

## Supporting Information for

# Application of stabilization effect of silyl group in radical-polar crossover reactions enabled by photoredox-neutral catalysis

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# 1 General Information

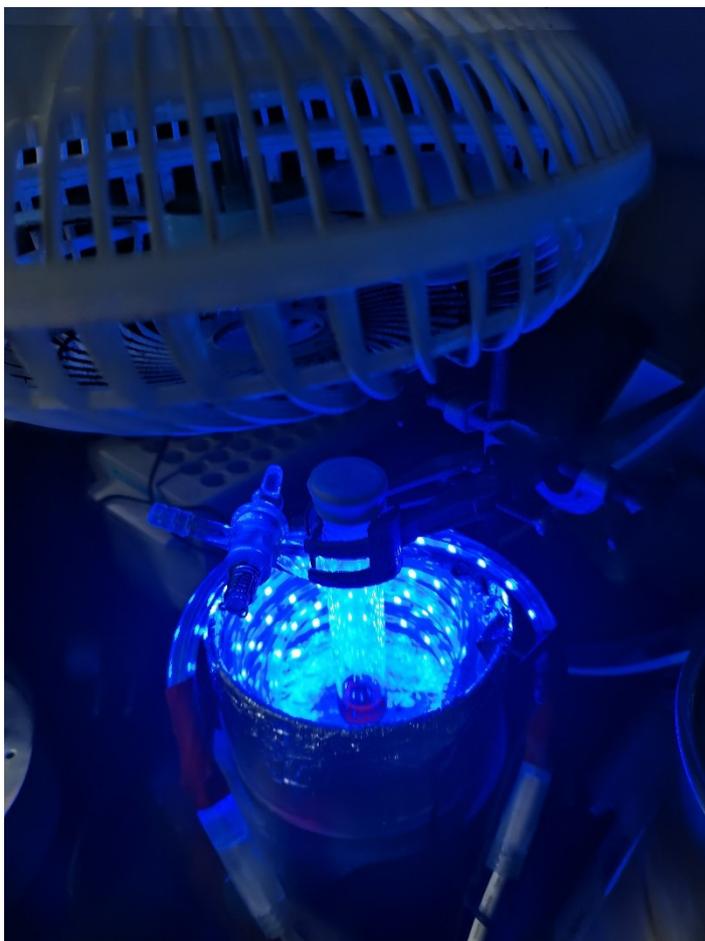
## 1.1 Solvents, Reagents, and Starting Materials

All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware. Photocatalysts Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub><sup>[1a]</sup>, 4CzIPN<sup>[1b]</sup> and Ru(bpz)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub><sup>[1c]</sup> were prepared according to published procedures.  $\alpha$ -Vinyl silanes were synthesized with reported procedures. Alkyl silicates were reported in our previous literatures.<sup>[2]</sup> Dried solvents were obtained from commercial sources and used without further purification unless otherwise noted.

## 1.2 Instruments

NMR spectra were recorded on a Bruker Avance 500 spectrometer (500 MHz) (500 MHz for <sup>1</sup>H NMR, 126 MHz for <sup>13</sup>C NMR, and 471 MHz for <sup>19</sup>F NMR). Chemical shifts were reported in ppm downfield from tetramethylsilane and calibrated using residue undeuterated solvent (Chloroform-*d* at 7.26 ppm <sup>1</sup>H NMR; 77.0 ppm <sup>13</sup>C NMR). Spectra were reported as follows: chemical shift ( $\delta$  ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad). Coupling constants are reported in Hertz where available. High resolution mass spectra (HRMS) were recorded on Waters Premier GC-TOF MS, Waters G2-Xs QTOF MS, and JEOL-AccuTOF-GCv4G-GCT MS. Analytical thin layer chromatography was performed on Polygram SIL G/UV254 plates. Visualization was accomplished with short wave UV light, or KMnO<sub>4</sub> staining solutions. Flash column chromatography was performed using silica gel (300-400 mesh) with solvents to use.

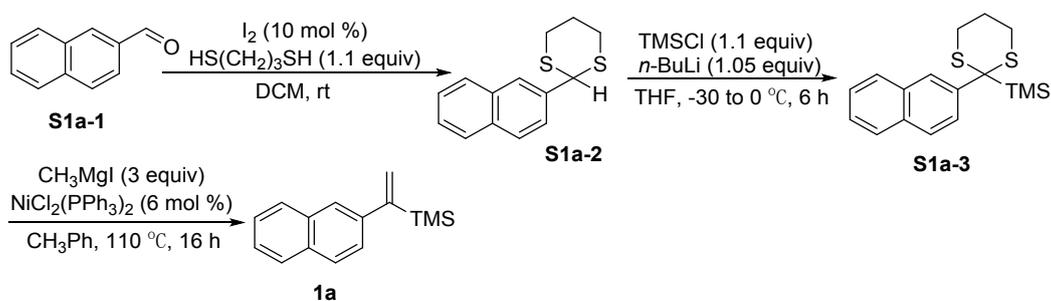
## 1.3 Picture of a Typical Reaction Setup



## 2 Synthesis of Vinylsilanes

### 2.1 General Procedure for the Preparation of Vinylsilanes

#### Method A:<sup>[3]</sup> Synthesis of Vinylsilanes 1a, 5a-5h, and 5k-5l.

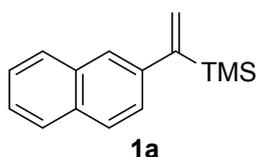


2-Naphthaldehyde **S1a-1** (5 g, 32.0 mmol, 1 equiv) and 1,3-dimercaptopropane (3.53

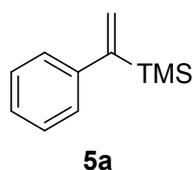
mL, 35.2 mmol, 1.1 equiv) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (80 mL) in a round-bottom flask. After 30 min, iodine (812 mg, 3.2 mmol, 0.1 equiv) was slowly added to the stirring solution as to prevent vigorous boiling of the solvent and the mixture was stirred at room temperature overnight. Then, the reaction was quenched with a 10% Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> aqueous solution (15 mL) and a 10% NaOH aqueous solution (15 mL). The reaction mixture was extracted by dichloromethane (5 x 20 mL) and dried over MgSO<sub>4</sub> and filtered. After evaporating the solvent, the product was recrystallized in isopropanol. The product **S1a-2** was collected by vacuum filtration in a yield of 66% (5.2 g) as a white solid.

To a stirred solution of **S1a-2** (4.4g, 18.0 mmol, 1 equiv) in THF (50 mL) was added *n*-butyl lithium (12 mL, 1.6 M, 1.1 equiv) dropwise at -30 °C and the reaction was stirred at this temperature for 1.5 h. Trimethylsilyl chloride (2.5 mL, 19.8 mmol, 1.1 equiv) was slowly added. The reaction was stirred at -30 °C for 3 h and then the temperature was raised to 0 °C for an additional 3 h. The reaction was quenched with saturated NH<sub>4</sub>Cl solution (1 mL), 0.5 M NaOH aqueous solution (10 mL) and extracted by ethyl acetate (4 x 20 mL). The combined organic layer was washed with brine. The organic layer was dried over MgSO<sub>4</sub>, filtered, and concentrated in vacuo. The product **S1a-3** was collected by vacuum filtration in a yield of 79% (4.5 g) as a white solid.

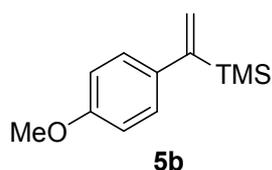
Methylmagnesium iodide in ether (8 mL, 3 M in ether, 24.0 mmol) was evacuated to remove ether. The residue was filled with nitrogen. A solution of **S1a-3** (2.54 g, 8.0 mmol, 1 equiv) and NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (314 mg, 0.48 mmol, 0.06 equiv) in toluene (40 mL) was then introduced. The resulting mixture was stirred at 110 °C and refluxed for 16 h. After cooling to room temperature, the reaction mixture was quenched with saturated NH<sub>4</sub>Cl solution (20 mL), and extracted by ethyl acetate (4 x 20 mL). The organic layer was dried over MgSO<sub>4</sub>, filtered, and concentrated in vacuo. The residue was purified by flash chromatography on a silica gel with petroleum ether as the eluent to give the product **1a** as a white solid in a yield of 71% (1.2 g).



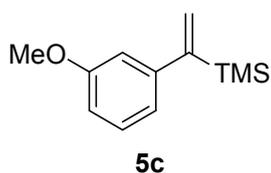
**Trimethyl(1-(naphthalen-2-yl)vinyl)silane (1a).**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82-7.77 (m, 3H), 7.61 (s, 1H), 7.48-7.41 (m, 2H), 7.36-7.34 (m, 1H), 5.93 (d,  $J = 2.9$  Hz, 1H), 5.70 (d,  $J = 2.9$  Hz, 1H), 0.21 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  153.5, 142.3, 133.4, 132.1, 127.8, 127.6, 127.5(8), 127.5(5), 125.9, 125.7, 125.3, 124.9, -0.8. These data are consistent with the published literature.<sup>[4]</sup>



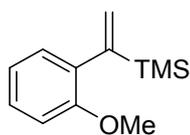
**Trimethyl(1-phenylvinyl)silane (5a).**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32-7.28 (m, 2H), 7.24-7.20 (m, 1H), 7.19-7.17 (m, 2H), 5.82 (d,  $J = 3.0$  Hz, 1H), 5.61 (d,  $J = 3.0$  Hz, 1H), 0.17 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  153.4, 144.7, 128.1, 127.1, 126.7, 126.2, -0.9. These data are consistent with the published literature.<sup>[4]</sup>



**(1-(4-Methoxyphenyl)vinyl)trimethylsilane (5b).**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.15-7.13 (m, 2H), 6.86-6.84 (m, 2H), 5.80 (d,  $J = 2.9$  Hz, 1H), 5.54 (d,  $J = 2.9$  Hz, 1H), 3.81 (s, 3H), 0.17 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  158.2, 152.4, 137.0, 127.7, 126.1, 113.5, 55.2, -0.8. This compound has been reported in the published literature.<sup>[12a]</sup>

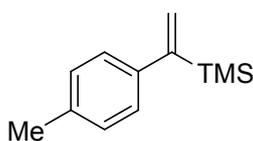


**(1-(3-Methoxyphenyl)vinyl)trimethylsilane (5c).**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.23-7.20 (m, 1H), 6.79-6.76 (m, 2H), 6.73-6.72 (m, 1H), 5.83 (d,  $J = 3.0$  Hz, 1H), 5.59 (d,  $J = 3.0$  Hz, 1H), 3.81 (s, 3H), 0.17 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.3, 153.3, 146.3, 129.0, 127.2, 119.3, 112.4, 111.5, 55.1, -0.9. These data are consistent with the published literature.<sup>[4]</sup>



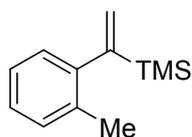
**5d**

**(1-(2-Methoxyphenyl)vinyl)trimethylsilane (5d).** Flash column chromatography to afford product **5d** as a pale yellow oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.22-7.19 (m, 1H), 7.02-7.00 (m, 1H), 6.93-6.91 (m, 1H), 6.84-6.82 (m, 1H), 5.77 (d,  $J = 3.2$  Hz, 1H), 5.64 (d,  $J = 3.2$  Hz, 1H), 3.78 (s, 3H), 0.09 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  155.6, 152.3, 134.5, 128.7, 127.5, 127.4, 120.6, 109.7, 54.8, -0.9. HRMS (ESI)  $[\text{M}+\text{H}]^+$ : calculated for  $\text{C}_{12}\text{H}_{19}\text{OSi}$ : 207.1200, found 207.1206.



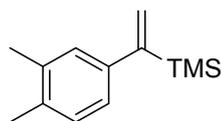
**5e**

**Trimethyl(1-(p-tolyl)vinyl)silane (5e).**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.12-7.08 (m, 4H), 5.81 (d,  $J = 3.0$  Hz, 1H), 5.57 (d,  $J = 3.0$  Hz, 1H), 2.34 (s, 3H), 0.16 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  153.0, 141.7, 135.8, 128.8, 126.6, 126.5, 21.1, -0.8. These data are consistent with the published literature.<sup>[4]</sup>



**5f**

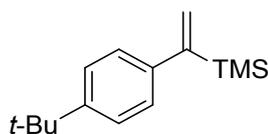
**Trimethyl(1-(o-tolyl)vinyl)silane (5f).**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.17-7.16 (m, 1H), 7.11-7.09 (m, 2H), 6.88-6.86 (m, 1H), 5.73 (d,  $J = 3.4$  Hz, 1H), 5.62 (d,  $J = 3.4$  Hz, 1H), 2.19 (s, 3H), 0.09 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  154.2, 144.4, 134.0, 129.9, 127.7, 127.5, 125.7, 125.0, 20.2, -1.4. This compound has been reported in the published literature.<sup>[12b]</sup>



**5g**

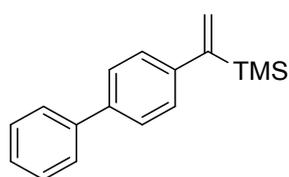
**(1-(3,4-Dimethylphenyl)vinyl)trimethylsilane (5g).** Flash column chromatography to afford product **5g** as a pale yellow oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.06 (d,  $J = 7.6$  Hz, 1H), 6.97 (d,  $J = 1.8$  Hz, 1H), 6.94-6.92 (m, 1H), 5.80 (d,  $J = 3.0$  Hz, 1H), 5.55 (d,  $J = 3.1$  Hz, 1H), 2.26 (s, 3H), 2.25 (s, 3H), 0.17 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,

CDCl<sub>3</sub>)  $\delta$  153.1, 142.2, 136.2, 134.5, 129.3, 127.9, 126.5, 124.1, 19.9, 19.4, -0.8.  
HRMS (EI) [M]<sup>+</sup>: calculated for C<sub>13</sub>H<sub>20</sub>Si: 204.1334, found 204.1324.



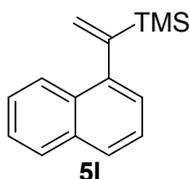
**5h**

**(1-(4-(*tert*-Butyl)phenyl)vinyl)trimethylsilane (5h).** Flash column chromatography to afford product **5h** as a colorless oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.33 -7.31 (m, 2H), 7.16-7.14 (m, 2H), 5.85 (d, *J* = 2.9 Hz, 1H), 5.57 (d, *J* = 3.0 Hz, 1H), 1.32 (s, 9H), 0.18 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  152.8, 149.1, 141.5, 126.6, 126.3, 125.0, 34.4, 31.4, -0.7. HRMS (EI) [M]<sup>+</sup>: calculated for C<sub>15</sub>H<sub>24</sub>Si: 232.1647, found 232.1643.



