Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information

Epoxy and aziridinyl enolsilanes in diastereoselective inter- and intramolecular Friedel-Crafts alkylations

Jesse Ling, Sze Kui Lam, Brian Lo, Sarah Lam, Wing-Tak Wong, Jian Sun, Guanhua Chen, and Pauline Chiu*

Table of Contents

General Experimental

Preparative:

All anhydrous reactions were performed in oven-dried round-bottomed flasks under a positive pressure of dry argon. Air and moisture-sensitive compounds were introduced via syringes or cannulae using standard inert atmosphere techniques. Reactions were monitored by thin layer chromatography (TLC) using E. Merck silica gel plates, Kieselgel 60 F_{254} with 0.2 mm thickness. Components were visualized by illumination with short-wavelength ultra-violet light and/or staining. Flash column chromatography was performed with Silicycle SiliaFlash® P60 40-63µm (230-400 mesh).

Solvents and chemicals were purified according to standard procedures. Tetrahydrofuran (THF), dichloromethane, 1,1,1,3,3,3-hexamethyldisilazane (HMDS), chlorotriethylsilane (TESCl) were distilled from CaH_2 under argon. Other reagents, including Grubbs' 2nd generation catalyst (**Grubbs II**), were used as received.

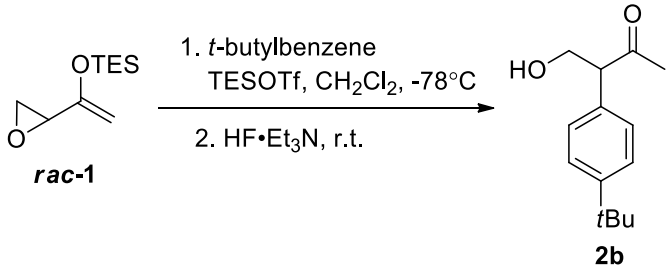
Analytical:

^{1}H and ^{13}C NMR nuclear magnetic resonance spectra were recorded at ambient temperature on a Bruker DX 300 spectrometer, Bruker Avance 400 spectrometer, Bruker DX 500 spectrometer, or Bruker Avance 600 operating at 300 MHz, 400 MHz, 500 MHz or 600 MHz respectively for ^{1}H, and at 75 MHz, 100 MHz, 125 MHz or 150 MHz respectively for ^{13}C. Electron impact mass spectrometry was recorded on a Finnigan MAT 95 mass spectrometer for both low resolution and high resolution, with accurate mass reported for the molecular ion (M^{+}) or next largest fragment thereof. IR absorption spectra were recorded as solutions in $CHCl_3$ on a Bio-Rad FTS 165 spectrometer from 4000 cm^{-1} to 400 cm^{-1}. Analytical HPLC was carried out on a Waters Analytical/Preparative HPLC system equipped with a 1525 Binary Pump, a 2707 Autosampler, and a variable wavelength Waters 2498 UV detector operated with Breeze 2 software.

Preparation of triethyl((1-(oxiran-2-yl)vinyl)oxy)silane (1)

Substrates **1** and (+)-**1** were synthesized according to literature procedures.[1]

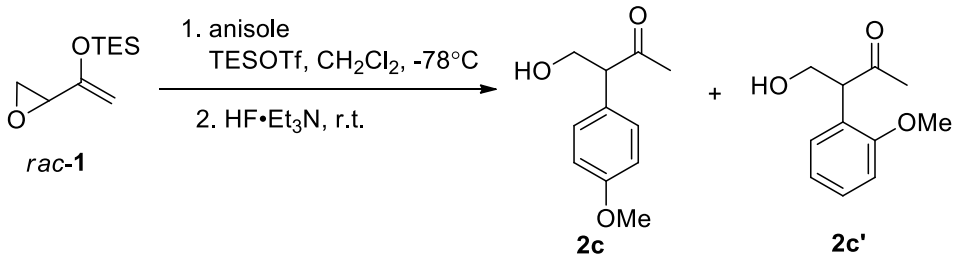
Scheme 1: Alkylation of *t*-butylbenzene



To a solution *t*-butylbenzene (0.39 mL, 2.50 mmol) in anhydrous CH_2Cl_2 (2.6 mL) was added *rac*-**1** (104.5 mg, 0.522 mmol). The mixture was cooled to –78 °C. TESOTf (0.25 mL, 0.2 M solution in CH_2Cl_2, 0.05 mmol) was added. The reaction progress was monitored by TLC. HF·Et_3N (0.18 mL) was added. The mixture was stirred for 1 h at r.t. Aqueous $NaHCO_3$ was added until effervescence ceased. The mixture was extracted with CH_2Cl_2, washed with brine and dried over anhydrous $MgSO_4$. The volatiles were removed in vacuo. The residue was purified by flash column chromatography using 20% EtOAc in hexane to afford **2b** (11.9 mg, 10% yield).

3-(4-(*tert*-butyl)phenyl)-4-hydroxybutan-2-one (2b): white solid; mp: 64-69 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 2H), 7.20 – 6.95 (m, 2H), 4.21 – 4.07 (m, 1H), 3.87 (quint, *J* = 4.2 Hz, 1H), 3.70 (ddd, *J* = 11.4, 8.2, 4.8 Hz, 1H), 2.37 – 2.26 (m, 1H), 2.09 (s, 3H), 1.31 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.7, 129.0, 128.3, 126.2, 125.7, 125.6, 125.0, 110.2, 110.1, 110.1, 64.3, 64.2, 62.0, 61.2, 31.4, 31.4, 29.7 ppm; HRMS (EI, m/z): calculated for [$C_{14}H_{20}O_2$] 220.1458, found 220.1458; FTIR: ν = 1036, 1363, 1508, 1705, 2966, 3612 cm^{-1}.

Scheme 1: Alkylation of anisole



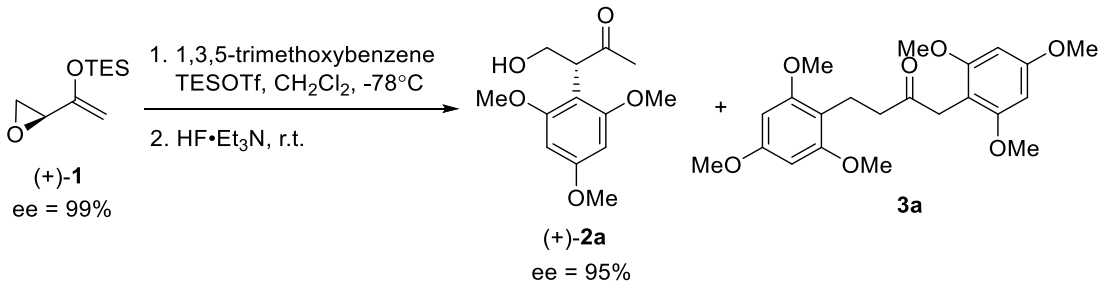
To a solution anisole (163 µL, 1.50 mmol) in anhydrous CH_2Cl_2 (1.5 mL) was added *rac*-**1** (60.1 mg, 0.300 mmol). The mixture was cooled to –78 °C. TESOTf (0.15 mL, 0.2 M solution in CH_2Cl_2, 0.030 mmol) was added. The reaction progress was

monitored by TLC. HF·Et_3N (0.12 mL) was added. The mixture was stirred for 1 h at r.t. Aqueous $NaHCO_3$ was added until effervescence ceased. The mixture was extracted with CH_2Cl_2, washed with brine and dried over anhydrous $MgSO_4$. The volatiles were removed in vacuo. The residue was purified by flash column chromatography using 40% EtOAc in hexane to afford **2c** (5.4 mg, 9% yield) and **2c′** (6.4 mg, 11% yield).

4-hydroxy-3-(4-methoxyphenyl)butan-2-one (2c): white solid; mp: 49–52 °C; R_f = 0.3 (50% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 4.11 (ddd, *J* = 11.3, 8.7, 5.3 Hz, 1H), 3.90 – 3.75 (m, 4H), 3.67 (ddd, *J* = 11.3, 8.2, 4.7 Hz, 1H), 2.29 (dd, *J* = 7.7, 5.9 Hz, 1H), 2.08 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 209.8, 159.4, 129.8, 127.6, 114.8, 64.2, 60.8, 55.4, 29.6; HRMS (EI, m/z): calculated for [$C_{11}H_{14}O_3$] 194.0937, found 194.0937; FTIR: ν = 1033, 1253, 1513, 1705, 2963, 3593 cm^{-1}.

4-hydroxy-3-(2-methoxyphenyl)butan-2-one (2c′): colourless oil; R_f = 0.4 (50% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 1H), 7.07 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.97 – 6.87 (m, 2H), 4.22 – 4.06 (m, 2H), 3.84 (s, 3H), 3.63 (s, 1H), 2.67 (s, 1H), 2.04 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 210.7, 157.2, 129.8, 129.2, 124.6, 121.2, 111.1, 63.2, 55.6 (2C), 29.2; HRMS (EI, m/z): calculated for [$C_{11}H_{14}O_3$] 194.0937, found 194.0941; FTIR: ν = 1027, 1250, 1498, 1707, 2963, 3587 cm^{-1}.

Table 1, entry 1:

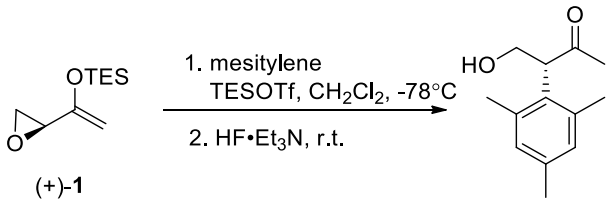


To a solution of 1,3,5-trimethoxybenzene (430 mg, 2.5 mmol) in anhydrous CH_2Cl_2 (2.5 mL) was added (+)-**1** (100 mg, 0.499 mmol). The mixture was cooled to − 78 °C. TESOTf (0.25 mL, 0.2 M solution in CH_2Cl_2, 0.05 mmol) was added. The reaction progress was monitored by TLC. When the reaction was complete, HF·Et_3N (0.2 mL) was added. The mixture was stirred for 1 h at r.t. Aqueous $NaHCO_3$ was added until effervescence ceased. The mixture was extracted with CH_2Cl_2, washed with brine and dried over anhydrous $MgSO_4$. The volatiles were removed in vacuo. The residue was purified by flash column chromatography using 50% EtOAc in hexane to afford **2a** (82.4 mg, 63% yield) and **3a** (28.0 mg, 13% yield).

(*R*)-4-hydroxy-3-(2,4,6-trimethoxyphenyl)butan-2-one (+)-**(2a):** White solid; mp: 99-103 °C; R_f = 0.4 (50% EtOAc in hexane);$[a]_D^{20} = +17.9$ (*c* = 15.22, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.13 (s, 2H), 4.21 – 4.08 (m, 2H), 3.32 (s, 3H), 3.78 (s, 6H), 3.43 (dt, *J* = 10.0, 3.4 Hz, 1H), 3.09 (dd, *J* = 10.0, 3.2 Hz, 1H), 1.96 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.3, 161.0, 158.8, 105.9, 90.8, 90.6, 62.4, 55.6, 55.4, 50.7, 28.0 ppm; HRMS (EI, m/z): calculated for [$C_{13}H_{18}O_5$] 254.1149, found 254.1147; FTIR: ν = 1122, 1206, 1465, 1609, 1701, 2841, 2942, 3570 cm^{-1}. The enantiomeric excess was determined by HPLC analysis [Daicel chiralcel OD, 1.0 mL/min, λ = 210 nm, 20% IPA in hexane, t_R (minor) = 35.85 min, t_R (major) = 38.08 min] to be 95% ee.

1,4-bis(2,4,6-trimethoxyphenyl)butan-2-one (3a): White solid; mp: 169-170 °C; R_f = 0.7 (50% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.15 (s, 2H), 6.10 (s, 2H), 3.83 (s, 3H), 3.80 (s, 3H), 3.77 (s, 6H), 3.75 (s, 6H), 3.64 (s, 2H), 2.82 (t, *J* = 8.4 Hz, 2H), 2.51 (t, *J* = 8.4 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.5, 160.3, 159.4, 159.0, 158.9, 110.3, 110.1, 105.2, 90.6, 90.6, 55.8, 55.7, 55.4, 55.4, 41.4, 37.2, 17.6 ppm; HRMS (EI, m/z): calculated for [$C_{22}H_{28}O_7$] 404.1830, found 404.1829; FTIR: ν = 1151, 1205, 1339, 1499, 1597, 1714, 2941 cm^{-1}.

Table 1, entry 2:



(+)-**1**
ee = 99%

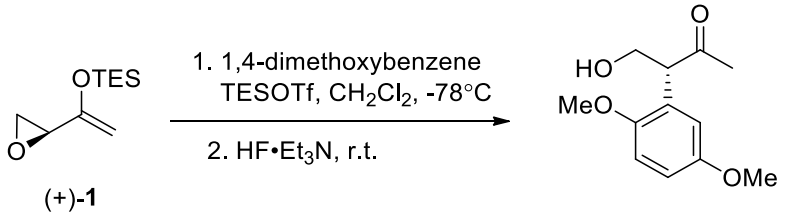
(+)-**2d**
ee = 97%

To a solution of mesitylene (0.35 mL, 2.5 mmol) in anhydrous CH_2Cl_2 (2.5 mL) was added (+)-**1** (95.9 mg, 0.479 mmol). The mixture was cooled to –78 °C. TESOTf (0.25 mL, 0.2 M solution in CH_2Cl_2, 0.05 mmol) was added. The reaction progress was monitored by TLC. HF·Et_3N (0.2 mL) was added. The mixture was stirred for 1 h at r.t. Aqueous $NaHCO_3$ was added until effervescence ceased. The mixture was extracted with CH_2Cl_2, washed with brine and dried over anhydrous $MgSO_4$. The volatiles were removed in vacuo. The residue was purified by flash column chromatography using 50% EtOAc in hexane to afford **2d** (63.1 mg, 64% yield).

(*R*)-4-hydroxy-3-mesitylbutan-2-one (+)-**(2d):** White solid; R_f = 0.4 (50% EtOAc in hexane);$[a]_D^{20} = +25.3$ (*c* = 11.96, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (s, 2H), 4.35 (t, *J* = 10.0 Hz, 1H), 4.06 (dd, *J* = 9.1, 4.4 Hz, 1H), 3.48 – 3.43 (m, 1H), 2.93 (d, *J* = 7.0 Hz, 1H), 2.26 (s, 9H), 2.02 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$)

δ 212.2, 137.4, 137.1, 130.3, 130.3, 61.9, 57.9, 29.1, 20.9, 20.7 ppm; HRMS (EI, m/z): calculated for [$C_{13}H_{18}O_2$] 206.1301, found 206.1296; FTIR: ν = 1172, 1026, 1458, 1612, 1697, 2947, 3572 cm^{-1}. The enantiomeric excess was determined by HPLC analysis [Daicel chiralcel OF, 0.5 mL/min, λ = 210 nm, 20% IPA in hexane, t_R (major) = 22.82 min, t_R (minor) = 24.40 min] to be 97% ee.

Table 1, entry 3:



(+)-**1**
ee = 99%

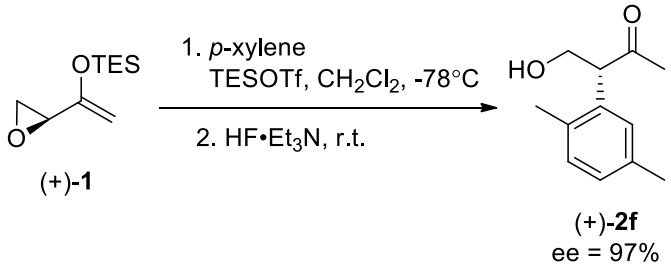
(+)-**2e**
ee = 93%

To a solution of 1,4-dimethoxybenzene (350 mg, 2.5 mmol) in anhydrous CH_2Cl_2 (2.5 mL) was added (+)-**1** (99.5 mg, 0.497 mmol). The mixture was cooled to –78 °C. TESOTf (0.25 mL, 0.2 M solution in CH_2Cl_2, 0.05 mmol) was added. The reaction progress was monitored by TLC. HF·Et_3N (0.2 mL) was added. The mixture was stirred for 1 h at r.t. Aqueous $NaHCO_3$ was added until effervescence ceased. The mixture was extracted with CH_2Cl_2

, washed with brine and dried over anhydrous $MgSO_4$. The volatiles were removed in vacuo. The residue was purified by flash column chromatography using 50% EtOAc in hexane to afford **2e** (45.8 mg, 43% yield).

(*R*)-3-(2,5-dimethoxyphenyl)-4-hydroxybutan-2-one (+)-**(2e)**: colourless oil; R_f = 0.3 (50% EtOAc in hexane); $[a]_D^{20} = +13.9$ (°$c = 3.3$, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 – 6.75 (m, 2H), 6.63 (d, *J* = 2.8 Hz, 1H), 4.16 – 4.07 (m, 2H), 3.77 (s, 3H), 3.72 (s, 3H), 3.66 – 3.60 (m, 1H), 2.79 (s, 1H), 2.03 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.2, 153.8, 151.3, 125.5, 115.8, 113.2, 112.0, 63.0, 56.0, 55.7, 55.4, 29.1 ppm; HRMS (EI, m/z): calculated for [$C_{12}H_{16}O_4$] 224.1043, found 224.1048; FTIR: ν = 1046, 1357, 1464, 1504, 1609, 1704, 2959 cm^{-1}. The enantiomeric excess was determined by HPLC analysis [Daicel chiralcel IC-3, 1.0 mL/min, λ = 210 nm, 15% IPA in hexane, t_R (minor) = 35.85 min, t_R (major) = 38.08 min] to be 93% ee.

Table 1, entry 4:



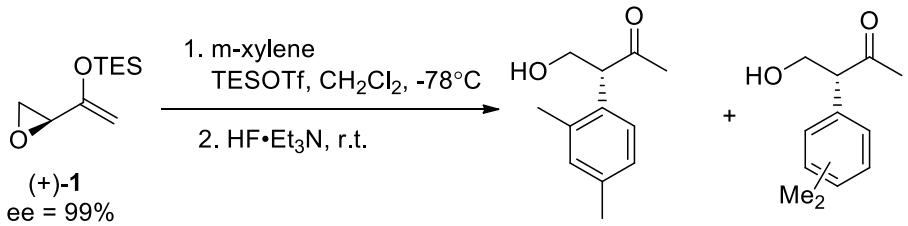
(+)-**1**

(+)-**2f**
ee = 97%

To a solution of *p*-xylene (1.25 mL, 10.2 mmol) in anhydrous CH_2Cl_2 (2.5 mL) was added (+)-**1** (105.3 mg, 0.524 mmol). The mixture was cooled to –78 °C. TESOTf (0.25 mL, 0.2 M solution in CH_2Cl_2, 0.05 mmol) was added. The reaction progress was monitored by TLC. HF·Et_3N (0.2 mL) was added. The mixture was stirred for 1 h at r.t. Aqueous $NaHCO_3$ was added until effervescence ceased. The mixture was extracted with CH_2Cl_2, washed with brine and dried over anhydrous $MgSO_4$. The volatiles were removed in vacuo. The residue was purified by flash column chromatography using 40% EtOAc in hexane to afford **2f** (58.3 mg, 58% yield).

