

## Electronic Supplementary Information

### A New C-anionic Tripodal Ligand, 2-{Bis(benzothiazolyl)(methoxy)methyl}phenyl and its Bismuth Complexes

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#### Table of Contents

|  |     |
|--|-----|
| 1. General   | S2  |
| 2. Synthesis of the ligand precursor <b>5</b> (Fig. S1)  | S2  |
| 3. Formation of rearranged ligands (Scheme S1, Fig. S2)  | S3  |
| 4. Synthesis of complexes <b>9a</b> and <b>9b</b> (Figs. S3, S4)   | S5  |
| 5. Survey of the reaction conditions suitable for the lithiation of <b>5</b> (Table S1)  | S6  |
| 6. Synthesis of complex <b>6</b> (Figs. S5 – S12)  | S7  |
| 7. Synthesis of complex <b>10</b> (Figs. S13 – S16)  | S12 |
| 8. Single crystal X-ray structure analysis   | S16 |
| 9. References  | S17 |
| 10. <sup>1</sup> H and <sup>13</sup> C NMR spectra of <b>4</b> (Figs. S17, S18), <b>5</b> (Figs. S19, S20), <b>6</b> ·THF (Figs. S21, S22), <b>7a</b> (Figs. S23, S24), <b>7b</b> (Figs. S25, S26), <b>9a</b> (Figs. S27, S28), <b>9b</b> (Figs. S29, S30), and <b>10</b> (Figs. S31, S32) | S18 |

## 1. General.

All manipulations of air-sensitive materials were carried out under a nitrogen atmosphere using standard Schlenk techniques or in a glovebox. Anhydrous toluene, hexane and THF were purchased from Kanto Chemicals and degassed before use.  $\text{CDCl}_3$ ,  $\text{DMSO-}d_6$ , and  $\text{THF-}d_8$  were dried over molecular sieves and degassed. NMR spectra were recorded on Jeol LA500 spectrometer. Chemical shifts are reported in  $\delta$  (ppm) and are referenced to internal tetramethylsilane (0.0 ppm) or the (residual) solvent signals for  $^1\text{H}$  (1.72 ppm for  $\text{THF-}d_8$ ) and  $^{13}\text{C}$  (77.16 ppm for  $\text{CDCl}_3$ , 67.21 ppm for  $\text{THF-}d_8$ ).<sup>S1</sup> Coupling constants were reported in Hertz. IR spectra were recorded on a JASCO FT IR-5300 spectrophotometer. Elemental analysis was performed by the Analytical Center at the National Institute of Advanced Industrial Science and Technology.

## 2. Synthesis of the Ligand precursor 5

### Benzo[*d*]thiazol-2-yl(2-bromophenyl)methanone 3.<sup>S2</sup>

This compound was synthesized based on the reported procedure for the preparation of similar ketones.<sup>S3</sup> To a THF (90 mL) solution of benzothiazole (10.9 mL, 13.52 g, 100 mmol) was added dropwise a hexane solution of *n*BuLi (1.58 M, 69.6 mL, 110 mmol) at  $-78^\circ\text{C}$ . The mixture was stirred at the same temperature for 1 h, followed by the addition of methyl 2-bromobenzoate (23.66 g, 110 mmol) dissolved in THF (6 mL). The mixture was stirred at  $-78^\circ\text{C}$  for 2 h, gradually warmed to rt over 8 h, and continued to stir for 1 h. After the addition of water, the product was extracted with toluene. The toluene solution was dried over  $\text{Na}_2\text{SO}_4$  and concentrated under vacuum to give a yellowish crude product, which was recrystallized from a mixture of  $\text{CH}_2\text{Cl}_2$  and hexane. After the filtration, washing with hexane, and drying under vacuum, **3** was obtained as colorless needle crystals (19.64 g, 62%).

Mp.:  $102\text{--}103.5^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 499.1 MHz):  $\delta$  7.42 (dt,  $J = 1.8, 7.7$ , 1H), 7.48 (dt,  $J = 1.2, 7.5$ , 1H), 7.52–7.59 (m, 2H), 7.69–7.75 (m, 2H), 7.99–8.05 (m, 1H), 8.14–8.20 (m, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125.4 MHz):  $\delta$  120.6, 122.3, 126.0, 127.04, 127.08, 128.0, 130.7, 132.4, 133.7, 137.5, 138.0, 153.7, 165.6 (CNS), 188.3 (CO). IR (KBr): 3036, 1671, 1483, 1294, 1260, 889, 762,  $727\text{ cm}^{-1}$ .

### Bis(benzo[*d*]thiazol-2-yl)(2-bromophenyl)methanol 4.

To a THF (100 ml) solution of benzothiazole (4.68 g, 34.6 mmol) was added dropwise a hexane solution of *n*BuLi (1.58 M, 24.0 mL, 37.9 mmol) at  $-78^\circ\text{C}$ . After the mixture was stirred at this temperature for 30 min, a THF solution (80 mL) of compound **5** (12.12 g, 38.1 mmol) was added. The reaction solution was stirred at  $-78^\circ\text{C}$  for 1 h, gradually warmed to rt, and continued to stir at rt overnight. After the addition of water, the product was extracted with toluene. The toluene solution was dried over  $\text{Na}_2\text{SO}_4$  and concentrated under vacuum to give a yellowish crude product, which was recrystallized from a mixture of  $\text{CH}_2\text{Cl}_2$  and hexane. After the filtration, washing with hexane, and drying under vacuum, **4** was obtained as colorless crystals (13.91 g, 89%).

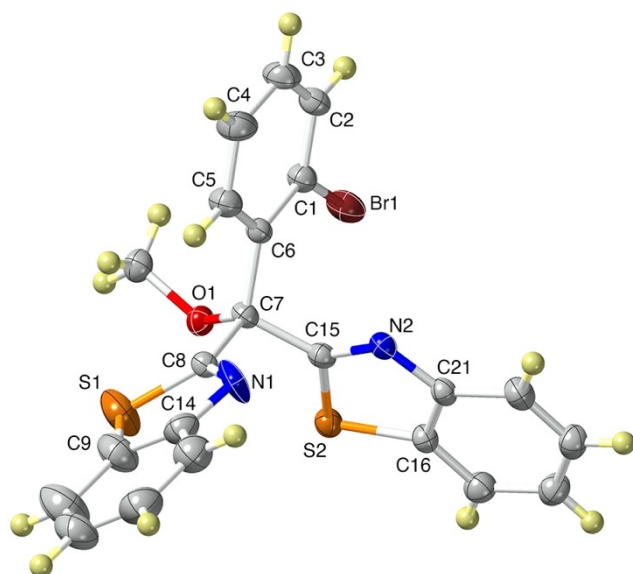
Mp.:  $162\text{--}163.3^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 499.1 MHz):  $\delta$  6.04 (s, 1H, OH), 7.13–7.18 (m, 1H), 7.20–7.27 (m, 2H), 7.39 (dt,  $J = 1.2, 7.6$ , 2H), 7.47–7.50 (dt,  $J = 1.2, 7.7$ , 2H), 7.62–7.67 (m, 1H), 7.88 (d,  $J = 7.8$ , 2H), 8.04 (d,  $J = 8.2$ , 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125.4 MHz):  $\delta$  81.8

(COH), 122.0, 123.64, 123.80, 123.85, 125.7, 126.4, 127.4, 130.65, 130.75, 135.4, 136.5, 140.8, 152.6, 174.1 (CNS). IR (KBr): 3436, 3050, 1564, 1495, 1435, 1318, 1154, 1034, 885, 758, 727  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{21}\text{H}_{13}\text{BrN}_2\text{OS}_2$ : C, 55.63; H, 2.89; N, 6.18%. Found: C, 55.51; H, 2.67; N, 5.98%.

### 2,2'-((2-bromophenyl)(methoxy)methylene)bis(benzo[*d*]thiazole) **5**.

A DMF solution of **4** (37.1 g, 81.8 mmol) was added to a NaH powder (7.5 g, 55% dispersion in paraffin, 0.17 mol, washed with hexane) in DMF (200 mL) at rt. After the mixture was stirred for 3 h,  $\text{CH}_3\text{I}$  (6.60 mL, 106 mmol) was added at rt. The mixture was stirred for 3 h at rt. Addition of  $\text{H}_2\text{O}$  (200 mL) and  $\text{Et}_2\text{O}$  (400 mL) to the mixture resulted in the separation of the product as a foam. The foamed substance was separated, washed with water, and dissolved into  $\text{CH}_2\text{Cl}_2$ . After drying over  $\text{Na}_2\text{SO}_4$ , volatiles were removed under vacuum to give a crude product as a colorless solid. Recrystallization of the crude product from a mixture of  $\text{CH}_2\text{Cl}_2$  and hexane afforded **5** as colorless crystals, 32.6 g (85.3% yield).

Mp.: 195.0-196.0  $^\circ\text{C}$  (dec).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 499.1 MHz):  $\delta$  3.45 (s, 3H), 7.29 (dd,  $J = 1.7$ , 7.6, 1H), 7.36-7.42 (m, 2H), 7.44-7.49 (m, 3H), 7.59 (dd,  $J = 1.4$ , 7.8, 1H), 7.88 (d,  $J = 8.1$ , 2H), 8.09 (d,  $J = 8.2$ , 2H), 8.14 (dd,  $J = 1.6$ , 8.0, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125.4 MHz):  $\delta$  53.9 (OCH<sub>3</sub>), 85.7 (C-OMe), 121.7, 124.2, 125.7, 126.1, 127.4, 130.7, 131.3, 135.0, 136.1, 139.3, 152.9, 171.4 (C=N). IR (KBr): 3054, 2990, 1512, 1435, 1314, 1080, 903, 758, 729  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{22}\text{H}_{15}\text{BrN}_2\text{OS}_2$ : C, 56.53; H, 3.23; N, 5.99%. Found: C, 56.53; H, 3.02; N, 5.85%.



**Fig. S1** Molecular structure of **5** determined by single crystal X-ray diffraction (thermal ellipsoids are shown at 50% probability level).

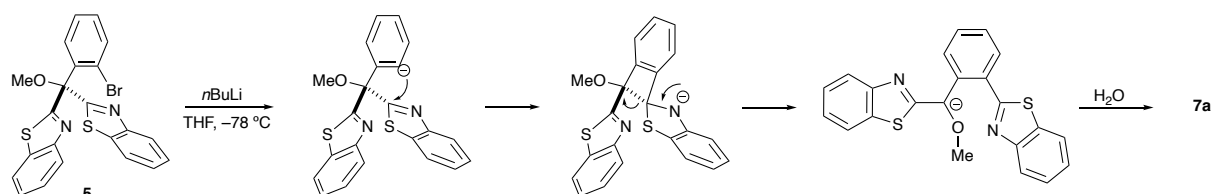
### 3. Formation of rearranged ligands

#### 2-(2-(benzo[*d*]thiazol-2-yl(methoxy)methyl)phenyl)benzo[*d*]thiazole **7a**

To a THF (6 mL) solution of **5** (234 mg, 0.50 mmol) was dropwise added a hexane solution of *n*-BuLi (1.57 M, 334  $\mu\text{L}$ , 0.52 mmol) at  $-78^\circ\text{C}$ . After the mixture was stirred at  $-78^\circ\text{C}$  for 1 h, the reaction was quenched with water at the same temperature. The mixture was gradually

warmed to rt. Aqueous work-up with CH<sub>2</sub>Cl<sub>2</sub> afforded a crude mixture, which was purified by a silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub> as an eluent) to give **7a** as a white powder. 162 mg, 83% yield.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 499.1 MHz): δ 3.53 (s, 3H, OCH<sub>3</sub>), 6.95 (s, 1H, CHOMe), 7.29-7.35 (m, 1H), 7.38-7.47 (m, 3H), 7.48-7.54 (m, 2H), 7.77 (dd, *J* = 1.2, 7.7, 1H), 7.80-7.84 (m, 2H), 7.92 (d, *J* = 7.9, 1H), 7.97 (d, *J* = 8.0, 1H), 8.11 (d, *J* = 8.2, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125.4 MHz): δ 58.0 (OCH<sub>3</sub>), 78.7 (COCH<sub>3</sub>), 121.55, 121.66, 123.49, 123.74, 125.02, 125.52, 125.88, 126.38, 128.71, 128.81, 130.82, 130.91, 132.9, 135.3, 135.8, 138.5, 153.4, 154.0, 167.1, 172.6. IR (KBr): 3061, 2992, 1514, 1435, 1314, 1084, 965, 760, 729 cm<sup>-1</sup>. HRMS *m/z* calcd for C<sub>22</sub>H<sub>16</sub>N<sub>2</sub>O<sub>5</sub><sup>+</sup> [M]<sup>+</sup>: 388.0699. Found: 388.0678.

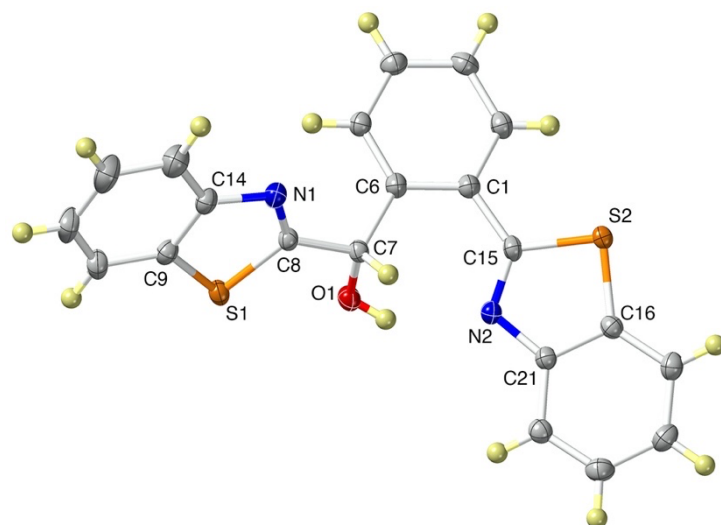


**Scheme S1.** A plausible mechanism for the formation of the rearranged compound **7a**.

### Benzo[*d*]thiazol-2-yl(2-(benzo[*d*]thiazol-2-yl)phenyl)methanol **7b**.

To a THF (10 ml) solution of **5** (0.227 g, 0.50 mmol) was dropwise added a hexane solution of *n*-BuLi (1.57 M, 668 μl, 1.0 mmol) at -78 °C. After the stirring at -78 °C for 1 h, the mixture was warmed to -15 °C and quenched with H<sub>2</sub>O at this temperature. After the usual work-up, **7b** was isolated by silica gel column chromatography (eluent, CH<sub>2</sub>Cl<sub>2</sub>) as a colorless solid, 0.125 g (67%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 499.1 MHz): δ 6.38 (d, *J* = 7.5, 1H), 7.28-7.33 (m, 1H), 7.36-7.46 (m, 3H), 7.48-7.54 (m, 3H), 7.71 (d, *J* = 7.6, 1H), 7.81-7.90 (m, 4H), 8.07 (d, *J* = 8.2, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125.4 MHz): δ 74.3 (COH), 121.74, 121.75, 123.07, 123.22, 124.8, 125.85, 125.97, 126.8, 129.2, 130.7, 131.5, 131.9, 132.6, 134.7, 135.3, 141.0, 152.6, 153.4, 169.2, 175.5.