**5k**

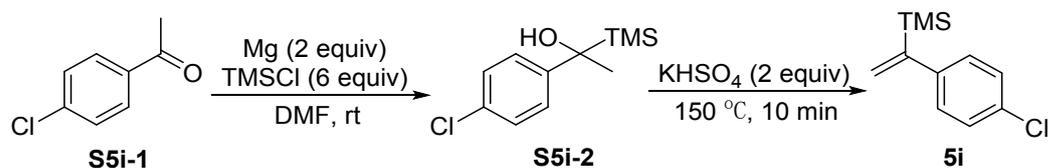
**(1-([1,1'-Biphenyl]-4-yl)vinyl)trimethylsilane (5k).** Flash column chromatography to afford product **5k** as a white solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.63-7.61 (m, 2H), 7.57-7.54 (m, 2H), 7.46-7.43 (m, 2H), 7.36-7.33 (m, 1H), 7.30-7.27 (m, 2H), 5.90 (d, *J* = 2.9 Hz, 1H), 5.65 (d, *J* = 2.9 Hz, 1H), 0.22 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  152.8, 143.7, 140.9, 139.0, 128.7, 127.2, 127.1(4), 127.1(0), 126.9, 126.8, -0.8. HRMS (EI) [M]<sup>+</sup>: calculated for C<sub>17</sub>H<sub>20</sub>Si: 252.1334, found 252.1331.



**5l**

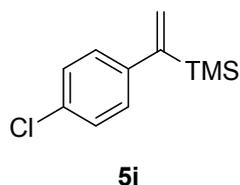
**Trimethyl(1-(naphthalen-1-yl)vinyl)silane (5l).** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.90-7.82 (m, 2H), 7.72-7.70 (m, 1H), 7.47-7.40 (m, 3H), 7.07-7.06 (m, 1H), 5.94 (d, *J* = 3.4 Hz, 1H), 5.79 (d, *J* = 3.4 Hz, 1H), 0.09 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  153.1, 142.9, 133.7, 131.3, 129.2, 128.1, 126.5, 126.0, 125.5, 125.2(1), 125.1(8), 123.9, -1.3. These data are consistent with the published literature.<sup>[3c]</sup>

#### Method B:<sup>[4]</sup> Synthesis of Vinylsilanes **5i** and **5j**.

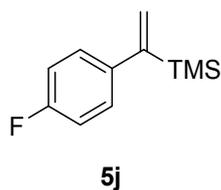


To a suspension of Mg dust (0.67 g, 28.0 mmol, 2 equiv) in DMF (7 mL) at rt was added a small particle of I<sub>2</sub> and several drops of TMSCl until deep color disappears. Then, TMSCl (9.3 mL, 84.0 mmol, 6 equiv) in DMF (20 mL) was added during 0.5 h. The mixture was kept for 2 h, then *p*-chloroacetophenone **S5i-1** (2.15 g, 14.0 mmol, 1 equiv) in DMF (27 mL) was added during 2 h. It was stirred at room temperature overnight, then quenched with saturated NH<sub>4</sub>Cl (10 mL). The mixture was extracted with ethyl acetate (4 x 20 ml), washed with water and brine, then dried over MgSO<sub>4</sub> and concentrated. The residue was purified by flash chromatography to afford the **S5i-2** with some inseparable impurities.

The stirred mixture of **S5i-2** (0.32 g, 1.4 mmol, 1 equiv) and KHSO<sub>4</sub> (0.38 g, 2.8 mmol, 2 equiv) was heated to 150 °C for 10 min, then it was cooled, filtered and washed with ethyl acetate. The organic phase was concentrated, and the residue was purified by flash chromatography on a silica gel with petroleum ether as the eluent to afford the product **5i** as a colorless oil.

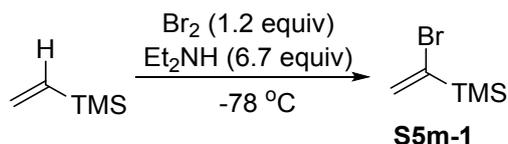


**(1-(4-Chlorophenyl)vinyl)trimethylsilane (5i).** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.26-7.24 (m, 2H), 7.09-7.07 (m, 2H), 5.60 (dd, *J* = 2.9, 1.6 Hz, 1H), 5.59 (dd, *J* = 2.9, 1.6 Hz, 1H), 0.14 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 152.4, 143.2, 132.0, 128.2, 128.0, 127.7, -1.0. These data are consistent with the published literature.<sup>[4]</sup>

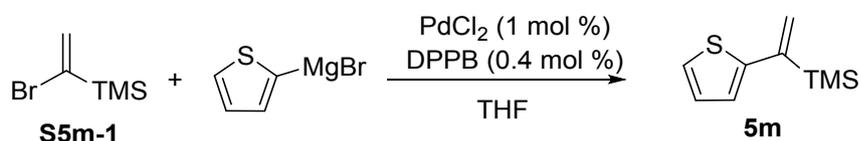


**(1-(4-Fluorophenyl)vinyl)trimethylsilane (5j).** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.15-7.11 (m, 2H), 7.01-6.97 (m, 2H), 5.79 (d, *J* = 2.9 Hz, 1H), 5.59 (d, *J* = 2.9 Hz, 1H), 0.16 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 161.7 (d, *J* = 244.4 Hz), 152.4, 140.6, 128.1 (d, *J* = 7.9 Hz), 127.4, 114.9 (d, *J* = 21.3 Hz), -1.0. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ -117.2. This compound has been reported in the published literature.

### Method C:<sup>[5]</sup> Synthesis of Vinylsilane 5m.



To an oven dried transparent 250 mL Schlenk tube equipped with stirring bar, trimethyl(vinyl)silane (6.5 g, 65.0 mmol, 1 equiv) was added. The reaction was stirred and cooled to  $-78^\circ\text{C}$  for 10 min. Bromine (4 mL, 78.0 mmol, 1.2 equiv) is added dropwise over 2 hours, then the temperature was raised to  $0^\circ\text{C}$  and diethylamine (45.5 mL, 435.0 mmol, 6.7 equiv) is cautiously added with continued stirring. After the addition is complete, the reaction mixture is heated at reflux for 12 hours, during which time a precipitate of diethylamine hydrochloride forms. The salts are separated from the cooled suspension by filtration and washed with diethyl ether. The combined extracts were quenched with 2M HCl (100 mL) until the aqueous layer remains acidic ( $\text{pH} = 2$ ). The reaction mixture was extracted with ethyl (4 x 50 mL). The combined extracts were washed with brine, dried over  $\text{MgSO}_4$  and filtered. The product **S5m-1** is obtained by atmospheric distillation.



To a suspension of Mg dust (0.26 g, 11.0 mmol, 1.1 equiv) in anhydrous THF (4 mL) at room temperature was added a small particle of  $\text{I}_2$  and several drops of 2-bromothiophene until deep color disappears. Then, 2-bromothiophene (1.63 g, 10.0 mmol, 1 equiv) in THF (4 mL) was added during 10 min. The resulting mixture was stirred at  $50^\circ\text{C}$  and refluxed for 1 h. After the formation of the Grignard reagent, the solution was cooled to room temperature and used for the next step.

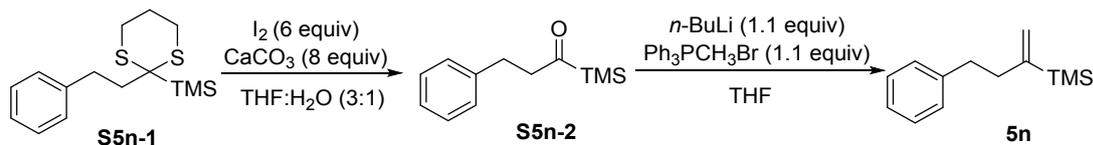
To a mixture of **S5m-1** (720 mg, 4.0 mmol, 1 equiv),  $\text{PdCl}_2$  (7 mg, 0.04 mmol, 1 mol %), 1,4-bis(diphenylphosphino)butane (DPPB) (7 mg, 0.016 mmol, 0.4 mol %), and dry THF (12 mL) was added an solution of 2-thienylmagnesium bromide (8 mL, 5.0 mmol, 1.25 equiv) at  $0^\circ\text{C}$  under an argon atmosphere. The mixture was refluxed for 2 h, hydrolyzed, and extracted with ether three times. After drying over  $\text{MgSO}_4$ , the

solvent was removed. The residue was purified by flash chromatography on a silica gel column with petroleum ether as the eluent to give the product **5m** as a colorless oil in 95% yield (692 mg).



**Trimethyl(1-(thiophen-2-yl)vinyl)silane (5m).** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.15-7.14 (m, 1H), 6.99-6.94 (m, 2H), 6.05 (d, *J* = 2.2 Hz, 1H), 5.48 (d, *J* = 2.2 Hz, 1H), 0.25 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 147.1, 144.3, 127.3, 125.5, 124.4, 123.5, -0.8. This compound has been reported in the published literature.<sup>[5]</sup>

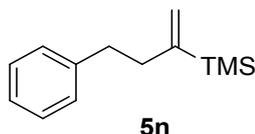
#### Method D:<sup>[6]</sup> Synthesis of Vinylsilane **5n**.



According to the method A, **S5n-1** was prepared using commercially available 3-phenylpropanal as the starting material. Under air, **S5n-1** (2.96 g, 10 mmol, 1.0 equiv) was dissolved in a mixture of THF (60 mL) and H<sub>2</sub>O (20 mL). CaCO<sub>3</sub> (8 g, 80 mmol, 8.0 equiv) was added and the mixture was cooled to 0 °C. Iodine (15.2 g, 60 mmol, 6.0 equiv) was added portionwise and the reaction mixture was stirred at room temperature overnight. The reaction was quenched with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution (30 mL) and extracted by ethyl acetate (4 x 20 mL). The combined organic were washed with brine, dried over MgSO<sub>4</sub>, concentrated under reduced pressure and purified by column chromatography on silica gel with petroleum ether as the eluent to give the product **S5n-2** as a pale yellow oil.

To a solution of methyltriphenylphosphonium bromide (1.18 g, 3.3 mmol, 1.1 equiv) in THF (26 mL) was added *n*-butyl lithium (2.5 mL, 1.6 M, 1.1 equiv) dropwise and the mixture was stirred for 1 hour at room temperature. Then **S5n-2** (618 mg, 3.0 mmol, 1 equiv) was added and the solution was stirred at 25 °C until the reaction is completed. The solvent was removed under reduced pressure and the residue was

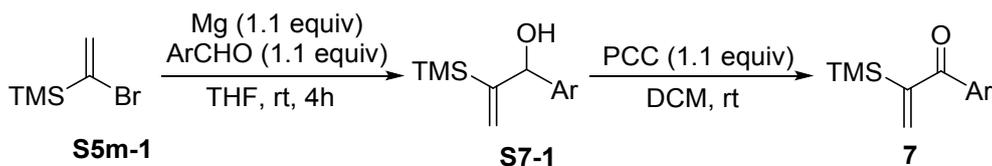
purified by flash chromatography on a silica gel with petroleum ether as the eluent to afford the product **5n** as a colorless oil.



**Trimethyl(4-phenylbut-1-en-2-yl)silane (5n).**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30-7.27 (m, 2H), 7.21-7.19 (m, 3H), 5.62 (d,  $J = 1.4$  Hz, 1H), 5.38 (d,  $J = 1.4$  Hz, 1H), 2.74-2.71 (m, 2H), 2.44-2.41 (m, 2H), 0.11 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  151.8, 142.5, 128.3(5), 128.2(9), 125.7, 124.0, 37.7, 35.5, -1.5. These data are consistent with the published literature.<sup>[6]</sup>

## 2.2 General Procedure for the Preparation of Silylated Vinylaryl Ketones **7a-7e**<sup>[8]</sup>

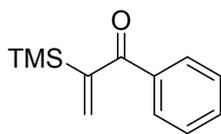
### Ketones **7a-7e**<sup>[8]</sup>



To an oven-dried Schlenk tube equipped with a stir bar was added Mg powder (132 mg, 5.5 mmol, 1.1 equiv), anhydrous THF (7 mL), and  $\alpha$ -bromovinyltrimethylsilane **S5m-1** (900 mg, 5.0 mmol, 1.0 equiv). The reaction was additionally heated with the heat gun to initiate Grignard reagent formation and left to stir at ambient temperature for 2 h. Then the mixture was cooled to 0 °C and THF (3 mL) solution of the corresponding aryl aldehyde (5.5 mmol, 1.1 equiv) was added slowly. The reaction mixture was allowed to slowly warm up to room temperature, stirred for an additional 2 h and quenched with 2M HCl (10 mL). Then, the organic phase was separated and the aqueous phase was extracted with ethyl acetate (3 x 20 mL). The organic phases were combined, dried over  $\text{MgSO}_4$  and concentrated. The residue was purified via column chromatography on Silica gel to yield the corresponding aryl alcohol **S7-1** as colorless oil.

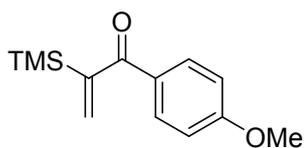
The aryl alcohol **S7-1** (3.4 mmol, 1 equiv) was diluted in  $\text{CH}_2\text{Cl}_2$  (10 mL). Then the reaction mixture was cooled to 0 °C and PCC (810 mg, 3.8 mmol, 1.1 equiv) was

added. The reaction was allowed to warm up to room temperature and stirred until disappearance of starting material. Then it was filtered through the short pad of silica gel and concentrated. The residue was purified via column chromatography on silica gel to afford the product **7**.



