

# Supporting Information

## **Palladium-catalyzed allylic alkylation with internal alkynes to construct C-C and C-N bonds in water**

Shang Gao, Hao Liu, Zijun Wu, Hequan Yao\* and Aijun Lin\*

*State Key Laboratory of Natural Medicines and Department of Medicinal Chemistry, School of  
Pharmacy, China Pharmaceutical University, Nanjing 210009, P. R. China.*

E-mail: ajlin@cpu.edu.cn, hyao@cpu.edu.cn and cpuyhao@126.com

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## 1. General Information

**Reagents and Solvents:** Pd(PPh<sub>3</sub>)<sub>4</sub> and ligands were commercially available. PE refers to petroleum ether (b.p. 60-90 °C), EA refers to ethyl acetate. All other starting materials and solvents were commercially available and were used without further purification unless otherwise stated.

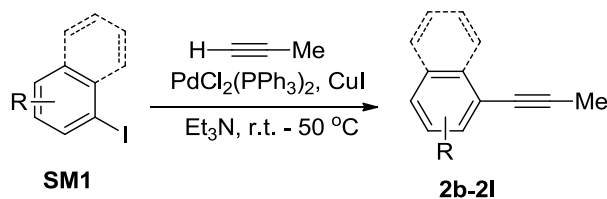
**Chromatography:** Flash column chromatography was carried out using commercially available 200-300 mesh under pressure unless otherwise indicated. Gradient flash chromatography was conducted eluting with PE/EA or DCM/MeOH, they are listed as volume/volume ratios.

**Data collection:** <sup>1</sup>H and <sup>13</sup>C NMR spectra were collected on BRUKER AV-300 (300 MHz) spectrometer using CDCl<sub>3</sub> or DMSO-*d*<sub>6</sub> as solvent. Chemical shifts of <sup>1</sup>H NMR were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ = 0.00 ppm) with the solvent resonance as the internal standard (CDCl<sub>3</sub>: δ = 7.26 ppm, DMSO-*d*<sub>6</sub>: δ = 2.50 ppm). Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz) and integration. Chemical shifts of <sup>13</sup>C NMR were reported in ppm with the solvent as the internal standard (CDCl<sub>3</sub>: δ = 77.16 ppm, DMSO-*d*<sub>6</sub>: δ = 39.52 ppm). High Resolution Mass measurement was performed on Agilent Q-TOF 6520 mass spectrometer with electron spray ionization (ESI) as the ion source. Melting point (mp) was measured on a microscopic melting point apparatus.

## 2. Preparation of Substrates

### 2.1 Preparation of alkynes

Substrates **2a** and **2m** are commercially available, and **2n** was synthesized according to the literature report. Substrates **2b-2l** were synthesized according to the following procedures:

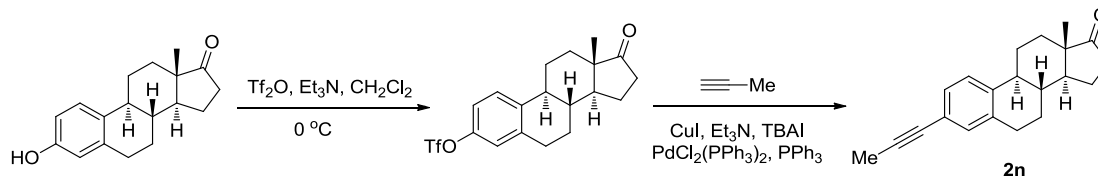


**Scheme S1.** Preparation of alkynes **2b-2l**

Substituted iodobenzene **SM1** (5 mmol, 1.0 equiv), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (2 mol %) and CuI (4 mol %) were dissolved in 15 mL Et<sub>3</sub>N and the reaction mixture was stirred under argon at r. t. for 5 min. Propyne (ca. 5% in tetrahydrofuran, ca. 1 mol/L, purchased from TCI) was added in one portion and the solution was stirred for 5 h. After the starting material was consumed completely which was detected by TLC, the reaction mixture was diluted with 60 mL ethyl acetate and filtered through a plug of Celite. The organic

phase was washed with water and brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The mixture was concentrated *in vacuo* and purified by flash chromatography on silica gel with PE to afford the alkylation products **2b-2l**.

Substrate **2n** was synthesized according to the literature reported procedure:<sup>1</sup>

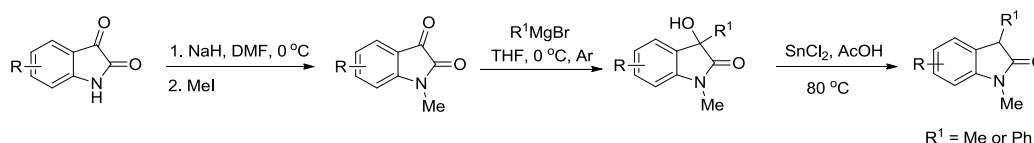


A solution of estrone (2.50 g, 9.26 mmol) and Et<sub>3</sub>N (2.60 mL, 18.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (46 mL) was stirred at 0 °C. Trifluoromethanesulfonic anhydride (1.71 mL, 10.2 mmol) was added dropwise. The reaction mixture was stirred at 0 °C for 60 min, and quenched with sat. aqueous NaHCO<sub>3</sub> (50 ml). The organic layer was separated, and the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 x 50 mL). The combined organic layers were washed with brine (50 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and the volatiles were removed in *vacuo*. The residue was then purified by flash column chromatography on silica gel (PE : EA = 4:1) to give estronyl triflate.

A mixture of estronyl triflate (804 mg, 2.0 mmol), triphenylphosphine (0.12 mmol), dichlorobis(triphenylphosphine)palladium(II) (0.1 mmol), triethylamine (3.7 mL), tetrabutylammonium iodide (4.0 mmol), copper(I) iodide (0.07 mmol), and DMF (2 mL) were added in a Schlenk tube. A solution of propyne in DMF (1 mol/L, 2.4 mL). The Schlenk tube was closed and heated under argon at 90 °C for 12 h. The reaction mixture was cooled to room temperature, filtered on celite, rinsed with ethyl acetate, and concentrated. The residue was then purified by flash column chromatography on silica gel (PE : EA = 20:1) to give **2n**. Yellow solid, m. p. 243 – 245 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.22 – 7.14 (m, 3H), 2.87 (AB, *J* = 3.7 Hz, 2H), 2.51 (dd, *J* = 18.3, 8.4 Hz, 1H), 2.43 – 2.38 (m, 1H), 2.27 (s, 1H), 2.22 – 2.11 (dd, *J* = 18.3, 9.3 Hz, 1H), 2.09 – 1.95 (m, 6H), 1.68 – 1.39 (m, 6H), 0.91 (s, 3H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 221.0, 139.5, 136.5, 132.1, 128.9, 125.4, 121.5, 85.2, 79.8, 50.6, 48.1, 44.5, 38.1, 36.0, 31.7, 29.2, 26.5, 25.7, 21.7, 14.0, 4.5 ppm.

## 2.2 Preparation of various nucleophiles

Substituted oxindoles were prepared according to the reported literature<sup>2</sup> as the following procedures:



1. (a) M. H. D. Postema, J. L. Piper, R. L. Betts, F. A. Valeriote and H. Pietraszkewicz, *J. Org. Chem.* 2005, **70**, 829; (b) L. Fernand; G. Sylvain; C. Julie; M. Josee; P. Steeves; D. Sylvain; S. Jean-Yves, PCT WO 2008/24922 A1, 2008.

