

## Supporting Information

# Synthesis, structure, and alkynylation reactivity of alkynyl-silicate, -germanate, and -stannate

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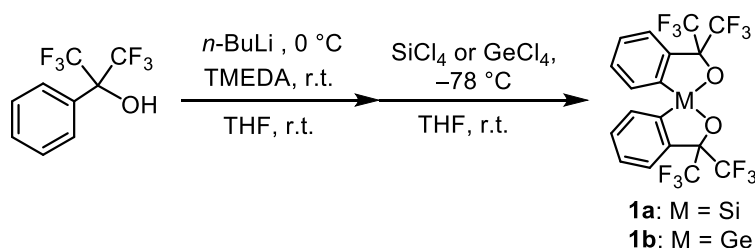
<b>1. General</b> .....	S2
<b>2. Synthesis of spirosilane 1a and spirogermane 1b</b> .....	S3
<b>3. Synthesis of fluorostannate 3</b> .....	S4
<b>4. Synthesis of alkynyl silicate 2a and germanate 2b</b> .....	S5
<b>5. Synthesis of alkynylstannate 2c</b> .....	S7
<b>6. Stability of alkynyl silicate, germanate, and stannate to acids</b> .....	S8
<b>7. Alkynylation of tropylium tetrafluoroborate</b> .....	S9
<b>7-1 Optimization of reaction conditions</b> .....	S9
<b>7-2 Alkynylation reactions with 2a-c</b> .....	S10
<b>8. Alkynylation of 2-benzyloxy-1-methylpyridinium trifluoromethanesulfonate</b> .....	S11
<b>8-1 Optimization of reaction conditions</b> .....	S11
<b>8-2 Alkynylation reactions of 7a-c</b> .....	S11
<b>9. Control experiments</b> .....	S14
<b>10. X-ray crystallographic analysis</b> .....	S15
<b>10-1 Data collection and structure determination</b> .....	S15
<b>11. NMR spectra</b> .....	S18
<b>12. References</b> .....	S49

## 1. General

Phenylacetylene, tetraethylammonium bromide, tropylium tetrafluoroborate, 2-benzyloxy-1-methylpyridinium trifluoromethanesulfonate (**7a**), 1,1,2,2-tetrachloroethane, MS4A, 2,6-lutidine, ethanol, phenol, acetic acid, trifluoroacetic acid, were commercially available. 3,3,3',3'-Tetrakis(trifluoromethyl)-1,1'-spirobi[2,1-benzoxasilole] (**1a**),<sup>1</sup> 3,3,3',3'-tetrakis(trifluoromethyl)-1,1'-spirobi[2,1-benzoxagermole] (**1b**),<sup>2</sup> tetrabutylammonium bis[ $\alpha,\alpha$ -bis(trifluoromethyl)benzenemethanolato(2-)- $C^2,O^6$ ]fluorostannate (**3**),<sup>3</sup> 2-benzyloxy(4-chlorophenyl)-1-methylpyridinium trifluoromethanesulfonate (**7b**)<sup>4</sup> and 2-benzyloxy(4-methylphenyl)-1-methylpyridinium trifluoromethanesulfonate (**7c**)<sup>4</sup> were synthesized according to the reported literature. Super dehydrated THF (Wako. Co.), super dehydrated  $CH_2Cl_2$  (Wako. Co.), and  $ClCH_2CH_2Cl$  (TCI) were used for solvents after drying with molecular sieves. Flash chromatography was carried out on a silica gel (Kanto Chem. Co., Silica Gel N, spherical, neutral, 40-100  $\mu m$ ). Preparative gel permeation chromatography (GPC) was carried out on Japan Analytical Industry LC-918 equipped with JAIGEL-1H and 2H using  $CHCl_3$  as an eluent. All NMR spectra were measured on Resonance ECZ 400S (JEOL, 400 MHz for  $^1H$ , 100 MHz for  $^{13}C$ ) or AVANCE III HD Nano Bay (Bruker Co., 400 MHz for  $^1H$ , 100 MHz for  $^{13}C$ ) at 22  $^\circ C$  using  $CDCl_3$  as a solvent unless otherwise noted.  $CDCl_3$  ( $\delta = 7.26$ ),  $CD_3CN$  ( $\delta = 1.94$ ) or acetone- $d_6$  ( $\delta = 2.05$ ) served as an internal standard for  $^1H$  NMR spectra, and  $CDCl_3$  ( $\delta = 77.16$ ) or acetone- $d_6$  ( $\delta = 206.26$ ) was used as an internal standard for  $^{13}C$  NMR spectra. All HRMS were measured on Micro-TOF (Bruker, TOF, ESI). Elemental analysis was performed by the One-Stop Facilities Center for Drug Discovery, Graduate School of Pharmaceutical Sciences, The University of Tokyo and A Rabbit Science Japan Co., Ltd.

## 2. Synthesis of spirosilane **1a** and spirogermane **1b**<sup>1,2</sup>

In a 300 mL Schlenk flask, to a stirred solution of *n*-BuLi (1.58 M hexane solution, 4.2 equiv.) was added TMEDA (0.4 equiv.). This mixture was stirred at 25 °C for 1 h until it became cloudy and cooled to 0 °C. 1,1,1,3,3,3-Hexafluoro-2-phenylpropan-2-ol (2.0 equiv.), dissolved in THF, was then added dropwise to the mixture. After 1 h, the ice bath was removed and the mixture was stirred for an additional 18 h. This mixture was then added to SiCl<sub>4</sub> or GeCl<sub>4</sub> (1.0 equiv.) dissolved in THF at –78 °C over 45 min. The reaction was stirred at –78 °C for 1 h, and stirred further at room temperature for 20 h. The reaction mixture was quenched with 7 mL of water, dissolved in ether (100 mL), and washed with 0.50 M HCl (4x100 mL) and water (100 mL). The organic phase was dried over MgSO<sub>4</sub>, filtered, and evaporated under reduced pressure to give a yellow solid. The residue was sublimed using a sublimation purifier and the resulting solid was crystallized from hot hexane to yield **1a** or **1b** as a white solid. The NMR data are in good agreement with those reported in the literature.<sup>1</sup>

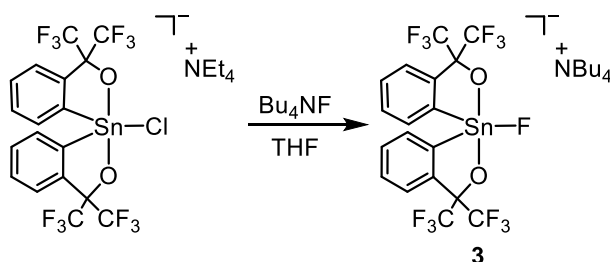


**Scheme S1**

<p><b>1a</b></p>	<p><b>3,3,3',3'-Tetrakis(trifluoromethyl)-1,1'-spirobi[2,1-benzoxasilole]<sup>1</sup></b>            Reaction of SiCl<sub>4</sub> (5.0 mL, 44.3 mmol) gave the title compound (7.0 g, 32%, colorless solid). 1.58 M <i>n</i>-BuLi in hexane (118 mL, 186 mmol), TMEDA (3.0 mL, 20.0 mmol), 1,1,1,3,3,3-hexafluoro-2-phenylpropan-2-ol (15.0 mL, 88.5 mmol) and THF (15 mL+18 mL) were used.  <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.83 (d, <i>J</i> = 8.0 Hz, 2H), 7.75-7.62 (m, 6H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ, –75.8 (q, <i>J</i><sub>F-F</sub> = 8.6 Hz, 6F), –76.2 (q, <i>J</i><sub>F-F</sub> = 8.6 Hz, 6F).</p>
<p><b>1b</b></p>	<p><b>3,3,3',3'-Tetrakis(trifluoromethyl)-1,1'-spirobi[2,1-benzoxasilole]<sup>2</sup></b>            Reaction of GeCl<sub>4</sub> (6.4 mL, 56.4 mmol) gave the title compound (10.2 g, 32%, colorless solid). 1.58 M <i>n</i>-BuLi in hexane (150 mL, 236 mmol), TMEDA (3.4 mL, 22.7 mmol), 1,1,1,3,3,3-hexafluoro-2-phenylpropan-2-ol (19.0 mL, 113.3 mmol) and THF (19 mL+45 mL) were used.  <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.79-7.67 (m, 6H), 7.93 (d, <i>J</i> = 7.6 Hz, 2H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ –76.2 (q, <i>J</i><sub>F-F</sub> = 8.3 Hz, 6F), –75.4 (q, <i>J</i><sub>F-F</sub> = 8.2 Hz, 6F).</p>

### 3. Synthesis of tetrabutylammonium bis[ $\alpha,\alpha$ -bis(trifluoromethyl)-benzenemethanolato(2-)- $C^2,O^a$ ]fluorostannate **3**<sup>3</sup>

A round-bottom flask equipped with a magnetic stirring bar and a septum was dried under vacuum with heating. After cooling the flask to room temperature, it was purged with argon gas. tetramethylammonium bis[ $\alpha,\alpha$ -bis(trifluoromethyl)-benzenemethanolato(2-)- $C^2,O^a$ ]chlorostannate (361 mg, 0.506 mmol, 1.0 equiv.) was dissolved in THF (30 mL) in the flask. To the solution was added 1.0 M of *n*-Bu<sub>4</sub>NF in THF (0.9 mL, 1.8 equiv.) at room temperature. The mixture was heated at 40 °C for 13 h and was cooled to room temperature. CH<sub>2</sub>Cl<sub>2</sub> and water was added to the mixture, and organic compounds were extracted with CH<sub>2</sub>Cl<sub>2</sub> for three times. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the solvents gave a crude material, which was washed with EtOH and dried under reduced pressure to give **3** (438 mg, 99%, colorless solid). The NMR data are in good agreement with those reported in the literature.<sup>3</sup>

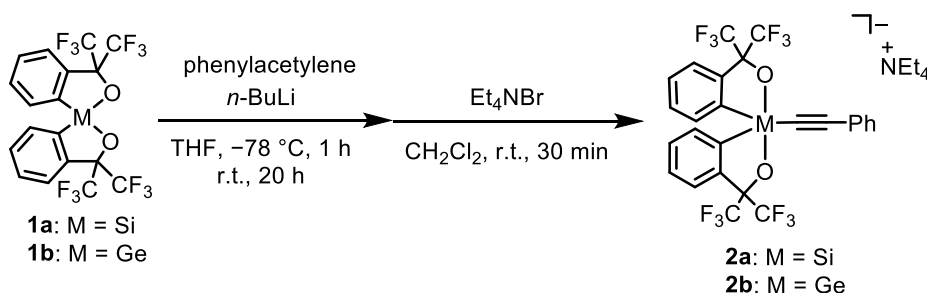


Scheme S2

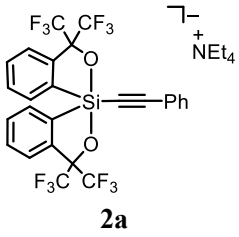
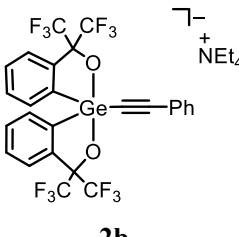
<p>Structure of <b>3</b>: A tin atom coordinated to two phenoxide rings, each substituted with two trifluoromethyl groups, and a fluorine atom. The counterion is tetrabutylammonium (NBu<sub>4</sub><sup>+</sup>).</p>	<p><b>tetrabutylammonium bis[<math>\alpha,\alpha</math>-bis(trifluoromethyl)-benzenemethanolato(2-)-<math>C^2,O^a</math>]fluorostannate<sup>3</sup></b></p> <p><sup>1</sup>H NMR (400 MHz, acetone-<i>d</i><sub>6</sub>): <math>\delta</math> 8.08 (d, <math>J</math> = 6.4 Hz and Sn-satellite: <math>J</math> = 69.0 Hz, 2H), 7.78 (d, <math>J</math> = 7.2 Hz, 2H), 7.54-7.48 (m, 4H), 3.43 (t, <math>J</math> = 8.0 Hz, 8H), 1.80 (quint, <math>J</math> = 8.0 Hz, 8H), 1.41 (sept, <math>J</math> = 7.4 Hz, 8H), 0.96 (t, <math>J</math> = 7.4 Hz, 12H). <sup>19</sup>F NMR (376 MHz, acetone-<i>d</i><sub>6</sub>): <math>\delta</math> -75.9 (s, 12F), -182.6 (s, <math>J_{F-119Sn}</math> = 2577 Hz, <math>J_{F-117Sn}</math> = 2461 Hz, 1F).</p>
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#### 4. Synthesis of alkynyl silicate **2a** and germanate **2b**

A round-bottom Schlenk flask (A) equipped with a magnetic stirring bar and a septum was dried under vacuum with heating. After cooling the flask to room temperature, it was purged with argon gas. Phenylacetylene (2.0 equiv.) was dissolved in THF (2.5 mL/mmol) in the Schlenk flask (A). The solution was stirred and *n*-BuLi (1.8 equiv.) was added to it at  $-78\text{ }^{\circ}\text{C}$ . The mixture was stirred at  $-78\text{ }^{\circ}\text{C}$  for 1 h. In another flask (B), 3,3,3',3'-tetrakis(trifluoromethyl)-1,1'-spirobi[2,1-benzoxasilole] (**1a**) (1.0 equiv.) or 3,3,3',3'-tetrakis(trifluoromethyl)-1,1'-spirobi[2,1-benzoxagermole] (**1b**) was dissolved in THF (5 mL/mmol of **1a** or **1b**) and stirred the solution in the flask (B) was added dropwise into the Schlenk flask (A) at  $-78\text{ }^{\circ}\text{C}$ . After stirring at  $-78\text{ }^{\circ}\text{C}$  for 1 h, the mixture was stirred at room temperature for 20 h. The mixture was quenched with EtOH (10 mL), and the solvents were evaporated under reduced pressure to give a yellow oil.  $\text{CH}_2\text{Cl}_2$  (15 mL/mmol of  $\text{Et}_4\text{NBr}$ ) and  $\text{Et}_4\text{NBr}$  (2.1 equiv.) were added to the oil and the mixture was stirred for 30 min. After evaporation of the solvent, water and hexane was added to the solid. Suction filtration of the mixture gave a solid product. The solid was washed with  $\text{CHCl}_3$  and EtOH. Recrystallization from a saturated THF solution and an excess of  $\text{Et}_2\text{O}$  at room temperature afforded the colorless solid of **2a** or **2b**.

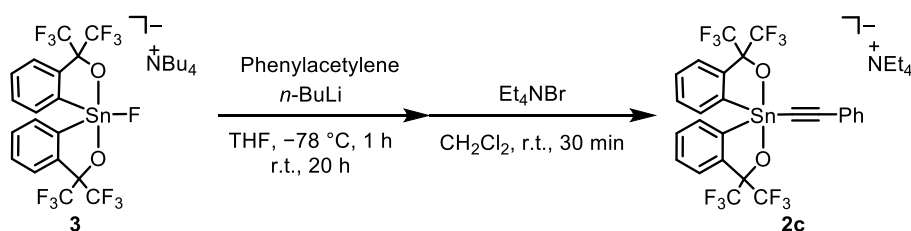


Scheme S3

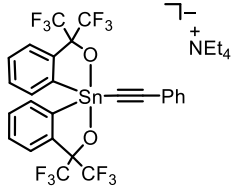
 <p style="text-align: center;"><b>2a</b></p>	<p style="text-align: center;"><b>tetraethylammonium bis[<math>\alpha,\alpha</math>-bis(trifluoromethyl)-benzenemethanolato(2-)-<math>C^2,O^\alpha</math>]phenylethynylsilicate</b></p> <p>Reaction of <b>1a</b> (1.54 g, 3.0 mmol) gave the title compound (0.85 g, 38%, colorless solid). Phenylacetylene (0.66 mL, 6.0 mmol), 1.57 M <i>n</i>-BuLi in hexane (3.5 mL, 5.4 mmol), and Et<sub>4</sub>NBr (1.3 g, 6.3 mmol) were used.</p> <p><sup>1</sup>H NMR (400 MHz, acetone-<i>d</i><sub>6</sub>): <math>\delta</math> 8.26 (dd, <math>J = 6.0, 2.8</math> Hz, 2H), 7.58 (d, <math>J = 5.6</math> Hz, 2H), 7.41-7.36 (m, 4H), 7.25-7.17 (m, 5H), 3.31 (q, <math>J = 7.3</math> Hz, 8H), 1.26-1.22 (m, 12H). <sup>13</sup>C NMR (100 MHz, acetone-<i>d</i><sub>6</sub>): <math>\delta</math> 143.9, 142.3, 138.2, 132.4, 129.4, 129.2, 128.9, 127.7, 127.1, 125.7 (q, <math>J_{F-C} = 258.9</math> Hz, C), 125.5 (q, <math>J_{F-C} = 287.9</math> Hz, C), 124.4, 104.0, 97.1, 82.5 (sept, <math>J_{F-C} = 28.8</math> Hz), 52.9, 7.5. <sup>19</sup>F NMR (376 MHz, acetone-<i>d</i><sub>6</sub>): <math>\delta</math> -74.4 (q, <math>J_{F-F} = 9.5</math> Hz, 6F), -75.6 (q, <math>J_{F-F} = 9.4</math> Hz, 6F). <sup>29</sup>Si NMR (79 MHz, acetone-<i>d</i><sub>6</sub>): <math>\delta</math> -88.2. HRMS (ESI, negative) <math>m/z</math> calcd for C<sub>26</sub>H<sub>13</sub>F<sub>12</sub>O<sub>2</sub>Si [M-Et<sub>4</sub>N]<sup>-</sup>: 613.0499, found: 613.0493; mp: 233-235 °C (decomp.). Anal. Calcd for C<sub>34</sub>H<sub>33</sub>F<sub>12</sub>NO<sub>2</sub>Si: C, 54.91; H, 4.47; N, 1.88. Found: C, 55.14; H, 4.68; N, 2.06.</p>
 <p style="text-align: center;"><b>2b</b></p>	<p style="text-align: center;"><b>tetraethylammonium bis[<math>\alpha,\alpha</math>-bis(trifluoromethyl)-benzenemethanolato(2-)-<math>C^2,O^\alpha</math>]phenylethynylgermanate</b></p> <p>Reaction of <b>1b</b> (4.10 g, 10.0 mmol) gave the title compound (2.10 g, 37%, colorless solid). Phenylacetylene (2.2 mL, 20 mmol), 1.58 M <i>n</i>-BuLi in hexane (11.5 mL, 18.0 mmol) and Et<sub>4</sub>NBr (4.4 g, 21 mmol) were used.</p> <p><sup>1</sup>H NMR (400 MHz, acetone-<i>d</i><sub>6</sub>): <math>\delta</math> 8.31 (dd, <math>J = 5.6, 2.4</math> Hz, 2H), 7.66 (d, <math>J = 5.6</math> Hz, 2H), 7.46-7.40 (m, 4H), 7.30-7.22 (m, 5H), 3.36 (q, <math>J = 7.3</math> Hz, 8H), 1.30-1.24 (m, 12H). <sup>13</sup>C NMR (100 MHz, acetone-<i>d</i><sub>6</sub>): <math>\delta</math> 141.3, 140.6, 135.9, 132.4, 129.7, 129.3, 128.9, 128.2, 126.1, 126.0 (q, <math>J_{F-C} = 289.9</math> Hz, C), 125.9 (q, <math>J_{F-C} = 288.3</math> Hz, C), 125.8, 100.9, 97.6, 82.4 (sept, <math>J = 28.0</math> Hz), 52.9, 7.54. <sup>19</sup>F NMR (376 MHz, acetone-<i>d</i><sub>6</sub>): <math>\delta</math> -75.0 (q, <math>J_{F-F} = 8.9</math> Hz, 6F), -75.5 (q, <math>J_{F-F} = 9.0</math> Hz, 6F). HRMS (ESI, negative) <math>m/z</math> calcd for C<sub>26</sub>H<sub>13</sub>F<sub>12</sub>O<sub>2</sub>Ge [M-Et<sub>4</sub>N]<sup>-</sup>: 658.9946, found: 658.9965; mp: 235-237 °C (decomp.). Anal. Calcd for C<sub>34</sub>H<sub>33</sub>F<sub>12</sub>NO<sub>2</sub>Ge: C, 51.81; H, 4.22; N, 1.78. Found: C, 51.74; H, 4.17; N, 1.83.</p>

