Supplementary Information

Cascade Cyclization of Alkene-tethered Acylsilanes and Allylic Sulfoxones Enabled by Unproductive Energy Transfer Photocatalysis

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1. General information

Chromatography: HaiLang Silica Flash P60 size 40–45 μm (300–400 mesh), TLC: HaiLang silica gel 60 (0.25 mm). Visualization of the chromatogram was performed by UV, phosphomolybdic acid and KMnO\textsubscript{4} staining. Mass spectra were recorded on Bruker UltiMate 3000 & Compact, Thermo ISQ LT, LTQ XL and VELOS pro & ORBITRAP mass spectrometers. \textsuperscript{1}H, \textsuperscript{13}C, \textsuperscript{19}F, \textsuperscript{29}Si were recorded on Bruker 400, Bruker 600 and JNM–ECZ 400 using CDCl\textsubscript{3} or DMSO-d\textsubscript{6} as solvent. Chemical shift values are reported in ppm with the solvent resonance as the internal standard (CDCl\textsubscript{3}: δ 7.26 for \textsuperscript{1}H, δ 77.16 for \textsuperscript{13}C). Data are reported as follows: chemical shifts, multiplicity (s = singlet, bs = broad singlet, d = doublet, dd = doublet of doublets, t = triplet, td = triplet of doublets, m = multiplet), coupling constants (Hz), and integration. Infrared spectra were recorded on an Agilent Technologies Cary 630 FTIR and wavelengths are reported in cm\textsuperscript{-1}. Melting point was measured by INESA SGW X–4. All reagents were used as received and solvents were dried and degassed according to standard procedure. If no special description, all reactions were conducted under nitrogen. Eosin Y (neutral eosin Y CAS: 15086-94-9), 4,4’-di-tert-butyl-2,2’-bipyridine was purchased from laajoo, IrCl\textsubscript{3}·xH\textsubscript{2}O was purchased from adamas, 1,3-Dithiane was purchased from bide, 1,3-Dithiane was purchased from adamas, 1,3-Dithiane was purchased from dide, all of the Chlorosilane and FeCl\textsubscript{3} were purchased from heows, PhSO\textsubscript{2}Na, K2S2O8, Chloramine T, Acetophenone were purchased from adamas, KOPiv was purchased from Ark, collidine (2,4,6-triMe-thypyrindine), n-BuLi were purchased from Energy chemical.

2. Synthesis of substrates

General procedure for preparation of Alkene-tethered Acylsilanes.
Alkene-tethered acylsilanes 1a–1f are all known compounds and they were synthesized according to reported procedures.[1] To a solution of 1,3-dithiane (4.8 g, 40 mmol) in dry THF (60 mL) was added n-butyllithium (17.6 mL, 2.5 M in hexane, 44 mmol) dropwise at –30 °C. After the mixture was stirred for 0.5 h, chlorosilane (40 mmol) was slowly added, and the reaction was warmed to ambient temperature. After being stirred for additional 12 h, the reaction mixture was cooled to –30 °C, and then n-butyllithium (17.6 mL, 2.5 M in hexane, 44 mmol) was added to the reaction mixture. After the mixture was stirred for 0.5 h, bromoalkyl olefin (40 mmol) was added dropwise at –30 °C. The reaction mixture was warmed to ambient temperature over 12 h, and then the reaction was quenched with H2O (100 mL). The aqueous layers were extracted with EA (70 mL×3), and the combined organic layers were washed with brine, dried over anhydrous Na2SO4, and concentrated in vacuo. Purification by flash silica gel column chromatography using PE/EA (v/v = 100:1) as an eluent gave crude product.

1-(Trimethylsilyl)hex-5-en-1-one 1a

Yellow oil. (2.5 g, 3 steps total yield: 36%), NMR Spectroscopy: 1H NMR (400 MHz, CDCl3, 25 °C) δ 5.79–5.68 (m, 1H), 5.02–4.91 (m, 2H), 2.59 (td, J = 7.3, 0.9 Hz, 2H), 2.05–1.95 (m, 2H), 1.65–1.56 (m, 2H), 0.18 (s, 9H). The characterization data is consistent to the reported data.[1]

1-(Triethylsilyl)hex-5-en-1-one 1b

Yellow oil. (3.1 g, 3 steps total yield: 36%), NMR Spectroscopy: 1H NMR (600 MHz, CDCl3, 25 °C) δ 5.76–5.66 (m, 1H), 4.99–4.92 (m, 2H), 2.56 (t, J = 7.2 Hz, 2H), 2.04–1.98 (m, 2H), 1.64–1.58 (m, 2H), 0.96 (t, J = 7.9 Hz, 9H), 0.72 (q, J = 7.9 Hz, 6H). The characterization data is consistent to the reported data.[1]

1-(tert-Butyldimethylsilyl)hex-5-en-1-one 1c

Yellow oil. (3.1 g, 3 steps total yield: 36%), NMR Spectroscopy: 1H NMR (600 MHz, CDCl3, 25 °C) δ 5.76–5.66 (m, 1H), 4.99–4.89 (m, 2H), 2.57 (t, J = 7.2 Hz, 2H), 2.02–1.95 (m, 2H), 1.62–1.55 (m, 2H), 0.89 (s, 9H), 0.14 (s, 6H). The characterization data is consistent to the reported data.[1]
1-(Dimethyl(phenyl)silyl)hex-5-en-1-one 1d

\[
\text{PhMe}_2\text{Si} \quad \text{O} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{O} \\
\]

Yellow oil. (3.3 g, 3 steps total yield: 36%), NMR Spectroscopy: \(^1\)H NMR (600 MHz, CDCl\(_3\), 25 °C) \(\delta\) 7.56–7.53 (m, 2H), 7.42–7.37 (m, 3H), 5.71–5.63 (m, 1H), 4.94–4.88 (m, 2H), 2.57 (t, \(J = 7.2\) Hz, 2H), 1.98–1.90 (m, 2H), 1.62–1.49 (m, 2H), 0.48 (s, 6H). The characterization data is consistent to the reported data.\(^{[1]}\)

1-(Methyldiphenylsilyl)hex-5-en-1-one 1e

\[
\text{Ph}_2\text{MeSi} \quad \text{O} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{O} \\
\]

R\(_f\) = 0.45 (PE/EA = 10/1 (v/v)). Yellow oil. (4.4 g, 3 steps total yield: 37%), NMR Spectroscopy: \(^1\)H NMR (600 MHz, CDCl\(_3\), 25 °C) \(\delta\) 7.46–7.42 (m, 4H), 7.42–7.38 (m, 6H), 5.71–5.63 (m, 1H), 4.94–4.85 (m, 2H), 2.67 (t, \(J = 7.2\) Hz, 2H), 1.98–1.92 (m, 2H), 1.62–1.53 (m, 2H), 0.76 (s, 3H). The characterization data is consistent to the reported data.\(^{[1]}\)

1-(Trimethylsilyl)pent-4-en-1-one 1f

\[
\text{Me}_3\text{Si} \quad \text{O} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{O} \\
\]

Yellow oil. (2.4 g, 3 steps total yield: 38%). NMR Spectroscopy: \(^1\)H NMR (400 MHz, CDCl\(_3\), 25 °C) \(\delta\) 5.84–5.69 (m, 1H), 5.02–4.91 (m, 2H), 2.74–2.64 (m, 2H), 2.32–2.20 (m, 2H), 0.19 (s, 9H). The characterization data is consistent to the reported data.\(^{[2]}\)

**General procedure for preparation of allylic sulfone.**

\[
\begin{align*}
\text{Me}(\text{CH}_2)\text{Cl}_2 \quad \text{SO}_2\text{Na} & \quad \text{FeCl}_3 (0.5 \text{ equiv}) \\
\quad & \quad \text{K}_2\text{S}_2\text{O}_8 (3.5 \text{ equiv}) \\
& \quad \text{Me(\text{CH}_2)\text{Cl}_2}\text{SO}_2\text{Na} (0.5 \text{ equiv}) \\
& \quad \text{DMAC, 110 °C, 16 h} \\
\end{align*}
\]

Allylic sulfones 2 were synthesized according to reported procedures.\(^{[3,4]}\) A 250 mL oven-dried reaction vessel was charged with \(\text{K}_2\text{S}_2\text{O}_8\) (9.45 g, 35 mmol), sodium dodecyl (1.74 g, 5 mmol), \(\text{FeCl}_3\) (0.81 g, 5 mmol), acetophenone (1.2 g, 10 mmol), Sodium benzenesulfinate (4.5 g, 25 mmol), and DMAC (50 mL) under air. The sealed reaction vessel was stirred at 110 °C for 12 h. After cooling to ambient temperature, the reaction was diluted with EA (100 mL) and washed with saturated sodium chloride solution. The organic layer was separated, and the aqueous layer was extracted with EA for three times. The combined organic layer was dried over magnesium sulfate and the volatiles were removed under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) with PE/EA = 10/1 (v/v) as eluent to afford the title compound as a white solid.

1-(2-Bromophenyl)-2-((phenylsulfonyl)methyl)prop-2-en-1-one 2l

\[
\begin{align*}
\text{Br} & \quad \text{O} \quad \text{C} \quad \text{S} \quad \text{Ph} \\
\end{align*}
\]
R<sub>t</sub> = 0.35 (PE/EA = 5/1 (v/v)). White solid, mp = 124.1–125.1 °C. (0.89 g, 81% yield). NMR Spectroscopy: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C) δ 7.98–7.91 (m, 2H), 7.69–7.63 (m, 1H), 7.60–7.55 (m, 3H), 7.37–7.28 (m, 2H), 7.11–7.05 (m, 1H), 6.55–6.50 (m, 1H), 6.03 (s, 1H), 4.36 (d, J = 0.8 Hz, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>, 25 °C) δ 194.4, 139.0, 138.8, 138.2, 136.0, 134.1, 133.3, 131.5, 129.3, 129.0, 128.7, 127.1, 119.4, 55.1. IR (ATR): v 3063, 2922, 1669, 1446, 1297, 1136, 1084, 980, 902, 708 cm<sup>−1</sup>.HRMS (APCI, m/z): calcd for C<sub>16</sub>H<sub>11</sub>BrO<sub>3</sub>S (M+H)<sup>+</sup>: 364.9842; found: 364.9855.

2-((Phenylsulfonyl)methyl)-1-(2-(trifluoromethyl)phenyl)prop-2-en-1-one 2n

![Image of 2-((Phenylsulfonyl)methyl)-1-(2-(trifluoromethyl)phenyl)prop-2-en-1-one 2n]

R<sub>t</sub> = 0.36 (PE/EA = 5/1 (v/v)). White solid, mp = 123.9–124.7 °C. (0.89 g, 83% yield). NMR Spectroscopy: <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25 °C) δ 7.98–7.93 (m, 2H), 7.75–7.64 (m, 3H), 7.61–7.56 (m, 4H), 6.52 (d, J = 0.9 Hz, 1H), 5.93 (s, 1H), 4.36 (s, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>, 25 °C) δ 194.2, 138.9, 138.1, 136.7, 136.6 (q, J = 2.1 Hz), 134.2, 131.5, 130.3, 129.4, 128.6, 128.5, 126.8 (q, J = 4.6 Hz), 123.5 (q, J = 273.9 Hz), 55.2. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>, 25 °C) δ −58.3 (s, 3F). IR (ATR): v 3063, 2922, 1669, 1446, 1297, 1136, 1084, 980, 902, 708 cm<sup>−1</sup>. HRMS (APCI, m/z): calcd for C<sub>17</sub>H<sub>13</sub>F<sub>3</sub>O<sub>2</sub>S (M+H)<sup>+</sup>: 355.0610; found: 355.0619.

1-Phenyl-2-((o-tolylsulfonyl)methyl)prop-2-en-1-one 2ac

![Image of 1-Phenyl-2-((o-tolylsulfonyl)methyl)prop-2-en-1-one 2ac]

R<sub>t</sub> = 0.37 (PE/EA = 5/1 (v/v)). mp = 62.2–63.6 °C. (1.8 g, 60 % yield). NMR Spectroscopy: <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25 °C) δ 7.95 (dd, J = 7.9, 1.4 Hz, 1H), 7.62–7.58 (m, 2H), 7.55–7.51 (m, 1H), 7.47–7.36 (m, 3H), 7.31–7.27 (m, 2H), 6.33 (s, 1H), 6.02 (s, 1H), 4.40 (d, J = 0.9 Hz, 2H), 2.76 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>, 25 °C) δ 195.0, 139.0, 137.0, 136.2, 135.6, 134.5, 134.1, 133.0, 132.8, 130.7, 129.7, 128.4, 126.5, 56.7, 20.5. IR (ATR): v 3060, 2993, 2929, 1654, 1468, 1397, 1304, 1248, 1148, 984, 756, 708. cm<sup>−1</sup>. HRMS (APCI, m/z): calcd for C<sub>17</sub>H<sub>11</sub>O<sub>2</sub>S (M+H)<sup>+</sup>: 301.0893; found: 301.0893.

2-((1,1'-Biphenyl)-4-ylsulfonyl)methyl)-1-phenylprop-2-en-1-one 2ai

![Image of 2-((1,1'-Biphenyl)-4-ylsulfonyl)methyl)-1-phenylprop-2-en-1-one 2ai]

R<sub>t</sub> = 0.38 (PE/EA = 5/1 (v/v)). White solid, mp = 87.5–88.1 °C. (1.4 g, 40% yield). NMR Spectroscopy: <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25 °C) δ 7.98–7.95 (m, 2H), 7.72–7.67 (m, 4H), 7.57–7.53 (m, 3H), 7.49–7.45 (m, 2H), 7.44–7.40 (m, 3H), 6.31 (d, J = 0.9 Hz, 1H), 6.06 (d, J = 0.6 Hz, 1H), 4.41 (d, J = 0.9 Hz, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>, 25 °C) δ 194.8, 146.9, 139.0, 137.3, 136.1, 135.6, 134.0, 132.7, 129.7, 129.1, 128.9, 128.7, 128.3, 127.8, 127.4, 57.9. IR (ATR): v 3063, 1654, 1595, 1479, 1446, 1394, 1304, 1203, 1092, 969, 756 cm<sup>−1</sup>. HRMS (APCI, m/z): calcd for C<sub>23</sub>H<sub>19</sub>O<sub>3</sub>S (M+H)<sup>+</sup>: 363.1044; found: 363.1049.
1-Phenyl-2-(((4-(trifluoromethoxy)phenyl)sulfonyl)methyl)prop-2-en-1-one 2aj

\[
\text{O} \quad \text{S} \quad \text{OCF}_3
\]

R\textsubscript{f} = 0.40 (PE/EA = 4/1 (v/v)). White solid, mp = 84.3–85.9 °C. (1.5 g, 41% yield). NMR Spectroscopy: \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}, 25 °C) δ 7.98–7.93 (m, 2H), 7.67–7.62 (m, 2H), 7.58–7.54 (m, 1H), 7.46–7.41 (m, 2H), 7.32 (d, J = 8.4 Hz, 2H), 6.35 (d, J = 1.4 Hz, 1H), 6.09 (s, 1H), 4.38 (s, 2H). \textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}, 25 °C) δ 194.7, 153.3, 137.1, 136.1, 135.4, 134.7, 133.0, 130.9, 129.7, 128.5, 121.1, 120.3 (q, J = 260.0 Hz), 58.0. \textsuperscript{19}F NMR (565 MHz, CDCl\textsubscript{3}, 25 °C) δ −57.7 (s, 3F). IR (ATR): ν 3052, 1654, 1587, 1490, 1446, 1297, 1256, 1203, 1148, 1084, 984, 741, 693 cm\textsuperscript{-1}. HRMS (APCI, m/z): calcd for C\textsubscript{17}H\textsubscript{14}F\textsubscript{3}O\textsubscript{4}S (M+H): 371.0551; found: 371.0559.

3. Substrate scope

3.1 Reaction setup

20 mL reaction vials are placed at the hole of photoreactive plant. Two parallel LED lamps (total 24 W) are placed perpendicularly to the sidewall of reaction vials (at approximately 1 cm away from the light source), so that the reactions vials can be equally exposed to the LEDs (about 6W was distributed to each hole). A clip fan at one end of the plant had been kept working during the reaction, offsetting the heat generated from the LED light and to stabilize reaction temperature for reproducible results.

Supplementary Figure 1: The device of photo-catalysis reaction

White LEDs were used for light irradiations (see figure S3).
3.2 Investigation of the reaction conditions.

Supplementary Table 1: Optimization of solvent.

| entry | solvent | Yield of 3d% (dr) | Yield of 4d% (dr) | Yield of 5a% (dr) | Yield of 6d% (dr) |
|-------|---------|-------------------|-------------------|-------------------|-------------------|
| 1     | DMF     | 36 (85/15)        | 0                 | 0                 | 0                 |
| 2     | MeCN    | 52 (88/12)        | 0                 | 0                 | 0                 |
| 3     | THF     | 44 (87/13)        | 0                 | 0                 | 0                 |
| 4     | DMSO    | 18 (87/13)        | 0                 | 0                 | 0                 |
| 5     | DCM     | 40 (87/13)        | 0                 | 0                 | 0                 |
| 6     | MeOH    | 58 (86/14)        | 0                 | 0                 | 0                 |
| 7     | H₂O     | 20 (80/20)        | 0                 | 0                 | 0                 |
| 8     | MeCN/H₂O 1/1 | 60 (90/10)    | 0                 | 0                 | 0                 |
| 9     | MeOH/H₂O 1/1 | 60 (90/10)      | 0                 | 0                 | 0                 |
| 10    | MeCN/MeOH 1/1 | 50 (88/12)     | 0                 | 0                 | 0                 |

\(^{a} \text{N}_{2} \) Reactions were run on 0.1 mmol scale in 1.5 mL dry solvent for 12 h. The yield was determined by \(^{1} \text{H} \) NMR spectroscopy with BrCH₂CH₂Br as an internal standard of the 3d.

Supplementary Table 2 Optimization of catalyst and light source.
Reactions were run on 0.1 mmol scale in 1.5 mL dry solvent for 12 h. The yield was determined by $^1$H NMR spectroscopy with BrCH$_2$CH$_2$Br as an internal standard of the 3d. $^b$PhSO$_2$Na (1 equiv.) was used. $^c$green LEDs was used. $^d$white LED was used.

### Supplementary Table 3 Optimization of base.

| Entry | base          | Yield of 3d% (dr) | Yield of 4d% (dr) | Yield of 5a% (dr) | Yield of 6d% |
|-------|---------------|-------------------|-------------------|-------------------|-------------|
| 1     | Cs$_2$CO$_3$   | 56 (89/11)        | 0                 | 0                 | 0           |
| 2     | CsOAc         | 58 (89/11)        | 0                 | 0                 | 0           |
| 3     | K$_2$PO$_4$   | 64 (90/10)        | 0                 | 0                 | 0           |
| 4     | tBuOK         | 24 (91/9)         | 0                 | 0                 | 0           |
| 5     | KOPiv         | 66 (90/10)        | 0                 | 0                 | 0           |
| 6     | collidine     | 64 (89/11)        | 0                 | 0                 | 0           |
| 7     | KOPiv (1 equiv.) | 66 (90/10)    | 0                 | 0                 | 0           |

$^b$N$_2$, Reactions were run on 0.1 mmol scale in 1.5 mL dry solvent for 12 h. The yield was determined by $^1$H NMR spectroscopy with BrCH$_2$CH$_2$Br as an internal standard of the 3d. $^d$white LED was used.

$^b$N$_2$, Reactions were run on 0.1 mmol scale in 1.5 mL dry solvent for 12 h. The yield was determined by $^1$H NMR spectroscopy with BrCH$_2$CH$_2$Br as an internal standard of the 3d. $^d$white LED was used.
**Supplementary Table 4** Optimization of ratio of MeCN/H$_2$O.

![Chemical structure and reaction conditions](image)

| Entry | Solvent       | Yield of 3d% (dr) | Yield of 4d% (dr) | Yield of 5a% (dr) | Yield of 6d% |
|-------|---------------|-------------------|-------------------|-------------------|-------------|
| 1     | MeCN/H$_2$O = 3:1 | 46 (88/12)        | 0                 | 0                 | 0           |
| 2     | MeCN/H$_2$O = 1:1 | 70 (90/10)        | 0                 | 0                 | 0           |
| 3     | MeCN/H$_2$O = 1:2 | 70 (89/12)        | 0                 | 0                 | 0           |
| 4     | MeCN/H$_2$O = 1:3 | 83 (88/12)        | 0                 | 0                 | 0           |
| 5     | MeCN/H$_2$O = 1:5 | 60 (88/12)        | 0                 | 0                 | 0           |
| 6     | MeCN/H$_2$O = 1:8 | 40 (87/13)        | 0                 | 0                 | 0           |

$^a_{N_2}$: Reactions were run on 0.1 mmol scale in 1.5 mL dry solvent for 12 h. The yield was determined by $^1$H NMR spectroscopy with BrCH$_2$CH$_2$Br as an internal standard of the 3d. $^b$Yield of isolated product is given within parentheses.

**Supplementary Table 5** Optimization of influence of silyl group.

![Chemical structure and reaction conditions](image)

| Entry | [Si] | Yield of 3% (dr) | Yield of 4% (dr) | Yield of 5a% (dr) | Yield of 6% (dr) |
|-------|------|------------------|------------------|-------------------|-----------------|
| 1     | TMS  | 86 (90/10) 82$^b$ | 0                | 0                 | 0               |
| 2     | TES  | 66 (86/14) 63$^b$ | 0                | 0                 | 0               |
| 3     | TBS  | 44 (86/14) 50$^b$ | 0                | 0                 | 0               |
| 4     | SiMe$_2$Ph | 83 (88/12) 82$^b$ | 0                | 0                 | 0               |
| 5     | SiMePh$_2$ | 73 (87/13) 71$^b$ | 0                | 0                 | 0               |

$^a_{N_2}$: Reactions were run on 0.1 mmol scale in 1.5 mL dry solvent for 12 h. The yield was determined by $^1$H NMR spectroscopy with BrCH$_2$CH$_2$Br as an internal standard of the 3. $^b$Yield of isolated product is given within parentheses.

**Supplementary Table 6** Control experiments.
Reactions were run on 0.1 mmol scale in 1.5 mL dry solvent for 12 h. The yield was determined by \(^1\)H NMR spectroscopy with \(\text{BrCH}_2\text{CH}_2\text{Br}\) as an internal standard of the \(3a\). Yield of isolated product is given within parentheses. \(^3\)no KOPiv was used, \(^4\)no light. \(^5\)no Eosin Y. \(^6\)Air atmosphere. \(^7\)reaction concentration (0.025 M).

### 3.3 Scope for the \(\beta\)-substituent cyclopentanol derivatives

**1-Phenyl-2-((2-((phenylsulfonyl)methyl)-1-((trimethylsilyl)oxy)cyclopentyl)methyl)prop-2-en-1-one (3a)**

In a glovebox, to an oven-dried 10 mL tube was added 2a (28.6 mg, 0.1 mmol), PhSO\(_2\)Na (3.2 mg, 0.02 mmol, 0.2 equiv.), Eosin Y (0.65 mg, 0.001 mmol, 1 mol%), KOPiv (14.2 mg, 0.1 mmol, 1 equiv.), MeCN/H\(_2\)O = 1:3 (0.067 M) and 1a (34.0 mg, 0.2 mmol, 2 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The dr was determined by the analysis of the unpurified crude mixture by \(^1\)H NMR. The crude product was purified with column chromatography on silica gel (300–400 mesh) with PE/EA = 5/1 (v/v) as eluent to afford the title compound as a colorless oil (37.5 mg, 82% yield in total, a mixture of two diastereoisomers).

Characterization of the major isomer: \(R_f = 0.48 (\text{PE/EA = 5/1 (v/v)})\). NMR Spectroscopy: \(^1\)H NMR (600 MHz, CDCl\(_3\), 25 °C) δ 7.93–7.88 (m, 2H), 7.65–7.62 (m, 2H), 7.58–7.52 (m, 2H), 7.51–7.47 (m, 2H), 7.44–7.41 (m, 2H), 5.77 (d, 2H).
= 1.0 Hz, 1H), 5.65 (d, J = 14.3, 2.0 Hz, 1H), 3.45 (dd, J = 14.3, 10.6 Hz, 1H), 2.84 (dd, J = 13.2, 0.9 Hz, 1H), 2.75 (dd, J = 13.1, 0.9 Hz, 1H), 2.12–1.91 (m, 2H), 1.77–1.66 (m, 2H), 1.65–1.54 (m, 2H), 1.55–1.45 (m, 1H), 0.08 (s, 9H). 1H NMR (151 MHz, CDCl3, 25 ºC) δ 197.3, 144.1, 140.1, 137.2, 133.5, 132.5, 130.6, 129.8, 129.2, 128.4, 128.1, 85.7, 57.8, 41.0, 40.2, 37.0, 29.6, 21.6, 2.2. 29Si NMR (119 MHz, CDCl3, 25 ºC) δ 10.7.

IR (ATR): ν 3063, 2959, 1654, 1446, 1304, 1252, 1148, 1069, 842, 752 cm⁻¹. HRMS (ESI, m/z): calcd for C25H33O4SSi (M+H)+: 457.1863; found: 457.1862.

2-((1-Hydroxy-2-((phenylsulfonyl)methyl)cyclopentyl)methyl)-1-phenylprop-2-en-1-one (3a′)

To a 4 mL tube was added 3a (22.8 mg, 0.05 mmol), EA (0.1 M) and TBAF (0.1 mL, 0.1 mmol, 1 M in THF, 2 equiv.) sequentially. The mixture was stirred at ambient temperature for the 0.5 h. The resulting mixture was filtered through a thin silica gel plug with EA (20 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300–400 mesh) with PE/EA = 2/1 (v/v) as eluent to afford the title compound as a colorless oil (18.8 mg, 97 % yield).

Characterization of the major isomer: Rf = 0.22 (PE/EA = 2/1 (v/v)). NMR Spectroscopy: 1H NMR (600 MHz, CDCl3, 25 ºC) δ 7.94–7.91 (m, 2H), 7.76–7.73 (m, 2H), 7.65–7.62 (m, 1H), 7.60–7.54 (m, 3H), 7.47–7.43 (m, 2H), 6.03 (d, J = 1.0 Hz, 1H), 5.79 (d, J = 0.7 Hz, 1H), 3.90 (s, 1H), 3.40 (dd, J = 14.3, 2.9 Hz, 1H), 3.17 (dd, J = 14.3, 9.7 Hz, 1H), 2.81 (d, J = 13.7 Hz, 1H), 2.54 (d, J = 13.7 Hz, 1H), 2.26–2.21 (m, 1H), 2.11–2.05 (m, 1H), 1.82–1.75 (m, 1H), 1.72–1.54 (m, 4H). 13C NMR (151 MHz, CDCl3, 25 ºC) δ 200.5, 144.1, 140.4, 137.0, 133.7, 133.1, 131.6, 130.1, 129.4, 128.5, 128.0, 81.6, 57.9, 43.3, 43.2, 38.9, 31.2, 21.7. IR (ATR): ν 3541, 3063, 2967, 2873, 1654, 1601, 1446, 1304, 1144, 1084, 909, 738, 689 cm⁻¹. HRMS (ESI, m/z): calcd for C22H25O4S (M+H)+: 385.1468; found: 385.1463.

1-Phenyl-2-((2-((phenylsulfonyl)methyl)-1-((triethylsilyl)oxy)cyclopentyl)methyl)prop-2-en-1-one (3b)

In a glovebox, to an oven-dried 10 mL tube was added 2a (57.2 mg, 0.2 mmol), PhSO2Na (6.4 mg, 0.04 mmol, 0.2 equiv.), Eosin Y (1.3 mg, 0.002 mmol, 1 mol%), KOPOiv (28.4 mg, 0.2 mmol, 1 equiv.), MeCN/H2O =1:3 (0.067 M) and 1b (82.8 mg, 0.4 mmol, 2 equiv.) sequentially. The mixture was sealed, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300–400 mesh) with PE/EA = 5/1 (v/v) as eluent to afford the title compound as a colorless oil (69.4 mg, 69 % yield in total, a mixture of two diasteroisomers).
Characterization of the major isomer: $R_f = 0.45$ (PE/EA = 5/1 (v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, CDCl$_3$, 25 °C) $\delta$ 7.92–7.89 (m, 2H), 7.67 (dd, $J = 8.3$, 1.4 Hz, 2H), 7.57–7.51 (m, 2H), 7.50–7.45 (m, 2H), 7.45–7.40 (m, 2H), 5.78 (d, $J = 0.9$ Hz, 1H), 5.67 (d, $J = 0.7$ Hz, 1H), 3.47 (dd, $J = 14.3$, 1.7 Hz, 1H), 3.09 (dd, $J = 14.3$, 10.2 Hz, 1H), 2.95 (dd, $J = 13.2$, 0.9 Hz, 1H), 2.70 (dd, $J = 13.0$, 0.8 Hz, 1H), 2.01–1.95 (m, 2H), 1.78–1.68 (m, 1H), 1.66–1.57 (m, 2H), 1.56–1.44 (m, 2H), 0.93 (t, $J = 7.9$ Hz, 9H), 0.66–0.54 (m, 6H). $^{13}$C NMR (151 MHz, CDCl$_3$, 25 °C) $\delta$ 197.3, 143.9, 140.1, 133.5, 132.5, 131.2, 129.7, 129.2, 128.4, 128.0, 85.5, 57.7, 40.8, 39.3, 37.1, 29.6, 21.5, 18.5, 7.3, 6.7. $^{29}$Si NMR (119 MHz, CDCl$_3$, 25 °C) $\delta$ 13.5. IR (ATR): $\nu$ 2981, 2929, 2862, 1610, 1513, 1356, 1248, 1170, 1080, 1002, 834 cm$^{-1}$. HRMS (ESI, m/z): calcd for C$_{28}$H$_{39}$O$_{3}$Si (M+H)$^+$: 499.2333; found: 499.2332.

2-((1-((Tert-butyldimethylsilyl)oxy)-2-((phenylsulfonyl)methyl)cyclopentyl)methyl)-1-phenylprop-2-en-1-one (3c)

![Diagram of 3c]

In a glovebox, to an oven-dried 10 mL tube was added 2a (57.2 mg, 0.2 mmol), PhSO$_2$Na (6.4 mg, 0.04 mmol, 0.2 equiv.), Eosin Y (1.3 mg, 0.002 mmol, 1 mol%), KOPiv (28.4 mg, 0.2 mmol, 1 equiv.), MeCN/H$_2$O =1:3 (0.067 M) and 1c (82.8 mg, 0.4 mmol, 2 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300–400 mesh) with PE/EA = 5/1 (v/v) as eluent to afford the title compound as a colorless oil (69.1 mg, 69 % yield in total, a mixture of two disteraoisomers).

Characterization of the major isomer: $R_f = 0.44$ (PE/EA = 5/1 (v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, CDCl$_3$, 25 °C) $\delta$ 7.96–7.88 (m, 2H), 7.64–7.59 (m, 2H), 7.58–7.51 (m, 2H), 7.50–7.46 (m, 2H), 7.45–7.42 (m, 2H), 5.80 (d, $J = 0.9$ Hz, 1H), 5.68 (d, $J = 0.7$ Hz, 1H), 3.47 (dd, $J = 14.4$, 1.8 Hz, 1H), 3.11 (dd, $J = 14.3$, 10.5 Hz, 1H), 3.01 (dd, $J = 13.2$, 0.9 Hz, 1H), 2.67 (dd, $J = 13.1$, 0.8 Hz, 1H), 2.01–1.93 (m, 2H), 1.77–1.69 (m, 1H), 1.66–1.61 (m, 1H), 1.60–1.55 (m, 1H), 1.53–1.44 (m, 2H), 0.84 (s, 9H), 0.15 (s, 3H), 0.13 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$, 25 °C) $\delta$ 197.3, 143.8, 140.1, 133.5, 132.5, 131.5, 129.7, 129.2, 128.4, 128.1, 85.8, 57.7, 41.0, 38.8, 36.5, 29.6, 26.0, 21.3, 18.5, 16.9, –2.6. $^{29}$Si NMR (119 MHz, CDCl$_3$, 25 °C) $\delta$ 12.5. IR (ATR): $\nu$ 2952, 2929, 2858, 1654, 1446, 1308, 1259, 1146, 1066, 913, 838, 775, 738, 711 cm$^{-1}$. HRMS (ESI, m/z): calcd for C$_{28}$H$_{39}$O$_{3}$Si (M+H)$^+$: 499.2333; found: 499.2332.

2-((1-((Dimethyl(phenyl)silyl)oxy)-2-((phenylsulfonyl)methyl)cyclopentyl)methyl)-1-phenylprop-2-en-1-one (3d)

![Diagram of 3d]

In a glovebox, to an oven-dried 10 mL tube was added 2a (28.6 mg, 0.1 mmol), PhSO$_2$Na (3.2 mg, 0.02 mmol, 0.2 equiv.), Eosin Y (0.65 mg, 0.001 mmol, 1 mol%), KOPiv (14.2 mg, 0.2 mmol, 1 equiv.), MeCN/H$_2$O =1:3 (0.067 M) and 1d (46.4 mg, 0.2 mmol, 2 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps.
The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300–400 mesh) with PE/EA = 5/1 (v/v) as eluent to afford the title compound as a colorless oil (34.2 mg, 66 % yield in total, a mixture of two diastereomers).

Characterization of the major isomer: \( R_f = 0.44 \) (PE/EA = 5/1 (v/v)). NMR Spectroscopy: \(^1\)H NMR (600 MHz, CDCl\(_3\), 25 °C) δ 7.92–7.87 (m, 2H), 7.61 (dd, \( J = 8.3, 1.4 \) Hz, 2H), 7.56–7.53 (m, 2H), 7.53–7.46 (m, 4H), 7.44–7.40 (m, 2H), 7.39–7.35 (m, 1H), 7.35–7.31 (m, 2H), 5.76–5.74 (m, 1H), 5.65 (d, \( J = 0.7 \) Hz, 1H), 3.50 (dd, \( J = 14.3, 2.0 \) Hz, 1H), 3.07 (dd, \( J = 14.3, 10.6 \) Hz, 1H), 2.91–2.84 (m, 1H), 2.77 (d, \( J = 12.9 \) Hz, 1H), 2.10–1.95 (m, 2H), 1.70–1.64 (m, 1H), 1.64–1.56 (m, 2H), 1.56–1.50 (m, 1H), 1.50–1.40 (m, 1H), 0.41 (s, 3H), 0.37 (s, 3H). \(^1\)C NMR (151 MHz, CDCl\(_3\), 25 °C) δ 197.2, 143.9, 140.1, 139.2, 137.2, 132.2, 132.4, 130.9, 129.7, 129.6, 129.2, 128.4, 128.0, 128.0, 86.4, 57.7, 41.0, 39.9, 36.9, 29.6, 21.4, 0.9, 0.8. \(^29\)Si NMR (119 MHz, CDCl\(_3\), 25 °C) δ 0.4. IR (ATR): ν 3062, 2959, 2859, 2925, 2929, 1654, 1446, 1304, 1252, 1192, 1144, 1058, 827, 786 cm\(^{-1}\). HRMS (ESI, m/z): calcd for C\(_38\)H\(_{35}\)O\(_3\)Si (M+H\(^+\)) \(^\ddagger\) : 519.2120; found: 519.2135.

Characterization of the minor isomer: \( R_f = 0.40 \) (PE/EA = 5/1 (v/v)). NMR Spectroscopy: \(^1\)H NMR (600 MHz, CDCl\(_3\), 25 °C) δ 7.86–7.82 (m, 2H), 7.67–7.61 (m, 3H), 7.52 (dt, \( J = 13.5, 7.6 \) Hz, 3H), 7.49–7.45 (m, 2H), 7.38 (dt, \( J = 10.0, 7.6 \) Hz, 3H), 7.28 (dd, \( J = 7.8, 6.5 \) Hz, 2H), 5.87 (s, 1H), 5.68 (d, \( J = 1.3 \) Hz, 1H), 3.43 (dd, \( J = 13.6, 1.9 \) Hz, 1H), 3.00 (dd, \( J = 13.5, 11.9 \) Hz, 1H), 2.57 (d, \( J = 13.1 \) Hz, 1H), 2.43–2.38 (m, 1H), 2.36 (d, \( J = 13.2 \) Hz, 1H), 2.13–2.05 (m, 1H), 1.71–1.64 (m, 1H), 1.61–1.57 (m, 3H), 1.47–1.37 (m, 1H), 0.21 (s, 3H), 0.20 (s, 3H). \(^1\)C NMR (151 MHz, CDCl\(_3\), 25 °C) δ 197.6, 144.2, 140.0, 139.0, 137.1, 133.7, 133.5, 132.4, 130.0, 129.6, 129.5, 129.4, 128.3, 128.1, 127.9, 85.5, 57.4, 44.6, 36.4, 35.6, 27.2, 19.8, 0.8, 0.6. IR (ATR): ν 3060, 2925, 2929, 1654, 1595, 1446, 1308, 1256, 1148, 834, 745, 700 cm\(^{-1}\). HRMS (ESI, m/z): calcd for C\(_38\)H\(_{35}\)O\(_3\)Si (M+H\(^+\)) \(^\ddagger\) : 519.2120; found: 519.2021.

\[ 2-(1-((Methylidiphenylsilyloxy)-2-((phenylsulfonyl)methyl)cyclopentyl)(methyl)-1-phenylprop-2-en-1-one \ (3e) \]

In a glovebox, to an oven-dried 10 mL tube was added \( 2a \) (28.6 mg, 0.1 mmol), PhSO\(_2\)Na (3.2 mg, 0.02 mmol, 0.2 equiv.), Eosin Y (0.65 mg, 0.001 mmol, 1 mol%), KOPiv (14.2 mg, 0.1 mmol, 1 equiv.), MeCN/H\(_2\)O =1:3 (0.067 M) and \( 1e \) (58.8 mg, 0.2 mmol, 2 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300–400 mesh) with PE/EA = 5/1 (v/v) as eluent to afford the title compound as a colorless oil (30.1 mg, 52 % yield in total, a mixture of two diastereomers).

Characterization of the major isomer: \( R_t = 0.44 \) (PE/EA = 5/1 (v/v)). NMR Spectroscopy: \(^1\)H NMR (600 MHz, CDCl\(_3\), 25 °C) δ 7.93–7.87 (m, 2H), 7.59–7.56 (m, 2H), 7.56–7.50 (m, 6H), 7.50–7.46 (m, 2H), 7.43–7.36 (m, 4H), 7.36–
7.30 (m, 4H), 5.73 (d, J = 0.9 Hz, 1H), 5.66 (d, J = 0.7 Hz, 1H), 3.55 (dd, J = 14.2, 1.7 Hz, 1H), 3.20 (dd, J = 14.2, 10.3 Hz, 1H), 2.94 (dd, J = 13.3, 0.8 Hz, 1H), 2.77 (dd, J = 13.2, 0.8 Hz, 1H), 2.04 (ddt, J = 14.4, 11.5, 5.0 Hz, 2H), 1.73–1.64 (m, 2H), 1.58–1.53 (m, 1H), 1.53–1.47 (m, 1H), 1.46–1.39 (m, 1H), 0.75 (s, 3H). 13C NMR (151 MHz, CDCl3, 25 ºC) δ 197.2, 143.7, 140.1, 137.6, 137.4, 137.2, 134.3, 133.5, 132.4, 131.5, 129.9, 129.7, 129.2, 128.4, 128.1, 128.0, 87.3, 57.7, 41.2, 39.5, 36.9, 29.7, 21.3, –0.3. 29Si NMR (119 MHz, CDCl3, 25 ºC) δ –10.1. IR (ATR): v 3067, 2963, 2926, 2873, 1654, 1446, 1304, 1259, 1058, 915, 738 cm⁻¹. HRMS (ESI, m/z): calcd for C35H37O3SSi (M+H)+: 581.2176; found: 581.2180.

2-((2-((Phenylsulfonyl)methyl)-1-((trimethylsilyl)oxy)cyclopentyl)methyl)-1-(p-tolyl)prop-2-en-1-one (3f)

In a glovebox, to an oven-dried 10 mL tube was added 2f (60 mg, 0.2 mmol), PhSO2Na (6.4 mg, 0.04 mmol, 0.2 equiv.), Eosin Y (2.6 mg, 0.004 mmol, 2 mol%), KOPiv (14.2 mg, 0.3 mmol, 1.5 equiv.), MeCN/H2O =1:3 (0.067 M) and 1a (68 mg, 0.4 mmol, 2 equiv.) sequentially. The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (300–400 mesh) with PE/EA = 5/1 (v/v) as eluent to afford the title compound as a colorless oil (51.9 mg, 55 % yield in total, a mixture of two diastereoisomers).

