Supporting Information

Simple and One-Pot Protocol for Synthesis of Indene-spiro-oxindoles Involving Tandem Prins and Friedel-Crafts Reactions

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EXPERIMENTAL SECTION

General Remarks: Melting points were recorded on a Superfit (India) capillary melting point apparatus and are uncorrected. IR spectra were recorded on a JASCO-FT-IR model 5300 spectrometer using solid samples as KBr plates. ^1H NMR (400 MHz) and ^{13}C NMR (50 MHz) spectra were recorded in deuteriochloroform (CDCl_3) on a Bruker-AVANCE-400 and Bruker-AC-200 spectrometer using tetramethylsilane (TMS, $\delta = 0$) as an internal standard. Elemental analyses were recorded on a Thermo-Finnigan Flash EA 1112 analyzer. Mass spectra were recorded on Shimadzu-LCMS-2010 A mass spectrometer. The X-ray diffraction measurements were carried out at 298 K on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a Mo-K α fine-focus sealed tube ($\lambda = 0.71073 \text{ \AA}$).

General procedure for the synthesis of (3-phenyl-1*H*-indene)-1-spiro-3'-(indolin-2'-one) (3): To a stirred solution of isatin (**1a**, 0.147g, 1 mmol), 1,1-diphenylethylene (**2a**, 0.180g, 1 mmol) in CH_2Cl_2 (3 mL), TiCl_4 (0.5 mL, 1 mmol, 2M solution in CH_2Cl_2) was added at 0°C . Reaction mixture was stirred at room temperature for 13 h and diluted with water (10 mL) and extracted with ether (3x15 mL). Combined organic layer was dried over anhydrous Na_2SO_4 . Solvent was evaporated and the residue thus obtained was purified by silica gel column-chromatography (30% EtOAc in hexanes) to provide the title compound **3** as a colorless solid.

Yield : 0.279g (90%); Reaction time: 13 h; mp: 192-194 $^\circ\text{C}$; ^1H NMR (400 MHz): δ 6.33 (s, 1H), 6.77 (d, 1H, $J = 7.6 \text{ Hz}$), 6.88-6.98 (m, 2H), 7.05 (d, 1H, $J = 7.6 \text{ Hz}$), 7.15-7.22 (m, 2H), 7.33-7.50 (m, 4H), 7.63 (d, 1H, $J = 7.6 \text{ Hz}$), 7.65-7.72 (m, 2H), 9.51 (s, 1H, D_2O exchangeable); ^{13}C NMR (50 MHz): δ 65.31, 110.74, 121.29, 122.67, 122.89, 123.64, 126.65, 127.77, 127.91, 128.33, 128.64, 128.76, 131.84, 134.68, 142.47, 144.00, 146.37, 148.51, 178.32; IR (KBr): ν 3250-2800 (multiple bands), 1701, 1610 cm^{-1} ; LCMS (m/z): 310 ($\text{M}+\text{H}$) $^+$; Anal calc'd for $\text{C}_{22}\text{H}_{15}\text{NO}$: C, 85.41; H, 4.89; N, 4.53; Found: C, 85.57; H, 4.88; N, 4.50.

Crystal data for 3: Empirical formula, C₂₂H₁₅NO; formula weight, 309.35; crystal color, habit: colorless, rectangular; crystal dimensions, 0.42 X 0.40 X 0.24 mm³; crystal system, monoclinic; lattice type, primitive; lattice parameters, $a = 12.2411(9)$ Å, $b = 8.0506(6)$ Å, $c = 16.9934(12)$ Å; $\alpha = 90.00$; $\beta = 97.3520(10)$; $\gamma = 90.00$; $V = 1660.9(2)$ Å³; space group, p 21/c; $Z = 4$; $D_{\text{calcd}} = 1.237$ g / cm³; $F_{000} = 648$; $\lambda(\text{Mo-K}\alpha) = 0.71073$ Å; R ($I \geq 2\sigma_I$) = 0.0425, $wR^2 = 0.1170$. Detailed X-ray crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (for compound **3** CCDC # 618512).

