Electronic Supplementary Material (ESI) for Chemical Communications.

Electronic Supplementary Information

Synthesis, Structure and Properties of Trivalent and Pentavalent Tricarbabismatranes

Shigeru Shimada,* Shuang-Feng Yin, and Yoong-Kee Choe

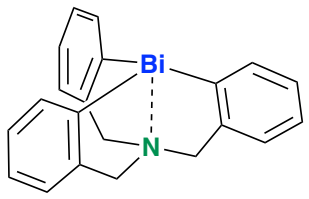
Table of Contents

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, Et_2O and CH_2Cl_2 were purchased from Kanto Chemicals and degassed before use. $CDCl_3$, C_6D_6, and DMSO-*d*$_6$ were dried over molecular sieves and degassed. XeF_2 was purchased from Acros Organics and used as received. NMR spectra were recorded on Jeol LA500 spectrometer or Bruker Avance Neo 400 spectrometer. Chemical shifts are reported in δ (ppm) and are referenced to internal tetramethylsilane (0.0 ppm) or the (residual) solvent signals for ^{1}H (7.16 ppm for C_6D_6) and ^{13}C (128.06 ppm for C_6D_6).[S1] Coupling constants were reported in Hertz. Elemental analysis was performed by the Analytical Center at the National Institute of Advanced Industrial Science and Technology. Tris(2-bromobenzyl)amine was synthesized according to the literature procedure.[S2]

2. Synthesis of compounds 4, 5, 7a, 8b, and 9

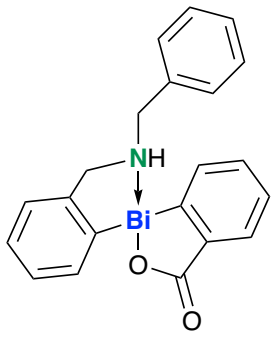
Bismatrane 4.



A hexane solution of *n*BuLi (1.57 M, 1.90 mL, 3.0 mmol) was added dropwise to a dry Et_2O solution (15 mL) of tris(2-bromobenzyl)amine **3** (521 mg, 0.994 mmol) at –30 ºC. The solution was stirred for 30 min at the same temperature and then gradually warmed to rt. The resulting solution was added to $BiCl_3$ (314 mg, 0.996 mmol) in Et_2O (5 mL) at –78 ºC. The reaction mixture was kept at –78 ºC for 3 h and then warmed to rt naturally and stirred overnight. After filtration, the filtrate was concentrated under vacuum to give a solid residue (360 mg). The residue was extracted with Et_2O (3 mL) and the extract was concentrated under vacuum to give bismatrane **4** as a colorless solid (130 mg, 27% yield). A similar experiment in lager scale (**3**, 3.1 g; $BiCl_3$, 1.86 g) afforded **4** in 25% isolated yield (0.72 g).

^{1}H NMR ($CDCl_3$, 499.1 MHz): δ 3.67 (6H, s), 7.23–7.26 (3H, m), 7.29–7.33 (6H, m), 7.99 (3H, d, *J* = 7.3). ^{1}H NMR (C_6D_6, 499.1 MHz): δ 3.34 (6H, s), 7.08 (3H, d, *J* = 7.3), 7.15 (3H, dt, *J* = 1.4, 7.3), 7.21 (3H, dt, *J* = 1.3, 7.1), 7.95 (3H, dd, *J* = 1.2, 7.1). ^{13}C NMR ($CDCl_3$, 125.4 MHz): δ 58.5 (*C*H_2), 128.1, 128.77, 128.84, 138.0, 145.2, 159.4 (br, *C*Bi). ^{13}C NMR (C_6D_6, 125.4 MHz): δ 58.6 (*C*H_2), 128.4, 129.24, 129.26, 138.5, 145.6, 159.3 (br, *C*Bi). Anal. Calcd for $C_{21}H_{18}BiN$: C, 51.12; H, 3.68; N, 2.84%. Found: C, 51.23; H, 3.61; N, 2.61%. HRMS Calcd for: 493.1243. Found: 493.1185

Oxidation product 5.



A CH_2Cl_2 solution of bismatrane **4** (20.0 mg, 0.0405 mmol) was stirred under air for 2 days to give colorless precipitates, which were separated by filtration and dried under vacuum to give compound **5** as a colorless solid (20.0 mg, 94% yield). Single crystals suitable for X-ray analysis were obtained by the recrystallization from a THF/heptane mixture.
^{1}H NMR (DMSO-d_6, 499.1 MHz): δ 4.04 (2H, br d, J = 5.9, NCH_2), 4.26 (2H, br d, J = 4.9, NCH_2), 5.68 (1H, quint, J = 5.7, NH), 7.25 (1H, dt, J = 1.2, 7.4), 7.33-7.52 (8H, m), 7.66 (1H, dt, J = 1.2, 7.3), 7.86 (2H, t, J = 7.2), 8.00 (1H, d, J = 7.3). ^{13}C NMR (DMSO-d_6, 125.4 MHz): δ 52.3 (CH$_2$), 55.8 (CH$_2$), 127.0, 127.5, 127.9, 128.4, 128.6 (2C), 129.2, 129.3 (2C), 133.5, 134.4, 135.2, 135.4, 137.1, 140.8, 148.9, 175.0, 178.5, 181.0. Anal. Calcd for $C_{21}H_{18}BiNO_2$: C, 48.01; H, 3.45; N, 2.67%. Found: C, 47.66; H, 3.43; N, 2.46%.

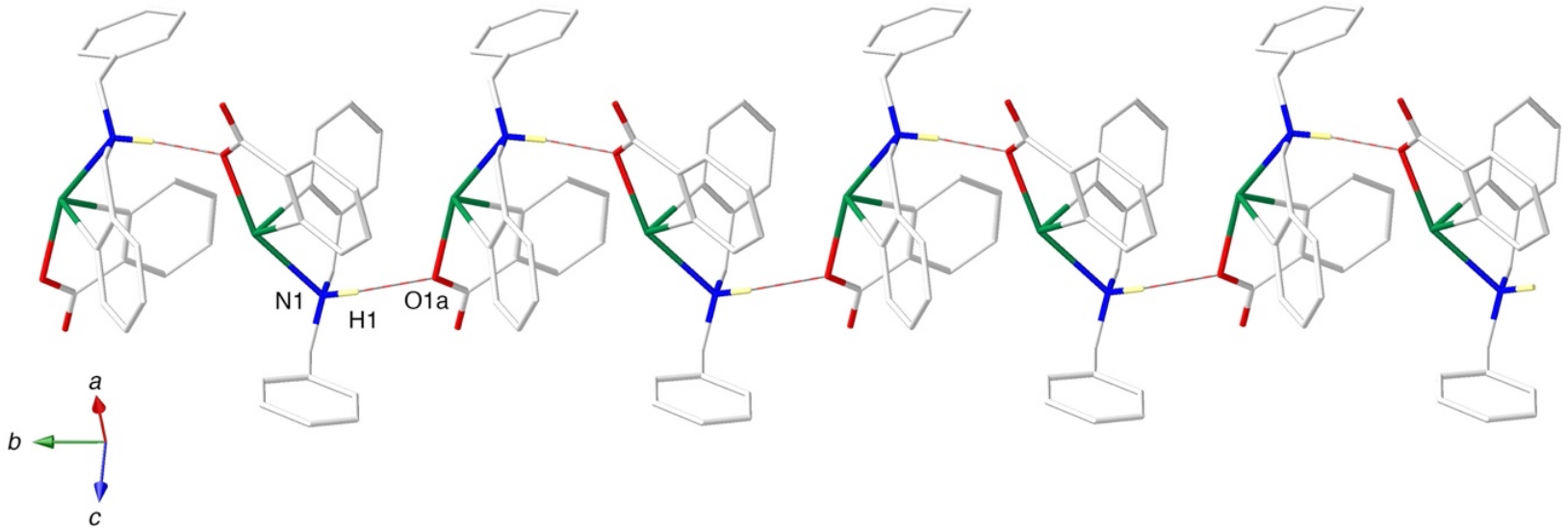
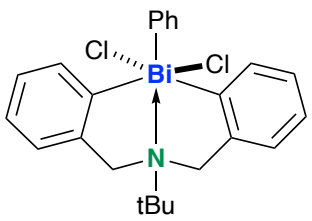


Fig. S1 1D arrangement of compound **5** in the crystal through intermolecular hydrogen bonds (N1···O1a (2.858(4) Å) , N1–H1–O1a (142.4º)). Symmetry transformations: a = 3/2 – x, –1/2 + y, 3/2 – z. Similar 1D arrangement was also observed in the crystal **5**·THF (N1···O1a (2.827(4) Å) , N1–H1–O1a (154.7º))

Compound 7a



To a dry Et_2O solution (10 mL) of dibenzazabismocine **6a** (81.2 mg, 0.151 mmol) was added SO_2Cl_2 (12 μl, 0.15 mmol) at –196 ºC. The mixture was warmed to –78 ºC and stirred for 1 h at the same temperature. Then the volatiles were removed under vacuum at rt to leave a colorless solid. The solid was washed with Et_2O and dried under vacuum to give **7a** (84.5 mg, 92% yield). Single crystals suitable for X-ray analysis were obtained by the recrystallization from Et_2O.
^{1}H NMR ($CDCl_3$, 499.1 MHz): δ 1.07 (9H, s), 4.62 (2H, d, J = 15.8), 4.70 (2H, d, J = 15.9), 7.38 (2H, tt, J = 2.0, 7.3), 7.42 (2H, tt, J = 1.3, 7.1), 7.45 (2H, dd, J = 2.0, 7.4), 7.59 (1H, tt, J = 1.3, 7.4), 7.71 (2H, d, J = 7.4), 7.74 (2H, t, J = 7.6), 8.71 (2H, dd, J = 1.0, 8.3). ^{13}C NMR ($CDCl_3$, 125.4 MHz): δ 26.3, 56.6, 59.7, 128.7, 129.0, 129.3, 129.8, 130.15, 130.19, 136.3, 141.7, 146.6, 162.7. Anal. Calcd for $C_{24}H_{16}BiCl_2N$: C, 47.38; H, 4.31; N, 2.30%. Found: C, 47.23; H, 4.22; N, 2.07%.