Characterization of the major isomer: Rf = 0.43 (PE/EA = 5/1 (v/v)). NMR Spectroscopy: 1H NMR (600 MHz, CDCl3, 25 ºC) δ 7.94–7.90 (m, 2H), 7.60–7.55 (m, 3H), 7.54–7.49 (m, 2H), 7.25–7.21 (m, 2H), 5.71 (d, J = 1.0 Hz, 1H), 5.61 (d, J = 0.9 Hz, 1H), 3.44 (dd, J = 14.4, 2.1 Hz, 1H), 3.02 (dd, J = 14.4, 10.8 Hz, 1H), 2.86 (dd, J = 13.2, 0.9 Hz, 1H), 2.72 (dd, J = 13.2, 0.9 Hz, 1H), 2.42 (s, 3H), 2.08–2.03 (m, 1H), 2.02–1.96 (m, 1H), 1.76–1.65 (m, 2H), 1.60–1.52 (m, 2H), 1.52–1.45 (m, 1H), 0.08 (s, 9H). 13C NMR (151 MHz, CDCl3, 25 ºC) δ 197.0, 144.2, 143.3, 140.2, 134.4, 133.5, 130.0, 129.7, 129.3, 129.1, 128.1, 85.7, 57.8, 40.9, 40.4, 37.0, 29.6, 21.8, 21.6, 2.3. 29Si NMR (119 MHz, CDCl3, 25 ºC) δ 10.6. IR (ATR): v 3063, 2959, 1654, 1606, 1446, 1408, 1304, 1252, 1148, 1066, 916, 842, 698 cm⁻¹. HRMS (ESI, m/z): calcd for C35H37O3SSi (M+H)+: 471.2020; found: 471.2025.

2-((2-((Phenylsulfonyl)methyl)-1-((trimethylsilyl)oxy)cyclopentyl)methyl)-1-(m-tolyl)prop-2-en-1-one (3g)

In a glovebox, to an oven-dried 10 mL tube was added 2g (90 mg, 0.3 mmol), PhSO2Na (9.84 mg, 0.06 mmol, 0.2 equiv.), Eosin Y (1.9 mg, 0.003 mmol, 1 mol%), KOPiv (42.6 mg, 0.3 mmol, 1 equiv.), MeCN/H2O =1:3 (0.067 M) and 1a (102 mg, 0.6 mmol, 2 equiv.) sequentially. The mixture was stirred, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase
was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300–400 mesh) with PE/EA = 5/1 (v/v) as eluent to afford the title compound as a colorless oil (98.7 mg, 70 % yield in total, a mixture of two disteraosiomers).

Charaterization of the major isomer: $R_t = 0.44$ (PE/EA = 5/1 (v/v)). NMR Spectroscopy: $^1$H NMR (400 MHz, CDCl$_3$, 25 °C) $\delta$ 7.94–7.89 (m, 2H), 7.58–7.53 (m, 1H), 7.52–7.46 (m, 3H), 7.42–7.34 (m, 2H), 7.32–7.26 (m, 1H), 5.76 (q, $J = 0.9$ Hz, 1H), 5.65 (d, $J = 0.9$ Hz, 1H), 3.46 (dd, $J = 14.3, 1.9$ Hz, 1H), 3.03 (dd, $J = 14.4, 10.5$ Hz, 1H), 2.85 (dd, $J = 13.3, 0.9$ Hz, 1H), 2.72 (dd, $J = 13.3, 0.9$ Hz, 1H), 2.41 (d, $J = 0.7$ Hz, 3H), 2.11–1.92 (m, 2H), 1.77–1.64 (m, 2H), 1.62–1.44 (m, 3H), 0.09 (s, 9H). $^{13}$C NMR (151 MHz, CDCl$_3$, 25 ºC) $\delta$ 197.5, 144.2, 140.2, 138.3, 137.3, 133.5, 133.2, 130.6, 130.2, 129.2, 128.2, 128.1, 127.1, 85.8, 57.8, 41.0, 40.1, 37.0, 29.7, 21.6, 21.5, 2.3. $^{29}$Si NMR (119 MHz, CDCl$_3$, 25 ºC) $\delta$ 10.6.

IR (ATR): $\nu$ 3063, 2955, 1654, 1446, 1304, 1252, 1144, 1066, 838, 749, 689 cm$^{-1}$. HRMS (ESI, m/z): calcd for C$_{26}$H$_{35}$O$_4$SSi (M+H)$^+$: 471.2120; found: 471.2119.

2-((2-((Phenylsulfonyl)methyl)-1-((trimethylsilyl)oxy)cyclopentyl)methyl)-1-(o-tolyl)prop-2-en-1-one (3h)

In a glovebox, to an oven-dried 10 mL tube was added 2h (90 mg, 0.3 mmol), PhSO$_2$Na (9.84 mg, 0.06 mmol, 0.2 equiv.), Eosin Y (1.9 mg, 0.003 mmol, 1 mol%), KO$_2$Piv (42.6 mg, 0.3 mmol, 1 equiv.), MeCN/H$_2$O = 1:3 (0.067 M) and 1a (102 mg, 0.6 mmol, 2 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300–400 mesh) with PE/EA = 5/1 (v/v) as eluent to afford the title compound as a colorless oil (105.0 mg, 75 % yield in total, a mixture of two disteraosiomers).

Charaterization of the major isomer: $R_t = 0.43$ (PE/EA = 5/1 (v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, CDCl$_3$, 25 °C) $\delta$ 7.93–7.88 (m, 2H), 7.55–7.49 (m, 1H), 7.48–7.44 (m, 2H), 7.34–7.31 (m, 1H), 7.22–7.21 (m, 1H), 7.18–7.15 (m, 1H), 7.08 (dd, $J = 7.6, 1.4$ Hz, 1H), 5.87 (d, $J = 0.9$ Hz, 1H), 5.65 (d, $J = 0.8$ Hz, 1H), 3.54 (dd, $J = 14.3, 1.9$ Hz, 1H), 3.05 (dd, $J = 14.3, 10.6$ Hz, 1H), 2.79 (dd, $J = 13.1, 0.8$ Hz, 1H), 2.72 (dd, $J = 13.1, 0.8$ Hz, 1H), 2.28 (s, 3H), 2.06–1.92 (m, 2H), 1.79–1.69 (m, 2H), 1.66–1.59 (m, 2H), 1.57–1.50 (m, 1H), 0.12 (s, 9H). $^{13}$C NMR (151 MHz, CDCl$_3$, 25 °C) $\delta$ 199.4, 145.3, 140.1, 138.2, 136.8, 134.0, 133.4, 133.4, 130.1, 129.2, 128.4, 128.1, 125.1, 86.0, 57.8, 41.0, 37.7, 36.6, 29.5, 21.4, 19.9, 2.3. $^{29}$Si NMR (119 MHz, CDCl$_3$, 25 °C) $\delta$ 10.4. IR (ATR): $\nu$ 3063, 2955, 1654, 1446, 1304, 1252, 1144, 1066, 838, 749, 689 cm$^{-1}$. HRMS (ESI, m/z): calcd for C$_{26}$H$_{35}$O$_3$SSi (M+H)$^+$: 471.2120; found: 471.2119.

1-(4-Fluorophenyl)-2-((2-((Phenylsulfonyl)methyl)-1-((trimethylsilyl)oxy)cyclopentyl)methyl)prop-2-en-1-one (3i)
In a glovebox, to an oven-dried 10 mL tube was added 2i (91.2 mg, 0.3 mmol), PhSO₃Na (9.8 mg, 0.06 mmol, 0.2 equiv.), Eosin Y (1.9 mg, 0.003 mmol, 1 mol%), KOPiv (42.6 mg, 0.3 mmol, 1 equiv.), MeCN/H₂O = 1:3 (0.067 M) and 1a (102 mg, 0.6 mmol, 2 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300–400 mesh) with PE/EA = 5/1 (v/v) as eluent to afford the title compound as a colorless oil (101.2 mg, 72 % yield in total, a mixture of two diastereomers).

Characterization of the major isomer: Rᵣ = 0.44 (PE/EA = 5/1 (v/v)). NMR Spectroscopy: ¹H NMR (600 MHz, CDCl₃, 25 ºC) δ 7.95–7.86 (m, 2H), 7.74–7.69 (m, 2H), 7.63–7.57 (m, 1H), 7.54–7.50 (m, 2H), 7.15–7.08 (m, 2H), 5.78 (d, J = 0.9 Hz, 1H), 5.63 (d, J = 0.8 Hz, 1H), 3.43 (dd, J = 14.3, 2.1 Hz, 1H), 2.99 (dd, J = 14.3, 10.9 Hz, 1H), 2.83–2.76 (m, 2H), 2.10–2.05 (m, 1H), 2.03–1.94 (m, 1H), 1.77–1.66 (m, 2H), 1.64–1.54 (m, 2H), 1.54–1.45 (m, 1H), 0.07 (s, 9H). ¹³C NMR (151 MHz, CDCl₃, 25 ºC) δ 195.8, 165.5 (d, J = 254.0 Hz), 144.1, 140.3, 133.6, 133.4 (d, J = 3.1 Hz), 132.4 (d, J = 8.9 Hz), 129.9, 129.3, 128.1, 115.6 (d, J = 21.8 Hz), 85.7, 57.8, 40.9, 40.6, 37.1, 29.6, 21.6, 2.2. ²⁹Si NMR (119 MHz, CDCl₃, 25 ºC) δ 10.83. ¹⁹F NMR (565 MHz, CDCl₃, 25 ºC) δ −106.2—106.7 (m, 1F). IR (ATR): ν 3067, 2939, 1654, 1599, 1505, 1446, 1408, 1304, 1252, 1151, 1066, 842 cm⁻¹. HRMS (ESI, m/z): calcd for C₂₅H₂₄FO₄SSi (M+H)⁺: 475.1769; found: 475.1771.

1-(2-Fluorophenyl)-2-((phenylsulfonyl)methyl)-1-((trimethylsilyl)oxy)cyclopentyl)methyl prop-2-en-1-one (3j) 9-147

In a glovebox, to an oven-dried 10 mL tube was added 2j (91.2 mg, 0.3 mmol), PhSO₃Na (9.84 mg, 0.06 mmol, 0.2 equiv.), Eosin Y (1.9 mg, 0.003 mmol, 1 mol%), KOPiv (42.6 mg, 0.3 mmol, 1 equiv.), MeCN/H₂O = 1:3 (0.067 M) and 1a (102 mg, 0.6 mmol, 2 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300–400 mesh) with PE/EA = 5/1 (v/v) as eluent to afford the title compound as a colorless oil (109.1 mg, 77 % yield in total, a mixture of two diastereomers).

Characterization of the major isomer: Rᵣ = 0.44 (PE/EA = 5/1 (v/v)). NMR Spectroscopy: ¹H NMR (600 MHz, CDCl₃, 25 ºC) δ 7.92–7.88 (m, 2H), 7.49–7.41 (m, 4H), 7.38–7.36 (m, 1H), 7.23–7.17 (m, 1H), 7.07–7.04 (m, 1H), 5.85 (s, 1H), 5.72 (d, J = 2.1 Hz, 1H), 3.50 (dd, J = 14.5, 2.1 Hz, 1H), 3.05 (dd, J = 14.4, 10.8 Hz, 1H), 2.75 (s, 2H), 2.04–1.95 (m, 1H), 1.94–1.87 (m, 1H), 1.78–1.57 (m, 4H), 1.57–1.48 (m, 1H), 0.11 (s, 9H). ¹³C NMR (151 MHz, CDCl₃, 25 ºC) δ 194.4, 159.7 (d, J = 251.4 Hz), 145.0, 139.9, 133.3, 132.9 (d, J = 2.3 Hz), 132.9, 130.6 (d, J = 2.9 Hz), 129.1, 128.1, 126.8 (d, J = 14.7 Hz), 124.4 (d, J = 3.6 Hz), 116.2 (d, J = 22.0 Hz), 85.9, 57.7, 40.8, 38.1, 36.5, 29.6, 21.4, 2.3. ¹⁹F NMR (565 MHz, CDCl₃, 25 ºC) δ −111.36—111.4 (m, 1F). ²⁹Si NMR (119 MHz, CDCl₃, 25 ºC) δ 10.3. IR (ATR): ν 3302, 3064, 2949, 1659, 1610, 1484, 1446, 1305, 1252, 1144, 1062, 987, 913, 835, 730 cm⁻¹. HRMS (ESI, m/z): calcd for C₂₅H₂₃FO₄SSi (M+H)⁺: 475.1769; found: 475.1770.
1-(2-Chlorophenyl)-2-((2-((phenylsulfonyl)methyl)-1-((trimethylsilyl)oxy)cyclopentyl)methyl)prop-2-en-1-one (3k)

In a glovebox, to an oven-dried 10 mL tube was added 2k (96 mg, 0.3 mmol), PhSO$_2$Na (9.84 mg, 0.06 mmol, 0.2 equiv.), Eosin Y (1.9 mg, 0.003 mmol, 1 mol%), KOPiv (42.6 mg, 0.3 mmol, 1 equiv.), MeCN/H$_2$O =1:3 (0.067 M) and 1a (102 mg, 0.6 mmol, 2 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300~400 mesh) with PE/EA = 5/1 (v/v) as eluent to afford the title compound as a colorless oil (101.4 mg, 69 % yield in total, a mixture of two diastereomers).

Characterization of the major isomer: $R_f = 0.44$ (PE/EA = 5/1 (v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, CDCl$_3$, 25 °C) $\delta$ 7.94–7.91 (m, 2H), 7.57–7.52 (m, 1H), 7.51–7.46 (m, 2H), 7.41–7.35 (m, 2H), 7.32–7.29 (m, 1H), 7.23–7.21 (m, 1H), 5.99 (s, 1H), 5.72 (s, 1H), 3.55 (dd, $J = 14.3, 1.8$ Hz, 1H), 3.05 (dd, $J = 14.3, 10.5$ Hz, 1H), 2.85–2.76 (m, 1H), 2.74–2.68 (m, 1H), 2.09–1.91 (m, 2H), 1.79–1.65 (m, 3H), 1.62–1.49 (m, 2H), 0.13 (s, 9H). $^{13}$C NMR (151 MHz, CDCl$_3$, 25 °C) $\delta$ 196.4, 144.2, 140.2, 138.4, 135.5, 133.5, 131.1, 131.0, 130.1, 129.3, 128.2, 126.7, 86.1, 57.9, 40.9, 37.2, 36.6, 29.8, 29.7, 21.4, 2.4. $^{29}$Si NMR (119 MHz, CDCl$_3$, 25 °C) $\delta$ 10.4. IR (ATR): $\nu$ 3060, 2955, 1666, 1617, 1591, 1446, 1304, 1252, 1146, 1062, 1025, 987, 842, 732 cm$^{-1}$. HRMS (ESI, m/z): calcd for C$_{25}$H$_{32}$ClO$_4$SSi (M+H)$^+$: 491.1474; found: 491.1471.

1-(2-Bromophenyl)-2-((2-((phenylsulfonyl)methyl)-1-((trimethylsilyl)oxy)cyclopentyl)methyl)prop-2-en-1-one (3l)

In a glovebox, to an oven-dried 10 mL tube was added 2l (108.9 mg, 0.3 mmol), PhSO$_2$Na (9.84 mg, 0.06 mmol, 0.2 equiv.), Eosin Y (1.9 mg, 0.003 mmol, 1 mol%), KOPiv (42.6 mg, 0.3 mmol, 1 equiv.), MeCN/H$_2$O =1:3 (0.067 M) and 1a (102 mg, 0.6 mmol, 2 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300~400 mesh) with PE/EA = 5/1 (v/v) as eluent to afford the title compound as a colorless oil (111.9 mg, 70 % yield in total, a mixture of two diastereomers).

Characterization of the major isomer: $R_f = 0.44$ (PE/EA = 5/1 (v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, CDCl$_3$, 25 °C) $\delta$ 7.95–7.91 (m, 2H), 7.60–7.53 (m, 2H), 7.51–7.47 (m, 2H), 7.36–7.33 (m, 1H), 7.30–7.28 (m, 1H), 7.18 (dd, $J = 7.5, 1.7$ Hz, 1H), 6.01 (s, 1H), 5.72 (s, 1H), 3.56 (dd, $J = 14.3, 2.0$ Hz, 1H), 3.04 (dd, $J = 14.3, 10.5$ Hz, 1H), 2.79
1-(4-Iodophenyl)-2-((2-((phenylsulfonyl)methyl)-1-((trimethylsilyl)oxy)cyclopentyl)methyl)prop-2-en-1-one (3m)

In a glovebox, to an oven-dried 10 mL tube was added 2m (123.3 mg, 0.3 mmol), PhSO_2Na (9.84 mg, 0.06 mmol, 0.2 equiv.), Eosin Y (1.9 mg, 0.003 mmol, 1 mol%), KOPiv (42.6 mg, 0.3 mmol, 1 equiv.), MeCN/H_2O =1:3 (0.067 M) and 1a (102 mg, 0.6 mmol, 2 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300~400 mesh) with PE/EA = 5/1 (v/v) as eluent to afford the title compound as a colorless oil (138.7 mg, 81 % yield in total, a mixture of two diasteroisomers).

Characterization of the major isomer: R_f = 0.44 (PE/EA = 5/1 (v/v)). NMR Spectroscopy: ^1H NMR (600 MHz, CDCl_3, 25 °C) δ 7.92–7.88 (m, 2H), 7.81–7.77 (m, 2H), 7.60–7.55 (m, 1H), 7.53–7.48 (m, 2H), 7.39–7.34 (m, 2H), 5.80–5.78 (m, 1H), 5.63 (d, J = 0.7 Hz, 1H), 3.41 (dd, J = 14.3, 1.9 Hz, 1H), 2.99 (dd, J = 14.3, 10.6 Hz, 1H), 2.77 (dd, J = 2.1, 0.9 Hz, 2H), 2.06–1.94 (m, 2H), 1.76–1.65 (m, 2H), 1.62–1.45 (m, 3H), 0.07 (s, 9H). ^13C NMR (151 MHz, CDCl_3, 25 °C) δ 196.4, 143.9, 140.1, 137.7, 136.5, 133.5, 131.2, 130.5, 129.3, 128.0, 100.1, 85.6, 57.7, 40.9, 40.3, 37.0, 29.6, 21.5. ^29Si NMR (119 MHz, CDCl_3, 25 °C) δ 10.82. IR (ATR): v 3063, 2955, 1654, 1580, 1446, 1304, 1148, 1062, 987, 842, 703 cm^-1. HRMS (ESI, m/z): calcd for C_{25}H_{32}IO_Si (M+H)^+ : 583.0830; found: 583.0838.

2-((2-((Phenylsulfonyl)methyl)-1-((trimethylsilyl)oxy)cyclopentyl)methyl)-1-(2-(trifluoromethyl)phenyl)prop-2-en-1-one (3n)

In a glovebox, to an oven-dried 10 mL tube was added 2n (70.8 mg, 0.2 mmol), PhSO_2Na (6.4 mg, 0.04 mmol, 0.2 equiv.), Eosin Y (1.3 mg, 0.002 mmol, 1 mol%), KOPiv (28.4 mg, 0.2 mmol, 1 equiv.), MeCN/H_2O =1:3 (0.067 M) and 1a (68 mg, 0.4 mmol, 2 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300~400 mesh) with PE/EA = 5/1 (v/v) as eluent to afford the title compound as a colorless oil (68.3 mg, 65 % yield.
in total, a mixture of two disteraosiomers).

Characterization of the major isomer: Rf = 0.44 (PE/EA = 5/1 (v/v)). NMR Spectroscopy: 1H NMR (600 MHz, CDCl3, 25 ºC) δ 7.97–7.87 (m, 2H), 7.74–7.68 (m, 1H), 7.59–7.56 (m, 4H), 7.52–7.50 (m, 2H), 7.30–7.26 (m, 1H), 6.07 (s, 1H), 5.65 (s, 1H), 3.55 (dd, J = 14.3, 1.6 Hz, 1H), 3.02 (dd, J = 14.3, 10.4 Hz, 1H), 2.85–2.66 (m, 2H), 2.15–1.96 (m, 2H), 1.80–1.71 (m, 2H), 1.70–1.62 (m, 1H), 1.62–1.53 (m, 2H), 0.13 (s, 9H). 13C NMR (151 MHz, CDCl3, 25 ºC) δ 196.8, 144.7, 140.3, 138.1, 136.1, 133.5, 131.4, 129.8, 129.3, 128.4, 128.2 (q, J = 31.7 Hz), 128.1, 126.7 (q, J = 4.5 Hz), 123.7 (q, J = 273.6 Hz), 86.1, 57.9, 40.9, 37.1, 36.6, 29.8, 21.4, 2.4. 19F NMR (565 MHz, CDCl3, 25 ºC) δ −58.1 (s, 3F). 29Si NMR (119 MHz, CDCl3, 25 ºC) δ 10.5. IR (ATR): ν 3068, 2959, 1647, 1599, 1510, 1446, 1305, 1252, 1133, 1059, 984, 913, 838, 730 cm⁻¹. HRMS (ESI, m/z): calcd for C29H32F3O5Si (M+H)+: 525.1737; found: 525.1740.

1-(4-Methoxyphenyl)-2-((2-((phenylsulfonyl)methyl)-1-(((trimethylsilyl)oxy)cyclopentyl)methyl)prop-2-en-1-one (3o)

In a glovebox, to an oven-dried 10 mL tube was added 2o (63.2 mg, 0.2 mmol), Eosin Y (1.3 mg, 0.002 mmol, 1 mol%), KOPiv (28.4 mg, 0.2 mmol, 1 equiv.), MeCN/H2O =1:3 (0.067 M) and 1a (68 mg, 0.4 mmol, 2 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300–400 mesh) with PE/EA = 5/1 (v/v) as eluent to afford the title compound as a colorless oil (70.4 mg, 72 % yield in total, a mixture of two disteraosiomers).

Characterization of the major isomer: Rf = 0.40 (PE/EA = 5/1 (v/v)). NMR Spectroscopy: 1H NMR (600 MHz, CDCl3, 25 ºC) δ 7.96–7.89 (m, 2H), 7.72–7.67 (m, 2H), 7.62–7.57 (m, 1H), 7.55–7.49 (m, 2H), 6.99–6.86 (m, 2H), 5.67 (d, J = 1.0 Hz, 1H), 5.58 (d, J = 0.9 Hz, 1H), 3.88 (s, 3H), 3.43 (dd, J = 14.3, 2.1 Hz, 1H), 3.01 (dd, J = 14.3, 10.9 Hz, 1H), 2.85 (dd, J = 13.2, 0.9 Hz, 1H), 2.73 (dd, J = 13.2, 0.9 Hz, 1H), 2.13–2.05 (m, 1H), 2.03–1.93 (m, 1H), 1.74–1.64 (m, 2H), 1.60–1.52 (m, 1H), 1.51–1.44 (m, 1H), 0.07 (s, 9H). 13C NMR (151 MHz, CDCl3, 25 ºC) δ 196.0, 163.3, 144.3, 140.3, 133.5, 132.2, 129.6, 129.3, 128.6, 128.1, 113.7, 85.7, 57.8, 55.6, 40.9, 37.1, 29.6, 21.6, 2.2. 29Si NMR (119 MHz, CDCl3, 25 ºC) δ 10.6. IR (ATR): ν 3064, 2959, 1647, 1599, 1510, 1446, 1305, 1252, 1144, 1066, 1029, 987, 838, 790, 730 cm⁻¹. HRMS (ESI, m/z): calcd for C29H35O3SSi (M+H)+: 487.1969; found: 487.1971.

1-Cyclopropyl-2-((2-((phenylsulfonyl)methyl)-1-(((trimethylsilyl)oxy)cyclopentyl)methyl)prop-2-en-1-one (3p)

In a glovebox, to an oven-dried 10 mL tube was added 2p (75 mg, 0.3 mmol), KOPiv (24.2 mg, 0.3 mmol, 1 equiv.), MeCN/H2O =1:3 (0.067 M) and 1a (102 mg, 0.6 mmol, 2 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps.
The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300–400 mesh) with PE/EA = 5/1 (v/v) as eluent to afford the title compound as a colorless oil (112.0 mg, 88 % yield in total, a mixture of two diasteroisomers).

Characterization of the major isomer: Rf = 0.45 (PE/EA = 5/1 (v/v)). NMR Spectroscopy: 1H NMR (600 MHz, CDCl3, 25 ºC) δ 8.00–7.90 (m, 2H), 7.69–7.62 (m, 1H), 7.61–7.54 (m, 2H), 6.20 (s, 1H), 5.70 (s, 1H), 3.43 (dd, J = 14.3, 1.7 Hz, 1H), 2.97 (dd, J = 14.3, 10.2 Hz, 1H), 2.69 (dd, J = 13.1, 0.9 Hz, 1H), 2.59–2.49 (m, 1H), 2.39–2.29 (m, 1H), 2.01–1.89 (m, 2H), 1.73–1.64 (m, 1H), 1.63–1.57 (m, 1H), 1.56–1.41 (m, 3H), 1.07–1.01 (m, 1H), 0.97–0.86 (m, 2H), 0.09 (s, 9H). 13C NMR (151 MHz, CDCl3, 25 ºC) δ 201.8, 145.9, 140.6, 133.5, 129.3, 128.1, 128.0, 86.0, 57.8, 40.8, 38.3, 36.4, 29.7, 21.5, 16.6, 11.6, 11.6, 2.3. 29Si NMR (119 MHz, CDCl3, 25 ºC) δ 10.0. IR (ATR): v 3086, 3004, 2959, 1662, 1621, 1446, 1394, 1304, 1252, 1148, 1066, 1025, 842 cm⁻¹. HRMS (ESI, m/z): calcd for C22H33O4SSi (M+H)+: 421.1863; found: 421.1872.

1-(Furan-2-yl)-2-((2-((phenylsulfonyl)methyl)-1-((trimethylsilyl)oxy)cyclopentyl)methyl)prop-2-en-1-one (3q)

In a glovebox, to an oven-dried 10 mL tube was added 2q (82.8 mg, 0.3 mmol), PhSO2Na (9.84 mg, 0.06 mmol, 0.2 equiv.), Eosin Y (1.9 mg, 0.003 mmol, 1 mol%), KOPiv (42.6 mg, 0.3 mmol, 1 equiv.), MeCN/H2O =1:3 (0.067 M) and 1a (102 mg, 0.6 mmol, 2 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300–400 mesh) with PE/EA = 5/1 (v/v) as eluent to afford the title compound as a colorless oil (109.1 mg, 82 % yield in total, a mixture of two diasteroisomers).

Characterization of the major isomer: Rf = 0.44 (PE/EA = 5/1 (v/v)). NMR Spectroscopy: 1H NMR (600 MHz, CDCl3, 25 ºC) δ 7.96–7.89 (m, 2H), 7.67–7.63 (m, 1H), 7.61 (dd, J = 1.7, 0.8 Hz, 1H), 7.59–7.55 (m, 2H), 7.09 (dd, J = 3.5, 0.8 Hz, 1H), 6.53 (dd, J = 3.5, 1.7 Hz, 1H), 5.92 (d, J = 0.8 Hz, 1H), 5.65 (q, J = 1.0 Hz, 1H), 3.42 (dd, J = 14.3, 2.0 Hz, 1H), 2.93 (dd, J = 14.3, 11.0 Hz, 1H), 2.79 (dd, J = 13.3, 1.0 Hz, 1H), 2.70 (dd, J = 13.2, 0.9 Hz, 1H), 2.12–2.07 (m, 1H), 1.99–1.94 (m, 1H), 1.72–1.65 (m, 2H), 1.62–1.56 (m, 1H), 1.55–1.40 (m, 2H), 0.04 (s, 9H). 13C NMR (151 MHz, CDCl3, 25 ºC) δ 183.7, 151.8, 147.2, 143.9, 140.4, 133.6, 129.3, 128.1, 127.6, 120.1, 112.2, 85.4, 58.0, 41.6, 41.2, 37.5, 30.2, 21.9, 2.1. 29Si NMR (119 MHz, CDCl3, 25 ºC) δ 110. IR (ATR): v 3131, 3067, 2955, 1647, 1561, 1464, 1390, 1304, 1252, 1135, 1148, 1036, 832 cm⁻¹. HRMS (ESI, m/z): calcd for C23H30O4SSi (M+H)+: 447.1656; found: 447.1672.
2-((2-((Phenylsulfonyl)methyl)-1-((trimethylsilyl)oxy)cyclopentyl)methyl)-1-(thiophen-2-yl)prop-2-en-1-one (3r)

In a glovebox, to an oven-dried 10 mL tube was added 2r (87.6 mg, 0.3 mmol), PhSO₂Na (9.84 mg, 0.06 mmol, 0.2 equiv.), Eosin Y (1.9 mg, 0.003 mmol, 1 mol%), KOPiv (42.6 mg, 0.3 mmol, 1 equiv.), MeCN/H₂O =1:3 (0.067 M) white LEDs (6 W), rt, 12 h. The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300~400 mesh) with PE/EA = 5/1 (v/v) to afford the title compound as a colorless oil (117.7 mg, 85 % yield in total, a mixture of two diastereomers).

Characterization of the major isomer: Rᵣ = 0.40 (PE/EA = 5/1 (v/v)). NMR Spectroscopy: ¹H NMR (600 MHz, CDCl₃, 25 °C) δ 7.99–7.91 (m, 2H), 7.67–7.61 (m, 2H), 7.59–7.52 (m, 3H), 7.11 (dd, J = 5.0, 3.8 Hz, 1H), 5.83 (d, J = 0.8 Hz, 1H), 5.64 (d, J = 1.0 Hz, 1H), 3.39 (dd, J = 14.3, 2.1 Hz, 1H), 2.96 (dd, J = 14.3, 11.0 Hz, 1H), 2.83–2.64 (m, 2H), 2.14–2.09 (m, 1H), 2.01–1.90 (m, 1H), 1.74–1.64 (m, 2H), 1.60–1.40 (m, 1H), 0.05 (s, 9H). ¹³C NMR (151 MHz, CDCl₃, 25 °C) δ 188.9, 144.5, 143.2, 140.4, 134.3, 134.0, 133.6, 129.3, 128.1, 127.6, 85.5, 57.9, 41.5, 41.0, 37.3, 29.9, 21.7, 21.4. ²⁹Si NMR (119 MHz, CDCl₃, 25 °C) δ 10.7. IR (ATR): ν 3093, 2955, 2877, 1636, 1513, 1412, 1304, 1148, 1066, 842, 749 cm⁻¹. HRMS (ESI, m/z): calcd for C₂₃H₃₁O₄S₂Si (M+H)⁺: 463.1428; found: 463.1423.

Ethyl 2-((2-((phenylsulfonyl)methyl)-1-((trimethylsilyl)oxy)cyclopentyl)methyl)acrylate (3s)

In a glovebox, to an oven-dried 10 mL tube was added 2s (76.2 mg, 0.3 mmol), PhSO₂Na (9.84 mg, 0.06 mmol, 0.2 equiv.), Eosin Y (1.9 mg, 0.003 mmol, 1 mol%), KOPiv (42.6 mg, 0.3 mmol, 1 equiv.), MeCN/H₂O =1:3 (0.067 M) white LEDs (6 W), rt, 12 h. The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300~400 mesh) with PE/EA = 5/1 (v/v) as eluent to afford the title compound as a colorless oil (91.6 mg, 72 % yield in total, a mixture of two diastereomers).

Characterization of the major isomer: Rᵣ = 0.50 (PE/EA = 5/1 (v/v)). NMR Spectroscopy: ¹H NMR (600 MHz, CDCl₃, 25 °C) δ 7.98–7.91 (m, 2H), 7.68–7.63 (m, 1H), 7.61–7.53 (m, 2H), 6.15 (d, J = 1.4 Hz, 1H), 5.40 (d, J = 1.2 Hz, 1H), 4.27–4.16 (m, 2H), 3.44 (dd, J = 14.4, 1.9 Hz, 1H), 2.98 (dd, J = 14.4, 10.6 Hz, 1H), 2.68 (dd, J = 13.4, 0.8 Hz, 1H), 2.52 (dd, J = 13.3, 0.9 Hz, 1H), 2.03–1.95 (m, 1H), 1.96–1.88 (m, 1H), 1.74–1.63 (m, 2H), 1.56–1.46 (m, 3H), 1.30
(t, J = 7.1 Hz, 3H), 0.09 (s, 9H). 13C NMR (151 MHz, CDCl3, 25 °C) δ 167.6, 140.5, 136.8, 133.6, 129.4, 129.0, 128.1, 86.1, 61.2, 58.0, 40.8, 39.3, 36.4, 29.9, 21.6, 14.3, 2.3. 29Si NMR (119 MHz, CDCl3, 25 °C) δ 10.1. IR (ATR): ν 3064, 2959, 1715, 1629, 1588, 1446, 1305, 1252, 1148, 1066, 1025, 947, 838, 749 cm⁻¹. HRMS (ESI, m/z): calcd for C_{21}H_{33}O_{5}SSi (M+H)^+: 425.1813; found: 425.1814.

2-Cyanoethyl 2-(((phenylsulfonyl)methyl)-1-((trimethylsilyloxy)cyclopentyl)methyl)acrylate (3t)

In a glovebox, to an oven-dried 10 mL tube was added 2t (27.9 mg, 0.1 mmol), PhSO2Na (3.2 mg, 0.02 mmol, 0.2 equiv.), Eosin Y (0.65 mg, 0.001 mmol, 1 mol%), KOPiv (14.2 mg, 0.1 mmol, 1 equiv.), MeCN/H2O =1:3 (0.067 M) and 1a (34 mg, 0.2 mmol, 2 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300~400 mesh) with PE/EA = 5/1 (v/v) to afford the title compound as a colorless oil (43.1 mg, 95 % yield in total, a mixture of two disteroisomers).

Characterization of the major isomer: Rf = 0.63 (PE/EA = 4/1 (v/v)). NMR Spectroscopy: 1H NMR (600 MHz, CDCl3, 25 °C) δ 7.96–7.91 (m, 2H), 7.69–7.63 (m, 1H), 7.60–7.54 (m, 2H), 6.27 (d, J = 1.1 Hz, 1H), 5.57 (d, J = 1.1 Hz, 1H), 4.45–4.41 (m, 1H), 4.38–4.34 (m, 1H), 3.44 (dd, J = 14.2, 1.6 Hz, 1H), 2.94 (dd, J = 14.3, 10.4 Hz, 1H), 2.85–2.72 (m, 2H), 2.62 (t, J = 1.1 Hz, 2H), 2.00–1.90 (m, 2H), 1.76–1.65 (m, 2H), 1.65–1.57 (m, 1H), 1.56–1.42 (m, 2H), 0.09 (s, 9H). 13C NMR (151 MHz, CDCl3, 25 °C) δ 166.9, 140.5, 135.8, 133.6, 130.4, 129.4, 128.0, 117.0, 86.0, 59.5, 57.9, 40.8, 39.3, 36.4, 30.0, 21.4, 18.1, 2.3. 29Si NMR (119 MHz, CDCl3, 25 °C) δ 10.3. IR (ATR): ν 3063, 2959, 2251, 1722, 1625, 1587, 1446, 1408, 1304, 1252, 1144, 1066, 1028, 842, 749, 689 cm⁻¹. HRMS (ESI, m/z): calcd for C_{22}H_{32}O_{5}N_{2}Si (M+H)^+: 450.1765; found: 450.1757.

Cyclobutyl 2-(((phenylsulfonyl)methyl)-1-((trimethylsilyloxy)cyclopentyl)methyl)acrylate (3u)

In a glovebox, to an oven-dried 10 mL tube was added 2u (28 mg, 0.1 mmol), PhSO2Na (3.2 mg, 0.06 mmol, 0.2 equiv.), Eosin Y (0.65 mg, 0.001 mmol, 1 mol%), KOPiv (14.2 mg, 0.1 mmol, 1 equiv.), MeCN/H2O =1:3 (0.067 M) and 1a (34 mg, 0.2 mmol, 2 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300~400 mesh) with PE/EA = 5/1 (v/v) as eluent to afford the title compound as a colorless oil (41.1 mg, 91 % yield in total, a mixture of two disteroisomers).
Charaterization of the major isomer: Rf = 0.50 (PE/EA = 5/1 (v/v)). NMR Spectroscopy: ¹H NMR (600 MHz, CDCl₃, 25 ºC) δ 7.96–7.91 (m, 2H), 7.67–7.63 (m, 1H), 7.60–7.55 (m, 2H), 6.16 (d, J = 1.4 Hz, 1H), 5.39 (d, J = 1.3 Hz, 1H), 5.07–4.96 (m, 1H), 5.42 (dd, J = 14.4, 2.0 Hz, 1H), 2.98 (dd, J = 14.4, 10.6 Hz, 1H), 2.68 (dd, J = 13.4, 0.8 Hz, 1H), 2.47 (dd, J = 13.4, 0.9 Hz, 1H), 2.42–2.32 (m, 2H), 2.15–2.04 (m, 2H), 2.03–1.96 (m, 1H), 1.96–1.88 (m, 1H), 1.85–1.77 (m, 1H), 1.72–1.60 (m, 3H), 1.55–1.43 (m, 3H), 0.09 (s, 9H). ¹³C NMR (151 MHz, CDCl₃, 25 ºC) δ 166.9, 140.5, 136.7, 133.6, 129.4, 129.2, 128.1, 86.0, 69.5, 58.0, 40.7, 39.1, 36.4, 30.4, 29.8, 21.6, 13.7, 2.3. ²⁹Si NMR (119 MHz, CDCl₃, 25 ºC) δ 10.1. IR (ATR): ν 3093, 3063, 2955, 1714, 1446, 1405, 1304, 1252, 1148, 1066, 1025, 946, 842, 749, 689 cm⁻¹. HRMS (ESI, m/z): calcld for C₂₃H₃₅O₃Si (M+H)⁺: 451.1969; found: 451.1964.

Naphthalen-1-ylmethyl 2-((2-((phenylsulfonyl)methyl)-1-((trimethylsilyl)oxy)cyclopentyl)methyl)acrylate (3v)

![Chemical structure](image)

In a glovebox, to an oven-dried 10 mL tube was added 2v (36.6 mg, 0.1 mmol), PhSO₂Na (3.2 mg, 0.02 mmol, 0.2 equiv.), Eosin Y (0.65 mg, 0.001 mmol, 1 mol%), KOPiv (14.2 mg, 0.1 mmol, 1 equiv.), MeCN/H₂O =1:3 (0.067 M) and 1a (34 mg, 0.2 mmol, 2 equiv.) sequentially. The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with PE/EA (30 mL) as the eluent. The organic phase was dried 10 mL tube was sealed, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with PE/EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300~400 mesh) with PE/EA = 5/1 (v/v) as eluent to afford the title compound as a colorless oil (35.1 mg, 65 % yield in total, a mixture of two disteraiosomers).

Charaterization of the major isomer: Rf = 0.48 (PE/EA = 5/1 (v/v)). NMR Spectroscopy: ¹H NMR (600 MHz, CDCl₃, 25 ºC) δ 8.04–8.02 (m, 1H), 7.94–7.91 (m, 2H), 7.91–7.88 (m, 1H), 7.89–7.84 (m, 1H), 7.63–7.59 (m, 1H), 7.58–7.49 (m, 5H), 7.46 (dd, J = 8.2, 7.0 Hz, 1H), 6.14 (d, J = 1.3 Hz, 1H), 5.71–5.61 (m, 2H), 5.40 (d, J = 1.2 Hz, 1H), 3.45 (dd, J = 14.4, 1.9 Hz, 1H), 2.98 (dd, J = 14.4, 10.6 Hz, 1H), 2.66 (dd, J = 13.3, 0.8 Hz, 1H), 2.54 (dd, J = 13.4, 0.8 Hz, 1H), 2.03–1.97 (m, 1H), 1.98–1.89 (m, 1H), 1.71–1.57 (m, 2H), 1.56–1.39 (m, 3H), 0.03 (s, 9H). ¹³C NMR (151 MHz, CDCl₃, 25 ºC) δ 167.5, 140.4, 136.5, 133.9, 133.5, 131.9, 131.5, 130.9, 129.5, 129.3, 128.3, 128.8, 121.1, 127.8, 126.7, 126.1, 125.4, 123.7, 86.0, 65.4, 58.0, 40.8, 39.4, 36.5, 29.9, 21.5, 2.2. ²⁹Si NMR (119 MHz, CDCl₃, 25 ºC) δ 10.2. IR (ATR): ν 3060, 2955, 1714, 1625, 1599, 1513, 1446, 1405, 1304, 1252, 1148, 1066, 957, 738, 689 cm⁻¹. HRMS (ESI, m/z): calcld for C₃₅H₃₇O₃Si (M+H)⁺: 537.2126; found: 537.2120.

6-Hydroxyhexyl 2-((2-((phenylsulfonyl)methyl)-1-((trimethylsilyl)oxy)cyclopentyl)methyl)acrylate (3w)

![Chemical structure](image)

In a glovebox, to an oven-dried 10 mL tube was added 2w (32.6 mg, 0.1 mmol), PhSO₂Na (3.2 mg, 0.02 mmol, 0.2 equiv.), Eosin Y (0.65 mg, 0.001 mmol, 1 mol%), KOPiv (14.2 mg, 0.1 mmol, 1 equiv.), MeCN/H₂O =1:3 (0.067 M) and 1a (34 mg, 0.2 mmol, 2 equiv.) sequentially. The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with PE/EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300~400 mesh) with PE/EA = 5/1 (v/v) as eluent to afford the title compound as a colorless oil (35.1 mg, 65 % yield in total, a mixture of two disteraiosomers).
off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300-400 mesh) with PE:EA = 5:1 (v/v) as eluent to afford the title compound as a colorless oil (41.1 mg, 82% yield in total, a mixture of two disteraosiomers).

