Supplementary Information for

Anthranilamide (aam)-substituted diboron: Palladium-catalyzed selective B(aam) transfer

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General Remarks.

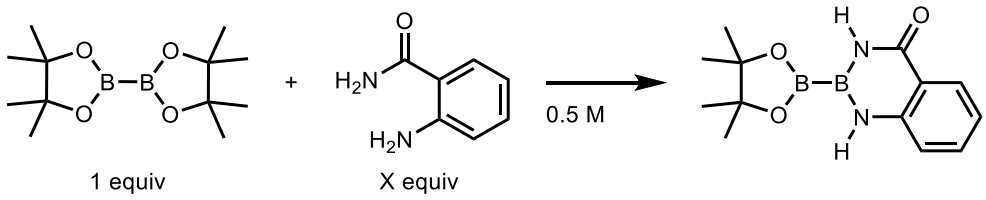
All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under an argon atmosphere. Nuclear magnetic resonance spectra were taken on a Varian System 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz; ^{11}B, 186 MHz) spectrometer using residual chloroform (^{1}H, δ = 7.26), $CDCl_3$ (^{13}C, δ = 77.16), a residual proton in DMSO-d_6 (^{1}H, δ = 2.50) and DMSO-d_6 (^{13}C, δ = 39.52) as an internal standard, and boron trifluoride diethyl etherate (^{11}B, δ = 0.00) as an external standard. ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration. High-resolution mass spectra were obtained with a Thermo Fisher Scientific LTQ Orbitrap XL spectrometer. Melting points were measured with Yanaco Micro Melting Point apparatus and uncorrected. Column chromatography was carried out using Florisil or Merk Kieselgel 60. All microwave reactions (Biotage, Initiator+) were conducted in a sealed tube, and the reaction temperature was maintained by an external infrared sensor. Unless otherwise noted, commercially available reagents were used without purification. 1,4-Dioxane was distilled from CaH_2, and other solvents were dried over activated molecular sieves 3Å. 2-Bromo-6-chloro-4-methoxypyridine was prepared according to a literature procedure.[1]

Synthesis of (pin)B–B(aam).

Conventional heating: A reaction tube equipped with a magnetic stirring bar was charged with bis(pinacolato)diboron (20 mmol), anthranilamide (60 mmol) and chlorobenzene (40 mL). After the mixture was stirred at reflux temperature for 48 h, the solvent was removed in vacuo at room temperature. The resulting mixture was diluted with ethyl acetate (200 mL) and filtered through a Celite plug. The organic solution was washed with saturated $CuSO_4$aq (100 mL × 5), dried over $MgSO_4$, and evaporated. Hexane (200 mL) was added into the solid residue and the mixture was sonicated. The product was isolated by filtration.

Microwave irradiation: A reaction tube equipped with a magnetic stirring bar was charged with bis(pinacolato)diboron (10 mmol), anthranilamide (5 mmol) and chlorobenzene (10 mL). After the mixture was stirred at 250 °C for 1.5 h under microwave irradiation, the solvent was removed in vacuo at room temperature. The resulting mixture was diluted with ethyl acetate (200 mL) and filtered through a Celite plug. The organic solution was washed with saturated $CuSO_4$aq (100 mL × 5), dried over $MgSO_4$, and evaporated. Hexane (200 mL) was added into the solid residue and the mixture was sonicated. The product was isolated by filtration and unreacted bis(pinacolato)diboron was recovered from filtrate.

Table S1. Synthesis of (pin)B–B(aam): Solvent Effect

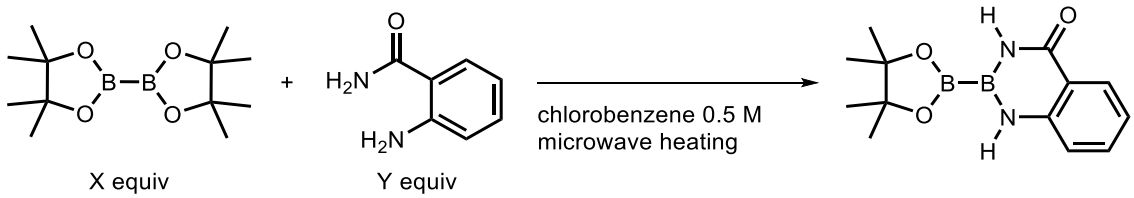


1 equiv X equiv

Entry	Solvent	X	Time (h)	Temp. (°C)	GC Yield (%)
1	heptane	1	48	98	0
2	DMF	1	48	100	0
3	diglyme	1	48	135	2
4	diglyme	1	48	162	0
5	THF	1	48	66	11
6	dimethoxyethane	1	48	83	7
7	dichloroethane	1	48	83	4
8	1,4-dioxane	1	48	100	4
9	chlorobenzene	1	48	131	16
10[a]	chlorobenzene	2	48	131	18
11	chlorobenzene	2	48	131	33
12	**chlorobenzene**	**3**	**48**	**131**	**44**
13	*p*-xylene	1	48	135	23
14[a]	*p*-xylene	2	48	135	13
15	*p*-xylene	2	48	100	23
16	*p*-xylene	2	48	135	29
17	benzene	1	48	80	0
18	benzene	2	48	80	0
19	anisole	2	48	135	12
20	anisole	2	20	154	18
21	pyridine	2	20	115	0
22	benzonitrile	2	20	135	13
23	benzonitrile	2	48	188	0
24	*o*-dichlorobenzene	2	20	135	10
25	*o*-dichlorobenzene	2	20	180	18
26	mesitylene	2	10	135	15
27	toluene	2	48	110	23

[a] 0.25 M

Table S2. Synthesis of (pin)B–B(aam): Effect of Other Conditions



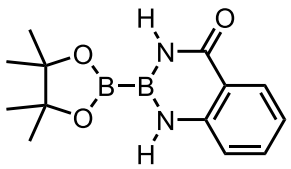
Entry	X	Y	Temp. (°C)	Time (min)	GC Yield (%)
1	1	3	200	10	3
2	1	1	250	10	11
3	1	1	200	20	3
4	1	1	250	60	15
5	1	1	250	90	40
6	1	1	250	120	31
7	1	1	250	180	trace
8	1	3	250	30	8
9	1	3	250	40	19
10	1	3	250	50	34
11	1	3	250	60	27
12	1	3	250	70	2
13	2	1	250	30	26
14	**2**	**1**	**250**	**90**	**43**
15	2	1	250	120	30

Pd-Catalyzed Borylation of Aryl Halides: A General Procedure.

A Schlenk tube equipped with a magnetic stirring bar was charged with potassium acetate (0.450 mmol), (pin)B–B(aam) (0.150 mmol), tris(dibenzylideneacetone)dipalladium (3.75 μmol), 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (0.0113 mmol), 1,4-dioxane (0.5 mL) and an aryl halide (0.225 mmol). After the mixture was stirred at 60 °C for 18 h, the mixture was diluted with ethyl acetate and the organic solution was washed with brine, dried over $MgSO_4$, and evaporated. The product was isolated by Florisil-column chromatography (hexane:ethyl acetate = 1:1 as an eluent).

The spectral data of the known Ar–B(aam) were found to be identical to those reported in the literature.

2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one [(pin)B–B(aam)]



Isolated in 40% yield as a white solid: mp 191.3–195.8 °C

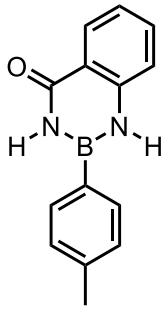
^{1}H NMR (400 MHz, Chloroform-d) δ 1.29 (s, 12H), 6.99 – 7.04 (m, 1H), 7.05 (brs, 1H), 7.16 (ddd, *J* = 8.2, 7.2, 1.0 Hz, 1H), 7.51 (ddd, *J* = 8.1, 7.2, 1.6 Hz, 1H), 7.55 (brs, 1H), 8.21 (dd, *J* = 8.0, 1.8 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-d) δ 25.23, 83.89, 117.61, 120.26, 122.31, 129.17, 133.71, 144.17, 165.77.

^{11}B NMR (160 MHz, Chloroform-d) δ 32.38.

HRMS Calcd for $C_{13}H_{19}B_2O_3$: $[M+H]^+$, 273.1576 Found: *m*/*z* 273.1582

2-(p-tolyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (1a)[2]



Isolated in 77% yield as a white solid: mp 267.4–270.3 °C

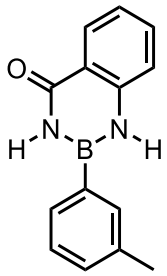
^{1}H NMR (500 MHz, DMSO-d6) δ 2.35 (s, 3H), 7.02 – 7.14 (m, 1H), 7.26 (d, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 1H), 7.56 (ddd, *J* = 8.5, 7.1, 1.7 Hz, 1H), 7.95 (d, *J* = 7.6 Hz, 2H), 8.00 (dd, *J* = 8.0, 1.6 Hz, 1H), 9.25 (brs, 1H), 9.63 (brs, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ 21.22, 118.09, 118.69, 120.70, 127.92, 128.52, 133.37, 140.16, 145.53, 166.30.

^{11}B NMR (160 MHz, DMSO-d6) δ 30.60.

HRMS Calcd for $C_{14}H_{14}BN_2O$: $[M+H]^+$, 237.1194 Found: *m*/*z* 237.1196

2-(m-tolyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (1b)[2]



Isolated in 72% yield as a white solid: mp 220.3–224.2 °C

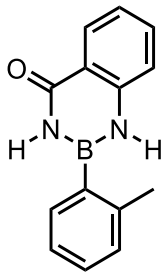
^{1}H NMR (500 MHz, DMSO-d6) δ 2.36 (s, 3H), 7.10 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 7.26 – 7.37 (m, 2H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.56 (ddd, *J* = 8.6, 7.5, 1.4 Hz, 1H), 7.83 (d, *J* = 7.1 Hz, 1H), 7.88 (s, 1H), 8.00 (dd, *J* = 7.9, 1.5 Hz, 1H), 9.29 (brs, 1H), 9.63 (brs, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ 21.15, 118.13, 118.76, 120.80, 127.77, 127.94, 130.41, 131.14, 133.40, 133.93, 136.69, 145.51, 166.29.

^{11}B NMR (160 MHz, DMSO-d6) δ 29.22.

HRMS Calcd for $C_{14}H_{14}BN_2O$: $[M+H]^+$, 237.1194 Found: *m*/*z* 237.1194

2-(o-tolyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (1c)[2]



Isolated in 60% yield as a white solid: mp 170.8–174.3 °C

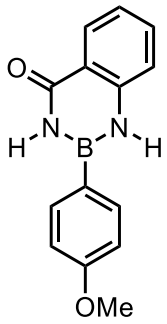
^{1}H NMR (500 MHz, DMSO-d6) δ 2.41 (s, 3H), 7.10 (dd, *J* = 8.1, 7.0 Hz, 1H), 7.16 – 7.25 (m, 2H), 7.26 – 7.36 (m, 2H), 7.44 (d, *J* = 6.3 Hz, 1H), 7.55 (ddd, *J* = 8.3, 7.1, 1.5 Hz, 1H), 8.01 (dd, *J* = 8.0, 1.5 Hz, 1H), 9.18 (brs, 1H), 9.43 (brs, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ 22.20, 118.05, 118.74, 120.85, 124.76, 127.92, 129.07, 129.16, 133.11, 133.29, 140.60, 145.41, 165.95.

^{11}B NMR (160 MHz, DMSO-d6) δ 30.48.

HRMS Calcd for $C_{14}H_{14}BN_2O$: $[M+H]^+$, 237.1194 Found: *m*/*z* 237.1194

2-(4-methoxyphenyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (1d)[2]



Isolated in 93% yield as a white solid: mp 230.1–233.3 °C

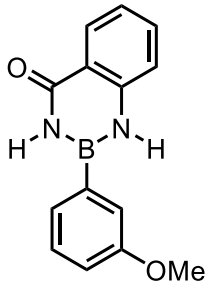
^{1}H NMR (500 MHz, DMSO-d6) δ 3.81 (s, 3H), 7.00 (d, *J* = 8.6 Hz, 2H), 7.07 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 7.40 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.55 (ddd, *J* = 8.5, 7.2, 1.6 Hz, 1H), 7.95 – 8.07 (m, 3H), 9.20 (brs, 1H), 9.61 (brs, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ 55.04, 113.46, 118.01, 118.58, 120.58, 127.93, 133.35, 135.09, 145.62, 161.34, 166.33.

^{11}B NMR (160 MHz, DMSO-d6) δ 29.00.

HRMS Calcd for $C_{14}H_{14}BN_2O_2$: $[M+H]^+$, 253.1143 Found: *m*/*z* 253.1143

2-(3-methoxyphenyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (1e)[3]



Isolated in 83% yield as a white solid: mp 184.2–186.4 °C

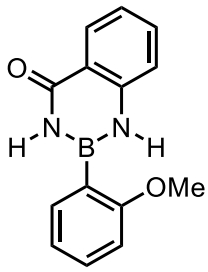
^{1}H NMR (500 MHz, DMSO-d6) δ 3.83 (s, 3H), 7.04 (ddd, *J* = 8.2, 2.7, 1.0 Hz, 1H), 7.10 (ddd, *J* = 8.0, 7.1, 1.1 Hz, 1H), 7.36 (dd, *J* = 8.2, 7.2 Hz, 1H), 7.43 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.57 (ddd, *J* = 8.5, 7.2, 1.6 Hz, 1H), 7.60 – 7.65 (m, 2H), 8.01 (dd, *J* = 7.9, 1.5 Hz, 1H), 9.30 (brs, 1H), 9.73 (brs, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ 55.13, 116.53, 118.13, 118.18, 118.78, 120.84, 125.52, 127.94, 129.01, 133.40, 145.43, 158.97, 166.31.

^{11}B NMR (160 MHz, DMSO-d6) δ 29.17.

HRMS Calcd for $C_{14}H_{14}BN_2O_2$: $[M+H]^+$, 253.1143 Found: *m*/*z* 253.1143

2-(2-methoxyphenyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (1f)



Isolated in 78% yield as a white solid: mp 220.2–224.0 °C

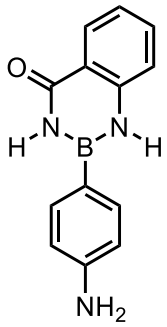
^{1}H NMR (500 MHz, DMSO-d6) δ 3.87 (s, 3H), 7.00 – 7.09 (m, 2H), 7.08 – 7.14 (m, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.45 – 7.49 (m, 1H), 7.53 – 7.60 (m, 1H), 7.81 (dd, *J* = 7.3, 1.8 Hz, 1H), 8.00 (dd, *J* = 7.9, 1.6 Hz, 1H), 9.06 (brs, 1H), 9.07 (brs, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ 55.13, 116.53, 118.13, 118.18, 118.78, 120.84, 125.52, 127.94, 129.01, 133.40, 145.43, 158.97, 166.31.

^{11}B NMR (160 MHz, DMSO-d6) δ 30.09.

HRMS Calcd for $C_{14}H_{14}BN_2O_2$: $[M+H]^+$, 253.1143 Found: *m*/*z* 253.1143

2-(4-aminophenyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (1g)



Isolated in 77% yield as a pale red solid: mp 202.1–205.4 °C

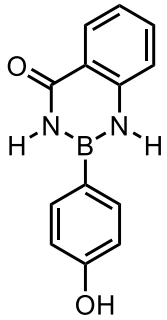
^{1}H NMR (500 MHz, DMSO-d6) δ 5.44 (brs, 2H), 6.58 (d, *J* = 8.4 Hz, 2H), 7.03 (ddd, *J* = 8.0, 7.1, 1.1 Hz, 1H), 7.36 (d, *J* = 7.7 Hz, 1H), 7.51 (ddd, *J* = 8.5, 7.1, 1.7 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.96 (dd, *J* = 7.9, 1.6 Hz, 1H), 8.95 (brs, 1H), 9.33 (brs, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ 113.04, 117.84, 118.37, 120.12, 127.89, 133.21, 134.68, 145.88, 151.16, 166.32.

^{11}B NMR (160 MHz, DMSO-d6) δ 29.86.

HRMS Calcd for $C_{13}H_{12}BN_3ONa$: $[M+Na]^+$, 260.0966 Found: *m*/*z* 260.0966

2-(4-hydroxyphenyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (1h)



Isolated in 59% yield as a pale yellow solid: mp 232.8–236.6 °C

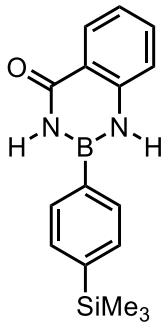
^{1}H NMR (500 MHz, DMSO-d6) δ 6.81 (dt, *J* = 8.8, 2.3 Hz, 2H), 7.06 (ddd, *J* = 8.1, 7.1, 1.2 Hz, 1H), 7.34 – 7.44 (m, 1H), 7.48 – 7.58 (m, 1H), 7.84 – 7.94 (m, 2H), 7.98 (dd, *J* = 7.9, 1.8 Hz, 1H), 9.11 (brs, 1H), 9.51 (brs, 1H), 9.74 (brs, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ 114.88, 117.97, 118.51, 120.45, 127.91, 133.30, 135.16, 145.69, 159.75, 166.32.

^{11}B NMR (160 MHz, DMSO-d6) δ 31.30.

HRMS Calcd for $C_{13}H_{11}BN_2O_2Na$: $[M+Na]^+$, 261.0806 Found: *m*/*z* 261.0807

2-(4-(trimethylsilyl)phenyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (1i)



Isolated in 58% yield as a white solid: mp 240.3–243.8 °C

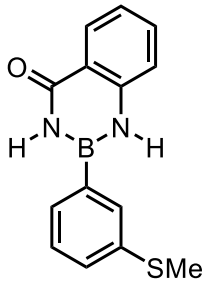
^{1}H NMR (500 MHz, DMSO-d6) δ 0.27 (s, 9H), 7.10 (ddd, *J* = 8.0, 7.1, 1.1 Hz, 1H), 7.43 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.54 – 7.60 (m, 3H), 8.01 (dd, *J* = 7.3, 0.9 Hz, 3H), 9.32 (brs, 1H), 9.69 (brs, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ -1.18, 118.16, 118.80, 120.85, 127.94, 132.46, 132.55, 133.40, 142.51, 145.45, 166.30.

^{11}B NMR (160 MHz, DMSO-d6) δ 30.35.

HRMS Calcd for $C_{16}H_{20}BN_2OSiNa$: $[M+Na]^+$, 317.1252 Found: *m*/*z* 317.1151

2-(3-(methylthio)phenyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (1j)



Isolated in 48% yield as a white solid: mp 187.5–191.9 °C

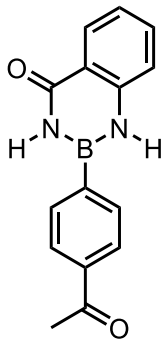
^{1}H NMR (500 MHz, DMSO-d6) δ 2.55 (s, 3H), 7.11 (dd, *J* = 8.0, 7.0 Hz, 1H), 7.35 – 7.41 (m, 2H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.57 (ddd, *J* = 8.3, 7.2, 1.6 Hz, 1H), 7.81 (dd, *J* = 5.3, 1.4 Hz, 1H), 7.92 (s, 1H), 8.01 (dd, *J* = 7.9, 1.5 Hz, 1H), 9.33 (brs, 1H), 9.77 (brs, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ 14.74, 118.13, 118.81, 120.89, 127.92, 128.05, 128.36, 129.75, 130.67, 133.40, 137.83, 145.39, 166.27.

^{11}B NMR (160 MHz, DMSO-d6) δ 29.87.

HRMS Calcd for $C_{14}H_{13}BN_2OSNa$: $[M+Na]^+$, 291.0734 Found: *m*/*z* 291.0735

2-(4-acetylphenyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (1k)



Isolated in 45% yield as a white solid: mp 265.7–269.1 °C

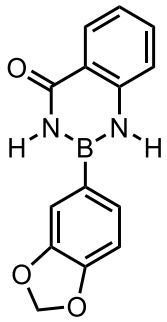
^{1}H NMR (500 MHz, DMSO-d6) δ 2.63 (s, 3H), 7.08 – 7.19 (m, 1H), 7.44 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.59 (ddd, *J* = 8.5, 7.2, 1.6 Hz, 1H), 7.96 – 8.08 (m, 3H), 8.19 (d, *J* = 8.2 Hz, 2H), 9.47 (brs, 1H), 9.84 (brs, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ 26.90, 118.24, 118.91, 121.11, 127.25, 127.95, 133.48, 133.58, 138.07, 145.28, 166.22, 198.22.

^{11}B NMR (160 MHz, DMSO-d6) δ 30.77.

HRMS Calcd for $C_{15}H_{13}BN_2O_2Na$: $[M+Na]^+$, 287.0962 Found: *m*/*z* 287.0964

2-(benzo[d][1,3]dioxol-5-yl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (1l)



Isolated in 84% yield as a white solid: mp 273.3–276.6 °C

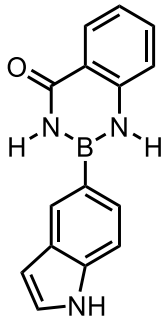
^{1}H NMR (500 MHz, DMSO-d6) δ 6.05 (s, 2H), 7.01 (d, *J* = 7.8 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 1H), 7.62 (d, *J* = 11.5 Hz, 2H), 7.99 (d, *J* = 7.9 Hz, 1H), 9.18 (brs, 1H), 9.61 (brs, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ 100.79, 108.34, 112.59, 118.01, 118.58, 120.66, 127.91, 128.18, 133.37, 145.48, 147.24, 149.30, 166.27.

^{11}B NMR (160 MHz, DMSO-d6) δ 30.77.

HRMS Calcd for $C_{14}H_{11}BN_2O_3Na$: $[M+Na]^+$, 289.0755 Found: *m*/*z* 289.0756

2-(1H-indol-5-yl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (1m)



Isolated in 73% yield as a white solid: mp 246.5–249.9 °C

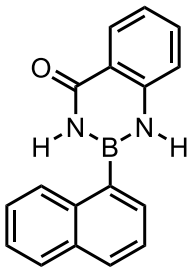
^{1}H NMR (500 MHz, DMSO-d6) δ 6.43 – 6.52 (m, 1H), 7.07 (dd, *J* = 8.0, 6.9 Hz, 1H), 7.37 (t, *J* = 2.6 Hz, 1H), 7.44 (dd, *J* = 7.1, 1.2 Hz, 1H), 7.55 (ddd, *J* = 8.5, 7.0, 1.5 Hz, 1H), 7.77 (dt, *J* = 8.2, 1.1 Hz, 1H), 8.00 (dd, *J* = 7.9, 1.8 Hz, 1H), 8.33 (s, 1H), 9.21 (brs, 1H), 9.55 (brs, 1H), 11.19 (brs, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ 101.51, 110.91, 118.02, 118.53, 120.36, 125.58, 125.90, 126.39, 127.54, 127.92, 133.27, 137.48, 145.84, 166.37.

^{11}B NMR (160 MHz, DMSO-d6) δ 30.53.

HRMS Calcd for $C_{15}H_{13}BN_3O$: $[M+H]^+$, 262.1146 Found: *m*/*z* 262.1147

2-(naphthalen-1-yl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (1n)[2]



Isolated in 86% yield as a white solid: mp 161.3–164.9 °C

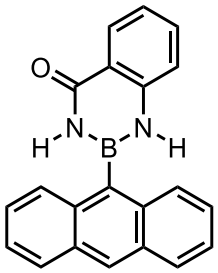
^{1}H NMR (500 MHz, DMSO-d6) δ 7.14 (ddd, *J* = 8.1, 7.1, 1.2 Hz, 1H), 7.34 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.49 – 7.62 (m, 4H), 7.71 (dd, *J* = 6.8, 1.4 Hz, 1H), 7.94 – 8.04 (m, 3H), 8.06 (dd, *J* = 8.0, 1.7 Hz, 1H), 9.43 (brs, 1H), 9.66 (brs, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ 118.17, 118.97, 120.99, 125.25, 125.71, 126.05, 127.98, 128.38, 129.08, 131.69, 132.73, 133.34, 135.05, 145.44, 166.03.

^{11}B NMR (160 MHz, DMSO-d6) δ 32.03.

HRMS Calcd for $C_{17}H_{14}BN_2O$: $[M+H]^+$, 273.1194 Found: *m*/*z* 273.1195

2-(anthracen-9-yl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (1o)



Isolated in 56% yield as a white solid: mp 267.9–271.2 °C

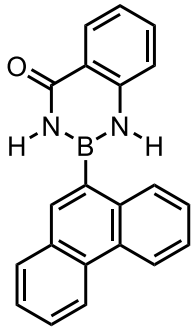
^{1}H NMR (500 MHz, DMSO-d6) δ 7.19 (t, *J* = 7.6 Hz, 1H), 7.29 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.45 – 7.56 (m, 4H), 7.60 (ddd, *J* = 8.5, 7.2, 1.7 Hz, 1H), 7.93 (dd, *J* = 8.6, 1.3 Hz, 2H), 8.13 (d, *J* = 7.8 Hz, 2H), 8.66 (s, 1H), 9.60 (brs, 1H), 9.84 (brs, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ 118.05, 119.17, 121.11, 125.25, 125.45, 127.20, 128.10, 128.56, 128.85, 130.72, 133.37, 133.84, 145.51, 165.91.

^{11}B NMR (160 MHz, DMSO-d6) δ 33.80.

HRMS Calcd for $C_{21}H_{15}BN_2ONa$: $[M+Na]^+$, 345.1170 Found: *m*/*z* 345.1171

2-(phenanthren-9-yl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (1p)



Isolated in 83% yield as a white solid: mp 190.5–193.8 °C

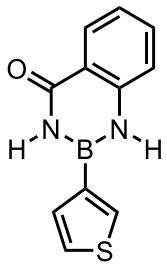
^{1}H NMR (500 MHz, DMSO-d6) δ 7.16 (td, *J* = 7.5, 6.9, 1.0 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.59 (td, *J* = 7.8, 7.1, 1.6 Hz, 1H), 7.63 – 7.79 (m, 5H), 7.97 – 8.15 (m, 5H), 8.89 (dd, *J* = 17.2, 8.1 Hz, 2H), 9.52 (brs, 1H), 9.73 (brs, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ 118.17, 119.02, 121.01, 122.78, 123.21, 126.52, 126.77, 126.90, 127.33, 128.00, 128.73, 129.18, 129.35, 130.18, 130.77, 133.08, 133.35, 145.44, 166.01.