**Fig. S2** Molecular structure of **7b** determined by single crystal X-ray diffraction (thermal ellipsoids are shown at 50% probability level).

#### 4. Synthesis of complexes **9a** and **9b**

##### Complex **9a**.

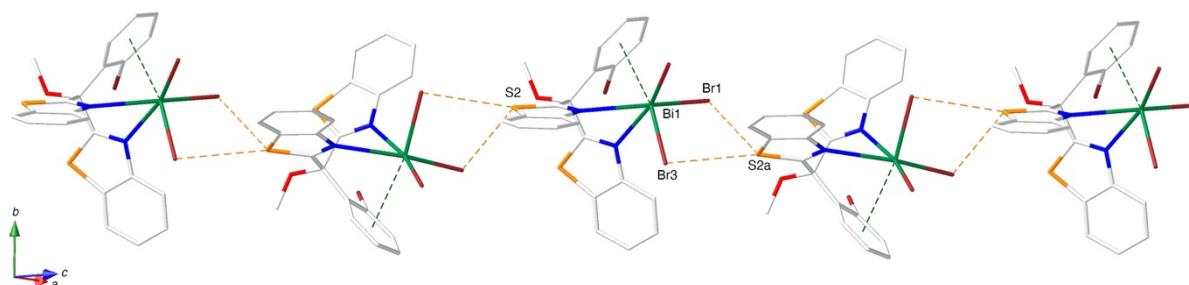
A mixture of **5** (156 mg, 0.334 mmol) and BiCl<sub>3</sub> (105 mg, 0.333 mmol) in THF (4 mL) was stirred at room temperature for 3 h. Then heptane was added to induce crystallization. After the filtration, colorless solids of **9a** was dried under vacuum (235 mg, 90% yield).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 499.1 MHz): δ 3.60 (s, 3H), 7.46 (t, *J* = 7.7, 2H), 7.52-7.59 (m, 3H), 7.64 (dt, *J* = 1.4, 7.6, 1H), 7.72 (dd, *J* = 1.5, 7.9, 1H), 7.87-7.92 (m, 3H), 8.40 (d, *J* = 8.4, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125.4 MHz): δ 55.4 (OCH<sub>3</sub>), 87.8 (COCH<sub>3</sub>), 121.7, 124.5, 126.0, 126.6, 127.3, 128.8, 132.7, 133.4, 133.8, 134.9, 137.5, 151.7 (CBr), 174.9 (C=N). Anal. Calcd for C<sub>22</sub>H<sub>15</sub>BiBrCl<sub>3</sub>N<sub>2</sub>OS<sub>2</sub>: C, 33.76; H, 1.93; N, 3.58%. Found: C, 33.95; H, 1.93; N, 3.40%.

##### Complex **9b**.

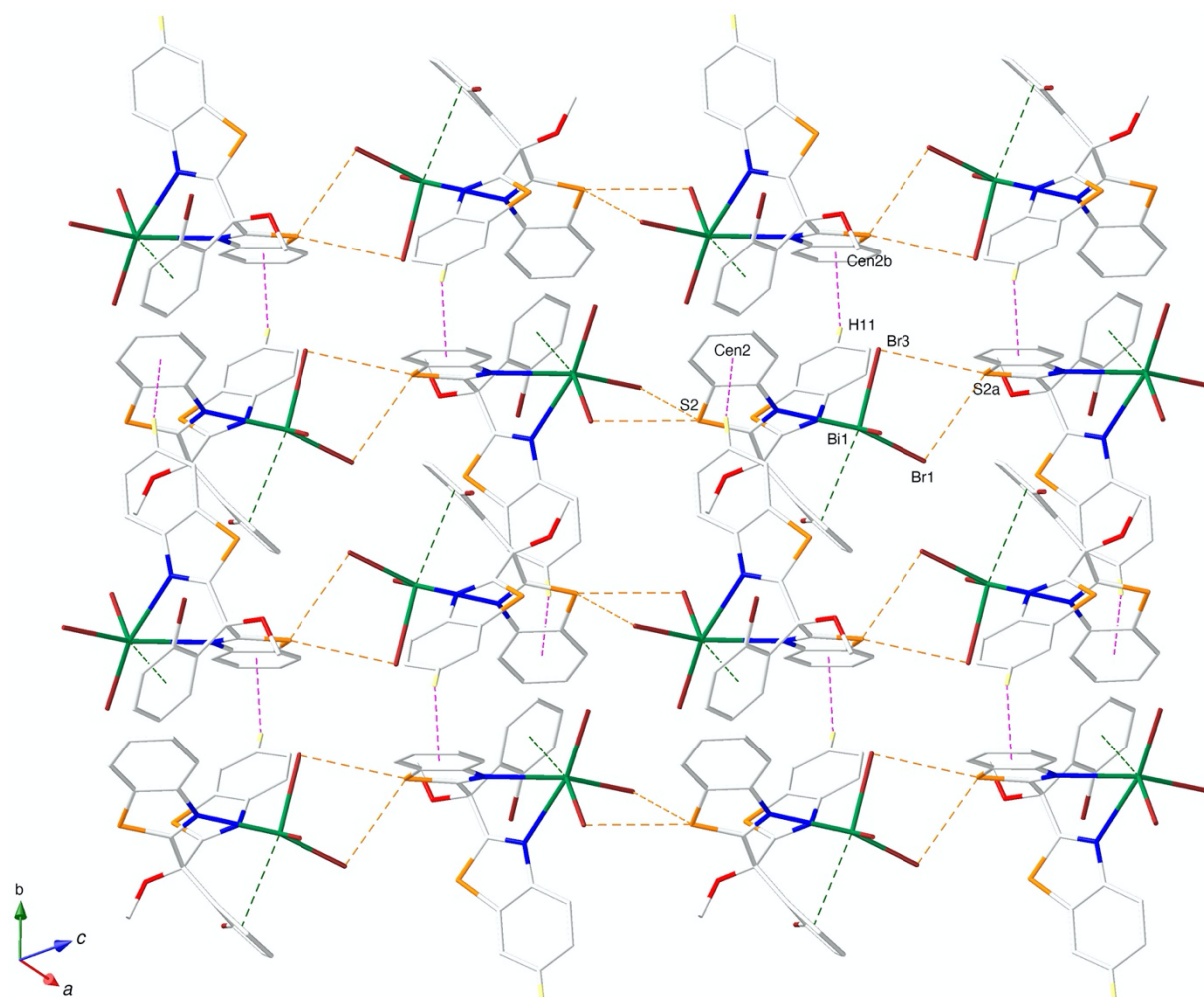
A mixture of **5** (156 mg, 0.334 mmol) and BiBr<sub>3</sub> (150 mg, 0.334 mmol) in THF (4 mL) was stirred at room temperature for 3 h. Then heptane was added to induce crystallization. After the filtration, colorless solids of **9b** was dried under vacuum (290 mg, 95% yield).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 499.1 MHz): δ 3.59 (s, 3H), 7.46 (t, *J* = 7.6, 2H), 7.52-7.58 (m, 3H), 7.68, (dt, *J* = 1.3, 7.6, 1H), 7.72 (dd, *J* = 1.0, 7.8, 1H), 7.86-7.92 (m, 3H), 8.38 (d, *J* = 8.3, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125.4 MHz): δ 55.4 (OCH<sub>3</sub>), 87.8 (COCH<sub>3</sub>), 121.7, 125.0, 125.9, 126.6, 127.2, 129.0, 132.4, 133.4, 133.6, 134.6, 137.5, 151.8 (CBr), 174.6 (C=N). Anal. Calcd for C<sub>22</sub>H<sub>15</sub>BiBr<sub>4</sub>N<sub>2</sub>OS<sub>2</sub>: C, 28.84; H, 1.65; N, 3.06%. Found: C, 29.15; H, 1.65; N, 2.75%.



**Fig. S3** 1D arrangement of complex **9b** in the crystal through intermolecular S···Br chalcogen bonds (S2···Br1 (3.5456(9) Å) and S2···Br3 (3.6120(9) Å)). Hydrogen atoms are omitted for clarity.

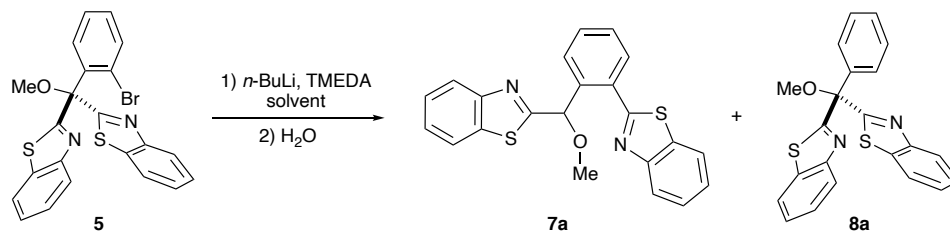
Symmetry transformations:  $a = 1/2 + x$ ,  $1/2 - y$ ,  $1/2 + z$ .



**Fig. S4** 2D arrangement of complex **9b** in the crystal through intermolecular S $\cdots$ Br chalcogen bond and intermolecular C–H $\cdots$  $\pi$  interaction (C11–H11 $\cdots$ Cen2, 2.60 Å). Hydrogen atoms except for H11 are omitted for clarity. Symmetry transformations: a = 1/2 + x, 1/2 – y, 1/2 + z. b = 1 1/2 – x, 1/2 + y, 1/2 – z.

## 5. Survey of the reaction conditions suitable for the lithiation of **5**

Table S1. Survey of the reaction conditions suitable for the lithiation of **5**



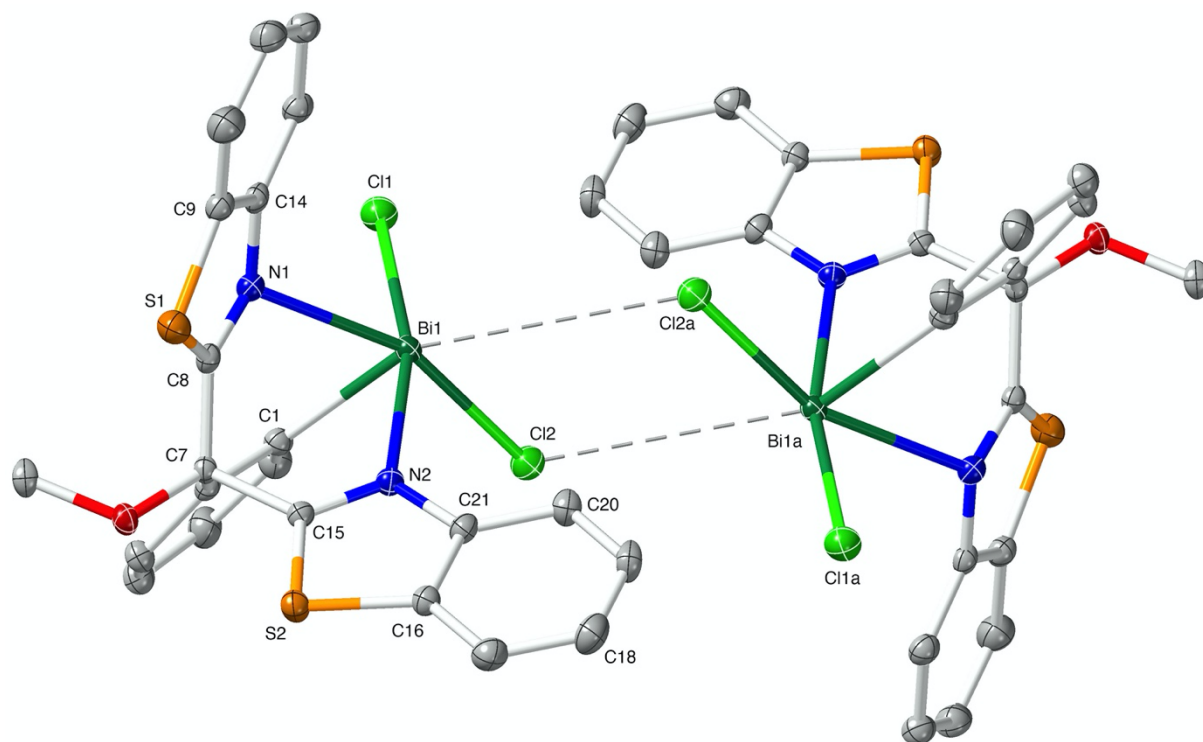
| Entry | Ratio<br>TMEDA:5:nBuLi | Temp<br>/°C | Time<br>/min | Solvent | Conversion of <b>5</b><br>/% | ratio<br><b>7a:8a</b> |
|-------|------------------------|-------------|--------------|---------|------------------------------|-----------------------|
| 1     | 1:1:1                  | –78         | 60           | toluene | 73                           | 91:9                  |
| 2     | 8:1:1.3                | –78         | 60           | THF     | 100                          | 93:7                  |
| 3     | 2:1:1.3                | –95         | 60           | THF     | 100                          | 43:57                 |

|    |           |      |     |           |     |       |
|----|-----------|------|-----|-----------|-----|-------|
| 4  | 0:1:1.03  | -104 | 30  | THF       | 81  | 0:100 |
| 5  | 1:1:1.18  | -104 | 30  | THF       | 99  | 7:93  |
| 6  | 2:1:1.3   | -104 | 60  | THF       | 100 | 2:98  |
| 7  | 0:1:1.03  | -104 | 120 | THF       | 88  | 25:75 |
| 8  | 2:1:1.03  | -104 | 120 | THF       | 88  | 5:95  |
| 9  | 2:1:1.11  | -104 | 180 | THF       | 93  | 29:71 |
| 10 | 0:1: 1.18 | -108 | 30  | THF       | 62  | 2:98  |
| 11 | 0:1: 1.03 | -108 | 120 | THF       | 90  | 10:90 |
| 12 | 0:1:1.18  | -108 | 360 | THF       | 99  | 35:65 |
| 13 | 2:1:1.3   | -114 | 240 | Ether     | 21  | 0:100 |
| 14 | 2:1:1.3   | -114 | 540 | Ether+THF | 22  | 0:100 |

