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# Heteroatom-Guided Torquoselective Olefination of $\alpha$ -Oxy and $\alpha$ -Amino Ketones via Ynolates

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## EXPERIMENTAL

**Materials.** Tetrahydrofuran was freshly distilled from sodium benzophenone ketyl. *tert*-Butyllithium was titrated with diphenylacetic acid.

**General Procedures.** <sup>1</sup>H-NMR spectra were measured in CDCl<sub>3</sub> solution and referenced to TMS (0.00 ppm) using AL400 (400 MHz) spectrometers, unless otherwise noted. <sup>13</sup>C-NMR spectra were measured in CDCl<sub>3</sub> solution and referenced to CDCl<sub>3</sub> (77.0 ppm) using AL400 spectrometers (100 MHz). IR spectra were recorded on JASCO FT/IR-410 spectrometer. Mass spectra were obtained on a JEOL GX303 and GCMS (JMS-AM SUN 200). Column chromatography was performed on silica gel (Kanto Chemical Co.). Thin-layer chromatography was performed on precoated plates (0.25 mm, silica gel Merck Kieselgel 60 F<sub>245</sub>). All reactions were performed in oven-dried glassware under positive pressure of argon, unless otherwise noted. Reaction mixtures were stirred magnetically. Solutions of alkyllithium reagents were transferred by syringe or cannula and were introduced into reaction vessels through rubber septa. The stereochemistry was determined by nOe experiments, otherwise noted.

The known  $\alpha$ -oxyketones (**6a**,<sup>[1]</sup> **6b**,<sup>[2]</sup> **6d**,<sup>[1]</sup> **6e**,<sup>[1]</sup> **6f**,<sup>[1]</sup> **6h**,<sup>[4]</sup> **8a**,<sup>[3]</sup> **8b**,<sup>[4]</sup> **8c**,<sup>[5]</sup> **8d**,<sup>[6]</sup> **8f**,<sup>[7]</sup> **8g**,<sup>[8]</sup> **8i**,<sup>[9]</sup> **8j**,<sup>[10]</sup> and **8k**,<sup>[11]</sup>) were prepared according to the literatures.

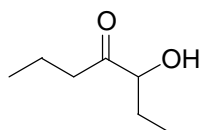
### Preparation of $\alpha$ -oxyketones (Table 1 and Table 2)

**2-(methoxyphenylmethoxy)-1-phenylpropan-1-one (6c).** To a solution of the 2-hydroxy-1-phenylpropan-1-one<sup>[12]</sup> (450 mg, 3.0 mmol) and 4-methoxyphenylmethyl-2,2,2-trichloroacetimidate (848 mg, 3.0 mmol) in cyclohexane-CH<sub>2</sub>Cl<sub>2</sub> (27 mL) was added a solution of triflic acid in cyclohexane-CH<sub>2</sub>Cl<sub>2</sub> until the solution was turned turbid at 0 °C. After being stirred at room temperature for 1 h, the reaction mixture was filtered, and water was added. The water phase was extracted with hexane. Organic layer was washed with a saturated NaHCO<sub>3</sub> solution, dried over MgSO<sub>4</sub>, filtered and concentrated to give a residue, which was purified by column chromatography (silica gel, hexane/AcOEt = 80/20), followed by distillation (Kügelrohr, 240 °C at 2.2 mmHg) to afford the methoxyphenylmethyl ether (**6c**, 481 mg, 59%) as a pale yellow oil: <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 1.51 (d, *J* = 6.8 Hz, 3H), 3.80 (s, 3H), 4.38 (d, *J* = 11.2 Hz, 1H), 4.57 (d, *J* = 11.2 Hz, 1H), 4.76 (q, *J* = 6.8 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.58 (tt, *J* = 1.2 Hz, 8.0 Hz, 1H), 8.04 (dd, *J* = 1.2 Hz, 8.0 Hz, 2H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 18.8, 55.2, 71.2, 77.8, 113.7, 128.4, 128.7, 129.2, 129.5,

133.2, 134.8, 159.2, 200.7; IR (Neat): 1694  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  270 ( $\text{M}^+$ ); HRMS (EI) calcd for  $\text{C}_{17}\text{H}_{18}\text{O}_3$ : 270.1256, found: 270.1236.

**2-Phenoxy-1-phenylpropan-1-one (6g).** To a suspension of sodium hydride (344 mg, 9.0 mmol, 62.7% in oil) in THF (15 mL) was added a solution of phenol (565 mg, 6.0 mmol) in THF (5 mL) at 0 °C. After 30 min, to the resulting mixture was added dropwise a solution of 2-bromo-1-phenylpropan-1-one<sup>[13]</sup> (1.07 g, 5.0 mmol) in THF (5 mL) at 0 °C. After being stirred at room temperature for 7.5 h, the reaction mixture was quenched with a saturated  $\text{NH}_4\text{Cl}$  solution and extracted with  $\text{Et}_2\text{O}$ . The organic phase was washed with water, a saturated  $\text{NaHCO}_3$  solution, brine, dried over  $\text{MgSO}_4$ , filtered and concentrated to give a residue, which was purified by column chromatography (silica gel, hexane/AcOEt = 80/20) to afford the compound **6g** (239 mg, 21%) as a colorless solid:  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.71 (d,  $J = 6.8$  Hz, 3H), 5.48 (q,  $J = 6.8$  Hz, 1H), 6.87 (dd,  $J = 0.8$  Hz, 8.8 Hz, 2H), 6.92 (tt,  $J = 1.2$  Hz, 7.2 Hz, 1H), 7.20-7.25 (m, 2H), 7.46 (tt,  $J = 1.6$  Hz, 8.0 Hz, 2H), 7.58 (tt,  $J = 1.6$  Hz, 7.2 Hz, 1H), 8.08 (dd,  $J = 1.6$  Hz, 8.4 Hz, 2H);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 18.8, 76.6, 115.1, 121.4, 128.7, 128.8, 129.5, 133.6, 134.1, 157.3, 198.8; IR ( $\text{CHCl}_3$ ): 1698  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  226 ( $\text{M}^+$ ), 121 (100%); HRMS (EI) calcd for  $\text{C}_{15}\text{H}_{14}\text{O}_2$ : 226.0994, found: 226.1012.

**3-Hydroxy-heptan-4-one (8e')**:



To a solution of diisopropylamine (2.62 mL, 26.0 mmol) in THF (45 mL) at -78 °C under argon, was added dropwise a solution of *n*-butyllithium (9.84 mL, 25.0 mmol, 2.54 M in hexane). The solution was stirred for 20 min at -78 °C and then trimethylsilyl chloride (freshly distilled from calcium hydride, 12.7 ml, 100 mmol) and a solution of 4-heptanone (2.28 g, 20.0 mmol) in THF (5 mL) were added. After 1 h, to the resulting reaction mixture was added triethylamine (14.0 mL, 100 mmol) and a saturated  $\text{NaHCO}_3$  solution (40 mL), and the mixture was allowed to warm to room temperature. The resulting mixture was filtered and then separated. The water phase was extracted with hexane (60 mL). The organic phase was washed with water, a saturated  $\text{NaHCO}_3$  solution, brine. The combined organic phase was dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated to afford the silyl enol ether as a pale yellow oil.

$\text{MMPP} \cdot 6\text{H}_2\text{O}$  (3.71 g, 7.5 mmol) was added to a solution of the silyl enol ether (5 mmol) in  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  (5:1, 18 mL), and the reaction mixture was stirred at room temperature. After 3.5 h, water was added, and the water phase was extracted with  $\text{CH}_2\text{Cl}_2$ . The organic phase was washed with a saturated  $\text{NaHCO}_3$  solution, dried over  $\text{MgSO}_4$ , filtered and concentrated to afford a pale yellow oil, which was purified by column chromatography (silica gel, hexane/AcOEt = 80/20) to afford the alcohol

**8e'** (323 mg, 50% in 2 steps) as a colorless oil: <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ: 0.94 (t, *J* = 7.2 Hz, 6H), 1.55-1.72 (m, 3H), 1.91 (d, sext, *J* = 4.4 Hz, 7.6 Hz, 1H), 2.44 (q, *J* = 7.2 Hz, 2H), 3.45 (d, *J* = 5.2 Hz, 1H, OH), 4.16 (dt, *J* = 4.4 Hz, 6.8 Hz, 1H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ: 8.9, 13.8, 17.1, 26.7, 39.7, 77.1, 212.1; IR (Neat): 3473 cm<sup>-1</sup>, 1712 cm<sup>-1</sup>; MS (EI) *m/z* 130 (M<sup>+</sup>), 59 (100%); HRMS (EI) calcd for C<sub>7</sub>H<sub>14</sub>O<sub>2</sub>: 130.0994, found: 130.0982.

**General procedure for the silylation of α-hydroxy ketone with tert-butyldimethylsilyl chloride.** To a mixture of the α-hydroxy ketone (1 eq.) and imidazole (2 eq.) in dry CH<sub>2</sub>Cl<sub>2</sub> were added *tert*-butyldimethylsilyl chloride (1.7 eq.) and 4-(dimethylamino)pyridine (0.05 eq.), and the resulting mixture was stirred at room temperature. The mixture was quenched with water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed with brine, dried over MgSO<sub>4</sub> and concentrated to give a residue, which was purified by column chromatography, followed by recrystallization or distillation to afford the silyl ether.

**3-(*tert*-Butyldimethylsiloxy)-heptan-4-one (8e):** According to the general procedure, 3-hydroxyheptan-4-one was converted into the silyl ether **8e** (91%) as a colorless oil, after purification by column chromatography (silica gel, hexane/AcOEt = 95/5), followed by distillation (Kügelrohr, 95-105 °C at 3.0 mmHg): Colorless oil. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ: 0.05 (s, 3H), 0.06 (s, 3H), 0.86-0.94 (m, 6H), 0.93 (s, 9H), 1.52-1.70 (m, 4H), 2.51 (t, *J* = 7.2 Hz, 2H), 3.96 (dd, *J* = 5.6 Hz, 6.4 Hz, 1H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ: -4.9, 9.3, 13.9, 16.6, 18.1, 25.8, 28.0, 39.4, 79.8, 213.8; IR (Neat): 1716 cm<sup>-1</sup>; MS (EI) *m/z* 229 (M<sup>+</sup>-Me), 187 (100%, M<sup>+</sup>-<sup>t</sup>Bu); HRMS (EI) calcd for C<sub>12</sub>H<sub>25</sub>O<sub>2</sub>Si (M<sup>+</sup>-Me): 229.1624, found: 229.1613.

**1-(*tert*-Butyldimethylsiloxy)-3,3-dimethyl-butan-2-one (8h):** According to the general procedure, 1-hydroxy-3,3-dimethyl-butan-2-one<sup>[14]</sup> was converted into the silyl ether **8h** as a colorless oil, after purification by column chromatography (silica gel, hexane/AcOEt = 95/5): <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ: 0.09 (s, 6H), 0.92 (s, 9H), 1.16 (s, 9H), 4.51 (s, 2H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ: -5.4 (q x 2), 18.6 (s), 25.9 (q x 3), 26.5 (q x 3), 42.7 (s), 65.6 (t), 212.7 (s); IR (Neat): 1726 cm<sup>-1</sup>; MS (EI) *m/z* 230 (M<sup>+</sup>), 173 (M<sup>+</sup>-<sup>t</sup>Bu, 100%); HRMS (EI) calcd for C<sub>12</sub>H<sub>26</sub>O<sub>2</sub>Si: 230.1702, found: 230.1712

***Cis*-2-(*tert*-butyldimethylsiloxy)-4-methyl-cyclohexanone (8l) and *trans*-2-(*tert*-butyldimethylsiloxy)-4-methyl-cyclohexanone (8m):** To a solution of diisopropylamine (3.25 mL, 23.2 mmol) in THF (40 mL), cooled to -78 °C under argon, was added dropwise a solution of *n*-butyllithium (15.6 ml, 22.3 mmol, 1.43 M in hexane). The solution was stirred for 20 min at -78 °C, and trimethylsilyl chloride (11.3 mL, 89.2 mmol) freshly distilled from calcium hydride and a solution of 4-methylcyclohexanone (2.0 g, 17.8 mmol) in THF (5 mL) were added. After 2 h, triethylamine (12.4 mL, 89.2 mmol) and a saturated NaHCO<sub>3</sub> solution (35 mL) were added to the reaction, which was allowed to warm to room temperature. Water was added to the resulting mixture, which was extracted with hexane

(90 mL). The organic phase was washed with water, a saturated NaHCO<sub>3</sub> solution, and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to afford the silyl enol ether as a pale yellow oil.

