Selective addition of carbamoylsilane to vicinal diketones:

Highly efficient synthesis of β-keto-α-hydroxyamides

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I  Experimental section
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I  Experimental section

$^1$H and $^{13}$C NMR spectra were recorded on Bruker AR600 MHz spectrometer in CDCl$_3$ as a solvent and TMS as an internal standard. Peak values are shown in δ (ppm). IR spectra were recorded on IMPACT-410 spectrophotometer. Elemental analysis was performed on an EA-1108 analyzer. Melting points were uncorrected. Toluene was distilled from sodium-benzophenone ketyl immediately before use. The monitoring of reaction and checking of purity of the product were done using pre-coated silica gel plates and visualization using iodine/UV lamp.

General procedure for the preparation of β-keto-α-siloxyamides 3 or 5

A Schlenk tube fitted with a Teflon vacuum stopcock and micro stirbar was flame-heated under vacuum and refilled with Ar. Vicinal diketones 2 (0.50 mmol) and 1.5 ml of anhydrous toluene was added at ice bath temperature. After 20 min, 1.2 equiv of carbamoylsilane (0.60 mmol) was added, and the reaction mixture was stirred at 110 °C until complete consumption of the carbamoylsilane (TLC). Volatiles were then removed under vacuum and the residue was chromatographed using petroleum ether–EtOAc as eluent to obtain β-keto-α-siloxyamides 3 (or 5).

II  $^1$H NMR data, $^{13}$C NMR data, IR and elemental analysis data of 3a-f and 5a-f

Compound 3a: White solid, mp 125–127 °C. IR: 1651, 1395, 1245, 1112 cm$^{-1}$. $^1$H NMR (600 MHz, CDCl$_3$): δ = 7.87–7.32 (m, 10H), 3.00 (s, 3H), 2.85 (s, 3H), 0.11 (s, 9H). $^{13}$C NMR (151 MHz, CDCl$_3$): δ = 197.2, 170.6, 139.1, 136.0, 132.2, 130.0, 128.3, 128.0, 127.8, 88.7, 38.3, 36.9, 2.0. Anal. Calcd for C$_{20}$H$_{25}$NO$_3$Si: C, 67.57; H, 7.09; N, 3.94. Found: C, 67.31; H, 7.13; N, 3.77.

Compound 3b: Colourless liquid. IR: 1719, 1653, 1255, 1153, 1098 cm$^{-1}$. $^1$H NMR: δ = 2.94 (s, 3H), 2.91 (s, 3H), 2.24(s, 3H), 1.58 (s, 3H), 0.16(s, 9H). $^{13}$C NMR: δ = 208.1, 170.1, 84.6, 37.3, 36.6, 24.2, 24.1, 1.5. Anal. Calcd for C$_{10}$H$_{21}$NO$_3$Si: C, 51.91; H, 9.15; N, 6.05. Found: C, 51.86; H, 9.09; N, 6.21.

Compound 3c: Colourless liquid. IR: 1720, 1655, 1393, 1254, 1150, 1105 cm$^{-1}$. $^1$H NMR: δ = 2.92 (s, 3H), 2.87 (s, 3H), 2.73, 2.52, 2.05 (qqq, J = 7.2 Hz, 2H), 2.19, 1.56 (ss, 3H), 1.06, 0.87 (tt, J = 7.2 Hz, 3H), 0.17, 0.15 (ss, 9H). $^{13}$C NMR: δ = 210.1, 207.6, 170.2, 169.7, 87.7, 84.6, 37.3, 36.7, 36.6, 30.1, 29.3, 25.6, 24.6, 8.2, 7.7, 1.6, 1.5. Anal. Calcd for C$_{11}$H$_{23}$NO$_3$Si: C, 53.84; H, 9.45; N, 5.71. Found: C, 53.62; H, 9.20; N, 5.48.

Compound 3d: Colourless liquid. IR: 1719, 1651, 1390, 1252, 1150 1099, 1058 cm$^{-1}$. $^1$H NMR: δ = 2.93 (s, 3H), 2.89 (s, 3H), 2.21, 1.57 (ss, 3H), 2.67–1.17 (m, 4H), 0.92 (t, J = 7.2 Hz, 3H), 0.17, 0.16 (ss, 9H). $^{13}$C NMR: δ = 210.0, 207.7, 170.2, 169.7, 87.4, 84.7, 39.4, 37.9, 37.4, 37.3, 36.7, 36.6, 25.6, 24.5, 17.0, 16.9, 14.3, 13.7, 1.6, 1.5. Anal. Calcd for C$_{12}$H$_{25}$NO$_3$Si: C, 55.56; H, 9.71; N, 5.40. Found: C, 55.64; H, 9.55; N, 5.31.