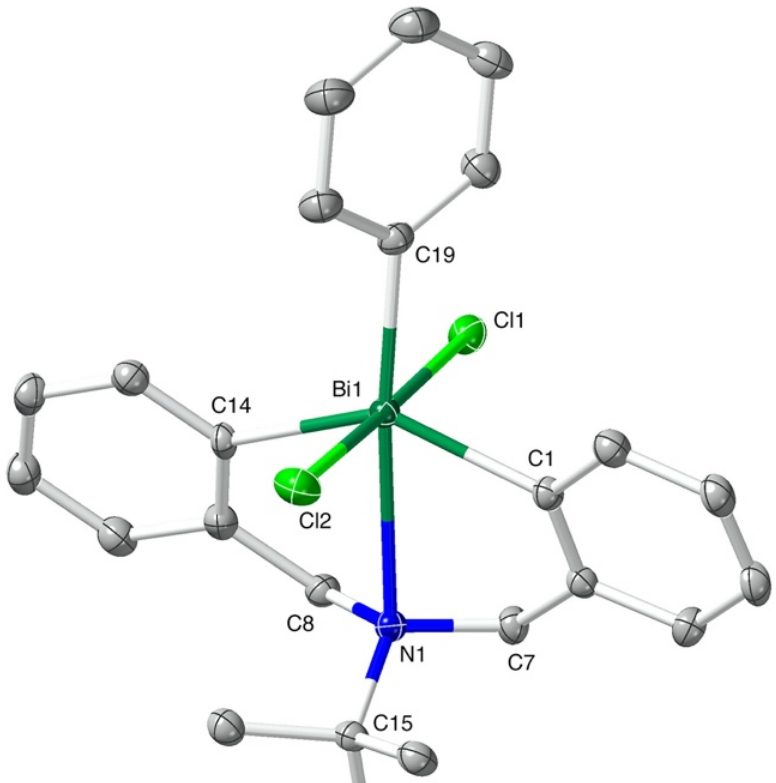
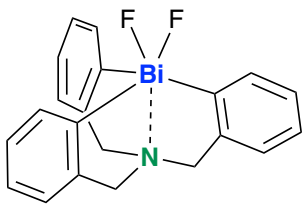


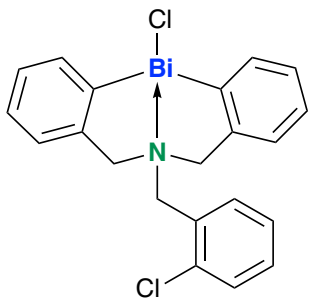
Fig. S2 Molecular structure of **7a** determined by single crystal X-ray diffraction (thermal ellipsoids are shown at 50% probability level). Hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (°): Bi1–Cl1 2.6261(8); Bi1–Cl2 2.5781(8); Bi1–N1 2.838(3); Bi1–C1 2.199(3); Bi1–C14 2.201(3); Bi1–C19 2.234(3); Cl1–Bi1–Cl2 178.48(3); Cl1–Bi1–N1 84.96(6); Cl2–Bi1–N1 95.51(6); Cl1–Bi1–C1 88.54(9); Cl1–Bi1–C14 88.12(8); Cl1–Bi1–C19 89.21(9); Cl2–Bi1–C1 92.98(9); Cl2–Bi1–C14 90.67(9); Cl2–Bi1–C19 90.39(9); N1–Bi1–C1 70.59(10); N1–Bi1–C14 70.66(10); N1–Bi1–C19 173.42(10); C1–Bi1–C14 141.25(12); C1–Bi1–C19 106.28(12); C14–Bi1–C19 112.26(12).

Difluorobismatrane 8b



To a stirred CH_2Cl_2 (30 mL) solution of bismatrane **4** (200 mg, 0.405 mmol) was added a CH_2Cl_2 solution (20 mL) of XeF_2 (75.5 mg, 0.446 mmol) at –94 ºC under N_2. The resulting mixture was stirred at –94 ºC for 1 h and warmed to rt naturally. The solvent was removed under vacuum to give a pale yellow solid residue. Recrystallization from a mixture of CH_2Cl_2 and heptane gave bismatrane **8b** as yellow crystals (200 mg, 93% yield).
Mp.: 162-163.3 °C. ^{1}H NMR ($CDCl_3$, 499.1 MHz): δ 4.19 (6H, s), 7.32 (3H, d, J = 7.3), 7.37 (3H, t, J = 7.3), 7.54 (3H, t, J = 7.0), 8.41 (3H, d, J = 7.6). ^{13}C NMR ($CDCl_3$, 125.4 MHz): δ 56.8 (CH_2), 128.5, 130.4, 131.1, 136.6, 140.3, 159.7 (br, *C*Bi). Anal. Calcd for $C_{21}H_{18}BiF_2N$: C, 47.47; H, 3.41; N, 2.64%. Found: C, 47.16; H, 3.21; N, 2.40%.

Chlorination of 4 with SO_2Cl_2; formation of 9



To a dry Et_2O solution (5 mL) of bismatrane **4** (72.0 mg, 0.146 mmol) was added SO_2Cl_2 (12 µl, 0.15 mmol) at –196 ºC. The mixture was warmed to –78 ºC and stirred for 2 h at the same temperature. Then the volatiles were removed under vacuum at rt to leave a yellowish solid. Then the solid residue was extracted with Et_2O (3 mL) and the Et_2O extract was evacuated to

give colorless solid (27 mg), which mainly consist of compound **9**. Single crystals suitable for X-ray analysis were obtained by the recrystallization from Et_2O.
^{1}H NMR ($CDCl_3$, 499.1 MHz): δ 4.16 (2H, s, NC*H*$_2$C$_6$H$_4$Cl), 4.21 (2H, d, *J* = 14.6), 4.37 (2H, d, *J* = 14.6), 7.27-7.37 (5H, m), 7.39-7.48 (3H, m), 7.53 (2H, t, *J* = 7.4), 8.65 (2H, dd, *J* = 1.1, 7.4). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 56.7 (*C*H$_2$), 62.8 (2C, *C*H$_2$), 127.3 (*C*H), 128.2 (2C, *C*H), 128.3 (2C, *C*H), 130.66 (*C*H), 130.72 (*C*H), 131.4 (2C, *C*H), 132.1, 133.4 (*C*H), 135.6, 138.5 (2C, *C*H), 147.9, 172.1.

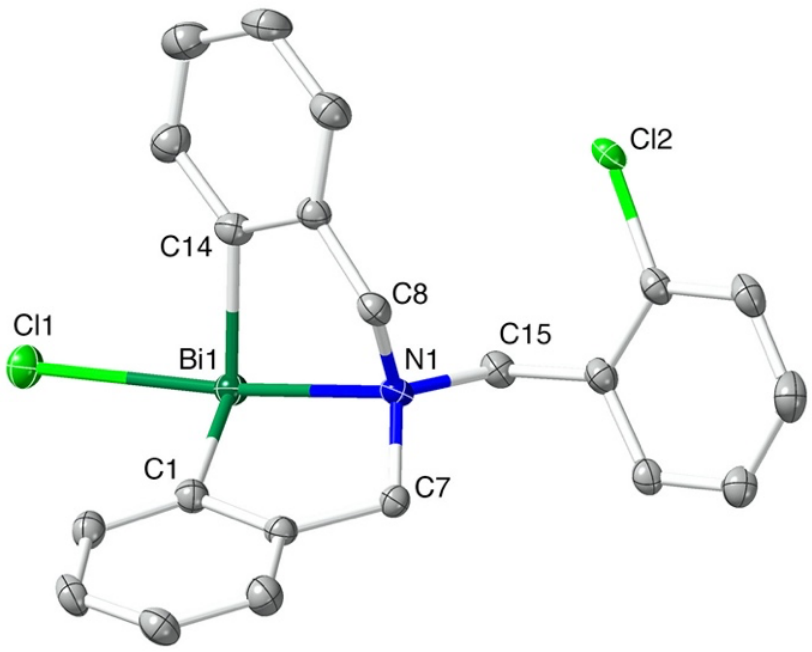


Fig. S3 Molecular structure of **9** determined by single crystal X-ray diffraction (thermal ellipsoids are shown at 50% probability level). Hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (°): Bi1–Cl1 2.6185(10); Bi1–N1 2.555(3); Bi1–C1 2.258(4); Bi1–C14 2.241(4); Cl1–Bi1–N1 154.57(8); Cl1–Bi1–C1 90.84(10); Cl1–Bi1–C14 90.94(10); N1–Bi1–C1 72.27(12); N1–Bi1–C14 73.78(12); C1–Bi1–C14 99.23(13).

3. Synthesis of a mixture of 8a and 9

To a dry CH_2Cl_2 solution (6 mL) of bismatrane **4** (120 mg, 0.243 mmol) was added SO_2Cl_2 (35 μl, 0.43 mmol) at –78 ºC. The mixture was gradually warmed to –10 ºC during 2.3 h with stirring. Then the volatiles were removed under vacuum with keeping the temperature between –10 and –5 ºC to give a pale yellow solid residue. The product was dissolved in dry CH_2Cl_2 (3 mL), and dry hexane (2 mL) was layered over the solution. The mixture was kept at –35 ºC overnight. The supernatant was removed. The resulted pale yellow solid was washed with CH_2Cl_2/hexane (1/1, 2 × 0.5 mL) and dried under vacuum (yield, 129 mg). ^{1}H NMR analysis of the solid suggested that it was a mixture of **8a** and **9** (**8a**/**9** = ca. 83/17).

The following NMR data was obtained from the spectra of a mixture of **8a** and **9** (ca. 3:1).
8a: ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 4.87 (6H, s, NC*H*$_2$), 7.57 (3H, t, *J* = 7.5), 7.65 (3H, t, *J* = 7.6), 7.83 (3H, d, *J* = 7.6), 7.96 (3H, d, *J* = 7.6). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 57.2, 132.1, 132.5, 133.5 (2C), 141.8, 142.4.

4. ^{1}H NMR monitoring of the composition change of the mixture of 8a and 9

The composition change (conversion of **8a** to **9**) of a mixture of **8a** and **9** in $CDCl_3$ (initial ratio of **8a** and **9** was ca. 83:17) was monitored by ^{1}H NMR analysis at 20 ºC for 6 days and then at 40 ºC for 47 h. The change of the ^{1}H NMR spectra is shown in Fig S4.