## 5. Synthesis of alkynylstannate **2c**

A round-bottom Schlenk flask (A) equipped with a magnetic stirring bar and a septum was dried under vacuum with heating. After cooling the flask to room temperature, it was purged with argon gas. Phenylacetylene (0.66 mL, 6.0 mmol, 2.0 equiv.) was dissolved in THF (15 mL) in the Schlenk flask (A). The solution was stirred and *n*-BuLi (3.5 mL, 5.4 mmol, 1.8 equiv.) was added to it at  $-78\text{ }^{\circ}\text{C}$ . The mixture was stirred at  $-78\text{ }^{\circ}\text{C}$  for 1 h. In another flask (B), tetrabutylammonium bis[ $\alpha,\alpha$ -bis(trifluoromethyl)benzenemethanolato(2-)- $C^2,O^{\alpha}$ ]fluorostannate (**3**) (2.6 g, 3.0 mmol, 1.0 equiv.) was dissolved in THF (10 mL/mmol of **3**) and stirred the solution in the flask (B) was added dropwise into the Schlenk flask (A) at  $-78\text{ }^{\circ}\text{C}$ . After stirring at  $-78\text{ }^{\circ}\text{C}$  for 1 h, the mixture was stirred at room temperature for 20 h. The mixture was quenched with EtOH (10 mL). After evaporation of the solvent, water and hexane was added to the solid. Suction filtration of the mixture gave a solid product. The solid was washed with  $\text{CHCl}_3$  and EtOH. The crude product was washed with  $\text{CHCl}_3$  and EtOH. Recrystallization from a saturated THF solution and an excess of  $\text{Et}_2\text{O}$  at room temperature afforded the colorless solid of **2c** (0.87 g, 35% yield).



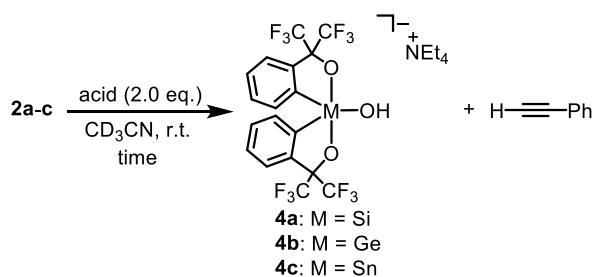
Scheme S4

	<b>tetraethylammonium bis[<math>\alpha,\alpha</math>-bis(trifluoromethyl)- benzenemethanolato(2-)-<math>C^2,O^{\alpha}</math>]phenylethynylstannate</b>
<b>2c</b>	<p><math>^1\text{H}</math> NMR (400 MHz, acetone-<math>d_6</math>): <math>\delta</math> 8.09 (d, <math>J = 6.4</math> Hz and Sn-satellite: <math>J = 63.4</math> Hz, 2H), 7.74 (d, <math>J = 7.2</math> Hz, 2H), 7.54-7.39 (m, 4H), 7.39-7.30 (m, 2H), 7.30-7.22 (m, 3H), 3.38 (q, <math>J = 7.2</math> Hz, 8H), 1.37-1.23 (m, 12H).</p> <p><math>^{13}\text{C}</math> NMR (100 MHz, acetone-<math>d_6</math>): <math>\delta</math> 141.9 (<math>J_{\text{Sn-C}} = 74.6</math> Hz), 141.8, 136.6 (<math>J_{\text{Sn-C}} = 50.9</math> Hz), 132.5, 129.4, 129.4, 129.1, 128.5, 127.0 (<math>J_{\text{Sn-C}} = 78.4</math> Hz), 125.5 (<math>J_{\text{Sn-C}} = 18.5</math> Hz), 126.3 (q, <math>J_{\text{C-F}} = 288.9</math> Hz, C), 126.1 (q, <math>J_{\text{C-F}} = 288.6</math> Hz, C), 104.6 (<math>J_{117\text{Sn-C}} = 179.2</math> Hz, <math>J_{119\text{Sn-C}} = 187.7</math> Hz), 100.9, 82.2 (sept, <math>J = 27.8</math> Hz), 52.9, 7.56. <math>^{19}\text{F}</math> NMR (376 MHz, acetone-<math>d_6</math>): <math>\delta</math> <math>-75.2</math> (q, <math>J_{\text{F-F}} = 8.4</math> Hz, 6F), <math>-75.8</math> (q, <math>J_{\text{F-F}} = 8.5</math> Hz, 6F). <math>^{119}\text{Sn}</math> NMR (149 MHz, acetone-<math>d_6</math>): <math>\delta</math> <math>-186.4</math> HRMS (ESI, negative) <math>m/z</math> calcd for <math>\text{C}_{26}\text{H}_{13}\text{F}_{12}\text{O}_2\text{Sn}</math> [M-Et<math>_4\text{N}</math>]: 704.9751, found: 704.9760; mp: 237-240 <math>^{\circ}\text{C}</math> (decomp.). Anal. Calcd for <math>\text{C}_{34}\text{H}_{33}\text{F}_{12}\text{NO}_2\text{Sn}</math>: C, 48.95; H, 3.99; N, 1.68. Found: C, 49.08; H, 4.14; N, 1.83.</p>

## 6. Stability of alkynyl silicate, germanate, and stannate to acids

A 30 mL round-bottom flask equipped with a magnetic stirring bar and a septum, was dried under vacuum with heating. After cooling the flask to room temperature, it was purged with argon gas. Alkynyl compounds **2a-c** (0.2 mmol), 1,1,2,2-tetrachloroethane (0.6 mmol) as internal standard and CD<sub>3</sub>CN (6 mL) were added to the flask. To four NMR tubes, an aliquot (ca. 0.5 mL) for each of the solution in the flask was transferred. An excess amount of acid (0.1 mmol) was added to the NMR tube and NMR spectra were measured after 15 min, 1 h, 3 h, 6 h, and 24 h. The NMR yield was determined based on the proton NMR spectra with 1,1,2,2-tetrachloroethane as the internal standard.

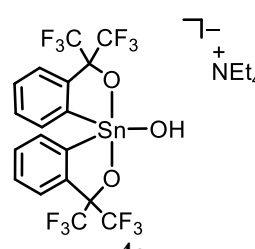
**Table S1**



Entry	acid	NMR yield (time)		
		<b>4a</b>	<b>4b</b>	<b>4c</b>
1	H <sub>2</sub> O	0% (24 h)	0% (24 h)	0% (24 h)
2	EtOH	0% (24 h)	0% (24 h)	0% (24 h)
3	PhOH	0% (24 h)	0% (24 h)	0% (24 h)
4	CH <sub>3</sub> COOH	0% (24 h)	0% (24 h)	100% (15 min)
5	TFA	54% (1 h) 100% (24h)	42% (6 h) 75% (24 h)	100% (15 min)

<p><b>4a</b></p>	<p><b>tetraethylammonium bis[<math>\alpha,\alpha</math>-bis(trifluoromethyl)-benzenemethanolate(2-)-C<sup>2</sup>,O<sup><math>\alpha</math></sup>]hydroxysilicate<sup>5</sup></b></p> <p><sup>1</sup>H NMR (400 MHz, acetonitrile-<i>d</i><sub>3</sub>): <math>\delta</math> 8.13-8.11 (m, 2H), 7.64 (m, 2H), 7.54-7.49 (m, 4H), 3.13 (q, <i>J</i> = 7.3 Hz, 8H), 1.22-1.17 (m, 12H). <sup>19</sup>F NMR (376 MHz, acetonitrile-<i>d</i><sub>3</sub>): <math>\delta</math> -76.1 (s, 12F).</p>
<p><b>4b</b></p>	<p><b>tetraethylammonium bis[<math>\alpha,\alpha</math>-bis(trifluoromethyl)-benzenemethanolate(2-)-C<sup>2</sup>,O<sup><math>\alpha</math></sup>]hydroxygermanate</b></p> <p><sup>1</sup>H NMR (400 MHz, acetonitrile-<i>d</i><sub>3</sub>): <math>\delta</math> 8.18-8.15 (m, 2H), 7.77-7.75 (m, 2H), 7.60-7.58 (m, 4H), 3.14 (q, <i>J</i> = 7.2 Hz, 8H), 1.21-1.16 (m, 12H). <sup>19</sup>F NMR (376 MHz, acetonitrile-<i>d</i><sub>3</sub>): <math>\delta</math> -76.1 (s, 12F).</p>



 <p style="text-align: center;"><b>4c</b></p>	<p><b>tetraethylammonium bis[<math>\alpha,\alpha</math>-bis(trifluoromethyl)-benzenemethanolate(2-)-C<sup>2</sup>,O<sup>2</sup>]hydroxystannate</b></p> <p><sup>1</sup>H NMR (400 MHz, acetonitrile-<i>d</i><sub>3</sub>): <math>\delta</math> 8.06-7.95 (m, 2H), 7.85-7.80 (m, 2H), 7.61-7.55 (m, 4H), 3.15-3.10 (m, 8H), 1.19-1.15 (m, 12H). <sup>19</sup>F NMR (376 MHz, acetonitrile-<i>d</i><sub>3</sub>): <math>\delta</math> -76.1 (s, 12F).</p>
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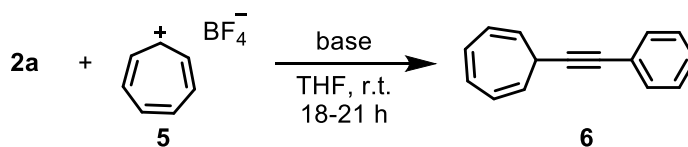
## 7. Alkynylation of tropylium tetrafluoroborate

### 7-1 Optimization of reaction conditions

#### General procedure

A 30 mL Schlenk tube equipped with a magnetic stirring bar and a septum, was dried under vacuum with heating. After cooling the tube to room temperature, it was purged with argon gas. Alkynyl compound **2a** (0.1 mmol, 1.0 equiv.) and THF (5 mL) were added to the tube. Then, base (0.2 mmol, 0.2 equiv.), additive and tropylium tetrafluoroborate (0.15 mmol, 1.5 equiv.) were added to the tube, and the mixture was stirred at room temperature for 21 h. Evaporation of the solvents under reduced pressure gave crude products, which were purified by flash chromatography (hexane) and/or GPC to give 7-(2-phenylethynyl)-1,3,5-cycloheptatriene (**6**) as yellow oil.

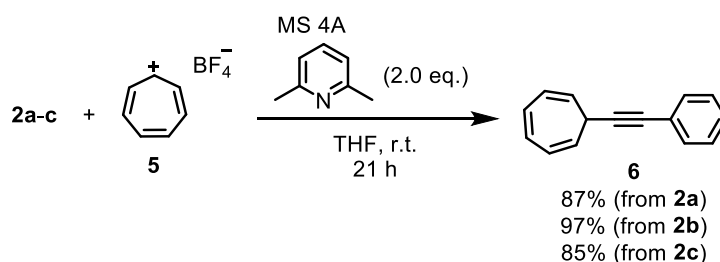
Table S2



entry	base	additive	time	yield (%)
1	none	-	18	34
2	2,6-lutidine (2.0 eq.)	-	20	65
3	2,6-lutidine (2.0 eq.)	MS 4A	21	87
4	2,6-lutidine (1.0 eq.)	MS 4A	21	78
5	2,6-Di- <i>tert</i> -butylpyridine	-	20	60
6	K <sub>2</sub> CO <sub>3</sub>	-	21	50
7	DBU	-	21	0
8	DIPEA	-	20	61
9	Na <sup>t</sup> OBu	-	20	0

## 7-2 Alkynylation reactions with 2a-c

A 30 mL Schlenk tube equipped with a magnetic stirring bar, MS4A (0.2 g) and a septum, was dried under vacuum with heating. After cooling the flask to room temperature, it was purged with argon gas, Alkynyl compounds **2a-c** (0.1 mmol, 1.0 equiv.) and THF (5 mL) were added to the tube. Then, 2,6-lutidine (0.2 mmol, 2.0 equiv.) and tropylium tetrafluoroborate (0.15 mmol, 1.5 equiv.) were added to the solution and the mixture was stirred at room temperature for 21 h. Evaporation of the solvents gave crude products, which were purified by flash chromatography (hexane) and/or GPC to give the 7-(2-phenylethynyl)-1,3,5-cycloheptatriene (**6**) as yellow oil.



Scheme S5

	<b>Reaction of 2a with 5</b> Reaction of <b>2a</b> (74.4 mg, 0.10 mmol) gave 7-(2-phenylethynyl)-1,3,5-cycloheptatriene ( <b>6</b> ) (16.8 mg, 87%, yellow oil). Tropylium tetrafluoroborate <b>5</b> (27.0 mg, 0.15 mmol), MS4A (0.1 g), and 2,6-lutidine (21.1 mg, 0.20 mmol) were used.
	<b>Reaction of 2b with 5</b> Reaction of <b>2b</b> (78.9 mg, 0.10 mmol) gave 7-(2-phenylethynyl)-1,3,5-cycloheptatriene ( <b>6</b> ) (18.7 mg, 97%, yellow oil). Tropylium tetrafluoroborate <b>5</b> (27.2 mg, 0.15 mmol), MS4A (0.1 g), and 2,6-lutidine (21.7 mg, 0.20 mmol) were used.
	<b>Reaction of 2c with 5</b> Reaction of <b>2c</b> (83.4 mg, 0.10 mmol) gave 7-(2-phenylethynyl)-1,3,5-cycloheptatriene ( <b>6</b> ) (16.4 mg, 85%, yellow oil). Tropylium tetrafluoroborate <b>5</b> (27.3 mg, 0.15 mmol), MS4A (0.1 g), and 2,6-lutidine (21.3 mg, 0.20 mmol) were used.
	<sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ): δ 7.48-7.46 (m, 2H), 7.34-7.29 (m, 3H), 6.70 (t, <i>J</i> = 4.4 Hz, 2H), 6.23-6.21 (m, 2H), 5.44 (dd, <i>J</i> = 8.8, 5.6 Hz, 2H), 2.71 (t, <i>J</i> = 8.2 Hz, 1H). <sup>13</sup> C NMR (100 MHz, CDCl <sub>3</sub> ): δ 131.9, 131.2, 128.4, 128.1, 124.9, 123.6, 123.4, 91.2, 80.7, 32.4.

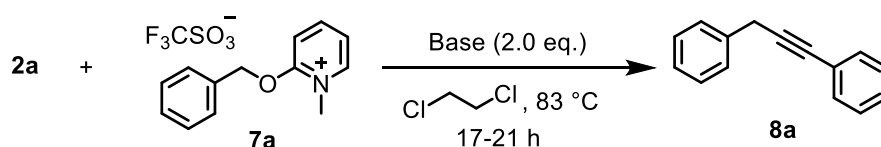
## 8. Alkynylation of 2-benzyloxy-1-methylpyridinium trifluoromethanesulfonate

### 8-1 Optimization of reaction conditions

#### General procedure

A 40 mL pressure tube equipped with a magnetic stirring bar and a septum, was dried under vacuum with heating. After cooling the flask to room temperature, it was purged with argon gas. Alkynylsilicate **2a** (0.1 mmol, 1.0 equiv.) and 1,2-dichloroethane (5 mL) were added to the tube. Then, base (0.2 mmol, 2.0 equiv.) and 2-benzyloxy-1-methylpyridinium trifluoromethanesulfonate **7a** (0.2 mmol, 2.0 equiv.) were added to the solution, and the mixture was stirred at 83 °C for 17 to 21 h. After cooling to room temperature, evaporation of the solvents under reduced pressure gave a crude product, which was purified by flash chromatography (hexane) and/or GPC to give 1,3-diphenylprop-1-yne as colorless oil.

