# **Supporting Information**

for

## Assembling the Carbon Skeleton of A-74528

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# Synthetic Procedures and Analytical Data

## General information

## **Experimental conditions**

All reactions were conducted with magnetic stirring at room temperature unless otherwise noted. Reactions at elevated temperatures were performed using an oil bath or aluminum block as the heat transfer medium, with the reported temperature corresponding to that of the heat transfer medium.

### Chemicals

All chemicals were obtained from common vendors and used without further purification unless otherwise noted. With the exception of dimethyl sulfoxide, which was purchased from Oakwood Chemical in standard quality, all solvents were purchased with "certified ACS" or higher quality. Anhydrous solvents were prepared with a solvent purification system by filtration of HPLC grade solvents through alumina according to the method of Grubbs<sup>1</sup> or purchased from Acros Organics in AcroSeal<sup>TM</sup> bottles. Dess-Martin periodinane,<sup>2</sup> nitroacetic acid,<sup>3</sup> 2-nitrobenzene sulfonyl hydrazide,<sup>4</sup> and TMS-dienolate  $A3^5$  were prepared according to a literature procedures.

### Chromatography

Retardation factors were determined by analytical thin-layer chromatography performed on pre-coated glass plates from Millipore Sigma (TLC Silica Gel 60 Plates, 250  $\mu$ m layer thickness, F254 fluorescence indicator), with visualization by exposure to ultraviolet light (254 nm) or by staining with a basic potassium permanganate solution.

Column chromatography was performed with silica gel obtained from Millipore Sigma (Geduran ® Si 60, 40 – 63  $\mu$ m) or from Teledyne Isco (RediSep<sup>®</sup> Gold, 20 – 40  $\mu$ m, spherical). Column chromatography was either performed manually or with an automated chromatography system (Teledyne Isco CombiFlash<sup>®</sup>).

### Nuclear magnetic resonance (NMR) spectroscopy

Proton and carbon (<sup>1</sup>H- and <sup>13</sup>C-) NMR spectra were recorded on Bruker Avance III (600/150 MHz, with TCI Cryoprobe<sup>TM</sup>) and Avance III HD (400/100 MHz, with BBFO Cryoprobe<sup>TM</sup>) spectrometers. All spectra were recorded at a temperature of 25 °C in 5 mm tubes in deuterated solvents purchased from Cambridge Isotope Laboratories, Inc. (chloroform-d or CDCl<sub>3</sub>, 99.8% D; dimethyl sulfoxide-d<sub>6</sub> or DMSO-d<sub>6</sub>, 99.9% D; methanol-d<sub>4</sub> or CD<sub>3</sub>OD, 99.8% D; acetone-d<sub>6</sub>, 99.9% D). For <sup>1</sup>H-NMR spectra chemical shifts ( $\delta$ ) in parts per million (ppm) relative to tetramethylsilane ( $\delta = 0$  ppm) are reported using the residual protic solvent (CHCl<sub>3</sub> in CDCl<sub>3</sub>:  $\delta = 7.26$  ppm, DMSO-d<sub>5</sub>:  $\delta = 2.50$  ppm, CHD<sub>2</sub>OD in CD<sub>3</sub>OD:  $\delta = 3.31$  ppm, acetone-d<sub>5</sub> in acetone-d<sub>6</sub>:  $\delta = 2.05$  ppm) as an internal reference. For <sup>13</sup>C-NMR spectra, chemical shifts in ppm relative to tetramethylsilane ( $\Delta = 0$  ppm) are reported using the central resonance of the solvent signal (CDCl<sub>3</sub>:  $\delta = 77.16$  ppm, DMSO-d<sub>6</sub>:  $\delta = 39.52$  ppm, CD<sub>3</sub>OD:  $\delta = 49.00$  ppm, acetone-d<sub>6</sub>:  $\delta = 29.84$  ppm) as an internal reference. NMR spectral data was analyzed with the program MestreNova 12.0.3 developed by Mestrelab Research S. L.

### Infrared spectroscopy

Infrared spectra were recorded on a Thermo-Fisher Nicolet 6700 Fourier Transform-IR spectrometer with Smart iTR<sup>™</sup> attenuated total reflectance unit. Samples were either measured

as a solid or as a thin film formed from a solution after evaporation of the solvent. IR data is reported as wave numbers with the unit  $cm^{-1}$ . The window of acquisition was 4000 to 700  $cm^{-1}$ .

#### Mass spectrometry

A Shimadzu TQ 8040 GC-MS/FID systems with electron ionization ion source was used to obtain low-resolution mass spectra. High-resolution mass spectra using either an electrospray ionization or atmospheric pressure chemical ionization ion source were obtained with an Agilent 6224 Accurate Mass time-of-flight LC/MS system. High-resolution mass spectra using an electron ionization source were measured on a Thermo Finnigan MAT 95 system at the analytic section of the Department of Chemistry of the Ludwig Maximilian University of Munich. All reported data refers to positive ionization mode.

## Benzyl alcohol SI-2



To a suspension of lithium aluminum hydride (19.3 g, 510 mmol, 1 eq.) in anhydrous tetrahydrofuran (250 mL) under nitrogen atmosphere was added ester **SI-1** (100 g, 510 mmol) in small portions within approx. 1 hour under ice bath cooling. After the addition was complete, the cooling bath was removed and the mixture was stirred overnight at room temperature. Then, ethyl acetate (50 mL), methanol (25 mL), water (200 mL) and diethyl ether (200 mL) were added carefully in the specified order and the mixture was stirred vigorously for 10 minutes. The resulting suspension was filtered and the filter cake was washed with several portions of diethyl ether (4×100 mL). The filtrate was washed with brine (200 mL), dried over magnesium sulfate and evaporated under reduced pressure to afford benzyl alcohol **SI-2** (83.1 g, 494 mmol, 97%) as white solid, which was used without further purification.

 $\mathbf{R}_{\mathbf{f}}$  = 0.29 (40% ethyl acetate in hexanes).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): 6.52 (d, J = 2.3, 2H), 6.38 (t, J = 2.3 Hz, 1H), 4.63 (s, 2H), 3.79 (s, 6H).

<sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>): 161.1, 143.5, 104.7, 99.8, 65.5, 55.5.

**IR**: 3352, 3000, 2939, 2838, 1595, 1458, 1428, 1345, 1318, 1295, 1262, 1203, 1148, 1058, 1035, 993, 952, 940, 918, 830, 703.

HRMS (APCI): C<sub>9</sub>H<sub>13</sub>O<sub>3</sub> [M+H]<sup>+</sup> calc. 169.0859, found 169.0865.

The spectroscopic data matched previously reported values.<sup>6</sup>

## Aldehyde SI-3



То benzyl alcohol **SI-2** (5.00 g, 29.7 mmol) in dichloromethane were added 2,2,6,6-tetramethylpiperidinyloxyl (467 mg, 2.97 mmol, 0.1 eq.) and phenyliodine(III) diacetate (10.5 g, 32.7 mmol, 1.1 eq.). After stirring for two hours, the reaction mixture was washed with 2 M aqueous sodium thiosulfate (40 mL) and saturated, aqueous sodium bicarbonate (40 mL), then dried over sodium sulfate and evaporated under reduced pressure. The residue was purified by column chromatography (0 to 20% ethyl acetate in hexanes) to afford aldehyde SI-3 (4.60 g, 27.7 mmol, 93%) as faint yellowish oil that solidified upon standing at room temperature.

 $\mathbf{R}_{\mathbf{f}} = 0.45$  (20% ethyl acetate in hexanes).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 9.90 (s, 1H), 7.01 (d, J = 2.4 Hz, 2H), 6.70 (t, J = 2.3 Hz, 1H), 3.84 (s, 6H).

<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): 192.1, 161.4, 138.5, 107.3, 107.2, 55.8.

**IR**: 2964, 2942, 2841, 1699, 1653, 1605, 1592, 1560, 1525, 1457, 1431, 1386, 1351, 1316, 1298, 1250, 1233, 1205, 1155, 1063, 1053, 990, 968, 954, 936, 923, 844, 720, 712.

**HRMS** (EI): C<sub>9</sub>H<sub>10</sub>O<sub>3</sub> [M]<sup>+-</sup> calc. 166.0625, found 166.0622.

The spectroscopic data matched previously reported values.<sup>7</sup>

## Cinnamic ester SI-4



To aldehyde **SI-3** (4.60 g, 27.7 mmol) and triethyl phosphonoacetate (5.77 mL, 29.1 mmol, 1.05 eq.) under nitrogen atmosphere was added 1,8-diazabicyclo[5.4.0]undec-7-ene (6.20 ml, 41.5 mmol, 1.5 eq.). After stirring overnight, the mixture was diluted with ethyl acetate (50 ml) and then washed with water (25 mL), 2 M hydrochloric acid (25 mL), saturated, aqueous sodium bicarbonate (25 mL) and brine (25 mL) and dried over sodium sulfate. The volatiles were evaporated under reduced pressure and the residue was purified by column chromatography (0 to 20% ethyl acetate in hexanes) to afford ester **SI-4** (6.30 g, 26.7 mmol, 96%) as colorless oil that solidified upon standing at room temperature.

 $R_f = 0.45$  (20% ethyl acetate in hexanes).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 7.60 (d, J = 16.0 Hz, 1H), 6.66 (d, J = 2.3 Hz, 2H), 6.49 (t, J = 2.3 Hz, 1H), 6.40 (d, J = 16.0 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.81 (s, 6H), 1.34 (t, J = 7.1 Hz, 3H).

<sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>): 167.0, 161.1, 144.7, 136.5, 118.9, 106.1, 102.7, 60.7, 55.5, 14.4.

**IR**: 2977, 2960, 2939, 2904, 2839, 1706, 1639, 1590, 1457, 1427, 1392, 1367, 1354, 1338, 1318, 1307, 1278, 1240, 1205, 1174, 1152, 1116, 1095, 1062, 1034, 978, 940, 925, 834, 770, 730.

**HRMS** (ESI): C<sub>13</sub>H<sub>17</sub>O<sub>4</sub> [M+H]<sup>+</sup> calc. 237.1121, found 237.1120.

The spectroscopic data matched previously reported values.<sup>8</sup>

## Cinnamic alcohol SI-5



To ester **SI-4** (6.30 g, 26.7 mmol) in anhydrous tetrahydrofuran (55 mL) under nitrogen atmosphere was dropwise added a 1.5 M toluene solution of diisobutylaluminum hydride (39.5 mL, 59.3 mmol, 2.2 eq.) under ice bath cooling within approximately 30 minutes. After stirring additional 50 minutes, ethyl acetate (2 mL), methanol (10 mL) and saturated, aqueous sodium potassium tartrate (50 mL) were carefully added in the specified order. The ice bath was removed and the mixture was stirred vigorously overnight. Then, the layers were separated and the aqueous layer was extracted with ethyl acetate ( $3 \times 30$  mL). The combined organic layers were washed with water (40 mL) and brine ( $40^{\circ}$ mL), dried over sodium sulfate and evaporated under reduced pressure. The residue was purified by column chromatography (0 to 30% ethyl acetate in dichloromethane) to afford alcohol **SI-5** (4.96 g, 25.5 mmol, 96%) as a colorless oil that solidified upon standing at room temperature.

 $\mathbf{R}_{\mathbf{f}}$  = 0.26 (40% ethyl acetate in hexanes).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 6.54 (d, J = 2.3 Hz, 2H), 6.54 (dt, J = 15.8, 1.5 Hz, 1H), 6.40 – 6.29 (m, 2H), 4.31 (d, J = 5.4 Hz, 2H), 3.79 (s, 6H).

<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): 161.0, 138.9, 131.1, 129.2, 104.7, 100.0, 63.7, 55.4.

**IR**: 3338, 3000, 2936, 2837, 1589, 1456, 1424, 1343, 1323, 1299, 1269, 1241, 1203, 1148, 1092, 1058, 1012, 992, 964, 941, 926, 829, 781, 726.

**HRMS** (APCI): C<sub>11</sub>H<sub>15</sub>O<sub>3</sub> [M+H]<sup>+</sup> calc. 195.1016, found 195.1018.

The spectroscopic data matched previously reported values.9

## Methyl carbonate 5



To alcohol **SI-5** (453 mg, 2.33 mmol), 4-dimethylaminopyridine (47.5 mg, 0.233 mmol, 0.1 eq.) and pyridine (564  $\mu$ L, 7.00 mmol, 3 eq.) in anhydrous dichloromethane (5 mL) under nitrogen atmosphere was dropwise added methyl chloroformate (361  $\mu$ L, 4.66 mmol, 2 eq.) under ice bath cooling. The mixture was stirred with warming to room temperature overnight, then diluted with water (10 mL) and ethyl acetate (25 mL) under ice bath cooling. The layers were separated and the organic layer was washed with 1 M hydrochloric acid (10 mL) and brine (10 mL) and dried over magnesium sulfate. The volatiles were evaporated under reduced pressure and the residue was purified by column chromatography (60% to 100% dichloromethane in pentane) to afford methyl carbonate **5** (562 mg, 2.23 mmol, 96%) as a colorless oil that solidified upon standing at room temperature.

 $\mathbf{R}_{\mathbf{f}}$  = 0.37 (20% ethyl acetate in hexanes).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 6.62 (dt, J = 15.6, 1.3 Hz, 1H), 6.54 (d, J = 2.3 Hz, 2H), 6.39 (t, J = 2.3 Hz, 1H), 6.27 (dt, J = 15.8, 6.4 Hz, 1H), 4.78 (dd, J = 6.4, 1.3 Hz, 2H), 3.81 (s, 3H), 3.79 (s, 6H).

<sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>): 161.1, 155.8, 138.2, 134.8, 123.1, 104.9, 100.6, 68.4, 55.5, 55.0.

**IR**: 2957, 2839, 1744, 1590, 1452, 1441, 1427, 1379, 1349, 1333, 1253, 1203, 1150, 1121, 1059, 1022, 1011, 966, 939, 903, 830, 790, 719.

**HRMS** (ESI): C<sub>13</sub>H<sub>17</sub>O<sub>5</sub> [M+H]<sup>+</sup> calc. 253.1071, found 253.1066.

The spectroscopic data matched previously reported values.<sup>10</sup>

## Diester SI-8



**Step 1:** To ester **SI-1** (7.50 g, 38.2 mmol) and acid chloride **SI-6** (8.63 g, 57.3 mmol, 1.5 eq.) in anhydrous 1,2-dichloroethane (500 mL) was added aluminum chloride (10.2 g, 76.5 mmol, 2 eq.) in 2 g portions within 5 minutes under ice bath cooling. The mixture was stirred for 3 hours, then the cooling bath was removed and stirring was continued at room temperature. After 2.5 hours, the mixture was poured onto water/ice (20 mL/30 g) and stirred until all ice had melted. The layers were separated and the aqueous layer was extracted with dichloromethane (75 mL). The combined organic layers were washed with saturated, aqueous sodium bicarbonate (50 mL) and brine (50 mL), dried over sodium sulfate and evaporated under reduced pressure to afford crude ketone **SI-7** (12.2 g) as an orange solid, which was used without further purification.

**Step 2:** To crude ketone **SI-7** were added triethylsilane (14.6 mL, 91.8 mmol, 2.4 eq.) and trifluoroacetic acid (29.5 mL, 382 mmol, 10 eq.). The mixture was stirred for 2.5 hours, then the volatiles were removed under reduced pressure. The residue, which contained diester **SI-8** and lactone **SI-9**, was purified by column chromatography (20% diethyl ether in pentane) to afford diester **SI-8** (8.14 g, 27.5 mmol, 72%) as a colorless oil that solidified upon extended standing at room temperature.

Analytical data for ketone SI-7

An analytical sample of ketone **SI-7** was isolated by column chromatography (30% ethyl acetate in pentane), which afforded a white solid.

 $\mathbf{R}_{\mathbf{f}}$  = 0.33 (40% ethyl acetate in hexanes).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 7.02 (d, J = 2.2 Hz, 1H), 6.63 (d, J = 2.3 Hz, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 3.80 (s, 3H), 3.70 (s, 3H), 3.13 (t, J = 7.3 Hz, 2H), 2.77 (t, J = 7.3 Hz, 2H).

<sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>): 203.5, 173.6, 166.4, 161.1, 157.3, 129.7, 126.2, 105.5, 103.1, 56.2, 55.8, 52.7, 51.8, 39.3, 28.4.

**IR**: 3002, 2952, 2843, 1720, 1639, 1601, 1579, 1455, 1436, 1422, 1329, 1295, 1249, 1215, 1174, 1149, 1065, 1049, 980, 950, 887, 844, 787, 763.

**HRMS** (ESI): C<sub>15</sub>H<sub>18</sub>NaO<sub>7</sub> [M+H]<sup>+</sup> calc. 333.0945, found 333.0957.

Analytical data for diester SI-8

 $\mathbf{R}_{\mathbf{f}}$  = 0.32 (20% ethyl acetate in hexanes).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 6.88 (d, J = 2.6 Hz, 1H), 6.57 (d, J = 2.5 Hz, 1H), 3.88 (s, 3H), 3.81 (s, 3H), 3.79 (s, 3H), 3.65 (s, 3H), 2.90 – 2.84 (m, 2H), 2.34 (t, J = 7.7 Hz, 2H), 1.86 (p, J = 7.7 Hz, 2H).

<sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>): 174.4, 168.4, 159.1, 158.4, 131.8, 124.5, 105.1, 102.2, 55.8, 55.6, 52.2, 51.5, 34.1, 25.57, 25.55.