(*R*)-3-(2,5-dimethylphenyl)-4-hydroxybutan-2-one (+)-**(2f)** : Colourless oil; R_f = 0.4 (50% EtOAc in hexane); $[a]_D^{20} = +40.0$ (*c* = 1.0, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11 (d, *J* = 7.7 Hz, 1H), 6.99 (d, *J* = 7.7 Hz, 1H), 6.74 (s, 1H), 4.17 – 4.09 (m, 2H), 3.63 – 3.50 (m, 1H), 2.62 (br, 1H), 2.41 (s, 3H), 2.28 (s, 3H), 2.07 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.9, 136.3, 133.6, 133.4, 131.1, 128.6, 128.1, 63.4, 57.6, 29.5, 21.0, 19.4 ppm; HRMS (EI, m/z): calculated for [$C_{12}H_{16}O_2$] 192.1145, found 192.1147; FTIR: ν = 1033, 1169, 1356, 1504, 1614, 1703, 2927, 3567 cm^{-1}; The enantiomeric excess was determined by HPLC analysis [Daicel chiralcel OD-3, 1.0 mL/min, λ = 210 nm, 2% IPA in hexane, t_R (major) = 15.26 min, t_R (minor) = 17.01 min] to be 97% ee.

Table 1, entry 5:



(+)-**1**
ee = 99%

(+)-**2g**
ee = 97%

2g'

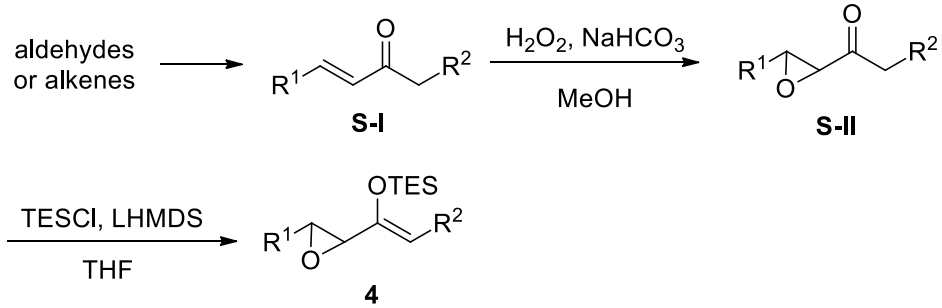
To a solution *m*-xylene (266.8 mg, 2.51 mmol) in anhydrous CH_2Cl_2 (2.5 mL) was added (+)-**1** (89.9 mg, 0.449 mmol). The mixture was cooled to –78 °C. TESOTf (0.25 mL, 0.2 M solution in CH_2Cl_2, 0.05 mmol) was added. The reaction progress was monitored by TLC. HF·Et_3N (0.2 mL) was added. The mixture was stirred for 1 h

at r.t. Aqueous $NaHCO_3$ was added until effervescence ceased. The mixture was extracted with CH_2Cl_2, washed with brine and dried over anhydrous $MgSO_4$. The volatiles were removed in vacuo. The residue was purified by flash column chromatography using 35% EtOAc in hexane to afford **2g** (47.7 mg, 41% yield) and an undetermined regioisomer **2g′** (6.6 mg, 15% yield).

(*R*)-3-(2,4-dimethylphenyl)-4-hydroxybutan-2-one (+)-**(2g)**: Colourless oil; R_f = 0.4 (50% EtOAc in hexane); $[a]_D^{20} = +14.3$ (*c* = 7.4, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (s, 1H), 6.97 (d, *J* = 7.7 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 4.15 – 4.00 (m, 2H), 3.62 – 3.50 (m, 1H), 2.45 (br, 1H), 2.40 (s, 3H), 2.30 (s, 3H), 2.02 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.3, 137.7, 136.5, 132.1, 130.8, 127.5, 127.5, 63.6, 57.4, 29.5, 21.1, 19.9 ppm; HRMS (EI, m/z): calculated for [$C_{12}H_{16}O_2$] 192.1145, found 192.1144; FTIR: ν = 1035, 1169, 1356, 1506, 1607, 1704, 2926, 3593 cm^{-1}; The enantiomeric excess was determined by HPLC analysis [Daicel chiralcel OD-3, 1.0 mL/min, λ = 210 nm, 15% IPA in hexane, t_R (major) = 25.46 min, t_R (minor) = 29.21 min] to be 97% ee.

(*R*)-3-(3,5-dimethylphenyl)-4-hydroxybutan-2-one or **(*R*)-3-(2,6-dimethylphenyl)-4-hydroxybutan-2-one (2g′)**: Colourless oil; R_f = 0.2 (50% EtOAc in hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07 (td, *J* = 8.1, 4.6 Hz, 3H), 4.38 (t, *J* = 10.6 Hz, 1H), 4.10 (dd, *J* = 9.1, 4.3 Hz, 1H), 3.49 (td, *J* = 11.0, 4.3 Hz, 1H), 3.01 – 2.83 (m, 1H), 2.31 (s, 6H), 2.02 (s, 3H). ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.1, 133.4, 129.6. 127.8. 61.9. 58.3. 29.1 ppm; HRMS (EI, m/z): calculated for [$C_{12}H_{14}O$] [M-H_2O]$^+$: 174.1039, found 174.1039; FTIR: ν = 1031, 1171, 1360, 1607, 1699, 2926, 2926 cm^{-1}. The enantiomeric excess was not determined.

General procedure for the preparation of epoxy enolsilanes (4)



Epoxy enolsilanes **4** were synthesized from epoxy ketone **S-II**, which in turn were prepared from enone **S-I**. The syntheses of **S-I** from aldehydes was via a Wittig reaction, or from alkenes via a Grubbs cross metathesis (CM) reaction.

General Procedure A for the preparation of enones (S-I) from terminal alkenes using Grubbs CM reaction

To a solution of a terminal alkene (1 equiv.) in CH_2Cl_2 (0.075 M) was added methyl vinyl ketone (4 equiv.) and Grubbs 2nd generation catalyst (**Grubbs II)** (0.03 equiv.). The reaction mixture was stirred under reflux for 12 h. The reaction progress was monitored with TLC. The crude product was concentrated in vacuo and purified by flash chromatography to afford **S-I**.

General Procedure B for the epoxidation of enones (S-I) to epoxy ketones (S-II)

To a solution of **S-I** (1 equiv.) in MeOH (0.25 M) was added $NaHCO_3$ (1 equiv.) and H_2O_2 (50% w/w, 3 equiv.). The reaction mixture was stirred at room temperature for 12-72 h. Aqueous Na_2SO_3 was added. The mixture was extracted with CH_2Cl_2, then the organics were dried over anhydrous $MgSO_4$. The crude product was concentrated in vacuo and purified by flash chromatography to afford epoxyketone **S-II**.

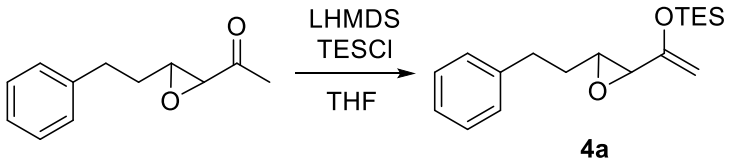
General Procedure C for the synthesis of epoxy enolsilanes (4)

To a solution of HMDS (2 equiv.) in anhydrous THF (0.2 M) at 0 ℃ was added *n*BuLi (1.95 equiv). The mixture was stirred for 30 minutes at 0 ℃ and was cooled to –78 ℃. To the cooled solution was added epoxyketone **S-II** (1.05 equiv.) in THF via cannula. The resulting solution was stirred for 1 h at –78 ℃. TESCl (1 equiv.) was added and the reaction was allowed to warm to r.t. After stirring for 1 h, water was added. The mixture was extracted with EtOAc, and the organics were dried over anhydrous $MgSO_4$. The volatiles were removed in vacuo. The residue was purified by flash chromatography to afford epoxy enolsilane **4**.

General Procedure D for Friedel-Crafts cyclizations of epoxy enolsilanes (4)

To a solution of epoxy enolsilane **4** (1 equiv.) in CH_2Cl_2 (0.2 M) at –78 ℃ was added TESOTf (0.2 M solution in CH_2Cl_2, 0.1 equiv.). The reaction progress was monitored by TLC. When the reaction was complete, $HF{\cdot}Et_3N$ (5 equiv.) was added. The mixture was warmed to room temperature and stirred for 1 h. $NaHCO_3$ solution was added until effervescence ceased. The reaction mixture was extracted by EtOAc, and the organics were dried with anhydrous $MgSO_4$. The crude product was concentrated in vacuo and then purified by flash chromatography to afford Friedel-Crafts products **5**.

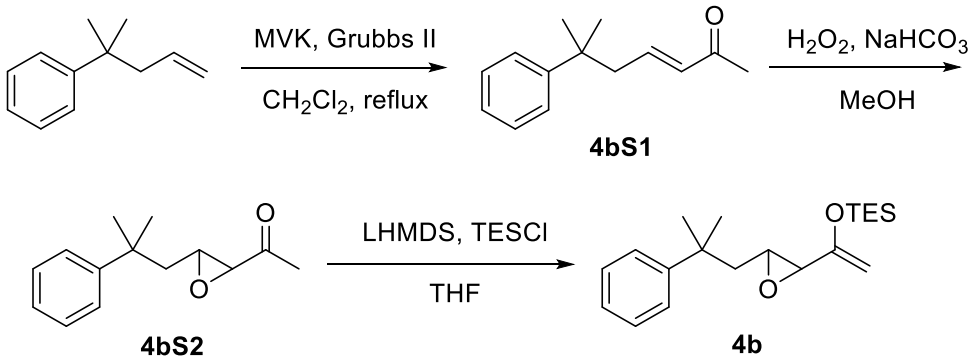
Preparation of triethyl((1-(3-phenethyloxiran-2-yl)vinyl)oxy)silane (4a)



4a

According to General Procedure C, the reaction of 1-(3-phenethyloxiran-2-yl)ethan-1-one[2] (210.9 mg, 2.211 mmol), HMDS (0.50 mL, 2.4 mmol), *n*BuLi (1.3M in hexane, 1.3 mL, 1.7 mmol) and TESCl (0.180 mL, 1.07 mmol) in THF (2.8 mL) afforded, after flash column chromatography using 2% EtOAc and 1% Et_3N in hexane, epoxy enolsilane **4a** (277.2 mg, 83% yield) as a colourless oil; R_f = 0.60 (5% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 2H), 7.21 – 7.17 (m, 3H), 4.41 (d, *J* = 1.4 Hz, 1H), 4.31 (d, *J* = 1.4 Hz, 1H), 3.07 (ddd, *J* = 7.0, 4.8, 1.9 Hz, 1H), 3.02 (d, *J* = 2.0 Hz, 1H), 2.80 – 2.73 (m, 2H), 1.90 – 1.86 (m, 2H), 0.97 (t, *J* = 8.0 Hz, 9H), 0.68 (q, *J* = 7.8 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 141.4, 128.6, 128.5, 126.1, 93.6, 58.2, 57.3, 33.8, 32.3, 6.7, 4.9 ppm; HRMS (EI, m/z) Calculated for $C_{18}H_{28}O_2Si$ [M^+] 304.1859, Found 304.1851; FTIR: ν = 3070, 2877, 1636, 1458, 1335, 1288, 1250, 1003 cm^{-1}.

Preparation of triethyl((1-(3-(2-methyl-2-phenylpropyl)oxiran-2-yl)vinyl) oxy)silane (4b)



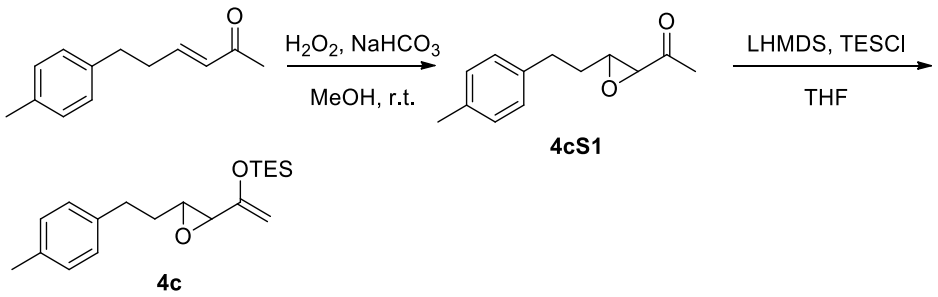
According to General Procedure A, reaction of (2-methylpent-4-en-2-yl)benzene[3] (173.7 mg, 1.08 mmol), methyl vinyl ketone (0.36 mL, 4.3 mmol) and **Grubbs II** (29.5 mg, 0.03 mmol) in CH_2Cl_2 (15 mL) afforded, after flash chromatography using 5% EtOAc in hexane, **4bS1** (156.9 mg, 66%) as a pale yellow oil. R_f = 0.3 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 8.0, 5.9 Hz, 4H), 7.25 – 7.16 (m, 1H), 6.50 (dt, *J* = 15.4, 7.5 Hz, 1H), 6.01 (d, *J* = 15.9 Hz, 1H), 2.53 (d, *J* = 7.5 Hz, 2H), 2.13 (s, 3H), 1.35 (s, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.5, 148.1, 145.3, 133.5, 128.4, 126.1, 125.7, 47.4, 38.1, 28.8, 26.8. ppm; HRMS (EI, m/z): calculated

for [$C_{14}H_{18}O$] 202.1352, found 202.1341; FTIR: ν = 1246, 1277, 1362, 1437, 1670, 2968 cm^{-1}.

According to General Procedure B, the reaction of **4bS1** (156.9 mg, 0.776 mmol) $NaHCO_3$ (62 mg, 0.74 mmol) and H_2O_2 (0.16 mL, 2.3 mmol) in MeOH (3 mL) over 48 h afforded, after purification by flash chromatography using 15% EtOAc in hexane, **4bS2** (144.9 mg, 86%) as a colourless oil. R_f = 0.4 (20% EtOAc in hexane) ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 – 7.29 (m, 3H), 7.28 – 7.19 (m, 2H), 3.04 (s, 1H), 2.79 (t, *J* = 5.6 Hz, 1H), 1.97 – 1.90 (m, 2H), 1.90 (s, 3H), 1.42 (d, *J* = 15.0 Hz, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.8, 140.4, 138.2, 128.0, 126.2, 60.0, 57.7, 33.6, 31.9, 24.6, 21.3 ppm; HRMS (EI, m/z): calculated for [$C_{14}H_{18}O_2$] 218.1301, found 218.1303; FTIR: ν = 1184, 1361, 1497, 1601, 1709, 2979 cm^{-1}.

According to General Procedure C, the reaction of **4bS2** (118.4 mg, 0.542 mmol), HMDS (0.25 mL, 1.1 mmol), *n*BuLi (2.10 M, 0.52 mL, 1.1 mmol) and TESCl (90 μL, 0.56 mmol) in anhydrous THF (3 mL) afforded, after flash chromatography using 3% EtOAc in hexane with 1% Et_3N, **4b** (120.2 mg, 62% yield) as a very pale yellow oil. R_f = 0.2 (5% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 4.32 (d, *J* = 1.1 Hz, 1H), 4.24 (d, *J* = 1.1 Hz, 1H), 2.88 (d, *J* = 2.0 Hz, 1H), 2.81 (td, *J* = 5.8, 2.0 Hz, 1H), 1.92 (dd, *J* = 14.0, 6.0 Hz, 1H), 1.81 (dd, *J* = 14.1, 5.7 Hz, 1H), 1.43 (s, 3H), 1.39 (s, 3H), 0.90 (t, *J* = 7.9 Hz, 9H), 0.62 (q, *J* = 7.8 Hz, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 128.4, 125.9, 125.8, 93.4, 57.9, 55.4, 46.5, 37.5, 29.5, 28.7, 6.7, 4.9 ppm; HRMS (EI, m/z): calculated for [$C_{20}H_{32}O_2Si$] 332.2166, found 332.2170; FTIR: ν = 1080, 1242, 1468, 1639 cm^{-1}.

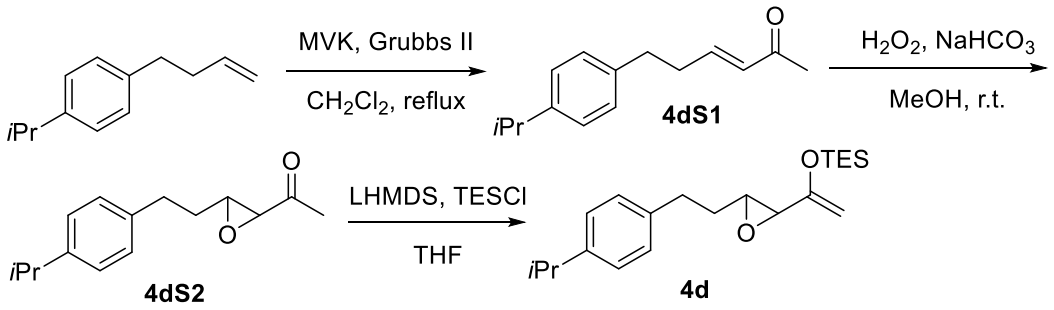
Preparation of triethyl((1-(3-(4-methylphenethyl)oxiran-2-yl)vinyl)oxy)silane (4c)



According to General Procedure B, the reaction of (*E*)-6-(*p*-tolyl)hex-3-en-2-one[4] (523.5 mg, 2.78 mmol), $NaHCO_3$ (236.0 mg, 2.81 mmol) and H_2O_2 (0.57 mL, 8.3 mmol) in MeOH (11 mL) overnight afforded, after purification by flash chromatography using 10% EtOAc in hexane, epoxy ketone **4cS1** (205.7 mg, 36%) as a colourless oil. R_f = 0.3 (10% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (dd, *J* = 18.7, 8.0 Hz, 4H), 3.17 (d, *J* = 2.0 Hz, 1H), 3.11 – 3.05 (m, 1H), 2.76 (dtd, *J* = 21.8, 14.0, 7.5 Hz, 2H), 2.32 (s, 3H), 2.01 (s, 3H), 1.96 – 1.90 (m, 2H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 205.7, 137.3, 135.9, 129.3, 128.2, 60.0, 57.6, 33.6, 31.6, 24.5, 21.0 ppm; HRMS (EI, m/z): calculated for [$C_{13}H_{16}O_2$] 204.1145, found 204.1143; FTIR: ν = 1361, 1516, 1709, 2862, 2926, 2990, 3057 cm^{-1}. The preparation of (+)-**4cS1** followed a modified literature procedure,[5] using (*E*)-6-(*p*-tolyl)hex-3-en-2-one as substrate. (+)-**4cS1**: $[a]_D^{20} = +19.0\,(c = 2.1, \mathrm{CH2Cl2})$; the enantiomeric excess was determined by HPLC analysis [Daicel chiralcel OD-3, 1.0 mL/min, λ = 210 nm, 10% IPA in hexane, t_R (major) = 6.99 min, t_R (minor) = 7.34 min] to be 96% ee.

