Synthesis of borinic acids and borinate adducts using diisopropylaminoborane

Ludovic Marciasini, Bastien Cacciuttolo, Michel Vaultier and Mathieu Pucheault*

Institut des Sciences Moléculaires, UMR 5255, Université de Bordeaux, IPB, CNRS, 351 Cours de la libération, F-33405 Talence Cedex, France

Supporting information

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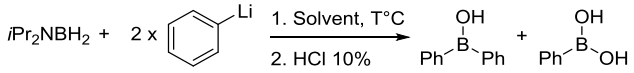
I. COMPLEMENTARY DATA

Table 1: Addition of Phenyllithium on iPr_2NBH_2



1 Li-2a 3a 4a

Entry	Solvent	T (°C)	^{11}B NMR ratio $Ph_2B(OH)$ **3**	$PhB(OH)_2$ **4**
1	THF	- 78	32	32
2	THF	- 20	84	16
3	THF	0	77	18
4	THF	40	71	29
5	MTBE	- 20	74	36
6	Et_2O	- 20	60	40
7	Toluene/THF 4:1	- 20	20	80

II. GENERALITIES

THF and diethyl ether were dried over sodium/benzophenone and freshly distilled before use. Acetonitrile, toluene, methylene chloride, and ethyl acetate were dried over calcium hydride and freshly distilled before use. Methanol was dried over magnesium/iodine and freshly distillated before use. All those process were done under an atmosphere of argon.

All commercially available reagents were use directly as received unless specified. Triethylamine and di*iso*propylamine for coupling reaction were dried over calcium hydride and freshly distilled before use. All the laboratory glassware was dried in oven and cooled under vacuum before use. After reaction involving metal (catalyst, additive …), glassware was washed with a solution of hydrochloric acid and hydrogen peroxide.

Analytical thin layer chromatography (TLC) was carried out using 0.25 mm silica plates purchased from Merck. Eluted plates were visualized using KMnO4 solution. Silica gel chromatography was performed using 230–400 mesh silica gel purchased from Merck.

^{1}H NMR were recorded on Brucker Advance 300, Advance 400 or Advance 600 spectrometer. Chemical shift (δ) are given in ppm relative to tetramethylsilane (external standard). The following abbreviations were used to explain the multiplicities: s = singlet, d =doublet, m = multiplet, t = triplet, dd = doublet of doublet, td = triplet of doublet, ddd = doublet of doublet of doublet, dt = doublet of triplet, q = qudruplet.

^{13}C NMR were recorded on Brucker Advance 300, Advance 400 or Advance 600 spectrometer. Chemical shift (δ) are given in ppm relative to tetramethylsilane (external standard).

^{11}B NMR were recorded on Brucker Advance 300 or Advance 400 spectrometer. Chemical shift (δ) are given in ppm relative to $BF_3.OEt_2$ (external standard).

^{19}F NMR were recorded on a Brucker Advance 400 spectrometer. Chemical shift (δ) are given in ppm relative to $BF_3.OEt_2$ (external standard).

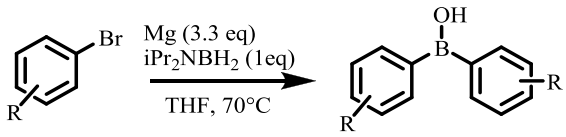
GC-MS analysis was realized on a Agilent 7890A equipped with a J&W Scientific DB-1701 capillary column, a Agilent 5975C triple axis detector (EI) using the following method : 50°C for 5 min then 10°C/min until 220°C

LC-MS analysis was performed on a Shimazu LCMS-2020 equipped with an ESI-MS detector and a UV deuterium lamp. The samples were analyzed using the following the procedure: bypass injection using CH_3CN/H_2O 70/30. Samples were diluted in CH_3CN (LC-MS grade) except if noticed.

The melting point was recorded on a Mettler Toledo DSC1-star system using the following method: 30°C to 300°C at 20°C/min.

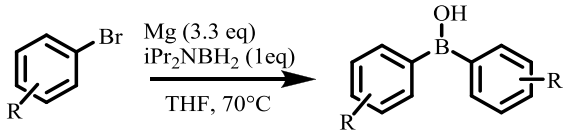
III. GENERAL PROCEDURES

1. General procedure A : borinic acid synthesis using liquid aryl bromides



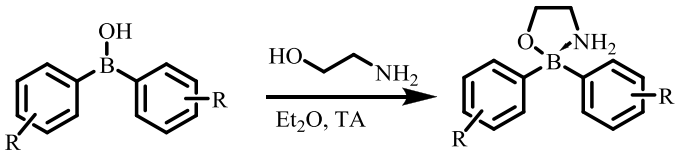
To a suspension of magnesium (16.5 mmol, 401 mg) in a solution of di*iso*propylaminoborane (5 mmol, 0.8 mL) in anhydrous THF (40 mL), at room temperature, was added aryl bromide (11 mmol). The mixture was then heated at 70°C under stirring during 20h, then cooled at 0°C and quenched with a 3M aqueous HCl solution (25 mL). The mixture was stirred for 45 minutes at room temperature. To this solution was added water (20 mL) and diethyl ether (20 mL) and the organic phase was separated. The aqueous phase was then extracted with DCM (6x30 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to afford crude borinic acid. The crude borinic acid can be used in the general procedures C or D to afford pure borinates derivatives.

2. General procedure B : borinic acid synthesis using solid aryl bromides



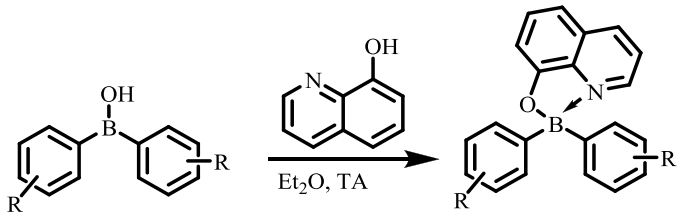
To a suspension of magnesium (16.5 mmol, 401 mg) in a solution of di*iso*propylaminoborane (5 mmol, 0.8 mL) in anhydrous THF (30 mL), at room temperature, was added a solution of aryl bromide (11 mmol) in anhydrous THF (10 mL). The mixture was then heated at 70°C under stirring during 20h, then cooled at 0°C and quenched with a 3M aqueous HCl solution (25 mL). The mixture was stirred for 45 minutes at room temperature. To this solution was added water (20 mL) and diethyl ether (20 mL) and the organic phase was separated. The aqueous phase was then extracted with DCM (6x30 mL) and the combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to afford crude borinic acid. The crude borinic acid can be used in the general procedures C or D to afford pure derivatives.

3. General procedure C : Ethanolamine workup



To a well stirred suspension of crude borinic acid (5 mmol) in diethyl ether (20 mL) was added ethanolamine (0.36 mL, 6 mmol).. After 15h of stirring at room temperature, in some cases, pentane was added to complete the formation of solid borinate, the reaction mixture was then filtered over a fritted glass, washed with cold pentane and dried under high vacuum to afford pure borinate adduct.

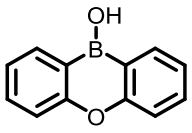
4. General procedure D : 8-hydroxyquinoline workup



To a well stirred suspension of crude borinic acid (5 mmol) in diethyl ether (20 mL) was added 8-hydroxyquinoline (726 mg, 5 mmol). A precipitate appeared immediately, otherwise, addition of pentane cause the precipitation. After 15h of stirring at room temperature, the reaction mixture was filtered over a fritted glass, washed with cold pentane and dried under high vacuum to afford pure borinate adduct.

5. Synthesis of borinic acids ethanolamine complexes

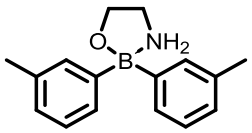
10H-dibenzo[b,e][1,4]oxaborinin-10-ol 3c



CAS 19014-28-9 White solid – 156 mg – 40%

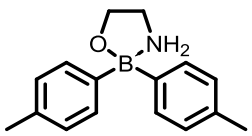
RMN ^{1}H (300 MHz, DMSO-d_6, 25° C)
9.84 (s, 1H), 8.13 (dd, *J* = 7.5, 1.7 Hz, 2H), 7.66 (ddd, *J* = 8.7, 7.1, 1.8 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.27 (td, *J* = 7.5, 0.9 Hz, 2H)
RMN ^{13}C (75 MHz, DMSO-d_6, 25° C)
162.1, 134.0, 132.3, 122.9, 118.0
RMN ^{11}B (64.2 MHz, DMSO-d_6, 25°C)
36.5 (s)

2-((di-m-tolylboryl)oxy)ethanamine 9e



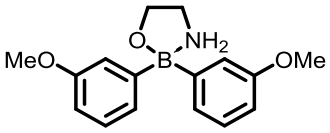
CAS 97979-11-8 White solid – 1.05 g – 82%
Melting point 193.4°C
RMN ^{1}H (300 MHz, DMSO-d_6, 25° C)
7.26 – 7.10 (m, 4H), 7.01 (t, *J* = 7.4 Hz, 2H), 6.84 (d, *J* = 7.4 Hz, 2H), 6.00 (bt, 2H), 3.74 (t, *J* = 6.4 Hz, 2H), 2.80 (p, *J* = 6.4 Hz, 2H), 2.22 (s, 6H)
RMN ^{13}C (75 MHz, $CDCl_3$, 25° C)
135.2, 132.7, 129.1, 126.9, 125.9, 62.80, 41.8, 21.9
RMN ^{11}B (64.2 MHz, 25°C)
4.8 (s)
LC-MS (ESI)
$C_{16}H_{20}BNO$ calculated for $[2M+H]^+$: 507.32, found 506.80

2-((di-o-tolylboryl)oxy)ethanamine 9d



CAS 19565-45-8 White solid – 1.04 g – 69%
Melting point 185.3°C
RMN ^{1}H (300 MHz, DMSO-d_6, 25° C)
7.25 (d, *J* = 7.7 Hz, 4H), 6.94 (d, *J* = 7.7 Hz, 4H), 5.92 (bt, 2H), 3.73 (t, *J* = 6.4 Hz, 2H), 2.80 (t, *J* = 6.4 Hz, 1H), 2.20 (s, 6H)
RMN ^{13}C (75 MHz, $CDCl_3$, 25° C)
148.2, 133.3, 131.6, 127.3, 62.4, 41.3, 20.9
RMN ^{11}B (64.2 MHz, 25°C)
5.7 (s)
LC-MS (ESI)
$C_{16}H_{20}BNO$ calculated for $[2M+H]^+$: 507.32, found 506.80

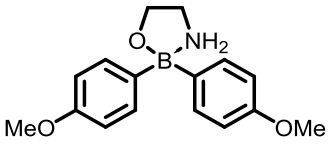
2-((bis(3-methoxyphenyl)boryl)oxy)ethanamine 9f



White solid – 1.12 g – 83%
Melting point 137.7°C
RMN ^{1}H (300 MHz, DMSO-d_6, 25° C)
7.06 (t, *J* = 7.8 Hz, 2H), 6.96 (m, 4H), 6.60 (dd, *J* = 7.8, 1.7 Hz, 2H), 6.05 (bt, 2H), 3.76 (t, *J* = 6.4 Hz, 2H), 3.68 (s, 6H), 2.81 (p, *J* = 6.4 Hz, 2H)

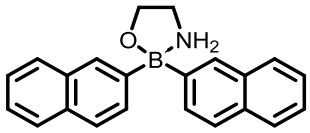
RMN ^{13}C (75 MHz, $CDCl_3$, 25° C)
158.2, 127.6, 123.9, 116.9, 110.1, 62.4, 54.5, 41.3
RMN ^{11}B (64.2 MHz, 25°C)
5.3 (s)
LC-MS (ESI)
$C_{16}H_{20}BNO_3$ calculated for $[2M+H]^+$: 570.30, found 570.70

2-((bis(4-methoxyphenyl)boryl)oxy)ethanamine 9b



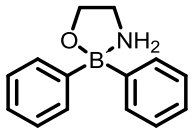
CAS 37763-62-5 White solid – 1.21 g – 84%
Melting point 181.7°C
RMN ^{1}H (300 MHz, DMSO-d_6, 25° C)
7.26 (d, *J* = 8.5 Hz, 4H), 6.72 (d, *J* = 8.5 Hz, 4H), 5.88 (bt, 2H), 3.74 (t, *J* = 6.35 Hz, 2H), 3.67 (s, 6H), 2.80 (t, *J* = 6.35 Hz, 2H)
RMN ^{13}C (75 MHz, $CDCl_3$, 25° C)
148.2, 133.3, 131.6, 127.3, 62.4, 41.3, 20.9
RMN ^{11}B (64.2 MHz, 25°C)
10.3 (s)
LC-MS (ESI)
$C_{16}H_{20}BNO_3$ calculated for $[2M+H]^+$: 570.30, found 570.70

2-((di(naphthalen-2-yl)boryl)oxy)ethanamine 9g



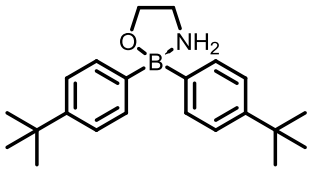
CAS 515157-62-7 White solid – 1.50 g – 92%
Melting point 206.2°C
RMN ^{1}H (300 MHz, DMSO-d_6, 25° C)
7.95 (s, 2H), 7.76 (d, *J* = 7.7 Hz, 4H), 7.73 – 7.61 (m, 4H), 7.44 – 7.30 (m, 4H), 6.34 (bt, 2H), 3.88 (t, *J* = 6.3 Hz, 2H), 3.02 – 2.88 (p, *J* = 6.3 Hz, 2H)
RMN ^{13}C (75 MHz, $CDCl_3$, 25° C)
132.9, 131.9, 130.8, 129.7, 127.4, 127.2, 125.4, 124.9, 124.3, 62.6, 41.6
RMN ^{11}B (64.2 MHz, 25°C)
6.0 (s)
LC-MS (ESI)
$C_{22}H_{20}BNO$ calculated for $[2M+H]^+$: 651.32, found 650.80

((diphenylboryl)oxy)ethanamine 9a



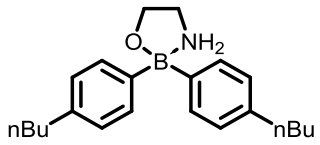
CAS 15614-89-8 White solid – 1.02 g – 91%
Melting point 192.5°C
RMN ^{1}H (300 MHz, DMSO-d_6, 25° C)
7.40 (d, *J* = 7.2 Hz, 4H), 7.13 (t, *J* = 7.2 Hz, 4H), 7.03 (t, *J* = 7.2 Hz, 2H), 6.07 (bt, 2H), 3.77 (t, *J* = 6.35 Hz, 2H), 2.90 – 2.75 (p, *J* = 6.35 Hz, 2H)
RMN ^{13}C (75 MHz, $CDCl_3$, 25° C)
131.5, 126.6, 124.9, 62.4, 41.3
RMN ^{11}B (64.2 MHz, , 25°C) 4.1 (s)

2-((bis(4-(tert-butyl)phenyl)boryl)oxy)ethanamine 9h



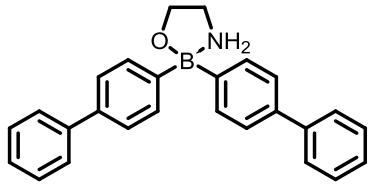
CAS 1379680-33-7 White solid – 1.24 g – 73%
Melting point 255.5°C
RMN ^{1}H (300 MHz, DMSO-d_6, 25° C)
7.32 (d, *J* = 8.2 Hz, 4H), 7.15 (d, *J* = 8.2 Hz, 4H), 5.98 (bt, 2H), 3.75 (t, *J* = 6.25 Hz, 2H), 2.80 (p, *J* = 6.25 Hz, 2H), 1.23 (s, 18H)
RMN ^{13}C (75 MHz, $CDCl_3$, 25° C)
146.7, 131.2, 123.3, 62.4, 41.4, 33.9, 31.4
RMN ^{11}B (64.2 MHz, 25°C)
6.1 (s)
LC-MS (ESI)
$C_{22}H_{32}BNO$ calculated for $[2M+H]^+$: 675.52, found 674.90

2-(bis(4-butylphenyl)boryl)oxy)ethanamine 9i



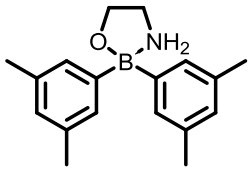
White solid – 1.48 g – 88%
Melting point 99.0°C
RMN ^{1}H (300 MHz, DMSO-d_6, 25° C)
7.29 (d, *J* = 7.7 Hz, 4H), 6.95 (d, *J* = 7.7 Hz, 4H), 5.96 (bt, 2H), 3.75 (t, *J* = 6.4 Hz, 2H), 2.88 – 2.77 (p, *J* = 6.4 Hz, 2H), 2.58 – 2.42 (m, 4H), 1.51 (m, 4H), 1.30 (m, 4H), 0.89 (t, *J* = 7.4 Hz, 6H)
RMN ^{13}C (75 MHz, $CDCl_3$, 25° C)
148.6, 138.4, 131.5, 126.6, 62.4, 41.3, 34.8, 33.5, 21.8, 13.8
RMN ^{11}B (64.2 MHz, 25°C)
5.8 (s)
LC-MS (ESI)
$C_{22}H_{32}BNO$ calculated for $[2M+H]^+$: 675.52, found 674.85

2-(dibiphenyl-4-ylboryloxy)ethanamine 9j



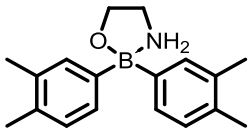
CAS 102032-41-7 White solid – 1.55 g – 82%
Melting point 232°C
RMN ^{1}H (300 MHz, DMSO-d_6, 25° C)
7.60 (d, *J* = 7.3 Hz, 4H), 7.55 (d, *J* = 8.0 Hz, 4H), 7.46 (d, *J* = 7.3 Hz, 4H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 2H), 6.19 (bt, 2H), 3.83 (t, *J* = 6.4 Hz, 2H), 2.95 – 2.83 (p, *J* = 6.4 Hz, 2H)
RMN ^{13}C (75 MHz, $CDCl_3$, 25° C)
151.0, 141.3, 137.0, 132.2, 128.8, 126.7, 126.4, 125.1, 62.6, 41.5
RMN ^{11}B (64.2 MHz, 25°C) : 7.8 (s)
LC-MS (ESI)
$C_{26}H_{24}BNO$ calculated for $[2M+H]^+$: 755.40, found 754.80

2-((bis(3,5-dimethylphenyl)boryl)oxy)ethanamine 9k



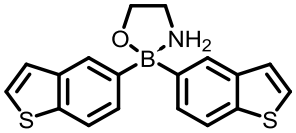
White solid – 1.02 g – 72%
Melting point 295°C
RMN ^{1}H (300 MHz, DMSO-d_6, 25° C)
6.97 (s, 4H), 6.65 (s, 2H), 5.92 (bt, 2H), 3.70 (t, *J* = 6.25 Hz, 2H), 2.78 (p, *J* = 6.25 Hz, 2H), 2.18 (s, 12H)
RMN ^{13}C (75 MHz, $CDCl_3$, 25° C)
134.6, 129.4, 126.3, 62.3, 41.3, 21.3
RMN ^{11}B (64.2 MHz, 25°C)
5.6 (s)
LC-MS (ESI)
$C_{18}H_{24}BNO$ calculated for $[2M+H]^+$: 563.40, found 562.75

2-((bis(3,4-dimethylphenyl)boryl)oxy)ethanamine 9l



CAS 99269-70-2 White solid – 1.11 g – 77%
Melting point 209°C
RMN ^{1}H (300 MHz, DMSO-d_6, 25° C)
7.12 (s, 2H), 7.06 (d, *J* = 7.4 Hz, 2H), 6.87 (d, *J* = 7.4 Hz, 2H), 5.87 (bt, 2H), 3.71 (t, *J* = 6.3 Hz, 2H), 2.78 (p, *J* = 6.3 Hz, 2H), 2.13 (s, 6H), 2.12 (s, 6H)
RMN ^{13}C (75 MHz, $CDCl_3$, 25° C)
133.4, 133.1, 131.9, 129.2, 127.8, 62.30, 41.3, 19.7, 19.2
RMN ^{11}B (64.2 MHz, 25°C)
5.9 (s)
LC-MS (ESI)
$C_{18}H_{24}BNO$ calculated for $[2M+H]^+$: 563.40, found 562.75

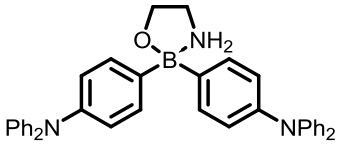
2-(dibenzo[b]thiophen-5-ylboryloxy)ethanamine 9m



White solid – 1.34 g – 79%
Melting point 228°C
RMN ^{1}H (300 MHz, DMSO-d_6, 25° C)
7.92 (s, 2H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.55 (d, *J* = 5.4 Hz, 2H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 5.4 Hz, 2H), 6.21 (bt, 2H), 3.85 (t, *J* = 6.4 Hz, 2H), 2.98 – 2.85 (p, *J* = 6.4 Hz, 2H)

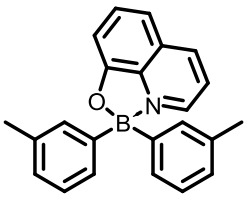
RMN ^{13}C (75 MHz, $CDCl_3$, 25° C)
147.3, 138.9, 136.4, 128.8, 126.4, 125.2, 124.0, 120.5, 62.6, 41
RMN ^{11}B (64.2 MHz, 25°C)
6.7 (s)
LC-MS (ESI)
$C_{18}H_{16}BNOS_2$ calculated for $[2M+H]^+$: 675.16, found 674.55

2-(ditriphenylamine-4-ylboryloxy)ethanamine 9n



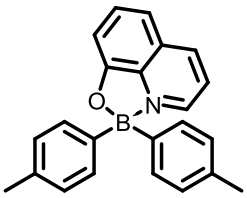
White solid – 2.64 g – 95%
Melting point 208°C
RMN ^{1}H (300 MHz, DMSO-d_6, 25° C)
7.40 (d, *J* = 8.1 Hz, 4H), 7.23 (dd, *J* = 10.6, 5.2 Hz, 8H), 7.01 – 6.86 (m, 16H), 5.87 (bs, 2H), 3.82 (t, *J* = 6.4 Hz, 2H), 2.95 – 2.84 (t, *J* = 6.4 Hz, 2H)
RMN ^{13}C (75 MHz, $CDCl_3$, 25° C)
147.7, 144.3, 132.8, 129.2, 123.69, 122.8, 121.9, 62.6, 41.5
RMN ^{11}B (64.2 MHz, 25°C) : 4.9 (s)
LC-MS (ESI)
$C_{38}H_{34}BN_3O$ calculated for $[2M+H]^+$: 1119.56, found 1118.85

8-((di-m-tolylboryl)oxy)quinolone 10e



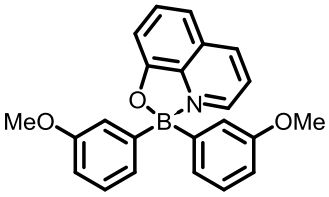
CAS 287200-17-3 Yellow solid – 1.22 g – 72%
Melting point 168°C
RMN ^{1}H (300 MHz, DMSO-d_6, 25° C)
9.11 (d, *J* = 5.0 Hz, 1H), 8.76 (d, *J* = 8.3 Hz, 1H), 7.89 (dd, *J* = 8.3, 5.0 Hz, 1H), 7.69 (t, *J* = 8.3 Hz, 1H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.24 – 7.05 (m, 7H), 6.97 (d, *J* = 7.0 Hz, 2H), 2.21 (s, 6H)
RMN ^{13}C (75 MHz, $CDCl_3$, 25° C)
157.8, 147.47, 141.3, 139.8, 136.4, 135.8, 132.3, 132.0, 128.5, 128.0, 127.2, 127.1, 124.1, 112.8, 108.6, 21.3
RMN ^{11}B (64.2 MHz, 25°C)
12.8 (s)
LC-MS (ESI)
$C_{23}H_{20}BNO$ calculated for $[M+H]^+$: 338.16, found 337.80 and calculated for $[2M+Na]^+$: 697.32, found 696.80

8-((di-p-tolylboryl)oxy)quinolone 10d



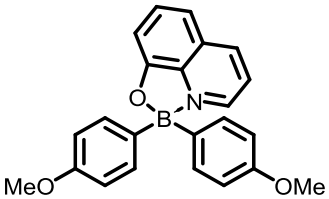
CAS 132722-18-0 Yellow solid – 1.25 g – 75%
Melting point 205°C
RMN ^{1}H (300 MHz, DMSO-d_6, 25° C)
9.02 (d, *J* = 5.0 Hz, 1H), 8.75 (d, *J* = 8.3 Hz, 1H), 7.87 (dd, *J* = 8.3, 5.0 Hz, 1H), 7.69 (t, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 4H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 4H), 2.22 (s, 6H)
RMN ^{13}C (75 MHz, $CDCl_3$, 25° C)
158.4, 144.6, 141.6, 140.2, 136.8, 135.8, 132.8, 132.0, 128.5, 128.4, 124.6, 113.2, 109.0, 21.3
RMN ^{11}B (64.2 MHz, 25°C)
13.0 (s)
LC-MS (ESI)
$C_{23}H_{20}BNO$ calculated for $[M+H]^+$: 338.16, found 337.85 and calculated for $[2M+Na]^+$: 697.32, found 696.65

8-((bis(3-methoxyphenyl)boryl)oxy)quinolone 10f



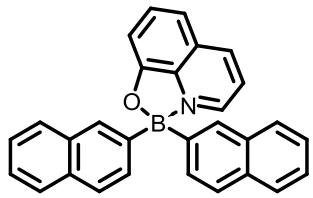
CAS 1345862-12-5 Yellow solid – 1.44 g – 78%
Melting point 133°C
RMN ^{1}H (300 MHz, DMSO-d_6, 25° C)
9.15 (d, *J* = 5.0 Hz, 1H), 8.78 (d, *J* = 8.2 Hz, 1H), 7.90 (dd, *J* = 8.2, 5.0 Hz, 1H), 7.71 (t, *J* = 8.2 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.16 (m, 3H), 6.94 (d, *J* = 7.5 Hz, 2H), 6.89 (d, *J* = 2.6 Hz, 2H), 6.74 (dd, *J* = 8.2, 2.6 Hz, 2H), 3.66 (s, 6H)
RMN ^{13}C (75 MHz, $CDCl_3$, 25° C)
158.6, 157.7, 149.0, 141.4, 140.0, 136.3, 132.3, 128.4, 128.0, 124.1, 123.6, 117.2, 113.0, 111.4, 108.7, 54.6
RMN ^{11}B (64.2 MHz, 25°C)
12.7 (s)
LC-MS (ESI)
$C_{23}H_{20}BNO_3$ calculated for $[M+H]^+$: 370.15, found 369.40 and calculated for $[2M+Na]^+$: 761.30, found 760.70

8-((bis(4-methoxyphenyl)boryl)oxy)quinolone 10b



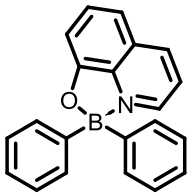
CAS 137001-21-9 Yellow solid – 1.21 g – 65%
Melting point 225°C
RMN ^{1}H (300 MHz, DMSO-d_6, 25° C)
8.99 (d, *J* = 5.0 Hz, 1H), 8.75 (d, *J* = 8.2 Hz, 1H), 7.87 (dd, *J* = 8.2, 5.0 Hz, 1H), 7.69 (t, *J* = 8.2 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 4H), 7.14 (d, *J* = 8.2 Hz, 1H), 6.78 (d, *J* = 8.2 Hz, 4H), 3.68 (s, 6H)
RMN ^{13}C (75 MHz, $CDCl_3$, 25° C)
158.3, 157.9, 141.1, 139.7, 138.8, 136.3, 132.7, 132.3, 128.0, 124.1, 112.9, 112.7, 108.5, 54.7
RMN ^{11}B (64.2 MHz,, 25°C)
12.4 (s)
LC-MS (ESI)
$C_{23}H_{20}BNO_3$ calculated for $[M+H]^+$: 370.15, found 369.80 and calculated for $[2M+Na]^+$: 761.30, found 760.65

8-((di(naphthalen-2-yl)boryl)oxy)quinolone 10g



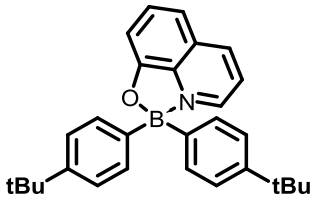
CAS 256664-74-1 Yellow solid – 1.24 g – 61%
Melting point 204°C
RMN ^{1}H (300 MHz, DMSO-d_6, 25° C)
9.31 (d, *J* = 5.0 Hz, 1H), 8.83 (d, *J* = 8.3 Hz, 1H), 7.97 (dd, *J* = 8.3, 5.0 Hz, 1H), 7.90 (s, 2H), 7.85 – 7.74 (m, 7H), 7.59 (dd, *J* = 8.2, 1.1 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.45 – 7.37 (m, 4H), 7.27 (d, *J* = 8.0 Hz, 1H)
RMN ^{13}C (75 MHz, $CDCl_3$, 25° C)
157.8, 147.4, 141.3, 139.9, 136.3, 132.3, 131.4, 128.0, 127.3, 126.5, 124.1, 112.8, 108.7
RMN ^{11}B (64.2 MHz, , 25°C)
12.4 (s)
LC-MS (ESI)
$C_{29}H_{20}BNO$ calculated for $[M+H]^+$: 410.16, found 408.95

8-((diphenylboryl)oxy)quinolone 10a



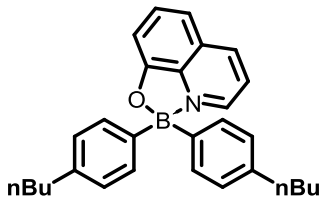
CAS 5123-16-0 Yellow solid – 1.25 g – 81%
Melting point 214°C
RMN ^{1}H (300 MHz, DMSO-d_6, 25° C)
9.13 (dd, *J* = 5.1, 0.9 Hz, 1H), 8.78 (dd, *J* = 8.4, 0.9 Hz, 1H), 7.90 (dd, *J* = 8.4, 5.1 Hz, 1H), 7.75 – 7.68 (m, 1H), 7.43 (dd, *J* = 8.4, 0.5 Hz, 1H), 7.40 – 7.33 (m, 4H), 7.26 – 7.13 (m, 7H)
RMN ^{13}C (75 MHz, $CDCl_3$, 25° C)
157.8, 147.4, 141.3, 139.9, 136.4, 132.3, 131.4, 128.0, 127.3, 126.52, 124.2, 112.9, 108.7
RMN ^{11}B (64.2 MHz, , 25°C)
11.3 (s)
LC-MS (ESI)
$C_{21}H_{16}BNO$ calculated for $[M+H]^+$: 310.13, found 309.85

8-((bis(4-(tert-butyl)phenyl)boryl)oxy)quinolone 10h



CAS 159122-13-1 Yellow solid – 1.67 g – 79%
Melting point 235°C
RMN ^{1}H (300 MHz, DMSO-d_6, 25° C)
9.10 (d, *J* = 5.0 Hz, 1H), 8.76 (d, *J* = 8.3 Hz, 1H), 7.88 (dd, *J* = 8.3, 5.0 Hz, 1H), 7.70 (t, *J* = 8.3 Hz, 1H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 4H), 7.23 (d, *J* = 8.3 Hz, 3H), 7.15 (d, *J* = 7.8 Hz, 1H), 1.22 (s, 18H)
RMN ^{13}C (75 MHz, $CDCl_3$, 25° C)
157.9, 148.6, 144.1, 141.2, 139.7, 136.4, 132.9, 131.2, 128.0, 124.0, 112.7, 108.5, 34.0, 31.2
RMN ^{11}B (64.2 MHz, , 25°C)
11.5 (s)
LC-MS (ESI)
$C_{29}H_{32}BNO$ calculated for $[M+H]^+$: 422.26, found 421.95 and calculated for $[2M+Na]^+$: 865.52, found 864.80

8-(bis(4-butylphenyl)boryloxy)quinolone 10i



Yellow solid – 1.53 g – 73%

Melting point 112°C

RMN ^{1}H (300 MHz, DMSO-d_6, 25° C)

9.07 (d, *J* = 4.5 Hz, 1H), 8.75 (d, *J* = 7.9 Hz, 1H), 7.87 (dd, *J* = 7.9, 4.5 Hz, 1H), 7.69 (t, *J* = 7.9 Hz, 1H), 7.40 (d, *J* = 7.9 Hz, 1H), 7.27 (d, *J* = 7.9 Hz, 4H), 7.15 (d, *J* = 7.9 Hz, 1H), 7.03 (d, *J* = 7.9 Hz, 4H), 2.55 – 2.42 (m, 4H), 1.56 – 1.42 (m, 4H), 1.26 (m, 4H), 0.85 (t, *J* = 7.3 Hz, 6H)

RMN ^{13}C (75 MHz, $CDCl_3$, 25° C)

157.9, 144.4, 141.1, 140.3, 139.7, 136.4, 132.3, 131.4, 128.0, 127.3, 124.1, 112.7, 108.5, 34.7, 33.3, 21.8, 13.7

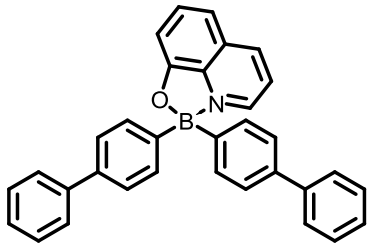
RMN ^{11}B (64.2 MHz, , 25°C)

13.5 (s)

LC-MS (ESI)

$C_{29}H_{32}BNO$ calculated for $[M+H]^+$: 422.26, found 421.90 and calculated for $[2M+Na]^+$: 865.52, found 865.00

8-((di([1,1'-biphenyl]-4-yl)boryl)oxy) 10j



CAS 1345864-85-8 Yellow solid – 1.91 g – 83%

Melting point 182°C

RMN ^{1}H (300 MHz, DMSO-d_6, 25° C)

9.22 (d, *J* = 5.0 Hz, 1H), 8.80 (d, *J* = 8.3 Hz, 1H), 7.93 (dd, *J* = 8.3, 5.0 Hz, 1H), 7.73 (t, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 7.4 Hz, 4H), 7.56 – 7.48 (m, 8H), 7.43 (m, 5H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 1H)

RMN ^{13}C (75 MHz, $CDCl_3$, 25° C)

157.8, 146.4, 141.4, 140.7, 140.0, 138.5, 136.4, 132.1, 128.8, 128.1, 127.0, 126.5, 125.8, 124.2, 113.0, 108.8

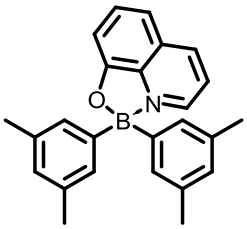
RMN ^{11}B (64.2 MHz, , 25°C)

14.1 (s)

LC-MS (ESI)

$C_{33}H_{24}BNO$ calculated for $[2M+Na]^+$: 945.40, found 944.65

8-((bis(3,5-dimethylphenyl)boryl)oxy)quinolone 10k



Yellow solid – 1.04 g – 58%

Melting point 221°C

RMN ^{1}H (300 MHz, DMSO-d_6, 25° C)

9.08 (d, *J* = 5 Hz, 1H), 8.75 (d, *J* = 8.3 Hz, 1H), 7.89 (dd, *J* = 8.3 Hz, 5.0 Hz 1H), 7.69 (t, *J* = 8 Hz 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 6.94 (s, 4H), 6.77 (s, 2H), 2.16 (s, 12H)

RMN ^{13}C (75 MHz, $CDCl_3$, 25° C)

157.9, 147.6, 141.2, 139.7, 136.4, 135.7, 132.3, 129.2, 128.0, 127.9, 124.1, 112.7, 108.6, 21.2

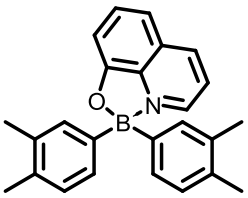
RMN ^{11}B (64.2 MHz, , 25°C)

12.7 (s)

LC-MS (ESI)

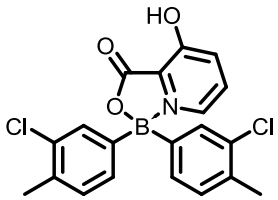
$C_{25}H_{24}BNO$ calculated for $[M+H]^+$: 366.20, found 365.70 and calculated for $[2M+Na]^+$: 753.40, found 752.95

8-((bis(3,4-dimethylphenyl)boryl)oxy)quinolone 10l



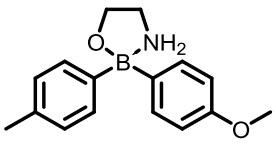
CAS 29190-60-1 Yellow solid – 1.50 g – 82%
Melting point 168°C
RMN ^{1}H (300 MHz, DMSO-d_6, 25° C)
9.01 (d, *J* = 5.0 Hz, 1H), 8.73 (d, *J* = 8.3 Hz, 1H), 7.86 (dd, *J* = 8.3, 5.0 Hz, 1H), 7.68 (t, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 7.10 (s, 2H), 7.04 (d, *J* = 7.5 Hz, 2H), 6.95 (d, *J* = 7.5 Hz, 2H), 2.13 (s, 6H), 2.11 (s, 6H)
RMN ^{13}C (75 MHz, $CDCl_3$, 25° C)
158.0, 144.8, 141.1, 139.6, 136.4, 134.5, 133.9, 132.8, 132.3, 129.0, 128.5, 128.0, 124.0, 112.6, 108.5, 19.5, 19.2
RMN ^{11}B (64.2 MHz, , 25°C)
13.8 (s)
LC-MS (ESI)
$C_{25}H_{24}BNO$ calculated for $[M+H]^+$: 366.20, found 365.85 and calculated for $[2M+Na]^+$: 753.56, found 752.95

AN0128



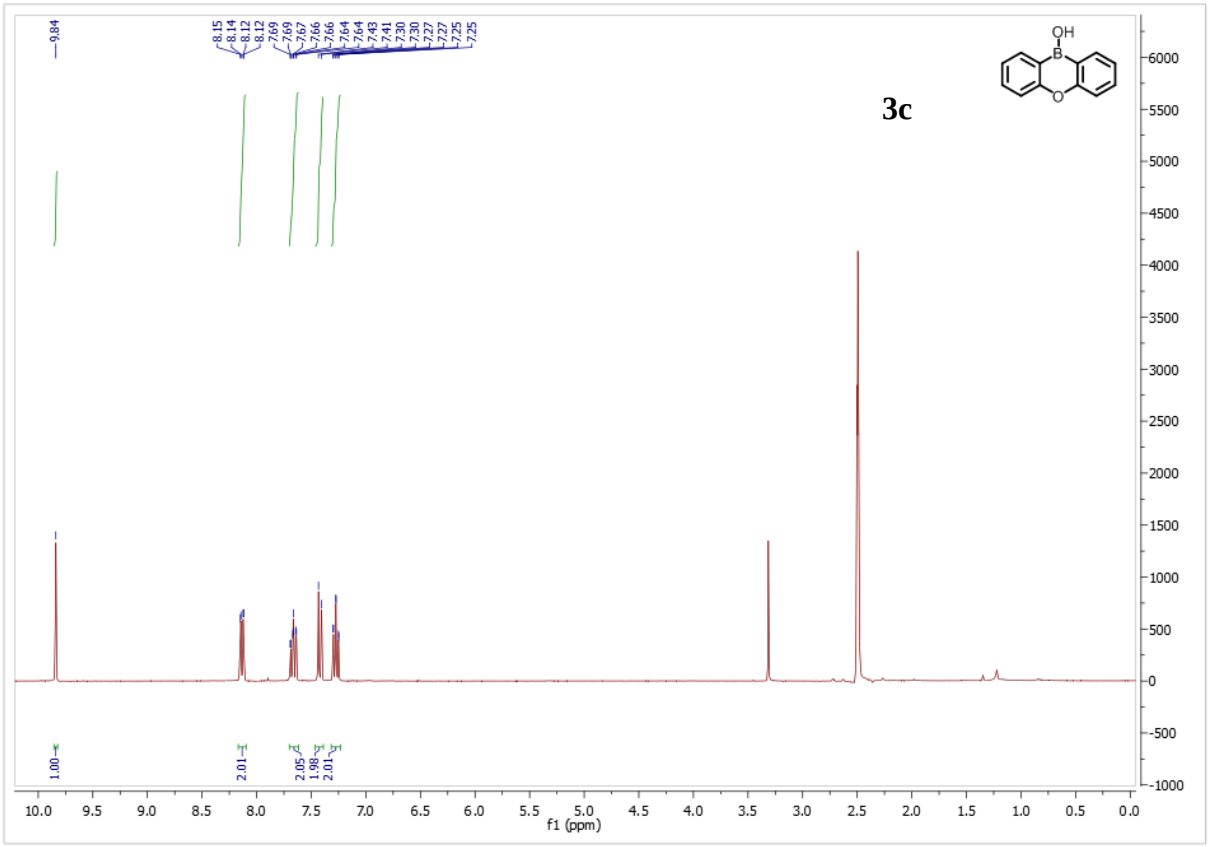
CAS 872044-70-7 White solid – 592 mg – 74%
RMN ^{1}H (300 MHz, DMSO-d_6, 25° C)
8.24 (t, *J* = 2.9 Hz, 1H), 8.14 (dd, *J* = 4.9, 1.3 Hz, 2H), 7.52 (m, 6H), 2.29 (s, 6H)
RMN ^{13}C (75 MHz, DMSO-d_6, 25° C)
173.1, 160.8, 132.1, 134.9, 135.0, 130.2, 129.4, 19.8
RMN ^{11}B (64.2 MHz, DMSO-d_6, 25°C)
6.46 (s)

2-(((4-methoxyphenyl)(p-tolyl)boryl)oxy)ethanamine 9p



CAS 7294-53-3 White solid – 1.05 g – 78%
Melting point 154°C
RMN ^{1}H (300 MHz, DMSO-d_6, 25° C)
7.26 (m, 4H), 6.94 (d, *J* = 7.5 Hz, 2H), 6.71 (d, *J* = 8.4, 1.8 Hz, 2H), 5.89 (bt, 2H), 3.74 (t, *J* = 6.1 Hz, 2H), 3.67 (s, 3H), 2.80 (p, *J* = 6.1 Hz, 2H), 2.21 (s, 3H)
RMN ^{13}C (75 MHz, $CDCl_3$, 25° C)
157.3, 133.3, 132.6, 131.6, 127.3, 112.3, 62.4, 54.6, 41.3, 20.9
RMN ^{11}B (64.2 MHz, 25°C)
5.19 (s)
LC-MS (ESI)
$C_{16}H_{20}BNO_2$ calculated for $[2M+H]^+$: 539.32, found 538.70

To a suspension of magnesium (18.7 mmol, 455 mg) in a solution of di*iso*propylaminoborane (7.5 mmol, 1.2 mL) in anhydrous THF (30 mL), at room temperature, was added 4-bromoanisole (5 mmol). The mixture was then heated at 70°C under stirring during 20h. After cooling at room temperature, all volatiles were removed under vacuum. To the resulting oil were added anhydrous THF (40 mL) and 4-bromotoluene (7.5 mmol), the mixture was heated at 70°C during 20h. After cooling at 0°C, the reaction was quenched with a 3M aqueous HCl solution (25 mL) and was stirred 45 minutes at room temperature. To this solution was added water (20 mL), diethyl ether (20 mL) and the organic phase was separated. The aqueous phase was then extracted with DCM (6x30 mL) and the combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was suspended in diethyl ether (20 mL) and ethanolamine (0.36 mL, 6 mmol) was slowly added to the mixture. After 15h of stirring at room temperature, the reaction mixture was filtered over a fritted glass, washed with cold pentane and dried under high vacuum to afford 1.05g of pure borinate (78% yield).


