Supporting Information

A Carbazolyl Dicyanobenzene Dye for the Photooxidation of Bis-Catecholato Silicates

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I. General informations

Unless otherwise noted, reactions were carried out under an argon atmosphere in oven-dried glassware. Methanol and toluene were distilled over CaH₂, THF and diethyl ether were distilled over sodium/benzophenone, triethylamine over potassium hydroxide. Catechol was purchased from commercial source and purified by crystallization from toluene followed by sublimation. Reagents and chemicals were purchased from commercial sources and used as received. Infrared (IR) spectra were recorded on a Bruker Tensor 27 (ATR diamond) spectrophotometer. Melting points were determined on a melting point apparatus SMP3 (Stuart scientific) and are uncorrected. \(^1\)H, \(^{19}\)F, \(^{31}\)P and \(^{13}\)C NMR spectra were recorded at room temperature at 400, 377, 162 and 100 MHz respectively, on a Bruker AVANCE 400 spectrometer. \(^{29}\)Si NMR spectra were recorded at 119 MHz on a Bruker AVANCE III 600 spectrometer. Chemical shifts (\(\delta\)) are reported in ppm and coupling constants (\(J\)) are given in Hertz (Hz). Abbreviations used for peak multiplicity are: s (singlet); bs (broad singlet); d (doublet); t (triplet); q (quartet); quint (quintet); sept (septet); m (multiplet). Thin layer chromatographies (TLC) were performed on Merck silica gel 60 F 254 and revealed with a UV lamp (\(\lambda = 254\) nm) and KMnO₄ staining. Flash Column Chromatographies were conducted on silica Geduran® Si 60 Å (40 – 63 \(\mu\)m). High resolution mass spectrometries were performed on a microTOF (ESI).
II. General procedures

1. General procedure A for silicate synthesis

**Method A:**

\[
R\text{Si}(OR')_3 + \begin{array}{c}
\text{catechol} \\
\text{OH} \\
\text{OH}
\end{array} \xrightarrow{\text{MeOK / MeOH}} \begin{array}{c}
\text{MeOK / MeOH} \\
18\text{-C-6, rt, 3h}
\end{array} \xrightarrow{\text{[18-C-6]}} \begin{array}{c}
\text{R} \\
\text{Si} \\
\text{K}^{+}
\end{array}
\]

To a stirred solution of catechol (2 eq.) in dry methanol (0.25 M) was added 18-C-6 (1 eq.). After dissolution of the crown ether, the trialkoxy organosilane (1 eq.) was added, followed by a solution of potassium methoxide in methanol (1 eq.). The reaction mixture was stirred for 3 hours and the solvent was removed under reduced pressure. The residue was dissolved in the minimum volume of acetone and diethyl ether was added until a cloudy solution was obtained (scrapping on the edge of the flask could be done to induce crystallization). The flask was placed at -20°C overnight. The crystals were collected by filtration, washed with cold diethyl ether and dried under vacuum to afford [18-C-6] silicate.

**Method B:**

\[
R\text{SiCl}_3 + \begin{array}{c}
\text{catechol} \\
\text{OH} \\
\text{OH}
\end{array} \xrightarrow{\text{1. Et}_3\text{N, THF}} \begin{array}{c}
\text{Et}_3\text{N, THF} \\
0^\circ\text{C to rt}
\end{array} \xrightarrow{\text{2. Et}_4\text{NBr, CH}_3\text{CN}} \begin{array}{c}
\text{Et}_4\text{NBr, CH}_3\text{CN} \\\	ext{rt}
\end{array} \xrightarrow{\text{[18-C-6]}} \begin{array}{c}
\text{R} \\
\text{Si} \\
\text{K}^{+}
\end{array}
\]

To a stirred solution of catechol (2 eq.) in dry THF (0.1 M) was added triethylamine (4 eq.). The reaction mixture was cooled to 0°C with an ice bath and organotrichlorosilane (1 eq.) was added dropwise. The mixture was stirred for an hour at 0°C and an additional hour at room temperature. The triethylamine hydrochloride salt was filtered off and the filtrate was evaporated under reduced pressure. The residue was taken up in acetonitrile (0.3 M) and tetraethylammonium bromide (1 eq.) was added. The mixture was stirred for an hour and the solvent was evaporated under reduced pressure. The solid was taken up in water, filtered, washed with water and dried under high vacuum to afford tetraethylammonium silicate.
2. Synthesis of Alkenyl bromides

1-Bromocyclooctene (7a)

The compound 7a has been synthesized following a previous reported procedure.[1] The spectroscopic data are in agreement with those reported in the literature.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 6.03 (t, $J = 8.5$, 1H), 2.63 – 2.59 (m, 2H), 2.13 – 2.07 (m, 2H), 1.64 – 1.62 (m, 2H), 1.55 – 1.50 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 131.8, 125.0, 35.3, 30.0, 28.8, 27.6, 26.6, 25.6.

((2-Bromoallyloxy)(tert-butyl)dimethylsilane (7b)

The compound 7b has been synthesized following a previous reported procedure.[2] The spectroscopic data are in agreement with those reported in the literature.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 5.85 (d, $J = 1.8$ Hz, 1H), 5.43 (d, $J = 1.6$ Hz, 1H), 4.11 – 4.10 (m, 2H), 0.82 (s, 9H), 0.00 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 132.0, 114.8, 67.6, 25.9 (3 C), 18.5, -5.2 (2 C). IR (neat): 2958, 2854, 1637, 1463, 124, 1085, 838, 774 cm$^{-1}$.

(E)-(2-bromovinyl)benzene (7d)

The compound 7d has been synthesized following a previous reported procedure.[3] The spectroscopic data are in agreement with those reported in the literature.
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.35 – 7.30 (m, 5H), 7.13 (d, $J = 14.0$ Hz, 1H), 6.79 (d, $J = 14.0$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 137.3, 136.0, 128.9 (2 C), 128.4, 126.2 (2 C), 106.6.

(Z)-(2-bromovinyl)benzene (7d')

The compound 7d' has been synthesized following a previous reported procedure. [4]

The spectroscopic data are in agreement with those reported in the literature.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.83 – 7.80 (m, 2H), 7.52 – 7.4 (m, 3H), 7.15 (d, $J = 8.1$ Hz, 1H), 6.52 (d, $J = 8.1$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 137.3, 136.0, 128.9 (2 C), 128.4, 126.2 (2 C), 106.6.

(2-chlorovinyl)benzene (7e)

The compound 7f has been synthesized following a previous reported procedure.[1]

A mixture of isomer was obtained (ratio Z/E 5:95). The spectroscopic data are in agreement with those reported in the literature.[1]

(E) isomer:

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.11 (d, $J = 8.6$ Hz, 2H), 6.74 (d, $J = 8.6$ Hz, 2H), 6.65 (d, $J = 13.6$ Hz, 1H), 6.38 (d, $J = 13.6$ Hz, 1H), 3.69 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 159.7, 132.8, 127.7, 127.5 (2 C), 116.5, 114.3 (2 C), 55.4.

(Z) isomer:

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.55 (d, $J = 8.7$ Hz, 2H), 6.80 (d, $J = 8.9$ Hz, 2H), 6.45 (d, $J = 8.1$ Hz, 1H), 6.04 (d, $J = 8.1$ Hz, 1H), 3.71 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 159.5, 130.8 (2 C), 128.7, 127.0, 115.5, 113.8 (2 C), 55.4.
1-(2,2-dichlorovinyl)-4-methoxybenzene (7f)

To a 250 mL round-bottom-flask was added the para-anisaldehyde (5 mmol, 0.607 mL) and 40 mL of MeCN. The reaction mixture was cooled with an ice bath to 0°C and BrCCl$_3$ (7.5 mmol, 0.740 mL) was added, followed by addition of a solution of triphenylphosphine (15 mmol, 3.95g) in the minimum of MeCN. The reaction mixture was stirred at room temperature for 3 hours and the solvent was removed under reduced pressure to afford the crude product. The residue was dissolved in 80 mL of pentane and the organic phase was washed with water (80 mL), brine (80 mL) and dried over MgSO$_4$. The solvent was removed under reduced pressure and the residue filtered on a pad of silica eluted with pentane, giving the pure material (559 mg, 55%). The spectroscopic data are in agreement with those reported in the literature.[6]

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.50 (d, $J = 8.8$ Hz, 2H), 6.90 (d, $J = 8.8$ Hz, 2H), 6.79 (s, 1H), 3.83 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 159.7, 130.2 (2 C), 128.2, 126.1, 118.9, 114.0 (2 C), 55.4.

