Supporting Information for the Paper

Efficient Entry to Diversely Functionalized Spirocyclic Oxindoles from Isatins through Carbonyl–Addition/Cyclization Reaction Sequences

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Table of Contents

Preparation of Homoallylic Alcohol 2	S2
Characterization of Homoallylic Alcohol 2	S2
Preparation of (Buta-1,3-dien-2-yl)methanol 3	S2
Characterization of (Buta-1,3-dien-2-yl)methanol 3	S3
General Procedure for the Synthesis of α -Allenic Alcohols 4	S3
Characterization of α -Allenyl Alcohols 4a–c	S3
General Procedure for the Reaction of Unsaturated Alcohols 2 and 3 with Allyl Bromide. Preparation of Diene 5 and Triene 8	S4
Characterization of Diene 5	S4
Characterization of Triene 8	S4
Reaction between Homoallylic Alcohol 2 and Methyl Propiolate. Preparation of Diene 6	S5
Characterization of Diene 6	S5
Reaction between Homoallylic Alcohol 2 and Acryloyl Chloride. Preparation of Diene 7	S5
Characterization of Diene 7	S5
Characterization of Spirocyclic Oxindole 9	S6
Characterization of Spirocyclic Oxindoles 10	S6

Characterization of Spirocyclic Oxindoles 15a	S6
Characterization of Spirocyclic Oxindoles 17b	S7
Characterization of Spirocyclic Oxindoles 22b	S7

All commercially available materials were obtained from Aldrich and used without further purification.

Preparation of Homoallylic Alcohol 2. Allyl bromide (121 mg, 1.0 mmol) was added to a well stirred suspension of the 2,3-indolinedione **1a** (73 mg, 0.5 mmol), indium powder (115 mg, 1.0 mmol) and hafnium(IV) chloride (32 mg, 0.1 mmol) in THF/H₂O (1:1, 5 mL) at 0 °C. The mixture was stirred at the same temperature until complete disappearance (30 min) of the α -keto- γ -lactam. 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. Chromatography of the residue eluting with hexanes/ethyl acetate or ethyl acetate/dichloromethane mixtures gave analytically pure compound **2**.

3-(1,1-Dimethylallyl)-3-hydroxy-1,3-dihydroindol-2-one, 2. From 81 mg (0.5 mmol) of 2,3-indolinedione **1a**, 101 mg (100%) of compound **2** was obtained as a colorless oil. ¹H-NMR: δ 7.35 (m, 2H), 7.09 (td, 1H, J = 7.4, 0.9 Hz), 6.82 (d, 1H, J = 7.8 Hz), 5.62 (m, 1H), 5.09 (m, 2H), 3.56 (br s, 1H), 3.17 (s, 3H), 2.77 (ddt, 1H, J = 13.3, 6.2, 1.2 Hz), 2.62 (dd, 1H, J = 13.3, 8.2 Hz). ¹³C-NMR: δ 177.8, 143.1, 130.4, 129.7, 129.5, 124.0, 122.9, 120.1, 108.2, 75.8, 42.7, 26.0. IR (CHCl₃, cm⁻¹): ν 3302, 1709. MS (EI), m/z : 204 (M^+ + 1, 7), 203 (M^+ , 100). Anal. Calcd for C₁₂H₁₃NO₂: C, 70.92; H, 6.45; N, 6.89. Found: C, 71.07; H, 6.40; N, 6.76.

Preparation of (Buta-1,3-dien-2-yl)methanol 3. 1,4-Dibromo-2-butyne (212 mg, 1.0 mmol) was added to a well stirred suspension of the α -keto lactam **1a** (81 mg, 0.5 mmol) and indium powder (115 mg, 1.0 mmol) in THF/H₂O (1:1, 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 (1:40) as an eluent gave 48 mg (44%) of compound **3**.

