Cooperative Organocatalysis of Mukaiyama-Type Aldol Reactions by Thioureas and Nitro Compounds

Supporting Information

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# 1. Nomenclature and abbreviations

**Table S1. Nomenclature and abbreviations**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Name/description</th>
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<tbody>
<tr>
<td>INEPT</td>
<td>Insensitive nuclei enhanced by polarization transfer</td>
</tr>
<tr>
<td>HMDS</td>
<td>Hexamethyldisilazane</td>
</tr>
<tr>
<td>HPLC</td>
<td>High Performance Liquid Chromatography</td>
</tr>
<tr>
<td>HRMS</td>
<td>High Resolution Mass Spectrometry</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>rps</td>
<td>Revolutions per second</td>
</tr>
<tr>
<td>TBS</td>
<td>tert-Butyldimethylsilyl</td>
</tr>
<tr>
<td>TIPS</td>
<td>Triisopropylsilyl</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>wt. %</td>
<td>Weight Percent</td>
</tr>
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</table>
2. Materials and methods

Materials and Synthetic Techniques
All reagents and solvents were provided by commercial suppliers (Sigma-Aldrich, Fisher Scientific and VWR) and used without further purification unless otherwise noted. Reactions requiring anhydrous conditions were performed under positive argon or nitrogen pressure using standard Schlenk line techniques. Nitromethane was distilled in the presence of P₂O₅ and stored over 4Å molecular sieves under argon. 1,3-Bis-(3,5-bis(trifluoromethyl)phenyl)thiourea (1a)¹ and 1-ethoxy-1-[(tert-butylidimethylsilyl)oxy]-1-ethoxyethene (3a)² were synthesized by previously reported techniques.

High Resolution Mass Spectrometry
HRMS analyses were performed by KAUST Analytical Core Labs (4700 King Abdullah University of Science and Technology, Thuwal, 23955-6900, Saudi Arabia).

NMR Spectroscopy
Data for routine characterization of small molecules and polymers were recorded at room temperature on Bruker Avance-III 400 MHz and 600 MHz NMR spectrometers equipped with a Z-axis gradient BBO probe. NMR chemical shifts are reported in ppm and are calibrated against residual solvent signals of CDCl₃ (¹H δ 7.26, ¹³C δ 77.16). ²⁹Si NMR experiments were run using INEPT to enhance ²⁹Si NMR signals for no-selective polarization transfer.
3. Synthesis of Thiourea Catalysts

Sodium hydride (72.4 mg, 3 mmol, 60 wt. % dispersion in mineral oil, 1.5 eq.) was added to a solution of 1,3-bis-(3,5-bis(trifluoromethyl)phenyl)thiourea (1a) (1.01 g, 2 mmol, 1 eq.) in 10 mL of dry THF under an argon atmosphere. The reaction mixture was stirred for 15 min at room temperature and iodomethane (856 mg, 0.376 mL, 6 mmol, 3 eq.) was added. The resulting mixture was stirred overnight at room temperature under argon. After this time, the solvent was removed in vacuo, and the residue was taken up in hexane (100 mL). The obtained suspension was filtered and evaporated. The crude mixture of products was purified by column chromatography (hexane:ethyl acetate, 100:1–80:20).

Methyl (Z)-N,N'-bis-(3,5-bis(trifluoromethyl)phenyl)-N-methylcarbamimidothioate (1c) (323 mg, 31 %) was obtained as the first fraction. Methyl (Z)-N,N'-bis-(3,5-bis(trifluoromethyl)phenyl)-carbamimidothioate (1b) (374 mg, 36 %) was obtained as the second fraction.