Table S3

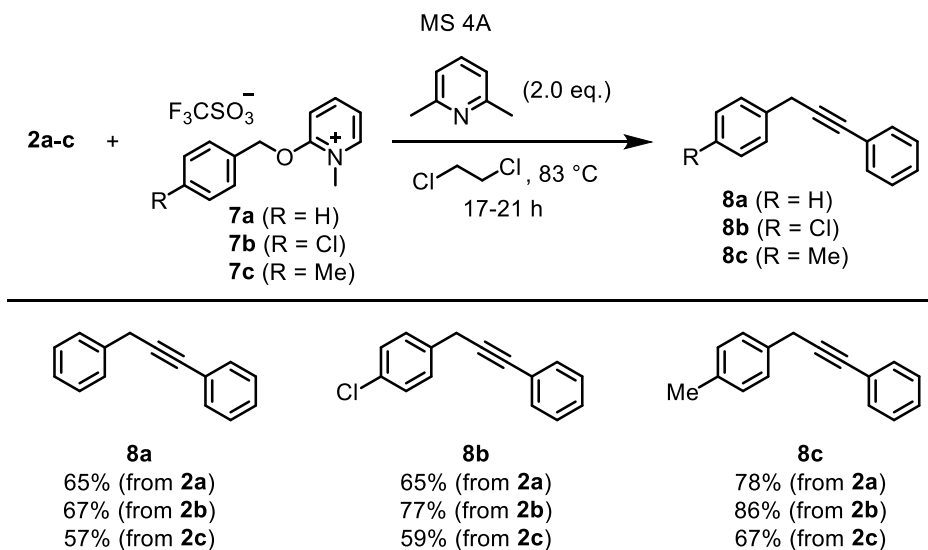


entry	Base	additive	time	yield (%)
1	MgO	-	18	31
2	2,6-lutidine (2.0 eq.)	-	17	60
3	2,6-lutidine (2.0 eq.)	MS 4A	21	65
4	2,6-lutidine (1.0 eq.)	MS 4A	20	46
5	2,6-Di- <i>tert</i> -butylpyridine	-	21	51
6	K <sub>2</sub> CO <sub>3</sub>	-	19	31
7	DBU	-	20	0
8	DIPEA	-	18	39
9	NaO <sup>t</sup> Bu	-	18	0
10	none	-	21	19

### 8-2 Alkynylation reactions of 7a-c

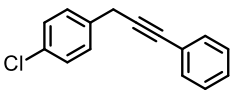
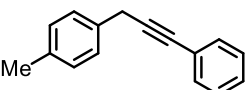
#### General procedure

A 40 mL Pressure tube equipped with a magnetic stirring bar, MS4A (0.2 g) and a septum, was dried under vacuum with heating. After cooling the flask to room temperature, it was purged with argon gas. Alkynyl compounds **2a-c** (0.1 mmol, 1.0 equiv.) and 1,2-dichloroethane (5 mL) were added to the flask. Then, 2,6-lutidine (0.2 mmol, 2.0 equiv.) and compound **7a-c** (0.2 mmol, 2.0 equiv.) were added and the mixture was stirred at 83 °C for 17 to 21 h. After cooling the flask to room temperature, evaporation of the solvents under reduced pressure gave crude products, which were purified by flash chromatography (hexane) and/or GPC to give the desired products.



**Scheme S6**

 <b>8a</b>	<p><b>Reaction of 2a with 7a</b>            Reaction of <b>2a</b> (74.7 mg, 0.10 mmol, 1.0 equiv.) for 20 h, gave Alkynyl <b>8a</b> (12.5 mg, 65%, colorless oil). MS4A (0.2 g), <b>7a</b> (64.9 mg, 0.20 mmol, 2.0 equiv.) and 2,6-lutidine (21.7 mg, 0.20 mmol, 2.0 equiv.) were used.</p>
	<p><b>Reaction of 2b with 7a</b>            Reaction of <b>2b</b> (78.9 mg, 0.10 mmol, 1.0 equiv.) for 17 h, gave Alkynyl <b>8a</b> (12.9 mg, 67%, colorless oil). MS4A (0.2 g), <b>7a</b> (65.1 mg, 0.20 mmol, 2.0 equiv.) and 2,6-lutidine (21.9 mg, 0.20 mmol, 2.0 equiv.) were used.</p>
	<p><b>Reaction of 2c with 7a</b>            Reaction of <b>2c</b> (83.4 mg, 0.10 mmol, 1.0 equiv.) for 19 h, gave Alkynyl <b>8a</b> (11.0 mg, 57%, colorless oil). MS4A (0.2 g), <b>7a</b> (65.0 mg, 0.20 mmol, 2.0 equiv.) and 2,6-lutidine (21.8 mg, 0.20 mmol, 2.0 equiv.) were used.</p>
	<p><math>^1\text{H NMR}</math> (400 MHz, <math>\text{CDCl}_3</math>): <math>\delta</math> 7.48-7.42 (m, 4H), 7.37-7.27 (m, 6H), 3.84 (s, 2H). <math>^{13}\text{C NMR}</math> (100 MHz, <math>\text{CDCl}_3</math>): <math>\delta</math> 136.9, 131.8, 128.7, 128.4, 128.1, 128.0, 126.8, 123.8, 87.7, 82.8, 25.9.</p>

 <p style="text-align: center;"><b>8b</b></p>	<p><b>Reaction of 2a with 7b</b> Reaction of <b>2a</b> (74.5 mg, 0.10 mmol, 1.0 equiv.) for 17 h, gave Alkynyl <b>8b</b> (15.4 mg, 68%, colorless oil). MS4A (0.2 g), <b>7b</b> (77.0 mg, 0.20 mmol, 2.0 equiv.) and 2,6-lutidine (22.0 mg, 0.2 mmol, 2.0 equiv.) were used.</p>
	<p><b>Reaction of 2b with 7b</b> Reaction of <b>2b</b> (79.1 mg, 0.10 mmol, 1.0 equiv.) for 18 h, gave Alkynyl <b>8b</b> (17.5 mg, 77%, colorless oil). MS4A (0.2 g), <b>7b</b> (76.9 mg, 0.20 mmol, 2.0 equiv.) and 2,6-lutidine (22.1 mg, 0.20 mmol, 2.0 equiv.) were used.</p>
	<p><b>Reaction of 2c with 7b</b> Reaction of <b>2c</b> (83.4 mg, 0.10 mmol, 1.0 equiv.) for 20 h, gave Alkynyl <b>8b</b> (13.4 mg, 59%, colorless oil). MS4A (0.2 g), <b>7b</b> (77.1 mg, 0.20 mmol, 2.0 equiv.) and 2,6-lutidine (21.9 mg, 0.20 mmol, 2.0 equiv.) were used.</p>
	<p><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.45-7.44 (m, 2H), 7.37-7.31 (m, 7H), 3.81 (s, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 135.4, 132.6, 131.8, 129.4, 128.8, 128.4, 128.1, 123.5, 87.0, 83.1, 25.3.</p>
 <p style="text-align: center;"><b>8c</b></p>	<p><b>Reaction of 2a with 7c</b> Reaction of <b>2a</b> (74.8 mg, 0.10 mmol, 1.0 equiv.) for 21 h, gave Alkynyl <b>8c</b> (16.1 mg, 78%, yellow oil). MS4A (0.2 g), <b>7c</b> (72.7 mg, 0.20 mmol, 2.0 equiv.) and 2,6-lutidine (21.9 mg, 0.20 mmol, 2.0 equiv.) were used.</p>
	<p><b>Reaction of 2b with 7c</b> Reaction of <b>2b</b> (79.1 mg, 0.10 mmol, 1.0 equiv.) for 20 h, gave Alkynyl <b>8c</b> gave the title compound (17.7 mg, 86%, yellow oil). MS4A (0.2 g), <b>7c</b> (73.1 mg, 0.20 mmol, 2.0 equiv.) and 2,6-lutidine (21.7 mg, 0.20 mmol, 2.0 equiv.) were used.</p>
	<p><b>Reaction of 2c with 7c</b> Reaction of <b>2c</b> (83.6 mg, 0.10 mmol, 1.0 equiv.) for 21 h, gave Alkynyl <b>8c</b> (13.8 mg, 67%, yellow oil). MS4A (0.2 g), <b>7c</b> (72.9 mg, 0.20 mmol, 2.0 equiv.) and 2,6-lutidine (22.3 mg, 0.20 mmol, 2.0 equiv.) were used.</p>
	<p><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.90-7.45 (m, 2H), 7.34-7.28 (m, 5H), 7.17 (d, 2H, <i>J</i> = 7.6 Hz), 3.81 (s, 2H), 2.36 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 136.3, 133.8, 131.8, 129.4, 128.3, 128.0, 127.9, 123.9, 88.0, 82.6, 25.5, 21.2.</p>

## 9. Control experiments

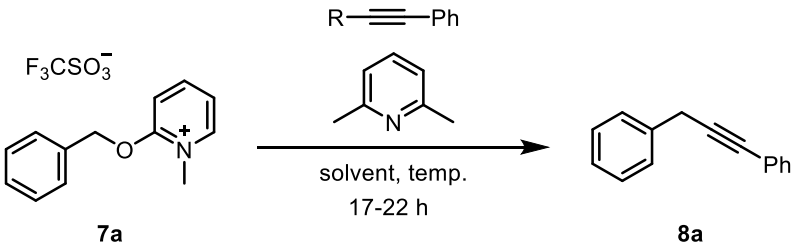
### General procedure (entries 1, 3, 4 and 5)

A 40 mL pressure tube equipped with a magnetic stirring bar and a septum, was dried under vacuum with heating. After cooling the tube to room temperature, it was purged with argon gas. Alkynyl compounds (0.1 mmol, 1.0 eq.) and 1,2-dichloroethane (5 mL) were added to the tube. Then, 2,6-lutidine (0.2 mmol, 2.0 eq.) and 2-benzyloxy-1-methylpyridinium trifluoromethanesulfonate (0.2 mmol, 2.0 eq.) were added to it and the mixture was stirred at 83 °C for 18 to 22 h. After cooling the flask to room temperature, evaporation of the solvents gave crude products, which were purified by flash chromatography (hexane) and/or GPC to give **8a**.

### Procedure for entry 2

A 30 mL flask equipped with a magnetic stirring bar and a septum, was dried under vacuum with heating. After cooling the flask to room temperature, it was purged with argon gas. Phenylacetylene (11  $\mu$ L, 0.1 mmol, 1.0 equiv.) was dissolved in THF (5 mL). The solution was stirred and *n*-BuLi (0.13 mL, 0.2 mmol, 2.0 equiv.) was added at  $-78$  °C. The mixture was stirred at  $-78$  °C for 1 h, and warmed up to room temperature. 2-Benzyloxy-1-methylpyridinium trifluoromethanesulfonate (69.9 mg, 0.2 mmol, 2.0 equiv.) was added to it, and the mixture was stirred at room temperature for 20 h. After evaporation of the solvents under reduced pressure gave crude products, which were subjected to NMR measurements.

Table S4



entry	R-C≡C-Ph	solvent	temp.	time	yield
1	H-C≡C-Ph	Cl-CH2-CH2-Cl	83 °C	20 h	no reaction
2	Li-C≡C-Ph	THF	r.t.	22 h	complex mixture
3	Me3Si-C≡C-Ph	Cl-CH2-CH2-Cl	83 °C	19 h	no reaction
4	KF3B-C≡C-Ph	Cl-CH2-CH2-Cl	83 °C	20 h	complex mixture
5	<b>2a</b>	Cl-CH2-CH2-Cl	83 °C	17 h	60%

## 10. X-ray crystallographic analysis

### 10-1 Data collection and structure determination

Colorless single crystals of **2a-c** were grown from a saturated THF/Et<sub>2</sub>O solution at room temperature. The intensity data were collected at 100 K on a Rigaku XtaLAB mini II diffractometer employing graphite-monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) for **2b** and **2c**, and on a Saxon CrysAlisPro-abstract goniometer imported SAXI images for **2a**. Structures were solved by direct methods (SHELXT)<sup>6</sup> and refined by full-matrix least-squares procedures on  $F^2$  for all reflections (SHELXL). Hydrogen atoms were located by assuming ideal geometry and were included in the structure calculations without further refinement of the parameters. The crystallographic data for the structures reported in this paper have been deposited with The Cambridge Crystallographic Data Centre as supplement publication.

**Table S5. Selected bond lengths [Å] and angles [°] of the X-ray crystal structure of 2a-c**

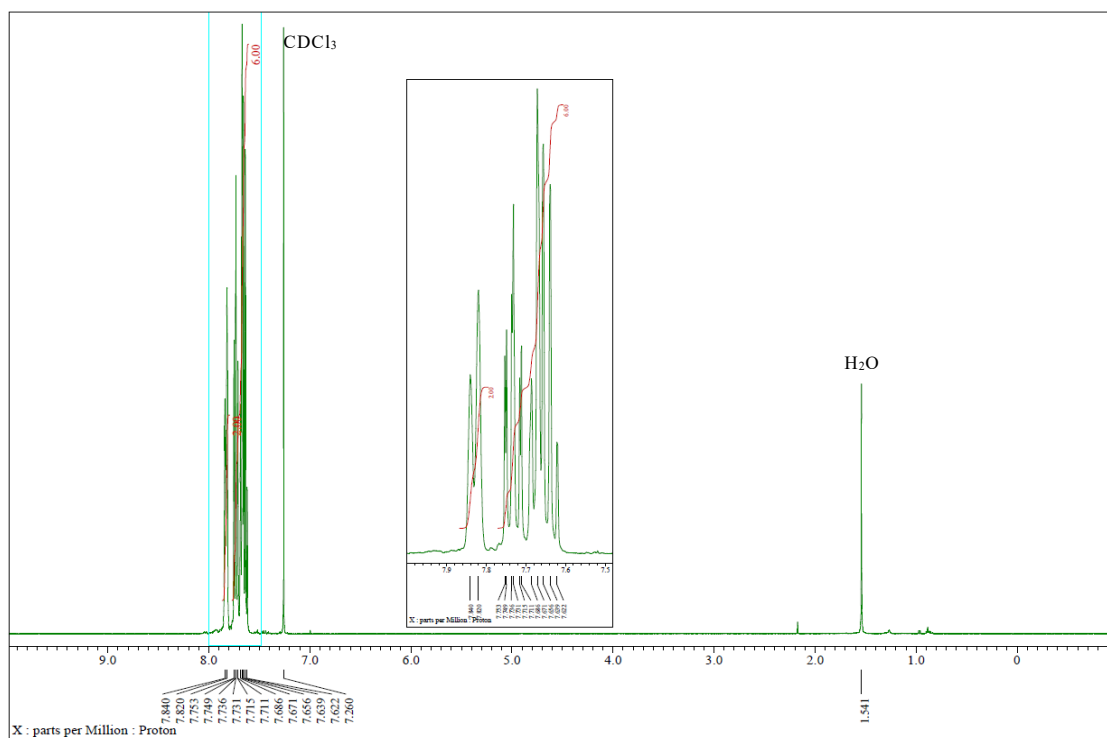
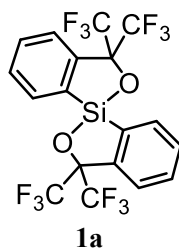
	bond lengths (Å)		
	<b>2a</b> (E = Si)	<b>2b</b> (E = Ge)	<b>2c</b> (E = Sn)
E1–C1	1.863(2)	1.917(2)	2.100(2)
E1–C4	1.897(2)	1.949(2)	2.113(2)
E1–C5	1.892(2)	1.917(2)	2.117(2)
E1–O1	1.820(1)	1.971(1)	2.101(1)
E1–O2	1.807(1)	1.955(1)	2.112(1)
C1–C2	1.206(3)	1.208(3)	1.208(3)
	bond angles (°)		
O1–E1–O2	175.96(6)	175.01(6)	169.66(5)
E1–C1–C2	177.2(2)	177.1(2)	176.4(2)
C1–C2–C3	179.7(2)	179.4(2)	179.3(2)



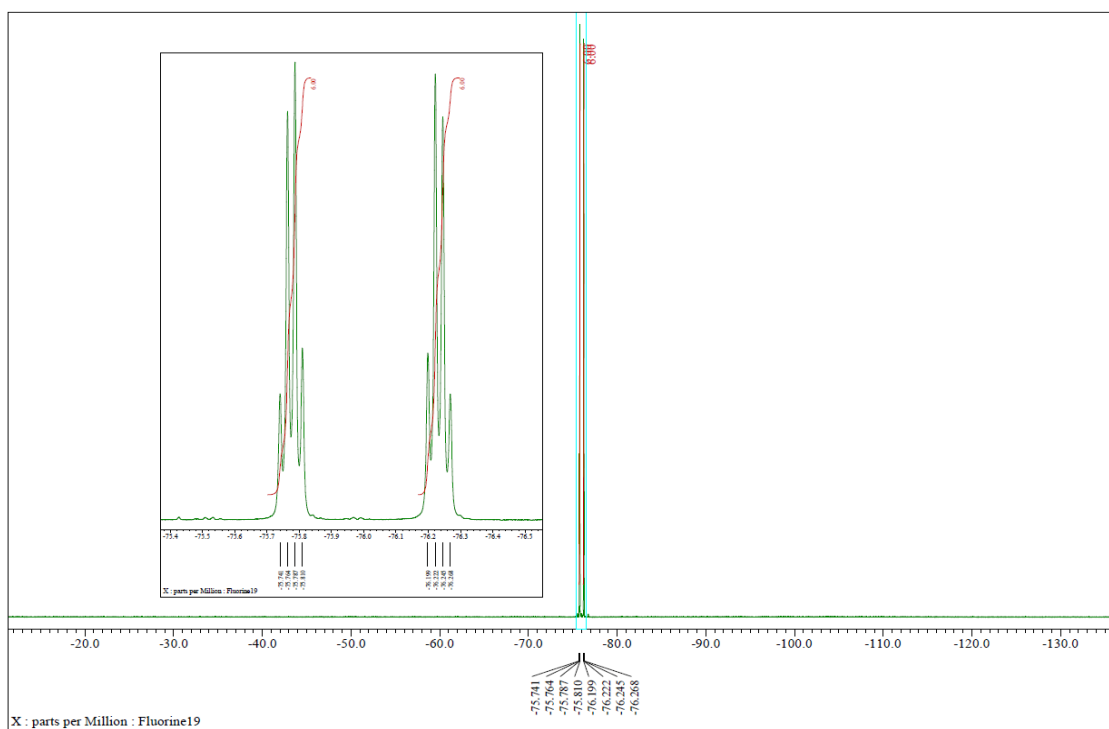
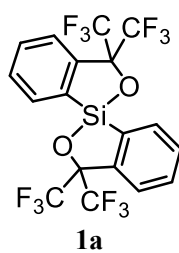
**Table S6.** Crystallographic data and details of refinement for **2a-c**

