m, 2H), 7.03-7.26 (m, 7H), 6.79-6.88 (m, 3H), 4.57 (d, $J = 7.2$ Hz, 1H), 3.71(d, $J = 16.4$ Hz, 1H), 3.47 (m, 1H), 3.28 (s, 3H), 3.10 (dd, $J = 16.4, 8.0$ Hz, 1H), 2.64-2.75 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm): 178.8, 145.2, 142.7, 142.5, 136.9, 134.2, 132.7, 129.8, 128.4, 128.0, 127.1, 126.9, 126.4, 126.3, 125.0, 124.8, 123.8, 122.4, 108.0, 48.7, 46.2, 45.5, 33.4, 32.5, 26.4. HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{22}\text{NO} [\text{M}+\text{H}]^+$ 352.1695, found: 352.1697. IR ν_{max} (KBr, film, cm^{-1}): 3445, 2923, 1709, 1610, 1491, 1471, 1375, 1350, 1254, 1088.



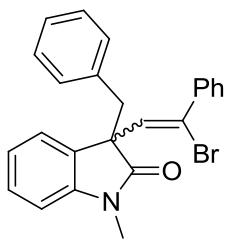
3-benzyl-1-methyl-3-(2-phenylallyl)indolin-2-one (7a)

White solid. Yield: 34.0 mg (49%), m.p. 89-90°C. ^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 6.97-7.10 (m, 7H), 6.85-6.93 (m, 3H), 6.79-6.83 (m, 3H), 6.37(d, $J = 7.6$ Hz, 1H), 4.88 (s, 3H), 4.39 (d, $J = 14.0$ Hz, 1H), 3.15 (d, $J = 13.2$ Hz, 1H), 3.06 (d, $J = 13.6$ Hz, 1H), 2.96 (d, $J = 13.2$ Hz, 1H), 2.95 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm): 178.3, 145.5, 143.7, 141.4, 135.7, 130.0, 129.9, 127.5, 127.4, 127.0, 126.7, 126.3, 124.8, 121.4, 116.9, 107.3, 54.5, 44.1, 42.7, 25.4. HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{24}\text{NO} [\text{M}+\text{H}]^+$ 354.1852, found: 354.1852. IR ν_{max} (KBr, film, cm^{-1}): 3447, 2927, 1708, 1613, 1494, 1470, 1377, 1360, 1088.



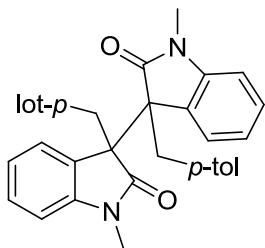
3-benzyl-3-(2,2-diphenylvinyl)-1-methylindolin-2-one (7b)

Yellow solid. Yield: 59.0 mg (72%), m.p. 120-122°C. ^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 7.16-7.24 (m, 4H), 7.10 (d, $J = 7.2$ Hz, 1H), 6.91-7.04 (m, 8H), 6.80(d, $J = 6.8$ Hz, 2H), 6.53-6.57 (m, 3H), 6.15 (d, $J = 7.6$ Hz, 1H), 3.38 (d, $J = 12.4$ Hz, 1H), 3.29 (d, $J = 12.4$ Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm): 177.6, 145.4, 143.1, 138.1, 135.0, 133.6, 130.1, 129.6, 128.7, 128.1, 127.5, 127.3, 127.0, 126.6, 126.5, 124.0, 121.8, 107.4, 54.8, 46.0, 25.3. HRMS (ESI): calcd for $\text{C}_{30}\text{H}_{26}\text{NO} [\text{M}+\text{H}]^+$ 416.2008, found: 416.2006. IR ν_{max} (KBr, film, cm^{-1}): 3455, 1639, 1493, 1469, 1376, 1088.



