Electronic Supplementary Information

Organocatalytic Amination of Alkyl Ethers via

\( n\)-Bu4NI/\( t\)-BuOOH-mediated Intermolecular Oxidative C(sp\(^3\))–N

Bond Formation: Novel Synthesis of Hemiaminal Ethers

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1. General Information

$^1$H NMR spectra were recorded on 600 MHz or 400 MHz spectrometers. The chemical shifts were reported in parts per million ($\delta$) relative to internal standard TMS (0 ppm) for CDCl$_3$. The peak patterns are indicated as follows: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, $J$, are reported in Hertz (Hz). $^{13}$C NMR spectra were obtained at 150 MHz or 100 MHz spectrometers and referenced to the internal solvent signals (central peak is 77.0 ppm in CDCl$_3$). CDCl$_3$ was used as the NMR solvent. High resolution mass spectrometry (HRMS) was obtained on a Q-TOF micro spectroMeter. Melting points were determined with a MicroMelting point apparatus without corrections. Organic solutions were concentrated by rotary evaporation below 40 °C in vacuum. TLC plates were visualized by exposure to ultraviolet light.

Reagents and solvents were purchased as reagent grade and were used without further purification unless otherwise stated. Flash column chromatography was performed over silica gel 200-300 m and the eluent was a mixture of ethyl acetate (EA) and petroleum ether (PE).
2. Experimental Section

2.1 Mechanistic Studies

Scheme 1. Investigation of the reaction mechanism. Reaction conditions: 1a (1 mmol), 2a (20 mmol), catalyst and oxidant, heated in a sealed tube at 75 °C.
2.1.1 General procedure for trapping experiment:

To a mixture of phthalimide 1a (0.5 mmol), 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 0.5 mmol) and n-Bu₄NI (0.2 mmol), tetrahydrofuran 2a (20 mmol) was added. Then anhydrous t-BuOOH (5 mmol) was dropped into the mixture. The reaction mixture was heated in a sealed tube at 75 °C and the process of the reaction was monitored by TLC. Upon completion, the reaction mixture was transferred to a round-bottom flask then the solvent was removed under vacuum without any workup and the residue was purified by silica gel chromatography (5% EA/PE) to afford the desired product 3aa and 4.

2-(Tetrahydrofuran-2-yl)isoindoline-1,3-dione (3aa)

3aa, 92% yield (based on 1a), white solid, mp. 73-75 °C. ¹H NMR (600 MHz, CDCl₃) δ 7.85 (dd, J = 5.4, 3.1 Hz, 2H), 7.72 (dd, J = 5.5, 3.0 Hz, 2H), 6.05 (dd, J = 8.0, 4.9 Hz, 1H), 4.21 (dd, J = 14.8, 7.7 Hz, 1H), 3.96 (td, J = 7.8, 4.7 Hz, 1H), 2.59-2.52 (m, 1H), 2.45-2.35 (m, 1H), 2.32-2.26 (m, 1H), 2.04-1.95 (m, 1H). ¹³C NMR (150 MHz, CDCl₃) δ 167.8, 134.1, 131.9, 123.3, 80.8, 69.7, 29.1, 26.0. HRMS (ESI) m/z calcd for C₁₂H₁₁NNaO₃ [M + Na⁺] 240.0631, found 240.0640.

2,2,6,6-Tetramethyl-1-(tetrahydrofuran-2-yl)oxy)piperidine (4)

4, 88% yield (based on TEMPO), yellow oil. ¹H NMR (600 MHz, CDCl₃) δ 5.42 – 5.30 (m, 1H), 3.87 (dd, J = 14.8, 7.1 Hz, 1H), 3.82 (td, J = 7.8, 5.1 Hz, 1H), 2.05 – 1.86 (m, 3H), 1.84 – 1.73 (m, 1H), 1.60 – 1.39 (m, 5H), 1.32 (d, J = 12.2 Hz, 1H), 1.22 (s, 3H), 1.11 (s, 3H), 1.07 (s, 3H), 1.04 (s, 3H).

