[Supporting Information]

Catalyst-free nucleophilic addition reactions of silyl glyoxylates in water

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1. General information

Chemicals and analytical grade solvents were purchased from commercial suppliers and used without further purification unless otherwise stated. General $^1$H and $^{13}$C NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer. Chemical shifts were reported in ppm and the coupling constants $J$ are given in Hz. CHCl$_3$ ($\delta = 7.26$ ppm) served as an internal standard for $^1$H NMR; while CDCl$_3$ ($\delta = 77.0$ ppm) was used as an internal standard for $^{13}$C NMR. HRMS data were obtained on a Bruker Apex II mass instrument (ESI).

Thiols were purchased from commercial suppliers. Silyl glyoxylates were prepared according to the literature procedures.$^1$

Reference

2. Filtration-based procedure for 3f

![Diagram of filtration process]

Figure 1. The appearance of the reaction for 3f.

The mixture of 4-methylbenzenethiol (0.3 mmol) and 4-bromobenzyl 2-oxo-2-(triethylsilyl)acetate (0.2 mmol) in 1 mL H₂O were stirred at room temperature. After stirring for 3 hours, the mixture was filtrated and washed with water to afford the desired product 3f.

3. Other nucleophile investigation
4. Mechanistic investigation

(1) Control experiments in homogeneous reaction condition.

![Figure 2](image1.png)

**Figure 2.** The appearance of the reaction in homogeneous reaction conditions.

The starting material of silyl glyoxylate is yellow oil and the reaction progress can be monitored approximately by visualization of the change of color (the yellow oil disappeared). The reaction between 1a and 2a was conducted under homogenous conditions and the reaction phenomenon have shown that the reaction rates order is: DMF/H$_2$O (100:1) > DMF. The ratio of addition product to Brook rearrangement product (41:1) in DMF/H$_2$O is also better than the reaction (11:1) in DMF. These results suggested that the solvent polarity and hydrogen bonding may be important for rate acceleration.

(2) Control experiments of nucleophilies

![Figure 3](image2.png)

**Figure 3.** The appearance of the reaction with different nucleophilies
The starting material of silyl glyoxylate is yellow oil and the reaction progress can be monitored approximately by visualization of the change of color (the yellow oil disappeared). The reaction phenomenon have shown that the reaction rates with \(n\)-propylthiol (lipophilicity) as the nucleophile is obviously faster than the reaction with 3-mercaptopropanol (hydrophilicity) as the nucleophile.

From two sets of control experiments, we can see that the rate acceleration and the higher ratio of addition product to Brook rearrangement product were observed when the reaction was performed in water or in DMF/H\(_2\)O. However, where the chemistry occurs at the interface or in an oil phase is currently unclear.

**The procedure for 3ad**

A mixture of 3-mercaptopropanol (0.2 mmol) and 4-bromobenzyl 2-oxo-2-(triethylsilyl)acetate (0.1 mmol) in H\(_2\)O (1 mL) were stirred at room temperature. After stirring for 20 hours, the mixture was extracted with EtOAc and washed with water to afford the desired product 3ad. Note: the product 3ad was not stable when the reaction mixture was purified by silica gel chromatography. However, the desired product could be purified by extraction and the crude product was identified by \(^1\)H NMR, \(^{13}\)C NMR and HRMS.
3ad: HRMS calcd. for [M+Na]⁺ 393.1532, found 393.1527.
5. General procedure for catalyst-free nucleophilic addition reactions of silyl glyoxylates with thiols in water

The mixture of thiols 1 (0.2 mmol), silyl glyoxylates 2 (0.1 mmol) in 1 mL H₂O were stirred at room temperature. After stirring for the indicated time, the mixture was further purified by silica gel chromatography to afford the desired product 3.

3a: 81% yield; yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 7.40 (s, 5H), 7.19 (d, J = 8.0 Hz, 2H), 7.05 (d, J = 8.0 Hz, 2H), 5.04 (dd, J = 12.0, 20.0 Hz, 2H), 3.59 (s, 1H), 2.33 (s, 3H), 0.94 (s, 9H), 0.33 (s, 3H), 0.20 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 174.7, 139.4, 136.2, 134.8, 129.6, 128.8, 128.6, 128.5, 125.9, 80.8, 67.8, 27.2, 21.3, 18.5, -5.9, -6.2; HRMS (ESI): calcd. for [C₂₂H₃₀O₃SSi+Na]+ 425.1583, found 425.1575.