Characterization of the major isomer: 

**R<sub>t</sub>** = 0.2 (PE:EA = 2/1 (v/v)). NMR Spectroscopy: ¹H NMR (600 MHz, CDCl₃, 25 °C) δ 7.96–7.92 (m, 2H), 7.67–7.62 (m, 1H), 7.60–7.55 (m, 2H), 6.15 (d, J = 1.4 Hz, 1H), 5.42 (d, J = 1.3 Hz, 1H), 4.18–4.12 (m, 2H), 3.69–3.60 (m, 2H), 3.44 (dd, J = 14.4, 2.0 Hz, 1H), 2.98 (dd, J = 14.3, 10.6 Hz, 1H), 2.67 (dd, J = 13.3, 0.7 Hz, 1H), 2.52 (dd, J = 13.3, 0.9 Hz, 1H), 2.03–1.96 (m, 1H), 1.73–1.64 (m, 4H), 1.60–1.54 (m, 2H), 1.54–1.45 (m, 2H), 1.44–1.39 (m, 4H), 1.33 (d, J = 5.0 Hz, 1H), 0.99 (s, 9H). ¹³C NMR (151 MHz, CDCl₃, 25 °C) δ 167.7, 140.5, 136.8, 133.6, 129.0, 128.1, 86.0, 65.2, 63.0, 58.0, 40.8, 39.4, 36.4, 29.9, 28.7, 25.9, 21.6, 2.3. ²⁹Si NMR (119 MHz, CDCl₃, 25 °C) δ 10.1.

IR (ATR): v 3544, 2940, 2862, 1714, 1625, 1446, 1408, 1304, 1252, 1148, 1066, 957, 842, 749, 689 cm⁻¹.

HRMS (ESI, m/z): calcd for C₂₅H₄₁O₆SSi (M+H)<sup>+</sup>: 497.2388; found: 497.2384.

**3-Hydroxy-3-methylbutyl 2-((2-((phenylsulfonyl)methyl)-1-(((trimethylsilyl)oxy)cyclopentyl)methyl)acrylate (3x)**

In a glovebox, to an oven-dried 10 mL tube was added 2x (31.2 mg, 0.1 mmol), PhSO₂Na (3.2 mg, 0.02 mmol, 0.2 equiv.), Eosin Y (0.65 mg, 0.001 mmol, 1 mol%), KO₃Piv (14.2 mg, 0.01 mmol, 1 equiv.), MeCN/H₂O = 1:3 (0.067 M) and 1a (34 mg, 0.2 mmol, 2 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300–400 mesh) with PE:EA = 5:1 (v/v) as eluent to afford the title compound as a colorless oil (42.5 mg, 88% yield in total, a mixture of two disteraosiomers).

Characterization of the major isomer: 

**R<sub>t</sub>** = 0.38 (PE:EA = 2/1 (v/v)). NMR Spectroscopy: ¹H NMR (600 MHz, CDCl₃, 25 °C) δ 7.98–7.90 (m, 2H), 7.67–7.61 (m, 1H), 7.58–7.54 (m, 2H), 6.14 (d, J = 1.3 Hz, 1H), 5.45 (d, J = 1.2 Hz, 1H), 4.40 (dt, J = 11.2, 6.9 Hz, 1H), 4.29 (dt, J = 11.2, 6.9 Hz, 1H), 3.46 (dd, J = 14.3, 1.6 Hz, 1H), 2.95 (dd, J = 14.2, 10.4 Hz, 1H), 2.68–2.54 (m, 2H), 2.01–1.91 (m, 2H), 1.89 (td, J = 6.9, 0.9 Hz, 2H), 1.73–1.63 (m, 2H), 1.61–1.54 (m, 1H), 1.53–1.45 (m, 2H), 1.27 (d, J = 3.0 Hz, 6H), 0.08 (s, 9H). ¹³C NMR (151 MHz, CDCl₃, 25 °C) δ 167.6, 140.5, 136.8, 129.3, 128.9, 128.0, 86.0, 70.0, 62.2, 57.9, 41.7, 40.8, 39.3, 36.3, 29.9, 28.9, 28.9, 21.4, 2.3. ²⁹Si NMR (119 MHz, CDCl₃, 25 °C) δ 10.1. IR (ATR): v 3511, 3064, 2963, 2862, 1714, 1625, 1446, 1408, 1304, 1252, 1148, 1066, 1025, 957, 842, 749, 689 cm⁻¹. HRMS (ESI, m/z): calcd for C₂₅H₄₀O₆Si (M+H)<sup>+</sup>: 483.2231; found: 483.2231.

**6-Oxohexyl 2-((2-((phenylsulfonyl)methyl)-1-(((trimethylsilyl)oxy)cyclopentyl)methyl)acrylate (3y)**
In a glovebox, to an oven-dried 10 mL tube was added 2y (34 mg, 0.1 mmol), PhSO₂Na (3.2 mg, 0.02 mmol, 0.2 equiv.), Eosin Y (0.65 mg, 0.001 mmol, 1 mol%), KOPiv (14.2 mg, 0.1 mmol, 1 equiv.), MeCN/H₂O = 1:3 (0.067 M) and 1a (34 mg, 0.2 mmol, 2 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300–400 mesh) with PE/EA = 5/1 (v/v) as eluent to afford the title compound as a colorless oil (39.6 mg, 80 % yield in total, a mixture of two diastereomers).

Characterization of the major isomer: Rf = 0.43 (PE/EA = 3/1 (v/v)). NMR Spectroscopy: ¹H NMR (600 MHz, CDCl₃, 25 ºC) δ 9.77 (t, J = 1.7 Hz, 1H), 7.95–7.92 (m, 2H), 7.67–7.63 (m, 1H), 7.59–7.54 (m, 2H), 6.15 (d, J = 1.3 Hz, 1H), 5.43 (d, J = 1.3 Hz, 1H), 4.20–4.11 (m, 2H), 3.44 (dd, J = 14.4, 1.9 Hz, 1H), 2.97 (dd, J = 14.4, 10.5 Hz, 1H), 2.68–2.64 (m, 1H), 2.53 (dd, J = 13.3, 0.8 Hz, 1H), 2.46 (td, J = 7.3, 1.7 Hz, 2H), 2.02–1.96 (m, 1H), 1.95–1.90 (m, 1H), 1.74–1.63 (m, 6H), 1.58–1.52 (m, 1H), 1.49 (ddt, J = 9.2, 7.8, 6.0 Hz, 2H), 1.45–1.37 (m, 2H), 0.09 (s, 9H). ¹³C NMR (151 MHz, CDCl₃, 25 ºC) δ 202.4, 167.6, 140.5, 136.8, 133.6, 129.4, 129.0, 128.1, 86.0, 64.9, 58.0, 43.8, 40.8, 39.3, 36.4, 29.9, 28.5, 25.7, 21.8, 21.5, 2.3. ²⁹Si NMR (119 MHz, CDCl₃, 25 ºC) δ 10.1. IR (ATR): ν 3063, 2955, 2870, 2721, 1718, 1628, 1446, 1408, 1304, 1252, 1148, 1069, 1025, 957, 842 cm⁻¹. HRMS (ESI, m/z): caled for C₂₅H₃₉O₆SSi (M+H)+: 495.2231; found: 495.2227.

(1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl-2-(((1S)-2-((phenylsulfonyl)methyl)-1-((trimethylsilyloxy)cyclopentyl)methyl)acylate (3z)

In a glovebox, to an oven-dried 10 mL tube was added 2z (35.7 mg, 0.1 mmol), PhSO₂Na (3.2 mg, 0.02 mmol, 0.2 equiv.), Eosin Y (0.65 mg, 0.001 mmol, 1 mol%), KOPiv (14.2 mg, 0.1 mmol, 1 equiv.), MeCN/H₂O = 1:3 (0.067 M) and 1a (34 mg, 0.2 mmol, 2 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300–400 mesh) with PE/EA = 5/1 (v/v) as eluent to afford the title compound as a colorless oil (30.3 mg, 56 % yield in total, a mixture of two diastereomers).

Characterization of the major isomer: Rf = 0.44 (PE/EA = 5/1 (v/v)). NMR Spectroscopy [mixture of rotamers]: ¹H NMR (600 MHz, CDCl₃, 25 ºC) δ 7.96–7.91 (m, 2H), 7.67–7.63 (m, 1H), 7.59–7.54 (m, 2H), 6.15 (d, J = 1.3 Hz, 1H), 5.34 (t, J = 1.2 Hz, 1H), 4.74–4.68 (m, 1H), 3.42–3.33 (m, 1H), 3.04–2.99 (m, 1H), 2.76 (dt, J = 13.3, 1.0 Hz, 1H), 2.40 (ddd, J = 30.4, 13.3, 0.8 Hz, 1H), 2.08–1.96 (m, 2H), 1.92–1.82 (m, 2H), 1.74–1.65 (m, 4H), 1.55–1.39 (m, 5H), 1.10–1.03 (m, 1H), 1.02–0.94 (m, 9H), 0.91–0.88 (m, 8H), 0.74 (dd, J = 6.9, 1.3 Hz, 3H), 0.10 (d, J = 2.7 Hz, 9H). ¹³C NMR (151 MHz, CDCl₃, 25 ºC) δ 167.1, 167.0 (C′), 140.4, 140.3(C′), 137.1, 137.0(C′), 133.7, 133.6(C′), 129.4, 129.0, 128.8(C′), 128.2, 128.1(C′), 86.0, 86.0(C′), 75.1, 75.1(C′), 58.2, 58.1(C′), 47.4, 47.3(C′), 41.0, 40.9, 40.6(C′), 39.1, 39.0(C′), 36.4, 36.3(C′), 34.4, 34.4(C′), 31.6, 31.5(C′), 29.9, 29.8(C′), 26.6, 26.4(C′), 23.6, 23.5(C′), 22.2, 21.7, 21.7(C′), 21.0, 20.9(C′), 16.5, 16.4(C′), 2.3, 2.3(C′). ²⁹Si NMR (119 MHz,
CDCl₃, 25 °C) δ 10.2, 10.1(Si'). IR (ATR): ν 2959, 2929, 2873, 1710, 1408, 1371, 1308, 1252, 1174, 1148, 1066, 1025, 749, 689 cm⁻¹. HRMS (ESI, m/z): calcd for C₂₉H₄₇O₅SSi (M+H)+: 535.2908; found: 535.2913.

(8R,9S,10R,13S,14S,17S)-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl 2-((2-((phenylsulfonyl)methyl)-1-((trimethylsilyl)oxy)cyclopentyl)methyl)acrylate (3aa)

In a glovebox, to an oven-dried 10 mL tube was added 2aa (49.6 mg, 0.1 mmol), PhSO₂Na (3.2 mg, 0.02 mmol, 0.2 equiv.), Eosin Y (0.65 mg, 0.001 mmol, 1 mol%), KOPiv (14.2 mg, 0.1 mmol, 1 equiv.), MeCN/H₂O = 1:3 (0.067 M) and 1a (34 mg, 0.2 mmol, 2 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300 ~ 400 mesh) with PE/EA = 5/1 (v/v) to afford the title compound as a colorless oil (34.1 mg, 52 % yield in total, a mixture of two disterosomers).

Characterization of the major isomer: Rf = 0.22 (PE/EA = 4/1 (v/v)). NMR Spectroscopy [mixture of rotamers]: ¹H NMR (600 MHz, CDCl₃, 25 °C) δ 7.97 – 7.91 (m, 2H), 7.68 – 7.62 (m, 1H), 7.60 – 7.53 (m, 2H), 6.15 (dd, J = 10.9, 1.4 Hz, 1H), 5.73 (t, J = 2.3 Hz, 1H), 5.43 (dd, J = 4.0, 1.3 Hz, 1H), 4.66–4.61 (m, 1H), 3.44–3.40 (m, 1H), 2.97 (dd, J = 14.4, 10.7 Hz, 1H), 2.67 (d, J = 13.3 Hz, 1H), 2.52–2.46 (m, 1H), 2.45–2.34 (m, 3H), 2.34–2.26 (m, 1H), 2.25–2.18 (m, 1H), 2.04–2.00 (m, 2H), 1.98–1.91 (m, 1H), 1.89–1.83 (m, 1H), 1.81–1.77 (m, 1H), 1.73–1.69 (m, 4H), 1.64–1.45 (m, 7H), 1.43–1.33 (m, 2H), 1.27–1.21 (m, 1H), 1.20–1.18 (m, 3H), 1.13–1.00 (m, 2H), 0.98–0.93 (m, 1H), 0.88 (d, J = 4.3 Hz, 3H), 0.08 (s, 9H). ¹³C NMR (151 MHz, CDCl₃, 25 °C) δ 199.6, 199.6(C'), 171.0, 167.5, 167.5(C'), 140.5, 140.5(C'), 137.0, 137.0(C'), 133.6, 133.6(C'), 129.4, 128.9, 128.7(C'), 128.1, 128.1(C'), 124.1, 86.0, 86.0(C'), 83.3, 83.2(C'), 58.1, 58.0(C'), 53.8, 53.8(C'), 50.4, 50.3(C'), 43.0, 42.8(C'), 41.1, 40.9(C'), 39.6, 39.4(C'), 38.7, 36.9, 36.8(C'), 36.7, 36.5(C'), 35.8, 35.8(C'), 35.6, 35.5(C'), 34.1, 32.9, 31.6, 30.0, 29.9(C'), 27.7, 27.6(C'), 23.7, 23.7(C'), 21.7, 21.6(C'), 20.7, 20.7(C'), 17.6, 12.4, 12.4(C'), 2.4, 2.3(C'). ²⁹Si NMR (119 MHz, CDCl₃, 25 °C) δ 10.0. IR (ATR): ν 2944, 2877, 2851, 1714, 1673, 1617, 1446, 1416, 1308, 1252, 1170, 1147, 1069, 842, 689 cm⁻¹. HRMS (ESI, m/z): calcd for C₃₈H₆₅O₅Si (M+H)+: 667.3483; found: 667.3480.

2-Methylene-1-phenylnon-8-ene-1,4-dione 5a

In a glovebox, to an oven-dried 10 mL tube was added 2a (57.2 mg, 0.2 mmol), sodium benzenesulfinate (3.6 mg, 0.04 mmol, 20 mol%), TBADT (6.6 mg, 0.002 mmol, 1 mol%), KOPiv (28.4 mg, 0.2 mmol, 1 equiv.), MeCN/H₂O
= 1:3 (0.067 M) and 1a (92.8 mg, 0.4 mmol, 2 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200~300 mesh) with PE/EA = 10/1 (v/v) as eluent to afford the title compound as a colorless oil (7.7 mg, 14 % yield).

R<sub>f</sub> = 0.48 (PE/EA = 10/1 (v/v)). NMR Spectroscopy: <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25 ºC) δ 7.83–7.80 (m, 2H), 7.56–7.52 (m, 1H), 7.46–7.42 (m, 2H), 5.92 (q, J = 1.0 Hz, 1H), 5.78 (s, 1H), 5.77–5.72 (m, 1H), 5.05–4.95 (m, 2H), 3.61 (d, J = 1.0 Hz, 2H), 2.54 (t, J = 7.4 Hz, 2H), 2.09–2.04 (m, 2H), 1.70 (p, J = 7.4 Hz, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>, 25 ºC) δ 207.8, 197.5, 142.1, 138.1, 137.4, 132.4, 129.9, 129.3, 128.3, 115.4, 46.6, 41.9, 33.1, 22.7. IR (ATR): ν 2933, 2875, 1714, 1654, 1446, 1341, 1216, 1170, 1118, 1077, 984, 752, 708 cm<sup>-1</sup>. HRMS (APCI+, m/z): calcd for C<sub>16</sub>H<sub>14</sub>O<sub>2</sub> (M+H)<sup>+</sup>: 243.1380; found: 243.1377.

3.4 Scope for the γ-substituted cyclopentanol derivatives

1-Phenyl-2-((3-(phenylsulfonyl)-1-(((trimethylsilyl)oxy)cyclopentyl)methyl)prop-2-en-1-one (7a)

In a glovebox, to an oven-dried 10 mL tube was added 2a (28.6 mg, 0.1 mmol), PhSO<sub>2</sub>Na (32.8 mg, 0.2 mmol, 2 equiv.), Eosin Y (1.3 mg, 0.002 mmol, 2 mol%), CsOOPiv (35.1 mg, 0.15 mmol, 1.5 equiv.), MeOH/H<sub>2</sub>O =1:2 (0.067 M) and 1f (31.2 mg, 0.2 mmol, 2 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300~400 mesh) with PE/E A = 5/1 (v/v) as eluent to afford the title compound as a colorless oil (27.5 mg, 62 % yield in total, a mixture of two diastereoisomers).

R<sub>f</sub> = 0.50 (PE/E A = 5/1 (v/v)). NMR Spectroscopy: <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25 ºC) δ 7.85–7.81 (m, 2H), 7.80–7.77 (m, 2H), 7.63–7.60 (m, 1H), 7.56–7.49 (m, 3H), 7.46–7.41 (m, 2H), 5.87 (q, J = 1.0 Hz, 1H), 5.64 (d, J = 1.0 Hz, 1H), 3.76–3.63 (m, 1H), 2.95–2.83 (m, 2H), 2.20–2.09 (m, 2H), 2.07–1.98 (m, 1H), 1.97–1.93 (m, 1H), 1.83–1.74 (m, 2H), 0.00 (s, 9H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>, 25 ºC) δ 197.8, 145.1, 138.7, 137.3, 132.5, 130.1, 129.3, 128.4, 128.3, 128.0, 84.9, 62.8, 42.7, 40.0, 38.3, 24.9, 2.0. <sup>29</sup>Si NMR (119 MHz, CDCl<sub>3</sub>, 25 ºC) δ 10.5. IR (ATR): ν 3063, 2952, 1654, 1599, 1446, 1304, 1252, 1200, 1144, 1056, 838, 699 cm<sup>-1</sup>. HRMS (ESI, m/z): calcd for C<sub>29</sub>H<sub>23</sub>O<sub>4</sub>Si (M+H)<sup>+</sup>: 443.1707; found: 443.1704.

R<sub>f</sub> = 0.35 (PE/E A = 5/1 (v/v)). NMR Spectroscopy: <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25 ºC) δ 7.90–7.85 (m, 2H), 7.73–7.70 (m, 2H), 7.63–7.57 (m, 1H), 7.55–7.49 (m, 3H), 7.43–7.38 (m, 2H), 5.82 (d, J = 1.1 Hz, 1H), 5.63 (d, J = 1.1 Hz, 1H), 3.73–3.45 (m, 1H), 2.78–2.51 (m, 2H), 2.27–2.14 (m, 2H), 2.03 (ddd, J = 13.3, 8.3, 1.5 Hz, 1H), 1.97–1.87 (m, 2H), 1.82–1.75 (m, 1H), 0.01 (s, 9H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>, 25 ºC) δ 198.0, 144.6, 138.4, 137.2, 133.7, 132.4, 130.0, 129.3, 128.6, 128.2, 83.3, 61.4, 42.5, 39.0, 37.9, 24.1, 2.1. <sup>29</sup>Si NMR (119 MHz, CDCl<sub>3</sub>, 25 ºC) δ
10.9. IR (ATR): ν 3302, 3063, 2952, 1658, 1446, 1304, 1248, 1144, 1103, 1084, 838, 699 cm⁻¹. HRMS (ESI, m/z): calcd for C₂₅H₃₁O₄Si (M+H)⁺: 443.1707; found: 443.1707.

**2-((1-Hydroxy-3-(phenylsulfonyl)cyclopentyl)methyl)-1-phenylprop-2-en-1-one (7a')**

To a 4 mL tube was added 3a (44.2 mg, 0.1 mmol), EA (0.1 M) and TBAF (0.2 mL, 0.2 mmol, 1 M in THF, 2 equiv.) sequentially. The mixture was stirred at ambient temperature for the 0.5 h. The resulting mixture was filtered through a thin silica gel plug with EA (20 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300–400 mesh) with PE/Ea = 2/1 (v/v) as eluent to afford the title compound as a colorless oil (36.4 mg, 98 % yield in total, a mixture of two disteraosiomers). Rf = 0.15 (PE/Ea = 2/1 (v/v)). NMR Spectroscopy: ¹H NMR (600 MHz, CDCl3, 25 ºC) δ 7.90–7.88 (m, 2H), 7.77–7.75 (m, 2H), 7.65–7.62 (m, 1H), 7.59–7.53 (m, 3H), 7.47–7.43 (m, 2H), 6.05 (s, 1H), 5.79 (s, 1H), 3.88–3.82 (m, 2H), 2.86–2.78 (m, 2H), 2.20 (dddd, J = 13.3, 9.4, 5.7, 3.4 Hz, 1H), 2.16–2.09 (m, 2H), 1.95 (ddd, J = 13.3, 7.8, 2.3 Hz, 1H), 1.88–1.81 (m, 1H), 1.76 (dddd, J = 13.2, 8.0, 3.3, 2.3 Hz, 1H). ¹³C NMR (151 MHz, CDCl3, 25 ºC) δ 200.5, 144.2, 139.1, 137.0, 133.7, 133.1, 131.2, 130.1, 129.4, 128.5, 128.4, 81.4, 43.7, 40.3, 38.9, 24.9. IR (ATR): ν 3496, 3067, 2937, 2858, 1654, 1607, 1446, 1304, 1207, 1148, 1084, 991, 838, 730, 687 cm⁻¹. HRMS (ESI, m/z): calcd for C₂₅H₂₃O₄S (M+H)⁺: 371.1312; found: 371.1300.

**2-((3-(phenylsulfonyl)-1-((trimethylsilyl)oxy)cyclopentyl)methyl)-1-(o-tolyl)prop-2-en-1-one (7b)**

In a glovebox, to an oven-dried 10 mL tube was added 2h (30 mg, 0.1 mmol), PhSO₂Na (32.8 mg, 0.2 mmol, 2 equiv.), Eosin Y (1.9 mg, 0.003 mmol, 3 mol%), CsOPiv (46.8 mg, 0.2 mmol, 2.0 equiv.), MeOH/H₂O =1:2 (0.067 M) and 1f (46.8 mg, 0.3 mmol, 3 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for the 24 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300–400 mesh) with PE/Ea = 5/1 (v/v) as eluent to afford the title compound as a colorless oil (26.3 mg, 58 % yield in total, a mixture of two disteraosiomers).
R<sub>f</sub> = 0.47 (PE/EA = 5/1 (v/v)). NMR Spectroscopy: <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25 °C) δ 7.90–7.85 (m, 2H), 7.66–7.63 (m, 1H), 7.58–7.53 (m, 2H), 7.33 (d, J = 7.5, 1.5 Hz, 1H), 7.29 (dd, J = 7.6, 1.4 Hz, 1H), 7.24–7.18 (m, 2H), 6.02 (d, J = 1.0 Hz, 1H), 5.69 (d, J = 1.0 Hz, 1H), 3.78–3.67 (m, 1H), 2.94–2.82 (m, 2H), 2.33 (s, 3H), 2.24–2.15 (m, 1H), 2.14–2.02 (m, 2H), 1.97 (dd, J = 13.4, 7.8, 1.9 Hz, 1H), 1.87–1.76 (m, 2H), 0.09 (s, 9H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>, 25 °C) δ 199.9, 146.3, 138.9, 138.5, 136.9, 133.7, 132.3, 131.0, 130.2, 129.4, 128.8, 128.5, 125.2, 85.1, 62.9, 40.3, 40.1, 38.3, 24.8, 20.1, 2.2. <sup>29</sup>Si NMR (119 MHz, CDCl<sub>3</sub>, 25 °C) δ 10.3. IR (ATR): ν 3063, 2952, 1446, 1408, 1304, 1252, 1196, 1148, 1069, 987, 913, 842, 760, 734 cm<sup>−1</sup>. HRMS (ESI, m/z): calcd for C<sub>25</sub>H<sub>19</sub>O<sub>3</sub>Si (M+H)<sup>+</sup>: 457.1863; found: 457.1861.

R<sub>f</sub> = 0.38 (PE/EA = 5/1 (v/v)). NMR Spectroscopy: <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25 °C) δ 7.94–7.88 (m, 2H), 7.66–7.60 (m, 1H), 7.58–7.52 (m, 2H), 7.31 (ddd, J = 7.7, 5.1, 3.7 Hz, 1H), 7.23–7.18 (m, 1H), 7.18–7.15 (m, 2H), 6.07 (d, J = 1.1 Hz, 1H), 5.72 (d, J = 1.2 Hz, 1H), 3.79–3.63 (m, 1H), 2.77–2.48 (m, 2H), 2.33–2.24 (m, 1H), 2.23–2.16 (m, 4H), 2.05–1.91 (m, 3H), 1.84–1.71 (m, 1H), 0.11 (s, 9H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>, 25 °C) δ 200.6, 145.3, 138.7, 138.6, 136.6, 133.7, 133.5, 131.0, 130.1, 129.3, 128.6, 128.5, 125.1, 83.3, 61.3, 39.4, 39.3, 38.2, 23.8, 19.9, 2.3. <sup>29</sup>Si NMR (119 MHz, CDCl<sub>3</sub>, 25 °C) δ 10.7. IR (ATR): ν 3056, 2959, 1658, 1446, 1304, 1252, 1181, 1148, 1103, 1084, 965, 913, 864, 842, 760 cm<sup>−1</sup>. HRMS (ESI, m/z): calcd for C<sub>25</sub>H<sub>19</sub>O<sub>3</sub>Si (M+H)<sup>+</sup>: 457.1863; found: 457.1861.

1-(2-Fluorophenyl)-2-((3-phenylsulfanyl)-1-((trimethylsilyl)oxy)cyclopentyl)methyl)prop-2-en-1-one (7c)

In a glovebox, to an oven-dried 10 mL tube was added <sup>2</sup>j (30.4 mg, 0.1 mmol), PhSO<sub>2</sub>Na (32.8 mg, 0.2 mmol, 2 equiv.), Eosin Y (1.9 mg, 0.003 mmol, 3 mol%), CsOPiv (46.8 mg, 0.2 mmol, 2 equiv.), MeOH/H<sub>2</sub>O =1:2 (0.067 M) and <sup>1</sup>f (46.8 mg, 0.3 mmol, 3 equiv.) sequentially. The mixture was stirred under white light irradiation at ambient temperature for the 24 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300–400 mesh) with PE/EA = 5/1 (v/v) as eluent to afford the title compound as a colorless oil (22.1 mg, 48 % yield in total, a mixture of two diastereoisomers).
calcd for C_{2}H_{5}FO_{4}SSi (M+H)^{+}: 461.1613; found: 461.1617.

R_{f} = 0.45 (PE/EA = 5/1 (v/v)). NMR Spectroscopy: \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}, 25 °C) \(\delta\) 7.93–7.88 (m, 2H), 7.65–7.59 (m, 1H), 7.57–7.52 (m, 2H), 7.45 (ddd, \(J = 8.3, 7.2, 5.2, 1.8\) Hz, 1H), 7.39–7.34 (m, 1H), 7.18 (td, \(J = 7.5, 1.0\) Hz, 1H), 7.08 (ddd, \(J = 9.6, 8.4, 1.1\) Hz, 1H), 6.06 (d, \(J = 1.0\) Hz, 1H), 5.80 (ddd, \(J = 1.9, 0.9\) Hz, 1H), 3.67–3.59 (m, 1H), 2.68–2.56 (m, 2H), 2.32–2.22 (m, 1H), 2.19 (ddd, \(J = 13.4, 9.9, 0.9\) Hz, 1H), 2.04–1.88 (m, 3H), 1.82–1.73 (m, 1H), 0.10 (s, 9H). \textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}, 25 °C) \(\delta\) 195.3, 159.9 (d, \(J = 252.1\) Hz), 145.0, 138.7, 133.8, 132.8 (d, \(J = 8.2\) Hz), 132.4, 130.6 (d, \(J = 3.1\) Hz), 129.3, 128.7, 127.0 (d, \(J = 14.9\) Hz), 124.2 (d, \(J = 3.5\) Hz), 116.3 (d, \(J = 21.8\) Hz), 83.2, 61.4, 39.9, 39.1, 38.0, 24.0, 2.2. \textsuperscript{19}F NMR (565 MHz, CDCl\textsubscript{3}, 25 °C) \(\delta\) 111.89–111.92 (m, 1F). \textsuperscript{29}Si NMR (119 MHz, CDCl\textsubscript{3}, 25 °C) \(\delta\) 10.7. IR (ATR): ν 3067, 2963, 1662, 1610, 1483, 1449, 1304, 1252, 1148, 1110, 965, 913, 864, 760 cm\textsuperscript{-1}. HRMS (ESI, m/z): calcd for C_{2}H_{5}FO_{4}SSi (M+H)^{+}: 461.1613; found: 461.1611.

1-(4-Iodophenyl)-2-((3-(phenylsulfonyl)-1-((trimethylsilyl)oxy)cyclopentyl)methyl)prop-2-en-1-one (7d)

In a glovebox, to an oven-dried 10 mL tube was added 2m (41.1 mg, 0.1 mmol), PhSO\textsubscript{2}Na (32.8 mg, 0.2 mmol, 2 equiv.), Eosin Y (1.9 mg, 0.003 mmol, 3 mol%), CsOPiv (46.8 mg, 0.2 mmol, 2 equiv.), MeOH/H\textsubscript{2}O =1:2 (0.067 M) and 1f (46.8 mg, 0.3 mmol, 3 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for the 24 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300–400 mesh) with PE/EA = 5/1 (v/v) as eluent to afford the title compound as a colorless oil (35.3 mg, 62 % yield in total, a mixture of two distersomers).

R_{f} = 0.45 (PE/EA = 5/1 (v/v)). NMR Spectroscopy: \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}, 25 °C) \(\delta\) 7.87–7.83 (m, 2H), 7.82–7.78 (m, 2H), 7.67–7.62 (m, 1H), 7.56–7.50 (m, 4H), 5.87 (d, \(J = 9.0\) Hz, 1H), 5.60 (d, \(J = 0.9\) Hz, 1H), 3.74–3.65 (m, 1H), 2.93–2.85 (m, 2H), 2.20–2.09 (m, 2H), 2.04–1.98 (m, 1H), 1.97–1.92 (m, 1H), 1.82–1.76 (m, 2H), 0.00 (s, 9H). \textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}, 25 °C) \(\delta\) 197.0, 145.1, 138.8, 137.7, 136.6, 133.8, 131.5, 129.4, 128.5, 128.0, 100.4, 84.9, 62.8, 42.8, 39.9, 38.4, 25.0, 2.0. \textsuperscript{29}Si NMR (119 MHz, CDCl\textsubscript{3}, 25 °C) \(\delta\) 10.7. IR (ATR): ν 3063, 2955, 2862, 1658, 1621, 1580, 1479, 1446, 1390, 1304, 1252, 1203, 1148, 1069, 842, 730 cm\textsuperscript{-1}. HRMS (ESI, m/z): calcd for C_{2}H_{5}FO_{4}SSi (M+H)^{+}: 569.0673; found: 569.0676.

R_{f} = 0.38 (PE/EA = 5/1 (v/v)). NMR Spectroscopy: \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}, 25 °C) \(\delta\) 7.90–7.87 (m, 2H), 7.80–7.76 (m, 2H), 7.66–7.59 (m, 1H), 7.56–7.52 (m, 2H), 7.47–7.42 (m, 2H), 5.81 (d, \(J = 1.0\) Hz, 1H), 5.59 (d, \(J = 1.0\) Hz, 1H), 3.59–3.51 (m, 1H), 2.68–2.56 (m, 2H), 2.31–2.20 (m, 1H), 2.18 (ddd, \(J = 13.3, 10.2, 0.9\) Hz, 1H), 2.01 (ddd, \(J = 13.3, 8.2, 1.6\) Hz, 1H), 1.97–1.85 (m, 2H), 1.80–1.75 (m, 1H), 0.01 (s, 9H). \textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}, 25 °C) \(\delta\) 197.2, 144.5, 138.5, 137.6, 136.6, 133.8, 131.5, 129.4, 128.7, 128.1, 100.2, 83.3, 61.5, 42.6, 39.0, 37.9, 24.1, 2.1. \textsuperscript{29}Si NMR (119 MHz, CDCl\textsubscript{3}, 25 °C) \(\delta\) 11.2. IR (ATR): ν 3063, 2959, 1662, 1580, 1429, 1446, 1390.
1304, 1252, 1148, 1103, 1084, 1058, 987, 913, 838, 730 cm⁻¹. HRMS (ESI, m/z): calcd for C₂₅H₂₉F₃O₄Si (M+H)⁺: 569.0673; found: 569.0676.

2-((3-(Phenylsulfonyl)-1-((trimethylsilyl)oxy)cyclopentyl)methyl)-1-(2-(trifluoromethyl)phenyl)-prop-2-en-1-one (7e)

In a glovebox, to an oven-dried 10 mL tube was added 2n (70.8 mg, 0.2 mmol), PhSO₂Na (65.6 mg, 0.4 mmol, 2 equiv.), Eosin Y (2.6 mg, 0.004 mmol, 2 mol%), CsOPiv (70.2 mg, 0.3 mmol, 1.5 equiv.), MeOH/H₂O = 1:2 (0.067 M) and 1f (62.4 mg, 0.4 mmol, 2 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LEDs. The mixture was stirred under white light irradiation at ambient temperature for 24 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300~400 mesh) with PE/EA = 5/1 (v/v) to afford the title compound as a colorless oil (53.8 mg, 52 % yield in total, a mixture of two disteraosiomers).

Rₖ = 0.51 (PE/EA = 5/1 (v/v)). NMR Spectroscopy: ¹H NMR (600 MHz, CDCl₃, 25 °C) δ 7.91–7.86 (m, 2H), 7.75–7.70 (m, 1H), 7.68–7.62 (m, 1H), 7.61–7.53 (m, 4H), 7.40–7.36 (m, 1H), 6.20 (d, J = 1.1 Hz, 1H), 5.68 (s, 1H), 3.76–3.71 (m, 1H), 2.91–2.83 (m, 2H), 2.24–2.21 (m, 1H), 2.14–2.03 (m, 2H), 1.97 (ddd, J = 13.5, 7.8, 2.2 Hz, 1H), 1.89–1.75 (m, 2H), 0.10 (s, 9H). ¹³C NMR (151 MHz, CDCl₃, 25 °C) δ 197.0, 145.5, 138.8, 138.4, 134.6, 133.7, 131.4, 129.9, 129.4, 128.6, 128.3 (q, J = 31.7 Hz), 128.5, 126.7 (q, J = 6.1 Hz), 123.7 (q, J = 273.3 Hz), 84.9, 63.0, 40.2, 39.3, 38.3, 24.8, 2.2. ¹⁹F NMR (565 MHz, CDCl₃, 25 °C) δ −58.2 (s, 3F). ²⁹Si NMR (119 MHz, CDCl₃, 25 °C) δ 10.5. IR (ATR): ν 3068, 2959, 1670, 1580, 1446, 1409, 1312, 1252, 1133, 1059, 984, 913, 838, 730 cm⁻¹. HRMS (ESI, m/z): calcd for C₂₅H₂₉F₃O₄Si (M+H)⁺: 569.0673; found: 569.0676.

Rₖ = 0.41 (PE/EA = 5/1 (v/v)). NMR Spectroscopy: ¹H NMR (600 MHz, CDCl₃, 25 °C) δ 7.94–7.88 (m, 2H), 7.71–7.68 (m, 1H), 7.66–7.61 (m, 1H), 7.58–7.52 (m, 4H), 7.25–7.21 (m, 1H), 6.27 (d, J = 1.0 Hz, 1H), 5.69 (d, J = 0.8 Hz, 1H), 3.74–3.66 (m, 1H), 2.65 (d, J = 14.1 Hz, 1H), 2.58–2.53 (m, 1H), 2.33–2.25 (m, 1H), 2.19 (ddd, J = 13.2, 10.0, 1.2 Hz, 1H), 2.06–1.95 (m, 2H), 1.92 (ddd, J = 13.2, 8.2, 1.7 Hz, 1H), 1.81–1.74 (m, 1H), 0.13 (s, 9H). ¹³C NMR (151 MHz, CDCl₃, 25 °C) δ 197.8, 144.6, 138.7, 138.2, 135.8, 133.7, 131.3, 129.8, 129.4, 128.6, 128.4, 128.2, 128.1, 128.1, 127.6 (q, J = 31.7 Hz), 126.7 (q, J = 4.5 Hz), 123.6 (q, J = 273.3 Hz), 83.3, 61.2, 39.2, 38.5, 38.3, 23.7, 2.3. ¹⁹F NMR (565 MHz, CDCl₃, 25 °C) δ −58.2. ²⁹Si NMR (119 MHz, CDCl₃, 25 °C) δ 10.8. IR (ATR): ν 3071, 2959, 1669, 1625, 1584, 1446, 1408, 1315, 1252, 1148, 1062, 1036, 987, 913, 864, 742 cm⁻¹. HRMS (ESI, m/z): calcd for C₂₅H₂₉F₃O₄Si (M+H)⁺: 511.1581; found: 511.1580.
**1-(4-Methoxyphenyl)-2-((3-(phenylsulfonyl)-1-((trimethylsilyl)oxy)cyclopentyl)methyl)prop-2-en-1-one (7f)**

In a glovebox, to an oven-dried 10 mL tube was added 2o (63.2 mg, 0.2 mmol), PhSO₂Na (65.6 mg, 0.4 mmol, 2 equiv.), Eosin Y (2.6 mg, 0.004 mmol, 2 mol%), CsOPiv (70.2 mg, 0.3 mmol, 1.5 equiv.), MeOH/H₂O = 1:2 (0.067 M) and 1f (62.4 mg, 0.4 mmol, 2 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for the 24 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300 ~ 400 mesh) with PE/EA = 5/1 (v/v) to afford the title compound as a colorless oil (26.3 mg, 58 % yield in total, a mixture of two diastereoisomers).

**Rₙ = 0.50 (PE/EA = 4/1 (v/v)). NMR Spectroscopy:** ¹H NMR (600 MHz, CDCl₃, 25 °C) δ 7.86 – 7.76 (m, 4H), 7.64 – 7.61 (m, 1H), 7.55 – 7.49 (m, 2H), 6.96 – 6.90 (m, 2H), 5.78 (d, J = 1.1 Hz, 1H), 5.58 (d, J = 1.1 Hz, 1H), 3.87 (s, 3H), 3.73 – 3.65 (m, 1H), 3.00 – 2.81 (m, 2H), 2.19 – 2.08 (m, 2H), 2.06 – 1.97 (m, 1H), 1.93 (ddd, J = 13.7, 7.9, 1.4 Hz, 1H), 1.79 (ddd, J = 8.5, 6.9, 1.7 Hz, 2H), 0.00 (s, 9H).

**13C NMR (151 MHz, CDCl₃, 25 °C) δ 196.5, 163.4, 145.3, 138.8, 133.7, 132.5, 132.2, 129.8, 129.4, 128.5, 126.4, 113.6, 85.0, 62.9, 55.6, 43.2, 40.1, 38.3, 24.9, 2.0.**

**²⁹Si NMR (119 MHz, CDCl₃, 25 °C) δ 10.5.**

**IR (ATR):** ν 3071, 2955, 2844, 1651, 1602, 1509, 1446, 1420, 1304, 1252, 1148, 1069, 1025, 957, 842, 700 cm⁻¹.

**HRMS (ESI, m/z):** calcd for C₂₅H₃₃O₅SSi(M+H)⁺: 473.1813; found: 473.1807.

**Rₙ = 0.38 (PE/EA = 4/1 (v/v)). NMR Spectroscopy:** ¹H NMR (600 MHz, CDCl₃, 25 °C) δ 7.90 – 7.85 (m, 2H), 7.80 – 7.73 (m, 2H), 7.65 – 7.59 (m, 1H), 7.55 – 7.50 (m, 2H), 6.94 – 6.88 (m, 2H), 5.73 (d, J = 1.2 Hz, 1H), 5.57 (d, J = 1.3 Hz, 1H), 3.87 (s, 3H), 3.60 – 3.50 (m, 1H), 2.74 – 2.57 (m, 2H), 2.29 – 2.13 (m, 2H), 2.04 (ddd, J = 13.3, 8.3, 1.5 Hz, 1H), 1.95 – 1.83 (m, 2H), 1.78 (ddd, J = 9.8, 5.8, 1.5 Hz, 1H), 0.01 (s, 9H).

**¹³C NMR (151 MHz, CDCl₃, 25 °C) δ 196.8, 163.3, 145.3, 138.8, 133.7, 132.5, 132.2, 129.8, 129.4, 128.5, 126.4, 113.5, 83.3, 61.6, 55.6, 43.2, 39.1, 37.9, 24.2, 2.1.**

**²⁹Si NMR (119 MHz, CDCl₃, 25 °C) δ 10.8.**

**IR (ATR):** ν 2955, 1654, 1602, 1572, 1509, 1446, 1420, 1304, 1259, 1166, 1148, 1107, 1084, 842, 700 cm⁻¹. HRMS (ESI, m/z): calcd for C₂₅H₃₃O₅SSi(M+H)⁺: 473.1813; found: 473.1810.