3. Synthesis of 4CzIPN

The 4CzIPN has been synthesized following a previous reported procedure.[7] To a 100 mL round-bottom-flask was added NaH (60% in mineral oil) (7.5 eq., 15 mmol, 600 mg). THF (40 mL) was added followed by the slow addition of carbazole (5.0 eq., 10 mmol, 1.67 g). After 30 min of stirring at room temperature the tetrafluoroisophtalonitrile (1.0 eq., 2 mmol, 400 mg) was added and the mixture was stirred at room temperature for 20 hours. A yellow precipitate progressively appeared. Water (1 mL) was added to neutralize the excess of NaH and the mixture was evaporated to give a yellow solid. The solid was successively washed with water and ethanol. The crude product was dissolved in the minimum of DCM
and crystallized by addition of pentane to give the pure 4CzIPN (1.13g, 71% yield). The spectroscopic data are in agreement with those reported in the literature.  

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.35 (dt, $J = 7.7$, 1.0 Hz, 1H), 8.19 (d, $J = 8.3$ Hz, 1H), 7.87 – 7.84 (m, 2H), 7.76 – 7.72 (m, 3H), 7.55 – 7.44 (m, 3H), 7.12 (dtd, $J = 17.9$, 7.3, 1.3 Hz, 4H), 6.83 – 6.79 (m, 1H), 6.72 – 6.68 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 145.6, 144.8, 139.9, 138.5, 137.6, 136.4, 126.8, 125.4, 124.1, 123.6, 123.2, 122.8, 121.9, 121.3, 121.0, 120.5, 120.1, 119.4, 116.7, 112.2, 111.1, 110.9, 110.8.

4. Spin trapping experiments with TEMPO for screening of photocatalyst:

To a schlenk flask was added the potassium [18-Crown-6] bis(catecholato)-benzylsilicate 1a (0.3 mmol), the appropriate photocatalyst (0.03 mmol) and TEMPO (0.66 mmol, 103 mg). The schlenk flask was sealed with a rubber septum, and evacuated / purged with vacuum / argon three times. Degassed DMF (3 mL) was introduced and the reaction mixture was irradiated with blue LED (477 nm) at room temperature for 24h under an argon atmosphere. The reaction mixture was diluted with diethyl ether (50 mL), washed with aqueous saturated Na$_2$CO$_3$ solution (2 times), brine (2 times), dried over MgSO$_4$ and evaporated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (pentane/Et$_2$O, 99/1) to afford 2a as a colorless oil.
Table 1: Screening of organic photocatalyst in spin trapping experiments with TEMPO

<table>
<thead>
<tr>
<th>Entry</th>
<th>Photocatalyst used</th>
<th>Photocatalyst loading (% mol)</th>
<th>Isolated yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Eosin Y</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Fluorescein</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>Fukuzumi’s catalyst</td>
<td>10</td>
<td>66</td>
</tr>
<tr>
<td>4</td>
<td>4CzIPN</td>
<td>10</td>
<td>92</td>
</tr>
<tr>
<td>5</td>
<td>4CzIPN</td>
<td>1</td>
<td>94</td>
</tr>
</tbody>
</table>

5. General procedure B for silicates additions on allylsulfone

To a schlenk flask was added the appropriate silicate (1 eq., 0.3 mmol), allyl sulfone 3a (4 eq., 1.2 mmol, 322 mg) and 4CzIPN (1 mol %, 3 μmol, 2.4 mg). Degassed DMF was added (3 mL) and the reaction mixture was irradiated with blue LED (477 nm) at room temperature for 24h under an argon atmosphere. The reaction mixture was diluted with diethyl ether (50 mL), washed with saturated aqueous NaHCO₃ (2 times), brine (2 times), dried over MgSO₄ and evaporated under reduced pressure. The crude product was purified by flash column chromatography to afford the adduct 4.

6. General procedure C for cyclohexylsilicate 1d vinylation and alkynylation reactions

To a schlenk flask was added potassium [18-C-6] bis(catecholato) cyclohexylsilicate 1d (1 eq., 0.3 mmol, 189.3 mg), 4CzIPN (1 mol %, 3 μmol, 2.4 mg) and the desired acceptor.
3 (4 eq., 1.2 mmol) (liquid alkenes were added with the solvent). Degassed DMF was added (3 mL). The reaction mixture was irradiated with blue LED (477 nm) for 24 hours. The reaction mixture was diluted with diethyl ether (50 mL), washed with saturated aqueous NaHCO₃ (2 times), brine (2 times), dried over MgSO₄ and evaporated under reduced pressure. The crude product was purified by flash column chromatography to afford the adduct 4.

7. General procedure D for cyclohexylsilicate 1d addition into activated alkenes

To a schlenk flask was added potassium [18-C-6] bis(catecholato) cyclohexylsilicate 1d (1 eq., 0.3 mmol, 189.3 mg), KH₂PO₄ (1.2 eq., 0.36 mmol, 49 mg), 4CzIPN (1 mol %, 3 µmol, 2.4 mg) and the desired alkene 3 (4 eq., 1.2 mmol) (liquid alkenes were added with the solvent). Degassed DMF was added (3 mL). The reaction mixture was irradiated with blue LED (477 nm) for 24 hours. The reaction mixture was diluted with diethyl ether (50 mL), washed with saturated aqueous NaHCO₃ (2 times), brine (2 times), dried over MgSO₄ and evaporated under reduced pressure. The crude product was purified by flash column chromatography to afford the 1,4 adduct 4.

8. General procedure E for photoredox/nickel cross-coupling dual catalysis with aryl/heteroaryl halide or vinyl bromide

To a schlenk flask was added aryl, heteroaryl halide 5 or alkenyl halide 7 (1 eq., 0.3 mmol), appropriate silicate 1 (1.5 eq., 0.45 mmol), 4CzIPN (1 mol%, 3 µmol, 2.4 mg), and 4,4′-di-tert-butyl-2,2′-bipyridine (2 mol %, 6 µmol, 1.6 mg). The schlenk flask was taken into
a glovebox and NiCl$_2$.dme (2 mol %, 6 µmol, 1.3 mg) was added. The schlenk flask was sealed with a rubber septum, removed from the glovebox, and evacuated / purged with vacuum / argon three times. Degassed DMF (3 mL) was introduced (followed by the aryl or heteroaryl halide if liquid) and the reaction mixture was irradiated with blue LEDs (477 nm) for 24 hours. The reaction mixture was diluted with diethyl ether (50 mL), washed with saturated NaHCO$_3$ (2 times), brine (2 times), dried over MgSO$_4$ and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the coupling adduct 6 or 8.


To a 100 mL schlenk flask was added 4'-bromoacetophenone 5a (1 eq., 3 mmol, 597 mg), acetoxypropylsilicate 1g (1.5 eq., 4.5 mmol, 2.92 g), 4CzIPN (1 mol%, 30 µmol, 23.7 mg) and 4,4'-di-tert-butyl-2,2'-bipyridine (2 mol %, 60 µmol, 16.1 mg). The schlenk flask was taken into a glovebox and NiCl$_2$.dme (2 mol %, 60 µmol, 13.2 mg) was added. The schlenk flask was sealed with a rubber septum, removed from the glovebox, and evacuated / purged with vacuum / argon three times. Degassed DMF (30 mL) was introduced and the reaction mixture was irradiated with blue LEDs (477 nm) for 48 hours. The reaction mixture was diluted with diethyl ether (200 mL) and washed with saturated NaHCO$_3$. The aqueous phase was extracted with diethyl ether and the combined organic phases were washed with saturated NaHCO$_3$ (2 times), brine (2 times), dried over MgSO$_4$ and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the 4'-(acetoxypropyl)acetophenone 6ag (503 mg, 76%).

