Supporting Information
Copper-Promoted Difunctionalization of Unactivated Alkenes with Silanes

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Table of Contents
1. General Information .......................................................................................................................2
2. General Procedure ..........................................................................................................................2
3. Optimization of the reaction ..........................................................................................................4
4. Characterization data of the products ............................................................................................5
5. Radical trapping experiment ........................................................................................................16
6. X-Ray crystallographic data of 3aa ..............................................................................................19
7. References ....................................................................................................................................21
8. 1H NMR, 13C NMR and 19F NMR spectra of the products............................................................21
1. General Information

All manipulations were performed in 25 mL Schlenk tube equipped with a magnetic stir bar unless otherwise noted. Solvents and reagents were purchased from commercial sources and used as received. Flash column chromatography was performed using silica gel (60-Å pore size, 32-63 µm, standard grade). Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25 mm 230-400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Melting points were recorded by XT4A micro melting point Measurement Instruments, thermometer was unrevised. The transformation progress and mass spectra were indicated by GC (Shimadzu GC-2010 Plus) or GC-MS (Thermo Fisher Scientific DSQ II). NMR spectra were obtained on Bruker AVANCE III systems using CDCl₃ as a solvent, CDCl₃ as an internal standard substance, at 400 MHz for ¹H NMR, 100 MHz for ¹³C NMR, and 376 MHz for ¹⁹F NMR. High-resolution mass spectrometry (HRMS) data were obtained on an Agilent Technologies 1290-6540 UHPLC/Accurate-Mass Quadrupole Time-of Flight (Q-TOF) LC/MS using ESI as ion source. X-ray analysis was performed with a single-crystal X-ray diffractometer. Preparative TLC was performed on silica gel plates and developed with ethyl acetate/petroleum ether.

2. General Procedure

2.1 Substrate Synthesis

Anilides, sulfonamides, and substrates 1 were prepared according to literature procedures.¹

\[
\begin{align*}
\text{NH}_2 \quad \text{R}^1 \quad \text{CH}_2\text{Cl}_2 & \quad \text{R}^2\text{Cl}, \text{Et}_3\text{N} & \quad \text{NHR}^2 \\
\text{R}^3 \quad \text{Br} & \quad \text{NaOH}, \text{DMF} & \quad \text{R}^3
\end{align*}
\]

A 250 mL flask, equipped with a magnetic stirring bar, was charged with aniline compound (20.0 mmol, 1.0 equiv.), CH₂Cl₂ (60.0 mL), and Et₃N (40.0 mmol, 2.0 equiv.), followed by the addition of acyl chloride (24.0 mmol, 1.2 equiv.) at 0 °C. The
reaction mixture was stirred at room temperature. After aniline compound was consumed, as indicated by TLC, the action mixture was quenched with aqueous NaHCO$_3$ (130 mL) and extracted with CH$_2$Cl$_2$ (130 mL) three times. The combined organic phase was washed with brine (70 mL). After removal of solvents, the solid of the crude product was further purified by washing with a petroleum ether/ethyl acetate mixture (7:1, v/v), affording N-acylaniline. To a stirred solution of N-acylaniline (15.0 mmol, 1.0 equiv.), and NaOH (22.5 mmol, 1.5 equiv.) in DMF (45.0 mL) was added 3-bromo-prop-1-ene (19.5 mmol, 1.3 equiv.), and the mixture was stirred at room temperature. After N-acylaniline was consumed, as indicated by TLC, the reaction mixture was quenched with brine (90 mL) and extracted with CH$_2$Cl$_2$ (90 mL) three times. The combined organic layers were dried with anhydrous Na$_2$SO$_4$, then filtered and concentrated under reduced pressure. The residue was purified by column chromatography (Petroleum/EtOAc = 8:1) on silica gel to afford 1a-1x.

2.2 Experimental Procedure

\[
\begin{align*}
\text{R}^1 & \quad \text{N} \quad \text{PG} \quad \text{R}^2 \\
\text{1} & \quad + \quad \text{[Si-H]} \\
\text{Cu(OAc)}_2 \text{ (5 mol%)} & \quad \text{DTBP} \text{ (2 equiv.)} \\
\text{KOAc} \text{ (0.5 equiv.)} & \quad \text{t-Butanol, 130 °C, 12 h} \\
\text{R}^1 & \quad \text{N} \quad \text{PG} \\
\text{2} & \quad \text{3} \\
\text{R}^2 & \quad \text{Si} \\
\end{align*}
\]

A dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with 1 (0.50 mmol, 1.0 equiv.), 2 (4.0 mmol, 8.0 equiv.), DTBP (1.0 mmol, 2.0 equiv.), KOAc (0.25 mmol, 0.5 equiv.), Cu(OAc)$_2$ (0.025 mmol, 5 mol%), and t-BuOH (3.0 mL). Subsequently, the tube was sealed and the resulting mixture was stirred at 130 °C for 12 h under Ar atmosphere. After cooling to room temperature, the reaction mixture was washed with water and extracted with CH$_2$Cl$_2$ three times. The combined organic layers were dried over anhydrous Na$_2$SO$_4$, concentrated in vacuo. The crude products were purified by flash column chromatography on silica gel (Petroleum ether/EtOAc) to afford desired products 3.

2.3 Scale-up Reaction
A mixture of $N$-(2-methyl-allyl)-$N$-phenylacetamide 1a (0.946 g, 5.0 mmol, 1.0 equiv.), triethylsilane 2a (4.651 g, 40 mmol, 8.0 equiv.), DTBP (1.462 g, 10 mmol, 2.0 equiv.), KOAc (0.245 g, 2.5 mmol, 0.5 equiv.), Cu(OAc)$_2$ (0.091 g, 0.25 mmol, 5 mol%), t-BuOH (30 mL), was taken in a dry round-bottomed flask. The reaction mixture was then stirred at 130 °C for 12 h under an argon atmosphere. After cooling down to room temperature, the reaction mixture was washed with water and extracted with CH$_2$Cl$_2$ three times. The combined organic layers dried over anhydrous Na$_2$SO$_4$, concentrated in vacuo. Then the crude reaction mixture was purified by flash silica gel column chromatography (Petroleum/EtOAc = 60:1-30:1) to afford the desired product 3aa (0.987 g, 65%).

