

## Supporting Information 1

### Ni-catalyzed cycloisomerization between 3-phenoxy acrylic acid derivatives and alkynes via intramolecular cleavage and formation of C-O bond to give 2,3-disubstituted benzofurans

Shohei Ohno,<sup>1</sup> Jiawei Qiu,<sup>1</sup> Ray Miyazaki,<sup>2</sup> Hiroshi Aoyama,<sup>1</sup> Kenichi Murai,<sup>1</sup> Jun-ya Hasegawa,<sup>2</sup> and Mitsuhiro Arisawa\*<sup>1</sup>

<sup>1</sup> Graduate School of Pharmaceutical Sciences, Osaka University, Yamada-oka 1-6, Suita, Osaka, 565-0871, JAPAN

<sup>2</sup> Institute for Catalysis, Hokkaido University, Kita 21 Nishi 10, Kita-ku, Sapporo, Hokkaido, 001-0021, JAPAN

\*Corresponding Author. Phone: +81-6-6879-8226

E-mail: [arisaw@phs.osaka-u.ac.jp](mailto:arisaw@phs.osaka-u.ac.jp)

#### Contents

• Computational Details	S2
• Energy Diagram for a Catalytic Cycle	S3
• Other Experiments	S3-S4
Experimental section	
• Preparation of <b>1aa-1ao</b> , <b>1ay</b> , <b>1ba-1be</b>	S5-S11
• Preparation of <b>precursors of 1ap-1ax</b>	S12-S14
• Preparation of <b>1ap-1ax</b>	S14-S16
• Preparation of <b>2aa-2ay</b>	S17-S23
• Preparation of <b>3</b> , <b>4</b> , <b>5</b>	S23-S24

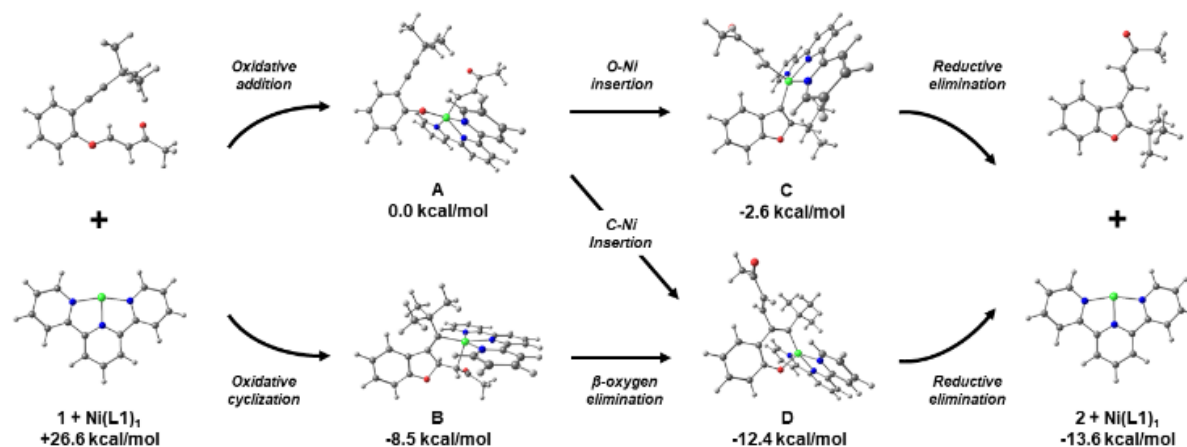
### **Computational Details**

Both geometry optimizations and single-point energy calculations were performed using DFT at the B3LYP functional level.<sup>1-2</sup> We employed the Stuttgart/Dresden basis set with effective core potential for Ni atom.<sup>3</sup> The 6-31G(d) basis sets<sup>4</sup> were used for the other atoms. The polarizable continuum model<sup>5</sup> was adopted to incorporate the solvation effect of tetrahydrofuran. All calculations were carried out using the Gaussian 16 program package.<sup>6</sup> The spin multiplicity of each structure which contains Ni atom was calculated to be triplet state.

### **References**

- (1) Becke, A. D. DENSITY-FUNCTIONAL THERMOCHEMISTRY .3. THE ROLE OF EXACT EXCHANGE. *J. Chem. Phys.* **1993**, 98, 5648.
- (2) Lee, C. T.; Yang, W. T.; Parr, R. G. DEVELOPMENT OF THE COLLE-SALVETTI CORRELATION-ENERGY FORMULA INTO A FUNCTIONAL OF THE ELECTRON-DENSITY. *Physical Review B* **1988**, 37, 785.
- (3) Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H. Energy-adjusted *ab initio* pseudopotentials for the first row transition elements. *J. Chem. Phys.* **1987**, 86, 866.
- (4) Hehre, W. J.; Ditchfield, R.; Pople, J. A. SELF-CONSISTENT MOLECULAR-ORBITAL METHODS .12. FURTHER EXTENSIONS OF GAUSSIAN-TYPE BASIS SETS FOR USE IN MOLECULAR-ORBITAL STUDIES OF ORGANIC-MOLECULES. *J. Chem. Phys.* **1972**, 56, 2257.
- (5) Tomasi, J.; Mennucci, B.; Cammi, R. Quantum Mechanical Continuum Solvation Models. *Chem. Rev.* **2005**, 105, 2999.
- (6) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; W.-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; and Fox, D. J. *Gaussian 16*, **2016**, Gaussian, Inc., Wallingford CT.

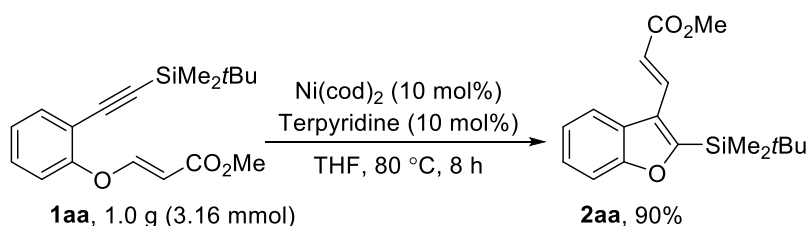
### Scheme S1. Energy Diagram for a Catalytic Cycle



The calculation was performed in THF with a substrate having a *tert*-butyl group on the alkyne and a methyl ketone on the alkene.

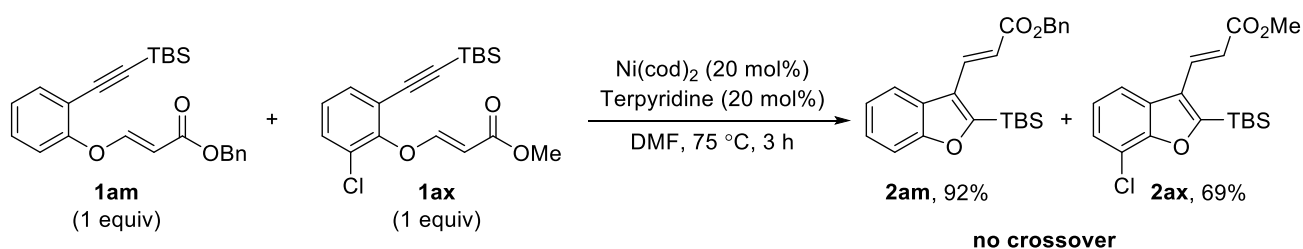
### Other Experiments

#### Scheme S2. Gram scale experiment

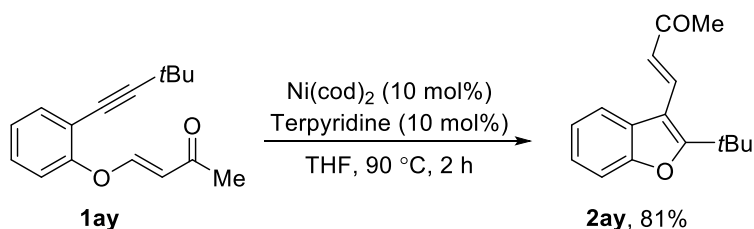


In glove box, to a round-bottom flask containing compound **1a** (1.0 g, 3.16 mmol) in THF (50 mL) was added Ni(cod)<sub>2</sub> (87 mg, 0.316 mmol) and terpyridine (74 mg, 0.316 mmol). The mixture was stirred for 8 h at 80 °C and removed from glove box, and concentrated in vacuo to remove the solvent. The obtained residue was purified by flash column chromatography on silica gel (*n*-hexane/AcOEt = 20:1) to give compound **2a**.

#### Scheme S3. Crossover experiment

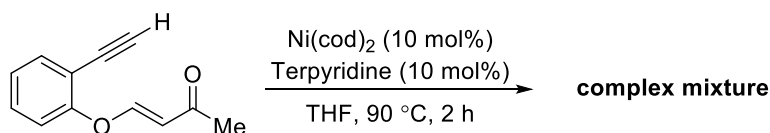


#### Scheme S4. Model reaction for DFT calculations



Complex mixture was obtained with the substrate **1ba** having a silyl group on the alkyne and a ketone on the alkene, but the reaction proceeded in 81% yield with the substrate **1ay** having a *t*Bu group on the alkyne and a ketone on the alkene.

#### Scheme S5. Examination with substrate with a terminal alkyne



**Table S1. Optimization of reaction temperatures**

Entry	Temp (°C)	Time (h)	Yield (%) <sup>[a-b]</sup>
1	25	20	15
2	50	12	94
3	80	3	92
4	130	1	84

[a] **1a** (0.09 mmol), [Ni(cod)<sub>2</sub>] (10 mol%), Terpyridine (10 mol%), in DMF (0.15 M) at 80°C. [b] Yields were determined by NMR using 2,4,6-trimethoxy benzene as internal standard.

**Table S2. Optimization of catalyst amounts**

Entry	X	Time (h)	Yield (%) <sup>[a-b]</sup>
1	1	12	73
2	5	6	84
3	10	3	92

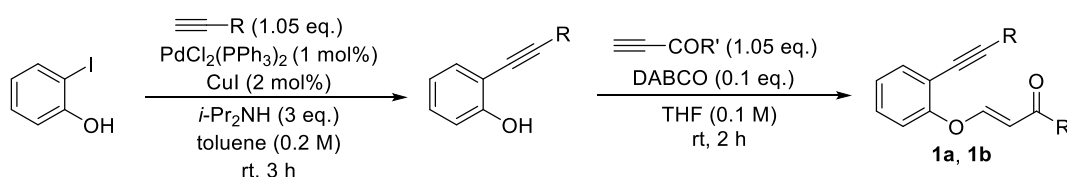
[a] **1a** (0.09 mmol), [Ni(cod)<sub>2</sub>] (10 mol%), Terpyridine (10 mol%), in DMF (0.15 M) at 80°C. [b] Yields were determined by NMR using 2,4,6-trimethoxy benzene as internal standard.

## Experimental Section

The following machines, equipments and chemicals were used for experiments of this study.

Melting Point	Yanaco MP-J3
Mass Spectrometer	JEOL JMS-3000 (MALDI-TOF)
Elemental analysis	J-SCIENCE LAB Co, MICRO CORDER JM10
<sup>1</sup> H NMR	JEOL JNM-LA 500 (500 MHz) JMN-ECS 400 (400 MHz) JEOL JMN-AL-300 (300 MHz)
<sup>13</sup> C NMR	JEOL JNM-LA 500 (125 MHz) JMN-ECS 400 (100 MHz) JEOL JMN-AL-300 (75 MHz)
Glove box	DBO-1NKP-TA (MIWA MFG CO., LTD)
Column Chromatography	Merck Kieselgel 60 Mesh (40-63µm) Kanto silica gel 60N (spherical, neutral, 40 - 50 µm)
PTLC Plate	Merck PLC silica gel 60 F <sub>254</sub> (0.5 mm)
TLC Plate	Merck DC Kieselgel 60 F <sub>254</sub>
Celite	Kanto Celite 545

### • Typical procedure A for the preparation of compounds 1aa-1ao, 1ay, 1ba-1bc

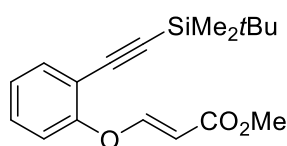


To a round-bottom flask containing 2-iodophenol (1.0 equiv) and mono-substituted acetylene (1.05 equiv) and diisopropylamine (3.0 equiv) in toluene (0.2 M) under nitrogen were added copper(I) iodide (2 mol%) and bis(triphenylphosphine) palladium(II) dichloride (1 mol%). The mixture was stirred at ambient temperature for 3 h. The mixture was diluted with ethyl acetate and the organic layer was washed with water and brine, dried over  $\text{Na}_2\text{SO}_4$ , and filtered. The filtrate was concentrated, and the residue was purified by short column chromatography ( $n\text{-hexane}/\text{AcOEt} = 10:1$ ) to give 2-substituted-ethynylphenol.