	<b>2a</b>	<b>2b</b>	<b>2c</b>
Formula	C <sub>34</sub> H <sub>33</sub> F <sub>12</sub> NO <sub>2</sub> Si	C <sub>34</sub> H <sub>33</sub> F <sub>12</sub> NO <sub>2</sub> Ge	C <sub>34</sub> H <sub>33</sub> F <sub>12</sub> NO <sub>2</sub> Sn
Formula weight	743.70	788.20	834.30
color	colorless	colorless	colorless
Crystal size/nm	0.10×0.05×0.05	0.07×0.07×0.03	0.12×0.08×0.08
Temperature/K	100	100	100
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> /Å	11.0531(2)	11.1071(5)	11.2117(4)
<i>b</i> /Å	16.2521(3)	16.2492(9)	16.2237(7)
<i>c</i> /Å	18.3816(3)	18.3357(8)	18.2776(8)
<i>a</i> /deg	90	90	90
<i>b</i> /deg	95.844(2)	95.828(4)	96.334(4)
<i>γ</i> /deg	90	90	90
<i>V</i> /Å <sup>3</sup>	3284.84(10)	3292.1(3)	3304.3(2)
<i>Z</i>	4	4	4
<i>D</i> <sub>calcd</sub> /g cm <sup>-3</sup>	1.504	1.590	1.677
No. of unique data	7533	9898	9946
No. of parameters	455	495	456
No. of restraints	0	0	0
<i>R</i> <sub>1</sub>	0.0558	0.0436	0.0317
<i>wR</i> <sub>2</sub>	0.0998	0.0819	0.0645
GOF	1.283	1.020	1.015

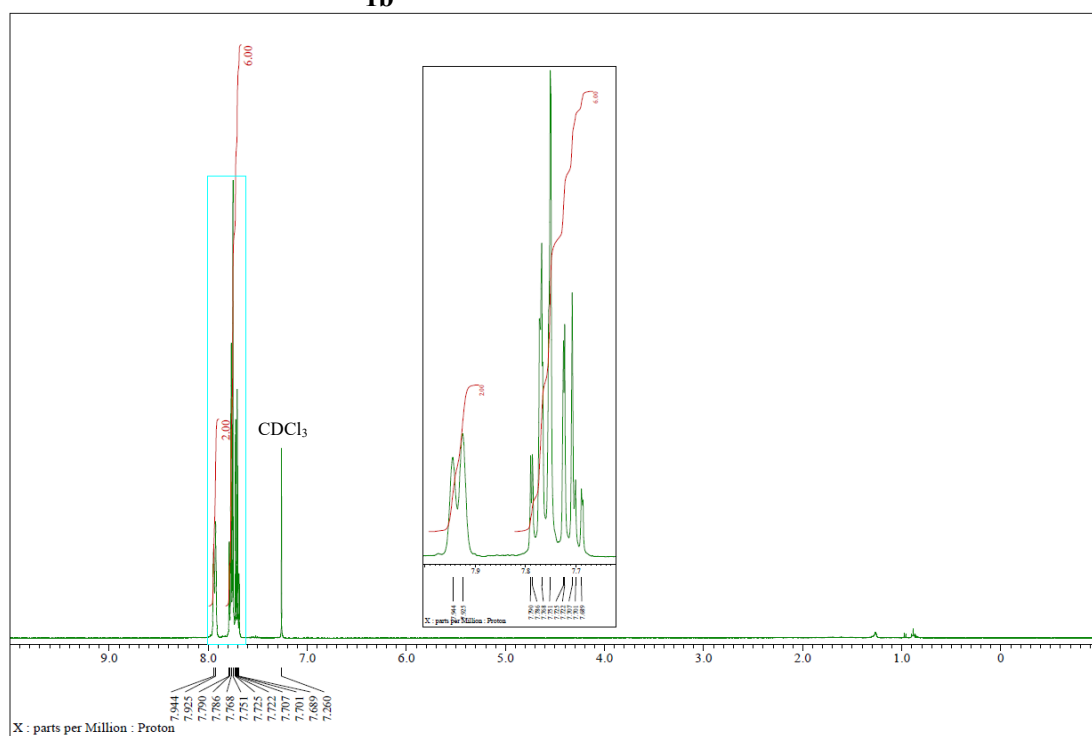
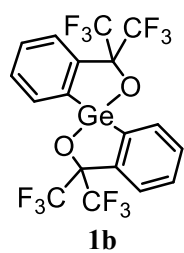
## 11. NMR spectra



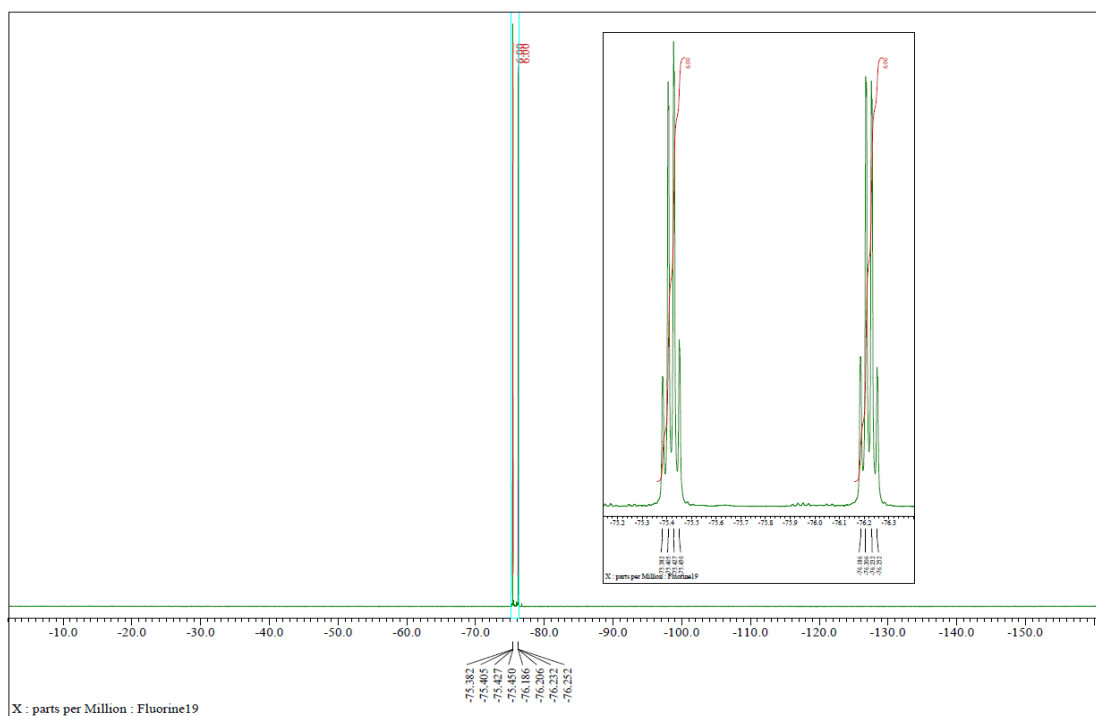
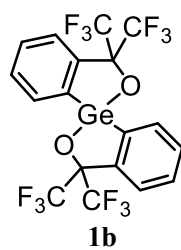
**Figure S1.** <sup>1</sup>H NMR (400 MHz) spectrum of **1a** in CDCl<sub>3</sub>



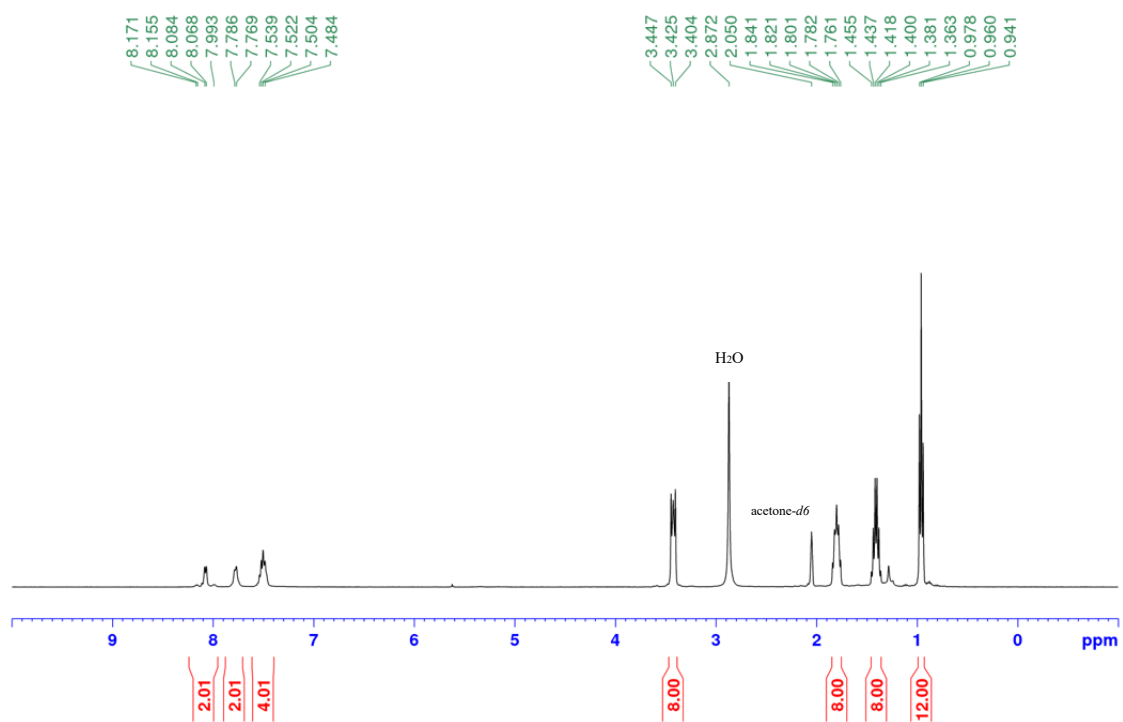
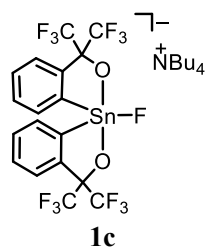
**Figure S2.**  $^{19}\text{F}$  NMR (376 MHz) spectrum of **1a** in  $\text{CDCl}_3$



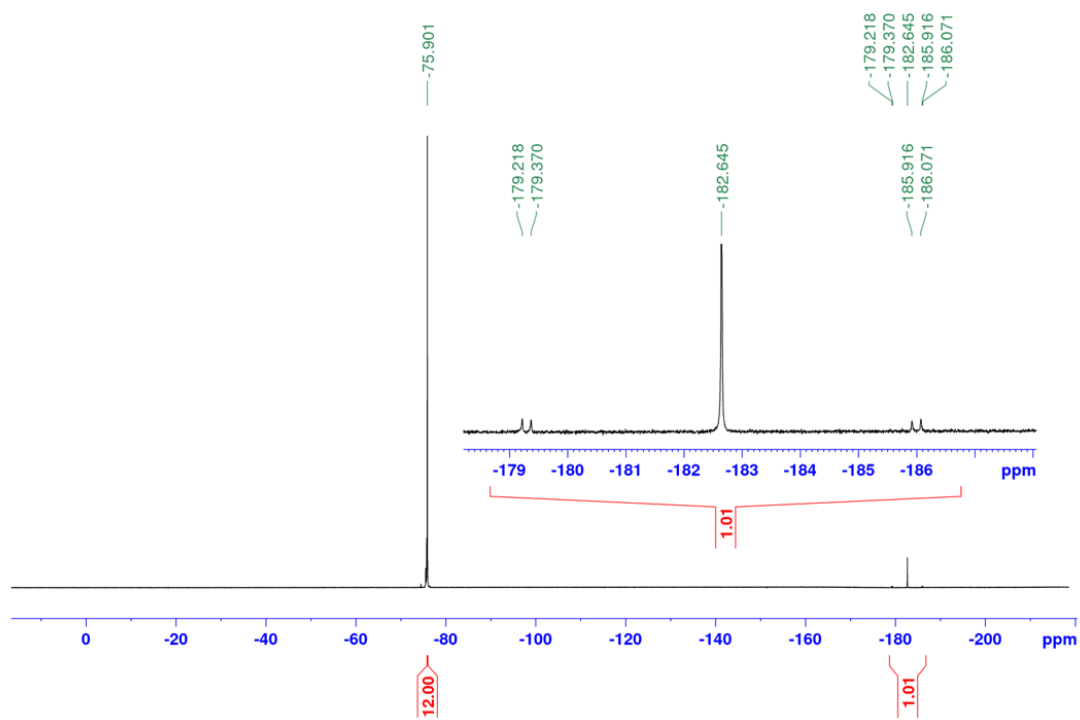
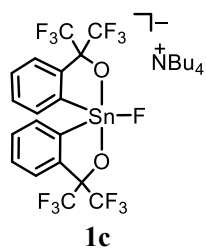
**Figure S3.**  $^1\text{H}$  NMR (400 MHz) spectrum of **1b** in  $\text{CDCl}_3$



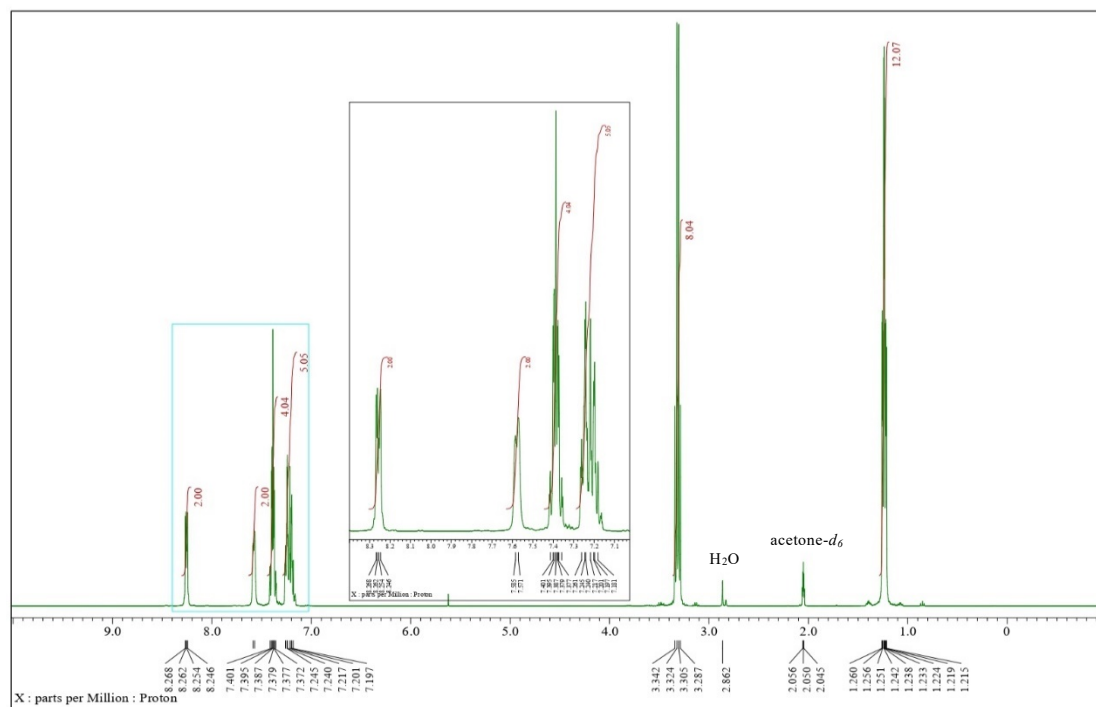
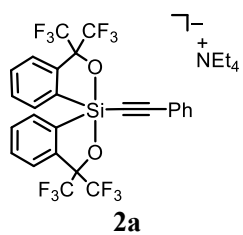
**Figure S4.**  $^{19}\text{F}$  NMR (376 MHz) spectrum of **1b** in  $\text{CDCl}_3$



**Figure S5.** <sup>1</sup>H NMR (376 MHz) spectrum of **1c** in acetone-*d*<sub>6</sub>.

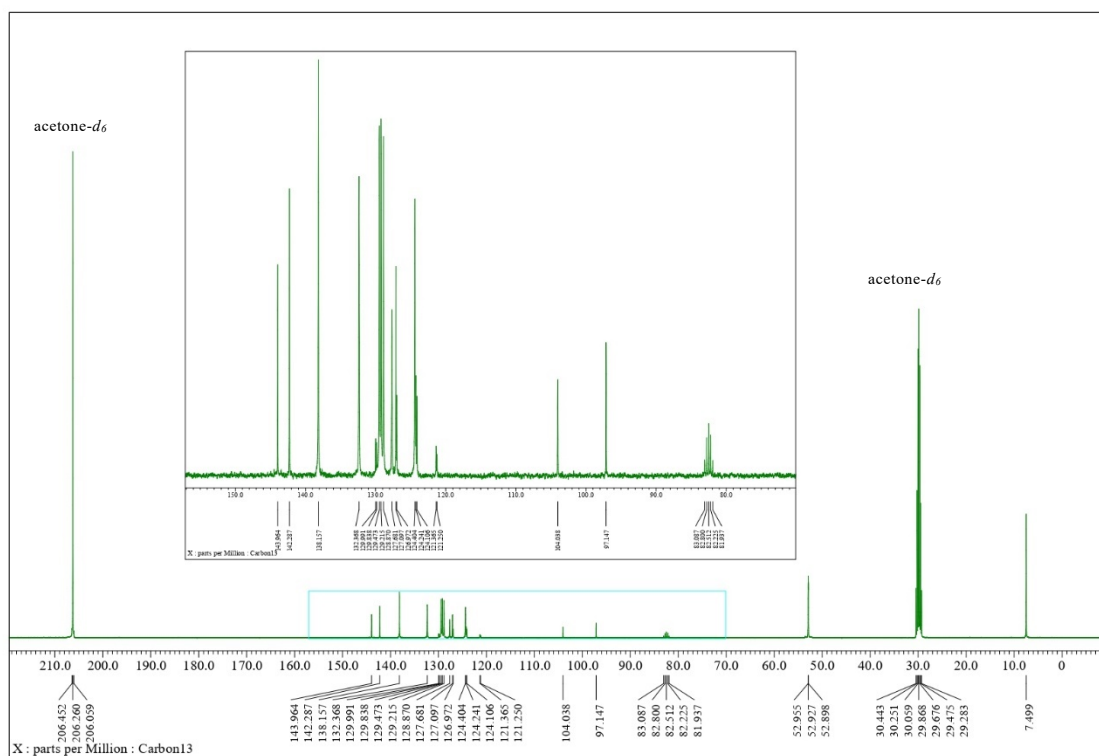
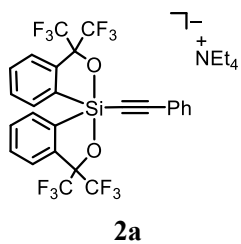