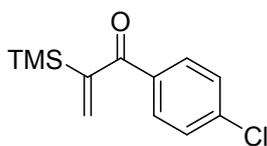
**7a**

**1-Phenyl-2-(trimethylsilyl)prop-2-en-1-one (7a).**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84-7.82 (m, 2H), 7.56-7.53 (m, 1H), 7.46-7.43 (m, 2H), 6.11 (d,  $J = 2.5$  Hz, 1H), 6.04 (d,  $J = 2.4$  Hz, 1H), 0.21 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  201.2, 153.7, 137.2, 133.4, 132.6, 129.7, 128.3, -1.4. These data are consistent with the published literature.<sup>[8]</sup>



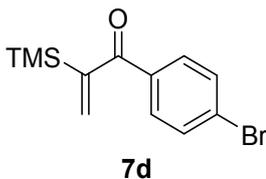
**7b**

**1-(4-Methoxyphenyl)-2-(trimethylsilyl)prop-2-en-1-one (7b).**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86-7.84 (m, 2H), 6.93-6.92 (m, 2H), 6.01 (d,  $J = 2.6$  Hz, 1H), 5.97 (d,  $J = 2.6$  Hz, 1H), 3.87 (s, 3H), 0.19 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  200.0, 163.4, 154.0, 132.1, 131.5, 129.9, 113.5, 55.4, -1.4. These data are consistent with the published literature.<sup>[8]</sup>

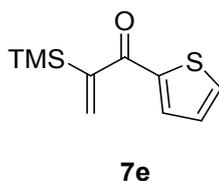


**7c**

**1-(4-Chlorophenyl)-2-(trimethylsilyl)prop-2-en-1-one (7c).**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78-7.76 (m, 2H), 7.43-7.41 (m, 2H), 6.11 (d,  $J = 2.4$  Hz, 1H), 6.02 (d,  $J = 2.4$  Hz, 1H), 0.20 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  199.9, 153.5, 139.1, 135.5, 133.5, 131.1, 128.6, -1.5. These data are consistent with the published literature.<sup>[8]</sup>



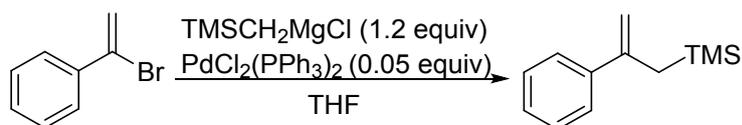
**1-(4-Bromophenyl)-2-(trimethylsilyl)prop-2-en-1-one(7d).**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70-7.68 (m, 2H), 7.60-7.57 (m, 2H), 6.11 (d,  $J = 2.4$  Hz, 1H), 6.02 (d,  $J = 2.4$  Hz, 1H), 0.20 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  200.1, 153.4, 135.9, 133.6, 131.6, 131.2, 127.8, -1.5. These data are consistent with the published literature.<sup>[8]</sup>



**1-(Thiophen-2-yl)-2-(trimethylsilyl)prop-2-en-1-one (7e).** Flash column chromatography to afford product **7e** as a pale yellow oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67-7.66 (m, 1H), 7.57-7.56 (m, 1H), 7.12-7.11 (m, 1H), 6.19 (d,  $J = 2.5$  Hz, 1H), 6.03 (d,  $J = 2.5$  Hz, 1H), 0.21 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  193.0, 153.7, 144.1, 134.2, 134.1, 132.2, 127.9, -1.5. HRMS (ESI)  $[\text{M}+\text{H}]^+$ : calculated for  $\text{C}_{10}\text{H}_{15}\text{OSSi}$ : 211.0607, found 211.0608.

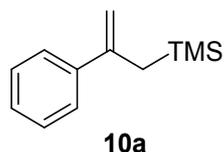
## 2.3 General Procedure for the Preparation of Allylsilanes<sup>[7]</sup>

### Method A': Synthesis of Allylsilane 10a.



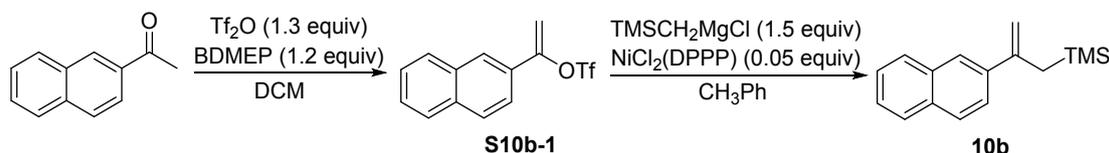
An oven-dried flask containing a stirring bar was charged with  $\alpha$ -bromostyrene (552 mg, 3.0 mmol, 1 equiv),  $\text{PdCl}_2(\text{PPh}_3)_2$  (105.3 mg, 0.15 mmol, 0.05 equiv) and dried THF (9 mL) under nitrogen. To the mixture was added commercially available (trimethylsilylmethyl)magnesium chloride in THF (2.8 mL, 1.3 M, 3.6 mmol, 1.2 equiv) dropwise by a syringe and the resulting mixture was stirred at room temperature for 3 h. Then the reaction was quenched with saturated aqueous solution of  $\text{NH}_4\text{Cl}$  (20 mL). The reaction mixture was extracted with ethyl acetate (3 x 20 mL). The combined extracts were washed with brine, dried over  $\text{MgSO}_4$ , filtered and

concentrated in vacuo. The residue was purified by flash chromatography on a silica gel column with petroleum ether as the eluent to give the product **10a** as a colorless liquid in 89% yield (505 mg).



**Trimethyl(2-phenylallyl)silane(10a).** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.42-7.39 (m, 2H), 7.32-7.29 (m, 2H), 7.26-7.24 (m, 1H), 5.13 (s, 1H), 4.87 (s, 1H), 2.03 (s, 2H), -0.09 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 146.6, 142.8, 128.0, 127.2, 126.3, 110.0, 26.1, -1.4. These data are consistent with the published literature.<sup>[7]</sup>

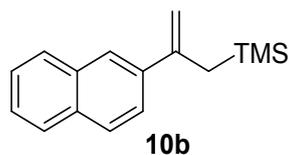
#### Method B': Synthesis of Allylsilane 10b.



To the solution of 1-(naphthalen-2-yl)ethan-1-one (1.36 g, 8.0 mmol, 1 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) at 0 °C was added 2,6-di-*tert*-butylpyridine (BDMEP) (1.85 g, 9.6 mmol, 1.2 equiv) and trifluoromethanesulfonic anhydride (1.75 mL, 10.4 mmol, 1.3 equiv) sequentially. The reaction mixture was warmed to room temperature and stirred overnight. Then the volatiles were removed under reduced pressure and petroleum ether was added to the residue. After filtration, the combined organic layer was washed with brine subsequently and dried over MgSO<sub>4</sub>. The organic phase was concentrated under reduced pressure and obtained product **S10b-1**.

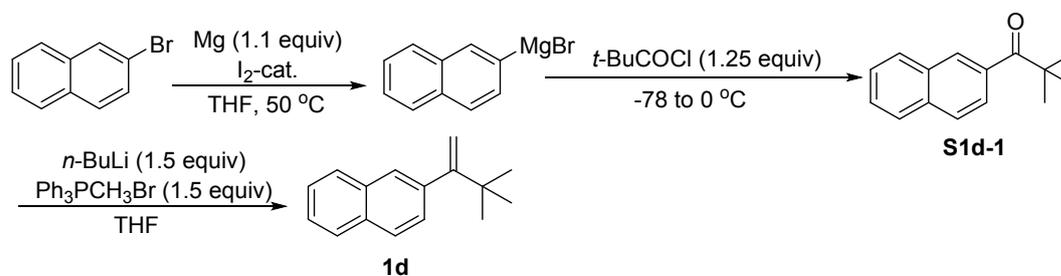
The product **S10b-1** was dissolved in toluene (20 mL) and transferred to a oven-dried flask with NiCl<sub>2</sub>(DPPP) (216.8 mg, 0.4 mmol) under inert atmosphere. To the mixture was added commercially available (trimethylsilylmethyl)magnesium chloride in THF (9.3 mL, 1.3 M, 12 mmol) dropwise by a syringe and the resulting mixture was stirred at room temperature overnight. Then the reaction was quenched with saturated aqueous solution of NH<sub>4</sub>Cl (20 mL). The reaction mixture was extracted with ethyl acetate (3 x 20 mL). The combined extracts were washed with brine, dried over MgSO<sub>4</sub>, filtered and concentrated in vacuo. The residue was purified by flash

chromatography on a silica gel column with petroleum ether as the eluent to give the product **10b** as a colorless oil.



**Trimethyl(2-(naphthalen-2-yl)allyl)silane (10b).**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83-7.77 (m, 4H), 7.61-7.59 (m, 1H), 7.47 -7.44 (m, 2H), 5.29 (d,  $J = 1.5$  Hz, 1H), 4.98 (d,  $J = 1.2$  Hz, 1H), 2.14 (s, 2H), -0.08 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  146.3, 139.8, 133.2, 132.7, 128.1, 127.6, 127.5, 126.0, 125.6, 124.9, 110.7, 26.0, -1.4. These data are consistent with the published literature.<sup>[7]</sup>

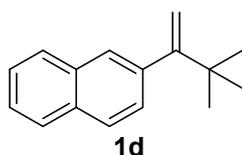
## 2.4 General Procedure for the Preparation of **1d**<sup>[10]</sup>



To a suspension of Mg dust (0.53 g, 22.0 mmol, 1.1 equiv) in anhydrous THF (5 mL) at room temperature was added a small particle of  $\text{I}_2$  and several drops of 2-bromonaphthalene until deep color disappears. 2-Bromonaphthalene (4.14 g, 20.0 mmol, 1 equiv) in THF (15 mL) was added during 20 min. Then, the resulting mixture was stirred at 50 °C for 1 h. After the formation of the Grignard reagent, the solution was cooled to room temperature and used for the next step.

The above prepared Grignard solution was transferred to a solution of pivaloyl chloride (3.1 mL, 25 mmol, 1.25 equiv) in THF (20 mL) dropwise at -78 °C. The reaction was stirred at -30 °C for 3 h and then the temperature was raised to 0 °C for an additional 3 h. The reaction was quenched with saturated  $\text{NH}_4\text{Cl}$  solution (20 mL), extracted with ethyl acetate (30 mL $\times$ 3), combined organic layers were dried over  $\text{MgSO}_4$ . The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel with petroleum ether as the eluent to give the product **S1d-1** as a white solid.

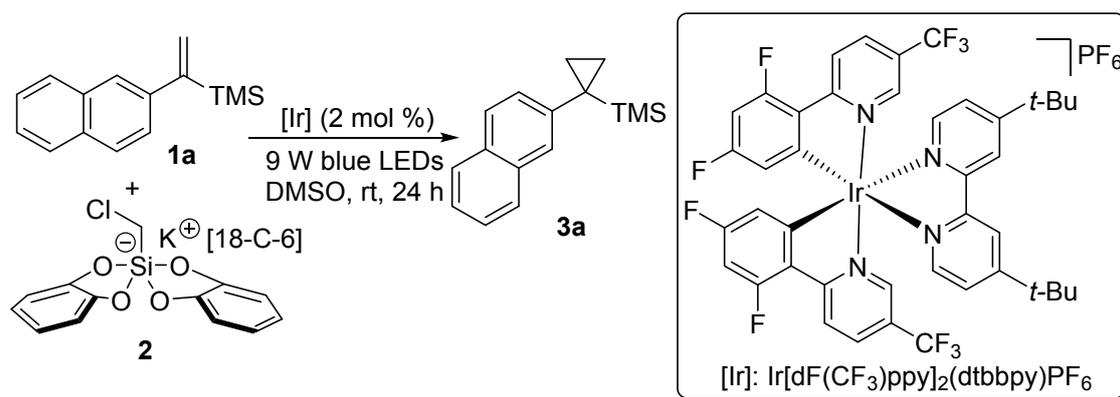
To a solution of methyltriphenylphosphonium bromide (2.68 g, 7.5 mmol, 1.5 equiv) in THF (30 mL) was added *n*-butyl lithium (4.7 mL, 1.6 M, 1.5 equiv) dropwise and the mixture was stirred for 0.5 h at room temperature. Then 2-pivalonaphthone **S1d-1** (1.06 g, 5.0 mmol, 1 equiv) was added and the solution was stirred at 25 °C until the reaction is completed. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel with petroleum ether as the eluent to give the product **1d** as a white solid in 83% yield (876 mg).



**2-(3,3-Dimethylbut-1-en-2-yl)naphthalene (1d).** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.86-7.76 (m, 3H), 7.62-7.61 (m, 1H), 7.51-7.45 (m, 2H), 7.35-7.32 (m, 1H), 5.29 (d, *J* = 2.1 Hz, 1H), 4.88 (d, *J* = 2.4 Hz, 1H), 1.20 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 159.8, 141.1, 132.9, 132.0, 127.9, 127.8, 127.5, 127.3, 126.5, 125.9, 125.4, 111.9, 36.4, 29.8. These data are consistent with the published literature.<sup>[10a]</sup>

### 3 General Procedures of Photoredox-Catalysed Reactions

#### 3.1 General Procedure of Cyclopropanation of Vinylsilanes for Preparation of 3a, 6a-e, and 6g-m



To an oven dried transparent 10 mL Schlenk tube equipped with stirring bar, Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (4.5 mg, 0.004 mmol, 0.02 equiv), potassium [18-Crown-6] bis(catecholato)chloromethylsilicate **2** (238.9 mg, 0.4 mmol, 2.0 equiv), the

vinylsilane **1a** (45.3 mg, 0.2 mmol, 1.0 equiv) were added. The tube was evacuated and filled with nitrogen for 3 times. The tube was then charged with degassed DMSO (6.0 mL, 0.033 M) via a syringe. The tube was irradiated with a 9 W blue LEDs strip spiraled within a bowel for 24 h (cooling with a fan). After the reaction was complete, the reaction solution was diluted with saturated Na<sub>2</sub>CO<sub>3</sub> aqueous solution (10 mL), and was extracted with EtOAc (5 x 10 mL). The organic layer was washed with brine, dried over MgSO<sub>4</sub>, filtered, and solvent was evaporated to obtain crude product. Flash chromatography over silica gel afforded the product **3a**.

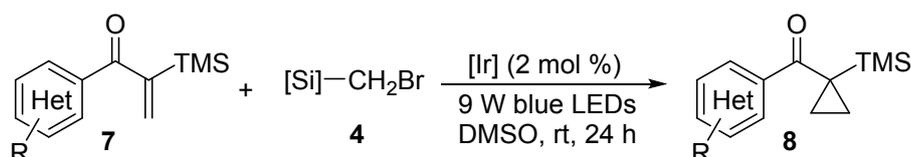
### 3.2 General Procedure of Cyclopropanation of Vinylsilanes for Preparation of **6f**, **6l**, and **6n**



To an oven dried transparent 10 mL Schlenk tube equipped with stirring bar, Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (4.5 mg, 0.004 mmol, 0.02 equiv), potassium [18-Crown-6] bis(catecholato)chloromethylsilicate **2** (238.9 mg, 0.4 mmol, 2.0 equiv) (**4** was used instead of **2** for the preparation of **6n**), the vinylsilane **5** (0.2 mmol, 1.0 equiv) were added. The tube was evacuated and filled with nitrogen for 3 times. The tube was then charged with degassed DMSO (6.0 mL, 0.033 M) via a syringe. The tube was irradiated with a 9 W blue LEDs strip spiraled within a bowel for 24 h (cooling with a fan). After 24 h, an additional portion of potassium [18-Crown-6] bis(catecholato)chloromethylsilicate **2** (119.5 mg, 0.2 mmol, 1 equiv) (**4** was used instead of **2** for the preparation of **6n**) and Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (2.3 mg, 0.002 mmol, 0.01 equiv) were added under N<sub>2</sub>, and the reaction was stirred for an additional 24 h under irradiation. After the reaction was complete, the reaction solution was diluted with saturated Na<sub>2</sub>CO<sub>3</sub> aqueous solution (10 mL), and was extracted with EtOAc (5 x 10 mL). The organic layer was washed with brine, dried

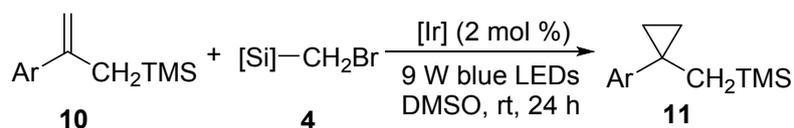
over MgSO<sub>4</sub>, filtered, and solvent was evaporated to obtain crude product. Flash chromatography over silica gel afforded the product **6**.

