Supporting Information for the Paper

Metal–Mediated Entry to Functionalized 3-Substituted 3-Hydroxyindolin-2-ones via Regiocontrolled Carbonyl-Allylation, Bromoallylation, 1,3-Butadien-2-ylation, Propargylation, or Allenylation Reactions of Isatins in Aqueous Media

Benito Alcaide,^{*a} Pedro Almendros,^{*b} and Raquel Rodríguez-Acebes,^a

^a*Departamento de Química Orgánica, Facultad de Química, Universidad Complutense de Madrid, 28040-Madrid, Spain*

^b*Instituto de Química Orgánica General, CSIC, Juan de la Cierva 3, 28006-Madrid, Spain*

E-mail: alcaideb@quim.ucm.es; iqoa392@iqog.csic.es

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Zinc Promoted Reaction between Allyl Bromide and Isatin 1a. Allyl bromide (121 mg, 1.0 mmol) was added to a well stirred suspension of the α -keto lactam **1a** (73 mg, 0.5 mmol) and zinc powder (65 mg, 1.0 mmol) in THF/H₂O (1:1, 5 mL) at room temperature. After 2 days, saturated aqueous sodium hydrogen carbonate (2.5 mL) was added at 0 °C, and the mixture was allowed to warm to room temperature, before being extracted with ethyl acetate (3 x 3 mL). The organic extract was washed with brine, dried (MgSO₄), and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/dichloromethane (1:4) as an eluent gave 33 mg (35%) of compound **2a**.

Zinc Promoted Reaction between Allyl Bromide and Isatin 1a in an Aqueous Medium Containing NH₄Cl. Allyl bromide (121 mg, 1.0 mmol) was added to a well stirred suspension of the α -keto lactam **1a** (73 mg, 0.5 mmol) and zinc powder (65 mg, 1.0 mmol) in THF/NH₄Cl (aq sat) (1:5, 5 mL) at room temperature. After 24 h, saturated aqueous sodium hydrogen carbonate (2.5 mL) was added at 0 °C, and the mixture was allowed to warm to room temperature, before being extracted with ethyl acetate (3 x 3 mL). The organic extract was washed with brine, dried (MgSO₄), and concentrated under reduced pressure to give 78 mg (83%) of compound **2a**.

Tin Promoted Reaction between Allyl Bromide and Isatin 1a. Allyl bromide (121 mg, 1.0 mmol) was added to a well stirred suspension of the α -keto lactam **1a** (73 mg, 0.5 mmol) and tin powder (119 mg, 1.0 mmol) in THF/H₂O (1:1, 5 mL) at room temperature. After 20 h, saturated aqueous sodium hydrogen carbonate (2.5 mL) was added at 0 °C, and the mixture was allowed to

warm to room temperature, before being extracted with ethyl acetate (3 x 3 mL). The organic extract was washed with brine, dried (MgSO₄), and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/dichloromethane (1:4) as an eluent gave 29 mg (31%) of compound **2a**.

Tin Promoted Reaction between Allyl Bromide and Isatin 1a in an Aqueous Medium Containing NH₄Cl. Allyl bromide (121 mg, 1.0 mmol) was added to a well stirred suspension of the α -keto lactam **1a** (73 mg, 0.5 mmol) and tin powder (119 mg, 1.0 mmol) in THF/NH₄Cl (aq sat) (1:5, 5 mL) at room temperature. After 24 h, saturated aqueous sodium hydrogen carbonate (2.5 mL) was added at 0 °C, and the mixture was allowed to warm to room temperature, before being extracted with ethyl acetate (3 x 3 mL). The organic extract was washed with brine, dried (MgSO₄), and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/dichloromethane (1:4) as an eluent gave 36 mg (40%) of compound **2a**.

Indium Promoted Reaction between Allyl Bromide and Isatin 1a. Allyl bromide (121 mg, 1.0 mmol) was added to a well stirred suspension of the α -keto lactam **1a** (73 mg, 0.5 mmol) and indium powder (115 mg, 1.0 mmol) in THF/H₂O (1:1, 5 mL) at 0 °C. After 2 h, saturated aqueous sodium hydrogen carbonate (2.5 mL) was added, and the mixture was allowed to warm to room temperature, before being extracted with ethyl acetate (3 x 3 mL). The organic extract was washed with brine, dried (MgSO₄), and concentrated under reduced pressure to give 93 mg (100%) of compound **2a**.