According to General Procedure C, the reaction of **4cS1** (203.6 mg, 1.00 mmol), HMDS (0.40 mL, 1.90 mmol), *n*BuLi (2.30 M, 0.82 mL, 1.89 mmol) and TESCl (150 μL, 0.95 mmol) in anhydrous THF (6 mL) afforded, after flash chromatography using 3% EtOAc in hexane with 1% Et_3N, epoxy enolsilane **4c** (188.7 mg, 66% yield) as a colourless oil. R_f = 0.4 (5% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (s, 4H), 4.41 (d, *J* = 1.2 Hz, 1H), 4.31 (d, *J* = 1.3 Hz, 1H), 3.11 – 3.05 (m, 1H), 3.02 (d, *J* = 2.1 Hz, 1H), 2.82 – 2.62 (m, 2H), 2.31 (s, 3H), 1.92 – 1.77 (m, 2H), 0.96 (t, *J* = 8.0 Hz, 9H), 0.68 (q, *J* = 7.9 Hz, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 138.3, 135.4, 129.2, 128.4, 93.5, 58.1, 57.4, 33.9, 31.8, 21.1, 6.7, 4.9 ppm; HRMS (EI, m/z): calculated for [$C_{19}H_{30}O_2Si$] 318.2010, found 318.200; FTIR: ν = 1153, 1368, 1385, 1425, 1495, 1598, 1697, 1761, 2989, 3065 cm^{-1}. (+)-**4cS2**: $[a]_D^{20} = +24.3^\circ$ $(c = 9.8, \mathrm{CH2Cl2})$.

Preparation of triethyl((1-(3-(4-isopropylphenethyl)oxiran-2-yl)vinyl)oxy)silane (4d)



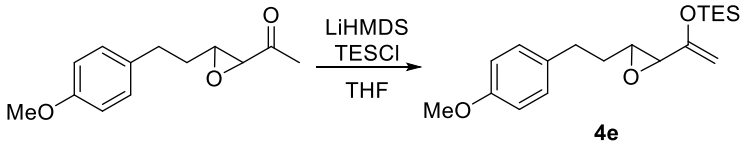
According to General Procedure A, the reaction of 1-(but-3-en-1-yl)-4-isopropylbenzene[6] (542.4 mg, 3.11 mmol), methyl vinyl ketone (1.00 mL, 12.5 mmol) and **Grubbs II** (64.0 mg, 0.08 mmol) in CH_2Cl_2 (41 mL) afforded, after flash chromatography using 20% EtOAc in hexane, enone **4dS1** (461.3 mg, 69% yield) as a pale yellow oil. R_f = 0.4 (20% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.04 (m, 4H), 6.92 – 6.75 (m, 1H), 6.10 (d, *J* = 16.0 Hz, 1H), 2.95 – 2.83 (m, 1H), 2.76 (t, *J* = 7.8 Hz, 2H), 2.54 (dd, *J* = 15.2, 7.0 Hz, 2H), 2.23 (s, 3H), 1.24 (d, *J* = 6.9 Hz, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.9, 147.6, 146.9, 138.1, 131.8, 128.4, 126.7, 34.3, 34.1, 33.8, 27.0, 24.2 ppm; HRMS (EI, m/z): calculated for [$C_{15}H_{20}O_2$] 216.1509, found 216.1509; FTIR: ν = 1186, 1514, 1626, 1672, 1757, 2963 cm^{-1}.

According to General Procedure B, the reaction of **4dS1** (475.4 mg, 2.198 mmol), $NaHCO_3$ (192.9 mg, 2.29 mmol) and H_2O_2 (0.45 mL, 6.6 mmol) in MeOH (9 mL) overnight afforded, after purification by flash chromatography using 20% EtOAc in hexane, epoxy ketone **4dS2** (505.2 mg, 78%) as a colourless oil. R_f = 0.5 (20% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.06 (m, 4H), 3.18 (d, *J* = 2.0 Hz, 1H), 3.10 (td, *J* = 5.6, 2.0 Hz, 1H), 2.88 (p, *J* = 6.9 Hz, 1H), 2.83 – 2.66 (m, 1H), 2.01 (s, 3H), 1.94 (td, *J* = 7.8, 5.6 Hz, 2H), 1.25 (s, 3H), 1.23 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 205.8, 147.1, 137.8, 128.4, 126.8, 60.1, 57.8, 33.9, 33.6, 31.7, 24.7, 24.2; HRMS (EI, m/z): calculated for [$C_{15}H_{20}O_2$] 232.1458, found 232.1454; FTIR: ν = 1362, 1514, 1606, 1709, 2964 cm^{-1}.

According to General Procedure C, the reaction of **4dS2** (384.0 mg, 1.55 mmol), HMDS (0.62 mL, 3.0 mmol), *n*BuLi (1.34 M, 2.2 mL, 2.9 mmol) and TESCl (250 µL, 1.49 mmol) in anhydrous THF (9 mL) afforded, after flash chromatography using 3% EtOAc in hexane with 1% Et_3N, epoxy enolsilane **4d** (216.8 mg, 42% yield) as a colourless oil. R_f = 0.5 (5% EtOAc in Hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.04 (m, 4H), 4.41 (d, *J* = 1.3 Hz, 1H), 4.31 (d, *J* = 1.3 Hz, 1H), 3.07 (td, *J* = 6.2, 2.1

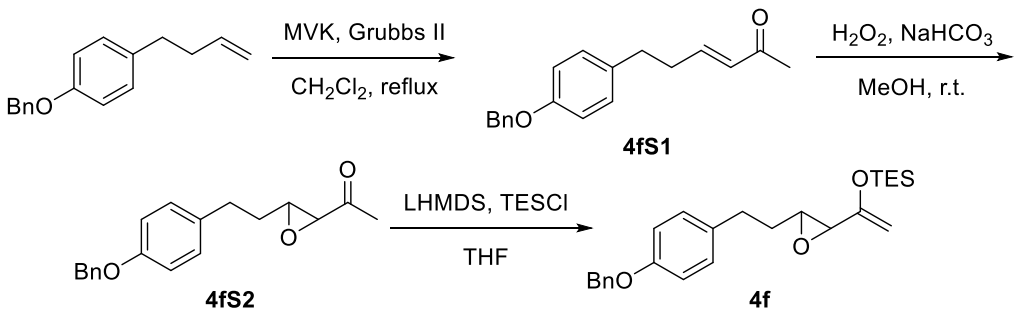
Hz, 1H), 3.01 (d, *J* = 2.1 Hz, 1H), 2.95 – 2.82 (m, 1H), 2.82 – 2.62 (m, 2H), 1.86 (tdd, *J* = 13.9, 8.4, 5.7 Hz, 2H), 1.24 (t, *J* = 5.6 Hz, 6H), 0.97 (t, *J* = 7.9 Hz, 9H), 0.77 – 0.60 (m, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4, 146.7, 138.6, 128.5, 126.6, 93.6, 58.2, 57.3, 33.8, 33.8, 31.8, 24.2, 6.7, 4.9 ppm; HRMS (EI, m/z): calculated for [$C_{21}H_{34}O_2Si$] 346.2323, found 346.2322; FTIR: ν = 1007, 1282, 1459, 1636, 2877, 2960, 3064 cm^{-1}.

Preparation of triethyl((1-(3-(4-methoxyphenethyl)oxiran-2-yl)vinyl)oxy)silane (4e)



According to General Procedure C, the reaction of 1-(3-(4-methoxyphenethyl)oxiran-2-yl)ethan-1-one[2] (920 mg, 4.18 mmol), HMDS (1.7 mL, 8.4 mmol), *n*BuLi (2.23 M, 3.6 mL, 8.3 mmol) and TESCl (0.65 mL, 4.1 mmol) in anhydrous THF (9 mL) afforded, after flash chromatography using 3% EtOAc in hexane with 1% Et_3N, epoxy enolsilane **4e** (739.8 mg, 57% yield) as a colourless oil. R_f = 0.2 (5% EtOAc in Hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (dd, *J* = 9.1, 2.5 Hz, 2H), 6.87 – 6.77 (m, 2H), 4.41 (d, *J* = 1.3 Hz, 1H), 4.30 (d, *J* = 1.4 Hz, 1H), 3.79 (s, 3H), 3.09 – 3.04 (m, 1H), 3.01 (d, *J* = 2.1 Hz, 1H), 2.81 – 2.61 (m, 2H), 1.91 – 1.74 (m, 2H), 0.96 (t, *J* = 7.9 Hz, 10H), 0.73 – 0.64 (m, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.9, 154.3, 133.2, 129.2, 113.8, 93.3, 57.9, 57.0, 55.1, 33.8, 31.2, 6.6, 4.8 ppm; HRMS (EI, m/z): calculated for [$C_{19}H_{30}O_3Si$] 334.1959, found 334.1958; FTIR: ν = 1033, 1178, 1331, 1457, 1513, 1612, 1635, 2878, 2959 cm^{-1}.

Preparation of ((1-(3-(4-(benzyloxy)phenethyl)oxiran-2-yl)vinyl)oxy)triethyl-silane (4f)

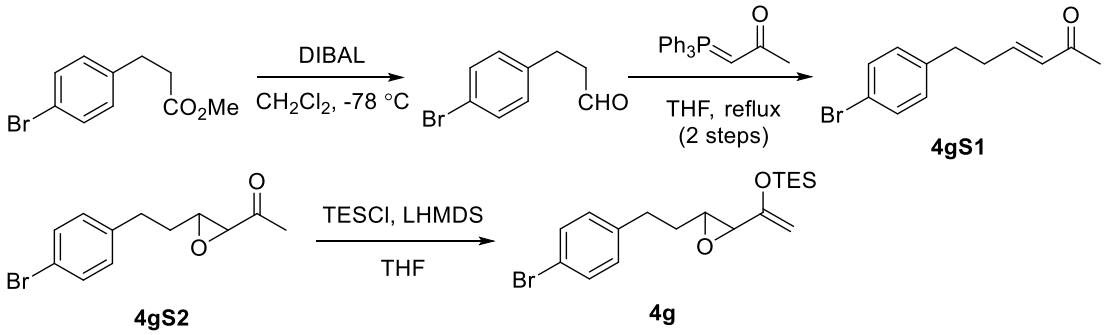


According to General Procedure A, the reaction of 1-(benzyloxy)-4-(but-3-en-1-yl)benzene[7] (967.7 mg, 4.06 mmol), methyl vinyl ketone (1.4 mL, 17 mmol) and **Grubbs II** (91.0 mg, 0.11 mmol) in CH_2Cl_2 (60 mL) afforded, after flash chromatography using 15% EtOAc in hexane, enone **4fS1** (998.6 mg, 88%) as a pale yellow oil. R_f = 0.5 (20% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.29 (m, 5H), 7.09 (d, *J* = 8.6 Hz, 2H), 6.95 – 6.86 (m, 2H), 6.81 (dt, *J* = 16.0, 6.8 Hz, 1H), 6.09 (dt, *J* = 16.0, 1.4 Hz, 1H), 5.05 (s, 2H), 2.74 (t, *J* = 7.7 Hz, 2H), 2.56 – 2.46 (m, 2H), 2.23 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.6, 157.3, 147.2, 137.1, 133.0, 131.7, 129.3, 128.6, 128.0, 127.5, 114.9, 70.1, 34.4, 33.6, 26.9 ppm; HRMS (EI, m/z): calculated for [$C_{19}H_{20}O_2$] 280.1458, found 280.1457. FTIR: ν = 1509, 1673, 1695 cm^{-1}.

According to General Procedure B, the reaction of **4fS1** (993.4 mg, 3.54 mmol), $NaHCO_3$ (295 mg, 3.54 mmol) and H_2O_2 (0.72 mL, 11 mmol) in MeOH (15 mL) afforded, after flash chromatography using 20% EtOAc in hexane, epoxy ketone **4fS2** (876.2mg, 83%) as a colourless oil. R_f = 0.3 (20% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.31 (m, 5H), 7.10 (d, *J* = 8.5 Hz, 2H), 6.92 (d, *J* = 8.5 Hz, 2H), 5.05 (s, 2H), 3.18 (d, *J* = 1.9 Hz, 1H), 3.09 (dd, *J* = 7.3, 3.9 Hz, 1H), 2.82 – 2.66 (m, 2H), 2.01 (s, 3H), 1.92 (dd, *J* = 10.3, 5.4 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.8, 157.4, 137.2, 132.8, 129.4, 128.7, 128.1, 127.6, 115.1, 109.7, 70.2, 60.0, 57.6, 33.8, 31.2, 24.7 ppm; HRMS (EI, m/z): calculated for [$C_{19}H_{20}O_3$] 296.1407, found 296.1405; FTIR: ν = 1510, 1607, 1709 cm^{-1}.

According to General Procedure C, the reaction of **4fS2** (145.1 mg, 0.49 mmol), HMDS (0.20 mL, 0.93 mmol), *n*BuLi (1.93 M, 0.50 mL, 0.47 mmol) and TESCl (80 μL, 0.47 mmol) in anhydrous THF (3 mL) afforded, after flash chromatography using 3% EtOAc in hexane with 1% Et_3N, epoxy enolsilane **4f** (38.5 mg, 19% yield) as a pale yellow oil. R_f = 0.2 (5% EtOAc in Hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.35 (m, 4H), 7.35 – 7.29 (m, 1H), 7.11 (d, *J* = 8.6 Hz, 2H), 6.94 – 6.86 (m, 2H), 5.04 (s, 2H), 4.41 (d, *J* = 1.3 Hz, 1H), 4.30 (d, *J* = 1.3 Hz, 1H), 3.06 (ddd, *J* = 6.4, 5.2, 2.1 Hz, 1H), 3.01 (d, *J* = 2.1 Hz, 1H), 2.80 – 2.60 (m, 2H), 1.91 – 1.76 (m, 2H), 0.96 (t, *J* = 7.9 Hz, 10H), 0.68 (q, *J* = 7.7 Hz, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.2, 154.3, 137.2, 133.6, 129.3, 128.6, 127.9, 127.5, 114.9, 93.4, 70.1, 58.0, 57.2, 33.8, 31.3, 6.6, 4.8 ppm; HRMS (EI, m/z): calculated for [$C_{25}H_{34}O_3Si$] 410.2272, found 410.2274; FTIR: ν = 1017, 1177, 1456, 1511, 1610, 2877, 2914, 2957 cm^{-1}.

Preparation of ((1-(3-(4-bromophenethyl)oxiran-2-yl)vinyl)oxy)triethylsilane (4g)



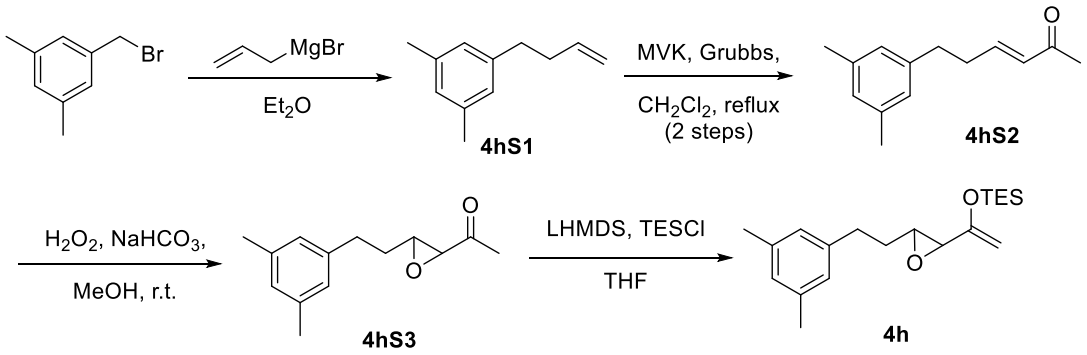
To a solution of methyl 3-(4-bromophenyl)propanoate[8] (1.947 g, 8.01 mmol) in CH_2Cl_2 (80 mL) was added DIBAL (1.0 M in PhMe, 8.8 mL, 8.8 mmol) at –78 °C dropwise. The reaction mixture was stirred at –78 °C for 1 h. HCl (2 M) was added at 0 °C, and the mixture was extracted with CH_2Cl_2. The organics were dried with anhydrous $MgSO_4$ and concentrated in vacuo. The crude product thus obtained was used in next step without further purification.

The crude product was dissolved in THF (32 mL). Acetylmethylenetriphenylphosphorane (3.1816 g, 9.99 mmol) was added and the mixture was stirred under reflux overnight. The crude product was concentrated in vacuo and purified by flash chromatography using 10% EtOAc in hexane to afford enone **4gS1** (614.3 mg, 30% over 2 steps) as a pale yellow oil. R_f = 0.2 (10% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.2 Hz, 2H), 7.05 (d, *J* = 8.1 Hz, 2H), 6.85 – 6.69 (m, 1H), 6.08 (d, *J* = 16.0 Hz, 1H), 2.75 (t, *J* = 7.6 Hz, 2H), 2.52 (dd, *J* = 14.7, 7.0 Hz, 2H), 2.23 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.4, 146.4, 139.6, 131.9, 131.6, 130.1, 120.1, 33.8, 27.0 ppm; HRMS (EI, m/z): calculated for [$C_{12}H_{13}O^{79}Br$] 252.0144, found 252.0144; FTIR: ν = 1362, 1489, 1673, 2929 cm^{-1}.

According to General Procedure B, the reaction of **4gS1** (609.2 mg, 2.41 mmol), $NaHCO_3$ (200.9 mg, 2.41 mmol) and H_2O_2 (0.49 mL, 7.2 mmol) in MeOH (10 mL) overnight afforded, after purification by flash chromatography using 10% EtOAc in hexane, epoxy ketone **4gS2** (465.5mg, 72%) as a colourless oil. R_f = 0.2 (10% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 3.19 (d, *J* = 2.0 Hz, 1H), 3.08 (ddd, *J* = 6.6, 4.7, 2.0 Hz, 1H), 2.86 – 2.61 (m, 2H), 2.03 (s, 3H), 2.00 – 1.80 (m, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.6, 139.5, 131.7, 130.2, 120.2, 59.9, 57.3, 33.3, 31.5, 24.6 ppm; HRMS (EI, m/z): calculated for [$C_{12}H_{13}{}^{79}BrO_2$] 268.0093, found 268.0091; FTIR: ν = 1012, 1246, 1284, 1425, 1489, 1710, 2982, 3045 cm^{-1}.