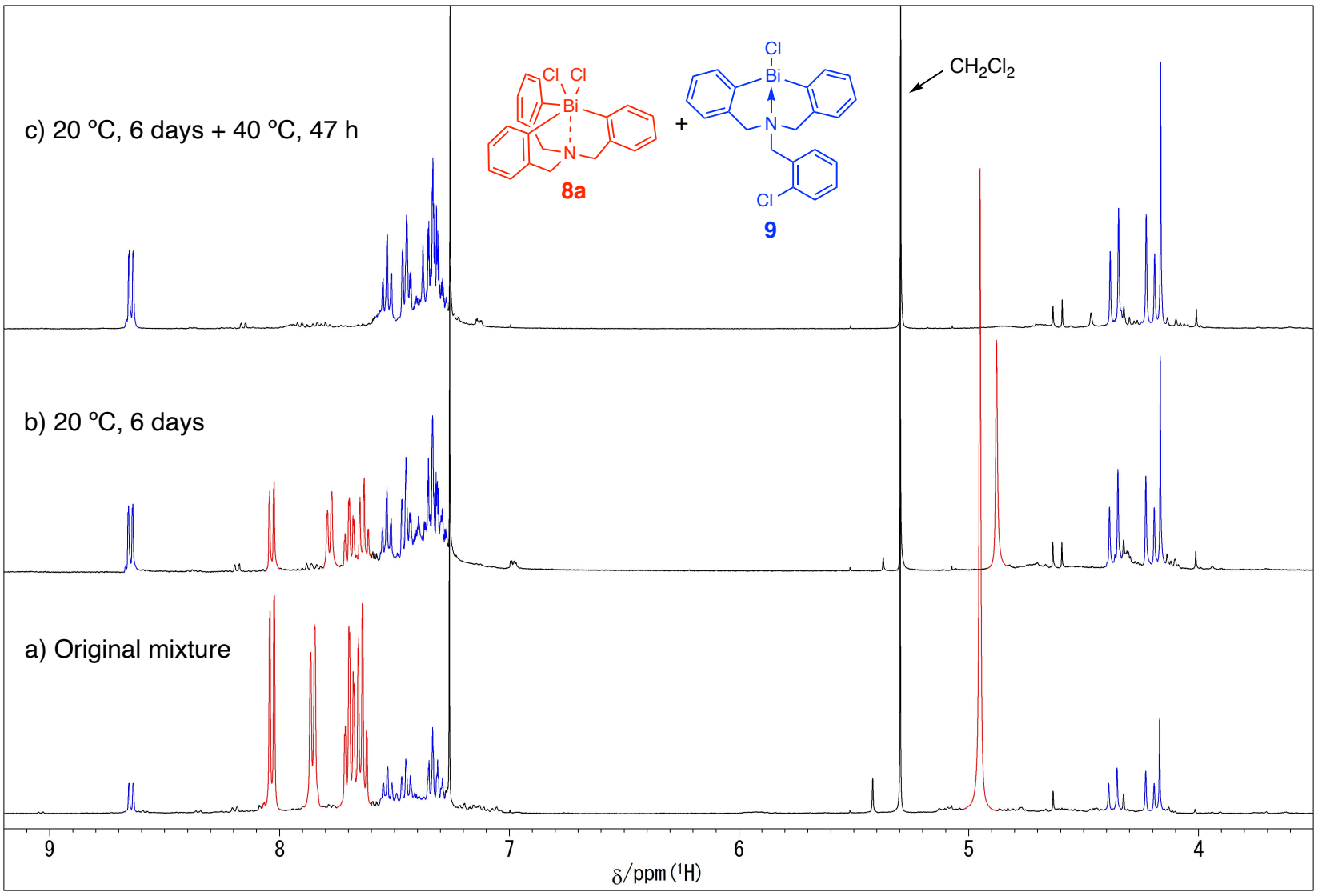
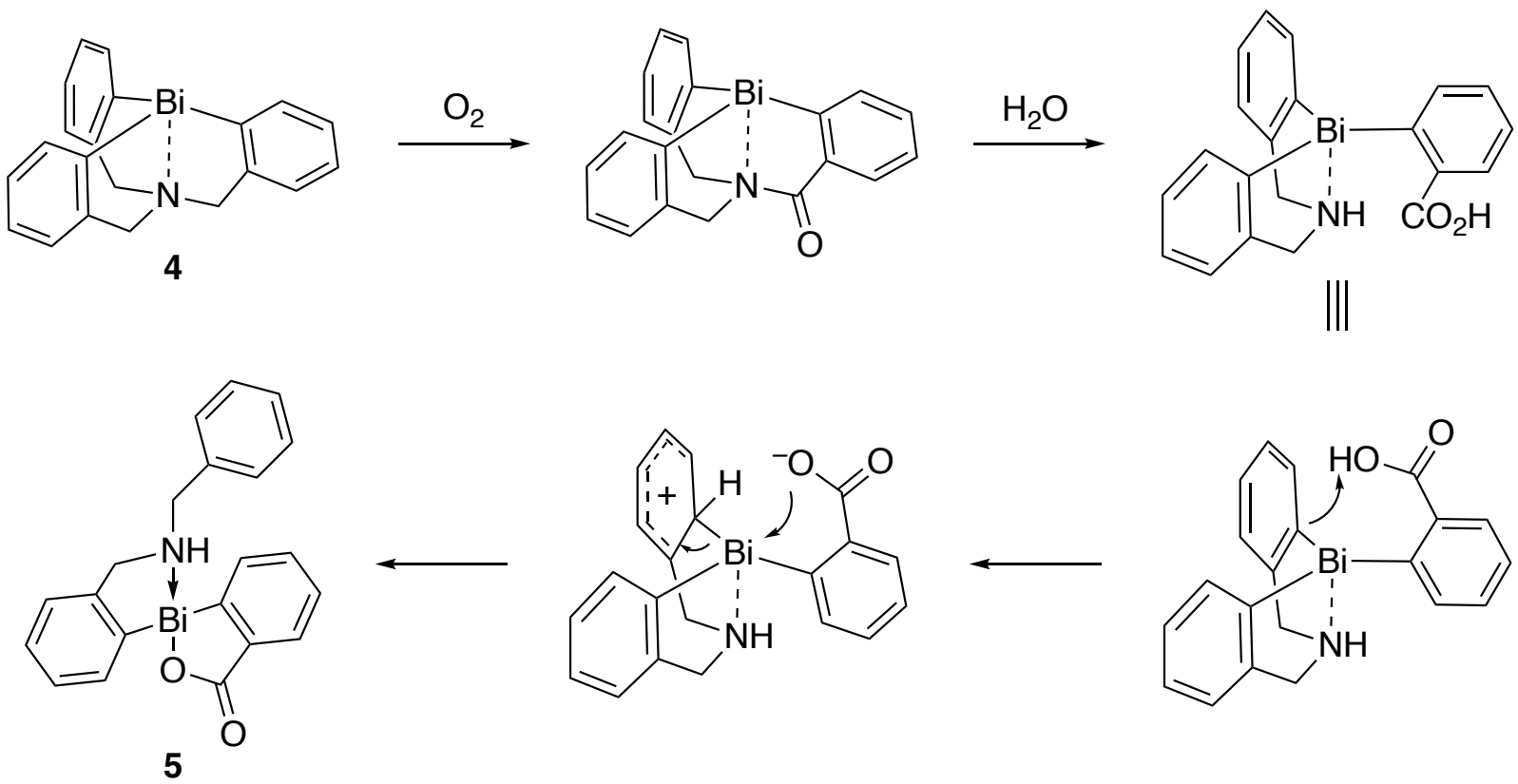


Fig. S4 Monitoring of the conversion of **8a** to **9** by ^{1}H NMR spectroscopy ($CDCl_3$, 400 MHz): a) Original mixture of **8a** and **9** in ca. 83:17 ratio. b) After 6 days at 20 ºC. c) After 6 days at 20 ºC and 47 h at 40 ºC; showing almost complete conversion of **8a**.

5. A plausible reaction pathway for the formation of compound 5



Scheme. S1 A plausible reaction pathway for the formation of compound **5** from bismatrane **4**.

6. Single crystal X-ray structure analysis

Single crystals of **5**, **5**·THF, **7a**, **8b** and **9** were covered with paratone-8236 oil and mounted on a glass fiber. Data collection was performed on a Bruker Smart Apex CCD diffractometer (Mo Kα radiation, graphite monochromator). The determination of crystal class and unit cell parameters was carried out with the CrysAlisPro program package.[S3] The raw frame data were processed using CrysAlisPro to yield the reduction data file. Structure solution and refinement were performed using Olex2 software package[S4] with SHELXT and SHELXL programs.[S5]

CCDC 2144020 – 2144024 respectively contain the supplementary crystallographic data for **8b**, **5**, **5**·THF, **7a**, and **9**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

7. Computational Details

Geometry optimizations and frequency calculations were performed using the density functional theory (DFT), as implemented in the Gaussian 16 quantum chemistry package.[S6] For the DFT calculations, the ωB97X-D functional was used.[S7] As for the basis sets, we used def2-SVP basis sets where core electrons of Bi were represented by effective core potential.[S8] To investigate bonding in the molecules, we carried out the Mayer bond order analysis.[S9]