To a stirred solution of the above obtained crude 2-substituted-ethynylphenol in THF (0.1 M) was added DABCO (10 mol%) and propiolic acid derivative (1.05 equiv). The mixture was stirred at ambient temperature for 2 h. The mixture was diluted with AcOEt and washed with water and brine. The combined organic layer was dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated. The residue was purified by flash column chromatography on

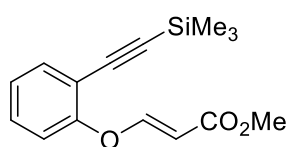
silica gel to give compounds **1aa-1ao**, **1ay**, **1ba-1bc**.

#### Compound 1aa



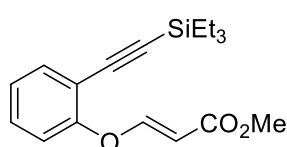
Following the typical procedure A on page S5, 2-iodophenol (550 mg, 2.50 mmol) was converted to **1aa** (570 mg, 72%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 20:1). Colorless oil.; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.77 (1H, d, *J* = 12.4 Hz), 7.50 (1H, dd, *J* = 7.8, 1.3 Hz), 7.33 (1H, ddd, *J* = 7.8, 7.8, 1.8 Hz), 7.15 (1H, ddd, *J* = 7.6, 7.6, 1.3 Hz), 7.06 (1H, dd, *J* = 8.2, 0.9 Hz), 5.48 (1H, d, *J* = 12.4 Hz), 3.71 (3H, s), 0.97 (9H, s), 0.16 (6H, s); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 167.50, 159.83, 156.39, 134.05, 129.96, 125.11, 118.80, 115.50, 101.37, 99.66, 99.38, 51.25, 26.01, 16.66, -4.82; HRMS (MALDI-TOF) calcd for C<sub>18</sub>H<sub>25</sub>O<sub>3</sub>Si (M+H): 317.1573, found: 317.1567.

#### Compound 1ab



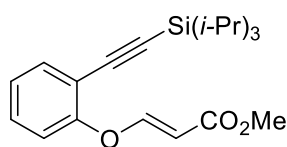
Following the typical procedure A on page S5, 2-iodophenol (550 mg, 2.50 mmol) was converted to **1ab** (480 mg, 70%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 20:1). Pale orange oil.; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.78 (1H, d, *J* = 12.4 Hz), 7.49 (1H, dd, *J* = 7.8, 1.4 Hz), 7.33 (1H, ddd, *J* = 7.9, 7.9, 1.7 Hz), 7.15 (1H, ddd, *J* = 7.6, 7.6, 1.2 Hz), 7.06 (1H, dd, *J* = 8.2, 1.4 Hz), 5.52 (1H, d, *J* = 12.4 Hz), 3.72 (3H, s), 0.23 (9H, s); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 167.55, 159.93, 156.41, 134.01, 130.01, 125.12, 118.92, 115.33, 101.31, 101.06, 99.10, 51.27, -0.31; HRMS (MALDI-TOF) calcd for C<sub>15</sub>H<sub>18</sub>O<sub>3</sub>NaSi (M+Na): 297.0916, found: 297.0917.

#### Compound 1ac



Following the typical procedure A on page S5, 2-iodophenol (550 mg, 2.50 mmol) was converted to **1ac** (570 mg, 72%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 20:1). Colorless oil.; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.77 (1H, d, *J* = 12.2 Hz), 7.50 (1H, dd, *J* = 7.8, 1.4 Hz), 7.32 (1H, ddd, *J* = 7.8, 7.8, 1.8 Hz), 7.15 (1H, dd, *J* = 7.6, 7.6 Hz), 7.06 (1H, d, *J* = 8.2 Hz), 5.48 (1H, d, *J* = 12.2 Hz), 3.71 (3H, s), 1.03 (9H, t, *J* = 7.9 Hz), 0.66 (6H, q, *J* = 7.9 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 167.52, 159.84, 156.39, 134.10, 129.89, 125.11, 118.82, 115.59, 101.29, 100.23, 98.55, 51.24, 7.41, 4.25; HRMS (MALDI-TOF) calcd for C<sub>18</sub>H<sub>24</sub>O<sub>3</sub>NaSi (M+Na): 339.1389, found: 339.1386.

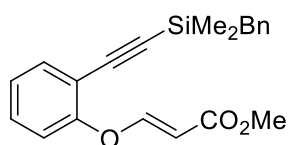
#### Compound 1ad



Following the typical procedure A on page S5, 2-iodophenol (550 mg, 2.50 mmol) was converted to **1ad** (708 mg, 79%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 20:1). Colorless oil.; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.77 (1H, d, *J* = 12.4 Hz), 7.51 (1H, dd, *J* = 7.6, 1.6 Hz), 7.33 (1H, ddd, *J* = 7.9, 7.9, 1.6 Hz), 7.15 (1H, dd, *J* = 7.6, 7.6 Hz), 7.06 (1H, d, *J* = 8.2 Hz), 5.46 (1H, d, *J* = 12.4 Hz), 3.71 (3H, s), 1.11 (21H, s); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 167.50, 159.84, 156.33, 134.15, 129.80, 125.12, 118.80, 115.84, 101.30,

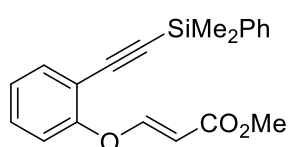
100.87, 97.42, 51.22, 18.56, 11.19; HRMS (MALDI-TOF) calcd for C<sub>21</sub>H<sub>30</sub>O<sub>3</sub>Si: 358.1956, found: 358.1958.

#### Compound 1ae



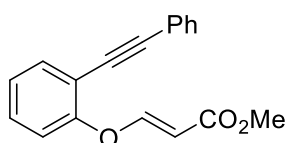
Following the typical procedure A on page S5, 2-iodophenol (550 mg, 2.50 mmol) was converted to **1ae** (429 mg, 45%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 20:1). Colorless oil.; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 7.78 (1H, d, J = 12.2 Hz), 7.48 (1H, dd, J = 7.6, 1.5 Hz), 7.35 (1H, ddd, J = 7.8, 7.8, 1.5 Hz), 7.23 (1H, dd, J = 7.6, 7.6 Hz), 7.16 (1H, ddd, J = 7.6, 7.6, 1.1 Hz), 7.11 (3H, d, J = 7.3 Hz), 7.07 (1H, dd, J = 8.2, 1.1 Hz), 5.53 (1H, d, J = 12.2 Hz), 3.72 (3H, s), 2.27 (2H, s), 0.19 (6H, s); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 167.51, 159.75, 156.38, 138.76, 134.11, 130.16, 128.37, 128.18, 125.10, 124.39, 118.79, 115.14, 101.52, 100.34, 99.35, 51.30, 25.99, -2.34; HRMS (MALDI-TOF) calcd for C<sub>21</sub>H<sub>22</sub>O<sub>3</sub>NaSi (M+Na): 373.1224, found: 373.1230.

#### Compound 1af



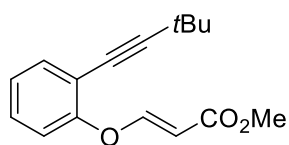
Following the typical procedure A on page S5, 2-iodophenol (550 mg, 2.50 mmol) was converted to **1af** (412 mg, 49%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 20:1). Colorless oil.; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 7.80 (1H, d, J = 12.2 Hz), 7.69-7.67 (2H, m), 7.53 (1H, dd, J = 7.6, 1.6 Hz), 7.40-7.38 (3H, m), 7.35 (1H, ddd, J = 7.8, 7.8, 1.6 Hz), 7.16 (1H, ddd, J = 7.5, 7.5, 1.0 Hz), 7.08 (1H, dd, J = 8.2, 1.0 Hz), 5.53 (1H, d, J = 12.2 Hz), 3.72 (3H, s), 0.48 (6H, s); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 167.42, 159.74, 156.50, 136.57, 134.07, 133.73, 130.25, 129.49, 127.89, 125.13, 118.79, 115.18, 101.52, 100.77, 98.78, 51.28, -1.04; HRMS (MALDI-TOF) calcd for C<sub>20</sub>H<sub>20</sub>O<sub>3</sub>NaSi (M+Na): 359.1074, found: 359.1073.

#### Compound 1ag



Following the typical procedure A on page S5, 2-iodophenol (550 mg, 2.50 mmol) was converted to **1ag** (598 mg, 86%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 10:1). Yellow oil.; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.86 (1H, d, J = 12.2 Hz), 7.57 (1H, dd, J = 7.9, 1.7 Hz), 7.53-7.49 (2H, m), 7.36-7.32 (4H, m), 7.20 (1H, ddd, J = 7.6, 7.6, 1.1 Hz), 7.11 (1H, dd, J = 8.1, 1.1 Hz), 5.57 (1H, d, J = 12.2 Hz), 3.72 (3H, s); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 167.57, 159.89, 155.86, 133.64, 131.58, 129.79, 128.61, 128.34, 125.26, 122.79, 118.92, 115.49, 101.49, 95.07, 83.85, 51.30; HRMS (MALDI-TOF) calcd for C<sub>18</sub>H<sub>14</sub>O<sub>3</sub>Na (M+Na): 301.0836, found: 301.0835.

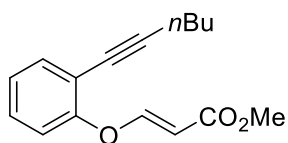
#### Compound 1ah



Following the typical procedure A on page S5, 2-iodophenol (550 mg, 2.50 mmol) was converted to **1ah** (458 mg, 71%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 20:1). Colorless oil.; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.78 (1H, d, J = 12.2 Hz), 7.41 (1H, dd, J = 7.9, 1.4 Hz), 7.27 (1H, ddd, J = 7.9, 7.9, 1.8 Hz), 7.13 (1H, ddd, J = 7.6, 7.6, 1.4 Hz), 7.04 (1H, dd, J = 8.0, 1.1 Hz), 5.48 (1H, d, J = 12.2 Hz), 3.72 (3H, s), 1.29 (9H, s); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 167.68, 160.58, 155.97, 133.57, 128.89, 125.19, 119.21, 116.24,

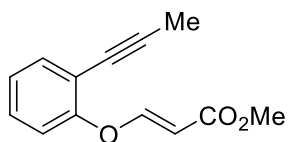
104.92, 100.67, 73.61, 51.21, 30.68, 28.16; HRMS (MALDI-TOF) calcd for C<sub>16</sub>H<sub>19</sub>O<sub>3</sub> (M+H): 259.1326, found: 259.1328.

#### Compound 1ai



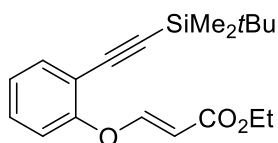
Following the typical procedure A on page S5, 2-iodophenol (550 mg, 2.50 mmol) was converted to **1ai** (432 mg, 67%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 20:1). Yellow oil.; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.77 (1H, d, J = 12.2 Hz), 7.42 (1H, dd, J = 7.8, 1.6 Hz), 7.27 (1H, ddd, J = 7.8, 7.8, 1.6 Hz), 7.13 (1H, ddd, J = 7.6, 7.6, 1.1 Hz), 7.03 (1H, d, J = 7.8 Hz), 5.47 (1H, d, J = 12.2 Hz), 3.71 (3H, s), 2.41 (3H, t, J = 6.9 Hz), 1.56 (2H, quin, J = 7.2 Hz), 1.46 (2H, sext, J = 7.2 Hz), 0.93 (3H, t, J = 7.3); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 167.66, 160.18, 155.88, 133.68, 128.92, 125.16, 118.91, 116.24, 100.99, 96.66, 75.04, 51.24, 30.49, 21.87, 19.23, 13.56; HRMS (MALDI-TOF) calcd for C<sub>16</sub>H<sub>19</sub>O<sub>3</sub> (M+H): 259.1324, found: 259.1328.