III. Compound characterizations

Potassium [18-Crown-6] bis(catecholato)-benzylsilicate (1a)

![Structure of 1a]
Silicate 1a was synthesized as described. The spectroscopic data are in agreement with those reported in the literature.\cite{8}

**Potassium [18-Crown-6] bis(catecholato)-anilinomethylsilicate (1b)**

![Structure of 1b]

Silicate 1b was synthesized as described. The spectroscopic data are in agreement with those reported in the literature.\cite{8}

**Tetraethylammonium bis(catecholato)-tertbutylsilicate (1c)**

![Structure of 1c]

Silicate 1c was synthesized as described. The spectroscopic data are in agreement with those reported in the literature.\cite{8}

**Potassium [18-Crown-6] bis(catecholato)-cyclohexylsilicate (1d)**

![Structure of 1d]

Silicate 1d was synthesized as described. The spectroscopic data are in agreement with those reported in the literature.\cite{8}
Potassium [18-Crown-6] bis(catecholato)-hexylsilicate (1e)

![Chemical structure](image)

Silicate 1e was synthesized as described. The spectroscopic data are in agreement with those reported in the literature.[8]

Potassium [18-Crown-6] bis(catecholato)-2-(diphenylphosphine oxide)ethylsilicate (1f)

![Chemical structure](image)

a) Oxidation of diphenyl(2-(triethoxysilyl)ethyl)phosphine

The oxidation step has been realized according to a previous reported procedure.[10] To a stirred solution of diphenyl(2-(triethoxysilyl)ethyl)phosphine (6 mmol, 2.15 mL) in 50 mL of toluene was added, at 0°C, a solution of m-chloroperbenzoic acid (6 mmol, 1.04 g) in 15 mL of toluene. After complete addition, the reaction mixture was warmed to room temperature and stirred for 5h. The reaction mixture was quenched with 50 mL of aqueous saturated Na₂CO₃ solution. The organic phase was then washed with 50 mL of saturated Na₂CO₃ solution (2 times), 50 mL of brine and dried over MgSO₄. Toluene was removed under reduced pressure to give a white waxy solid. The crude material was dissolved in the minimum volume of DCM and crystallized by slow addition of pentane. The Diphenyl(2-(triethoxysilyl)ethyl)phosphine oxide was collected by filtration and washed with pentane (1.28 g, 54%).

\[ ^1H \text{ NMR} \ (400 \text{ MHz, Acetone-d}_6) : \delta \ 7.86 - 7.81 \ (m, 4H), \ 7.58 - 7.49 \ (m, 6H), \ 3.80 \ (q, \ J = 6.9 \ Hz, \ 6H), \ 2.34 - 2.27 \ (m, \ 2H), \ 1.17 \ (t, \ J = 6.9 \ Hz, \ 9H), \ 0.78 - 0.71 \ (m, \ 2H). \]

\[ ^13C \text{ NMR} \ (150 \text{ MHz, Acetone-d}_6) : \delta \ 135.37 \ (d, \ J = 95.1 \ Hz, \ 2C), \ 132.4 \ (d, \ J = 2.5 \ Hz, \ 2C), \ 131.8 \ (d, \ J = 9.1 \ Hz, \ 4C), \ 129.6 \ (d, J = 11.1 \ Hz, \ 4C), \ 59.2, \ 23.7 \ (d, J = 71.0 \ Hz), \ 18.9 \ (3C), \ 2.13 \ (d, \ J = 6.4 \ Hz). \]

\[ ^31P \text{ NMR} \ (162 \text{ MHz, Acetone-d}_6) : \delta \ 29.92. \]

\[ ^29Si \text{ NMR} \ (119 \text{ MHz, Acetone-d}_6) : \delta - 47.22 \ (d, J = 29.8 \ Hz). \]

HRMS calc. for [C\text{20}H\text{20}NaO\text{4}PSi]^+ 415.1465; found 415.1461. \textbf{M.p.} 72°C. \textbf{IR} (neat): 3053, 2973, 2924, 1482, 1167, 1064, 758, 748, 729, 692 cm⁻¹.
b) Silicate synthesis

Following the general procedure A, with 2-(diphenylphosphine oxide)ethylsilane (2.5 mmol, 981 mg), catechol (5 mmol, 550.6 mg), 18-Crown-6 (2.5 mmol, 660 mg) and potassium methoxide (2.5 mmol, 700 μL of a 3.56 M solution in methanol) in 10 mL of dry methanol at room temperature. The crude product was purified according the general procedure to afford 1e (1.41 g, 72%) as a white solid.

$^1$H NMR (400 MHz, Methanol-d4): δ 7.57 – 7.47 (m, 6H), 7.42 – 7.39 (m, 4H), 6.71 – 6.70 (m, 4H), 6.60 – 6.59 (m, 4H), 3.52 (s, 24H), 2.38 – 2.33 (m, 2H), 0.83 – 0.79 (m, 2H). $^{13}$C NMR (100 MHz, Methanol-d4): δ 150.8 (4 C), 133.3 (d, $J = 97.5$ Hz, 2 C), 133.0 (d, $J = 2.6$ Hz, 2 C), 131.8 (d, $J = 9.3$ Hz, 4 C), 129.8 (d, $J = 11.6$ Hz, 4 C), 119.6 (4 C), 111.7 (4 C), 71.2 (12 C), 25.1 (d, $J = 70.4$ Hz), 8.2 (d, $J = 7.3$ Hz, 2 C). $^{31}$P NMR (162 MHz, Methanol-d4): δ 40.12. $^{29}$Si NMR (119 MHz, Methanol-d4): δ -78.10 (d, $J = 34.8$ Hz). HRMS calc. for [C$_{26}$H$_{22}$O$_5$PSi]$^-$: 473.0980; found 473.0964. M.p. 229°C. IR (neat): 2990, 2895, 1482, 1238, 1103, 826, 734, 723 cm$^{-1}$.

Potassium [18-Crown-6] bis(catecholato)-acetoxypropylsilicate (1g)

Silicate 1g was synthesized as described. The spectroscopic data are in agreement with those reported in the literature.[9]

Potassium [18-Crown-6] bis(catecholato)-acetoxyethylsilicate (1h)

Silicate 1h was synthesized as described. The spectroscopic data are in agreement with those reported in the literature.[9]
Potassium [18-Crown-6] bis(catecholato)-chloromethylsilicate (1i)

Silicate 1i was synthesized as described. The spectroscopic data are in agreement with those reported in the literature.\textsuperscript{[8]}

Potassium [18-Crown-6] bis(catecholato)-hex-5-enylsilicate (1j)

Silicate 1j was synthesized as described. The spectroscopic data are in agreement with those reported in the literature.\textsuperscript{[8]}

$\text{1-(Benzyloxy)-2,2,6,6-tetramethylpiperidine (2a)}$

Following procedure of spin-trapping experiments with 1a (0.3 mmol, 192 mg). The crude product was purified by flash column chromatography (pentane/Et$_2$O, 99/1) to afford 2a as a colorless oil. The spectroscopic data are in agreement with those reported in the literature.\textsuperscript{[8]}

$\text{^1H NMR (400 MHz, CDCl}_3\text{): } \delta 7.40 – 7.26 \text{ (m, 5H), 4.85 \text{ (s, 2H), 1.58 – 1.50 \text{ (m, 5H), 1.38 – 1.35 \text{ (m, 1H), 1.28 \text{ (s, 6H), 1.21 \text{ (s, 6H).}}}}$

$\text{^{13}C NMR (100 MHz, CDCl}_3\text{): } \delta 138.6, 128.4 \text{ (2 C), 127.7 \text{ (2 C), 127.5, 79.0, 60.2 \text{ (2 C), 40.0 \text{ (2 C), 33.4 \text{ (2 C), 20.6 \text{ (2 C), 17.4.}}}}$

Ethyl 2-methylene-4-(phenylamino)butanoate (4ab)
Following general procedure B with 1b (0.3 mmol, 196.2 mg). The crude product was purified by flash column chromatography (pentane/ethyl acetate, 95/5) to afford 4ab as a colorless oil (62 mg, 93%). The spectroscopic data are in agreement with those reported in the literature.\[8\]

$^1$H NMR (300 MHz, CDCl$_3$): \(\delta\) 7.22 – 7.16 (m, 2H), 7.74 – 7.69 (m, 2H), 6.65 – 6.62 (m, 2H), 6.27 (d, \(J = 1.4\) Hz, 1H), 6.54 (d, \(J = 1.3\) Hz, 1H), 4.25 (q, \(J = 7.1\) Hz, 2H), 3.68 (bs, 1H), 3.31 (d, \(J = 6.8\) Hz, 2H), 2.64 (td, \(J = 6.8, 1.1\) Hz, 2H), 1.33 (t, \(J = 7.1\) Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$): \(\delta\) 167.1, 148.0, 138.4, 129.3 (2 C), 126.7, 117.4, 112.9 (2 C), 61.0, 43.0, 32.1, 14.3.