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**2-((3-(Phenylsulfonyl)-1-((trimethylsilyl)oxy)cyclopentyl)methyl)-1-((thiophen-2-yl)prop-2-en-1-one (7g))**

In a glovebox, to an oven-dried 10 mL tube was added 2r (29.2 mg, 0.1 mmol), PhSO₂Na (32.8 mg, 0.2 mmol, 2 equiv.), Eosin Y (1.9 mg, 0.003 mmol, 3 mol%), CsOPiv (46.8 mg, 0.2 mmol, 2 equiv.), MeOH/H₂O = 1:2 (0.067 M) and 1f (46.8 mg, 0.3 mmol, 3 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps.
The mixture was stirred under white light irradiation at ambient temperature for the 24 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300–400 mesh) with PE/EA = 5/1 (v/v) as eluent to afford the title compound as a colorless oil (32.1 mg, 71 % yield in total, a mixture of two diastereomers).

\[ R_f = 0.48 \ (\text{PE/EA} = 5/1 \ (v/v)). \]

NMR Spectroscopy: \(^1H\) NMR (600 MHz, CDCl\(_3\), 25 °C) \( \delta \) 7.83–7.78 (m, 2H), 7.71–7.65 (m, 2H), 7.66–7.60 (m, 1H), 7.56–7.50 (m, 2H), 7.13 (dd, \( J = 4.9, 3.8 \) Hz, 1H), 5.83 (d, \( J = 1.0 \) Hz, 1H), 5.76 (d, \( J = 1.0 \) Hz, 1H), 3.71–3.63 (m, 1H), 2.93–2.81 (m, 2H), 2.19–2.12 (m, 1H), 2.08 (dd, \( J = 13.6, 9.5 \) Hz, 1H), 2.06–1.97 (m, 1H), 1.94–1.88 (m, 1H), 1.85–1.77 (m, 2H), 0.00 (s, 9H). \(^13C\) NMR (151 MHz, CDCl\(_3\), 25 °C) \( \delta \) 189.5, 145.5, 143.4, 138.8, 134.6, 134.3, 133.5, 133.7, 129.4, 128.5, 128.1, 125.7, 84.8, 62.9, 43.4, 40.1, 38.3, 24.8. HRMS (ESI, m/z): calcd for C\(_{22}H\(_25\)O\(_3\)Si (M+H): 449.1271; found: 449.1278.

In a glovebox, a mixture of two diastereomers (300 mesh) with PE/EA = 5/1 (v/v) as eluent to afford the title compound as a co-

\[ R_f = 0.42 \ (\text{PE/EA} = 5/1 \ (v/v)). \]

NMR Spectroscopy: \(^1H\) NMR (600 MHz, CDCl\(_3\), 25 °C) \( \delta \) 7.90–7.86 (m, 2H), 7.68–7.59 (m, 3H), 7.57–7.51 (m, 2H), 7.11 (dd, \( J = 4.9, 3.8 \) Hz, 1H), 5.84 (d, \( J = 1.1 \) Hz, 1H), 5.71 (d, \( J = 1.1 \) Hz, 1H), 3.57–3.48 (m, 1H), 2.69–2.54 (m, 2H), 2.27–2.12 (m, 2H), 2.03 (dd, \( J = 13.4, 8.3, 1.5 \) Hz, 1H), 1.95–1.84 (m, 2H), 1.81–1.74 (m, 1H), 0.01 (s, 9H). \(^13C\) NMR (151 MHz, CDCl\(_3\), 25 °C) \( \delta \) 189.6, 145.0, 143.4, 138.5, 134.3, 134.1, 133.8, 129.4, 128.7, 127.9, 125.9, 83.2, 61.5, 43.1, 39.0, 37.8, 24.1, 2.0. \(^29Si\) NMR (119 MHz, CDCl\(_3\), 25 °C) \( \delta \) 10.9. IR (ATR): ν 3090, 2955, 1640, 1513, 1446, 1412, 1356, 1304, 1252, 1200, 1148, 1069, 842, 699 cm\(^{-1}\).

HRMS (ESI, m/z): calcd for C\(_{22}H\(_25\)O\(_3\)Si (M+H): 449.1271; found: 449.1280.

\[ S32 \]

\[ \text{1-(Naphthalen-2-yl)-2-)-(3-(phenylsulfonyl)-1-}-((trimethylsilyloxy)cyclopentyl)methyl)prop-2-en-1-one (7h) \]

In a glovebox, to an oven-dried 10 mL tube was added 2h° (67.6 mg, 0.2 mmol), PhSO\(_2\)Na (65.6 mg, 0.4 mmol, 2 equiv.), Eosin Y (2.6 mg, 0.004 mmol, 2 mol%), CsOPiv (70.2 mg, 0.3 mmol, 1.5 equiv.), MeOH/H\(_2\)O =1:2 (0.067 M) and 1f (62.4 mg, 0.4 mmol, 2 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for the 24 h. The result was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300–400 mesh) with PE/EA = 5/1 (v/v) as eluent to afford the title compound as a colorless oil (50.7 mg, 51 % yield in total, a mixture of two diastereomers).

\[ R_f = 0.48 \ (\text{PE/EA} = 5/1 \ (v/v)). \]

NMR Spectroscopy: \(^1H\) NMR (600 MHz, CDCl\(_3\), 25 °C) \( \delta \) 8.35–8.34 (m, 1H), 7.98 (dd, \( J = 8.0, 1.3 \) Hz, 1H), 7.89 (dd, \( J = 12.6, 1.0 \) Hz, 3H), 7.85–7.82 (m, 2H), 7.63–7.52 (m, 3H), 7.51–7.45 (m, 2H), 5.92 (d, \( J = 1.0 \) Hz, 1H), 5.72 (d, \( J = 1.0 \) Hz, 1H), 3.77–3.67 (m, 1H), 2.98 (d, \( J = 0.9 \) Hz, 2H), 2.25–2.13 (m, 2H), 2.09–2.02 (m, 1H), 2.02–1.96 (m, 1H), 1.90–1.79 (m, 2H), 0.04 (s, 9H). \(^13C\) NMR
Ethyl 2-((3-(phenylsulfonyl)-1-((trimethylsilyl)oxy)cyclopentyl)methyl)acrylate (7i)

In a glovebox, to an oven-dried 10 mL tube was added 2s (25.4 mg, 0.1 mmol), PhSO₃Na (32.8 mg, 0.2 mmol, 2 equiv.), Eosin Y (1.9 mg, 0.003 mmol, 3 mol%), CsOIPv (46.8 mg, 0.2 mmol, 2 equiv.), MeOH/H₂O = 1:2 (0.067 M) and 1f (46.8 mg, 0.3 mmol, 3 equiv.) sequentially. The mixture was stirred under white light irradiation at ambient temperature for 24 h. The crude product was purified with column chromatography on silica gel (300–400 mesh) with PE/EA = 5/1 (v/v) as eluent to afford the title compound as a colorless oil (19.8 mg, 48 % yield in total, a mixture of two diastereomers).

Rₛ = 0.51 (PE/EA = 5/1 (v/v)). NMR Spectroscopy: ¹H NMR (600 MHz, CDCl₃, 25 °C) δ 7.89–7.85 (m, 2H), 7.67–7.62 (m, 1H), 7.58–7.52 (m, 2H), 6.25 (d, J = 1.5 Hz, 1H), 5.63 (d, J = 1.4 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.75–3.66 (m, 1H), 2.71 (dd, J = 2.4, 1.0 Hz, 2H), 2.19–2.14 (m, 1H), 2.09–2.02 (m, 1H), 1.99 (ddd, J = 13.4, 9.9 Hz, 1H), 1.87 (ddd, J = 13.4, 7.7, 2.3 Hz, 1H), 1.79–1.66 (m, 2H), 1.30 (t, J = 7.1 Hz, 3H), 0.09 (s, 9H). ¹³C NMR (151 MHz, CDCl₃, 25 °C) δ 167.5, 138.9, 138.2, 137.1, 134.2, 129.4, 128.4, 84.9, 62.9, 61.0, 41.0, 40.1, 37.8, 24.5, 14.4, 22. ²⁹Si NMR (119 MHz, CDCl₃, 25 °C) δ 10.0. IR (ATR): ν 3075, 2955, 1718, 1628, 1446, 1304, 1252, 1177, 1148, 1069, 1002, 957, 913, 842, 730 cm⁻¹. HRMS (ESI, m/z): calcd for C₂₃H₂₃O₃Si (M+H⁺): 411.1656; found: 411.1667.

Rₛ = 0.46 (PE/EA = 5/1 (v/v)). NMR Spectroscopy: ¹H NMR (600 MHz, CDCl₃, 25 °C) δ 7.92–7.86 (m, 2H), 7.66–7.62 (m, 1H), 7.59–7.53 (m, 2H), 6.25 (d, J = 1.8 Hz, 1H), 5.65 (d, J = 1.8 Hz, 1H), 4.13 (q, J = 7.1 Hz, 2H), 3.57 (ddt, J = 9.5, 8.4, 6.1 Hz, 1H), 2.54–2.41 (m, 2H), 2.30–2.20 (m, 1H), 2.13 (ddd, J = 13.3, 9.8, 0.9 Hz, 1H), 1.96–1.82 (m, 3H), 1.75–1.69 (m, 1H), 1.25 (t, J = 7.1 Hz, 3H), 0.11 (s, 9H). ¹³C NMR (151 MHz, CDCl₃, 25 °C) δ 186.0, 138.7, 136.5, 133.7, 129.3, 128.8, 128.7, 83.2, 61.4, 61.0, 40.7, 39.1, 37.9, 23.9, 14.3, 2.2. ²⁹Si NMR (119 MHz, CDCl₃, 25 °C) δ 10.5. IR (ATR): ν 3060, 2955, 1654, 1625, 1595, 1446, 1409, 1304, 1252, 1148, 1069, 998, 913, 842, 700 cm⁻¹. HRMS (ESI, m/z): calcd for C₃₀H₂₇O₃S (M+H⁺): 493.1863; found: 493.1861.
CDCl₃, 25 °C) δ 10.5. IR (ATR): ν 2963, 1714, 1628, 1543, 1446, 1304, 1252, 1148, 1088, 1028, 842, 726 cm⁻¹. HRMS (ESI, m/z): calcd for C₂₁H₃₁O₄Si (M+H)+: 411.1656; found: 411.1661.

3.5 Scope for the synthesis different sulfonyl group-substituted cyclopentyl siloxanes.

1-Phenyl-2-((2-(tosylmethyl)-1-((trimethylsilyl)oxy)cyclopentyl)methyl)prop-2-en-1-one 3ab

In a glovebox, to an oven-dried 10 mL tube was added 2ab (60.0 mg, 0.2 mmol), PhSO₂Na (0.7 mg, 0.004 mmol, 2 mol%), Eosin Y (1.3 mg, 0.002 mmol, 1 mol%), KOPiv (28.0 mg, 0.2 mmol, 1 equiv.), MeCN/H₂O =1:3 (0.05 M) and 1a (68.0 mg, 0.4 mmol, 2 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The crude product was concentrated under reduced pressure.

The crude product was purified with column chromatography on silica gel (200~300 mesh) with PE/EA = 5/1 (v/v) to afford the title compound as a colorless oil (75.1 mg, 80 % yield in total, a mixture of two disterasiosomers).

Characterization of the major isomer: R$_f$ = 0.55 (PE/EA = 5/1 (v/v)). NMR Spectroscopy: ¹H NMR (600 MHz, CDCl₃, 25 °C) δ 7.81–7.75 (m, 2H), 7.67–7.61 (m, 2H), 7.57–7.53 (m, 1H), 7.45–7.41 (m, 2H), 7.30–7.26 (m, 2H), 5.79 (d, J = 1.0 Hz, 1H), 5.65 (d, J = 0.8 Hz, 1H), 3.43 (dd, J = 14.4, 2.0 Hz, 1H), 3.01 (dd, J = 14.4, 10.7 Hz, 1H), 2.89–2.82 (m, 1H), 2.74 (dd, J = 13.0, 0.8 Hz, 1H), 2.39 (s, 3H), 2.09–1.91 (m, 2H), 1.76–1.65 (m, 2H), 1.61–1.46 (m, 3H), 0.08 (s, 9H). ¹³C NMR (151 MHz, CDCl₃, 25 °C) δ 197.4, 144.4, 144.1, 137.2, 137.2, 132.5, 130.7, 129.9, 129.8, 128.4, 128.1, 85.7, 57.9, 41.0, 40.1, 37.0, 29.6, 21.8, 21.6. ²⁹Si NMR (119 MHz, CDCl₃, 25 °C) δ 10.6. IR (ATR): ν 3086, 3063, 2959, 1654, 1599, 1446, 1312, 1252, 1144, 1066, 842, 730 cm⁻¹. HRMS (ESI, m/z): calcd for C₂₆H₃₅O₄Si (M+H)+: 471.2020; found: 471.2023.

1-Phenyl-2-((2)-(o-tolylsulfonyl)methyl)-1-((trimethylsilyl)oxy)cyclopentyl)methyl)prop-2-en-1-one 3ac

In a glovebox, to an oven-dried 10 mL tube was added 2ac (60.0 mg, 0.2 mmol), PhSO₂Na (0.7 mg, 0.004 mmol, 2 mol%), Eosin Y (1.3 mg, 0.002 mmol, 1 mol%), KOPiv (28.0 mg, 0.2 mmol, 1 equiv.), MeCN/H₂O =1/3 (0.05 M) and 1a (68.0 mg, 0.4 mmol, 2 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200~300 mesh) with PE/EA = 5/1 (v/v) as eluent to afford the title compound as a colorless oil (81.6 mg, 87 % yield in total, a mixture of two disterasiosomers).
Characterization of the major isomer: 

R_t = 0.52 (PE/EA = 5/1 (v/v)). NMR Spectroscopy: 

^1^H NMR (600 MHz, CDCl_3, 25 °C) δ 7.99 (dd, J = 7.9, 1.4 Hz, 1H), 7.69–7.66 (m, 2H), 7.57–7.52 (m, 1H), 7.48–7.40 (m, 3H), 7.35 (t, J = 7.6 Hz, 1H), 7.30 (d, J = 7.6 Hz, 1H), 5.82 (s, 1H), 5.68 (s, 1H), 3.45 (dd, J = 14.4, 2.1 Hz, 1H), 3.04 (dd, J = 14.3, 10.8 Hz, 1H), 2.91 (d, J = 13.2 Hz, 1H), 2.72 (d, J = 5.6 Hz, 4H), 2.18 (ddd, J = 10.8, 8.6, 2.1 Hz, 1H), 1.96 (ddd, J = 12.5, 8.5, 3.7 Hz, 1H), 1.69 (qq, J = 7.7, 3.7, 3.1 Hz, 2H), 1.62–1.46 (m, 3H), 0.08 (s, 9H).

^1^C NMR (151 MHz, CDCl_3, 25 °C) δ 197.4, 144.1, 138.2, 138.1, 137.1, 133.6, 132.8, 132.5, 130.3, 130.1, 129.8, 128.4, 126.6, 85.7, 56.8, 40.7, 40.3, 37.1, 29.7, 21.6, 20.6, 2.2. ^2^9^Si NMR (119 MHz, CDCl_3, 25 °C) δ 10.73. IR (ATR): ν 3063, 2952, 1654, 1595, 1446, 1312, 1252, 1151, 1107, 842, 730 cm⁻¹. HRMS (ESI, m/z): calcd for C_{36}H_{33}O_{4}Si (M+H)^+: 471.2016; found: 471.2020; found: 471.2016.

2-((2-(((4-(tert-Butyl)phenyl)sulfonyl)methyl)-1-((trimethylsilyl)oxy)cyclopentyl)methyl)-1-phenylprop-2-en-1-one 3ad

In a glovebox, to an oven-dried 10 mL tube was added 2ad (68.4 mg, 0.2 mmol), sodium 4-(tert-butyl)benzenesulfinate (9.9 mg, 0.04 mmol, 20 mol%), Eosin Y (1.3 mg, 0.002 mmol, 1 mol%), KOPiv (28.0 mg, 0.2 mmol, 1 equiv.), MeCN/H_2O =1:3 (0.05 M) and 1a (68.0 mg, 0.4 mmol, 2 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then, the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) with PE/EA = 5/1 (v/v) as eluent to afford the title compound as a colorless oil (86.0 mg, 84 % yield in total, a mixture of two diastereoisomers).

Characterization of the major isomer: 

R_t = 0.58 (PE/EA = 5/1 (v/v)). NMR Spectroscopy: 

^1^H NMR (600 MHz, CDCl_3, 25 °C) δ 7.88–7.83 (m, 2H), 7.71–7.67 (m, 2H), 7.59–7.52 (m, 3H), 7.47–7.41 (m, 2H), 5.70 (d, J = 0.9 Hz, 1H), 5.62 (d, J = 0.8 Hz, 1H), 3.43 (dd, J = 14.3, 2.0 Hz, 1H), 3.00 (dd, J = 14.3, 10.9 Hz, 1H), 2.90 (dd, J = 13.2, 0.9 Hz, 1H), 2.69 (dd, J = 13.2, 0.9 Hz, 1H), 2.23–2.12 (m, 1H), 2.07–1.98 (m, 1H), 1.75–1.66 (m, 2H), 1.56–1.47 (m, 2H), 1.33 (s, 9H), 1.28–1.23 (m, 1H), 0.07 (s, 9H). ^1^C NMR (151 MHz, CDCl_3, 25 °C) δ 197.5, 157.5, 144.1, 137.3, 137.2, 132.5, 130.3, 129.8, 128.4, 127.9, 126.4, 85.7, 57.9, 40.8, 40.3, 37.1, 35.4, 31.2, 29.8, 21.7, 2.2. ^2^9^Si NMR (119 MHz, CDCl_3, 25 °C) δ 10.64. IR (ATR): ν 3060, 2959, 1654, 1595, 1446, 1401, 1312, 1252, 1151, 1107, 842, 731 cm⁻¹. HRMS (ESI, m/z): calcd for C_{36}H_{33}O_{4}Si (M+H)^+: 513.2489; found: 513.2492.

2-((2-(((4-Methoxyphenyl)sulfonyl)methyl)-1-((trimethylsilyl)oxy)cyclopentyl)methyl)-1-phenylprop-2-en-1-one 3ae

In a glovebox, to an oven-dried 10 mL tube was added 2ae (63.2 mg, 0.2 mmol), PhSO_3Na (0.7 mg, 0.004 mmol, 2 mol%), Eosin Y (1.3 mg, 0.002 mmol, 1 mol%), KOPiv (28.0 mg, 0.2 mmol, 1 equiv.), MeCN/H_2O =1:3 (0.05 M) and 1a (68.0 mg, 0.4 mmol, 2 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps.
The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200~300 mesh) with PE/EA = 5/1 (v/v) as eluent to afford the title compound as a colorless oil (80.0 mg, 82 % yield in total, a mixture of two disteraosiomers).

Characterization of the major isomer: \( R_t = 0.32 \) (PE/EA = 5/1 (v/v)). NMR Spectroscopy: \(^1\)H NMR (600 MHz, CDCl\(_3\), 25 °C) \(^1\)H NMR (600 MHz, Chloroform-d) \( \delta \) 7.85–7.79 (m, 2H), 7.65–7.61 (m, 2H), 7.56–7.52 (m, 1H), 7.45 – 7.40 (m, 2H), 6.96 – 6.92 (m, 2H), 5.81 (d, \( J = 1.0 \) Hz, 1H), 5.67 (d, \( J = 0.8 \) Hz, 1H), 3.84 (s, 3H), 3.43 (dd, \( J = 14.3, 2.0 \) Hz, 1H), 3.00 (dd, \( J = 14.3, 10.6 \) Hz, 1H), 2.87 – 2.82 (m, 1H), 2.75 (dd, \( J = 13.2, 0.9 \) Hz, 1H). 2O2–1.93 (m, 2H), 1.77–1.64 (m, 2H), 1.62 – 1.53 (m, 3H), 1.53–1.46 (m, 1H), 0.08 (s, 9H). \(^1\)^13\(^C\) NMR (151 MHz, CDCl\(_3\), 25 °C) \( \delta \) 197.4, 163.6, 144.1, 137.2, 132.5, 131.7, 130.7, 129.7, 128.4, 114.4, 85.7, 58.0, 55.7, 41.1, 40.1, 37.0, 29.6, 21.6, 2.3. \(^29\)\(^Si\) NMR (119 MHz, CDCl\(_3\), 25 °C) \( \delta \) 10.6. IR (ATR): \( \nu \) 3097, 3063, 2955, 1654, 1591, 1490, 1446, 1412, 1297, 1259, 1140, 1088, 1028, 838, 730 cm\(^{-1}\). HRMS (APCI, \( m/z \)): calcd for C\(_{26}\)H\(_{35}\)O\(_3\)Si (M+H): 487.1969; found: 487.1963.

2-((2-(((4-Fluorophenyl)sulfonyl)methyl)-1-(((trimethylsilyl)oxy)cyclopentyl)methyl)-1-phenylprop-2-en-1-one 3af

In a glovebox, to an oven-dried 10 mL tube was added 2af (60.8 mg, 0.2 mmol), PhSO\(_2\)Na (0.7 mg, 0.004 mmol, 2 mol%), Eosin Y (1.3 mg, 0.002 mmol, 1 mol%), KOPiv (28.0 mg, 0.2 mmol, 1 equiv.), MeCN/H\(_2\)O =1:3 (0.05 M) and 1a (68.0 mg, 0.4 mmol, 2 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200~300 mesh) with PE/EA = 5/1 (v/v) as eluent to afford the title compound as a colorless oil (80.5 mg, 85 % yield in total, a mixture of two disteraosiomers).

Characterization of the major isomer: \( R_t = 0.56 \) (PE/EA = 5/1 (v/v)). NMR Spectroscopy: \(^1\)H NMR (600 MHz, CDCl\(_3\), 25 °C) \( \delta \) 7.91–7.84 (m, 2H), 7.60–7.58 (m, 2H), 7.57 (d, \( J = 1.4 \) Hz, 1H), 7.43 (t, \( J = 7.7 \) Hz, 2H), 7.11–7.04 (m, 2H), 5.85 (d, \( J = 1.1 \) Hz, 1H), 5.70 (d, \( J = 0.9 \) Hz, 1H), 5.85 (d, \( J = 1.1 \) Hz, 1H), 5.70 (d, \( J = 0.9 \) Hz, 1H), 3.47 (dd, \( J = 14.3, 2.2 \) Hz, 1H), 3.03 (dd, \( J = 14.3, 11.0 \) Hz, 1H), 2.84 (d, \( J = 13.2 \) Hz, 1H), 2.75 (d, \( J = 13.2 \) Hz, 1H), 1.98 (dd, \( J = 12.5, 8.4, 3.5 \) Hz, 1H), 1.86 (ddd, \( J = 10.7, 8.9, 8.1, 2.2 \) Hz, 1H), 1.80–1.59 (m, 5H), 1.56–1.48 (m, 1H), 0.09 (s, 9H). \(^1\)^13\(^C\) NMR (151 MHz, CDCl\(_3\), 25 °C) \( \delta \) 197.3, 166.5, 164.8, 144.1, 137.1, 135.9 (d, \( J = 3.2 \) Hz), 132.6, 131.1, 130.9 (d, \( J = 9.5 \) Hz), 129.0 (d, \( J = 19.1 \) Hz), 116.4 (d, \( J = 22.4 \) Hz), 85.8, 57.7, 41.1, 39.9, 36.6, 29.4, 21.4, 2.3. \(^19\)\(^F\) NMR (565 MHz, CDCl\(_3\), 25 °C) \( \delta \) –103.73 (tt, \( J = 9.1, 4.8 \) Hz). \(^29\)\(^Si\) NMR (119 MHz, CDCl\(_3\), 25 °C) \( \delta \) 10.7. IR (ATR): \( \nu \) 3071, 2955, 1654, 1591, 1490, 1446, 1405, 1315, 1252, 1140, 1060, 913, 838, 752 cm\(^{-1}\). HRMS (ESI, \( m/z \)): calcd for C\(_{26}\)H\(_{35}\)O\(_3\)Si (M+H): 475.1769; found: 475.1758.
2-((2-(((4-Chlorophenyl)sulfonyl)methyl)-1-((trimethylsilyl)oxy)cyclopentyl)methyl)-1-phenylprop-2-en-1-one 3ag

In a glovebox, to an oven-dried 10 mL tube was added 2ag (64.0 mg, 0.2 mmol), PhSO$_2$Na (1.6 mg, 0.01 mmol, 5 mol%), Eosin Y (1.3 mg, 0.002 mmol, 1 mol%), KOPiv (28.4 mg, 0.2 mmol, 1 equiv.), MeCN/H$_2$O = 1:3 (0.05 M) and 1a (68.0 mg, 0.4 mmol, 2 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) with PE/EA = 5/1 (v/v) as eluent to afford the title compound as a colorless oil (61.1 mg, 62 % yield in total, a mixture of two diastereomers).

Characterization of the major isomer: $R_f = 0.55$ (PE/EA = 5/1 (v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, CDCl$_3$, 25 ºC) $\delta$ 7.83–7.78 (m, 2H), 7.63–7.58 (m, 2H), 7.58–7.55 (m, 1H), 7.46–7.41 (m, 2H), 7.41–7.36 (m, 2H), 5.85 (d, $J = 1.0$ Hz, 1H), 5.71 (d, $J = 0.8$ Hz, 1H), 3.48 (dd, $J = 14.3$, 2.3 Hz, 1H), 3.03 (dd, $J = 14.3$, 11.0 Hz, 1H), 2.84 (dd, $J = 13.2$, 0.9 Hz, 1H), 1.98 (dtd, $J = 16.8$, 8.4, 3.3 Hz, 1H), 1.92–1.86 (m, 1H), 1.80–1.63 (m, 4H), 1.57–1.47 (m, 1H), 1.77–1.62 (m, 4H), 1.57–1.47 (m, 1H), 0.10 (s, 9H). $^{13}$C NMR (151 MHz, CDCl$_3$, 25 ºC) $\delta$ 197.3, 144.1, 140.2, 138.5, 137.1, 132.6, 131.1, 129.6, 129.6, 129.5, 128.4, 85.8, 57.7, 41.0, 39.9, 36.7, 29.4, 21.4, 2.3. $^{29}$Si NMR (119 MHz, CDCl$_3$, 25 ºC) $\delta$ 10.75. IR (ATR): $\nu$ 3086, 3060, 3030, 2955, 1654, 1580, 1476, 1446, 1394, 1312, 1252, 1148, 1088, 838, 752 cm$^{-1}$. HRMS (ESI, m/z): calcd for C$_{25}$H$_{32}$ClO$_4$SSi (M+H)$^+$: 491.1474; found: 491.1469.

2-((2-(((4-Bromophenyl)sulfonyl)methyl)-1-((trimethylsilyl)oxy)cyclopentyl)methyl)-1-phenylprop-2-en-1-one 3ah

In a glovebox, to an oven-dried 10 mL tube was added 2ah (73.0 mg, 0.2 mmol), PhSO$_2$Na (1.6 mg, 0.01 mmol, 5 mol%), Eosin Y (1.3 mg, 0.002 mmol, 1 mol%), KOPiv (28.4 mg, 0.2 mmol, 1 equiv.), MeCN/H$_2$O = 1:3 (0.05 M) and 1a (68.0 mg, 0.4 mmol, 2 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) with PE/EA = 5/1 (v/v) as eluent to afford the title compound as a colorless oil (58.4 mg, 54 % yield in total, a mixture of two diastereomers).

Characterization of the major isomer: $R_f = 0.53$ (PE/EA = 5/1 (v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, CDCl$_3$, 25 ºC) $\delta$ 7.76–7.70 (m, 2H), 7.63–7.58 (m, 2H), 7.46–7.41 (m, 2H), 7.41–7.36 (m, 2H), 5.85 (d, $J = 1.0$ Hz, 1H), 5.71 (d, $J = 0.8$ Hz, 1H), 3.48 (dd, $J = 14.3$, 2.3 Hz, 1H), 3.03 (dd, $J = 14.3$, 11.0 Hz, 1H), 2.84 (dd, $J = 13.2$, 0.9 Hz, 1H), 2.77 (dd, $J = 13.1$, 0.9 Hz, 1H), 1.98 (dtd, $J = 12.4$, 8.4, 3.3 Hz, 1H), 1.92–1.86 (m, 1H), 1.80–1.63 (m, 4H), 1.57–1.47 (m, 1H), 0.10 (s, 9H). $^{13}$C NMR (151 MHz, CDCl$_3$, 25 ºC) $\delta$ 197.4, 144.0, 139.0, 137.1, 132.7, 132.5, 131.1, 129.7, 129.7, 128.4, 128.5,
85.8, 57.6, 41.0, 39.9, 36.7, 29.4, 21.4, 2.3. $^{29}$Si NMR (119 MHz, CDCl$_3$, 25 °C) δ 10.76. IR (ATR): ν 3086, 3060, 2955, 1654, 1572, 1468, 1390, 1315, 1252, 1148, 1066, 913, 842, 752 cm$^{-1}$. HRMS (ESI, m/z): calcd for C$_{23}$H$_{32}$BrO$_3$Si (M+H)$^+$: 535.0969; found: 535.0965.

2-((1,1′-Biphenyl)-4-ylsulfonyl)methyl)-1-((trimethylsilyl)oxy)cyclopentyl)methyl)-1-phenylprop-2-en-1-one 3ai

In a glovebox, to an oven-dried 10 mL tube was added 2ai (72.4 mg, 0.2 mmol), sodium [[1,1′-biphenyl]]-4-sulfinate (9.6 mg, 0.04 mmol, 20 mol%), Eosin Y (1.3 mg, 0.002 mmol, 1 mol%), KOPiv (28.0 mg, 0.2 mmol, 1 equiv.), MeCN/H$_2$O = 1:3 (0.05 M) and 1a (68.0 mg, 0.4 mmol, 2 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) with PE/EA = 5/1 (v/v) as eluent to afford the title compound as a colorless oil (30.8 mg, 58 % yield in total, a mixture of two diasteroisomers).

Characterization of the major isomer: $R_f = 0.56$ (PE/EA = 5/1 (v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, CDCl$_3$, 25 °C) δ 7.99–7.94 (m, 2H), 7.73–7.68 (m, 2H), 7.67–7.62 (m, 2H), 7.61–7.56 (m, 2H), 7.51–7.43 (m, 4H), 7.37 (t, J = 7.6 Hz, 2H), 5.81 (s, 1H), 5.67 (s, 1H), 3.50 (dd, J = 14.3, 2.0 Hz, 1H), 3.07 (dd, J = 14.3, 10.6 Hz, 1H), 2.86 (dd, J = 13.2 Hz, 1H). 13C NMR (151 MHz, CDCl$_3$, 25 °C) δ 197.4, 146.4, 144.1, 139.3, 138.7, 137.2, 132.5, 130.7, 129.7, 129.2, 128.8, 128.6, 128.4, 127.9, 127.5, 85.7, 57.9, 41.0, 40.2, 37.0, 29.7, 21.6, 2.3. $^{29}$Si NMR (119 MHz, CDCl$_3$, 25 °C) δ 10.7. IR (ATR): ν 3063, 2955, 1654, 1572, 1446, 1441, 1393, 1387, 1372, 132.5, 130.7, 129.7, 129.2, 128.8, 128.6, 128.4, 127.9, 127.5, 85.7, 57.9, 41.0, 40.2, 37.0, 29.7, 21.6, 2.3. $^{29}$Si NMR (119 MHz, CDCl$_3$, 25 °C) δ 10.7. HRMS (ESI, m/z): calcd for C$_{31}$H$_{37}$O$_3$Si (M+H)$^+$: 533.2176; found: 533.2174.

1-Phenyl-2-((2-(((4-(trifluoromethoxy)phenyl)sulfonyl)methyl)-1-((trimethylsilyl)oxy)cyclopentyl)methyl)-1-phenylprop-2-en-1-one 3aj

In a glovebox, to an oven-dried 10 mL tube was added 2aj (74.0 mg, 0.2 mmol), sodium 4-(trifluoromethoxy)benzenesulfitinate (9.6 mg, 0.04 mmol, 20 mol%), Eosin Y (1.3 mg, 0.002 mmol, 1 mol%), KOPiv (28.0 mg, 0.2 mmol, 1 equiv.), MeCN/H$_2$O = 1:3 (0.05 M) and 1a (68.0 mg, 0.4 mmol, 2 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) with PE/EA = 5/1 (v/v) as eluent to afford the title compound as a colorless oil (31.7 mg, 58 % yield in total, a mixture of two diasteroisomers).

Characterization of the major isomer: $R_f = 0.48$ (PE/EA = 5/1 (v/v)). NMR Spectroscopy: $^1$H NMR (600 MHz, CDCl$_3$, 25 °C) δ 7.96–7.90 (m, 2H), 7.66–7.60 (m, 2H), 7.57–7.54 (m, 1H), 7.45–7.42 (m, 2H), 7.28 (t, J = 1.2 Hz, 1H), 5.84...
(d, J = 1.0 Hz, 1H), 5.71 (d, J = 0.8 Hz, 1H), 3.49 (dd, J = 14.3, 2.2 Hz, 1H), 3.03 (dd, J = 14.3, 10.9 Hz, 1H), 2.84–2.77 (m, 2H), 2.02–1.94 (m, 2H), 1.76–1.68 (m, 2H), 1.67–1.62 (m, 2H), 1.56–1.51 (m, 1H), 0.10 (s, 9H). 13C NMR (151 MHz, CDCl3, 25 ºC) δ 197.4, 152.8, 144.1, 138.4, 137.1, 132.6, 131.0, 130.4, 129.7, 128.4, 120.9, 120.3 (q, J = 257.8 Hz), 85.8, 57.7, 41.0, 40.0, 36.7, 29.5, 21.5, 2.3. 19F NMR (565 MHz, CDCl3, 25 ºC) δ −57.59. 29Si NMR (119 MHz, CDCl3, 25 ºC) δ 10.8.

IR (ATR): ν 3052, 1587, 1490, 1446, 1306, 1284, 1203, 1148, 1084, 984, 741, 693 cm−1. HRMS (ESI, m/z): calcd for C26H32F3O5SSi (M+H)+: 541.1686; found: 541.1678.

1-Phenyl-2-(((3-tosyl-1-((trimethylsilyl)oxy)cyclopentyl)methyl)prop-2-en-1-one)7j

In a glovebox, to an oven-dried 10 mL tube was added 2ab (60.0 mg, 0.2 mmol), sodium 4-methylbenzenesulinate (71.2 mg, 0.4 mmol, 2 equiv.), Eosin Y (1.3 mg, 0.02 mmol, 1 mol%), KOPiv (28.0 mg, 0.2 mmol, 1 equiv.), MeOH/H2O = 1:2 (0.075 M) and 1f (62.4 mg, 0.4 mmol, 2 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200–300 mesh) with PE/EA = 5/1 (v/v) to afford the title compound as a colorless oil (47.0 mg, 52 % yield in total, a mixture of two disteraosiomers).

Rf = 0.47 (PE/EA = 5/1 (v/v)). NMR Spectroscopy: 1H NMR (600 MHz, CDCl3, 25 ºC) δ 7.78–7.70 (m, 4H), 7.53 (ddt, J = 8.7, 7.0, 1.3 Hz, 1H), 7.44–7.38 (m, 2H), 7.33–7.29 (m, 2H), 5.82 (t, J = 1.1 Hz, 1H), 5.63 (dd, J = 1.1 Hz, 1H), 3.55 (dd, J = 9.9, 8.3, 6.3 Hz, 1H), 2.69–2.60 (m, 2H), 2.42 (s, 3H), 2.27–2.13 (m, 2H), 2.03 (dd, J = 13.3, 8.3, 1.5 Hz, 1H), 1.95–1.85 (m, 2H), 1.84–1.73 (m, 1H), 0.01 (s, 9H). 13C NMR (151 MHz, CDCl3, 25 ºC) δ 198.1, 144.7, 137.3, 135.7, 132.6, 130.1, 130.0, 128.5, 128.3, 128.0, 85.0, 62.9, 42.7, 40.1, 38.3, 25.0, 21.8, 2.0. 29Si NMR (119 MHz, CDCl3, 25 ºC) δ 10.9. IR (ATR): ν 3056, 2952, 1584, 1595, 1446, 1300, 1252, 1144, 1066, 838, 701 cm−1. HRMS (ESI, m/z): calcd for C25H33O4Si (M+H)+: 457.1863; found: 457.1864.
2-((3-((4-Fluorophenyl)sulfonyl)-1-((trimethylsilyloxy)cyclopentyl)methyl)-1-phenylprop-2-en-1-one 7k

In a glovebox, to an oven-dried 10 mL tube was added 2af (60.8 mg, 0.2 mmol), sodium 4-fluorobenzenesulfinate (72.8 mg, 0.4 mmol, 2 equiv.), Eosin Y (1.3 mg, 0.002 mmol, 1 mol%), KOPiv (28.0 mg, 0.2 mmol, 1 equiv.), MeOH/H₂O = 1:2 (0.05 M) and 1b (62.4 mg, 0.4 mmol, 2 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200 ~ 300 mesh) with PE/EA = 5/1 (v/v) to afford the title compound as a colorless oil (51.5 mg, 56% yield in total, a mixture of two diastereomers).

Rₐ = 0.53 (PE/EA = 5/1 (v/v)). NMR Spectroscopy: ¹H NMR (600 MHz, CDCl₃, 25 ºC) δ 7.86–7.76 (m, 4H), 7.57–7.54 (m, 1H), 7.48–7.41 (m, 2H), 7.22–7.15 (m, 2H), 5.88 (d, J = 1.0 Hz, 1H), 5.65 (d, J = 1.0 Hz, 1H), 3.68 (tdd, J = 9.7, 7.9, 5.7 Hz, 1H), 2.96–2.86 (m, 2H), 2.15 (ddt, J = 13.4, 7.5, 5.5 Hz, 1H), 2.10–2.00 (m, 2H), 1.93 (dd, J = 13.5, 7.9, 1.5 Hz, 1H), 1.86–1.77 (m, 2H), 0.02 (s, 9H). ¹³C NMR (151 MHz, CDCl₃, 25 ºC) δ 197.81, 166.71, 165.01, 145.05, 137.21, 134.78 (d, J = 3.3 Hz), 132.66, 131.29 (d, J = 9.6 Hz), 129.23 (d, J = 257.9 Hz), 128.19, 116.71 (d, J = 22.4 Hz), 84.93, 63.06, 42.60, 40.18, 38.27, 24.85, 2.04. ²⁹Si NMR (119 MHz, CDCl₃, 25 ºC) δ 10.7. ¹⁹F NMR (565 MHz, CDCl₃, 25 ºC) δ –102.4–108.2 (m). IR (ATR): ν3075, 2952, 1654, 1591, 1490, 1312, 1248, 1144, 1060, 834, 730 cm⁻¹. HRMS (ESI, m/z): calcd for C₂₄H₃₀FO₄SSi (M+H)+: 461.1613; found: 461.1612.

2-((3-((4-Methoxyphenyl)sulfonyl)-1-((trimethylsilyloxy)cyclopentyl)methyl)-1-phenylprop-2-en-1-one 7l

In a glovebox, to an oven-dried 10 mL tube was added 2ae (63.2 mg, 0.2 mmol), sodium 4-fluorobenzenesulfinate (77.6 mg, 0.4 mmol, 2 equiv.), Eosin Y (1.3 mg, 0.002 mmol, 1 mol%), KOPiv (28.0 mg, 0.2 mmol, 1 equiv.),
MeOH/H₂O = 1:2 (0.075 M) and If (62.4 mg, 0.4 mmol, 2 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (200~300 mesh) with PE/EA = 5/1 (v/v) as eluent to afford the title compound as a colorless oil (55.8 mg, 59 % yield in total, a mixture of two diastereoisomers).

Rf = 0.28 (PE/EA = 5/1 (v/v)). NMR Spectroscopy: 1H NMR (600 MHz, CDCl₃, 25 °C) δ 7.81–7.78 (m, 2H), 7.76–7.72 (m, 2H), 7.56–7.53 (m, 1H), 7.47–7.42 (m, 2H), 6.99–6.96 (m, 2H), 5.87 (d, J = 1.0 Hz, 1H), 5.63 (d, J = 1.0 Hz, 1H), 3.87 (s, 3H), 3.67 (tdd, J = 9.6, 8.0, 5.8 Hz, 1H), 2.99–2.83 (m, 2H), 2.17–2.00 (m, 3H), 1.96 (ddd, J = 13.6, 8.0, 1.6 Hz, 1H), 1.83–1.77 (m, 2H), 0.01 (s, 9H). 13C NMR (151 MHz, CDCl₃, 25 °C) δ 197.9, 163.7, 145.2, 137.3, 132.6, 130.6, 130.2, 130.1, 128.3, 128.0, 114.5, 85.0, 63.1, 55.8, 42.7, 40.2, 38.3, 25.0, 2.0. 29Si NMR (119 MHz, CDCl₃, 25 °C) δ 10.5.

IR (ATR): ν 3063, 2955, 2844, 1658, 1595, 1498, 1461, 1297, 1140, 1088, 1025, 834, 699 cm⁻¹. HRMS (ESI, m/z): calcd for C₂₅H₃₃O₅Si (M+H)+: 473.1813; found: 473.1822.