Compound 3e: Yellowish solid, mp 82.0–83.0 °C. IR: 1731, 1639, 1395, 1253, 1182, 1132 cm$^{-1}$. $^1$H NMR: δ = 7.39–7.33 (m, 5H), 3.00, 2.99 (ss, 3H), 2.78, 2.77 (ss, 3H), 2.05, 2.04 (ss,
Compound 3e: Colourless liquid. IR: 1696, 1646, 1448, 1393, 1250, 1160 cm$^{-1}$. $^1$H NMR: $\delta = 8.06–7.41$ (m, 5H), 2.99 (s, 3H), 2.95 (s, 3H), 1.81 (s, 3H), 0.15 (s, 9H). $^{13}$C NMR: $\delta = 198.0, 171.1, 134.2, 132.9, 129.5, 128.9, 128.6, 125.9, 81.7, 44.1, 37.7, 37.2, 24.6, 23.9, 23.4, 22.2. Anal. Calcd for C$_{15}$H$_{23}$NO$_3$Si: C, 68.42; H, 8.04; N, 5.32. Found: C, 68.20; H, 7.98; N, 5.57.

Compound 5a: Yellowish liquid. IR: 1661, 1593, 1446, 1394, 1248, 1104 cm$^{-1}$. $^1$H NMR: $\delta = 7.93–7.34$ (m, 10H), 4.90–4.65(m, 2H), 3.18, 2.97 (ss, 3H), 2.86 (s, 3H), 0.09, 0.02 (ss, 9H). $^{13}$C NMR: $\delta = 197.0, 171.9, 138.9, 135.6, 132.6, 130.2, 128.5, 127.9, 89.0, 79.9, 79.4, 56.2, 54.6, 34.4, 33.1, 2.1. Anal. Calcd for C$_{21}$H$_{27}$NO$_4$Si: C, 65.42; H, 7.06; N, 3.63. Found: C, 65.18; H, 7.19; N, 3.41.

Compound 5b: Colourless liquid. IR: 1721, 1666, 1458, 1439, 1253, 1151 cm$^{-1}$. $^1$H NMR: $\delta = 4.95–4.47$ (m, 2H), 3.29, 3.28, 3.18, 3.17 (ssss, 3H), 2.94, 2.93, 2.89, 2.88 (ssss, 3H), 2.26, 2.25, 2.18, 2.17 (ssss, 3H), 1.59, 1.58, 1.57, 1.56 (ssss, 3H), 0.16, 0.15, 0.15, 0.14 (ssss, 9H). $^{13}$C NMR: $\delta = 208.2, 206.5, 171.5, 170.9, 85.1, 84.8, 80.3, 78.8, 55.8, 55.1, 33.7, 33.5, 24.3, 24.1, 24.0, 23.9, 1.6, 1.5. Anal. Calcd for C$_{11}$H$_{23}$NO$_4$Si: C, 50.54; H, 7.06; N, 3.63. Found: C, 50.28; H, 8.65; N, 5.12.

Compound 5c: Yellowish liquid. IR: 1723, 1663, 1458, 1393, 1253, 1151 cm$^{-1}$. $^1$H NMR: $\delta = 5.02–4.48$ (m, 2H), 3.33, 3.32, 3.21, 3.19 (ssss, 3H), 2.97, 2.94, 2.89, 2.85 (ssss, 3H), 2.83–2.05 (m, 2H), 2.26, 2.17, 1.63, 1.60 (ssss, 3H), 1.09, 0.92 (tt, $J = 7.8$ Hz, 3H), 0.20, 0.18 (ss, 9H). $^{13}$C NMR: $\delta = 211.3, 207.8, 171.8, 88.7, 84.9, 80.4, 80.3, 79.1, 78.9, 56.1, 56.0, 55.2, 34.1, 33.8, 33.5, 30.1, 29.8, 29.7, 29.2, 25.7, 25.4, 24.5, 8.4, 8.1, 7.7, 7.6, 1.8, 1.7. Anal. Calcd for C$_{12}$H$_{25}$NO$_4$Si: C, 52.33; H, 9.15; N, 5.09. Found: C, 52.58; H, 9.36; N, 5.30.

