

## Supplementary Information

### NHC-catalyzed reactions of enals with water as solvent

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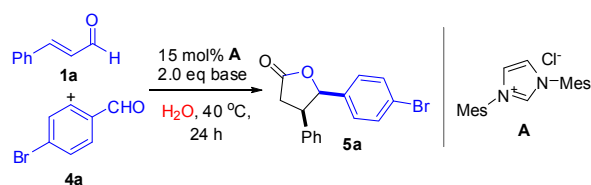
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#### General Information.

Commercially available materials purchased from Alfa Aesar or Aldrich were used as received. Proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra were recorded on Bruker AMX 400 (400 MHz) and Bruker BBFO 400 (400 MHz) spectrometers. Chemical shifts were recorded in parts per million (ppm,  $\delta$ ) relative to tetramethylsilane ( $\delta$  0.00) or chloroform ( $\delta$  = 7.26, singlet).  $^1\text{H}$  NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), dd (doublet of doublets), m (multiplets), and etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). Carbon nuclear magnetic resonance ( $^{13}\text{C}$  NMR) spectra were recorded on Bruker BBFO 400 (100 MHz) spectrometer. High resolution mass spectral analysis (HRMS) was performed on a Finnigan MAT 95 XP mass spectrometer (Thermo Electron Corporation). Analytical thin-layer chromatography (TLC) was carried out on Merck 60 F254 pre-coated silica gel plate (0.2 mm thickness). Visualization was performed using UV radiation (254 nm). Compounds **3a-h**,<sup>1</sup> **5a-c**,<sup>2</sup> and **7a**<sup>3</sup> have been previously reported in the literature.

**Table S1.** Optimization of reaction conditions for the reactions between enals and aldehydes<sup>a</sup>



entry	base	dr ( <i>cis:trans</i> ) <sup>b</sup>	yield (%) <sup>c</sup>
1	NaOH	-	N.R.
2	DBU	-	N.R.
3	$\text{K}_2\text{CO}_3$	3:1	74
4	$\text{Et}_3\text{N}$	3:1	70
5	$\text{K}_3\text{PO}_4$	3:1	62
6	DMAP	3:1	56
7	DIEA	3:1	72
8 <sup>d</sup>	$\text{K}_2\text{CO}_3$	3:1	80

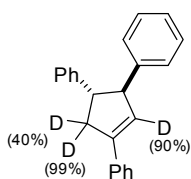
<sup>a</sup> Reaction conditions: **1** (0.1 mmol), **5** (2 eq), catalyst **A** (15 mol%), base (2.0 equiv), and water (0.5 mL, 0.2 M). <sup>b</sup> Determined by  $^1\text{H}$  NMR analysis of crude mixture. <sup>c</sup> Yield estimated by  $^1\text{H}$  NMR spectroscopy with 1,3,5-trimethoxybenzene as internal standard. <sup>d</sup> 5 mol% catalyst loading.

### General procedure for the catalytic reactions between enals and chalcones (for Scheme 1):

A borosilicate glass test tube (16 X 150 mm) containing a stir bar was successively charged with enal **1** (0.37 mmol), chalcone **2** (0.25 mmol), catalyst **A** (8.6 mg, 0.0125 mmol), NaOH (20 mg, 0.5 mmol) and water (0.5 mL). The test tube was capped with a rubber septum and the resulting milky emulsion was stirred vigorously at 40 °C for 24 h. The reaction mixture was cooled to room temperature and extracted using minimal amount of EtOAc, dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated under vacuum. The crude product was purified by flash column chromatography to afford the pure cyclopentene product **3**.

### General procedure for deuteration reaction between enals and chalcones (for scheme 2):

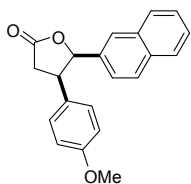
A dry 10 mL Schlenk tube equipped with stir bar was successively charged with enal **1** (0.375 mmol), chalcone **2** (0.25 mmol), catalyst **A** (8.6 mg, 0.0125 mmol), and NaOH (20 mg, 0.5 mmol). The flask was then evacuated and refilled with N<sub>2</sub> and D<sub>2</sub>O (0.5 mL) was added via a syringe. The resulting mixture was stirred vigorously at 40 °C for 48 h. The reaction mixture was cooled to room temperature and extracted using minimal amount of EtOAc, dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated under vacuum. The crude product was purified by flash column chromatography to afford the deuterated cyclopentene product **D-3a**.



**Deuterated compound (D-3a):** Colorless oil, *trans:cis* = 11:1, 73% combined yield of both isomers; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.59-7.53 (m, 2H), 7.40-7.14 (m, 13H), 6.27 (s, 0.1H), 4.13 (d, *J* = 7.2 Hz, 1H), 3.44 (t, *J* = 8.3 Hz, 1H), 3.33 (d, *J* = 9.2 Hz, 0.6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 145.7, 145.2, 142.3, 136.2, 128.7, 127.7, 127.6, 127.5, 126.6, 126.5, 126.0, 61.0, 57.0, 54.6, 54.5, 42.0, 41.8, 41.6; HRMS (ESI) calcd for C<sub>23</sub>H<sub>18</sub>D<sub>3</sub>[M+1]<sup>+</sup>: 300.1832, Found: 300.1828.

