Supporting Information

Chemoselective *N*-arylation of Aminobenzamides via Copper Catalysed Chan–Evans–Lam Reactions

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1 General considerations

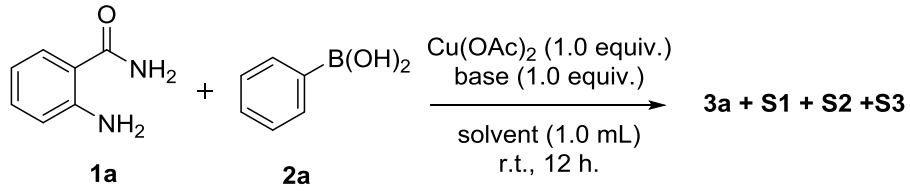
General. Unless otherwise noted, all reactions were carried out under an air atmosphere. Analytical thin-layer chromatography (TLC) was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator. Visualization was accomplished by exposure to a UV lamp. All 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.

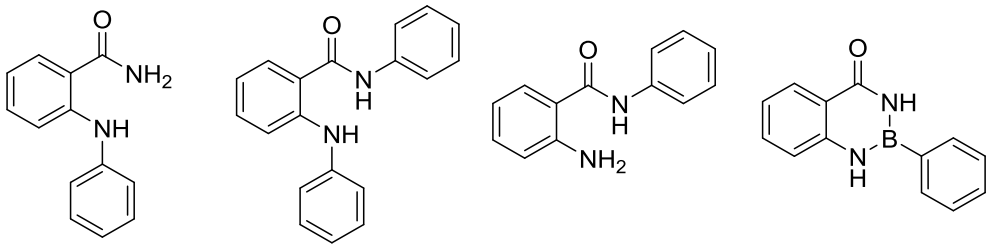
Structural analysis. NMR spectra were measured on a Bruker Ascend 400 spectrometer and chemical shifts (δ) are reported in parts per million (ppm). ^{1}H NMR spectra were recorded at 400 MHz in NMR solvents and referenced internally to corresponding solvent resonance, and ^{13}C NMR spectra were recorded at 100 MHz and referenced to corresponding solvent resonance. 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 on Thermo Scientific LTQ Orbitrap XL with an ESI source.

Materials. Commercial reagents and solvent were purchased from Adamas, J&K, Energy, Sigma-Aldrich, Alfa Aesar, Acros Organics, TCI and used as received unless otherwise stated.

2 *Cu-catalysed selective N-arylation reactions*

2.1 Table S1: Preliminary attempts for *N*-arylation reactions

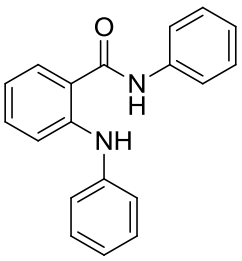




Entry	Cu source	Base	Solvent	Yields (%)[isolated] **1a : S1 : S2 : S3 : 3a**
1	$Cu(OAc)_2$	TEA	MeOH	**17 : 10 : 8 : 16 : 35**
2	$Cu(OAc)_2$	TEA	DCM	**18 : 6 : 7 : 17 : 30**
3	$Cu(OAc)_2$	$CsCO_3$	MeOH	**17 : 13 : 15 : 4 : 41**

A flame-dried 25 mL pear shaped flask were placed with a stirring bar. Then, 2-aminobenzamide (68.1 mg, 0.5 mmol, 1.0 eq.), $Cu(OAc)_2$ (90.8 mg, 0.5 mmol, 1.0 eq.), Bases (1.0 eq.), arylboronic acid (0.75 mmol, 1.5 eq.) and Solvents (1.0 mL) were added .The resulting mixture was stirred vigorously at ambient temperature for 12 hours. The reaction mixture was filtered, concentrated and then purified by column chromatography on silica gel to give the target product.

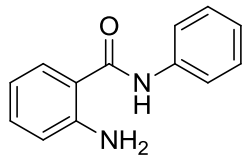
(S1) N-phenyl-2-(phenylamino)benzamide (CAS: 34237-88-2)



^{1}H NMR (400 MHz, DMSO) δ 10.34 (s, 1H), 9.11 (s, 1H), 7.77 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.74 – 7.69 dd, *J* = 8.8, 1.2Hz), 7.42 – 7.26 (m, 6H), 7.16 (dd, *J* = 8.8 Hz, 1.2H, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.94 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.72, 144.33, 133.94, 131.91, 131.10, 129.25, 128.61, 121.94, 119.01, 117.63.

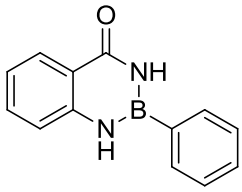
(S2) 2-amino-N-phenylbenzamide (CAS: 4424-17-3)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.56 (dd, *J* = 8.8, 1.2 Hz, 2H), 7.47 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.25 (dd, *J* = 15.4, 1.5 Hz, 1H), 7.18 – 7.11 (m, 1H), 6.75 – 6.68 (m, 2H), 5.49 (br, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.61, 148.98, 137.87, 132.77, 129.08, 127.19, 124.52, 120.57, 117.56, 116.86, 116.27.

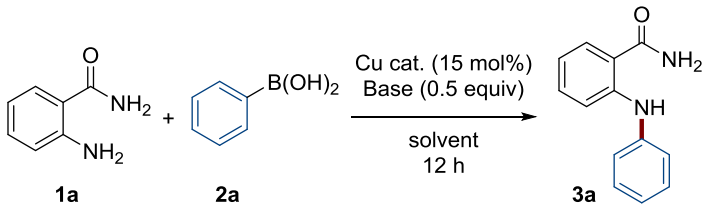
(S3) 2-phenyl-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one (CAS: 28249-75-4)



^{1}H NMR (400 MHz, DMSO) δ 9.68 (s, 1H), 9.31 (s, 1H), 8.03 (m, 3H), 7.60 – 7.54 (td, *J* = 6.8, 1.6, 1H), 7.46 (m, 4H), 7.14 – 7.08 (td, *J* =7.2, 1.2, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.54, 150.71, 138.59, 138.56, 138.51, 137.53, 135.73, 133.19, 133.13, 133.03, 126.04, 124.00, 123.38.

2.2 Table S2: Detailed table of reaction condition optimization for *o*-aminobenzamides

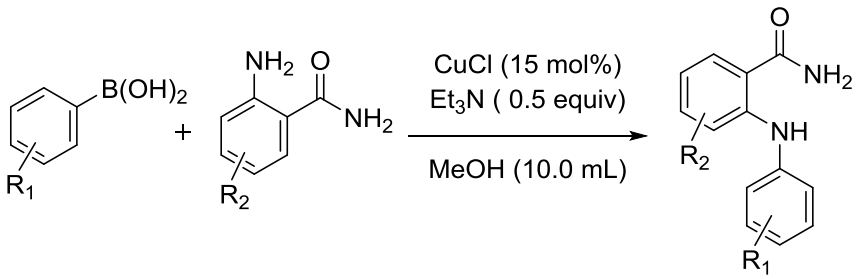


Entry	Catalyst	Base	Oxidant	Solvent	Isolated yields (%)
1	$Cu(OAc)_2$	TEA	Air	DCM	N.R.
2	$Cu(OTf)_2$	TEA	Air	MeOH	34
3	$Cu(OTf)_2$		Air	MeOH	54
4	$Cu(OTf)_2$		Air	DMF	N.R.
5	$Cu(OTf)_2$		Air	DMSO	N.R.
6	$Cu(OTf)_2$		DTBP	MeOH	60
7	$Cu(OTf)_2$		TBHP	MeOH	14
8	Cu_2O		Air	MeOH	N.R.
9	CuI		Air	MeOH	N.R.
10	CuTC		Air	MeOH	N.R.
11	CuCl		Air	MeOH	63
12	CuCl	2,2'-Dipyridyl	Air	MeOH	70
13	CuCl	4-Phenylpyridine	Air	MeOH	69
14	CuCl	K_2CO_3	Air	MeOH	81
15	CuCl	Na_2CO_3	Air	MeOH	75
16	CuCl	$KHCO_3$	Air	MeOH	68
17	CuCl	DBU	Air	MeOH	68
18	CuCl	Ag_2CO_3	Air	MeOH	64
19	CuCl	t-BuOK	Air	MeOH	64
20	CuCl	TEA	Air	MeOH (1.0 mL)	66
21	CuCl	TEA	Air	MeOH (70 °C)	24
22	**CuCl**	**TEA**	**Air**	**MeOH**	**90**
23	CuCl	TEA	Air	DCM	N.R.
24	CuCl	TEA	Air	THF	N.R.

25	CuCl	TEA	Air	toluene	N.R.
26	CuCl	TEA	Air	MeOH	79% [a, b]
27	CuCl	TEA	Air	MeOH	9% [a, c]
28	CuCl	TEA	O_2	MeOH	83% [a]

[a] NMR yield. [b] phenyl boronic acid pinacol ester was used instead of free boronic acid. [c] potassium phenyl trifluoroborate was used.

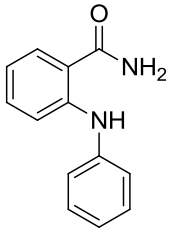
2.3 General procedure A for Cu-catalysed selective arylation of *o*-aminobenzamides



A flame-dried 100 mL pear shaped flask were placed with a stirring bar. Then, 2-aminobenzamide (68.1 mg, 0.5 mmol, 1.0 eq.), CuCl (7.4 mg, 0.075 mmol, 15 mol%), Et_3N (35.0 μL, 0.25 mmol, 0.5 eq.), arylboronic acid (0.75 mmol, 1.5 eq.), and MeOH (10.0 mL) were added .The resulting mixture was stirred vigorously at ambient temperature for 12 hours. The reaction mixture was filtered, concentrated and then purified by column chromatography on silica gel to give the target product.

2.4 Cu-catalysed selective arylation of ortho-aminobenzamides

(3a) 2-(phenylamino)benzamide (CAS : 1211-19-4)



2-(phenylamino)benzamide
Chemical Formula: $C_{13}H_{12}N_2O$
Exact Mass: 212.0950
Molecular Weight: 212.2472

The general procedure A was followed using phenylboronic acid **2a** (91.4 mg, 0.75 mmol.) as starting material. **3a** was obtained as yellow solid (95.2 mg, 90%) after purification by silica gel flash chromatography (PE:EA = 3:1).

Melting point(°C): 124.6-132.3

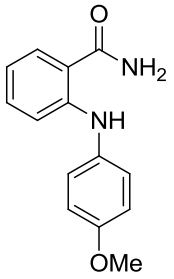
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.50 (s, 1H), 7.46 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.34–7.26 (m, 4H), 7.23–7.18 (m, 2H), 7.08–6.99 (m, 1H), 6.74 (td, *J* = 6.8, 1.2 Hz, 1H), 5.92 (br, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.07, 146.46, 141.30, 132.93, 129.34, 128.37, 122.89, 121.51, 117.61, 116.07, 115.34.

HRMS (ESI) m/z calcd for $C_{13}H_{13}N_2O^+$ $(M+H)^+$ 213.10224, found 213.10234.

IR (cm^{-1}): 3469, 3330, 1665, 1606, 1585, 1510, 756, 743.

(3b) 2-((4-methoxyphenyl)amino)benzamide (CAS : 16328-60-2)



2-((4-methoxyphenyl)amino)benzamide
Chemical Formula: $C_{14}H_{14}N_2O_2$
Exact Mass: 242.1055
Molecular Weight: 242.2732

The general procedure A was followed using (4-methoxyphenyl)boronic acid **2b** (114.0 mg, 0.75 mmol.) as starting material. **3b** was obtained as yellow solid (86.1 mg, 72%) after purification by silica gel flash chromatography (PE:EA = 3:1).

Melting point(°C): 128.4-129.8

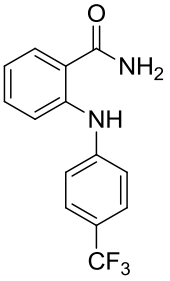
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (s, 1H), 7.43 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.25–7.19 (m, 1H), 7.18–7.12 (m, 2H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.92–6.86 (m, 2H), 6.69–6.62 (m, 1H), 5.96 (br, 2H), 3.81 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.14, 156.33, 148.41, 133.93, 133.08, 128.28, 125.26, 116.40, 114.64, 114.32, 114.27, 55.54.

HRMS (ESI) m/z calcd for $C_{14}H_{15}N_2O_2^+$ $(M+H)^+$ 243.11280, found 243.11205.

IR (cm^{-1}): 3479, 3149, 1681, 1596, 1506, 1230, 1022, 838, 732.

(3c) 2-((4-(trifluoromethyl)phenyl)amino)benzamide (CAS : 1382353-86-7)



2-((4-(trifluoromethyl)phenyl)amino)benzamide
Chemical Formula: $C_{14}H_{11}F_3N_2O$
Exact Mass: 280.0823
Molecular Weight: 280.2451

The general procedure A was followed using (4-(trifluoromethyl)phenyl)boronic acid **2c** (142.5 mg, 0.75 mmol.) as starting material. **3c** was obtained as white solid (105.1 mg, 75%) after purification by silica gel flash chromatography (PE:EA = 3:1).

Melting point(°C): 178.2-181.2

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (s, 1H), 7.52–7.45 (dd, *J*=7.6,1.2Hz,1H), 7.39 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.36–7.30 (m, 1H), 7.24 (ddd, *J* = 10.4, 7.6, 4.4 Hz, 1H), 6.99–6.90 (m, 2H), 6.82 (ddd, *J* = 8.1, 7.2, 1.3 Hz, 1H), 6.69 (m, 1H), 5.94 (br, 2H).

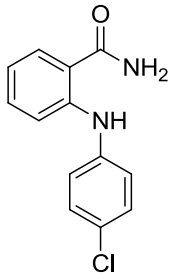
^{13}C NMR (100 MHz, DMSO-d_6) δ 171.29, 146.33, 142.82, 132.44, 129.86, 127.06 (q, J = 3 Hz), 125.17 (q, J = 269 Hz), 121.18, 120.82 (q, J = 32 Hz), 120.55, 117.80, 117.61

^{19}F NMR (376 MHz, $CDCl_3$) δ -61.72.

HRMS (ESI) m/z calcd for $C_{14}H_{12}F_3N_2O^+$ $(M+H)^+$ 281.08962, found 281.08969.

IR (cm^{-1}): 3415, 3361, 3198, 1640, 1614, 1527, 1330, 1102, 1068, 834,755.

(3d) 2-((4-chlorophenyl)amino)benzamide (CAS: 13799-33-2)



2-((4-chlorophenyl)amino)benzamide
Chemical Formula: $C_{13}H_{11}ClN_2O$
Exact Mass: 246.0560
Molecular Weight: 246.6922

The general procedure A was followed using (4-chlorophenyl)boronic acid **2d** (117.3 mg, 0.75 mmol.) as starting material. **3d** was obtained as white solid (102.9 mg, 83%) after purification by silica gel flash chromatography (PE:EA = 3:1).

Melting point(°C): 160.2-162.3

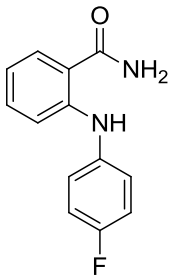
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.54 (s, 1H), 7.48 (dd, J = 8.0, 1.2 Hz, 1H), 7.38–7.21 (m, 4H), 7.14 (d, J = 8.8 Hz, 2H), 6.84–6.71 (m, 1H), 5.83 (br, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.83, 146.11, 139.93, 133.04, 129.33, 128.36, 127.60, 122.60, 117.99, 116.17, 115.27.

HRMS (ESI) m/z calcd for $C_{13}H_{12}ClN_2O^+$ $(M+H)^+$ 247.06327, found 247.06357.

IR (cm^{-1}): 3401, 3364, 3191, 1638, 1587, 1509, 1321, 1092, 827, 755.

(3e) 2-((4-fluorophenyl)amino)benzamide (CAS: 18201-71-3)



2-((4-fluorophenyl)amino)benzamide
Chemical Formula: $C_{13}H_{11}FN_2O$
Exact Mass: 230.0855
Molecular Weight: 230.2376

The general procedure A was followed using (4-fluorophenyl)boronic acid **2e** (105.0 mg, 0.75 mmol.) as starting material. **3e** was obtained as yellow solid (93.6 mg, 82%) after purification by silica gel flash chromatography (PE:EA = 3:1).

Melting point(°C): 123.5-125.4

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (s, 1H), 7.45 (dd, J = 8.0, 1.2 Hz, 1H), 7.30–7.22 (td, J = 8.8, 1.2 Hz, 1H), 7.20–7.08 (m, 3H), 7.05–6.95 (m, 2H), 6.79–6.67 (m, 1H), 6.02 (br, 2H).

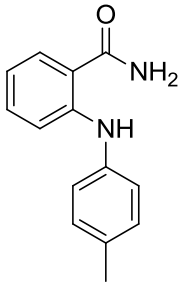
^{13}C NMR (100 MHz, $CDCl_3$) δ 172.03, 159.16 (d, J = 241 Hz), 147.39, 137.11 (d, J = 3 Hz), 133.11, 128.33, 124.36 (d, J = 8 Hz), 117.23, 116.03 (d, J = 23 Hz), 115.15, 114.56.

^{19}F NMR (376 MHz, $CDCl_3$) δ -119.48.

HRMS (ESI) m/z calcd for $C_{13}H_{12}FN_2O^+$ $(M+H)^+$ 231.09282, found 231.09275.

IR (cm^{-1}): 3469, 3171, 1866, 1620, 1506, 1218, 818, 737.

(3f) 2-(p-tolylamino)benzamide (CAS: 193265-70-2)



2-(*p*-tolylamino)benzamide
Chemical Formula: $C_{14}H_{14}N_2O$
Exact Mass: 226.1106
Molecular Weight: 226.2738

The general procedure A was followed using p-tolylboronic acid **2f** (102.0 mg, 0.75 mmol.) as starting material. **3f** was obtained as yellow solid (86.9 mg, 77%) after purification by silica gel flash chromatography (PE:EA = 3:1).

Melting point(°C): 119.7-121.2

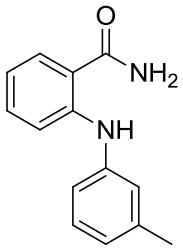
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.44 (s, 1H), 7.44 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.30–7.17 (m, 2H), 7.16–7.07 (m, 4H), 6.70 (ddd, *J* = 8.0, 6.7, 1.6 Hz, 1H), 5.90 (br, 2H), 2.33 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.07, 147.28, 138.48, 132.97, 132.85, 129.90, 128.32, 122.41, 116.97, 115.25, 114.87, 20.87.

HRMS (ESI) m/z calcd for $C_{14}H_{15}N_2O^+$ $(M+H)^+$ 227.11789, found 227.11789.

IR (cm^{-1}): 3466, 3349, 3197, 1635, 1610, 1514, 1287, 747.

(3g) 2-(m-tolylamino)benzamide (CAS: 1188890-42-7)



2-(*m*-tolylamino)benzamide
Chemical Formula: $C_{14}H_{14}N_2O$
Exact Mass: 226.1106
Molecular Weight: 226.2738

The general procedure A was followed using m-tolylboronic acid **2g** (102.0 mg, 0.75 mmol.) as starting material. **3g** was obtained as white solid (93.1 mg, 82%) after purification by silica gel flash chromatography (PE:EA = 3:1).

Melting point(°C): 118.4-120.1

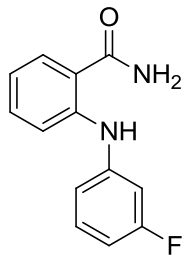
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.46 (s, 1H), 7.46 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.31 (ddd, *J* = 8.2, 7.6, 1.5 Hz, 2H), 7.24–7.16 (m, 1H), 7.02 (t, *J* = 2.2, 2H), 6.86 (d, *J* = 7.2 Hz, 1H), 6.74 (ddd, *J* = 8.1, 6.7, 1.6 Hz, 1H), 5.75 (br, 2H), 2.33 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.90, 146.59, 141.19, 139.22, 132.92, 129.10, 128.32, 123.75, 122.28, 118.51, 117.42, 115.91, 115.46, 21.48.

HRMS (ESI) m/z calcd for $C_{14}H_{15}N_2O^+$ $(M+H)^+$ 227.11789, found 227.11783.

IR (cm^{-1}): 3373, 3317, 3139, 1660, 1601, 1508, 1487, 1282, 766, 691.

(3h) 2-((3-fluorophenyl)amino)benzamide



2-((3-fluorophenyl)amino)benzamide
Chemical Formula: $C_{13}H_{11}FN_2O$
Exact Mass: 230.0855
Molecular Weight: 230.2376

The general procedure A was followed using (3-fluorophenyl)boronic acid **2h** (105.0 mg, 0.75 mmol.) as starting material. **3h** was obtained as white solid (83.2 mg, 73%) after purification by silica gel flash chromatography (PE:EA = 3:1).

Melting point(°C): 112.5-114.1

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (s, 1H), 7.48 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.39 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.36–7.30 (m, 1H), 7.24 (ddd, *J* = 10.4, 7.6, 4.4 Hz, 1H), 7.00–6.89 (m, 2H), 6.82 (ddd, *J* = 8.1, 7.2, 1.3 Hz, 1H), 6.69 (tdd, *J* = 8.4, 2.3, 0.9 Hz, 1H), 5.94 (br, 2H).

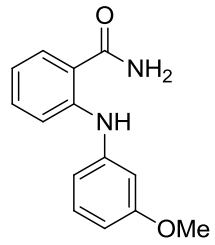
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.90, 163.57 (d, *J* = 244 Hz), 145.27, 143.33 (d, *J* = 11 Hz), 132.97, 130.43 (d, *J* = 10 Hz), 128.37, 118.60, 117.05, 116.14 (d, *J* = 3 Hz), 116.08, 109.00 (d, *J* = 21 Hz), 107.14 (d, *J* = 24 Hz)

^{19}F NMR (376 MHz, $CDCl_3$) δ -112.16.

HRMS (ESI) m/z calcd for $C_{13}H_{12}FN_2O^+$ $(M+H)^+$ 231.09282, found 231.09291.

IR (cm^{-1}): 3445, 3361, 2976, 2360, 1650, 1619, 1529, 1340, 845, 766.

(3i) 2-((3-methoxyphenyl)amino)benzamide (CAS: 1376246-78-4)



2-((3-methoxyphenyl)amino)benzamide
Chemical Formula: $C_{14}H_{14}N_2O_2$
Exact Mass: 242.1055
Molecular Weight: 242.2732

The general procedure A was followed using (3-methoxyphenyl)boronic acid **2i** (114.0 mg, 0.75 mmol.) as starting material. **3i** was obtained as yellow solid (103.6 mg, 86%) after purification by silica gel flash chromatography (PE:EA = 3:1).

Melting point(°C): 80.9-82.4

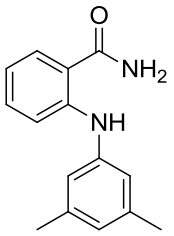
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.50 (s, 1H), 7.47 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.38 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.33–7.27 (m, 1H), 7.21 (t, *J* = 8.0 Hz, 1H), 6.86–6.72 (m, 3H), 6.63–6.56 (m, 1H), 5.78 (br, 2H), 3.79 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.89, 160.60, 146.13, 142.63, 132.92, 130.00, 128.31, 117.81, 116.32, 115.87, 113.60, 108.33, 106.83, 55.30.

HRMS (ESI) m/z calcd for $C_{14}H_{15}N_2O_2^+$ $(M+H)^+$ 243.11280, found 243.11259.

IR (cm^{-1}): 3328, 3155, 2829, 1661, 1586, 1489, 1268, 1157, 858.

(3j) 2-((3,5-dimethylphenyl)amino)benzamide



2-((3,5-dimethylphenyl)amino)benzamide
Chemical Formula: $C_{15}H_{16}N_2O$
Exact Mass: 240.1263
Molecular Weight: 240.3003

The general procedure A was followed using (3,5-dimethylphenyl)boronic acid **2j** (112.0 mg, 0.75 mmol.) as starting material. **3j** was obtained as white solid (98.9 mg, 82%) after purification by silica gel flash chromatography (PE:EA = 3:1).

Melting point(°C): 161.6-165.2

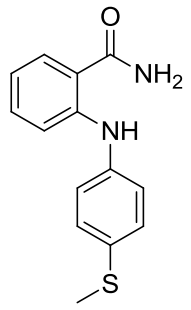
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (s, 1H), 7.45 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.30 (ddd, *J* = 8.2, 7.6, 1.5 Hz, 2H), 6.85 (s, 2H), 6.73 (ddd, *J* = 14.1, 7.8, 4.5 Hz, 2H), 5.80 (br, 2H), 2.29 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.00, 146.64, 141.15, 138.99, 132.88, 128.34, 124.71, 119.24, 117.34, 115.95, 115.61, 21.39.

HRMS (ESI) m/z calcd for $C_{15}H_{17}N_2O^+$ $(M+H)^+$ 241.13354, found 241.13361.

IR (cm^{-1}): 3374, 3328, 3143, 2914, 1592, 1511, 1328, 768.

(3k) 2-((4-(methylthio)phenyl)amino)benzamide (CAS: 1382353-90-3)



2-((4-(methylthio)phenyl)amino)benzamide
Chemical Formula: $C_{14}H_{14}N_2OS$
Exact Mass: 258.0827
Molecular Weight: 258.3388

The general procedure A was followed using (4-(methylthio)phenyl)boronic acid **2k** (126.0 mg, 0.75 mmol.) as starting material. **3k** was obtained as yellow solid (89.5 mg, 70%) after purification by silica gel flash chromatography (PE:EA = 3:1).

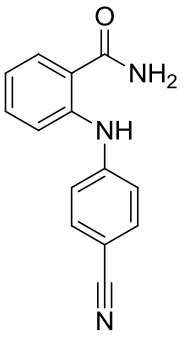
Melting point(°C): 151.4-153.2

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.52 (s, 1H), 7.49–7.43 (dd, *J* =8.4, 1.2Hz, 1H), 7.29 (m, 3H), 7.26–7.24 (m, 1H), 7.20–7.12 (m, 2H), 6.75 (ddd, *J* = 8.0, 6.3, 2.0 Hz, 1H), 5.77 (br, 2H), 2.48 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.89, 146.50, 139.10, 132.99, 131.63, 128.96, 128.34, 122.28, 117.59, 115.83, 115.22, 17.20.

HRMS (ESI) m/z calcd for $C_{14}H_{15}N_2OS^+$ $(M+H)^+$ 259.08996, found 259.08994.
IR (cm^{-1}): 3407, 3369, 3203, 1630, 1581, 1504, 1314, 804, 755.

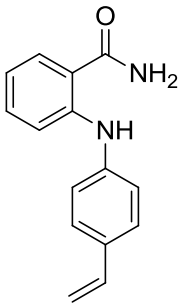
(3l) 2-((4-cyanophenyl)amino)benzamide (CAS: 564483-27-8)



2-((4-cyanophenyl)amino)benzamide
Chemical Formula: $C_{14}H_{11}N_3O$
Exact Mass: 237.0902
Molecular Weight: 237.2566

The general procedure A was followed using (4-cyanophenyl)boronic acid **2l** (110.2 mg, 0.75 mmol.) as starting material. **3l** was obtained as white solid (60.8 mg, 51%) after purification by silica gel flash chromatography (PE:EA = 3:1).
Melting point(°C): 158.0-180.0
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92–9.63 (m, 1H), 7.55–7.43 (m, 4H), 7.42–7.34 (m, 1H), 7.21–7.14 (m, 2H), 6.97–6.87 (m, 1H), 5.84 (d, *J* = 130.0 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.26, 146.03, 143.10, 133.64, 132.90, 128.43, 120.47, 119.61, 119.03, 118.01, 117.60, 103.40.
HRMS (ESI) m/z calcd for $C_{14}H_{12}N_3O^+$ $(M+H)^+$ 238.09749, found 238.09811.
IR (cm^{-1}): 3442, 3328, 2829, 1661, 1586, 1489, 1268, 1157, 858.

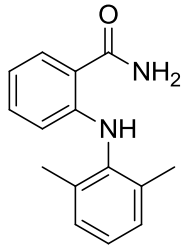
(3m) 2-((4-vinylphenyl)amino)benzamide



2-((4-vinylphenyl)amino)benzamide
Chemical Formula: $C_{15}H_{14}N_2O$
Exact Mass: 238.1106
Molecular Weight: 238.2845

The general procedure A was followed using (4-vinylphenyl)boronic acid **2m** (111.0 mg, 0.75 mmol.) as starting material. **3m** was obtained as yellow solid (78.4 mg, 66%) after purification by silica gel flash chromatography (PE:EA = 2:1).
Melting point(°C): 173.2-175.6
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.56 (s, 1H), 7.47 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.35 (ddd, *J* = 5.9, 4.8, 1.5 Hz, 3H), 7.32–7.27 (m, 1H), 7.21–7.13 (m, 2H), 6.76 (ddd, *J* = 8.1, 7.1, 1.3 Hz, 1H), 6.68 (dd, *J* = 17.6, 10.9 Hz, 1H), 6.21–5.53 (m, 3H), 5.16 (dd, *J* = 10.8, 0.8 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.85, 146.07, 140.95, 136.31, 132.95, 132.19, 128.34, 127.20, 121.00, 117.81, 116.23, 115.61, 112.07.
HRMS (ESI) m/z calcd for $C_{15}H_{15}N_2O^+$ $(M+H)^+$ 239.11789, found 239.11768.
IR (cm-1): 3402, 3365, 3202, 1633, 1583, 1515, 1325, 898, 834.

(3n) 2-((2,6-dimethylphenyl)amino)benzamide (CAS:13625-38-2)

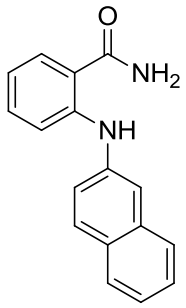


Chemical Formula: $C_{15}H_{16}N_2O$
Exact Mass: 240.1263
Molecular Weight: 240.3003

The general procedure A was followed using ((2,6-dimethylphenyl) boronic acid **2n** (112.5 mg, 0.75 mmol.) as starting material. **3n** was obtained as yellow solid (44.6 mg, 37%) after purification by silica gel flash chromatography (PE:EA = 3:1).
Melting point(°C): 156.7-158.8
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 (s, 1H), 7.44 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.20–7.07 (m, 4H), 6.66–6.57 (m, 1H), 6.23 (d, *J* = 8.4 Hz, 1H), 5.81 (br, 2H), 2.21 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.16, 149.11, 137.53, 136.69, 133.43, 128.41, 128.18, 126.27, 115.44, 113.30, 112.69, 18.34.
HRMS (ESI) m/z calcd for $C_{15}H_{17}N_2O^+$ $(M+H)^+$ 241.13354, found 241.13353.

IR (cm^{-1}): 3480, 3377, 3249, 1651, 1558, 1278, 766, 730.

(3o) N-methyl-2-(naphthalen-2-ylamino)benzamide (CAS:1382353-91-4)



Chemical Formula: $C_{17}H_{14}N_2O$
Exact Mass: 262.1106
Molecular Weight: 262.3059

The general procedure A was followed using naphthalen-2-ylboronic acid **2o** (129 mg, 0.75 mmol.) as starting material. **3o** was obtained as white solid (73.3 mg, 56%) after purification by silica gel flash chromatography (PE:EA = 3:1).

Melting point(°C): 141.6-145.5

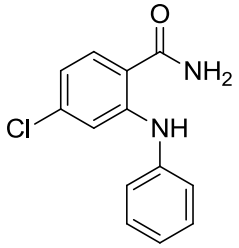
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.70 (s, 1H), 7.83–7.73 (m, 2H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.62 (s, 1H), 7.53–7.28 (m, 6H), 6.79 (t, *J* = 7.4 Hz, 1H), 5.93 (br, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.92, 146.26, 138.95, 134.41, 133.01, 130.12, 129.12, 128.39, 127.67, 126.89, 126.40, 124.29, 122.44, 117.97, 116.40, 116.38, 115.68.

HRMS (ESI) m/z calcd for $C_{17}H_{15}N_2O^+$ $(M+H)^+$ 263.11789, found 263.11789.

IR (cm^{-1}): 3481, 3152, 2360, 1644, 1528, 1387, 860, 731.

(3p) 4-chloro-2-(phenylamino)benzamide (CAS: 64445-26-7)



Chemical Formula: $C_{13}H_{11}ClN_2O$
Exact Mass: 246.0560
Molecular Weight: 246.6922

The general procedure A was followed using 2-amino-4-chlorobenzamideas **1b** (85.3mg, 0.5mmol.) starting material. **3p** was obtained as white solid (74.9 mg, 60%) after purification by silica gel flash chromatography (PE:EA = 3:1).

Melting point(°C): 137.3-139.7

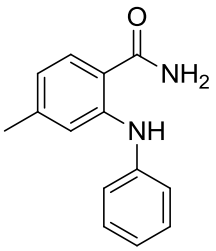
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.69 (s, 1H), 7.42–7.31 (t, *J* = 8.4Hz, 3H), 7.25–7.17 (m, 3H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.68 (dd, *J* = 8.4, 2.0 Hz, 1H), 5.80 (br, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.32, 148.04, 140.22, 139.28, 129.55, 129.50, 123.97, 122.54, 117.28, 114.29, 113.53.

HRMS (ESI) m/z calcd for $C_{13}H_{12}ClN_2O^+$ $(M+H)^+$ 247.06327, found 247.06325.

IR (cm^{-1}): 3440, 3165, 2360, 1620, 1589, 1563, 1505, 1273, 1075, 929, 774.

(3q) 4-methyl-2-(phenylamino)benzamide (CAS: 95216-63-0)



Chemical Formula: $C_{14}H_{14}N_2O$
Exact Mass: 226.1106
Molecular Weight: 226.2738

The general procedure A was followed using 2-amino-4-methylbenzamide **1c** (75.1mg, 0.5mmol.) starting material. **3q** was obtained as yellow solid (86.5 mg, 77%) after purification by silica gel flash chromatography (PE:EA = 3:1).