Figure 1. ORTEP diagram of compound **3**

(Hydrogen atoms were omitted for clarity)

[6-Methyl-3-(4-methylphenyl)-1*H*-indene]-1-spiro-3'-(indolin-2'-one) (4**)**

Yield: 82%; Reaction time: 13 h; mp: 182-184 °C; ¹H NMR (400 MHz): δ 2.29 (s, 3H), 2.41 (s, 3H), 6.23 (s, 1H), 6.81 (d, 1H, $J = 7.6$ Hz), 6.86 (s, 1H), 6.92-6.98 (m, 1H), 7.00 (d, 1H, $J = 7.6$ Hz), 7.15 (d, 1H, $J = 8.0$ Hz), 7.22-7.29 (m, 3H), 7.49 (d, 1H, $J = 8.0$ Hz), 7.58 (d, 2H, $J = 8.8$ Hz), 7.87 (s, 1H, D₂O exchangeable); ¹³C NMR (50 MHz): δ 21.42, 64.89, 110.35, 121.19, 122.92, 123.69, 124.06, 127.77, 128.64, 128.79, 129.39, 130.19, 132.11, 136.65, 138.22, 141.57, 142.15, 146.66, 148.53, 178.25; IR (KBr): ν 3300-2800 (multiple bands), 1714, 1614 cm⁻¹; LCMS (m/z): 338(M+H)⁺; Anal calc'd for C₂₄H₁₉NO: C, 85.43; H, 5.68; N, 4.15; Found: C, 85.28; H, 5.65; N, 4.16.

[6-Methoxy-3-(4-methoxyphenyl)-1*H*-indene]-1-spiro-3'-(indolin-2'-one) (5)

Yield: 69%; Reaction time: 13 h; mp: 204-206 °C; ¹H NMR (400 MHz) : δ 3.73 (s, 3H), 3.86 (s, 3H), 6.15 (s, 1H), 6.61(d, 1H, *J* = 2.4Hz), 6.80 (d, 1H, *J* = 7.6 Hz), 6.89 (dd, 1H, *J* = 8.4 Hz & 2.4 Hz), 6.91-7.04 (m, 4H), 7.19-7.24 (m, 1H), 7.52 (d, 1H, *J* = 8.4 Hz), 7.63 (d, 2H, *J* = 8.8 Hz), 9.02 (s, 1H, D₂O exchangeable); ¹³C NMR (50 MHz): δ 55.38, 55.58, 64.94, 109.33, 110.59, 113.38, 114.06, 121.87, 122.82, 123.91, 127.48, 128.45, 128.59, 128.93, 129.42, 137.01, 142.25, 147.63, 148.10, 159.04, 159.72, 178.66; IR (KBr): ν 3300-2800 (multiple bands), 1714, 1610 cm⁻¹; LCMS (m/z): 370 (M+H)⁺; Anal calc'd for C₂₄H₁₉NO₃: C, 78.03; H, 5.18; N, 3.79 Found: C, 78.30; H, 5.16; N, 3.77.

Crystal data for **5**: Single crystal X-ray structure revealed the presence of two molecules in the asymmetric unit. For clarity we have shown one molecule in the ORTEP diagram (Figure 2). Empirical formula, C₂₄H₁₉NO₃; formula weight, 369.40; crystal color, habit: colorless, rectangular; crystal dimensions, 0.29 X 0.12 X 0.08 mm³; crystal system, monoclinic; lattice type, primitive; lattice parameters, *a* = 23.3988(15) Å, *b* = 9.0998(6) Å, *c* = 19.3653(13) Å; α = 90.00; β = 113.2430(10); γ = 90.00; *V* = 3788.7(4) Å³; space group, *P* 21/c; *Z* = 8; *D*_{calcd} = 1.295 g / cm³; *F*₀₀₀ = 1552; λ(Mo-K_α) = 0.71073 Å; *R* (*I* ≥ 2σ_{*I*}) = 0.0661, *wR*² = 0.1138. Detailed X-ray crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (for compound **5** CCDC # 618513).