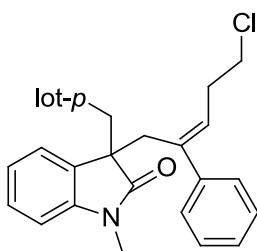
3-benzyl-3-(2-bromo-2-phenylvinyl)-1-methylindolin-2-one (7c)

Pale yellow solid. Yield: 36.0 mg (44%), m.p. 130-132°C. ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 7.52-7.58 (m, 4H), 7.30-7.34 (m, 6H), 7.25 (s, 1H), 7.18-7.21 (m, 1H), 7.02-7.10 (m, 11H), 6.80-6.83 (m, 4H), 6.74 (s, 1H), 6.53-6.57 (m, 2H), 3.39 (d, J = 12.4 Hz, 2H), 3.30 (d, J = 12.4 Hz, 2H), 2.96 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ (ppm): 176.9, 176.5, 144.4, 144.1, 139.7, 137.6, 136.0, 134.4, 134.3, 131.2, 131.1, 131.0, 130.1, 129.0, 128.9, 128.2, 128.2, 128.0, 128.0, 127.7, 127.4, 127.4, 127.2, 126.8, 126.8, 126.6, 123.7, 123.7, 122.2, 122.2, 107.6, 56.6, 56.4, 46.1, 45.7, 26.0. HRMS (ESI): calcd for C₂₄H₂₁NOBr [M+H]⁺ 418.0801, found: 418.0801. IR ν_{max} (KBr, film, cm⁻¹): 3466, 1639, 1492, 1469, 1373, 1087.



1,1'-dimethyl-3,3'-bis(4-methylbenzyl)-[3,3'-biindoline]-2,2'-dione (8)

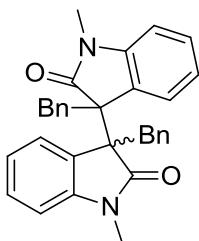
White solid. Yield: 30.0 mg (30%), m.p. 250-252°C. ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 7.12 (d, J = 8.4 Hz, 2H), 6.82-6.89 (m, 4H), 6.73 (d, J = 8.1 Hz, 4H), 6.68 (d, J = 8.1 Hz, 4H), 6.42 (d, J = 7.2 Hz, 2H), 4.19 (d, J = 12.3 Hz, 2H), 3.44 (d, J = 12.3 Hz, 2H), 2.68 (s, 6H), 2.13 (s, 6H); ¹³C NMR (CDCl₃, 75 MHz) δ (ppm): 176.0, 144.5, 135.5, 132.3, 130.2, 128.7, 128.4, 127.9, 124.6, 121.2, 107.7, 58.2, 36.3, 25.5, 20.9. HRMS (ESI): calcd for C₃₄H₃₃N₂O₂ [M+H]⁺ 501.2536, found: 501.2534. IR ν_{max} (KBr, film, cm⁻¹): 3447, 2922, 1702, 1636, 1492, 1469, 1374, 1350, 1086.



(E)-3-(5-chloro-2-phenylpent-2-en-1-yl)-1-methyl-3-(4-methylbenzyl)indolin-2-one (9)

White solid. Yield: 7.0 mg (8%), m.p. 80-82°C. ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 7.02-7.07 (m, 4H), 6.78-6.90 (m, 6H), 6.68 (d, J = 8.1 Hz, 2H), 6.36 (d, J = 7.8 Hz, 1H), 5.27 (t, J = 7.2 Hz, 1H), 3.43-3.49 (m, 2H), 3.28 (d, J = 13.8 Hz, 1H), 3.17 (d, J = 13.8 Hz, 1H), 3.08 (d, J = 13.2 Hz,

1H), 2.96 (d, $J = 13.2$ Hz, 1H), 2.47-2.57 (m, 2H), 2.53 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 178.4, 143.6, 142.6, 139.7, 135.8, 132.5, 130.0, 128.1, 127.9, 127.5, 127.4, 127.0, 126.7, 124.4, 121.2, 107.3, 54.2, 44.0, 43.4, 36.8, 32.2, 25.3, 20.9. HRMS (ESI): calcd for $\text{C}_{28}\text{H}_{29}\text{ClNO} [\text{M}+\text{H}]^+$ 430.1932, found: 430.1933. IR ν_{max} (KBr, film, cm^{-1}): 3443, 2922, 1635, 1493, 1470, 1377, 1129.

