Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Direct introduction of naphthalene-1,8-diamino boryl [B(dan)] group by a Pd-catalysed selective boryl transfer reaction

Table of Contents

1. General considerations

General. Unless otherwise noted, all reactions were carried out in a flame-dried, sealed Schlenk reaction tube under an atmosphere of nitrogen. Analytical thin-layer chromatography (TLC) was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator. Preparative thin-layer chromatography (PTLC) was performed on pre-coated, glass-backed GF254 silica gel plates. Visualization was accomplished by exposure to a UV lamp. All the products in this article are compatible with standard silica gel chromatography. Column chromatography was performed on silica gel (200–300 mesh) using standard methods.

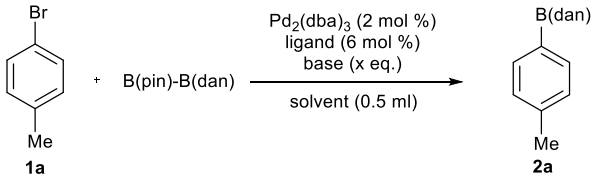
Structural analysis. NMR spectra were measured on a Bruker Avance-400 spectrometer and chemical shifts (δ) are reported in parts per million (ppm). ^{1}H NMR spectra were recorded at 400 MHz in NMR solvents and referenced internally to corresponding solvent resonance, and ^{13}C NMR spectra were recorded at 100 MHz and referenced to corresponding solvent resonance. Carbons bearing boron substituents were generally not observed due to quadrupolar relaxation. Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Infrared spectra were collected on a Thermo Fisher Nicolet 6700 FT-IR spectrometer using ATR (Attenuated Total Reflectance) method. Absorption maxima (ν max) are reported in wavenumbers (cm^{-1}). High resolution mass spectra (HRMS) were acquired with an ESI source or APCI source.

Materials. Commercial reagents and solvent were purchased from J&K, Energy, Sigma-Aldrich, Alfa Aesar, Acros Organics, Strem Chemicals, TCI and used as received unless otherwise stated. B(pin)-B(dan) was synthesized according to literature.[1]

2. Pd-catalyzed selective boryl transfer of B(pin)-B(dan)

A. Optimization of reaction conditions

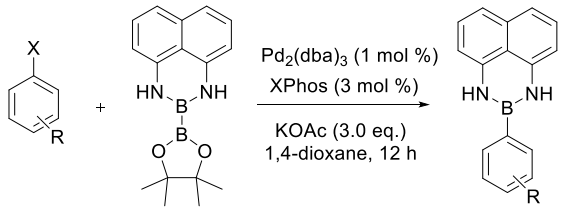
Table S1. Optimization of reaction conditions



Entry	Ligand	Base	T (^{o}C)	t(h)	solvent	Yields (%)[b]
1	PPh_3	KOAc (3.0 eq.)	80	12	1.4-dioxane	19
2	*t*Bu-XPhos	KOAc (3.0 eq.)	100	12	1.4-dioxane	20
3	SPhos	KOAc (3.0 eq.)	100	12	1.4-dioxane	95
4	XantPhos	KOAc (3.0 eq.)	100	12	1.4-dioxane	29
5	XPhos	KOAc (3.0 eq.)	100	12	1.4-dioxane	99
6	XPhos	KO*t*Bu (3.0 eq.)	100	12	1.4-dioxane	Trace[f]
7	XPhos	KOAc (3.0 eq.)	r.t.	12	1.4-dioxane	18
8	XPhos	KOAc (3.0 eq.)	50	12	1.4-dioxane	76
9	**XPhos**	**KOAc (3.0 eq.)**	**60**	**12**	1.4-dioxane	**99(98)**[e]
10	XPhos	KOAc (3.0 eq.)	60	8	1.4-dioxane	95(92)[e]
11	XPhos	NaOAc (3.0 eq.)	60	8	1.4-dioxane	N.R.
12	XPhos	K_2CO_3 (3.0 eq.)	60	8	1.4-dioxane	36
13	XPhos	$KHCO_3$ (3.0 eq.)	60	8	1.4-dioxane	21
14	XPhos	PhCOONa (3.0 eq.)	60	8	1.4-dioxane	N.R.
15	XPhos	Na_2CO_3 (3.0 eq.)	60	8	1.4-dioxane	N.R.
16	XPhos	K_3PO_4 (3.0 eq.)	60	8	1.4-dioxane	65(59)[e]
17	XPhos	KO*t*Bu (3.0 eq.)	60	8	1.4-dioxane	Trace[f]
18	XPhos	KOAc (1.5 eq.)	60	8	1.4-dioxane	81(79)[e]
19	XPhos	KOAc (3.0 eq.)	60	8	Toluene	84(81)[e]
20	XPhos	KOAc (3.0 eq.)	60	8	DCE	79
21[c]	XPhos	KOAc (3.0 eq.)	60	12	1.4-dioxane	64
22[d]	-	KOAc (3.0 eq.)	60	12	1.4-dioxane	N.R.

[a] Reaction conditions: 4-Bromotoluene (0.12mmol), B(pin)-B(dan) (0.10mmol), solvent (0.5 ml) under N_2 atomosphere. [b] Yields based on ^{1}H NMR analysis of the crude products with 1,3,5-trimethoxybenzene added as an internal standard. [c] 4 mol% $Pd(OAc)_2$ was used as catalyst. [d] catalyst and ligand were not added. [e] Isolated yield shown in parenthesis. [f] B(pin)-B(dan) was completely consumed according to crude ^{1}H-NMR analysis.

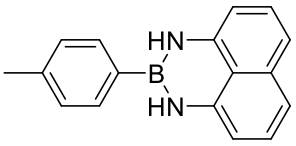
B. General procedure A for Pd-catalyzed selective boryl transfer:



In a dried Schlenk flask (25 mL in volume) equipped with a stirring bar were placed with B(pin)-B(dan) (73.5 mg, 0.25 mmol, 1.0 eq.), $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol, 1 mol %), XPhos (3.6 mg, 0.0075 mmol, 3 mol %), KOAc (73.6 mg, 0.75 mmol, 3.0 eq.) and aryl halide (0.3 mmol, 1.2 eq., if solid). After evacuation and refill with dry nitrogen for three times, aryl halide (0.3 mmol, 1.2 eq., if liquid) and 1,4-dioxane (1.0 mL) were added with syringes under a stream of nitrogen. The resulting mixture was allowed to stir at 60 ℃ (for aryl bromides) or 100 ℃ (for aryl chlorides and orth-substituted aryl bromides) for 12 h. After cooling to room temperature, the reaction mixture was filtered, concentrated and then purified by column chromatography on silica gel to give the target product.

C. Spectra data:

(2a) 2-(*p*-tolyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (CAS: 1159803-47-0)[2]



2-(*p*-tolyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine
Chemical Formula: $C_{17}H_{15}BN_2$
Exact Mass: 258.1328
Molecular Weight: 258.1310

The general procedure A was followed using 1-bromo-4-methylbenzene **1a** (36.9 uL, 0.3 mmol, 1.2 eq.) as starting material. **2a** was obtained as white solid (64.6 mg, quant.) after purification by silica gel flash chromatography (PE:EA = 15:1).

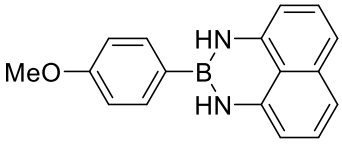
The general procedure A was followed using 1-chloro -4-methylbenzene **1a-Cl** (35.5 uL, 0.3 mmol, 1.2 eq.) as starting material. **2a** was obtained as white solid (52.9 mg, 82%) after purification by silica gel flash chromatography (PE:EA = 15:1).Melting point(°C): 193.6-195.9

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.6 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.06 (t, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.33 (d, *J* = 7.6 Hz, 2H), 5.93 (br, 2H), 2.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.29, 140.52, 136.49, 131.58, 129.17, 127.74, 119.92, 117.85, 106.08, 21.71.

HRMS (APCI) m/z calcd for $C_{17}H_{14}BN_2$ (M-): 257.1256, found: 257.1256.IR (cm^{-1}): 3413, 1594, 1490, 1407, 1328, 1083.

(2b) 2-(4-methoxyphenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (CAS: 1159803-53-8)[2]



2-(4-methoxyphenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine
Chemical Formula: $C_{17}H_{15}BN_2O$
Exact Mass: 274.1277
Molecular Weight: 274.1300

The general procedure A was followed using 1-bromo-4-methoxybenzene **1b** (37.6 uL, 0.3 mmol, 1.2 eq.) as starting material. **2b** was obtained as white solid (65.1 mg, 95%) after purification by silica gel flash chromatography (PE:EA = 10:1).

Melting point(°C): 163.2-165.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.8 Hz, 2H), 7.15 (t, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.42 (d, *J* = 7.2 Hz, 2H), 5.99 (br, 2H), 3.86 (s, 3H).

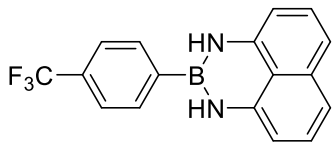
^{13}C NMR (100 MHz, $CDCl_3$) δ 161.54, 141.33, 136.48, 133.13, 127.75, 119.80, 117.81, 114.00, 106.05, 55.31.

^{11}B NMR (128 MHz, $CDCl_3$) δ 29.1.

HRMS (APCI) m/z calcd for $C_{17}H_{14}BN_2O$ (M-): 273.1205, found: 273.1203.

IR (cm^{-1}): 3407, 1594, 1495, 1407, 1224, 1181, 1029.

(2c) 2-(4-(trifluoromethyl)phenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine



2-(4-(trifluoromethyl)phenyl)-2,3-dihydro-1
naphtho[1,8-*de*][1,3,2]diazaborinine
Chemical Formula: $C_{17}H_{12}BF_3N_2$
Exact Mass: 312.1046
Molecular Weight: 312.1022

The general procedure A was followed using 1-bromo-4-(trifluoromethyl)benzene **1c** (42.0 uL, 0.3 mmol, 1.2 eq.) as starting material. **2c** was obtained as white solid (73.4 mg, 94%) after purification by silica gel flash chromatography (PE:EA = 20:1).

Melting point(^{o}C): 127.0-130.3

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.16 (t, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 7.6 Hz, 2H), 6.44 (dd, *J* = 7.2, 0.8 Hz, 2H), 6.01 (br, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.76, 136.47, 132.17 (q, J = 32 Hz), 131.91, 127.79, 125.06 (q, J = 4 Hz), 124.23 (q, J = 272 Hz), 120.10, 118.40, 106.44.

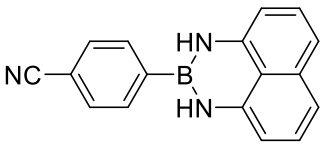
^{19}F NMR (377 MHz, CDCl3): δ ppm -62.88.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.1.

HRMS (APCI) m/z calcd for $C_{17}H_{11}BF_3N_2$ (M-): 311.0973, found: 311.0974.

IR (cm^{-1}): 3414, 2923, 1600, 1400, 1318, 1105, 1087, 1065, 1015.

(2d) 4-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)benzonitrile



4-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-
2(3*H*)-yl)benzonitrile
Chemical Formula: $C_{17}H_{12}BN_3$
Exact Mass: 269.1124
Molecular Weight: 269.1140

The general procedure A was followed using 4-bromobenzonitrile **1d** (54.6 mg, 0.3 mmol, 1.2 eq.) as starting material. **2c** was obtained as white solid (62.3 mg, 97%) after purification by silica gel flash chromatography (PE:EA = 14:1).

The general procedure A was followed using 4-chlorobenzonitrile **1d-Cl** (41.3 mg, 0.3 mmol, 1.2 eq.) as starting material. **2c** was obtained as white solid (45.7 mg, 68%) after purification by silica gel flash chromatography (PE:EA = 14:1).

Melting point (^{o}C): 220.4-225.1

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 8.0, 3.2 Hz, 4H), 7.15 (t, *J* = 7.8, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.43 (d, *J* = 7.2 Hz, 2H), 5.99 (br, 2H).

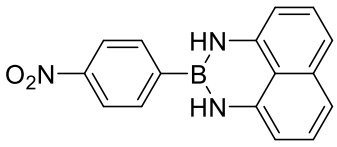
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.56, 136.46, 132.14, 131.86, 127.79, 120.14, 118.86, 118.59, 113.86, 106.55.

^{11}B NMR (128 MHz, $CDCl_3$) δ 28.8.

HRMS (ESI) m/z calcd for $C_{17}H_{12}BN_3Na$ (M+): 292.1022, found: 292.1014.

IR (cm^{-1}): 3383, 2924, 2231, 1595, 1527, 1408, 1397, 1084.

(2e) 2-(4-nitrophenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine



2-(4-nitrophenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine
Chemical Formula: $C_{16}H_{12}BN_3O_2$
Exact Mass: 289.1023
Molecular Weight: 289.1010

The general procedure A was followed using 1-bromo-4-nitrobenzene **1e** (60.6 mg, 0.3 mmol, 1.2 eq.) as starting material. **2e** was obtained as dark-red solid (70.1 mg, 97%) after purification by silica gel flash chromatography (PE:EA = 5:1).

Melting point (^{o}C): 135.4-138.2

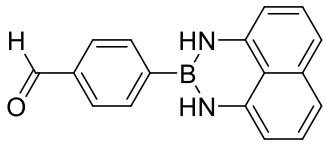
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.50 (s, 2H), 8.30 (d, J = 8.8 Hz, 2H), 8.20 (d, J = 8.4 Hz, 2H), 7.11 (t, J = 8.0 Hz, 2H), 6.94 (d, J = 8.4 Hz, 2H), 6.60 (d, J = 7.6 Hz, 2H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 148.59, 141.97, 135.93, 133.94, 127.69, 122.31, 119.94, 116.69, 105.91.

HRMS (APCI) m/z calcd for $C_{16}H_{11}BN_3O_2$ (M-): 288.0950, found: 288.0949.

IR (cm^{-1}): 3401, 1595, 1515, 1500, 1333, 1086.

(2f) 4-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)benzaldehyde



4-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)benzaldehyde
Chemical Formula: $C_{17}H_{13}BN_2O$
Exact Mass: 272.1121
Molecular Weight: 272.1140

The general procedure A was followed using 4-bromobenzaldehyde **1f** (55.5 mg, 0.3 mmol, 1.2 eq.) as starting material. **2f** was obtained as white solid (57.1 mg, 84%) after purification by silica gel flash chromatography (PE:EA = 3:1).

Melting point (^{o}C): > 250

^{1}H NMR (400 MHz, Acetone-d_6) δ 10.08 (s, 1H), 8.07 (d, J = 8.0 Hz, 2H), 7.94 (d, J = 8.0 Hz, 2H), 7.80 (s, 2H), 7.11 (t, J = 7.8 Hz, 2H), 7.01 (d, J = 8.4 Hz, 2H), 6.62 (d, J = 7.2 Hz, 2H).

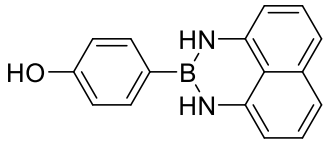
^{13}C NMR (100 MHz, Acetone-d_6) δ 193.14, 142.87, 138.57, 137.44, 133.70, 129.46, 128.49, 121.25, 118.12, 106.99.

^{11}B NMR (128 MHz, $CDCl_3$) δ 29.7.

HRMS (APCI) m/z calcd for $C_{17}H_{12}BN_2O$ (M-): 271.1038, found: 271.1052.

IR (cm^{-1}): 3382, 1666, 1592, 1522, 1406, 1172, 1086.

(2g) 4-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)phenol (CAS: 1492899-94-1)[3]



4-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)phenol
Chemical Formula: $C_{16}H_{13}BN_2O$
Exact Mass: 260.1121
Molecular Weight: 260.1030

The general procedure A was followed using 4-bromophenol **1g** (51.9 mg, 0.3 mmol, 1.2 eq.) as starting material. **2g** was obtained as white solid (65.0 mg, quant.) after purification by silica gel flash chromatography (PE:EA = 3:1).

Melting point (^{o}C): 222.6-225.7

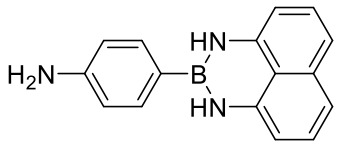
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.0 Hz, 2H), 7.14 (t, J = 7.8 Hz, 2H), 7.05 (d, J = 8.4 Hz, 2H), 6.91 (d, J = 8.4 Hz, 2H), 6.41 (d, J = 7.6 Hz, 2H), 5.98 (br, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.76, 141.49, 136.68, 133.59, 127.96, 120.01, 118.05, 115.65, 106.27.

HRMS (APCI) m/z calcd for $C_{16}H_{12}BN_2O$ (M-): 259.1048, found: 259.1049.

IR (cm^{-1}): 3523, 3398, 2923, 1595, 1489, 1405, 1210,1175, 1083.

(2h) 4-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(*3H*)-yl)aniline



4-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)aniline
Chemical Formula: $C_{16}H_{14}BN_3$
Exact Mass: 259.1281
Molecular Weight: 259.1190

The general procedure A was followed using 4-bromo aniline **1h** (51.6 mg, 0.3 mmol, 1.2 eq.) as starting material. **2h** was obtained as yellow solid (54.4 mg, 84%) after purification by silica gel flash chromatography (PE:EA = 2:1).

Melting point (^oC): 230.1-236.5

^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.12 (t, *J* = 7.2 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.74 (d, *J* = 8.4 Hz, 2H), 6.39 (d, *J* = 7.2 Hz, 2H), 5.97 (br, 2H), 3.84 (br, 2H).

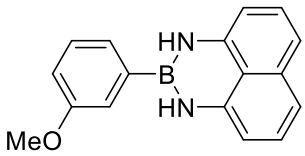
^{13}C NMR (100 MHz, $CDCl_3$) δ 148.51, 141.37, 136.35, 132.91, 127.62, 119.59, 117.48, 114.67, 105.79.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.0.

HRMS (APCI) m/z calcd for $C_{16}H_{12}BN_2O$ (M-): 258.1208, found: 258.1208.

IR (cm^{-1}): 3417, 3331, 2954, 2922, 2853, 1593, 1492, 1405, 1226, 1086.

(2i) 2-(3-methoxyphenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine



2-(3-methoxyphenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine
Chemical Formula: $C_{17}H_{15}BN_2O$
Exact Mass: 274.1277
Molecular Weight: 274.1300

The general procedure A was followed using 1-bromo-3-methoxybenzene **1i** (37.7 uL, 0.3 mmol, 1.2 eq.) as starting material. **2i** was obtained as white solid (63.7 mg, 93%) after purification by silica gel flash chromatography (PE:EA = 15:1).

The general procedure A was followed using 1-chloro-3-methoxybenzene **1i-Cl** (37.6 uL, 0.3 mmol, 1.2 eq.) as starting material. **2i** was obtained as white solid (59.6 mg, 87%) after purification by silica gel flash chromatography (PE:EA = 15:1).

Melting point (^oC): 113.7-116.4

^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 7.2 Hz, 1H), 7.16-7.13 (m, 3H), 7.06 (d, *J* = 8.0 Hz, 2H), 7.01 (ddd, *J* = 8.4, 2.8, 0.8 Hz, 1H), 6.42 (d, *J* = 7.2 Hz, 2H), 6.01 (br, 2H), 3.87 (s, 3H).

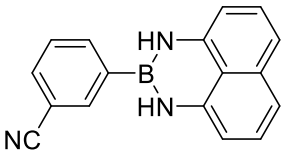
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.62, 141.17, 136.47, 129.69, 127.77, 123.87, 120.03, 118.01, 117.11, 115.64, 106.18, 55.42.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.1.

HRMS (APCI) m/z calcd for $C_{17}H_{14}BN_2O$ (M-): 273.1205, found: 273.1207.

IR (cm^{-1}): 3453, 3411, 1594, 1418, 1407, 1244, 1041.

(2j) 3-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)benzonitrile (CAS: 1352304-46-1)[5]



3-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)benzonitrile
Chemical Formula: $C_{17}H_{12}BN_3$
Exact Mass: 269.1124
Molecular Weight: 269.1140

The general procedure A was followed using 3-bromobenzonitrile **1j** (54.6 mg, 0.3 mmol, 1.2 eq.) as starting material. **2j** was obtained as white solid (57.8 mg, 86%) after purification by silica gel flash chromatography (PE:EA = 7:1).

Melting point (^oC): 228.6-233.5

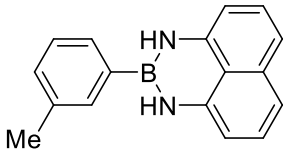
^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.16 (t, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.44 (d, *J* = 7.2 Hz, 2H), 6.00 (br, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.56, 136.44, 135.72, 135.30, 133.61, 129.11, 127.79, 120.09, 118.98, 118.57, 112.78, 106.56.

HRMS (APCI) m/z calcd for $C_{17}H_{11}BN_3$ (M-): 268.1052, found: 268.1048.

IR (cm^{-1}): 3399, 2222, 1595, 1407, 1160, 1083.

(2k) 2-(*m*-tolyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine



2-(*m*-tolyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine
Chemical Formula: $C_{17}H_{15}BN_2$
Exact Mass: 258.1328
Molecular Weight: 258.1310

The general procedure A was followed using 1-bromo-3-methylbenzene **1k** (36.4 uL, 0.3 mmol, 1.2 eq.) as starting material. **2k** was obtained as white solid (62.6 mg, 97%) after purification by silica gel flash chromatography (PE:EA = 20:1).

Melting point (^{o}C): 103.8-106.3

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.15 (t, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.42 (d, *J* = 7.6 Hz, 2H), 6.03 (br, 2H), 2.43 (s, 3H).

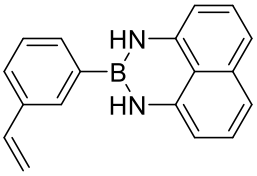
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.27, 137.82, 136.50, 132.29, 131.19, 128.61, 128.35, 127.76, 119.99, 117.91, 106.12, 21.66.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.4.

HRMS (APCI) m/z calcd for $C_{17}H_{14}BN_2$ (M-): 257.1256, found: 257.1257.

IR (cm^{-1}): 3410, 1593, 1409, 1372, 1084.

(2l) 2-(3-vinylphenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine



2-(3-vinylphenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine
Chemical Formula: $C_{18}H_{15}BN_2$
Exact Mass: 270.1328
Molecular Weight: 270.1420

The general procedure A was followed using 1-bromonaphthalene **1l** (54.9 mg, 0.3 mmol, 1.2 eq.) as starting material. **2l** was obtained as white solid (61.4 mg, 91%) after purification by silica gel flash chromatography (PE:EA = 20:1).

Melting point (^{o}C): 86.3-87.9

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.54 (dd, *J* = 7.6, 1.2 Hz, 2H), 7.42 (t, *J* = 7.6 Hz 1H), 7.15 (t, *J* = 8.4 Hz 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.79 (dd, *J* = 17.6, 10.8 Hz, 1H), 6.43 (dd, *J* = 7.2, 0.8 Hz, 2H), 6.04 (br, 2H), 5.83 (d, *J* = 17.6 Hz, 1H), 5.32 (d, *J* = 10.8 Hz, 1H).

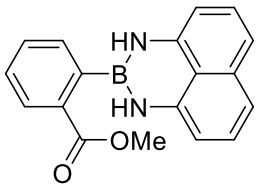
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.03, 137.35, 136.77, 136.36, 130.90, 129.47, 128.50, 127.93, 127.65, 119.88, 117.89, 114.35, 106.07.

^{11}B NMR (128 MHz, $CDCl_3$) δ 29.9.

HRMS (APCI) m/z calcd for $C_{18}H_{14}BN_2$ (M-): 269.1256, found: 269.1257.

IR (cm^{-1}): 3413, 2925, 1596, 1409, 1305, 1129.

(2m) methyl 2-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)benzoate



methyl 2-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)benzoate
Chemical Formula: $C_{18}H_{15}BN_2O_2$
Exact Mass: 302.1227
Molecular Weight: 302.1400

The general procedure A was followed using methyl 2-bromobenzoate **1m** (64.5 mg 0.3 mmol, 1.2 eq.) as starting material. **2m** was obtained as white solid (58.2 mg, 77%) after purification by silica gel flash chromatography (PE:EA = 14:1).

Melting point (^{o}C): 160.3-164.5

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.0 Hz, 1H), 7.59-7.55 (m, 2H), 7.49-7.46 (m, 1H), 7.12 (t, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.32 (d, *J* = 7.2 Hz, 2H), 5.73 (br, 2H), 3.86 (s, 3H).

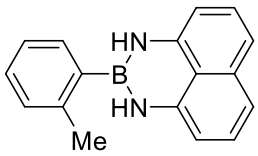
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.44, 141.40, 136.57, 133.33, 132.84, 132.20, 129.71, 129.01, 127.68, 119.78, 117.70, 105.92, 52.49.

^{11}B NMR (128 MHz, $CDCl_3$) δ 31.0.

HRMS (APCI) m/z calcd for $C_{18}H_{14}BN_2O_2$ (M-): 301.1154, found: 301.1157.

IR (cm^{-1}): 3381, 1706, 1600, 1515, 1269, 1069.

(2n) 2-(*o*-tolyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine



2-(*o*-tolyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine
Chemical Formula: $C_{17}H_{15}BN_2$
Exact Mass: 258.1328
Molecular Weight: 258.1310

The general procedure A was followed using 1-bromo-2-methylbenzene **1n** (36.1 uL, 0.3 mmol, 1.2 eq.) as starting material. **2n** was obtained as white solid (58.7 mg, 91%) after purification by silica gel flash chromatography (PE:EA = 20:1).

Melting point (^{o}C): 73.2-75.1

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.36 (m, 1H), 7.25-7.22 (m, 1H), 7.15-7.12 (m, 2H), 7.05 (t, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.26 (dd, *J* = 7.2, 0.8 Hz, 2H), 5.74 (br, 2H), 2.41 (s, 3H).

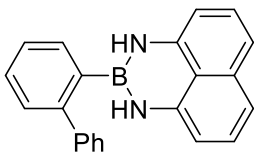
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.21, 140.76, 136.48, 132.36, 129.81, 129.44, 127.74, 125.41, 119.89, 117.95, 106.03, 22.52.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.0.

HRMS (APCI) m/z calcd for $C_{17}H_{14}BN_2$ (M-): 257.1256, found: 257.1257.

IR (cm^{-1}): 3420, 3405, 1599, 1506, 1407, 1319, 1079.

(2o) 2-([1,1'-biphenyl]-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine



2-([1,1'-biphenyl]-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine
Chemical Formula: $C_{22}H_{17}BN_2$
Exact Mass: 320.1485
Molecular Weight: 320.2020

The general procedure A was followed using 2-bromo-1,1'-biphenyl **1o** (69.9 mg, 0.3 mmol, 1.2 eq.) as starting material. **2o** was obtained as white solid (55.2 mg, 69%) after purification by silica gel flash chromatography (PE:EA = 20:1).

Melting point (^{o}C): 97.7-99.4

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.6 Hz, 1H), 7.54 – 7.32 (m, 8H), 7.06 (t, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.11 (d, *J* = 7.2 Hz, 2H), 5.47 (br, 2H).

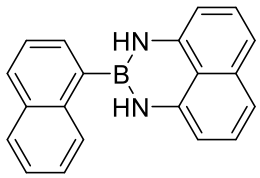
^{13}C NMR (100 MHz, $CDCl_3$) δ 146.42, 142.67, 141.07, 136.21, 132.77, 129.70, 129.42, 129.09, 128.38, 127.56, 127.46, 126.93, 119.47, 117.52, 105.75.

^{11}B NMR (128 MHz, $CDCl_3$) δ 29.9.

HRMS (APCI) m/z calcd for $C_{22}H_{16}BN_2$ (M-): 319.1412, found: 2319.1416.

IR (cm^{-1}): 3416, 1596, 1507, 1404, 1329, 1082.**(2p)**

2-(naphthalen-1-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine



2-(naphthalen-1-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine
Chemical Formula: $C_{20}H_{15}BN_2$
Exact Mass: 294.1328
Molecular Weight: 294.1640

The general procedure A was followed using 1-bromonaphthalene **1p** (62.1 mg, 0.3 mmol, 1.2 eq.) as starting material. **2p** was obtained as white solid (66.9 mg, 91%) after purification by silica gel flash chromatography (PE:EA = 30:1).

Melting point (^oC): 140.2-143.6

^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 6.4, 3.2 Hz, 1H), 7.92-7.89 (m, 2H), 7.70 (d, *J* = 6.4 Hz, 1H), 7.53-7.50 (m, 3H), 7.17 (t, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.38 (d, *J* = 7.2 Hz, 2H), 6.02 (br, 2H).

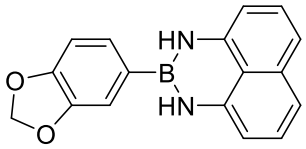
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.23, 136.55, 135.54, 133.41, 130.79, 129.65, 128.91, 128.03, 127.79, 126.36, 125.97, 125.52, 120.09, 118.12, 106.17.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.7.

HRMS (ESI) m/z calcd for $C_{20}H_{16}BN_2$ (M+): 295.1407, found: 295.1399.

IR (cm^{-1}): 3420, 3402, 1594, 1508, 1498, 1315, 1167.

(2q) 2-(benzo[*d*][1,3]dioxol-5-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine



2-(benzo[*d*][1,3]dioxol-5-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine
Chemical Formula: $C_{17}H_{13}BN_2O_2$
Exact Mass: 288.1070
Molecular Weight: 288.1130

The general procedure A was followed using 5-bromobenzo[*d*][1,3]dioxole **1q** (60.3 mg, 0.3 mmol, 1.2 eq.) as starting material. **2q** was obtained as white solid (69.0 mg, 93%) after purification by silica gel flash chromatography (PE:EA = 15:1).

The general procedure A was followed using benzo[*d*][1,3]dioxol-5-yl trifluoromethanesulfonate **1q-OTf** (81.1 mg, 0.3 mmol, 1.2 eq.) as starting material. **2q** was obtained as white solid (69.9 mg, 97%) after purification by silica gel flash chromatography (PE:EA = 15:1).

Melting point (^oC): 173.5-175.8

^1H NMR (400 MHz, $CDCl_3$) δ 7.16-7.12 (m, 3H), 7.06 (t, *J* = 8.4 Hz, 3H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.41 (d, *J* = 7.2 Hz, 2H), 6.00 (s, 2H), 5.94 (br, 2H).

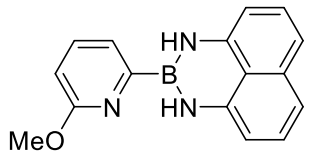
^{13}C NMR (100 MHz, $CDCl_3$) δ 149.53, 147.95, 141.19, 136.47, 127.75, 125.90, 119.83, 117.92, 111.04, 108.90, 106.12, 101.06.

^{11}B NMR (128 MHz, $CDCl_3$) δ 29.7.

HRMS (ESI) m/z calcd for $C_{17}H_{14}BN_2O_2$ (M+): 289.1148, found: 289.1147.

IR (cm^{-1}): 3399, 1594, 1478, 1402, 1232, 1034.

(2r) 2-(6-methoxypyridin-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine



2-(6-methoxypyridin-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine
Chemical Formula: $C_{16}H_{14}BN_3O$
Exact Mass: 275.1230
Molecular Weight: 275.1180

The general procedure A was followed using 2-bromo-6-methoxypyridine **1r** (36.9 uL, 0.3 mmol, 1.2 eq.) as starting material. **2r** was obtained as white solid (62.6 mg, 91%) after purification by silica gel flash chromatography (PE:Acetone = 20:1).

The general procedure A was followed using 2-chloro-6-methoxypyridine **1r-Cl** (35.7 uL, 0.3 mmol, 1.2 eq.) as starting material. **2r** was obtained as white solid (37.8 mg, 55%)

after purification by silica gel flash chromatography (PE:Acetone = 20:1).

Melting point (^{o}C): 142.3-144.9

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 8.4, 7.2 Hz, 1H), 7.24 (d, *J* = 7.2 Hz, 1H), 7.15 (t, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 1H), 6.47-6.44 (m, 4H), 4.05 (s, 3H).

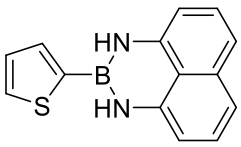
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.97, 141.18, 137.73, 136.63, 127.76, 120.49, 117.97, 112.45, 106.26, 53.38.

^{11}B NMR (128 MHz, $CDCl_3$) δ 27.6.

HRMS (APCI) m/z calcd for $C_{16}H_{13}BN_3O$ (M-): 274.1157, found: 274.1157.

IR (cm^{-1}): 3419, 1595, 1454, 1407, 1308, 1033, 1010.

(2s) 2-(thiophen-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (CAS: 1159803-80-1)[4]



2-(thiophen-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin
Chemical Formula: $C_{14}H_{11}BN_2S$
Exact Mass: 250.0736
Molecular Weight: 250.1260

The general procedure A was followed using 2-chlorothiophene **1s-Cl** (27.7 uL, 0.3 mmol, 1.2 eq.) as starting material. **2s** was obtained as white solid (31.9 mg, 51%) after purification by silica gel flash chromatography (PE:EA = 20:1).

Melting point (^{o}C): 78.6-80.3

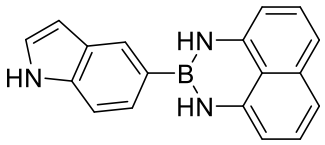
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 4.8 Hz, 1H), 7.50 (d, *J* = 3.2 Hz, 1H), 7.26-7.24 (m, 1H), 7.14 (t, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.41 (d, *J* = 7.2 Hz, 2H), 5.97 (br, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.86, 136.46, 132.98, 130.24, 128.70, 127.73, 119.91, 118.14, 106.28.

HRMS (APCI) m/z calcd for $C_{14}H_{10}BNS$ (M-): 249.0663, found: 249.0664.

IR (cm^{-1}): 3400, 1595, 1523, 1399, 1232.

(2t) 2-(1*H*-indol-5-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine



2-(1*H*-indol-5-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine
Chemical Formula: $C_{18}H_{14}BN_3$
Exact Mass: 283.1281
Molecular Weight: 283.1410

The general procedure A was followed using 5-Bromoindole **1t** (58.8 mg, 0.3 mmol, 1.2 eq.) as starting material. **2t** was obtained as white solid (47.8 mg, 68%) after purification by silica gel flash chromatography (PE:EA = 4:1).

Melting point (^{o}C): 170.4-174.1

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (br, 1H), 8.00 (s, 1H), 7.48 (s, 2H), 7.25 (s, 1H), 7.16 (t, *J* = 7.6 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.63 (t, *J* = 2.4 Hz, 1H), 6.44 (d, *J* = 7.2 Hz, 2H), 6.12 (br, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.62, 137.31, 136.53, 128.10, 127.78, 125.10, 124.77, 124.71, 119.82, 117.63, 111.19, 105.97, 103.10.

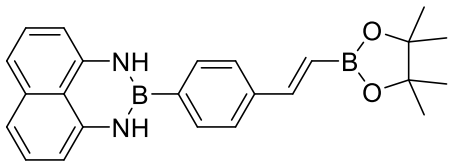
^{11}B NMR (128 MHz, $CDCl_3$) δ 30.4.