3c
OH
B
O
9.84
8.15
8.14
8.12
8.12
7.69
7.69
7.67
7.66
7.66
7.64
7.64
7.43
7.41
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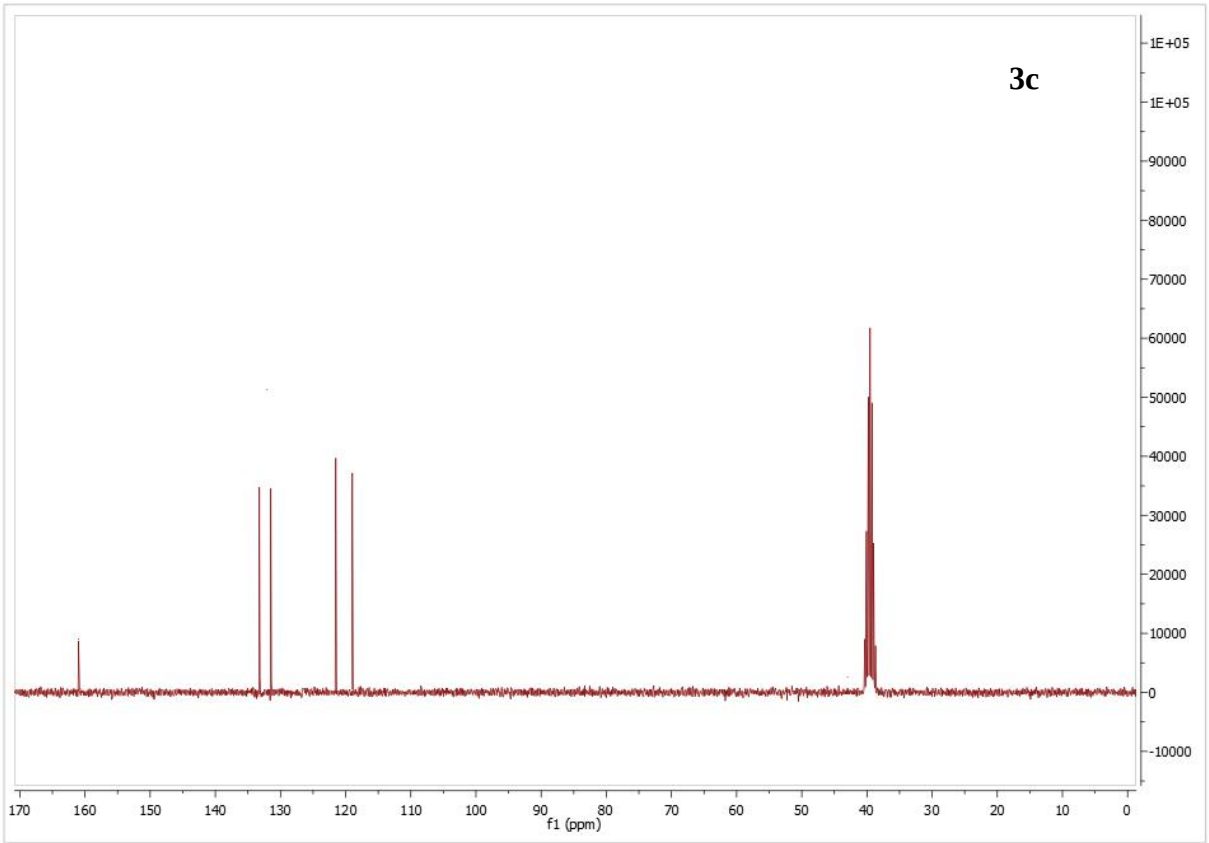
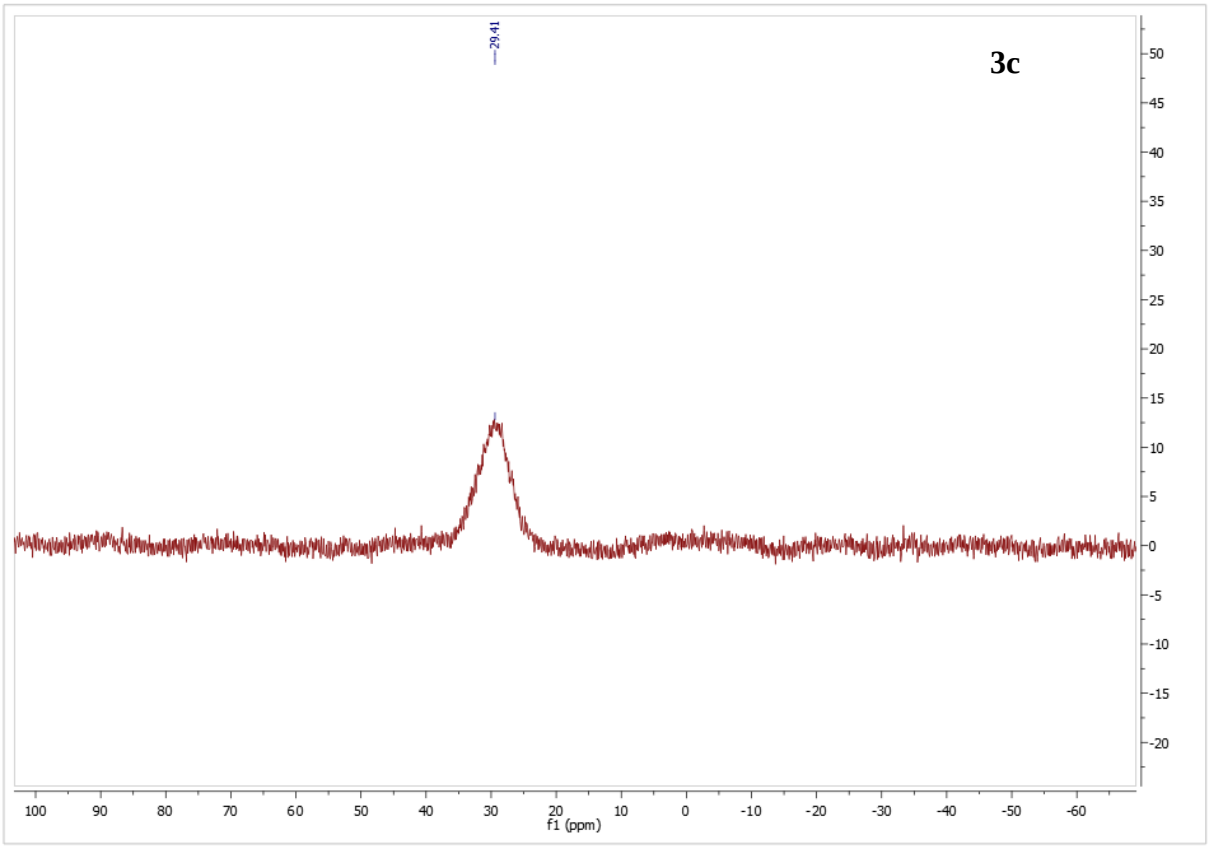
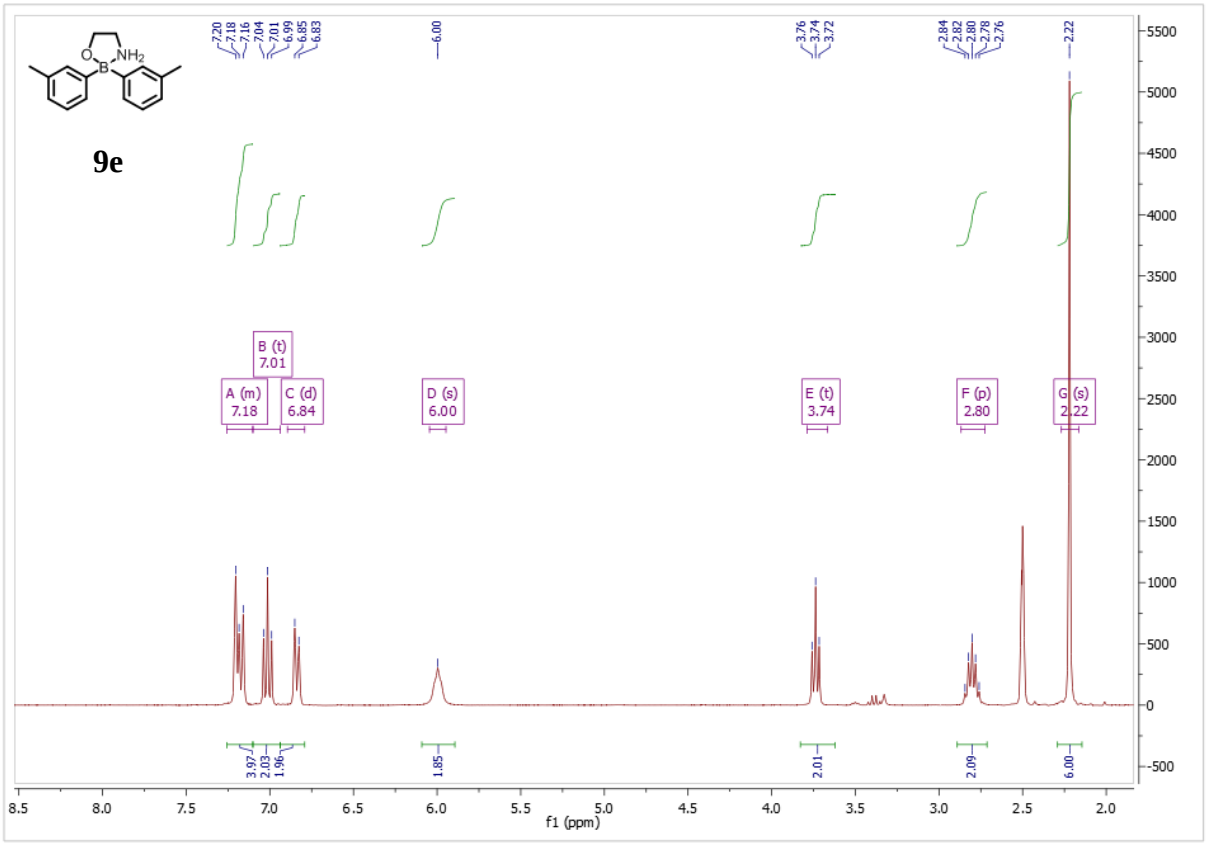
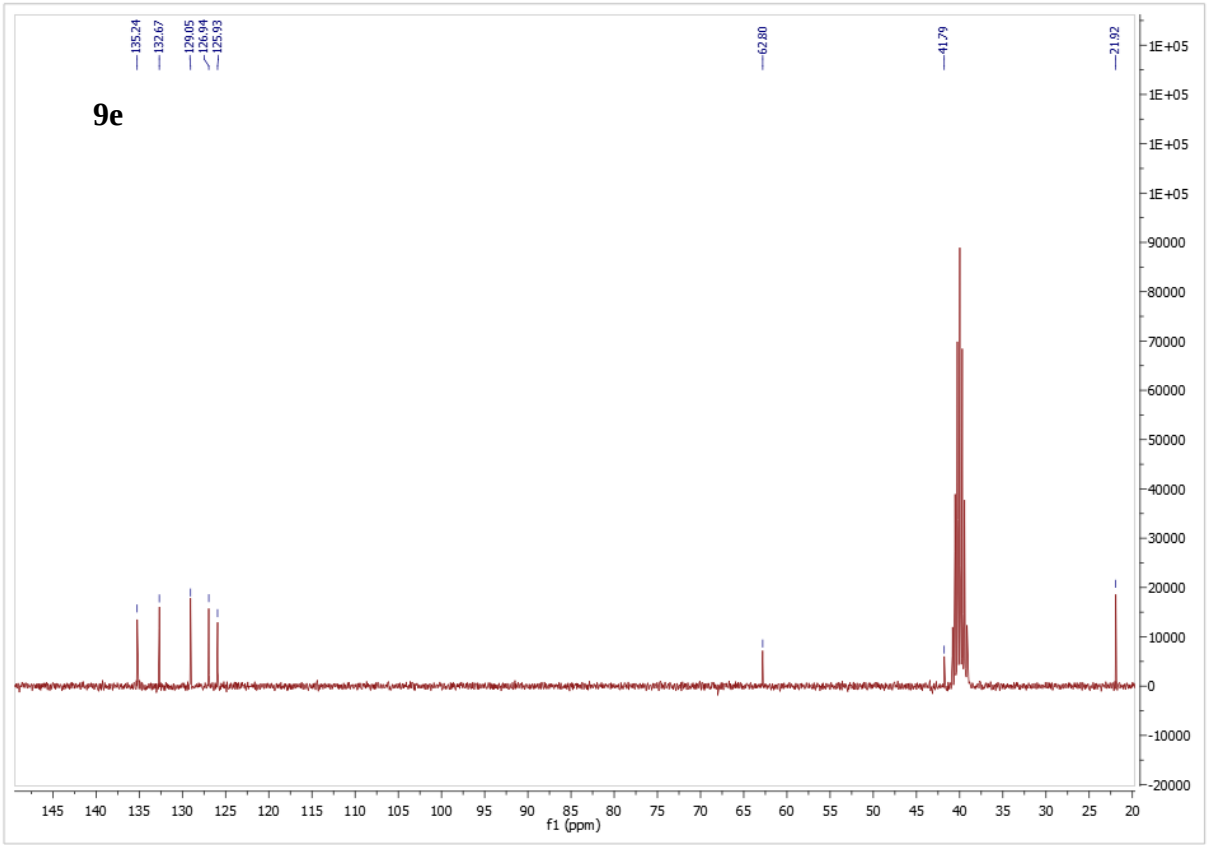
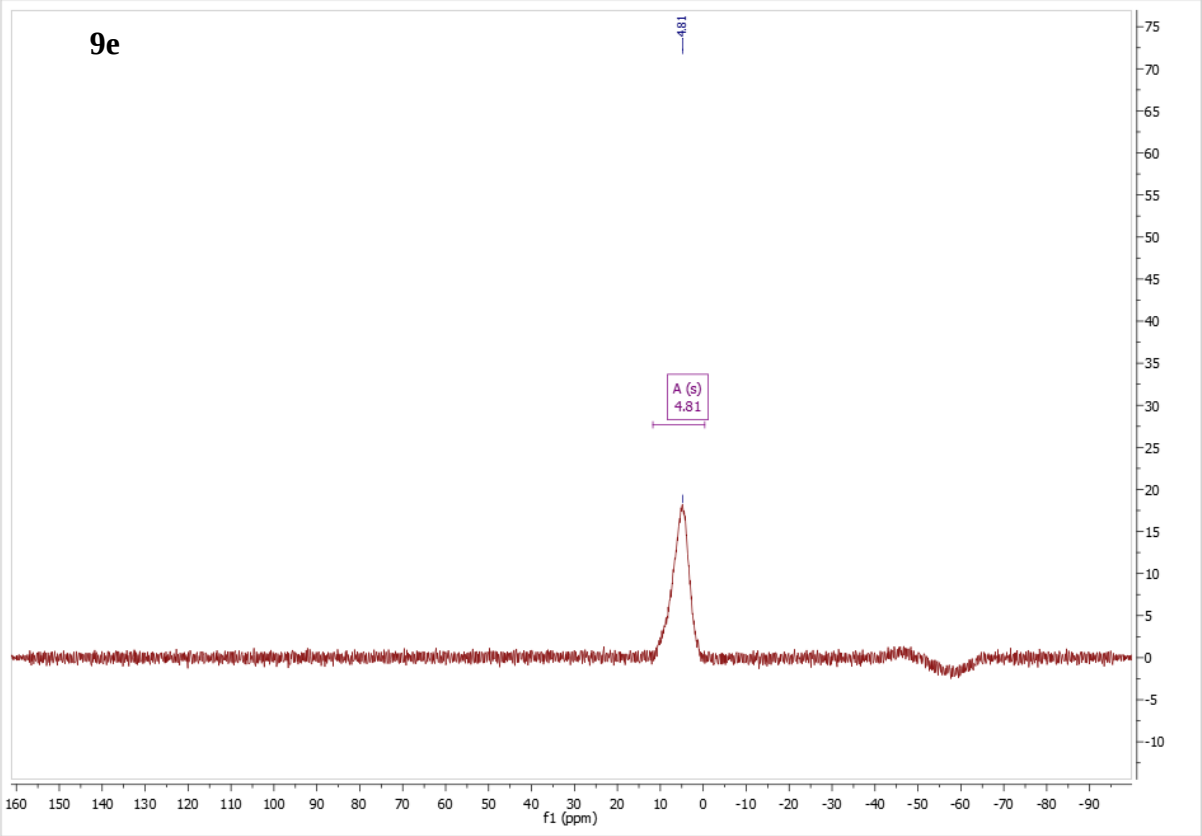
2.01
2.05
1.98
2.01
f1 (ppm)

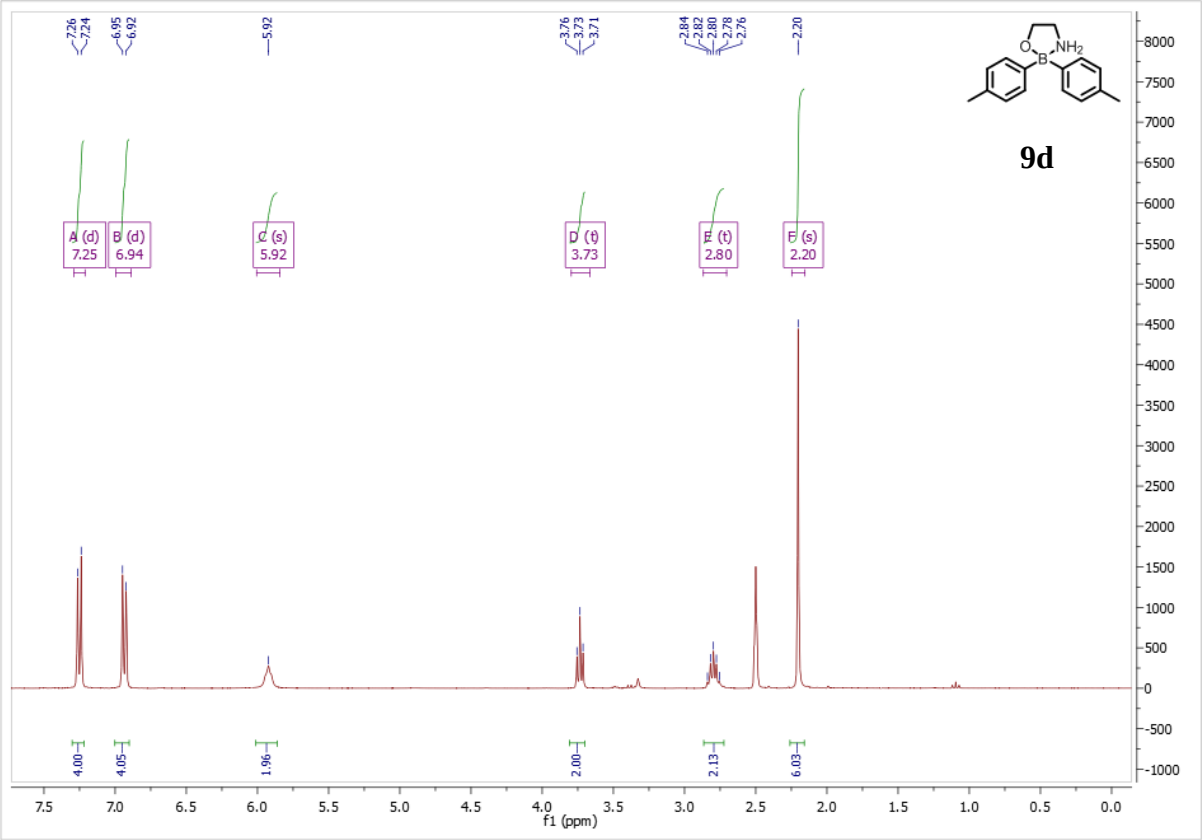

3c
f1 (ppm)

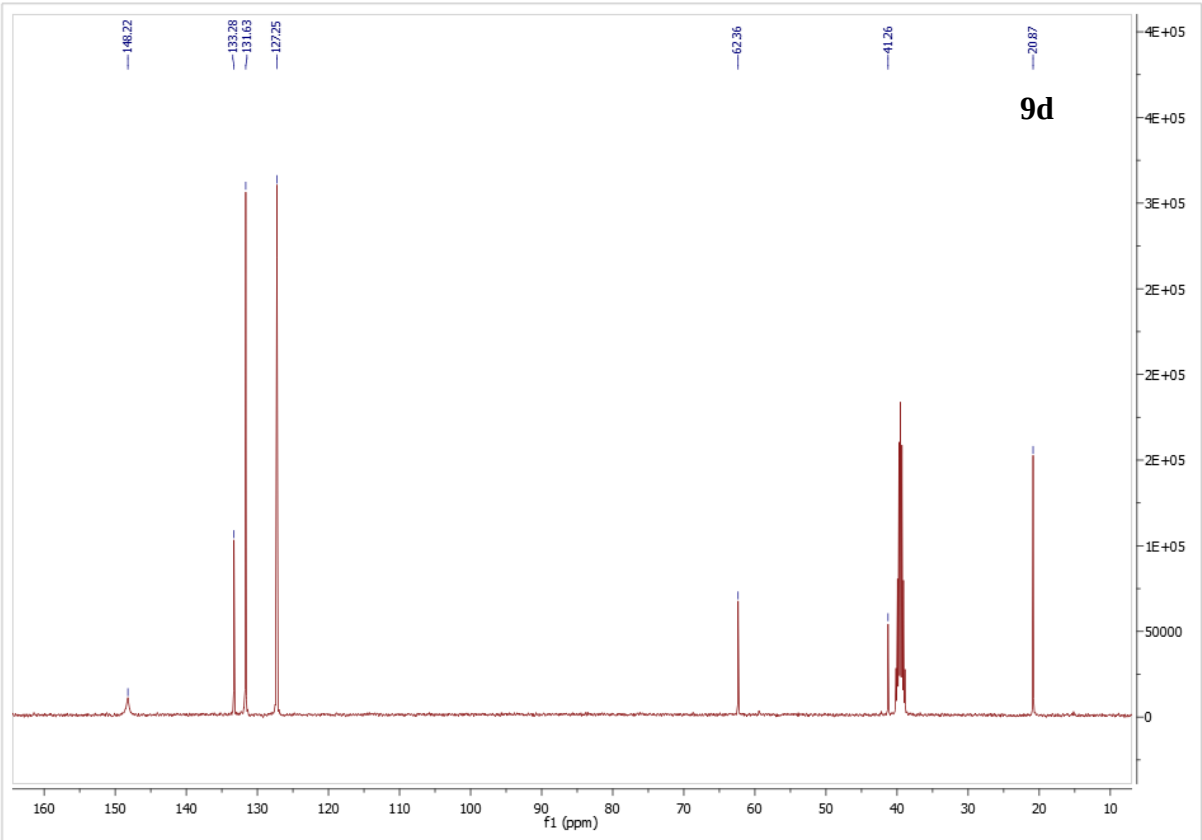

29.41
3c
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
f1 (ppm)

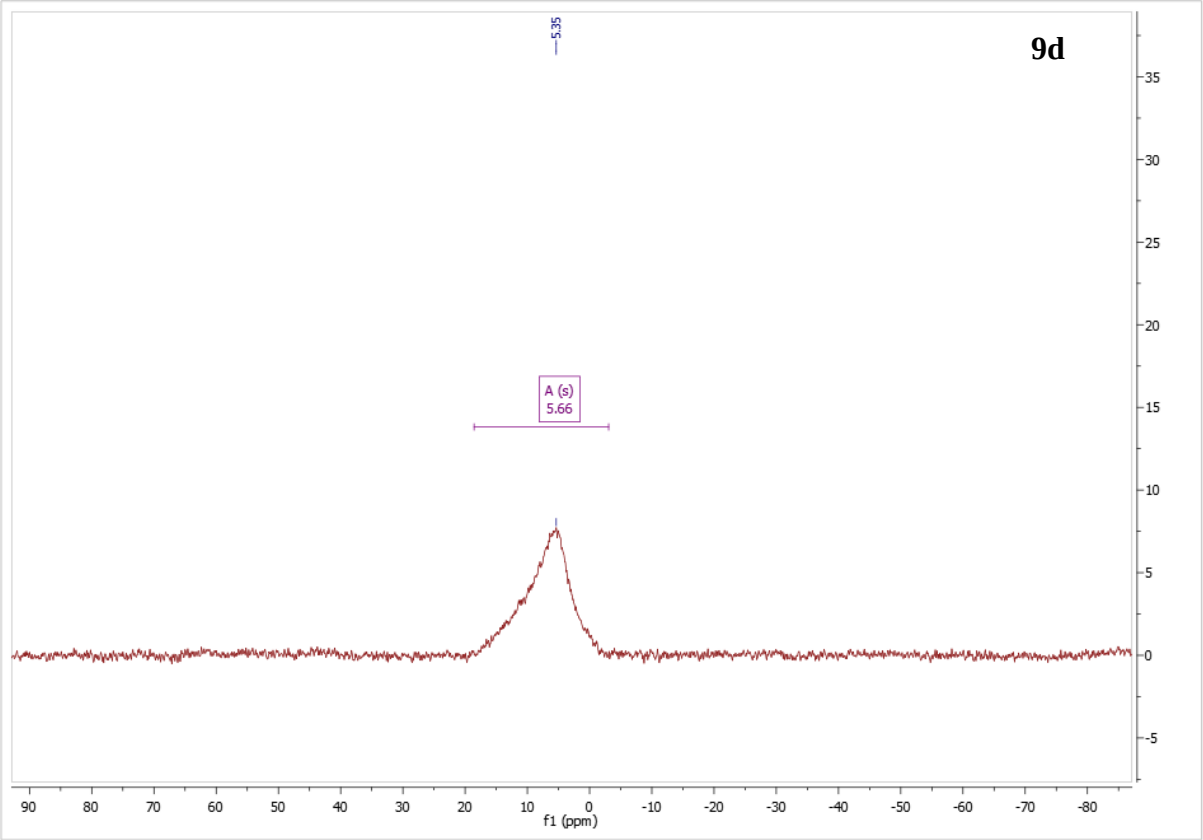

9e
7.20
7.18
7.16
7.04
7.01
6.99
6.85
6.83
6.00
3.76
3.74
3.72
2.84
2.82
2.80
2.78
2.76
2.22
B (t)
7.01
A (m)
7.18
C (d)
6.84
D (s)
6.00
E (t)
3.74
F (p)
2.80
G (s)
2.22
3.97
2.03
1.96
1.85
2.01
2.09
6.00
f1 (ppm)

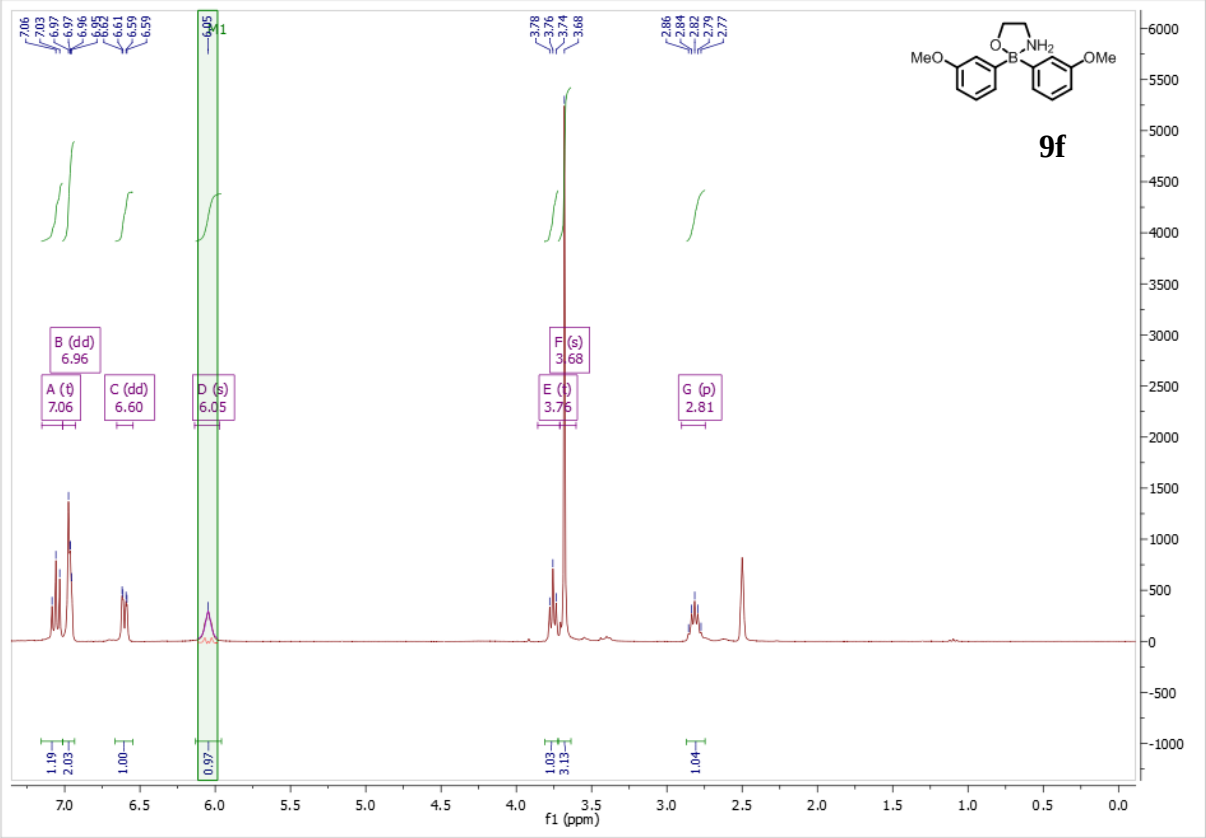

9e
135.24
132.67
129.05
126.94
125.93
62.80
41.79
21.92
f1 (ppm)

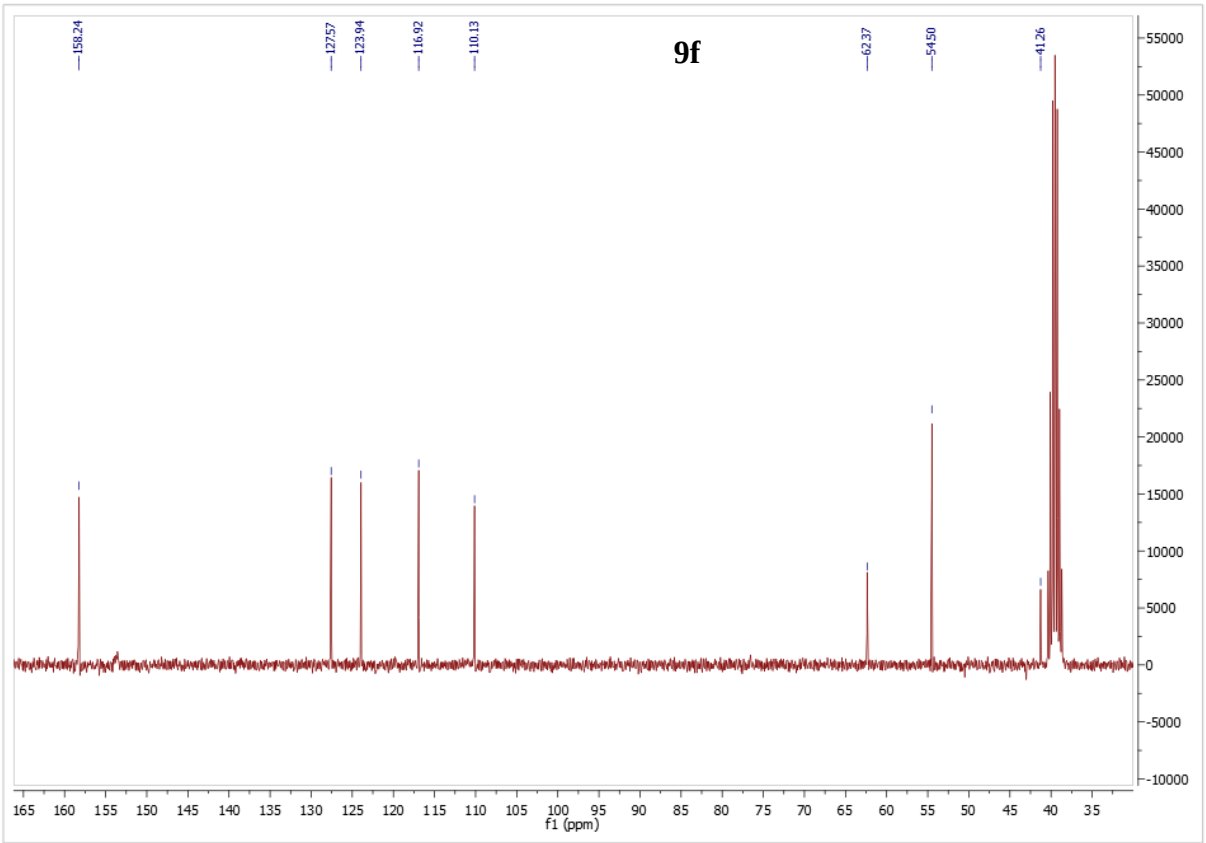

9e
4.81
A (s)
4.81
f1 (ppm)