#### Compound 1aj



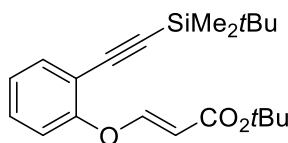
Following the typical procedure A on page S5, 2-iodophenol (550 mg, 2.50 mmol) was converted to **1aj** (346 mg, 64%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 15:1). Colorless oil.; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.79 (1H, d, J = 12.2 Hz), 7.44 (1H, dd, J = 7.6, 1.5 Hz), 7.29 (1H, ddd, J = 7.1, 7.1, 1.5 Hz), 7.14 (1H, ddd, J = 7.6, 7.6, 1.1 Hz), 7.04 (1H, dd, J = 8.0, 1.1 Hz), 5.50 (1H, d, J = 12.2 Hz), 3.73 (3H, s), 2.07 (3H, s); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 167.64, 159.97, 155.85, 133.77, 128.99, 125.14, 118.79, 116.09, 101.25, 91.96, 74.19, 51.27, 4.58; HRMS (MALDI-TOF) calcd for C<sub>13</sub>H<sub>12</sub>O<sub>3</sub>Na (M+Na): 239.0679, found: 239.0678.

#### Compound 1ak



Following the typical procedure A on page S5, 2-iodophenol (550 mg, 2.50 mmol) was converted to **1ak** (554 mg, 67%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 30:1). Colorless oil.; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.76 (1H, d, J = 12.2 Hz), 7.49 (1H, dd, J = 7.6, 1.5 Hz), 7.33 (1H, ddd, J = 7.8, 7.8, 1.5 Hz), 7.15 (1H, dd, J = 7.6, 7.6 Hz), 7.06 (1H, d, J = 8.2 Hz), 5.46 (1H, d, J = 12.2 Hz), 4.18 (2H, q, J = 7.3), 1.27 (3H, t, J = 7.3), 0.97 (9H, s), 0.16 (6H, s); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 167.09, 159.65, 156.39, 134.03, 129.95, 125.09, 118.89, 115.57, 101.73, 99.70, 99.32, 59.99, 26.03, 16.66, 14.32, -4.79; HRMS (MALDI-TOF) calcd for C<sub>19</sub>H<sub>27</sub>O<sub>3</sub>Si (M+H): 331.1727, found: 331.1724.

#### Compound 1al

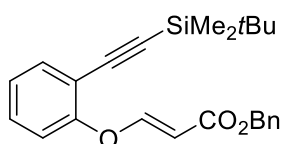


Following the typical procedure A on page S5, 2-iodophenol (550 mg, 2.50 mmol) was converted to **1al** (457 mg, 51%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 40:1). Colorless oil.; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.65 (1H, d, J = 12.4 Hz), 7.49 (1H, dd, J = 7.8, 1.8 Hz), 7.32 (1H, ddd, J = 7.9, 7.9, 1.8 Hz), 7.14 (1H, ddd, J = 7.6, 7.6, 1.0 Hz), 7.05 (1H, dd, J = 8.2, 1.0 Hz), 5.35 (1H, d, J = 12.4 Hz), 1.47 (9H, s), 0.98



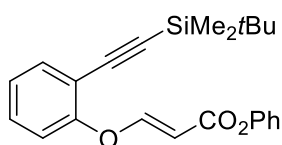
(9H, s), 0.17 (6H, s);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 166.43, 158.90, 156.41, 133.98, 129.93, 124.98, 118.98, 115.65, 103.36, 99.79, 99.14, 80.07, 28.23, 26.07, 16.67, -4.76; HRMS (MALDI-TOF) calcd for  $\text{C}_{21}\text{H}_{30}\text{O}_3\text{Si}$ : 358.1954, found: 358.1958.

#### Compound 1am



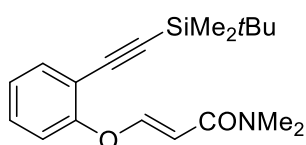
Following the typical procedure A on page S5, 2-iodophenol (550 mg, 2.50 mmol) was converted to **1am** (687 mg, 70%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 30:1). Colorless oil.;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.82 (1H, d,  $J$  = 12.4 Hz), 7.50 (1H, dd,  $J$  = 7.8, 1.4 Hz), 7.37-7.30 (6H, m), 7.15 (1H, ddd,  $J$  = 7.8, 7.8, 1.1 Hz), 7.05 (1H, d,  $J$  = 8.2 Hz), 5.51 (1H, d,  $J$  = 12.4 Hz), 5.17 (2H, s), 0.97 (9H, s), 0.16 (6H, s);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 166.91, 160.13, 156.27, 136.12, 134.04, 129.95, 128.52, 128.23, 128.14, 125.19, 118.94, 115.61, 101.34, 99.63, 99.38, 65.87, 26.01, 16.65, -4.81; HRMS (MALDI-TOF) calcd for  $\text{C}_{24}\text{H}_{28}\text{O}_3\text{NaSi}$  ( $\text{M}+\text{Na}$ ): 415.1696, found: 415.1699.

#### Compound 1an



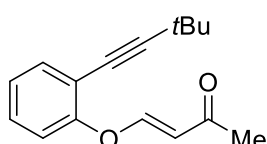
Following the typical procedure A on page S5, 2-iodophenol (550 mg, 2.50 mmol) was converted to **1an** (738 mg, 74%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 30:1). Colorless oil.;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.95 (1H, d,  $J$  = 12.2 Hz), 7.53 (1H, dd,  $J$  = 7.8, 1.4 Hz), 7.39 (2H, d,  $J$  = 7.8 Hz), 7.35 (2H, d,  $J$  = 7.8 Hz), 7.24-7.17 (2H, m), 7.13-7.09 (3H, m), 5.63 (1H, d,  $J$  = 12.2 Hz), 1.00 (9H, s), 0.19 (6H, s);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 165.51, 161.40, 156.19, 150.59, 134.09, 130.03, 129.36, 125.63, 125.47, 121.69, 119.14, 115.72, 100.79, 99.62, 99.56, 26.07, 16.70, -4.75; HRMS (MALDI-TOF) calcd for  $\text{C}_{23}\text{H}_{26}\text{O}_3\text{NaSi}$  ( $\text{M}+\text{Na}$ ): 401.1544, found: 401.1543.

#### Compound 1ao



Following the typical procedure A on page S5, 2-iodophenol (550 mg, 2.50 mmol) was converted to **1ao** (387 mg, 47%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 2:1). Colorless oil.;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.75 (1H, d,  $J$  = 11.5 Hz), 7.48 (1H, dd,  $J$  = 7.6, 1.6 Hz), 7.32 (1H, ddd,  $J$  = 7.9, 7.9, 1.6 Hz), 7.11 (1H, d,  $J$  = 7.6 Hz), 7.06 (1H, d,  $J$  = 8.3 Hz), 6.05 (1H, d,  $J$  = 11.5 Hz), 3.02 (6H, s), 0.99 (9H, s), 0.17 (6H, s);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 166.53, 157.34, 156.99, 133.87, 129.95, 124.32, 117.50, 114.90, 101.58, 100.12, 98.62, 26.07, 16.74, -4.76; HRMS (MALDI-TOF) calcd for  $\text{C}_{19}\text{H}_{27}\text{O}_2\text{NaSi}$  ( $\text{M}+\text{Na}$ ): 352.1702, found: 352.1703.

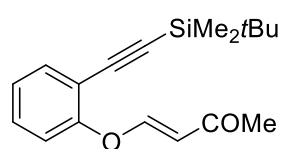
#### Compound 1ay



Following the typical procedure A on page S5, 2-iodophenol (550 mg, 2.50 mmol) was converted to **1ay** (210 mg, 32%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 15:1). Yellow oil.;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.69 (1H, d,  $J$  =

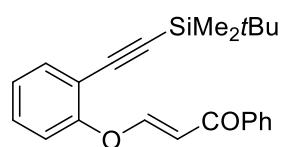
12.3 Hz), 7.42 (1H, dd,  $J = 7.6, 1.7$  Hz), 7.27 (1H, ddd,  $J = 7.7, 7.7, 1.7$  Hz), 7.14 (1H, ddd,  $J = 7.5, 7.5, 1.2$  Hz), 7.05 (1H, dd,  $J = 8.3, 1.2$  Hz), 5.82 (1H, d,  $J = 12.3$  Hz), 2.21 (3H, s), 1.28 (9H, s);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 197.12, 160.69, 155.92, 133.66, 128.95, 125.39, 119.45, 116.38, 110.99, 104.99, 73.58, 30.71, 28.15, 27.91; HRMS (MALDI-TOF) calcd for  $\text{C}_{16}\text{H}_{18}\text{O}_2\text{Na}$  ( $\text{M}+\text{Na}$ ): 265.1197, found: 265.1199.

#### Compound 1ba



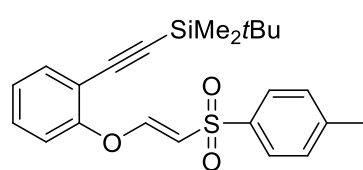
Following the typical procedure A on page S5, 2-iodophenol (550 mg, 2.50 mmol) was converted to **1ba** (593 mg, 79%) after flash column chromatography on silica gel ( $n$ -hexane/AcOEt = 10:1). Colorless oil.;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.70 (1H, d,  $J = 12.4$  Hz), 7.51 (1H, dd,  $J = 7.6, 1.6$  Hz), 7.34 (1H, ddd,  $J = 7.8, 7.8, 1.6$  Hz), 7.17 (1H, ddd,  $J = 7.6, 7.6, 1.1$  Hz), 7.07 (1H, dd,  $J = 8.2, 1.1$  Hz), 5.81 (1H, d,  $J = 12.4$  Hz), 2.22 (3H, s), 0.97 (9H, s), 0.16 (6H, s);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 197.07, 159.98, 156.26, 134.13, 130.00, 125.36, 119.14, 115.67, 111.41, 99.59, 99.44, 27.97, 26.01, 16.66, -4.79; HRMS (MALDI-TOF) calcd for  $\text{C}_{18}\text{H}_{24}\text{O}_2\text{NaSi}$  ( $\text{M}+\text{Na}$ ): 323.1439, found: 323.1437.

#### Compound 1bb



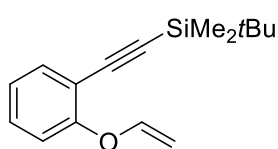
Following the typical procedure A on page S5, 2-iodophenol (550 mg, 2.50 mmol) was converted to **1bb** (716 mg, 79%) after flash column chromatography on silica gel ( $n$ -hexane/AcOEt = 10:1). Colorless oil.;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.94 (1H, d,  $J = 11.5$  Hz), 7.90 (2H, d,  $J = 7.8$  Hz), 7.53 (2H, d,  $J = 8.2$  Hz), 7.46 (2H, dd,  $J = 7.8, 7.8$  Hz), 7.35 (1H, dd,  $J = 8.2, 8.2$  Hz), 7.17 (1H, dd,  $J = 7.8, 7.8$ ), 7.11 (1H, d,  $J = 7.8$ ), 6.64 (1H, d,  $J = 11.5$  Hz), 0.97 (9H, s), 0.16 (6H, s);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 190.19, 160.76, 156.58, 138.34, 134.06, 132.50, 129.99, 128.47, 128.02, 125.17, 118.66, 115.47, 106.43, 99.69, 99.39, 26.02, 16.65, -4.79; HRMS (MALDI-TOF) calcd for  $\text{C}_{23}\text{H}_{27}\text{O}_2\text{Si}$  ( $\text{M}+\text{H}$ ): 363.1774, found: 363.1774.

#### Compound 1bc



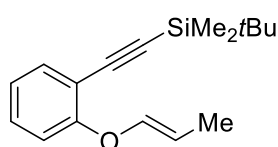
Following the typical procedure A on page S5, 2-iodophenol (550 mg, 2.50 mmol) was converted to **1bc** (505 mg, 49%) after flash column chromatography on silica gel ( $n$ -hexane/AcOEt = 10:1). White solid. m.p. 92-93 °C (from  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.77 (1H, d,  $J = 11.7$  Hz), 7.76 (2H, d,  $J = 7.7$  Hz), 7.49 (1H, dd,  $J = 7.6, 1.7$  Hz), 7.35 (1H, dd,  $J = 7.7, 1.7$  Hz), 7.31 (2H, d,  $J = 8.6$  Hz), 5.90 (1H, d,  $J = 11.7$  Hz), 2.42 (3H, s), 0.94 (9H, s), 0.14 (6H, s);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 157.99, 155.74, 143.89, 139.04, 134.15, 130.05, 129.80, 127.08, 125.75, 119.05, 115.79, 111.78, 99.62, 99.17, 26.04, 21.55, 16.63, -4.83; HRMS (MALDI-TOF) calcd for  $\text{C}_{23}\text{H}_{28}\text{O}_3\text{NaSi}$  ( $\text{M}+\text{Na}$ ): 435.1419, found: 435.1420.