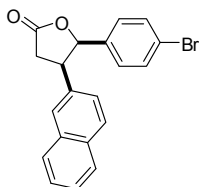
### General Procedure for reaction between enals and aldehydes (for Scheme 3):

A borosilicate glass test tube (16 X 150 mm) containing a stir bar was successively charged with enal **1** (0.1 mmol), aldehyde **4** (0.2 mmol), catalyst **A** (3.4 mg, 0.005 mmol) and K<sub>2</sub>CO<sub>3</sub> (28 mg, 0.2 mmol). The test tube was capped with a rubber septum, flushed with N<sub>2</sub>, and water (0.5 mL) was added via a syringe. The resulting milky emulsion was stirred vigorously at 40 °C for 24 h. The reaction mixture was cooled to room temperature and extracted using minimal amount of EtOAc, dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated under vacuum. The crude product was purified by flash column chromatography to afford the pure lactone products **5**.

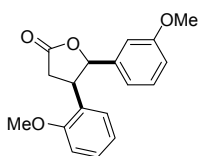


**cis-4-(4-methoxyphenyl)-5-(naphthalen-2-yl)dihydrofuran-2(3H)-one (5d):** White solid, *cis:trans*

= 4:1, 75% combined yield of both isomers;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74-7.71 (m, 1H), 7.56 (d,  $J = 8.8$  Hz, 2H), 7.46-7.43 (m, 2H), 6.82 (dd,  $J = 8.4, 1.6$  Hz, 1H), 6.75 (d,  $J = 8.4$  Hz, 2H), 6.57 (d,  $J = 6.8$  Hz, 2H), 5.94 (d,  $J = 7.2$  Hz, 1H), 4.13-4.08 (m, 1H), 3.65 (s, 3H), 3.07 (dd,  $J = 17.6, 8.2$  Hz, 1H), 2.94 (dd,  $J = 17.2, 6.8$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  177.0, 159.0, 133.4, 133.0, 129.2, 128.7, 128.2, 127.8, 126.4, 126.3, 125.0, 123.9, 114.0, 85.0, 55.3, 46.4, 35.4; HRMS (ESI) calcd for  $\text{C}_{21}\text{H}_{19}\text{O}_3[\text{M}+1]^+$ : 319.1334, Found: 319.1331.



**cis-5-(4-bromophenyl)-4-(naphthalen-2-yl)dihydrofuran-2(3H)-one (5e)**: White solid, *cis:trans* = 3:1, 57% yield of both isomers;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72-7.68 (m, 2H), 7.57 (d,  $J = 8.4$  Hz, 1H), 7.47-7.39 (m, 3H), 7.20 (d,  $J = 8.4$  Hz, 2H), 6.83-6.80 (m, 3H), 5.85 (d,  $J = 6.8$  Hz, 1H), 4.23-4.19 (m, 1H), 3.14 (dd,  $J = 17.5, 8.2$  Hz, 1H), 3.03 (dd,  $J = 17.5, 5.9$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  176.5, 134.8, 134.2, 133.2, 132.7, 131.4, 128.4, 127.9, 127.8, 127.6, 127.0, 126.6, 126.4, 125.9, 122.2; HRMS (ESI) calcd for  $\text{C}_{20}\text{H}_{16}\text{BrO}_2[\text{M}+1]^+$ : 369.0313, Found: 369.0310.



**cis-4-(2-methoxyphenyl)-5-(3-methoxyphenyl)dihydrofuran-2(3H)-one (5f)**: White solid, *cis:trans* = 4:1, 80% combined yield of both isomers;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.15-7.10 (m, 1H), 7.04-7.00 (m, 1H), 6.81-6.73 (m, 2H), 6.69-6.62 (m, 2H), 6.57 (d,  $J = 7.6$  Hz, 1H), 6.40 (s, 1H), 5.90 (d,  $J = 7.2$  Hz, 1H), 4.45-4.40 (m, 1H), 3.69 (s, 3H), 3.58 (s, 3H), 3.08-2.70 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  177.3, 159.2, 157.2, 137.8, 128.8, 128.1, 125.7, 120.6, 118.3, 114.0, 111.0, 110.3, 83.8, 55.3, 41.4, 33.5; HRMS (ESI) calcd for  $\text{C}_{18}\text{H}_{19}\text{O}_4[\text{M}+1]^+$ : 299.1283, Found: 299.1281.

#### General Procedure for reaction between enals and isatin derivatives (for Scheme 4):

A borosilicate glass test tube (16 X 150 mm) containing a stir bar was successively charged with enal **1** (0.2 mmol), isatin derivative **6a** (0.1 mmol), catalyst **A** (3.4 mg, 0.005 mmol),  $\text{K}_2\text{CO}_3$  (28 mg, 0.2 mmol) and water (0.5 mL). The test tube was capped with a rubber septum and the resulting milky emulsion was stirred vigorously at 40 °C for 24 h. The reaction mixture was cooled to room temperature and extracted using minimal amount of EtOAc, dried over  $\text{Na}_2\text{SO}_4$  and evaporated under vacuum. The crude product was purified by flash column chromatography to afford the pure product **7a**.

#### References

1. (a) V. Nair, S. Vellalath, M. Poonoth, E. Suresh, *J. Am. Chem. Soc.* **2006**, *128*, 8736-8737; (b) B. Cardinal-David, D. E. A. Raup, K. A. Scheidt, *J. Am. Chem. Soc.* **2010**, *132*, 5345-5347.
2. S. S. Sohn, E. L. Rosen, J. W. Bode, *J. Am. Chem. Soc.* **2004**, *126*, 14370-14371.
3. V. Nair, S. Vellalath, M. Poonoth, R. Mohan, E. Suresh, *Org. Lett.* **2006**, *8*, 507 – 509.