According General Procedure C, **4gS2** (462.6 mg, 1.67 mmol), HMDS (0.67 mL, 3.19 mmol), *n*BuLi (2.16 M, 1.5 mL, 3.2 mmol) and TESCl (270 μL, 1.59 mmol) in anhydrous THF (9 mL) afforded, after flash chromatography using 3% EtOAc in hexane with 1% Et_3N, epoxy enolsilane **4g** (510.8 mg, 83% yield) as a pale yellow oil. R_f = 0.2 (5% EtOAc in Hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.34 (m, 2H), 7.07 (d, *J* = 8.3 Hz, 2H), 4.41 (d, *J* = 1.4 Hz, 1H), 4.31 (d, *J* = 1.4 Hz, 1H), 3.04 (ddd, *J* = 10.8, 5.6, 3.1 Hz, 1H), 3.00 (d, *J* = 2.1 Hz, 1H), 2.81 – 2.62 (m, 2H), 1.93 – 1.74 (m, 2H), 0.96 (t, *J* = 7.9 Hz, 9H), 0.68 (q, *J* = 7.9 Hz, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 140.3, 131.6, 130.3, 119.9, 93.7, 58.1, 57.0, 33.5, 31.7, 6.7, 4.9 ppm; HRMS (EI, m/z): calculated for [$C_{12}H_{13}O_2{}^{79}Br$] 268.0093, found 268.0093; FTIR: ν = 1011, 1072, 1331, 1489, 1636, 2878, 2958 cm^{-1}.

Preparation of ((1-(3-(3,5-dimethylphenethyl)oxiran-2-yl)vinyl)oxy)triethylsilane (4h)



To a solution of allylmagnesium bromide (1.0 M in Et_2O, 5.0 mL, 5.0 mmol) in anhydrous Et_2O (14 mL) was added 1-(bromomethyl)-3,5-dimethylbenzene (830.6 mg, 4.17 mmol, dissolved in 1.4 mL Et_2O) dropwise at 0 °C. The reaction mixture was stirred at room temperature for 20 h. The reaction was quenched with H_2O and extracted with Et_2O. The organics were dried over anhydrous $MgSO_4$ and concentrated in vacuo. The crude product was filtered through a silica gel plug using 2% EtOAc in hexane to afford **4hS1** (579.9 mg, 87% yield) as a pale yellow oil. R_f = 0.9 (5% EtOAc in hexane). This product was used in the next step without further purification or characterization.

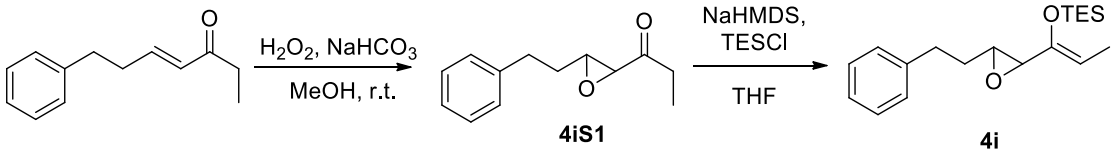
According to General Procedure A, the reaction of **4hS1** (570.7 mg, 3.43 mmol), methyl vinyl ketone (1.15 mL, 13.7 mmol) and **Grubbs II** (88.9 mg, 0.10 mmol) in CH_2Cl_2 (50 mL) afforded, after flash chromatography using 20% EtOAc in hexane, enone **4hS2** (597.3 mg, 83% yield as a colourless oil. R_f = 0.5 (20% EtOAc in hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.92 – 6.73 (m, 4H), 6.10 (dt, *J* = 16.0, 1.4 Hz,

1H), 2.77 – 2.65 (m, 2H), 2.59 – 2.44 (m, 2H), 2.31 (d, *J* = 7.0 Hz, 6H), 2.24 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.7, 147.5, 140.7, 138.1, 131.6, 127.9, 126.2, 34.3, 34.3, 26.9, 21.4 ppm; HRMS (EI, m/z): calculated for [$C_{14}H_{18}O$] 202.1352, found 202.1344; FTIR: ν = 1258, 1362, 1663, 1693, 2922 cm^{-1}.

According to General Procedure B, the reaction of **4hS2** (550 mg, 2.72 mmol), $NaHCO_3$ (244.9 mg, 2.72 mmol) and H_2O_2 (0.55 mL, 8.2 mmol) in MeOH (11 mL) overnight afforded, after purification by flash chromatography using 20% EtOAc in hexane, epoxy ketone **4hS3** (505.2 mg, 85%) as a colourless oil. R_f = 0.5 (20% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (s, 1H), 6.80 (s, 2H), 3.17 (d, *J* = 2.0 Hz, 1H), 3.09 (td, *J* = 5.6, 2.0 Hz, 1H), 2.85 – 2.59 (m, 2H), 2.30 (d, *J* = 10.3 Hz, 6H), 2.03 (s, *J* = 10.7 Hz, 3H), 1.92 (tt, *J* = 21.8, 10.9 Hz, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.9, 140.4, 138.2, 128.0, 126.3, 60.1, 57.7, 33.7, 31.9, 24.7, 21.4 ppm; HRMS (EI, m/z): calculated for [$C_{14}H_{18}O_2$] 218.1301, found 218.1302; FTIR: ν = 1183, 1361, 1606, 1709, 2922, 2987 cm^{-1}.

According to General Procedure C, the reaction of **4hS3** (493.7 mg, 2.26 mmol), HMDS (0.90 mL, 4.3 mmol), *n*BuLi (2.16 M, 2.0 mL, 4.3 mmol) and TESCl (360 μL, 2.15 mmol) in anhydrous THF (13 mL) afforded, after flash chromatography using 3% EtOAc in hexane with 1% Et_3N, epoxy enolsilane **4h** (410.7 mg, 58% yield) as a colourless oil. R_f = 0.2 (5% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (d, *J* = 6.2 Hz, 3H), 4.41 (s, 1H), 4.31 (s, 1H), 3.08 (t, *J* = 5.7 Hz, 1H), 3.01 (d, *J* = 1.8 Hz, 1H), 2.81 – 2.56 (m, 2H), 2.28 (s, 6H), 1.99 – 1.73 (m, 2H), 0.97 (t, *J* = 7.9 Hz, 9H), 0.68 (q, *J* = 7.9 Hz, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4, 141.3, 138.0, 127.8, 126.4, 93.7, 58.2, 57.3, 33.9, 32.1, 21.4, 6.7, 4.9 ppm; HRMS (EI, m/z): calculated for [$C_{20}H_{32}O_2Si$] 332.2166, found 332.2165; FTIR: ν = 1007, 1332, 1457, 1606, 1636, 2958 cm^{-1}.

Preparation of (*Z*)-triethyl((1-(3-phenethyloxiran-2-yl)prop-1-en-1-yl)oxy)silane (4i)

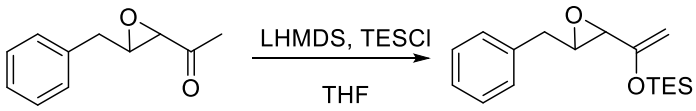


According to General Procedure B, the reaction of (*E*)-7-phenylhept-4-en-3-one[9] (225.6 mg, 1.20 mmol), $NaHCO_3$ (96.6 mg, 1.15 mmol) and H_2O_2 (0.25 mL, 3.6

mmol) in MeOH (5 mL) overnight afforded, after flash chromatography using 10% EtOAc in hexane, epoxy ketone **4iS1** (160.3 mg, 65%) as a colourless oil. R_f = 0.3 (10% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.10 (m, 5H), 3.21 (d, *J* = 2.0 Hz, 1H), 3.07 (td, *J* = 5.6, 2.0 Hz, 1H), 2.88 – 2.68 (m, 2H), 2.47 – 2.17 (m, 2H), 2.01 – 1.88 (m, 2H), 1.03 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.0, 140.6, 128.7, 128.5, 126.4, 110.1, 59.6, 58.0, 33.7, 32.1, 30.9 ppm; HRMS (EI, m/z): calculated for [$C_{13}H_{16}O_2$] 204.1145, found 204.1141; FTIR: ν = 1030, 1360, 1455, 1497, 1709, 2984 cm^{-1}.

To a solution of **4iS1** (165.4 mg, 0.81 mmol) in anhydrous THF (8 mL) at –78 °C was added NaHMDS (1.0 M, 1.5 mL, 1.5 mmol). The mixture was stirred for 1 h at –78 °C. TESCl (0.17 mL, 0.77 mmol) was added and the reaction was allowed to warm to room temperature. After stirring for 1 h, water was added. The mixture was extracted with EtOAc, and the organics were dried over anhydrous $MgSO_4$. The volatiles were removed in vacuo. The residue was purified by flash chromatography using 2% EtOAc in hexane with 1% Et_3N to afford epoxy enolsilane **4i** (174.9 mg, 75% yield) as a colourless oil. R_f = 0.2 (5% EtOAc in Hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.35 (m, 4H), 7.35 – 7.29 (m, 1H), 7.11 (d, *J* = 8.6 Hz, 2H), 6.94 – 6.86 (m, 2H), 5.04 (s, 2H), 4.41 (d, *J* = 1.3 Hz, 1H), 4.30 (d, *J* = 1.3 Hz, 1H), 3.06 (ddd, *J* = 6.4, 5.2, 2.1 Hz, 1H), 3.01 (d, *J* = 2.1 Hz, 1H), 2.80 – 2.60 (m, 2H), 1.91 – 1.76 (m, 2H), 0.96 (t, *J* = 7.9 Hz, 9H), 0.68 (q, *J* = 7.7 Hz, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.0, 141.4, 128.6 (2 carbons), 126.1, 107.0, 58.9, 56.8, 33.8, 32.3, 10.9, 6.9, 5.4 ppm; HRMS (EI, m/z): calculated for [$C_{19}H_{30}O_2Si$] 318.2010, found 318.2012; FTIR: ν = 1008, 1340, 1384, 1415, 1455, 1602, 1727, 2877, 2957, 3672 cm^{-1}.

Preparation of ((1-(3-benzyloxiran-2-yl)vinyl)oxy)triethylsilane (4j)

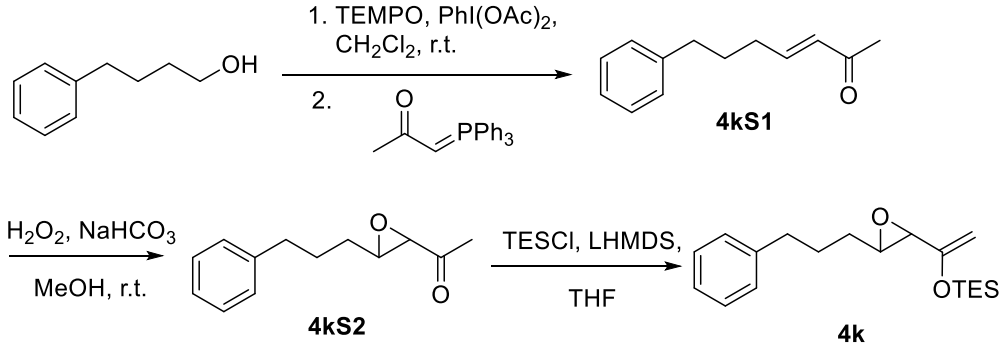


4j

According to General Procedure C, the reaction of 1-(3-benzyloxiran-2-yl)ethan-1-one[10] (362.7 mg, 2.06 mmol), HMDS (0.82 mL, 3.9 mmol), *n*BuLi (1.93 M, 2.0 mL, 3.9 mmol) and TESCl (350 µL, 1.96 mmol) in anhydrous THF (12 mL) afforded, after flash chromatography using 3% EtOAc in hexane with 1% Et_3N, epoxy enolsilane **4j** (381 mg, 67% yield) as a colourless oil. R_f = 0.2 (5% EtOAc in Hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.20 (m, 5H), 4.45 (d, *J* = 1.3 Hz, 1H), 4.31 (d, *J* = 1.4 Hz, 1H), 3.27 (td, *J* = 5.5, 2.0 Hz, 1H), 3.08 (d, *J* = 2.0 Hz, 1H), 2.98 – 2.84 (m, 2H), 0.94

(t, J = 7.9 Hz, 9H), 0.67 (q, J = 7.8 Hz, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 137.1, 129.1, 128.6, 126.7, 93.5, 57.9, 57.8, 38.1, 6.7, 4.9 ppm; HRMS (EI, m/z): calculated for [$C_{17}H_{26}O_2Si$] 290.1697, found 290.1706; FTIR: ν = 1007, 1018, 1334, 1456, 1497, 1636, 2877, 2958 cm^{-1}.

Preparation of triethyl((1-(3-(3-phenylpropyl)oxiran-2-yl)vinyl)oxy)silane (4k)



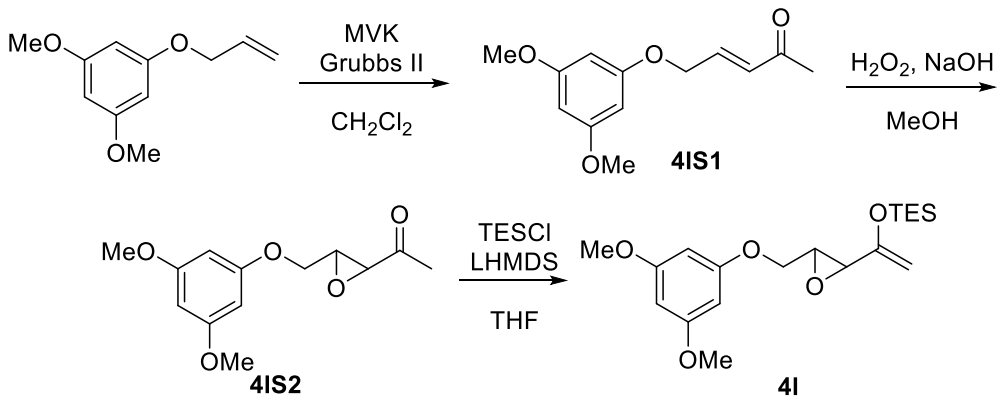
To a solution of 4-phenylbutan-1-ol (0.38 mL, 2.5 mmol) in CH_2Cl_2 (10 mL) was added $PhI(OAc)_2$ (0.8438 g, 2.62 mmol) and TEMPO (39.3 mg, 0.25 mmol). The reaction mixture was stirred for 4 h at room temperature. Acetylmethylenetriphenyl-phosphorane (0.95 g, 3.0 mmol) was added at 0 °C. The mixture was warmed to room temperature and stirred overnight. The crude product was concentrated in vacuo and purified by flash chromatography using 10% EtOAc in hexane to afford **4kS1** (466.6 mg, 97% yield) as a yellowish oil. R_f = 0.4 (10% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, J = 7.4 Hz, 2H), 7.19 (dd, J = 13.0, 7.2 Hz, 3H), 6.80 (dt, J = 15.9, 6.8 Hz, 1H), 6.08 (d, J = 16.0 Hz, 1H), 2.66 (t, J = 7.6 Hz, 2H), 2.30 – 2.24 (m, 2H), 2.23 (s, 3H), 1.87 – 1.75 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.6, 147.9, 141.6, 131.5, 128.4, 128.4, 126.0, 35.3, 31.9, 29.6, 26.8 ppm; HRMS (EI, m/z): calculated for [$C_{12}H_{13}O$] [M-CH_3]$^+$ 173.0961, found 173.0960; FTIR: ν = 1161, 1248, 1331, 1418, 1513, 1612, 1713, 2957 cm^{-1}.

According to General Procedure B, the reaction of **4kS1** (463.1 mg, 2.46 mmol), $NaHCO_3$ (210 mg, 2.50 mmol) and H_2O_2 (0.51 mL, 7.5 mmol) in MeOH (10 mL) overnight afforded, after purification by flash chromatography using 10% EtOAc in hexane, epoxy ketone **4kS2** (265.6 mg, 53% yield) as a colourless oil. R_f = 0.4 (10% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 2H), 7.23 – 7.14 (m, 3H), 3.18 (d, J = 2.0 Hz, 1H), 3.07 (ddd, J = 6.4, 4.6, 2.0 Hz, 1H), 2.68 (t, J = 7.5 Hz, 2H), 2.05 (s, 3H), 1.89 – 1.55 (m, 4H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.2, 141.6, 128.6, 128.5, 126.1, 59.9, 58.0, 35.5, 31.3, 27.6, 24.5 ppm; HRMS (EI, m/z):

calculated for [$C_{13}H_{14}O$] [M-H_2O]$^+$ 186.1039, found 186.1029; FTIR: ν = 1184, 1361, 1454, 1709, 2862, 2943 cm^{-1}.

According to General Procedure C, the reaction of **4kS2** (876.7 mg, 4.29 mmol), HMDS (1.8 mL, 8.2 mmol), *n*BuLi (1.97 M, 4.1 mL, 8.2 mmol) and TESCl (0.69 mL, 4.1 mmol) in anhydrous THF (24 mL) afforded, after flash chromatography using 3% EtOAc in hexane with 1% Et_3N, epoxy enolsilane **4k** (764.1 mg, 54% yield) as a colourless oil. R_f = 0.2 (5% EtOAc in Hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.13 (m, 5H), 4.45 (d, *J* = 1.3 Hz, 1H), 4.32 (d, *J* = 1.3 Hz, 1H), 3.14 – 2.96 (m, 2H), 2.67 (t, *J* = 7.6 Hz, 2H), 1.93 – 1.70 (m, 2H), 1.70 – 1.54 (m, 3H), 0.98 (t, *J* = 7.9 Hz, 9H), 0.70 (q, *J* = 7.8 Hz, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 142.1, 128.5, 128.,5 126.0, 93.3, 57.9, 57.8, 35.7, 31.3, 27.8, 6.7, 4.9 ppm; HRMS (EI, m/z): calculated for [$C_{19}H_{30}O_2Si$] 318.2010, found 318.2010; FTIR: ν = 1008, 1456, 1636, 2959 cm^{-1}.

Preparation of ((1-(3-((3,5-dimethoxyphenoxy)methyl)oxiran-2-yl)vinyl)oxy) triethylsilane (4l)



According to General Procedure A, the reaction of 1-(allyloxy)-3,5-dimethoxy-benzene[11] (519.0 mg, 2.67 mmol), methyl vinyl ketone (0.89 mL, 11 mmol) and **Grubbs II** (68.0 mg, 0.08 mmol) in CH_2Cl_2 (36 mL) afforded, after flash chromatography using 25% EtOAc in hexane, **4lS1** (105.3 mg, 32% yield) as a yellowish oil, along with 49% recovered 1-(allyloxy)-3,5-dimethoxybenzene. R_f = 0.3 (20% EtOAc in hexane); ^{1}H NMR (400 MHz, CDCl3) δ 6.89 (dt, *J* = 16.0, 4.2 Hz, 1H), 6.43 (d, *J* = 16.1 Hz, 1H), 6.11 (d, *J* = 1.9 Hz, 1H), 6.09 (d, *J* = 2.0 Hz, 2H), 4.68 (dd, *J* = 4.1, 1.8 Hz, 2H), 3.77 (s, 6H), 2.30 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 161.5, 159.8, 141.0, 130.5, 93.4, 93.3, 66.4, 55.2, 27.2 ppm; HRMS (EI, m/z): calculated for [$C_{13}H_{16}O_4$] 236.1043, found 236.1042; FTIR: ν = 1159, 1552, 1676 cm^{-1}.

