Electric Supporting Information

Thieno[1,3,2]oxazaborinine-containing aza-BODIPYs with near infrared absorption bands; synthesis, photophysical properties, and device application

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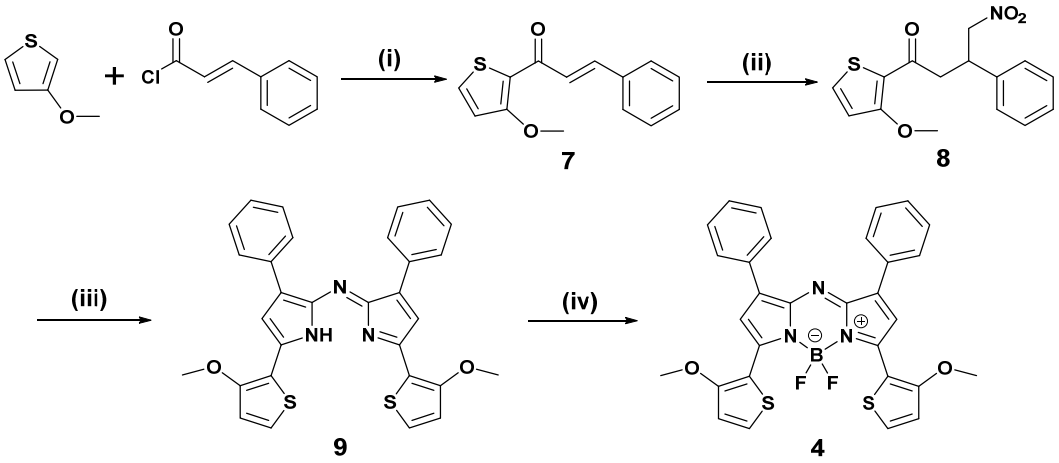
Synthesis of 4

Dye **4** was prepared from 3-methoxythiophene through a chalcone intermediate. (Scheme S1).



Scheme S1. Synthesis of **4**. *Reaction and Conditions*; (i) $SnCl_4$, dry CH_2Cl_2, (ii) $MeNO_2$, KOH, EtOH, (iii) NH_4OAc, dry EtOH, (iv) $BF_3{\cdot}OEt_2$, DIPEA, dry CH_2Cl_2.

(*E*)-1-(3-Methoxythiophen-2-yl)-3-phenyl-2-propen-1-one 7[1]

To a solution of 3-methoxythiophene (4.0 mL, 40.6 mmol) and cinnamoyl chloride (6.78 g, 40.7 mmol) in dry CH_2Cl_2 (50 mL) was added $SnCl_4$ (4.75 mL, 40.7 mmol) under water bath cooling. The resulting mixture was stirred for 45 min under water bath conditions. After pouring into 2M HCl aq. the solution, the solution was extracted with CH_2Cl_2. The organic phase was washed with 2M HCl aq. and then with sat. $NaHCO_3$ and dried with Na_2SO_4. After evaporation of the filtrate, the residue was precipitated with hexane to give 9.30 g of **7** in 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.80 (1H, d, J = 15.8 Hz), 7.79 (1H, d, J = 15.6 Hz), 7.64–7.62 (2H, m), 7.57 (1H, d, J = 5.49 Hz), 7.43–7.37 (3H, m), 6.90 (1H, d, J = 5.49 Hz), 4.06 (s, 3H). FAB-MS: m/z = 245 $[M+1]^+$.

1-(3-Methoxythiophen-2-yl)-4-nitro-3-phenylbutan-1-one 8

To a solution of **7** (7.70 g, 31.5 mmol) in EtOH (150 mL) were added nitromethane (33.5 mL, 620 mmol) and KOH (0.390 g, 6.95 mmol). The mixture was stirred at 60 ºC overnight. The resulting solution was concentrated *in vacuo* and extracted with $CHCl_3$, washed with sat. NaCl aq., with NH_4Cl aq. then with water, and dried with Na_2SO_4. After filtration on silica gel, the filtrate was evaporated and dispersed with hexane. In this way, 7.81 g of **8** was obtained in 81% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.55 (1H, d, J = 5.60 Hz), 7.35–7.32 (m, 2H), 7.29–7.24 (3H, m), 6.86 (1H, d, J = 5.44 Hz), 4.81 (1H, dd, J = 12.5 and 6.30 Hz), 4.68 (1H, dd, J = 12.6 and 8.55 Hz), 4.16 (1H, tt, J = 8.21 and 6.29 Hz), 3.99 (3H, s), 3.37 (1H, dd, J = 17.1 and 6.19 Hz), 3.29 (1H, dd, J = 17.1 and 7.92 Hz); ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 189.7, 160.7, 139.5, 133.7, 128.9, 127.7, 127.5, 122.2, 115.9, 79.7, 58.9, 44.3, 39.5; FAB-MS: m/z = 306 $[M+1]^+$.

[5-(3-Methoxythiophen-2-yl)-3-phenyl-1*H*-pyrrol-2-yl]-[5-(3-methoxythiophen-2-yl)-3-phenyl-2*H*-pyrrol-2-ylidene]amine 9

Under a N_2 atmosphere, **8** (2.03 g, 6.65 mmol) and NH_4OAc (19.0 g, 246 mmol) were dissolved in dry EtOH (150 mL). The mixture was refluxed for 65 hours. After the resultant solution was concentrated *in vacuo*, the resultant solid was collected by filtration and washed with EtOH. After filtration on silica gel, reprecipitated with CH_2Cl_2/hexane to give **9** as a fraction A. On the other hand, the filtrate was extracted with $CHCl_3$, the resultant organic layer being washed with water and dried with Na_2SO_4. After evaporation, the residue was chromatographed on silica gel (Wakogel C-300) using CH_2Cl_2/hexane (1:2 v/v) as am eluent to give **9** as a fraction B. Combined A and B fractions, 0.499 g of **9** was collected (29% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.05–8.02 (m, 4H), 7.40–7.37 (m, 4H), 7.33 (2H, d, J = 5.55 Hz), 7.33–7.28 (2H, m), 7.19 (2H, s), 6.94 (2H, d, J = 5.54 Hz), 4.10 (6H, s). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 158.1, 148.4, 148.1, 141.1, 134.1, 129.2, 128.1, 127.5, 126.7, 116.7, 115.1, 114.9, 59.2.

Difluoroboron chelated [5-(3-methoxythiophen-2-yl)-3-phenyl-1*H*-pyrrol-2-yl]-[5-(3-methoxythiophen-2-yl)-3-phenyl-2*H*-pyrrol-2-ylidene]amine 4

To a solution of **9** (0.610 g, 1.17 mmol) in dry CH_2Cl_2 (80 mL) was added DIPEA (2.5 mL, 14.7 mmol) under a N_2 atmosphere. The resulting mixture was stirred for 20 min and BF_3·OEt_2 (2.5 mL, 20.26 mmol) was further added to the solution. After the mixture was stirred at room temperature overnight, it was then poured into water. Resultant organic phase was washed with water and concentrated *in vacuo*. Adding MeOH into the residue allowed us to collect desired **4** (0.626 g) in 94% yield as a crude compound, which was used in the next reaction without further purification. Purity and identification were verified by several analytical data after reprecipitation with CH_2Cl_2 and hexane. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.08–8.05 (4H, m), 7.70 (2H, s), 7.60 (2H, d, J = 5.60 Hz), 7.46–7.42 (4H, m), 7.38 (tt, 2H, J = 7.29 and 1.58 Hz), 6.93 (2H,d, J = 5.60 Hz), 4.06 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 162.2, 148.4, 144.7, 140.9, 132.9, 132.0, 129.2, 128.7, 128.4, 120.0, 115.0, 111.9, 59.1. ^{11}B NMR ($CDCl_3$, 160 MHz): δ (ppm) 0.927 (t, J = 33.4 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) : δ (ppm) 30.8 (q, J = 33.2 Hz). FAB-MS: m/z = 569 $[M]^+$. Elemental analysis: Calcd for $C_{30}H_{22}BF_2N_3O_2S_2$·0.5$H_2O$: C, 62.29; H, 4.01; N, 7.26. Found: C, 62.26; H, 3.90; N, 7.25.

1. G. Henrio and J. Morel, *Tetrahedron Lett.*, 1974, **15**, 2167-2168.

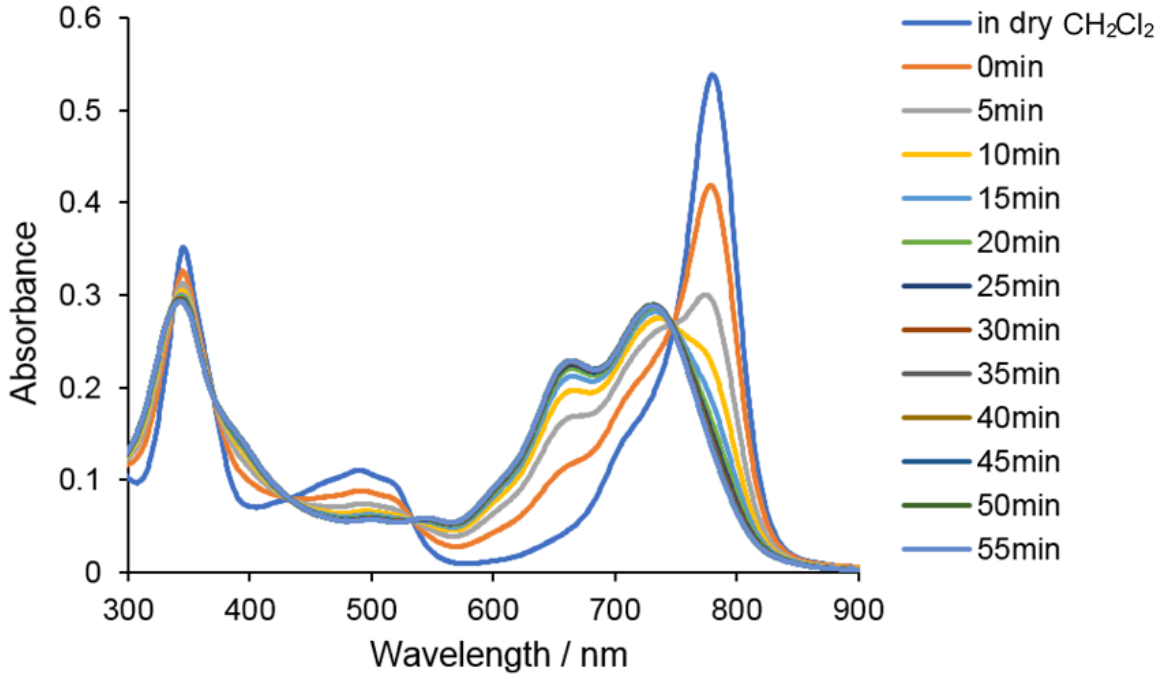


Figure S1. Time-dependent change in absorption spectra of **1** in water saturated CH_2Cl_2.

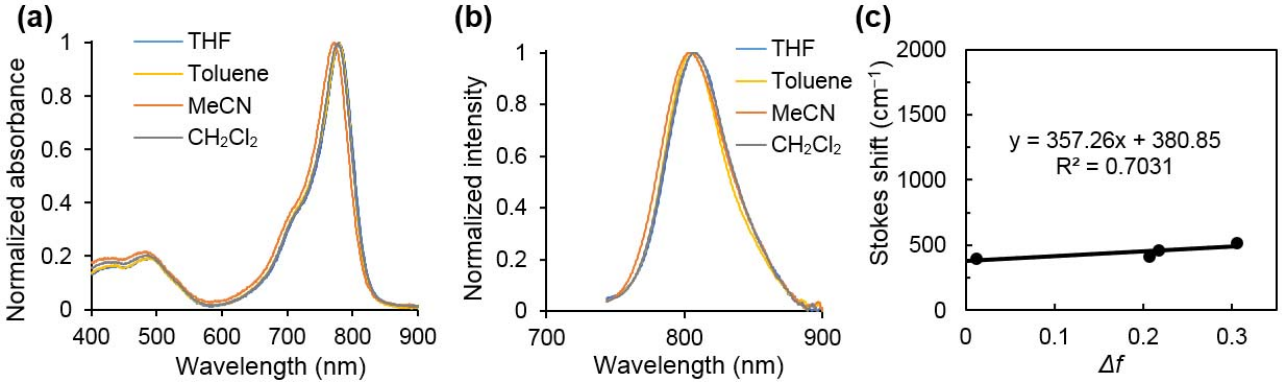


Figure S2. Normalized UV-vis absorption spectra (a) and normalized emission spectra (b) of **3** in various solvents (1 μM). λ_{ex} = 730 nm. (c) Lippert-Mataga plot of **3**.

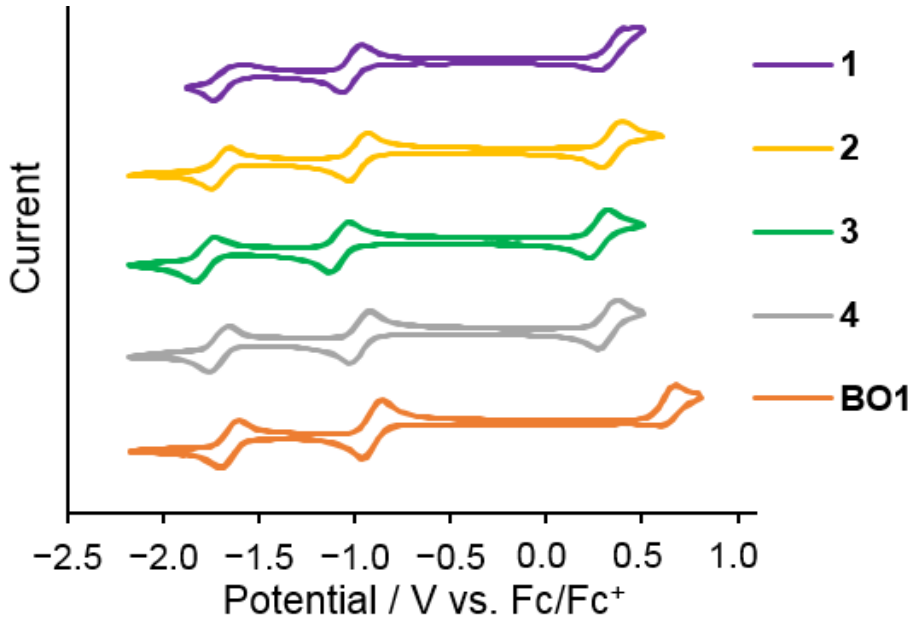


Figure S3. Cyclic voltammograms of dyes in CH_2Cl_2 solution containing 0.1 M $TBAPF_6$. The scan rate is 0.05 V s^{-1}.

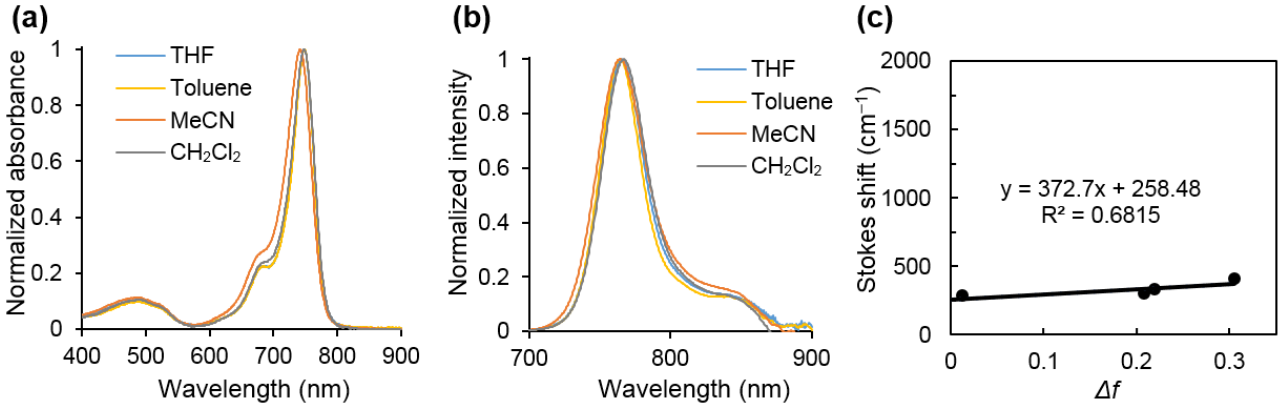


Figure S4. Normalized UV-vis absorption spectra (a) and normalized emission spectra (b) of **4** in various solvents (ca. 1 μM). λ_{ex} = 650 nm. (c) Lippert-Mataga plot of **4**.

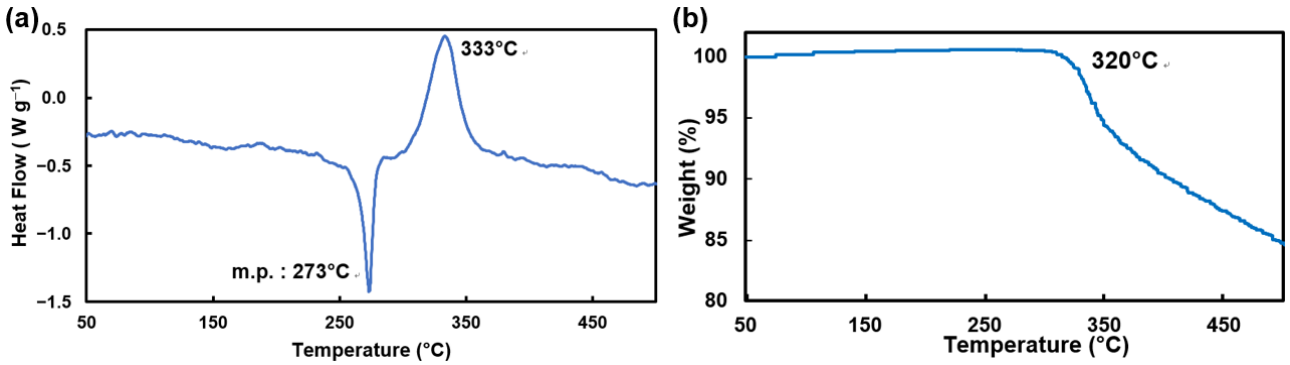


Figure S5. DSC (a) and TGA (b) plots of **3**.

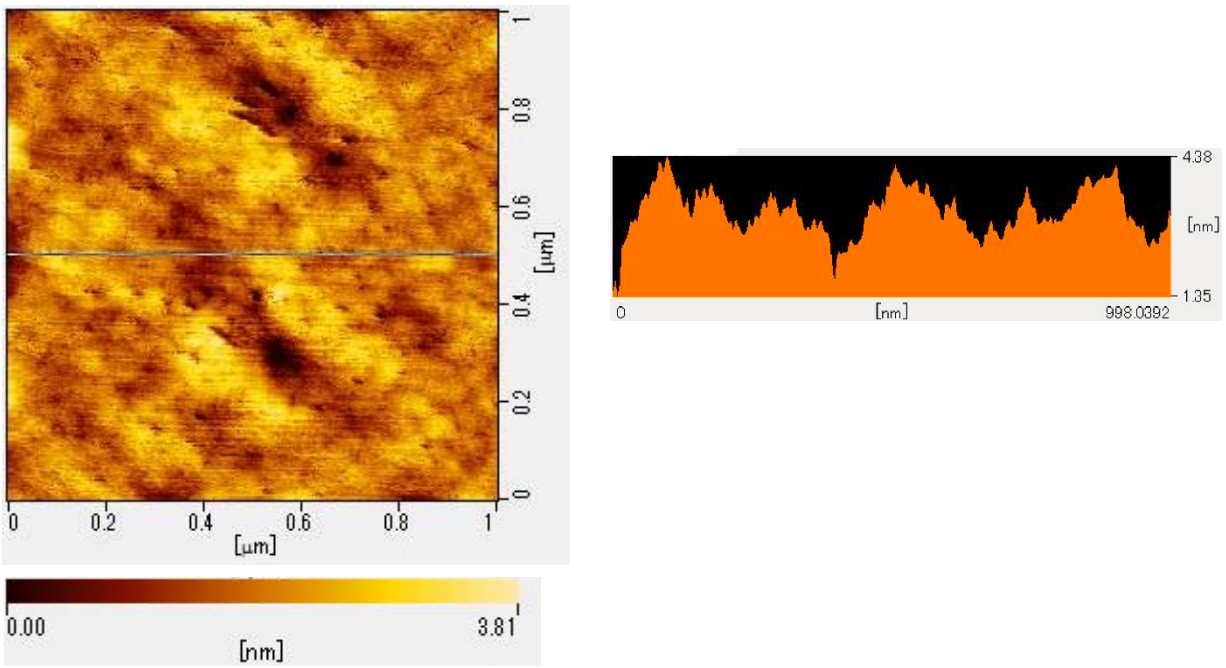


Figure S6. AFM images of film **3**.

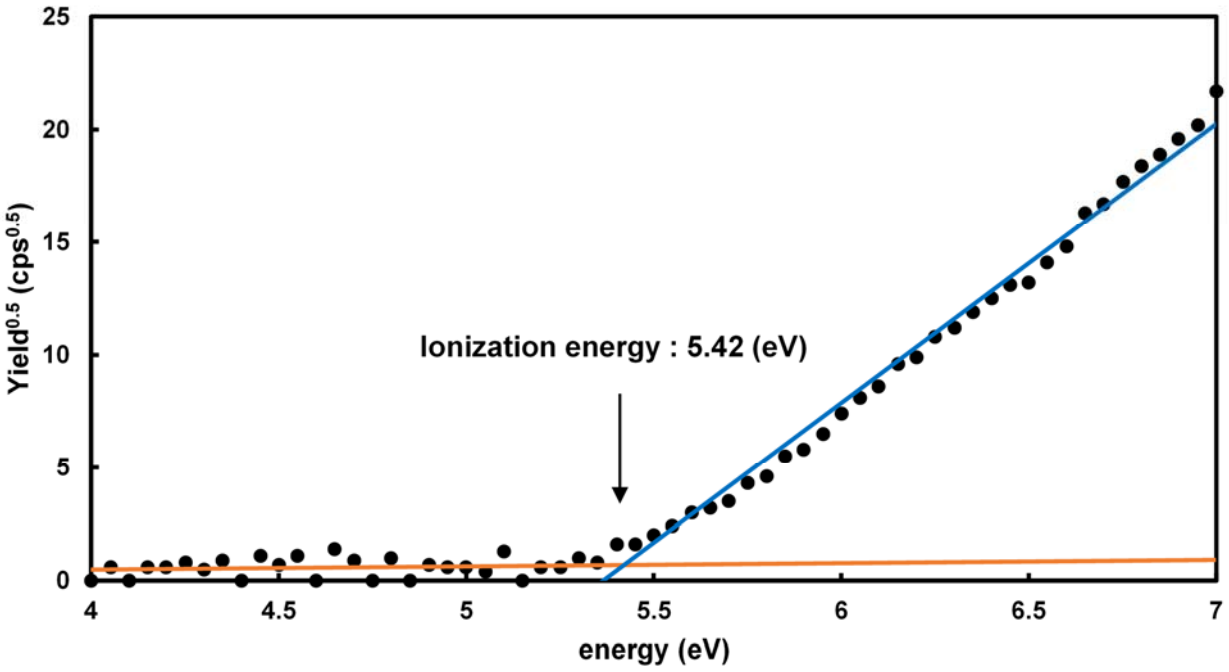


Figure S7. Photoelectron spectroscopic analysis of film **3**.