**Methyl (Z)-N,N'-bis-(3,5-bis(trifluoromethyl)phenyl)-carbamimidothioate (1b)**

White solid. Isolated yield 36 %. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.58 (s, 5H), 6.74 (s, 1H), 2.36 (s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 171.90, 151.50, 132.52 (q, $J = 33.4$ Hz), 123.27 (q, $J = 272.8$ Hz), 121.19, 117.29, 15.15. $^{19}$F NMR (377 MHz, CDCl$_3$): $\delta$ -63.02 (s, 12F) ppm. HRMS (ESI+) calculated for [C$_{18}$H$_{11}$N$_2$F$_{12}$S]$^+$: 515.04458, found: 515.04500.

**Methyl (Z)-N,N'-bis-(3,5-bis(trifluoromethyl)phenyl)-N-methylcarbamimidothioate (1c)**

White solid. Isolated yield 31 %. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.60 (s, 1H), 7.53 (s, 2H), 7.42 (s, 1H), 7.24 (s, 2H), 3.49 (s, 3H), 2.12 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 159.08, 150.03, 146.77, 132.66 (q, $J = 33.8$ Hz), 132.05 (q, $J = 33.2$ Hz), 124.74, 124.56, 123.20 (q, $J = 272.7$ Hz), 122.78 (q, $J = 272.9$ Hz), 121.33, 118.79, 116.06, 116.02, 115.98, 41.13, 15.71. $^{19}$F NMR (377 MHz, CDCl$_3$): $\delta$ -63.16 (s, 6F), -63.19 (s, 6F) ppm. HRMS (ESI+) calculated for [C$_{19}$H$_{13}$N$_2$F$_{12}$S]$^+$: 529.06023, found: 529.06018.
4. Catalytic reactions

Screening of solvents

Acetone (10 μL, 7.86 mg, 135 μmol, 1 eq.) and 1a (6.77 mg, 13.5 μmol, 0.1 eq.) in 80 μL of solvent (see table 1, main text) were combined in an HPLC vial (1.8 ml), followed by the addition of 3a (46 μL, 41 mg, 203 μmol, 1.5 eq.) under air; 3a was added in a single portion. The vial was closed by screw cap and the reaction was stirred at room temperature for 1 hour. After this time 0.5 mL of CDCl₃ was added; the resulting solution was analyzed by NMR directly. Conversion was estimated by the ratio of ¹H signals at 1.35 (s, 6H) for ethyl 3-((tert-butyldimethylsilyl)oxy)-3-methylbutanoate (4a) and 2.17 (s, 6H) for acetone (2a).

Screening of catalysts

Acetone (10 μL, 7.86 mg, 135 μmol, 1 eq.), catalyst 1 (13.5 μmol, 0.1 eq., see table 2, main text) and nitromethane (73 μL, 82.61 mg, 1.35 mmol, 10 eq.) were combined in an HPLC vial (1.8 ml), followed by the addition of 3a (46 μL, 41 mg, 203 μmol, 1.5 eq.) under air; 3a was added in a single portion. The vial was closed by screw cap and the reaction was stirred at room temperature for 1 hour. 0.5 mL of CDCl₃ was added after this time and the resulting solution was analyzed by NMR directly. Conversion was estimated by the ratio of ¹H signals at 1.35 (s, 6H) for ethyl 3-((tert-butyldimethylsilyl)oxy)-3-methylbutanoate (4a) and 2.17 (s, 6H) for acetone (2a).
5. Kinetic experiments

General procedure

The compounds were mixed in a vial until the reaction mixture became homogeneous (10 – 20 seconds) and then the solution was transferred into an NMR tube equipped with a thinner internal tube (the internal tube was filled with 0.02 mL of HMDS ($^{29}$Si NMR $\delta = 2.2$ ppm) in 0.1 mL of CDCl$_3$). The combined tubes were placed into a Bruker 600 MHz NMR spectrometer, spun at 20 rps and analyzed every 2-20 minutes. The first recorded point of each analysis was ~5 minutes after the reaction started.

Figure S1. NMR tube set-up for kinetic experiments.