### 3. Optimization of the reaction

Table S1. Reaction Optimization

<table>
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<th>entry</th>
<th>2a (equiv.)</th>
<th>solvent</th>
<th>Catalyst (mol%)</th>
<th>Oxidant (equiv.)</th>
<th>Base (equiv.)</th>
<th>yield (%)$^b$</th>
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<td>NaOAc(3)</td>
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<td>DTBP(2)</td>
<td>KOAc(3)</td>
<td>88</td>
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<td>Cu(OAc)₂(10)</td>
<td>DTBP(1.5)</td>
<td>KOAc(3)</td>
<td>35</td>
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<td>DTBP(2)</td>
<td>KOAc(3)</td>
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<td>Cu(OAc)₂(10)</td>
<td>DTBP(2)</td>
<td>KOAc(3)</td>
<td>88</td>
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<td>t-Butanol</td>
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<td>DTBP(2)</td>
<td>KOAc(3)</td>
<td>65</td>
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<td>KOAc(3)</td>
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<td>DTBP(2)</td>
<td>KOAc(3)</td>
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<td>Cu(OAc)₂(2)</td>
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<td>t-Butanol</td>
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<td>DTBP(2)</td>
<td>KOAc(1.5)</td>
<td>87</td>
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<td>37</td>
<td>t-Butanol</td>
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<td>Cu(OAc)₂(5)</td>
<td>DTBP(2)</td>
<td>KOAc(0.5)</td>
<td>88(80)</td>
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<tr>
<td>38</td>
<td>t-Butanol</td>
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<td>Cu(OAc)₂(5)</td>
<td>DTBP(2)</td>
<td>KOAc(0.25)</td>
<td>63</td>
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</tbody>
</table>

aReaction conditions: 1a (0.5 mmol, 1.0 equiv.), 2a, oxidant, catalyst, base, solvent (3.0 mL), 130 °C, under Ar, 12 h (DTBP = di-tert-butylperoxide, TBHP = tert-butyl hydroperoxide, TBPB = tert-butyl peroxybenzoate, LPO = dilauroyl peroxide).

bYields determined by GC analysis with naphthalene as the internal standard, isolated yield of 3aa was shown in parentheses.

4. Characterization data of the products
1-(3-methyl-3-((triethylsilyl)methyl)indolin-1-yl)ethan-1-one (3aa). White solid, 80% yield (121.6 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 10:1). M.p. = 47-49 °C. $^1$H NMR (400 MHz, CDCl$_3$, ppm) present in 5.0:1 ratio of rotational isomer about the amide: $\delta$ 8.17 (d, $J = 8.0$ Hz, 1 H), 7.20-7.16 (m, 1 H), 7.14-7.12 (m, 1 H), 7.05-7.01 (m, 1 H), 3.93-3.83 (m, 0.33 H), 3.83-3.72 (m, 1.66 H), 2.44 (s, 0.50 H), 2.21 (s, 2.49 H), 1.33 (s, 2.54 H), 1.39 (s, 0.51 H), 1.17 (d, $J = 14.8$ Hz, 1 H), 1.07 (d, $J = 14.8$ Hz, 1 H), 0.88 (t, $J = 8.0$ Hz, 9 H), 0.51-0.36 (m, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm), major rotational isomer: $\delta$ 168.6, 141.8, 141.1, 127.6, 123.8, 122.0, 116.9, 63.4, 42.5, 30.9, 26.2, 24.2, 7.4, 4.4; minor rotational isomer: $\delta$ 168.4, 144.6, 140.0, 127.2, 123.4, 123.3, 114.0, 62.0, 40.9, 30.2, 25.3, 24.5, 7.3, 4.4; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for C$_{18}$H$_{30}$NOSi 304.2091; Found 304.2093.

1-(3,5-dimethyl-3-((triethylsilyl)methyl)indolin-1-yl)ethan-1-one (3ba). Light yellow liquid, 81% yield (128.4 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 10:1). $^1$H NMR (400 MHz, CDCl$_3$, ppm) present in 5.0:1 ratio of rotational isomers about the amide: $\delta$ 8.03 (d, $J = 8.4$ Hz, 1 H), 6.99-6.93 (m, 2 H), 3.92-3.83 (m, 0.34 H), 3.81-3.71 (m, 1.69 H), 2.41 (s, 0.50 H), 2.31 (s, 3 H), 2.19 (s, 2.50 H), 1.38 (s, 2.52 H), 1.31 (s, 0.50 H), 1.16 (d, $J = 15.2$ Hz, 1 H), 1.05 (d, $J = 15.2$ Hz, 1 H), 0.88 (t, $J = 8.0$ Hz, 9 H), 0.52-0.39 (m, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm), major rotational isomer: $\delta$ 168.3, 141.9, 138.8, 133.4, 128.1, 122.6, 116.6, 63.5, 42.5, 30.8, 26.2, 24.1, 21.1, 7.4, 4.4; minor rotational isomer: $\delta$ 168.2, 144.8, 137.7, 133.1, 127.6, 124.0, 113.8, 62.1, 40.9, 30.1, 25.2, 24.4, 20.9, 7.3, 4.5; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for C$_{19}$H$_{32}$NOSi 318.2248; Found 318.2248.
1-(5-ethyl-3-methyl-3-((triethylsilyl)methyl)indolin-1-yl)ethan-1-one (3ca). Light yellow liquid, 71% yield (117.4 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 10:1). \(^1\)H NMR (400 MHz, CDCl\(_3\), ppm) present in 4.5:1 ratio of rotational isomers about the amide: \(\delta\) 8.06 (d, \(J = 8.0\) Hz, 1 H), 7.02-6.95 (m, 2 H), 3.92-3.84 (m, 0.36 H), 3.82-3.71 (m, 1.63 H), 2.64-2.58 (m, 2 H), 2.42 (s, 0.54 H), 2.19 (s, 2.46 H), 1.39 (s, 2.50 H), 1.33 (s, 0.55 H), 1.21 (t, \(J = 7.6\) Hz, 3 H), 1.18-1.05 (m, 2 H), 0.88 (t, \(J = 7.8\) Hz, 9 H), 0.50-0.37 (m, 6 H); \(^1\)C NMR (100 MHz, CDCl\(_3\), ppm), major rotational isomer: \(\delta\) 168.3, 141.8, 139.9, 139.1, 127.0, 121.5, 116.7, 63.6, 42.5, 31.0, 28.6, 26.2, 24.1, 15.9, 7.4, 4.3; minor rotational isomer: \(\delta\) 144.7, 139.6, 138.0, 126.5, 122.8, 113.9, 62.2, 40.9, 30.3, 28.4, 25.2, 24.4, 4.4. \(\text{HRMS (ESI-TOF) m/z: } [\text{M + H}]^+ \text{ Calcd for C}_{20}\text{H}_{34}\text{NOSi 332.2404; Found 332.2402.}\)

