Supporting Information

**A Novel Pyrrolidine Imide Catalyzed Direct Formation of
 α , β -Unsaturated Ketones from Simple Ketones and Aldehydes**

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General Information: Commercial reagents were used as received, unless otherwise stated. Merck 60 silica gel was used for chromatography, and Whatman silica gel plates with fluorescence F₂₅₄ were used for thin-layer chromatography (TLC) analysis. ¹H and ¹³C NMR spectra were recorded on Broker Advance 500, and tetramethylsilane (TMS) was used as a reference. Data for ¹H are reported as follows: chemical shift (ppm), and multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). Data for ¹³C NMR are reported as ppm.

Preparation of Catalysis I

(S)-tert-Butyl 2-((2,2,2-trifluoroacetyl)carbamoyl)pyrrolidine-1-carboxylate. To a solution of (S)-tert-butyl 2-carbamoylpyrrolidine-1-carboxylate (1165 mg, 5.44 mmol) and sodium carbonate (577 mg, 5.44 mmol) in 21 mL of dichloromethane at 0 °C was added dropwise trifluoroacetic anhydride (1.55 mL, 11.1 mmol) for 30 min. The resulting mixture was stirred at room temperature for 45 min. The precipitate was filtered off. The resulting residue was then purified by silica gel chromatography (EtOAc / Hexane = 1/7) and fractions were collected and concentrated *in vacuo* to provide product as a clear oil in 68% yield (1.15g, 3.70 mmol).

(S)-N-((2,2,2-Trifluoroacetyl)amino)pyrrolidine-2-carboxamide (I). A solution of trifluoroacetic acid (14 mL) in 48 mL of dichloromethane was added dropwise in 45 min into a stirring mixture of (S)-tert-butyl 2-((2,2,2-trifluoroacetyl)carbamoyl)pyrrolidine-1-carboxylate (1.15g, 3.70 mmol) and 28 mL of dichloromethane at room temperature. The solution was stirred for 2 h at room temperature, and the volatiles were removed under reduced pressure. The remaining viscous product was treated with ethyl ether (3 × 20 mL) to provide a white solid in 57% yield. (441 mg, 2.10 mmol). ¹H NMR (500 MHz, CD₃OD): δ 4.57 (t, 1H, *J* = 7.5 Hz), 3.36-3.24 (m, 2H), 2.39-2.33 (m, 1H), 2.21-2.14 (m, 1H), 2.12-1.97 (m, 2H). ¹³C NMR (125 MHz, CD₃OD): δ 163.5, 163.3, 163.0, 162.7, 121.6, 119.3, 116.9, 116.5, 114.6, 47.9, 47.0, 31.2, 24.5.

General Procedure for Synthesis of α, β-Unsaturated Cyclopentanones: A mixture of aldehyde (0.15 mmol), ketone (0.30 mmol) and catalyst **I** (0.03 mmol) in 0.5 mL of anhydrous DMSO was vigorously stirred for 6-132 hr. The endpoint of the reaction was monitored by TLC. The resulting mixture was then directly purified by silica gel

chromatography and fractions were collected and concentrated *in vacuo* to provide a solid or clear oil.

(E)-2-Benzylidenecyclopentanone (Table 1, entry 1)¹: The title compound was prepared according to the general procedure in 84% yield. ¹H NMR (500 MHz, CDCl₃): δ 7.53 (d, 2H, *J* = 7.45 Hz), 7.43-7.34 (m, 4H), 2.98 (dt, 2H, *J* = 7.2, 2.65 Hz), 2.40 (t, 2H, *J* = 7.9 Hz), 2.07-2.00 (m, 2H). ¹³C NMR (125 MHz, CDCl₃): δ 207.8, 136.1, 135.6, 132.3, 130.5, 129.3, 128.7, 37.7, 29.3, 20.2.

(E)-2-(4-Methoxybenzylidene)cyclopentanone (Table 1, entry 2)¹: The title compound was prepared according to the general procedures in 94% yield. ¹H NMR (500 MHz, CDCl₃): δ 7.49 (d, 2H, *J* = 8.7 Hz), 7.35 (t, 1H, *J* = 2.6 Hz), 6.94 (d, 2H, *J* = 8.8 Hz), 3.84 (s, 3H), 2.95 (dt, 2H, *J* = 7.3 Hz, 2.6 Hz), 2.38 (t, 2H, *J* = 7.9 Hz), 2.06-1.99 (m, 2H). ¹³C NMR (125 MHz, CDCl₃): δ 207.8, 160.6, 133.7, 132.2, 132.1, 128.3, 114.2, 55.3, 37.7, 29.2, 20.1.