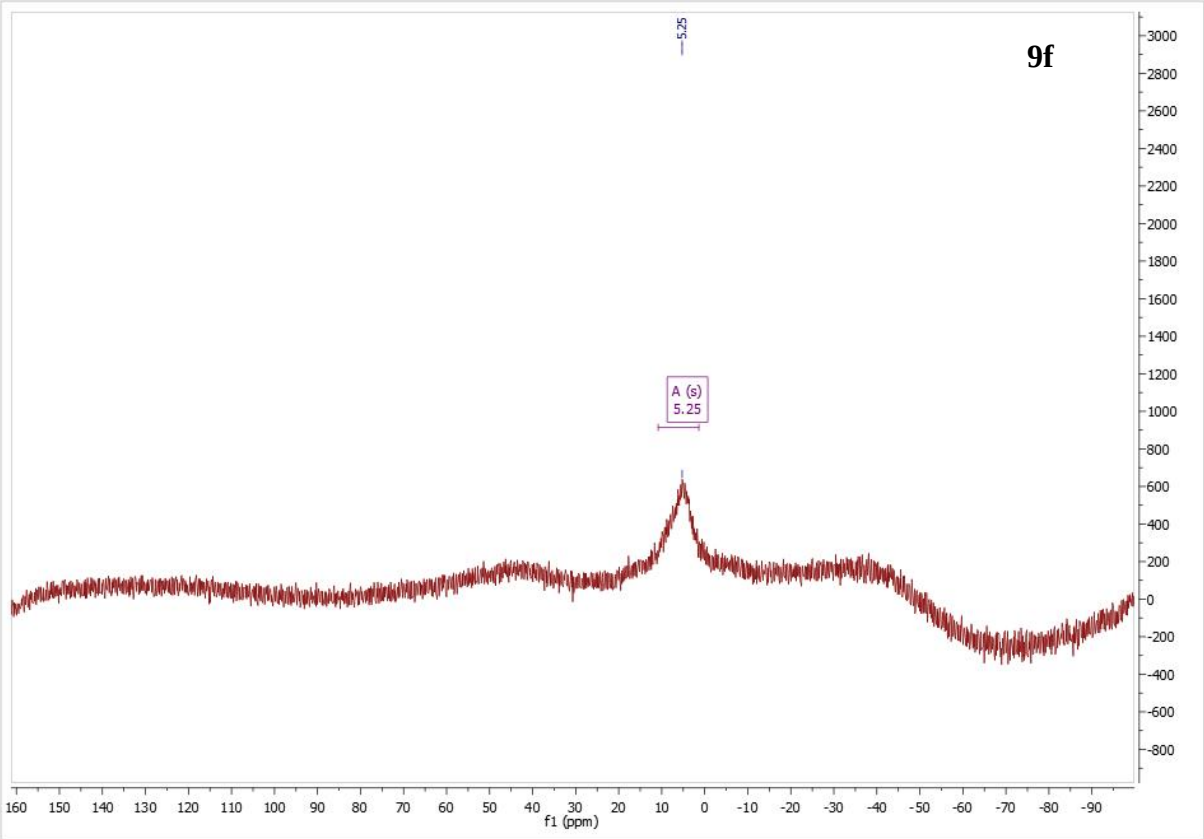

9d
A (d) 7.25
B (d) 6.94
C (s) 5.92
D (t) 3.73
E (t) 2.80
F (s) 2.20
f1 (ppm)

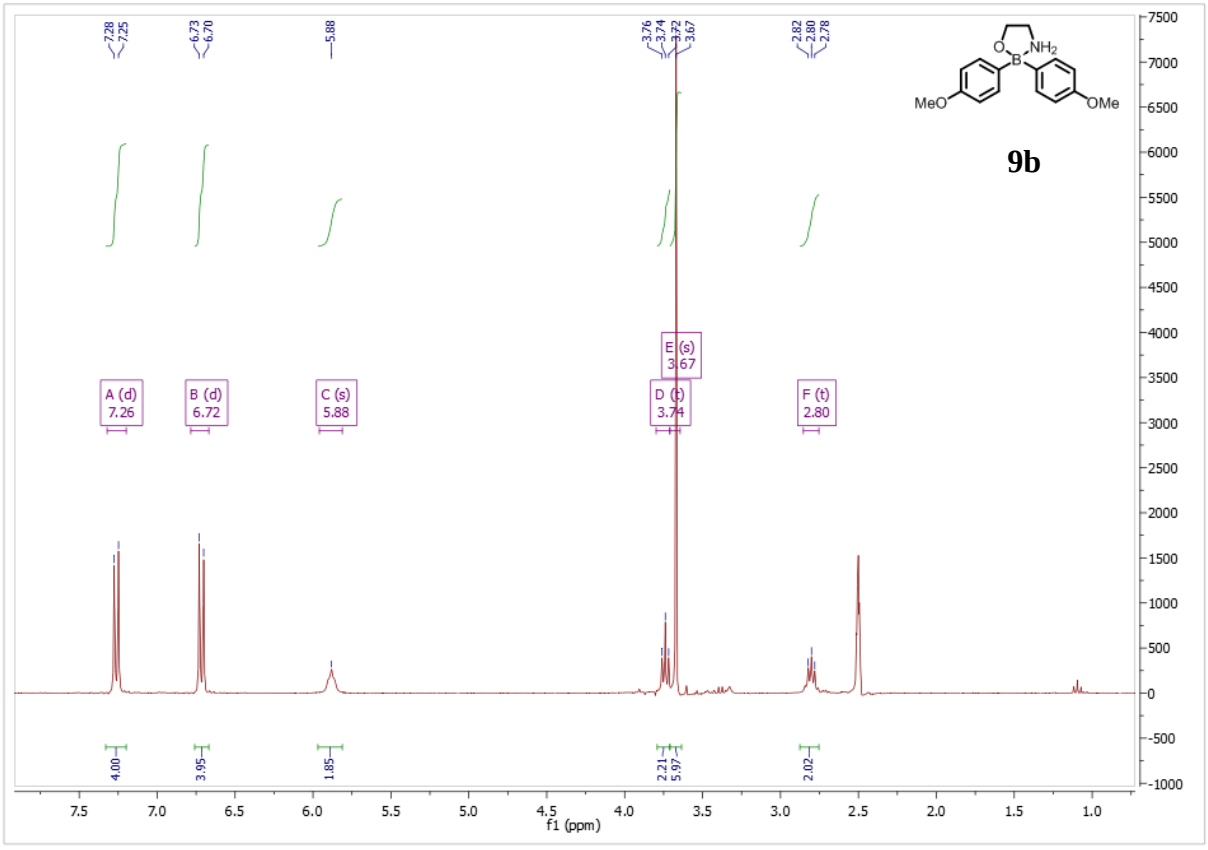

9d
148.22
133.28
131.63
127.25
62.36
41.26
20.87
f1 (ppm)

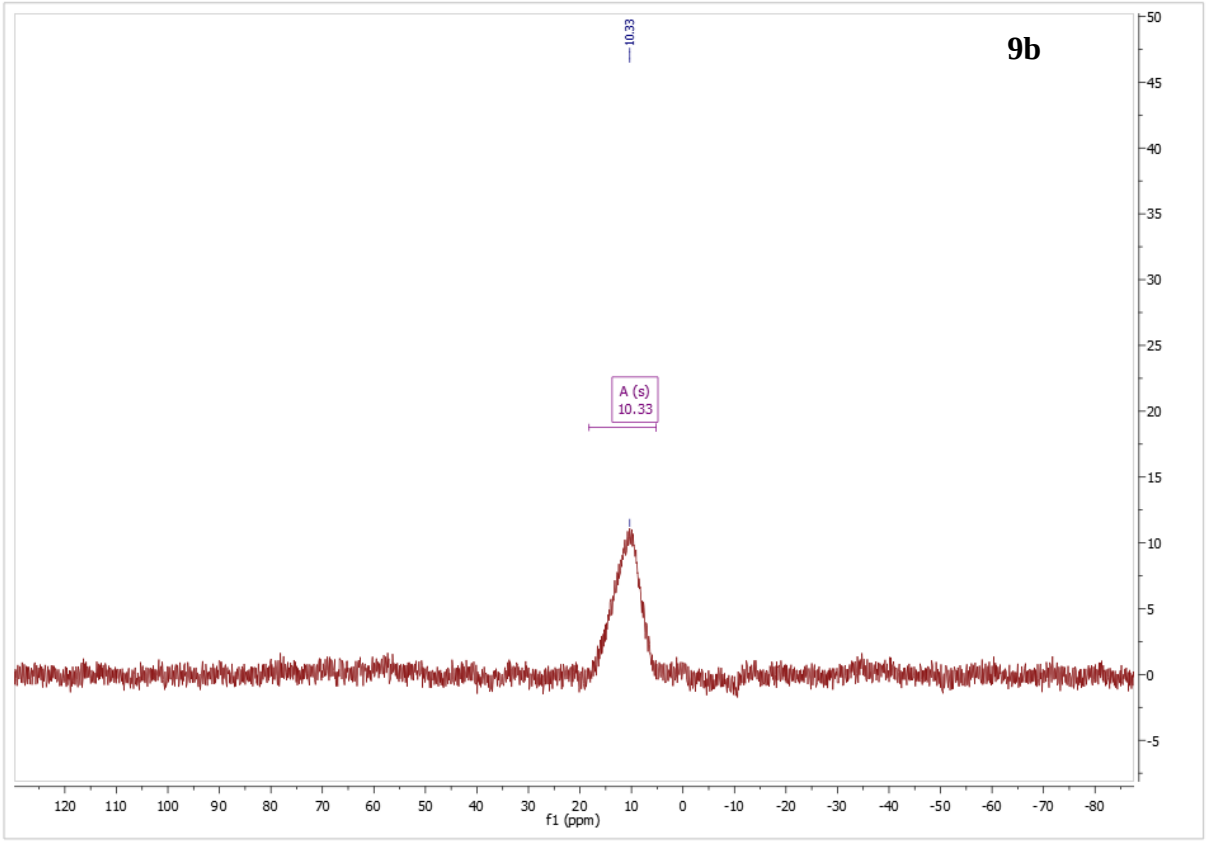

9d
5.35
A (s)
5.66
35
30
25
20
15
10
5
0
-5
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
f1 (ppm)

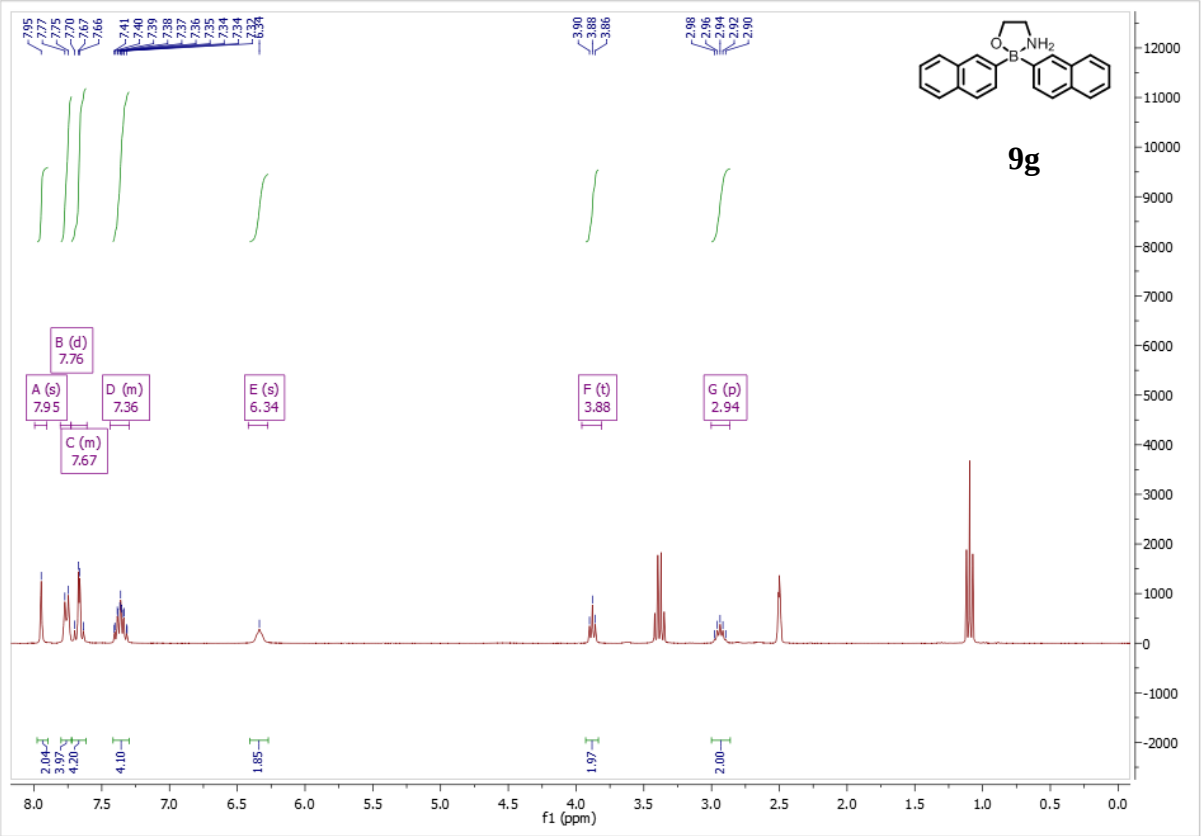

9f
MeO
OMe
NH2
B (dd) 6.96
A (t) 7.06
C (dd) 6.60
D (s) 6.05
F (s) 3.68
E (t) 3.76
G (p) 2.81
f1 (ppm)

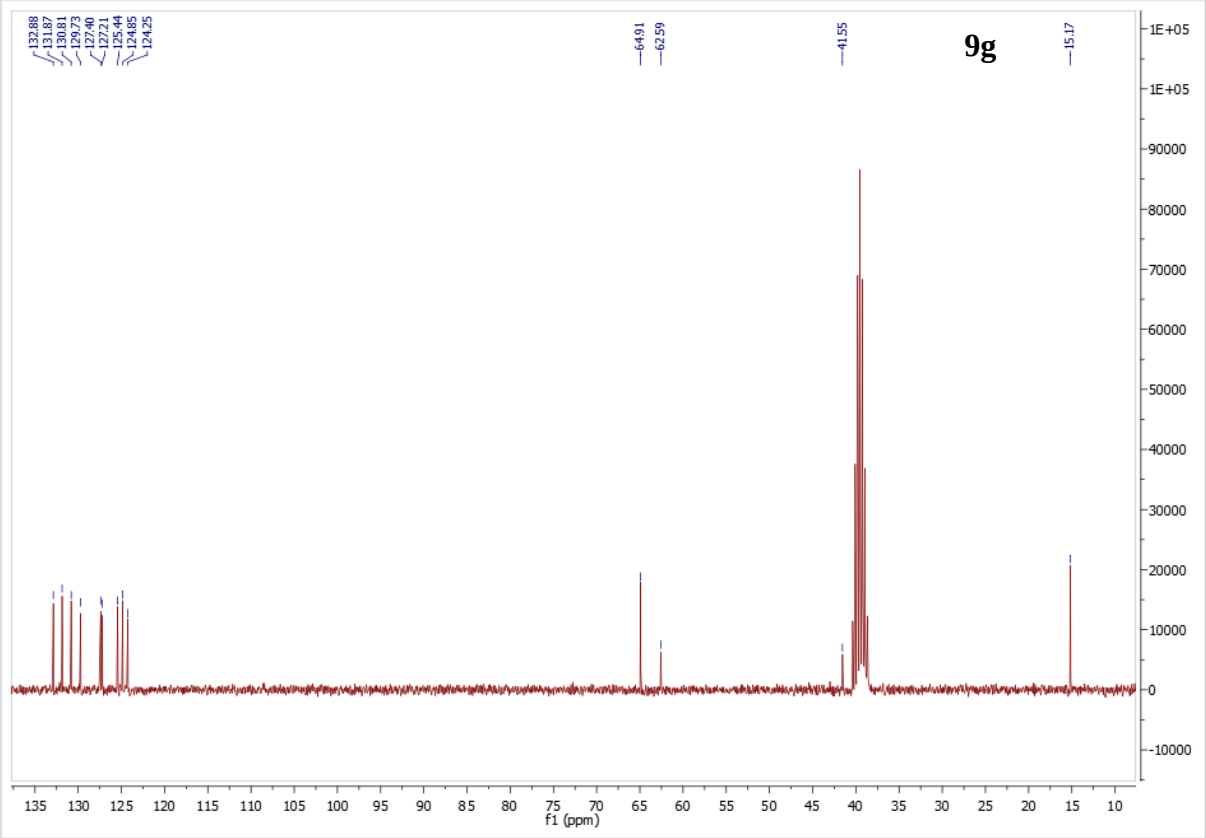

9f
158.24
127.57
123.94
116.92
110.13
62.37
54.50
41.26
f1 (ppm)

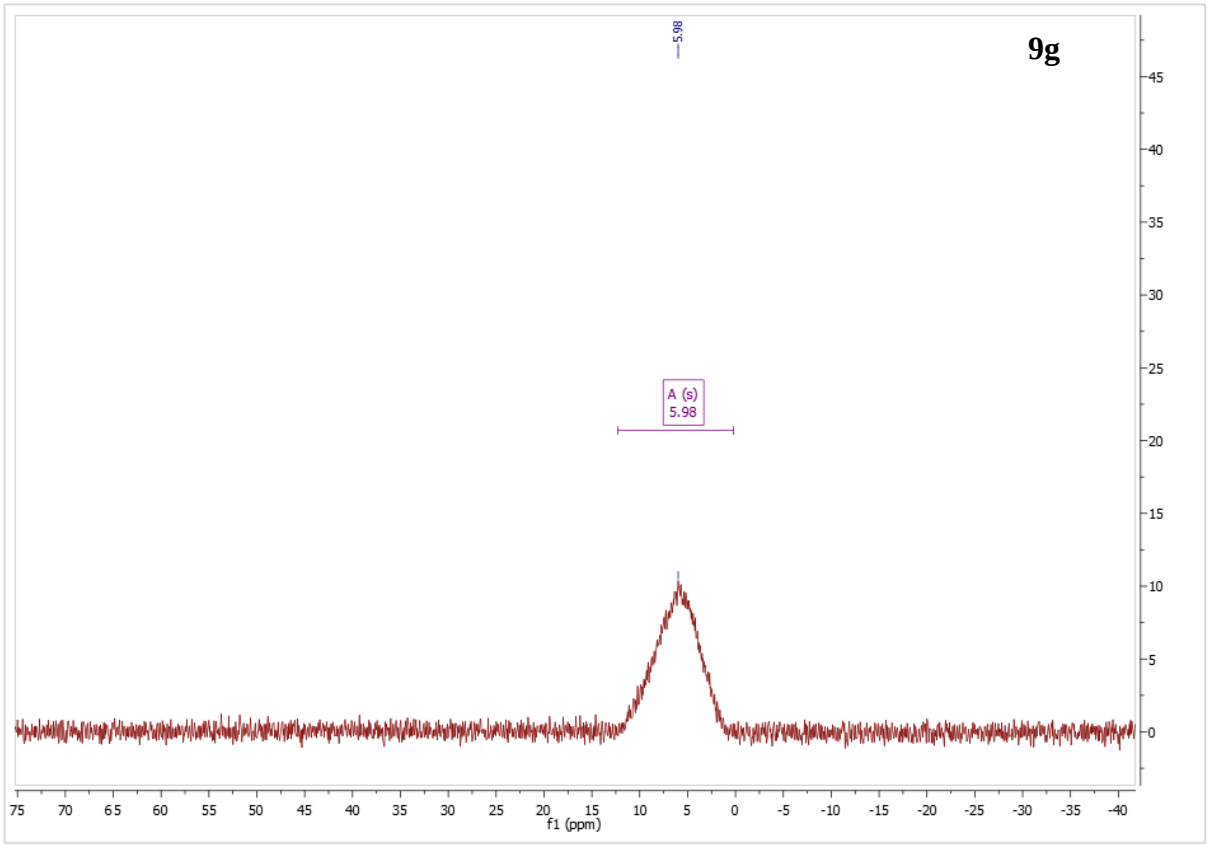

9f
5.25
A (s)
5.25
f1 (ppm)

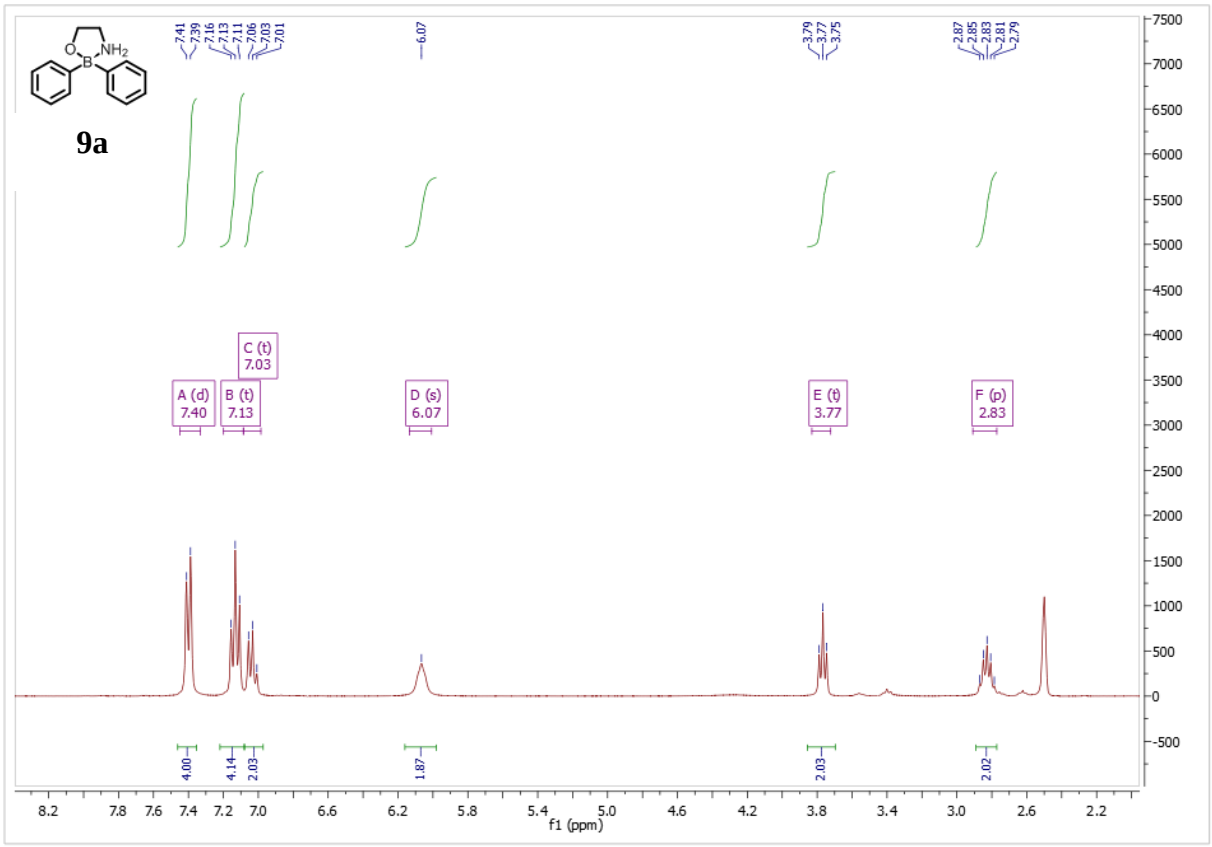

9b
A (d) 7.26
B (d) 6.72
C (s) 5.88
D (t) 3.74
E (s) 3.67
F (t) 2.80
f1 (ppm)

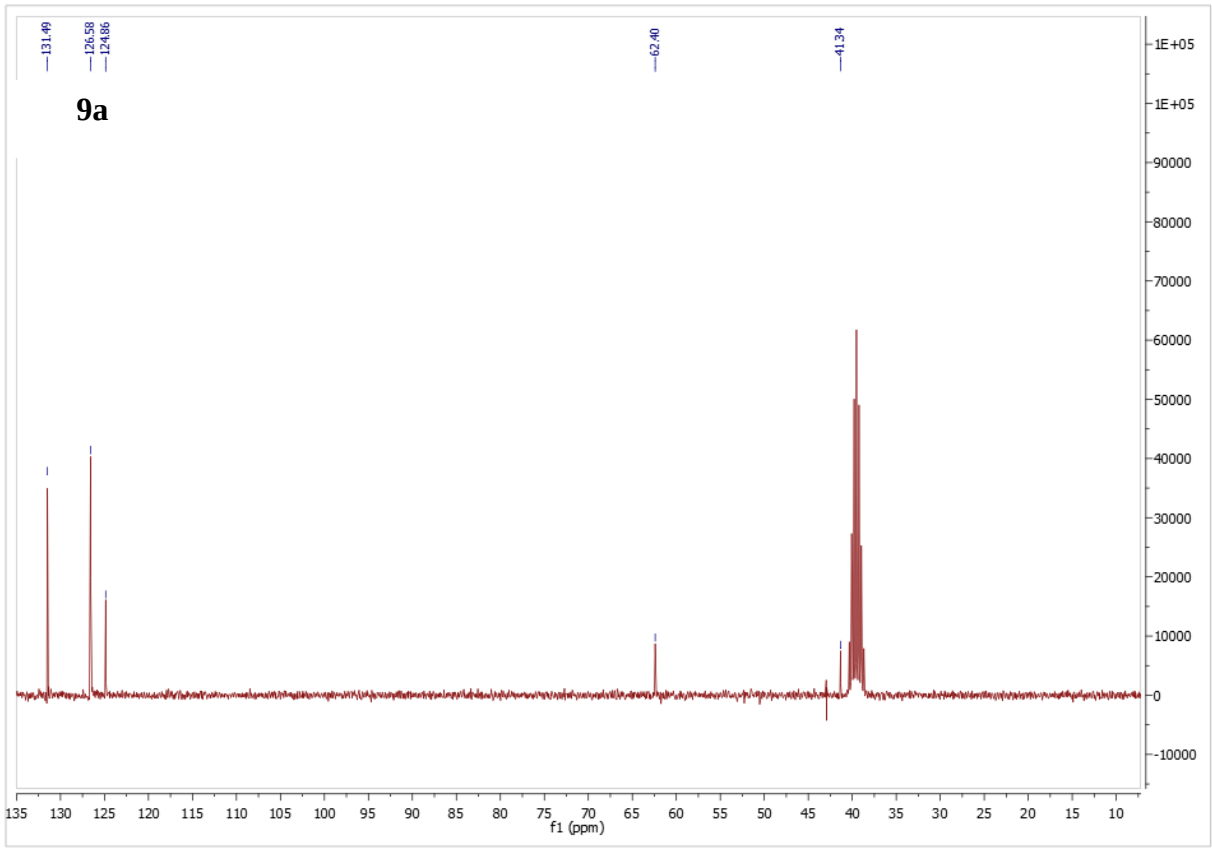

9b
A (s) 10.33
f1 (ppm)

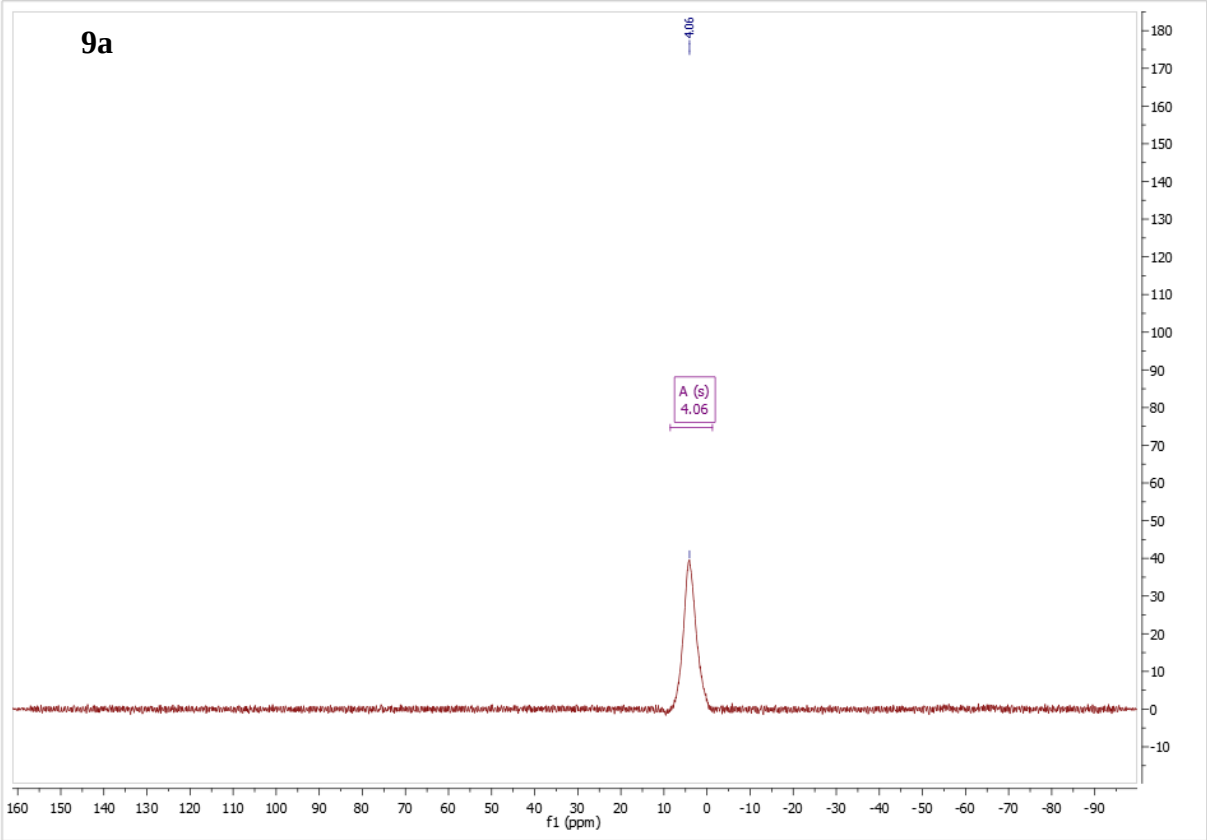

9g
B (d) 7.76
A (s) 7.95
D (m) 7.36
E (s) 6.34
F (t) 3.88
G (p) 2.94
C (m) 7.67
f1 (ppm)

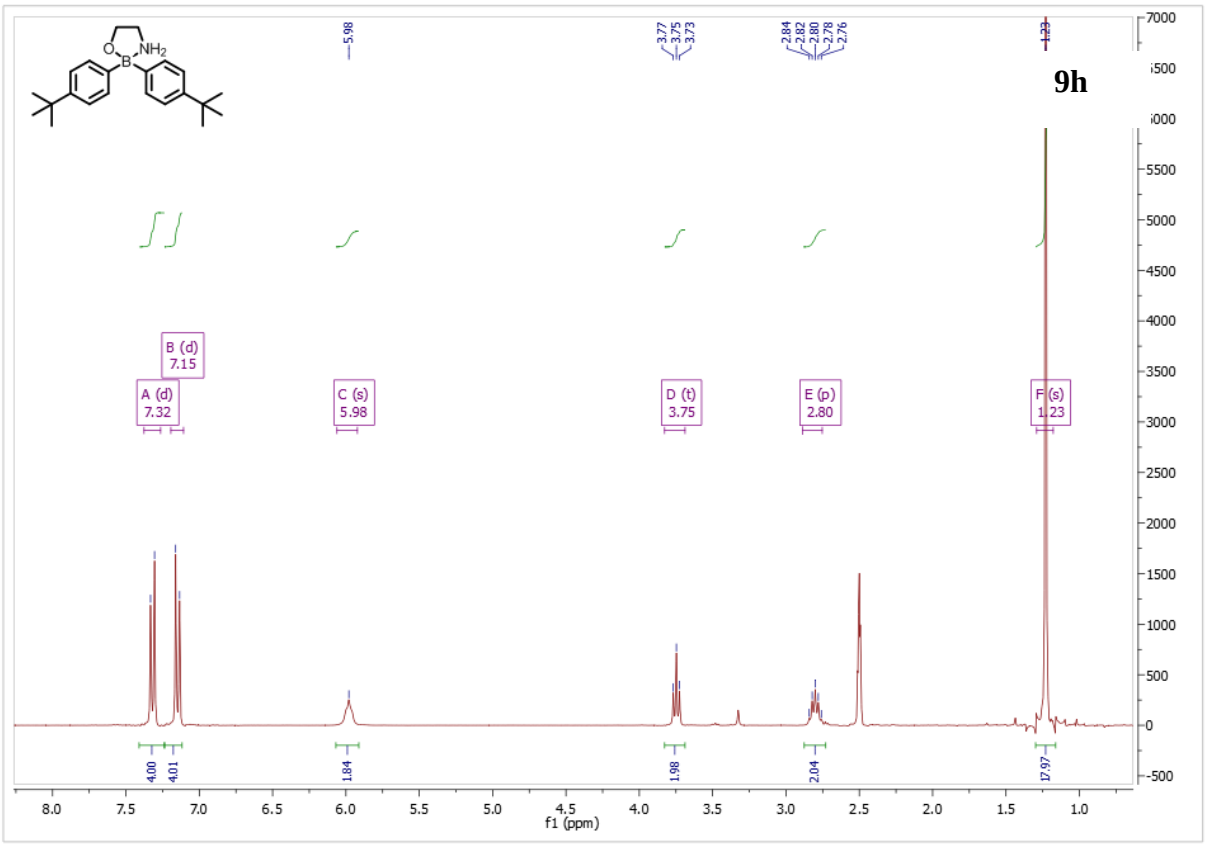

9g
f1 (ppm)

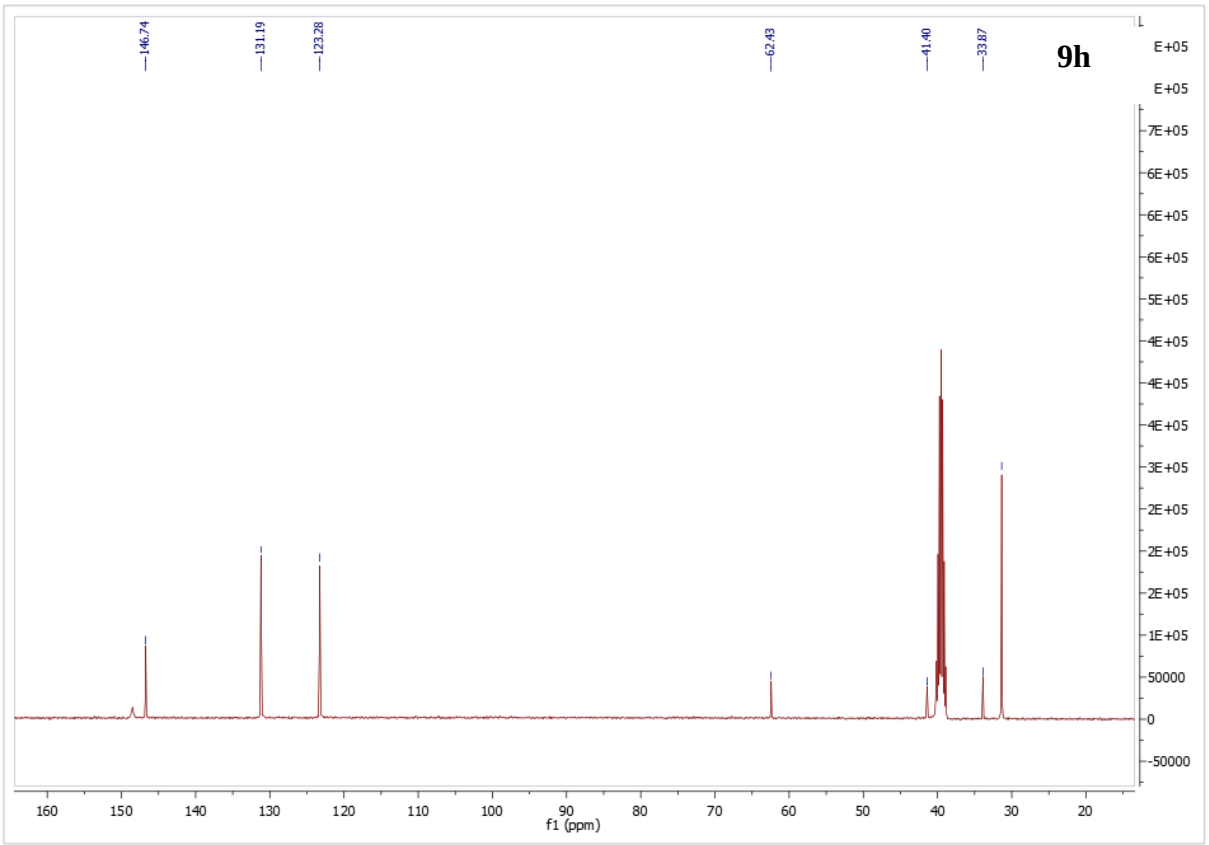

9g
5.98
A (s)
5.98
f1 (ppm)

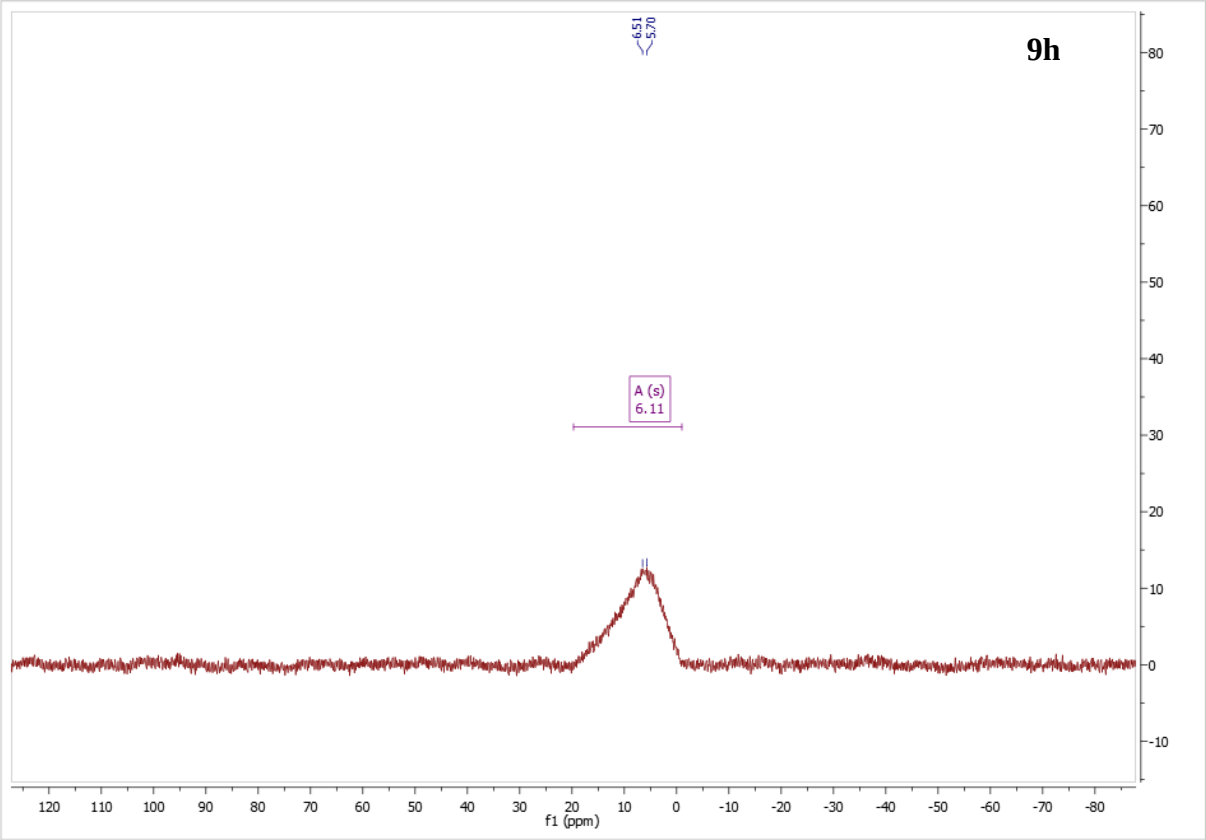

9a
7.41
7.39
7.16
7.13
7.11
7.06
7.03
7.01
6.07
3.79
3.77
3.75
2.87
2.85
2.83
2.81
2.79
A (d) 7.40
B (t) 7.13
C (t) 7.03
D (s) 6.07
E (t) 3.77
F (p) 2.83
4.00
4.14
2.03
1.87
2.03
2.02
f1 (ppm)