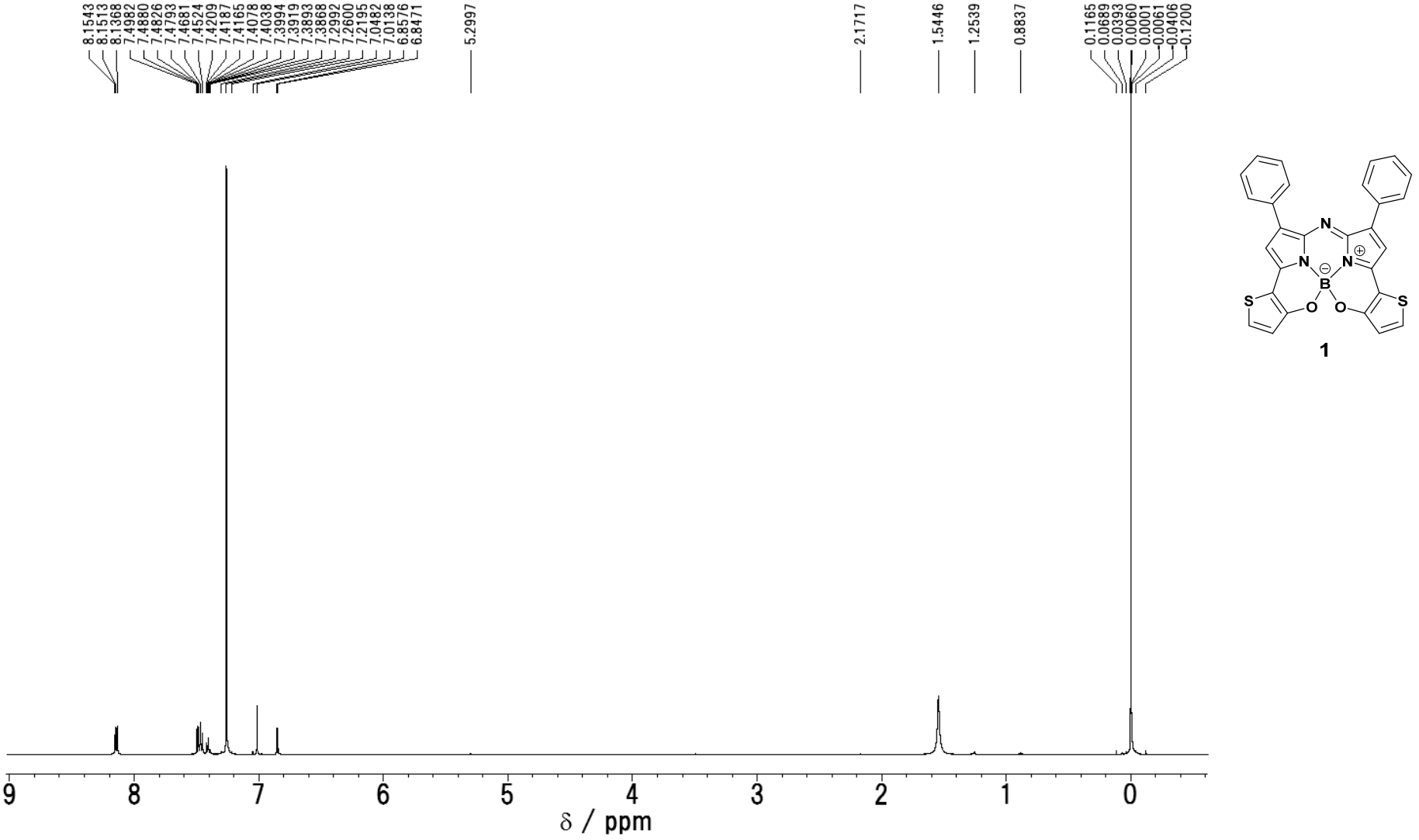


Figure S8. ^{1}H NMR spectrum of **1** (500 MHz) in $CDCl_3$.

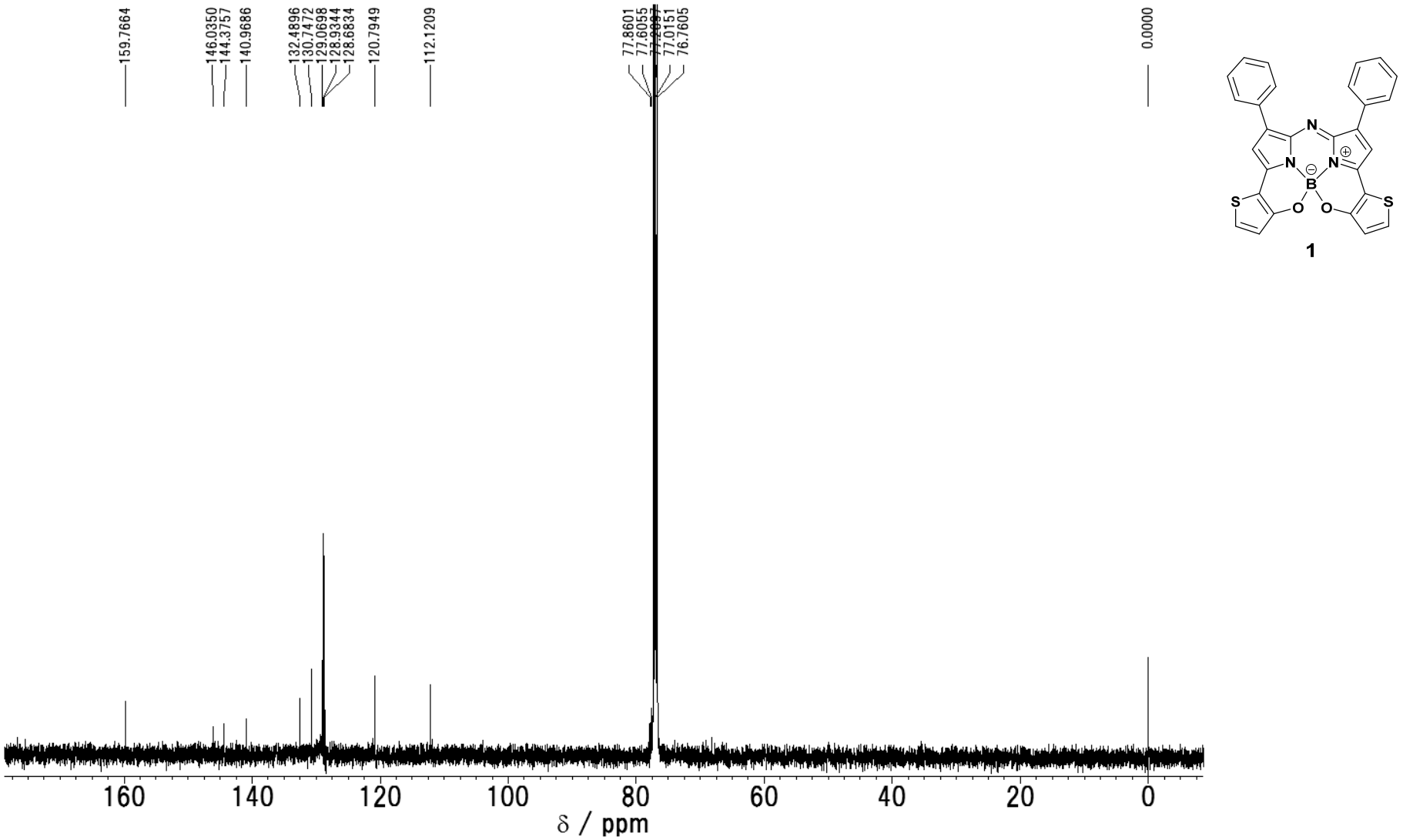


Figure S9. ^{13}C NMR spectrum of **1** (126 MHz) in $CDCl_3$.

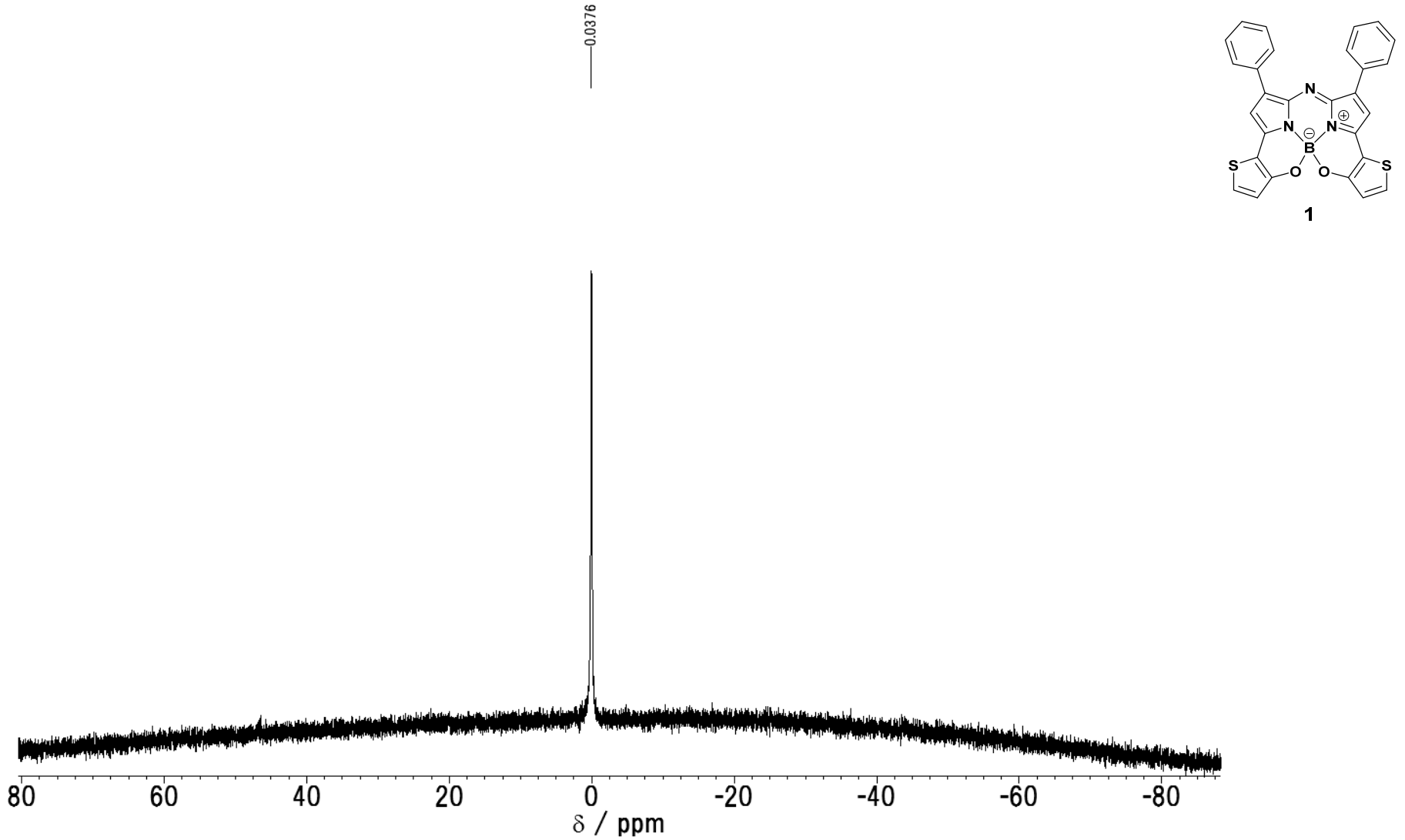


Figure S10. ^{11}B NMR spectrum of **1** (160 MHz) in $CDCl_3$.

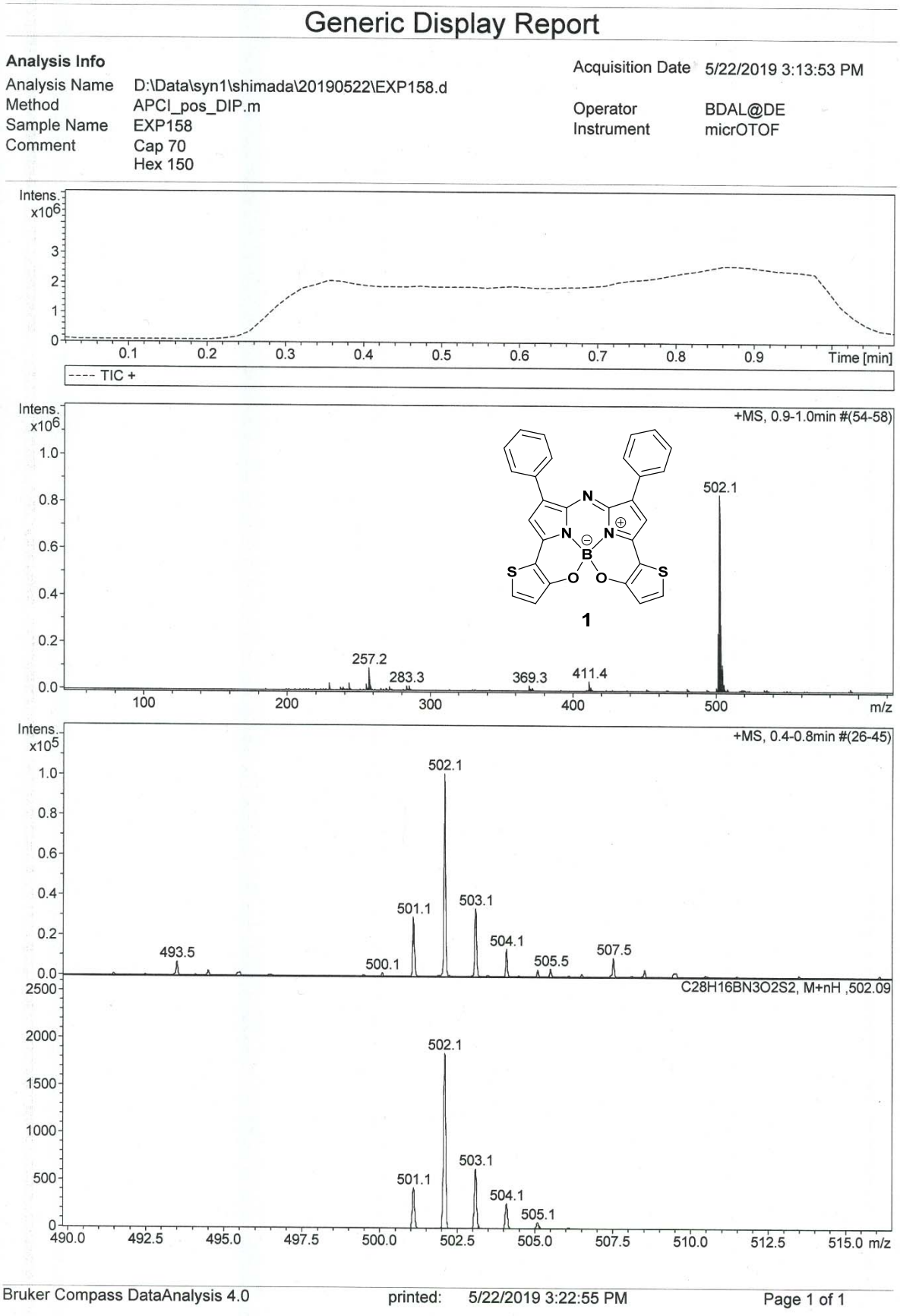


Figure S11. APCI mass spectrum (positive mode) of **1**.

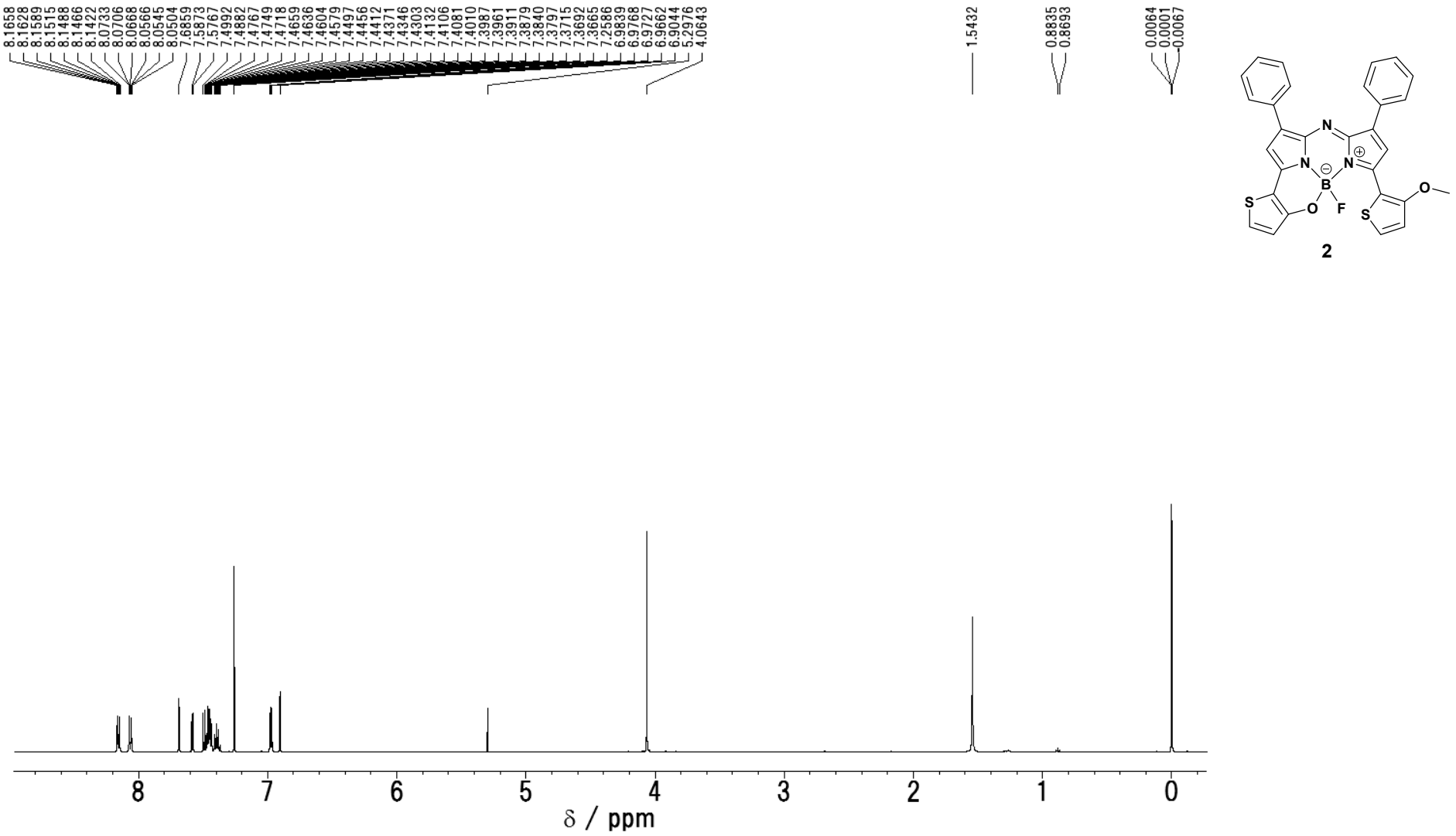


Figure S12. ^{1}H NMR spectrum of **2** (500 MHz) in $CDCl_3$.

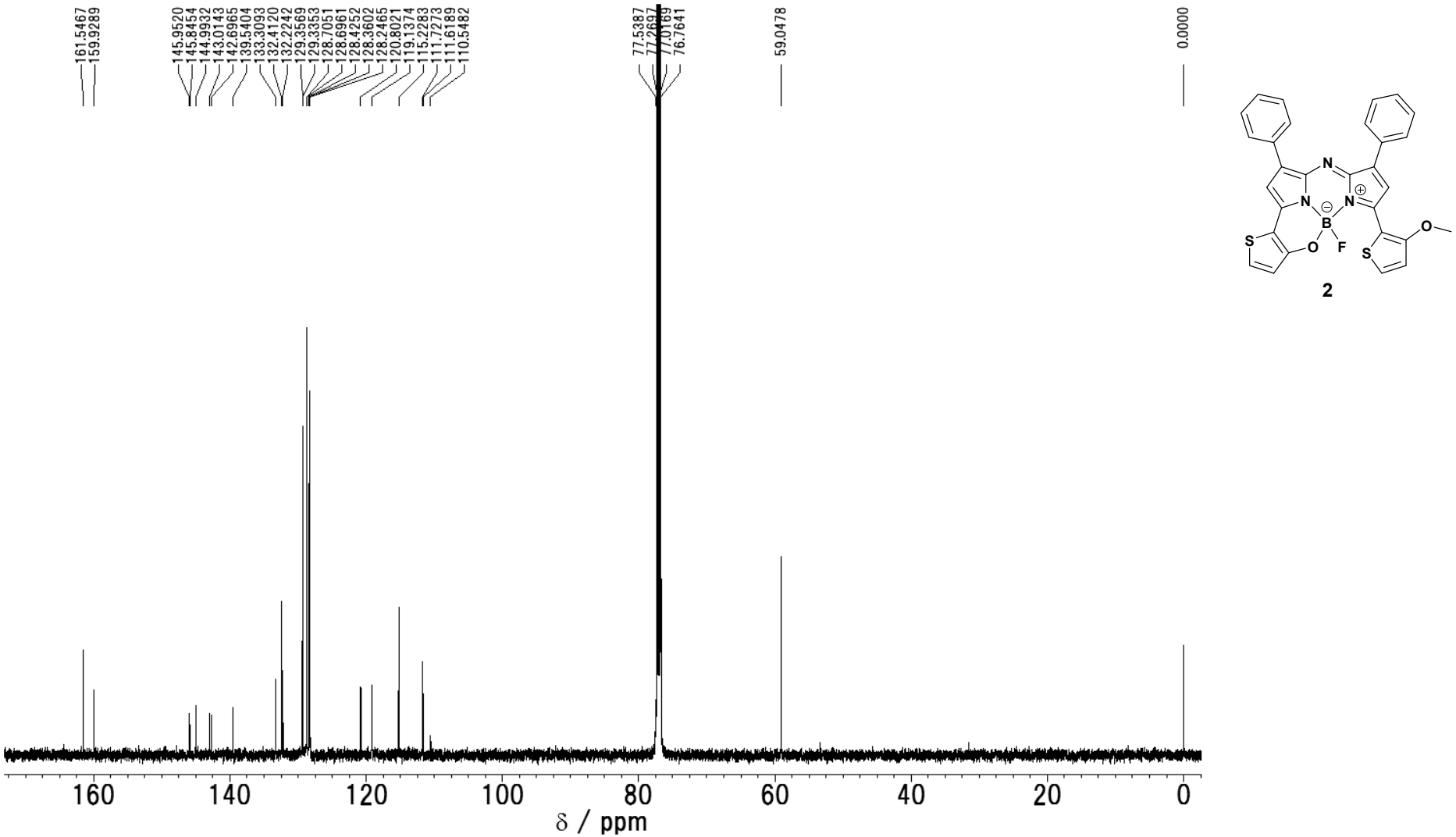
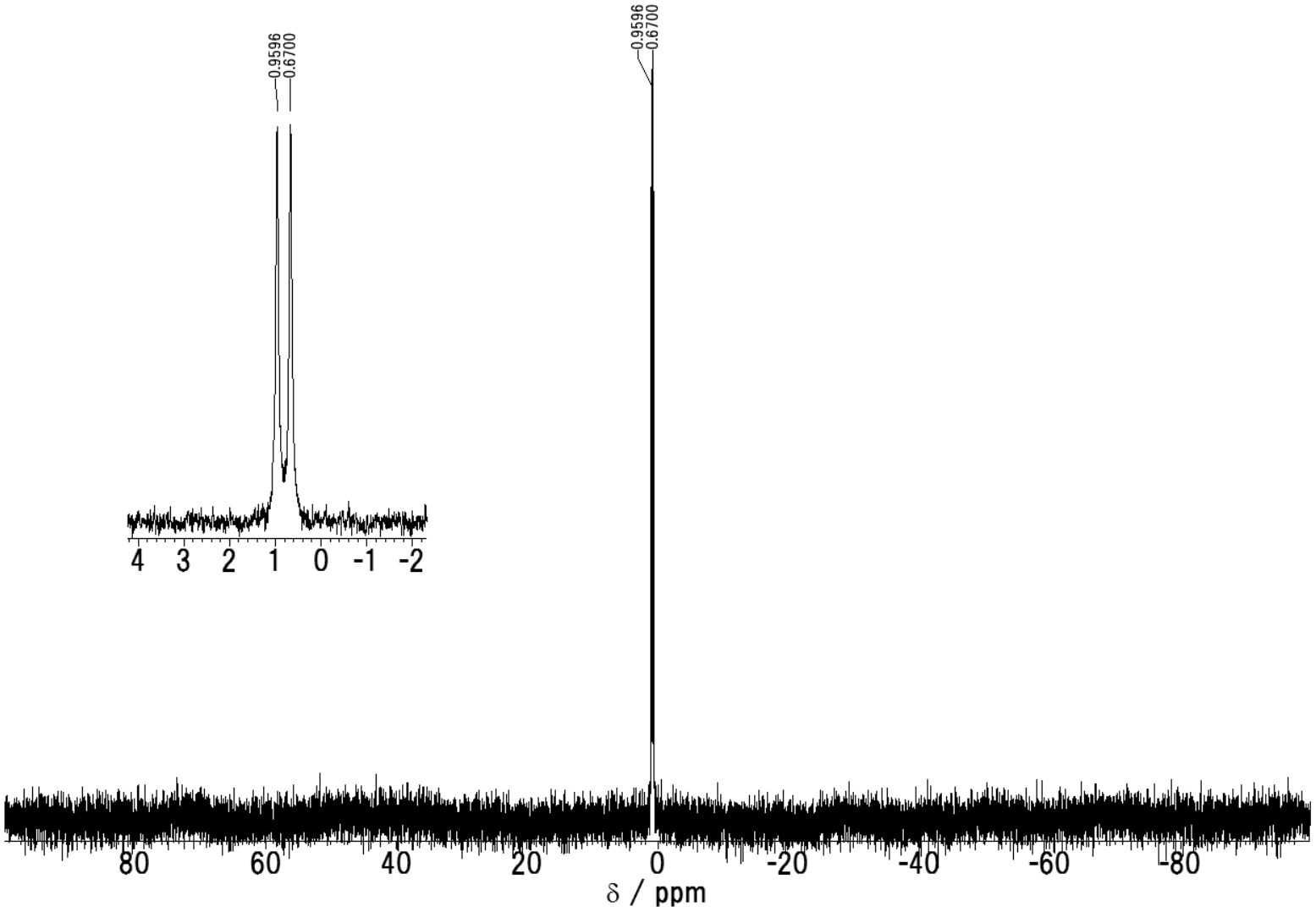
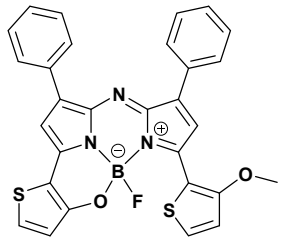


Figure S13. ^{13}C NMR spectrum of **2** (126 MHz) in $CDCl_3$.