**Figure S6.** <sup>19</sup>F NMR (376 MHz) spectrum of **1c** in acetone-*d*<sub>6</sub>.

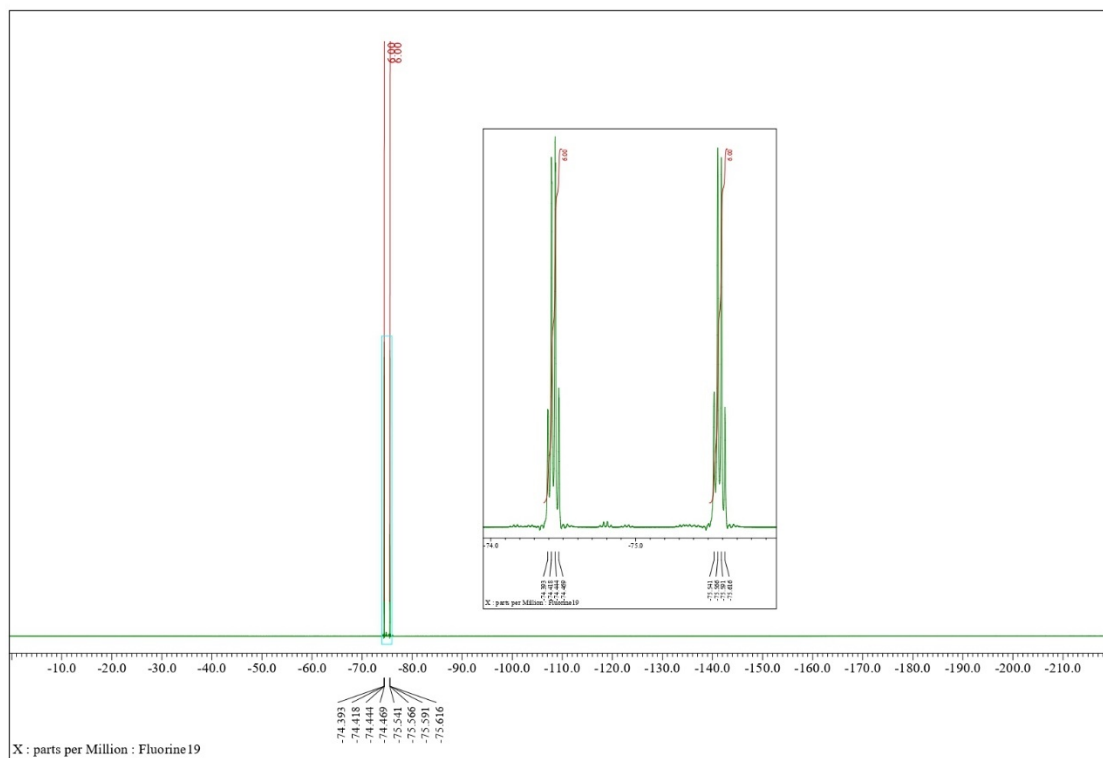
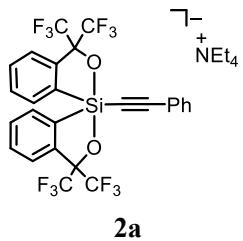


**Figure S7.**  $^1\text{H}$  NMR (400 MHz) spectrum of **2a** in acetone- $d_6$ .

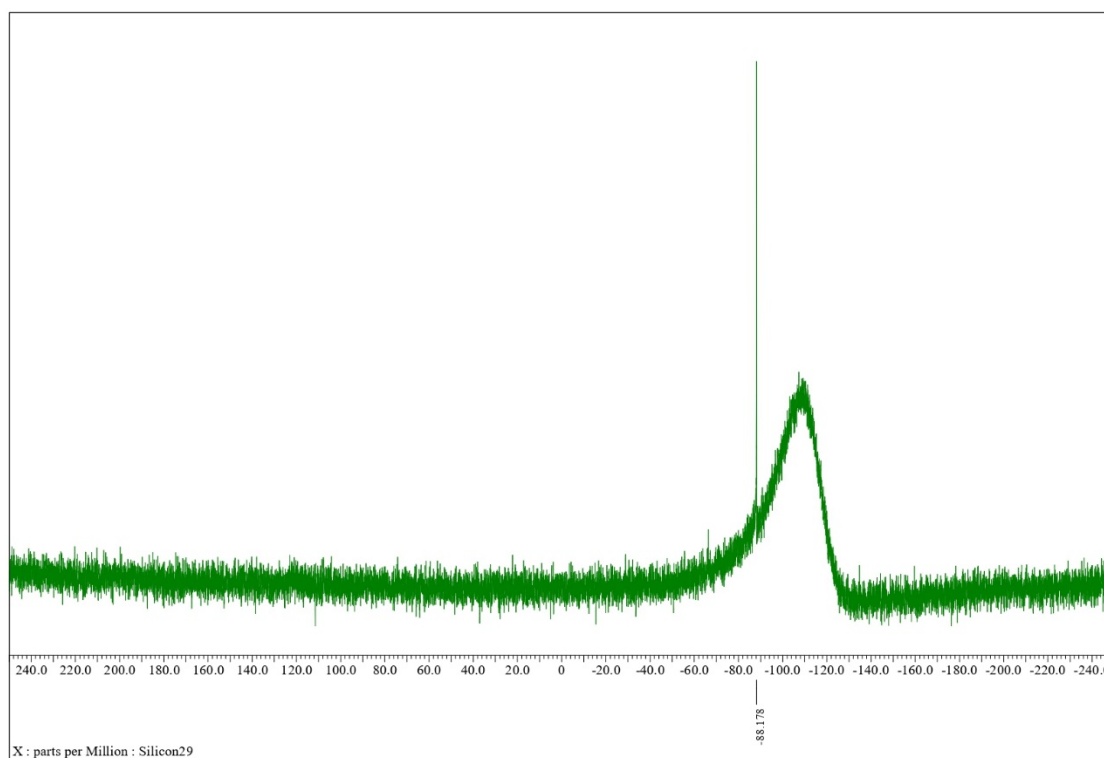
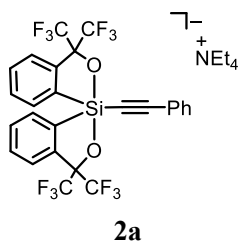




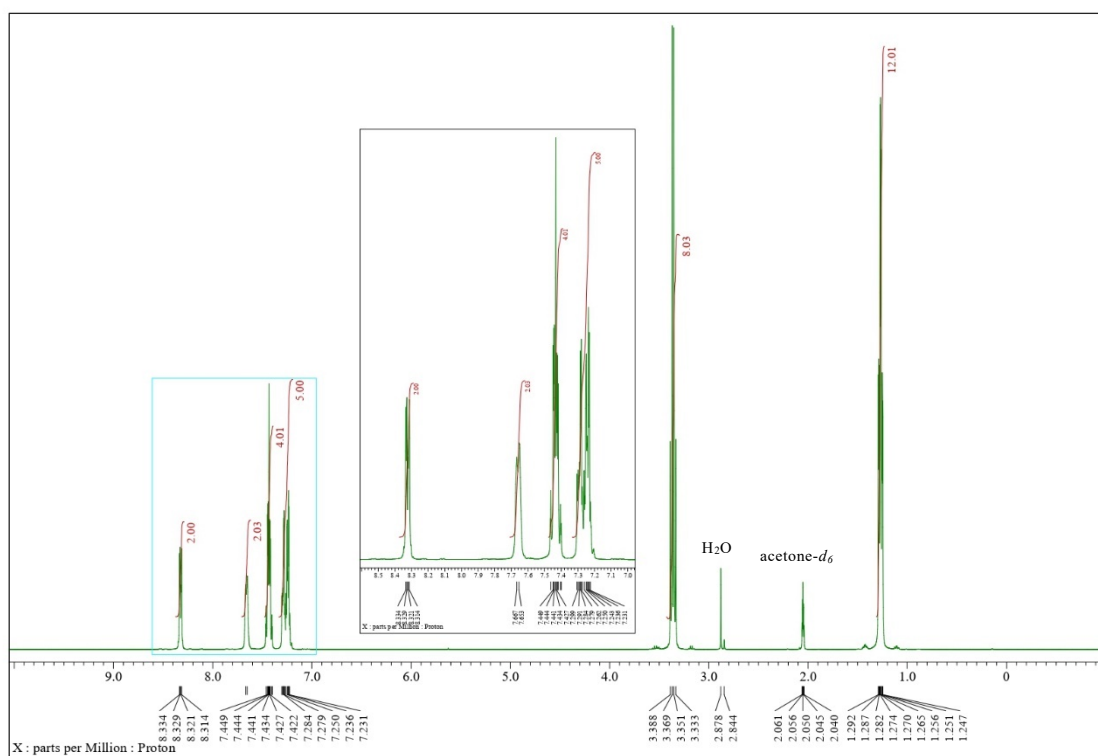
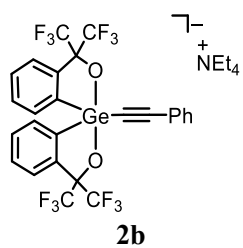
**Figure S8.** <sup>13</sup>C NMR (100 MHz) spectrum of **2a** in acetone-*d*<sub>6</sub>.



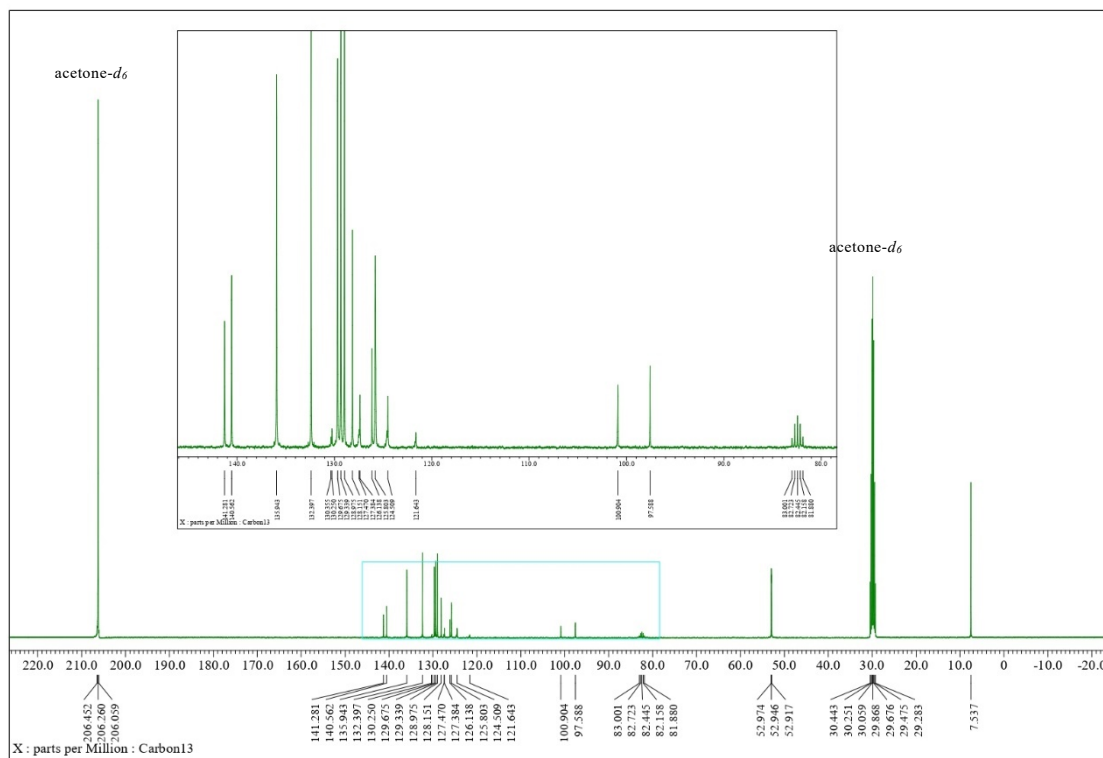
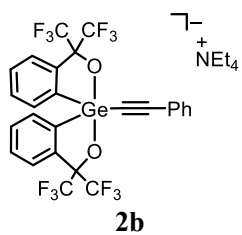
**Figure S9.**  $^{19}\text{F}$  NMR (376 MHz) spectrum of **2a** in acetone- $d_6$ .



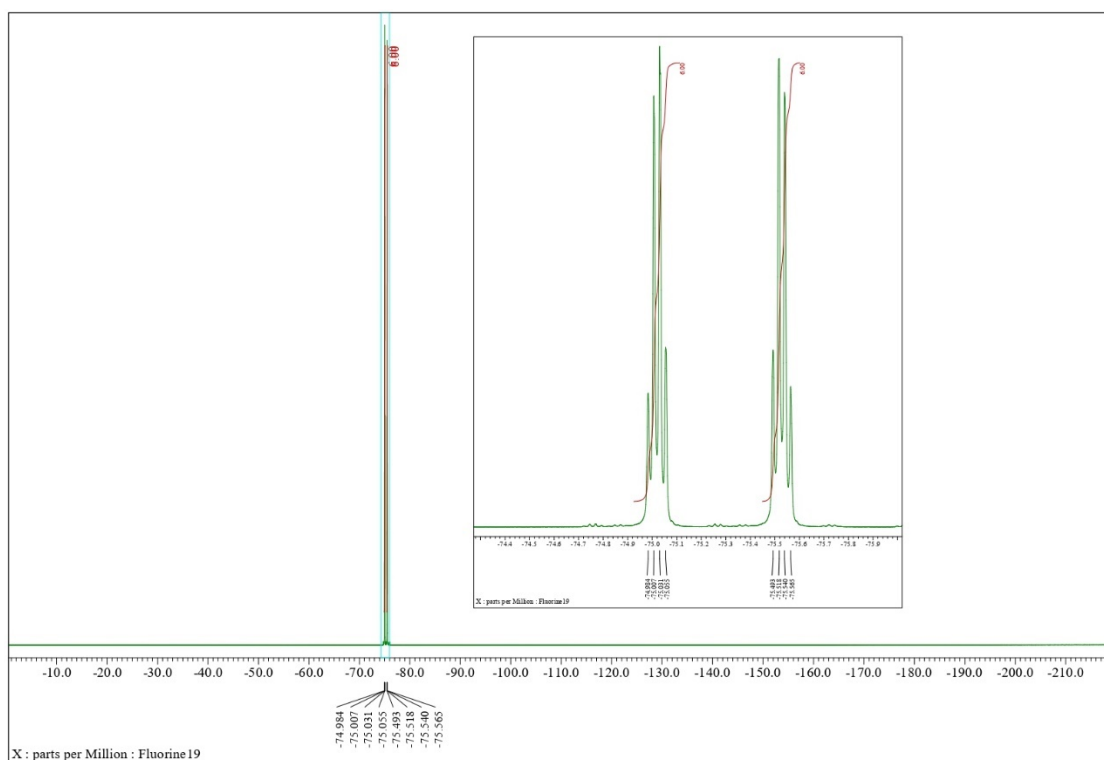
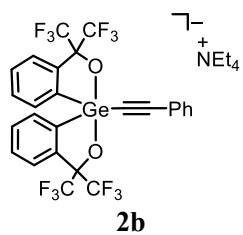
**Figure S10.**  $^{29}\text{Si}$  NMR (80 MHz) spectrum of **2a** in acetone- $d_6$ .



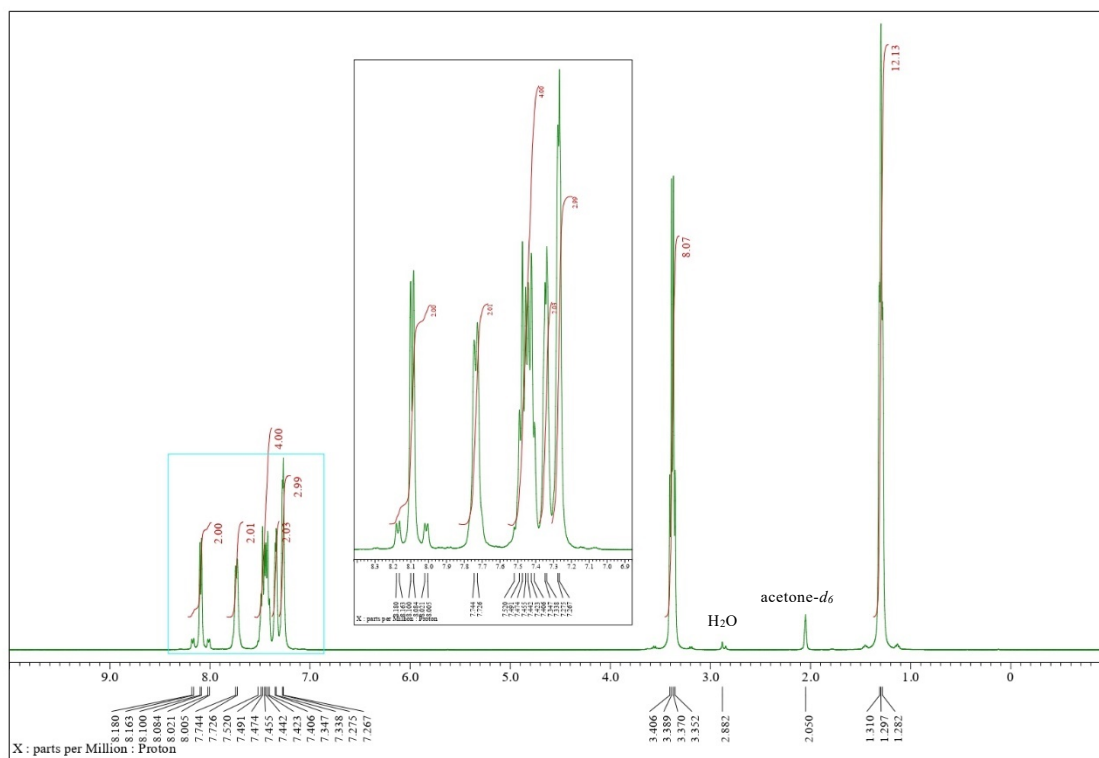
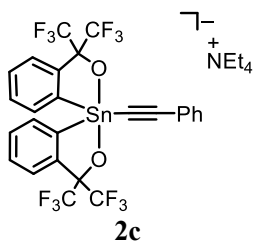
**Figure S11.**  $^1\text{H}$  NMR (400 MHz) spectrum of **2b** in acetone- $d_6$ .