(E)-2-(4-Nitrobenzylidene)cyclopentanone (Table 1, entry 3)¹: The title compound was prepared according to the general procedure in 93% yield. ¹H NMR (500 MHz, CDCl₃): δ 8.27 (d, 2H, *J* = 8.7 Hz), 7.67 (d, 2H, *J* = 8.7 Hz), 7.39 (t, 1H, *J* = 2.6 Hz), 3.01 (dt, 2H, *J* = 7.2, 2.7 Hz), 2.46 (t, 2H, *J* = 7.9 Hz), 2.13-2.06 (m, 2H). ¹³C NMR (125 MHz, CDCl₃): δ 207.3, 147.5, 141.9, 139.8, 130.8, 129.3, 123.9, 37.7, 29.4, 20.0.

(E)-2-(4-Bromobenzylidene)cyclopentanone (Table 1, entry 4)²: The title compound was prepared according to the general procedure in 88% yield. ¹H NMR (500 MHz,

CDCl₃): δ 7.54 (d, 2H, J = 8.3 Hz), 7.38 (d, 2H, J = 8.3 Hz), 7.30 (t, 1H, J = 2.4 Hz), 2.93 (dt, 2H, J = 7.2, 2.4 Hz), 2.40 (t, 2H, J = 7.9 Hz), 2.08-2.01 (m, 2H). ¹³C NMR (125 MHz, CDCl₃): δ 207.5, 136.7, 134.5, 131.9, 131.8, 130.9, 123.6, 37.7, 29.3, 20.1.

(E)-2-(1-Naphthylidene)cyclopentanone (Table 1, entry 5)²: The title compound was prepared according to the general procedure in 85% yield. ¹H NMR (500 MHz, CDCl₃): δ 8.14-8.12 (m, 2H), 7.88-7.84 (m, 2H), 7.60-7.47 (m, 4H), 2.90 (dt, 2H, J = 7.1 Hz, 2.6Hz), 2.46 (t, 2H, J = 7.8Hz), 2.03-1.96 (m, 2H). ¹³C NMR (125 MHz, CDCl₃): δ 207.4, 138.4, 133.6, 132.4, 132.3, 129.6, 128.9, 128.7, 126.9, 126.6, 126.2, 125.1, 124.0, 38.2, 29.6, 20.5.

(E)-2-(Cyclohexylmethylidene)cyclopentanone (Table 1, entry 6)³: The title compound was prepared according to the general procedure in 82% yield. ¹H NMR (500 MHz, CDCl₃): δ 6.39 (d, 1H, J = 9.6 Hz), 2.61 (dt, 2H, J = 7.2 Hz, 2.0Hz), 2.32 (t, 2H, J = 7.7 Hz), 2.16 (m, 1H), 1.93 (m, 2H), 1.76-1.64 (m, 5H), 1.34-1.14 (m, 5H). ¹³C NMR (125 MHz, CDCl₃): δ 207.8, 140.9, 135.2, 38.8, 38.5, 31.6, 26.6, 25.8, 25.5, 19.8.

(E)-2-(Cyclopentylmethylidene)cyclopentanone (Table 1, entry 7)⁴: The title compound was prepared according to the general procedure in 61% yield. ¹H NMR (500 MHz, CDCl₃): δ 6.48 (dt, 1H, J = 9.7 Hz, 2.5Hz), 2.64-2.55 (m, 3H), 2.31 (t, 2H, J = 7.9Hz), 1.96-1.89 (m, 2H), 1.87-1.33 (m, 8H). ¹³C NMR (125 MHz, CDCl₃): δ 207.2, 141.0, 135.5, 40.3, 38.4, 32.7, 26.6, 25.4, 19.7.