3-Hydroxy-1-methyl-3-(1-methylene-allyl)-1,3-dihydro-indol-2-one, 3. Colorless solid. Mp: 119–120 °C (hexanes/ethyl acetate). ¹H-NMR: δ 7.37 (td, 1H, *J* = 7.7, 1.3 Hz), 7.30 (m, 1H), 7.10 (td, 1H, *J* = 7.6, 1.0 Hz), 6.88 (d, 1H, *J* = 7.8 Hz), 6.06 (ddd, 1H, *J* = 17.5, 11.2, 1.0 Hz), 5.58 and 5.50 (s, each 1H), 5.21 (dd, 1H, *J* = 17.6, 1.2 Hz), 4.99 (dd, 1H, *J* = 11.0, 1.0 Hz), 3.25 (s, 3H). ¹³C-NMR: δ 176.7, 145.1, 143.9, 133.3, 130.2, 129.6, 124.6, 123.5, 116.8, 114.1, 108.7, 78.0, 26.5. IR (CHCl₃, cm⁻¹): ν 3295, 1718. MS (EI), *m/z*: 216 (*M*⁺ + 1, 7), 215 (*M*⁺, 100). Anal. Calcd for C₁₃H₁₃NO₂: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.41; H, 6.05; N, 6.55.

General Procedure for the Synthesis of α-Allenic Alcohols 4. The appropriate 3-substituted prop-2-ynyl bromide (1.5 mmol) was added to a well stirred suspension of the corresponding 2,3-indolinedione **1** (0.5 mmol) and indium powder (344 mg, 3.0 mmol) in THF/H₂O (1:1, 5 mL) at 5 °C. 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 eluting with hexanes/ethyl acetate or ethyl acetate/dichloromethane mixtures gave analytically pure compounds **4**. Spectroscopic and analytical data for some representative forms of **4** follow.

3-Hydroxy-1-methyl-3-(1-methyl-propa-1,2-dienyl)-1,3-dihydro-indol-2-one, 4a. From 90 mg (0.56 mmol) of 2,3-indolinedione **1a**, 108 mg (90%) of compound **4a** was obtained as a colorless oil. ¹H-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). ¹³C-NMR: δ 204.8, 176.7, 143.8, 129.9, 129.1, 124.5, 123.2, 108.4, 100.7, 80.3, 77.1, 26.3, 13.7. IR (CHCl₃, cm⁻¹): ν 3298, 1715. MS (EI), *m/z*: 216 (*M*⁺ + 1, 9), 215 (*M*⁺, 100). Anal. Calcd for C₁₃H₁₃NO₂: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.66; H, 6.05; N, 6.45.

3-Hydroxy-3-(1-methyl-propa-1,2-dienyl)-1,3-dihydro-indol-2-one, 4b. From 73 mg (0.5 mmol) of 2,3-indolinedione **1b**, 90 mg (90%) of compound **4b** was obtained as a colorless solid. Mp: 179–180 °C (hexanes/ethyl acetate). ¹H-NMR (d₆-acetone): δ 9.24 (br s, 1H), 7.18 (dd, 1H, *J* = 7.4, 1.2 Hz), 7.10 (td, 1H, *J* = 7.7, 1.3 Hz), 6.87 and 6.77 (td, each 1H, *J* = 7.5, 1.0 Hz), 4.98 (s,

1H), 4.69 (qd, 2H, $J = 3.1, 1.3$ Hz), 1.59 (t, 3H, $J = 3.1$ Hz). ^{13}C -NMR (d_6 -acetone): δ 207.1, 178.7, 143.1, 132.6, 130.5, 126.0, 123.1, 110.9, 102.0, 78.5, 77.6, 14.3. IR (CHCl_3 , cm^{-1}): ν 3423, 3296, 1714. MS (EI), m/z : 202 ($\text{M}^+ + 1$, 7), 201 (M^+ , 100). Anal. Calcd for $\text{C}_{12}\text{H}_{11}\text{NO}_2$: C, 71.63; H, 5.51; N, 6.96. Found: C, 71.52; H, 5.54; N, 7.00.