HRMS (APCI) m/z calcd for $C_{18}H_{13}BN_3$ (M-): 282.1208, found: 282.1211.

IR (cm^{-1}): 3407, 3362, 1592, 1406, 1328, 1163, 1075.

3. The application of B(dan)-containing molecules

(3a)(*E*)-2-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine



(*E*)-2-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine
Chemical Formula: $C_{24}H_{26}B_2N_2O_2$
Exact Mass: 396.2180
Molecular Weight: 396.1040

The general procedure A was followed using (*E*)-2-(4-chlorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (79.4 mg, 0.3 mmol, 1.2 eq.) as starting material. **3a** was obtained as white solid (79.2 mg, 80%) after purification by silica gel flash chromatography (PE:EA = 10:1).

Melting point (^{o}C): 200.5-203.8

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 18.4 Hz, 1H), 7.14 (t, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.41 (d, *J* = 7.2 Hz, 2H), 6.26 (d, *J* = 18.4 Hz, 1H), 6.02 (br, 2H), 1.33 (s, 12H).

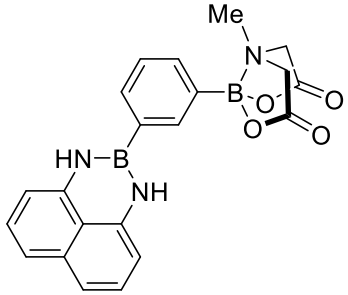
^{13}C NMR (100 MHz, $CDCl_3$) δ 149.06, 141.01, 139.26, 136.36, 131.76, 127.63, 126.84, 119.87, 117.88, 106.06, 83.47, 24.84.

^{11}B NMR (128 MHz, $CDCl_3$) δ 29.6.

HRMS (ESI) m/z calcd for $C_{24}H_{27}B_2N_2O_2$ (M+): 397.2259, found: 397.2249.

IR (cm^{-1}): 3413, 2976, 1597, 1406, 1347, 1318, 1139.

(3b)8-(3-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)phenyl)-4-methyldihydro-4λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione



Chemical Formula: $C_{21}H_{19}B_2N_3O_4$
Exact Mass: 399.1562
Molecular Weight: 399.0200

The general procedure A was followed using 3-chlorophenyl MIDA boronate (80.2 mg, 0.3 mmol, 1.2 eq.) as starting material. **3b** was obtained as white solid (78.8 mg, 79%) after purification by silica gel flash chromatography (PE:Acetone = 3:2).

Melting point (^{o}C): > 250

^{1}H NMR (400 MHz, Acetone-d_6) δ 8.04 (s, 1H), 7.88 (d, *J* = 7.2 Hz, 1H), 7.73 (s, 2H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.56 (d, *J* = 7.2 Hz, 2H), 4.35 (d, *J* = 16.8 Hz, 2H), 4.16 (d, *J* = 16.8 Hz, 2H), 2.73 (s, 3H).

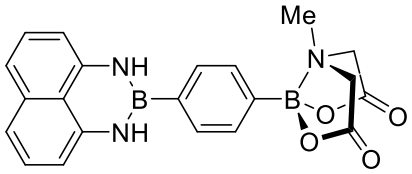
^{13}C NMR (100 MHz, Acetone-d_6) δ 169.40, 143.21, 137.45, 137.25, 135.06, 133.87, 128.45, 128.12, 121.02, 117.71, 106.65, 62.76, 48.34.

^{11}B NMR (128 MHz, $CDCl_3$) δ 12.0, 31.3.

HRMS (APCI) m/z calcd for $C_{21}H_{18}B_2N_3O_4$ (M-): 398.1489, found: 398.1498.

IR (cm^{-1}): 3392, 3373, 1749, 1600, 1282, 1203, 1042, 990.

(3c)8-(4-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)phenyl)-4-methyldihydro-4λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione



Chemical Formula: $C_{21}H_{19}B_2N_3O_4$
Exact Mass: 399.1562
Molecular Weight: 399.0200

The general procedure A was followed using 4-bromophenyl MIDA boronate (93.6 mg, 0.3 mmol, 1.2 eq.) as starting material. **3c** was obtained as white solid (66.8 mg, 67%) after purification by silica gel flash chromatography (PE:Acetone = 3:2).

Melting point (°C): > 250

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.88 (d, *J* = 7.9 Hz, 2H), 7.68 (s, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.16 (t, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.61 (d, *J* = 7.2 Hz, 2H), 4.37 (d, *J* = 17.2 Hz, 2H), 4.15 (d, *J* = 17.2 Hz, 2H), 2.74 (s, 3H).

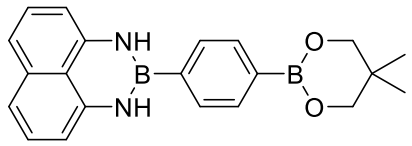
^{13}C NMR (100 MHz, Acetone-d_6) δ 169.35, 143.14, 137.43, 132.84, 132.45, 128.45, 121.06, 117.77, 106.76, 62.78, 48.30.

^{11}B NMR (128 MHz, $CDCl_3$) δ 11.9, 31.0.

HRMS (ESI) m/z calcd for $C_{21}H_{20}B_2N_3O_4$ (M+): 400.1640, found: 400.1630.

IR (cm^{-1}): 3373, 1746, 1598, 1282, 1204, 1040, 990.

(3d)2-(4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine



Chemical Formula: $C_{21}H_{22}B_2N_2O_2$
Exact Mass: 356.1867
Molecular Weight: 356.0390

The product **3d** was synthesized according to the method of a published literature.[5]

In a dried Schlenk flask (10 mL in volume) equipped with a stirring bar were placed with p-B(dan) benzonitrile (53.8 mg, 0.20 mmol, 1.0 eq.), bis(neopentylglycolato)diboron (90.4 mg, 0.40 mmol, 2.0 eq.), $[RhCl(cod)]_2$ (4.9 mg, 0.01 mmol, 5 mol %), XantPhos (23.1 mg, 0.04 mmol, 20 mol %), DABCO (22.5 mg, 0.20 mmol, 1.0 eq.). After evacuation and refill with dry nitrogen for three times, toluene (0.2 mL) were added with syringes under a stream of nitrogen. The resulting mixture was allowed to stir at 100 ℃ for 15 h. After cooling to room temperature, the reaction mixture was concentrated and then purified by column chromatography on silica gel to give the target product as white solid (32.0 mg, 45%) after purification by silica gel flash chromatography (PE:EA = 10:1).

Melting point (°C): 173.5-176.8

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.14 (t, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.42 (d, *J* = 7.6 Hz, 2H), 6.07 (br, 2H), 3.80 (s, 4H), 1.05 (s, 6H).

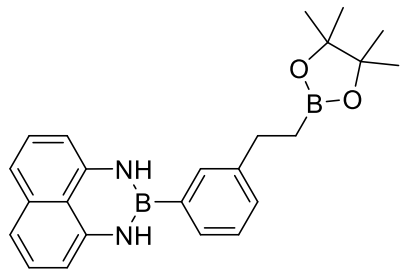
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.23, 136.48, 133.70, 130.72, 127.76, 120.03, 117.91, 106.15, 72.49, 32.05, 22.05.

^{11}B NMR (128 MHz, $CDCl_3$) δ 32.3.

HRMS (APCI) m/z calcd for $C_{21}H_{21}B_2N_2O_2$ (M-): 355.1795, found: 355.1790.

IR (cm^{-1}): 3413, 2925, 1596, 1409, 1305, 1129.

(3e) 2-(3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine



Chemical Formula: $C_{24}H_{28}B_2N_2O_2$
Exact Mass: 398.2337
Molecular Weight: 398.1200

The product **3e** was synthesized according to the method of a published literature.[6]

CuCl (1.0 mg, 0.01 mmol, 5 mol %), NaOt-Bu (2.9 mg, 0.03 mmol, 15 mol %) and DPEphos (5.4 mg, 0.01 mmol, 5 mol %) were placed in an oven-dried Schlenk tube and THF (0.20 ml) were added under nitrogen. The reaction mixture was stirred for 30 min at room temperature and then, bis(pinacolato)diboron and THF (0.20 ml) were added. The reaction mixture was stirred for 10 min and **2l** compound (54.0 mg, 0.20 mmol) was added, followed by MeOH (12.8 mg, 0.40 mmol). The reaction tube was washed with THF (0.40 mL), sealed, and stirred for 20 hours at 30°C. Then reaction mixture was concentrated and purified by column chromatography on silica gel to give the target product as white solid (78.0 mg, 98%) after purification by silica gel flash chromatography (PE:EA = 15:1).

Melting point (°C): 158.7-162.6

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.45 (d, *J* = 5.2 Hz, 1H), 7.37-7.34 (m, 2H), 7.15 (t, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.42 (d, *J* = 7.2 Hz, 2H), 6.05 (br, 2H), 2.82 (t, *J* = 8.4 Hz, 2H), 1.27-1.19 (m, 14H).

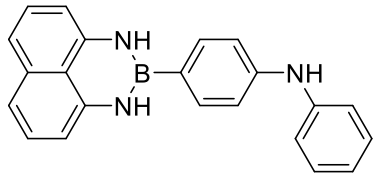
^{13}C NMR (100 MHz, $CDCl_3$) δ 144.20, 141.20, 136.36, 131.20, 130.15, 128.68, 128.20, 127.65, 119.86, 117.72, 105.97, 83.20, 30.05, 24.85.

^{11}B NMR (128 MHz, $CDCl_3$) δ 34.6, 30.7.

HRMS (APCI) m/z calcd for $C_{24}H_{28}B_2N_2O_2$ (M-): 397.2264, found: 397.2269.

IR (cm^{-1}): 3429, 3382, 1596, 1407, 1371, 1321, 1237, 1139.

(4) 4-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)-N-phenylaniline



Chemical Formula: $C_{22}H_{18}BN_3$
Exact Mass: 335.1594
Molecular Weight: 335.2170

The product **4** was synthesized according to the method of a published literature.[7]

In a dried Schlenk flask (25 mL in volume) equipped with a stirring bar were placed with p-B(dan)aniline (64.8 mg, 0.25 mmol, 1.0 eq.), $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol, 1 mol %), XPhos (4.8 mg, 0.01 mmol, 4 mol %), K_2CO_3 (103.7 mg, 0.75 mmol, 3.0 eq.). After evacuation and refill with dry nitrogen for three times, phenylbromide (0.3 mmol, 1.2 eq.) and *t*-BuOH (0.5 mL) were added with syringes under a stream of nitrogen. The resulting mixture was allowed to stir at 110 ℃ for 20 h. After cooling to room temperature, the reaction mixture was filtered, concentrated and then purified by column chromatography on silica gel to give the target product as yellow solid (62.8 mg, 75 %) after purification by silica gel flash chromatography (PE:EA = 15:1).

Melting point (°C): 164.8-169.2

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.4 Hz, 2H), 7.32 (t, *J* = 8.0 Hz, 2H), 7.20 – 7.02 (m, 9H), 6.41 (d, *J* = 7.2 Hz, 2H), 5.99 (br, 2H).

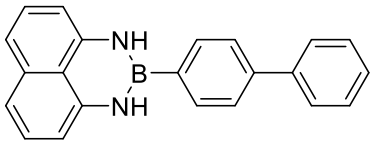
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.46, 142.06, 141.40, 136.50, 132.97, 129.59, 127.75, 122.22, 119.80, 119.23, 117.74, 116.46, 106.02.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.9.

HRMS (APCI) m/z calcd for $C_{22}H_{16}B_2N_2$ (M-): 334.1521, found: 334.1526.

IR (cm^{-1}): 3433, 3416, 3367, 1595, 1495, 1405, 1326, 1084.

(5) 2-([1,1'-biphenyl]-4-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (CAS: 950511-20-3)[8]



Chemical Formula: $C_{22}H_{17}BN_2$
Exact Mass: 320.1485
Molecular Weight: 320.2020

The product **5** was synthesized according to the method of a published literature.[9]

Melting point (^oC): 185.3-188.5

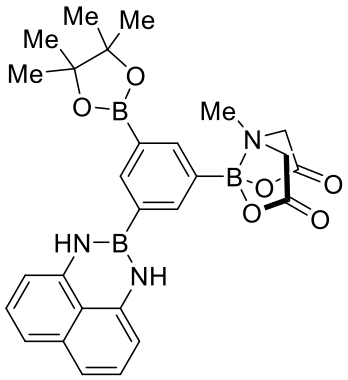
^1H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.63 (m, 6H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.15 (t, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.44 (d, *J* = 7.2 Hz, 2H), 6.08 (br, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.17, 141.20, 140.88, 136.50, 132.10, 129.01, 127.78, 127.31, 127.11, 120.00, 118.00, 106.19.

HRMS (APCI) m/z calcd for $C_{22}H_{16}B_2N_2$ (M-): 319.1412, found: 319.1416.

IR (cm^{-1}): 3426, 3410, 1597, 1396, 1331, 1165, 1083.

(6) 8-(3-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenyl)-4-methyldihydro-4λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione



Chemical Formula: $C_{27}H_{30}B_3N_3O_6$
Exact Mass: 525.2414
Molecular Weight: 524.9820

The general procedure A was followed at 0.10 mmol scale using 1-B(pin)-3-B(MIDA)phenyl cloride (47.2 mg, 0.12 mmol, 1.2 eq.) as starting material. **6** was obtained as white solid (22.0 mg, 42%) after purification by silica gel flash chromatography (PE:Acetone = 1:1).

Melting point (^oC): >250

^1H NMR (400 MHz, Acetone-d_6) δ 8.22 (s, 1H), 8.13 (s, 1H), 8.08 (s, 1H), 7.86 (s, 2H), 7.06 (t, *J* = 7.6 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.58 (d, *J* = 7.2 Hz, 2H), 4.38 (d, *J* = 16.8 Hz, 2H), 4.19 (d, *J* = 17.2 Hz, 2H), 2.77 (s, 3H), 1.36 (s, 12H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 168.51, 142.40, 140.69, 139.49, 139.40, 136.56, 127.56, 120.19, 116.79, 105.77, 83.56, 61.99, 47.62, 24.37.

^{11}B NMR (128 MHz, $CDCl_3$) δ 12.2, 30.7.

HRMS (APCI) m/z calcd for $C_{22}H_{16}B_2N_2$ (M-): 524.2341, found: 524.2349.

IR (cm^{-1}): 3390, 2920, 1765, 1599, 1362, 1204, 1024.

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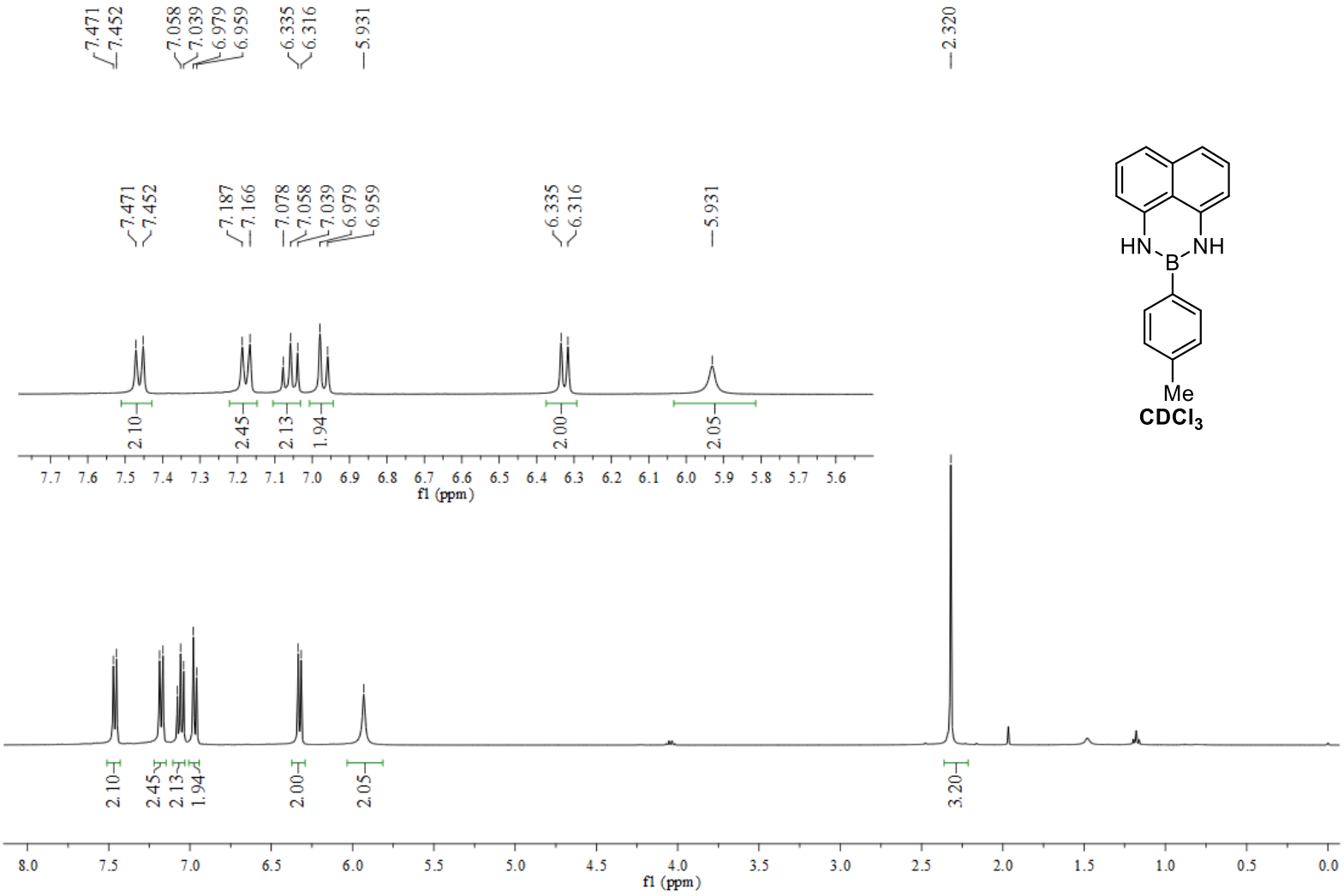