**IR**: 2998, 2951, 2840, 1722, 1603, 1584, 1483, 1460, 1434, 1421, 1350, 1315, 1275, 1237, 1199, 1153, 1131, 1068, 1055, 989, 941, 886, 844, 810, 787, 762.

**HRMS** (ESI): C<sub>15</sub>H<sub>20</sub>NaO<sub>6</sub> [M+Na]<sup>+</sup> calc. 319.1152, found 319.1165.

Analytical data for lactone SI-9

An analytical sample of lactone **SI-9** was isolated by column chromatography (0 to 30% ethyl acetate in hexanes).

 $\mathbf{R}_{f}$  = 0.40 (40% ethyl acetate in hexanes), 0.13 (20% ethyl acetate in hexanes).

<sup>1</sup>**H-NMR** (600 MHz, CDCl<sub>3</sub>): 6.90 (d, J = 1.9 Hz, 1H), 6.66 (d, J = 1.9 Hz, 1H), 5.49 (dd, J = 8.1, 3.3 Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.66 (s, 3H), 2.65 – 2.58 (m, 1H), 2.47 (ddd, J = 15.8, 9.1, 6.6 Hz, 1H), 2.40 (ddd, J = 16.6, 9.4, 5.5 Hz, 1H), 2.03 – 1.95 (m, 1H).

<sup>13</sup>**C-NMR** (150 MHz, CDCl<sub>3</sub>): 173.4, 170.5, 162.8, 155.2, 130.3, 128.7, 105.0, 98.7, 79.4, 56.1, 55.9, 51.9, 29.5, 28.4.

**IR**: 2950, 2843, 1763, 1735, 1679, 1626, 1606, 1502, 1454, 1435, 1331, 1302, 1257, 1228, 1202, 1154, 1117, 1070, 1037, 991, 944, 892, 845, 768, 727, 704.

**HRMS** (ESI): C<sub>14</sub>H<sub>17</sub>O<sub>6</sub> [M+H]<sup>+</sup> calc. 281.1020, found 281.1031.

## Tetralone 4



To potassium *tert*-butoxide (81.0 g, 722 mmol, 3 eq.) in anhydrous tetrahydrofuran (240 mL) under nitrogen atmosphere was dropwise added ester **SI-8** (71.3 g, 241 mmol) in anhydrous tetrahydrofuran (80 mL) under ice bath cooling. The mixture was stirred for two hours, then poured onto ice-cold 2 M hydrochloric acid (650 mL)-and the resulting suspension was filtered. The solids were washed with water (2×100 mL) followed by ethanol (100 mL) and dried to afford a mixture of tetralone **4** and its tautomer **4-enol** (43.5 g, 165 mmol, 68%) as a white powder, with the enol tautomer **4-enol** as the primary component (≈95% by <sup>1</sup>H-NMR). The combined filtrate and washings were extracted with ethyl acetate (2×150 mL). The extracts were washed with water (200 mL) and brine (200 mL), dried over sodium sulfate and evaporated under reduced pressure. The residue was purified by recrystallization from ethanol to afford a mixture of tautomer **4** as the primary component (≈80% by <sup>1</sup>H-NMR). The mother liquors of the recrystallization were evaporated under reduced pressure. The residue was the primary component (≈80% by <sup>1</sup>H-NMR). The mother liquors of the recrystallization were evaporated under reduced pressure. The residue was the primary component (≈80% by <sup>1</sup>H-NMR). The mother liquors of the recrystallization were evaporated under reduced pressure. The residue was the primary component (≈80% by <sup>1</sup>H-NMR). The mother liquors of the recrystallization were evaporated under reduced pressure. The residue was washed with ethanol and dried to afford further material (5.27 g, 19.9 mmol, 8%) as an off-white solid, which contained roughly equal amounts of the tautomers **4** and **4-enol**.

Analytical data for keto-tautomer 4

 $R_f$  = 0.44 (20% ethyl acetate in hexanes).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 7.12 (d, J = 2.5 Hz, 1H), 6.63 (d, J = 2.5 Hz, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 3.77 (s, 3H), 3.58 (dd, J = 10.3, 4.7 Hz, 1H), 2.98 (ddd, J = 17.7, 5.9, 4.8 Hz, 1H), 2.78 – 2.68 (m, 1H), 2.48 – 2.38 (m, 1H), 2.36 – 2.27 (m, 1H).

<sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>): 193.5, 170.9, 159.2, 157.9, 133.0, 126.4, 104.6, 100.4, 55.9, 55.7, 54.3, 52.4, 25.9, 20.9.

**IR**: 3001, 2951, 2840, 1739, 1682, 1650, 1605, 1583, 1487, 1453, 1434, 1366, 1326, 1312, 1283, 1241, 1211, 1196, 1149, 1128, 1116, 1072, 1042, 1005, 969, 940, 915, 889, 843, 768, 754, 728.

**HRMS** (ESI): C<sub>14</sub>H<sub>17</sub>O<sub>5</sub> [M+H]<sup>+</sup> calc. 265.1071, found 265.1083.

Analytical data for enol-tautomer 4-enol

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 12.45 (s, 1H), 6.99 (d, J = 2.4 Hz, 1H), 6.53 (d, J = 2.4 Hz, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 3.82 (s, 3H), 2.72 (dd, J = 9.0, 6.9 Hz, 2H), 2.51 (dd, J = 8.8, 7.1 Hz, 3H).

<sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>): 173.3, 165.1, 159.2, 157.0, 131.4, 120.7, 101.5, 99.8, 97.3, 55.8, 55.7, 51.8, 20.3, 19.7.

**IR**: 3000, 2900, 2841, 1648, 1595, 1580, 1489, 1453, 1437, 1422, 1373, 1352, 1322, 1287, 1236, 1211, 1200, 1152, 1126, 1070, 1052, 1029, 1010, 941, 918, 900, 852, 828, 801, 769, 756, 731.

**HRMS** (ESI): C<sub>14</sub>H<sub>17</sub>O<sub>5</sub> [M+H]<sup>+</sup> calc. 265.1071, found 265.1076.

## Ketoester 3



**Catalyst preparation:** Molybdenum hexacarbonyl (528 mg, 2.00 mmol, 0.08 eq.) and racemic ligand *rac*-L1 (1.38 g, 3.00 mmol, 0.12 eq.) were placed in a 40 mL screw-cap vial, which was closed with an open-top cap with a PTFE/silicone septum. The vial was evacuated and refilled with argon three times. Anhydrous, degassed<sup>a</sup> toluene (13 mL) was added, the vial was disconnected from the argon line and the sealed vial was stirred at 85 °C behind a blast shield for 4 hours. Then, the mixture was taken up in a syringe and directly used for the coupling of carbonate **5** and tetralone **4**.

**Coupling:** Tetralone **4**<sup>b</sup> (8.59 g, 32.5 mmol, 1.3 eq.), carbonate **5** (6.31 g, 25.0 mmol) and a 60% suspension of sodium hydride in paraffin oil (1.35 g, 33.8 mmol, 1.35 eq.) were placed in a 350 mL pressure vessel, which was closed as described below. The vessel was evacuated and refilled with argon three times. Anhydrous, degassed\* tetrahydrofuran (100 mL) was added, the mixture was stirred until no more gas evolved and kept at room temperature until the catalyst solution was added. Then, the reaction vessel was disconnected from the argon line and the sealed vessel was stirred at 55 °C for 52 hours behind a blast shield. After this time, the pressure vessel was carefully vented through a needle and the reaction mixture was purified as described below.

Assembly of the reaction vessel:



A 350 mL pressure vessel with #15 opening (item **A**, highest pressure 88 psig) was closed with a 14/20 natural rubber septum (item **B**), which had been trimmed to properly fit the opening of the pressure vessel (**B uncut**  $\rightarrow$  **B cut**). A PTFE plug with a central opening (item **C**, PTFE connecting adapter #15 ACE-thread to 8-425 GPI thread by Ace Glass Inc., product # 13290-11) was used to hold the rubber septum in place, while still allowing access to the rubber septum. The outer opening of PTFE plug was sealed with 8 mm OD natural rubber septum and the space between both rubber septa was evacuated and refilled with protective gas in the same way as the inside of the pressure vessel.

**Purification:** Catalyst preparation and coupling as described above were performed in parallel for two batches, which were then combined for purification. Silica (30 g) was added to the combined reaction mixtures and the volatiles were removed under reduced pressure. Then, the

<sup>&</sup>lt;sup>a</sup>By three cycles of evacuating/refilling with argon under sonication.

<sup>&</sup>lt;sup>b</sup>For reasons of simplicity the term "tetralone **4**" here refers to both tautomeric forms and mixtures thereof.

resulting slurry was suspended in dichloromethane (50 mL), filtered over additional silica (20 g) and the filter cake was washed with plenty dichloromethane (450 mL). The dichloromethane was evaporated and ethanol (200 mL) was added to the residue. The mixture was warmed to reflux, then coolet to room temperature overnight and filtered. The solids were washed with ethanol (25 mL) and dried to afford ketoester **3** (18.4 g, 41.8 mmol, 84%) as a white solid. The filtrate was discarded.

After purification of ketoester **3** a minor impurity remained, which was tentatively assigned to be the alternative diastereomer. A corresponding diastereomeric ratio of  $\approx 20/1$  was observed by <sup>1</sup>H-NMR. The impurity or any corresponding products thereof were removed during conversions to stilbene **6**.

 $R_f = 0.61$  (40% ethyl acetate in hexanes).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 7.12 (d, J = 2.5 Hz, 1H), 6.58 (d, J = 2.3 Hz, 2H), 6.56 (d, J = 2.5 Hz, 1H), 6.36 – 6.26 (m, 2H), 5.18 – 5.08 (m, 2H), 4.33 (d, J = 10.0 Hz, 1H), 3.83 (s, 3H), 3.78 (s, 3H), 3.76 (s, 6H), 3.56 (s, 3H), 2.91 (ddd, J = 18.2, 5.6, 3.3 Hz, 1H), 2.79 (ddd, J = 18.2, 11.0, 4.8 Hz, 1H), 2.55 (ddd, J = 13.7, 4.8, 3.3 Hz, 1H), 2.01 (ddd, J = 13.8, 11.1, 5.6 Hz, 1H).

<sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>): 193.5, 170.0, 160.4, 159.0, 157.9, 142.2, 136.6, 133.7, 125.6, 117.8, 108.5, 104.2, 100.9, 98.8, 62.3, 55.8, 55.6, 55.4, 53.7, 52.5, 28.4, 19.9.

**IR**: 3000, 2950, 2837, 1729, 1687, 1604, 1594, 1503, 1487, 1456, 1430, 1367, 1347, 1328, 1283, 1230, 1199, 1152, 1127, 1055, 992, 964, 909, 884, 846, 787, 769, 729.

**HRMS** (ESI): C<sub>25</sub>H<sub>29</sub>O<sub>7</sub> [M+H]<sup>+</sup> calc. 441.1908, found 441.1919.

#### Stilbene 6



**Step 1:** To a suspension of ketoester **3** (16.0 g, 36.3 mmol) and trimethyl sulfonium iodide (8.66 g, 42.4 mmol, 1.17 eq.) under nitrogen atmosphere in anhydrous dimethyl sulfoxide (75 mL) was added a 1.66 M tetrahydrofuran solution of potassium *tert*-butoxide (24.4 mL, 40.5 mmol, 1.12 mmol) in five equal portions each 10 minutes. After the addition, the mixture was stirred for 25 minutes. The resulting solution was diluted with water (320 mL) and brine (80 mL) and extracted with dichloromethane (200 mL and 2×100 mL). The extracts were washed with water (2×150 mL), dried over sodium sulfate and evaporated under reduced pressure to afford crude epoxide **SI-10** as an off-white solid, which was directly used without further purification.

**Step 2:** Crude epoxide **SI-10** in toluene (75 mL) was heated to 105 °C, then p-toluenesulfonic acid monohydrate (734 mg, 3.86 mmol, 0.11 eq.) was added, After stirring at 105 °C for 35 minutes, the reaction mixture was cooled to room temperature, filtered over silica (40 g) and the silica was washed with dichloromethane (350 mL). The filtrate was evaporated under reduced pressure, ethanol (350 mL) was added to the residue and the mixture was warmed to reflux for one hour. After cooling to room temperature overnight, the mixture was filtered. The filtrate was discarded and the solids were dried to afforded stilbene **6**, which still contained lactone **SI-11** as a minor impurity that was removed by another treatment with ethanol as described below.

**Purification:** Two batches of impure stilbene **6**, which had prepared in parallel as described above (36.3 mmol ketoester **3** per batch), were combined. Ethanol (350 mL) was added and the mixture was warmed to reflux for one hour, then cooled to room temperature overnight and filtered. The filtrate was discarded and the solids were dried to afford pure stilbene **6** (18.4 g, 43.5 mmol, 60%) as a white solid.

Analytical data for stilbene **6** 

 $\mathbf{R}_{\mathbf{f}}$  = 0.57 (40% ethyl acetate in hexanes).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 7.59 (s, 1H), 7.08 (d, J = 2.2 Hz, 1H), 6.35 (d, J = 2.2 Hz, 1H), 6.33 (d, J = 2.4 Hz, 1H), 6.31 (d, J = 2.3 Hz, 1H), 5.69 (dt, J = 17.0, 9.8 Hz, 1H), 5.21 (ddd, J = 17.0, 1.9, 0.6 Hz, 1H), 4.95 (dd, J = 10.0, 1.9 Hz, 1H), 3.89 (s, 3H), 3.85 (s, 3H), 3.81 (s, 3H), 3.80 (s, 3H), 3.80 (d, J = 9.7 Hz, 1H), 3.48 (s, 3H), 3.08 – 2.98 (m, 1H), 2.25 – 2.07 (m, 2H), 1.94 – 1.84 (m, 1H).

<sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>): 176.6, 160.4, 158.7, 158.0, 157.0, 139.5, 136.8, 135.3, 129.2, 118.8, 117.1, 116.1, 115.8, 104.4, 98.5, 97.4, 97.2, 55.6, 55.4, 53.5, 52.4, 50.5, 30.4, 20.2.

**IR**: 3000, 2949, 2837, 1721, 1599, 1570, 1491, 1463, 1455, 1426, 1364, 1338, 1322, 1302, 1287, 1278, 1234, 1213, 1195, 1168, 1148, 1120, 1089, 1058, 999, 981, 961, 946, 912, 874, 861, 827, 792, 764, 731.

**HRMS** (ESI): C<sub>26</sub>H<sub>29</sub>O<sub>6</sub> [M+H]<sup>+</sup> calc. 437.1959, found 437.1965.

Analytical data for lactone **SI-11** 

An analytical sample of lactone **SI-11** was isolated from the ethanol mother liquors by column chromatography (0 to 30% ethyl acetate in hexanes) and successive precipitation from dichloromethane solution by addition of hexanes, which afforded a white solid.

 $\mathbf{R}_{\mathbf{f}}$  = 0.51 (40% ethyl acetate in hexanes).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 6.96 (d, J = 2.4 Hz, 1H), 6.44 (d, J = 2.1 Hz, 1H), 6.36 (d, J = 2.4 Hz, 1H), 6.30 (d, J = 2.1 Hz, 1H), 5.36 – 5.17 (m, 2H), 5.16 (d, J = 9.2 Hz, 1H), 4.96 (dd, J = 9.1, 2.5 Hz, 1H), 4.10 (d, J = 9.1 Hz, 1H), 4.09 (d, J = 9.2 Hz, 1H), 3.94 (s, 4H), 3.79 (s, 3H), 3.77 (s, 3H), 3.75 (s, 3H), 3.03 (ddd, J = 16.8, 7.1, 5.7 Hz, 1H), 2.51 (ddd, J = 16.8, 8.2, 5.9 Hz, 1H), 2.10 (ddd, J = 13.3, 7.0, 5.8 Hz, 1H), 2.00 (ddd, J = 14.2, 8.2, 5.8 Hz, 1H).

<sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>): 183.3, 162.0, 158.9, 157.5, 157.2, 147.9, 139.6, 138.1, 122.6, 117.3, 117.0, 104.5, 101.6, 99.2, 97.1, 75.0, 58.1, 57.7, 57.5, 55.7, 55.6, 55.3, 55.2, 26.1, 20.1.

**IR**: 2939, 2837, 1762, 1606, 1585, 1487, 1462, 1454, 1436, 1424, 1363, 1330, 1322, 1308, 1285, 1240, 1201, 1177, 1150, 1111, 1077, 1057, 1021, 1003, 984, 946, 907, 832, 780, 763, 726.

**HRMS** (ESI): C<sub>25</sub>H<sub>27</sub>O<sub>6</sub> [M+H]<sup>+</sup> calc. 423.1802, found 423.1806.

## Triene **SI-12**



To stilbene **6** (16.9 g, 38.7 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzo-quinone (9.67 g, 42.6 mmol, 1.1 eq.) under nitrogen atmosphere was added anhydrous toluene (155 mL). The mixture was stirred until all solids had been properly suspended, then warmed to 65°C. After stirring for 3 hours, the mixture was cooled to room temperature and filtered. The solids were washed thoroughly with several portions of dichloromethane (425 mL total) and discarded. The filtrate was evaporated under reduced pressure and ethanol (200 mL) was added to the residue. Then, the mixture was sonicated for 15 minutes and filtered. The solids were washed with ethanol (30 mL) and dried to afford diene **SI-12** (14.8 g, 34.1 mmol, 88%) as a yellow solid. The filtrate was evaporated under reduced pressure and the residue purified by column chromatography (70 to 100% dichloromethane in hexanes and 0 to 10% ethyl acetate in dichloromethane) to afford additional diene **SI-12** (680 mg, 1.57 mmol, 4%) as a yellow foam.