Figure 2. ORTEP diagram of compound **5**

(Hydrogen atoms were omitted for clarity)

(3-Phenyl-1*H*-indene)-1-spiro-3'-(5'-chloroindolin-2'-one) (6)

Yield: 77%; Reaction time: 18 h; mp: 205-207 °C; ¹H NMR (400 MHz): δ 6.30 (s, 1H), 6.77 (s, 1H), 6.91 (d, 1H, *J* = 8.4 Hz), 7.05 (d, 1H, *J* = 7.6 Hz), 7.18-7.25 (m, 2H), 7.35-7.55 (m, 4H), 7.63 (d, 1H, *J* = 7.6 Hz), 7.69 (d, 2H, *J* = 7.6 Hz), 8.87 (s, 1H, D₂O exchangeable); ¹³C NMR (50 MHz): δ 65.23, 111.71, 121.63, 122.94, 124.15, 126.94, 127.84, 128.23, 128.37, 128.71, 128.81, 130.70, 130.92, 134.44, 140.89, 144.00, 145.67, 149.26, 178.13; IR (KBr): ν 3250-2800 (multiple bands), 1716, 1614 cm⁻¹; LCMS (m/z): 344 (M+H)⁺, 346 (M+2+H)⁺; Anal calc'd for C₂₂H₁₄ClNO: C, 76.86; H, 4.10; N, 4.07; Found: C, 76.74; H, 4.12; N, 4.02.

[6-Methyl-3-(4-methylphenyl)-1*H*-indene]-1-spiro-3'-(5'-chloroindolin-2'-one) (7)

Yield: 80%; Reaction time: 18 h; mp: 130-132 °C; ¹H NMR (400 MHz): δ 2.31 (s, 3H), 2.42 (s, 3H), 6.19 (s, 1H), 6.78 (d, 1H, *J* = 2.0 Hz), 6.85 (s, 1H), 6.93 (d, 1H, *J* = 8.4 Hz), 7.17 (d, 1H, *J* = 8.0 Hz), 7.22 (dd, 1H, *J* = 8.4 Hz & 2.4 Hz), 7.27 (d, 2H, *J* = 8.0 Hz), 7.50 (d, 1H, *J* = 8.0 Hz), 7.58 (d, 2H, *J* = 8.0 Hz), 8.24 (s, 1H, D₂O exchangeable); ¹³C NMR (50 MHz): δ 21.40, 64.97, 111.64, 121.34, 123.69, 124.18, 127.67, 128.13, 128.57, 129.03, 129.44, 131.19, 131.75, 136.86, 138.42, 140.87, 141.43, 145.94, 148.99, 178.49; IR (KBr): ν 3300-2800 (multiple bands), 1714, 1610 cm⁻¹; LCMS (m/z): 370 (M-H)⁺, 372 (M+2-H)⁺; Anal calc'd for C₂₄H₁₈ClNO: C, 77.52; H, 4.88; N, 3.77; Found: C, 77.63; H, 4.89; N, 3.73.

[6-Methoxy-3-(4-methoxyphenyl)-1*H*-indene]-1-spiro-3'-(5'-chloroindolin-2'-one) (8)

Yield: 88%; Reaction time: 18 h; mp: 128-130 °C; ¹H NMR (400 MHz): δ 3.75 (s, 3H), 3.87 (s, 3H), 6.11 (s, 1H), 6.60 (d, 1H, *J* = 2.4 Hz), 6.79 (s, 1H), 6.86-6.95 (m, 2H), 6.99 (d, 2H, *J* = 8.4 Hz), 7.22 (dd, 1H, *J* = 8.4 Hz & 2.4 Hz), 7.51 (d, 1H, *J* = 8.4 Hz), 7.62 (d, 2H, *J* = 8.4 Hz), 8.20 (s, 1H, D₂O exchangeable); ¹³C NMR (50 MHz): δ 55.46, 55.68, 64.85, 109.55, 111.49, 113.51, 114.18, 122.19, 124.37, 127.23, 127.55, 128.30, 128.64, 129.01, 131.36, 136.94, 140.65, 147.47, 148.34, 159.23, 159.93, 178.17; IR (KBr): ν 3300-2800 (multiple bands), 1714, 1610 cm⁻¹; LCMS (m/z): 404 (M+H)⁺; 406 (M+2+H)⁺; Anal calc'd for C₂₄H₁₈ClNO₃: C, 71.38; H, 4.49; N, 3.47; Found: C, 71.60; H, 4.49; N, 3.49.