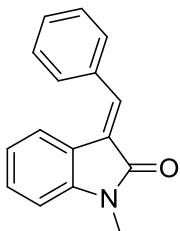


3,3'-dibenzyl-1,1'-dimethyl-[3,3'-biindoline]-2,2'-dione (6-anti)

White solid. Yield: 36.0 mg (40%). ^1H NMR (CDCl_3 , 300 MHz) δ (ppm): 7.19 (d, $J = 7.5$ Hz, 1H), 6.82-6.95 (m, 6H), 6.76 (t, $J = 6.6$ Hz, 1H), 6.14 (d, $J = 7.5$ Hz, 1H), 4.32 (d, $J = 12.6$ Hz, 1H), 3.76 (d, $J = 12.6$ Hz, 1H), 2.89 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 177.0, 143.0, 136.0, 130.3, 128.2, 127.9, 127.2, 126.0, 123.9, 121.4, 107.1, 57.5, 35.3, 25.5.

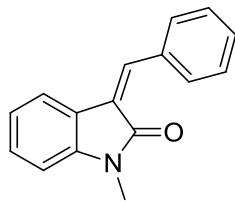
3,3'-dibenzyl-1,1'-dimethyl-[3,3'-biindoline]-2,2'-dione (6-syn)

White solid. Yield: 25.0 mg (28%). ^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 7.14 (d, $J = 8.4$ Hz, 1H), 6.78-6.99 (m, 7H), 6.42 (d, $J = 8.0$ Hz, 1H), 4.24 (d, $J = 12.4$ Hz, 1H), 3.49 (d, $J = 12.4$ Hz, 1H), 2.68 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm): 175.9, 144.4, 135.4, 130.3, 128.5, 127.2, 126.2, 124.6, 121.3, 107.7, 57.9, 36.9, 25.5.



(E)-3-benzylidene-1-methylindolin-2-one (4)

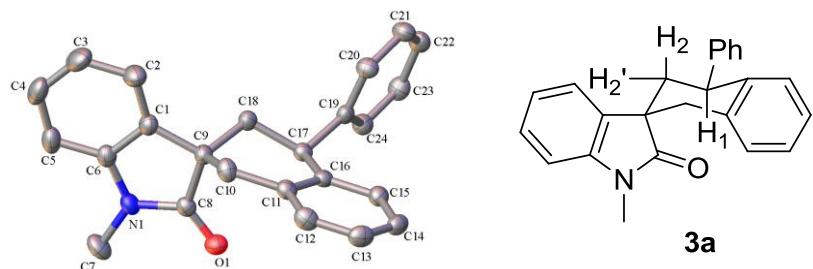
Red solid. Yield: 28.0 mg (61%). ^1H NMR (CDCl_3 , 300 MHz) δ (ppm): 7.65 (s, 1H), 7.61-7.63 (m, 3H), 7.41-7.48 (m, 3H), 7.26 (t, $J = 8.2$ Hz, 1H), 6.79 (t, $J = 8.4$ Hz, 1H), 6.81-6.90 (m, 2H), 3.28 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 168.5, 144.2, 137.1, 135.0, 129.8, 129.5, 129.3, 128.6, 127.2, 122.7, 121.8, 121.6, 108.1, 26.2.



(Z)-3-benzylidene-1-methylindolin-2-one (4)

Red solid. Yield: 9.0 mg (21%). ^1H NMR (CDCl_3 , 300 MHz) δ (ppm): 8.27 (d, $J = 7.8$ Hz, 2H), 7.40-7.54 (m, 5H), 7.02-7.30 (m, 2H), 6.79 (d, $J = 7.6$ Hz, 1H), 3.27 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm): 166.1, 142.3, 137.0, 133.8, 131.9, 130.4, 128.8, 128.2, 126.3, 124.8, 121.8, 118.9, 107.9, 25.9;

5. X-ray crystallography of compound 3a



The methods of recrystallisation of **3a**:

The crystal of compounds **3a** was prepared from the solution in petroleum ether (2 mL) with dichloromethane (1 mL).