Indium Promoted Reaction between Allyl Bromide and Isatin 1a in an Aqueous Medium Containing NH₄Cl. Allyl bromide (121 mg, 1.0 mmol) was added to a well stirred suspension of the α -keto lactam **1a** (73 mg, 0.5 mmol) and indium powder (115 mg, 1.0 mmol) in THF/NH₄Cl (aq sat) (1:5, 5 mL) at room temperature. After 4 h, saturated aqueous sodium hydrogen carbonate (2.5 mL) was added at 0 °C, and the mixture was allowed to warm to room temperature, before being extracted with ethyl acetate (3 x 3 mL). The organic extract was washed with brine, dried (MgSO₄), and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/dichloromethane (1:4) as an eluent gave 39 mg (42%) of compound **2a**.

3-(2-Methyl-3-buten-2-yl)-3-hydroxy-1,3-dihydro-2H-indol-2-one, 2b. From 73 mg (0.5 mmol) of 2,3-indolinedione **1a**, 92 mg (86%) of compound **2b** was obtained as a colorless solid by

flash chromatography (ethyl acetate/dichloromethane, 1/4). Mp: 182–183 °C (hexanes/ethyl acetate). $^1\text{H-NMR}$ (d_6 -acetone): δ 9.22 (br s, 1H), 7.33 (dd, 1H, $J = 7.4, 1.3$ Hz), 7.21 (td, 1H, $J = 7.7, 1.3$ Hz), 6.94 (td, 1H, $J = 7.6, 1.0$ Hz), 6.85 (d, 1H, $J = 7.8$ Hz), 6.16 (dd, 1H, $J = 17.6, 11.0$ Hz), 5.01 (dd, 1H, $J = 11.0, 1.5$ Hz), 4.94 (dd, 1H, $J = 17.8, 1.5$ Hz), 4.65 (s, 1H), 1.23 and 1.08 (s, each 3H). $^{13}\text{C-NMR}$ (d_6 -acetone): δ 179.7, 144.0, 143.4, 131.7, 129.9, 127.0, 122.0, 113.7, 110.2, 80.7, 44.2, 22.2, 20.7. IR (CHCl_3 , cm^{-1}): ν 3422, 3298, 1708. MS (EI), m/z : 218 ($\text{M}^+ + 1$, 9), 217 (M^+ , 100). Anal. Calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.96; H, 6.92; N, 6.42.

3-Allyl-3-hydroxy-1-methyl-1,3-dihydro-2H-indol-2-one, 2c.^{11a} From 81 mg (0.5 mmol) of 2,3-indolinedione **1b**, 101 mg (100%) of compound **2c** was obtained as a colorless oil.

Indium Promoted Reaction between 2,3-Dibromopropene and Isatin 1a. 2,3-Dibromopropene (300 mg, 1.5 mmol) was added to a well stirred suspension of the α -keto lactam **1a** (73 mg, 0.5 mmol) and indium powder (86 mg, 0.75 mmol) in THF/ H_2O (1:1, 5 mL) at room temperature. After 7 days, saturated aqueous sodium hydrogen carbonate (2.5 mL) was added at 0 °C, and the mixture was allowed to warm to room temperature, before being extracted with ethyl acetate (3 x 3 mL). The organic extract was washed with brine, dried (MgSO_4), and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/dichloromethane (1:4) as an eluent gave 27 mg (20%) of compound **3a**.

Zinc Promoted Reaction between 2,3-Dibromopropene and Isatin 1a. Synthesis of Compound 10. 2,3-Dibromopropene (300 mg, 1.5 mmol) was added to a well stirred suspension of the α -keto lactam **1a** (73 mg, 0.5 mmol) and zinc powder (65 mg, 1.0 mmol) in THF/ H_2O (1:1, 5 mL) at room temperature. After 7 days, saturated aqueous sodium hydrogen carbonate (2.5 mL) was added at 0 °C, and the mixture was allowed to warm to room temperature, before being extracted with ethyl acetate (3 x 3 mL). The organic extract was washed with brine, dried (MgSO_4), and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/dichloromethane (1:1) as an eluent gave 136 mg (96%) of compound **10**.