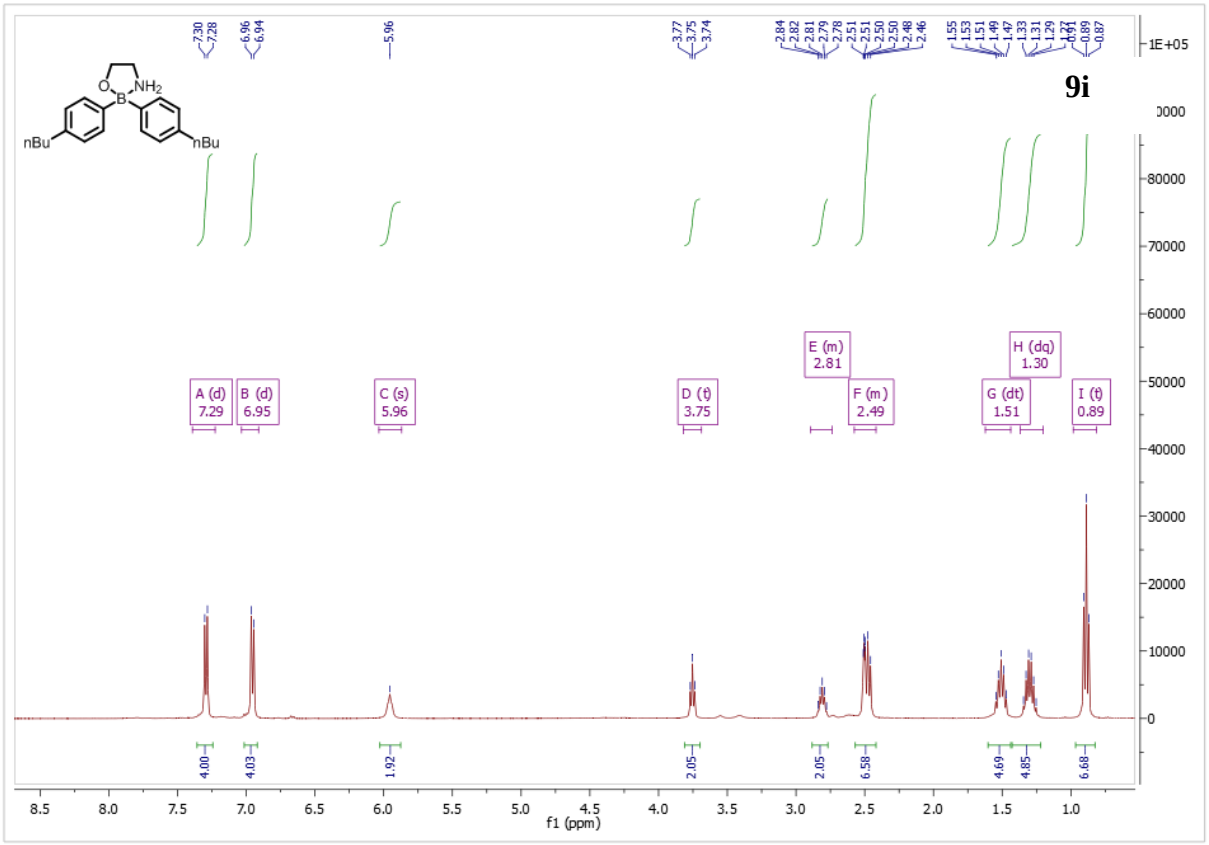

9a
131.49
126.58
124.86
62.40
41.34
f1 (ppm)

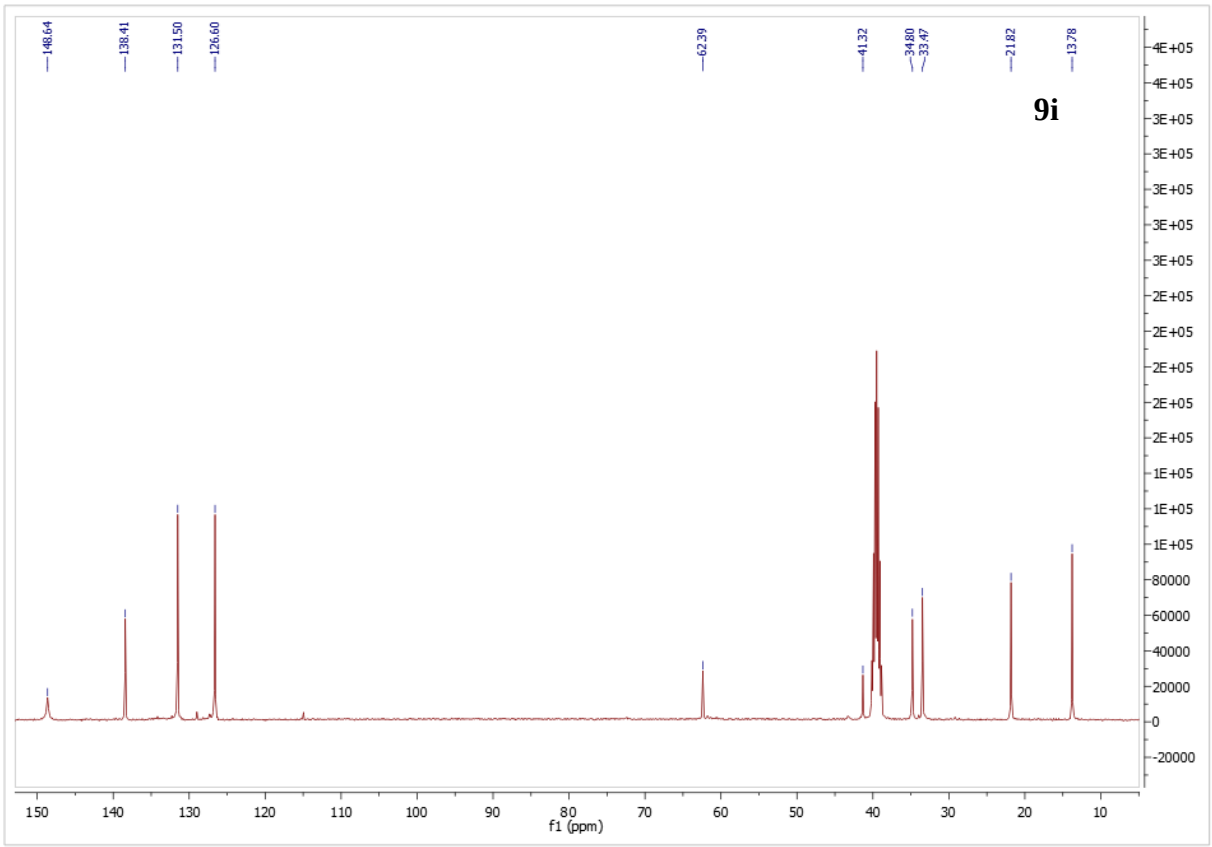

9a
4.06
A (s)
4.06
f1 (ppm)

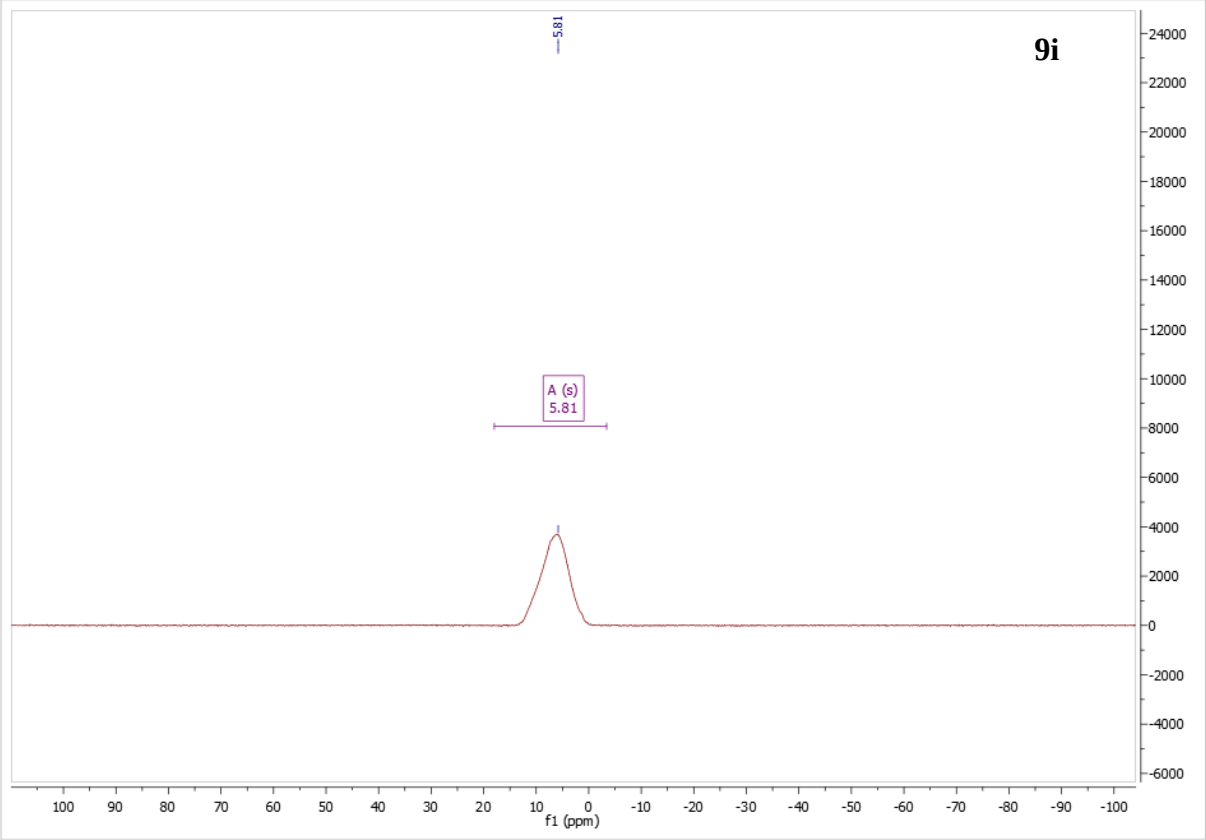

9h
B (d) 7.15
A (d) 7.32
C (s) 5.98
D (t) 3.75
E (p) 2.80
F (s) 1.23
f1 (ppm)

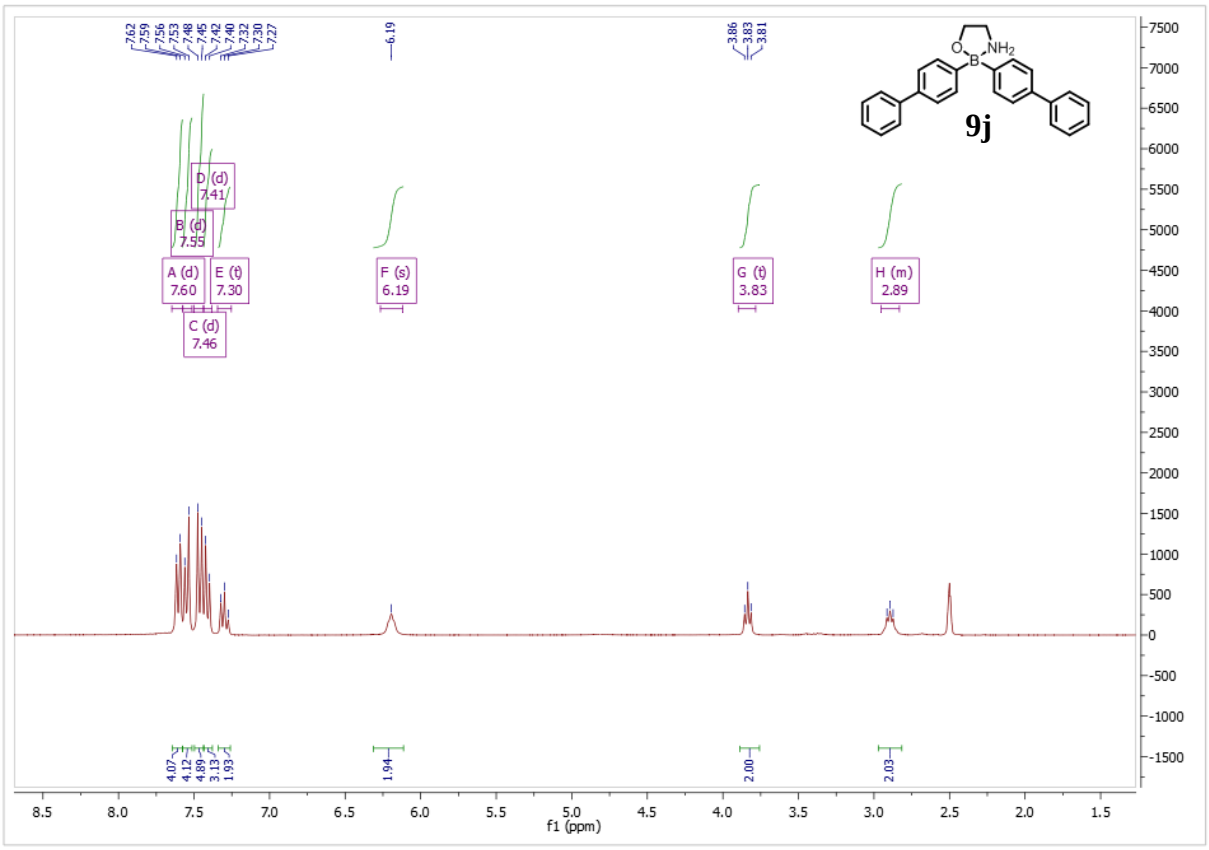

9h
146.74
131.19
123.28
62.43
41.40
33.87
f1 (ppm)

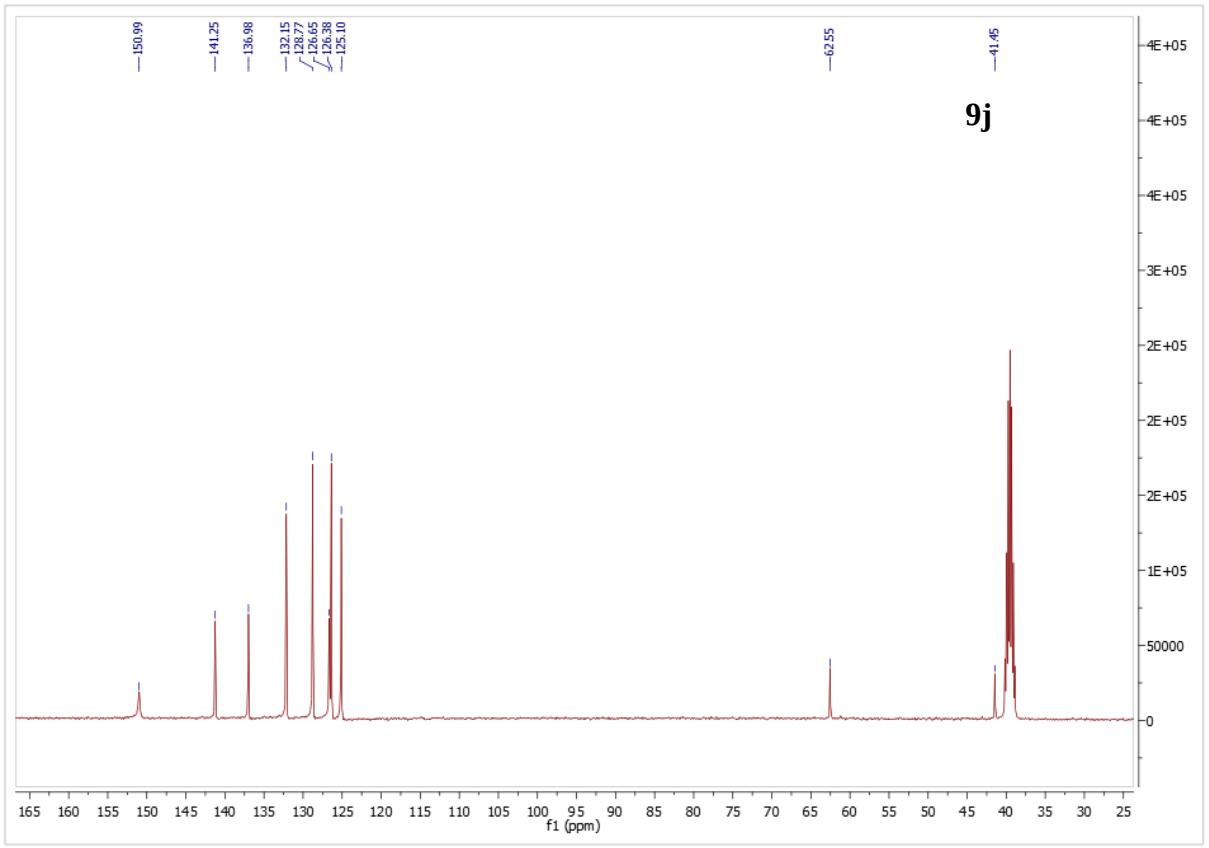

9h
6.51
5.70
A (s)
6.11
f1 (ppm)

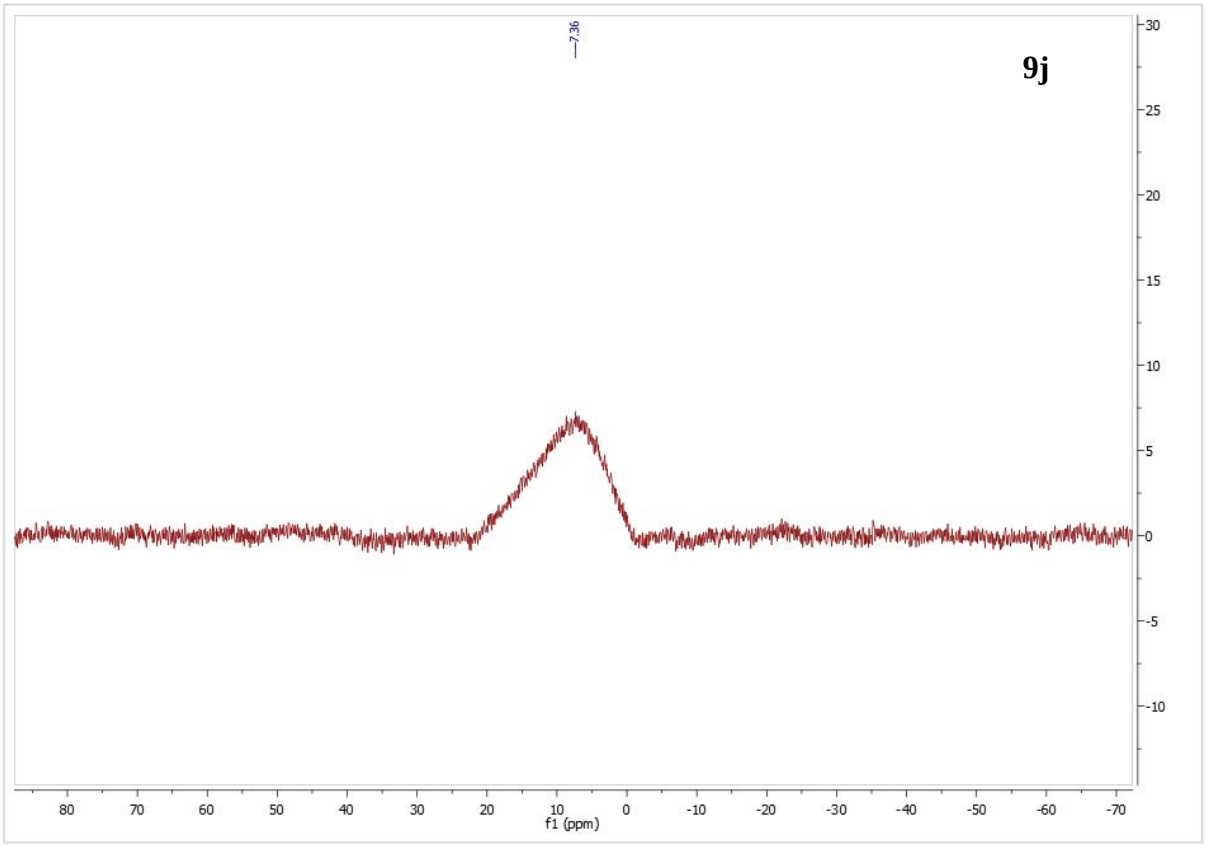

9i
nBu
nBu
O
B
NH2
A (d) 7.29
B (d) 6.95
C (s) 5.96
D (t) 3.75
E (m) 2.81
F (m) 2.49
G (dt) 1.51
H (dq) 1.30
I (t) 0.89
4.00
4.03
1.92
2.05
2.05
6.58
4.69
4.85
6.68
f1 (ppm)

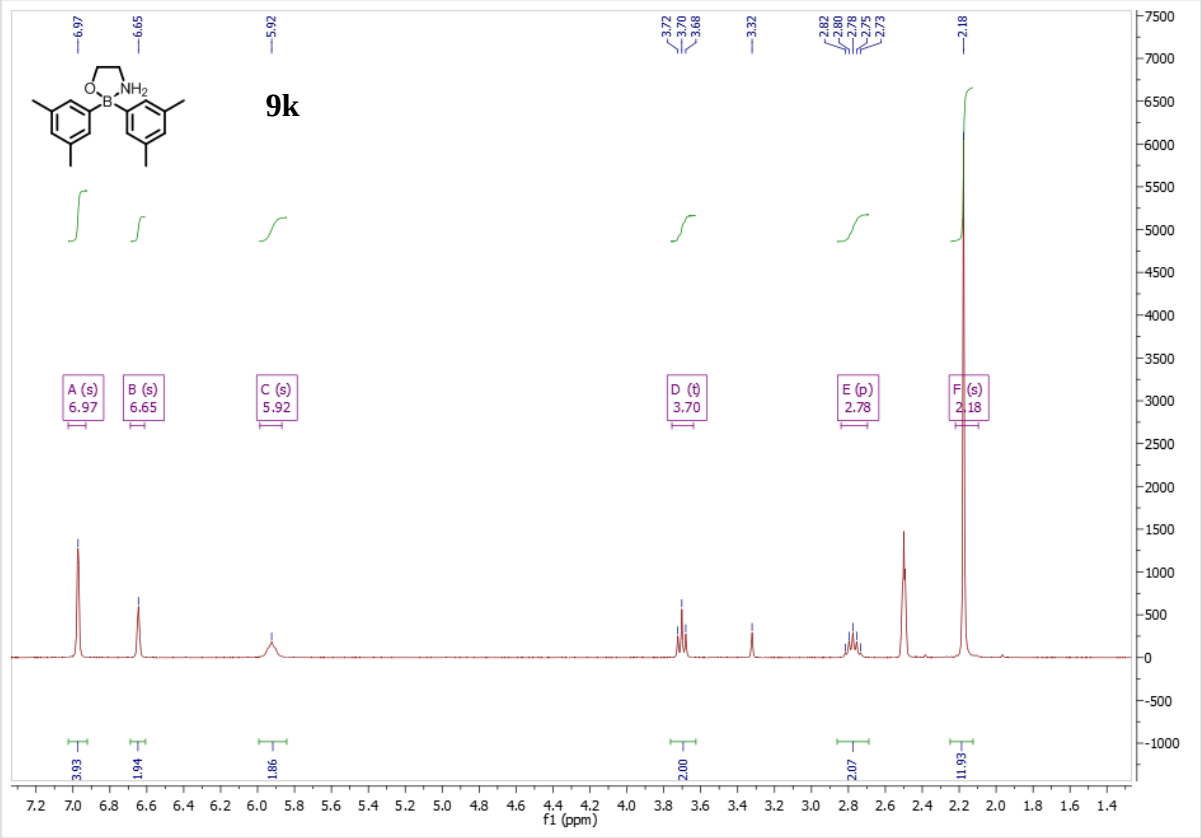

9i
148.64
138.41
131.50
126.60
62.39
41.32
34.80
33.47
21.82
13.78
f1 (ppm)

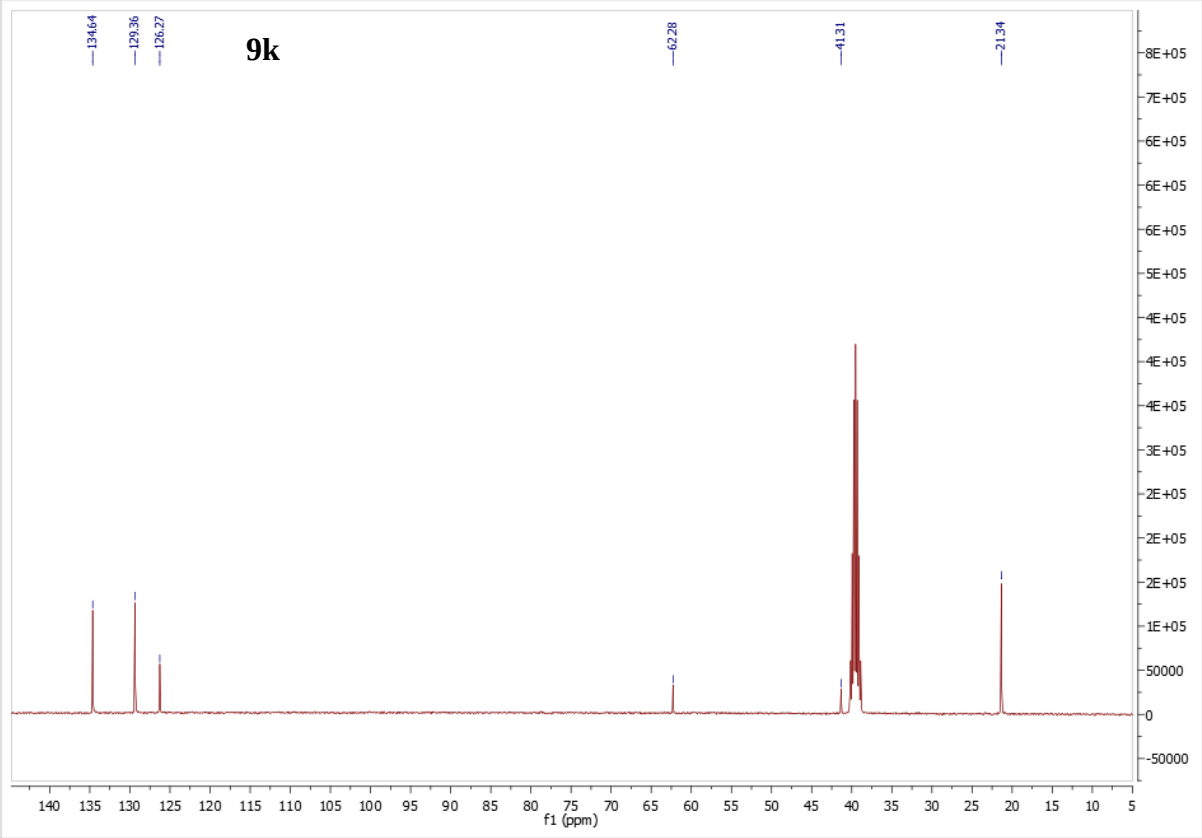

9i
5.81
A (s)
5.81
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
-4000
-6000
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
f1 (ppm)

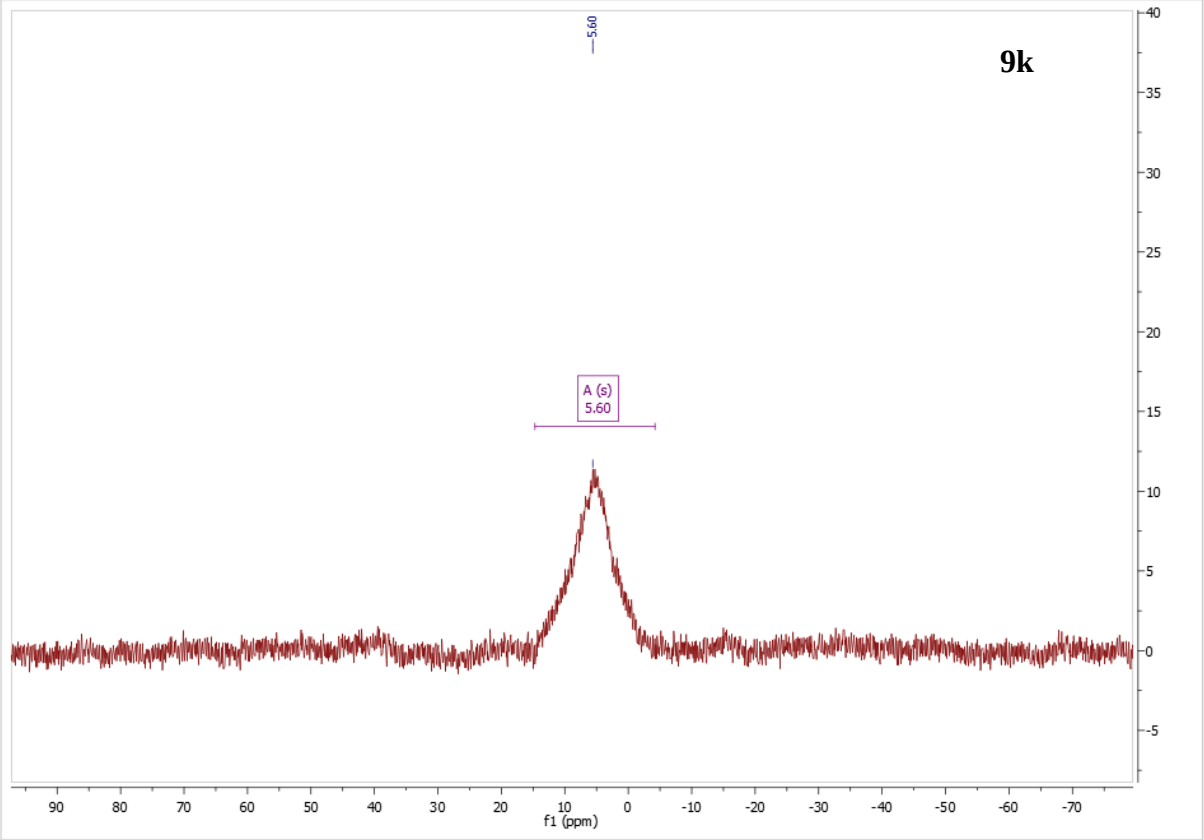

9j
D (d) 7.41
B (d) 7.55
A (d) 7.60
E (t) 7.30
C (d) 7.46
F (s) 6.19
G (t) 3.83
H (m) 2.89
f1 (ppm)

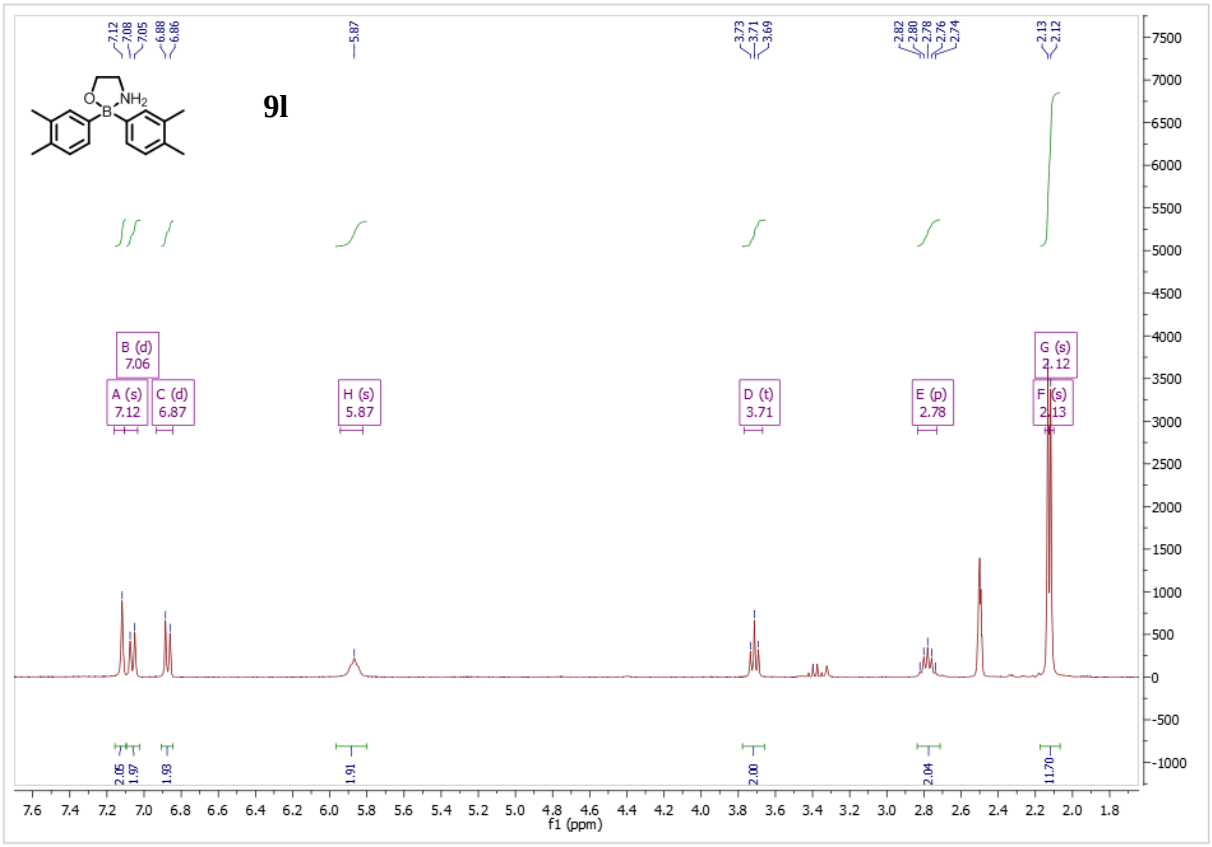

9j
150.99
141.25
136.98
132.15
128.77
126.65
126.38
125.10
62.55
41.45
f1 (ppm)

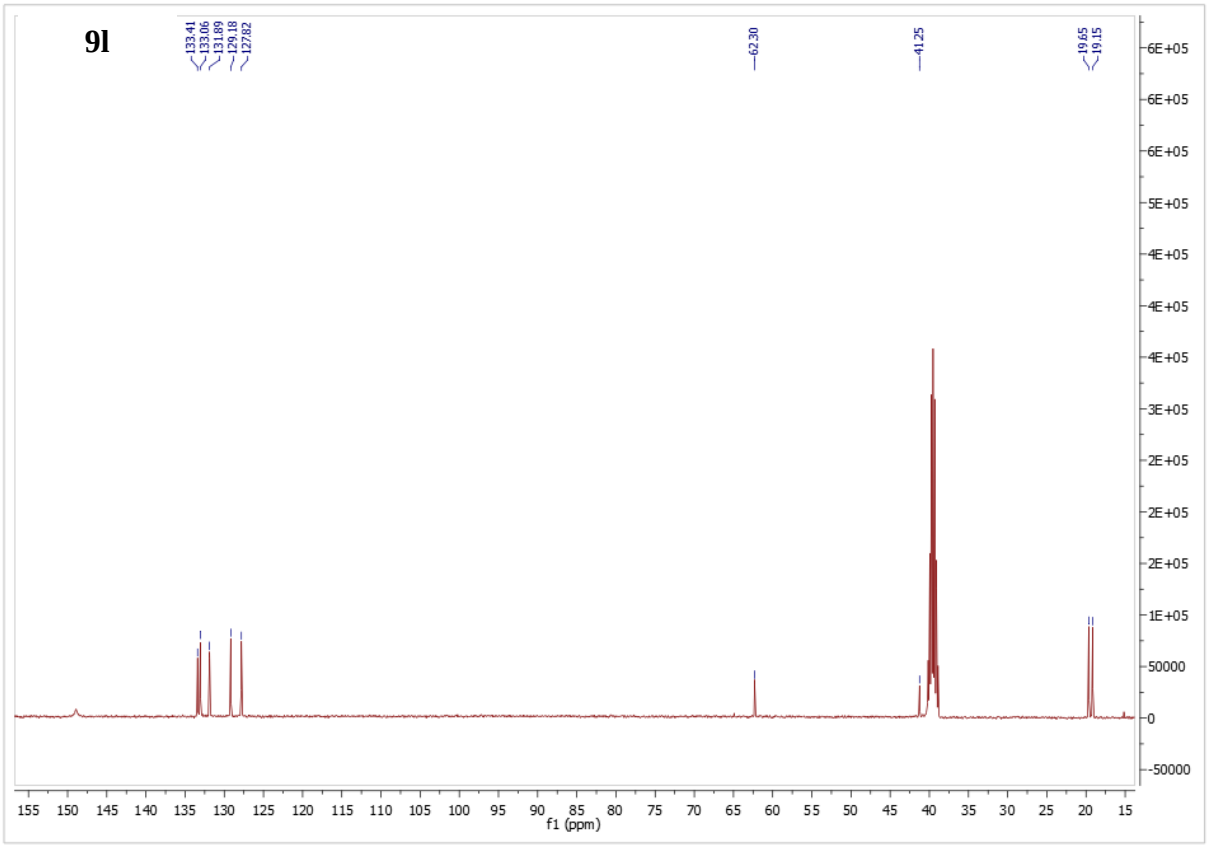

9j
7.36
30
25
20
15
10
5
0
-5
-10
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
f1 (ppm)