Melting point(°C): 143.8-145.9

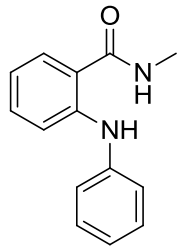
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.57 (s, 1H), 7.37–7.28 (m, 3H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.12 (s, 1H), 7.04 (t, *J*= 7.4 Hz, 1H), 6.55 (d, *J* = 8.0 Hz, 1H), 5.98 (br, 2H), 2.25 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.97, 146.65, 143.70, 141.37, 129.31, 128.36, 122.82, 121.70, 118.73, 115.39, 113.19, 21.84.

HRMS (ESI) m/z calcd for $C_{14}H_{15}N_2O^+$ $(M+H)^+$ 227.11789, found 227.11795.

IR (cm^{-1}): 3409, 3331, 3169, 2975, 1619, 1587, 1511, 1278, 743, 690.

(3r) N-methyl-2-(phenylamino)benzamide (CAS:4-61-7）



Chemical Formula: $C_{14}H_{14}N_2O$
Exact Mass: 226.1106
Molecular Weight: 226.2738

The general procedure A was followed using 2-amino-N-methylbenzamide **1d** (75.1mg, 0.5mmol.) starting material. **3r** was obtained as white solid (90.4 mg, 80%) after purification by silica gel flash chromatography (PE:EA = 3:1).

Melting point(°C): 87.2-88.8

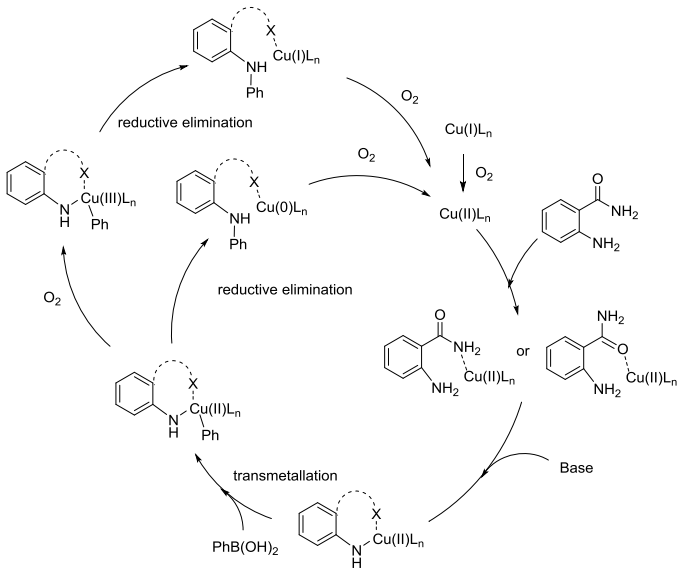
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.29 (s, 1H), 7.37 (ddd, *J* = 15.0, 8.1, 1.2 Hz, 2H), 7.33–7.27 (m, 2H), 7.24 (d, *J* = 1.5 Hz, 1H), 7.22–7.14 (m, 2H), 7.00 (t, *J* = 7.4 Hz, 1H), 6.80–6.71 (m, 1H), 6.15 (s, 1H), 2.99 (d, *J* = 4.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.23, 145.28, 141.61, 132.07, 129.29, 127.44, 122.33, 120.64, 118.64, 117.97, 115.53, 26.65.

HRMS (ESI) m/z calcd for $C_{14}H_{15}N_2O^+$ $(M+H)^+$ 227.11789, found 227.11786.

IR (cm^{-1}): 3379, 3260, 3065, 2882, 2361, 1620, 1551, 1508, 1310, 759, 695.

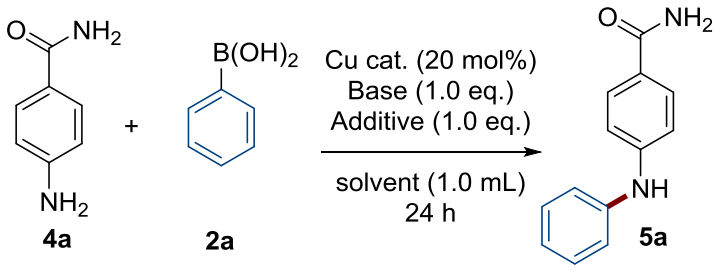
2.5 Proposed mechanism for C-N coupling of *o*-aminobenzamide



The "n" value in "$Cu(X)L_n$" might vary in the catalytic cycle.

Although it is hard to propose a precise and inerrant catalytic mechanism for this reaction, especially considering the lability of valence state of Cu under air atmosphere, we would like to proposed a possible reaction mechanism based on our experimental observations and literature survey. The plausible reaction mechanism was depicted above. Cu(II) species was thought to be catalytic active complex. After complexation of **1a** with copper catalyst and deprotonation of aniline NH_2, Cu(II) cyclometalated species was formed. Then, the transmetallation process proceeded with $PhB(OH)_2$, generating Cu(II) species coordinated by nitranion and carbanion. The following reductive elimination would afford the product and Cu(0) complex, which was then oxidized to Cu(II) catalyst. A higher oxidation Cu(III) complex might also participate in this catalytic cycle, due to the oxidation effect of air.

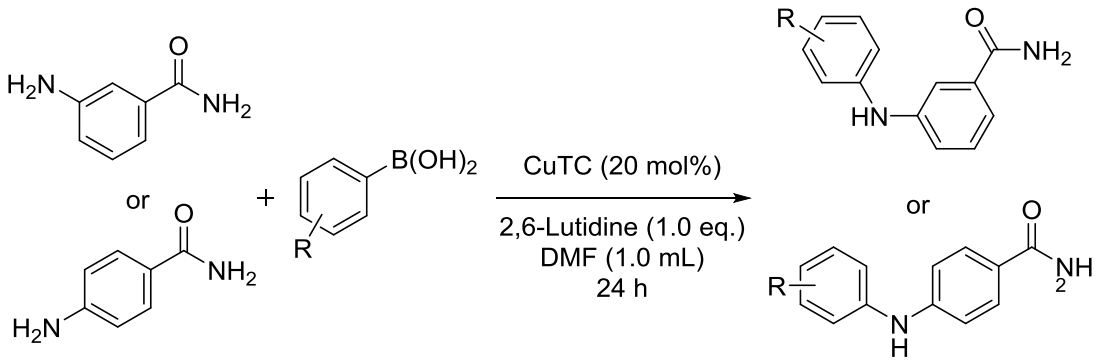
2.6 Table S3: Detailed table of reaction condition optimization for *p*-aminobenzamides



Entry	Catalyst	Base	Additive	Solvent	Isolated yields (%)
1	CuCl	TEA	—	MeOH	N.R.
2	$Cu(OTf)_2$	TEA	—	MeOH	N.R.

3	$Cu(OAc)_2$	2,6-Lutidine	Myristic acid	toluene	23
4	$Cu(OAc)_2$	TEA	Myristic acid	toluene	8
5	$Cu(OAc)_2$	K_2CO_3/TEA	—	MeCN	12
6	$Cu(OAc)_2$	DMAP	Myristic acid	toluene	N.R.
7	$Cu(OAc)_2$	Cs_2CO_3	benzoic acid	MeOH	57
8	CuCl	2,6-Lutidine	Myristic acid	toluene	N.R.
9	CuTC	2,6-Lutidine	—	MeOH	49
10	CuTC	pyridine	—	MeOH	31
11	CuTC	2,6-Lutidine	—	1,4-dioxane	64
12	CuTC	2,6-Lutidine	—	THF	49
13	**CuTC**	**2,6-Lutidine**	—	**DMF**	**88**

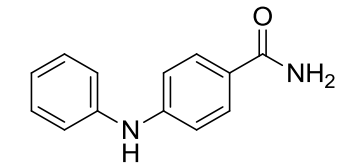
2.7 General procedure B for Cu-catalyzed selective arylation



A flame-dried 100 mL pear shaped flask were placed with a stirring bar. Then, 4-aminobenzamide (68.1 mg, 0.5 mmol, 1.0 eq.), CuTC (19.1 mg, 0.1 mmol, 20 mol%), 2,6-Lutidine (58.0 μL, 0.5 mmol, 1.0 eq.), arylboronic acid (0.75 mmol, 1.5 eq.), and DMF (1.0 mL) were added. The resulting mixture was stirred vigorously at ambient temperature for 24 hours. The reaction mixture was treated with EtOAc (5.0 mL) and water (5.0 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc (3 × 5.0 mL). The combined organic phase was washed with brine (2 × 5.0 mL), dried over anhydrous Na_2SO_4, and concentrated to afford residue, which was purified by column chromatography on silica gel to give the target product.

2.8 Cu-catalysed selective arylation of *p*- and *m*-aminobenzamides

(5a) 4-(phenylamino)benzamide (CAS: 183557-73-5)



Chemical Formula: $C_{13}H_{12}N_2O$
Exact Mass: 212.0950
Molecular Weight: 212.2472

The general procedure B was followed using phenylboronic acid **2a** (91.4 mg, 0.75 mmol.) as starting material. **6a** was obtained as gray solid (93.7 mg, 88%) after purification by silica gel flash chromatography (PE:EA = 1:2).

Melting point(°C): 165.1-169.6

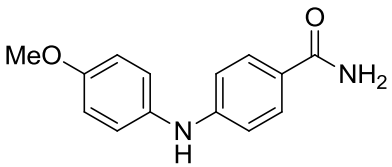
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.62 (m, 2H), 7.37–7.30 (m, 2H), 7.16 (dt, *J* = 8.7, 1.7 Hz, 2H), 7.09–6.99 (m, 3H), 5.90 (d, *J* = 95.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.92, 147.35, 141.04, 129.54, 129.23, 124.11, 122.99, 120.19, 115.05.

HRMS (ESI) m/z calcd for $C_{13}H_{13}N_2O^+$ $(M+H)^+$ 213.10224, found 213.10207.

IR (cm^{-1}): 3473, 3325, 2976, 2360, 1652, 1621, 1586, 1525, 1387, 1329, 765, 693.

(5b) 4-((4-methoxyphenyl)amino)benzamide (CAS: 183723-13-9)



Chemical Formula: $C_{14}H_{14}N_2O_2$
Exact Mass: 242.1055
Molecular Weight: 242.2732

The general procedure B was followed using phenylboronic acid **2b** (114.0 mg, 0.75 mmol.) as starting material. **6b** was obtained as yellow solid (78.4 mg, 65%) after purification by silica gel flash chromatography (PE:EA = 1:2).

Melting point(°C): 166.1-170.1

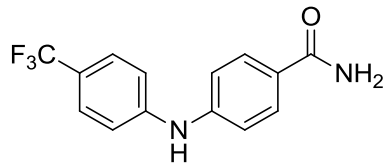
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.8 Hz, 2H), 7.10 (d, *J* = 8.9 Hz, 2H), 6.87 (d, *J* = 8.9 Hz, 2H), 6.83–6.77 (m, 2H), 5.78 (br, 3H), 3.79 (s, 3H).

^{13}C NMR (101 MHz, DMSO) δ 168.17, 155.16, 148.63, 135.12, 129.63, 123.67, 122.46, 115.06, 113.19, 55.69.

HRMS (ESI) m/z calcd for $C_{14}H_{15}N_2O_2^+$ $(M+H)^+$ 243.11280, found 243.11259.

IR (cm^{-1}): 3479, 3362, 3327, 2977, 1664, 1591, 1525, 1510, 1374, 1337, 1243, 825, 765.

(5c) 4-((4-(trifluoromethyl)phenyl)amino)benzamide



Chemical Formula: $C_{14}H_{11}F_3N_2O$
Exact Mass: 280.0823
Molecular Weight: 280.2451

The general procedure B was followed using (4-(trifluoromethyl)phenyl)boronic acid **2c** (142.5 mg, 0.75 mmol.) as starting material. **6c** was obtained as white solid (49.6 mg, 41%) after purification by silica gel flash chromatography (PE:EA = 1:2).

Melting point(°C): 135.0-141.2

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 8.8 Hz, 2H), 7.15 (dd, *J* = 18.0, 8.4 Hz, 4H), 6.24 (s, 1H), 5.84 (br, 2H).

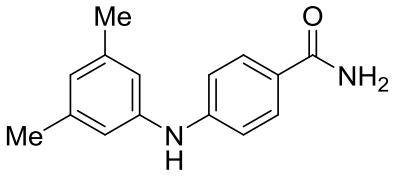
^{13}C NMR (100 MHz, DMSO-d_6) δ 167.88, 146.71, 145.09, 129.58, 127.05 (q, *J* = 3 Hz), 126.90, 125.25 (q, *J* = 269 Hz), 120.20 (q, *J* = 32 Hz), 116.98, 116.64.

^{19}F NMR (376 MHz, $CDCl_3$) δ -61.75.

HRMS (ESI) m/z calcd for $C_{14}H_{12}F_3N_2O^+$ $(M+H)^+$ 281.08962, found 281.08963.

IR (cm^{-1}):3388, 3209, 1640, 1602, 1526, 1320, 1110, 1067, 837.

(5d) 4-((3,5-dimethylphenyl)amino)benzamide (CAS: 564483-29-0)



Chemical Formula: $C_{15}H_{16}N_2O$
Exact Mass: 240.1263
Molecular Weight: 240.3003

The general procedure B was followed using 4-((3,5-dimethylphenyl)amino)benzamide **2j** (112.5 mg, 0.75 mmol.) as starting material. **6d** was obtained as white solid (106.5 mg, 88%) after purification by silica gel flash chromatography (PE:EA = 1:2).

Melting point(°C): 201.1-204.6

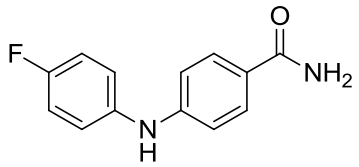
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.79 (s, 2H), 6.71 (s, 1H), 5.90 (br, 3H), 2.30 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.07, 147.73, 140.83, 139.28, 129.27, 124.91, 123.47, 118.05, 115.06, 21.38.

HRMS (ESI) m/z calcd for $C_{15}H_{17}N_2O^+$ $(M+H)^+$ 241.13354, found 241.13339.

IR (cm^{-1}): 3382, 3178, 2976, 1682, 1591, 1335, 855, 773.

(5e) 4-((4-fluorophenyl)amino)benzamide (CAS: 852927-43-6)



Chemical Formula: $C_{13}H_{11}FN_2O$
Exact Mass: 230.0855
Molecular Weight: 230.2376

The general procedure B was followed using (4-fluorophenyl)boronic acid **2e** (105.0 mg, 0.75 mmol.) as starting material. **6d** was obtained as white solid (76.6 mg, 67%) after purification by silica gel flash chromatography (PE:EA = 1:2).

Melting point(°C): 167.5-170.6

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.8 Hz, 2H), 7.14 (dd, *J* = 8.8, 4.6 Hz, 2H), 7.04 (t, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 5.87 (s, 1H), 5.67 (br, 2H).

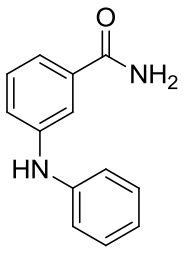
^{13}C NMR (100 MHz, CDCl3) δ 168.96, 159.15 (d, *J* = 241 Hz), 148.09, 136.86 (d, *J* = 2 Hz), 129.30, 123.82, 123.15 (d, *J* = 8 Hz), 116.27 (d, *J* = 23 Hz), 114.32,

^{19}F NMR (376 MHz, $CDCl_3$) δ -119.05.

HRMS (ESI) m/z calcd for $C_{13}H_{12}FN_2O^+$ $(M+H)^+$ 231.09282, found 231.09279.

IR (cm^{-1}): 3417, 3335, 2976, 1698, 1598, 1507, 1338, 1194, 821.

(7a) 3-(phenylamino)benzamide (CAS: 935688-08-7)



Chemical Formula: $C_{13}H_{12}N_2O$
Exact Mass: 212.0950
Molecular Weight: 212.2472

The general procedure B was followed using phenylboronic acid **2a** (91.4 mg, 0.75 mmol.) as starting material. **7a** was obtained as white solid (92.0 mg, 87%) after purification by silica gel flash chromatography (PE:EA = 1:2).

Melting point(°C): 154.4-159.6

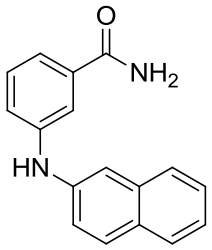
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (t, *J* = 2.0 Hz, 1H), 7.34–7.24 (m, 5H), 7.21 (ddd, *J* = 7.8, 2.3, 1.3 Hz, 1H), 7.10 (dd, *J* = 8.4, 1.0 Hz, 2H), 7.02–6.96 (m, 1H), 5.91 (d, *J* = 120.0 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.44, 143.99, 142.07, 134.55, 129.54, 122.14, 120.37, 119.05, 118.89, 116.19, 100.00.

HRMS (ESI) m/z calcd for $C_{13}H_{13}N_2O^+$ $(M+H)^+$ 213.10224, found 213.10213.

IR (cm^{-1}): 3338, 3154, 2363, 1657, 1599, 1417, 789, 683.

(7b) 3-(naphthalen-2-ylamino)benzamide (CAS:5-94-4)



Chemical Formula: $C_{17}H_{14}N_2O$
Exact Mass: 262.1106
Molecular Weight: 262.3059

The general procedure B was followed using phenylboronic acid **2o** (131.6 mg, 0.75 mmol.) as starting material. **7b** was obtained as gray solid (101.4 mg, 80%) after purification by silica gel flash chromatography (PE:EA = 1:2).

Melting point(°C): 148.6-149.9

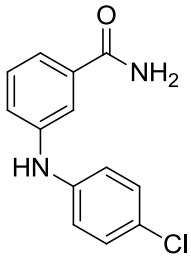
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 8.8, 5.6 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.58 (t, *J* = 18 Hz, 1H), 7.49–7.39 (m, 2H), 7.38–7.29 (m, 4H), 7.24 (d, *J* = 2.4 Hz, 1H), 5.88 (d, *J* = 143.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.44, 143.78, 139.77, 134.56, 134.46, 129.69, 129.44, 127.70, 126.70, 126.60, 124.07, 120.78, 120.41, 119.52, 116.77, 113.37.

HRMS (ESI) m/z calcd for $C_{17}H_{15}N_2O^+$ $(M+H)^+$ 263.11789, found 263.11783.

IR (cm^{-1}): 3331, 3153, 2977, 2360, 1660, 1578, 1540, 1421, 1393, 739.

(7c) 3-((4-chlorophenyl)amino)benzamide



Chemical Formula: $C_{13}H_{11}ClN_2O$
Exact Mass: 246.0560
Molecular Weight: 246.6922

The general procedure B was followed using phenylboronic acid **2d** (131.6 mg, 0.75 mmol.) as starting material. **7c** was obtained as gray solid (58.4 mg, 47%) after purification by silica gel flash chromatography (PE:EA = 1:2).

Melting point(°C): 125.9-127.6

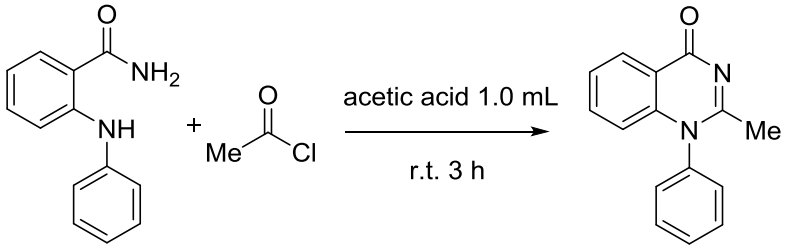
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (t, *J* = 2 Hz, 1H), 7.35–7.27 (m, 2H), 7.26–7.22 (m, 2H), 7.18 (ddd, *J* = 7.8, 2.4, 1.2 Hz, 1H), 7.06–6.99 (m, 2H), 5.84 (d, *J* = 152.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.53, 143.63, 140.87, 134.61, 129.67, 129.47, 126.61, 120.46, 119.85, 119.33, 116.54.

HRMS (ESI) m/z calcd for $C_{13}H_{12}ClN_2O^+$ $(M+H)^+$ 247.06327, found 247.06326.

IR (cm^{-1}): 3382, 2976, 2361, 1644, 1531, 1332, 1090, 787.

3 The application of mono-arylated aminobenzamides



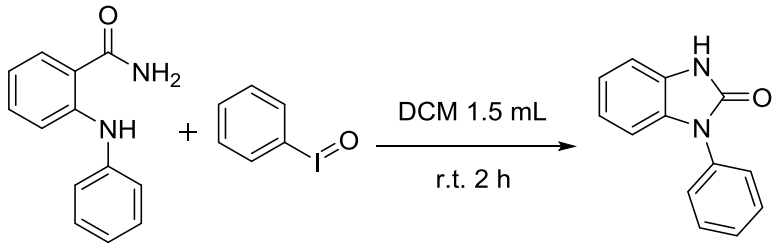
According to literature Chem. Pharm. Bull. 28(3) 702-707 (1980), a flame-dried 25 mL vial were placed with a stirring bar. Then, **3a** (63.6 mg, 0.3 mmol), acetyl chloride 65 μL (3.0 eq.) and acetic acid (1.0 mL) were added .The resulting mixture was stirred vigorously at ambient temperature for 3 hours and the solvent was evaporated off in vacuo. The residue was dissolved in H_2O and neutralized with aqueous K_2CO_3, to give a crude product. Recrystallization from EtOH gave a pure sample as colorless needles (54.2 mg, 77%).

(12) 2-methyl-1-phenylquinazolin-4(1H)-one (CAS: 1086-20-0)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.71–7.61 (m, 3H), 7.50 (ddd, *J* = 8.6, 7.2, 1.7 Hz, 1H), 7.44–7.38 (m, 1H), 7.36–7.32 (m, 2H), 6.59 (d, *J* = 8.3 Hz, 1H), 2.27 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.10, 161.07, 142.43, 137.99, 133.39, 130.93, 130.32, 128.34, 128.00, 125.78, 119.11, 116.53, 24.63.

HRMS (ESI) m/z calcd for $C_{15}H_{13}N_2O^+$ $(M+H)^+$ 237.10224, found 237.10214.



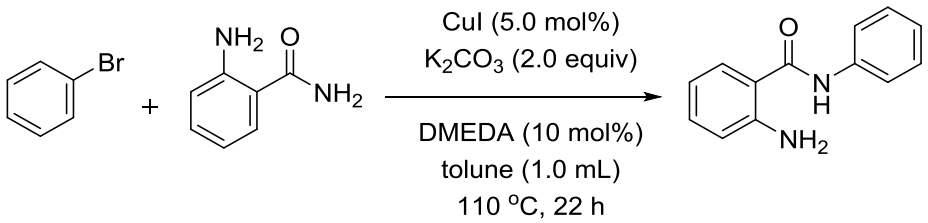
According to literature Eur. J. Org. Chem. 2012, 1994–2000, a flame-dried 25 mL vial were placed with a stirring bar. Then, **3a** (63.6 mg, 0.3 mmol), iodosylbenzene (99.0 mg, 1.5equiv) and DCM (1.5 mL) were added .The resulting mixture was stirred vigorously at ambient temperature for 2 hours. The reaction mixture was filtered, concentrated and then purified by column chromatography on silica gel to give the target product as white solid (58.6mg, 93%).

(13) 1-phenyl-1H-benzo[d]imidazol-2(3H)-one (CAS: 14813-85-5)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.1 Hz, 1H), 7.62 (t, *J* = 8.9 Hz, 3H), 7.54 (t, *J* = 7.9 Hz, 2H), 7.49–7.43 (m, 1H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.23, 134.44, 130.52, 129.66, 128.19, 127.93, 126.30, 122.32, 121.47, 110.14, 108.87.

HRMS (ESI) m/z calcd for $C_{13}H_{11}N_2O^+$ $(M+H)^+$ 211.08659, found 211.08650.



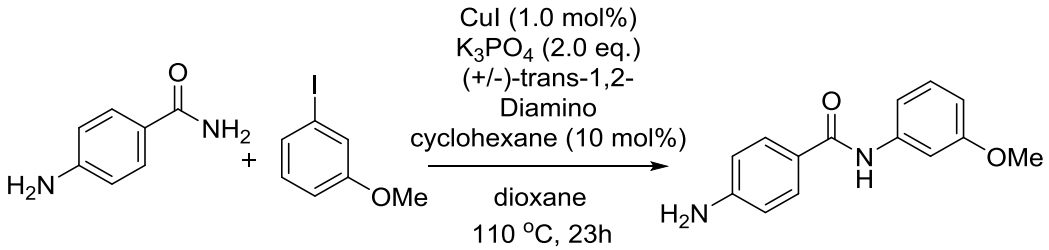
According to literature J. AM. CHEM. SOC. 2003, 125, 6653-6655•6653, a Schlenk tube was charged with CuI (9.7 mg, 0.050 mmol, 5.0 mol%), 2-aminobenzamide (167 mg, 1.2 mmol), K_2CO_3 (276 mg, 2.0 equiv), evacuated and backfilled with argon. N,N'-dimethylethylenediamine (11 μL, 0.10 mmol, 10 mol%), bromobenzene (106 μL, 1.0 mmol) and toluene (1.0 mL) were added under argon. The Schlenk tube was sealed with a Teflon valve and the reaction mixture was stirred at 110 °C for 22 h. Product was obtained as white solid (172mg, 85%) after purification by silica gel flash chromatography (PE:EA = 8:1).

(8) 2-amino-N-phenylbenzamide (CAS: 4424-17-3)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.56 (dd, *J* = 8.8, 1.2 Hz, 2H), 7.47 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.25 (dd, *J* = 15.4, 1.5 Hz, 1H), 7.18 – 7.11 (m, 1H), 6.75 – 6.68 (m, 2H), 5.49 (br, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.61, 148.98, 137.87, 132.77, 129.08, 127.19, 124.52, 120.57, 117.56, 116.86, 116.27.

HRMS (ESI) m/z calcd for $C_{13}H_{13}N_2O^+$ $(M+H)^+$ 213.10224, found 213.10252.



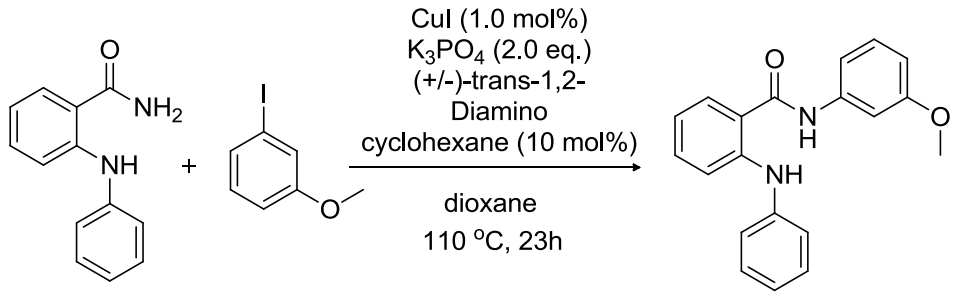
According to literature J. Am. Chem. Soc. 2001, 123, 7727-7729, a Schlenk tube was charged with CuI (1.0 mg, 0.005 mmol, 1.0 mol%), 4-aminobenzamide (83.4 mg, 1.2 mmol), K_3PO_4 (212.5 mg, 2 equiv), evacuated and backfilled with argon. rac-trans-1,2-cyclohexanediamine (7 μL, 0.05 mmol, 10 mol%), 1-iodo-3-methoxybenzene (70 uL, 0.5 mmol) and toluene (0.5 mL) were added under argon. The Schlenk tube was sealed with a Teflon valve and the reaction mixture was stirred at 110 °C for 23 h. Product was obtained as white solid (90.3mg, 75%) after purification by silica gel flash chromatography (PE:EA = 1:1).

(10) 4-amino-N-(3-methoxyphenyl)benzamide (CAS: 897594-57-9)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.8 Hz, 3H), 7.44 (t, *J* = 2.0 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.06 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.74 – 6.65 (m, 3H), 4.03 (br, 2H), 3.83 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.41, 160.23, 149.99, 139.61, 129.66, 128.88, 124.26, 114.27, 112.08, 110.17, 105.56, 55.34.

HRMS (ESI) m/z calcd for $C_{14}H_{15}N_2O_2^+$ $(M+H)^+$ 243.11280, found 243.11275.



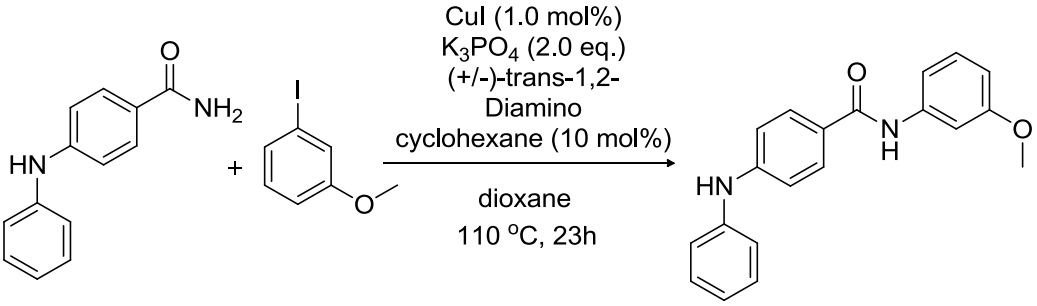
According to literature J. Am. Chem. Soc. 2001, 123, 7727-7729, a Schlenk tube was charged with CuI (1.0 mg, 0.005 mmol, 1.0 mol%), 2-(phenylamino)benzamide (127.2 mg, 1.2 mmol), K_3PO_4 (212.5 mg, 2 equiv), evacuated and backfilled with argon. rac-trans-1,2-cyclohexanediamine (7 μL, 0.05 mmol, 10 mol%), 1-iodo-3-methoxybenzene (70 uL, 0.5 mmol) and toluene (0.5 mL) were added under argon. The Schlenk tube was sealed with a Teflon valve and the reaction mixture was stirred at 110 °C for 23 h Product was obtained as yellow viscous liquid (93.7mg, 59%) after purification by silica gel flash chromatography (PE:EA = 8:1).

(9) N-(3-methoxyphenyl)-2-(phenylamino)benzamide (CAS: 1181002-63-0)

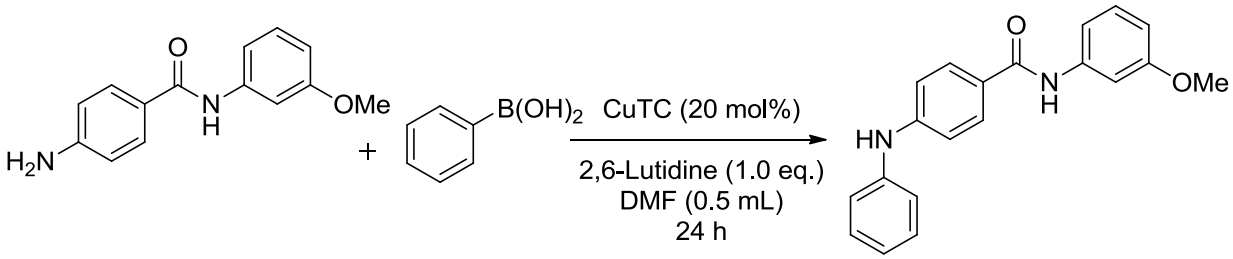
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (s, 1H), 7.94 (s, 1H), 7.54 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.37 – 7.32 (m, 1H), 7.28 (dt, *J* = 11.9, 5.7 Hz, 4H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 2H), 7.02 (m, 2H), 6.83 – 6.77 (m, 1H), 6.69 (dd, *J* = 8.4, 2.0 Hz, 1H), 3.79 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.78, 160.24, 145.72, 141.40, 138.92, 132.68, 129.81, 129.37, 127.66, 122.71, 120.91, 118.86, 118.32, 116.00, 112.86, 110.57, 106.44, 55.38.

HRMS (ESI) m/z calcd for $C_{20}H_{19}N_2O_2^+$ $(M+H)^+$ 319.14410, found 319.14423.



According to literature J. Am. Chem. Soc. 2001, 123, 7727-7729, a Schlenk tube was charged with CuI (1.0 mg, 0.005 mmol, 1.0 mol%), 4-(phenylamino)benzamide (127.2 mg, 1.2 mmol), K_3PO_4 (212.5 mg, 2 equiv), evacuated and backfilled with argon. rac-trans-1,2-cyclohexanediamine (7 μL, 0.05 mmol, 10 mol%), 1-iodo-3-methoxybenzene (70 uL, 0.5 mmol) and toluene (0.5 mL) were added under argon. The Schlenk tube was sealed with a Teflon valve and the reaction mixture was stirred at 110 °C for 23 h. Product was obtained as white solide (155.1mg, 97%) after purification by silica gel flash chromatography (PE:EA = 3:1).