To a solution of the silyl enol ether in CHCl<sub>3</sub>/H<sub>2</sub>O (1:1, 100 mL) were added MMPP· 6H<sub>2</sub>O (8.8 g, 17.8 mmol) and TBAC (tetrabutylammonium chloride, 742 mg, 2.67 mmol), and the reaction mixture was warmed to 50 °C. After 13 h, the resulting mixture was separated. The water phase was extracted with CHCl<sub>3</sub> (2 x 25 mL). The organic phase was washed with a saturated NaHCO<sub>3</sub> solution, dried over MgSO<sub>4</sub>, filtered and concentrated to afford an orange oil, which was purified by column chromatography (silica gel, hexane/AcOEt = 60/40) to provide the 1.2 : 1 mixture of *cis*-2-hydroxy-4-methylcyclohexanone<sup>[15]</sup> and *trans*-2-hydroxy-4-methylcyclohexanone (1.04g, 46%, for 2 steps) as a pale yellow oil.

To a solution of the 1.2 : 1 mixture of *syn*- and *anti*- 2-hydroxy-4-methylcyclohexanones (700 mg, 5.5 mmol) and imidazole (749 mg, 11 mmol) in CH<sub>2</sub>Cl<sub>2</sub> were added *tert*-butyldimethylsilyl chloride (1.23 g, 8.2 mmol) and 4-(dimethylamino)pyridine (cat.), and the resulting mixture was stirred at room temperature for 24 h. The mixture was quenched with a saturated NaHCO<sub>3</sub> solution and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed with brine, dried over MgSO<sub>4</sub> and concentrated to give a residue, which was purified by column chromatography (silica gel, hexane/CHCl<sub>3</sub> = 60/40) to provide **8l** (547 mg, 41%) and **8m** (617 mg, 46%), respectively.

**8l**: colorless oil; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ: 0.02 (s, 3H), 0.14 (s, 3H), 0.90 (s, 9H), 1.02 (d, *J* = 6.8 Hz, 3H), 1.34 (dq, *J* = 4.4 Hz, 13.2 Hz, 1H), 1.47 (q, *J* = 12.4 Hz, 1H), 1.92-2.04 (m, 2H), 2.15-2.22 (m, 1H), 2.31 (td, *J* = 1.2 Hz, 13.6 Hz, 1H), 2.39 (ddd, *J* = 2.4 Hz, 4.8 Hz, 14.0 Hz, 1H), 4.20 (ddd, *J* = 1.2 Hz, 6.4 Hz, 12.0 Hz, 1H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ: -5.3 (q), -4.4 (q), 18.6 (s), 21.1 (q), 25.9 (qx3), 31.1 (d), 35.2 (t), 39.6 (t), 45.4 (t), 76.1 (d), 209.2 (s); IR (Neat): 1731 cm<sup>-1</sup>; MS (EI) *m/z* 242 (M<sup>+</sup>), 185 (M<sup>+</sup>-<sup>t</sup>Bu, 100%); HRMS (EI) calcd for C<sub>13</sub>H<sub>26</sub>O<sub>2</sub>Si: 242.1702, found: 242.1662.

**8m**: colorless oil; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ: 0.02 (s, 3H), 0.05 (s, 3H), 0.88 (s, 9H), 0.97 (d, *J* = 6.8 Hz, 3H), 1.38 (dtd, *J* = 4.4 Hz, 10.8 Hz, 12.4 Hz, 1H), 1.49 (ddd, *J* = 3.2 Hz, 10.8 Hz, 14.0 Hz, 1H), 1.90-1.98 (m, 2H), 2.16 (dtd, *J* = 1.2 Hz, 4.4 Hz, 13.2 Hz, 1H), 2.21-2.33 (m, 1H), 2.81 (td, *J* = 5.6 Hz, 12.8 Hz, 1H), 3.96 (t, *J* = 4.0 Hz, 1H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ: -5.0 (q), -4.9 (q), 18.1 (s), 20.6 (q), 25.7 (qx3), 25.8 (d), 35.3 (t), 36.7 (t), 44.0 (t), 74.8 (d), 211.6 (s); IR (Neat): 1730 cm<sup>-1</sup>; MS (EI) *m/z* 242 (M<sup>+</sup>), 185 (M<sup>+</sup>-<sup>t</sup>Bu, 100%); HRMS (EI) calcd for C<sub>13</sub>H<sub>26</sub>O<sub>2</sub>Si: 242.1702, found: 242.1701.

**2-(*tert*-Butyldimethylsiloxy)cycloheptanone (8n)**: The silylation of 2-hydroxycycloheptanone<sup>[14]</sup> gave **8n** (69%) as a colorless oil, after purification by column chromatography (silica gel, hexane/AcOEt = 90/10), followed by distillation (Kügelrohr, 105 °C at 3.0 mmHg): <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ: 0.03 (s, 3H), 0.05 (s, 3H), 0.89 (s, 9H), 1.30-1.39 (m, 1H), 1.53-1.81 (m, 6H), 1.85-1.94 (m, 1H), 2.33

(ddd,  $J = 9.2$  Hz, 8.8 Hz, 15.6 Hz, 1H), 2.66 (ddd,  $J = 7.2$  Hz, 6.4 Hz, 15.2 Hz, 1H), 4.26 (dd,  $J = 2.4$  Hz, 7.2 Hz, 1H);  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : -5.1 (q), -4.9 (q), 18.2 (s), 22.8 (t), 25.0 (t), 25.8 (qx3), 28.3 (t), 33.8 (t), 40.4 (t), 79.0 (d), 213.5 (s); IR (Neat): 1713  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  242 ( $\text{M}^+$ ), 185 ( $\text{M}^+ - \text{tBu}$ ), 75 (100%); HRMS (EI) calcd for  $\text{C}_{13}\text{H}_{26}\text{O}_2\text{Si}$ : 242.1702, found: 242.1701.

**2-(tert-Butyldimethylsiloxy)-cyclooctanone (8o)**: Silylation of 2-hydroxycyclooctanone<sup>[11]</sup> gave **8o** (93%) as a colorless oil, after purification by column chromatography (silica gel, hexane/AcOEt = 90/10), followed by distillation (Kügelrohr, 110-140 °C at 3.0 mmHg):  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 0.04 (s, 3H), 0.05 (s, 3H), 0.91 (s, 9H), 1.13-1.21 (m, 1H), 1.45-1.56 (m, 4H), 1.66-1.78 (m, 2H), 1.82-1.98 (m, 2H), 2.20-2.31 (m, 2H), 2.70-2.77 (m, 1H), 4.19 (dd,  $J = 3.2, 6.4$  Hz, 1H);  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : -5.0 (q), -4.9 (q), 18.2 (s), 20.9 (t), 25.2 (t), 25.3 (t), 25.8 (q), 27.3 (t), 35.5 (t), 39.3 (t), 78.1 (d), 218.0 (s); IR (Neat): 1714  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  256 ( $\text{M}^+$ ), 199 ( $\text{M}^+ - \text{tBu}$ ), 75 (100%); HRMS (EI) calcd for  $\text{C}_{14}\text{H}_{28}\text{O}_2\text{Si}$ : 256.1859, found: 256.1906.

**2-(tert-Butyldimethylsiloxy)-cyclododecanone (8p)**: Silylation of 2-hydroxy-cyclododecanone<sup>[11]</sup> gave **8p** (96%) as a colorless solid, after purification by column chromatography (silica gel, hexane/AcOEt = 99/1 to 95/5), followed by distillation (Kügelrohr, 205-210 °C at 2.0 mmHg): mp 28-29 °C:  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 0.03 (s, 3H), 0.03 (s, 3H), 0.89 (s, 9H), 1.04-1.36 (m, 14H), 1.47-1.56 (m, 1H), 1.60-1.80 (m, 2H), 1.84-1.95 (m, 1H), 2.29 (ddd,  $J = 3.4$  Hz, 6.6 Hz, 16.4 Hz, 1H), 2.89 (ddd,  $J = 3.4$  Hz, 13.0 Hz, 14.4 Hz, 1H), 4.01 (dd,  $J = 4.0$  Hz, 9.2 Hz, 1H);  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : -5.0 (q), -4.9 (q), 18.1 (s), 19.8 (t), 21.2 (t), 22.3 (t), 22.5 (t), 22.8 (t), 23.9 (t), 25.7 (q x 3), 26.5 (t), 26.6 (t), 32.8 (t), 33.2 (t), 79.2 (d), 212.9 (s); IR (Neat): 1714  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  312 ( $\text{M}^+$ ), 255 ( $\text{M}^+ - \text{tBu}$ ), 75 (100%); Anal. Calcd for  $\text{C}_{18}\text{H}_{36}\text{O}_2\text{Si}$ : H, 11.61; C, 69.17, found: H, 11.49; C, 69.11.

**(Z)-Methyl 4-methoxymethoxy-2-methyl-3-phenyl-2-pentenoate (7b)**: Pale yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.24$  (d,  $J = 6.4$  Hz, 3H), 1.69 (s, 3H), 3.35 (s, 3H), 3.81 (s, 3H), 4.53 (d,  $J = 6.4$  Hz, 1H), 4.78 (d,  $J = 6.4$  Hz, 1H), 4.91 (q,  $J = 6.4$  Hz, 1H), 7.10 (dd,  $J = 1.6$  Hz, 8.4 Hz, 2H), 7.28-7.38 (m, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 17.7, 20.0, 51.8, 55.3, 71.7, 93.9, 127.2, 128.0, 128.0, 128.9, 137.3, 145.3, 170.6$ ; IR (Neat):  $\nu = 1729$   $\text{cm}^{-1}$ . MS (EI)  $m/z$  264 ( $\text{M}^+$ ), 219 (100%,  $\text{M}^+ - \text{MOM}$ ); HRMS (EI) calcd for  $\text{C}_{15}\text{H}_{20}\text{O}_4$ : 264.1362, found: 264.1379.

**(Z)-Methyl 4-methoxyphenylmethoxy-2-methyl-3-phenyl-2-pentenoate (7c)**: Colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.22$  (d,  $J = 6.4$  Hz, 3H), 1.73 (s, 3H), 3.72 (s, 3H), 3.80 (s, 3H), 4.38 (d,  $J = 12.0$  Hz, 1H), 4.59 (q,  $J = 6.4$  Hz, 1H), 4.62 (d,  $J = 12.0$  Hz, 1H), 6.86 (d,  $J = 8.8$  Hz, 2H), 7.14 (dd,  $J = 1.2$  Hz, 8.0 Hz, 2H), 7.24 (d,  $J = 8.8$  Hz, 2H), 7.27-7.38 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 17.8, 20.3, 51.8, 55.3, 70.1, 74.8, 113.6, 127.1, 128.0, 128.1, 128.9, 129.0, 130.7, 137.3, 145.8,$

158.9, 170.7; IR (Neat):  $\nu = 1715 \text{ cm}^{-1}$ ; MS (EI):  $m/z$  340 ( $M^+$ ); HRMS (EI) calcd for  $C_{21}H_{24}O_4$ : 340.1675, found: 340.1653.

**(Z)-Methyl 2-methyl-3-phenyl-4-triethylsiloxy-2-pentenoate (7d)**: Colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.59$  (q,  $J = 8.0$  Hz, 6H), 0.93 (t,  $J = 8.0$  Hz, 9H), 1.21 (d,  $J = 6.0$  Hz, 3H), 1.63 (s, 3H), 3.79 (s, 3H), 5.10 (q,  $J = 6.0$  Hz, 1H), 7.12 (dd,  $J = 1.2$  Hz, 8.0 Hz, 2H), 7.27-7.36 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 4.8, 6.9, 17.6, 23.0, 51.6, 68.4, 124.7, 126.9, 127.6, 129.2, 137.7, 150.3, 170.4$ ; IR (Neat):  $\nu = 1720 \text{ cm}^{-1}$ ; MS (EI):  $m/z$  334 ( $M^+$ ); HRMS (EI): calcd for  $C_{19}H_{30}O_3\text{Si}$ : 334.1964, found: 334.1964.

**(Z)-Methyl 4-(tert-butyldimethylsiloxy)-2-methyl-3-phenyl-2-pentenoate (7e)**: Pale yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.05$  (s, 3H), 0.06 (s, 3H), 0.84 (s, 9H), 1.19 (d,  $J = 6.0$  Hz, 3H), 1.63 (s, 3H), 3.79 (s, 3H), 5.14 (q,  $J = 6.4$  Hz, 1H), 7.11 (dd,  $J = 1.2$  Hz, 8.0 Hz, 2H), 7.27-7.35 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = -4.8, -4.7, 17.6, 18.3, 23.0, 25.9, 51.6, 68.4, 124.9, 126.9, 127.6, 129.2, 137.7, 150.4, 170.2$ ; IR (Neat):  $\nu = 1722 \text{ cm}^{-1}$ ; MS (EI):  $m/z$  334 ( $M^+$ ), 277 (100%,  $M^+ - t\text{Bu}$ ); HRMS (EI) calcd for  $C_{19}H_{30}O_3\text{Si}$ : 334.1964, found: 334.1958.

