Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Hypervalent iodine initiated intramolecular alkene dimerisation: a stereodivergent entry to cyclobutanes

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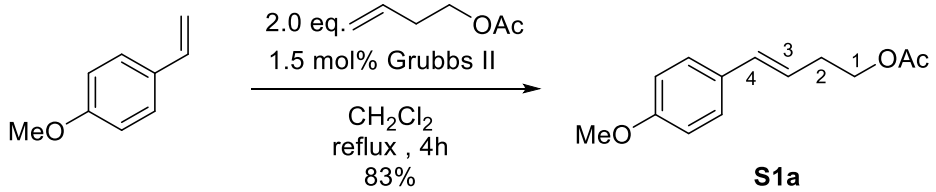
1. General experimental details

^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz or 500MHz spectrometer in $CDCl_3$ and referenced to residual solvent peaks. Chemical shifts are quoted in ppm (parts per million) to the nearest 0.01 ppm with signal splitting recorded as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint) septet (sept), multiplet (m) and broad singlet (br s). Coupling constants, *J*, are measured in Hz to the nearest 0.1 Hz. ^{1}H and ^{13}C NMR spectra were recorded at room temperature. Infrared spectra were recorded as thin films of neat samples on a Bruker Tensor 27 FT-IR spectrometer equipped with Attenuated Total Reflectance sampling accessories. High resolution mass spectra are given to four decimal places and were recorded on a Bruker MicroTof (resolution = 10000 FWHM) under conditions of electrospray ionization (ESI), electronic ionization (EI) or chemical ionization (CI). Melting points (m.p.) were obtained from recrystallized samples using a Lecia VMTG heated-stage microscope and are uncorrected. The solvent systems used for recrystallization are quoted in parentheses. Flash column chromatography was performed using silica gel (60 Å, 0.033-0.070 mm, BDH) or using basic alumina (pH 9.5, 58 Å, 150 mesh, Sigma-Aldrich). TLC analyses were performed on Merck Kiesegel 60 F_{254} 0.25 mm precoated silica plates or Macherey-Nagel Alugram Alox N/UV_{254} 0.20 mm precoated alumina plates. Reagents obtained from Sigma-Aldrich, Alfa, Fluorochem and TCI suppliers were used directly as supplied All anhydrous reactions were carried out in flame dried glassware and under an inert atmosphere of argon provided by a balloon. All reactions were stirred with magnetic followers. THF, toluene and CH_2Cl_2 were dried by purification through two activated alumina purification columns. Brine refers to a saturated aqueous solution of NaCl.

2. General procedure for the synthesis of styrenes using a Ru-catalyzed methatesis reaction

To a flame-dried flask, charged with 1.5 mol% of Ru-catalyst, under Ar, at room temperature, was added 4.0 mL/mmol of dry CH_2Cl_2 (previously degassed, bubling Ar for 30 min.). A solution of the mixture of alkenes in dry and degassed CH_2Cl_2 (1.0 mL/mmol) was added and the mixture was stirred at the appropriate temperature. The reaction was monitored by TLC until completion, and the solvent was evaporated under reduced pressure to give the corresponding styrene, that was purified by chromatography on silica gel using the appropriate mixture of eluents.

2.1. (1*E*)-4-(4-Methoxyphenyl)but-3-en-1-yl acetate, S1a.

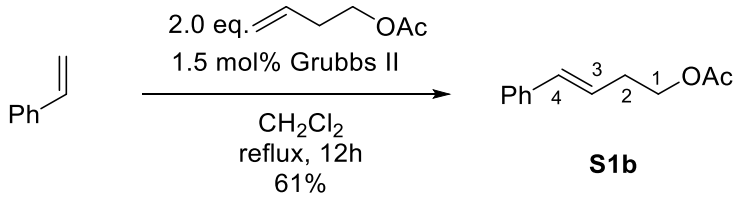


S1a

From 4-methoxystyrene (5.000 g, 37.31 mmol), 3-butenyl acetate (8.500 g, 74.60 mmol) and Grubbs II (1.500 g, 1.769 mmol), in 150 mL of CH_2Cl_2, following the general procedure, styrene **S1a** was obtained. Chromatographic purification (gradient elution: 1:99 → 10:90 Et_2O – pentane) gave **S1a** (6.800 g, 83%), as a colorless oil. Spectral properties matched those previously reported.[1]

Data for **S1a**: R_f 0.30 (10% Et_2O – pentane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.28 (2H, d, *J* = 8.4 Hz, Ar), 6.84 (2H, d, *J* = 8.8 Hz, Ar), 6.41 (1H, d, *J* = 15.9 Hz, 4-H), 6.02 (1 H, dt, *J* = 15.8, 7.0 Hz, 3-H), 4.17 (2H, t, *J* = 6.8 Hz, 1-H_2), 3.79 (3H, s, OMe), 2.52 (2H, qd, *J* = 6.9, 1.5 Hz, 2-H_2), 2.05 (3H, s, Me OAc). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 171.1 (C=O), 159.0 (C Ar), 131.8 (C-4), 130.1 (C Ar), 127.2 (2 x CH Ar), 123.3 (C-3), 114.0 (2 x CH Ar), 63.9 (C-1), 55.3 (OMe), 32.4 (C-2), 21.0 (Me OAc). **HRMS** (ESI): calculated for $C_{13}H_{16}O_3Na$ $[M+Na]^+$ requires *m/z* 243.0991, found *m/z* 243.0994.

2.2. (*E*)-4-Phenylbut-3-en-1-yl acetate, S1b.

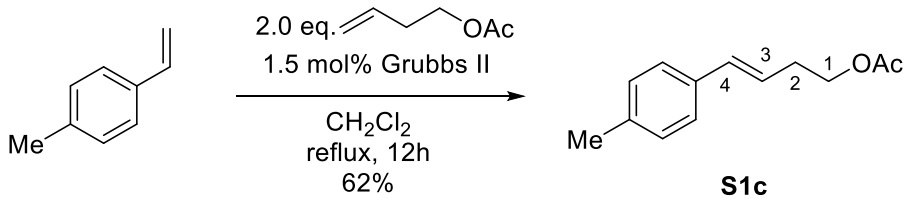


S1b

From styrene (0.456 g, 4.38 mmol), but-3-en-1-yl acetate (1.000 g, 8.772 mmol) and Grubbs II (56.0 mg, 0.0660 mmol) following the general procedure, styrene **S1b** was obtained. Chromatographic purification (gradient elution: 5% → 8% Et_2O - pentane) gave **S1b** as a white solid (510.0 mg, 61%). Spectral properties matched those previously reported.[2]

Data for **S1b**: R_f 0.50 (20% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.28-7.38 (4 H, m, Ar), 7.19-7.25 (1 H, m, Ar), 6.48 (1H, d, *J* = 15.9 Hz, 4-H), 6.18 (1H, dt, *J* = 15.9, 7.0 Hz, 3-H), 4.20 (2H, t, *J* = 6.7 Hz, 1-H_2), 2.55 (2H, qd, *J* = 6.8, 1.5 Hz, 2-H_2), 2.06 (3H, s, Me Ac). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 171.1 (C=O), 137.3 (C Ar), 132.4 (C-4), 128.6 (2 x CH Ar), 127.3 (CH Ar), 126.1 (2 x CH Ar), 125.6 (C-3), 63.8 (C-1), 32.4 (C-2), 21.0 (Me Ac). **HRMS** (ESI): calculated for $C_{12}H_{14}O_2Na$ $[M+Na]^+$ requires *m/z* 213.0886, found *m/z* 213.0888.

2.3. (*E*)-4-(*p*-Tolyl)but-3-en-1-yl acetate, S1c.



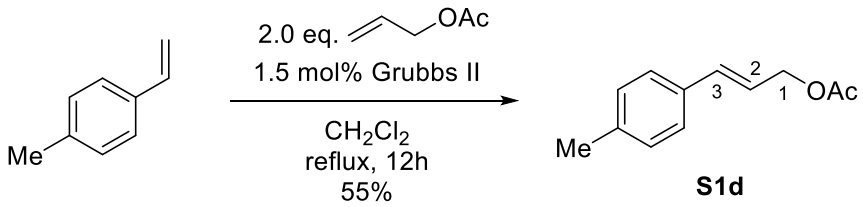
S1c

From 1-methyl-4-vinylbenzene (0.520 g, 4.41 mmol), but-3-en-1-yl acetate (1.000 g, 8.850 mmol) and Grubbs II (56.0 mg, 0.0660 mmol) following the general procedure, styrene **S1c** was

obtained. Chromatographic purification (gradient elution: 5% → 8% Et_2O - pentane) gave **S1c** as a white solid (552.0 mg, 62%).

Data for **S1c**: R_f 0.40 (20% Et_2O - pentane). **M.p.**: 49 °C (solvent: 5% diethyl ether in pentane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.25 (2H, d, *J* = 8.2 Hz, Ar), 7.12 (2H, d, *J* = 8.2 Hz, Ar), 6.44 (1H, d, *J* = 15.9 Hz, 4-H), 6.12 (1H, dt, *J* = 15.9, 7.0 Hz, 3-H), 4.18 (2H, t, *J* = 6.8 Hz, 1-H_2), 2.53 (2H, qd, *J* = 6.8, 1.5 Hz, 2-H_2), 2.33 (3H, s, Me), 2.06 (3H, s, Me Ac). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 171.3 (C=O), 137.2 (C Ar), 134.6 (C Ar), 132.4 (C-4), 129.3 (2 x CH Ar), 126.1 (2 x CH Ar), 124.6 (C-3), 63.9 (C-1), 32.5 (C-2), 21.3 (Me), 21.1 (Me Ac). **IR** (film) ν_{max} 2955, 2360, 2341, 1736, 1232, 1033, 967, 799 cm^{-1}. **HRMS** (ESI): calculated for $C_{13}H_{16}O_2Na$ $[M+Na]^+$ requires *m/z* 227.1043, found *m/z* 227.1044.

2.4. (*E*)-3-(*p*-Tolyl)allyl acetate, S1d.



S1d

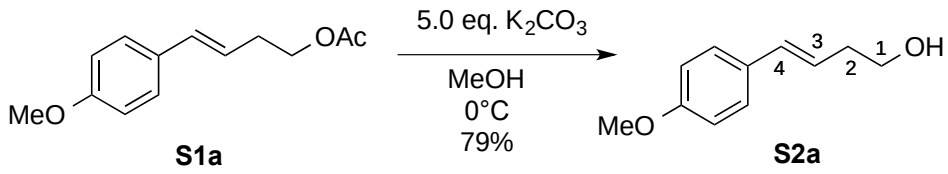
From 1-methyl-4-vinylbenzene (1.000 g, 8.475 mmol), allyl acetate (1.450 g, 14.50 mmol) and Grubbs II (108.0 mg, 0.1273 mmol) following the general procedure, styrene **S1d** was obtained. Chromatographic purification (gradient elution: 5% → 8% Et_2O - pentane) gave **S1d** as a white solid (871.0 mg, 55%). Spectral properties matched those previously reported.[3]

Data for **S1d**: R_f 0.5 (15% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.29 (2H, d, *J* = 8.1 Hz, Ar), 7.13 (2H, d, *J* = 7.6 Hz, Ar), 6.63 (1H, d, *J* = 15.9 Hz, 3-H), 6.24 (1H, dt, *J* = 15.9, 6.6 Hz, 2-H), 4.72 (2H, dd, *J* = 6.6, 1.3 Hz, 1-H_2), 2.34 (3H, s, Me), 2.10 (3H, s, Me Ac). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.9 (C=O), 138.0 (C Ar), 134.3 (C-3), 133.4 (C Ar), 129.3 (2 x CH Ar), 126.5 (2 x CH Ar), 122.1 (C-2), 65.3 (C-1), 21.3 (Me), 21.1 (Me Ac). **HRMS** (Cl): calculated for $C_{12}H_{15}O_2$ $[M+H]^+$ requires *m/z* 191.1072, found *m/z* 191.1069.

3. General procedure for acetate deprotection

To a solution of acetate in MeOH (10.0 mL/mmol), 5.0 equiv of K_2CO_3 were added in one portion at room temperature. The reaction was monitored by TLC until completion. The mixture was filtered and the solvent was evaporated under reduced pressure to give the corresponding alcohol, that was purified by chromatography on silica gel using the appropriate mixture of eluents.

3.1. (*E*)-4-(4-Methoxyphenyl)but-3-en-1-ol, S2a.

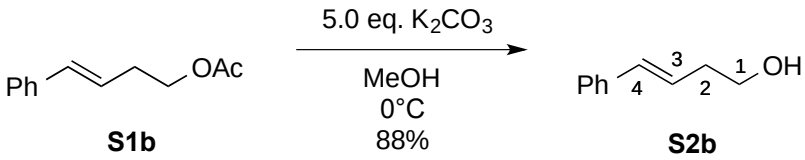


S1a **S2a**

From acetate **S1a** (3.510 g, 15.95 mmol) and K_2CO_3 (6.580 g, 47.68 mmol) following the general procedure, alcohol **S2a** was obtained. Chromatographic purification (gradient elution: 50% → 100% Et_2O - pentane) gave **S2a** as a white solid (2.230 g, 79%). Spectral properties matched those previously reported.[4]

Data for **S2a**: R_f 0.33 (75 % Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.30 (2H, d, *J* = 8.9 Hz, Ar), 6.84 (2H, d, *J* = 8.8 Hz, Ar), 6.45 (1H, d, *J* = 15.9 Hz, 4-H), 6.05 (1H, dt, *J* = 15.8, 7.2 Hz, 3-H), 3.80 (3H, s, OMe), 3.75 (2H, t, *J* = 7.5 Hz, 1-H_2), 2.43-2.50 (2 H, m, 2-H_2), 1.47 (1H, br s, OH). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.0 (C Ar), 132.3 (C-4), 130.1 (C Ar), 127.2 (2 x CH Ar), 124.0 (C-3), 114.0 (2 x CH Ar), 62.1 (C-1), 55.3 (OMe), 36.4 (C-2). **HRMS** (Cl): calculated for $C_{11}H_{15}O_2$ $[M+H]^+$ requires *m/z* 179.1072, found *m/z* 179.1067.

3.2. (*E*)-4-Phenylbut-3-en-1-ol, S2b.

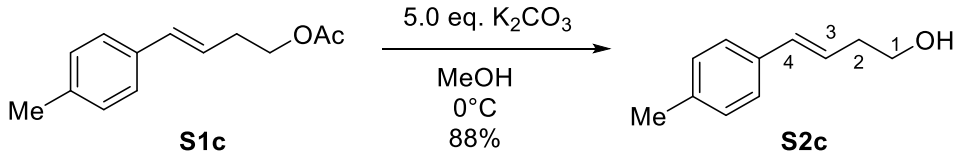


S1b **S2b**

From acetate **S1b** (0.541 g, 2.85 mmol) and K_2CO_3 (1.970 g, 14.28 mmol) following the general procedure, alcohol **S2b** was obtained. Chromatographic purification (gradient elution: 40% → 60% Et_2O - pentane) gave **S2b** as a colorless oil (0.369 g, 88%). Spectral properties matched those previously reported.[5]

Data for **S2b**: R_f 0.4 (75% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.28-7.39 (4H, m, Ar), 7.19-7.25 (1H, m, Ar), 6.51 (1H, d, *J* = 15.8 Hz, 4-H), 6.21 (1H, dt, *J* = 15.9, 7.1 Hz, 3-H), 3.73-3.81 (2H, m, 1-H_2), 2.47-2.53 (2H, m, 2-H_2), 1.47 (1H, br s, OH). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 137.2 (C Ar), 132.9 (C-4), 128.6 (2 x CH Ar), 127.3 (CH Ar), 126.3 (C-3), 126.1 (2 x CH Ar), 62.0 (C-1), 36.4 (C-2). **HRMS** (CI): calculated for $C_{10}H_{17}ON$ $[M+NH_4]^+$ requires *m/z* 166.1232, found *m/z* 166.1227.

3.3. (*E*)-4-(*p*-Tolyl)but-3-en-1-ol, S2c.

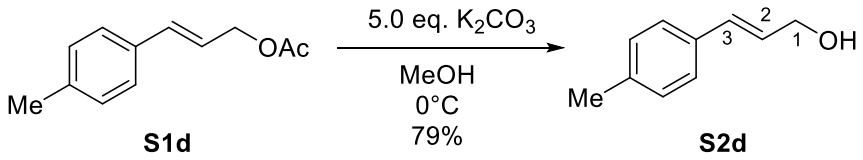


S1c **S2c**

From acetate **S1c** (0.452 g, 2.22 mmol) and K_2CO_3 (1.530 g, 11.09 mmol) following the general procedure, styrene **S2c** was obtained. Chromatographic purification (gradient elution: 50% → 100% Et_2O - pentane) gave **S2c** as a white solid (0.317 g, 88%). Spectral properties matched those previously reported.[6]

Data for **S2c**: R_f 0.5 (80% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.29 (2H, d, *J* = 8.2 Hz, Ar), 7.14 (2H, d, *J* = 7.9 Hz, Ar), 6.48 (1H, d, *J* = 15.9 Hz, 4-H), 6.17 (1H, dt, *J* = 15.9, 7.1 Hz, 3-H), 3.75 (2H, t, *J* = 6.4 Hz, 1-H_2), 2.48 (2H, qd, *J* = 6.5, 1.4 Hz, 2-H_2), 2.44 (1 H, br s, OH), 2.37 (3 H, s, Me). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 137.0 (C Ar), 134.6 (C Ar), 132.5 (C-4), 129.3 (2 x CH Ar), 126.0 (2 x CH Ar), 125.4 (C-3), 62.1 (C-1), 36.5 (C-2), 21.2 (Me). **HRMS** (ESI): calculated for $C_{11}H_{14}ONa$ $[M+Na]^+$ requires *m/z* 185.0937, found *m/z* 185.0935.

3.4. (*E*)-3-(*p*-Tolyl)prop-2-en-1-ol, S2d.



S1d **S2d**

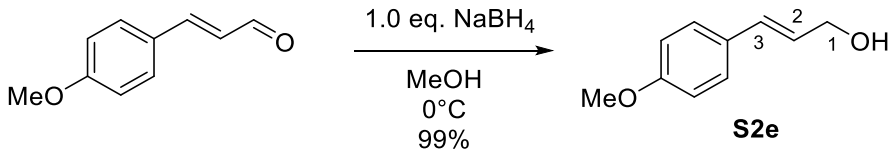
From acetate **S1d** (0.440 g, 2.14 mmol) and K_2CO_3 (1.480 g, 10.72 mmol) following the general procedure, styrene **S2d** was obtained. Chromatographic purification (gradient elution: 50% → 100% Et_2O - pentane) gave **S2d** as a light yellow solid (250.0 mg, 79%). Spectral properties matched those previously reported.[7]

Data for **S2d**: R_f 0.5 (80% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.30 (2H, d, *J* = 8.1 Hz, Ar), 7.15 (2H, d, *J* = 7.9 Hz, Ar), 6.58 (1H, d, *J* = 15.9 Hz, 3-H), 6.32 (1H, dt, *J* = 15.8, 5.8 Hz, 2-H), 4.30 (2H, dd, *J* = 5.8, 1.5 Hz, 1-H_2), 2.92 (1H, br s, OH), 2.38 (3H, s, Me). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 137.5 (C Ar), 134.0 (C Ar), 131.0 (C-3), 129.4 (2 x CH Ar), 127.6 (C-2), 126.5 (2 x CH Ar), 63.6 (C-1), 21.3 (Me). **HRMS** (Cl): calculated for $C_{10}H_{16}ON$ $[M+NH_4]^+$ requires *m/z* 166.1232, found *m/z* 166.1232.

4. General procedure for the reduction of α, β-unsaturated aldehydes to allylic alcohols

To a solution of 1.0 eq. of aldehyde in MeOH (1.5 mL/mmol) under Ar, 1.0 eq. of $NaBH_4$ was slowly added at 0 °C. The reaction was stirred for 30 min. and let it warmed up slowly to rt. until completion (usually 12 hours)**.** The reaction was quenched with saturated NH_4Cl solution (5.0 mL/mmol) and the aqueous layer was extracted with Et_2O (3 x 5.0 mL/mmol). The combined organic layers were washed with brine (5.0 mL/mmol), dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. Recrystalization afforded the corresponding alcohol.

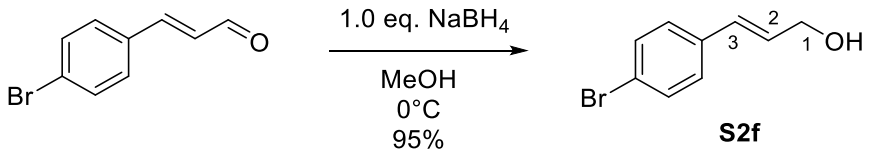
4.1. (*E*)-3-(4-Methoxyphenyl)prop-2-en-1-ol, S2e.



From *p*-methoxycinnamaldehyde (4.800 g, 29.63 mmol) and $NaBH_4$ (1.125 g, 29.63 mmol) following the general procedure, gave alcohol **S2e** (4.850 g, 99%) as a white solid. Spectral properties matched those previously reported.[8]

Data for **S2e**: $\boldsymbol{R_f}$ 0.5 (80% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.32 (2H, d, *J* = 8.7 Hz, Ar), 6.86 (2H, d, *J* = 8.7 Hz, Ar), 6.56 (1H, d, *J* = 15.9 Hz, 3-H), 6.24 (1H, dt, *J* = 15.8, 6.0 Hz, 2-H), 4.29 (2H, dd, *J* = 5.9, 1.2 Hz, 1-H_2), 3.81 (3H, s, OMe), 1.53 (1H, br s, OH). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.5 (C Ar), 131.1 (C-3), 129.6 (C Ar), 127.8 (2 x CH Ar), 126.4 (C-2), 114.2 (2 x CH Ar), 64.07 (C-1), 55.43 (OMe). **HRMS** (Cl): calculated for $C_{10}H_{13}O_2$ $[M+H]^+$ requires *m/z* 165.0916, found *m/z* 165.0919.

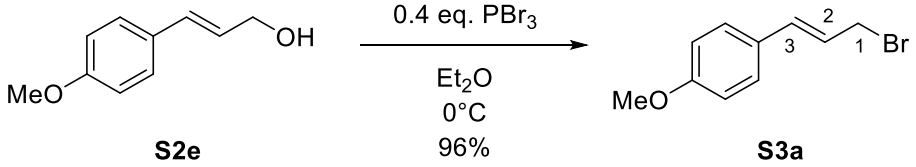
4.2. (*E*)-3-(4-Bromophenyl)prop-2-en-1-ol, S2f.



From (*E*)-3-(4-Bromophenyl)acrylaldehyde (0.500 g, 2.38 mmol) and $NaBH_4$ (91.0 mg, 2.39 mmol) following the general procedure gaver alcohol **S2f** as a yellow solid (479.0 mg, 95%). Spectral properties matched those previously reported.[9]

Data for **S2f**: $\boldsymbol{R_f}$ 0.45 (80% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.38 (2H, d, *J* = 8.4 Hz, Ar), 7.15 (2H, d, *J* = 8.5 Hz, Ar), 6.48 (1H, d, *J* = 15.9 Hz, 3-H), 6.27 (1H, dt, *J* = 15.9, 5.5 Hz, 2-H), 4.26 (2H, dd, *J* = 5.6, 1.6 Hz, 1-H_2), 3.28 (1H, br s, OH). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 135.5 (C Ar), 131.6 (2 x CH Ar), 129.4 (C-3), 129.3 (C-2), 127.9 (2 x CH Ar), 121.3 (C Ar), 63.1 (C-1).

5. (*E*)-1-(3-Bromoprop-1-en-1-yl)-4-methoxybenzene, S3a.



To a stirred solution of alcohol **S2e** (1.060 g, 6.463 mmol) in dry Et_2O (2.0 mL) at 0 °C under Ar was added PBr_3 (0.24 mL, 2.6 mmol). The reaction was stirred until completion, monitored by TLC analysis and quenched with $NaHCO_3$. The layers were separated and the aqueous layer extracted

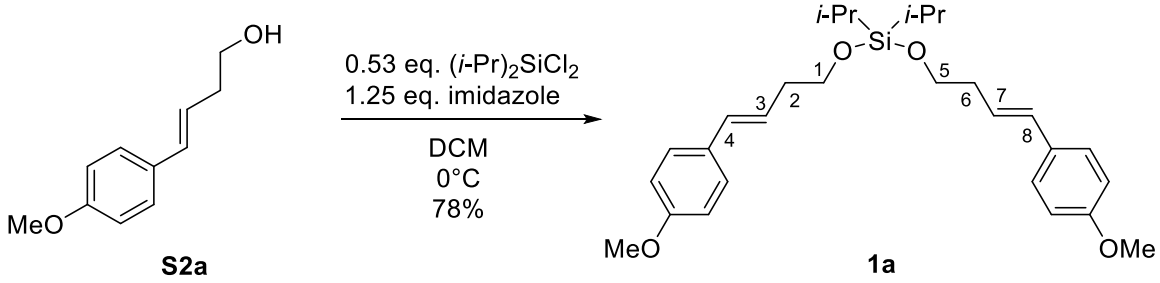
with Et_2O twice. The combined organics were washed with brine, dried over $MgSO_4$, filtered and the solvent was evaporated to give the pure bromide **S3a** as a white solid (1.400 g, 96%). Spectral properties matched those previously reported.[10]

Data for **S3a**: R_f 0.80 (80% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.33 (2H, d, *J* = 8.4 Hz, Ar), 6.87 (2H, d, *J* = 8.8 Hz, Ar), 6.60 (1H, d, *J* = 15.5 Hz, 3-H), 6.27 (1H, dt, *J* = 15.7, 7.9 Hz, 2-H), 4.17 (2H, dd, *J* = 7.8, 1.0 Hz, 1-H_2), 3.82 (3H, s, OMe). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.8 (C Ar), 134.2 (C-3), 128.5 (C Ar), 128.1 (2 x CH Ar), 123.0 (C-2), 114.1 (2 x CH Ar), 55.4 (OMe), 34.3 (C-1). **HRMS** (Cl): calculated for $C_{10}H_{12}BrO$ $[M+H]^+$ requires *m/z* 227.0072, found *m/z* 227.0069.