#### Compound 1bd



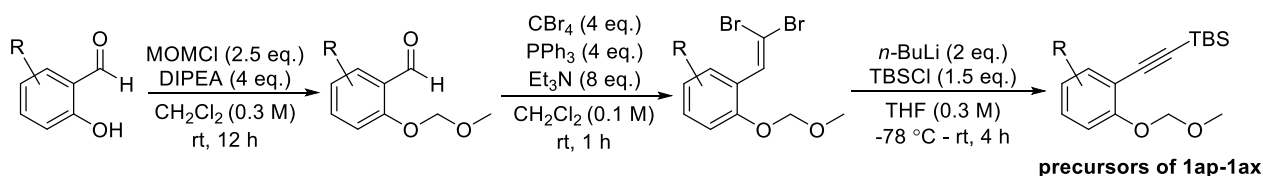
Following the previously reported procedure<sup>1</sup>, 2-iodophenol (550 mg, 2.50 mmol) was converted to **1bd** (136 mg, 21%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 40:1). Colorless oil.; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.46 (1H, dd, *J* = 7.6, 1.6 Hz), 7.28 (1H, ddd, *J* = 7.9, 7.9, 1.6 Hz), 7.03 (1H, ddd, *J* = 7.6, 7.6, 1.0 Hz), 6.98 (1H, d, *J* = 8.3 Hz), 6.65 (1H, dd, *J* = 13.7, 6.0 Hz), 4.71 (1H, dd, *J* = 13.7, 1.8 Hz), 4.41 (1H, dd, *J* = 6.0, 1.8 Hz), 1.00 (9H, s), 0.19 (6H, s); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 157.51, 148.44, 133.87, 129.74, 123.10, 117.01, 114.62, 100.86, 97.88, 94.67, 26.09, 16.79, -4.67; HRMS (MALDI-TOF) calcd for C<sub>16</sub>H<sub>23</sub>OSi (M+H): 259.1515, found: 259.1512.

### Compound 1be



Following the previously reported procedure<sup>2</sup>, 2-iodophenol (550 mg, 2.50 mmol) was converted to **1be** (497 mg, 73%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 100:1). Colorless oil.; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 7.46 (1H, dd, *J* = 7.7, 1.7 Hz), 7.27 (1H, ddd, *J* = 8.3, 7.2, 1.7 Hz), 6.97 (1H, ddd, *J* = 7.6, 7.5, 1.2 Hz), 6.94 (1H, dd, *J* = 8.3, 0.6 Hz), 6.43 (1H, dq, *J* = 6.0, 1.8 Hz), 4.89 (1H, dq, *J* = 6.9, 6.0 Hz), 1.75 (3H, dd, *J* = 6.9, 1.8 Hz), 1.02 (9H, s), 0.20 (6H, s); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 158.41, 140.66, 133.78, 129.69, 121.96, 114.59, 113.52, 107.42, 101.15, 97.38, 26.11, 16.74, 9.39, -4.62; HRMS (MALDI-TOF) calcd for C<sub>17</sub>H<sub>25</sub>OSi (M+H): 273.1664, found: 273.1669.

### Typical procedure B for the preparation of 1-(methoxymethoxy)-2-(2-*tert*-butyldimethylsilylethynyl) - benzene (precursors of 1ap-1ax)



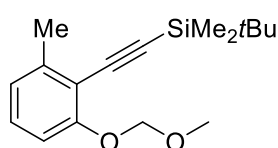
To a round-bottom flask containing salicylaldehyde (1.0 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (0.3 M) were added *N,N*-diisopropyl ethylamine (4.0 equiv) and chloromethyl methyl ether (2.5 equiv). The mixture was stirred at ambient temperature for 12 h. The mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> and washed with water and brine. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated to give 2-(methoxymethoxy) -benzaldehyde.

To a flame dried round-bottom flask containing triphenylphosphine (4.0 equiv) and anhydrous dichloromethane (0.1 M) at 0 °C was added carbon tetrabromide (4.0 equiv) and triethylamine (8.0 equiv). After stirring at 0 °C for 10 min, the above obtained crude 2-(methoxymethoxy)benzaldehyde (1.0 equiv) in dichloromethane (2.0 M) was added to this solution. The mixture was stirred at 0 °C for 10 min, then warmed to ambient temperature and stirred until TLC showed complete consumption of the starting material. The filtrate was concentrated, and the residue was purified by short column chromatography to give 1-(2,2-dibromoethenyl)-2-(methoxymethoxy) -benzene.

To a stirred solution of the above obtained crude 1-(2,2-dibromoethenyl)-2-(methoxymethoxy)benzene (1.0

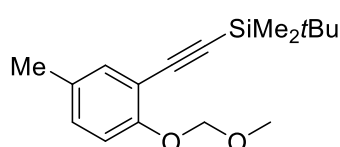
equiv) in anhydrous THF (0.3 M) under nitrogen at  $-78\text{ }^{\circ}\text{C}$  was added *n*-butyllithium (2.0 equiv, 2.76 M in hexanes). The mixture was stirred at  $-78\text{ }^{\circ}\text{C}$  for 1 h, and then *tert*-butyldimethylchlorosilane (1.5 equiv) was added. The reaction mixture was allowed to warm to ambient temperature, and stirred for 3 h. The mixture was quenched with water, and concentrated to remove the solvent. The residue was diluted with ethyl acetate and the organic layer was washed with water and brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated. The residue was purified by flash column chromatography to give 1-(methoxymethoxy)-2-(2-*tert*-butyldimethylsilyl-ylethynyl)benzene (precursors of **1ap-1ax**).

#### Precursor of **1ap**



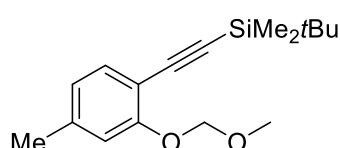
Following the typical procedure B on page S11, 6-methyl-salicylaldehyde (680 mg, 5.0 mmol) was converted to **precursor of 1ap** (886 mg, 61%) after flash column chromatography on silica gel (*n*-hexane/ $\text{Et}_2\text{O}$  = 40:1). Yellow oil.;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.13 (1H, dd,  $J$  = 7.8, 7.8 Hz), 6.89 (1H, d,  $J$  = 8.4 Hz), 6.87 (1H, d,  $J$  = 7.8 Hz), 5.23 (2H, s), 3.52 (3H, s), 2.44 (3H, s), 1.02 (9H, s), 0.20 (6H, s);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 158.33, 142.63, 128.78, 123.06, 114.14, 112.49, 101.26, 100.37, 94.95, 56.19, 26.12, 20.92, 16.71, -4.48; HRMS (MALDI-TOF) calcd for  $\text{C}_{17}\text{H}_{26}\text{O}_2\text{NaSi}$  ( $\text{M}+\text{Na}$ ): 313.1591, found: 313.1594.

#### Precursor of **1aq**



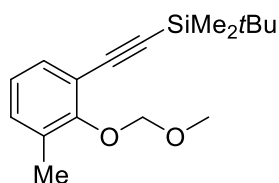
Following the typical procedure B on page S11, 5-methyl-salicylaldehyde (680 mg, 5.0 mmol) was converted to **precursor of 1aq** (842 mg, 58%) after flash column chromatography on silica gel (*n*-hexane/ $\text{Et}_2\text{O}$  = 40:1). Colorless oil.;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.25 (1H, d,  $J$  = 1.8 Hz), 7.05 (1H, dd,  $J$  = 8.2, 2.3 Hz), 6.95 (1H, d,  $J$  = 8.7 Hz), 5.20 (2H, s), 3.51 (3H, s), 2.26 (3H, s), 1.01 (9H, s), 0.19 (6H, s);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 156.01, 134.10, 131.28, 130.37, 115.70, 113.86, 101.96, 96.42, 95.18, 56.17, 26.10, 20.31, 16.77, -4.59; HRMS (MALDI-TOF) calcd for  $\text{C}_{17}\text{H}_{26}\text{O}_2\text{NaSi}$  ( $\text{M}+\text{Na}$ ): 313.1591, found: 313.1594.

#### Precursor of **1ar**



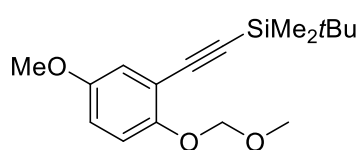
Following the typical procedure B on page S11, 4-methyl-salicylaldehyde (680 mg, 5.0 mmol) was converted to **precursor of 1ar** (1016 mg, 70%) after flash column chromatography on silica gel (*n*-hexane/ $\text{Et}_2\text{O}$  = 40:1). Yellow oil.;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.32 (1H, d,  $J$  = 7.8 Hz), 6.88 (1H, s), 6.76 (1H, d,  $J$  = 7.8 Hz), 5.22 (2H, s), 3.52 (3H, s), 2.33 (3H, s), 1.01 (9H, s), 0.18 (6H, s);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 158.06, 140.34, 133.49, 122.65, 116.12, 111.05, 102.00, 95.92, 94.86, 56.22, 26.09, 21.77, 16.78, -4.57; HRMS (MALDI-TOF) calcd for  $\text{C}_{17}\text{H}_{26}\text{O}_2\text{NaSi}$  ( $\text{M}+\text{Na}$ ): 313.1594, found: 313.1594.

#### Precursor of **1as**



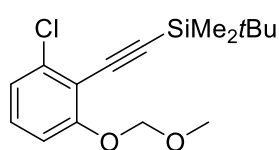
Following the typical procedure B on page S11, 3-methyl-salicylaldehyde (680 mg, 5.0 mmol) was converted to **precursor of 1as** (813 mg, 56%) after flash column chromatography on silica gel (*n*-hexane/Et<sub>2</sub>O = 40:1). Yellow oil.; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 7.30 (1H, d, *J* = 7.2 Hz), 7.14 (1H, d, *J* = 7.4 Hz), 6.95 (1H, dd, *J* = 7.5, 7.2 Hz), 5.26 (2H, s), 3.61 (3H, s), 2.31 (3H, s), 1.00 (9H, s), 0.18 (6H, s); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 157.55, 131.90, 131.70, 131.56, 123.64, 116.61, 102.53, 99.39, 96.81, 57.54, 26.13, 16.73, 16.69, -4.63; HRMS (MALDI-TOF) calcd for C<sub>17</sub>H<sub>26</sub>O<sub>2</sub>NaSi (M+Na): 313.1592, found: 313.1594.

#### Precursor of **1at**



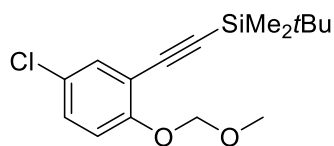
Following the typical procedure B on page S11, 5-methoxy-salicylaldehyde (760 mg, 5.0 mmol) was converted to **precursor of 1at** (582 mg, 38%) after flash column chromatography on silica gel (*n*-hexane/Et<sub>2</sub>O = 30:1). Colorless oil.; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 6.99 (1H, d, *J* = 9.2 Hz), 6.95 (1H, d, *J* = 3.1 Hz), 6.81 (1H, dd, *J* = 8.9, 3.1 Hz), 5.16 (2H, s), 3.76 (3H, s), 3.52 (3H, s), 1.01 (9H, s), 0.19 (6H, s); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 154.29, 152.37, 117.84, 117.78, 116.10, 115.01, 101.66, 96.89, 95.89, 56.19, 55.69, 26.08, 16.75, -4.64; HRMS (MALDI-TOF) calcd for C<sub>17</sub>H<sub>26</sub>O<sub>3</sub>NaSi (M+Na): 329.1542, found: 329.1543.