**Ethyl 4,4-dimethyl-2-methylenepentanoate (4ac)**

Following general procedure B with 1c (0.3 mmol, 129.5 mg). The crude product was purified by flash column chromatography (pentane/ethyl acetate, 95/5) to afford 4ac as a colorless oil (48 mg, 94%). The spectroscopic data are in agreement with those reported in the literature.\[8\]

$^1$H NMR (400 MHz, CDCl$_3$): \(\delta\) 6.17 (d, \(J = 1.4\) Hz, 1H), 5.44 – 5.44 (m, 1H), 4.19 (q, \(J = 7.1\) Hz, 2H), 2.28 (d, \(J = 0.8\) Hz, 2H), 1.29 (t, \(J = 7.1\) Hz, 3H), 0.88 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$): \(\delta\) 168.2, 139.1, 126.8, 60.6, 53.4, 44.5, 31.5, 29.2 (3 C), 14.2.

**Ethyl 2-(cyclohexylmethyl)acrylate (4ad)**

Following general procedure B with 1d (0.3 mmol, 189.3 mg). The crude product was purified by flash column chromatography (pentane/diethyl ether, 95/5) to afford 4ad as a colorless oil (52 mg, 88%). The spectroscopic data are in agreement with those reported in the literature.\[8\]

$^1$H NMR (400 MHz, CDCl$_3$): \(\delta\) 6.13 (d, \(J = 1.8\) Hz, 1H), 5.45 (m, 1H), 4.19 (q, \(J = 7.1\) Hz, 2H), 2.18 (dd, \(J = 7.1, 1.1\) Hz, 2H), 1.72 – 1.61 (m, 5H), 1.46 – 1.41 (m, 1H), 1.29 (t, \(J = 7.1\) Hz, 3H), 1.23 – 1.08 (m, 3H), 0.92 – 0.85 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): \(\delta\) 167.7, 139.8, 125.6, 125.5, 60.6, 40.1, 36.8, 33.4, 33.2, 26.7, 26.4, 14.3.
Ethyl 2-methylenenonanoate (4ae)

Following general procedure B with 1e (0.3 mmol, 184.7 mg). The crude product was purified by flash column chromatography (pentane/diethyl ether, 95/5) to afford 4ae as a colorless oil (34 mg, 57%). The spectroscopic data are in agreement with those reported in the literature.[8]

^1H NMR (400 MHz, CDCl3): \( \delta \) 6.11 (d, \( J = 1.5 \) Hz, 1H), 5.50 (q, \( J = 1.5 \) Hz, 1H), 4.20 (q, \( J = 7.1 \) Hz, 2H), 2.31 – 2.27 (m, 2H), 1.47 – 1.42 (m, 2H), 1.32 – 1.25 (m, 12H), 0.87 (t, \( J = 7.1 \) Hz, 3H).

^13C NMR (100 MHz, CDCl3): \( \delta \) 167.7, 141.3, 124.2, 60.7, 32.0, 32.0, 29.3, 29.2, 28.6, 22.8, 14.4, 14.2.

Ethyl 5-(diphenylphosphoryl)-2-methylenepentanoate (4af)

Following general procedure B with 1f (0.3 mmol, 233.1 mg). The crude product was purified by flash column chromatography (pentane/ethyl acetate, 80/20) to afford 4af as a colorless oil (48 mg, 46%).

^1H NMR (400 MHz, CDCl3): \( \delta \) 7.74 – 7.69 (m, 4H), 7.52 – 7.42 (m, 6H), 6.14 (d, \( J = 1.3 \) Hz, 1H), 5.49 (d, \( J = 1.3 \) Hz, 1H), 4.14 (q, \( J = 7.1 \) Hz, 2H), 2.42 – 2.38 (m, 2H), 2.29 – 2.22 (m, 2H), 1.84 – 1.80 (m, 2H), 1.22 (t, \( J = 7.1 \) Hz, 3H).

^13C NMR (100 MHz, CDCl3): \( \delta \) 167.0, 139.7, 133.1 (d, \( J = 98.2 \) Hz, 2 C), 131.8 (d, \( J = 2.7 \) Hz, 2 C), 130.9 (d, \( J = 9.2 \) Hz, 4 C), 128.7 (d, \( J = 11.6 \) Hz, 4 C), 125.6, 60.8, 32.9 (d, \( J = 15.3 \) Hz), 29.2 (d, \( J = 72.2 \) Hz), 20.5 (d, \( J = 3.4 \) Hz), 14.3. ^31P NMR (162 MHz, CDCl3): \( \delta \) 32.2. IR (neat): 3120, 2944, 1903, 1710, 1629, 1437, 1176, 1105, 717, 694 cm\(^{-1}\). HRMS calc. for [C\(_{20}\)H\(_{23}\)NaO\(_3\)P]\(^+\) 365.1277; found 365.1268, for [(C\(_{20}\)H\(_{23}\)O\(_3\)P)\(_2\)Na]\(^+\) 707.2662; found 707.2366.

Ethyl 5-(diphenylphosphoryl)-2-methylenepentanoate (4ag)

Following general procedure B with 1g (0.3 mmol, 194.6 mg). The crude product was purified by flash column chromatography (pentane/diethyl ether, 90/10) to afford 4ag as a colorless oil (24 mg, 37%).
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 6.15 (d, $J = 1.5$ Hz, 1H), 5.52 (d, $J = 1.4$ Hz, 1H), 4.20 (q, $J = 7.1$ Hz, 2H), 4.07 (t, $J = 6.5$ Hz, 2H), 2.35 – 2.31 (m, 2H), 2.04 (s, 3H), 1.69 – 1.62 (m, 2H), 1.58 – 1.50 (m, 2H), 1.30 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 171.3, 167.3, 140.6, 124.8, 64.4, 60.8, 31.6, 28.3, 25.0, 21.1, 14.4. IR (neat): 2995, 2949, 1741, 1710, 1630, 1368, 1234, 1187, 1146, 1028, 944, 813 cm$^{-1}$. HRMS calc. for [C$_{11}$H$_{18}$NaO$_4$]$^{+}$ 237.1097; found 237.1097.

(Cyclohexylethynyl)benzene (4bd)

Following general procedure C with 1-phenyl-2-p-toluenesulfonylthene 3b (1.2 mmol, 307.6 mg). The crude product was purified by flash column chromatography (pentane) to afford 4bd as a colorless oil (44 mg, 78%). The spectroscopic data are in agreement with those reported in the literature.[8]

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.42 – 7.39 (m, 2H), 7.31 – 7.24 (m, 3H), 2.64 – 2.55 (m, 1H), 1.92 – 1.85 (m, 2H), 1.79 – 1.74 (m, 2H), 1.58 – 1.52 (m, 3H), 1.40 – 1.33 (m, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 131.7 (2 C), 128.3 (2 C), 127.5, 124.3, 94.6, 80.7, 32.9, 29.8, 26.1 (2 C), 25.1 (2 C).

(2,2-Dichlorovinyl)cyclohexane (4cd)

Following general procedure C with trichloroethylene 3c (1.2 mmol, 108 μL). The crude product was purified by flash column chromatography (pentane) to afford 4cd as a colorless oil (39 mg, 70%). The spectroscopic data are in agreement with those reported in the literature.[8]

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 5.70 (d, $J = 9.2$ Hz, 1H), 2.43 – 2.32 (m, 1H), 1.77 – 1.62 (m, 5H), 1.37 – 1.04 (m, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 135.2, 118.7, 39.3, 31.8 (2 C), 25.9, 25.7 (2 C).
Dimethyl 2-cyclohexylsuccinate (4dd)

Following general procedure D with dimethyl maleate 3d (1.2 mmol, 150 µL). The crude product was purified by flash column chromatography (pentane/ethyl acetate, 95/5) to afford 4dd as a colorless oil (84 mg, 78%). The spectroscopic data are in agreement with those reported in the literature.\textsuperscript{[8]}

\( ^1\text{H NMR} \) (300 MHz, CDCl\(_3\)): \( \delta \) 3.67 (s, 3 H), 3.64 (s, 3 H), 2.76 – 2.65 (m, 2 H), 2.48 – 2.38 (m, 1 H), 1.74 – 1.85 (m, 6 H), 1.29 – 0.97 (m, 5 H). \( ^{13}\text{C NMR} \) (100 MHz, CDCl\(_3\)): \( \delta \) 175.0, 173.0, 51.80, 51.6, 47.1, 40.03, 33.3, 30.7, 30.2, 29.8, 26.4, 26.2.