2-(2-Aminophenyl)-4-bromo-2-hydroxypent-4-enoic acid, 10. Colorless oil. $^1\text{H-NMR}$ (acetone- d_6): δ 7.62 (td, 1H, $J = 7.7, 1.2$ Hz), 7.55 (d, 1H, $J = 7.6$ Hz), 7.13 (td, 1H, $J = 7.6, 0.7$ Hz), 7.03 (dt, 1H, $J = 7.8, 0.7$ Hz), 6.05 (dt, 1H, $J = 2.0, 0.7$ Hz), 5.84 (d, 1H, $J = 2.0$ Hz), 3.36 (d, 2H, $J = 0.7$ Hz). $^{13}\text{C-NMR}$ (acetone- d_6): δ 184.8, 151.6, 139.2, 125.9, 125.4, 125.3, 123.9, 119.0, 113.2, 65.9, 49.2. IR (CHCl_3 , cm^{-1}): ν 3504, 3410, 1694. MS (EI), m/z : 287 ($\text{M}^+ + 2$, 98), 285 (M^+ , 100). Anal. Calcd for $\text{C}_{11}\text{H}_{12}\text{BrNO}_3$: C, 46.18; H, 4.23; N, 4.90. Found: C, 46.29; H, 4.20; N, 4.86.

Tin Promoted Reaction between 2,3-Dibromopropene and Isatin 1a. 2,3-Dibromopropene (300 mg, 1.5 mmol) was added to a well stirred suspension of the α -keto lactam **1a** (73 mg, 0.5 mmol) and tin powder (89 mg, 0.75 mmol) in THF/ H_2O (1:1, 5 mL) at room temperature. After 27 h, saturated aqueous sodium hydrogen carbonate (2.5 mL) was added at 0 °C, and the mixture was allowed to warm to room temperature, before being extracted with ethyl acetate (3 x 3 mL). The organic extract was washed with brine, dried (MgSO_4), and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/dichloromethane (1:4) as an eluent gave 40 mg (30%) of compound **3a**.

Tin Promoted Reaction between 2,3-Dibromopropene and Isatin 1a in an Aqueous Medium Containing NH_4Cl . 2,3-Dibromopropene (300 mg, 1.5 mmol) was added to a well stirred suspension of the α -keto lactam **1a** (73 mg, 0.5 mmol) and tin powder (89 mg, 0.75 mmol) in THF/ NH_4Cl (aq sat) (1:5, 5 mL) at room temperature. After 24 h, saturated aqueous sodium hydrogen carbonate (2.5 mL) was added at 0 °C, and the mixture was allowed to warm to room temperature, before being extracted with ethyl acetate (3 x 3 mL). The organic extract was washed with brine, dried (MgSO_4), and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/dichloromethane (1:4) as an eluent gave 65 mg (49%) of compound **3a**.

Tin Promoted Reaction between 2,3-Dibromopropene and Isatin 1a in an Aqueous Medium Containing HBr . 2,3-Dibromopropene (300 mg, 1.5 mmol) was added to a well stirred suspension of the α -keto lactam **1a** (73 mg, 0.5 mmol), tin powder (89 mg, 0.75 mmol) and 48% HBr (cat.) in THF/ NH_4Cl (aq satd) (1:5, 5 mL) at 5 °C. After 2 days, saturated aqueous sodium hydrogen carbonate (2.5 mL) was added at 0 °C, and the mixture was allowed to warm to room temperature, before being extracted with ethyl acetate (3 x 3 mL). The organic extract was washed

with brine, dried (MgSO_4), and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/dichloromethane (1:4) as an eluent gave 86 mg (65%) of compound **3a**.