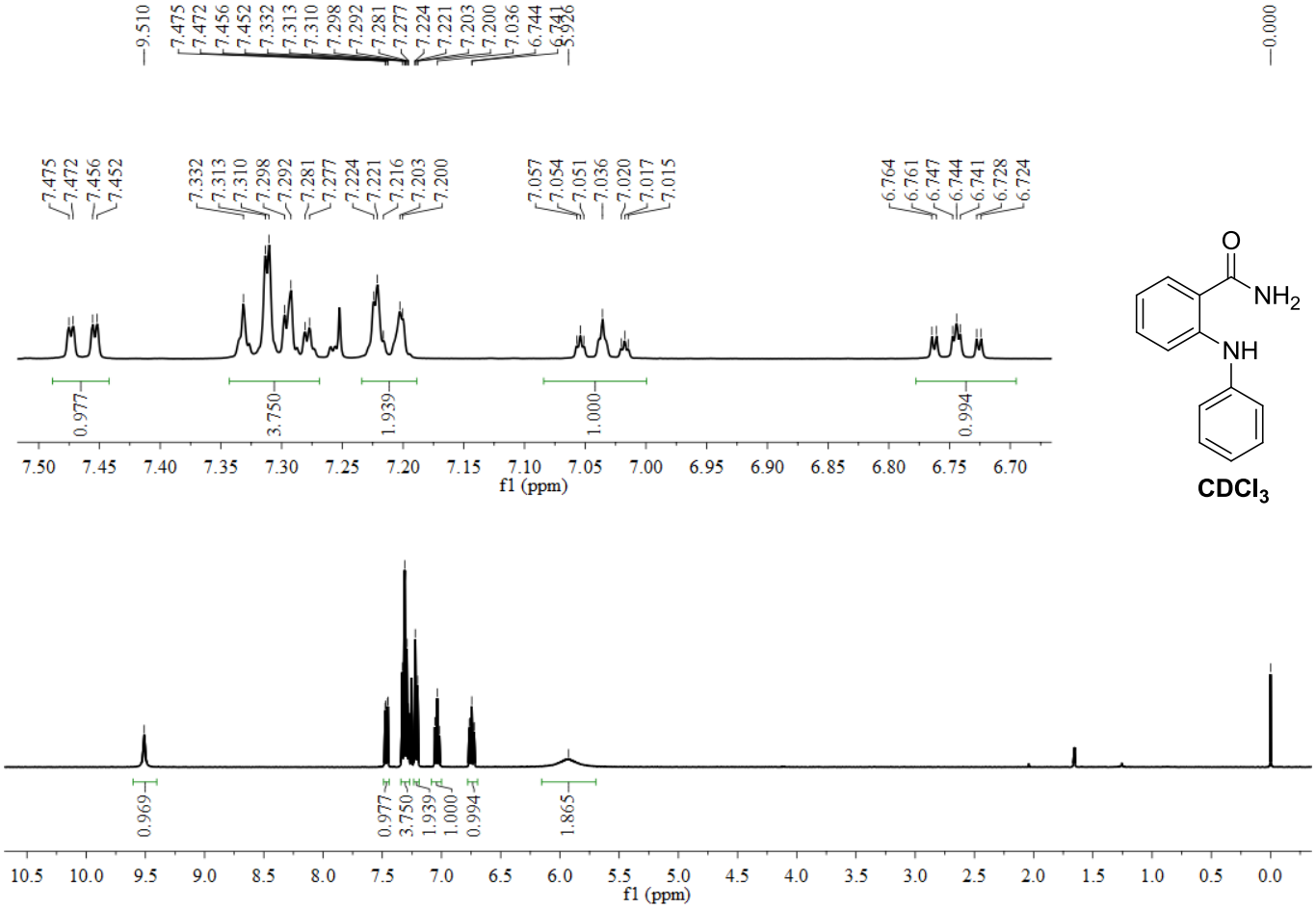
A flame-dried 100 mL pear shaped flask were placed with a stirring bar. Then, 4-amino-N-(3-methoxyphenyl)benzamide (48.4 mg, 0.2 mmol, 1.0 eq.), CuTC (7.6 mg, 0.04 mmol, 20 mol%), 2,6-Lutidine (23 μL, 0.2 mmol, 1.0 eq.), arylboronic acid (36.6 mg, 0.75 mmol, 1.5 eq.), and DMF (0.5 mL) were added. The resulting mixture was stirred vigorously at ambient temperature for 24 hours. The reaction mixture was treated with EtOAc (5.0 mL) and water (5.0 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc (3 × 5.0 mL). The combined organic phase was washed with brine (2 × 5.0 mL), dried over anhydrous Na_2SO_4, and concentrated to afford residue, which was purified by column chromatography on silica gel to give the target product, Product was obtained as white solide (59.3 mg, 93%) after purification by silica gel flash chromatography (PE:EA = 3:1).

(11) N-(3-methoxyphenyl)-4-(phenylamino)benzamide

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.8 Hz, 2H), 7.73 (s, 1H), 7.45 (t, *J* = 4.0, 2.0 Hz, 1H), 7.34 (t, *J* = 16, 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.17 (d, *J* = 7.2 Hz, 2H), 7.06 (t, *J* = 16.8, 8.0 Hz, 4H), 6.69 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.02 (s, 1H), 3.83 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.25, 160.24, 147.24, 141.04, 139.53, 129.69, 129.55, 128.80, 125.66, 122.98, 120.14, 115.24, 112.16, 110.27, 105.64, 55.35.

4 Copies of NMR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7.472
7.456
7.452
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NH
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1.000
0.994
1.865
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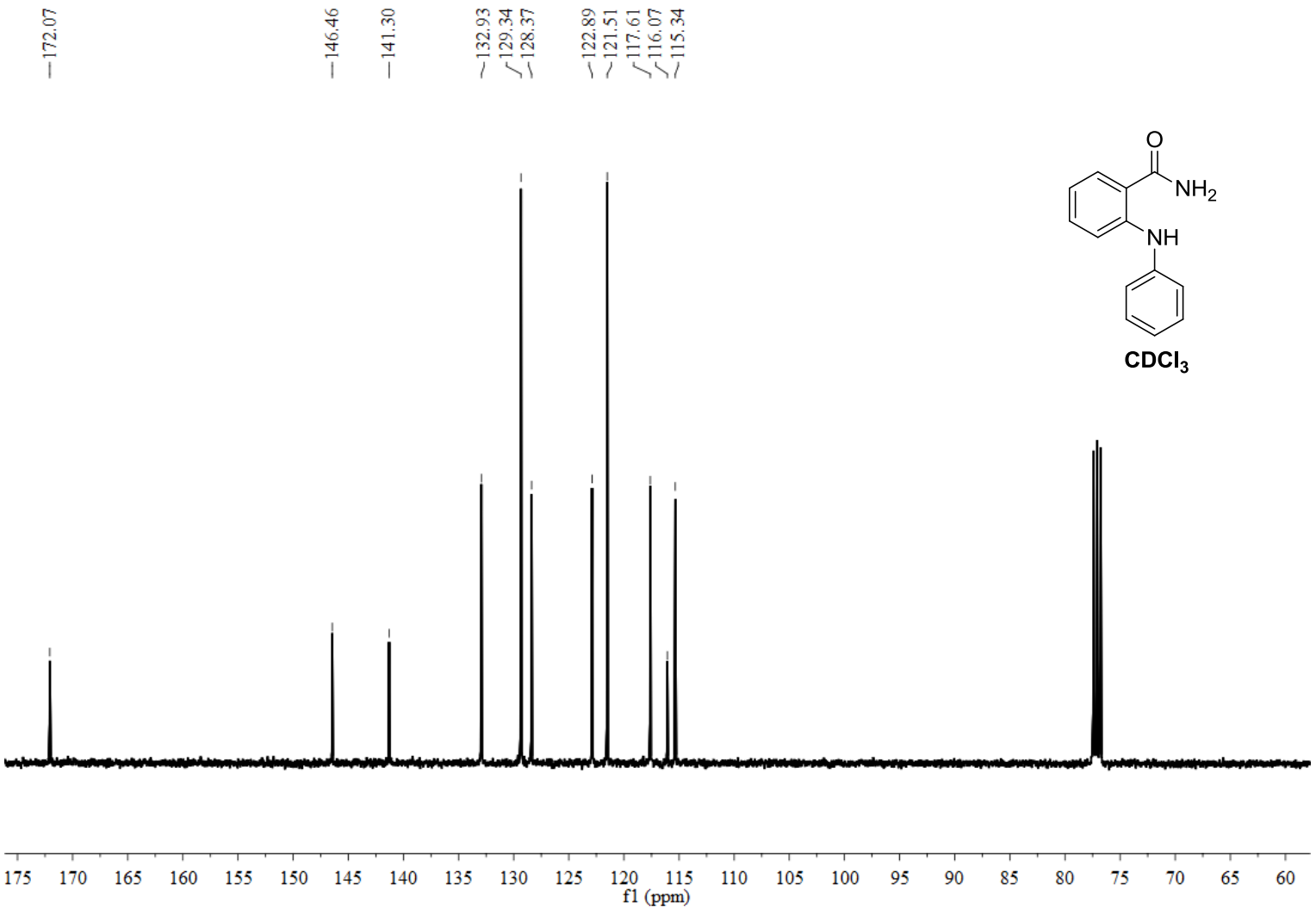
f1 (ppm)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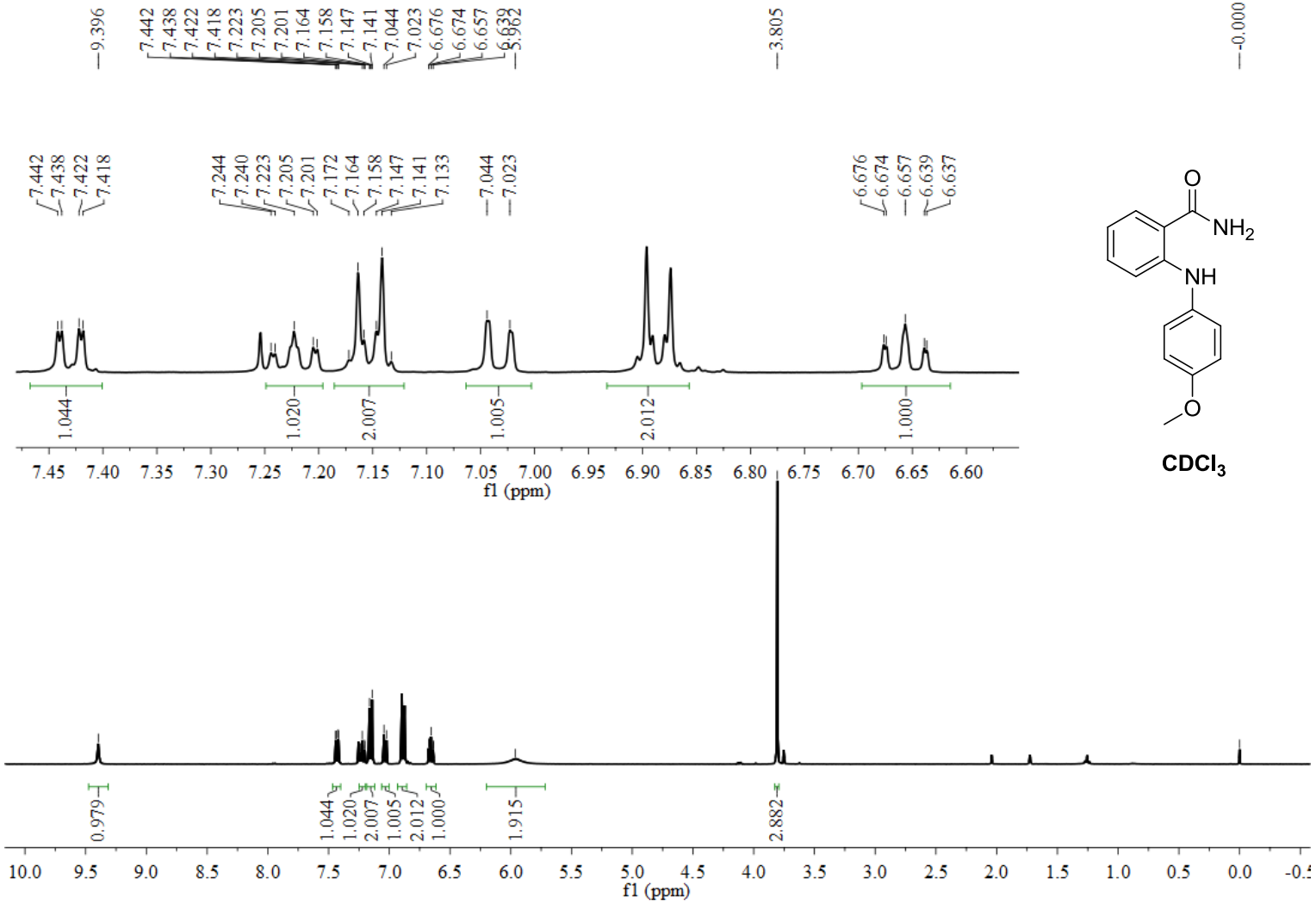
128.37
122.89
121.51
117.61
116.07
115.34
O
NH2
NH
CDCl3
175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60
f1 (ppm)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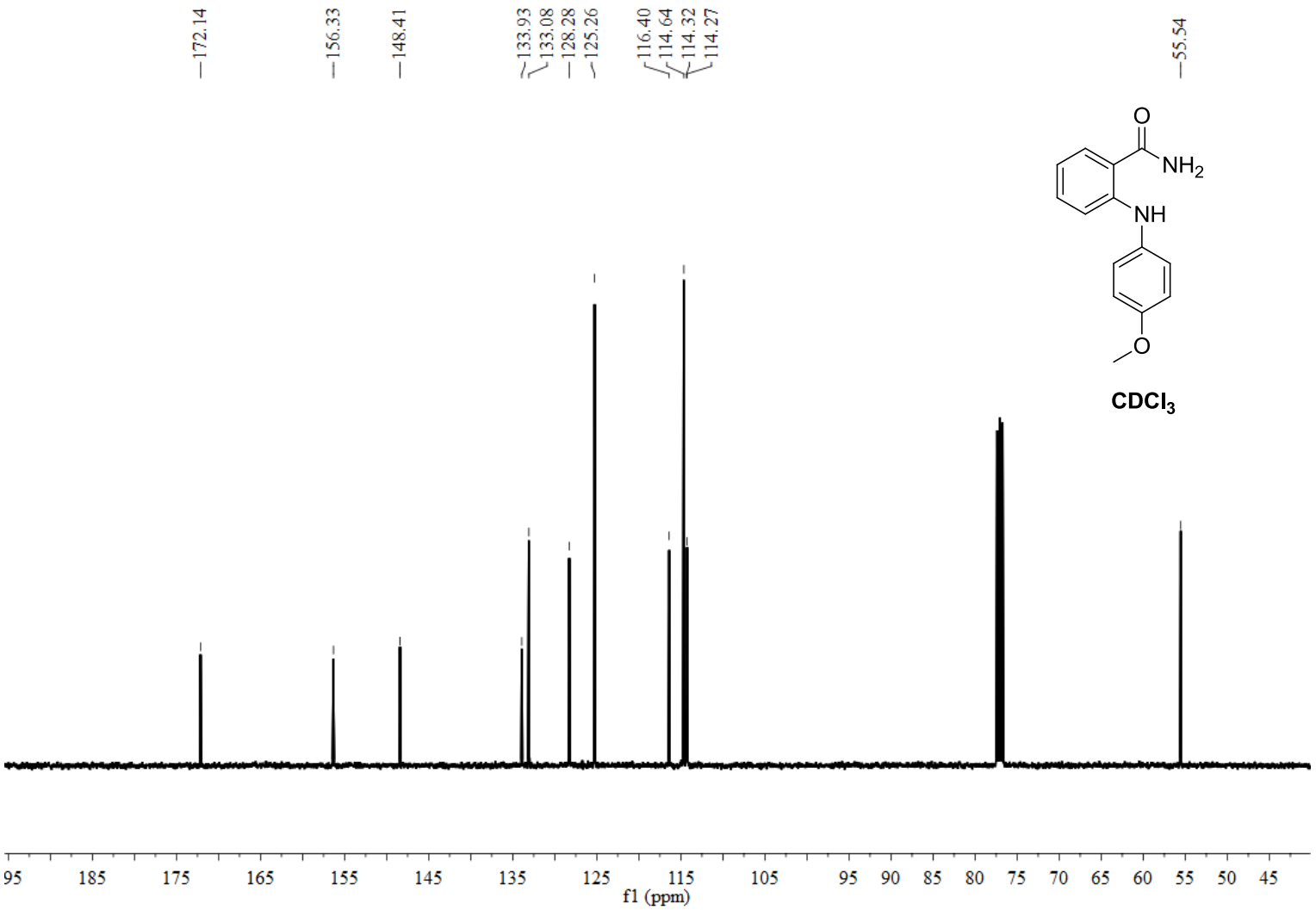
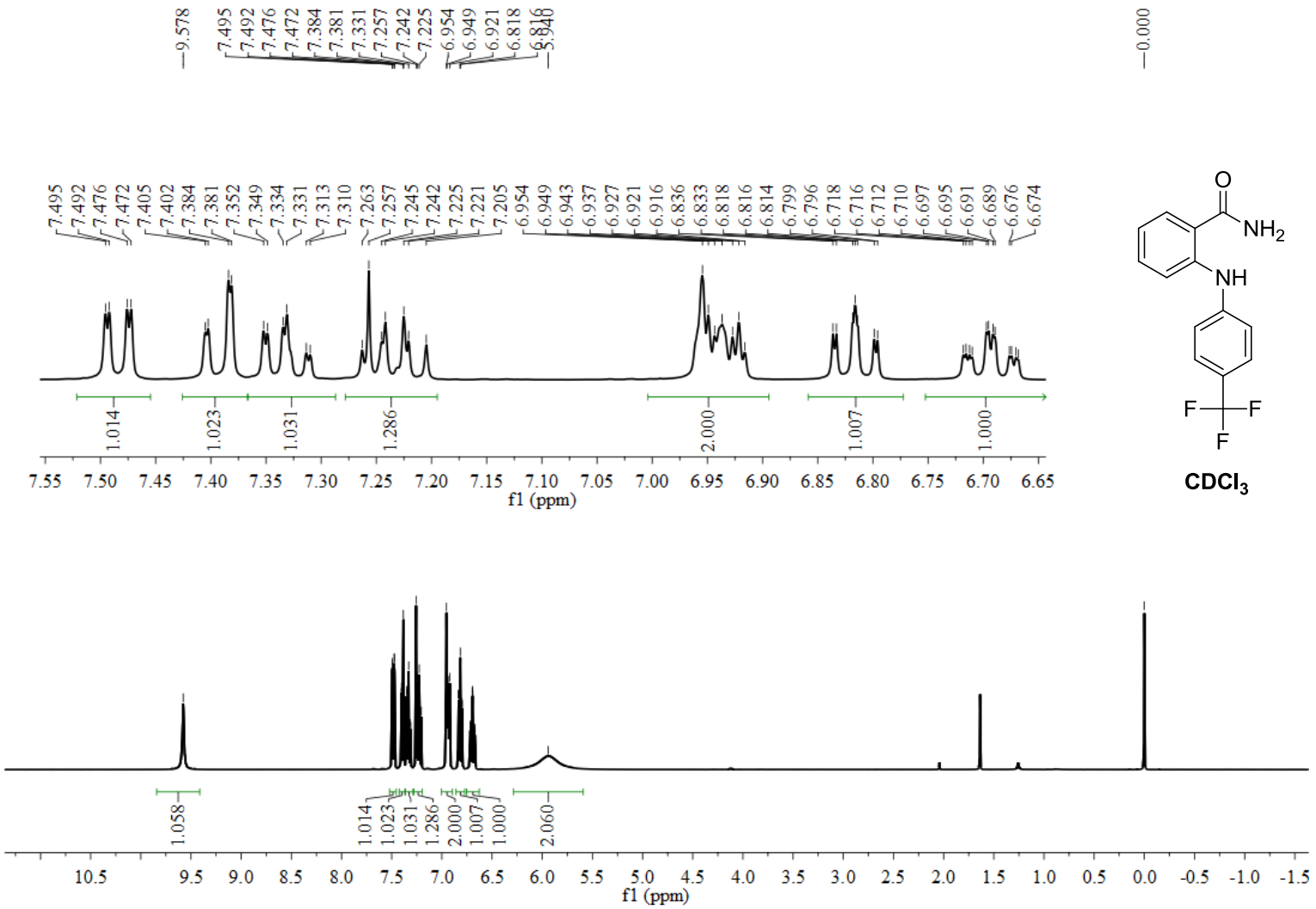
7.442
7.438
7.422
7.418
7.223
7.205
7.201
7.164
7.158
7.147
7.141
7.044
7.023
6.676
6.674
6.657
6.639
5.982
3.805
0.000
7.442
7.438
7.422
7.418
7.244
7.240
7.223
7.205
7.201
7.172
7.164
7.158
7.147
7.141
7.133
7.044
7.023
6.676
6.674
6.657
6.639
6.637
1.044
1.020
2.007
1.005
2.012
1.000
7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90 6.85 6.80 6.75 6.70 6.65 6.60
f1 (ppm)
O
NH2
NH
O
CDCl3
0.979
1.044
1.020
2.007
1.005
2.012
1.000
1.915
2.882
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 0.0
f1 (ppm)


172.14
156.33
148.41
133.93
133.08
128.28
125.26
116.40
114.64
114.32
114.27
55.54
O
NH2
NH
O
CDCl3
95 185 175 165 155 145 135 125 115 105 95 90 85 80 75 70 65 60 55 50 45
f1 (ppm)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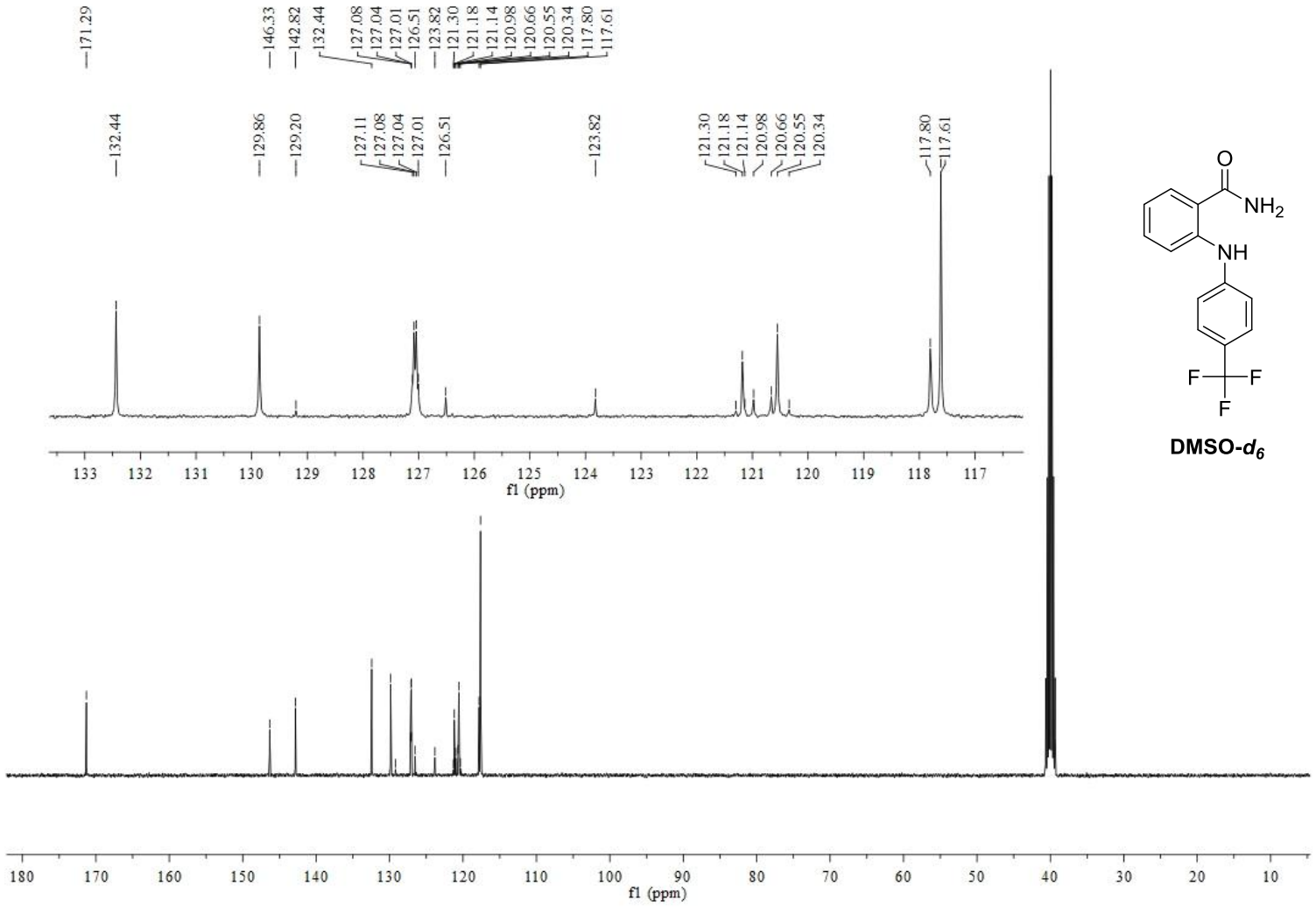
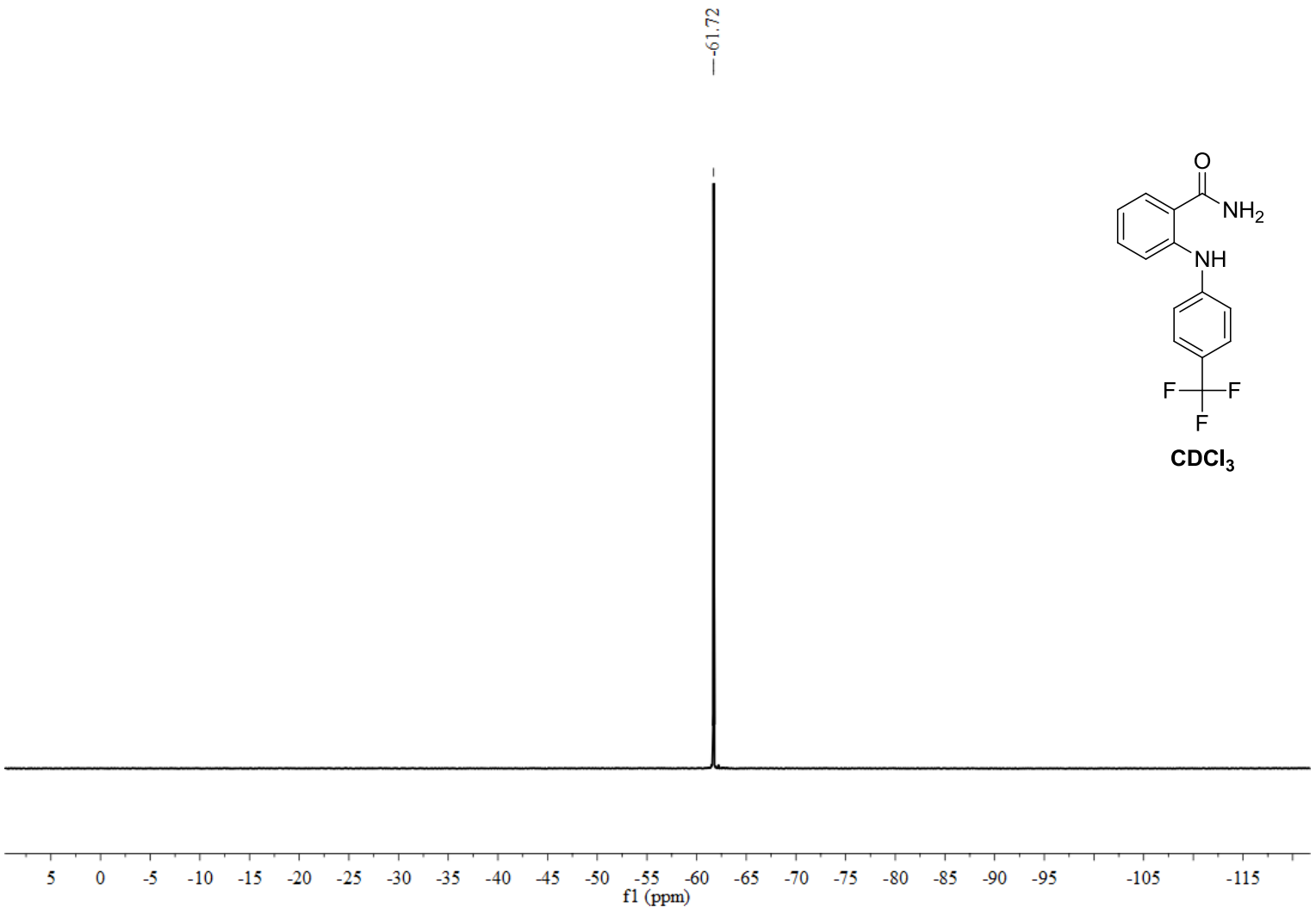
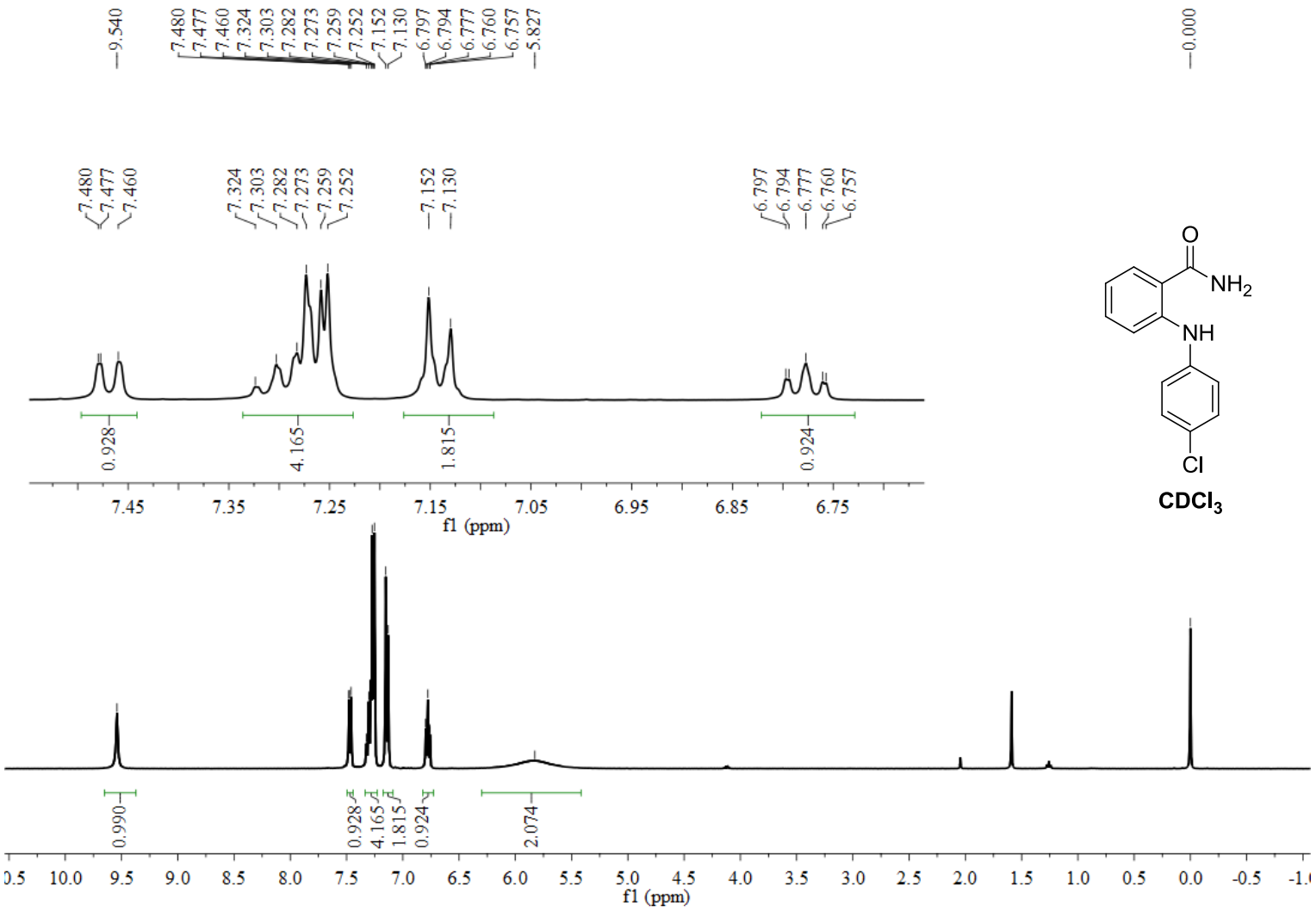
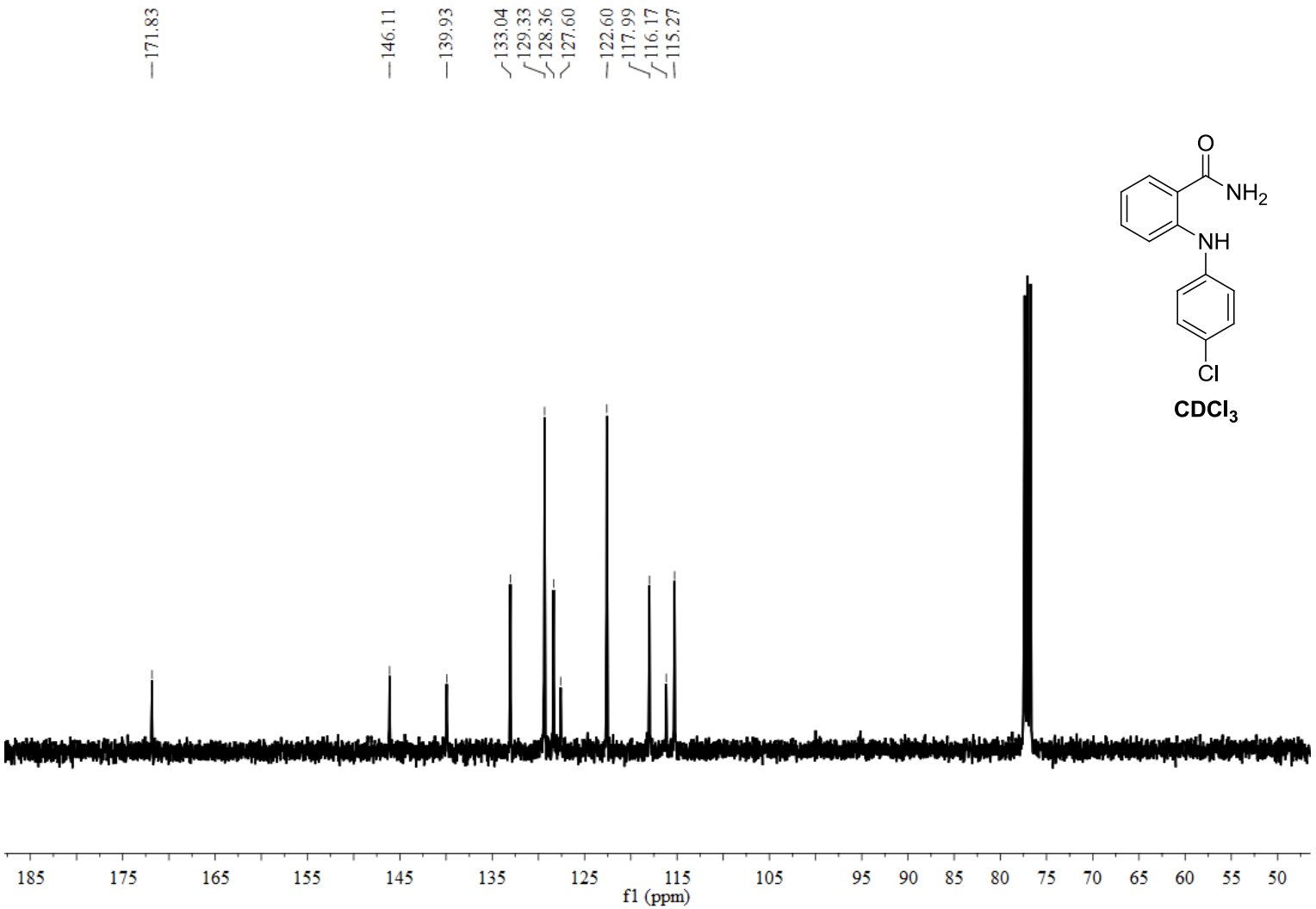
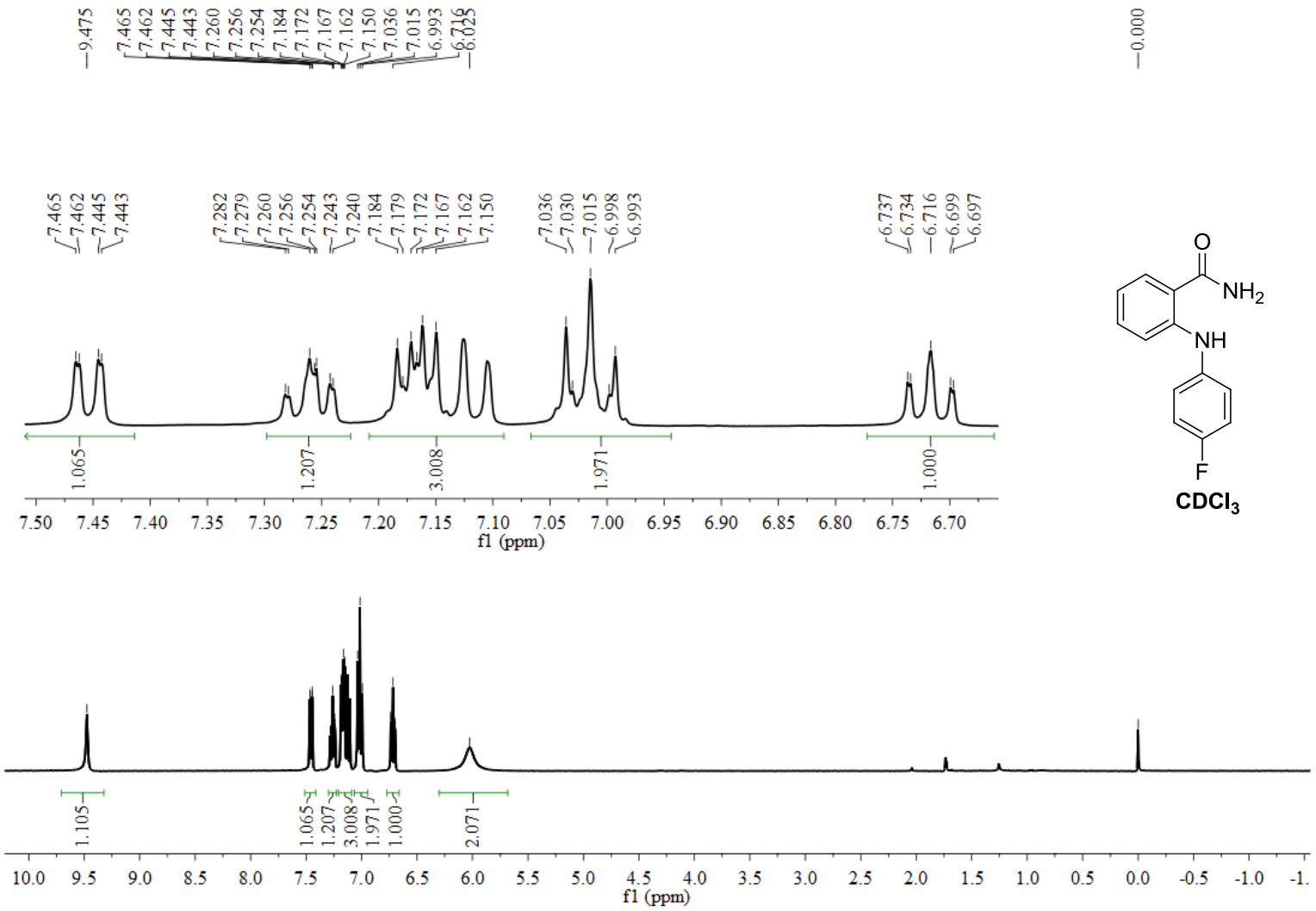
7.495
7.492
7.476
7.472
7.384
7.381
7.331
7.257
7.242
7.225
6.954
6.949
6.921
6.818
5.946
0.000
7.495
7.492
7.476
7.472
7.405
7.402
7.384
7.381
7.352
7.349
7.334
7.331
7.313
7.310
7.263
7.257
7.245
7.242
7.225
7.221
7.205
6.954
6.949
6.943
6.937
6.927
6.921
6.916
6.836
6.833
6.818
6.816
6.814
6.799
6.796
6.718
6.716
6.712
6.710
6.697
6.695
6.691
6.689
6.676
6.674
1.014
1.023
1.031
1.286
2.000
1.007
1.000
7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90 6.85 6.80 6.75 6.70 6.65
f1 (ppm)
O
NH2
NH
F
F
F
CDCl3
1.058
1.014
1.023
1.031
1.286
2.000
1.007
1.000
2.060
10.5 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 0.0 -0.5 -1.0 -1.5
f1 (ppm)