2

Figure S14. ^{11}B NMR spectrum of **2** (160 MHz) in $CDCl_3$.

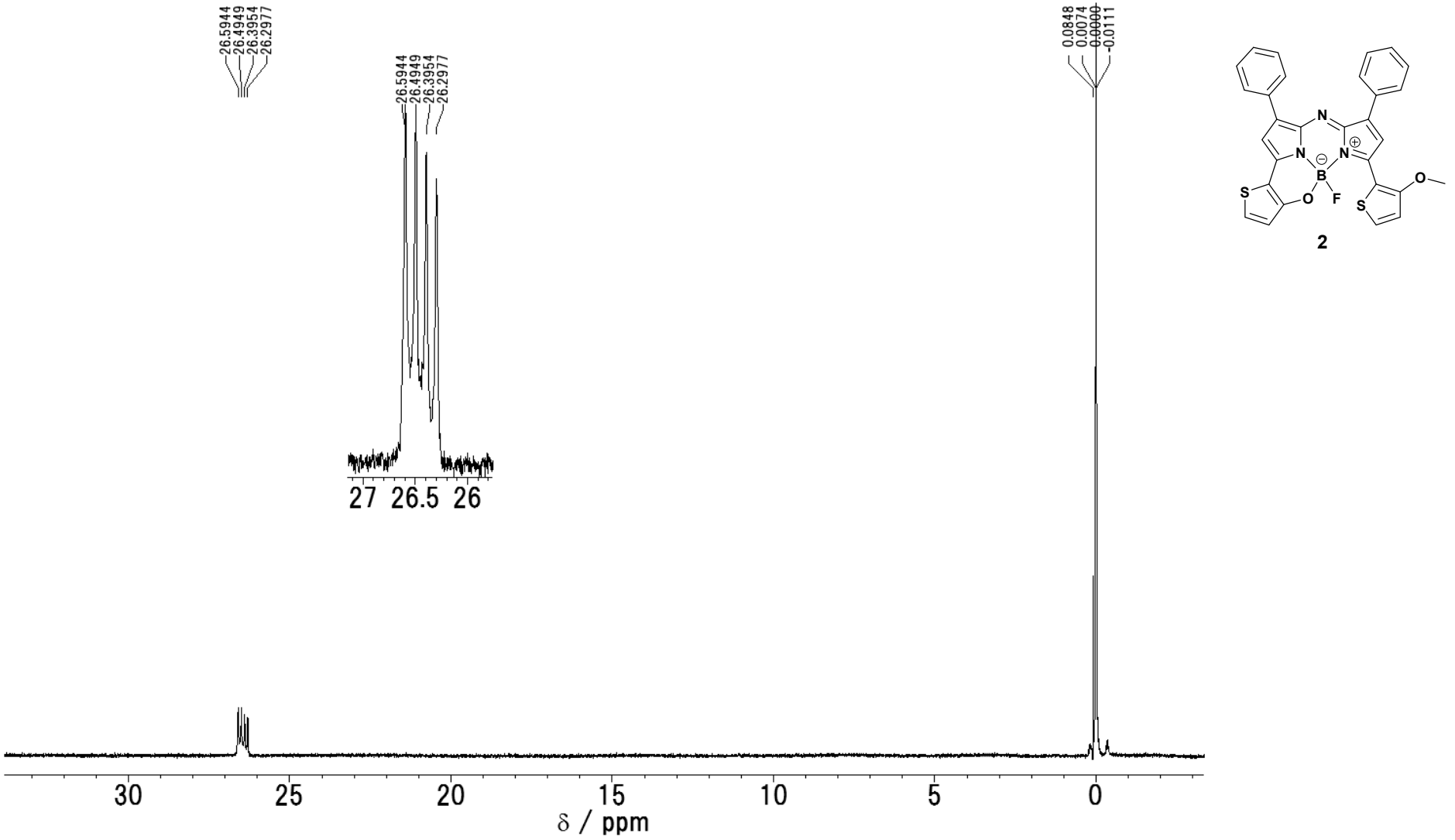


Figure S15. ^{19}F NMR spectrum of **2** (471 MHz) in $CDCl_3$.

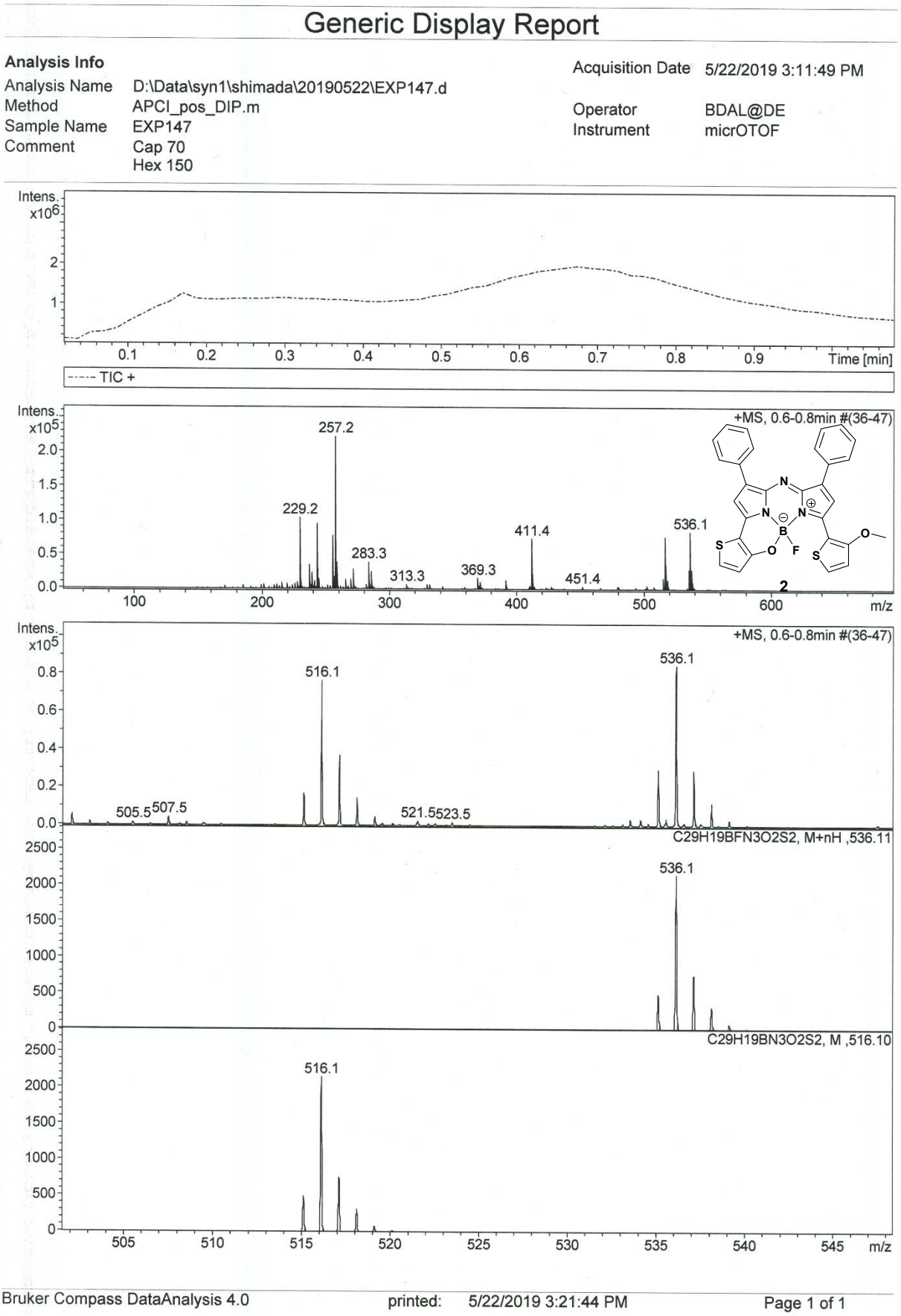


Figure S16. APCI mass spectrum (positive mode) of **2**.

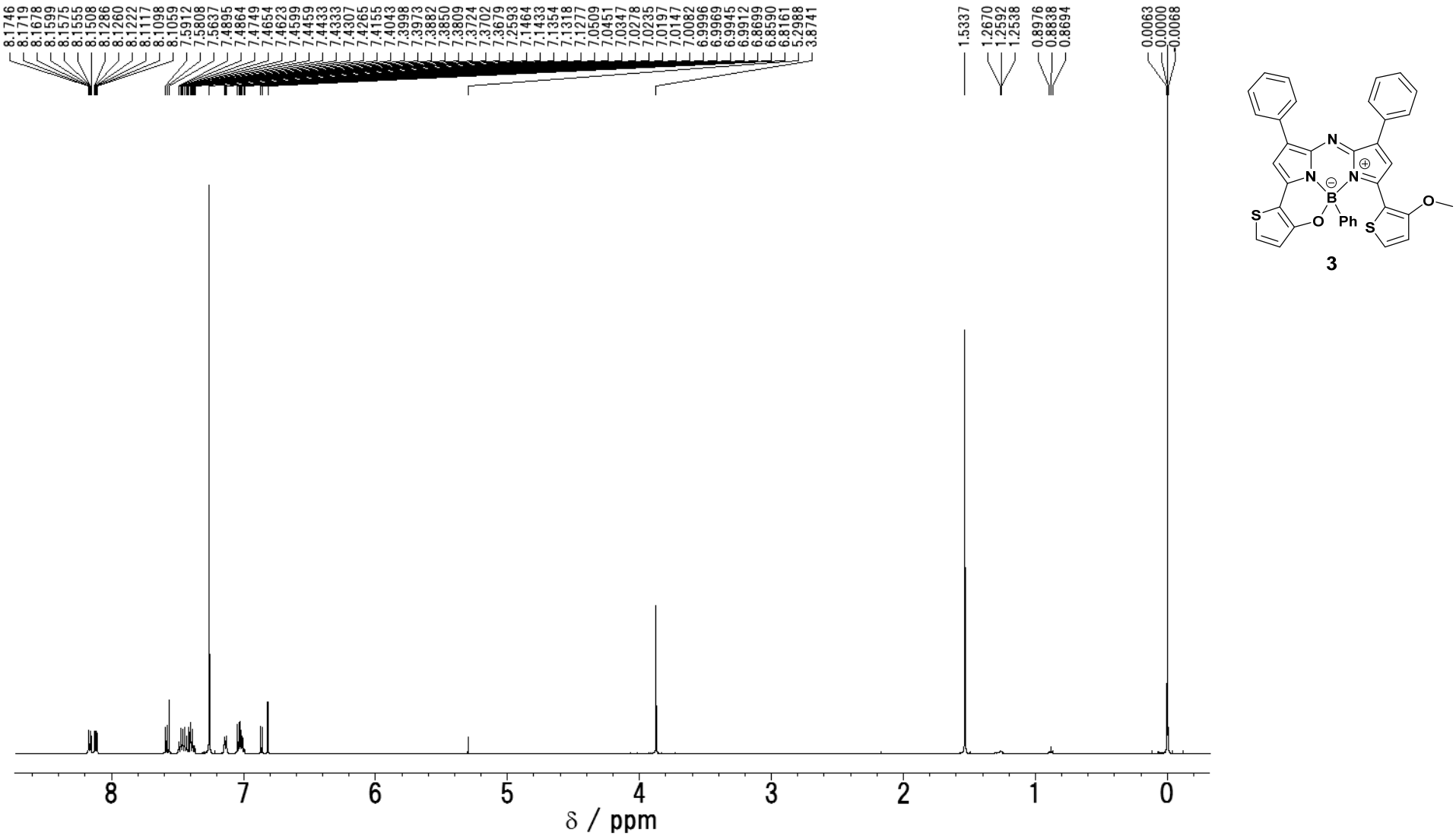


Figure S17. ^{1}H NMR spectrum of **3** (500 MHz) in $CDCl_3$.

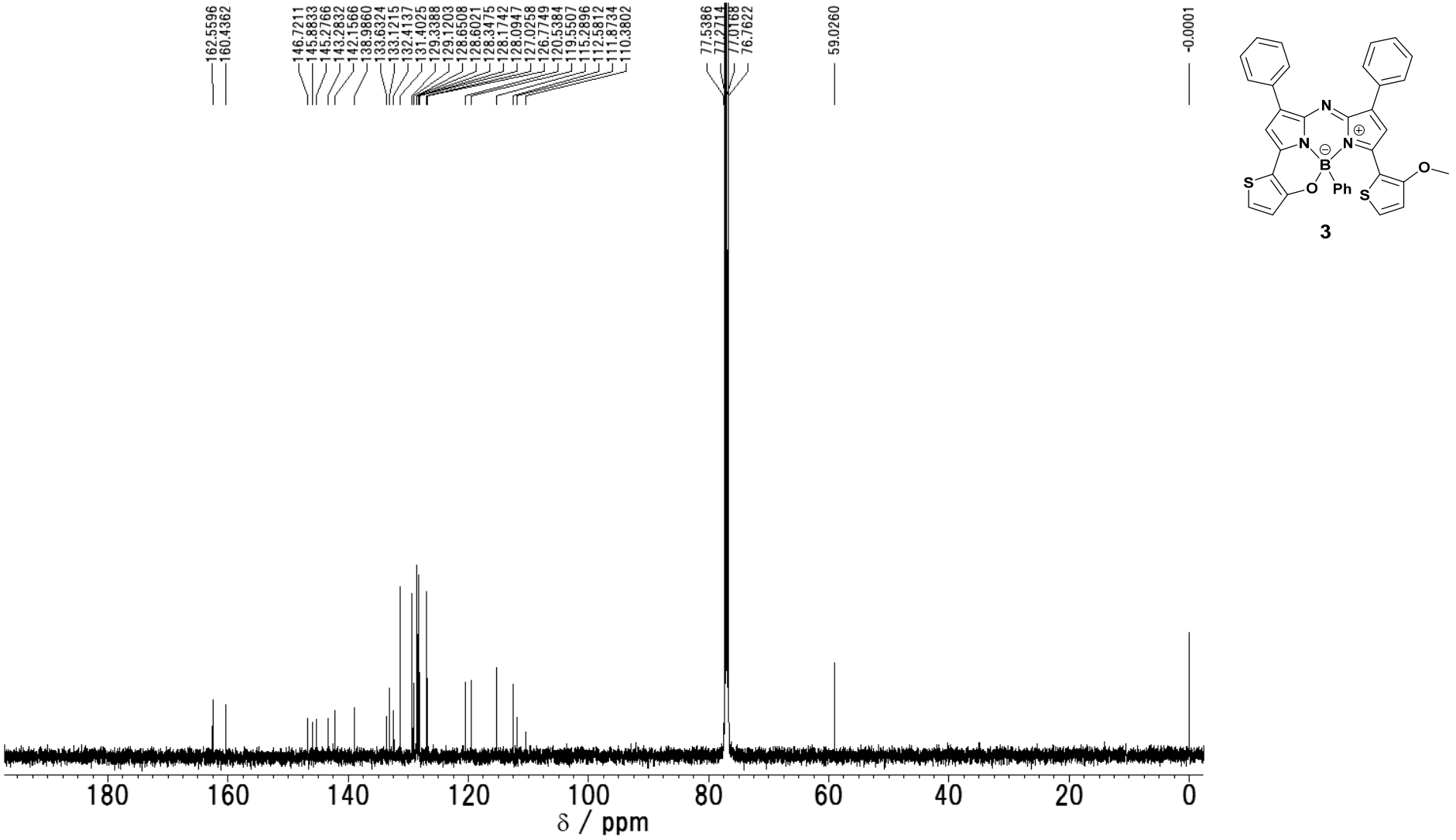
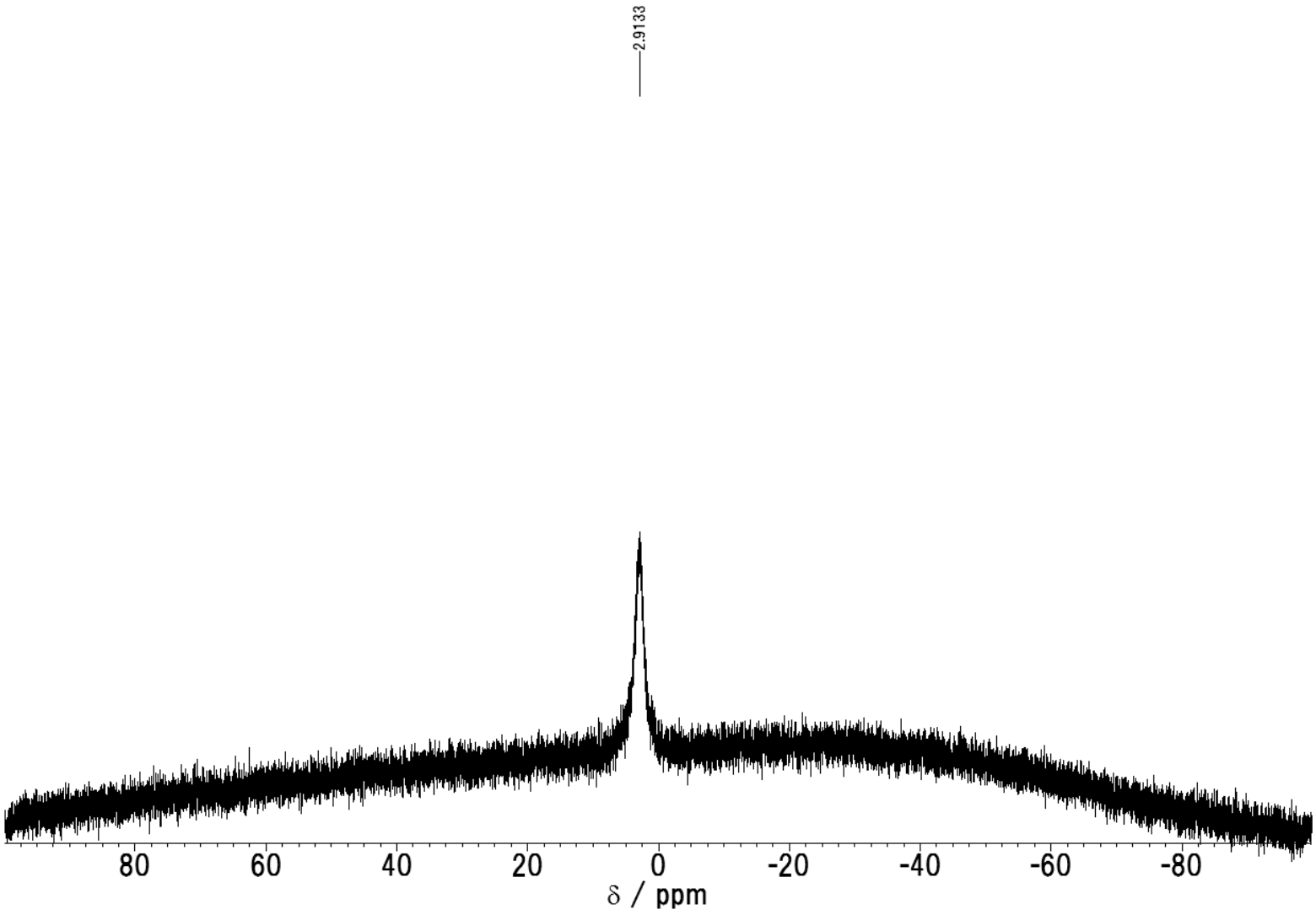
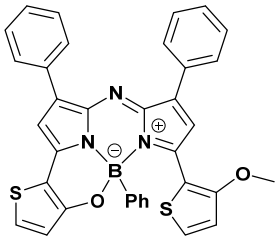


Figure S18. ^{13}C NMR spectrum of **3** (126 MHz) in $CDCl_3$.





3

Figure S19. ^{11}B NMR spectrum of **3** (160 MHz) in $CDCl_3$.