6. General procedure for the preparation of symmetric silyl ethers

To a flame-dried round bottom flask with a stirring bar, a solution of 1.25 eq. of imidazole in dry DCM (5.0 mL/mmol) was added under argon. The solution was stirred and cooled down to 0 °C, and 0.53 eq. of silane was added dropwise. After 10 min. of stirring, a solution of 1.0 eq. of alcohol in dry DCM (2 mL/mmol) was added dropwise over 1 hour using syringe pump. The reaction was stirred for 10 min. at 0 °C after the addition of alcohol was completed, and monitored by TLC. The solvent was evaporated under reduced pressure and the crude reaction was purified by chromatography on silica gel using the appropriate mixture of eluents.

6.1. (*E*)-4-Diisopropylbis[(4-methoxyphenyl)but-3-en-1-yloxy)]silane, 1a.



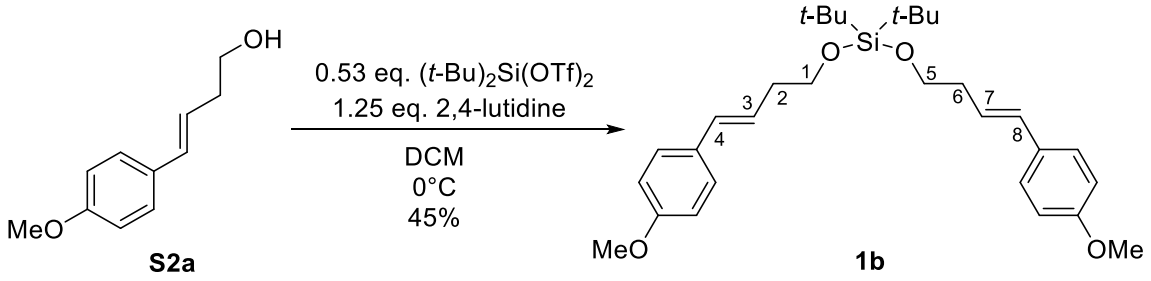
S2a **1a**

From alcohol **S2a** (102.0 mg, 0.573 mmol), imidazole (48.7 mg, 0.716 mmol) and dichlorodiisopropylsilane (0.054 mL, 0.30 mmol) following the general procedure, diene **1a** was obtained. Chromatographic purification (3% Et_2O - pentane) gave **1a** as a colorless oil (76.9 mg, 78%).

Data for **1a**: R_f 0.45 (10% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.25 (4H, d, *J* = 8.8 Hz, Ar), 6.82 (4H, d, *J* = 8.7 Hz, Ar), 6.38 (2H, d, *J* = 15.9 Hz, 4-H and 8-H), 6.08 (2H, dt, *J* = 15.8, 7.1 Hz, 3-H and 7-H), 3.84 (4H, t, *J* = 6.8 Hz, 1-H_2 and 5-H_2), 3.79 (6H, s, 2 x OMe), 2.45 (4H, qd, *J* = 6.9, 1.4 Hz, 2-H_2 and 6-H_2), 1.01-1.08 (14H, m, 4 x *i*-Pr). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.9 (2 x C Ar), 131.2 (C-4 and C-8), 130.6 (2 x C Ar), 127.2 (4 x CH Ar), 124.9 (C-3 and C-7),

114.0 (4 x C-H Ar), 63.0 (C-1 and C-5), 55.4 (2 x OMe), 36.7 (C-2 and C-6), 17.5 (4 x CH_3 *i*-Pr), 12.3 (2 x CH *i*-Pr). **IR** (film) ν_{max} 3657, 2980, 2888, 1382, 1251, 1152, 1072, 954 cm^{-1}. **HRMS** (ESI): calculated for $C_{28}H_{40}O_4SiNa$ $[M+Na]^+$ requires *m/z* 491.2588, found *m/z* 491.2586.

6.2. (*E*)-4-Di*tert*-butylbis[(4-methoxyphenyl)but-3-en-1-yloxy]silane, 1b.

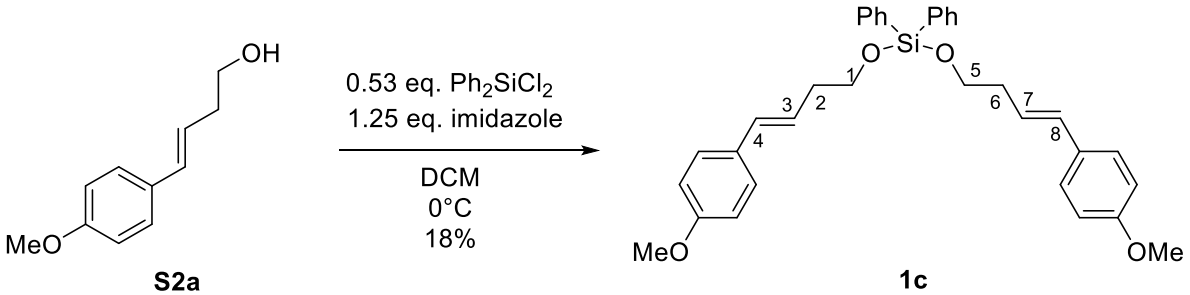


S2a 1b

From alcohol **S2a** (100.0 mg, 0.561 mmol), di-*tert*-butylsilanediylbis(trifluoromethanesulfonate) (0.096 mL, 0.30 mmol) and 2,4-lutidine (0.08 mL, 0.7 mmol), following the general procedure, diene **1b** was obtained. Chromatographic purification (5% Et_2O - pentane) gave **1b** as a colorless oil (62.1 mg, 45%).

Data for **1b**: R_f 0.40 (10% Et_2O - pentane). **M.p.**: 45 °C (solvent: 10% diethyl ether in pentane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.25 (4H, d, *J* = 8.7 Hz, Ar), 6.82 (4H, d, *J* = 8.8 Hz, Ar), 6.38 (2H, d, *J* = 15.9 Hz, 4-H and 8-H), 6.10 (2H, dt, *J* = 15.8, 7.1 Hz, 3-H and 7-H), 3.93 (4H, t, *J* = 6.7 Hz, 1-H_2 and 5-H_2), 3.79 (6H, s, 2 x OMe), 2.45 (4H, qd, *J* = 6.8, 1.4 Hz, 2-H_2 and 6-H_2), 1.03 (18H, s, 6 x CH_3 *t*-Bu). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.8 (2 x C Ar), 131.1 (C-4 and C-8), 130.7 (2 x C Ar), 127.2 (4 x CH Ar), 125.2 (C-3 and C-7), 114.0 (4 x CH Ar), 63.9 (C-1 and C-5), 55.4 (2 x OMe), 36.9 (C-2 and C-6), 28.0 (6 x CH_3 *t*-Bu), 21.3 (2 x C *t*-Bu). **IR** (film) ν_{max} 3667, 2980, 2360, 1382, 1249, 1151, 1086, 955 cm^{-1}. **HRMS** (ESI): calculated for $C_{30}H_{44}O_4SiNa$ $[M+Na]^+$ requires *m/z* 519.2901, found *m/z* 519.2899.

6.3. (*E*)-Bis[4-(4-methoxyphenyl)but-3-en-1-yloxy]diphenylsilane, 1c.

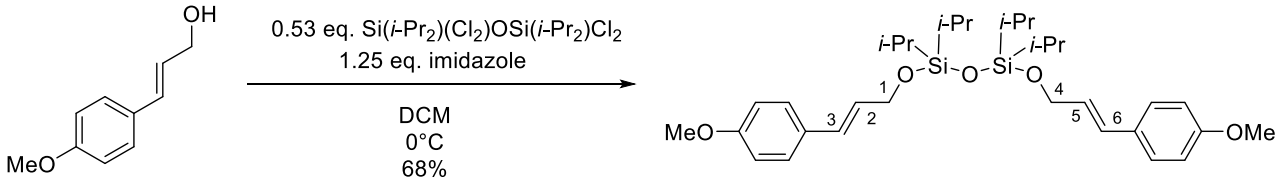


S2a 1c

From alcohol **S2a** (80.0 mg, 0.449 mmol), imidazole (38.2 mg, 0.562 mmol) and dichlorodiphenylsilane (0.049 mL, 0.24 mmol) following the general procedure, diene **1c** was obtained. Chromatographic purification (5% Et_2O - pentane) gave **1c** as a colorless oil (21.7 mg, 18%).

Data for **1c**: R_f 0.45 (30% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65-7.70 (4H, m, Ar), 7.30-7.45 (6H, m, Ar), 7.24 (4H, d, *J* = 8.7 Hz, Ar), 6.82 (4H, d, *J* = 8.8 Hz, Ar), 6.37 (2H, d, *J* = 15.9 Hz, 4-H and 8-H), 6.05 (2H, dt, *J* = 15.8, 7.0 Hz, 3-H and 7-H), 3.90 (4H, t, *J* = 6.7 Hz, 1-H_2 and 5-H_2), 3.79 (6H, s, 2 x OMe), 2.49 (4H, qd, *J* = 6.8, 1.4 Hz, 2-H_2 and 6-H_2). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.9 (2 x C Ar), 135.1 (4 x CH Ar), 133.0 (2 x C Ar), 131.4 (C-4 and C-8), 130.6 (2 x C Ar), 130.4 (2 x CH Ar), 128.0 (4 x CH Ar), 127.2 (4 x CH Ar), 124.8 (C-3 and C-7), 114.0 (4 x CH Ar), 63.1 (C-1 and C-5), 55.4 (2 x OMe), 36.4 (C-2 and C-6). **IR** (film) ν_{max} 3028, 2360, 1509, 1246, 1116, 1080, 700 cm^{-1}. **HRMS** (ESI): calculated for $C_{34}H_{36}O_4SiNa$ $[M+Na]^+$ requires *m/z* 559.2275, found *m/z* 559.2277.

6.4. 1,1,3,3-Tetraisopropyl-1,3-bis{(*E*)-3-[4-methoxyphenyl)allyloxy]}disiloxane, 1e.

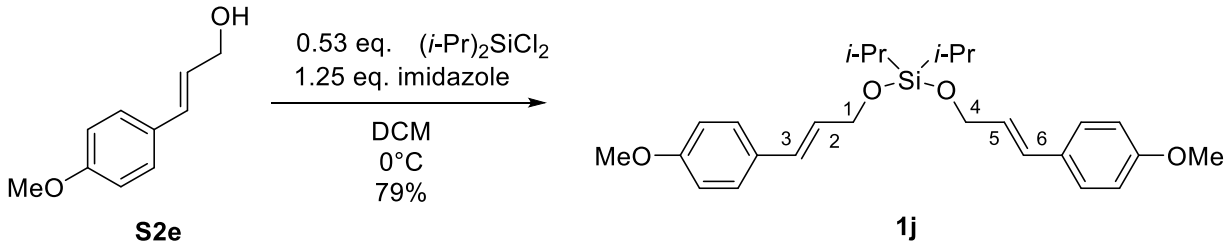


S2e **1e**

From alcohol **S2e** (80.0 mg, 0.488 mmol), imidazole (41.5 mg, 0.610 mmol) and 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane (0.082 mL, 0.26 mmol) following the general procedure, diene **1e** was obtained. Chromatographic purification (6% Et_2O - pentane) gave **1e** as a white solid (95.1 mg, 68%).

Data for **1e**: R_f 0.45 (20% Et_2O - pentane). **M.p.**: 27 °C (solvent: 10% diethyl ether in pentane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.29 (4H, d, *J* = 8.7 Hz, Ar), 6.83 (4H, d, *J* = 8.7 Hz, Ar), 6.56 (2H, d, *J* = 15.8 Hz, 3-H and 6-H), 6.16 (2H dt, *J* = 15.8, 5.1 Hz, 2-H and 5-H), 4.47 (4H, dd, *J* = 5.1, 1.8 Hz, 1-H_2 and 4-H_2), 3.80 (6H, s, 2 x OMe), 0.93-1.17 (28H, m, 4 x ^{i}Pr). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.1 (2 x C Ar), 130.1 (2 x C Ar), 129.0 (C-3 and C-6), 127.7 (4 x CH Ar), 126.9 (C-2 and C-5), 114.0 (4 x CH Ar), 63.4 (C-1 and C-4), 55.4 (2 x OMe), 17.6 (4 x CH_3 ^{i}Pr), 17.5 (4 x CH_3 ^{i}Pr), 13.2 (4 x CH ^{i}Pr). **IR** (film) ν_{max} 2980, 2866, 2360, 2341, 1511, 1249, 1050, 966 cm^{-1}. **HRMS** (CI): calculated for $C_{32}H_{51}O_5Si_2$ $[M+H]^+$ requires *m/z* 571.3275, found *m/z* 571.3266.

6.5. (*E*)-Diisopropylbis[3-(4-methoxyphenyl)allyloxy]silane, 1j.

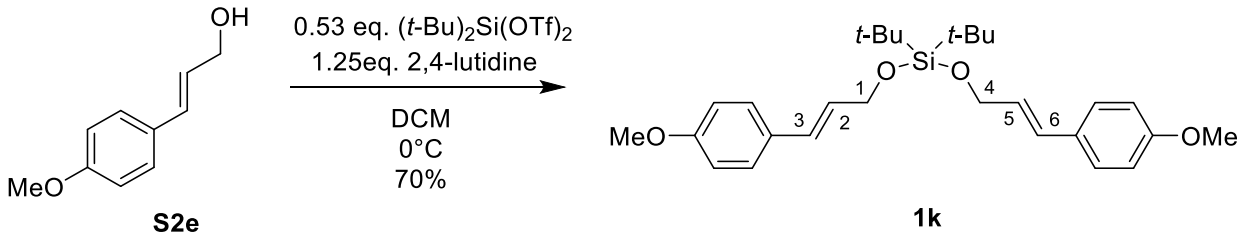


S2e **1j**

From alcohol **S2e** (100.0 mg, 0.609 mmol), imidazole (51.9 mg, 0.763 mmol) and dichlorodiisopropylsilane (0.058 mL, 0.32 mmol) following the general procedure, diene **1j** was obtained. Chromatographic purification (gradient elution: 3% → 5% Et_2O - pentane) gave **1j** as a colorless oil (105.4 mg, 79%).

Data for **1j**: $\boldsymbol{R_f}$ 0.5 (15% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.31 (4H, d, *J* = 8.7 Hz, Ar), 6.85 (4H, d, *J* = 8.7 Hz, Ar), 6.58 (4H, d, *J* = 15.8 Hz, 3-H and 6-H), 6.19 (2H, dt, *J* = 15.8, 5.3 Hz, 2-H and 5-H), 4.48 (4H, dd, *J* = 5.3, 1.7 Hz, 1-H_2 and 4-H_2), 3.81 (6H, s, 2 x OMe), 1.13 (14H, m, 2 x ^{i}Pr). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.2 (2 x C Ar), 129.9 (2 x C Ar), 129.4 (C-3 and C-6), 127.7 (4 x CH Ar), 126.7 (C-2 and C-5), 114.0 (4 x CH Ar), 63.8 (C-1 and C-4), 55.4 (2 x OMe), 17.6 (4 x CH_3 ^{i}Pr), 12.4 (2 x CH ^{i}Pr). **IR** (film) ν_{max} 2970, 1739, 1368, 1229, 1216, 835 cm^{-1}. **HRMS** (ESI): calculated for $C_{26}H_{36}O_4SiNa$ $[M+Na]^+$ requires *m/z* 463.2275, found *m/z* 463.2273.

6.6. (*E*)-Di*tert*-butylbis[3-(4-methoxyphenyl)allyloxy]silane, 1k.

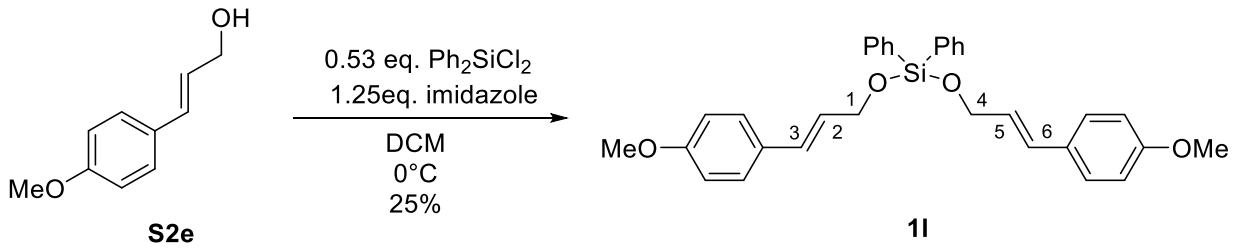


S2e **1k**

From alcohol **S2e** (80.0 mg, 0.488 mmol), di*tert*-butylsilanediyl bis(trifluoromethanesulfonate) (0.070 mL, 0.26 mmol) and 2,4-lutidine (0.07 mL, 0.6 mmol) following the general procedure, diene **1k** was obtained. Chromatographic purification (gradient elution: 4% → 8% Et_2O - pentane) gave **1k** as a colorless oil (80.1 mg, 70%).

Data for **1k**: $\boldsymbol{R_f}$ 0.43 (15% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.31 (4H, d, *J* = 8.7 Hz, Ar), 6.85 (4H, d, *J* = 8.8 Hz, Ar), 6.60 (2H, d, *J* = 15.8 Hz, 3-H and 6-H), 6.18 (2H, dt, *J* = 15.8, 4.9 Hz, 2-H and 5-H), 4.55 (4H, dd, *J* = 5.0, 1.8 Hz, 1-H_2 and 4-H_2), 3.81 (6H, s, 2 x OMe), 1.10 (18H, s, 6 x CH_3 *t*Bu). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.1 (2 x C Ar), 130.1 (2 x C Ar), 128.8 (C-3 and C-6), 127.7 (4 x CH Ar), 127.0 (C-2 and C-5), 114.0 (4 x CH Ar), 64.6 (C-1 and C-4), 55.4 (2 x OMe), 28.1 (6 x CH_3 *t*-Bu), 21.5 (2 x C *t*-Bu). **IR** (film) ν_{max} 2970, 2360, 1738, 1463, 1230, 857 cm^{-1}. **HRMS** (ESI): calculated for $C_{28}H_{40}O_4SiNa$ $[M+Na]^+$ requires *m/z* 491.2588, found *m/z* 491.2586

6.7. (*E*)-Bis-[3-(4-methoxyphenyl)allyloxy]diphenylsilane, 1l.

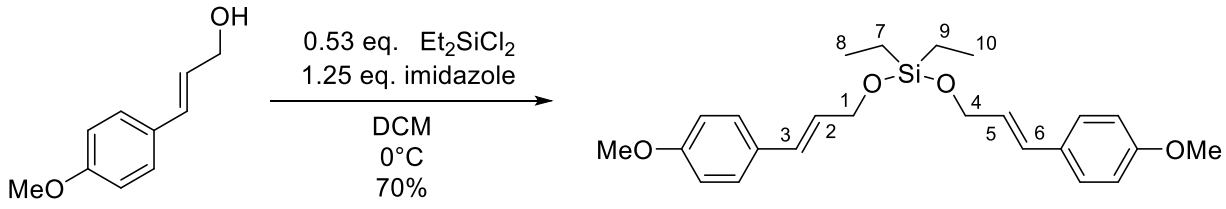


S2e **1l**

From alcohol **S2e** (100.0 mg, 0.609 mmol), imidazole (51.9 mg, 0.763 mmol) and dichlorodiphenylsilane (0.08 mL, 0.3 mmol) following the general procedure, diene **1l** was obtained. Chromatographic purification (gradient elution: 7% → 9% Et_2O - pentane) gave **1l** as a colorless oil (38.5 mg, 25%).

Data for **1l**: R_f 0.58 (10% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.72-7.77 (4H, m, Ar), 7.35-7.48 (6H, m, Ar), 7.26 (4H, d, *J* = 8.6 Hz, Ar), 6.82 (4H, d, *J* = 8.8 Hz, Ar), 6.54 (2H, d, *J* = 15.8 Hz, 3-H and 6-H), 6.19 (2H, dt, *J* = 15.8, 5.6 Hz, 2-H and 5-H), 4.50 (4H, dd, *J* = 5.6, 1.6 Hz, 1-H_2 and 4-H_2), 3.81 (6H, s, 2 x OMe). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.3 (2 x C Ar), 135.1 (4 x CH Ar), 132.8 (2 x C Ar), 130.5 (3 x CH Ar), 130.3 (C-3 and C-6), 129.8 (2 x C Ar), 128.1 (3 x CH Ar), 127.8 (4 x CH Ar), 126.0 (C-2 and C-5), 114.0 (4 x CH Ar), 64.3 (C-1 and C-4), 55.4 (2 x OMe). **IR** (film) ν_{max} 2980, 2360, 1738, 1510, 1249, 837 cm^{-1}. **HRMS** (ESI): calculated for $C_{32}H_{32}O_4SiNa$ $[M+Na]^+$ requires *m/z* 531.1962, found *m/z* 531.1961.

6.8. (*E*)-Diethylbis[3-(4-methoxyphenyl)allyloxy]silane, 1m.



S2e **1m**

From alcohol **S2e** (80.0 mg, 0.488 mmol), imidazole (41.5 mg, 0.610 mmol) and dichlorodiethylsilane (0.038 mL, 0.26 mmol) following the general procedure, diene **1m** was obtained. Chromatographic purification (gradient elution: 8% → 10% Et_2O - pentane) gave **1m** as a colorless solid (70.6 mg, 70%).

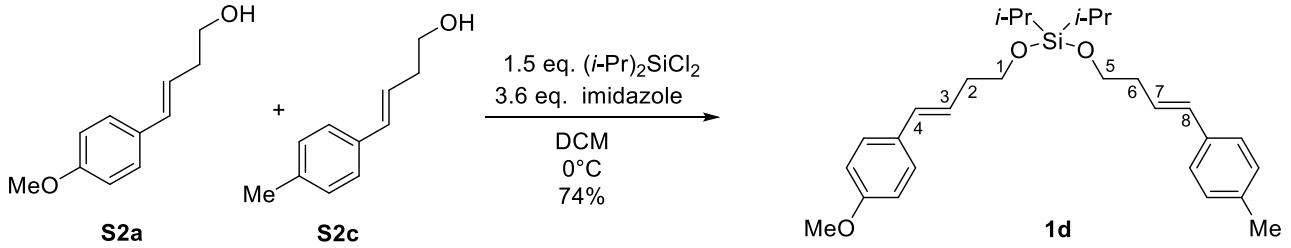
Data for **1m**: R_f 0.58 (30% Et_2O - pentane). **M.p.**: 49 °C (solvent: 5% diethyl ether in pentane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.29 (4H, d, *J* = 8.7 Hz, Ar), 6.83 (4H, d, *J* = 8.7 Hz, Ar), 6.54 (2H, d, *J* = 15.8 Hz, 3-H and 6-H), 6.18 (2H, dt, *J* = 15.8, 5.6 Hz, 2-H and 5-H), 4.42 (4H, dd, *J* = 5.6, 1.6 Hz, 1-H_2 and 4-H_2), 3.80 (6H, s, 2 x OMe), 1.03 (6H t, *J* = 8.0 Hz, 8-H_3 and 10-H_3), 0.72 (4H, q, *J* = 8.0 Hz, 7-H_2 and 9-H_2). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 159.2 (2 x C Ar), 130.0 (2 x C Ar), 129.8 (C-3 and C-6), 127.8 (4 x CH Ar), 126.4 (C-2 and C-5), 114.0 (4 x CH Ar), 63.7 (C-1 and C-4), 55.4 (2 x OMe), 6.7 (C-8 and C-10), 4.1 (C-7 and C-9). **IR** (film) ν_{max} 2960, 2360, 2341, 1607, 1249, 1035,

833 cm^{-1}; **HRMS** (CI): calculated for $C_{24}H_{32}O_4Si$ $[M+H]^+$ requires *m/z* 413.2148, found *m/z* 413.2145.

7. General procedure for the preparation of non-symmetric silyl ethers

To a flame-dried flask with a stirring bar, a solution of 3.6 eq. of imidazole in dry DCM (5.0 mL/mmol) was added under argon**.** The solution was stirred and cooled to 0 °C, and then 1.5 eq. of silane was added dropwise. After 10 min. of stirring, a solution of 1.0 eq. of the first alcohol in dry DCM (2 mL/mmol) was added dropwise over 20 min. by using syringe pump. The solution was stirred for 15 min. at 0 °C after the addition of the first alcohol was completed. Then a solution of 1.0 eq. of the second alcohol in dry DCM (1 mL/mmol) was added dropwise. The reaction was monitored by TLC, until completion. The solvent was evaporated under reduced pressure and the crude reaction was purified by chromatography on silica gel using the appropriate mixture of eluents.

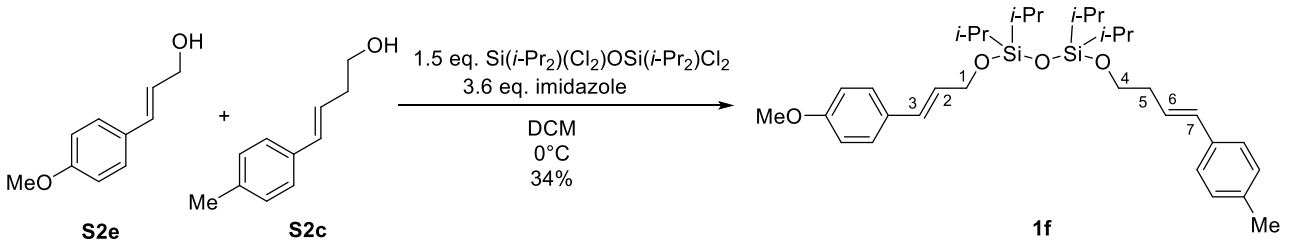
7.1. (*E*)-4-Diisopropyl[(4-methoxyphenyl)but-3-en-1-yloxy](*E*)-4-[(*p*-tolyl)but-3-en-1-yloxy]silane, 1d.



From alcohols **S2a** (44.0 mg, 0.247 mmol), **S2c** (40.0 mg, 0.247 mmol), imidazole (60.5 mg, 0.890 mmol) and dichlorodiisopropylsilane (0.067 mL, 0.37 mmol) following the general procedure, diene **1d** was obtained. Chromatographic purification (gradient elution: 0.6% → 1.5% Et_2O - pentane) gave **1d** as a colorless oil (80.8 mg, 74%).