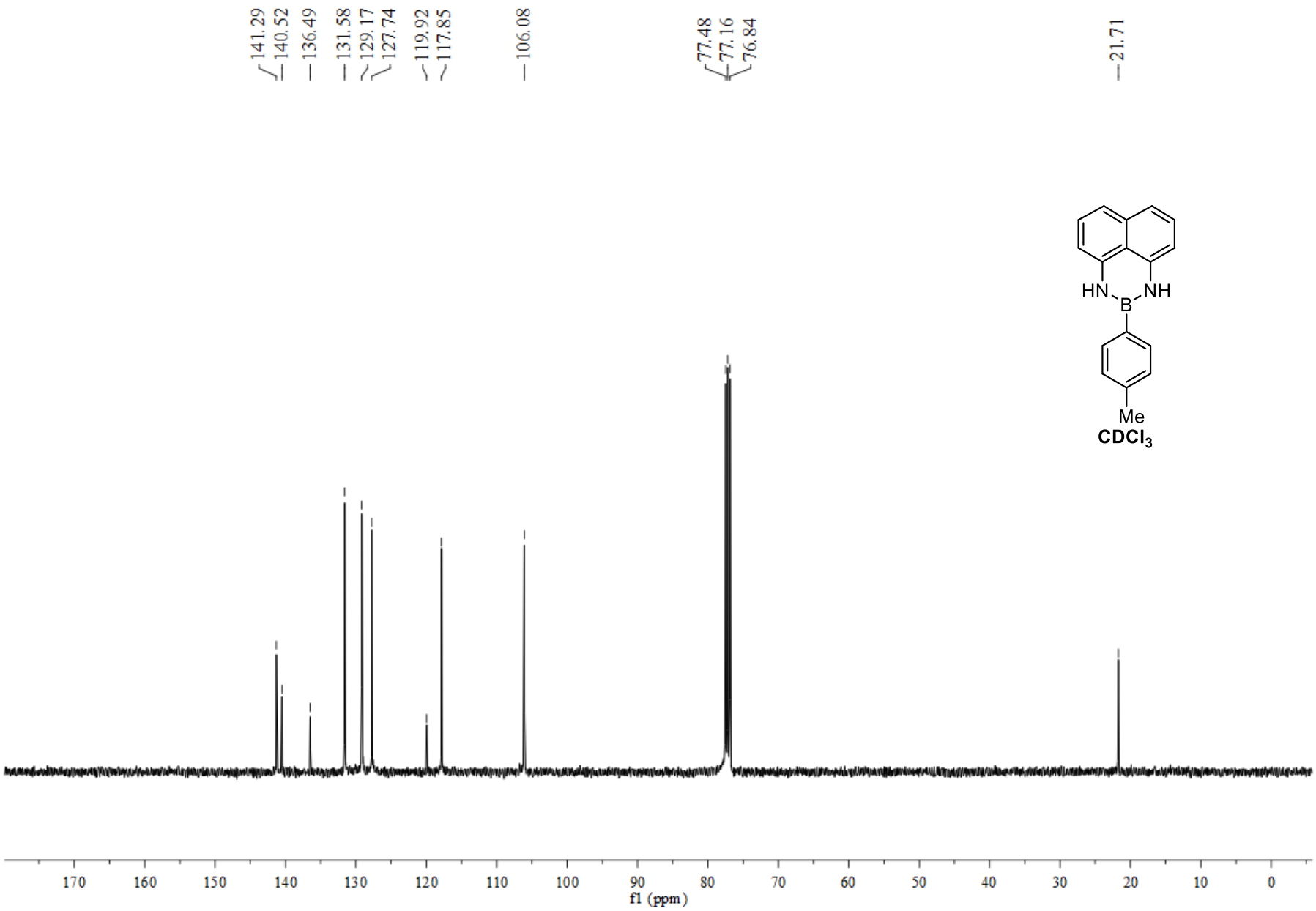
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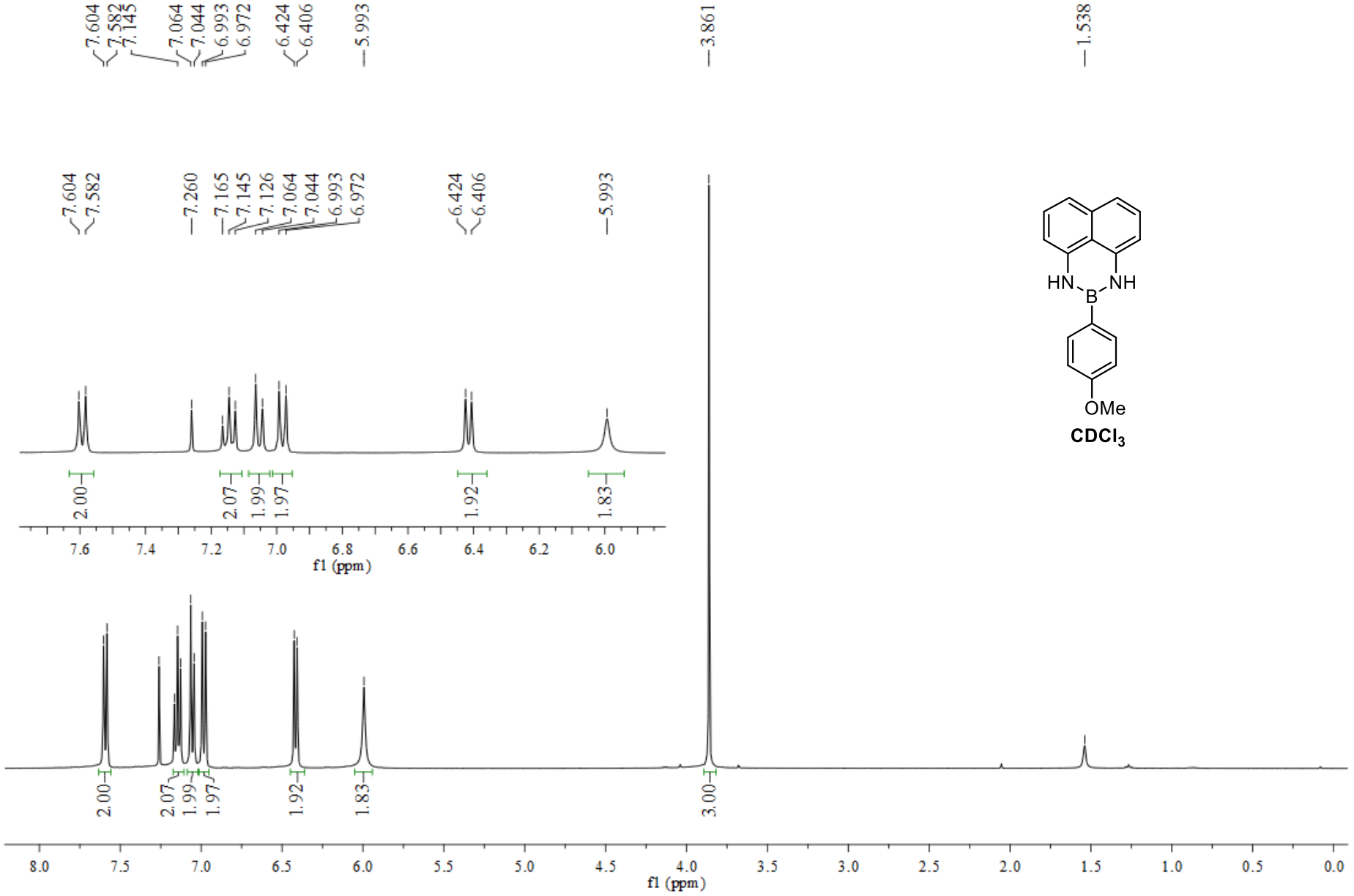
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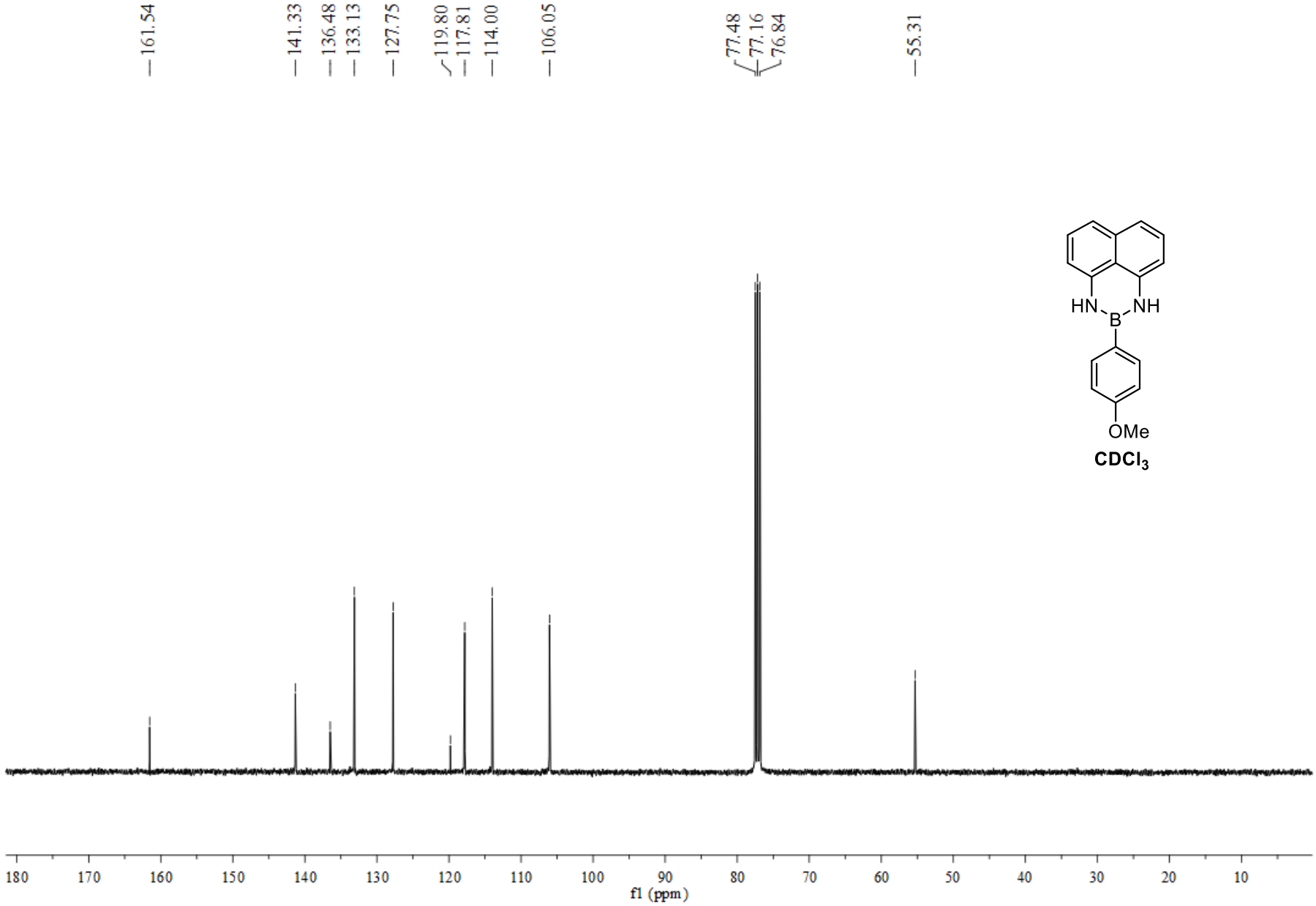
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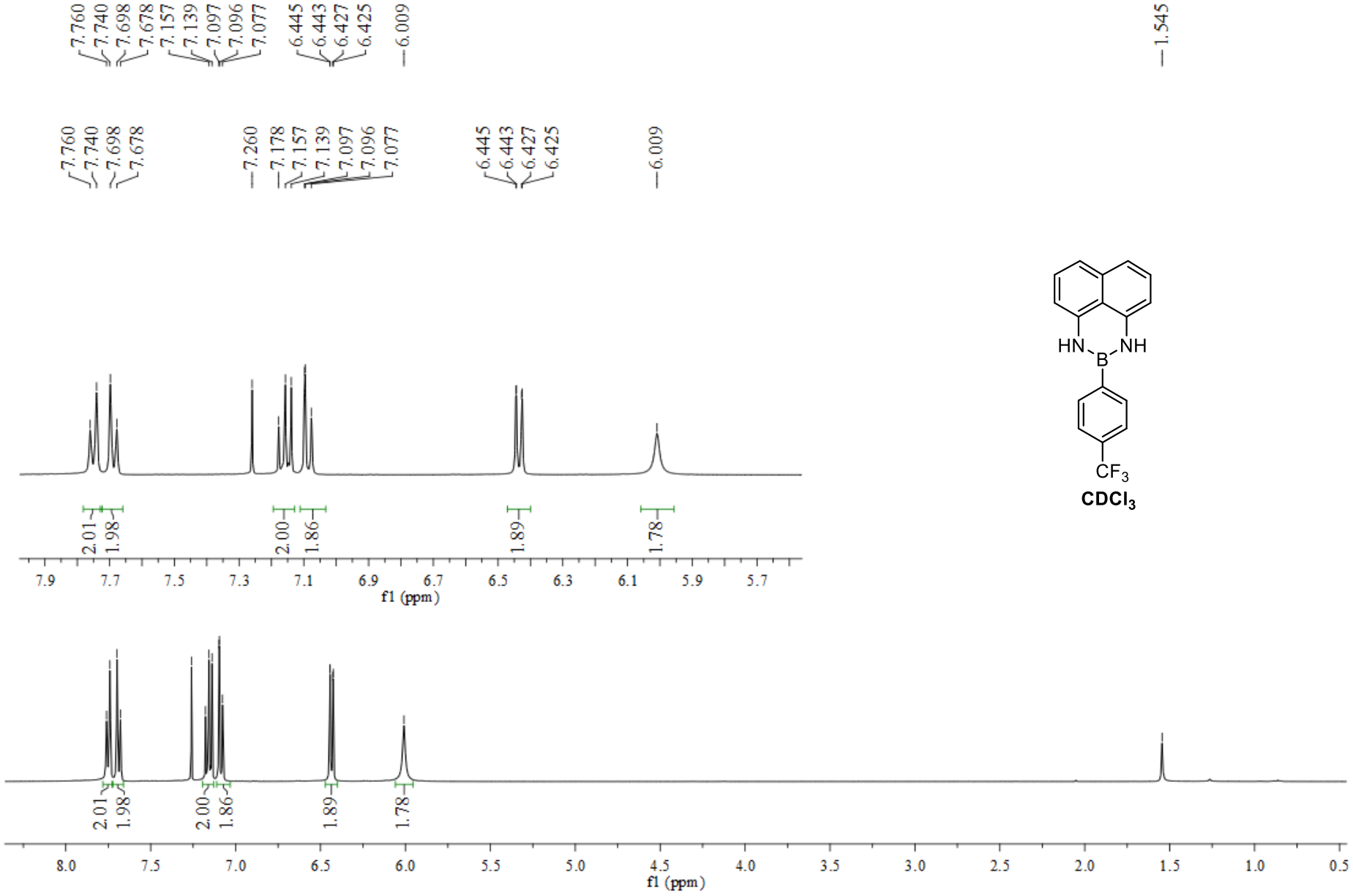
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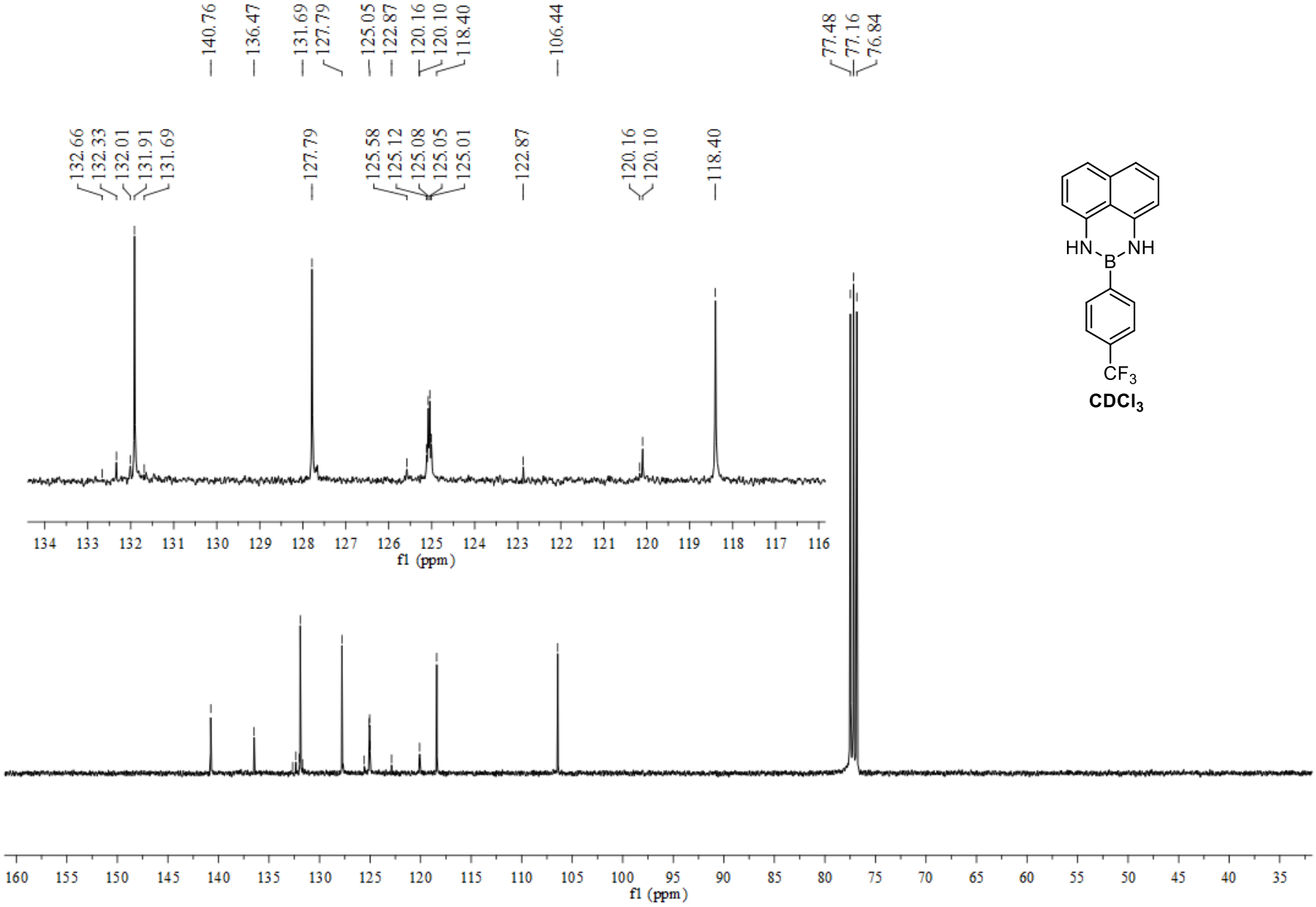
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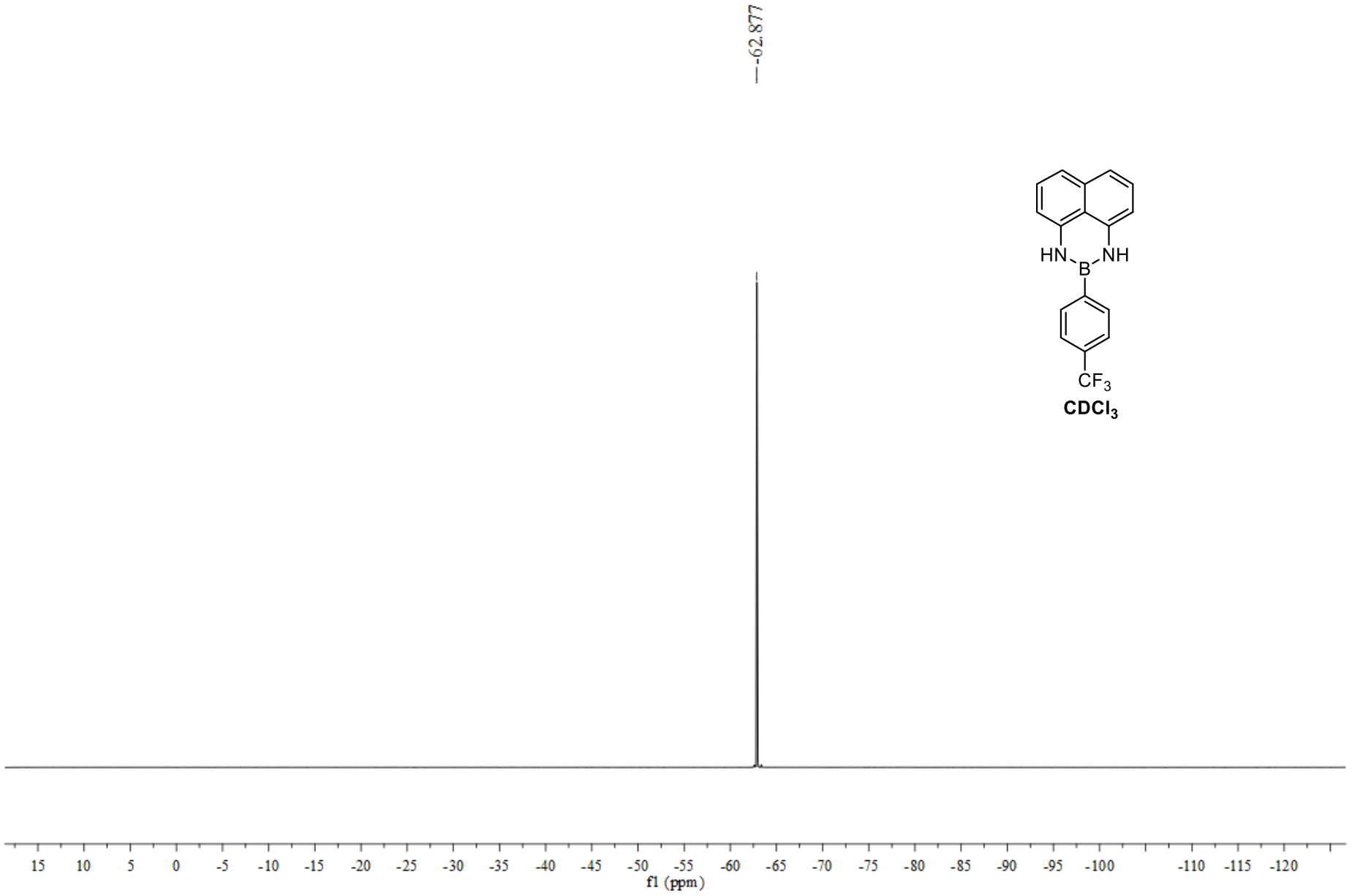
f1 (ppm)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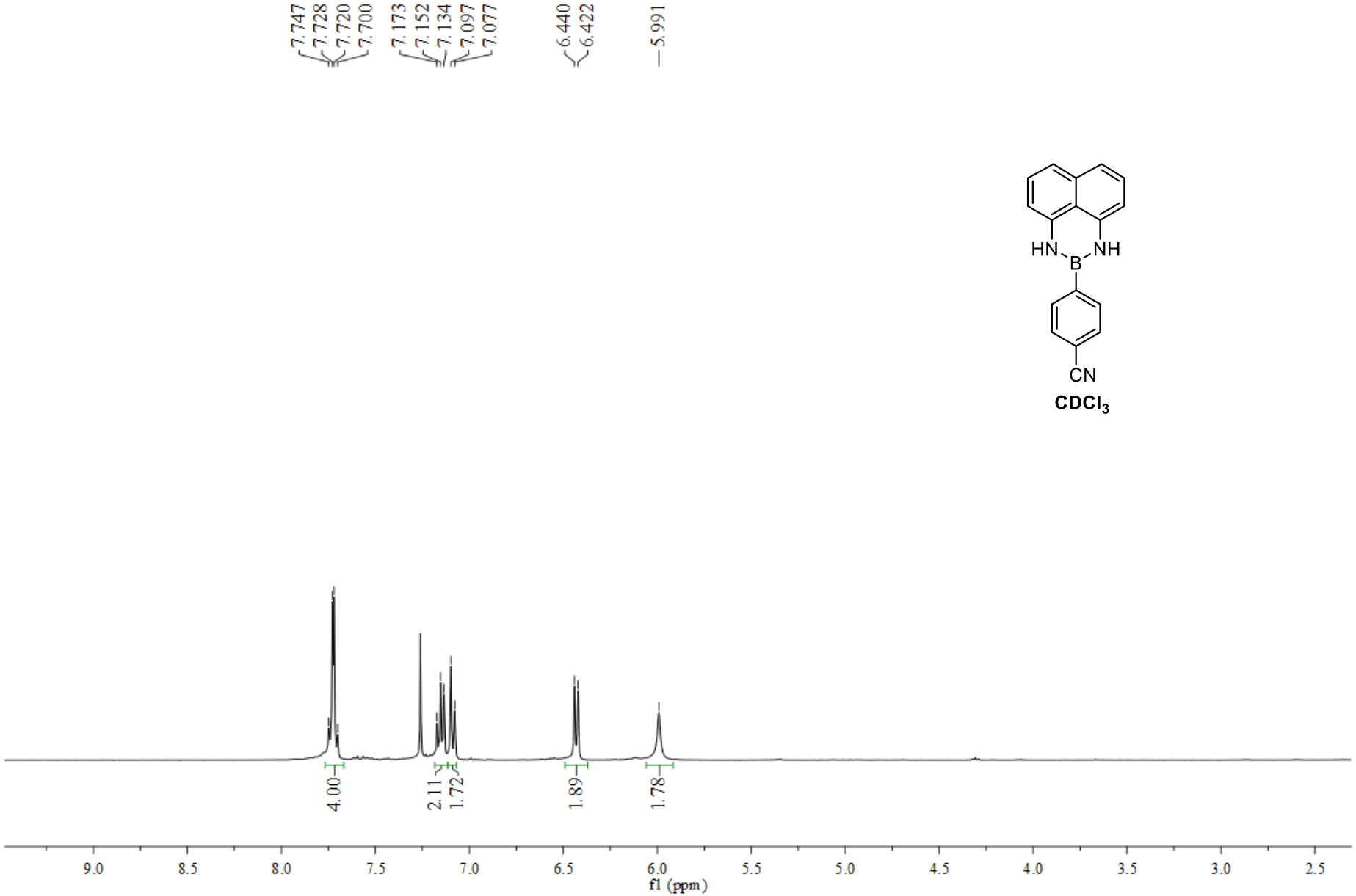
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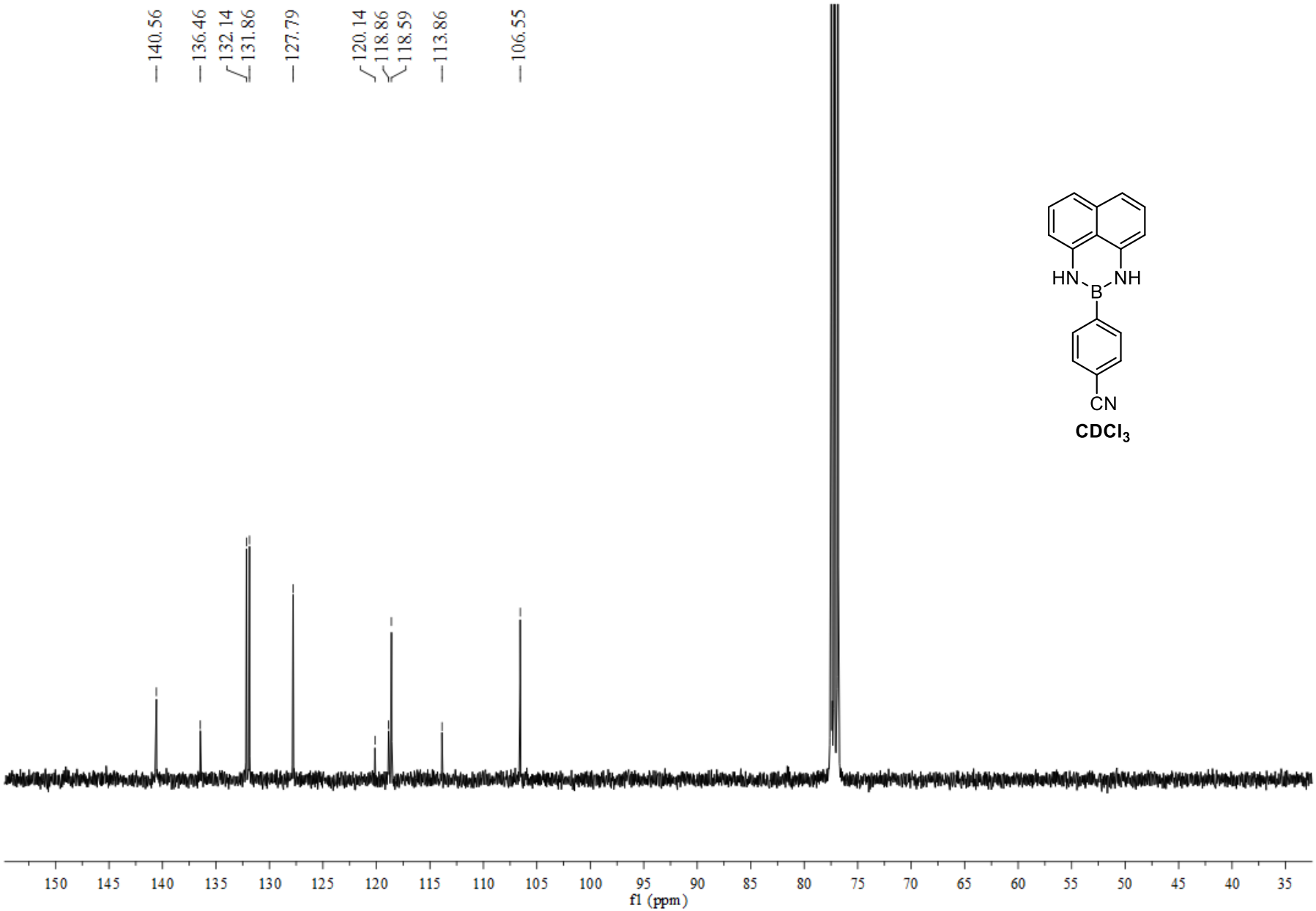
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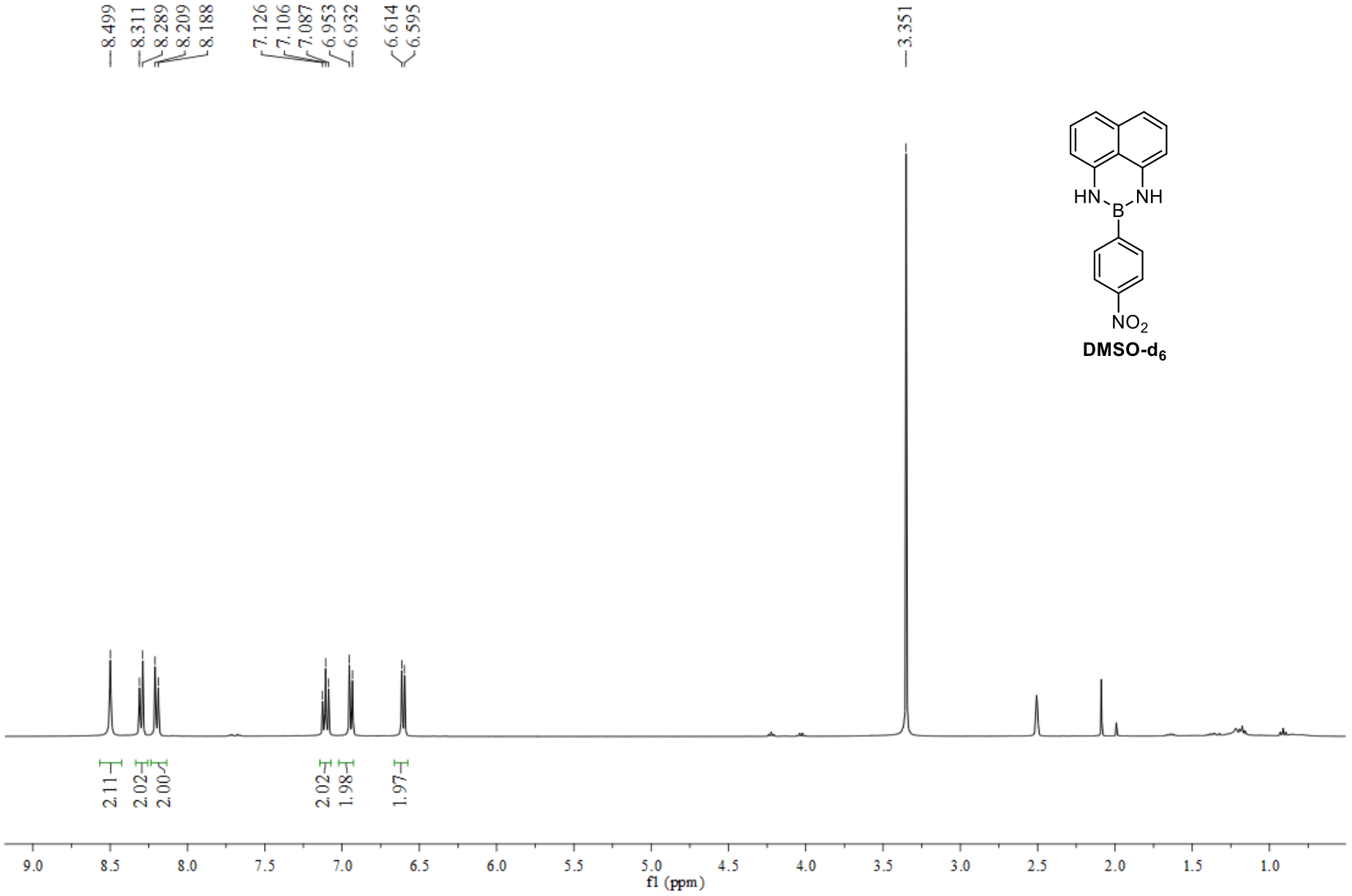
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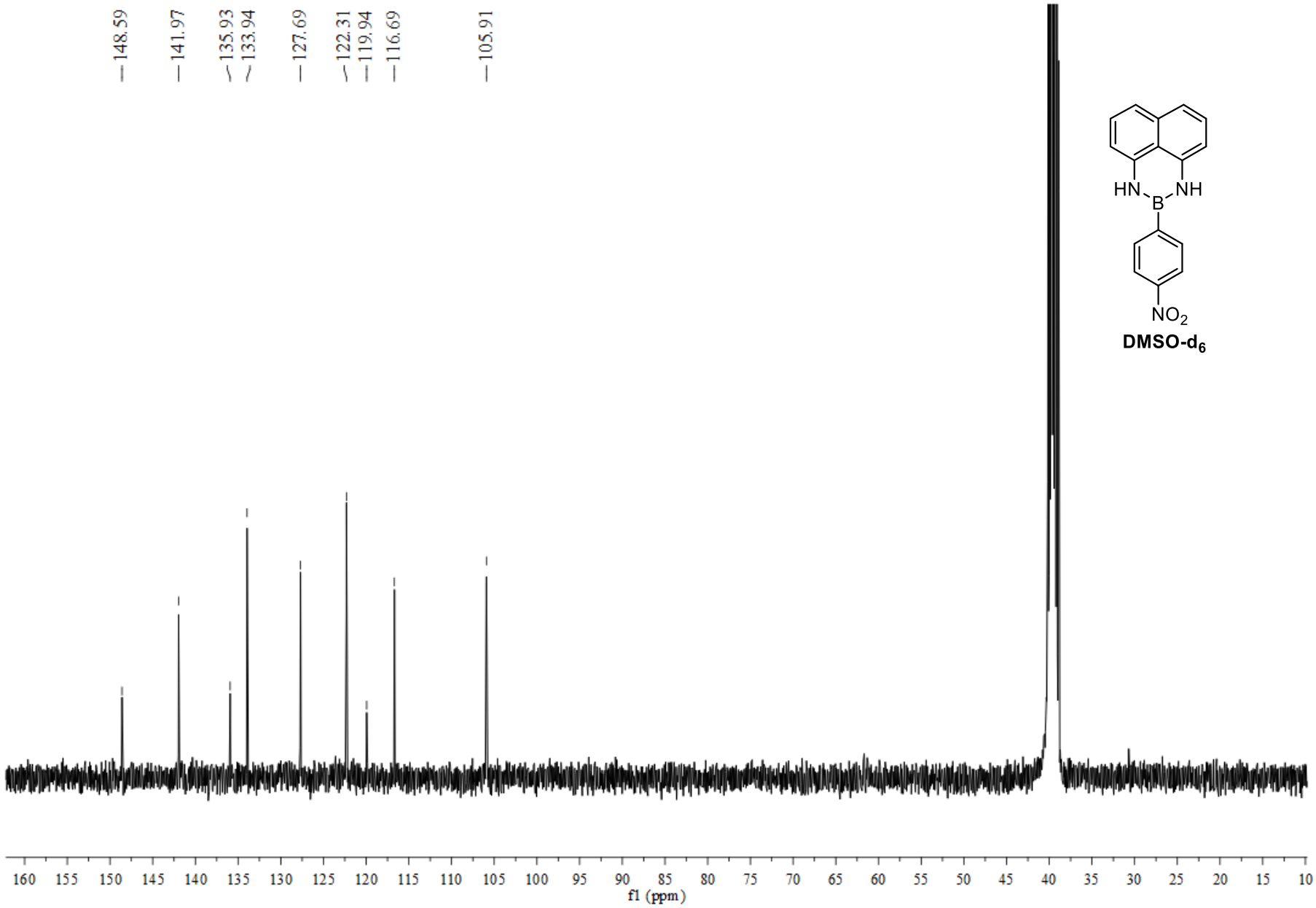
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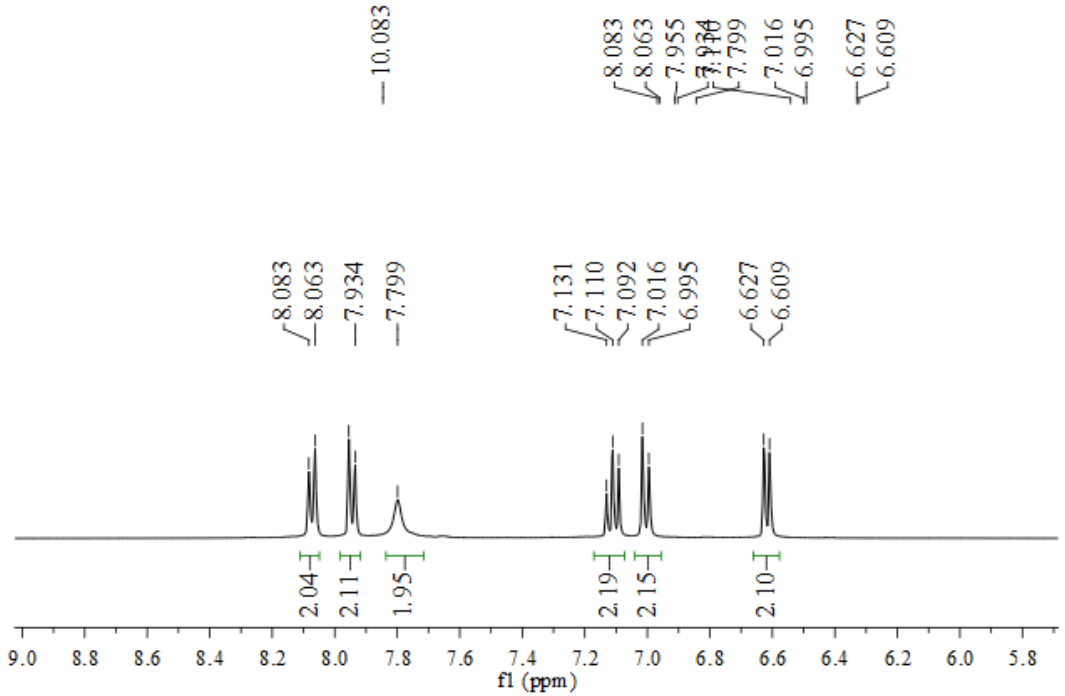
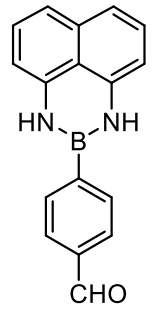
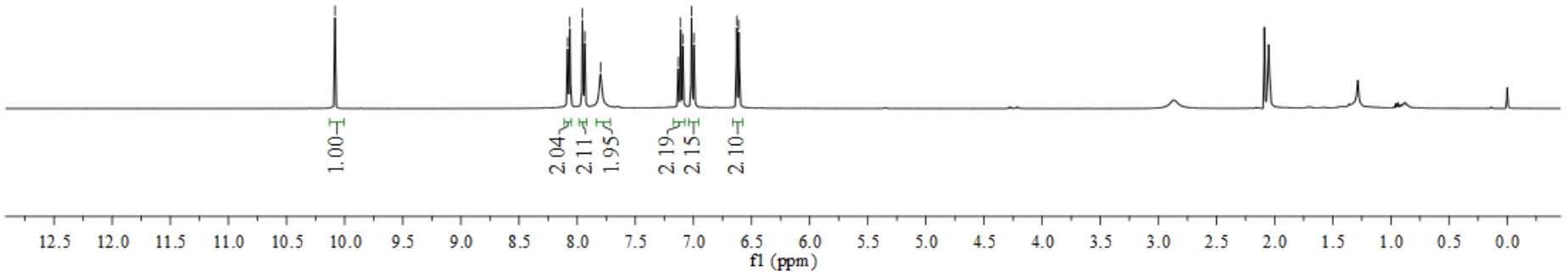
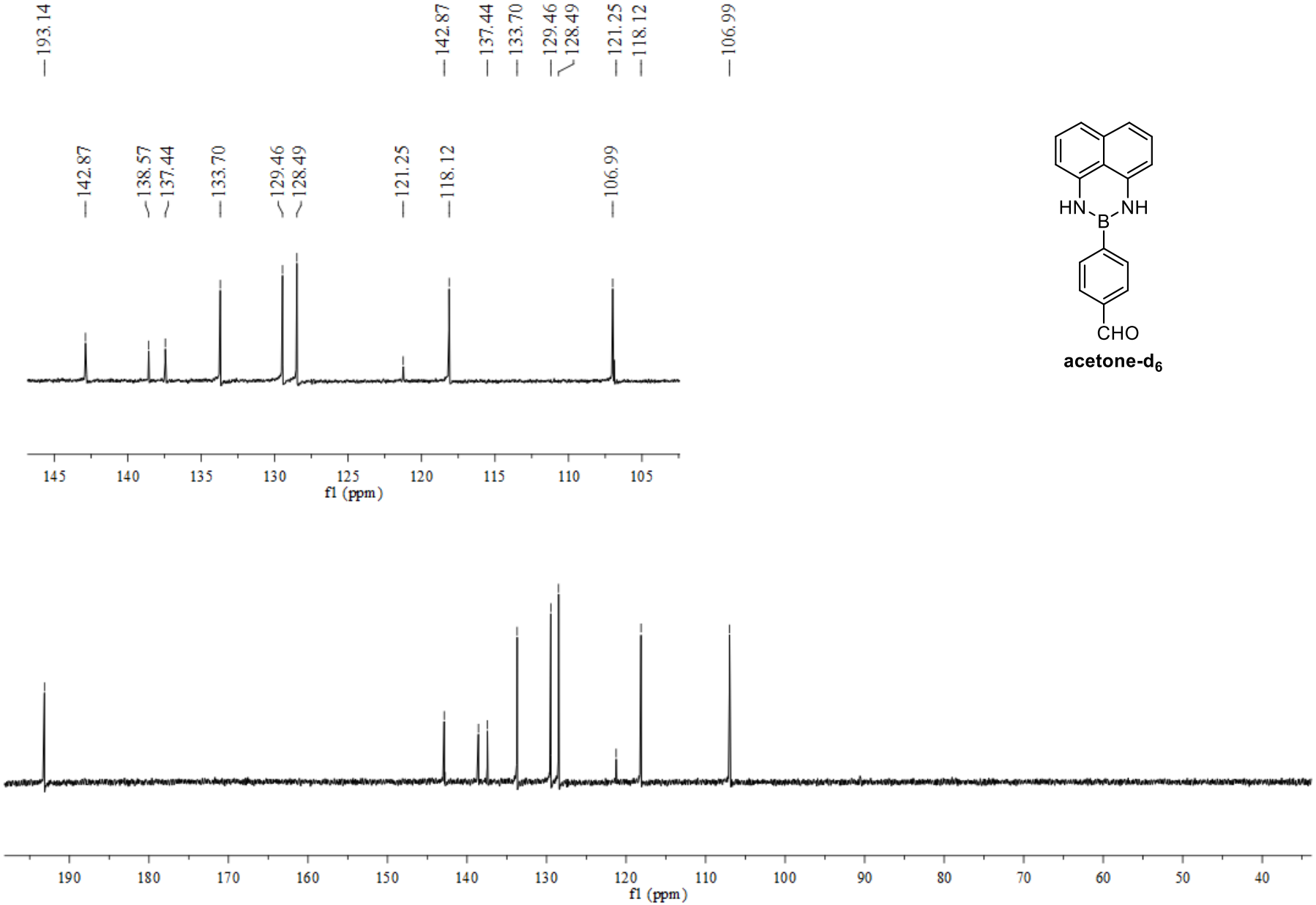
119.94
116.69
105.91
HN
B
NH
NO2
DMSO-d6
160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)

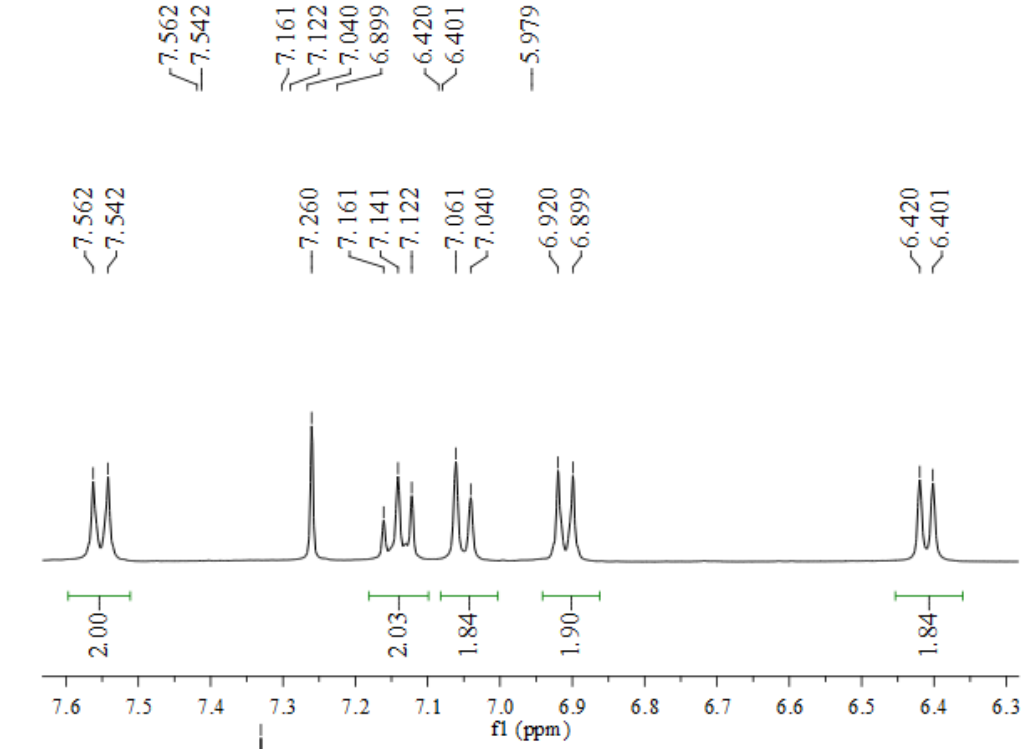

10.083
8.083
8.063
7.955
7.934
7.799
7.016
6.995
6.627
6.609
8.083
8.063
7.934
7.799
7.131
7.110
7.092
7.016
6.995
6.627
6.609
2.04
2.11
1.95
2.19
2.15
2.10
f1 (ppm)

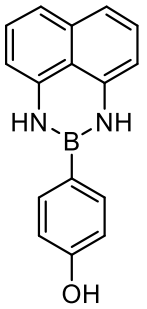

HN
B
NH
CHO

acetone-d_6

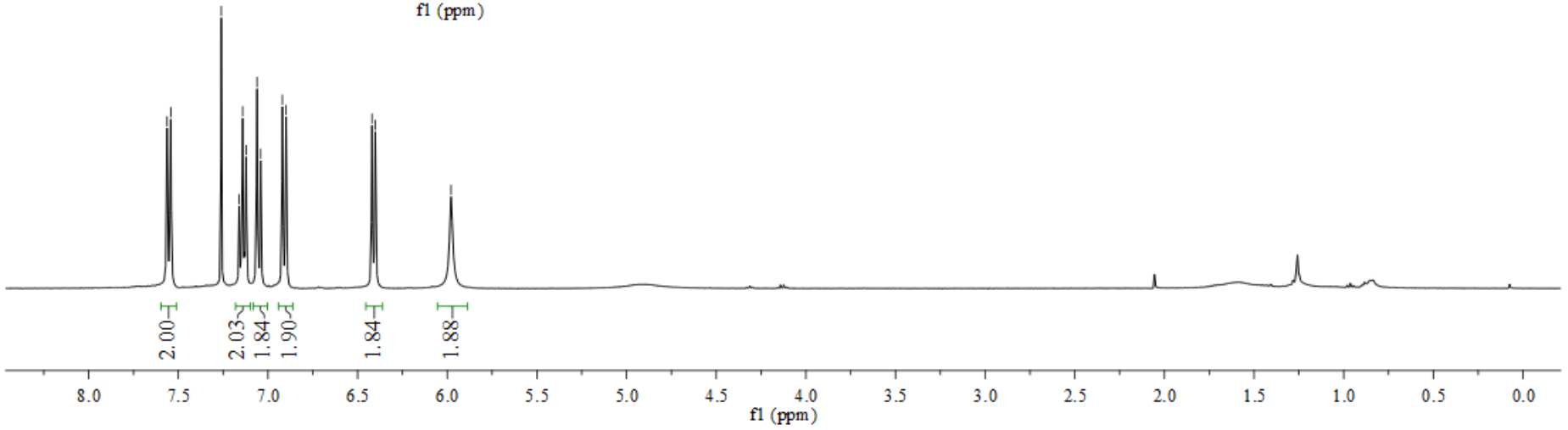

1.00
2.04
2.11
1.95
2.19
2.15
2.10
f1 (ppm)