Rf = 0.30 (PE/EA = 5/1 (v/v)). NMR Spectroscopy: 1H NMR (600 MHz, CDCl₃, 25 °C) δ 7.82–7.77 (m, 2H), 7.76–7.71 (m, 2H), 7.55–7.51 (m, 1H), 7.45–7.39 (m, 2H), 7.00–6.95 (m, 2H), 5.82 (d, J = 1.2 Hz, 1H), 5.63 (d, J = 1.1 Hz, 1H), 3.86 (s, 3H), 3.53 (tdd, J = 9.9, 8.6, 6.2 Hz, 1H), 2.64 (q, J = 13.4 Hz, 2H), 2.26–2.12 (m, 2H), 2.04 (ddd, J = 13.3, 8.3, 1.5 Hz, 1H), 1.95–1.86 (m, 2H), 1.83–1.74 (m, 1H), 0.01 (s, 9H). 13C NMR (151 MHz, CDCl₃, 25 °C) δ 198.1, 163.8, 144.7, 137.3, 132.5, 130.8, 130.1, 129.9, 128.2, 128.2, 114.5, 83.3, 61.7, 55.8, 42.5, 39.2, 37.9, 24.1, 2.1. 29Si NMR (119 MHz, CDCl₃, 25 °C) δ 10.85. IR (ATR): ν 3060, 2922, 2847, 1651, 1595, 1498, 1461, 1297, 1259, 1140, 1088, 1025, 834, 699 cm⁻¹. HRMS (ESI, m/z): calcd for C₂₅H₃₃O₅Si (M+H)+: 473.1813; found: 473.1812.

4. Down-stream transformations of products

Phenyl(7-(phenylsulfonyl)-3a-((trimethylsilyl)oxy)octahydro-1H-inden-5-yl)methanone (8)

In a glovebox, to an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was added 3a (0.05 mmol, 22.8 mg). THF (1 mL, dry), LiHMDS (0.1 mL, 1 M in THF, 2.0 equiv.) The tube was then sealed and moved out of the glovebox, and the resulting mixture was stirred at 70 °C in a heating block for 12 h, after which the mixture was cooled to room temperature. The reaction mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300~400 mesh) with PE/EA=5/1 (v/v) as eluent to afford the title compound as a colorless oil (16.4 mg, 82 % yield).

Rf = 0.38 (PE/EA = 5/1 (v/v)). NMR Spectroscopy: 1H NMR (600 MHz, CDCl₃, 25 °C) δ 8.02–7.97 (m, 2H), 7.91–
Phenyl((1S,5S)-1-(phenylsulfonyl)-5-((trimethylsilyl)oxy)bicyclo[3.2.1]octan-3-yl)methanone (9)

![Diagram of the reaction](image_url)

In a glovebox, to an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was added 7a (0.05 mmol, 22.1 mg), THF (1 mL, dry), LiHDMDS (0.1 mL, 1 M in THF, 2.0 equiv.) The tube was then sealed and moved out of the glovebox, and the resulting mixture was stirred at 70 °C in a heating block for 12 h, after which the mixture was cooled to room temperature. The reaction mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The crude product was purified with column chromatography on silica gel (300–400 mesh) with PE/EA=5/1 (v/v) as eluent to afford the title compound as a colorless oil (16.3 mg, 74 % yield).

Rf = 0.40 (PE/EA = 5/1 (v/v)). NMR Spectroscopy: 1H NMR (600 MHz, CDCl3, 25 °C) δ 7.87–7.82 (m, 2H), 7.73–7.68 (m, 2H), 7.68–7.62 (m, 1H), 7.57–7.51 (m, 3H), 7.46–7.41 (m, 2H), 3.71–3.65 (m, 1H), 2.50–2.44 (m, 2H), 2.41–2.31 (m, 2H), 2.12 (ddd, J = 13.5, 9.4, 2.2 Hz, 1H), 2.07–2.01 (m, 1H), 1.76 (ddd, J = 8.2, 6.6, 2.6 Hz, 2H), 1.65–1.50 (m, 2H), 0.08 (s, 9H). 13C NMR (151 MHz, CDCl3, 25 °C) δ 202.3, 136.2, 136.1, 133.9, 132.9, 130.0, 129.1, 128.9, 128.5, 80.0, 68.1, 44.9, 40.2, 39.7, 35.5, 30.6, 27.0, 2.3. 29Si NMR (119 MHz, CDCl3, 25 °C) δ 12.1. IR (ATR): ν 3063, 2959, 1684, 1595, 1446, 1345, 1304, 1252, 1222, 1148, 842 cm⁻¹. HRMS (ESI, m/z): calcd for C24H30O3Si (M+H)⁺: 443.1707; found: 443.1717.

5. Mechanism study

5.1 Reaction of 1a and 2a in the presence of TEMPO.

![Diagram of the reaction](image_url)

In a glovebox, to an oven-dried 10 mL tube was added 2a (28.6 mg, 0.1 mmol), PhSO2Na (3.2 mg, 0.02 mmol, 0.2 equiv.), Eosin Y (0.65 mg, 0.001 mmol, 1 mol%), KOPiv (14.2 mg, 0.1 mmol, 1 equiv.), TEMPO (15.6 mg, 0.1 mmol, 1 equiv.). MeCN/H2O =1:3 (0.067 M) white LEDs (6 W), rt, 12 h

40% conv. of 2a, 0% yield of 3a X, detected by HRMS.
(30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The conversion of 2a and yield of 3a were determined by $^1$H NMR analysis of the unpurified mixture with BrCH$_2$CH$_2$Br as an internal standard.

5.2 Time profile of the transformation with the light ON/OFF over time.

Supplementary Figure 3: Time profile of the transformation with the light ON/OFF over time of 3a.

In a glovebox, to 6 identical oven-dried 10 mL tubes respectively add 2a (28.6 mg, 0.1 mmol), PhSO$_2$Na (3.2 mg, 0.02 mmol, 0.2 equiv.), Eosin Y (0.65 mg, 0.001 mmol, 1 mol%), KOPiv (14.2 mg, 0.1 mmol, 1 equiv.), MeCN/H$_2$O = 1:3 (0.067 M) and 1a (34.0 mg, 0.2 mmol, 2 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps. All the reactions were stirred under blue light irradiation at ambient temperature for the 10 minutes. Then the light was turned off. Remove one of the tubes. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The remaining mixture was stirred in the absence of light for an additional 10 minutes. Then remove one of the tubes. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. NMR analysis was performed every 10 minutes until the reaction time reached 1 h. The conversion of 2a and yield of 3a were determined by $^1$H NMR analysis of the unpurified mixture with BrCH$_2$CH$_2$Br as an internal standard.
**Supplementary Figure 4: Light and darkness control experiment**

In a glovebox, to three identical oven-dried 10 mL tubes respectively added 2a (28.6 mg, 0.1 mmol), PhSO₂Na (3.2 mg, 0.02 mmol, 0.2 equiv.), Eosin Y (0.65 mg, 0.001 mmol, 1 mol%), KOPiv (14.2 mg, 0.1 mmol, 1 equiv.). MeCN/H₂O =1:3 (0.067 M) and 1a (34.0 mg, 0.2 mmol, 2 equiv.) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps. All the reactions were stirred under white light irradiation at ambient temperature for the 10 minutes. Then the light was turned off. Remove one of the tubes. The resulting mixture of reaction 1 was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The remaining mixtures of reactions 2 and 3 were stirred in the absence of light for an additional 1 hour and 2 hours. Then remove the tube. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The conversion of 2a and yield of 3a were determined by ¹H NMR analysis of the unpurified mixture with BrCH₂CH₂Br as an internal standard.

### 5.3 Determination of Quantum Yield

In a glovebox, to an oven-dried 10 mL tube was added 2a (28.6 mg, 0.1 mmol), Eosin Y (1.3 mg, 0.002 mmol, 2 mol%), dry DCM (2 mL) and KOPiv (14.2 mg, 0.1 mmol, 1.0 equiv.) and MeCN (1 mL) and 1a (34.0 mg, 0.2 mmol, 2 equiv.) and H₂O (3 mL), sequentially. The tube was sealed, the sample was irradiated (λ = 460 nm, slit width = 3.0 mm, slit height 5.0 mm with intensity of 0.662 mW·cm⁻²) for 10800 s. After irradiation, the yield of product formed was determined by ¹H NMR with BrCH₂CH₂Br as an internal standard. The quantum yield was determined as follows.

$$\phi = \frac{\text{Mole number for product}}{\text{Mole number for absorption of photons}} = 1.46$$

\(\phi\): the mole number of the product 3a; t: reaction time (10800 s); NA: 6.02×10²³/mol; f: 1-10⁻⁸ (460 nm, A = 4.8); P: P = E*S (E: illumination intensity, E = 0.662 mW/cm²; S: the area that irradiated S = 0.15 cm²); λ: wavelength (λ = 4.6 ×10⁻⁷ m); h: planck constant (h = 6.626 ×10⁻³⁴ J*s); c: velocity of light (c = 3 ×10⁸ m/s). This result reveals that the radical chain process is not main pathway.
5.4 Experiments on the light-induced decomposition of 1a

![Supplementary Figure 5: Experiments on the light-induced decomposition of 1a](image)

In a glovebox, 0.5 mL CDCl₃ was added to the NMR tubes labeled 1, 2, and 3, followed by 1a (0.05 mmol, 8.5 mg) and BrCH₂CH₂Br (0.025 mmol, 4.7 mg). The No. 1 NMR tube is completely covered with tin foil. Eosin Y (0.0005 mmol, 0.32 mg) was added to the No. 2 NMR tube. The No. 3 NMR tube is only added by 1a (0.05 mmol, 8.5 mg) and BrCH₂CH₂Br (0.025 mmol, 4.7 mg). Illuminate the NMR tubes with a white LED lamp. The conversion of 1a was measured at 2 h, 6 h and 30 h respectively. The conversion of 1a were determined by ¹H NMR analysis of the unpurified mixture with BrCH₂CH₂Br as an internal standard.

5.5 Luminescence Quenching Experiments

![Supplementary Figure 6: Eosin Y emission quenching by 2a](image)
Fluorescence spectra was collected on Agilent Fluorescence Spectrophotometer G9800AS24 for all experiments. All Eosin Y solutions were excited at 350 nm and the emission intensity was collected at 550 nm. In a typical experiment, the emission spectrum of a 1×10^{-4} M solution of Eosin Y in MeOH/H_{2}O=1/2 (v/v) was collected. The significant decrease of Eosin Y luminescence could be observed in the presence of substrate 2a.

**Supplementary Figure 7:** Eosin Y emission quenching by PhSO_{2}Na

Fluorescence spectra was collected on Agilent Fluorescence Spectrophotometer G9800AS24 for all experiments. All Eosin Y solutions were excited at 350 nm and the emission intensity was collected at 550 nm. In a typical experiment, the emission spectrum of a 1×10^{-3} M solution of Eosin Y in MeCN/H_{2}O=1/2 (v/v) was collected. The significant decrease of Eosin Y luminescence could be observed in the presence of substrate PhSO_{2}Na.

**Supplementary Figure 8:** 1a emission quenching by Eosin Y
Fluorescence spectra was collected on Agilent Fluorescence Spectrophotometer G9800AS24 for all experiments. All 1a solutions were excited at 350 nm and the emission intensity was collected at 416 nm. In a typical experiment, the emission spectrum of a $1 \times 10^{-3}$ M solution of 1a in MeCN was collected. The significant decrease of 1a luminescence could be observed in the presence of substrate Eosin Y.

5.6 Cyclic voltammograms

![Cyclic voltammogram study for 1a in MeCN](image)

|        | SCE  |
|--------|------|
| $E_p$  | 1.183 V |
| $E_{p/2}$ | 1.226 V |
| $E_s$  | 1.277 V |

Supplementary Figure 9: Cyclic voltammogram study for 1a in MeCN

Cyclic voltammetry experiments were performed on a CH Instruments Electrochemical Analyzer (CHI660E model) at room temperature under nitrogen atmosphere. The 0.1 M MeCN solution of 1a was prepared with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte, using a glassy carbon working electrode, a Pt counter electrode, and an SCE reference electrode. Scan Rate (V/s) = 0.10.
5.7 UV/Vis of 1a and Eosin Y.

**Supplementary Figure 10:** Individual absorption Spectra of acylsilane 1a, Eosin Y (0.005 M in MeCN/H2O = 1/3).

The UV-Vis spectra of 1a and 2a in DCM were collected by using the following parameter set: scan rate 600 nm·min⁻¹, band width 2.0 nm, baseline correction.

5.8 Reaction in the presence of E-stilbene instead of Eosin Y.

In a glovebox, to an oven-dried 10 mL tube was added 2a (28.6 mg, 0.1 mmol), PhSO₂Na (3.2 mg, 0.02 mmol, 0.2 equiv.), E-stilbene (18.0 mg, 0.1 mmol, 1 equiv.), KOPiv (14.2 mg, 0.1 mmol, 1 equiv.), MeCN (1 mL) and 1a (34.0 mg, 0.2 mmol, 2 equiv.) and H₂O (3 mL) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The conversion of 2a and stereochemical scrambling/conversion to Z-stilbene were determined by ¹H NMR analysis of the unpurified mixture with BrCH₂CH₂Br as an internal standard.

In a glovebox, to an oven-dried 10 mL tube was added 2a (28.6 mg, 0.1 mmol), E-stilbene (18.0 mg, 0.1 mmol, 1
equiv.), MeCN (1 mL) and 1a (34.0 mg, 0.2 mmol, 2 equiv.) and H₂O (3 mL) sequentially. The tube was sealed, then irradiated with 6 W white LED lamps. The mixture was stirred under white light irradiation at ambient temperature for the 12 h. Then the light was turned off. The resulting mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The organic phase was concentrated under reduced pressure. The conversion of 2a and stereochemical scrambling/conversion to Z-stilbene were determined by ¹H NMR analysis of the unpurified mixture with BrCH₂CH₂Br as an internal standard.

5.9 Transient absorption spectra of 1a/Eosin Y/1a+ Eosin Y.

**Supplementary Figure 11:** Transient absorption spectra of 1a/Eosin Y/1a+ Eosin Y.

The nanosecond transient absorption spectra were measured using Laser Flash Photolysis Spectrometer (LP980-KS, Edinburgh Instruments, UK). The samples were pumped by the third harmonic output of a frequency-doubled Q-switched Nd:YAG laser at 355 nm (LAB 190, Spectraphysics), with pulse energy at 10 mJ/pulse. The samples were probed by a pulsed Xe lamp. The transient absorption spectra were recorded by an iStar CCD camera (Andor Technology). The transient absorption kinetics were recorded by a R928 PMT (Hamamatsu Photonics) connected to a 500 MHz 5 GS/s oscilloscope (Tektronix TDS 3052). All samples were carried out at room temperature, in a standard 1.0 cm path length quartz cell cuvette with screwed cap and degassed with Ar for 30 min before the measurement.

Transient absorption spectra observed after laser excitation (λex = 355 nm) of a) 1a (1.0 × 10⁻³ M); b) Eosin Y (1.0 × 10⁻⁴ M); c) 1a (1 × 10⁻³ M)+Eosin Y (1.0 × 10⁻⁴ M)
5.10 Proposed mechanism of the synthesis of $\gamma$-substituted cyclopentanol derivatives.

**Supplementary Figure 12**: Proposed mechanism of the synthesis of $\gamma$-substituted cyclopentanol derivatives.
5.10 NOE of 7a

Supplementary Figure 13: NOE spectra of 7a

H11 is not correlated with H13, suggesting that the two H atoms are not on the same plane, indicating that the configuration of the product is trans.
5.11 NOE of 7a'

Supplementary Figure 14: NOE spectra of 7a'

H11 is correlated with H13, suggesting that these H atoms are located on the same plane, indicating that the product is a cis-structure.
5.12 COSY of 8.

Supplementary Figure 15: COSY spectra of 8

5.13 NOE of 8.

Supplementary Figure 16: NOE spectra of 8
According to the COSY: H18 is correlated with H20.

According to the NOE: H18 is not correlated with H19, suggesting that these H atoms are located on the different plane. H18 is correlated with H20, suggesting that these two H atoms are located on the same plane.

5.14 ORTEP diagram of compound 3j.

Supplementary Figure 17: ORTEP diagram of compound 3j. (CCDC 2076884)

Table 1. Crystal data and structure refinement for final-zyx-9-147-250k-20210113.

| Characteristic                        | Value                        |
|--------------------------------------|------------------------------|
| Identification code                  | zyx-9-147-250k-20210113      |
| Empirical formula                    | C25 H31 F O4 S Si            |
| Formula weight                       | 474.65                       |
| Temperature                          | 249.98(10) K                |
| Wavelength                           | 1.54184 Å                    |
| Crystal system                       | Triclinic                    |
| Space group                          | P-1                          |
| Unit cell dimensions                 | a = 9.46640(10) Å            |
|                                     | α = 78.518(2)°               |
|                                     | b = 11.3418(2) Å             |
|                                     | β = 68.875(2)°               |
|                                     | c = 12.7977(2) Å             |
|                                     | γ = 78.0470(10)°             |
Volume \( 1242.20(4) \text{ Å}^3 \)

\( Z \quad 2 \)

Density (calculated) \( 1.269 \text{ Mg/m}^3 \)

Absorption coefficient \( 1.919 \text{ mm}^{-1} \)

\( F(000) \quad 504 \)

Crystal size \( 0.08 \times 0.06 \times 0.04 \text{ mm}^3 \)

Theta range for data collection \( 3.738 \text{ to } 75.298^\circ \).

Index ranges \(-11 \leq h \leq 11, -14 \leq k \leq 14, -15 \leq l \leq 15\)

Reflections collected \( 44512 \)

Independent reflections \( 4930 \) [\( R(\text{int}) = 0.0468 \)]

Completeness to theta = 67.684° \( 98.3\% \)

Absorption correction Semi-empirical from equivalents

Max. and min. transmission 1.00000 and 0.84796

Refinement method Full-matrix least-squares on \( F^2 \)

Data / restraints / parameters 4930 / 0 / 413

Goodness-of-fit on \( F^2 \) 1.053

Final R indices \([I>2\sigma(I)]\) \( R1 = 0.0441, wR2 = 0.1180 \)

R indices (all data) \( R1 = 0.0454, wR2 = 0.1189 \)

Extinction coefficient \( \text{n/a} \)

Largest diff. peak and hole \( 0.389 \) and \( -0.604 \text{ e.Å}^{-3} \)

Table 2. Atomic coordinates \((x \times 10^4)\) and equivalent isotropic displacement parameters \((\text{Å}^2 x 10^3)\)

for final-zyx-9-147-250k-20210113. \( U(\text{eq}) \) is defined as one third of the trace of the orthogonalized \( U^{ij} \) tensor.

|       | x      | y      | z      | U(eq)  |
|-------|--------|--------|--------|--------|
| S(1)  | 6001(1)| 8203(1)| 7538(1)| 49(1)  |
| Si(1) | -306(1)| 10674(1)| 7987(1)| 43(1)  |
| O(2)  | 1145(1)| 9560(1)| 7860(1)| 45(1)  |
| F(1)  | 3334(2)| 5249(1)| 6449(1)| 69(1)  |
| O(1)  | 2887(2)| 5723(1)| 9480(1)| 58(1)  |
| O(3)  | 6505(2)| 9155(1)| 6627(1)| 65(1)  |
| O(4)  | 6435(2)| 8108(2)| 8520(2)| 72(1)  |
| C(16) | 3970(2)| 8340(2)| 7995(2)| 44(1)  |
| C(2)  | 3286(2)| 8079(2)| 7173(1)| 40(1)  |
| C(1)  | 1520(2)| 8333(1)| 7604(1)| 40(1)  |
| C(10) | 3172(2)| 4285(2)| 8293(2)| 47(1)  |
|   |   |   |   |   |
|---|---|---|---|---|
| C(9) | 2412(2) | 5430(2) | 8816(2) | 46(1) |
| C(6) | 710(2)   | 7506(2) | 8672(2) | 47(1) |
| C(5) | 1152(2)  | 8236(2) | 6560(2) | 49(1) |
| C(7) | 1048(2)  | 6163(2) | 8562(2) | 46(1) |
| C(17) | 6703(2)  | 6804(2) | 6984(2) | 52(1) |
| C(11) | 3602(2)  | 4228(2) | 7151(2) | 51(1) |
| C(15) | 3552(2)  | 3231(2) | 8964(2) | 57(1) |
| C(3) | 3702(2)  | 8829(2) | 5997(2) | 53(1) |
| C(13) | 4699(2)  | 2151(2) | 7350(2) | 67(1) |
| C(14) | 4294(2)  | 2172(2) | 8502(2) | 68(1) |
| C(24) | -1947(3) | 10321(2) | 9274(2) | 67(1) |
| C(22) | 6543(2)  | 5720(2) | 7705(2) | 62(1) |
| C(12) | 4364(2)  | 3191(2) | 6663(2) | 62(1) |
| C(8) | 111(2)   | 5595(2) | 8351(2) | 64(1) |
| C(18) | 7425(3)  | 6818(2) | 5828(2) | 68(1) |
| C(25) | 457(3)   | 11999(2) | 8115(3) | 68(1) |
| C(4) | 2414(3)  | 8769(3) | 5555(2) | 67(1) |
| C(23) | -985(3)  | 11063(2) | 6756(2) | 66(1) |
| C(21) | 7111(3)  | 4631(2) | 7244(3) | 83(1) |
| C(20) | 7817(3)  | 4647(3) | 6098(4) | 94(1) |
| C(19) | 7984(3)  | 5725(3) | 5381(3) | 88(1) |

Table 3. Bond lengths [Å] and angles [°] for final-zyx-9-147-250k-20210113.
S(1)-O(3) 1.4360(14) C(13)-C(14) 1.387(4)
S(1)-O(4) 1.4352(15) C(13)-C(12) 1.378(3)
S(1)-C(16) 1.7793(18) C(13)-H(13) 0.97(3)
S(1)-C(17) 1.769(2) C(14)-H(14) 0.88(3)
Si(1)-O(2) 1.6470(12) C(24)-H(24A) 0.99(3)
Si(1)-C(24) 1.854(2) C(24)-H(24B) 1.01(3)
Si(1)-C(25) 1.854(2) C(24)-H(24C) 1.03(4)
Si(1)-C(23) 1.851(2) C(22)-C(21) 1.396(4)
O(2)-C(1) 1.4361(19) C(22)-H(22) 0.91(2)
F(1)-C(11) 1.357(2) C(12)-H(12) 0.94(3)
O(1)-C(9) 1.218(2) C(8)-H(8A) 0.95(3)
C(16)-C(2) 1.519(2) C(8)-H(8B) 0.94(3)
C(16)-H(16A) 0.99(2) C(18)-C(19) 1.391(4)
C(16)-H(16B) 0.92(2) C(18)-H(18) 0.99(3)
C(2)-C(1) 1.543(2) C(25)-H(25A) 0.96(3)
C(2)-C(3) 1.532(2) C(25)-H(25B) 0.91(3)
C(2)-H(2) 0.974(19) C(25)-H(25C) 1.00(3)
C(1)-C(6) 1.539(2) C(4)-H(4A) 0.96(3)
C(1)-C(5) 1.526(2) C(4)-H(4B) 1.05(3)
C(10)-C(9) 1.504(2) C(23)-H(23A) 0.94(3)
C(10)-C(11) 1.380(3) C(23)-H(23B) 0.96(3)
C(10)-C(15) 1.390(3) C(23)-H(23C) 0.97(3)
C(9)-C(7) 1.489(2) C(21)-C(20) 1.373(5)
C(6)-C(7) 1.514(2) C(21)-H(21) 0.87(3)
C(6)-H(6A) 0.98(2) C(20)-C(19) 1.375(5)
C(6)-H(6B) 1.04(3) C(20)-H(20) 0.93(3)
C(5)-C(4) 1.526(3) C(19)-H(19) 0.98(3)
C(5)-H(5A) 0.98(2)
C(5)-H(5B) 0.98(2) O(3)-S(1)-C(16) 109.38(9)
C(7)-C(8) 1.324(3) O(3)-S(1)-C(17) 107.48(10)
C(17)-C(22) 1.382(3) O(4)-S(1)-O(3) 117.96(10)
C(17)-C(18) 1.387(3) O(4)-S(1)-C(16) 107.60(9)
C(11)-C(12) 1.382(3) O(4)-S(1)-C(17) 107.92(10)
C(15)-C(14) 1.385(3) C(17)-S(1)-C(16) 105.86(8)
C(15)-H(15) 0.94(2) O(2)-Si(1)-C(24) 111.02(9)
C(3)-C(4) 1.536(3) O(2)-Si(1)-C(25) 104.16(9)
C(3)-H(3A) 1.01(2) O(2)-Si(1)-C(23) 114.24(10)
C(3)-H(3B) 0.95(3) C(25)-Si(1)-C(24) 110.11(13)
| Bond                        | Angle (°) |
|-----------------------------|-----------|
| C(7)-C(8)-H(8B)             | 121.7(15) |
| H(8A)-C(8)-H(8B)            | 117(2)    |
| C(17)-C(18)-C(19)           | 119.7(3)  |
| C(17)-C(18)-H(18)           | 121.6(16) |
| C(19)-C(18)-H(18)           | 118.7(16) |
| Si(1)-C(25)-H(25A)          | 114.5(17) |
| Si(1)-C(25)-H(25B)          | 103.0(17) |
| Si(1)-C(25)-H(25C)          | 110.9(16) |
| H(25A)-C(25)-H(25B)         | 104(2)    |
| H(25A)-C(25)-H(25C)         | 110(2)    |
| C(5)-C(4)-C(3)              | 106.57(16) |
| C(5)-C(4)-H(4A)             | 110.0(17) |
| C(5)-C(4)-H(4B)             | 109.2(18) |
| C(3)-C(4)-H(4A)             | 108.6(17) |
| C(3)-C(4)-H(4B)             | 110.5(18) |
| H(4A)-C(4)-H(4B)            | 112(2)    |
| Si(1)-C(23)-H(23A)          | 106.3(17) |
| Si(1)-C(23)-H(23B)          | 115.5(18) |
| Si(1)-C(23)-H(23C)          | 107.8(19) |
| H(23A)-C(23)-H(23B)         | 101(2)    |
| H(23A)-C(23)-H(23C)         | 112(3)    |
| H(23B)-C(23)-H(23C)         | 114(3)    |
| C(22)-C(21)-H(21)           | 117.8(19) |
| C(20)-C(21)-C(22)           | 120.3(3)  |
| C(20)-C(21)-H(21)           | 121.8(18) |
| C(21)-C(20)-C(19)           | 121.2(3)  |
| C(21)-C(20)-H(20)           | 122.2(19) |
| C(19)-C(20)-H(20)           | 116.6(19) |
| C(18)-C(19)-H(19)           | 124.6(19) |
| C(20)-C(19)-C(18)           | 119.2(3)  |
| C(20)-C(19)-H(19)           | 116.1(18) |
Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (Å² x 10³) for final-zyx-9-147-250k-20210113.

The anisotropic displacement factor exponent takes the form: 

\[-2\pi²[ h² a*² U^{11} + ... + 2 h k a* b* U^{12} ]\]

|      | \(U^{11}\) | \(U^{22}\) | \(U^{33}\) | \(U^{23}\) | \(U^{13}\) | \(U^{12}\) |
|------|-----------|-----------|-----------|-----------|-----------|-----------|
| S(1) | 46(1)     | 43(1)     | 65(1)     | 1(1)      | -27(1)    | -13(1)    |
| Si(1)| 41(1)     | 38(1)     | 55(1)     | -5(1)     | -22(1)    | -3(1)     |
| O(2) | 44(1)     | 39(1)     | 53(1)     | -9(1)     | -20(1)    | 0(1)      |
| F(1) | 95(1)     | 53(1)     | 56(1)     | -2(1)     | -30(1)    | 1(1)      |
| O(1) | 64(1)     | 58(1)     | 58(1)     | -2(1)     | -29(1)    | -10(1)    |
| O(3) | 58(1)     | 50(1)     | 83(1)     | 9(1)      | -20(1)    | -22(1)    |
| O(4) | 74(1)     | 79(1)     | 86(1)     | -5(1)     | -52(1)    | -20(1)    |
| C(16)| 46(1)     | 43(1)     | 44(1)     | -3(1)     | -18(1)    | -8(1)     |
| C(2) | 37(1)     | 41(1)     | 39(1)     | -5(1)     | -13(1)    | -4(1)     |
| C(1) | 40(1)     | 36(1)     | 44(1)     | -6(1)     | -14(1)    | -2(1)     |
| C(10)| 38(1)     | 43(1)     | 57(1)     | 1(1)      | -17(1)    | -8(1)     |
| C(9) | 42(1)     | 45(1)     | 46(1)     | 5(1)      | -12(1)    | -12(1)    |
| C(6) | 41(1)     | 44(1)     | 50(1)     | -4(1)     | -9(1)     | -4(1)     |
| C(5) | 52(1)     | 49(1)     | 53(1)     | -8(1)     | -27(1)    | -3(1)     |
| C(7) | 39(1)     | 43(1)     | 52(1)     | -1(1)     | -11(1)    | -7(1)     |
| C(17)| 36(1)     | 48(1)     | 76(1)     | -1(1)     | -26(1)    | -6(1)     |
| C(11)| 50(1)     | 44(1)     | 61(1)     | -5(1)     | -21(1)    | -4(1)     |
| C(15)| 45(1)     | 53(1)     | 67(1)     | 7(1)      | -20(1)    | -8(1)     |
| C(3) | 52(1)     | 60(1)     | 42(1)     | 4(1)      | -14(1)    | -10(1)    |
| C(13)| 45(1)     | 48(1)     | 99(2)     | -12(1)    | -15(1)    | -2(1)     |
| C(14)| 48(1)     | 44(1)     | 103(2)    | 15(1)     | -28(1)    | -6(1)     |
| C(24)| 51(1)     | 67(1)     | 72(1)     | -14(1)    | -10(1)    | -1(1)     |
| C(22)| 44(1)     | 49(1)     | 94(2)     | 4(1)      | -29(1)    | -8(1)     |
| C(12)| 56(1)     | 55(1)     | 74(1)     | -16(1)    | -17(1)    | -5(1)     |
| C(8) | 48(1)     | 50(1)     | 98(2)     | -2(1)     | -32(1)    | -10(1)    |
| C(18)| 52(1)     | 65(1)     | 81(2)     | -11(1)    | -21(1)    | 4(1)      |
| C(25)| 66(1)     | 48(1)     | 101(2)    | -12(1)    | -41(1)    | -8(1)     |
| C(4) | 62(1)     | 96(2)     | 42(1)     | -2(1)     | -22(1)    | -9(1)     |
| C(23)| 74(2)     | 56(1)     | 78(2)     | -4(1)     | -46(1)    | 2(1)      |
Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for final-zyx-9-147-250k-20210113.

|      | x     | y     | z     | U(eq) |
|------|-------|-------|-------|-------|
| H(6A)| 970(20)| 7633(18)| 9313(17)| 47(5) |
| H(2) | 3620(20)| 7226(18)| 7066(15)| 43(5) |
| H(5A)| 1260(20)| 7360(20)| 6535(17)| 52(5) |
| H(16A)| 3700(20)| 7782(19)| 8720(18)| 54(5) |
| H(15) | 3290(30)| 3260(20)| 9744(19)| 59(6) |
| H(5B) | 100(30)| 8620(20)| 6619(18)| 58(6) |
| H(16B)| 3670(30)| 9140(20)| 8126(18)| 60(6) |
| H(6B) | -460(30)| 7790(20)| 8840(20)| 70(7) |
| H(14) | 4480(30)| 1480(20)| 8930(20)| 72(7) |
| H(13) | 5230(30)| 1420(20)| 7010(20)| 73(7) |
| H(3A) | 4770(30)| 8470(20)| 5533(19)| 65(6) |
| H(12) | 4650(30)| 3220(30)| 5870(20)| 85(8) |
| H(3B) | 3720(30)| 9640(30)| 6090(20)| 80(8) |
| H(23A)| -100(30)| 11110(20)| 6110(20)| 83(8) |
| H(24A)| -1590(40)| 10100(30)| 9940(30)| 104(10)|
| H(23B)| -1400(30)| 10430(30)| 6610(20)| 91(9) |
| H(23C)| -1660(40)| 11840(30)| 6830(30)| 108(10)|
| H(24B)| -2790(40)| 11030(30)| 9400(20)| 99(9) |
| H(24C)| -2400(40)| 9610(30)| 9190(30)| 110(10)|
| H(22) | 6130(20)| 5736(18)| 8468(18)| 47(6) |
| H(25A)| 990(30)| 11840(30)| 8650(20)| 90(9) |
| H(18) | 7560(30)| 7590(30)| 5310(20)| 85(8) |
| H(25B)| 1210(30)| 12120(30)| 7440(20)| 75(8) |
| H(21) | 6970(30)| 3950(30)| 7700(20)| 80(8) |
| H(4A) | 2810(30)| 8240(30)| 4980(20)| 86(8) |
| H(20) | 8190(40)| 3940(30)| 5760(30)| 99(10)|
| H(25C)| -370(30)| 12710(30)| 8290(20)| 84(8)|
6. Computational Details

Computational methods

All density functional theory (DFT) calculations were carried out using the Gaussian 16 software package.\[^5\] All geometries were optimized using the M06-2X functional\[^6\] with a basis set of 6-31G(d) for all atoms. Frequencies were calculated for all the stationary points to confirm if each optimized structure is a local minimum on the respective potential energy surface or a transition state structure with only one imaginary frequency. Solvation energy correction was calculated in water solvent with the SMD continuum solvation model\[^7\] based on the gas phase optimized geometries. The M06-2X functional with a basis set of 6-311+G(d,p) for all atoms was used for single point energy calculations. The 3D structures were plot using CYLview.\[^8\]

DFT study of 1f involved Cascade Cyclization of Alkene-tethered Acylsilanes and Allylic Sulfones
**Supplementary Figure 18:** DFT study of 1f involved Cascade Cyclization of Alkene-tethered Acylsilanes and Allylic Sulfones

**Cartesian coordinates (Å) and energies of optimized structures**

**Supplementary Table 7:** Cartesian coordinates of 1a

M062X SCF energy: -718.25357354 a.u.
M062X enthalpy: -717.984996 a.u.
M062X free energy: -718.048885 a.u.
M062X SCF energy in solution: -718.42153480 a.u.
M062X enthalpy in solution: -718.152957 a.u.
M062X free energy in solution: -718.216846 a.u.

Cartesian coordinates

| ATOM | X      | Y      | Z      |
|------|--------|--------|--------|
| C    | -0.590713 | -0.542117 | -0.053078 |
| O    | -0.440958 | -1.749113 | 0.021584 |
| Si   | -2.395180 | 0.150987 | 0.036134 |
| C    | -2.888733 | 0.095453 | 1.851290 |
| H    | -3.927356 | 0.415682 | 1.984629 |
| H    | -2.795887 | -0.923690 | 2.239078 |
| H    | -2.256093 | 0.748160 | 2.461467 |
| C    | -3.462294 | -1.009553 | -0.980843 |
| H    | -4.528128 | -0.815752 | -0.824538 |
| H    | -3.253241 | -0.912499 | -2.050625 |
| H    | -3.252432 | -2.043406 | -0.690486 |
| C    | -2.449131 | 1.918296 | -0.613804 |
| H    | -3.464191 | 2.324426 | -0.550235 |
| H    | -1.792987 | 2.577055 | -0.035077 |
| H    | -2.137643 | 1.970145 | -1.662254 |
| C    | 0.609561 | 0.384968 | -0.171898 |
| H    | 0.484893 | 0.975368 | -1.093047 |
| H    | 0.546454 | 1.120802 | 0.645493 |
| C    | 1.948310 | -0.340443 | -0.157819 |
| H    | 1.962317 | -1.080029 | -0.966789 |
| H    | 2.043195 | -0.912259 | 0.771442 |
| C    | 3.135305 | 0.618062 | -0.300456 |
| H    | 3.020472 | 1.189788 | -1.232552 |
| H    | 3.128973 | 1.346729 | 0.520065 |
| C    | 4.449051 | -0.108583 | -0.315484 |
| H    | 4.580110 | -0.837951 | -1.115576 |
| C    | 5.420697 | 0.061078 | 0.575988 |
| H    | 5.322229 | 0.775517 | 1.389844 |
| H    | 6.347171 | -0.501976 | 0.527239 |
**Supplementary Table 8**: Cartesian coordinates of 2
M062X SCF energy: -779.98659512 a.u.
M062X enthalpy: -779.877940 a.u.
M062X free energy: -779.919945 a.u.
M062X SCF energy in solution: -780.14285358 a.u.
M062X enthalpy in solution: -780.034198 a.u.
M062X free energy in solution: -780.076203 a.u.

| ATOM | X          | Y          | Z          |
|------|------------|------------|------------|
| C    | 0.757061   | -1.220539  | -0.054153  |
| C    | 0.091394   | 0.000004   | -0.084172  |
| C    | 0.757140   | 1.220601   | -0.054318  |
| C    | 2.145977   | 1.210668   | 0.032037   |
| C    | 2.835818   | -0.000048  | 0.073159   |
| C    | 2.145989   | -1.210680  | 0.032182   |
| H    | 0.193521   | -2.147138  | -0.077284  |
| H    | 0.193391   | 2.147072   | -0.077576  |
| H    | 2.689093   | 2.149063   | 0.070296   |
| H    | 3.919070   | 0.000029   | 0.138405   |
| H    | 2.688914   | -2.149180  | 0.070543   |
| S    | -1.696862  | 0.000023   | -0.253260  |
| O    | -2.183423  | -1.289617  | 0.266034   |
| O    | -2.183385  | 1.289586   | 0.266386   |

**Supplementary Table 9**: Cartesian coordinates of TS-1a
M062X SCF energy: -1498.23957830 a.u.
M062X enthalpy: -1497.861593 a.u.
M062X free energy: -1497.946251 a.u.
M062X SCF energy in solution: -1498.57100884 a.u.
M062X enthalpy in solution: -1498.193024 a.u.
M062X free energy in solution: -1498.277682 a.u.
Imaginary frequency: 361.7383 cm⁻¹

| ATOM | X          | Y          | Z          |
|------|------------|------------|------------|
| C    | 3.445214   | -0.773429  | 0.372141   |
| O    | 3.616108   | -1.788454  | 1.023831   |
| Si   | 5.000784   | 0.220143   | -0.209536  |
Supplementary Table 10: Cartesian coordinates of TS-1f

| Element | X    | Y    | Z    |
|---------|------|------|------|
| C       | 5.581328 | -0.594293 | -1.804182 |
| H       | 6.492675  | -0.114827  | -2.176565 |
| H       | 5.801177  | -1.653173  | -1.636697 |
| H       | 4.822870  | -0.526191  | -2.590861 |
| C       | 6.285176  | 0.044411   | 1.144653  |
| H       | 7.264767  | 0.408212   | 0.819318  |
| H       | 5.997120  | 0.600286   | 2.042166  |
| H       | 6.380765  | -1.009845  | 1.421082  |
| C       | 4.530776  | 2.017496   | -0.522757 |
| H       | 5.395748  | 2.588701   | -0.875931 |
| H       | 4.822870  | -1.009845  | 1.421082  |
| C       | 2.041038  | -0.326820  | -0.011275 |
| H       | 1.886786  | 0.683685   | 0.397755  |
| H       | 2.015615  | -0.198190  | -1.104897 |
| C       | 0.951488  | -1.282083  | 0.456775  |
| H       | 1.028376  | -1.408236  | 1.542653  |
| H       | 1.126516  | -2.273676  | 0.026202  |
| C       | -0.452181 | -0.787203  | 0.083986  |
| H       | -0.602218 | 0.214872   | 0.517110  |
| H       | -0.535015 | -0.670152  | -1.004408 |
| C       | -1.521963 | -1.709343  | 0.574240  |
| H       | -1.553862 | -1.901984  | 1.645292  |
| C       | -2.494922 | -2.259004  | -0.228838 |
| H       | -2.371749 | -2.230908  | -1.310734 |
| H       | -3.122431 | -3.059618  | 0.155785  |
| C       | -3.229302 | 1.157425   | 1.290393  |
| C       | -3.446760 | 0.752339   | -0.022689 |
| C       | -2.918828 | 1.442383   | -1.108788 |
| C       | -2.155407 | 2.581267   | -0.867611 |
| C       | -1.924909 | 3.003008   | 0.441520  |
| C       | -2.463793 | 2.298155   | 1.517654  |
| H       | -3.667737 | 0.591260   | 2.106091  |
| H       | -3.119702 | 1.092394   | -2.116541 |
| H       | -1.742778 | 3.141684   | -1.700252 |
| H       | -1.327152 | 3.890482   | 0.624159  |
| H       | -2.289991 | 2.638895   | 2.533226  |
| S       | -4.277330 | -0.802240  | -0.311125 |
| O       | -5.133138 | -1.068618  | 0.852503  |
| O       | -4.824018 | -0.772280  | -1.675995 |
M062X SCF energy: -1498.23563088 a.u.
M062X enthalpy: -1497.858045 a.u.
M062X free energy: -1497.943373 a.u.
M062X SCF energy in solution: -1498.56491357 a.u.
M062X enthalpy in solution: -1498.187328 a.u.
M062X free energy in solution: -1498.272656 a.u.
Imaginary frequency: -408.3714 cm⁻¹