Tin Promoted Reaction between 2,3-Dibromopropene and Isatin 1a in an Aqueous Medium Containing HfCl_4 . 2,3-Dibromopropene (300 mg, 1.5 mmol) was added to a well stirred suspension of the α -keto lactam **1a** (73 mg, 0.5 mmol), tin powder (89 mg, 0.75 mmol) and hafnium(IV) chloride (32 mg, 0.1 mmol) in THF/ NH_4Cl (aq satd) (1:5, 5 mL) at 5 °C. After 22 h, saturated aqueous sodium hydrogen carbonate (2.5 mL) was added at 0 °C, and the mixture was allowed to warm to room temperature, before being extracted with ethyl acetate (3 x 3 mL). The organic extract was washed with brine, dried (MgSO_4), and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/dichloromethane (1:4) as an eluent gave 82 mg (62%) of compound **3a**.

3-(2-Bromoallyl)-3-hydroxy-1-methyl-1,3-dihydro-2H-indol-2-one, 3b. From 53 mg (0.33 mmol) of 2,3-indolinedione **1b**, 69 mg (74%) of compound **3b** was obtained as a colorless oil after purification by flash chromatography (ethyl acetate/dichloromethane, 1/40). $^1\text{H-NMR}$: δ 7.45 (ddd, 1H, $J = 7.3, 1.3, 0.6$ Hz), 7.35 (td, 1H, $J = 7.7, 1.3$ Hz), 7.12 (td, 1H, $J = 7.4, 0.9$ Hz), 6.85 (d, 1H, $J = 7.8$ Hz), 6.53 (dt, 1H, $J = 1.7, 0.9$ Hz), 5.42 (d, 1H, $J = 1.7$ Hz), 3.19 (m, 5H). $^{13}\text{C-NMR}$: δ 177.2, 143.6, 130.9, 130.1, 128.6, 125.0, 124.8, 123.1, 122.2, 108.6, 76.1, 49.1, 26.3. IR (CHCl_3 , cm^{-1}): ν 3292, 1714. MS (EI), m/z : 283 ($\text{M}^+ + 1$, 100), 281 ($\text{M}^+ - 1$, 98). Anal. Calcd for $\text{C}_{12}\text{H}_{12}\text{BrNO}_2$: C, 51.09; H, 4.29; N, 4.96. Found: C, 51.20; H, 4.26; N, 4.92.

Tin Promoted Reaction between Propargyl Bromide and Isatin 1a. Propargyl bromide (178 mg, 1.5 mmol) was added to a well stirred suspension of the α -keto lactam **1a** (73 mg, 0.5 mmol) and tin powder (348 mg, 3.0 mmol) in THF/ H_2O (1:1, 5 mL) at room temperature. After 9 ds, saturated aqueous sodium hydrogen carbonate (2.5 mL) was added at 0 °C, and the mixture was allowed to warm to room temperature, before being extracted with ethyl acetate (3 x 3 mL). The organic extract was washed with brine, dried (MgSO_4), and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/dichloromethane (1:20) as an eluent gave 23 mg (25%) of compound **4a** containing 52% of its regioisomer **5a**.

Indium Promoted Reaction between Propargyl Bromide and Isatin 1a. Propargyl bromide (178 mg, 1.5 mmol) was added to a well stirred suspension of the α -keto lactam **1a** (73

mg, 0.5 mmol) and indium powder (344 mg, 3.0 mmol) in THF/H₂O (1:1, 5 mL) at room temperature. After 7 ds, saturated aqueous sodium hydrogen carbonate (2.5 mL) was added at 0 °C, and the mixture was allowed to warm to room temperature, before being extracted with ethyl acetate (3 x 3 mL). The organic extract was washed with brine, dried (MgSO₄), and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/dichloromethane (1:20) as an eluent gave 37 mg (40%) of compound **4a** containing 22% of its regioisomer **5a**.

Tin Promoted Promoted Reaction between Propargyl Bromide and Isatin 1a in an Aqueous Medium Containing NH₄Cl. Propargyl bromide (178 mg, 1.5 mmol) was added to a well stirred suspension of the α -keto lactam **1a** (73 mg, 0.5 mmol) and tin powder (348 mg, 3.0 mmol) in THF/NH₄Cl (aq sat) (1:5, 5 mL) at room temperature. After 1 d, saturated aqueous sodium hydrogen carbonate (2.5 mL) was added at 0 °C, and the mixture was allowed to warm to room temperature, before being extracted with ethyl acetate (3 x 3 mL). The organic extract was washed with brine, dried (MgSO₄), and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/dichloromethane (1:20) as an eluent gave 30 mg (32%) of compound **4a** containing 54% of its regioisomer **5a**.