3b: 83% yield; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.31–7.44 (m, 5H), 7.20 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 8.0 Hz, 2H), 5.08 (s, 2H), 3.57 (s, 1H), 2.32 (s, 3H), 1.02 (t, J = 8.0 Hz, 9H), 0.78–0.84 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 174.4, 139.3, 136.0, 129.6, 128.9, 128.5, 126.1, 80.3, 67.8, 21.2, 7.4, 2.5; HRMS (ESI): calcd. for [C₂₂H₃₀O₃SSi+NH₄]+ 420.2029, found 420.2020.
3c: 90% yield; yellow solid; $^1$H NMR (400 MHz, CDCl₃) δ 7.37 (dd, $J = 8.0, 12.0$ Hz, 1H), 7.15–7.20 (m, 3H), 7.04–7.09 (m, 4H), 5.02 (dd, $J = 12.0, 32.0$ Hz, 2H), 3.56 (s, 1H), 2.32 (s, 3H), 0.94 (s, 9H), 0.34 (s, 3H), 0.21 (s, 3H); $^{13}$C NMR (100 MHz, CDCl₃) δ 174.6, 162.8 (d, $J = 245$ Hz), 139.5, 137.2 (d, $J = 7$ Hz), 129.6, 125.9, 124.2 (d, $J = 3$ Hz), 115.5 (q, $J = 12$ Hz), 80.8, 66.8, 27.2, 21.2, 18.5, -5.9, -6.6; HRMS (ESI): calcd. for [C$_{22}$H$_{29}$FO$_3$Si+Na]$^+$ 443.1488, found 443.1480.

3d: 83% yield; yellow solid; $^1$H NMR (400 MHz, CDCl₃) δ 7.34–7.38 (m, 2H), 7.18 (d, $J = 8.0$ Hz, 2H), 7.03–7.10 (m, 4H), 5.01 (dd, $J = 16.0, 20.0$ Hz, 2H), 3.56 (s, 1H), 2.32 (s, 3H), 0.93 (s, 9H), 0.32 (s, 3H), 0.18 (s, 3H); $^{13}$C NMR (100 MHz, CDCl₃) δ 174.7, 162.8 (d, $J = 246$ Hz), 139.5, 136.1, 130.9 (d, $J = 8$ Hz), 129.6, 125.9, 115.5 (d, $J = 21$ Hz), 80.7, 67.0, 27.2, 21.3, 18.5, -5.9, -6.6; HRMS (ESI): calcd. for [C$_{22}$H$_{29}$FO$_3$Si+NH$_4$]$^+$ 438.1934, found 438.1917.

3e: 74% yield; yellow solid; $^1$H NMR (400 MHz, CDCl₃) δ 7.30–7.37 (m, 2H), 7.02–7.12 (m, 2H), 6.97 (d, $J = 8.0$ Hz, 2H), 6.84 (d, $J = 8.0$ Hz, 2H), 4.79 (dd, $J = 12.0, 32.0$ Hz, 2H), 3.35 (s, 1H), 2.13 (s, 3H), 0.75 (s, 9H), 0.13 (s, 3H), 0.00 (s, 3H); $^{13}$C
**NMR** (100 MHz, CDCl₃) δ 174.7, 139.5, 136.1, 133.9, 131.8, 130.5, 129.6, 126.0, 122.7, 80.7, 66.9, 27.2, 21.2, 18.5, -5.9, -6.6; **HRMS (ESI)**: calcd. for [C₂₂H₂₉BrO₃SSi+Na]⁺ 503.0688, found 503.0685.

![Image of 3f](3f.png)

**3f**: 76% yield; yellow solid; **¹H NMR** (400 MHz, CDCl₃) δ 7.44–7.50 (m, 2H), 7.20–7.26 (m, 2H), 7.15 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 8.0 Hz, 2H), 4.99 (dd, J = 12.0, 24.0 Hz, 2H), 3.50 (s, 1H), 2.30 (s, 3H), 1.00 (t, J = 8.0 Hz, 9H), 0.82–0.75 (m, 6H); **¹³C NMR** (100 MHz, CDCl₃) δ 174.4, 139.4, 135.8, 134.0, 131.7, 130.5, 129.6, 126.1, 122.7, 80.2, 66.9, 21.2, 7.4, 2.5; **HRMS (ESI)**: calcd. for [C₂₂H₂₉BrO₃SSi+NH]⁺ 498.1134, found 498.1129.