1-(5-isopropyl-3-methyl-3-((triethylsilyl)methyl)indolin-1-yl)ethan-1-one (3da). Light yellow liquid, 67% yield (116.1 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 10:1). \(^1\)H NMR (400 MHz, CDCl\(_3\), ppm) present in 4.2:1 ratio of rotational isomers about the amide: \(\delta\) 8.06 (d, \(J = 8.4\) Hz, 1 H), 7.06-6.97 (m, 2 H), 3.92-3.84 (m, 0.38 H), 3.82-3.71 (m, 1.61 H), 2.92-2.84 (m, 1 H), 2.42 (s, 0.57 H), 2.19 (s, 2.41 H), 1.40 (s, 2.46 H), 1.33 (s, 0.59 H), 1.24-1.22 (m, 6 H), 1.16 (d, \(J = 14.8\) Hz, 1 H), 1.07 (d, \(J = 15.2\) Hz, 1 H), 0.87 (t, \(J = 7.8\) Hz, 9 H), 0.49-0.34 (m, 6 H); \(^1\)C NMR (100 MHz, CDCl\(_3\), ppm), major rotational isomer: \(\delta\) 168.3, 144.6, 141.5, 139.2, 125.6, 120.0, 116.7, 63.7, 42.6, 34.0, 31.1, 26.3, 24.2, 24.1, 7.4, 4.3; minor rotational isomer: \(\delta\) 144.5, 144.3, 138.1, 125.1, 121.3, 113.8, 62.3, 41.0, 33.8, 30.4, 25.3, 24.4, 4.4; \(\text{HRMS (ESI-TOF) m/z: } [\text{M + H}]^+ \text{ Calcd for C}_{21}\text{H}_{36}\text{NOSi 346.2561; Found 346.2560.}\)
1-(5-(tert-butyl)-3-methyl-3-((triethylsilyl)methyl)indolin-1-yl)ethan-1-one (3ea).

Light yellow liquid, 64% yield (114.3 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 15:1). $^1$H NMR (400 MHz, CDCl$_3$, ppm) present in 4.0:1 ratio of rotational isomers about the amide: $\delta$ 8.07 (d, $J = 8.4$ Hz, 1 H), 7.23-7.12 (m, 2 H), 3.92-3.85 (m, 0.40 H), 3.82-3.72 (m, 1.60 H), 2.42 (s, 0.60 H), 2.19 (s, 2.39 H), 1.40 (s, 2.44 H), 1.34 (s, 0.61 H), 1.30 (s, 9 H), 1.15 (d, $J = 14.8$ Hz, 1 H), 1.08 (d, $J = 15.2$ Hz, 1 H), 0.86 (t, $J = 7.8$ Hz, 9 H), 0.49-0.32 (m, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm), major rotational isomer: $\delta$ 168.3, 146.9, 141.0, 138.9, 124.6, 118.8, 116.3, 63.7, 42.7, 34.6, 31.5, 31.3, 26.4, 24.1, 7.5, 4.3; minor rotational isomer: $\delta$ 146.5, 144.0, 137.8, 124.1, 120.2, 113.5, 62.3, 41.0, 34.5, 31.5, 30.6, 25.3, 24.4, 4.4; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for C$_{22}$H$_{38}$NOSi 360.2717; Found 360.2717.

1-(5-methoxy-3-methyl-3-((triethylsilyl)methyl)indolin-1-yl)ethan-1-one (3fa).

Light brown liquid, 70% yield (116.0 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). $^1$H NMR (400 MHz, CDCl$_3$, ppm) present in 6.3:1 ratio of rotational isomers about the amide: $\delta$ 8.08 (d, $J = 8.8$ Hz, 1 H), 6.74-6.67 (m, 2 H), 3.93-3.83 (m, 0.29 H), 3.81-3.71 (m, 4.83 H), 2.38 (s, 0.41 H), 2.17 (s, 2.59 H), 1.37 (s, 2.60 H), 1.30 (s, 0.41 H), 1.14 (d, $J = 15.2$ Hz, 1 H), 1.04 (d, $J = 14.8$ Hz, 1 H), 0.88 (t, $J = 7.8$ Hz, 9 H), 0.52-0.36 (m, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm), major rotational isomer: $\delta$ 167.9, 156.5, 143.5, 134.9, 117.5, 111.9, 108.5, 63.5, 55.6, 42.6, 30.7, 26.0, 23.9, 7.4, 4.3; minor rotational isomer: $\delta$ 156.3, 146.4, 133.7, 114.7, 111.7, 109.6, 62.2, 55.5, 41.2, 30.0, 25.0, 24.1, 7.3, 4.4; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for C$_{19}$H$_{32}$NO$_2$Si 334.2197; Found 334.2197.
1-(3-methyl-3-((triethylsilyl)methyl)-5-(trifluoromethoxy)indolin-1-yl)ethan-1-one (3ga). Yellow liquid, 79% yield (153.7 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 10:1). $^1$H NMR (400 MHz, CDCl$_3$, ppm) present in 10.1:1 ratio of rotational isomers about the amide: $\delta$ 8.17 (d, $J = 8.8$ Hz, 1 H), 7.04-7.01 (m, 1 H), 6.95 (s, 1 H), 3.92-3.90 (m, 0.18 H), 3.86-3.76 (m, 1.82 H), 2.42 (s, 0.27 H), 2.20 (s, 2.72 H), 1.39 (s, 2.72 H), 1.33 (s, 0.27 H), 1.15 (d, $J = 14.8$ Hz, 1 H), 1.06 (d, $J = 15.2$ Hz, 1 H), 0.88 (t, $J = 8.0$ Hz, 9 H), 0.50-0.36 (m, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta$ 168.7, 145.4, 143.7, 139.9, 120.6 (q, $^1J_{(C-F)} = 254.7$ Hz), 120.4, 117.6, 115.5, 63.6, 42.7, 30.9, 26.2, 24.1, 7.4, 4.4; $^{19}$F NMR (376 MHz, CDCl$_3$, ppm): $\delta$ -61.58; HRMS (ESI-TOF) $m/z$: [M + H]$^+$ Calcd for C$_{19}$H$_{29}$F$_3$NO$_2$Si 388.1914; Found 388.1914.