2.1.2 Procedure of competition experiments between THF and [D₈]-THF:

To a mixture of phthalimide 1a (0.25 mmol) and n-Bu₄NI (0.05 mmol, 20 mol%), tetrahydrofuran 2a (2.5 mmol, 10 equiv.) and ds-tetrahydrofuran [D₈]-2a (2.5 mmol,
10 equiv.) was added followed by the dropwise addition of anhydrous $t$-BuOOH (1.25 mmol, 5 equiv.). Then the reaction mixture was stirred at 75 °C under air atmosphere in a sealed tube and the process of the reaction was monitored by TLC. Upon completion, the reaction mixture was transferred to a round-bottom flask then the solvent was removed under vacuum without any workup and the residue was purified by silica gel chromatography, using a mixture of PE/EA to afford the desired product 3aa and [D$_7$]-3aa in 76% yield. The ratio (3aa/[D$_7$]-3aa=15.7 : 1) was calculated from $^1$H NMR spectra.
## 2.2 A Full Description of the Reaction Optimization Conditions.\textsuperscript{a}

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\textsuperscript{a} Reaction conditions: 1\textit{a} (1 mmol), 2\textit{a} (20 mmol), catalyst and oxidant were heated in a sealed tube at 75 °C unless otherwise stated. \textit{t-BuOOH}: anhydrous \textit{tert}-butyl hydroperoxide, H₂O₂ 30% in water, DTBP: \textit{di-tert}-butyl peroxide 98%. \textsuperscript{b} Isolated yields. \textsuperscript{c} \textit{t-BuOOH}, 70% in H₂O. \textsuperscript{d} EtOAc (0.3 M) was used as the solvent. \textsuperscript{e} DCE was used as the solvent.
2.3 General Procedure

All the known amides 1b, 1c, 1d, 1g and 3i were prepared following literature procedure and the analytical data were in agreement with those that have been previously reported.

2.3.1 General procedure for the amination of alkyl ethers

To the mixture of ether 2 (10 mmol) and n-Bu₄NI (0.1 mmol, 36.9 mg) into a sealed tube, amine 1 (0.5 mmol) and t-BuOOH (2.5 mmol) were added. The reaction mixture was stirred at 75 °C under air atmosphere in a sealed tube and the process of the reaction was monitored by TLC. Upon completion, the reaction mixture was transferred to a round-bottom flask. Then the solvent was removed under vacuum and the residue was purified by silica gel chromatography, using a mixture of PE/EA to afford the desired product 3.

2.3.2 Data and references.

5-Methyl-2-(tetrahydrofuran-2-yl)isoindoline-1,3-dione (3ba)

Following the general procedure, 3ba was purified by silica gel chromatography (10% EA/PE). Yield: 80%. 3ba, white solid, mp. 74-76 °C. ¹H NMR (600 MHz, CDCl₃) δ 7.72 (d, J = 7.6 Hz, 1H), 7.64 (s, 1H), 7.51 (d, J = 7.6 Hz, 1H), 6.03 (dd, J = 8.0, 5.0 Hz, 1H), 4.20 (dd, J = 14.9, 7.7 Hz, 1H), 3.95 (td, J = 7.8, 4.7 Hz, 1H), 2.59-2.52 (m, 1H), 2.51 (s, 3H), 2.43-2.35 (m, 1H), 2.32-2.22 (m, 1H), 2.06-1.95 (m, 1H). ¹³C NMR (150 MHz, CDCl₃) δ 167.8, 167.7, 145.3, 134.6, 132.2, 129.2, 123.6, 123.0, 80.7, 69.5, 28.9, 25.9, 21.8. HRMS (ESI) m/z calcd for C₁₃H₁₃NNaO₃ [M+Na⁺] 254.0788, found 254.0790.

5-Chloro-2-(tetrahydrofuran-2-yl)isoindoline-1,3-dione (3ca)
Following the general procedure, **3ca** was purified by silica gel chromatography (10% EA/PE). Yield: 87%. **3ca**, white solid, mp. 90-93 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.82 (d, $J = 1.4$ Hz, 1H), 7.79 (d, $J = 7.9$ Hz, 1H), 7.69 (dd, $J = 8.0$, 1.7 Hz, 1H), 6.03 (dd, $J = 7.9$, 4.9 Hz, 1H), 4.20 (dd, $J = 14.8$, 7.7 Hz, 1H), 3.96 (td, $J = 7.8$, 4.7 Hz, 1H), 2.53 (tdd, $J = 13.0$, 7.9, 5.0 Hz, 1H), 2.39 (dt, $J = 10.1$, 6.1 Hz, 1H), 2.34-2.23 (m, 1H), 2.03 (ddd, $J = 11.8$, 8.3, 4.3 Hz, 1H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 166.8, 166.4, 140.7, 134.2, 133.5, 129.9, 124.6, 123.7, 81.0, 69.8, 29.0, 25.9. HRMS (ESI) m/z calcd for C$_{12}$H$_{10}$ClINaO$_3$ [M + Na$^+$] 274.0241, found 274.0243.