![Image of 3g](3g.png)

**3g**: 71% yield; yellow solid; **¹H NMR** (400 MHz, CDCl₃) δ 7.29–7.35 (m, 2H), 7.19 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 8.0 Hz, 2H), 6.87–6.92 (m, 2H), 7.98 (s, 2H), 3.84 (s, 3H), 3.60 (s, 1H), 2.32 (s, 3H), 0.93 (s, 9H), 0.31 (s, 3H), 0.17 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 174.7, 159.8, 139.4, 136.3, 130.6, 129.6, 127.0, 126.0, 113.9, 80.8, 67.6, 55.3, 27.3, 21.3, 18.5, -5.9, -6.6; **HRMS (ESI)**: calcd. for [C₂₃H₃₂O₄SSi+H]⁺ 433.1869, found 433.1862.
3h: 69% yield; yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.28–7.35 (m, 2H), 7.19 (d, $J = 8.0$ Hz, 2H), 7.03 (d, $J = 8.0$ Hz, 2H), 6.88–6.92 (m, 2H), 5.01 (dd, $J = 11.6, 12.8$ Hz, 2H), 3.84 (s, 3H), 3.56 (s, 1H), 2.32 (s, 3H), 1.01 (t, $J = 8.0$ Hz, 9H), 0.76–0.83 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 174.5, 159.9, 139.2, 136.0, 130.7, 129.5, 127.2, 126.2, 113.9, 80.3, 67.6, 55.3, 21.2, 7.4, 2.5; HRMS (ESI): calcd. for [C$_{23}$H$_{32}$O$_4$SSi+Na]$^+$ 455.1688, found 455.1653.

3i: 76% yield; yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37–7.42 (m, 5H), 7.20 (d, $J = 8.0$ Hz, 2H), 7.04 (d, $J = 8.0$ Hz, 2H), 5.07 (s, 2H), 3.56 (s, 1H), 2.32 (s, 3H), 1.01 (t, $J = 8.0$ Hz, 9H), 0.77–0.84 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 174.5, 159.3, 136.0, 135.0, 129.6, 128.9, 128.5, 126.1, 80.3, 67.8, 21.2, 7.4, 2.5; HRMS(ESI): calcd. for [C$_{22}$H$_{29}$NO$_5$SSi+Na]$^+$ 470.1433, found 470.1431.

3j: 70% yield; yellow solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.32 (d, $J = 8.0$ Hz, 2H), 7.10 (d, $J = 8.0$ Hz, 2H), 4.61–4.67 (m, 2H), 3.66 (s, 1H), 2.32 (s, 3H), 1.72–1.81 (m, 4H), 1.45–1.56 (m, 3H), 1.29–1.37 (m, 3H), 0.99 (s, 9H), 0.35 (s, 3H), 0.23 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 174.4, 139.2, 136.0, 129.5, 126.4, 80.3, 75.3, 31.7,
31.5, 27.4, 25.3, 23.7, 21.2, 18.7, -6.0, -6.4; HRMS (ESI): calcd. for 
[C$_{21}$H$_{34}$O$_{3}$Si+NH$_{4}$]$^+$ 412.2342, found 412.2341.

3k: 41% yield; colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.33–7.41 (m, 5H), 7.22–7.26 (m, 2H), 7.06 (d, $J = 8.0$ Hz, 2H), 5.10 (dd, $J = 12.0, 32.0$ Hz, 2H), 3.53 (s, 1H), 2.33 (s, 3H), 0.20 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 174.4, 139.4, 136.0, 135.1, 129.6, 128.7, 128.6, 128.5, 126.1, 80.1, 67.8, 21.2, -3.3; HRMS (ESI): calcd. for 
[C$_{19}$H$_{24}$O$_{3}$Si+NH$_{4}$]$^+$ 378.1559, found 378.1547.

3m: 92% yield; yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34–7.42 (m, 5H), 7.19 (s, 1H), 7.10–7.14 (m, 3H), 5.06 (s, 2H), 3.61 (s, 1H), 2.27 (s, 3H), 1.02 (t, $J = 8.0$ Hz, 9H), 0.78-0.84 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 174.4, 138.5, 136.6, 134.9, 132.8, 130.0, 128.7, 128.6, 80.4, 67.8, 21.2, 7.4, 2.5; HRMS (ESI): calcd. for 
[C$_{22}$H$_{30}$O$_{3}$Si+H]$^+$ 425.1583, found 425.1583.