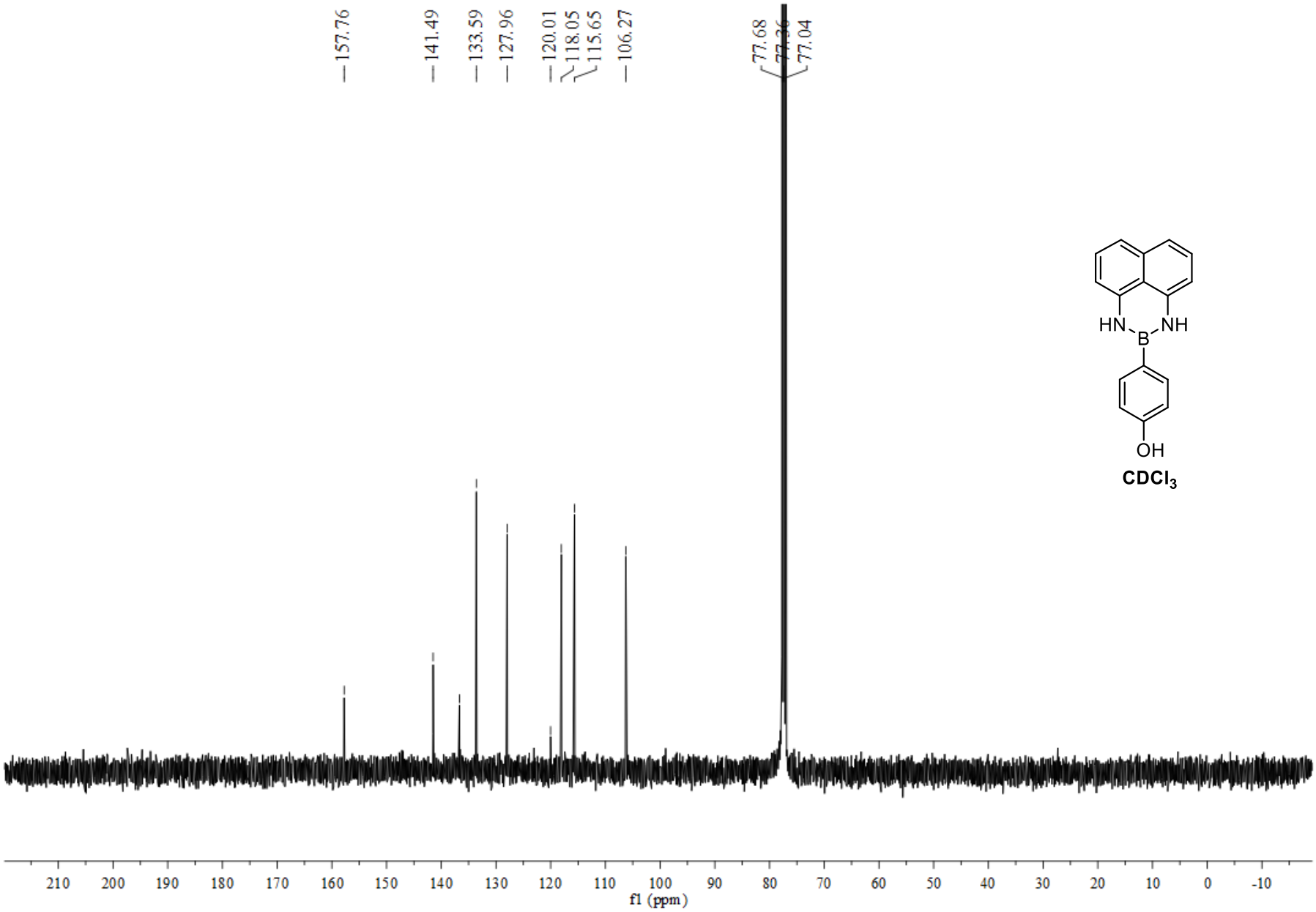

193.14
142.87
137.44
133.70
129.46
128.49
121.25
118.12
106.99
142.87
138.57
137.44
133.70
129.46
128.49
121.25
118.12
106.99
145
140
135
130
125
120
115
110
105
f1 (ppm)
HN
B
NH
CHO
acetone-d6
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
f1 (ppm)

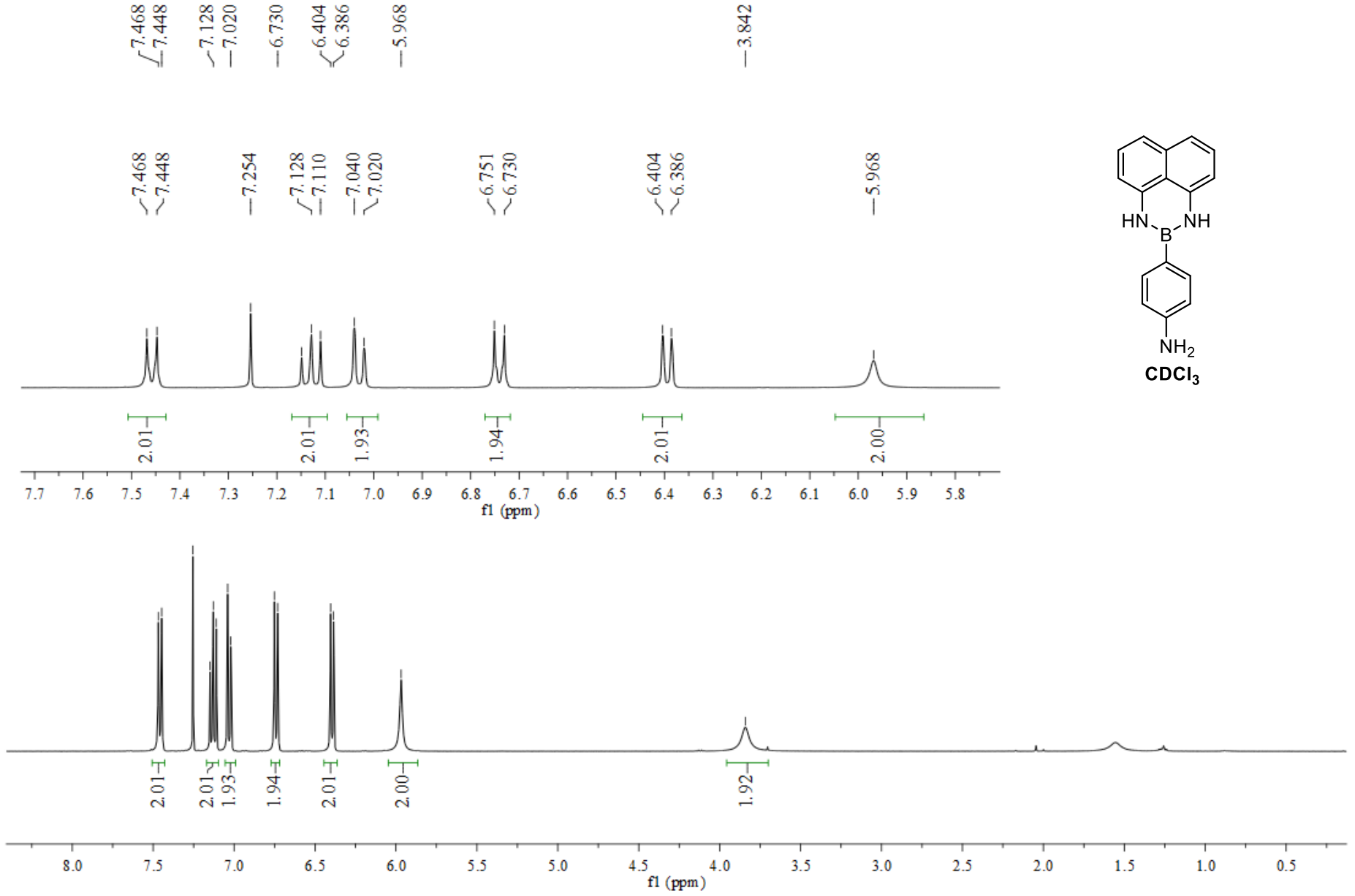

7.562
7.542
7.260
7.161
7.141
7.122
7.061
7.040
6.920
6.899
6.420
6.401
2.00
2.03
1.84
1.90
1.84
f1 (ppm)

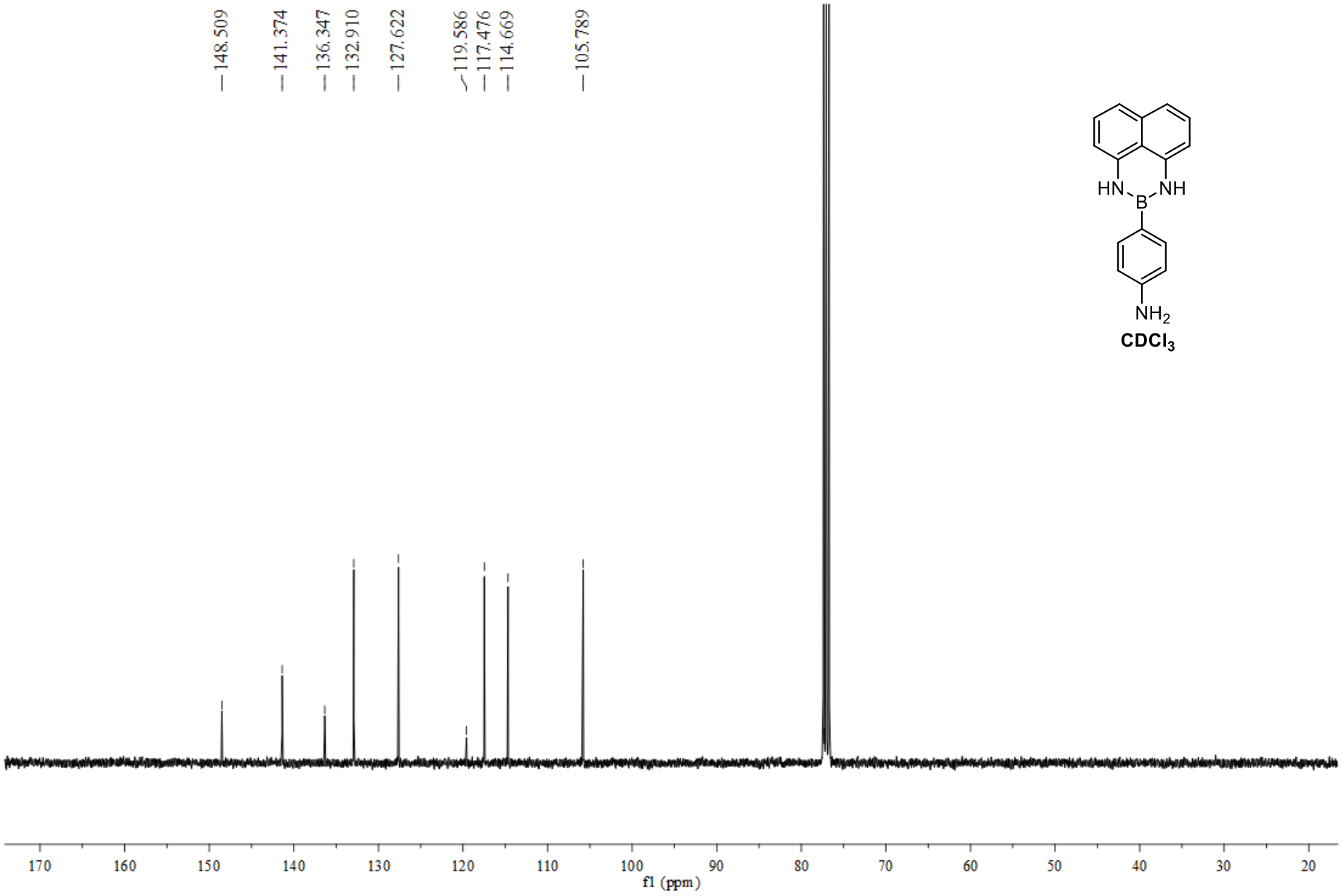

HN
B
NH
OH

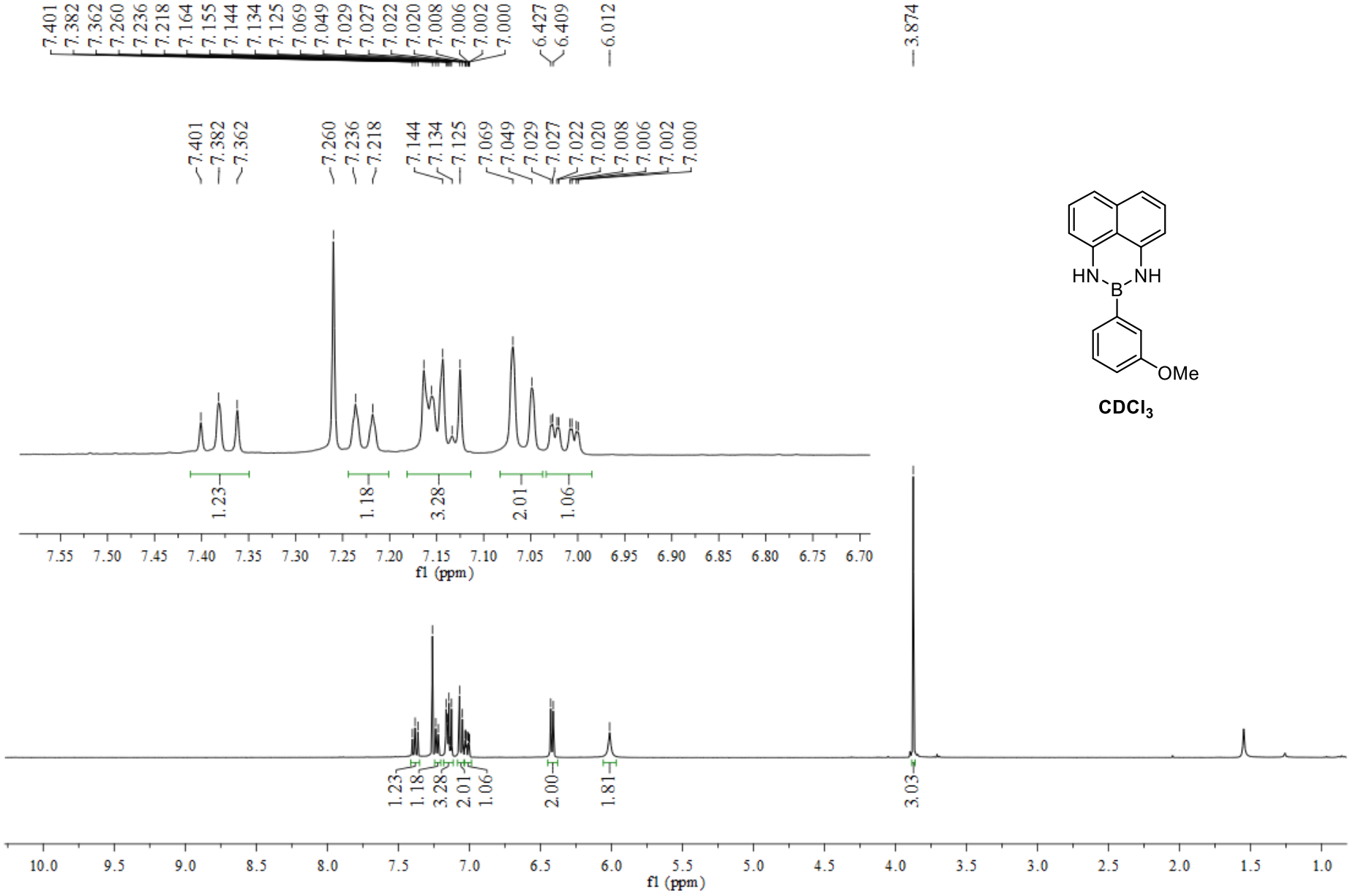
$CDCl_3$

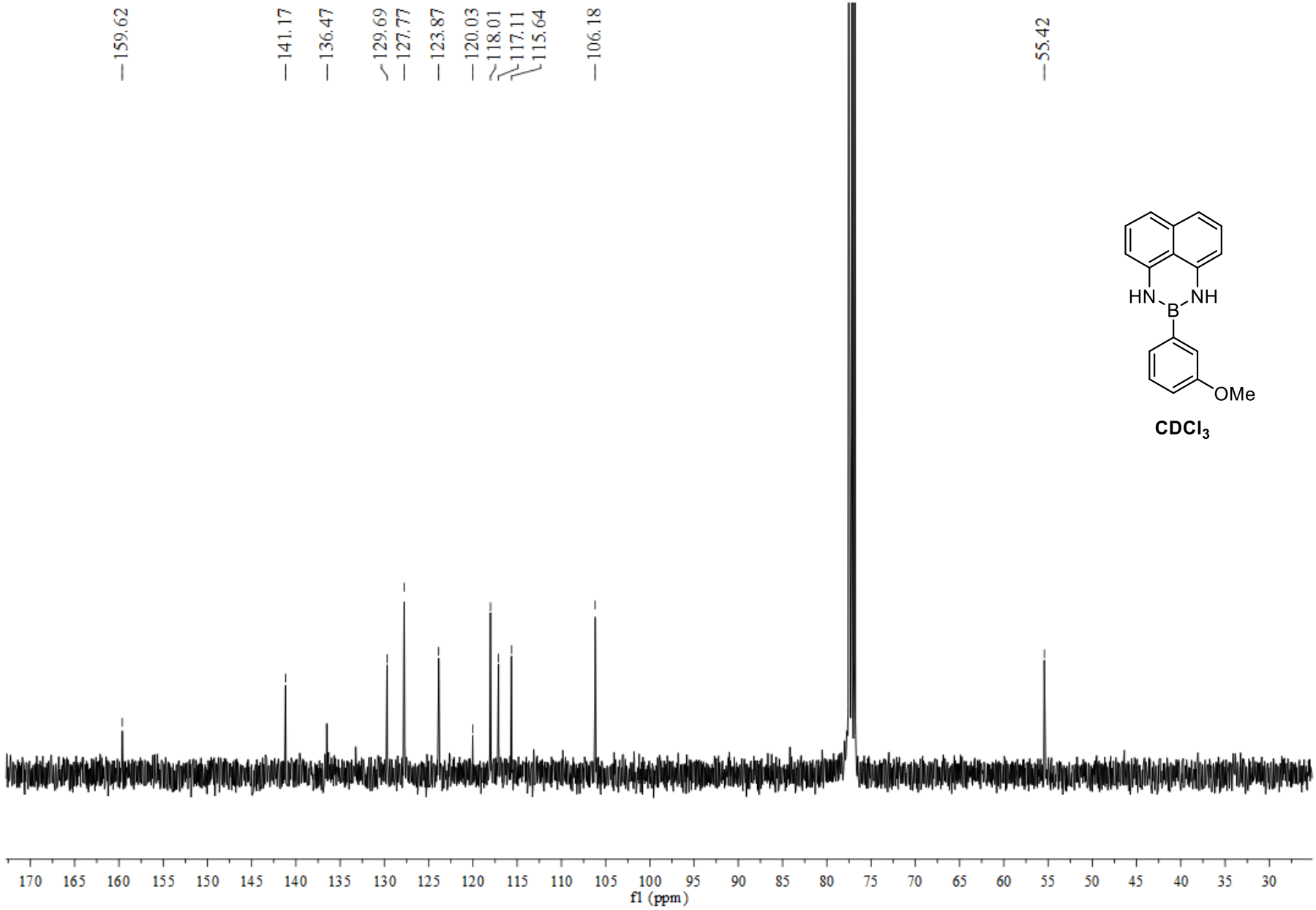

7.562
7.542
7.161
7.122
7.040
6.899
6.420
6.401
5.979
2.00
2.03
1.84
1.90
1.84
1.88
f1 (ppm)

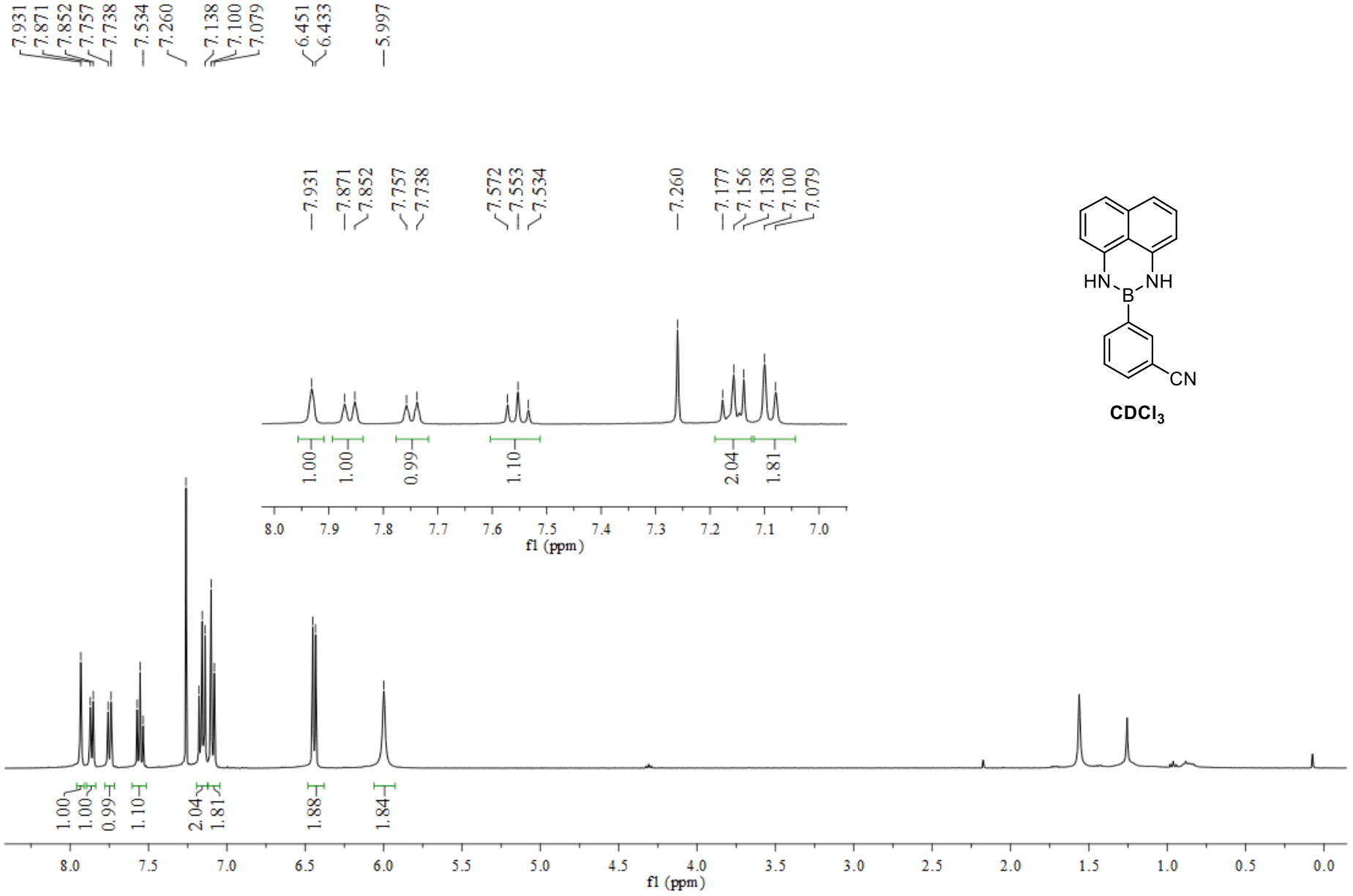

157.76
141.49
133.59
127.96
120.01
118.05
115.65
106.27
77.68
77.36
77.04
HN
B
NH
OH
CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

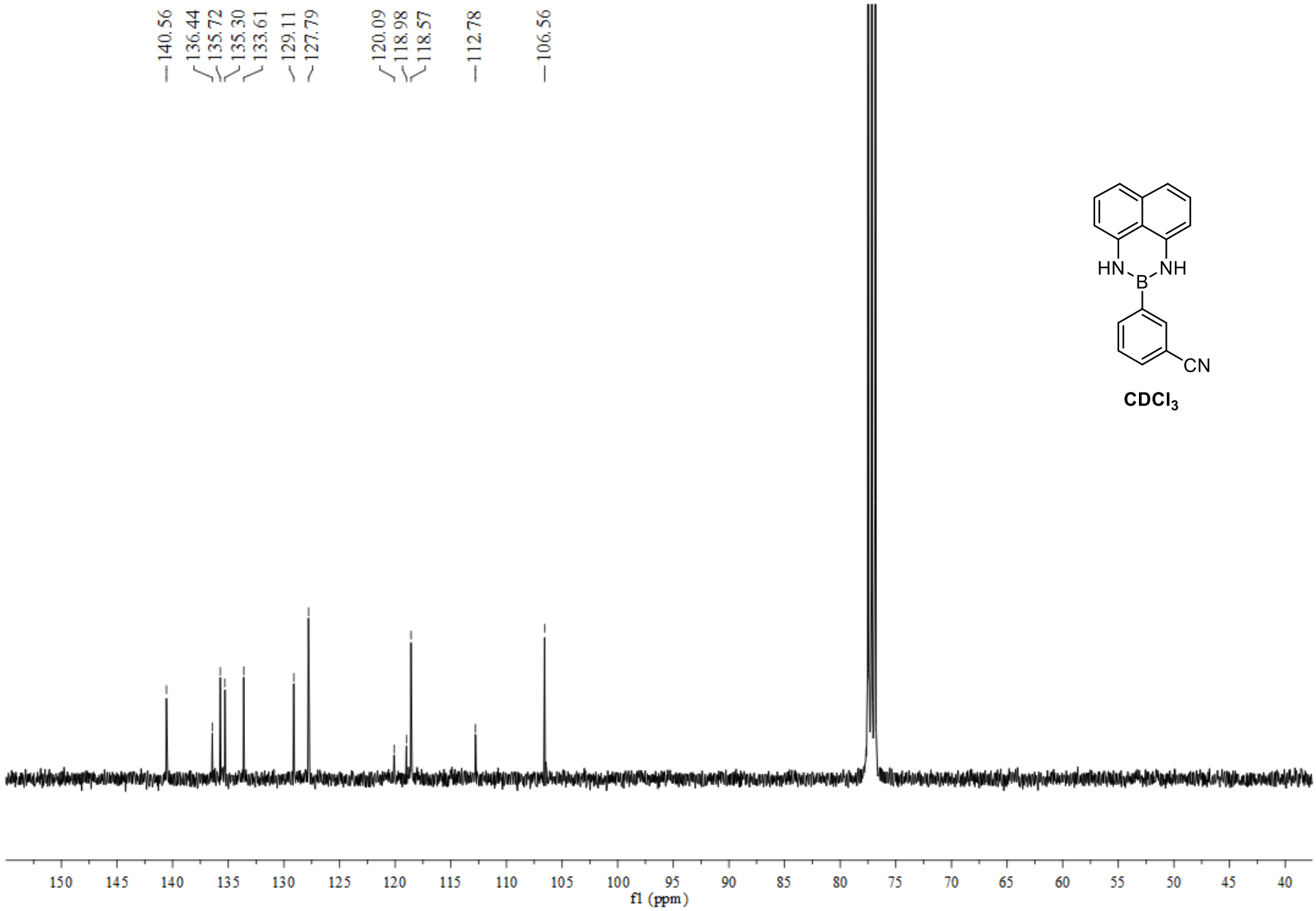

7.468
7.448
7.128
7.020
6.730
6.404
6.386
5.968
3.842
7.254
7.110
7.040
6.751
6.730
2.01
2.01
1.93
1.94
2.01
2.00
f1 (ppm)
HN
B
NH
NH2
CDCl3
1.92

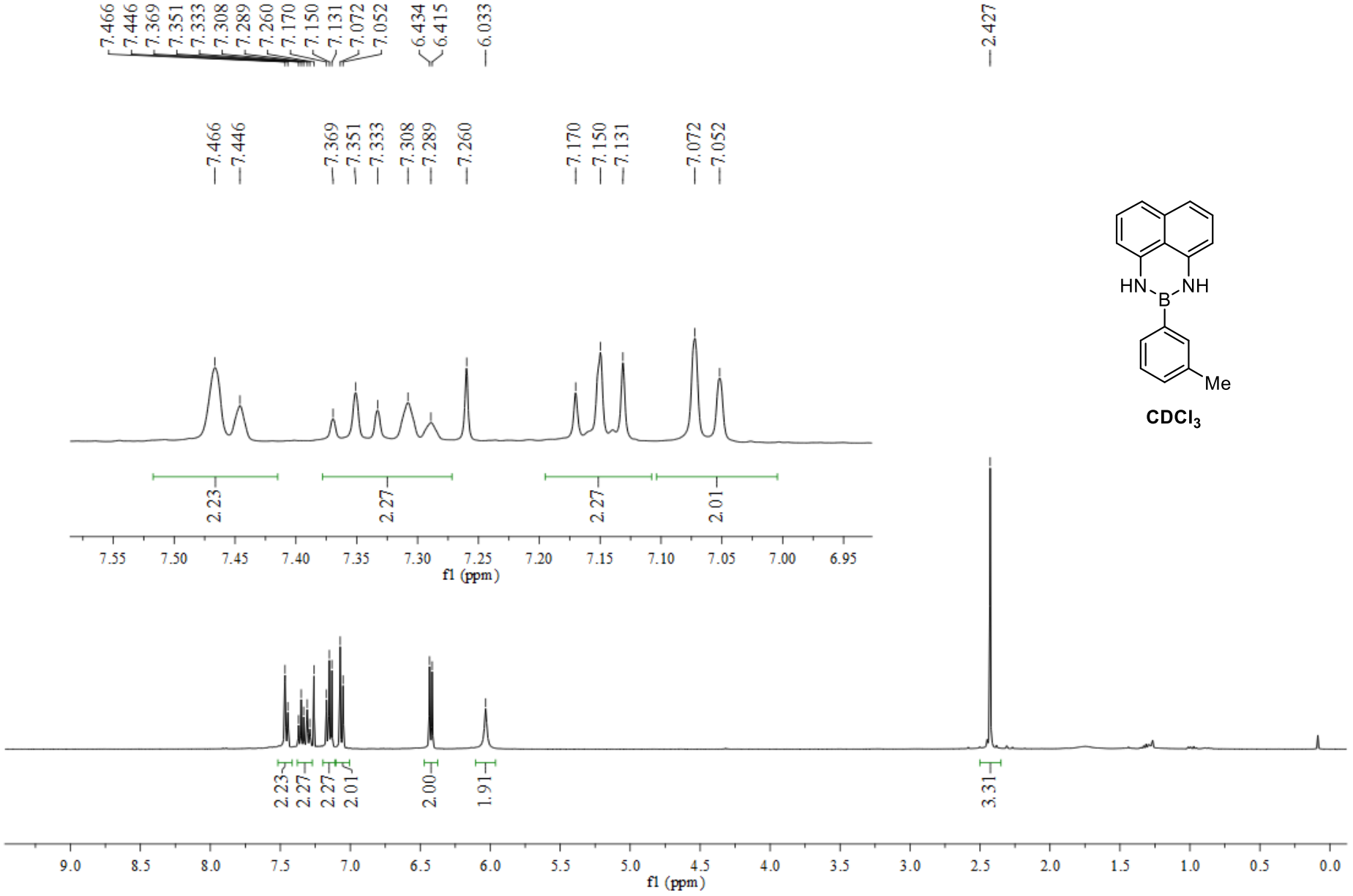

148.509
141.374
136.347
132.910
127.622
119.586
117.476
114.669
105.789
HN
B
NH
NH2
CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

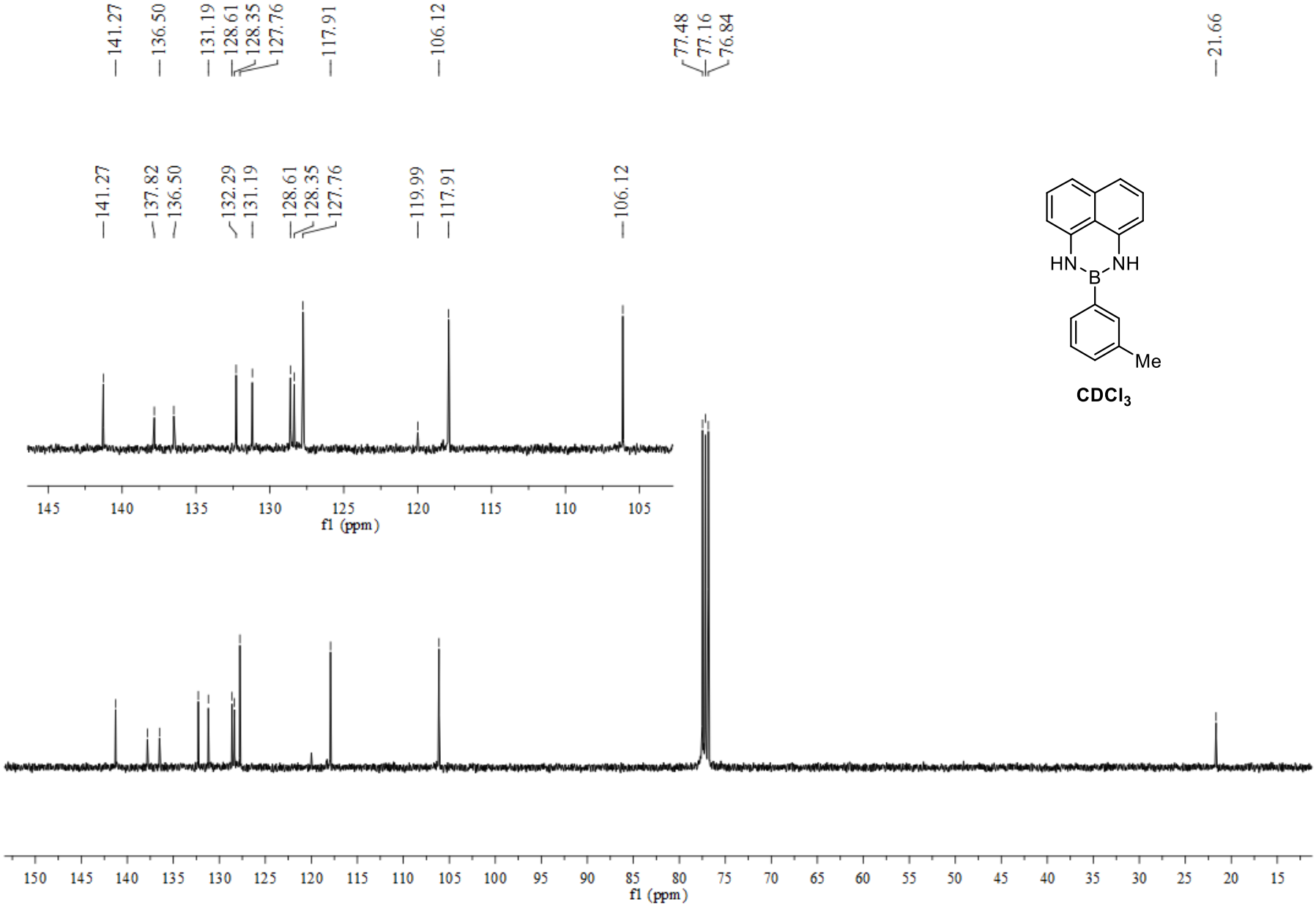

7.401
7.382
7.362
7.260
7.236
7.218
7.164
7.155
7.144
7.134
7.125
7.069
7.049
7.029
7.027
7.022
7.020
7.008
7.006
7.002
7.000
6.427
6.409
6.012
3.874
HN
B
NH
OMe
CDCl3
1.23
1.18
3.28
2.01
1.06
2.00
1.81
3.03
f1 (ppm)