**5-Iodo-2-(tetrahydrofuran-2-yl)isoindoline-1,3-dione (3da)**

![3da](image)

Following the general procedure, **3da** was purified by silica gel chromatography (10% EA/PE). Yield: 58%. **3da**, white solid, mp. 100-103 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.19 (d, $J = 0.7$ Hz, 1H), 8.09 (dd, $J = 7.8$, 1.2 Hz, 1H), 7.57 (d, $J = 7.8$ Hz, 1H), 6.02 (dd, $J = 7.9$, 4.9 Hz, 1H), 4.19 (dd, $J = 14.8$, 7.7 Hz, 1H), 3.96 (td, $J = 7.8$, 4.7 Hz, 1H), 2.57-2.47 (m, 1H), 2.43-2.33 (m, 1H), 2.33-2.22 (m, 1H), 2.02 (ddd, $J = 11.9$, 8.3, 4.3 Hz, 1H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 167.2, 166.4, 143.1, 133.2, 132.4, 131.0, 124.6, 101.1, 81.0, 69.8, 29.1, 26.0. HRMS (ESI) m/z calcd for C$_{12}$H$_{10}$INaO$_3$ [M + Na$^+$] 365.9598, found 365.9601.

**5-Nitro-2-(tetrahydrofuran-2-yl)isoindoline-1,3-dione (3ea)**

![3ea](image)

Following the general procedure, **3ea** was purified by silica gel chromatography (10% EA/PE). Yield: 24%, 89% brsm. **3ea**, white solid, mp. 75-78 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.67 (s, 1H), 8.62 (d, $J = 8.1$ Hz, 1H), 8.06 (d, $J = 8.1$ Hz, 1H), 6.07 (dd, $J = 7.6$, 5.0 Hz, 1H), 4.26-4.15 (m, 1H), 3.98 (dd, $J = 7.5$, 5.0 Hz, 1H), 2.59-2.47 (m, 1H), 2.47-2.26 (m, 2H), 2.11-1.97 (m, 1H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 165.7, 165.4, 151.7, 136.2, 133.2, 129.4, 124.6, 118.8, 81.4, 70.0, 29.2, 25.9. HRMS (ESI) m/z calcd for C$_{12}$H$_{10}$N$_2$NaO$_3$ [M+Na$^+$] 285.0482, found 285.0485.

**1-(Tetrahydrofuran-2-yl)pyrrolidine-2,5-dione (3fa)**
Following the general procedure, 3fa was purified by silica gel chromatography (10% EA/PE). Yield: 90%. 3fa, colorless oil. $^1$H NMR (600 MHz, CDCl$_3$) δ 5.87 (dd, $J = 7.7$, 5.3 Hz, 1H), 4.16 (dd, $J = 15.0$, 7.4 Hz, 1H), 3.92 (td, $J = 7.6$, 4.8 Hz, 1H), 2.68 (s, 4H), 2.41 (dt, $J = 17.1$, 6.5 Hz, 1H), 2.35-2.26 (m, 1H), 2.24-2.14 (m, 1H), 2.03-1.91 (m, 1H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 176.8, 81.3, 70.0, 28.2, 28.0, 26.0. HRMS (ESI) m/z calcd for C$_8$H$_{11}$NNaO$_3$ [M + Na$^+$] 192.0631, found 192.0640.

$N$-benzoyl-$N$-(tetrahydrofuran-2-yl)benzamide (3ga)

Following the general procedure, 3ga was purified by silica gel chromatography (10% EA/PE). Yield: 59%. 3ga, white solid, mp. 92-94 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.47 (d, $J = 8.0$ Hz, 4H), 7.27 (d, $J = 8.7$ Hz, 2H), 7.18 (t, $J = 7.5$ Hz, 4H), 6.42-6.26 (m, 1H), 4.23 (q, $J = 7.2$ Hz, 1H), 3.91 (dd, $J = 12.9$, 7.5 Hz, 1H), 2.56 (dd, $J = 12.5$, 5.2 Hz, 1H), 2.43-2.19 (m, 2H), 2.13-1.85 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 173.9, 137.1, 131.9, 128.7, 128.3, 88.6, 69.6, 30.2, 25.6. HRMS (ESI) m/z calcd for C$_{18}$H$_{17}$NNaO$_3$ [M + Na$^+$] 318.1101, found 318.1007.