3n: 66% yield; yellow solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36–7.42 (m, 5H), 7.21–7.25 (m, 2H), 6.86–6.91 (m, 2H), 5.09 (dd, $J = 12.0, 28.0$ Hz, 2H), 3.58 (s, 1H), 1.02 (t, $J = 8.0$ Hz, 9H), 0.78–0.84 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 174.4, 163.3
(d, J = 210 Hz), 138.0 (d, J = 9 Hz), 134.8, 129.0, 128.7, 128.6, 125.0, 115.8 (d, J = 22 Hz), 80.3, 67.9, 7.4, 2.5; **HRMS** (ESI): calcd. for [C_{21}H_{27}FO_3SSi+Na]^+ 429.1332, found 429.1337.

![Chemical structure of 3o](image)

**3o**: 74% yield; yellow oil; **^1H NMR** (400 MHz, CDCl₃) δ 7.35–7.41 (m, 6H), 7.28–7.31 (m, 1H), 7.12–7.19 (m, 2H), 5.07 (d, J = 4.0 Hz, 2H), 3.67 (s, 1H), 1.01 (t, J = 8.0 Hz, 9H), 0.76–0.84 (m, 6H); **^13C NMR** (100 MHz, CDCl₃) δ 174.3, 135.3, 134.7, 134.2, 133.7, 132.0, 129.7, 129.3, 128.9, 128.7, 128.6, 80.6, 68.1, 7.4, 2.4; **HRMS** (ESI): calcd. for [C_{21}H_{27}ClO_3SSi+H]^+ 423.1217, found 423.1212.

![Chemical structure of 3p](image)

**3p**: 82% yield; yellow oil; **^1H NMR** (400 MHz, CDCl₃) δ 7.31–7.39 (m, 5H), 7.19–7.23 (m, 2H), 6.72–6.77 (m, 2H), 5.09 (dd, J = 12.0, 16.0 Hz, 2H), 3.78 (s, 3H), 3.52 (s, 1H), 1.01 (t, J = 8.0 Hz, 9H), 0.77–0.83 (m, 6H); **^13C NMR** (100 MHz, CDCl₃) δ 174.5, 160.6, 137.7, 135.0, 128.9, 128.6, 120.2, 114.3, 80.4, 67.8, 55.2, 7.5, 2.5; **HRMS** (ESI): calcd. for [C_{22}H_{30}O_4SSi+H]^+ 419.1712, found 419.1716.

![Chemical structure of 3q](image)

**3q**: 70% yield; yellow oil; **^1H NMR** (400 MHz, CDCl₃) δ 7.36–7.44 (m, 5H), 7.20–
7.24 (m, 2H), 6.74–6.78 (m, 2H), 5.06 (dd, J = 12.0, 28.0 Hz, 2H), 3.78 (s, 3H), 3.58 (s, 1H), 0.95 (s, 9H), 0.34 (s, 3H), 0.21 (s, 3H); \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)) \(\delta\) 174.7, 160.6, 137.9, 134.9, 128.8, 128.6, 128.5, 120.0, 114.3, 80.8, 67.8, 55.2, 27.2, 18.5, -5.9, -6.6; \(\text{HRMS(ESI)}\): calcd. for \([\text{C}_{22}\text{H}_{30}\text{O}_{4}\text{SSi}+\text{H}]^+\) 419.1712, found 419.1716.

![3r](image)

3r: 72% yield; light yellow oil; \(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 7.27–7.37 (m, 5H), 7.12–7.19 (m, 1H), 7.04–7.07 (m, 2H), 6.81–6.84 (m, 1H), 5.51 (s, 1H), 5.12 (dd, \(J = 12.0, 24.0\) Hz, 2H), 3.74 (s, 3H), 0.92 (t, \(J = 8.0\) Hz, 9H), 0.62 (dd, \(J = 8.0, 16.0\) Hz, 6H); \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)) \(\delta\) 170.0, 159.5, 135.3, 132.9, 128.5, 128.3, 125.9, 118.6, 114.7, 78.6, 67.1, 55.2, 6.5, 4.6; \(\text{HRMS (ESI)}\): calcd. for \([\text{C}_{22}\text{H}_{30}\text{O}_{4}\text{SSi}+\text{Na}]^+\) 441.1532, found 441.1523.