(3-Phenyl-1*H*-indene)-1-spiro-3'-(5'-methylindolin-2'-one) (9)

Yield: 61%; Reaction time: 13 h; mp: 188-190 °C; ¹H NMR (400 MHz): δ 2.20 (s, 3H), 6.34 (s, 1H), 6.61 (s, 1H), 6.89 (d, 1H, *J* = 8.0 Hz), 7.03 (d, 1H, *J* = 7.6 Hz), 7.08 (d, 1H, *J* = 7.2 Hz), 7.18-7.25 (m, 1H), 7.35-7.51 (m, 4H), 7.64 (d, 1H, *J* = 7.6 Hz), 7.71 (d, 2H, *J* = 7.2 Hz), 8.73 (s, 1H, D₂O exchangeable); ¹³C NMR (50 MHz): δ 20.96, 65.33, 110.40, 121.36, 122.97, 124.40, 126.68, 127.87, 127.99, 128.37, 128.69, 128.84, 129.03, 132.01, 132.35, 134.75, 139.90, 144.02, 146.52, 148.48, 178.39; IR (KBr): ν 3250-2800 (multiple bands), 1707, 1622 cm⁻¹; LCMS (m/z): 346 (M+Na)⁺; Anal calc'd for C₂₃H₁₇NO: C, 85.42; H, 5.30; N, 4.33; Found: C, 85.22; H, 5.31; N, 4.35.

[6-Methyl-3-(4-methylphenyl)-1*H*-indene]-1-spiro-3'-(5'-methylindolin-2'-one) (10)

Yield: 79%; Reaction time: 13 h; mp: 184-186 °C; ¹H NMR (400 MHz): δ 2.21 (s, 3H), 2.30 (s, 3H), 2.41 (s, 3H), 6.22 (s, 1H), 6.62 (s, 1H), 6.86-6.93 (m, 2H), 7.05 (d, 1H, *J* = 8.0 Hz), 7.16 (d, 1H, *J* = 7.6 Hz), 7.27 (d, 2H, *J* = 8.0 Hz), 7.50 (d, 1H, *J* = 7.6 Hz), 7.59 (d, 2H, *J* = 8.0 Hz), 7.85 (s, 1H, D₂O exchangeable); ¹³C NMR (50 MHz): δ 20.92, 21.35, 65.11, 110.38, 121.05, 123.69, 124.35, 127.67, 128.64, 128.88, 129.30, 130.46, 132.06, 132.18, 136.50, 138.05, 139.95, 141.47, 146.79, 148.17, 178.88; IR (KBr): ν 3250-2800 (multiple

bands), 1707, 1622 cm^{-1} ; LCMS (m/z): 352 (M+H)⁺; Anal calc'd for $\text{C}_{25}\text{H}_{21}\text{NO}$: C, 85.44; H, 6.02; N, 3.99; Found: C, 85.27; H, 6.03; N, 4.04.