### 3.3 General Procedure of Cyclopropanation of Silylated Vinylaryl Ketones for Preparation of **8a-8e**



To an oven dried transparent 10 mL Schlenk tube equipped with stirring bar, Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (4.5 mg, 0.004 mmol, 0.02 equiv), potassium [18-Crown-6] bis(catecholato)bromomethylsilicate **4** (257.1 mg, 0.4 mmol, 2.0 equiv), the silylated vinylaryl ketone **7** (0.2 mmol, 1.0 equiv) were added. The tube was evacuated and filled with nitrogen for 3 times. The tube was then charged with degassed DMSO (6.0 mL, 0.033 M) via a syringe. The tube was irradiated with a 9 W blue LEDs strip spiraled within a bowel for 24 h (cooling with a fan). After the reaction was complete, the reaction solution was diluted with saturated Na<sub>2</sub>CO<sub>3</sub> aqueous solution (10 mL), and was extracted with EtOAc (5 x 10 mL). The organic layer was washed with brine, dried over MgSO<sub>4</sub>, filtered, and solvent was evaporated to obtain crude product. Flash chromatography over silica gel afforded the product **8**.

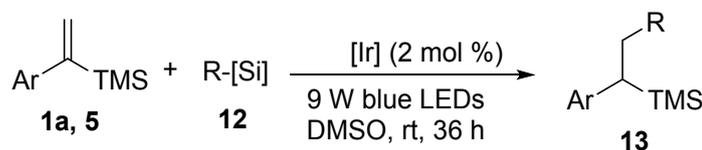
### 3.4 General Procedure of Cyclopropanation of Allylsilanes for Preparation of **11a** and **11b**



To an oven dried transparent 10 mL Schlenk tube equipped with stirring bar, Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (4.5 mg, 0.004 mmol, 0.02 equiv), potassium [18-Crown-6] bis(catecholato)bromomethylsilicate **4** (257.1 mg, 0.4 mmol, 2.0 equiv), the allylsilane **10** (0.2 mmol, 1.0 equiv) were added. The tube was evacuated and filled

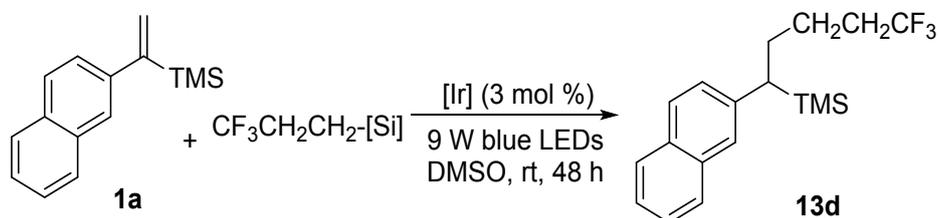
with nitrogen for 3 times. The tube was then charged with degassed DMSO (6.0 mL, 0.033 M) via a syringe. The tube was irradiated with a 9 W blue LEDs strip spiraled within a bowel for 24 h (cooling with a fan). After the reaction was complete, the reaction solution was diluted with saturated Na<sub>2</sub>CO<sub>3</sub> aqueous solution (10 mL), and was extracted with EtOAc (5 x 10 mL). The organic layer was washed with brine, dried over MgSO<sub>4</sub>, filtered, and solvent was evaporated to obtain crude product. Flash chromatography over silica gel afforded the product **11**.

### 3.5 General Procedure of Radical Addition of Vinylsilanes for Preparation of 13a-13c and 13e-13l



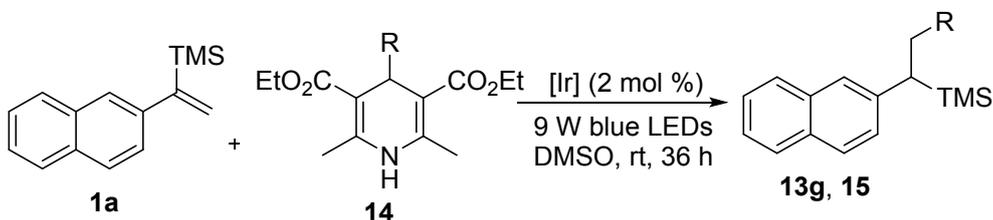
To an oven dried transparent 10 mL Schlenk tube equipped with stirring bar, Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (4.5 mg, 0.004 mmol, 0.02 equiv), potassium [18-Crown-6] bis(catecholato)-alkylsilicate **12** (0.4 mmol, 2.0 equiv), the vinylsilane **1a** or **5** (0.2 mmol, 1.0 equiv) were added. The tube was evacuated and filled with nitrogen for 3 times. The tube was then charged with degassed DMSO (6.0 mL, 0.033 M) via a syringe. The tube was irradiated with a 9 W blue LEDs strip spiraled within a bowel for 36 h (cooling with a fan). After the reaction was complete, the reaction solution was diluted with saturated Na<sub>2</sub>CO<sub>3</sub> aqueous solution (10 mL), and was extracted with EtOAc (5 x 10 mL). The organic layer was washed with brine, dried over MgSO<sub>4</sub>, filtered, and solvent was evaporated to obtain crude product. Flash chromatography over silica gel afforded the product **13**.

### 3.6 General Procedure of Radical Addition of Vinylsilane for Preparation of 13d

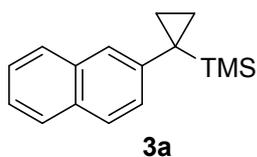


To an oven dried transparent 10 mL Schlenk tube equipped with stirring bar,  $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$  (4.5 mg, 0.004 mmol, 0.02 equiv), potassium [18-Crown-6] bis(catecholato)-3,3,3-trifluoropropylsilicate (258 mg, 0.4 mmol, 2.0 equiv), the vinylsilane **1a** (45.2 mg, 0.2 mmol, 1.0 equiv) were added. The tube was evacuated and filled with nitrogen for 3 times. The tube was then charged with degassed DMSO (6.0 mL, 0.033 M) via a syringe. The tube was irradiated with a 9 W blue LEDs strip spiraled within a bowel for 24 h (cooling with a fan). After 24 h, an additional portion of potassium [18-Crown-6] bis(catecholato)-3,3,3-trifluoropropylsilicate (129 mg, 0.2 mmol, 1 equiv) and  $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$  (2.3 mg, 0.002 mmol, 0.01 equiv) were added under  $\text{N}_2$ , and the reaction was stirred for an additional 24 h under irradiation. After the reaction was complete, the reaction solution was diluted with saturated  $\text{Na}_2\text{CO}_3$  aqueous solution (10 mL), and was extracted with EtOAc (5 x 10 mL). The organic layer was washed with brine, dried over  $\text{MgSO}_4$ , filtered, and solvent was evaporated to obtain crude product. Flash chromatography over silica gel afforded the product **13d**.

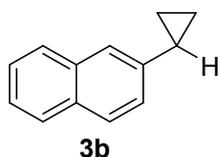
### 3.7 General Procedure of Radical Addition of Vinylsilanes for Preparation of 13g and 15



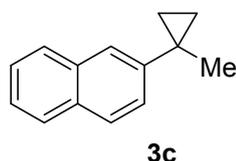
To an oven dried transparent 10 mL Schlenk tube equipped with stirring bar, Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (4.5 mg, 0.004 mmol, 0.02 equiv), 4-alkyldihydropyridine **14** (0.4 mmol, 2.0 equiv), the vinylsilane **1a** (45.2 mg, 0.2 mmol, 1.0 equiv) were added. The tube was evacuated and filled with nitrogen for 3 times. The tube was then charged with degassed DMSO (6.0 mL, 0.033 M) via a syringe. The tube was irradiated with a 9 W blue LEDs strip spiraled within a bowel for 36 h (cooling with a fan). After the reaction was complete, the reaction solution was diluted with saturated Na<sub>2</sub>CO<sub>3</sub> aqueous solution, and was extracted with EtOAc (5 x 10 mL). The organic layer was washed with brine, dried over MgSO<sub>4</sub>, filtered, and solvent was evaporated to obtain crude product. Flash chromatography over silica gel afforded the product **13g** or **15**.



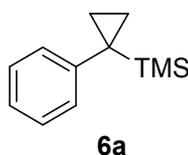
**Trimethyl(1-(naphthalen-2-yl)cyclopropyl)silane (3a).** Flash column chromatography to afford product **3a** as a white solid (39.9 mg, 83% yield); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.78-7.69 (m, 3H), 7.61-7.60 (m, 1H), 7.44-7.35 (m, 3H), 0.90-0.85 (m, 4H), -0.05 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 144.3, 133.4, 131.5, 129.5, 128.1, 127.5, 127.3, 127.1, 125.7, 124.8, 15.5, 9.8, -3.1. HRMS (ESI) [M+H]<sup>+</sup>: calculated for C<sub>16</sub>H<sub>21</sub>Si: 241.1407, found 241.1409.



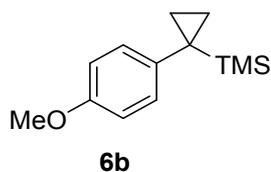
**2-Cyclopropylnaphthalene (3b).**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80-7.74 (m, 3H), 7.55 (s, 1H), 7.46-7.38 (m, 2H), 7.21 (dd,  $J = 8.5, 1.9$  Hz, 1H), 2.10-2.05 (m, 1H), 1.06-1.02 (m, 2H), 0.84-0.82 (m, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  141.4, 133.5, 131.9, 127.8, 127.6, 127.2, 125.9, 124.8, 124.6, 123.7, 15.6, 9.2. These data are consistent with the published literature.<sup>[10a]</sup>



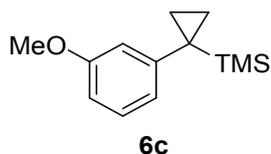
**2-(1-Methylcyclopropyl)naphthalene (3c).**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81-7.76 (m, 3H), 7.72 (d,  $J = 1.8$  Hz, 1H), 7.47-7.37 (m, 3H), 1.52 (s, 3H), 1.00-0.98 (m, 2H), 0.82-0.80 (m, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  144.5, 133.4, 131.7, 127.7, 127.5, 127.4, 125.9, 125.6, 125.1, 124.9, 25.7, 20.0, 15.5. This compound has been reported in the published literature.<sup>[12c]</sup>



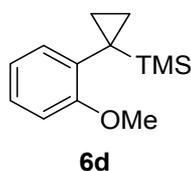
**Trimethyl(1-phenylcyclopropyl)silane (6a).** Flash column chromatography to afford product **6a** as a yellow oil (27.8 mg, 73% yield);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.23-7.17 (m, 4H), 7.12-7.09 (m, 1H), 0.78 (br, 4H), -0.09 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  146.6, 130.3, 127.8, 124.9, 15.2, 9.6, -3.2. This compound has been reported in the published literature.<sup>[12d]</sup>



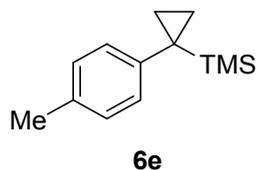
**(1-(4-Methoxyphenyl)cyclopropyl)trimethylsilane (6b).** Flash column chromatography to afford product **6b** as a pale yellow solid (31.3 mg, 71% yield);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.11-7.10 (m, 2H), 6.79-6.77 (m, 2H), 3.78 (s, 3H), 0.75-0.73 (m, 2H), -0.09 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  157.0, 138.6, 131.1, 113.2, 55.2, 14.0, 9.6, -3.2. HRMS (EI)  $[\text{M}]^+$ : calculated for  $\text{C}_{13}\text{H}_{20}\text{OSi}$ : 220.1283, found 220.1284.



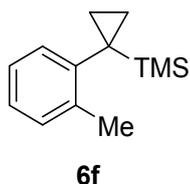
**(1-(3-Methoxyphenyl)cyclopropyl)trimethylsilane (6c).** Flash column chromatography to afford product **6c** as a pale yellow oil (34.8 mg, 79% yield);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.15-7.12 (m, 1H), 6.80-6.78 (m, 1H), 6.76-6.75 (m, 1H), 6.68-6.65 (m, 1H), 3.79 (s, 3H), 0.81-0.76 (m, 4H), -0.07 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.0, 148.3, 128.7, 122.8, 116.0, 110.2, 55.1, 15.4, 9.6, -3.2. HRMS (EI)  $[\text{M}]^+$ : calculated for  $\text{C}_{13}\text{H}_{20}\text{OSi}$ : 220.1283, found 220.1281.



**(1-(2-Methoxyphenyl)cyclopropyl)trimethylsilane (6d).** Flash column chromatography to afford product **6d** as a pale yellow oil (30.4 mg, 69% yield);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.14-7.10 (m, 2H), 6.86-6.83 (m, 1H), 6.80-6.78 (m, 1H), 3.79 (s, 3H), 0.83-0.81 (m, 2H), 0.74-0.72 (m, 2H), -0.11 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  158.7, 134.5, 131.7, 126.0, 119.9, 109.8, 54.8, 10.4(2), 10.4(0), -3.0. HRMS (EI)  $[\text{M}]^+$ : calculated for  $\text{C}_{13}\text{H}_{20}\text{OSi}$ : 220.1283, found 220.1282.

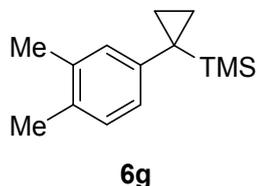


**Trimethyl(1-(p-tolyl)cyclopropyl)silane (6e).** Flash column chromatography to afford product **6e** as a colorless oil (27.8 mg, 68% yield);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.10-7.03 (m, 4H), 2.31 (s, 3H), 0.78-0.74 (m, 4H), -0.08 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  143.5, 134.4, 130.2, 128.6, 21.0, 14.6, 9.6, -3.2. HRMS (EI)  $[\text{M}]^+$ : calculated for  $\text{C}_{13}\text{H}_{20}\text{Si}$ : 204.1334, found 204.1332.

