

Electronic Supplementary Information

A mild and convenient synthesis of *N*-carbobenzyloxy ketimines

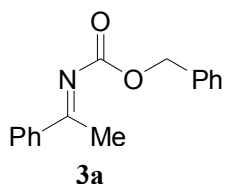
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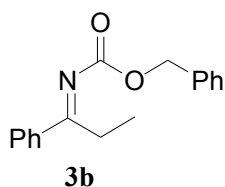
General. Infrared (IR) spectra were recorded on a Shimadzu FTIR-8100. ¹H NMR spectra were recorded on a JEOL EX270 (270 MHz) spectrometer; chemical shifts (δ) are reported in parts per million relative to tetramethylsilane. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. ¹³C NMR spectra were recorded on a JEOL JNM EX270 (67.5 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in parts per million relative to tetramethylsilane with the solvent resonance as the internal standard (CDCl₃; δ 77.0 ppm). High resolution mass spectra (HRMS) were recorded on a JEOL JMS-SX-102A mass spectrometer. Analytical TLC was performed on Merck precoated TLC plates (silica gel 60 GF254, 0.25 mm). Silica-gel column chromatography was carried out on silica gel 60N (Kanto Kagaku Co., Ltd., spherical, neutral, 63–210 μ m). Preparative thin-layer chromatography (PTLC) was carried out on silica gel Wakogel B-5F. THF was distilled under argon from sodium/benzophenone ketyl. All oxidation reactions were carried out under argon in dried glassware with magnetic stirring. Kugelrohr distillation was conducted by using Shibata glass tube oven GTO-350RS.

N-*tert*-Butylbenzenesufinimidoyl chloride (**1**)¹ was prepared according to the modified literature procedure of employing 1.3 equivalents of *N,N*-dichloro-*t*-butylamine, and **1** was stored in a refrigerator. *N*-Cbz amines (**2a-i**, **4a-d**) were prepared by the reaction of amines and benzyl chloroformate under Schotten-Baumann's method (Et₂O, aq. NaOH). Some primary amines were prepared by Leuckart's method.²

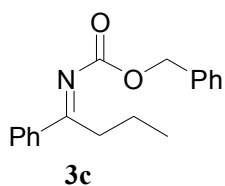
Oxidation of *N*-Cbz amines was performed by the procedure described in the text. The *N*-Cbz ketimines should be purified rapidly. Spectrum data were shown below.



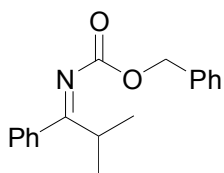
Mp 71-72 °C; ^1H NMR (270 MHz, CDCl_3) δ 2.34 (s, 3H), 5.28 (s, 2H), 7.31-7.46 (m, 8H), 7.86 (d, J = 7.0, 2H); ^{13}C NMR (67.8 MHz, CDCl_3) δ 19.8, 68.1, 127.5, 128.3, 128.4, 128.5, 131.8, 135.5, 136.7, 163.0, 169.3; IR (CHCl_3 , cm^{-1}) 1717, 1647, 1233, 1204, 698; HRMS (FAB+) Calculated for $\text{C}_{16}\text{H}_{16}\text{O}_2\text{N}$: 254.11810. Found 254.11793.



^1H NMR (270 MHz, CDCl_3) δ 1.18 (t, J = 7.6 Hz, 3H), 2.71 (q, J = 7.6 Hz, 2H), 5.25 (s, 2H), 7.24-7.48 (m, 8H), 7.77 (d, J = 7.0 Hz, 2H); ^{13}C NMR (67.8 MHz, CDCl_3) δ 12.2, 28.1, 68.0, 127.65, 128.3, 128.5, 131.4, 135.3, 135.6, 162.8, 174.5; IR (CHCl_3 , cm^{-1}) 1713, 1644, 1225, 1208, 698; HRMS (FAB+) Calculated for $\text{C}_{17}\text{H}_{18}\text{O}_2\text{N}$: 268.13375. Found 268.13358.

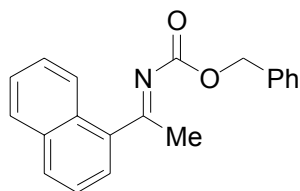


^1H NMR (270 MHz, CDCl_3) δ 0.87 (t, J = 7.3 Hz, 3H), 1.59 (m, 2H), 2.64 (dd, J = 7.8, 7.8 Hz, 2H), 5.26 (s, 2H), 7.33-7.47 (m, 8H), 7.77 (d, J = 7.3 Hz, 2H); ^{13}C NMR (67.8 MHz, CDCl_3) δ 13.9, 21.1, 36.4, 68.0, 127.7, 128.3, 128.4, 128.6, 131.4, 135.6, 136.0, 162.8, 173.5; IR (CHCl_3 , cm^{-1}) 1713, 1644, 1224, 698; HRMS (FAB+) Calculated for $\text{C}_{18}\text{H}_{20}\text{O}_2\text{N}$: 282.14940. Found 282.14934.