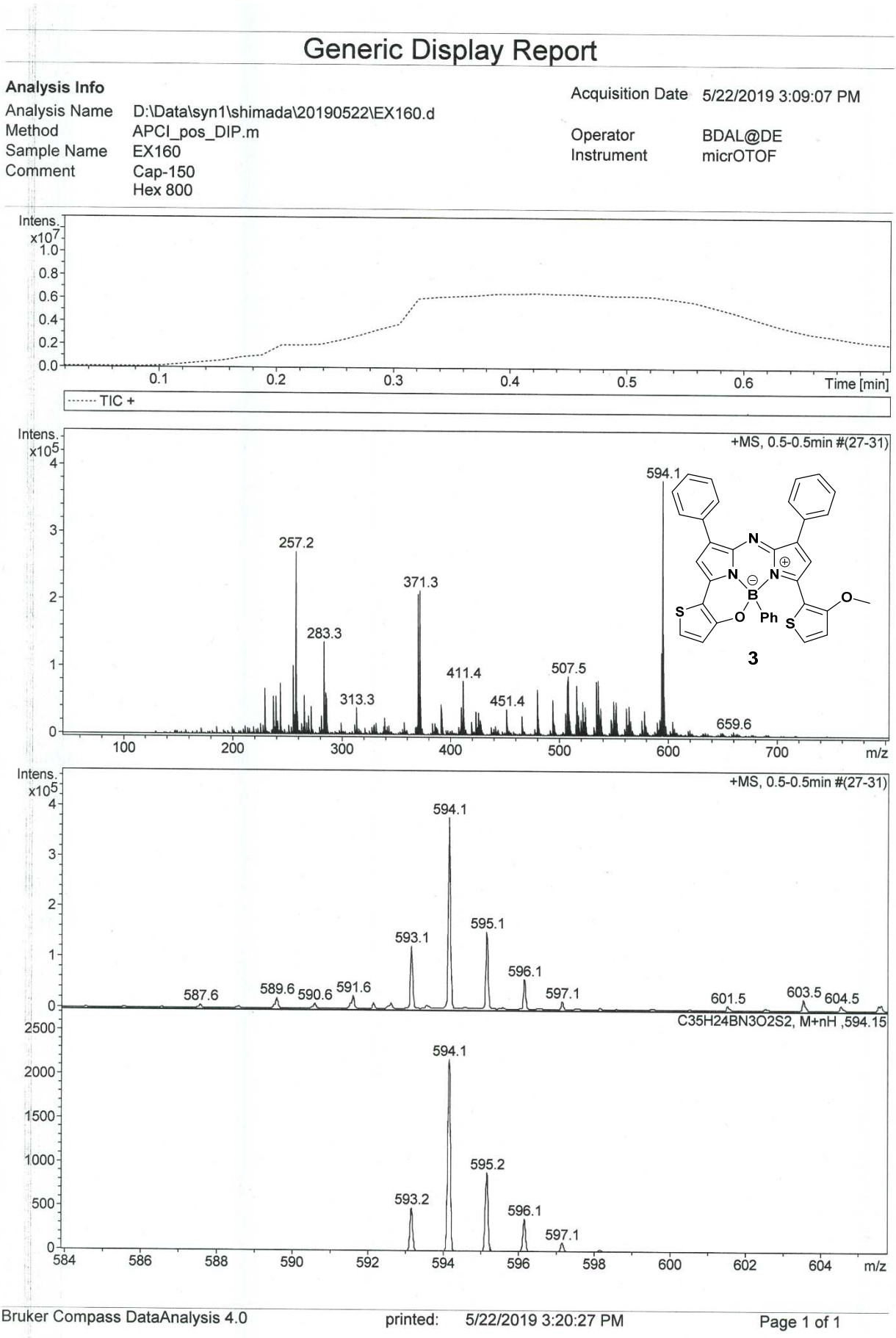


Figure S20. APCI mass spectrum (positive mode) of **3**.

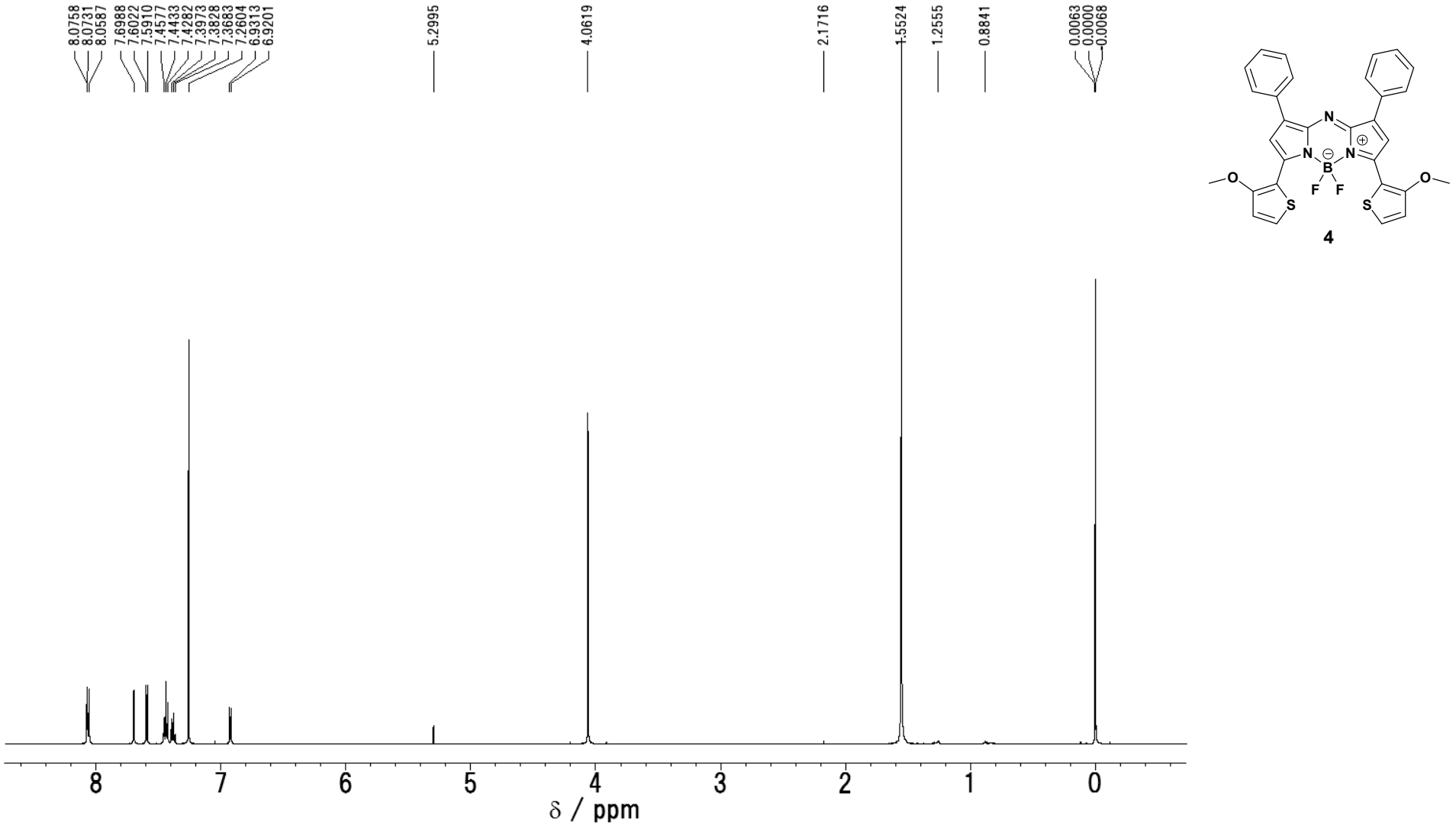
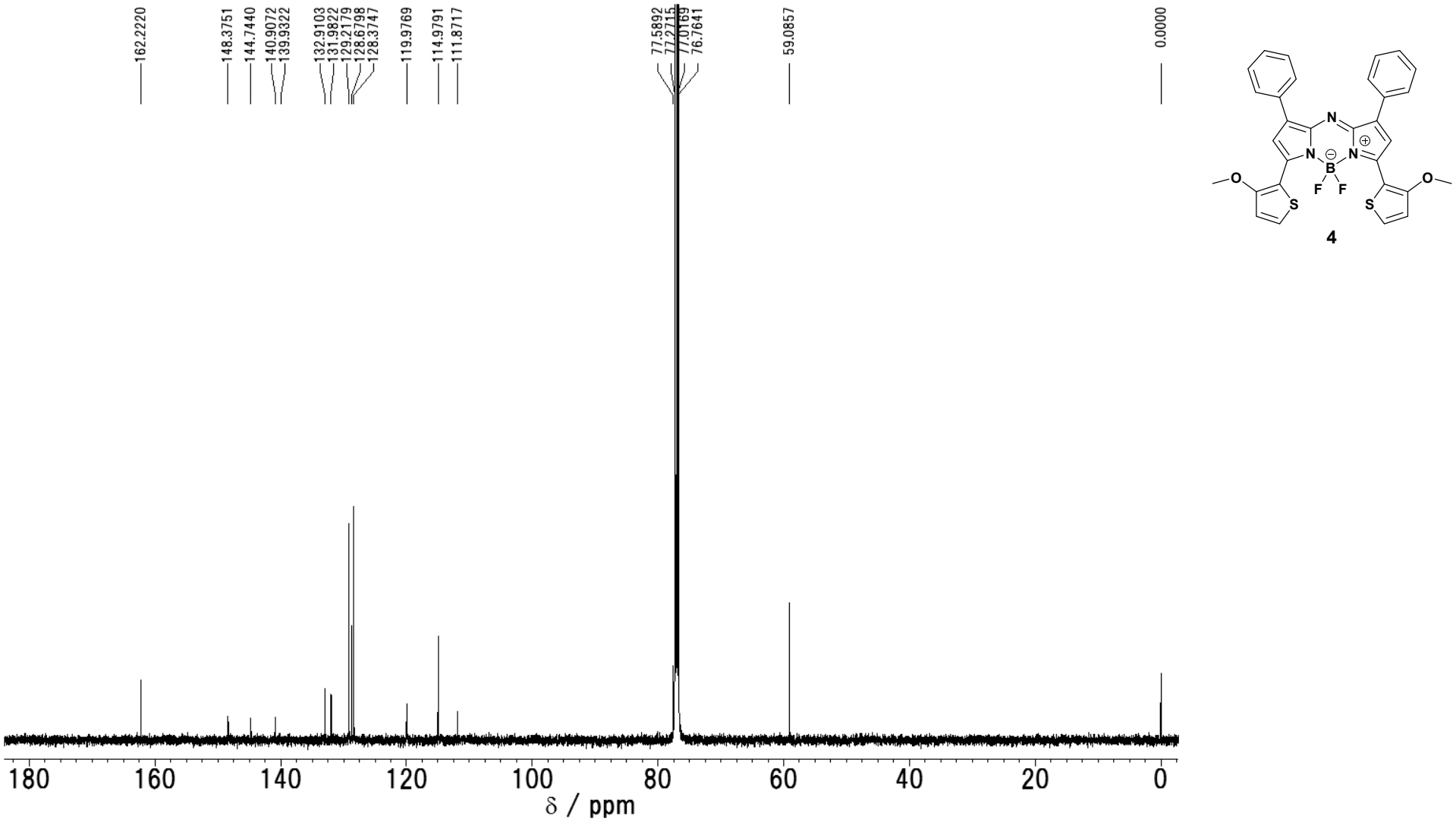


Figure S21. ^{1}H NMR spectrum of **4** (500 MHz) in $CDCl_3$.



4

Figure S22. ^{13}C NMR spectrum of **4** (126 MHz) in $CDCl_3$.

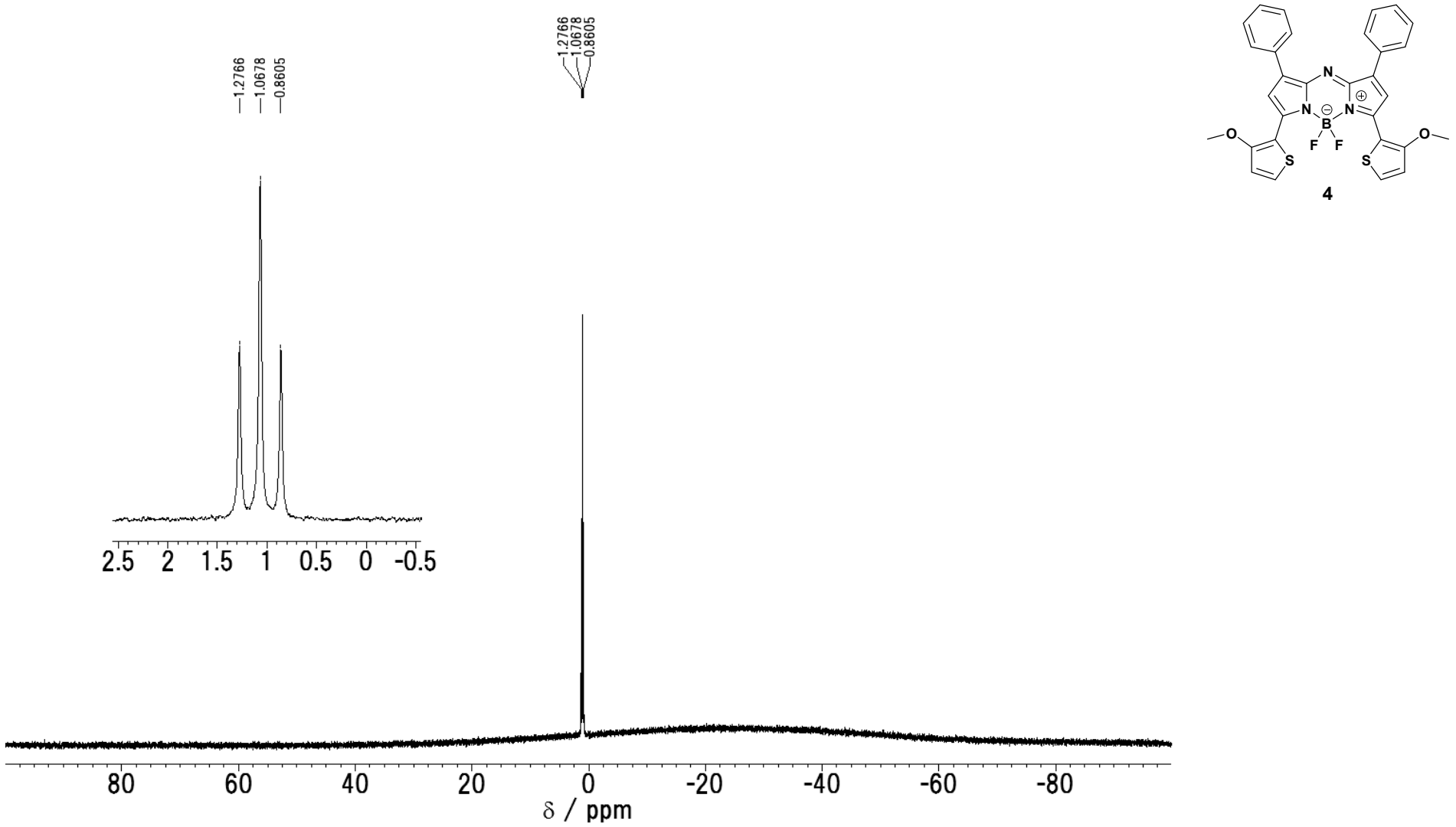


Figure S23. ^{11}B NMR spectrum of **4** (160 MHz) in $CDCl_3$.

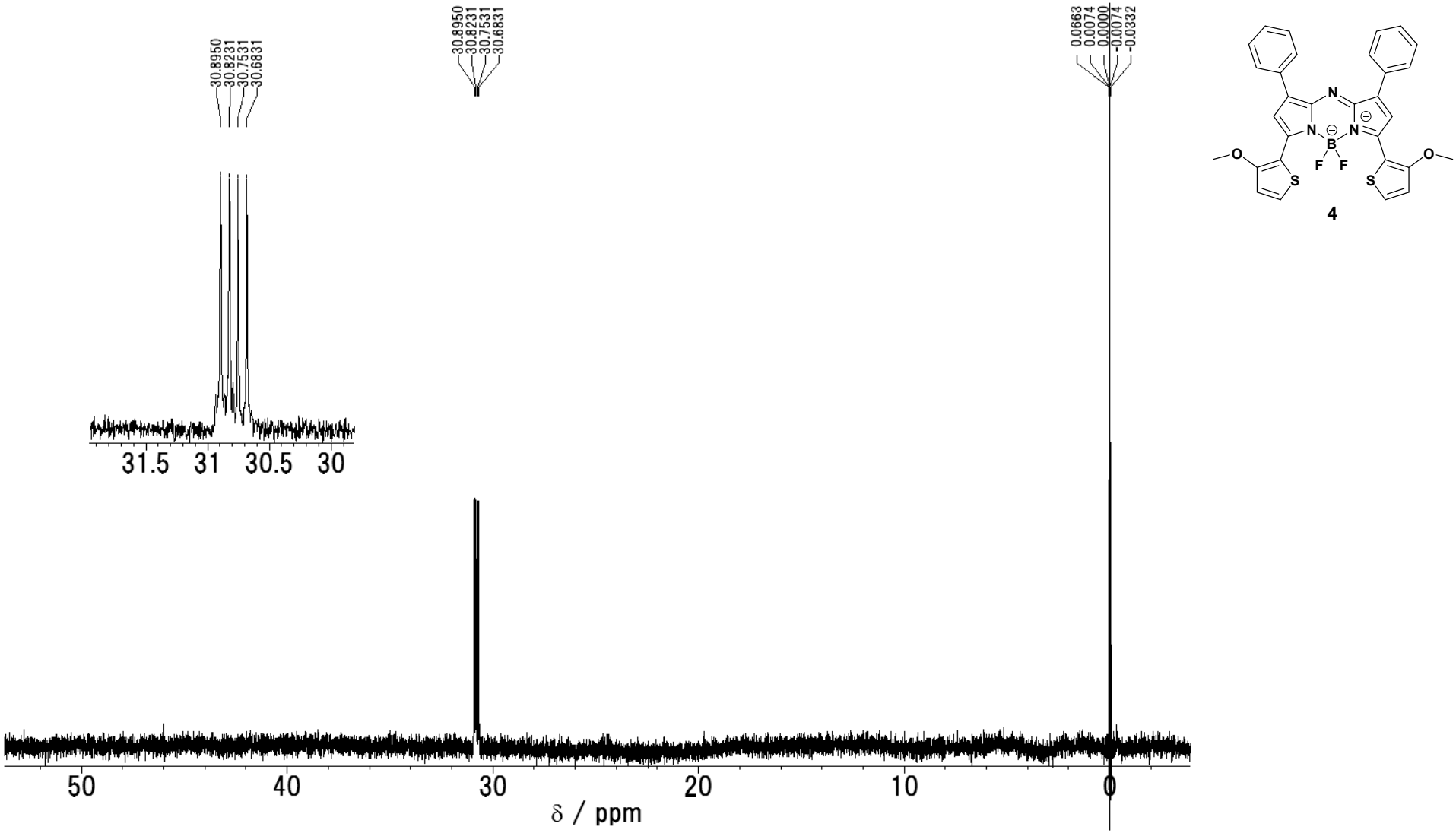
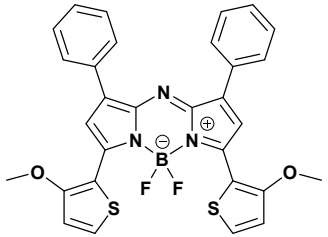


Figure S24. ^{19}F NMR spectrum of **4** (471 MHz) in $CDCl_3$.

[Mass Spectrum]
Data : 20190829-EXP116-001 Date : 29-Aug-2019 09:33
Instrument : MStation
Sample : -
Inlet : Direct Ion Mode : FAB+
Spectrum Type : Normal Ion [MF-Linear]
Scan# : (4,9)
BP : m/z 154 Int. : 178.80 (1874853)
Output m/z range : 50 to 642 Cut Level : 0.00 %



4

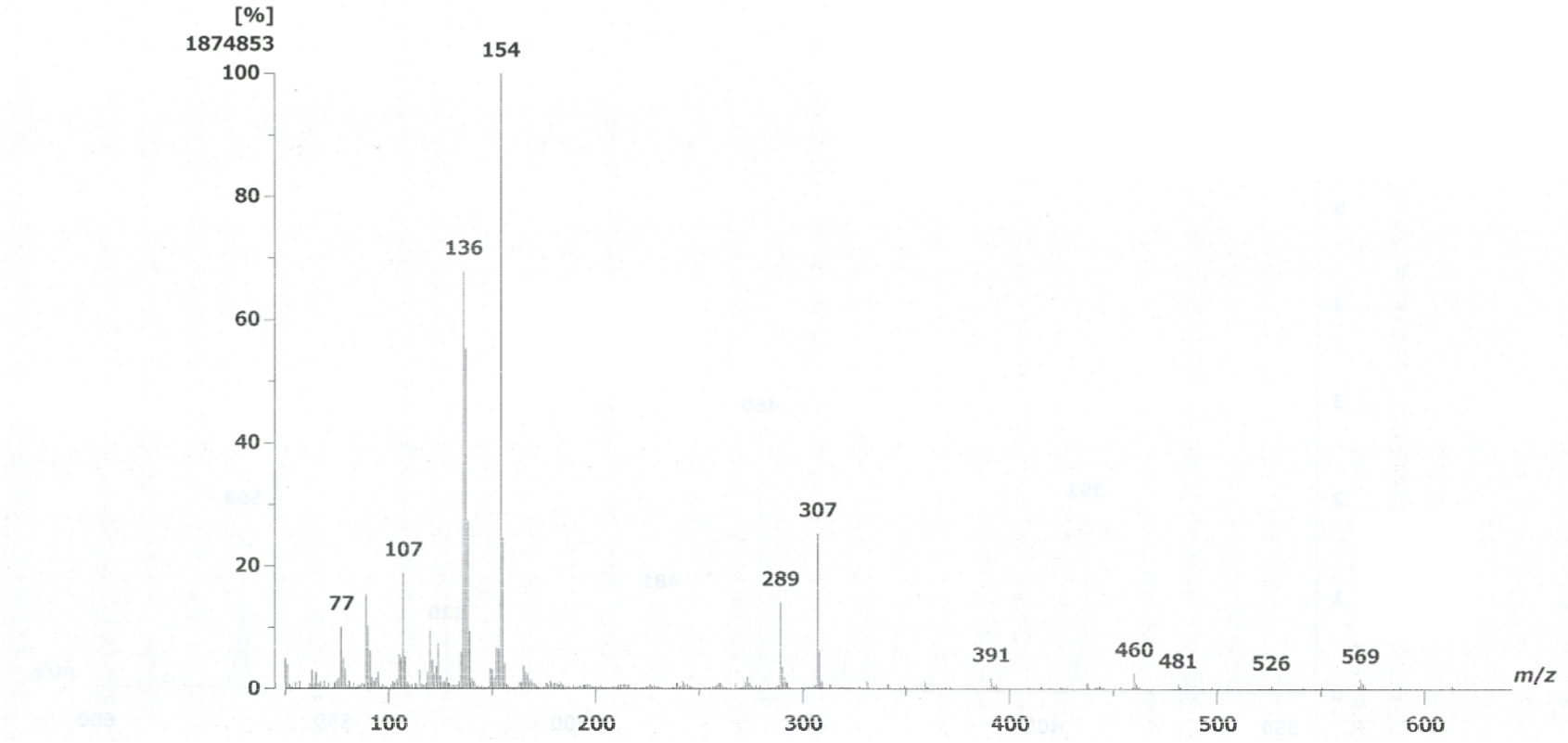


Figure S25. APCI mass spectrum (positive mode) of **4**.

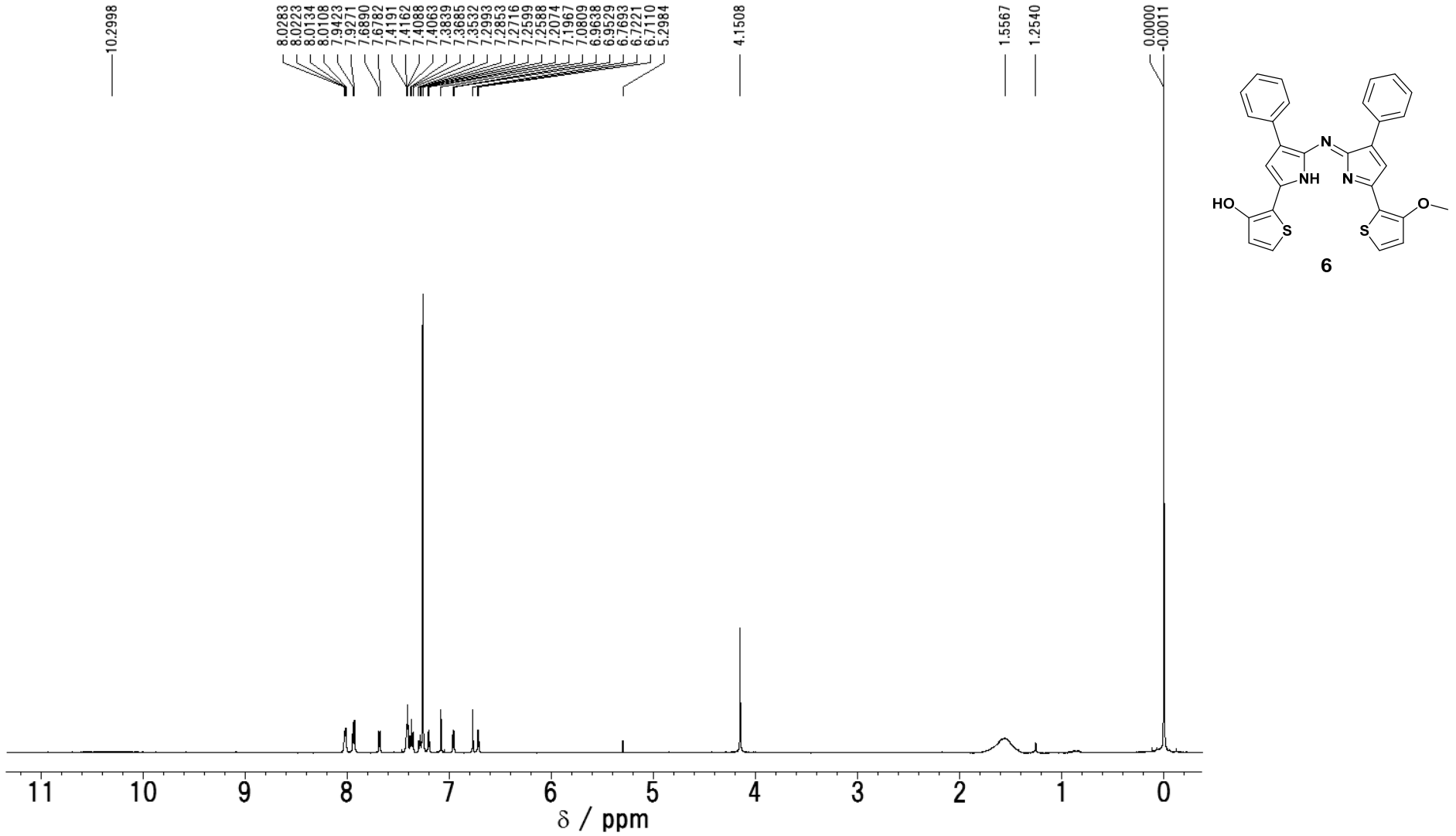


Figure S26. ^{1}H NMR spectrum of **6** (500 MHz) in $CDCl_3$.