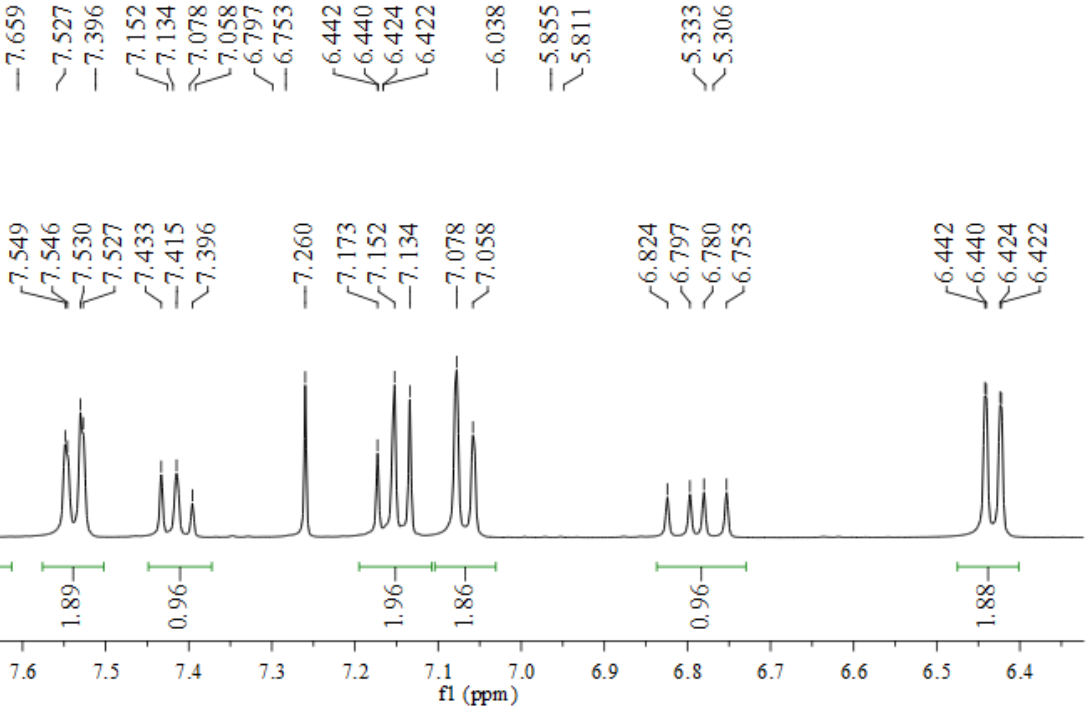

159.62
141.17
136.47
129.69
127.77
123.87
120.03
118.01
117.11
115.64
106.18
55.42
HN
B
NH
OMe
CDCl3
170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30
f1 (ppm)

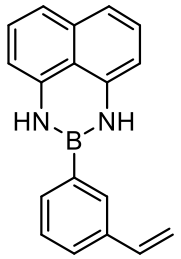

7.931
7.871
7.852
7.757
7.738
7.534
7.260
7.138
7.100
7.079
6.451
6.433
5.997
7.572
7.553
7.534
7.177
7.156
1.00
1.00
0.99
1.10
2.04
1.81
1.88
1.84
f1 (ppm)
HN
B
NH
CN
CDCl3


140.56
136.44
135.72
135.30
133.61
129.11
127.79
120.09
118.98
118.57
112.78
106.56
HN
B
NH
CN
CDCl3
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40
f1 (ppm)

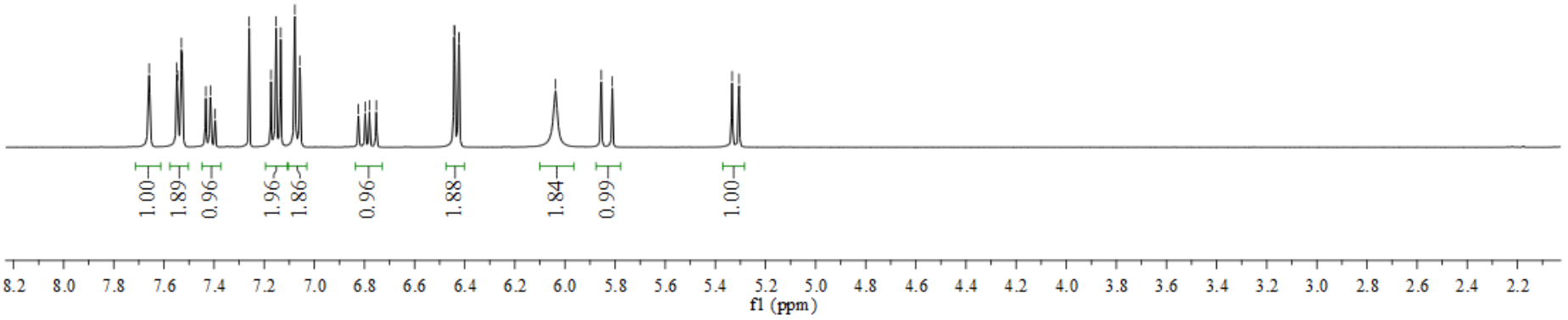

7.466
7.446
7.369
7.351
7.333
7.308
7.289
7.260
7.170
7.150
7.131
7.072
7.052
6.434
6.415
6.033
2.427
HN
B
NH
Me
CDCl3
2.23
2.27
2.27
2.01
f1 (ppm)
2.23
2.27
2.27
2.01
2.00
1.91
3.31
f1 (ppm)

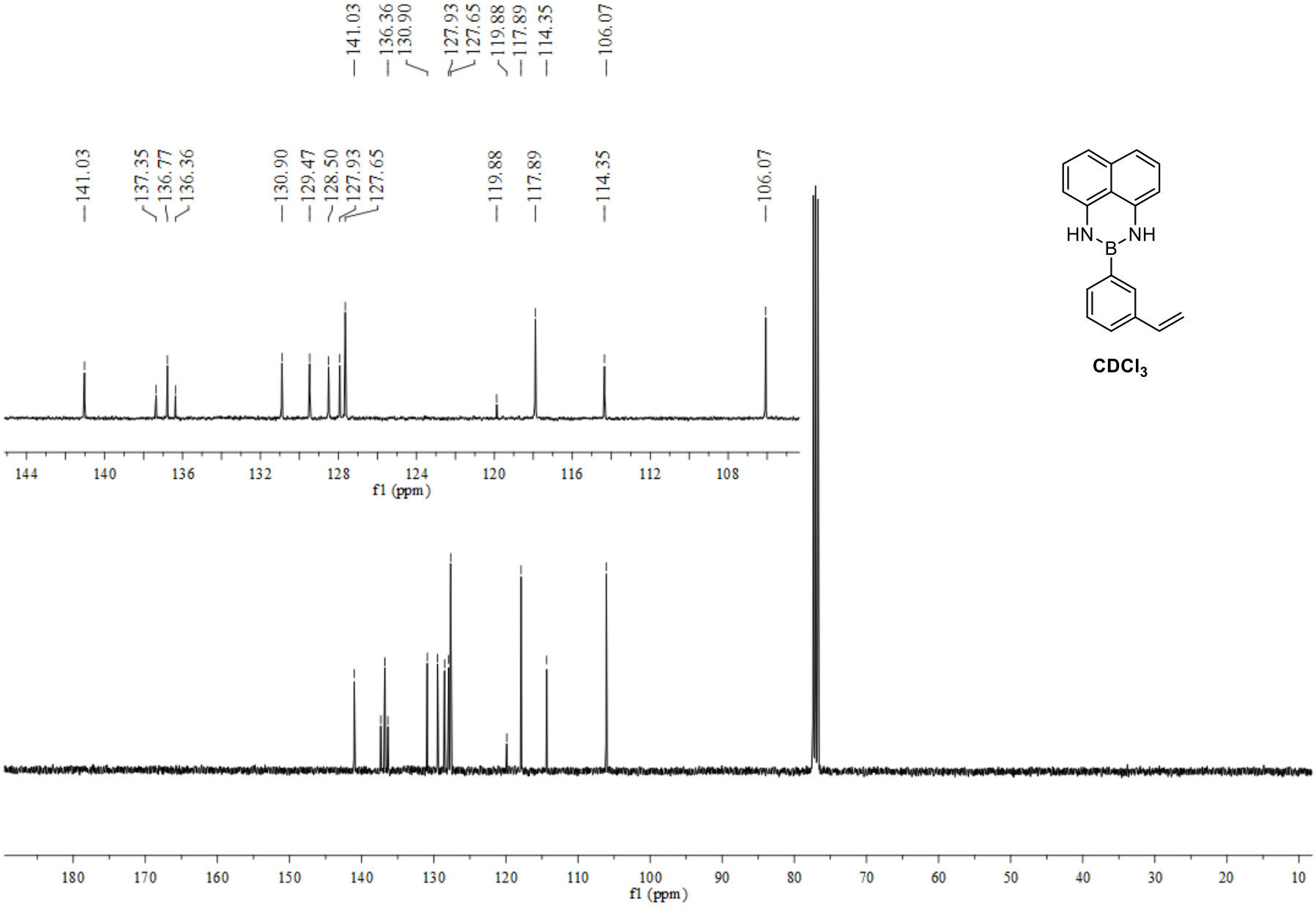

141.27
136.50
131.19
128.61
128.35
127.76
117.91
106.12
77.48
77.16
76.84
21.66
141.27
137.82
136.50
132.29
131.19
128.61
128.35
127.76
119.99
117.91
106.12
HN
B
NH
Me
CDCl3
f1 (ppm)
f1 (ppm)

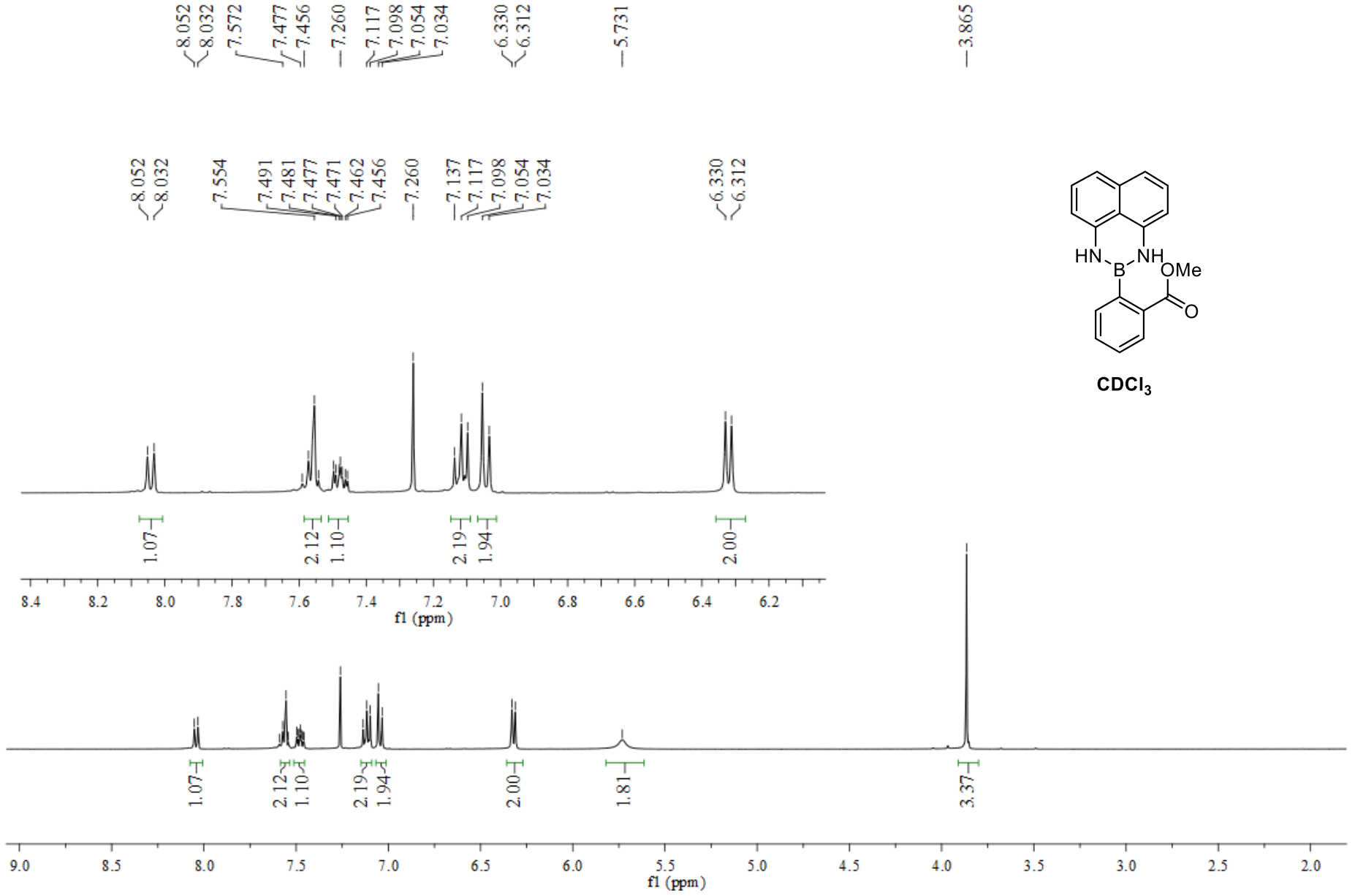

7.659
7.549
7.546
7.530
7.527
7.433
7.415
7.396
7.260
7.173
7.152
7.134
7.078
7.058
6.824
6.797
6.780
6.753
6.442
6.440
6.424
6.422
1.00
1.89
0.96
1.96
1.86
0.96
1.88
f1 (ppm)


HN
B
NH

$CDCl_3$


7.659
7.527
7.396
7.152
7.134
7.078
7.058
6.797
6.753
6.442
6.440
6.424
6.422
6.038
5.855
5.811
5.333
5.306
1.00
1.89
0.96
1.96
1.86
0.96
1.88
1.84
0.99
1.00
f1 (ppm)


141.03
136.36
130.90
127.93
127.65
119.88
117.89
114.35
106.07
141.03
137.35
136.77
136.36
130.90
129.47
128.50
127.93
127.65
119.88
117.89
114.35
106.07
HN
B
NH
CDCl3
144
140
136
132
128
124
120
116
112
108
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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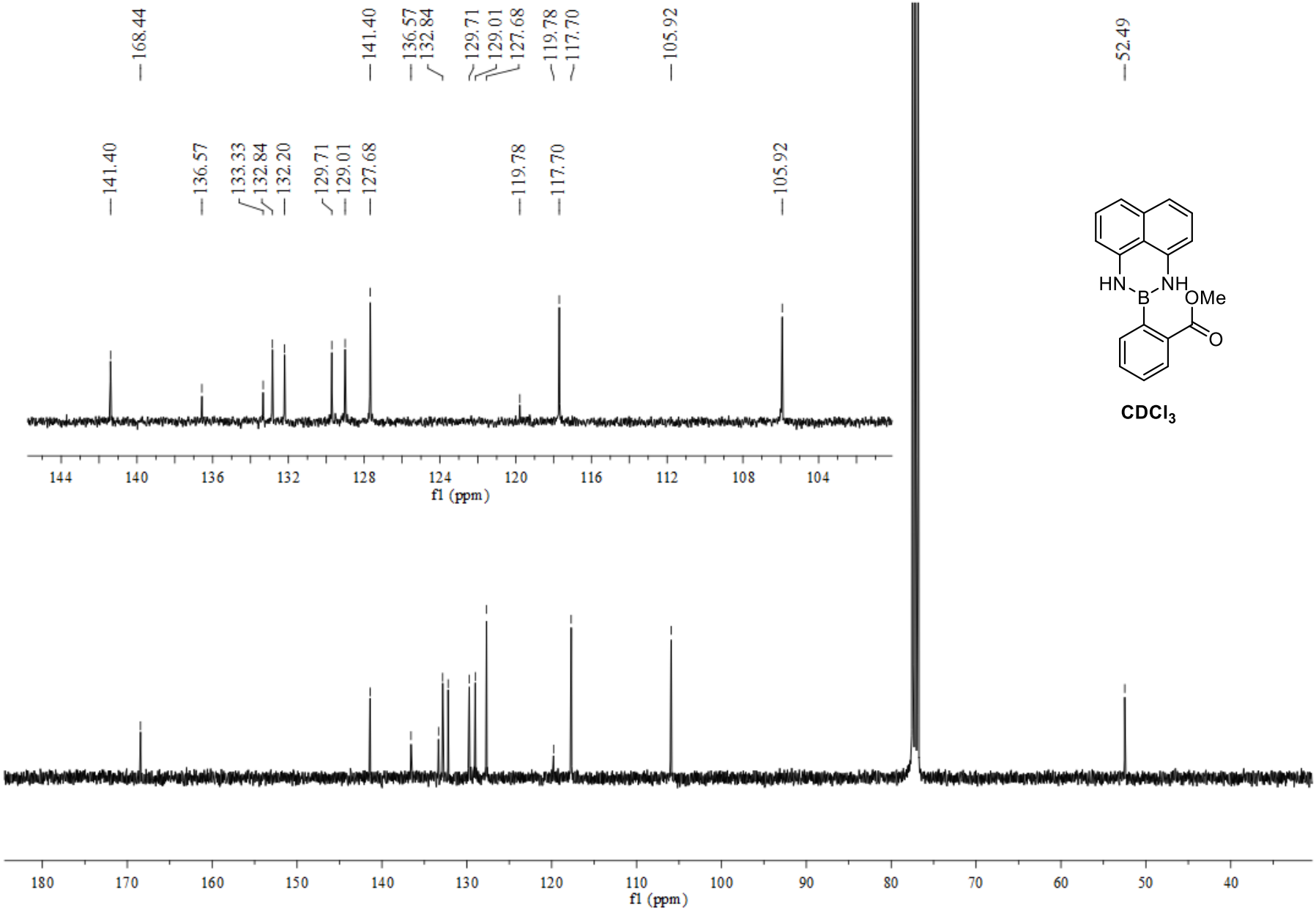
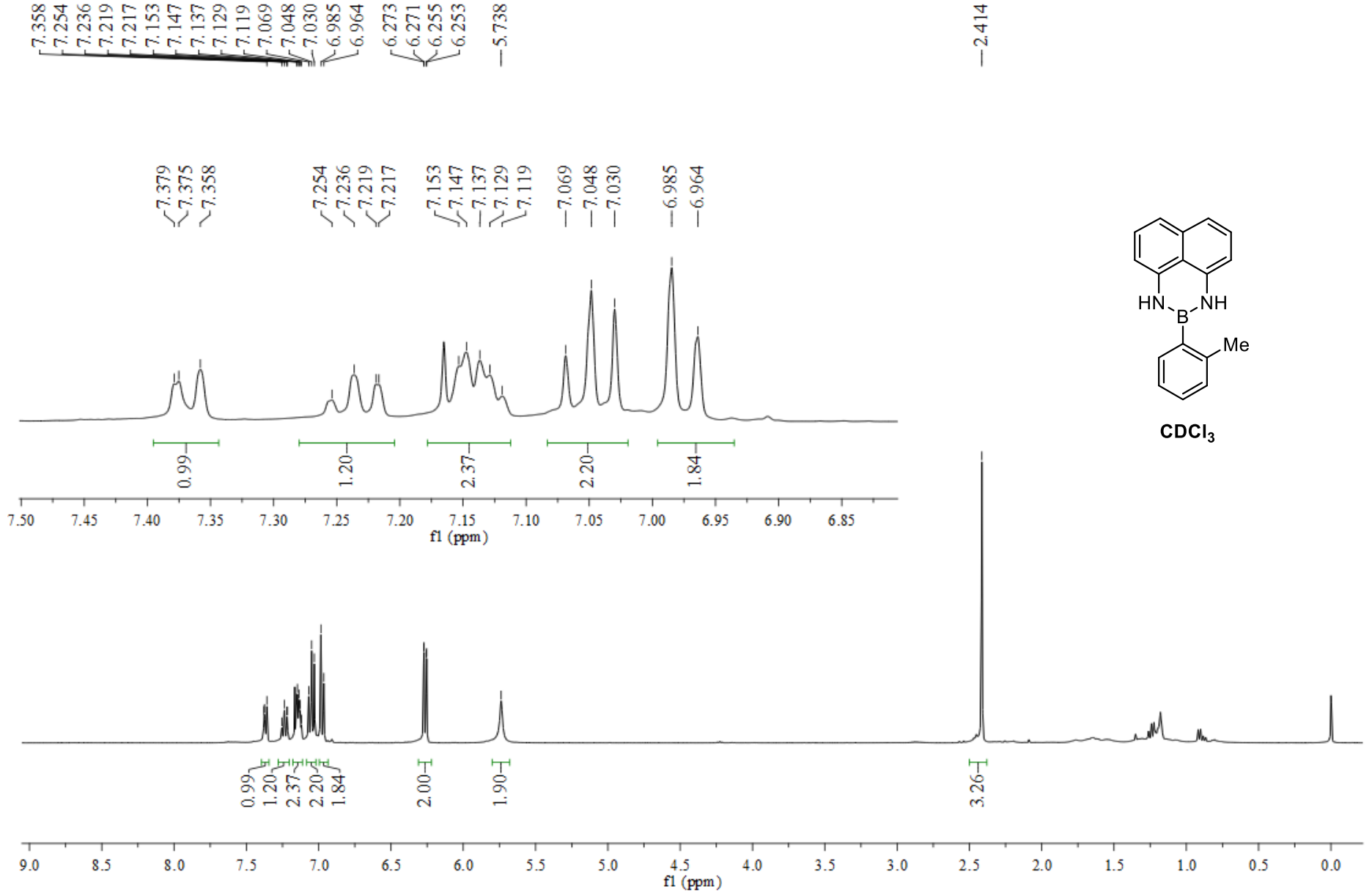
7.572
7.477
7.456
7.260
7.117
7.098
7.054
7.034
6.330
6.312
5.731
3.865
8.052
8.032
7.554
7.491
7.481
7.477
7.471
7.462
7.456
7.260
7.137
7.117
7.098
7.054
7.034
6.330
6.312
HN
B
NH
OMe
O
CDCl3
1.07
2.12
1.10
2.19
1.94
2.00
1.81
3.37
f1 (ppm)
f1 (ppm)


168.44
141.40
136.57
132.84
129.71
129.01
127.68
119.78
117.70
105.92
52.49
141.40
136.57
133.33
132.84
132.20
129.71
129.01
127.68
119.78
117.70
105.92
144
140
136
132
128
124
120
116
112
108
104
f1 (ppm)
HN
B
NH
OMe
O
CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
f1 (ppm)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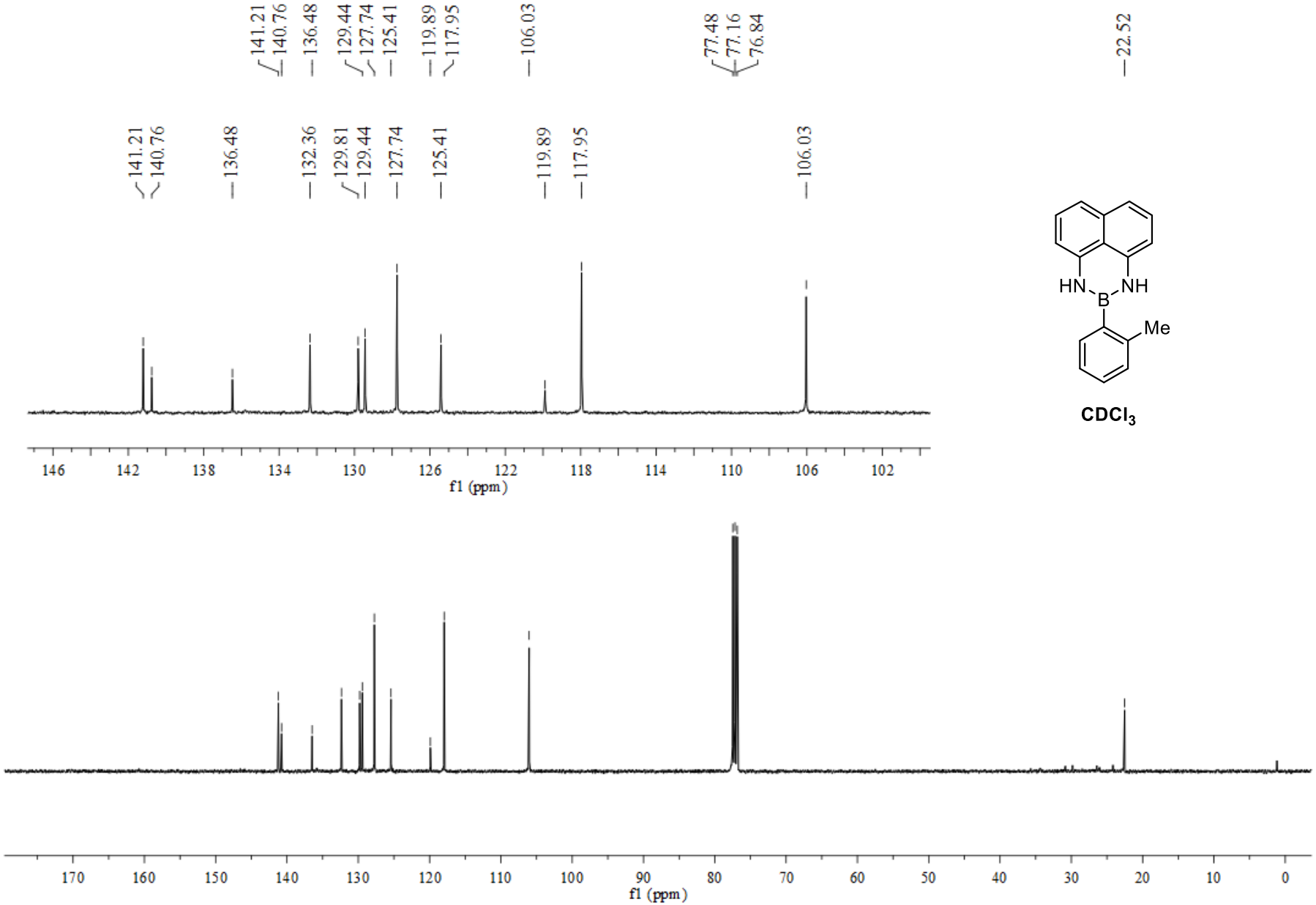
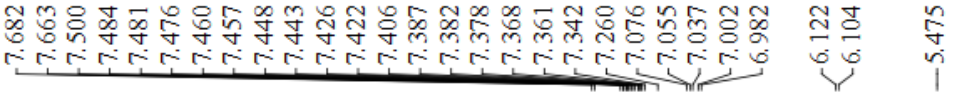
7.254
7.236
7.219
7.217
7.153
7.147
7.137
7.129
7.119
7.069
7.048
7.030
6.985
6.964
6.273
6.271
6.255
6.253
5.738
2.414
HN
B
NH
Me
CDCl3
0.99
1.20
2.37
2.20
1.84
2.00
1.90
3.26
f1 (ppm)


141.21
140.76
136.48
129.44
127.74
125.41
119.89
117.95
106.03
77.48
77.16
76.84
22.52
HN
NH
B
Me
CDCl3
f1 (ppm)
f1 (ppm)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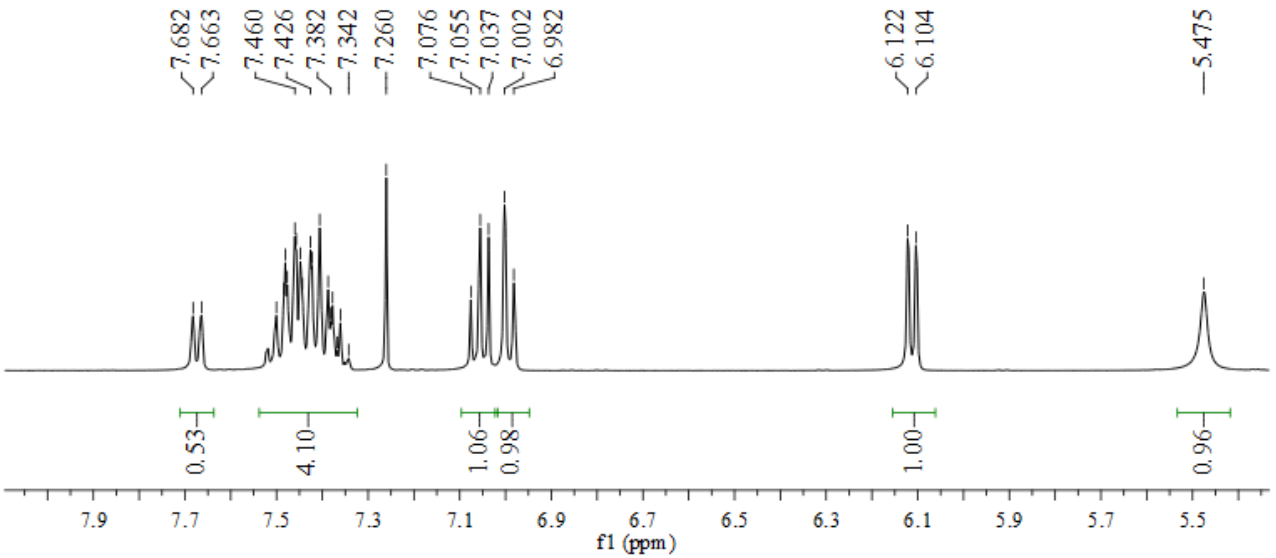
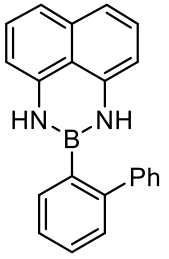
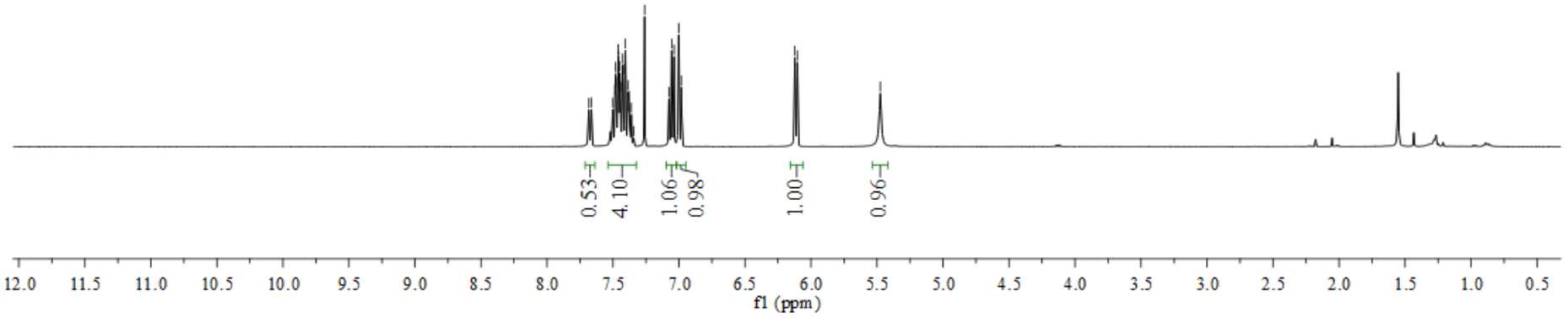
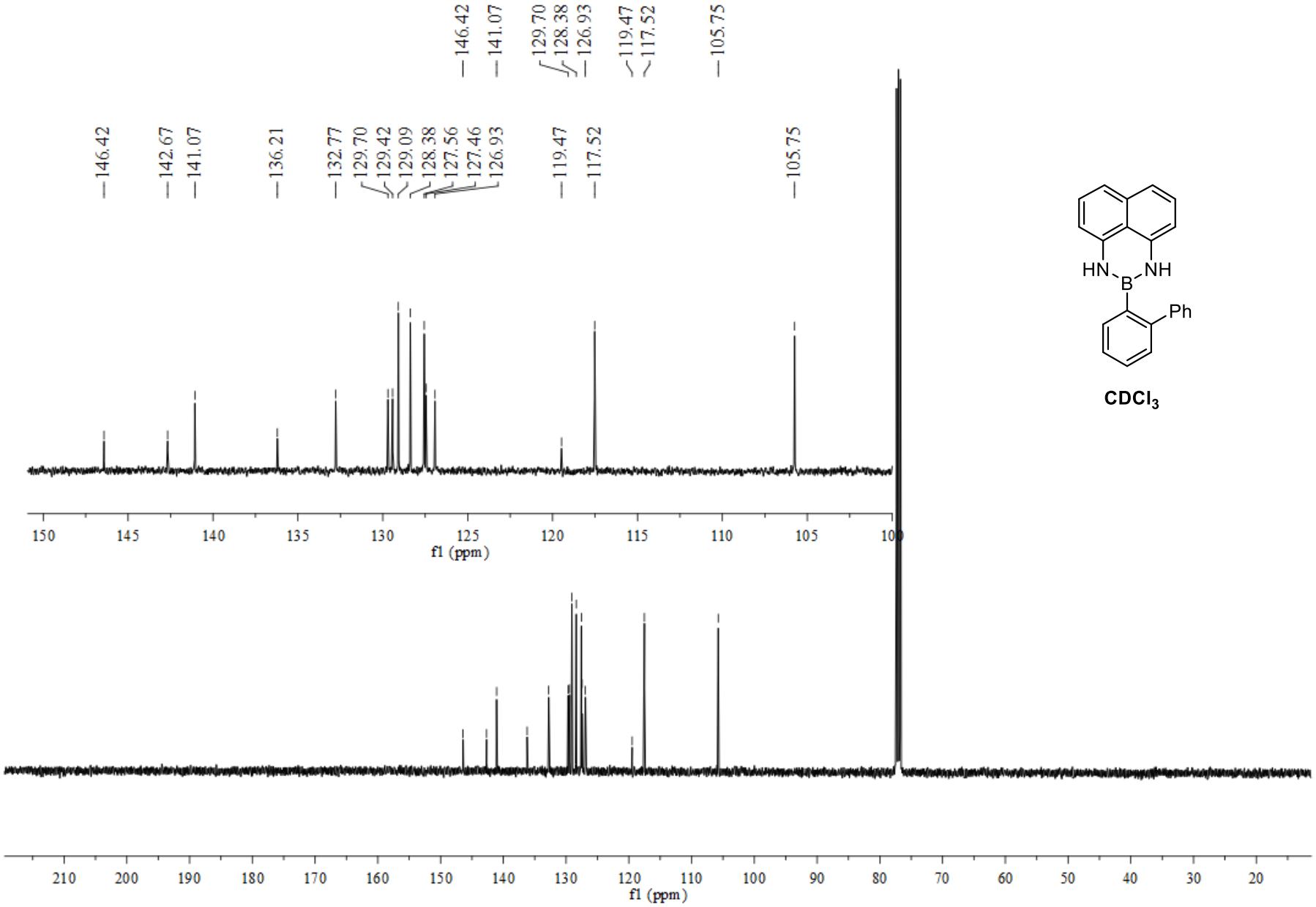
7.663
7.500
7.484
7.481
7.476
7.460
7.457
7.448
7.443
7.426
7.422
7.406
7.387
7.382
7.378
7.368
7.361
7.342
7.260
7.076
7.055
7.037
7.002
6.982
6.122
6.104
5.475