3-Hydroxy-1-methyl-3-(1-phenyl-propa-1,2-dienyl)-1,3-dihydro-indol-2-one, 4c. From 112 mg (0.70 mmol) of 2,3-indolinedione **1a**, 158 mg (82%) of compound **4c** was obtained as a colorless solid. Mp: 106–108 °C (hexanes/ethyl acetate). ^1H -NMR: δ 7.30 (m, 2H), 7.15 (m, 5H), 7.04 (td, 1H, $J = 7.6, 1.0$ Hz), 6.77 (d, 1H, $J = 7.3$ Hz), 5.28 (s, 2H), 3.12 (s, 3H). ^{13}C -NMR: δ 206.9, 176.3, 143.7, 133.1, 130.1, 129.2, 128.4, 128.2, 127.6, 124.9, 123.2, 108.5, 108.0, 81.3, 77.2, 26.3. IR (CHCl_3 , cm^{-1}): ν 3295, 1712. MS (EI), m/z : 278 ($\text{M}^+ + 1$, 15), 277 (M^+ , 100). Anal. Calcd for $\text{C}_{18}\text{H}_{15}\text{NO}_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 78.07; H, 5.41; N, 5.10.

General Procedure for the Reaction of Unsaturated Alcohols 2 and 3 with Allyl Bromide. Preparation of Diene 5 and Triene 8. Tetrabutyl ammonium iodide (32 mg, 0.086 mmol), 50% aqueous sodium hydroxide (100 mL) and allyl bromide (1.67 g, 13.8 mmol) were sequentially added at room temperature to a solution of the appropriate hydroxy compound **2** or **3** (8.64 mmol) in dichloromethane (100 mL). The reaction was stirred for 20 h and then water was added (50 mL), before being partitioned between dichloromethane and water. The aqueous phase was extracted with dichloromethane (3 x 50 mL), the combined organic extracts were dried (MgSO_4) and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/hexanes (1:4) as an eluent gave analytically pure compounds **5** and **8**. Spectroscopic and analytical data for compounds **5** and **8** follow.

Diene 5. From 450 mg (2.22 mmol) of alcohol **2**, 480 mg (89%) of compound **5** was obtained as a colorless oil. ^1H -NMR: δ 7.35 (m, 2H), 7.11 (td, 1H, $J = 7.5, 0.9$ Hz), 6.84 (d, 1H, $J = 7.6$ Hz), 5.84 (ddt, 1H, $J = 17.1, 10.3, 5.7$ Hz), 5.53 (m, 1H), 5.16 (dq, 1H, $J = 17.2, 1.6$ Hz), 5.08 (dq, 1H, $J = 10.3, 1.4$ Hz), 5.00 (m, 2H), 3.70 and 3.59 (ddt, each 1H, $J = 11.6, 5.8, 1.4$ Hz), 3.19 (s, 3H), 2.79 (ddt, 1H, $J = 13.3, 6.3, 1.3$ Hz), 2.63 (dd, 1H, $J = 13.3, 8.2$ Hz). ^{13}C -NMR: δ 175.8, 143.9, 134.3, 130.7, 129.8, 127.1, 124.6, 122.7, 119.7, 117.1, 108.3, 81.9, 66.8, 42.2, 26.1. IR (CHCl_3 , cm^{-1}): ν 1710. MS (EI), m/z : 244 ($\text{M}^+ + 1$, 5), 243 (M^+ , 100). Anal. Calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_2$: C, 74.05; H, 7.04; N, 5.76. Found: C, 74.17; H, 7.01; N, 5.74.