4’-(Anilinomethyl)acetophenone (6ab)

Following general procedure E with anilinomethylsilicate 1b (0.45 mmol, 294 mg) and 4’-bromoacetophenone 5a (0.3 mmol, 60 mg). The crude product was purified by flash column chromatography (pentane/diethyl ether, 80/20) to afford 6ab as a colorless oil (53 mg, 78 %). The spectroscopic data are in agreement with those reported in the literature.\textsuperscript{[9]}

\( ^1\text{H NMR} \) (400 MHz, CDCl\(_3\)): \( \delta \) 7.94 (d, \( J = 8.3 \text{ Hz}, 2\text{H} \)), 7.47 (d, \( J = 8.3 \text{ Hz}, 2\text{H} \)), 7.21 – 7.15 (m, 2H), 6.76 – 6.72 (m, 1H), 6.63 – 6.60 (m, 2H), 4.42 (s, 2H), 4.19 (s, 1H), 2.60 (s, 3H). \( ^{13}\text{C NMR} \) (100 MHz, CDCl\(_3\)): \( \delta \) 197.8, 147.8, 145.4, 136.3, 129.4 (2 C), 128.8 (2 C), 127.4 (2 C), 117.9, 113.0 (2 C), 48.0, 26.7.

1-(3-(2-(Diphenylphosphoryl)ethyl)phenyl)ethan-1-one (6af)

Following general procedure F with 2-(diphenylphosphine oxide)ethylsilicate 1f (0.45 mmol, 350 mg) and 4’-bromoacetophenone 5a (0.3 mmol, 60 mg). The crude product was purified by flash column chromatography (dichloromethane/ethyl acetate, 60/40 to 40/60)) to
afford 6af contaminated with 15% of ethyldiphenylphosphine oxide as a white solid (79 mg, 68%).

**1H NMR (400 MHz, CDCl₃):** δ 7.82 (d, J = 8.3 Hz, 2H), 7.77 – 7.72 (m, 4H), 7.53 – 7.43 (m, 6H), 7.23 (d, J = 8.3 Hz, 2H), 3.06 – 2.87 (m, 2H), 2.60 – 2.54 (m, 2H), 2.53 (s, 3H).  

**13C NMR (100 MHz, CDCl₃):** δ 197.7, 146.8 (d, J = 14.6 Hz), 135.5, 132.6 (d, J = 98.8 Hz, 2 C), 132.0 (d, J = 2.7 Hz, 2 C), 130.8 (d, J = 9.2 Hz, 4 C), 128.8 (d, J = 11.2 Hz, 4 C), 128.8 (2 C), 128.4 (2 C), 31.5 (d, J = 69.8 Hz), 27.7 (d, J = 3.0 Hz), 26.6.  

**31P NMR (162 MHz, CDCl₃):** 31.11.  

**IR (neat):** 3015, 2895, 2257, 1904, 1674, 1601, 1437, 1264, 1174, 1111, 747, 725 cm⁻¹.  

**HRMS calc. for [C₂₂H₂₁NaO₂P]+ 371.1171; found 371.1159.**

**Ethyldiphenylphosphine oxide**

![Ph₂P=O](image)

Ethyldiphenylphosphine oxide has been obtained as a contaminant of 6af. The spectroscopic data are in agreement with those reported in the literature.[11]

**1H NMR (400 MHz, CDCl₃):** δ 7.73 – 7.69 (m, 4H), 7.51 – 7.41 (m, 6H), 2.30 – 2.21 (m, 2H), 1.21 – 1.13 (m, 2H).  

**13C NMR (100 MHz, CDCl₃):** δ 132.9 (d, J = 97.8 Hz, 2 C), 131.7 (d, J = 2.7 Hz, 2 C), 130.9 (d, J = 9.0 Hz, 4 C), 128.7 (d, J = 11.6 Hz, 4 C), 22.7 (d, J = 72.9 Hz), 5.7 (d, J = 5.0 Hz).  

**31P NMR (162 MHz, CDCl₃):** 34.09.  

**HRMS calc. for [C₁₄H₁₅NaOP]+ 253.0753; found 253.0755.**

**4’-(Acetoxypropyl)acetophenone (6ag)**

![image]

Following general procedure E with acetoxypropylsilicate 1ge (0.45 mmol, 292 mg) and 4’-bromoacetophenone 5a (0.3 mmol, 60 mg). The crude product was purified by flash column chromatography (pentane/diethyl ether, 80/20) to afford 6ag as a colorless oil (55 mg, 83%). The spectroscopic data are in agreement with those reported in the literature.[9]

**1H NMR (400 MHz, CDCl₃):** δ 7.88 (d, J = 8.5 Hz, 2H), 7.27 (d, J = 8.5 Hz, 2H), 4.08 (t, J = 6.5 Hz, 2H), 2.76 – 2.72 (m, 2H), 2.57 (s, 3H), 2.04 (s, 3H), 2.00 – 1.93 (m, 2H).  

**13C NMR (100 MHz, CDCl₃):** δ 197.9, 171.2, 147.1, 135.4, 128.8, 128.7, 63.7, 32.4, 30.0, 26.7, 21.1.
4’-(Acetoxymethyl)acetophenone (6ah)

Following general procedure F with acetoxymethylsilicate 1h (0.45 mmol, 279 mg) and 4’-bromoacetophenone 5a (0.3 mmol, 60 mg). The crude product was purified by flash column chromatography (pentane/diethyl ether, 90/10) to afford 6ah as a colorless oil (51 mg, 88%). The spectroscopic data are in agreement with those reported in the literature.\[9\]

\[\text{\textsuperscript{1}H NMR (400 MHz, CDCl}_{3}\text{): }\delta 7.95 (d, J = 8.4 \text{ Hz, 2H}), 7.43 (d, J = 8.4 \text{ Hz, 2H}), 5.15 (s, 2H), 2.60 (s, 3H), 2.12 (s, 3H). \text{\textsuperscript{13}C NMR (100 MHz, CDCl}_{3}\text{): }\delta 197.6, 170.8, 141.3, 137.0, 128.7 (2 \text{ C}), 128.0 (2 \text{ C}), 65.6, 26.8, 21.0.\]

4’-(Acetoxymethyl)acetophenone (6aj), 1-(4-(hex-4-en-1-yl)phenyl)ethan-1-one (6aj’) and 1-(4-(cyclopentylmethyl)phenyl)ethan-1-one (6aj’’)

Following general procedure F with hex-5-enylsilicate 1j (0.45 mmol, 279 mg) and 4’-bromoacetophenone 5a (0.3 mmol, 60 mg). The crude product was purified by flash column chromatography (pentane/diethyl ether, 90/10) to afford a mixture of 6aj, 6aj’ and 6aj’’ in a ratio of 10:13:77 as a colorless oil (51 mg, 88%). The spectroscopic data are in agreement with those reported in the literature.\[9\]

**Compound 6aj**

\[\text{\textsuperscript{1}H NMR (400 MHz, C}_{6}D_{6}\text{): }\delta 7.80 (d, J = 8.3 \text{ Hz, 2H}), 6.97 (d, J = 8.4 \text{ Hz, 2H}), 5.72 (ddt, J = 16.9, 10.2, 6.7 \text{ Hz, 1H}), 5.03 – 4.96 (m, 2H), 2.15 (s, 3H), 1.98 – 1.83 (m, 2H). \text{\textsuperscript{13}C NMR (100 MHz, CDCl}_{3}\text{): }\delta 196.2, 138.8, 114.8.\]

**Compound 6aj’**

\[\text{\textsuperscript{1}H NMR (400 MHz, C}_{6}D_{6}\text{): }\delta 5.54 – 5.35 (m, 2H), 1.97 – 1.85 (m, 2H), 1.45 – 1.39 (m, 3H). \text{\textsuperscript{13}C NMR (100 MHz, CDCl}_{3}\text{): }\delta 196.2, 130.3, 124.6, 12.9.\]

**Compound 6aj’’**
$^1$H NMR (400 MHz, C$_6$D$_6$): $\delta$ 7.80 (d, $J = 8.3$ Hz, 2H), 6.97 (d, $J = 8.4$ Hz, 2H), 2.40 (d, $J = 7.5$ Hz, 2H), 2.16 (s, 3H), 1.94 – 1.83 (m, 1H), 1.61 – 1.38 (m, 5H), 1.08 – 0.99 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 196.2, 147.7, 135.7, 129.1, 128.7, 42.2, 42.0, 32.7, 26.2, 25.2. HRMS calc. for [C$_{14}$H$_{18}$NaO$_2$]$^+$ 225.1250; found 225.1247.