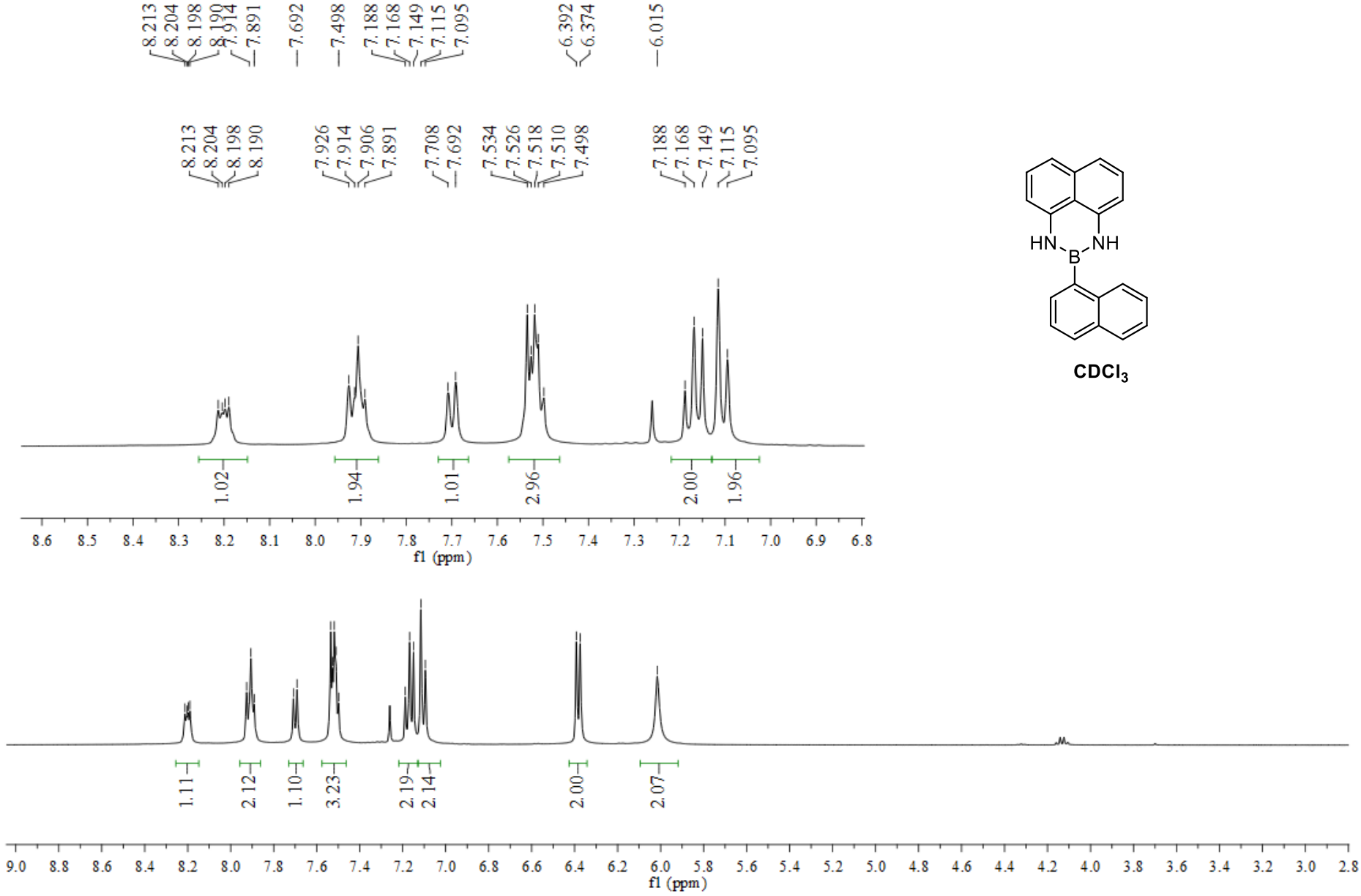

7.682
7.663
7.460
7.426
7.382
7.342
7.260
7.076
7.055
7.037
7.002
6.982
6.122
6.104
5.475
0.53
4.10
1.06
0.98
1.00
0.96
7.9
7.7
7.5
7.3
7.1
6.9
6.7
6.5
6.3
6.1
5.9
5.7
5.5
f1 (ppm)

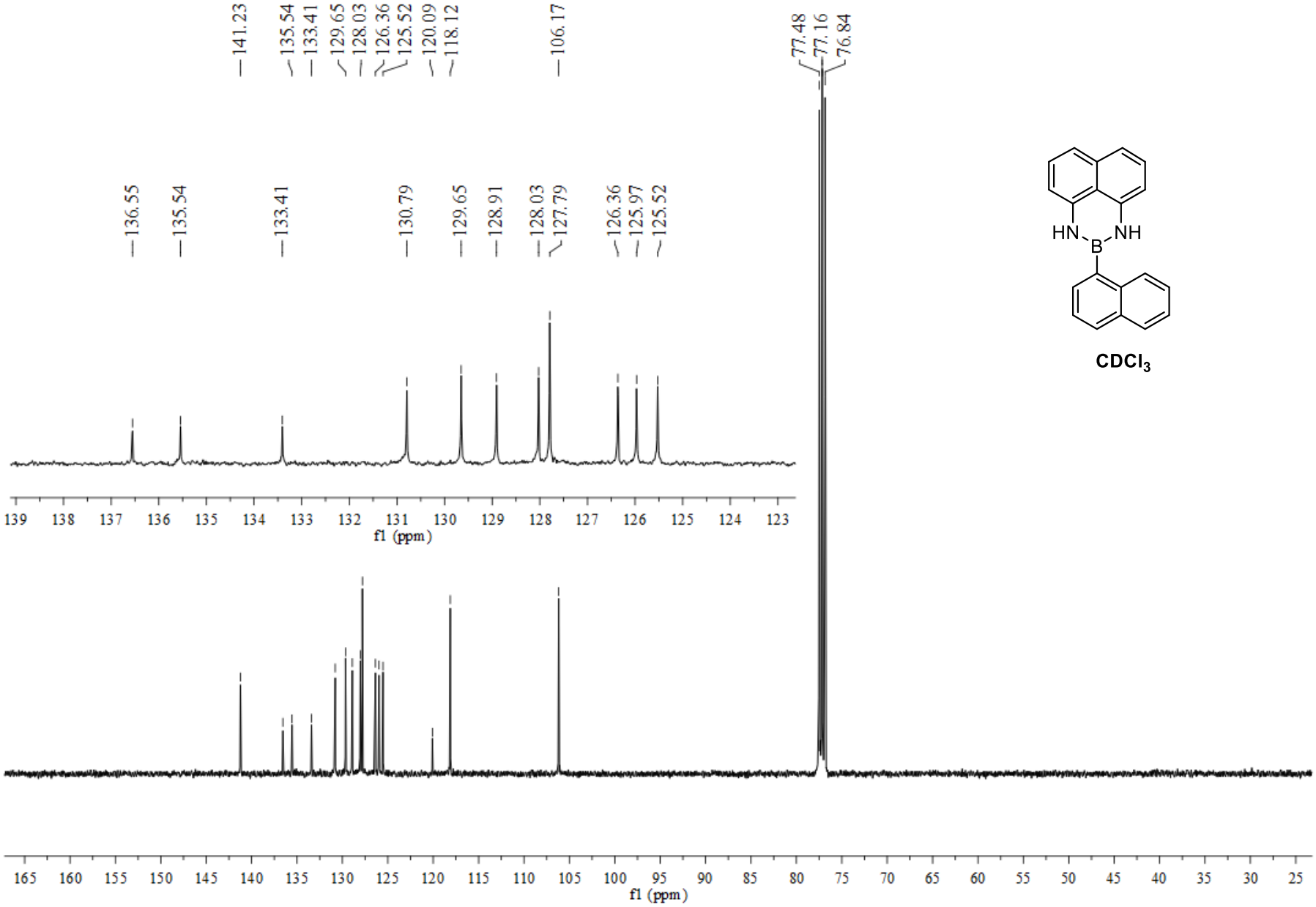

HN
B
NH
Ph

$CDCl_3$


0.53
4.10
1.06
0.98
1.00
0.96
12.0
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)


146.42
141.07
129.70
128.38
126.93
119.47
117.52
105.75
146.42
142.67
141.07
136.21
132.77
129.70
129.42
129.09
128.38
127.56
127.46
126.93
119.47
117.52
105.75
HN
B
NH
Ph
CDCl3
150
145
140
135
130
125
120
115
110
105
100
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


8.213
8.204
8.198
8.190
7.914
7.891
7.692
7.498
7.188
7.168
7.149
7.115
7.095
6.392
6.374
6.015
7.926
7.914
7.906
7.891
7.708
7.692
7.534
7.526
7.518
7.510
7.498
1.02
1.94
1.01
2.96
2.00
1.96
f1 (ppm)
1.11
2.12
1.10
3.23
2.19
2.14
2.00
2.07
f1 (ppm)
HN
B
NH
CDCl3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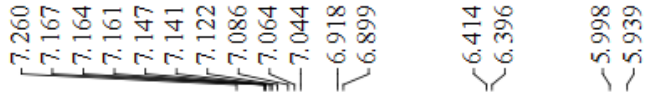
133.41
129.65
128.03
126.36
125.52
120.09
118.12
106.17
77.48
77.16
76.84
136.55
135.54
133.41
130.79
129.65
128.91
128.03
127.79
126.36
125.97
125.52
HN
B
NH
CDCl3
f1 (ppm)
f1 (ppm)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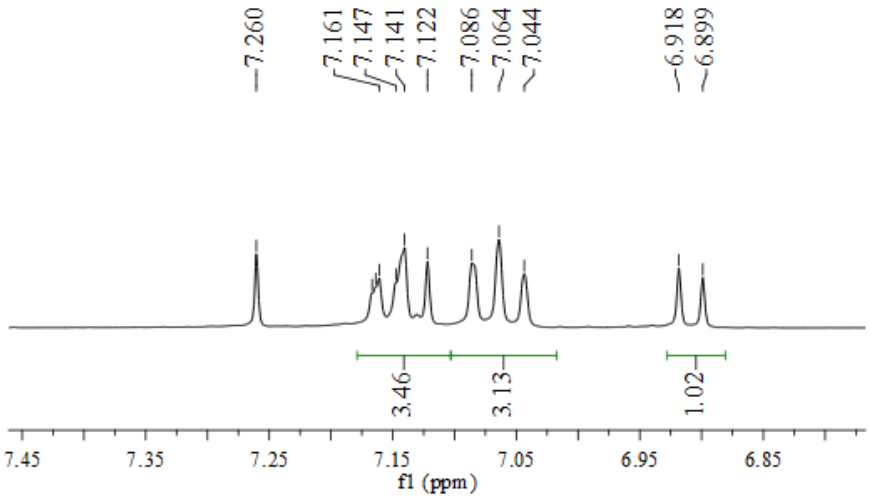
7.167
7.164
7.161
7.147
7.141
7.122
7.086
7.064
7.044
6.918
6.899
6.414
6.396
5.998
5.939


7.260
7.161
7.147
7.141
7.122
7.086
7.064
7.044
6.918
6.899
3.46
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1.02
7.45
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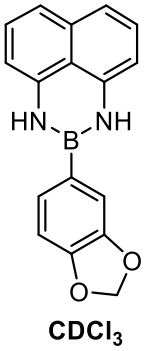
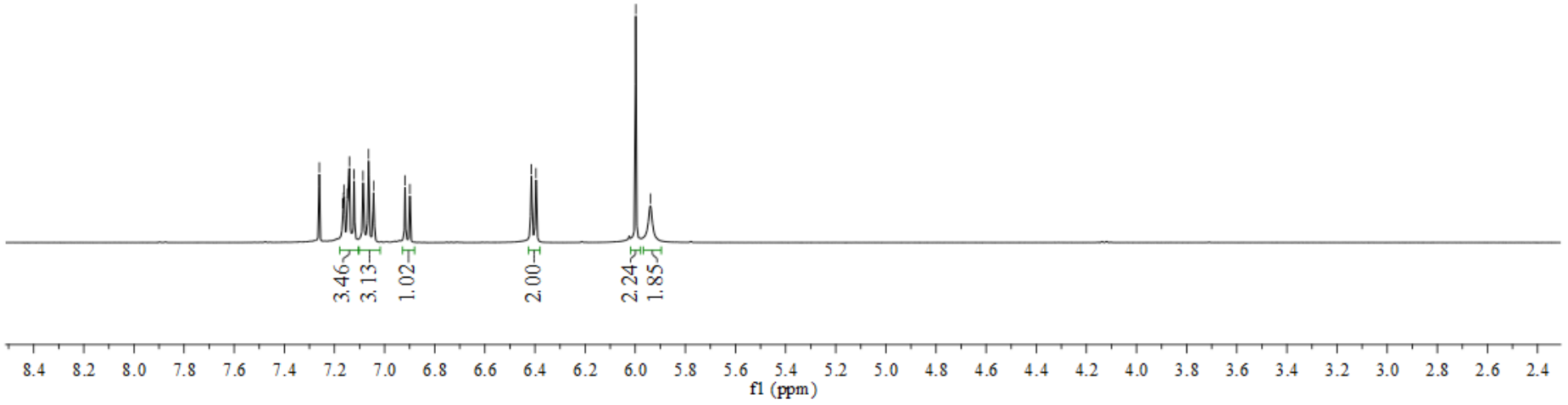
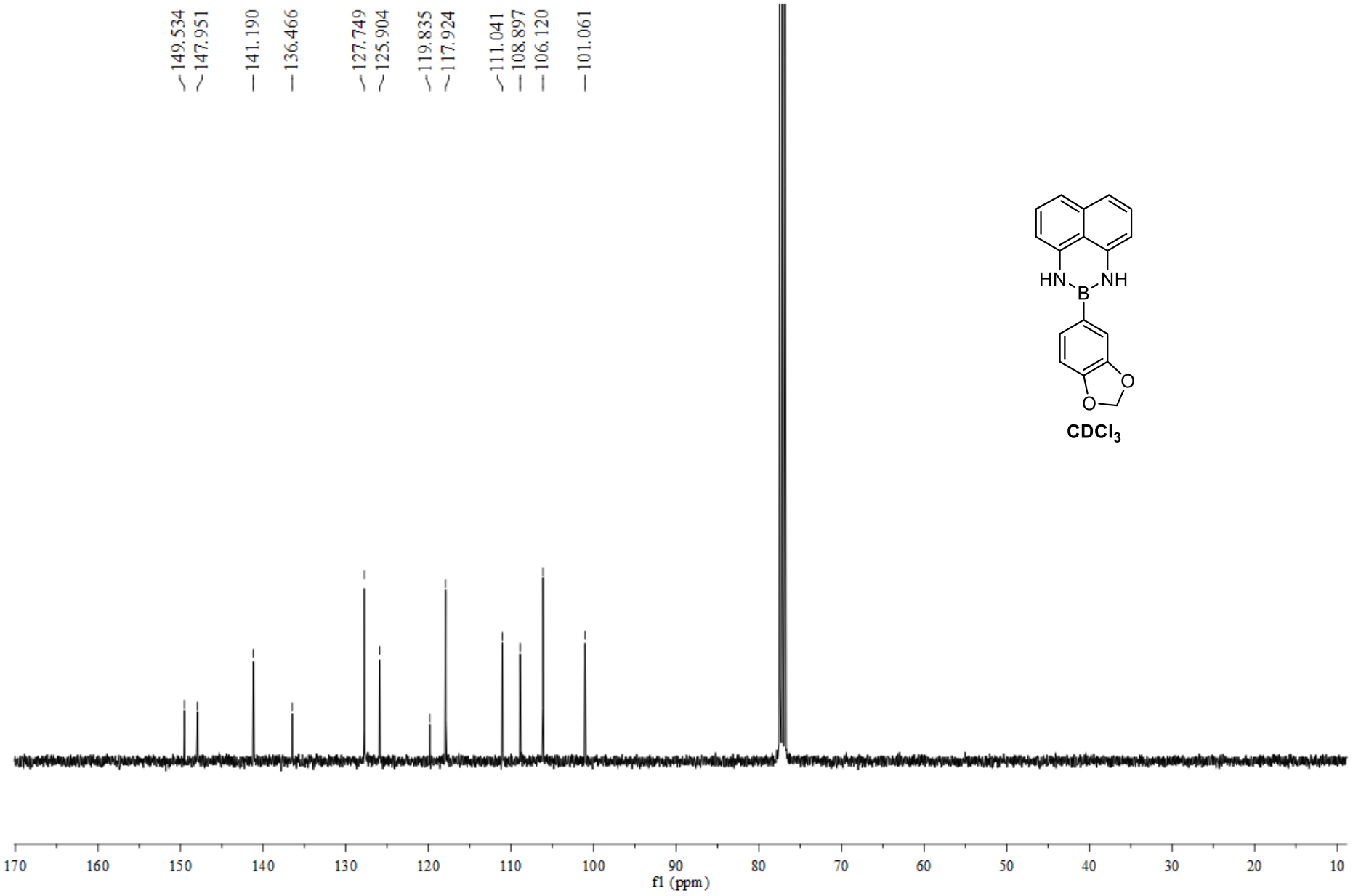
7.15
7.05
6.95
6.85
f1 (ppm)


HN
B
NH
O
O
CDCl3


3.46
3.13
1.02
2.00
2.24
1.85
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
f1 (ppm)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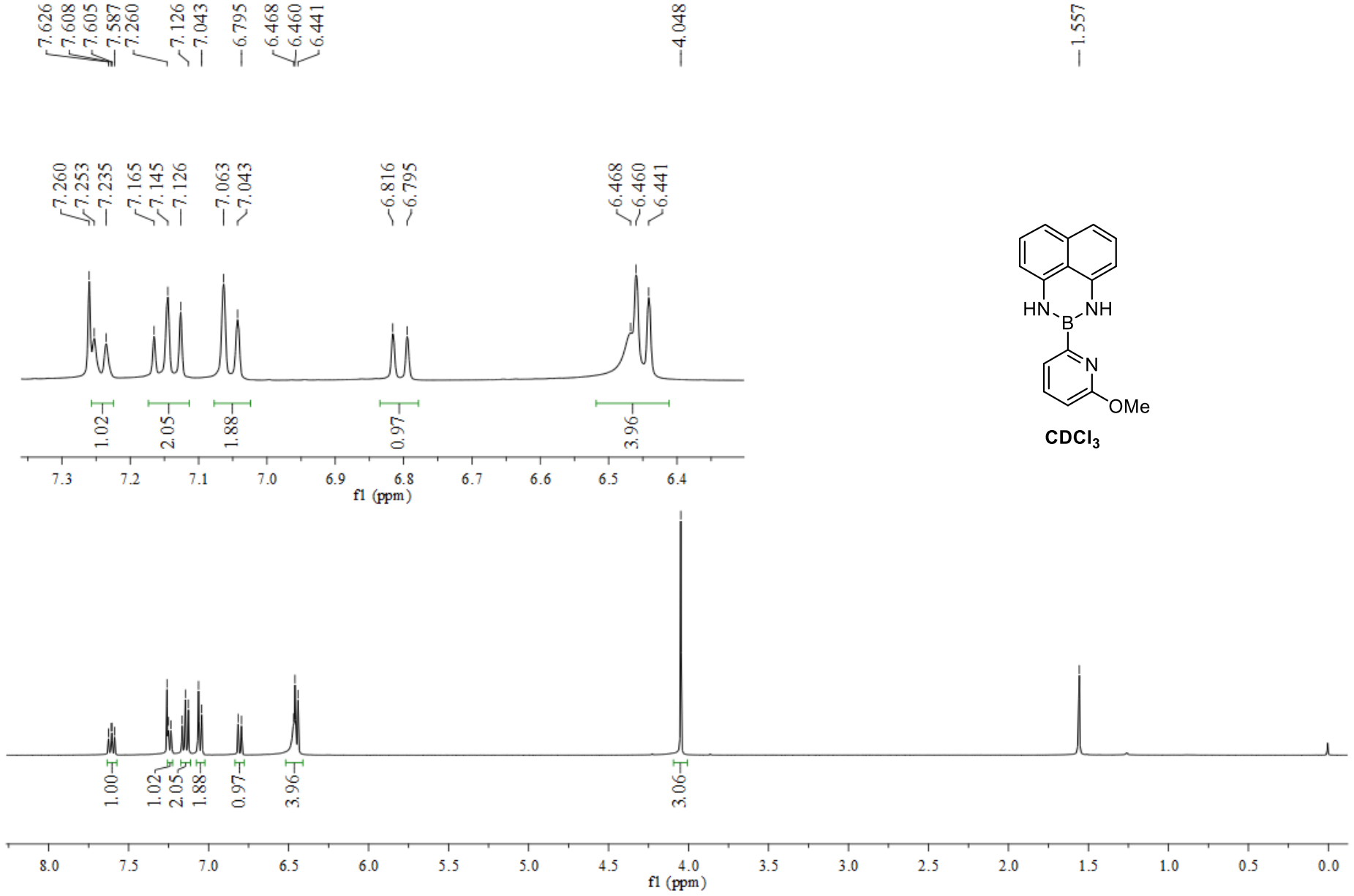
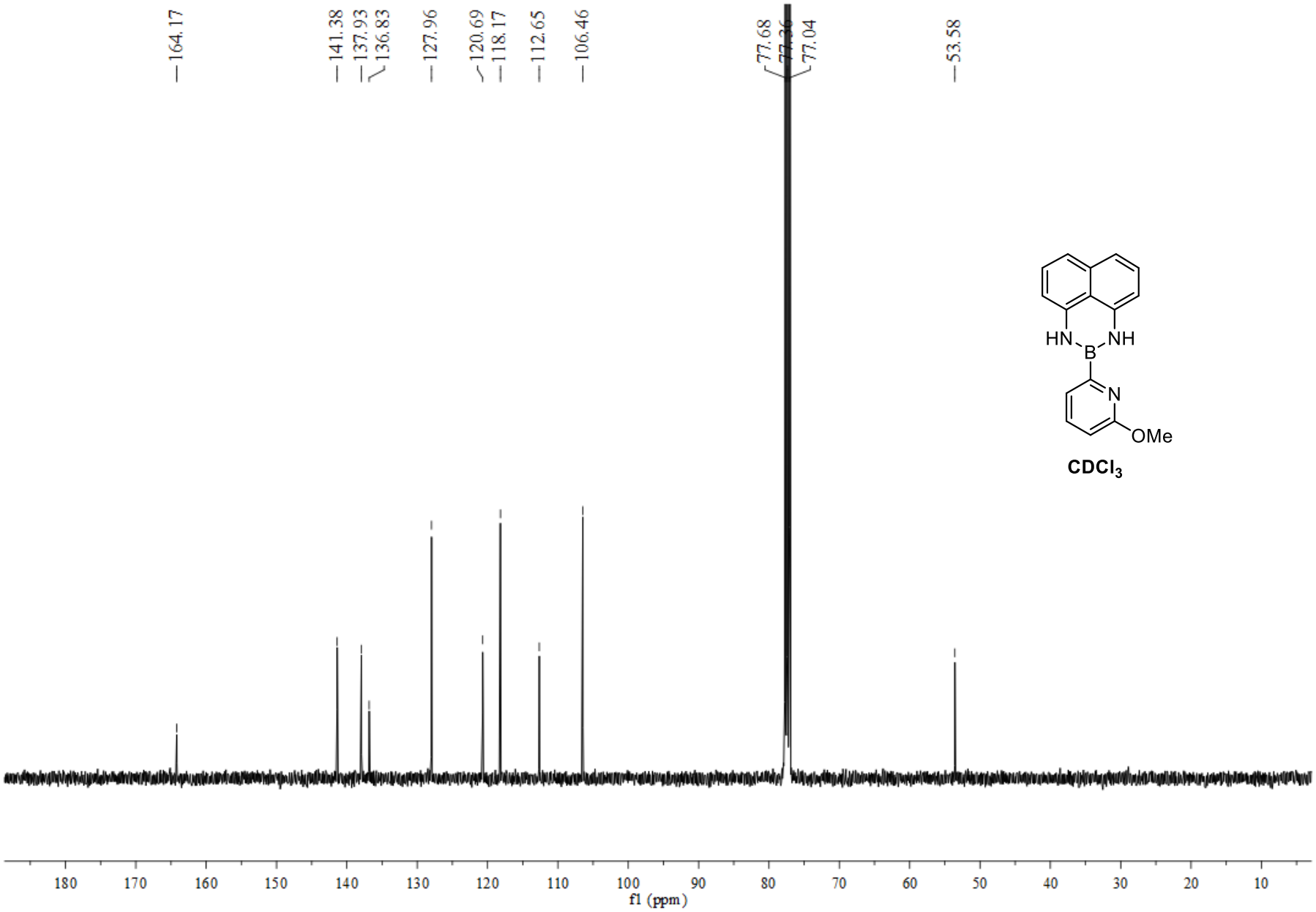
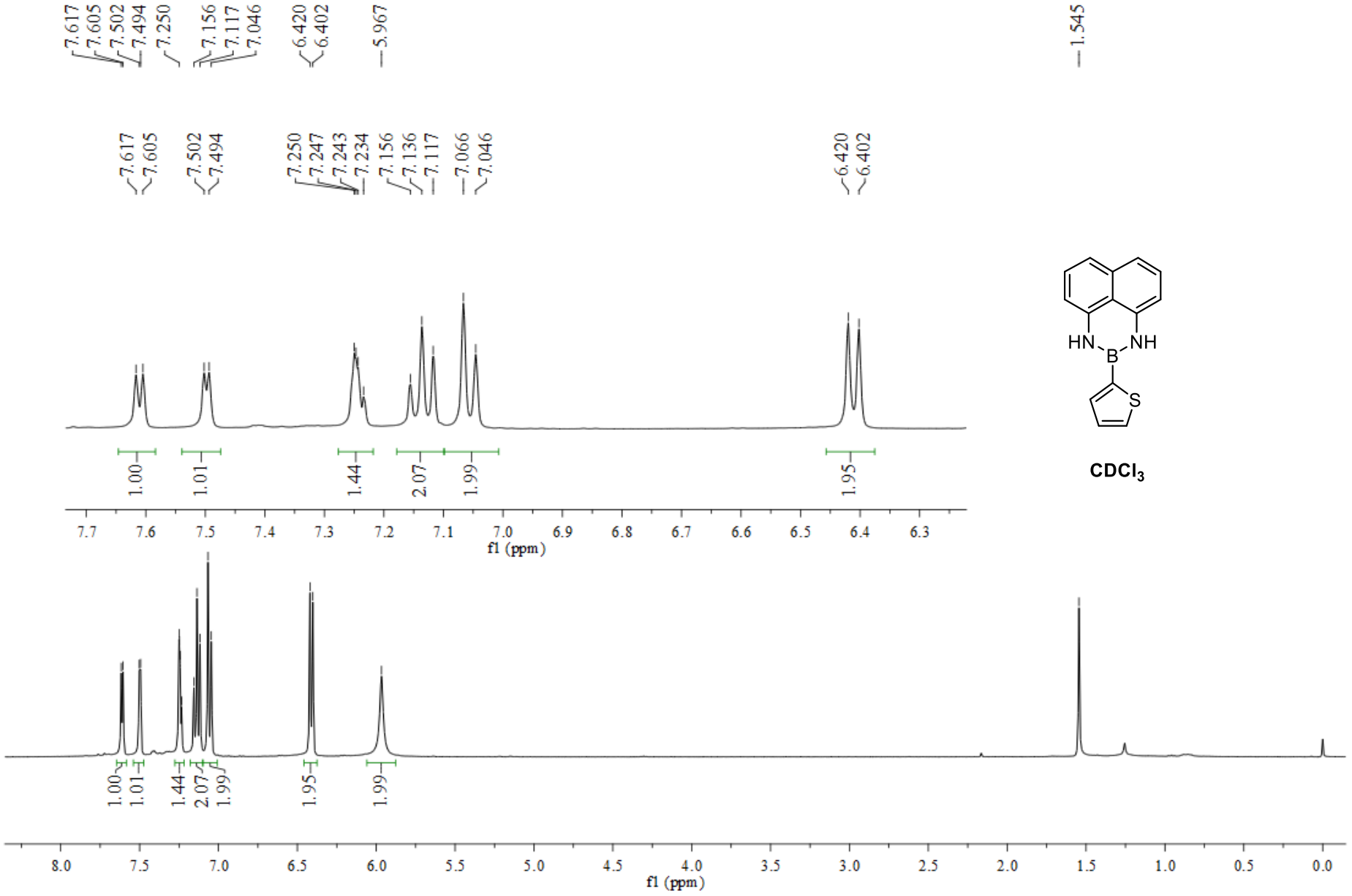
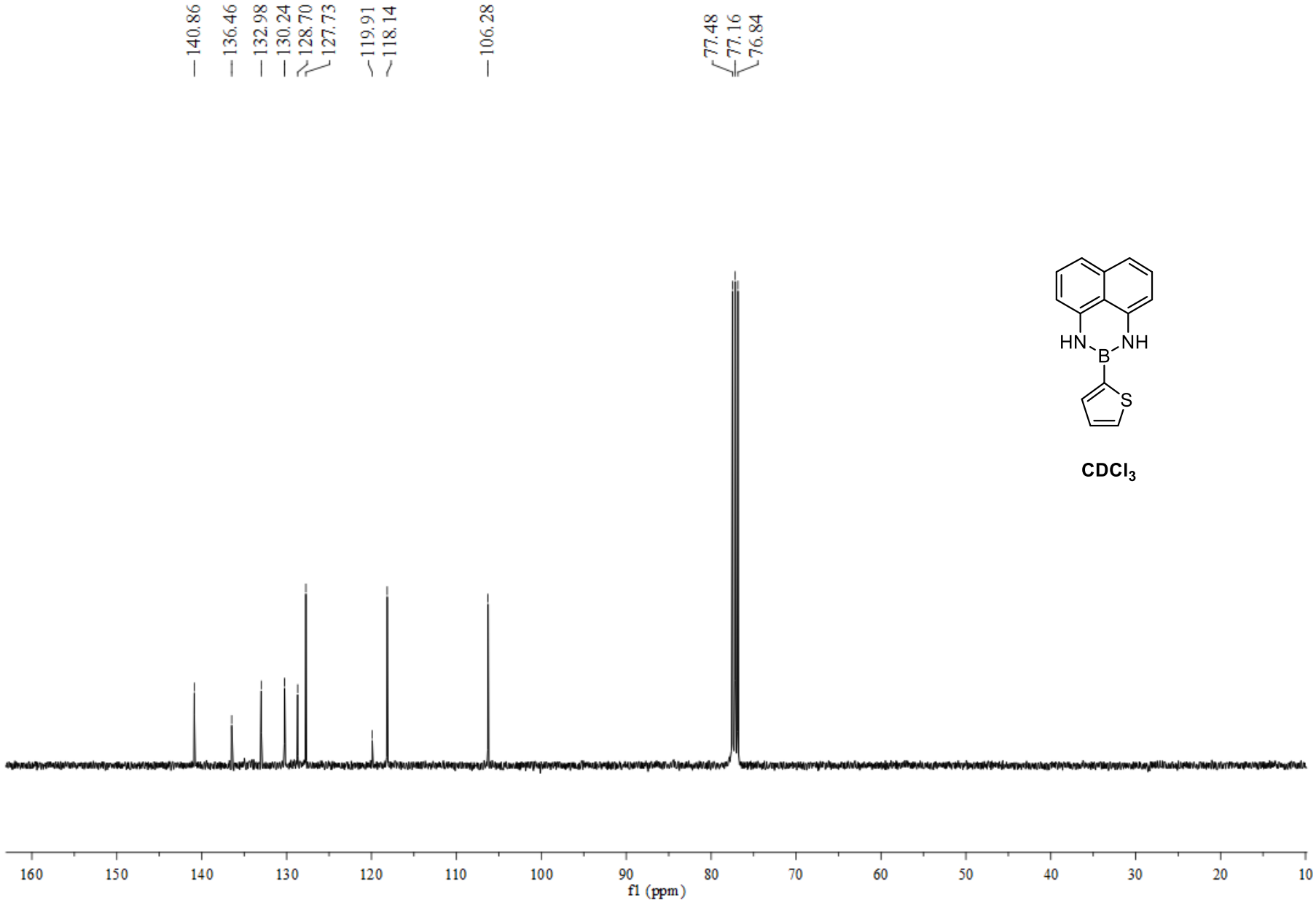
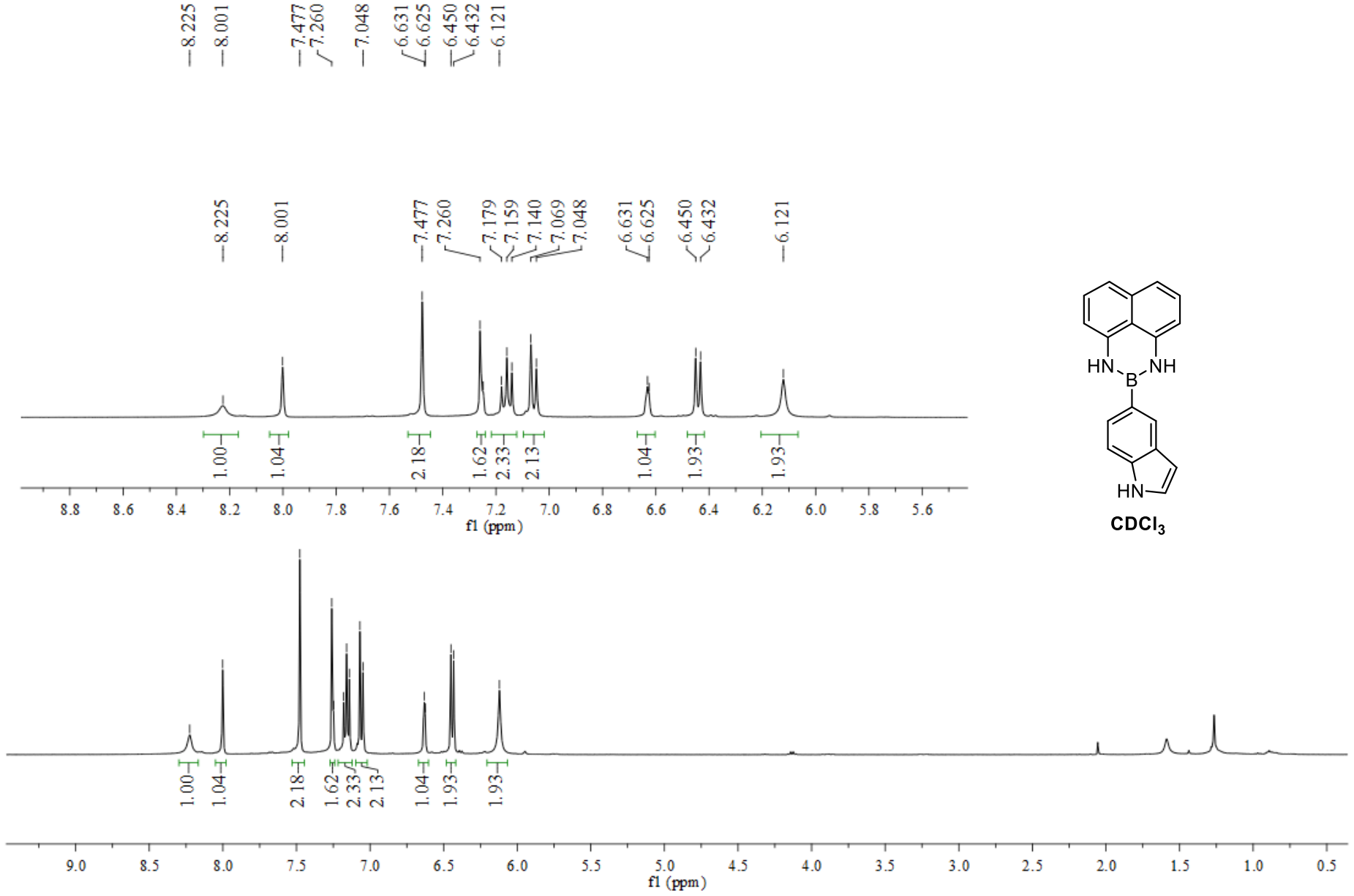
147.951
141.190
136.466
127.749
125.904
119.835
117.924
111.041
108.897
106.120
101.061
HN
B
NH
O
O
CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