1-(Tetrahydrofuran-2-yl)-1H-benzo[d][1,2,3]triazole (3ha) and 2-(tetrahydrofuran-2-yl)-2H-benzo[d][1,2,3]triazole (3h'a)

Following the general procedure, 3ha and 3h'a was purified by silica gel chromatography (10% EA/PE). Yield: 3ha, 67% and 3h'a, 20%, 87% in total. 3ha, colorless oil.$^1$H NMR (600 MHz, CDCl$_3$) δ 8.07 (d, $J = 8.3$ Hz, 1H), 7.72 (d, $J = 8.3$ Hz, 1H), 7.51 (t, $J = 7.6$ Hz, 1H), 7.39 (t, $J = 7.6$ Hz, 1H), 6.52 (dd, $J = 6.8$, 1.8 Hz, 1H), 4.11 (dd, $J = 14.8$, 7.7 Hz, 1H), 4.04 (dd, $J = 14.5$, 8.1 Hz, 1H), 3.25-3.13 (m, 1H), 2.53 (dt, $J = 15.5$, 8.7 Hz, 1H), 2.46-2.34 (m, 1H), 2.19 (dd, $J = 9.3$, 4.7 Hz, 1H). 3h'a, white solid, mp. 47-50 °C. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.88 (dd, $J = 6.5$, 3.1 Hz, 2H), 7.39 (dd, $J = 6.6$, 3.1 Hz, 2H), 6.60 (dd, $J = 6.5$, 2.0 Hz, 1H), 4.34 (dd, $J =$
13.9, 7.8 Hz, 1H), 4.15 (dd, J = 14.5, 7.4 Hz, 1H), 2.76 (ddd, J = 8.0, 6.6, 2.5 Hz, 1H), 2.61-2.44 (m, 2H), 2.25-2.08 (m, 1H).

4-Methyl-N-(tetrahydrofuran-2-yl)-N-p-tolylbenzenesulfonamide (3ia)

Following the general procedure, 3ia was purified by silica gel chromatography (10% EA/PE). Yield: 42%, 61% brsm. 3ia, white solid, mp. 98-100 °C. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.64 (d, J = 7.6 Hz, 2H), 7.23 (d, J = 7.6 Hz, 2H), 7.07 (d, J = 7.6 Hz, 2H), 6.97 (d, J = 7.4 Hz, 2H), 6.25 (t, J = 5.7 Hz, 1H), 3.62 (dd, J = 16.5, 7.6 Hz, 2H), 2.42 (s, 3H), 2.33 (s, 3H), 2.18-2.06 (m, 1H), 1.74-1.60 (m, 2H), 1.22 (dt, J = 12.9, 6.5 Hz, 1H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 143.0, 138.7, 136.9, 132.5, 131.8, 129.3, 129.0, 128.1, 89.3, 68.3, 30.2, 24.6, 21.5, 21.1. HRMS (ESI) m/z calcd for C$_{18}$H$_{21}$NNaO$_3$S [M + Na$^+$] 354.1134, found 354.1140.

2-((Tetrahydro-2H-pyran-2-yl)isoindoline-1,3-dione (3ab)

Following the general procedure, 3ab was purified by silica gel chromatography (10% EA/PE). Yield: 54%, white solid, mp. 115-118 °C. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.87 (dd, J = 5.4, 3.1 Hz, 2H), 7.70 (dd, J = 5.4, 3.1 Hz, 2H), 5.33 (dd, J = 11.4, 2.2 Hz, 1H), 4.17-4.05 (m, 1H), 3.66 (td, J = 12.1, 2.2 Hz, 1H), 2.76 (dd, J = 11.6, 4.1 Hz, 1H), 2.04 (dd, J = 13.3, 2.3 Hz, 1H), 1.80-1.51 (m, 4H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 167.4, 134.2, 131.8, 123.5, 79.3, 69.0, 27.9, 24.9, 23.6. HRMS (ESI) calcd for C$_{13}$H$_{13}$NNaO$_3$ [M + Na$^+$] 254.0788, found 254.0782.