Cartesian coordinates

| ATOM | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | 3.291929| -0.606298| 0.134470|
| O    | 3.449677| -1.753825| -0.242563|
| Si   | 4.770669| 0.626281 | -0.055499|
| C    | 4.561315| 2.077142 | 1.129011|
| H    | 4.558008| 1.746519 | 2.172830|
| H    | 5.380585| 2.794304 | 1.011524|
| H    | 3.624431| 2.612580 | 0.941845|
| C    | 4.733383| 1.221413 | -1.840134|
| H    | 4.799636| 0.371882 | -2.526779|
| H    | 3.809329| 1.764015 | -2.064231|
| H    | 5.574684| 1.891196 | -2.046900|
| C    | 6.331549| -0.353008| 0.295094|
| H    | 7.229336| 0.209707 | 0.020825|
| H    | 6.407307| -0.618558| 1.354030|
| H    | 6.314574| -1.281963| -0.282653|
| C    | 1.954496| -0.151686| 0.701602|
| H    | 2.131331| 0.174183 | 1.739075|
| H    | 1.647216| 0.757233 | 0.161343|
| C    | 0.869945| -1.216314| 0.625707|
| H    | 1.242810| -2.145997| 1.069664|
| H    | 0.661894| -1.433186| -0.427124|
| C    | -0.414742| -0.783874| 1.330158|
| H    | -0.236258| -0.696355| 2.409199|
| H    | -0.711528| 0.219930 | 0.992860|
| S    | -2.319414| -0.993729| -0.929321|
| O    | -1.216273| -0.451687| -1.742052|
| O    | -3.206219| -2.044977| -1.442161|
| C    | -3.335167| 0.391324 | -0.438168|
| C    | -4.627614| 0.142262 | 0.015150|
| C    | -2.786711| 1.670191 | -0.445358|
| C    | -5.392041| 1.212412 | 0.470341|
| H    | -5.023322| -0.868010| -0.016179|
| C    | -3.563931| 2.731596 | 0.011307|
| H    | -1.781178| 1.819840 | -0.825599|
### Supplementary Table 11: Cartesian coordinates of 10a

M062X SCF energy: -1498.25337970 a.u.
M062X enthalpy: -1497.873907 a.u.
M062X free energy: -1497.960304 a.u.
M062X SCF energy in solution: -1498.58188403 a.u.
M062X enthalpy in solution: -1498.202411 a.u.
M062X free energy in solution: -1498.288808 a.u.

| ATOM | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | 4.258159 | -0.530398 | -0.337391 |
| O    | 4.403963 | -1.614172 | -0.875293 |
| Si   | 5.843791 | 0.491034   | 0.094879  |
| C    | 6.386209 | 1.320303  | -1.505765 |
| H    | 7.320991 | 1.872309  | -1.362402 |
| H    | 6.551674 | 0.571447   | -2.286501 |
| H    | 5.632726 | 2.027002  | -1.868405 |
| C    | 7.130858 | -0.742244 | 0.678564 |
| H    | 8.120125 | -0.281273  | 0.760991 |
| H    | 6.868690 | -1.160283  | 1.655309 |
| H    | 7.192180 | -1.569764  | -0.034529 |
| C    | 5.446385 | 1.782382  | 1.407140 |
| H    | 6.331010 | 2.384352  | 1.640292 |
| H    | 4.660878 | 2.466473  | 1.068825 |
| H    | 5.108072 | 1.316740  | 2.338563 |
| C    | 2.866785 | 0.016649  | -0.057171 |
| H    | 2.797220 | 0.224811  | 1.021417 |
| H    | 2.792761 | 1.003724  | -0.541035 |
| C    | 1.744898 | -0.906016 | -0.513031 |
| H    | 1.857915 | -1.876489  | -0.016108 |
| H    | 1.850311 | -1.103942  | -1.585182 |
| C    | 0.359766 | -0.327535  | -0.216979 |
| H    | 0.279197 | -0.096559  | 0.858746 |
| ATOM | X     | Y     | Z     |
|------|-------|-------|-------|
| C    | 3.244037 | -0.592946 | -0.037108 |
| O    | 3.334544  | -1.656085  | -0.624171  |
| Si   | 4.797128  | 0.559750   | 0.016527   |
| C    | 4.788252  | 1.533536   | -1.594340  |
| H    | 5.668711  | 2.180875   | -1.664177  |
| H    | 4.798641  | 0.854286   | -2.452305  |
| H    | 3.899365  | 2.167437   | -1.676500  |
| C    | 6.295167  | -0.563563  | 0.117138   |
| H    | 7.225243  | -0.009548  | -0.043698  |
| H    | 6.357961  | -1.057533  | 1.091614   |
| H    | 6.217951  | -1.342013  | -0.647739  |
| C    | 4.680299  | 1.727229   | 1.491207   |

**Supplementary Table 12: Cartesian coordinates of 10b**

M062X SCF energy: -1498.2496091 a.u.
M062X enthalpy: -1497.871137 a.u.
M062X free energy: -1497.955147 a.u.
M062X SCF energy in solution: -1498.57848026 a.u.
M062X enthalpy in solution: -1498.199656 a.u.
M062X free energy in solution: -1498.283666 a.u.
Supplementary Table 13: Cartesian coordinates of TS-2a
M062X SCF energy: -1498.24928606 a.u.
M062X enthalpy: -1498.24928606 a.u.
M062X free energy: -1498.24928606 a.u.
M062X SCF energy in solution: -1498.57758325 a.u.
M062X enthalpy in solution: -1498.57758325 a.u.
M062X free energy in solution: -1498.57758325 a.u.
Imaginary frequency: -523.3122 cm⁻¹

Cartesian coordinates
ATOM       X           Y           Z
C           -0.965107    1.018566    0.171900
C   -2.423311  0.084033  -1.136063
C   -3.232924  1.359408  -1.397538
C   -2.916837  2.417232  -0.338728
C   -1.395032  2.418427  -0.147658
H   -1.222004  0.666676   1.171236
H   -2.955921  1.713613  -2.397112
H   -4.302891  1.113375  -1.410297
H   -3.282568  3.404098  -0.636371
H   -3.400687  2.164626   0.612158
H   -0.906558  2.754597  -1.069934
H   -1.088756  3.102089   0.654615
O   -1.742323  -0.412167  -2.054605
Si  -2.976543  -1.198875   0.213352
C   -1.496890  -2.216086   0.762606
H   -0.789331  -1.656142   1.384414
H   -1.840551  -3.079118   1.343216
H   -0.965839  -2.599971  -0.115257
C   -3.863740  -0.399479   1.671735
H   -4.708073   0.211607   1.334106
H   -4.268302  -1.184702   2.320331
H   -3.211303   0.228612   2.285946
C   -4.193107  -2.301700  -0.709417
H   -3.710327  -2.739345  -1.588514
H   -4.547929  -3.117136  -0.069968
H   -5.068240  -1.738844  -1.050677
C   0.319875  0.474553  -0.354591
H   0.271531  -0.604556  -0.533905
H   0.636346   0.972205  -1.275138
S   1.601926   0.739793   0.890841
O   1.834992   2.179286   0.997795
O   1.214929  -0.043345   2.066186
C   3.048070  -0.012027   0.175445
C   3.936567   0.782716  -0.541929
C   3.239113  -1.382388   0.331116
C   5.047867   0.180608  -1.125178
H   3.759864   1.850927  -0.617208
C   4.352471  -1.971578  -0.259429
H   2.534622  -1.961229   0.920747
C   5.250789  -1.191225  -0.986307
H   5.757619   0.782239  -1.683218
H   4.523492  -3.037051  -0.147190
H   6.119000  -1.655565  -1.443140
**Supplementary Table 14: Cartesian coordinates of TS-2b**

M062X SCF energy: -1498.24643096 a.u.
M062X enthalpy: -1497.867567 a.u.
M062X free energy: -1497.944563 a.u.
M062X SCF energy in solution: -1498.57393452 a.u.
M062X enthalpy in solution: -1498.195071 a.u.
M062X free energy in solution: -1498.272067 a.u.

Imaginary frequency: -498.7734 cm$^{-1}$

| ATOM | X      | Y      | Z      |
|------|--------|--------|--------|
| C    | 0.570637 | 2.398891 | -0.521486 |
| C    | 2.013600 | 1.912732 | -0.648758 |
| C    | 2.349596 | 0.843839 | 0.399198  |
| C    | 0.983823 | -0.667162 | -0.331641 |
| C    | -0.305924 | 0.051898  | -0.112250 |
| C    | -0.446521 | 1.331407  | -0.936303 |
| H    | 2.218133 | 1.538562  | -1.660029 |
| H    | 2.706326 | 2.746783  | -0.470141 |
| H    | 0.401034 | 2.685210  | 0.521861  |
| H    | 0.417291 | 3.290033  | -1.138145 |
| H    | -0.445202 | 0.244641  | 0.958244  |
| H    | -0.319355 | 1.071356  | -1.994636 |
| H    | -1.460157 | 1.731527  | -0.821178 |
| O    | 1.927268 | 1.003517  | 1.560457  |
| Si   | 3.930527 | -0.261492 | 0.219971  |
| C    | 5.346217 | 0.915955  | 0.621333  |
| H    | 6.306147 | 0.388649  | 0.623901  |
| H    | 5.413289 | 1.727288  | -0.111123 |
| H    | 5.201428 | 1.362999  | 1.609884  |
| C    | 3.805148 | -1.616762 | 1.511251  |
| H    | 3.285490 | -1.219897 | 2.389134  |
| H    | 3.249761 | -2.486769 | 1.147661  |
| H    | 4.796481 | -1.959902 | 1.822949  |
| C    | 4.154957 | -0.943904 | -1.522025 |
| H    | 4.044065 | -0.162557 | -2.281674 |
| H    | 5.162356 | -1.360893 | -1.628676 |
| H    | 3.443616 | -1.744000 | -1.748737 |
| S    | -1.630943 | -1.136223 | -0.549566 |
| O    | -1.693605 | -1.212526 | -2.009262 |
| O    | -1.409837 | -2.333812 | 0.259008  |
| C    | -3.127124 | -0.356511 | 0.025339  |
| C    | -3.918602 | 0.344917  | -0.879369 |
| C    | -3.465945 | -0.468700 | 1.371306  |
Supplementary Table 15: Cartesian coordinates of 11a
M062X SCF energy: -1498.27995893 a.u.
M062X enthalpy: -1497.898070 a.u.
M062X free energy: -1497.974397 a.u.
M062X SCF energy in solution: -1498.60512700 a.u.
M062X enthalpy in solution: -1498.223238 a.u.
M062X free energy in solution: -1498.299565 a.u.

Cartesian coordinates

| ATOM | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | -5.078659 | 0.959340 | -0.415772 |
| H    | -3.627887 | 0.383886 | -1.924495 |
| C    | -4.626002 | 0.152987 | 1.822188 |
| H    | -2.839766 | -1.053162 | 2.038425 |
| C    | -5.426469 | 0.866198 | 0.930596 |
| H    | -5.713323 | 1.505602 | -1.105683 |
| H    | -4.910296 | 0.074160 | 2.866245 |
| H    | -6.332081 | 1.346731 | 1.287013 |
| H    | 1.200342  | -1.496633 | 0.333845 |
| H    | 1.307015  | -0.781327 | -1.364432 |
| Si   | -2.953306 | -1.237536 | 0.181598 |
| C    | -1.529178 | -2.322498 | 0.733660 |
| H    | -0.787917 | -1.758904 | 1.312842 |
| H    | -1.898846 | -3.135729 | 1.367988 |
| H    | -1.032537 | -2.769169 | -0.133283 |
| C    | -3.814376 | -0.444715 | 1.656439 |
| H    | -4.607382 | 0.242190 | 1.343999 |
| H    | -4.276561 | -1.230913 | 2.264675 |
| H    | -3.115762 | 0.100886 | 2.298057 |
Supplementary Table 16: Cartesian coordinates of 11b
M062X SCF energy: -1498.28761133 a.u.
M062X enthalpy: -1497.905109 a.u.
M062X free energy: -1497.981681 a.u.
M062X SCF energy in solution: -1498.61426597 a.u.
M062X enthalpy in solution: -1498.231764 a.u.
M062X free energy in solution: -1498.308336 a.u.

| ATOM | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| C    | -0.608903 | 2.450631  | 0.177562  |
| C    | -2.009354 | 1.864282  | 0.398152  |
| C    | -2.094997 | 0.518579  | -0.346384 |
| C    | -1.048017 | -0.482565 | 0.182799  |
| C    | 0.338119  | 0.131723  | -0.048312 |
| C    | 0.483544  | 1.484211  | 0.647914  |
| H    | -2.189888 | 1.723647  | 1.472116  |
| H    | -2.769997 | 2.545900  | 0.005106  |
| H    | -0.487603 | 2.651514  | -0.893973 |
| H    | -0.506192 | 3.405193  | 0.703711  |
| H    | -1.181377 | -0.664538 | 1.256627  |
Supplementary Table 17: Cartesian coordinates of TS-3a

M062X SCF energy: -1498.27715880 a.u.

M062X enthalpy: -1497.896196 a.u.

M062X free energy: -1497.971249 a.u.

M062X SCF energy in solution: -1498.59949439 a.u.

M062X enthalpy in solution: -1498.218532 a.u.

M062X free energy in solution: -1498.293585 a.u.

Imaginary frequency: -246.5142 cm⁻¹

Cartesian coordinates
| ATOM | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | -1.026771 | 0.973408 | 0.006960 |
| C    | -2.170518 | 0.317957 | -0.822442 |
| C    | -3.143490 | 1.430378 | -1.235102 |
| C    | -2.788522 | 2.596249 | -0.307786 |
| C    | -1.264845 | 2.482692 | -0.158054 |
| H    | -1.142044 | 0.715349 | 1.069945 |
| H    | -2.924360 | 1.681601 | -2.281579 |
| H    | -4.194964 | 1.128064 | -1.186586 |
| H    | -3.105200 | 3.565643 | -0.700059 |
| H    | -3.268811 | 2.458482 | 0.668740 |
| H    | -0.777889 | 2.828387 | -1.079036 |
| H    | -0.854541 | 3.064820 | 0.669599 |
| O    | -1.910398 | -0.692062 | -1.639247 |
| Si   | -2.966217 | -1.262071 | 0.125244 |
| C    | -1.578952 | -2.315193 | 0.810321 |
| H    | -0.834007 | -1.705290 | 1.336450 |
| H    | -1.978137 | -3.035407 | 1.533052 |
| H    | -1.077747 | -2.868860 | 0.011895 |
| C    | -3.884609 | -0.443210 | 1.570264 |
| H    | -4.671352 | 0.231467 | 1.216429 |
| H    | -4.360316 | -1.219648 | 2.181566 |
| H    | -3.208443 | 0.123765 | 2.217861 |
| C    | -4.226871 | -2.173944 | -0.913580 |
| H    | -3.736014 | -2.812600 | -1.650997 |
| H    | -4.876984 | -2.789073 | -0.282582 |
| H    | -4.860318 | -1.464042 | -1.455640 |
| C    | 0.326378  | 0.453348 | -0.458290 |
| H    | 0.294382  | -0.627857 | -0.625227 |
| H    | 0.665354  | 0.942957 | -1.376642 |
| S    | 1.558487  | 0.754333 | 0.809165 |
| O    | 1.802995  | 2.194198 | 0.890347 |
| O    | 1.141088  | 0.002439 | 1.995629 |
| C    | 3.024100  | -0.020368 | 0.155946 |
| C    | 3.935433  | 0.753257 | -0.555511 |
| C    | 3.212500  | -1.384610 | 0.360102 |
| C    | 5.065077  | 0.135668 | -1.085237 |
| H    | 3.761369  | 1.818725 | -0.667340 |
| C    | 4.344463  | -1.989877 | -0.176367 |
| H    | 2.490417  | -1.946138 | 0.945187 |
| C    | 5.264747  | -1.230827 | -0.898361 |
| H    | 5.791956  | 0.721455 | -1.638151 |
| H    | 4.513075  | -3.050969 | -0.025287 |
| H    | 6.147609  | -1.707316 | -1.312658 |
**Supplementary Table 18:** Cartesian coordinates of **TS-3b**

M062X SCF energy: -1498.28435507 a.u.
M062X enthalpy: -1497.902739 a.u.
M062X free energy: -1497.978298 a.u.
M062X SCF energy in solution: -1498.60831168 a.u.
M062X enthalpy in solution: -1498.226696 a.u.
M062X free energy in solution: -1498.302255 a.u.
Imaginary frequency: -245.6018 cm⁻¹

| ATOM | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | -0.586288 | 2.471164 | 0.053189 |
| C    | -1.971593 | 1.908859 | 0.410833 |
| C    | -2.074674 | 0.503945 | -0.172489 |
| C    | -1.018926 | -0.443038 | 0.393584 |
| C    | 0.356772  | 0.139154 | 0.030207 |
| C    | 0.532661  | 1.558955 | 0.567880 |
| H    | -2.09137 | 1.875223 | 1.501274 |
| H    | -2.757696 | 2.544961 | -0.006954 |
| H    | -0.521210 | 2.556842 | -1.038367 |
| H    | -0.463430 | 3.476487 | 0.468477 |
| H    | -1.102165 | -0.510626 | 1.485466 |
| H    | -1.120634 | -1.443226 | -0.035766 |
| H    | 0.480048  | 0.107964 | -1.059921 |
| H    | 0.509589  | 1.516567 | 1.664225 |
| H    | 1.509868  | 1.957958 | 0.274431 |
| O    | -2.324368 | 0.409990 | -1.477811 |
| Si   | -3.921385 | -0.272454 | -0.240722 |
| C    | -5.145448 | 0.949946 | -0.955172 |
| H    | -6.167969 | 0.596619 | -0.782164 |
| H    | -5.053751 | 1.931973 | -0.480449 |
| H    | -4.992164 | 1.073304 | -2.029314 |
| C    | -3.948748 | -1.949721 | -1.067852 |
| H    | -3.137676 | -2.587298 | -0.702257 |
| H    | -4.892962 | -2.460461 | -0.849391 |
| H    | -3.841062 | -1.852080 | -2.150172 |
| C    | -4.312158 | -0.507819 | 1.602217 |
| H    | -4.275040 | 0.440781 | 2.147236 |
| H    | -5.322499 | -0.920221 | 1.711359 |
| H    | -3.612159 | -1.203992 | 2.075001 |
| S    | 1.615030  | -0.980575 | 0.689989 |
| O    | 1.649833  | -0.802345 | 2.142580 |
Supplementary Table 19: Cartesian coordinates of 12a

M062X SCF energy: -1498.31652454 a.u.
M062X enthalpy: -1497.934514 a.u.
M062X free energy: -1498.013398 a.u.
M062X SCF energy in solution: -1498.63684444 a.u.
M062X enthalpy in solution: -1498.254834 a.u.
M062X free energy in solution: -1498.333718 a.u.

Cartesian coordinates

| ATOM | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | 1.871536| 2.939651| 1.143207|
| C    | 0.854590| 2.936147| -0.012082|
| C    | 0.820962| 1.473149| -0.508006|
| C    | 2.135165| 0.910388| -0.026495|
| C    | 2.952226| 1.952980| 0.680615|
| H    | 2.262423| 3.937494| 1.355772|
| H    | 1.403014| 2.564763| 2.060942|
| H    | 1.228088| 3.570394| -0.822864|
| H    | -0.130279| 3.311608| 0.274300|
| H    | 0.758189| 1.409355| -1.602151|
| H    | 3.561274| 1.556760| 1.500400|
| H    | 3.644774| 2.436995| -0.028904|
| O    | 2.703021| -0.102734| -0.737020|
| Si   | 3.256188| -1.519449| -0.011943|
| C    | 4.536335| -1.134075| 1.304044|
| H    | 5.023246| -2.056950| 1.638508|
| H    | 5.313450| -0.466505| 0.917975|
| H    | 4.087251| -0.660971| 2.183204|
| C    | 1.795372| -2.406493| 0.762218|
| H    | 1.059160| -2.696747| 0.005146|
Supplementary Table 20: Cartesian coordinates of 12b
M062X SCF energy: -1498.32824986 a.u.
M062X enthalpy: -1497.945334 a.u.
M062X free energy: -1498.022582 a.u.
M062X SCF energy in solution: -1498.64745913 a.u.
M062X enthalpy in solution: -1498.264543 a.u.
M062X free energy in solution: -1498.341791 a.u.

| ATOM | X     | Y     | Z     |
|------|-------|-------|-------|
| C    | 0.504190 | 2.142133 | 1.409275 |
| C    | 1.787911 | 2.251146 | 0.560829 |
| C    | 2.001388 | 0.952032 | -0.156600 |
| C    | 0.880253 | 0.524973 | -1.057599 |
| C    | -0.394188 | 0.412968 | -0.191227 |
| C    | -0.689428 | 1.723479 | 0.541022 |
| H    | 1.670915 | 3.061005 | -0.170227 |
| H    | 2.650908 | 2.482797 | 1.193143 |
| H    | 0.667204 | 1.394560 | 2.194874 |
| H    | 0.285981 | 3.094846 | 1.902895 |
|    |   x   |   y   |   z   |
|----|-------|-------|-------|
|   H |  0.705727 |  1.277210 | -1.836501 |
|   H |  1.093884 | -0.434587 | -1.536381 |
|   H | -0.276716 | -0.418264 |  0.515276 |
|   H | -0.898047 |  2.496602 | -0.209719 |
|   H | -1.586719 |  1.617530 |  1.160821 |
|   O |  2.508984 | -0.055588 |  0.632537 |
|   Si|  4.029044 | -0.688420 |  0.260004 |
|   C |  5.299104 |  0.682942 |  0.406527 |
|   H |  6.302205 |  0.326465 |  0.149586 |
|   H |  5.054226 |  1.509029 | -0.269970 |
|   H |  5.333074 |  1.080565 |  1.426064 |
|   C |  4.319738 | -2.033273 |  1.524709 |
|   H |  3.553600 | -2.811116 |  1.451727 |
|   H |  5.295757 | -2.506652 |  1.375683 |
|   H |  4.293278 | -1.627668 |  2.540672 |
|   C |  4.001336 | -1.374050 | -1.483748 |
|   H |  3.754154 | -0.590766 | -2.208469 |
|   H |  4.977794 | -1.786632 | -1.759399 |
|   H |  3.258329 | -2.171875 | -1.584223 |
|   S | -1.757209 | -0.067529 | -1.275615 |
|   O | -2.095575 |  1.090187 | -2.105452 |
|   O | -1.394961 | -1.347180 | -1.884579 |
|   C | -3.125057 | -0.360884 | -0.167961 |
|   C | -4.045561 |  0.658087 |  0.058474 |
|   C | -3.236269 | -1.604595 |  0.447669 |
|   C | -5.099591 |  0.424686 |  0.937618 |
|   H | -3.935126 |  1.602713 | -0.464854 |
|   C | -4.293140 | -1.824803 |  1.325696 |
|   H | -2.517353 | -2.384797 |  0.217221 |
|   C | -5.218579 | -0.811191 |  1.570782 |
|   H | -5.831139 |  1.204240 |  1.123190 |
|   H | -4.400431 | -2.789060 |  1.811469 |
|   H | -6.043004 | -0.989042 |  2.254071 |

**Supplementary Table 21:** Cartesian coordinates of **TS-4a**

M06X SCF energy: -2739.83894765 a.u.
M06X enthalpy: -2739.171321 a.u.
M06X free energy: -2739.290341 a.u.
M06X SCF energy in solution: -2740.46846123 a.u.
M06X enthalpy in solution: -2739.800835 a.u.
M06X free energy in solution: -2739.919855 a.u.
Imaginary frequency: -226.7798 cm⁻¹
| ATOM | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | -2.019714 | 1.183641 | -0.205109 |
| C    | -0.818060 | 0.899714 | 0.680313  |
| C    | -0.469978 | 2.106277 | 1.505886  |
| C    | -1.073127 | 3.257154 | 0.692387  |
| C    | -2.369070 | 2.653127 | 0.127067  |
| H    | -1.758756 | 1.087144 | -1.268882 |
| H    | -0.953631 | 2.048276 | 2.497182  |
| H    | 0.607955  | 2.200689 | 1.682713  |
| H    | -1.256081 | 4.148683 | 1.296532  |
| H    | -0.385837 | 3.546785 | -0.111301 |
| H    | -3.148944 | 2.670937 | 0.897465  |
| H    | -2.765698 | 3.191284 | -0.736631 |
| O    | -0.625157 | -0.364269 | 1.114700  |
| Si   | -0.195457 | -0.912376 | 2.663170  |
| C    | 0.271701  | -2.703863 | 2.395640  |
| H    | 0.338736  | -3.224977 | 3.356796  |
| H    | -0.480623 | -3.216525 | 1.788295  |
| H    | 1.240447  | -2.809410 | 1.896887  |
| C    | 1.223057  | 0.055542  | 3.409650  |
| H    | 0.886549  | 0.991390  | 3.866102  |
| H    | 1.681717  | -0.549232 | 4.201058  |
| H    | 2.009547  | 0.303488  | 2.687789  |
| C    | -1.728071 | -0.788833 | 3.739395  |
| H    | -2.540773 | -1.400119 | 3.333104  |
| H    | -1.520433 | -1.139508 | 4.756204  |
| H    | -2.087336 | 0.243412  | 3.814404  |
| C    | -3.145961 | 0.186756  | 0.069179  |
| H    | -2.817312 | -0.837706 | -0.128177 |
| H    | -3.517743 | 0.254955  | 1.097476  |
| S    | -4.544713 | 0.513317  | -1.015889 |
| O    | -5.276694 | 1.665302  | -0.490793 |
| O    | -4.038231 | 0.509258  | -2.387607 |
| C    | -5.571443 | -0.928881 | -0.801724 |
| C    | -6.559735 | -0.913478 | 0.177619  |
| C    | -5.351766 | -2.038785 | -1.612806 |
| C    | -7.341638 | -2.051419 | 0.355499  |
| H    | -6.718135 | -0.015180 | 0.765971  |
| C    | -6.140079 | -3.169832 | -1.424557 |
| H    | -4.591175 | -1.996856 | -2.386378 |
| C    | -7.128347 | -3.175136 | -0.440985 |
| H    | -8.122326 | -2.058308 | 1.108977  |
| H    | -5.989955 | -4.043328 | -2.050403 |
Supplementary Table 22: Cartesian coordinates of TS-4b

M062X SCF energy: -2739.83740962 a.u.
M062X enthalpy: -2739.168777 a.u.
M062X free energy: -2739.293792 a.u.
M062X SCF energy in solution: -2740.45590295 a.u.
M062X enthalpy in solution: -2739.787270 a.u.
M062X free energy in solution: -2739.912285 a.u.

|   | x   | y   | z   |
|---|-----|-----|-----|
| H | -7.742580 | -4.058910 | -0.300262 |
| C | 2.558272  | -0.628629  | 0.018552  |
| H | 3.267636  | -0.639327  | 0.850425  |
| H | 1.749170  | -1.346525  | 0.179799  |
| C | 2.823031  | 1.855916   | 0.377948  |
| O | 3.556000  | 1.638534   | 1.334729  |
| C | 2.626005  | 3.258027   | -0.112600 |
| C | 2.563345  | 4.283060   | 0.835007  |
| C | 2.544659  | 3.564071   | -1.473760 |
| C | 2.370668  | 5.598473   | 0.428926  |
| H | 2.665406  | 4.028133   | 1.885848  |
| C | 2.373360  | 4.885108   | -1.879020 |
| H | 2.641105  | 2.769096   | -2.207833 |
| C | 2.272061  | 5.899365   | -0.929188 |
| H | 2.304447  | 6.390765   | 1.167874  |
| H | 2.321380  | 5.122455   | -2.936720 |
| H | 2.126373  | 6.926907   | -1.247618 |
| S | 3.445258  | -1.204314  | -1.452466 |
| O | 2.444609  | -1.564319  | -2.456848 |
| O | 4.491774  | -0.231091  | -1.754788 |
| C | 4.223019  | -2.704121  | -0.885319 |
| C | 3.524085  | -3.904112  | -0.978269 |
| C | 5.497872  | -2.631977  | -0.331524 |
| C | 4.121375  | -5.064352  | -0.493758 |
| H | 2.543477  | -3.919297  | -1.443750 |
| C | 6.084163  | -3.799704  | 0.147536  |
| H | 6.014710  | -1.677884  | -0.298298 |
| C | 5.395649  | -5.009418  | 0.068751  |
| H | 3.597054  | -6.011838  | -0.562831 |
| H | 7.080081  | -3.767199  | 0.576879  |
| H | 5.858422  | -5.917316  | 0.442596  |
| C | 2.061520  | 0.755969   | -0.254458 |
| C | 0.911876  | 0.948371   | -0.950818 |
| H | 0.411563  | 0.101647   | -1.412960 |
| H | 0.588460  | 1.937119   | -1.256922 |
Imaginary frequency: -116.4562 cm⁻¹

Cartesian coordinates

| ATOM | X     | Y     | Z     |
|------|-------|-------|-------|
| O    | 0.387454 | -0.151967 | 1.933279 |
| Si   | -0.511892 | -0.020385 | 3.368315 |
| C    | -0.918078 | 1.802791 | 3.470996 |
| H    | -1.657061 | 2.102130 | 2.720620 |
| H    | -1.332216 | 2.045918 | 4.455380 |
| H    | -0.020204 | 2.411155 | 3.325384 |
| C    | -2.072030 | -1.055252 | 3.333383 |
| H    | -2.749245 | -0.693714 | 4.116523 |
| H    | -2.610643 | -0.997888 | 2.380926 |
| H    | -1.871171 | -2.111475 | 3.537377 |
| C    | 0.596833  | -0.537280 | 4.788921 |
| H    | 0.910074  | -1.582749 | 4.697629 |
| H    | 1.499799  | 0.080048  | 4.826055 |
| H    | 0.074886  | -0.431997 | 5.746376 |
| C    | 2.758722  | -0.172986 | 0.128593 |
| H    | 2.384493  | -0.110186 | -0.897704 |
| H    | 2.521656  | 0.751235  | 0.665713 |
| S    | 4.551131  | -0.270736 | 0.008892 |
| O    | 5.083773  | -0.291875 | 1.370988 |
| O    | 4.881635  | -1.333897 | -0.939443 |
| C    | 4.993496  | 1.287368  | -0.734286 |
| C    | 5.278949  | 2.371519  | 0.090442 |
| C    | 5.027806  | 1.385136  | -2.122140 |
| C    | 5.596969  | 3.591996  | -0.497644 |
| H    | 5.269122  | 2.242794  | 1.168219 |
| C    | 5.345360  | 2.611914  | -2.697501 |
| H    | 4.827865  | 0.507187  | -2.728374 |
| C    | 5.625294  | 3.710407  | -1.886377 |
| H    | 5.829086  | 4.448561  | 0.126599 |
| H    | 5.380537  | 2.709269  | -3.777453 |
| H    | 5.874126  | 4.664461  | -2.340160 |
| C    | -0.433836 | -0.823539 | -0.855762 |
| C    | -1.727853 | -0.720093 | -0.470385 |
| C    | -2.280334 | 0.599947  | -0.027786 |
| H    | -3.220118 | 0.471961  | 0.515864 |
| H    | -1.564173 | 1.183026  | 0.558359 |
| C    | -2.648082 | -1.876931 | -0.363297 |
| O    | -3.642993 | -1.817738 | 0.346743 |
| C    | -2.313829 | -3.151662 | -1.076689 |
| C    | -2.560773 | -4.356014 | -0.411945 |
Supplementary Table 23: Cartesian coordinates of 13a

M062X SCF energy: -2739.88391899 a.u.
M062X enthalpy: -2739.212161 a.u.
M062X free energy: -2739.332941 a.u.
M062X SCF energy in solution: -2740.49855632 a.u.
M062X enthalpy in solution: -2739.826798 a.u.
M062X free energy in solution: -2739.947578 a.u.

| ATOM | X      | Y      | Z      |
|------|--------|--------|--------|
| C    | -1.781511 | 0.846691 | -0.927599 |
| C    | -0.578912 | 0.676986 | 0.040629  |
| C    | -0.792175 | 1.828047 | 1.038304  |
| C    | -1.272901 | 3.006658 | 0.175141  |
| C    | -1.898489 | 2.376021 | -1.101906 |
| H    | -1.583157 | 0.334394 | -1.875317 |
| H    | -1.569002 | 1.532436 | 1.755372  |
| H    | 0.104945  | 2.061970 | 1.618584  |
| H    | -1.991064 | 3.626056 | 0.717512  |
| H    | -0.429986 | 3.655995 | -0.084476 |
| H    | -2.936929 | 2.679392 | -1.248784 |
| H    | -1.350601 | 2.691379 | -1.994167 |
| O    | -0.535511 | -0.616639 | 0.600707 |
| O    | -0.585237 | -1.155905 | 2.186776 |
| Si   | 0.035593  | -2.920956 | 2.080213 |
| H    | 1.107424  | -2.961280 | 1.860197 |
| H    | -0.126450 | -3.445967 | 3.027713  |
| H    | -0.490543 | -3.472891 | 1.295037  |
| C    | 0.506381  | -0.155888 | 3.341721  |
| H    | 0.036566  | 0.783278  | 3.649582  |
| H    | 0.688250  | -0.743448 | 4.249602  |
| H    | 1.482994  | 0.085748  | 2.906500  |
| C    | -2.350842 | -1.165409 | 2.838493  |
| H    | -3.011869 | -1.774589 | 2.211931  |
| H    | -2.367724 | -1.592365 | 3.847976  |
| H    | -2.782393 | -0.160823 | 2.903824  |
| C    | -3.026632 | 0.210759  | -0.314185 |
| H    | -2.824567 | -0.828766 | -0.042674 |
| H    | -3.399288 | 0.748769  | 0.564676  |
| S    | -4.396227 | 0.153829  | -1.480860 |
| O    | -5.015111 | 1.477758  | -1.557488 |
| O    | -3.921558 | -0.522202 | -2.686815 |
| C    | -5.546726 | -0.931251 | -0.653684 |
| C    | -6.517497 | -0.378880 | 0.175623  |
| C    | -5.430286 | -2.305956 | -0.840505 |
| C    | -7.389555 | -1.233015 | 0.845315  |
| H    | -6.591193 | 0.699943  | 0.269604  |
| C    | -6.307363 | -3.148835 | -0.164812 |
| H    | -4.677791 | -2.693587 | -1.520503 |
Supplementary Table 24: Cartesian coordinates of 13b
M062X SCF energy: -2739.87905137 a.u.
M062X enthalpy: -2739.207395 a.u.
M062X free energy: -2739.328823 a.u.
M062X SCF energy in solution: -2740.49424004 a.u.
M062X enthalpy in solution: -2739.822584 a.u.
M062X free energy in solution: -2739.944012 a.u.

Cartesian coordinates

| ATOM | X        | Y        | Z        |
|------|----------|----------|----------|
| O    | -0.501024| 1.583027 | -1.622095|
| Si   | -1.452100| 2.936670 | -1.875985|
| C    | -2.588083| 2.407718 | -3.268088|
| H    | -3.252287| 1.594940 | -2.956157|
| H    | -3.216532| 3.242132 | -3.597097|
| H    | -2.011048| 2.057498 | -4.129262|
| C    | -2.489344| 3.443601 | -0.391761|
| H    | -1.899054| 3.774961 | 0.468760 |
| H    | -3.117787| 4.289972 | -0.696187|
| H    | -3.155033| 2.652458 | -0.035379|
| C    | -0.442660| 4.424768 | -2.419594|
| H    | 0.139583 | 4.217086 | -3.322653|
| H    | -1.123157| 5.253413 | -2.647969|
| H    | 0.245594 | 4.773798 | -1.643641|
| C    | 2.691566 | -0.045930| -0.643845|
| H    | 2.956714 | 0.416972 | 0.313447 |
| H    | 2.269691 | -1.037027| -0.451408|
| S    | 4.254258 | -0.336149| -1.496967|
| O    | 3.938766 | -0.775402| -2.854903|
| O    | 5.130049 | 0.812868 | -1.262962|
| C    | 4.940678 | -1.723490| -0.610490|
| C    | 4.592895 | -3.012950| -1.003551|
| C    | 5.799227 | -1.482762| 0.457465 |
| C    | 5.112963 | -4.090473| -0.293503|
| H    | 3.943626 | -3.157480| -1.861639|
| C    | 6.313805 | -2.569862| 1.158668 |
| H    | 6.067609 | -0.461878| 0.709970 |
| C    | 5.967612 | -3.867178| 0.785466 |
| H    | 4.857989 | -5.103693| -0.585842|
| H    | 6.990107 | -2.404759| 1.990920 |
| H    | 6.372439 | -4.711400| 1.334553 |
| C    | -0.091143| 0.036435 | 0.157445 |
| H    | 0.613023 | -0.195014| 0.959418 |
| H    | -0.159849| -0.839308| -0.500098|
| C    | -1.452725| 0.319514 | 0.707808 |
| C    | -2.630596| -0.139040| -0.070134|
| H    | -3.546739| 0.345571 | 0.275488 |
| H    | -2.493661| -0.041883| -1.151254|
### Supplementary Table 25: Cartesian coordinates of TS-5a

M062X SCF energy: -2739.86217583 a.u.
M062X enthalpy: -2739.192517 a.u.

| Element | X-Coordinate | Y-Coordinate | Z-Coordinate |
|---------|--------------|--------------|--------------|
| C       | 87.8413      | 0.992599     | 1.972312     |
| O       | -2.855508    | 1.463309     | 2.184262     |
| C       | -0.658684    | 1.145062     | 2.998839     |
| C       | -0.476608    | 2.390450     | 3.602702     |
| C       | 0.114380     | 0.054086     | 3.403524     |
| C       | 0.510995     | 2.558000     | 4.567486     |
| H       | -1.113888    | 3.217548     | 3.303504     |
| C       | 1.088415     | 0.219463     | 4.384291     |
| H       | -0.077228    | -0.926332    | 2.973773     |
| C       | 1.296877     | 1.473544     | 4.954967     |
| H       | 0.663736     | 3.530733     | 5.024025     |
| H       | 1.679082     | -0.631472    | 4.708244     |
| H       | 2.063735     | 1.603372     | 5.712214     |
| S       | -2.827394    | -1.926848    | 0.259691     |
| O       | -1.914597    | -2.50172     | -0.626203    |
| O       | -2.749248    | -2.103593    | 1.708800     |
| C       | -4.494269    | -2.261889    | -0.262426    |
| C       | 1.751500     | -2.733947    | -1.552205    |
| C       | 5.535393     | -2.020610    | 0.630383     |
| C       | 6.025950     | -2.966633    | -1.959491    |
| H       | -3.870394    | -2.928572    | -2.205224    |
| C       | -6.039786    | -2.255870    | 0.208554     |
| H       | -5.315352    | 1.671695     | 1.634839     |
| C       | 7.081615     | -2.725020    | -1.082444    |
| H       | 6.222419     | -3.341081    | -2.958623    |
| H       | -7.666977    | -2.079573    | 0.887993     |
| H       | -8.101514    | -2.908540    | -1.405196    |
| C       | 0.481894     | 1.211706     | -0.671663    |
| C       | 0.990321     | 2.398067     | 0.186942     |
| C       | 1.737681     | 0.806009     | -1.488952    |
| C       | 2.213720     | 2.984414     | -0.564945    |
| H       | 1.277707     | 2.039899     | 1.181131     |
| H       | 0.196364     | 3.132392     | 0.352558     |
| C       | 2.313496     | 2.177014     | -1.868942    |
| H       | 1.432968     | 0.222930     | -2.362375    |
| H       | 2.123710     | 4.057222     | -0.749633    |
| H       | 3.125007     | 2.843289     | 0.025648     |
| H       | 1.667628     | 2.609293     | -2.638010    |
| H       | 3.329280     | 2.137736     | -2.265435    |
M062X free energy: -2739.313084 a.u.
M062X SCF energy in solution: -2740.47514580 a.u.
M062X enthalpy in solution: -2739.805487 a.u.
M062X free energy in solution: -2739.926054 a.u.
Imaginary frequency: -236.9438 cm$^{-1}$

| ATOM | X      | Y      | Z      |
|------|--------|--------|--------|
| C    | -1.889675 | 0.856502 | -0.777355 |
| C    | -0.761038 | 0.264980 | 0.112118  |
| C    | -0.717148 | 1.256468 | 1.288603  |
| C    | -0.920527 | 2.638125 | 0.643621  |
| C    | -1.663176 | 2.380736 | -0.698547 |
| H    | -1.805275 | 0.476993 | -1.801553 |
| H    | -1.544288 | 1.023882 | 1.972118  |
| H    | 0.204172  | 1.187263 | 1.875319  |
| H    | -1.486466 | 3.301489 | 1.301984  |
| H    | 0.045462  | 3.121693 | 0.464321  |
| H    | -2.607433 | 2.925357 | -0.762045 |
| H    | -1.053127 | 2.710999 | -1.543918 |
| O    | -1.021709 | -1.074694 | 0.450213 |
| Si   | -1.142978 | -1.875088 | 1.915799 |
| C    | -0.808243 | -3.667249 | 1.488307 |
| O    | 0.240409  | -3.816179 | 1.211117 |
| H    | -1.023938 | -4.320495 | 2.340507 |
| H    | -1.427805 | -3.992704 | 0.646976 |
| C    | 0.078098  | -1.287815 | 3.215435 |
| H    | -0.228527 | -0.348481 | 3.685619 |
| H    | 0.130435  | -2.046095 | 4.006227 |
| H    | 1.090880  | -1.154744 | 2.819114 |
| C    | -2.892687 | -1.702574 | 2.589219 |
| H    | -3.640410 | -2.066112 | 1.875479 |
| H    | -3.001415 | -2.287758 | 3.509530 |
| H    | -3.141003 | -0.663467 | 2.833096 |
| C    | -3.249176 | 0.418789  | -0.237324 |
| H    | -3.282254 | -0.669301 | -0.137394 |
| H    | -3.501559 | 0.877964  | 0.725122 |
| S    | -4.585886 | 0.852464  | -1.361994 |
| O    | -4.909024 | 2.270552  | -1.197642 |
| O    | -4.250318 | 0.309200  | -2.677168 |
| C    | -5.951456 | -0.091354 | -0.706692 |
| C    | -6.802556 | 0.504634  | 0.218257 |
| C    | -6.118864 | -1.409675 | -1.121923 |
| C    | -7.845754 | -0.249204 | 0.749475 |
Supplementary Table 26: Cartesian coordinates of **TS-5b**

|   |          |          |          |
|---|----------|----------|----------|
| H | -6.652426| 1.544117 | 0.492159 |
| C | -7.164293| -2.152685| -0.582562|
| H | -5.450041| -1.826695| -1.868671|
| C | -8.021622| -1.573279| 0.352302 |
| H | -8.524783| 0.198567 | 1.467619 |
| H | -7.316065| -3.179882| -0.897367|
| H | -8.837271| -2.156327| 0.768166 |
| C | 0.557840 | 0.286354 | -0.701442|
| H | 0.744540 | 1.306522 | -1.043067|
| H | 0.403695 | -0.336494| -1.589116|
| C | 1.713701 | -0.256631| 0.085371 |
| C | 2.051062 | -1.578788| 0.006758 |
| H | 2.790532 | -1.987516| 0.692072 |
| H | 1.412133 | -2.276913| -0.528977|
| C | 2.531364 | 0.594154 | 1.004929 |
| O | 3.059453 | 0.103830 | 1.991659 |
| C | 2.679562 | 2.058885 | 0.729428 |
| C | 2.720815 | 2.928776 | 1.822709 |
| C | 2.821000 | 2.560722 | -0.569368|
| C | 2.853672 | 4.297378 | 1.619234|
| H | 2.638953 | 2.513651 | 2.822734 |
| C | 2.979468 | 3.930450 | -0.766202|
| H | 2.831976 | 1.878799 | -1.417575|
| C | 2.979854 | 4.798583 | 0.323755 |
| H | 2.863673 | 4.973985 | 2.467763 |
| H | 3.099387 | 4.319008 | -1.772282|
| H | 3.085778 | 5.867149 | 0.164554 |
| S | 3.619012 | -1.467128| -1.864812|
| O | 3.618396 | -2.699077| -2.666673|
| O | 3.363323 | -0.153637| -2.475083|
| C | 5.167781 | -1.373086| -0.983271|
| C | 5.882579 | -2.546423| -0.761154|
| C | 5.560303 | -0.147569| -0.453620|
| C | 7.045079 | -2.478144| 0.000020 |
| H | 5.538142 | -3.479307| -1.195169|
| C | 6.721273 | -0.98926 | 0.311771 |
| H | 4.978669 | 0.747516 | -0.652220|
| C | 7.458978 | -1.259621| 0.536690 |
| H | 7.628176 | -3.376380| 0.174176 |
| H | 7.047779 | 0.846285 | 0.731961 |
| H | 8.362720 | -1.214998| 1.135879 |
M062X SCF energy: -2739.85738844 a.u.
M062X enthalpy: -2739.187695 a.u.
M062X free energy: -2739.309179 a.u.
M062X SCF energy in solution: -2740.47046907 a.u.
M062X enthalpy in solution: -2739.800776 a.u.
M062X free energy in solution: -2739.922260 a.u.
Imaginary frequency: -237.9154 cm$^{-1}$