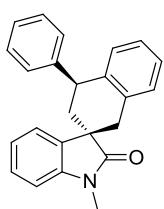
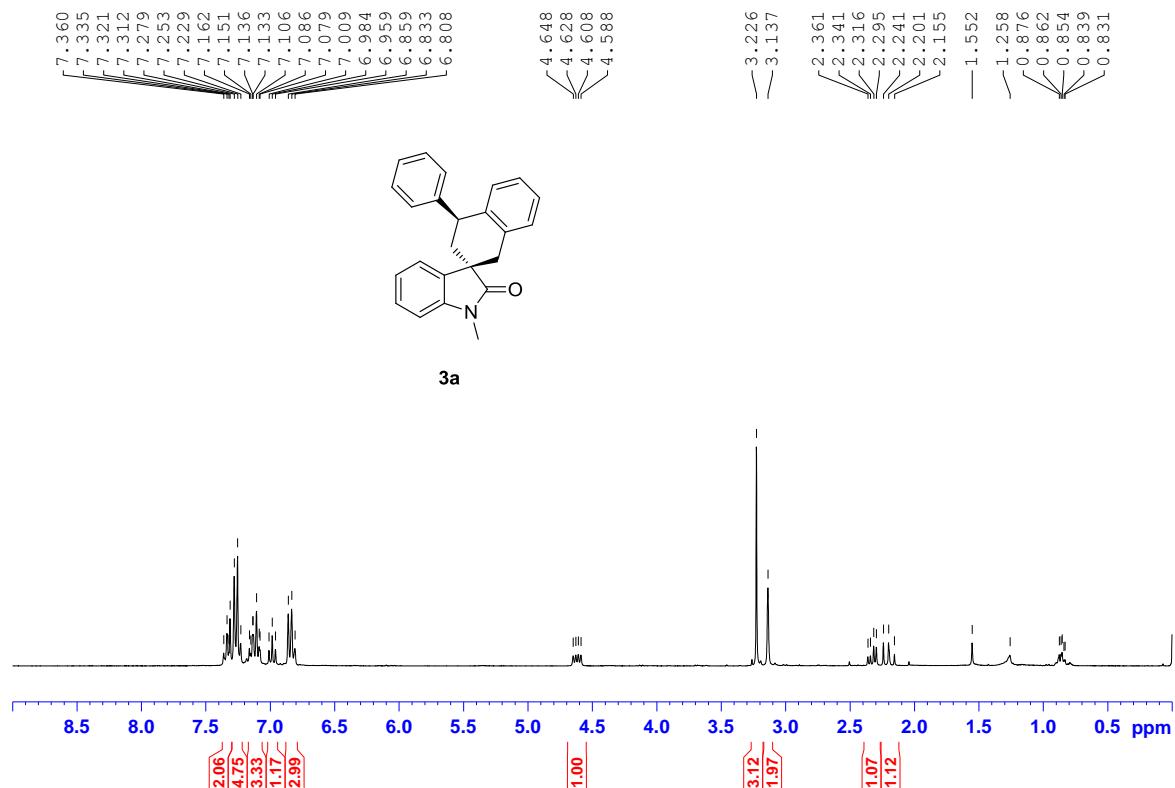
Table 1. Crystal data and structure refinement for sa4060.

Identification code	sa4060
Empirical formula	$\text{C}_{24} \text{H}_{21} \text{NO}$
Formula weight	339.42
Temperature	173.1500 K
Wavelength	0.71073 Å
Crystal system	Trigonal
Space group	$\text{R}-3$
Unit cell dimensions	$a = 34.203(2)$ Å $\alpha = 90^\circ$ $b = 34.203(2)$ Å $\beta = 90^\circ$ $c = 7.9236(6)$ Å $\gamma = 120^\circ$