3-(4-Methoxyphenyl)propyl acetate (6bg)

Following general procedure F with acetoxypropylsilicate 1g (0.45 mmol, 292 mg) and 4-iodoanisole 5b (0.3 mmol, 70 mg). The crude product was purified by flash column chromatography (pentane/diethyl ether, 90/10) to afford 6bg as a colorless oil (34 mg, 54%). The spectroscopic data are in agreement with those reported in the literature.$^{[9]}$

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.10 (d, $J = 8.6$ Hz, 2H), 6.83 (d, $J = 8.6$ Hz, 2H), 4.08 (t, $J = 6.6$ Hz, 2H), 3.79 (s, 3H), 2.65 – 2.61 (m, 2H), 2.05 (s, 3H), 1.96 – 1.89 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 171.3, 158.1, 133.4, 129.4 (2 C), 114.0 (2 C), 64.0, 55.4, 31.4, 30.6, 21.1.

3-Phenylpropyl acetate (6cg)

Following general procedure F with acetoxypropylsilicate 1g (0.45 mmol, 292 mg) and bromobenzene 5c (0.3 mmol, 32 µl). The crude product was purified by flash column chromatography (pentane/diethyl ether, 95/5) to afford 6cg as a colorless oil (41 mg, 76%). The spectroscopic data are in agreement with those reported in the literature.$^{[12]}$

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.30 – 7.23 (m, 2H), 7.20 – 7.15 (m, 2H), 4.07 (t, $J = 6.5$ Hz, 2H), 2.70 – 2.65 (m, 2H), 2.04 (s, 3H), 2.03 – 1.90 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 171.2, 141.3, 128.5 (2C), 128.5 (2C), 126.1, 63.9, 32.3, 30.3, 21.1.
3-(Naphthalen-1-yl)propyl acetate (6dg)

Following general procedure F with acetoxypropylsilicate 1g (0.45 mmol, 292 mg) and 1-bromonaphthalene 5d (0.3 mmol, 42 µl). The crude product was purified by flash column chromatography (pentane/diethyl ether, 95/5) to afford 6dg as a colorless oil (43 mg, 63%). The spectroscopic data are in agreement with those reported in the literature.\textsuperscript{[13]}

\textbf{\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}): \(\delta\) 8.03 (dt, \(J = 7.8, 0.9\) Hz, 1H), 7.87 (dd, \(J = 8.2, 1.3\) Hz, 1H), 7.74 – 7.72 (m, 1H), 7.55 – 7.46 (m, 2H), 7.42 – 7.39 (m, 1H), 7.34 – 7.32 (m, 1H), 4.17 (t, \(J = 6.5\) Hz, 2H), 3.18 – 3.15 (m, 2H), 2.14 – 2.07 (m, 2H), 2.09 (s, 3H). \textbf{\textsuperscript{13}C NMR} (100 MHz, CDCl\textsubscript{3}): \(\delta\) 171.2, 137.2, 133.9, 131.8, 128.8, 126.9, 126.1, 125.9, 125.5, 125.5, 123.6, 64.1, 29.5, 29.3, 21.0. \textbf{IR} (neat): 2052, 2953, 1930, 1733, 1592, 1360, 1234, 1040, 738 cm\textsuperscript{-1}. \textbf{HRMS} calc. for [C\textsubscript{15}H\textsubscript{16}NaO\textsubscript{2}]\(^+\) 251.1043; found 251.1041.

3-(Phenanthren-9-yl)propyl acetate (6eg)

Following general procedure F with acetoxypropylsilicate 1g (0.45 mmol, 292 mg) and 9-bromophenanthrene 5e (0.3 mmol, 77 mg). The crude product was purified by flash column chromatography (pentane/diethyl ether, 95/5) to afford 6eg as a colorless oil (38 mg, 45%).

\textbf{\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}): \(\delta\) 8.76 – 8.74 (m, 1H), 8.68 – 8.65 (m, 1H), 8.11 – 8.07 (m, 1H), 7.85 – 7.82 (m, 1H), 7.70 – 7.56 (m, 5H), 4.23 (t, \(J = 6.5\) Hz, 2H), 3.23 – 3.19 (m, 2H), 2.20 – 2.14 (m, 2H), 2.10 (s, 3H). \textbf{\textsuperscript{13}C NMR} (100 MHz, CDCl\textsubscript{3}): \(\delta\) 171.3, 135.5, 131.9, 131.28, 130.9, 129.9, 128.2, 126.8, 126.8, 126.4, 126.4, 126.3, 124.3, 123.5, 122.6, 64.3, 29.9, 29.1, 21.2.\textbf{IR} (neat): 2917, 2957, 1929, 1722, 1245, 1067, 1031, 755, 736 cm\textsuperscript{-1}. \textbf{HRMS} calc. for [C\textsubscript{19}H\textsubscript{18}NaO\textsubscript{2}]\(^+\) 301.1199; found 301.1195.
3-(Pyren-1-yl)propyl acetate (6fg)

Following general procedure F with acetoxypropylsilicate 1g (0.45 mmol, 292 mg) and 9-bromophenanthrene 5f (0.3 mmol, 84.3 mg). The crude product was purified by flash column chromatography (pentane/diethyl ether, 95/5) to afford 6fg as a colorless oil (58 mg, 64%).

$^1$H NMR (600 MHz, CDCl$_3$): δ 8.26 (d, $J = 9.2$ Hz, 1H), 8.18 – 8.16 (m, 2H), 8.12 (d, $J = 9.2$ Hz, 2H), 8.05 – 8.02 (m, 2H), 8.00 (t, $J = 7.6$ Hz, 1H), 7.87 (d, $J = 7.7$ Hz, 1H), 4.21 (t, $J = 6.4$ Hz, 2H), 3.45 – 3.42 (m, 2H), 2.23 – 2.19 (m, 2H), 2.11 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ 171.3, 135.5, 131.6, 131.0, 128.8, 127.6, 127.3, 126.9, 126.0, 125.3, 125.1, 125.0, 124.9, 123.2, 64.1, 30.6, 29.9, 21.2. IR (neat): 3140, 2953, 2895, 1728, 1361, 1238, 1036, 836, 769, 708 cm$^{-1}$. HRMS calc. for [C$_{21}$H$_{18}$NaO$_2$]$^+$ 325.1199; found 325.1209.

3-(2-Fluoropyridin-4-yl)propyl acetate (6gg)

Following general procedure F with acetoxypropylsilicate 1g (0.45 mmol, 292 mg) and 4-bromo-2-fluoropyridine 5g (0.3 mmol, 31 μl). The crude product was purified by flash column chromatography (pentane/EtOAc, 80/20) to afford 6gg as a colorless oil (43 mg, 73%). The spectroscopic data are in agreement with those reported in the literature.$^9$

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.10 (d, $J = 5.1$ Hz, 1H), 7.01 – 6.99 (m, 1H), 6.75 (m, 1H), 4.09 (t, $J = 6.4$ Hz, 2H), 2.74 – 2.70 (m, 2H), 2.04 (s, 3H), 2.01 – 1.94 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 171.1, 164.3 (d, $J = 238.6$ Hz), 156.4 (d, $J = 7.7$ Hz), 147.6 (d, $J = 15.3$ Hz), 121.7 (d, $J = 3.9$ Hz), 109.2 (d, $J = 36.9$ Hz), 63.4, 31.6 (d, $J = 3.0$ Hz), 29.0, 21.0. $^{19}$F NMR (376 MHz, CDCl$_3$): δ -68.81.
Methyl 5-(3-acetoxypropyl)nicotinate (6hg)

Following general procedure F with acetoxypropylsilicate 1g (0.45 mmol, 292 mg) and methyl 5-bromonicotinate 5h (0.3 mmol, 65 mg). The crude product was purified by flash column chromatography (pentane/diethyl ether, 40/60) to afford 6gh as a colorless oil (39 mg, 54%). The spectroscopic data are in agreement with those reported in the literature.[9]

\[ ^1H \text{ NMR (400 MHz, CDCl}_3\]: \delta 9.05 (d, \text{ J} = 2.0 \text{ Hz}, 1\text{H}), 8.60 (d, \text{ J} = 2.2 \text{ Hz}, 1\text{H}), 8.11 (d d, \text{ J} = 2.2, 2.0 \text{ Hz}, 1\text{H}), 4.09 (t, \text{ J} = 6.4 \text{ Hz}, 2\text{H}), 3.93 (s, 3\text{H}), 2.77 – 2.73 (m, 2\text{H}), 2.04 (s, 3\text{H}), 2.01 – 1.94 (m, 2\text{H}). \]

\[ ^{13}C \text{ NMR (100 MHz, CDCl}_3\]: \delta 171.1, 166.0, 153.7, 148.8, 136.8, 136.5, 125.9, 63.4, 25.5, 29.8, 29.3, 21.0. \]