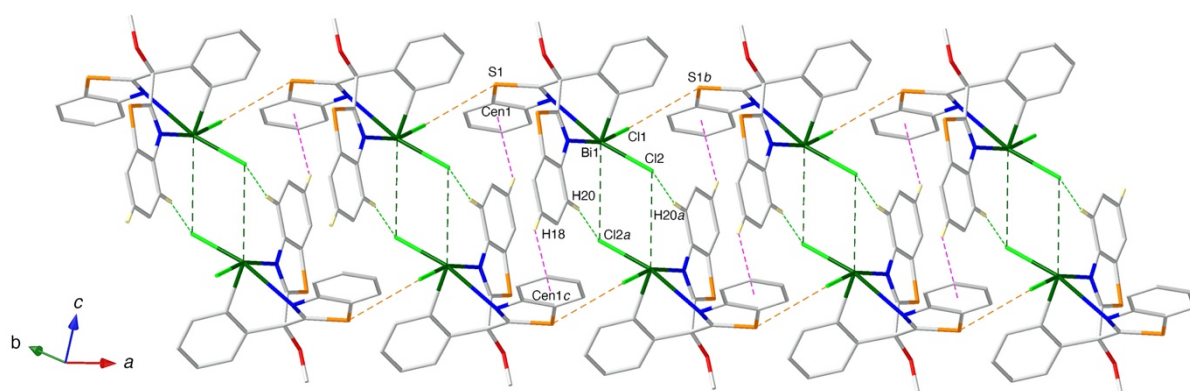
## 6. Synthesis of complex 6

To a THF solution (30 mL) of **5** (2.0 g, 4.3 mmol) and *N,N,N',N'*-tetramethylethylenediamine (646  $\mu$ L, 4.3 mmol) was dropwise added a hexane solution of *n*BuLi (1.58 M, 2.8 mL, 4.4 mmol) at  $-104$  °C (cyclohexene cooling bath). After the stirring at  $-104$  °C for 30 min, BiCl<sub>3</sub> powder (2.0 g, 6.3 mmol) was quickly added to the mixture. The mixture was stirred at  $-104$  °C for 2 h and then warmed naturally to rt within 10 h. Then BiCl<sub>3</sub> powder (1.3 g, 4.1 mmol) was added. The mixture was refluxed for 1 h in an oil bath heated at 75 °C with stirring. Volatiles were removed under vacuum and the residue was washed with water repeatedly. Complex **5** was obtained by the extraction of the residue with THF and recrystallization with a mixture of THF and toluene as colorless crystals, which contain one molecule of THF as a co-crystallization solvent (2.1 g, 66%).

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 499.1 MHz):  $\delta$  3.64 (s, 3H, OCH<sub>3</sub>), 7.35 (dt,  $J = 1.1, 7.6$ , 1H), 7.52-7.62 (m, 3H), 7.66 (dt,  $J = 1.2, 7.7$ , 2H), 7.85 (dt,  $J = 1.1, 7.4$ , 1H), 8.25 (d,  $J = 8.0$ , 2H), 8.33 (2H, d,  $J = 8.2$ ), 9.67 (dd,  $J = 1.2, 7.5$ , 1H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 125.4 MHz):  $\delta$  55.2 (OCH<sub>3</sub>), 92.0 (C-OMe), 122.7, 123.6, 126.5, 126.8, 128.0, 128.4, 133.6, 134.9, 140.5, 147.3, 150.3, 170.3, 215.6 (C*Bi*). IR (KBr): 3057, 2974, 1496, 1435, 1317, 1276, 1245, 1084, 906, 758, 730 cm<sup>-1</sup>. Anal. Calcd for C<sub>22</sub>H<sub>15</sub>BiCl<sub>2</sub>N<sub>2</sub>OS<sub>2</sub>·C<sub>4</sub>H<sub>8</sub>O: C, 42.23; H, 3.14; N, 3.79%. Found: C, 42.38; H, 3.05; N, 3.54%.

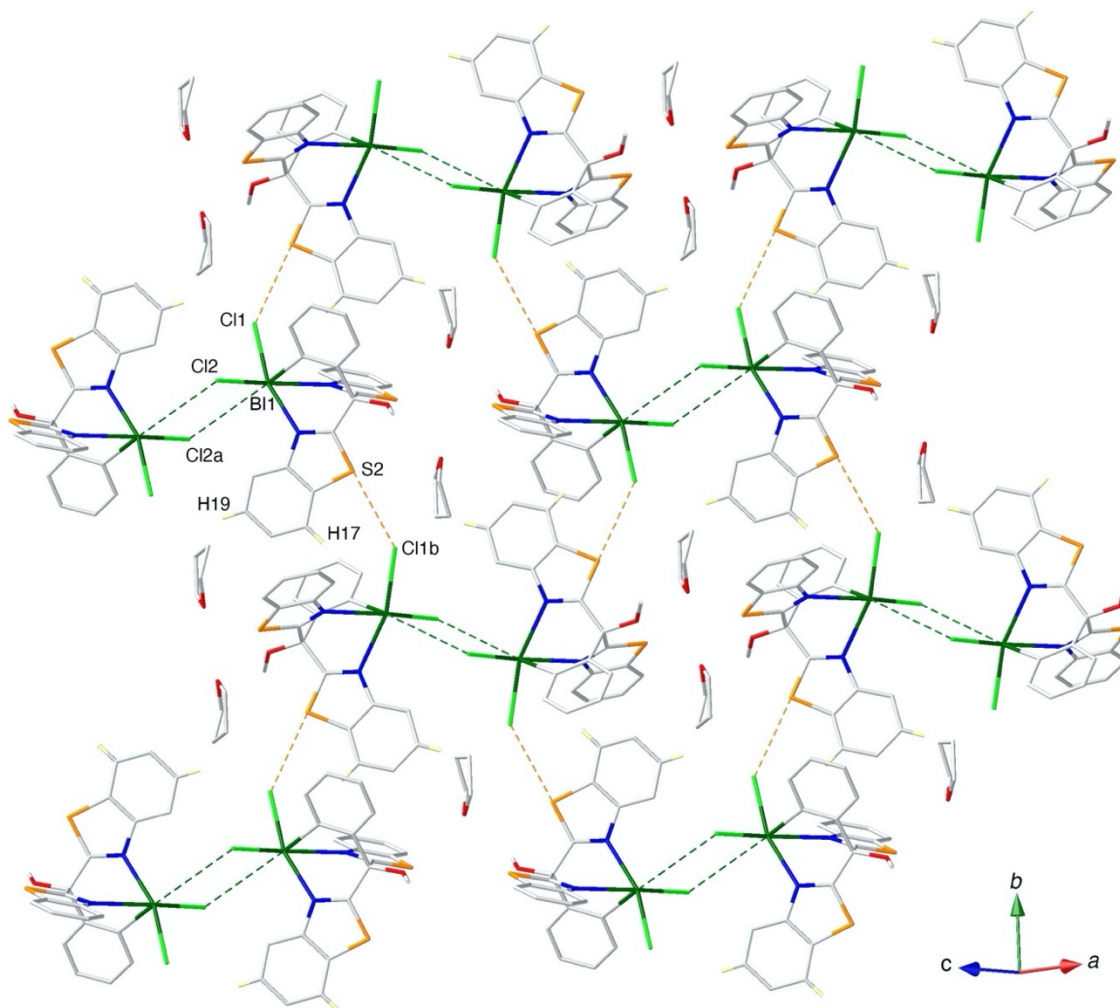


**Fig. S5** Dimeric structure of complex **6** in the crystal (thermal ellipsoids are shown at 50% probability level). Hydrogen atoms are omitted for clarity. Symmetry transformations:  $a = 1 - x, 1 - y, 2 - z$ .

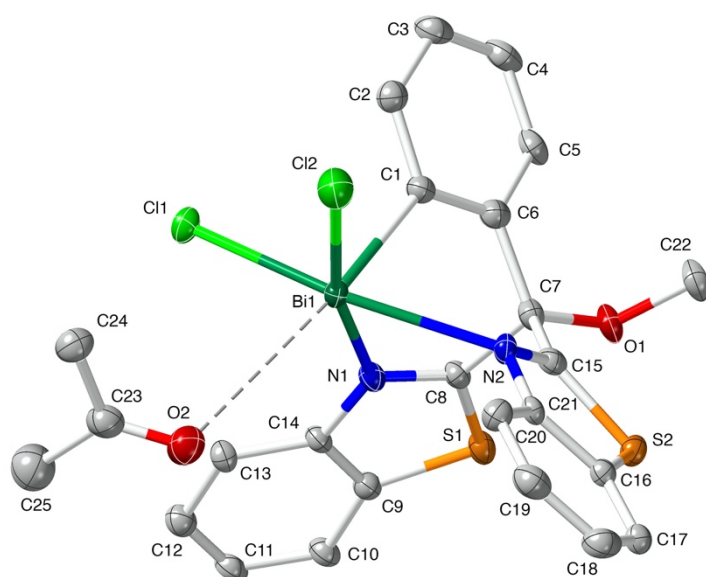


**Fig. S6** 1D arrangement of the dimer of complex **6** in the crystal along the  $a$  axis through intermolecular  $S \cdots Cl$  chalcogen bond  $S1 \cdots Cl1$  (3.385(1) Å),  $Cl \cdots H$  interaction ( $Cl2 \cdots H20$ , 2.88 Å), and  $C-H \cdots \pi$  interaction ( $H18 \cdots Cen1$ , 2.74 Å,  $a' = 12.7^\circ$ ). Hydrogen atoms except for H18 and H20 are omitted for clarity. Symmetry transformations:  $a = 1 - x, 1 - y, 2 - z$ .  $b = -1 + x, y, z$ .  $c = 2 - x, 1 - y, 2 - z$ .



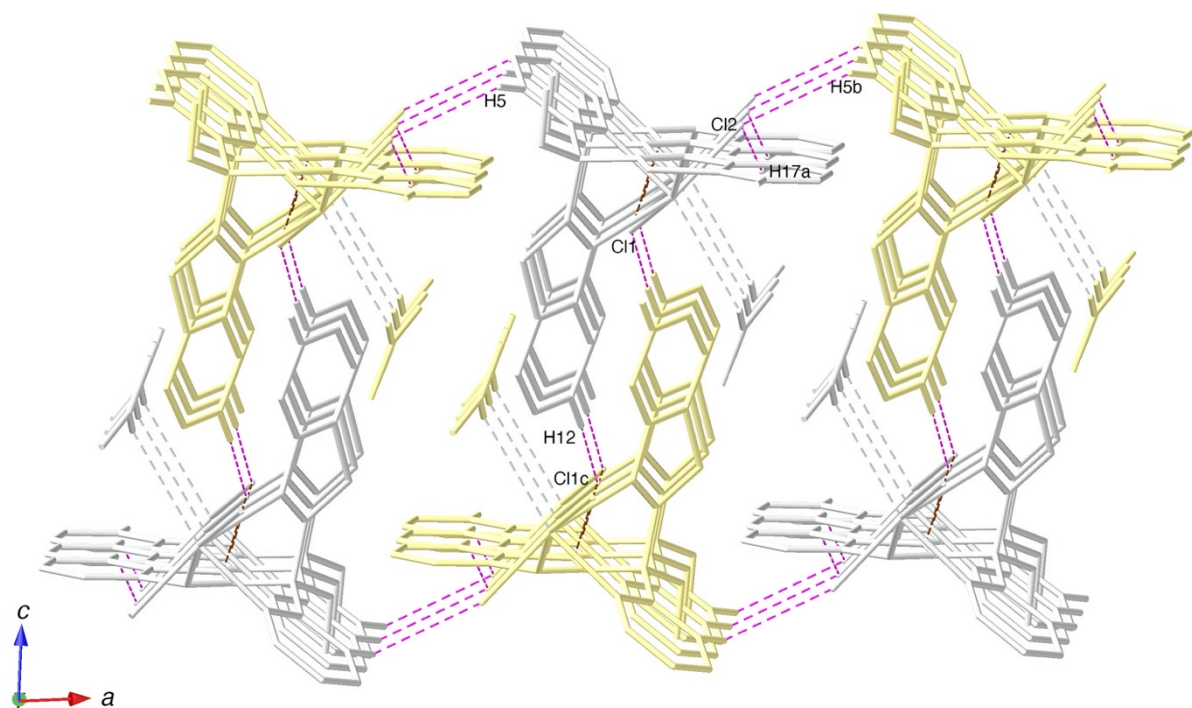


**Fig. S7** 2D arrangement of the dimer of complex **6**·THF in the crystal through intermolecular S···Cl chalcogen bond S2···Cl1 (3.4414 (25) Å). Hydrogen atoms except for H17 and H19 are omitted for clarity. Symmetry transformations: a = 1 - x, 1 - y, 2 - z. b = 1/2 - x, -1/2 + y, 1 1/2 - z.