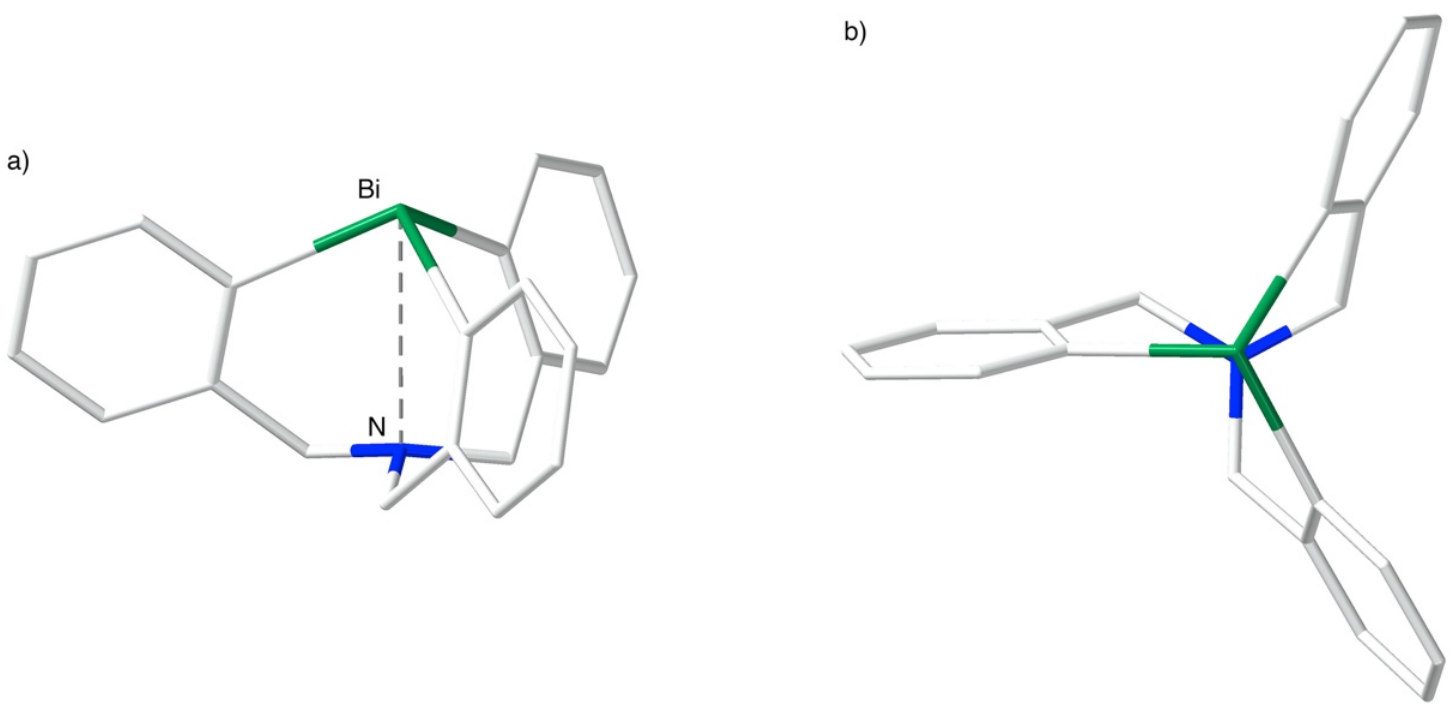


Fig. S5 Two views of the molecular structure of compound **4** obtained by the DFT calculations.

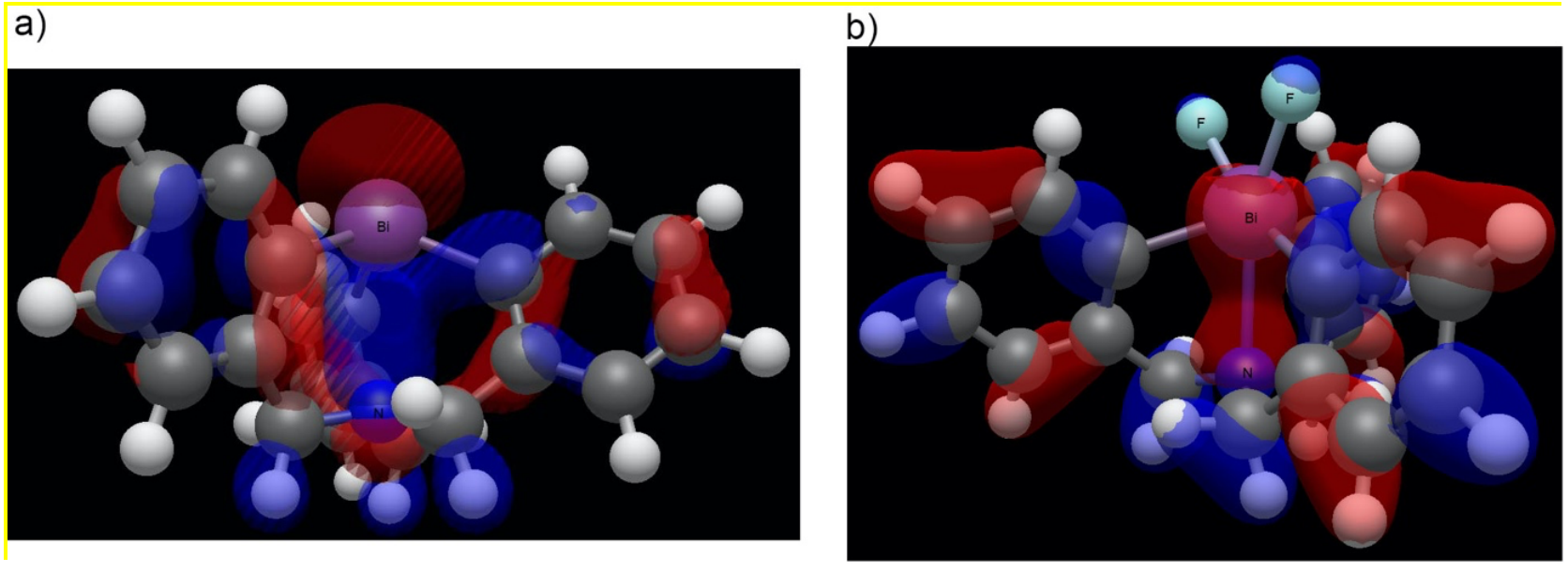


Fig. S6 Views of molecular orbitals relating to the Bi–N interactions. a) A view of MO85 (HOMO–1) for compound **4**. b) A view of MO55 (HOMO–41) for compound **8b**.

8. Coordinates of compounds 4 and 8b in XYZ format

Compound 4

```
41

 H     2.801421     6.338994    -0.081929
Bi     6.748843     5.667738     3.371146
 C     7.674737     3.627862     3.821928
 C     8.785635     3.302925     3.036860
 C     9.027817     1.192010     4.168336
 C     7.922653     1.506386     4.957796
 C     7.243245     2.717750     4.800105
 C     6.067869     3.040733     5.701322
 C     4.296507     4.727055     5.799837
 C     5.147832     5.891638     6.265408
 C     4.905255     6.468338     7.515374
 C     5.646645     7.561841     7.960384
 C     6.650852     8.088353     7.153296
 C     6.899888     7.513742     5.905548
 C     6.163362     6.415655     5.449654
 C     4.729830     5.102178     2.461893
 C     4.316164     5.915101     1.401599
 C     3.108282     5.687537     0.739606
 C     2.298906     4.627986     1.138813
 C     2.702190     3.810287     2.193342
 C     3.912509     4.031063     2.856885
 C     4.334841     3.097686     3.974138
 H     9.142162     4.002293     2.272241
 H     7.576305     0.793725     5.712494
```

H	4.121394	6.049911	8.154029
H	5.442319	7.996827	8.941324
H	7.242793	8.941582	7.492554
H	7.692607	7.941525	5.281459
H	4.942663	6.752349	1.073896
H	1.348519	4.439204	0.634495
H	2.061526	2.982256	2.511653
H	5.010098	2.334714	3.551866
H	3.449343	2.548879	4.359377
H	6.432071	3.660753	6.537615
H	5.675591	2.106298	6.155904
H	3.485685	5.122246	5.165101
H	3.802405	4.250654	6.673125
N	5.053862	3.792469	5.009494
C	9.462868	2.093219	3.201115
H	10.324277	1.856525	2.572291
H	9.543558	0.239035	4.306415

Compound 8b

43

H	2.849901	6.131300	-0.302676
Bi	6.475532	5.605629	3.508492
C	7.639901	3.676411	3.821106
C	8.763331	3.401469	3.042113
C	9.003016	1.268293	4.149634
C	7.884921	1.550258	4.931867
C	7.196821	2.757714	4.780510
C	6.022202	3.086870	5.674454
C	4.296450	4.810172	5.826358
C	5.198010	5.911554	6.352412
C	5.003757	6.449840	7.627740
C	5.797798	7.500691	8.082750
C	6.793879	8.032049	7.264994
C	6.999364	7.507217	5.989257
C	6.217397	6.441118	5.553589
C	4.659124	5.053203	2.361393
C	4.299383	5.836612	1.266692
C	3.137145	5.528630	0.561459
C	2.332918	4.467820	0.977012
C	2.683497	3.718028	2.097564
C	3.857449	3.998300	2.804280
C	4.250480	3.155557	4.000559

F	8.131127	6.115613	2.370593
F	6.022528	7.568082	2.911603
H	9.098634	4.144266	2.318036
H	7.539539	0.823115	5.672612
H	4.217532	6.042733	8.269776
H	5.635036	7.909236	9.082308
H	7.410172	8.861853	7.617169
H	7.759973	7.939614	5.335634
H	4.915301	6.696576	0.998112
H	1.414106	4.233199	0.435227
H	2.033985	2.905081	2.434616
H	4.871802	2.317080	3.645712
H	3.349806	2.706947	4.462364
H	6.385373	3.668898	6.536765
H	5.571570	2.162839	6.085476
H	3.494098	5.262617	5.219196
H	3.801934	4.283039	6.665611
N	5.039662	3.898787	4.971513
C	9.443957	2.194391	3.206676
H	10.321133	1.978488	2.592634
H	9.529457	0.319811	4.276807

9. References:

S1 G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics*, 2010, **29**, 2176-2179.

S2 Q. Chen, C. E. Buss, V. G. Young and S. Fox, *J. Chem. Crystallogr.*, 2005, **35**, 177-181.

S3 CrysAlisPro 1.171.40.67a. Rigaku OD, 2019.

S4 Olex2 1.5: 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.