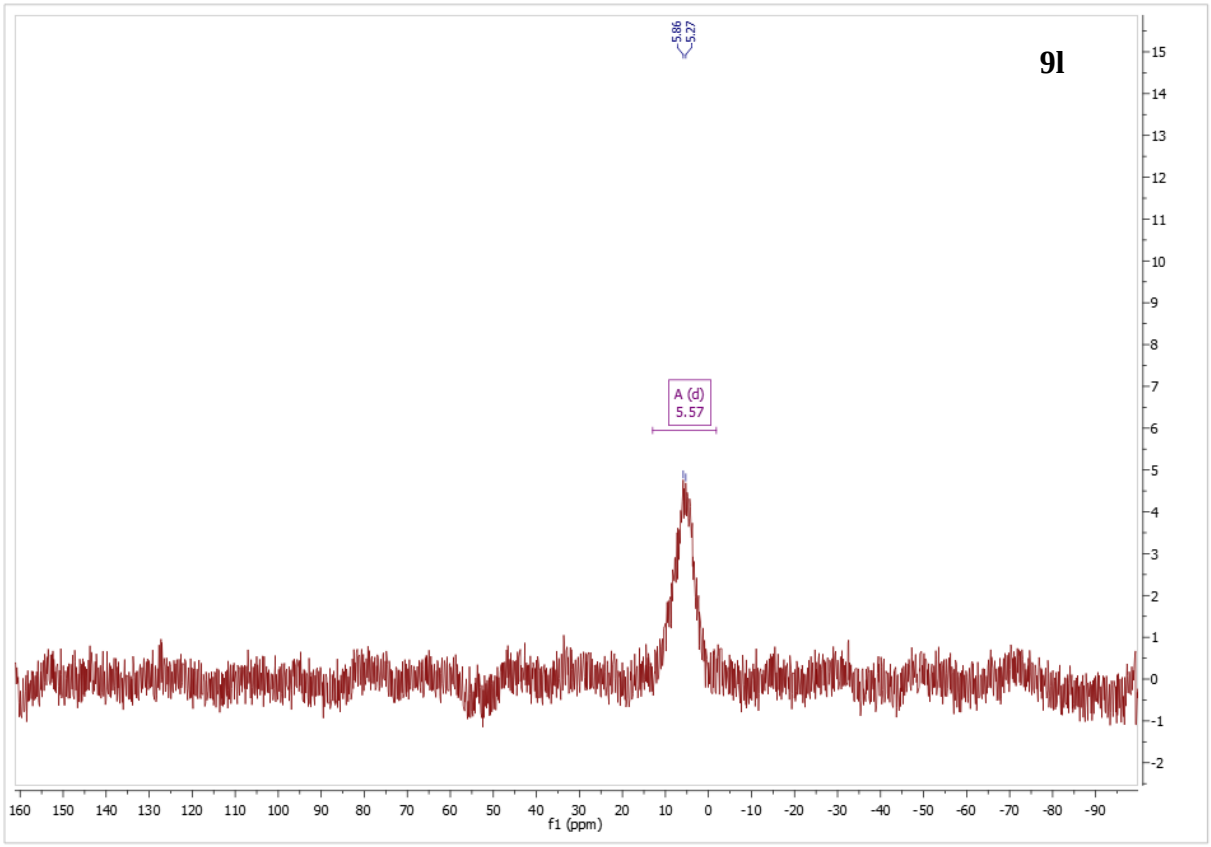

9k
6.97
6.65
5.92
3.72
3.70
3.68
3.32
2.82
2.80
2.78
2.75
2.73
2.18
A (s) 6.97
B (s) 6.65
C (s) 5.92
D (t) 3.70
E (p) 2.78
F (s) 2.18
3.93
1.94
1.86
2.00
2.07
11.93
f1 (ppm)

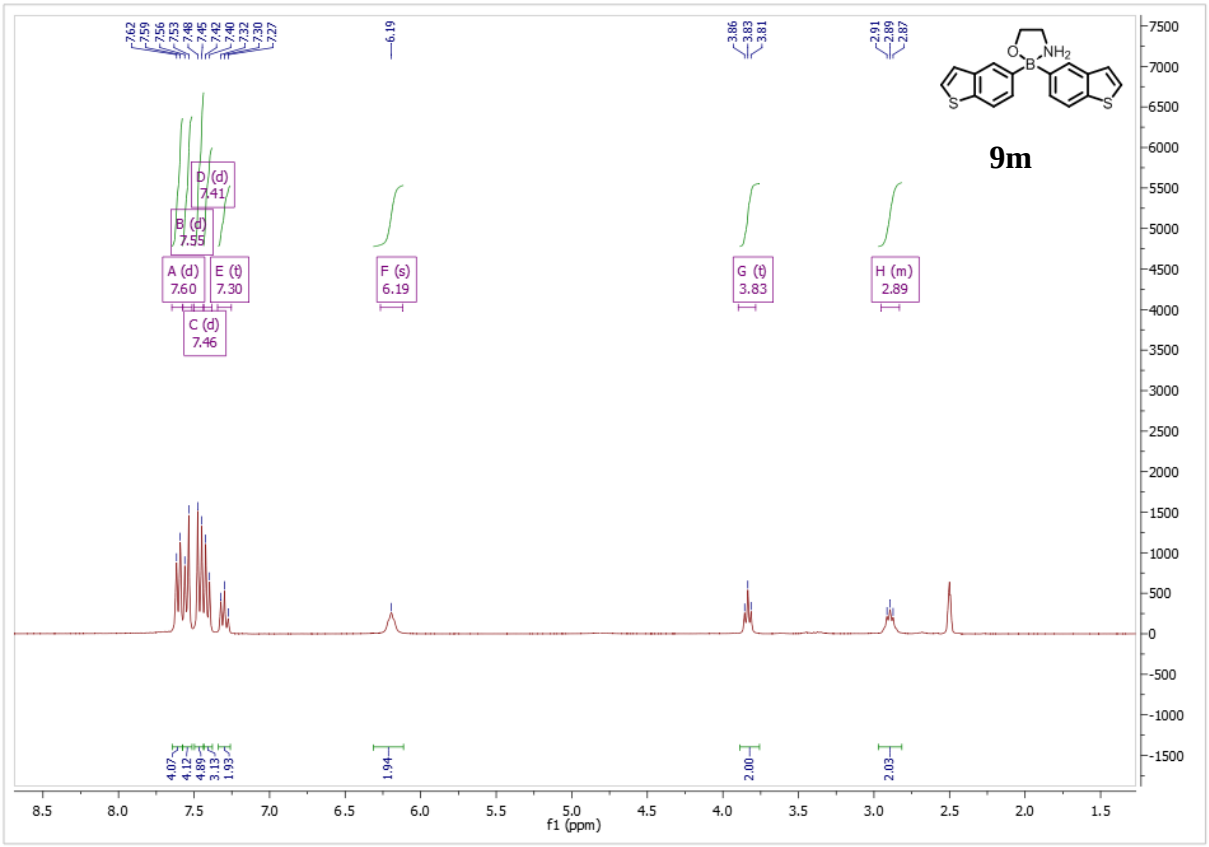

9k
134.64
129.36
126.27
62.28
41.31
21.34
f1 (ppm)

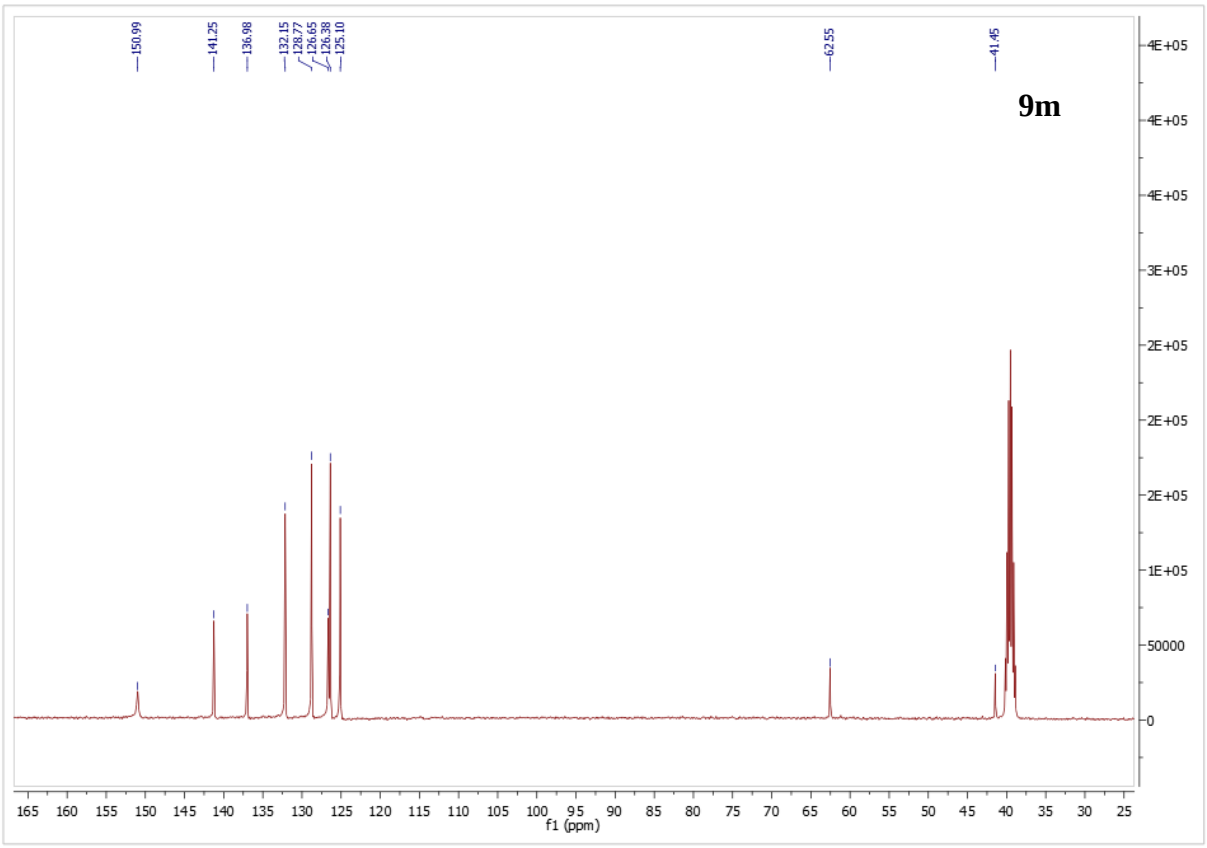

9k
5.60
A (s)
5.60
40
35
30
25
20
15
10
5
0
-5
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
f1 (ppm)

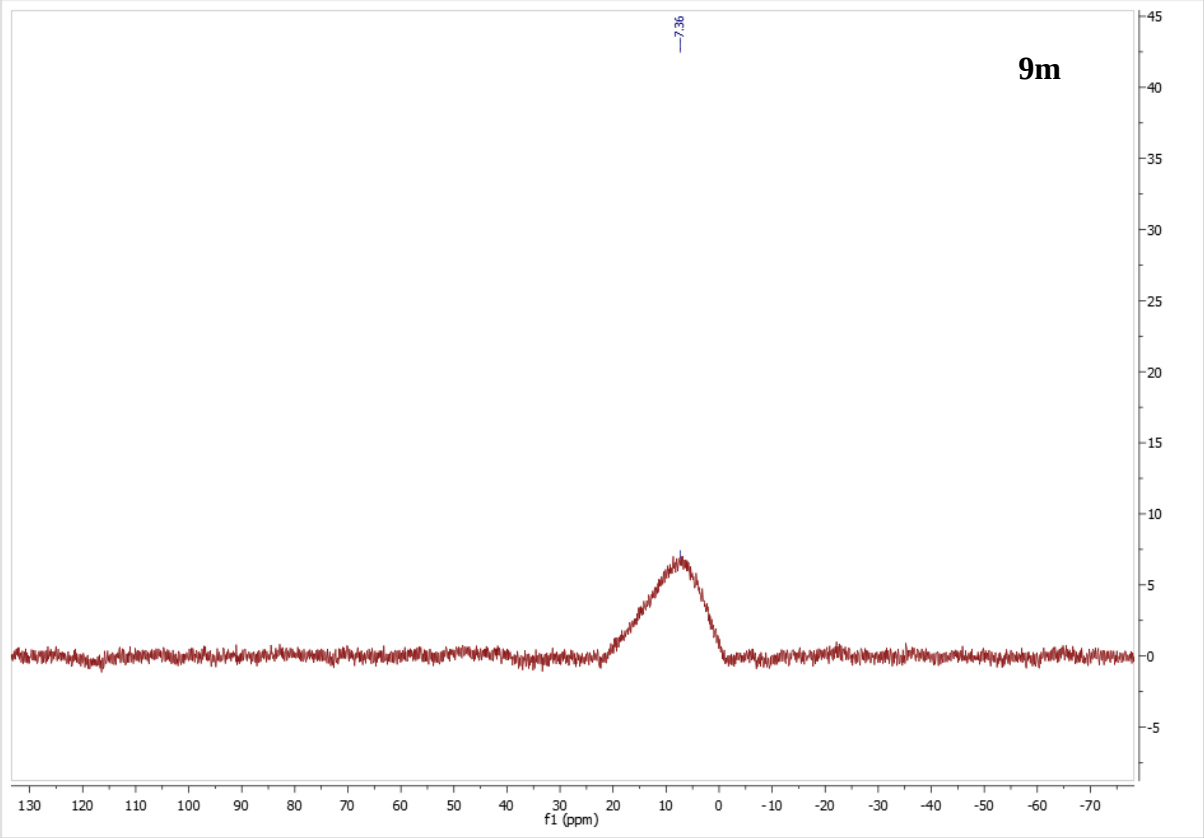

9l
B (d) 7.06
A (s) 7.12
C (d) 6.87
H (s) 5.87
D (t) 3.71
E (p) 2.78
G (s) 2.12
F (s) 2.13
f1 (ppm)

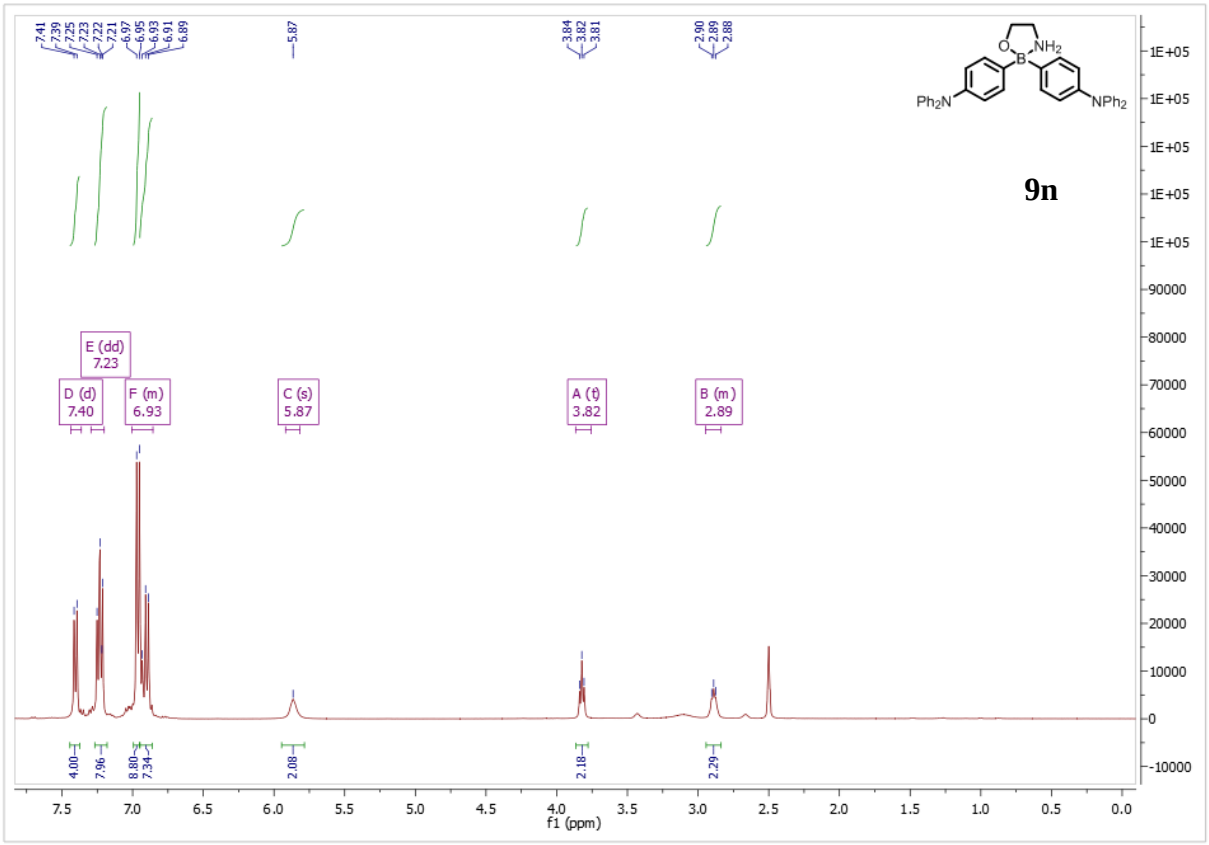

9l
f1 (ppm)

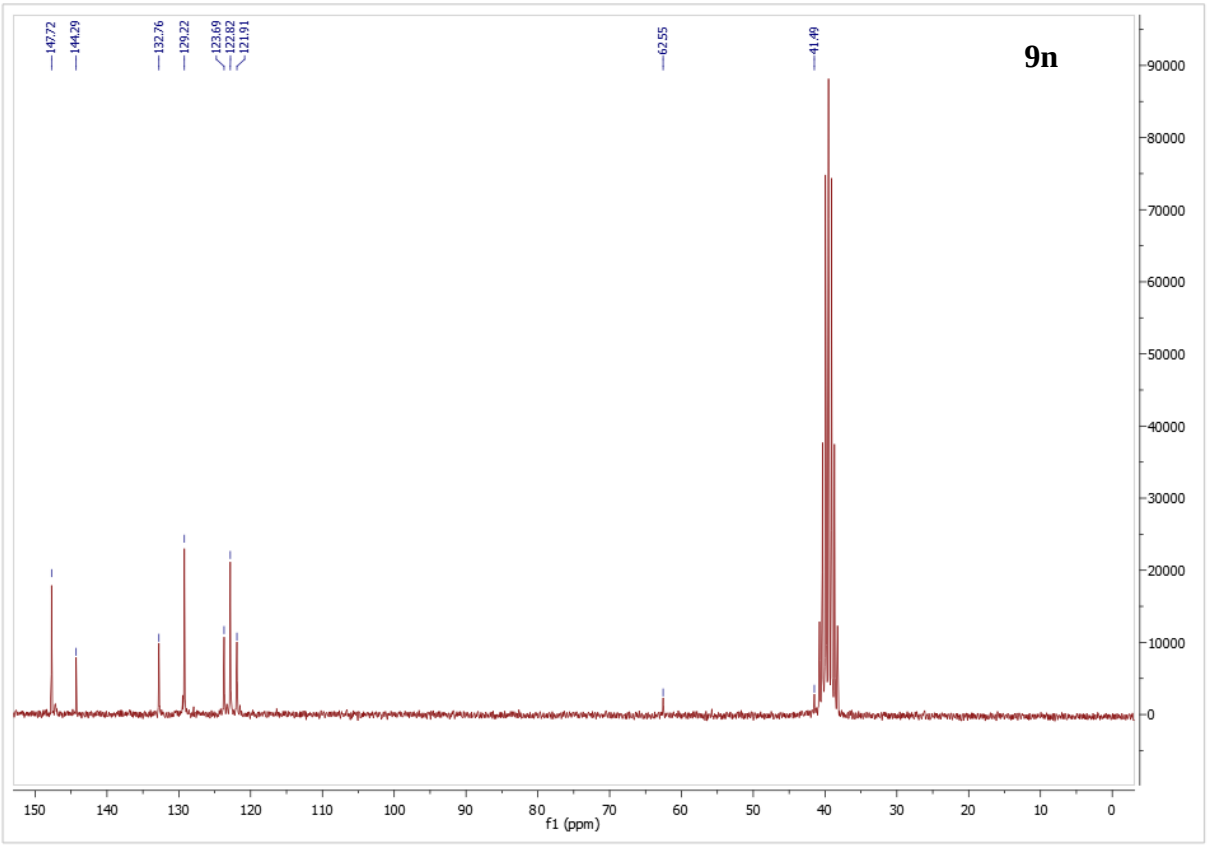

9l
5.86
5.27
A (d)
5.57
f1 (ppm)

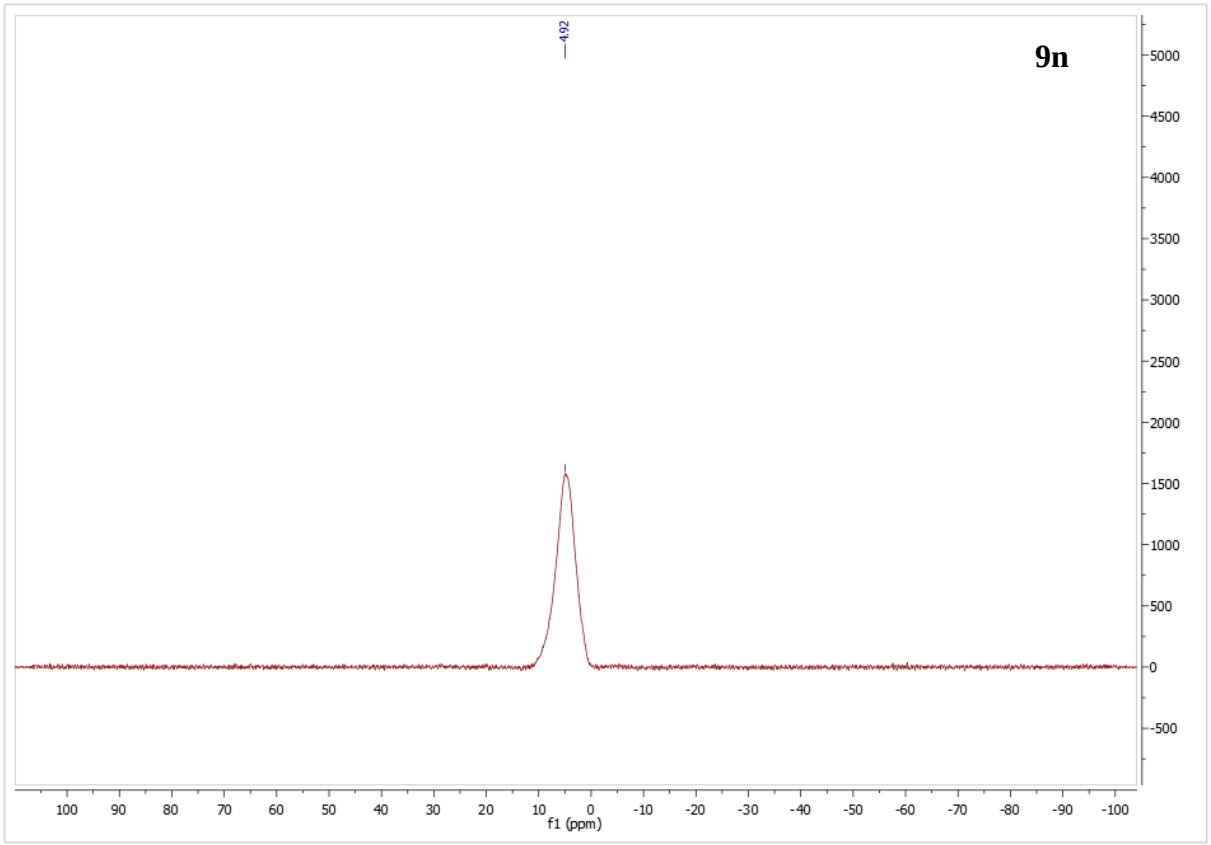

9m
D (d) 7.41
B (d) 7.55
A (d) 7.60
E (t) 7.30
C (d) 7.46
F (s) 6.19
G (t) 3.83
H (m) 2.89
f1 (ppm)

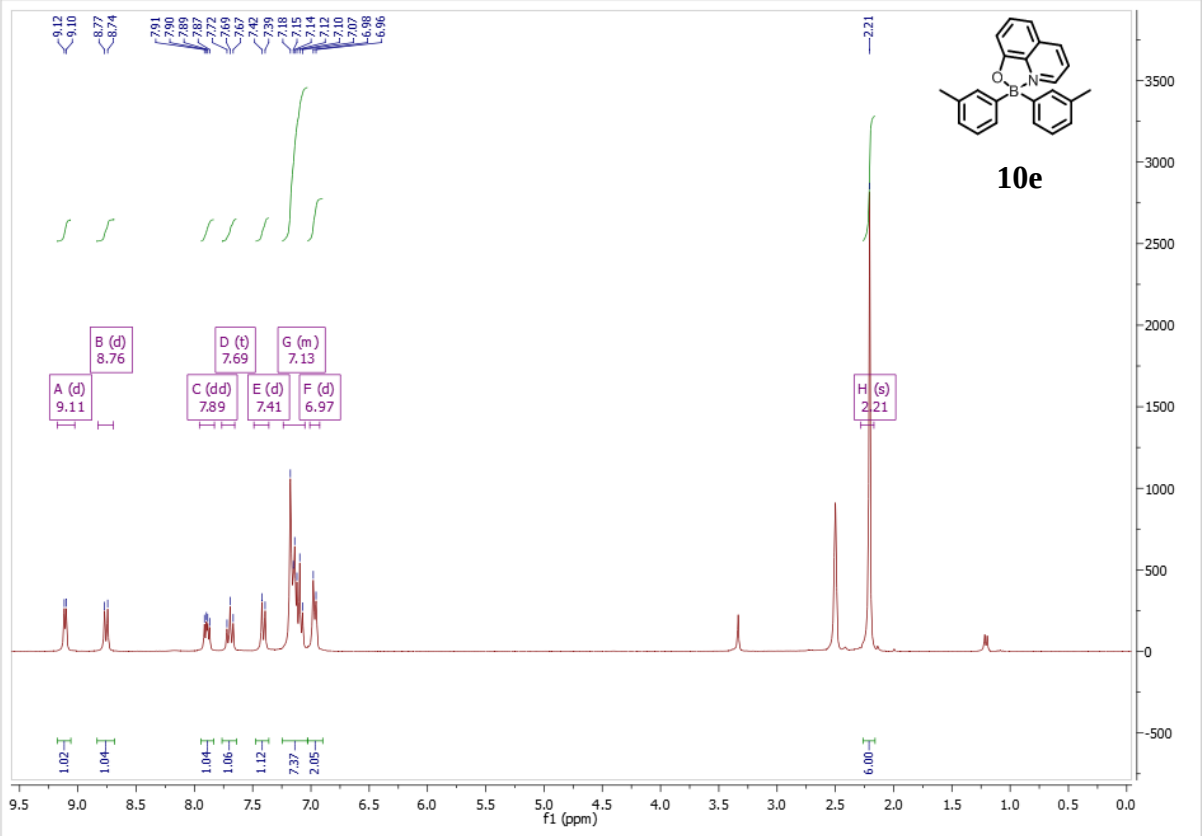

9m
f1 (ppm)

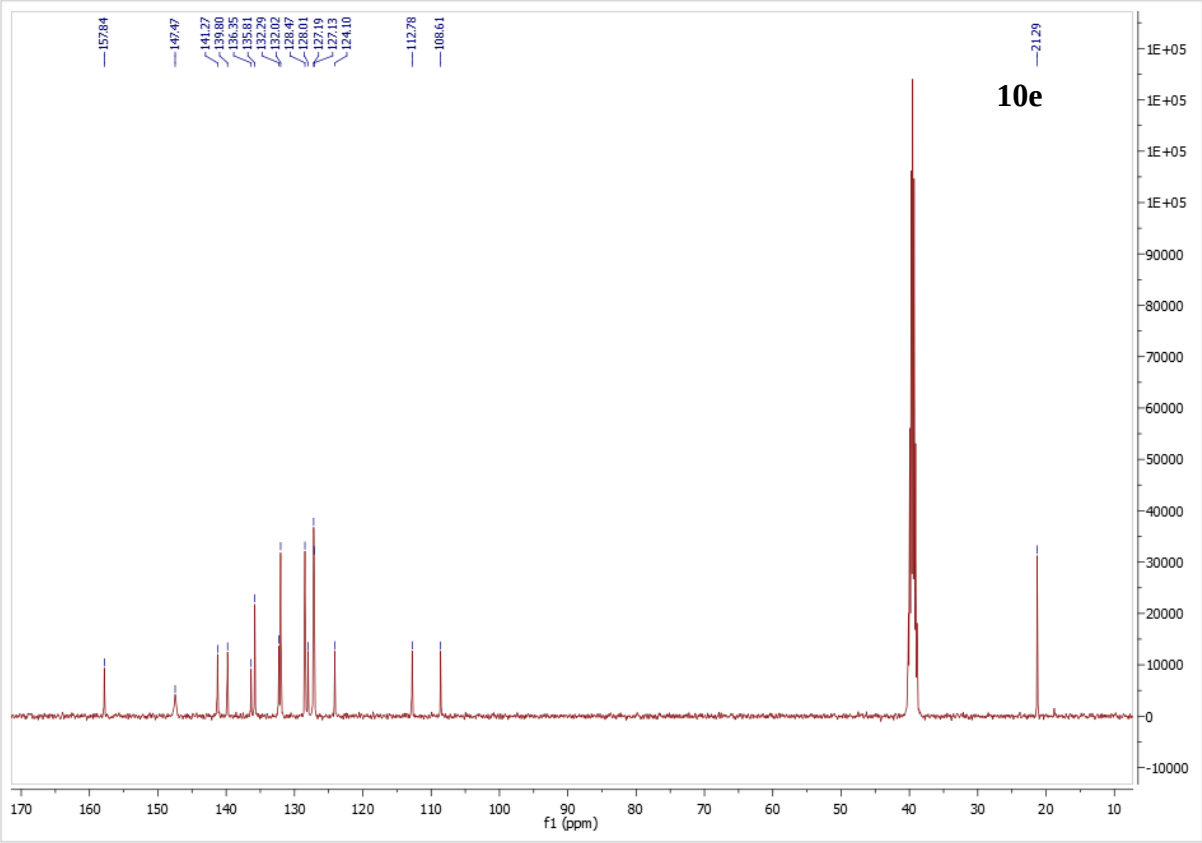

9m
7.36
45
40
35
30
25
20
15
10
5
0
-5
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
f1 (ppm)

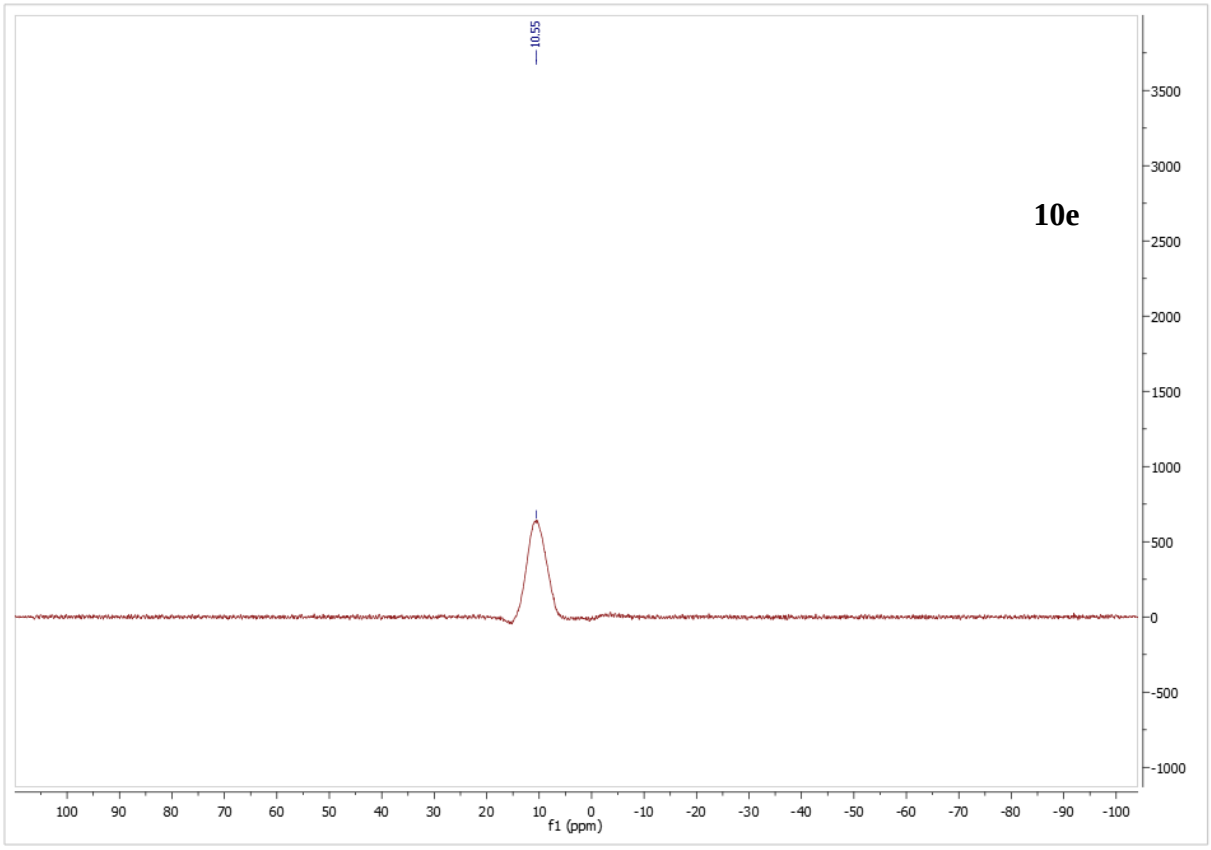

9n
E (dd) 7.23
D (d) 7.40
F (m) 6.93
C (s) 5.87
A (t) 3.82
B (m) 2.89
f1 (ppm)

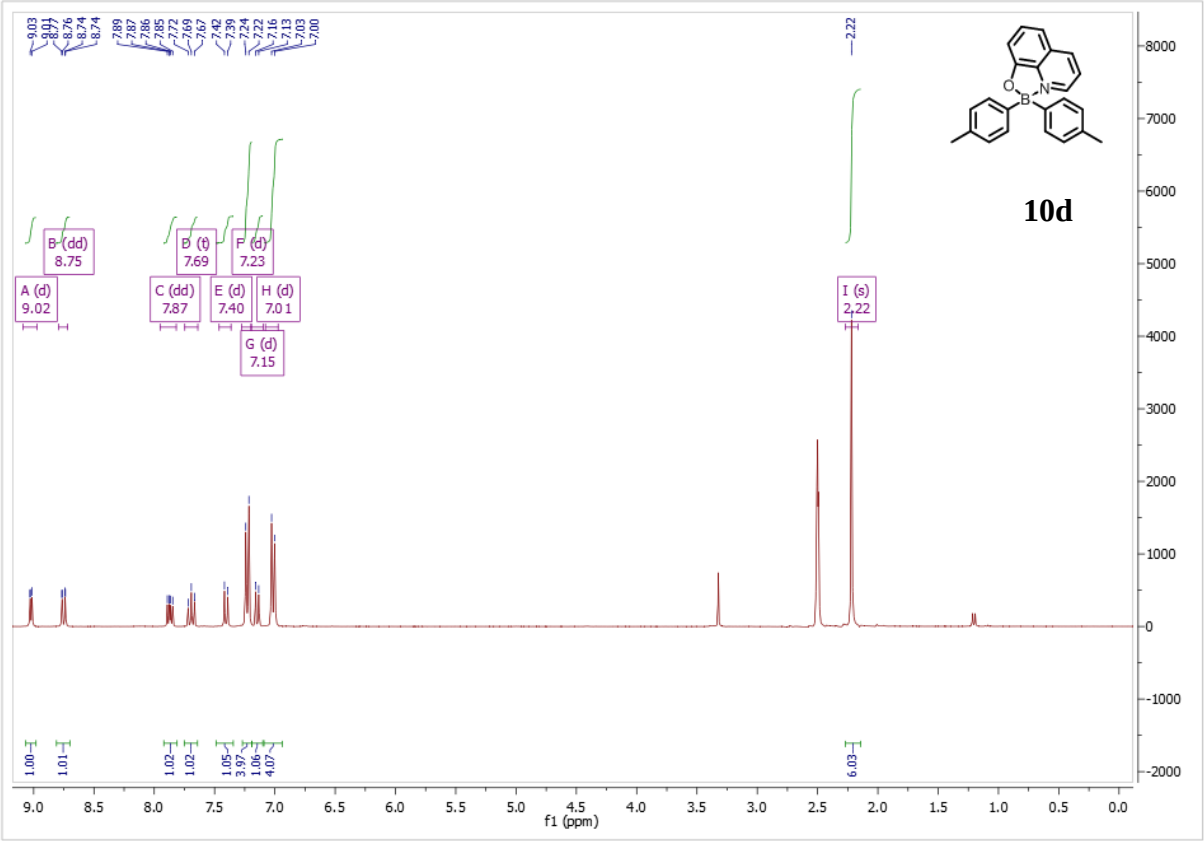

9n
f1 (ppm)

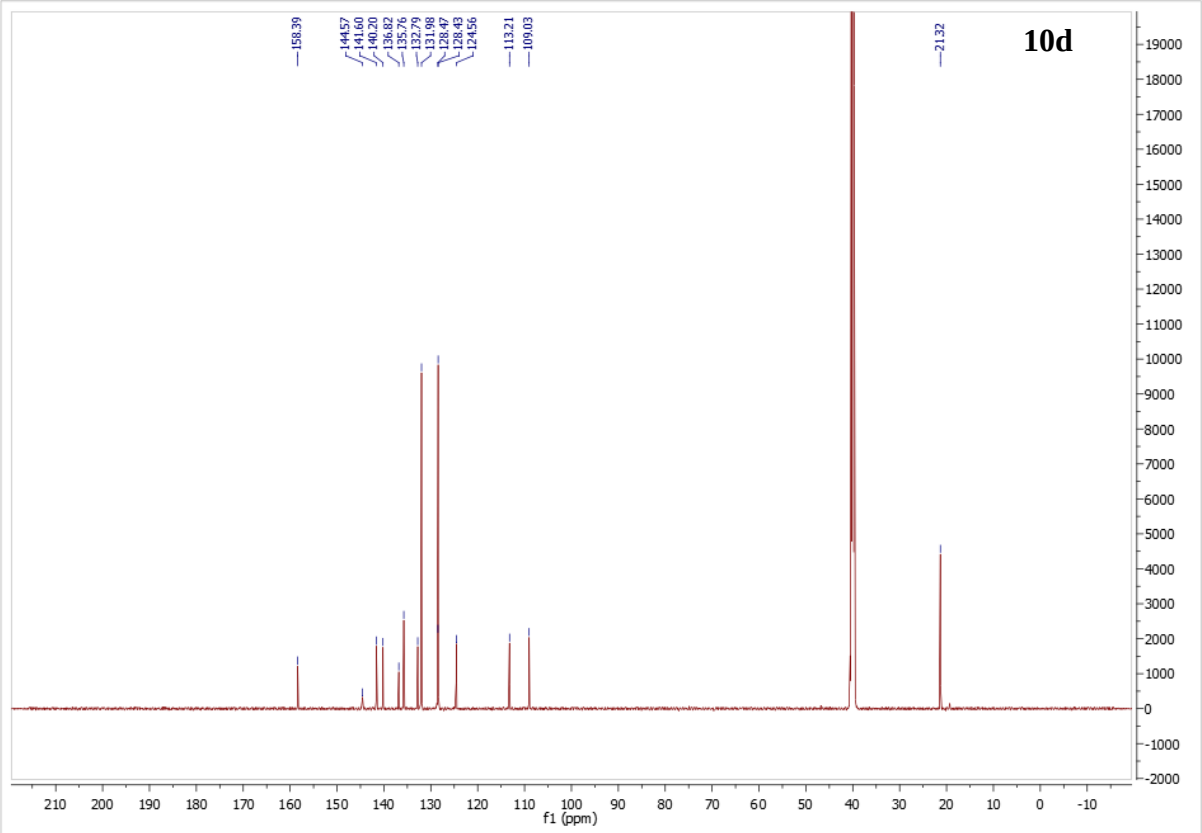

9n
4.92
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
f1 (ppm)