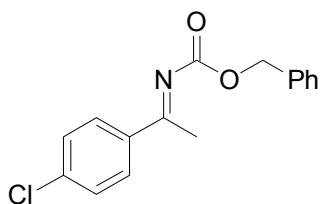
3d

^1H NMR (270 MHz, CDCl_3) δ 1.17 (d, $J = 6.9$ Hz, 6H), 3.03 (sept, $J = 6.9$ Hz, 1H), 5.05 (s, 2H), 7.11-7.37 (m, 10H); ^{13}C NMR (67.8 MHz, CDCl_3) δ 19.6, 36.8, 67.7, 126.4, 128.1, 128.3, 128.3, 128.4, 129.9, 135.4, 137.2, 162.6, 180.4; IR (CHCl_3 , cm^{-1}) 1713, 1651, 1210, 909, 785; HRMS (FAB+) Calculated for $\text{C}_{18}\text{H}_{20}\text{O}_2\text{N}$: 282.14940. Found 282.14912.



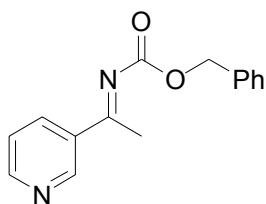
3e

^1H NMR (270 MHz, CDCl_3) δ 2.49 (s, 3H), 5.16 (brs, 2H), 7.26-7.51 (10H, m), 7.84 (d, $J = 6.5$ Hz, 2H); ^{13}C NMR (67.8 MHz, CDCl_3) δ 68.0, 124.6, 125.1, 126.3, 127.0, 128.2, 128.4, 133.5, 135.3, 136.1, 161.9; IR (CHCl_3 , cm^{-1}) 3019, 1732, 1509, 1225, 1208, 785, 738; HRMS (FAB+) Calculated for $\text{C}_{20}\text{H}_{18}\text{O}_2\text{N}$: 304.13375. Found 304.13206.



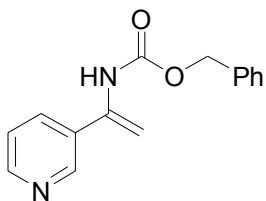
3g

^1H NMR (270 MHz, CDCl_3) δ 2.33 (s, 3H), 5.29 (s, 2H), 7.33-7.44 (m, 7H), 7.81 (d, $J = 8.9$ Hz, 2H); ^{13}C NMR (67.8 MHz, CDCl_3) δ 19.8, 68.2, 128.5, 128.5, 128.6, 128.7, 129.0, 135.1, 135.4, 138.2, 162.8, 168.2; IR (CHCl_3 , cm^{-1}) 1717, 1649, 1229, 909



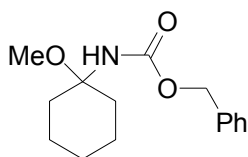
3i

^1H NMR (270 MHz, CDCl_3) δ 2.38 (s, 3H), 5.30 (s, 2H), 7.33-7.45 (m, 6H), 8.20 (m, 1H), 8.70 (dd, J = 1.6, 4.8 Hz, 1H), 9.06 (d, J = 2.3 Hz, 1H); ^{13}C NMR (67.8 MHz, CDCl_3) δ 19.6, 68.3, 123.3, 128.5, 128.6, 132.3, 134.8, 135.3, 149.0, 152.5, 162.5, 167.5; IR (CHCl_3 , cm^{-1}) 1721, 1653, 1231, 754; Calculated for $\text{C}_{15}\text{H}_{15}\text{O}_2\text{N}_2$: 255.11336. Found 255.11384.



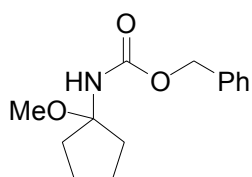
3i'

^1H NMR (270 MHz, CDCl_3) δ 4.99 (s, 1H), 5.17 (s, 2H), 5.63 (s, 1H), 6.59 (brs, 1H), 7.24-7.36 (m, 6H), 7.71 (m, 1H), 8.54 (dd, J = 1.5, 4.8 Hz, 1H), 8.67 (d, J = 1.6 Hz, 1H); ^{13}C NMR (67.8 MHz, CDCl_3) δ 67.2, 123.2, 128.3, 128.4, 128.6, 133.5, 133.7, 135.8, 138.1, 147.5, 149.7; IR (CHCl_3 , cm^{-1}) 3432, 1783, 1514; HRMS (FAB+) Calculated for $\text{C}_{15}\text{H}_{15}\text{O}_2\text{N}_2$: 255.11336. Found 255.11293.