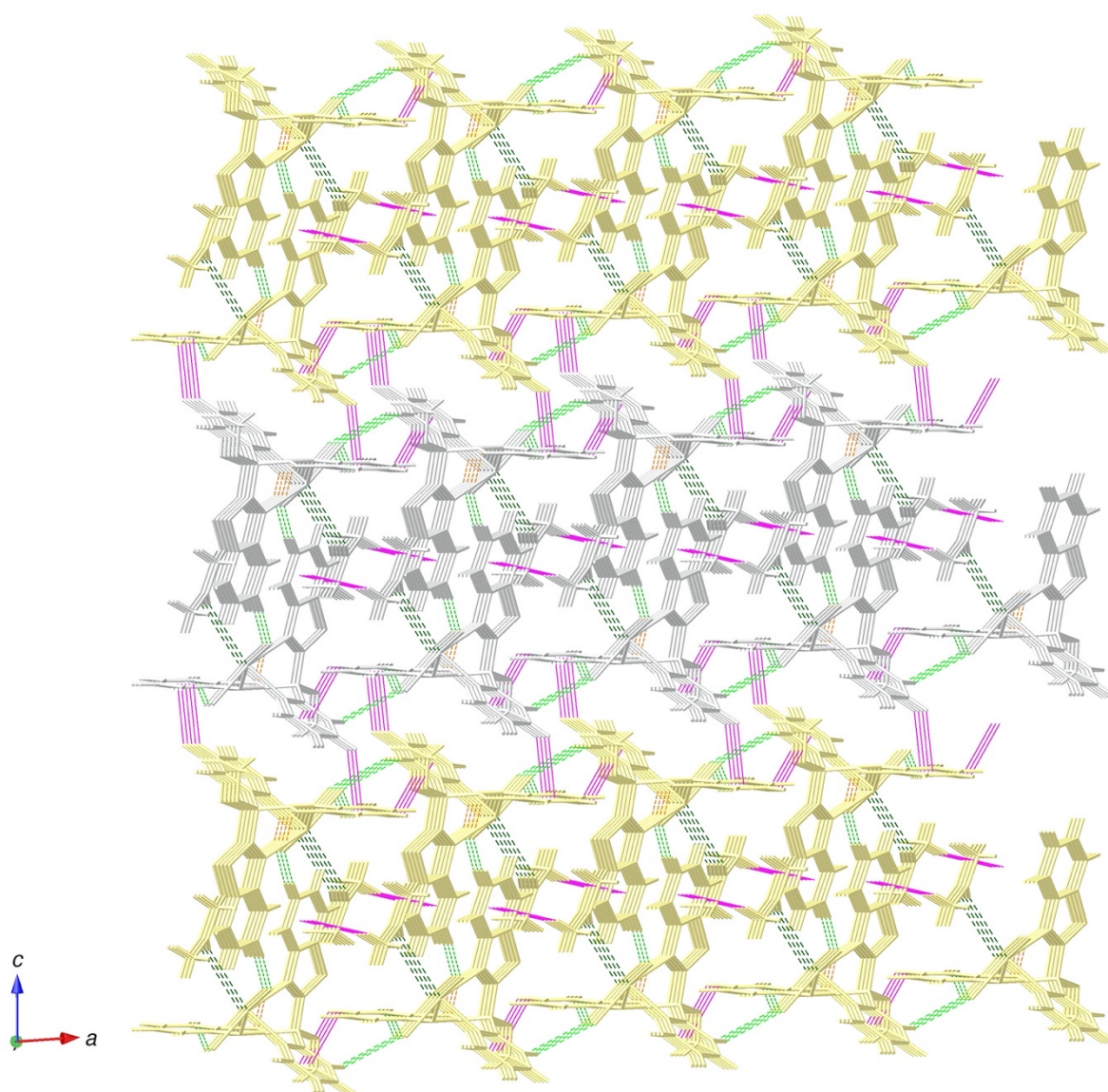


**Fig. S8** Structure of complex **6**·acetone (thermal ellipsoids are shown at 50% probability level). Hydrogen atoms are omitted for clarity.





**Fig. S11** 2D bilayer arrangement of 1D chain of complex **6**·acetone in the crystal through intermolecular C–H···Cl interactions (broken lines in pink). Hydrogen atoms except for H5, H12 and H17 are omitted for clarity. Symmetry transformations:  $a = x, -1 + y, z$ ;  $b = -1 + x, y, z$ ;  $c = 1 - x, -y, 1 - z$ .

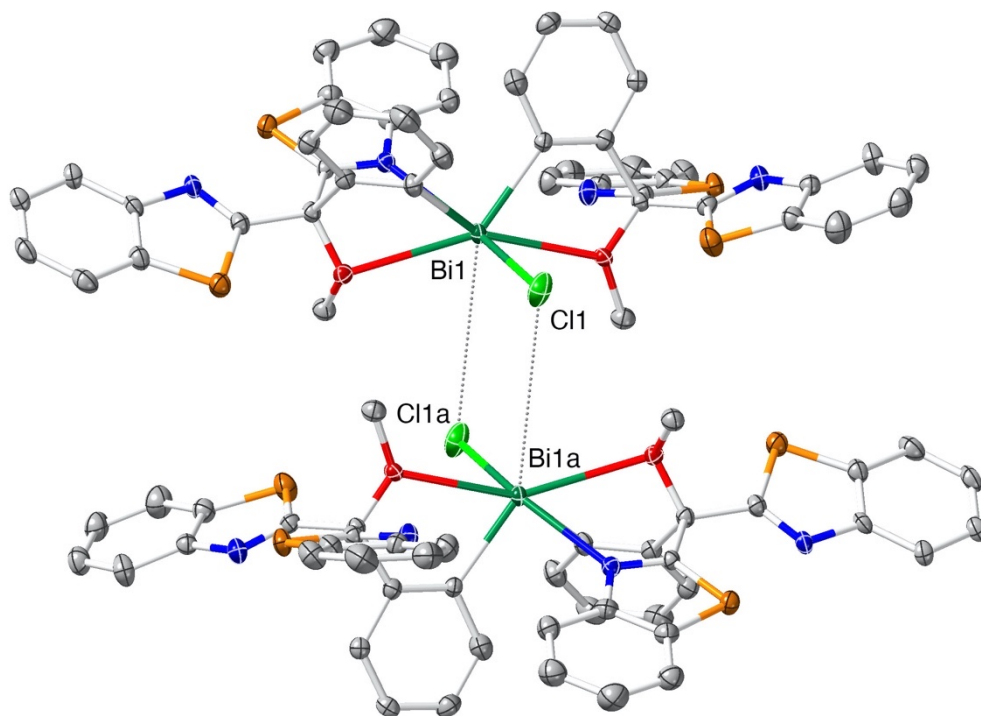


**Fig. S12** Connection of 2D bilayers of complex **6**·acetone in the crystal through the intermolecular C–H··· $\pi$  interactions (lines in pink).

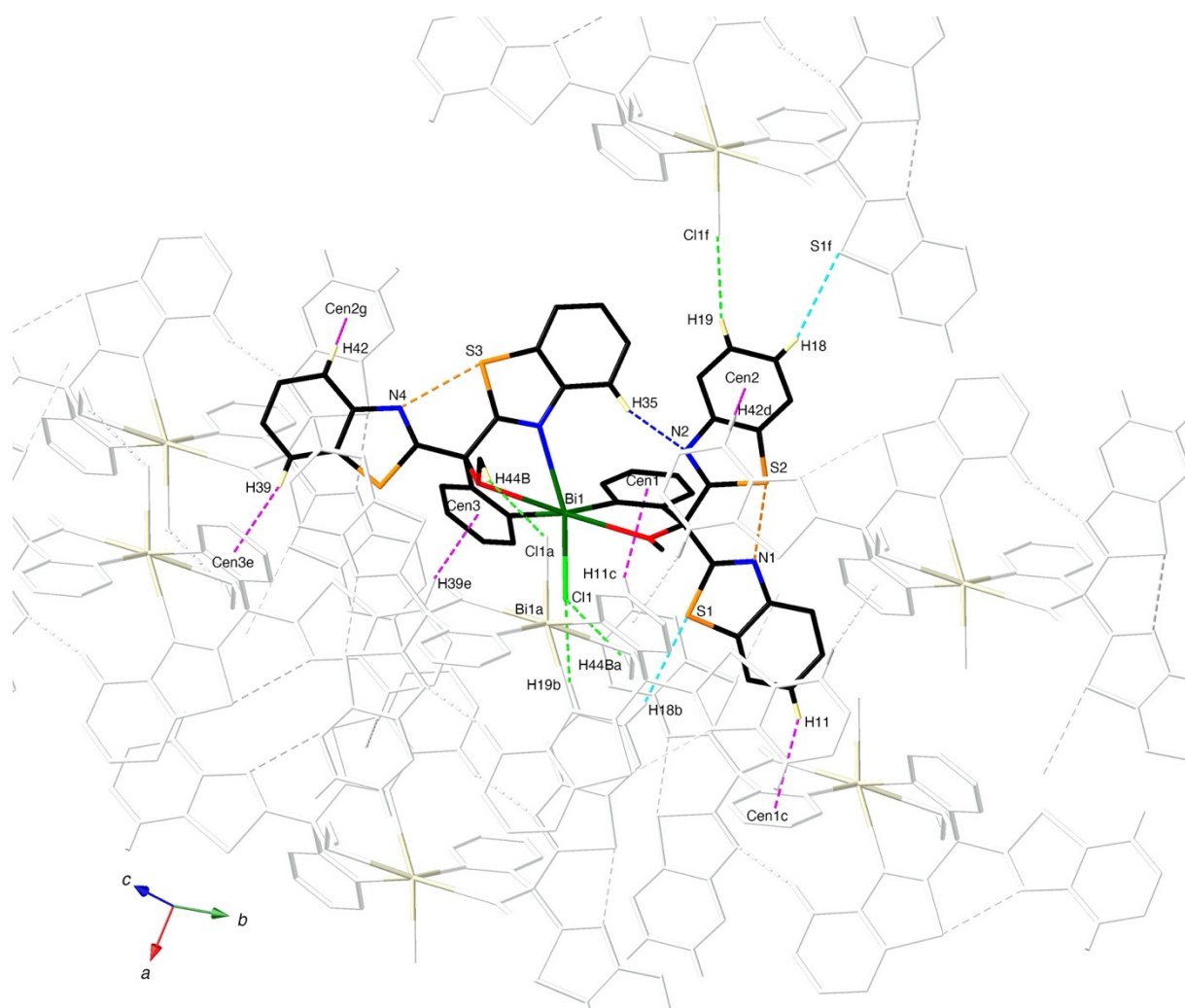
## 7. Synthesis of complex **10**

To a THF solution (60 mL) of **5** (1.00 g, 2.14 mmol) and *N,N,N',N'*-tetramethylethylenediamine (0.70 mL, 4.7 mmol) was dropwise added a hexane solution of *n*-BuLi (1.58 M, 1.5 mL, 2.4 mmol) at  $-104\text{ }^{\circ}\text{C}$ . After the stirring at  $-104\text{ }^{\circ}\text{C}$  for 30 min,  $\text{BiCl}_3$  powder (0.69 g, 2.2 mmol) was quickly added to the reaction mixture. The mixture was stirred at  $-104\text{ }^{\circ}\text{C}$  for 2 h and then warmed naturally to rt within 10 h. Volatiles were removed under vacuum and the residue was washed with water ( $5 \times 10\text{ mL}$ ). The residue was extracted with  $\text{CHCl}_3$  (50 mL). The extract was washed with saturated aqueous  $\text{NH}_4\text{Cl}$  solution, dried over  $\text{Na}_2\text{SO}_4$ , and removal of the solvent afforded complex **10** as a colorless solid, 1.15 g (80%).  $^1\text{H}$  NMR (THF- $d_3$ , 499.1 MHz):  $\delta$  3.68 (s, 6H), 7.13 (ddd,  $J = 1.4, 7.2, 7.9$ , 2H), 7.26 (dt,  $J = 1.2, 7.3$ , 2H), 7.28-7.38(m, 4H), 7.40-7.55 (m, 6H), 7.86 (d,  $J = 7.8$ , 2H), 7.95 (d,  $J = 7.9$ , 2H), 8.05 (d,  $J = 8.1$ , 2H), 8.18 (d,  $J = 7.8$ , 2H), 8.83 (dd,  $J = 1.2, 7.5$ , 2H).  $^{13}\text{C}$  NMR (THF-

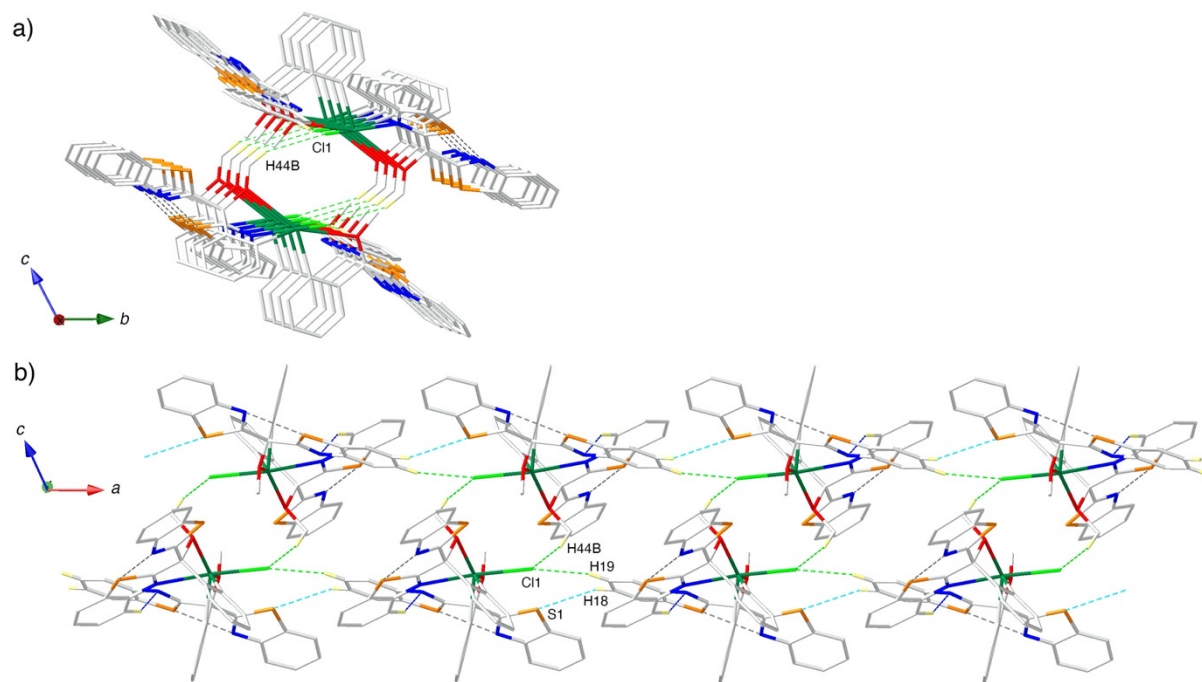
$d_8$ , 125.4 MHz):  $\delta$  54.4 (OCH<sub>3</sub>), 91.3 (C-OMe), 122.41, 122.52, 124.27, 124.48, 126.41, 126.73, 127.7, 128.8, 129.8, 132.4, 137.00, 137.31, 142.5, 149.1, 152.72, 152.99, 171.8 (C=N), 189.8 (C=O). IR (KBr): 3060, 2993, 1455, 1433, 1315, 1072, 908, 756, 727 cm<sup>-1</sup>. Anal. Calcd for C<sub>44</sub>H<sub>30</sub>BiClN<sub>4</sub>O<sub>2</sub>S<sub>4</sub>: C, 51.84; H, 2.97; N, 5.50%. Found: 52.05; H, 2.88; N, 5.06%.