[6-Methoxy-3-(4-methoxyphenyl)-1*H*-indene]-1-spiro-3'-(5'-methylin-dolin-2'-one) (11)

Yield: 76%; Reaction time: 13 h; mp: 156-158 $^{\circ}\text{C}$; ^1H NMR (400 MHz): δ 2.21 (s, 3H), 3.74 (s, 3H), 3.87 (s, 3H), 6.15 (s, 1H), 6.62 (s, 2H), 6.86-6.92 (m, 2H), 6.99 (d, 2H, $J = 8.8$ Hz), 7.03 (d, 1H, $J = 8.0$ Hz), 7.52 (d, 1H, $J = 8.4$ Hz), 7.64 (d, 2H, $J = 8.8$ Hz), 8.53 (s, 1H, D_2O exchangeable); ^{13}C NMR (50 MHz): δ 20.96, 55.38, 55.58, 65.09, 109.41, 110.33, 113.34, 114.09, 121.85, 124.49, 127.57, 128.74, 128.96, 129.44, 132.35, 137.03, 139.82, 147.49, 148.31, 159.04, 159.72, 178.68; IR (KBr): ν 3250-2800 (multiple bands), 1707, 1610 cm^{-1} ; LCMS (m/z): 382 (M-H)⁺; Anal calc'd for $\text{C}_{25}\text{H}_{21}\text{NO}_3$: C, 78.31; H, 5.52; N, 3.65; Found: C, 78.09; H, 5.49; N, 3.61.

[6-Methoxy-3-(4-methoxyphenyl)-1*H*-indene]-1-spiro-3'-(5'-bromoindolin-2'-one) (12)

Yield: 64%; Reaction time: 18 h; mp: 164-166 $^{\circ}\text{C}$; ^1H NMR (400 MHz): δ 3.75 (s, 3H), 3.87 (s, 3H), 6.10 (s, 1H), 6.60 (d, 1H, $J = 2.4$ Hz), 6.83 (d, 1H, $J = 8.4$ Hz), 6.89-6.95 (m, 2H), 7.00 (d, 2H, $J = 8.8$ Hz), 7.31 (dd, 1H, $J = 8.4$ Hz & 2.0 Hz), 7.53 (d, 1H, $J = 8.4$ Hz), 7.63 (d, 2H, $J = 8.4$ Hz), 9.33 (s, 1H, D_2O exchangeable); ^{13}C NMR (50 MHz): δ 55.38, 55.60, 64.85, 109.58, 112.17, 113.41, 114.18, 115.40, 122.09, 126.90, 127.16, 127.55, 128.93, 131.46, 131.60, 136.89, 141.30, 147.42, 148.19, 159.18, 159.91, 178.27; IR (KBr): ν 3250-2800 (multiple bands), 1712, 1610 cm^{-1} ; LCMS (m/z): 446 (M-H)⁺, 448 (M+2-H)⁺; Anal calc'd for $\text{C}_{24}\text{H}_{18}\text{BrNO}_3$: C, 64.30; H, 4.05; N, 3.12; Found: C, 64.14; H, 4.09; N, 3.18.

[6-Methoxy-3-(4-methoxyphenyl)-1*H*-indene]-1-spiro-3'-(1'-methylin-dolin-2'-one) (13)

Yield: 72%; Reaction time: 18 h; mp: 96-98 °C; ¹H NMR (400 MHz): δ 3.35 (s, 3H), 3.72 (s, 3H), 3.86 (s, 3H), 6.09 (s, 1H), 6.51 (d, 1H, *J* = 2.4 Hz), 6.81-6.89 (m, 2H), 6.95-7.02 (m, 4H), 7.30-7.37 (m, 1H), 7.50 (d, 1H, *J* = 8.4 Hz), 7.60-7.64 (m, 2H); ¹³C NMR (50 MHz): δ 26.98, 55.36, 55.58, 64.36, 108.39, 109.48, 113.07, 114.06, 121.83, 122.97, 123.72, 127.60, 128.64, 128.71, 128.96, 137.18, 144.87, 147.51, 148.29, 159.01, 159.72, 175.29; IR (KBr): ν 1714, 1608 cm⁻¹; LCMS (m/z): 384 (M+H)⁺; Anal calc'd for C₂₅H₂₁NO₃: C, 78.31; H, 5.52; N, 3.65; Found: C, 78.53; H, 5.50; N, 3.69.