Indium Promoted Promoted Reaction between Propargyl Bromide and Isatin 1a in an Aqueous Medium Containing NH₄Cl. Propargyl bromide (178 mg, 1.5 mmol) was added to a well stirred suspension of the α -keto lactam **1a** (73 mg, 0.5 mmol) and indium powder (344 mg, 3.0 mmol) in THF/NH₄Cl (aq sat) (1:5, 5 mL) at room temperature. After 2 h, saturated aqueous sodium hydrogen carbonate (2.5 mL) was added at 0 °C, and the mixture was allowed to warm to room temperature, before being extracted with ethyl acetate (3 x 3 mL). The organic extract was washed with brine, dried (MgSO₄), and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/dichloromethane (1:20) as an eluent gave 53 mg (57%) of compound **4a** containing 18% of its regioisomer **5a**.

Zinc Promoted Reaction between Propargyl Bromide and Isatin 1a. Propargyl bromide (178 mg, 1.5 mmol) was added to a well stirred suspension of the α -keto lactam **1a** (73 mg, 0.5 mmol) and zinc powder (195 mg, 3.0 mmol) in THF/H₂O (1:1, 5 mL) at room temperature. After 9 ds, saturated aqueous sodium hydrogen carbonate (2.5 mL) was added at 0 °C, and the mixture was allowed to warm to room temperature, before being extracted with ethyl acetate (3 x 3 mL). The

organic extract was washed with brine, dried (MgSO₄), and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/dichloromethane (1:20) as an eluent gave 43 mg (46%) of compound **4a** containing 7% of its regioisomer **5a**.

Zinc Promoted Reaction between Propargyl Bromide and Isatin 1a in an Aqueous Medium Containing NH₄Cl. Propargyl bromide (178 mg, 1.5 mmol) was added to a well stirred suspension of the α -keto lactam **1a** (73 mg, 0.5 mmol) and zinc powder (195 mg, 3.0 mmol) in THF/NH₄Cl (aq sat) (1:5, 5 mL) at room temperature. After 1 h, saturated aqueous sodium hydrogen carbonate (2.5 mL) was added at 0 °C, and the mixture was allowed to warm to room temperature, before being extracted with ethyl acetate (3 x 3 mL). The organic extract was washed with brine, dried (MgSO₄), and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/dichloromethane (1:20) as an eluent gave 60 mg (64%) of compound **4a**.

Zinc Promoted Reaction between Propargyl Bromide and Isatin 1a in an Aqueous Medium Containing HfCl₄. Propargyl bromide (178 mg, 1.5 mmol) was added to a well stirred suspension of the α -keto lactam **1a** (73 mg, 0.5 mmol), zinc powder (195 mg, 3.0 mmol) and hafnium(IV) chloride (32 mg, 0.1 mmol) in THF/H₂O (1:1, 5 mL) at room temperature. After 7 d, saturated aqueous sodium hydrogen carbonate (2.5 mL) was added at 0 °C, and the mixture was allowed to warm to room temperature, before being extracted with ethyl acetate (3 x 3 mL). The organic extract was washed with brine, dried (MgSO₄), and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/dichloromethane (1:20) as an eluent gave 55 mg (59%) of compound **4a**.