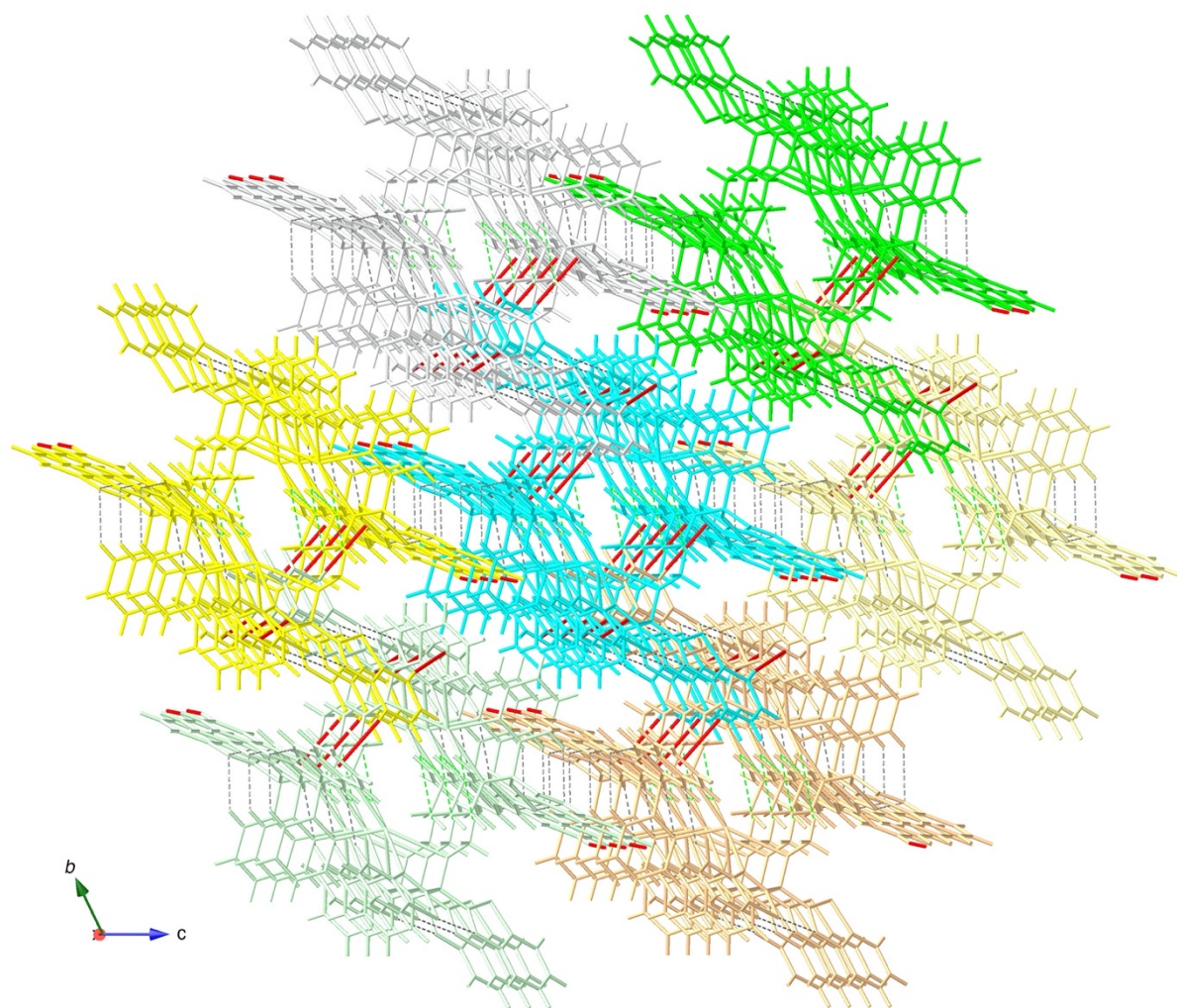
**Fig. S13** Dimeric arrangement of complex **10** in the crystal (Bi1 $\cdots$ Cl1a, 4.4504(16) Å). Hydrogen atoms are omitted for clarity. Symmetry transformations: a = 2 - x, 2 - y, 1 - z.



**Fig. S14** Various inter- and intramolecular interactions of complex **10** in the crystal. Orange broken line,  $N \cdots S$ ; light green broken line,  $C-H \cdots Cl$ ; light blue broken line,  $C-H \cdots S$ ; blue broken line,  $C-H \cdots N$ ; pink broken line,  $C-H \cdots \pi$ . Hydrogen atoms except for H11, H18, H19, H35, H39, H42 and H44B are omitted for clarity. Symmetry transformations:  $a = 2 - x, 2 - y, 1 - z$ ;  $b = 1 + x, y, z$ ;  $c = 2 - x, 2 - y, 1 - z$ ;  $d = x, 1 + y, z$ ;  $e = 2 - x, 1 - y, 1 - z$ ;  $f = -1 + x, y, z$ ;  $g = x, -1 + y, z$



**Fig. S15** 1D columnar arrangement of complex **10** in the crystal through C–H $\cdots$ Cl (C19–H19 $\cdots$ Cl1 and C44–H44B $\cdots$ Cl1) and C–H $\cdots$ S (C18–H18 $\cdots$ S1) interactions. Hydrogen atoms except for H18, H19 and H44B are omitted for clarity. a) A view from *a* axis. b) A view from *b* axis.



**Fig. S16** 3D connection of complex **10** in the crystal. 1D columns shown in Fig. S15 are further connected through C–H··· $\pi$  interactions (red lines).

### 8. Single crystal X-ray structure analysis

Single crystals of **5**, **6**, **6**·THF, **6**·acetone, **7b**, **9b** and **10** were covered with paratone-8236 oil and mounted on a glass fiber. Data collection was performed on a Bruker Smart Apex CCD diffractometer (Mo K $\alpha$  radiation, graphite monochromator). Data were corrected for absorption. Structure solution and refinement were performed using Olex2 software package<sup>S4</sup> with SHELXT and SHELXL programs.<sup>S5</sup>

CCDC 2073386–2073391 and 2073586 contain the supplementary crystallographic data for **5**, **6**, **6**·THF, **6**·acetone, **7b**, **9b** and **10**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).



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- S3 H Chikashita and K Itoh, *Heterocycles*, 1985, **29**, 295-300.
- S4 Olex2 1.3: O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339.
- S5 Shelxl Version 2018/3: G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112.

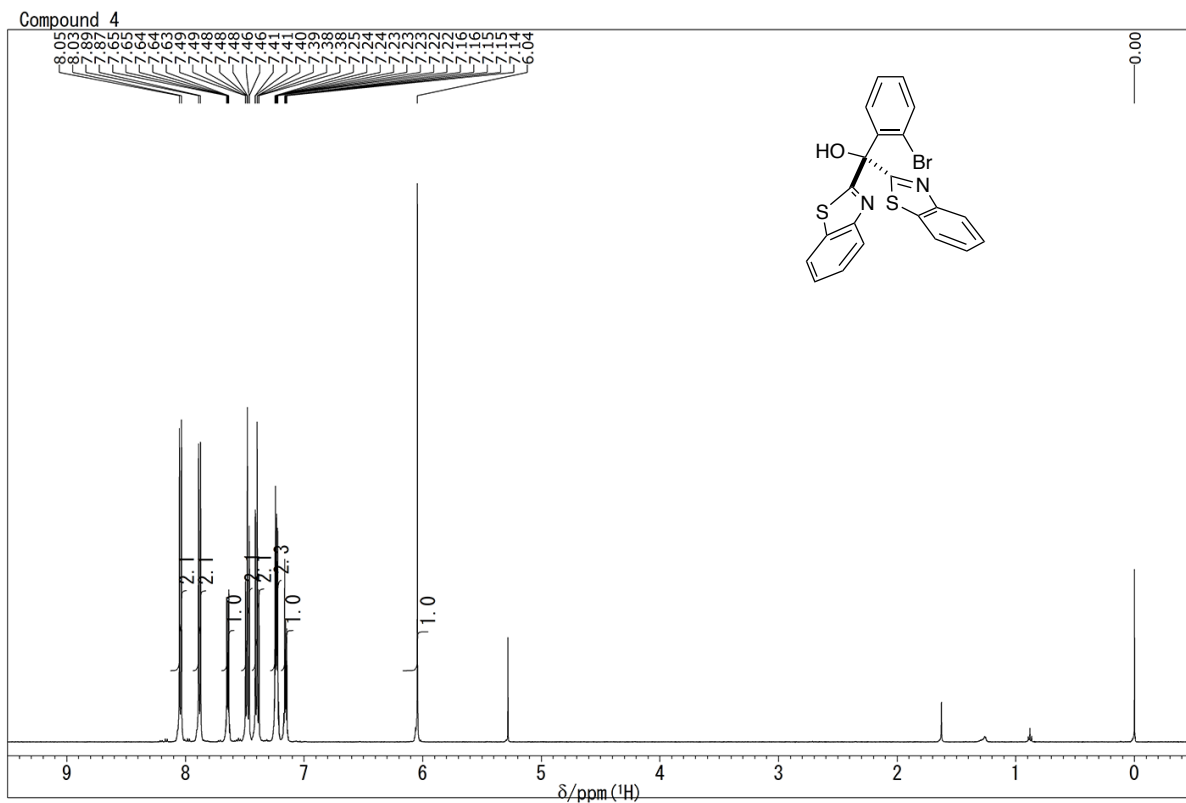


Fig. S17  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 499.1 MHz) spectrum of compound 4.

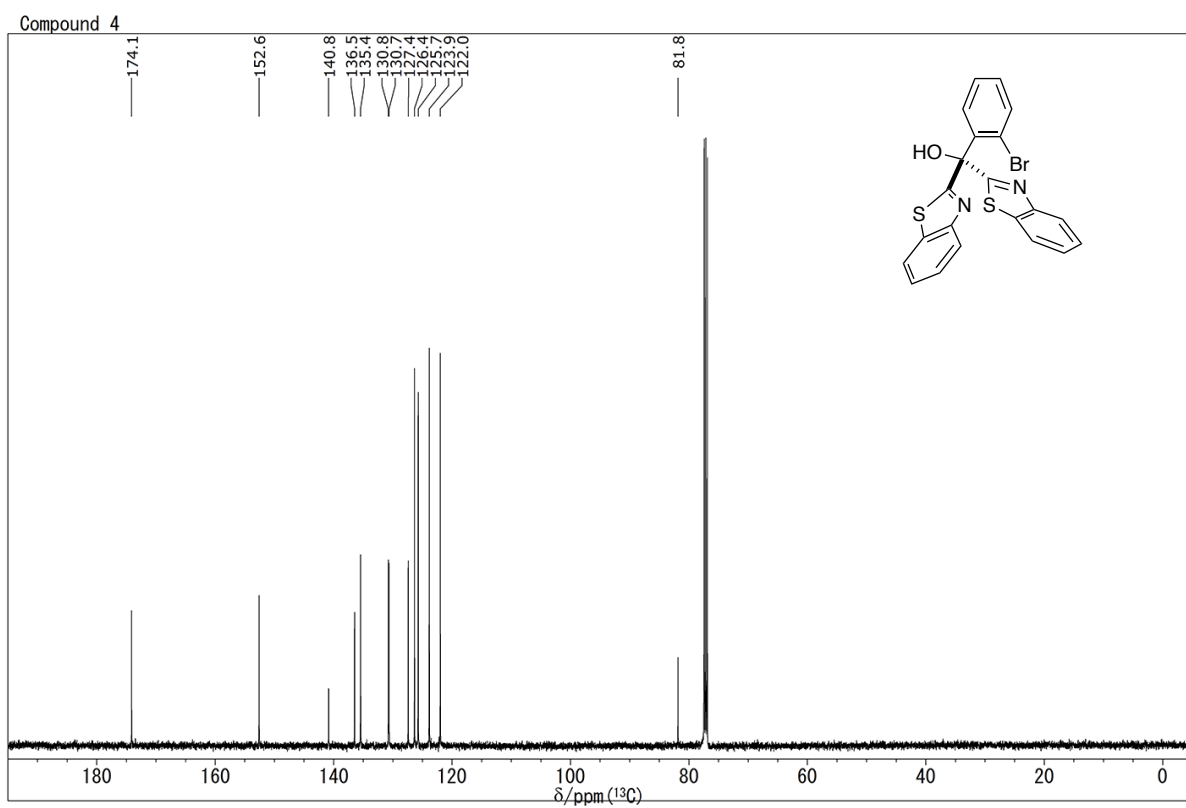


Fig. S18  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125.4 MHz) spectrum of compound 4.