S6 M. J. Frisch , G. W. Trucks , H. B. Schlegel , G. E. Scuseria , M. A. Robb , J. R. Cheeseman , G. Scalmani , V. Barone , G. A. Petersson , H. Nakatsuji , X. Li , M. Caricato , A. V. Marenich , J. Bloino , B. G. Janesko , R. Gomperts , B. Mennucci , H. P. Hratchian , J. V. Ortiz , A. F. Izmaylov , J. L. Sonnenberg , D. Williams , F. Ding , F. Lipparini , F. Egidi , J. Goings , B. Peng , A. Petrone , T. Henderson , D. Ranasinghe , V. G. Zakrzewski , J. Gao , N. Rega , G. Zheng , W. Liang , M. Hada , M. Ehara , K. Toyota , R. Fukuda , J. Hasegawa , M. Ishida , T. Nakajima , Y. Honda , O. Kitao , H. Nakai , T. Vreven , K. Throssell , J. A. Montgomery Jr , J. E. Peralta , F. Ogliaro , M. J. Bearpark , J. J. Heyd , E. N. Brothers , K. N. Kudin , V. N. Staroverov , T. A. Keith , R. Kobayashi , J. Normand , K. Raghavachari , A. P. Rendell , J. C. Burant , S. S. Iyengar , J. Tomasi , M. Cossi , J. M. Millam , M. Klene , C. Adamo , R. Cammi , J. W. Ochterski , R. L. Martin , K. Morokuma , O. Farkas , J. B. Foresman and D. J. Fox , *Gaussian 16* , Wallingford, CT, 2016.

S7 J.-D. Chai and M. Head-Gordon , *Phys. Chem. Chem. Phys.*, 2008, **10** , 6615 —6620.

S8 F. Weigend and R. Ahlrichs, Phys. Chem. Chem. Phys., 2005, 7, 3297–3305.

S9 (a) I. Mayer *Chem. Phys. Lett.*, 1983, **97** , 270 (b) I. Mayer *Int. J. Quantum Chem.*, 1984, **26** , 151

10. ^{1}H and ^{13}C NMR spectra of compounds 4, 5, 7a, 8b, and 9

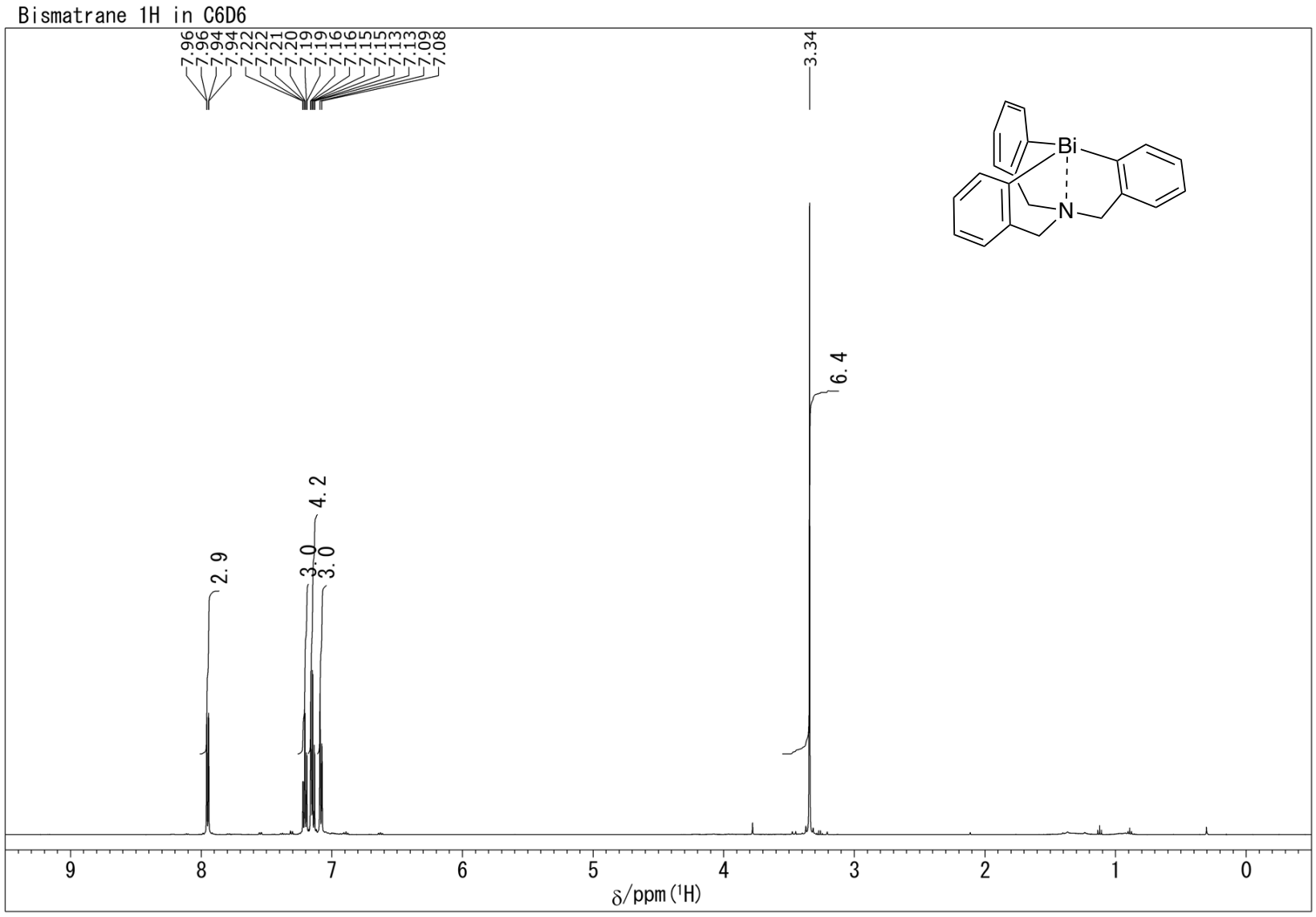


Fig. S7 ^{1}H NMR (C_6D_6, 499.1 MHz) spectrum of compound **4**.

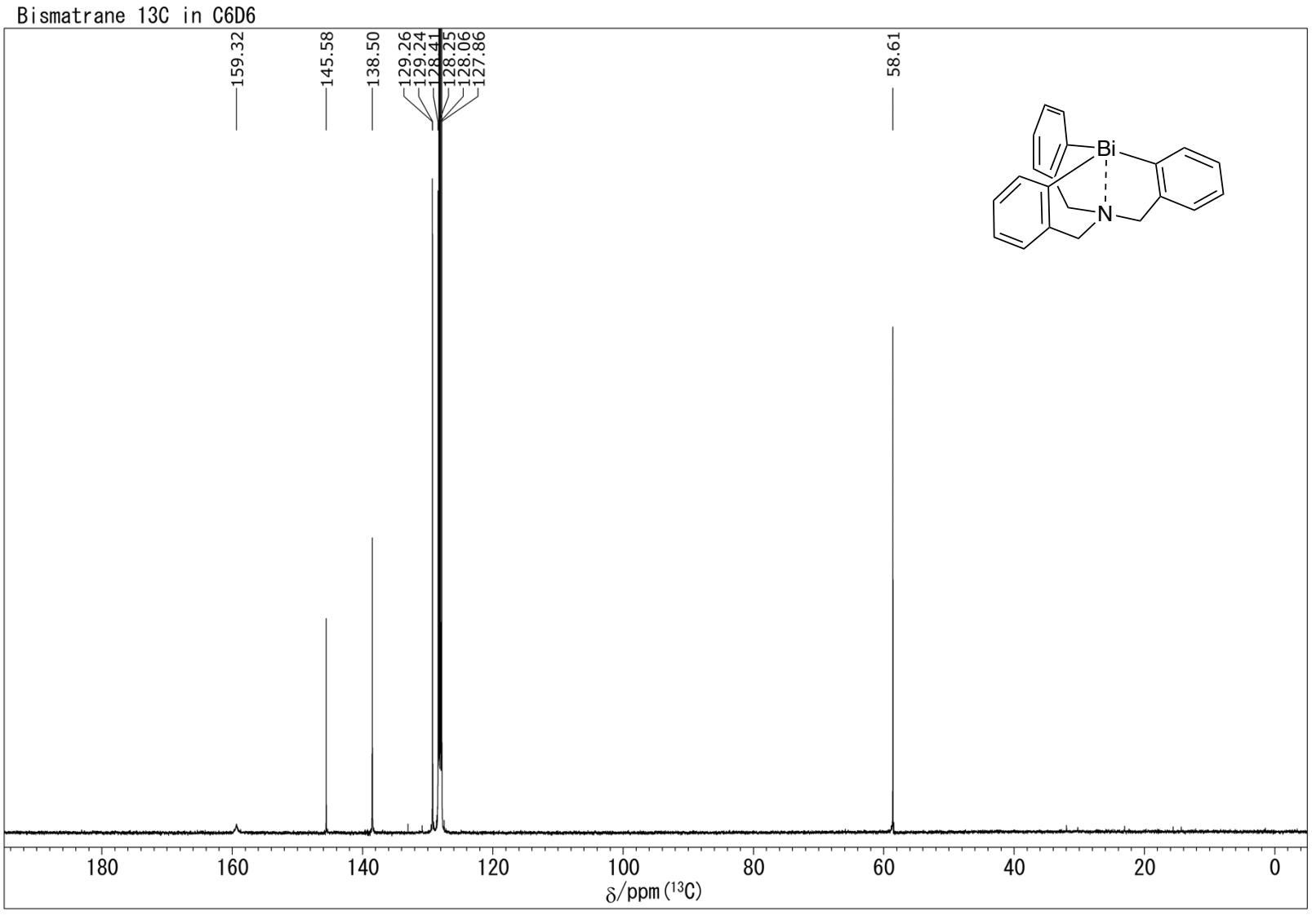


Fig. S8 ^{13}C NMR (C_6D_6, 125.4 MHz) spectrum of compound **4**.