Data for **1d**: R_f 0.6 (10% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.25 (2H, d, *J* = 8.8 Hz, Ar), 7.22 (2H, d, *J* = 8.1 Hz, Ar), 7.09 (2H, d, *J* = 7.9 Hz, Ar), 6.82 (2H, d, *J* = 8.7 Hz, Ar), 6.41 (1H, d, J = 15.9 Hz, 8-H), 6.38 (1H, d, *J* = 15.8 Hz, 4-H), 6.17 (1H, dt, *J* = 15.9, 7.1 Hz, 7-H), 6.08 (1H, dt, *J* = 15.8, 7.0 Hz, 3-H), 3.82-3.88 (4H, m, 1-H_2 and 5-H_2), 3.79 (3H, s, OMe), 2.46 (2H, qd, *J* = 6.8, 1.5 Hz, 6-H_2), 2.45 (2H, qd, *J* = 6.8, 1.2 Hz, 2-H_2), 2.32 (3H, s, Me), 1.00-1.10 (14 H, m, 2 x ^{i}Pr). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.9 (C Ar), 136.8 (C Ar), 135.0 (C Ar), 131.7 (C-8), 131.2 (C-4), 130.7 (C Ar), 129.3 (2 x CH Ar), 127.2 (2 x CH Ar), 126.1 (C-7), 126.0 (2 x CH Ar), 124.9 (C-3), 114.0 (2 x CH Ar), 63.0 and 62.9 (C-1 and C-5), 55.4 (OMe), 36.8 (C-2 and C-6), 21.3 (Me), 17.5 (4 x CH_3 *i*-Pr), 12.3 (2 x CH *i*-Pr). **IR** (film) ν_{max} 2980, 2360, 1510, 1382, 1247, 1088, 964, 796 cm^{-1}. **HRMS** (ESI): calculated for $C_{28}H_{40}O_3SiNa$ $[M+Na]^+$ requires *m/z* 475.2639, found *m/z* 475.2633.

7.2. 1,1,3,3-Tetraisopropyl-1-(*E*)-3-[(4-methoxyphenyl)allyloxy]-3-(*E*)-4-[(*p*-tolyl)but-3-en-1-yloxy]disiloxane, 1f.

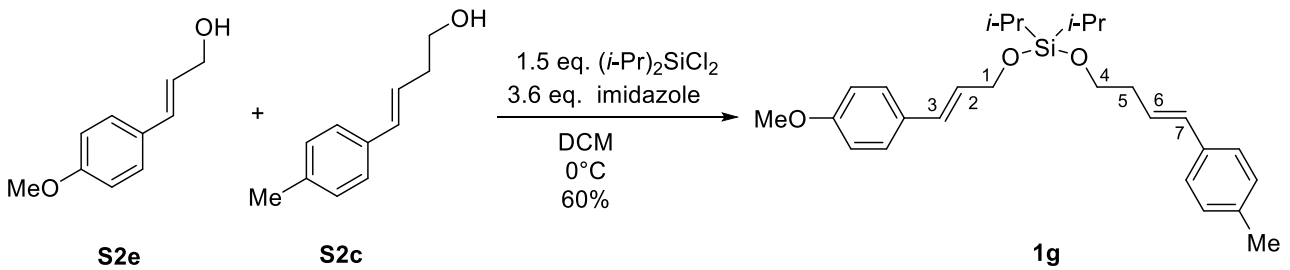


S2e S2c 1f

From alcohols **S2e** (60.0 mg, 0.366 mmol), **S2c** (61.0 mg, 0.377 mmol), imidazole (90.5 mg, 1.33 mmol) and 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane (0.177 mL, 0.562 mmol) following the general procedure, diene **1f** was obtained. Chromatographic purification (gradient elution: 1.5% → 2.5% Et_2O - pentane) to yield **1f** as a colorless oil (76.2 mg, 34%).

Data for **1f**: R_f 0.55 (10% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.29 (2H, d, *J* = 8.7 Hz, Ar), 7.21 (2H, d, *J* = 8.1 Hz, Ar), 7.09 (2H, d, *J* = 7.8 Hz, Ar), 6.83 (2H, d, *J* = 8.7 Hz, Ar), 6.56 (1H, d, *J* = 15.8 Hz, 3-H), 6.40 (1H, d, *J* = 15.9 Hz, 7-H), 6.16-6.23 (1 H, m, 6-H), 6.10-6.16 (1H, m, 2-H), 4.46 (2H, dd, *J* = 5.1, 1.8 Hz, 1-H_2), 3.86 (2H, t, *J* = 6.8 Hz, 4-H_2), 3.80 (3H, s, OMe), 2.46 (2H, qd, *J* = 6.9, 1.4 Hz, 5-H_2) 2.32 (3H, s, Me), 0.88-1.16 (28 H, m, 4 x *i*-Pr). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.1 (C Ar), 136.8 (C Ar), 135.0 (C Ar), 131.6 (C-7), 130.1 (C Ar), 129.3 (2 x CH Ar), 129.0 (C-3), 127.6 (2 x CH Ar), 126.9 (C-2), 126.2 (C-6), 126.0 (2 x CH Ar), 114.0 (2 x CH Ar), 63.3 (C-1), 62.6 (C-4), 55.4 (OMe), 36.7 (C-5), 21.3 (Me), 17.6 (4 x CH_3 *i*-Pr), 17.5 (4 x CH_3 *i*-Pr), 13.2 (2 x CH *i*-Pr), 13.1 (2 x CH *i*-Pr). **IR** (film) ν_{max} 2980, 2889, 1382, 1250, 1151, 1081, 965 cm^{-1}. **HRMS** (ESI): calculated for $C_{33}H_{52}O_4Si_2Na$ $[M+Na]^+$ requires *m/z* 591.3296, found *m/z* 591.3291.

7.3. (*E*)-3-Diisopropyl[(4-methoxyphenyl)allyloxy](*E*)-4-[(*p*-tolyl)but-3-en-1-yloxy]silane, 1g.



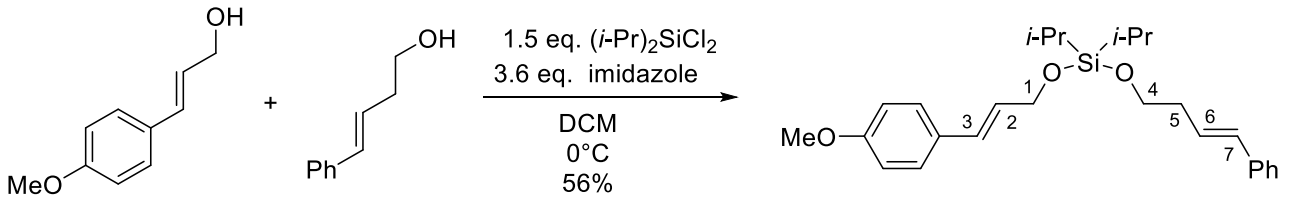
S2e S2c 1g

From alcohols **S2e** (50.0 mg, 0.304 mmol), **S2c** (49.0 mg, 0.302 mmol), imidazole (74.7 mg, 1.10 mmol) and dichlorodiisopropylsilane (0.083 mL, 0.46 mmol) following the general procedure, diene **1g** was obtained. Chromatographic purification (gradient elution: 3% → 5% Et_2O - pentane) to yield **1g** as a colorless oil (80.5 mg, 60%).

Data for **1g**: R_f 0.45 (15% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.30 (2H, d, *J* = 8.8 Hz, Ar), 7.21 (2H, d, *J* = 8.2 Hz, Ar), 7.09 (2H, d, *J* = 7.9 Hz, Ar), 6.84 (2H, d, *J* = 8.8 Hz, Ar),

6.55 (1H, d, *J* = 15.8 Hz, 3-H), 6.40 (1H, d, *J* = 15.9 Hz, 7-H), 6.17-6.22 (1 H, m, 6-H), 6.12-6.17 (1H, m, 2-H), 4.45 (2H, dd, *J* = 5.3, 1.7 Hz, 1-H_2), 3.87 (2H, t, *J* = 6.8 Hz, 4-H_2), 3.80 (3H, s, OMe), 2.47 (2H, qd, *J* = 6.9, 1.4 Hz, 5-H_2), 2.32 (3H, s, Me), 1.05-1.11 (14H, m, 2 x *i*-Pr). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.2 (C Ar), 136.8 (C Ar), 135.0 (C Ar), 131.7 (C-7), 130.0 (C Ar), 129.30 (2 x CH Ar), 129.27 (C-3), 127.7 (2 x CH Ar), 126.8 (C-2), 126.1 (C-6), 126.0 (2 x CH Ar), 114.1 (2 x CH Ar), 63.7 (C-1), 62.9 (C-4), 55.4 (OMe), 36.7 (C-5), 21.3 (Me), 17.6 (4 x CH_3 *i*-Pr), 12.3 (2 x CH *i*-Pr). **IR** (film) ν_{max} 2970, 1736, 1436, 1368, 1228, 1216 cm^{-1}. **HRMS** (ESI): calculated for $C_{27}H_{38}O_3SiNa$ $[M+Na]^+$ requires *m/z* 461.2482, found *m/z* 461.2482.

7.4. (*E*)-3-Diisopropyl[(4-methoxyphenyl)allyloxy](*E*)-4-(phenylbut-3-en-1-yloxy)silane, 1h.

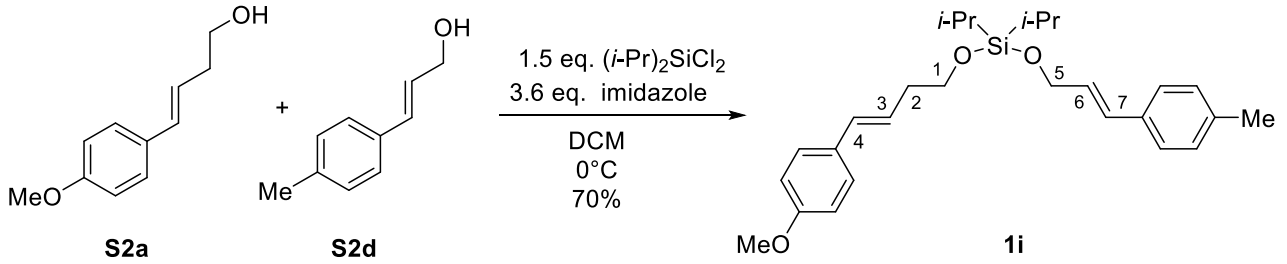


S2e **S2b** **1h**

From alcohols **S2e** (50.0 mg, 0.305 mmol), **S2b** (45.0 mg, 0.304 mmol), imidazole (82.7 mg, 1.22 mmol) and dichlorodiisopropylsilane (0.091 mL, 0.51 mmol) following the general procedure, diene **1h** was obtained. Chromatographic purification (radient elution: 1.5% → 3% Et_2O - pentane) to yield **1h** as a colorless oil (78.8 mg, 56%).

Data for **1h**: R_f 0.6 (10% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.26-7.35 (6H, m, Ar), 7.16-7.23 (1H, m, Ar), 6.85 (2H, d, *J* = 8.8 Hz, Ar), 6.56 (1H, d, *J* = 15.8 Hz, 3-H), 6.44 (1H, d, *J* = 15.9 Hz, 7-H), 6.25 (1H, dt, *J* = 16.0, 7.0 Hz, 6-H), 6.17 (1H, dt, *J* = 15.8, 5.2 Hz, 2-H), 4.46 (2H, dd, *J* = 5.2, 1.7 Hz, 1-H_2), 3.89 (2H, t, *J* = 6.8 Hz, 4-H_2), 3.81 (3H, s, OMe), 2.49 (2H, qd, *J* = 6.8, 1.4 Hz, 5-H_2), 1.06-1.12 (14H, m, 2 x *i*-Pr). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.2 (C Ar), 137.8 (C Ar), 131.9 (C-7), 130.0 (C Ar), 129.3 (C-3), 128.6 (2 x CH Ar), 127.7 (2 x CH Ar), 127.2 (CH Ar), 127.1 (C-6), 126.8 (C-2), 126.1 (2 x CH Ar), 114.1 (2 x CH Ar), 63.7 (C-1), 62.8 (C-4), 55.4 (OMe), 36.7 (C-5), 17.6 (4 x CH_3 *i*-Pr), 12.3 (2 x CH *i*-Pr). **IR** (film) ν_{max} 2864, 2360, 1607, 1510, 1247, 1101, 1037, 963, 691 cm^{-1}. **HRMS** (ESI): calculated for $C_{26}H_{36}O_3SiNa$ $[M+Na]^+$ requires *m/z* 447.2326, found *m/z* 447.2326.

7.5. (*E*)-4-Diisopropyl[(4-methoxyphenyl)but-3-en-1-yloxy](*E*)-3-[(*p*-tolyl)allyloxy]silane, 1i.

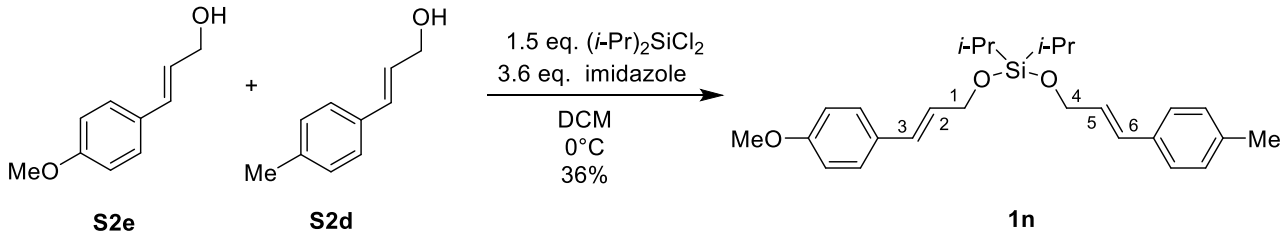


S2a **S2d** **1i**

From alcohols **S2a** (72.0 mg, 0.404 mmol), **S2d** (60.0 mg, 0.405 mmol), imidazole (99.1 mg, 1.46 mmol) and dichlorodiisopropylsilane (0.083 mL, 0.46 mmol) following the general procedure, diene **1i** was obtained. Chromatographic purification (gradient elution: 1.5% → 2.5% Et_2O - pentane) to yield **1i** as a colorless oil (121.5 mg, 70%).

Data for **1i**: R_f 0.45 (10% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.23-7.30 (4H, m, Ar), 7.13 (2H, d, *J* = 7.8 Hz, Ar), 6.83 (2H, d, *J* = 8.7 Hz, Ar), 6.60 (1H, d, *J* = 15.8 Hz, 7-H), 6.39 (1H, d, *J* = 15.9 Hz, 4-H), 6.26 (1H, dt, *J* = 15.8, 5.1 Hz, 6-H), 6.10 (1H, dt, *J* = 15.8, 7.1 Hz, 3-H), 4.48 (2H, dd, *J* = 5.1, 1.8 Hz, 5-H_2), 3.88 (2H, t, *J* = 6.8 Hz, 1-H_2), 3.80 (3H, s, OMe), 2.47 (2H, qd, *J* = 6.8, 1.4 Hz, 2-H_2), 2.35 (3H, s, Me), 1.08-1.12 (14H, m, 2 x *i*-Pr). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.9 (C Ar), 137.2 (C Ar), 134.4 (C Ar), 131.2 (C-4), 130.6 (C Ar), 129.5 (C-7), 129.3 (2 x CH Ar), 127.9 (C-6), 127.2 (2 x CH Ar), 126.4 (2 x CH Ar), 124.9 (C-3), 114.0 (2 x CH Ar), 63.6 (C-5), 63.0 (C-1), 55.4 (OMe), 36.7 (C-2), 21.3 (Me), 17.6 (4 x CH_3 *i*-Pr), 12.3 (2 x CH *i*-Pr). **IR** (film) ν_{max} 2980, 1382, 1250, 1151, 1072, 965 cm^{-1}. **HRMS** (ESI): calculated for $C_{27}H_{38}O_3SiNa$ $[M+Na]^+$ requires *m/z* 461.2482, found *m/z* 461.2478.

7.6. (*E*)-3-Diisopropyl[(4-methoxyphenyl)allyloxy] (*E*)-3- [(*p*-tolyl)allyloxy]silane, 1n.



S2e **S2d** **1n**

From alcohols **S2e** (50.0 mg, 0.304 mmol), **S2f** (45.0 mg, 0.304 mmol), imidazole (74.7 mg, 1.10 mmol) and dichlorodiisopropylsilane (0.080 mL, 0.46 mmol) following the general procedure, diene **1n** was obtained. Chromatographic purification (gradient elution: 2% → 4% Et_2O - pentane) gave **1n** as a colorless oil (45.9 mg, 36%).

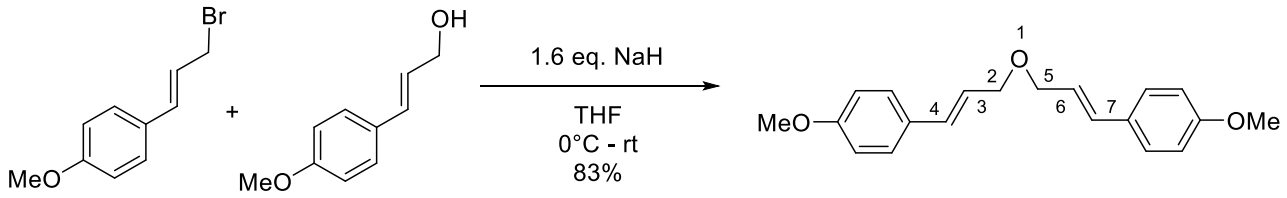
Data for **1n**: R_f 0.4 (10% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.30 (2H, d, *J* = 8.7 Hz, Ar), 7.26 (2H, d, *J* = 8.1 Hz, Ar), 7.11 (2H, d, *J* = 7.8 Hz, Ar), 6.84 (2H, d, *J* = 8.7 Hz, Ar), 6.60 (1H, d, *J* = 15.8 Hz, 6-H), 6.57 (1H, d, *J* = 15.8 Hz, 3-H), 6.27 (1H, dt, *J* = 15.8, 5.1 Hz, 5-H), 6.18 (1H, dt, *J* = 15.8, 5.3 Hz, 2-H), 4.48 (2H, dd, *J* = 5.1, 1.8 Hz, 4-H_2), 4.47 (2H, dd, *J* = 5.2, 1.7 Hz, 1-H_2), 3.81 (3H, s, OMe), 2.34 (3H, s, Me), 1.07-1.14 (14H, m, 2 x *i*-Pr). **^{13}C NMR (100 MHz, $CDCl_3$)**

δ 159.2 (C Ar), 137.3 (C Ar), 134.4 (C Ar), 130.0 (C Ar), 129.7 and 129.4 (C-3 and C-6), 129.3 (2 x CH Ar), 127.8 (C-5), 127.7 (C-2), 126.7 (2 x CH Ar), 126.5 (2 x CH Ar), 114.0 (2 x CH Ar), 63.8 and 63.7 (C-1 and C-4), 55.4 (OMe), 21.3 (Me), 17.6 (4 x CH_3 *i*-Pr), 12.4 (2 x CH *i*-Pr). **IR** (film) ν_{max} 2943, 2865, 2360, 1510, 1249, 1117, 1055, 965 cm^{-1}. **HRMS** (ESI): calculated for $C_{26}H_{36}O_3SiNa$ $[M+Na]^+$ requires *m/z* 447.2326, found *m/z* 447.2327.

8. General procedure for the synthesis of ethers by alkylation of alcohols with bromides.

A flame-dried flask was charged with 1.6 eq. of NaH (60% in mineral oil) and 2 mL/mmol of dry THF. To this suspension a solution of 1.0 eq. of alcohol in 3.0 mL/mmol of THF was added dropwise, and the reaction was stirred for 30 min. The flask was cooled to 0 °C, and a solution of 1.4 eq. of bromide in 3.0 mL/mmol THF was added dropwise. The mixture was gradually warmed to r.t. After 12 h, the reaction was quenched by slow addition of saturated NH_4Cl. The phases were separated, and the aqueous phase was extracted with Et_2O (2 x 5 mL/mmol). The combined organic layers were washed with brine, dried over $MgSO_4$, and the solvent was evaporated to give the corresponding ether, that was purified by chromatography on silica gel using the appropriate mixture of eluents.

8.1. 4,4'-[(1*E*,1'*E*)-Oxybis(prop-1-ene-3,1-diyl)]bis(methoxybenzene, 4a.

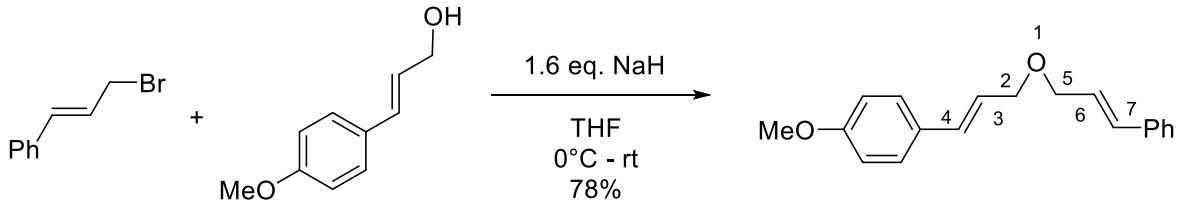


S3a **S2e** **4a**

From bromide **S3a** (1.290 g, 5.708 mmol), alcohol **S2e** (0.670 g, 4.09 mmol) and NaH (261.0 mg, 6.525 mmol, 60% in mineral oil) following the general procedure, diene **4a** was obtained. Chromatographic purification (gradient elution: 15% → 20% Et_2O - pentane) gave **4a** as a white solid (1.052 g, 83%). Spectral properties matched those previously reported. [11]

Data for **4a**: R_f 0.5 (50% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.35 (4H, d, *J* = 8.8 Hz, Ar), 6.87 (4H, d, *J* = 8.8 Hz, Ar), 6.59 (2H, d, *J* = 15.9 Hz, 4-H and 7-H), 6.21 (2H, dt, *J* = 15.9, 6.2 Hz, 3-H and 6-H), 4.19 (4H, dd, *J* = 6.2, 1.4 Hz, 2-H_2 and 5-H_2), 3.81 (6H, s, 2 x OMe). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.3 (2 x C Ar), 132.3 (C-4 and C-7), 129.6 (2 x C Ar), 127.7 (4 x CH Ar), 123.8 (C-3 and C-6), 114.0 (4 x CH Ar), 70.9 (C-2 and C-5), 55.3 (2 x OMe). **HRMS** (CI): calculated for $C_{20}H_{23}O_3$ $[M+H]^+$ requires *m/z* 311.1647, found *m/z* 311.1646.

8.2. 1-[(*E*)-3-(Cinnamyloxy)prop-1-en-1-yl]-4-methoxybenzene, 4b.

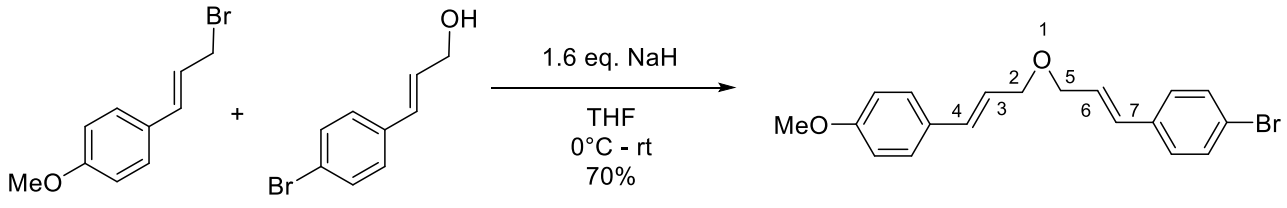


S2e **4b**

From (*E*)-(3-bromoprop-1-en-1-yl)benzene (273.0 mg, 1.393 mmol), alcohol **S2e** (164.0 mg, 1.000 mmol) and NaH (64.0 mg, 1.60 mmol, 60% in mineral oil) following the general procedure, diene **4b** was obtained. Chromatographic purification (8% Et_2O - pentane) gave **4b** as a colorless oil (218.0 mg, 78%). Spectral properties matched those previously reported.[11]

Data for **4b**: ***R*****$_f$** 0.50 (30% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44 (2H, d, *J* = 8.5 Hz, Ar), 7.38 (2H, d, *J* = 8.6 Hz, Ar), 7.36 (2H, d, *J* = 8.5 Hz, Ar), 7.30-7.25 (1H, m, Ar), 6.89 (2H, d, *J* = 8.8 Hz, Ar), 6.68 (1H, d, *J* = 15.9 Hz, 7-H), 6.62 (1H, d, *J* = 15.9 Hz, 4-H), 6.37 (1H, dt, *J* = 15.9, 6.0 Hz, 6-H), 6.24 (1H, dt, *J* = 15.9, 6.0 Hz, 3-H), 4.23 (2H, dd, *J* = 5.1, 1.3 Hz, 5-H_2), 4.22 (2H, dd, *J* = 5.1, 1.3 Hz, 2-H_2), 3.82 (3 H, s, OMe). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.3 (C Ar), 136.8 (C Ar), 132.5 and 132.4 (C-4 and C-7), 129.5 (C Ar), 128.6 (2 x CH Ar), 127.8 (2 x CH Ar), 127.7 (CH Ar), 126.5 (2 x CH Ar), 126.2 (C-6), 123.7 (C-3), 114.0 (2 x CH Ar), 71.0 and 70.7 (C-2 and C-5), 55.3 (OMe). **HRMS** (Cl): calculated for $C_{19}H_{21}O_2$ $[M+H]^+$ requires *m/z* 281.1542, found *m/z* 281.1530.

8.3. 1-Bromo-4-{(*E*)-3-[(*E*)-3-(4-methoxyphenyl)allyloxyprop-1-en-1-yl]}benzene, 4c.