#### Precursor of **1au**



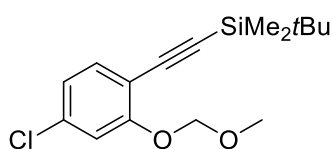
Following the typical procedure B on page S11, 6-chloro-salicylaldehyde (783 mg, 5.0 mmol) was converted to **precursor of 1au** (933 mg, 60%) after flash column chromatography on silica gel (*n*-hexane/Et<sub>2</sub>O = 50:1). Yellow oil.; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 7.15 (1H, dd, *J* = 8.2, 8.2 Hz), 7.05 (1H, dd, *J* = 8.2, 0.8 Hz), 6.98 (1H, dd, *J* = 8.2, 0.8 Hz), 5.23 (2H, s), 3.51 (3H, s), 1.03 (9H, s), 0.21 (6H, s); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 159.31, 137.37, 129.29, 122.65, 114.43, 113.13, 103.15, 97.80, 94.97, 56.34, 26.07, 16.77, -4.66; HRMS (MALDI-TOF) calcd for C<sub>16</sub>H<sub>23</sub>O<sub>2</sub>NaSiCl (M+Na): 333.1044, found: 333.1048.

#### Precursor of **1av**



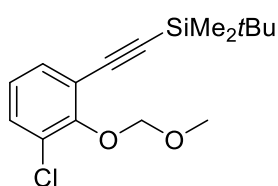
Following the typical procedure B on page S11, 5-chloro-salicylaldehyde (783 mg, 5.0 mmol) was converted to **precursor of 1av** (870 mg, 56%) after flash column chromatography on silica gel (*n*-hexane/Et<sub>2</sub>O = 50:1). Yellow oil.; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 7.39 (1H, d, *J* = 2.7 Hz), 7.20 (1H, dd, *J* = 8.8, 2.7 Hz), 7.00 (1H, d, *J* = 8.8 Hz), 5.20 (2H, s), 3.50 (3H, s), 1.00 (9H, s), 0.18 (6H, s); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 156.78, 133.15, 129.56, 126.55, 116.53, 115.56, 100.21, 98.42, 95.06, 56.28, 26.06, 16.75, -4.71; HRMS (FAB) calcd for C<sub>16</sub>H<sub>24</sub>O<sub>2</sub>SiCl (M+H): 333.1234, found: 333.1234.

#### Precursor of **1aw**



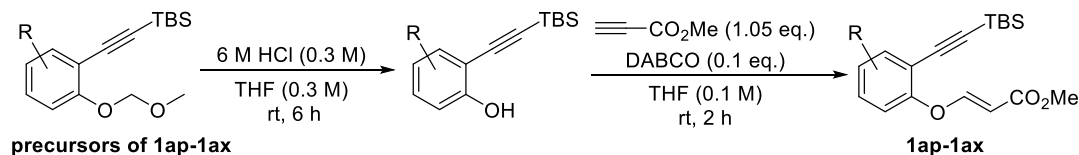
Following the typical procedure B on page S11, 4-chloro-salicylaldehyde (783 mg, 5.0 mmol) was converted to **precursor of 1aw** (1041 mg, 67%) after flash column chromatography on silica gel (*n*-hexane/Et<sub>2</sub>O = 50:1). Yellow oil.; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.34 (1H, d, *J* = 8.2 Hz), 7.09 (1H, d, *J* = 2.3 Hz), 6.93 (1H, dd, *J* = 8.2, 1.8 Hz), 5.21 (2H, s), 3.51 (3H, s), 1.00 (9H, s), 0.18 (6H, s); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 158.66, 135.07, 134.26, 121.96, 115.72, 112.49, 100.63, 97.93, 94.89, 56.34, 26.06, 16.75, -4.67; HRMS (FAB) calcd for C<sub>16</sub>H<sub>24</sub>O<sub>2</sub>SiCl (M+H): 333.1234, found: 333.1234.

#### Precursor of 1ax



Following the typical procedure B on page S11, 3-chloro-salicylaldehyde (783 mg, 5.0 mmol) was converted to **precursor of 1ax** (777 mg, 50%) after flash column chromatography on silica gel (*n*-hexane/Et<sub>2</sub>O = 50:1). Yellow oil.; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 7.35 (2H, dd, *J* = 6.5, 6.5 Hz), 6.98 (1H, dd, *J* = 7.8, 7.8 Hz), 5.32 (2H, s), 3.68 (3H, s), 0.99 (9H, s), 0.18 (6H, s); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 154.56, 132.74, 130.79, 128.21, 124.42, 118.99, 101.07, 99.23, 98.54, 57.98, 26.09, 16.69, -4.74; HRMS (MALDI-TOF) calcd for C<sub>16</sub>H<sub>23</sub>O<sub>2</sub>NaSiCl (M+Na): 333.1049, found: 333.1048.

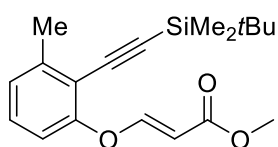
#### • Typical procedure C for the preparation of compounds 1ap-1ax



To a round-bottom flask containing 1-(methoxymethoxy)-2-(2-*tert*-butyldimethylsilylethynyl)benzene (precursors of **1ap-1ax**) (1.0 equiv) in THF (0.3 M) was slowly added 6 M HCl (0.3 M). The mixture was vigorously stirred at ambient temperature for 6 h. The mixture was diluted with ethyl acetate and the organic layer was washed with water and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to give 2-*tert*-butyldimethylsilylethynylphenol.

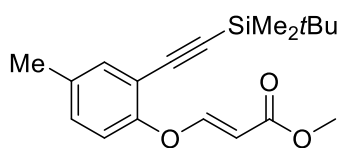
To a stirred solution of the above obtained crude 2-*tert*-butyldimethylsilylethynylphenol in THF (0.1 M) was added DABCO (10 mol%) and methyl propiolate (1.05 equiv). The mixture was stirred at ambient temperature for 2 h. The mixture was diluted with AcOEt and washed with water and brine. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated. The residue was purified by flash column chromatography on silica gel to give compounds **1ap-1ax**.

#### Compound 1ap



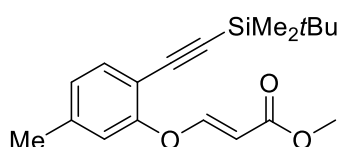
Following the typical procedure C on page S14, **precursor of 1ap** (581 mg, 2.0 mmol) was converted to **1ap** (291 mg, 44%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 20:1). Colorless oil.; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.76 (1H, d, *J* = 12.4 Hz), 7.20 (1H, dd, *J* = 7.8, 7.8 Hz), 7.05 (1H, d, *J* = 7.8 Hz), 6.89 (1H, d, *J* = 7.8 Hz), 5.47 (1H, d, *J* = 12.4 Hz), 3.71 (3H, s), 2.45 (3H, s), 0.98 (9H, s), 0.17 (6H, s); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 167.62, 160.14, 156.62, 143.19, 128.97, 126.23, 115.93, 115.54, 103.58, 101.04, 98.44, 51.22, 26.02, 20.78, 16.61, -4.73; HRMS (MALDI-TOF) calcd for C<sub>19</sub>H<sub>27</sub>O<sub>3</sub>Si (M+H): 331.1724, found: 331.1724.

#### Compound 1aq



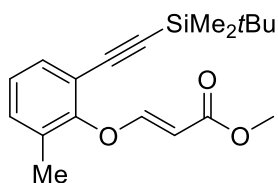
Following the typical procedure C on page S14, **precursor of 1aq** (581 mg, 2.0 mmol) was converted to **1aq** (370 mg, 56%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 20:1). Colorless oil.; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.74 (1H, d, *J* = 12.2 Hz), 7.30 (1H, d, *J* = 2.3 Hz), 7.11 (1H, dd, *J* = 8.3, 2.3 Hz), 6.93 (1H, d, *J* = 8.3 Hz), 5.44 (1H, d, *J* = 12.2 Hz), 3.71 (3H, s), 2.30 (3H, s), 0.97 (9H, s), 0.15 (6H, s); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 167.61, 160.33, 154.29, 134.92, 134.28, 130.61, 118.78, 115.13, 100.90, 99.89, 98.85, 51.99, 26.01, 20.52, 16.65, -4.81; HRMS (MALDI-TOF) calcd for C<sub>19</sub>H<sub>27</sub>O<sub>3</sub>Si (M+H): 331.1729, found: 331.1724.

#### Compound 1ar



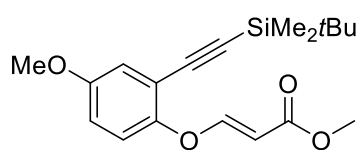
Following the typical procedure C on page S14, **precursor of 1ar** (581 mg, 2.0 mmol) was converted to **1ar** (291 mg, 44%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 20:1). Colorless oil.; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 7.76 (1H, d, *J* = 12.2 Hz), 7.37 (1H, d, *J* = 7.9 Hz), 6.95 (1H, d, *J* = 7.9 Hz), 6.86 (1H, s), 5.47 (1H, d, *J* = 12.2 Hz), 3.72 (3H, s), 2.35 (3H, s), 0.97 (9H, s), 0.15 (6H, s); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 167.61, 159.94, 156.30, 140.84, 133.70, 125.93, 119.41, 112.38, 101.21, 99.89, 98.35, 51.24, 26.02, 21.47, 16.68, -4.77; HRMS (MALDI-TOF) calcd for C<sub>19</sub>H<sub>27</sub>O<sub>3</sub>Si (M+H): 331.1722, found: 331.1724.

#### Compound 1as



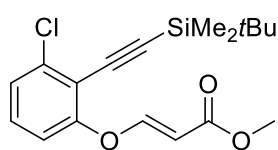
Following the typical procedure C on page S14, **precursor of 1as** (581 mg, 2.0 mmol) was converted to **1as** (218 mg, 33%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 20:1). Colorless oil.; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.72 (1H, d, *J* = 12.4 Hz), 7.34 (1H, d, *J* = 7.8 Hz), 7.18 (1H, d, *J* = 7.3 Hz), 7.07 (1H, dd, *J* = 7.8, 7.8 Hz), 5.21 (1H, d, *J* = 12.4 Hz), 3.68 (3H, s), 2.20 (3H, s), 0.95 (9H, s), 0.14 (6H, s); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 167.59, 160.91, 154.00, 131.66, 131.57, 130.43, 125.59, 116.45, 100.02, 99.45, 99.03, 51.12, 25.97, 16.61, 15.94, -4.85; HRMS (MALDI-TOF) calcd for C<sub>19</sub>H<sub>27</sub>O<sub>3</sub>Si (M+H): 331.1722, found: 331.1724.

### Compound 1at



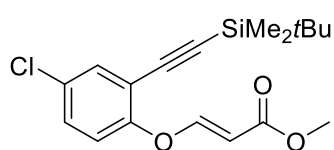
Following the typical procedure C on page S14, **precursor of 1at** (613 mg, 2.0 mmol) was converted to **1at** (388 mg, 56%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 15:1). Colorless oil.; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.71 (1H, d, *J* = 12.2 Hz), 6.97 (1H, d, *J* = 3.1 Hz), 6.95 (1H, s), 6.85 (1H, dd, *J* = 9.0, 3.1 Hz), 5.38 (1H, d, *J* = 12.2 Hz), 3.79 (3H, s), 3.69 (3H, s), 0.96 (9H, s), 0.16 (6H, s); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 167.62, 160.95, 156.50, 150.26, 120.46, 117.66, 116.28, 100.49, 99.63, 99.27, 55.72, 51.18, 25.98, 16.64, -4.85; HRMS (MALDI-TOF) calcd for C<sub>19</sub>H<sub>27</sub>O<sub>4</sub>Si (M+H): 347.1677, found: 347.1673.

### Compound 1au



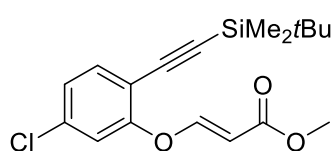
Following the typical procedure C on page S14, **precursor of 1au** (622 mg, 2.0 mmol) was converted to **1au** (309 mg, 44%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 25:1). Colorless oil.; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.73 (1H, d, *J* = 12.4 Hz), 7.28-7.25 (1H, m), 7.23 (1H, d, *J* = 7.4 Hz), 6.98 (1H, dd, *J* = 7.4, 1.0 Hz), 5.52 (1H, d, *J* = 12.4, 1.0 Hz), 3.72 (3H, s), 0.99 (9H, s), 0.18 (6H, s); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 167.25, 159.14, 157.36, 137.84, 129.45, 126.02, 116.82, 116.12, 105.77, 102.09, 96.03, 51.33, 25.99, 16.66, -4.89; HRMS (MALDI-TOF) calcd for C<sub>18</sub>H<sub>24</sub>O<sub>3</sub>SiCl (M+H): 351.1178, found: 351.1177.