2. B. M. Trost, J. Xie and J. D. Sieber, *J. Am. Chem. Soc.* 2011, **133**, 20611.

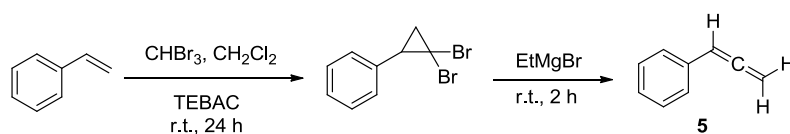
Substituted isatins (20.0 mmol) were dissolved in anhydrous DMF (30 mL), and the resultant solution was cooled to 0 °C, whereupon sodium hydride (60% dispersion in oil, 0.95 g, 24.0 mmol) was added in one portion and stirred for 5 minutes. Iodomethane (1.87 mL, 30.0 mmol) was added and the reaction was stirred at 0 °C for 30 min. The reaction mixture was then poured into saturated aqueous NH<sub>4</sub>Cl and extracted with EA (4 x 30 mL). The combined organic layers were washed with water and brine, then dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated to give the crude substituted *N*-methyl isatins which was used without further purification. *R<sub>f</sub>* = 0.50 (PE : EA = 1 : 1).

The crude substituted *N*-methyl isatins (20 mmol) were dissolved in anhydrous THF (30 mL) and cooled to 0 °C followed by dropwise addition of a 2.0 M solution of R<sup>1</sup>MgBr in THF (12.0 mL, 24.0 mmol). Then, the ice-bath was removed, and the reaction was stirred under argon atmosphere for 30 min at which point TLC analysis indicated consumption of the starting material. The reaction mixture was poured into saturated aqueous NH<sub>4</sub>Cl (20 mL), and extracted with ethyl acetate (3 x 30 mL). The combined organic layers were washed with brine (20 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated to give the crude alcohol. *R<sub>f</sub>* = 0.45 (PE : EA = 1 : 1).

The crude alcohol (5.0 mmol) was dissolved in 30 mL of glacial acetic acid and SnCl<sub>2</sub>•2 H<sub>2</sub>O (10.0 mmol) was added. The reaction mixture was stirred at 80 °C for 2 h at which point TLC analysis indicated consumption of the starting material. Next, the solution was cooled to room temperature, concentrated *in vacuo*, and then diluted with EA (100 mL). The solution was washed with water (3 x 20 mL) and brine (30 mL). The organic layer was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography with EA/PE to afford the oxindoles as solid.

### 2.3 Preparation of phenyl allene

Phenyl allene **5** was prepared according to the literature reported procedure.<sup>3</sup>

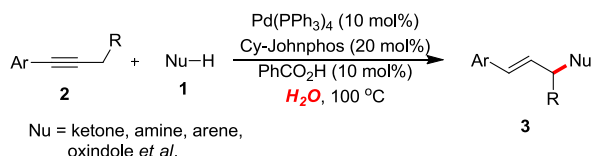


#### *propa-1,2-dien-1-ylbenzene (5)*

Colorless oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.33 – 7.29 (m, 4H), 7.23 – 7.16 (m, 1H), 6.16 (t, *J* = 6.8 Hz, 1H), 5.14 (d, *J* = 6.8 Hz, 2H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 209.9, 134.0, 128.8, 127.0, 126.8, 94.1, 78.9 ppm.

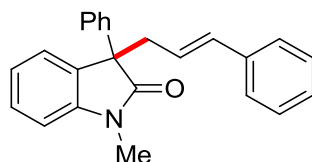
<sup>3</sup> T. Kippo, T. Fukuyama and I. Ryu, *Org. Lett.* 2011, **13**, 3864.

### 3. General Procedure of Allylic Alkylation of Nucleophiles with Alkynes in Water



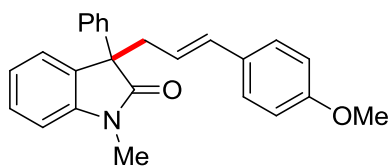
A sealed tube was charged with nucleophiles **1** (0.25 mmol, 1.0 equiv), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.025 mmol, 10 mol %), benzoic acid (0.025 mmol, 10 mol %), alkynes **2** (0.5 mmol, 2.0 equiv) and water (1.0 mL). The reaction mixture was vigorously stirred at 100 °C or 120 °C (oil temperature) for 24 h to 36 h under argon. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate (20 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The mixture was concentrated *in vacuo* and purified by flash chromatography on silica gel with PE/EA to afford the allylic alkenylated product **3**.

### 4. Characterization of the Allylic Alkylation Products



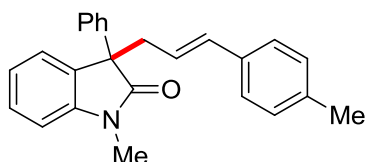
#### (*E*)-3-cinnamyl-1-methyl-3-phenylindolin-2-one (**3aa**)

Yellow solid, m. p. 94 – 96 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.42 (d, *J* = 7.1 Hz, 2H), 7.32 – 7.23 (m, 5H), 7.20 – 7.06 (m, 6H), 6.83 (d, *J* = 7.7 Hz, 1H), 6.35 (d, *J* = 15.8 Hz, 1H), 5.83 – 5.73 (m, 1H), 3.23 – 3.07 (m, 5H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 178.0, 143.9, 139.4, 137.3, 134.2, 131.7, 128.6, 128.4, 128.4, 127.4, 127.3, 127.2, 126.2, 125.3, 124.1, 122.6, 108.3, 56.8, 41.4, 26.4 ppm. HRMS (ESI) calcd for [C<sub>24</sub>H<sub>21</sub>NO+H]<sup>+</sup> 340.1696, found 340.1695.



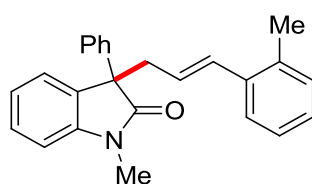
#### (*E*)-3-(3-(4-methoxyphenyl)allyl)-1-methyl-3-phenylindolin-2-one (**3ab**)

Yellow solid, 138 – 140 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.42 (d, *J* = 7.2 Hz, 2H), 7.32– 7.21 (m, 5H), 7.10 (d, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 7.7 Hz, 1H), 6.73 (d, *J* = 8.7 Hz, 2H), 6.29 (d, *J* = 15.8 Hz, 1H), 5.68 – 5.58 (m, 1H), 3.72 (s, 3H), 3.22 – 3.04 (m, 5H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 178.1, 159.0, 143.9, 139.5, 133.5, 131.8, 130.1, 128.6, 128.3, 127.4, 127.3, 127.2, 125.4, 122.5, 121.8, 113.9, 108.3, 56.9, 55.3, 41.4, 26.4 ppm. HRMS (ESI) calcd for [C<sub>25</sub>H<sub>23</sub>NO<sub>2</sub>+H]<sup>+</sup> 370.1802, found 370.1803.



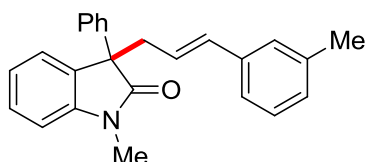
***(E)*-1-methyl-3-phenyl-3-(3-(*p*-tolyl)allyl)indolin-2-one (3ac)**

Yellow solid, 75 – 77 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 (d,  $J = 7.1$  Hz, 2H), 7.33 – 7.22 (m, 5H), 7.09 (t,  $J = 7.4$  Hz, 1H), 7.01 (s, 4H), 6.85 (d,  $J = 7.7$  Hz, 1H), 6.32 (d,  $J = 15.8$  Hz, 1H), 5.78 – 5.68 (m, 1H), 3.23 – 3.05 (m, 5H), 2.27 (s, 3H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  178.06, 143.9, 139.5, 137.1, 134.5, 134.0, 131.7, 129.2, 128.7, 128.4, 127.5, 127.2, 126.1, 125.4, 123.0, 122.6, 108.3, 56.9, 41.4, 26.5, 21.2 ppm. HRMS (ESI) calcd for  $[\text{C}_{25}\text{H}_{23}\text{NO}+\text{H}]^+$  354.1852, found 354.1853.