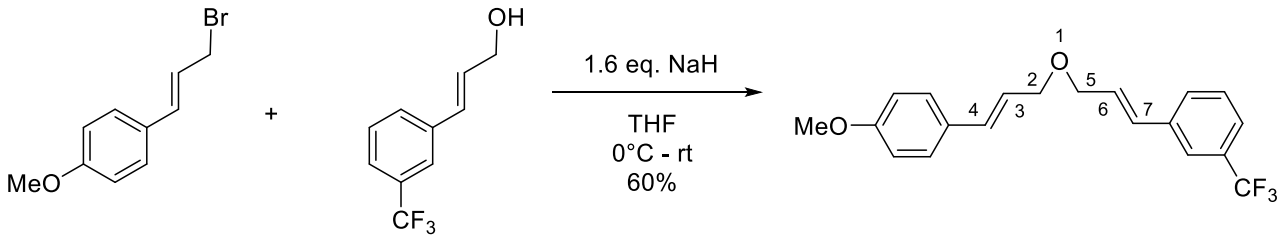
S3a **S2f** **4c**

From bromide **S3a** (150.0 mg, 0.664 mmol), alcohol **S2f** (100.0 mg, 0.4717 mmol) and NaH (30.4 mg, 0.760 mmol, 60% in mineral oil) following the general procedure, diene **4c** was obtained. Chromatographic purification (gradient elution: 15% → 20% Et_2O - pentane) gave **4c** as a white foam (119.0 mg, 70%).

Data for **4c**: ***R*****$_f$** 0.5 (50% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44 (2H, d, *J* = 8.5 Hz, Ar), 7.34 (2H, d, *J* = 8.7 Hz, Ar), 7.25 (2H, d, *J* = 8.4 Hz, Ar), 6.86 (2H, d, *J* = 8.7 Hz, Ar), 6.58 (2H, d, *J* = 15.2 Hz, 4-H and 7-H), 6.32 and 6.19 (2H, dt, *J* = 15.9, 6.2 Hz, 3-H and 6-H), 4.15-4.21 (4H, m, 2-H_2 and 5-H_2), 3.81 (3H, s, OMe). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.5 (C Ar), 135.8 (C Ar), 132.6 and 131.8 (C-4 and C-7), 131.3 (2 x CH Ar), 129.5 (C Ar), 128.1 (2 x CH Ar), 127.9 (2 x CH Ar), 127.1 and 123.7 (C-3 and C-6), 121.6 (C Ar), 114.1 (2 x CH Ar), 71.3 and 70.5 (C-2 and C-

5), 55.4 (OMe). **IR** (film) ν_{max} 2982, 2890, 1380, 1255, 1150, 1081, 970 cm^{-1}. **HRMS** (CI): calculated for $C_{19}H_{20}BrO_2$ $[M+H]^+$ requires *m/z* 359.0647, found *m/z* 359.0632.

8.4. 1-((*E*)-3-{[(*E*)-3-(4-Methoxyphenyl)allyloxy]prop-1-en-1-yl}-3-(trifluoromethyl)benzene, 4d.

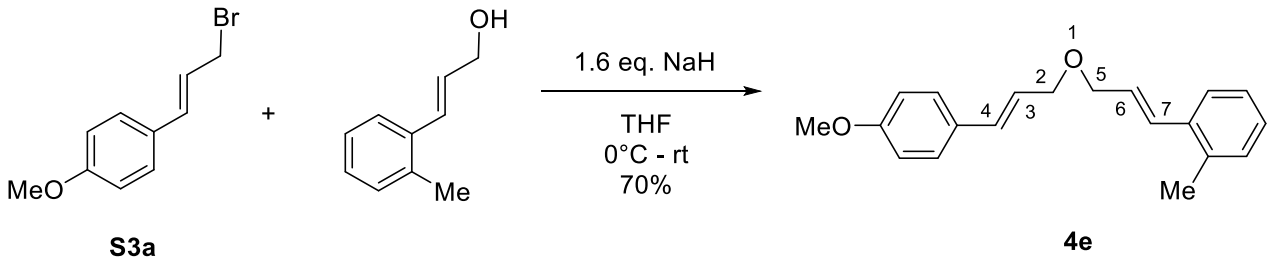


S3a **4d**

From bromide **S3a** (125.0 mg, 0.553 mmol), 3-(trifluoromethyl) cinnamic alcohol (80.0 mg, 0.396 mmol) and NaH (25.2 mg, 0.630 mmol, 60% in mineral oil) following the general procedure, diene **4d** was obtained. Chromatographic purification (15% Et_2O - pentane) gave **4d** as a colorless oil (83.8 mg, 60%).

Data for **4d**: R_f 0.50 (50% Et_2O - pentane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.64 (1H, s, Ar), 7.56 (1H, d, *J* = 7.7 Hz, Ar), 7.49 (1H, d, *J* = 7.8 Hz, Ar), 7.43 (1H, t, *J* = 7.7 Hz, Ar), 7.35 (2H, d, *J* = 8.7 Hz, Ar), 6.87 (2H, d, *J* = 8.7 Hz, Ar), 6.68 (1H, d, *J* = 16.0 Hz, 7-H), 6.60 (1H, d, *J* = 15.9 Hz, 4-H), 6.41 (1H, dt, *J* = 15.9, 5.7 Hz, 6-H), 6.21 (1H, dt, *J* = 15.9, 6.3 Hz, 3-H), 4.22 (2H, dd, *J* = 5.9, 1.6 Hz, 5-H_2), 4.21 (2H, dd, *J* = 5.9, 1.6 Hz, 2-H_2), 3.81 (3H, s, OMe). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 159.5 (C Ar), 137.7 (C Ar), 132.6 (C-4), 131.1 (CF_3, q, *J* = 32.1 Hz), 130.8 (C-7), 129.7 (CH Ar), 129.5 (CH Ar), 129.1 (C Ar), 128.4 (C-6), 127.9 (2 x CH Ar), 124.3 (CH Ar, q, *J* = 3.8 Hz), 123.6 (C-3), 123.3 (CH Ar, q, *J* = 3.8 Hz), 114.1 (2 x CH Ar), 71.4 and 70.3 (C-2 and C-5), 55.4 (OMe). **IR** (film) ν_{max} 2980, 2890, 1378, 1252, 1151, 1081, 965 cm^{-1}. **HRMS** (EI): calculated for $C_{20}H_{20}F_3O_2$ $[M+H]^+$ requires *m/z* 349.1415, found *m/z* 349.1409.

8.5. 1-{(*E*)-3-[(*E*)-3-(4-Methoxyphenyl)allyloxy]prop-1-en-1-yl}-2-methylbenzene, 4e.



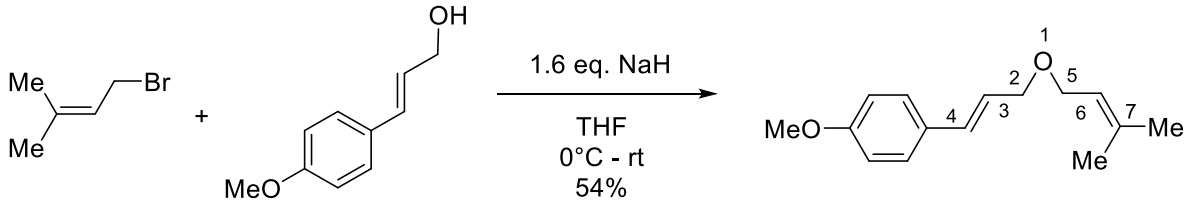
S3a **4e**

From bromide **S3a** (170.0 mg, 0.7522 mmol), (*E*)-3-(*o*-tolyl)prop-2-en-1-ol (80.0 mg, 0.541 mmol) and NaH (34.8 mg, 0.870 mmol, 60% in mineral oil) following the general procedure, diene

4e was obtained. Chromatographic purification (gradient elution: 15% → 20% Et_2O - pentane) gave **4e** as a colorless oil (111.0 mg, 70 %).

Data for **4e**: $\boldsymbol{R_f}$ 0.50 (50% Et_2O - pentane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.47-7.52 (2H, m, Ar), 7.37 (2H, d, *J* = 8.7 Hz, Ar), 7.14-7.23 (2H, m, Ar), 6.89 (2H, d, *J* = 8.8 Hz, Ar), 6.87 (1H, d, *J* = 15.9 Hz, 7-H), 6.62 (1H, d, *J* = 15.9 Hz, 4-H), 6.25 (1H, dt, *J* = 15.6, 6.0 Hz, 6-H), 6.24 (1H, dt, *J* = 15.6, 6.0 Hz, 3-H), 4.25 and 4.23 (4H, dd, *J* = 6.2, 1.4 Hz, 2-H_2 and 5-H_2), 3.82 (3H, s, OMe), 2.39 (3H, s, Me). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 159.5 (C Ar), 136.0 (C Ar), 135.6 (C Ar), 132.5 (C Ar), 130.6 (C-4), 130.4 (C-7), 129.6 (CH Ar), 127.9 (2 x CH Ar), 127.7 (CH Ar), 127.6 (CH Ar), 126.2 (CH Ar), 125.9 (C-6), 123.9 (C-3), 114.1 (2 x CH Ar), 71.1 and 71.0 (C-2 and C-5), 55.4 (OMe), 20.0 (Me). **IR** (film) ν_{max} 2985, 2889, 1380, 1251, 1151, 1080, 960 cm^{-1}. **HRMS** (CI): calculated for $C_{20}H_{23}O_2$ $[M+H]^+$ requires *m/z* 295.1698, found *m/z* 295.1688.

8.6. (*E*)-1-Methoxy-4-[3-(3-methylbut-2-en-1-yloxy)prop-1-en-1-yl]benzene, 4f.

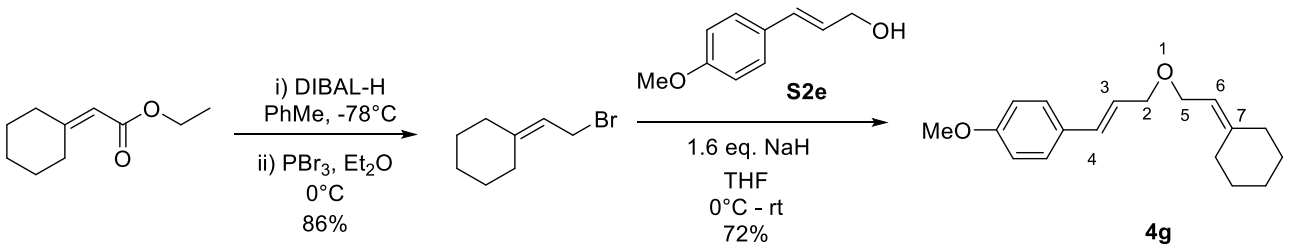


S2e **4f**

From 1-bromo-3-methylbut-2-ene (101.0 mg, 0.682 mmol), alcohol **S2e** (80.0 mg, 0.488 mmol) and NaH (31.2 mg, 0.78 mmol, 60% in mineral oil) following the general procedure, diene **4f** was obtained. Chromatographic purification (8% Et_2O - pentane) gave **4f** as a colorless oil (60.4 mg, 54%). Spectral properties matched those previously reported.[11]

Data for **4f**: $\boldsymbol{R_f}$ 0.55 (30% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.33 (2H, d, *J* = 8.7 Hz, Ar), 6.85 (2H, d, *J* = 8.8 Hz, Ar), 6.55 (1H, d, *J* = 15.9 Hz, 4-H), 6.18 (1H, dt, *J* = 15.9, 6.3 Hz, 3-H), 5.40 (1H, tt, *J* = 7.0, 1.3 Hz, 6-H), 4.11 (2H, dd, *J* = 6.2, 1.4 Hz, 2-H_2), 4.01 (2H, d, *J* = 6.9 Hz, 5-H_2), 3.80 (3H, s, OMe), 1.76 (3H, s, Me), 1.69 (3H, s, Me). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.2 (C Ar), 137.1 (C-7), 132.1 (C-4), 129.6 (C Ar), 127.7 (2 x CH Ar), 124.1 (C-3), 121.1 (C-6), 114.0 (2 x CH Ar), 70.8 (C-2), 66.5 (C-5), 55.3 (OMe), 25.9 (Me), 18.1 (Me). **HRMS** (Cl): calculated for $C_{15}H_{20}O_2$ $[M+H]^+$ requires *m/z* 233.1542, found *m/z* 233.1538.

8.7. (*E*)-1-[3-(2-Cyclohexylideneethoxy)prop-1-en-1-yl]-4-methoxybenzene, 4g.



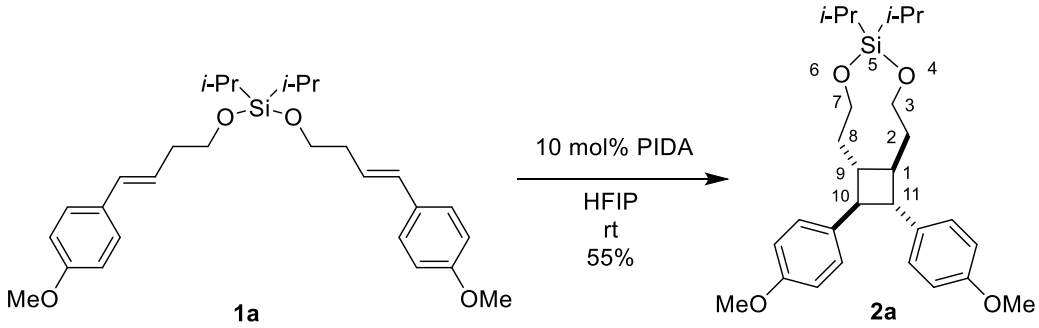
To a solution of ethyl cyclohexylideneacetate (0.525 g, 3.13 mmol) in anhydrous PhMe (25 mL) under an atmosphere of argon at –78 °C was added 1 M DIBAL-H in PhMe (7.9 mL, 7.8 mmol), and the reaction was stirred at this temperature for 3 h. The reaction mixture was warmed to r.t. and H_2O (1 mL), then aqueous 1M NaOH solution (7.5 mL), followed again by H_2O (2.5 mL), were added, with 5 minutes between each addition, maintaining vigorous stirring. The mixture was then poured into a separating funnel, and after phase separation, the aqueous phase was extracted with PhMe (2 x 25 mL). The combined organic layers were then washed with brine, dried over $MgSO_4$, filtered through a plug of silica gel, and the solvent removed in vacuo to yield a colourless oil, which is then added a stirring bar and dry Et_2O (25 mL). The solution was cooled to 0 °C and 1M PBr_3 (1.25 mL, 1.25 mmol) was added under Ar. The reaction was stirred until completion, monitored by TLC analysis and quenched with $NaHCO_3$. The layers were separated and the aqueous layer extracted with Et_2O twice. The combined organics were washed with brine, dried over $MgSO_4$, filtered and the solvent was evaporated to give the pure bromide as a colourless oil (0.51 g, 86%). Then From (2-bromoethylidene)cyclohexane (529.2 mg, 2.800 mmol), alcohol **S2e** (328.0 mg, 2.000 mmol) and NaH (128.0 mg, 3.200 mmol, 60% in mineral oil) following the general procedure, diene **4g** was obtained. Chromatographic purification (8% Et_2O - pentane) gave **4g** as a colorless oil (390.6 mg, 72%).

Data for **S3b**: $\boldsymbol{R_f}$ 0.50 (20% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.32 (2H, d, *J* = 8.7 Hz, Ar), 6.85 (2H, d, *J* = 8.7 Hz, Ar), 6.55 (1H, d, *J* = 15.9 Hz, 4-H), 6.17 (1H, dt, *J* = 15.9, 6.2 Hz, 3-H), 5.32 (1H, t, *J* = 7.0 Hz, 6-H), 4.11 (2H, dd, *J* = 6.2, 1.4 Hz, 2-H_2), 4.03 (2H, d, *J* = 7.0 Hz, 5-H_2), 3.80 (3H, s, OMe), 2.16-2.21 (2H, m, CH_2 cyclohexyl), 2.11-2.15 (2H, m, CH_2 cyclohexyl), 1.51-1.59 (6H, m, 3 x CH_2 cyclohexyl).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.3 (C Ar), 145.1 (C Ar), 132.1 (C-4), 129.7 (C-7), 127.8 (2 x CH Ar), 124.3 (C-3), 117.9 (C-6), 114.1 (2 x CH Ar), 70.8 (C-2), 65.7 (C-5), 55.4 (OMe), 37.2 (CH_2 cyclohexyl), 29.2 (CH_2 cyclohexyl), 28.5 (CH_2 cyclohexyl), 27.9 (CH_2 cyclohexyl), 26.8 (CH_2 cyclohexyl). **IR** (film) ν_{max} 2923, 2849, 1380, 1251, 1151, 1178, 1037 cm^{-1}.**HRMS** (ESI): calculated for $C_{18}H_{25}O_2$ $[M+H]^+$ requires *m/z* 273.1849, found *m/z* 273.1839.

9. General procedure C - hypervalent iodine promoted cycloaddition:

To a solution of 1.0 eq. of diene in HFIP (10 mL/mmol), under argon, 10 mol% of hypervalent iodine reagent was added. The reaction was monitored by TLC until completion, and the solvent was evaporated under reduced pressure to give the corresponding cyclobutane, that was purified by chromatography on silica gel using the appropriate mixture of eluents.

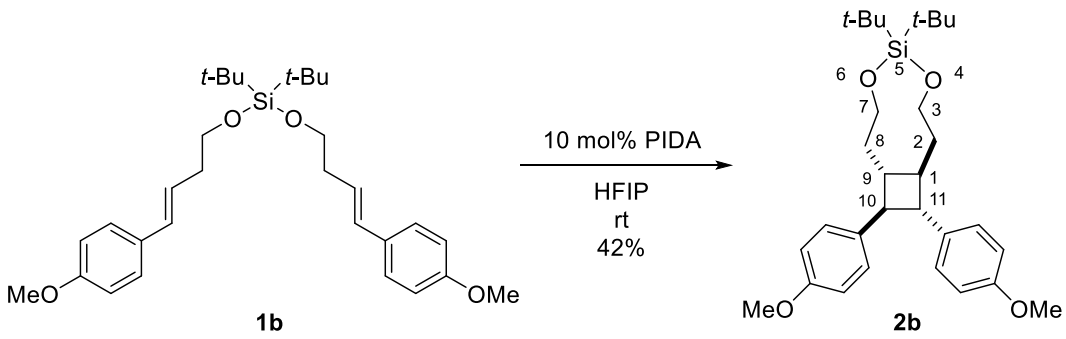
9.1. (±)-(1*R*,9*R*,10*S*,11*S*)-5,5-Diisopropyl-10,11-bis(4-methoxyphenyl)-4,6-dioxa-5-silabicyclo[7.2.0]undecane, 2a.



From diene **1a** (20.0 mg, 0.0427 mmol) and PIDA (1.38 mg, 0.00429 mmol) following the general procedure, cyclobutane **2a** was obtained. Chromatographic purification (gradient elution: 8% → 10% Et_2O - pentane) gave **2a** as a colorless oil (11.4 mg, 55%).

Data for **2a**: R_f 0.5 (30% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.10-7.16 (4H, m, Ar), 6.78-6.84 (4H, m, Ar), 3.78 (6H, s, 2 x OMe), 3.71 (4H, t, J = 7.1 Hz, 3-H_2 and 7-H_2), 2.83-2.89 (2H, m, 10-H and 11-H), 2.19-2.09 (2 H, m, 1-H and 9-H), 1.84-1.94 (4H, m, 2-H_2 and 8-H_2), 0.86-1.03 (14 H, m, 2 x *i*-Pr). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.2 (2 x C Ar), 136.0 (2 x C Ar), 128.0 (4 x CH Ar), 113.8 (4 x CH Ar), 60.9 (C-3 and C-7), 55.4 (2 x OMe), 52.04 and 51.96 (C-10 and C-11), 42.5 (C-1 and C-9), 39.6 (C-2 and C-8), 17.6, 17.52 and 17.48 (4 x CH_3 *i*-Pr), 12.2 and 12.0 (2 x CH *i*-Pr). **IR** (film) ν_{max} 2926, 2865, 1511, 1462, 1245, 1176, 1088 cm^{-1}. **HRMS** (EI): calculated for $C_{28}H_{40}O_4Si$ $[M]^+$ requires *m/z* 468.2696, found *m/z* 468.2689.

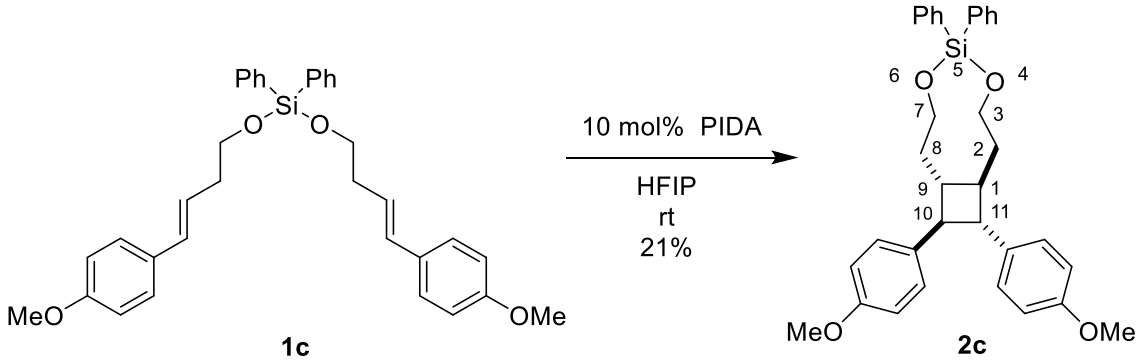
9.2. (±)-(1*R*,9*R*,10*S*,11*S*)-5,5-Di*tert*-butyl-10,11-bis(4-methoxyphenyl)-4,6-dioxa-5-silabicyclo[7.2.0]undecane, 2b.



From diene **1b** (20.5 mg, 0.0413 mmol) and PIDA (1.33 mg, 0.00413 mmol) following the general procedure, cyclobutane **2b** was obtained. Chromatographic purification (gradient elution: 8% → 10% Et_2O - pentane) gave **2b** as a colorless oil (8.6 mg, 42%).

Data for **2b**: $\boldsymbol{R_f}$ 0.45 (30% Et_2O - pentane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.16 (2H, d, *J* = 8.7 Hz, Ar), 7.14 (2H, d, *J* = 8.7 Hz, Ar), 6.81 (4H, d, *J* = 8.5 Hz, Ar), 3.78-3.84 (4H, m, 3-H_2 and 7-H_2), 3.77 (6H, s, 2 x OMe), 2.83-2.90 (2H, m, 10-H and 11-H), 2.12-2.19 (2H, m, 1-H and 9-H), 1.94-1.83 (4H, m, 2-H_2 and 8-H_2), 0.87-0.96 (18H, m, 6 x CH_3 *t*-Bu). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 158.2 (2 x C Ar), 136.06 (C Ar), 136.04 (C Ar), 128.00 (2 x CH Ar), 127.97 (2 x CH Ar), 113.87 (2 x CH Ar), 113.85 (2 x CH Ar), 61.82 and 61.80 (C-3 and C-7), 55.4 (2 x OMe), 52.2 and 52.0 (C-10 and C-11), 42.6 and 42.4 (C-1 and C-9), 40.1 and 39.8 (C-2 and C-8), 27.98 (4 x CH_3 *t*-Bu), 27.95 (2 x CH_3 *t*-Bu), 21.2 (2 x C *t*-Bu). **IR** (film) ν_{max} 2980, 2888, 2360, 2341, 1383, 1249, 1151, 1087, 668 cm^{-1}. **HRMS:** calculated for $C_{30}H_{45}O_4Si$ $[M]^+$ requires *m/z* 497.3087, found *m/z* 497.3091.

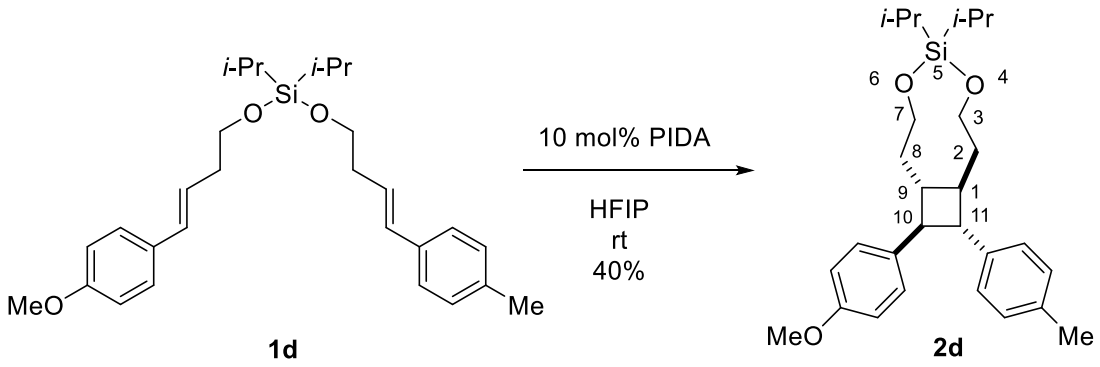
9.3. (±)-(1*R*,9*R*,10*S*,11*S*)-10,11-Bis(4-methoxyphenyl)-5,5-diphenyl-4,6-dioxa-5-silabicyclo[7.2.0]undecane, 2c.



From diene **1c** (14.0 mg, 0.0261 mmol) and PIDA (0.84 mg, 0.0026 mmol) following the general procedure, cyclobutane **2c** was obtained. Chromatographic purification (gradient elution: 10% → 30% Et_2O - pentane) gave **2c** as a colorless oil (3.1 mg, 21%).

Data for **2c**: $\boldsymbol{R_f}$ 0.5 (30% Et_2O - pentane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.47-7.59 (4H, m, Ar), 7.28-7.43 (6H, m, Ar), 7.06-7.10 (4H, m, Ar), 6.74-6.82 (4H, m, Ar), 3.74-3.90 (4H, m, 3-H_2 and 7-H_2), 3.77 (6H, s, 2 x OMe), 2.80-2.86 (2H, m, 10-H and 11-H), 2.18-2.23 (2H, m, 1-H and 9-H), 1.89-1.99 (4H, m, 2-H_2 and 8-H_2). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 158.2 (C Ar), 158.1 (C Ar), 135.92 (C Ar), 135.85 (C Ar), 135.0 (2 x CH Ar), 134.9 (C Ar), 133.1 (C Ar), 130.0 (2 x CH Ar), 128.03 (2 x CH Ar), 128.01 (2 x CH Ar), 128.0 (2 x CH Ar), 127.9 (2 x CH Ar), 113.84 (2 x CH Ar), 113.84 (2 x CH Ar), 61.4 and 61.3 (C-3 and C-7), 55.4 (2 x OMe), 52.1 and 51.9 (C-10 and C-11), 42.5 (C-1 and C-9), 39.2 and 39.1 (C-2 and C-8). **IR** (film) ν_{max} 2980, 2360, 2341, 1510, 1249, 1075 cm^{-1}. **HRMS:** calculated for $C_{34}H_{37}O_4Si$ $[M]^+$ requires *m/z* 537.2461, found *m/z* 537.2465.