2-((1,3-Dioxolan-2-yl)isoindoline-1,3-dione (3ac)

Following the general procedure, 3ac was purified by silica gel chromatography (10% EA/PE). Yield: 65%, white solid, mp. 95-98 °C. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.87 (dd, J = 5.4, 3.1 Hz, 2H), 7.75 (dd, J = 5.5, 3.0 Hz,
2H), 6.79 (s, 1H), 4.46 (t, J = 6.6 Hz, 2H), 4.10 (t, J = 6.0 Hz, 2H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 166.8, 134.3, 131.7, 123.5, 100.5, 66.5. HRMS (ESI) calcd for C\(_{11}\)H\(_9\)NNaO\(_4\) [M + Na\(^+\)] 242.0424, found 242.0431.

2-(1-Ethoxyethyl)isoindoline-1,3-dione (3ad)

\[\text{Following the general procedure, 3ad was purified by silica gel chromatography (10\% EA/PE). Yield: 90\%, white solid, mp. 63-65 ^\circ\text{C}.} \]

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.88 (dd, \(J = 5.4, 3.0\) Hz, 2H), 7.75 (dd, \(J = 5.4, 3.0\) Hz, 2H), 5.59 (q, \(J = 6.3\) Hz, 1H), 3.59-3.45 (m, 2H), 1.79 (d, \(J = 6.3\) Hz, 3H), 1.20 (t, \(J = 7.0\) Hz, 3H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 167.8, 134.1, 131.9, 123.3, 80.8, 69.7, 29.1, 26.0. HRMS (ESI) m/z calcd for C\(_{12}\)H\(_{13}\)NNaO\(_3\) [M + Na\(^+\)] 298.1415, found 298.1415.

2-(1-Butoxybutyl)isoindoline-1,3-dione (3ae)

\[\text{Following the general procedure, 3ae was purified by silica gel chromatography (10\% EA/PE). Yield: 72\%, colorless oil.} \]

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.88 (dd, \(J = 5.4, 3.0\) Hz, 2H), 7.76 (dd, \(J = 5.4, 3.0\) Hz, 2H), 5.38 (t, \(J = 7.1\) Hz, 1H), 3.52-3.39 (m, 2H), 2.32-2.21 (m, 1H), 2.15-2.04 (m, 1H), 1.55 (td, \(J = 13.4, 6.8\) Hz, 2H), 1.50-1.40 (m, 1H), 1.39-1.28 (m, 3H), 0.95 (t, \(J = 7.4\) Hz, 3H), 0.87 (t, \(J = 7.4\) Hz, 3H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 168.2, 134.2, 131.7, 123.5, 82.0, 68.9, 34.6, 31.4, 19.3, 18.9, 13.8, 13.6. HRMS (ESI) m/z calcd for C\(_{16}\)H\(_{21}\)NNaO\(_3\) [M + Na\(^+\)] 298.1414, found 298.1415.

2-(1-(Isopentyloxy)-3-methylbutyl)isoindoline-1,3-dione (3af)

\[\text{Following the general procedure, 3af was purified by silica gel chromatography (10\% EA/PE). Yield: 72\%, colorless oil.} \]

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.88 (dd, \(J = 5.4,
3.0 Hz, 2H), 7.75 (dt, J = 5.4, 2.7 Hz, 2H), 5.55 – 5.35 (m, 1H), 3.50 – 3.44 (m, 1H), 2.22 – 2.13 (m, 1H), 2.05 – 1.93 (m, 1H), 1.70 – 1.60 (m, 2H), 1.45 (dt, J = 14.1, 6.9 Hz, 2H), 0.98-0.92 (m, 6H), 0.88 – 0.79 (m, 7H). 13C NMR (150 MHz, CDCl3) δ 167.0, 134.1, 131.5, 123.3, 80.6, 67.1, 41.0, 37.9, 24.7, 24.6, 22.3, 22.2. HRMS (ESI) m/z calcd for C18H25NNaO3 [M + Na+] 326.1727, found 326.1735.