### Compound 1av



Following the typical procedure C on page S14, **precursor of 1av** (622 mg, 2.0 mmol) was converted to **1av** (329 mg, 47%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 25:1). Colorless oil.; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.71 (1H, d, *J* = 11.9 Hz), 7.47 (1H, d, *J* = 2.6 Hz), 7.28 (1H, dd, *J* = 8.7, 2.6 Hz), 6.99 (1H, d, *J* = 8.7 Hz), 5.48 (1H, d, *J* = 11.9 Hz), 3.71 (3H, s), 0.96 (9H, s), 0.16 (6H, s); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 167.25, 159.34, 154.88, 133.52, 130.31, 129.91, 120.04, 117.06, 101.86, 101.09, 98.24, 51.34, 25.96, 16.63, -4.92; HRMS (MALDI-TOF) calcd for C<sub>18</sub>H<sub>24</sub>O<sub>3</sub>SiCl (M+H): 351.1169, found: 351.1177.

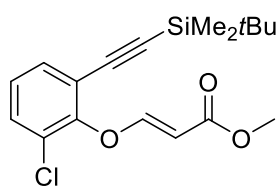
### Compound 1aw



Following the typical procedure C on page S14, **precursor of 1aw** (622 mg, 2.0 mmol) was converted to **1aw** (295 mg, 42%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 25:1). Colorless oil.; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.72 (1H, d, *J* = 12.4 Hz), 7.42 (1H, d, *J* = 8.4 Hz), 7.13 (1H, dd, *J* = 8.4, 2.0 Hz), 7.08 (1H, d, *J* = 2.0 Hz), 5.53 (1H, d, *J* = 12.4 Hz), 3.73 (3H, s), 0.97 (9H, s), 0.16 (6H, s); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 167.16, 158.81, 156.69, 135.19, 134.65, 125.41, 119.26, 114.03, 102.35, 100.57, 98.62, 51.38, 25.99, 16.65, -4.88; HRMS (MALDI-TOF) calcd for C<sub>18</sub>H<sub>24</sub>O<sub>3</sub>SiCl (M+H): 351.1181, found: 351.1177.

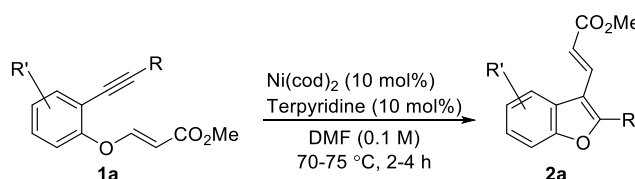
### Compound 1ax





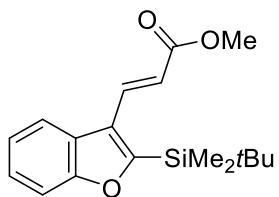
Following the typical procedure C on page S14, **precursor of 1ax** (622 mg, 2.0 mmol) was converted to **1ax** (316 mg, 45%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 25:1). Colorless oil.; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.67 (1H, d, *J* = 12.4 Hz), 7.40 (2H, d, *J* = 7.9 Hz), 7.12 (1H, dd, *J* = 8.0, 8.0 Hz), 5.29 (1H, d, *J* = 12.4 Hz), 3.69 (3H, s), 0.95 (9H, s), 0.15 (6H, s); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 167.19, 160.02, 151.75, 132.21, 130.78, 127.07, 126.42, 118.72, 100.97, 100.61, 98.62, 51.27, 25.95, 16.61, -4.94; HRMS (MALDI-TOF) calcd for C<sub>18</sub>H<sub>24</sub>O<sub>3</sub>SiCl (*M*+*H*): 351.1179, found: 351.1177.

• **Typical procedure D for the preparation of compounds 2aa-2ay**



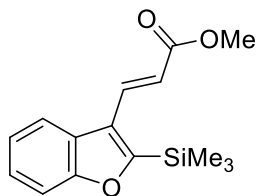
In glove box, to a round-bottom flask containing compound **1a** (1.0 equiv) in DMF (or THF) was added Ni(cod)<sub>2</sub> (10 mol%) and terpyridine (10 mol%). The mixture was stirred for 2-4 h at 70-75 °C and removed from glove box, and concentrated in vacuo to remove the solvent. The obtained residue was purified by flash column chromatography to give compound **2a**.

**Compound 2aa**

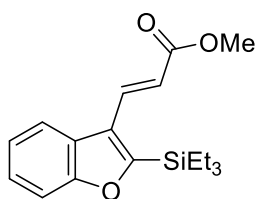


Following the typical procedure D on page S17, **1aa** (50 mg, 0.158 mmol) was converted to **2aa** (46 mg, 92%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 20:1). White solid. m.p. 93-94 °C (from Hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.99 (1H, d, *J* = 16.0 Hz), 7.86 (1H, dd, *J* = 6.9, 1.0 Hz), 7.53 (1H, d, *J* = 7.3 Hz), 7.36 (1H, ddd, *J* = 7.6, 7.6, 1.7 Hz), 7.31 (1H, ddd, *J* = 7.4, 7.4, 1.0 Hz), 6.60 (1H, d, *J* = 16.0 Hz), 3.83 (3H, s), 0.97 (9H, s), 0.46 (6H, s); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 167.78, 166.63, 158.39, 136.94, 127.26, 125.54, 125.27, 123.31, 121.11, 117.64, 111.75, 51.65, 26.40, 17.57, -5.36; HRMS (MALDI-TOF) calcd for C<sub>18</sub>H<sub>25</sub>O<sub>3</sub>Si (*M*+*H*): 317.1566, found: 317.1567.

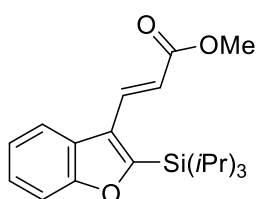
**Compound 2ab** (Solvent is THF)



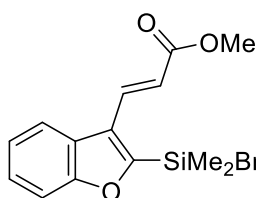
Following the typical procedure D on page S17, **1ab** (50 mg, 0.182 mmol) was converted to **2ab** (33.5 mg, 67%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 20:1). White solid. m.p. 62-64 °C (from Hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.98 (1H, d, *J* = 16.0 Hz), 7.84 (1H, d, *J* = 7.3 Hz), 7.52 (1H, d, *J* = 7.8 Hz), 7.35 (1H, ddd, *J* = 7.7, 7.7, 1.5 Hz), 7.30 (1H, ddd, *J* = 7.4, 7.4, 1.1 Hz), 6.58 (1H, d, *J* = 16.0 Hz), 3.83 (3H, s), 0.46 (9H, s); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 167.76, 167.72, 158.25, 136.39, 126.16, 125.61, 125.29, 123.35, 121.11, 117.59, 111.73, 51.67, -1.03; HRMS (MALDI-TOF) calcd for C<sub>15</sub>H<sub>19</sub>O<sub>3</sub>Si (*M*+*H*): 275.1098, found: 275.1098.

**Compound 2ac** (Solvent is THF)

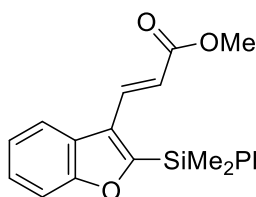
Following the typical procedure D on page S17, **1ac** (50 mg, 0.158 mmol) was converted to **2ac** (42 mg, 84%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 20:1). Colorless oil.; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 7.96 (1H, d, J = 16.0 Hz), 7.86 (1H, d, J = 7.4 Hz), 7.53 (1H, d, J = 8.0 Hz), 7.35 (1H, ddd, J = 7.7, 7.7, 1.2 Hz), 7.31 (1H, ddd, J = 7.4, 7.4, 1.2 Hz), 6.60 (1H, d, J = 16.0 Hz), 3.84 (3H, s), 1.06-0.95 (15H, m); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 167.81, 166.66, 158.57, 136.62, 127.13, 125.54, 125.18, 123.28, 121.07, 117.53, 111.73, 51.64, 7.24, 3.54; HRMS (MALDI-TOF) calcd for C<sub>18</sub>H<sub>25</sub>O<sub>3</sub>Si (M+H): 317.1561, found: 317.1567.

**Compound 2ad**

Following the typical procedure D on page S17, **1ad** (50 mg, 0.139 mmol) was converted to **2ad** (17 mg, 34%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 20:1). Colorless oil.; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.94 (1H, d, J = 15.8 Hz), 7.88 (1H, dd, J = 6.5, 2.0 Hz), 7.54 (1H, dd, J = 6.7, 2.0 Hz), 7.36 (1H, ddd, J = 6.4, 6.4, 1.6 Hz), 7.31 (1H, ddd, J = 6.4, 6.4, 1.6 Hz), 6.61 (1H, d, J = 15.8 Hz), 3.83 (3H, s), 1.57 (3H, sep, J = 7.6), 1.15 (18H, d, J = 7.6); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 167.86, 165.89, 158.59, 137.29, 127.59, 125.61, 125.09, 123.26, 121.08, 117.53, 111.74, 51.66, 18.56, 11.64; HRMS (MALDI-TOF) calcd for C<sub>21</sub>H<sub>30</sub>O<sub>3</sub>Si : 358.1956, found: 358.1958.

**Compound 2ae** (Solvent is THF)

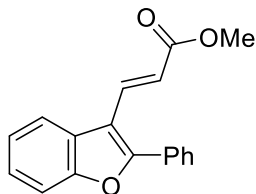
Following the typical procedure D on page S17, **1ae** (50 mg, 0.143 mmol) was converted to **2ae** (32.5 mg, 65%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 20:1). White solid. m.p. 79-80 °C (from Hexane); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 7.84 (1H, d, J = 7.4 Hz), 7.80 (1H, d, J = 16.0 Hz), 7.53 (1H, dd, J = 8.0, 1.0 Hz), 7.37 (1H, ddd, J = 7.7, 7.7, 1.3 Hz), 7.32 (1H, ddd, J = 7.4, 7.4, 1.1 Hz), 7.18 (1H, dd, J = 7.4, 7.4 Hz), 7.08 (1H, dd, J = 7.3, 7.3 Hz), 6.99 (2H, d, J = 8.3 Hz), 6.55 (1H, d, J = 16.0 Hz), 3.82 (3H, s), 2.48 (2H, s), 0.43 (6H, s); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 167.61, 165.83, 158.34, 138.11, 136.12, 128.36, 128.29, 127.03, 125.55, 125.46, 124.58, 123.41, 121.17, 117.96, 111.78, 51.66, 25.21, -3.08; HRMS (MALDI-TOF) calcd for C<sub>21</sub>H<sub>23</sub>O<sub>3</sub>Si (M+H): 351.1420, found: 351.1411.

**Compound 2af** (Solvent is THF)

Following the typical procedure D on page S17, **1af** (50 mg, 0.149 mmol) was converted to **2af** (35.5 mg, 71%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 20:1). White solid. m.p. 85-86 °C (from Hexane); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.84 (1H, d, J = 6.9 Hz), 7.75 (1H, d, J = 16.0 Hz), 7.63 (2H, dd, J = 7.2, 2.1 Hz), 7.54 (1H, d, J = 7.2 Hz), 7.47-7.28 (4H, m), 7.31 (1H, ddd, J = 7.5, 7.5, 1.3 Hz), 6.52 (1H, d, J = 16.0 Hz), 3.77 (3H, s), 0.75 (6H, s); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 167.49, 165.43, 158.41,

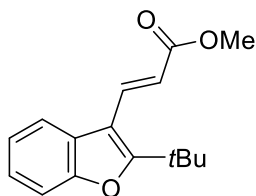
136.35, 135.26, 134.09, 129.94, 128.19, 127.01, 125.59, 125.45, 123.40, 121.20, 118.01, 111.83, 51.54, -2.44; HRMS (MALDI-TOF) calcd for C<sub>20</sub>H<sub>21</sub>O<sub>3</sub>Si (M+H): 337.1230, found: 337.1254.