 $\mathbf{R}_{\mathbf{f}}$  = 0.53 (40% ethyl acetate in hexanes).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 7.46 (s, 1H), 6.96 (d, J = 2.2 Hz, 1H), 6.88 (d, J = 9.8 Hz, 1H), 6.34 (d, J = 2.3 Hz, 1H), 6.30 (d, J = 2.2 Hz, 1H), 6.29 (d, J = 2.3 Hz, 1H), 5.92 (ddd, J = 17.0, 10.1, 8.4 Hz, 1H), 5.58 (dd, J = 9.9, 1.1 Hz, 1H), 5.06 (ddd, J = 17.0, 1.8, 1.0 Hz, 1H), 4.99 (ddd, J = 10.1, 1.8, 0.8 Hz, 1H), 4.00 (d, J = 8.4 Hz, 1H), 3.90 (s, 3H), 3.84 (s, 3H), 3.81 (s, 3H), 3.80 (s, 3H), 3.51 (s, 3H).

<sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>): 173.6, 160.8, 160.5, 157.0, 156.8, 137.7, 136.8, 134.3, 129.0, 124.7, 121.9, 118.0, 116.5, 115.6, 113.9, 104.6, 99.3, 97.8, 97.2, 55.7, 55.61, 55.55, 55.5, 52.9, 52.2, 51.8.

**IR**: 3001, 2939, 2836, 1719, 1633, 1595, 1568, 1491, 1454, 1424, 1387, 1324, 1304, 1288, 1217, 1204, 1166, 1142, 1116, 1082, 1071, 1051, 1027, 994, 972, 947, 907, 828, 801, 784, 760, 727.

**HRMS** (ESI): C<sub>26</sub>H<sub>27</sub>O<sub>6</sub> [M+H]<sup>+</sup> calc. 435.1802, found 435.1813.

## Alcohol SI-13



To triene **SI-12** (15.5 g, 35.7 mmol) in anhydrous tetrahydrofuran (200 mL) under nitrogen atmosphere was added a 0.5 M tetrahydrofuran solution of 9-borabicyclo-[3.3.1]nonane (78.5 mL, 39.2 mmol, 1.1 eq.) and the mixture was stirred overnight. Then, 20% aqueous sodium acetate (100 mL) and 30% hydrogen peroxide (23 mL) were added carefully under ice bath cooling. The cooling bath was removed and the mixture was stirred vigorously for 1 hour, diluted with water (400 mL) and extracted with dichloromethane (3×200 mL). The extracts were dried over sodium sulfate and evaporated under reduced pressure. Hexanes (430 mL) and ethanol (60 mL) were added to the remaining orange oil. The mixture was warmed to reflux until all of the oil had been consumed and a large amount of solids had formed. Then, the mixture was cooled to room temperature and filtered. The filtrate was discarded. The solids were washed with hexanes and dried to afford alcohol **SI-13** (15.5 g, 34.3 mmol, 96%) as a yellow solid.

 $\mathbf{R}_{\mathbf{f}}$  = 0.35 (6% acetone in dichloromethane).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 7.45 (s, 1H), 6.97 (d, J = 2.2 Hz, 1H), 6.91 (d, J = 9.8 Hz, 1H), 6.36 (d, J = 2.3 Hz, 1H), 6.30 (d, J = 2.2 Hz, 1H), 6.28 (d, J = 2.3 Hz, 1H), 5.58 (d, J = 9.9 Hz, 1H), 3.89 (s, 3H), 3.83 (s, 3H), 3.81 (s, 3H), 3.80 (s, 3H), 3.63 – 3.55 (m, 1H), 3.54 – 3.46 (m, 4H), 3.44 (dd, J = 11.2, 3.4 Hz, 1H), 2.05 – 1.85 (m, 1H), 1.74 – 1.64 (m, 1H).

<sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>): 173.9, 160.6, 160.2, 157.1, 156.8, 138.8, 134.1, 129.2, 124.2, 122.6, 117.9, 115.4, 114.0, 105.5, 99.2, 97.8, 96.9, 60.9, 55.7, 55.6, 55.52, 55.50, 53.1, 52.8, 43.3, 33.2.

**IR**: 3001, 2940, 2838, 1720, 1639, 1596, 1568, 1491, 1455, 1425, 1388, 1338, 1289, 1219, 1205, 1149, 1121, 1090, 1051, 993, 946, 932, 910, 887, 872, 829, 803, 786, 764, 730.

**HRMS** (ESI): C<sub>26</sub>H<sub>29</sub>O<sub>7</sub> [M+H]<sup>+</sup> calc. 453.1908, found 453.1916.

Silyl ether SI-14



To alcohol **SI-13** (7.00 g, 15.5 mmol) and 2,6-lutidine (2.15 mL, 18.6 mmol, 1.2 eq.) in anhydrous dichloromethane (75 mL) under nitrogen atmosphere was dropwise added *tert*-butyldimethylsilyl trifluoromethanesulfonate (3.90 mL, 18.6 mmol, 1.1 eq.) under ice bath cooling. The mixture was stirred for 1.5 hours, before additional 2,6-lutidine (0.350 mL, 3.02 mmol, 0.2 eq.) and *tert*-butyl-dimethylsilyl trifluoromethanesulfonate (0.700 mL, 3.05 mmol, 0.2 eq.) were added dropwise. Stirring with cooling was continued for 50 minutes. Then, the mixture was diluted with dichloromethane (50 mL), washed with 2 M hydrochloric acid (100 mL), dried over sodium sulfate and evaporated under reduced pressure. Hexanes (150 mL) were added to the residue, the mixture was sonicated for 20 minutes and filtered. The filtrate was discarded. The solids were washed with hexanes and dried to afford silyl ether **SI-14** (8.27 g, 14.6 mmol,94%) as a yellow solid.

 $\mathbf{R}_{\mathbf{f}}$  = 0.63 (40% ethyl acetate in hexanes).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 7.44 (s, 1H), 6.97 (d, J = 2.2 Hz, 1H), 6.91 (dd, J = 9.8, 0.6 Hz, 1H), 6.37 (d, J = 2.3 Hz, 1H), 6.30 (d, J = 2.2 Hz, 1H), 6.27 (d, J = 2.3 Hz, 1H), 5.57 (dd, J = 9.9, 1.1 Hz, 1H), 3.89 (s, 3H), 3.83 (s, 3H), 3.81 (s, 3H), 3.80 (s, 3H), 3.58 – 3.38 (m, 6H), 2.03 – 1.92 (m, 1H), 1.59 – 1.49 (m, 1H), 0.91 (s, 9H), 0.02 (s, 6H).

<sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>): 174.1, 160.5, 160.1, 156.9, 156.8, 139.2, 134.2, 129.2, 124.5, 122.4, 117.9, 115.4, 114.1, 105.6, 99.2, 97.8, 96.9, 60.6, 55.7, 55.6, 55.5, 55.4, 53.1, 52.8, 42.8, 33.2, 26.1, 18.4, -5.0, -5.1.

**IR**: 3000, 2951, 2934, 2855, 2838, 1722, 1639, 1596, 1568, 1491, 1462, 1425, 1387, 1329, 1307, 1286, 1217, 1204, 1166, 1144, 1086, 1050, 1026, 1005, 962, 948, 938, 907, 889, 830, 801, 775, 729.

HRMS (ESI): C<sub>32</sub>H<sub>43</sub>O<sub>7</sub>Si [M+H]<sup>+</sup> calc. 567.2773, found 567.2785.

#### Nitroacetic acid ester 7



**Step 1:** To a suspension of ester **SI-14** (7.60 g, 13.4 mmol) in anhydrous toluene (65 mL) under nitrogen atmosphere was dropwise added a 1.2 M toluene solution of diisobutylaluminum hydride (23.5 mL, 28.2 mmol, 2.1 eq.) under ice bath cooling. The resulting solution was stirred for 1.5 hours, before ethyl acetate (4 mL), methanol (3.5 mL), and saturated, aqueous potassium sodium tartrate (65 mL) were added carefully in the specified order. The cooling bath was removed and the mixture was stirred vigorously for 45 minutes. Then, the layers were separated and the aqueous layer was extracted with toluene ( $2 \times 50$  mL). The combined organic layers were washed with water (65 mL) and brine (65 mL), dried over sodium sulfate and evaporated under reduced pressure to afford crude alcohol **SI-15** as yellow foam, which was directly used without further purification.

Step 2: To crude alcohol SI-15 in anhydrous dichloromethane (90 mL) was added *N*,*N*′-diisopropylcarbodiimide (6.20 mL, 40.0 mmol, 3 eq.) under ice/brine bath cooling. Then, freshly prepared nitroacetic acid (4.23 g, 40.3 mmol, 3 eq.) in anhydrous tetrahydrofuran (23 mL) was added via syringe pump within 25 minutes. The mixture was stirred for one hour, then the cooling bath as removed and the mixture was filtered. The solids were washed with dichloromethane and discarded. The filtrate was concentrated under reduced pressure and the residue was subjected to column chromatography (0 to 40% ethyl acetate in hexanes), which afforded diester SI-16 (879 mg, 1.47 mmol, 11%) in the form of an orange-yellow foam and ester 7 with minor impurities. Diethyl ether (25 mL) was added to the impure ester 7, the mixture was sonicated for several minutes and filtered. The solids were washed with diethyl ether (2×5 mL) and dried to afford ester 7 (2.11 g, 3.37 mmol, 25%) as a yellow solid. The filtrate was evaporated under reduced pressure, hexanes (40 mL) were added, the mixture was sonicated for several minutes and then filtered. The solids were washed with hexanes and dried to afford additional ester 7 (4.50 g, 7.19 mmol, 54%) in the form of a yellow solid. The filtrate was evaporated under reduced pressure and the residue again purified by column chromatography (0 to 40% ethyl acetate in hexanes) to afford further ester 7 (660 mg, 1.05 mmol, 8%) as an orange-yellow foam.

Analytical data for nitroacetic acid ester 7

 $\mathbf{R}_{\mathbf{f}}$  = 0.58 (40% ethyl acetate in hexanes).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 7.39 (s, 1H), 6.90 (d, J = 10.0 Hz, 1H), 6.87 (d, J = 2.2 Hz, 1H), 6.34 (d, J = 2.3 Hz, 1H), 6.32 (d, J = 2.2 Hz, 1H), 6.31 (d, J = 2.4 Hz, 1H), 5.53 (dd, J = 10.0, 1.1 Hz, 1H), 4.89 (d, J = 14.4 Hz, 1H), 4.81 (d, J = 14.4 Hz, 1H), 4.33 (d, J = 10.3 Hz, 1H), 4.07 (d, J = 10.3 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.83 (s, 3H), 3.82 (s, 3H), 3.52 (ddd, J = 9.9, 6.3, 3.3 Hz, 1H), 3.39 (td, J = 10.2, 4.7 Hz, 1H), 2.92 (dd, J = 10.9, 3.0 Hz, 1H), 1.99 (dddd, J = 13.4, 9.7, 6.4, 3.1 Hz, 1H), 1.61 (dddd, J = 13.9, 11.0, 4.6, 3.3 Hz, 1H), 0.92 (s, 9H), 0.03 (s, 6H).

<sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>): 161.9, 160.4, 160.3, 156.9, 156.8, 138.5, 133.9, 130.2, 126.2, 121.8, 118.1, 114.7, 106.4, 99.4, 97.9, 96.9, 76.0, 70.9, 60.2, 55.8, 55.6, 55.5, 44.1, 41.0, 33.9, 26.1, 18.4, - 5.07, -5.14.

**IR**: 3001, 2951, 2933, 2884, 2855, 2839, 1756, 1642, 1596, 1564, 1491, 1462, 1425, 1407, 1387, 1330, 1309, 1287, 1253, 1219, 1205, 1147, 1103, 1094, 1053, 1006, 978, 939, 911, 890, 833, 810, 776, 733.

**HRMS** (ESI): C<sub>33</sub>H<sub>44</sub>NO<sub>9</sub>Si [M+H]<sup>+</sup> calc. 626.2780, found 626.2774.

Analytical data for diester SI-16

 $\mathbf{R}_{\mathbf{f}}$  = 0.31 (40% ethyl acetate in hexanes).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 7.40 (s, 1H), 6.91 (d, J = 10.0 Hz, 1H), 6.86 (d, J = 2.2 Hz, 1H), 6.43 – 6.26 (m, 2H), 6.22 (d, J = 2.2 Hz, 1H), 5.53 (d, J = 10.0 Hz, 1H), 5.24 (d, J = 14.4 Hz, 1H), 5.17 (d, J = 14.4 Hz, 1H), 5.04 (d, J = 14.4 Hz, 1H), 4.96 (d, J = 14.4 Hz, 1H), 4.29 (d, J = 10.3 Hz, 1H), 4.20 (ddd, J = 10.1, 5.9, 3.8 Hz, 1H), 4.11 (td, J = 10.6, 4.5 Hz, 1H), 4.05 (d, J = 10.3 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.83 (s, 3H), 3.82 (s, 3H), 2.78 (dd, J = 11.1, 3.1 Hz, 1H), 2.22 – 2.10 (m, 1H), 1.85 (ddt, J = 15.0, 11.1, 4.2 Hz, 1H).

<sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>): 161.7, 161.6, 160.7, 160.5, 157.2, 156.9, 136.8, 133.4, 129.5, 125.3, 122.2, 118.3, 114.6, 114.5, 106.0, 99.5, 98.1, 97.4, 76.5, 76.2, 70.1, 65.1, 55.8, 55.67, 55.65, 55.6, 43.8, 41.0, 29.7.

**IR**: 2941, 2840, 1752, 1641, 1596, 1561, 1491, 1462, 1456, 1426, 1406, 1369, 1333, 1312, 1286, 1238, 1205, 1148, 1108, 1083, 1050, 1013, 979, 946, 937, 911, 878, 832, 790, 732.

**HRMS** (ESI): C<sub>29</sub>H<sub>31</sub>N<sub>2</sub>O<sub>12</sub> [M+H]<sup>+</sup> calc. 599.1872, found 599.1862.

#### Isoxazoline 8



To nitroacetic ester 7 (6.46 g, 10.3 mmol) and 4-chlorophenyl isocyanate (3.80 g, 24.8 mmol, in anhydrous toluene (205 mL) under nitrogen atmosphere was added 2.4 eq.) diisopropylethylamine (270  $\mu$ L, 1.55 mmol, 0.15 eq.) and the mixture was stirred at 105 °C for 60 hours, with addition of further diisopropylethylamine after 12 hours (270  $\mu$ L, 1.55 mmol, 0.15 eq.) and 36 h(540 µL, 3.10 mmol, 0.3 eq.). Then, the mixture was cooled to room temperature and filtered. The solids were washed with toluene and discarded. The filtrate was evaporated under reduced pressure and the residue was partially purified by column chromatography (0 to 40% ethyl acetate in hexanes) yielding a brown-red solid. This material was dissolved in dichloromethane and the solvent was removed under reduced pressure, providing an orange-red oil. Diethyl ether (30 mL) was added and the mixture was sonicated until all of the oil had dissolved. Upon standing at room temperature for several minutes a white solid formed. The mixture was kept at room temperature until no further material crystallized and then filtered. The solids were washed with diethyl ether and dried to afford isoxazoline 8 (3.96 g, 6.52 mmol, 63%) as a yellow solid. The filtrate was evaporated under reduced pressure and the residue was purified by column chromatography (0 to 50% ethyl acetate in hexanes) to afford additional isoxazoline 8 (828 mg, 1.36 mmol, 13%) as an orange foam.

 $\mathbf{R}_{\mathbf{f}}$  = 0.48 (40% ethyl acetate in hexanes).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 7.38 (s, 1H), 6.84 (d, J = 2.2 Hz, 1H), 6.47 (d, J = 2.2 Hz, 1H), 6.39 (d, J = 2.3 Hz, 1H), 6.37 (d, J = 2.3 Hz, 1H), 6.18 (d, J = 12.7 Hz, 1H), 4.18 (d, J = 12.0 Hz, 1H), 4.01 (d, J = 12.7 Hz, 1H), 3.92 (s, 3H), 3.89 (s, 3H), 3.87 (s, 3H), 3.85 (s, 3H), 3.67 (d, J = 12.1 Hz, 1H), 3.55 (ddd, J = 10.1, 5.9, 3.1 Hz, 1H), 3.47 (td, J = 10.2, 4.1 Hz, 1H), 3.05 (dd, J = 10.0, 2.0 Hz, 1H), 1.80 – 1.70 (m, 1H), 1.45 (ddt, J = 13.7, 9.9, 3.7 Hz, 1H), 0.89 (s, 9H), 0.05 (s, 3H), 0.03 (s, 3H).

<sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>): 161.8, 161.5, 161.0, 160.2, 157.3, 148.2, 139.8, 134.0, 125.1, 120.4, 113.7, 112.8, 106.1, 99.4, 99.1, 97.2, 79.0, 70.0, 60.3, 56.3, 55.7, 55.6, 45.3, 43.0, 41.2, 33.3, 26.1, 18.35, -5.1, -5.2.

**IR**: 2951, 2934, 1760, 1608, 1598, 1580, 1567, 1529, 1492, 1457, 1426, 1368, 1329, 1319, 1303, 1278, 1258, 1242, 1215, 1203, 1150, 1117, 1100, 1074, 1052, 1028, 1010, 988, 906, 873, 833, 809, 776, 726.