To a solution of **4lS1** (202.0 mg, 0.855 mmol) in MeOH (3.4 mL) was added aqueous NaOH (2.0 M, 43 µL, 0.086 mmol) and H_2O_2 (50% w/w, 0.12 mL, 1.7 mmol) at 0 ℃. The reaction mixture was stirred at 0 ℃ for 45 minutes. Aqueous Na_2SO_3 was added, and the mixture was extracted with CH_2Cl_2. The organics were dried over anhydrous $MgSO_4$. The crude product was concentrated in vacuo and purified by flash chromatography with 35% EtOAc in hexane to afford **4lS2** (157.0 mg, 73% yield) as a pale brown oil. R_f = 0.5 (35% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.12 (s, 1H), 6.08 (d, *J* = 1.7 Hz, 2H), 4.26 (dd, *J* = 11.4, 2.1 Hz, 1H), 4.00 (dd, *J* = 11.4, 4.6 Hz, 1H), 3.77 (s, 6H), 3.52 – 3.45 (m, 2H), 2.12 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.8, 161.5, 159.9, 93.6, 93.5, 67.0, 57.0, 55.4, 55.3, 24.4 ppm; HRMS (EI, m/z): calculated for [$C_{13}H_{16}O_5$] 252.0992, found 252.0992; FTIR: ν = 1201, 1544, 1710 cm^{-1}.

According to General Procedure C, the reaction of **4lS2** (155.0 mg 0.614 mmol), HMDS, (0.24 mL, 1.2 mmol), *n*BuLi (2.17 M, 0.53 mL, 1.2 mmol) and TESCl (98 µL, 0.59 mmol) in THF (3.6 mL) afforded, after flash chromatography with 5% EtOAc in hexane with 1%Et_3N, epoxy enolsilane **4l** (87.5 mg, 41% yield) as a pale yellow oil. R_f = 0.2 (5% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.10 (s, 3H), 4.53 (d, *J* = 1.5 Hz, 1H), 4.39 (d, *J* = 1.5 Hz, 1H), 4.21 (dd, *J* = 11.1, 3.0 Hz, 1H), 3.96 (dd, *J* = 11.1, 5.4 Hz, 1H), 3.76 (s, 6H), 3.46 (ddd, *J* = 5.2, 2.9, 2.1 Hz, 1H), 3.33 (d, *J* = 2.1 Hz, 1H), 0.98 (t, *J* = 7.9 Hz, 9H), 0.71 (q, *J* = 7.8 Hz, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.5, 160.4, 153.2, 94.5, 93.6, 93.6, 67.8, 55.7, 55.4, 55.1, 6.6, 4.8 ppm; HRMS (EI, m/z): calculated for [$C_{19}H_{30}O_5Si$] 366.1857, found 366.1862; FTIR: ν = 1012, 2918 cm^{-1}.

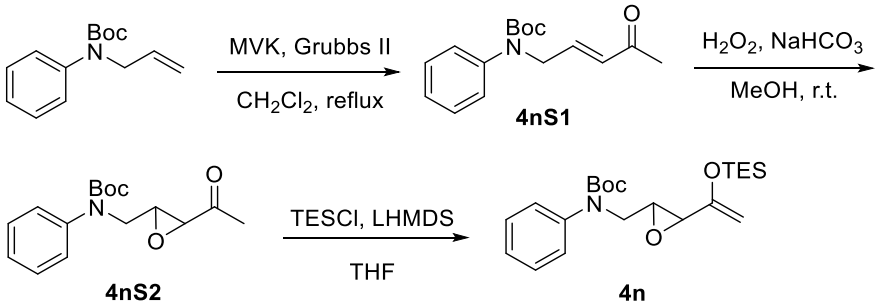
Preparation of triethyl((1-(3-(phenoxymethyl)oxiran-2-yl)vinyl)oxy)silane (4m)

4m

According to General Procedure C, the reaction of 1-(3-(phenoxymethyl)oxiran-2-yl)ethan-1-one[12] (447.5 mg, 2.33 mmol), HMDS (1.0 mL, 4.8 mmol), *n*BuLi (2.23 M, 2.0 mL, 4.6 mmol) and TESCl (0.375 mL, 2.28 mmol) in anhydrous THF (12 mL) afforded, after flash chromatography using 5% EtOAc in hexane with 1% Et_3N, epoxy enolsilane **4m** (550.1 mg, 77% yield) as a colourless oil; R_f = 0.4 (5% EtOAc in hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (m, 2H), 6.95 (m, 3H), 4.53 (s, 1H), 4.39

(s, 1H), 4.25 (dd, *J* = 11.2, 2.9 Hz, 1H), 4.02 (dd, *J* = 11.2, 5.2 Hz, 1H), 3.49 (t, *J* = 2.3 Hz, 1H), 3.34 (d, *J* = 1.2 Hz, 1H), 0.97 (t, *J* = 7.7 Hz, 9H), 0.71 (q, *J* = 7.9 Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.7, 153.4, 129.6, 121.4, 114.8, 94.6, 67.8, 55.8, 55.4, 6.7, 4.9 ppm; HRMS (EI, m/z): calculated for [$C_{17}H_{26}O_3Si$] 306.1646, found 306.1646; FTIR: ν = 1009, 1174, 1456, 1497, 1637, 2878, 2959 cm^{-1}.

Preparation of *tert*-butyl phenyl((3-(1-(triethylsiloxyvinyl)oxiran-2-yl)methyl)-carbamate (4n)

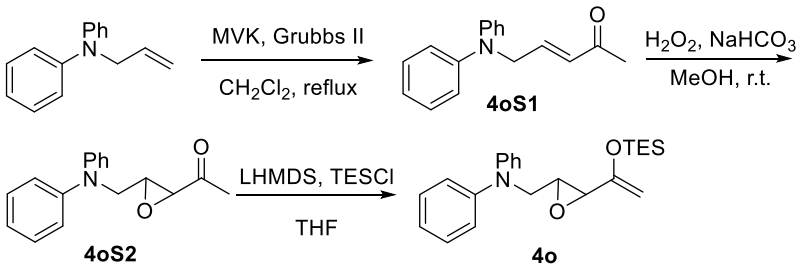


According to General Procedure A, the reaction of *N*-Boc-allylaniline (302.1 mg, 1.30 mmol), methyl vinyl ketone (0.45 mL, 5.4 mmol) and **Grubbs II** (33.0 mg, 0.04 mmol) in CH_2Cl_2 (17 mL) afforded, after flash chromatography using 20% EtOAc in hexane, **4nS1** (105.3 mg, 30% yield) as a yellowish oil, together with 68% recovered *N*-Boc-allylaniline. R_f = 0.4 (20% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 10.8, 4.9 Hz, 2H), 7.23 – 7.15 (m, 3H), 6.80 (dt, *J* = 16.0, 5.2 Hz, 1H), 6.17 (d, *J* = 16.0 Hz, 1H), 4.41 (dd, *J* = 5.2, 1.7 Hz, 2H), 2.26 (s, 3H), 1.44 (s, 9H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.0, 154.3, 142.9, 142.4, 131.3, 128.9, 126.2, 81.02, 51.4, 28.3, 27.2 ppm; HRMS (EI, m/z): calculated for [$C_{16}H_{21}NO_3$] 275.1516, found 275.1510; FTIR: ν = 1158, 1385, 1497, 1597, 1697, 2931, 3686 cm^{-1}.

According to General Procedure B, the reaction of **4nS1** (105.3 mg, 0.382 mmol), $NaHCO_3$ (32.6 mg, 0.39 mmol) and H_2O_2 (50% w/w, 0.08 mL, 1 mmol) in MeOH (1.6 mL) over 2 days afforded, after flash chromatography using 20% EtOAc in hexane, epoxy ketone **4nS2** (74.6 mg, 67% yield) as a colourless oil. R_f = 0.3 (20% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.8 Hz, 2H), 7.25 – 7.18 (m, 3H), 3.92 (dd, *J* = 14.9, 4.2 Hz, 1H), 3.72 (dd, *J* = 15.9, 4.8 Hz, 1H), 3.44 – 3.36 (m, 1H), 3.23 (d, *J* = 2.0 Hz, 1H), 2.06 (s, 3H), 1.44 (s, 9H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.7, 154.5, 142.4, 129.0, 126.8, 126.6, 58.6, 55.9, 51.7, 28.3, 24.7 ppm; HRMS (EI, m/z): calculated for [$C_{16}H_{21}NO_4$] 291.1465, found 291.1470; FTIR: ν = 1153, 1368, 1385, 1495, 1598, 1697, 2932 cm^{-1}.

According to General Procedure C, the reaction of **4nS2** (74.4 mg, 0.26 mmol), HMDS (0.10 mL, 0.49 mmol), *n*BuLi (2.30 M, 0.11 mL, 0.25 mmol) and TESCl (0.040 mL, 0.24 mmol) in anhydrous THF (1.5 mL) afforded, after flash chromatography using 3% EtOAc in hexane with 1% Et_3N, epoxy enolsilane **4n** (25.3 mg, 26% yield) as a pale yellow oil. R_f = 0.2 (5% EtOAc in Hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 4.41 (d, *J* = 1.3 Hz, 1H), 4.33 (d, *J* = 1.3 Hz, 1H), 3.76 (d, *J* = 5.0 Hz, 2H), 3.36 (d, *J* = 2.0 Hz, 1H), 3.06 (d, *J* = 1.7 Hz, 1H), 1.45 (s, 9H), 0.96 (t, *J* = 7.9 Hz, 9H), 0.68 (q, *J* = 7.9 Hz, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.5, 142.7, 128.8, 126.94, 126.2, 93.8, 57.2, 55.4, 51.9, 28.3, 6.6, 6.2, 4.8, ppm; HRMS (EI, m/z): calculated for [$C_{22}H_{35}NO_4Si$] 405.2330, found 405.2333; FTIR: ν = 1010, 1152, 1387, 1456, 1495, 1598, 1636, 1696, 2959 cm^{-1}.

Preparation of *N*-phenyl-*N*-((3-(1-(triethylsiloxy)vinyl)oxiran-2-yl)methyl)aniline (4o)

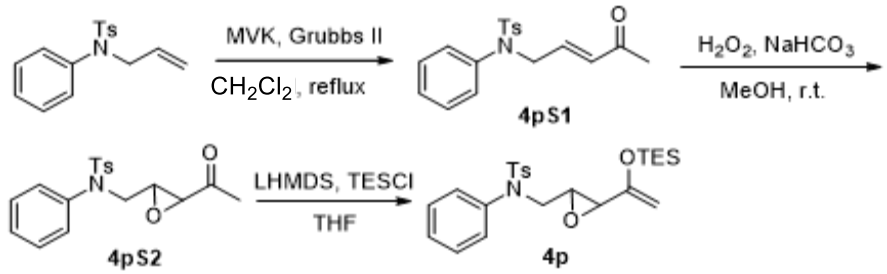


According to General Procedure A, the reaction of *N*-allyl-*N*-phenylaniline (382.2 mg, 1.83 mmol), methyl vinyl ketone (0.65 mL, 7.8 mmol) and **Grubbs II** (48.0 mg, 0.06 mmol) in CH_2Cl_2 (25 mL) afforded, after flash chromatography using 20% EtOAc in hexane, enone **4oS1** (333.0 mg, 73% yield) as a yellowish oil. R_f = 0.2 (20% EtOAc in hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 5H), 6.98 (dd, *J* = 13.7, 7.5 Hz, 5H), 6.86 (dt, *J* = 16.0, 4.5 Hz, 1H), 6.31 (dt, *J* = 16.0, 1.6 Hz, 1H), 4.54 (dd, *J* = 4.4, 1.8 Hz, 2H), 2.24 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.1, 147.3, 143.7, 131.5, 129.4, 121.9, 120.6, 53.5, 27.4 ppm; HRMS (EI, m/z): calculated for [$C_{17}H_{17}NO$] 251.1305, found 251.1302; FTIR: ν = 1339, 1456, 1497, 1605, 2980 cm^{-1}.

According to General Procedure B, the reaction of **4oS1** (314.4 mg, 1.25 mmol), $NaHCO_3$ (127.8 mg, 1.52 mmol) and H_2O_2 (0.26 mL, 3.8 mmol) in MeOH (5 mL) overnight afforded, after flash chromatography using 35% EtOAc in hexane, epoxy ketone **4oS2** (178.3mg, 53%) as a colourless oil. R_f = 0.5 (35% EtOAc in hexane); the product was used immediately to avoid decomposition.

According to General Procedure C, the reaction of **4oS2** (170 mg, 0.64 mmol), HMDS (0.25 mL, 1.2 mmol), *n*BuLi (2.16 M, 0.56 mL, 1.2 mmol) and TESCl (0.10 mL, 0.61 mmol) in anhydrous THF (4 mL) afforded, after flash chromatography using 3% EtOAc in hexane with 1% Et_3N, epoxy enolsilane **4o** (157.8 mg, 69% yield) as a pale yellow oil. R_f = 0.2 (5% EtOAc in Hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 4H), 7.05 – 7.00 (m, 4H), 6.99 – 6.95 (m, 2H), 4.36 (d, *J* = 1.4 Hz, 1H), 4.28 (d, *J* = 1.4 Hz, 1H), 3.93 (dd, *J* = 4.2, 1.0 Hz, 2H), 3.33 (td, *J* = 4.3, 2.1 Hz, 1H), 3.10 (d, *J* = 2.1 Hz, 1H), 0.93 (t, *J* = 7.9 Hz, 9H), 0.65 (q, *J* = 8.0 Hz, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.6, 147.9, 129.4, 121.7, 121.1, 93.6, 56.9, 55.8, 53.3, 6.6, 4.8 ppm; HRMS (EI, m/z): calculated for [$C_{23}H_{31}NO_2Si$] 381.2119, found 381.2118; FTIR: ν = 1007, 1425, 1497, 1591, 2878, 2959 cm^{-1}.

Preparation of 4-methyl-*N*-phenyl-*N*-((3-(1-(triethylsiloxyvinyl)oxiran-2-yl) methyl)- benzenesulfonamide (4p)



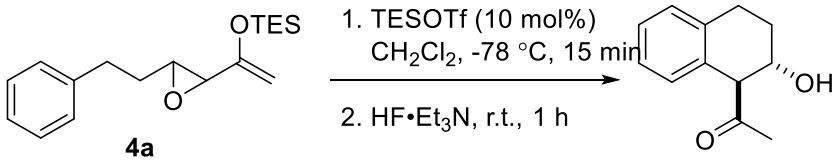
According to General Procedure A, the reaction of *N*-allyl-4-methyl-*N*-phenylbenzene- sulfonamide[13] (219.3 mg, 0.76 mmol), methyl vinyl ketone (0.25 mL, 3.0 mmol) and **Grubbs II** (27.8 mg, 0.03 mmol) in CH_2Cl_2 (10 mL) afforded, after flash chromatography using 20% EtOAc in hexane, enone **4pS1** (132.4 mg, 53% yield) as a yellowish oil. R_f = 0.2 (20% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.2 Hz, 2H), 7.34 – 7.24 (m, 5H), 7.10 – 6.98 (m, 2H), 6.64 (dt, *J* = 16.0, 5.8 Hz, 1H), 6.10 (d, *J* = 16.0 Hz, 1H), 4.34 (d, *J* = 5.7 Hz, 2H), 2.43 (s, 3H), 2.18 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 143.9, 141.2, 139.1, 134.8, 132.6, 129.6, 129.1, 128.4, 128.1, 127.6, 51.9, 27.1, 21.5 ppm; HRMS (EI, m/z): calculated for [$C_{18}H_{19}NO_3S$] 329.1080, found 329.1081; FTIR: ν = 1507, 1555, 1605 cm^{-1}.

According to General Procedure B, the reaction of **4pS1** (132.4 mg, 0.40 mmol), $NaHCO_3$ (34.0 mg, 0.40 mmol) and H_2O_2 (0.08 mL, 1 mmol) in MeOH (1.6 mL) for 4 days afforded, after purification by flash chromatography using 50% EtOAc in hexane, epoxy ketone **4pS2** (114.7 mg, 83% yield) as a colourless oil. R_f = 0.1 (20% EtOAc in

hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 2.4 Hz, 3H), 7.28 – 7.22 (m, 2H), 7.07 (d, *J* = 3.3 Hz, 2H), 3.75 (qd, *J* = 14.5, 5.1 Hz, 2H), 3.35 (s, 1H), 3.15 (s, 1H), 2.43 (s, 3H), 2.01 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.2, 144.1, 139.7, 135.1, 129.7, 129.5, 128.9, 128.6, 127.8, 58.3, 56.2, 52.9, 24.9, 21.7 ppm; HRMS (EI, m/z): calculated for [$C_{18}H_{19}NO_4S$] 345.1029, found 345.1029; FTIR: ν = 1166, 1354, 1489, 1597, 1713 cm^{-1}.

According to General Procedure C, the reaction of **4pS2** (111.3 mg, 0.29 mmol), HMDS (0.12 mL, 0.55 mmol), *n*BuLi (2.28 M, 0.21 mL, 0.48 mmol) and TESCl (0.047 mL, 0.28 mmol) in anhydrous THF (1.7 mL) afforded, after flash chromatography using 10% EtOAc in hexane with 1% Et_3N, epoxy enolsilane **4p** (39.5 mg, 27% yield) as a pale yellow oil. R_f = 0.2 (5% EtOAc in Hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.2 Hz, 2H), 7.37 – 7.18 (m, 5H), 7.12 – 7.03 (m, 2H), 4.31 (s, 1H), 4.27 (s, 1H), 3.81 (dd, *J* = 14.2, 5.4 Hz, 1H), 3.63 (dd, *J* = 14.2, 5.5 Hz, 1H), 3.24 (s, 1H), 2.93 (s, 1H), 2.42 (s, 3H), 0.92 (t, *J* = 7.9 Hz, 9H), 0.63 (q, *J* = 7.9 Hz, 6H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.9, 143.6, 139.6, 135.5, 129.5, 129.2, 129.0, 128.3, 127.7, 94.2, 57.0, 55.0, 52.9, 21.6, 6.6, 4.7 ppm; HRMS (EI, m/z): calculated for [$C_{24}H_{33}NO_4SSi$] 459.1894, found 459.1903; FTIR: ν = 1019, 1091, 1166, 1350, 1425, 1493, 1598, 1636, 1714, 2877, 2959 cm^{-1}.

Friedel-Crafts Cyclization of 4a

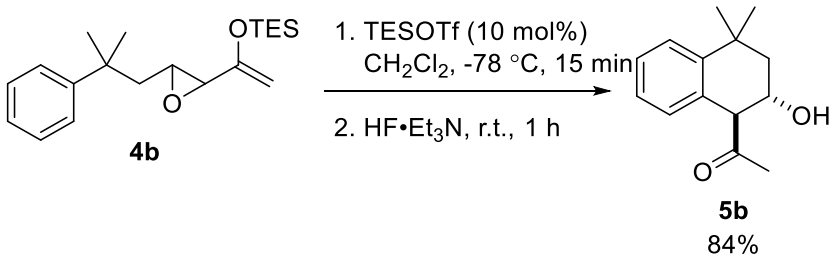


According to General Procedure D, the reaction of **4a** (100.2 mg, 0.329 mmol) and TESOTf (0.2 M solution in CH_2Cl_2, 0.164 mL, 0.03 mmol) in CH_2Cl_2 (1.8 mL) afforded, after flash chromatography using 35% EtOAc in hexane, **5a** (35.8 mg, 57% yield).