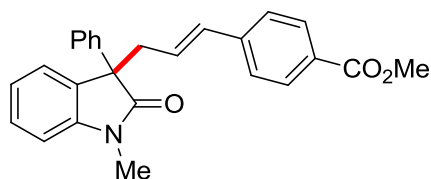
***(E)*-1-methyl-3-phenyl-3-(3-(*o*-tolyl)allyl)indolin-2-one (3ad)**

Yellow oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 – 7.42 (m, 2H), 7.32 – 7.20 (m, 5H), 7.12 – 7.00 (m, 5H), 6.85 (d,  $J = 7.6$  Hz, 1H), 6.52 (d,  $J = 15.6$  Hz, 1H), 5.68 – 5.58 (m, 1H), 3.24 – 3.11 (m, 5H), 2.13 (s, 3H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  178.0, 143.9, 139.5, 136.7, 135.3, 132.7, 131.7, 130.0, 128.6, 128.4, 127.5, 127.2, 127.2, 126.0, 125.9, 125.6, 125.4, 122.5, 108.4, 57.0, 41.7, 26.4, 19.7 ppm. HRMS (ESI) calcd for  $[\text{C}_{25}\text{H}_{23}\text{NO}+\text{H}]^+$  354.1852, found 354.1857.



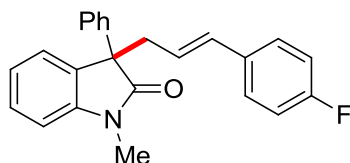
***(E)*-1-methyl-3-phenyl-3-(3-(*m*-tolyl)allyl)indolin-2-one (3ae)**

Colorless oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 (d,  $J = 7.1$  Hz, 2H), 7.33– 7.22 (m, 5H), 7.10 (t,  $J = 8.4$  Hz, 2H), 6.94 (t,  $J = 9.0$  Hz, 3H), 6.85 (d,  $J = 7.7$  Hz, 1H), 6.32 (d,  $J = 15.7$  Hz, 1H), 5.83 – 5.73 (m, 1H), 3.24 – 3.05 (m, 5H), 2.23 (s, 3H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  178.1, 143.9, 139.5, 138.0, 137.2, 134.3, 131.7, 128.7, 128.4, 128.1, 127.5, 127.2, 127.1, 125.4, 123.9, 123.3, 122.6, 108.4, 56.8, 41.4, 26.5, 21.4 ppm. HRMS (ESI) calcd for  $[\text{C}_{25}\text{H}_{23}\text{NO}+\text{H}]^+$  354.1852, found 354.1855.



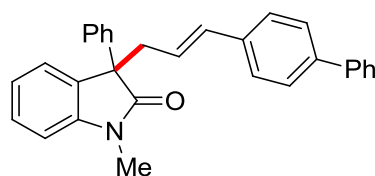
**(E)-methyl 4-(3-(1-methyl-2-oxo-3-phenylindolin-3-yl)prop-1-en-1-yl)benzoate (3af)**

Yellow solid, 122 – 124 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 (d,  $J = 8.3$  Hz, 2H), 7.42 (d,  $J = 7.1$  Hz, 2H), 7.35 – 7.23 (m, 5H), 7.16 (s, 2H), 7.11 (t,  $J = 7.4$  Hz, 1H), 6.87 (d,  $J = 7.7$  Hz, 1H), 6.39 (d,  $J = 15.8$  Hz, 1H), 6.02 – 5.79 (m, 1H), 3.86 (s, 3H), 3.25– 3.11 (m, 5H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  177.8, 166.9, 143.8, 141.6, 139.2, 133.3, 131.5, 129.8, 128.8, 128.7, 128.5, 127.6, 127.1, 127.1, 126.0, 125.3, 122.7, 108.4, 56.7, 52.1, 41.4, 26.5 ppm. HRMS (ESI) calcd for  $[\text{C}_{26}\text{H}_{23}\text{NO}_3+\text{H}]^+$  398.1751, found 398.1758.



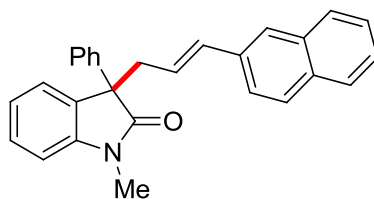
**(E)-3-(3-(4-fluorophenyl)allyl)-1-methyl-3-phenylindolin-2-one (3ag)**

Brown oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44– 7.41 (m, 2H), 7.33 – 7.24 (m, 5H), 7.12 (dd,  $J = 7.5, 0.7$  Hz, 1H), 7.11 – 7.04 (m, 2H), 6.87 (t,  $J = 8.4$  Hz, 3H), 6.31 (d,  $J = 15.8$  Hz, 1H), 5.80 – 5.63 (m, 1H), 3.23 – 3.06 (m, 5H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  178.0, 162.1 (d,  $J = 244.8$  Hz), 143.8, 139.3, 133.33 (d,  $J = 3.3$  Hz), 133.0, 131.6, 128.7, 128.4, 127.6 (d,  $J = 7.9$  Hz), 127.5, 127.2, 125.3, 123.79, 123.76, 122.6, 115.3 (d,  $J = 21.4$  Hz), 108.4, 56.8, 41.2, 26.4 ppm. HRMS (ESI) calcd for  $[\text{C}_{24}\text{H}_{20}\text{FNO}+\text{H}]^+$  358.1602, found 358.1601.



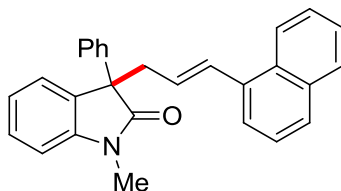
**(E)-3-(3-([1,1'-biphenyl]-4-yl)allyl)-1-methyl-3-phenylindolin-2-one (3ah)**

White solid, 158 – 159 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 – 7.18 (m, 16H), 7.11 (t,  $J = 7.4$  Hz, 1H), 6.86 (d,  $J = 7.6$  Hz, 1H), 6.39 (d,  $J = 15.7$  Hz, 1H), 5.83 (dt,  $J = 15.1, 7.5$  Hz, 1H), 3.26 – 3.09 (m, 5H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  178.0, 143.9, 140.8, 140.1, 139.4, 136.3, 133.7, 131.7, 128.8, 128.7, 128.4, 127.5, 127.3, 127.2, 127.2, 127.0, 126.7, 125.4, 124.3, 122.6, 108.4, 56.9, 41.5, 26.5 ppm. HRMS (ESI) calcd for  $[\text{C}_{30}\text{H}_{25}\text{NO}+\text{H}]^+$  416.2009, found 416.2011.



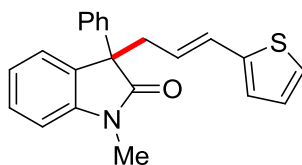
**(E)-1-methyl-3-(3-(naphthalen-2-yl)allyl)-3-phenylindolin-2-one (3ai)**

Yellow solid, 58 – 60 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 (d,  $J = 6.4$  Hz, 2H), 7.64 (d,  $J = 8.6$  Hz, 1H), 7.49(s, 1H), 7.44(d,  $J = 7.2$  Hz, 2H), 7.40 – 7.16 (m, 8H), 7.19 (t,  $J = 7.4$  Hz, 1H), 6.83 (d,  $J = 7.9$  Hz, 1H), 6.50 (d,  $J = 15.8$  Hz, 1H), 5.96 – 5.86 (m, 1H), 3.28 – 3.13 (m, 5H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  178.0, 143.9, 139.4, 134.6, 134.3, 133.6, 132.8, 131.7, 128.7, 128.4, 128.1, 128.0, 127.6, 127.5, 127.2, 126.3, 126.0, 125.8, 125.4, 124.5, 123.5, 122.6, 108.4, 56.9, 41.5, 26.5 ppm. HRMS (ESI) calcd for  $[\text{C}_{30}\text{H}_{25}\text{NO}+\text{H}]^+$  416.2009, found 416.2011.