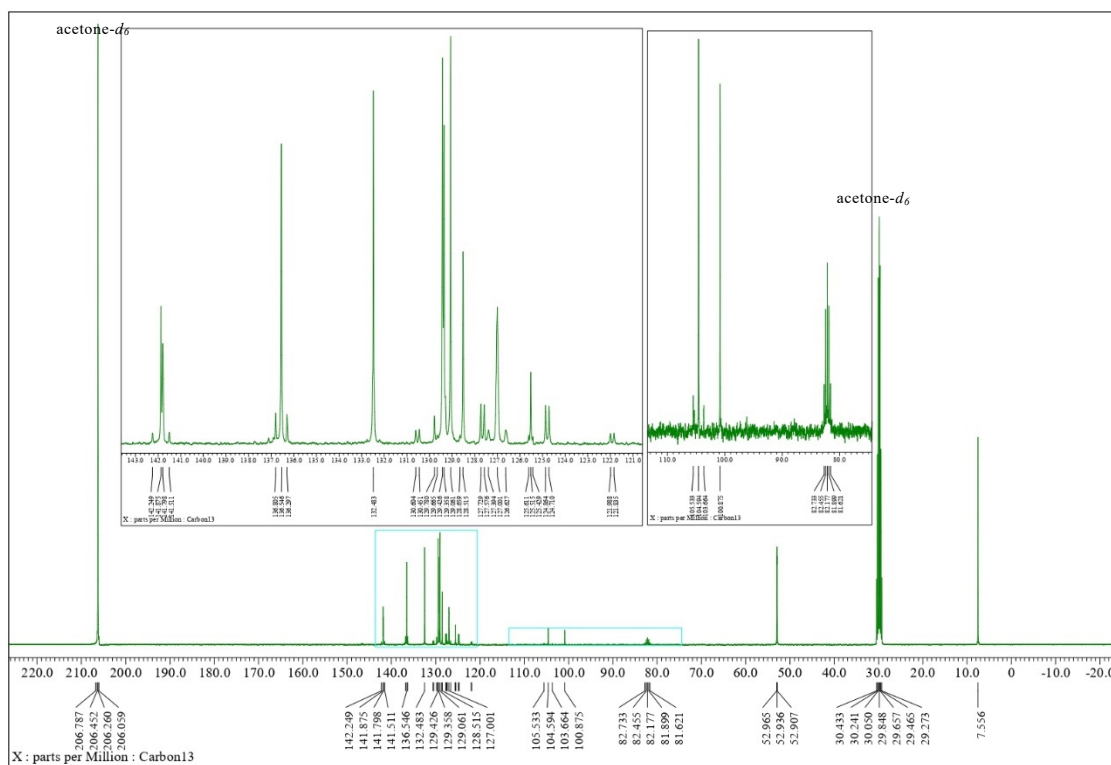
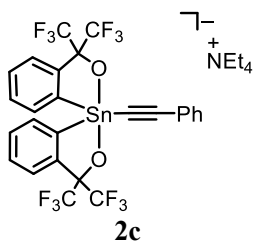
**Figure S12.** <sup>13</sup>C NMR (100 MHz) spectrum of **2b** in acetone-*d*<sub>6</sub>.



**Figure S13.**  $^{19}\text{F}$  NMR (376 MHz) spectrum of **2b** in acetone- $d_6$ .

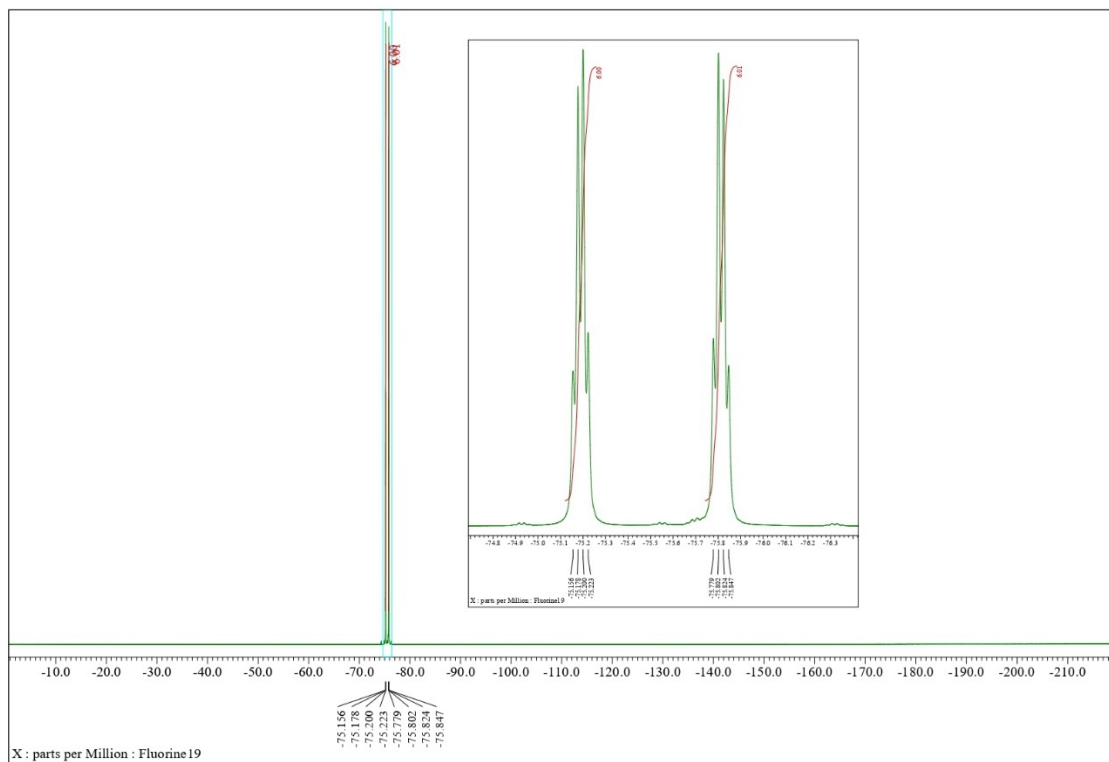
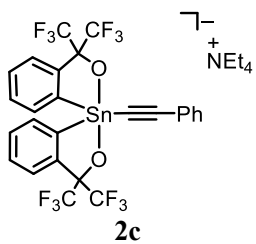


**Figure S14.**  $^1\text{H}$  NMR (400 MHz) spectrum of **2c** in acetone- $d_6$ .

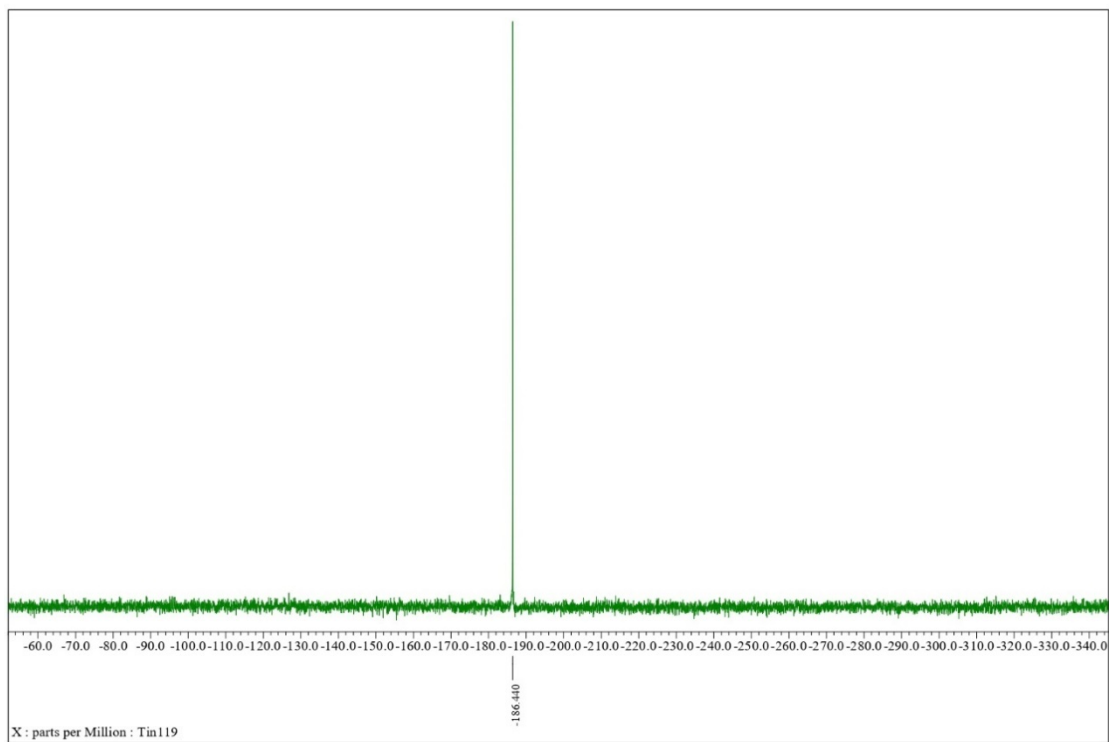
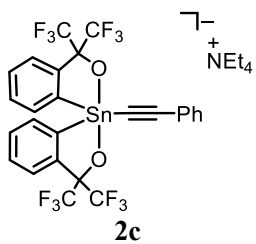


**Figure S15.** <sup>13</sup>C NMR (400 MHz) spectrum of **2c** in acetone-*d*<sub>6</sub>.

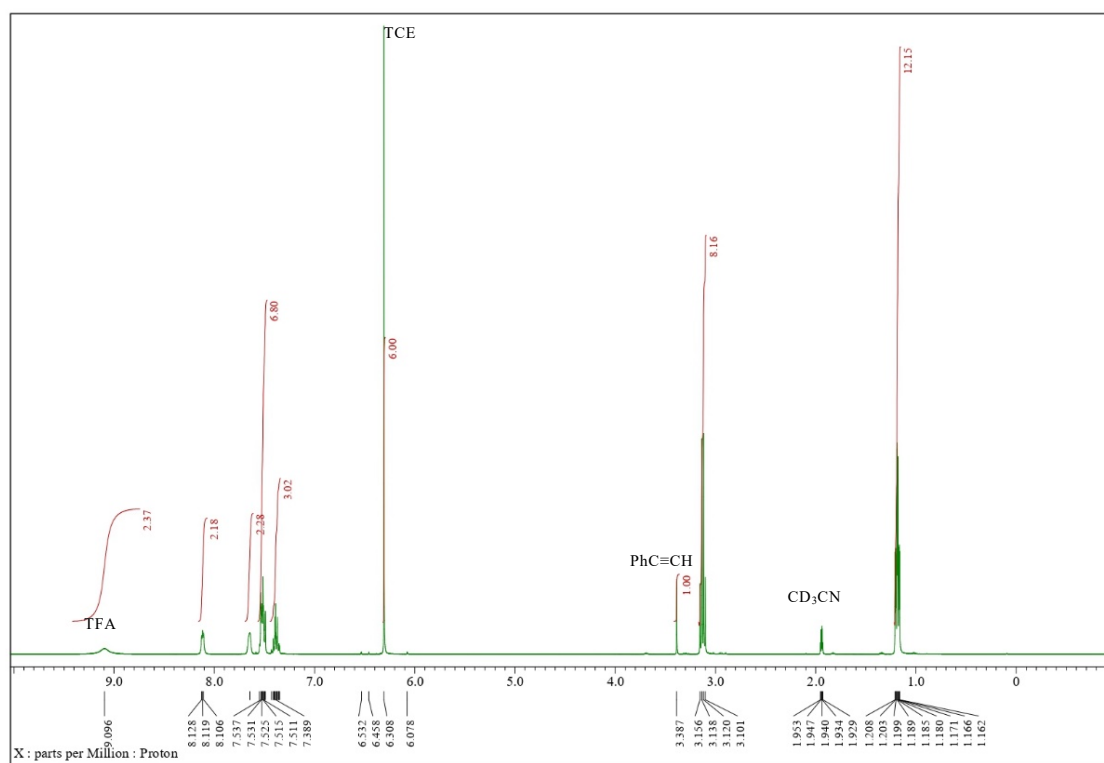
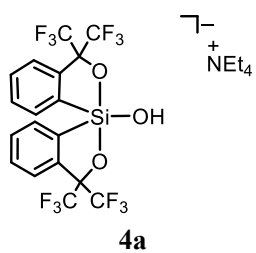




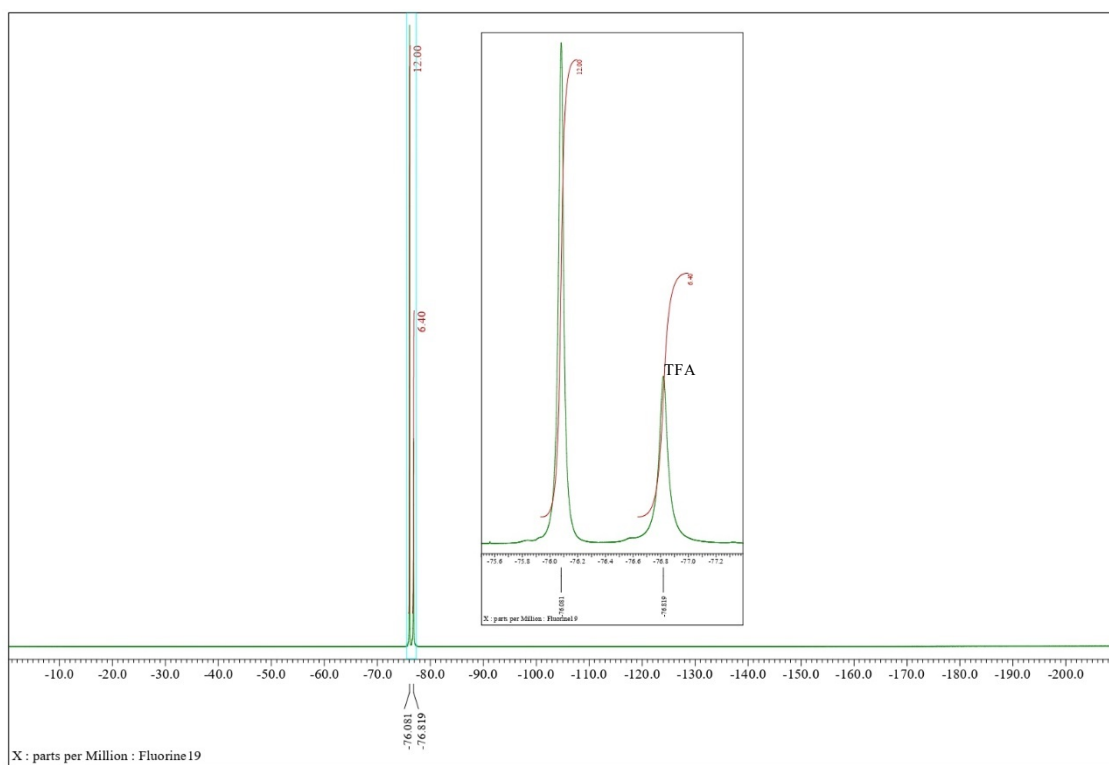
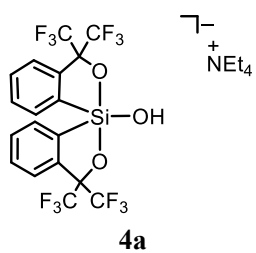
**Figure S16.**  $^{19}\text{F}$  NMR (376 MHz) spectrum of **2c** in acetone- $d_6$ .



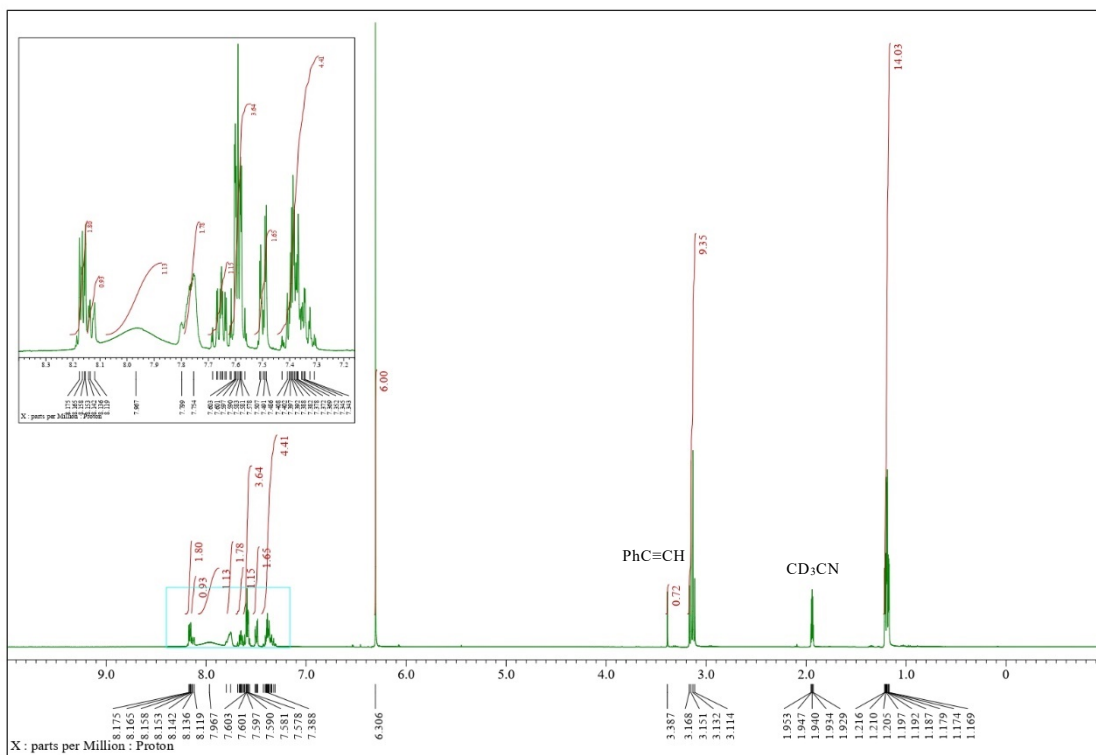
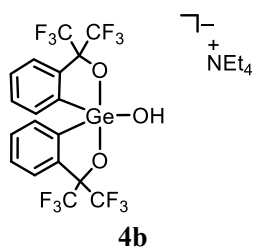
**Figure S17.**  $^{119}\text{Sn}$  NMR (149 MHz) spectrum of **2c** in acetone- $d_6$ .