Reaction 3a with 1a

Thiourea 1a (49 mg, 0.097 mmol, 1 eq.) was dissolved in 3a (334 $\mu$L, 298 mg, 1.470 mmol, 15 eq.) and analyzed via $^{29}$Si NMR every 20 minutes for 17 hours. No degradation was observed (figure S2).

Figure S2. $^{29}$Si NMR spectra showing the stability of 3a in presence of thiourea 1a. Z axis: time from 0.1-17 hours.
Reaction of 3a with nitromethane

Nitromethane (302 μL, 341 mg, 5.590 mmol, 10 eq.) was mixed with 3a (190 μL, 170 mg, 0.838 mmol, 1.5 eq.) and analyzed by $^{29}$Si NMR every 20 minutes for 17 hours (Figure S3).

After 23 hours 0.1 mL of the reaction mixture was diluted with 0.5 mL of CDCl$_3$ and analyzed by $^1$H NMR (Figure S12). The molar ratio between 6 (peak at 3.27 ppm, 2H) and ethyl acetate (peak at 2.03 ppm, 3H) is 1:1. The peak at 5.73 ppm corresponds to 5. A similar structure (TIPS instead of TBS) was synthetized previously$^3$ and has the same shift ($\delta = 5.75$ ppm, s, 2H) for CH$_2$N protons. The reaction mixture was evaporated under vacuum yielding 120 mg (76 %) of ethyl 3-(bis(tert-butyldimethylsilyl)oxy)amino)propanoate (6) as slightly yellow oil. $^1$H NMR (600 MHz; CDCl$_3$): $\delta$ 4.11 (q, $J = 7.1$ Hz, 2H), 3.27 (t, $J = 6.9$ Hz, 2H), 2.60 (t, $J = 6.9$ Hz, 2H), 1.23 (t, $J = 7.1$ Hz, 3H), 0.88 (s, 18H), 0.15 (s, 6H), 0.13 (s, 6H). $^{13}$C NMR (151 MHz; CDCl$_3$): $\delta$ 172.3, 62.2, 60.5, 29.9, 26.1, 17.9, 14.3, -3.8, -4.5. $^{29}$Si NMR (119 MHz; CDCl$_3$): $\delta$ 23.7 (s, 2Si). HRMS (ESI$^+$) calculated for [C$_{17}$H$_{39}$NO$_5$Si$_2$K]$^+$: 416.20492, found: [C$_{17}$H$_{39}$NO$_5$Si$_2$K]$^+$: 416.20492.
Reaction of 3a with nitromethane in the presence of 1a

Thiourea 1a (28 mg, 0.056 mmol, 0.1 eq.) was dissolved in nitromethane (302 μL, 341 mg, 5.590 mmol, 10 eq.). The resulting mixture was mixed with 3a (190 μL, 170 mg, 0.838 mmol, 1.5 eq.) and analyzed by 29Si NMR every 5 minutes for 17 hours (Figure S4).

Figure S4. 29Si NMR spectra for the degradation of 3a in nitromethane in presence of 1a. Z axis: time from 0.1-17 hours.

After 17 hours the reaction mixture was evaporated under high vacuum (0.8 mBar) at 120 °C to give a 110 mg of mixture of 6 and 7 as a yellow oil. Purification of 7 via column chromatography failed and therefore the structure of 7 was determined by NMR in as a mixture with 6. (Bis((tert-butyldimethylsilyl)oxy)amino)methyl (Z)-N,N'-bis(3,5-bis(trifluoromethyl)phenyl)-N-(tert-butyldimethylsilyl) carbamimido thioate (7): 1H NMR (600 MHz; CDCl3): δ 7.77 (s, 1H), 7.64 (s, 2H), 7.48 (s, 1H), 7.37 (s, 2H), 3.74 (s, 2H), 1.02 (s, 9H), 0.76 (s, 18H), 0.14 (s, 6H), 0.05 (s, 6H), -0.09 (s, 6H). 13C NMR (101 MHz; CDCl3): δ 159.9, 149.38, 145.44, 132.64, 130.59, 124.7, 121.61, 120.79, 115.99, 115.94, 68.4, 28.3, 25.8, 20.2, 17.85, -1.8, -4.5, -4.9. 29Si NMR (119 MHz; CDCl3): δ 25.4 (s, 2Si), 17.0 (s, 1Si). 19F NMR (377 MHz; CDCl3): δ -63.1 (s, 12F).
Mukaiyama reaction