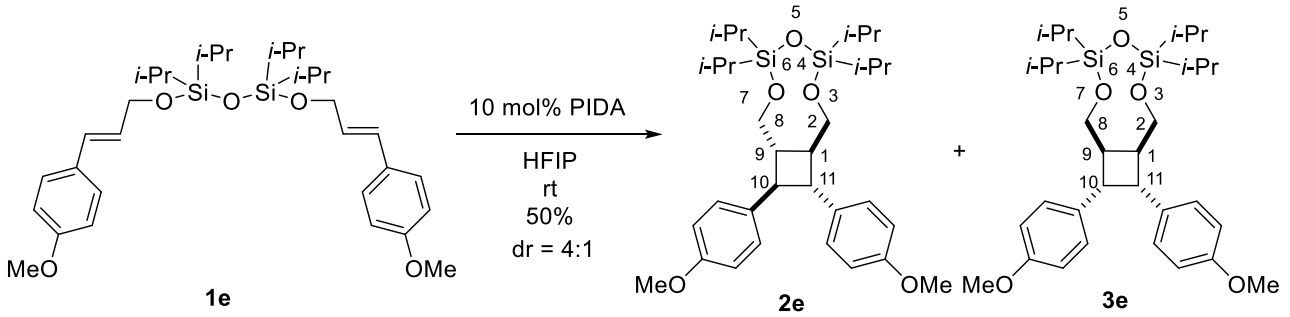
9.4. (±)-(1*R*,9*R*,10*S*,11*S*)-5,5-Diisopropyl-10-(4-methoxyphenyl)-11-(*p*-tolyl)-4,6-dioxa-5-silabicyclo[7.2.0]undecane, 2d.



From diene **1d** (20.0 mg, 0.043 mmol) and PIDA (1.40 mg, 0.0043 mmol) following the general procedure except using 0.02M of HFIP, cyclobutane **2d** was obtained. Chromatographic purification (gradient elution: 1.5% →3% Et_2O - pentane) gave **2d** as a colorless oil (8.0 mg, 40%).

Data for **2d**: R_f 0.55 (20% Et_2O - pentane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.13 (2H, d, *J* = 8.7 Hz, Ar), 7.07-7.11 (4H, m, Ar), 6.83 (2H, d, *J* = 8.7 Hz, Ar), 3.99 (2H, ddd, *J* = 11.1, 7.6, 2.2 Hz, 3-H_A and 7-H_A), 3.84-3.89 (2H, m, 3-H_B and 7-H_B), 3.78 (3H, s, OMe), 2.90 (2H, d, *J* = 8.7 Hz, 10-H and 11-H), 2.28-2.33 (2H, m, 1-H and 9-H), 2.31 (3H, s, Me), 2.00-2.10 (2 H, m, 2-H_A and 8-H_A), 1.81-1.72 (2H, m, 2-H_B and 8-H_B), 1.05-1.08 (14 H, m, 2 x *i*-Pr). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 158.2 (C Ar), 140.8 (C Ar), 136.1 (C Ar), 135.8 (C Ar), 129.2 (2 x CH Ar), 128.0 (2 x CH Ar), 126.9 (2 x CH Ar), 113.9 (2 x CH Ar), 62.58 and 62.55 (C-3 and C-7), 55.4 (OMe), 52.1 and 51.6 (C-10 and C-11), 44.4 and 44.2 (C-1 and C-9), 38.83 and 38.79 (C-2 and C-8), 21.2 (Me), 17.7 (2 x CH_3 *i*-Pr), 17.6 (2 x CH_3 *i*-Pr), 12.1 (2 x CH *i*-Pr). **IR** (film) ν_{max} 2926, 2867, 1512, 1249, 1124, 1035 cm^{-1}. **HRMS** (El): calculated for $C_{28}H_{40}O_3Si$ $[M]^+$ requires *m/z* 452.2747, found *m/z* 452.2751

9.5. (±)-(1*S*,9*S*,10*R*,11*R*)-4,4,6,6-Tetraisopropyl-10,11-bis(4-methoxyphenyl)-3,5,7-trioxa-4,6-disilabicyclo[7.2.0]undecane, 2e and (±)-(1*R*,9*S*,10*R*,11*S*)-4,4,6,6-Tetraisopropyl-10,11-bis(4-methoxyphenyl)-3,5,7-trioxa-4,6-disilabicyclo[7.2.0]undecane, 3e.

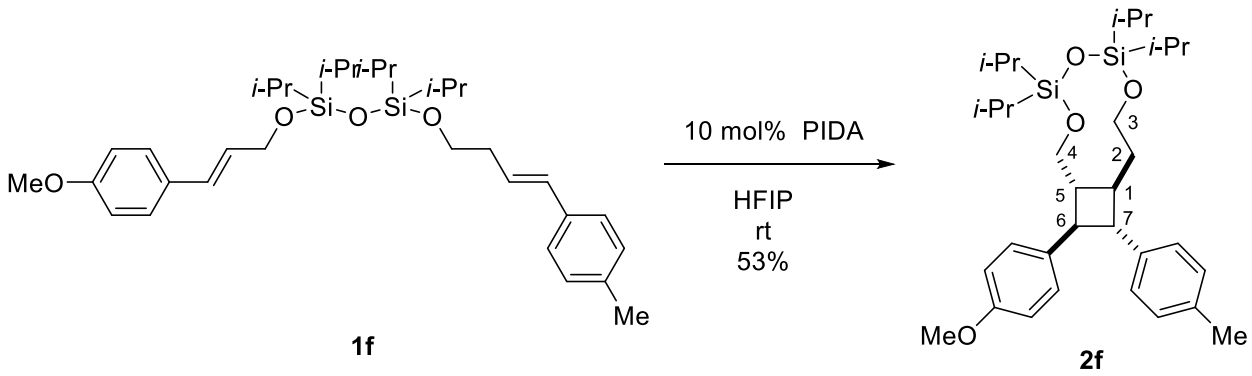


From diene **1e** (18.1 mg, 0.0318 mmol) and PIDA (1.00 mg, 0.00310 mmol) following the general procedure, a 4:1 mixture of cyclobutanes **2e**:**3e** was obtained. Chromatographic purification (8% Et_2O - pentane) gave an inseparable 4:1 mixture of **2e**:**3e** as a colorless oil (7.5 mg, 50%).

Data for **2e** (from the mixture): R_f 0.55 (30% Et_2O - pentane). **M.p.**: 60 °C (solvent: 5% diethyl ether in pentane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.12 (4H, d, *J* = 8.7 Hz, Ar), 6.81 (4H, d, *J* = 8.6 Hz, Ar), 4.10 (2H, dd, *J* = 11.5, 2.8 Hz, 2-H_A and 8-H_A), 3.78-3.81 (2H, m, 2-H_B and 8-H_B), 3.78 (6H, s, 2 x OMe), 3.03-3.07 (2H, m, 10-H and 11-H), 2.47-2.11 (2H, m, 1-H and 9-H), 0.99-1.13 (28H, m, 4 x *i*-Pr). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 158.2 (2 x C Ar), 134.9 (2 x C Ar), 128.1 (4 x CH Ar), 113.9 (4 x CH Ar), 64.9 (C-2 and C-8), 55.4 (2 x OMe), 46.5 (C-10 and C-11), 45.4 (C-1 and C-9), 17.7 (4 x CH_3 *i*-Pr), 17.5 (4 x CH_3 *i*-Pr), 13.3 (2 x CH *i*-Pr), 13.2 (2 x CH *i*-Pr). **IR** (film) ν_{max} 2980, 2969, 2360, 2341, 1513, 1248, 1045 cm^{-1}. **HRMS** (ESI): calculated for $C_{32}H_{51}O_5Si$ $[M]^+$ requires *m/z* 571.3270, found *m/z* 571.3269.

Data for **3e** (from the mixture): **^{1}H NMR (500 MHz, $CDCl_3$)** δ 6.85 (4H, d, *J* = 8.7 Hz, Ar), 6.64 (4H, d, *J* = 8.7 Hz, Ar), 4.20 (2H, dd, *J* = 7.4, 3.1 Hz, 2-H_A and 8-H_A), 4.10 (2H, dd, *J* = 11.5, 2.8 Hz, 2-H_B and 8-H_B), 3.75 (2H, d, *J* = 6.1 Hz, 10-H and 11-H), 3.70 (6H, s, 2 x OMe), 2.96-3.00 (2H, m, 1-H and 9-H), 0.99-1.13 (28H, m, 4 x *i*-Pr). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 157.6 (2 x C Ar), 133.1 (2 x C Ar), 129.3 (4 x CH Ar), 113.3 (4 x CH Ar), 62.4 (C-2 and C-8), 55.4 (2 x OMe), 42.5 (C-10 and C-11), 41.4 (C-1 and C-9), 17.6 (4 x CH_3 *i*-Pr), 17.5 (4 x CH_3 *i*-Pr), 13.3 (4 x CH *i*-Pr).

9.6. (±)-(1*R*,10*S*,11*S*,12*R*)-4,4,6,6-Tetraisopropyl-12-(4-methoxyphenyl)-11-(*p*-tolyl)-3,5,7-trioxa-4,6-disilabicyclo[8.2.0]dodecane, 2f.



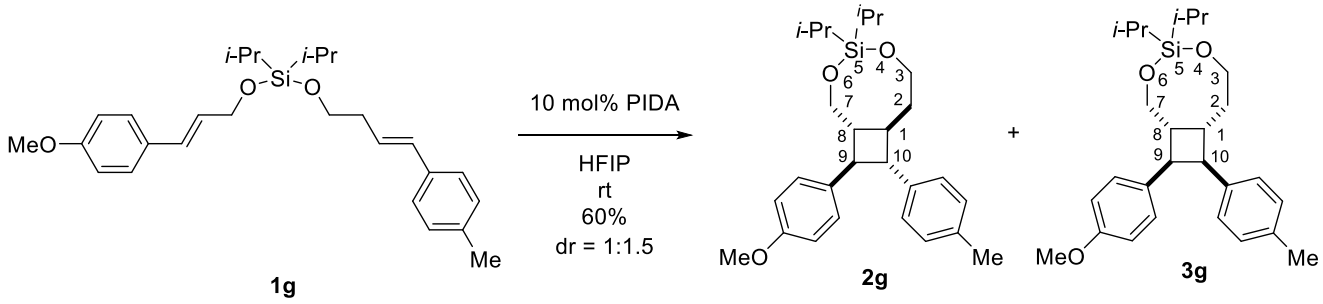
1f **2f**

From diene **1f** (39.9 mg, 0.0702 mmol) and PIDA (2.26 mg, 0.00702 mmol) following the general procedure, cyclobutane **2f** was obtained. Chromatographic purification (3% Et_2O - pentane) gave **2f** as a colorless oil (21.0 mg, 53%).

Data for **2f**: R_f 0.6 (30% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.15 (2H, d, *J* = 8.6 Hz, Ar), 7.05-7.12 (4H, m, Ar), 6.83 (2H, d, *J* = 8.7 Hz, Ar), 4.00 (1H, ddd, *J* = 11.8, 9.9, 2.1 Hz, 3-H_A), 3.94 (1H, dd, *J* = 10.8, 2.4 Hz, 4-H_A), 3.79-3.84 (2H, m, 3-H_B and 4-H_B), 3.78 (3H, s, OMe), 3.06 (1H, t, *J* = 9.7 Hz, 6-H), 2.89 (1H, t, *J* = 9.7 Hz, 7-H), 2.60 (1H, dtd, *J* = 11.7, 9.0, 2.8 Hz, 1-H), 2.30 (3H, s, Me), 2.13-2.00 (2H, m, 2-H_A and 5-H), 1.50 (1H, dtd, *J* = 14.0, 11.5, 2.6 Hz, 2-H_B), 1.00-1.12 (28H, m, 4 x *i*-Pr). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 158.2 (C Ar), 140.4 (C Ar), 135.7 (C Ar),

135.5 (C Ar), 129.1 (2 x CH Ar), 128.3 (2 x CH Ar), 127.0 (2 x CH Ar), 113.9 (2 x CH Ar), 64.5 (C-4), 60.4 (C-3), 55.4 (OMe), 50.8 (C-7), 49.7 (C-5), 45.7 (C-6), 40.2 (C-1), 37.8 (C-2), 21.2 (Me), 17.73 (CH_3 *i*-Pr), 17.71 (CH_3 *i*-Pr), 17.68 (CH_3 *i*-Pr), 17.66 (3 x CH_3 *i*-Pr), 17.64 (CH_3 *i*-Pr), 17.58 (CH_3 *i*-Pr), 13.7 (CH *i*-Pr), 13.5 (CH *i*-Pr), 13.3 (CH *i*-Pr), 13.2 (CH *i*-Pr). **IR** (film) ν_{max} 2980, 2889, 2360, 1462, 1250, 1151, 1073 cm^{-1}. **HRMS** (CI): calculated for $C_{33}H_{53}O_4Si_2$ $[M+H]^+$ requires *m/z* 569.3482, found *m/z* 569.3469.

9.7. (±)(1*R*,8*S*,9*S*,10*R*)-4,4-Diisopropyl-9-(4-methoxyphenyl)-10-(*p*-tolyl)-3,5-dioxa-4 silabicyclo[6.2.0]decane, 2g and (±)-(1*R*,8*R*,9*R*,10*R*)-4,4-diisopropyl-9-(4-methoxy phenyl)-10-(*p*-tolyl)-3,5-dioxa-4-silabicyclo[6.2.0]decane, 3g.



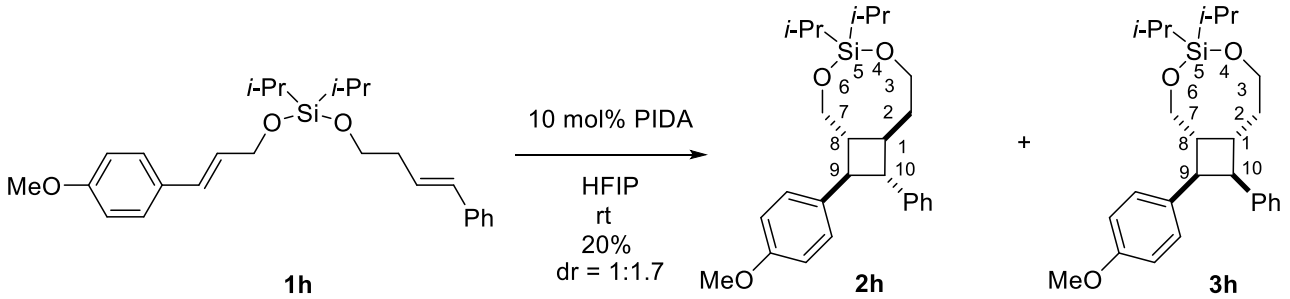
From diene **1g** (19.4 mg, 0.0443 mmol) and PIDA (1.40 mg, 0.00435 mmol) following the general procedure, a 1:1.5 mixture of cyclobutanes **2g**:**3g** was obtained. Chromatographic purification (gradient elution: 2% → 6% Et_2O - pentane) gave an inseparable 1:1 mixture of **2g**:**3g** as a colorless oil (11.9 mg, 60%).

Data for **2g (**from the mixture): R_f 0.6 (10% Et_2O - pentane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.08-7.13 (6 H, m, Ar), 6.83 (2H, d, *J* = 6.3 Hz, Ar), 4.12-4.15 (1H, m, 7-H_A), 3.97-4.01 (1H, m, 3-H_A), 3.84-3.89 (1H, m, 3-H_B), 3.74-3.80 (1H, m, 7-H_B), 3.78 (3H, s, OMe), 2.98 (1H, t, *J* = 9.4 Hz, 10-H), 2.91 (1H, t, *J* = 9.4 Hz, 9-H), 2.49 (1H, dtd, *J* = 10.7, 8.6, 4.1 Hz, 8-H), 2.32 (3H, s, Me), 2.18-2.26 (1H, m, 1-H), 2.08 (1H, ddt, *J* = 15.6, 7.9, 4.0 Hz, 2-H_A), 1.61 (1H, m, 2-H_B), 1.02-1.11 (14H, m, 2 x *i*-Pr). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 158.1 (C Ar), 140.2 (C Ar), 135.9 (C Ar), 135.2 (C Ar), 129.1 (2 x CH Ar), 128.6 (2 x CH Ar), 126.7 (2 x CH Ar), 113.8 (2 x CH Ar), 68.6 (C-7), 61.6 (C-3), 55.3 (OMe), 51.8 (C-10), 47.5 (C-9), 46.4 (C-8), 44.3 (C-1), 36.6 (C-2), 21.0 (Me), 17.72 (CH_3 *i*-Pr), 17.71 (CH_3 *i*-Pr), 17.67 (CH_3 *i*-Pr), 17.65 (CH_3 *i*-Pr), 12.69 (CH *i*-Pr), 12.67 (CH *i*-Pr). **IR** (film) ν_{max} 2926, 2360, 2341, 1513, 1248, 1112 cm^{-1}. **HRMS (Cl):** calculated for $C_{27}H_{39}O_3Si$ $[M+H]^+$ requires *m/z* 439.2668, found *m/z* 439.2269.

Data for **3g** (from the mixture): **^{1}H NMR (500 MHz, $CDCl_3$)** δ 6.89 (4H, m, Ar), 6.81 (2H, d, *J* = 6.3 Hz, Ar), 6.65 (2H, d, *J* = 8.6 Hz, Ar), 4.21 (1H, t, *J* = 11.5 Hz, 7-H_A), 4.08-4.12 (1H, m, 3-H_A), 3.92-3.96 (1H, m, 7-H_B), 3.80-3.84 (1H, m, 3-H_B), 3.71 (3H, s, OMe), 3.44 (1H, dd, *J* = 9.8, 6.4 Hz, 10-H), 3.40 (1H, dd, *J* = 9.9, 6.5 Hz, 9-H), 3.16 (1H, dtd, *J* = 15.3, 7.6, 6.6, 4.0 Hz, 8-H), 2.83-

2.88 (1H, m, 1-H), 2.32-2.39 (1H, m, 2-H_A), 2.21 (3H, s, Me), 1.67-1.71 (1H, m, 2-H_B), 1.02-1.11 (14H, m, 2 x *i*-Pr). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 157.6 (C Ar), 137.3 (C Ar), 135.2 (C Ar), 132.1 (C Ar), 129.0 (4 x CH Ar), 128.0 (2 x CH Ar), 113.2 (2 x CH Ar), 64.9 (C-3), 64.1 (C-7), 55.1 (OMe), 48.8 (C-10), 44.3 (C-9), 41.9 (C-8), 40.0 (C-1), 33.5 (C-2), 21.0 (Me), 17.61 (CH_3 *i*-Pr), 17.57 (CH_3 *i*-Pr), 17.54 (CH_3 *i*-Pr), 17.49 (CH_3 *i*-Pr), 12.4 (CH *i*-Pr), 11.8 (CH *i*-Pr).

9.8. (±)-(1*R*,8*S*,9*S*,10*R*)-4,4-Diisopropyl-9-(4-methoxyphenyl)-10-phenyl-3,5-dioxa-4-silabicyclo[6.2.0]decane, 2h and (±)-(1*R*,8*R*,9*R*,10*R*)-4,4-diisopropyl-9-(4-methoxy phenyl)-10-phenyl-3,5-dioxa-4-silabicyclo[6.2.0]decane, 3h.



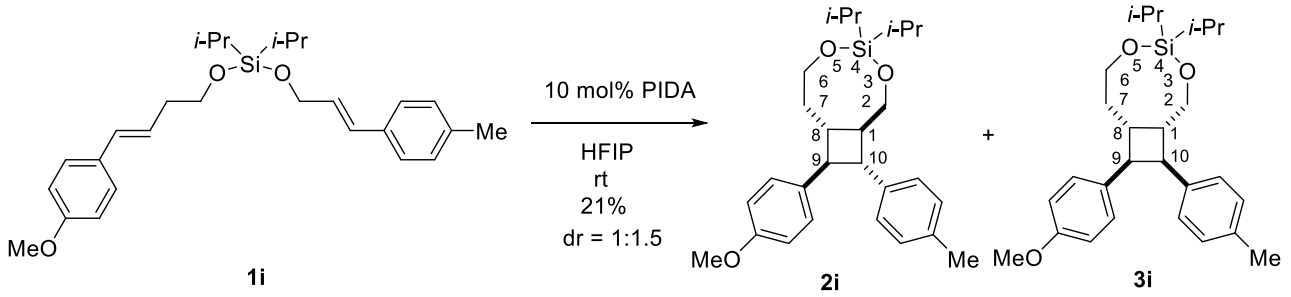
From diene **1h** (16.7 mg, 0.0394 mmol) and PIDA (1.30 mg, 0.00404 mmol) following the general procedure, a 1:1.7 mixture of cyclobutanes **2h**:**3h** was obtained. Chromatographic purification (gradient elution: 3% → 20% Et_2O - pentane) gave an inseparable 1:1.7 mixture of **2h**:**3h** as a colorless oil (3.6 mg, 20%).

Data for **2h** (from the mixture): R_f 0.45 (10% Et_2O - pentane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.27-7.31 (2H, m, Ar), 7.18-7.22 (3H, m, Ar), 7.10-7.14 (2H, m, Ar), 6.83 (2H, d, *J* = 8.8 Hz, Ar), 4.12-4.14 (1H, m, 7-H_A), 3.97-4.01 (1H, m, 3-H_A), 3.88 (1H, dt, J = 9.5, 2.7 Hz, 3-H_B), 3.79-3.81 (1H, m, 7-H_B), 3.78 (3H, s, OMe), 3.03 (1H, t, *J* = 9.5 Hz, 10-H), 2.93 (1H, t, *J* = 9.4 Hz, 9-H), 2.47-2.51 (1H, m, 8-H), 2.24-2.28 (1H, m, 1-H), 2.06-2.14 (1H, m, 2-H_A), 1.58-1.67 (1H, m, 2-H_B), 1.02-1.11 (14H, m, 2 x *i*-Pr). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 158.3 (C Ar), 143.3 (C Ar), 135.2 (C Ar), 128.6 (2 x CH Ar), 127.9 (2 x CH Ar), 126.8 (3 x CH Ar), 113.9 (2 x CH Ar), 68.6 (C-7), 61.6 (C-3), 55.4 (OMe), 52.2 (C-10), 47.5 (C-9), 46.6 (C-8), 44.2 (C-1), 36.7 (C-2), 17.8 (CH_3 *i*-Pr), 17.7 (CH_3 *i*-Pr), 17.5 (CH_3 *i*-Pr), 17.3 (CH_3 *i*-Pr), 12.5 (CH *i*-Pr), 11.9 (CH *i*-Pr). **NOESY- 2D (500 MHz, $CDCl_3$)**: between 9-H and 1-H, between 10-H and 8-H, between 10-H and 2-H_B. **IR** (film) ν_{max} 3026, 2942, 1738, 1513, 1365, 1228 cm^{-1}. **HRMS (Cl):** calculated for $C_{26}H_{37}O_3Si$ $[M+H]^+$ requires *m/z* 425.2512, found *m/z* 425.2500.

Data for **3h** (from the mixture): **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.09 (2H, d, *J* = 7.7 Hz, Ar), 6.99-7.05 (1H, m, Ar), 6.93 (2H, d, *J* = 7.2 Hz, Ar), 6.86 (2H, d, *J* = 8.6 Hz, Ar), 6.63 (2H, d, *J* = 8.7 Hz, Ar), 4.21 (1H, t, *J* = 11.4 Hz, 7-H_A), 4.07-4.11 (1H, m, 3-H_A), 3.92-3.97 (1H, m, 7-H_B), 3.81-3.85 (1H, m, 3-H_B), 3.69 (3H, s, OMe), 3.48 (1H, dd, *J* = 9.9, 6.6 Hz, 10-H), 3.42 (1H, dd, *J* = 9.9,

6.6 Hz, 9-H), 3.12-3.22 (1H, m, 8-H), 2.88-2.92 (1H, m, 1-H), 2.31-2.42 (1H, m, 2-H_A), 1.69-1.73 (1H, m, 2-H_B), 1.02-1.11 (14H, m, 2 x *i*-Pr). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 157.8 (C Ar), 140.5 (C Ar), 132.0 (C Ar), 129.1 (2 x CH Ar), 128.2 (2 x CH Ar), 127.9 (2 x CH Ar), 125.9 (CH Ar), 113.3 (2 x CH Ar), 64.9 (C-3), 64.1 (C-7), 55.2 (OMe), 49.2 (C-10), 44.5 (C-9), 42.0 (C-8), 39.8 (C-1), 33.7 (C-2), 17.8 (CH_3 *i*-Pr), 17.7 (CH_3 *i*-Pr), 17.68 (CH_3 *i*-Pr), 17.62 (CH_3 *i*-Pr), 12.82 (CH *i*-Pr), 12.80 (CH *i*-Pr). **NOESY- 2D (500 MHz, $CDCl_3$)**: between 9-H and 2-H_A, between 9-H and 7-H_A & 7-H_B, between 10-H and 2-H_A & 2-H_B, between 10-H and 7-H_A.

9.9. (±)-(1*R*,8*S*,9*S*,10*R*)-4,4-Diisopropyl-9-(4-methoxyphenyl)-10-(*p*-tolyl)-3,5-dioxa-4-silabicyclo[6.2.0]decane, 2i and (±)-(1*S*,8*S*,9*S*,10*S*)-4,4-Diisopropyl-9-(4-methoxy phenyl)-10-(*p*-tolyl)-3,5-dioxa-4-silabicyclo[6.2.0]decane, 3i.