1-((*1S*,2S)-2-hydroxy-1,2,3,4-tetrahydronaphthalen-1-yl)ethan-1-one (5a)**: white solid; mp: 77–78 °C; R_f = 0.20 (35% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21-7.14 (m, 3H), 6.69 (d, *J* = 8.0 Hz, 1H), 4.29-4.23 (m, 1H), 3.82 (d, *J* = 8.1 Hz, 1H), 2.93 (dd, *J* = 7.9, 5.2 Hz, 2H), 2.20 (s, 3H), 2.19-2.14 (m, 1H), 1.96 (d, *J* = 4.9 Hz, 1H), 1.86-1.78 (m, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.1, 135.9, 132.2, 129.2, 128.7, 127.3, 126.5, 69.6, 62.8, 30.5, 28.7, 27.4 ppm; HRMS (EI, m/z)

Calculated for [$C_{12}H_{14}O_2$] 190.0994, Found 190.0989; IR (CH_2Cl_2) 3441 (OH), 3024, 2932, 1713 (C=O), 1489, 1358, 1227, 1165, 1042 cm^{-1}.

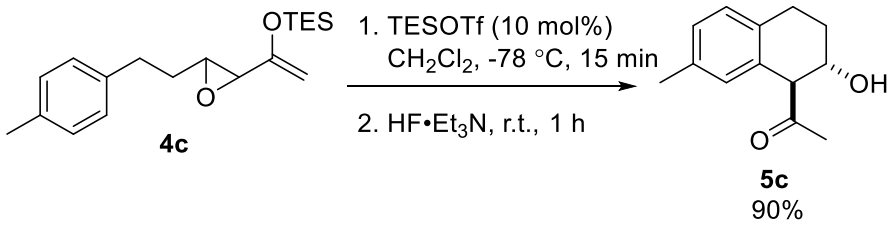
Friedel-Crafts Cyclization of 4b



According to General Procedure D, the reaction of **4b** (46.3 mg, 0.139 mmol) and TESOTf (0.2 M solution in CH_2Cl_2, 0.075 mL, 0.02 mmol) in CH_2Cl_2 (0.8 mL) afforded, after flash chromatography using 35% EtOAc in hexane, **5b** (23.9 mg, 84% yield).

1-((*1S*,2S)-2-hydroxy-4,4-dimethyl-1,2,3,4-tetrahydronaphthalen-1-yl)ethan-1-one (5b)**: white solid; mp: 81-84 °C; R_f = 0.4 (35% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.8 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 4.33 (s, 1H), 3.76 (d, *J* = 9.5 Hz, 1H), 2.21 (s, 3H), 1.98 (dd, *J* = 12.6, 3.5 Hz, 1H), 1.82 – 1.65 (m, 2H), 1.37 (d, *J* = 11.1 Hz, 6H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 210.8, 144.8, 131.1, 128.0, 127.6, 126.8, 126.5, 67.2, 64.3, 46.6, 36.0, 32.6, 31.8, 28.2 ppm; HRMS (EI, m/z): calculated for [$C_{14}H_{18}O_2$] 218.1301, found 218.1298; FTIR: ν = 1060, 1363, 1489, 1705, 3596 cm^{-1}.

Friedel-Crafts Cyclization of 4c

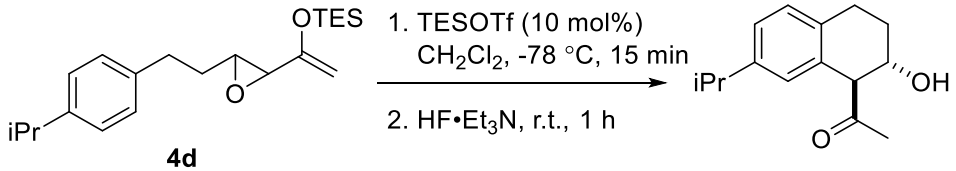


According to General Procedure D, the reaction of **4c** (99.9 mg, 0.314 mmol) and TESOTf (0.2 M solution in CH_2Cl_2, 0.157 mL, 0.03 mmol) in CH_2Cl_2 (1.7 mL) afforded, after flash chromatography using 35% EtOAc in hexane, **5c** (57.4 mg, 90% yield).

1-((*1S*,2S)-2-hydroxy-7-methyl-1,2,3,4-tetrahydronaphthalen-1-yl)ethan-1-one (5c)**: white solid; mp: 82-86 °C; R_f = 0.3 (35% EtOAc in hexane); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.02 (q, *J* = 8.7, 8.3 Hz, 2H), 6.74 (s, 1H), 4.22 (ddd, *J* = 9.8, 8.2, 3.4 Hz, 1H), 3.77 (d, *J* = 8.2 Hz, 1H), 2.87 (dd, *J* = 8.1, 5.1 Hz, 2H), 2.50 – 2.34

(m, 1H), 2.27 (s, 3H), 2.20 (s, 3H), 2.18 – 2.09 (m, 1H), 1.78 (ddt, *J* = 12.6, 9.8, 8.3 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.8, 136.1, 132.9, 132.1, 129.1, 129.0, 128.2, 69.9, 62.9, 30.8, 28.7, 27.2, 21.1 ppm; HRMS (EI, m/z): calculated for [$C_{13}H_{16}O_2$] 204.1145, found 204.1143; FTIR: ν = 1043, 1161, 1355, 1418, 1504, 1606, 1705, 2934, 3600, 3688 cm^{-1}. (–)-**5c**: $[a]_D^{20} = -27.0\,(c = 1.0, \mathrm{CH2Cl2})$; The enantiomeric excess was determined by HPLC analysis [Daicel chiralcel OD-3, 1.0 mL/min, λ = 210 nm, 10% IPA in hexane, t_R (minor) = 7.00 min, t_R (major) = 7.38 min] to be 96% ee.

Friedel-Crafts Cyclization of 4d

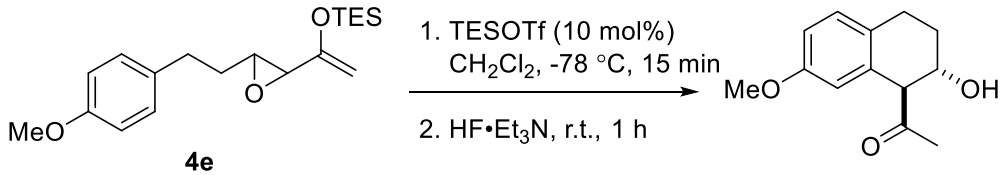


4d **5d** 72%

According to General Procedure D, the reaction of **4d** (61.8 mg, 0.178 mmol) and TESOTf (0.2 M solution in CH_2Cl_2, 0.088 mL, 0.02 mmol) in CH_2Cl_2 (0.9 mL) afforded, after flash chromatography using 40% EtOAc in hexane, **5d** (29.9 mg, 72% yield).

1-((*1S*,2S)-2-hydroxy-7-isopropyl-1,2,3,4-tetrahydronaphthalen-1-yl)ethan-1-one (5d)**: colourless oil; R_f = 0.3 (35% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 – 7.04 (m, 2H), 6.79 (s, 1H), 4.24 (t, *J* = 7.4 Hz, 1H), 3.79 (d, *J* = 8.1 Hz, 1H), 2.89 (dd, *J* = 8.0, 5.0 Hz, 2H), 2.82 (dq, *J* = 13.9, 7.0 Hz, 1H), 2.19 (s, 3H), 2.18 – 2.12 (m, 1H), 1.96 (s, 1H), 1.81 (ddt, *J* = 12.7, 9.9, 8.2 Hz, 1H), 1.20 (dd, *J* = 6.9, 2.3 Hz, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.3, 147.2, 133.2, 131.9, 129.1, 126.7, 125.4, 69.8, 63.0, 33.7, 30.7, 28.4, 27.1, 24.0, 24.0 ppm; HRMS (EI, m/z): calculated for [$C_{15}H_{20}O_2$] 232.1458, found 232.1458; FTIR: ν = 1044, 1356, 1501, 1603, 1704, 2963, 3607, 3690 cm^{-1}.

Friedel-Crafts Cyclization of 4e

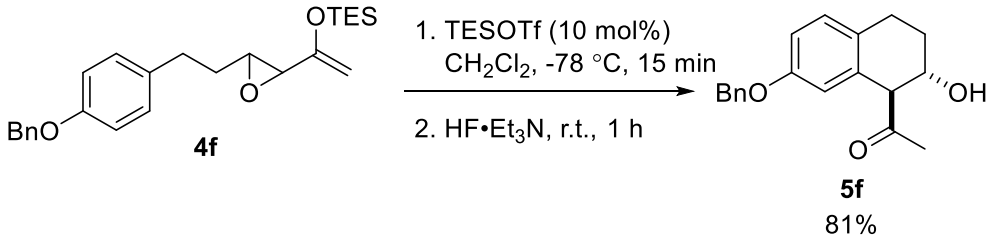


4e **5e** 81%

According to General Procedure D, the reaction of **4e** (154.2 mg, 0.461 mmol) and TESOTf (0.2 M solution in CH_2Cl_2, 0.200 mL, 0.04 mmol) in CH_2Cl_2 (2.5 mL) afforded, after flash chromatography using 35% EtOAc in hexane, **5e** (81.9 mg, 81% yield).

1-((*1S*,2S)-2-hydroxy-7-methoxy-1,2,3,4-tetrahydronaphthalen-1-yl)ethan-1-one (5e)**: colourless oil; R_f = 0.2 (35% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.5 Hz, 1H), 6.77 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.48 (d, *J* = 2.3 Hz, 1H), 4.30 – 4.18 (m, 1H), 3.81 – 3.69 (m, 4H), 2.85 (dd, *J* = 7.7, 5.3 Hz, 2H), 2.20 (s, 3H), 2.15 (ddd, *J* = 13.5, 8.7, 5.1 Hz, 1H), 1.86 – 1.73 (m, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 143.9, 141.2, 139.1, 134.8, 132.6, 129.6, 129.1, 128.4, 128.1, 127.6, 51.9, 27.1, 21.5 ppm; HRMS (EI, m/z): calculated for [$C_{13}H_{16}O_3$] 220.1094, found 220.1093; FTIR: ν = 1038, 1163, 1355, 1504, 1611, 1706, 2937, 3599 cm^{-1}.

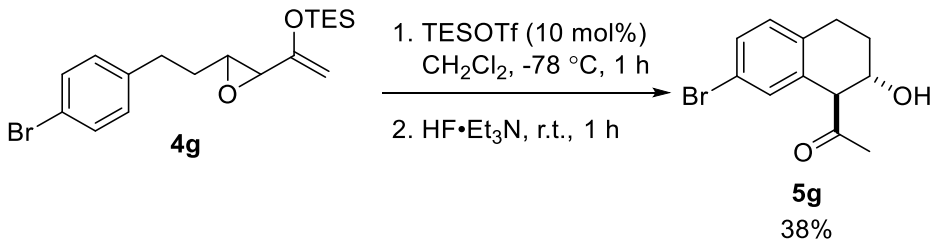
Friedel-Crafts Cyclization of 4f



According to General Procedure D, the reaction of **4f** (34.9 mg, 0.085 mmol) and TESOTf (0.2 M solution in CH_2Cl_2, 0.042 mL, 0.01 mmol) in CH_2Cl_2 (0.4 mL) afforded, after flash chromatography using 40% EtOAc in hexane, **5f** (20.3 mg, 81% yield).

1-((*1S*,2S)-7-(benzyloxy)-2-hydroxy-1,2,3,4-tetrahydronaphthalen-1-yl)ethan-1-one (5f)**: white solid; mp: 68-72 °C; R_f = 0.3 (50% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.33 (m, 4H), 7.33 – 7.28 (m, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 6.84 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.53 (d, *J* = 2.3 Hz, 1H), 5.05 – 4.96 (m, 2H), 4.22 (td, *J* = 10.0, 3.4 Hz, 1H), 3.75 (d, *J* = 8.0 Hz, 1H), 2.84 (dd, *J* = 7.9, 5.1 Hz, 2H), 2.17 – 2.10 (m, 4H), 2.01 (d, *J* = 17.7 Hz, 1H), 1.78 (ddt, *J* = 12.7, 9.9, 8.1 Hz, 1H) ppm; ^{13}C NMR (126 MHz, MeOH) δ 209.9, 157.2, 136.9, 133.1, 130.1, 128.6, 128.2, 128.0, 127.4, 114.5, 114.5, 70.1, 69.6, 63.0, 30.8, 28.4, 26.6 ppm; HRMS (EI, m/z): calculated for [$C_{19}H_{20}O_3$] 296.1407, found 296.1410; FTIR: ν = 1026, 1165, 1356, 1504, 1609, 1705, 2935, 3600, 3689 cm^{-1}.

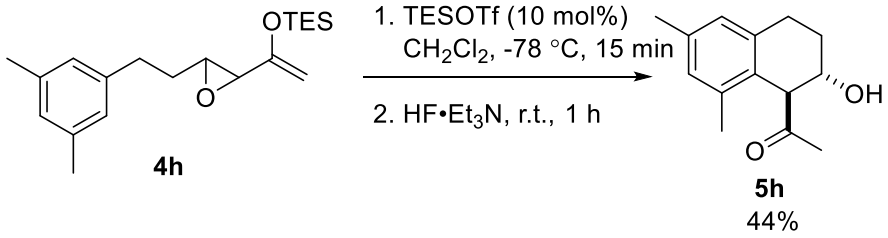
Friedel-Crafts Cyclization of 4g



According to modified General Procedure B, the reaction of **4g** (110.0 mg, 0.287 mmol) and TESOTf (0.2 M solution in CH_2Cl_2, 0.131 mL, 0.03 mmol) in CH_2Cl_2 (1.3 mL) for 1 h afforded, after flash chromatography using 35% EtOAc in hexane, **5g** (27.6 mg, 38% yield) and the desilylated substrate **4gS2** (25.7 mg, 35% yield).

1-((*1S*,2S)-7-bromo-2-hydroxy-1,2,3,4-tetrahydronaphthalen-1-yl)ethan-1-one (5g)**: white solid; mp: 92-96 °C; R_f = 0.3 (50% EtOAc in hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 1H), 7.13 – 7.07 (m, 1H), 7.03 (d, *J* = 8.2 Hz, 1H), 4.32 – 4.23 (m, 1H), 3.82 (t, *J* = 7.2 Hz, 1H), 2.93 – 2.78 (m, 2H), 2.25 (s, 3H), 2.16 – 2.09 (m, 1H), 1.88 – 1.77 (m, 2H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 209.1, 135.0, 134.4, 131.6, 130.8, 130.4, 119.9, 69.1, 61.9, 30.0, 29.3, 26.6 ppm; HRMS (EI, m/z): calculated for [$C_{12}H_{13}O_2{}^{79}Br$] 268.0093, found 268.0089; FTIR: ν = 1046, 1155, 1356, 1605, 1707, 3599, 3689 cm^{-1}.

Friedel-Crafts Cyclization of 4h

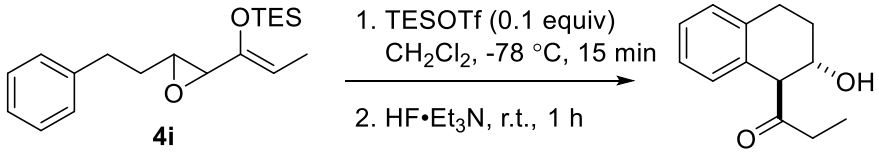


According to General Procedure D, the reaction of **4h** (95.4 mg, 0.301 mmol) and TESOTf (0.15 mL, 0.2 M solution in CH_2Cl_2, 0.03 mmol) in CH_2Cl_2 (1.4 mL) afforded, after flash chromatography using 35% EtOAc in hexane, **5h** (35.8 mg, 44% yield).

1-((*1S*,2S)-2-hydroxy-6,8-dimethyl-1,2,3,4-tetrahydronaphthalen-1-yl)ethan-1-one 5h:** white solid; mp: 27-30 °C; R_f = 0.4 (35% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.85 (d, *J* = 6.8 Hz, 2H), 4.33 – 4.18 (m, 1H), 3.87 (d, *J* = 4.8 Hz, 1H), 2.86 (ddd, *J* = 16.8, 7.8, 5.6 Hz, 1H), 2.76 (dt, *J* = 16.9, 6.3 Hz, 1H), 2.27 (s, 3H), 2.24 – 2.17 (b, 1H), 2.16 – 2.10 (s, 3H), 2.09 (s, *J* = 6.6 Hz, 3H), 2.01 – 1.91 (m, 1H), 1.79 (td, *J* = 12.9, 7.1 Hz, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.9, 137.1, 136.6, 136.3, 129.4, 128.0, 127.5, 68.8, 60.1, 28.6, 28.2, 25.7, 20.9, 19.8 ppm; HRMS

(EI, m/z): calculated for [$C_{14}H_{18}O_2$] 218.1301, found 218.1292; FTIR: ν = 1159, 1356, 1607, 1711, 2932, 3600, 3689 cm^{-1}.

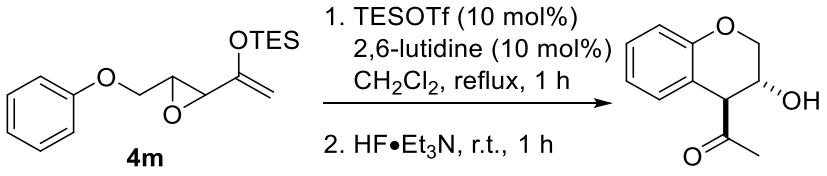
Friedel-Crafts Cyclization of 4i



5i
37%

According to General Procedure D, the reaction of **4i** (51.0 mg, 0.160 mmol) and TESOTf (0.2 M solution in CH_2Cl_2, 0.087 mL, 0.02 mmol) in CH_2Cl_2 (3.3 mL) afforded, after flash chromatography using 50% EtOAc in hexane, **5i** (12.9 mg, 37%).
1-((*1S*,2S)-2-hydroxy-1,2,3,4-tetrahydronaphthalen-1-yl)propan-1-one (5i)**: white solid; mp: 73-76 °C; R_f = 0.4 (50% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 – 7.10 (m, 3H), 6.92 (d, *J* = 7.0 Hz, 1H), 4.32 – 4.22 (m, 1H), 3.87 (d, *J* = 7.8 Hz, 1H), 2.92 (dd, *J* = 7.5, 5.5 Hz, 2H), 2.63 – 2.47 (m, 2H), 2.16 (dtd, *J* = 12.8, 5.3, 3.6 Hz, 1H), 1.87 – 1.77 (m, 2H), 1.08 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.6, 136.1, 132.6, 129.1, 128.7, 127.1, 126.4, 69.8, 61.8, 35.3, 30.5, 27.3, 7.8 ppm; HRMS (EI, m/z): calculated for [$C_{13}H_{16}O_2$] 204.1145, found 204.1145; FTIR: ν = 1050, 1109, 1715, 2939, 3600 cm^{-1}.