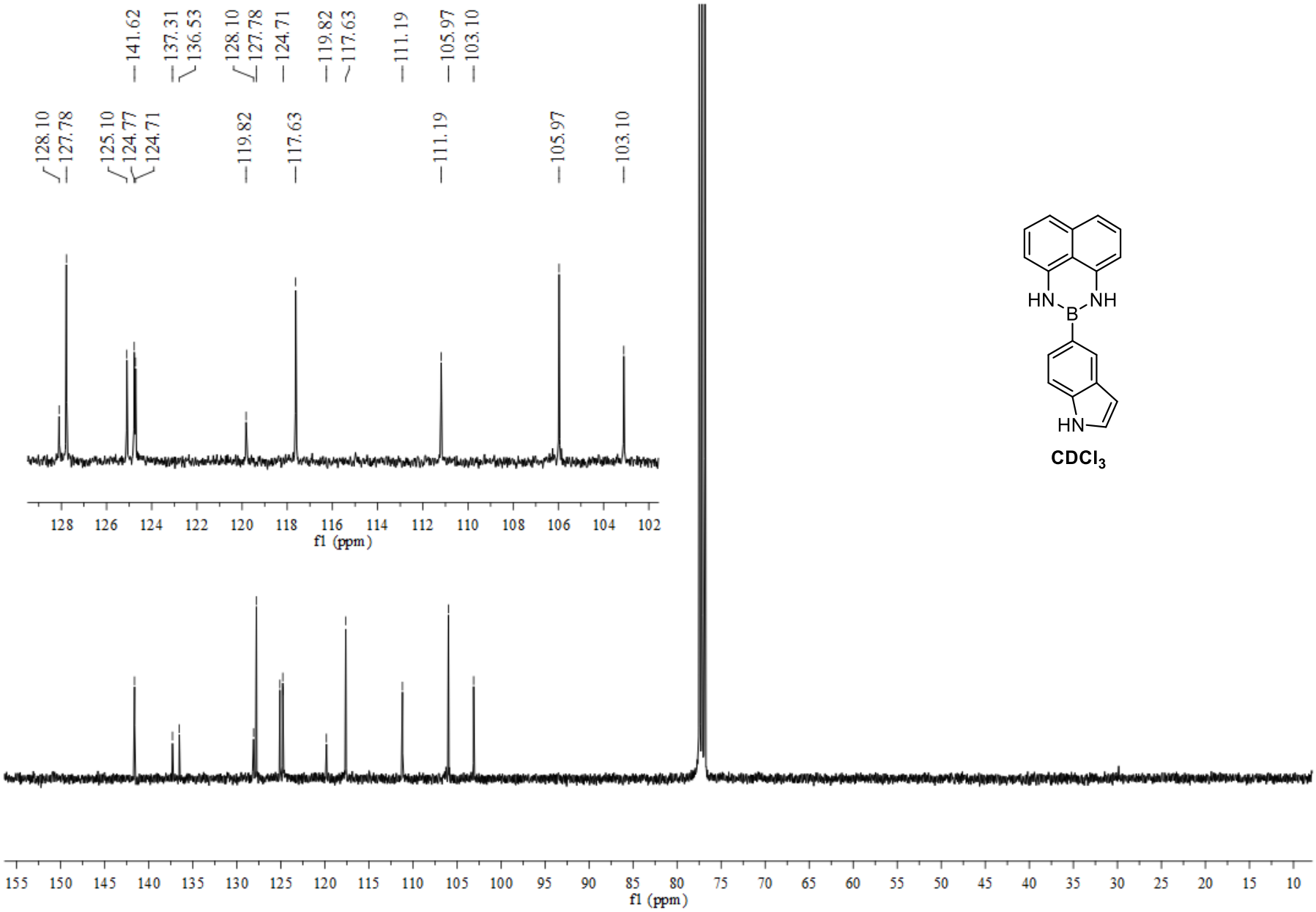

7.626
7.608
7.605
7.587
7.260
7.126
7.043
6.795
6.468
6.460
6.441
4.048
1.557
7.260
7.253
7.235
7.165
7.145
7.126
7.063
7.043
6.816
6.795
6.468
6.460
6.441
1.02
2.05
1.88
0.97
3.96
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
f1 (ppm)
HN
B
NH
N
OMe
CDCl3
1.00
1.02
2.05
1.88
0.97
3.96
3.06
8.0
7.5
7.0
6.5
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)


164.17
141.38
137.93
136.83
127.96
120.69
118.17
112.65
106.46
77.68
77.36
77.04
53.58
HN
B
NH
N
OMe
CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.617
7.605
7.502
7.494
7.250
7.156
7.117
7.046
6.420
6.402
5.967
1.545
HN
B
NH
S
CDCl3
1.00
1.01
1.44
2.07
1.99
1.95
f1 (ppm)


140.86
136.46
132.98
130.24
128.70
127.73
119.91
118.14
106.28
77.48
77.16
76.84
HN
B
NH
S
CDCl3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.225
8.001
7.477
7.260
7.048
6.631
6.625
6.450
6.432
6.121
1.00
1.04
2.18
1.62
2.33
2.13
1.04
1.93
1.93
f1 (ppm)
HN
B
NH
HN
CDCl3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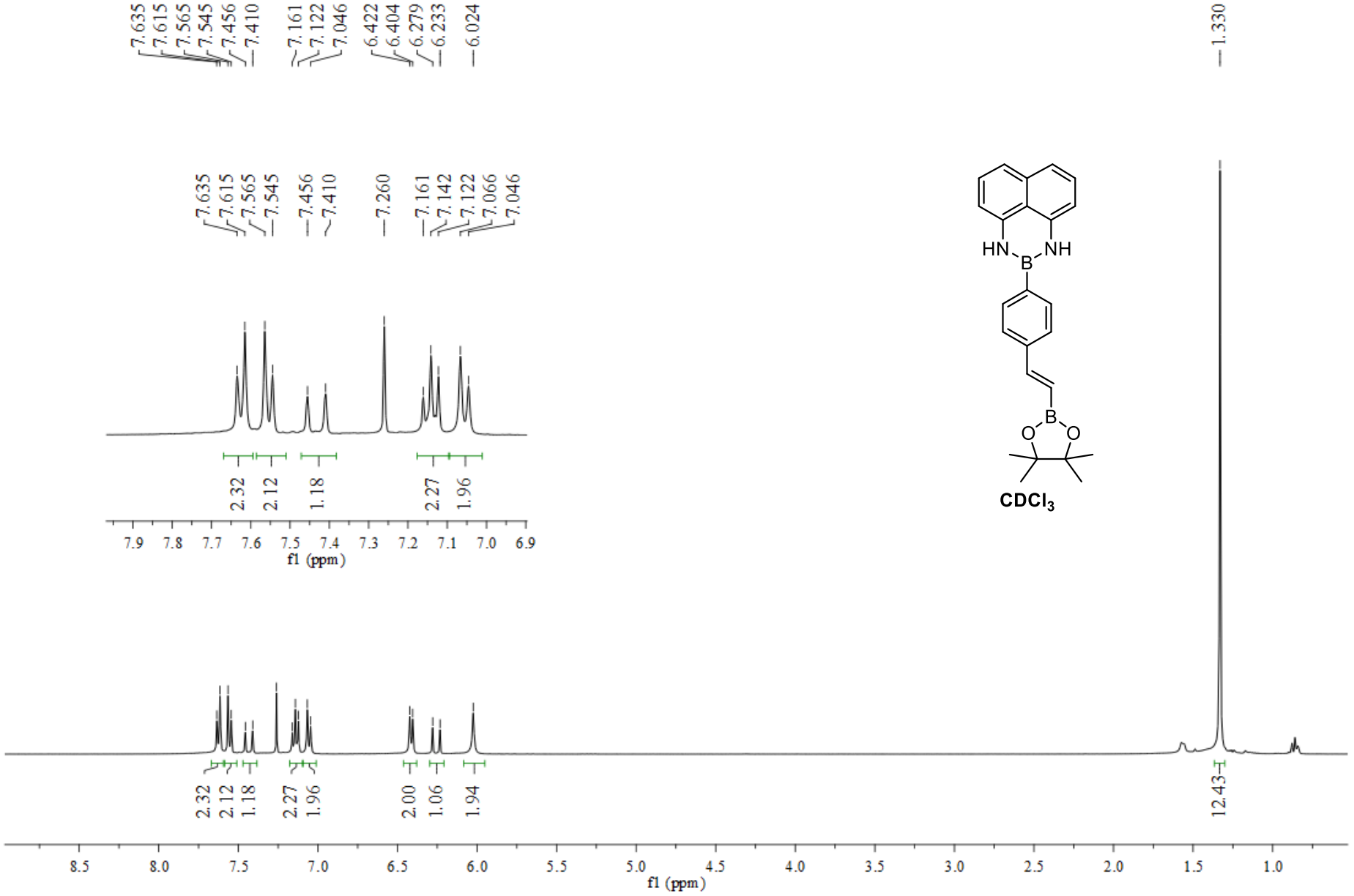
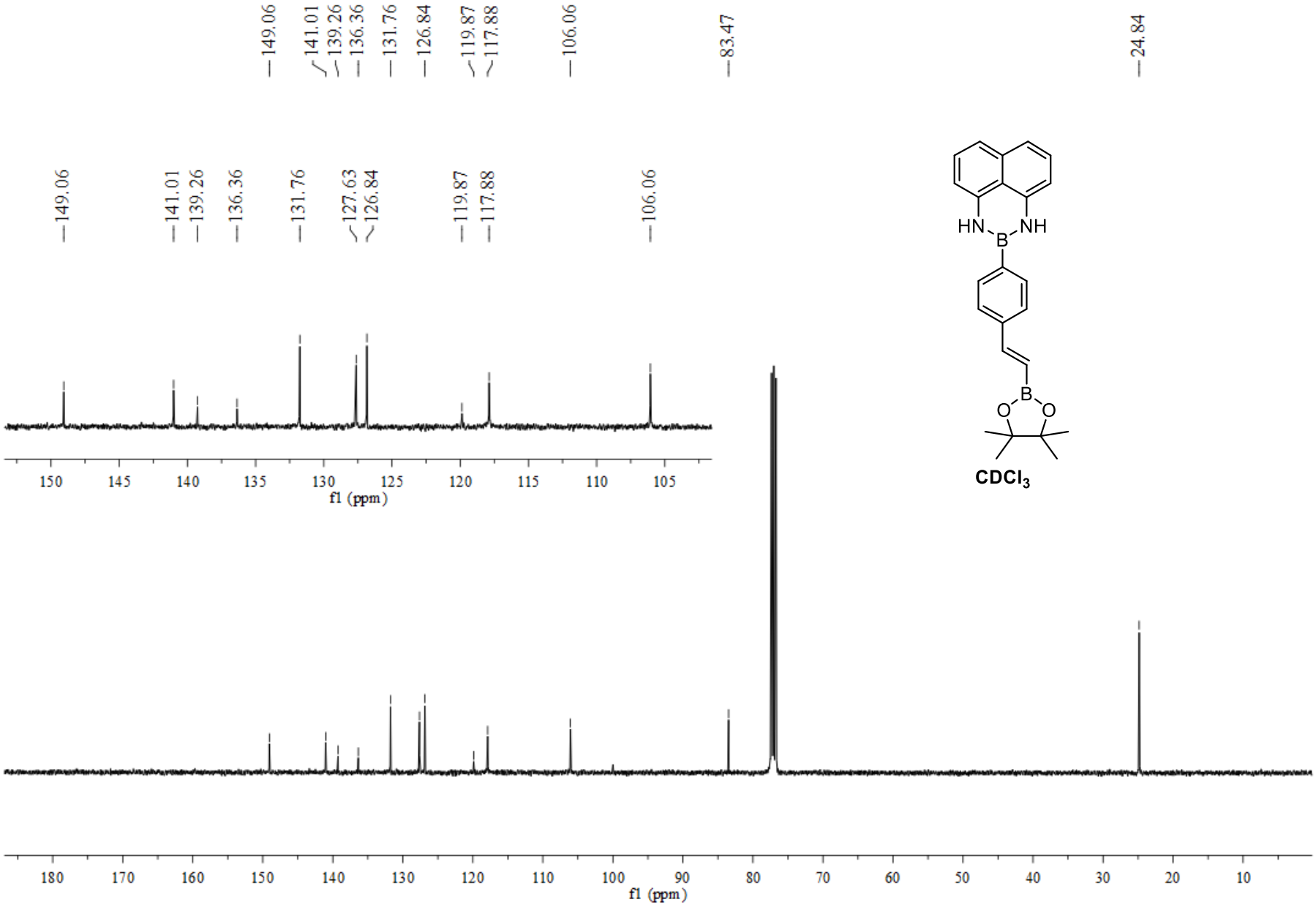
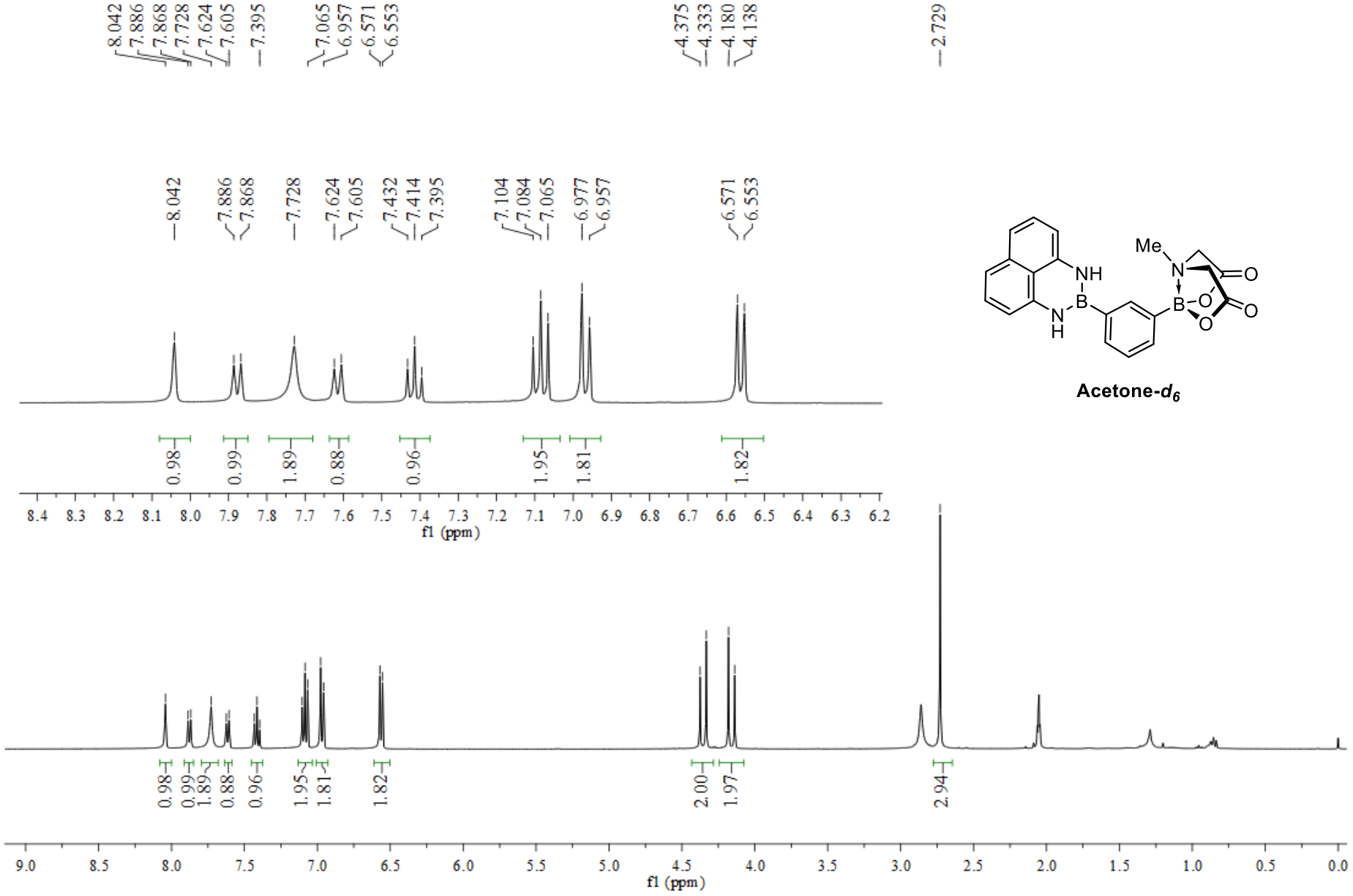
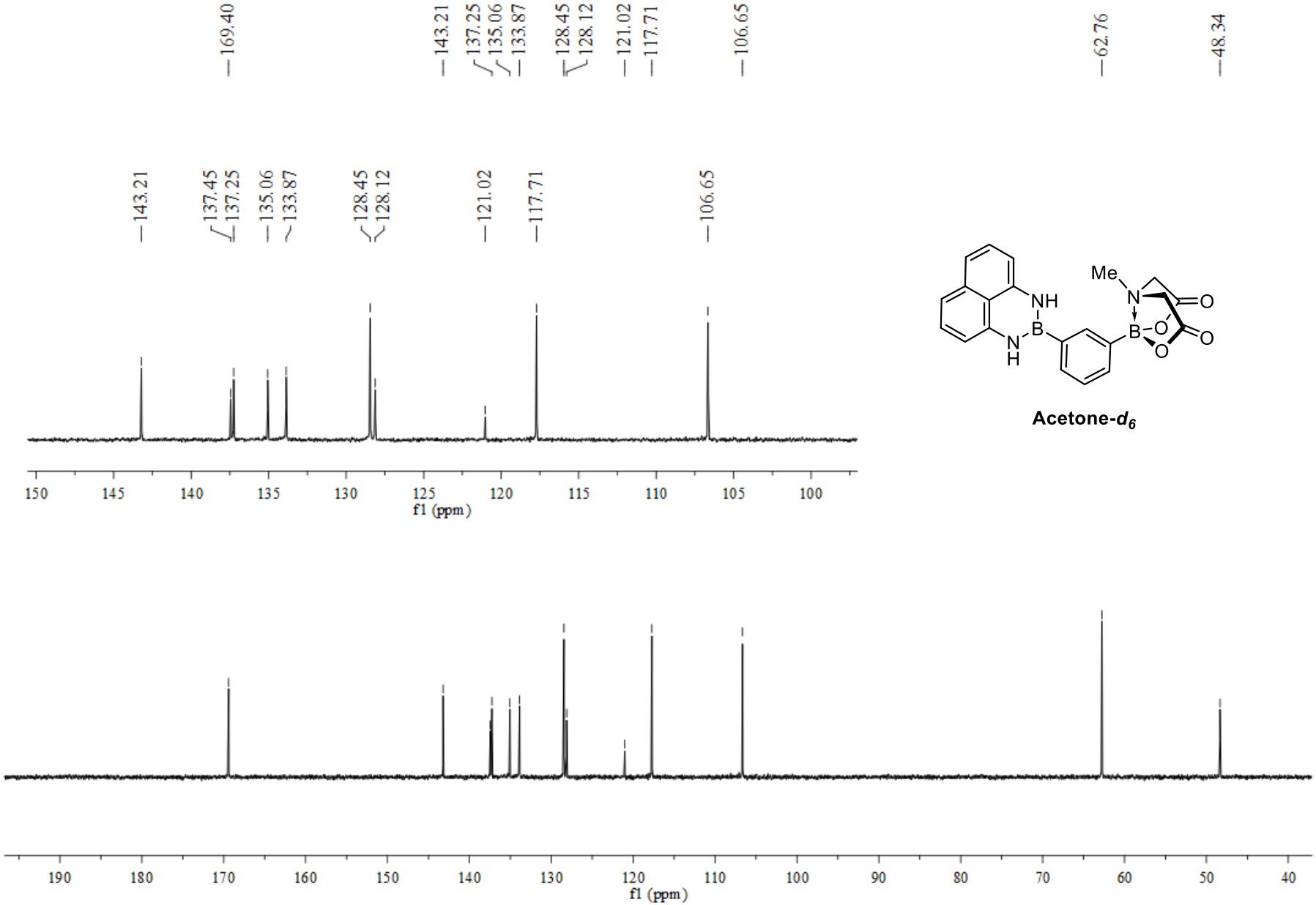
137.31
136.53
128.10
127.78
124.71
119.82
117.63
111.19
105.97
103.10
128.10
127.78
125.10
124.77
124.71
119.82
117.63
111.19
105.97
103.10
HN
B
NH
HN
CDCl3
f1 (ppm)
f1 (ppm)


7.635
7.615
7.565
7.545
7.456
7.410
7.161
7.122
7.046
6.422
6.404
6.279
6.233
6.024
1.330
HN
B
NH
O
O
CDCl3
2.32
2.12
1.18
2.27
1.96
2.00
1.06
1.94
12.43
f1 (ppm)


149.06
141.01
139.26
136.36
131.76
126.84
119.87
117.88
106.06
83.47
24.84
HN
B
NH
O
O
CDCl3
f1 (ppm)


8.042
7.886
7.868
7.728
7.624
7.605
7.395
7.065
6.957
6.571
6.553
4.375
4.333
4.180
4.138
2.729
0.98
0.99
1.89
0.88
0.96
1.95
1.81
1.82
2.00
1.97
2.94
f1 (ppm)
Me
N
NH
B
O
Acetone-d6


169.40
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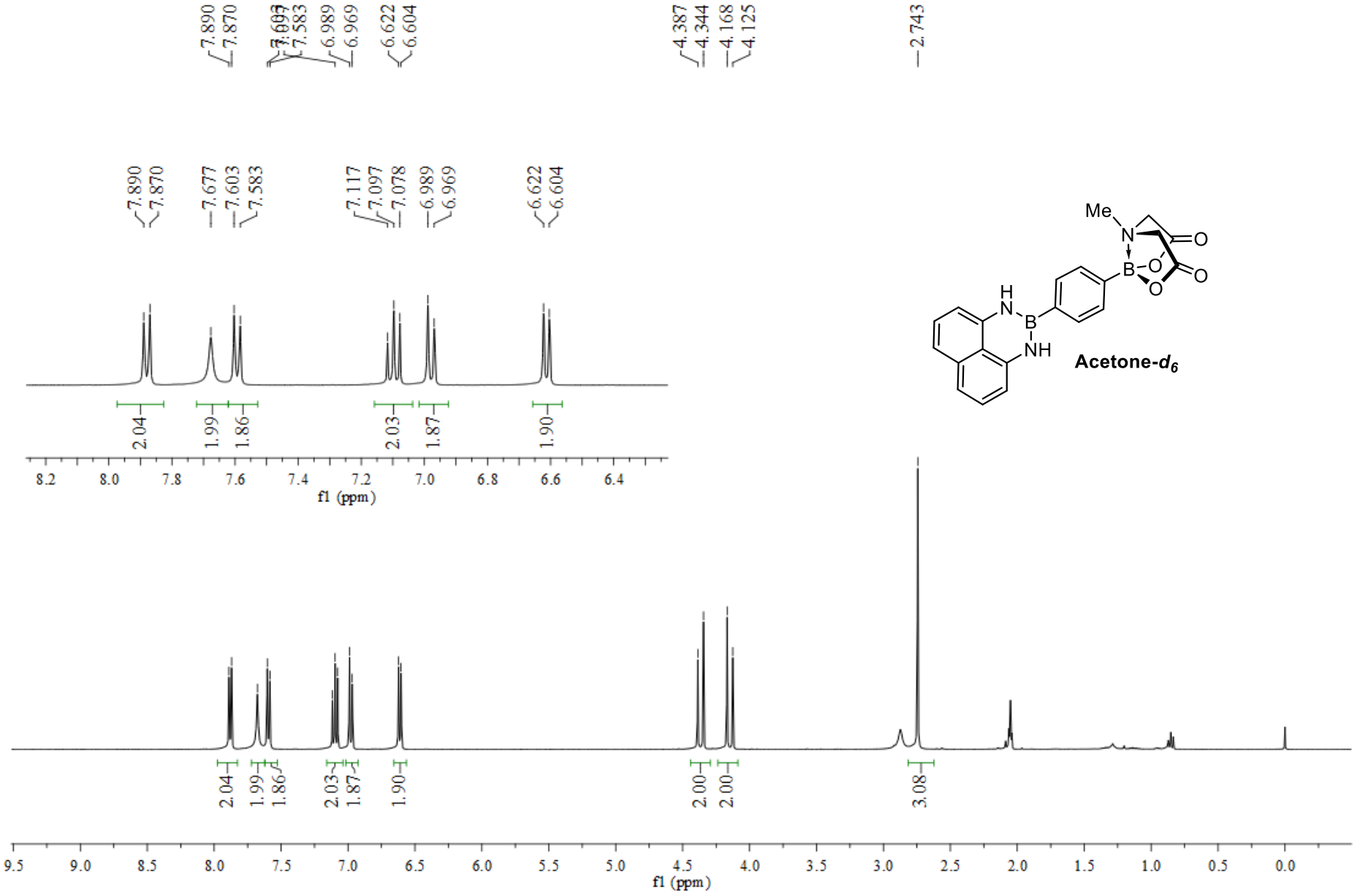
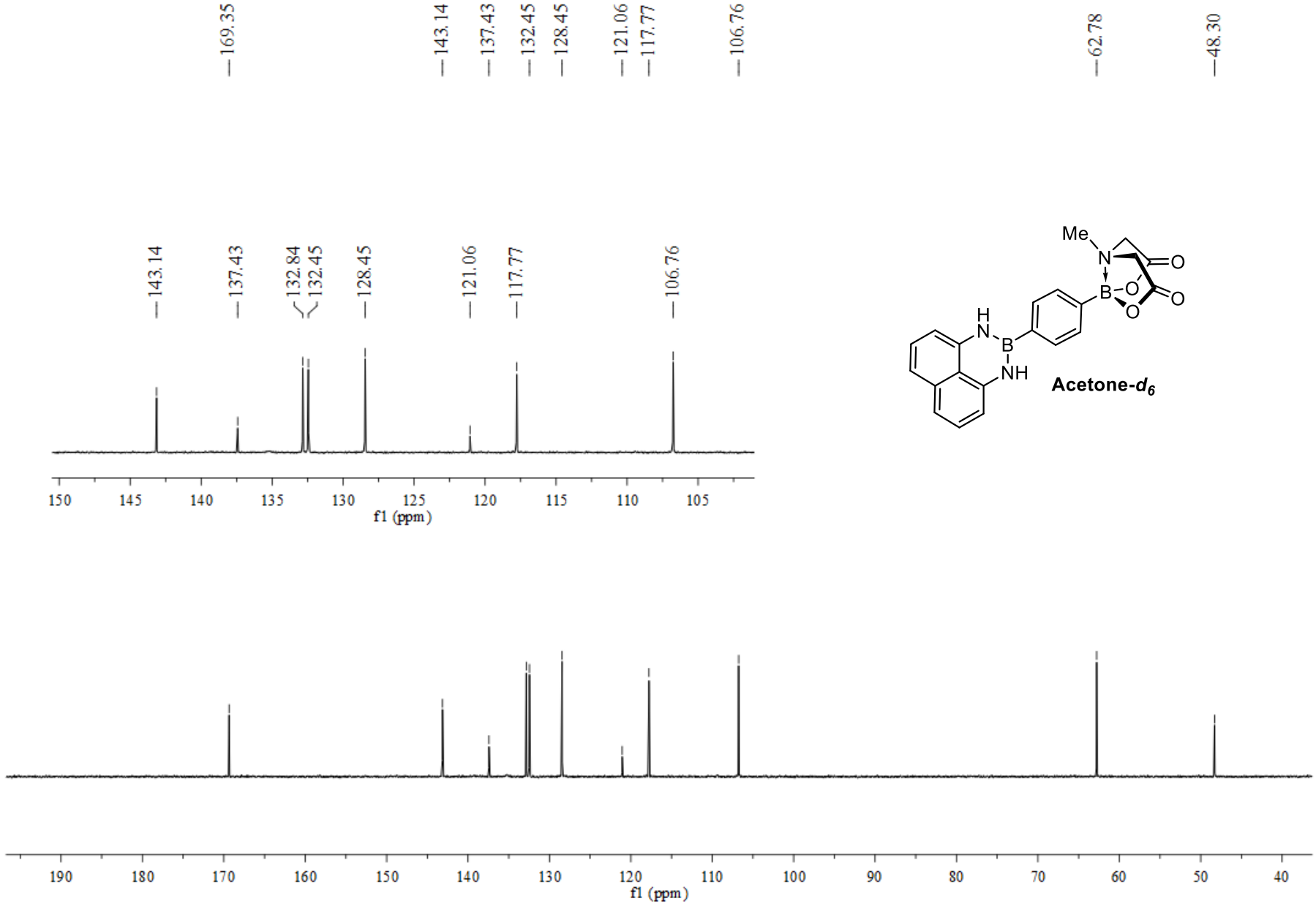
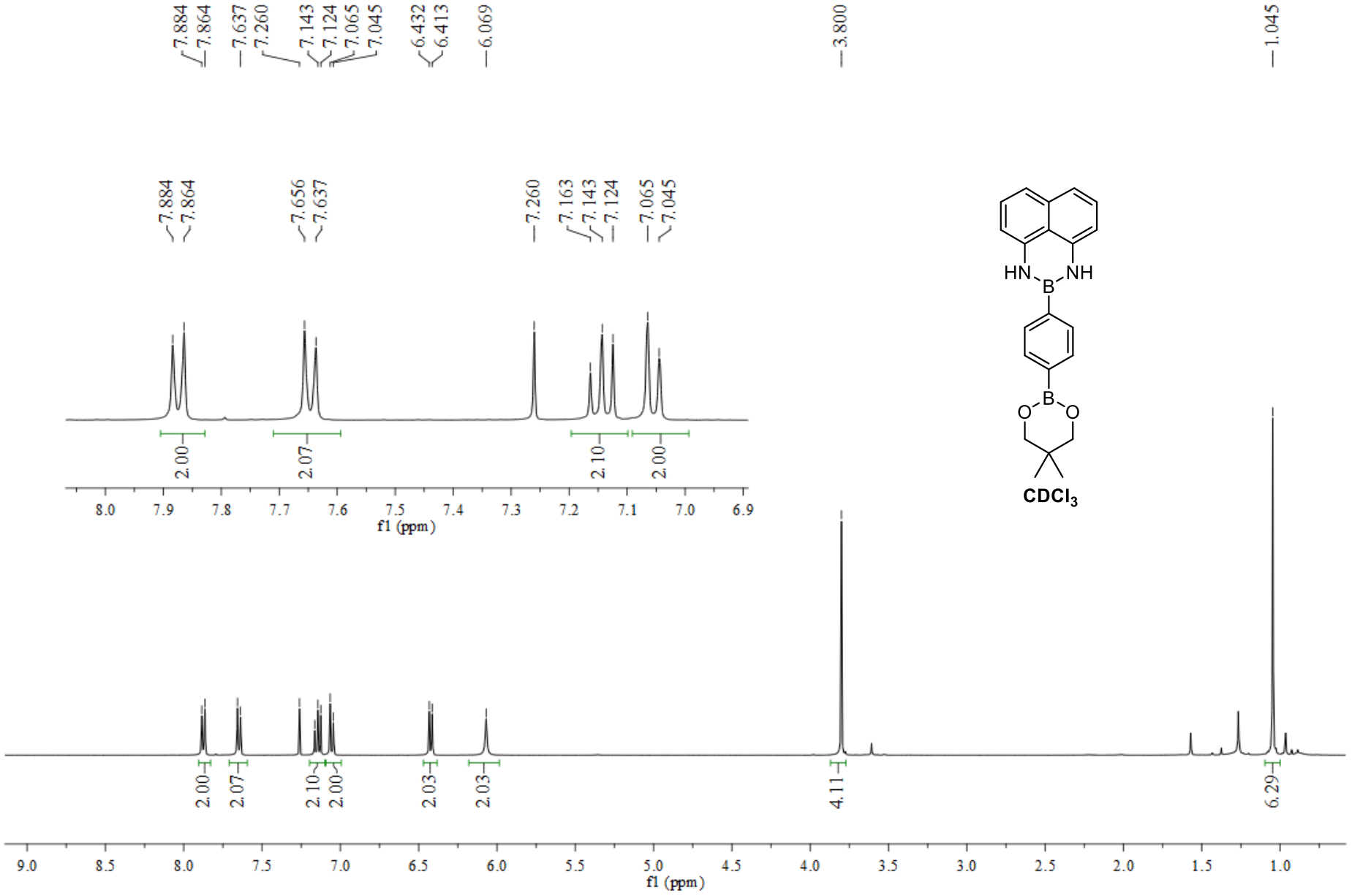
137.25
135.06
133.87
128.45
128.12
121.02
117.71
106.65
62.76
48.34
143.21
137.45
137.25
135.06
133.87
128.45
128.12
121.02
117.71
106.65
150
145
140
135
130
125
120
115
110
105
100
f1 (ppm)
Me
N
NH
B
N
H
B
O
O
O
O
Acetone-d6
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
f1 (ppm)


7.890
7.870
7.677
7.603
7.583
7.117
7.097
7.078
6.989
6.969
6.622
6.604
4.387
4.344
4.168
4.125
2.743
2.04
1.99
1.86
2.03
1.87
1.90
2.00
2.00
3.08
f1 (ppm)
Me
N
O
B
O
O
O
H
N
B
NH
Acetone-d6