^{11}B NMR (160 MHz, DMSO-d6) δ 33.16.

HRMS Calcd for $C_{21}H_{15}BN_2ONa$: $[M+Na]^+$, 345.1170 Found: *m*/*z* 345.1171

2-(thiophen-3-yl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (1q)[2]



Isolated in 44% yield as a white solid: mp 210.1–213.1 °C

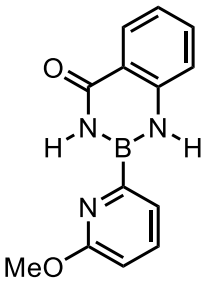
^{1}H NMR (500 MHz, DMSO-d6) δ 7.09 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 7.35 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.56 (ddd, *J* = 8.4, 7.1, 1.6 Hz, 1H), 7.65 (dd, *J* = 4.9, 2.7 Hz, 1H), 7.80 (dd, *J* = 4.8, 1.2 Hz, 1H), 8.00 (dd, *J* = 7.9, 1.5 Hz, 1H), 8.41 (dd, *J* = 2.6, 1.1 Hz, 1H), 9.28 (brs, 1H), 9.73 (brs, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ 117.93, 118.73, 120.71, 126.11, 127.98, 131.70, 133.43, 134.83, 145.50, 166.25.

^{11}B NMR (160 MHz, DMSO-d6) δ 28.02.

HRMS Calcd for $C_{11}H_{10}BN_2OS$: $[M+H]^+$, 229.0601 Found: *m*/*z* 229.0601

2-(6-methoxypyridin-2-yl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (1r)



Isolated in 64% yield as a white solid: mp 209.1–212.4 °C

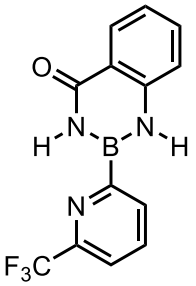
^{1}H NMR (500 MHz, DMSO-d6) δ 4.02 (s, 3H), 6.89 (d, *J* = 8.0 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.51 (d, *J* = 8.2 Hz, 1H), 7.60 (t, *J* = 7.7 Hz, 1H), 7.72 – 7.85 (m, 2H), 8.04 (d, *J* = 7.9 Hz, 1H), 9.27 (brs, 1H), 9.34 (brs, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ 53.14, 112.51, 118.48, 119.09, 121.17, 122.75, 128.04, 133.50, 138.21, 145.12, 163.23, 165.89.

^{11}B NMR (160 MHz, DMSO-d6) δ 29.03.

HRMS Calcd for $C_{13}H_{13}BN_3O_2$: $[M+H]^+$, 254.1095 Found: *m*/*z* 254.1096

2-(6-(trifluoromethyl)pyridin-2-yl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (1s)



Isolated in 63% yield as a white solid: mp 283.7–286.7 °C

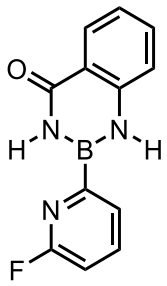
^{1}H NMR (400 MHz, DMSO-d6) δ 7.16 (ddd, *J* = 8.1, 6.4, 1.8 Hz, 1H), 7.53 – 7.66 (m, 2H), 7.97 (dd, *J* = 8.0, 1.0 Hz, 1H), 8.05 (dd, *J* = 7.6, 1.2 Hz, 1H), 8.17 (t, *J* = 7.8 Hz, 1H), 8.44 (d, *J* = 7.6 Hz, 1H), 9.42 (brs, 1H), 9.53 (brs, 1H).

^{13}C NMR (101 MHz, DMSO-d6) δ 118.70, 119.19, 121.46, 121.81 (q, *J* = 274.4 Hz), 127.98, 131.86, 133.59, 137.40, 145.00, 146.92 (q, *J* = 33.6 Hz), 165.85.

^{11}B NMR (160 MHz, DMSO-d6) δ 29.17.

HRMS Calcd for $C_{13}H_9BF_3N_3ONa$: $[M+Na]^+$, 314.0683 Found: *m*/*z* 314.0684

2-(6-fluoropyridin-2-yl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (1t)



Isolated in 51% yield as a white solid: mp 245.8–249.1 °C

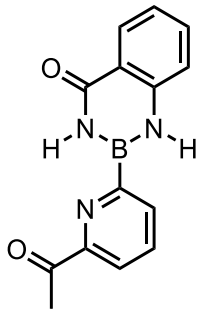
^{1}H NMR (500 MHz, DMSO-d6) δ 7.13 (ddd, *J* = 8.1, 5.9, 2.2 Hz, 1H), 7.26 (dd, *J* = 8.2, 2.4 Hz, 1H), 7.54 – 7.62 (m, 2H), 7.99 – 8.11 (m, 2H), 8.16 (dd, *J* = 7.2, 3.2 Hz, 1H), 9.43 (brs, 1H), 9.69 (brs, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ 111.24 (d, *J* = 38.1 Hz), 118.70, 119.12, 121.28, 127.25, 127.91, 133.49, 141.47 (d, *J* = 7.6 Hz), 145.09, 163.07 (d, *J* = 236.0 Hz), 166.02.

^{11}B NMR (160 MHz, DMSO-d6) δ 28.47.

HRMS Calcd for $C_{12}H_9BFN_3ONa$: $[M+Na]^+$, 264.0715 Found: *m*/*z* 264.0716

2-(6-acetylpyridin-2-yl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (1u)



Isolated in 59% yield as a white solid: mp 262.5–265.9 °C

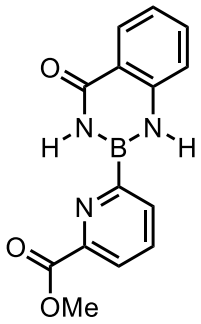
^{1}H NMR (400 MHz, DMSO-d6) δ 2.85 (s, 3H), 7.16 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H), 7.54 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.62 (ddd, *J* = 8.5, 7.0, 1.6 Hz, 1H), 7.99 (dd, *J* = 7.9, 1.2 Hz, 1H), 8.03 – 8.13 (m, 2H), 8.40 (dd, *J* = 7.5, 1.3 Hz, 1H), 9.45 (brs, 1H), 9.61 (brs, 1H).

^{13}C NMR (101 MHz, DMSO-d6) δ 25.99, 118.54, 119.22, 121.34, 121.86, 128.05, 132.07, 133.55, 136.42, 145.03, 153.34, 165.93, 200.30.

^{11}B NMR (160 MHz, DMSO-d6) δ 28.94.

HRMS Calcd for $C_{14}H_{12}BN_3O_2Na$: $[M+Na]^+$, 288.0915 Found: *m*/*z* 288.0916

methyl 6-(4-oxo-3,4-dihydrobenzo[d][1,3,2]diazaborinin-2(1H)-yl)picolinate (1v)



Isolated in 41% yield as a white solid: mp 245.8–249.1 °C

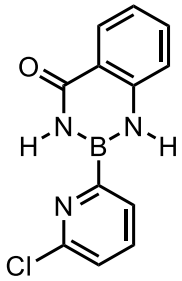
^{1}H NMR (400 MHz, DMSO-d6) δ 3.95 (d, *J* = 0.6 Hz, 3H), 7.16 (ddd, *J* = 8.0, 7.0, 1.2 Hz, 1H), 7.54 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.61 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H), 7.99 – 8.16 (m, 3H), 8.35 (ddd, *J* = 7.0, 1.8, 0.6 Hz, 1H), 9.33 (brs, 1H), 9.44 (brs, 1H).

^{13}C NMR (101 MHz, DMSO-d6) δ 52.54, 118.61, 119.13, 121.38, 125.55, 128.00, 131.76, 133.60, 136.52, 145.06, 148.03, 165.55, 165.73.

^{11}B NMR (160 MHz, DMSO-d6) δ 29.30.

HRMS Calcd for $C_{14}H_{13}BN_3O_3$: $[M+H]^+$, 282.1045 Found: *m*/*z* 282.1045

2-(6-chloropyridin-2-yl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (1w)



Isolated in 62% yield as a white solid: mp 215.7–219.2 °C

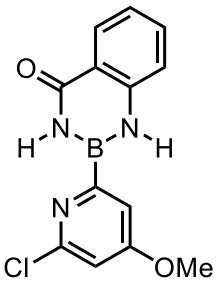
^{1}H NMR (500 MHz, DMSO-d6) δ 7.14 (ddd, *J* = 8.1, 5.1, 3.2 Hz, 1H), 7.56 – 7.63 (m, 3H), 7.94 (t, *J* = 7.7 Hz, 1H), 8.00 – 8.07 (m, 1H), 8.19 (dd, *J* = 7.3, 0.9 Hz, 1H), 9.40 (brs, 1H), 9.62 (brs, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ 118.71, 119.13, 121.33, 125.58, 127.92, 128.14, 133.52, 138.98, 145.06, 150.98, 165.96.

^{11}B NMR (160 MHz, DMSO-d6) δ 29.17.

HRMS Calcd for $C_{12}H_9BClN_3ONa$: $[M+Na]^+$, 280.0419 Found: *m*/*z* 280.0421

2-(6-chloro-4-methoxypyridin-2-yl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (1x)



Isolated in 40% yield as a white solid: mp 212.4–215.8 °C

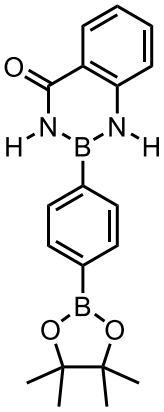
^{1}H NMR (500 MHz, DMSO-d6) δ 3.92 (s, 3H), 7.14 (ddd, *J* = 8.1, 6.3, 1.9 Hz, 1H), 7.17 (d, *J* = 2.2 Hz, 1H), 7.54 – 7.64 (m, 2H), 7.87 (d, *J* = 2.2 Hz, 1H), 8.02 (d, *J* = 8.5 Hz, 1H), 9.33 (brs, 1H), 9.65 (brs, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ 56.16, 110.38, 115.87, 118.73, 119.10, 121.31, 127.90, 133.51, 145.02, 151.95, 165.99, 166.87.

^{11}B NMR (160 MHz, DMSO-d6) δ 29.03.

HRMS Calcd for $C_{13}H_{11}BClN_3O_2Na$: $[M+Na]^+$, 310.0525 Found: *m*/*z* 310.0526

2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (1y)



Isolated in 90% yield as a white solid: mp 286.0–289.3 °C

^{1}H NMR (500 MHz, DMSO-d6) δ 1.30 (s, 12H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 7.3 Hz, 2H), 8.00 (d, *J* = 7.9 Hz, 1H), 8.04 (d, *J* = 7.4 Hz, 2H), 9.36 (brs, 1H), 9.68 (brs, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ 24.69, 83.74, 118.18, 118.84, 120.92, 127.91, 132.63, 133.38, 133.58, 145.38, 166.20.

^{11}B NMR (160 MHz, DMSO-d6) δ 31.49.

HRMS Calcd for $C_{19}H_{23}B_2N_2O_3$: $[M+H]^+$, 349.1889 Found: *m*/*z* 349.1891

X-ray Crystallographic Analyses: The diffraction data of the single crystal of (pin)B–B(aam) and (pin)B–B(dan) were collected on a Bruker APEX-II Ultra CCD-based diffractometer at 173 K. The structures were solved by the direct method and expanded using Fourier techniques. Non-hydrogen atomas were refined anisotropically, while hydrogen atoms were located at ideal positions and refined isotropically. All calculations were performed using SHELXL-97 crystallographic software package.[a]

a) Scheldrick, G. M. SHELX-97: Programs for Crystal Structure Analysis. University of Göttingen, Germany, 1997.

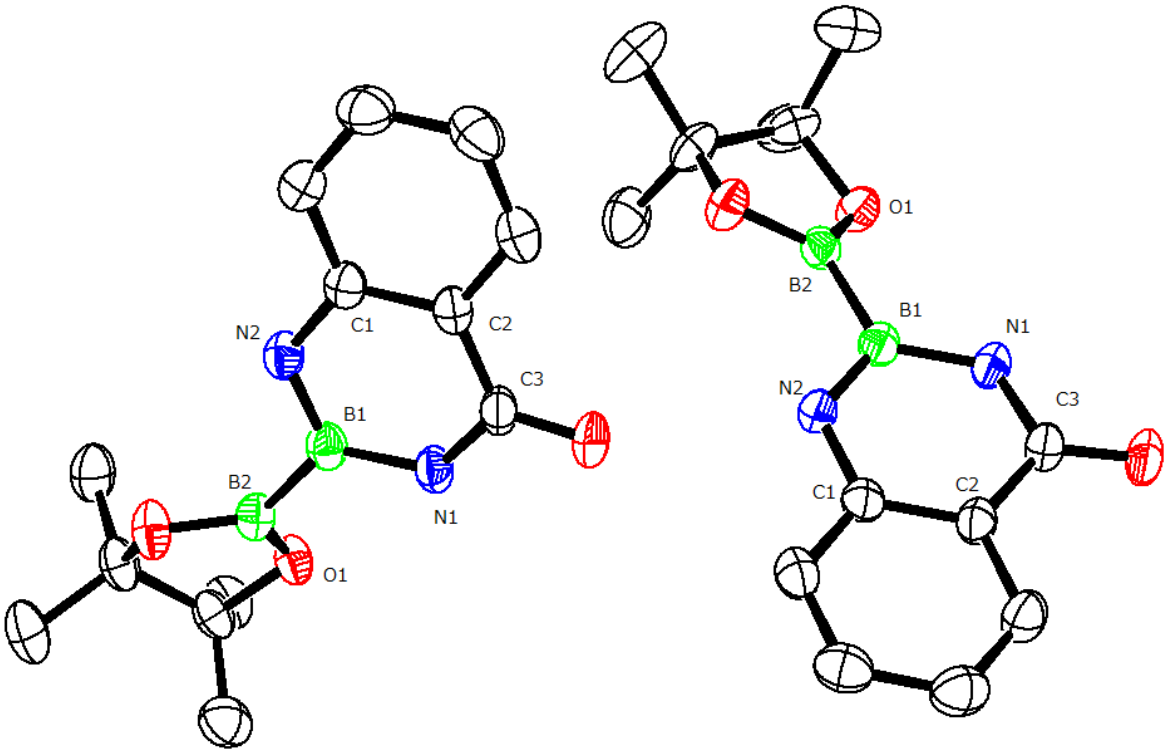
Table S3. Crystal Data and Structure Refinement for (pin)B–B(aam)

Identification code	(pin)B–B(aam)	
Empirical formula	C13 H18 B2 N2 O3	
Formula weight	271.91	
Temperature	173 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 2_1/c 1	
Unit cell dimensions	a = 13.5677(11) Å	α = 90°.
	b = 17.9941(15) Å	β = 99.3700(10)°.
	c = 12.3197(10) Å	γ = 90°.
Volume	2967.6(4) $Å^3$	
Z	8	
Density (calculated)	1.217 Mg/m^3	
Absorption coefficient	0.084 mm^{-1}	
F(000)	1152	
Crystal size	0.150 x 0.050 x 0.050 mm^3	
Theta range for data collection	1.52 to 23.25°.	
Index ranges	-15<=h<=15, -19<=k<=15, -12<=l<=13	
Reflections collected	12299	
Independent reflections	4253 [R(int) = 0.0291]	
Completeness to theta = 23.25°	100 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.09 and 0.10	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4253 / 0 / 369	
Goodness-of-fit on F^2	1.027	
Final R indices [I>2sigma(I)]	R1 = 0.0463, wR2 = 0.1171	
R indices (all data)	R1 = 0.0640, wR2 = 0.1280	
Largest diff. peak and hole	0.613 and -0.165 e.$Å^{-3}$	

Table S4. Crystal Data and Structure Refinement for (pin)B–B(dan)

Identification code	(pin)B–B(dan)	
Empirical formula	C16 H20 B2 N2 O2	
Formula weight	293.96	
Temperature	173 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 2_1/c 1	
Unit cell dimensions	a = 13.217(5) Å	α = 90°.
	b = 11.608(5) Å	β = 102.985(6)°.
	c = 10.778(4) Å	γ = 90°.
Volume	1611.3(11) $Å^3$	
Z	4	
Density (calculated)	1.212 Mg/m^3	
Absorption coefficient	0.078 mm^{-1}	
F(000)	624	
Crystal size	0.200 x 0.200 x 0.200 mm^3	
Theta range for data collection	1.58 to 27.18°.	
Index ranges	-8<=h<=16, -13<=k<=14, -13<=l<=12	
Reflections collected	8224	
Independent reflections	3529 [R(int) = 0.0248]	
Completeness to theta = 27.18°	98.4 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.02 and 0.02	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3529 / 0 / 279	
Goodness-of-fit on F^2	1.003	
Final R indices [I>2sigma(I)]	R1 = 0.0485, wR2 = 0.1200	
R indices (all data)	R1 = 0.0656, wR2 = 0.1331	
Largest diff. peak and hole	0.332 and -0.218 $e.Å^{-3}$	

Figure S1. Solid-state structure of (pin)B–B(aam) with 50% probability ellipsoids. All hydrogen atoms are omitted for clarity.



Selected Bond Distances and Bond Angles

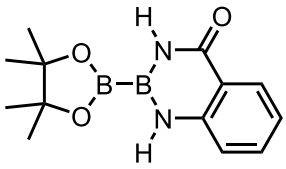
	left	right
Bond distance (Å)		
B1–B2	1.694 (4)	1.700 (4)
B1–N1	1.444 (3)	1.441 (4)
B1–N2	1.414 (3)	1.411 (3)
N1–C3	1.375 (3)	1.376 (3)
N2–C1	1.390 (3)	1.390 (3)
C1–C2	1.405 (3)	1.407 (3)
C2–C3	1.473 (4)	1.468 (3)
Bond angle (°)		
N1–B1–N2	116.3 (2)	116.4 (2)
B1–N1–C3	124.4 (2)	124.4 (2)
B1–N2–C1	122.0 (2)	122.1 (2)
N1–C3–C2	116.3 (2)	116.3 (2)
N2–C1–C2	120.2 (2)	120.1 (2)
C1–C2–C3	120.4 (2)	120.5 (2)
Torsion angle (°)		
N1–B1–B2–O1	-35.5 (4)	24.9 (4)

References

(1) S. Choppin, P. Gros and Y. Fort, *Org. Lett*., 2000, **2**, 803.

(2) H. Ihara, M. Koyanagi and M. Suginome, *Org. Lett*., 2011, **13**, 2662.