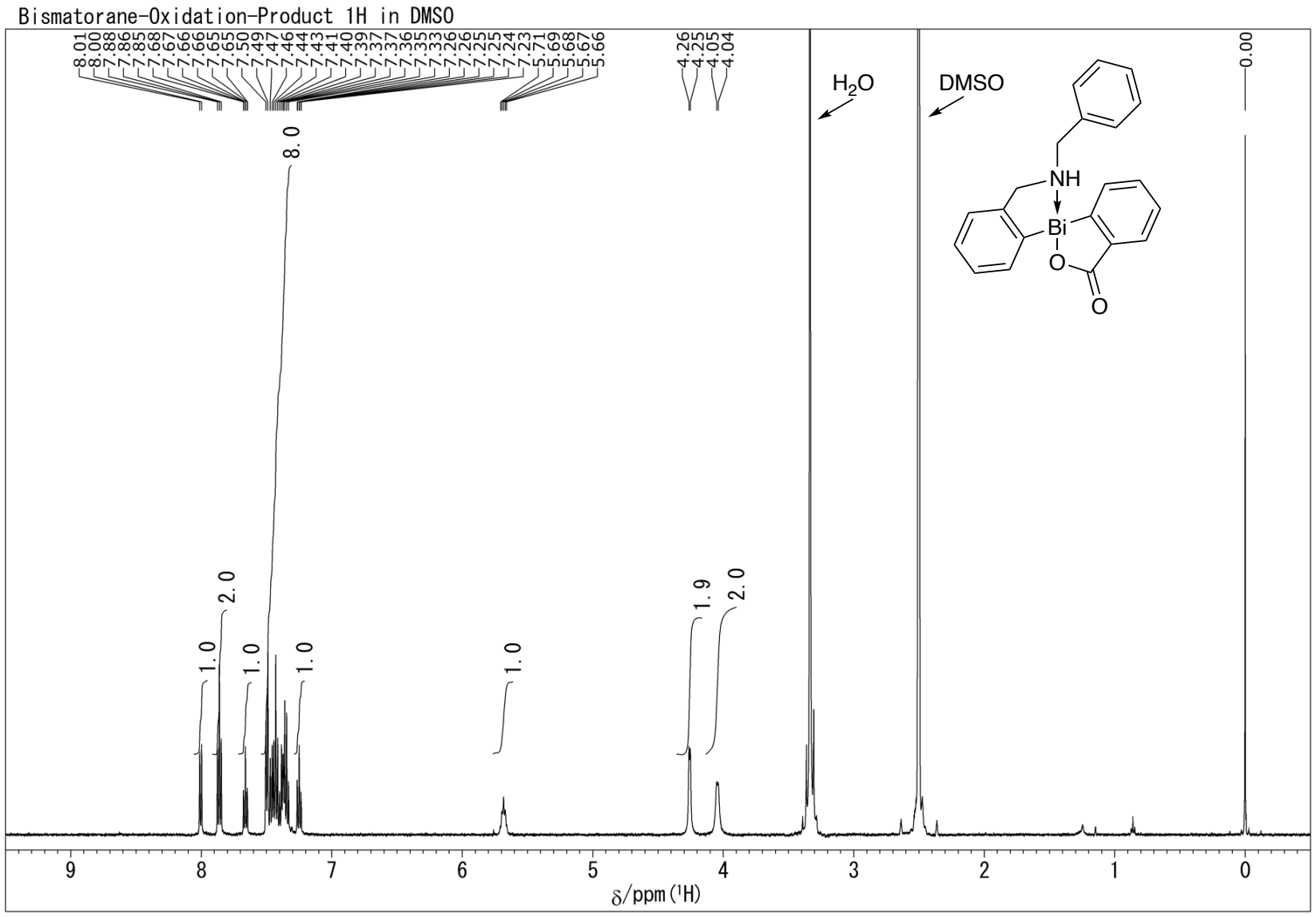


Fig. S9 ^{1}H NMR (DMSO-d_6, 499.1 MHz) spectrum of compound **5**.

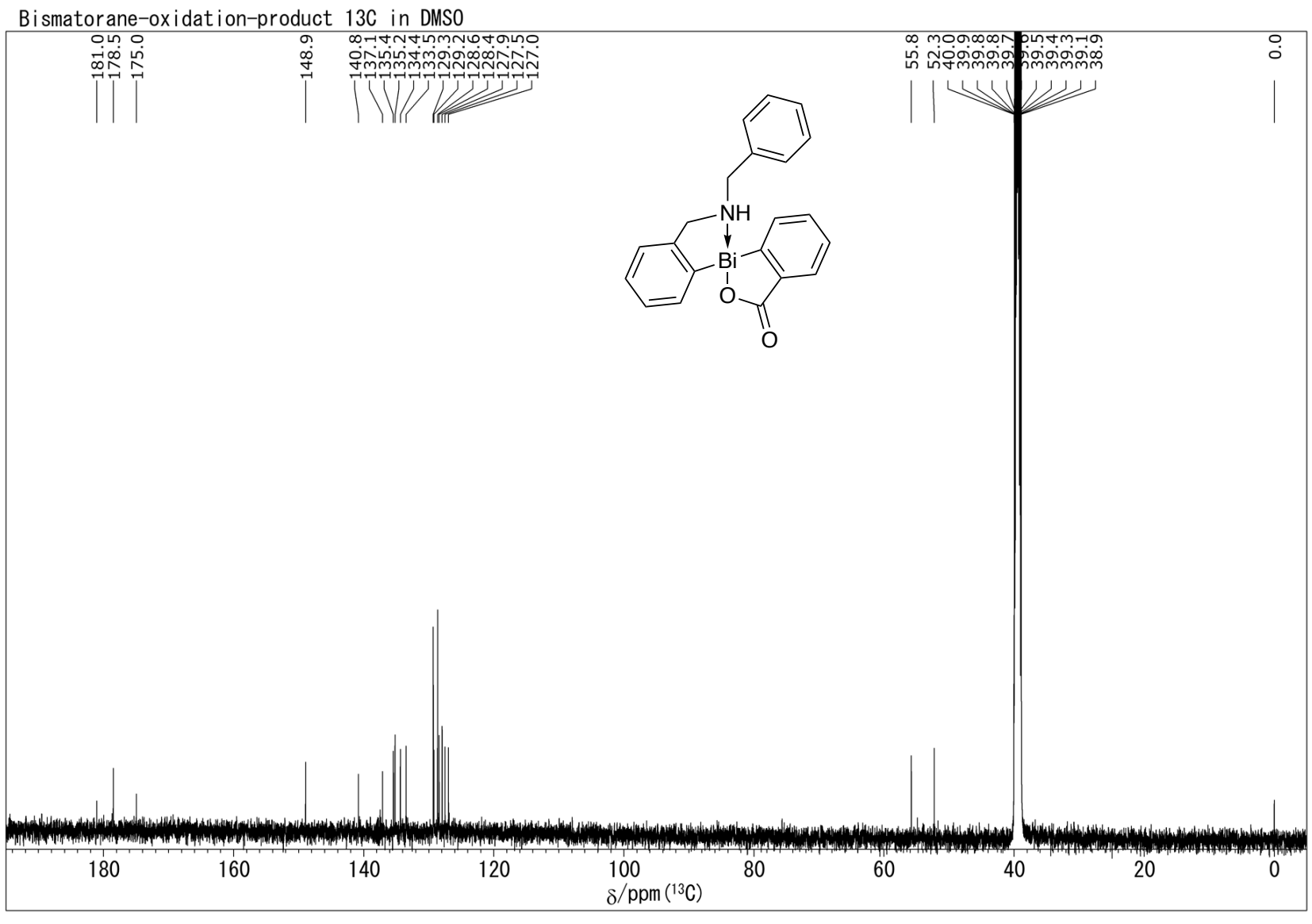


Fig. S10 ^{13}C NMR (DMSO-d_6, 125.4 MHz) spectrum of compound **5**.

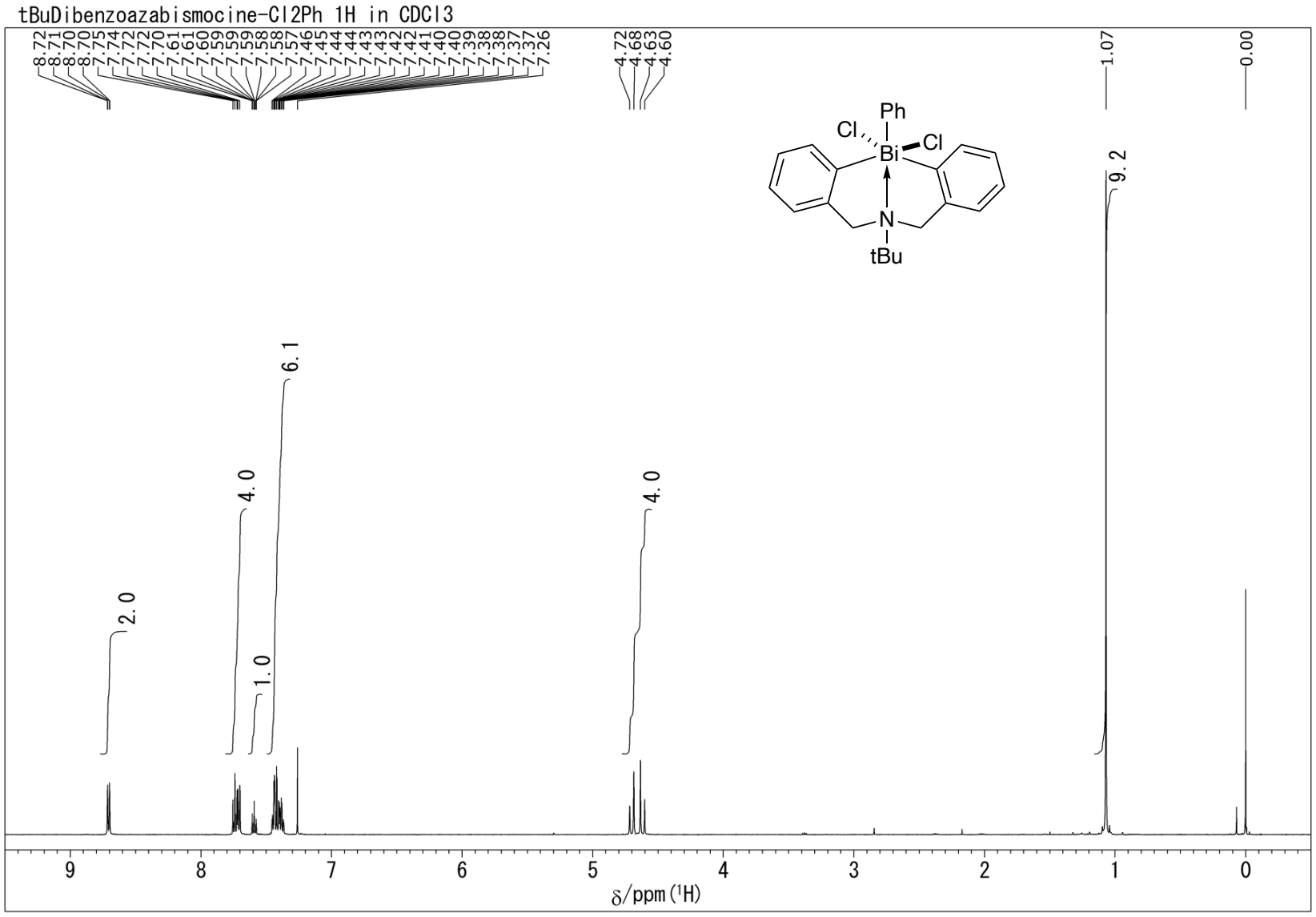


Fig. S11 ^{1}H NMR ($CDCl_3$, 499.1 MHz) spectrum of compound **7a**.