(E)-2-(2-Methylpentylidene)cyclopentanone (Table 1, entry 8): The title compound was prepared according to the general procedure in 69% yield. ¹H NMR (500 MHz,

CDCl₃): δ 6.34 (dt, 1H, J = 10.2 Hz, 2.5 Hz), 2.62-2.57 (m, 2H), 2.33 (t, 2H, J = 7.9 Hz), 1.97-1.90 (m, 2H), 1.40-1.20 (m, 5H), 1.01 (d, 3H, J = 6.7 Hz), 0.87 (t, 3H, J = 7.2 Hz). ¹³C NMR (125 MHz, CDCl₃): δ 207.6, 141.9, 135.7, 38.9, 38.6, 34.3, 26.8, 20.6, 19.9, 19.8, 14.1.

(E)-2-(3-Methylbutylidene)cyclopentanone (Table 1, entry 9)⁵: The title compound was prepared according to the general procedure in 71% yield. ¹H NMR (500 MHz, CDCl₃): δ 6.60-6.55 (m, 1H), 2.58 (dt, 2H, J = 7.2, 1.2 Hz), 2.33 (t, 2H, J = 7.9 Hz), 2.06-2.02 (m, 2H), 1.96-1.89 (m, 2H), 1.83-1.74 (m, 1H), 0.93 (d, 6H, J = 6.7 Hz). ¹³C NMR (125 MHz, CDCl₃): δ 206.9, 137.9, 135.1, 38.8, 38.6, 28.3, 26.9, 22.5, 19.8.

(E)-2-Hexylidenecyclopentanone (Table 1, entry 10)⁵: The title compound was prepared according to the general procedure in 79% yield. ¹H NMR (500 MHz, CDCl₃): δ 6.57-6.53 (m, 1H), 2.58 (dt, 2H, J = 6.3, 1.4 Hz), 2.33 (t, 2H, J = 7.9 Hz), 2.17-2.11 (m, 2H), 1.97-1.90 (m, 2H), 1.50-1.43 (m, 2H), 1.34-1.29 (m, 4H), 0.89 (t, 3H, J = 6.9 Hz). ¹³C NMR (125 MHz, CDCl₃): δ 207.2, 137.1, 136.4, 38.6, 31.5, 29.6, 28.0, 26.7, 22.4, 19.8, 13.9.

(E)-2-heptylidenecyclopentanone (Table 1, entry 11)⁵: The title compound was prepared according to the general procedure in 64% yield. ¹H NMR (500 MHz, CDCl₃): δ 6.58-6.53 (m, 1H), 2.58 (dt, 2H, J = 6.0, 1.1 Hz), 2.33 (t, 2H, J = 7.9 Hz), 2.14 (q, 2H, J = 7.4 Hz), 1.97-1.90 (m, 2H), 1.49-1.42 (m, 2H), 1.35-1.25 (m, 6H), 0.88 (t, 3H, J = 6.9 Hz). ¹³C NMR (125 MHz, CDCl₃): δ 207.3, 137.2, 136.4, 38.6, 31.6, 29.7, 29.0, 28.3, 26.7, 22.6, 19.8, 14.0.

(E)-2-Octylidenecyclopentanone (Table 1, entry 12)⁵: The title compound was prepared according to the general procedure in 55% yield. ¹H NMR (500 MHz, CDCl₃): δ 6.57-6.53 (m, 1H), 2.58 (dt, 2H, J = 6.0, 1.1 Hz), 2.33 (t, 2H, J = 7.9 Hz), 2.14 (q, 2H, J = 7.4 Hz), 1.97-1.90 (m, 2H), 1.47-1.42 (m, 2H), 1.35-1.25 (m, 8H), 0.88 (t, 3H, J = 6.8 Hz).

^{13}C NMR (125 MHz, CDCl_3): δ 207.2, 137.2, 136.4, 38.6, 31.7, 29.6, 29.3, 29.1, 28.4, 26.7, 22.6, 19.8, 14.0.

(E)-2-((Benzyloxy)methylene)cyclopentanone (Table 1, entry 13): The title compound was prepared according to the general procedure in 66% yield. ^1H NMR (500 MHz, CDCl_3): δ 7.38-7.28 (m, 5H), 6.66-6.63 (m, 1H), 4.54 (s, 2H), 4.18 (d, 2H, J = 5.9 Hz), 2.60 (dt, 2H, J = 7.2, 2.0 Hz), 2.33 (t, 2H, J = 7.9 Hz), 1.98-1.91 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 206.9, 138.2, 137.8, 131.1, 128.4, 127.8, 127.7, 72.8, 67.5, 38.1, 27.0, 19.8.