**(E)-1-methyl-3-(3-(naphthalen-1-yl)allyl)-3-phenylindolin-2-one (3aj)**

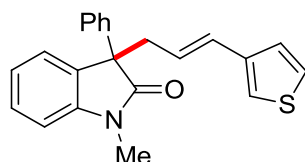
White solid, 59 – 61 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 (td,  $J = 7.6, 4.2$  Hz, 2H), 7.68 (d,  $J = 8.1$  Hz, 1H), 7.49 – 7.41 (m, 4H), 7.39 – 7.27 (m, 6H), 7.23 – 7.11 (m, 3H), 7.03 (d,  $J = 15.5$  Hz, 1H), 6.85 (d,  $J = 7.7$  Hz, 1H), 5.76 (dt,  $J = 15.2, 7.5$  Hz, 1H), 3.28 (d,  $J = 7.4$  Hz, 2H), 3.15 (s, 3H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  178.0, 143.9, 139.4, 134.6, 134.3, 133.5, 132.8, 131.6, 128.7, 128.4, 128.0, 127.9, 127.6, 127.5, 127.2, 126.3, 126.0, 125.8, 125.4, 124.4, 123.5, 122.6, 108.4, 56.9, 41.5, 26.5 ppm. HRMS (ESI) calcd for  $[\text{C}_{28}\text{H}_{23}\text{NO}+\text{H}]^+$  390.1852, found 390.1858.



**(E)-1-methyl-3-phenyl-3-(3-(thiophen-2-yl)allyl)indolin-2-one (3ak)**

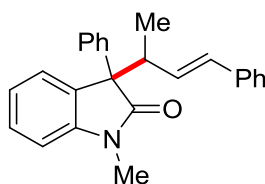
Brown solid, 154 – 156 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41 (d,  $J = 7.0$  Hz, 2H), 7.34 - 7.27 (m, 4H), 7.26 - 7.24 (m, 1H), 7.11 (t,  $J = 7.5$  Hz, 1H), 7.08 – 6.99 (m, 1H), 6.86 (dd,  $J = 7.9, 4.1$  Hz, 2H), 6.75 (d,  $J = 3.2$  Hz, 1H), 6.46 (d,  $J = 15.6$  Hz, 1H), 5.66 – 5.56 (m, 1H), 3.23 – 3.12 (m, 4 H), 3.07 (dd,  $J = 13.4, 8.6$  Hz, 1H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  178.0, 143.9, 142.2, 139.3, 131.5, 128.7, 128.7, 128.5, 127.5, 127.3, 127.2, 125.3, 125.2, 123.8, 123.8, 122.7, 108.4, 56.8, 41.3, 26.5 ppm. HRMS (ESI) calcd for  $[\text{C}_{22}\text{H}_{19}\text{NOS}+\text{H}]^+$  346.1260, found 346.1265.





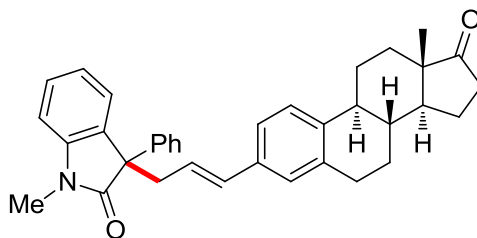
**(E)-1-methyl-3-phenyl-3-(3-(thiophen-3-yl)allyl)indolin-2-one (3al)**

White solid, 158 – 160 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.41 (d, *J* = 7.1 Hz, 2H), 7.35 – 7.23 (m, 6H), 7.16 – 7.09 (m, 2H), 6.93 (t, *J* = 4.4 Hz, 2H), 6.87 (d, *J* = 7.8 Hz, 1H), 6.36 (d, *J* = 15.7 Hz, 1H), 5.68 – 5.58 (m, 1H), 3.23 – 3.15 (m, 4H), 3.07 (dd, *J* = 13.5, 8.6 Hz, 1H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 178.1, 143.9, 139.9, 139.4, 131.7, 128.7, 128.4, 128.4, 127.5, 127.2, 125.8, 125.4, 125.1, 123.9, 122.6, 121.6, 108.4, 56.8, 41.3, 26.5 ppm. HRMS (ESI) calcd for [C<sub>22</sub>H<sub>19</sub>NOS+H]<sup>+</sup> 346.1260, found 346.1261.



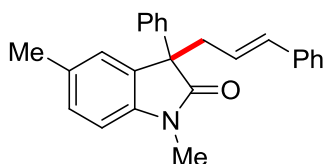
**1-methyl-3-phenyl-3-(E)-4-phenylbut-3-en-2-ylindolin-2-one (3am)**

Colorless oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.54- 7.45 (m, 5H), 7.39 – 7.05 (m, 21H), 6.89- 6.82 (m, 2H), 6.45 (d, *J* = 15.8 Hz, 1H), 6.26 – 6.11 (m, 2H), 5.50 (dd, *J* = 15.8, 8.8 Hz, 1H), 3.69 – 3.55 (m, 2H), 3.18 (s, 3H), 3.04 (s, 3H), 1.14 (d, *J* = 6.9 Hz, 3H), 0.88 (d, *J* = 6.5 Hz, 3H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 179.2, 177.8, 144.4, 138.7, 138.0, 137.5, 137.5, 131.7, 131.4, 130.4, 130.3, 129.1, 128.9, 128.6, 128.5, 128.4, 127.9, 127.7, 127.4, 127.4, 127.3, 127.2, 126.5, 126.3, 126.2, 126.2, 122.1, 122.1, 108.4, 108.3, 61.0, 60.5, 45.3, 43.7, 26.4, 26.3, 15.8, 14.5 ppm. HRMS (ESI) calcd for [C<sub>25</sub>H<sub>23</sub>NO+H]<sup>+</sup> 354.1852, found 354.1854.



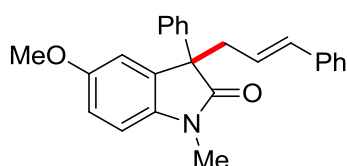
**1-methyl-3-((E)-3-((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)allyl)-3-phenylindolin-2-one (3an)**

Yellow solid, m. p. 70 – 72 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.42 (d, *J* = 7.3 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 3H), 7.26 – 7.22 (m, 3H), 6.92 (d, *J* = 8.2 Hz, 1H), 6.87 (s, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.30 (d, *J* = 15.7 Hz, 1H), 5.81 – 5.71 (m, 1H), 3.23 – 3.04 (m, 5H), 2.82 (AB, *J* = 3.4 Hz, 2H), 2.36 – 2.33 (m, 1H), 2.30 – 2.18 (m, 1H), 2.17 (t, *J* = 9.0 Hz, 1H), 2.07 – 1.92 (m, 4H), 1.62 – 1.30 (m, 6H), 0.86 (s, 3H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 220.5, 177.8, 143.6, 139.2, 138.7, 136.2, 134.6, 133.7, 131.4, 128.4, 128.1, 127.2, 126.9, 126.7, 125.2, 125.1, 123.3, 123.2, 122.3, 108.1, 76.5, 56.5, 50.3, 47.7, 44.2, 41.2, 37.9, 35.6, 31.4, 29.1, 26.3, 26.2, 25.5, 21.4, 13.6 ppm. HRMS (ESI) calcd for [C<sub>36</sub>H<sub>37</sub>O<sub>2</sub>+H]<sup>+</sup> 516.2897, found 516.2901.