(3) M. Koyanagi, N. Eichenauer, H. Ihara, T. Yamamoto and M. Suginome, *Chem. Lett*., 2013, **42**, 541.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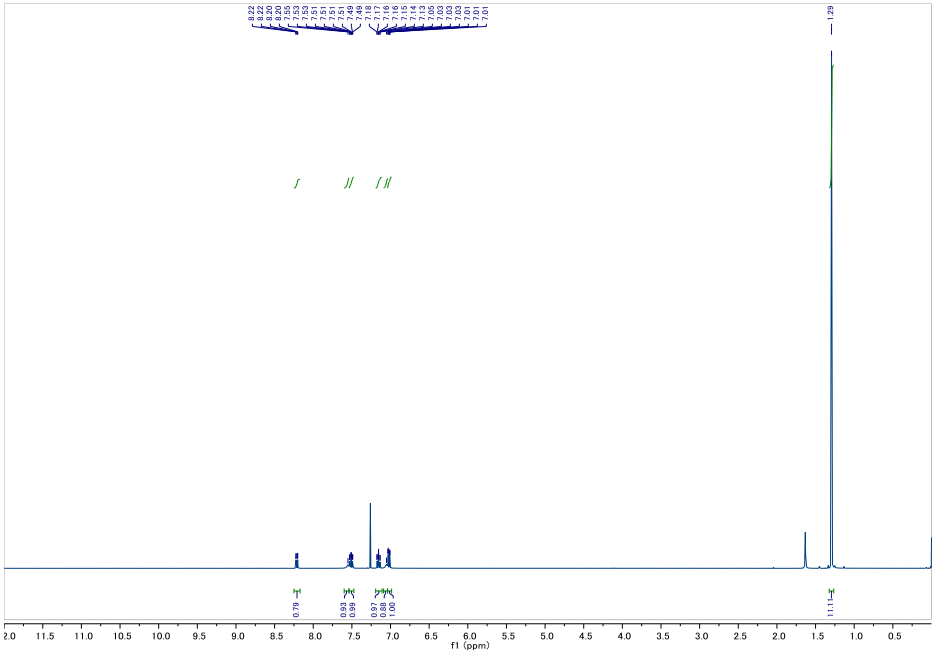
O
N
O
B
B
O
N
H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7.51
7.49
7.49
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7.17
7.16
7.16
7.15
7.14
7.13
7.05
7.03
7.03
7.01
7.01
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0.93
0.99
0.97
0.88
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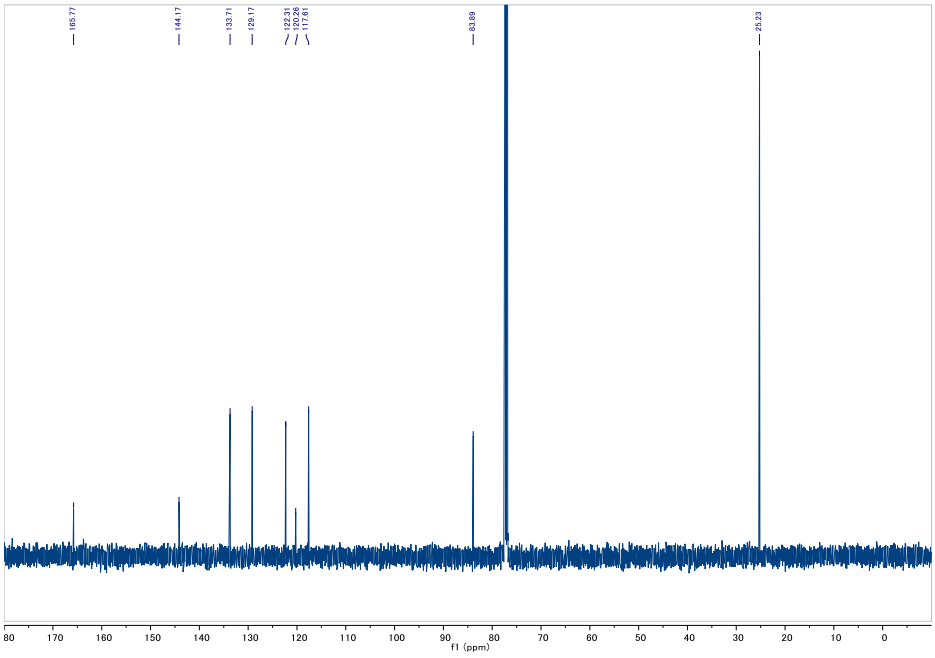
11.11
f1 (ppm)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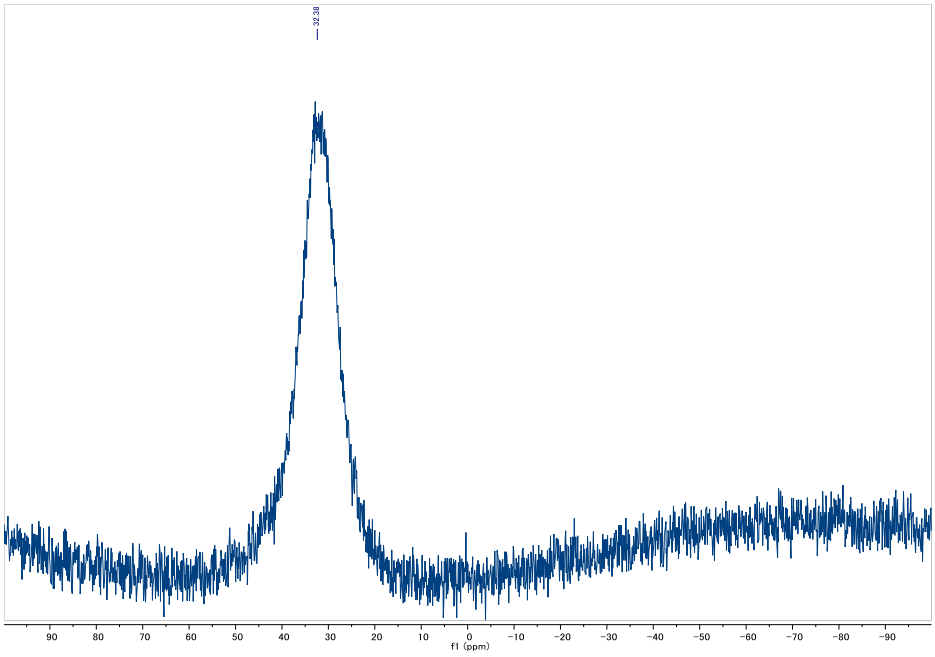
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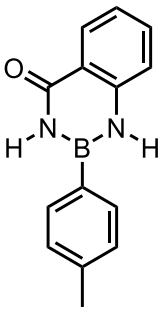
f1 (ppm)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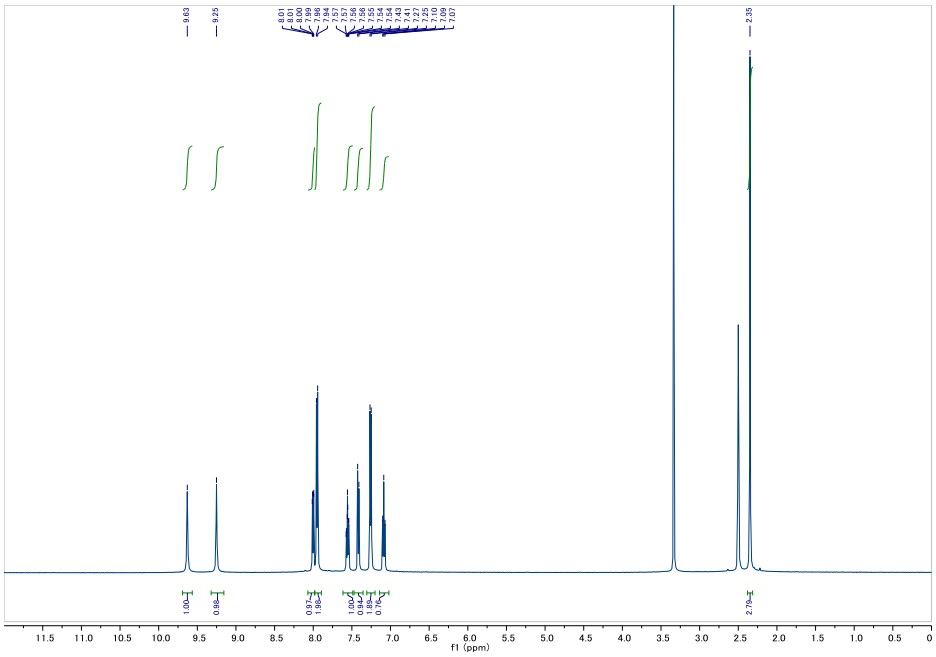
N
B
N
H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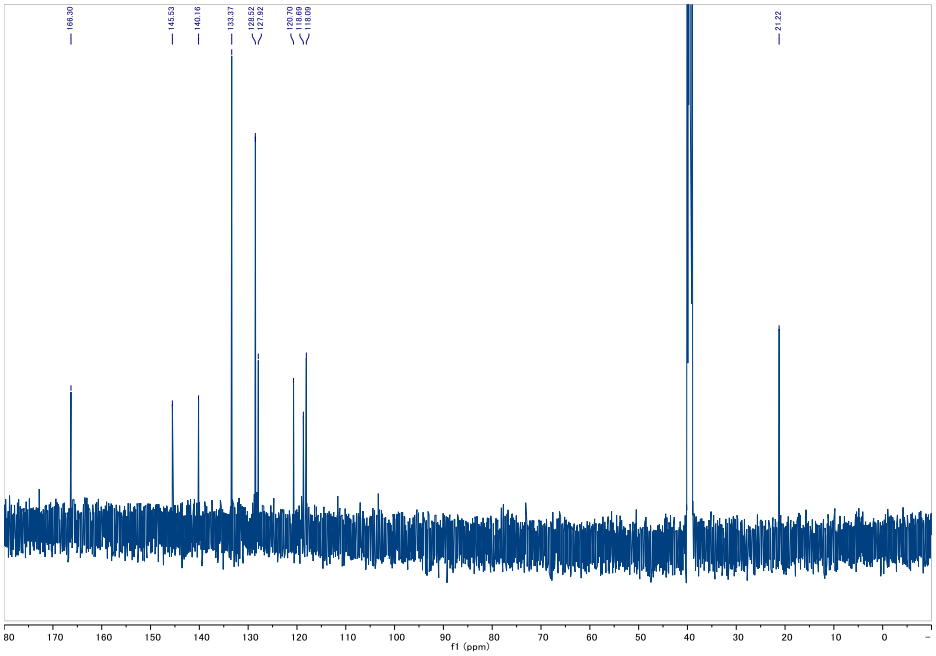
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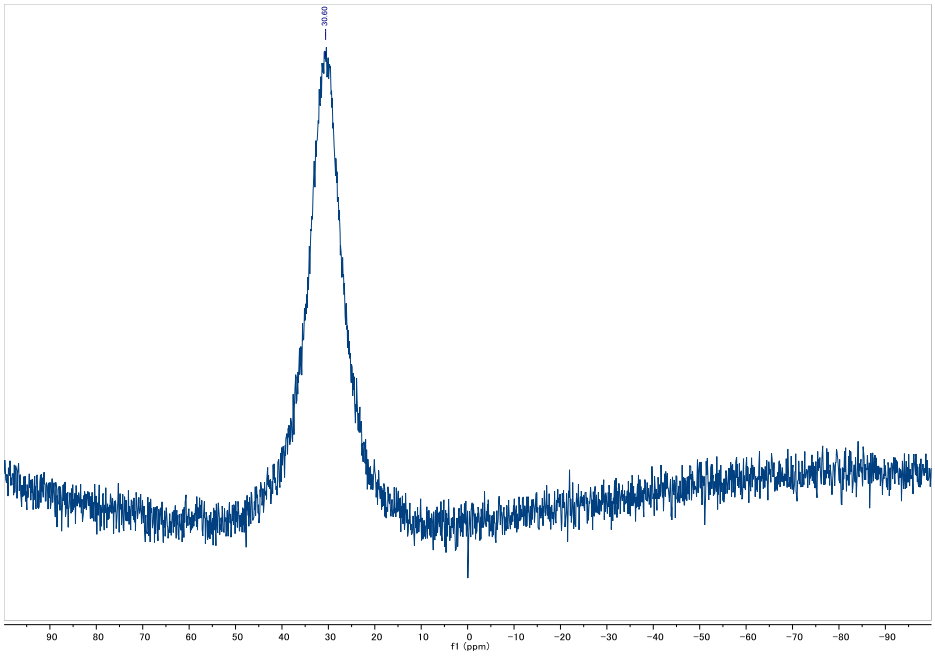
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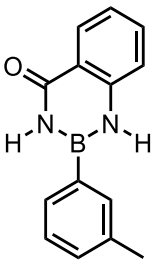
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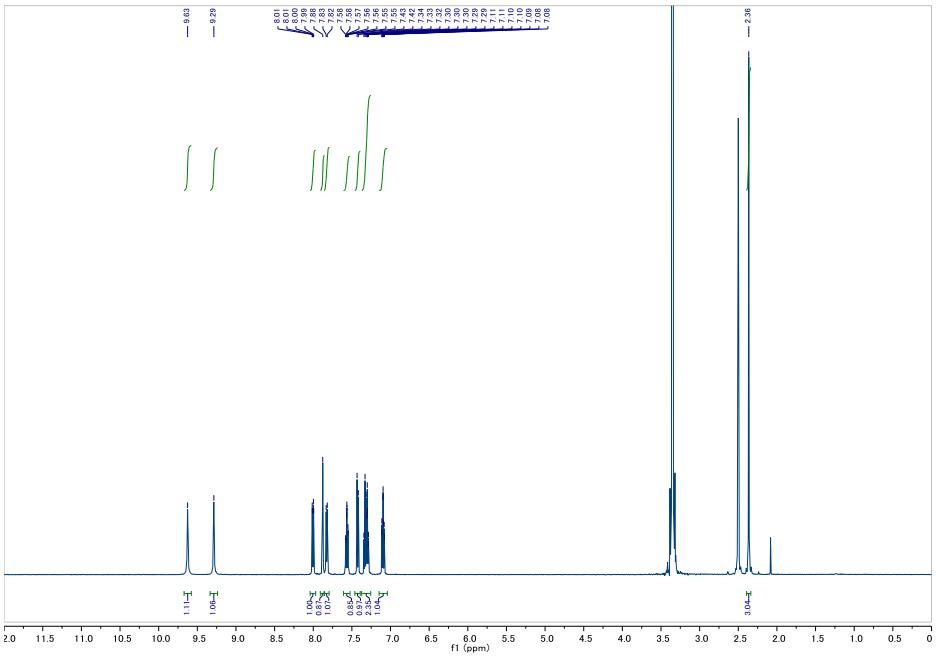
B
N
H
H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7.08
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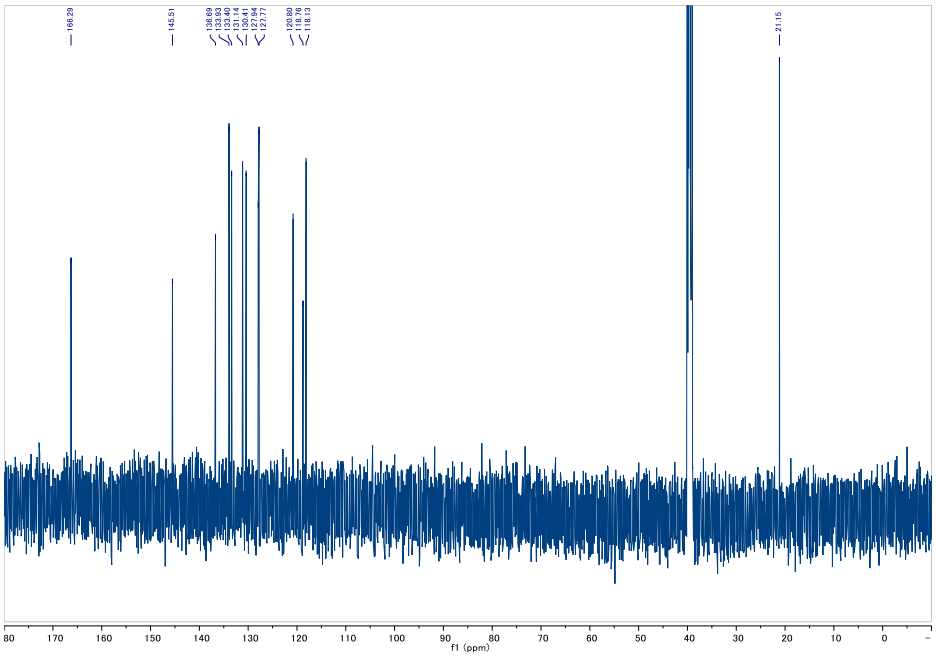
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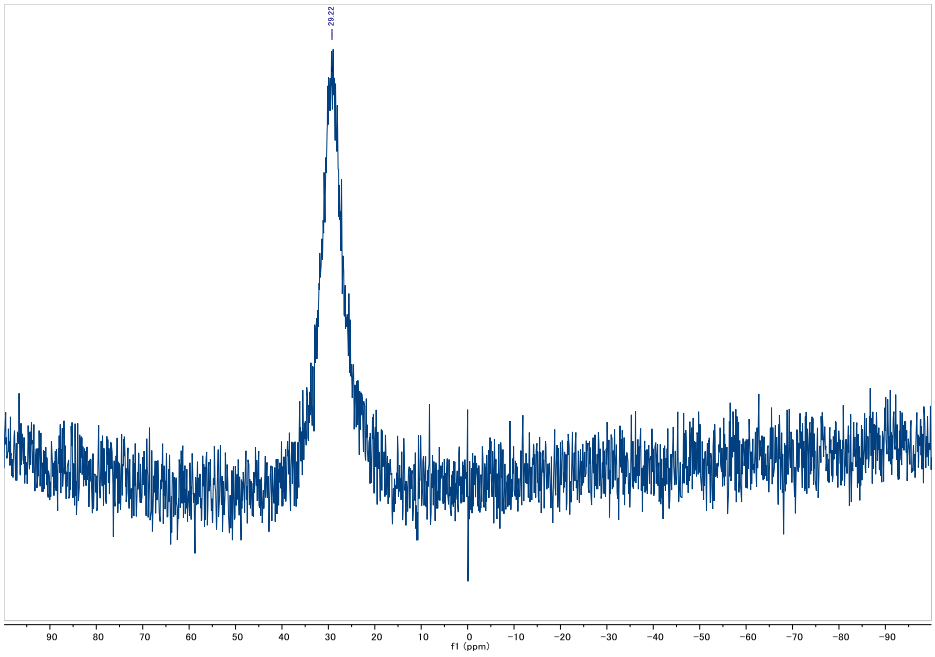
f1 (ppm)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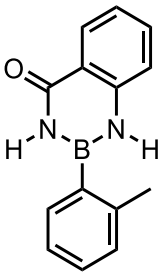
f1 (ppm)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H
B
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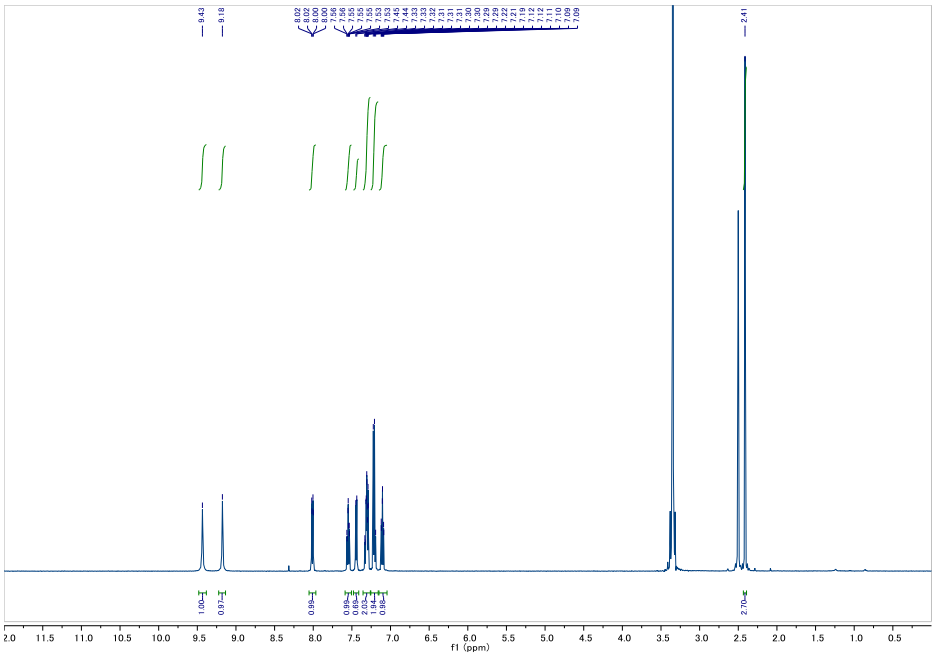
H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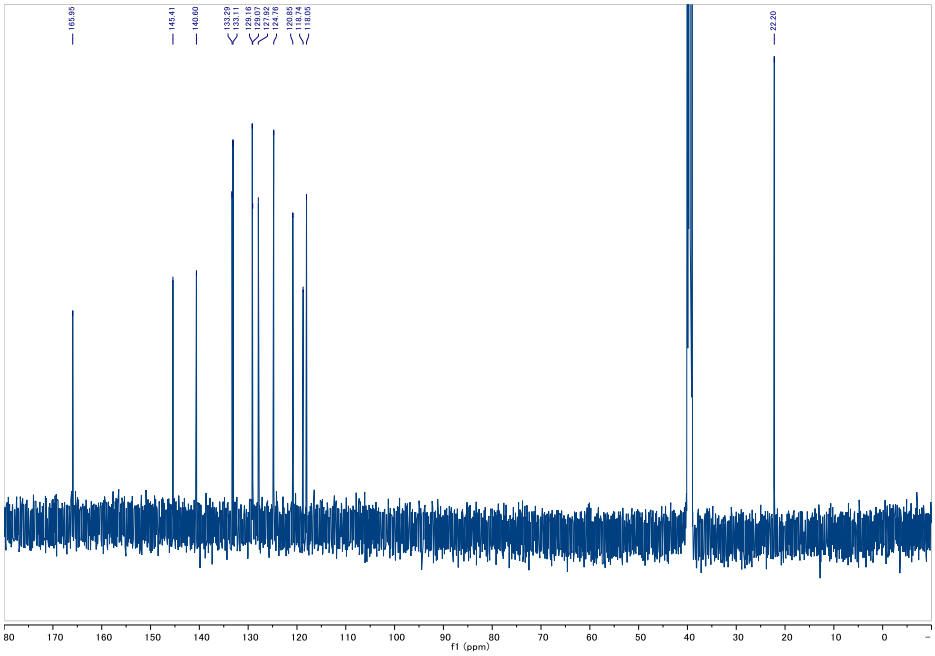
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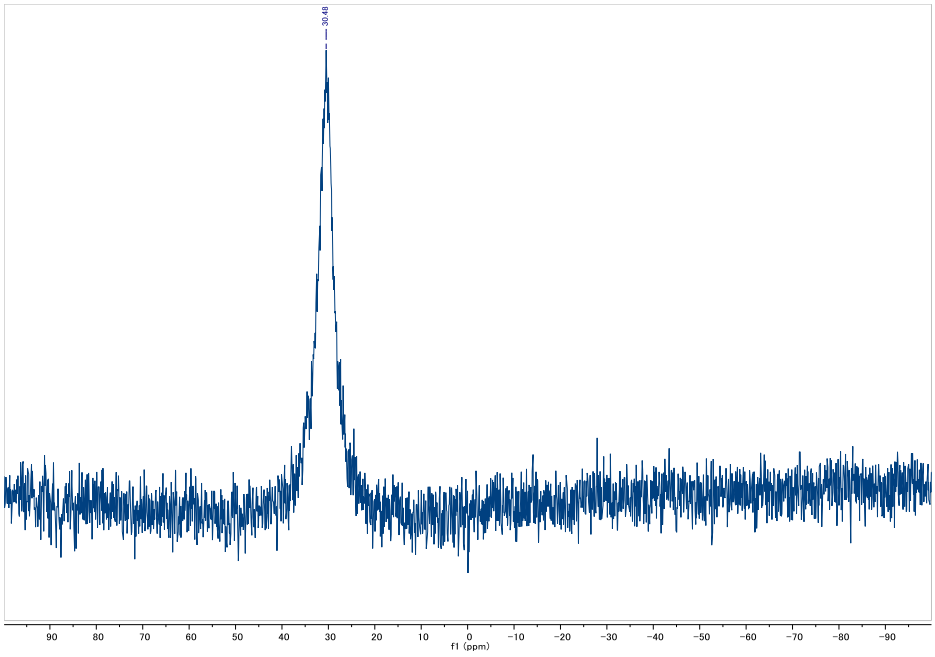
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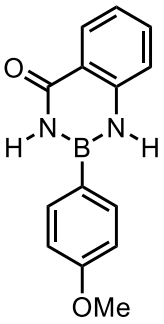