HRMS (ESI): C<sub>33</sub>H<sub>42</sub>NO<sub>8</sub>Si [M+H]<sup>+</sup> calc. 608.2681, found 608.2674.

#### Isoxazole 9



**Step 1:** To isoxazoline **8** (1.88 g, 3.09 mmol) in anhydrous chloroform (60 mL) under nitrogen atmosphere was dropwise added *tert*-butyldimethylsilyl trifluoro-methanesulfonate (852  $\mu$ L, 3.71 mmol, 1.2 eq.). The mixture was stirred for 25 minutes, 2,6-lutidine (537  $\mu$ L, 4.64 mmol, 1.5 eq.) was added and stirring was continued for 1 hour. Then, the mixture was diluted with dichloromethane (50 mL), washed with water (60 mL), 2 M hydrochloric acid (2×60 mL) and again with water (60 mL). After drying over sodium sulfate, the volatiles were evaporated under reduced pressure to afford crude silyl oxime **SI-17** as an orange-yellow solid.

**Step 2:** To crude silyl oxime **SI-17** in anhydrous 1,2-dichloroethane (40 mL) was added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (738 mg, 3.25 mmol, 1.05 eq.). The mixture was stirred at 75°C for 18 hours, then cooled to room temperature and filtered. The solids were washed with dichloromethane and discarded. The filtrate was evaporated under reduced pressure and the residue was partially purified by column chromatography (0 to 100% ethyl acetate in hexanes). Diethyl ether (20 mL) was added to the resulting material, the mixture was sonicated and filtered. The solids were washed with diethyl ether ( $2 \times 5$  mL) and dried to afford isoxazole **9** (1.67 g, 2.76 mmol, 89%) as an orange-yellow solid. The filtrate was evaporated under reduced pressure and the residue was again purified by column chromatography (0 to 40% ethyl acetate in hexanes) to afford additional isoxazole **9** (88.0 mg, 0.145 mmol, 5%) as an orange solid.

#### Analytical data for silyl oxime SI-17

An analytical sample of silyl oxime **SI-17** was obtained by column chromatography (0 to 20% ethyl acetate in hexanes).

 $\mathbf{R}_{\mathbf{f}}$  = 0.62 (40% ethyl acetate in hexanes).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 8.11 (s, 1H), 7.33 (s, 1H), 6.83 (d, J = 2.2 Hz, 1H), 6.36 (d, J = 2.3 Hz, 1H), 6.30 (d, J = 2.3 Hz, 1H), 6.28 (d, J = 2.2 Hz, 1H), 4.35 (d, J = 10.6 Hz, 1H), 4.28 (d, J = 10.7 Hz, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 3.80 (s, 3H), 3.79 (s, 3H), 3.47 (ddd, J = 10.3, 6.8, 3.6 Hz, 1H), 3.34 (td, J = 9.8, 5.6 Hz, 1H), 3.06 (dd, J = 10.7, 3.8 Hz, 1H), 1.95 – 1.70 (m, 2H), 1.04 (s, 9H), 0.85 (s, 9H), 0.35 (s, 3H), 0.31 (s, 3H), -0.04 (s, 3H).

<sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>): 162.0, 161.0, 160.9, 158.2, 156.8, 147.0, 136.6, 134.4, 127.6, 126.5, 122.3, 119.1, 114.3, 113.9, 106.4, 99.1, 97.8, 97.7, 70.5, 60.3, 55.7, 55.60, 55.58, 42.7, 40.2, 32.5, 26.09, 26.07, 25.9, 18.2, 18.0, -4.99, -5.02, -5.04, -5.3.

**IR**: 2950, 2929, 2894, 2886, 2856, 2840, 1742, 1596, 1567, 1491, 1461, 1425, 1383, 1360, 1331, 1306, 1289, 1252, 1236, 1219, 1204, 1168, 1148, 1102, 1076, 1038, 1002, 987, 955, 937, 909, 828, 809, 787, 775, 731.

HRMS (ESI): C<sub>39</sub>H<sub>56</sub>NO<sub>8</sub>Si<sub>2</sub> [M+H]<sup>+</sup> calc. 722.3539, found 722.3539.

Analytical data for isoxazole 9

 $\mathbf{R}_{\mathbf{f}} = 0.40$  (40% ethyl acetate in hexanes).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 7.46 (s, 1H), 6.97 (d, J = 2.2 Hz, 1H), 6.44 (d, J = 2.3 Hz, 1H), 6.41 (d, J = 2.1 Hz, 1H), 6.35 (d, J = 2.3 Hz, 1H), 4.60 (d, J = 10.6 Hz, 1H), 4.03 – 3.97 (m, 4H), 3.91 (s, 3H), 3.88 (s, 3H), 3.84 (s, 3H), 3.55 – 3.35 (m, 3H), 1.84 – 1.63 (m, 2H), 0.85 (s, 9H), -0.03 (s, 3H), -0.05 (s, 3H).

<sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>): 167.0, 163.0, 161.8, 158.0, 158.0, 157.6, 149.5, 138.5, 137.8, 125.4, 123.1, 115.7, 114.5, 106.9, 106.5, 101.8, 97.7, 97.5, 74.1, 60.1, 56.3, 55.8, 55.7, 55.6, 40.4, 40.1, 32.5, 26.0, 18.3, -5.1, -5.3.

**IR**: 2950, 2931, 2885, 2856, 2840, 1765, 1653, 1604, 1592, 1564, 1489, 1459, 1435, 1425, 1388, 1323, 1297, 1253, 1236, 1205, 1175, 1150, 1101, 1075, 1050, 1029, 998, 982, 954, 907, 832, 810, 792, 776, 757, 728.

**HRMS** (ESI): C<sub>33</sub>H<sub>40</sub>NO<sub>8</sub>Si [M+H]<sup>+</sup> calc. 606.2518, found 606.2524.

#### Lactone **2**



To isoxazole **9** (2.50 g, 4.13 mmol), tris(2,2,6,6-tetramethyl-3,5-heptanedionato)-manganese(III) (250 mg, 0.413 mmol, 0.1 eq.), anhydrous, degassed<sup>a</sup> 1,2-dichloroethane (50 mL) and anhydrous, degassed<sup>a</sup> isopropanol (10 mL) under nitrogen atmosphere was added phenylsilane (764  $\mu$ L, 0.670 mmol, 1.5 eq.) and the mixture was stirred for 5 minutes. Then, a 5.5 M decane solution of *tert*-butyl hydroperoxide (1.50 mL, 8.25 mmol, 2 eq.) was added dropwise, the mixture was stirred for 1.5 hours and evaporated under reduced pressure. The residue was partially purified by column chromatography (0 to 100% ethyl acetate in hexanes). Diethyl ether (20 mL) was added to the resulting material, the mixture was sonicated and filtered. The solids were washed with diethyl ether (2×5 mL) and dried to afford lactone **2** (1.94 g, 3.19 mmol, 77%) as a yellowish solid. The filtrate was evaporated under reduced pressure. The residue was purified by column chromatography (0 to 40% ethyl acetate in hexanes) and again treated with diethyl ether to afford additional lactone **2** (102 mg, 0.168 mmol, 4%) as a yellow solid.

 $\mathbf{R}_{\mathbf{f}}$  = 0.43 (40% ethyl acetate in hexanes).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 6.67 (br, 1H), 6.43 (d, J = 2.1 Hz, 1H), 6.41 (d, J = 2.3 Hz, 1H), 6.36 (d, J = 2.4 Hz, 1H), 4.18 (d, J = 10.7 Hz, 1H), 4.04 (d, J = 10.7 Hz, 1H), 4.00 (s, 3H), 3.88 (s, 3H), 3.86 (s, 3H), 3.80 (s, 3H), 3.55 (dd, J = 17.1, 9.8 Hz, 1H), 3.35 – 3.31 (m, 2H), 3.27 (dd, J = 11.0, 3.4 Hz, 1H), 3.14 (dd, J = 9.7, 5.3 Hz, 1H), 3.01 (dd, J = 17.1, 5.3 Hz, 1H), 1.59 – 1.49 (m, 1H), 1.31 – 1.21 (m, 1H), 0.79 (s, 9H), -0.09 (s, 3H), -0.13 (s, 3H).

<sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>): 167.0, 163.6, 159.0, 157.9, 157.8, 157.6, 148.7, 146.0, 139.8, 116.8, 113.2, 107.5, 106.4, 105.9, 97.6, 96.0, 80.7, 60.5, 56.2, 55.7, 55.54, 55.51, 40.8, 38.9, 37.2, 32.5, 25.9, 22.8, 18.2, -5.2, -5.3.

**IR**: 3002, 2951, 2930, 2884, 2855, 1764, 1718, 1700, 1684, 1654, 1600, 1571, 1495, 1452, 1436, 1424, 1388, 1353, 1311, 1277, 1254, 1200, 1147, 1102, 1061, 1044, 1005, 981, 965, 948, 910, 883, 834, 811, 796, 776, 760, 730, 705.

**HRMS** (ESI): C<sub>33</sub>H<sub>42</sub>NO<sub>8</sub>Si [M+H]<sup>+</sup> calc. 608.2674, found 608.2677.

<sup>&</sup>lt;sup>a</sup>By sparging with nitrogen under sonication.

Diol SI-18



To lactone **2** (2.00 g, 3.29 mmol) in anhydrous tetrahydrofuran (35 mL) under nitrogen atmosphere was added a 1.2 M toluene solution of diisobutylaluminum hydride (6.00 mL, 7.20 mmol, 2.2 eq.) under ice bath cooling. The mixture was stirred for 35 minutes, then ethyl acetate (1 mL), methanol (1 mL) and saturated, aqueous sodium potassium tartrate (35 mL) were added carefully in the specified order. After stirring vigorously overnight, the volatiles were evaporated under reduced pressure. The residue was diluted with water (40 mL) and extracted with dichloromethane (50 mL and  $2 \times 20$  mL). The extracts were dried over sodium sulfate and evaporated under reduced pressure. The residue was partially purified by column chromatography (0 to 2.5% methanol in dichloromethane). Diethyl ether (20 mL) was added to the resulting material, the mixture was sonicated and filtered. The solids were washed with diethyl ether (2 × 5 mL) and dried to afford diol **SI-18** (1.70 g, 2.78 mmol, 84%) as a white solid. The filtrate was evaporated under reduced pressure, then diethyl ether (2 mL) and hexanes (2 mL) were added to the residue. The mixture was sonicated, filtered and the filtrate was discarded. The solids were washed with a minimal amount of diethyl ether and dried to afford additional diol **SI-18** (216 mg, 0.353 mmol, 11%) as a yellowish solid.

 $\mathbf{R}_{\mathbf{f}} = 0.31$  (5% methanol in dichloromethane).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 6.65 (d, J = 1.7 Hz, 1H), 6.40 – 6.35 (m, 2H), 6.33 (d, J = 2.3 Hz, 1H), 4.83 (d, J = 13.1 Hz, 1H), 4.78 (d, J = 13.1 Hz, 1H), 3.93 (s, 3H), 3.86 (s, 3H), 3.83 (s, 3H), 3.79 (s, 3H), 3.69 (d, J = 11.7 Hz, 1H), 3.53 – 3.39 (m, 3H), 3.36 – 3.30 (m, 2H), 3.21 (dd, J = 10.4, 3.1 Hz, 1H), 2.79 (dd, J = 15.5, 6.5 Hz, 1H), 1.67 – 1.56 (m, 1H), 1.39 – 1.28 (m, 1H), 0.86 (s, 9H), -0.02 (s, 3H), -0.04 (s, 3H).

<sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>): 166.9, 162.3, 159.4, 158.7, 157.6, 157.4, 145.2, 141.0, 115.8, 110.9, 106.9, 105.5, 105.3, 96.7, 96.3, 68.9, 60.9, 56.8, 56.1, 55.6, 55.54, 55.50, 44.8, 41.9, 39.1, 33.4, 26.1, 25.5, 18.4, -5.2, -5.3.

**IR**: 3513, 3276, 2999, 2952, 2932, 2883, 2856, 2840, 1767, 1653, 1598, 1571, 1495, 1452, 1430, 1423, 1388, 1359, 1337, 1309, 1285, 1256, 1206, 1162, 1149, 1083, 1051, 1006, 982, 939, 910, 833, 810, 776, 730.

**HRMS** (ESI): C<sub>33</sub>H<sub>46</sub>NO<sub>8</sub>Si [M+H]<sup>+</sup> calc. 612.2987, found 612.2985.

Tris-silyl ether SI-19



To diol **SI-18** (1.5 g, 2.45 mmol) and 2,6-lutidine (1.14 mL, 9.84 mmol, 4 eq.) in anhydrous dichloromethane (20 mL) under nitrogen atmosphere was dropwise added *tert*-butyldimethylsilyl trifluoromethanesulfonate (1.35 mL, 5.88 mmol, 2.4 eq.) under ice bath cooling. After stirring with cooling for 2.5 hours, the mixture was diluted with dichloromethane (80 mL), washed with saturated, aqueous sodium bicarbonate (100 mL), 2 M hydrochloric acid (2×100 mL) and water (100 mL), then dried over sodium sulfate and evaporated under reduced pressure. The residue was purified by column chromatography (0 to 10% ethyl acetate in hexanes) to afford tris-silyl ether **SI-19** (2.06 g, 2.45 mmol, quantitative) as an off-white foam.

 $R_f = 0.47$  (20% ethyl acetate in hexanes).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 6.62 (dd, J = 2.2, 1.0 Hz, 1H), 6.37 (d, J = 2.2 Hz, 1H), 6.33 (d, J = 2.3 Hz, 1H), 6.22 (d, J = 2.3 Hz, 1H), 4.85 (d, J = 12.4 Hz, 1H), 4.76 (d, J = 12.4 Hz, 1H), 3.93 (s, 3H), 3.87 (d, J = 10.1 Hz, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 3.78 (s, 3H), 3.53 (t, J = 7.3 Hz, 1H), 3.45 (d, J = 10.0 Hz, 1H), 3.38 (td, J = 9.7, 4.7 Hz, 1H), 3.27 (ddd, J = 10.0, 8.8, 7.0 Hz, 1H), 3.20 (dd, J = 17.4, 7.8 Hz, 1H), 2.96 (dd, J = 17.3, 6.8 Hz, 1H), 2.89 (dd, J = 9.8, 3.7 Hz, 1H), 1.76 – 1.65 (m, 1H), 1.39 – 1.27 (m, 1H), 0.96 (s, 9H), 0.76 (s, 9H), 0.67 (s, 9H), 0.17 (s, 3H), 0.15 (s, 3H), -0.12 (s, 6H), -0.14 (s, 3H), -0.15 (s, 3H).

<sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>): 166.1, 162.0, 159.7, 158.4, 157.7, 157.1, 145.1, 142.0, 115.8, 112.6, 107.8, 105.5, 105.2, 96.3, 96.1, 67.5, 62.8, 58.1, 56.0, 55.6, 55.5, 55.4, 44.5, 42.7, 38.8, 35.0, 26.2, 26.0, 25.8, 24.6, 18.6, 18.3, 18.1, -4.9, -5.0, -5.18, -5.24, -5.3, -5.4.

**IR**: 2954, 2929, 2884, 2856, 1599, 1572, 1493, 1463, 1432, 1423, 1389, 1361, 1338, 1324, 1311, 1286, 1255, 1207, 1163, 1148, 1081, 1054, 1005, 961, 939, 907, 832, 814, 775, 728.

HRMS (APCI): C<sub>45</sub>H<sub>74</sub>NO<sub>8</sub>Si<sub>3</sub> [M+H]<sup>+</sup> calc. 840.4717, found 840.4707.

Diol 10



To silyl ether **SI-19** (400 mg, 0.476 mmol) in tetrahydrofuran (6 mL) was added 1 M hydrochloric acid (2 mL) and the mixture was stirred for 4 hours. Then, 2 M sodium hydroxide (0.4 mL) and saturated, aqueous sodium bicarbonate (5 mL) were added. The tetrahydrofuran was evaporated under reduced pressure and the residue was extracted with dichloromethane (3×4 mL). The extracts were dried over sodium sulfate and evaporated under reduced pressure. The residue was purified by column chromatography (0 to 10% methanol in dichloromethane) to afford diol **10** (224 mg, 0.366 mmol, 77%) and triol **SI-20** (39.6 mg,79.6 µmol, 17%), which were both obtained in the form of a yellowish solid.

Analytical data for diol 10

 $\mathbf{R}_{\mathbf{f}}$  = 0.29 (5% methanol in dichloromethane).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 6.62 (d, J = 1.5 Hz, 1H), 6.41 – 6.35 (m, 3H), 4.87 (s, 2H), 3.94 (s, 3H), 3.86 (s, 3H), 3.85 (s, 3H), 3.80 (s, 3H), 3.70 (d, J = 9.9 Hz, 1H), 3.45 – 3.28 (m, 5H), 3.24 (t, J = 7.4 Hz, 1H), 2.86 (dd, J = 16.3, 7.8 Hz, 1H), 1.74 (dddd, J = 14.6, 9.1, 5.8, 3.3 Hz, 1H), 1.30 (ddt, J = 14.5, 10.3, 4.1 Hz, 1H), 0.70 (s, 9H), -0.10 (s, 3H), -0.12 (s, 3H).

<sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>): 165.7, 162.1, 160.5, 158.7, 157.6, 157.2, 144.5, 141.9, 115.7, 112.4, 107.3, 105.8, 105.6, 96.8, 96.2, 69.6, 60.7, 57.0, 56.1, 55.59, 55.56, 55.5, 44.6, 41.4, 40.1, 34.7, 25.8, 25.4, 18.3, -5.41, -5.44.