![3s](image)

3s: 74% yield; yellow oil; \(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 7.31–7.42 (m, 5H), 7.16 (t, \(J = 8.0\) Hz, 1H), 6.87–6.96 (m, 3H), 5.02 (dd, \(J = 12.0, 20.0\) Hz, 2H), 3.71 (s, 4H), 0.96 (s, 9H), 0.35 (s, 3H), 0.21 (s, 3H); \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)) \(\delta\) 174.6, 159.4, 134.8, 130.9, 129.4, 128.6, 128.5, 128.4, 128.1, 120.8, 115.5, 81.1, 67.8, 55.2, 27.2, 18.5, -5.9, -6.6; \(\text{HRMS (ESI)}\): calcd. for \([\text{C}_{22}\text{H}_{30}\text{O}_{4}\text{SSi}+\text{Na}]^+\) 441.1532, found 441.1523.
3t: 85% yield; yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.88 (s, 1H), 7.79–7.81 (m, 1H), 7.67–7.72 (m, 2H), 7.45–7.50 (m, 2H), 7.31–7.49 (m, 6H), 5.02 (dd, $J = 12.0$, 12.0 Hz, 2H), 3.68 (s, 1H), 1.05 (t, $J = 8.0$ Hz, 9H), 0.80–0.88 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 174.4, 135.7, 134.9, 133.4, 133.3, 132.4, 128.8, 128.6, 128.2, 127.9, 127.7, 127.4, 126.8, 126.3, 80.8, 67.9, 7.5, 2.5; HRMS (ESI): calcd. for [C$_{25}$H$_{30}$O$_3$SSi+Na]$^+$ 461.1583, found 461.1547.

3u: 67% yield; yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.29–7.38 (m, 5H), 7.16–7.24 (m, 5H), 5.01 (dd, $J = 12.0$, 12.0 Hz, 2H), 3.85 (s, 1H), 3.73 (d, $J = 12.0$ Hz, 1H), 3.46 (d, $J = 12.0$ Hz, 1H), 0.92 (s, 9H), 0.23 (s, 3H), 0.10 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 176.1, 137.2, 129.3, 128.6, 128.3, 127.0, 78.1, 67.9, 31.9, 27.3, 18.5, -6.2, -6.7; HRMS (ESI): calcd. for [C$_{22}$H$_{30}$O$_2$SSi+Na]$^+$ 425.1583, found 425.1575.

3v: 72% yield; yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.35–7.39 (m, 5H), 7.11 (d, $J = 8.0$ Hz, 2H), 6.77 (d, $J = 8.0$ Hz, 2H), 5.07 (dd, $J = 12.0$, 20.0 Hz, 2H), 3.81 (s, 1H), 3.75 (s, 3H), 3.71 (d, $J = 12.0$ Hz, 1H), 3.43 (d, $J = 12.0$ Hz, 1H), 0.96 (t, $J = 8.0$ Hz, 3H).
Hz, 9H), 0.70–0.76 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 175.7, 158.6, 135.1, 130.3, 129.0, 128.6, 128.5, 113.8, 77.8, 67.9, 55.2, 31.5, 7.4, 2.3; HRMS(ESI): calcd. for [C$_{23}$H$_{32}$O$_4$SSi+Na]$^+$ 455.1688, found 455.1647.

3w: 67% yield; yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.32–7.43 (m, 5H), 5.24 (dd, $J = 12.0$, 36.0 Hz, 2H), 3.71 (s, 1H), 2.43–2.50 (m, 1H), 2.15–2.22 (m, 1H), 1.41–1.50 (m, 2H), 0.97 (t, $J = 8.0$ Hz, 9H), 0.87 (t, $J = 8.0$ Hz, 3H), 0.70–0.77 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 176.1, 135.0, 128.7, 128.5, 128.6, 67.9, 67.2, 29.4, 22.5, 13.6, 7.4, 2.3; HRMS (ESI): calcd. for [C$_{18}$H$_{30}$O$_3$SSi+Na]$^+$ 377.1583, found 377.1594.