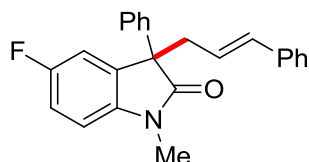
**(E)-3-cinnamyl-1,5-dimethyl-3-phenylindolin-2-one (3ba)**

White solid, m. p. 66 – 68 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 – 7.34 (m, 2H), 7.36 – 7.27 (m, 2H), 7.33 – 7.08 (m, 9H), 6.74 (d,  $J = 7.7$  Hz, 1H), 6.37 (d,  $J = 15.8$  Hz, 1H), 5.81 – 5.71 (m, 1H), 3.21 – 3.08 (m, 5H), 2.34 (s, 3H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  178.0, 141.5, 139.7, 137.3, 134.1, 132.1, 131.8, 128.7, 128.5, 127.4, 127.3, 127.2, 126.2, 126.0, 124.2, 115.0, 108.1, 57.0, 41.2, 26.5, 21.4 ppm. HRMS (ESI) calcd for  $[\text{C}_{25}\text{H}_{23}\text{NO}+\text{H}]^+$  354.1852, found 354.1860.



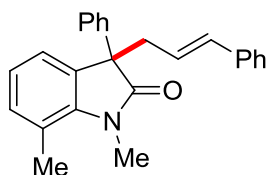
**(E)-3-cinnamyl-5-methoxy-1-methyl-3-phenylindolin-2-one (3ca)**

Brown solid, m. p. 60 – 62 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 (d,  $J = 7.3$  Hz, 2H), 7.25 – 7.03 (m, 8H), 6.81 (d,  $J = 2.0$  Hz, 1H), 6.75 (dd,  $J = 8.5, 2.3$  Hz, 1H), 6.67 (d,  $J = 8.4$  Hz, 1H), 6.29 (d,  $J = 15.8$  Hz, 1H), 5.74 – 5.64 (m, 1H), 3.65 (s, 3H), 3.13 – 3.04 (m, 5H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  177.7, 156.0, 139.4, 137.5, 137.3, 134.2, 133.1, 128.7, 128.5, 127.5, 127.3, 127.2, 126.2, 124.1, 112.7, 112.7, 108.6, 57.3, 55.9, 41.2, 26.5 ppm. HRMS (ESI) calcd for  $[\text{C}_{25}\text{H}_{24}\text{NO}_2+\text{H}]^+$  370.1802, found 370.1799.



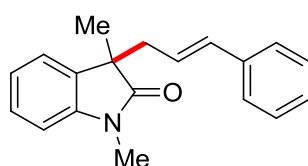
**(E)-3-cinnamyl-5-fluoro-1-methyl-3-phenylindolin-2-one (3da)**

Yellow oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 (d,  $J = 7.5$  Hz, 2H), 7.32 (t,  $J = 7.2$  Hz, 2H), 7.28 – 7.25 (m, 1H), 7.23 – 7.18 (m, 2H), 7.17 – 7.11 (m, 3H), 7.04 – 6.97 (m, 2H), 6.76 (dd,  $J = 8.2, 4.2$  Hz, 1H), 6.37 (d,  $J = 15.8$  Hz, 1H), 5.81 – 5.70 (m, 1H), 3.19 – 3.14 (m, 5H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  177.7, 159.3 (d,  $J = 239.2$  Hz), 139.9 (d,  $J = 1.8$  Hz), 138.9, 137.1, 134.6, 133.4 (d,  $J = 8.0$  Hz), 128.8, 128.5, 127.7, 127.4, 127.0, 126.2, 123.5, 114.7 (d,  $J = 23.3$  Hz), 113.3 (d,  $J = 24.6$  Hz), 108.8 (d,  $J = 8.1$  Hz), 57.3, 41.2, 26.6 ppm. HRMS (ESI) calcd for  $[\text{C}_{24}\text{H}_{20}\text{FNO}+\text{H}]^+$  358.1602, found 358.1598.



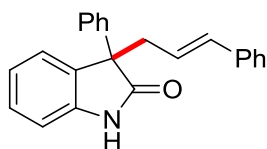
**(E)-3-cinnamyl-1,7-dimethyl-3-phenylindolin-2-one (3ea)**

Yellow solid, 131 – 133 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40– 7.07(m, 11H), 7.03 – 6.94 (m, 2H), 6.36 (d,  $J = 15.7$  Hz, 1H), 5.83 – 5.73 (m, 1H), 3.42 (s, 3H), 3.15 (d,  $J = 4.8$  Hz, 2H), 2.54 (s, 3H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  178.8, 141.7, 139.9, 137.4, 134.1, 132.4, 132.1, 128.6, 128.5, 127.4, 127.2, 126.2, 124.3, 123.3, 122.5, 119.9, 56.2, 41.5, 29.9, 19.2 ppm. HRMS (ESI) calcd for  $[\text{C}_{25}\text{H}_{24}\text{NO}+\text{H}]^+$  354.1852, found 354.1846.



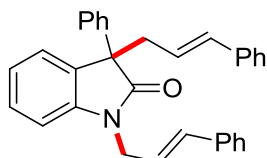
**(E)-3-cinnamyl-1,3-dimethylindolin-2-one (3fa)**

Yellow oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27 – 7.12 (m, 7H), 7.06 (t,  $J = 7.2$  Hz, 1H), 6.80 (d,  $J = 7.7$  Hz, 1H), 6.34 (d,  $J = 15.7$  Hz, 1H), 5.92 – 5.83 (m, 1H), 3.16 (s, 3H), 2.64 (d,  $J = 7.5$  Hz, 2H), 1.41 (s, 3H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  180.3, 143.2, 137.4, 133.8, 133.7, 128.5, 127.9, 127.3, 126.2, 124.3, 123.0, 122.5, 108.1, 48.7, 41.7, 26.2, 22.6 ppm. HRMS (ESI) calcd for  $[\text{C}_{19}\text{H}_{19}\text{NO}+\text{H}]^+$  278.1539, found 278.1539.



**(E)-3-cinnamyl-3-phenylindolin-2-one (3ga)**

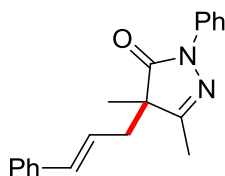
White solid, 45 – 47 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  9.17 (s, 1H), 7.41– 7.02 (m, 13H), 6.90 (d,  $J = 7.8$  Hz, 1H), 6.37 (d,  $J = 15.7$  Hz, 1H), 5.85 (dt,  $J = 15.2, 7.5$  Hz, 1H), 3.21 (dd,  $J = 13.4, 6.1$  Hz, 1H), 3.09 (dd,  $J = 13.4, 8.5$  Hz, 1H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  180.8, 141.1, 139.4, 137.2, 134.4, 132.5, 128.8, 128.5, 128.4, 127.6, 127.4, 127.2, 126.3, 125.6, 124.0, 122.6, 110.4, 57.4, 41.0 ppm. HRMS (ESI) calcd for  $[\text{C}_{23}\text{H}_{19}\text{NO}+\text{H}]^+$  326.1539, found 326.1538.