3-Hydroxy-1-methyl-3-(2-propynyl)-1,3-dihydro-2H-indol-2-one, 4b. From 58 mg (0.36 mmol) of 2,3-indolinedione **1b**, 65 mg (90%) of compound **4b** was obtained as a colorless solid. after purification by flash chromatography (ethyl acetate/hexanes, 1/2). Mp: 152–153 °C (hexanes/ethyl acetate). ¹H-NMR: δ 7.58 (dd, 1H, J = 7.3, 1.2 Hz), 7.37 (td, 1H, J = 7.7, 1.3 Hz), 7.13 (td, 1H, J = 7.6, 1.0 Hz), 6.86 (d, 1H, J = 7.8 Hz), 3.21 (s, 3H), 2.94 and 2.73 (dd, each 1H, J = 16.5, 2.7 Hz), 1.99 (t, 1H, J = 2.7 Hz). ¹³C-NMR: δ 176.9, 143.5, 130.2, 129.2, 124.3, 123.4, 108.6, 77.8, 74.5, 71.6, 28.9, 26.4. IR (CHCl₃, cm⁻¹): ν 3295, 1712. MS (EI), m/z : 202 (M⁺ + 1,

12), 201 (M^+ , 100). Anal. Calcd for $C_{12}H_{11}NO_2$: C, 71.63; H, 5.51; N, 6.96. Found: C, 71.73; H, 5.47; N, 6.99.

Tin Promoted Reaction between 1-Bromo-2-butyne and Isatin 1a. 1-Bromo-2-butyne (200 mg, 1.5 mmol) was added to a well stirred suspension of the α -keto lactam **1a** (73 mg, 0.5 mmol) and tin powder (348 mg, 3.0 mmol) in THF/H₂O (1:1, 5 mL) at room temperature. After 18 h, saturated aqueous sodium hydrogen carbonate (2.5 mL) was added at 0 °C, and the mixture was allowed to warm to room temperature, before being extracted with ethyl acetate (3 x 3 mL). The organic extract was washed with brine, dried (MgSO₄), and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/dichloromethane (1:10) as an eluent gave 42 mg (42%) of compound **6a**.

Tin Promoted Reaction between 1-Bromo-2-butyne and Isatin 1a in an Aqueous Medium Containing NH₄Cl. 1-Bromo-2-butyne (200 mg, 1.5 mmol) was added to a well stirred suspension of the α -keto lactam **1a** (73 mg, 0.5 mmol) and tin powder (348 mg, 3.0 mmol) in THF/NH₄Cl (aq sat) (1:5, 5 mL) at 5 °C. After 36 h, saturated aqueous sodium hydrogen carbonate (2.5 mL) was added at 0 °C, and the mixture was allowed to warm to room temperature, before being extracted with ethyl acetate (3 x 3 mL). The organic extract was washed with brine, dried (MgSO₄), and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/dichloromethane (1:10) as an eluent gave 57 mg (57%) of compound **6a** containing 18% of its regioisomer **7a**.

Tin Promoted Reaction between 1-Bromo-2-butyne and Isatin 1a in an Aqueous Medium Containing HfCl₄. 1-Bromo-2-butyne (200 mg, 1.5 mmol) was added to a well stirred suspension of the α -keto lactam **1a** (73 mg, 0.5 mmol), tin powder (348 mg, 3.0 mmol) and hafnium(IV) chloride (32 mg, 0.1 mmol) in THF/H₂O (1:1, 5 mL) at 5 °C. After 6 h, saturated aqueous sodium hydrogen carbonate (2.5 mL) was added at 0 °C, and the mixture was allowed to warm to room temperature, before being extracted with ethyl acetate (3 x 3 mL). The organic extract was washed with brine, dried (MgSO₄), and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/dichloromethane (1:10) as an eluent gave 60 mg (60%) of compound **6a** containing 28% of its regioisomer **7a**.

3-(2,3-Butadien-2-yl)-3-hydroxy-1-methyl-1,3-dihydro-2H-indol-2-one, 6b. From 90 mg (0.56 mmol) of 2,3-indolinedione **1b**, 108 mg (90%) of compound **6b** was obtained as a colorless oil. $^1\text{H-NMR}$: δ 7.37 (dd, 1H, $J = 7.6, 1.3$ Hz), 7.35 and 7.10 (td, each 1H, $J = 7.5, 1.0$ Hz), 6.85 (d, 1H, $J = 7.6$ Hz), 5.04 (q, 2H, $J = 3.1$ Hz), 3.21 (s, 3H), 1.55 (t, 3H, $J = 3.1$ Hz). $^{13}\text{C-NMR}$: δ 204.8, 176.7, 143.8, 129.9, 129.1, 124.5, 123.2, 108.4, 100.7, 77.2, 80.3, 26.3, 13.7. IR (CHCl_3 , cm^{-1}): ν 3298, 1954, 1715. MS (EI), m/z : 216 ($\text{M}^+ + 1$, 9), 215 (M^+ , 100). Anal. Calcd for $\text{C}_{13}\text{H}_{13}\text{NO}_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.66; H, 6.05; N, 6.45.