3x: 72% yield; yellow solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.32–7.42 (m, 5H), 5.24 (dd, $J = 12.0$, 36.0 Hz, 2H), 3.71 (s, 1H), 2.47–2.53 (m, 1H), 2.16–2.23 (m, 1H), 1.38–1.46 (m, 2H), 1.23–1.33 (m, 2H), 0.96 (t, $J = 8.0$ Hz, 9H), 0.83 (t, $J = 8.0$ Hz, 3H), 0.67–0.77 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 176.1, 135.1, 128.7, 128.6, 128.5, 77.4, 68.0, 31.1, 27.1, 22.2, 13.6, 7.4, 2.4; HRMS (ESI): calcd. for [C$_{19}$H$_{32}$O$_3$SSi+H]$^+$ 369.1920, found 369.1902.

3y: 76% yield; yellow solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.32–7.42 (m, 5H), 5.24
(dd, $J = 12.0, 36.0$ Hz, 2H), 3.71 (s, 1H), 2.46–2.53 (m, 1H), 2.15–2.21 (m, 1H), 1.40–1.48 (m, 2H), 1.22–1.27 (m, 4H), 0.96 (t, $J = 8.0$ Hz, 9H), 0.83–0.86 (m, 3H), 0.69–0.77 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 176.1, 135.0, 128.7, 128.6, 128.5, 77.5, 67.9, 31.3, 28.7, 27.4, 22.2, 13.9, 7.4, 2.4; HRMS (ESI): calcd. for [C$_{20}$H$_{34}$O$_3$SSi+H]$^+$ 383.2076, found 338.2075.

3z: 74% yield; yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.32–7.43 (m, 5H), 5.24 (dd, $J = 12.0, 36.0$ Hz, 2H), 3.71 (s, 1H), 2.46–2.53 (m, 1H), 2.15–2.22 (m, 1H), 1.39–1.47 (m, 2H), 1.16–1.30 (m, 6H), 0.97 (t, $J = 8.0$ Hz, 9H), 0.86 (t, $J = 8.0$ Hz, 3H), 0.70–0.76 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 176.1, 135.1, 128.7, 128.6, 128.5, 77.4, 67.9, 31.3, 29.0, 28.8, 27.4, 22.5, 14.0, 7.4, 2.4; HRMS (ESI): calcd. for [C$_{21}$H$_{36}$O$_3$SSi+H]$^+$ 397.2233, found 397.2254.

3aa: 46% yield; yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34–7.42 (m, 5H), 5.24 (dd, $J = 12.0, 36.0$ Hz, 2H), 3.70 (s, 1H), 2.46–2.52 (m, 1H), 2.15–2.21 (m, 1H), 1.37–1.47 (m, 2H), 1.21–1.30 (m, 12H), 0.96 (t, $J = 8.0$ Hz, 9H), 0.87 (t, $J = 8.0$ Hz, 3H), 0.69–0.75 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 176.1, 135.1, 128.7, 128.6, 128.5, 77.5, 67.9, 31.8, 27.5, 22.6, 14.1, 7.4, 2.4; HRMS(ESI): calcd. for [C$_{23}$H$_{40}$O$_3$SSi+Na]$^+$ 447.2365, found 447.2356.
3ab: 64% yield; yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34–7.43 (m, 5H), 5.24 (dd, $J = 12.0, 52.0$ Hz, 2H), 3.68 (s, 1H), 2.36 (t, $J = 8.0, 12.0$ Hz, 1H), 2.06 (t, $J = 8.0, 12.0$ Hz, 1H), 1.60–1.67 (m, 1H), 0.97 (t, $J = 8.0$ Hz, 9H), 0.87 (t, $J = 8.0$ Hz, 6H), 0.70–0.76 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 176.2, 135.1, 128.7, 128.6, 128.5, 77.1, 67.9, 36.0, 28.3, 22.2, 22.1, 7.4, 2.4; HRMS(ESI): calcd. for [C$_{19}$H$_{32}$O$_3$Si+H]$^+$ 369.1920, found 369.1911.

4a: colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.29–7.40 (m, 7H), 7.07 (d, $J = 8.0$ Hz, 2H), 5.44 (s, 1H), 5.11 (dd, $J = 12.0, 40.0$ Hz, 2H), 2.32 (s, 3H), 0.87 (s, 9H), 0.07 (s, 3H), 0.02 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.9, 138.8, 135.3, 134.8, 129.5, 128.4, 128.3, 127.6, 78.9, 67.0, 25.5, 21.2, 18.1, -4.8, -5.5; HRMS(ESI): calcd. for [C$_{22}$H$_{30}$O$_3$Si+NH$_4$]$^+$ 420.2029, found 420.2027.
6. NMR spectra
3ab