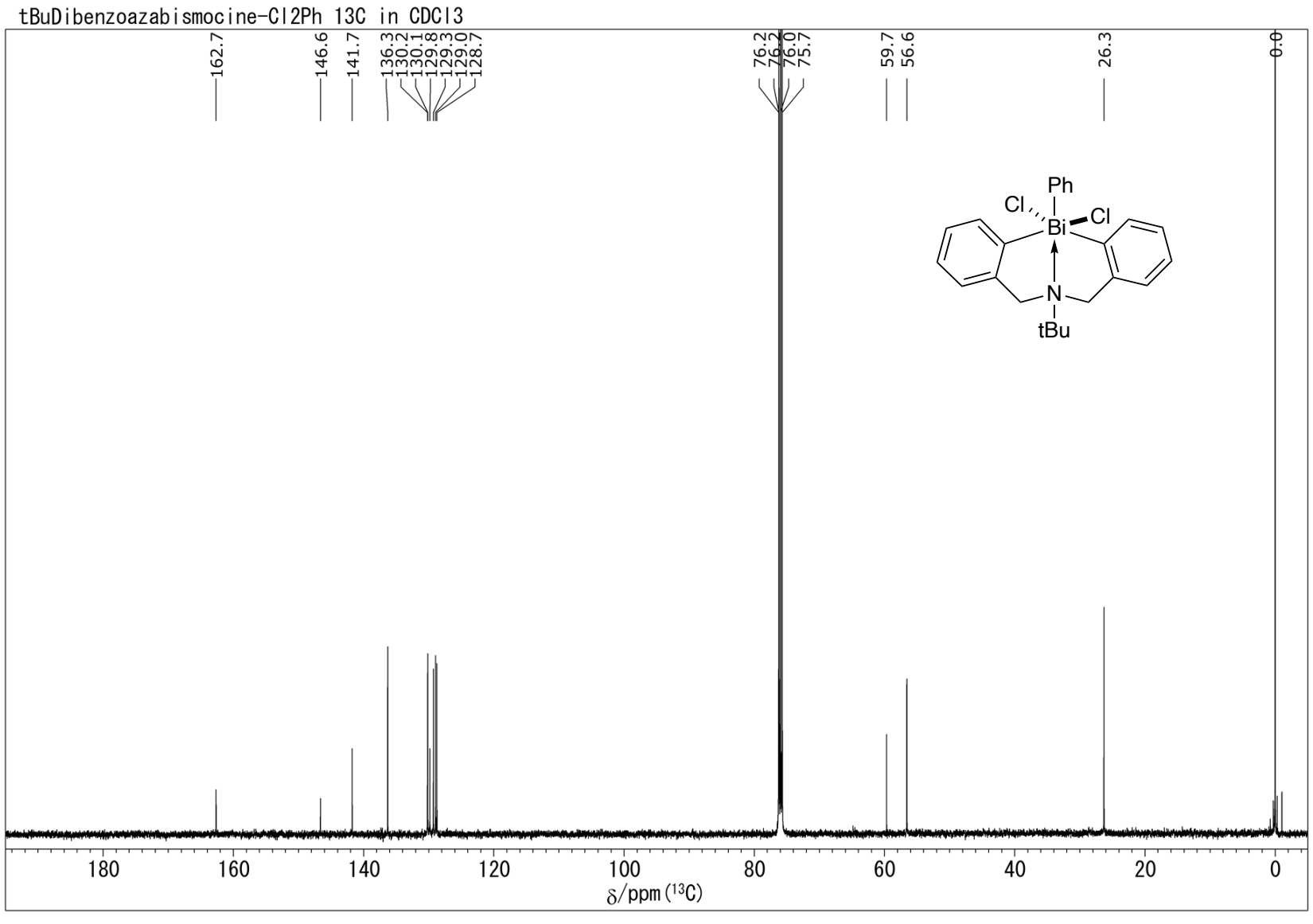


Fig. S12 ^{13}C NMR ($CDCl_3$, 125.4 MHz) spectrum of compound **7a**.

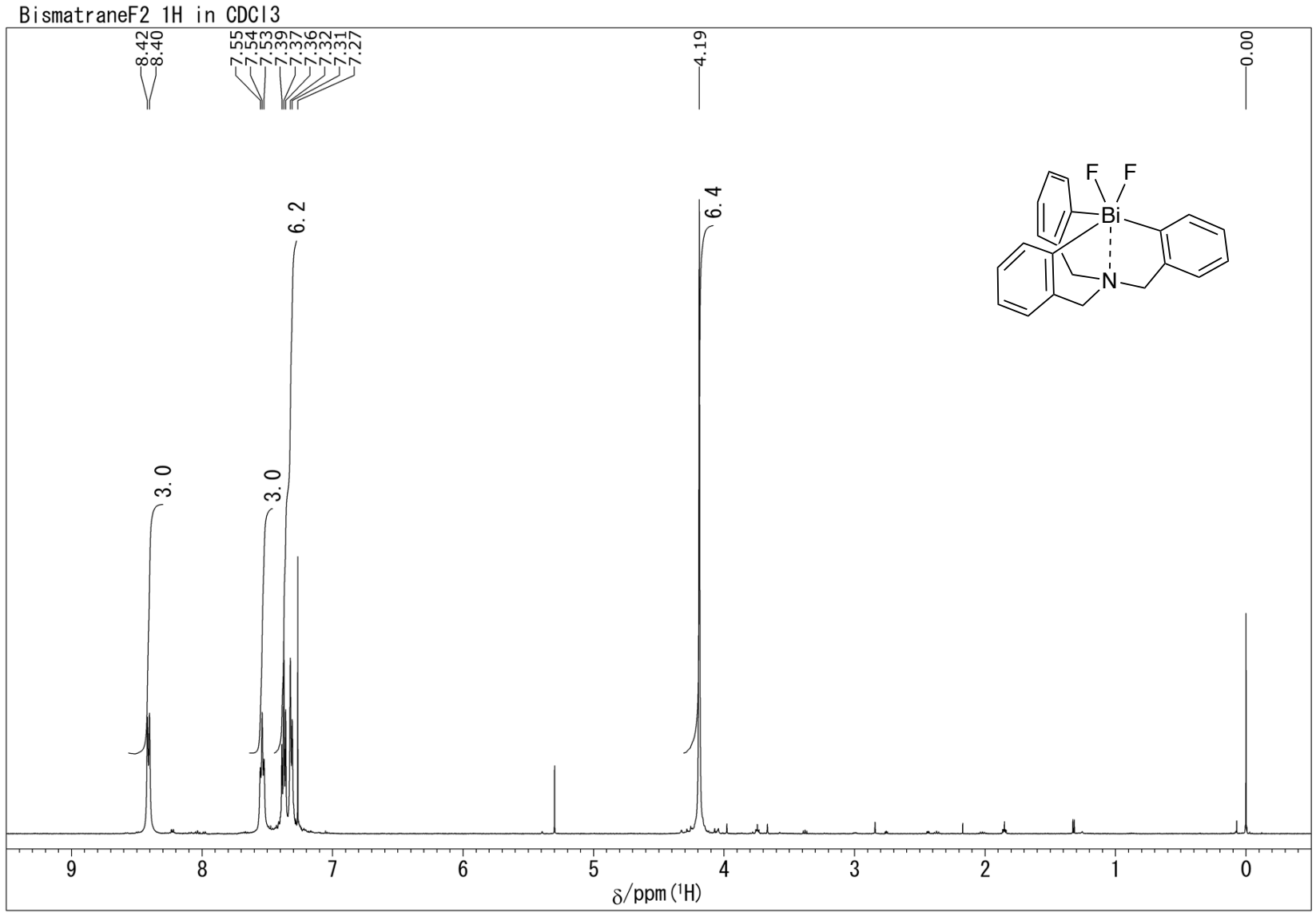


Fig. S13 ^{1}H NMR ($CDCl_3$, 499.1 MHz) spectrum of compound **8b**.