f1 (ppm)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N
B
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H
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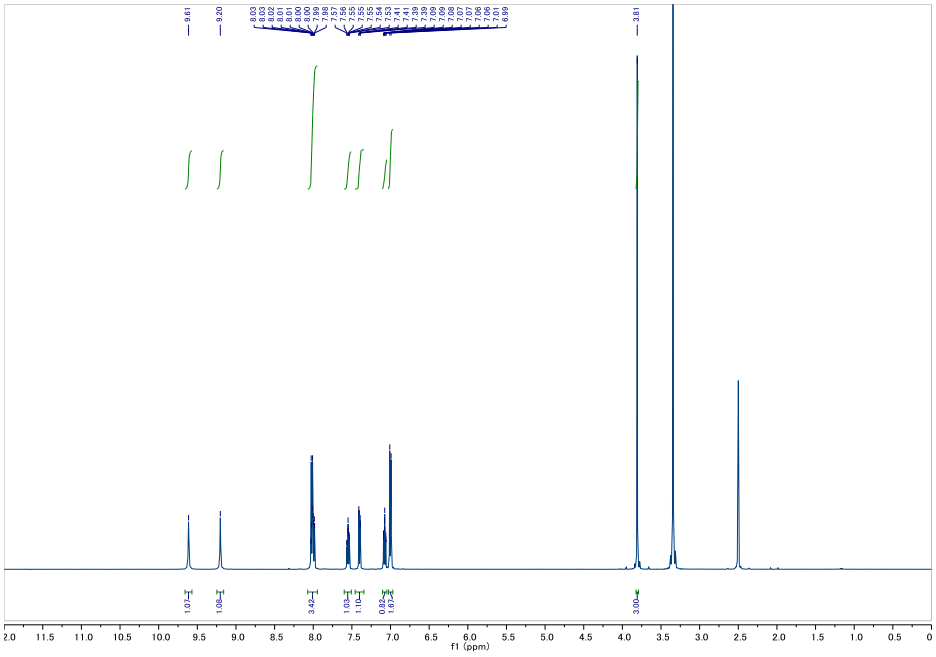
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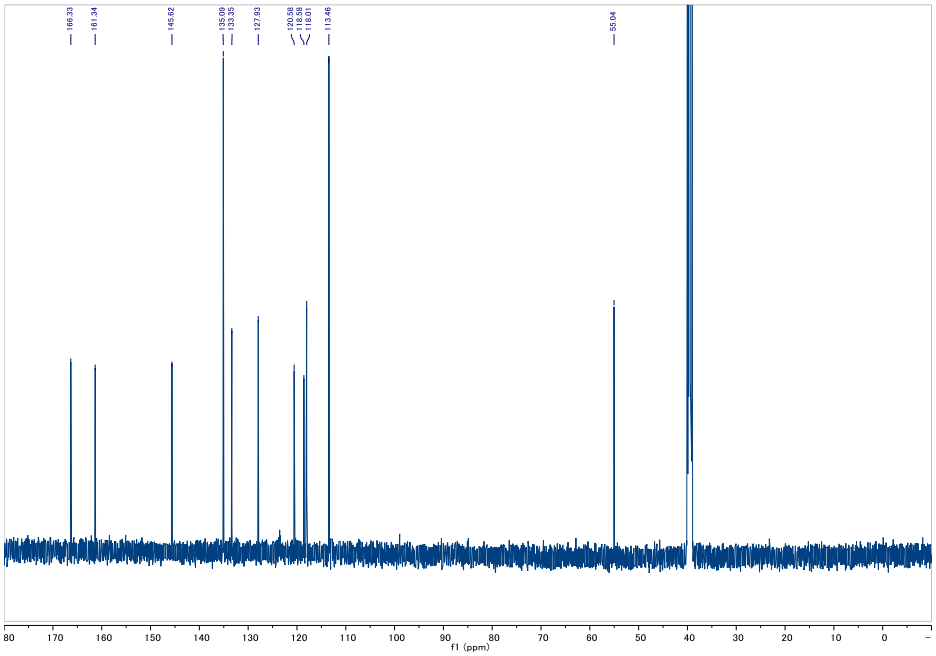
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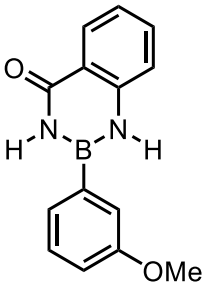
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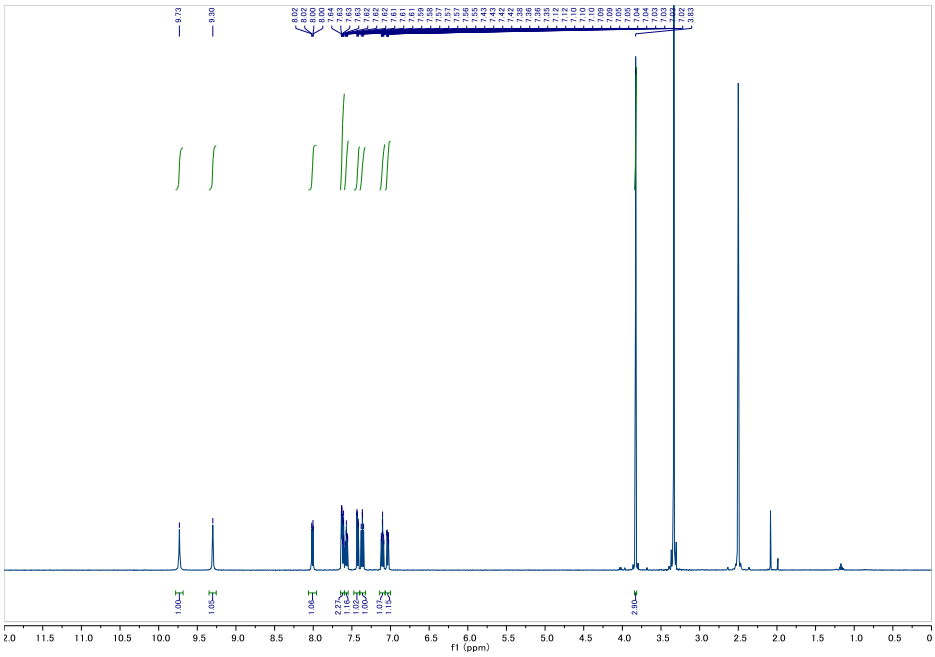
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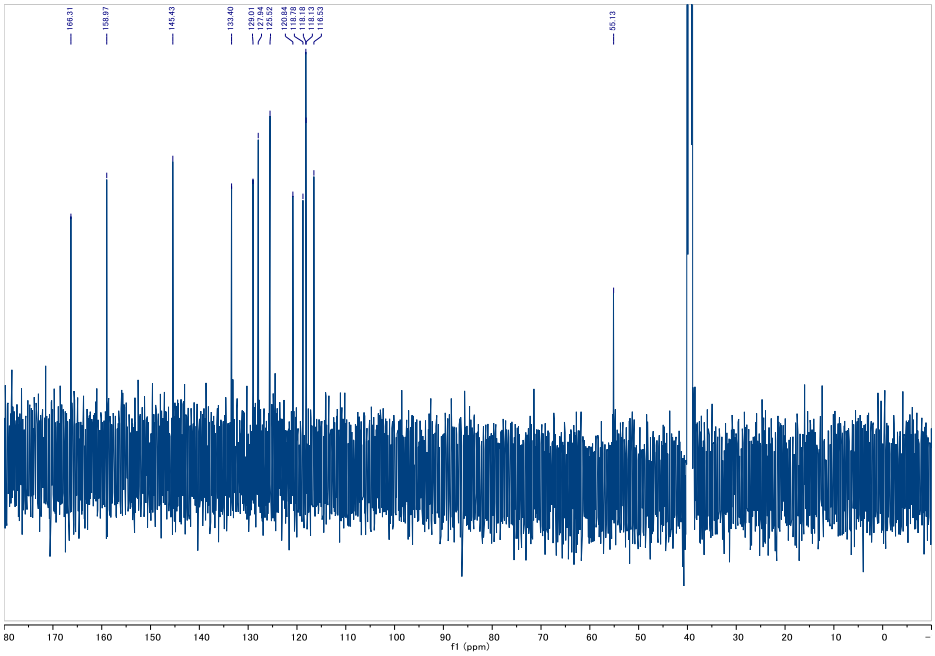
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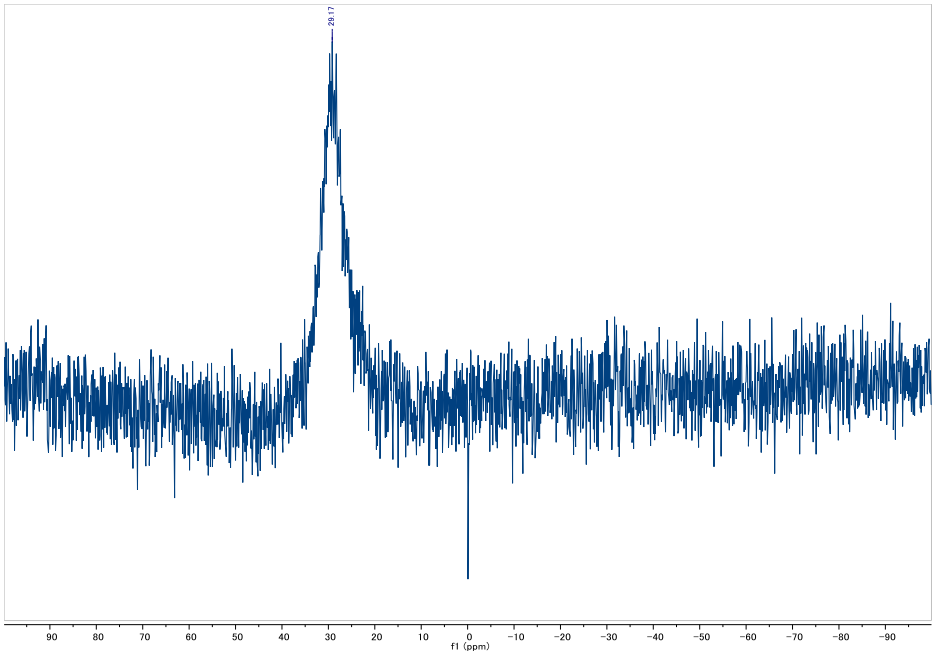
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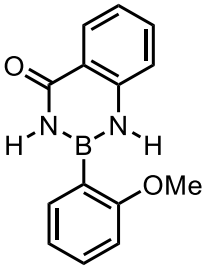
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B
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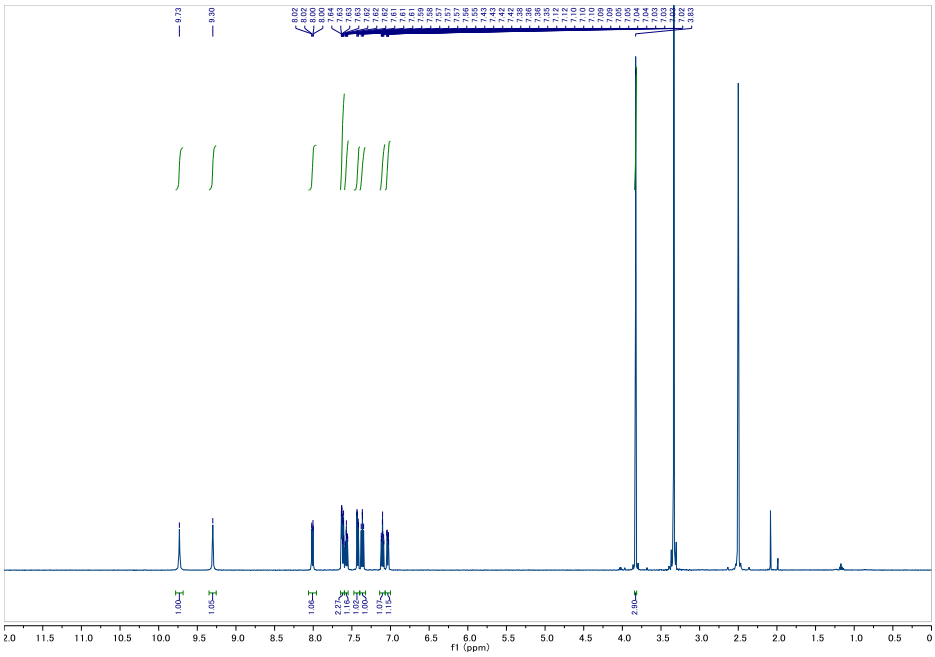
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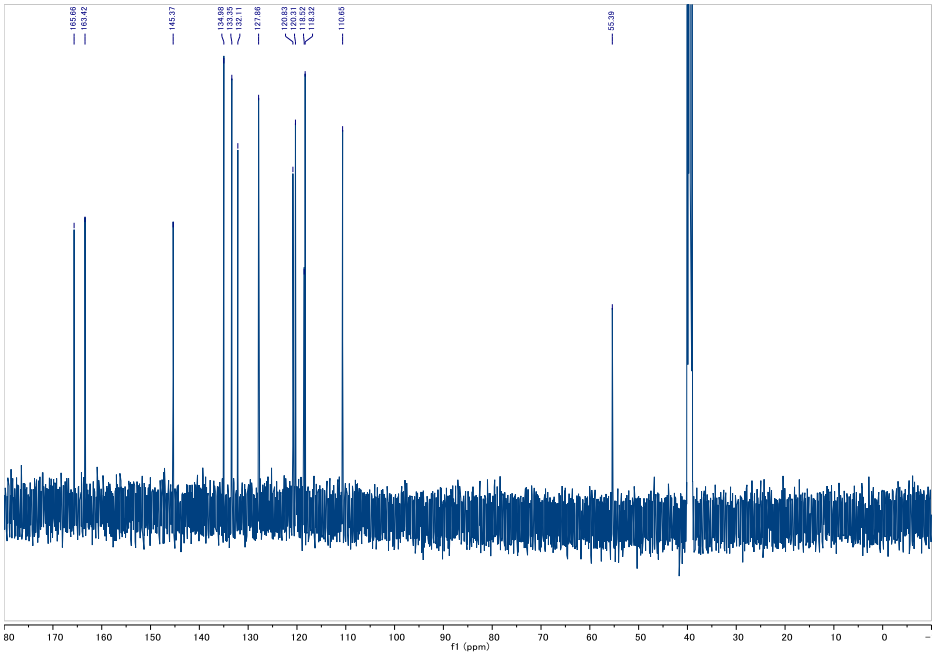
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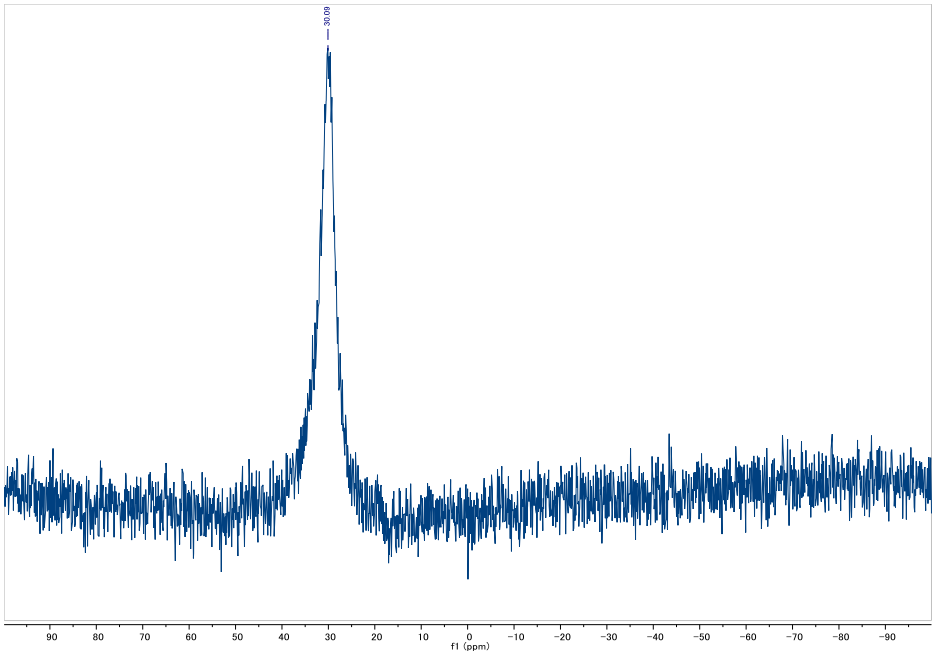
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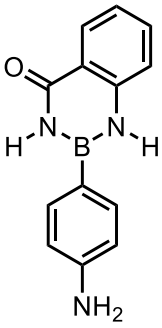
O
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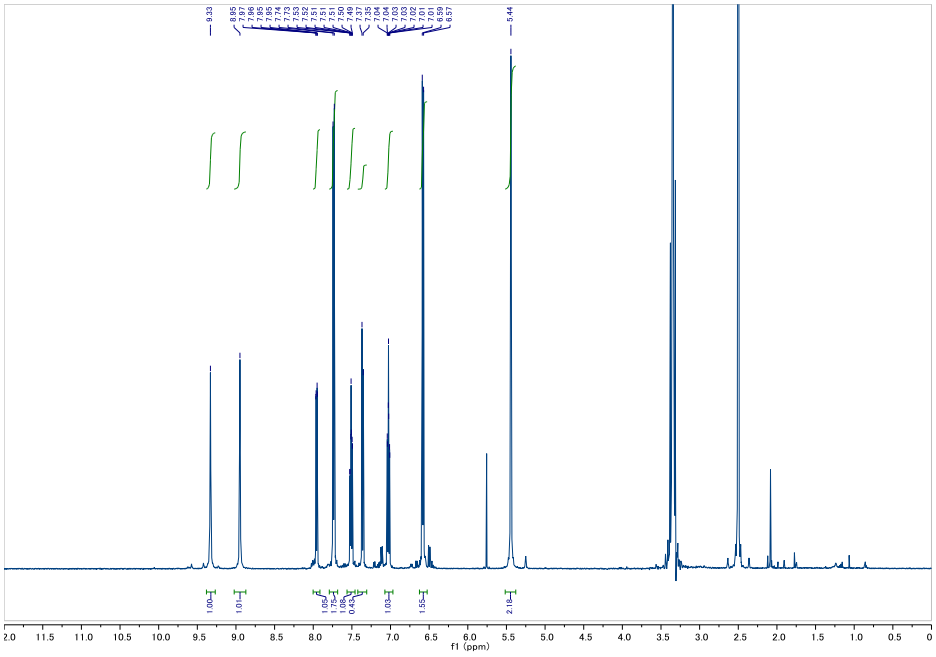
B
N
H
NH2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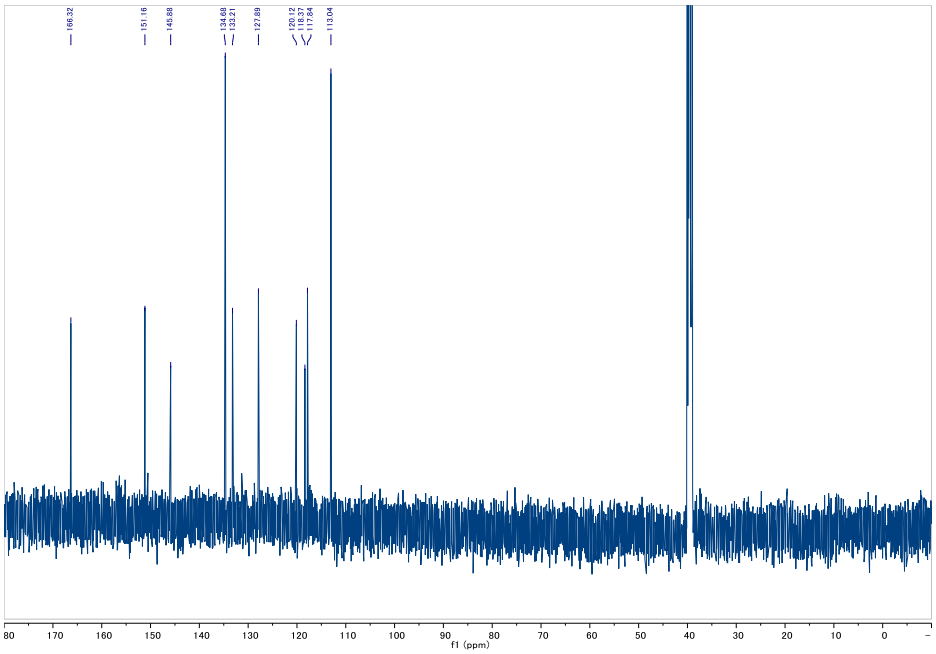
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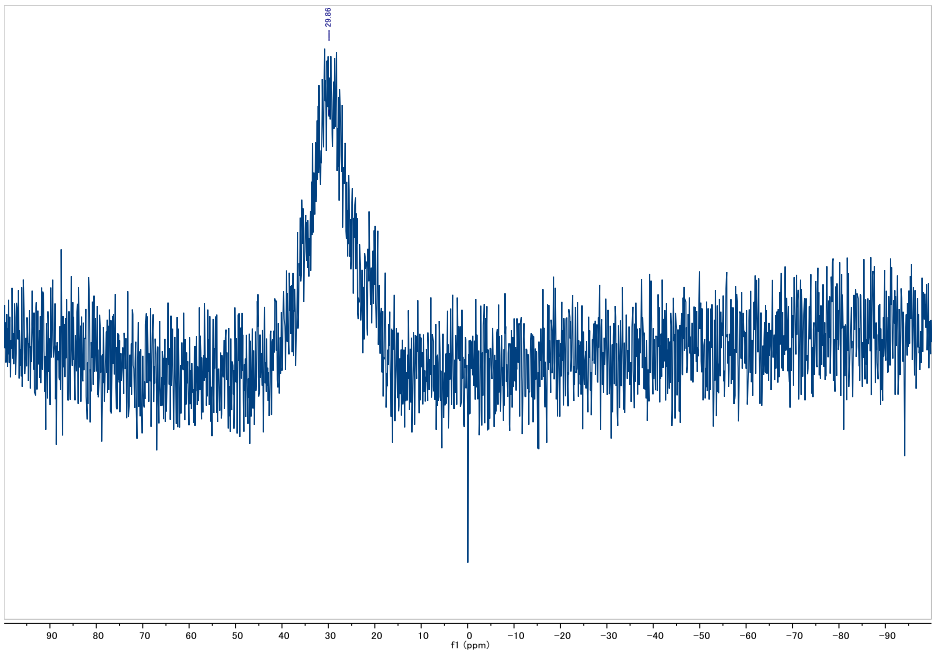
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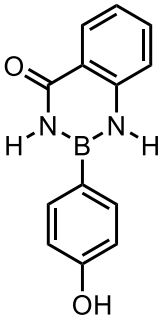
f1 (ppm)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B
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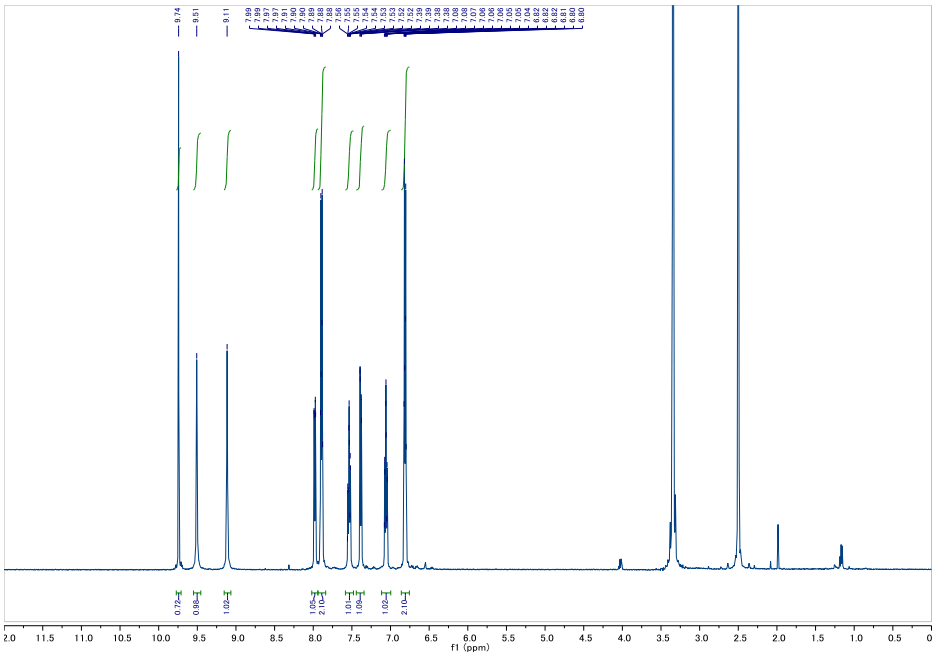
H
OH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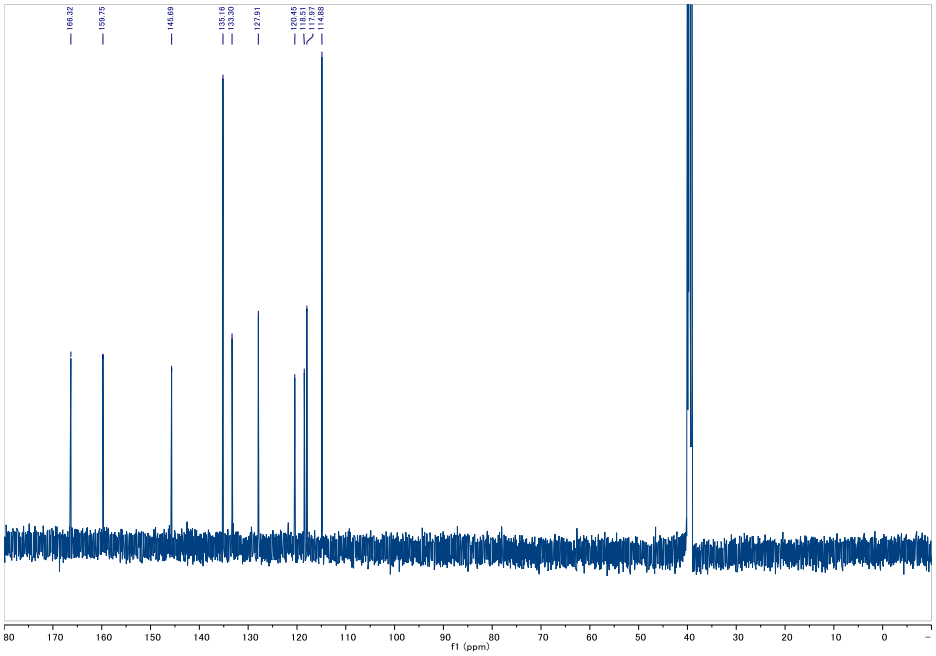
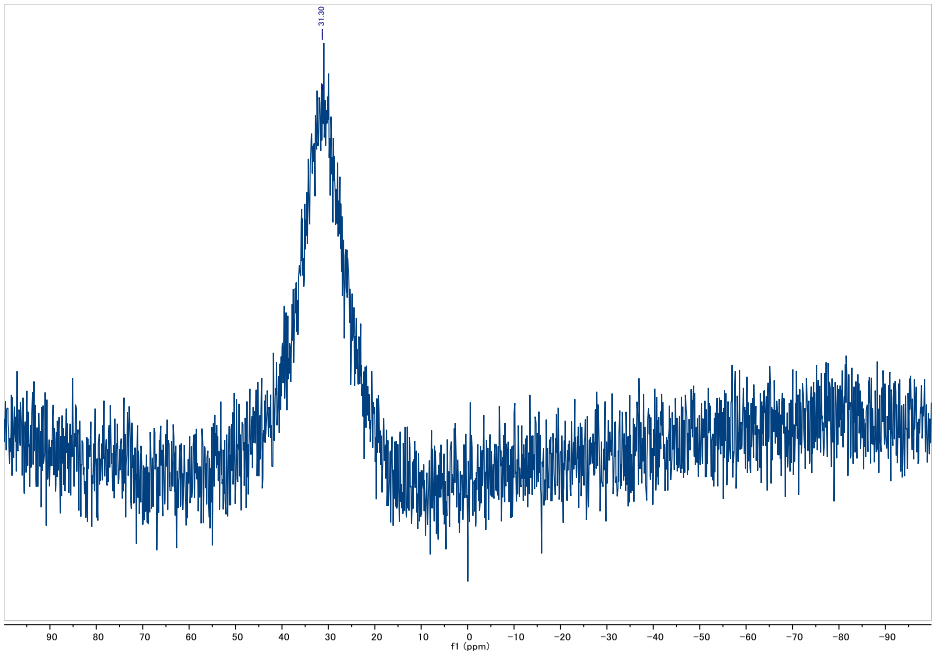
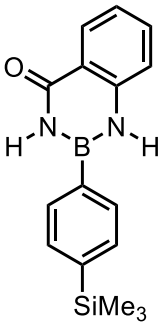
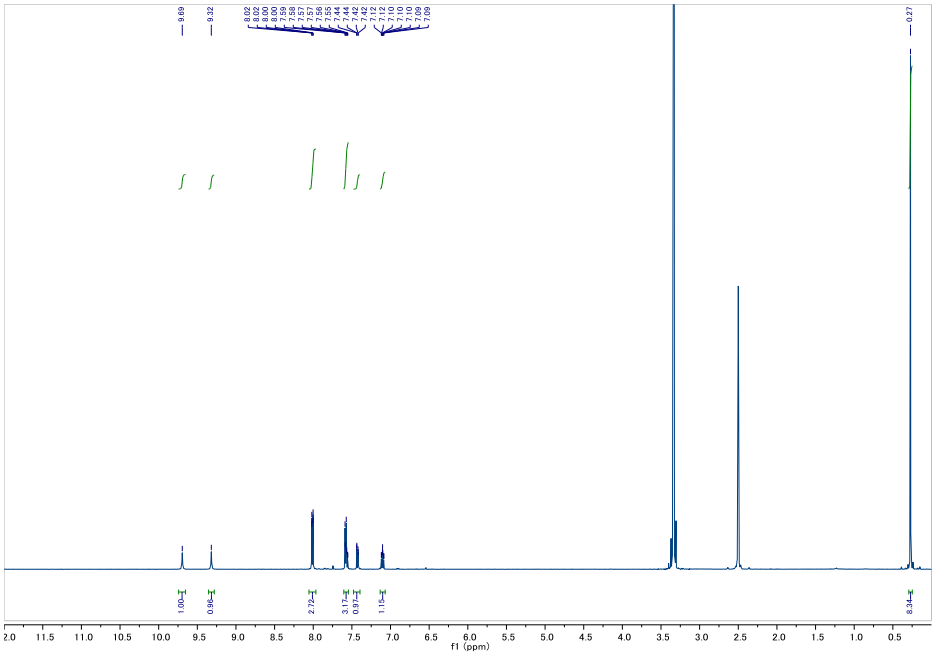
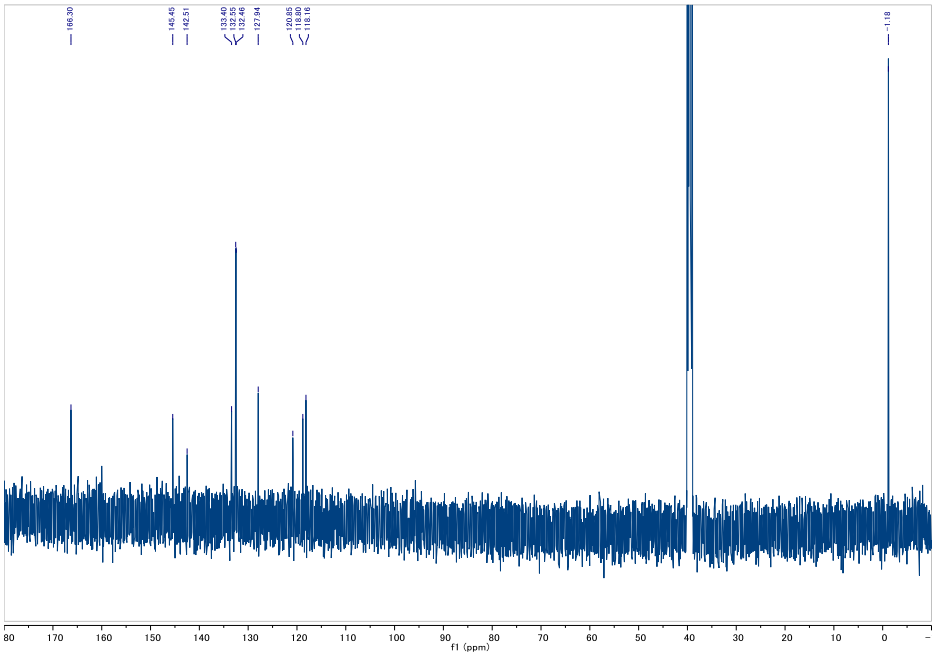
6.82
6.81
6.80
6.64
0.72
0.88
1.02
1.05
2.10
1.01
1.08
1.02
2.10
f1 (ppm)