**(Z)-Methyl 4-(triisopropylsiloxy)-2-methyl-3-phenyl-2-pentenoate (7f)**: Colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.96$ -1.06 (m, 21H), 1.27 (d,  $J = 6.4$  Hz, 3H), 1.64 (s, 3H), 3.77 (s, 3H), 5.34 (q,  $J = 6.4$  Hz, 1H), 7.15 (dd,  $J = 1.6$  Hz, 8.4 Hz, 2H), 7.27-7.34 (m, 3H);  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 12.4, 17.6, 18.09, 18.14, 23.4, 51.6, 68.3, 124.5, 126.8, 127.4, 129.3, 137.6, 151.6, 169.9$ ; IR (Neat):  $\nu = 1721 \text{ cm}^{-1}$ ; MS (EI):  $m/z$  376 ( $M^+$ ); HRMS (EI) calcd for  $C_{22}H_{36}O_3\text{Si}$ : 376.2434, found: 376.2470.

**(Z)-Methyl 2-methyl-4-phenoxy-3-phenyl-2-pentenoate (7g)**: Colorless oil;  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 1.48$  (d,  $J = 6.4$  Hz, 3H), 1.65 (s, 3H), 3.84 (s, 3H), 5.77 (q,  $J = 6.4$  Hz, 1H), 6.85-6.99 (m, 5H), 7.22-7.32 (m, 5H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 17.7, 20.3, 51.9, 73.0, 115.4, 120.5, 127.2, 127.5, 127.8, 128.7, 129.3, 136.8, 149.1, 158.0, 169.6$ ; IR (Neat):  $\nu = 1716 \text{ cm}^{-1}$ ; MS (EI):  $m/z$  296 ( $M^+$ ); HRMS (EI) calcd for  $C_{19}H_{20}O_3$ : 296.1412, found: 296.1427.

**(Z)-Methyl 4-(4-methoxyphenoxy)-2-methyl-3-phenyl-2-pentenoate (7h)**: Colorless oil;  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.44$  (d,  $J = 6.4$  Hz, 3H), 1.65 (s, 3H), 3.77 (s, 3H), 3.83 (s, 3H), 5.64 (q,  $J = 6.4$  Hz, 1H), 6.80 (s, 4H), 6.97-7.00 (m, 2H), 7.27-7.33 (m, 3H);  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 17.7, 20.3, 51.9, 55.7, 73.8, 114.5, 116.5, 127.2, 127.5, 127.8, 128.7, 136.9, 149.0, 152.2, 153.6, 169.7$ ; IR (Neat):  $\nu = 1718 \text{ cm}^{-1}$ ; MS (EI):  $m/z$  326 ( $M^+$ ); HRMS (EI): calcd for  $C_{20}H_{22}O_4$ : 326.1518, found: 326.1527.

**(Z)-Methyl 2-butyl-4-(tert-butyldimethylsiloxy)-3-methyl-2-butenolate (10):** 59% yield as a colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.05 (s, 6H), 0.88-0.92 (m, 12H), 1.25-1.41 (m, 4H), 1.84 (s, 3H), 2.29 (t,  $J$  = 7.2 Hz, 2H), 3.72 (s, 3H), 4.40 (s, 2H);  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = -5.3 (qx2), 13.9 (q), 15.7 (q), 18.4 (s), 22.6 (t), 25.9 (qx3), 29.7 (t), 30.9 (t), 51.3 (q), 64.6 (t), 128.1 (s), 145.0 (s), 169.5 (s); IR (neat):  $\nu$  = 1715  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  300 ( $\text{M}^+$ ), 243 (100%,  $\text{M}^+ - t\text{Bu}$ ); HRMS (EI) calcd for  $\text{C}_{16}\text{H}_{32}\text{O}_3\text{Si}$ : 300.2121, found: 300.2100.

**(Z)-Methyl 4-(tert-butyldiphenylsiloxy)-2,3-dimethyl-2-butenolate (11):** 66% yield as a colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.05 (s, 9H), 1.85 (s, 3H), 1.94 (s, 3H), 3.54 (s, 3H), 4.53 (s, 2H), 7.34-7.70 (m, 10H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 15.8 (q), 16.5 (q), 19.4 (s), 26.9 (qx3), 51.2 (q), 65.1 (t), 122.9 (s), 127.5 (d), 129.5 (d), 133.6 (s), 135.5 (d), 146.1 (s), 169.1 (s); IR (Neat):  $\nu$  = 1714  $\text{cm}^{-1}$ ; MS (EI):  $m/z$  382 ( $\text{M}^+$ ), 325 (100%,  $\text{M}^+ - t\text{Bu}$ ); HRMS (EI): calcd for  $\text{C}_{23}\text{H}_{30}\text{O}_3\text{Si}$ : 382.1964, found: 382.1971.

**(Z)-Methyl 4-(tert-butyldimethylsiloxy)-2,3-dimethyl-2-pentenoate (12):** >99% yield as a colorless oil:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : -0.04 (s, 3H), 0.00 (s, 3H), 0.86 (s, 9H), 1.20 (d,  $J$  = 6.4 Hz, 3H), 1.75 (s, 3H), 1.83 (s, 3H), 3.72 (s, 3H), 5.14 (q,  $J$  = 6.4 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = -5.0 (q), -5.0 (q), 13.2 (q), 15.8 (q), 18.2 (s), 22.7 (q), 25.8 (qx3), 51.3 (q), 68.2 (d), 121.2 (s), 150.2 (s), 169.3 (s); IR (Neat):  $\nu$  = 1716  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  272 ( $\text{M}^+$ ), 215 (100%,  $\text{M}^+ - t\text{Bu}$ ); HRMS (EI): calcd for  $\text{C}_{14}\text{H}_{28}\text{O}_3\text{Si}$ : 272.1808, found: 272.1788.

**(Z)-Methyl 4-(tert-butyldimethylsiloxy)-2,3,4-trimethyl-2-pentenoate (13):** 98% yield as a colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.09 (s, 6H), 0.87 (s, 9H), 1.38 (s, 6H), 1.71 (q,  $J$  = 1.2 Hz, 3H), 1.82 (q,  $J$  = 1.2 Hz, 3H), 3.71 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = -2.1 (qx2), 15.8 (q), 18.4 (s), 18.6 (q), 26.1 (qx3), 29.4 (qx2), 51.6 (q), 76.4 (s), 121.1 (s), 142.3 (s), 173.2 (s); IR (Neat):  $\nu$  = 1732  $\text{cm}^{-1}$ ; MS (EI):  $m/z$  286 ( $\text{M}^+$ ), 229 (100%,  $\text{M}^+ - t\text{Bu}$ ); HRMS (EI) calcd for  $\text{C}_{15}\text{H}_{30}\text{O}_3\text{Si}$ : 286.1964, found: 286.1960.

**(Z)-Methyl 4-(tert-butyldimethylsiloxy)-2-methyl-3-propyl-hex-2-enoate (14):** 60% yield as a colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = -0.05 (s, 3H), 0.01 (s, 3H), 0.86 (t,  $J$  = 7.6 Hz, 3H), 0.87 (s, 9H), 0.95 (t,  $J$  = 7.6 Hz, 3H), 1.36-1.61 (m, 4H), 1.86 (s, 3H), 2.04 (dt,  $J$  = 5.2 Hz, 12.0 Hz, 1H), 2.23 (dt,  $J$  = 5.2 Hz, 12.0 Hz, 1H), 3.72 (s, 3H), 4.80 (dd,  $J$  = 5.2 Hz, 7.6 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = -5.0 (q), -4.7 (q), 10.6 (q), 14.9 (q), 15.9 (q), 18.2 (s), 22.7 (t), 25.9 (qx3), 29.8 (t), 30.2 (t), 51.3 (q), 73.8 (d), 123.6 (s), 151.5 (s), 170.0 (s); IR (Neat):  $\nu$  = 1717  $\text{cm}^{-1}$ ; MS (EI):  $m/z$  314 ( $\text{M}^+$ ), 257 (100%,  $\text{M}^+ - t\text{Bu}$ ); HRMS (EI): calcd for  $\text{C}_{17}\text{H}_{34}\text{O}_3\text{Si}$ : 314.2277, found: 314.2284.

**(Z)-Methyl 4-(tert-butyldimethylsiloxy)-2-isopropyl-3-phenyl-2-pentenoate (15):** 76% as a colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.06 (s, 3H), 0.10 (s, 3H), 0.86 (s, 9H), 0.94 (d,  $J$  = 6.8 Hz, 3H), 0.95 (d,  $J$  = 6.8 Hz, 3H), 1.15 (d,  $J$  = 6.4 Hz, 3H), 2.35 (hept,  $J$  = 6.8 Hz, 1H), 3.79 (s, 3H), 4.56 (q,  $J$  = 6.0 Hz, 1H), 7.13 (dd,  $J$  = 2.0 Hz, 8.0 Hz, 2H), 7.27-7.35 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = -4.9 (q), -4.6 (q), 18.3 (s), 21.1 (q), 21.1 (q), 22.8 (q), 26.0 (qx3), 29.8 (d), 51.1 (q), 70.1 (d), 126.8 (d), 127.5 (d), 129.5 (d), 136.4 (s), 137.0 (s), 143.5 (s), 169.8 (s); IR (Neat):  $\nu$  = 1730  $\text{cm}^{-1}$ ; MS (EI):  $m/z$  362 ( $\text{M}^+$ ), 305 ( $\text{M}^+ - t\text{Bu}$ ), 89 (100%); HRMS (EI): calcd for  $\text{C}_{21}\text{H}_{34}\text{O}_3\text{Si}$ : 362.2277, found: 362.2294.

**(Z)-Methyl 4-(tert-butyldimethylsiloxy)-2,3-diphenyl-2-pentenoate (16):** 75% as a colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.13 (s, 3H), 0.15 (s, 3H), 0.92 (s, 9H), 1.27 (d,  $J$  = 4.4 Hz, 3H), 3.78 (s, 3H), 5.02 (q,  $J$  = 6.4 Hz, 1H), 6.97-7.14 (m, 10H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = -4.8 (q), -4.6 (q), 18.4 (s), 22.9 (q), 26.0 (qx3), 52.0 (q), 70.1 (d), 126.9 (dx2), 127.3 (d), 127.7 (d), 129.4 (d), 130.3 (d), 131.7 (s), 136.6 (s), 137.1 (s), 148.9 (s), 169.6 (s); IR (Neat):  $\nu$  = 1730  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  396 ( $\text{M}^+$ ), 339 ( $\text{M}^+ - t\text{Bu}$ , 100%); HRMS (EI): calcd for  $\text{C}_{24}\text{H}_{32}\text{O}_3\text{Si}$ : 396.2121, found: 396.2136.

**(Z)-Methyl 4-(tert-butyldimethylsiloxy)-2,4-dimethyl-3-phenyl-2-pentenoate (17):** 91% as a pale yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.03 (s, 6H), 0.79 (s, 9H), 1.42 (s, 6H), 1.50 (s, 3H), 3.77 (s, 3H), 7.07 (dd,  $J$  = 1.6 Hz, 8.4 Hz, 2H), 7.24 (t,  $J$  = 7.2 Hz, 1H), 7.31 (t,  $J$  = 7.2 Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = -1.7 (qx2), 18.4 (s), 20.0 (q), 26.2 (qx3), 30.5 (qx2), 51.7 (q), 76.1 (s), 124.8 (s), 126.4 (d), 127.8 (d), 128.8 (d), 140.2 (s), 148.3 (s), 172.3 (s); IR (Neat):  $\nu$  = 1731  $\text{cm}^{-1}$ ; MS (EI):  $m/z$  348 ( $\text{M}^+$ ), 291 ( $\text{M}^+ - t\text{Bu}$ ), 89 (100%); HRMS (EI) calcd for  $\text{C}_{20}\text{H}_{32}\text{O}_3\text{Si}$ : 348.2121, found: 348.2084.

**(Z)-Methyl 4-(tert-butyldimethylsiloxy)-2-methyl-3,4-diphenyl-2-butenoate (18):** 93% yield as a pale yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = -0.02 (s, 3H), 0.12 (s, 3H), 0.88 (s, 9H), 1.65 (s, 3H), 3.89 (s, 3H), 6.35 (s, 1H), 6.66 (dd,  $J$  = 1.2 Hz, 8.0 Hz, 2H), 7.11-7.23 (m, 8H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = -5.0 (q), -4.7 (q), 17.7 (q), 18.3 (s), 25.9 (q x 3), 51.8 (q), 72.5 (d), 125.8 (s), 126.2 (d), 126.6 (d), 126.7 (d), 126.9 (d), 127.4 (d), 136.5 (s), 142.2 (s), 149.3 (s), 170.2 (s); IR (Neat):  $\nu$  = 1716  $\text{cm}^{-1}$ ; MS (EI):  $m/z$  396 ( $\text{M}^+$ ), 339 ( $\text{M}^+ - t\text{Bu}$ ), 205 (100%); HRMS (EI): calcd for  $\text{C}_{24}\text{H}_{32}\text{O}_3\text{Si}$ : 396.2121, found: 396.2126.