1-(3-methyl-3-((triethylsilyl)methyl)-5-(trifluoromethyl)indolin-1-yl)ethan-1-one (3ha). Yellow liquid, 43% yield (80.3 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 5:1). $^1$H NMR (400 MHz, CDCl$_3$, ppm) present in 10.5:1 ratio of rotational isomers about the amide: $\delta$ 8.25 (d, $J = 8.4$ Hz, 1 H), 7.47-7.44 (m, 1 H), 7.35 (s, 1 H), 3.87 (d, $J = 10.0$ Hz, 1 H), 3.80 (d, $J = 10.0$ Hz, 1 H), 2.46 (s, 0.26 H), 2.23 (s, 2.74 H), 1.42 (s, 2.74 H), 1.36 (s, 0.26 H), 1.18 (d, $J = 14.8$ Hz, 1 H), 1.08 (d, $J = 14.8$ Hz, 1 H), 0.88 (t, $J = 8.0$ Hz, 9 H), 0.52-0.35 (m, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta$ 169.2, 143.9, 142.4, 125.7 (q, $^2J_{(C-F)} = 32.0$ Hz), 125.3 (d, $^3J_{(C-F)} = 3.6$ Hz), 124.4 (q, $^1J_{(C-F)} = 270.0$ Hz), 119.2 (d, $^3J_{(C-F)} = 3.4$ Hz), 116.6, 63.5, 42.6, 30.9, 26.2, 24.2, 7.3, 4.3; $^{19}$F NMR (376 MHz, CDCl$_3$, ppm): $\delta$ -58.12; HRMS (ESI-TOF) $m/z$: [M + H]$^+$ Calcd for C$_{19}$H$_{29}$F$_3$NOSi 372.1965; Found 372.1964.
1-acetyl-3-methyl-3-((triethylsilyl)methyl)indoline-5-carbonitrile (3ia). Colorless liquid, 48% yield (78.5 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 7:1). $^1$H NMR (400 MHz, CDCl$_3$, ppm) δ 8.22 (d, $J$ = 8.4 Hz, 1 H), 7.48-7.45 (m, 1 H), 7.37 (s, 1 H), 3.85 (d, $J$ = 10.0 Hz, 1 H), 3.78 (d, $J$ = 10.0 Hz, 1 H), 2.22 (s, 3 H), 1.38 (s, 3 H), 1.16 (d, $J$ = 15.2 Hz, 1 H), 1.03 (d, $J$ = 15.2 Hz, 1 H), 0.88 (t, $J$ = 8.0 Hz, 9 H), 0.50-0.36 (m, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ 169.4, 144.8, 143.1, 132.7, 126.0, 119.3, 117.1, 106.5, 63.3, 42.6, 30.7, 26.2, 24.3, 7.4, 4.4; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for C$_{19}$H$_{29}$N$_2$OSi 329.2044; Found 329.2042.

ethyl 1-acetyl-3-methyl-3-((triethylsilyl)methyl)indoline-5-carboxylate (3ja). Yellow liquid, 41% yield (76.9 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 7:1). $^1$H NMR (400 MHz, CDCl$_3$, ppm) present in 9.2:1 ratio of rotational isomers about the amide: δ 8.18 (d, $J$ = 8.4 Hz, 1 H), 7.91-7.89 (m, 1 H), 7.80 (s, 1 H), 4.37-4.31 (m, 2 H), 3.87-3.77 (m, 2 H), 2.45 (s, 0.30 H), 2.22 (s, 2.75 H), 1.40-1.36 (m, 6 H), 1.20 (d, $J$ = 14.8 Hz, 1 H), 1.07 (d, $J$ = 15.2 Hz, 1 H), 0.87 (t, $J$ = 7.8 Hz, 9 H), 0.50-0.37 (m, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ 169.2, 166.4, 145.0, 142.1, 130.1, 125.8, 123.6, 116.1, 63.7, 60.8, 42.4, 30.9, 26.2, 24.3, 14.4, 7.4, 4.4; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for C$_{21}$H$_{34}$NO$_3$Si 376.2302; Found 376.2304.

1-(3-methyl-5-phenyl-3-((triethylsilyl)methyl)indolin-1-yl)ethan-1-one (3la). Yellow liquid, 67% yield (127.4 mg). Column chromatography on silica gel
(Petroleum ether/EtOAc = 10:1). $^1$H NMR (400 MHz, CDCl$_3$, ppm) present in 5.4:1 ratio of rotational isomers about the amide: $\delta$ 8.26 (d, $J = 8.4$ Hz, 1 H), 7.60-7.58 (m, 2 H), 7.46-7.30 (m, 5 H), 4.00-3.92 (m, 0.31 H), 3.89-3.79 (m, 1.68 H), 2.48 (s, 0.47 H), 2.24 (s, 2.55 H), 1.46 (s, 2.54 H), 1.40 (s, 0.47 H), 1.24 (d, $J = 14.8$ Hz, 1 H), 1.15 (d, $J = 15.2$ Hz, 1 H), 0.92 (t, $J = 8.0$ Hz, 9 H), 0.58-0.40 (m, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta$ 168.6, 142.5, 141.2, 140.7, 137.0, 128.8, 126.9 (2 C), 126.7, 120.8, 117.1, 63.7, 42.7, 31.0, 26.4, 24.2, 7.5, 4.4; HRMS (ESI-TOF) $m/z$: [M + H]$^+$ Calcd for C$_{24}$H$_{34}$NOSi 380.2404; Found 380.2402.