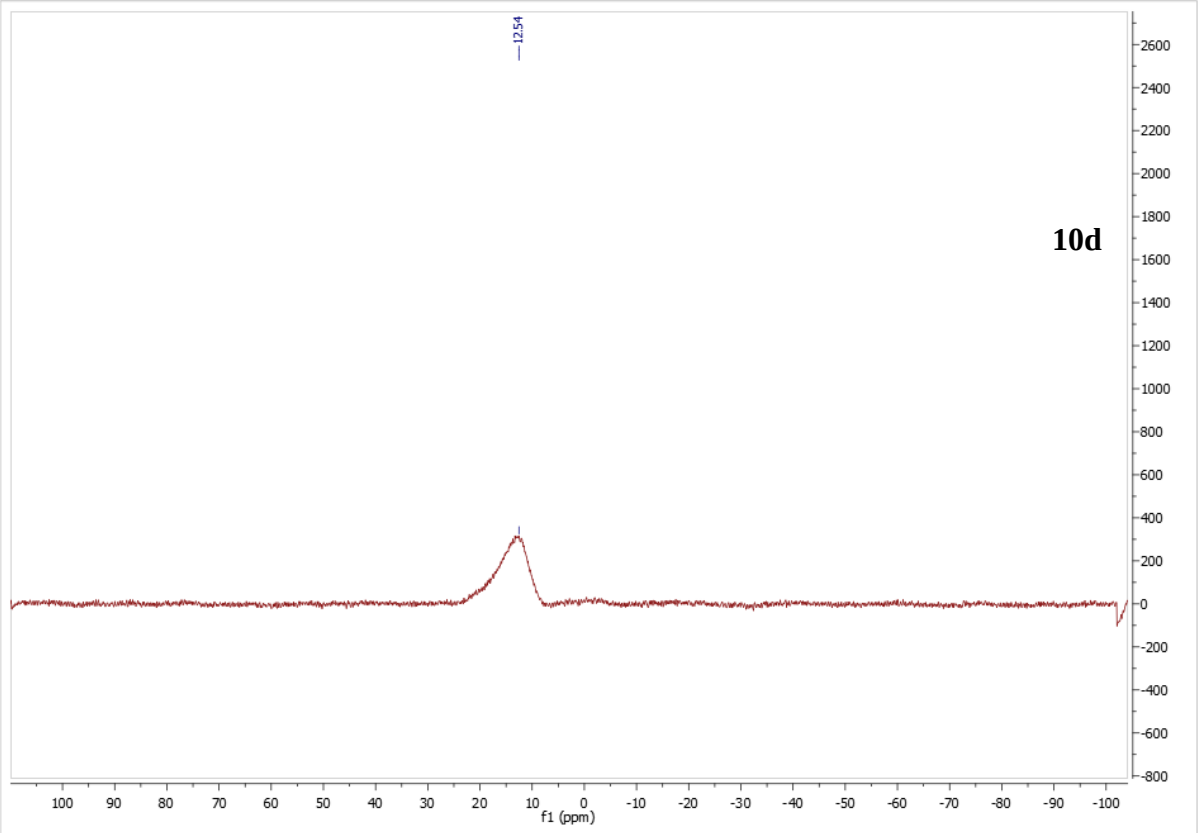

10e
A (d) 9.11
B (d) 8.76
C (dd) 7.89
D (t) 7.69
E (d) 7.41
F (d) 6.97
G (m) 7.13
H (s) 2.21
f1 (ppm)

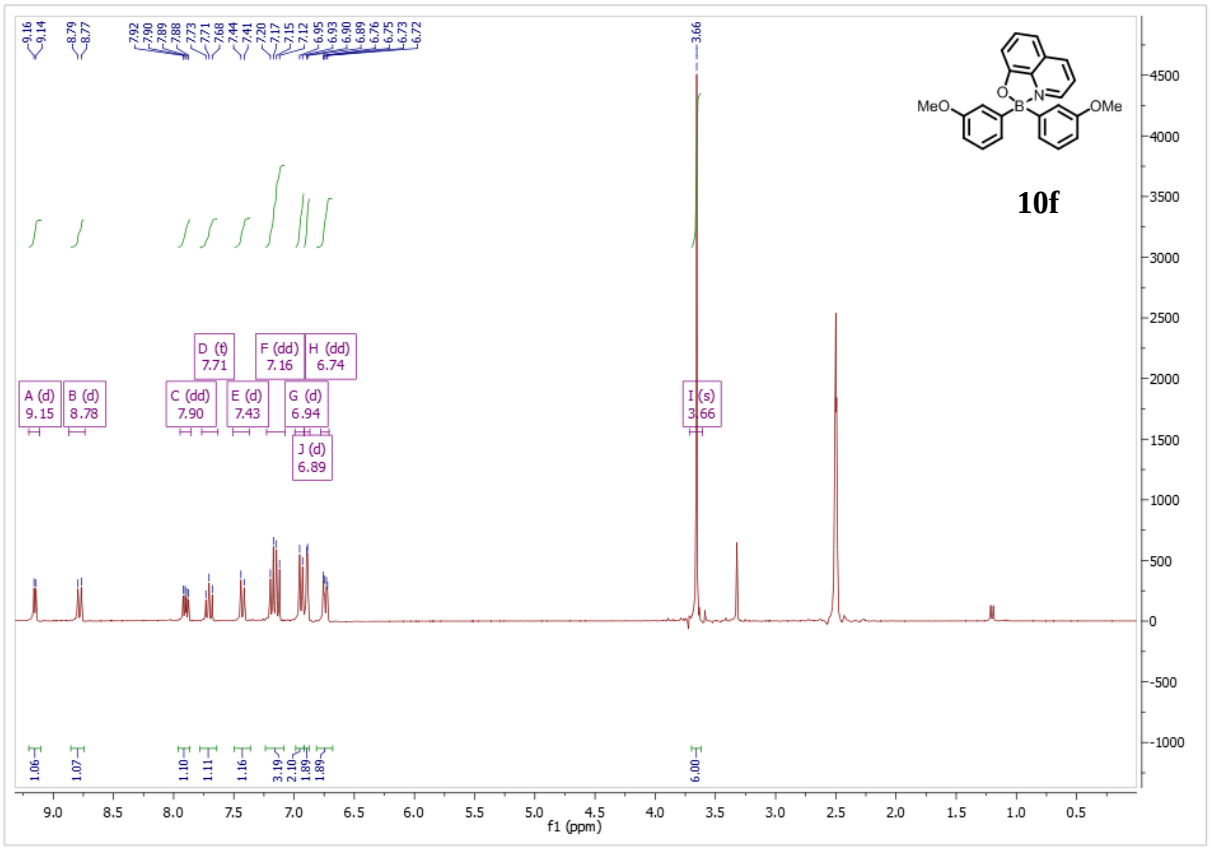

10e
157.84
147.47
141.27
139.80
136.35
135.81
132.29
132.02
128.47
128.01
127.19
127.13
124.10
112.78
108.61
21.29
f1 (ppm)

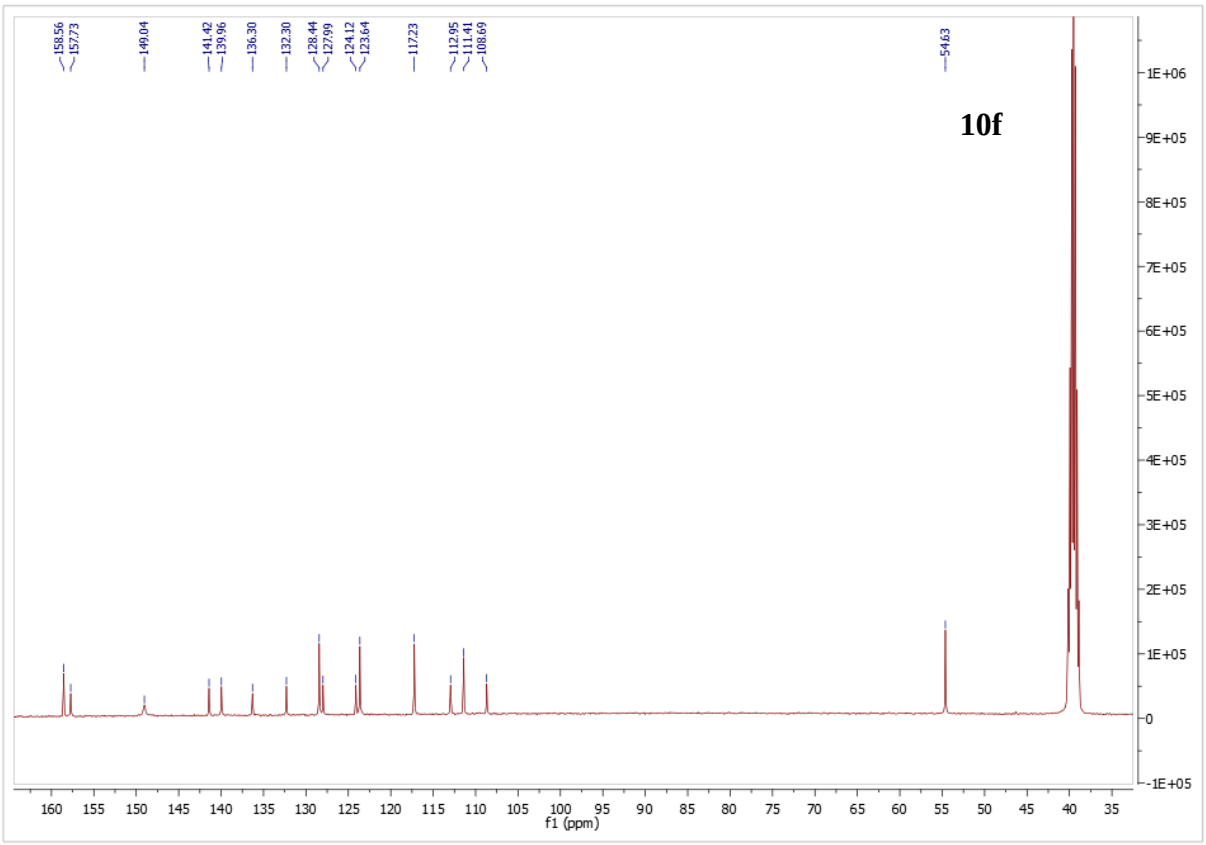

10.55
10e
3500
3000
2500
2000
1500
1000
500
0
-500
-1000
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)

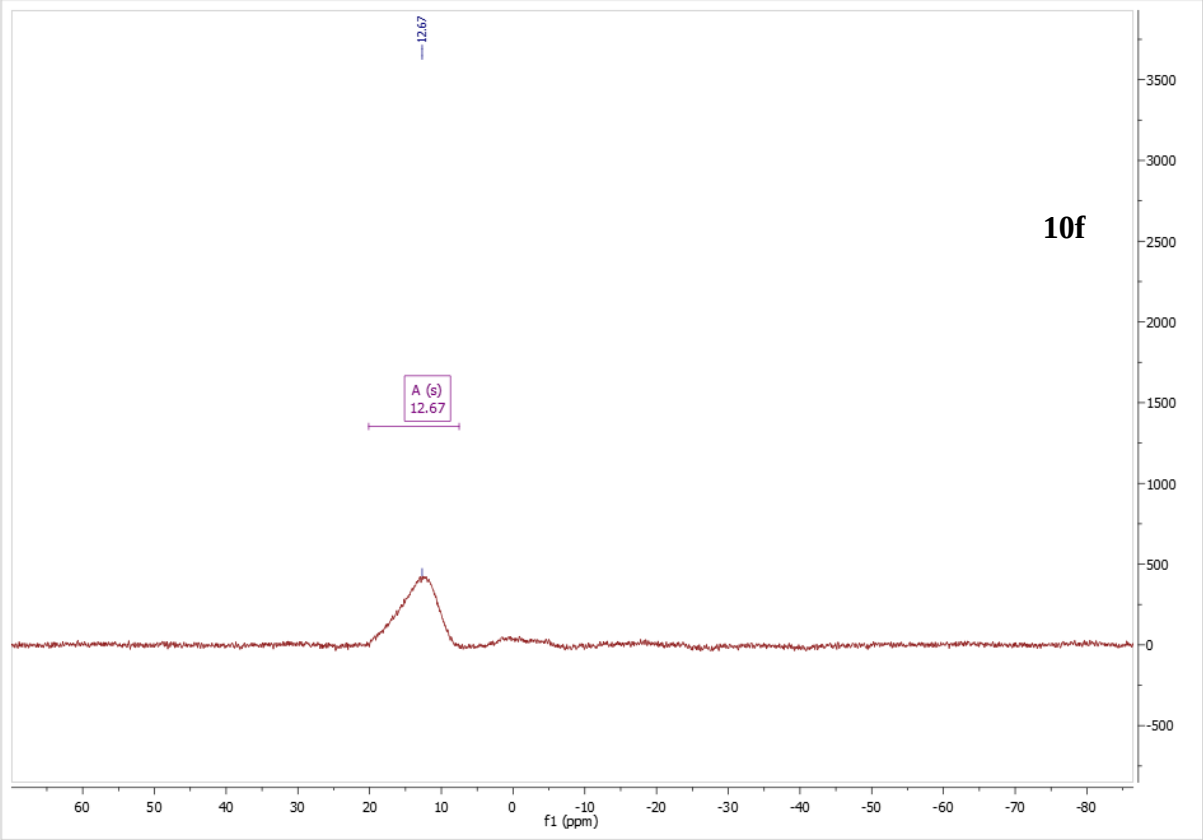

10d
A (d) 9.02
B (dd) 8.75
C (dd) 7.87
D (t) 7.69
E (d) 7.40
F (d) 7.23
G (d) 7.15
H (d) 7.01
I (s) 2,22
f1 (ppm)

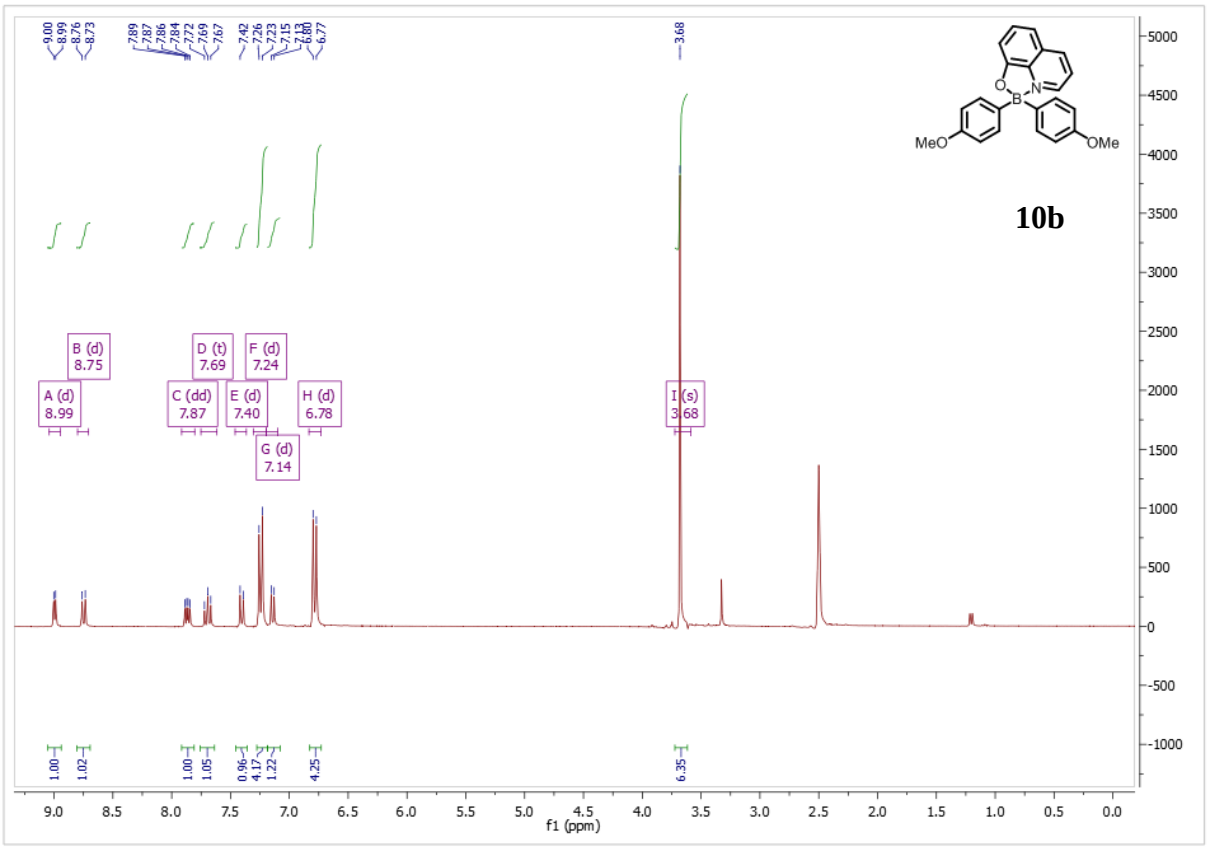

10d
158.39
144.57
141.60
140.20
136.82
135.76
132.79
131.98
128.47
128.43
124.56
113.21
109.03
21.32
f1 (ppm)

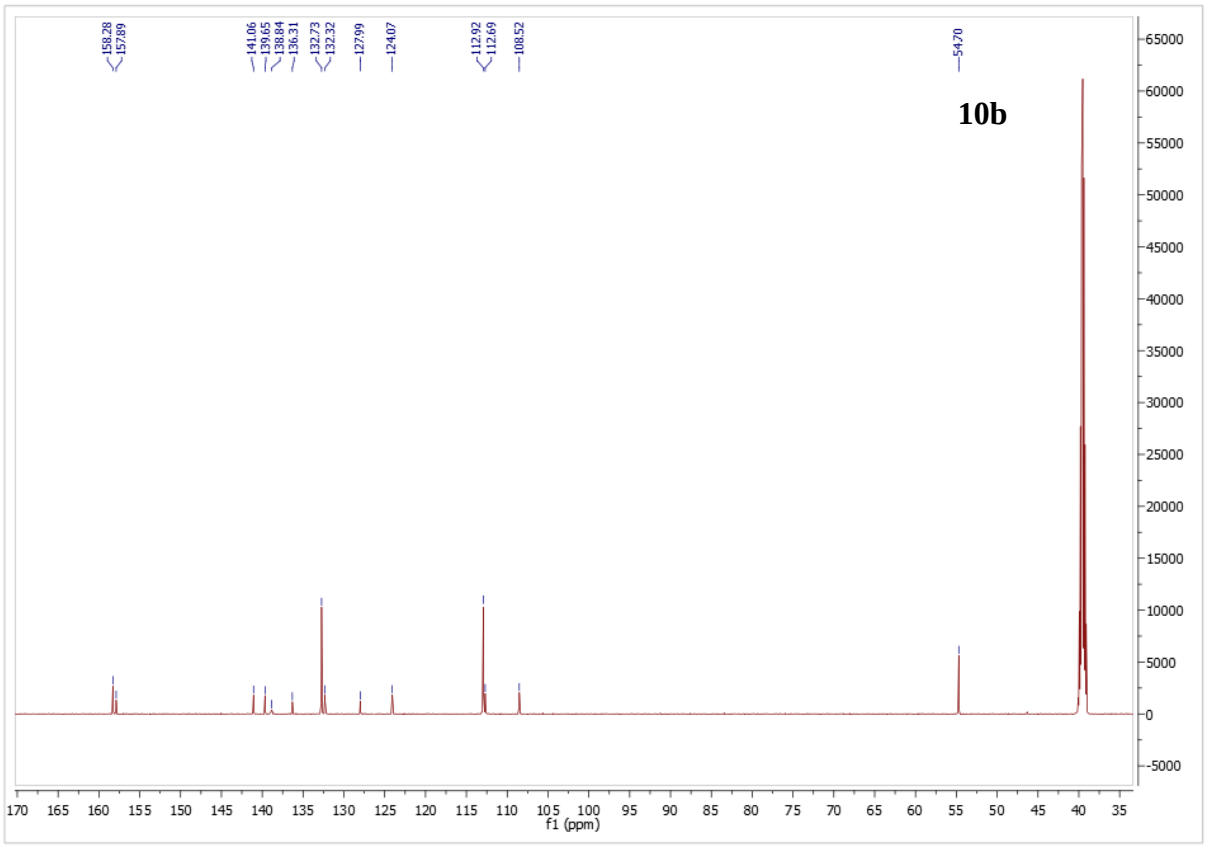

12.54
10d
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
-600
-800
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
f1 (ppm)

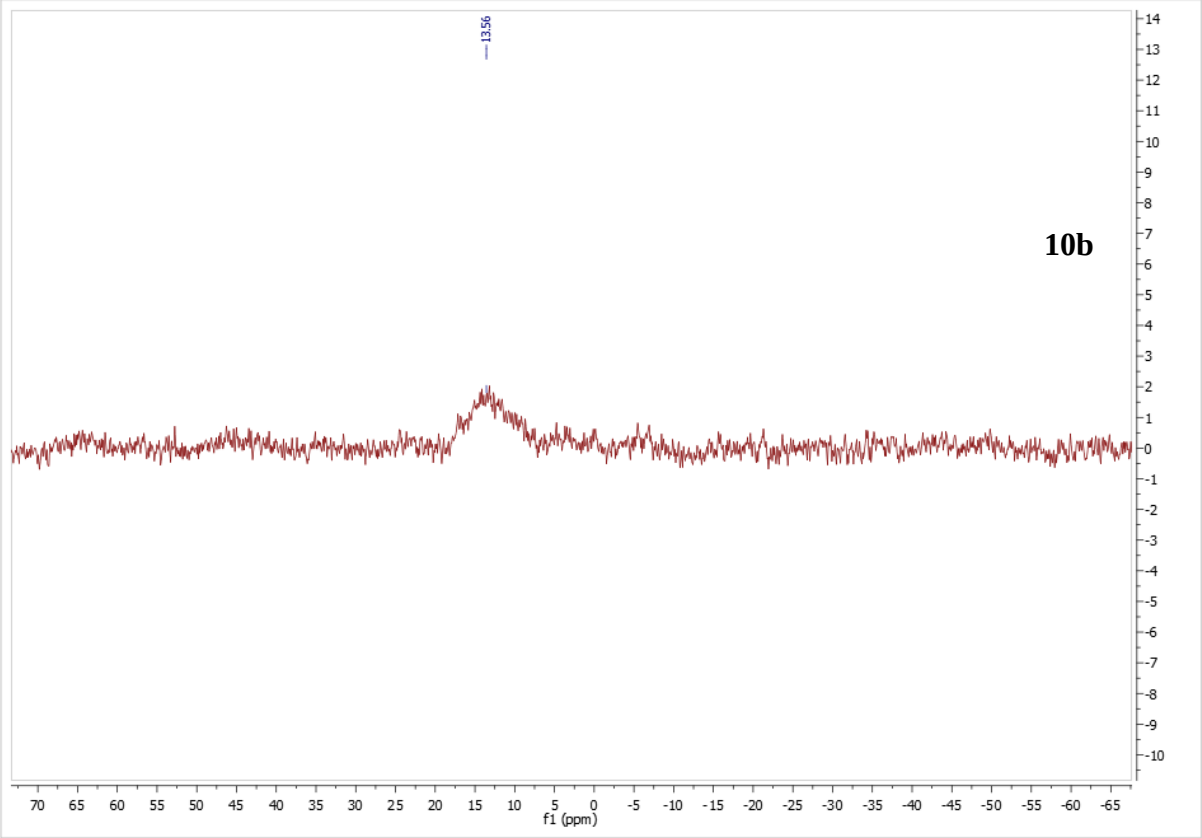

10f
MeO
OMe
A (d) 9.15
B (d) 8.78
C (dd) 7.90
D (t) 7.71
E (d) 7.43
F (dd) 7.16
G (d) 6.94
H (dd) 6.74
J (d) 6.89
I (s) 3.66
f1 (ppm)

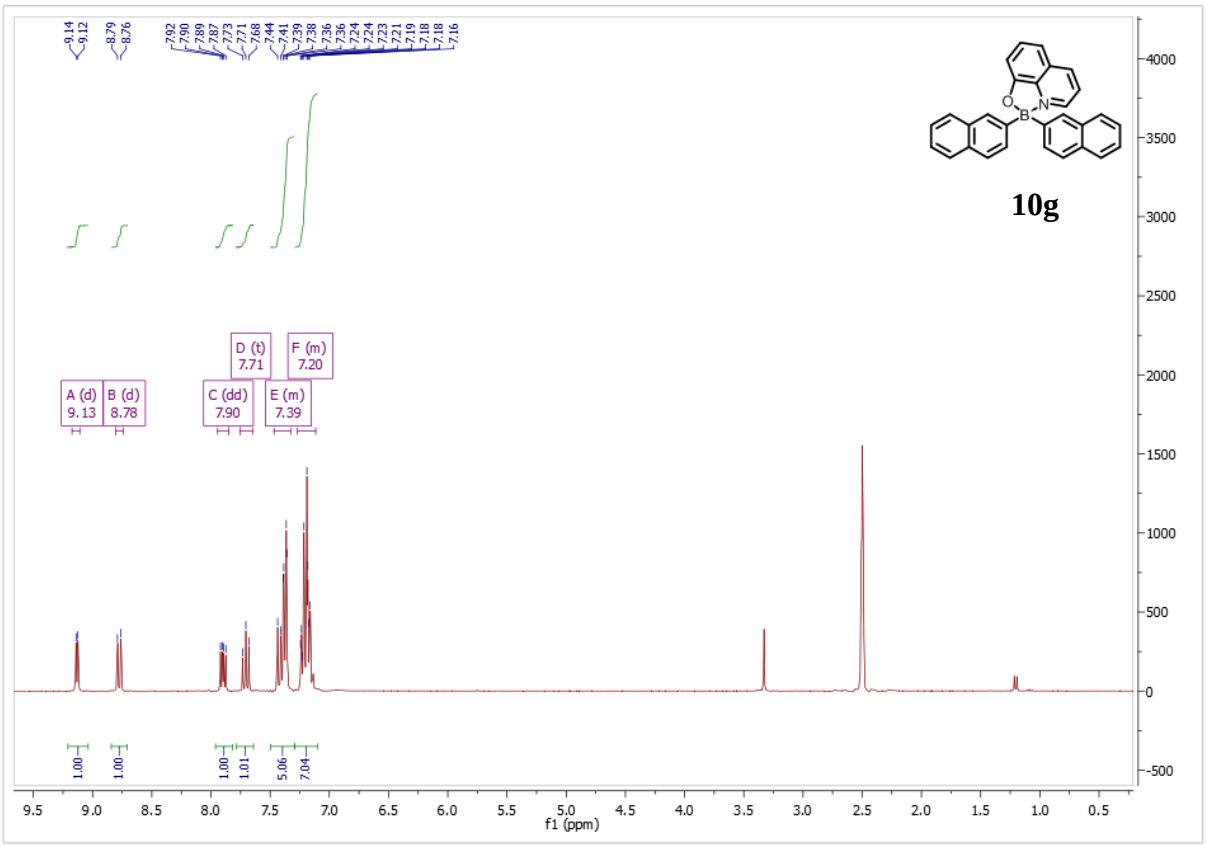

10f
158.56
157.73
149.04
141.42
139.96
136.30
132.30
128.44
127.99
124.12
123.64
117.23
112.95
111.41
108.69
54.63
f1 (ppm)

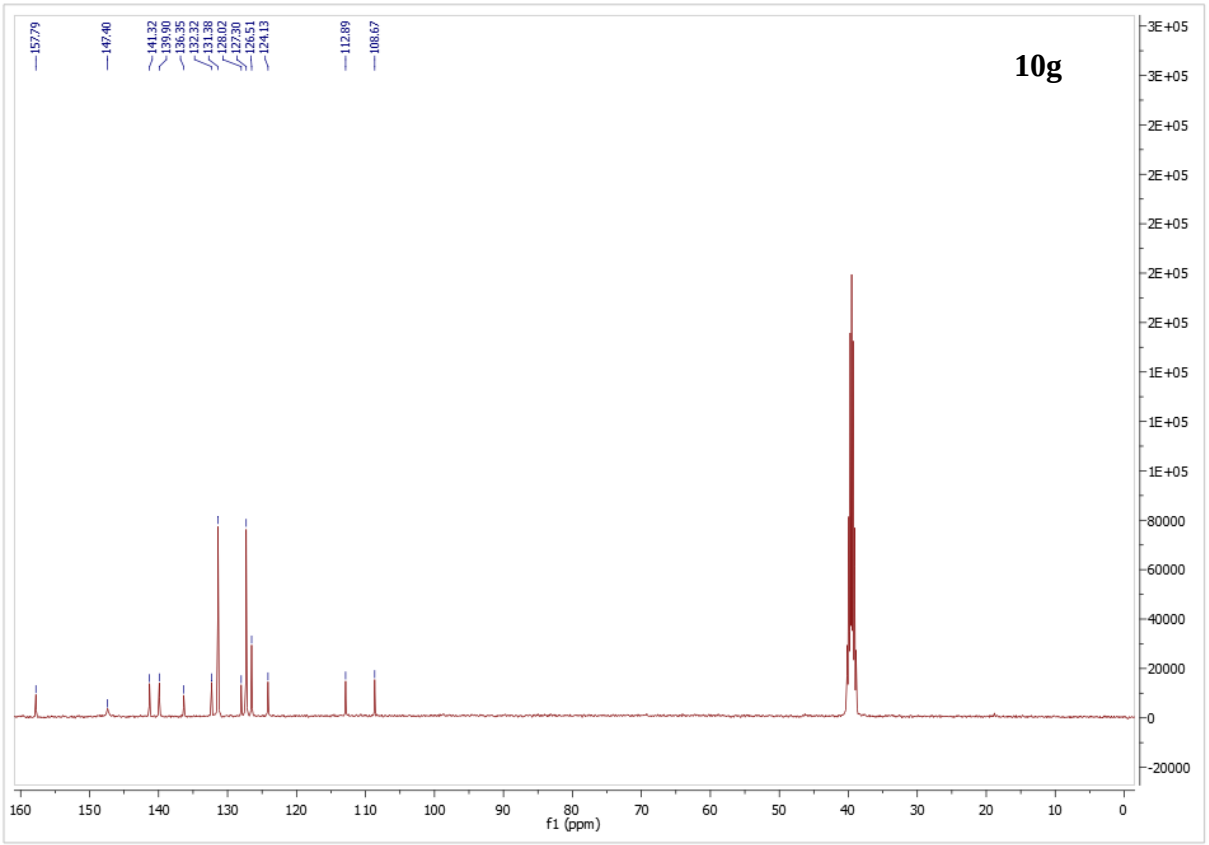

12.67
10f
A (s)
12.67
3500
3000
2500
2000
1500
1000
500
0
-500
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
f1 (ppm)

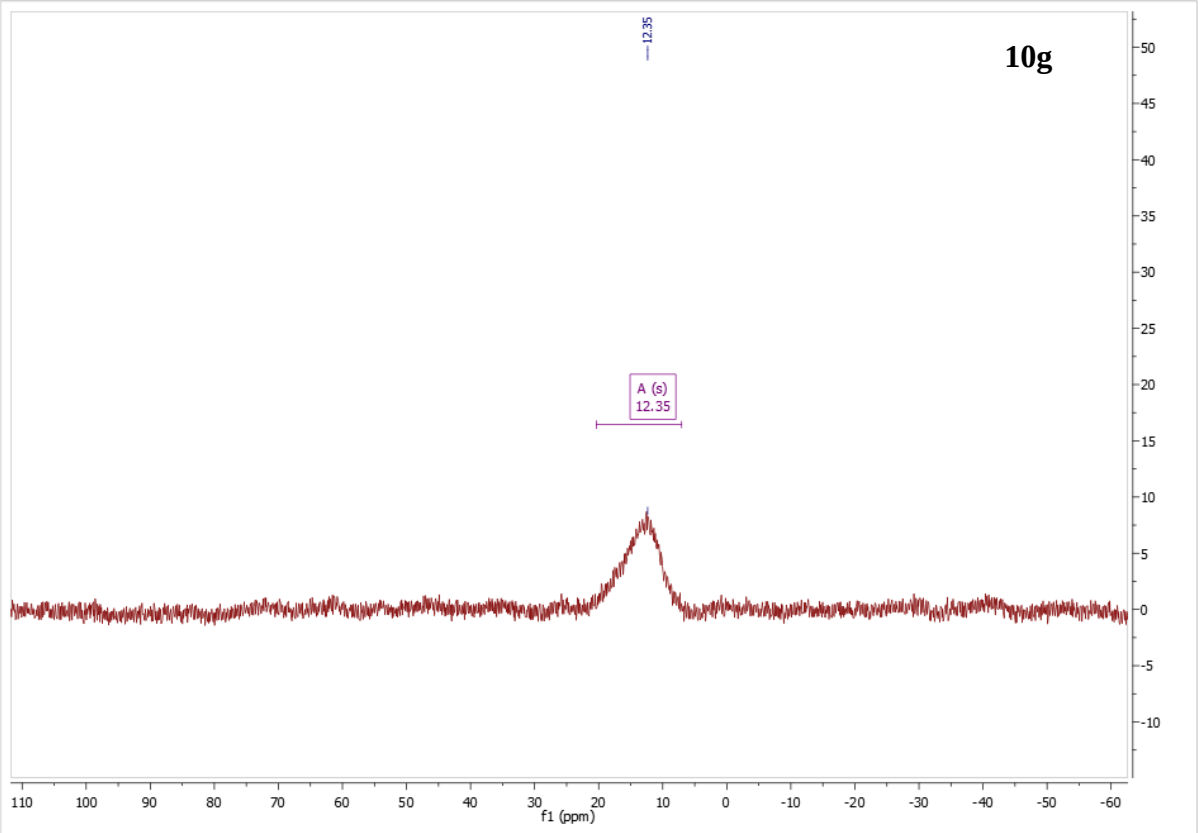

10b
MeO
OMe
A (d) 8.99
B (d) 8.75
C (dd) 7.87
D (t) 7.69
E (d) 7.40
F (d) 7.24
G (d) 7.14
H (d) 6.78
I (s) 3.68
f1 (ppm)

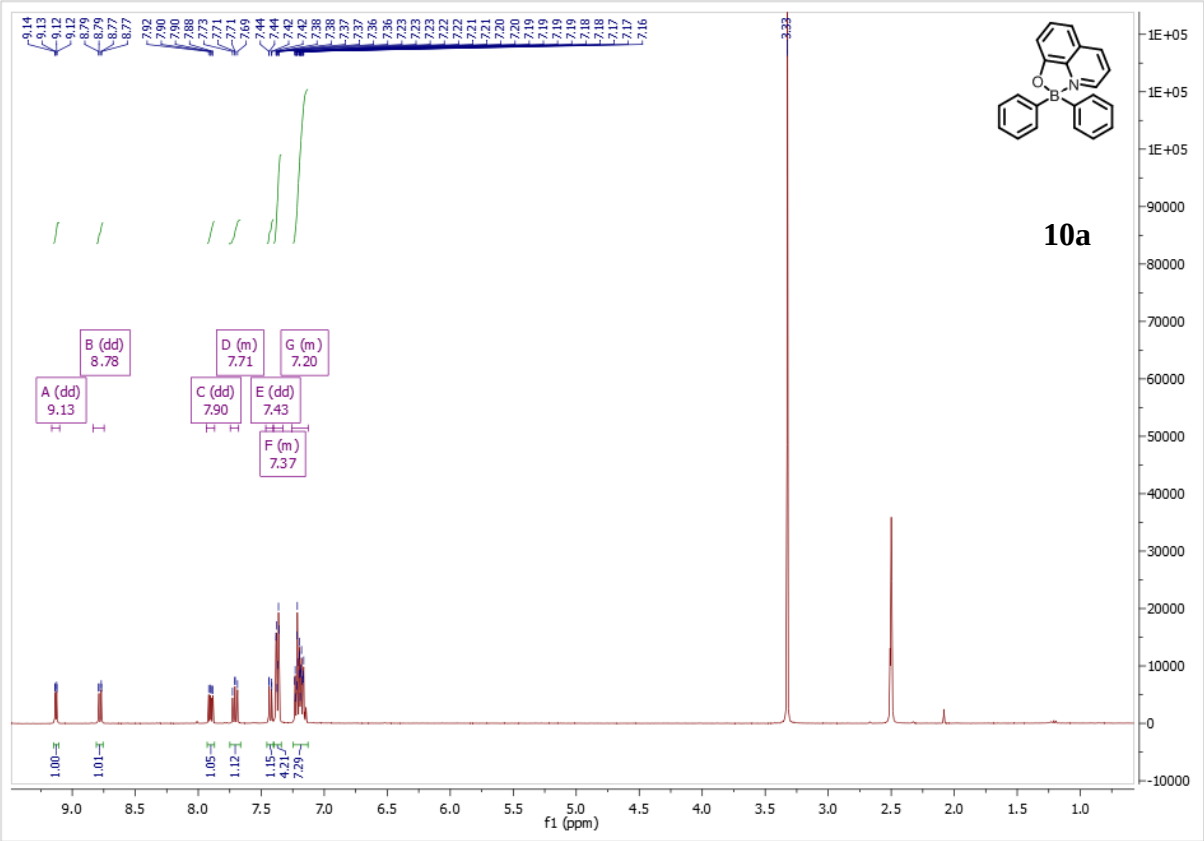

10b
158.28
157.89
141.06
139.65
138.84
136.31
132.73
132.32
127.99
124.07
112.92
112.69
108.52
54.70
f1 (ppm)