Cartesian coordinates

| ATOM | X       | Y       | Z       |
|------|---------|---------|---------|
| O    | 0.145965| 2.711512| -0.497958|
| Si   | -0.686878| 4.084967| -0.041299|
| C    | -1.834345| 4.455025| -1.478503|
| H    | -2.693065| 3.776379| -1.495185|
| H    | -2.222385| 5.477079| -1.407791|
| H    | -1.308333| 4.361098| -2.433839|
| C    | -1.707702| 3.901114| 1.524913 |
| H    | -1.101665| 3.937905| 2.436059 |
| H    | -2.412180| 4.740621| 1.570279 |
| H    | -2.295346| 2.975721| 1.535119 |
| C    | 0.504249 | 5.526305| 0.150895 |
| H    | 1.113750 | 5.653362| -0.749919|
| H    | -0.060178| 6.453347| 0.304286 |
| H    | 1.181891 | 5.410163| 1.002531 |
| C    | 2.902207 | 0.245282| -0.087655|
| H    | 2.889346 | -0.097052| 0.953126|
| H    | 2.460537 | -0.528230| -0.723526|
| S    | 4.642810 | 0.307618| -0.568573|
| O    | 4.707039 | 0.917714| -1.895218|
| O    | 5.424065 | 0.845587| 0.545432 |
| C    | 5.065592 | -1.418022| -0.733915|
| C    | 4.865963 | -2.046145| -1.960050|
| C    | 5.575509 | -2.095932| 0.368835 |
| C    | 5.175272 | -3.397787| -2.076433|
| H    | 4.495127 | -1.472411| -2.803857|
| C    | 5.881347 | -3.447897| 0.239008 |
| H    | 5.745223 | -1.559546| 1.297025 |
| C    | 5.677680 | -4.094953| -0.978422|
| H    | 5.032284 | -3.905038| -3.024799|
| H    | 6.285837 | -3.993963| 1.084879 |
| H    | 5.919889 | -5.148582| -1.075147|
| C    | -0.056668| 0.337335 | -0.424037|
| H    | 0.390634 | -0.566964| -0.006348|
| H    | 0.045697 | 0.296992 | -1.514794|
C  -1.508937  0.432557  -0.058468
C  -2.421350  0.960812  -0.927592
H  -3.431620  1.173639  -0.584108
H  -2.090505  1.429960  -1.851234
C  -2.012107  0.011302  1.286843
O  -2.938636  0.611273  1.809881
C  -1.377534 -1.142824  2.000976
C  -1.349914 -1.112247  3.398443
C  -0.893384 -2.263982  1.317341
C  -0.809625 -2.177675  4.108237
H  -1.756059 -0.243996  3.908053
C  -0.375722 -3.339922  2.034772
H  -0.954776 -2.307951  0.231686
C  -0.322342 -3.292456  3.425921
H  -0.773931 -2.145015  5.192470
H  -0.014886 -4.215626  1.505031
H   0.093141 -4.127873  3.980908
S   -3.073020 -1.051436 -2.135085
O   -3.438703  -0.759481 -3.528393
O   -2.029194  -2.035551 -1.808367
C   -4.555279  -1.499918 -1.249080
C   -5.785564  -1.089618 -1.754238
C   -4.429292  -2.147360  -0.023634
C   -6.929579  -1.363322 -1.011371
H   -5.834649  -0.586520 -2.714330
C   -5.583053  -2.406076  0.709774
H   -3.452403  -2.455543  0.336371
C   -6.826658  -2.015060  0.216967
H   -7.901741  -1.066904 -1.391085
H   -5.508686  -2.912513  1.666162
H   -7.722446  -2.218011  0.794998
C    0.717721   1.566428  0.096408
C    0.773403   1.641518  1.630183
C    2.218009   1.598112 -0.295544
C    1.953083   2.587413  1.943417
H    0.970466   0.635634  2.020446
H   -0.178370   1.960130  2.062450
C    2.760586   2.709361  0.624919
H    2.307036   1.864496 -1.352798
H    1.599794   3.567474  2.279209
H    2.567958   2.184734  2.752727
H    2.563331   3.672119  0.147503
H    3.837249   2.635803  0.787678
**Supplementary Table 27: Cartesian coordinates of 3a**

M062X SCF energy: -1959.87004392 a.u.
M062X enthalpy: -1959.309930 a.u.
M062X free energy: -1959.408241 a.u.
M062X SCF energy in solution: -1960.32519728 a.u.
M062X enthalpy in solution: -1959.765083 a.u.
M062X free energy in solution: -1959.863394 a.u.

| ATOM | X     | Y     | Z     |
|------|-------|-------|-------|
| C    | 0.341703 | -0.965350 | -0.655970 |
| C    | -0.656403 | 0.199072  | -0.397022  |
| C    | -1.117805 | -0.083659 | 1.043923  |
| C    | -1.266391 | -1.613007 | 1.112090  |
| C    | -0.323099 | -2.185179 | 0.015977  |
| H    | 0.482640  | -1.109329 | -1.733062 |
| H    | -0.333720 | 0.258541  | 1.732474  |
| H    | -2.031048 | 0.452465  | 1.319481  |
| H    | -1.015089 | -1.991471 | 2.105804  |
| H    | -2.303940 | -1.903943 | 0.918084  |
| H    | 0.425591  | -2.866474 | 0.425496  |
| H    | -0.893702 | -2.755732 | -0.722197 |
| O    | -0.048657 | 1.446613  | -0.611473 |
| Si   | 0.130876  | 2.815784  | 0.334078  |
| C    | 0.319915  | 4.210310  | -0.901373 |
| H    | -0.619671 | 4.383012  | -1.436025 |
| H    | 0.598966  | 5.144105  | -0.401752 |
| H    | 1.091645  | 3.978073  | -1.641784 |
| C    | -1.312223 | 3.163556  | 1.480217  |
| H    | -1.304609 | 2.528561  | 2.371442  |
| H    | -1.238115 | 4.203662  | 1.820625  |
| H    | -2.282042 | 3.044321  | 0.984952  |
| C    | 1.705764  | 2.656724  | 1.354955  |
| H    | 2.585755  | 2.488477  | 0.723919  |
| H    | 1.879981  | 3.573931  | 1.929007  |
| H    | 1.646647  | 1.829965  | 2.072130  |
| C    | 1.703686  | -0.619710 | -0.059094 |
| H    | 2.030763  | 0.363220  | -0.408076 |
| H    | 1.713101  | -0.636547 | 1.036561  |
| S    | 2.974806  | -1.777044 | -0.589689 |
| O    | 2.852762  | -3.014955 | 0.181746  |
| O    | 2.962139  | -1.804687 | -2.051729 |
| C    | 4.471672  | -0.958763 | -0.065537 |
Supplementary Table 28: Cartesian coordinates of 3a'
M062X SCF energy: -1959.87314402 a.u.
M062X enthalpy: -1959.312840 a.u.
M062X free energy: -1959.412258 a.u.
M062X SCF energy in solution: -1960.32441451 a.u.
M062X enthalpy in solution: -1959.764110 a.u.
M062X free energy in solution: -1959.863528 a.u.

Cartesian coordinates

| ATOM | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | 1.111656| -1.388307| -1.654666|
| C    | 0.347387| -0.679407| -0.525918|
Supplementary Table 29: Cartesian coordinates of 1f
M062X SCF energy: -678.96162613 a.u.
M062X enthalpy: -678.723221 a.u.
M062X free energy: -678.782717 a.u.
M062X SCF energy in solution: -679.11804772 a.u.
M062X enthalpy in solution: -678.879643 a.u.
M062X free energy in solution: -678.939139 a.u.

| ATOM | X        | Y        | Z        |
|------|----------|----------|----------|
| C    | -0.098085| -0.594420| 0.016424 |
| O    | -0.025100| -1.809996| -0.027017|
| Si   | -1.859904| 0.204573 | -0.043784|
| C    | -1.732691| 2.042250 | -0.436256|
| H    | -2.724848| 2.505764 | -0.447174|
| H    | -1.129665| 2.569903 | 0.310263 |
| H    | -1.277386| 2.212327 | -1.417397|
| C    | -2.612983| -0.063988| 1.659509 |
| H    | -3.648440| 0.290769 | 1.690229 |
| H    | -2.611769| -1.129280| 1.910217 |
| H    | -2.053600| 0.467331 | 2.436204 |
| C    | -2.822966| -0.732010| -1.353529|
| H    | -3.886701| -0.475337| -1.328324|
| H    | -2.446030| -0.517131| -2.358174|
| H    | -2.722503| -1.807614| -1.179869|
Supplementary Table 30: Cartesian coordinates of TS-6a
M062X SCF energy: -1458.94390364 a.u.
M062X enthalpy: -1458.596475 a.u.
M062X free energy: -1458.678407 a.u.
M062X SCF energy in solution: -1459.26267550 a.u.
M062X enthalpy in solution: -1458.915247 a.u.
M062X free energy in solution: -1458.997179 a.u.
Imaginary frequency: -358.1462 cm⁻¹

Cartesian coordinates

| ATOM | X     | Y     | Z     |
|------|-------|-------|-------|
| C    | 1.156455 | 0.254472 | 0.152953 |
| H    | 1.180582 | 0.970187 | -0.681564 |
| H    | 1.043217 | 0.874396 | 1.056408 |
| C    | 2.443445 | -0.568761 | 0.205184 |
| H    | 2.535516 | -1.154885 | -0.715001 |
| H    | 2.357324 | -1.293110 | 1.024004 |
| C    | 3.653446 | 0.297928 | 0.394030 |
| H    | 3.690300 | 0.876087 | 1.318399 |
| C    | 4.645780 | 0.415354 | -0.483381 |
| H    | 4.643364 | -0.144117 | -1.415707 |
| H    | 5.495690 | 1.065718 | -0.302999 |

C  3.162592 -0.380808 -0.178725
O  3.077824 -1.556580 -0.482808
Si -4.919704 0.357552 0.159192
C  4.884986 2.227520 -0.066353
H  5.868618 2.661189 0.142681
H  4.165709 2.698342 0.612267
H  4.612796 2.503437 -1.090411
C  5.341479 -0.084392 1.939237
H  6.350777 0.253859 2.196181
H  5.300812 -1.168301 2.084424
H  4.644056 0.377898 2.645353
C  6.089418 -0.483168 -1.040668
H  7.135362 -0.274650 -0.794960
H  5.909861 -0.154752 -2.068955
H  5.933118 -1.565381 -1.003190
C -1.910760 0.472771 -0.027351
H -1.988951 1.321533 -0.722313
H -1.927160 0.921722 0.977929
C -0.619162 -0.309698 -0.261996
H -0.619900 -0.731332 -1.272726
Supplementary Table 31: Cartesian coordinates of TS-6b

M062X SCF energy: -1458.94796654 a.u.
M062X enthalpy: -1458.600232 a.u.
M062X free energy: -1458.681181 a.u.
M062X SCF energy in solution: -1459.26786562 a.u.
M062X enthalpy in solution: -1458.920131 a.u.
M062X free energy in solution: -1459.001080 a.u.
Imaginary frequency: -370.9533 cm⁻¹

Cartesian coordinates

| ATOM | X      | Y      | Z      |
|------|--------|--------|--------|
| C    | -2.508260 | 0.085021 | 0.136397 |
| O    | -2.091214 | 1.103811 | 0.658064 |
| Si   | -4.422412 | -0.172061 | -0.000090 |
| C    | -4.804703 | -1.346960 | -1.421015 |
| H    | -5.882984 | -1.520646 | -1.500390 |
| H    | -4.463619 | -0.942698 | -2.379702 |
| H    | -4.323796 | -2.320035 | -1.274854 |
| C    | -5.171047 | 1.527566 | -0.256110 |
| H    | -6.260326 | 1.506108 | -0.152320 |
| H    | -4.765651 | 2.221022 | 0.486664 |
| H    | -4.932310 | 1.922612 | -1.248293 |
Supplementary Table 32: Cartesian coordinates of 14a

M062X SCF energy: -1458.95924292 a.u.
M062X enthalpy: -1458.610484 a.u.
M062X free energy: -1458.691132 a.u.
M062X SCF energy in solution: -1459.27693951 a.u.
M062X enthalpy in solution: -1458.928181 a.u.
M062X free energy in solution: -1459.008829 a.u.

Cartesian coordinates

| ATOM | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | -3.106840 | -0.462736 | -0.067542 |
| O    | -3.139291 | -1.676193 | -0.162101 |
| Si   | -4.787372 | 0.483407  | 0.095132  |
| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| C    | -4.549369 | 2.303587 | -0.328621 |
| H    | -5.490273 | 2.852823 | -0.217508 |
| H    | -3.812559 | 2.775116 | 0.330383 |
| H    | -4.210496 | 2.434487 | -1.361559 |
| C    | -5.328048 | 0.282864 | 1.885947 |
| H    | -6.312260 | 0.734012 | 2.049705 |
| H    | -5.394016 | -0.777970 | 2.146564 |
| H    | -4.623121 | 0.757482 | 2.576140 |
| C    | -5.987898 | -0.364540 | -1.069362 |
| H    | -7.014644 | -0.023054 | -0.904748 |
| H    | -5.731056 | -0.175521 | -2.116168 |
| C    | -1.776170 | 0.276644 | -0.040741 |
| H    | -1.767708 | 0.988162 | -0.880197 |
| H    | -1.754989 | 0.901318 | 0.865888 |
| C    | -0.573760 | -0.657994 | -0.094981 |
| H    | -0.625312 | -1.279888 | -0.994999 |
| H    | -0.592485 | -1.339788 | 0.760536 |
| C    | 0.739901 | 0.132809 | -0.102579 |
| H    | 0.841887 | 0.728048 | 0.812781 |
| C    | 0.934178 | 0.953516 | -1.316825 |
| S    | 2.093104 | -1.109775 | 0.039291 |
| O    | 1.946004 | -1.778380 | 1.331573 |
| O    | 2.120396 | -1.871139 | -1.208494 |
| C    | 3.568212 | -0.109643 | 0.106199 |
| C    | 4.039956 | 0.311215 | 1.345708 |
| C    | 4.202453 | 0.239845 | -1.082895 |
| C    | 5.175113 | 1.115925 | 1.391163 |
| H    | 3.532747 | -0.010243 | 2.250031 |
| C    | 5.336002 | 1.045036 | -1.023809 |
| H    | 3.815891 | -0.134557 | -2.025683 |
| C    | 5.816663 | 1.483207 | 0.209537 |
| H    | 5.563443 | 1.449202 | 2.347946 |
| H    | 5.849117 | 1.324098 | -1.938248 |
| H    | 6.702830 | 2.108718 | 0.250236 |
| H    | 1.438979 | 1.909422 | -1.277159 |
| H    | 0.710250 | 0.519796 | -2.284276 |

**Supplementary Table 33:** Cartesian coordinates of 14b
M062X SCF energy: -1458.9639855 a.u.
M062X enthalpy: -1458.614428 a.u.
M062X free energy: -1458.695455 a.u.
M062X SCF energy in solution: -1459.27894308 a.u.
M062X enthalpy in solution: -1458.929383 a.u.
M062X free energy in solution: -1459.010410 a.u.

Cartesian coordinates

| ATOM | X      | Y      | Z      |
|------|--------|--------|--------|
| C    | -3.172415 | 0.663779 | -0.588933 |
| O    | -3.502502 | 1.118910 | -1.669823 |
| Si   | -4.169340 | -0.795109 | 0.195791 |
| C    | -4.192973 | -0.597423 | 2.068560 |
| H    | -4.731913 | -1.426760 | 2.538772 |
| H    | -3.176530 | -0.589883 | 2.476052 |
| H    | -4.685863 | 0.332640 | 2.369661 |
| C    | -3.230408 | -2.354667 | -0.283674 |
| H    | -3.671758 | -3.240256 | 0.185599 |
| H    | -3.251337 | -2.500916 | -1.368106 |
| H    | -2.181324 | -2.294059 | 0.025955 |
| C    | -5.889397 | -0.758215 | -0.550584 |
| H    | -6.453008 | -1.665387 | -0.311419 |
| H    | -6.459202 | 0.102392 | -0.186990 |
| H    | -5.815349 | -0.671751 | -1.638689 |
| C    | -1.925612 | 1.167063 | 0.122953 |
| H    | -2.249810 | 1.724325 | 1.014710 |
| H    | -1.363200 | 0.301550 | 0.495447 |
| C    | -1.039511 | 2.036219 | -0.781217 |
| H    | -1.631378 | 2.898958 | -1.112139 |
| H    | -0.797026 | 1.461349 | -1.681598 |
| C    | 0.206934 | 2.479139 | -0.095785 |
| H    | 0.127771 | 3.087703 | 0.799097 |
| C    | 1.517671 | 1.862374 | -0.387395 |
| S    | 1.645684 | 0.232576 | 0.444455 |
| O    | 1.352752 | 0.461601 | 1.883573 |
| O    | 0.725499 | -0.682157 | -0.236429 |
| C    | 3.308079 | -0.298328 | 0.088993 |
| C    | 4.328057 | 0.045517 | 0.971653 |
| C    | 3.551552 | -1.015128 | -1.079148 |
| C    | 5.631012 | -0.337404 | 0.667793 |
| H    | 4.089511 | 0.581466 | 1.885044 |
| C    | 4.859295 | -1.391107 | -1.371260 |
| H    | 2.723055 | -1.286784 | -1.725775 |
| C    | 5.893750 | -1.049749 | -0.501419 |
| H    | 6.439949 | -0.086885 | 1.346076 |
| H    | 5.070322 | -1.956600 | -2.272840 |
| H    | 6.911573 | -1.347203 | -0.732967 |
| H    | 2.362701 | 2.444899 | -0.008688 |
Supplementary Table 34: Cartesian coordinates of TS-7a

M062X SCF energy: -1458.94780929 a.u.
M062X enthalpy: -1458.599229 a.u.
M062X free energy: -1458.674220 a.u.
M062X SCF energy in solution: -1459.26692907 a.u.
M062X enthalpy in solution: -1458.918349 a.u.
M062X free energy in solution: -1458.993340 a.u.

Imaginary frequency: -558.0129 cm⁻¹

| ATOM | X        | Y        | Z        |
|------|----------|----------|----------|
| C    | 1.660428 | 1.642253 | -1.451356|

Cartesian coordinates
Supplementary Table 35: Cartesian coordinates of TS-7b

M062X SCF energy: -1458.94059880 a.u.
M062X enthalpy: -1458.592159 a.u.
M062X free energy: -1458.668180 a.u.
M062X SCF energy in solution: -1459.25827072 a.u.
M062X enthalpy in solution: -1458.909831 a.u.
M062X free energy in solution: -1458.985852 a.u.
Imaginary frequency: -568.9261 cm$^{-1}$

| ATOM | X    | Y    | Z    |
|------|------|------|------|
| C    | -3.310985 | -0.420426 | 1.352837 |
| C    | -3.557112 | -0.140380 | -1.054279 |
| C    | -4.357407 | -1.337778 | 1.346315 |
| H    | -2.813946 | -0.132010 | 2.273925 |
| C    | -4.603220 | -1.058535 | -1.046511 |
| H    | -3.239304 | 0.356919  | -1.965430 |
| C    | -4.997278 | -1.656694 | 0.149387 |
| H    | -4.679988 | -1.796329 | 2.275201 |
| H    | -5.115217 | -1.301773 | -1.971636 |
| H    | -5.814984 | -2.370439 | 0.150156 |

*S102*
Supplementary Table 36: Cartesian coordinates of 15a
M062X SCF energy: -1458.98293083 a.u.
M062X enthalpy: -1458.631308 a.u.
M062X free energy: -1458.705316 a.u.
M062X SCF energy in solution: -1459.30063746 a.u.
M062X enthalpy in solution: -1458.949015 a.u.
M062X free energy in solution: -1459.023023 a.u.

Cartesian coordinates

| ATOM | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | 0.090473| -0.269760| -0.020185|
| C    | 0.056281| 0.253925 | -1.459438|
| C    | -1.409256| 0.675401 | -1.630748|
| C    | -2.216811| -0.360750| -0.783672|
| C    | -1.178984| -1.113958| 0.105068|
| H    | 0.102148| 0.551693 | 0.706437|
| H    | 0.295256| -0.576500| -2.133676|
| H    | 0.768497| 1.064535 | -1.634822|
| H    | -1.539384| 1.704594 | -1.273313|
| H    | -1.759547| 0.634048 | -2.664221|
| H    | -1.480877| -1.268453| 1.144205|
| H    | -1.017669| -2.098443| -0.349931|
| O    | -3.113106| -1.096259| -1.405046|
| ATOM | X       | Y       | Z       |
|------|---------|---------|---------|
| Si   | -3.527789 | 0.589656 | 0.367745 |
| C    | -4.535029 | -0.690892 | 1.287130 |
| H    | -3.895960 | -1.360563 | 1.871019 |
| H    | -5.235043 | -0.209717 | 1.978407 |
| H    | -5.104080 | -1.300370 | 0.580666 |
| C    | -4.579842 | 1.654194 | -0.757655 |
| H    | -5.337911 | 2.195695 | -0.181962 |
| H    | -3.978533 | 2.392880 | -1.296702 |
| H    | -5.088240 | 1.026230 | -1.494306 |
| C    | -2.519834 | 1.636985 | 1.568388 |
| H    | -1.883250 | 2.364024 | 1.053964 |
| H    | -3.201035 | 2.197398 | 2.218919 |
| H    | -1.887555 | 1.015808 | 2.211572 |
| S    | 1.538218  | -1.267748 | 0.361906 |
| O    | 1.446759  | -1.634558 | 1.774288 |
| O    | 1.666339  | -2.289227 | -0.676773 |
| C    | 2.894687  | -0.125507 | 0.175173 |
| C    | 3.270804  | 0.654690  | 1.264814 |
| C    | 3.536774  | -0.030812 | -1.056420 |
| C    | 4.311821  | 1.565045  | 1.108466 |
| H    | 2.766627  | 0.524866  | 2.217436 |
| C    | 4.576303  | 0.883783  | -1.199828 |
| H    | 3.231285  | -0.680463 | -1.870697 |
| C    | 4.958111  | 1.680216  | -0.121391 |
| H    | 4.624982  | 2.177622  | 1.947484 |
| H    | 5.093683  | 0.969108  | -2.149727 |
| H    | 5.771228  | 2.389773  | -0.237649 |

**Supplementary Table 37: Cartesian coordinates of 15b**

M062X SCF energy: -1458.95454573 a.u.
M062X enthalpy: -1458.604075 a.u.
M062X free energy: -1458.679642 a.u.
M062X SCF energy in solution: -1459.27189048 a.u.
M062X enthalpy in solution: -1458.921420 a.u.
M062X free energy in solution: -1458.996987 a.u.

Cartesian coordinates

| ATOM | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | 1.700870  | 2.560684  | 0.064067  |
| C    | 1.016890  | 1.185960  | 0.289016  |
| C    | 2.011835  | 0.580015  | -0.770759 |
| C    | 2.604802  | 1.999063  | -1.057884 |
| H    | 1.021518  | 3.356020  | -0.254611 |
Supplementary Table 38: Cartesian coordinates of TS-8a

|     |        |        |        |
|-----|--------|--------|--------|
| H   | 2.252213 | 2.903117 | 0.942915 |
| H   | 1.110084 | 0.816580 | 1.316660 |
| H   | 2.325011 | 2.326830 | -2.062273 |
| H   | 3.681750 | 2.140713 | -0.928565 |
| O   | 1.597182 | -0.180747 | -1.739759 |
| Si  | 3.298658 | -0.619508 | 0.127939 |
| C   | 2.329106 | -2.061286 | 0.810559 |
| H   | 3.000602 | -2.794293 | 1.271142 |
| H   | 1.606857 | -1.736417 | 1.567396 |
| H   | 1.758751 | -2.545279 | 0.013723 |
| C   | 4.085573 | 0.399758 | 1.504636 |
| H   | 3.344257 | 0.728890 | 2.240019 |
| H   | 4.820751 | -0.216470 | 2.034694 |
| H   | 4.608605 | 1.281485 | 1.121065 |
| C   | 4.565304 | -1.106532 | -1.162498 |
| H   | 5.350157 | -1.734122 | -0.727730 |
| H   | 4.080963 | -1.662428 | -1.969659 |
| H   | 5.042737 | -0.223447 | -1.599398 |
| C   | -0.439469 | 1.091557 | -0.137288 |
| H   | -1.035492 | 1.909962 | 0.280789 |
| H   | -0.551526 | 1.060492 | -1.225806 |
| S   | -1.184639 | -0.417163 | 0.517152 |
| O   | -0.686037 | -1.575907 | -0.215355 |
| O   | -1.051676 | -0.350366 | 1.974517 |
| C   | -2.908341 | -0.210925 | 0.109389 |
| C   | -3.365034 | -0.678929 | -1.119175 |
| C   | -3.750663 | 0.420450 | 1.019575 |
| C   | -4.705297 | -0.495354 | -1.446872 |
| H   | -2.679370 | -1.191983 | -1.786505 |
| C   | -5.088943 | 0.596123 | 0.680277 |
| H   | -3.357928 | 0.742947 | 1.978875 |
| C   | -5.561324 | 0.142488 | -0.550479 |
| H   | -5.083387 | -0.856759 | -2.397507 |
| H   | -5.764810 | 1.079344 | 1.378193 |
| H   | -6.606345 | 0.280273 | -0.809602 |
Imaginary frequency: -235.5897 cm⁻¹

| ATOM | X        | Y        | Z        |
|------|----------|----------|----------|
| C    | -0.116847| 0.284367 | -0.056674|
| C    | -0.098885| -0.371165| -1.443085|
| C    | 1.379491 | -0.744813| -1.642935|
| C    | 2.167375 | 0.287763 | -0.800730|
| C    | 1.144678 | 1.147894 | -0.034116|
| H    | -0.104344| -0.462192| 0.746312 |
| H    | -0.401712| 0.381259 | -2.179987|
| H    | -0.779181| -1.223216|-1.517155 |
| H    | 1.560786 | -1.773676|-1.307600 |
| H    | 1.704707 | -0.676993|-2.684259 |
| H    | 1.451718 | 1.433303 | 0.975438 |
| H    | 0.977265 | 2.067887 | -0.610594|
| O    | 3.267322 | 0.843832 | -1.277838|
| Si   | 3.584978 | -0.513865| 0.365177 |
| C    | 4.536923 | 0.791253 | 1.306030 |
| H    | 3.862937 | 1.556966 | 1.703448 |
| H    | 5.069001 | 0.344531 | 2.152638 |
| H    | 5.258624 | 1.287815 | 0.653955 |
| C    | 4.643055 | -1.673845| -0.651456|
| H    | 5.224823 | -2.334627| -0.000039|
| H    | 4.027088 | -2.305883| -1.299591|
| H    | 5.330257 | -1.109596| -1.285770|
| C    | 2.572894 | -1.524394| 1.614182 |
| H    | 1.944189 | -2.276570| 1.126263 |
| H    | 3.254679 | -2.050121| 2.293383 |
| H    | 1.931503 | -0.878732| 2.223916 |
| S    | -1.570859| 1.298902 | 0.249208 |
| O    | -1.472465| 1.788418 | 1.623105 |
| O    | -1.714127| 2.224762 | -0.874133|
| C    | -2.917424| 0.133206 | 0.171364 |
| C    | -3.272636| -0.561247| 1.324358 |
| C    | -3.572708| -0.065147| -1.040704|
| C    | -4.306067| -1.490675| 1.253777 |
| H    | -2.758996| -0.351383| 2.257463 |
| C    | -4.604721| -0.997531| -1.097862|
| H    | -3.283501| 0.520503 | -1.907719|
| C    | -4.965673| -1.709101| 0.045158 |
| H    | -4.602888| -2.037521| 2.142654 |
| H    | -5.132449| -1.162669| -2.031378|
| H    | -5.773024| -2.432890| -0.004075|
Supplementary Table 39: Cartesian coordinates of TS-8b

M062X SCF energy: -1458.95067370 a.u.
M062X enthalpy: -1458.601067 a.u.
M062X free energy: -1458.675386 a.u.
M062X SCF energy in solution: -1459.26457270 a.u.
M062X enthalpy in solution: -1458.914966 a.u.
M062X free energy in solution: -1458.989285 a.u.

Imaginary frequency: -243.3426 cm$^{-1}$

| ATOM | X       | Y       | Z        |
|------|---------|---------|----------|
| C    | 1.588772| 2.068385| 0.729178 |
| C    | 1.066876| 1.231494| -0.462103|
| C    | 2.492459| 0.663306| -0.594661|
| C    | 3.040778| 1.839031| 0.246074 |
| H    | 1.234294| 3.097570| 0.786167 |
| H    | 1.387283| 1.571455| 1.682193 |
| H    | 3.393550| 2.634872| -0.419557|
| H    | 3.809236| 1.640528| 0.999371 |
| O    | 3.019899| 0.089632| -1.652164|
| Si   | 3.064908|-1.141587| 0.059261 |
| C    | 2.148661|-2.540931|-0.782430 |
| H    | 2.350018|-3.484190|-0.262830 |
| H    | 1.065684|-2.382825|-0.766038 |
| H    | 2.462373|-2.639239|-1.823908 |
| C    | 2.591125|-1.137043| 1.901999 |
| H    | 1.512303|-1.081184| 2.075108 |
| H    | 2.952861|-2.069200| 2.353810 |
| H    | 3.063885|-0.305022| 2.434149 |
| C    | 4.929386|-1.273392|-0.019168 |
| H    | 5.295816|-2.051267| 0.658828 |
| H    | 5.259894|-1.500306|-1.035120 |
| H    | 5.391859|-0.326109| 0.277620 |
| C    | -0.116637| 0.298833|-0.286110 |
| H    | -0.300094|-0.290188|-1.190661 |
| H    | -0.002325| -0.369638| 0.573175 |
| S    | -1.598455| 1.274861| 0.024466 |
| O    | -1.493245| 1.819849| 1.377423 |
| O    | -1.793692| 2.153955|-1.126726 |
| C    | -2.902996| 0.060160| 0.020937 |
| C    | -3.261704| -0.547509| 1.220397 |
| C    | -3.521864| -0.260374|-1.184076 |
Supplementary Table 40: Cartesian coordinates of 16a

M062X SCF energy: -1459.02671650 a.u.
M062X enthalpy: -1458.675177 a.u.
M062X free energy: -1458.749820 a.u.
M062X SCF energy in solution: -1459.33735261 a.u.
M062X enthalpy in solution: -1458.985813 a.u.
M062X free energy in solution: -1459.060456 a.u.

Cartesian coordinates

| ATOM | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | -0.082261 | -0.237299 | 1.799101 |
| C    | 1.002312  | -1.331550 | 1.861703 |
| C    | 1.098462  | -1.917469 | 0.437306 |
| C    | -0.296175 | -1.744342 | -0.184951|
| H    | -0.664660 | -0.190238 | 2.728109 |
| H    | 0.345798  | 0.764301  | 1.648103 |
| H    | 0.688436  | -2.136490 | 2.533178 |
| H    | 1.969171  | -0.970369 | 2.223425 |
| H    | 1.448541  | -2.954965 | 0.435993 |
| H    | -0.256616 | -1.527826 | -1.259255|
| H    | -0.850266 | -2.689054 | -0.082777|
| C    | -0.914194 | -0.625303 | 0.612273 |
| O    | -1.693831 | 0.313359  | 0.004007 |
| Si   | -3.359806 | 0.076053  | -0.123714|
| C    | -3.974165 | 1.537195  | -1.113203|
| H    | -3.527141 | 1.549192  | -2.112075|
| H    | -5.062066 | 1.505455  | -1.231678|
| H    | -3.716401 | 2.477839  | -0.616814|
| C    | -4.089082 | 0.042167  | 1.601957 |
| H    | -3.631749 | -0.756495 | 2.196203 |
| H    | -3.912916 | 0.989928  | 2.120416 |
| H    | -5.169306 | -0.135706 | 1.577875 |
| C    | -3.691142 | -1.543404 | -1.009080|
| ATOM | X     | Y     | Z     |
|------|-------|-------|-------|
| C    | -1.041144 | -2.886573 | -0.386798 |
| C    | -1.004890 | -1.463574 | 0.237214  |
| C    | -2.240908 | -1.172641 | -0.591180 |
| C    | -2.078649 | -2.402973 | -1.440628 |
| H    | -0.085241 | -3.248922 | -0.767529 |
| H    | -1.453334 | -3.624195 | 0.303053  |
| H    | -1.095253 | -1.400516 | 1.327995  |
| H    | -1.628966 | -2.183413 | -2.419469 |
| H    | -2.959885 | -3.031620 | -1.603086 |
| O    | -2.601417 | 0.049717 | -1.052300 |
| Si   | -3.354221 | 1.164462 | -0.022609 |
| C    | -3.118862 | 2.819544 | -0.858557 |
| H    | -3.630566 | 3.614752 | -0.306654 |
| H    | -2.058070 | 3.081783 | -0.921392 |
| H    | -3.521212 | 2.801891 | -1.876021 |

**Supplementary Table 41:** Cartesian coordinates of 16b
M062X SCF energy: -1458.99257145 a.u.
M062X enthalpy: -1458.641533 a.u.
M062X free energy: -1458.718589 a.u.
M062X SCF energy in solution: -1459.30160370 a.u.
M062X enthalpy in solution: -1458.950565 a.u.
M062X free energy in solution: -1459.027621 a.u.
Supplementary Table 42: Cartesian coordinates of TS-9a

M062X SCF energy: -2700.54889401 a.u.
M062X enthalpy: -2699.910300 a.u.
M062X free energy: -2700.025635 a.u.
M062X SCF energy in solution: -2701.16428893 a.u.
M062X enthalpy in solution: -2700.525695 a.u.
M062X free energy in solution: -2700.641030 a.u.
Imaginary frequency: -234.0747 cm⁻¹

Cartesian coordinates

| ATOM | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | 1.902522| 0.746749| -0.413675|
| C    | 0.692960| 0.898708| 0.487220 |
| C    | 0.890419| 0.106331| 1.759855 |
| C    | 2.302519| -0.497821| 1.626935 |
| C    | 2.504918| -0.559417| 0.110866 |
| H    | 1.682578| 0.710721| -1.484442 |
| Symbol | X-C | Y-C | Z-C |
|--------|-----|-----|-----|
| H      | 0.790619 | 0.762713 | 2.629845 |
| H      | 0.129985  | -0.680831 | 1.859850 |
| H      | 3.039977  | 0.184947  | 2.066195 |
| H      | 2.415194  | -1.477745 | 2.093263 |
| H      | 1.971397  | -1.423043 | -0.308168 |
| O      | 0.061084  | 2.078434  | 0.620561 |
| Si     | -0.378958 | 3.300991  | -0.467936 |
| C      | -2.247601 | 3.325785  | -0.521122 |
| H      | -2.660340 | 2.452965  | -1.041219 |
| H      | -2.657186 | 3.350872  | 0.495082 |
| H      | -2.600120 | 4.221833  | -1.044615 |
| C      | 0.297910  | 4.880145  | 0.270830 |
| H      | 1.390924  | 4.852939  | 0.324814 |
| H      | 0.011581  | 5.748278  | -0.332282 |
| H      | -0.084827 | 5.032878  | 1.284517 |
| C      | 0.335537  | 3.023672  | -2.179283 |
| H      | 0.010541  | 2.080809  | -2.630244 |
| H      | -0.017507 | 3.831034  | -2.831540 |
| H      | 1.429530  | 3.050945  | -2.185593 |
| C      | 4.188600  | -0.886917 | -0.420996 |
| O      | 4.184181  | -0.863019 | -1.833318 |
| O      | 4.658151  | -2.059554 | 0.316695 |
| C      | 5.147843  | 0.511052  | 0.139293 |
| C      | 5.732819  | 0.467970  | 1.402283 |
| C      | 5.311318  | 1.604042  | -0.708432 |
| C      | 6.480316  | 1.560452  | 1.833311 |
| H      | 5.617487  | -0.420557 | 2.015145 |
| C      | 6.061988  | 2.689692  | -0.266694 |
| H      | 4.874092  | 1.579783  | -1.702039 |
| C      | 6.639051  | 2.667987  | 1.002270 |
| H      | 6.947183  | 1.543006  | 2.812543 |
| H      | 6.205964  | 3.547240  | -0.915667 |
| H      | 7.226186  | 3.515632  | 1.341204 |
| H      | 2.592582  | 1.589553  | -0.238087 |
| C      | -0.840386 | -0.373083 | -0.815043 |
| C      | -1.652088 | -1.093373 | 0.007025 |
| C      | -2.924475 | -0.494438 | 0.525033 |
| H      | -2.809493 | 0.551461  | 0.830107 |
| H      | -3.326391 | -1.093363 | 1.345941 |
| C      | -1.299939 | -2.423425 | 0.558381 |
| O      | -1.940215 | -2.911596 | 1.477943 |
| C      | -0.056575 | -3.099889 | 0.059555 |
| C      | 0.238576  | -3.245532 | -1.299111 |
| C      | 0.851525  | -3.561967 | 1.016717 |
## Supplementary Table 43: Cartesian coordinates of TS-9b

| ATOM | X     | Y     | Z     |
|------|-------|-------|-------|
| C    | 1.059150 | 1.568915 | 1.226424 |
| C    | 0.402947 | 1.950754 | -0.069398 |
| C    | 1.436791 | 2.273901 | -1.119480 |
| C    | 2.760401 | 1.771931 | -0.495665 |
| C    | 2.396761 | 0.976233 | 0.775169 |
| H    | 0.463386 | 0.860060 | 1.813101 |
| H    | 1.475508 | 3.353367 | -1.309495 |

M062X SCF energy: -2700.55129857 a.u.
M062X enthalpy: -2699.912814 a.u.
M062X free energy: -2700.030295 a.u.
M062X SCF energy in solution: -2701.15926507 a.u.
M062X enthalpy in solution: -2700.520780 a.u.
M062X free energy in solution: -2700.638261 a.u.