Acetone (41.3 μL, 32.46 mg, 0.558 mmol, 1 eq.) and thiourea 1a (28 mg, 0.056 mmol, 0.1 eq.) was dissolved in nitromethane (302 μL, 341 mg, 5.590 mmol, 10 eq.). The resulting mixture was combined with 3a (190 μL, 170 mg, 0.838 mmol, 1.5 eq.) and analyzed by \(^{29}\text{Si} \) NMR every 2 minutes for 2 hours (Figure S5). The reaction completed after 60 minutes.

Figure S5. \(^{29}\text{Si} \) NMR spectra for the Mukaiyama reaction. Z axis; time from 5-120 minutes.
6. Exploration of Scope

General procedure

A solution of carbonyl compound 2 (1 mmol, 1 eq., see table 3, main text) and 1a (50 mg, 0.1 mmol, 0.1 eq.) in 0.54 mL of nitromethane were combined in an HPLC vial (1.8 mL). 3 (1.5 mmol, 1.5 eq.) was then added in one portion under air. The vial was closed by screw cap and the reaction was stirred at room temperature. After the reaction was complete, nitromethane was evaporated in vacuo. The products were purified by column chromatography.

Ethyl 3-((tert-butyldimethylsilyl)oxy)-3-methylbutanoate (4a)

Colorless oil. Isolated yield: 88%. Purification by column chromatography, hexane:ethyl acetate, 100:1. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 4.10 (q, $J = 7.2$ Hz, 2H), 2.44 (s, 2H), 1.35 (s, 6H), 1.25 (t, $J = 7.2$ Hz, 3H), 0.83 (s, 9H), 0.07 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 171.4, 72.7, 60.2, 49.8, 30.3, 25.8, 18.1, 14.3, -2.1. HRMS (ESI+) calculated for [C$_{13}$H$_{29}$O$_3$Si]$^+$: 261.18805, found: 261.18803.

Ethyl 2-1-((tert-butyldimethylsilyl)oxy)cyclopentyl)acetate (4b)

Colorless oil. Isolated yield: 56%. Purification by column chromatography, hexane:ethyl acetate, 100:1. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 4.10 (q, $J = 7.1$ Hz, 2H), 2.58 (s, 2H), 1.85-1.65 (m, 6H), 1.64-1.51 (m, 2H), 1.26 (t, $J = 7.1$ Hz, 3H), 0.83 (s, 9H), 0.08 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 171.5, 82.9, 60.2, 46.2, 39.8, 25.6, 23.3, 18.0, 14.1, -2.5. HRMS (ESI+) calculated for [C$_{15}$H$_{30}$O$_3$SiNa]$^+$: 309.18564, found: 309.18534.

Ethyl 2-1-((tert-butyldimethylsilyl)oxy)cyclohexyl)acetate (4c)

Colorless oil. Isolated yield: 88%. Purification by column chromatography, hexane:ethyl acetate, 100:1. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 4.10 (q, $J = 7.1$ Hz, 2H), 2.51 (s, 2H), 1.78-1.70 (m, 2H), 1.70-1.61 (m, 2H), 1.61-1.50 (m, 2H), 1.45-1.31 (m, 4H), 1.25 (t, $J = 7.1$ Hz, 3H), 0.86 (s, 9H), 0.09 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 171.6, 74.8, 60.4, 46.6, 38.7, 26.1, 25.8, 23.1, 18.5, 14.4, -1.7. NMR data corresponded to peaks previously reported.
Ethyl 3-((tert-butyldimethylsilyl)oxy)-3-phenylbutanoate (4d)