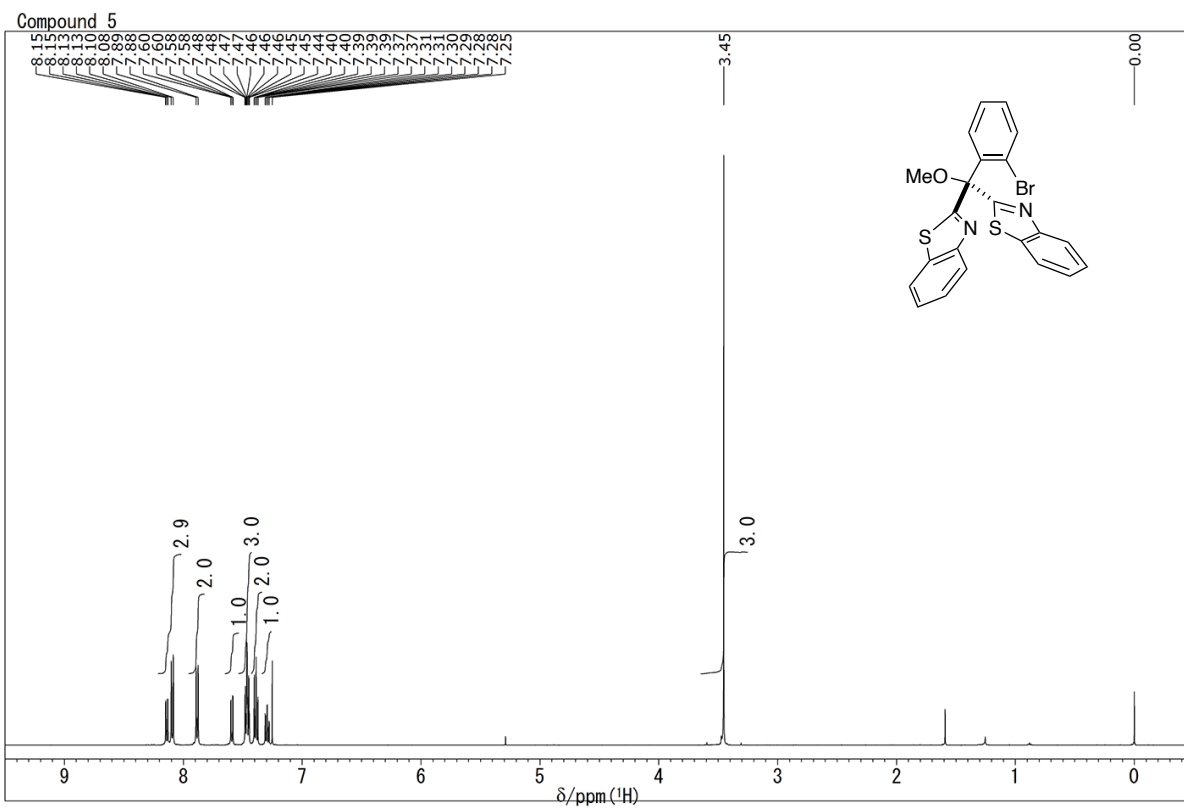


Fig. S19  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 499.1 MHz) spectrum of compound 5.

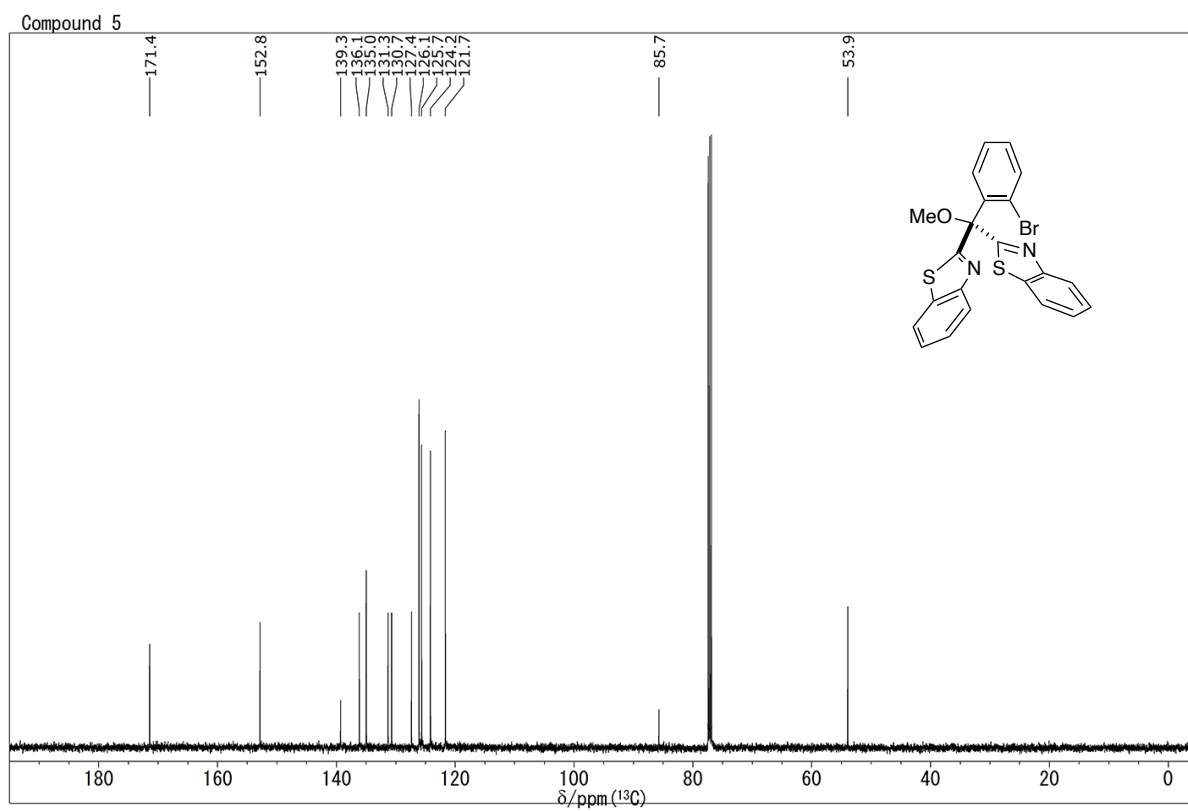


Fig. S20  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125.4 MHz) spectrum of compound 5.

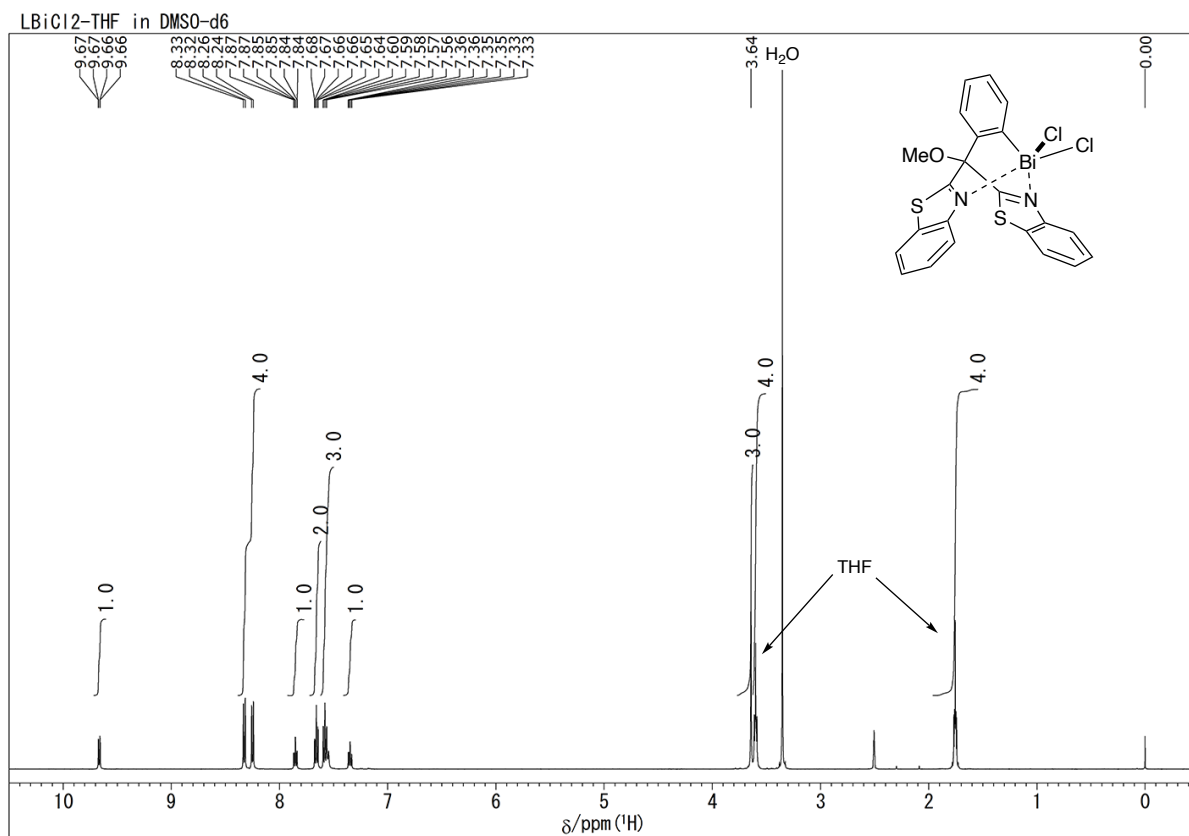


Fig. S21 <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 499.1 MHz) spectrum of complex 6·THF.

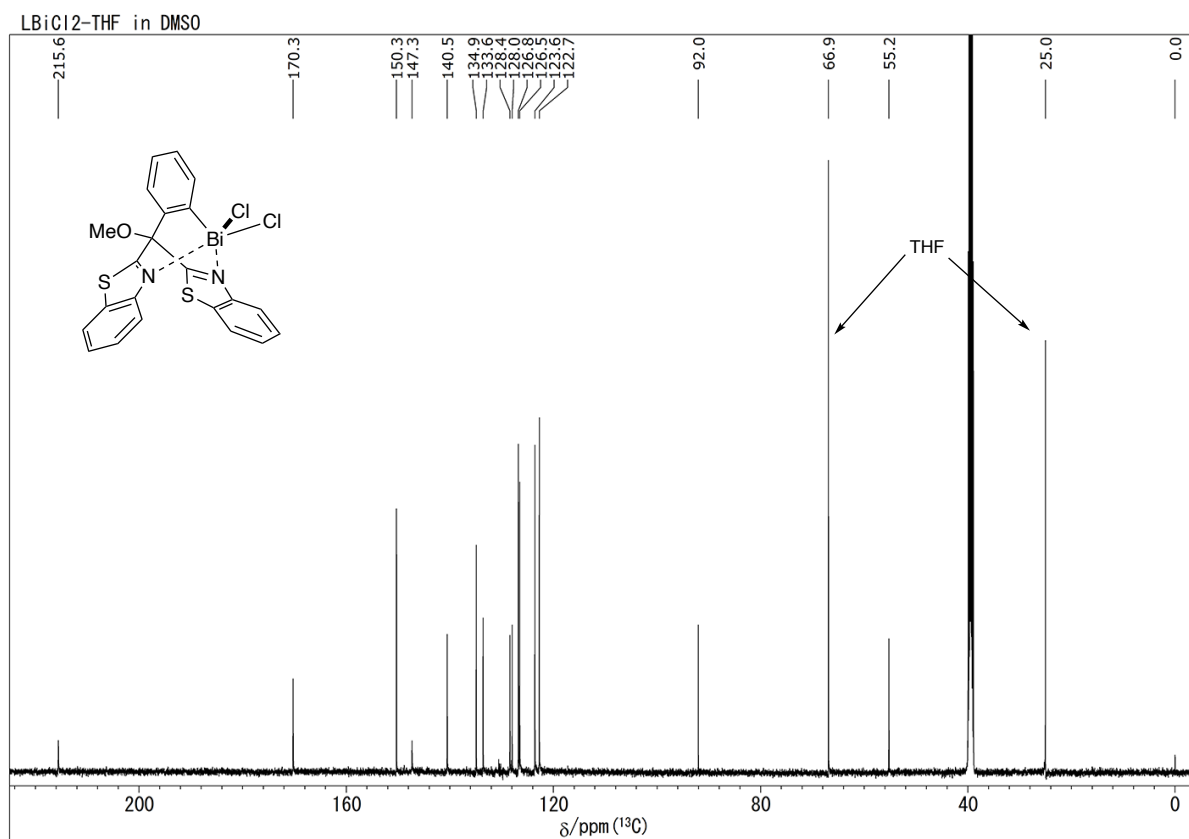


Fig. S22 <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 125.4 MHz) spectrum of complex 6·THF.

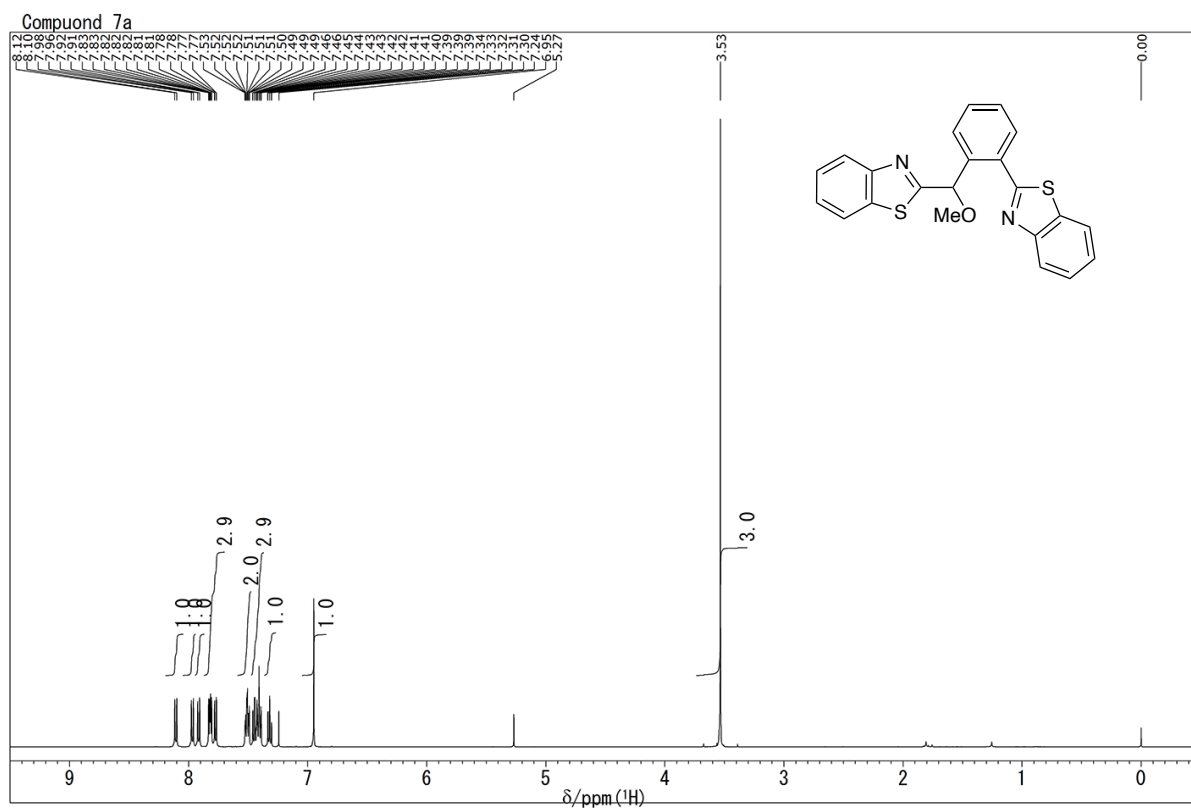


Fig. S23  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 499.1 MHz) spectrum of compound 7a.