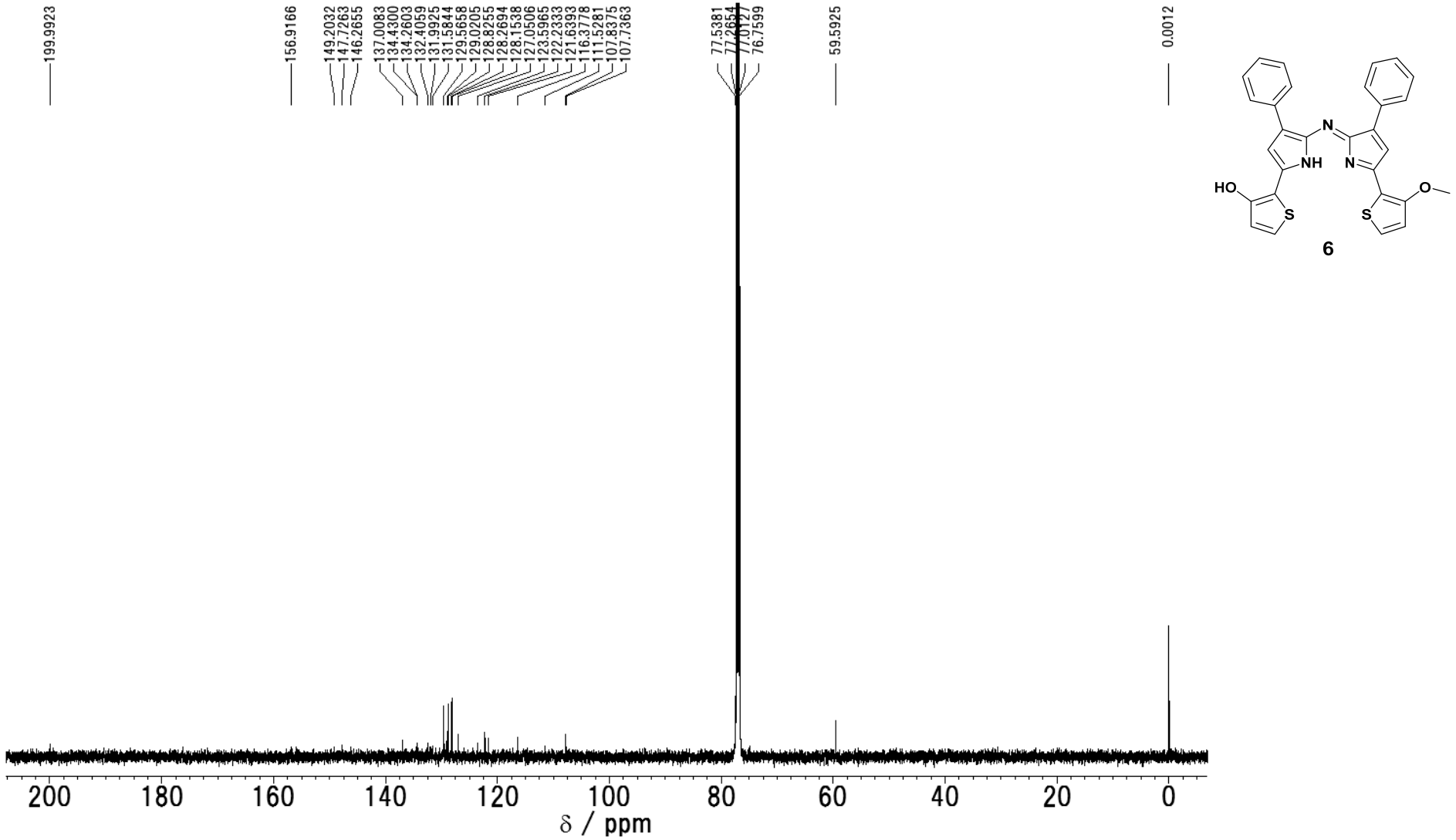


Figure S27. ^{13}C NMR spectrum of **6** (126 MHz) in $CDCl_3$

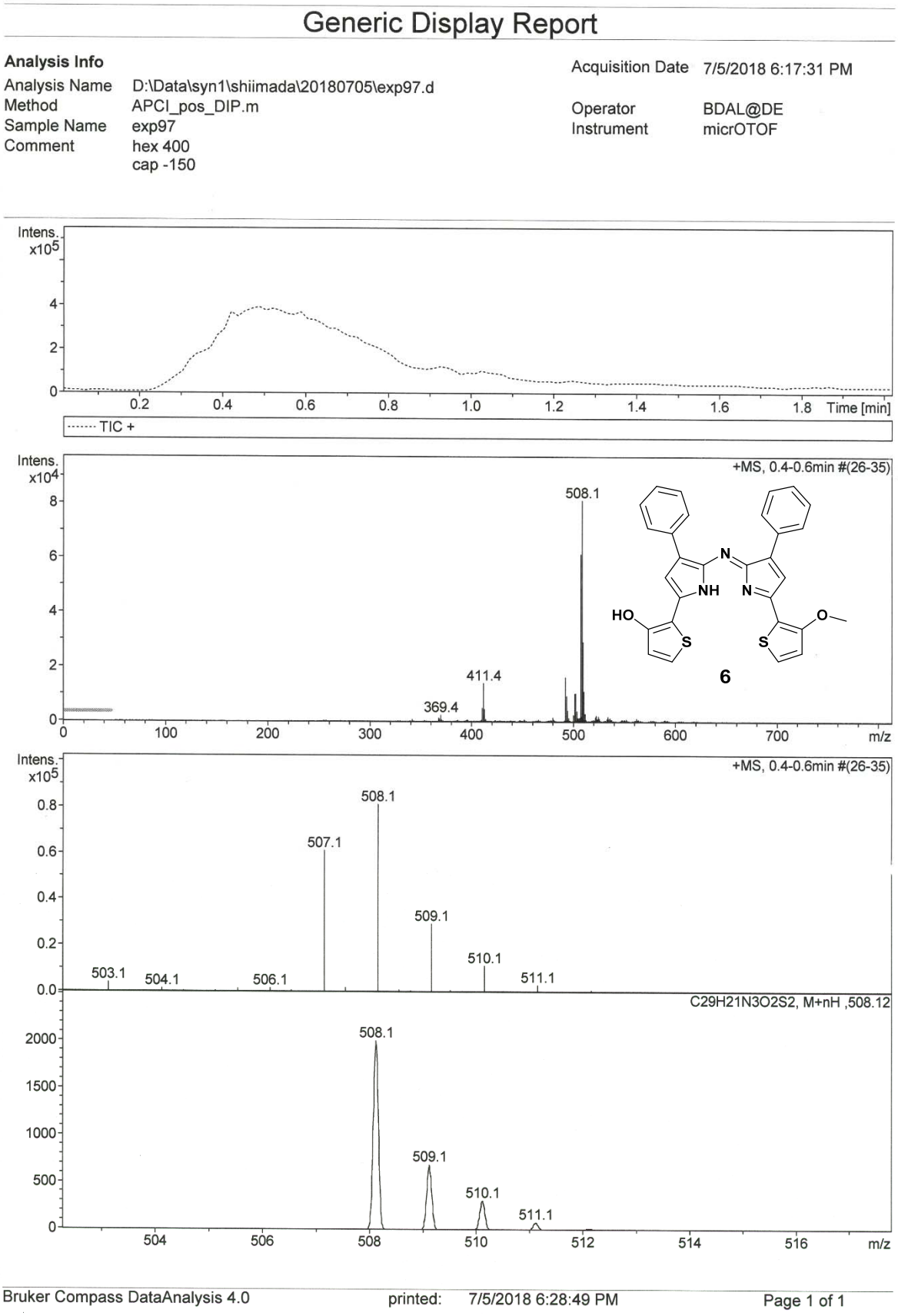


Figure S28. APCI mass spectrum (positive mode) of **6**.

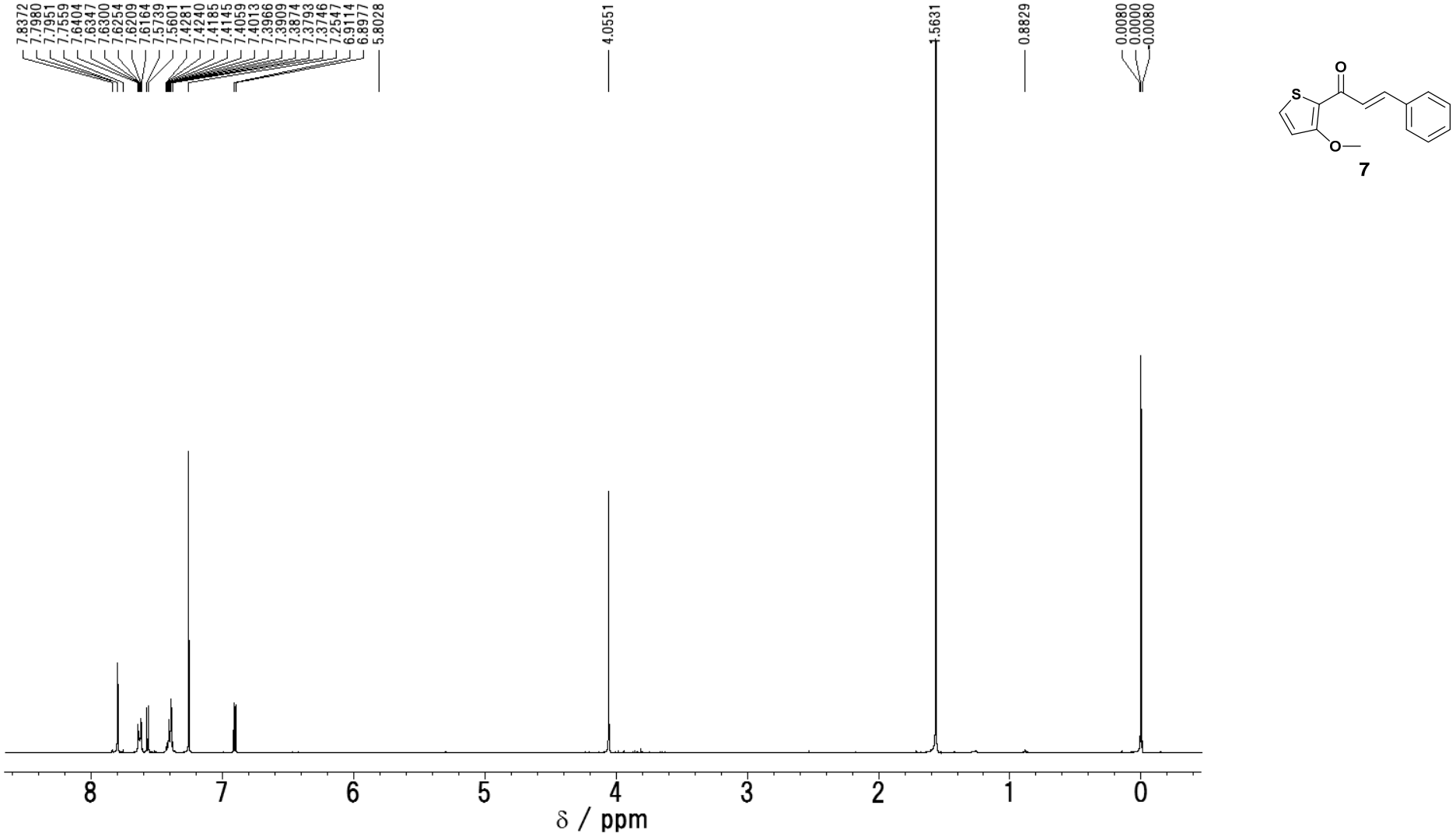
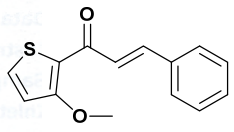


Figure S29. ^{1}H NMR spectrum of **7** (400 MHz) in $CDCl_3$.

[Mass Spectrum]
Data : 190827-Shimada EXP113-002 Date : 27-Aug-2019 19:51
Instrument : MStation
Sample : -
Inlet : Direct Ion Mode : FAB+
Spectrum Type : Normal Ion [MF-Linear]
Scan# : (4,7)
BP : m/z 154 Int. : 26.34 (276224)
Output m/z range : 50 to 720 Cut Level : 0.00 %



7

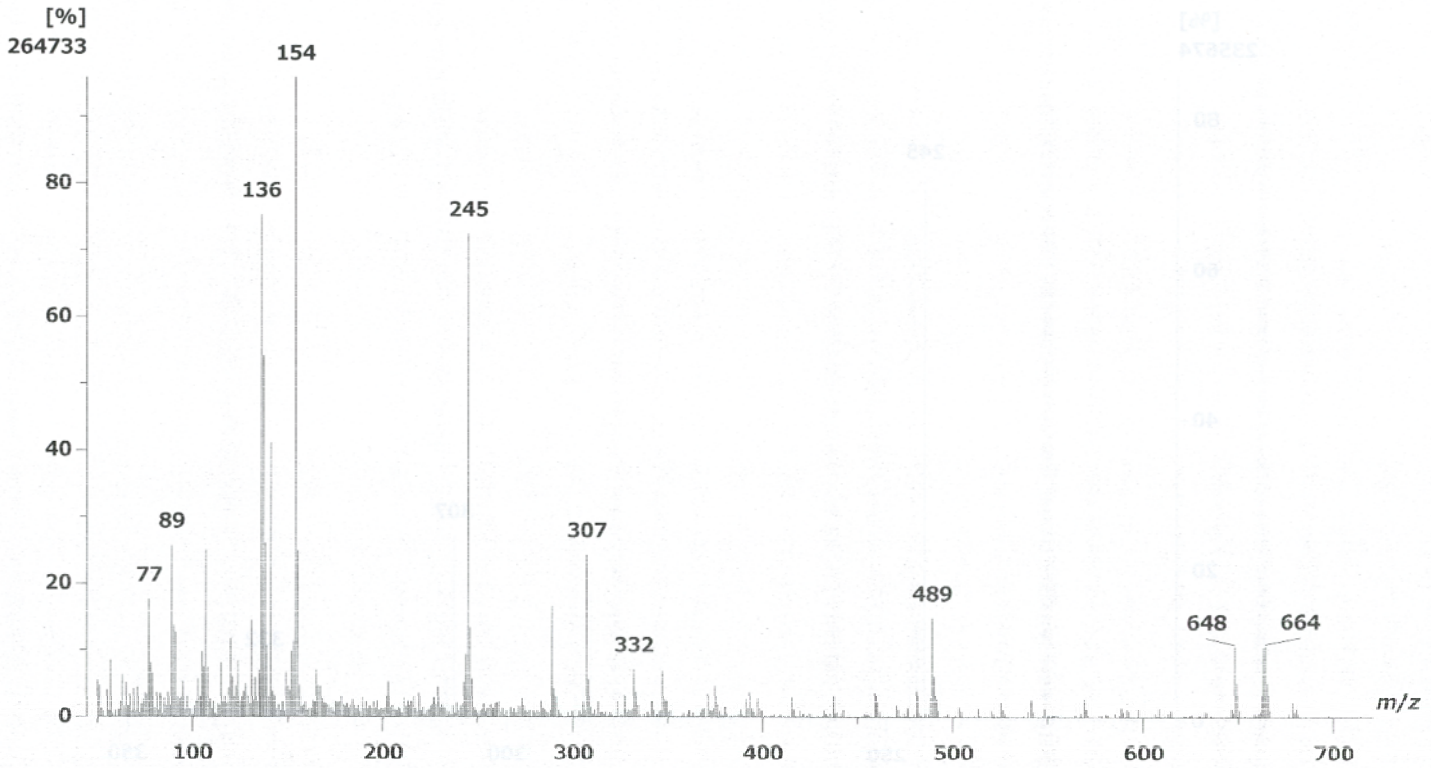


Figure S30. FAB mass spectrum (positive mode) of **7**.

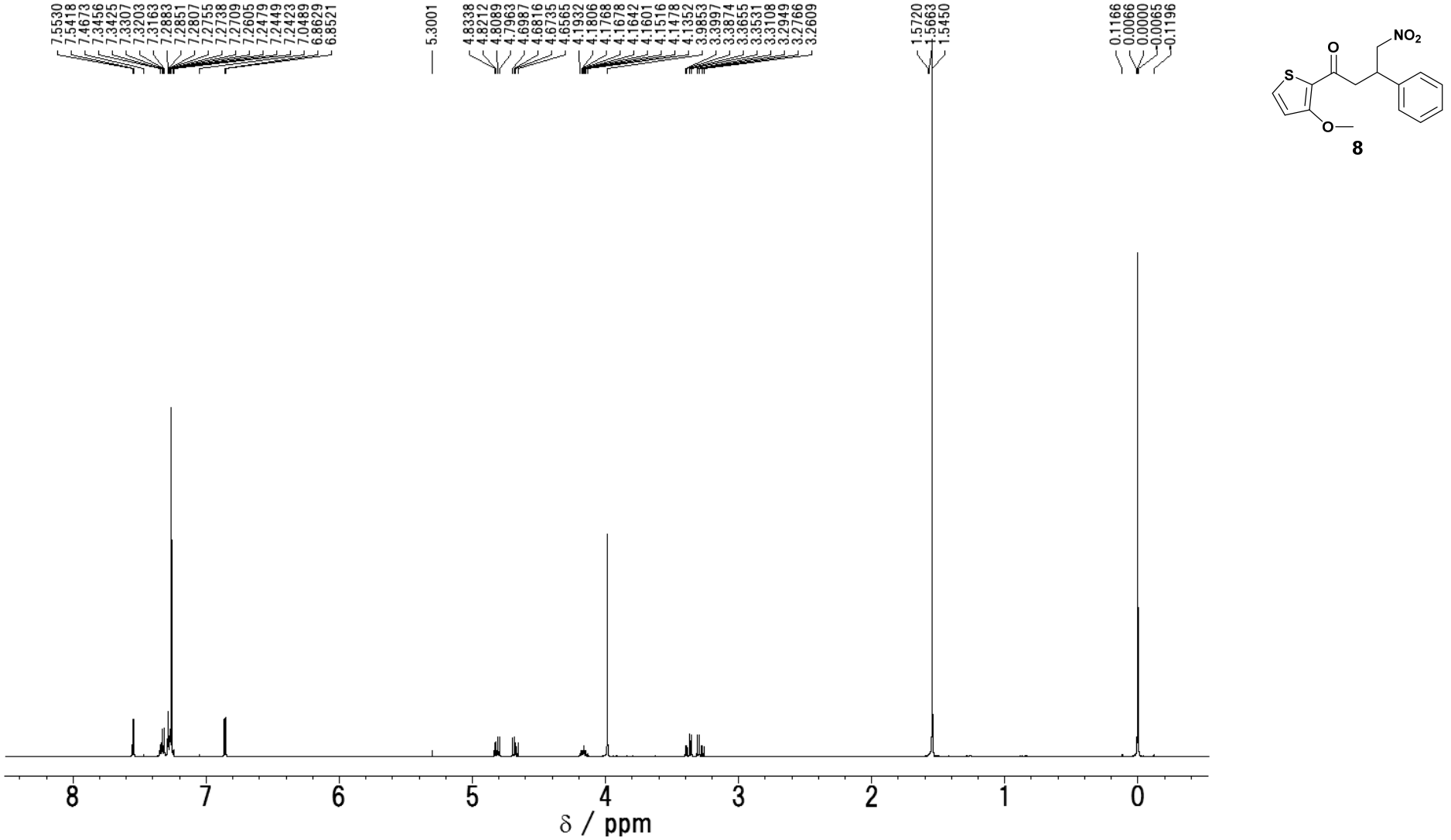


Figure S31. ^{1}H NMR spectrum of **8** (500 MHz) in $CDCl_3$.

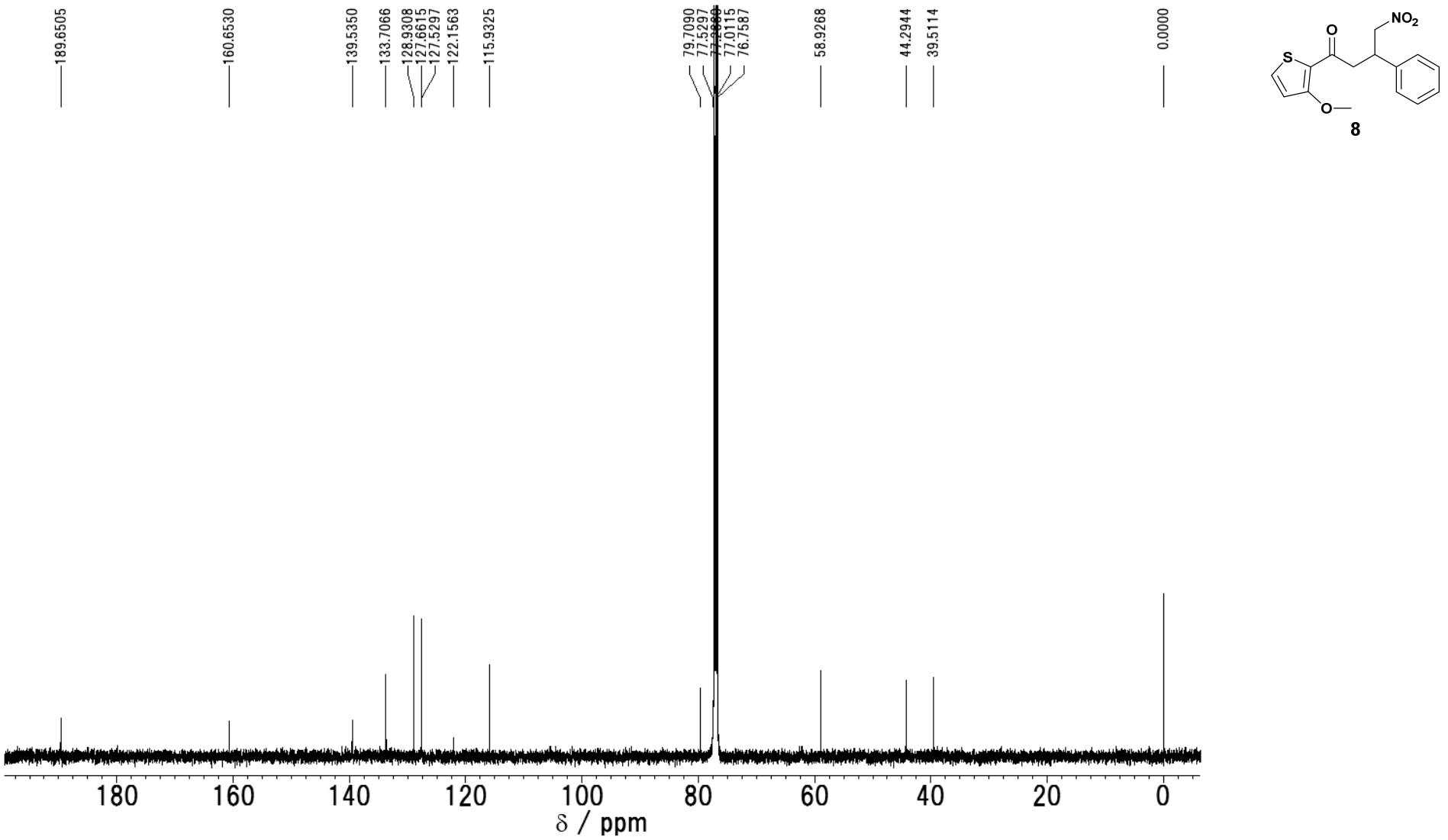
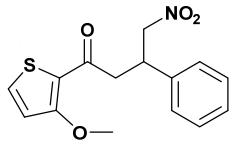


Figure S32. ^{13}C NMR spectrum of **8** (126 MHz) in $CDCl_3$.