Colorless oil. Isolated yield: 71 %. Purification by column chromatography, hexane:ethyl acetate, 100:1. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.47-7.45 (m, 2H), 7.33-7.21 (m, 3H), 3.97 (q, $J = 7.0$ Hz, 2H), 2.75 (dd, $J = 51.0$, 13.5 Hz, 2H), 1.82 (s, 3H), 1.09 (t, $J = 7.2$ Hz, 3H), 0.93 (s, 9H), 0.08 (s, 3H), -0.12 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 170.5, 147.5, 127.9, 127.0, 125.5, 75.8, 60.2, 51.3, 28.5, 26.1, 18.5, 14.1, -1.9, -2.4. HRMS (ESI$^+$) calculated for [C$_{18}$H$_{30}$O$_3$SiNa]$^+$: 345.18544, found: [C$_{18}$H$_{30}$O$_3$SiNa]$^+$: 345.18549.

Ethyl 2-(3-((tert-butyldimethylsilyl)oxy)cyclopent-2-en-1-yl)acetate (4e)

Colorless oil. Isolated yield: 87 %. Purification by column chromatography, hexane:ethyl acetate:triethylamine, 98:1:1. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 4.60 (d, $J = 1.8$ Hz, 1H), 4.11 (q, $J = 7.1$ Hz, 2H), 3.05-3.00 (m, 1H), 2.34-2.22 (m, 4H), 2.14-2.07 (m, 1H), 1.52-1.43 (m, 1H), 1.24 (t, $J = 7.1$ Hz, 3H), 0.90 (s, 9H), 0.13 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 173.5, 156.5, 106.5, 60.6, 42.3, 39.1, 33.5, 28.5, 26.1, 18.7, 14.8, -4.1, -4.2. NMR data corresponded to peaks previously reported.

Ethyl 2-(3-((tert-butyldimethylsilyl)oxy)cyclohex-2-en-1-yl)acetate (4f)

Colorless oil. Isolated yield: 99 %. Purification by column chromatography, hexane:ethyl acetate:triethylamine, 98:1:1. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 4.85-4.69 (m, 1H), 4.12 (q, $J = 7.1$ Hz, 2H), 2.70-2.57 (m, 1H), 2.33-2.18 (m, 2H), 2.04-1.90 (m, 2H), 1.75-1.70 (m, 2H), 1.62-1.52 (m, 1H), 1.25 (t, $J = 7.2$ Hz, 3H), 1.22-1.06 (m, 1H), 0.90 (s, 9H), 0.11 (s, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 172.9, 151.8, 107.9, 60.3, 41.7, 32.0, 29.9, 28.7, 25.8, 21.3, 18.2, 14.4, -4.26, -4.34. NMR data corresponded to peaks previously reported.

Ethyl 3-((tert-butyldimethylsilyl)oxy)-3-phenylpropanoate (4g)

Colorless oil. Isolated yield: 99 %. Purification by column chromatography, hexane:ethyl acetate, 100:1. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.35-7.24 (m, 5H), 5.14 (dd, $J = 9.4$, 4.0 Hz, 1H), 4.17-4.08 (m, 2H), 2.72 (dd, $J = 14.6$, 9.4 Hz, 1H), 2.54 (dd, $J = 14.6$, 4.0 Hz, 1H), 1.25 (t, $J = 7.2$ Hz, 3H), 0.84 (s, 9H), 0.02 (s, 3H), -0.18 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 171.7,
144.1, 128.4, 127.7, 125.9, 72.4, 60.8, 46.7, 25.8, 18.2, 14.3, -4.6, -5.2. NMR data corresponded to peaks previously reported. 