Friedel-Crafts Cyclization of 4m

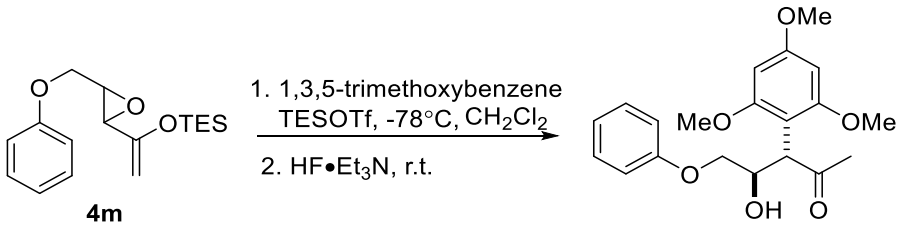


5m
18%

To a solution of epoxy enolsilane **4m** (42.0 mg, 0.137 mmol) in CH_2Cl_2 (0.9 mL) was added 0.087 mL of a 1:1 mixture of 0.2 M TESOTf in CH_2Cl_2 and 0.2 M 2,6-lutidine in CH_2Cl_2. It was stirred for 1 h under reflux, then HF·Et_3N (0.07 mL) was added. The mixture was cooled down to room temperature and stirred for 1 h. $NaHCO_3$ solution was added until effervescence ceased. The reaction mixture was extracted by CH_2Cl_2, and the organics were dried over anhydrous $MgSO_4$. The crude product was concentrated in vacuo and then purified by preparative TLC using 35% EtOAc in hexane to afford **5m** (5.1 mg, 18%) and desilylated substrate **4mS1** (11.6 mg, 41%).

1-((*3R*,4S)-3-hydroxychroman-4-yl)ethan-1-one (5m)**: colourless oil; R_f = 0.3 (35% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.5 Hz, 1H), 7.09 (t, *J* = 9.1 Hz, 1H), 7.01 – 6.86 (m, 2H), 4.42 – 4.29 (m, 1H), 4.26 – 4.18 (m, 1H), 4.09 (dd, *J* = 11.3, 4.8 Hz, 1H), 3.87 (d, *J* = 3.6 Hz, 1H), 2.29 (s, 3H), 2.15 (s, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.4, 153.6, 130.5, 129.0, 121.5, 117.4, 117.0, 67.8, 64.2, 56.7, 29.3 ppm; HRMS (EI, m/z): calculated for [$C_{11}H_{12}O_3$] 192.0781, found 192.0779; FTIR: ν = 1160, 1606, 1709, 3690 cm^{-1}.

Reaction of 4m with 1,3,5-trimethoxybenzene

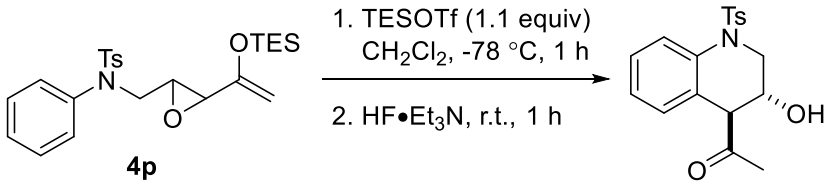


4m **6**

To a solution 1,3,5-trimethoxybenzene (188.2 mg, 1.12 mmol) in anhydrous CH_2Cl_2 (2.5 mL) was added **4m** (73.9 mg, 0.241 mmol). The mixture was cooled to –78 °C. TESOTf (0.2 M solution in CH_2Cl_2, 0.25 mL, 0.05 mmol) was added. The reaction progress was monitored by TLC. HF·Et_3N (0.2 mL) was added. Aqueous $NaHCO_3$ was added until effervescence ceased. The mixture was extracted with CH_2Cl_2. The organics were washed with brine and dried over anhydrous $MgSO_4$.The volatiles were removed in vacuo. The residue was purified by flash column chromatography using 20-60% EtOAc in hexane to afford **6** (31.7 mg, 36% yield).

(*3S*,4R)-4-hydroxy-5-phenoxy-3-(2,4,6-trimethoxyphenyl)pentan-2-one (6)**: colourless oil; R_f = 0.5 (50% EtOAc in hexane) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (dd, *J* = 8.7, 7.4 Hz, 2H), 6.86 (t, *J* = 7.3 Hz, 1H), 6.74 (dd, *J* = 8.7, 0.9 Hz, 2H), 6.09 (s, 2H), 4.76 – 4.68 (m, 1 H), 4.33 (s, 1H), 4.26 (d, *J* = 8.9 Hz, 1H), 3.80 (s, 3H), 3.75 – 3.72 (m, 2H), 3.70 (s, 6H), 1.93 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.0, 161.2, 158.9, 129.1, 120.4, 114.5, 105.4, 90.7, 69.5, 55.6, 55.3, 51.1, 28.1 ppm; HRMS (EI, m/z): calculated for [$C_{20}H_{24}O_6$] 360.1567, found 360.1580; FTIR: ν = 1124, 1464, 1497, 1599, 1699, 2941, 3689 cm^{-1}.

Friedel-Crafts Cyclization of 4p

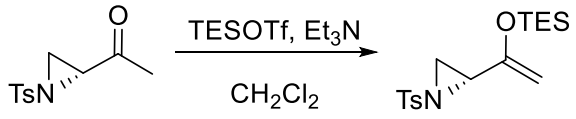


4p **5p** 23%

To a solution of epoxy enolsilane **4p** (38.9 mg, 0.085 mmol) in CH_2Cl_2 (0.45 mL) at –78 °C was added TESOTf (0.2 M solution in CH_2Cl_2, 0.465 mL, 0.09 mmol). It was stirred for 1 h at –78 °C, then HF·Et_3N (0.07 mL) was added. The mixture was warmed to room temperature and stirred for 1 h. $NaHCO_3$ solution was added until effervescence ceased. The reaction mixture was extracted by EtOAc, and the organics were dried over anhydrous $MgSO_4$. The crude product was concentrated in vacuo and then purification by flash chromatography using 50% EtOAc in hexane to afford **5p** (6.6 mg, 23% yield) and the desilylated substrate **4pS2** (15.5 mg, 53% yield).

1-((*3R*,4S)-3-hydroxy-1-tosyl-1,2,3,4-tetrahydroquinolin-4-yl)ethan-1-one (5p)**: white waxy solid; R_f = 0.3 (50% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 1H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.31-7.24 (m, 3H), 7.16 – 7.09 (m, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 4.23 (dd, *J* = 13.4, 4.2 Hz, 1H), 4.17 – 4.06 (m, 1H), 3.61 – 3.47 (m, 2H), 2.39 (s, 3H), 2.16 (d, *J* = 5.3 Hz, 1H), 1.80 (s, 3H) ppm; ^{13}C NMR (151 MHz, Acetone) δ 206.2, 144.2, 136.8, 136.4, 129.8, 129.4, 127.5, 127.3, 126.2, 124.9, 123.3, 64.2, 64.1, 60.2, 60.1, 50.7, 50.7, 26.9, 20.5 ppm; HRMS (EI, m/z): calculated for $[C_{18}H_{17}NO_3S]$ $[M\text{-}H_2O]^+$ 327.0924, found 327.0923; FTIR: ν = 1090, 1167, 1356, 1489, 1599, 1709, 2928, 3588 cm^{-1}.

Preparation of (*R*)-1-tosyl-2-(1-((triethylsilyl)oxy)vinyl)aziridine (+)-**7**

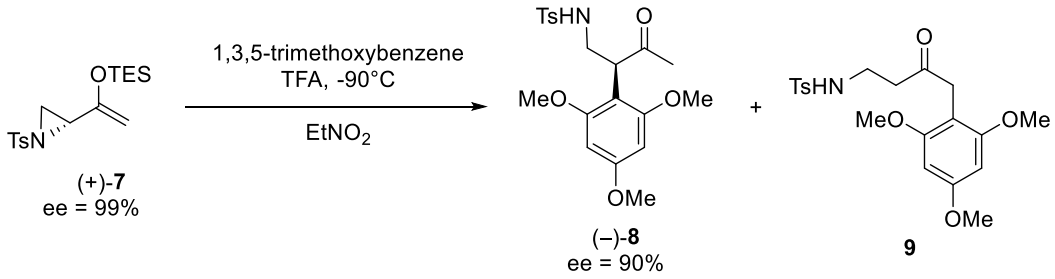


(+)-**7**

To a solution of (*R*)-1-(1-tosylaziridin-2-yl)ethanone[15] (1.3550 g, 5.6695 mmol, >99% *ee* [OF column, 40% IPA/hexane, 1.00 mL/min]) in CH_2Cl_2 (50 mL) at –78 °C was added Et_3N (2.4 mL, 17 mmol) and TESOTf (2.5 mL, 11 mmol). The resulting mixture was warmed to room temperature and stirred overnight. The reaction was quenched with dilute $NaHCO_3$ and extracted with Et_2O. The combined organic layers were dried over anhydrous $MgSO_4$. The volatiles were removed in vacuo and the residue was purification by flash chromatography using 4% EtOAc and 0.1% Et_3N in hexane to afford **7** (1.9062 g, 95% yield) as a colourless oil: R_f = 0.45 (10% EtOAc in

hexane); ;$[a]_D^{20} = +42.8$ (*c* = 1.12, $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6) δ 7.84 (d, *J* = 8.2 Hz, 2H), 6.77 (d, *J* = 8.1Hz, 2H), 4.27 (d, *J* = 1.4 Hz, 1H), 4.17 (d, *J* = 1.4 Hz, 1H), 3.26 (dd, *J* = 7.0, 4.4 Hz, 1H), 2.50 (d, *J* = 7.0 Hz, 1H), 2.17 (d, *J* = 4.4 Hz, 1H), 1.86 (s, 3H), 0.85 (t, *J* = 7.9 Hz, 9H), 0.51 (q, *J* = 7.9 Hz, 6H) ppm; ^{13}C NMR (100 MHz, C_6D_6) δ 152.4, 144.1, 136.5, 129.7, 128.2, 94.6, 41.2, 31.3, 21.1, 6.7, 5.0 ppm; HRMS (EI, m/z): calculated for [$C_{17}H_{27}NO_3SSi$] 353.1480, found 353.1480; FTIR: ν = 3067, 2960, 2914, 2878, 1636, 1598 cm^{-1}.

Alkylation of 1,3,5-trimethoxybenzene with (+)-**7**



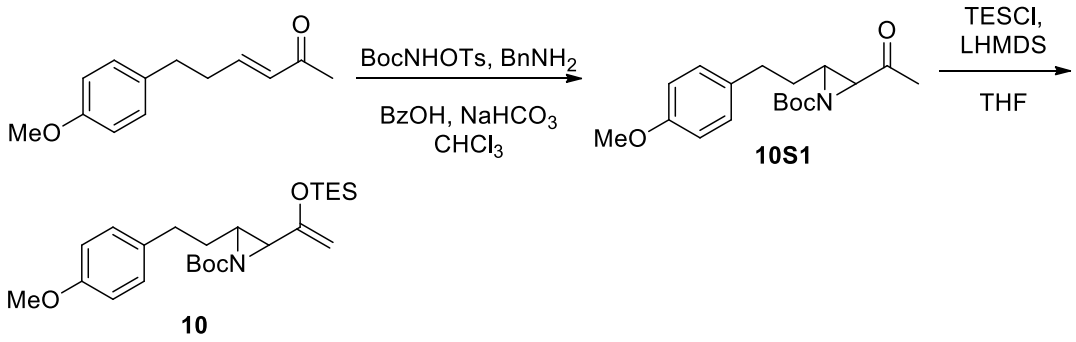
To a solution of (+)-**7** (0.3537 g, 1.002 mmol) in $EtNO_2$ (10 mL) at –90 °C was added 1,3,5-trimethoxybenzene (0.8411 g, 5.007 mmol) and trifluoroacetic acid (0.37 mL, 5.0 mmol). The resulting mixture was stirred for 5 h at –90 °C. The reaction was quenched with dilute $NaHCO_3$ and extracted with Et_2O. The combined organic layers were dried over anhydrous $MgSO_4$. The solvent was removed in vacuo and the residue was purified by flash chromatography using 25% EtOAc in hexane to afford **8** (0.3275 g, 80% yield) and **9** (0.0773 g, 19% yield).

(*S*)-4-methyl-*N*-(3-oxo-2-(2,4,6-trimethoxyphenyl)butyl)benzenesulfonamide (8): White solid; mp: 94°C; R_f (20% IPA in hexane) 0.37; $[a]_D^{20} = -105.6$ (*c* = 4.67, $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 6.07 (s, 2H), 5.20 (dd, *J* = 8.0, 4.8 Hz, 1H), 4.02 (dd, *J* = 8.0, 5.0 Hz, 1H), 3.80 (s, 3H), 3.70 (s, 6H), 3.42-3.36 (m, 1H), 3.09-3.03 (m, 1H), 2.40 (s, 3H), 1.84 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.6, 161.3, 158.9, 143.0, 137.7, 129.6, 127.1, 105.8, 90.8, 55.7, 55.5, 48.4, 42.8, 27.6, 21.6 ppm; HRMS (EI, m/z): calculated for [$C_{20}H_{25}NO_6S$] 407.1397; Found 407.1395; FTIR: ν = 3672, 3060, 3051, 1705, 1610, 1595 cm^{-1}; The enantiomeric excess was determined by HPLC analysis [Daicel chiralcel IC-3, 0.4 mL/min, λ = 210 nm, 60% IPA in hexane, t_R (major) = 87.53 min, t_R (minor) = 97.57 min] to be 90% ee.

4-methyl-*N*-(3-oxo-4-(2,4,6-trimethoxyphenyl)butyl)benzenesulfonamide (9): colourless oil; R_f (20% IPA in hexane) 0.40; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 6.13 (s, 2H), 5.11 (t, *J* = 6.4 Hz, 1H), 3.81 (s,

3H), 3.76 (s, 6H), 3.57 (s, 2H), 3.07 (q, *J* = 6.0 Hz, 2H), 2.62 (t, *J* = 5.7 Hz, 2H), 2.41 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.5, 160.7, 158.8, 143.4, 137.0, 129.8, 127.1, 103.7, 90.6, 55.8, 55.5, 40.6, 38.5, 37.6, 21.6 ppm; HRMS (EI, m/z): calculated for [$C_{20}H_{25}NO_6S$] 407.1397; Found 407.1393; FTIR: ν = 3047, 1716, 1610, 1596, 1500 cm^{-1}.

Preparation of *tert*-butyl 2-(4-methoxyphenethyl)-3-(1-(triethylsiloxy)vinyl) aziridine-1- carboxylate (10):

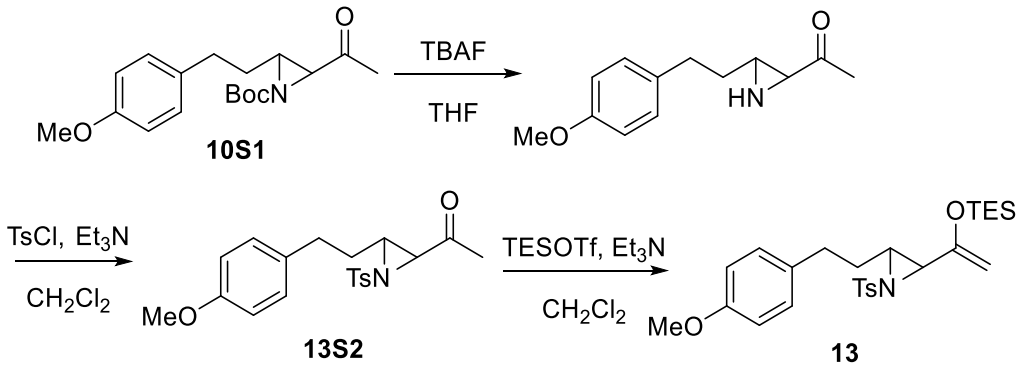


To a solution of $BnNH_2$ (0.62 mL, 5.0 mmol) in $CHCl_3$ (19 mL) was added BzOH (286.6 mg, 2.35 mmol). The mixture was stirred at room temperature for 10 min. (*E*)-6-(4-methoxyphenyl)hex-3-en-2-one (958.6 mg, 4.69 mmol) was added and stirred for 10 min, then BocNHOTs[14] (1.60g, 5.63 mmol) was added. After 5 min, $NaHCO_3$ (2.813 g, 33.5 mmol) was added, and the mixture was stirred at room temperature overnight. Another portion of BocNHOTs (308 mg, 1.07 mmol) was added, and the mixture was stirred overnight. The crude mixture was filtered through a short column of silica gel with EtOAc. The organics were collected, and the volatiles were removed in vacuo. The residue was purified by flash column chromatography using 15% EtOAc in hexane to afford **10S1** as a yellowish oil (1.2446 g , 83% yield). R_f = 0.4 (20% EtOAc in hexane); ^{1}H NMR (300 MHz, C_6D_6) δ 7.10 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 2.93 – 2.56 (m, 4H), 2.15 (s, 3H), 1.95 (dt, *J* = 13.9, 5.8 Hz, 1H), 1.68 (td, *J* = 14.3, 8.1 Hz, 1H), 1.46 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.3, 159.1, 158.0, 132.7, 129.4, 114.0, 81.7, 55.3, 46.6, 45.0, 33.3, 32.1, 29.3, 28.0 ppm; HRMS (EI, m/z): calculated for [$C_{18}H_{25}NO_4$] 319.1778, found 319.1771; FTIR: ν = 1153, 1314, 1369, 1513, 1612, 1724, 2936 cm^{-1}.

According to General Procedure C, the reaction of **10S1** (485.0 mg, 1.52 mmol), HMDS (0.60 mL, 2.9 mmol), *n*BuLi (1.91 M, 1.4 mL, 2.8 mmol) and TESCl (240 μL,

1.45 mmol) in anhydrous THF (9 mL) afforded, after flash chromatography using 3% EtOAc in hexane with 1% Et_3N, **10** (296.9 mg, 48% yield) as a pale yellow oil. R_f = 0.4 (5% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 4.41 (s, 1H), 4.30 (s, 1H), 3.78 (s, 3H), 2.83 – 2.68 (m, 2H), 2.68 – 2.60 (m, 2H), 1.85 (td, *J* = 14.4, 6.5 Hz, 1H), 1.67 (dt, *J* = 14.0, 6.9 Hz, 1H), 1.45 (s, 9H), 0.94 (t, *J* = 7.9 Hz, 9H), 0.66 (q, *J* = 7.9 Hz, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 158.0, 152.7, 133.5, 129.5, 113.9, 94.0, 80.7, 55.4, 46.1, 40.6, 33.5, 32.4, 28.2, 6.8, 5.0 ppm; HRMS (EI, m/z): calculated for [$C_{24}H_{39}NO_4Si$] 433.2643, found 433.2643; FTIR: ν = 1151, 1326, 1510, 1713, 2960 cm^{-1}.