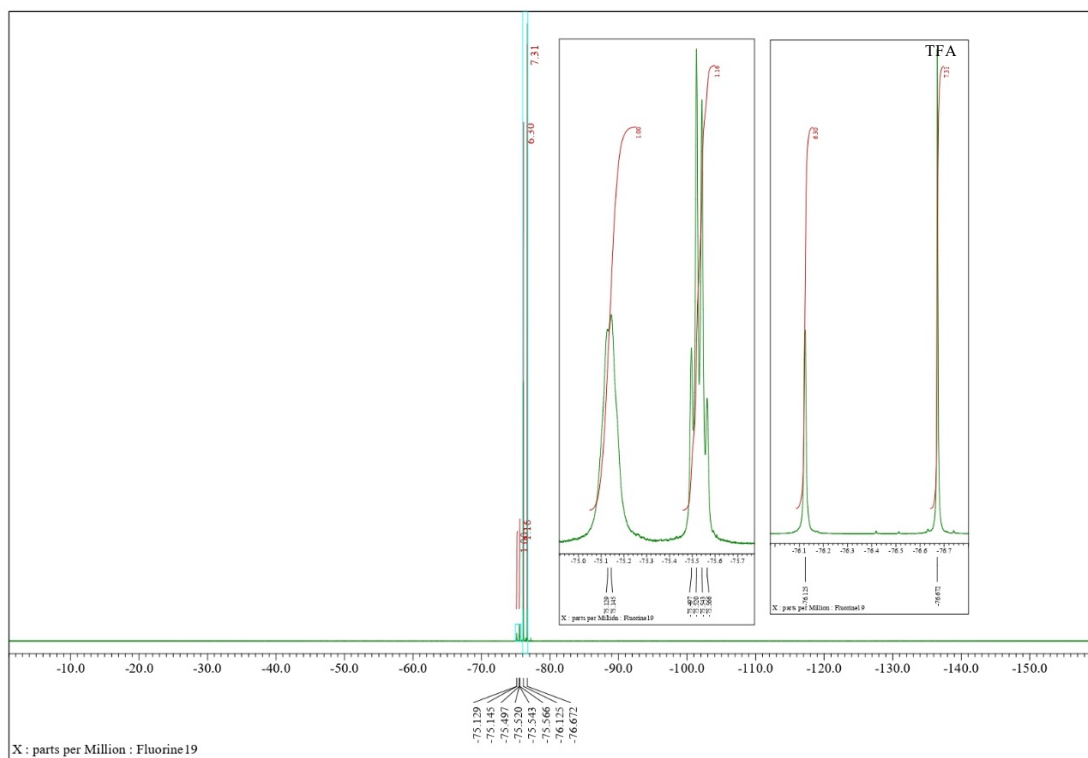
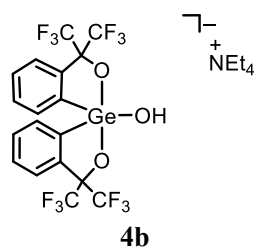


**Figure S18.** <sup>1</sup>H NMR (400 MHz) spectrum of reaction of **4a** with TFA in CD<sub>3</sub>CN.

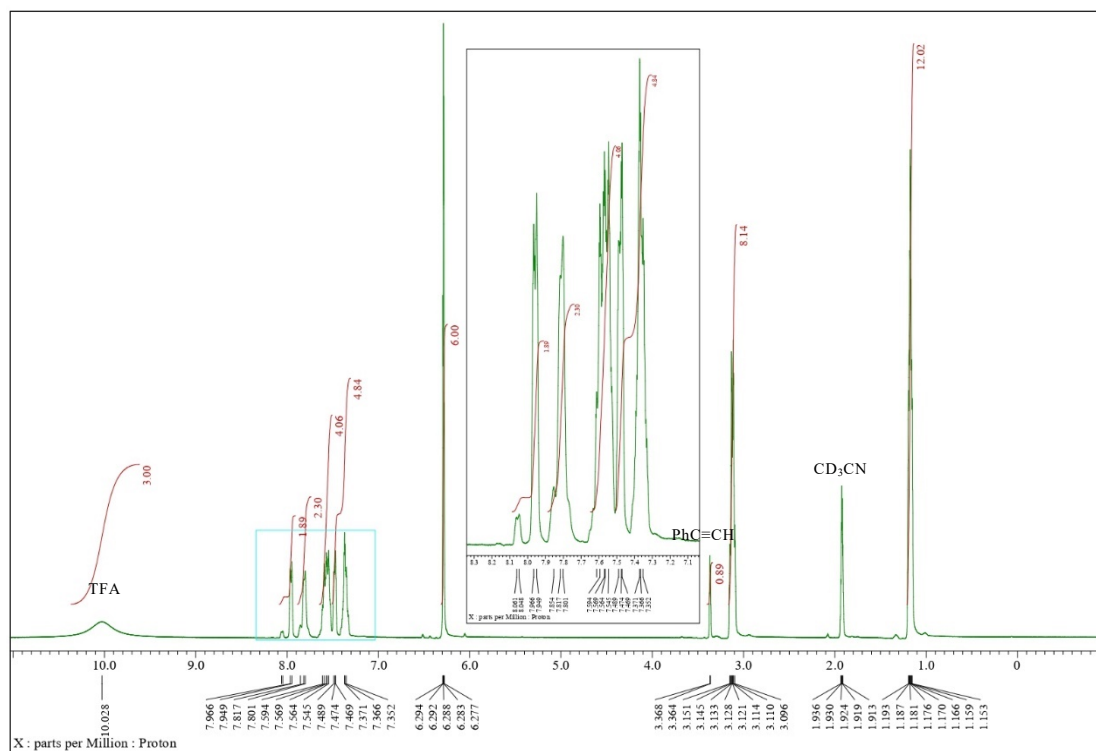
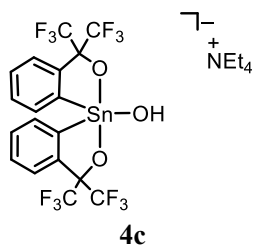


**Figure S19.**  $^{19}\text{F}$  NMR (376 MHz) spectrum of reaction of **4a** with TFA in  $\text{CD}_3\text{CN}$ .

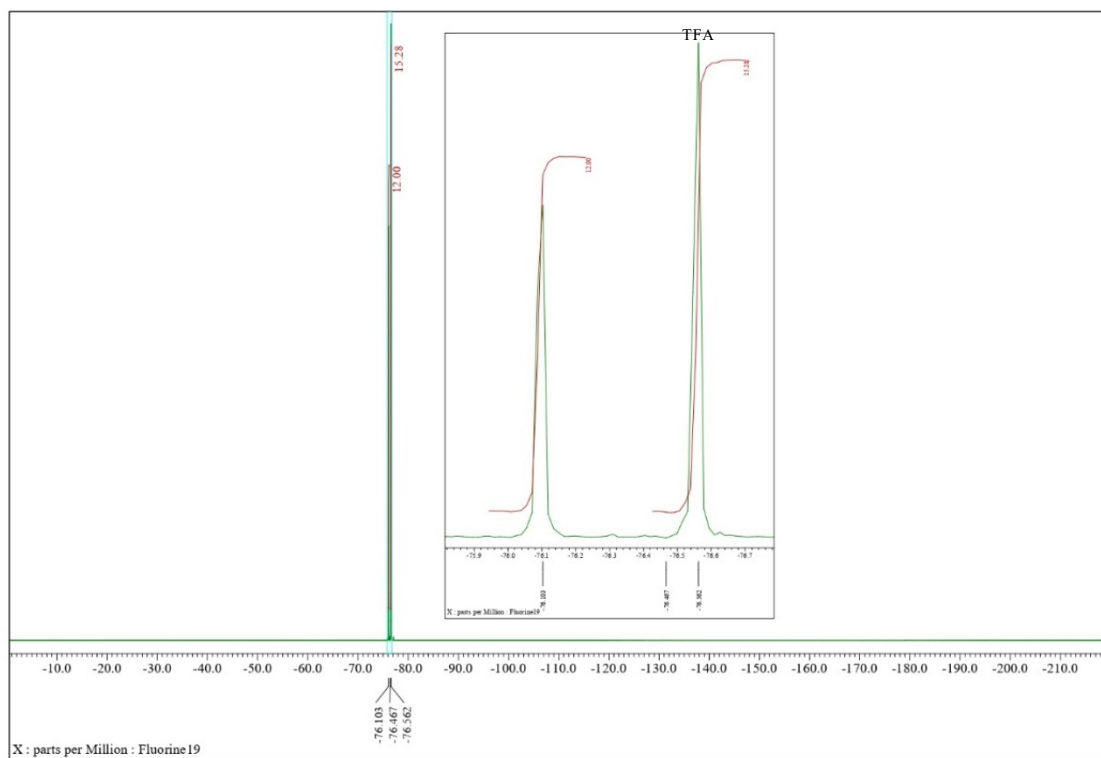
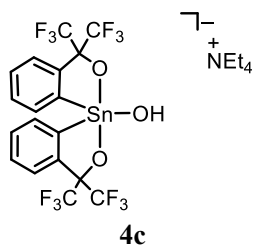