1-(5-fluoro-3-methyl-3-((triethylsilyl)methyl)indolin-1-yl)ethan-1-one (3ma).
White solid, 83% yield (132.7 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 10:1). M.p. = 32-34 °C. $^1$H NMR (400 MHz, CDCl$_3$, ppm) present in 9.0:1 ratio of rotational isomers about the amide: $\delta$ 8.14-8.11 (m, 1 H), 6.88-6.80 (m, 2 H), 3.96-3.85 (m, 0.20 H), 3.85-3.74 (m, 1.80 H), 2.40 (s, 0.30 H), 2.19 (s, 2.70 H), 1.38 (s, 2.69 H), 1.31 (s, 0.30 H), 1.14 (d, $J = 14.8$ Hz, 1 H), 1.04 (d, $J = 15.2$ Hz, 1 H), 0.89 (t, $J = 7.8$ Hz, 9 H), 0.52-0.42 (m, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta$ 168.3, 159.6 (d, $^1J_{(C-F)} = 240.6$ Hz), 144.0 (d, $^3J_{(C-F)} = 7.1$ Hz), 137.2 (d, $^4J_{(C-F)} = 1.8$ Hz), 117.8 (d, $^3J_{(C-F)} = 7.8$ Hz), 113.7 (d, $^2J_{(C-F)} = 22.5$ Hz), 109.3 (d, $^2J_{(C-F)} = 27.3$ Hz), 63.4, 42.6, 30.6, 26.0, 23.9, 7.4, 4.3; $^{19}$F NMR (376 MHz, CDCl$_3$, ppm): $\delta$ -118.83; HRMS (ESI-TOF) $m/z$: [M + H]$^+$ Calcd for C$_{18}$H$_{29}$FNOSi 322.1997; Found 322.1995.

1-(5-chloro-3-methyl-3-((triethylsilyl)methyl)indolin-1-yl)ethan-1-one (3na).
Yellow liquid, 90% yield (151.5 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 7:1). $^1$H NMR (400 MHz, CDCl$_3$, ppm) present in 8.7:1 ratio of rotational isomers about the amide: $\delta$ 8.10 (d, $J = 8.4$ Hz, 1 H), 7.15-7.07 (m,
2 H), 3.94-3.84 (m, 0.21 H), 3.84-3.74 (m, 1.81 H), 2.41 (s, 0.31 H), 2.20 (s, 2.70 H), 1.38 (s, 2.70 H), 1.32 (s, 0.31 H), 1.15 (d, J = 15.2 Hz, 1 H), 1.04 (d, J = 15.2 Hz, 1 H), 0.90 (t, J = 8.0 Hz, 9 H), 0.53-0.38 (m, 6 H); \( 1^3 \)C NMR (100 MHz, CDCl\(_3\), ppm): \( \delta \) 168.6, 143.9, 139.7, 128.6, 127.4, 122.4, 117.8, 63.4, 42.6, 30.6, 26.1, 24.0, 7.4, 4.3; HRMS (ESI-TOF) \( m/z \): [M + H]\(^+\) Calcd for C\(_{18}\)H\(_{29}\)ClNOSi 338.1701; Found 338.1700.

1-(4,6-dichloro-3-methyl-3-((triethylsilyl)methyl)indolin-1-yl)ethan-1-one (3pa). Colorless liquid, 47% yield (88.4 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 7:1). \( 1^H \) NMR (400 MHz, CDCl\(_3\), ppm): \( \delta \) 8.21 (d, J = 1.2 Hz, 1 H), 6.95 (d, J = 2.0 Hz, 1 H), 3.84 (d, J = 10.4 Hz, 1 H), 3.74 (d, J = 10.4 Hz, 1 H), 2.18 (s, 3 H), 1.54 (s, 3 H), 1.38-1.29 (m, 2 H), 0.88 (t, J = 7.8 Hz, 9 H), 0.45-0.40 (m, 6 H); \( 1^3 \)C NMR (100 MHz, CDCl\(_3\), ppm): \( \delta \) 168.9, 143.8, 135.4, 133.9, 130.3, 124.9, 115.9, 64.1, 43.9, 28.8, 24.3, 23.7, 7.4, 4.3; HRMS (ESI-TOF) \( m/z \): [M + H]\(^+\) Calcd for C\(_{18}\)H\(_{28}\)ClNOSi 372.1312; Found 372.1307.

1-(3-((triethylsilyl)methyl)indolin-1-yl)ethan-1-one (3qa). White solid, 67% yield (97.0 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 7:1). M.p. = 51-53 °C. \( 1^H \) NMR (400 MHz, CDCl\(_3\), ppm) present in 4.6:1 ratio of rotational isomers about the amide: \( \delta \) 8.17 (d, J = 8.0 Hz, 1 H), 7.23-7.01 (m, 3 H), 4.39 (t, J = 10.6 Hz, 0.18 H), 4.16 (t, J = 9.2 Hz, 0.82 H), 3.57-3.31 (m, 2 H), 2.42 (s, 0.53 H), 2.21 (s, 2.46 H), 1.23-1.18 (m, 1 H), 0.98 (t, J = 7.8 Hz, 9 H), 0.88-0.82 (m, 1 H), 0.63-0.56 (m, 6 H); \( 1^3 \)C NMR (100 MHz, CDCl\(_3\), ppm): \( \delta \) 168.5, 141.9, 137.9, 127.6, 123.7, 123.3, 116.8, 57.2, 36.4, 24.2, 18.3, 7.4, 3.9; HRMS (ESI-TOF) \( m/z \): [M + H]\(^+\) Calcd for C\(_{17}\)H\(_{28}\)NOSi 290.1935; Found 290.1932.
1-(3-methyl-3-((triethylsilyl)methyl)indolin-1-yl)propan-1-one (3ra). Yellow liquid, 79% yield (124.9 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 10:1). \(^1\)H NMR (400 MHz, CDCl\(_3\), ppm) present in 7.1:1 ratio of rotational isomers about the amide: \(\delta 8.20\) (d, \(J = 8.0\) Hz, 1 H), 7.20-7.12 (m, 2 H), 7.04-7.00 (m, 1 H), \(\delta 3.93\)-3.86 (m, 0.24 H), 3.82-3.71 (m, 1.71 H), 2.69 (s, 0.24 H), 2.45-2.39 (m, 1.71 H), 1.38 (s, 2.64 H), 1.33 (s, 0.37 H), 1.23 (t, \(J = 7.4\) Hz, 3 H), 1.17 (d, \(J = 15.2\) Hz, 1 H), 1.06 (d, \(J = 15.2\) Hz, 1 H), 0.88 (t, \(J = 7.8\) Hz, 9 H), 0.49-0.39 (m, 6 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), ppm): \(\delta 171.9\), 141.7, 141.4, 127.6, 123.6, 122.0, 116.8, 62.4, 42.6, 30.9, 29.2, 26.1, 8.7, 7.4, 4.4; HRMS (ESI-TOF) \(m/z\): [M + H]\(^+\) Calcd for C\(_{19}\)H\(_{32}\)NOSi 318.2248; Found 318.2245.