169.35
143.14
137.43
132.45
128.45
121.06
117.77
106.76
62.78
48.30
143.14
137.43
132.84
132.45
128.45
121.06
117.77
106.76
150
145
140
135
130
125
120
115
110
105
f1 (ppm)
Me
N
O
O
B
O
O
H
N
B
NH
Acetone-d6
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
f1 (ppm)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7.143
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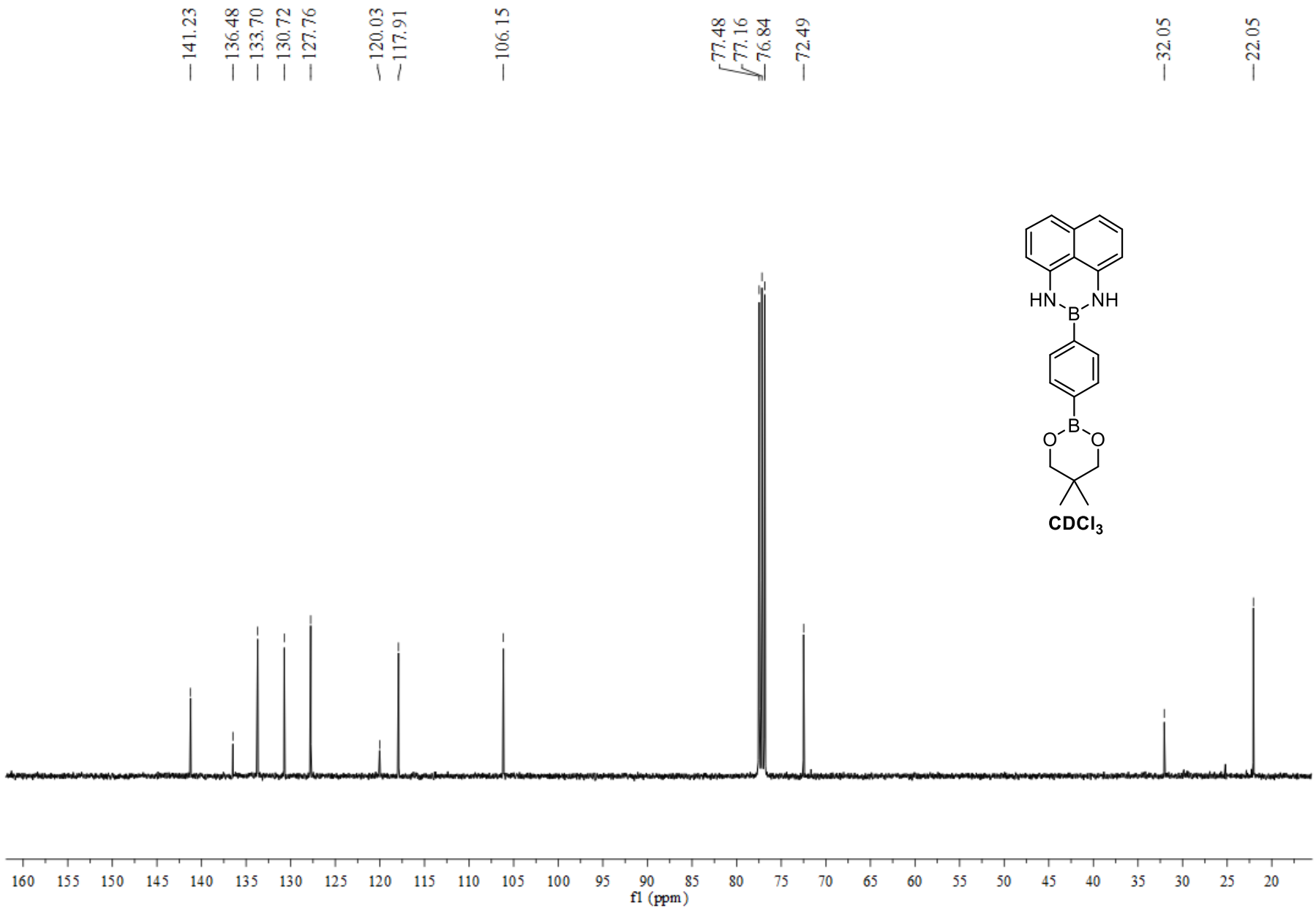
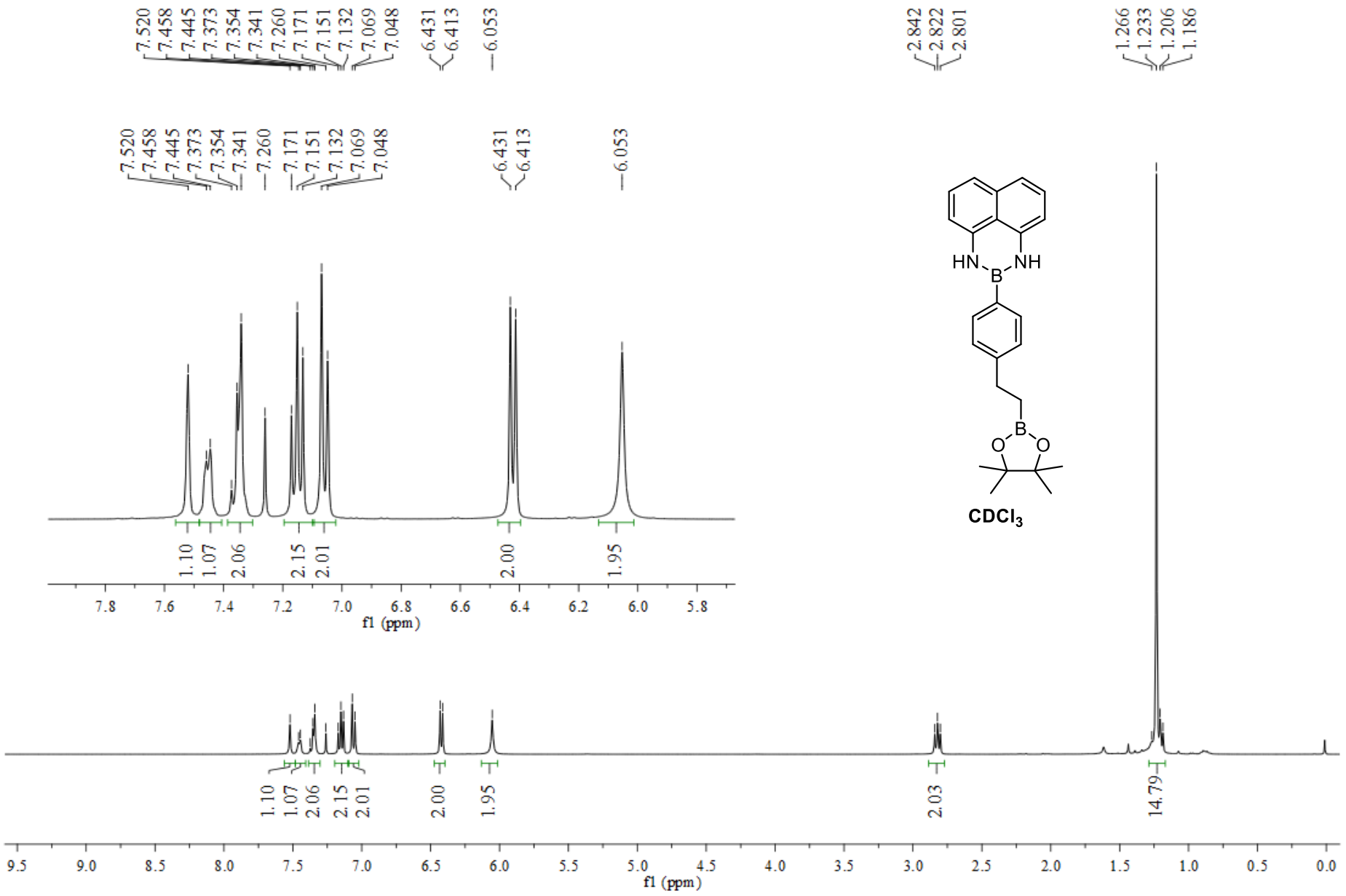
7.065
7.045
6.432
6.413
6.069
3.800
1.045
7.656
7.637
7.163
2.00
2.07
2.10
2.00
2.03
2.03
4.11
6.29
HN
NH
B
O
O
CDCl3
f1 (ppm)


141.23
136.48
133.70
130.72
127.76
120.03
117.91
106.15
77.48
77.16
76.84
72.49
32.05
22.05
HN
B
NH
B
O
O
CDCl3
160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20
f1 (ppm)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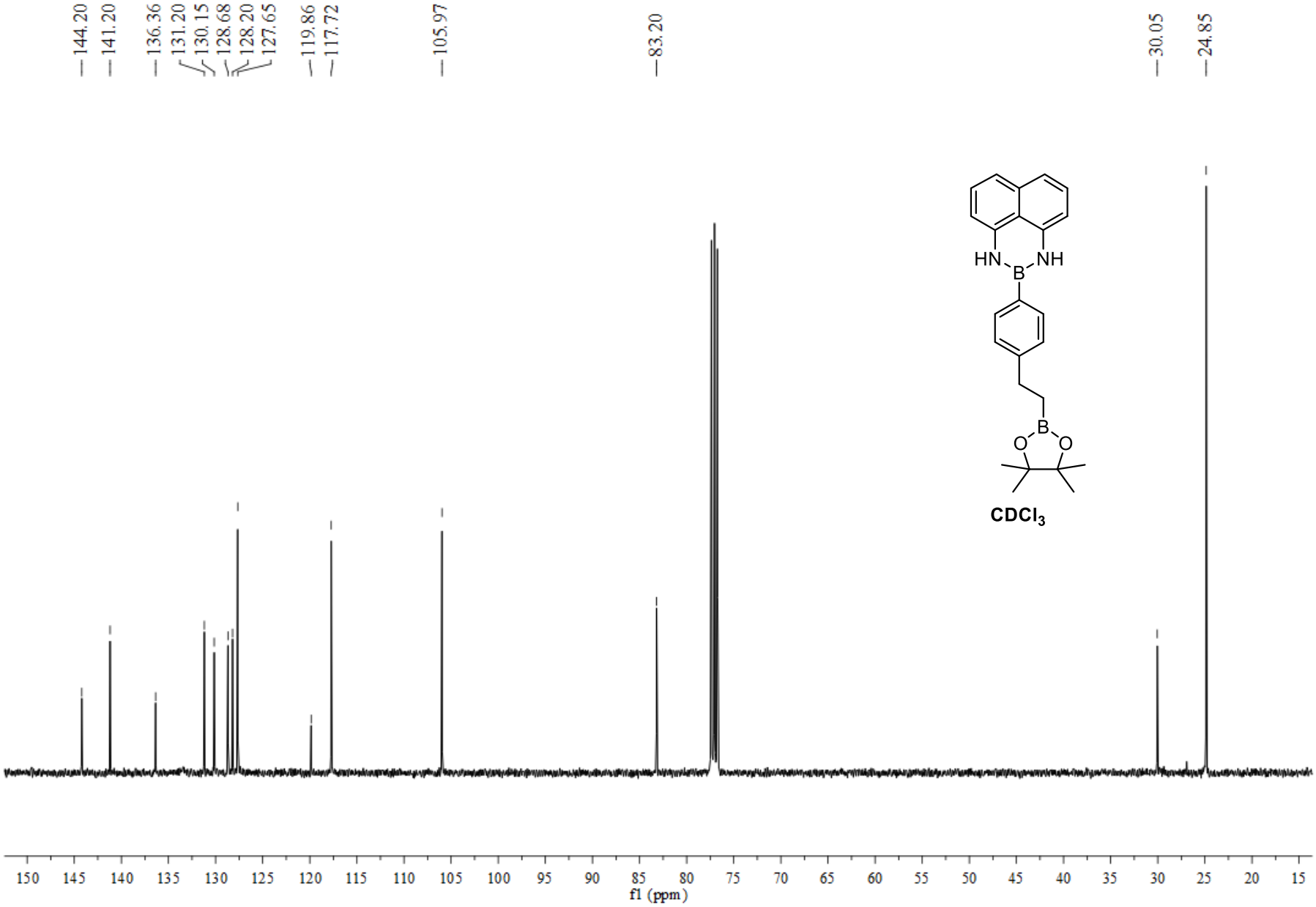
7.445
7.373
7.354
7.341
7.260
7.171
7.151
7.132
7.069
7.048
6.431
6.413
6.053
2.842
2.822
2.801
1.266
1.233
1.206
1.186
HN
B
NH
O
O
CDCl3
1.10
1.07
2.06
2.15
2.01
2.00
1.95
2.03
14.79
f1 (ppm)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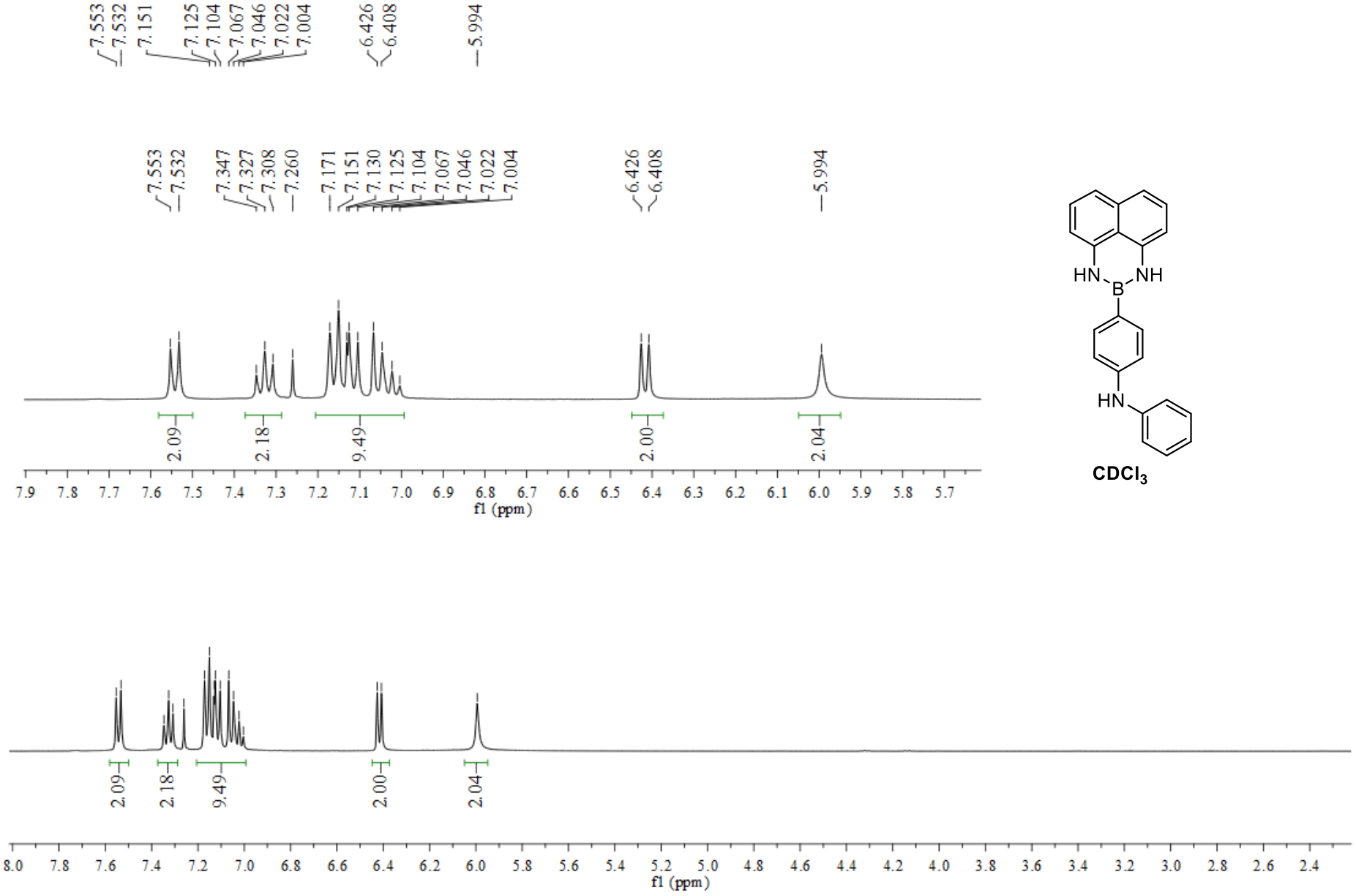
141.20
136.36
131.20
130.15
128.68
128.20
127.65
119.86
117.72
105.97
83.20
30.05
24.85
HN
B
NH
B
O
O
CDCl3
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
f1 (ppm)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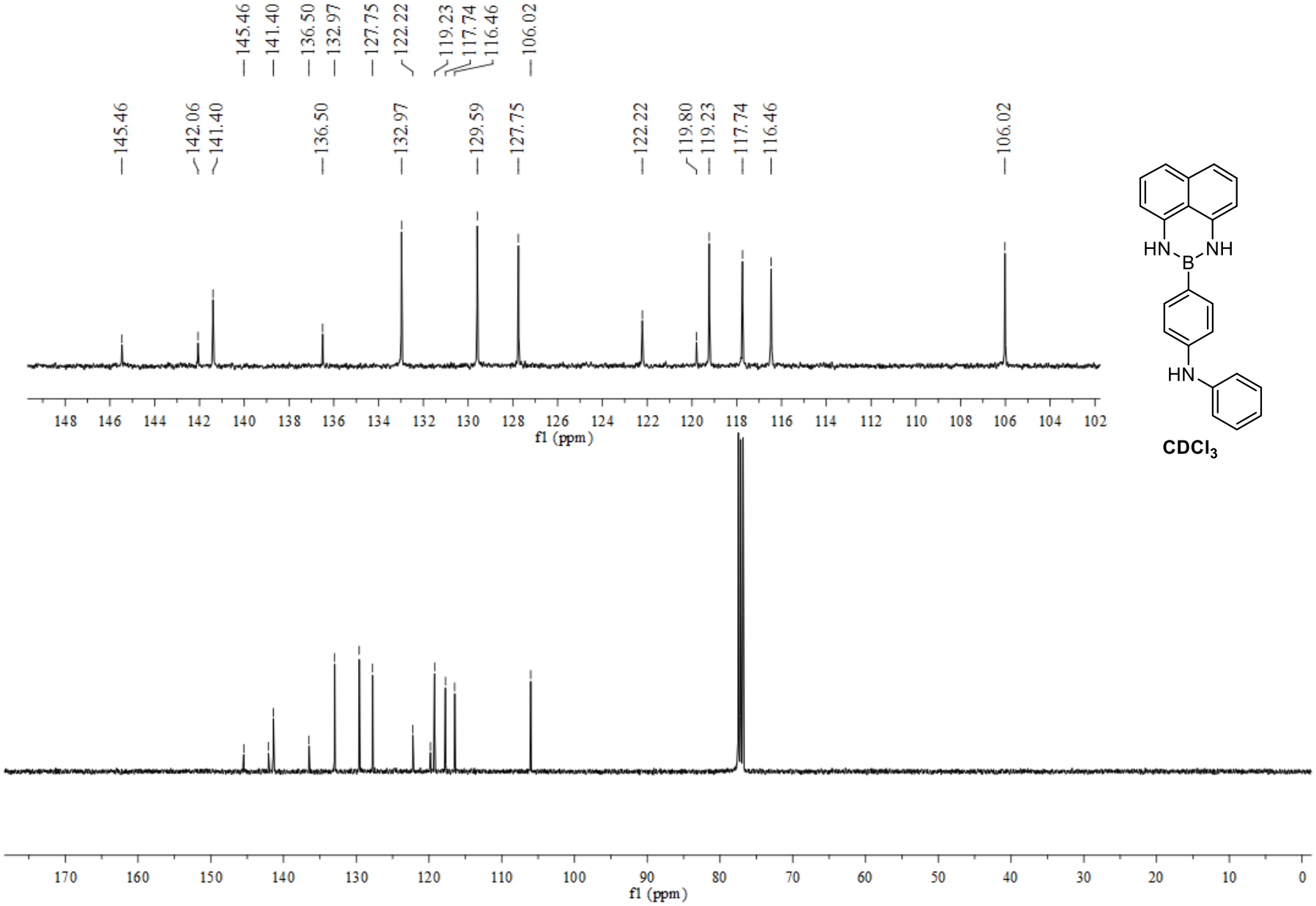
7.532
7.151
7.125
7.104
7.067
7.046
7.022
7.004
6.426
6.408
5.994
7.553
7.532
7.347
7.327
7.308
7.260
7.171
7.151
7.130
7.125
7.104
7.067
7.046
7.022
7.004
6.426
6.408
5.994
2.09
2.18
9.49
2.00
2.04
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7
f1 (ppm)
HN
B
NH
HN
CDCl3
2.09
2.18
9.49
2.00
2.04
8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4
f1 (ppm)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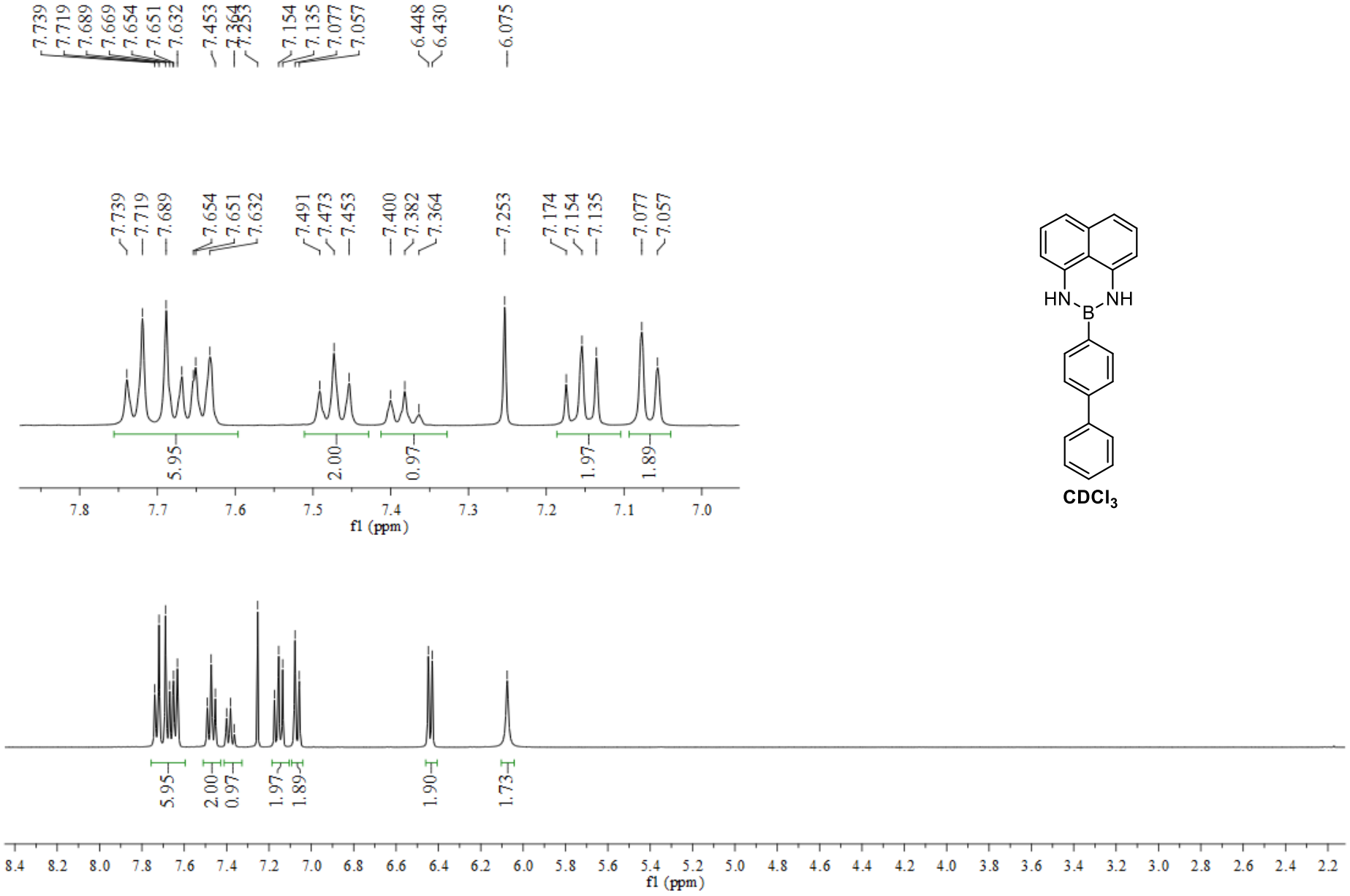
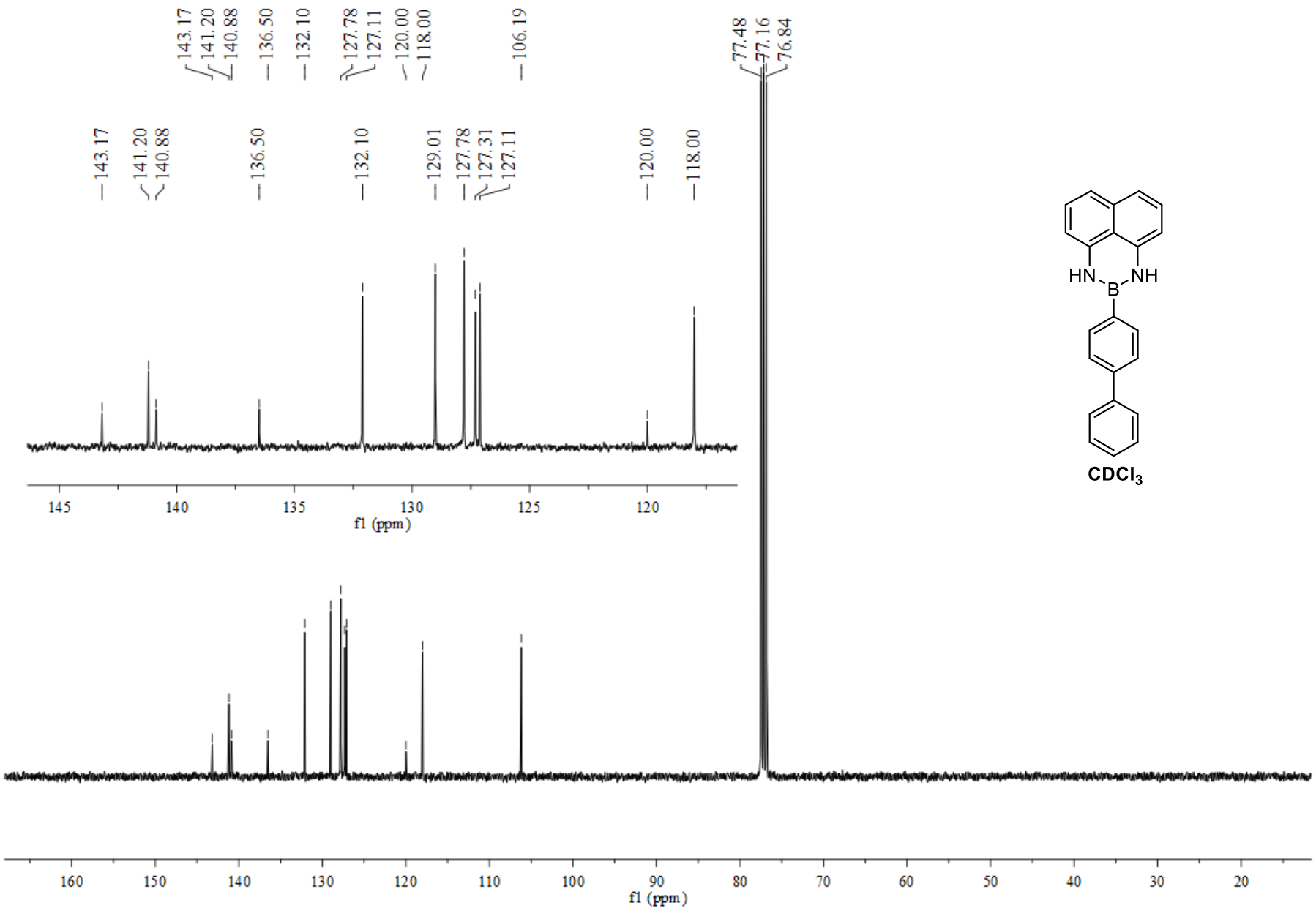
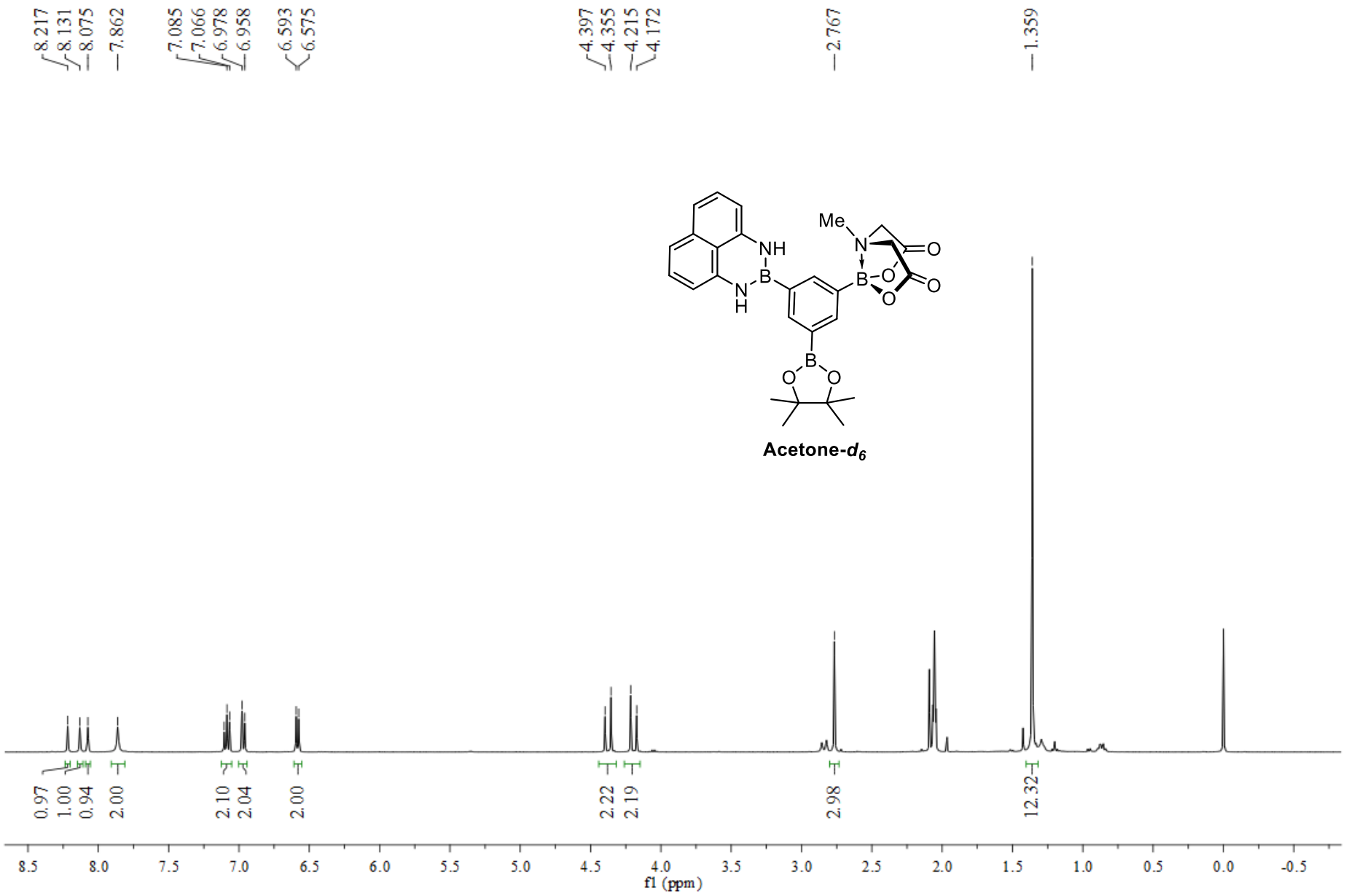
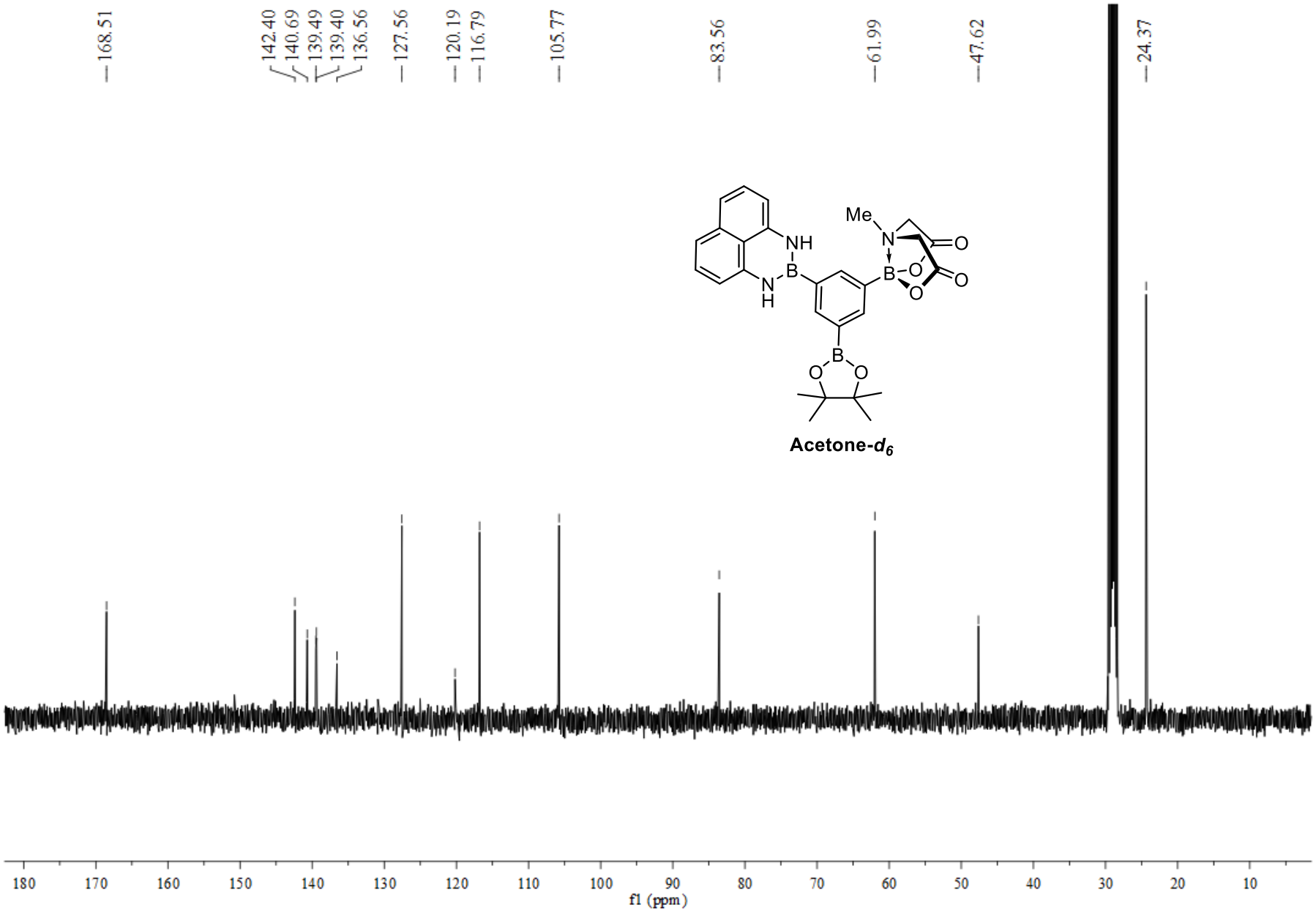
136.50
132.97
127.75
122.22
119.23
117.74
116.46
106.02
145.46
142.06
141.40
136.50
132.97
129.59
127.75
122.22
119.80
119.23
117.74
116.46
106.02
148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114 112 110 108 106 104 102
f1 (ppm)
HN
B
NH
HN
CDCl3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.739
7.719
7.689
7.669
7.654
7.651
7.632
7.453
7.364
7.253
7.154
7.135
7.077
7.057
6.448
6.430
6.075
5.95
2.00
0.97
1.97
1.89
1.90
1.73
f1 (ppm)
HN
B
NH
CDCl3


143.17
141.20
140.88
136.50
132.10
127.78
127.11
120.00
118.00
106.19
77.48
77.16
76.84
143.17
141.20
140.88
136.50
132.10
129.01
127.78
127.31
127.11
120.00
118.00
145
140
135
130
125
120
f1 (ppm)
HN
B
NH
CDCl3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


8.217
8.131
8.075
7.862
7.085
7.066
6.978
6.958
6.593
6.575
4.397
4.355
4.215
4.172
2.767
1.359
Me
N
NH
B
N
H
O
O
O
B
O
O
B
O
O
Acetone-d_6
0.97
1.00
0.94
2.00
2.10
2.04
2.00
2.22
2.19
2.98
12.32
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
-0.5
f1 (ppm)


168.51
142.40
140.69
139.49
139.40
136.56
127.56
120.19
116.79
105.77
83.56
61.99
47.62
24.37
Me
N
NH
N
H
B
B
O
O
O
O
O
B
O
O
Acetone-d_6
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)