#### Compound 2ag



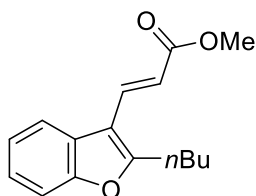
Following the typical procedure D on page S17, **1ag** (50 mg, 0.179 mmol) was converted to **2ag** (45.5 mg, 91%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 20:1). White solid. m.p. 125-126 °C (from Hexane/AcOEt = 4:1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 8.03 (1H, d, J = 16.0 Hz), 7.88 (1H, d, J = 7.4 Hz), 7.78 (2H, d, J = 6.9 Hz), 7.57-7.47 (4H, m), 7.39 (1H, ddd, J = 7.6, 7.6, 1.6 Hz), 7.36 (1H, ddd, J = 7.5, 7.5, 1.4 Hz), 6.69 (1H, d, J = 16.0 Hz), 3.84 (3H, s); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 167.72, 157.67, 154.51, 136.14, 129.76, 129.67, 128.94, 128.58, 126.74, 125.33, 123.78, 120.97, 118.79, 112.62, 111.61, 51.69; HRMS (MALDI-TOF) calcd for C<sub>18</sub>H<sub>14</sub>O<sub>3</sub>: 278.0931, found: 278.0937.

#### Compound 2ah



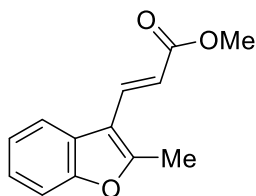
Following the typical procedure D on page S17, **1ah** (50 mg, 0.194 mmol) was converted to **2ah** (47.5 mg, 95%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 20:1). Colorless oil.; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 8.18 (1H, d, J = 16.0 Hz), 7.76 (1H, dd, J = 6.3, 2.6 Hz), 7.45 (1H, dd, J = 6.0, 1.7 Hz), 7.31-7.27 (2H, m), 6.50 (1H, d, J = 16.0 Hz), 3.83 (3H, s), 1.52 (9H, s); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 167.82, 167.02, 153.35, 136.57, 127.11, 124.27, 123.26, 120.57, 117.53, 111.11, 110.55, 51.62, 35.25, 30.01; HRMS (MALDI-TOF) calcd for C<sub>16</sub>H<sub>18</sub>O<sub>3</sub>: 258.1252, found: 258.1250.

#### Compound 2ai



Following the typical procedure D on page S17, **1ai** (50 mg, 0.158 mmol) was converted to **2ai** (37.5 mg, 75%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 20:1). Colorless oil.; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.81 (1H, d, J = 15.8 Hz), 7.78 (1H, dd, J = 6.0, 3.3 Hz), 7.46 (1H, dd, J = 6.0, 3.3 Hz), 7.30 (1H, dd, J = 6.0, 3.3 Hz), 6.53 (1H, d, J = 15.8 Hz), 3.83 (3H, s), 2.92 (2H, t, J = 7.6 Hz), 1.75 (2H, quin, J = 7.6 Hz), 1.41 (2H, sext, J = 7.4 Hz), 0.95 (3H, t, J = 7.4 Hz); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 167.96, 162.96, 154.35, 135.34, 126.03, 124.35, 123.47, 120.44, 116.24, 112.23, 111.21, 51.60, 30.35, 26.52, 22.33, 13.74; HRMS (MALDI-TOF) calcd for C<sub>16</sub>H<sub>18</sub>O<sub>3</sub>: 258.1246, found: 258.1250.

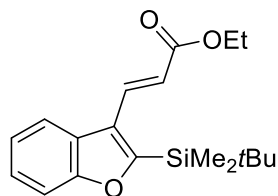
#### Compound 2aj



Following the typical procedure D on page S17, **1aj** (50 mg, 0.231 mmol) was converted to **2aj** (36.5 mg, 73%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 20:1). Colorless oil.; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 7.80 (1H, d, J = 15.9 Hz), 7.76 (1H, dd, J = 5.9, 3.3 Hz), 7.44 (1H, dd, J = 5.9, 3.3 Hz), 7.30 (1H, dd, J = 5.9, 3.3 Hz), 6.51 (1H, d, J = 15.9 Hz), 3.83 (3H, s), 2.59 (3H, s); <sup>13</sup>C NMR (125 MHz,

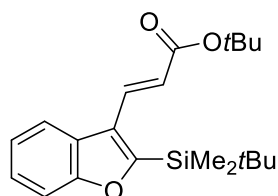
CDCl<sub>3</sub>)  $\delta$ : 167.91, 158.89, 154.32, 135.36, 126.07, 124.38, 123.53, 120.29, 116.32, 112.59, 111.13, 51.63, 12.71; HRMS (MALDI-TOF) calcd for C<sub>13</sub>H<sub>13</sub>O<sub>3</sub>: 217.0860, found: 217.0859.

### Compound 2ak



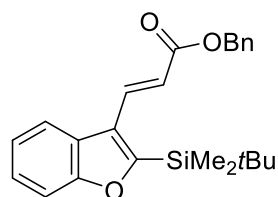
Following the typical procedure D on page S17, **1ak** (50 mg, 0.151 mmol) was converted to **2ak** (44 mg, 88%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 20:1). Colorless oil.; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.99 (1H, d, *J* = 16.0 Hz), 7.88 (1H, d, *J* = 7.2 Hz), 7.53 (1H, d, *J* = 8.0 Hz), 7.35 (1H, ddd, *J* = 7.7, 7.7, 1.2 Hz), 7.31 (1H, ddd, *J* = 7.4, 7.4, 1.2 Hz), 6.59 (1H, d, *J* = 16.0 Hz), 4.29 (2H, q, *J* = 7.2 Hz), 1.36 (3H, t, *J* = 7.2 Hz), 0.98 (9H, s), 0.47 (6H, s); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$ : 167.31, 166.53, 158.40, 136.69, 127.32, 125.56, 125.25, 123.28, 121.17, 118.06, 111.73, 60.37, 26.41, 17.56, 14.33, -5.37; HRMS (MALDI-TOF) calcd for C<sub>19</sub>H<sub>27</sub>O<sub>3</sub>Si (M+H): 331.1727, found: 331.1724.

### Compound 2al



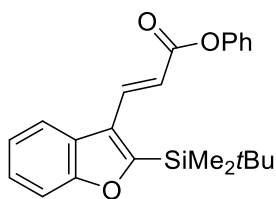
Following the typical procedure D on page S17, **1al** (50 mg, 0.139 mmol) was converted to **2al** (33.5 mg, 67%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 20:1). Colorless oil.; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.89 (1H, d, *J* = 16.1 Hz), 7.88 (1H, d, *J* = 7.5 Hz), 7.52 (1H, d, *J* = 8.0 Hz), 7.35 (1H, ddd, *J* = 7.7, 7.7, 1.2 Hz), 7.30 (1H, ddd, *J* = 7.5, 7.5, 0.9 Hz), 6.50 (1H, d, *J* = 16.1 Hz), 1.56 (9H, s), 0.97 (9H, s), 0.46 (6H, s); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$ : 166.55, 166.05, 158.38, 135.62, 127.38, 125.64, 125.15, 123.19, 121.26, 120.02, 111.67, 80.26, 28.26, 26.43, 17.57, -5.35; HRMS (MALDI-TOF) calcd for C<sub>21</sub>H<sub>30</sub>O<sub>3</sub>Si: 358.1953, found: 358.1958.

### Compound 2am



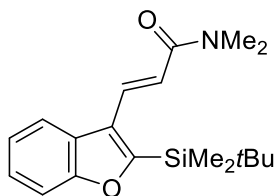
Following the typical procedure D on page S17, **1am** (50 mg, 0.127 mmol) was converted to **2am** (45.5 mg, 91%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 20:1). Colorless oil.; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.05 (1H, d, *J* = 15.8 Hz), 7.87 (1H, d, *J* = 7.8 Hz), 7.54 (1H, dd, *J* = 7.3, 0.9 Hz), 7.44 (2H, ddd, *J* = 7.4, 7.4, 1.4 Hz), 7.41-7.36 (3H, m), 7.33 (1H, dd, *J* = 5.3, 1.6 Hz), 7.30 (1H, dd, *J* = 7.3, 0.9 Hz), 6.64 (1H, d, *J* = 15.8 Hz), 5.29 (2H, s), 0.97 (9H, s), 0.46 (6H, s); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 167.07, 166.85, 158.39, 137.28, 136.15, 128.56, 128.19, 128.17, 127.28, 125.47, 125.28, 123.33, 121.16, 117.58, 111.74, 66.26, 26.38, 17.55, -5.37; HRMS (MALDI-TOF) calcd for C<sub>24</sub>H<sub>28</sub>O<sub>3</sub>NaSi (M+Na): 415.1697, found: 415.1699.

### Compound 2an



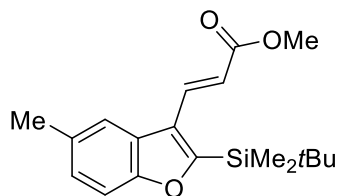
Following the typical procedure D on page S17, **1an** (50 mg, 0.132 mmol) was converted to **2an** (32 mg, 64%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 20:1). Colorless oil.; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 8.18 (1H, d, *J* = 16.0 Hz), 7.93 (1H, dd, *J* = 6.0, 1.9 Hz), 7.56 (1H, dd, *J* = 7.7, 1.5 Hz), 7.45-7.35 (5H, m), 7.21 (2H, d, *J* = 8.4, 1.2 Hz), 6.78 (1H, d, *J* = 16.0 Hz), 0.99 (9H, s), 0.48 (6H, s); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 167.65, 165.81, 158.49, 150.93, 138.74, 129.40, 127.27, 125.71, 125.44, 125.42, 123.51, 121.67, 121.19, 116.78, 111.84, 26.41, 17.58, -5.34; HRMS (MALDI-TOF) calcd for C<sub>23</sub>H<sub>26</sub>O<sub>3</sub>NaSi (M+Na): 401.1544, found: 401.1543.

### Compound 2ao



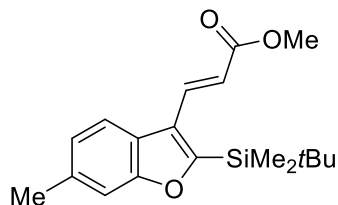
Following the typical procedure D on page S17, **1ao** (50 mg, 0.152 mmol) was converted to **2ao** (29.3 mg, 59%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 3:1). White solid. m.p. 107-109 °C (from CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 7.99 (1H, d, *J* = 15.5 Hz), 7.81 (1H, d, *J* = 7.4 Hz), 7.53 (1H, d, *J* = 8.3 Hz), 7.35 (1H, ddd, *J* = 7.6, 7.6, 1.4 Hz), 7.30 (1H, ddd, *J* = 7.5, 7.5, 1.1 Hz), 7.04 (1H, d, *J* = 15.5 Hz), 3.22 (3H, s), 3.10 (3H, s), 0.97 (9H, s), 0.46 (6H, s); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 166.89, 165.58, 158.35, 134.55, 127.84, 125.91, 122.99, 120.79, 117.30, 111.82, 37.38, 35.88, 26.46, 17.59, -5.33; HRMS (MALDI-TOF) calcd for C<sub>19</sub>H<sub>28</sub>NO<sub>2</sub>Si (M+H): 330.1881, found: 318.1883.

### Compound 2aq



Following the typical procedure D on page S17, **1aq** (50 mg, 0.151 mmol) was converted to **2aq** (39 mg, 78%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 20:1). White solid. m.p. 94-95 °C (from Hexane); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 7.97 (1H, d, *J* = 16.1 Hz), 7.64 (1H, s), 7.40 (1H, d, *J* = 8.4 Hz), 7.16 (1H, d, *J* = 8.4 Hz), 6.58 (1H, d, *J* = 16.1 Hz), 3.84 (3H, s), 2.49 (3H, s), 0.96 (9H, s), 0.45 (6H, s); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 167.84, 166.85, 156.89, 137.18, 132.91, 127.01, 126.54, 125.62, 120.95, 117.33, 111.19, 51.64, 26.40, 21.43, 17.57, -5.37; HRMS (MALDI-TOF) calcd for C<sub>19</sub>H<sub>27</sub>O<sub>3</sub>Si (M+H): 331.1719, found: 331.1724.