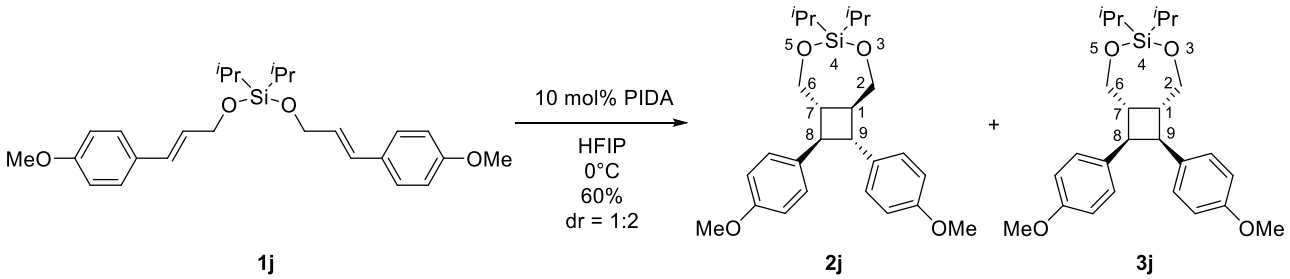
From diene **1i** (33.9 mg, 0.0774 mmol) and PIDA (2.50 mg, 0.00776 mmol) following the general procedure, a 1:1.5 mixture of cyclobutanes **2i**:**3i** was obtained. Chromatographic purification (gradient elution: 3% → 4% Et_2O - pentane) gave an inseparable 1:1.5 mixture of **2i**:**3i** as a colorless oil (6.9 mg, 21%).

Data for **2i (**from the mixture): ***R**$_f$* 0.6 (10% Et_2O - pentane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.13 (2H, d, *J* = 8.6 Hz, Ar), 7.04-7.11 (4H, m, Ar), 6.81-6.83 (2H, m, Ar), 4.12-4.15 (1H, m, 2-H_A), 3.97-4.00 (1H, m, 6-H_A), 3.85-3.89 (1H, m, 6-H_B), 3.76-3.79 (1H, m, 2-H_B), 3.78 (3H, s, OMe), 2.97 (1H, t, *J* = 9.4 Hz, 9-H), 2.91 (1H, t, *J* = 9.3 Hz, 10-H), 2.50 (1H, dtd, *J* = 10.9, 8.6, 4.2 Hz, 1-H), 2.31 (3H, s, Me), 2.18-2.23 (1H, m, 8-H), 2.01-2.12 (1H, m, 7-H_A), 1.59-1.64 (1H, m, 7-H_B), 1.02-1.10 (14H, m, 2 x *i*-Pr). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 158.3 (C Ar), 140.1 (C Ar), 136.0 (C Ar), 135.3 (C Ar), 129.24 (2 x CH Ar), 127.9 (2 x CH Ar), 126.8 (2 x CH Ar), 114.0 (2 x CH Ar), 68.8 (C-2), 61.7 (C-6), 55.4 (OMe), 51.5 (C-9), 48.2 (C-10), 46.3 (C-1), 44.6 (C-8), 36.7 (C-7), 21.2 (Me), 17.72 (CH_3 *i*-Pr), 17.6 (CH_3 *i*-Pr), 17.5 (CH_3 *i*-Pr), 17.0 (CH_3 *i*-Pr), 12.6 (CH *i*-Pr), 11.9 (CH *i*-Pr). **IR** (film) ν_{max} 2926, 2360, 2341, 1513, 1248, 1112 cm^{-1}. **HRMS (ESI)**: calculated for $C_{27}H_{38}O_3SiNa$ $[M+Na]^+$ requires *m/z* 461.2482, found *m/z* 461.2484.

Data for **3i** (from the mixture): **^{1}H NMR (500 MHz, $CDCl_3$)** δ 6.91 (2H, d, *J* = 8.0 Hz, Ar), 6.83-6.96 (4H, m, Ar), 6.64 (2H, d, *J* = 8.7 Hz, Ar), 4.21 (1H, t, *J* = 11.4 Hz, 2-H_A), 4.07-4.14 (1H, m, 6-H_A), 3.93-3.97 (1H, m, 2-H_B), 3.80-3.84 (1H, m, 6-H_B), 3.70 (3H, s, OMe), 3.44 (1H, dd, *J* =

10.0, 6.7 Hz, 9-H), 3.39 (1H, dd, *J* = 9.9, 6.6 Hz, 10-H), 3.13-3.22 (1H, m, 1-H), 2.82-2.89 (1H, m, 8-H), 2.30-2.33 (1H, m, 7-H_A), 2.21 (3H, s, Me), 1.65-1.72 (1H, m, 7-H_B), 1.02-1.10 (14H, m, 2 x *i*-Pr). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 157.7 (C Ar), 137.0 (C Ar), 135.5 (C Ar), 132.7 (C Ar), 129.20 (2 x CH Ar), 128.7 (2 x CH Ar), 128.1 (2 x CH Ar), 113.4 (2 x CH Ar), 65.0 (C-6), 64.2 (C-2), 55.3 (OMe), 48.5 (C-9), 44.9 (C-10), 41.7 (C-1), 40.5 (C-8), 33.7 (C-7), 21.7 (Me), 17.9 (CH_3 *i*-Pr), 17.80 (CH_3 *i*-Pr), 17.75 (CH_3 *i*-Pr), 17.6 (CH_3 *i*-Pr), 12.85 (CH *i*-Pr), 12.81 (CH *i*-Pr).

9.10. (±)-(1*S*,7*S*,8*R*,9*R*)-4,4-Diisopropyl-8,9-bis(4-methoxyphenyl)-3,5-dioxa-4-silabicyclo[5.2.0]nonane, 2j and (±)-(1*R*,7*S*,8*R*,9*S*)-4,4-Diisopropyl-8,9-bis(4-methoxyphenyl)-3,5-dioxa-4-silabicyclo[5.2.0]nonane, 3j.



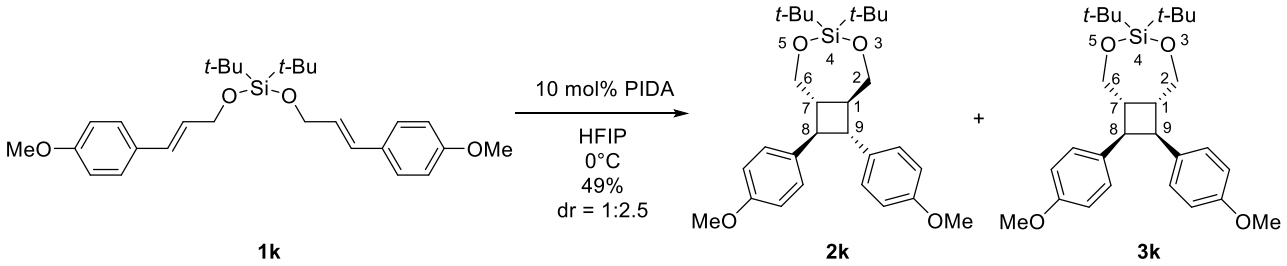
1j **2j** **3j**

From diene **1j** (21.2 mg, 0.0482 mmol) and PIDA (1.60 mg, 0.00497 mmol) following the general procedure except conducting the reaction at 0°C, a 1:2 mixture of cyclobutanes **2j**:**3j** was obtained. Chromatographic purification (gradient elution: 5% → 10% Et_2O - pentane) gave a separable 1:2 mixture of **2j**:**3j** as a colorless oil (13.0 mg, 60%).

Data for **2j**: ***R*$_f$** 0.54 (30% Et_2O - pentane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.11 (4H, d, *J* = 8.6 Hz, Ar), 6.84 (4H, d, *J* = 8.5 Hz, Ar), 4.17-4.21 (2H, m, 2-H_A and 6-H_A), 3.74-3.81 (2H, m, 2-H_B and 6-H_B), 3.79 (6H, s, 2 x OMe), 3.02 (2H, d, *J* = 9.4 Hz, 8-H and 9-H), 2.33-2.41 (2H, m, 1-H and 7-H), 1.03-1.06 (14 H, m, 2 x *i*-Pr). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 158.5 (2 x C Ar), 134.5 (2 x C Ar), 127.8 (4 x C-H Ar), 114.1 (4 x CH Ar), 68.6 (C-2 and C-6), 55.4 (2 x OMe), 49.9 (C-1 and C-7), 47.1 (C-8 and C-9), 17.6 (2 x CH_3 *i*-Pr), 17.5 (2 x CH_3 *i*-Pr), 13.4 (2 x CH *i*-Pr**)**. **IR** (film) ν_{max} 2980, 2360, 1611, 1513, 1247, 1121 cm^{-1}**.** **HRMS** (CI): calculated for $C_{26}H_{37}O_4Si$ $[M+H]^+$ requires 441.2461, found 441.2463.

Data for **3j**: **^{1}H NMR (500 MHz, $CDCl_3$)** δ 6.83 (4H, d, *J* = 8.6 Hz, Ar), 6.64 (4H, d, *J* = 8.7 Hz, Ar), 4.21-4.23 (2H, m, 2-H_A and 6-H_A), 4.07-4.11 (2H, m, 2-H_B and 6-H_B), 3.71 (6H, s, 2 x OMe), 3.60 (2H, d, *J* = 6.0 Hz, 8-H and 9-H), 3.12 (2 H, m, 1-H and 7-H), 1.06-1.09, 1.07-1.16 (14H, m, 2 x *i*-Pr). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 157.8 (2 x C Ar), 132.4 (2 x C Ar), 129.2 (4 x CH Ar), 113.4 (4 x CH Ar), 64.2 (C-2 and C-6), 55.3 (2 x OMe), 42.9 (C-8 and C-9), 42.0 (C-1 and C-7), 17.6 (2 x CH_3 *i*-Pr), 17.3 (2 x CH_3 *i*-Pr), 12.3 (CH *i*-Pr), 11.9 (CH *i*-Pr).

9.11. (±)-(1*S*,7*S*,8*R*,9*R*)-4,4-Di-*tert*-butyl-8,9-bis(4-methoxyphenyl)-3,5-dioxa-4-silabicyclo[5.2.0]nonane, 2k and (±)-(1*R*,7*S*,8*R*,9*S*)-4,4-Di-*tert*-butyl-8,9-bis(4-methoxyphenyl) -3,5-dioxa-4-silabicyclo[5.2.0]nonane, 3k.

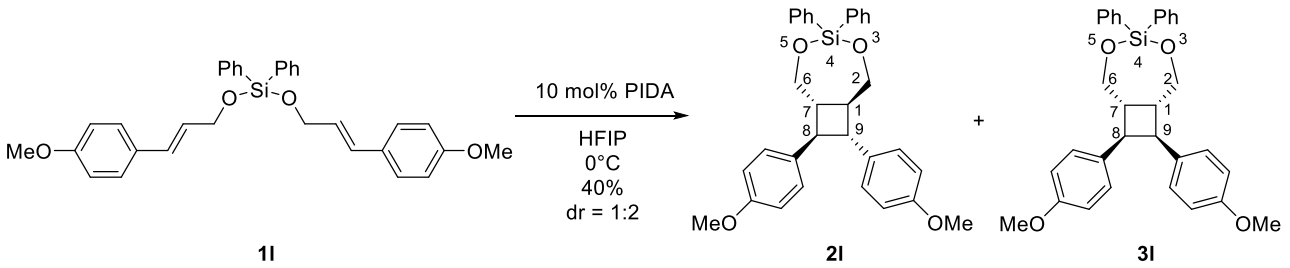


From diene **1k** (15.6 mg, 0.0333 mmol) and PIDA (1.10 mg, 0.00333 mmol) following the general procedure except conducting the reaction at 0°C, a 1:2.5 mixture of cyclobutanes **2k**:**3k** was obtained. Chromatographic purification (gradient elution: 4% → 9% Et_2O - pentane) gave a separable 1:2.5 mixture of **2k**:**3k** as a colorless oil (7.5 mg, 49%).

Data for **2k**: R_f 0.45 (30% Et_2O - pentane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.10 (4H, d, *J* = 8.6 Hz, Ar), 6.84 (4H, d, *J* = 8.7 Hz, Ar), 4.22 (2H, dd, *J* = 10.6, 3.4 Hz, 2-H_A and 6-H_A), 3.85 (2H, t, *J* = 10.4 Hz, 2-H_B and 6-H_B), 3.78 (6H, s, OMe), 3.02 (2H, d, *J* = 9.5 Hz, 8-H and 9-H), 2.28-2.37 (2H, m, 1-H and 7-H), 1.00 (18 H, s, 6 x CH_3 *t*-Bu). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 158.4 (2 x C Ar), 134.6 (2 x C Ar), 127.9 (4 x C-H Ar), 114.1 (4 x C-H Ar), 69.6 (C-2 and C-6), 55.4 (2 x OMe), 50.3 (C-1 and C-7), 46.8 (C-8 and C-9), 27.9 (6 x CH_3 *t*-Bu), 22.0 (2 x C *t*-Bu). **IR** (film) ν_{max} 2980, 2932, 1513, 1249, 1124, 1078, 826cm^{-1}. **HRMS (Cl):** calculated for $C_{28}H_{40}O_4Si$ $[M+H]^+$ requires 469.2744, found 469.2767.

Data for **3k**: **^{1}H NMR (500 MHz, $CDCl_3$)** δ 6.83 (4H, d, *J* = 7.9 Hz, Ar), 6.64 (4H, d, *J* = 8.7 Hz, Ar), 4.34-4.43 (2H, m, 2-H_A and 6-H_A), 4.10 (2H, dd, *J* = 11.7, 4.7 Hz, 2-H_B and 6-H_B), 3.70 (6H, s, OMe), 3.42 (2H, d, *J* = 5.7 Hz, 8-H and 9-H), 3.15-3.25 (2H, m, 1-H and 7-H), 1.10 (9H, s, 3 x CH_3 *t*-Bu), 1.04 (9 H, s, 3 x CH_3 *t*-Bu). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 157.7 (2 x C Ar), 132.5 (2 x C Ar), 129.1 (4 x C-H Ar), 113.4 (4 x C-H Ar), 66.0 (C-2 and C-6), 55.3 (2 x OMe), 42.6 (C-8 and C-9), 41.7 (C-1 and C-7), 28.1 (3 x CH_3 *t*-Bu), 27.5 (3 x CH_3 *t*-Bu), 22.8 (C *t*-Bu), 20.3 (C *t*-Bu). **NOESY- 2D (500 MHz, $CDCl_3$)**: between 1-H/7-H and 8-H/9-H, between 1-H/7-H and 2-H_2, between 1-H/7-H and 6-H_2.

9.12. (±)-(1*S*,7*S*,8*R*,9*R*)-8,9-Bis(4-methoxyphenyl)-4,4-diphenyl-3,5-dioxa-4-silabicyclo[5.2.0]nonane, 2l and (±)-(1*R*,7*S*,8*R*,9*S*)-8,9-Bis(4-methoxyphenyl)-4,4-diphenyl-3,5-dioxa-4-silabicyclo[5.2.0]nonane, 3l.

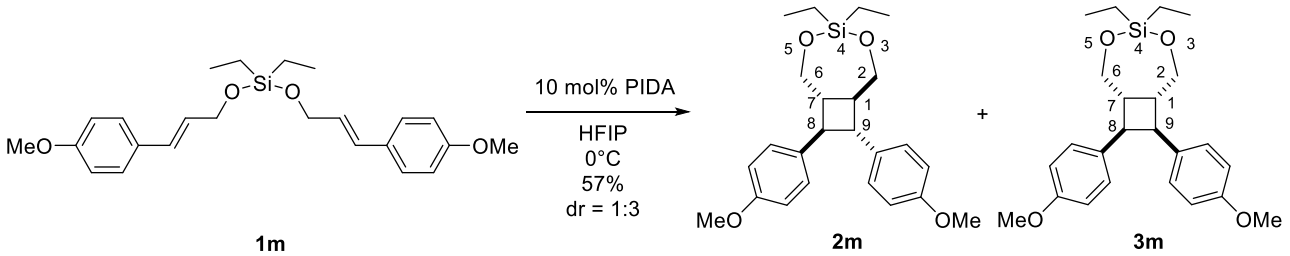


From diene **1l** (16.1 mg, 0.0317 mmol) and PIDA (1.10 mg, 0.00317 mmol) following the general procedure except conducting the reaction at 0°C, a 1:2 mixture of cyclobutanes **2l**:**3l** was obtained. Chromatographic purification (15% Et_2O - pentane) gave an inseparable 1:2 mixture of **2l**:**3l** as a colorless oil (6.5 mg, 40%).

Data for **2l** (from the mixture): R_f 0.54 (30% Et_2O - pentane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.79 (3H, dd, *J* = 7.9, 1.5 Hz, Ar), 7.79 (7H, dd, *J* = 7.9, 1.5 Hz, Ar), 7.00-7.05 (4H, m, Ar), 6.79-6.82 (4H, m, Ar), 4.39 (2H, dd, *J* = 10.7, 3.8 Hz, 2-H_A and 6-H_A), 3.92 (2H, t, *J* = 10.7 Hz, 2-H_B and 6-H_B), 3.77 (6H, s, 2 x OMe), 2.95 (2H, d, *J* = 9.3 Hz, 8-H and 9-H), 2.48-2.55 (2H, m, 1-H and 7-H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 158.5 (2 x C Ar), 134.5 (2 x C Ar), 132.0 (2 x C Ar), 135.1 (2 x CH Ar), 134.8 (2 x CH Ar), 134.5 (6 x CH Ar), 127.8 (4 x CH Ar), 114.1 (4 x CH Ar), 68.8 (C-2 and C-6), 55.4 (2 x OMe), 48.8 (C-1 and C-7), 47.4 (C-8 and C-9). **IR** (film) ν_{max} 2980, 1513, 1382, 1249, 1125, 830 cm^{-1}. **HRMS** (CI): calculated for $C_{32}H_{33}O_4Si$ $[M+H]^+$ requires 509.2148, found 509.2147.

Data for **3l** (from the mixture): **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.35-7.52 (10H, m, Ar), 6.82-6.85 (4H, m, Ar), 6.63-6.67 (4H, m, Ar), 4.25-4.31 (2H, m, 2-H_A and 6-H_A), 4.19-4.25 (2H, m, 2-H_B and 6-H_B), 3.71 (6H, s, 2 x OMe), 3.67-3.70 (2 H, m, 8-H and 9-H), 3.21-3.26 (2 H, m, 1-H and 7-H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 157.8 (2 x C Ar), 132.6 (2 x C Ar), 130.4 (2 x C Ar), 129.3 (4 x CH Ar), 128.3 (2 x C-H Ar), 128.27 (2 x CH Ar), 128.20 (4 x CH Ar), 128.15 (2 x CH Ar), 113.4 (4 x CH Ar), 64.2 (C-2 and C-6), 55.3 (2 x OMe), 43.1 (C-8 and C-9), 42.0 (C-1 and C-7).

9.13. (±)-(1*S*,7*S*,8*R*,9*R*)-4,4-Diethyl-8,9-bis(4-methoxyphenyl)-3,5-dioxa-4-silabicyclo[5.2.0]nonane, 2m and (±)-(1*R*,7*S*,8*R*,9*S*)-4,4-Diethyl-8,9-bis(4-methoxyphenyl)-3,5-dioxa-4-silabicyclo[5.2.0]nonane, 3m.



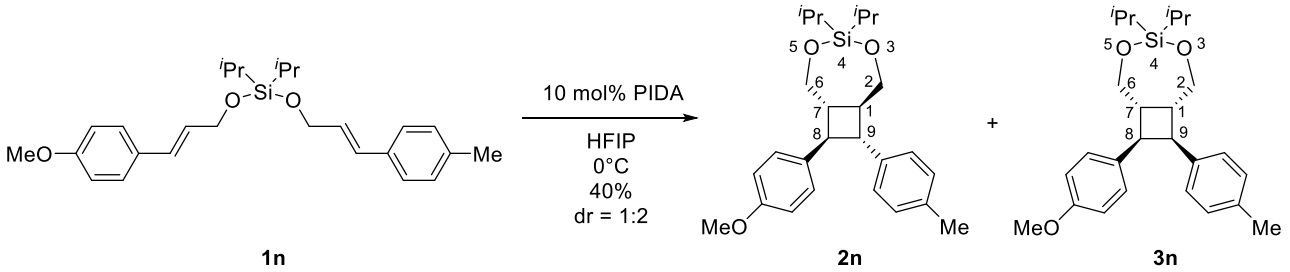
From diene **1m** (22.0 mg, 0.0534 mmol) and PIDA (1.70 mg, 0.00534 mmol) following the general procedure except conducting the reaction at 0°C, a 1:3 mixture of cyclobutanes **2m**:**3m** was obtained. Chromatographic purification (gradient elution: 5% → 9% Et_2O - pentane) gave separable

cyclobutanes **2m** and **3m** as colorless oils (12.5 mg, 57%).

Data for **2m**: R_f 0.54 (30% Et_2O - pentane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.10 (4H, d, *J* = 8.6 Hz, Ar), 6.81-6.87 (4H, m, Ar), 4.17 (2H, dd, *J* = 10.8, 3.8 Hz, 2H, m, 2-H_A and 6-H_A), 3.71-3.81 (2H, m, 2-H_B and 6-H_B), 3.79 (6H, s, 2 x OMe), 2.98-3.04 (2H, m, 8-H and 9-H), 2.40-2.47 (2H, m, 1-H and 7-H), 0.99 (6H, t, *J* = 8.0 Hz, 2 x CH_3 Et), 0.66 (4H, q, *J* = 8.0 Hz, 2 x CH_2 Et). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 158.5 (2 x C Ar), 134.4 (2 x C Ar), 127.8 (4 x CH Ar), 114.1 (4 x CH Ar), 68.1 (C-2 and C-6), 55.4 (2 x OMe), 49.5 (C-1 and C-7), 47.3 (C-8 and C-9), 6.8 (2 x CH_3 Et), 5.7 (2 x CH_2 Et). **IR** (film) ν_{max} 2980, 2360, 1513, 1247, 1122, 828 cm^{-1}. **HRMS (Cl):** calculated for $C_{24}H_{33}O_4Si$ $[M+H]^+$ requires *m/z* 413.2148, found *m/z* 413.2139.

Data for **3m**: **^{1}H NMR (500 MHz, $CDCl_3$)** δ 6.83 (4H, d, *J* = 6.2 Hz, Ar), 6.64 (4H, d, *J* = 8.7 Hz, Ar), 4.11-4.16 (2H, m, 2-H_A and 6-H_A), 4.04-4.10 (2H, m, 2-H_B and 6-H_B), 3.71 (6H, s, 2 x OMe), 3.66 (2H, d, *J* = 6.0 Hz, 8-H and 9-H), 3.11 (2H, ddd, *J* = 7.6, 4.6, 2.3 Hz, 1-H and 7-H), 1.08 (3H, t, *J* = 8.0 Hz, CH_3 Et), 1.03 (3 H, t, *J* = 8.0 Hz, CH_3 Et), 0.76 (2H, q, *J* = 8.0 Hz, CH_2 Et), 0.70 (2H, q, *J* = 8.0 Hz, CH_2 Et). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 157.8 (2 x C Ar), 132.3 (2 x C Ar), 129.3 (4 x CH Ar), 113.4 (4 x CH Ar), 63.6 (C-2 and C-6), 55.3 (2 x OMe), 43.1 (C-8 and C-9), 42.0 (C-1 and C-7), 6.7 (CH_3 Et), 6.5 (CH_3 Et), 3.9 (CH_2 Et), 3.8 (CH_2 Et).

9.14. (±)-(1*S*,7*S*,8*R*,9*R*)-4,4-Diisopropyl-8-(4-methoxyphenyl)-9-(*p*-tolyl)-3,5-dioxa-4-silabicyclo[5.2.0]nonane, 2n and (±)-(1*R*,7*S*,8*R*,9*S*)-4,4-diisopropyl-8-(4-methoxyphenyl) -9-(*p*-tolyl)-3,5-dioxa-4-silabicyclo[5.2.0]nonane, 3n.



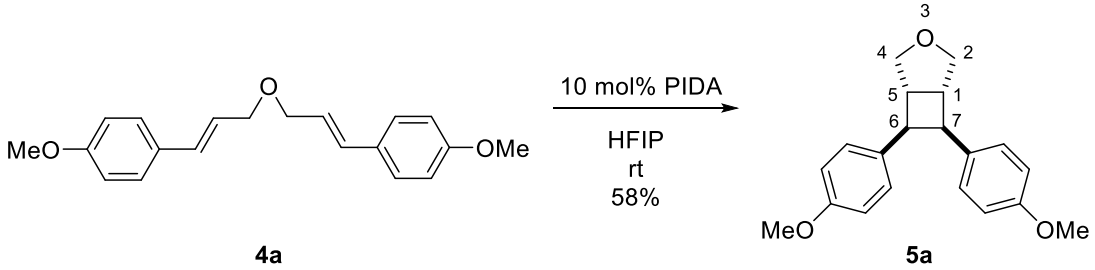
From diene **1n** (19.2 mg, 0.0453 mmol) and PIDA (1.50 mg, 0.00453 mmol) following the general procedure except conducting the reaction at 0°C and using 0.02M of HFIP, a 1:2 mixture (d.r. was based on crude NMR) of cyclobutanes **2n**:**3n** was obtained. Chromatographic purification (3% Et_2O - pentane) gave an inseparable 1:4 mixture of **2n** and **3n** as a colorless oils (7.7 mg, 40%).

Data for **2n** (from the mixture): R_f 0.35 (10% Et_2O - pentane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.07-7.13 (6H, m, Ar), 6.81-6.86 (2H, m, Ar), 4.16-4.22 (2H, m, 2-H_A and 6-H_A), 3.77-3.82 (2H, m, 2-H_B and 6-H_B), 3.78 (3H, s, OMe), 3.04 (2H, d, *J* = 9.4 Hz, 8-H and 9-H), 2.35-2.42 (2H, m, 1-H and 7-H), 2.32 (3H, s, Me), 1.01-1.06 (14H, m, 2 x *i*-Pr). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 157.7 (C Ar), 139.3 (C Ar), 135.3 (C Ar), 134.5 (C Ar), 129.4 (2 x CH Ar), 127.9 (2 x CH Ar), 126.8 (2 x CH Ar), 114.0 (2 x CH Ar), 68.6 (C-2 and C-6), 55.3 (OMe), 49.9 and 49.7 (C-1 and C-7), 47.4 and 46.8

(C-8 and C-9), 21.1 (Me), 17.6 and 17.5 (4 x CH_3 *i*-Pr), 13.4 (2 x CH *i*-Pr). **IR** (film) ν_{max} 2980, 2360, 1513, 1462, 1382, 1250, 1511, 1073, 954 cm^{-1}. **HRMS** (ESI): calculated for $C_{26}H_{37}O_3Si$ $[M]^+$ requires *m/z* 425.2507, found *m/z* 425.2506.