166.32
159.75
145.69
135.16
133.50
127.91
120.45
118.51
117.97
114.88
f1 (ppm)


31.30
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
f1 (ppm)


O
H
N
B
N
H
SiMe3


9.99
9.32
8.02
8.02
8.00
8.00
7.59
7.58
7.57
7.57
7.56
7.55
7.44
7.44
7.43
7.42
7.12
7.10
7.10
7.10
7.09
7.09
0.27
1.00
0.86
2.72
3.17
0.97
1.15
8.34
f1 (ppm)


166.30
145.45
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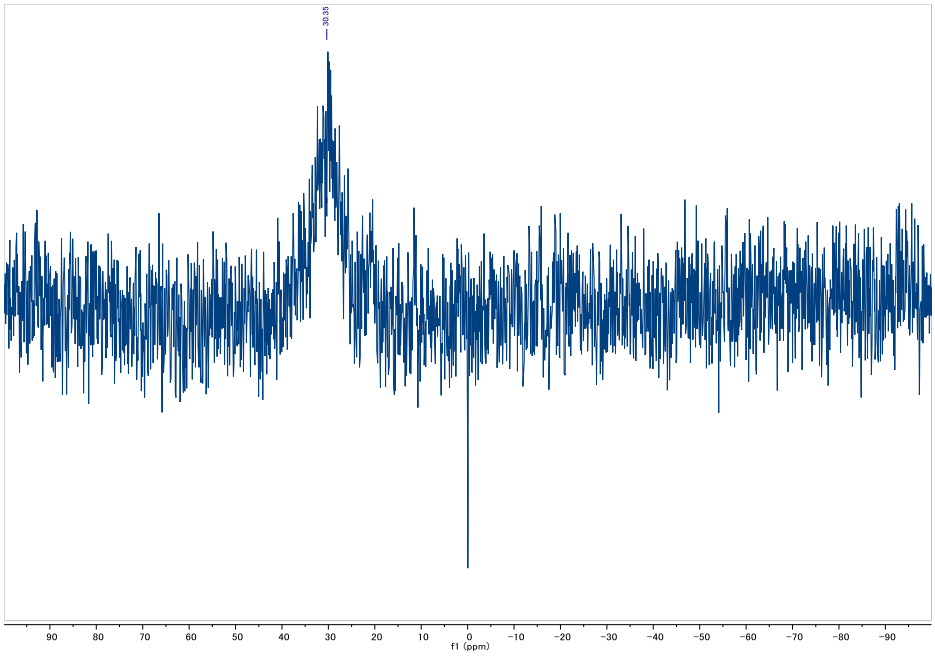
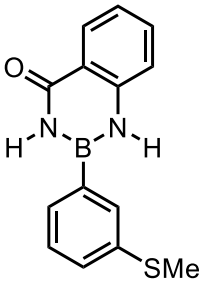
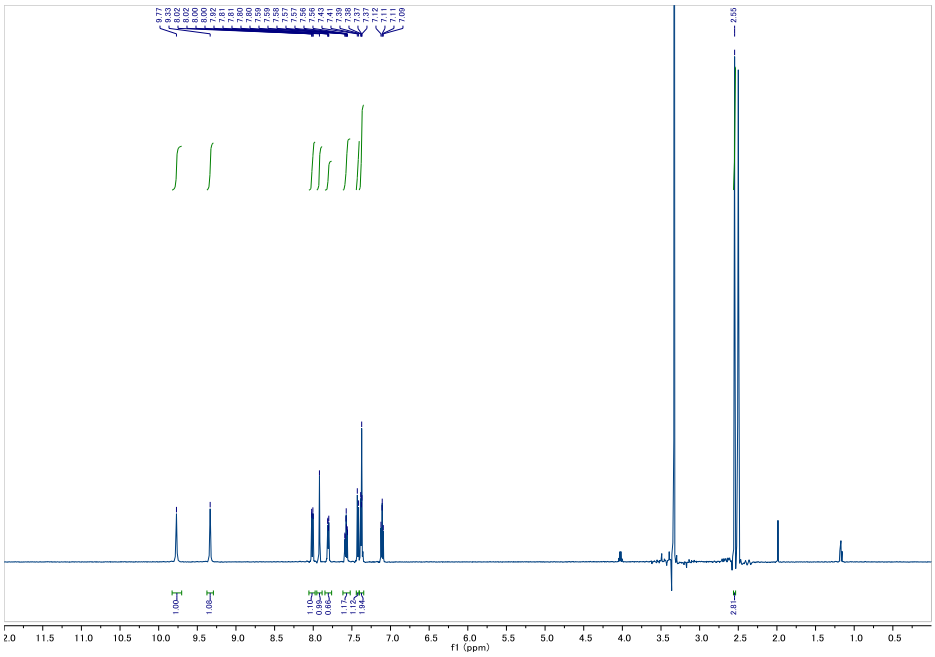
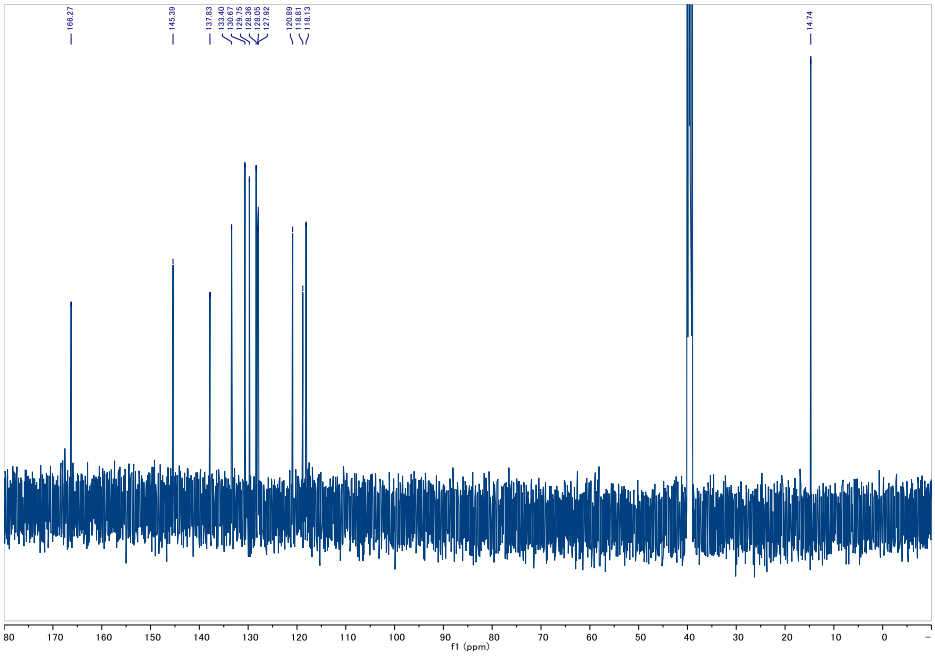
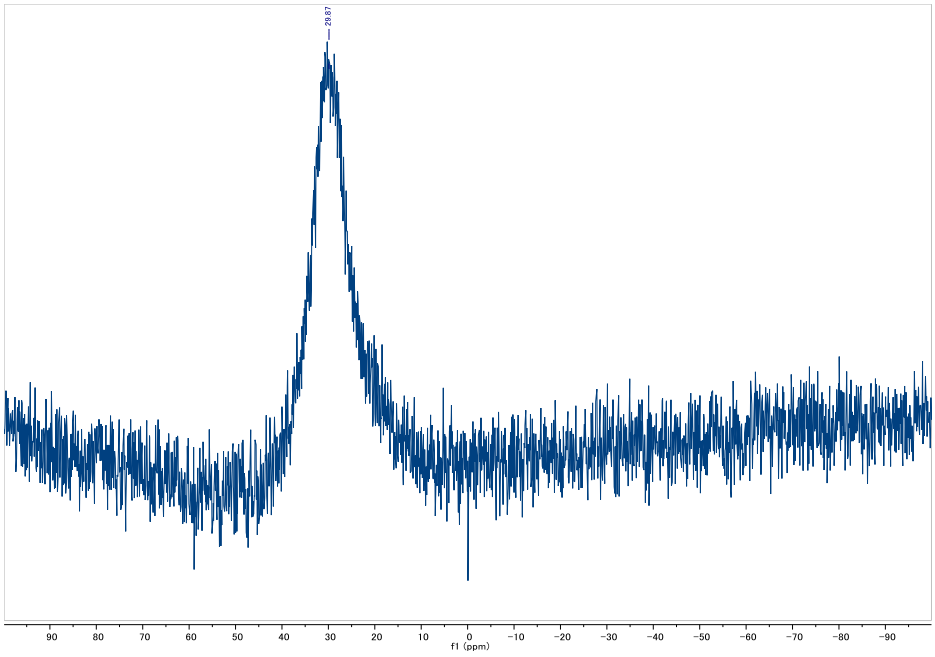
133.49
132.55
132.46
127.94
120.85
118.80
118.16
1.18
f1 (ppm)

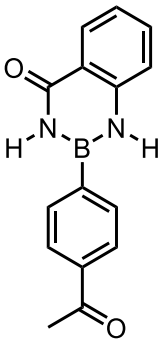

30.35
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
f1 (ppm)

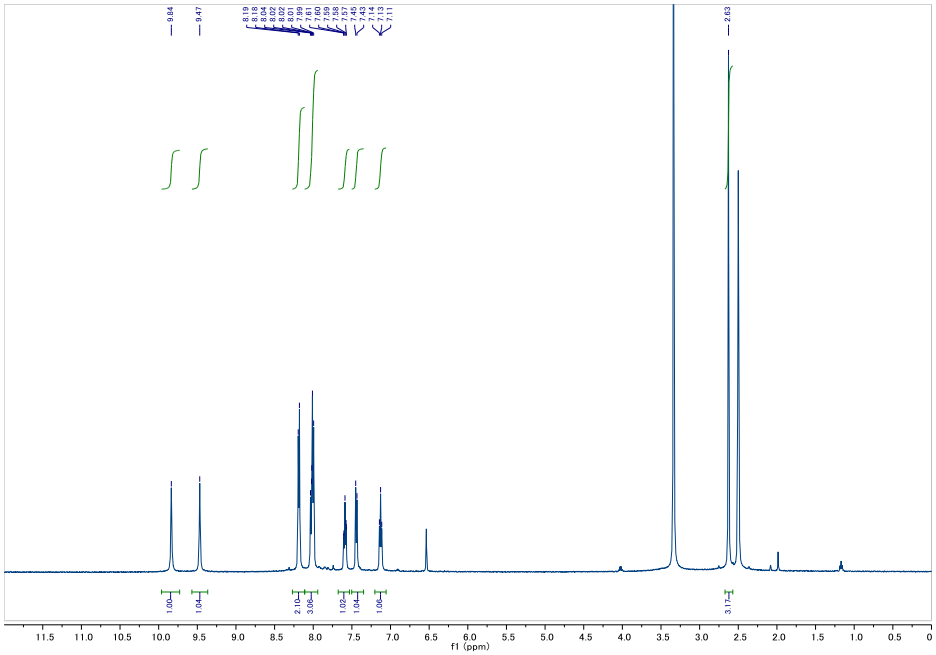

O
N
H
B
N
H
SMe

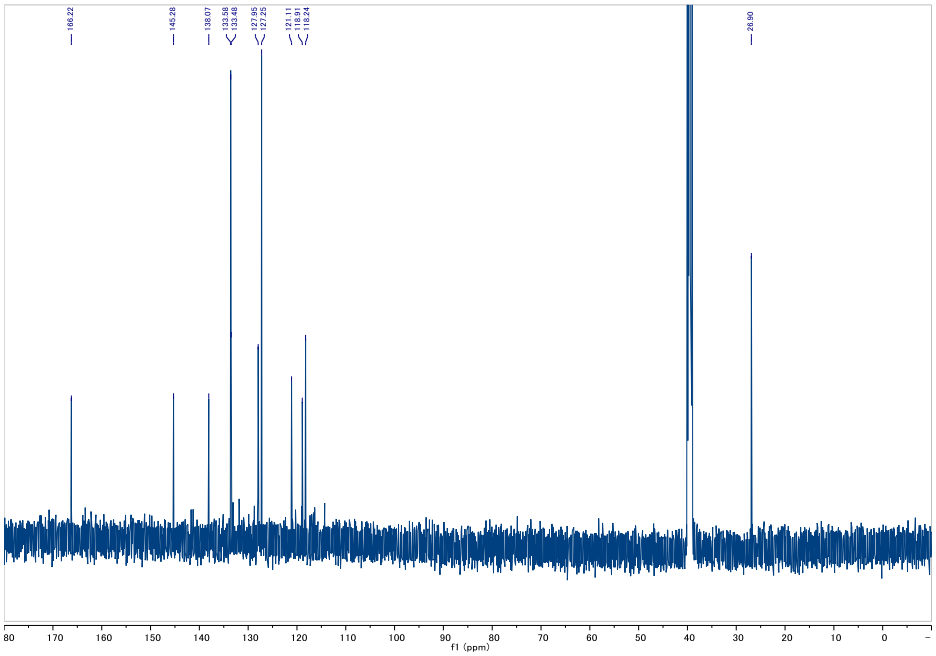

9.77
9.33
8.02
8.02
8.00
8.00
7.92
7.81
7.81
7.80
7.80
7.59
7.59
7.58
7.58
7.57
7.57
7.56
7.56
7.43
7.44
7.39
7.38
7.37
7.37
7.12
7.11
7.11
7.09
2.55
1.00
1.08
1.10
0.94
0.88
1.17
1.15
1.84
2.81
f1 (ppm)

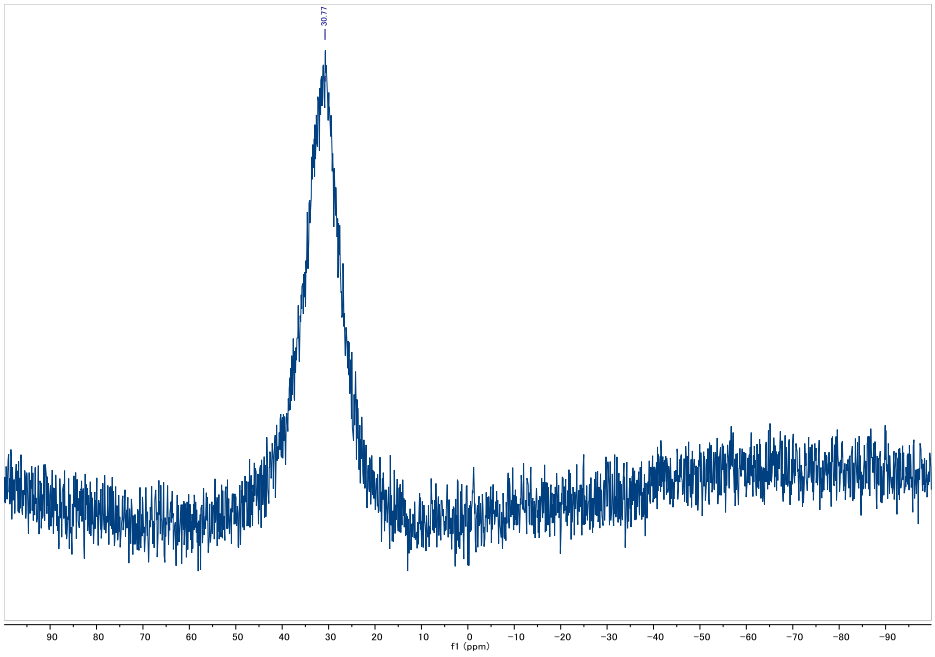

168.27
145.39
137.83
134.40
133.47
129.75
129.36
128.05
127.92
120.89
118.81
118.13
14.74
f1 (ppm)

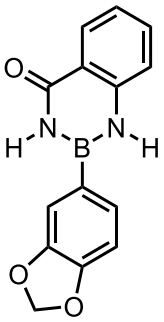

29.87
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
f1 (ppm)

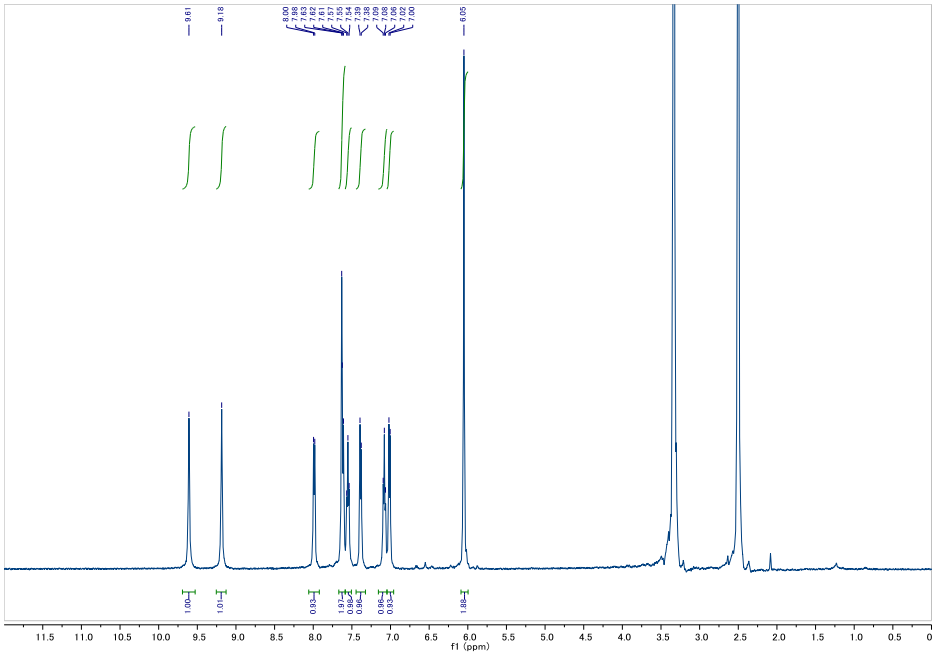


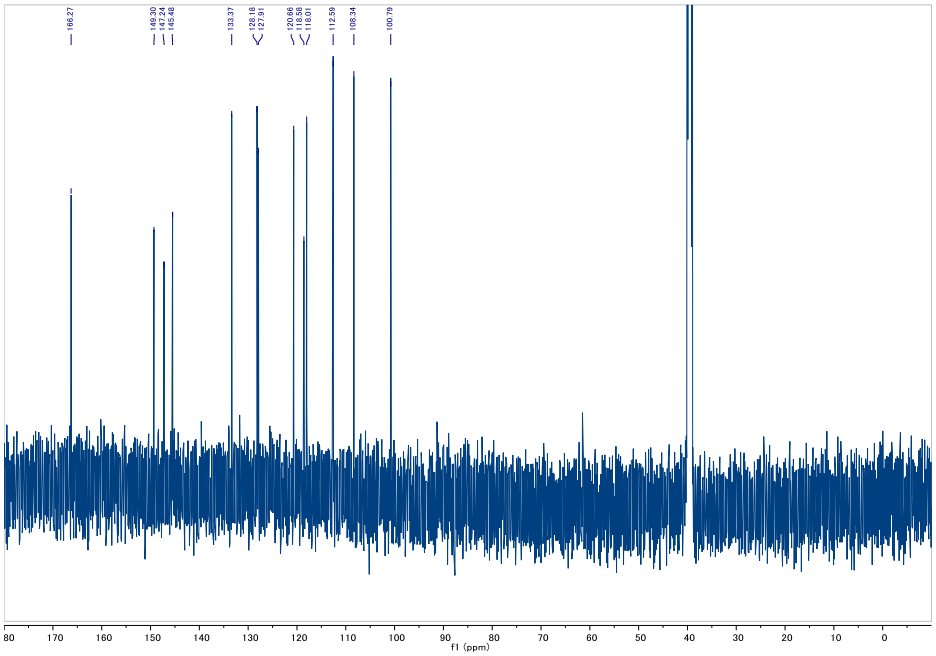


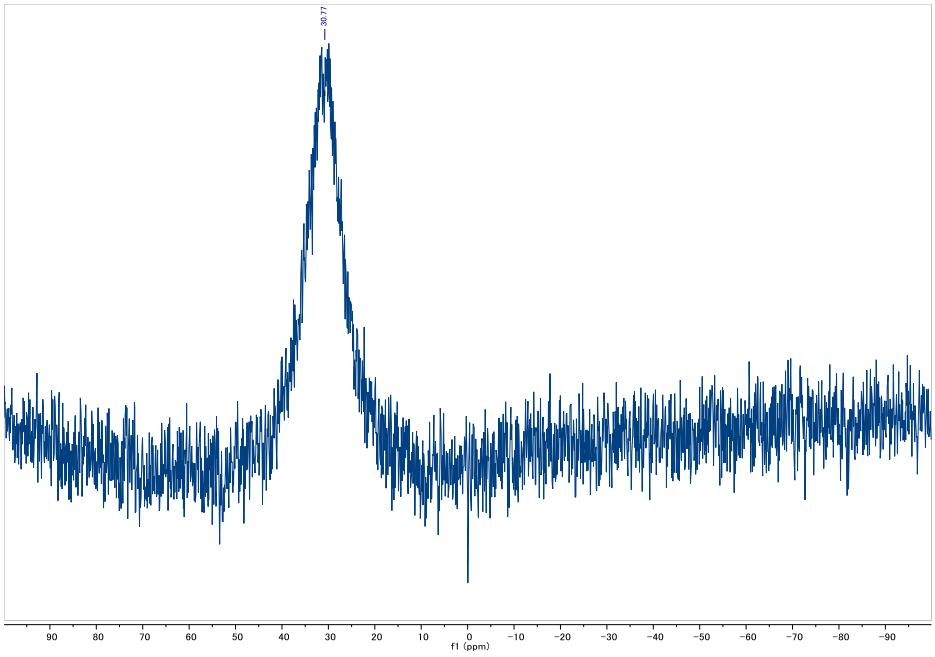


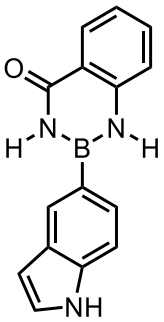

30.77
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
f1 (ppm)

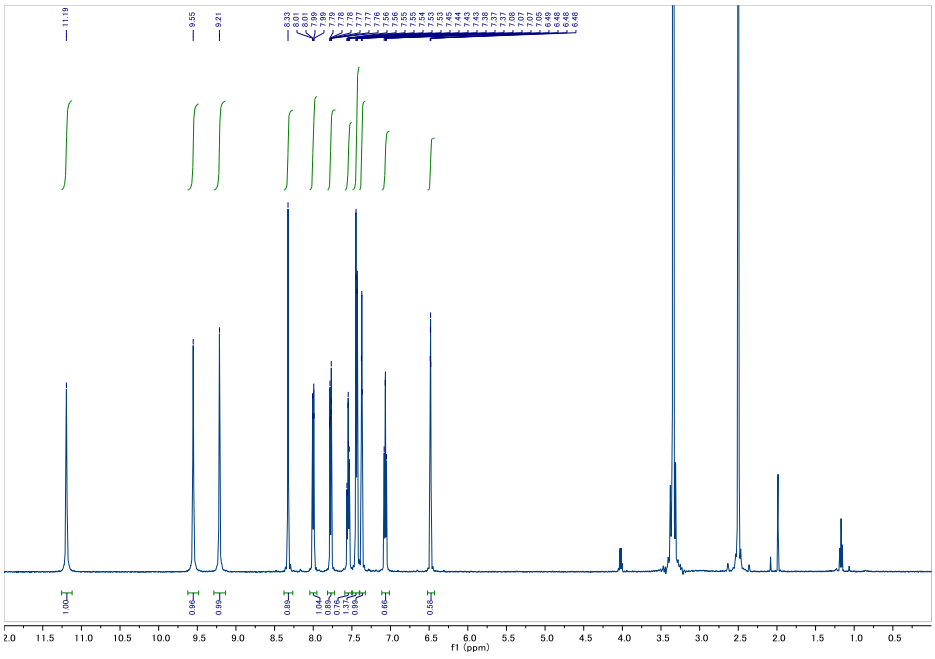

O
H
N
B
N
H
O
O

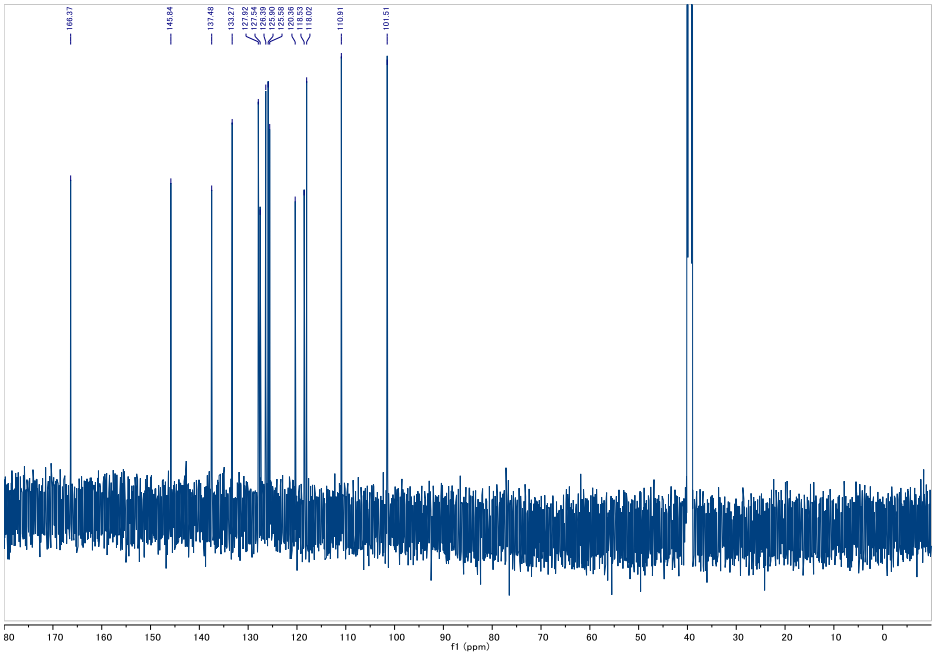

9.61
9.18
8.00
7.98
7.65
7.62
7.61
7.57
7.55
7.54
7.39
7.38
7.09
7.08
7.06
7.03
7.00
6.05
1.00
1.01
0.93
1.97
0.89
0.94
0.96
0.83
1.88
f1 (ppm)

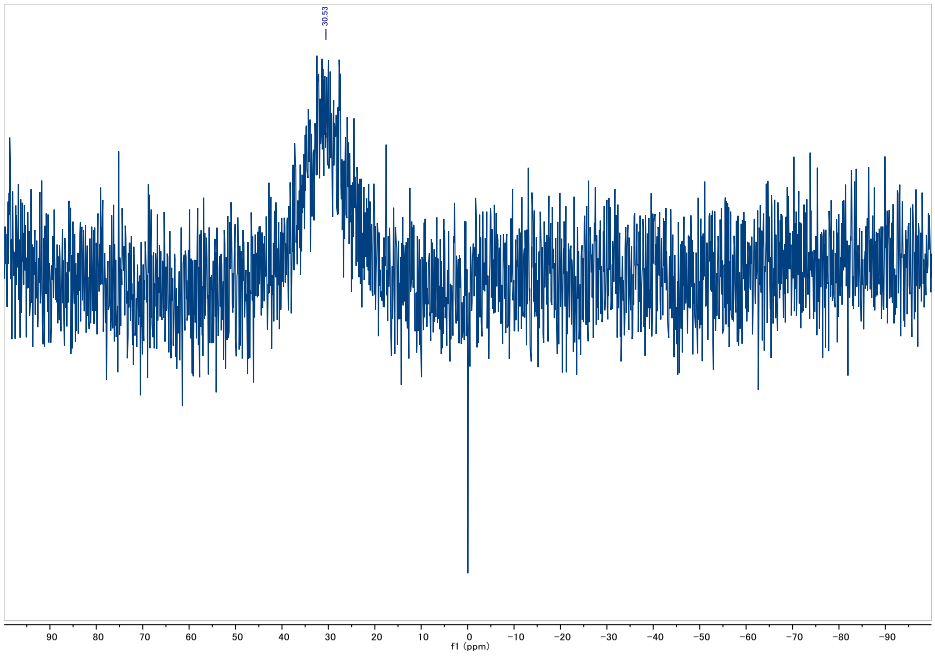

166.27
149.30
147.34
145.48
133.37
128.18
127.91
120.66
118.58
118.01
112.59
108.34
100.79
f1 (ppm)

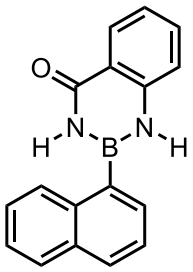

30.77
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
−10
−20
−30
−40
−50
−60
−70
−80
−90