5-Methyltetrahydrofuran-2-yl)isoindoline-1,3-dione (3ag) and 2-(5-methyltetrahydrofuran-2-yl)isoindoline-1,3-dione (3ag')

Following the general procedure, 3ag and 3ag' was purified by silica gel chromatography (10% EA/PE). Yield: 63%. 3ag, white solid, mp. 103-105 °C, a mixture of two diastereomers (dr=1.6:1). Major: 1H NMR (600 MHz, CDCl3) δ 7.90-7.81 (dd, J = 5.3, 3.0 Hz, 2H), 7.73 (dd, J = 5.3, 3.0 Hz, 2H), 6.11 (dd, J = 7.8, 6.0 Hz 0.6H), 5.99 (dd, J = 8.6, 3.5 Hz, 0.4H), 4.62-4.50 (m, 0.6H), 4.13-4.10 (m, 0.4H), 2.71-2.60 (m, 0.6H), 2.58-2.49 (m, 0.4H), 2.45-2.27 (m, 1.6H), 2.21-2.14 (m, 0.4H), 2.10-2.02 (m, 1H), 1.64-1.57 (m, 0.6H), 1.37 (d, J = 6.0 Hz, 1.1H), 1.28 (d, J = 6.1 Hz, 1.9H). 13C NMR (150 MHz, CDCl3) δ 167.8, 167.3, 134.0, 131.7, 131.7, 123.1, 123.1, 80.4, 80.0, 77.1, 33.8, 32.3, 29.7, 29.3, 20.6, 20.1. HRMS (ESI) calcd for C13H13NNaO3 [M + Na+] 254.0788, found 254.0783. 3ag', white solid, mp. 84-85 °C 1H NMR (600 MHz, CDCl3) δ 7.82 (dd, J = 5.4, 3.0 Hz, 2H), 7.70 (dd, J = 5.4, 3.0 Hz, 2H), 4.13-3.97 (m, 2H), 3.31-3.15 (m, 1H), 2.11-1.91 (m, 3H), 1.86 (s, 3H). 13C NMR (150 MHz, CDCl3) δ 168.3, 133.8, 132.0, 122.9, 97.0, 68.8, 37.2, 25.7, 24.6. HRMS (ESI) calcd for C13H13NNaO3 [M + Na+] 254.0788, found 254.0786.

2-(1,2-Dimethoxyethyl)isoindoline-1,3-dione (3ah) and 2-((2-methoxyethoxy)methyl)isoindoline-1,3-dione (3ah')

Following the general procedure, 3ah and 3ah' was purified by silica gel chromatography (10% EA/PE). Yield: 3ah, 48% and 3ah', 32%, 80% in total. 3ah, colorless oil. 1H NMR (600 MHz, CDCl3) δ 7.90 (dd, J = 5.4, 3.0 Hz, 2H), 7.77 (dd, J = 5.4, 3.0 Hz, 2H), 5.48 (t, J = 6.5 Hz, 1H), 4.01 (dd, J = 12.4, 6.5 Hz, 2H), 3.42 (s,
3H), 3.39 (s, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 168.0, 134.3, 131.6, 123.6, 81.2, 70.9, 59.2, 56.9. HRMS (ESI) m/z calcd for C$_{12}$H$_{13}$NNaO$_4$ [M + Na$^+$] 258.0737, found 258.0744. 3ah', white solid, mp. 78-80 °C. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.91 (dd, $J = 5.4$, 2.9 Hz, 2H), 7.77 (dd, $J = 5.4$, 2.9 Hz, 2H), 5.19 (s, 2H), 3.83-3.72 (m, 2H), 3.58-3.48 (m, 2H), 3.31 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ 167.9, 134.3, 131.9, 123.6, 71.6, 69.4, 67.7, 59.0. HRMS (ESI) m/z calcd for C$_{12}$H$_{13}$NNaO$_4$ [M + Na$^+$] 258.0737, found 258.0742.

2-(Tert-butoxymethyl)isoindoline-1,3-dione (3ai)$^8$ and 2-(hydroxymethyl)isoindoline-1,3-dione (3ai')$^9$

Following the general procedure, 3ai and 3ai' was purified by silica gel chromatography (10% EA/PE). Yield: 65% in total. 3ai, white solid, mp. 80-83 °C. $^1$H NMR (600 MHz, CDCl$_3$) $^1$H NMR (600 MHz, CDCl$_3$) δ 7.89 (dd, $J = 5.4$, 3.0 Hz, 2H), 7.74 (dd, $J = 5.4$, 3.0 Hz, 2H), 5.12 (s, 2H), 1.31 (s, 9H). 3ai', white solid, mp. 140-145 °C. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.90 (dd, $J = 5.4$, 3.1 Hz, 2H), 7.80 (dd, $J = 5.4$, 3.1 Hz, 2H), 5.27 (s, 2H).

3. Reference

4. $^1$H NMR and $^{13}$C NMR Spectra of the Products
3ea
The ratio of $3\text{aa}$/$[\text{D}_2]$-$3\text{aa}$ = 15.7 : 1