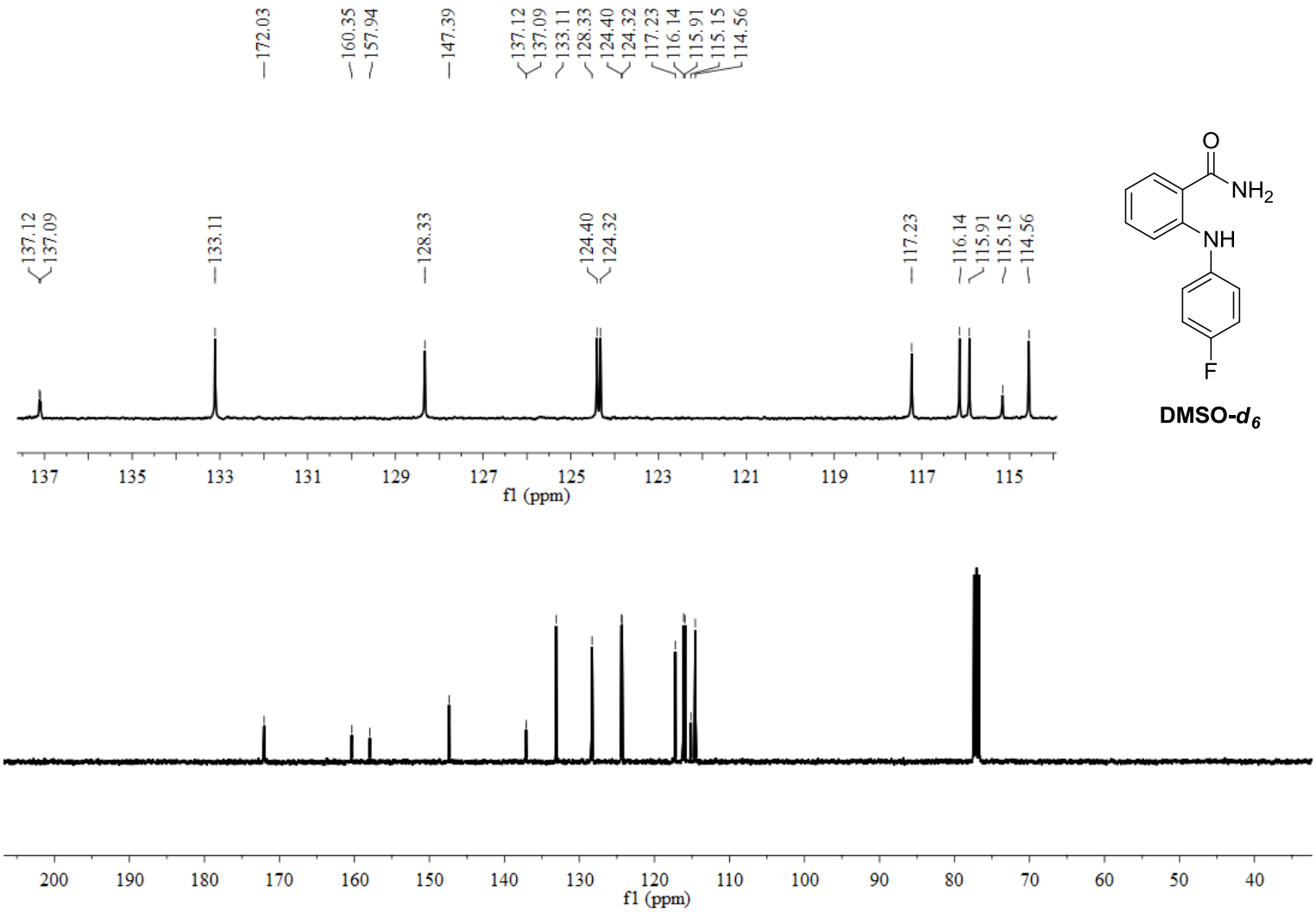

171.29
146.33
142.82
132.44
127.08
127.04
127.01
126.51
123.82
121.30
121.18
121.14
120.98
120.66
120.55
120.34
117.80
117.61
132.44
129.86
129.20
127.11
127.08
127.04
127.01
126.51
123.82
121.30
121.18
121.14
120.98
120.66
120.55
120.34
117.80
117.61
133 132 131 130 129 128 127 126 125 124 123 122 121 120 119 118 117
f1 (ppm)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)
O
NH2
NH
F
F
F
DMSO-d6


-61.72
O
NH2
NH
F
F
F
CDCl3
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-105
-115
f1 (ppm)


9.540
7.480
7.477
7.460
7.324
7.303
7.282
7.273
7.259
7.252
7.152
7.130
6.797
6.794
6.777
6.760
6.757
5.827
0.000
0.928
4.165
1.815
0.924
f1 (ppm)
O
NH2
NH
Cl
CDCl3
0.990
0.928
4.165
1.815
0.924
2.074
f1 (ppm)


171.83
146.11
139.93
133.04
129.33
128.36
127.60
122.60
117.99
116.17
115.27
O
NH2
NH
Cl
CDCl3
185
175
165
155
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
f1 (ppm)


9.475
7.465
7.462
7.445
7.443
7.260
7.256
7.254
7.184
7.172
7.167
7.162
7.150
7.036
7.015
6.993
6.716
6.025
0.000
7.465
7.462
7.445
7.443
7.282
7.279
7.260
7.256
7.254
7.243
7.240
7.184
7.179
7.172
7.167
7.162
7.150
7.036
7.030
7.015
6.998
6.993
6.737
6.734
6.716
6.699
6.697
1.065
1.207
3.008
1.971
1.000
7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90 6.85 6.80 6.75 6.70
f1 (ppm)
O
NH2
NH
F
CDCl3
1.105
1.065
1.207
3.008
1.971
1.000
2.071
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 0.0 -0.5 -1.0 -1.
f1 (ppm)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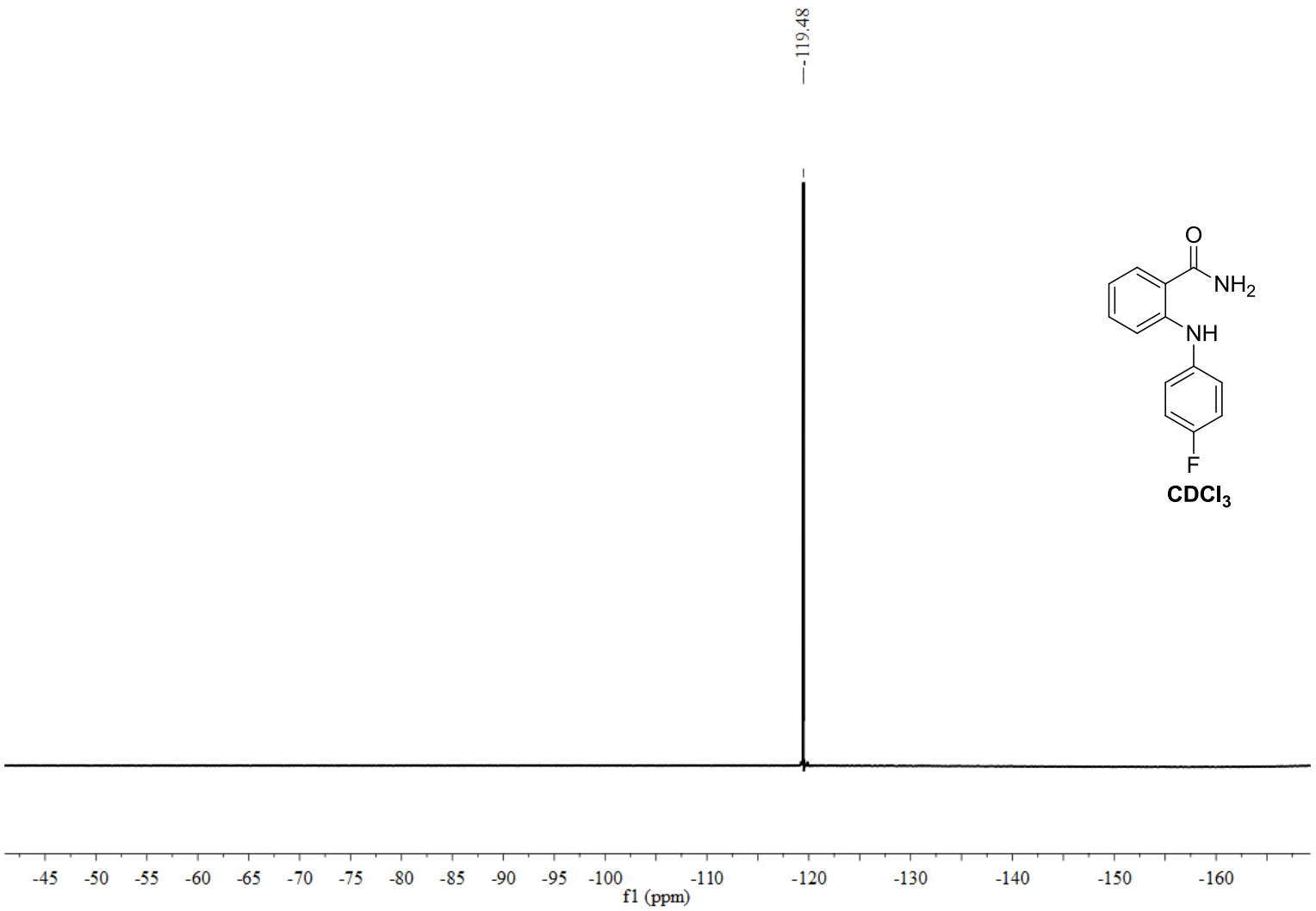
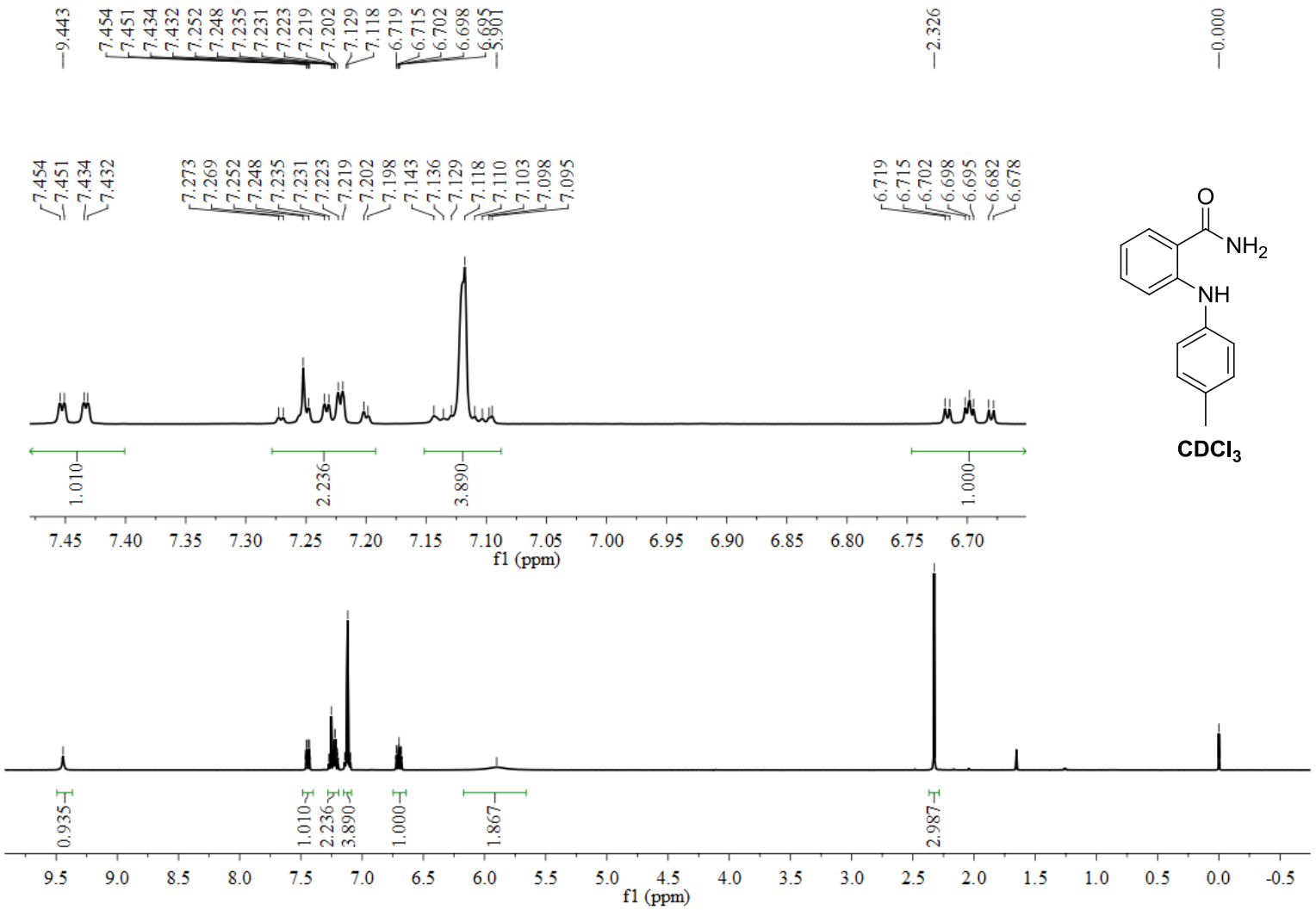
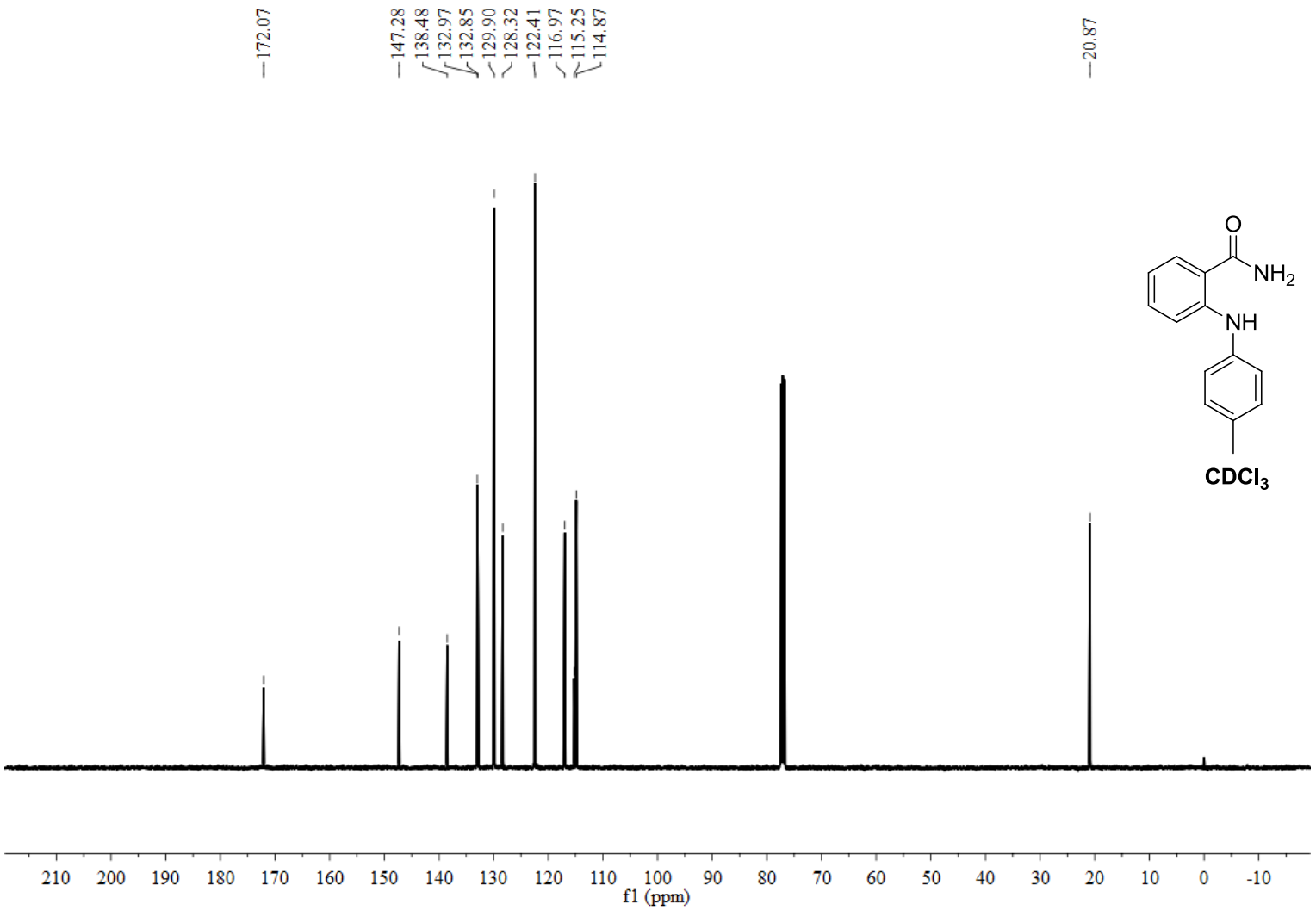
160.35
157.94
147.39
137.12
137.09
133.11
128.33
124.40
124.32
117.23
116.14
115.91
115.15
114.56
137
135
133
131
129
127
125
123
121
119
117
115
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
f1 (ppm)
O
NH2
NH
F
DMSO-d6


-119.48
O
NH2
NH
F
CDCl3
-45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)