[Mass Spectrum]
Data : 20180824-EXP110001 Date : 24-Aug-2018 17:25
Instrument : MStation
Sample : -
Inlet : Direct Ion Mode : FAB+
Spectrum Type : Normal Ion [MF-Linear]
Scan# : 1
BP : m/z 154 Int. : 5.79 (60703)
Output m/z range : 50 to 684 Cut Level : 0.00 %



8

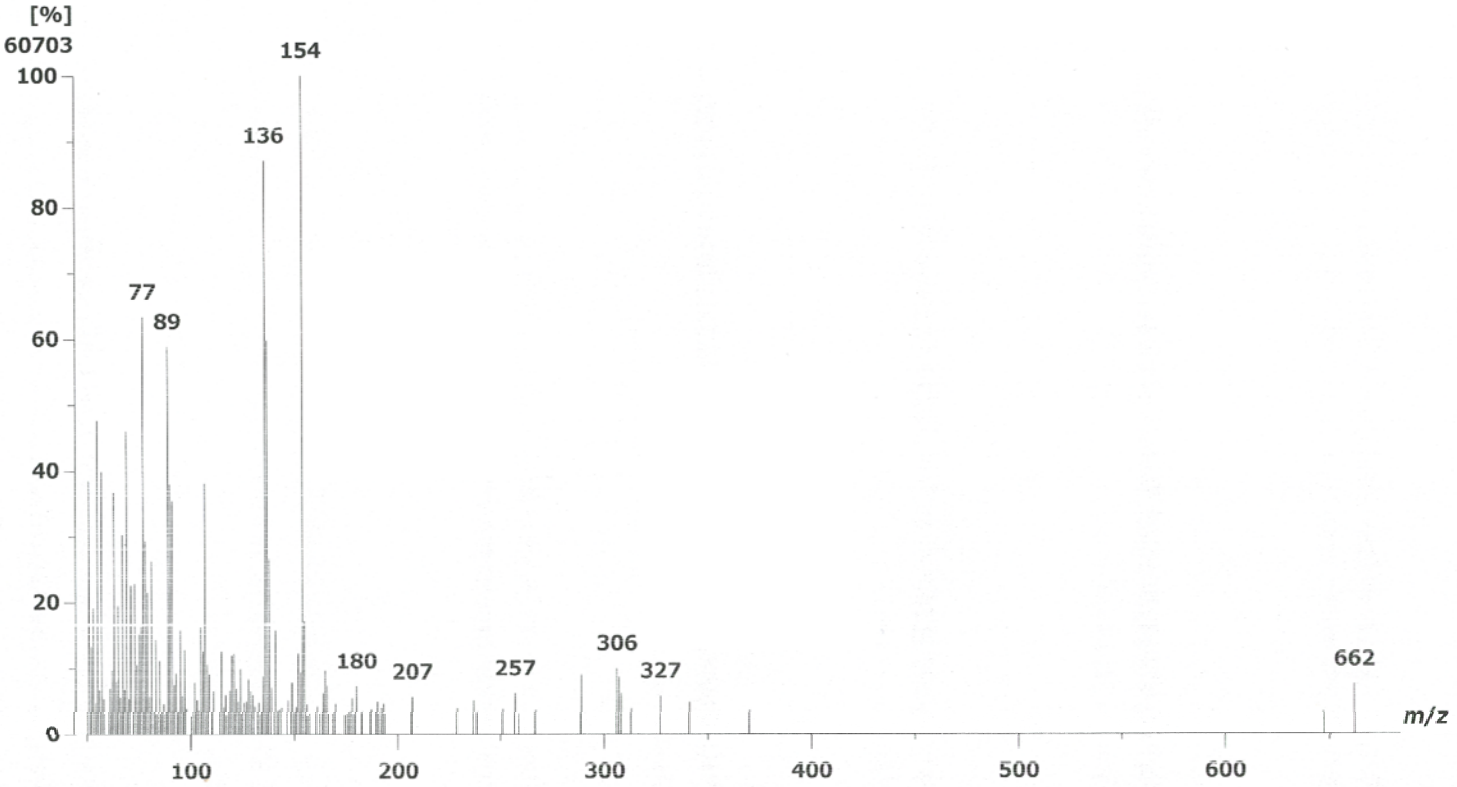


Figure S33. FAB mass spectrum (positive mode) of **8**.

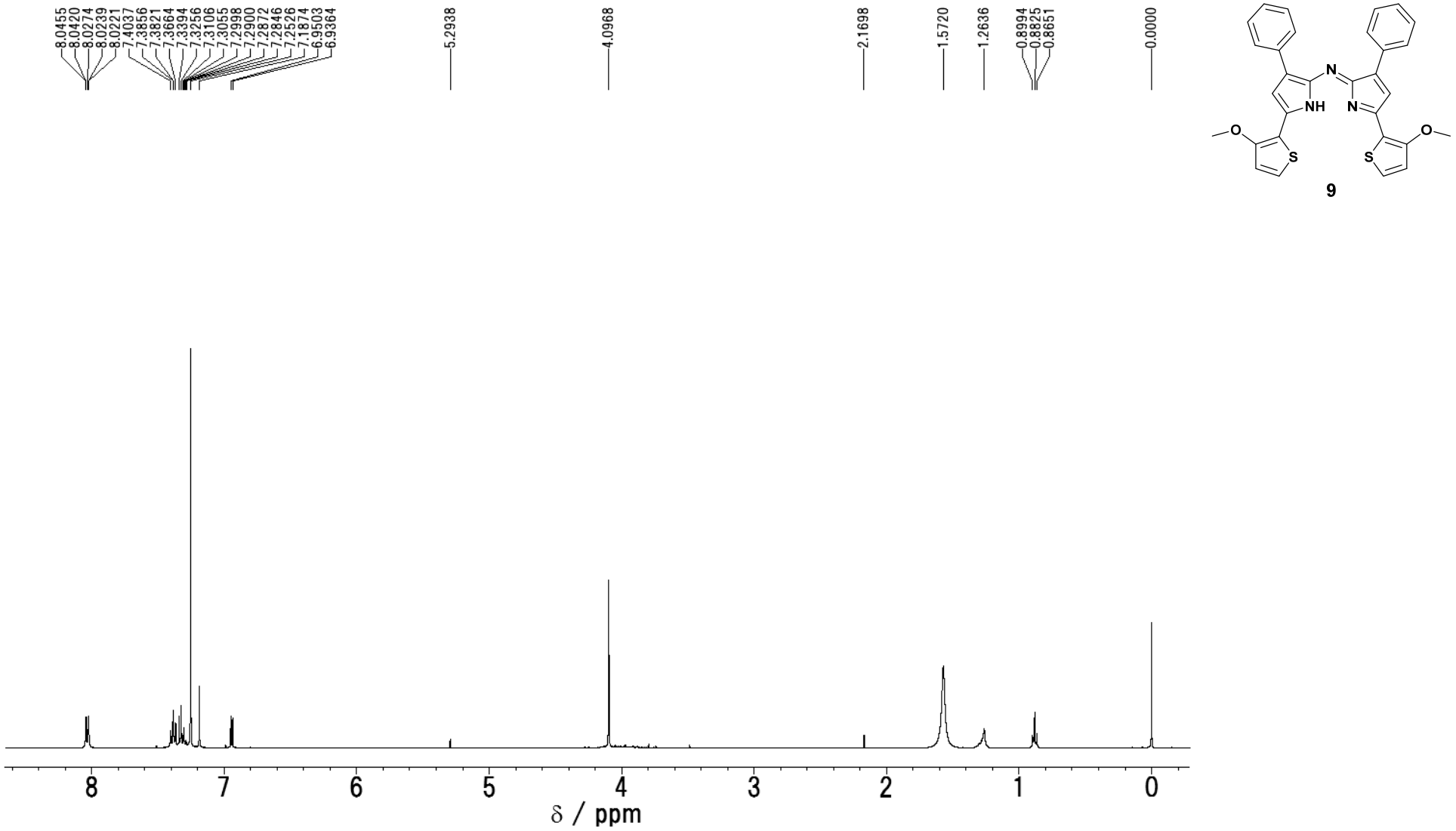


Figure S34. ^{1}H NMR spectrum of **9** (400 MHz) in $CDCl_3$.

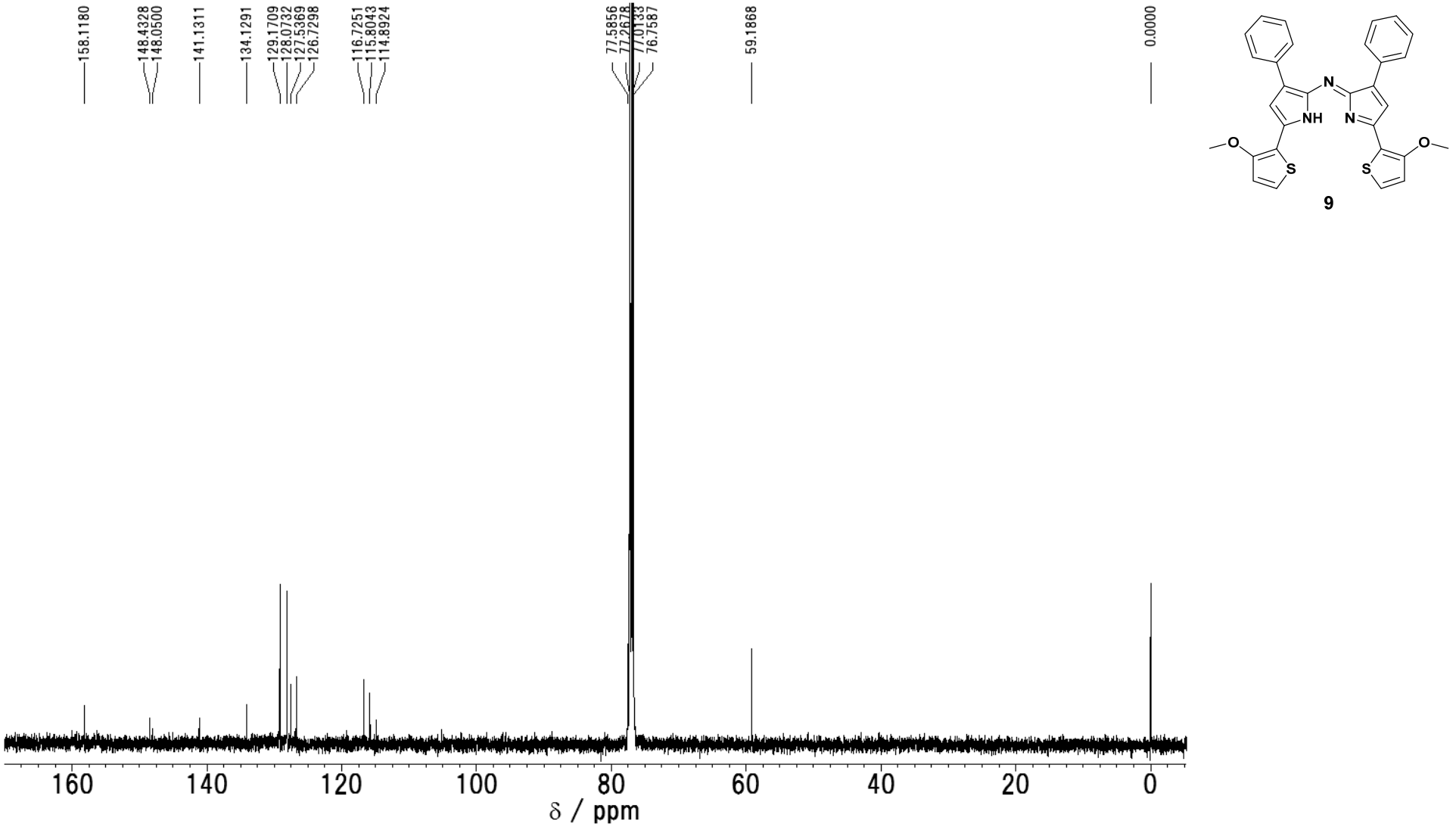
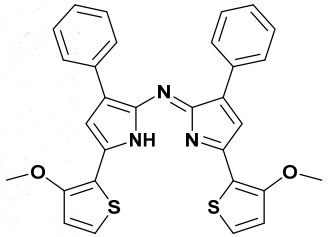


Figure S35. ^{13}C NMR spectrum of **9** (126 MHz) in $CDCl_3$.

[Mass Spectrum]
Data : 190827-Shimada EXP100-001 Date : 27-Aug-2019 19:43
Instrument : MStation
Sample : -
Inlet : Direct Ion Mode : FAB+
Spectrum Type : Normal Ion [MF-Linear]
Scan# : (3,7)
BP : m/z 154 Int. : 57.89 (607027)
Output m/z range : 50 to 580 Cut Level : 0.00 %



9

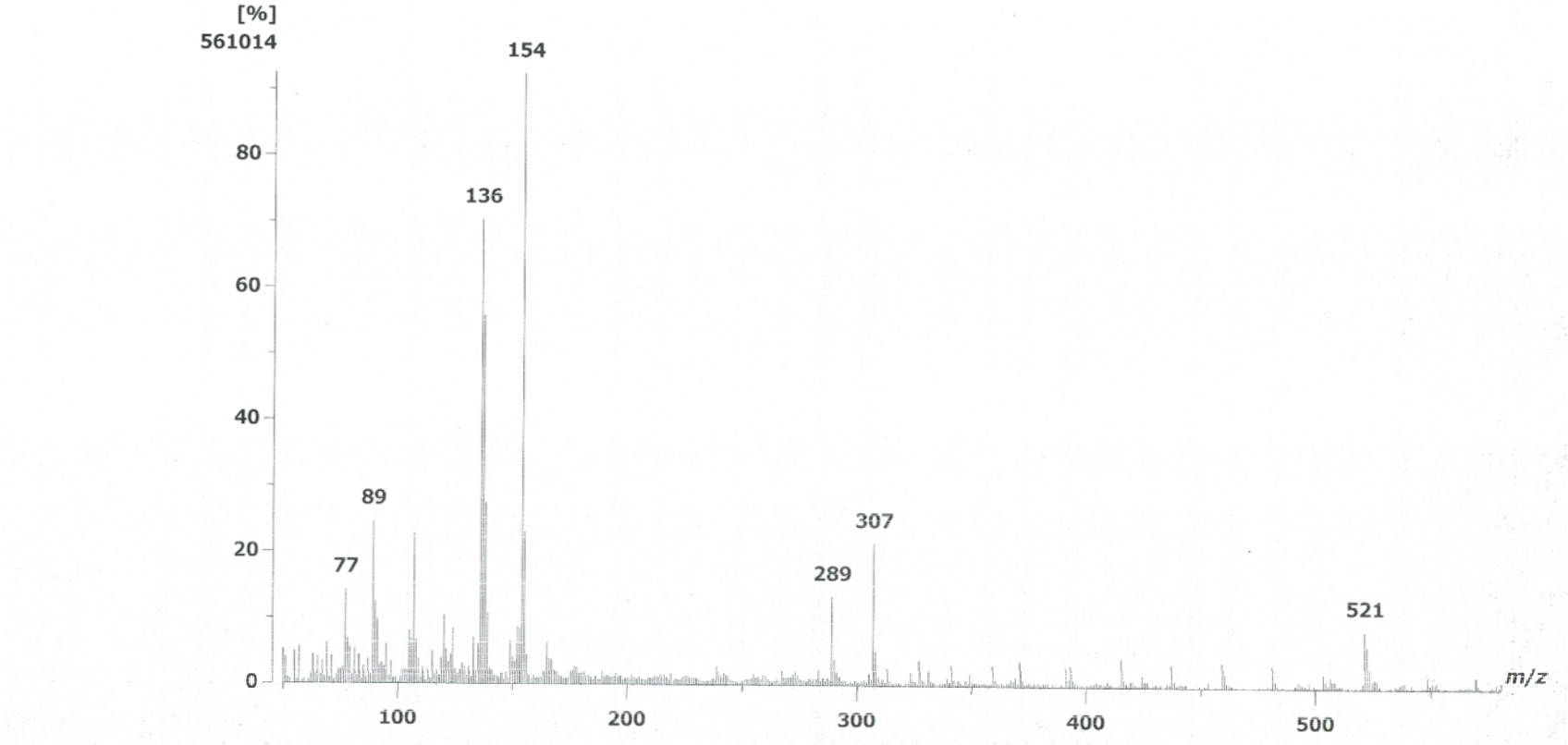


Figure S36. FAB mass spectrum (positive mode) of **9**.

Single crystal X-ray diffraction study for 2
(CCDC No. 1948374)

Data Collection

A brown platelet crystal of $C_{29}H_{19}BFN_3O_2S_2$ having approximate dimensions of 0.430 × 0.140 × 0.070 mm was mounted on a glass fiber. All measurements were made on a Rigaku XtaLAB mini diffractometer using graphite monochromated Mo-Kα radiation.

The crystal-to-detector distance was 49.91 mm.

Cell constants and an orientation matrix for data collection corresponded to an I-centered monoclinic cell with dimensions:

a = 24.542(14) Å
b = 7.437(4) Å β = 109.69(4)°
c = 27.588(12) Å
V = 4741(4) Å^3

For Z = 8 and F.W. = 535.42, the calculated density is 1.500 g/cm^3. Based on the reflection conditions of:

hkl: h+k+l = 2n
h0l: h = 2n

packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

I2/a (#15)

The data were collected at a temperature of −173 + 1°C to a maximum 2θ value of 55.0°. A total of 540 oscillation images were collected. A sweep of data was done using ω scans from −60.0 to 120.0° in 1.00° step, at χ=54.0° and ϕ = 0.0°. The exposure rate was 16.0 [sec./°]. The detector swing angle was 29.97°. A second sweep was performed using ω scans from −60.0 to 120.0° in 1.00° step, at χ=54.0° and ϕ = 120.0°. The exposure rate was 16.0 [sec./°]. The detector swing angle was 29.97°. Another sweep was performed using ω scans from −60.0 to 120.0° in 1.00° step, at χ=54.0° and ϕ = 240.0°. The exposure rate was 16.0 [sec./°]. The detector swing angle was 29.97°. The crystal-to-detector distance was 49.91 mm. Readout was performed in the 0.073 mm pixel mode.

Data Reduction

Of the 24242 reflections were collected, where 5427 were unique (Rint = 0.0824); equivalent reflections were merged. Data were collected and processed using CrystalClear (Rigaku). [1]

The linear absorption coefficient, μ, for Mo-Kα radiation is 2.684 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.876 to 0.981. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods[2] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement[3] on F^2 was based on 5427 observed reflections and 343 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$R1 = \Sigma \, ||Fo| - |Fc|| \, / \, \Sigma \, |Fo| = 0.0577$

$wR2 = [\, \Sigma \, (\, w \, (Fo^2 - Fc^2)^2 \,) / \, \Sigma \, w(Fo^2)^2]^{1/2} = 0.1195$

The goodness of fit[4] was 1.09. Unit weights were used. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.38 and −0.36 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from International Tables for Crystallography (IT), Vol. C, Table 6.1.1.4 [5]. Anomalous dispersion effects were included in Fcalc[6]; the values for Δf' and Δf'' were those of Creagh and McAuley[7]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[8]. All calculations were performed using the CrystalStructure[9] crystallographic software package except for refinement, which was performed using SHELXL Version 2014/7[10].

References

(1) CrystalClear: Data Collection and Processing Software, Rigaku Corporation (1998–2015). Tokyo 196–8666, Japan.

(2) SHELXS Version 2014/5: Sheldrick, G. M. (2014). Acta Cryst. A70, C1437.

(3) Least Squares function minimized: (SHELXL Version 2014/7)

$\Sigma w(F_o^2 - F_c^2)^2$ where w = Least Squares weights.

(4) Goodness of fit is defined as:

$[\Sigma w(F_o^2 - F_c^2)^2/(N_o - N_v)]^{1/2}$

where: N_o = number of observations
N_v = number of variables

(5) International Tables for Crystallography, Vol.C (1992). Ed. A.J.C. Wilson, Kluwer Academic Publishers, Dordrecht, Netherlands, Table 6.1.1.4, pp. 572.

(6) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).

(7) Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219–222 (1992).

(8) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200–206 (1992).

(9) CrystalStructure 4.3: Crystal Structure Analysis Package, Rigaku Corporation (2000–2018). Tokyo 196–8666, Japan.

(10) SHELXL Version 2014/7: Sheldrick, G. M. (2008). Acta Cryst. A64, 112–122.

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{29}H_{19}BFN_3O_2S_2$
Formula Weight	535.42
Crystal Color, Habit	brown, platelet
Crystal Dimensions	0.430 × 0.140 × 0.070 mm
Crystal System	monoclinic
Lattice Type	I-centered
Lattice Parameters	a = 24.542(14) Å
	b = 7.437(4) Å
	c = 27.588(12) Å
	β = 109.69(4)°
	V = 4741(4) Å^3
Space Group	I2/a (#15)
Z value	8
D_{calc}	1.500 g/cm^3
F_{000}	2208.00
μ(MoKα)	2.684 cm^{-1}

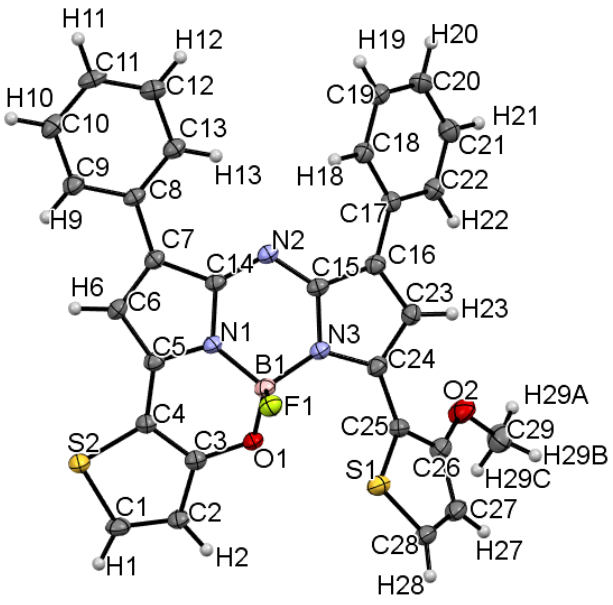
B. Intensity Measurements

Diffractometer	XtaLAB mini
Radiation	MoKα (λ = 0.71075 Å) graphite monochromated
Voltage, Current	50 kV, 12 mA
Temperature	−173.0°C
Detector Aperture	75.0 mm (diameter)
Data Images	540 exposures
ω oscillation Range (χ=54.0, ϕ=0.0)	−60.0 – 120.0°
Exposure Rate	16.0 sec./°
Detector Swing Angle	29.97°
ω oscillation Range (χ=54.0, ϕ=120.0)	−60.0 – 120.0°
Exposure Rate	16.0 sec./°
Detector Swing Angle	29.97°
ω oscillation Range (χ=54.0, ϕ=240.0)	−60.0 – 120.0°
Exposure Rate	16.0 sec./°
Detector Swing Angle	29.97°
Detector Position	49.91 mm
Pixel Size	0.073 mm
$2\theta_{max}$	55.0°
No. of Reflections Measured	Total: 24242 Unique: 5427 (R_{int} = 0.0824)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.876 – 0.981)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SHELXT Version 2014/5)
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\Sigma\ w\ (Fo^2 - Fc^2)^2$
Least Squares Weights	$w = 1/[\ \sigma^2\ (Fo^2) + (0.0304 \cdot P)^2 + 8.2160 \cdot P\ ]$ where $P = (Max(Fo^2,0) + 2Fc^2)/3$
$2\theta_{max}$ cutoff	55.0°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	5427
No. Variables	343
Reflection/Parameter Ratio	15.82
Residuals: R1 (I>2.00σ(I))	0.0577
Residuals: R (All reflections)	0.0795
Residuals: wR2 (All reflections)	0.1195
Goodness of Fit Indicator	1.087
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map	0.38 $e^-/Å^3$
Minimum peak in Final Diff. Map	−0.36 $e^-/Å^3$

Atom numbering of **2**.