(3-methyl-3-((triethylsilyl)methyl)indolin-1-yl)(phenyl)methanone (3sa). Colorless liquid, 45% yield (81.7 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 10:1). \(^1\)H NMR (400 MHz, CDCl\(_3\), ppm) \(\delta 8.08\) (s, 1 H), 7.63-7.61 (m, 2 H), 7.55-7.52 (m, 3 H), 7.32-7.30 (m, 1 H), 7.21-7.15 (m, 1 H), 7.10-7.06 (m, 1 H), 3.91-3.85 (m, 2 H), 1.41 (s, 3 H), 1.23(d, \(J = 14.9\) Hz, 1 H), 1.11 (d, \(J = 14.9\) Hz, 1 H), 0.86 (t, \(J = 7.9\) Hz, 9 H), 0.49-0.38 (m, 6 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), ppm): \(\delta\) 168.0, 143.0, 141.5, 137.6, 130.1, 128.4, 127.1, 127.0, 123.9, 122.5, 116.7, 64.6, 42.4, 29.5, 25.2, 6.8, 4.0; HRMS (ESI-TOF) \(m/z\): [M + H]\(^+\) Calcd for C\(_{23}\)H\(_{32}\)NOSi 366.2248; Found 366.2244.

tert-butyl 3-methyl-3-((triethylsilyl)methyl)indoline-1-carboxylate (3ta). Colorless liquid, 54% yield (97.6 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 10:1). \(^1\)H NMR (400 MHz, CDCl\(_3\), ppm) present in 7.1:1 ratio of rotational isomers about the amide: \(\delta 8.18\) (d, \(J = 8.0\) Hz, 1 H), 7.20-7.12 (m, 2 H), 7.04-7.00 (m, 1 H), \(\delta 3.93\)-3.86 (m, 0.24 H), 3.82-3.71 (m, 1.71 H), 2.69 (s, 0.24 H), 2.45-2.39 (m, 1.71 H), 1.38 (s, 2.64 H), 1.33 (s, 0.37 H), 1.23 (t, \(J = 7.4\) Hz, 3 H), 1.17 (d, \(J = 15.2\) Hz, 1 H), 1.06 (d, \(J = 15.2\) Hz, 1 H), 0.88 (t, \(J = 7.8\) Hz, 9 H), 0.49-0.39 (m, 6 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), ppm): \(\delta 171.9\), 141.7, 141.4, 127.6, 123.6, 122.0, 116.8, 62.4, 42.6, 30.9, 29.2, 26.1, 8.7, 7.4, 4.4; HRMS (ESI-TOF) \(m/z\): [M + H]\(^+\) Calcd for C\(_{19}\)H\(_{32}\)NOSi 318.2248; Found 318.2245.
ether/EtOAc = 100:1). $^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta$ 7.62 (s, 1 H), 7.17-7.10 (m, 2 H), 6.97-6.93 (m, 1 H), 3.78-3.65 (m, 2 H), 1.56 (s, 9 H), 1.36 (s, 3 H), 1.11-1.00 (m, 2 H), 0.87 (t, $J$ = 8.0 Hz, 9 H), 0.43 (s, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta$ 152.5, 142.6, 141.4, 127.4, 122.3, 114.6, 80.4, 61.9, 41.7, 30.8 (2 C), 28.5, 26.7, 7.4, 4.3; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for C$_{21}$H$_{36}$NO$_2$SiNa 384.2329; Found 384.2325.

**tert-butyl 5-chloro-3-methyl-3-((triethylsilyl)methyl)indoline-1-carboxylate (3ua).**

Yellow liquid, 90% yield (178.6 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 100:1). $^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta$ 7.53 (s, 1 H), 7.11-7.04 (m, 2 H), 3.78-3.65 (m, 2 H), 1.55 (s, 9 H), 1.35 (s, 3 H), 1.10 (d, $J$ = 14.4 Hz, 1 H), 1.00 (d, $J$ = 14.8 Hz, 1 H), 0.88 (t, $J$ = 8.0 Hz, 9 H), 0.46-0.44 (m, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta$ 152.3, 143.5, 140.0, 127.3, 122.6, 115.6, 80.7, 62.1, 41.8, 30.5 (2 C), 28.4, 26.5, 7.4, 4.3; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for C$_{21}$H$_{35}$ClNO$_2$SiNa 418.1940; Found 418.1939.