(3-Phenyl-1*H*-indene)-1-spiro-3'-(1'-ethylindolin-2'-one) (14)

Yield: 63%; Reaction time: 24 h; mp: 122-124 °C; ¹H NMR (400 MHz): δ 1.37 (t, 3H, *J* = 7.2 Hz), 3.84-4.00 (m, 2H), 6.29 (s, 1H), 6.80-6.88 (m, 1H), 6.92-7.04 (m, 3H), 7.16-7.20 (m, 1H), 7.28-7.50 (m, 5H), 7.61 (d, 1H, *J* = 7.6 Hz), 7.65-7.75 (m, 2H); ¹³C NMR (50 MHz): δ 12.72, 35.23, 64.51, 108.48, 121.17, 122.43, 122.58, 123.67, 126.43, 127.70, 128.18, 128.52, 131.89, 134.71, 143.90, 146.66, 148.39, 174.22; IR (KBr): ν 1716, 1610 cm⁻¹; LCMS (m/z): 338 (M+H)⁺; Anal calc'd for C₂₄H₁₉NO: C, 85.43; H, 5.68; N, 4.15; Found: C, 85.20; H, 5.65; N, 4.13.

Crystal data for **14**: Empirical formula, C₂₄H₁₉NO; formula weight, 337.40; crystal color, habit: colorless, rectangular; crystal dimensions 0.31 X 0.25 X 0.20 mm³; crystal system, monoclinic; lattice type, primitive; lattice parameters, *a* = 12.038(2) Å, *b* = 12.112(2) Å, *c* = 14.089(2) Å; α = 90.00; β = 114.892(3); γ = 90.00; *V* = 1863.5(5) Å³; space group, *p* 21/n; *Z* = 4; *D*_{calcd} = 1.203 g / cm³; *F*₀₀₀ = 712; λ(Mo-Kα) = 0.71073 Å; *R* (*I* ≥ 2σ_{*I*}) = 0.0522, *wR*² = 0.1397. Detailed X-ray crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (for compound **14** CCDC # 618514).

Figure 3. ORTEP diagram of compound **14**

(Hydrogen atoms were omitted for clarity)

[This reaction also provides 3,3-bis(2,2-diphenylvinyl)-1-ethylindolin-2-one (**18**) in 23% isolated yield (based on alkene). Spectral data is given on page S11. We have also recovered 11% of *N*-ethylisatin (**1f**)]

[6-Methoxy-3-(4-methoxyphenyl)-1*H*-indene]-1-spiro-3'-(1'-ethylindolin-2'-one) (15**)**

Yield: 71%; Reaction time: 18 h; mp: 96-98 °C; ¹H NMR (400 MHz): δ 1.37 (t, 3H, *J* = 7.2 Hz), 3.72 (s, 3H), 3.84-4.04 (m, 5H), 6.10 (s, 1H), 6.49 (s, 1H), 6.82-6.89 (m, 2H), 6.92-7.04 (m, 4H), 7.28-7.35 (m, 1H), 7.50 (d, 1H, *J* = 8.0 Hz), 7.62 (d, 2H, *J* = 8.8 Hz); ¹³C NMR (50 MHz): δ 12.57, 35.03, 54.97, 55.17, 64.09, 108.34, 109.24, 112.51, 113.84, 121.51, 122.43, 123.52, 127.28, 128.37, 128.47, 128.62, 128.88, 136.79, 143.66, 147.20, 148.34, 158.74, 159.50, 174.39; IR (KBr): ν 1714, 1608 cm⁻¹; LCMS (*m/z*): 398 (*M*+H)⁺; Anal calc'd for C₂₆H₂₃NO₃: C, 78.57; H, 5.83; N, 3.52; Found : C, 78.82; H, 5.80; N, 3.60.