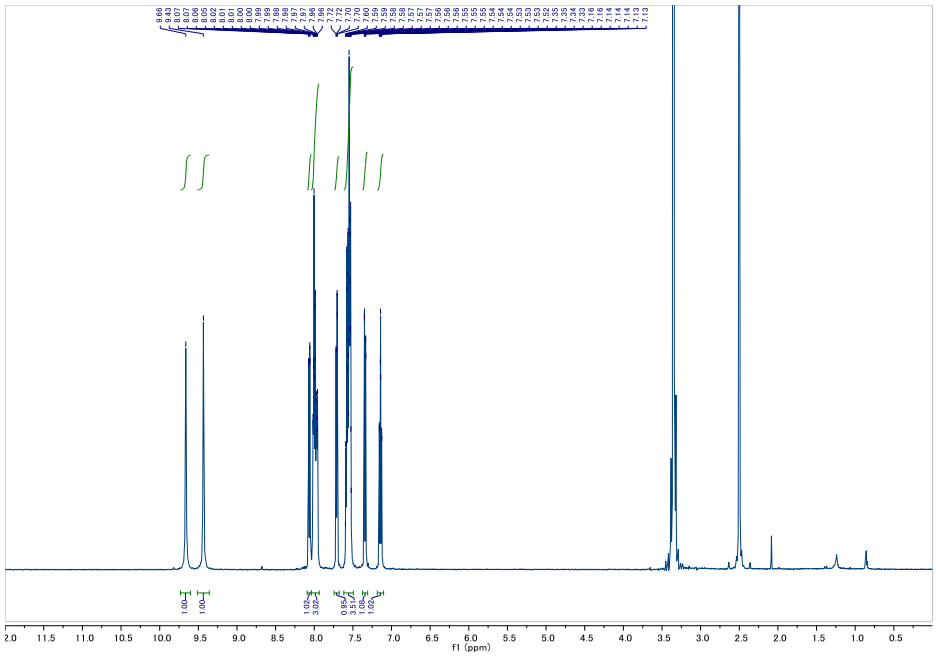

O
H
N
B
N
H
NH

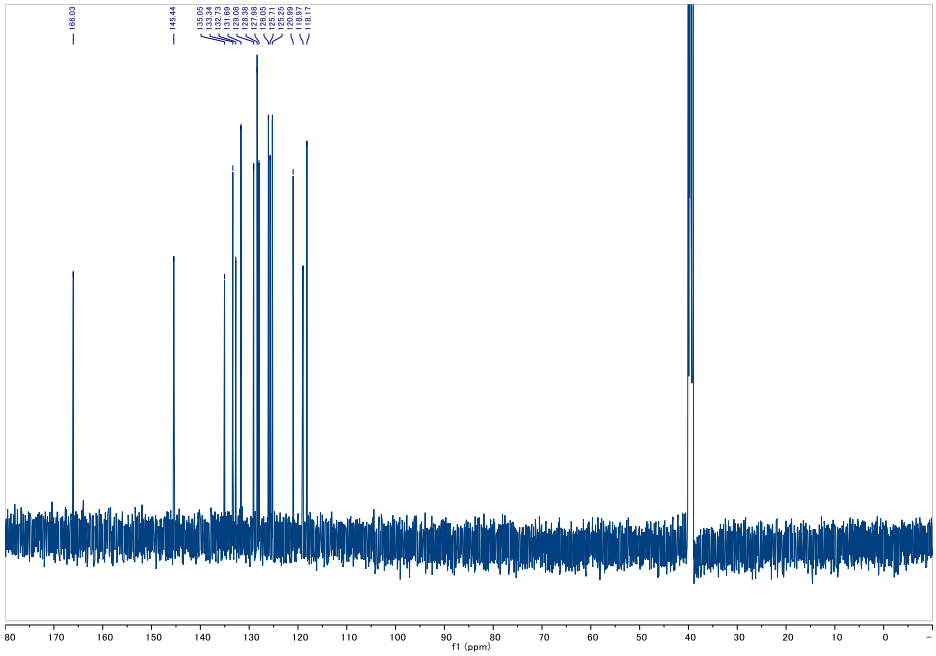

11.19
9.55
9.21
8.33
8.01
7.99
7.79
7.78
7.77
7.76
7.56
7.55
7.54
7.53
7.45
7.44
7.43
7.38
7.37
7.08
7.07
7.06
6.49
6.48
6.46
6.48
1.00
0.96
0.99
0.89
1.47
0.98
0.75
1.15
0.84
0.66
0.56
f1 (ppm)

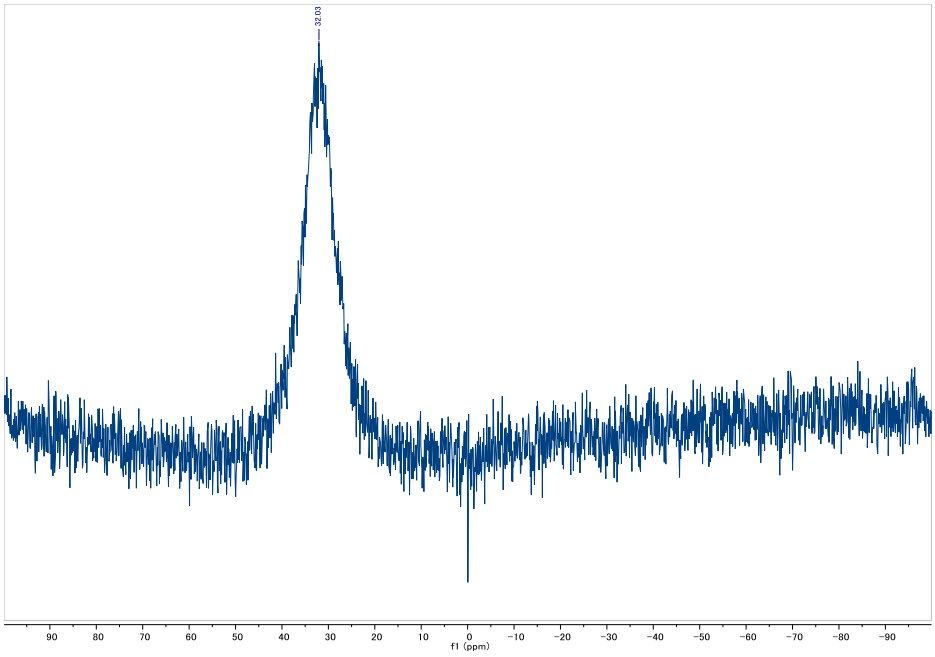

166.37
145.84
137.48
133.27
127.92
127.54
127.50
125.90
125.58
125.35
118.53
118.02
110.91
101.51
f1 (ppm)

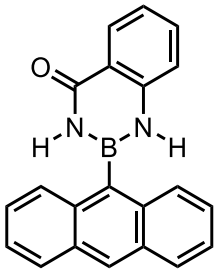

30.53
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
f1 (ppm)

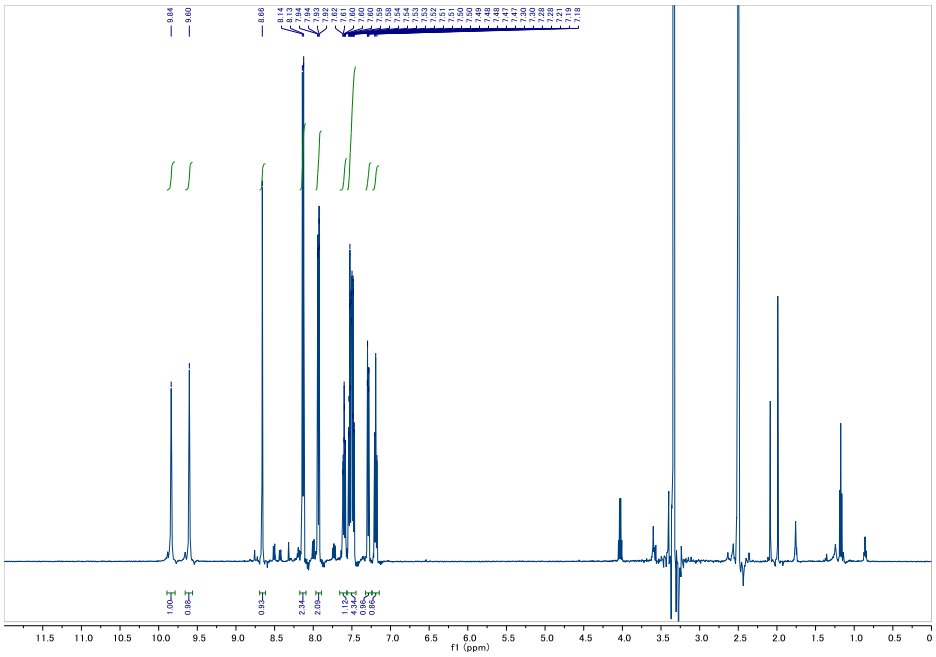

O
N
H
B
N
H

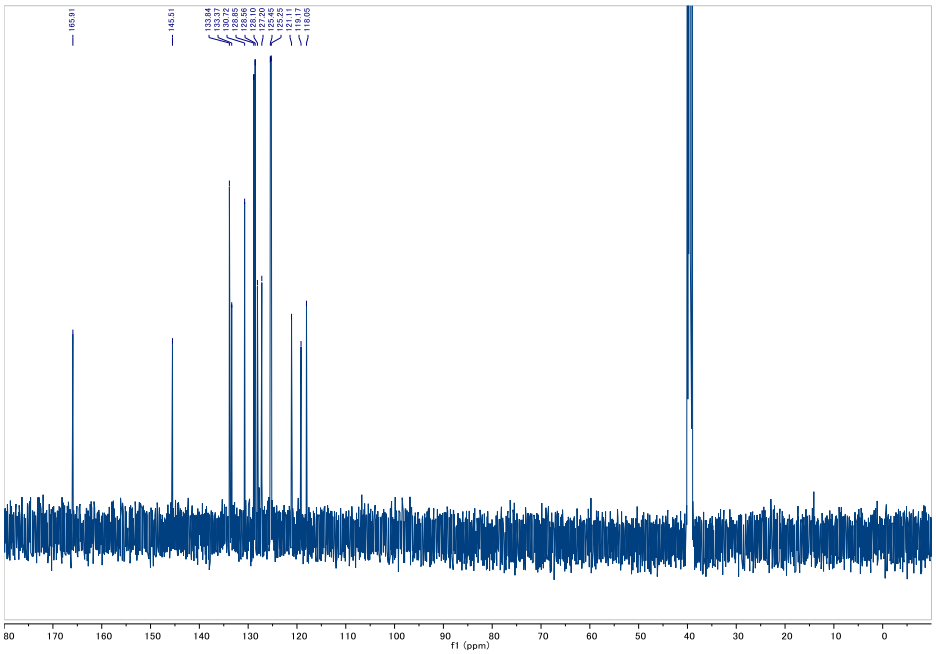

f1 (ppm)

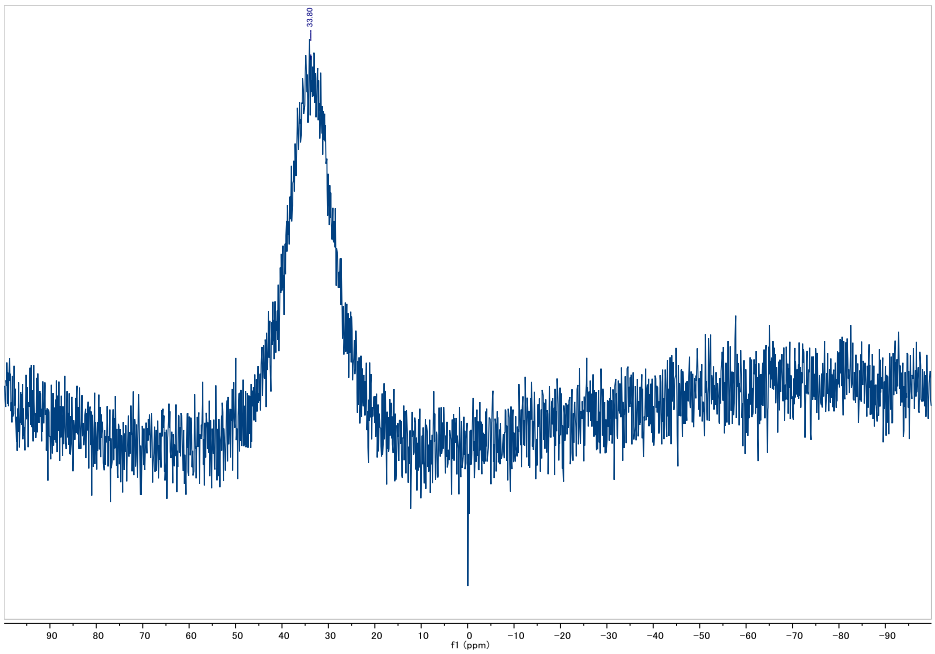

166.03
145.44
135.05
133.34
132.20
131.69
130.90
128.38
127.98
126.65
125.71
125.25
120.69
118.97
118.17
f1 (ppm)

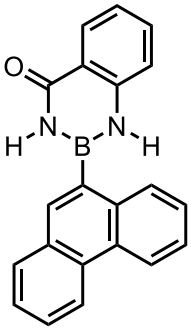

32.03
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
f1 (ppm)

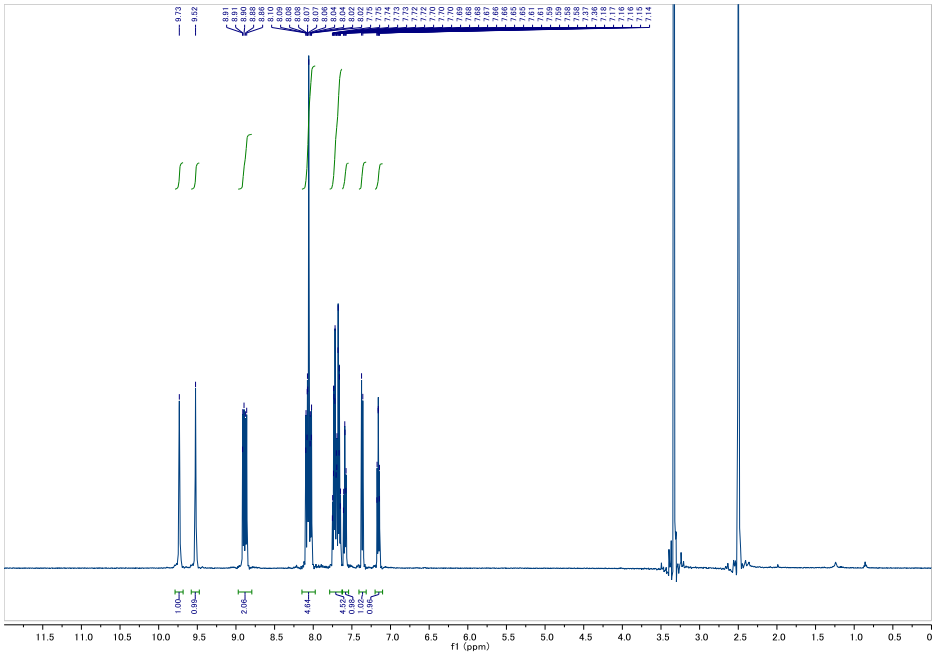

O
N
H
B
N
H

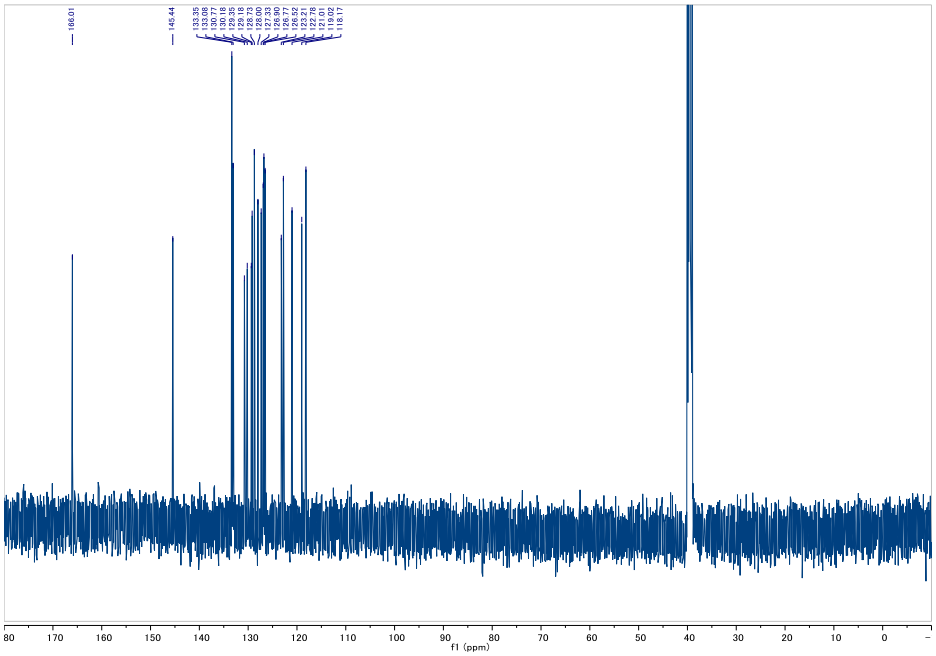

9.84
9.60
8.66
8.14
8.13
7.94
7.93
7.92
7.62
7.61
7.60
7.60
7.60
7.59
7.59
7.58
7.54
7.54
7.53
7.53
7.52
7.51
7.51
7.50
7.50
7.50
7.49
7.48
7.48
7.47
7.47
7.30
7.30
7.29
7.28
7.21
7.19
7.18
1.00
0.98
0.93
2.34
2.09
1.12
4.34
0.98
0.96
f1 (ppm)

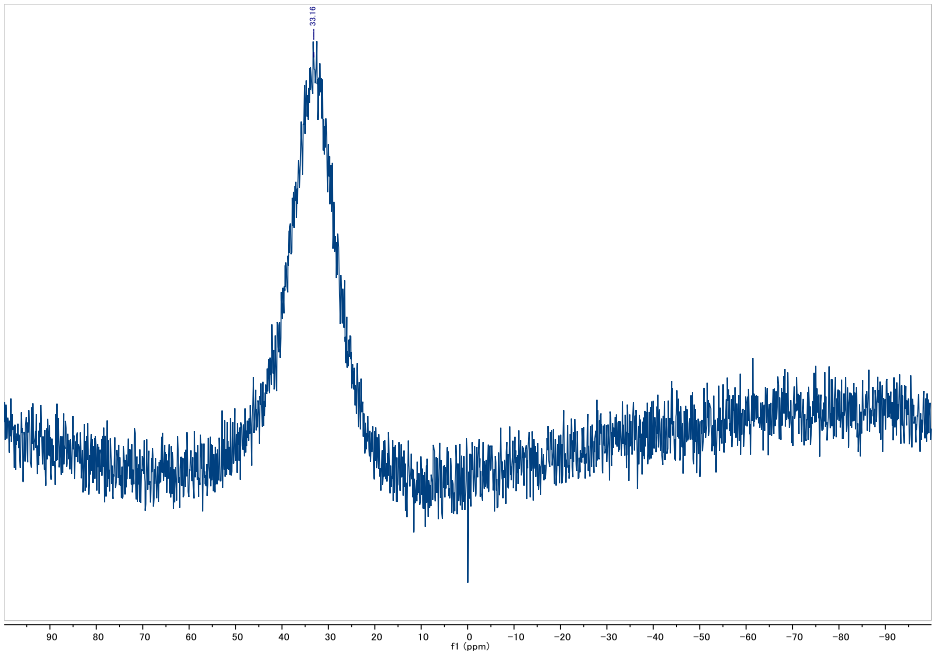

165.91
145.51
133.84
133.37
130.72
129.85
128.95
128.10
127.20
125.45
125.25
121.11
119.17
118.05
f1 (ppm)

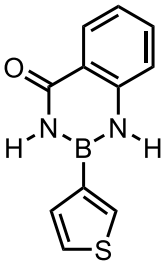

33.80
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
−10
−20
−30
−40
−50
−60
−70
−80
−90

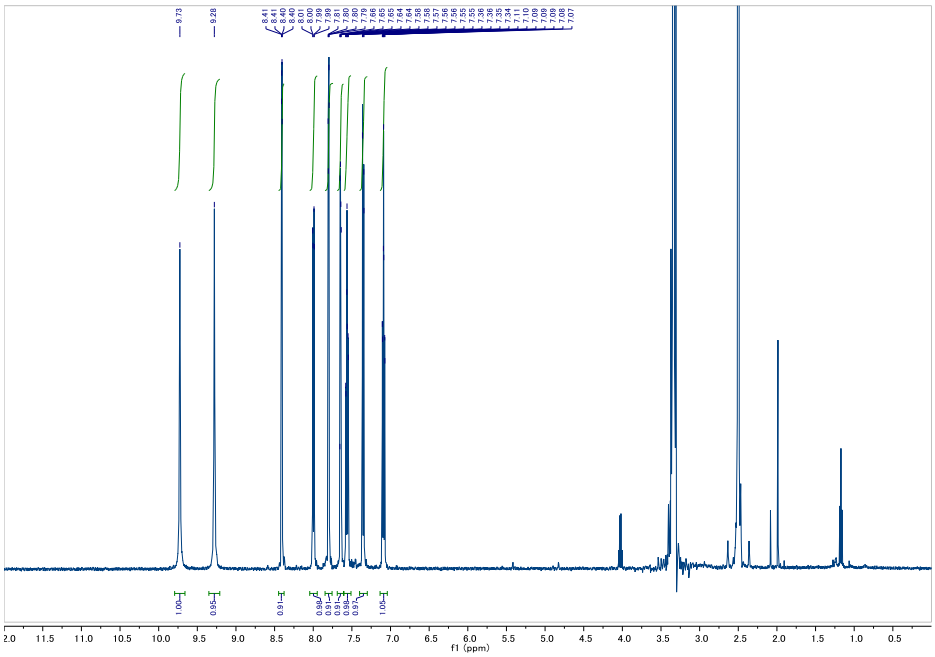

O
N
H
B
N
H


f1 (ppm)


f1 (ppm)


33.16
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
f1 (ppm)


O
N
B
N
H
H
S


9.73
9.28
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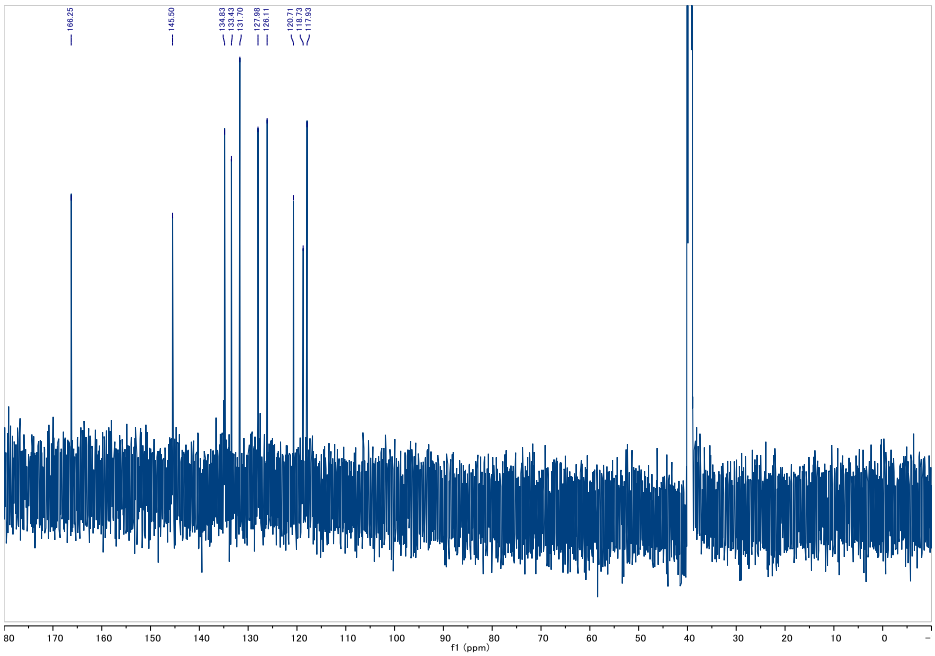
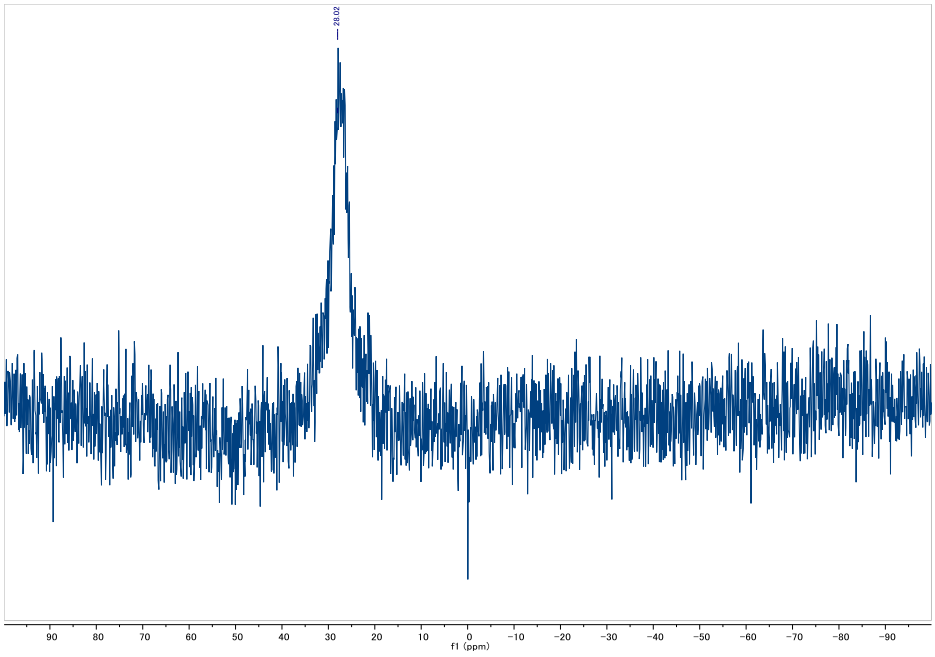
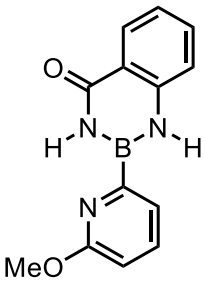
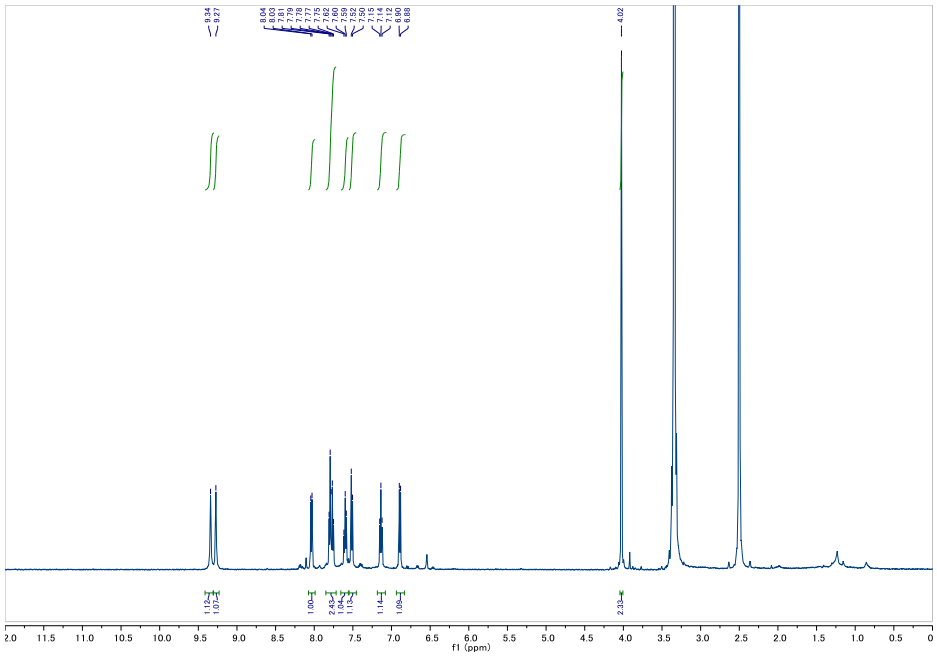
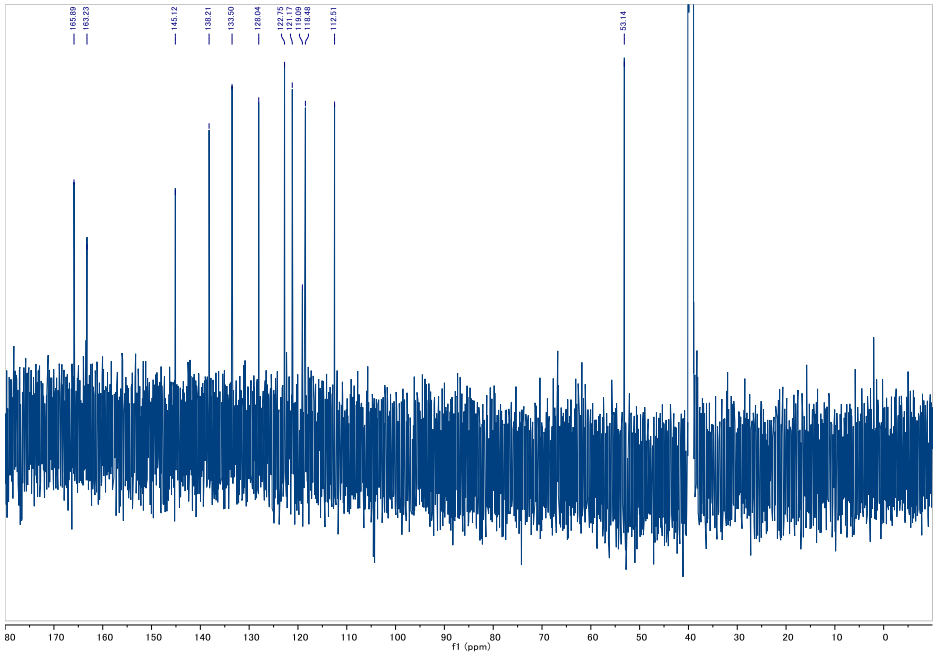
8.40
8.00
7.99
7.79
7.78
7.77
7.76
7.75
7.74
7.73
7.72
7.71
7.70
7.69
7.68
7.67
1.00
0.95
0.91
0.94
0.93
0.94
0.98
0.93
1.04
f1 (ppm)