3-(Quinolin-3-yl)propyl acetate (6ig)

Following general procedure F with acetoxypropylsilicate 1g (0.45 mmol, 292 mg) and 4-bromoquinoline 5i (0.3 mmol, 41 µl). The crude product was purified by flash column chromatography (pentane/diethyl ether, 90/10) to afford 6ig as a colorless oil (31 mg, 45%). The spectroscopic data are in agreement with those reported in the literature.[9]

\[ ^1H \text{ NMR (400 MHz, CDCl}_3\]: \delta 8.78 (d, \text{ J} = 2.3 \text{ Hz}, 1\text{H}), 8.07 (d, \text{ J} = 8.3 \text{ Hz}, 1\text{H}), 7.92 (d, \text{ J} = 3.2 \text{ Hz}, 1\text{H}), 7.75 (d d, \text{ J} = 8.2, 1.4 \text{ Hz}, 1\text{H}), 7.65 (d d d, \text{ J} = 8.4, 6.9, 1.5 \text{ Hz}, 1\text{H}), 7.51 (d d d, \text{ J} = 8.1, 6.9, 1.2 \text{ Hz}, 1\text{H}), 4.14 (t, \text{ J} = 6.4 \text{ Hz}, 2\text{H}), 2.90 – 2.86 (m, 2\text{H}), 2.09 – 2.02 (m, 2\text{H}), 2.05 (s, 3\text{H}). \]

\[ ^{13}C \text{ NMR (100 MHz, CDCl}_3\]: \delta 171.1, 151.9, 147.1, 134.4, 133.9, 129.3, 128.9, 128.2, 127.4, 126.8, 63.6, 30.0, 29.7, 21.0. \]

3-(Benzofuran-5-yl)propyl acetate (6jg)

Following general procedure F with acetoxypropylsilicate 1j (0.45 mmol, 292 mg) and 5-bromobenzofuran 5j (0.3 mmol, 38 µl). The crude product was purified by flash column
chromatography (pentane/diethyl ether, 90/10) to afford 6jg as a colorless oil (31 mg, 45%). The spectroscopic data are in agreement with those reported in the literature.\[^9\]

**\(^1\)H NMR** (400 MHz, CDCl\(_3\)): \(\delta 7.60 \text{ (d, } J = 2.2 \text{ Hz, 1H), 7.48 – 7.34 \text{ (m, 2H), 7.12 \text{ (dd, } J = 8.4, 1.8 \text{ Hz, 1H), 6.71 \text{ (dd, } J = 2.2, 1.0 \text{ Hz, 1H), 4.11 \text{ (t, } J = 6.6 \text{ Hz, 2H), 2.80 – 2.77 \text{ (m, 2H), 2.06 \text{ (s, 3H), 2.03 – 1.96 \text{ (m, 2H).} \)** \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 171.3, 153.8, 145.3, 135.8, 127.7, 125.0, 120.6, 111.3, 106.5.\)

(E)-3-((Cyclooct-1-en-1-yl)propyl acetate (8ag)

Following general procedure F with acetoxypropylsilicate 1g (0.45 mmol, 292 mg) and (E)-1-bromocyclooct-1-ene 7a (0.3 mmol, 44 µl). The crude product was purified by flash column chromatography (pentane/diethyl ether, 95/5) to afford 8ag as a colorless oil (29 mg, 46%). The spectroscopic data are in agreement with those reported in the literature.\[^1\]

**\(^1\)H NMR** (400 MHz, CDCl\(_3\)): \(\delta 5.34 \text{ (t, } J = 8.1 \text{ Hz, 1H), 4.05 \text{ (t, } J = 6.7 \text{ Hz, 2H), 2.15 – 2.12 \text{ (m, 2H), 2.09 – 2.01 \text{ (m, 4H), 2.04 \text{ (s, 3H), 1.78 – 1.70 \text{ (m, 2H), 1.53 – 1.43 \text{ (m, 8H).} \)** \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 171.3, 139.6, 124.5, 64.6, 33.7, 30.1, 29.0, 28.9, 27.1, 26.7, 26.4, 26.4, 21.2.\)

4-(((tert-butyldimethylsilyl)oxy)methyl)pent-4-en-1-yl acetate (8bg)

Following general procedure F with acetoxypropylsilicate 1g (0.45 mmol, 292 mg) and ((2-bromoallyl)oxy)(tert-butyl)dimethylsilane 7b (0.3 mmol, 68 µl). The crude product was purified by flash column chromatography (pentane/diethyl ether, 95/5) to afford 8bg as a colorless oil (46 mg, 56%).

**\(^1\)H NMR** (300 MHz, CDCl\(_3\)): \(\delta 5.05 \text{ (dt, } J = 1.6, 0.8 \text{ Hz, 1H), 4.83 \text{ (t, } J = 1.5 \text{ Hz, 1H), 4.10 – 4.05 \text{ (m, 4H), 2.11 – 2.06 \text{ (m, 2H), 2.04 \text{ (s, 3H), 1.84 – 1.74 \text{ (m, 2H), 0.91 \text{ (s, 9H), 0.07 \text{ (s, 6H).} \)** \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta 171.3, 147.6, 109.3, 66.0, 64.3, 29.1, 26.9, 26.1 \text{ (3 C), 21.1, 18.5, -5.2 \text{ (2 C).} \)** IR (neat): 2972, 2945, 2885, 2852, 1740, 1653, 1465, 1361, 1237, 1116, 1078, 1039, 839, 773 cm\(^{-1}\). \textbf{HRMS} calc. for [C\(_{14}\)H\(_{28}\)NaSiO\(_3\)]\(^+\) 295.1700; found 295.1710.
Cyclohexylidenebutyl acetate (8cg)

Following general procedure F with acetoxypropylsilicate 1g (0.45 mmol, 292 mg) and bromomethylenecyclohexane 7c (0.3 mmol, 40 µl). The crude product was purified by flash column chromatography (pentane/diethyl ether, 95/5) to afford 8cg as a colorless oil (32 mg, 55%). The spectroscopic data are in agreement with those reported in the literature.\[1\]

\[1\]H NMR (400 MHz, CDCl₃): δ 5.09 – 4.93 (m, 1H), 4.04 (t, J = 6.8 Hz, 2H), 2.12 – 2.03 (m, 6H), 2.04 (s, 3H), 1.65 (p, J = 6.8 Hz, 2H), 1.56 – 1.45 (m, 6H). 13C NMR (100 MHz, CDCl₃): δ 171.2, 140.8, 119.7, 64.0, 37.2, 28.9, 28.7, 28.6, 27.8, 26.90, 23.3, 21.

(E)-5-Phenylpent-4-en-1-yl acetate (8dg)

Following general procedure F with acetoxypropylsilicate 1g (0.45 mmol, 292 mg) and (E)-(2-bromovinyl)benzene 7e (0.3 mmol, 39 µl). The crude product was purified by flash column chromatography (pentane/diethyl ether, 90/10) to afford 8dg as a colorless oil (46 mg, 75%). The spectroscopic data are in agreement with those reported in the literature.\[1\]

\[1\]H NMR (400 MHz, CDCl₃): δ 7.41 – 7.31 (m, 4H), 7.28 – 7.23 (m, 1H), 6.50 – 6.44 (m, 1H), 6.25 (dt, J = 15.8, 6.8 Hz, 1H), 4.18 (t, J = 6.6 Hz, 2H), 2.93 – 2.31 (m, 2H), 2.11 (s, 3H), 1.92 – 1.83 (m, 2H). 13C NMR (100 MHz, CDCl₃): δ 171.2, 137.7, 130.8, 129.5, 128.6 (2C), 127.2, 126.1 (2C), 64.1, 29.5, 28.5, 21.1.

(Z)-5-Phenylpent-4-en-1-yl acetate (8d’g)

Following general procedure F with acetoxypropylsilicate 1g (0.45 mmol, 292 mg) and (Z)-(2-bromovinyl)benzene 7d’ (0.3 mmol, 39 µl). The crude product was purified by flash column chromatography (pentane/diethyl ether, 90/10) to afford 8d’g as a colorless oil (39 mg, 65%). The spectroscopic data are in agreement with those reported in the literature.\[1\]

\[1\]H NMR (400 MHz, CDCl₃): δ 7.41 – 7.36 (m, 2H), 7.34 – 7.26 (m, 3H), 6.53 – 6.51 (m, 1H), 5.70 (dt, J = 11.5, 7.3 Hz, 1H), 4.13 (t, J = 6.6 Hz, 2H), 2.46 (qd, J = 7.4, 1.8 Hz, 2H),
2.05 (s, 3H), 1.87 – 1.80 (m, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 171.2, 137.5, 131.4, 130.0, 128.8 (2 C), 128.3 (2 C), 126.8, 64.0, 28.9, 25.1, 21.0.