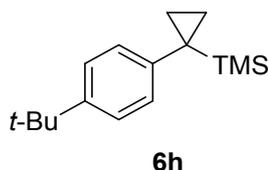


**Trimethyl(1-(o-tolyl)cyclopropyl)silane (6f).** Flash column chromatography to afford product **6f** as a pale yellow oil (28.6 mg, 70% yield);  $^1\text{H}$  NMR (500 MHz,

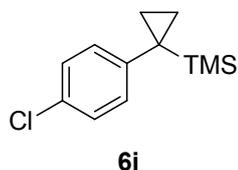
CDCl<sub>3</sub>)  $\delta$  7.14 (d,  $J=7.4$  Hz, 1H), 7.09-7.02 (m, 3H), 2.34 (s, 3H), 0.89 (br, 2H), 0.78 (br, 2H), -0.08 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  144.1, 137.6, 131.5, 130.0, 125.3, 125.0, 19.9, 13.3, 11.4, -2.8. HRMS (EI) [M]<sup>+</sup>: calculated for C<sub>13</sub>H<sub>20</sub>Si: 204.1334, found 204.1330.



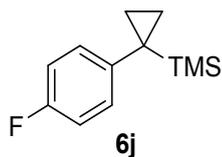
**(1-(3,4-Dimethylphenyl)cyclopropyl)trimethylsilane (6g).** Flash column chromatography to afford product **6g** as a pale yellow oil (41.4 mg, 95% yield); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.00-6.97 (m, 2H), 6.94-6.93 (m, 1H), 2.23 (s, 3H), 2.22 (s, 3H), 0.76 (br, 4H), -0.07 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  144.0, 135.8, 133.0, 131.6, 129.1, 127.7, 19.8, 19.3, 14.5, 9.5, -3.2. HRMS (EI) [M]<sup>+</sup>: calculated for C<sub>14</sub>H<sub>22</sub>Si: 218.1491, found 218.1492.



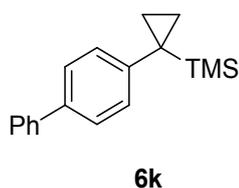
**(1-(4-(tert-Butyl)phenyl)cyclopropyl)trimethylsilane (6h).** Flash column chromatography to afford product **6h** as a white solid (42.3 mg, 86% yield); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.24-7.22 (m, 2H), 7.11-7.10 (m, 2H), 1.30 (s, 9H), 0.78-0.74 (m, 4H), -0.08 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  147.6, 143.3, 129.9, 124.6, 34.3, 31.4, 14.5, 9.5, -3.2. HRMS (EI) [M]<sup>+</sup>: calculated for C<sub>16</sub>H<sub>26</sub>Si: 246.1804, found 246.1805.



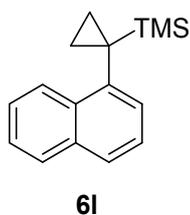
**(1-(4-Chlorophenyl)cyclopropyl)trimethylsilane (6i).** Flash column chromatography to afford product **6i** as a pale yellow oil (26.0 mg, 58% yield); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.20-7.17 (m, 2H), 7.12-7.10 (m, 2H), 0.80-0.78 (m, 2H), 0.76-0.74 (m, 2H), -0.09 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  145.2, 131.6, 130.5, 127.9, 14.8, 9.7, -3.3. HRMS (ESI) [M+H]<sup>+</sup>: calculated for C<sub>16</sub>H<sub>18</sub>ClSi: 225.0861, found 225.0870.



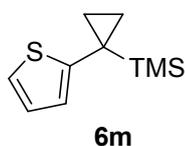
**(1-(4-Fluorophenyl)cyclopropyl)trimethylsilane (6j).** Flash column chromatography to afford product **6j** as a colorless oil (21.6 mg, 52% yield);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.15-7.11 (m, 2H), 6.93-6.88 (m, 2H), 0.79-0.77 (m, 2H), 0.75-0.74 (m, 2H), -0.09 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  160.6 (d,  $J = 242.8$  Hz), 142.2 (d,  $J = 3.1$  Hz), 131.5 (d,  $J = 7.7$  Hz), 114.5 (d,  $J = 21.0$  Hz), 14.4, 9.8, -3.3.  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -118.5. HRMS (EI)  $[\text{M}]^+$ : calculated for  $\text{C}_{12}\text{H}_{17}\text{FSi}$ : 208.1084, found 208.1080.



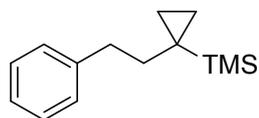
**(1-([1,1'-Biphenyl]-4-yl)cyclopropyl)trimethylsilane (6k).** Flash column chromatography to afford product **6k** as a white solid (34.6 mg, 65% yield);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60-7.58 (m, 2H), 7.49-7.46 (m, 2H), 7.44-7.41 (m, 2H), 7.34-7.30 (m, 1H), 7.28-7.26 (m, 2H), 0.83 (br, 4H), -0.04 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  145.8, 141.1, 137.8, 130.7, 128.6, 126.9, 126.8, 126.5, 15.0, 9.7, -3.2. HRMS (EI)  $[\text{M}]^+$ : calculated for  $\text{C}_{18}\text{H}_{22}\text{Si}$ : 266.1491, found 266.1490.



**Trimethyl(1-(naphthalen-1-yl)cyclopropyl)silane (6l).** Flash column chromatography to afford product **6l** as a yellow oil (25 mg, 52% yield);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.37-8.35 (m, 1H), 7.83-7.82 (m, 1H), 7.67-7.65 (m, 1H), 7.49-7.43 (m, 2H), 7.40-7.35 (m, 2H), 0.96 (br, 4H), -0.08 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  143.0, 133.7, 133.0, 128.4, 128.1, 126.0, 125.7, 125.3, 125.2, 124.7, 12.7, 11.5, -2.6. HRMS (ESI)  $[\text{M}+\text{H}]^+$ : calculated for  $\text{C}_{16}\text{H}_{21}\text{Si}$ : 241.1407, found 241.1402.

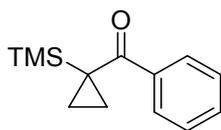


**Trimethyl(1-(thiophen-2-yl)cyclopropyl)silane (6m).** Flash column chromatography to afford product **6m** as a colorless oil (27 mg, 69% yield);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.00-6.99 (m, 1H), 6.87-6.85 (m, 1H), 6.74-6.73 (m, 1H), 0.92-0.91 (m, 2H), 0.86-0.83 (m, 2H), -0.02 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  151.4, 126.4, 124.8, 122.0, 11.9, 9.1, -3.1. HRMS (FI)  $[\text{M}]^+$ : calculated for  $\text{C}_{10}\text{H}_{16}\text{SSi}$ : 196.0742, found 196.0740.



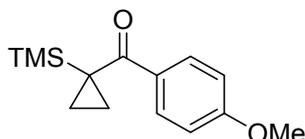
**6m**

**Trimethyl(1-phenethylcyclopropyl)silane (6n).** Flash column chromatography to afford product **6n** as a colorless oil (19.8 mg, 45% yield);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28-7.25 (m, 2H), 7.18-7.14 (m, 3H), 2.64-2.61 (m, 2H), 1.54-1.51 (m, 2H), 0.43-0.41 (m, 2H), 0.32-0.27 (m, 2H), 0.03 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  143.0, 128.3, 128.1, 125.6, 40.7, 35.5, 9.5, 5.8, -2.2. HRMS (FI)  $[\text{M}]^+$ : calculated for  $\text{C}_{14}\text{H}_{22}\text{Si}$ : 218.1491, found 218.1487.



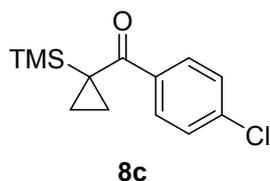
**8a**

**Phenyl(1-(trimethylsilyl)cyclopropyl)methanone (8a).** Flash column chromatography to afford product **8a** as a pale yellow oil (28.4 mg, 65% yield);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00-7.99 (m, 2H), 7.53-7.50 (m, 1H), 7.43-7.40 (m, 2H), 1.17-1.15 (m, 2H), 0.97-0.95 (m, 2H), -0.02 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  202.6, 137.7, 132.5, 129.1, 128.0, 21.0, 9.8, -2.2. HRMS (ESI)  $[\text{M}+\text{H}]^+$ : calculated for  $\text{C}_{13}\text{H}_{19}\text{OSi}$ : 219.1200, found 219.1200.

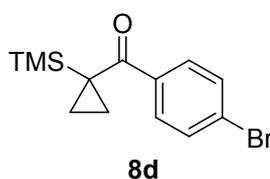


**8b**

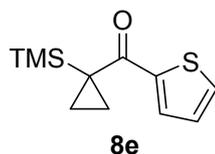
**(4-Methoxyphenyl)(1-(trimethylsilyl)cyclopropyl)methanone (8b).** Flash column chromatography to afford product **8b** as a pale yellow solid (34.7 mg, 70% yield);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02-8.01 (m, 2H), 6.91-6.89 (m, 2H), 3.86 (s, 3H), 1.12-1.10 (m, 2H), 0.94-0.92 (m, 2H), -0.02 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  200.9, 163.1, 131.5, 130.5, 113.2, 55.4, 20.8, 9.7, -2.3. HRMS (ESI)  $[\text{M}+\text{H}]^+$ : calculated for  $\text{C}_{14}\text{H}_{21}\text{O}_2\text{Si}$ : 249.1305, found 249.1305.



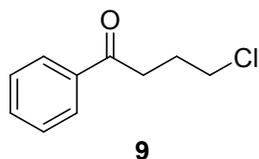
**(4-Chlorophenyl)(1-(trimethylsilyl)cyclopropyl)methanone (8c).** Flash column chromatography to afford product **8c** as a white solid (36.3 mg, 72% yield);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96-7.94 (m, 2H), 7.41-7.39 (m, 2H), 1.14-1.12 (m, 2H), 0.98-0.96 (m, 2H), -0.02 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  201.2, 138.9, 135.9, 130.6, 128.4, 21.0, 9.8, -2.2. HRMS (ESI)  $[\text{M}+\text{H}]^+$ : calculated for  $\text{C}_{13}\text{H}_{18}\text{ClOSi}$ : 253.0810, found 253.0810.



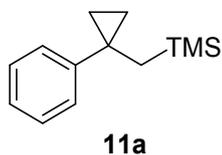
**(4-Bromophenyl)(1-(trimethylsilyl)cyclopropyl)methanone (8d).** Flash column chromatography to afford product **8d** as a white solid (41.4 mg, 70% yield);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88-7.85 (m, 2H), 7.57-7.54 (m, 2H), 1.13-1.11 (m, 2H), 0.96-0.94 (m, 2H), -0.03 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  201.4, 136.3, 131.4, 130.7, 127.6, 21.0, 9.8, -2.2. HRMS (ESI)  $[\text{M}+\text{H}]^+$ : calculated for  $\text{C}_{13}\text{H}_{18}\text{BrOSi}$ : 297.0305, found 297.0305.



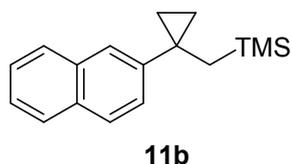
**Thiophen-2-yl(1-(trimethylsilyl)cyclopropyl)methanone (8e).** Flash column chromatography to afford product **8e** as a pale yellow solid (30.5 mg, 68% yield);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78-7.77 (m, 1H), 7.58-7.56 (m, 1H), 7.10-7.08 (m, 1H), 1.19-1.17 (m, 2H), 0.93-0.91 (m, 2H), 0.02 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  195.1, 144.8, 133.0, 132.8, 127.6, 22.2, 9.4, -2.5. HRMS (ESI)  $[\text{M}+\text{H}]^+$ : calculated for  $\text{C}_{11}\text{H}_{17}\text{OSSi}$ : 225.0764, found 225.0763.



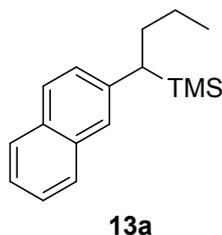
**4-Chloro-1-phenylbutan-1-one (9).**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00-7.97 (m, 2H), 7.59-7.56 (m, 1H), 7.49-7.46 (m, 2H), 3.69 (t,  $J = 6.2$  Hz, 2H), 3.19 (t,  $J = 7.0$  Hz, 2H), 2.27-2.21 (m, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  199.0, 136.7, 133.2, 128.6, 128.0, 44.7, 35.3, 26.7. This compound is known and data is consistent with the published literature.<sup>[11b]</sup>



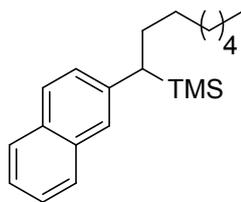
**Trimethyl((1-phenylcyclopropyl)methyl)silane (11a).** Flash column chromatography to afford product **11a** as a yellow oil (23.2 mg, 57% yield);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36-7.33 (m, 2H), 7.29-7.26 (m, 2H), 7.19-7.16 (m, 1H), 1.05 (s, 2H), 0.89-0.87 (m, 2H), 0.67-0.65 (m, 2H), -0.17 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  146.6, 128.4, 128.0, 125.7, 29.4, 22.4, 14.9, -0.7. HRMS (FI)  $[\text{M}]^+$ : calculated for  $\text{C}_{13}\text{H}_{20}\text{Si}$ : 204.1334, found 204.1331.



**Trimethyl((1-(naphthalen-2-yl)cyclopropyl)methyl)silane (11b).** Flash column chromatography to afford product **11b** as a yellow oil (31.3 mg, 62% yield)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80-7.75 (m, 3H), 7.69 (s, 1H), 7.53-7.51 (m, 1H), 7.47-7.40 (m, 2H), 1.14 (s, 2H), 0.98-0.96 (m, 2H), 0.74-0.72 (m, 2H), -0.19 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  144.2, 133.4, 131.9, 127.6, 127.5(2), 127.4(9), 127.4(2), 126.0, 125.8, 125.1, 29.0, 22.6, 15.2, -0.6. HRMS (EI)  $[\text{M}]^+$ : calculated for  $\text{C}_{17}\text{H}_{22}\text{Si}$ : 254.1491, found 254.1489.

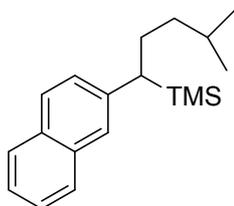


**Trimethyl(1-(naphthalen-2-yl)butyl)silane (13a).** Flash column chromatography to afford product **13a** as a yellow oil (42.0 mg, 82% yield);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80-7.72 (m, 3H), 7.45-7.42 (m, 2H), 7.39-7.36 (m, 1H), 7.22-7.20 (m, 1H), 2.22 (dd,  $J = 12.1, 3.6$  Hz, 1H), 1.95-1.92 (m, 1H), 1.76-1.73 (m, 1H), 1.37-1.35 (m, 1H), 1.21-1.18 (m, 1H), 0.87 (t,  $J = 7.3$  Hz, 3H), -0.03 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  141.7, 133.7, 131.3, 127.6, 127.5, 127.3, 127.1, 125.6, 125.2, 124.3, 36.9, 31.5, 22.4, 13.9, -2.9. HRMS (EI)  $[\text{M}]^+$ : calculated for  $\text{C}_{17}\text{H}_{24}\text{Si}$ : 256.1647, found 256.1648.



