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. $^1$H NMR spectra were recorded on a JEOL EX270 (270 MHz) spectrometer; chemical shifts ($\delta$) 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. $^{13}$C 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 (CDCl$_3$; $\delta$ 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 $\mu$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-Butylenesulfimidoyl 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 (Et$_2$O, 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.

\[
\text{Ph} \quad \text{O} \quad \text{O} \quad \text{Ph} \\
\text{Me}
\]

\[3a\]

Mp 71-72 °C; \(^1\)H NMR (270 HHz, CDCl\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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 C\(_{16}\)H\(_{16}\)O\(_2\)N: 254.11810. Found 254.11793.

\[
\text{Ph} \quad \text{O} \quad \text{O} \quad \text{Ph} \\
\]

\[3b\]

\(^1\)H NMR (270 HHz, CDCl\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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 C\(_{17}\)H\(_{18}\)O\(_2\)N: 268.13375. Found 268.13358.

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\text{Ph} \quad \text{O} \quad \text{O} \quad \text{Ph} \\
\]

\[3c\]

\(^1\)H NMR (270 HHz, CDCl\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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 C\(_{18}\)H\(_{20}\)O\(_2\)N: 282.14940. Found 282.14934.
$^1$H NMR (270 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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 C$_{18}$H$_{20}$O$_2$N: 282.14940. Found 282.14912.

$^1$H NMR (270 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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 C$_{20}$H$_{18}$O$_2$N: 304.13375. Found 304.13206.

$^1$H NMR (270 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 19.8, 68.2, 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

$^1$H 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, 149.0, 152.5, 162.5, 167.5; IR (CHCl$_3$, cm$^{-1}$) 1721, 1653, 1231, 754; Calculated for C$_{15}$H$_{15}$O$_2$N$_2$: 255.11336. Found 255.11384.

3i’

$^1$H 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 C$_{15}$H$_{15}$O$_2$N$_2$: 255.11336. Found 255.11293.

7a

$^1$H 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 C$_{15}$H$_{22}$O$_3$N: 264.15997. Found 264.15951.
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')

H 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.