**(Z)-Methyl 3-(tert-butyldimethylsiloxy)-2,4,4-trimethyl-2-pentenoate (19):** 94% as a colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 0.03 (s, 6H), 0.89 (s, 9H), 1.26 (s, 9H), 2.02 (s, 3H), 3.72 (s, 3H), 4.11 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = -5.4 (qx2), 18.3 (s), 18.5 (q), 25.9 (qx3), 30.2 (q x 3), 35.4 (s), 51.7 (q), 63.5 (t), 128.9 (s), 146.1 (s), 172.7 (s); IR (Neat):  $\nu$  = 1728  $\text{cm}^{-1}$ ; MS (FAB)  $m/z$  323 ( $\text{M}^+ + \text{Na}$ ), 73 (100%); HRMS (FAB): calcd for  $\text{C}_{16}\text{H}_{32}\text{O}_3\text{SiNa}$ : 323.2018, Found: 323.2016.

**(Z)-(4S)-Methyl 4,5-dihydroxy-4,5-O-isopropylidene-2-methyl-3-phenyl-2-pentenoate (20):** 26% as a pale yellow oil; [entry 1: >99% ee: DAISEL, CHIRALCEL<sup>®</sup> OJ (0.46 x 25 cm), 0.5% *i*PrOH/hexane (v/v), flow rate; 0.5 ml/min; retention time, 11 min for (*S*)-isomer and 13 min for (*R*)-isomer, monitored by UV absorbance at 254 nm]; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 1.37 (s, 3H), 1.49 (s, 3H), 1.82 (d, *J* = 0.4 Hz, 3H), 1.89 (d, *J* = 0.4 Hz, 3H), 3.58 (dd, *J* = 7.2 Hz, 8.4 Hz, 1H), 3.73 (s, 3H), 4.25 (dd, *J* = 7.2 Hz, 8.4 Hz, 1H), 5.27 (t, *J* = 7.2 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 14.1 (q), 16.0 (q), 25.2 (q), 26.2 (q), 51.6 (q), 68.7 (t), 76.0 (d), 109.4 (s), 125.5 (s), 144.6 (s), 168.9 (s); IR (Neat): ν = 1713 cm<sup>-1</sup>; [α]<sub>D</sub><sup>27</sup>: +47.4° (*c* 1.39, CHCl<sub>3</sub>); MS (EI): *m/z* 214 (M<sup>+</sup>), 43 (100%); HRMS (EI): calcd for C<sub>11</sub>H<sub>18</sub>O<sub>4</sub>: 214.1205, found: 214.1175.

**(2Z,4S)-Methyl 4,5-dihydroxy-4,5-O-isopropylidene-2-methyl-3-phenyl-2-pentenoate (21):** 66% as a pale yellow oil: [>99% ee: DAISEL, CHIRALCEL<sup>®</sup> OJ (0.46 x 25 cm), 0.5% *i*PrOH/hexane (v/v), flow rate; 0.5 ml/min; retention time, 10 min for (*S*)-isomer and 12 min for (*R*)-isomer, monitored by UV absorbance at 254 nm]; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 0.91 (s, 3H), 1.32 (s, 3H), 1.70 (s, 3H), 3.72 (dd, *J* = 7.2 Hz, 8.4 Hz, 1H), 3.81 (s, 3H), 4.24 (dd, *J* = 6.8 Hz, 8.4 Hz, 1H), 5.30 (t, *J* = 6.8 Hz, 1H), 7.11 (dd, *J* = 2.0 Hz, 8.8 Hz, 2H), 7.30 (tt, *J* = 1.6 Hz, 6.8 Hz, 1H), 7.35 (tt, *J* = 1.6 Hz, 6.8 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 17.7 (q), 25.5 (q), 25.7 (q), 51.9 (q), 68.9 (t), 75.9 (d), 109.7 (s), 127.2 (d), 127.8 (d), 128.5 (s), 129.1 (d), 137.0 (s), 146.8 (s), 169.4 (s); IR (Neat): ν = 1713 cm<sup>-1</sup>; [α]<sub>D</sub><sup>27</sup> = +95.1° (*c* 0.64, CHCl<sub>3</sub>); MS (EI): *m/z* 276 (M<sup>+</sup>), 186 (100%); HRMS (EI): calcd for C<sub>16</sub>H<sub>20</sub>O<sub>4</sub>: 276.1362, found: 276.1360.

**(Z)-Methyl 2-[2-(*tert*-butyldimethylsiloxy)-cyclohexylidene]propionate (22):** 60% as a colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = -0.04 (s, 3H), 0.01 (s, 3H), 0.87 (s, 9H), 1.27 (qt, *J* = 4.0 Hz, 12.8 Hz, 1H), 1.43-1.51 (m, 2H), 1.79-1.95 (m, 3H), 1.84 (s, 3H), 2.31-2.42 (m, 2H), 3.73 (s, 3H), 5.02 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = -5.1 (q), -4.8 (q), 15.3 (q), 18.1 (s), 20.1 (t), 25.8 (qx3), 26.0 (t), 27.8 (t), 35.9 (t), 51.4 (q), 67.8 (d), 119.5 (s), 149.7 (s), 170.3 (s); IR (Neat): ν = 1719 cm<sup>-1</sup>; MS (EI): *m/z* 298 (M<sup>+</sup>), 241 (100%, M<sup>+</sup>-*t*Bu); HRMS (EI): calcd for C<sub>16</sub>H<sub>30</sub>O<sub>3</sub>Si: 298.1964, found: 298.1952.

**(Z)-*syn*-Methyl 2-[2-(*tert*-butyldimethylsiloxy)-4-methyl-cyclohexylidene]-propionate (23):** 40% as a colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 0.03 (s, 3H), 0.07 (s, 3H), 0.89 (s, 9H), 1.11 (d, *J* = 6.8 Hz, 3H), 1.37-1.49 (m, 1H), 1.55-1.69 (m, 2H), 1.73-1.83 (m, 2H), 1.97 (s, 3H), 2.25 (ddd, *J* = 4.4 Hz, 6.8 Hz, 13.2 Hz, 1H), 2.55 (dddd, *J* = 0.8 Hz, 4.4 Hz, 9.2 Hz, 13.2 Hz, 1H), 3.73 (s, 3H), 4.54 (dd, *J* = 3.6 Hz, 6.0 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = -4.8 (q), -4.7 (q), 15.2 (q), 18.1 (s), 21.5 (q), 25.9 (q x 3), 26.5 (t), 28.7 (d), 34.8 (t), 42.9 (t), 51.5 (q), 70.9 (d), 120.6 (s), 146.7 (s), 171.3 (s); IR (Neat): ν = 1722 cm<sup>-1</sup>; MS (EI): *m/z* 312 (M<sup>+</sup>), 255 (100%, M<sup>+</sup>-*t*Bu); HRMS (EI) calcd for C<sub>17</sub>H<sub>32</sub>O<sub>3</sub>Si: 312.2121, found: 312.2125.

**(Z)-anti-Methyl 2-[2-(tert-butyldimethylsiloxy)-4-methyl-cyclohexylidene]-propionate (24):** 33% as a colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = -0.05 (s, 3H), 0.00 (s, 3H), 0.85 (d, *J* = 6.8 Hz, 3H), 0.87 (s, 9H), 0.88-1.02 (m, 1H), 1.15 (dt, *J* = 2.0 Hz, 12.0 Hz, 1H), 1.80 (dq, *J* = 2.0 Hz, 13.2 Hz, 2H), 1.85 (d, *J* = 1.2 Hz, 3H), 2.02-2.15 (m, 1H), 2.34 (dt, *J* = 3.2 Hz, 12.8 Hz, 1H), 2.42 (ddt, *J* = 1.2 Hz, 4.4 Hz, 13.2 Hz, 1H), 3.73 (s, 3H), 5.02 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = -5.1 (q), -4.8 (q), 15.4 (q), 18.1 (s), 21.8 (q), 25.6 (t), 25.8 (q x 3), 26.1 (d), 36.0 (t), 44.2 (t), 51.4 (q), 67.9 (d), 119.7 (s), 149.3 (s), 170.2 (s); IR (Neat): ν = 1722 cm<sup>-1</sup>; MS (EI): *m/z* 312 (M<sup>+</sup>), 255 (100%, M<sup>+</sup>-*t*Bu); HRMS (EI): calcd for C<sub>17</sub>H<sub>32</sub>O<sub>3</sub>Si: 312.2121, Found: 312.2153.

**(Z)-Methyl 2-[2-(tert-butyldimethylsiloxy)-cycloheptylidene]-propionate (25):** 83% as a colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = -0.05 (s, 3H), 0.00 (s, 3H), 0.86 (s, 9H), 1.26-1.41 (m, 2H), 1.48-1.56 (m, 1H), 1.58-1.76 (m, 5H), 1.86 (s, 3H), 2.24 (dt, *J* = 5.2 Hz, 14.4 Hz, 1H), 2.54-2.62 (m, 1H), 3.72 (s, 3H), 5.10 (t, *J* = 4.4 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = -5.0 (q x 2), 15.3 (q), 18.1 (s), 22.6 (t), 25.0 (t), 25.8 (q x 3), 27.9 (t), 37.5 (t), 51.3 (q), 70.5 (d), 122.6 (s), 151.2 (s), 169.9 (s); IR (Neat): ν = 1715 cm<sup>-1</sup>; MS (EI): *m/z* 312 (M<sup>+</sup>), 255 (100%, M<sup>+</sup>-*t*Bu); HRMS (EI): calcd for C<sub>17</sub>H<sub>32</sub>O<sub>3</sub>Si: 312.2121, found: 312.2126.

**(Z)-Methyl 2-[2-(tert-butyldimethylsiloxy)-cyclooctylidene]-propionate (26):** 90% as a colorless oil; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ = -0.08 (s, 3H), -0.02 (s, 3H), 0.84 (s, 9H), 1.25-1.72 (m, 10H), 1.87 (s, 3H), 2.20 (dt, *J* = 4.4 Hz, 14.0 Hz, 1H), 2.59 (ddd, *J* = 6.0 Hz, 12.0 Hz, 14.4 Hz, 1H), 3.73 (s, 3H), 4.92 (dd, *J* = 3.2 Hz, 8.0 Hz, 1H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ = -5.0 (q), -4.9 (q), 15.9 (q), 18.1 (s), 20.8 (t), 24.3 (t), 25.7 (t), 25.8 (qx3), 26.7 (t), 26.9 (t), 33.4 (t), 51.3 (q), 70.2 (d), 124.1 (s), 151.4 (s), 170.1 (s); IR (Neat): ν = 1715 cm<sup>-1</sup>; MS (EI): *m/z* 326 (M<sup>+</sup>), 269 (100%, M<sup>+</sup>-*t*Bu); HRMS (EI): calcd for C<sub>18</sub>H<sub>34</sub>O<sub>3</sub>Si: 326.2277, found: 326.2285.

**(Z)-Methyl 2-[2-(tert-butyldimethylsiloxy)-cyclododecylidene]-propionate (27):** 70% as a colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = -0.07 (s, 3H), -0.02 (s, 3H), 0.85 (s, 9H), 1.18-1.69 (m, 18H), 1.90 (s, 3H), 2.10 (ddd, *J* = 6.0 Hz, 10.0 Hz, 14.0 Hz, 1H), 2.53 (dt, *J* = 5.2 Hz, 13.6 Hz, 1H), 3.71 (s, 3H), 4.80 (dd, *J* = 5.2 Hz, 9.2 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = -5.0 (q), -4.9 (q), 17.0 (q), 18.2 (s), 21.2 (t), 23.0 (t), 23.1 (t), 23.8 (t), 25.1(t), 25.4 (t), 25.5 (t), 25.9 (q x 3), 26.3 (t), 26.5 (t), 36.3 (t), 51.3 (q), 72.3 (d), 126.5 (s), 148.3 (s), 170.5 (s); IR (Neat): ν = 1724 cm<sup>-1</sup>; MS (EI): *m/z* 382 (M<sup>+</sup>), 325 (M<sup>+</sup>-*t*Bu), 73 (100%); HRMS (EI): calcd for C<sub>22</sub>H<sub>42</sub>O<sub>3</sub>Si: 382.2903, found: 382.2888.

**3,4,5-Trimethyl-2(5H)-furanone (35)<sup>[16]</sup>** (Table 4, entry 2): Colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 1.40 (d, *J* = 6.8 Hz, 3H), 1.81 (s, 3H), 1.95 (s, 3H), 4.79 (q, *J* = 6.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz,

CDCl<sub>3</sub>):  $\delta$  = 8.3 (q), 11.7 (q), 18.0 (q), 79.4 (d), 122.6 (s), 160.3 (s), 174.2 (s); IR (Neat):  $\nu$  = 1747 cm<sup>-1</sup>; MS (EI):  $m/z$  126 (M<sup>+</sup>), 55 (100%).