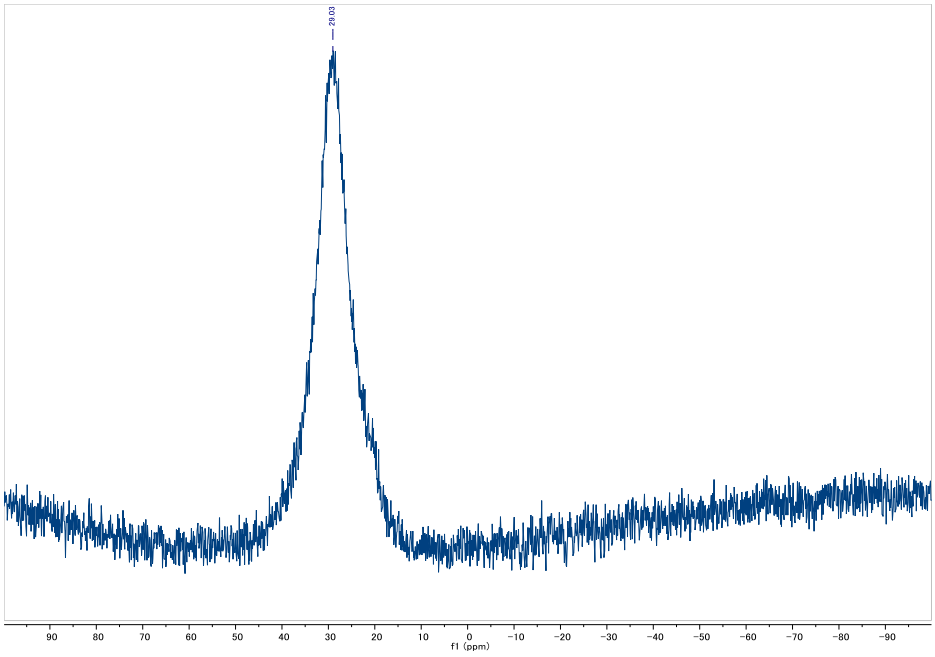

166.25
145.50
134.83
134.52
131.70
127.98
126.11
120.71
118.73
117.93
f1 (ppm)

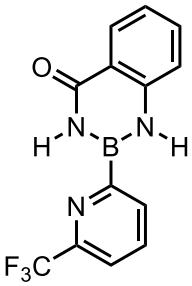

28.02
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
f1 (ppm)

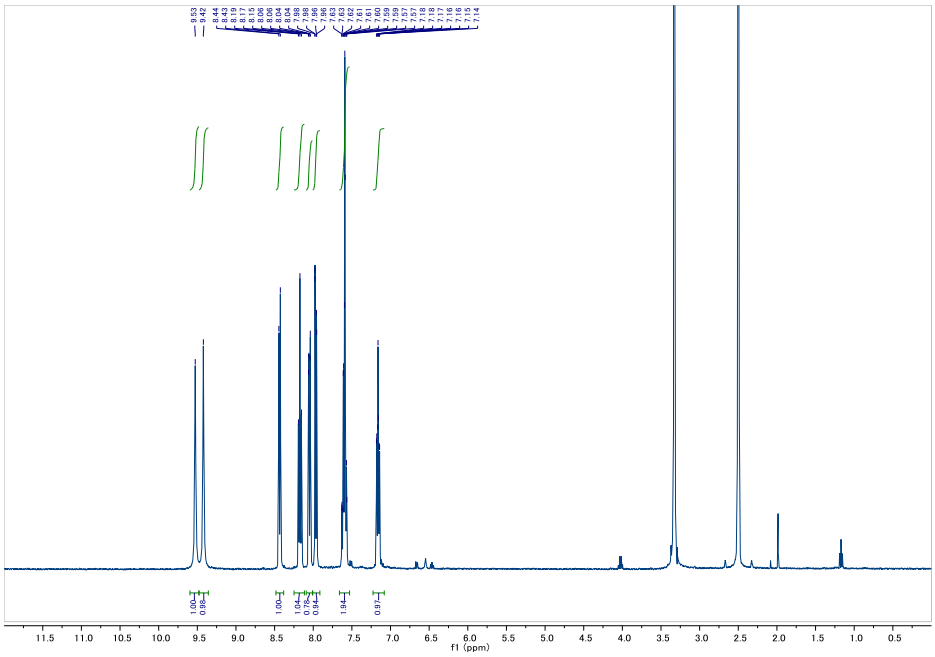

O
N
H
B
N
H
N
MeO

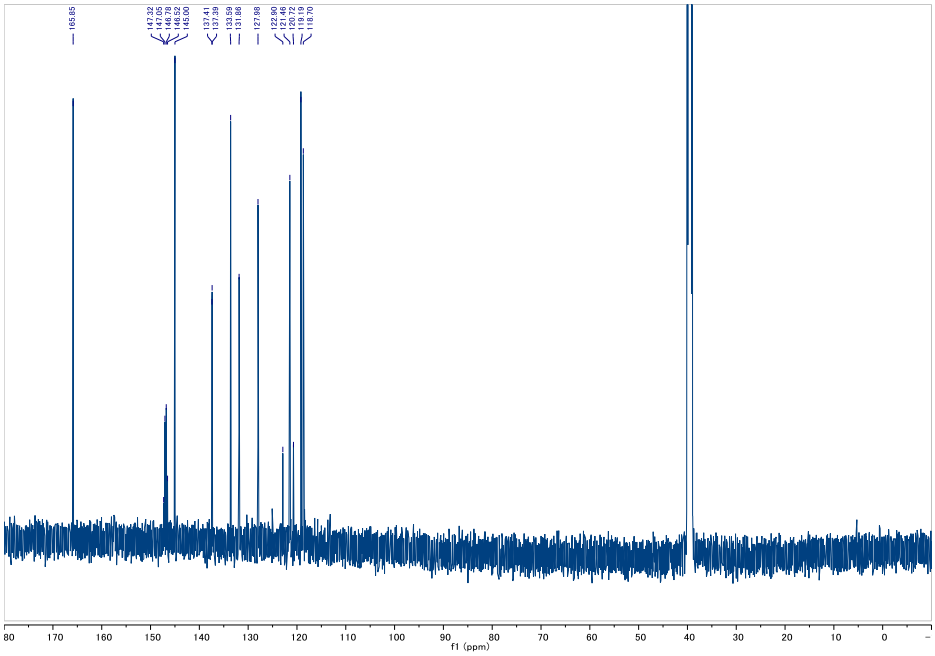

9.34
9.27
8.04
8.03
7.81
7.79
7.78
7.77
7.75
7.62
7.60
7.58
7.52
7.50
7.15
7.14
7.13
6.90
6.88
4.02
f1 (ppm)

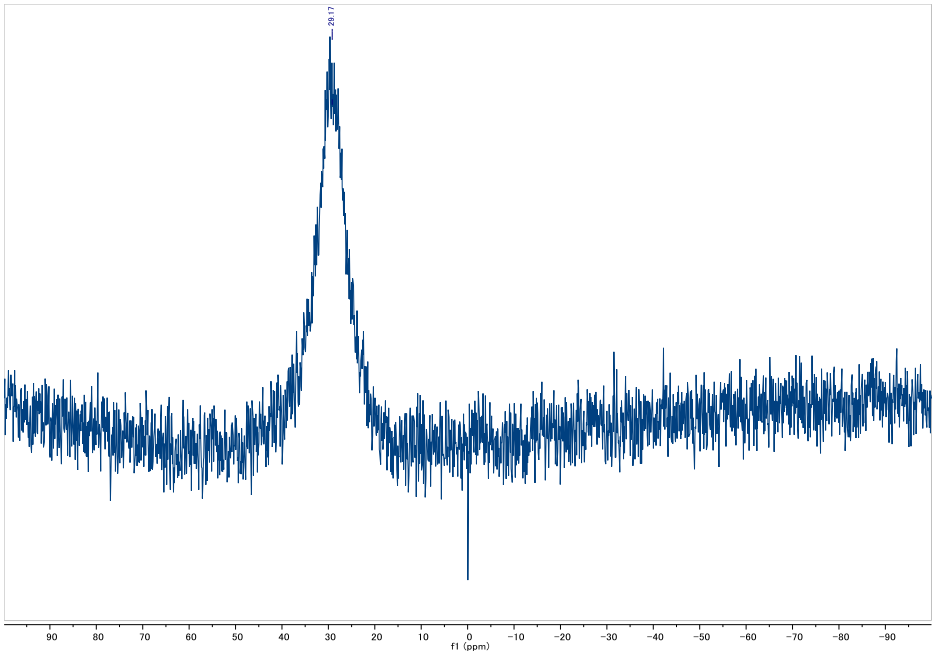

155.89
163.23
145.12
138.21
133.50
128.04
122.75
121.77
119.09
118.48
112.51
53.14
f1 (ppm)

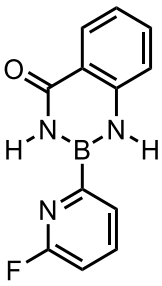

29.03
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
−10
−20
−30
−40
−50
−60
−70
−80
−90

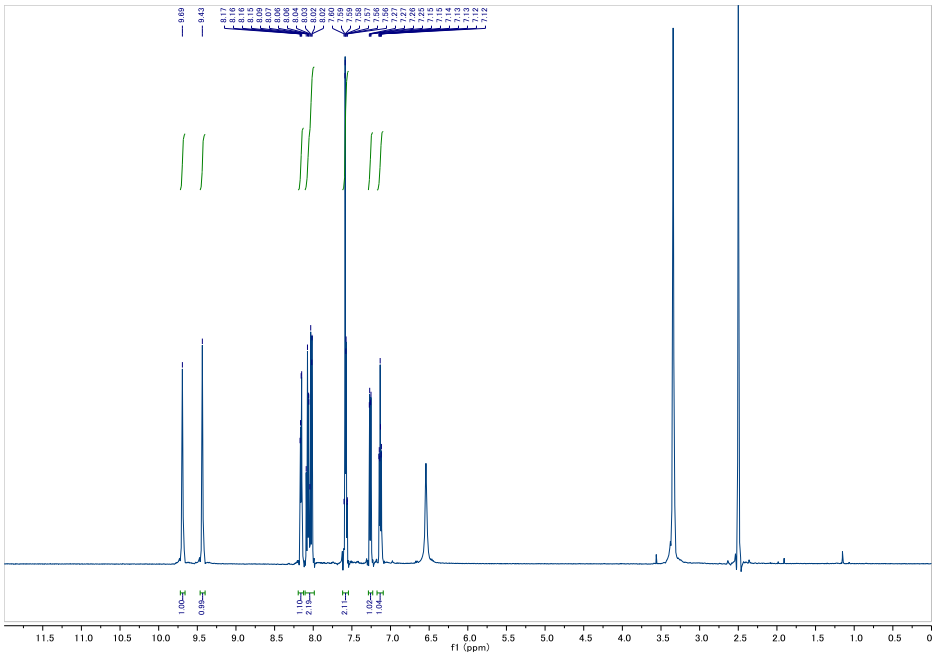

O
N
H
B
N
H
N
F3C

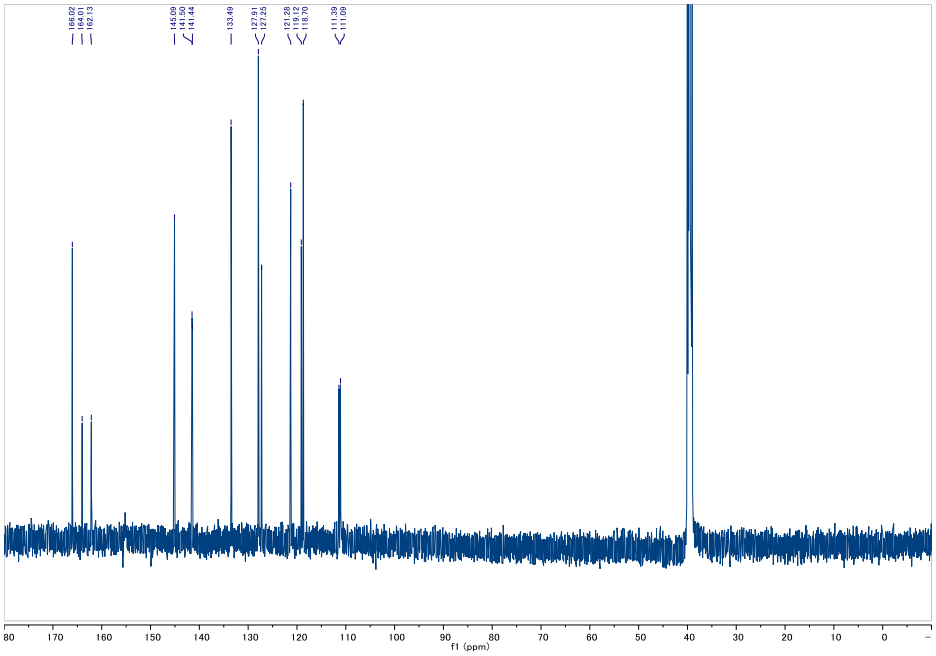

f1 (ppm)

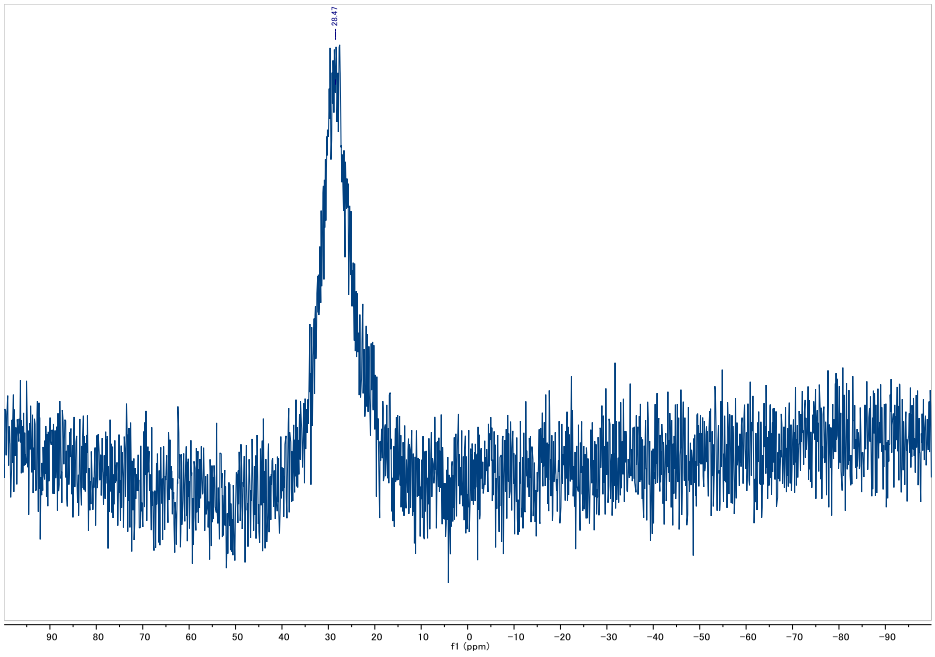

f1 (ppm)

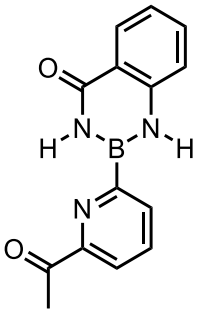

29.17
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
−10
−20
−30
−40
−50
−60
−70
−80
−90

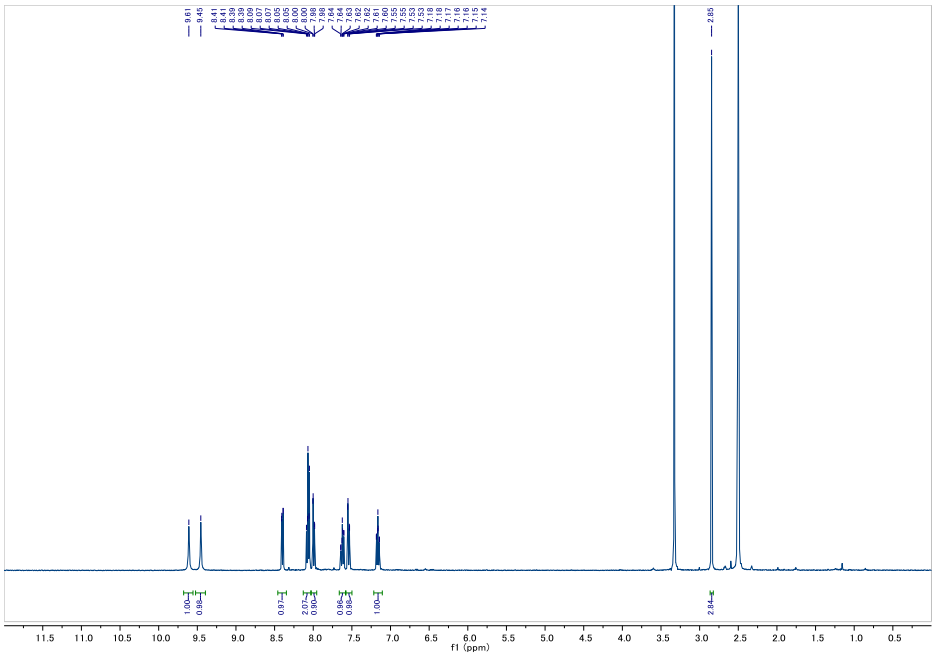

O
N
H
B
N
H
N
F

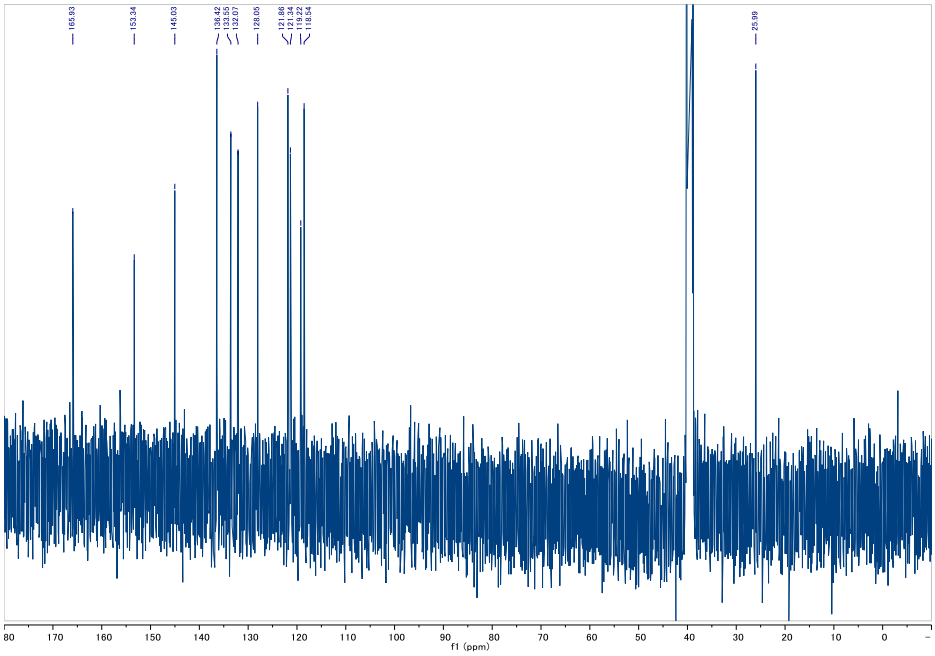

9.69
9.43
8.17
8.16
8.15
8.09
8.07
8.06
8.04
8.03
8.02
7.60
7.59
7.58
7.57
7.56
7.56
7.27
7.26
7.25
7.15
7.14
7.13
7.13
7.12
7.12
1.00
0.99
1.10
2.19
2.11
1.02
1.04
f1 (ppm)

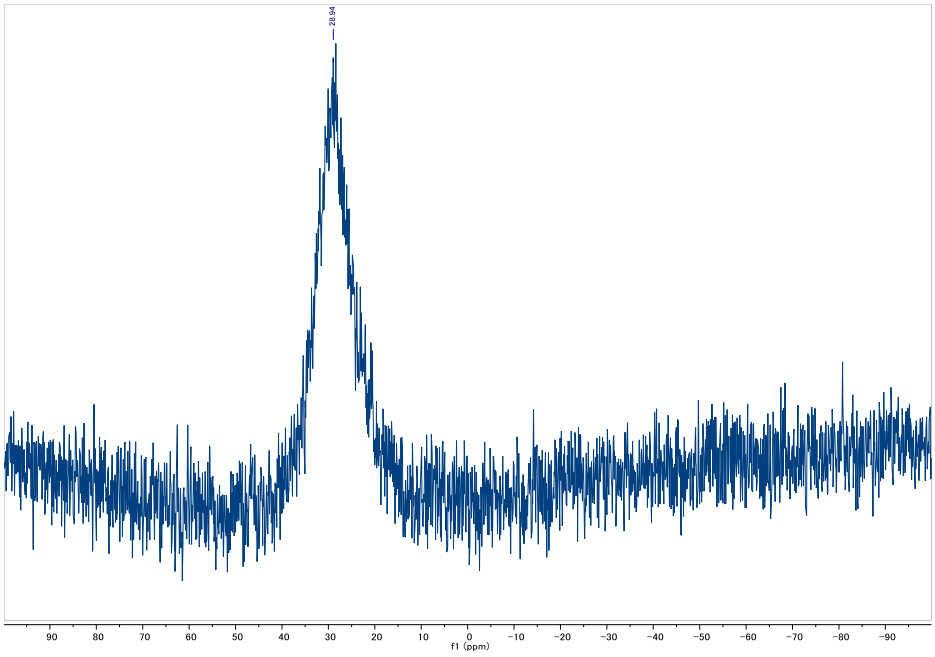

156.02
154.61
152.13
145.09
141.50
141.44
133.49
127.91
127.25
121.28
119.12
118.70
111.39
111.09
f1 (ppm)

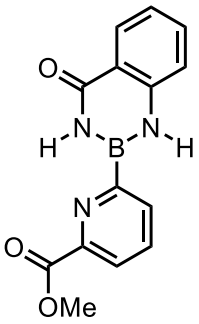

28.47
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
f1 (ppm)