Ethyl (E)-3-((tert-butyldimethylsilyl)oxy)-5-phenylpent-4-enoate (4h)

Colorless oil. Isolated yield: 99%. Purification by column chromatography, hexane:ethyl acetate, 100:1. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.38-7.22 (m, 5H), 6.58 (d, $J = 15.9$ Hz, 1H), 6.20 (dd, $J = 15.9, 6.7$ Hz, 1H), 4.78 (qd, $J = 6.6, 1.2$ Hz, 1H), 4.16-4.12 (m, 2H), 2.66-2.50 (m, 2H), 1.27 (t, $J = 7.2$ Hz, 3H), 0.90 (s, 9H), 0.09 (s, 3H), 0.07 (s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 171.2, 136.8, 131.8, 130.0, 128.7, 127.7, 126.6, 70.9, 60.6, 44.2, 25.9, 18.2, 14.4, -4.1, -4.9. NMR data corresponded to peaks previously reported.

Ethyl 3-((tert-butyldimethylsilyl)oxy)-5-phenylpentanoate (4i)

Colorless oil. Isolated yield: 41%. Purification by column chromatography, hexane:ethyl acetate, 100:1. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.30-7.26 (m, 2H), 7.20-7.17 (m, 3H), 4.22 (dd, $J = 6.6, 5.9$ Hz, 1H), 4.13 (qd, $J = 7.1, 2.6$ Hz, 2H), 2.71-2.64 (m, 2H), 2.50 (qd, $J = 12.9, 6.3$ Hz, 2H), 1.89-1.80 (m, 2H), 1.27 (t, $J = 7.2$ Hz, 3H), 0.94-0.85 (m, 9H), 0.07 (d, $J = 13.6$ Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 171.8, 142.3, 128.52, 128.43, 125.9, 69.2, 60.5, 42.8, 39.5, 31.5, 25.9, 18.2, 14.3, -4.4, -4.6. HRMS (ESI$^+$) calculated for [C$_{19}$H$_{32}$O$_3$SiNa]$^+$: 359.20129, found: [C$_{19}$H$_{32}$O$_3$SiNa]$^+$: 359.20114.

1,3-Diphenyl-3-((trimethylsilyl)oxy)propan-1-one (4k)

Colorless oil. Isolated yield: 99%. Purification by column chromatography, hexane:ethyl acetate, 100:1. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.98-7.96 (m, 2H), 7.57-7.53 (m, 1H), 7.47-7.42 (m, 4H), 7.34 (t, $J = 7.5$ Hz, 2H), 7.28-7.24 (m, 1H), 5.40 (dd, $J = 8.8, 3.8$ Hz, 1H), 3.57 (dd, $J = 15.6, 8.8$ Hz, 1H), 3.03 (dd, $J = 15.6, 3.8$ Hz, 1H), -0.02 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 198.6, 144.8, 137.7, 133.1, 128.56, 128.49, 128.43, 127.4, 125.8, 71.7, 49.8, 0.0. NMR data corresponded to peaks previously reported.

(E)-1,5-diphenyl-3-((trimethylsilyl)oxy)pent-4-en-1-one (4l)

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Colorless oil. Isolated yield: 99%. Purification by column chromatography, hexane:ethyl acetate, 100:1. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.99-7.96 (m, 2H), 7.58-7.21 (m, 8H), 6.62 (d, $J = 15.8$ Hz, 1H), 6.29 (dd, $J = 15.8$, 6.0 Hz, 1H), 5.02-4.97 (m, 1H), 3.42 (dd, $J = 15.5$, 7.8 Hz, 1H), 3.03 (dd, $J = 15.5$, 4.9 Hz, 1H), 0.07 (s, 8H). $^{13}$C NMR (101 MHz, CDCl$_3$): δ 198.7, 137.8, 137.0, 133.3, 132.3, 129.8, 128.82, 128.78, 128.66, 127.8, 126.7, 70.5, 47.4, 0.4. HRMS (ESI$^+$) calculated for $[\text{C}_{20}\text{H}_{24}\text{O}_2\text{SiNa}]^+$: 347.14378, found: $[\text{C}_{20}\text{H}_{24}\text{O}_2\text{SiNa}]^+$: 347.14339.
7. NMR spectra

Figure S6. $^1$H-NMR spectrum of 1b in CDCl$_3$.