**3,4,5,5-Tetramethyl-2(5H)-furanone (36)** (Table 4, entry 3): Yellow oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.41 (s, 6H), 1.79 (dd,  $J$  = 1.2 Hz, 2.0 Hz, 3H), 1.92 (dd,  $J$  = 1.2 Hz, 2.0 Hz, 3H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.6 (q), 11.0 (q), 24.7 (q x 2), 85.7 (q), 121.8 (s), 163.6 (s), 173.5 (s); IR (Neat):  $\nu$  = 1748 cm<sup>-1</sup>; MS (EI):  $m/z$  140 (M<sup>+</sup>), 43 (100%); HRMS (EI): calcd for C<sub>8</sub>H<sub>12</sub>O<sub>2</sub>: 140.0837; found: 140.0815.

**3,5-Dimethyl-4-phenyl-2(5H)-furanone (37)**<sup>[17]</sup> (Table 4, entry 4): Colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.38 (d,  $J$  = 6.8 Hz, 3H), 2.00 (d,  $J$  = 1.6 Hz, 3H), 5.42 (dq,  $J$  = 1.6 Hz, 6.8 Hz, 1H), 7.35 (t,  $J$  = 1.6 Hz, 1H), 7.37 (d,  $J$  = 1.6 Hz, 1H), 7.44-7.52 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.9 (q), 19.1 (q), 78.1 (d), 122.9 (s), 127.6 (d), 128.8 (d), 129.6 (d), 131.2 (s), 160.4 (s), 174.2 (s); IR (Neat):  $\nu$  = 1749 cm<sup>-1</sup>; MS (EI):  $m/z$  188 (M<sup>+</sup>), 145 (100%).

**4-Methyl-2,3-diphenyl-2(5H)-furanone (38)**<sup>[18]</sup> (Table 4, entry 5): Colorless solid mp. 136-137 °C (lit.<sup>[18]</sup> mp. 139-140 °C), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.45 (d,  $J$  = 6.8 Hz, 3H), 5.52 (q,  $J$  = 6.8 Hz, 1H), 7.22-7.42 (m, 10H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 19.0 (q), 78.0 (d), 125.8 (d), 127.9 (d), 128.3 (d), 128.4 (d), 128.8 (d), 129.1 (d), 129.7 (s), 129.8 (d), 130.9 (s), 161.5 (s), 172.0 (s); IR (Neat):  $\nu$  = 1747 cm<sup>-1</sup>; MS (EI)  $m/z$  250 (M<sup>+</sup>), 179 (100%); HRMS (EI): calcd for C<sub>17</sub>H<sub>14</sub>O<sub>2</sub>: 250.0994; found: 250.1003.

**3-Methyl-5,6,7,7a-tetrahydro-(4H)-benzofuran-2-one (39)**<sup>[19]</sup> (Table 4, entry 6): Colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.15-1.33 (m, 2H), 1.46 (ddt,  $J$  = 3.2 Hz, 13.2 Hz, 27.2 Hz, 1H), 1.81 (t,  $J$  = 1.5 Hz, 3H), 1.90 (ddd,  $J$  = 2.8 Hz, 5.2 Hz, 14 Hz, 1H), 2.00 (dt,  $J$  = 2.4 Hz, 13.2 Hz, 1H), 2.14 (dt,  $J$  = 5.6 Hz, 13.6 Hz, 1H), 2.47-2.53 (m, 1H), 2.82 (dt,  $J$  = 2.4 Hz, 14.0 Hz, 1H), 4.57 (dd,  $J$  = 6.4 Hz, 10.4 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.2 (q), 22.8 (t), 26.2 (tx2), 34.2 (t), 80.1 (d), 119.4 (s), 162.4 (s), 174.6 (s); IR (Neat):  $\nu$  = 1747 cm<sup>-1</sup>; MS (EI):  $m/z$  152 (M<sup>+</sup>, 100%).

**3-Methyl-4,5,6,7,8,8a-hexahydro-cyclohepta[b]furan-2-one (40)**<sup>[20]</sup> (Table 4, entry 7): Colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.28 (q,  $J$  = 11.2 Hz, 1H), 1.39-1.57 (m, 2H), 1.78 (s, 3H), 1.78-1.96 (m, 4H), 2.33 (d,  $J$  = 10.4 Hz, 1H), 2.53 (t,  $J$  = 12.4 Hz, 1H), 2.66 (d,  $J$  = 17.6 Hz, 1H), 4.85 (d,  $J$  = 7.2 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.3 (q), 25.5 (t), 26.2 (t), 27.6 (t), 29.8 (t), 33.7 (t), 83.3 (d), 122.1 (s), 165.4 (s), 174.4 (s); IR (Neat):  $\nu$  = 1747 cm<sup>-1</sup>; MS (EI):  $m/z$  166 (M<sup>+</sup>, 100%).

**3-Methyl-5,6,7,8,9,9a-hexahydro-(4H)-cycloocta[b]furan-2-one (41)** (Table 4, entry 8): Pale yellow oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 1.36-1.56 (m, 7H), 1.74-1.81 (m, 2H), 1.83 (d, *J* = 2.0 Hz, 3H), 1.90-2.18 (m, 1H), 2.27 (ddd, *J* = 5.6 Hz, 8.8 Hz, 14.4 Hz, 1H), 2.70 (dt, *J* = 6.0 Hz, 14.4 Hz, 1H), 4.85-4.89 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 8.6 (q), 20.7 (t), 25.0 (t), 25.9 (t), 26.7 (t), 27.0 (t), 28.6 (t), 82.6 (d), 124.1 (s), 164.0 (s), 174.5 (s); IR (Neat): ν = 1747 cm<sup>-1</sup>; MS (EI): *m/z* 180 (M<sup>+</sup>), 95 (100%); HRMS (EI): calcd for C<sub>11</sub>H<sub>16</sub>O<sub>2</sub>: 180.1150; found: 180.1157.

**3-Methyl-5,6,7,8,9,10,11,12,13,13a-decahydro-(4H)-cyclododeca[b]furan-2-one (42)** (Table 4, entry 9): Colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 1.07-1.16 (m, 1H), 1.24-1.73 (m, 16H), 1.86 (s, 3H), 2.05-2.17 (m, 1H), 2.37-2.45 (m, 2H), 4.90 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 9.1 (q), 19.4 (t), 22.3 (t), 22.8 (t), 23.4 (t), 24.2 (t), 24.2 (t), 24.4 (t), 25.2 (t), 25.2 (t), 29.9 (t), 82.5 (d), 124.8 (s), 162.0 (s), 174.7 (s); IR (Neat): ν = 1746 cm<sup>-1</sup>; MS (EI): *m/z* 236 (M<sup>+</sup>), 41 (100%); HRMS (EI): calcd for C<sub>15</sub>H<sub>24</sub>O<sub>2</sub>: 236.1776; found: 236.1801.

**3-Methyl-4,5-diphenyl-2(5H)-furanone (44)**<sup>[171]</sup> (Table 5, entry 2): Yellow oil, <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ: 2.17 (d, *J* = 1.6 Hz, 3H), 6.20 (dd, *J* = 1.6 Hz, 3.2 Hz, 1H), 7.21-7.38 (m, 10H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ: 10.3 (q), 83.6 (d), 124.0 (s), 127.4 (d), 127.9 (d), 128.6 (d), 129.0 (d), 129.5 (d), 131.3 (s), 134.9 (s), 158.2 (s), 174.3 (s); IR (Neat): ν = 1748 cm<sup>-1</sup>; MS (EI): *m/z* 250 (M<sup>+</sup>), 145 (100%); HRMS (EI): calcd for C<sub>17</sub>H<sub>14</sub>O<sub>2</sub>: 250.0994; found: 250.0979.

**3,5,5-Trimethyl-4-phenyl-2(5H)-furanone (45)**<sup>[21]</sup>: Colorless solid, <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ: 1.52 (s, 6H), 1.80 (s, 3H), 7.22 (dd, *J* = 1.6, 7.6 Hz, 2H), 7.41-7.49 (m, 3H); IR (CHCl<sub>3</sub>): ν = 1746 cm<sup>-1</sup>;

#### **General procedure for the preparation of α-amino ketone (A).**

To a solution of the amine (2 eq.) and triethylamine (2 eq.) in dimethoxyethane (DME) was added the α-halo-ketone at room temperature, and then the solution was refluxed. After addition of a saturated NaHCO<sub>3</sub> solution, the mixture was extracted with AcOEt. The organic phase was washed with brine, dried over MgSO<sub>4</sub>, filtered and concentrated to afford a residue, which was purified by column chromatography followed by distillation to afford the amino ketone.

#### **General procedure for the preparation of α-amino ketone (B).**

To a solution of the amine (3 eq.) in dimethoxyethane (DME) was added the α-halo-ketone at room temperature, and then the solution was refluxed. After addition of a saturated NaHCO<sub>3</sub> solution, the

mixture was extracted with AcOEt. The organic phase was washed with brine, dried over MgSO<sub>4</sub>, filtered and concentrated to afford a residue, which was purified by column chromatography followed by distillation to afford the amino ketone.

**2-(Benzyl-methyl-amino)-propiofenone (46):** According to *the General procedure for the preparation of  $\alpha$ -amino ketone (A)*, 2-chloro-propiofenone<sup>[22]</sup> was converted into the amino ketone **46** (81%), a yellow oil, after purification by column chromatography (silica gel, hexane/AcOEt = 80/20), followed by distillation (Kügelrohr, 170-210 °C at 1.5 mmHg): <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 1.31 (d,  $J$  = 6.4 Hz, 3H), 2.21 (s, 3H), 3.63 (s, 2H), 4.29 (q,  $J$  = 6.4 Hz, 1H), 7.19-7.27 (m, 5H), 7.42 (t,  $J$  = 6.4 Hz, 2H), 7.53 (t,  $J$  = 6.8 Hz, 1H), 7.99 (d,  $J$  = 7.2 Hz, 2H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.0 (q), 37.6 (q), 58.3 (t), 62.2 (d), 126.9 (d), 128.1 (d), 128.1 (d), 128.8 (d), 128.8 (d), 132.6 (d), 136.4 (s), 139.0 (s), 200.6 (s); IR (Neat): 1683 cm<sup>-1</sup>; MS (EI)  $m/z$  253 (M<sup>+</sup>), 91 (100%); HRMS (EI) calcd for C<sub>17</sub>H<sub>19</sub>NO: 253.1467, found: 253.1461.

**2-Dibenzylamino-propiofenone (48):** According to *the General procedure for the preparation of  $\alpha$ -amino ketone (A)*, 2-chloro-propiofenone was converted into the amino ketone **48** (68%), a yellow oil, after purification by column chromatography (silica gel, hexane/AcOEt = 80/20), followed by distillation (Kügelrohr, 250 °C at 1.5 mmHg): <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 1.35 (d,  $J$  = 6.8 Hz, 3H), 3.54 (d,  $J$  = 13.6 Hz, 2H), 3.68 (d,  $J$  = 13.2 Hz, 2H), 4.35 (q,  $J$  = 6.8 Hz, 1H), 7.16 (dd,  $J$  = 2.0 Hz, 8.0 Hz, 4H), 7.21-7.35 (m, 8H), 7.51 (tt,  $J$  = 1.2 Hz, 7.6 Hz, 1H), 7.60 (dd,  $J$  = 1.2 Hz, 8.4 Hz, 2H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.4 (q), 54.3 (t), 57.1 (d), 127.0 (d), 127.9 (d), 128.0 (d), 128.7 (d), 129.1 (d), 132.3 (d), 136.7 (s), 139.1 (s), 201.7 (s); IR (Neat): 1682 cm<sup>-1</sup>; MS (EI)  $m/z$  329 (M<sup>+</sup>), 181 (100%); HRMS (EI) calcd for C<sub>23</sub>H<sub>23</sub>NO: 329.1780, found: 329.1760.