Data for **3n** (from the mixture): **^{1}H NMR (500 MHz, $CDCl_3$)** δ 6.90 (2H, d, *J* = 7.8 Hz, Ar), 6.78-6.86 (4H, m, Ar), 6.62-6.66 (2H, m, Ar), 4.21 (2H, m, 2-H_A and 6-H_A), 4.09 (2H, dd, *J* = 11.9, 3.9 Hz, 2-H_B and 6-H_B), 3.70 (3H, s, OMe), 3.56-3.64 (2H, m, 8-H and 9-H), 3.07-3.19 (2H, m, 1-H and 7-H), 2.21 (3H, s, Me), 1.12-1.16 (7H, m, *i*-Pr), 1.06-1.10 (7H, m, *i*-Pr). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 157.7 (C Ar), 137.2 (C Ar), 135.3 (C Ar), 132.5 (C Ar), 129.2 (2 x CH Ar), 128.7 (2 x CH Ar), 128.1 (2 x CH Ar), 113.4 (2 x CH Ar), 64.3 and 64.2 (C-2 and C-6), 55.3 (OMe), 43.3 and 42.9 (C-8 and C-9), 42.2 and 41.8 (C-1 and C-7), 21.1 (Me), 17.6 (2 x CH_3 *i*-Pr), 17.3 (2 x CH_3 *i*-Pr), 12.3 (CH *i*-Pr), 11.9 (CH *i*-Pr).

9.15. (±)-(1*R*,5*S*,6*R*,7*S*)-6,7-Bis(4-methoxyphenyl)-3-oxabicyclo[3.2.0]heptanes, 5a.

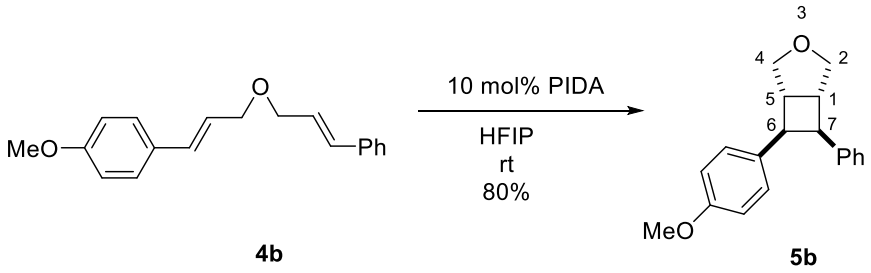


4a **5a**

From diene **4a** (50.5 mg, 0.163 mmol) and PIDA (5.30 mg, 0.0163 mmol) following the general procedure, cyclobutane **5a** was obtained. Chromatographic purification (gradient elution: 15% → 20% Et_2O - pentane) gave **5a** as a white solid (29.1 mg, 58%). Spectral properties matched those previously reported.[11]

Data for **5a**: R_f 0.4 (50% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.85 (4H, d, *J* = 8.7 Hz, Ar), 6.64 (4H, d, *J* = 8.7 Hz, Ar), 4.08 (2H, d, *J* = 9.4 Hz, 2-H_A and 4-H_A), 3.70 (6H, s, 2 x OMe), 3.66-3.71 (2H, m, 2-H_B and 4-H_B), 3.65 (2H, d, *J* = 4.4 Hz, 6-H and 7-H), 3.20-3.24 (2H, m, 1-H and 5-H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.4 (2 x C Ar), 133.1 (2 x C Ar), 129.0 (4 x CH Ar), 113.2 (4 x CH Ar), 74.0 (C-2 and C-4), 55.1 (2 x OMe), 46.5 (C-6 and C-7), 42.5 (C-1 and C-5). **HRMS** (Cl): calculated for $C_{20}H_{26}O_3N_4$ $[M+NH_4]^+$ requires *m/z* 328.1913, found *m/z* 328.1903.

9.16. (±)-(1*R*,5*S*,6*R*,7*S*)-6-(4-Methoxyphenyl)-7-phenyl-3-oxabicyclo[3.2.0]heptanes, 5b.

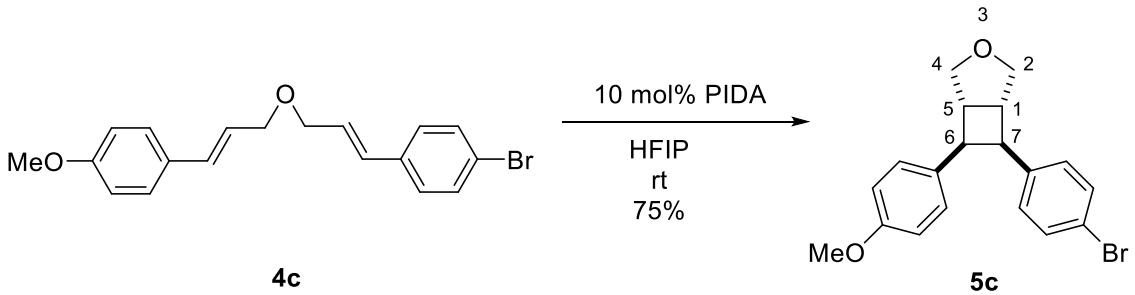


4b **5b**

From diene **4b** (21.4 mg, 0.0764 mmol) and PIDA (2.50 mg, 0.00764 mmol) following the general procedure, cyclobutane **5b** was obtained. Chromatographic purification (gradient elution: 11% → 14% Et_2O - pentane) gave **5b** as a colorless oil (17.1 mg, 80%). Spectral properties matched those previously reported.[11]

Data for **5b**: R_f 0.4 (40% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.06-7.12 (2H, m, Ar), 6.98-7.03 (1H, m, Ar), 6.92-6.96 (2H, m, Ar), 6.85 (2H, d, *J* = 8.6 Hz, Ar), 6.62 (2H, d, *J* = 8.7 Hz, Ar), 4.09 (2H, d, *J* = 9.4 Hz, 2-H_A and 4-H_A), 3.68-3.74 (4H, m, 2-H_B, 4-H_B, 1-H and 5-H), 3.69 (3H, s, OMe), 3.21-3.33 (2H, m, 6-H and 7-H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.5 (C Ar), 140.9 (C Ar), 133.0 (C Ar), 129.1 (2 x CH Ar), 128.1 (2 x CH Ar), 127.7 (2 x CH Ar), 125.6 (CH Ar), 113.1 (2 x CH Ar), 74.0 (C-2 and C-4), 55.1 (OMe), 49.5 and 47.2 (C-1 and C-5), 42.6 and 42.0 (C-6 and C-7). **HRMS** (Cl): calculated for $C_{19}H_{20}O_2$ $[M+H]^+$ requires *m/z* 281.1542, found *m/z* 281.1531.

9.17. (±)-(1*S*,5*R*,6*S*,7*R*)-6-(4-Bromophenyl)-7-(4-methoxyphenyl)-3-oxabicyclo[3.2.0]heptane, 5c.



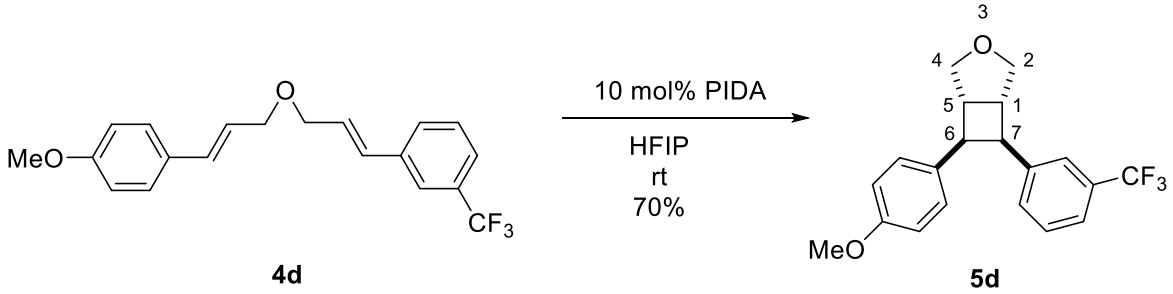
4c **5c**

From diene **4c** (17.5 mg, 0.0489 mmol) and PIDA (1.60 mg, 0.00489 mmol) following the general procedure, cyclobutane **5c** was obtained. Chromatographic purification (gradient elution: 15% → 30% Et_2O - pentane) gave **5c** as a colorless oil (13.1 mg, 75%).

Data for **5c**: R_f 0.5 (50 % Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.20 (2H, d, *J* = 8.5 Hz, Ar), 6.84 (2H, d, *J* = 8.7 Hz, Ar), 6.80 (2H, d, *J* = 8.4 Hz, Ar), 6.65 (2H, d, *J* = 8.7 Hz, Ar), 4.08 (2H, dd, *J* = 9.5, 3.0 Hz, 2-H_A and 4-H_A), 3.71 (3H, s, OMe), 3.67-3.73 (2H, m, 1-H and 5-H), 3.63-3.67 (2H, m, 2-H_B and 4-H_B), 3.18-3.26 (2H, m, 6-H and 7-H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.7 (C Ar), 140.1 (C Ar), 132.7 (C Ar), 130.9 (2 x CH Ar), 129.9 (2 x CH Ar), 129.1 (2 x CH Ar), 121.5 (C Ar), 113.5 (2 x CH Ar), 74.1 and 73.1 (C-2 and C-4), 55.2 (OMe), 46.7 and 46.5 (C-1 and C-5),

42.6 and 42.3 (C-6 and C-7). **IR** (film) ν_{max} 2980, 2894, 1380, 1255, 1150, 1081, 970 cm^{-1}. **HRMS** (Cl): calculated for $C_{19}H_{23}BrNO_2$ $[M+NH_4]^+$ requires *m/z* 376.0912, found *m/z* 376.0911.

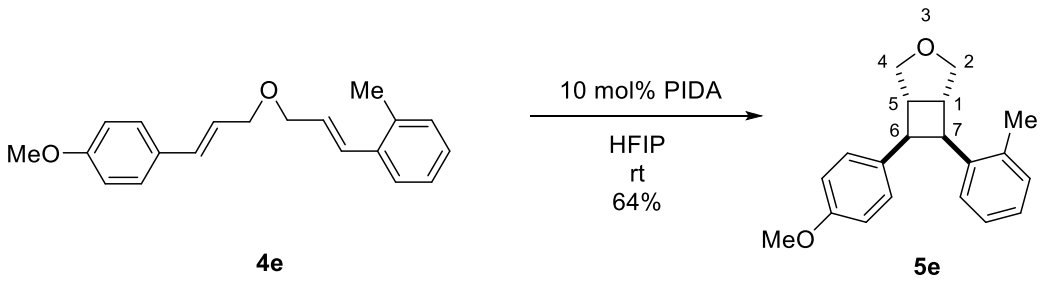
9.18. (±)-(1R,5S,6R,7S)-6-(4-Methoxyphenyl)-7-(3-(trifluoromethyl)phenyl)-3-oxabicyclo[3.2.0]heptane, 5d.



From diene **4d** (44.6 mg, 0.128 mmol) and PIDA (4.10 mg, 0.0128 mmol) following the general procedure, cyclobutane **5d** was obtained. Chromatographic purification (gradient elution: 15% → 20% Et_2O - pentane) to yield **5d** as a colorless oil (30.9 mg, 70%).

Data for **5d**: R_f 0.45 (50% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.25 (1H, d, *J* = 7.5 Hz, Ar), 7.17 (2H, t, *J* = 7.8 Hz, Ar), 7.06 (1H, d, *J* = 7.7 Hz, Ar), 6.83 (2H, d, *J* = 8.6 Hz, Ar), 6.62 (2H, d, *J* = 8.7 Hz, Ar), 4.11 (2H, dd, *J* = 9.3, 2.0 Hz, 2-H_A and 4-H_A), 3.72-3.76 (2H, m, 1-H and 5-H), 3.69-3.72 (2H, m, 2-H_B and 4-H_B), 3.23-3.34 (2H, m, 6-H and 7-H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.9 (C Ar), 141.0 (C Ar), 132.3 (C Ar), 131.7 (CH Ar), 130.0 (CF_3, q, *J* = 31.9 Hz), 129.1 (CH Ar and C Ar), 128.2 (2 x CH Ar), 124.8 (CH Ar, q, *J* = 3.8 Hz), 122.5 (CH Ar, q, *J* = 3.8 Hz), 113.5 (2 x CH Ar), 74.1 and 74.0 (C-2 and C-4), 55.3 (OMe), 47.1 and 46.7 (C-1 and C-5), 42.3 and 42.0 (C-6 and C-7). **IR** (film) ν_{max} 2980, 2889, 1382, 1250, 1150, 1081 cm^{-1}. **HRMS** (Cl): calculated for $C_{20}H_{23}F_3NO_2$ $[M+NH_4]^+$ requires *m/z* 366.1681, found *m/z* 366.1670.

9.19. (±)- (1*R*,5*S*,6*R*,7*S*)-6-(4-Methoxyphenyl)-7-(*o*-tolyl)-3-oxabicyclo[3.2.0]heptane, 5e.

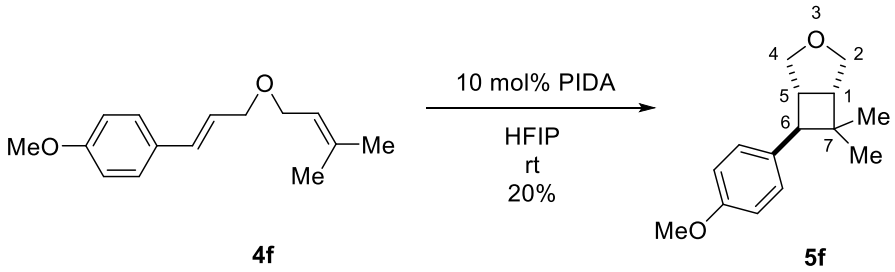


From diene **4e** (38.3 mg, 0.130 mmol) and PIDA (4.20 mg, 0.0130 mmol) following the general procedure, cyclobutane **5e** was obtained. Chromatographic purification (gradient elution: 10% → 20% Et_2O - pentane) gave **5e** as a colorless oil (18.3 mg, 64%).

Data for **5e**: R_f 0.45 (50% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.29 (1H, d, *J* = 7.7 Hz, Ar), 7.09 (1H, t, *J* = 8.5 Hz, Ar), 6.96 (1H, t, *J* = 7.5 Hz, Ar), 6.86-6.91 (3H, m, Ar), 6.58

(2H, d, J = 8.7 Hz, Ar), 4.13 (1H, d, J = 9.4 Hz, 4-H_A), 4.03 (1H, d, J = 9.2 Hz, 2-H_A), 3.81-3.90 (1H, m, 7-H), 3.70 (2H, dd, J = 9.4, 5.5 Hz, 2-H_A and 4-H_A), 3.67 (3H, s, OMe), 3.63 (1H, dd, J = 10.0, 4.6 Hz, 6-H), 3.53-3.60 (1H, m, 1-H), 2.99-3.07 (1H, m, 5-H), 2.01 (3H, s, Me). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.7 (C Ar), 138.3 (C Ar), 136.5 (C Ar), 133.7 (C Ar), 130.0 (CH Ar), 129.3 (2 x CH Ar), 126.5 (CH Ar), 126.0 (CH Ar), 125.3 (CH Ar), 113.1 (2 x CH Ar), 74.3 (C-2 and C-4), 55.2 (OMe), 47.5 (C-6), 44.6 (C-7), 44.0 (C-5), 40.2 (C-1), 20.0 (Me). **IR** (film) ν_{max} 2982, 2890, 1380, 1250, 1151, 1081, 970 cm^{-1}. **HRMS** (Cl): calculated for $C_{20}H_{26}NO_2$ $[M+NH_4]^+$ requires *m/z* 312.1964, found *m/z* 312.1962.

9.20. (±)-(1*S*,5*S*,7*S*)-7-(4-Methoxyphenyl)-6,6-dimethyl-3-oxabicyclo[3.2.0]heptane, 5f.

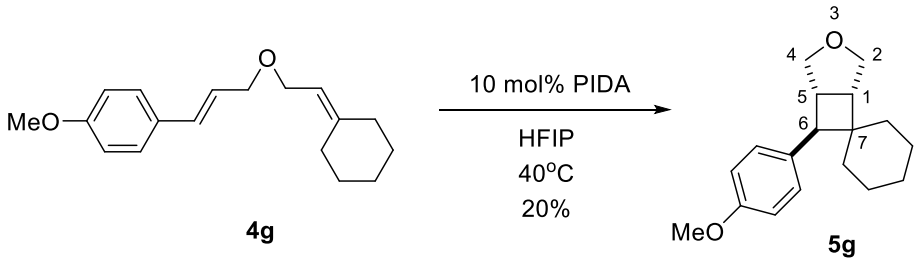


4f **5f**

From diene **4f** (20.0 mg, 0.0862 mmol) and PIDA (2.80 mg, 0.00862 mmol) following the general procedure, cyclobutane **5f** was obtained. Chromatographic purification gradient elution: 11% → 20% Et_2O - pentane) gave **5f** as a colorless oil (4.0 mg, 20%). Spectral properties matched those previously reported.[11]

Data for **5f**: R_f 0.5 (40% Et_2O - pentane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.06 (2H, d, J = 8.8 Hz, Ar), 6.85 (2H, d, J = 8.8 Hz, Ar), 4.16 (1H, d, J = 10.1 Hz, 2-H_A), 3.80 (3H, s, OMe), 3.78 (1H, d, J = 9.1 Hz, 4-H_A), 3.50 (1H, dd, J = 10.1, 7.0 Hz, 2-H_B), 3.43 (1H, dd, J = 9.1, 4.3 Hz, 4-H_B), 3.18-3.24 (1H, m, 5-H), 2.91 (1H, d, J = 7.4 Hz, 6-H), 2.39 (1H, t, J = 7.5 Hz, 1-H), 1.08 (3H, s, Me), 0.73 (3H, s, Me). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 157.9 (C Ar), 132.7 (C Ar), 128.6 (2 x CH Ar), 113.4 (2 x CH Ar), 72.0 (C-4), 69.1 (C-2), 55.2 (OMe), 51.2 (C-6), 46.5 (C-1), 38.4 (C-5), 37.2 (C-7), 26.2 (Me), 24.1 (Me).

9.21. (±)-(1*S*,5*S*,7*S*)-7-(4-Methoxyphenyl)-3-oxaspiro{bicyclo[3.2.0]heptane-6,1'-cyclohexane}, 5g



4g **5g**

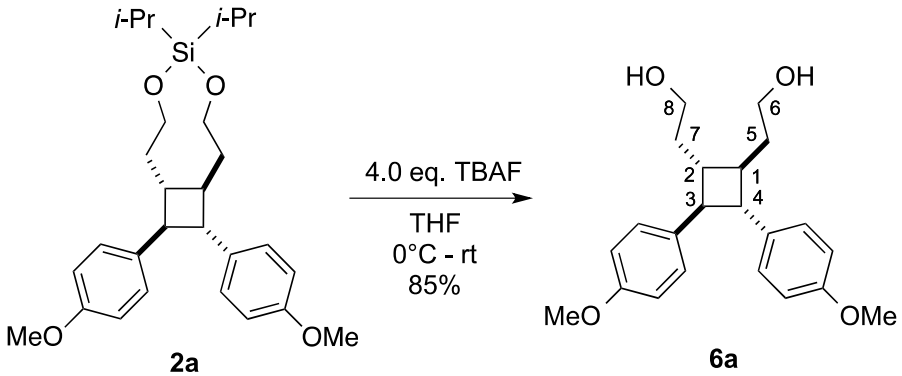
From diene **4g** (60.0 mg, 0.221 mmol) and PIDA (7.1 mg, 0.022 mmol) following the general procedure except conducting the reaction at 40°C, cyclobutane **5g** was obtained. Chromatographic purification gradient elution: 4% → 6% Et_2O - pentane) gave **5g** as a colorless oil (12.0 mg, 20%).

Data for **5g**: $\boldsymbol{R_f}$ 0.4 (20% Et_2O - pentane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.08 (2H, d, *J* = 8.7 Hz, Ar), 6.85 (2H, d, *J* = 8.7 Hz, Ar), 4.13 (1H, dd, *J* = 9.9, 1.2 Hz, 2-H_A), 3.80 (3H, s, OMe), 3.76 (1H, dd, *J* = 9.0, 1.2 Hz, 4-H_A), 3.57 (1H, dd, *J* = 10.0, 6.8 Hz, 2-H_B), 3.43 (1H, dd, *J* = 9.0, 4.5 Hz, 4-H_B), 3.18 (1H, td, *J* = 7.8, 4.4 Hz, 5-H), 2.84 (1H, d, *J* = 7.5 Hz, 6-H), 2.45- 2.54 (1H, m, 1-H), 1.74-1.94 (1H, m, 1/2 x CH_2 cyclohexyl), 1.45-1.53 (2H, m, CH_2 cyclohexyl), 1.27-1.39 (3H, m, 1/2 x CH_2 and CH_2 cyclohexyl), 1.12-1.23 (2H, m, CH_2 cyclohexyl), 1.00-1.09 (1H, m, 1/2 x CH_2 cyclohexyl), 0.81-0.92 (1H, m, 1/2 x CH_2 cyclohexyl). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 158.1 (C Ar), 132.5 (C Ar), 129.2 (2 x CH Ar), 113.5 (2 x CH Ar), 72.4 (C-4), 69.2 (C-2), 55.4 (OMe), 51.7 (C-6), 44.4 (C-1), 41.0 (C-7), 39.0 (C-5), 34.7 (CH_2 cyclohexyl), 33.4 (CH_2 cyclohexyl), 26.0 (CH_2 cyclohexyl), 23.2 (CH_2 cyclohexyl), 21.9 (CH_2 cyclohexyl). **IR** (film) ν_{max} 2923, 2849, 1512, 1447, 1246, 1178, 1037 cm^{-1}.**HRMS** (ESI): calculated for $C_{18}H_{25}O_2$ $[M+H]^+$ requires *m/z* 273.1849, found *m/z* 273.1839.

10. General procedure for silyl ether deprotection

To a cold (0 °C) solution of 1.0 eq. of cyclobutane in 20 mL/mmol of dry THF, under Ar, 3.0 eq. of TBAF (1 M in THF) was added slowly. After 10 min. the reaction was let to warm up to rt and was stirred for 3 hours. The reaction was quenched with phosphate buffer and extract with Et_2O. The combined organic layer was washed with brine and dry with $MgSO_4$, and the solvent was evaporated under reduced pressure to give the corresponding diol, that was purified by chromatography on silica gel using the appropriate mixture of eluents.

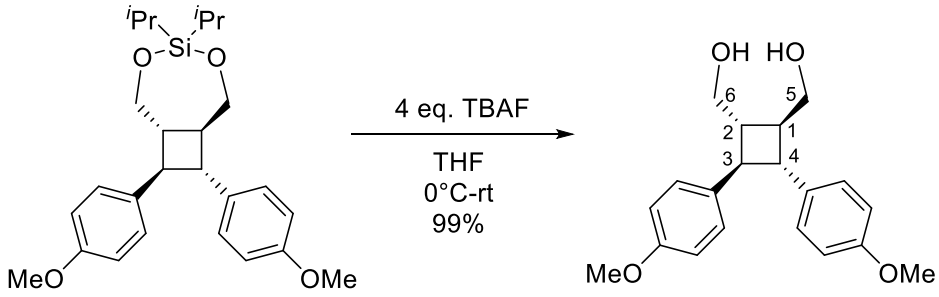
10.1. (±)-[(1*R*,2*R*,3*S*,4*S*)-3,4-Bis(4-methoxyphenyl)cyclobutane]-1,2-bis(2-hydroxyethyl), 6a.



From cyclobutane **2a** (19.9 mg, 0.0425 mmol) and 1.0 M TBAF (0.17 ml, 0.17 mmol) following the general procedure, diol **6a** was obtained. Chromatographic purification (gradient elution: 50% → 100% EtOAc - pentane) gave **6a** as a colorless oil (12.9 mg, 85%).

Data for **6a**: R_f 0.5 (100% EtOAc). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.13 (4H, d, *J* = 8.7 Hz, Ar), 6.82 (4H, d, *J* = 8.7 Hz, Ar), 3.77 (6H, s, 2 x OMe), 3.56-3.70 (4H, m, 6-H_2 and 8-H_2), 2.86 (2H, d, *J* = 9.2 Hz, 3-H and 4-H), 2.16-2.20 (2H, m, 1-H and 2-H), 1.86-1.90 (4H, m, 5-H_2 and 7-H_2), 1.66 (2H, br s, OH). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.3 (2 x C Ar), 135.4 (2 x C Ar), 128.0 (4 x CH Ar), 114.0 (4 x CH Ar), 61.0 (C-6 and C-8), 55.4 (2 x OMe), 52.2 (C-3 and C-4), 43.0 (C-1 and C-2), 38.1 (C-5 and C-7). **IR** (film) ν_{max} 2980, 2360, 1738, 1378, 1230, 1152, 954 cm^{-1}.**HRMS** (ESI): calculated for $C_{22}H_{29}O_4Si$ $[M]^+$ requires *m/z* 357.2060, found *m/z* 357.2061.

10.2. (±)-(1*S*,2*S*,3*R*,4*R*)-3,4-bis(4-methoxyphenyl)cyclobutane]-1,2-bis(hydroxylmethyl), 6b.