Preparation of 2-(4-methoxyphenethyl)-1-tosyl-3-(1-((triethylsilyl)oxy)vinyl) aziridine (13):



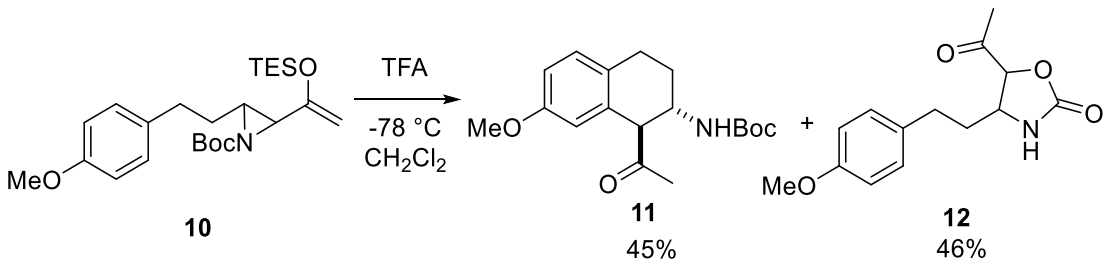
To a solution of **10S1** (1.2446 g, 3.90 mmol) in THF (19 mL) was added TBAF (1 M in THF, 4.3 mL; 4 mmol). The mixture was stirred under reflux for 6 h. $NaHCO_3$ solution was added. The mixture was extracted with CH_2Cl_2, and the organics were dried over anhydrous $MgSO_4$. The volatiles were removed in vacuo, and the residue was purified by flash column chromatography using 70% EtOAc in hexane to afford the crude product (610.2 mg, 71% yield) as a brown oil. The crude product was used in the next step directly.

The crude product (306.7 mg, 1.40 mmol) was dissolved in 3.5 mL of CH_2Cl_2. TsCl (463.0 mg, 2.43 mmol) and Et_3N (0.23 mL, 1.7 mmol) were added. The mixture was stirred at room temperature for 3 h. $NaHCO_3$ solution was added. The reaction mixture was extracted with CH_2Cl_2, and the organics were dried over anhydrous $MgSO_4$. The crude product was then concentrated in vacuo, and purified by flash column chromatography using 35% EtOAc in hexane to afford aziridinyl ketone **13S2** (377.0 mg, 72% yield) as a yellowish oil. R_f = 0.5 (35% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 3.76 (s, 3H), 3.23 (d, *J* = 4.0 Hz, 1H), 2.97 –

2.81 (m, 2H), 2.79 – 2.67 (m, 1H), 2.48 (dq, *J* = 7.6, 5.8 Hz, 1H), 2.41 (s, 3H), 2.25 (dq, *J* = 15.9, 7.9 Hz, 1H), 1.83 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.9, 158.1, 144.7, 136.7, 131.9, 129.7, 129.4, 127.4, 114.0, 55.2, 49.7, 49.1, 32.9, 29.7, 26.2, 21.6 ppm; HRMS (EI, m/z): calculated for [$C_{20}H_{23}NO_4S$] 373.1342, found 373.1342; FTIR: ν = 1161, 1248, 1331, 1418, 1513, 1612, 1713, 2957 cm^{-1}.

To a solution of **13S2** (375.0 mg, 1.00 mmol) in CH_2Cl_2 (10 mL) was added Et_3N (0.56 mL, 4.0 mmol) and TESOTf (0.45 mL, 2.0 mmol) at –78 ℃. The reaction was warmed to room temperature and stirred for 2 h. $NaHCO_3$ solution was added. The mixture was extracted with CH_2Cl_2, and the organics were dried over anhydrous $MgSO_4$. The volatiles were removed in vacuo. The residue was purified by flash column chromatography using 8% EtOAc in hexane with 1% Et_3N to afford aziridinyl enolsilane **13** (185.4 mg, 38% yield) as a colourless syrup. R_f = 0.3 (10% EtOAc in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.6 Hz, 2H), 6.84 – 6.79 (m, 2H), 4.22 (d, *J* = 1.5 Hz, 1H), 4.14 (d, *J* = 1.5 Hz, 1H), 3.78 (s, 3H), 3.16 (d, *J* = 4.4 Hz, 1H), 2.92 – 2.84 (m, 2H), 2.80 – 2.72 (m, 1H), 2.52 – 2.43 (m, 1H), 2.41 (s, 3H), 2.22 (dt, *J* = 15.9, 8.2 Hz, 1H), 0.82 (t, *J* = 7.9 Hz, 9H), 0.56 – 0.42 (m, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.0, 152.2, 143.7, 138.1, 132.8, 129.5, 129.4, 127.3, 113.9, 93.6, 55.3, 48.8, 48.3, 33.3, 30.0, 21.6, 6.5, 4.6 ppm; HRMS (EI, m/z): calculated for [$C_{26}H_{37}NO_4SiS$] 487.2207, found 487.2203; FTIR: ν = 1020, 1159, 1417, 1504, 1611, 1626, 2958 cm^{-1}.

Friedel Crafts Cyclization of 10

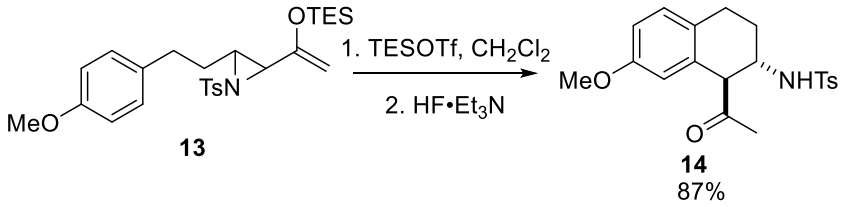


To a solution of aziridinyl enolsilane **10** (60.4 mg, 0.138 mmol) in CH_2Cl_2 (0.7 mL) at –78 ℃ was added TFA (11 µL, 0.14 mmol). It was stirred for 15 minutes at –78 ˚C. $NaHCO_3$ solution was added at –78 ˚C, and the reaction mixture was warmed to room temperature. The product mixture was extracted with CH_2Cl_2, and the organics were dried over anhydrous $MgSO_4$. The crude product was concentrated in vacuo and then purified by flash chromatography using 30% EtOAc in hexane to afford **11** (13.6 mg, 45% yield) and **12** (16.8 mg, 46% yield).

***tert*-Butyl ((*1S*,2S**)-1-acetyl-7-methoxy-1,2,3,4-tetrahydronaphthalen-2-yl)carbamate (11)**: white solid; mp: 138-139 °C; R_f = 0.5 (35% EA in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.4 Hz, 1H), 6.78 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.47 (d, *J* = 1.7 Hz, 1H), 4.63 (s, 1H), 4.25 (d, *J* = 7.0 Hz, 1H), 3.75 (s, 3H), 3.63 (d, *J* = 8.1 Hz, 1H), 2.90 (dd, *J* = 15.9, 6.5 Hz, 1H), 2.78 (dt, *J* = 16.8, 5.3 Hz, 1H), 2.16 (s, 3H), 1.70 – 1.60 (m, 2H), 1.43 (s, 9H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.6, 158.1, 155.2, 132.7, 130.4, 127.9, 113.8, 113.4, 79.8, 63.6, 61.5, 55.3, 48.5, 28.3, 28.2, 26.9, 26.7 ppm; HRMS (EI, m/z): calculated for [$C_{18}H_{25}NO_4$] 319.1778, found 319.1785; FTIR: ν = 1165, 1419, 1501, 1611, 1707, 3435 cm^{-1}.

5-acetyl-4-(4-methoxyphenethyl)oxazolidin-2-one (12): pale yellow oil; R_f = 0.1 (35% EA in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 5.67 – 5.40 (m, 1H), 4.42 (d, *J* = 5.3 Hz, 1H), 3.83 (dd, *J* = 12.8, 5.6 Hz, 1H), 3.79 (s, 3H), 2.74 – 2.59 (m, 2H), 2.33 (s, 3H), 2.09 – 1.86 (m, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.0, 158.3, 158.2, 132.0, 129.4, 114.3, 84.2, 55.4, 54.9, 37.8, 30.7, 26.6 ppm; HRMS (EI, m/z): calculated for [$C_{14}H_{17}NO_4$] 263.1152, found 263.1158; FTIR: ν = 1510, 1727, 1775, 3451 cm^{-1}.

Friedel Crafts Cyclization of 13



To a solution of aziridinyl enolsilane **13** (65.2 mg, 0.134 mmol) in CH_2Cl_2 (0.68 mL) at –78 °C was added 0.071 mL of a 1:1 mixture 0.2 M TESOTf in CH_2Cl_2 and 0.02 M 2,6-lutidine in CH_2Cl_2. The reaction was stirred for 5 min at –78 °C, then triethylamine trihydrofluoride (0.04 mL) was added. The mixture was warmed to room temperature and stirred for 1 h. $NaHCO_3$ solution was added until effervescence ceased. The reaction mixture was extracted by CH_2Cl_2, and the organics were dried over anhydrous $MgSO_4$. The crude product was concentrated in vacuo and then purified by flash chromatography using 35% EtOAc in hexane to afford **14** (43.3 mg, 87% yield).

***N*-((*1S*,2S**)-1-acetyl-7-methoxy-1,2,3,4-tetrahydronaphthalen-2-yl)-4-methylbenzenesulfonamide (14)**: white solid; mp: 147-149 °C; R_f = 0.4 (35% EA in hexane). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 6.45 (d, *J* = 2.1

Hz, 1H), 4.95 – 4.82 (m, 1H), 3.93 (q, *J* = 9.9 Hz, 1H), 3.74 (s, 3H), 3.64 (d, *J* = 6.4 Hz, 1H), 2.79 – 2.62 (m, 2H), 2.44 (s, 3H), 2.04 – 1.97 (m, 1H), 1.94 (s, 3H), 1.72 – 1.65 (m, 1H), 1.59 (td, *J* = 14.0, 7.9 Hz, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 207.7, 158.0, 143.7, 137.7, 131.9, 130.3, 129.8, 127.7, 127.1, 114.2, 114.1, 113.9, 60.4, 55.3, 50.8, 27.8, 27.6, 25.5, 21.6 ppm; calculated for [$C_{20}H_{23}NO_4S$] 373.1342, found 373.1337; FTIR: ν = 1093, 1161, 1336, 1419, 1505, 1611, 1706, 2936 cm^{-1}.

Experimental for Computations

Conformer Distribution: Conformational searches of compound **4a** and **4m** were performed using the Conformer Distribution function of Spartan 14, using MMFFaq force field with implicit solvent model. Conformers were organized according to population and the distance (d1) between atoms C1 and C2. The orientation of the atoms is not considered. The conformational distribution of **4a** and **4m** at 298K is shown in Table S1 and Table S2 respectively. The conformations of the ground state conformers are depicted in Figure 2 in the main text.

Table S1

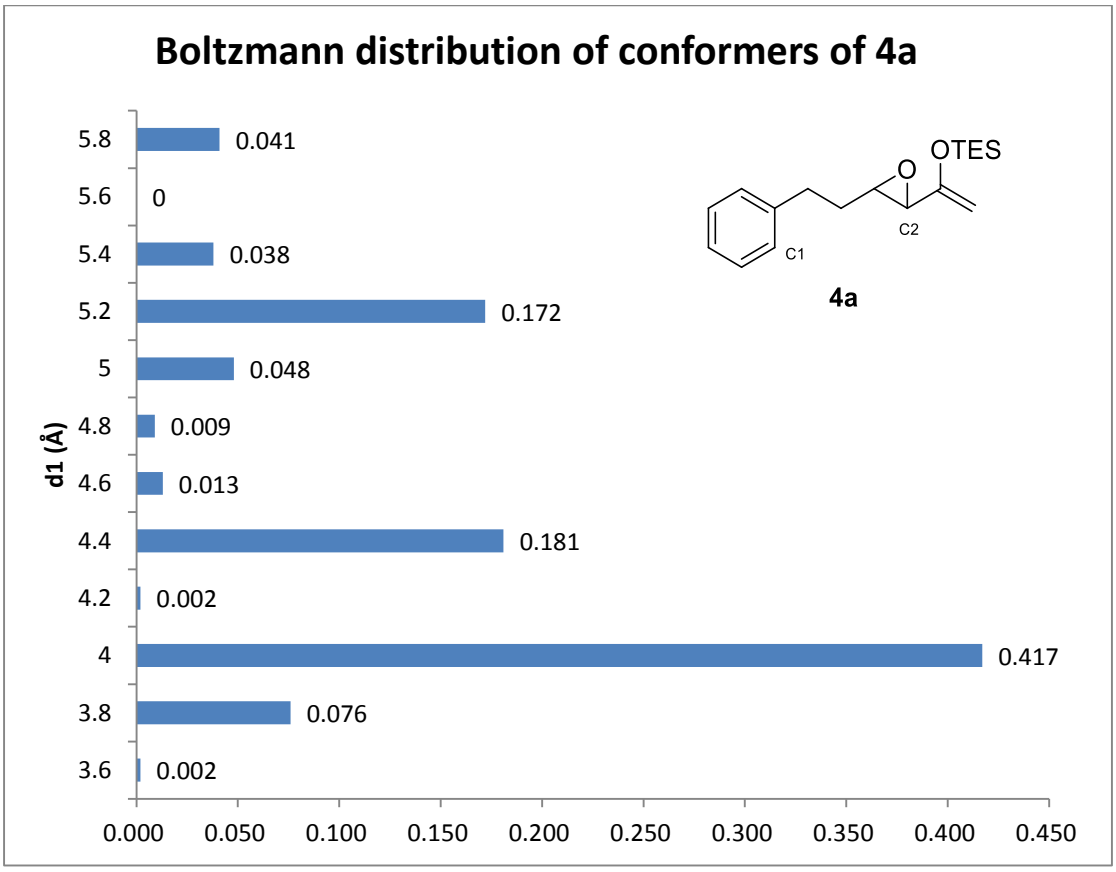
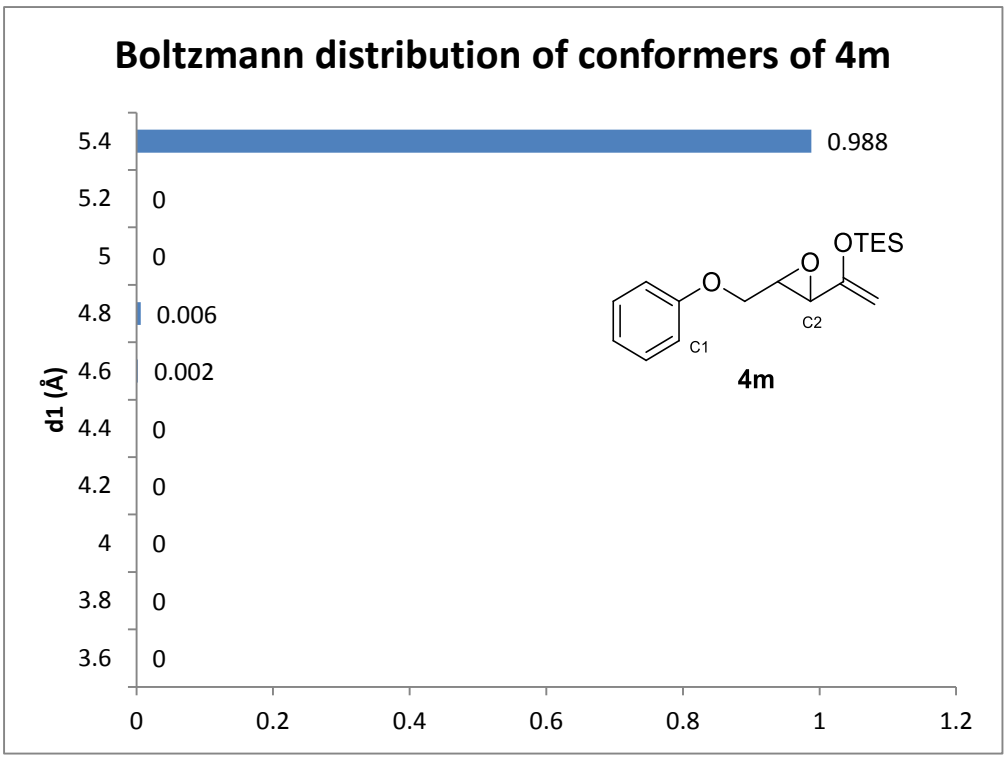


Table S2


Boltzmann distribution of conformers of 4m
d1 (Å)
5.4
5.2
5
4.8
4.6
4.4
4.2
4
3.8
3.6
0.988
0
0
0.006
0.002
0
0
0
0
0
0
0.2
0.4
0.6
0.8
1
1.2
OTES
O
O
C1
C2
4m

References:

1 B. Lo, S. Lam, W.-T. Wong and P. Chiu, *Angew. Chem. Int. Ed.*, 2012, **51**, 12120.

2 Y. Lu, C. Zheng, Y. Yang, G. Zhao and G. Zou, *Adv. Synth. Catal.*, 2011, **353**, 3129.

3 J. A. Cella, *J. Org. Chem.*, 1982, **47**, 2125.

4 A. Sato, H. Noguchi, S. Mitsui, I. Kaneko and Y. Shimada, *Chem. Pharm. Bull.*, 1980, **28**, 1509.

5 C. M. Reisinger, X. Wang and B. List, *Angew. Chem. Int. Ed.*, 2008, **47**, 8112.

6 Y. Li, Y.-Y. Hu and S.-L. Zhang, *Chem. Commun.*, 2013, **49**, 10635.

7 J. Kashanna, P. Jangili, R. A. Kumar and B. Das, *Helv. Chim. Acta*, 2012, **95**, 1666.

8 W. Cao, X. Liu, R. Peng, P. He, L. Lin and X. Feng, *Chem. Commun.*, 2013, **49**, 3470.

9 M. Yamane, K. Uera and K. Narasaka, *Bull. Chem. Soc. Jpn.*, 2005, **78**, 477.

10 O. Lifchits, M. Mahlau, C. M. Reisinger, A. Lee, C. Farès, I. Polyak, G. Gopakumar, W. Thiel and B. List, *J. Am. Chem. Soc.*, 2013, **135**, 6677.

11 K. S. Reddy, O.-H. Ko, D. Ho, P. E. Persons and J. M. Cassady, *Tetrahedron Lett.*, 1987, **28**, 3075.

12 I. Shibata, H. Yamasaki, A. Baba and H. Matsuda, *J. Org. Chem.*, 1992, **57**, 6909.

13 K. C. Majumdar, B. Chattopadhyay and S. Samanta, *Tetrahedron Lett.*, 2009, **50**, 3178.

14 J. P. Lajiness, W. M. Robertson, I. Dunwiddie, M. A. Broward, G. A. Vielhauer, S. J. Weir and D. L. Boger, *J. Med. Chem.*, 2010, **53**, 7731.

15 A. B. Smith and D.-S. Kim, *Org. Lett.*, 2005, **7**, 3247.