**IR**: 3359, 2954, 2930, 2884, 2856, 2840, 1599, 1572, 1494, 1462, 1452, 1423, 1390, 1359, 1336, 1309, 1285, 1257, 1206, 1162, 1148, 1107, 1083, 1051, 1007, 984, 961, 939, 906, 833, 813, 776, 727.

**HRMS** (ESI): C<sub>33</sub>H<sub>46</sub>NO<sub>8</sub>Si [M+H]<sup>+</sup> calc. 612.2987, found 612.3017.

Analytical data for triol **SI-20** 

 $\mathbf{R}_{\mathbf{f}}$  = 0.13 (5% methanol in dichloromethane).

<sup>1</sup>**H-NMR** (400 MHz, CD<sub>3</sub>OD): 6.66 (dd, J = 2.2, 1.0 Hz, 1H), 6.53 (d, J = 2.2 Hz, 1H), 6.44 (d, J = 2.3 Hz, 1H), 6.33 (d, J = 2.3 Hz, 1H), 4.82 (d, J = 13.0 Hz, 1H), 4.78 (d, J = 13.1 Hz, 1H), 3.94 (s, 3H), 3.87 (s, 3H), 3.86 (s, 3H), 3.85 (d, J = 11.4 Hz, 1H), 3.78 (s, 3H), 3.56 – 3.43 (m, 2H), 3.32 (d, J = 12.2 Hz, 1H), 3.29 – 3.17 (m, 2H), 3.04 (dd, J = 10.5, 3.7 Hz, 1H), 2.98 (dd, J = 16.3, 5.7 Hz, 1H), 1.54 (dtd, J = 13.7, 7.9, 3.7 Hz, 1H), 1.27 – 1.15 (m, 1H).

<sup>13</sup>**C-NMR** (100 MHz, CD<sub>3</sub>OD): 167.9, 164.1, 161.3, 160.1, 159.1, 158.6, 146.5, 142.4, 115.9, 113.1, 108.0, 107.0, 106.4, 97.5, 97.1, 68.4, 61.1, 57.1, 56.4, 56.0, 55.9, 55.7, 45.7, 44.2, 39.1, 35.1, 25.2.

**IR**: 3443, 3312, 2933, 2883, 2831, 1613, 1598, 1565, 1493, 1468, 1449, 1426, 1343, 1328, 1308, 1299, 1291, 1255, 1229, 1205, 1161, 1148, 1110, 1098, 1084, 1075, 1056, 1036, 1018, 995, 975, 951, 940, 905, 873, 865, 857, 834, 803, 792, 760, 727.

**HRMS** (APCI): C<sub>27</sub>H<sub>32</sub>NO<sub>8</sub> [M+H]<sup>+</sup> calc. 498.2122, found 498.2125.

Enal **11** 



**Step 1:** To diol **10** (536 mg, 0.876 mmol) and sodium bicarbonate (515 mg, 6.13 mmol, 2.5 eq.) in dichloromethane (7.5 mL) was added Dess-Martin periodinane (929 mg, 2.19 mmol, 2.5 eq.) under ice bath cooling. The mixture was stirred for 30 minutes, then the cooling bath was removed and stirring was continued at room temperature for another 30 minutes. After this time, 2 M aqueous sodium thiosulfate (2.0 mL) and saturated, aqueous sodium bicarbonate (2.0 mL) were added. After stirring for 15 minutes, the mixture was diluted with dichloromethane (10 mL) and the organic layer was separated, dried over sodium sulfate and evporated under reduced pressure. The resulting crude dialdehyde **SI-21** (530 mg, 0.872 mmol, quantitative) was used without further purification.

**Step 2:** To crude dialdehyde **SI-21** (468 mg, 0.770 mmol) in methanol (7 mL) was added potassium carbonate (479 mg, 3.47 mmol, 4.5 eq.). This mixture was stirred for 8 hours, before saturated, aqueous ammonium chloride (4 mL) was added and the mixture was concentrated under reduced pressure to remove methanol. The residue was extracted with dichloromethane (3×5 mL), then the extracts were dried over sodium sulfate and evaporated under reduced pressure. The residue was purified by column chromatography (0 to 5% ethyl acetate in dichloromethane) to afford enal **11** (373 mg, 0.632 mmol, 82%) as a yellowish foam.

Analytical data for dialdehyde SI-21

<sup>1</sup>**H-NMR** (400 MHz, in neutralized CDCl<sub>3</sub>): 10.22 (s, 1H), 9.32 (s, 1H), 6.63 (s, 1H), 6.41 (d, J = 2.2 Hz, 1H), 6.36 (d, J = 2.3 Hz, 1H), 6.31 (d, J = 2.3 Hz, 1H), 4.18 (d, J = 9.8 Hz, 1H), 3.99 (s, 3H), 3.87 (s, 3H), 3.85 (s, 3H), 3.78 (s, 3H), 3.55 – 3.50 (m, 1H), 3.41 (d, J = 9.8 Hz, 1H), 3.20 (dd, J = 17.1, 6.6 Hz, 1H), 3.00 (d, J = 7.0 Hz, 1H), 2.27 (dd, J = 17.2, 5.3 Hz, 1H), 2.18 – 2.10 (m, 1H), 0.6 (s, 9H), -0.15 (s, 3H), -0.23 (s, 3H).

Analytical data for enal **11** 

 $\mathbf{R}_{\mathbf{f}}$  = 0.49 (5% ethyl acetate in dichloromethane).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 9.95 (s, 1H), 7.49 (s, 1H), 6.59 (d, J = 2.1 Hz, 1H), 6.46 – 6.42 (m, 2H), 6.23 (d, J = 2.3 Hz, 1H), 4.87 (s, 1H), 3.97 (s, 3H), 3.88 (s, 3H), 3.71 (s, 3H), 3.68 (s, 3H), 3.37 – 3.27 (m, 1H) 3.30 (d, J = 3.9 Hz, 2H), 3.00 (dd, J = 17.2, 5.9 Hz, 1H), 2.13 (dd, J = 17.3, 12.0 Hz, 1H), 0.80 (s, 9H), -0.11 (s, 3H), -0.12 (s, 3H).

<sup>13</sup>**C-NMR** (101 MHz, CDCl<sub>3</sub>): 194.7, 163.7, 162.7, 158.8, 157.4, 157.3, 155.8, 150.0, 146.3, 137.6, 133.8, 117.2, 113.2, 107.6, 106.7, 104.0, 97.2, 96.6, 64.8, 56.1, 55.7, 55.4, 55.4, 41.2, 36.8, 35.4, 27.9, 25.9, 18.4, -5.5, -5.6.

IR: 2945, 2852, 1677, 1596, 1455, 1308, 1086, 1062, 837.

**HRMS** (ESI): C<sub>33</sub>H<sub>40</sub> NO<sub>7</sub>Si [M+H]<sup>+</sup> calc. 590.2574, found 590.2563.

## Propargylic alcohol 12



To enal **11** (58 mg, 98 µmol) in anhydrous tetrahydrofuran (250 µL) under nitrogen atmosphere was added a 0.5 M tetrahydrofuran solution of ethynylmagnesium bromide (255 µL, 128 µmol, 1.3 eq.) under ice bath cooling. The resulting mixture was stirred for 1.5 hours, then the cooling bath was removed. After stirring for 10 minutes at room temperature, saturated, aqueous ammonium chloride (2 mL) was added and the mixture was extracted with ethyl acetate (2×2 mL). The extracts were washed with brine (3 mL), dried over magnesium sulfate and evaporated under reduced pressure. The residue (d.r. > 20/1) was purified by column chromatography (0 to 60% ethyl acetate in dichloromethane) to afford propargylic alcohol **12** (46 mg, 75 µmol, 76%) as a white solid.

 $\mathbf{R}_{\mathbf{f}}$  = 0.42 (15% ethyl acetate in dichloromethane).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 7.09 (s, 1H), 6.61 (d, J = 2.2 Hz, 1H), 6.55 (d, J = 2.1 Hz, 1H), 6.41 (d, J = 2.1 Hz, 1H), 6.25 (d, J = 2.2 Hz, 1H), 5.50 (d, J = 6.5 Hz, 1H), 4.46 (s, 1H), 3.94 (s, 3H), 3.85 (s, 3H), 3.77 (s, 3H), 3.67 (s, 3H), 3.55 (d, J = 9.8 Hz, 1H), 3.39 (d, J = 9.8 Hz, 1H), 3.30 (dd, J = 10.5, 5.5 Hz, 1H), 2.87 (dd, J = 16.4, 5.7 Hz, 1H), 2.67 (d, J = 2.2 Hz, 1H), 2.55 (d, J = 6.3 Hz, 1H), 2.38 (dd, J = 16.4, 10.3 Hz, 1H), 0.82 (s, 9H), -0.07 (s, 3H), -0.09 (s, 3H).

<sup>13</sup>**C-NMR** (101 MHz, CDCl<sub>3</sub>): 162.4, 162.2, 158.5, 157.4, 156.9, 156.3, 149.6, 145.9, 138.1, 118.8, 112.9, 111.2, 107.5, 107.4, 104.8, 97.1, 96.4, 82.8, 75.6, 65.1, 64.8, 56.0, 55.6, 55.6, 55.4, 42.7, 41.2, 38.2, 27.7, 26.0, 18.4, -5.3, -5.4.

**IR:** 3275, 2925, 2850, 1660, 1598, 1491, 1457, 1309, 1154, 1084, 1070, 891.

HRMS (ESI): C<sub>35</sub>H<sub>42</sub>NO<sub>7</sub>Si [M+H]<sup>+</sup> calc. 616.2731, found 616.2698.

## Pentadienol 13



To propargylic alcohol **12** (50 mg, 81  $\mu$ mol) and triphenylphosphinegold(I) bis(trifluoromethanesulfonyl)imidate (6.0 mg, 8.1  $\mu$ mol, 0.1 eq.) under nitrogen atmosphere was added anhydrous toluene (2.8 mL) and the mixture was stirred at 80 °C for 3 hours, followed by 3 hours at room temperature. Then, the solvent was removed under reduced pressure and the residue was purified by column chromatography (0 to 20% ethyl acetate in dichloromethane) to afford pentadienol **13** (43 mg, 70  $\mu$ mol, 86%) as a white foam/colorless film.

 $\mathbf{R}_{\mathbf{f}}$  = 0.35 (10% ethyl acetate in dichloromethane).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 6.60 (d, J = 2.2 Hz, 1H), 6.57 (s, 1H), 6.44 (d, J = 2.2 Hz, 1H), 6.32 (s, 1H), 6.00 (s, 1H), 5.91 (d, J = 1.7 Hz, 1H), 4.94 (s, 1H), 3.96 (s, 3H), 3.94 (m, 1H), 3.87 (s, 3H), 3.83 (s, 3H), 3.75 (s, 3H), 3.52 (d, J = 9.8 Hz, 1H), 3.39 (d, J = 9.7 Hz, 1H), 3.38 (d, J = 12.0 Hz, 1H), 3.02 (dd, J = 17.0, 5.9 Hz, 1H), 2.10 (dd, J = 15.9, 12.1 Hz, 1H), 0.80 (s, 9H), -0.08 (s, 3H), -0.09 (s, 3H).

<sup>13</sup>**C-NMR** (101 MHz, CDCl<sub>3</sub>): 162.2, 161.9, 157.0, 156.9, 156.4, 156.2, 151.0, 145.5, 141.3, 137.2, 117.0, 115.4, 114.7, 112.1, 110.3, 107.7, 107.1, 97.2, 93.4, 73.2, 65.3, 56.1, 55.9, 55.6, 55.5, 40.0, 37.0, 35.1, 27.4, 26.0, 18.4, -5.4, -5.4.

**IR:** 2927, 2852, 1598, 1457, 1310, 1209, 1078, 834.

**HRMS** (ESI): C<sub>35</sub>H<sub>42</sub> NO<sub>7</sub>Si [M+H]<sup>+</sup> calc. 616.2731, found 616.2712.

## Allylic alcohols 14a and 14b



To pentadienol **13** (720 mg, 1.17 mmol) in anhydrous 1,2-dichloroethane (23.5 mL) under nitrogen atmosphere were added 2-nitrobenzene sulfonyl hydrazide (2.37 g, 11.7 mmol, 10 eq.) and triethylamine (3.3 mL, 24 mmol, 20 eq.). This mixture was stirred at 50 °C in the dark for 3 hours. After this time, the mixture was diluted with dichloromethane (60 mL), washed with 0.5 M hydrochloric acid (50 mL), water (3×40 mL), and brine, dried over sodium sulfate and evaporated under reduced pressure. The residue (**14a/14b**  $\approx$  1/2.3) was purified by column chromatography (0 to 15% ethyl acetate in dichloromethane) to give **14a** (199 mg, 0.322 mmol, 28%) and **14b** (376 mg, 0.609 mmol, 52%) as pale yellowish oils.

Analytical data for 14a

 $\mathbf{R}_{\mathbf{f}}$  = 0.39 (5% ethyl acetate in dichloromethane).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 6.61 (d, J = 2.1 Hz, 1H), 6.55 (s, 1H), 6.43 (d, J = 2.2 Hz, 1H), 6.26 (s, 1H), 4.59 (s, 1H), 4.37 (s, 1H), 3.95 (s, 3H), 3.87 (s, 3H), 3.80 (s, 3H), 3.73 (s, 3H), 3.52 (dd, J = 12.2, 6.9 Hz, 1H), 3.43 (d, J = 9.7 Hz, 1H), 3.38 (dd, J = 7.0, 1.9 Hz, 1H), 3.27 (d, J = 9.7 Hz, 1H), 3.17 (dd, J = 16.8, 6.8 Hz, 1H), 2.20 – 2.07 (m, 1H), 1.16 (d, J = 6.9 Hz, 3H), 0.81 (d, J = 0.9 Hz, 9H), -0.08 (s, 6H).

<sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>): 162.1, 161.7, 157.0, 156.6, 156.4, 155.7, 151.6, 145.6, 136.4, 119.9, 114.2, 111.2, 109.7, 107.9, 107.1, 97.1, 93.3, 78.3, 64.8, 56.1, 55.6, 55.6, 55.5, 41.4, 39.1, 34.6, 34.2, 27.9, 26.0, 19.9, 18.4, -5.3, -5.4.

IR: 3360, 2926, 2853, 1596, 1458, 1310, 1195, 1076, 834.

HRMS (ESI): C<sub>35</sub>H<sub>44</sub>NO<sub>7</sub>Si [M+H]<sup>+</sup> calc. 618.2887, found 618.2864.

#### Analytical data for **14b**

 $\mathbf{R}_{f}$  = 0.40 (10% ethyl acetate in dichloromethane).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 6.60 (d, J = 2.1 Hz, 1H), 6.49 (s, 1H), 6.44 (d, J = 2.2 Hz, 1H), 6.27 (s, 1H), 4.70 (dd, *J* = 9.0, 3.0 Hz, 1H), 4.28 (s, 1H), 3.96 (s, 3H), 3.94 – 3.90 (m, 1H), 3.88 (s, 3H), 3.81 (s, 3H), 3.72 (s, 3H), 3.47 (d, J = 9.9 Hz, 1H), 3.47 – 3.41 (m, 1H), 3.38 (d, J = 9.7 Hz, 1H), 3.02 (dd, J = 17.0, 6.1 Hz, 1H), 2.09 (dd, J = 17.0, 12.1 Hz, 1H), 1.36 (d, J = 7.5 Hz, 3H), 0.83 (s, 9H), -0.04 (s, 3H), -0.07 (s, 3H).

<sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>): 162.2, 161.8, 157.0, 156.4, 155.8, 155.2, 154.4, 145.6, 136.9, 120.9, 114.7, 111.0, 110.2, 107.8, 107.2, 97.1, 92.8, 71.5, 64.9, 56.1, 55.8, 55.7, 55.5, 39.9, 34.9, 34.8, 32.3, 27.6, 26.0, 18.4, 15.1, -5.4, -5.5.

IR: 3362, 2927, 2849, 1654, 1595, 1455, 1487, 1194, 1149, 835.

**HRMS** (ESI): C<sub>35</sub>H<sub>44</sub>NO<sub>7</sub>Si [M+H]<sup>+</sup> calc. 618.2887, found 618.2869.

## Alcohol 15a



To allylic alcohol **14a** (120 mg, 194  $\mu$ mol), tris(2,2,6,6-tetramethyl-3,5-heptanedionato)manganese(III) (35 mg, 58  $\mu$ mol, 0.3 eq.), anhydrous, degassed<sup>a</sup> 1,2-dichloroethane (2.3 mL) and anhydrous, degassed<sup>a</sup> isopropanol (0.47 mL) under nitrogen atmosphere was added phenylsilane (72  $\mu$ L, 0.58  $\mu$ mol, 3 eq.). After the mixture had stirred for 5 minutes, a 5.5 M decane solution of *tert*-butyl hydroperoxide (60  $\mu$ L, 0.33 mmol, 1.7 eq.) was added dropwise and stirring was continued for 25 minutes. Then, the mixture was filtered through a pad of silica with a ¼-mixture of ethyl acetate/dichloromethane. The filtrate was evaporated under reduced pressure and purification of the residue by column chromatography (0 to 10% ethyl acetate in dichloromethane)<sup>b</sup> recovered remaining allylic alcohol **14a** (26 mg, 42  $\mu$ mol, 22%) and afforded alcohol **15a** (42 mg, 68  $\mu$ mol, 35%, based on recovered starting material: 45%) as a yellowish foam.