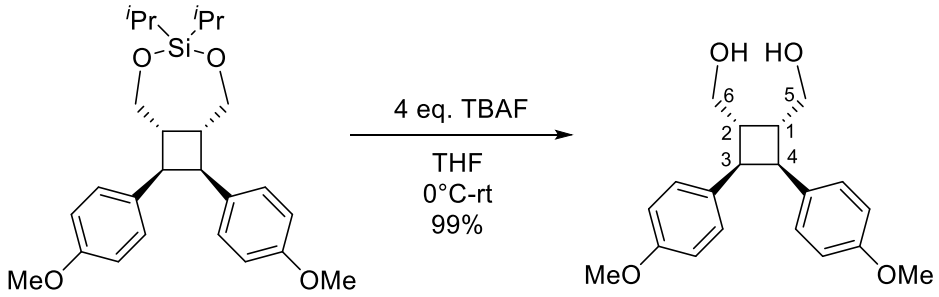


2j **6b**

From cyclobutane **2j** (20.0 mg, 0.0454 mmol) and 1.0 M TBAF (0.19 ml, 0.19 mmol) following the general procedure, diol **6b** was obtained. Chromatographic purification (gradient elution: 40% → 100% acetone - pentane) gave **6b** as a colorless oil (15.8 mg, 99%).

Data for **6b**: R_f 0.5 (50% acetone - pentane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.12 (4H, d, *J* = 8.6 Hz, Ar), 6.84 (4H, d, *J* = 8.6 Hz, Ar), 3.92 (2H, dd, *J* = 10.2, 3.3 Hz, 5-H_A and 6-H_A), 3.78 (6H, s, 2 x OMe), 3.58-3.64 (2H, m, 5-H_B and 6-H_B), 3.03 (2H, d, *J* = 9.4 Hz, 3-H and 4-H), 2.28-2.36 (2H, m, 1-H and 2-H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 158.4 (2 x C Ar), 134.6 (2 x C Ar), 127.9 (4 x CH Ar), 114.0 (4 x CH Ar), 65.6 (C-5 and C-6), 55.4 (2 x OMe), 47.8 (C-1 and C-2), 47.3 (C-3 and C-4). **IR** (film) ν_{max} 2980, 2360, 1738, 1378, 1230, 1152, 954 cm^{-1}. **HRMS** (ESI): calculated for $C_{20}H_{24}O_4Na$ $[M+Na]^+$ requires *m/z* 351.1567, found *m/z* 351.1568.

10.3. (±)-[(1*R*,2*S*,3*R*,4*S*)-3,4-Bis(4-methoxyphenyl)cyclobutane]-1,2-bis(hydroxymethyl), 7a.



3j **7a**

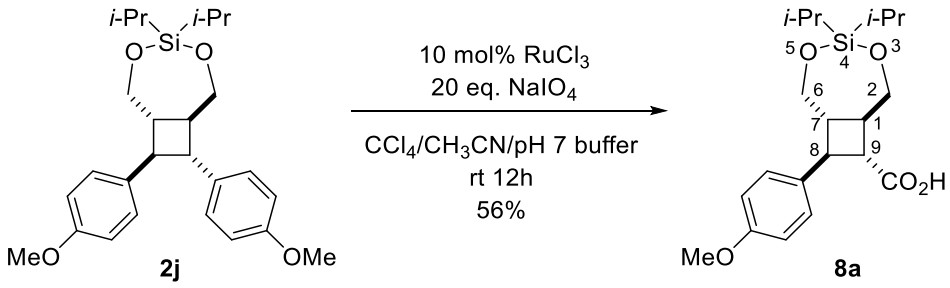
From cyclobutane **3j** (20.0 mg, 0.0454 mmol) and 1.0 M TBAF (0.19 ml, 0.19 mmol) following the general procedure, diol **7a** was obtained. Chromatographic purification (gradient elution: 40% → 100% acetone - pentane) gave **7a** as a colorless oil (15.8 mg, 99%).

Data for **7a**: R_f 0.5 (50% acetone - pentane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 6.83 (4H, d, *J* = 8.6 Hz, Ar), 6.64 (4H, d, *J* = 8.7 Hz, Ar), 4.05 (2H, dd, *J* = 11.3, 9.9 Hz, 5-H_A and 6-H_A), 3.85-3.89 (2H, m, 5-H_B and 6-H_B), 3.70 (6H, s, 2 x OMe), 3.51 (2H, d, *J* = 6.0 Hz, 3-H and 4-H), 3.10-3.14 (2H, m, 1-H and 2-H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 157.8 (2 x C Ar), 132.1 (2 x C Ar), 129.1 (4 x CH Ar), 113.4 (4 x CH Ar), 62.9 (C-5 and C-6), 55.3 (2 x OMe), 43.7 (C-3 and C-4), 40.8 (C-1 and C-2). **IR** (film) ν_{max} 2980, 2360, 1738, 1378, 1230, 1152, 954 cm^{-1}. **HRMS** (ESI): calculated for $C_{20}H_{24}O_4Na$ $[M+Na]^+$ requires *m/z* 351.1567, found *m/z* 351.1568.

11. General procedure for the Ru-catalyzed oxidation of aromatic rings to carboxylic acids

To a cold (0 °C) solution of cyclobutane in 10.0 mL/mmol of a 2:2:3 mixture of CCl_4:MeCN:pH 7 buffer (Na_2HPO_4), $NaIO_4$ (20.0 equiv) was added in one portion. The mixture was stirred at that temperature for 15 min and $RuCl_3$ (5 or 10 mol%) was added in one portion. The mixture was warmed up to room temperature. The reaction was monitored by TLC until completion, diluted with Et_2O and H_2O and extracted with Et_2O (3 x 3 mL/mmol). The water layer was acidified until pH 1 using concentrated HCl, and extracted with Et_2O (3 x 3 mL/mmol). The combined organic layers were dried using Na_2SO_4, filtered and the solvent was evaporated under reduced pressure to give the corresponding carboxylic acid, that was purified by chromatography on silica gel using the appropriate mixture of eluents.

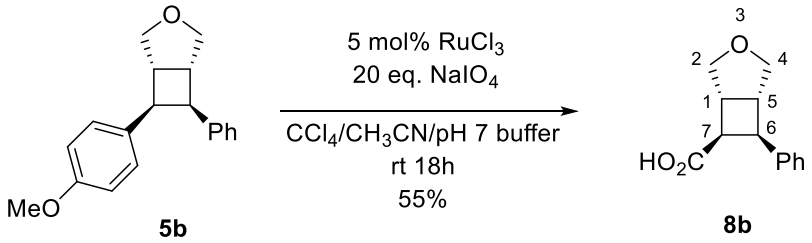
11.1. (±)-(1*S*,7*R*,8*R*,9*S*)-4,4-Diisopropyl-9-(4-methoxyphenyl)-3,5-dioxa-4-silabicyclo[5.2.0]nonane-8-carboxylic acid, 8a.



From cyclobutane **2j** (10.0 mg, 0.0227 mmol), $RuCl_3$ (0.47 mg, 0.0023 mmol) and $NaIO_4$ (98.0 mg, 0.454 mmol) following the general procedure, carboxylic acid **8a** was obtained. Chromatographic purification (gradient elution: 2% → 4% methanol - DCM) gave **8a** as a colorless oil (3.7 mg, 56%).

Data for **8a**: R_f 0.5 (10% MeOH - DCM).**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.16 (2H, d, *J* = 8.5 Hz, Ar), 6.87 (2H, d, *J* = 8.6 Hz, Ar), 4.13-4.20 (2H, m, 2-H_A and 6-H_A), 3.79 (3H, s, OMe), 3.66-3.78 (2H, m, 2-H_B and 6-H_B), 3.27 (1H, t, *J* = 9.6 Hz, 9-H), 2.73 (1H, t, *J* = 9.5 Hz, 8-H), 2.49-2.57 (1H, m, 7-H), 2.32-2.42 (1H, m, 1-H), 0.92-1.07 (14H, m, 2 x *i*-Pr). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 177.0 (C=O), 158.7 (C Ar), 133.2 (C Ar), 127.7 (2 x CH Ar), 114.2 (2 x CH Ar), 68.1 and 68.0 (C-2 and C-6), 55.5 (OMe), 49.2 (C-1), 45.4 (C-7), 44.9 (C-8), 42.7 (C-9), 17.57, 17.55, 17.5, 17.4 and 13.4 (2 x *i*-Pr). **NOESY- 2D (500 MHz, $CDCl_3$)**: between 9-H and 2-H_B, between 9-H and 7-H, between 9-H and Ar C-H, between 8-H and 1-H, between 8-H and 6-H_B. **IR** (film) ν_{max} 2935, 2857, 1722, 1712, 1033 cm^{-1}. **HRMS** (ESI): calculated for $C_{20}H_{29}O_5Si$ $[M-H]^+$ requires *m/z* 377.17897, found *m/z* 377.17892.

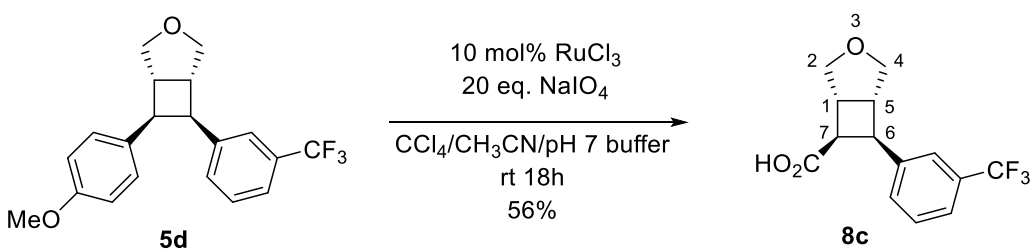
11.2. (±)-(1*R*,5*R*,6*R*,7*R*)-7-Phenyl-3-oxabicyclo[3.2.0]heptane-6-carboxylic acid, 8b.



5b **8b**

From cyclobutane **5b** (20.0 mg, 0.0714 mmol), $RuCl_3$ (0.70 mg, 0.0036 mmol) and $NaIO_4$ (302.0 mg, 1.422 mmol) following the general procedure, carboxylic acid **8b** was obtained. Chromatographic purification (gradient elution: 5% → 20% methanol - DCM) gave **8b** as a colorless oil (8.5 mg, 55%). Data for **8b**: R_f 0.5 (10% MeOH - DCM). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.14-7.34 (5H, m, Ar), 3.98 (2H, d, *J* = 9.6 Hz, 2-H_A and 4-H_A), 3.52-3.63 (3H, m, 2-H_A, 4-H_A and 7-H), 3.34-3.42 (1H, m, 6-H), 3.24-3.32 (1H, m, 1-H), 3.10-3.24 (1H, m, 5-H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 183.7 (C=O), 140.2 (C Ar), 128.4 (2 x CH Ar), 127.7 (2 x CH Ar), 126.9 (CH Ar), 73.7 and 73.1 (C-2 and C-4), 45.3 (C-7), 43.2 (C-5), 41.6 (C-6), 38.1 (C-1). **IR** (film) ν_{max} 2925, 2853, 1725, 1702, 1412, 1611, 699 cm^{-1}. **HRMS** (CI): calculated for $C_{13}H_{18}O_3N$ $[M+NH_4]^+$ requires *m/z* 236.1287, found *m/z* 236.1285.

11.3. (±)-(1*R*,5*R*,6*R*,7*R*)-7-[3-(Trifluoromethyl)phenyl]-3-oxabicyclo[3.2.0]heptane-6-carboxylic acid, 8c.

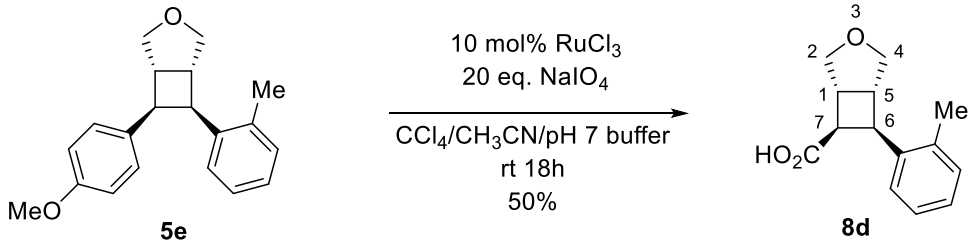


5d **8c**

From cyclobutane **5d** (18.0 mg, 0.0517 mmol), $RuCl_3$ (0.54 mg, 0.0052 mmol) and $NaIO_4$ (226.0 mg, 1.034 mmol) following the general procedure, carboxylic acid **8c** was obtained. Chromatographic purification (gradient elution: 5% → 20% methanol - DCM) gave **8c** as a colorless oil (8.3 mg, 56%)

Data for **8c**: R_f 0.5 (10% MeOH - DCM). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.45-7.50 (2H, m, Ar), 7.38-7.45 (2H, m, Ar), 4.01 (2H, dd, *J* = 9.7, 3.9 Hz, 2-H_A and 4-H_A), 3.66 (1H, dd, *J* = 10.6, 5.5 Hz, 7-H), 3.55-3.64 (2H, m, 2-H_B and 4-H_B), 3.37-3.43 (1H, m, 1-H), 3.33 (1H, dd, *J* = 10.5, 4.9 Hz, 6-H), 3.21-3.27 (1H, m, 5-H). **^{13}C NMR (^{19}F-decoupled, 125 MHz, $CDCl_3$)** δ 174.9 (C=O), 141.1 (C Ar), 131.2 (CH Ar and CF_3), 128.9 (C Ar and CH Ar), 124.6 (CH Ar), 123.9 (CH Ar), 73.6 and 73.1 (C-2 and C-4), 46.3 (C-6), 44.9 (C-7), 43.1 (C-5), 38.2 (C-5). **NOESY- 2D (500 MHz, $CDCl_3$)**: between 5-H and 1-H, between 5-H and Ar C-H, between 6-H and 7-H, between 6-H and 2-H_B & 4-H_B, between 7-H and 2-H_B & 4-H_B. **IR** (film) ν_{max} 2925, 2855, 1725, 1705, 1412, 701 cm^{-1}. **HRMS** (CI): calculated for $C_{14}H_{17}F_3NO_3$ $[M+NH_4]^+$ requires *m/z* 304.1161, found *m/z* 304.1157.

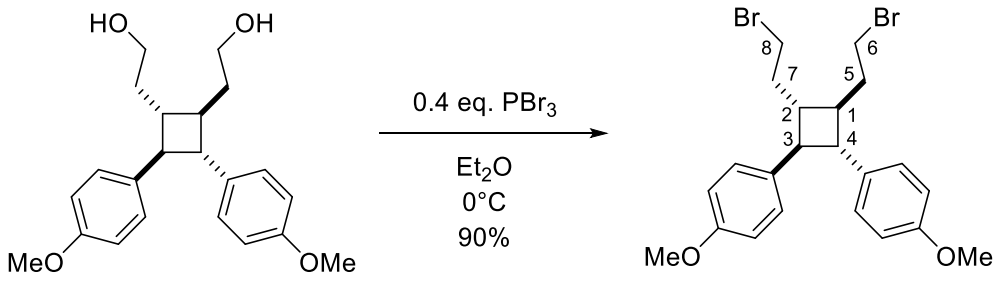
11.4. (±)-(1*R*,5*R*,6*R*,7*R*)-7-(*o*-Tolyl)-3-oxabicyclo[3.2.0]heptane-6-carboxylic acid, 8d.



From cyclobutane **5e** (11.3 mg, 0.0384 mmol), $RuCl_3$ (0.80 mg, 0.0038 mmol) and $NaIO_4$ (164.0 mg, 0.768 mmol) following the general procedure, carboxylic acid **5e** was obtained. Chromatographic purification (gradient elution: 5% → 20% methanol - DCM) gave **8d** as a colorless oil (4.4 mg, 50%).

Data for **8d**: R_f 0.5 (10% MeOH - DCM). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.34 (1 H, d, *J* = 7.6 Hz, Ar), 7.15-7.20 (1H, m, Ar), 7.10-7.14 (2H, m, Ar), 4.04 (1H, d, *J* = 9.7 Hz, 4-H_A), 4.12 (1H, d, *J* = 9.7 Hz, 2-H_A), 3.79-3.89 (1H, m, 7-H), 3.65 (1H, dd, *J* = 9.8, 6.0 Hz, 4-H_B), 3.56 (1H, dd, *J* = 9.6, 5.1 Hz, 2-H_B), 3.42-3.48 (1H, m, 6-H), 3.27-3.33 (2H, m, 1-H and 5-H), 2.26 (3H, s, Me). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 175.3 (C=O), 137.4 (C Ar), 136.9 (C Ar), 130.2 (CH Ar), 126.9 (CH Ar), 126.4 (CH Ar), 125.9 (CH Ar), 73.9 and 73.2 (C-2 and C-4), 46.2 and 37.2 (C-1 and C-5), 41.6 and 41.5 (C-6 and C-7), 19.9 (Me). **IR** (film) ν_{max} 2925, 2853, 1725, 1702, 1412, 1611, 699 cm^{-1}. **HRMS** (CI): calculated for $C_{14}H_{20}NO_3$ $[M+NH_4]^+$ requires *m/z* 250.1443, found *m/z* 250.1433.

12. (±)-(1S,2S,3R,4R) 3,4-Bis(2-bromoethyl)-1,2-bis(4-methoxyphenyl)cyclobutane, 9



6a **9**

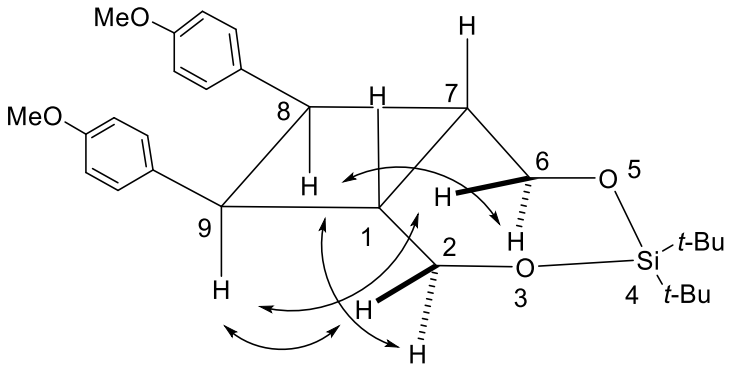
To a stirred solution of diol **6a** (28.8 mg, 0.0809 mmol) in dry Et_2O (0.5 mL) at 0 °C under Ar was added PBr_3 (0.07 mL, 0.7 mmol). The reaction was stirred until completion, monitored by TLC analysis and quenched with $NaHCO_3$. The layers were separated and the aqueous layer extracted with Et_2O twice. The combined organics were washed with brine, dried over $MgSO_4$, filtered and the solvent was evaporated to give the pure bromide **9** as a white solid (34.9 mg, 90%). Spectral properties matched those previously reported.[1]

Data for **9**: R_f 0.25 (5% Et_2O – pentane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.11 (4H, d, *J* = 8.6 Hz, Ar), 6.83 (4H, d, *J* = 8.6 Hz, Ar), 3.78 (6H, s, 2 x OMe), 3.40-3.18 (4H, m, 6-H_2 and 8-H_2), 2.83 (2 H, m, 3-H and 4-H), 2.30-2.12 (6H, m, 1-H, 2-H, 6-H_2 and 8-H_2). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.4 (2 x C Ar), 134.7 (2 x C Ar), 128.0 (4 x CH Ar), 114.0 (4 x CH Ar), 55.4 (2 x OMe), 52.5 (C-3 and C-4), 43.8 (C-1 and C-2), 39.4 (C-5 and C-7), 31.1 (C-6 and C-8). HRMS (ESI): calculated for $C_{22}H_{26}O_2{}^{79}Br_2Na$ [M+Na]+ requires m/z 503.0192, found m/z 503.0193.

13. NMR study of compound 3k, 8a and 8c.

The ^{1}H NMR spectrum of **3k** presents 1-H and 7-H as a multiplet that has COSY cross peaks with 8-H, 9-H, 2-H_A and 6-H_A, while 8-H and 9-H is a doublet (J = 5.7 Hz) that has COSY cross-peaks with 1-H and 7-H.

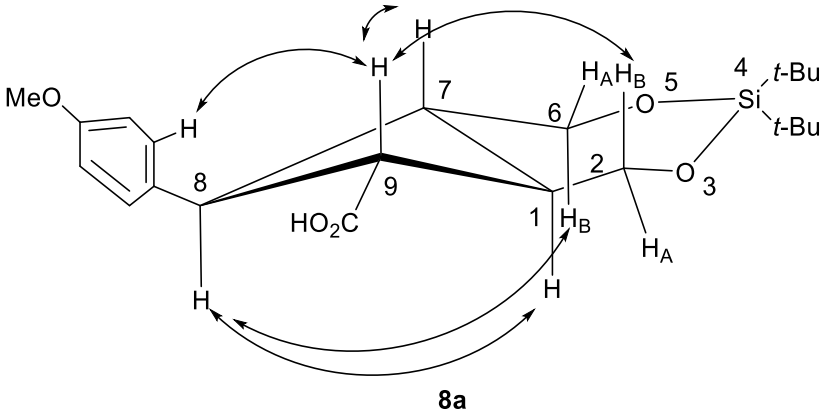
Additional support for the structure was found upon inspection of the NOESY 2D spectra of **3k**, that showed interactions between 8-H/9-H and 2-H_2, between 8-H/9-H and 6-H_2, but no interactions between 1-H/7-H and 8-H/9-H, among others, confirming the *trans-cis-trans* relative stereochemistry.



3k

The ^{1}H NMR spectrum of **8a** presents 1-H and 7-H as a multiplet that has COSY cross peaks with 7-H, 9-H, 2-H_2 and 1-H and 8-H, 6-H_2 respectively, while 8-H and 9-H is a triplet (J = 9.6 Hz) that has COSY cross-peaks with 9-H, 7-H and 1-H, 8-H respectively.

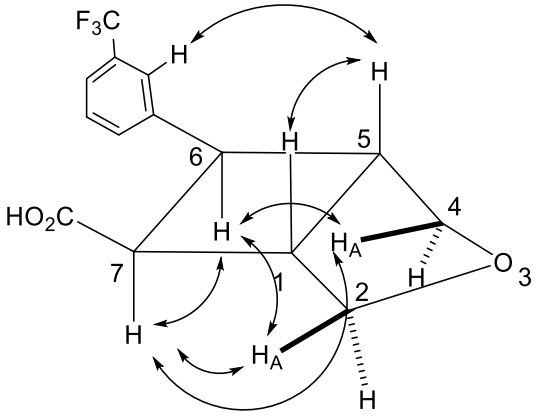
Additional support for the structure was found upon inspection of the NOESY 2D spectra of **8a**, that showed interactions between 9-H and 2-H_B, between 9-H and 7-H, between 9-H and Ar C-H, between 8-H and 1-H, between 8-H and 6-H_B, confirming the all-*trans* relative stereochemistry.



8a

The ^{1}H NMR spectrum of **8c** presents 1-H and 5-H as a multiplet that has COSY cross peaks with 7-H, 5-H, 2-H_2 and 1-H and 4-H, 6-H_2 respectively, while 6-H and 7-H is a doublet of doublet (J = 10.5, 9.6 Hz and J = 10.5, 5.5 Hz) that has COSY cross-peaks with 5-H, 7-H and 1-H, 6-H respectively.

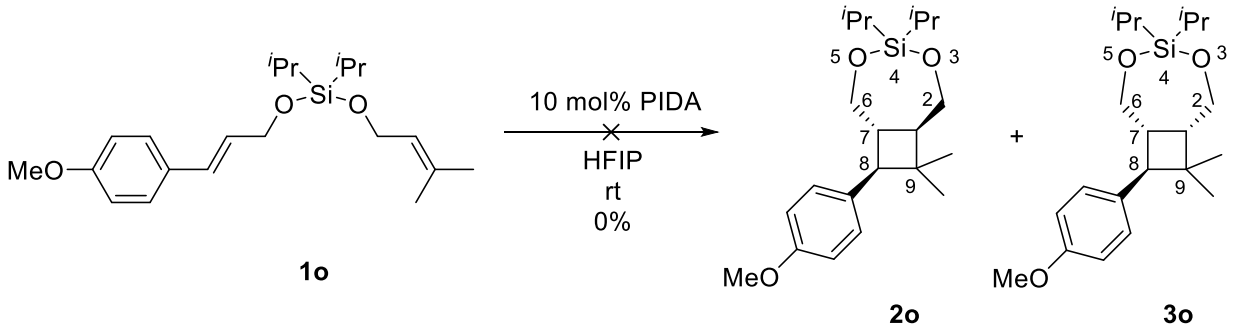
Additional support for the structure was found upon inspection of the NOESY 2D spectra of **8a**, that showed interactions between 5-H and 1-H, between 5-H and Ar C-H, between 6-H and 7-H, between 6-H and 2-H_B & 4-H_B, between 7-H and 2-H_B & 4-H_B.



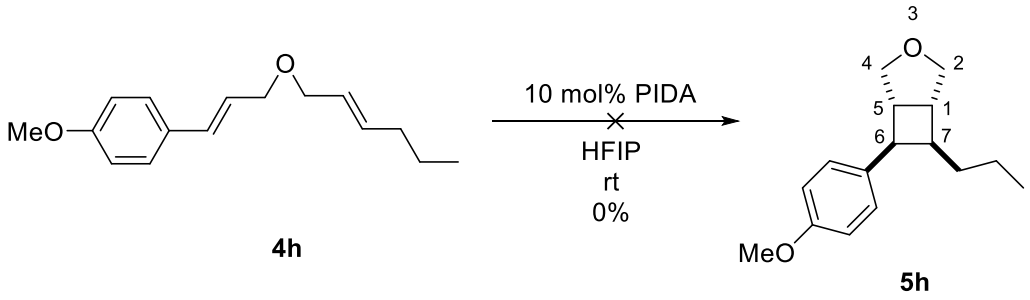
8c

14. Limitations in the scope of [2+2] cycloaddition

For the silicon tethered [2+2]-cycloaddition, the silyl ether **1o** bearing a tri-substituted aliphatic allyl alcohol gave a complex mixture under standard conditions; no desired cyclobutene was observed.



For the intramolecular bis-allylether [2+2]-cycloaddition, the ether **4h** bearing a di-substituted aliphatic allyl alcohol gave recovery of starting material under standard conditions, no desired cyclobutene was observed. However, an ether bearing a tri-substituted aliphatic allyl alcohol gave desired cyclobutene product (see cycloaddition of ethers **4f** and **4g**).



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