9.443
7.454
7.451
7.434
7.432
7.252
7.248
7.235
7.231
7.223
7.219
7.202
7.129
7.118
6.719
6.715
6.702
6.698
6.695
5.801
2.326
0.000
7.454
7.451
7.434
7.432
7.273
7.269
7.252
7.248
7.235
7.231
7.223
7.219
7.202
7.198
7.143
7.136
7.129
7.118
7.110
7.103
7.098
7.095
6.719
6.715
6.702
6.698
6.695
6.682
6.678
O
NH2
NH
CDCl3
1.010
2.236
3.890
1.000
7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90 6.85 6.80 6.75 6.70
f1 (ppm)
0.935
1.010
2.236
3.890
1.000
1.867
2.987
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 0.0 -0.5
f1 (ppm)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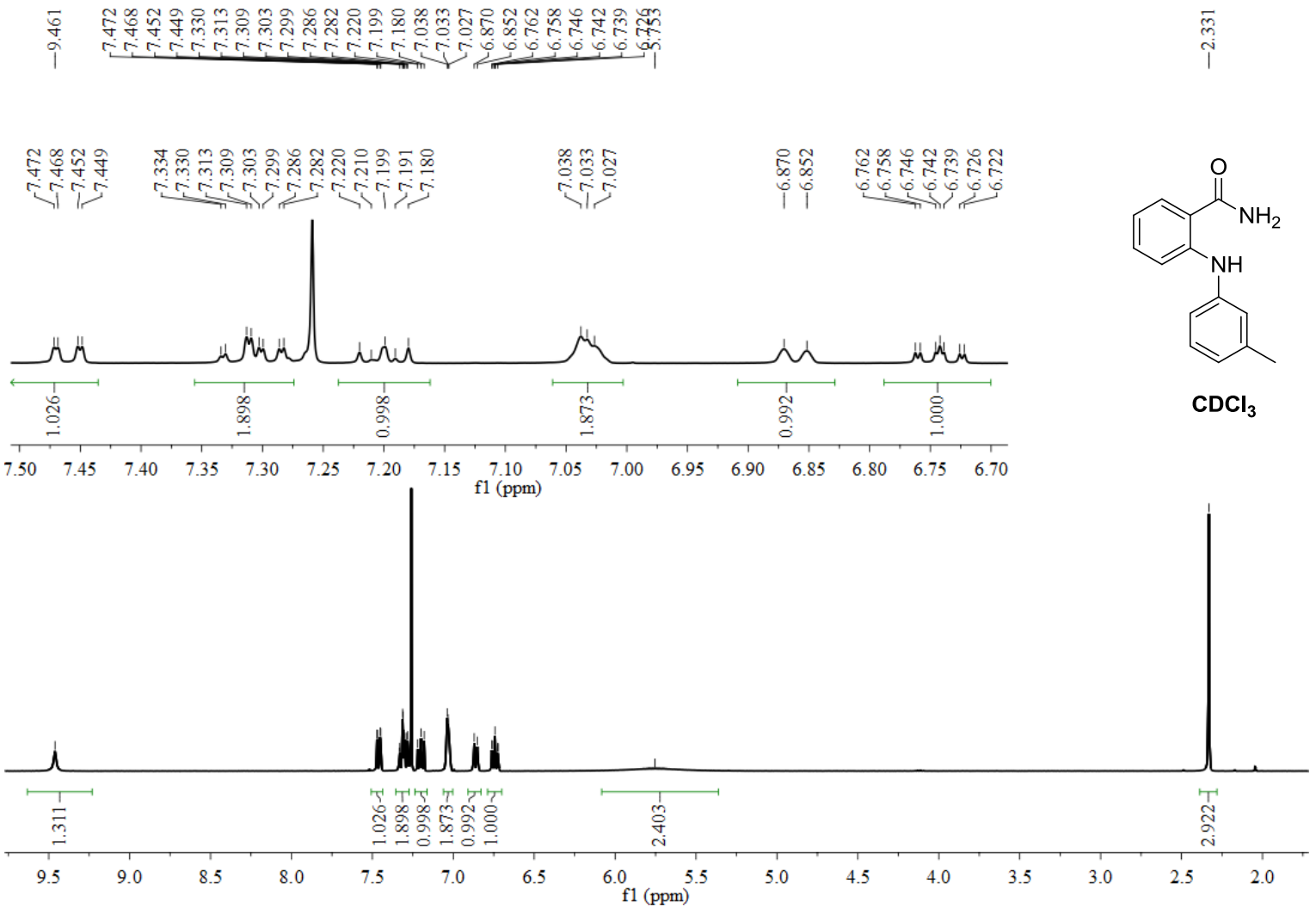
147.28
138.48
132.97
132.85
129.90
128.32
122.41
116.97
115.25
114.87
20.87
O
NH2
NH
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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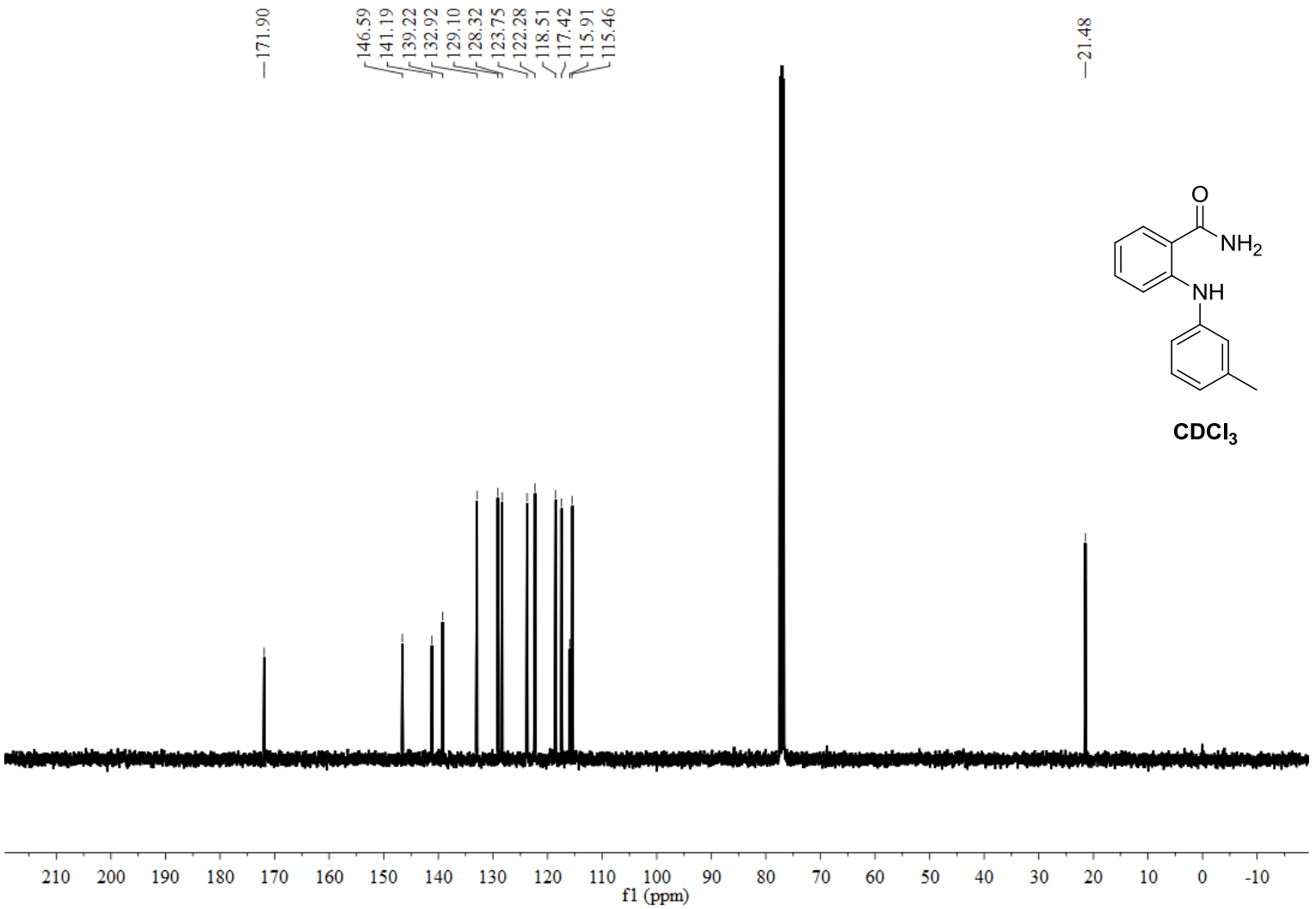
7.452
7.449
7.330
7.313
7.309
7.303
7.299
7.286
7.282
7.220
7.199
7.180
7.038
7.033
7.027
6.870
6.852
6.762
6.758
6.746
6.742
6.739
6.726
6.722
5.753
2.331
1.026
1.898
0.998
1.873
0.992
1.000
f1 (ppm)
1.311
2.403
2.922
O
NH2
NH
CDCl3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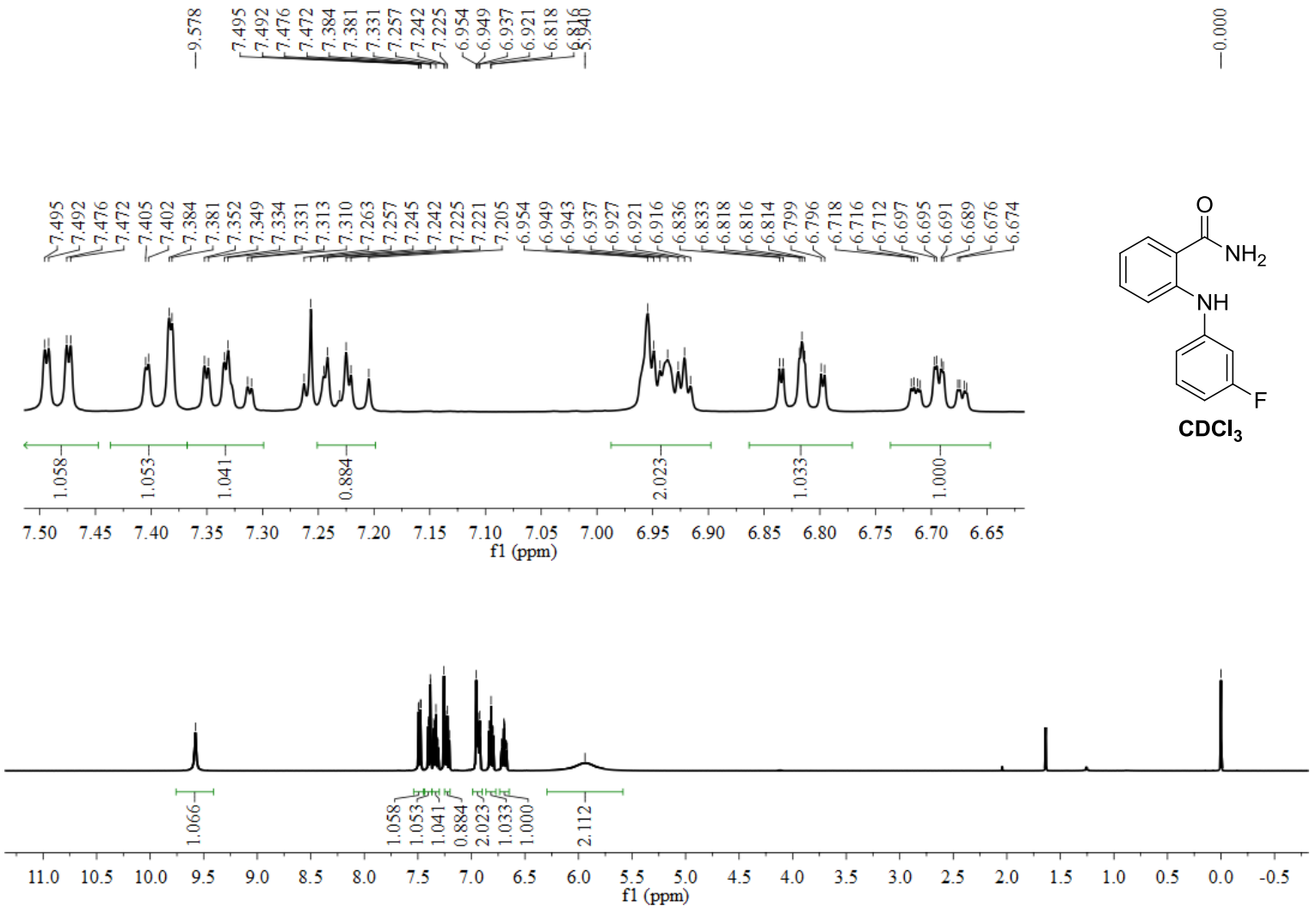
146.59
141.19
139.22
132.92
129.10
128.32
123.75
122.28
118.51
117.42
115.91
115.46
21.48
O
NH2
NH
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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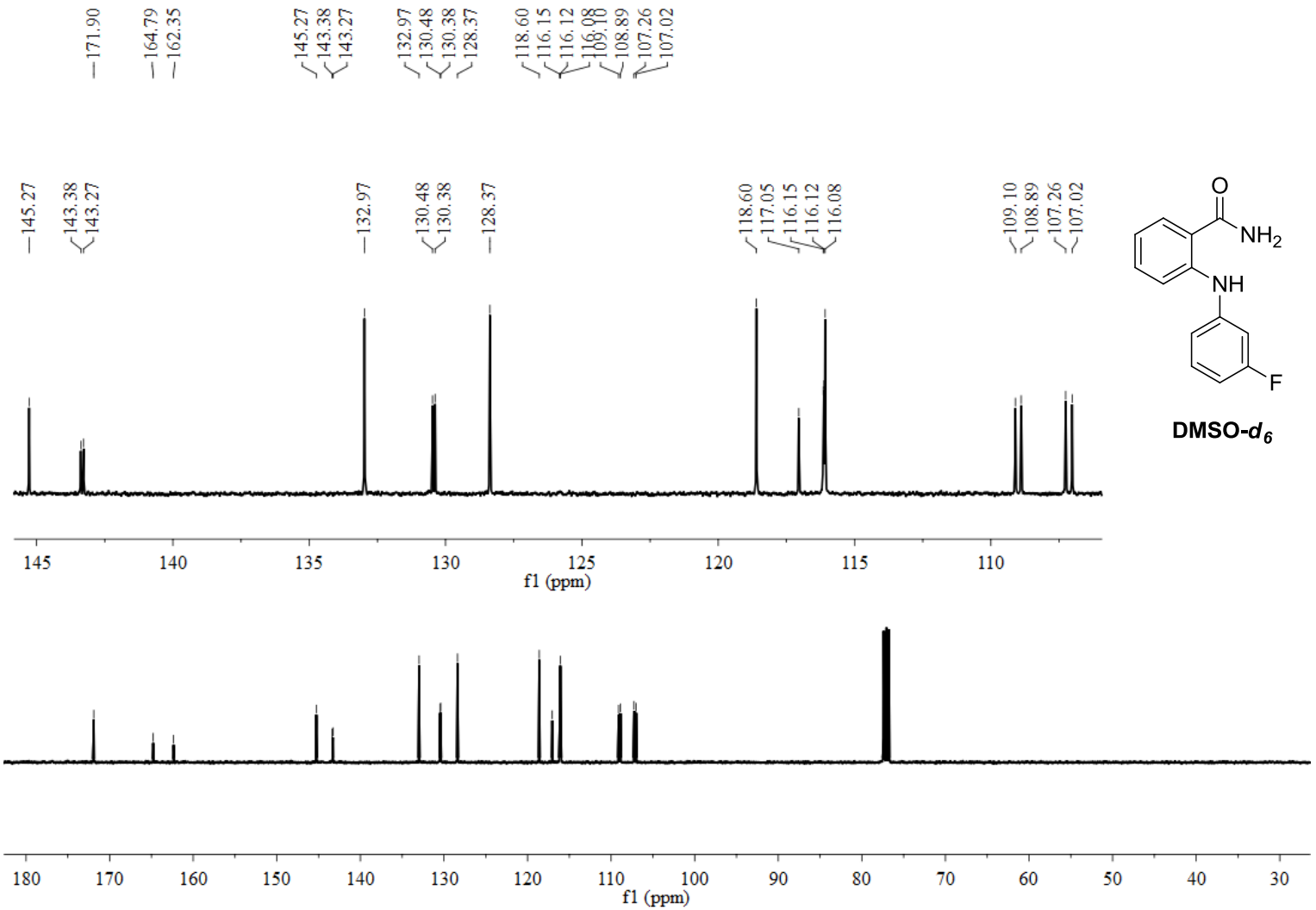
7.495
7.492
7.476
7.472
7.384
7.381
7.331
7.257
7.242
7.225
6.954
6.949
6.937
6.921
6.818
6.816
5.940
0.000
7.495
7.492
7.476
7.472
7.405
7.402
7.384
7.381
7.352
7.349
7.334
7.331
7.313
7.310
7.263
7.257
7.245
7.242
7.225
7.221
7.205
6.954
6.949
6.943
6.937
6.927
6.921
6.916
6.836
6.833
6.818
6.816
6.814
6.799
6.796
6.718
6.716
6.712
6.697
6.695
6.691
6.689
6.676
6.674
1.058
1.053
1.041
0.884
2.023
1.033
1.000
7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90 6.85 6.80 6.75 6.70 6.65
f1 (ppm)
O
NH2
NH
F
CDCl3
1.066
1.058
1.053
1.041
0.884
2.023
1.033
1.000
2.112
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 0.0 -0.5
f1 (ppm)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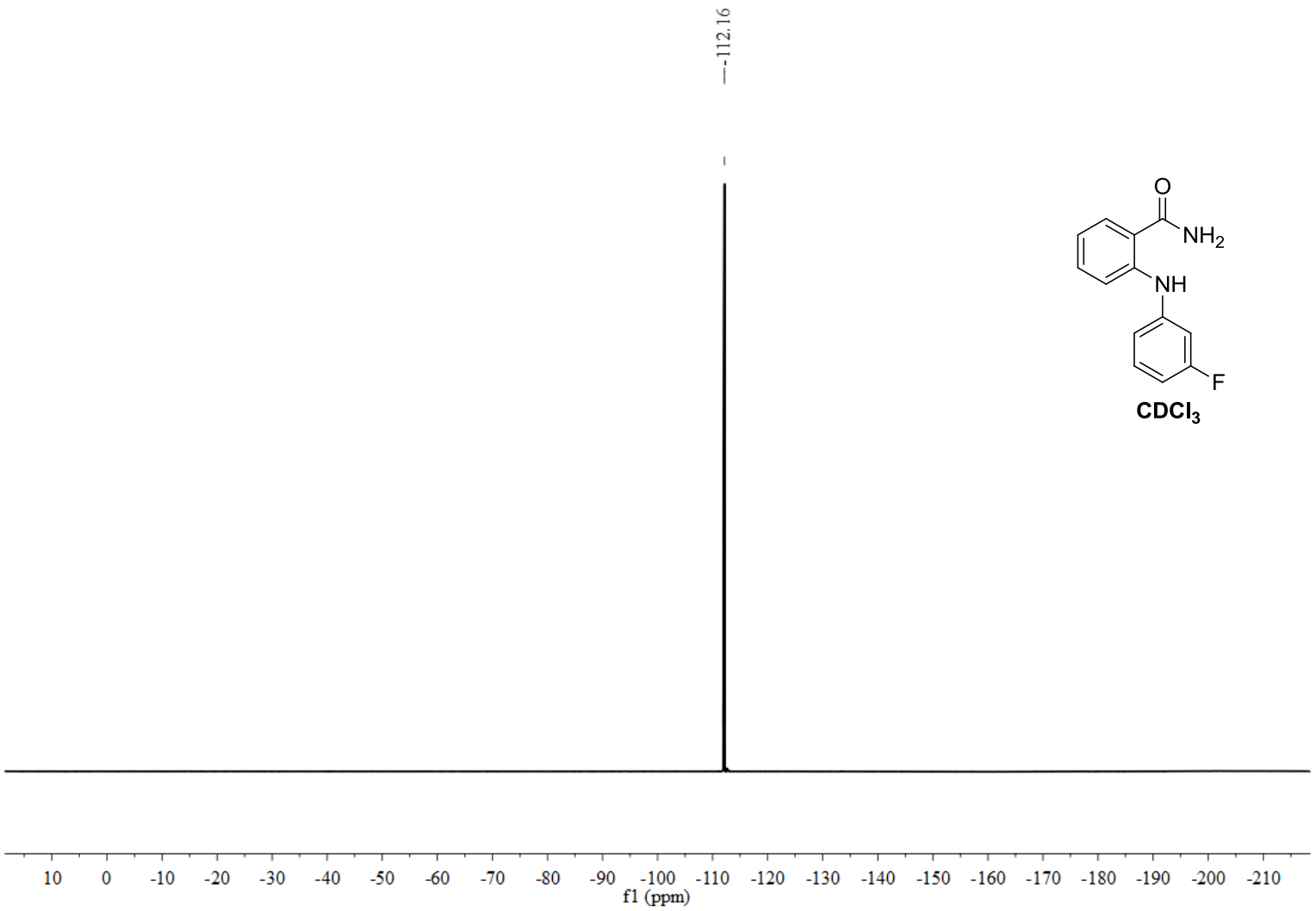
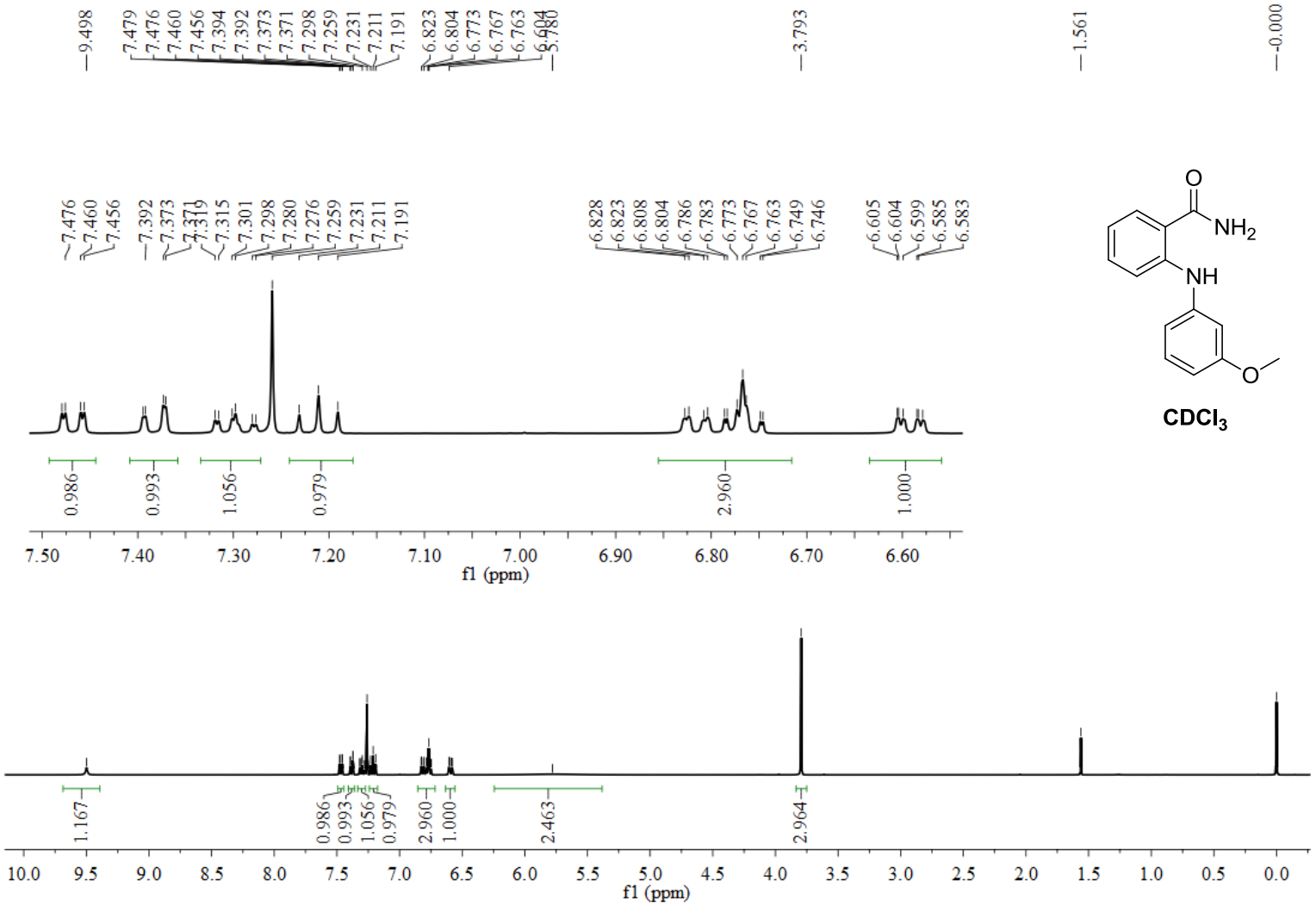
164.79
162.35
145.27
143.38
143.27
132.97
130.48
130.38
128.37
118.60
116.15
116.12
116.08
109.10
108.89
107.26
107.02
O
NH2
NH
F
DMSO-d6
f1 (ppm)
f1 (ppm)


-112.16
O
NH2
NH
F
CDCl3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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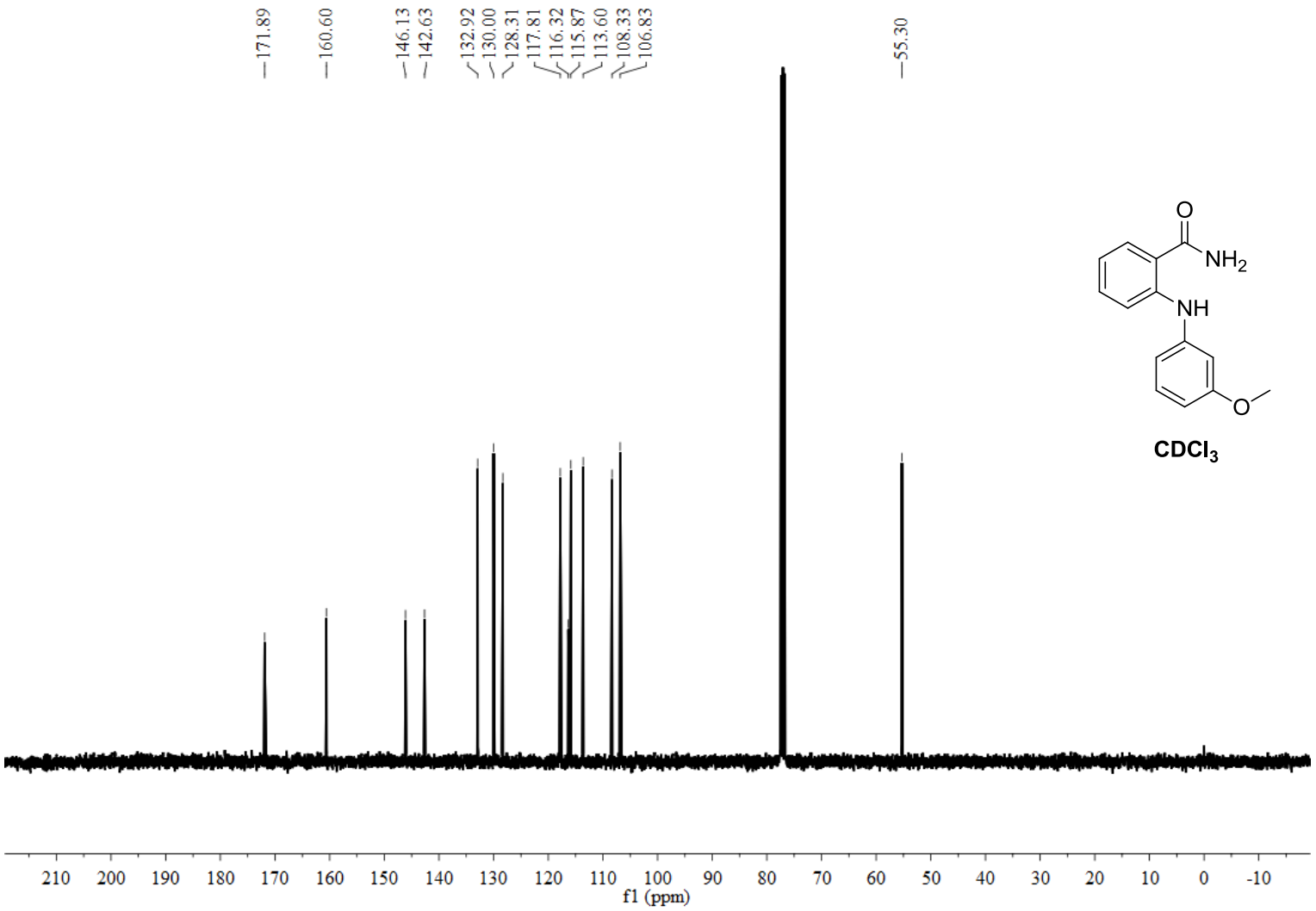
7.373
7.371
7.298
7.259
7.231
7.211
7.191
6.823
6.804
6.773
6.767
6.763
6.604
5.780
3.793
1.561
0.000
7.476
7.460
7.456
7.392
7.373
7.371
7.319
7.315
7.301
7.298
7.280
7.276
7.259
7.231
7.211
7.191
6.828
6.823
6.808
6.804
6.786
6.783
6.773
6.767
6.763
6.749
6.746
6.605
6.604
6.599
6.585
6.583
0.986
0.993
1.056
0.979
2.960
1.000
7.50
7.40
7.30
7.20
7.10
7.00
6.90
6.80
6.70
6.60
f1 (ppm)
O
NH2
NH
O
CDCl3
1.167
0.986
0.993
1.056
0.979
2.960
1.000
2.463
2.964
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
0.0
f1 (ppm)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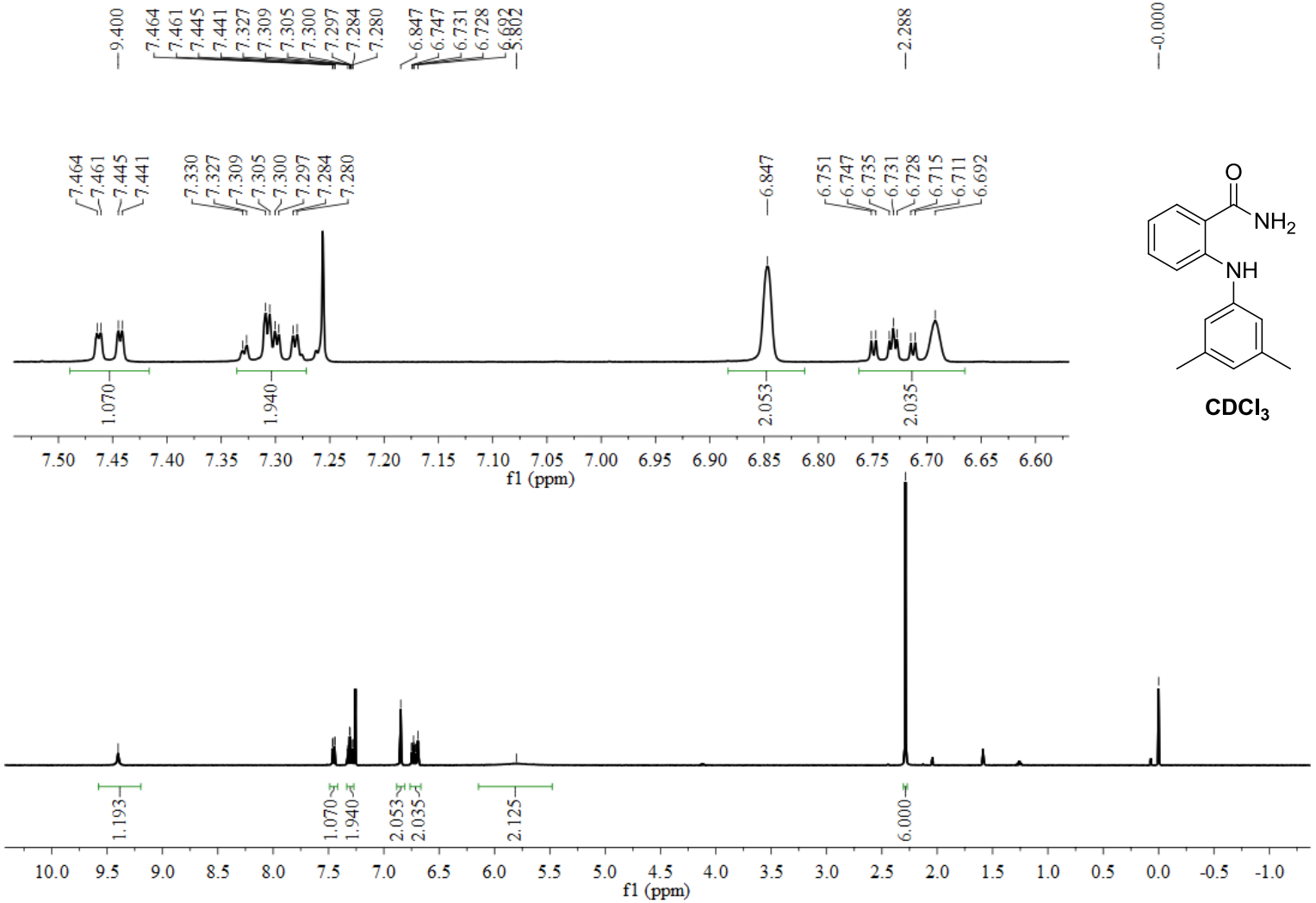
160.60
146.13
142.63
132.92
130.00
128.31
117.81
116.32
115.87
113.60
108.33
106.83
55.30
O
NH2
NH
O
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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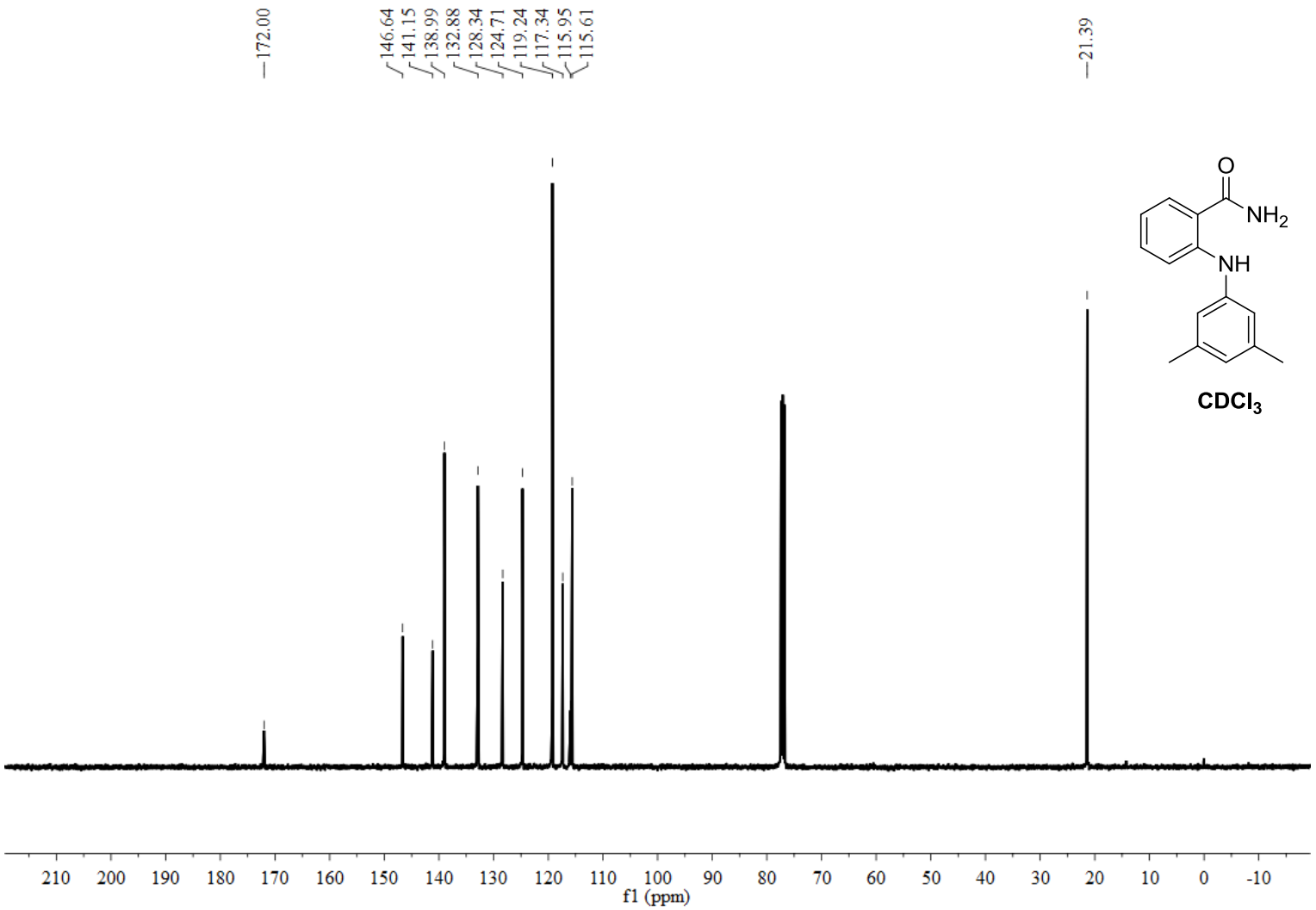
7.445
7.441
7.327
7.309
7.305
7.300
7.297
7.284
7.280
6.847
6.747
6.731
6.728
6.682
5.802
2.288
0.000
7.464
7.461
7.445
7.441
7.330
7.327
7.309
7.305
7.300
7.297
7.284
7.280
6.847
6.751
6.747
6.735
6.731
6.728
6.715
6.711
6.692
1.070
1.940
2.053
2.035
7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90 6.85 6.80 6.75 6.70 6.65 6.60
f1 (ppm)
O
NH2
NH
CDCl3
1.193
1.070
1.940
2.053
2.035
2.125
6.000
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 0.0 -0.5 -1.0
f1 (ppm)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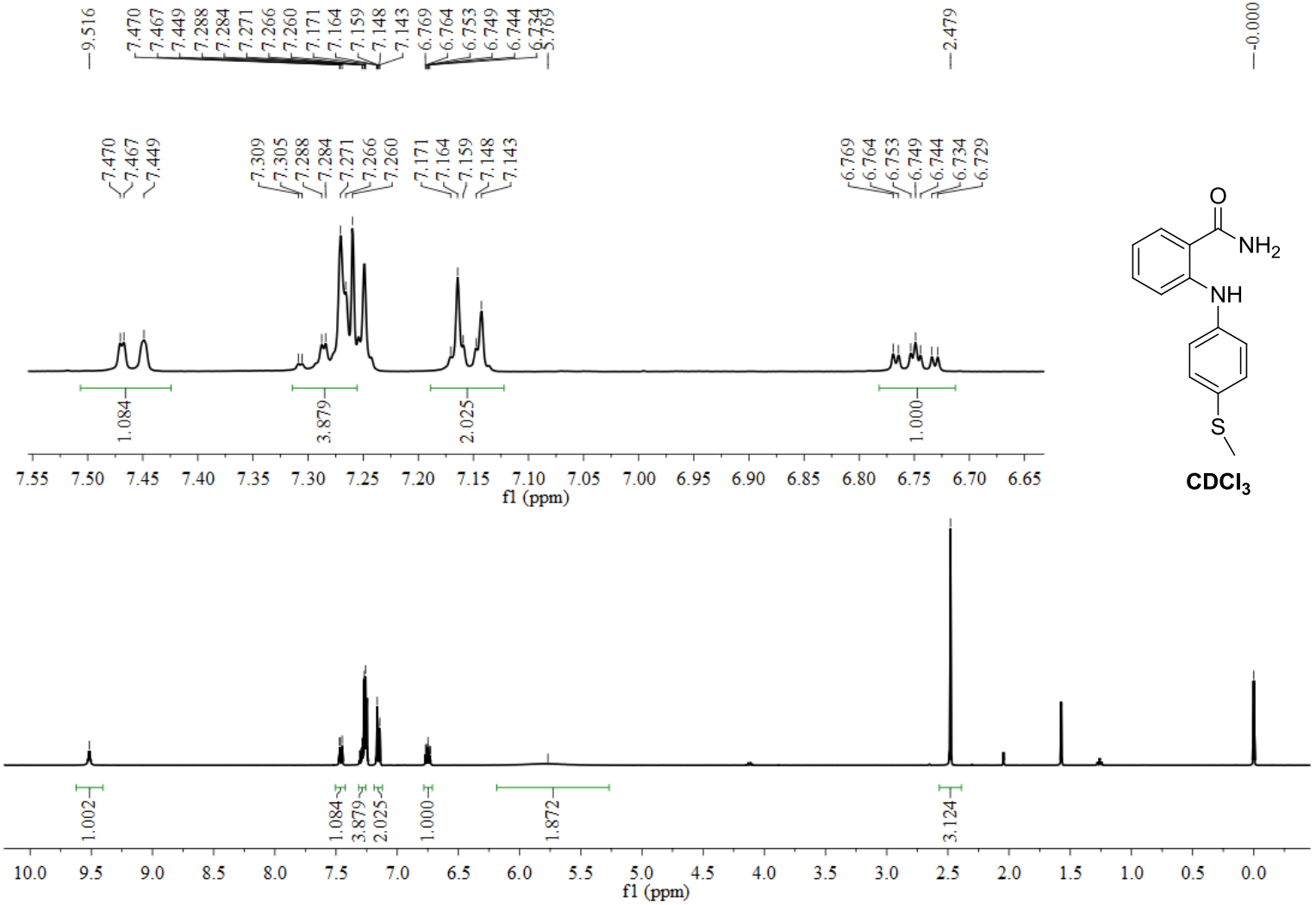
141.15
138.99
132.88
128.34
124.71
119.24
117.34
115.95
115.61
21.39
O
NH2
NH
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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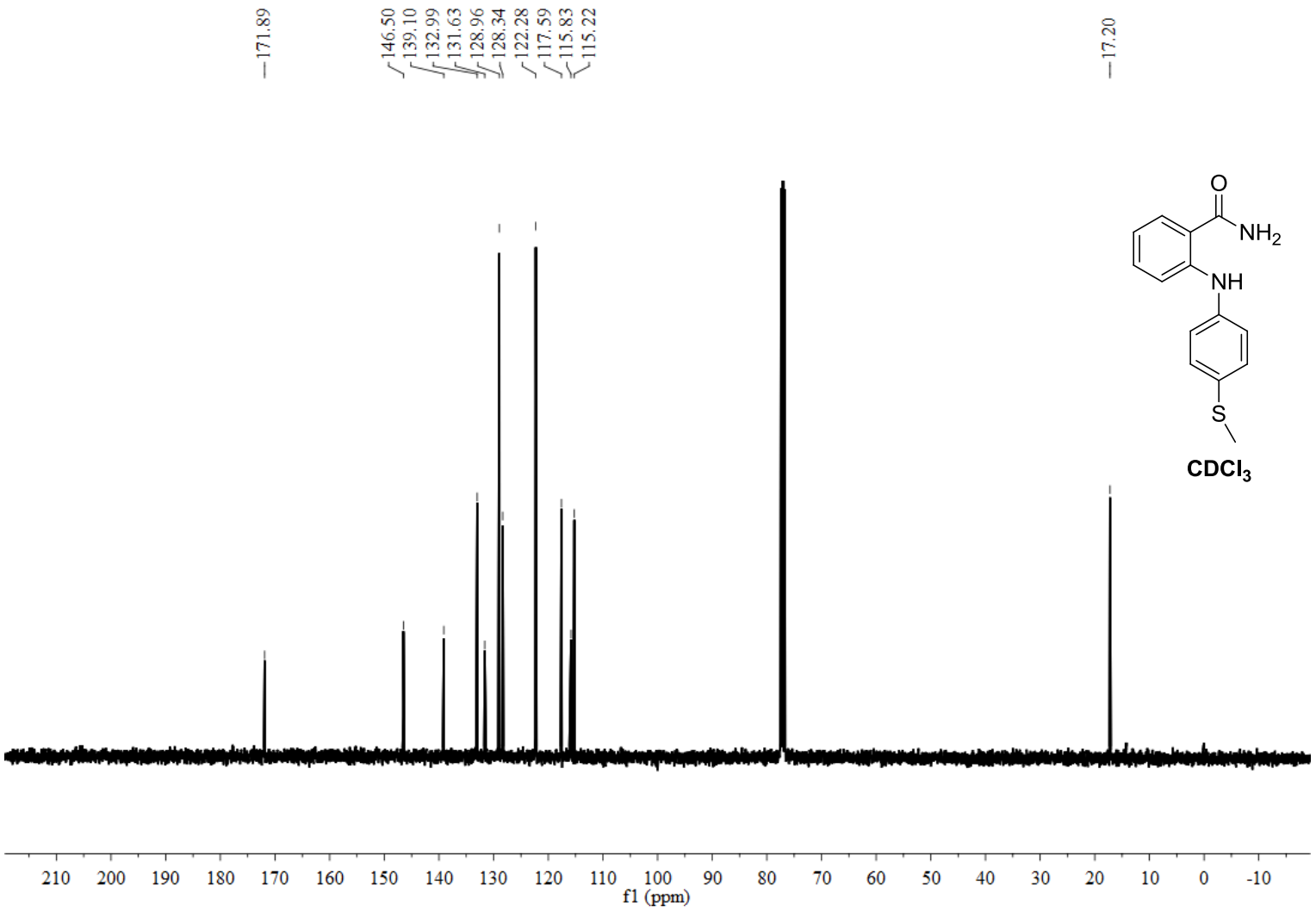
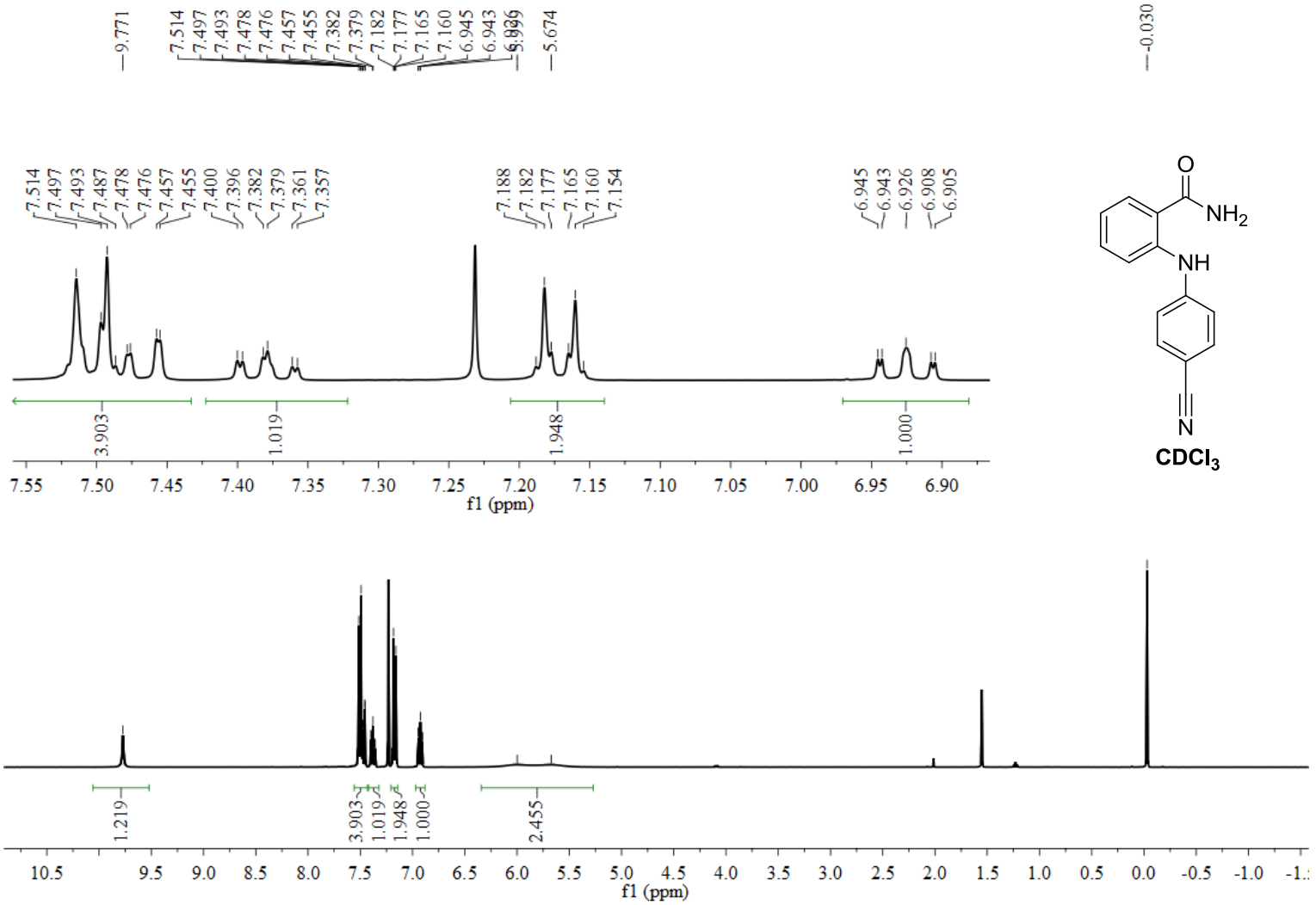
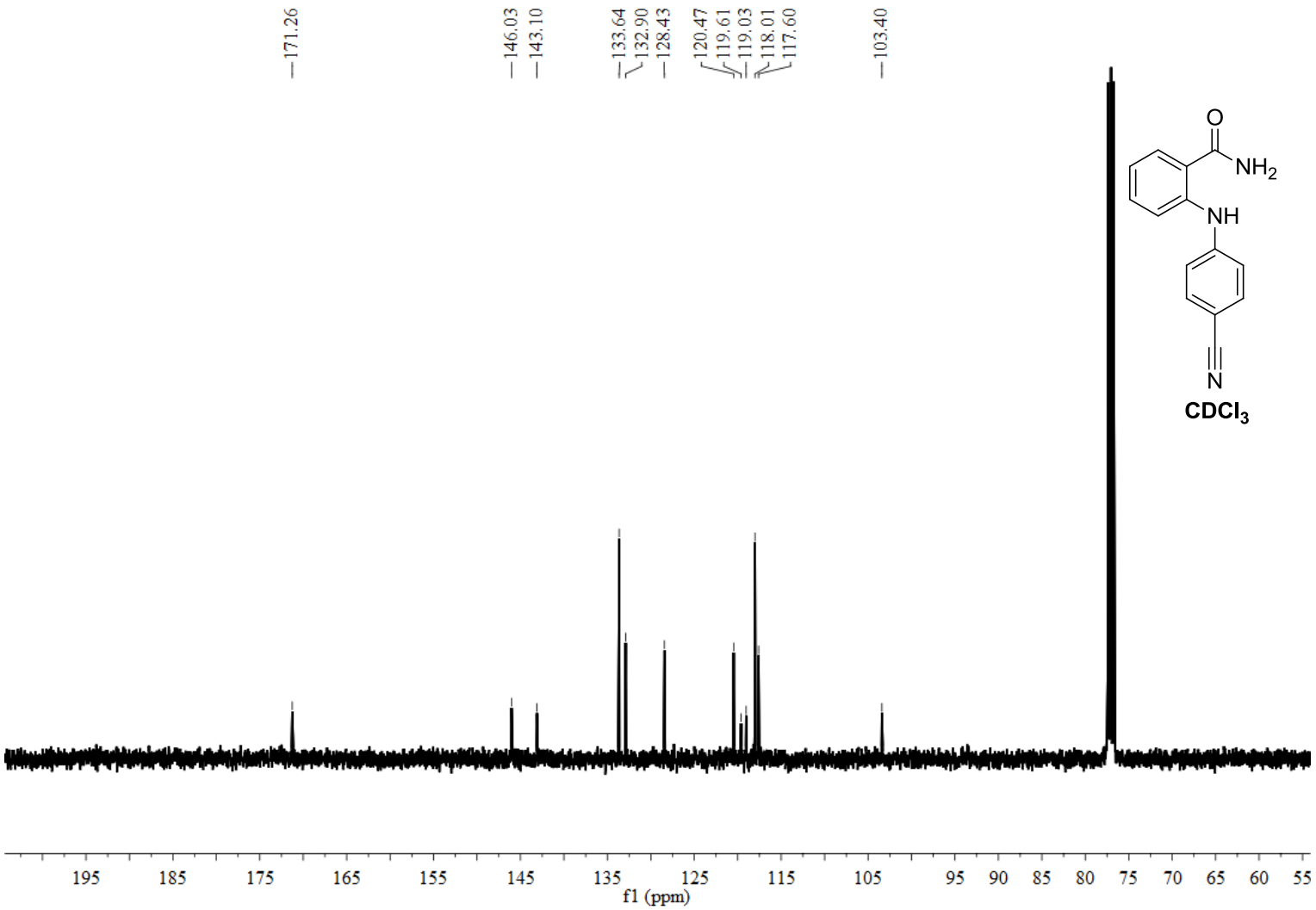
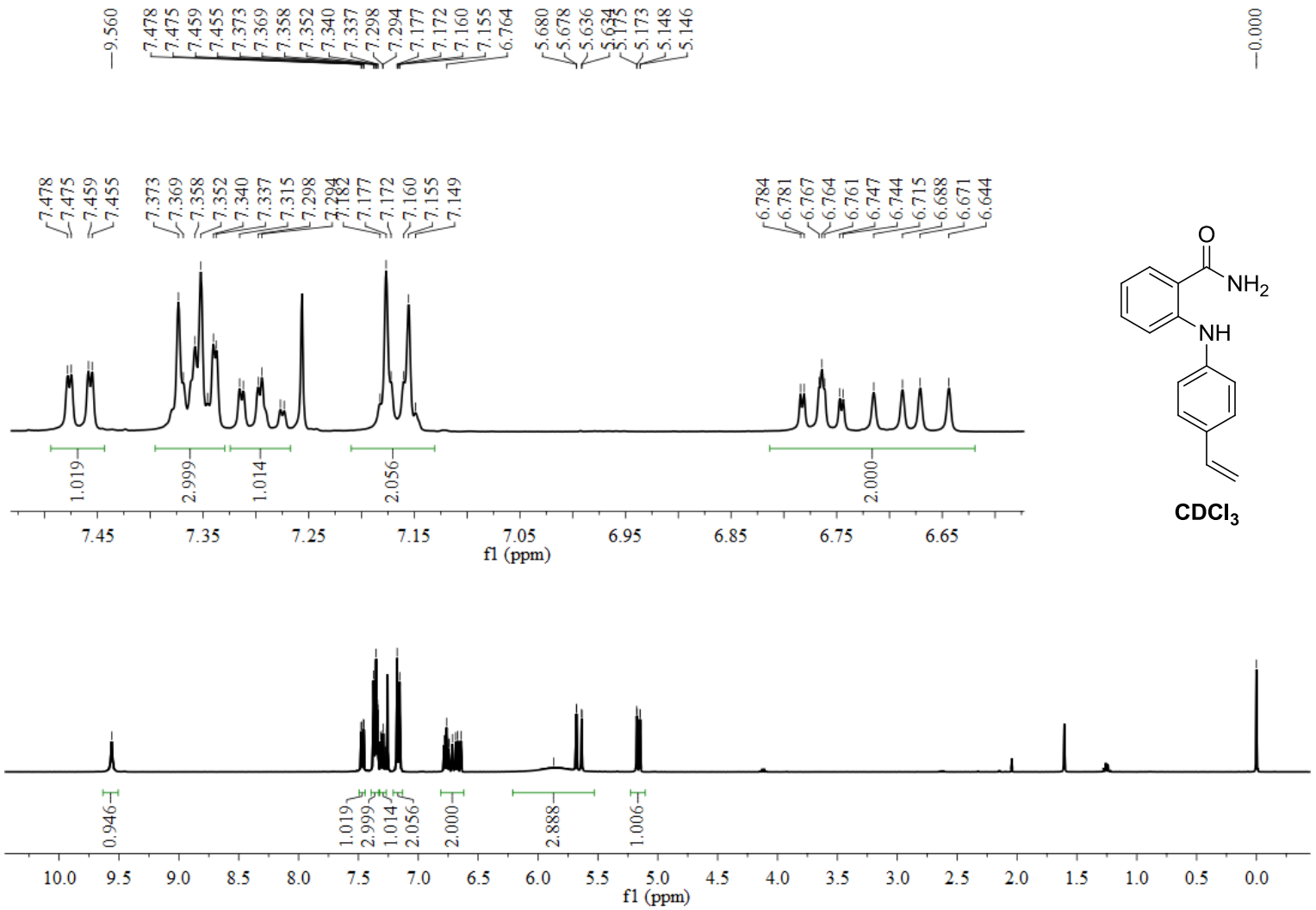
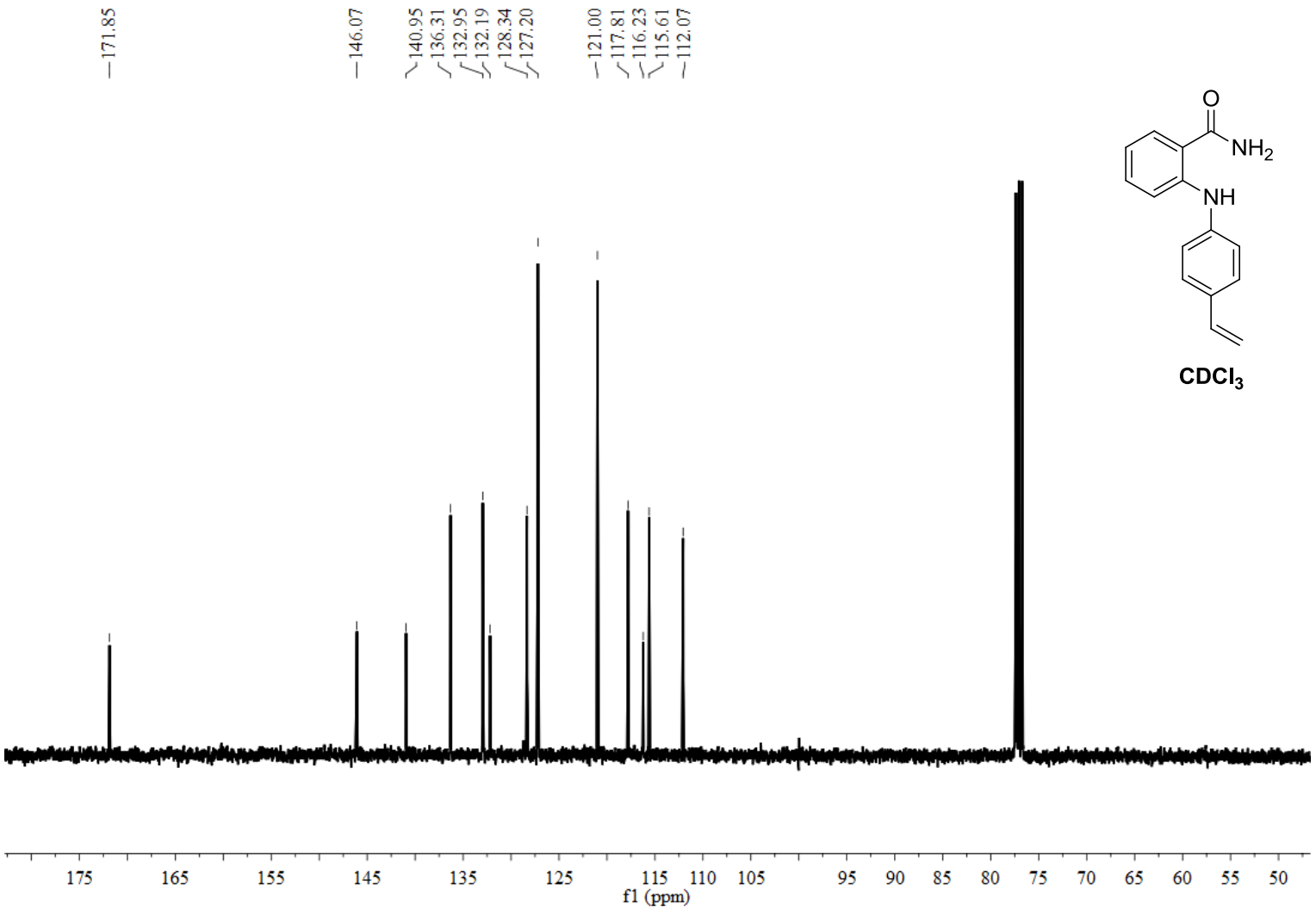
7.470
7.467
7.449
7.288
7.284
7.271
7.266
7.260
7.171
7.164
7.159
7.148
7.143
6.769
6.764
6.753
6.749
6.744
6.734
3.769
2.479
0.000
7.309
7.305
6.729
1.084
3.879
2.025
1.000
1.002
1.872
3.124
f1 (ppm)
O
NH2
NH
S
CDCl3