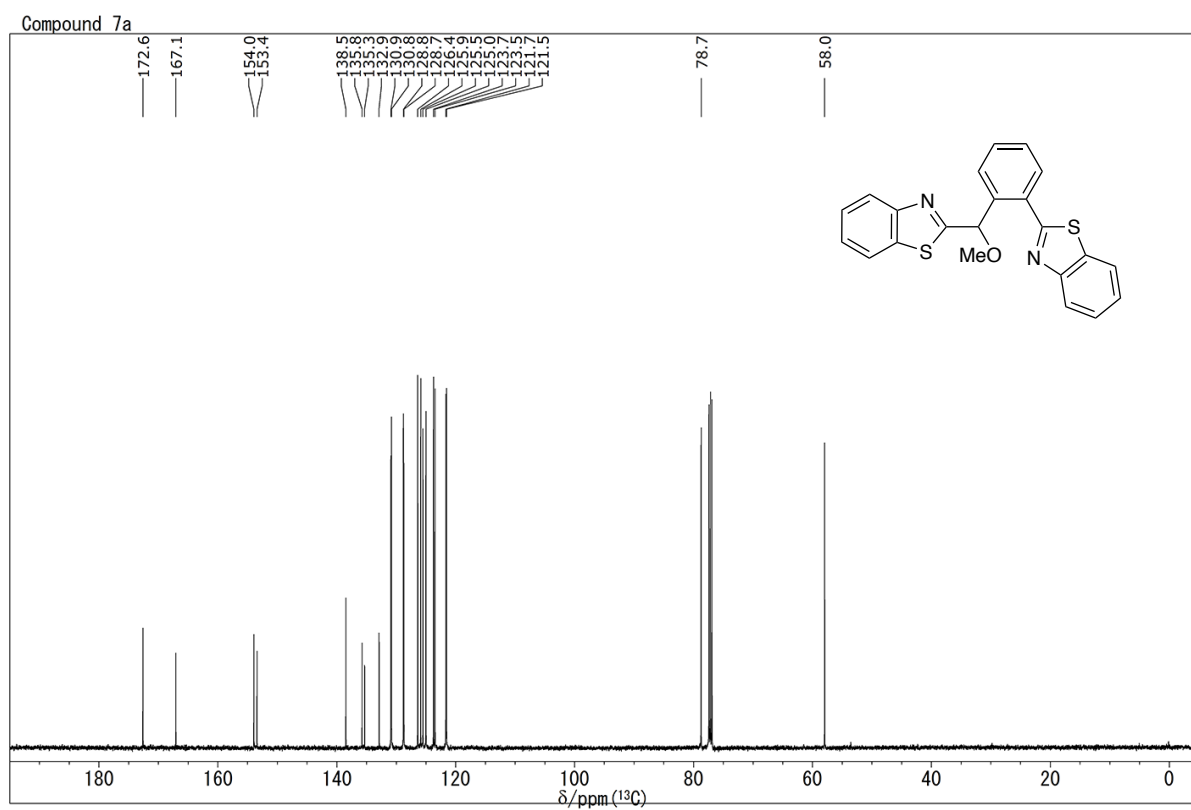


Fig. S24  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125.4 MHz) spectrum of compound 7a.

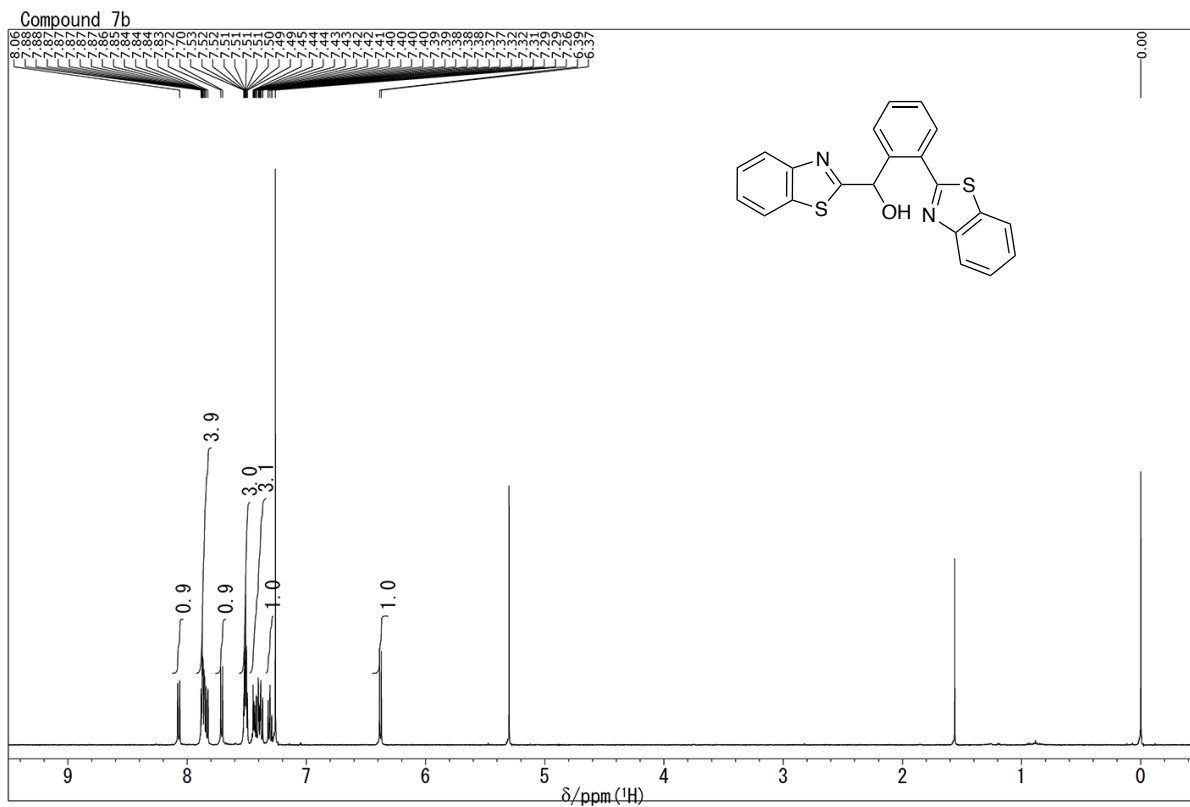


Fig. S25  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 499.1 MHz) spectrum of compound 7b.

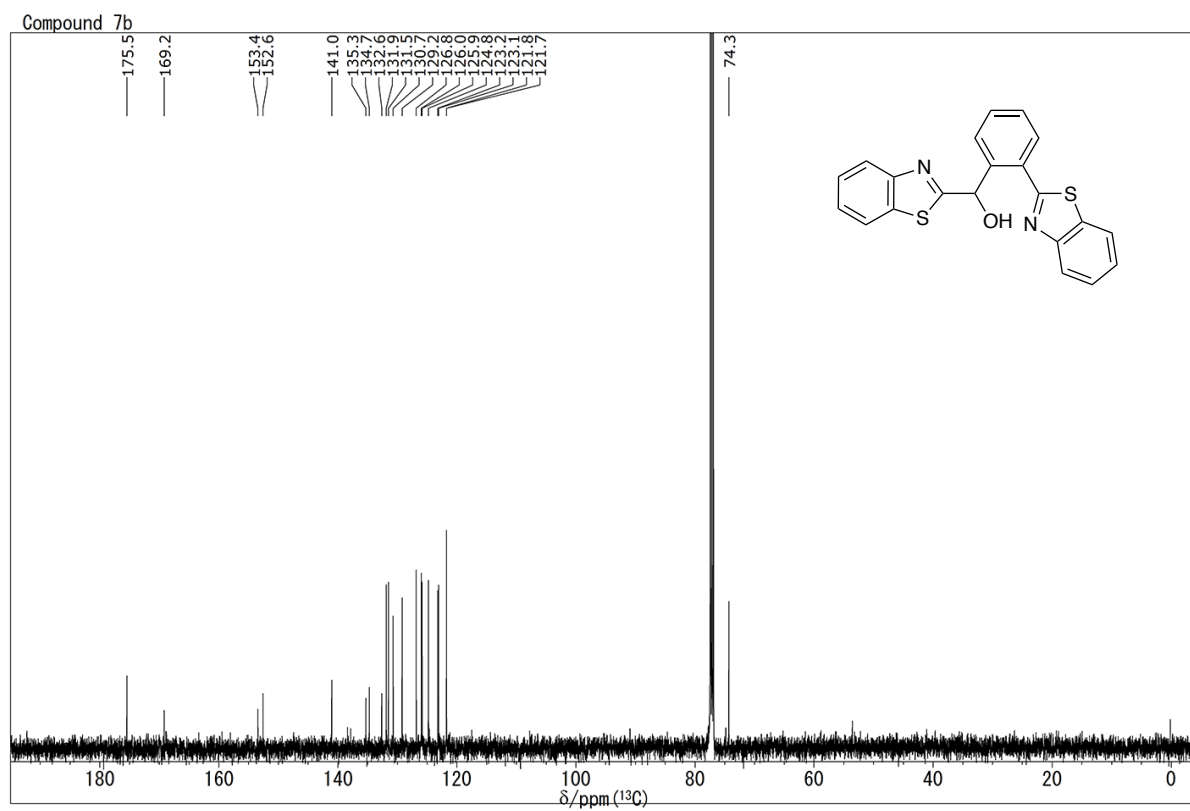


Fig. S26  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125.4 MHz) spectrum of compound 7b.

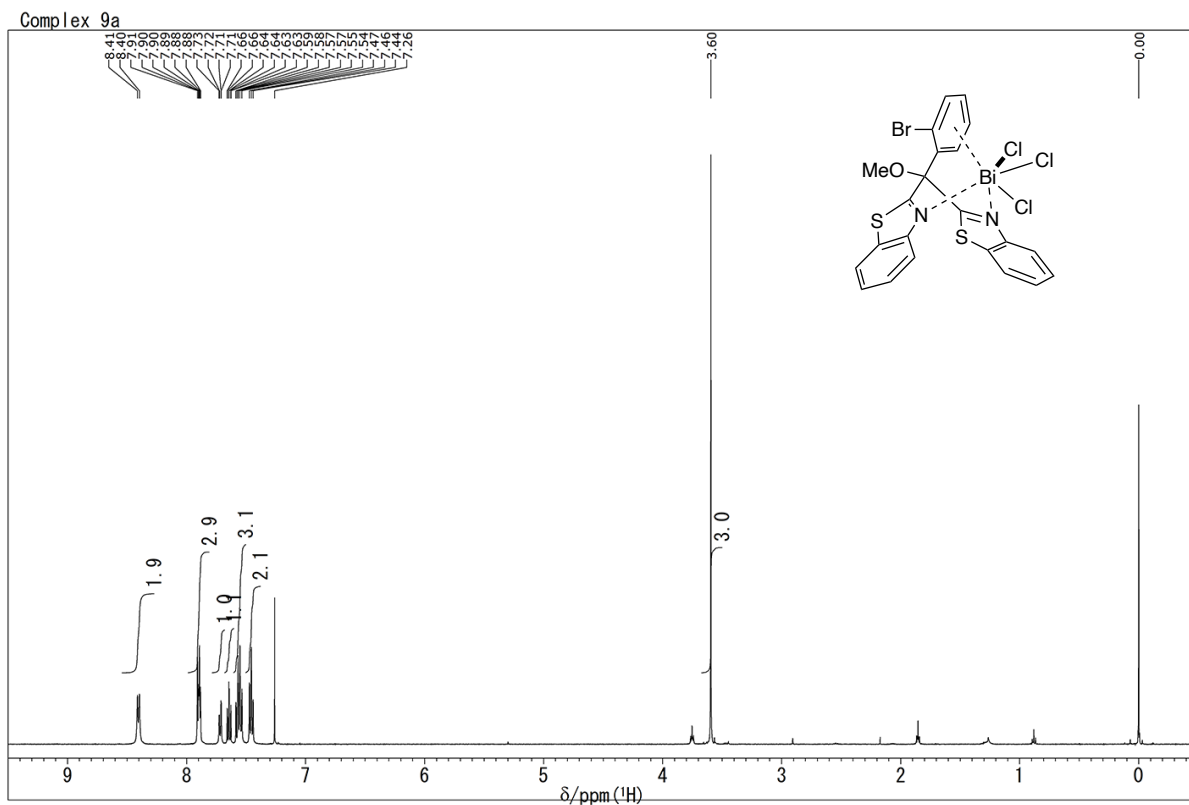


Fig. S27  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 499.1 MHz) spectrum of compound 9a.