Compound 5d: Colourless liquid. IR: 1719, 1664, 1393, 1256, 1147, 1100 cm$^{-1}$. $^1$H NMR: $\delta = 5.02–4.50$ (m, 2H), 3.33, 3.31, 3.21, 3.20 (ssss, 3H), 2.96, 2.89 (ss, 3H), 2.74–1.97 (m, 2H), 2.25, 2.17, 1.62, 1.59 (ssss, 3H), 1.74–1.24 (m, 4H), 0.94, 0.93 (ss, 3H), 0.19, 0.18 (ss, 9H). $^{13}$C NMR: $\delta = 210.4, 208.9, 171.7, 171.0, 88.35, 87.8, 85.3, 85.0, 80.4, 80.2, 79.1, 78.9, 56.1, 56.0, 55.2, 39.3, 39.0, 38.2, 37.8, 33.7, 33.6, 25.7, 25.4, 24.6, 24.4, 17.2, 16.9, 16.7, 14.3, 14.2, 13.7, 1.8, 1.7, 1.3. Anal. Calcd for C$_{13}$H$_{27}$NO$_4$Si: C, 53.94; H, 9.40; N, 4.84. Found: C, 53.68; H, 9.16; N, 4.60.

Compound 5e: Colourless liquid. IR: 1730, 1648, 1449, 1396, 1251, 1125 cm$^{-1}$. $^1$H NMR:
\[ \delta = 7.47 - 7.36 \text{ (m, 5H), 4.89 - 4.38 \text{ (m, 2H), 3.42, 2.99 \text{ (ss, 3H), 2.79, 2.71 \text{ (ss, 3H), 2.12, 2.09 \text{ (ss, 3H), 0.26, 0.23 \text{ (ss, 9H).} }}] \\
\] 13C NMR: \[ \delta = 203.7, 203.6, 172.2, 172.0, 138.6, 138.5, 128.9, 128.6, 128.5, 126.2, 125.8, 89.0, 88.8, 80.3, 79.0, 56.6, 55.1, 34.6, 32.0, 27.6, 27.4, 2.3, 2.2. \]


Compound 5e': Slightly brown liquid. IR: 1651, 1451, 1396, 1254, 1172 cm\(^{-1}\). 1H NMR: \[ \delta = 8.10 - 7.42 \text{ (m, 5H), 4.95 - 4.70 \text{ (m, 2H), 3.28, 3.19 \text{ (ss, 3H), 3.01, 2.98 \text{ (ss, 3H), 1.85, 1.83 \text{ (ss, 3H), 0.18, 0.14 \text{ (ss, 9H).} }}] } \\
\] 13C NMR: \[ \delta = 197.8, 196.7, 172.5, 172.2, 134.2, 134.0, 133.1, 132.9, 129.8, 129.7, 128.3, 84.4, 84.3, 80.2, 79.0, 56.1, 55.1, 33.8, 33.6, 25.3, 25.0, 1.8. \]


Compound 5f: Yellowish liquid. IR: 1655, 1446, 1393, 1251, 1104 cm\(^{-1}\). 1H NMR: \[ \delta = 7.45 - 7.35 \text{ (m, 5H), 4.88 - 4.36 \text{ (m, 2H), 3.41, 2.97 \text{ (ss, 3H), 2.77, 2.69 \text{ (ss, 3H), 2.65 - 2.57 \text{ (m, 1H), 2.06 - 1.87 \text{ (m, 2H), 0.88, 0.85 \text{ (dd, } J = 6.6 \text{ Hz, 3H), 0.55, 0.51 \text{ (dd, } J = 6.6 \text{ Hz, 3H), 0.26, 0.23 \text{ (ss, 9H).} }}] } \\
\] 13C NMR: \[ \delta = 197.3, 195.8, 172.1, 135.1, 132.9, 132.6, 129.8, 128.5, 128.2, 128.1, 126.3, 125.9, 87.1, 86.7, 80.1, 79.5, 56.4, 55.2, 46.7, 34.2, 33.9, 24.2, 24.1, 24.0, 22.4, 22.3, 1.9. \]

Anal. Caled for C19H31NO4Si: C, 62.43; H, 8.55; N, 3.83. Found: C, 62.28; H, 8.75; N, 3.62.

### III 1H NMR and 13C NMR spectra of 3a-f and 5a-f

**1H NMR of 3a**

![1H NMR spectrum of 3a](image-url)
$^{13}$C NMR of 3a

$^1$H NMR of 3b
$^{13}$C NMR of 3b

$^1$H NMR of 3c
$^{13}$C NMR of 3c

$^1$H NMR of 3d
$^{13}$C NMR of 3d

$^1$H NMR of 3e
$^{13}$C NMR of 3e'

$^1$H NMR of 3f
$^{13}$C NMR of 3f

$^1$H NMR of 5a
$^{13}$C NMR of $5b$

$^1$H NMR of $5c$
$^{13}$C NMR of 5c

$^{1}$H NMR of 5d
$^{13}$C NMR of 5d

$^1$H NMR of 5e
$^{13}$C NMR of 5f