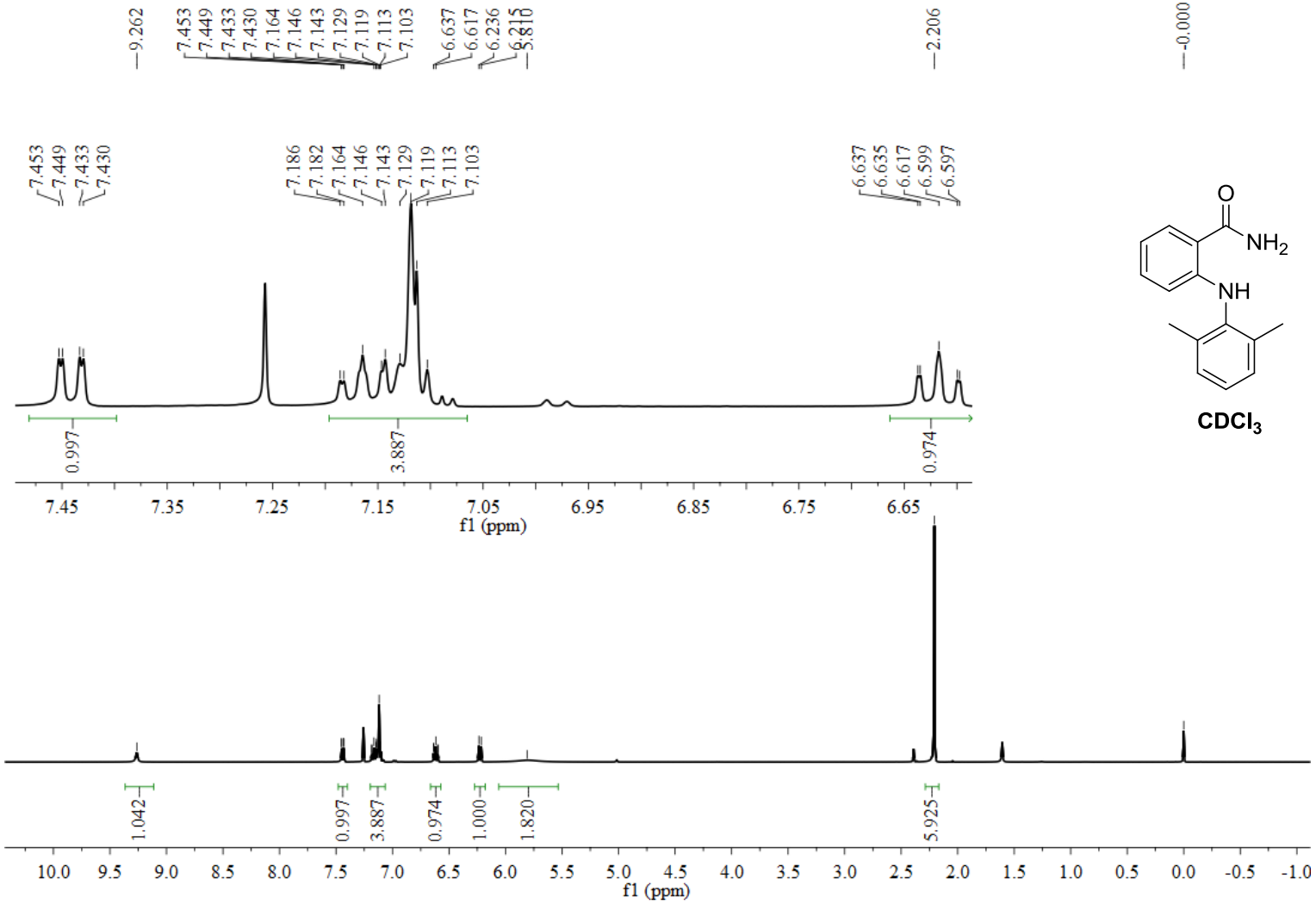

171.89
146.50
139.10
132.99
131.63
128.96
128.34
122.28
117.59
115.83
115.22
17.20
O
NH2
NH
S
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

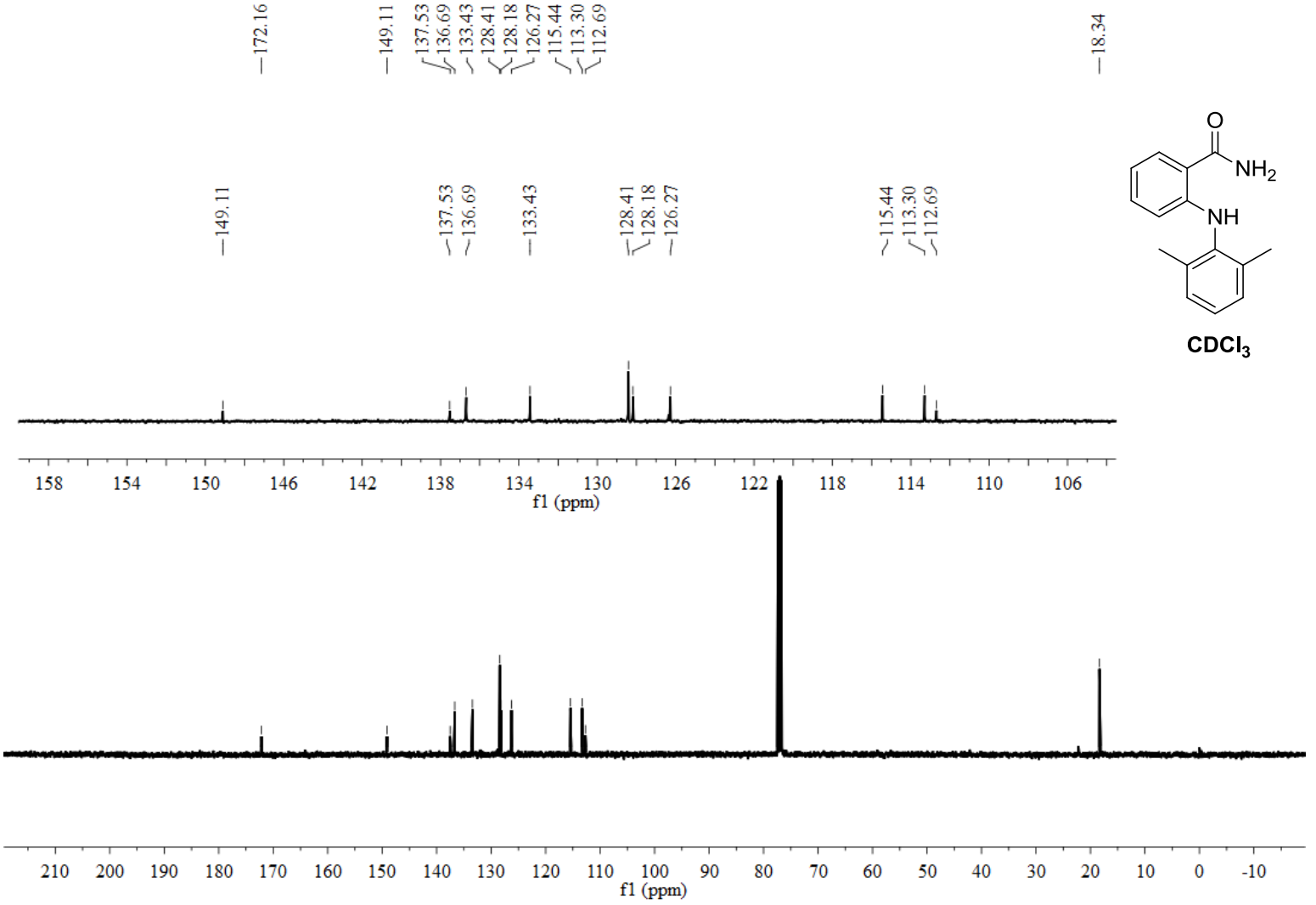

9.771
7.514
7.497
7.493
7.478
7.476
7.457
7.455
7.382
7.379
7.182
7.177
7.165
7.160
6.945
6.943
5.674
-0.030
7.514
7.497
7.493
7.487
7.478
7.476
7.457
7.455
7.400
7.396
7.382
7.379
7.361
7.357
7.188
7.182
7.177
7.165
7.160
7.154
6.945
6.943
6.926
6.908
6.905
3.903
1.019
1.948
1.000
7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90
f1 (ppm)
O
NH2
NH
N
CDCl3
1.219
3.903
1.019
1.948
1.000
2.455
10.5 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 0.0 -0.5 -1.0
f1 (ppm)

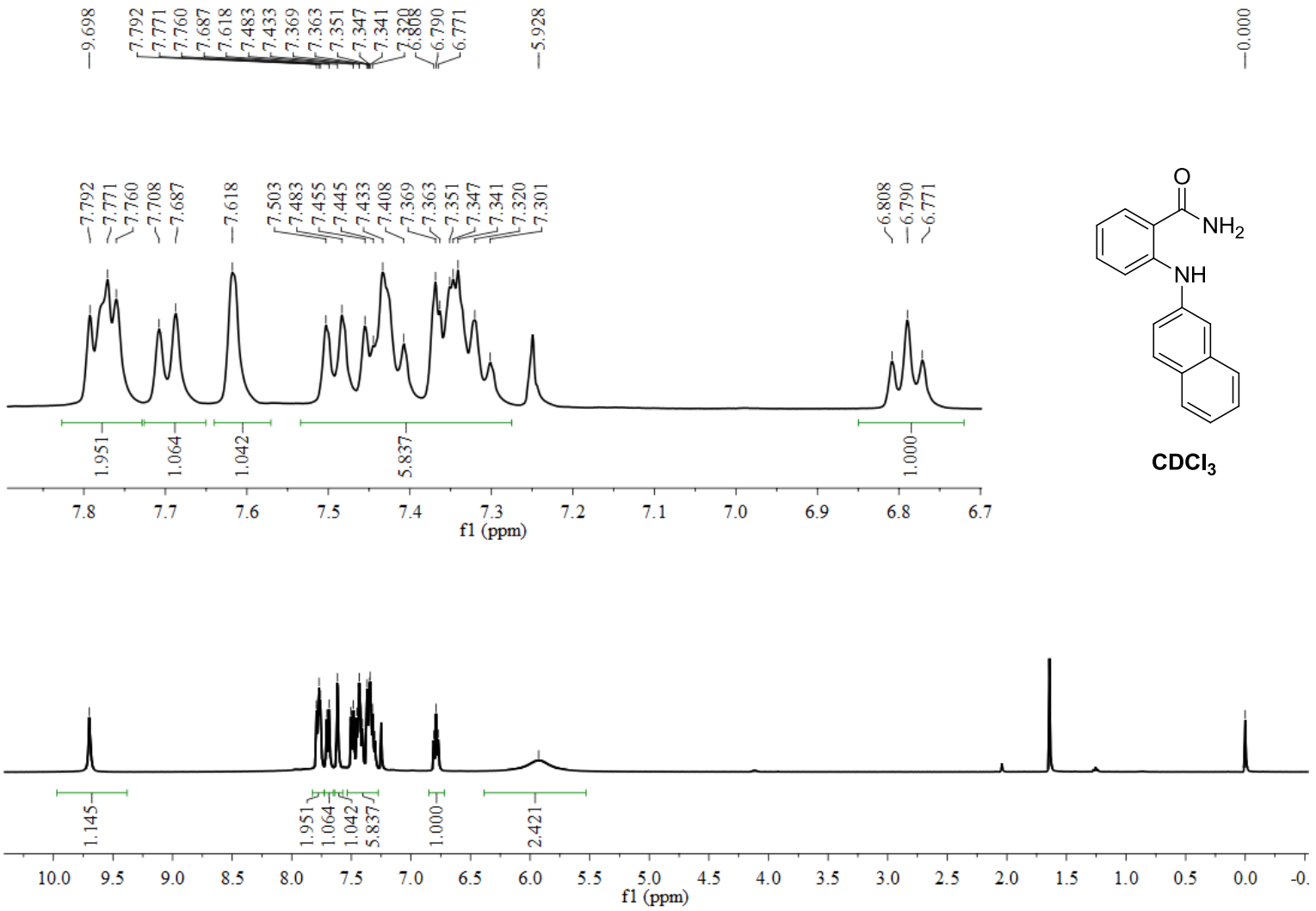

171.26
146.03
143.10
133.64
132.90
128.43
120.47
119.61
119.03
118.01
117.60
103.40
O
NH2
NH
N
CDCl3
195
185
175
165
155
145
135
125
115
105
95
90
85
80
75
70
65
60
55
f1 (ppm)

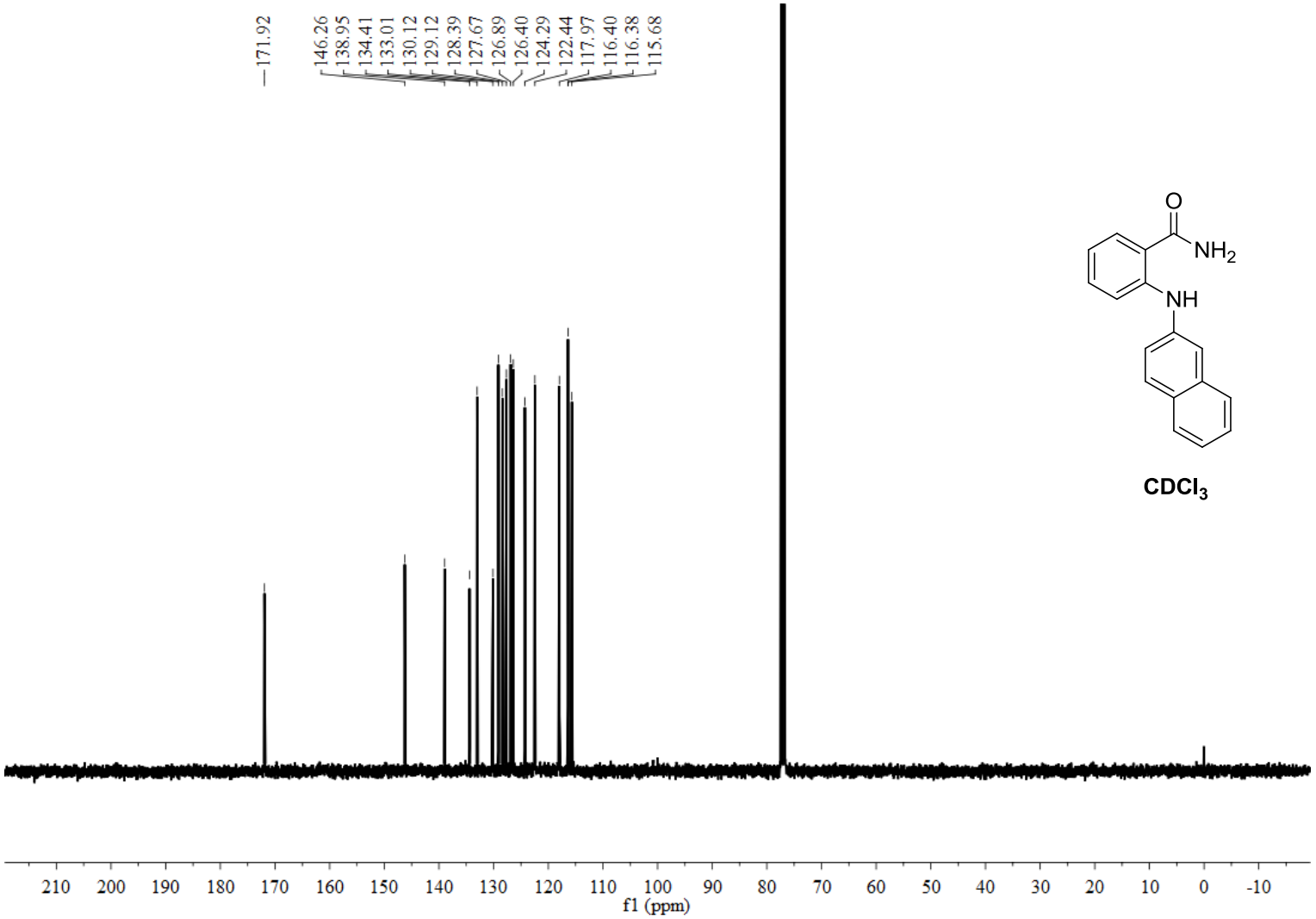

9.560
7.478
7.475
7.459
7.455
7.373
7.369
7.358
7.352
7.340
7.337
7.298
7.294
7.177
7.172
7.160
7.155
6.764
5.680
5.678
5.636
5.634
5.175
5.173
5.148
5.146
0.000
7.478
7.475
7.459
7.455
7.373
7.369
7.358
7.352
7.340
7.337
7.315
7.298
7.294
7.182
7.177
7.172
7.160
7.155
7.149
6.784
6.781
6.767
6.764
6.761
6.747
6.744
6.715
6.688
6.671
6.644
1.019
2.999
1.014
2.056
2.000
7.45
7.35
7.25
7.15
7.05
6.95
6.85
6.75
6.65
f1 (ppm)
O
NH2
NH
CDCl3
0.946
1.019
2.999
1.014
2.056
2.000
2.888
1.006
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
0.0
f1 (ppm)