**Figure S21.**  $^{19}\text{F}$  NMR (376 MHz) spectrum of reaction of **4b** with TFA in  $\text{CD}_3\text{CN}$ .

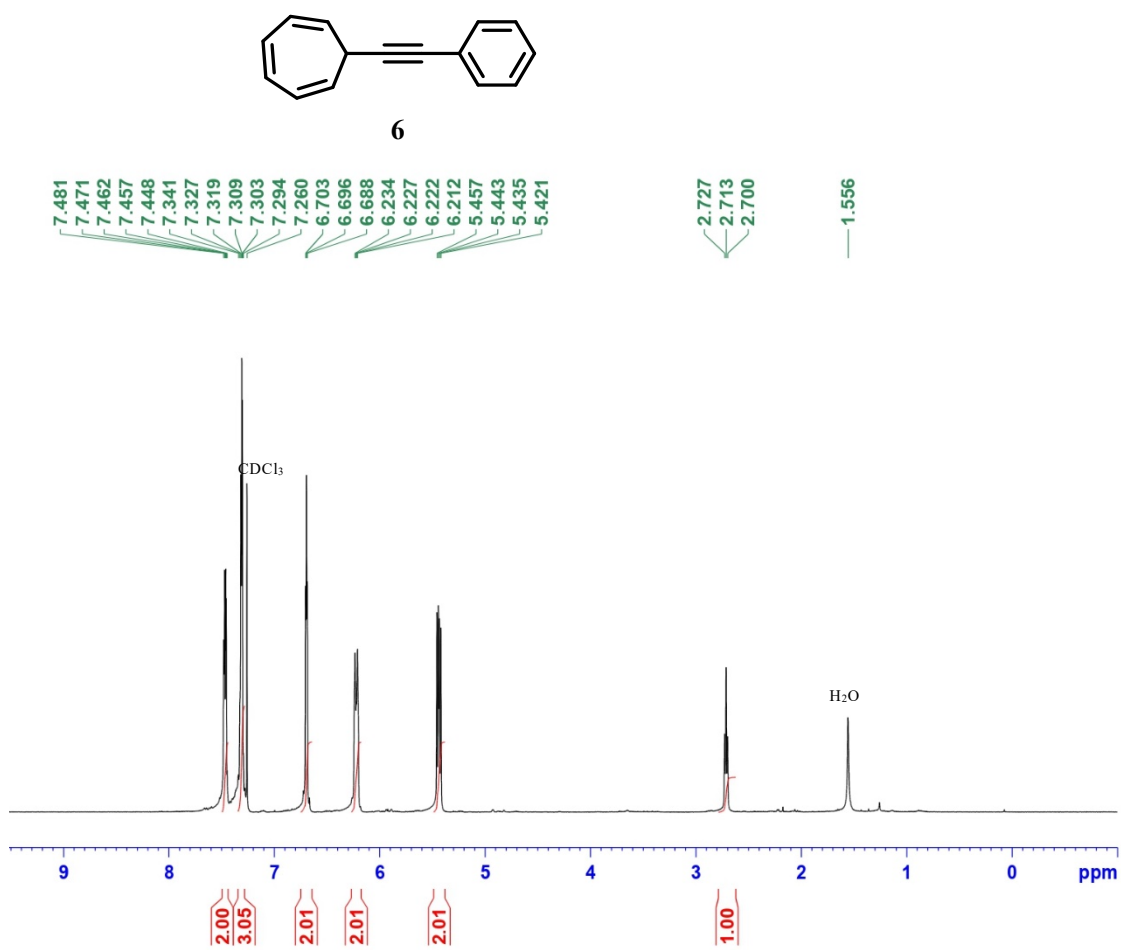


**Figure S22.**  $^1\text{H}$  NMR (400 MHz) spectrum reaction of **4c** with TFA in  $\text{CD}_3\text{CN}$ .

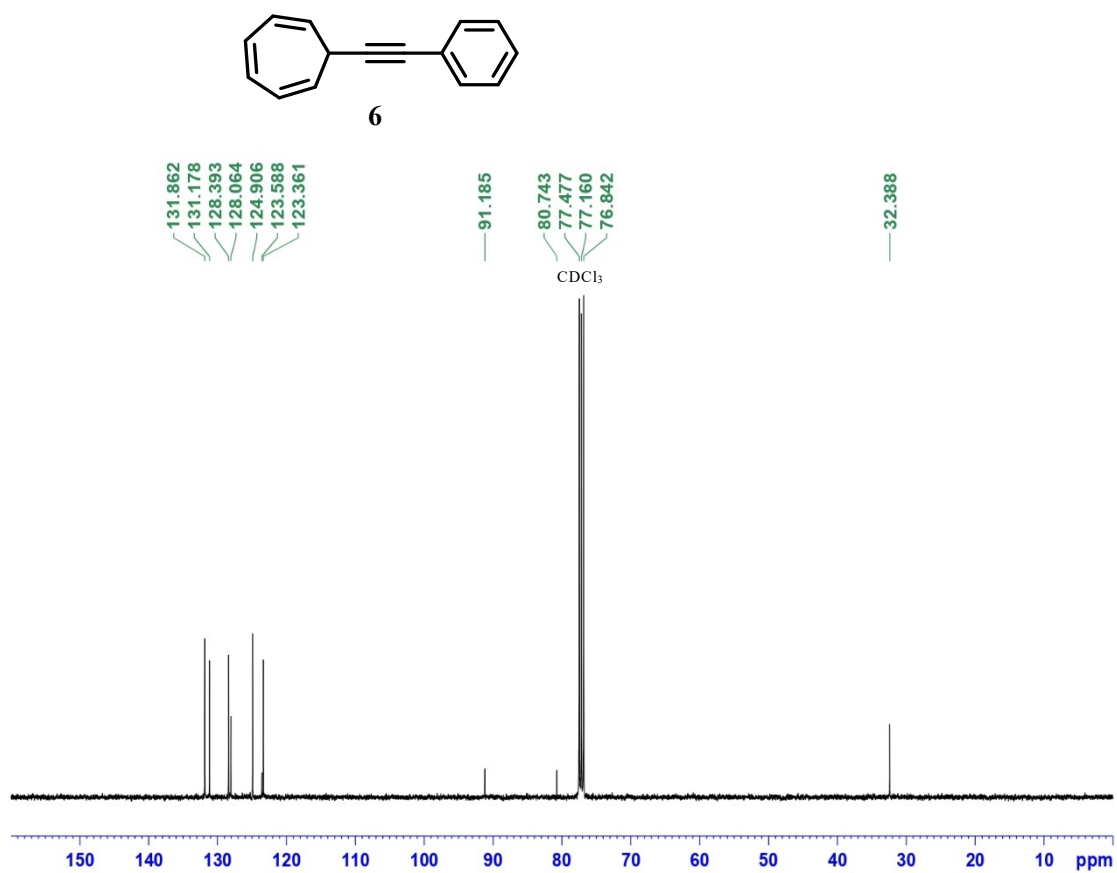


**Figure S23.** <sup>19</sup>F NMR (376 MHz) spectrum of reaction of **4c** with TFA in CD<sub>3</sub>CN.

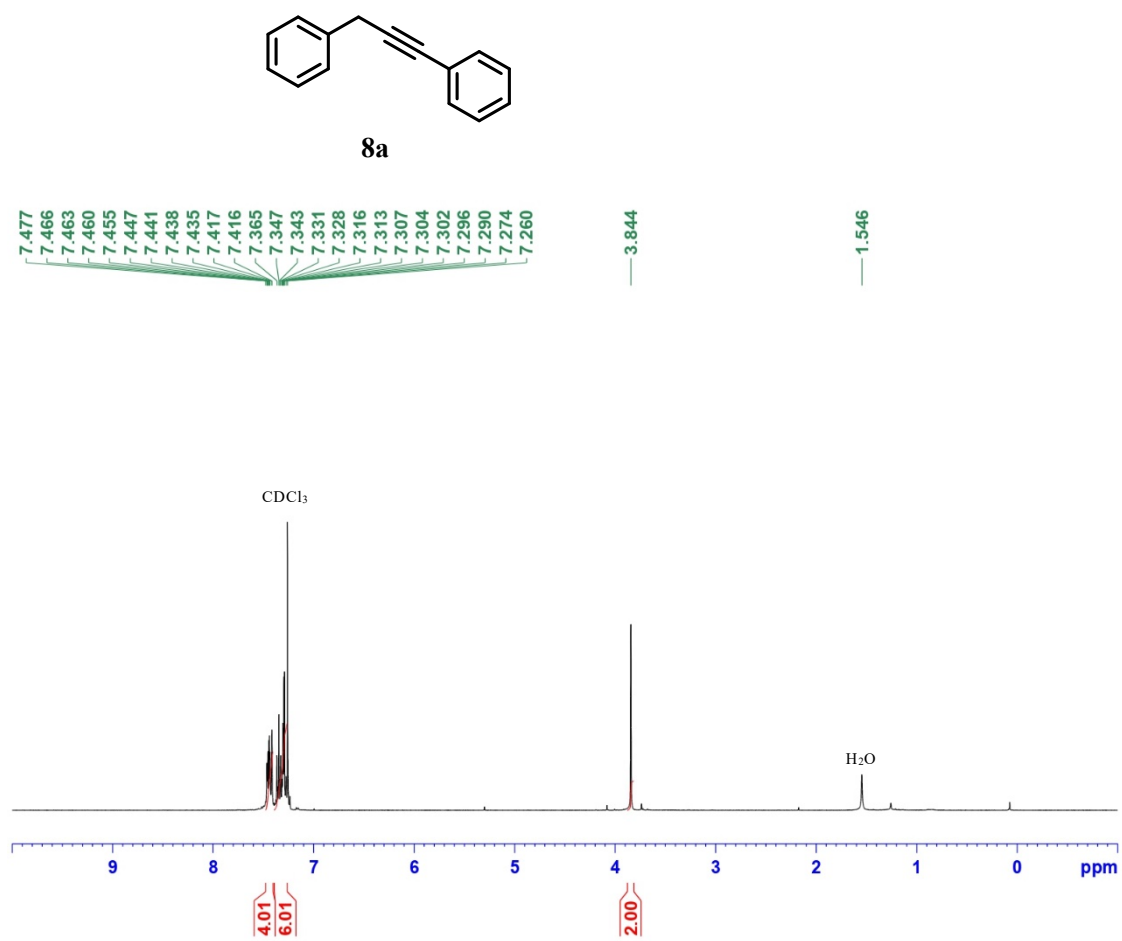




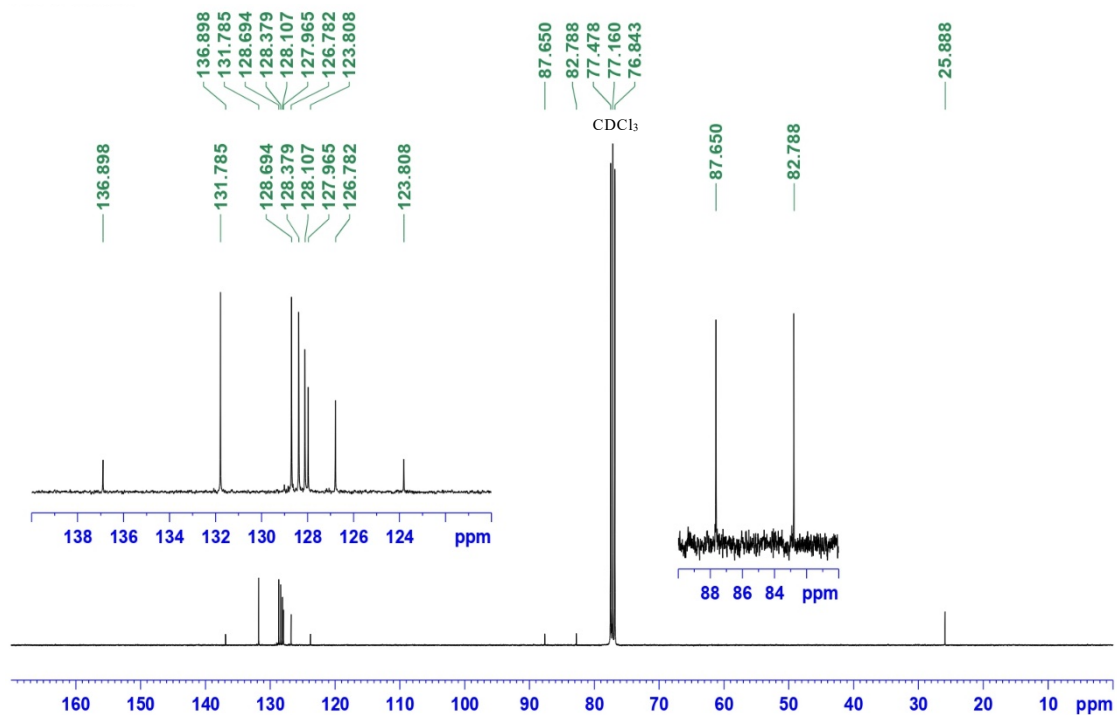
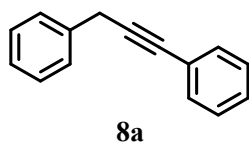
**Figure S24.** <sup>1</sup>H NMR (400 MHz) spectrum of **6** in CDCl<sub>3</sub>



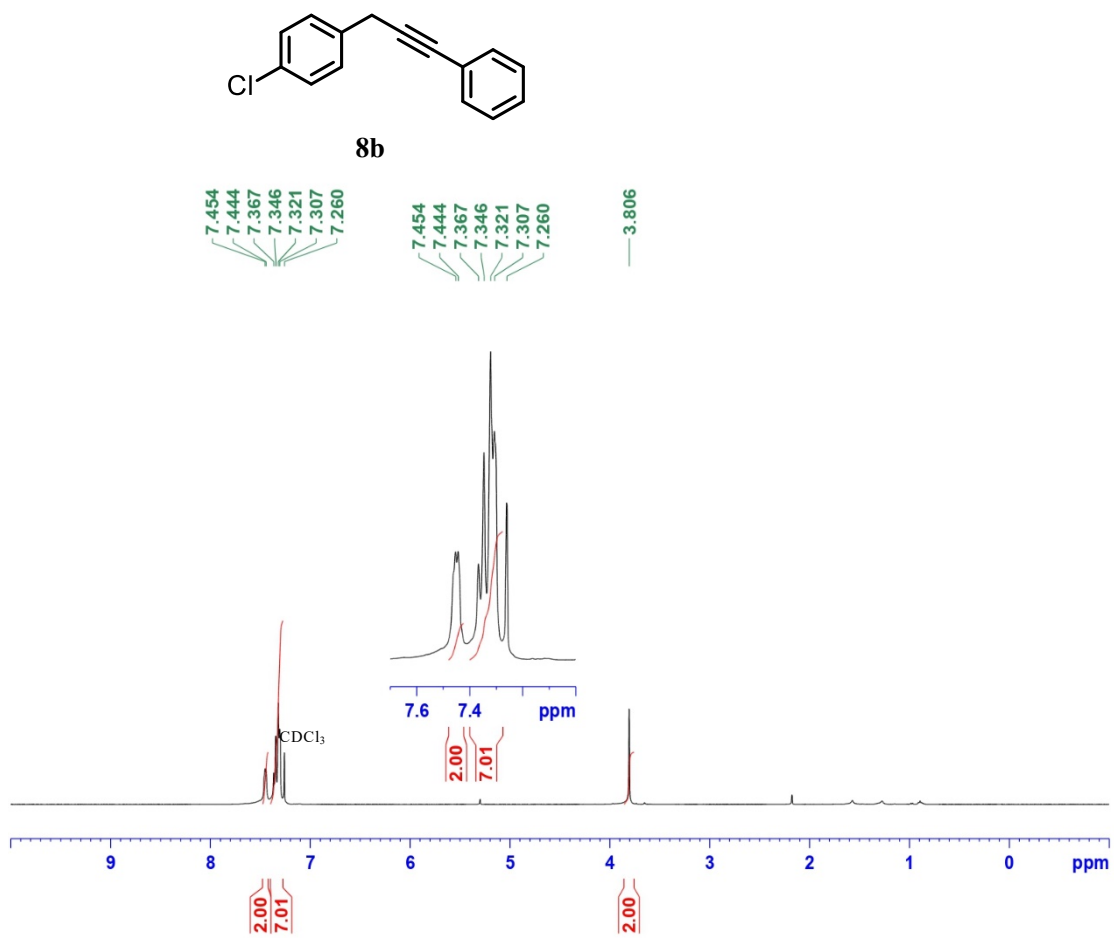
**Figure S25.** <sup>13</sup>C NMR (100 MHz) spectrum of **6** in CDCl<sub>3</sub>



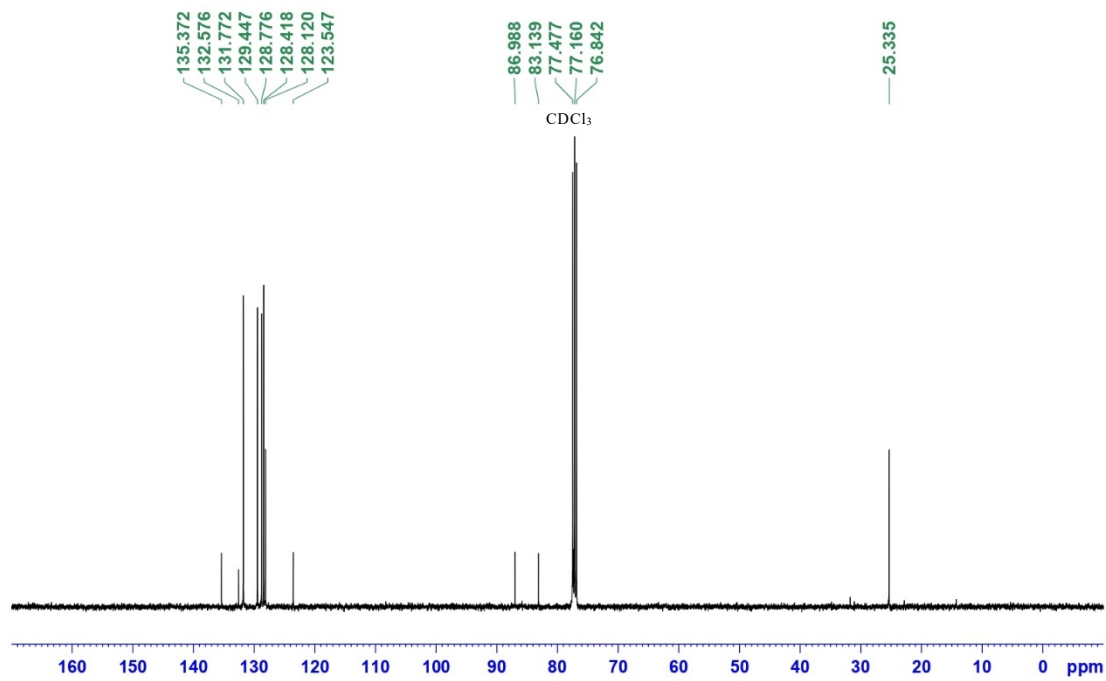
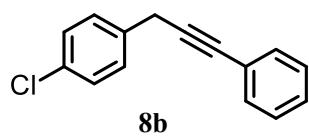
**Figure S26.** <sup>1</sup>H NMR (400 MHz) spectrum of **8a** in CDCl<sub>3</sub>



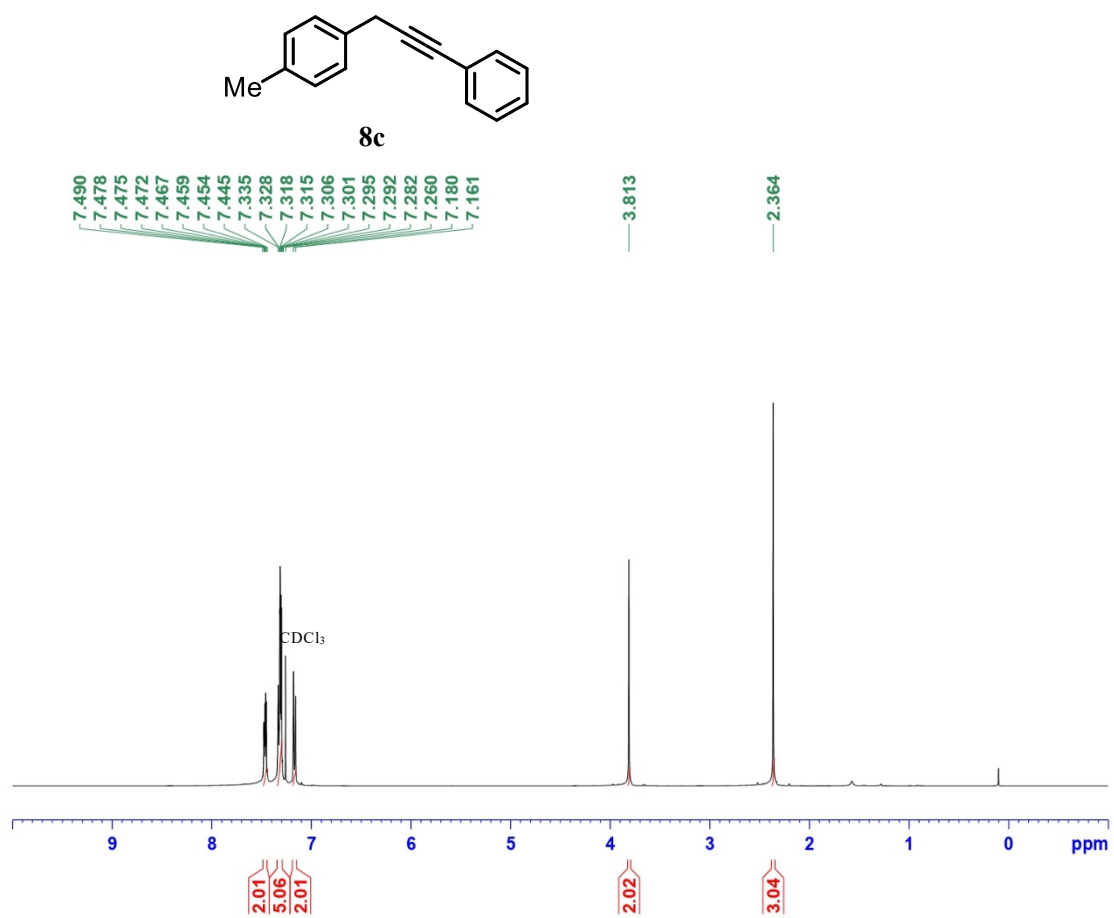
**Figure S27.** <sup>13</sup>C NMR (100 MHz) spectrum of **8a** in CDCl<sub>3</sub>



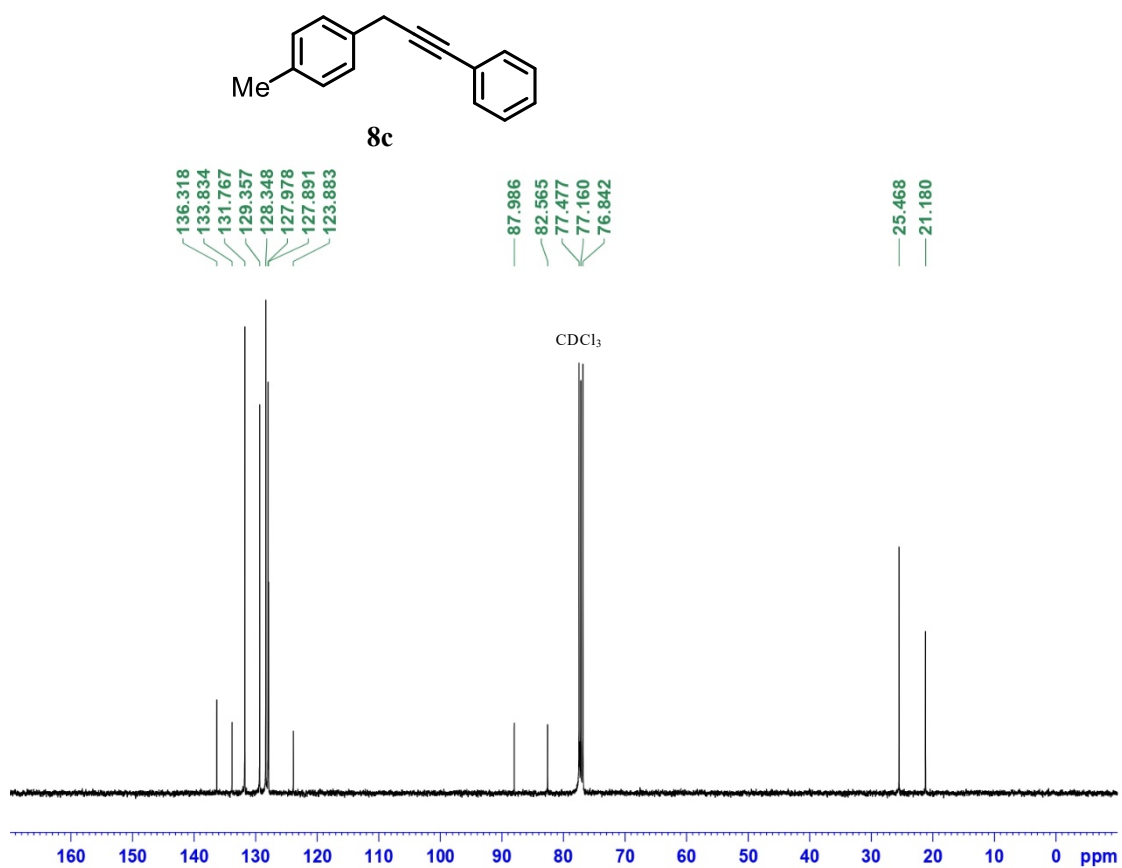
**Figure S28.** <sup>1</sup>H NMR (400 MHz) spectrum of **8b** in CDCl<sub>3</sub>



**Figure S29.** <sup>13</sup>C NMR (100 MHz) spectrum of **8b** in CDCl<sub>3</sub>.



**Figure S30.** <sup>1</sup>H NMR (400 MHz) spectrum of **8c** in CDCl<sub>3</sub>



**Figure S31.** <sup>13</sup>C NMR (100 MHz) spectrum of **8c** in CDCl<sub>3</sub>



## 12. References

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