**1-(3-methyl-3-((trihexylsilyl)methyl)indolin-1-yl)ethan-1-one (3ab).** Light yellow liquid, 58% yield (136.5 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 7:1). $^1$H NMR (400 MHz, CDCl$_3$, ppm) present in 5.3:1 ratio of rotational isomers about the amide: $\delta$ 8.17 (d, $J$ = 8.0 Hz, 1 H), 7.20-7.12 (m, 2 H), 7.05-7.01 (m, 1 H), 3.92-3.85 (m, 0.31 H), 3.83-3.72 (m, 1.66 H), 2.44 (s, 0.48 H), 2.21 (s, 2.55 H), 1.39-1.14 (m, 28 H), 1.05 (d, $J$ = 14.8 Hz, 1 H), 0.88 (t, $J$ = 6.8 Hz, 9 H), 0.48-0.34 (m, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta$ 168.5, 141.8, 141.2, 127.6, 123.8, 122.0, 116.9, 63.4, 42.6, 33.6, 31.5, 31.0, 27.2, 24.2, 23.8, 22.6, 14.1, 13.6; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for C$_{30}$H$_{54}$NOSi 472.3969; Found 472.3970.
**1-(3-methyl-3-((triisopropylsilyl)methyl)indolin-1-yl)ethan-1-one (3ac).** Colorless liquid, 31% yield (54.3 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 10:1). $^1$H NMR (400 MHz, CDCl$_3$, ppm) present in 5.1:1 ratio of rotational isomers about the amide: δ 8.17 (d, $J = 8.0$ Hz, 1 H), 7.24-7.16 (m, 2 H), 7.10-7.03 (m, 1 H), 4.01-3.92 (m, 0.33 H), 3.92-3.76 (m, 1.67 H), 2.44 (s, 0.49 H), 2.21 (s, 2.51 H), 1.41 (s, 2.51 H), 1.36 (s, 0.49 H), 1.28 (d, $J = 15.2$ Hz, 1 H), 1.15 (d, $J = 15.2$ Hz, 1 H), 1.06-1.03 (m, 21 H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ 168.6, 142.8, 140.9, 127.6, 123.9, 121.9, 116.9, 63.6, 42.5, 31.0, 24.3, 23.4, 19.1, 19.0, 11.9; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for C$_{21}$H$_{36}$NOSiNa 368.2380; Found 368.2378.

**1-(3-(((tert-butyldimethylsilyl)methyl)-3-methylindolin-1-yl)ethan-1-one (3ad).** Colorless liquid, 25% yield (37.8 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 10:1). $^1$H NMR (400 MHz, CDCl$_3$, ppm) present in 5.1:1 ratio of rotational isomers about the amide: δ 8.18 (d, $J = 8.0$ Hz, 1 H), 7.21-7.17 (m, 1 H), 7.13-7.09 (m, 1 H), 7.06-7.02 (m, 1 H), 3.97-3.83 (m, 0.33 H), 3.83-3.74 (m, 1.67 H), 2.44 (s, 0.49 H), 2.21 (s, 2.49 H), 1.40 (s, 2.49 H), 1.34 (s, 0.49 H), 1.18-1.08 (m, 2 H), 0.83 (s, 9 H), 0.00 (s, 3 H), -0.18 (s, 0.50 H), -0.25 (s, 2.50 H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ 168.6, 141.7, 141.2, 127.7, 123.8, 122.2, 116.9, 63.2, 42.5, 31.4, 26.4, 26.2, 24.3, 16.5, -4.1, -4.9; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for C$_{18}$H$_{30}$NOSi 304.2092; Found 304.2092.

**1-(3-(((dimethyl(phenyl)silyl)methyl)-3-methylindolin-1-yl)ethan-1-one (3ae).** Colorless liquid, 77% yield (125.0 mg). Column chromatography on silica gel
(Petroleum ether/EtOAc = 7:1). $^1$H NMR (400 MHz, CDCl$_3$, ppm) present in 9.2:1 ratio of rotational isomers about the amide: $\delta$ 8.18 (d, $J = 8.0 \text{ Hz}$, 1 H), 7.46-7.35 (m, 5 H), 7.22-7.18 (m, 1 H), 7.12-7.10 (m, 1 H), 7.04-7.00 (m, 1 H), 3.90-3.80 (m, 0.19 H), 3.54-3.42 (m, 1.75 H), 2.39 (s, 0.29 H), 1.72 (s, 2.67 H), 1.42-1.27 (m, 5 H), 0.25 (s, 0.29 H), 0.19 (s, 3 H), -0.02 (s, 2.67 H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta$ 169.9, 142.7, 142.0, 140.2, 134.7, 130.3, 129.1, 128.9, 124.9, 123.4, 118.0, 63.5, 43.7, 33.1, 32.7, 24.9, -0.0, -1.7; HRMS (ESI-TOF) $m/z$: [M + H]$^+$ Calcd for C$_{20}$H$_{26}$NOSi 324.1778; Found 324.1774.

1-(3-methyl-3-((methyldiphenylsilyl)methyl)indolin-1-yl)ethan-1-one (3af). Colorless liquid, 66% yield (128.0 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 7:1). $^1$H NMR (400 MHz, CDCl$_3$, ppm) present in 12.6:1 ratio of rotational isomers about the amide: $\delta$ 8.17 (d, $J = 8.0 \text{ Hz}$, 1 H), 7.50-7.30 (m, 10 H), 7.24-7.14 (m, 2 H), 7.05-7.02 (m, 1 H), 3.90-3.75 (m, 0.15 H), 3.57-3.38 (m, 1.85 H), 2.33 (s, 0.22 H), 1.77 (d, $J = 15.2 \text{ Hz}$, 1 H), 1.63 (d, $J = 14.8 \text{ Hz}$, 1 H), 1.58 (s, 2.78 H), 1.45 (s, 2.78 H), 1.31 (s, 0.22 H), 0.47 (s, 0.22 H), 0.19 (s, 2.78 H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta$ 168.8, 141.6, 140.7, 137.7, 136.8, 134.6, 134.3, 129.5, 129.3, 128.0, 127.9 (2 C), 123.8, 122.3, 116.9, 62.2, 42.5, 31.7, 29.8, 23.6, -3.9; HRMS (ESI-TOF) $m/z$: [M + H]$^+$ Calcd for C$_{25}$H$_{28}$NOSi 386.1935; Found 386.1933.