**2-(*N,N*-Diallylamino)propiofenone (53):** According to *the General procedure for the preparation of  $\alpha$ -amino ketone (B)*, 2-bromo-propiofenone<sup>[23]</sup> was converted into the amino ketone **53** (92%), a pale yellow oil, after purification by column chromatography (silica gel, hexane/AcOEt = 90/10), followed by distillation (Kügelrohr, 140-160 °C at 2.0 mmHg): <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 1.23 (d,  $J$  = 6.8 Hz, 3H), 3.08 (dd,  $J$  = 7.2 Hz, 14.0 Hz, 2H), 3.23 (ddt,  $J$  = 1.6 Hz, 5.6 Hz, 14.4 Hz, 2H), 4.45 (q,  $J$  = 6.4 Hz, 1H), 5.09 (dq,  $J$  = 1.2 Hz, 10.0 Hz, 2H), 5.15 (dq,  $J$  = 1.2 Hz, 17.2 Hz, 2H), 5.73 –5.83 (m, 2H), 7.43 (tt,  $J$  = 1.2 Hz, 7.6 Hz, 2H), 7.53 (tt,  $J$  = 1.6 Hz, 7.2 Hz, 1H), 8.01 (dd,  $J$  = 1.2 Hz, 8.4 Hz, 2H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.7 (q), 53.4 (tx2), 58.7 (d), 117.2 (tx2), 128.0 (d), 128.7 (d), 132.4 (d), 136.3 (d), 136.7 (s), 201.5 (s); IR (Neat): 1684 cm<sup>-1</sup>; MS (EI)  $m/z$  229 (M<sup>+</sup>), 42 (100%); HRMS (EI) calcd for C<sub>15</sub>H<sub>19</sub>NO: 229.1467, found: 229.1467.

**2-(*N*-Benzyl-*N*-methylamino)acetophenone (61):** According to *the General procedure for the preparation of  $\alpha$ -amino ketone (B)*, phenacylchloride was converted into the amino ketone **61** (80%), a yellow oil, after purification by column chromatography (silica gel, hexane/AcOEt = 70/30), followed by distillation (Kügelrohr, 210-220 °C at 1.3 mmHg): <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 2.37 (s, 3H), 3.68 (s, 2H), 3.79 (s, 2H), 7.22-7.36 (m, 5H), 7.43 (t, *J* = 8.0 Hz, 2H), 7.55 (tt, *J* = 1.2 Hz, 7.2 Hz, 1H), 7.96 (dd, *J* = 0.8 Hz, 8.4 Hz, 2H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 42.8 (q), 62.0 (t), 63.1 (t), 127.2 (d), 128.2 (dx2), 128.3 (d), 129.1 (d), 133.0 (d), 136.0 (s), 138.2 (s), 197.6 (s); IR (Neat): 1682 cm<sup>-1</sup>, 1694 cm<sup>-1</sup>; MS (EI) *m/z* 239 (M<sup>+</sup>), 91 (100%); HRMS (EI) calcd for C<sub>16</sub>H<sub>17</sub>NO: 239.1310, found: 239.1306.

**2-(*N*-Benzyl-*N*-methylamino)-3,3-dimethyl-2-butanone (62):** According to *the General procedure for the preparation of  $\alpha$ -amino ketone (B)*, 1-chloropinacolone was converted into the amino ketone **62** (92%), a pale yellow oil, after purification by column chromatography (silica gel, hexane/AcOEt = 70/30), followed by distillation (Kügelrohr, 155-160 °C at 2.0 mmHg): <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 1.12 (s, 9H), 2.32 (s, 3H), 3.43 (s, 2H), 3.62 (s, 2H), 7.21-7.35 (m, 5H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 26.4 (qx3), 42.4 (q), 43.5 (s), 60.2 (t), 61.4 (t), 127.0 (d), 128.1 (d), 129.0 (d), 138.2 (s), 212.9 (s); IR (Neat): 1680 cm<sup>-1</sup>, 1714 cm<sup>-1</sup>; MS (EI) *m/z* 219 (M<sup>+</sup>), 91 (100%); HRMS (EI) calcd for C<sub>14</sub>H<sub>21</sub>NO: 219.1623, found: 219.1613.

**3-*N,N*-Diallylamino-4-heptenone (63):** According to *the General procedure for the preparation of  $\alpha$ -amino ketone (B)*, 3-bromo-4-heptanone was converted into the amino ketone **63** (63%), a yellow oil, after purification by column chromatography (silica gel, hexane/AcOEt = 95/5), followed by distillation (Kügelrohr, 95-110 °C at 3.0 mmHg): <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 0.84 (t, *J* = 7.2 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H), 1.48 (d.hept, *J* = 1.2 Hz, 6.4 Hz, 1H), 1.58 (sext, *J* = 7.6 Hz, 2H), 1.70 (d.hept, *J* = 1.2 Hz, 7.6 Hz, 1H), 2.41 (dt, *J* = 7.6 Hz, 16.8 Hz, 1H), 2.58 (dt, *J* = 7.2 Hz, 16.8 Hz, 1H), 3.05 (dd, *J* = 7.2 Hz, 14.4 Hz, 2H), 3.17 (dd, *J* = 5.6 Hz, 14.4 Hz, 2H), 3.23 (dd, *J* = 5.2 Hz, 8.8 Hz, 1H), 5.11 (dd, *J* = 1.2 Hz, 10.4 Hz, 2H), 5.17 (d, *J* = 17.2 Hz, 2H), 5.73-5.38 (m, 2H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 11.6 (q), 13.8 (q), 17.2 (q), 17.3 (q), 42.8 (t), 53.4 (tx2), 68.6 (d), 116.8 (tx2), 136.5 (dx2), 211.7 (s); IR (Neat): 1714 cm<sup>-1</sup>; MS (EI) *m/z* 209 (M<sup>+</sup>), 41 (100%); HRMS (EI) calcd for C<sub>13</sub>H<sub>23</sub>NO: 209.1780, found: 209.1806.

#### **General procedure for one-pot synthesis of $\gamma$ -lactam from $\alpha$ -amino ketone (A).**

To a solution of ethyl 2,2-dibromopropionate (1.2 eq.) in THF, cooled to -78 °C under argon, was added dropwise a solution of *tert*-butyllithium (4.8 eq.). The yellow solution was stirred for 3 h at -78 °C and allowed to warm to 0 °C. After 30 min, the resulting colorless or pale yellow reaction mixture was

warmed to room temperature and a solution of  $\alpha$ -amino ketone (1.0 eq.) in THF was added. After 0.5 h, MeOSOCl (ca. 3 eq.), prepared from MeOH and SOCl<sub>2</sub> at -10 °C, was added at room temperature. After 15-20 h, the reaction mixture was concentrated in vacuo, and MeOH was added and the solution was concentrated in vacuo. The residue was diluted with Et<sub>2</sub>O, acidified with 5% HCl and extracted with Et<sub>2</sub>O. The water phase was basified with 28% NH<sub>3</sub> and extracted with Et<sub>2</sub>O. The combined organic layer was dried over MgSO<sub>4</sub>, filtered and concentrated to give a residue, which was purified by column chromatography to afford the lactam.

**1,3,5-Trimethyl-4-phenyl-1,5-dihydro-2-pyrrolone (54):** According to *the general procedure for one-pot synthesis of  $\gamma$ -lactam from  $\alpha$ -amino ketone (A)*, the amino ketone **46** was converted into the  $\gamma$ -lactam **54** (quant.) as a pale yellow oil, after purification by column chromatography (silica gel, hexane/AcOEt = 50/50): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 1.17 (d,  $J$  = 6.8 Hz, 3H), 2.02 (d,  $J$  = 2.0 Hz, 3H), 3.07 (s, 3H), 4.33 (dq,  $J$  = 1.6 Hz, 6.8 Hz, 1H), 7.31 (dd,  $J$  = 1.2 Hz, 6.8 Hz, 2H), 7.37 (tt,  $J$  = 1.6 Hz, 7.2 Hz, 1H), 7.44 (tt,  $J$  = 1.6 Hz, 7.2 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 10.2 (q), 16.9 (q), 27.1 (q), 59.1 (d), 127.9 (d), 128.3 (d), 128.5 (d), 128.9 (s), 133.1 (s), 152.1 (s), 171.3 (s); IR (Neat):  $\nu$  = 1682 cm<sup>-1</sup>; MS (EI):  $m/z$  201 (M<sup>+</sup>), 186 (M<sup>+</sup>-Me, 100%); HRMS (EI): calcd for C<sub>13</sub>H<sub>15</sub>NO: 201.1154; found: 201.1149.

**1-Benzyl-3,5-dimethyl-4-diphenyl-1,5-dihydro-2-pyrrolone (55):** According to *the General procedure for one-pot synthesis of  $\gamma$ -lactam from  $\alpha$ -amino ketone (B)*, the amino ketone **48** was converted into the  $\gamma$ -lactam **55** (68%) as a pale yellow oil, after purification by column chromatography (silica gel, hexane/AcOEt = 80/20): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 1.12 (d,  $J$  = 6.8 Hz, 3H), 2.07 (d,  $J$  = 1.6 Hz, 3H), 4.22 (d,  $J$  = 15.2 Hz, 1H), 4.28 (dq,  $J$  = 1.6 Hz, 8.0 Hz, 1H), 5.23 (d,  $J$  = 15.2 Hz, 1H), 7.25-7.43 (m, 10H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 10.3 (q), 17.0 (q), 43.9 (t), 56.6 (d), 127.3 (d), 127.9 (d), 128.0 (d), 128.4 (d), 128.5 (s), 128.5 (d), 128.6 (d), 133.0 (s), 137.6 (s), 152.7 (s), 171.3 (s); IR (Neat):  $\nu$  = 1682 cm<sup>-1</sup>; MS (EI):  $m/z$  277 (M<sup>+</sup>), 91 (Bn, 100%); HRMS (EI): calcd for C<sub>19</sub>H<sub>19</sub>NO: 277.1467, found: 277.1475.

**1-Allyl-3,5-dimethyl-4-phenyl-1,5-dihydro-2-pyrrolone (60):** According to *the General procedure for one-pot synthesis of  $\gamma$ -lactam from  $\alpha$ -amino ketone (B)*, the amino ketone **53** was converted into the  $\gamma$ -lactam **60** (87%) as a pale yellow oil, after purification by column chromatography (silica gel, hexane/AcOEt = 70/30): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.14 (d,  $J$  = 6.8 Hz, 3H), 2.04 (d,  $J$  = 1.6 Hz, 3H), 3.75 (dd,  $J$  = 7.2 Hz, 15.6 Hz, 1H), 4.44 (dq,  $J$  = 1.6 Hz, 6.4 Hz, 1H), 4.57 (dd,  $J$  = 4.8 Hz, 16.0 Hz, 1H), 5.22 (dt,  $J$  = 1.2 Hz, 13.2 Hz, 2H), 5.80-5.90 (m, 1H), 7.32 (dd,  $J$  = 1.2 Hz, 6.8 Hz, 2H), 7.37 (t,  $J$  = 8.0 Hz, 1H), 7.44 (t,  $J$  = 8.0 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 10.2 (q), 17.0 (q), 42.8

(t), 56.9 (d), 117.3 (t), 128.0 (d), 128.4 (d), 128.5 (d), 128.6 (s), 133.0 (s), 133.7 (d), 152.6 (s), 171.0 (s); IR (Neat):  $\nu = 1682 \text{ cm}^{-1}$ ; MS (EI):  $m/z$  227 ( $M^+$ ), 226 (100%); HRMS (EI): calcd for  $C_{15}H_{17}NO$ : 227.1310; found: 227.1338.

**1,3-Dimethyl-4-phenyl-1,5-dihydro-2-pyrrolone (64):** According to the *General procedure for one-pot synthesis of g-lactam from  $\alpha$ -amino ketone (A)*, the amino ketone **61** was converted into the  $\gamma$ -lactam **64** (52%) as colorless needles, after purification by column chromatography (silica gel, hexane/AcOEt = 50/50), followed by recrystallization from ethyl acetate in hexane: mp 95-96 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 2.11$  (t,  $J = 1.6$  Hz, 3H), 3.13 (s, 3H), 4.17 (d,  $J = 2.0$  Hz, 2H), 7.34-7.48 (m, 5H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 10.7$  (q), 29.3 (q), 54.1 (t), 127.1 (d), 128.6 (d), 128.7 (d), 129.8 (s), 133.7 (s), 145.4 (s), 172.4 (s); IR ( $\text{CHCl}_3$ ):  $\nu = 1673 \text{ cm}^{-1}$ ; MS (EI):  $m/z$  187 ( $M^+$ , 100%); HRMS (EI): calcd for  $C_{12}H_{13}NO$ : 187.0997, found: 187.0983; elemental analysis calcd (%) for  $C_{12}H_{13}NO$ : H 7.00; C 76.98; N 7.48; found: H 6.99; C 76.64; N 7.37.

**4-tert-Butyl-1,3-dimethyl-1,5-dihydro-2-pyrrolone (65):** According to the *General procedure for one-pot synthesis of g-lactam from  $\alpha$ -amino ketone (A)*, the amino ketone **62** was converted into the  $\gamma$ -lactam **65** (53%) as a yellow oil, after purification by column chromatography (silica gel, hexane/AcOEt = 50/50):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 1.23$  (s, 9H), 1.95 (t,  $J = 1.6$  Hz, 3H), 3.02 (s, 3H), 3.76 (dd,  $J = 0.4$  Hz, 1.6 Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 10.7$  (q), 29.1 (q), 29.2 (qx3), 33.5 (s), 53.1 (t), 127.1 (s), 156.3 (s), 173.1 (s); IR (Neat):  $\nu = 1686 \text{ cm}^{-1}$ ; MS (EI):  $m/z$  167 ( $M^+$ ), 111 (100%); HRMS (EI): calcd for  $C_{10}H_{17}NO$ : 167.1310; found: 167.1292.