Towards understanding mechanism:

Reaction of isatin (**1a**, 1 mmol) with 1,1-diphenylethylene (**2a**, 1 mmol) in the presence of TiCl₄ (1 mmol, 0.5mL, 2M solution in CH₂Cl₂) at 0 °C for five minutes provided (3-phenyl-1*H*-indene)-1-spiro-3'-(indolin-2'-one) (**3**) in 17% (based on isatin **1a**) isolated yield and 3,3-bis(2,2-diphenylvinyl)-indolin-2-one (**16**) in 45%

(based on alkene **2a**) isolated yields. We have also recovered isatin (**1a**) in 31% and alkene (**2a**) in 17% isolated yields.

3,3-Bis(2,2-diphenylvinyl)indolin-2-one (**16**)

Yield: 45%; Reaction time: 5 min; mp: 218-220 °C; ^1H NMR (400 MHz): δ 6.30-6.36 (m, 3H), 6.61 (s, 1H, D_2O exchangeable), 6.84-7.24 (m, 23H); ^{13}C NMR (50 MHz): δ 56.28, 109.72, 122.48, 124.76, 127.21, 127.33, 127.60, 127.96, 129.54, 130.07, 136.53, 138.32, 140.19, 142.86, 144.46, 178.66; IR (KBr): ν 3350-2950 (multiple bands), 1716, 1614 cm^{-1} ; LCMS (m/z): 490 ($\text{M}+\text{H}^+$); Anal calc'd for $\text{C}_{36}\text{H}_{27}\text{NO}$: C, 88.31; H, 5.56; N, 2.86; Found: C, 88.11; H, 5.59; N, 2.89.

Crystal data for **16**: Empirical formula, $\text{C}_{36}\text{H}_{27}\text{NO}$; formula weight, 489.59; crystal color, habit: colorless, rectangular; crystal dimensions, 0.42 X 0.36 X 0.05 mm^3 ; crystal system, monoclinic; lattice type, primitive; lattice parameters, $a = 11.237(3)$ Å, $b = 17.495(4)$ Å, $c = 14.195(4)$ Å; $\alpha = 90.00$; $\beta = 94.841(5)$; $\gamma = 90.00$; $V = 2780.6(12)$ Å 3 ; space group, $P 2_1/n$; $Z = 4$; $D_{\text{calc'd}} = 1.169$ g / cm^3 ; $F_{000} = 1032$; $\lambda(\text{Mo-K}\alpha) = 0.71073$ Å; R ($I \geq 2\sigma_I$) = 0.0482, $wR^2 = 0.1060$. Detailed X-ray crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (for compound **16** CCDC # 618515).

Figure 4. ORTEP diagram of compound **16**

(Hydrogen atoms were omitted for clarity)

Reaction of 5-chloroisatin (**1b**, 1 mmol) with 1,1-diphenylethylene (**2a**, 1 mmol) in the presence of TiCl_4 (1 mmol, 0.5mL, 2M solution in CH_2Cl_2) at 0°C for five minutes provided (3-phenyl-1*H*-indene)-1-spiro-3'-(5'-chloroindolin-2'-one) (**6**) in 16% isolated yield (based on **1b**) and 3,3-bis(2,2-diphenylvinyl)-5-chloroindolin-2-one (**17**) in 37% (based on alkene) isolated yields. We also recovered isatin (**1a**) in 25% and alkene (**2a**) in about 6% isolated yields.

3,3-Bis(2,2-diphenylvinyl)-5-chloroindolin-2-one (**17**)

Yield: 37%; Reaction time: 5 min, mp: 168-170 $^\circ\text{C}$; ^1H NMR (400 MHz): δ 6.22 (d, 1H, $J = 8.4$ Hz), 6.36 (s, 2H), 6.85-6.90 (m, 5H), 6.91-6.96 (m, 1H), 7.00-7.06 (m, 5H), 7.07-7.18 (m, 6H), 7.19-7.24 (m, 6H); ^{13}C NMR (50 MHz): δ 56.57, 110.72, 125.56, 127.26, 127.38, 127.62, 128.06, 128.62, 129.73, 136.69, 138.00, 138.93, 142.40, 144.92, 179.36; IR (KBr): ν 3300-2800 (multiple bands), 1711, 1614 cm^{-1} ; LCMS (m/z): 524 ($\text{M}+\text{H}$) $^+$, 526 ($\text{M}+2\text{H}$) $^+$; Anal calc'd for $\text{C}_{36}\text{H}_{26}\text{ClNO}$: C, 82.51; H, 5.00; N, 2.67; Found: C, 82.79; H, 5.03; N, 2.64.