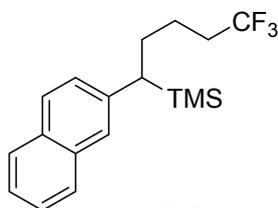
**13b**

**Trimethyl(1-(naphthalen-2-yl)octyl)silane (13b).** Flash column chromatography to afford product **13b** as a colorless oil (50.6 mg, 81% yield);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80-7.72 (m, 3H), 7.45-7.42 (m, 2H), 7.40-7.36 (m, 1H), 7.22-7.20 (m, 1H), 2.19 (dd,  $J = 12.0, 3.6$  Hz, 1H), 1.94-1.90 (m, 1H), 1.80-1.77 (m, 1H), 1.33-1.18 (m, 10H), 0.86 (t,  $J = 7.1$  Hz, 3H), -0.03 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  141.8, 133.7, 131.3, 127.5, 127.3(2), 127.3(0), 127.2, 125.6, 125.1, 124.3, 37.2, 31.9, 29.5, 29.4, 29.3, 29.1, 22.6, 14.1, -2.8. HRMS (EI)  $[\text{M}]^+$ : calculated for  $\text{C}_{21}\text{H}_{32}\text{Si}$ : 312.2273, found 312.2264.



**13c**

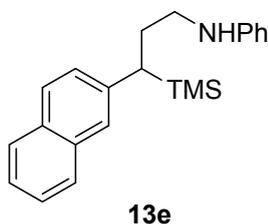
**Trimethyl(4-methyl-1-(naphthalen-2-yl)pentyl)silane (13c).** Flash column chromatography to afford product **13c** as a colorless oil (40.9 mg, 72% yield);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81-7.73 (m, 3H), 7.46-7.43 (m, 2H), 7.40-7.37 (m, 1H), 7.22-7.20 (m, 1H), 2.16 (dd,  $J = 11.7, 3.7$  Hz, 1H), 1.93-1.90 (m, 1H), 1.83-1.81 (m, 1H), 1.56-1.54 (m, 1H), 1.20-1.11 (m, 2H), 0.86-0.84 (m, 6H), -0.02 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  141.8, 133.7, 131.3, 127.5, 127.3(3), 127.2(6), 127.2, 125.6, 125.1, 124.3, 38.7, 37.4, 27.9, 27.0, 22.9, 22.2, -2.8. HRMS (EI)  $[\text{M}]^+$ : calculated for  $\text{C}_{19}\text{H}_{28}\text{Si}$ : 284.1960, found 284.1957.



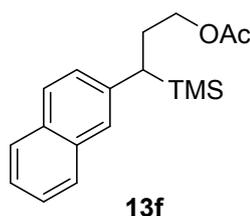
**13d**

**Trimethyl(5,5,5-trifluoro-1-(naphthalen-2-yl)pentyl)silane (13d).** Flash column chromatography to afford product **13d** as a pale yellow oil (59.6 mg, 92% yield);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80-7.78 (m, 1H), 7.76-7.73 (m, 2H), 7.46-7.43 (m, 2H), 7.41-7.38 (m, 1H), 7.19-7.17 (m, 1H), 2.18 (dd,  $J = 12.3, 3.4$  Hz, 1H), 2.08-1.99 (m, 3H), 1.86-1.84 (m, 1H), 1.61-1.60 (m, 1H), 1.45-1.43 (m, 1H), -0.03 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  140.5, 133.7, 131.5, 127.7, 127.6, 127.1(7), 127.1(6) (q,  $J$

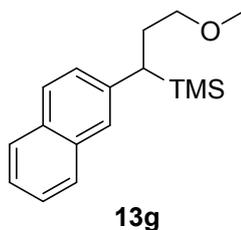
= 277.2 Hz), 126.9, 125.8, 125.1, 124.6, 36.9, 33.4 (q,  $J = 28.3$  Hz) 28.4, 21.7 (q,  $J = 2.8$  Hz), -2.9.  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -66.0. HRMS (EI)  $[\text{M}]^+$ : calculated for  $\text{C}_{18}\text{H}_{23}\text{F}_3\text{Si}$ : 324.1521, found 324.1517.



***N*-(3-(Naphthalen-2-yl)-3-(trimethylsilyl)propyl)aniline (13e).** Flash column chromatography to afford product **13e** as a pale yellow oil (51.3 mg, 77% yield);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82-7.75 (m, 3H), 7.50-7.39 (m, 3H), 7.26-7.23 (m, 1H), 7.14-7.10 (m, 2H), 6.67-6.64 (m, 1H), 6.50-6.48 (m, 2H), 3.60 (br, 1H), 3.17-3.11 (m, 1H), 3.05-2.99 (m, 1H), 2.32 (dd,  $J = 12.4, 3.0$  Hz, 1H), 2.27-2.20 (m, 1H), 2.14-2.09 (m, 1H), -0.01 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  148.2, 140.7, 133.7, 131.5, 129.1, 127.7, 127.6, 127.2, 127.0, 125.9, 125.0, 124.7, 117.1, 112.7, 43.8, 34.9, 29.2, -2.9. HRMS (ESI)  $[\text{M}+\text{H}]^+$ : calculated for  $\text{C}_{22}\text{H}_{28}\text{NSi}$ : 334.1986, found 334.1995.

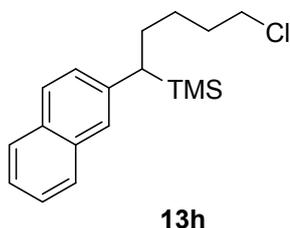


**3-(Naphthalen-2-yl)-3-(trimethylsilyl)propyl acetate (13f).** Flash column chromatography to afford product **13f** as a yellow oil (54.0 mg, 90% yield);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80-7.73 (m, 3H), 7.46-7.38 (m, 3H), 7.21-7.19 (m, 1H), 4.06-4.02 (m, 1H), 3.97-3.94 (m, 1H), 2.29-2.25 (m, 2H), 2.14-2.12 (m, 1H), 1.97 (d,  $J = 1.3$  Hz, 3H), 0.00 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  171.0, 140.1, 133.7, 131.5, 127.7, 127.5, 127.2, 126.9, 125.8, 125.1, 124.7, 64.3, 33.5, 28.3, 20.9, -3.0. HRMS (EI)  $[\text{M}]^+$ : calculated for  $\text{C}_{18}\text{H}_{24}\text{O}_2\text{Si}$ : 300.1546, found 300.1546.

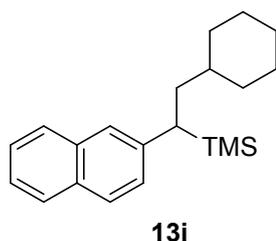


**(3-Methoxy-1-(naphthalen-2-yl)propyl)trimethylsilane (13g).** Flash column chromatography to afford product **13g** as a yellow solid (45.5 mg, 84% yield);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80-7.78 (m, 1H), 7.75 (t,  $J = 8.1$  Hz, 2H), 7.47-7.37 (m, 3H), 7.23-7.21 (m, 1H), 3.35-3.30 (m, 1H), 3.25-3.20 (m, 1H), 3.24 (s, 3H), 2.32 (dd,

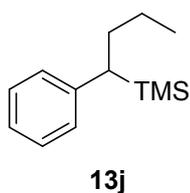
$J = 12.2, 3.6$  Hz, 1H), 2.19-2.10 (m, 2H), -0.02 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  140.8, 133.7, 131.4, 127.5(69), 127.5(66), 127.2, 127.1, 125.7, 125.0, 124.5, 72.2, 58.5, 33.2, 29.2, -3.0. HRMS (EI)  $[\text{M}]^+$ : calculated for  $\text{C}_{17}\text{H}_{24}\text{OSi}$ : 272.1596, found 272.1595.



**(5-Chloro-1-(naphthalen-2-yl)pentyl)trimethylsilane (13h).** Flash column chromatography to afford product **13h** as a white solid (42.0 mg, 69% yield);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79-7.77 (m, 1H), 7.75-7.72 (m, 2H), 7.45-7.42 (m, 2H), 7.39-7.36 (m, 1H), 7.19-7.17 (m, 1H), 3.47-3.41 (m, 2H), 2.18 (dd,  $J = 12.2, 3.6$  Hz, 1H), 1.97-1.94 (m, 1H), 1.82-1.72 (m, 3H), 1.44-1.43 (m, 1H), 1.33-1.32 (m, 1H), -0.04 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  141.2, 133.7, 131.4, 127.5(3), 127.5(1), 127.2, 127.1, 125.7, 125.1, 124.5, 44.9, 37.1, 32.6, 28.6, 26.7, -2.9. HRMS (EI)  $[\text{M}]^+$ : calculated for  $\text{C}_{18}\text{H}_{25}\text{ClSi}$ : 304.1414, found 304.1411.

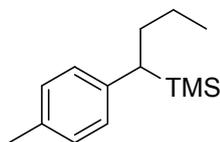


**(2-Cyclohexyl-1-(naphthalen-2-yl)ethyl)trimethylsilane (13i).** Flash column chromatography to afford product **13i** as a white solid (44.7 mg, 72% yield);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80-7.71 (m, 3H), 7.45-7.36 (m, 3H), 7.21-7.19 (m, 1H), 2.36 (dd,  $J = 12.5, 3.3$  Hz, 1H), 1.96-1.90 (m, 1H), 1.84-1.81 (m, 1H), 1.63-1.55 (m, 4H), 1.18-0.78 (m, 7H), -0.05 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  141.8, 133.7, 131.3, 127.5, 127.4, 127.3, 127.2, 125.6, 125.2, 124.3, 36.9, 35.5, 34.7, 33.8, 31.8, 26.7, 26.3, 26.0, -2.9. HRMS (EI)  $[\text{M}]^+$ : calculated for  $\text{C}_{21}\text{H}_{30}\text{Si}$ : 310.2117, found 310.2119.



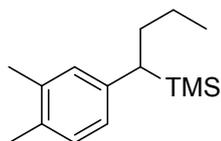
**Trimethyl(1-phenylbutyl)silane (13j).** Flash column chromatography to afford product **13j** as a pale yellow oil (25.6 mg, 62% yield);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.24-7.21 (m, 2H), 7.09-7.06 (m, 1H), 7.02-7.00 (m, 2H), 2.03 (dd,  $J = 12.0, 3.7$  Hz,

1H), 1.81-1.77 (m, 1H), 1.67-1.64 (m, 1H), 1.36-1.31 (m, 1H), 1.17-1.13 (m, 1H), 0.85 (t,  $J = 7.3$  Hz, 3H), -0.07 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  143.9, 127.9, 127.7, 124.1, 36.7, 31.5, 22.3, 13.9, -3.0. This compound has been reported in the published literature.<sup>[12d]</sup>



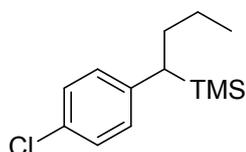
**13k**

**Trimethyl(1-(*p*-tolyl)butyl)silane (13k).** Flash column chromatography to afford product **13k** as a colorless oil (23.3 mg, 53% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.06-7.03 (m, 2H), 6.91-6.89 (m, 2H), 2.30 (s, 3H), 1.97 (dd,  $J = 11.9, 3.7$  Hz, 1H), 1.78-1.74 (m, 1H), 1.65-1.61 (m, 1H), 1.35-1.29 (m, 1H), 1.16-1.11 (m, 1H), 0.84 (t,  $J = 7.3$  Hz, 3H), -0.08 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  140.6, 133.4, 128.7, 127.6, 36.0, 31.5, 22.3, 20.9, 13.9, -2.9. HRMS (EI)  $[\text{M}]^+$ : calculated for  $\text{C}_{14}\text{H}_{24}\text{Si}$ : 220.1647, found 220.1643.



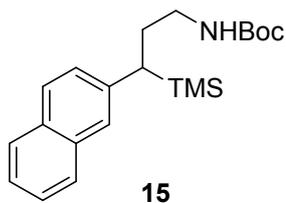
**13l**

**(1-(3,4-Dimethylphenyl)butyl)trimethylsilane (13l).** Flash column chromatography to afford product **13l** as a colorless oil (31.8 mg, 68% yield);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.98 (d,  $J = 7.6$  Hz, 1H), 6.77-6.73 (m, 2H), 2.22 (s, 3H), 2.21 (s, 3H), 1.94 (dd,  $J = 11.9, 3.7$  Hz, 1H), 1.79-1.72 (m, 1H), 1.66-1.61 (m, 1H), 1.36-1.31 (m, 1H), 1.16-1.12 (m, 1H), 0.84 (t,  $J = 7.3$  Hz, 3H), -0.07 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  141.1, 135.8, 132.0, 129.2(0), 129.1(9), 125.0, 36.0, 31.6, 22.3, 19.9, 19.2, 14.0, -2.9. HRMS (EI)  $[\text{M}]^+$ : calculated for  $\text{C}_{15}\text{H}_{26}\text{Si}$ : 234.1804, found 234.1802.



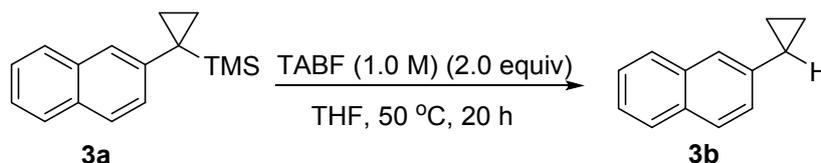
**13m**

**(1-(4-Chlorophenyl)butyl)trimethylsilane (13m).** Flash column chromatography to afford product **13m** as a colorless oil (43.2 mg, 90% yield);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.20-7.18 (m, 2H), 6.95-6.93 (m, 2H), 2.01 (dd,  $J = 12.0, 3.8$  Hz, 1H), 1.75-1.70 (m, 1H), 1.67-1.63 (m, 1H), 1.33-1.27 (m, 1H), 1.16-1.10 (m, 1H), 0.84 (t,  $J = 7.3$  Hz, 3H), -0.08 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  142.5, 129.6, 128.9, 128.1, 36.2, 31.4, 22.2, 13.8, -3.1. This compound has been reported in the published literature.