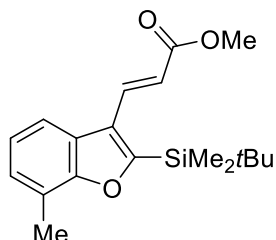
### Compound 2ar



Following the typical procedure D on page S17, **1ar** (50 mg, 0.151 mmol) was converted to **2ar** (38.6 mg, 77%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 20:1). White solid. m.p. 88-89 °C (from Hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.97 (1H, d, *J* = 15.8 Hz), 7.72 (1H, d, *J* = 8.2 Hz), 7.34 (1H, s), 7.14 (1H, d, *J* = 8.7 Hz), 6.57 (1H, d, *J* = 15.8 Hz), 3.83 (3H, s), 2.48 (3H, s), 0.97 (9H, s), 0.45 (6H, s); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 167.82, 166.05, 158.87, 137.07, 135.71,

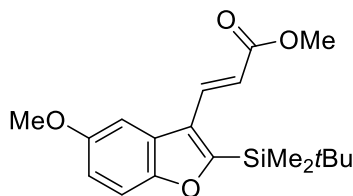
127.24, 124.74, 123.03, 120.57, 117.38, 111.94, 51.61, 26.39, 21.54, 17.55, -5.36; HRMS (MALDI-TOF) calcd for  $C_{19}H_{27}O_3Si$  (M+H): 331.1727, found: 331.1724.

#### Compound 2as



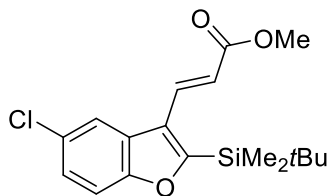
Following the typical procedure D on page S17, **1as** (50 mg, 0.151 mmol) was converted to **2as** (38.4 mg, 77%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 20:1). White solid. m.p. 61-63 °C (from Hexane);  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$ : 7.99 (1H, d, *J* = 16.1 Hz), 7.68 (1H, d, *J* = 7.6 Hz), 7.22 (1H, dd, *J* = 7.5, 7.5 Hz), 7.15 (1H, d, *J* = 7.3 Hz), 6.58 (1H, d, *J* = 16.1 Hz), 3.83 (3H, s), 2.54 (3H, s), 0.99 (9H, s), 0.47 (6H, s);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$ : 167.84, 166.19, 165.81, 157.42, 137.11, 127.54, 126.05, 124.95, 123.40, 121.99, 118.56, 117.45, 51.62, 26.40, 17.52, 14.94, -5.33; HRMS (MALDI-TOF) calcd for  $C_{19}H_{27}O_3Si$  (M+H): 331.1719, found: 331.1724.

#### Compound 2at



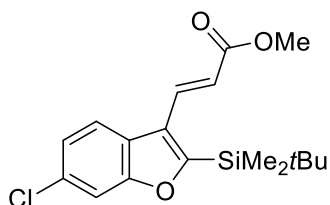
Following the typical procedure D on page S17, **1at** (50 mg, 0.144 mmol) was converted to **2at** (40 mg, 80%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 15:1). White solid. m.p. 88-90 °C (from Hexane);  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$ : 7.97 (1H, d, *J* = 16.1 Hz), 7.42 (1H, d, *J* = 9.2 Hz), 7.26 (1H, s), 6.96 (1H, dd, *J* = 9.0, 2.5 Hz), 6.51 (1H, d, *J* = 16.1 Hz), 3.89 (3H, s), 3.83 (3H, s), 0.96 (9H, s), 0.45 (6H, s);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$ : 167.78, 167.67, 156.44, 153.52, 137.13, 127.24, 126.03, 117.14, 113.97, 112.08, 103.67, 56.12, 51.64, 26.39, 17.58, -5.39; HRMS (MALDI-TOF) calcd for  $C_{19}H_{27}O_4Si$  (M+H): 347.1674, found: 347.1673.

#### Compound 2av



Following the typical procedure D on page S17, **1av** (50 mg, 0.142 mmol) was converted to **2av** (32.5 mg, 65%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 25:1). White solid. m.p. 142-143 °C (from Hexane);  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$ : 7.93 (1H, d, *J* = 16.1 Hz), 7.81 (1H, d, *J* = 1.9 Hz), 7.44 (1H, d, *J* = 8.6 Hz), 7.30 (1H, dd, *J* = 8.6, 1.9 Hz), 6.51 (1H, d, *J* = 16.1 Hz), 3.84 (3H, s), 0.96 (9H, s), 0.45 (6H, s);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$ : 168.19, 167.50, 156.76, 136.20, 129.02, 126.92, 126.76, 125.46, 120.73, 118.13, 112.59, 51.73, 26.36, 17.57, -5.45; HRMS (MALDI-TOF) calcd for  $C_{18}H_{24}O_3SiCl$  (M+H): 351.1180, found: 351.1177.

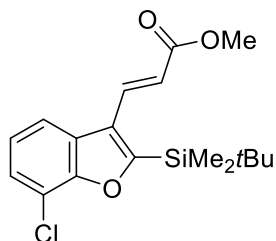
#### Compound 2aw



Following the typical procedure D on page S17, **1aw** (50 mg, 0.142 mmol) was converted to **2aw** (18 mg, 36%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 25:1). White solid. m.p. 89-90 °C (from Hexane);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$ : 7.93 (1H, d, *J* = 16.0 Hz), 7.74 (1H, d, *J* = 8.7 Hz), 7.54

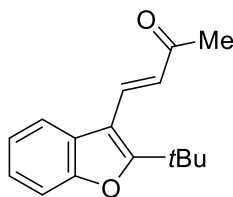
(1H, d, J = 1.5 Hz), 7.29 (1H, dd, J = 8.0, 1.5 Hz), 6.53 (1H, d, J = 16.0 Hz), 3.83 (3H, s), 0.96 (9H, s), 0.45 (6H, s);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 167.51, 167.44, 158.47, 136.29, 131.28, 127.03, 124.26, 123.99, 121.49, 118.19, 112.27, 51.72, 26.36, 17.56, -5.45; HRMS (MALDI-TOF) calcd for  $\text{C}_{18}\text{H}_{24}\text{O}_3\text{SiCl}$  (M+H): 351.1171, found: 351.1177.

### Compound 2ax



Following the typical procedure D on page S17, **1ax** (50 mg, 0.142 mmol) was converted to **2ax** (38 mg, 76%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 25:1). White solid. m.p. 100-101 °C (from Hexane);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.95 (1H, d, J = 16.1 Hz), 7.73 (1H, d, J = 8.0, 1.1 Hz), 7.35 (1H, dd, J = 7.8, 1.0 Hz), 7.24 (1H, dd, J = 7.8, 7.8 Hz), 6.56 (1H, d, J = 16.1 Hz), 3.83 (3H, s), 1.00 (9H, s), 0.48 (6H, s);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 167.49, 167.46, 154.12, 136.29, 127.68, 127.25, 125.36, 124.17, 119.49, 118.41, 117.43, 51.73, 26.38, 17.52, -5.41; HRMS (MALDI-TOF) calcd for  $\text{C}_{18}\text{H}_{24}\text{O}_3\text{SiCl}$  (M+H): 351.1175, found: 351.1177.

### Compound 2ay

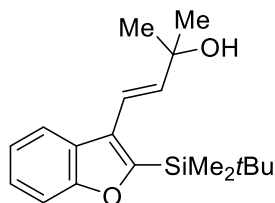


Following the typical procedure D on page S17, **1ay** (50 mg, 0.206 mmol) was converted to **2ay** (40.6 mg, 81%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 15:1). Yellow oil.;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.01 (1H, d, J = 16.2 Hz), 7.74 (1H, dd, J = 6.0, 2.3 Hz), 7.42 (1H, dd, J = 6.4, 2.1 Hz), 7.29-7.23 (2H, m), 6.77 (1H, d, J = 16.2 Hz), 2.34 (3H, s), 1.49 (9H, s);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 198.12, 167.61, 153.42, 135.16, 126.95, 126.92, 124.39, 123.34, 120.71, 111.17, 110.69, 35.36, 30.07, 27.67; HRMS (MALDI-TOF) calcd for  $\text{C}_{16}\text{H}_{19}\text{O}_2$  (M+H): 243.1377, found: 243.1379.

### Compound 3

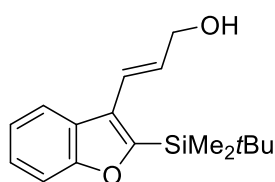
Following the previously reported procedure<sup>3</sup>, **2aa** (50 mg, 0.158 mmol) was converted to **3** (20.1 mg, 41%) after flash column chromatography on silica gel (*n*-hexane/AcOEt = 15:1). White solid. m.p. 99-100 °C (from Hexane/AcOEt = 4:1);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.01 (1H, d, J = 16.0 Hz), 7.85 (1H, dd, J = 6.3, 2.1 Hz), 7.72 (2H, dd, J = 6.7, 1.9 Hz), 7.54 (1H, ddd, J = 6.7, 6.7, 2.0 Hz), 7.36 (1H, ddd, J = 9.3, 9.3, 3.2 Hz), 7.33 (1H, ddd, J = 8.9, 8.9, 3.1 Hz), 7.06 (1H, d, J = 9.3 Hz), 7.06 (1H, d, J = 4.6 Hz), 6.66 (1H, d, J = 16.0 Hz), 3.89 (3H, s), 3.83 (3H, s);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 167.87, 160.92, 158.04, 136.43, 130.10, 126.91, 124.99, 123.69, 122.23, 120.78, 118.08, 114.49, 111.56, 111.45, 55.44, 51.66; HRMS (MALDI-TOF) calcd for  $\text{C}_{19}\text{H}_{16}\text{O}_4$ : 308.1040, found: 308.1043.

### Compound 4



To a round-bottom flask containing **2aa** (50 mg, 0.158 mmol) in Et<sub>2</sub>O (0.3 M) was slowly added methylmagnesium bromide (105  $\mu$ L, 3.0 M in Et<sub>2</sub>O) at 0 °C. The mixture was stirred at ambient temperature for 2 h. The obtained residue was purified by flash column chromatography on silica gel (*n*-hexane/AcOEt = 8:1) to give compound **4** (48.6 mg, 97%). White solid. m.p. 83-84 °C (from CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.84 (1H, d, *J* = 7.4 Hz), 7.49 (1H, d, *J* = 8.3 Hz), 7.31 (1H, ddd, *J* = 7.6, 7.6, 1.3 Hz), 7.25 (1H, ddd, *J* = 7.4, 7.4, 1.1 Hz), 6.84 (1H, d, *J* = 16.2 Hz), 6.50 (1H, d, *J* = 16.2 Hz), 1.48 (6H, s), 0.97 (9H, s), 0.41 (6H, s); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$ : 159.98, 158.21, 138.86, 128.45, 126.59, 124.59, 122.40, 120.92, 118.45, 111.48, 71.23, 29.86, 26.47, 17.82, -5.40; HRMS (MALDI-TOF) calcd for C<sub>19</sub>H<sub>28</sub>O<sub>2</sub>Si: 316.1829, found: 316.1853.

### Compound 5



To a round-bottom flask containing **2aa** (50 mg, 0.158 mmol) in Et<sub>2</sub>O (0.1 M) was added lithium aluminium hydride (6.5 mg, 0.171 mmol) and aluminium chloride (32 mg, 0.240 mmol) at 0 °C. The mixture was stirred at ambient temperature for 2 h. The mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> and washed with water and brine. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated. The obtained residue was purified by flash column chromatography on silica gel (*n*-hexane/AcOEt = 12:1) to give compound **5** (39.6 mg, 87%). Yellow oil.; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.85 (1H, d, *J* = 7.4 Hz), 7.49 (1H, d, *J* = 8.3 Hz), 7.31 (1H, ddd, *J* = 7.7, 7.7, 1.4 Hz), 7.25 (1H, ddd, *J* = 7.4, 7.4, 1.1 Hz), 6.85 (1H, dt, *J* = 16.0, 1.4 Hz), 6.52 (1H, dt, *J* = 16.0, 5.7 Hz), 4.37 (2H, dd, *J* = 5.7, 1.4 Hz), 1.26 (1H, s), 0.97 (9H, s), 0.41 (6H, s); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$ : 160.39, 158.15, 129.75, 128.35, 126.53, 124.65, 123.09, 122.52, 120.97, 111.49, 64.39, 26.47, 17.74, -5.36; HRMS (MALDI-TOF) calcd for C<sub>17</sub>H<sub>25</sub>O<sub>2</sub>Si (M+H): 289.1620, found: 289.1618.

### References

- [1] Sakiyama, N.; Noguchi, K.; Tanaka, K. *Angew. Chem. Int. Ed.* **2012**, *51*, 5976.
- [2] Ohno, S.; Takamoto, K.; Fujioka, H.; Arisawa, M. *Org. Lett.* **2017**, *19*, 2422.
- [3] Komiyama, T.; Minami, Y.; Furuya, Y.; Hiyama, T. *Angew. Chem. Int. Ed.* **2018**, *57*, 1987.