**(E, E)-1,3-dicinnamyl-3-phenylindolin-2-one (3ha)**

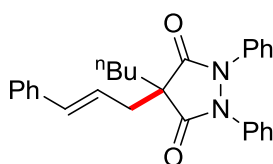
White solid, m.p. 123 – 125 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 (d,  $J = 7.2$  Hz, 2H), 7.35– 7.24 (m, 5H), 7.21– 7.10 (m, 9H), 7.01 (s, 2H), 6.91 (d,  $J = 7.6$  Hz, 1H), 6.50 (d,  $J = 16.1$  Hz, 1H), 6.43 (d,  $J = 16.0$  Hz, 1H), 5.95 (dt,  $J = 15.7, 5.7$  Hz, 1H), 5.87 – 5.68

(m, 1H), 4.65 (dd,  $J = 15.9, 4.3$  Hz, 1H), 4.27 (dd,  $J = 16.0, 6.4$  Hz, 1H), 3.31 – .315 (m, 2H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  177.7, 143.0, 139.7, 137.1, 136.1, 134.4, 133.1, 131.7, 128.8, 128.6, 128.6, 128.4, 127.8, 127.6, 127.4, 127.2, 126.4, 126.2, 125.2, 123.8, 123.2, 122.7, 109.4, 57.0, 42.3, 41.3 ppm. HRMS (ESI) calcd for  $[\text{C}_{32}\text{H}_{27}\text{NO}+\text{H}]^+$  442.2165, found 442.2177.



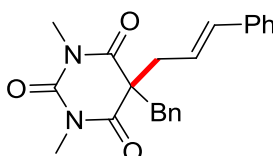
**(E)-4-cinnamyl-1,3,4-trimethyl-1H-pyrazol-5(4H)-one (3ia)**

Brown solid, m. p. 85 – 87 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89 (d,  $J = 7.8$  Hz, 2H), 7.35 (t,  $J = 7.9$  Hz, 2H), 7.22 – 7.11 (m, 6H), 6.46 (d,  $J = 15.7$  Hz, 1H), 5.92 – 5.77 (dt,  $J = 15.7, 7.5$  Hz, 1H), 2.72 (dd,  $J = 13.6, 6.8$  Hz, 1H), 2.49 (dd,  $J = 13.9, 7.8$  Hz, 1H), 2.08 (s, 3H), 1.32 (s, 3H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  175.8, 163.5, 138.2, 136.7, 134.4, 128.9, 128.6, 127.7, 126.4, 125.0, 122.6, 119.0, 54.8, 39.2, 20.0, 14.0 ppm. HRMS (ESI) calcd for  $[\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}+\text{H}]^+$  305.1648, found 305.1643.



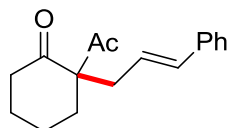
**(E)-4-butyl-4-cinnamyl-1,2-diphenylpyrazolidine-3,5-dione (3ja)**

Yellow oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27 – 7.19 (m, 13H), 7.12 (td,  $J = 8.6, 4.5$  Hz, 2H), 6.53 (d,  $J = 15.8$  Hz, 1H), 6.06 (dt,  $J = 15.6, 7.7$  Hz, 1H), 2.78 (d,  $J = 7.6$  Hz, 2H), 1.96 (t,  $J = 8.0$  Hz, 2H), 1.34 - 1.25 (m, 4H), 0.87 (t,  $J = 6.7$  Hz, 3H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  173.2, 136.7, 135.6, 135.5, 129.0, 128.6, 127.8, 126.9, 126.5, 123.0, 122.2, 55.4, 39.8, 35.4, 27.2, 22.8, 13.8 ppm. HRMS (ESI) calcd for  $[\text{C}_{28}\text{H}_{28}\text{N}_2\text{O}_2+\text{H}]^+$  425.2224, found 425.2236.



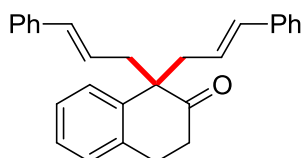
**(E)-5-benzyl-5-cinnamyl-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (3ka)**

Yellow oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27 – 7.19 (m, 8H), 7.00 – 6.97 (m, 2H), 6.51 (d,  $J = 15.7$  Hz, 1H), 5.92 (dt,  $J = 15.5, 7.6$  Hz, 1H), 3.28 (s, 2H), 3.13 – 3.04 (m, 8H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  170.9, 150.3, 136.6, 135.4, 134.7, 129.0, 128.6, 128.6, 128.0, 127.8, 126.4, 122.2, 59.4, 46.5, 41.4, 28.2 ppm. HRMS (ESI) calcd for  $[\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_3+\text{H}]^+$  363.1703, found 363.1704.



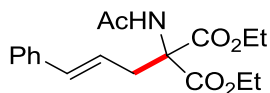
**(E)-2-acetyl-2-cinnamylcyclohexanone (3la)**

Faint yellow oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 – 7.19 (m, 5H), 6.39 (d,  $J = 15.8$  Hz, 1H), 6.07– 5.97 (m, 1H), 2.72 (dd,  $J = 14.0, 7.5$  Hz, 1H), 2.59 (dd,  $J = 14.3, 7.6$  Hz, 1H), 2.50 (d,  $J = 13.1$  Hz, 2H), 2.35 – 2.27 (m, 1H), 2.12 (s, 3H), 1.99 (d,  $J = 5.0$  Hz, 1H), 1.76 – 1.49 (m, 4H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  209.7, 206.2, 137.1, 133.6, 128.6, 127.5, 126.3, 124.5, 68.0, 41.9, 38.0, 34.2, 27.2, 26.5, 22.2 ppm.



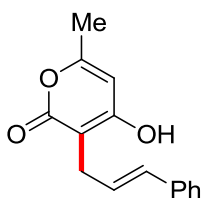
**1,1-dicinnamyl-3,4-dihydronaphthalen-2(1H)-one (3ma)**

Yellow solid, 83 – 85 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 (d,  $J = 7.6$  Hz, 1H), 7.34 (t,  $J = 7.6$  Hz, 1H), 7.24 – 7.13 (m, 12H), 6.25 (d,  $J = 15.8$  Hz, 2H), 5.81 – 5.71 (m, 2H), 2.98 (dd,  $J = 13.4, 8.7$  Hz, 2H), 2.88 – 2.84 (m, 2H), 2.70 (dd,  $J = 13.0, 6.1$  Hz, 2H), 2.50 – 2.46 (m, 2H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  214.2, 139.1, 137.3, 137.3, 133.4, 128.5, 128.3, 127.3, 127.2, 127.0, 126.6, 126.2, 124.9, 56.8, 44.4, 40.6, 27.8 ppm. HRMS (ESI) calcd for  $[\text{C}_{28}\text{H}_{26}\text{O}+\text{H}]^+$  379.2056, found 379.2056.



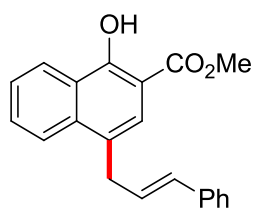
**(E)-diethyl 2-acetamido-2-cinnamylmalonate (3na)**

Yellow solid, m. p. 77 – 79 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30 – 7.23 (m, 5H), 6.82 (s, 1H), 6.44 (d,  $J = 15.7$  Hz, 1H), 5.94 (dt,  $J = 15.5, 7.6$  Hz, 1H), 4.30 – 4.23 (m, 4H), 3.24 (d,  $J = 7.4$  Hz, 2H), 2.04 (s, 3H), 1.27 (t,  $J = 7.1$  Hz, 6H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  169.3, 167.7, 137.0, 134.8, 128.6, 127.6, 126.3, 122.7, 66.5, 62.7, 36.4, 23.1, 14.1 ppm. HRMS (ESI) calcd for  $[\text{C}_{18}\text{H}_{23}\text{NO}_5+\text{H}]^+$  334.1649, found 334.1646.