Triene 8. From 350 mg (1.63 mmol) of alcohol **3**, 410 mg (98%) of compound **8** was obtained as a colorless oil. $^1\text{H-NMR}$: δ 7.37 (td, 1H, $J = 7.7, 1.3$ Hz), 7.29 (dd, 1H, $J = 7.4, 0.7$ Hz), 7.11 (td, 1H, $J = 7.5, 1.0$ Hz), 6.87 (d, 1H, $J = 7.8$ Hz), 6.24 (dd, 1H, $J = 17.4, 11.1$ Hz), 5.87 (m, 1H), 5.46 (s, 1H), 5.40 (dd, 1H, $J = 17.4, 1.5$ Hz), 5.33 (s, 1H), 5.20 (dq, 1H, $J = 17.2, 1.7$ Hz), 5.10 and 5.05 (dd, each 1H, $J = 10.0, 1.5$ Hz), 3.83 and 3.76 (ddt, each 1H, $J = 12.0, 5.5, 1.5$ Hz), 3.23 (s, 3H). $^{13}\text{C-NMR}$: δ 174.4, 144.1, 143.8, 134.1, 133.4, 130.1, 127.2, 125.2, 123.1, 116.8, 116.4, 114.3, 108.4, 83.1, 66.2, 26.2. IR (CHCl_3 , cm^{-1}): ν 1715. MS (EI), m/z : 256 ($\text{M}^+ + 1$, 4), 255 (M^+ , 100). Anal. Calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_2$: C, 75.27; H, 6.71; N, 5.49. Found: C, 75.14; H, 6.74; N, 5.46.

Reaction between Homoallylic Alcohol 2 and Methyl Propiolate. Preparation of Diene 6. Triethylamine (344 mg, 3.40 mmol) and methyl propiolate (172 mg, 2.04 mmol) were sequentially added to a solution of the hydroxyindolone **2** (345 mg, 1.70 mmol) in dichloromethane (10 mL) at 0 °C. The reaction was stirred for 1 h at RT and then water (5 mL) was added. The mixture was diluted with dichloromethane (20 mL), before being partitioned between dichloromethane and water. The organic layer was dried (MgSO_4) and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/hexanes (1:3) as an eluent gave 485 mg (quantitative yield) of compound **6** as a colorless oil.

Diene 6. $^1\text{H-NMR}$: δ 7.40 (td, 1H, $J = 7.7, 1.4$ Hz), 7.32 (dd, 1H, $J = 7.4, 1.3$ Hz), 7.17 (d, 1H, $J = 12.0$ Hz), 7.13 (td, 1H, $J = 7.4, 1.0$ Hz), 6.89 (d, 1H, $J = 7.8$ Hz), 5.51 (m, 1H), 5.38 (d, 1H, $J = 12.0$ Hz), 5.07 (m, 2H), 3.61 and 3.23 (s, each 3H), 2.91 (ddt, 1H, $J = 13.4, 6.2, 1.3$ Hz), 2.73 (dd, 1H, $J = 13.4, 8.1$ Hz). $^{13}\text{C-NMR}$: δ 173.4, 167.6, 157.4, 143.7, 131.0, 129.2, 125.8, 124.8, 123.5, 121.0, 108.9, 101.3, 83.2, 51.1, 41.1, 26.4. IR (CHCl_3 , cm^{-1}): ν 1755, 1710. MS (EI), m/z : 288 ($\text{M}^+ + 1$, 3), 287 (M^+ , 100). Anal. Calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_4$: C, 66.89; H, 5.96; N, 4.88. Found: C, 67.01; H, 5.99; N, 4.86.

Reaction between Homoallylic Alcohol 2 and Acryloyl Chloride. Preparation of Diene 7. Hydroxyindolone **2** (204 mg, 1.0 mmol) was added to a stirred suspension of sodium hydride (48 mg, 2.0 mmol) in THF (12 mL), and the reaction was stirred for 30 min. Then, the mixture was cooled at 0 °C and acryloyl chloride (118 mg, 1.3 mmol) was added. After 1 h at RT, 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 (10 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/hexanes (1:4) as an eluent gave 224 mg (86%) of compound **7** as a colorless oil.