 $\mathbf{R}_{\mathbf{f}}$  = 0.40 (5% ethyl acetate in dichloromethane).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 6.60 (d, J = 2.2 Hz, 1H), 6.43 (d, J = 2.2 Hz, 1H), 6.29 (s, 1H), 4.04 (s, 1H), 3.94 (s, 3H), 3.87 (s, 3H), 3.81 (s, 3H), 3.75 (s, 1H), 3.72 (s, 3H), 3.63 (d, J = 10.3 Hz, 1H), 3.46 (dd, J = 11.9, 7.0 Hz, 1H), 3.38 (d, J = 10.3 Hz, 1H), 3.13 – 3.05 (m, 2H), 2.83 (dd, J = 16.6, 5.0 Hz, 1H), 2.78 – 2.71 (m, 1H), 2.49 (dd, J = 16.6, 13.0 Hz, 1H), 1.94 – 1.84 (m, 1H), 1.70 (d, J = 3.9 Hz, 1H), 1.43 (d, J = 7.4 Hz, 3H), 0.83 (s, 9H), -0.05 (s, 3H), -0.06 (s, 3H).

<sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>): 163.6, 162.2, 159.3, 157.2, 156.7, 155.4, 146.9, 132.9, 119.4, 116.3, 112.5, 107.4, 107.3, 97.2, 93.3, 75.9, 63.7, 56.1, 55.6, 55.5, 55.4, 40.0, 37.1, 36.8, 35.6, 29.5, 27.5, 26.0, 21.5, 21.2, 18.4, -5.3, -5.4.

**IR:** 2928, 2854, 1592, 1453, 1308, 1209, 1149, 1051, 832.

HRMS (ESI): C<sub>35</sub>H<sub>46</sub>NO<sub>7</sub>Si [M+H]<sup>+</sup> calc. 620.3044, found 620.3035.

<sup>&</sup>lt;sup>a</sup>By sparging with nitrogen under sonication for 15 minutes.

<sup>&</sup>lt;sup>b</sup> Multiple purifications by flash column chromatography on silica gel were required to separate the product from starting material.

## Benzyl ether 16a



Alcohol **15a** (76 mg, 0.12 mmol) in anhydrous tetrahydrofuran (200  $\mu$ L + rinse with 50  $\mu$ L) was slowly added to sodium hydride (60% suspension in paraffin oil, 8.8 mg, 0.22 mmol, 1.8 eq., paraffin oil removed by washing with hexane) in anhydrous tetrahydrofuran (150  $\mu$ L) under nitrogen atmosphere under ice bath cooling. After stirring for 45 minutes, the cooling bath was removed and stirring was continued at room temperature for 15 minutes, before benzyl bromide (32  $\mu$ L, 0.27 mmol, 2.2 eq.) followed by tetra-*n*-butylammonium iodide (2.3 mg, 6.1  $\mu$ mol, 0.05 eq.) were added under ice bath cooling and the mixture was stirred for 8 hours at reflux. After this time, saturated, aqueous ammonium chloride (2 mL) was added under ice bath cooling and the mixture was extracted with diethyl ether (3×2 mL). The extracts were washed with brine, dried over sodium sulfate and evaporated under reduced pressure. The residue was purified by column chromatography (20 to 50% ethyl acetate in hexanes) to recover remaining alcohol **15a** (10 mg, 16 mmol, 13%) and afford benzyl ether **16a** (54 mg, 76 µmol, 62%, based on recovered starting material: 71%) as a yellowish solid.

 $\mathbf{R}_{\mathbf{f}}$  = 0.50 (30% ethyl acetate in hexanes).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 7.41 – 7.30 (m, 4H), 7.30 – 7.24 (m, 1H), 6.60 (d, J = 2.2 Hz, 1H), 6.43 (d, J = 2.2 Hz, 1H), 6.30 (s, 1H), 4.70 (s, 2H), 3.95 (s, 3H), 3.86 (s, 3H), 3.83 – 3.78 (m, 4H), 3.72 (s, 3H), 3.70 – 3.65 (m, 2H), 3.47 (dd, J = 11.8, 7.0 Hz, 1H), 3.38 – 3.34 (m, 2H), 3.10 (dd, J = 17.2, 7.1 Hz, 1H), 2.99 – 2.90 (m, 1H), 2.76 (dd, J = 16.7, 5.0 Hz, 1H), 2.52 (dd, J = 16.8, 13.2 Hz, 1H), 1.98 – 1.77 (m, 1H), 1.40 (d, J = 7.4 Hz, 3H), 0.78 (s, 9H), –0.10 (s, 3H), –0.12 (s, 3H).

<sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>): 163.6, 162.1, 159.4, 157.2, 156.6, 155.3, 146.9, 139.0, 132.9, 128.4, 127.6, 127.4, 119.9, 116.3, 112.6, 107.4 (2 C), 97.2, 93.2, 82.6, 70.3, 63.9, 56.0, 55.6, 55.5, 55.4, 40.0, 35.7, 33.9, 33.1, 30.2, 27.6, 26.0, 21.8, 21.3, 18.4, -5.4, -5.5.

**IR:** 2928, 2854, 1593, 1452, 1309, 1198, 1082.

HRMS (ESI): C<sub>42</sub>H<sub>52</sub>NO<sub>7</sub>Si [M+H]<sup>+</sup> calc. 710.3513, found 710.3495.

## Alcohol 15b



To allylic alcohol **14b** (68 mg, 110  $\mu$ mol), tris(2,2,6,6-tetramethyl-3,5-heptanedionato)manganese(III) (20 mg, 33  $\mu$ mol, 0.3 eq.), anhydrous, degassed<sup>a</sup> 1,2-dichloroethane (1.3 mL) and anhydrous, degassed<sup>a</sup> isopropanol (0.3 mL) under nitrogen atmosphere was added phenylsilane (41  $\mu$ L, 0.33 mmol, 3 eq.). After the mixture had stirred for 5 minutes, a 5.5 M decane solution of *tert*-butyl hydroperoxide (34  $\mu$ L, 0.19 mmol, 1.7 eq.) was added dropwise and stirring was continued for 25 minutes. Then, the mixture was filtered through a pad of silica with a ¼-mixture of ethyl acetate/dichloromethane. The filtrate was evaporated under reduced pressure and purification of the residue by column chromatography (0 to 10% ethyl acetate in dichloromethane)<sup>b</sup> recovered remaining allylic alcohol **14b** (10 mg, 16  $\mu$ mol, 21%) and affored alcohol **SI-22b** (32 mg, 52  $\mu$ mol, 47%, based on recovered starting material 55%) as a yellowish foam.

 $\mathbf{R}_{\mathbf{f}}$  = 0.40 (10% ethyl acetate in dichloromethane).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>):

6.58 (d, J = 2.2 Hz, 1H), 6.43 (d, J = 2.2 Hz, 1H), 6.26 (s, 1H), 4.10 (d, J = 7.2 Hz, 1H), 3.94 (s, 3H), 3.86 (s, 3H), 3.81 (s, 3H), 3.77 (d, J = 3.5 Hz, 1H), 3.70 (s, 3H), 3.66 – 3.59 (m, 2H), 3.49 – 3.37 (m, 2H), 2.96 (dd, J = 17.7, 7.0 Hz, 1H), 2.83 (dd, J = 16.9, 5.6 Hz, 1H), 2.76 – 2.64 (m, 1H), 1.96 (dd, J = 16.9, 12.7 Hz, 1), 1.87 (ddd, J = 16.7, 11.5, 1.4 Hz, 1), 1.32 (d, J = 7.3 Hz, 3H), 0.85 (s, 9H), -0.02 (s, 3H), -0.04 (s, 3H).

<sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>): 163.8, 162.2, 159.3, 157.2, 155.5, 155.4, 147.1, 133.5, 120.1, 116.9, 112.3, 107.4, 107.3, 97.1, 92.8, 72.4, 63.6, 56.0, 55.7, 55.6, 55.2, 40.2, 40.2, 35.9, 30.6, 29.8, 27.7, 26.0, 22.6, 18.4, 14.7, -5.4, -5.4.

**IR:** 2929, 2854, 1641, 1597, 1453, 1422, 1310, 1208, 1150, 1072, 835.

**HRMS** (ESI): C<sub>35</sub>H<sub>46</sub>NO<sub>7</sub>Si [M+H]<sup>+</sup> calc. 620.3044, found 620.3032.

<sup>&</sup>lt;sup>a</sup>By sparging with nitrogen under sonication for 15 minutes.

<sup>&</sup>lt;sup>b</sup> Multiple purifications by flash column chromatography on silica gel were required to separate the product from starting material.
#### Benzyl ether 16b



Alcohol **15b** (67 mg, 0.11 mmol) in anhydrous tetrahydrofuran (150  $\mu$ L + 50  $\mu$ L for rinse) was slowly added to sodium hydride (8.7 mg of 60% suspension in paraffin oil, 0.22 mmol, 2 eq., paraffin oil removed by washing with hexane) in anhydrous tetrahydrofuran (200  $\mu$ L) under nitrogen atmosphere under ice bath cooling. After stirring for 45 minutes, the cooling bath was removed and stirring was continued at room temperature for 15 minutes, before benzyl bromide (28  $\mu$ L, 0.24  $\mu$ mol, 2.2 eq.) followed by tetra-*n*-butylammonium iodide (4.0 mg, 11  $\mu$ mol, 0.1 eq.) were added under ice bath cooling and the mixture was stirred for 5 hours at reflux. After this time, saturated, aqueous ammonium chloride (2.5 mL) was added under ice bath cooling and the mixture was extracted with diethyl ether (3×2 mL). The extracts were washed with brine, dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography (20 to 50% ethyl acetate in hexanes) to afford benzyl ether **16b** (60 mg, 85  $\mu$ mol, 78%) as a yellowish solid.

 $\mathbf{R}_{\mathbf{f}}$  = 0.50 (30% ethyl acetate in hexanes).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 7.45 – 7.40 (m, 2H), 7.39 – 7.32 (m, 2H), 7.31 – 7.27 (m, 1H), 6.58 (d, J = 2.2 Hz, 1H), 6.44 (d, J = 2.2 Hz, 1H), 6.27 (s, 1H), 4. 75 – 4.65 (m, 2H), 3.95 (s, 3H), 3.94 – 3.89 (m, 1H), 3.88 – 3.84 (m, 1H), 3.87 (s, 3H), 3.82 (s, 3H), 3.71 (s, 3H), 3.64 – 3.61 (m, 1H), 3.60 (d, J = 10.3 Hz, 1H), 3.42 (d, J = 10.0 Hz, 1H), 3.38 (dd, J = 11.9, 6.2 Hz, 1H), 2.96 – 2.75 (m, 3H), 2.01 – 1.76 (m, 2H), 1.32 (d, J = 7.3 Hz, 3H), 0.83 (s, 9H), -0.04 (s, 3H), -0.07 (s, 3H).

<sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>): 163.7, 162.2, 159.3, 157.2, 155.4, 155.1, 146.8, 139.0, 134.5, 128.5, 127.5, 127.4, 120.4, 117.0, 112.0, 107.5, 107.3, 97.1, 92.7, 81.0, 71.0, 63.9, 56.0, 55.9, 55.6, 55.3, 40.7, 37.7, 36.0, 30.9, 28.7, 27.4, 25.9, 24.4, 18.4, 14.7, -5.4, -5.5.

**IR:** 2930, 2854, 1597, 1452, 1309, 1203, 1071, 833.

**HRMS** (ESI): C<sub>42</sub>H<sub>52</sub>NO<sub>7</sub>Si [M+H]<sup>+</sup> calc. 710.3513, found 710.3498.

## Neopentylic alcohol 17b



To silyl ether **16b** (145 mg, 204 µmol) in acetonitrile (8.2 mL) was added 70% aqueous hydrogen fluoride-pyridine (300 µL, 10.2 mmol, 50 eq.) and the mixture was stirred for 12 hours. After this time, another portion of 70% aqueous hydrogen fluoride-pyridine (150 µL, 5.10 mmol, 25 eq.) was added under ice bath cooling. After stirring further 24 hours at room temperature, saturated, aqueous sodium bicarbonate was added under ice bath cooling until no further formation of gas was observed and the mixture was extracted with ethyl acetate ( $3 \times 5$  mL). The extracts were washed with brine, dried over sodium sulfate and evaporated under reduced pressure. The residue was purified by column chromatography (20 to 50% ethyl acetate in hexanes) to afford neopentylic alcohol **17b** (106 mg, 178 µmol, 87%) as a white solid.

 $R_f$  = 0.50 (50% ethyl acetate in hexanes).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 7.43 – 7.40 (m, 2H), 7.40 – 7.33 (m, 2H), 7.32 – 7.28 (m, 1H), 6.62 (d, J = 2.2 Hz, 1H), 6.42 (d, J = 2.2 Hz, 1H), 6.26 (s, 1H), 4.74 (d, J = 11.9 Hz, 1H), 4.64 (d, J = 12.0 Hz, 1H), 3.94 (s, 3H), 3.87 (s, 3H), 3.89 – 3.80 (m, 1H), 3.82 (s, 3H), 3.76 – 3.64 (m, 3H), 3.70 (s, 3H), 3.49 (dd, J = 11.1, 5.1 Hz, 1H), 3.33 (m, 1H), 2.94 (dd, J = 17.5, 6.6 Hz, 1H), 2.85 – 2.75 (m, 2H), 2.00 – 1.78 (m, 2H), 1.33 (d, J = 7.3 Hz, 3H).

<sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>): 163.8, 162.4, 159.2, 157.3, 155.4, 155.3, 146.6, 138.9, 133.6, 128.6, 127.8, 127.7, 120.1, 116.9, 111.8, 107.4, 107.2, 97.2, 92.9, 80.7, 71.6, 64.3, 56.1, 55.8, 55.7, 55.3, 40.7, 37.9, 35.9, 31.2, 28.9, 27.5, 23.9, 15.0.

IR: 3392, 2922, 1599, 1451, 1347, 1108, 1071, 1047.

**HRMS** (ESI): C<sub>36</sub>H<sub>38</sub>NO<sub>7</sub> [M+H]<sup>+</sup> calc. 596.2648, found 596.2635.

#### Aldehyde SI-22b



A mixture of neopentylic alcohol **17b** (99 mg, 0.17 mmol), tetrakis(acetonitrile)copper(I) triflate(6.3 mg, 17  $\mu$ mol, 0.1 eq.), 4-4'-dimethoxy-2-2'-bipyridine (3.6 mg, 17  $\mu$ mol, 0.1 eq.), 9-azabicyclo[3.3.1]nonane *N*-oxyl (2.8 mg, 17  $\mu$ mol, 0.1 eq.) and *N*-methylimidazole (2.7 mg, 33  $\mu$ mol, 0.2 eq.) in acetonitrile/tetrahydrofuran (12.6mL/4.2 mL), was stirred under oxygen atmosphere (balloon) for 4.5 hours. The reaction mixture was filtered through the pad of silica (50% ethyl acetate in hexanes). Then, the volatiles were evaporated under reduced pressure. The residue was purified by column chromatography (0 to 5% ethyl acetate in dichloromethane) to afford aldehyde **SI-22b** (75 mg, 0.13 mmol, 76%) as a white solid.

 $R_f$  = 0.68 (50% ethyl acetate in hexanes).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 9.66 (s, 1H), 7.39 – 7.33 (m, 2H), 7.32 – 7.27 (m, 2H), 7.31 – 7.26 (m, 1H), 6.55 (d, J = 2.2 Hz, 1H), 6.43 (d, J = 2.2 Hz, 1H), 6.28 (s, 1H), 4.75 – 4.51 (m, 2H), 3.95 (s, 3H), 3.90 (d, J = 3.9 Hz, 1H), 3.86 (s, 3H), 3.81 (s, 3H), 3.71 (s, 3H), 3.75 – 3.66 (m, 2H), 3.25 (dd, J = 10.9, 7.0 Hz, 1H), 3.03 (dd, J = 17.7, 7.0, 1H), 2.78 (dd, J = 17.0, 5.5 Hz, 1H), 2.66 – 2.54 (m, 1H), 2.07 – 1.88 (m, 2H), 1.36 (d, J = 6.9 Hz, 3H).

<sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>): 202.2, 164.6, 162.6, 159.1, 157.6, 155.8, 155.4, 144.9, 138.8, 131.1, 128.5, 127.7, 127.7, 119.8, 115.8, 108.4, 107.4, 106.8, 97.6, 93.2, 79.3, 71.5, 56.1, 55.7, 55.7, 55.3, 46.6, 40.6, 38.2, 30.2, 29.6, 28.2, 22.7, 15.4.

IR: 2936, 1723, 1644, 1598, 1568, 1453, 1423, 1357, 1208, 1073.

HRMS (ESI): C<sub>36</sub>H<sub>36</sub>NO<sub>7</sub> [M+H]<sup>+</sup> calc. 594.2492, found 594.2487.