Tin Promoted Reaction between 1-Bromo-2-butyne and Isatin 1b in an Aqueous Medium Containing BiCl_3 . 1-Bromo-2-butyne (200 mg, 1.5 mmol) was added to a well stirred suspension of the α -keto lactam **1b** (81 mg, 0.5 mmol), tin powder (348 mg, 3.0 mmol) and bismuth(III) chloride (31 mg, 0.1 mmol) in THF/ H_2O (1:1, 5 mL) at 5 °C. After 19 h, saturated aqueous sodium hydrogen carbonate (2.5 mL) was added at 0 °C, and the mixture was allowed to warm to room temperature, before being extracted with ethyl acetate (3 x 3 mL). The organic extract was washed with brine, dried (MgSO_4), and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/dichloromethane (1:40) as an eluent gave 6.5 mg (6%) of the less polar compound **7b** and 45 mg (42%) of the more polar regioisomer **6b**.

3-(2-Butynyl)-3-hydroxy-1-methyl-1,3-dihydro-2H-indol-2-one, 7b. Colorless oil. $^1\text{H-NMR}$ (d_6 -acetone): δ 7.49 (dd, 1H, $J = 7.3, 1.9$ Hz), 7.34 and 7.07 (td, each 1H, $J = 7.5, 1.0$ Hz), 6.96 (d, 1H, $J = 7.8$ Hz), 2.88 (s, 3H), 2.80 and 2.61 (dq, each 1H, $J = 16.0, 2.6$ Hz), 1.58 (t, 3H, $J = 2.5$ Hz). IR (CHCl_3 , cm^{-1}): ν 3301, 1716. MS (EI), m/z : 216 ($\text{M}^+ + 1$, 11), 215 (M^+ , 100). Anal. Calcd for $\text{C}_{13}\text{H}_{13}\text{NO}_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.41; H, 6.06; N, 6.56.

Indium Promoted Reaction between 1-Bromo-2-butyne and Isatin 1a in an Aqueous Medium Containing NH_4Cl . 1-Bromo-2-butyne (200 mg, 1.5 mmol) was added to a well stirred suspension of the α -keto lactam **1a** (73 mg, 0.5 mmol) and indium powder (344 mg, 3.0 mmol) in THF/ NH_4Cl (aq sat) (1:5, 5 mL) at 5 °C. After 24 h, saturated aqueous sodium hydrogen carbonate (2.5 mL) was added at 0 °C, and the mixture was allowed to warm to room temperature, before being extracted with ethyl acetate (3 x 3 mL). The organic extract was washed with brine, dried (MgSO_4), and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/dichloromethane (1:10) as an eluent gave 57 mg (57%) of compound **6a**.

Indium Promoted Reaction between 1-Bromo-3-phenyl-2-propyne and Isatin 1b at Room Temperature. 1-Bromo-3-phenyl-2-propyne (293 mg, 1.5 mmol) was added to a well stirred suspension of the α -keto lactam **1b** (81 mg, 0.5 mmol) and indium powder (344 mg, 3.0 mmol) in THF/H₂O (1:1, 5 mL) at room temperature. After 1 h, saturated aqueous sodium hydrogen carbonate (2.5 mL) was added at 0 °C, and the mixture was allowed to warm to room temperature, before being extracted with ethyl acetate (3 x 3 mL). The organic extract was washed with brine, dried (MgSO₄), and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/dichloromethane (1:40) as an eluent gave 103 mg (74%) of the less polar compound **6c** and 5 mg (4%) of the more polar regioisomer **7c**.