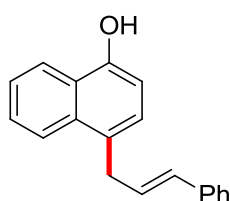
**3-cinnamyl-4-hydroxy-6-methyl-2H-pyran-2-one (3oa)**

Yellow solid, m. p. 228 – 230 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ )  $\delta$  11.30 (s, 1H), 7.35 – 7.18 (m, 5H), 6.38 – 6.21 (m, 2H), 6.04 (s, 1H), 3.17 (d,  $J = 5.3$  Hz, 2H), 2.16 (s, 3H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{DMSO}-d_6$ )  $\delta$  165.9, 165.0, 160.8, 137.6, 130.0, 129.0, 127.7, 127.4, 126.3, 100.4, 99.3, 26.6, 19.8 ppm. HRMS (ESI) calcd for  $[\text{C}_{15}\text{H}_{14}\text{O}_3+\text{H}]^+$  243.1016, found 243.1013.



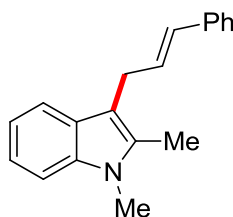
**(E)-methyl 4-cinnamyl-1-hydroxy-2-naphthoate (3pa)**

Colorless oil;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  11.90 (s, 1H), 8.47 (d,  $J = 7.9$  Hz, 1H), 7.98 (d,  $J = 8.4$  Hz, 1H), 7.66 – 7.61 (m, 2H), 7.54 (t,  $J = 7.2$  Hz, 1H), 7.32 (t,  $J = 6.5$  Hz, 2H), 7.26 (d,  $J = 7.0$  Hz, 2H), 7.21 – 7.18 (m, 1H), 6.47 – 6.39 (m, 2H), 3.98 (s, 3H), 3.87 (d,  $J = 4.3$  Hz, 2H) ppm.  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  171.5, 160.2, 137.5, 136.0, 131.4, 129.6, 128.9, 128.6, 127.3, 126.7, 126.2, 125.7, 125.3, 124.6, 124.2, 105.2, 52.4, 36.1 ppm. HRMS (ESI) calcd for  $[\text{C}_{19}\text{H}_{16}\text{O}-\text{H}]^-$  259.1128, found 259.1127.



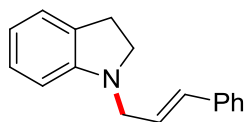
**4-cinnamyl-naphthalen-1-ol (3qa)**

White solid, m. p. 77 – 78 °C;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.18 – 8.14 (m, 1H), 7.79 (dd,  $J = 5.4, 3.9$  Hz, 1H), 7.50 – 7.40 (m, 3H), 7.36 – 7.20 (m, 6H), 6.59 (d,  $J = 16.0$  Hz, 1H), 6.43 (dt,  $J = 15.9, 6.2$  Hz, 1H), 5.56 (s, 1H), 3.73 (d,  $J = 5.6$  Hz, 2H) ppm.  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  149.7, 136.9, 134.0, 132.1, 128.7, 128.6, 127.8, 127.7, 127.6, 126.4, 126.0, 125.5, 125.0, 121.4, 120.6, 118.4, 34.9 ppm. HRMS (ESI) calcd for  $[\text{C}_{21}\text{H}_{18}\text{O}_3+\text{H}]^+$  319.1329, found 319.1324.



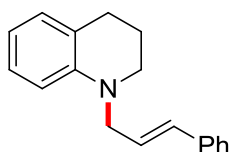
**3-cinnamyl-1,2-dimethyl-1H-indole (3ra)**

Yellow oil;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 (d,  $J = 7.7$  Hz, 1H), 7.31 – 7.26 (m, 4H), 7.22 (d,  $J = 4.0$  Hz, 1H), 7.17 – 7.12 (m, 2H), 7.08 – 7.03 (m, 1H), 6.43 (d,  $J = 16.0$  Hz, 1H), 6.40 (dt,  $J = 15.8$  Hz, 5.2 Hz, 1H), 3.65 (s, 3H), 3.63 (d,  $J = 5.3$  Hz, 1H), 2.37 (s, 3H) ppm.  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  138.0, 136.8, 133.4, 130.0, 129.6, 128.5, 127.9, 126.9, 126.2, 120.7, 119.0, 118.3, 108.7, 108.7, 29.6, 28.2, 10.4 ppm. HRMS (ESI) calcd for  $[\text{C}_{19}\text{H}_{20}\text{N}+\text{H}]^+$  262.1590, found 262.1587.



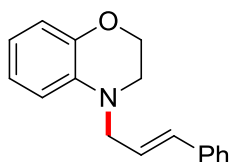
**(E)-1-cinnamylindoline (3sa)**

Brown solid, m. p. 48 – 50 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27- 7.05 (m, 6H), 6.97 (t,  $J = 7.8$  Hz, 2H), 6.59- 6.44 (m, 3H), 6.19 (dt,  $J = 15.8, 6.2$  Hz, 1H), 3.75 (d,  $J = 6.1$  Hz, 2H), 3.26 (t,  $J = 8.3$  Hz, 2H), 2.85 (t,  $J = 8.2$  Hz, 2H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  152.3, 137.0, 132.4, 130.4, 128.7, 127.6, 127.4, 126.5, 126.1, 124.6, 117.9, 107.5, 53.4, 51.7, 28.7 ppm. HRMS (ESI) calcd for  $[\text{C}_{17}\text{H}_{17}\text{N}+\text{H}]^+$  236.1434, found 236.1419.



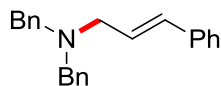
**1-cinnamyl-1,2,3,4-tetrahydroquinoline (3ta)**

Brown solid, m. p. 38 – 40 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 (d,  $J = 7.1$  Hz, 2H), 7.26 (t,  $J = 7.3$  Hz, 2H), 7.23 – 7.12 (m, 1H), 7.02 (t,  $J = 7.7$  Hz, 1H), 6.94 (d,  $J = 7.1$  Hz, 1H), 6.60 (dd,  $J = 11.6, 7.8$  Hz, 2H), 6.51 (d,  $J = 16.1$  Hz, 1H), 6.22 (dt,  $J = 15.9, 5.4$  Hz, 1H), 3.99 (dd,  $J = 5.3, 1.3$  Hz, 2H), 3.37 – 3.20 (m, 2H), 2.76 (t,  $J = 6.3$  Hz, 2H), 1.96 (dt,  $J = 11.7, 6.2$  Hz, 2H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  145.5, 137.1, 131.2, 129.2, 128.6, 127.4, 127.3, 126.4, 125.8, 122.7, 116.0, 111.2, 53.6, 49.3, 28.3, 22.5 ppm. HRMS (ESI) calcd for  $[\text{C}_{18}\text{H}_{19}\text{N}+\text{H}]^+$  250.1590, found 250.1585.



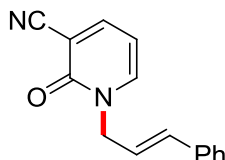
**4-cinnamyl-3,4-dihydro-2H-benzo[b][1,4]oxazine (3ua)**

Yellow solid, m. p. 56 – 58 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35– 7.18 (m, 5H), 6.85 – 6.73 (m, 3H), 6.66 – 6.60 (m, 1H), 6.56 (d,  $J = 15.9$  Hz, 1H), 6.23 (dt,  $J = 15.9, 5.8$  Hz, 1H), 4.25 (t,  $J = 4.4$  Hz, 2H), 3.99 (dd,  $J = 5.7, 1.0$  Hz, 2H), 3.33 (t,  $J = 4.5$  Hz, 2H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  144.4, 136.8, 135.3, 132.4, 128.7, 127.7, 126.5, 125.0, 121.7, 118.0, 116.5, 112.9, 64.7, 53.3, 46.9 ppm. HRMS (ESI) calcd for  $[\text{C}_{17}\text{H}_{17}\text{NO}+\text{H}]^+$  252.1383, found 252.1379.