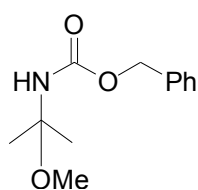
7a

^1H NMR (270 MHz, CDCl_3) δ 1.3-2.0 (m, 10H), 3.20 (s, 3H), 5.03 (brs, 1H), 5.08 (s, 2H), 7.2-7.4 (m, 5H); ^{13}C NMR (67.8 MHz, CDCl_3) δ 22.3, 25.2, 34.1, 48.1, 66.2, 85.2, 128.0, 128.4, 136.4, 154.2; IR (CHCl_3 , cm^{-1}) 3440, 1732, 1505; HRMS (FAB+) Calculated for $\text{C}_{15}\text{H}_{22}\text{O}_3\text{N}$: 264.15997. Found 264.15951.



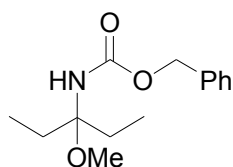
7b

^1H NMR (270 MHz, CDCl_3) δ 1.6-2.2 (m, 8H), 3.19 (s, 3H), 5.09 (s, 2H), 5.48 (brs, 1H), 7.3-7.4 (m, 5H); ^{13}C NMR (67.8 MHz, CDCl_3) δ 22.7, 36.5, 49.7, 94.4, 127.9, 128.0, 128.4, 136.3; IR (CHCl_3 , cm^{-1}) 1732, 1503; HRMS (FAB+) Calculated for $\text{C}_{14}\text{H}_{20}\text{O}_3\text{N}$: 250.14432. Found 250.14426.



7c

^1H NMR (270 MHz, CDCl_3) δ 1.53 (s, 6H), 3.21 (s, 3H), 5.07 (s, 2H), 5.22 (brs, 1H), 7.3-7.4 (m, 5H); ^{13}C NMR (67.8 MHz, CDCl_3) δ 25.9, 28.6, 49.2, 66.2, 84.4, 128.0, 128.0, 128.4, 136.3, 154.2; IR (CHCl_3 , cm^{-1}) 1732, 1507; HRMS (FAB+) Calculated for $\text{C}_{12}\text{H}_{18}\text{O}_3\text{N}$: 224.12867. Found 224.12805.



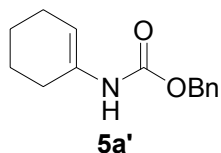
7d

^1H NMR (270 MHz, CDCl_3) δ 0.83 (t, $J = 7.4$ Hz, 6H), 1.69-1.99 (m, 4H), 3.16 (s, 3H), 4.95 (brs, 1H), 5.08 (s, 2H), 7.31-7.35 (m, 5H); ^{13}C NMR (67.8 MHz, CDCl_3) δ 7.4, 25.9, 48.4, 66.2, 89.3, 127.9, 127.9, 128.4, 136.4, 154.0; IR (CHCl_3 , cm^{-1}) 3441, 1734, 1507, 909; Calculated for $\text{C}_{14}\text{H}_{22}\text{O}_3\text{N}$: 252.15997. Found 252.15906.

Typical experimental procedure for synthesis of ene carbamate **5a** (Table 2, Entry 1, Scheme 3): to a stirred solution of *N*-Cbz cyclohexylamine (100.2 mg, 0.43 mmol) in dry THF (2 mL) was added a solution of *n*-BuLi (1.60 N in hexane, 0.31 mL, 0.50 mmol) at -78 °C, and the yellow solution was stirred for 20 min at the same temperature. A solution of **1** (136 mg, 0.63 mmol) in THF (1 mL) was added at -78 °C, and the reaction mixture was stirred for 30 min at the same temperature. MeOH (0.5 mL) was then added at -78 °C and the mixture was stirred at room temperature for 1 h. The reaction

was quenched by adding saturated NaHCO₃, and the mixture was extracted with AcOEt (three times). The combined organic extracts were washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuo. The crude product was purified by thin layer chromatography on silica gel (hexane/AcOEt) to afford **7a** (90.8 mg, 0.34 mmol).

Kugelrohr distillation of **7a** (90.8 mg, 0.34 mmol) gave **5a'** (79.1 mg, 0.34 mmol) as a colorless oil.



Cyclohex-1-enylcarbamic acid benzyl ester (**5a'**)³

¹H NMR (500 MHz, C₆D₆) δ 1.27-1.44 (m, 4H), 1.70-2.00 (m, 4H), 5.04 (s, 2H) 5.59 (brs, 1H), 6.03 (brs, 1H), 7.05-7.24 (m, 5H); ¹³C NMR (125 MHz, C₆D₆) δ 22.4, 22.8, 24.1, 27.7, 66.5, 109.5, 128.2, 128.5, 128.6, 132.5, 137.3, 153.4.

¹ Matsuo, J.-i.; Iida, D.; Tatani, K.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 223.

² Dalmolen, J.; Tiemersma-Wegman, T. D.; Nieuwenhuijzen, J. W.; van der Sluis, M.; van Echten, E.; Vries, T. R.; Kaptein, B.; Broxterman, Q. B.; Kellogg, R. M. *Chem. Eur. J.* **2005**, *11*, 5619-5624.

³ Matsubara, R.; Vital, P.; Nakamura, Y.; Kiyohara, H.; Kobayashi, S. *Tetrahedron* **2004**, *60*, 9769-9784.