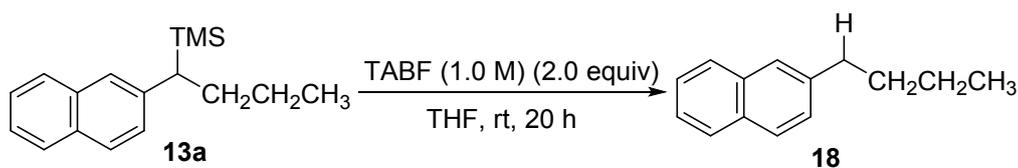


**tert-Butyl (3-(naphthalen-2-yl)-3-(trimethylsilyl)propyl)carbamate (15).** Flash column chromatography to afford product **15** as a yellow solid (40.2 mg, 56% yield);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79-7.73 (m, 3H), 7.45-7.37 (m, 3H), 7.21-7.19 (m, 1H), 4.51 (br, 1H), 3.12 (br, 1H), 2.96 (br, 1H), 2.23 (dd,  $J = 11.6, 4.1$  Hz, 1H), 2.09-2.01 (m, 2H), 1.41 (s, 9H), -0.02 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  155.8, 140.4, 133.7, 131.4, 127.7, 127.5, 127.1, 126.8, 125.8, 125.1, 124.6, 78.9, 40.4, 34.5, 29.4, 28.3, -3.0. HRMS (ESI)  $[\text{M}+\text{Na}]^+$ : calculated for  $\text{C}_{21}\text{H}_{31}\text{NO}_2\text{NaSi}$ : 380.2016, found 380.2029.

#### 4 Desilylation of Organosilanes<sup>[9]</sup>

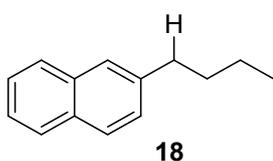


To an oven-dried Schlenk tube equipped with a stir bar was added **3a** (24 mg, 0.1 mmol, 1 equiv), TBAF (0.2 mL, 0.2 mmol, 2 equiv) and anhydrous THF (1 mL). The resulting mixture was stirred at 50 °C for 20 h. After cooling to room temperature, the reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (5 x 10 mL). The combined organic layer was dried over anhydrous  $\text{MgSO}_4$  and concentrated under reduced pressure. The residue was purified by flash chromatography on a silica gel column with petroleum ether as the eluent to give the product **3b** as a colorless oil in 96% (16.1 mg) yield.



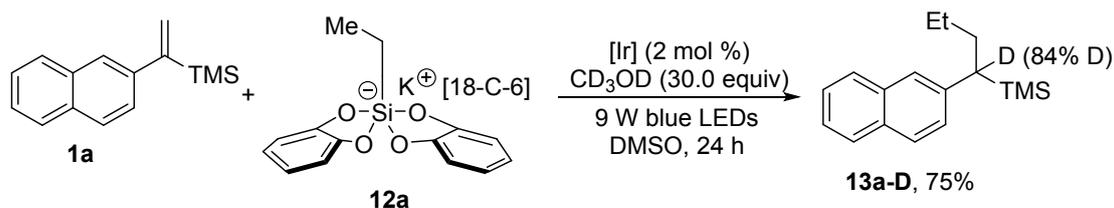
To an oven-dried Schlenk tube equipped with a stir bar was added **13a** (25.6 mg, 0.1

mmol, 1 equiv), TBAF (0.2 mL, 0.2 mmol, 2 equiv) and anhydrous THF (1 mL). The resulting mixture was stirred at room temperature for 20 h. After the reaction was complete, the reaction mixture was quenched by water (10 mL) and extracted by ethyl acetate (5 x 10 mL). The combined organic layer was dried over anhydrous MgSO<sub>4</sub> and concentrated under reduced pressure. The residue was purified by flash chromatography on a silica gel column with petroleum ether as the eluent to give the product **18** as a colorless oil in 95% (17.5 mg) yield.



**2-Butylnaphthalene (18).** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.83-7.77 (m, 3H), 7.63 (s, 1H), 7.48-7.41 (m, 2H), 7.35 (dd, *J* = 8.4, 1.8 Hz, 1H), 2.81-2.78 (m, 2H), 1.74-1.68 (m, 2H), 1.44-1.40 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 140.4, 133.6, 131.9, 127.7, 127.6, 127.4(4), 127.3(6), 126.3, 125.8, 124.9, 35.8, 33.5, 22.4, 14.0. These data are consistent with the published literature.<sup>[11c]</sup>

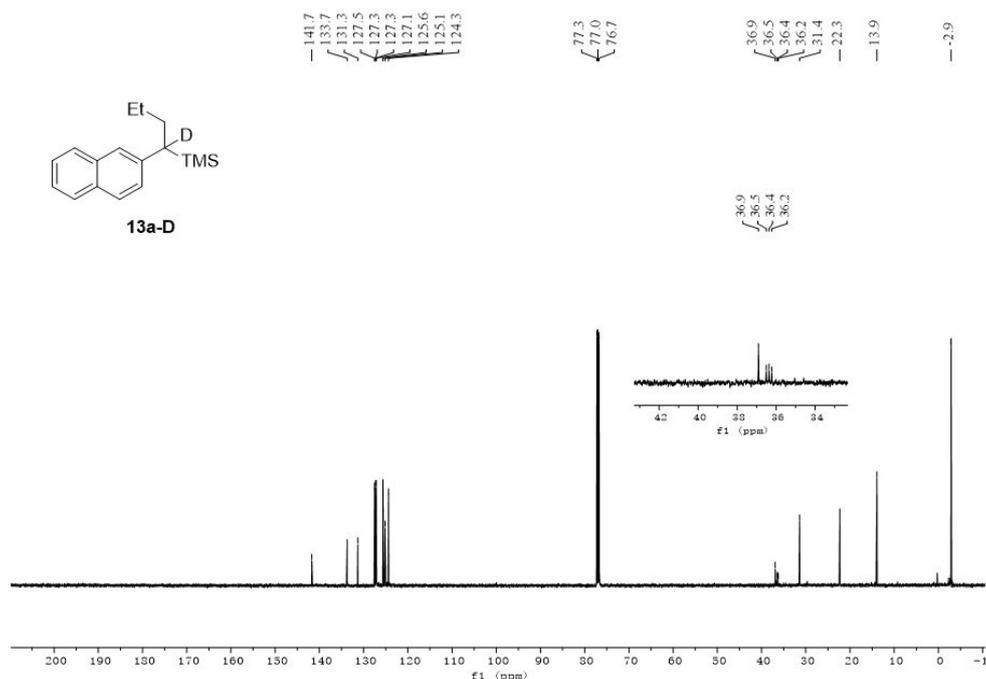
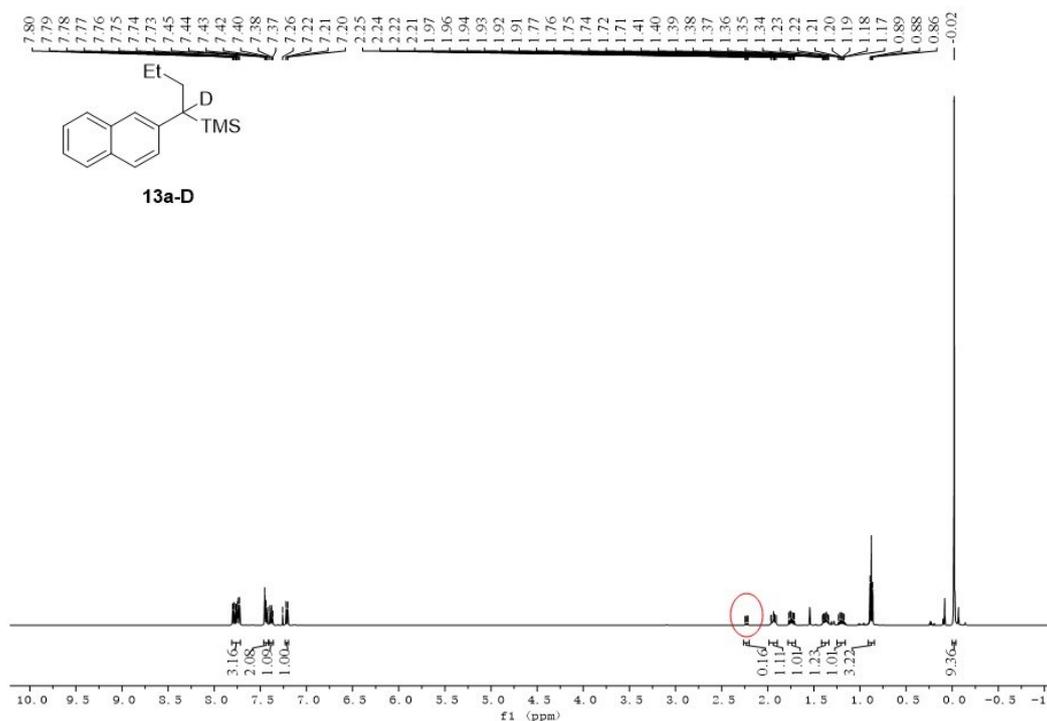
## 5 Deuteration Studies



To an oven dried transparent 10 mL Schlenk tube equipped with stirring bar, Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (4.5 mg, 0.004 mmol, 0.02 equiv), potassium [18-Crown-6] bis(catecholato)-ethylsilicate **12a** (230 mg, 0.4 mmol, 2.0 equiv), the vinylsilane **1a** (45.2 mg, 0.2 mmol, 1.0 equiv) were added. The tube was evacuated and filled with nitrogen for 3 times. The tube was then charged with degassed DMSO (6.0 mL, 0.033 M) via a syringe. Then CD<sub>3</sub>OD (250 μL, 6 mmol, 30.0 equiv) was added via a microsyringe. The tube was irradiated with a 9 W blue LEDs strip spiraled within a bowel for 24 h (cooling with a fan). After 24 h, the reaction solution was diluted with saturated Na<sub>2</sub>CO<sub>3</sub> aqueous solution (10 mL), and was extracted with EtOAc (5 x 10 mL). The organic layer was washed with brine, dried over MgSO<sub>4</sub>, filtered, and solvent was evaporated to obtain crude product. Flash chromatography

over silica gel afforded the product **13a-D** (38.4 mg, 75%). The product **13a-D** with 84% D-incorporation was determined by  $^1\text{H}$  NMR.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80-7.73 (m, 3H), 7.45-7.42 (m, 2H), 7.40-7.37 (m, 1H), 7.22-7.20 (m, 1H), 1.97-1.91 (m, 1H), 1.77-1.71 (m, 1H), 1.41-1.34 (m, 1H), 1.23-1.17 (m, 1H), 0.88 (t,  $J = 7.3$  Hz, 3H), -0.02 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  141.7, 133.7, 131.3, 127.5, 127.3, 127.3, 127.1, 125.6, 125.1, 124.3, 36.4 (t,  $J = 18.0$  Hz), 31.4, 22.3, 13.9, -2.9. HRMS (EI)  $[\text{M}]^+$  : calculated for  $\text{C}_{17}\text{H}_{23}\text{DSi}$ : 257.1701, found 257.1704.