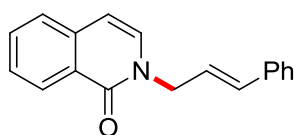
**(E)-N,N-dibenzyl-3-phenylprop-2-en-1-amine (3va)**

Yellow oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 – 7.18 (m, 15H), 6.51 (d,  $J = 15.9$  Hz, 1H), 6.28 (dt,  $J = 15.8, 6.4$  Hz, 1H), 3.61 (s, 4H), 3.21 (d,  $J = 6.1$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  139.8, 137.4, 132.6, 128.9, 128.6, 128.3, 127.9, 127.4, 127.0, 126.4, 58.1, 55.9 ppm. HRMS (ESI) calcd for  $[\text{C}_{23}\text{H}_{23}\text{N}+\text{H}]^+$  314.1903, found 314.1901.



**(E)-1-cinnamyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (3wa)**

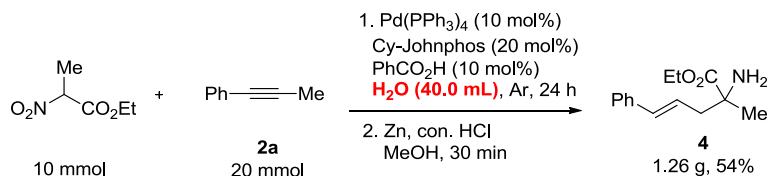
Yellow solid, m. p. 80 – 82 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (dd,  $J = 7.1, 2.0$  Hz, 1H), 7.69 (dd,  $J = 6.8, 2.0$  Hz, 1H), 7.38 – 7.26 (m, 5H), 6.66 (d,  $J = 15.9$  Hz, 1H), 6.33 – 6.22 (m, 2H), 4.75 (dd,  $J = 6.7, 0.8$  Hz, 2H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  159.6, 147.2, 142.6, 135.8, 135.5, 128.7, 128.5, 126.7, 121.9, 115.8, 105.7, 105.5, 51.8 ppm. HRMS (ESI) calcd for  $[\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}+\text{H}]^+$  237.1022, found 237.1022.



**2-cinnamylisoquinolin-1(2H)-one (3xa)**

Brown solid, m. p. 81 – 83 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.46 (d,  $J = 8.0$  Hz, 1H), 7.63 (t,  $J = 7.4$  Hz, 1H), 7.51 – 7.46 (m, 2H), 7.36 (d,  $J = 7.2$  Hz, 2H), 7.31 – 7.22 (m, 3H), 7.11 (d,  $J = 7.4$  Hz, 1H), 6.60 (d,  $J = 15.9$  Hz, 1H), 6.50 (d,  $J = 7.4$  Hz, 1H), 6.34 (dt,  $J = 15.8, 6.3$  Hz, 1H), 4.79 (d,  $J = 6.3$  Hz, 2H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  162.1, 137.2, 136.3, 133.7, 132.3, 131.1, 128.7, 128.1, 127.0, 126.6, 126.4, 126.0, 124.2, 106.5, 50.4 ppm. HRMS (ESI) calcd for  $[\text{C}_{18}\text{H}_{15}\text{NO}+\text{H}]^+$  262.1226, found 262.1225.

**5. Further Study of This Allylic Alkylation**

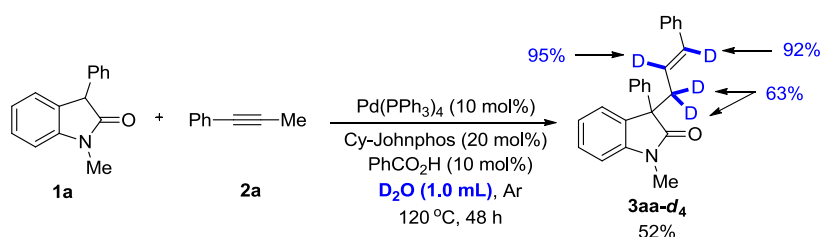


A 100 mL sealed tube was charged with ethyl 2-nitropropionate (1.47 g, 10 mmol, 1.0 equiv.), **2a** (2.32 g, 20 mmol, 2.0 equiv.),  $\text{Pd}(\text{PPh}_3)_4$  (1.156 g, 1 mmol, 10 mol%), Cy-Johnphos (0.700 g, 2 mmol, 20 mol%),  $\text{PhCO}_2\text{H}$  (0.122 g, 1 mmol, 10 mol%),  $\text{H}_2\text{O}$  (40.0 mL) and a stir bar. The reaction mixture was vigorously stirred at 100 °C (oil temperature) for 24 h under argon. After cooling to room temperature, the reaction



mixture was diluted with ethyl acetate (200 mL). The organic phase was separated and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The mixture was concentrated *in vacuo* and submitted to the next step without further purification.

Reduction of the nitro group was conducted according to the literature's procedure:<sup>4</sup> Dissolving aforementioned mixture with 150 mL MeOH in a 500 mL round-bottom flask in a 20°C water bath. To the flask was added concentrated HCl (19.6 mL, 4.0 mmol, 20 equiv). Zinc dust (25.6 g, 0.4 mol) was added slowly with vigorous stirring. The reaction vial was capped with a needle connected to the air and stirred for 1 h at room temperature. The reaction was filtered and the filtrate was concentrated to about 20 mL. Adjusting pH of the solution to 9 with saturated aqueous NaHCO<sub>3</sub>. Extracted the aqueous phase with ethyl acetate (3 x 100 mL) and the combined organics were dried over Na<sub>2</sub>SO<sub>4</sub>. The mixture was filtered and concentrated *in vacuo*. Purification by flash chromatography on silica gel (1% MeOH, 0.5% NH<sub>4</sub>OH/CH<sub>2</sub>Cl<sub>2</sub>) provided the pure product **4** as paint yellow oil in 54% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.35 – 7.27 (m, 4H), 7.23 – 7.19 (m, 1H), 6.48 (d, *J* = 15.8 Hz, 1H), 6.22 – 5.97 (m, 1H), 4.19 (qd, *J* = 7.1, 1.7 Hz, 2H), 2.68 (dd, *J* = 13.1, 6.3 Hz, 1H), 2.42 (dd, *J* = 13.5, 8.4 Hz, 1H), 1.74 (s, 2H), 1.38 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 177.3, 137.2, 134.3, 128.6, 127.5, 126.3, 124.5, 61.2, 57.9, 44.5, 26.4, 14.4 ppm. HRMS (ESI) calcd for [C<sub>14</sub>H<sub>19</sub>NO<sub>2</sub>+H]<sup>+</sup> 234.1488, found 234.1499.



A sealed tube was charged with **1a** (0.25 mmol, 1.0 equiv), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.025 mmol, 10 mol %), benzoic acid (0.025 mmol, 10 mol %), **2a** (0.5 mmol, 2.0 equiv) and D<sub>2</sub>O (1.0 mL). The reaction mixture was vigorously stirred at 120 °C (oil temperature) for 48 h under argon. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate (20 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The mixture was concentrated *in vacuo* and purified by flash chromatography on silica gel with PE/EA (20:1~10:1) to afford the allylic alkenylated product **3aa-d<sub>4</sub>** in 52% yield.

## 6. $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of Titled Compounds