**1,5-Dimethyl-3,4-diphenyl-1,5-dihydro-2-pyrrolone (66):** According to the *General procedure for one-pot synthesis of g-lactam from  $\alpha$ -amino ketone (A)*, the amino ketone **46** was converted into the  $\gamma$ -lactam **66** (90%) as a pale yellow oil, after purification by column chromatography (silica gel, hexane/AcOEt = 50/50):  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.23 (d,  $J = 6.8$  Hz, 3H), 3.13 (s, 3H), 4.47 (q,  $J = 6.8$  Hz, 1H), 7.16-7.40 (m, 10H);  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 16.9 (q), 27.3 (q), 59.3 (d), 127.7 (d), 127.9 (d), 128.3 (d), 128.5 (d), 128.6 (d), 129.4 (d), 131.4 (s), 131.5 (s), 132.7 (s), 153.6 (s), 169.5 (s); IR ( $\text{CHCl}_3$ ):  $\nu = 1683 \text{ cm}^{-1}$ ; MS (EI)  $m/z$  263 ( $M^+$ , 100%); HRMS (EI) calcd for  $C_{18}H_{17}NO$ : 263.1310, found: 263.1304.

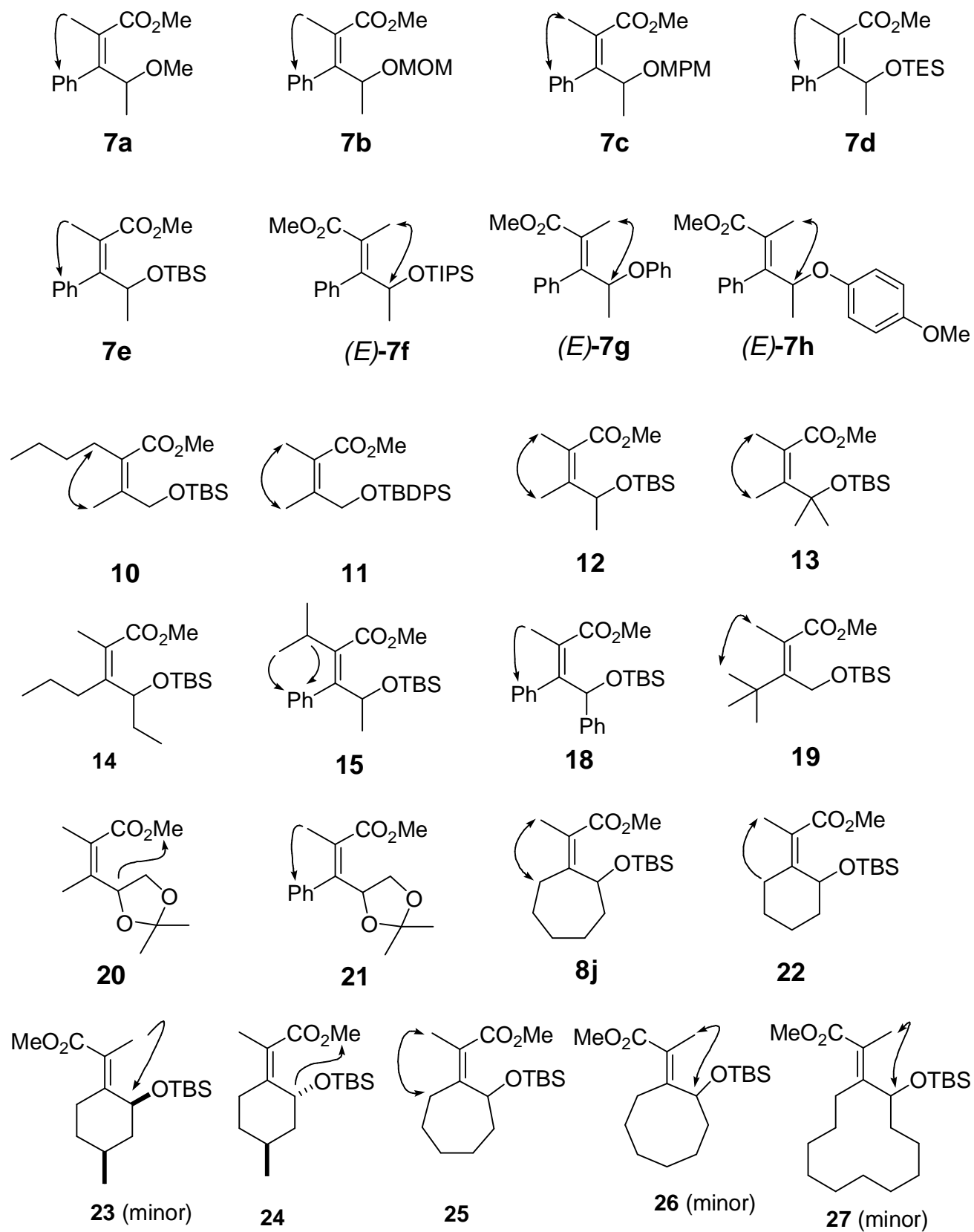
**3-Isopropyl-1,5-dimethyl-4-phenyl-1,5-dihydro-2-pyrrolone (67):** According to the *General procedure for one-pot synthesis of g-lactam from  $\alpha$ -amino ketone (A)*, the amino ketone **46** was converted into the  $\gamma$ -lactam **67** (60%) as a pale yellow oil, after purification by column chromatography

(silica gel, hexane/AcOEt = 80/20 to 70/30):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.10 (d,  $J$  = 6.8 Hz, 3H), 1.21 (d,  $J$  = 6.8 Hz, 3H), 1.30 (d,  $J$  = 6.8 Hz, 3H), 2.91 (hept,  $J$  = 7.2 Hz, 1H), 3.02 (s, 3H), 4.20 (q,  $J$  = 6.8 Hz, 1H), 7.21 (dd,  $J$  = 2.0 Hz, 6.4 Hz, 2H), 7.35-7.45 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 16.6 (q), 20.6 (q), 20.8 (q), 25.8 (d), 26.6 (q), 59.4 (d), 128.1 (d), 128.1 (d), 128.4 (d), 133.6 (s), 137.8 (s), 151.8 (s), 170.2 (s); IR (Neat):  $\nu$  = 1682  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  229 ( $\text{M}^+$ ), 186 ( $\text{M}^+ - i\text{Pr}$ , 100%); HRMS (EI): calcd for  $\text{C}_{15}\text{H}_{19}\text{NO}$ : 229.1467; found: 229.1483.

**3-Butyl-1,5-dimethyl-4-phenyl-1,5-dihydro-2-pyrrolone (68):** According to the *General procedure for one-pot synthesis of  $\gamma$ -lactam from  $\alpha$ -amino ketone (A)*, the amino ketone **46** was converted into the  $\gamma$ -lactam **68** (79%) as a pale yellow oil, after purification by column chromatography (silica gel, hexane/AcOEt = 60/40):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 0.87 (t,  $J$  = 7.2 Hz, 3H), 1.14 (d,  $J$  = 6.8 Hz, 3H), 1.24-1.66 (m, 4H), 2.34-2.47 (m, 2H), 3.05 (s, 3H), 4.29 (q,  $J$  = 6.4 Hz, 1H), 7.26-7.45 (m, 5H);  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 13.8 (q), 16.8 (q), 22.8 (t), 24.2 (t), 26.9 (q), 30.7 (t), 59.3 (d), 127.8 (d), 128.2 (d), 128.5 (d), 133.3 (s), 133.5 (s), 152.3 (s), 170.9 (s); IR (Neat):  $\nu$  = 1682  $\text{cm}^{-1}$ ; MS (EI):  $m/z$  243 ( $\text{M}^+$ ), 186 ( $\text{M}^+ - \text{Bu}$ , 100%); HRMS (EI): calcd for  $\text{C}_{16}\text{H}_{21}\text{NO}$ : 243.1623; found: 243.1644.

**1-Allyl-5-ethyl-3-methyl-4-propyl-1,5-dihydro-2-pyrrolone (69):** According to the *General procedure for one-pot synthesis of  $\gamma$ -lactam from  $\alpha$ -amino ketone (B)*, the amino ketone **63** was converted into the  $\gamma$ -lactam **69** (73%) as a yellow oil, after purification by column chromatography (silica gel, hexane/AcOEt = 70/30);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.51 (t,  $J$  = 7.2 Hz, 3H), 0.94 (t,  $J$  = 7.2 Hz, 3H), 1.43 (sext,  $J$  = 7.6 Hz, 1H), 1.51-1.60 (m, 1H), 1.69 (d. quint,  $J$  = 2.4 Hz, 7.2 Hz, 1H), 1.79-1.90 (m, 1H), 1.83 (s, 3H), 2.05-2.13 (m, 1H), 2.41 (dt,  $J$  = 8.0 Hz, 13.6 Hz, 1H), 3.50 (dd,  $J$  = 7.6 Hz, 15.6 Hz, 1H), 4.00 (s, 1H), 4.51 (dd,  $J$  = 4.8 Hz, 15.6 Hz, 1H), 5.15 (t,  $J$  = 10.0 Hz, 2H), 5.73-5.85 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 5.7 (q), 8.7 (q), 14.0 (q), 20.4 (t), 21.8 (t), 28.3 (t), 42.5 (t), 60.4 (d), 116.9 (t), 129.2 (s), 133.8 (d), 152.3 (s), 172.1 (s); IR (Neat):  $\nu$  = 1682  $\text{cm}^{-1}$ ; MS (EI):  $m/z$  207 ( $\text{M}^+$ ), 178 (100%); HRMS (EI): calcd for  $\text{C}_{13}\text{H}_{21}\text{NO}$ : 207.1623; found: 207.1622.

## NOE experiments



## Theoretical Calculations

TSZ1

E(RB+HF-LYP) = -816.650219152 hartree

Value of imaginary frequency = 0.08511i cm<sup>-1</sup>

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Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z
1	6	0.397712	-1.126808	-0.798177
2	6	2.237233	-0.745364	0.220687
3	6	2.709891	0.621487	-0.218918
4	8	0.357301	-0.201983	0.211055
5	3	-1.529341	-0.055138	-0.306238
6	8	-0.663988	-1.353164	-1.451275
7	1	3.092160	-3.016150	-1.758250
8	1	2.354671	-3.664758	-0.290047
9	1	1.391420	-3.494099	-1.763027
10	8	2.612252	1.593254	0.811270
11	1	3.775731	0.501237	-0.502604
12	1	2.164148	0.928667	-1.120110
13	6	3.272805	2.796052	0.484959
14	1	3.137141	3.480299	1.327344
15	1	4.352306	2.641095	0.322343
16	1	2.854992	3.261372	-0.423112
17	8	-1.988949	1.851298	-0.464060
18	6	-0.912381	2.778944	-0.304740
19	6	-3.081056	2.381031	-1.201655

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20	1	-0.098668	2.236970	0.179559
21	1	-1.234415	3.630739	0.310313
22	1	-0.579667	3.148102	-1.284793
23	1	-2.766122	2.675086	-2.212542
24	1	-3.836577	1.594992	-1.271575
25	1	-3.510242	3.255380	-0.692052
26	6	2.851859	-1.235332	1.505626
27	1	2.367187	-2.150457	1.854704
28	1	3.918107	-1.453208	1.342103
29	1	2.792841	-0.462302	2.276204
30	8	-3.048750	-0.920397	0.584805
31	6	-3.733379	-0.429199	1.727550
32	6	-3.078291	-2.345546	0.474518
33	1	-3.300703	-0.839723	2.650695
34	1	-4.800693	-0.688848	1.686213
35	1	-3.621569	0.657283	1.726535
36	1	-4.105631	-2.693552	0.300018
37	1	-2.689472	-2.808067	1.392057
38	1	-2.433270	-2.599490	-0.367844
39	6	1.704141	-1.638817	-0.779641
40	6	2.168369	-3.010983	-1.159840