Atomic coordinates and B_{iso}/B_{eq}.

atom	x	y	z	B_{eq}
S1	0.31326(3)	0.17833(10)	0.55129(2)	2.236(13)
S2	0.09250(3)	0.74533(10)	0.53109(2)	2.225(13)
F1	0.21655(6)	0.22480(19)	0.60361(5)	1.99(3)
O1	0.24053(7)	0.4958(2)	0.57286(6)	1.82(3)
O2	0.45755(8)	0.4110(3)	0.62666(8)	2.95(4)
N1	0.21174(9)	0.4976(3)	0.64872(7)	1.62(3)
N2	0.27639(9)	0.4422(3)	0.73251(8)	1.63(3)
N3	0.30426(9)	0.3654(3)	0.65798(7)	1.58(3)
C1	0.12190(12)	0.7294(4)	0.48271(10)	2.22(5)
C2	0.17348(11)	0.6425(4)	0.49717(9)	1.90(4)
C3	0.19051(11)	0.5828(3)	0.54906(9)	1.73(4)
C4	0.15081(11)	0.6306(3)	0.57312(9)	1.82(4)
C5	0.16416(11)	0.6004(3)	0.62670(9)	1.73(4)
C6	0.14374(11)	0.6644(4)	0.66600(9)	1.85(4)
C7	0.18025(10)	0.5996(3)	0.71283(9)	1.62(4)
C8	0.17333(11)	0.6279(3)	0.76306(9)	1.64(4)
C9	0.12058(11)	0.6930(4)	0.76514(10)	2.00(4)
C10	0.11292(12)	0.7269(4)	0.81176(10)	2.23(5)
C11	0.15787(12)	0.6941(4)	0.85706(10)	2.32(5)
C12	0.21008(12)	0.6257(4)	0.85607(10)	2.28(5)
C13	0.21791(11)	0.5927(3)	0.80929(9)	1.95(4)
C14	0.22576(11)	0.5012(3)	0.70166(9)	1.59(4)
C15	0.31493(11)	0.3827(3)	0.71130(9)	1.64(4)
C16	0.37486(11)	0.3476(3)	0.73814(9)	1.71(4)
C17	0.40575(11)	0.3687(3)	0.79361(9)	1.72(4)
C18	0.37917(11)	0.3441(3)	0.83093(9)	1.81(4)
C19	0.40966(11)	0.3717(4)	0.88258(10)	2.05(4)
C20	0.46747(12)	0.4252(4)	0.89850(10)	2.41(5)
C21	0.49458(11)	0.4488(4)	0.86223(10)	2.32(5)
C22	0.46412(11)	0.4208(4)	0.81049(10)	2.09(5)
C23	0.39910(11)	0.3087(4)	0.70091(9)	1.93(4)
C24	0.35576(11)	0.3177(3)	0.65231(10)	1.82(4)
C25	0.36335(11)	0.2831(3)	0.60326(9)	1.84(4)
C26	0.41279(11)	0.3226(4)	0.59182(10)	2.17(5)
C27	0.40974(12)	0.2679(4)	0.54153(10)	2.35(5)
C28	0.35841(12)	0.1884(4)	0.51587(10)	2.34(5)
C29	0.50401(12)	0.4631(5)	0.60948(12)	3.11(6)
B1	0.24333(13)	0.3921(4)	0.61902(11)	1.74(5)

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Atomic coordinates and B_{iso} involving hydrogen atoms

atom	x	y	z	B_{iso}
H1	0.10375	0.77688	0.44915	2.666
H2	0.19559	0.62375	0.47521	2.283
H6	0.11081	0.73869	0.66106	2.221
H9	0.08953	0.71432	0.73400	2.406
H10	0.07707	0.77234	0.81260	2.672
H11	0.15298	0.71857	0.88915	2.780
H12	0.24050	0.60148	0.88741	2.730
H13	0.25372	0.54594	0.80874	2.338
H18	0.33976	0.30801	0.82058	2.171
H19	0.39108	0.35416	0.90737	2.462
H20	0.48816	0.44533	0.93397	2.898
H21	0.53406	0.48421	0.87286	2.781
H22	0.48312	0.43721	0.78598	2.504
H23	0.43864	0.28054	0.70714	2.314
H27	0.43994	0.28500	0.52768	2.823
H28	0.34858	0.14310	0.48180	2.805
H29A	0.53373	0.52530	0.63739	3.732
H29B	0.52085	0.35596	0.59940	3.732
H29C	0.48934	0.54387	0.57984	3.732

Anisotropic displacement parameters.

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S1	0.0296(4)	0.0354(4)	0.0219(3)	0.0006(3)	0.0111(3)	−0.0032(3)
S2	0.0277(3)	0.0377(4)	0.0215(3)	0.0084(3)	0.0114(3)	0.0052(3)
F1	0.0268(8)	0.0252(8)	0.0246(7)	−0.0022(6)	0.0100(6)	−0.0028(6)
O1	0.0228(9)	0.0296(10)	0.0192(8)	0.0031(7)	0.0103(7)	0.0026(7)
O2	0.0292(11)	0.0538(13)	0.0352(11)	−0.0081(10)	0.0190(9)	−0.0070(10)
N1	0.0200(11)	0.0265(11)	0.0175(10)	0.0007(9)	0.0095(8)	0.0013(9)
N2	0.0228(11)	0.0206(11)	0.0203(10)	−0.0012(9)	0.0096(9)	−0.0006(8)
N3	0.0215(11)	0.0225(11)	0.0183(10)	0.0004(8)	0.0096(9)	−0.0006(8)
C1	0.0355(15)	0.0330(15)	0.0187(12)	0.0008(12)	0.0128(11)	0.0031(11)
C2	0.0266(13)	0.0284(14)	0.0211(12)	0.0011(11)	0.0130(11)	0.0033(11)
C3	0.0237(13)	0.0219(13)	0.0207(12)	−0.0010(10)	0.0083(10)	−0.0003(10)
C4	0.0230(13)	0.0271(13)	0.0199(12)	0.0029(10)	0.0083(10)	0.0022(10)
C5	0.0223(13)	0.0248(13)	0.0204(12)	−0.0016(10)	0.0095(10)	0.0009(10)
C6	0.0217(13)	0.0279(14)	0.0242(13)	0.0025(11)	0.0123(10)	−0.0002(11)
C7	0.0212(12)	0.0214(12)	0.0217(12)	−0.0018(10)	0.0107(10)	−0.0002(10)
C8	0.0250(13)	0.0212(12)	0.0200(12)	−0.0030(10)	0.0126(10)	−0.0009(10)
C9	0.0269(14)	0.0283(14)	0.0250(13)	0.0010(11)	0.0141(11)	0.0019(11)
C10	0.0306(14)	0.0280(14)	0.0330(14)	0.0000(12)	0.0200(12)	−0.0004(12)
C11	0.0410(16)	0.0317(15)	0.0225(13)	−0.0056(12)	0.0201(12)	−0.0037(11)
C12	0.0356(15)	0.0312(14)	0.0217(13)	−0.0026(12)	0.0124(12)	−0.0019(11)
C13	0.0273(14)	0.0265(14)	0.0239(13)	−0.0011(11)	0.0134(11)	0.0003(11)
C14	0.0216(12)	0.0224(12)	0.0185(12)	−0.0020(10)	0.0097(10)	0.0006(10)
C15	0.0238(13)	0.0212(12)	0.0190(12)	−0.0022(10)	0.0095(10)	−0.0008(10)
C16	0.0221(13)	0.0224(13)	0.0222(12)	−0.0009(10)	0.0096(10)	0.0013(10)
C17	0.0215(13)	0.0226(13)	0.0210(12)	0.0020(10)	0.0067(10)	0.0005(10)
C18	0.0230(13)	0.0227(13)	0.0244(13)	0.0013(10)	0.0096(11)	0.0006(10)
C19	0.0268(14)	0.0300(14)	0.0231(13)	0.0028(11)	0.0109(11)	0.0000(11)
C20	0.0302(15)	0.0358(16)	0.0223(13)	0.0033(12)	0.0042(12)	−0.0042(12)
C21	0.0223(13)	0.0342(15)	0.0299(14)	−0.0010(11)	0.0065(11)	−0.0015(12)
C22	0.0238(13)	0.0310(14)	0.0260(13)	0.0016(11)	0.0104(11)	0.0001(11)
C23	0.0202(12)	0.0290(14)	0.0255(13)	0.0021(10)	0.0097(11)	0.0018(11)
C24	0.0252(13)	0.0239(13)	0.0232(13)	0.0014(10)	0.0124(11)	0.0014(10)
C25	0.0244(13)	0.0283(14)	0.0178(12)	0.0042(11)	0.0079(10)	0.0013(10)
C26	0.0268(14)	0.0314(14)	0.0270(13)	0.0036(12)	0.0127(11)	0.0004(12)
C27	0.0325(15)	0.0352(16)	0.0272(14)	0.0073(12)	0.0174(12)	0.0033(12)
C28	0.0356(15)	0.0342(15)	0.0228(13)	0.0091(12)	0.0147(12)	0.0013(12)
C29	0.0287(15)	0.0492(19)	0.0444(18)	−0.0021(14)	0.0177(14)	0.0043(15)
B1	0.0245(15)	0.0251(15)	0.0197(13)	0.0003(12)	0.0115(12)	0.0013(12)

The general temperature factor expression:

$\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Bond lengths (Å)

atom	atom	distance	atom	atom	distance
S1	C25	1.728(2)	S1	C28	1.708(3)
S2	C1	1.722(3)	S2	C4	1.733(2)
F1	B1	1.404(3)	O1	C3	1.347(3)
O1	B1	1.471(4)	O2	C26	1.360(3)
O2	C29	1.428(4)	N1	C5	1.356(3)
N1	C14	1.383(3)	N1	B1	1.522(4)
N2	C14	1.322(3)	N2	C15	1.344(4)
N3	C15	1.410(3)	N3	C24	1.371(4)
N3	B1	1.532(3)	C1	C2	1.356(4)
C2	C3	1.420(3)	C3	C4	1.397(4)
C4	C5	1.420(4)	C5	C6	1.421(4)
C6	C7	1.387(3)	C7	C8	1.467(4)
C7	C14	1.452(4)	C8	C9	1.401(4)
C8	C13	1.397(3)	C9	C10	1.384(4)
C10	C11	1.382(3)	C11	C12	1.387(4)
C12	C13	1.389(4)	C15	C16	1.430(3)
C16	C17	1.469(3)	C16	C23	1.380(4)
C17	C18	1.404(4)	C17	C22	1.403(4)
C18	C19	1.383(3)	C19	C20	1.394(4)
C20	C21	1.387(5)	C21	C22	1.386(4)
C23	C24	1.404(3)	C24	C25	1.450(4)
C25	C26	1.384(4)	C26	C27	1.423(4)
C27	C28	1.355(4)			

Bond lengths involving hydrogens (Å)

atom	atom	distance	atom	atom	distance
C1	H1	0.950	C2	H2	0.950
C6	H6	0.950	C9	H9	0.950
C10	H10	0.950	C11	H11	0.950
C12	H12	0.950	C13	H13	0.950
C18	H18	0.950	C19	H19	0.950
C20	H20	0.950	C21	H21	0.950
C22	H22	0.950	C23	H23	0.950
C29	H29A	0.980	C29	H29B	0.980
C29	H29C	0.980			

Bond angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
C25	S1	C28	92.16(14)	C1	S2	C4	91.00(14)
C3	O1	B1	116.3(2)	C26	O2	C29	116.2(2)
C5	N1	C14	109.4(2)	C5	N1	B1	124.6(2)
C14	N1	B1	126.0(2)	C14	N2	C15	118.4(2)
C15	N3	C24	106.75(19)	C15	N3	B1	120.9(2)
C24	N3	B1	132.3(2)	S2	C1	C2	113.5(2)
C1	C2	C3	112.0(3)	O1	C3	C2	123.5(3)
O1	C3	C4	123.9(2)	C2	C3	C4	112.6(2)
S2	C4	C3	110.99(18)	S2	C4	C5	128.6(2)
C3	C4	C5	120.1(2)	N1	C5	C4	114.7(3)
N1	C5	C6	108.6(2)	C4	C5	C6	136.4(2)
C5	C6	C7	108.1(2)	C6	C7	C8	125.9(2)
C6	C7	C14	106.2(2)	C8	C7	C14	127.9(2)
C7	C8	C9	119.4(2)	C7	C8	C13	122.1(2)
C9	C8	C13	118.5(3)	C8	C9	C10	121.2(2)
C9	C10	C11	119.4(3)	C10	C11	C12	120.5(3)
C11	C12	C13	120.1(2)	C8	C13	C12	120.3(3)
N1	C14	N2	121.2(3)	N1	C14	C7	107.4(2)
N2	C14	C7	130.8(2)	N2	C15	N3	125.0(2)
N2	C15	C16	125.9(2)	N3	C15	C16	108.7(2)
C15	C16	C17	126.8(3)	C15	C16	C23	106.2(2)
C17	C16	C23	126.7(2)	C16	C17	C18	123.1(2)
C16	C17	C22	119.1(3)	C18	C17	C22	117.8(2)
C17	C18	C19	120.8(2)	C18	C19	C20	120.4(3)
C19	C20	C21	119.6(2)	C20	C21	C22	120.0(2)
C17	C22	C21	121.3(3)	C16	C23	C24	108.8(2)
N3	C24	C23	109.5(2)	N3	C24	C25	124.4(2)
C23	C24	C25	126.0(3)	S1	C25	C24	125.1(2)
S1	C25	C26	109.9(2)	C24	C25	C26	125.0(2)
O2	C26	C25	120.2(3)	O2	C26	C27	126.3(3)
C25	C26	C27	113.5(2)	C26	C27	C28	111.6(3)
S1	C28	C27	112.8(2)	F1	B1	O1	108.8(2)
F1	B1	N1	110.4(2)	F1	B1	N3	110.1(2)
O1	B1	N1	108.2(2)	O1	B1	N3	115.2(2)
N1	B1	N3	104.1(2)				

Bond angles involving hydrogens (°)

atom	atom	atom	angle	atom	atom	atom	angle
S2	C1	H1	123.3	C2	C1	H1	123.3
C1	C2	H2	124.0	C3	C2	H2	124.0
C5	C6	H6	125.9	C7	C6	H6	125.9
C8	C9	H9	119.4	C10	C9	H9	119.4
C9	C10	H10	120.3	C11	C10	H10	120.3
C10	C11	H11	119.7	C12	C11	H11	119.7
C11	C12	H12	120.0	C13	C12	H12	120.0
C8	C13	H13	119.9	C12	C13	H13	119.9
C17	C18	H18	119.6	C19	C18	H18	119.6
C18	C19	H19	119.8	C20	C19	H19	119.8
C19	C20	H20	120.2	C21	C20	H20	120.2
C20	C21	H21	120.0	C22	C21	H21	120.0
C17	C22	H22	119.4	C21	C22	H22	119.4
C16	C23	H23	125.6	C24	C23	H23	125.6
C26	C27	H27	124.2	C28	C27	H27	124.2
S1	C28	H28	123.6	C27	C28	H28	123.6
O2	C29	H29A	109.5	O2	C29	H29B	109.5
O2	C29	H29C	109.5	H29A	C29	H29B	109.5
H29A	C29	H29C	109.5	H29B	C29	H29C	109.4

Torsion Angles(°) (Those having bond angles > 160 or < 20 degrees are excluded.)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
C25	S1	C28	C27	−0.14(19)	C28	S1	C25	C24	−177.48(19)
C28	S1	C25	C26	0.14(17)	C1	S2	C4	C3	−0.38(17)
C1	S2	C4	C5	172.5(2)	C4	S2	C1	C2	−0.27(19)
C3	O1	B1	F1	81.8(3)	C3	O1	B1	N1	−38.2(3)
C3	O1	B1	N3	−154.1(2)	B1	O1	C3	C2	−160.3(2)
B1	O1	C3	C4	22.3(3)	C29	O2	C26	C25	−173.5(2)
C29	O2	C26	C27	4.3(4)	C5	N1	C14	N2	−166.4(2)
C5	N1	C14	C7	5.7(3)	C14	N1	C5	C4	170.50(19)
C14	N1	C5	C6	−3.9(3)	C5	N1	B1	F1	−84.1(3)
C5	N1	B1	O1	34.8(3)	C5	N1	B1	N3	157.7(2)
B1	N1	C5	C4	−10.9(3)	B1	N1	C5	C6	174.7(2)
C14	N1	B1	F1	94.3(3)	C14	N1	B1	O1	−146.8(2)
C14	N1	B1	N3	−23.9(3)	B1	N1	C14	N2	15.0(4)
B1	N1	C14	C7	−172.9(2)	C14	N2	C15	N3	−4.9(3)
C14	N2	C15	C16	167.1(2)	C15	N2	C14	N1	1.8(3)
C15	N2	C14	C7	−168.3(2)	C15	N3	C24	C23	−1.4(3)
C15	N3	C24	C25	178.8(2)	C24	N3	C15	N2	174.2(2)
C24	N3	C15	C16	1.1(2)	C15	N3	B1	F1	−98.8(3)
C15	N3	B1	O1	137.7(2)	C15	N3	B1	N1	19.5(3)
B1	N3	C15	N2	−7.9(3)	B1	N3	C15	C16	178.94(19)
C24	N3	B1	F1	78.4(3)	C24	N3	B1	O1	−45.1(4)
C24	N3	B1	N1	−163.3(2)	B1	N3	C24	C23	−178.9(2)
B1	N3	C24	C25	1.3(4)	S2	C1	C2	C3	0.8(3)
C1	C2	C3	O1	−178.8(2)	C1	C2	C3	C4	−1.1(3)
O1	C3	C4	S2	178.55(19)	O1	C3	C4	C5	5.0(4)
C2	C3	C4	S2	0.9(3)	C2	C3	C4	C5	−172.6(2)
S2	C4	C5	N1	177.00(17)	S2	C4	C5	C6	−10.7(4)
C3	C4	C5	N1	−10.7(3)	C3	C4	C5	C6	161.6(2)
N1	C5	C6	C7	0.5(3)	C4	C5	C6	C7	−172.2(3)
C5	C6	C7	C8	−177.4(2)	C5	C6	C7	C14	3.0(3)
C6	C7	C8	C9	14.0(4)	C6	C7	C8	C13	−165.8(2)
C6	C7	C14	N1	−5.3(3)	C6	C7	C14	N2	165.8(2)
C8	C7	C14	N1	175.0(2)	C8	C7	C14	N2	−13.9(4)
C14	C7	C8	C9	−166.5(2)	C14	C7	C8	C13	13.8(4)
C7	C8	C9	C10	−178.0(2)	C7	C8	C13	C12	178.3(2)
C9	C8	C13	C12	−1.4(4)	C13	C8	C9	C10	1.8(4)
C8	C9	C10	C11	−0.7(4)	C9	C10	C11	C12	−0.8(4)

Torsion angles (°) (continued)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
C10	C11	C12	C13	1.2(4)	C11	C12	C13	C8	−0.1(4)
N2	C15	C16	C17	0.2(4)	N2	C15	C16	C23	−173.4(2)
N3	C15	C16	C17	173.3(2)	N3	C15	C16	C23	−0.4(3)
C15	C16	C17	C18	31.1(4)	C15	C16	C17	C22	−147.0(2)
C15	C16	C23	C24	−0.5(3)	C17	C16	C23	C24	−174.2(2)
C23	C16	C17	C18	−156.4(2)	C23	C16	C17	C22	25.5(4)
C16	C17	C18	C19	−177.7(2)	C16	C17	C22	C21	177.7(2)
C18	C17	C22	C21	−0.6(4)	C22	C17	C18	C19	0.4(3)
C17	C18	C19	C20	0.2(4)	C18	C19	C20	C21	−0.7(4)
C19	C20	C21	C22	0.6(4)	C20	C21	C22	C17	0.1(4)
C16	C23	C24	N3	1.2(3)	C16	C23	C24	C25	−179.0(2)
N3	C24	C25	S1	−36.9(4)	N3	C24	C25	C26	145.8(2)
C23	C24	C25	S1	143.3(2)	C23	C24	C25	C26	−34.0(4)
S1	C25	C26	O2	177.89(17)	S1	C25	C26	C27	−0.1(3)
C24	C25	C26	O2	−4.5(4)	C24	C25	C26	C27	177.5(2)
O2	C26	C27	C28	−177.8(2)	C25	C26	C27	C28	0.0(3)
C26	C27	C28	S1	0.1(3)					

Intramolecular contacts less than 3.60 Å

atom	atom	distance	atom	atom	distance
S1	F1	3.185(2)	S1	O1	3.136(2)
S1	N3	3.329(3)	S1	B1	3.335(4)
S2	C6	3.555(3)	F1	C3	3.019(3)
F1	C4	3.391(3)	F1	C5	3.227(3)
F1	C14	3.344(3)	F1	C15	3.347(3)
F1	C24	3.296(3)	O1	C1	3.577(3)
O1	C5	2.864(4)	O1	C24	3.222(3)
O1	C25	3.254(3)	O2	C23	2.969(4)
O2	C24	2.901(4)	N1	C3	2.696(3)
N1	C15	2.679(3)	N2	C5	3.474(3)
N2	C6	3.559(4)	N2	C8	3.233(4)
N2	C13	3.138(4)	N2	C17	3.100(4)
N2	C18	3.107(3)	N2	C23	3.548(4)
N2	C24	3.529(4)	N2	B1	2.981(4)
N3	C14	2.784(4)	C4	C14	3.534(4)
C4	B1	2.823(4)	C6	C9	2.983(4)
C8	C11	2.788(4)	C9	C12	2.767(4)
C10	C13	2.785(4)	C13	C14	3.115(4)
C15	C18	3.155(4)	C17	C20	2.809(4)
C18	C21	2.780(4)	C19	C22	2.769(5)
C22	C23	3.021(4)	C23	C26	3.140(4)
C25	B1	3.223(5)	C27	C29	2.837(4)