Diene 7. $^1\text{H-NMR}$: δ 7.35 (td, 1H, $J = 7.8, 1.2$ Hz), 7.23 (d, 1H, $J = 6.6$ Hz), 7.04 (t, 1H, $J = 7.6$ Hz), 6.86 (d, 1H, $J = 7.8$ Hz), 6.38 (dd, 1H, $J = 17.2, 1.6$ Hz), 6.12 (dd, 1H, $J = 17.1, 10.2$ Hz), 5.85 (dd, 1H, $J = 10.3, 1.5$ Hz), 5.63 (m, 1H), 5.09 (m, 2H), 3.25 (s, 3H), 2.89 (dd, 1H, $J = 13.4, 6.3$ Hz), 2.63 (dd, 1H, $J = 13.4, 8.0$ Hz). $^{13}\text{C-NMR}$: δ 174.4, 164.1, 144.0, 132.3, 130.0, 129.6, 127.5, 127.2, 123.2, 122.7, 120.8, 108.5, 79.6, 41.0, 26.6. IR (CHCl_3 , cm^{-1}): ν 1760, 1712. MS (EI), m/z : 258 ($\text{M}^+ + 1$, 5), 257 (M^+ , 100). Anal. Calcd for $\text{C}_{15}\text{H}_{15}\text{NO}_3$: C, 70.02; H, 5.88; N, 5.44. Found: C, 70.14; H, 5.86; N, 5.42.

Spectroscopic and analytical data for some representative pure forms of **9–12** follow.

Spirocyclic Oxindole 9. From 48 mg (0.198 mmol) of diene **5**, 35 mg (83%) of compound **9** was obtained as a colorless oil after chromatography eluting with ethyl acetate/hexanes (1:3). $^1\text{H-NMR}$: δ 7.44 (ddd, 1H, $J = 7.3, 1.2, 0.5$ Hz), 7.34 and 7.05 (td, each 1H, $J = 7.8, 1.0$ Hz), 6.86 (d, 1H, $J = 7.8$ Hz), 6.00 (m, 2H), 4.59 (d, 1H, $J = 16.0$ Hz), 4.41 (d, 1H, $J = 17.1$ Hz), 3.20 (s, 3H), 2.75 and 2.18 (d, each 1H, $J = 17.0$ Hz). $^{13}\text{C-NMR}$: δ 174.9, 143.4, 129.6, 129.5, 125.8, 124.2, 122.6, 121.4, 108.4, 73.9, 62.5, 29.9, 26.1. IR (CHCl_3 , cm^{-1}): ν 1711. MS (EI), m/z : 216 ($\text{M}^+ + 1$, 3), 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, 72.65; H, 6.06; N, 6.54.

Spirocyclic Oxindole 10. From 40 mg (0.139 mmol) of diene **6**, 16 mg (57%) of compound **10** was obtained as a colorless oil after chromatography eluting with ethyl acetate/dichloromethane (1:80). $^1\text{H-NMR}$: δ 7.41 (d, 1H, $J = 8.1$ Hz), 7.33 (dd, 1H, $J = 7.7, 1.3$ Hz), 7.09 (td, 1H, $J = 7.6, 1.0$ Hz), 6.83 (d, 1H, $J = 7.8$ Hz), 6.52 and 5.14 (q, each 1H, $J = 2.5$ Hz), 3.21 (s, 3H), 3.20 and 2.90 (dt, each 1H, $J = 15.5, 2.3$ Hz). $^{13}\text{C-NMR}$: δ 175.6, 145.3, 143.4, 130.6, 130.2, 123.6, 123.4, 108.4, 99.6, 77.2, 39.9, 26.3. IR (CHCl_3 , cm^{-1}): ν 1712. MS (EI), m/z : 202 ($\text{M}^+ + 1$, 5), 201 (M^+ , 100). Anal. Calcd for $\text{C}_{12}\text{H}_{11}\text{NO}_2$: C, 71.63; H, 5.51; N, 6.96. Found: C, 71.74; H, 5.49; N, 6.93.

Spectroscopic and analytical data for some representative pure forms of **15** follow.