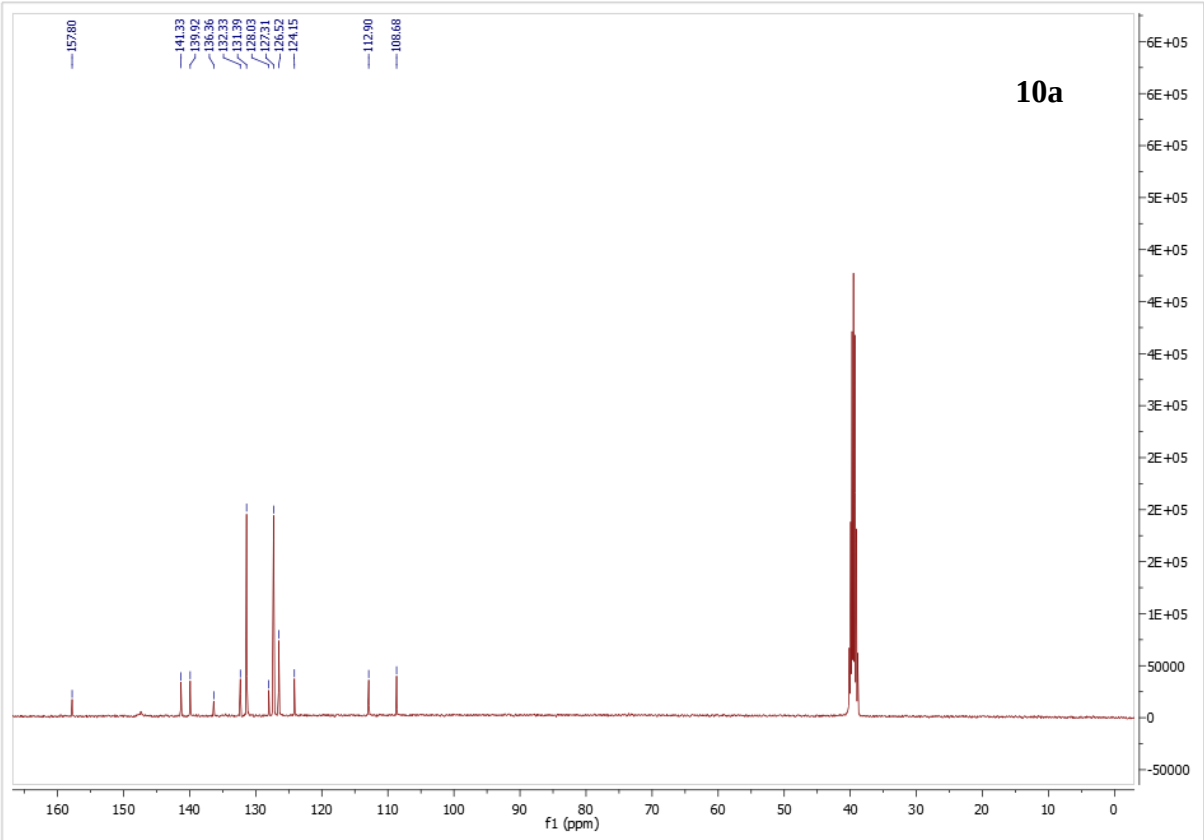

13.56
10b
f1 (ppm)

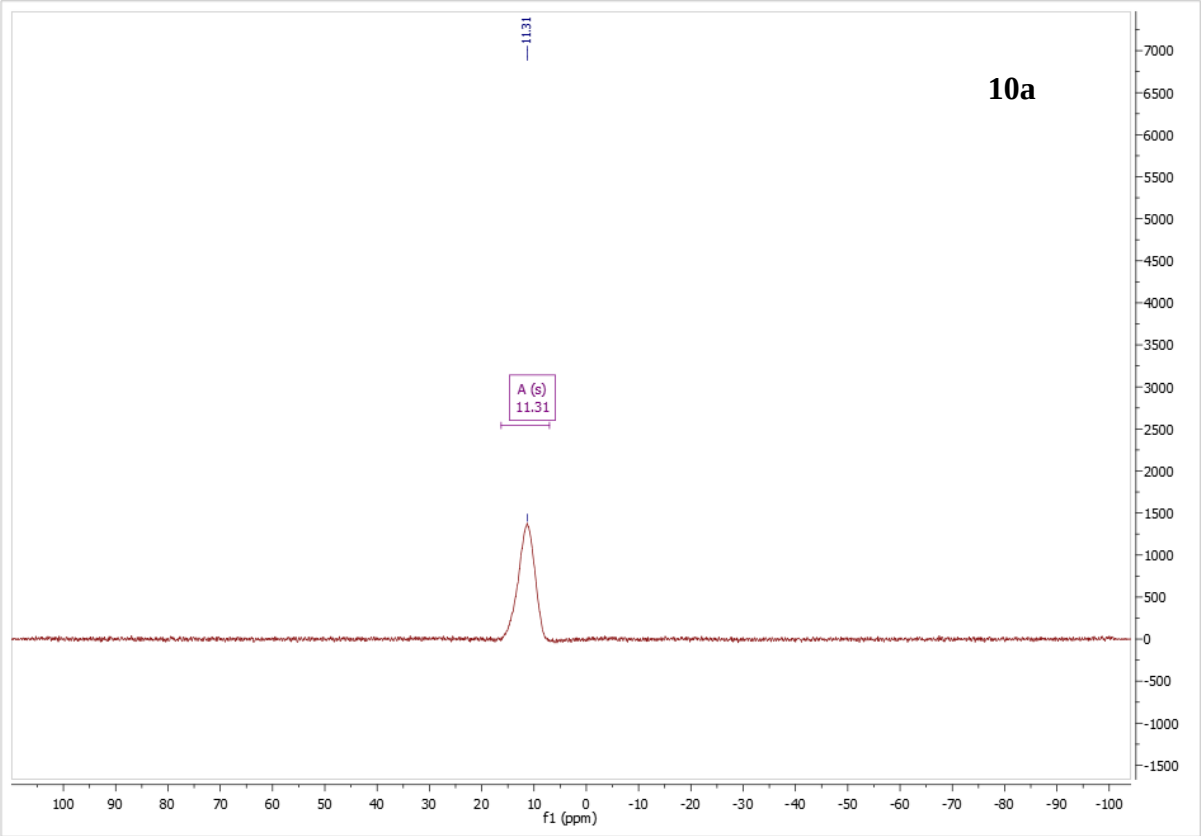

10g
A (d) 9.13
B (d) 8.78
C (dd) 7.90
D (t) 7.71
E (m) 7.39
F (m) 7.20
f1 (ppm)

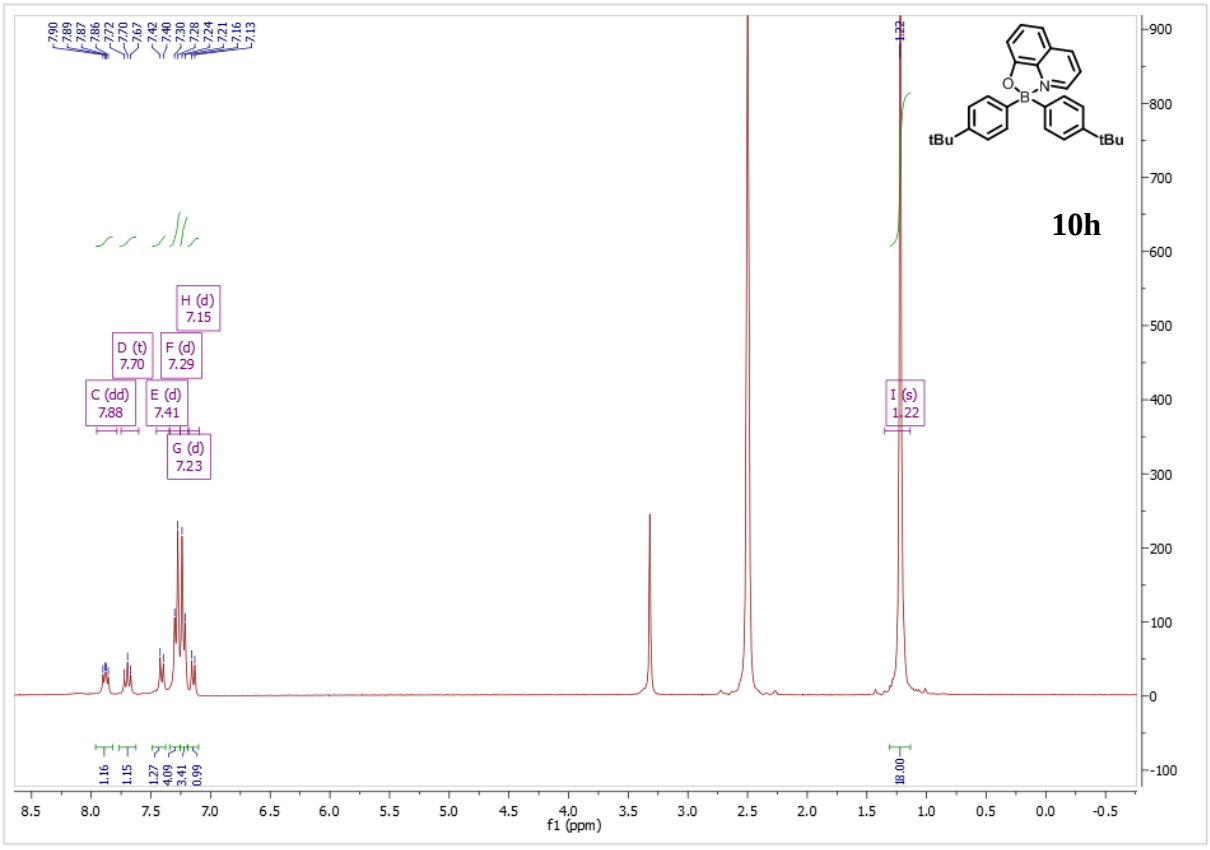

10g
157.79
147.40
141.32
139.90
136.35
132.32
131.38
128.02
127.30
126.51
124.13
112.89
108.67
f1 (ppm)

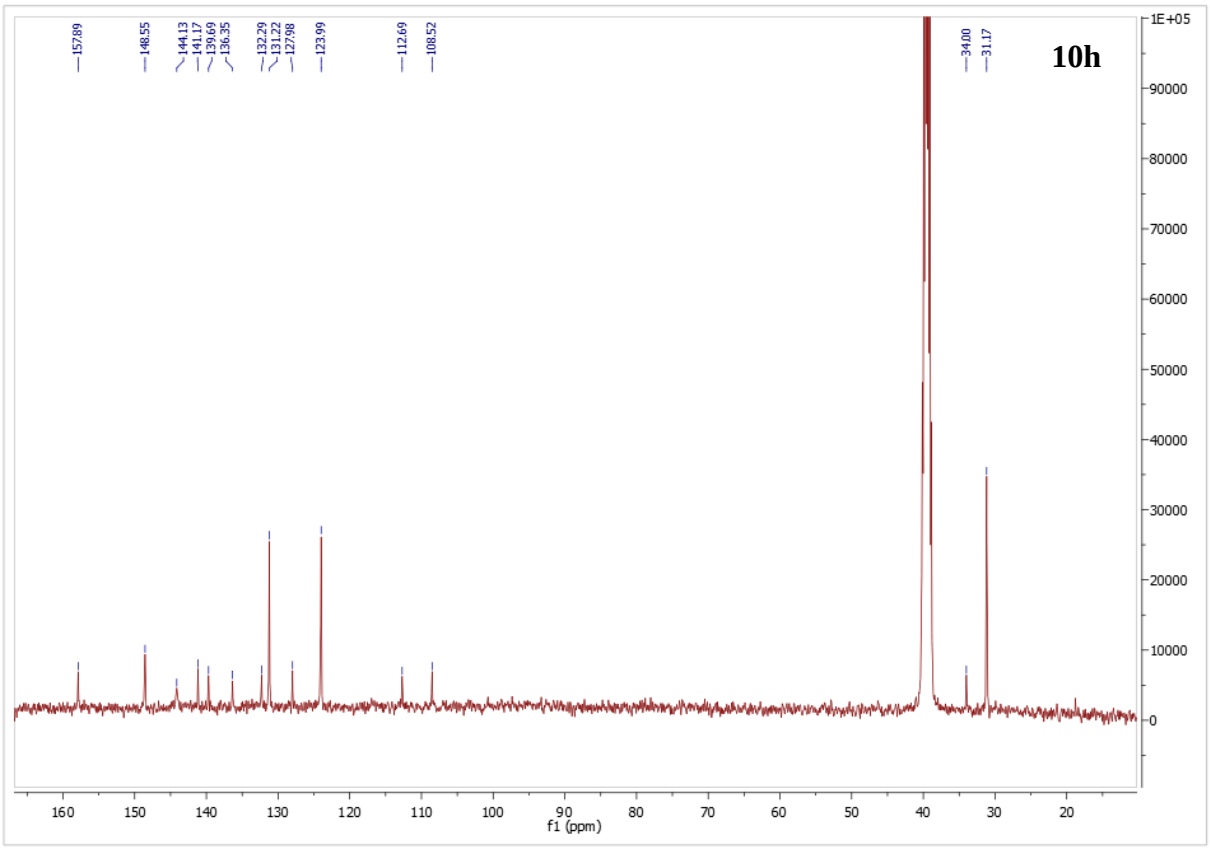

12.35
10g
A (s)
12.35
50
45
40
35
30
25
20
15
10
5
0
-5
-10
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
f1 (ppm)

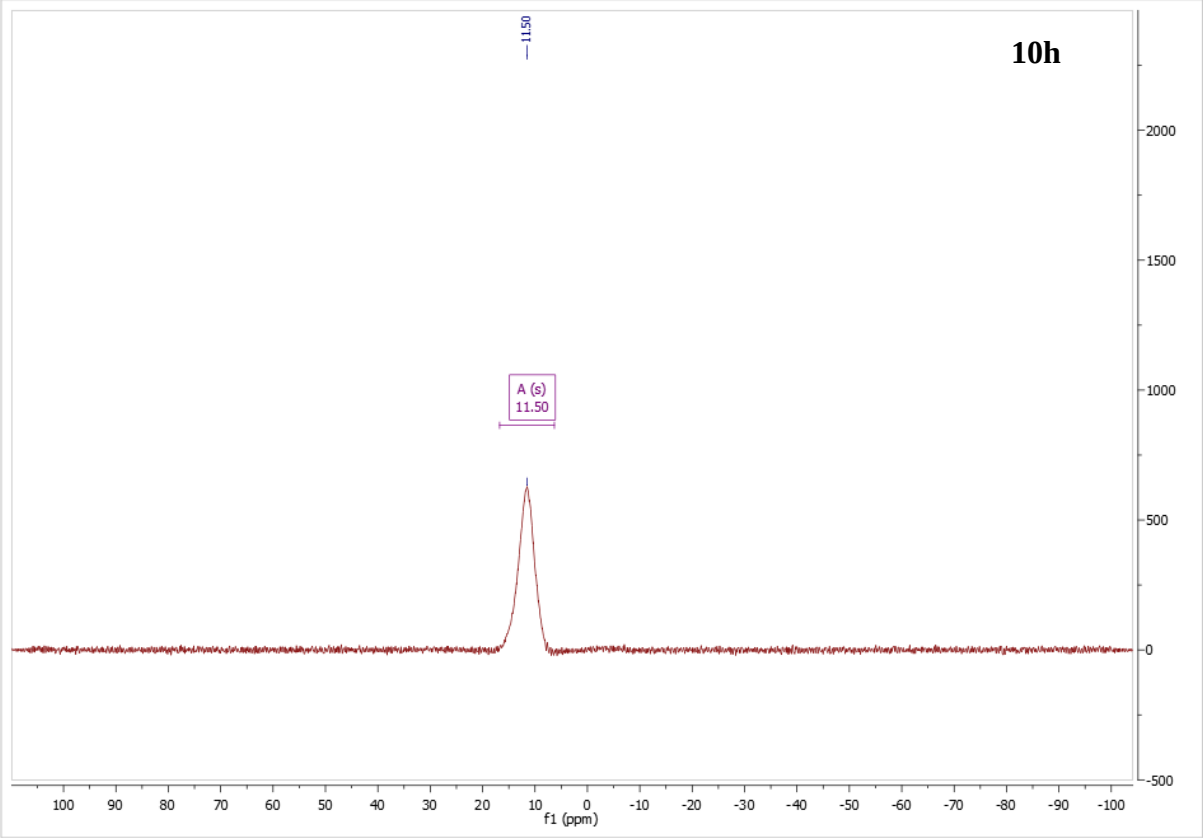

10a
A (dd) 9.13
B (dd) 8.78
C (dd) 7.90
D (m) 7.71
E (dd) 7.43
F (m) 7.37
G (m) 7.20
f1 (ppm)

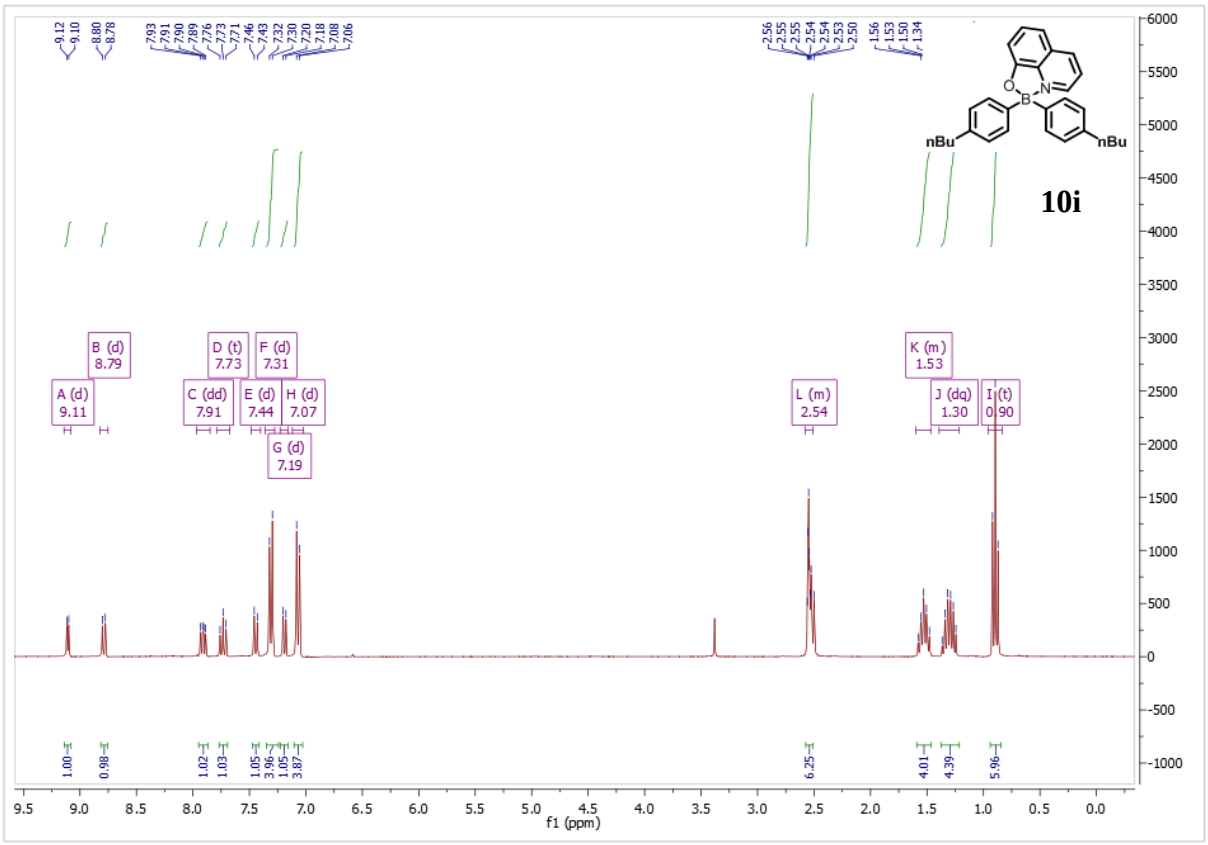

10a
f1 (ppm)

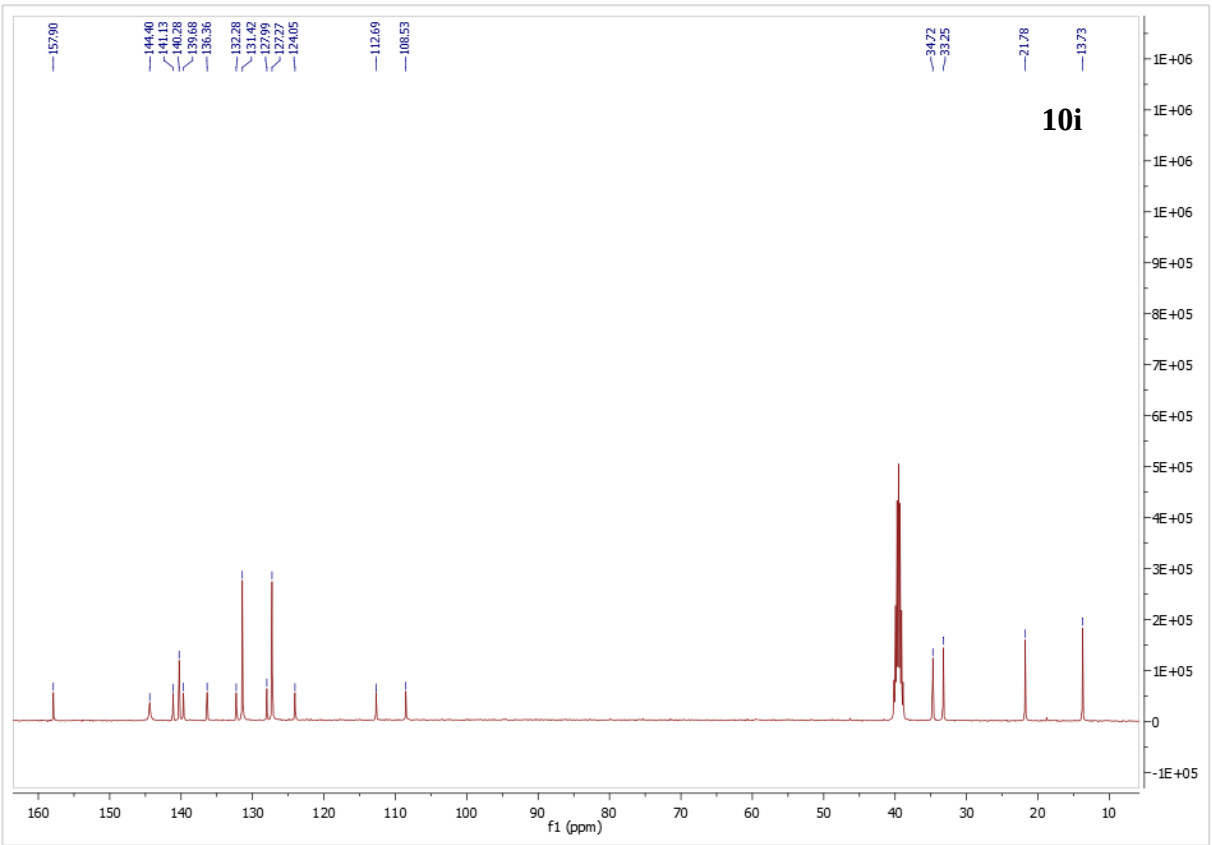

11.31
10a
A (s)
11.31
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-1000
-1500
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
f1 (ppm)

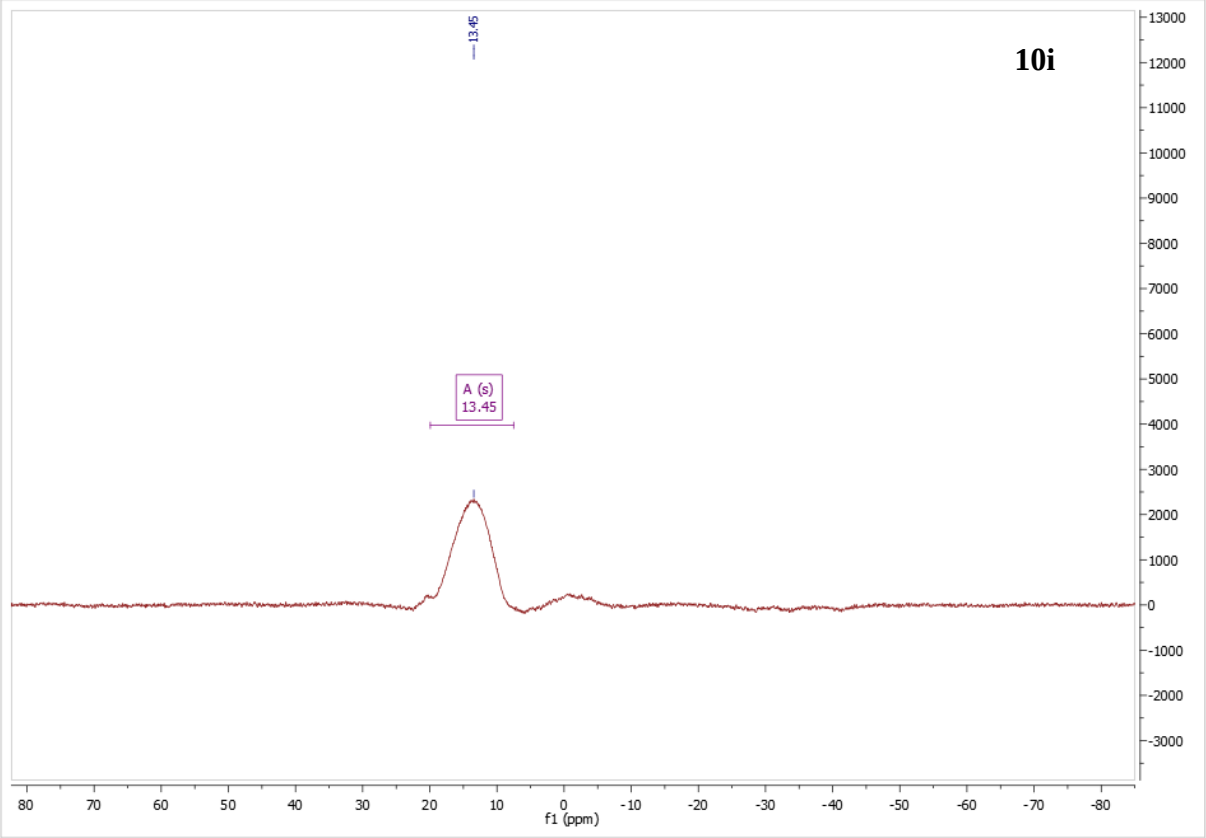

10h
H (d) 7.15
D (t) 7.70
F (d) 7.29
C (dd) 7.88
E (d) 7.41
G (d) 7.23
I (s) 1.22
tBu
tBu
f1 (ppm)

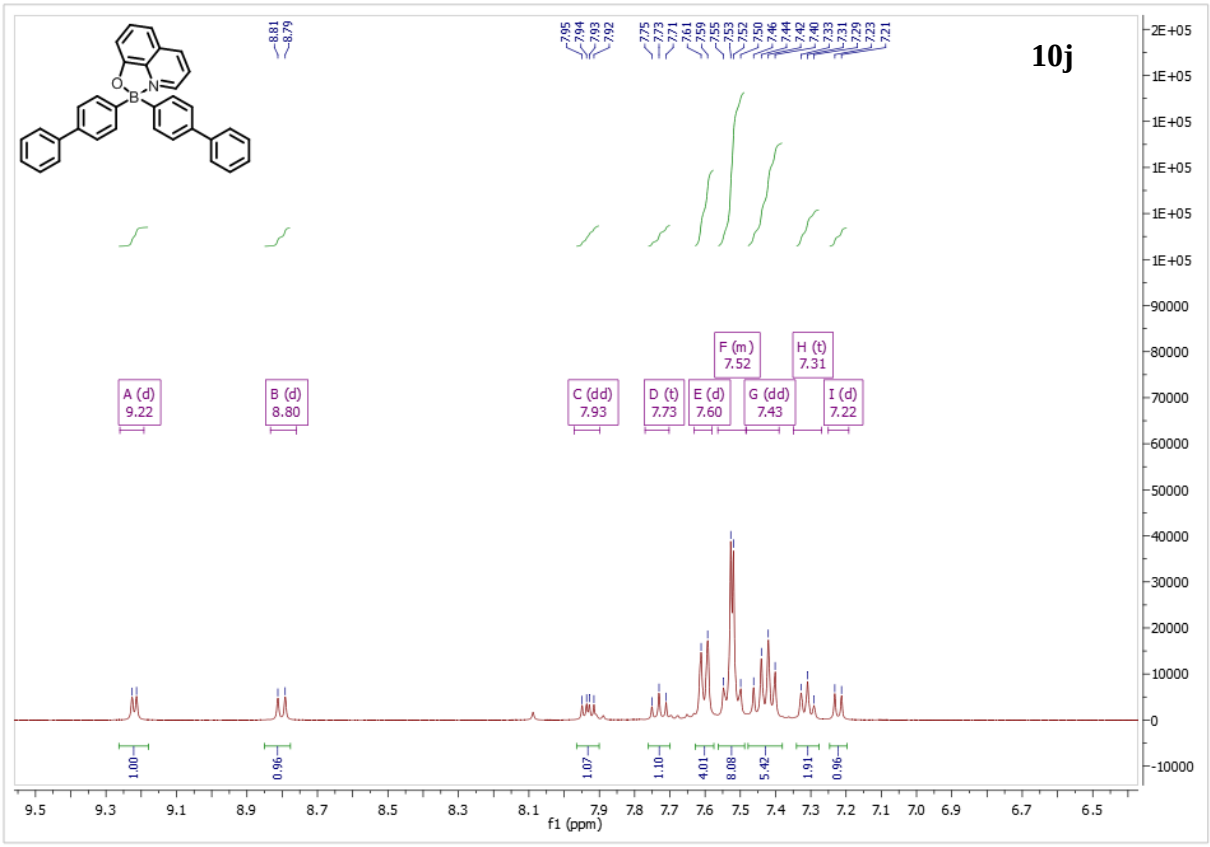

10h
157.89
148.55
144.13
141.17
139.69
136.35
132.29
131.22
127.98
123.99
112.69
108.52
34.00
31.17
f1 (ppm)

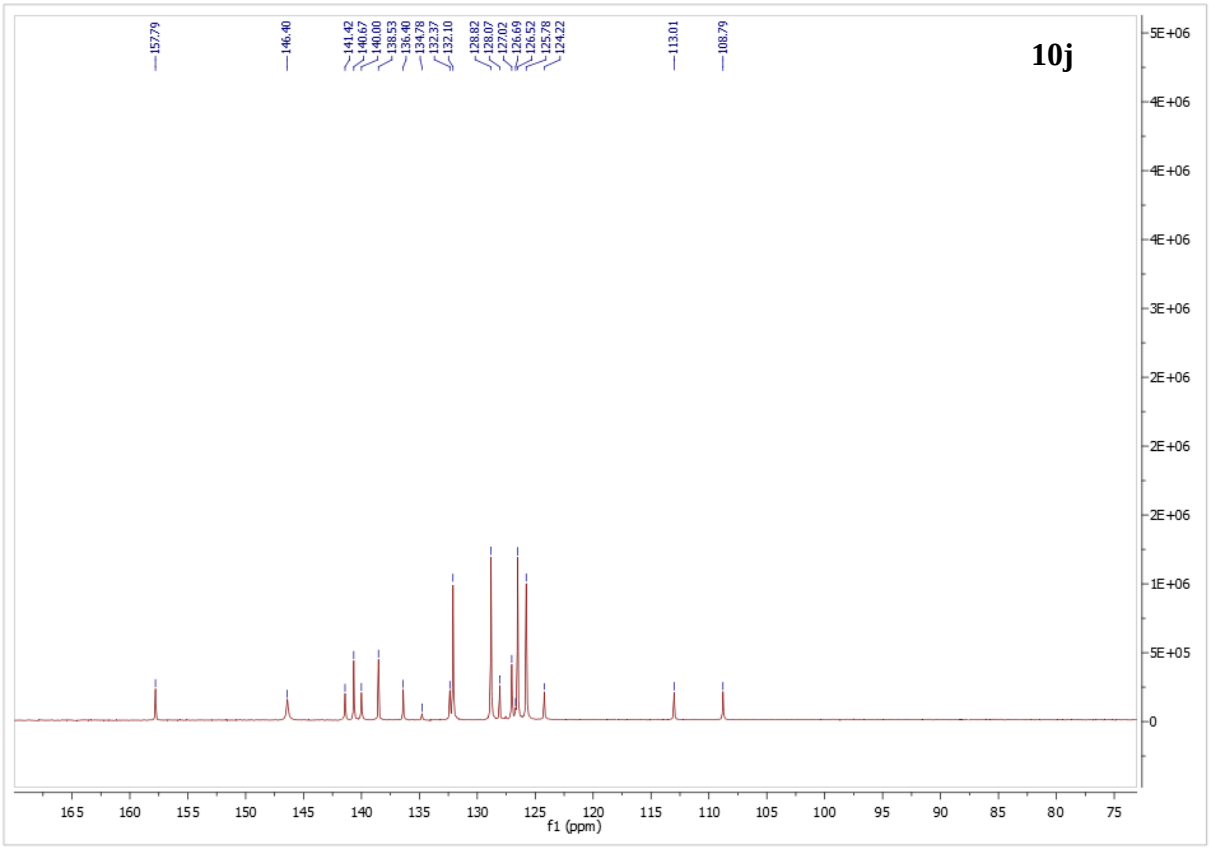

11.50
10h
A (s)
11.50
2000
1500
1000
500
0
-500
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
f1 (ppm)

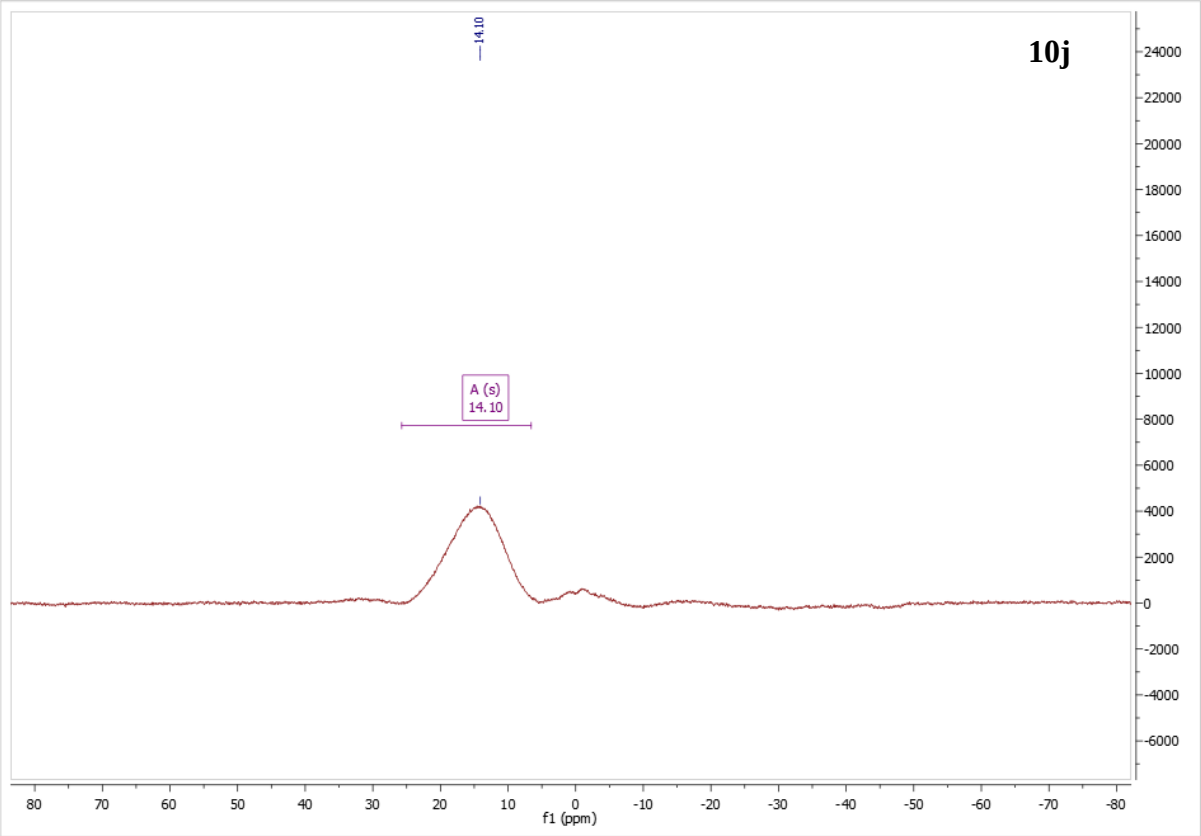

10i
nBu
nBu
A (d) 9.11
B (d) 8.79
C (dd) 7.91
D (t) 7.73
E (d) 7.44
F (d) 7.31
G (d) 7.19
H (d) 7.07
L (m) 2.54
J (dq) 1.30
K (m) 1.53
f1 (ppm)

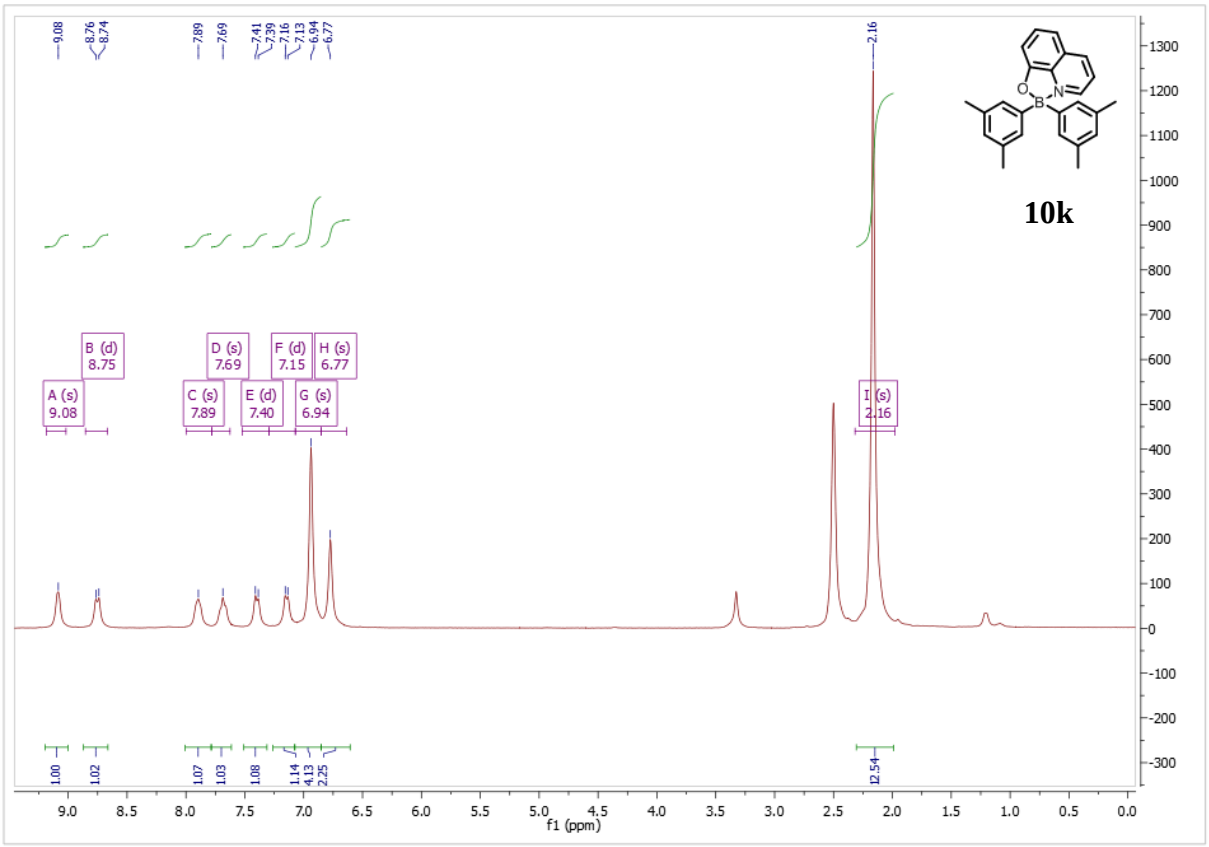

10i
f1 (ppm)