Figure S7. $^{13}$C-NMR spectrum of 1b in CDCl$_3$. 
Figure S8. $^{19}$F-NMR spectrum of 1b in CDCl$_3$.

Figure S9. $^1$H-NMR spectrum of 1c in CDCl$_3$. 
Figure S10. $^1$H-NMR spectrum of 1c in CDCl$_3$.

Figure S11. $^{19}$F-NMR spectrum of 1c in CDCl$_3$.
Figure S12. $^1$H NMR spectra for the reaction mixture of degradation of 3a in nitromethane after 23 hours in CDCl$_3$.

Figure S13. $^1$H NMR spectrum of 6 in CDCl$_3$. 
Figure S14. $^{13}$C NMR spectrum of 6 in CDCl$_3$.

Figure S15. $^{29}$Si NMR spectrum of 6 in CDCl$_3$. 
Figure S16. $^1$H NMR spectrum of mixture 6 and 7 in CDCl$_3$.

Figure S17. $^{13}$C NMR spectrum of mixture 6 and 7 in CDCl$_3$. 
Figure S18. HMBC spectrum of mixture 6 and 7 in CDCl₃.

Figure S19. HSQC spectrum of mixture 6 and 7 in CDCl₃.
Figure S20. $^{29}$Si NMR spectrum of mixture 6 and 7 in CDCl$_3$.

Figure S21. $^{19}$F NMR spectrum of mixture 6 and 7 in CDCl$_3$. 
Figure S22. $^1$H-NMR spectrum of 4a in CDCl$_3$.

Figure S23. $^{13}$C-NMR spectrum of 4a in CDCl$_3$. 
Figure S24. $^1$H-NMR spectrum of 4b in CDCl$_3$.

Figure S25. $^{13}$C-NMR spectrum of 4b in CDCl$_3$. 
Figure S26. $^1$H-NMR spectrum of 4c in CDCl$_3$.

Figure S27. $^{13}$C-NMR spectrum of 4c in CDCl$_3$. 

Figure S28. $^1$H-NMR spectrum of 4d in CDCl$_3$.

Figure S29. $^{13}$C-NMR spectrum of 4d in CDCl$_3$. 
Figure S30. $^1$H-NMR spectrum of 4e in CDCl$_3$.

Figure S31. $^{13}$C-NMR spectrum of 4e in CDCl$_3$. 
Figure S32. $^1$H-NMR spectrum of 4f in CDCl$_3$.

Figure S33. $^{13}$C-NMR spectrum of 4f in CDCl$_3$. 
Figure S34. $^1$H-NMR spectrum of 4g in CDCl$_3$.

Figure S35. $^{13}$C-NMR spectrum of 4g in CDCl$_3$. 
Figure S36. $^1$H-NMR spectrum of 4h in CDCl$_3$.

Figure S37. $^{13}$C-NMR spectrum of 4h in CDCl$_3$. 
Figure S38. $^1$H-NMR spectrum of 4i in CDCl$_3$.

Figure S39. $^{13}$C-NMR spectrum of 4i in CDCl$_3$. 
Figure S40. $^1$H-NMR spectrum of 4k in CDCl$_3$.

Figure S41. $^{13}$C-NMR spectrum of 4k in CDCl$_3$. 
Figure S42. $^1$H-NMR spectrum of 4l in CDCl$_3$.

Figure S43. $^{13}$C-NMR spectrum of 4l in CDCl$_3$. 
9. References

(3) Han, X.; Dong, L.; Geng, C.; Jiao, P. Org. Lett. 2015, 17, 3194.