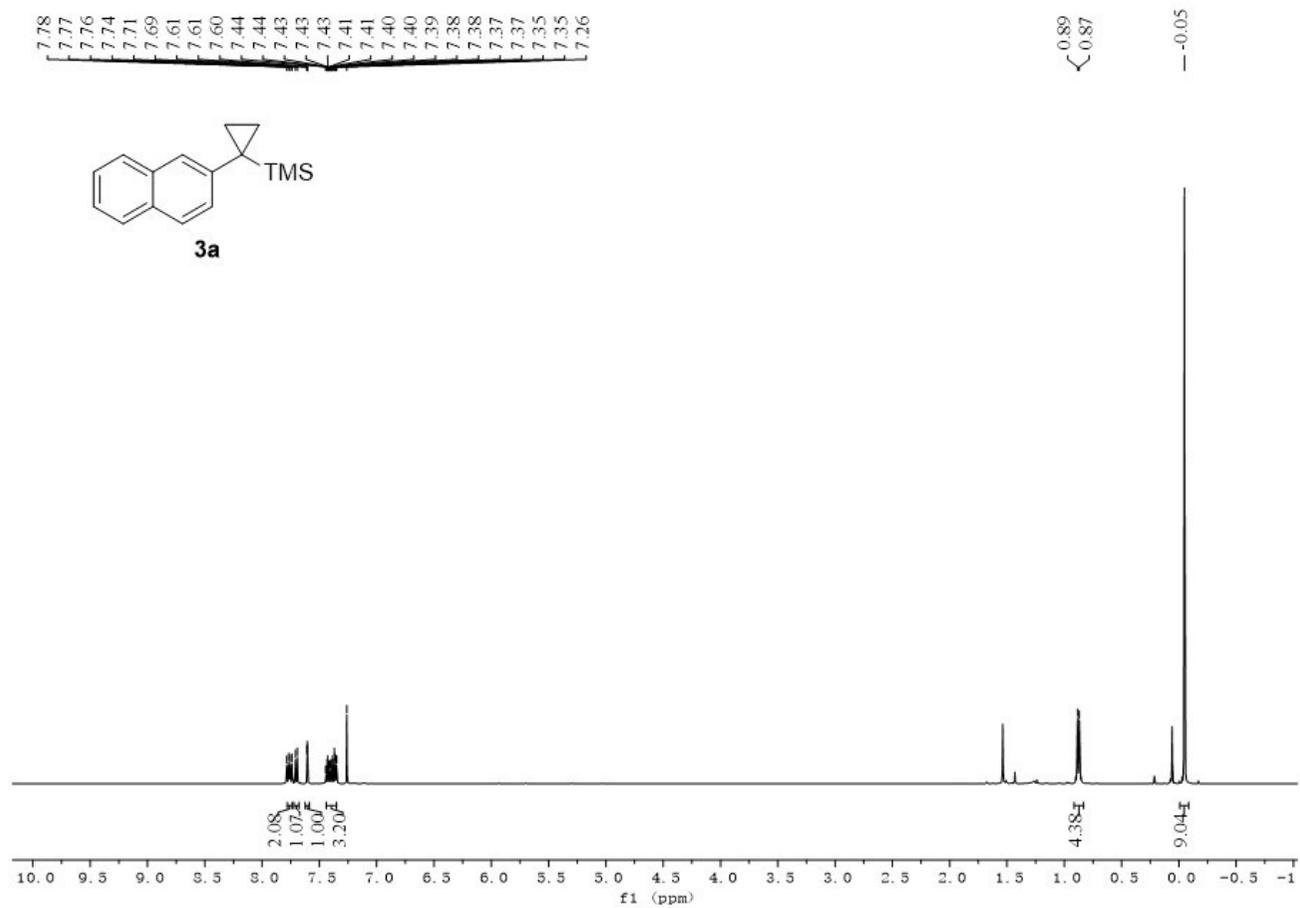


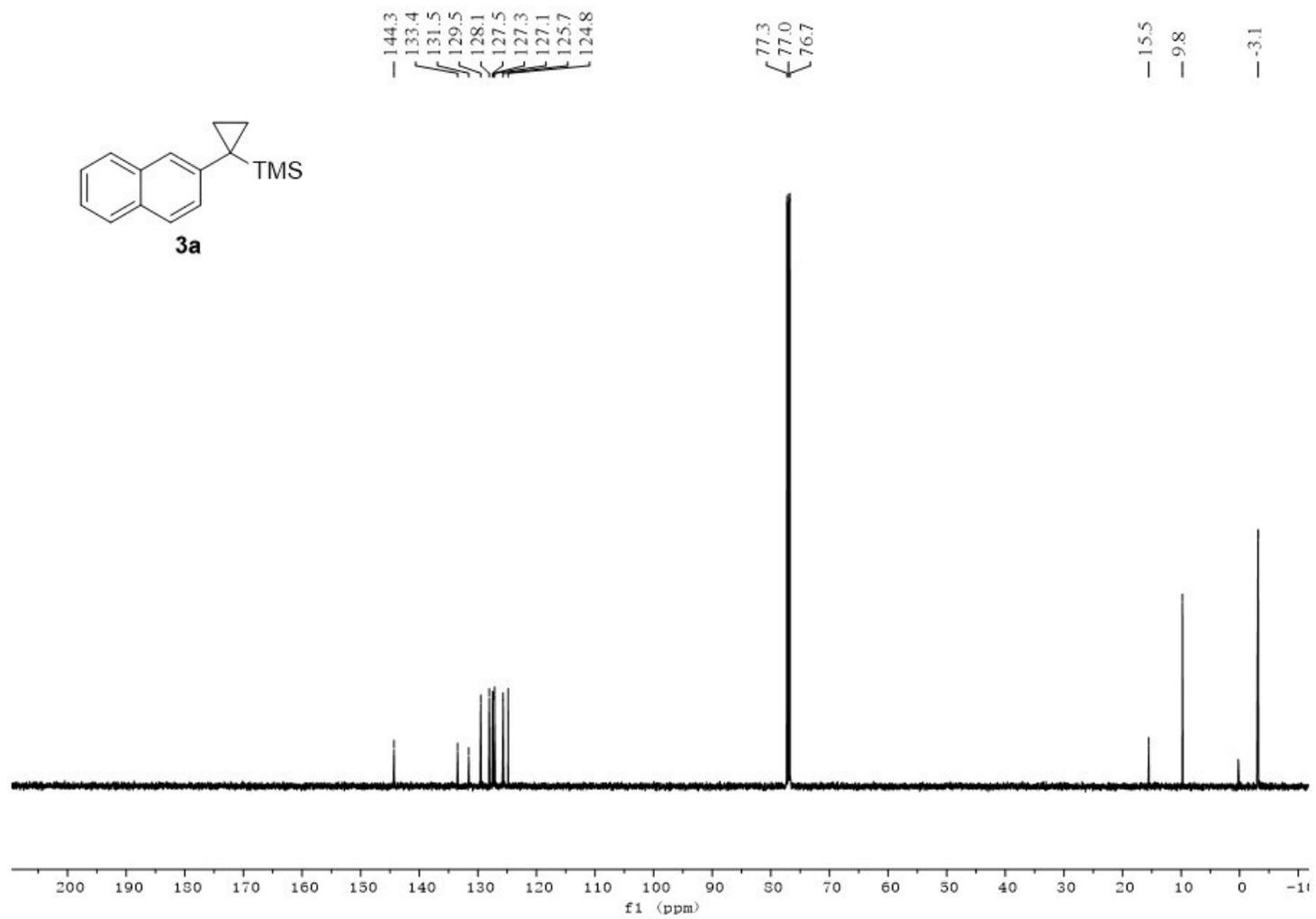
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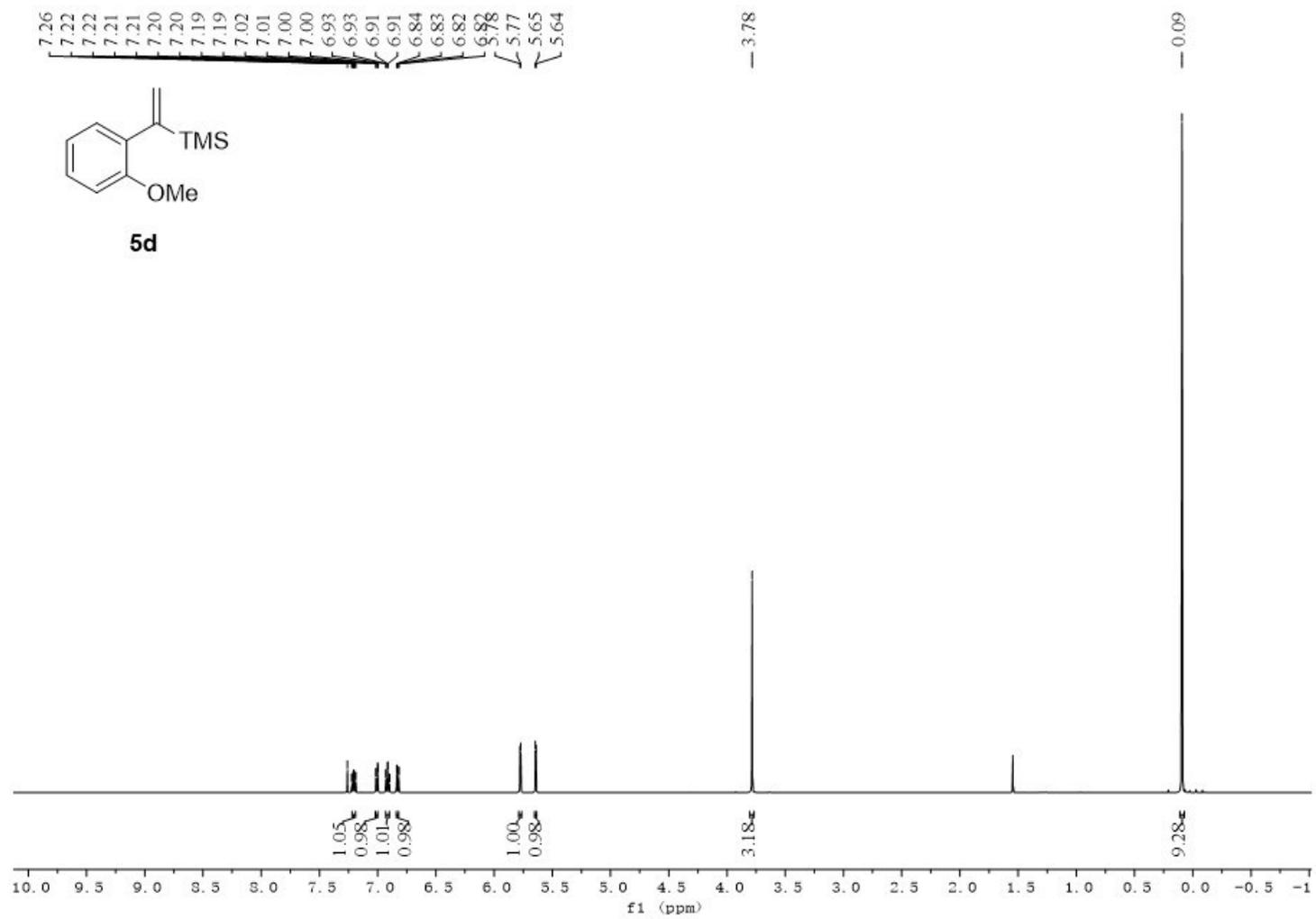
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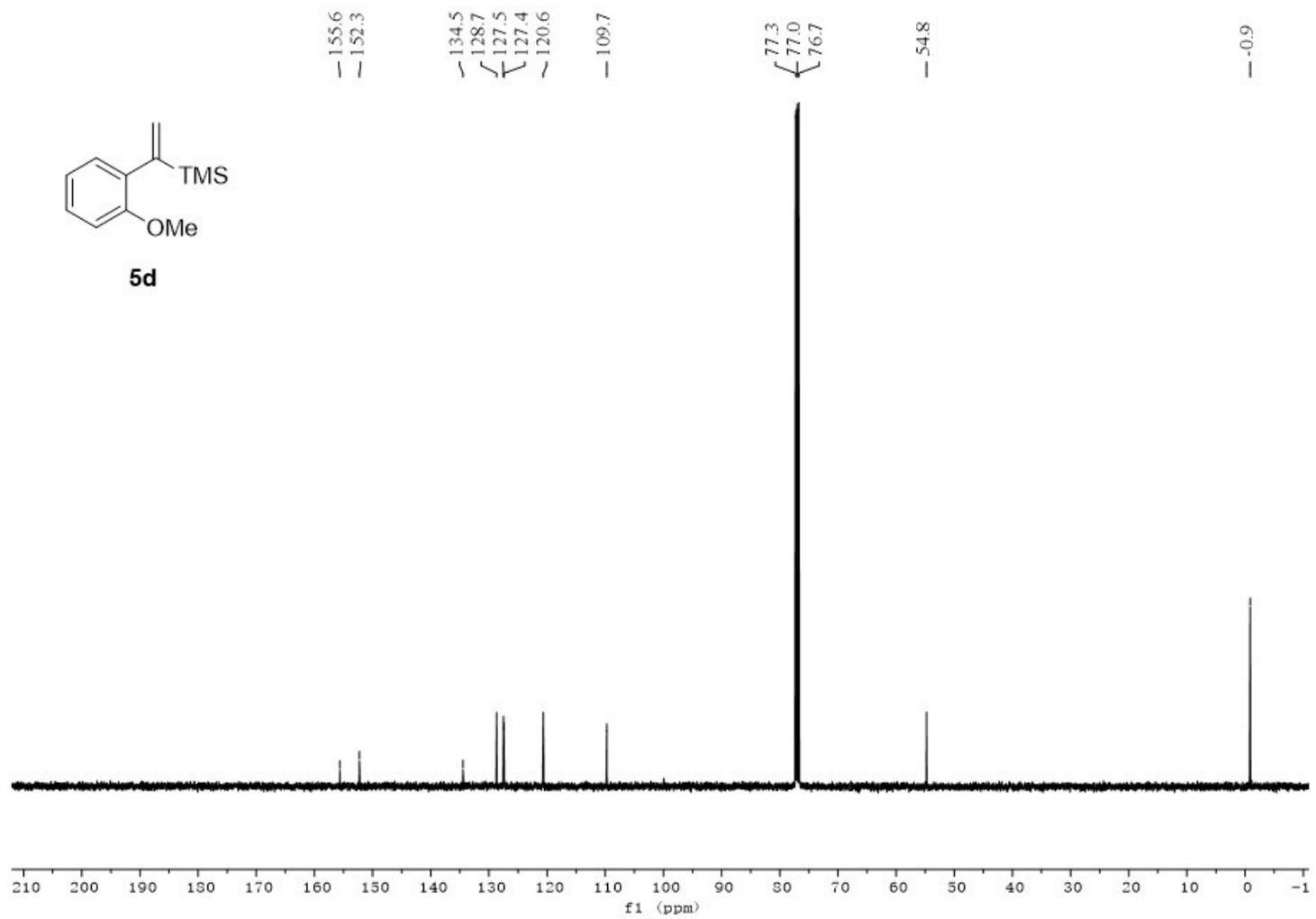
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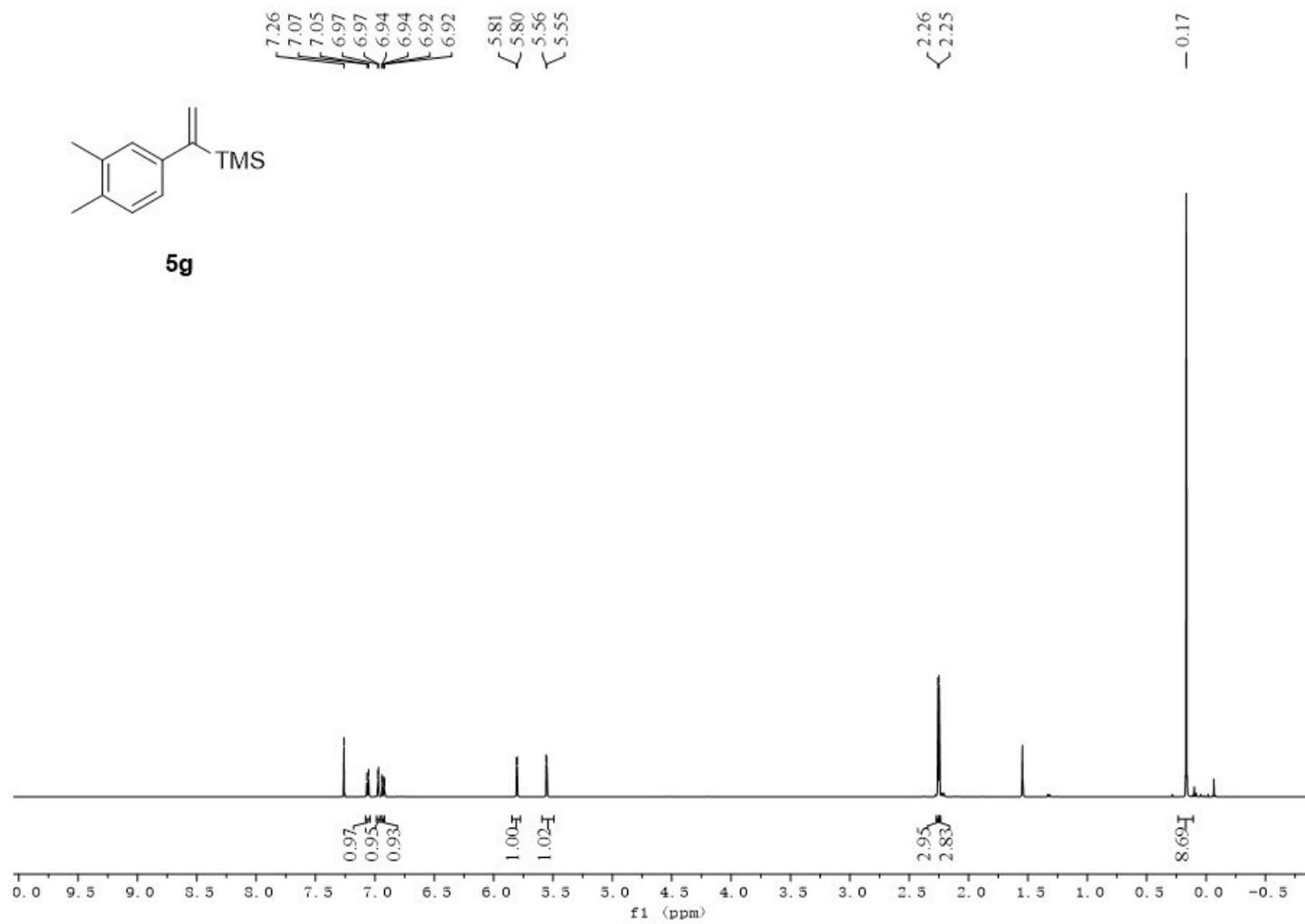
## 7 NMR Spectra of New Compounds

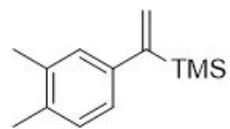












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