#### Vinyl boronate SI-23b



To 2,2,6,6-tetramethylpiperidine (29  $\mu$ L, 0.17 mmol, 3.5 eq.) in anhydrous tetrahydrofuran (50  $\mu$ L) under nitrogen atmosphere was added a 2.5 M hexane solution of *n*-butyl lithium (69  $\mu$ L, 0.17 mmol, 3.5 eq.) under ice bath cooling. The mixture was stirred for 5 minutes, before bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (46 mg, 0.17 mmol, 3.5 eq.) in anhydrous tetrahydrofuran (200  $\mu$ L + 100  $\mu$ L for rinse) was added and the mixture was stirred for additional 5 minutes. Then, the ice bath was replaced with a acetone/dry ice bath and aldehyde SI-22b (29 mg, 49 µmol) in anhydrous tetrahydrofuran (200 µL + 100 µL for rinse) was added dropwise. The mixture was stirred with cooling for additional 4 hours and then warmed to -10 °C over 3 hours. After this time, saturated, aqueous ammonium chloride was added and the mixture was extracted with diethyl ether (3×15 mL). The extracts were washed with brine, dried over sodium sulfate and evaporated under reduced pressure. The residue was purified by column chromatography (20 to 40% ethyl acetate in hexanes) to afford vinyl boronate SI-23b (24 mg,  $33 \mu mol, 66\%$ ) as a white solid.

 $R_f$  = 0.70 (50% ethyl acetate in hexanes).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 7.41 – 7.31 (m, 4H), 7.30 – 7.24 (m, 1H), 6.59 (d, J = 17.4 Hz, 1H), 6.50 (d, J = 2.2 Hz, 1H), 6.38 (d, J = 2.2 Hz, 1H), 6.25 (s, 1H), 5.24 (d, J = 17.9 Hz, 1H), 4.64 (d, J = 11.6 Hz, 1H), 4.51 (d, J = 11.6 Hz, 1H), 3.93 (s, 3H), 3.85 (s, 3H), 3.80 (s, 3H), 3.68 (s, 3H), 3.73 – 3.60 (m, 2H), 3.40 (d, J = 3.4 Hz, 1H), 3.09 (dd, J = 10.7, 7.2 Hz, 1H), 2.95 (dd, J = 17.8, 7.2 Hz, 1H), 2.80 (m, 1H), 2.68 (dd, J = 16.9, 5.6 Hz, 1H), 1.97 (dd, J = 16.9, 12.7 Hz, 1H), 1.84 (dd, J = 17.9, 10.7 Hz, 1H), 1.34 (d, J = 7.1 Hz, 3H), 1.19 (d, J = 5.5 Hz, 12H).

<sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>): 164.1, 162.0, 159.1, 157.3, 156.7, 155.7, 155.3, 146.9, 138.9, 131.7, 128.5, 127.8, 127.6, 119.9, 116.6, 111.9, 107.4, 107.0, 97.0, 93.1, 83.3, 79.2, 75.2, 71.3, 56.0, 55.7, 55.6, 55.2, 44.1, 39.8, 35.7, 34.5, 30.0, 28.6, 25.0, 25.0, 24.9, 22.2, 15.7.

IR: 2975, 2932, 2837, 1598, 1453, 1309, 1201, 1141, 1065, 969.

**HRMS** (ESI): C<sub>43</sub>H<sub>49</sub>NBO<sub>8</sub> [M+H]<sup>+</sup> calc. 718.3551, found 718.3550.

## Aldehyde 18b



To boronate **SI-23b** (71 mg, 98 µmol, 1 eq.) in tetrahydrofuran (1 mL) was added sodium perborate (107 mg, 695 µmol, 7 eq.) in water (1 mL) under ice bath cooling. After stirring for 10 minutes, the cooling bath was removed and the mixture was stirred at room temperature for 2.5 hours. Then, water (5 mL) and 2 M aqueous sodium sulfite (3 mL) were added. After stirring further 15 minutes, the mixture was extracted with dichloromethane (4×10 mL). The extracts were dried over sodium sulfate and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (0 to 5% ethyl acetate in dichloromethane) to afford aldehyde **18b** (32 mg, 53 µmol, 53%) as a colorless oil.

 $R_f$  = 0.42 (30% ethyl acetate in hexanes).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 9.64 (t, J = 2.44 Hz, 1H), 7.44 – 7.33 (m, 4H), 7.31 – 7.26 (m, 1H), 6.57 (d, J = 2.2 Hz, 1H), 6.45 (d, J = 2.2 Hz, 1H), 6.26 (s, 1H), 4.73 – 4.59 (m, 2H), 3.95, (s, 3H), 3.87 (s, 3H), 3.84 – 3.74 (m, 1H), 3.81 (s, 3H), 3.70 (s, 3H), 3.72 – 3.64 (m, 2H), 3.28 (dd, J = 11.0, 6.6 Hz, 1H), 2.92 (dd, J = 17.7, 6.6 Hz, 1H), 2.85 – 2.75 (m, 2H), 2.73 – 2.63 (m, 2H), 1.94 (dd, J = 18.4, 14.0 Hz, 1H), 1.80 (dd, J = 16.8, 11.2 Hz, 1H), 1.30 (d, J = 7.2 Hz, 3H).

<sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>): 201.3, 163.4, 162.7, 158.4, 157.6, 155.5, 155.4, 146.2, 138.8, 132.4, 128.6, 127.8, 127.7, 119.9, 116.6, 113.2, 107.2, 107.1, 97.5, 93.1, 80.1, 71.8, 56.1, 55.8, 55.7, 55.3, 49.8, 44.0, 38.1, 34.9, 33.9, 29.1, 27.8, 23.3, 15.2.

**IR:** 2927, 1714, 1598, 1452, 1310, 1206, 1073, 751.

**HRMS** (ESI): C<sub>37</sub>H<sub>38</sub>NO<sub>7</sub> [M+H]<sup>+</sup> calc. 608.2648, found 608.2635.

## Ketone SI-25b



**Step 1:** A 1 M dichloromethane solution of titanium tetrachloride (20  $\mu$ L, 20  $\mu$ mol, 1.5 eq.) was added to a aldehyde **18b** (8.0 mg, 13  $\mu$ mol, 1 eq.) and TMS-dienolate **A3** (7.1 mg, 33  $\mu$ mol, 2.5 eq.) in anhydrous dichloromethane (850  $\mu$ L) under nitrogen atmosphere with acetone/dry ice bath cooling. The mixture was stirred with cooling for 1 hour, before diethyl ether (4 mL), phosphate buffered saline (pH=7.4) and a few drops of saturated, aqueous sodium bicarbonate were added. Then, the mixture was extracted with diethyl ether (4×4 mL) and the extracts were washed with brine, dried over sodium sulfate and evaporated under reduced pressure. The residue was purified by column chromatography (30 to 50% ethyl acetate in hexanes) to afford a mixture of diastereomers of alcohol **SI-24b** (8.2 mg, 11  $\mu$ mol, 83%) as a white solid.

**Step 2:** To alcohol **SI-24b** (3.9 mg, 5.2 µmol) and sodium bicarbonate (1.3 mg, 16 µmol, 3 eq.) in dichloromethane (104 µL) was added Dess-Martin periodinane (5.5 mg, 13 µmol, 2.5 eq.) under ice bath cooling. After stirring 15 minutes, the cooling bath was removed and stirring was continued at room temperature for 1 hour, before more Dess-Martin periodinane (3.0 mg, 7.1 µmol, 1.4 eq.) and sodium bicarbonate (1.3 mg, 15 µmol, 3 eq.) were added. After stirring further 15 minutes at room temperature, the mixture was diluted with dichloromethane (2 mL), then 2 M aqueous sodium sulfite (2 mL) and saturated, aqueous sodium bicarbonate (2 mL) were added under ice bath cooling. After stirring with cooling for 15 min, the organic phase was separated, dried over sodium sulfate and evaporated under reduced pressure. The residue was purified by column chromatography (30 to 50% ethyl acetate in hexanes) to afford ketone **SI-25b** (3.5 mg, 4.7 µmol, 90%) as a white solid.

Analytical data for alcohol SI-24b

 $\mathbf{R}_{\mathbf{f}}$  = 0.32 (50% ethyl acetate in hexanes).

Analytical data for ketone **SI-25b** 

 $R_f$  = 0.38 (50% ethyl acetate in hexanes).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 7.42 – 7.33 (m, 4H), 7.32 – 7.28 (m, 1H), 6.58 (d, J = 2.2 Hz, 1H), 6.45 (d, J = 2.3 Hz, 1H), 6.26 (s, 1H), 5.13 (s, 1H), 4.76 (d, J = 11.8 Hz, 1H), 4.62 (d, J = 11.8 Hz, 1H), 3.95 (s, 3H), 3.91 – 3.81 (m, 1H), 3.87 (s, 3H), 3.82 (s, 3H), 3.78 – 3.76 (m, 1H), 3.70 (s, 3H), 3.51 (dd, *J* = 11.1, 6.5 Hz, 1H), 3.23 (d, J = 16.5 Hz, 1H), 3.12 (d, J = 16.5 Hz, 1H), 2.90 – 2.78 (m, 2H), 2.80 (d, J = 16.3 Hz, 1H), 2.75 – 2.69 (m, 1H), 2.67 (d, J = 16.7 Hz, 1H), 1.91 (dd, J = 17.0, 12.7 Hz, 1H), 1.75 (dd, J = 17.6, 11.2 Hz, 1H), 1.59 (s, 3H), 1.57 (s, 3H), 1.29 (d, J = 7.3 Hz, 3H).

<sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>): 202.5, 164.2, 163.1, 162.6, 160.7, 158.2, 157.5, 155.5, 155.2, 146.5, 138.6, 132.9, 128.7, 127.9, 127.6, 119.7, 116.8, 113.7, 107.4, 107.3, 107.0, 97.2, 96.8, 92.9, 80.4, 71.9, 56.1, 55.8, 55.7, 55.3, 49.3, 46.7, 42.4, 38.9, 34.5, 33.7, 28.7, 27.6, 25.2, 24.8, 23.7, 15.1.

**IR:** 2923, 2853, 1726, 1599, 1455, 1312, 1206, 1073.

**HRMS** (ESI): C<sub>44</sub>H<sub>46</sub>NO<sub>10</sub> [M+H]<sup>+</sup> calc. 748.3122, found 748.3109.

#### Pyrone 19b



To refluxing, degassed toluene (1.5 mL) was added ketone **SI-25b** (14.6 mg, 19.5  $\mu$ mol) in degassed toluene (0.8 mL + 0.5 mL for rinse). This mixture was refluxed for 15 minutes, then the solvent was removed under reduced pressure. The residue was purified by column chromatography (30 to 50% ethyl acetate in hexanes) to afford pyrone **19b** (9.3 mg, 13  $\mu$ mol, 69%) as a white solid.

 $R_f = 0.60$  (ethyl acetate).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 9.67 (br. s, 1H), 7.45 – 7.41 (m, 2H), 7.38 – 7.34 (m, 2H), 7.30 – 7.25 (m, 1H), 6.71 (d, J = 2.2 Hz, 1H), 6.40 (d, J = 2.2 Hz, 1H), 6.24 (s, 1H), 5.71 (d, J = 2.0 Hz, 1H), 5.31 (s, 1H), 4.76 (d, J = 11.1 Hz, 1H), 4.65 (d, J = 11.6 Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.87 – 3.83 (m, 1H), 3.80 (s, 3H), 3.70 – 3.65 (m, 4H), 3.60 – 3.57 (m, 1H), 3.17 (dd, J = 11.1, 6.5 Hz, 1H), 2.90 (dd, J = 17.6, 6.5 Hz, 1H), 2.84 – 2.77 (m, 2H), 2.72 – 2.63 (m, 2H), 1.96 – 1.90 (m, 1H) 1.75 (dd, J = 17.6, 11.2 Hz, 1H), 1.29 (d, J = 7.2 Hz, 3H).

<sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>): 170.3, 166.1, 164.1, 163.2, 162.9, 158.5, 157.4, 155.5, 155.4, 146.4, 138.8, 132.5, 128.7, 127.9, 127.7, 119.7, 116.5, 113.3, 107.1, 106.9, 104.0, 98.0, 93.0, 90.7, 80.3, 71.8, 56.1, 55.9, 55.8, 55.3, 43.4, 40.7, 38.3, 35.2, 33.9, 28.8, 27.9, 23.6, 15.0.

**IR:** 2924, 1694, 1598, 1567, 1453, 1435, 1311, 1071.

**HRMS** (ESI): C<sub>41</sub>H<sub>40</sub>NO<sub>9</sub> [M+H]<sup>+</sup> calc. 690.2703, found 690.2707.

## Enamine 20b



Platinum dioxide (0.8 mg, 4  $\mu$ mol, 0.1 eq.) was added to pentadienol **13** (22.9 mg, 37.2 mmol) in dichloromethane (750  $\mu$ L) and the mixture was stirred under hydrogen atmosphere (balloon) for 8 hours. Then, the mixture was filtered through a pad of Celite<sup>®</sup> and concentrated under reduced pressure. The residue was purified by preperative thin layer chromatography (10% methanol in dichloromethane) to yield enamine **20b** (18.2 mg, 29.3 mmol. 79%) as a yellowish solid.

 $\mathbf{R}_{\mathbf{f}}$  = 0.55 (10% methanol in dichloromethane).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 6.39 (d, J = 2.32 Hz, 1H), 6.36 (d, J = 2.34 Hz, 1H), 3.90 (s, 3H), 3.83 (s, 3H), 3.82 (s, 3H), 3.88 – 3.80 (m, 1H), 3.75 (s, 3H), 3.75 – 3.65 (m, 1H), 3.64 – 3.56 (m, 1H), 3.51 (d, J = 11.3 Hz, 1H), 3.44 (d, J = 11.1 Hz, 1H), 3.18 (dd, *J* = 12.3, 5.5 Hz, 1H), 2.98 (dd, J = 17.2, 5.5 Hz, 1H), 2.54 – 2.47 (m, 1H), 2.37 (ddd, J = 17.3, 12.4, 1.7 Hz, 1H), 2.02 (dd, J = 17.0, 5.5 Hz, 1H), 1.86 (dd, J = 16.9, 12.9 Hz, 1H), 1.27 (d, J = 7.3 Hz, 3H), 0.80 (s, 9H), -0.10 (s, 3H), -0.20 (s, 3H).

<sup>13</sup>**C-NMR** (101 MHz, CDCl<sub>3</sub>): 186.8, 162.7, 161.7, 159.5, 155.6, 155.3, 149.6, 135.3, 119.9, 117.7, 116.1, 104.7, 100.7, 97.9, 92.8, 72.5, 65.4, 56.1, 55.8, 55.4, 55.3, 40.9, 39.9, 36.8, 33.0, 31.9, 30.3, 29.1, 25.9, 18.3, 14.6, -5.5, -5.7.

**IR:** 3420, 2926, 2853, 1594, 1484, 1311, 1250, 1197, 1080, 1051, 834.

**HRMS** (ESI): C<sub>35</sub>H<sub>48</sub>NO<sub>7</sub>Si [M+H]<sup>+</sup> calc. 622.3200, found 622.3207.

#### Keto-enol 21b



To enamine **20b** (54.7 mg, 88.0 µmol) and *tert*-butyl nitrite(21 µL, 0.18 mmol, 2 eq.) in dimethyl sulfoxide (1.1 mL) was added triflic acid (78 µL, 0.88 mmol, 10 eq.) and the mixture was stirred for 15 minutes. After this time, saturated, aqueous sodium bicarbonate (4 mL) was added and the mixture was extracted with ethyl acetate (3×3 mL). The extracts were washed with water (5 mL) and brine (5 mL), dried over sodium sulfate and evaporated under reduced pressure. The residue was purified by column chromatography (hexanes/ethyl acetate/dichloromethane = 3/1/1) to afford the keto-enol **21b** (33.5 mg, 53.8 mmol, 61%) as a colorless solid.

 $\mathbf{R}_{\mathbf{f}}$  = 0.32 (hexanes/ethyl acetate/dichloromethane = 3/1/1).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 6.41 (s, 2H), 6.32 (s, 1H), 3.93 – 3.90 (m, 4H), 3.86 (s, 3H), 3.82 (s, 3H), 3.76 (s, 3H), 3.69 (d, J = 4.1 Hz, 1H), 3.62 – 3.55 (m, 1H), 3.57 (d, J = 10.2 Hz, 1H), 3.40 (d, J = 10.4 Hz, 1H), 3.27 (dd, J = 12.2, 5.9 Hz, 1H), 3.02 (dd, J = 17.4, 5.9 Hz, 1H), 2.59 – 2.51 (m, 1H), 2.32 – 2.19 (m, 2H), 1.86 (dd, J = 18.4, 12.8 Hz, 1H), 1.28 (d, J = 7.3 Hz, 3H), 0.82 (s, 9H), -0.06 (s, 3H), -0.16 (s, 3H).

<sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>): 187.4, 182.2, 164.3, 162.4, 155.9, 155.3, 151.2, 134.5, 120.0, 117.1, 112.6, 105.6, 105.2, 97.8, 92.9, 71.9, 65.0, 56.2, 55.8, 55.6, 55.3, 40.2, 39.3, 36.7, 32.5, 31.0, 30.2, 29.3, 25.9, 18.3, 14.7, -5.5, -5.6.

IR: 2929, 2854, 1592, 1460, 1313, 1254, 1209, 1080, 835.

**HRMS** (ESI): C<sub>35</sub>H<sub>47</sub>O<sub>8</sub>Si [M+H]<sup>+</sup> calc. 623.3040, found 623.3029.

## Tetraphenol 22b



To keto-enol **21b** (37.0 mg, 59.4 µmol) in anhydrous dichloromethane (1.9 mL) was dropwise added boron tribromide (56 µL, 0.59 mmol, 10 eq.) under acetone/dry ice bath cooling. The mixture was stirred with cooling for 4 hours, then the cooling bath was removed and stirring was continued at room temperature for 22 hours. After this time, the reaction mixture was cooled with an ice bath, diluted with dichloromethane (3 mL) and ice was added. The cooling bath was removed and stirring was continued for 1 hour at room temperature. The layers were separated and the aqueous layer was extracted with dichloromethane/methanol = 10/1 (2×3 mL). The combined organic layers were dried over sodium sulfate and evaporated under reduced pressure. The residue was purified by column chromatography (10% methanol in dichloromethane) to afford tetraphenol **22b** (9.8 mg, 22 mmol, 36%) as a redish oil.