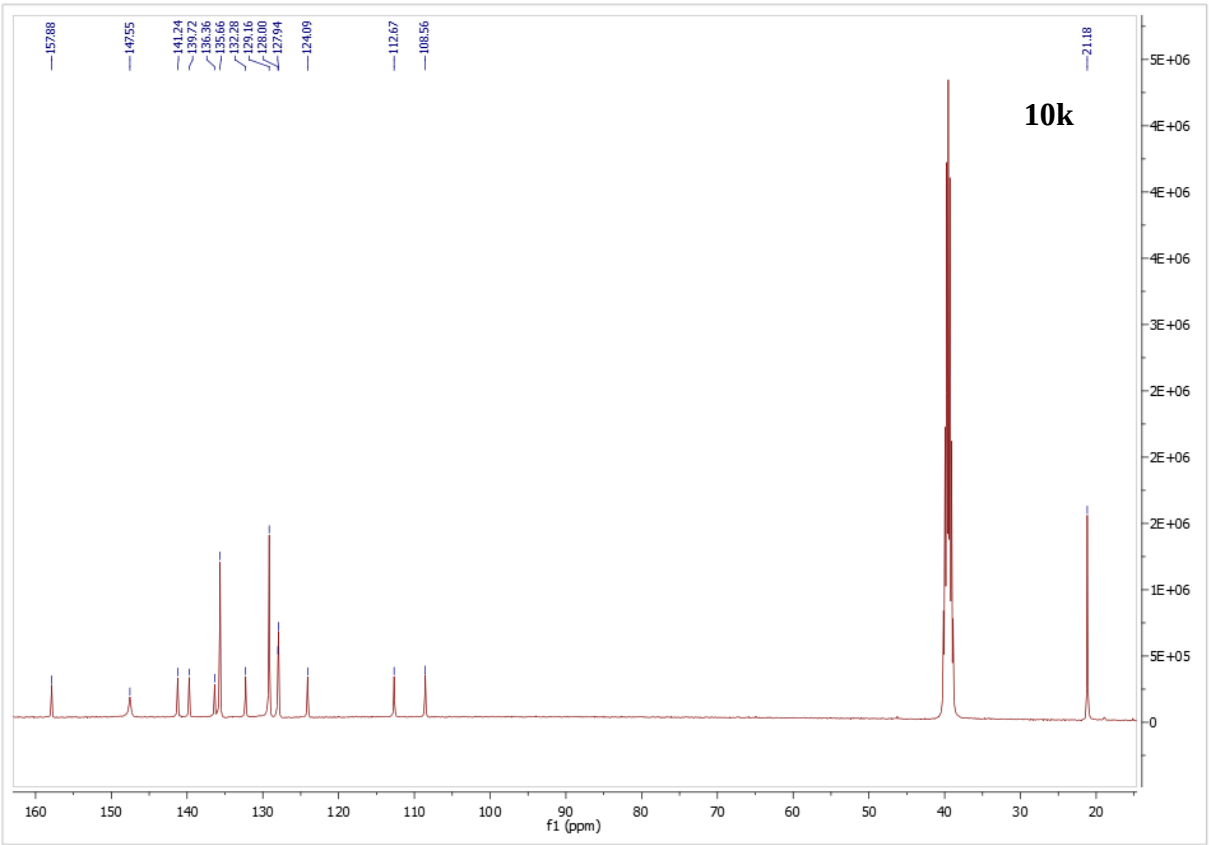

13.45
10i
A (s)
13.45
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
-3000
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
f1 (ppm)

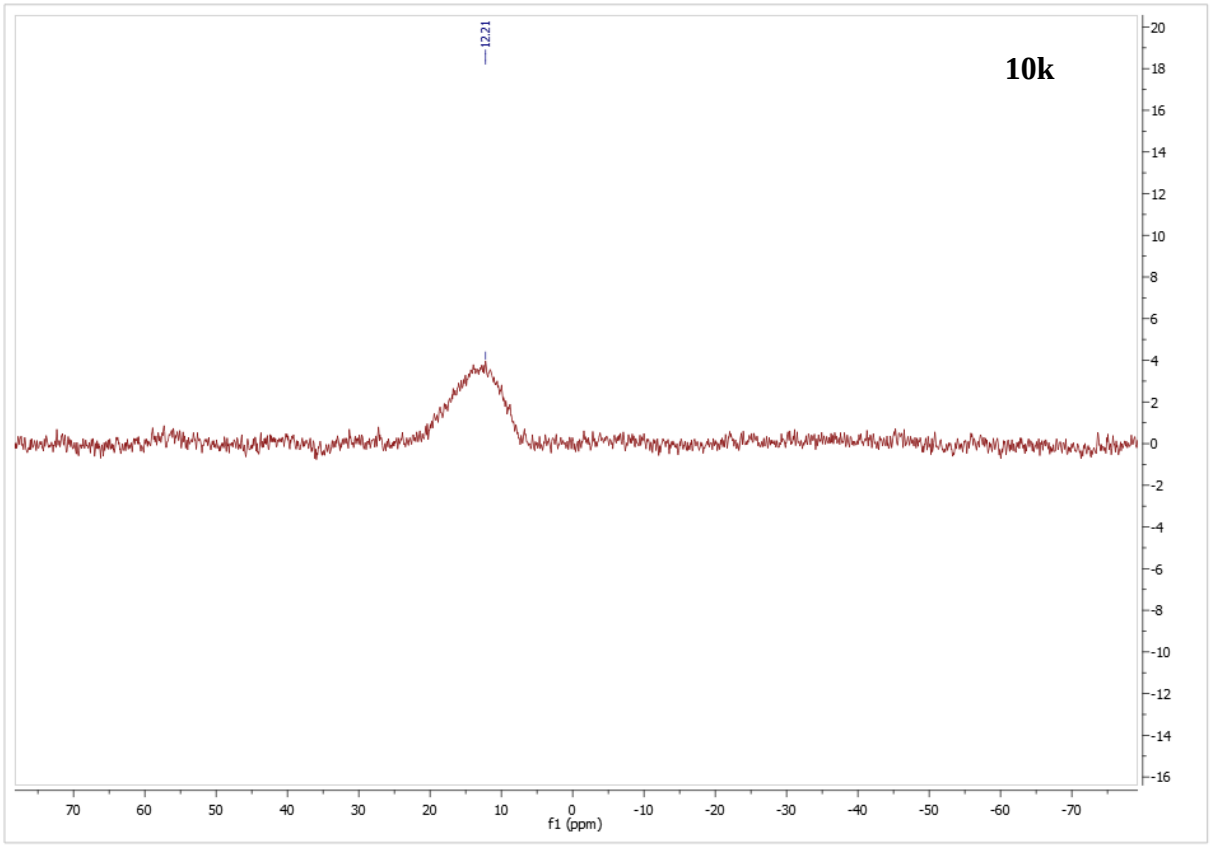

10j
A (d) 9.22
B (d) 8.80
C (dd) 7.93
D (t) 7.73
E (d) 7.60
F (m) 7.52
G (dd) 7.43
H (t) 7.31
I (d) 7.22
f1 (ppm)

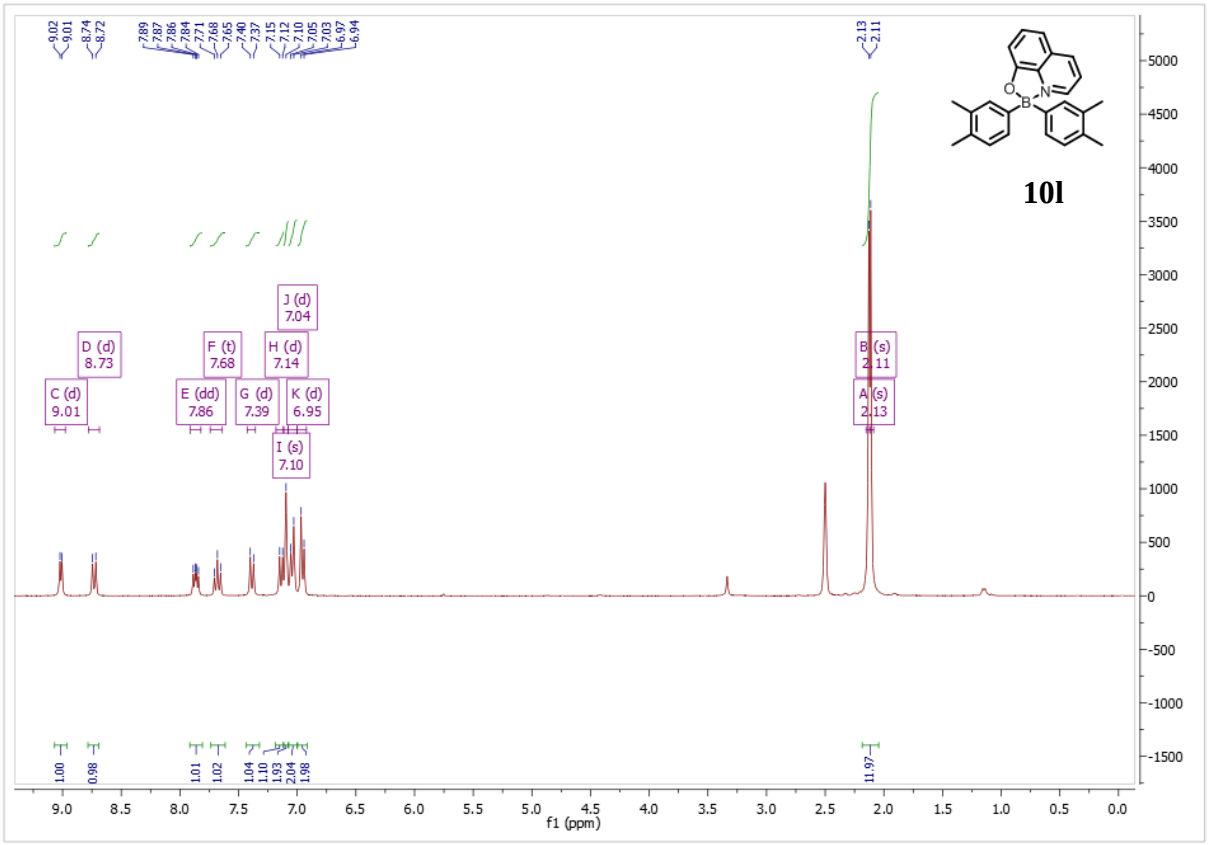

10j
157.79
146.40
141.42
140.67
140.00
138.53
136.40
134.78
132.37
132.10
128.82
128.07
127.02
126.69
126.52
125.78
124.22
113.01
108.79
f1 (ppm)

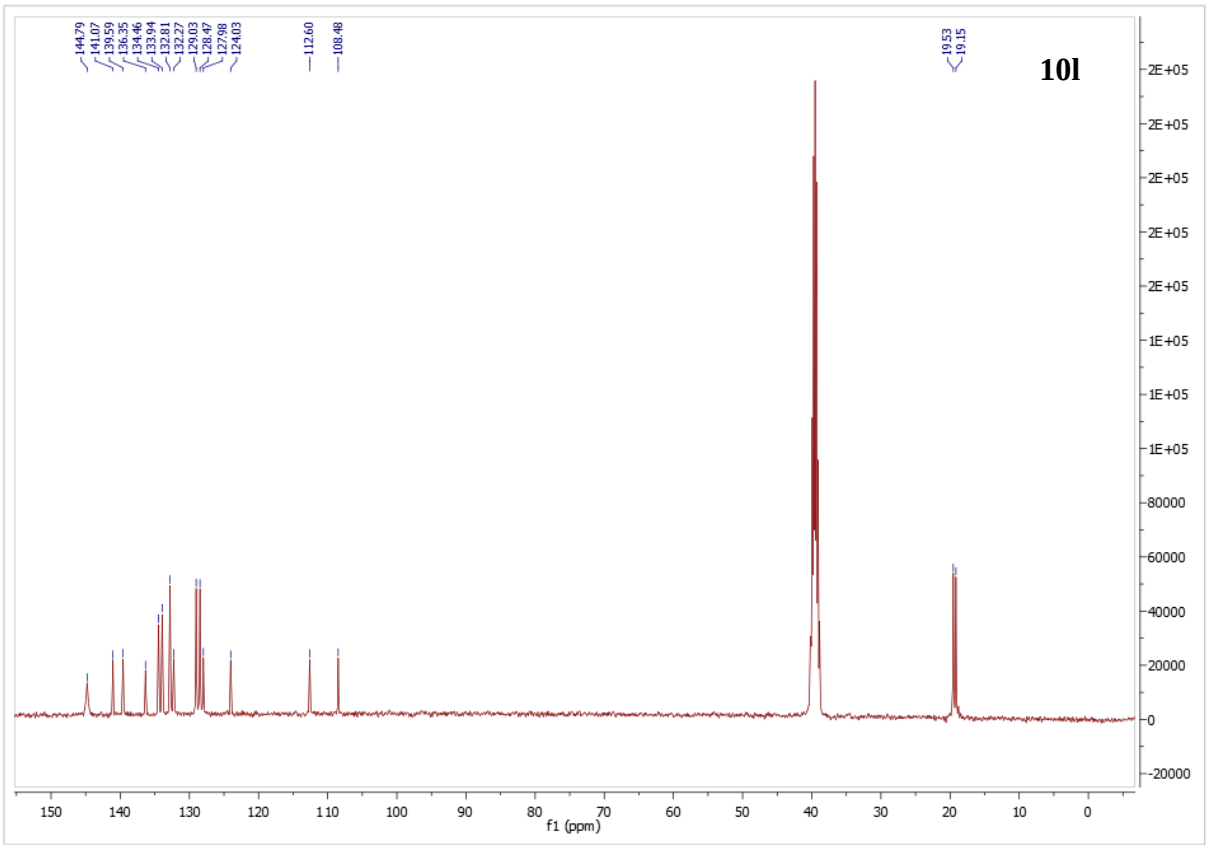

14.10
10j
A (s)
14.10
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
-4000
-6000
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
f1 (ppm)

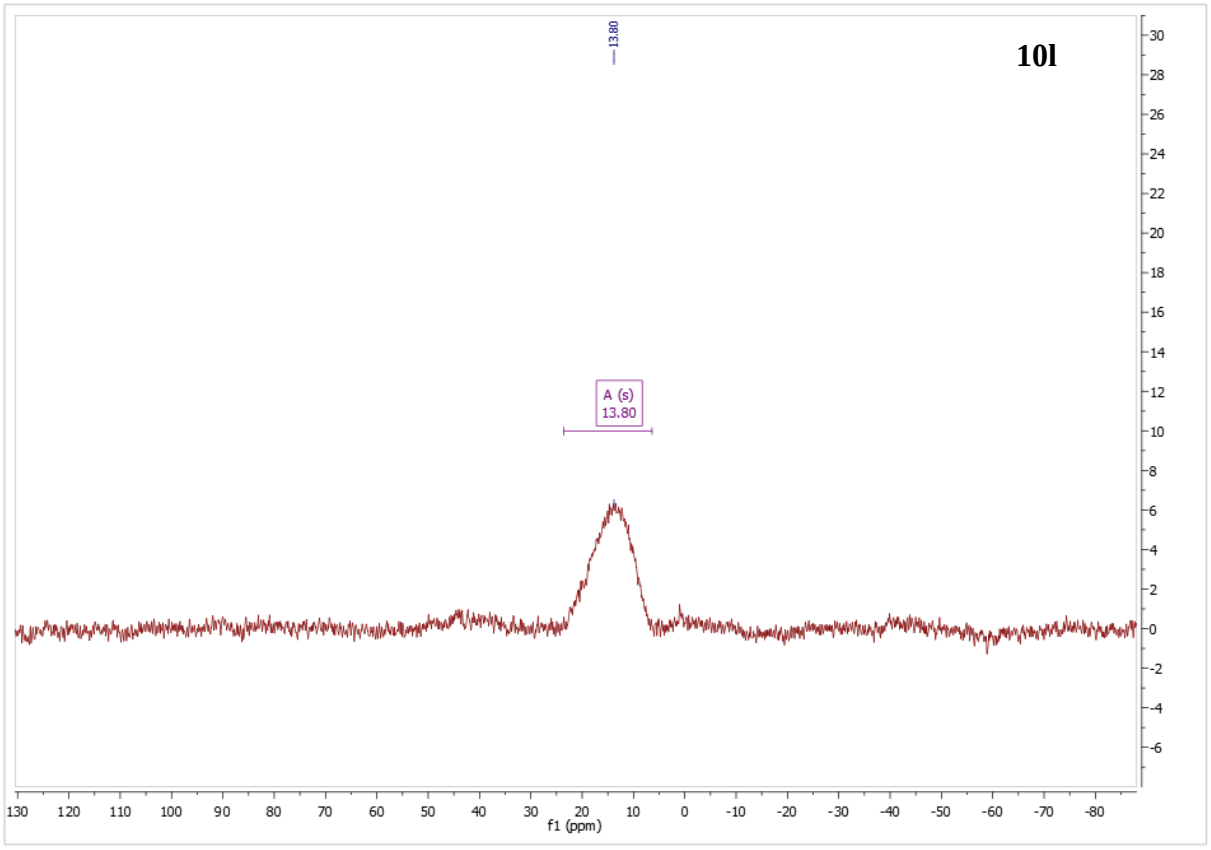

10k
A (s) 9.08
B (d) 8.75
C (s) 7.89
D (s) 7.69
E (d) 7.40
F (d) 7.15
G (s) 6.94
H (s) 6.77
I (s) 2.16
f1 (ppm)

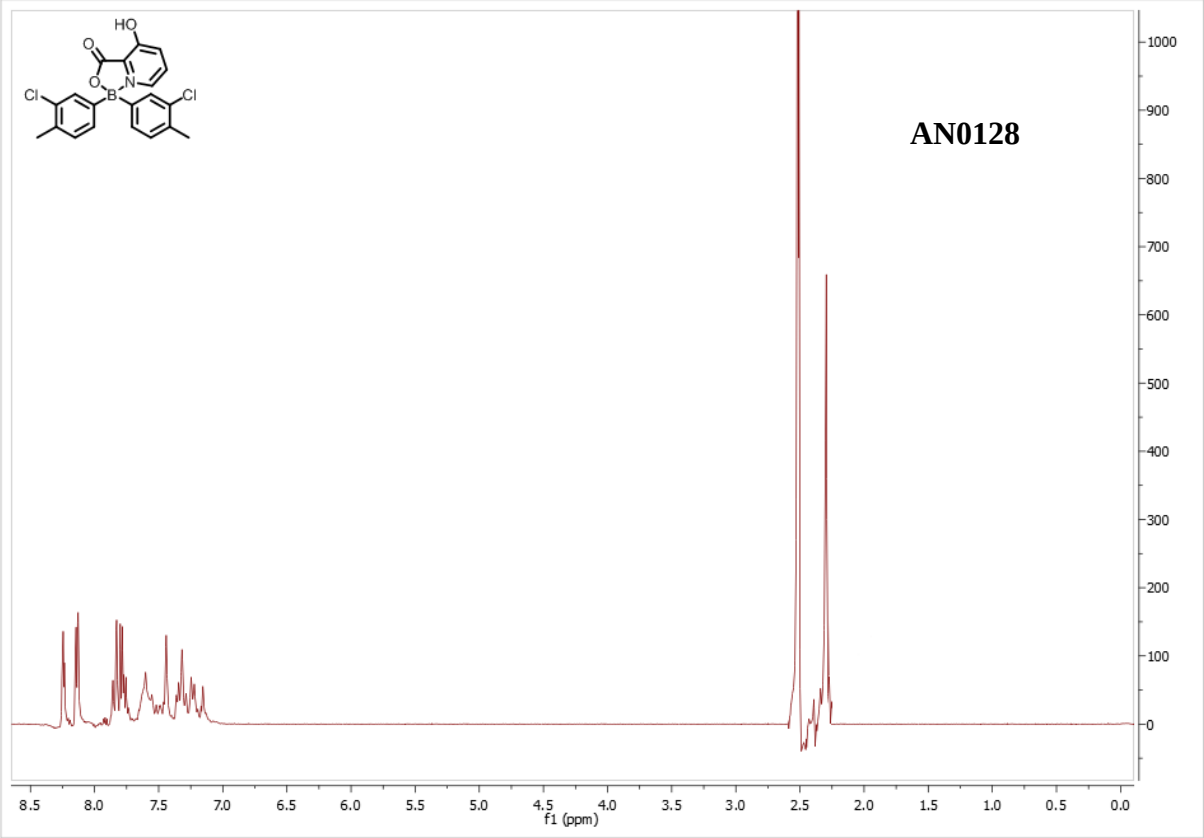

10k
f1 (ppm)

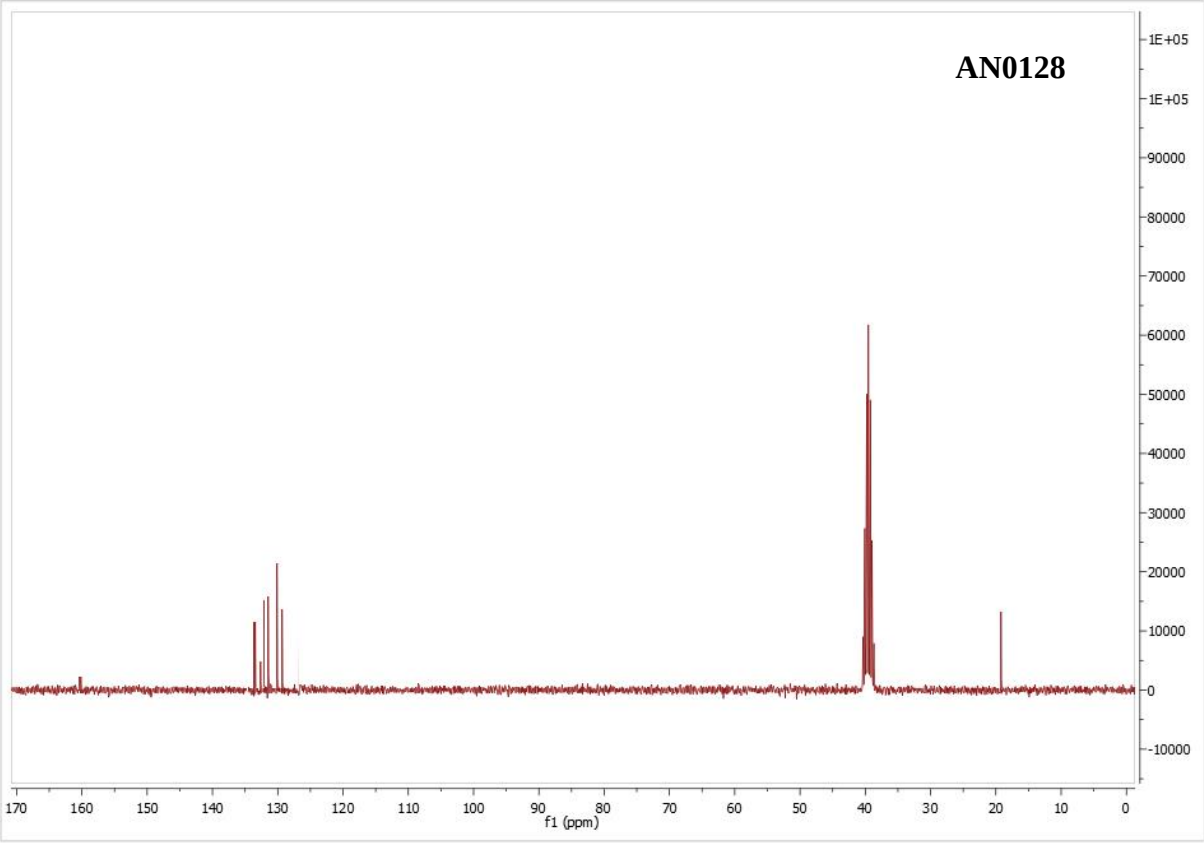

12.21
10k
20
18
16
14
12
10
8
6
4
2
0
-2
-4
-6
-8
-10
-12
-14
-16
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
f1 (ppm)

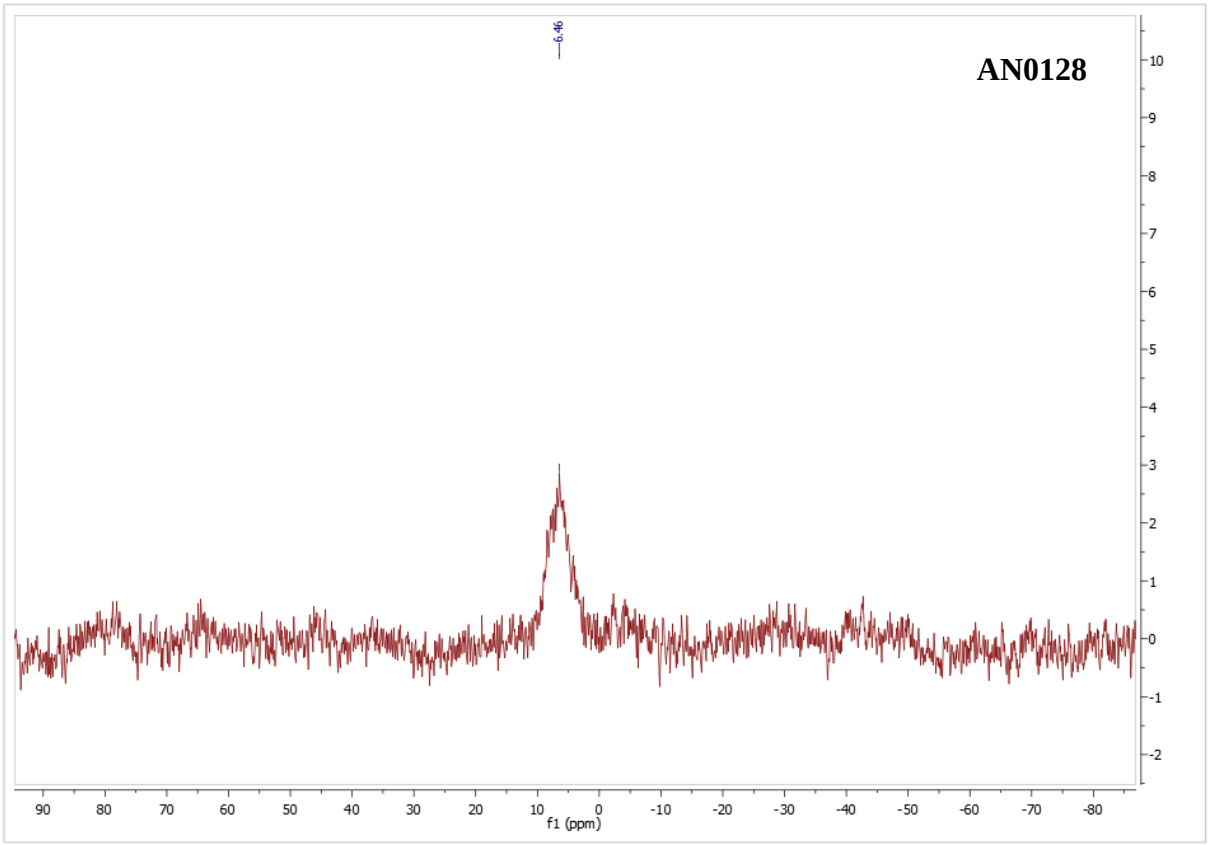

10l
C (d) 9.01
D (d) 8.73
E (dd) 7.86
F (t) 7.68
G (d) 7.39
H (d) 7.14
I (s) 7.10
J (d) 7.04
K (d) 6.95
A (s) 2.13
B (s) 2.11
f1 (ppm)

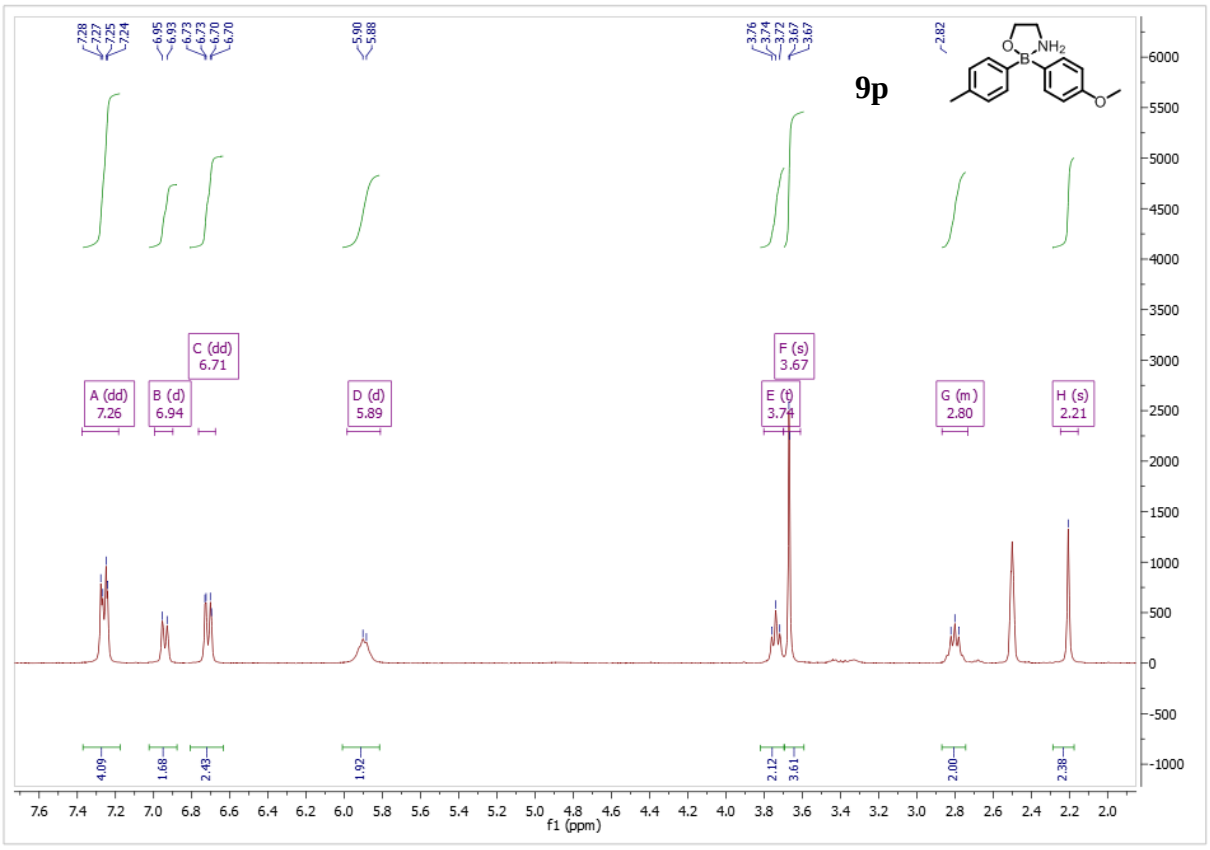

10l
f1 (ppm)

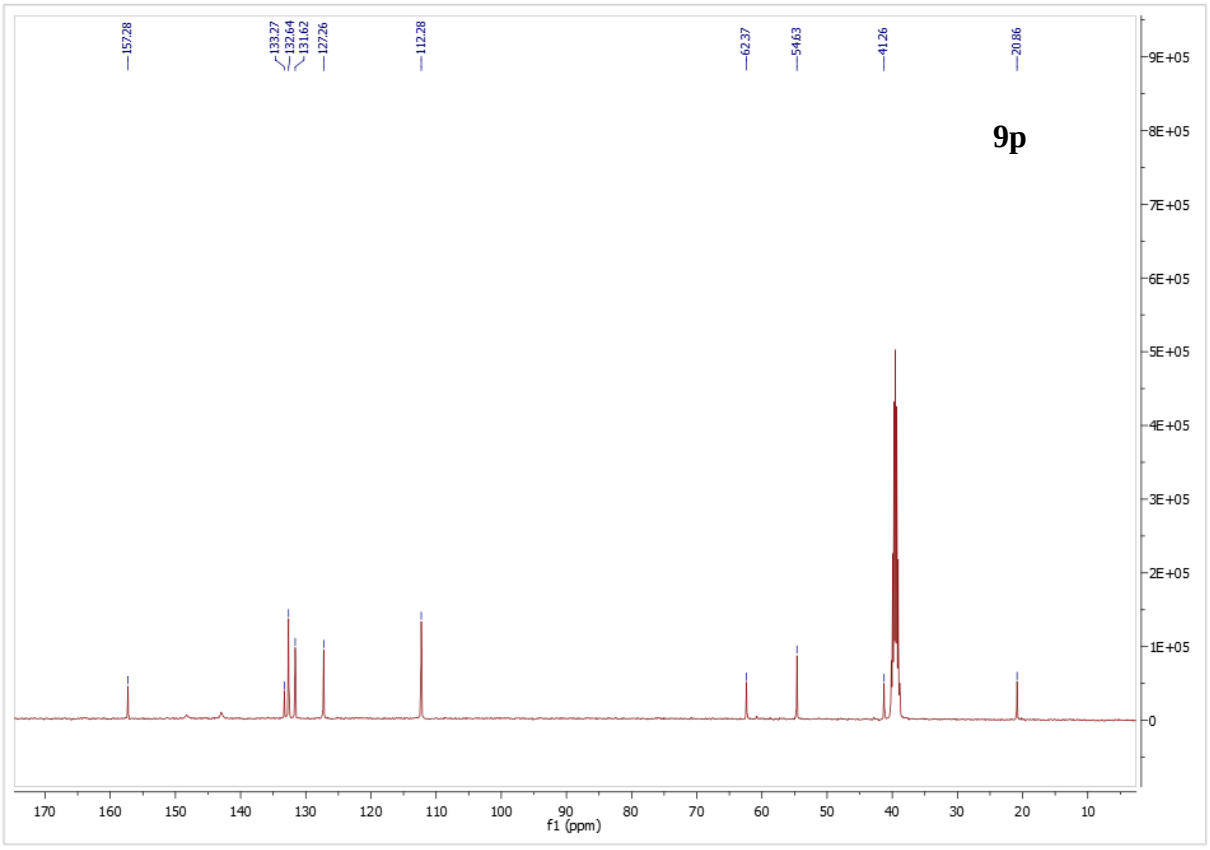

10l
13.80
A (s)
13.80
f1 (ppm)

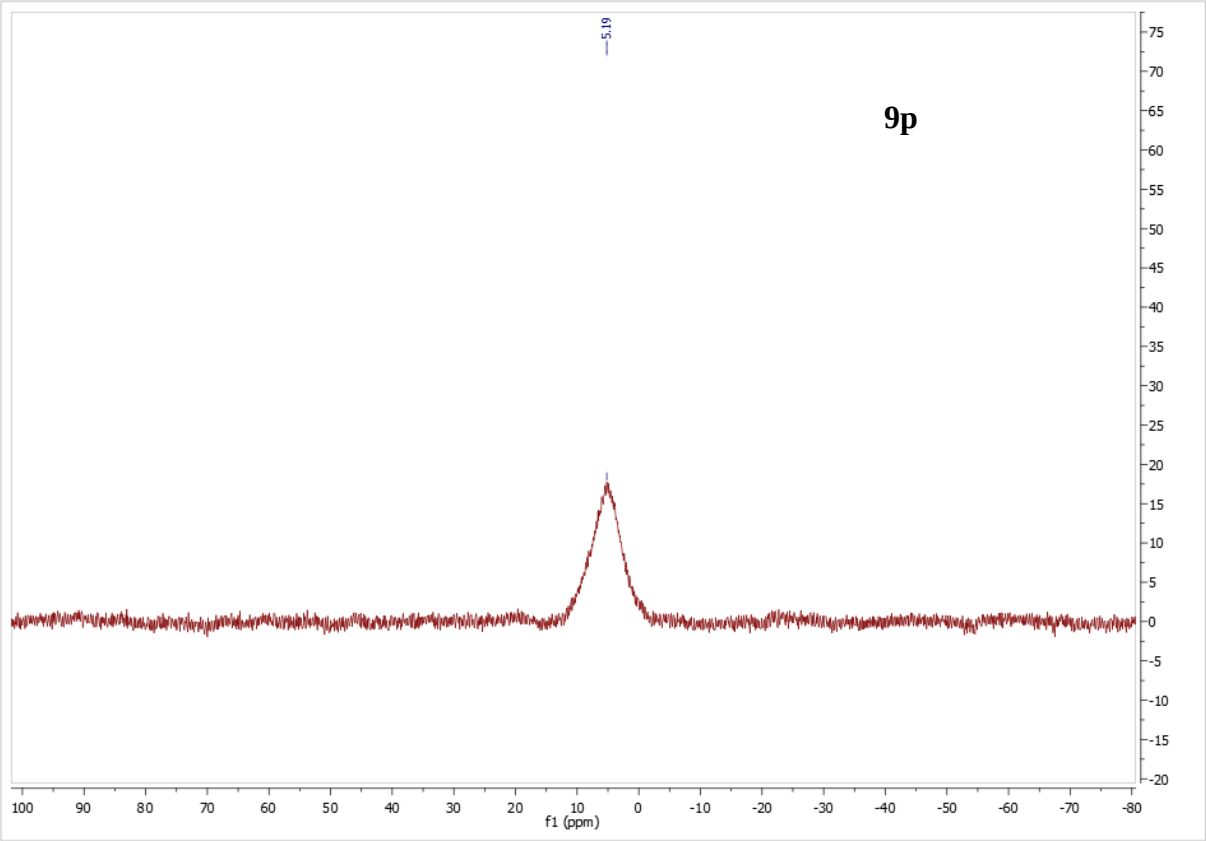

HO
O
O
N
B
Cl
Cl
AN0128
1000
900
800
700
600
500
400
300
200
100
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


AN0128
1E+05
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


AN0128
6.46
10
9
8
7
6
5
4
3
2
1
0
-1
-2
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
f1 (ppm)


9p
A (dd) 7.26
B (d) 6.94
C (dd) 6.71
D (d) 5.89
E (t) 3.74
F (s) 3.67
G (m) 2.80
H (s) 2.21
f1 (ppm)


9p
157.28
133.27
132.64
131.62
127.26
112.28
62.37
54.63
41.26
20.86
f1 (ppm)


9p
5.19
f1 (ppm)