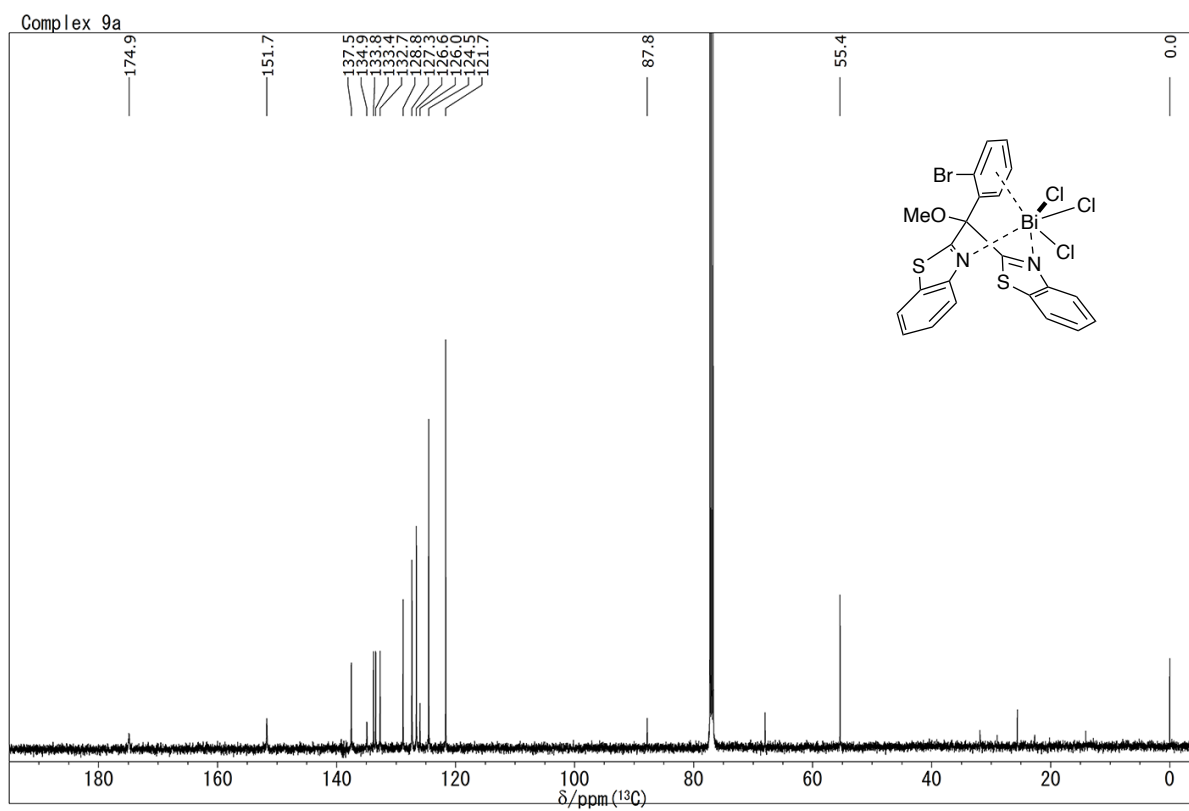
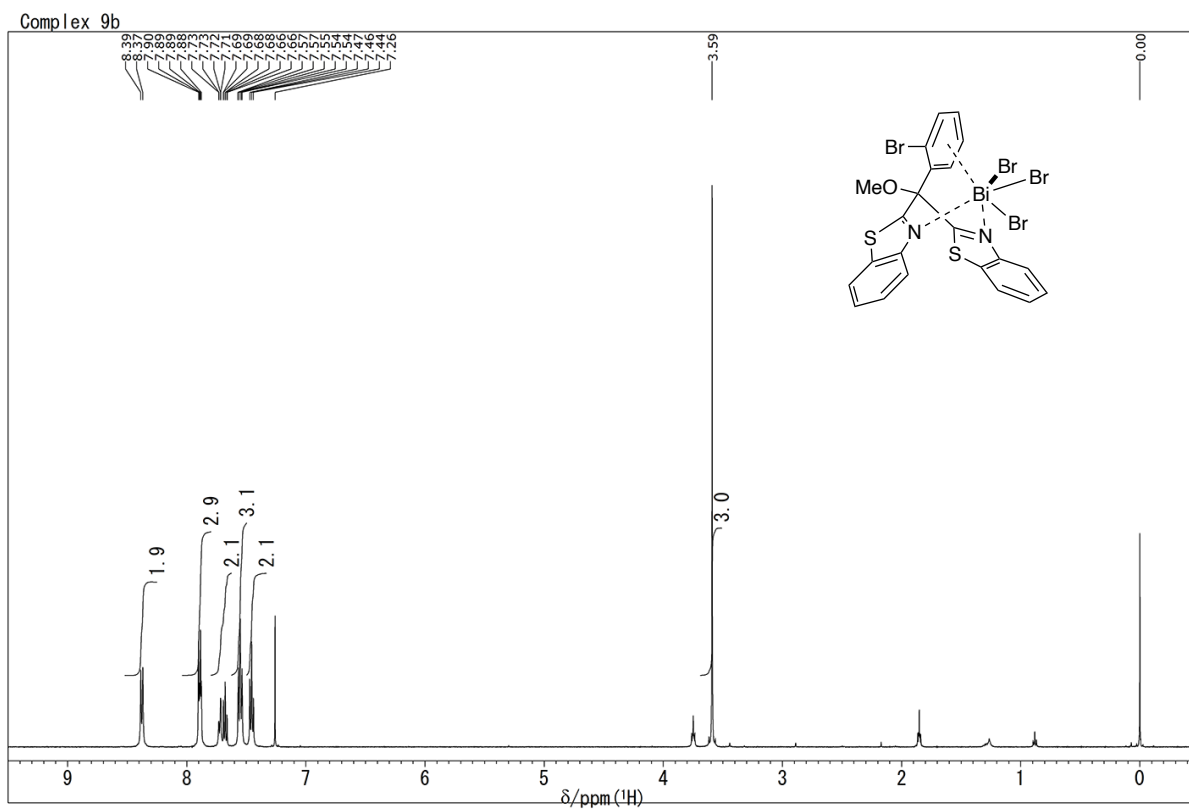
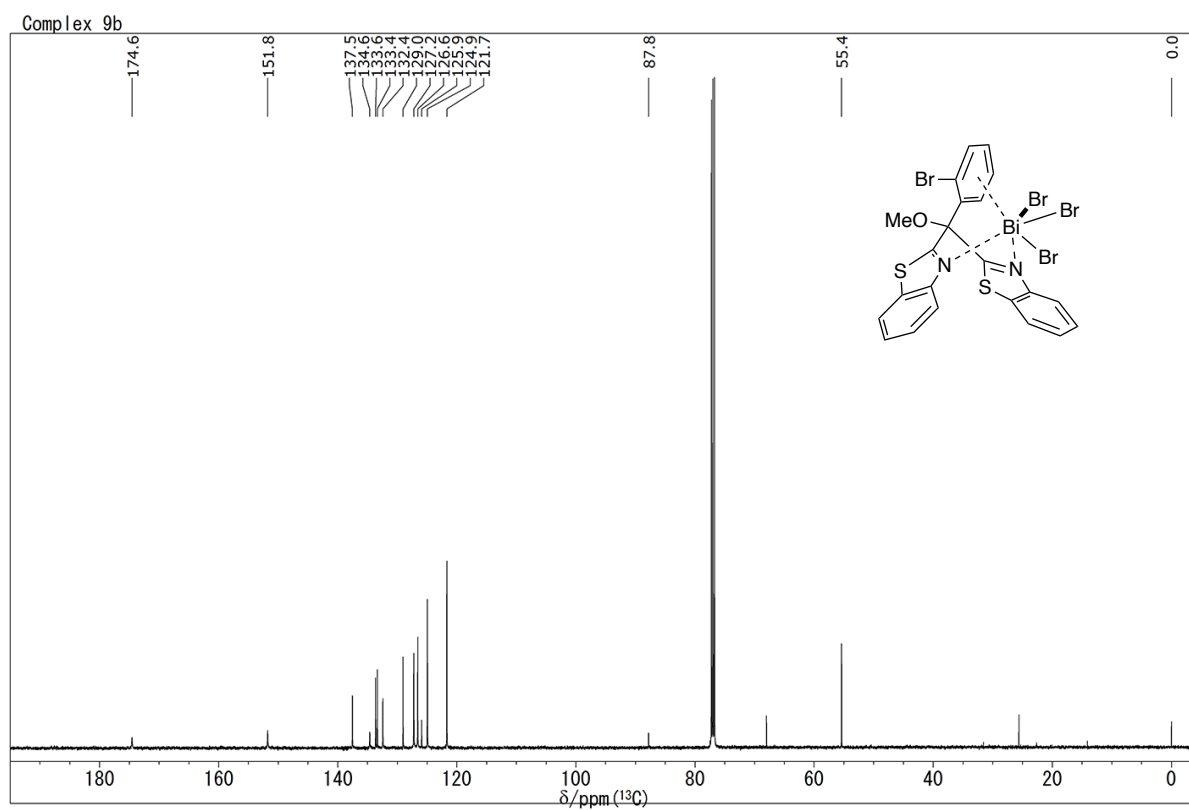


Fig. S28  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125.4 MHz) spectrum of compound 9a.



**Fig. S29**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 499.1 MHz) spectrum of compound **9b**.



**Fig. S30**  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125.4 MHz) spectrum of compound **9b**.



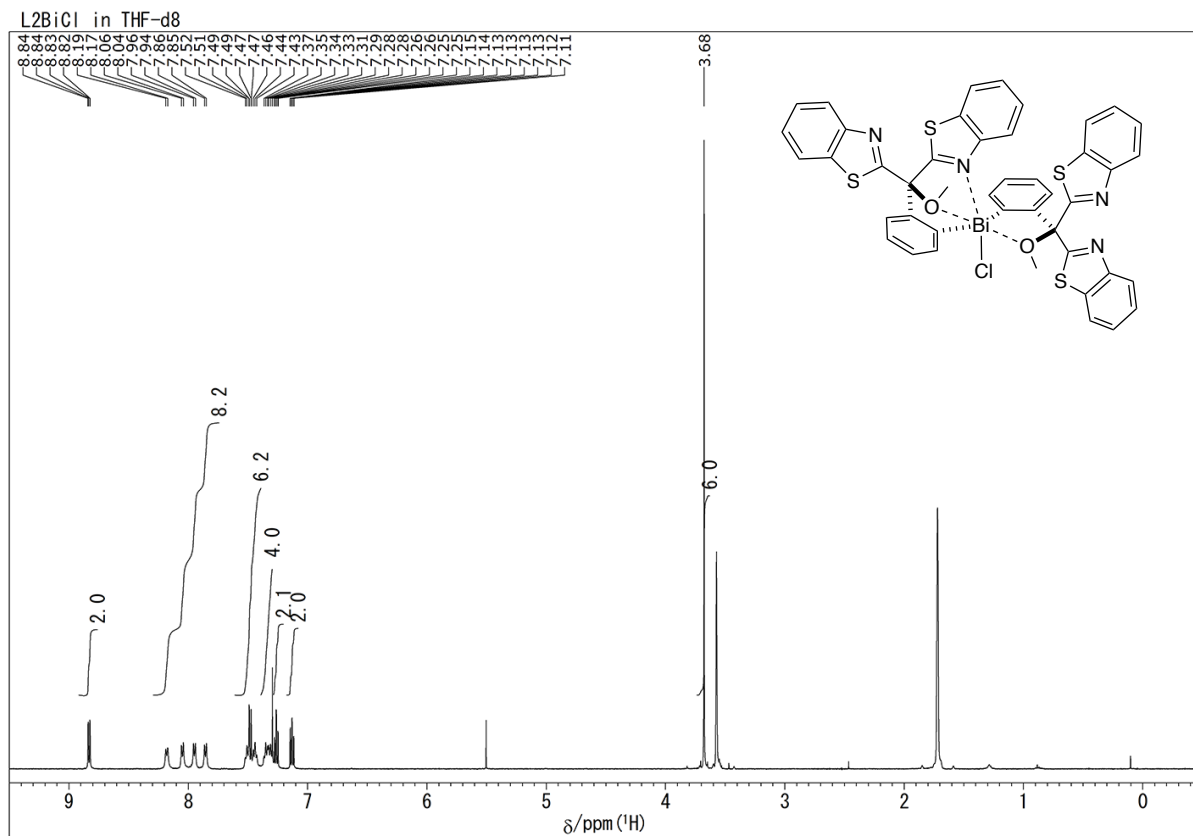


Fig. S31  $^1\text{H}$  NMR (THF- $d_8$ , 499.1 MHz) spectrum of compound 10.

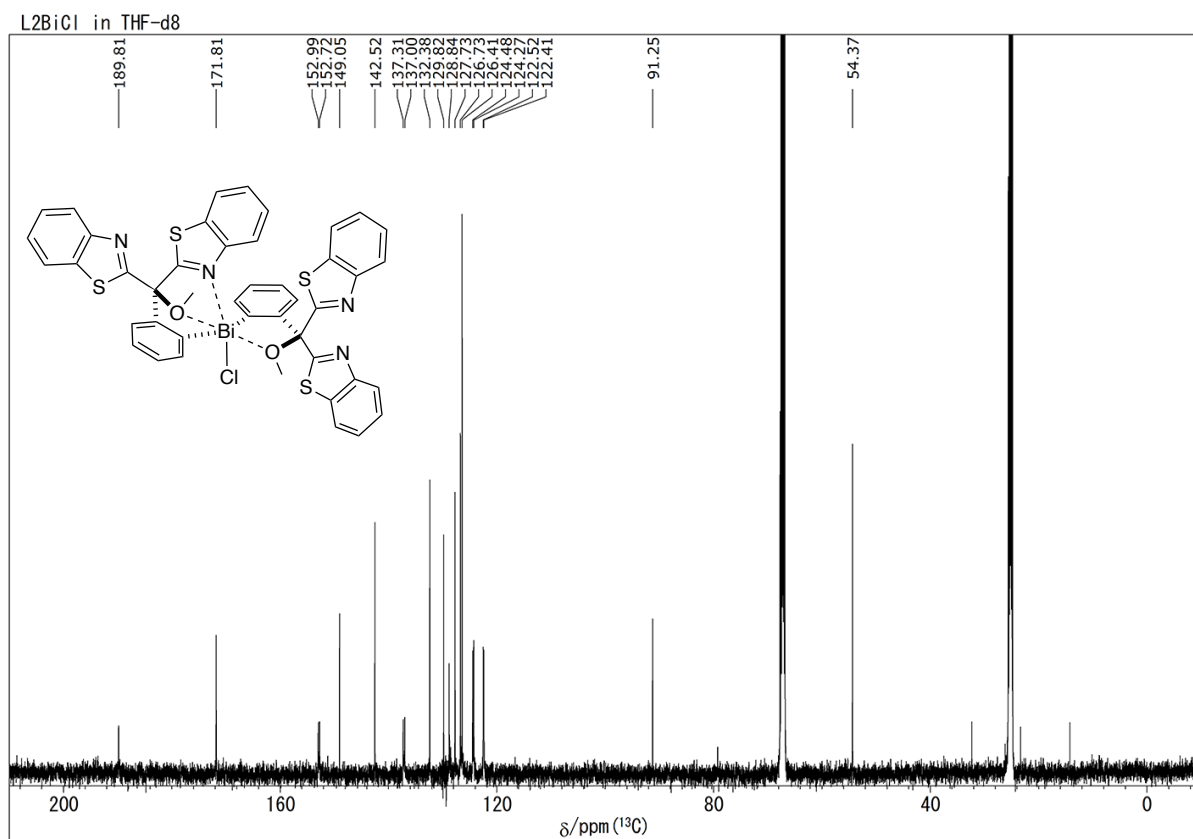


Fig. S32  $^{13}\text{C}$  NMR (THF- $d_8$ , 125.4 MHz) spectrum of compound 10.