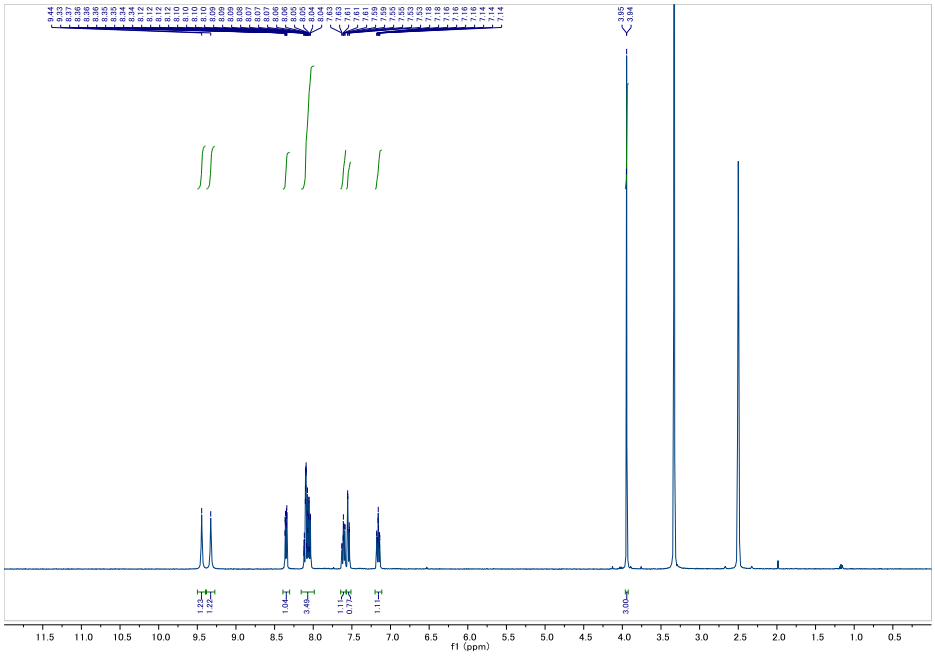


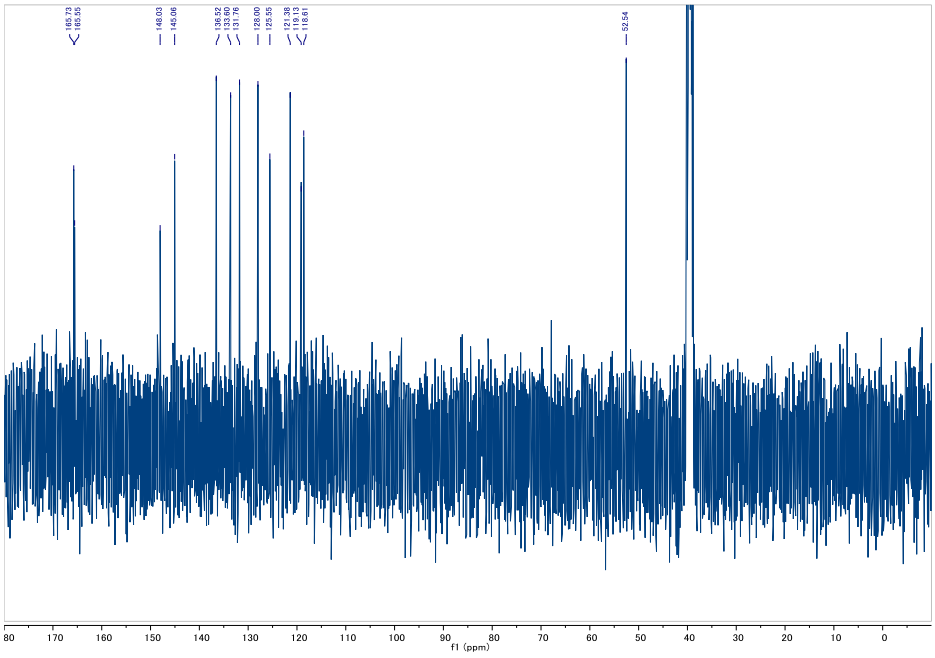

9.61
9.45
8.41
8.41
8.39
8.39
8.09
8.07
8.07
8.05
8.05
8.00
8.00
7.99
7.98
7.64
7.64
7.63
7.63
7.62
7.62
7.61
7.61
7.60
7.55
7.55
7.53
7.53
7.18
7.17
7.17
7.16
7.16
7.15
7.15
7.14
2.65
1.00
0.98
0.97
2.07
0.97
0.98
0.98
1.00
2.64
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

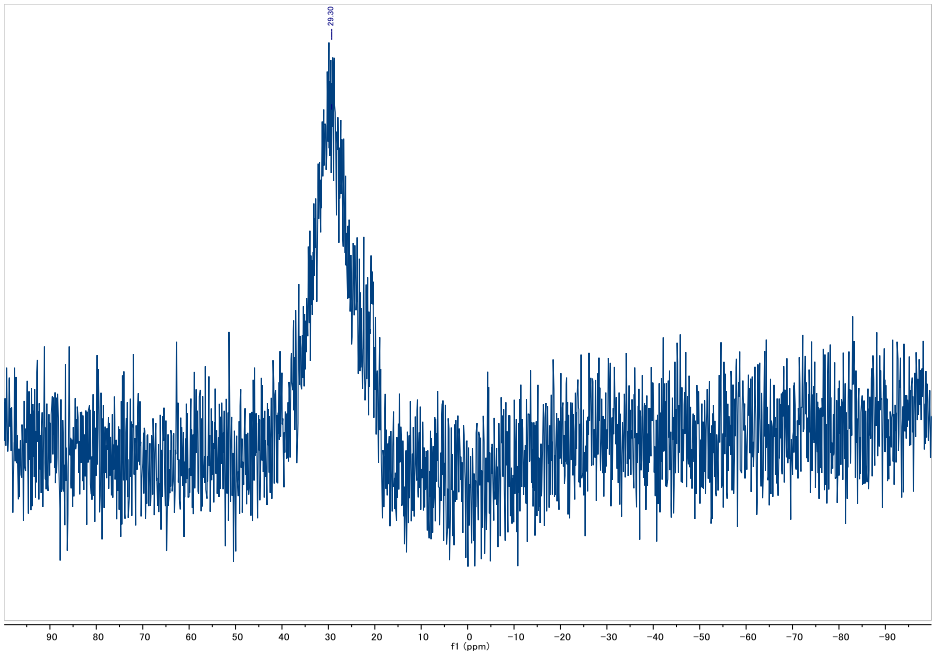

165.93
153.34
145.03
138.42
133.55
132.07
128.05
121.86
121.34
119.22
118.54
25.99
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

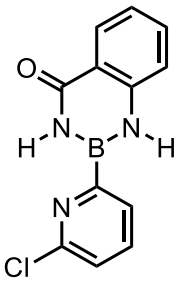

28.94
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
f1 (ppm)

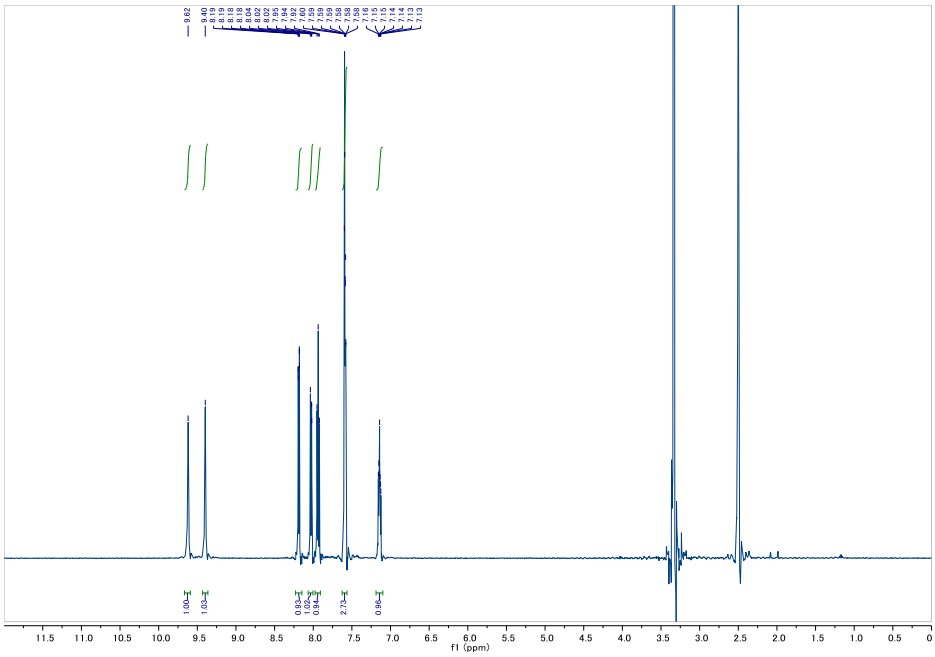

O
H
N
B
N
H
N
O
OMe

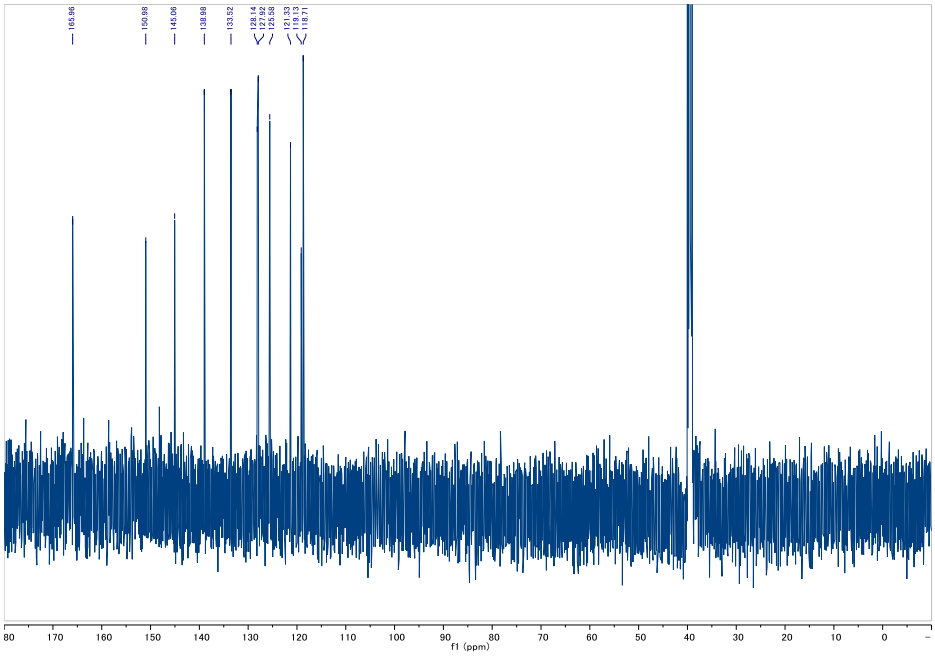

f1 (ppm)

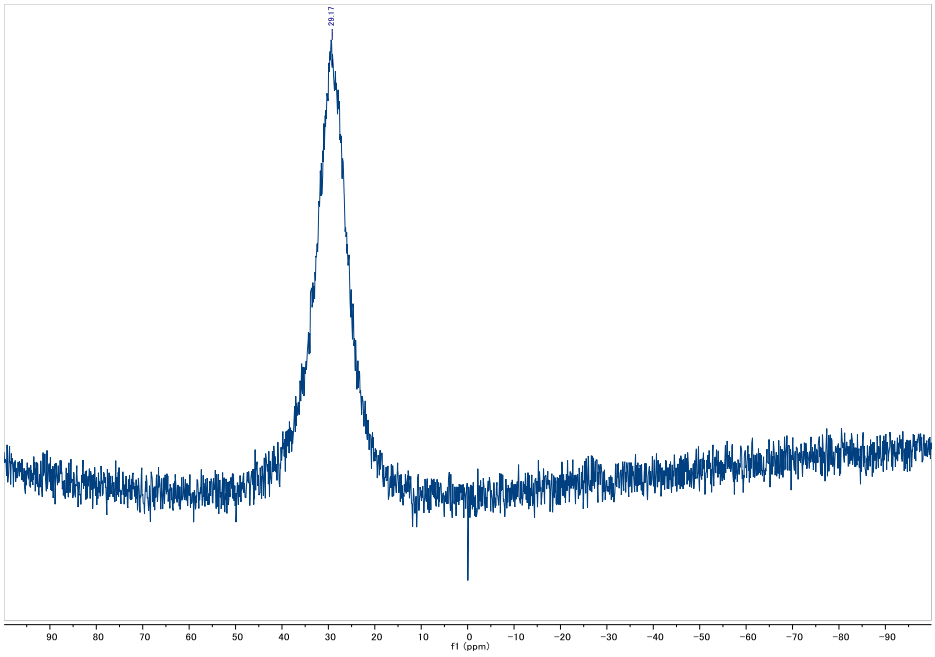

f1 (ppm)

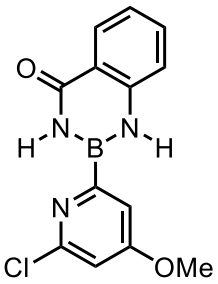

29.30
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
−10
−20
−30
−40
−50
−60
−70
−80
−90

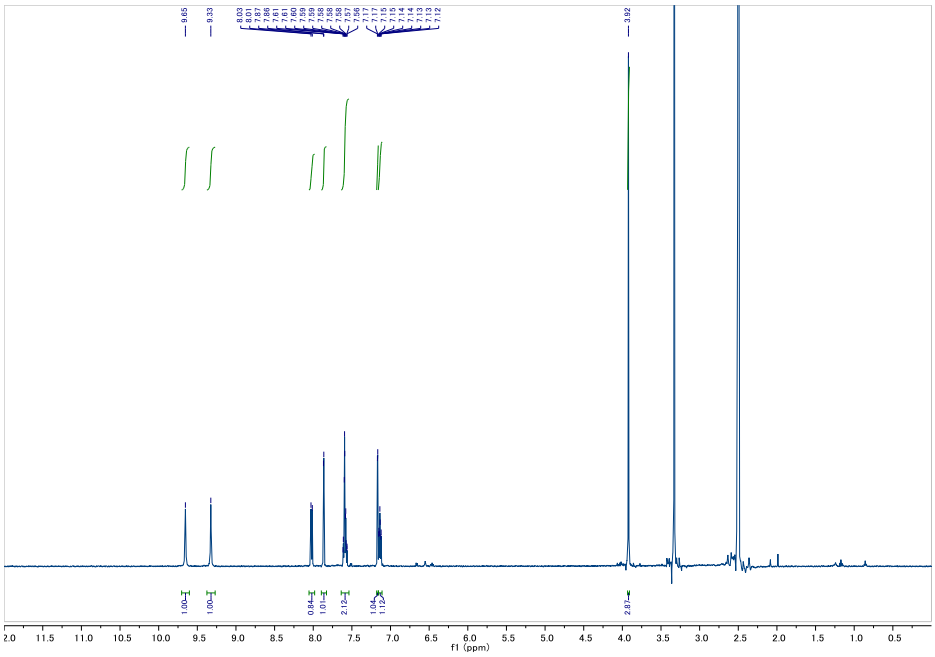

O
N
H
B
N
H
N
Cl

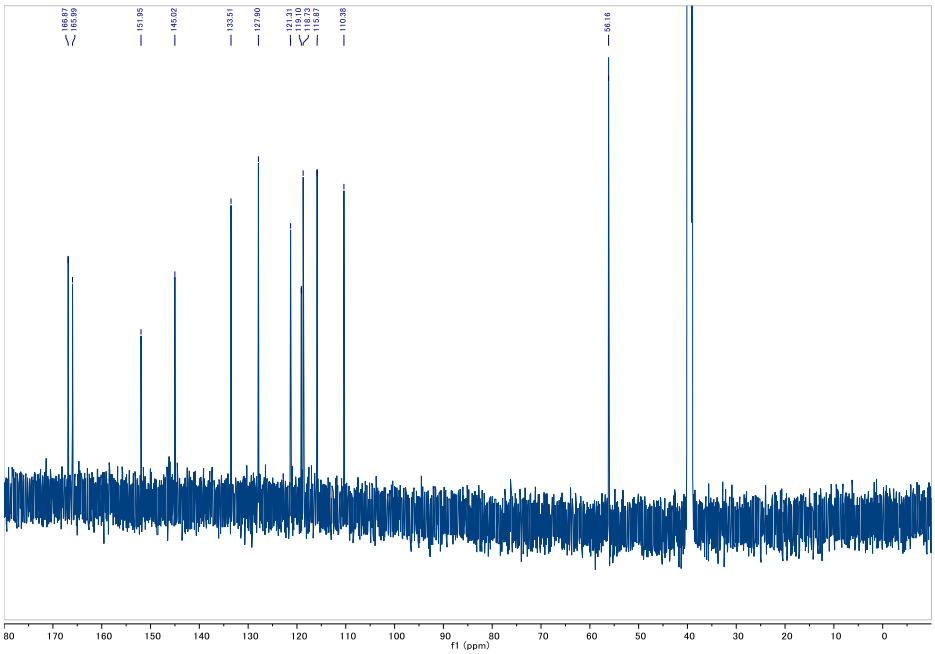

9.62
9.40
8.19
8.19
8.18
8.18
8.04
8.02
8.02
8.00
7.94
7.92
7.60
7.59
7.59
7.58
7.58
7.16
7.15
7.15
7.14
7.14
7.14
7.13
1.00
1.03
0.93
1.02
1.04
2.75
0.86
f1 (ppm)

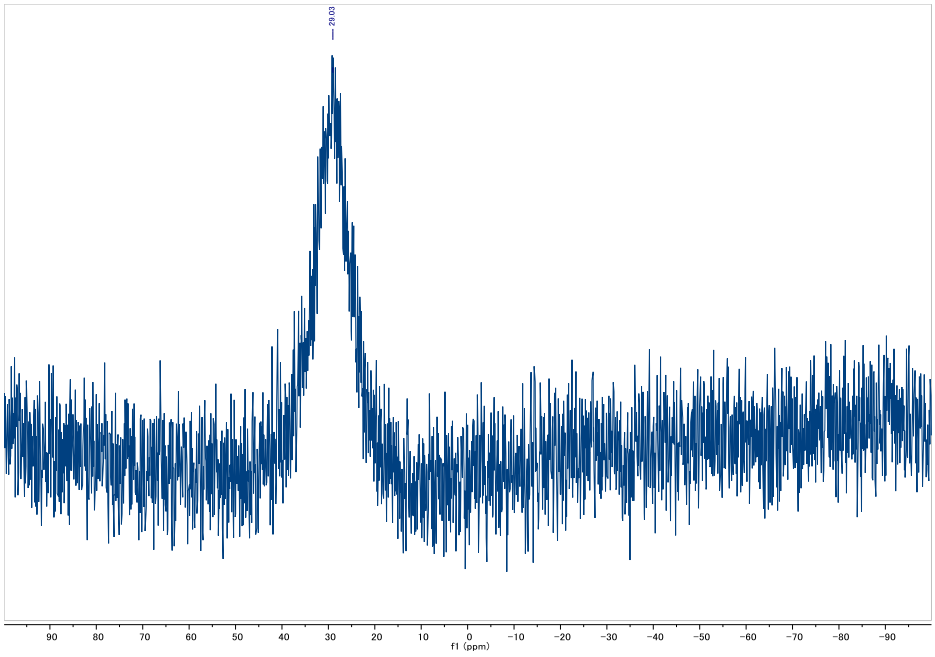

165.96
150.88
145.06
138.88
133.52
129.14
127.20
125.58
121.33
119.13
118.71
f1 (ppm)

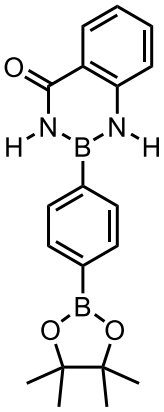

29.17
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
−10
−20
−30
−40
−50
−60
−70
−80
−90

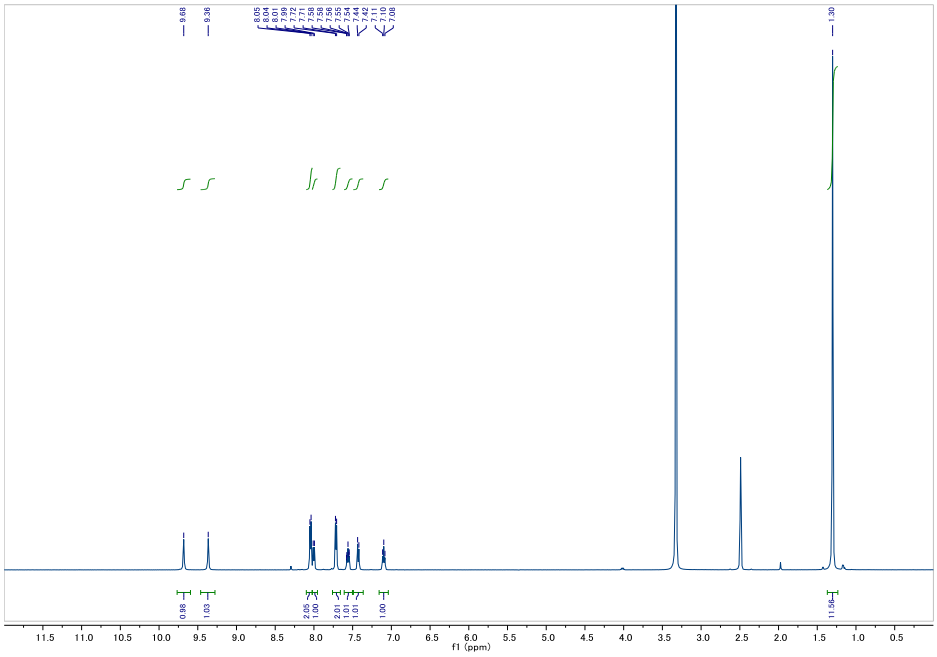

O
N
H
B
N
H
N
Cl
OMe

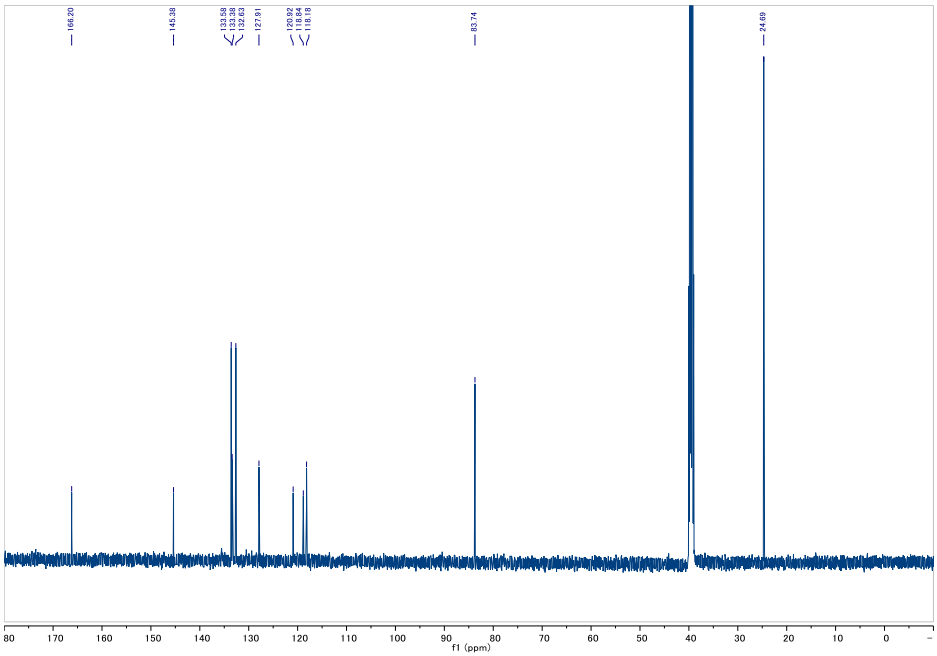

9.65
9.33
8.03
8.01
7.87
7.86
7.61
7.60
7.59
7.59
7.58
7.58
7.57
7.56
7.17
7.17
7.15
7.15
7.14
7.14
7.13
7.13
7.12
3.92
1.00
1.00
0.84
1.01
2.12
1.04
1.12
2.01
f1 (ppm)

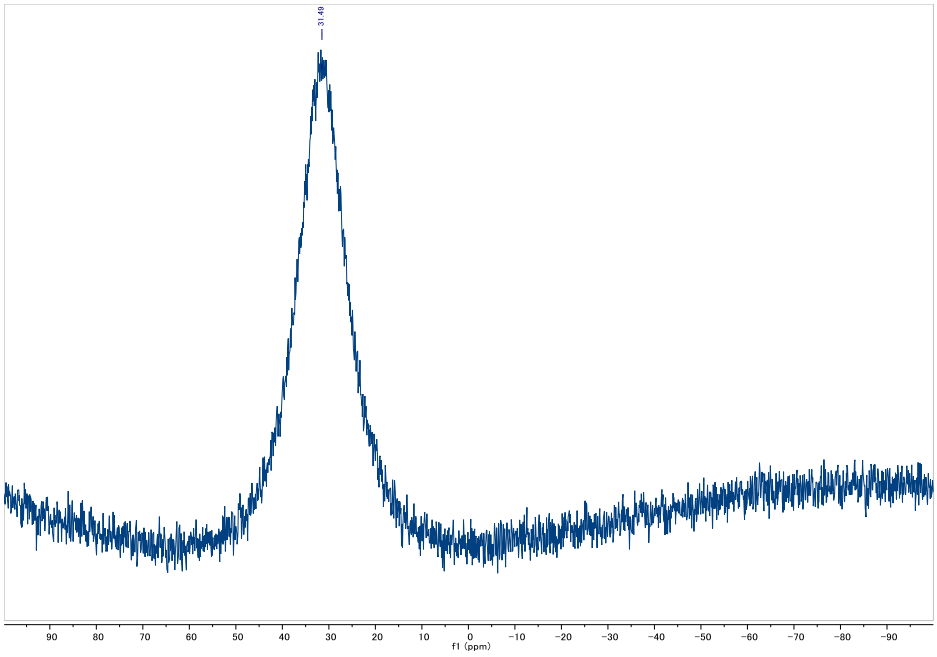

166.87
165.99
151.95
145.02
133.51
127.90
121.31
119.10
118.73
118.67
110.38
56.16
f1 (ppm)


29.03
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
f1 (ppm)




9.68
9.36
8.05
8.04
8.01
7.99
7.72
7.71
7.58
7.58
7.56
7.55
7.54
7.44
7.42
7.11
7.10
7.08
1.30
0.88
1.03
2.05
2.00
2.01
1.02
1.01
1.00
11.56
f1 (ppm)


166.20
145.38
133.58
133.38
132.63
127.91
120.92
118.84
118.18
83.74
24.69
f1 (ppm)


31.49
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
−10
−20
−30
−40
−50
−60
−70
−80
−90