 $\mathbf{R}_{\mathbf{f}}$  = 0.15 (10% methanol in dichloromethane).

<sup>1</sup>**H-NMR** (400 MHz, DMSO-*d*<sub>6</sub>): 14.43 (s, 1H), 11.88 (s, 1H), 10.62 (s, 1H), 8.83 (s, 1H), 8.82 (s, 1H), 6.32 (d, J = 2.2 Hz, 1H), 6.19 (s, 1H), 6.12 (d, J = 2.2 Hz, 1H), 4.81 (t, J = 5.0 Hz, 1H), 4.67 (d, J = 4.1 Hz, 1H), 3.66 (ddd, J = 7.0, 3.9, 2.0 Hz, 1H), 3.49 (d, J = 4.1 Hz, 1H), 3.41 (dd, J = 10.4, 4.7 Hz, 1H), 3.21 (dd, J = 11.2, 5.2 Hz, 1H), 3.17 (d, J = 4.6 Hz, 2H), 3.10 (dd, J = 12.0, 6.0 Hz, 1H), 2.75 (dd, J = 17.0, 6.0 Hz, 1H), 2.21 (dd, J = 18.6, 5.7 Hz, 1H), 1.96 (dd, J = 17.0, 12.1 Hz, 1H), 1.70 (dd, J = 18.7, 12.5 Hz, 1H), 1.13 (d, J = 7.2 Hz, 3H).

<sup>13</sup>**C-NMR** (100 MHz, DMSO-*d*<sub>6</sub>): 190.8, 177.9, 164.7, 164.1, 152.8, 151.9, 150.6, 133.6, 117.0, 113.0, 108.4, 106.4, 104.6, 100.6, 100.0, 70.4, 63.9, 48.6, 37.5, 35.6, 31.6, 30.8, 30.3, 29.9, 15.0.

**IR:** 3338, 2923, 1597, 1348, 1266, 1223, 1163.

HRMS (ESI): C<sub>25</sub>H<sub>25</sub>O<sub>8</sub> [M+H]<sup>+</sup> calc. 453.1549, found 453.1562.

#### Amide SI-26b



To enamine **20b** (14.9 mg, 24.0 µmol) in dichloromethane (150 µL) were added pyridine (19 µL, 0.24 mmol, 10 eq.) and benzoyl chloride (8 µL, 0.072 mmol, 3 eq.) under ice bath cooling. Then, the mixture was stirred with warming to room temperature for 40 hours. After this time, more dichloromethane (100 µL) and *N*,*N*-dimethylethylenediamine (11 mg, 0.12 mmol, 5.00 eq.) were added under ice bath cooling. After stirring for additional 1.5 hours at room temperature, the mixture was diluted with dichloromethane (3 mL), washed with saturated, aqueous ammonium chloride and dried over sodium sulfate. The volatiles were evaporated under reduced pressure and the residue was purified by column chromatography (30 to 50% ethyl acetate in hexanes) to afford amide **SI-26b** (17.1 mg, 20.6 µmol, 86%) as a yellowish solid.

 $R_f$  = 0.50 (50% ethyl acetate in hexanes).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 14.44 (s, 1H), 8.14 – 8.06 (m, 2H), 8.02 – 7.97 (m, 2H), 7.58 – 7.37 (m, 6H), 6.45 – 6.38 (m, 2H), 6.35 (s, 1H), 5.40 (dd, J = 8.6, 1.3 Hz, 1H), 4.00 (dd, J = 8.5, 7.2 Hz, 1H), 3.95 (s, 3H), 3.86 (s, 3H), 3.84 (s, 3H), 3.80 – 3.75 (m, 4H), 3.61 – 3.47 (m, 3H), 3.33 (dd, J = 12.5, 5.5 Hz, 1H), 3.11 (dd, J = 17.3, 5.6 Hz, 1H), 2.70 – 2.63 (m, 1H), 2.54 (dd, J = 19.0, 12.7 Hz, 1H), 2.33 (dd, J = 17.3, 12.7, 1.7 Hz, 1H), 1.30 (d, J = 7.3 Hz, 3H), 0.72 (s, 9H), -0.27 (s, 3H), -0.30 (s, 3H).

<sup>13</sup>**C-NMR** (101 MHz, CDCl<sub>3</sub>): 189.0, 166.2, 166.2, 164.1, 162.7, 156.0, 155.4, 155.1, 150.7, 134.7, 134.4, 133.0, 132.1, 130.7, 129.8, 128.8, 128.4, 128.1, 119.5, 116.5, 115.3, 110.9, 105.0, 98.0, 93.1, 74.7, 65.2, 56.4, 55.7, 55.6, 55.3, 42.0, 39.7, 34.6, 31.5, 29.8, 29.8, 28.3, 25.8, 18.3, 16.3, -5.8, -5.9.

**IR:** 2927, 2837, 1572, 1450, 1233, 1158, 1045.

HRMS (ESI): C<sub>49</sub>H<sub>59</sub>N<sub>2</sub>O<sub>9</sub>Si [M+NH<sub>4</sub>]<sup>+</sup> calc. 847.3990, found 847.3993.

## Picolinamide SI-29 (racemic)



A mixture of chloropicolinic acid SI-27 (16.7 g, 106 mmol, 2.2 eq.) and carbonyldiimidazole (16.4 g, 0.101 mmol, 2.1 eq.) in anhydrous tetrahydrofuran (172 mL) under nitrogen atmosphere was warmed to 50 °C. After stirring for 2 hours, racemic diaminocyclohexane SI-28 (5.78 mL, 48.1 mmol) was added. After stirring further 6.5 hours, the mixture was cooled to room temperature and the volatiles were removed under reduced pressure. Water (200 mL) was added to the residue, the mixture was stirred overnight and filtered. The solids were washed with additional water (2×50 mL) and the filtrate was discarded. Then, the solids were dissolved in plenty dichloromethane and the remaining insoluble material was discarded. The resulting solution was dried over sodium sulfate and filtered over a short plug of silica. The silica was washed with additional dichloromethane and 5% ethyl acetate in dichloromethane until no further material eluted. Then, the volatiles were evaporated under reduced pressure. The residue was suspended in ethanol (150 mL), warmed to reflux for 15 minutes, cooled with an ice bath for 1 hour and the resulting suspension was filtered. The solids were washed with ethanol (2×10 mL) and dried to afford amide SI-29 (12.8 g 32.5 mmol, 68%) as an off-white solid. Additional amide SI-29 (1.20 g, 3.05 mmol, 6%) was isolate from the filtrate after removal of the solvent under reduced pressure and purification of the residue by column chromatography (0 to 40% ethyl acetate in hexanes).

 $\mathbf{R}_{\mathbf{f}}$  = 0.51 (50% ethyl acetate in hexanes).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 8.42 (dd, J = 5.3, 0.6 Hz, 2H), 8.22 – 8.09 (m, 2H), 8.05 (dd, J = 2.1, 0.6 Hz, 2H), 7.35 (dd, J = 5.2, 2.1 Hz, 2H), 4.14 – 3.94 (m, 2H), 2.29 – 2.11 (m, 2H), 1.92 – 1.73 (m, 2H), 1.63 – 1.33 (m, 4H).

<sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>): 163.5, 151.3, 149.2, 145.7, 126.3, 122.9, 53.6, 32.7, 24.9.

**IR**: 3342, 2930, 2857, 1653, 1578, 1554, 1517, 1461, 1451, 1395, 1366, 1349, 1338, 1321, 1286, 1266, 1231, 1209, 1169, 1139, 1095, 1064, 1047, 994, 959, 938, 904, 878, 859, 847, 836, 795, 782, 747, 730.

HRMS (ESI): C<sub>18</sub>H<sub>19</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>2</sub> [M+H]<sup>+</sup> calc. 393.0880, found 393.0896.

The spectroscopic data matched previously reported values.<sup>13</sup>

## Pyrrolidinopyridine L1 (racemic)



Chloropyridine **SI-29** (14.2 g, 36.1 mmol) and pyrrolidine (15 mL, 181 mmol, 5 eq.) in anhydrous toluene (14 mL) were stirred at 85 °C under nitrogen atmosphere for 44 hours. After cooling to room temperature, the mixture was diluted with diethyl ether (120 mL) and water (120 mL). Then, the mixture was stirred vigorously for 7.5 hours and the resulting suspension was filtered. The filtrate was discared. The solids were washed with water (2×50 mL) and diethyl ether (2×50 mL), then thoroughly dried at 80 °C under high vacuum to afford ligand L1 (16.2 g, 35.0 mmol, 97%) as an off-white powder.

 $\mathbf{R}_{\mathbf{f}}$  = 0.28 (5% methanol in dichloromethane).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>): 8.34 – 8.16 (m, 2H), 8.07 (d, J = 5.8 Hz, 2H), 7.21 (d, J = 2.5 Hz, 2H), 6.32 (dd, J = 5.8, 2.6 Hz, 2H), 4.12 – 3.90 (m, 2H), 3.39 – 3.21 (m, 8H), 2.23 – 2.13 (m, 2H), 2.03 – 1.92 (m, 8H), 1.86 – 1.72 (m, 2H), 1.52 – 1.35 (m, 4H).

<sup>13</sup>**C-NMR** (100 MHz, CDCl<sub>3</sub>): 165.6, 152.6, 150.0, 148.2, 108.3, 105.7, 53.1, 47.2, 32.8, 25.4, 24.9.

**IR**: 3351, 2933, 2856, 1661, 1636, 1604, 1515, 1484, 1460, 1391, 1350, 1321, 1287, 1275, 1249, 1230, 1181, 1154, 1111, 1006, 981, 922, 868, 862, 837, 819, 785, 768, 728.

HRMS (ESI): C<sub>26</sub>H<sub>35</sub>N<sub>6</sub>O<sub>2</sub> [M+H]<sup>+</sup> calc. 463.2816, found 463.2810.

The spectroscopic data matched previously reported values.<sup>11</sup>

# X-Ray Crystallography

## General information

X-ray diffraction data were collected on a Bruker D8 VENTURE diffractometer using Mo K radiation. Crystal data, data collection and structure solution/refinement for componds **16a** and **SI-26b** was performed by Dr. Michelle C. Neary at Hunter College, New York. The structure was solved using a dual-space method and standard difference map techniques, and was refined by full-matrix least-squares procedures on  $F^2$  with SHELXTL (Version 2018/3).<sup>12</sup> All hydrogen atoms were placed in calculated positions. Most were refined with a riding model [ $U_{iso}$ (H) = 1.2–1.5 $U_{eq}$ (C)], while a rigid model was used for the hydrogen atoms in the disordered -OTBS group in **16a** and the hydrogen atom bound to nitrogen was located on the difference map and freely refined in **SI-26b**.

## Compound 16a



lattice	Triclinic
formula	$C_{42}H_{51}NO_7Si$
formula weight	709.92
space group	P-1
a/Å	9.7148(3)
b/Å	11.2996(3)
c/Å	18.1294(5)
α/°	85.6710(10)
β/°	81.1060(10)
γ/°	69.2720(10)
V/Å <sup>3</sup>	1838.46(9)
Ζ	2
temperature (K)	100(2)
radiation (λ, Å)	0.71073
$\rho$ (calcd.) g cm $^3$	1.282
μ (Mo Kα), mm <sup>-1</sup>	0.117
θ max, deg.	36.292
no. of data collected	67111
no. of data	15771
no. of parameters	493
$R_1\left[I > 2 \boxed{2}(I)\right]$	0.0502
$wR_2[I > 2\square(I)]$	0.1397
$R_1$ [all data]	0.0644
$wR_2$ [all data]	0.1501
GOF	1.030
R <sub>int</sub>	0.0459

## Compound $SI-26b \cdot CH_2Cl_2$



lattice	Monoclinic
formula	$C_{50}H_{57}Cl_2NO_9Si$
formula weight	914.95
space group	$P2_{l}/c$
a/Å	13.5277(17)
b/Å	26.159(4)
c/Å	14.8755(19)
α/°	90
β/°	116.018(3)
γ/°	90
V/Å <sup>3</sup>	4730.5(11)
Ζ	4
temperature (K)	130(2)
radiation (λ, Å)	0.71073
$\rho$ (calcd.) g cm $^{-3}$	1.285
$\mu$ (Mo K $\alpha$ ), mm <sup>-1</sup>	0.219
$\theta$ max, deg.	33.266
no. of data collected	151597
no. of data	17812
no. of parameters	749
$R_{I} [I > 2\sigma(I)]$	0.0738
$wR_2 \left[ I > 2\sigma(I) \right]$	0.2033
$R_I$ [all data]	0.1083
$wR_2$ [all data]	0.2390
GOF	1.042
Rind	0.0391

# **NMR Spectra**

Compound SI-2 – <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (100 MHz) in  $CDCl_3$ 



## Compound SI-3 – <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (100 MHz) in $CDCl_3$



Compound SI-4 – <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (100 MHz) in  $CDCl_3$ 



## Compound SI-5 – <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (100 MHz) in $CDCl_3$



## Compound 5 – <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (100 MHz) in $CDCl_3$



## Compound SI-7 – <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (100 MHz) in $CDCl_3$



## Compound SI-8 – <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (100 MHz) in $CDCl_3$



## Compound SI-9 – <sup>1</sup>H-NMR (600 MHz) and <sup>13</sup>C-NMR (150 MHz) in $CDCl_3$



90 80 f1 (ppm) •1 ò

Compound 4 – <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (100 MHz) in  $CDCl_3$ 



Compound 4-enol – <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (100 MHz) in  $CDCl_3$ 





Compound 3 – <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (100 MHz) in  $CDCl_3$ 



## Compound 6 – <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (100 MHz) in $CDCl_3$









Compound SI-13 – <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (100 MHz) in CDCl<sub>3</sub>





### Compound SI-14 – <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (100 MHz) in CDCl<sub>3</sub>



### Compound 7 – <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (100 MHz) in CDCl<sub>3</sub>







#### Compound 8 – <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (100 MHz) in CDCl<sub>3</sub>


Compound SI-17 – <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (100 MHz) in CDCl<sub>3</sub>







Compound 2 – <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (100 MHz) in CDCl<sub>3</sub>









#### Compound 10 – <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (100 MHz) in CDCl<sub>3</sub>



#### Compound SI-20 – <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (100 MHz) in CD<sub>3</sub>OD





## Compound 11 – <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (100 MHz) in $CDCl_3$





## Compound 12 – <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (100 MHz) in $CDCl_3$



## Compound 13 – <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (100 MHz) in $CDCl_3$





## Compound ${\bf 14b}$ – ${}^1{\bf H}{\textbf{-}NMR}$ (400 MHz) and ${}^{13}{\bf C}{\textbf{-}NMR}$ (100 MHz) in ${\rm CDCl}_3$





Compound  $15a - {}^{1}H$ -NMR (400 MHz) and  ${}^{13}C$ -NMR (100 MHz) in CDCl<sub>3</sub>

∎OH

́′Ме

ОМе

398

6.5

1636

6.0

5.5

5.0 4.5

-132.9-116.3-116.3-116.3-116.3-116.3-116.3-116.3-12.5-12.5-9.2

Ĥ

MeO

.0 8.5

TBSO

MeO

8.0

7.5 7.0

15a



STREET STREET

3.5

4.0 f1 (ppm)

F-1500

525 555 555 555 555 555 555 555

3.0

2.5

¥-7670 Teore

1.5

2.0

F-05'6

0.5

1.0

LESS SESS

624H

0.0

-0.5

CSA SA



#### Compound 16a – <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (100 MHz) in CDCl<sub>3</sub>

## Compound $15b - {}^{1}H$ -NMR (400 MHz) and ${}^{13}C$ -NMR (100 MHz) in CDCl<sub>3</sub>





10 200 190

## Compound 16b – <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (100 MHz) in $CDCl_3$



## Compound ${\bf 17b}$ – ${}^1{\rm H}{\rm -NMR}$ (400 MHz) and ${}^{13}{\rm C}{\rm -NMR}$ (100 MHz) in ${\rm CDCl}_3$

#### Compound SI-22b – <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (100 MHz) in CDCl<sub>3</sub>





## Compound SI-23b – <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (100 MHz) in $CDCl_3$



## Compound ${\bf 18b}$ – ${}^1{\rm H}{\rm -NMR}$ (400 MHz) and ${}^{13}{\rm C}{\rm -NMR}$ (100 MHz) in ${\rm CDCl}_3$



## Compound SI-25b – <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (100 MHz) in $CDCl_3$

## Compound ${\bf 19b}$ – ${}^1{\rm H}{\rm -NMR}$ (400 MHz) and ${}^{13}{\rm C}{\rm -NMR}$ (100 MHz) in ${\rm CDCl}_3$



## Compound **20b** – <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (100 MHz) in $CDCl_3$



Compound **21b** – <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (100 MHz) in CDCl<sub>3</sub>



Compound **22b** – <sup>1</sup>**H-NMR** (400 MHz) and <sup>13</sup>**C-NMR** (100 MHz) in DMSO-d<sub>6</sub>



#### Compound SI-26b – <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (100 MHz) in CDCl<sub>3</sub>

#### 





## Compound SI-29 – <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (100 MHz) in $CDCl_3$



## Compound L1 – <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (100 MHz) in $CDCl_3$

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