3-Hydroxy-1-methyl-3-(3-phenyl-2-propynyl)-1,3-dihydro-2H-indol-2-one, 7c. Colorless oil. ¹H-NMR: δ 7.62 (dd, 1H, J = 7.3, 1.2 Hz), 7.39 (td, 1H, J = 7.7, 1.4 Hz), 7.28 (m, 5H), 7.15 (td, 1H, J = 7.6, 1.0 Hz), 6.88 (d, 1H, J = 7.6 Hz), 3.23 (s, 3H), 3.15 and 2.93 (d, each 1H, J = 16.6 Hz). IR (CHCl₃, cm⁻¹): ν 3302, 1714. MS (EI), m/z : 278 (M^+ + 1, 12), 277 (M^+ , 100). Anal. Calcd for C₁₈H₁₅NO₂: C, 77.96; H, 5.45; N, 5.05. Found: C, 77.85; H, 5.40; N, 5.10.

Zinc Promoted Reaction between 1,4-Dibromo-2-butyne and Isatin 1b in an Aqueous Medium Containing NH₄Cl. 1,4-Dibromo-2-butyne (212 mg, 1.0 mmol) was added to a well stirred suspension of the α -keto lactam **1b** (81 mg, 0.5 mmol) and zinc powder (65 mg, 1.0 mmol) in THF/NH₄Cl (aq sat) (1:5, 5 mL) at room temperature. After 24 h, saturated aqueous sodium hydrogen carbonate (2.5 mL) was added at 0 °C, and the mixture was allowed to warm to room temperature, before being extracted with ethyl acetate (3 x 3 mL). The organic extract was washed with brine, dried (MgSO₄), and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/dichloromethane (1:40) as an eluent gave 22 mg (20%) of compound **8**.

Zinc Promoted Reaction between 1,4-Dibromo-2-butyne and Isatin 1b. 1,4-Dibromo-2-butyne (212 mg, 1.0 mmol) was added to a well stirred suspension of the α -keto lactam **1b** (81 mg, 0.5 mmol) and zinc powder (65 mg, 1.0 mmol) in THF/H₂O (1:1, 5 mL) at room temperature. After 24 h, saturated aqueous sodium hydrogen carbonate (2.5 mL) was added at 0 °C, and the mixture was allowed to warm to room temperature, before being extracted with ethyl acetate (3 x 3 mL). The organic extract was washed with brine, dried (MgSO₄), and concentrated under reduced

pressure. Chromatography of the residue using ethyl acetate/dichloromethane (1:40) as an eluent gave 16 mg (15%) of compound **8**.

Indium Promoted Reaction between 1,4-Bis(methanesulfonyl)-2-butyne and Isatin 1b in an Aqueous Medium Containing NH₄Cl. 1,4-Bis(methanesulfonyl)-2-butyne (726 mg, 3.0 mmol) was added to a well stirred suspension of the α -keto lactam **1b** (81 mg, 0.5 mmol), sodium iodide (6.0 mmol) and indium powder (344 mg, 3.0 mmol) in THF/NH₄Cl (aq sat) (1:5, 5 mL) at room temperature. After 24 h, saturated aqueous sodium hydrogen carbonate (2.5 mL) was added at 0 °C, and the mixture was allowed to warm to room temperature, before being extracted with ethyl acetate (3 x 3 mL). The organic extract was washed with brine, dried (MgSO₄), and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/dichloromethane (1:40) as an eluent gave 27 mg (25%) of compound **8**.

Indium Promoted Reaction between 1,4-Dibromo-2-butyne and Isatin 1b in an Aqueous Medium Containing NH₄Cl. 1,4-Dibromo-2-butyne (212 mg, 1.0 mmol) was added to a well stirred suspension of the α -keto lactam **1b** (81 mg, 0.5 mmol) and indium powder (115 mg, 1.0 mmol) in THF/NH₄Cl (aq sat) (1:5, 5 mL) at room temperature. After 14 h, saturated aqueous sodium hydrogen carbonate (2.5 mL) was added at 0 °C, and the mixture was allowed to warm to room temperature, before being extracted with ethyl acetate (3 x 3 mL). The organic extract was washed with brine, dried (MgSO₄), and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/dichloromethane (1:40) as an eluent gave 12 mg (11%) of compound **8**.