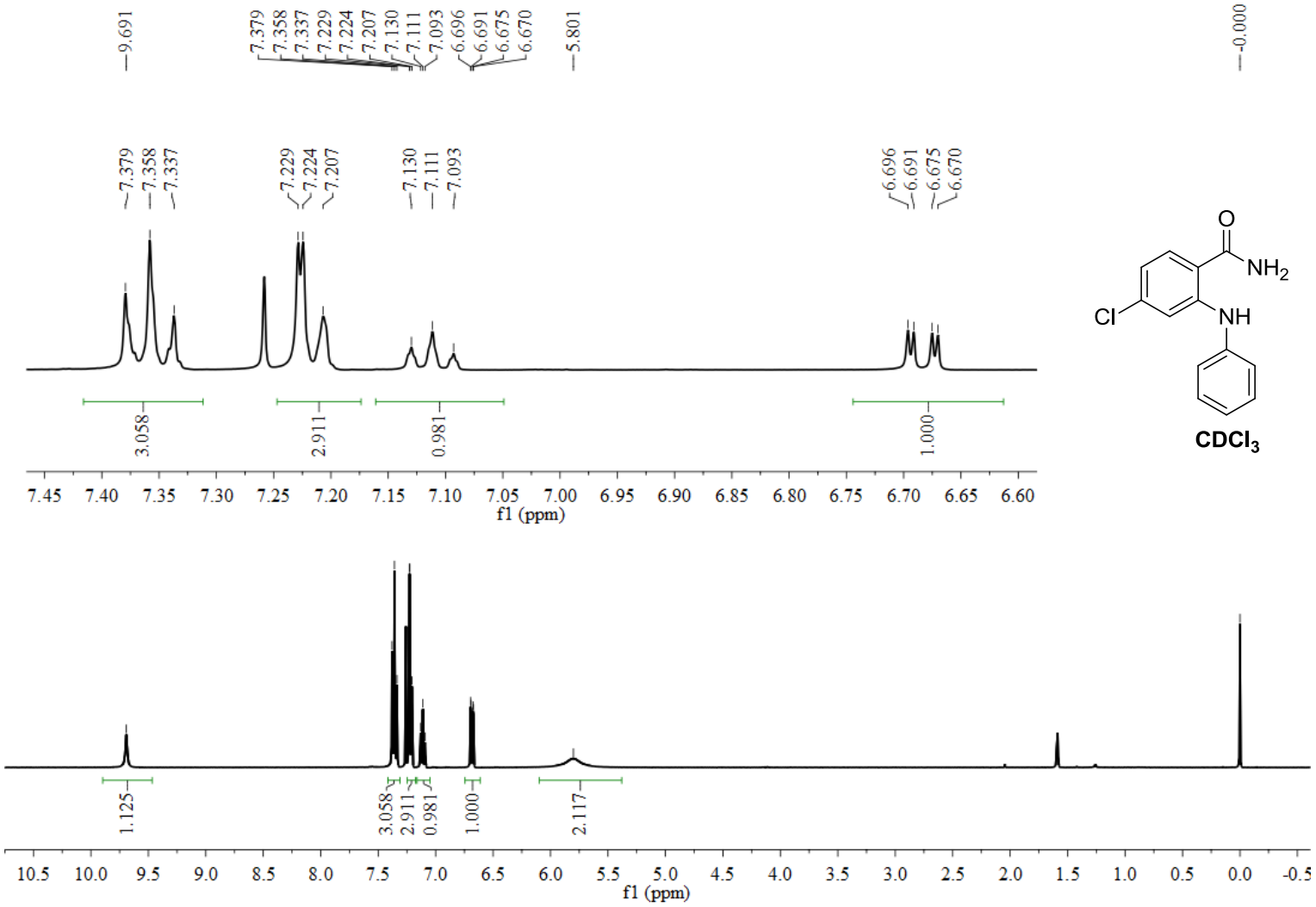

171.85
146.07
140.95
136.31
132.95
132.19
128.34
127.20
121.00
117.81
116.23
115.61
112.07
O
NH2
NH
CDCl3
175
165
155
145
135
125
115
110
105
95
90
85
80
75
70
65
60
55
50
f1 (ppm)

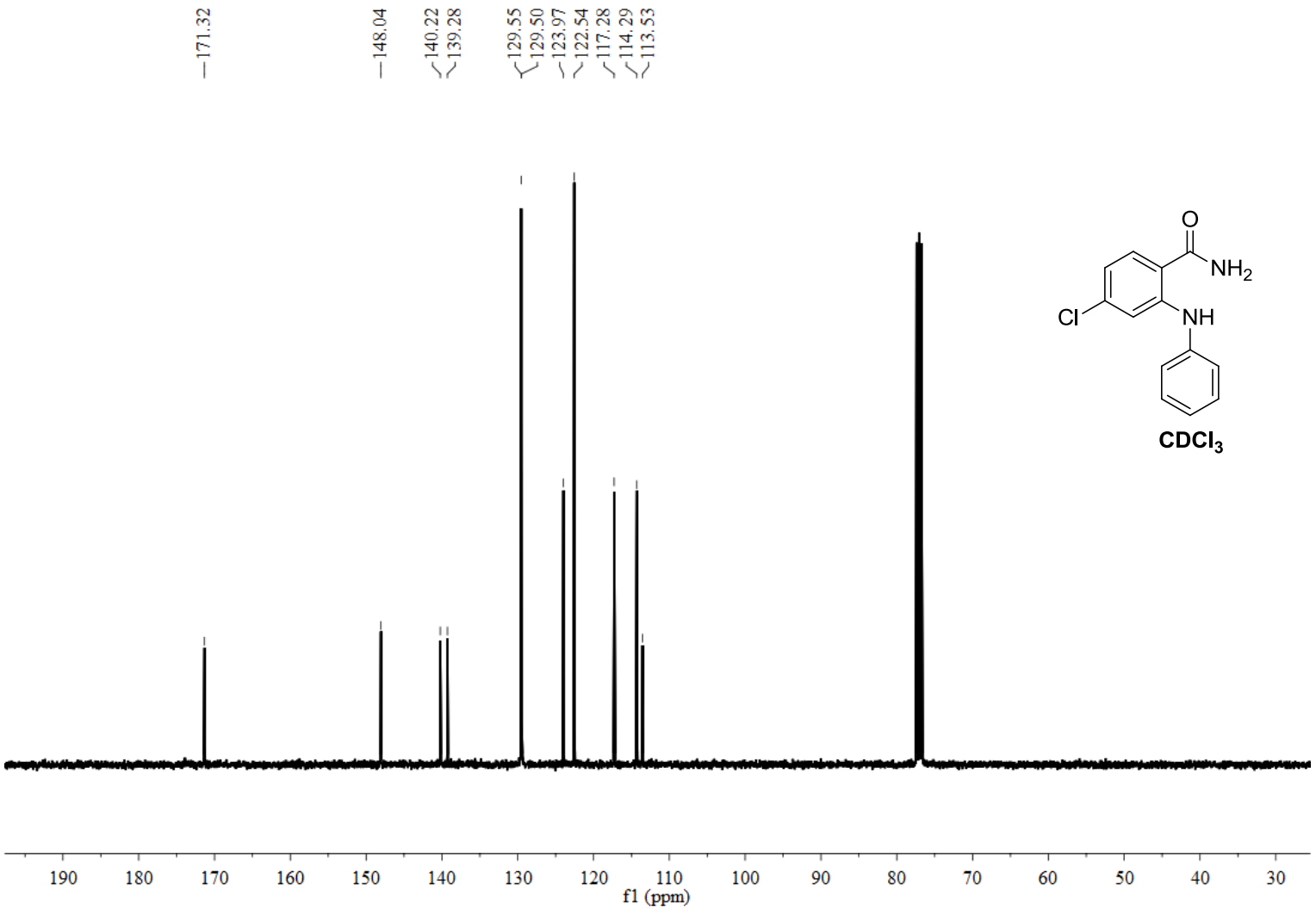

9.262
7.453
7.449
7.433
7.430
7.164
7.146
7.143
7.129
7.119
7.113
7.103
6.637
6.617
6.236
6.215
5.810
2.206
0.000
7.186
7.182
7.164
7.146
7.143
7.129
7.119
7.113
7.103
6.637
6.635
6.617
6.599
6.597
0.997
3.887
0.974
7.45
7.35
7.25
7.15
7.05
6.95
6.85
6.75
6.65
f1 (ppm)
O
NH2
NH
CDCl3
1.042
0.997
3.887
0.974
1.000
1.820
5.925
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
0.0
-0.5
-1.0
f1 (ppm)

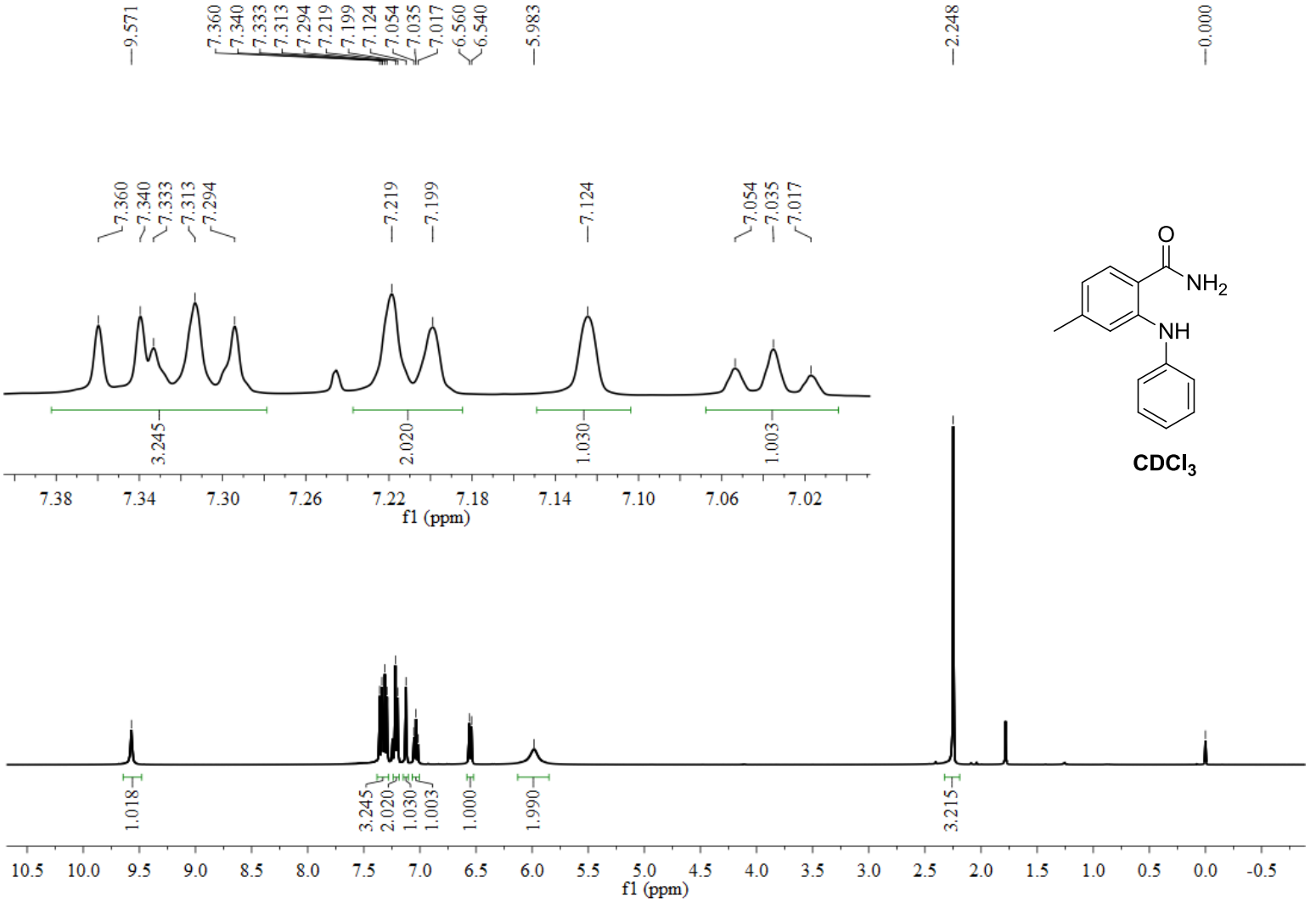

172.16
149.11
137.53
136.69
133.43
128.41
128.18
126.27
115.44
113.30
112.69
18.34
O
NH2
NH
CDCl3
158 154 150 146 142 138 134 130 126 122 118 114 110 106
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

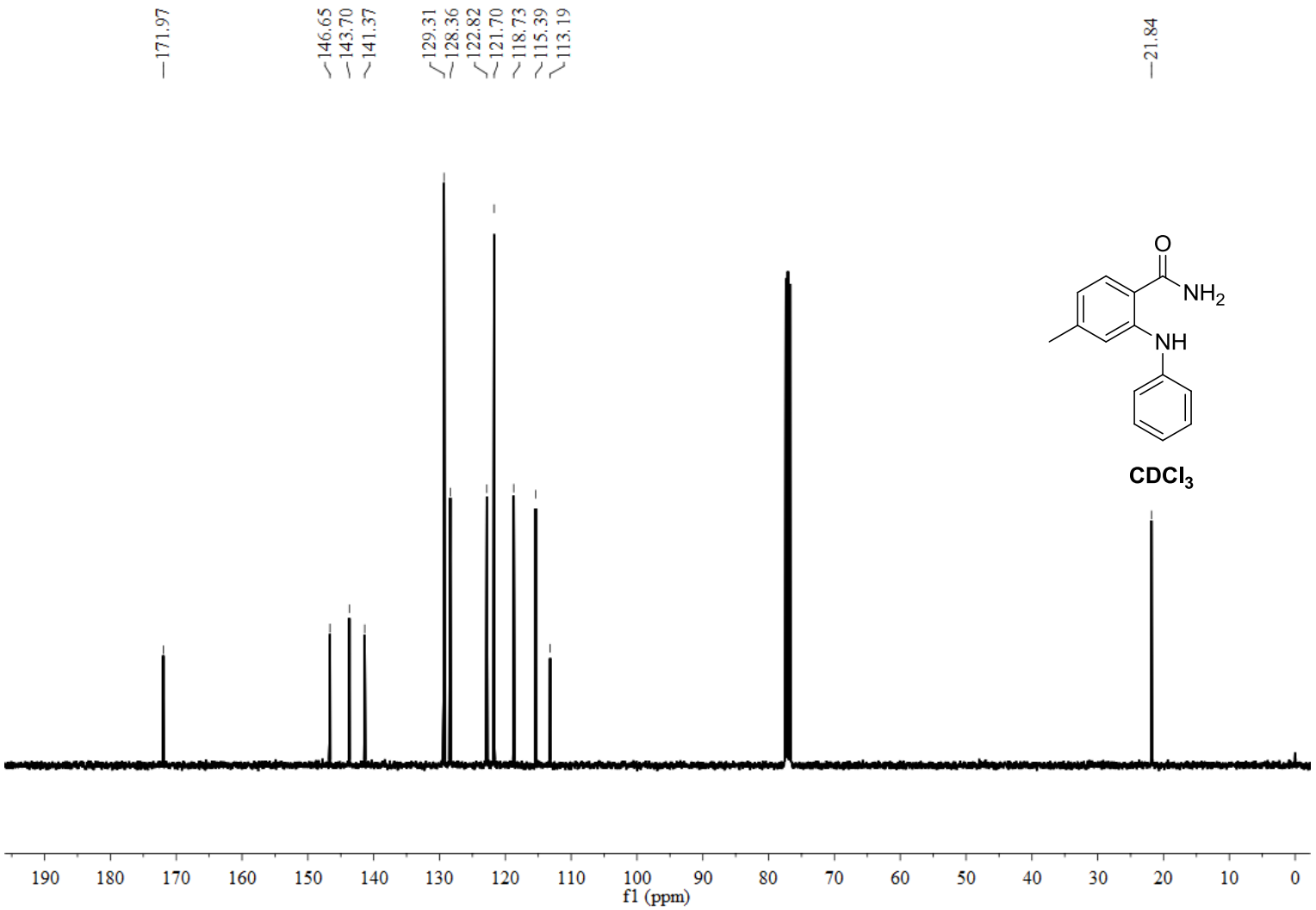

9.698
7.792
7.771
7.760
7.687
7.618
7.483
7.433
7.369
7.363
7.351
7.347
7.341
6.808
6.790
6.771
5.928
0.000
7.792
7.771
7.760
7.708
7.687
7.618
7.503
7.483
7.455
7.445
7.433
7.408
7.369
7.363
7.351
7.347
7.341
7.320
7.301
6.808
6.790
6.771
1.951
1.064
1.042
5.837
1.000
f1 (ppm)
O
NH2
NH
CDCl3
1.145
1.951
1.064
1.042
5.837
1.000
2.421
f1 (ppm)

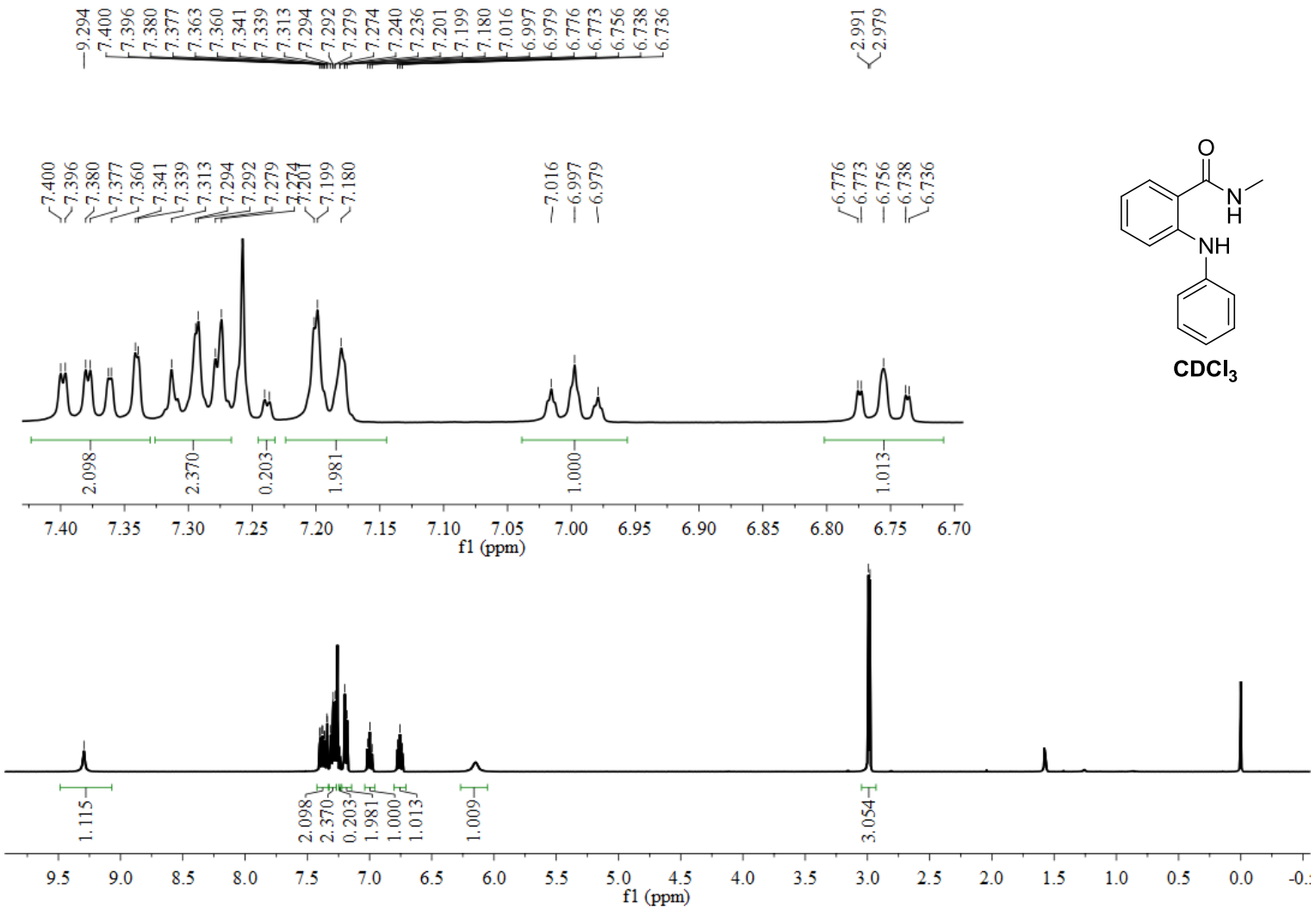

171.92
146.26
138.95
134.41
133.01
130.12
129.12
128.39
127.67
126.89
126.40
124.29
122.44
117.97
116.40
116.38
115.68
O
NH2
NH
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

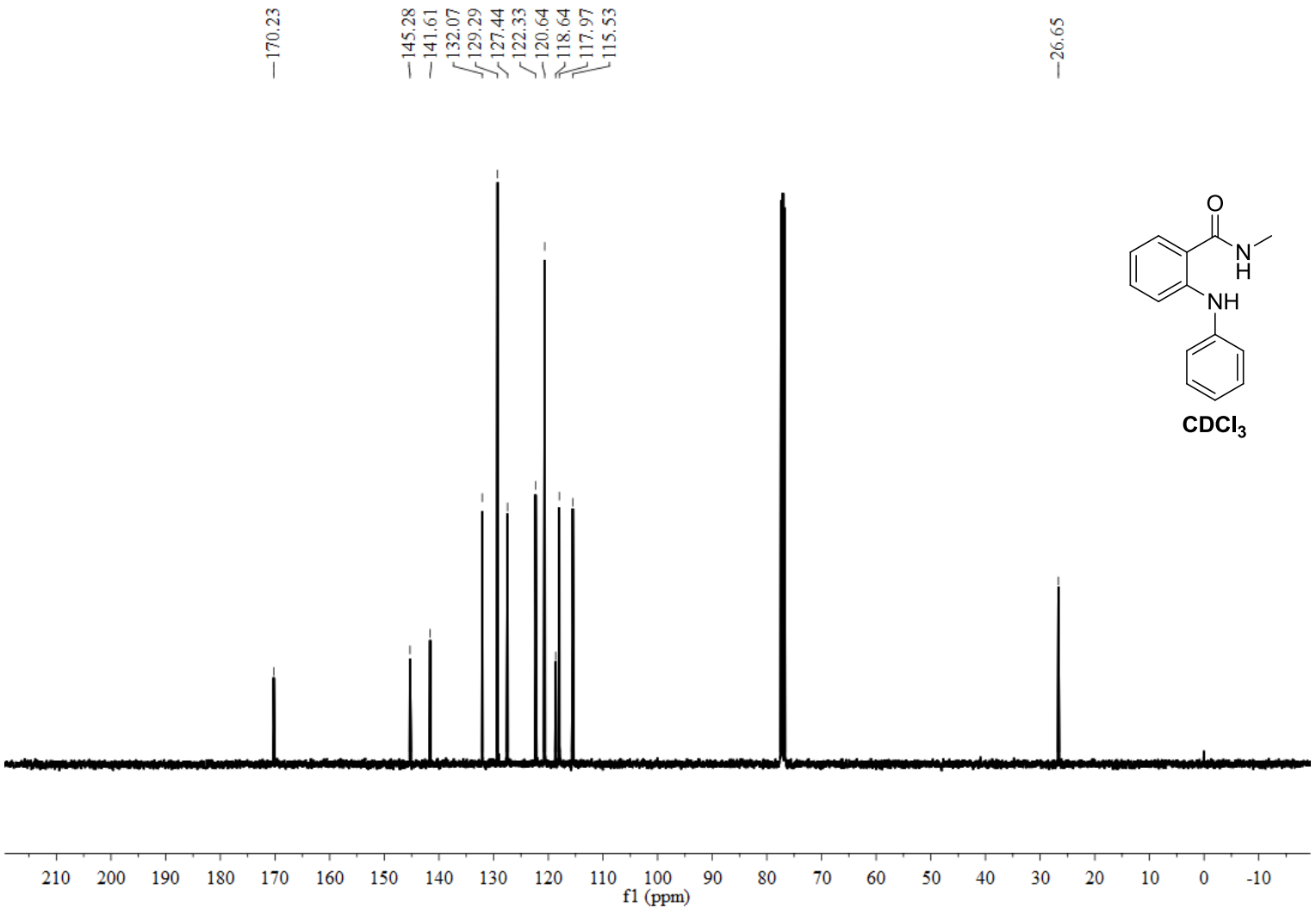

9.691
7.379
7.358
7.337
7.229
7.224
7.207
7.130
7.111
7.093
6.696
6.691
6.675
6.670
5.801
0.000
3.058
2.911
0.981
1.000
f1 (ppm)
O
NH2
Cl
NH
CDCl3
1.125
3.058
2.911
0.981
1.000
2.117
f1 (ppm)

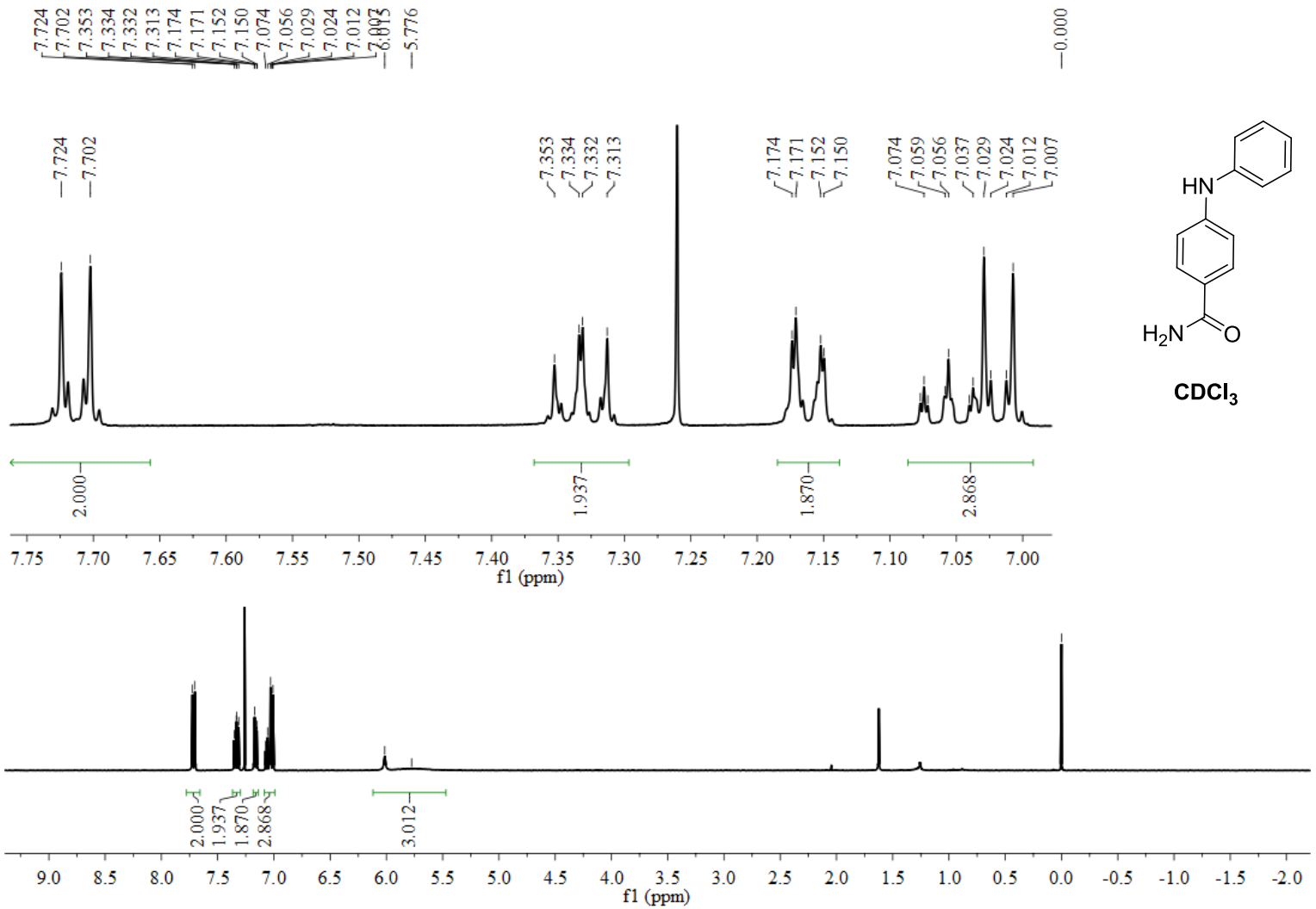

171.32
148.04
140.22
139.28
129.55
129.50
123.97
122.54
117.28
114.29
113.53
O
NH2
Cl
NH
CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
f1 (ppm)

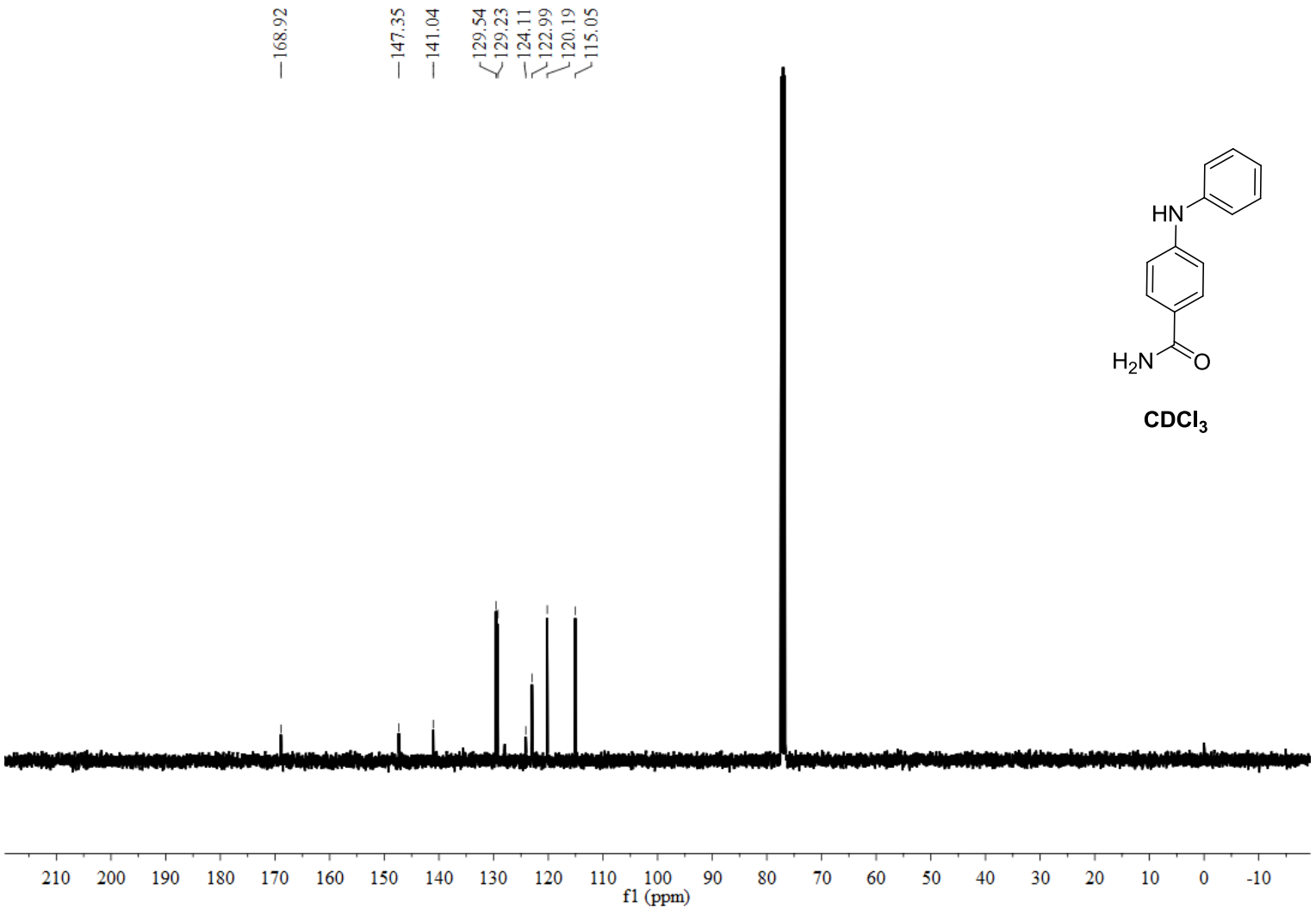

9.571
7.360
7.340
7.333
7.313
7.294
7.219
7.199
7.124
7.054
7.035
7.017
6.560
6.540
5.983
2.248
0.000
3.245
2.020
1.030
1.003
f1 (ppm)
1.018
3.245
2.020
1.030
1.003
1.000
1.990
3.215
f1 (ppm)
O
NH2
NH
CDCl3

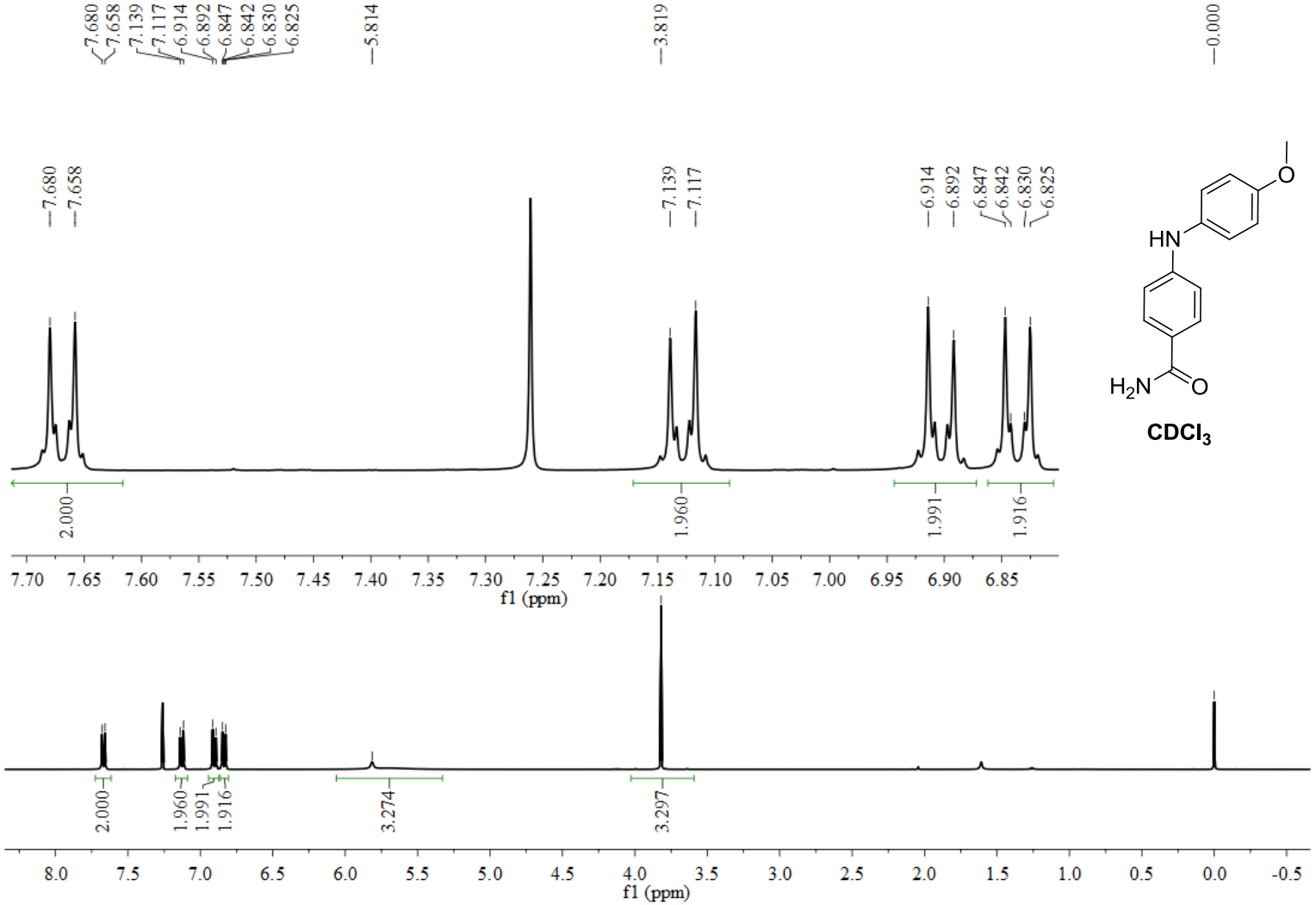

171.97
146.65
143.70
141.37
129.31
128.36
122.82
121.70
118.73
115.39
113.19
21.84
O
NH2
NH
CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