Spirocyclic Oxindole 15a. From 54 mg (0.25 mmol) of α -allenol **4a**, 52 mg (96%) of compound **15a** was obtained as a colorless oil. $^1\text{H-NMR}$: δ 7.32 (td, 1H, $J = 7.6, 1.5$ Hz), 7.20 (ddd, 1H, $J = 7.3, 1.5, 0.5$ Hz), 7.07 (td, 1H, $J = 7.4, 1.0$ Hz), 6.82 (d, 1H, $J = 7.8$ Hz), 5.96 (q, 1H, $J = 1.5$ Hz), 5.02 and 4.90 (dq, each 1H, $J = 12.2, 2.0$ Hz), 3.20 (s, 3H), 1.43 (q, 3H, $J = 2.0$ Hz). $^{13}\text{C-NMR}$: δ 176.1, 144.4, 136.2, 130.5, 128.7, 125.3, 124.9, 123.6, 108.7, 92.9, 76.8, 26.7, 11.6. IR (CHCl_3 , cm^{-1}): ν 1711. MS (EI), m/z : 216 ($\text{M}^+ + 1$, 3), 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, 72.65; H, 6.06; N, 6.55.

Spectroscopic and analytical data for some representative pure forms of **17** follow.

Spirocyclic Oxindole 17b. From 23 mg (0.114 mmol) of α -allenol **4b**, 21 mg (75%) of compound **17b** was obtained as a colorless oil after chromatography eluting with ethyl acetate/hexanes (1:5). $^1\text{H-NMR}$: δ 8.59 (br s, 1H), 7.25 (td, 1H, $J = 7.7, 1.3$ Hz), 7.17 (d, 1H, $J = 6.8$ Hz), 7.05 (td, 1H, $J = 7.5, 1.0$ Hz), 6.89 (d, 1H, $J = 7.7$ Hz), 5.85 (ddt, 1H, $J = 17.0, 10.0, 6.3$ Hz), 5.19 (dq, 1H, $J = 17.0, 1.5$ Hz), 5.11 (dq, 1H, $J = 10.0, 1.5$ Hz), 4.98 and 4.89 (dq, each 1H, $J = 12.0, 2.0$ Hz), 3.05 and 2.96 (dd, 1H, $J = 15.9, 6.2$ Hz), 1.39 (t, 3H, $J = 1.8$ Hz). $^{13}\text{C-NMR}$: δ 178.4, 141.0, 134.5, 134.1, 130.0, 129.1, 128.6, 124.8, 123.1, 116.3, 110.3, 94.3, 78.7, 29.6, 8.7. IR (CHCl_3 , cm^{-1}): ν 1712. MS (ES), m/z : 242 ($\text{M}^+ + 1$, 100), 241 (M^+ , 12). Anal. Calcd for $\text{C}_{15}\text{H}_{15}\text{NO}_2$: C, 74.67; H, 6.27; N, 5.81. Found: C, 74.80; H, 6.23; N, 5.84.

Spectroscopic and analytical data for some representative pure forms of **22** follow.

Spirocyclic Oxindole 22b. From 31 mg (0.11 mmol) of α -allenol **4c**, 24 mg (38%) of compound **22b** was obtained as a colorless oil after chromatography eluting with ethyl acetate/dichloromethane (1:40). $^1\text{H-NMR}$: δ 7.49 (d, 1H, $J = 7.7$ Hz), 7.43 (m, 5H), 7.39 and 7.15 (td, each 1H, $J = 7.7, 1.0$ Hz), 6.84 (d, 1H, $J = 7.8$ Hz), 4.03 and 3.97 (d, each 1H, $J = 10.7$ Hz), 3.21 (s, 3H). $^{13}\text{C-NMR}$: δ 174.7, 145.6, 145.2, 136.1, 130.4, 129.4, 128.8, 128.6, 128.7, 124.1, 123.5, 121.9, 108.7, 96.9, 78.3, 26.3. IR (CHCl_3 , cm^{-1}): ν 1710. MS (ES), m/z : 358 ($\text{M}^+ + 2 + \text{H}$, 100), 356 ($\text{M}^+ + \text{H}$, 98). Anal. Calcd for $\text{C}_{18}\text{H}_{14}\text{BrNO}_2$: C, 60.69; H, 3.96; N, 3.93. Found: C, 60.56; H, 3.98; N, 3.91.