General Procedure for Synthesis of α , β -Unsaturated Acetones: A mixture of aldehyde (0.15 mmol) and catalyst **I** (0.03 mmol) in 0.5 mL of anhydrous acetone was vigorously stirred for 10 or 46 hr. The endpoint of the reaction was monitored by TLC. The resulting mixture was then purified by silica gel chromatography and fractions were collected and concentrated *in vacuo* to provide a solid or clear oil.

(E)-4-(4-Nitrophenyl)-3-buten-2-one (Table 2, entry 2)⁷: The title compound was prepared according to the general procedure in 95% yield. ^1H NMR (500 MHz, CDCl_3): δ 8.26 (d, 2H, J = 8.6 Hz), 7.71 (d, 2H, J = 8.6 Hz), 7.55 (d, 1H, J = 16.3 Hz), 6.83 (d, 1H, J = 16.3 Hz), 2.43 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 197.5, 148.5, 140.6, 140.0, 130.3, 128.8, 124.1, 28.0.

(E)-4-(4-Chlorophenyl)-3-buten-2-one (Table 2, entry 3)⁷: The title compound was prepared according to the general procedure in 89% yield. ^1H NMR (500 MHz, CDCl_3): δ 7.49-7.44 (m, 3H), 7.38 (d, 2H, J = 8.5 Hz), 6.69 (d, 1H, J = 16.3 Hz), 2.38 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 198.0, 141.8, 136.4, 132.9, 129.4, 129.3, 127.5, 27.7.

(E)-5-Methyloct-3-en-2-one (Table 2, entry 4): The title compound was prepared according to the general procedure in 41% yield. ^1H NMR (500 MHz, CDCl_3): δ 6.68 (dd, 1H, $J = 16.0, 7.9$ Hz), 6.03 (d, 1H, $J = 16.0$ Hz), 2.33 (m, 1H), 2.25 (s, 3H), 1.48-1.23 (m, 4H), 1.06 (d, 3H, $J = 6.7$ Hz), 0.90 (t, 3H, $J = 7.1$ Hz). ^{13}C NMR (125 MHz, CDCl_3): δ 198.9, 153.8, 129.5, 38.3, 36.5, 26.9, 20.3, 19.4, 14.0.

(E)-4-Cyclohexylbut-3-en-2-one (Table 2, entry 5)⁷: The title compound was prepared according to the general procedure in 60% yield. ^1H NMR (500 MHz, CDCl_3): δ 6.73 (dd, 1H, $J = 16.1, 6.8$ Hz), 6.02 (dd, 1H, $J = 16.1, 1.2$ Hz), 2.24 (s, 3H), 2.18-2.11 (m, 1H), 1.79-1.75 (m, 4H), 1.36-1.07 (m, 6H). ^{13}C NMR (125 MHz, CDCl_3): δ 199.1, 153.4, 128.8, 40.6, 31.8, 26.8, 25.9, 25.7.

(E)-Non-3-en-2-one (Table 2, entry 6)⁸: The title compound was prepared according to the general procedure in 67% yield. ^1H NMR (500 MHz, CDCl_3): δ 6.84-6.77 (m, 1H), 6.07 (d, 1H, $J = 15.5$ Hz), 2.25-2.20 (m, 5H), 1.51-1.44 (m, 2H), 1.35-1.29 (m, 4H), 0.90 (t, 3H, $J = 7.0$ Hz). ^{13}C NMR (125 MHz, CDCl_3): δ 198.7, 148.6, 131.3, 32.4, 31.3, 27.8, 26.8, 22.4, 13.9.

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These compounds are known and have been reported in the following papers.

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^1H NMR (500 MHz, CD_3OD)

^1H NMR (500 MHz, CDCl_3)

^1H NMR (500 MHz, CDCl_3)

^1H NMR (500 MHz, CDCl_3)

¹H NMR (500 MHz, CDCl₃)

^1H NMR (500 MHz, CDCl_3)

^1H NMR (500 MHz, CDCl_3)