Imaginary frequency: -265.2724 cm⁻¹
| Atom | x        | y        | z        |
|------|----------|----------|----------|
| H    | 1.216420 | 1.792870 | -2.081592|
| H    | 3.430494 | 2.606645 | -0.270317|
| H    | 2.256432 | -0.081734| 0.528018 |
| O    | -0.770219| 2.611558 | -0.118856|
| Si   | -1.701797| 3.267903 | 1.138602 |
| C    | -3.383719| 3.541520 | 0.368011 |
| H    | -3.287782| 4.033421 | -0.604706|
| H    | -3.993849| 4.184698 | 1.011476 |
| H    | -3.934322| 2.606614 | 0.22479  |
| C    | -0.929803| 4.907458 | 1.622527 |
| H    | 0.092906 | 4.778821 | 1.992897 |
| H    | -1.510105| 5.388071 | 2.417863 |
| H    | -0.894987| 5.591994 | 0.769354 |
| C    | -1.806206| 2.137646 | 2.631968 |
| H    | -1.860803| 1.072337 | 2.381474 |
| H    | -2.710387| 2.389824 | 3.198737 |
| H    | -0.952193| 2.273596 | 3.303130 |
| H    | 1.217681 | 2.460415 | 1.858203 |
| S    | 3.656679 | 0.759216 | -1.689357|
| O    | 2.806424 | -0.391215| -2.007671|
| O    | 4.144514 | 1.643308 | -2.745148|
| C    | 5.050046 | 0.161471 | -0.756741|
| C    | 6.211294 | 0.927404 | -0.709690|
| C    | 4.928804 | -1.043654| -0.070255|
| C    | 7.278431 | 0.473195 | 0.060027 |
| H    | 6.274543 | 1.845670 | -1.285404|
| C    | 6.001532 | -1.482507| 0.699572 |
| H    | 4.016129 | -1.626567| -0.154539|
| C    | 7.169833 | -0.724842| 0.765447 |
| H    | 8.196315 | 1.049981 | 0.104968 |
| H    | 5.923601 | -2.418728| 1.243424 |
| H    | 8.005213 | -1.073131| 1.364709 |
| H    | 3.177271 | 1.038311 | 1.536295 |
| C    | -0.315531| -0.152681| -0.903956|
| C    | -1.134952| -0.644304| 0.062083 |
| C    | -2.589315| -0.293208| 0.073347 |
| H    | -3.031033| -0.436912| 1.062817 |
| H    | -2.787942| 0.713572 | -0.304960|
| C    | -0.649231| -1.429811| 1.216592 |
| O    | -1.250632| -1.402854| 2.284158 |
| C    | 0.619842 | -2.221062| 1.099101 |
| C    | 1.418758 | -2.351721| 2.239735 |
| C    | 0.981250 | -2.879600| -0.079836|
| C    | 2.582316 | -3.110858| 2.196214 |
Supplementary Table 44: Cartesian coordinates of 17a
M062X SCF energy: -2700.59026980 a.u.
M062X enthalpy: -2699.948730 a.u.
M062X free energy: -2700.064798 a.u.
M062X SCF energy in solution: -2701.19617395 a.u.
M062X enthalpy in solution: -2700.554634 a.u.
M062X free energy in solution: -2700.670702 a.u.

| ATOM | X     | Y     | Z     |
|------|-------|-------|-------|
| C    | 1.790271 | -0.203455 | -1.087173 |
| C    | 0.778321 | 0.330936 | -0.052592 |
| C    | 0.785671 | -0.794564 | 0.993928 |
| C    | 0.732910 | -2.076223 | 0.157856 |
| C    | 1.492609 | -1.712105 | -1.145292 |
| H    | 1.718785 | 0.284778 | -2.062249 |
| H    | 1.735211 | -0.741496 | 1.538891 |
| H    | -0.016354 | -0.693933 | 1.729777 |
| H    | 1.165532 | -2.944149 | 0.660749 |
| Element | X    | Y    | Z    |
|---------|------|------|------|
| H       | -0.295800 | -2.344744 | -0.105415 |
| H       | 0.905568  | -1.976166 | -2.031766 |
| O       | 1.079887  | 1.587534  | 0.498710  |
| Si      | 2.554244  | 2.277128  | 0.901246  |
| C       | 2.106339  | 3.852594  | 1.801222  |
| H       | 1.430098  | 3.646051  | 2.636872  |
| H       | 3.002125  | 4.340048  | 2.200947  |
| H       | 1.606278  | 4.555158  | 1.127701  |
| C       | 3.552342  | 1.147064  | 2.023245  |
| H       | 3.800211  | 0.192801  | 1.545671  |
| H       | 4.500651  | 1.628136  | 2.290767  |
| H       | 3.012387  | 0.931932  | 2.951597  |
| C       | 3.554243  | 2.691658  | -0.636801 |
| H       | 2.914582  | 3.138189  | -1.405358 |
| H       | 4.329166  | 3.424870  | -0.385252 |
| H       | 4.054366  | 1.821781  | -1.074419 |
| S       | 2.978970  | -2.700390 | -1.427305 |
| O       | 3.516880  | -2.277189 | -2.719168 |
| O       | 2.636491  | -4.096235 | -1.164660 |
| C       | 4.161405  | -2.197880 | -0.181228 |
| C       | 4.112401  | -2.773244 | 1.086581  |
| C       | 5.151708  | -1.281818 | -0.530554 |
| C       | 5.064710  | -2.399025 | 2.031726  |
| H       | 3.365498  | -3.528507 | 1.309613  |
| C       | 6.104673  | -0.923987 | 0.419239  |
| H       | 5.176464  | -0.887207 | -1.541836 |
| C       | 6.056490  | -1.478180 | 1.697486  |
| H       | 5.042661  | -2.839314 | 3.023094  |
| H       | 6.886093  | -0.217101 | 0.160180  |
| H       | 6.800140  | -1.196267 | 2.436122  |
| H       | 2.800920  | -0.034386 | -0.698814 |
| C       | -0.593817 | 0.492555  | -0.757466 |
| H       | -0.456852 | 1.310168  | -1.469607 |
| H       | -0.828779 | -0.414528 | -1.325003 |
| C       | -1.707081 | 0.800583  | 0.189755  |
| C       | -2.560871 | -0.297390 | 0.721079  |
| H       | -3.255872 | 0.087805  | 1.471142  |
| H       | -2.010275 | -1.156111 | 1.119634  |
| C       | -1.994982 | 2.143546  | 0.700535  |
| O       | -2.544466 | 2.273868  | 1.791652  |
| C       | -1.636698 | 3.347065  | -0.111364 |
| C       | -1.157816 | 4.483137  | 0.541781  |
| C       | -1.881839 | 3.384355  | -1.486179 |
| C       | -0.873557 | 5.634852  | -0.183840 |
| ATOM | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | -0.083816 | -1.131584 | -2.011871 |
| C    | 0.806419  | -1.310525  | -0.773569  |
| C    | 0.012594  | -2.348761  | 0.060012   |
| C    | -1.467937 | -2.185018  | -0.368037  |
| C    | -1.503848 | -1.084533  | -1.448178  |
| H    | 0.196415  | -0.266227  | -2.617541  |
| H    | 0.339708  | -3.356665  | -0.199906  |
| H    | 0.160164  | -2.220122  | 1.137889   |
| H    | -1.867452 | -3.128800  | -0.750993  |
| H    | -1.702532 | -0.110999  | -0.981173  |
| O    | 2.083149  | -1.728316  | -1.187678  |

**Supplementary Table 45: Cartesian coordinates of 17b**

M062X SCF energy: -2700.59216076 a.u.
M062X enthalpy: -2699.950790 a.u.
M062X free energy: -2700.065595 a.u.
M062X SCF energy in solution: -2701.19455209 a.u.
M062X enthalpy in solution: -2700.553181 a.u.
M062X free energy in solution: -2700.667986 a.u.
| Element | X     | Y     | Z     |
|---------|-------|-------|-------|
| Si      | 3.153372 | -2.847630 | -0.538905 |
| C       | 4.686877  | -2.689301  | -1.593907  |
| H       | 5.072867  | -1.667991  | -1.587655  |
| C       | 5.477029  | -3.353911  | -1.228039  |
| H       | 4.467819  | -2.963585  | -2.630739  |
| C       | 3.493534  | -2.505501  | 1.272026   |
| H       | 2.577893  | -2.524029  | 1.874357   |
| H       | 1.507909  | -1.136559  | -0.726992  |
| C       | 1.843111  | -1.923613  | 0.082790   |
| C       | 0.953334  | -0.005211  | 0.059207   |
| H       | 3.163476  | -0.259090  | 0.894844   |
| C       | -0.021951 | 0.259230   | 0.488479   |
| C       | 1.507909  | 1.136559   | -0.726992  |
| C       | 0.607831  | 2.098049   | -1.408474  |
| H       | 1.107371  | 2.574791   | -2.255906  |
| C       | -0.357965 | 1.683422   | -1.708870  |
| C       | 2.944849  | 1.383881   | -0.908838  |
| O       | 3.343715  | 1.916854   | -1.939142  |
| C       | 3.912242  | 1.023839   | 0.174707   |
| C       | 5.200303  | 0.621102   | -0.183503  |
| C       | 3.588675  | 1.207001   | 1.522481   |
| C       | 6.140129  | 0.332032   | 0.799852   |
| H       | 5.448571  | 0.552678   | -1.238219  |
| C       | 4.540364  | 0.943840   | 2.504318   |
| C       | 2.610391  | 1.597555   | 1.790948   |
| C       | 5.808236  | 0.489711   | 2.145462   |
| H       | 7.134470  | -0.000953  | 0.519356   |
| H       | 4.293401  | 1.098373   | 3.549730   |
| H       | 6.543852  | 0.273061   | 2.913926   |
| S       | 0.225777  | 3.499815   | -0.256250  |
| O       | 0.943602  | 3.240382   | 0.992611   |
| O       | 0.416700  | 4.742955   | -0.996622  |
| C       | -1.519783 | 3.342874   | 0.079953   |
| C       | -1.942412 | 2.480693   | 1.086308   |
| C       | -2.415527 | 4.092003   | -0.679117  |
| C       | -3.307986 | 2.365636   | 1.336882   |
| H       | -1.222905 | 1.920433   | 1.674240   |
| C       | -3.776680 | 3.969445   | -0.417139  |
| H       | -2.038812 | 4.769740   | -1.438282  |
| C       | -4.219234 | 3.108483   | 0.587595   |
**Supplementary Table 46: Cartesian coordinates of TS-10a**

M062X SCF energy: -2700.56959603 a.u.
M062X enthalpy: -2699.930259 a.u.
M062X free energy: -2700.046688 a.u.
M062X SCF energy in solution: -2701.17588074 a.u.
M062X enthalpy in solution: -2700.536544 a.u.
M062X free energy in solution: -2700.652973 a.u.
Imaginary frequency: -250.4821 cm⁻¹

| ATOM | X      | Y      | Z      |
|------|--------|--------|--------|
| C    | -2.114782 | -0.318558 | 1.028083 |
| C    | -0.984584 | -0.103248 | 0.003020 |
| C    | -1.448145 | -0.975300 | -1.175989 |
| C    | -1.982208 | -2.253123 | -0.519653 |
| C    | -2.484411 | -1.801659 | 0.876478 |
| H    | -1.837811 | -0.046697 | 2.049595 |
| H    | -2.260514 | -0.451753 | -1.690632 |
| H    | -0.651161 | -1.151246 | -1.903143 |
| H    | -2.766721 | -2.739915 | -1.103559 |
| H    | -1.192062 | -2.998399 | -0.390998 |
| H    | -2.048305 | -2.410389 | 1.675988 |
| O    | -0.767095 | 1.240233 | -0.352825 |
| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| Si   | -1.837530 | 2.494637 | -0.659431 |
| C    | -0.759131 | 3.848893 | -1.364046 |
| H    | -0.129133 | 4.288747 | -0.584867 |
| H    | -0.102863 | 3.448227 | -2.143822 |
| H    | -1.366530 | 4.647887 | -1.802440 |
| C    | -3.159623 | 1.993979 | -1.897063 |
| H    | -3.786724 | 1.173355 | -1.531389 |
| H    | -3.824558 | 2.844346 | -2.090201 |
| H    | -2.719406 | 1.688669 | -2.852149 |
| C    | -2.658342 | 3.091263 | 0.924350 |
| H    | -1.932793 | 3.143944 | 1.742821 |
| H    | -3.059508 | 4.099999 | 0.772500 |
| H    | -3.487930 | 2.452749 | 1.244947 |
| S    | -4.243742 | -2.108768 | 1.152336 |
| O    | -4.531513 | -1.668019 | 2.516112 |
| O    | -4.523226 | -3.475416 | 0.717824 |
| C    | -5.119997 | -1.005771 | 0.049204 |
| C    | -5.366152 | -1.399228 | -1.264261 |
| C    | -5.594295 | 0.205113 | 0.550788 |
| C    | -6.081127 | -0.543722 | -2.099242 |
| H    | -5.038037 | -2.375408 | -1.606817 |
| C    | -6.314757 | 1.047876 | -0.290863 |
| H    | -5.417491 | 0.454102 | 1.592910 |
| C    | -6.552092 | 0.674873 | -1.613099 |
| H    | -6.284471 | -0.836092 | -3.124053 |
| H    | -6.694978 | 1.991454 | 0.086780 |
| H    | -7.113991 | 1.334210 | -2.266977 |
| H    | -2.962571 | 0.309802 | 0.732321 |
| C    | 0.357334 | -0.591769 | 0.598007 |
| H    | 0.529334 | 0.002616 | 1.499036 |
| H    | 0.281563 | -1.641863 | 0.903689 |
| C    | 1.479830 | -0.431685 | -0.383775 |
| C    | 1.974976 | -1.494965 | -1.086067 |
| C    | 2.072580 | 0.915191 | -0.685071 |
| O    | 2.393815 | 1.187142 | -1.828490 |
| C    | 2.312150 | 1.900526 | 0.418210 |
| C    | 2.393586 | 3.253103 | 0.075219 |
| C    | 2.555962 | 1.504874 | 1.737742 |
| C    | 2.663519 | 4.207492 | 1.048357 |
| H    | 2.243484 | 3.533625 | -0.962138 |
| C    | 2.848881 | 2.462533 | 2.706651 |
| H    | 2.561182 | 0.449804 | 2.001736 |
| C    | 2.887786 | 3.812484 | 2.367437 |
| H    | 2.709742 | 5.258321 | 0.779527 |
Supplementary Table 47: Cartesian coordinates of TS-10b

M062X SCF energy: -2700.57253083 a.u.
M062X enthalpy: -2699.933178 a.u.
M062X free energy: -2700.047400 a.u.
M062X SCF energy in solution: -2701.17181321 a.u.
M062X enthalpy in solution: -2700.532460 a.u.
M062X free energy in solution: -2700.646682 a.u.
Imaginary frequency: -319.9239 cm$^{-1}$

Cartesian coordinates

| ATOM | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | -0.154291 | -1.790840 | 1.809986 |
| C    | -0.815627 | -1.642804 | 0.431766 |
| C    | 0.093402  | -2.521810 | -0.465447 |
| C    | 1.491270  | -2.481340 | 0.203714 |
| C    | 1.338386  | -1.667880 | 1.505985 |
| H    | -0.520726 | -1.063011 | 2.538550 |
| H    | -0.273263 | -3.550636 | -0.448899 |
| H    | 0.110012  | -2.186164 | -1.507950 |
| H    | 1.855558  | -3.492386 | 0.407631 |
| H    | 1.600819  | -0.617435 | 1.331671 |
| O    | -2.154665 | -2.071540 | 0.511135 |
| Si   | -3.126079 | -2.743542 | -0.685024 |
| C    | -4.878885 | -2.541966 | -0.074837 |
|   |   |   |   |
|---|---|---|---|
| H | -5.230966 | -1.519689 | -0.241120 |
| H | -5.553543 | -3.224160 | -0.603297 |
| H | -4.950749 | -2.752692 | 0.996648  |
| C | -2.923596 | -1.885669 | -2.345229 |
| H | -1.899505 | -1.910794 | -2.731369 |
| H | -3.559540 | -2.393290 | -3.080443 |
| H | -3.249179 | -0.841355 | -2.296128 |
| C | -2.736645 | -4.575393 | -0.893024 |
| H | -2.608319 | -5.064421 | 0.078381  |
| H | -3.569924 | -5.070939 | -1.404125 |
| H | -1.837166 | -4.757776 | -1.489386 |
| C | -0.779757 | -0.177551 | -0.071127 |
| H | -1.438991 | -0.119233 | -0.945191 |
| H | 0.226996  | 0.069779  | -0.423930 |
| C | -1.176773 | 0.810662  | 0.983971  |
| C | -0.286921 | 1.759015  | 1.428646  |
| C | -2.510888 | 0.746732  | 1.677390  |
| O | -2.517629 | 0.665096  | 2.893441  |
| C | -3.785234 | 0.829037  | 0.906893  |
| C | -4.978361 | 0.574172  | 1.592013  |
| C | -3.819541 | 1.238922  | -0.428910 |
| C | -6.197241 | 0.708275  | 0.941705  |
| H | -4.921882 | 0.278386  | 2.634336  |
| C | -5.045919 | 1.365899  | -1.079705 |
| H | -2.902408 | 1.507992  | -0.947082 |
| C | -6.230942 | 1.098425  | -0.398620 |
| H | -7.122061 | 0.507152  | 1.473004  |
| H | -5.073180 | 1.692596  | -2.114343 |
| H | -7.183820 | 1.203128  | -0.908519 |
| C | -0.380588 | 3.441092  | -0.222562 |
| O | -1.044098 | 2.790827  | -1.362648 |
| O | -0.843795 | 4.738389  | 0.288604  |
| C | 1.358568  | 3.581220  | -0.604363 |
| C | 1.957410  | 2.538752  | -1.305442 |
| C | 2.088193  | 4.644509  | -0.081258 |
| C | 3.335960  | 2.571308  | -1.497736 |
| H | 1.364105  | 1.719134  | -1.697397 |
| C | 3.463213  | 4.672076  | -0.297331 |
| H | 1.577962  | 5.430246  | 0.466165  |
| C | 4.083687  | 3.636867  | -0.996930 |
| H | 3.812546  | 1.756541  | -2.033127 |
| H | 4.051426  | 5.500232  | 0.084571  |
| H | 5.157934  | 3.661162  | -1.151887 |
| H | -0.389681 | -2.794484 | 2.182616  |
Supplementary Table 48: Cartesian coordinates of 7a
M062X SCF energy: -1920.58424114 a.u.
M062X enthalpy: -1920.054331 a.u.
M062X free energy: -1920.149777 a.u.
M062X SCF energy in solution: -1920.58424114 a.u.
M062X enthalpy in solution: -1920.054331 a.u.
M062X free energy in solution: -1920.149777 a.u.

| ATOM | X      | Y      | Z       |
|------|--------|--------|---------|
| C    | -1.106100 | -1.065656 | -1.460423 |
| C    | 0.253020   | -1.062716 | -0.724893 |
| C    | -0.087587  | -0.362042 | 0.600560  |
| C    | -1.003004  | 0.788440  | 0.184130  |
| C    | -1.843418  | 0.203244  | -0.974039 |
| H    | -0.998651  | -1.089848 | -2.547407 |
| H    | -0.658129  | -1.054777 | 1.230217  |
| H    | 0.797661   | -0.030040 | 1.149404  |
| H    | -1.619765  | 1.153030  | 1.010127  |
| H    | -0.408582  | 1.630593  | -0.176191 |
| H    | -2.028569  | 0.922761  | -1.776579 |
| O    | 0.761891   | -2.370142 | -0.602397 |
| Si   | 0.569612   | -3.497316 | 0.622696  |
| C    | 1.528709   | -4.978871 | -0.006295 |
| H    | 2.590900   | -4.739427 | -0.123251 |
H  1.450616 -5.821845  0.688474
H  1.148552 -5.306228 -0.978751
C  1.352499 -2.898473  2.225901
H  0.717822 -2.199651  2.777906
H  1.558077 -3.752118  2.881748
H  2.305848 -2.398636  2.020516
C  -1.234154 -3.944340  0.872734
H  -1.642629 -4.410438 -0.030877
H  -1.332101 -4.668810  1.689611
H  -1.867164 -3.082431  1.112067
C   1.289524 -0.276730 -1.557410
H   0.878594  0.701426 -1.825910
H   1.434286 -0.846487 -2.481591
C   2.900271  1.260676 -0.297736
O   1.970657  1.992398  0.002380
C   4.307717  1.725814 -0.072085
C   5.375955  1.338091 -0.886646
C   4.524382  2.651519  0.953852
C   6.648049  1.858392 -0.663899
H   5.207246  0.648019 -1.706688
C   5.797631  3.154842  1.186639
H   3.677990  2.963980  1.556717
C   6.861795  2.757656  0.377284
H   7.471416  1.562850 -1.306158
H   5.962269  3.861521  1.993711
H   7.856170  3.155680  0.554319
C   2.622260 -0.094634 -0.870743
C   3.469541 -1.110784 -0.665495
H   3.228133 -2.108566 -1.018041
H   4.398101 -0.979431 -0.118427
H  -1.644277 -1.973523 -1.165963
S  -3.483422 -0.300030 -0.414025
O  -4.190207 -0.861706 -1.563579
O  -3.310889 -1.087396  0.811139
C  -4.290436  1.225106  0.036770
C  -4.858195  2.003631 -0.968480
C  -4.344044  1.599083  1.375896
C  -5.477107  3.199835 -0.620264
H  -4.832238  1.658744 -1.997681
C  -4.969039  2.797039  1.711952
H  -3.918249  0.944563  2.129838
C  -5.527834  3.595225  0.715993
H  -5.928289  3.818688 -1.388795
H  -5.024707  3.103985  2.751128
H   -6.014380  4.528001  0.983030

Supplementary Table 49: Cartesian coordinates of 7a'
M062X SCF energy: -1920.58267289 a.u.
M062X enthalpy: -1920.052744 a.u.
M062X free energy: -1920.148756 a.u.
M062X SCF energy in solution: -1921.02361389 a.u.
M062X enthalpy in solution: -1920.493685 a.u.
M062X free energy in solution: -1920.589697 a.u.

Cartesian coordinates

| ATOM | X      | Y      | Z      |
|------|--------|--------|--------|
| C    | -1.194407 | 1.853257 | 0.922425 |
| C    | 0.216381 | 1.501679 | 0.393343 |
| C    | -0.070556 | 1.037396 | -1.045089 |
| C    | -1.333486 | 0.186293 | -0.907048 |
| C    | -2.176546 | 0.960532 | 0.127932 |
| H    | -1.272091 | 1.725272 | 2.006771 |
| H    | -0.287642 | 1.917419 | -1.664451 |
| H    | 0.762245 | 0.492776 | -1.496465 |
| H    | -1.868051 | 0.046708 | -1.849251 |
| H    | -1.053807 | -0.800150 | -0.525501 |
| O    | 1.074464 | 2.616179 | 0.503968 |
| Si   | 1.559510 | 3.758823 | -0.610411 |
| C    | 2.770419 | 4.822943 | 0.341625 |
| H    | 3.645620 | 4.241122 | 0.648841 |
| H    | 3.123671 | 5.661849 | -0.267306 |
| H    | 2.305757 | 5.231033 | 1.244287 |
| C    | 2.432134 | 2.983571 | -2.084938 |
| H    | 1.741511 | 2.538965 | -2.807179 |
| H    | 3.020679 | 3.744317 | -2.610353 |
| H    | 3.120941 | 2.199374 | -1.752034 |
| C    | 0.108589 | 4.810056 | -1.185087 |
| H    | -0.382579 | 5.290121 | -0.331976 |
| H    | 0.456054 | 5.602658 | -1.857391 |
| H    | -0.647856 | 4.231075 | -1.725421 |
| C    | 0.835385 | 0.384316 | 1.259771 |
| H    | 0.127299 | -0.443233 | 1.356404 |
| H    | 0.969468 | 0.816715 | 2.257255 |
| C    | 2.165992 | -1.428018 | 0.032012 |
| O    | 1.162261 | -1.792630 | -0.558731 |
| C    | 3.391957 | -2.291343 | 0.008764 |
| C    | 4.314346 | -2.325495 | 1.058933 |
Computational methods of triplet energy

All density functional theory (DFT) calculations were carried out using the Gaussian 16 software package. All geometries were optimized using the B3LYP functional with a basis set of def2-TZVPP for all atoms with the SMD continuum solvation model. Frequencies were calculated for all the stationary points to confirm if each optimized structure is a local minimum on the respective potential energy surface or a transition state structure with only one imaginary frequency. The 3D structures were plot using CYLview.

All energies were calculated at B3LYP/def2-TZVPP/SMD(acetonitrile) level of theory.
Supplementary Table 50: Cartesian coordinates of 2a-singlet

B3LYP SCF energy in solution: -718.7455380 a.u.
B3LYP enthalpy in solution: -718.482242 a.u.
B3LYP free energy in solution: -718.544551 a.u.

Cartesian coordinates

| ATOM | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | -0.589779 | -0.566217 | -0.003183 |
| O    | -0.475468 | -1.782851 | 0.063850  |
| Si   | -2.398411 | 0.162605  | 0.035262  |
| C    | -3.174127 | -0.427212 | 1.640112  |
| H    | -4.217945 | -0.108026 | 1.700192  |
| H    | -3.152401 | -1.516540 | 1.711524  |
| H    | -2.651382 | -0.021350 | 2.509349  |
| C    | -3.291450 | -0.565862 | -1.447275 |
| H    | -4.337900 | -0.249813 | -1.456457 |
| H    | -2.837211 | -0.240745 | -2.386183 |
| H    | -3.271417 | -1.657333 | -1.422782 |
| C    | -2.390268 | 2.038292  | -0.050341 |
| H    | -3.415294 | 2.418839  | -0.028805 |
| H    | -1.857631 | 2.480658  | 0.794361  |
| H    | -1.924732 | 2.399854  | -0.969820 |
| C    | 0.619823  | 0.334276  | -0.114799 |
| H    | 0.479256  | 0.946848  | -1.014447 |
| H    | 0.561978  | 1.049963  | 0.715100  |
| C    | 1.971726  | -0.368417 | -0.138584 |
| H    | 2.003214  | -1.069528 | -0.976120 |
| H    | 2.089368  | -0.966869 | 0.767616  |
| C    | 3.142574  | 0.618972  | -0.252462 |
| H    | 2.998183  | 1.225047  | -1.154242 |
| H    | 3.133650  | 1.306125  | 0.597772  |
| C    | 4.472581  | -0.066683 | -0.335119 |
| H    | 4.603602  | -0.741698 | -1.178106 |
| C    | 5.469929  | 0.077669  | 0.532023  |
| H    | 5.386052  | 0.736834  | 1.389762  |
| H    | 6.406051  | -0.454840 | 0.414589  |
Supplementary Table 51: Cartesian coordinates of 2a-triplet

B3LYP SCF energy in solution: -718.65230204 a.u.
B3LYP enthalpy in solution: -718.390455 a.u.
B3LYP free energy in solution: -718.454209 a.u.

| ATOM | X      | Y      | Z      |
|------|--------|--------|--------|
| C    | -0.590724 | -0.645944 | -0.064171 |
| O    | -0.650105 | -1.913765 | 0.066810 |
| Si   | -2.350232 | 0.177126 | -0.044350 |
| C    | -3.101056 | 0.069818 | 1.673963 |
| H    | -4.105165 | 0.504882 | 1.675059 |
| H    | -3.186267 | -0.968066 | 2.002860 |
| H    | -2.500846 | 0.610911 | 2.408420 |
| C    | -3.405953 | -0.764742 | -1.271227 |
| H    | -4.399735 | -0.312017 | -1.330302 |
| H    | -2.970067 | -0.749866 | -2.272138 |
| H    | -3.530371 | 1.806775 | -0.969967 |
| C    | -2.117832 | 1.960928 | -0.569382 |
| H    | -3.105960 | 2.410849 | 0.706426 |
| H    | -1.588301 | 2.547663 | 0.182653 |
| H    | -1.579721 | 2.042382 | 1.515235 |
| C    | 0.609470 | 0.141538 | 0.467797 |
| H    | 0.407089 | 1.205504 | 0.357128 |
| H    | 0.715812 | -0.064862 | 1.540745 |
| C    | 1.913308 | -0.220022 | -0.255393 |
| H    | 1.798788 | -0.025581 | -1.324735 |
| H    | 2.109038 | 1.288880 | 0.144761 |
| C    | 3.107381 | 0.579177 | 0.289014 |
| H    | 2.879627 | 1.647130 | 0.196138 |
| H    | 3.239615 | 0.370802 | 1.353648 |
| C    | 4.378813 | 0.284703 | -0.447741 |
| H    | 4.369570 | 0.506695 | -1.512479 |
| C    | 5.481102 | -0.225005 | 0.093115 |
| H    | 5.538622 | -0.465169 | 1.149666 |
| H    | 6.367102 | -0.417955 | -0.499687 |
7. Spectroscopic Data

Supplementary Figure 19: $^1$H NMR of 21 (600 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 20: $^{13}$C NMR of 21 (151 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 21: $^1$H NMR of 2n (600 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 22: $^{13}$C NMR of 2n (151 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 23: $^{19}$F NMR of $2n$ (565 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 24: $^1$H NMR of $2ac$ (600 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 25: $^{13}$C NMR of 2ac (151 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 26: $^1$H NMR of 2ai (600 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 27: $^{13}$C NMR of 2ai (101 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 28: $^1$H NMR of 2aj (600 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 29: $^{13}$C NMR of 2aj (151 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 30: $^{19}$F NMR of 2aj (565 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 31: $^1$H NMR of 3a (600 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 32: $^{13}$C NMR of 3a (151 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 33: $^{29}$Si NMR of 3a (119 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 34: $^1$H NMR of 3a' (600 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 35: $^{13}$C NMR of 3a' (151 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 36: $^1$H NMR of 3b (600 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 37: $^{13}$C NMR of 3b (151 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 38: $^{29}$Si NMR of 3b (119 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 39: $^1$H NMR of 3c (600 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 40: $^{13}$C NMR of 3c (151 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 41: $^{29}$Si NMR of 3c (119 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 42: $^{1}$H NMR of 3d (600 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 43: $^{13}$C NMR of 3d (151 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 44: $^{29}$Si NMR of 3d (119 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 45: $^1$H NMR of 3d' (600 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 46: $^{13}$C NMR of 3d' (151 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 47: $^{29}$Si NMR of 3d’ (119 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 48: $^1$H NMR of 3e (600 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 49: \(^{13}\)C NMR of 3e (151 MHz, CDCl\(_3\), 25 °C)

Supplementary Figure 50: \(^{29}\)Si NMR of 3e (119 MHz, CDCl\(_3\), 25 °C)
Supplementary Figure 51: $^1$H NMR of 3f (600 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 52: $^{13}$C NMR of 3f (151 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 53: $^{29}$Si NMR of 3f (119 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 54: $^1$H NMR of 3g (600 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 55: $^1$C NMR of 3g (151 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 56: $^{29}$Si NMR of 3g (119 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 57: $^1$H NMR of 3h (600 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 58: $^{13}$C NMR of 3h (151 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 59: \(^{29}\)Si NMR of 3h (119 MHz, CDCl\(_3\), 25 °C)

Supplementary Figure 60: \(^{1}\)H NMR of 3i (600 MHz, CDCl\(_3\), 25 °C)
Supplementary Figure 61: $^{13}$C NMR of 3i (151 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 62: $^{29}$Si NMR of 3i (119 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 63: $^{19}$F NMR of 3i (565 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 64: $^1$H NMR of 3j (600 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 65: $^{13}$C NMR of 3j (151 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 66: $^{29}$Si NMR of 3j (119 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 67: $^{19}$F NMR of 3j (565 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 68: $^1$H NMR of 3k (600 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 69: $^{13}$C NMR of 3k (151 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 70: $^{29}$Si NMR of 3k (119 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 71: $^1$H NMR of 3i (600 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 72: $^{13}$C NMR of 3i (151 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 73: $^29$Si NMR of 3l (119 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 74: $^1$H NMR of 3m (600 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 75: $^{13}$C NMR of 3m (151 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 76: $^{29}$Si NMR of 3m (119 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 77: $^1$H NMR of 3n (600 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 78: $^{13}$C NMR of 3n (151 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 79: $^{29}$Si NMR of 3n (119 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 80: $^{19}$F NMR of 3n (565 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 81: $^1$H NMR of 3o (600 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 82: $^{13}$C NMR of 3o (151 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 83: $^{29}$Si NMR of 3o (119 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 84: $^1$H NMR of 3p (600 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 85: $^{13}$C NMR of 3p (151 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 86: $^{29}$Si NMR of 3p (119 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 87: $^1$H NMR of 3q (600 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 88: $^{13}$C NMR of 3q (151 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 89: $^{29}$Si NMR of 3q (119 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 90: $^1$H NMR of 3r (600 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 91: $^{13}$C NMR of 3$r$ (151 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 92: $^{29}$Si NMR of 3$r$ (119 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 93: $^1$H NMR of 3s (600 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 94: $^{13}$C NMR of 3s (151 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 95: $^{29}$Si NMR of 3s (119 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 96: $^1$H NMR of 3t (600 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 97: $^{13}$C NMR of 3t (151 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 98: $^{29}$Si NMR of 3t (119 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 99: $^1$H NMR of 3u (600 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 100: $^{13}$C NMR of 3u (151 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 101: $^{29}$Si NMR of 3u (119 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 102: $^1$H NMR of 3v (600 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 103: $^{13}$C NMR of 3v (151 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 104: $^{29}$Si NMR of 3v (119 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 105: $^1$H NMR of 3w (600 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 106: $^{13}$C NMR of 3w (151 MHz, CDCl$_3$, 25 °C)
**Supplementary Figure 107:** $^{29}$Si NMR of 3w (119 MHz, CDCl$_3$, 25 ºC)

**Supplementary Figure 108:** $^1$H NMR of 3x (600 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 109: $^{13}$C NMR of 3x (151 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 110: $^{29}$Si NMR of 3x (119 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 111: $^1$H NMR of 3y (600 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 112: $^{13}$C NMR of 3y (151 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 113: $^{29}$Si NMR of 3y (119 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 114: $^1$H NMR of 3z (600 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 115: $^{13}$C NMR of 3z (151 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 116: $^{29}$Si NMR of 3z (119 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 117: $^1$H NMR of 3aa (600 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 118: $^{13}$C NMR of 3aa (151 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 119: $^{29}$Si NMR of 3aa (119 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 120: $^1$H NMR of 5a (600 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 121: $^{13}$C NMR of 5a (600 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 122: $^1$H NMR of 7a (600 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 123: $^{13}$C NMR of 7a (151 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 124: $^{29}$Si NMR of 7a (119 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 125: $^1$H NMR of 7a' (600 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 126: $^{13}$C NMR of 7a' (151 MHz, CDCl$_3$, 25 °C)
**Supplementary Figure 127:** $^{29}$Si NMR of 7a' (119 MHz, CDCl$_3$, 25 ºC)

**Supplementary Figure 128:** $^1$H NMR of 7a'' (600 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 129: $^{13}$C NMR of 7a" (151 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 130: $^1$H NMR of 7b (600 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 131: $^{13}$C NMR of 7b (151 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 132: $^{29}$Si NMR of 7b (119 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 133: $^1$H NMR of 7b' (600 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 134: $^{13}$C NMR of 7b' (151 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 135: $^{29}$Si NMR of $7b'$ (119 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 136: $^1$H NMR of $7c$ (600 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 137: $^{13}$C NMR of 7c (151 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 138: $^{29}$Si NMR of 7c (119 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 139: $^{19}$F NMR of 7c (565 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 140: $^1$H NMR of 7c’ (600 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 141: $^{13}$C NMR of 7c' (151 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 142: $^{29}$Si NMR of 7c' (119 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 143: $^{19}$F NMR of 7c' (565 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 144: $^1$H NMR of 7d (600 MHz, CDCl$_3$, 25 ºC)
**Supplementary Figure 145:** $^{13}$C NMR of 7d (151 MHz, CDCl$_3$, 25 °C)

**Supplementary Figure 146:** $^{29}$Si NMR of 7d (119 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 147: $^1$H NMR of $7d'$ (600 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 148: $^{13}$C NMR of $7d'$ (151 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 149: $^{29}$Si NMR of 7d' (119 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 150: $^1$H NMR of 7e (600 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 151: $^{13}$C NMR of 7e (151 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 152: $^{29}$Si NMR of 7e (119 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 153: $^{19}$F NMR of 7e (565 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 154: $^1$H NMR of 7e' (600 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 155: $^{13}$C NMR of 7e' (151 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 156: $^{29}$Si NMR of 7e' (119 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 157: $^{19}$F NMR of 7e' (565 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 158: $^1$H NMR of 7f (600 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 159: $^{13}$C NMR of 7f (151 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 160: $^{29}$Si NMR of 7f (119 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 161: $^1$H NMR of 7f' (600 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 162: $^{13}$C NMR of 7f' (151 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 163: $^{29}$Si NMR of 7f (119 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 164: $^1$H NMR of 7g (600 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 165: $^{13}$C NMR of 7g (151 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 166: $^{29}$Si NMR of 7g (119 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 167: $^1$H NMR of 7g$'$ (600 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 168: $^{13}$C NMR of 7g$'$ (151 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 169: $^{29}$Si NMR of 7g' (119 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 170: $^1$H NMR of 7h (600 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 171: $^{13}$C NMR of $7h$ (151 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 172: $^{29}$Si NMR of $7h$ (119 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 173: $^1$H NMR of 7h' (600 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 174: $^{13}$C NMR of 7h' (151 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 175: $^{29}$Si NMR of $7h$ (119 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 176: $^1$H NMR of $7i$ (600 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 177: $^{13}$C NMR of 7i (151 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 178: $^{29}$Si NMR of 7i (119 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 179: $^1$H NMR of 7i' (600 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 180: $^{13}$C NMR of 7i' (151 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 181: $^{29}$Si NMR of 7' (119 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 182: $^1$H NMR of 3ab (600 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 183: $^{13}$C NMR of 3ab (151 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 184: $^{29}$Si NMR of 3ab (119 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 185: $^1$H NMR of 3ac (600 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 186: $^{13}$C NMR of 3ac (151 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 187: $^{29}$Si NMR of 3ac (119 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 188: $^1$H NMR of 3ad (600 MHz, CDCl$_3$, 25 ºC)
**Supplementary Figure 189:** $^{13}$C NMR of 3ad (151 MHz, CDCl$_3$, 25 ºC)

**Supplementary Figure 190:** $^{29}$Si NMR of 3ad (119 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 191: $^1$H NMR of 3ae (600 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 192: $^{13}$C NMR of 3ae (151 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 193: $^{29}$Si NMR of 3ae (119 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 194: $^1$H NMR of 3af (600 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 195: $^{13}$C NMR of 3af (151 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 196: $^{19}$F NMR of 3af (565 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 197: $^{29}$Si NMR of 3af (119 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 198: $^1$H NMR of 3ag (600 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 199: $^{13}\text{C}$ NMR of 3ag (151 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 200: $^{29}\text{Si}$ NMR of 3ag (119 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 201: $^1$H NMR of 3ah (600 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 202: $^{13}$C NMR of 3ah (151 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 203: $^{29}$Si NMR of 3ah (119 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 204: $^1$H NMR of 3ai (600 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 205: $^{13}$C NMR of 3ai (151 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 206: $^{29}$Si NMR of 3ai (119 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 207: $^1$H NMR of 3aj (600 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 208: $^{13}$C NMR of 3aj (151 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 209: $^{19}$F NMR of 3aj (565 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 210: $^{29}$Si NMR of 3aj (119 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 211: $^1$H NMR of 7j (600 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 212: $^{13}$C NMR of 7j (151 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 213: $^{29}$Si NMR of 7j (119 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 214: $^1$H NMR of 7j' (600 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 215: $^{13}$C NMR of 7j’ (151 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 216: $^{29}$Si NMR of 7j’ (119 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 217: $^1$H NMR of 7k (600 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 218: $^{13}$C NMR of 7k (151 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 219: $^{19}$F NMR of 7k (565 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 220: $^{29}$Si NMR of 7k (119 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 221: $^1$H NMR of 7k' (600 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 222: $^{13}$C NMR of 7k' (151 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 223: $^{19}$F NMR of 7k' (565 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 224: $^1$H NMR of 7l (600 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 225: $^{13}$C NMR of 7l (151 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 226: $^{29}$Si NMR of 7l (119 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 227: $^1$H NMR of 7l$'$ (600 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 228: $^{13}$C NMR of 7l$'$ (151 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 229: $^{29}$Si NMR of 7l' (119 MHz, CDCl$_3$, 25 ºC)

Supplementary Figure 230: $^1$H NMR of 8 (600 MHz, CDCl$_3$, 25 ºC)
**Supplementary Figure 231**: $^{13}$C NMR of 8 (151 MHz, CDCl$_3$, 25 ºC)

$^{29}$Si NMR of 8 (119 MHz, CDCl$_3$, 25 ºC)
Supplementary Figure 233: $^1$H NMR of 9 (600 MHz, CDCl$_3$, 25 °C)

Supplementary Figure 234: $^{13}$C NMR of 9 (151 MHz, CDCl$_3$, 25 °C)
Supplementary Figure 235: $^{29}$Si NMR of 9 (119 MHz, CDCl$_3$, 25 °C)
8. Supplementary References

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