1-(3-methyl-3-((triphenylsilyl)methyl)indolin-1-yl)ethan-1-one (3ag). White solid, 78% yield (175.4 mg). Column chromatography on silica gel (Petroleum ether/EtOAc = 15:1). M.p. = 156-158 °C. $^1$H NMR (400 MHz, CDCl$_3$, ppm) present in 14.0:1 ratio of rotational isomers about the amide: $\delta$ 8.11-8.09 (m, 1 H), 7.58-7.56 (m, 6 H), 7.44-7.35 (m, 9 H), 7.17-7.14 (m, 2 H), 6.99-6.95 (m, 1 H), 3.76-3.65 (m, 0.13 H), 3.51-3.18 (m, 1.90 H), 2.29 (s, 0.20 H), 2.16 (d, $J = 15.2 \text{ Hz}$, 1 H), 1.95 (d, $J = 15.2 \text{ Hz}$, 1
H, 1.71 (s, 2.80 H), 1.32 (s, 2.80 H), 1.28 (s, 0.20 H); \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\), ppm): \(\delta\) 168.6, 142.0, 141.0, 135.8, 134.8, 129.7, 128.1, 127.7, 123.8, 122.1, 116.8, 62.5, 42.7, 30.9, 27.0, 23.8; \textbf{HRMS (ESI-TOF)} \(m/z\): [M + H]\(^+\) Calcd for C\(_{39}\)H\(_{30}\)NOSi 448.2091; Found 448.2093.

5. Radical trapping experiment

To study the reaction mechanism, several control experiments were carried out under the optimized reaction conditions (Scheme S2). When 2.0 equiv. of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) was added to the system, the reaction was completely inhibited. By adding 2.0 equiv. of radical scavenger 1,1-diphenylethylene to the reaction mixture, the reaction was totally suppressed and corresponding adducts 4 and 5 could be detected by GC-MS. When 2.0 equiv. of BHT (2,6-di-tert-butyl-4-methylphenol) was added to the reaction, no target product was obtained and GC-MS analysis indicated that compounds 6 and 7 were formed. These results showed that the reaction system proceeded in a free radical way.

Scheme S2. Radical trapping experiment
Figure S1. GC-MS (EI, m/z) of compound 4

Figure S2. GC-MS (EI, m/z) of compound 5
Figure S3. GC-MS (EI, m/z) of compound 6

Figure S4. GC-MS (EI, m/z) of compound 7

6. X-Ray crystallographic data of 3aa

The product 3aa was recrystallized from petroleum ether. Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC2120950.
Figure S5. Single-crystal X-ray Molecular Structure of 3aa

Table S2. Crystal data and structure refinement for 3aa

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2Θ range for data collection/° 8.068 to 134.14
Index ranges -26 ≤ h ≤ 26, -5 ≤ k ≤ 8, -26 ≤ l ≤ 26
Reflections collected 12393
Independent reflections 3274 [R_{int} = 0.0402, R_{sigma} = 0.0365]
Data/restraints/parameters 3274/0/195
Goodness-of-fit on F² 1.037
Final R indexes [I>=2σ (I)] R$_1$ = 0.0470, wR$_2$ = 0.1276
Final R indexes [all data] R$_1$ = 0.0606, wR$_2$ = 0.1415
Largest diff. peak/hole / e Å⁻³ 0.32/-0.17

7. References


8. $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra of the products
Figure S6. $^1$H NMR (400 MHz, CDCl$_3$) of compound 3aa
Figure S7. $^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3aa
Figure S8. $^1$H NMR (400 MHz, CDCl$_3$) of compound 3ba
Figure S9. $^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3ba
Figure S10. $^1$H NMR (400 MHz, CDCl$_3$) of compound 3ca
Figure S11. $^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3ca
Figure S12. $^1$H NMR (400 MHz, CDCl$_3$) of compound 3da
Figure S13. $^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3da
Figure S14. $^1$H NMR (400 MHz, CDCl$_3$) of compound 3ea
Figure S15. $^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3ea
Figure S16. $^1$H NMR (400 MHz, CDCl$_3$) of compound 3fa
Figure S17. $^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3fa
Figure S18. $^1$H NMR (400 MHz, CDCl$_3$) of compound 3ga
Figure S19. $^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3ga
Figure S20. $^{19}$F NMR (376 MHz, CDCl$_3$) of compound 3ga
Figure S21. $^1$H NMR (400 MHz, CDCl$_3$) of compound 3ha
Figure S22. $^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3ha
Figure S23. $^{19}$F NMR (376 MHz, CDCl$_3$) of compound 3ha
Figure S24. $^1$H NMR (400 MHz, CDCl$_3$) of compound 3ia
Figure S25. $^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3ia
Figure S26. $^1$H NMR (400 MHz, CDCl$_3$) of compound 3ja
Figure S27. $^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3ja
Figure S28. $^1$H NMR (400 MHz, CDCl$_3$) of compound 3la
Figure S29. $^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3la
Figure S30. $^1$H NMR (400 MHz, CDCl$_3$) of compound 3ma
Figure S31. $^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3ma
Figure S32. $^{19}\text{F NMR (376 MHz, CDCl}_3$) of compound 3ma
Figure S33. $^1$H NMR (400 MHz, CDCl$_3$) of compound 3na
Figure S34. $^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3na
Figure S35. $^1$H NMR (400 MHz, CDCl$_3$) of compound 3pa
Figure S36. $^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3ba
Figure S37. ^1^H NMR (400 MHz, CDCl\textsubscript{3}) of compound 3qa
Figure S38. $^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3qa
Figure S39. $^1$H NMR (400 MHz, CDCl$_3$) of compound 3ra
Figure S40. $^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3ra
Figure S41. $^1$H NMR (400 MHz, CDCl$_3$) of compound 3sa
Figure S42. $^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3sa
Figure S43. $^1$H NMR (400 MHz, CDCl$_3$) of compound 3ta
Figure S44. $^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3ta
Figure S45. $^1$H NMR (400 MHz, CDCl$_3$) of compound 3ua
Figure S46. $^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3ua
Figure S47. $^1$H NMR (400 MHz, CDCl$_3$) of compound 3ab
Figure S48. $^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3ab
Figure S49. $^1$H NMR (400 MHz, CDCl$_3$) of compound 3ac
Figure S50. $^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3ac
Figure S51. $^1$H NMR (400 MHz, CDCl$_3$) of compound 3ad
Figure S52. $^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3ad
Figure S53. $^1$H NMR (400 MHz, CDCl$_3$) of compound 3ae
Figure S54. $^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3ae
Figure S55. $^1$H NMR (400 MHz, CDCl$_3$) of compound 3af
Figure S56. $^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3af
Figure S57. $^{1}$H NMR (400 MHz, CDCl$_3$) of compound 3ag
Figure S58. $^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3ag