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TSZ2

E(RB+HF-LYP) = -816.648705042 hartree

Value of imaginary frequency = 0.08765i cm<sup>-1</sup>

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	0.299525	-0.666694	-0.855495
2	6	2.041039	-0.647659	0.370518
3	6	2.539947	0.789307	0.464823
4	8	0.207410	-0.028630	0.365993
5	3	-1.700753	0.130910	-0.173213
6	8	-0.729211	-0.694452	-1.595868
7	1	3.044632	-2.196485	-2.164669
8	1	1.359382	-2.687083	-2.385862
9	8	3.960308	0.727579	0.339383
10	1	2.110537	1.386840	-0.348399
11	1	2.272296	1.248200	1.432013
12	6	4.554001	2.004645	0.306920
13	1	5.633419	1.859341	0.206634
14	1	4.193838	2.601621	-0.546998
15	1	4.355028	2.573472	1.231004
16	8	-3.112431	-1.064103	0.479658
17	6	-3.784257	-0.949544	1.725951
18	6	-2.967469	-2.416610	0.036920
19	1	-2.348172	-2.379810	-0.860532
20	1	-2.466978	-3.019302	0.806799
21	1	-3.951176	-2.852335	-0.184418
22	1	-4.806561	-1.346880	1.656360

23	1	-3.242678	-1.489632	2.515033
24	1	-3.823459	0.113449	1.974815
25	6	2.550871	-1.522304	1.486726
26	1	2.258865	-1.102737	2.456416
27	1	2.176892	-2.546065	1.408556
28	1	3.648128	-1.534654	1.462876
29	8	-2.393522	1.965632	-0.124246
30	6	-1.373670	2.966244	-0.114309
31	6	-3.564013	2.366827	-0.825537
32	1	-0.496156	2.505817	0.341583
33	1	-1.700312	3.839029	0.467256
34	1	-1.131754	3.279551	-1.138790
35	1	-4.021486	3.244618	-0.348456
36	1	-3.330309	2.605347	-1.872113
37	1	-4.262651	1.528037	-0.791178
38	6	1.586185	-1.202677	-0.883160
39	6	2.100009	-2.389188	-1.634971
40	1	2.277499	-3.265365	-0.987963

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TSZ3

E(RB+HF-LYP) = -816.644611755 hartree

Value of imaginary frequency = 0.08674i cm<sup>-1</sup>

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Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z

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1	6	0	-0.525612	-0.776094	0.757539
2	6	0	-2.232449	-0.832939	-0.530527
3	6	0	-2.719967	0.553914	-0.906016
4	8	0	-0.343329	-0.322955	-0.523567
5	3	0	1.489410	0.025711	0.133610
6	8	0	0.460436	-0.755372	1.554127
7	1	0	-3.415132	-1.943599	2.143860
8	1	0	-2.621455	-3.237363	1.238012
9	1	0	-1.764513	-2.422600	2.548108
10	8	0	-2.332665	1.569782	-0.014832
11	1	0	-2.421218	0.798406	-1.939960
12	1	0	-3.827517	0.472118	-0.912221
13	6	0	-3.037097	2.771935	-0.232538
14	1	0	-2.674184	3.495106	0.502965
15	1	0	-2.866476	3.175007	-1.244842
16	1	0	-4.122848	2.640898	-0.094047
17	8	0	2.042074	1.898555	0.087444
18	6	0	0.928090	2.787842	0.220459
19	6	0	3.237952	2.411076	0.656202
20	1	0	0.045834	2.244061	-0.122408
21	1	0	1.092080	3.690526	-0.384474
22	1	0	0.793231	3.073054	1.272424
23	1	0	3.103387	2.625077	1.725720
24	1	0	4.008009	1.645833	0.534703
25	1	0	3.551273	3.331094	0.142861

26	6	0	-2.705952	-1.871533	-1.524996
27	1	0	-3.342729	-2.609027	-1.024478
28	1	0	-3.250354	-1.456058	-2.381632
29	1	0	-1.826758	-2.405439	-1.903456
30	8	0	3.014280	-1.124229	-0.335160
31	6	0	3.754541	-1.092516	-1.546069
32	6	0	2.910458	-2.433916	0.231114
33	1	0	3.290180	-1.734564	-2.307626
34	1	0	4.789472	-1.423981	-1.380910
35	1	0	3.756538	-0.058133	-1.897898
36	1	0	3.896051	-2.781865	0.569263
37	1	0	2.509709	-3.139587	-0.509265
38	1	0	2.217025	-2.349579	1.069428
39	6	0	-1.843790	-1.234713	0.798893
40	6	0	-2.451876	-2.255183	1.711097

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TSZ4

E(RB+HF-LYP) = -816.643992492 hartree

Value of imaginary frequency = 0.08098i cm<sup>-1</sup>

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Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.015059	-0.175206	-1.223642
2	6	0	-2.397260	0.517518	0.253114
3	6	0	-1.623396	0.538618	1.576419

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4	8	0	-0.802520	1.073114	-0.695124
5	3	0	0.863909	0.144796	-0.140143
6	8	0	-0.095495	-0.723274	-1.882999
7	1	0	-3.867301	-2.035940	-0.539894
8	1	0	-4.079606	-0.918999	-1.893431
9	1	0	-2.829940	-2.160088	-1.962501
10	8	0	-0.412777	-0.217505	1.603056
11	1	0	-1.363519	1.569076	1.843753
12	1	0	-2.297386	0.160028	2.364977
13	6	0	-0.582670	-1.561667	2.048698
14	1	0	0.392113	-2.044946	1.957173
15	1	0	-0.901512	-1.584926	3.100785
16	1	0	-1.312406	-2.088533	1.424609
17	8	0	2.240921	-1.332912	0.077871
18	6	0	2.115863	-2.545509	-0.666539
19	6	0	3.367206	-1.313340	0.940035
20	1	0	1.238289	-2.418321	-1.301781
21	1	0	1.988142	-3.402056	0.011360
22	1	0	3.011781	-2.709152	-1.282068
23	1	0	3.289262	-2.094473	1.710595
24	1	0	4.296508	-1.469562	0.373156
25	1	0	3.393364	-0.329262	1.411307
26	6	0	-3.645897	1.369537	0.321044
27	1	0	-3.694137	2.018891	1.203415
28	1	0	-3.701923	1.995821	-0.575788
29	1	0	-4.531681	0.721724	0.317677

30	8	0	2.202173	1.669921	-0.021120
31	6	0	1.633821	2.870880	0.498597
32	6	0	2.762559	1.861224	-1.320272
33	1	0	3.164440	0.897330	-1.638265
34	1	0	3.571344	2.604316	-1.282572
35	1	0	1.993164	2.187418	-2.031677
36	1	0	2.401570	3.653518	0.576304
37	1	0	0.808394	3.213981	-0.135887
38	1	0	1.252628	2.637433	1.495193
39	6	0	-2.273884	-0.548341	-0.700450
40	6	0	-3.319904	-1.445783	-1.290253

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TSE1

E(RB+HF-LYP) = -816.646128093 hartree

Value of imaginary frequency = 0.09617i cm<sup>-1</sup>

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Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z
1	6	0.157500	-0.943067	0.907279
2	6	1.792502	-1.247107	-0.432793
3	6	2.817599	-0.313171	-1.037479
4	8	-0.104992	-0.730582	-0.425694
5	3	-1.697587	0.160813	0.338438
6	8	-0.769577	-0.729097	1.743469
7	1	3.041297	-1.966862	2.375489

8	1	3.166877	-0.245740	1.978792
9	1	1.866189	-0.824004	3.034078
10	8	2.907945	0.904445	-0.328626
11	1	3.795502	-0.833810	-1.037527
12	1	2.565052	-0.126565	-2.095050
13	6	3.899016	1.759665	-0.857505
14	1	3.892485	2.671375	-0.254621
15	1	4.901323	1.304392	-0.805716
16	1	3.694801	2.023563	-1.908318
17	8	-1.490820	2.119989	0.305820
18	6	-1.526836	2.720462	-0.984036
19	6	-0.321872	2.493074	1.049402
20	1	-2.429714	2.360588	-1.483147
21	1	-1.568968	3.815324	-0.899567
22	1	-0.644777	2.434772	-1.572949
23	1	0.586693	2.192974	0.512979
24	1	-0.371037	1.954371	1.996213
25	1	-0.320535	3.577231	1.225942
26	6	1.545915	-2.459074	-1.307482
27	1	2.468360	-3.061776	-1.336173
28	1	0.756821	-3.078879	-0.880054
29	1	1.289741	-2.193743	-2.340533
30	8	-3.404241	-0.426007	-0.419239
31	6	-4.679780	-0.146508	0.143061
32	6	-3.303810	-1.746684	-0.958873
33	1	-4.644385	0.872256	0.535734

34	1	-4.909801	-0.845365	0.958981
35	1	-5.465186	-0.214537	-0.622399
36	1	-2.259706	-1.880739	-1.246695
37	1	-3.573531	-2.493282	-0.200059
38	1	-3.964730	-1.853162	-1.829780
39	6	1.519201	-1.248384	0.983659
40	6	2.452811	-1.066005	2.140307

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TSE2

E(RB+HF-LYP) = -816.645620811 hartree

Value of imaginary frequency = 0.08726i cm<sup>-1</sup>

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Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z
1	6	2.134452	-1.095251	2.604943
2	6	1.482527	-0.957737	1.260946
3	6	0.166950	-0.592369	0.968358
4	6	2.064280	-0.676354	-0.037675
5	6	3.150885	0.368304	-0.096011
6	8	0.198163	-0.072416	-0.293807
7	3	-1.743542	0.124675	-0.006867
8	8	-0.941308	-0.603028	1.594239
9	1	2.851355	-1.927894	2.659168
10	1	2.667600	-0.193880	2.953983

11	1	1.351157	-1.297555	3.344544
12	8	3.851376	0.375627	-1.324618
13	1	2.677956	1.347531	0.089264
14	1	3.843856	0.186842	0.745389
15	6	4.840989	1.378570	-1.376381
16	1	5.321531	1.309094	-2.356011
17	1	4.408603	2.386163	-1.260938
18	1	5.605317	1.241582	-0.593388
19	8	-3.084980	-1.133977	-0.715099
20	6	-3.785796	-1.171190	-1.946666
21	6	-3.142961	-2.368801	0.004309
22	1	-3.673379	-0.191841	-2.418585
23	1	-3.372077	-1.942024	-2.612063
24	1	-4.854038	-1.373696	-1.784916
25	1	-2.757027	-3.190175	-0.614836
26	1	-4.178583	-2.590285	0.296918
27	1	-2.512523	-2.238817	0.885563
28	6	2.019182	-1.647606	-1.189583
29	1	1.996345	-1.144027	-2.159873
30	1	1.170212	-2.324500	-1.083891
31	1	2.946167	-2.241476	-1.158312
32	8	-2.423553	1.956095	0.273146
33	6	-2.775933	2.946225	-0.679107
34	6	-1.969423	2.506413	1.512699
35	1	-1.126148	3.189668	1.343134
36	1	-1.641570	1.661652	2.120895

37	1	-2.785318	3.050165	2.008204
38	1	-1.914466	3.583849	-0.922887
39	1	-3.594355	3.576710	-0.303900
40	1	-3.108473	2.429261	-1.582738

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TSE3

E(RB+HF-LYP) = -816.638140831 hartree

Value of imaginary frequency = 0.06946i cm<sup>-1</sup>

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Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z
1	6	-1.337877	0.915647	-1.157030
2	8	-0.363604	-0.064633	-1.378615
3	3	0.742356	0.010474	0.125910
4	8	-1.180401	2.089795	-1.506667
5	6	-1.762769	-1.096045	-0.450376
6	6	-1.379917	-1.801729	0.844916
7	8	-0.346426	-1.032801	1.487185
8	6	0.052565	-1.576185	2.736984
9	1	0.830155	-0.921887	3.139011
10	1	-0.792815	-1.605347	3.438153
11	1	0.454684	-2.593244	2.622562
12	1	-2.253258	-1.858318	1.513277
13	1	-1.009563	-2.823258	0.676431

14	1	-4.304690	0.416948	0.496463
15	1	-2.993878	0.714602	1.644614
16	1	-3.350546	1.898610	0.382486
17	8	1.273657	1.805777	0.790195
18	6	1.829627	2.551792	-0.304823
19	6	0.251772	2.555955	1.459072
20	1	-0.166440	1.908185	2.232526
21	1	0.688048	3.449100	1.927290
22	1	-0.529666	2.842487	0.747818
23	1	1.046372	2.759895	-1.042452
24	1	2.278771	3.483219	0.066076
25	1	2.609158	1.926830	-0.746484
26	6	-1.987961	-2.038974	-1.612027
27	1	-2.862174	-2.671303	-1.381453
28	1	-1.136847	-2.708169	-1.791338
29	1	-2.213657	-1.477939	-2.520358
30	6	-2.312431	0.226710	-0.386039
31	6	-3.284924	0.823102	0.584708
32	8	2.428065	-0.897452	-0.419606
33	6	2.552742	-1.223892	-1.806466
34	6	3.623591	-1.105026	0.315502
35	1	3.424423	-0.818720	1.350761
36	1	3.928354	-2.160608	0.280593
37	1	4.441315	-0.485657	-0.079596
38	1	2.772016	-2.293581	-1.928809
39	1	3.359826	-0.636171	-2.265643

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