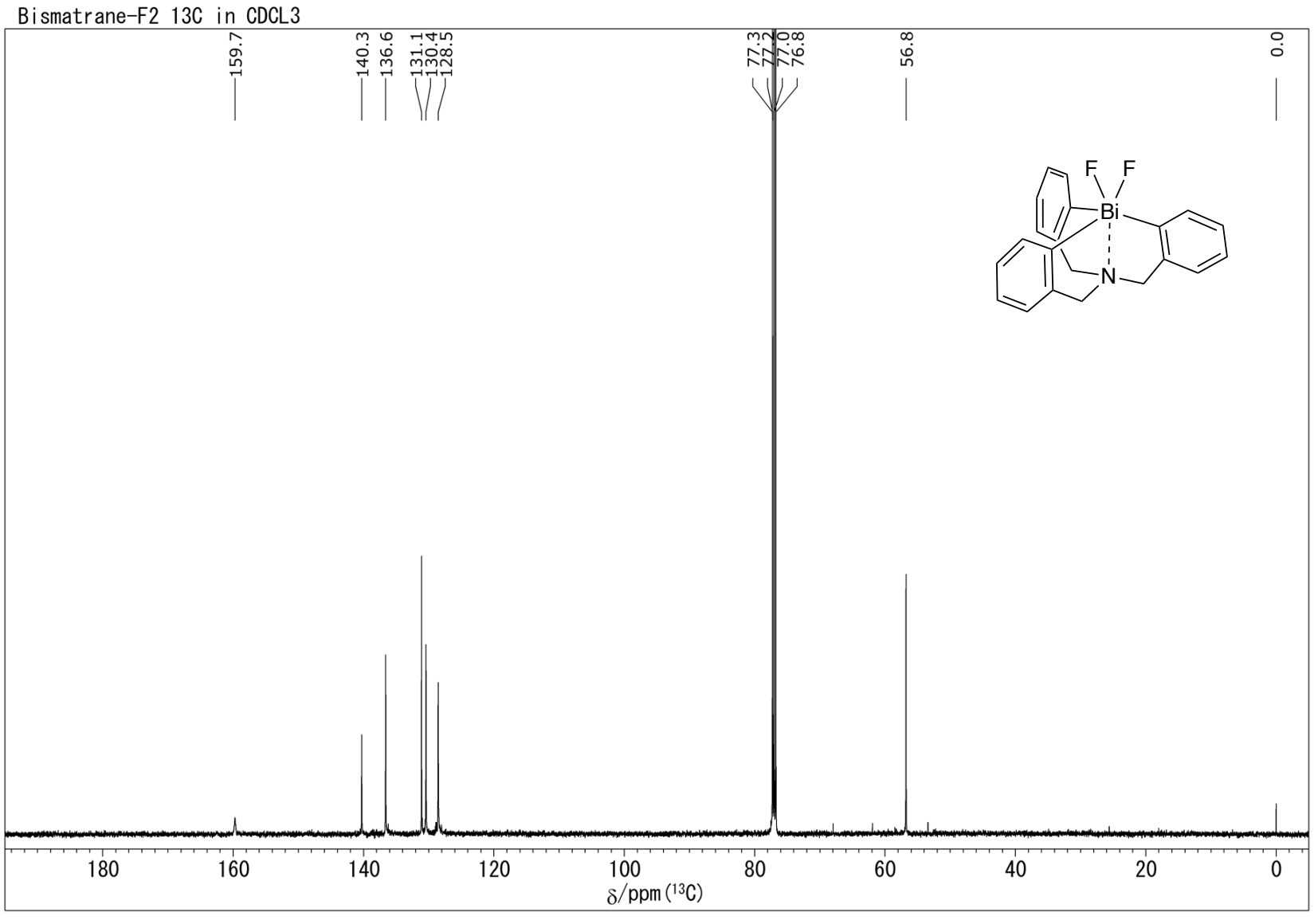


Fig. S14 ^{13}C NMR ($CDCl_3$, 125.4 MHz) spectrum of compound **8b**.

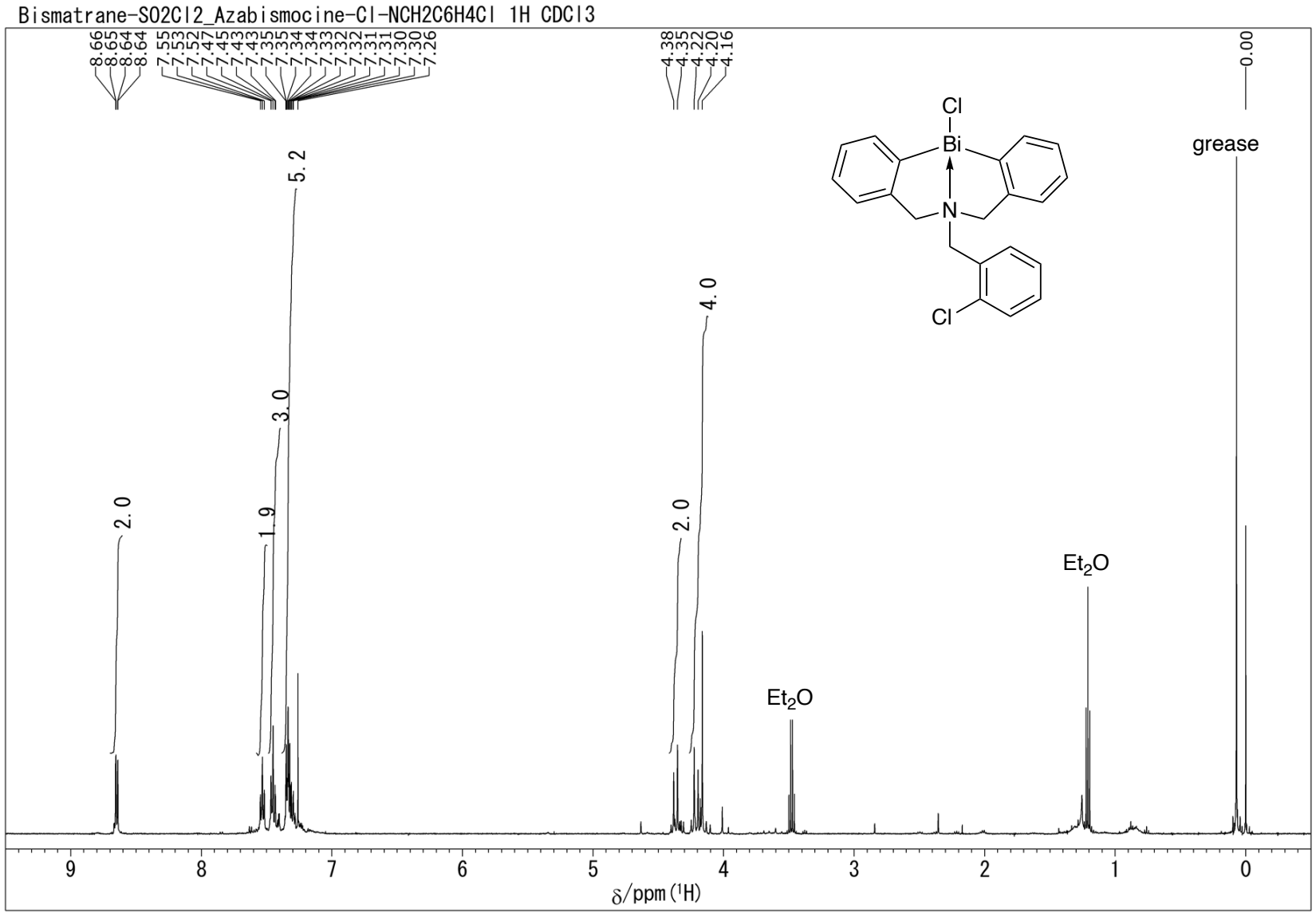


Fig. S15 ^{1}H NMR ($CDCl_3$, 499.1 MHz) spectrum of compound **9**.

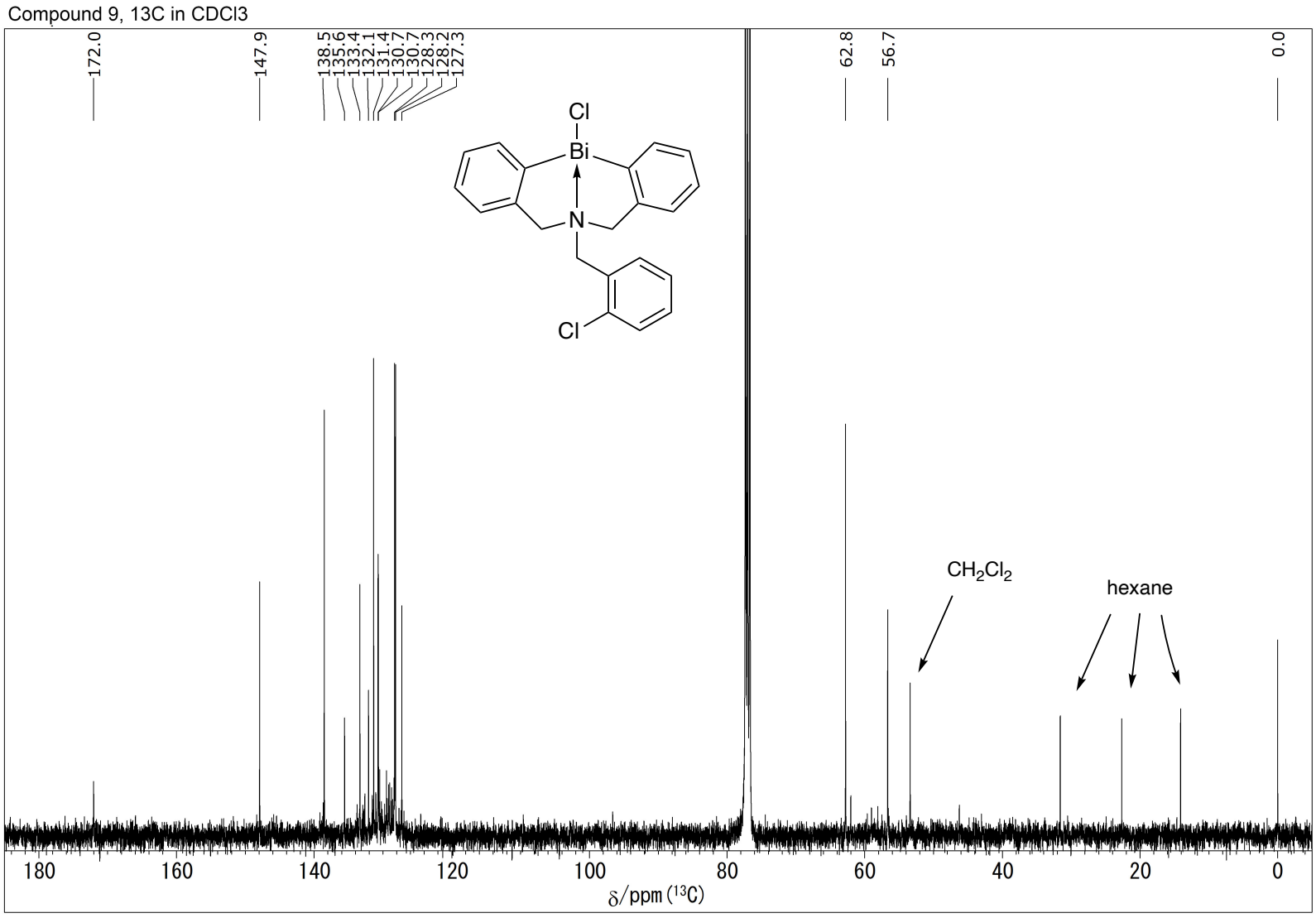


Fig. S16 ^{13}C NMR ($CDCl_3$, 100.6 MHz) spectrum of compound **9**.