3,3-Bis(2,2-diphenylvinyl)-1-ethylindolin-2-one (**18**)

Yield: 23%; Reaction time: 24 h; mp: 80-82 $^\circ\text{C}$; ^1H NMR (400 MHz): δ 0.91 (t, 3H, $J = 7.2$ Hz), 2.99 (q, 2H, $J = 7.2$ Hz), 6.19 (s, 2H), 6.41 (d, 1H, $J = 7.6$ Hz), 6.82-7.02 (m, 9H), 7.08-7.23 (m, 14H); ^{13}C NMR (50 MHz): δ 12.62, 34.96, 55.92, 108.14, 122.41, 124.57, 127.21, 127.28, 127.43, 127.67, 127.89, 129.49, 130.10, 136.57, 138.49, 141.98, 143.27, 144.04, 175.53; IR (KBr): ν 1712, 1606 cm^{-1} ; LCMS (m/z): 518 ($\text{M}+\text{H}$) $^+$; Anal calc'd for $\text{C}_{38}\text{H}_{31}\text{NO}$: C, 88.17; H, 6.04; N, 2.71; Found: C, 88.03; H, 6.06; N, 2.76

We have also carried out the following experiments with a view to prove the mechanistic path-way (**Y**)

Reaction of 3,3-bis(2,2-diphenylvinyl)indolin-2-one (**16**) with TiCl_4 in dichloromethane for 13 h at room temperature provided (3-phenyl-1*H*-indene)-1-spiro-3'-(indolin-2'-one) (**3**) in 85% isolated yield and 3-methyl-1,1,3-triphenylindane (**19**) in 60% isolated yield.

Similar reaction of 3,3-bis(2,2-diphenylvinyl)-5-chloroindolin-2-one (**17**), with TiCl_4 in dichloromethane for 18 h at room temperature provided (3-phenyl-1*H*-indene)-1-spiro-3'-(5-chloroindolin-2'-one) (**6**) in 88% isolated yield and 3-methyl-1,1,3-triphenylindane (**19**) in 70% isolated yield.

Similar reaction of 3,3-bis(2,2-diphenylvinyl)-1-ethylindolin-2-one (**18**), with TiCl_4 in dichloromethane for 48 h at room temperature provided [3-phenyl-1*H*-indene]-1-spiro-3'-(1'-ethylindolin-2'-one) (**14**) and 3-methyl-1,1,3-triphenylindane (**19**) in 36% and 22% isolated yields respectively. We have also recovered the starting material **18** in 47% isolated yield.

3-Methyl-1,1,3-triphenylindane (**19**)

mp: 138-140 °C (lit. 143-144 °C)^s; ^1H NMR (400 MHz): δ 1.54 (s, 3H), 3.09 & 3.39 (ABq, 2H, $J = 13.5$ Hz), 6.98-7.34 (m, 19H); ^{13}C NMR (50 MHz): δ 28.99, 51.29, 61.06, 61.45, 125.12, 125.68, 126.07, 126.97, 127.53, 127.67, 127.96, 128.04, 128.76, 128.86, 147.59, 148.68, 148.97, 149.43, 150.62; IR (KBr): ν 2968, 1595 cm^{-1} ; LCMS (m/z): 361 ($\text{M}+\text{H}^+$); Anal calc'd for $\text{C}_{28}\text{H}_{24}$: C, 93.29; H, 6.71; Found: C, 93.42; H, 6.74.

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150.6236
149.4350
148.9741
148.6830
147.5915

128.8649
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76.4693

61.4541
61.0660

51.2903

28.9980