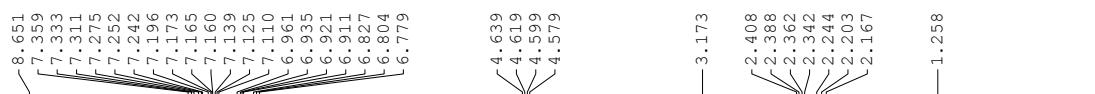
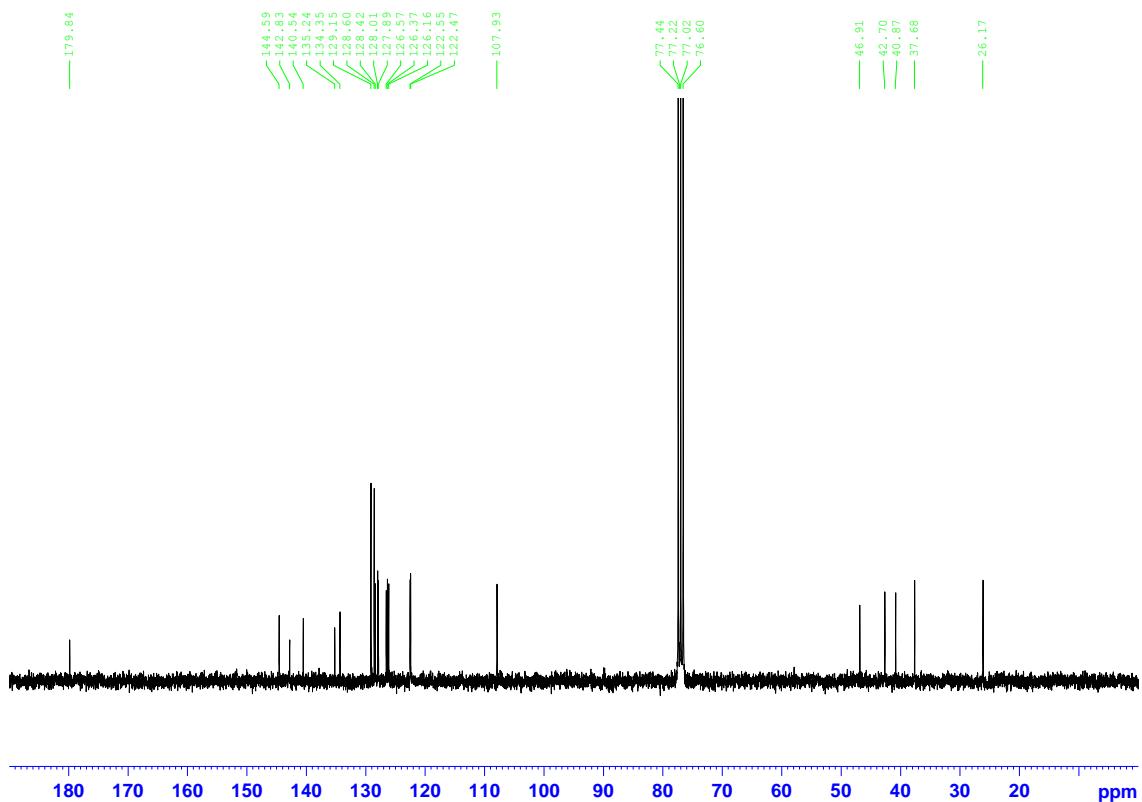
Volume	8027.6(12) Å ³
Z	18
Density (calculated)	1.264 Mg/m ³
Absorption coefficient	0.077 mm ⁻¹
F(000)	3240
Crystal size	0.61 x 0.27 x 0.17 mm ³
Theta range for data collection	2.382 to 27.464°
Index ranges	-44<=h<=44, -44<=k<=44, -10<=l<=10
Reflections collected	17421
Independent reflections	4076 [R(int) = 0.0351]
Completeness to theta = 26.000°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.8714
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4076 / 0 / 236
Goodness-of-fit on F ²	1.222
Final R indices [I>2sigma(I)]	R1 = 0.0594, wR2 = 0.1180
R indices (all data)	R1 = 0.0625, wR2 = 0.1196
Extinction coefficient	n/a
Largest diff. peak and hole	0.196 and -0.183 e. Å ⁻³

CCDC deposition number: 1060529

6. NMR Spectra



3a



3b