(E)-5-Phenylpent-4-en-1-yl acetate (8eg)

Following general procedure F with acetoxypropylsilicate 1g (0.45 mmol, 292 mg) and (E)-1-(2-chlorovinyl)-4-methoxybenzene 7e (0.3 mmol, 50.6 mg). The crude product was purified by flash column chromatography (pentane/diethyl ether, 90/10) to afford 8eg as a colorless oil (46 mg, 65%, Z/E:8/92). The spectroscopic data are in agreement with those reported in the literature.\(^{[1]}\)

(E) isomer:

\(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 7.27 (d, \(J = 8.8\) Hz, 2H), 6.84 (d, \(J = 8.7\) Hz, 2H), 6.35 (d, \(J = 15.8\) Hz, 1H), 6.05 (dt, \(J = 15.8, 7.1\) Hz, 1H), 4.12 (t, \(J = 6.6\) Hz, 2H), 3.80 (s, 3H), 2.26 (qd, \(J = 7.1, 1.5\) Hz, 1H), 2.05 (s, 3H), 1.82 – 1.78 (m, 2H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 171.3, 158.9, 130.5, 130.2, 127.2, 127.2 (2 C), 114.0 (2 C), 64.1, 554, 29.5, 28.6, 21.1.

(Z) isomer:

\(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 7.21 (d, \(J = 8.7\) Hz, 2H), 6.87 (d, \(J = 8.7\) Hz, 2H), 6.39 (d, \(J = 11.7\) Hz, 1H), 5.54 (dt, \(J = 11.6, 7.3\) Hz, 1H), 4.08 (t, \(J = 6.6\) Hz, 2H), 3.81 (s, 3H), 2.40 (qd, \(J = 7.3, 1.9\) Hz, 2H), 2.01 (s, 3H), 1.80 – 1.76 (m, 2H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 171.2, 158.4, 130.1, 130.0, 129.8, 129.4 (2 C), 113.7 (2 C), 64.0, 55.4, 29.0, 25.1, 21.0.

(E)-5-Phenylpent-4-en-1-yl acetate (8fg)

Following general procedure F with acetoxypropylsilicate 1f (0.45 mmol, 292 mg) and (E)-1-(2-chlorovinyl)-4-methoxybenzene 7g (0.3 mmol, 61 mg). The crude product was purified by flash column chromatography (pentane/diethyl ether, 90/10) to afford 8fg as a colorless oil (44 mg, 54%). Geometry of the double bond determined by NOESY experiment.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.55 (d, \(J = 8.7\) Hz, 2H), 6.88 (d, \(J = 8.7\) Hz, 2H), 6.43 (s, 1H), 4.14 (t, \(J = 6.4\) Hz, 2H), 3.82 (s, 3H), 2.55 (td, \(J = 7.3, 0.9\) Hz, 2H), 2.06 (s, 3H), 2.04 – 1.98 (m, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 171.2, 159.1, 131.6, 130.4 (2 C), 127.6, 124.7, 113.7 (2 C), 63.4, 55.4, 37.8, 26.9, 21.1. IR (neat): 2948, 2846, 1734, 1605, 1508, 1361,
1240, 1175, 1032, 819, 609 cm\(^{-1}\). **HRMS** calc. for [C\(_{14}\)H\(_{17}\)ClNaO\(_3\)]\(^+\) 291.0758; found 291.0763.
IV. $^1$H, $^{13}$C, $^{19}$F, $^{29}$Si and $^{31}$P NMR spectra

$^1$H spectrum of diphenyl(2-(triethoxysilyl)ethyl)phosphine oxide

$^{13}$C spectrum of diphenyl(2-(triethoxysilyl)ethyl)phosphine oxide
$^{31}$P spectrum of diphenyl(2-(triethoxysilyl)ethyl)phosphine oxide

![$^{31}$P spectrum of diphenyl(2-(triethoxysilyl)ethyl)phosphine oxide](image)

$^{29}$Si spectrum of diphenyl(2-(triethoxysilyl)ethyl)phosphine oxide

![$^{29}$Si spectrum of diphenyl(2-(triethoxysilyl)ethyl)phosphine oxide](image)
$^{1}H$ spectrum of 1f

![$^{1}H$ spectrum of 1f](image)

$^{13}C$ spectrum of 1f

![$^{13}C$ spectrum of 1f](image)
$^{31}$P spectrum of 1f

$^{29}$Si spectrum of 1f
$^{1}H$ spectrum of 4ab

$^{13}C$ spectrum of 4ab
$^1$H spectrum of 4ac

$^{13}$C spectrum of 4ac
$^1$H spectrum of 4ad

$^{13}$C spectrum of 4ad
$^1$H spectrum of 4ae

\[
\text{CO}_2\text{Et} \\
\text{4ae}
\]

$^{13}$C spectrum of 4ae

\[
\text{CO}_2\text{Et} \\
\text{4ae}
\]
$^1$H spectrum of 4af

$^{13}$C spectrum of 4af
$^{31}$P spectrum of 4af

$^1$H spectrum of 4ag
$^{13}$C spectrum of 4ag

\[
\text{CO}_2\text{Et} \quad \text{OAc}
\]

4ag

$^1$H spectrum of 4bd

\[
\text{O}
\]

4bd
$^{13}$C spectrum of 4bd

4bd

$^1$H spectrum of 4cd

4cd
$^{13}$C spectrum of 4cd

$^1$H spectrum of 4dd
$^{13}$C spectrum of 4dd

\[ \text{4dd} \]

$^1$H spectrum of 6ab

\[ \text{6ab} \]
$^{13}$C spectrum of 6ab

![Carbon spectrum of 6ab](image)

$^1$H spectrum of 6af

![Proton spectrum of 6af](image)
$^1$H NMR spectrum of 6af

$^{31}$P NMR spectrum of 6af
$^1$H spectrum of 6ag

6ag

$^{13}$C spectrum of 6ag

6ag
$^1$H spectrum of 6ah

$^{13}$C spectrum of 6ah
$^1$H spectrum of 6aj

$^{13}$C spectrum of 6aj

6aj
\(^1\)H spectrum of 6bg

\[^{13}\text{C}\) spectrum of 6bg
$^1$H spectrum of 6cg

$^{13}$C spectrum of 6cg
$^1$H spectrum of 6dg

$^{13}$C spectrum of 6dg
$^1$H spectrum of 6eg

$^{13}$C spectrum of 6eg
$^1$H spectrum of 6fg

$^{13}$C spectrum of 6fg
$^1$H spectrum of 6gg

![H spectrum of 6gg](image)

$^{13}$C spectrum of 6gg

![C spectrum of 6gg](image)
$^{19}$F spectrum of 6gg

$^{1}$H spectrum of 6hg
$^{13}$C spectrum of 6hg

$^1$H spectrum of 6ig

6hg

6ig
$^{13}$C spectrum of 6ig

![Carbon Spectrum of 6ig](image)

$^{1}$H spectrum of 6jg

![Proton Spectrum of 6jg](image)
$^{13}$C spectrum of 6jg

$^1$H spectrum of 8ag
$^{13}$C spectrum of $8ag$

![$8ag$ spectrum](image)

$^1H$ spectrum of $8bg$

![$8bg$ spectrum](image)
$^{13}$C spectrum of 8bg

AcO\(\text{C}相连\)OTBDMS

8bg

$^1$H spectrum of 8cg

S59
$^{13}$C spectrum of $8\text{cg}$

$\text{H}$ spectrum of $8\text{dg}$
$^{13}$C spectrum of dg

\[ \text{8dg} \]

$^1$H spectrum of 8d’g

\[ \text{8d’g} \]
$^{13}\text{C}$ spectrum of 8d’g

$^{1}\text{H}$ spectrum of 8eg
$^{13}$C spectrum of 8eg

![13C spectrum of 8eg](image)

$^1$H spectrum of 8fg

![1H spectrum of 8fg](image)

S63
NOESY of 8fg

$\{^{13}\text{C}}$ spectrum of 8fg

8fg
V. References