Intramolecular contacts less than 3.60 Å involving hydrogens

atom	atom	distance	atom	atom	distance
S1	H27	3.476	S2	H2	3.496
S2	H6	3.460	O1	H2	2.716
O2	H23	2.604	O2	H27	2.779
N1	H6	3.168	N2	H13	2.473
N2	H18	2.602	N3	H23	3.178
C3	H1	3.203	C4	H1	3.399
C4	H2	3.241	C4	H6	3.017
C6	H9	2.666	C7	H9	2.627
C7	H13	2.682	C8	H6	2.836
C8	H10	3.283	C8	H12	3.273
C9	H6	2.820	C9	H11	3.246
C9	H13	3.267	C10	H12	3.260
C11	H9	3.244	C11	H13	3.262
C12	H10	3.263	C13	H9	3.263
C13	H11	3.261	C13	H18	3.591
C14	H6	3.194	C14	H13	2.818
C15	H18	2.921	C15	H23	3.169
C16	H18	2.706	C16	H22	2.623
C17	H19	3.279	C17	H21	3.285
C17	H23	2.841	C18	H13	3.292
C18	H20	3.268	C18	H22	3.265
C19	H21	3.263	C20	H18	3.265
C20	H22	3.255	C21	H19	3.260
C22	H18	3.266	C22	H20	3.261
C22	H23	2.899	C23	H22	2.722
C25	H23	2.839	C25	H27	3.244
C25	H28	3.409	C26	H23	3.043
C26	H28	3.202	C26	H29A	3.185
C26	H29B	2.601	C26	H29C	2.601
C27	H29B	2.735	C27	H29C	2.785
C29	H27	2.632	H1	H2	2.409
H6	H9	2.250	H9	H10	2.330
H10	H11	2.332	H11	H12	2.333
H12	H13	2.337	H13	H18	2.689
H18	H19	2.325	H19	H20	2.344
H20	H21	2.340	H21	H22	2.326
H22	H23	2.383	H27	H28	2.415
H27	H29A	3.600	H27	H29B	2.343
H27	H29C	2.464			

Intermolecular contacts less than 3.60 Å

atom	atom	distance	atom	atom	distance
S1	S1[1]	3.425(2)	F1	C12[2]	3.150(3)
F1	C13[2]	3.366(3)	F1	C18[2]	3.450(4)
F1	C19[2]	3.324(4)	F1	C28[1]	3.199(3)
O1	C2[1]	3.482(4)	O1	C11[3]	3.467(3)
O1	C12[3]	3.411(3)	N1	C12[3]	3.423(4)
N1	C13[3]	3.501(4)	N1	C18[2]	3.549(4)
N2	N2[2]	3.410(3)	N2	C8[3]	3.414(4)
N3	C10[3]	3.589(4)	N3	C11[3]	3.468(4)
C1	C26[1]	3.595(4)	C1	C27[1]	3.533(4)
C1	C28[4]	3.446(4)	C2	O1[1]	3.482(4)
C2	C26[1]	3.559(4)	C2	C27[1]	3.406(4)
C2	C28[1]	3.458(4)	C3	C28[1]	3.436(4)
C5	C12[3]	3.593(4)	C6	C29[5]	3.389(4)
C7	C13[3]	3.590(4)	C8	N2[3]	3.414(4)
C9	C15[3]	3.491(4)	C9	C16[3]	3.421(4)
C10	N3[3]	3.589(4)	C10	C15[3]	3.568(4)
C10	C16[3]	3.504(4)	C10	C23[3]	3.474(4)
C10	C24[3]	3.540(4)	C11	O1[3]	3.467(3)
C11	N3[3]	3.468(4)	C12	F1[2]	3.150(3)
C12	O1[3]	3.411(3)	C12	N1[3]	3.423(4)
C12	C5[3]	3.593(4)	C13	F1[2]	3.366(3)
C13	N1[3]	3.501(4)	C13	C7[3]	3.590(4)
C13	C14[3]	3.377(4)	C14	C13[3]	3.377(4)
C14	C18[2]	3.532(4)	C15	C9[3]	3.491(4)
C15	C10[3]	3.568(4)	C16	C9[3]	3.421(4)
C16	C10[3]	3.504(4)	C18	F1[2]	3.450(4)
C18	N1[2]	3.549(4)	C18	C14[2]	3.532(4)
C19	F1[2]	3.324(4)	C20	C29[6]	3.529(5)
C21	C26[7]	3.544(4)	C23	C10[3]	3.474(4)
C24	C10[3]	3.540(4)	C26	C1[1]	3.595(4)
C26	C2[1]	3.559(4)	C26	C21[6]	3.544(4)
C27	C1[1]	3.533(4)	C27	C2[1]	3.406(4)
C28	F1[1]	3.199(3)	C28	C1[8]	3.446(4)
C28	C2[1]	3.458(4)	C28	C3[1]	3.436(4)
C29	C6[9]	3.389(4)	C29	C20[7]	3.529(5)

Symmetry Operators:

(1) −X+1/2,Y,−Z+1 (2) −X+1,−Y+1,−Z+2

(3) −X+1,−Y+2,−Z+2 (4) −X+1/2,Y+1,−Z+1

(5) X,−Y+1,Z (6) −X+1,Y+1/2−1,−Z+1/2+1

(7) −X+1,Y+1/2,−Z+1/2+1 (8) −X+1/2,Y−1,−Z+1

(9) X+1,−Y+1,Z

Intermolecular contacts less than 3.60 Å involving hydrogens

atom	atom	distance	atom	atom	distance
S1	H2[1]	3.383	S1	H11[2]	3.344
S1	H12[2]	3.230	S2	H19[3]	3.385
S2	H20[4]	3.365	S2	H20[3]	3.380
S2	H28[5]	3.364	S2	H29B[6]	3.073
S2	H29C[1]	3.391	F1	H12[2]	2.624
F1	H13[2]	3.040	F1	H18[2]	2.880
F1	H19[2]	2.622	F1	H28[1]	2.437
O1	H2[1]	2.554	O1	H11[3]	3.255
O1	H12[3]	3.169	O1	H28[1]	3.423
O2	H1[1]	3.453	O2	H10[3]	3.168
O2	H21[7]	3.180	N1	H12[3]	3.471
N1	H13[3]	3.599	N1	H18[2]	2.864
N2	H18[2]	3.305	C1	H11[8]	2.953
C1	H20[4]	3.491	C1	H28[5]	3.236
C1	H29C[1]	3.026	C2	H2[1]	3.045
C2	H11[8]	3.032	C3	H2[1]	3.101
C3	H12[3]	3.074	C3	H28[1]	3.434
C4	H12[3]	3.212	C4	H29B[6]	3.502
C5	H12[3]	3.340	C5	H13[3]	3.426
C5	H18[2]	3.383	C5	H29A[6]	3.441
C5	H29B[6]	3.355	C6	H13[3]	3.206
C6	H18[2]	3.542	C6	H29A[6]	2.910
C6	H29B[6]	2.960	C7	H13[3]	3.253
C7	H18[2]	3.158	C10	H21[6]	3.354
C10	H22[6]	3.258	C11	H1[9]	3.246
C11	H2[9]	3.359	C11	H21[6]	3.475
C14	H13[3]	3.432	C14	H18[2]	2.754
C15	H13[2]	3.561	C16	H9[3]	3.394
C16	H10[3]	3.529	C17	H6[3]	3.255
C17	H9[3]	3.205	C17	H29A[7]	3.232
C18	H6[3]	3.115	C18	H29A[7]	3.114
C19	H6[3]	3.113	C19	H28[10]	3.538
C19	H29A[7]	3.064	C19	H29C[7]	3.381
C20	H1[11]	3.347	C20	H6[3]	3.242
C20	H29A[7]	3.132	C20	H29B[12]	3.215
C20	H29C[7]	3.016	C21	H1[11]	3.199
C21	H6[3]	3.374	C21	H10[13]	3.248

Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
C21	H29A[7]	3.226	C21	H29B[12]	3.272
C21	H29C[7]	3.370	C22	H6[3]	3.374
C22	H9[3]	3.084	C22	H10[13]	3.105
C22	H29A[7]	3.267	C23	H10[3]	3.215
C24	H10[3]	3.446	C25	H2[1]	3.330
C25	H21[7]	3.255	C26	H1[1]	3.542
C26	H2[1]	3.492	C26	H21[7]	2.851
C27	H20[7]	3.369	C27	H21[7]	3.120
C28	H1[14]	3.249	C28	H2[1]	3.538
C28	H19[15]	3.365	C29	H1[1]	3.489
C29	H6[13]	2.938	B1	H18[2]	3.382
B1	H28[1]	3.467	H1	O2[1]	3.453
H1	C11[8]	3.246	H1	C20[4]	3.347
H1	C21[4]	3.199	H1	C26[1]	3.542
H1	C28[5]	3.249	H1	C29[1]	3.489
H1	H11[8]	2.356	H1	H20[4]	2.999
H1	H21[4]	2.703	H1	H28[5]	3.304
H1	H29C[1]	2.762	H2	S1[1]	3.383
H2	O1[1]	2.554	H2	C2[1]	3.045
H2	C3[1]	3.101	H2	C11[8]	3.359
H2	C25[1]	3.330	H2	C26[1]	3.492
H2	C28[1]	3.538	H2	H2[1]	2.558
H2	H11[8]	2.536	H6	C17[3]	3.255
H6	C18[3]	3.115	H6	C19[3]	3.113
H6	C20[3]	3.242	H6	C21[3]	3.374
H6	C22[3]	3.374	H6	C29[6]	2.938
H6	H13[3]	3.528	H6	H18[3]	3.561
H6	H19[3]	3.560	H6	H29A[6]	2.651
H6	H29B[6]	2.394	H9	C16[3]	3.394
H9	C17[3]	3.205	H9	C22[3]	3.084
H9	H22[6]	3.560	H9	H22[3]	3.088
H9	H23[6]	3.523	H9	H29A[6]	3.114
H9	H29B[6]	3.562	H10	O2[3]	3.168
H10	C16[3]	3.529	H10	C21[6]	3.248
H10	C22[6]	3.105	H10	C23[3]	3.215
H10	C24[3]	3.446	H10	H21[6]	2.950
H10	H22[6]	2.673	H10	H22[3]	3.397

Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H10	H23[3]	3.371	H11	S1[2]	3.344
H11	O1[3]	3.255	H11	C1[9]	2.953
H11	C2[9]	3.032	H11	H1[9]	2.356
H11	H2[9]	2.536	H11	H21[6]	3.180
H12	S1[2]	3.230	H12	F1[2]	2.624
H12	O1[3]	3.169	H12	N1[3]	3.471
H12	C3[3]	3.074	H12	C4[3]	3.212
H12	C5[3]	3.340	H12	H28[10]	3.531
H13	F1[2]	3.040	H13	N1[3]	3.599
H13	C5[3]	3.426	H13	C6[3]	3.206
H13	C7[3]	3.253	H13	C14[3]	3.432
H13	C15[2]	3.561	H13	H6[3]	3.528
H18	F1[2]	2.880	H18	N1[2]	2.864
H18	N2[2]	3.305	H18	C5[2]	3.383
H18	C6[2]	3.542	H18	C7[2]	3.158
H18	C14[2]	2.754	H18	B1[2]	3.382
H18	H6[3]	3.561	H19	S2[3]	3.385
H19	F1[2]	2.622	H19	C28[10]	3.365
H19	H6[3]	3.560	H19	H27[10]	3.293
H19	H28[10]	2.598	H19	H29A[7]	3.528
H20	S2[11]	3.365	H20	S2[3]	3.380
H20	C1[11]	3.491	H20	C27[12]	3.369
H20	H1[11]	2.999	H20	H20[16]	3.584
H20	H27[12]	3.059	H20	H29B[12]	3.176
H20	H29C[7]	3.083	H21	O2[12]	3.180
H21	C10[13]	3.354	H21	C11[13]	3.475
H21	C25[12]	3.255	H21	C26[12]	2.851
H21	C27[12]	3.120	H21	H1[11]	2.703
H21	H10[13]	2.950	H21	H11[13]	3.180
H21	H23[12]	3.343	H21	H27[12]	3.429
H21	H29B[12]	3.277	H22	C10[13]	3.258
H22	H9[13]	3.560	H22	H9[3]	3.088
H22	H10[13]	2.673	H22	H10[3]	3.397
H22	H23[12]	3.162	H23	H9[13]	3.523
H23	H10[3]	3.371	H23	H21[7]	3.343
H23	H22[7]	3.162	H27	H19[15]	3.293
H27	H20[7]	3.059	H27	H21[7]	3.429

Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H28	S2[14]	3.364	H28	F1[1]	2.437
H28	O1[1]	3.423	H28	C1[14]	3.236
H28	C3[1]	3.434	H28	C19[15]	3.538
H28	B1[1]	3.467	H28	H1[14]	3.304
H28	H12[15]	3.531	H28	H19[15]	2.598
H29A	C5[13]	3.441	H29A	C6[13]	2.910
H29A	C17[12]	3.232	H29A	C18[12]	3.114
H29A	C19[12]	3.064	H29A	C20[12]	3.132
H29A	C21[12]	3.226	H29A	C22[12]	3.267
H29A	H6[13]	2.651	H29A	H9[13]	3.114
H29A	H19[12]	3.528	H29B	S2[13]	3.073
H29B	C4[13]	3.502	H29B	C5[13]	3.355
H29B	C6[13]	2.960	H29B	C20[7]	3.215
H29B	C21[7]	3.272	H29B	H6[13]	2.394
H29B	H9[13]	3.562	H29B	H20[7]	3.176
H29B	H21[7]	3.277	H29C	S2[1]	3.391
H29C	C1[1]	3.026	H29C	C19[12]	3.381
H29C	C20[12]	3.016	H29C	C21[12]	3.370
H29C	H1[1]	2.762	H29C	H20[12]	3.083

Symmetry Operators:

(1) −X+1/2,Y,−Z+1
(2) −X+1,−Y+1,−Z+2
(3) −X+1,−Y+2,−Z+2
(4) X+1/2−1,Y+1/2,Z+1/2−1
(5) −X+1/2,Y+1,−Z+1
(6) X,−Y+1,Z
(7) −X+1,Y+1/2−1,−Z+1/2+1
(8) X,−Y+2,Z
(9) X,−Y+2,Z+1
(10) X,−Y+1,Z+1
(11) X+1/2,Y+1/2−1,Z+1/2
(12) −X+1,Y+1/2,−Z+1/2+1
(13) X+1,−Y+1,Z
(14) −X+1/2,Y−1,−Z+1
(15) X,−Y+1,Z
(16) −X+1,−Y+1,−Z+2

Calculation results

Table S1. Atom coordinates and absolute energy levels for **1** optimized in the S_0 state.
E(RB3LYP) = −2212.68176939

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z	Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−0.707609	1.101103	0.302383	27	8	0	2.524488	−0.418993	1.104804
2	7	0	0.683806	1.164468	0.271090	28	8	0	2.524316	0.418233	−1.104925
3	5	0	1.617166	−0.000375	0.000885	29	6	0	3.004245	−1.661303	1.012157
4	7	0	0.683004	−1.165215	−0.269646	30	6	0	4.183512	−2.106128	1.682921
5	6	0	−0.708320	−1.101143	−0.301369	31	6	0	4.431108	−3.432574	1.470595
6	7	0	−1.388637	0.000219	0.000461	32	16	0	3.243866	−4.198266	0.453458
7	6	0	−1.201353	2.449357	0.469172	33	16	0	3.245085	4.197521	−0.453417
8	6	0	−0.084059	3.284319	0.411960	34	6	0	4.430002	3.431983	−1.473270
9	6	0	1.061509	2.472864	0.208203	35	6	0	4.181962	2.105649	−1.685655
10	6	0	1.060174	−2.473691	−0.206711	36	6	0	3.004274	1.660265	−1.012341
11	6	0	−0.085754	−3.284656	−0.410349	37	1	0	−0.078073	4.364412	0.453930
12	6	0	−1.202679	−2.449214	−0.468153	38	1	0	−0.080161	−4.364750	−0.452307
13	6	0	2.373468	2.690644	−0.292157	39	1	0	−2.261684	4.875128	−0.089902
14	6	0	2.372173	−2.691891	0.293621	40	1	0	−4.600164	5.597443	0.187048
15	6	0	−2.604170	2.854745	0.598856	41	1	0	−6.317916	3.992657	1.007308
16	6	0	−2.605595	−2.854043	−0.598557	42	1	0	−5.654428	1.657225	1.555241
17	6	0	−2.996838	4.171263	0.289142	43	1	0	−3.306173	0.937564	1.294532
18	6	0	−4.319931	4.577336	0.436001	44	1	0	−2.263796	−4.875541	0.087441
19	6	0	−5.284695	3.676031	0.892702	45	1	0	−4.602380	−5.596752	−0.190536
20	6	0	−4.911738	2.365555	1.197759	46	1	0	−6.319659	−3.990470	−1.008791
21	6	0	−3.587826	1.956108	1.055219	47	1	0	−5.655448	−1.654493	−1.553747
22	6	0	−2.998676	−4.170871	−0.290627	48	1	0	−3.307088	−0.935813	−1.291875
23	6	0	−4.321859	−4.576388	−0.438112	49	1	0	4.804652	−1.451245	2.282069
24	6	0	−5.286366	−3.674248	−0.893724	50	1	0	5.268761	−4.013199	1.833426
25	6	0	−4.913010	−2.363498	−1.197081	51	1	0	5.267340	4.012467	−1.837080
26	6	0	−3.589001	−1.954587	−1.053891	52	1	0	4.801855	1.451019	−2.286376

Table S2. Atom coordinates and absolute energy levels for **3** optimized in the S_0 state.
E(RB3LYP) = −2484.22787245

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z	Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−1.712327	−0.814470	0.029011	36	6	0	1.581319	−0.890742	1.454495
2	7	0	−0.518959	−1.498470	−0.040810	37	8	0	3.546084	3.620102	0.244461
3	7	0	0.642832	0.591000	−0.501585	38	6	0	3.394458	3.415687	1.657363
4	6	0	−0.640928	1.161828	−0.389546	39	6	0	0.913230	−0.315884	2.552119
5	7	0	−1.765817	0.495600	−0.116728	40	6	0	1.478041	−0.290303	3.827322
6	6	0	1.523459	1.621870	−0.688331	41	6	0	2.849805	−1.440416	1.699077
7	6	0	0.816777	2.846012	−0.727016	42	6	0	3.426262	−1.421870	2.971992
8	6	0	−0.537467	2.582292	−0.553955	43	6	0	2.741726	−0.846159	4.041791
9	6	0	−2.787796	−1.788848	0.096623	44	1	0	1.280459	3.800953	−0.917425
10	6	0	−2.176894	−3.033625	−0.016323	45	1	0	−2.662497	−3.998450	−0.034092
11	6	0	−0.771561	−2.825664	−0.134857	46	1	0	−3.164503	2.211527	−1.223542
12	6	0	−1.627449	3.564836	−0.550772	47	1	0	−4.949079	3.919155	−1.246768
13	6	0	−4.220927	−1.503521	0.198063	48	1	0	−4.449206	6.264246	−0.584801
14	6	0	0.343404	−3.630714	−0.481664	49	1	0	−2.137460	6.879663	0.102606
15	6	0	2.958982	1.521996	−0.857669	50	1	0	−0.359766	5.170638	0.138692
16	6	0	−2.940289	3.230403	−0.933870	51	1	0	−4.831546	−3.407997	−0.621136
17	6	0	−3.943773	4.196700	−0.942839	52	1	0	−7.246163	−2.974283	−0.395091
18	6	0	−3.663989	5.513948	−0.574586	53	1	0	−8.047021	−0.805261	0.524214
19	6	0	−2.366088	5.859546	−0.192292	54	1	0	−6.395257	0.917642	1.224709
20	6	0	−1.360706	4.897062	−0.180528	55	1	0	−3.973188	0.476622	1.015514
21	6	0	−5.168676	−2.466872	−0.198113	56	1	0	6.199628	0.637782	−2.028169
22	6	0	−6.532573	−2.218630	−0.079892	57	1	0	6.037488	2.892243	−0.634700
23	6	0	−6.982431	−0.999588	0.432926	58	1	0	2.474553	−6.135137	−1.773123
24	6	0	−6.054620	−0.032528	0.823769	59	1	0	3.360946	−3.659754	−1.996134
25	6	0	−4.688232	−0.277796	0.710771	60	1	0	4.332314	3.061978	2.101941
26	16	0	3.793427	0.270058	−1.763108	61	1	0	3.134788	4.387947	2.079981
27	6	0	5.311088	1.078691	−1.597655	62	1	0	2.599399	2.694686	1.873585
28	6	0	5.210853	2.234575	−0.873568	63	1	0	−0.074301	0.119779	2.412311
29	6	0	3.875719	2.493778	−0.462447	64	1	0	0.932952	0.158309	4.653965
30	16	0	0.408710	−5.365010	−0.695667	65	1	0	4.410190	−1.857411	3.127137
31	6	0	1.963944	−5.234607	−1.460950	66	1	0	3.185510	−0.831513	5.033655
32	6	0	2.414592	−3.948108	−1.556558	67	1	0	3.401070	−1.887171	0.876681
33	6	0	1.499490	−3.010880	−0.988367						
34	8	0	1.696720	−1.694444	−0.993263						
35	5	0	0.899825	−0.881427	−0.017295						

Table S3. Atom coordinates and absolute energy levels for **4** optimized in the S_0 state.
E(RB3LYP) = −2492.22331622

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z	Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−1.097772	−1.145100	0.045016	37	6	0	3.581456	−1.540322	2.974843
2	7	0	0.290921	−1.240356	0.118572	38	5	0	1.259379	0.000119	0.000162
3	7	0	0.290924	1.240350	−0.118391	39	9	0	2.040358	−0.167840	−1.130731
4	6	0	−1.097751	1.145096	−0.044819	40	9	0	2.040223	0.168045	1.131156
5	7	0	−1.759226	−0.000025	0.000115	41	1	0	−0.588353	4.411559	0.074927
6	6	0	0.609588	2.560555	−0.065534	42	1	0	−0.588286	−4.411551	−0.075399
7	6	0	−0.570102	3.331457	0.066091	43	1	0	−3.810255	1.075392	−0.899273
8	6	0	−1.661547	2.469558	0.046998	44	1	0	−6.183114	1.757000	−0.807792
9	6	0	−1.661532	−2.469624	−0.046990	45	1	0	−6.828428	3.909217	0.259175
10	6	0	−0.570077	−3.331450	−0.066326	46	1	0	−5.069083	5.373156	1.235947
11	6	0	0.609618	−2.560504	0.065443	47	1	0	−2.702059	4.685114	1.158472
12	6	0	−3.078832	2.833841	0.112013	48	1	0	−2.702102	−4.685042	−1.158703
13	6	0	−3.078818	−2.833895	−0.112004	49	1	0	−5.069153	−5.373034	−1.236184
14	6	0	1.965448	−3.075657	0.148509	50	1	0	−6.828429	−3.909182	−0.259187
15	6	0	1.965422	3.075743	−0.148632	51	1	0	−6.183053	−1.757092	0.808001
16	6	0	−4.085376	2.013113	−0.432876	52	1	0	−3.810174	−1.075534	0.899485
17	6	0	−5.421901	2.400985	−0.376931	53	1	0	4.926223	4.820680	0.739507
18	6	0	−5.785032	3.610513	0.218739	54	1	0	4.995205	3.543813	−1.553988
19	6	0	−4.797036	4.433739	0.763573	55	1	0	4.995276	−3.543831	1.553794
20	6	0	−3.460456	4.050148	0.711086	56	1	0	4.926210	−4.820824	−0.739464
21	6	0	−3.460479	−4.050121	−0.711216	57	1	0	3.089752	1.050460	−3.815935
22	6	0	−4.797065	−4.433680	−0.763707	58	1	0	4.374740	2.194676	−3.357174
23	6	0	−5.785029	−3.610498	−0.218743	59	1	0	3.998386	0.779941	−2.309879
24	6	0	−5.421862	−2.401044	0.377053	60	1	0	3.090020	−1.050729	3.816069
25	6	0	−4.085328	−2.013203	0.433003	61	1	0	4.374907	−2.194864	3.356815
26	16	0	2.607473	4.108167	1.113184						
27	6	0	4.126552	4.243317	0.296808						
28	6	0	4.142406	3.563283	−0.887677						
29	6	0	2.898387	2.906127	−1.156622						
30	6	0	2.898461	−2.905931	1.156432						
31	6	0	4.142411	−3.563267	0.887568						
32	6	0	4.126470	−4.243561	−0.296757						
33	16	0	2.607405	−4.108445	−1.113191						
34	8	0	2.561556	2.284813	−2.310341						
35	8	0	2.561666	−2.284447	2.310033						
36	6	0	3.581257	1.540332	−2.974906						