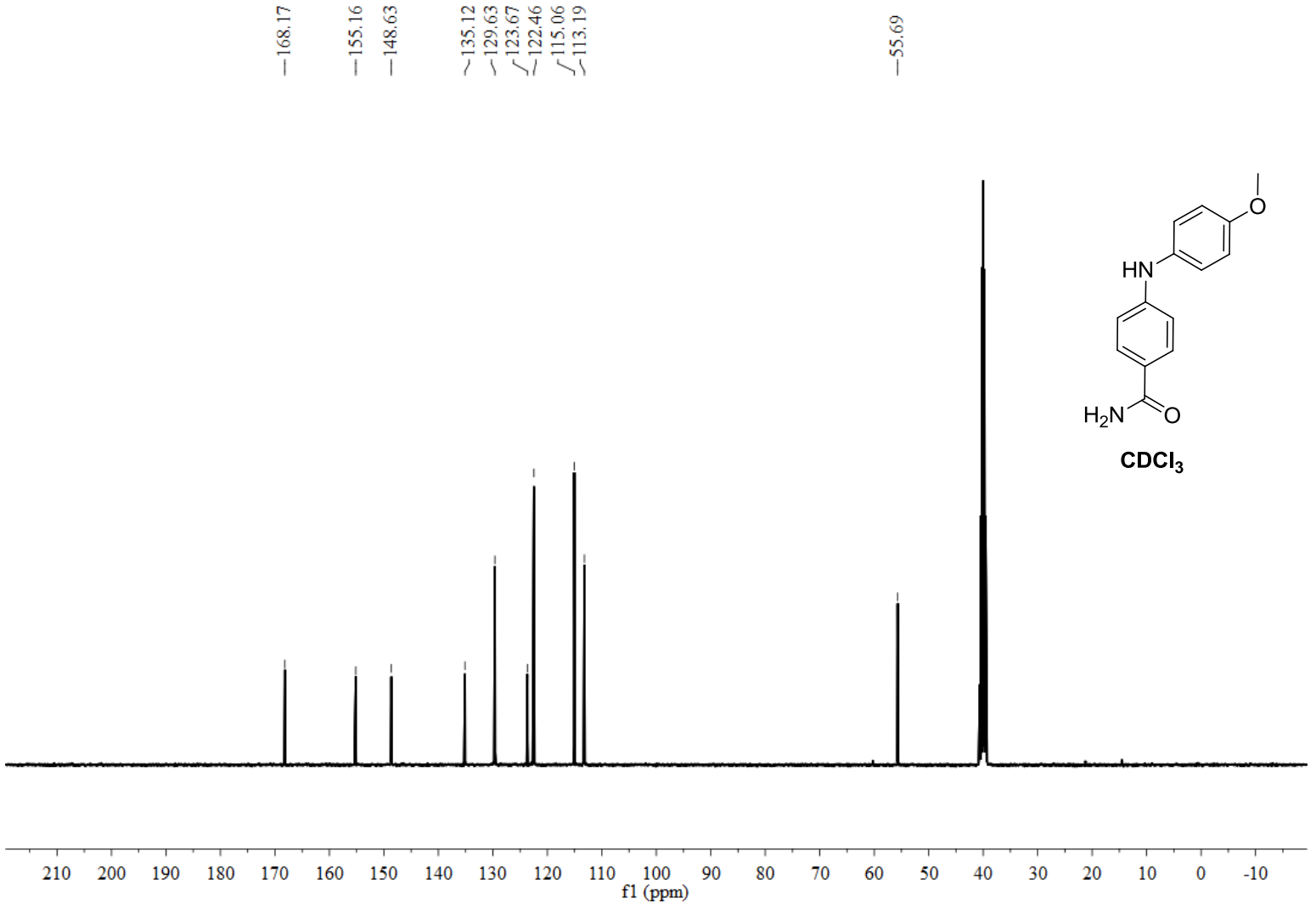

9.294
7.400
7.396
7.380
7.377
7.363
7.360
7.341
7.339
7.313
7.294
7.292
7.279
7.274
7.240
7.236
7.201
7.199
7.180
7.016
6.997
6.979
6.776
6.773
6.756
6.738
6.736
2.991
2.979
O
N
H
NH
CDCl3
2.098
2.370
0.203
1.981
1.000
1.013
f1 (ppm)
1.115
1.009
3.054

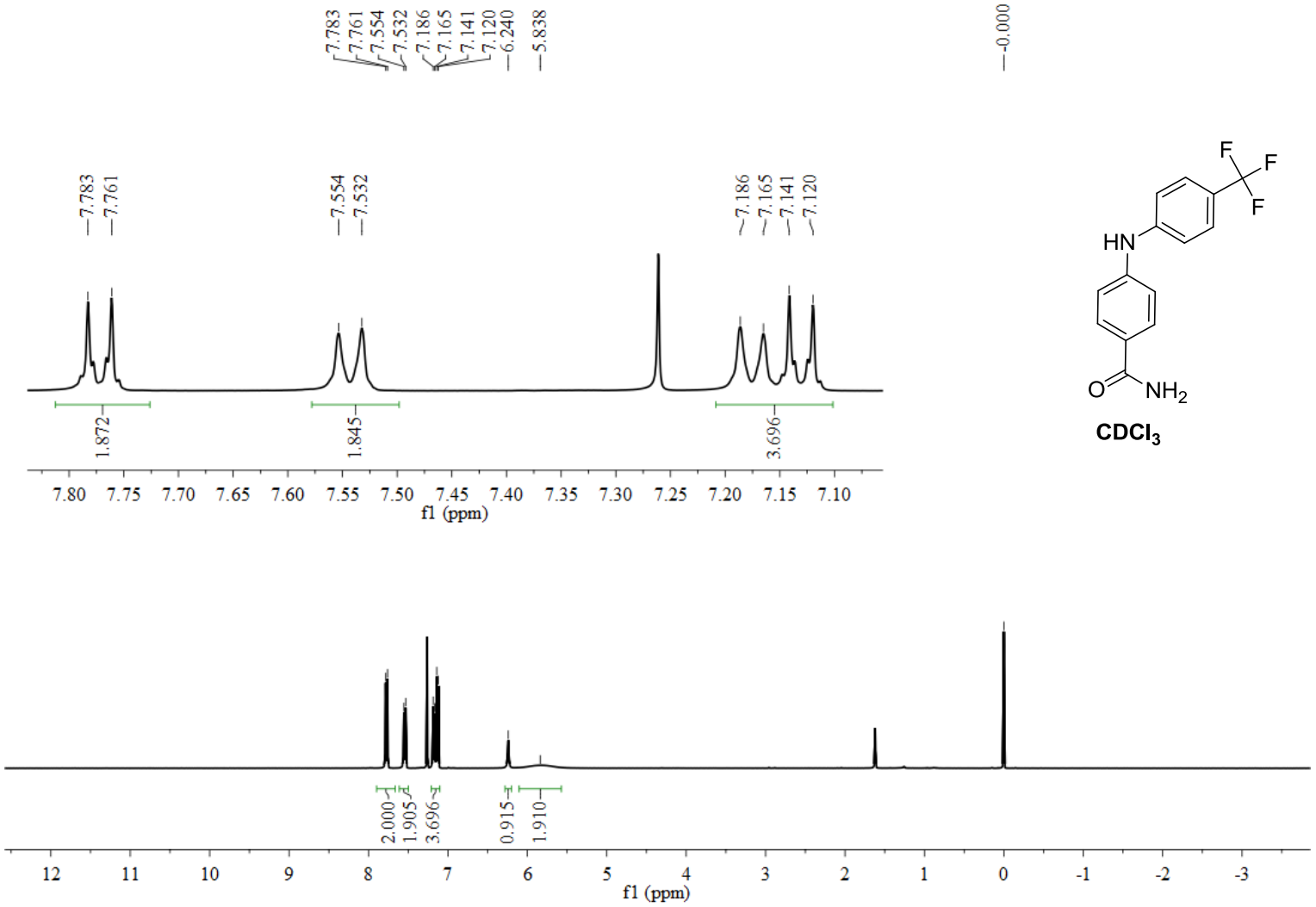

170.23
145.28
141.61
132.07
129.29
127.44
122.33
120.64
118.64
117.97
115.53
26.65
O
N
H
NH
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

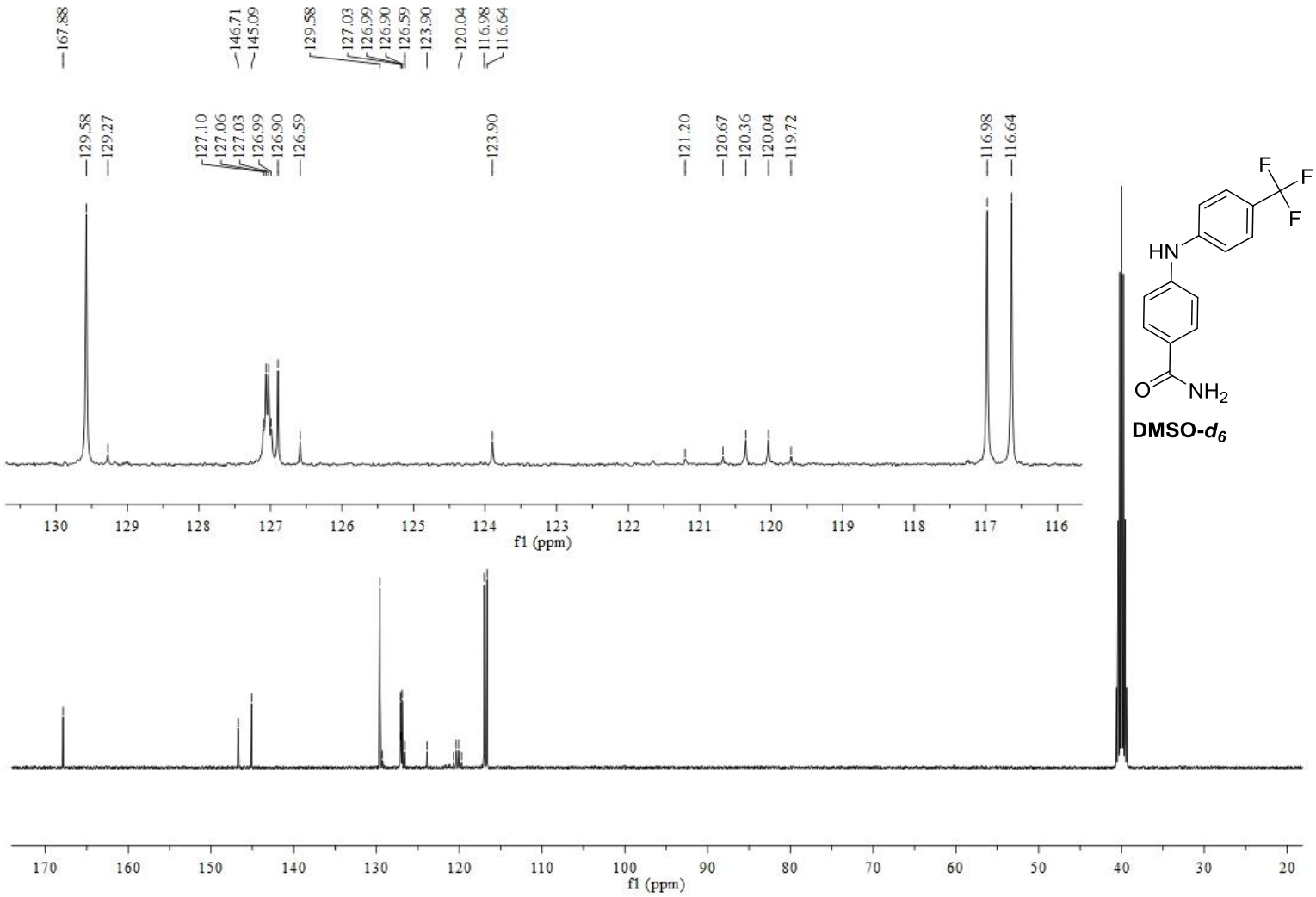

7.724
7.702
7.353
7.334
7.332
7.313
7.174
7.171
7.152
7.150
7.074
7.056
7.029
7.024
7.012
5.776
0.000
2.000
1.937
1.870
2.868
f1 (ppm)
3.012
HN
H2N
O
CDCl3

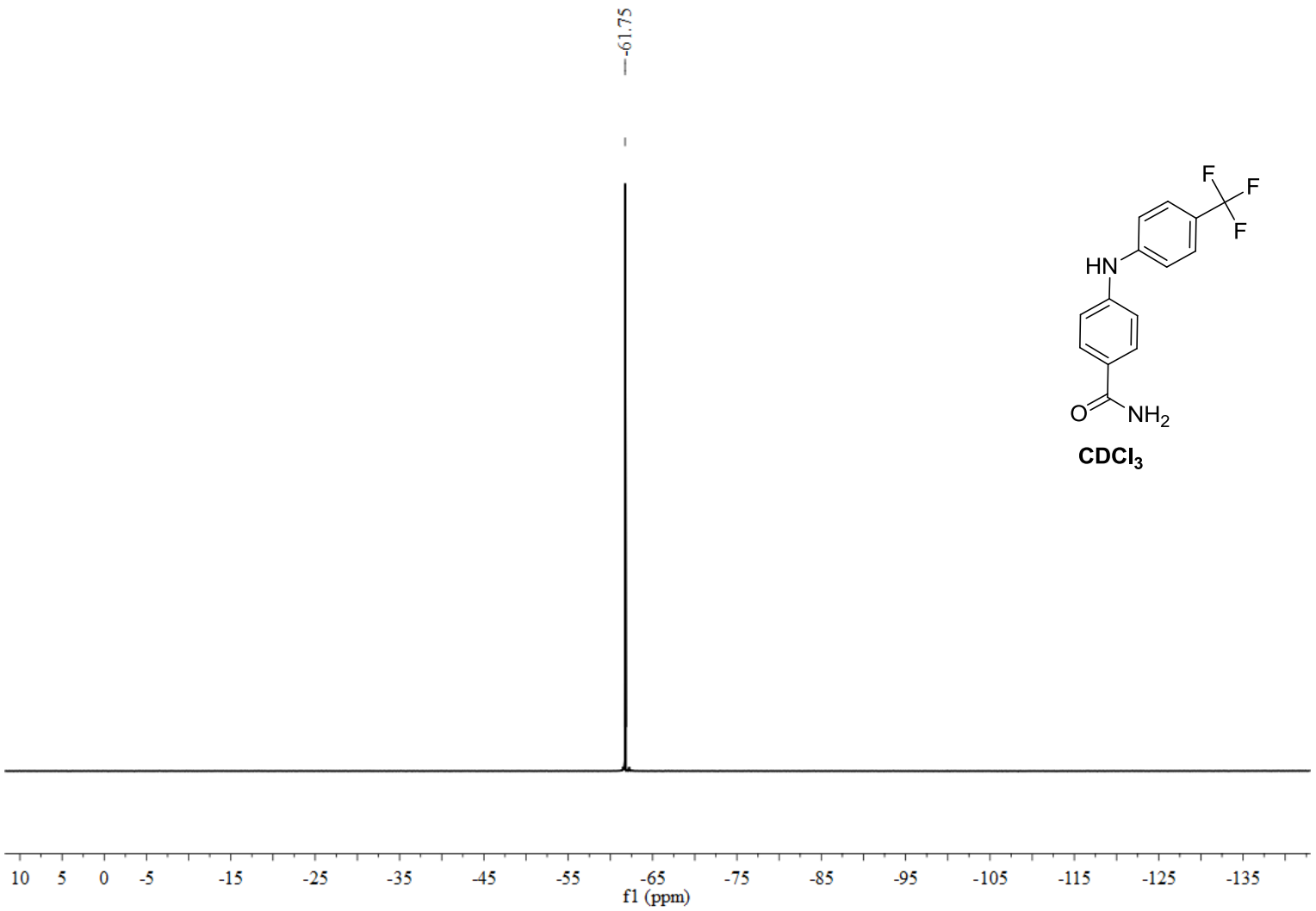

168.92
147.35
141.04
129.54
129.23
124.11
122.99
120.19
115.05
HN
H2N
O
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

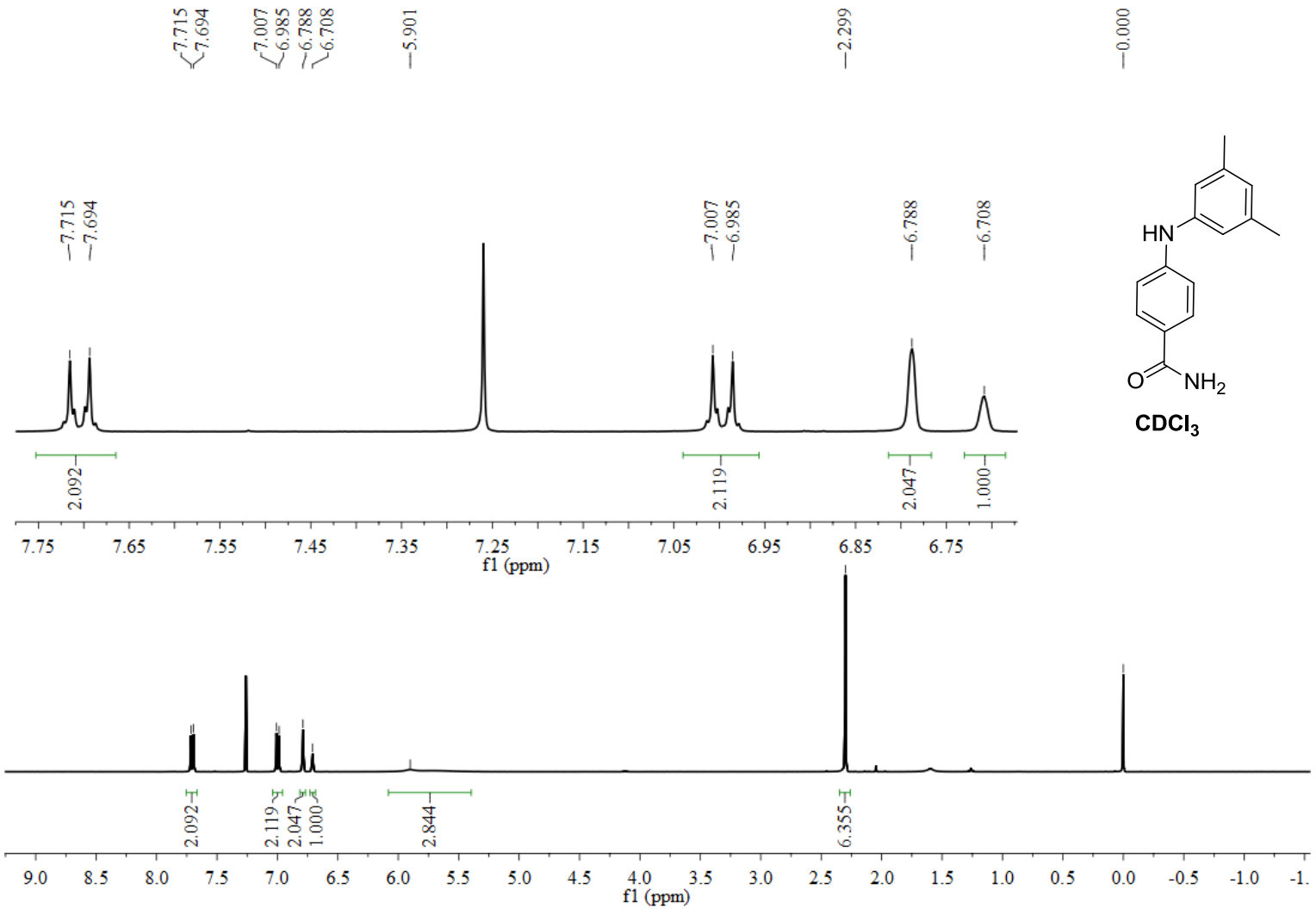

7.680
7.658
7.139
7.117
6.914
6.892
6.847
6.842
6.830
6.825
5.814
3.819
0.000
2.000
1.960
1.991
1.916
f1 (ppm)
3.274
3.297
HN
O
H2N
O
CDCl3

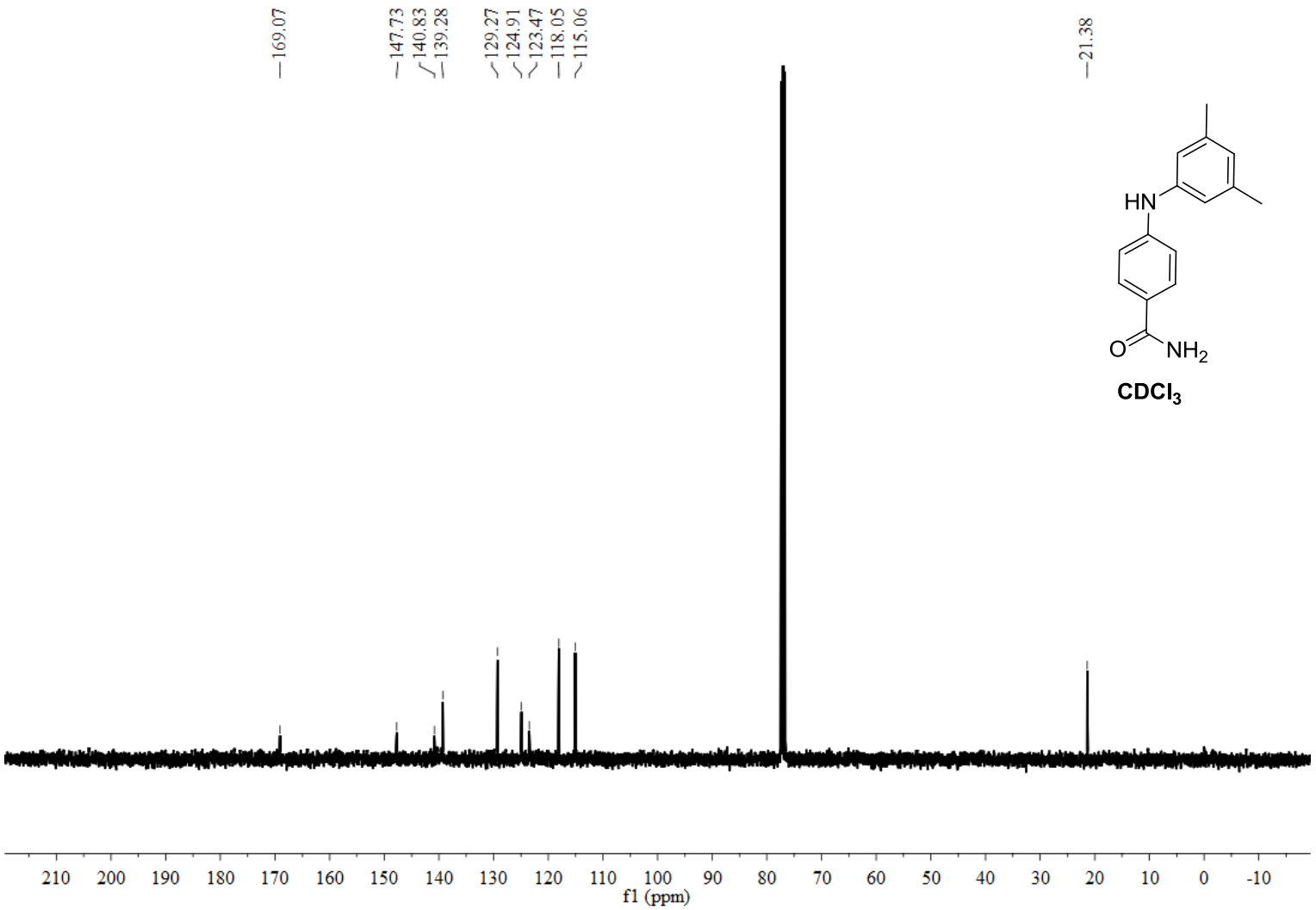

168.17
155.16
148.63
135.12
129.63
123.67
122.46
115.06
113.19
55.69
HN
O
H2N
O
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

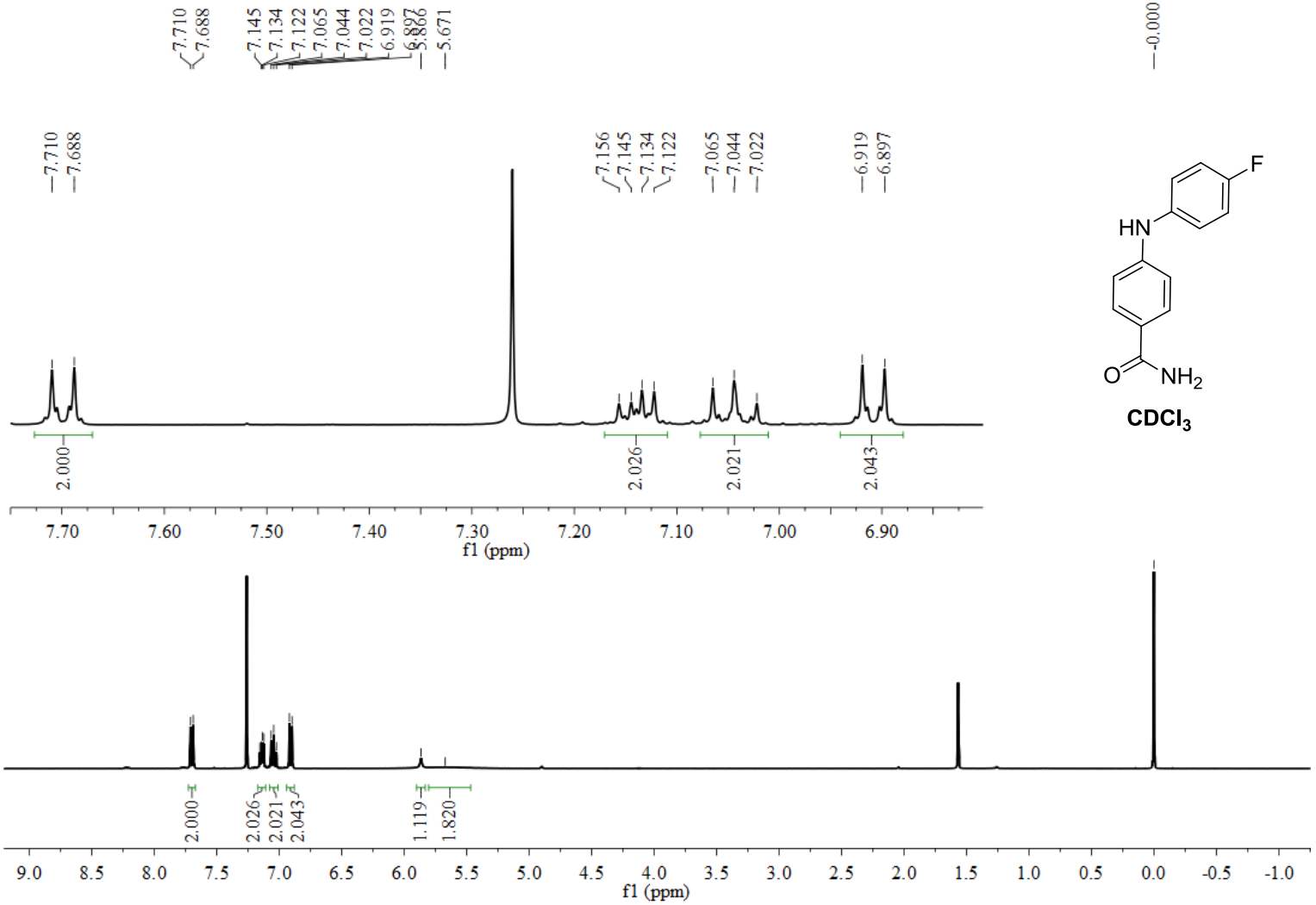

7.783
7.761
7.554
7.532
7.186
7.165
7.141
7.120
6.240
5.838
0.000
1.872
1.845
3.696
f1 (ppm)
F
F
F
HN
O
NH2
CDCl3
2.000
1.905
3.696
0.915
1.910
f1 (ppm)

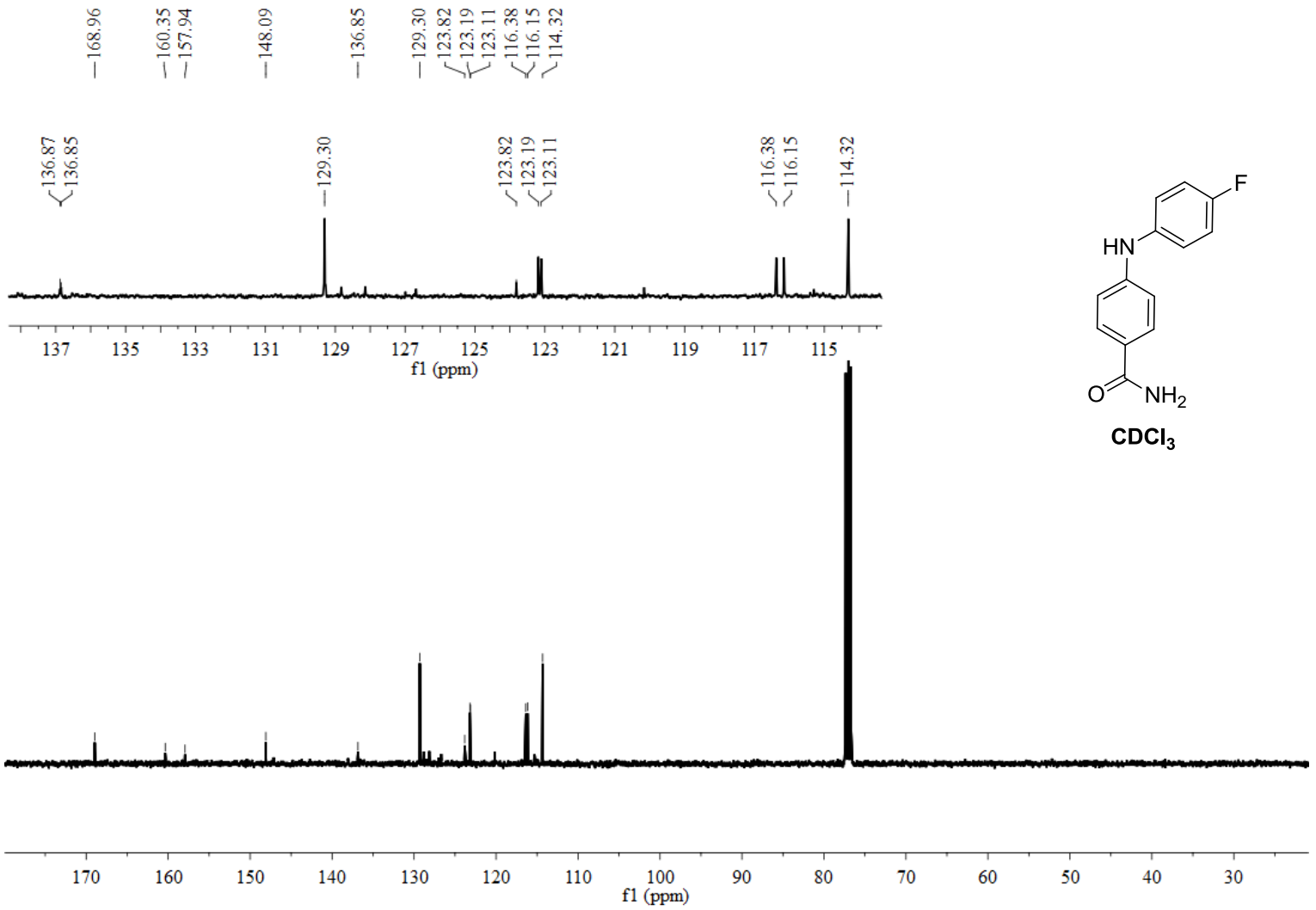

167.88
146.71
145.09
129.58
127.03
126.99
126.90
126.59
123.90
120.04
116.98
116.64
129.58
129.27
127.10
127.06
127.03
126.99
126.90
126.59
123.90
121.20
120.67
120.36
120.04
119.72
116.98
116.64
130 129 128 127 126 125 124 123 122 121 120 119 118 117 116
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)
F
F
F
HN
O
NH2
DMSO-d6


-61.75
F
F
F
HN
O
NH2
CDCl3
10
5
0
-5
-15
-25
-35
-45
-55
-65
-75
-85
-95
-105
-115
-125
-135
f1 (ppm)


7.715
7.694
7.007
6.985
6.788
6.708
5.901
2.299
0.000
2.092
2.119
2.047
1.000
f1 (ppm)
HN
O
NH2
CDCl3
2.092
2.119
2.047
1.000
2.844
6.355
f1 (ppm)


169.07
147.73
140.83
139.28
129.27
124.91
123.47
118.05
115.06
21.38
HN
O
NH2
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)


7.710
7.688
7.145
7.134
7.122
7.065
7.044
7.022
6.919
6.897
5.671
0.000
2.000
2.026
2.021
2.043
1.119
1.820
f1 (ppm)
HN
F
O
NH2
CDCl3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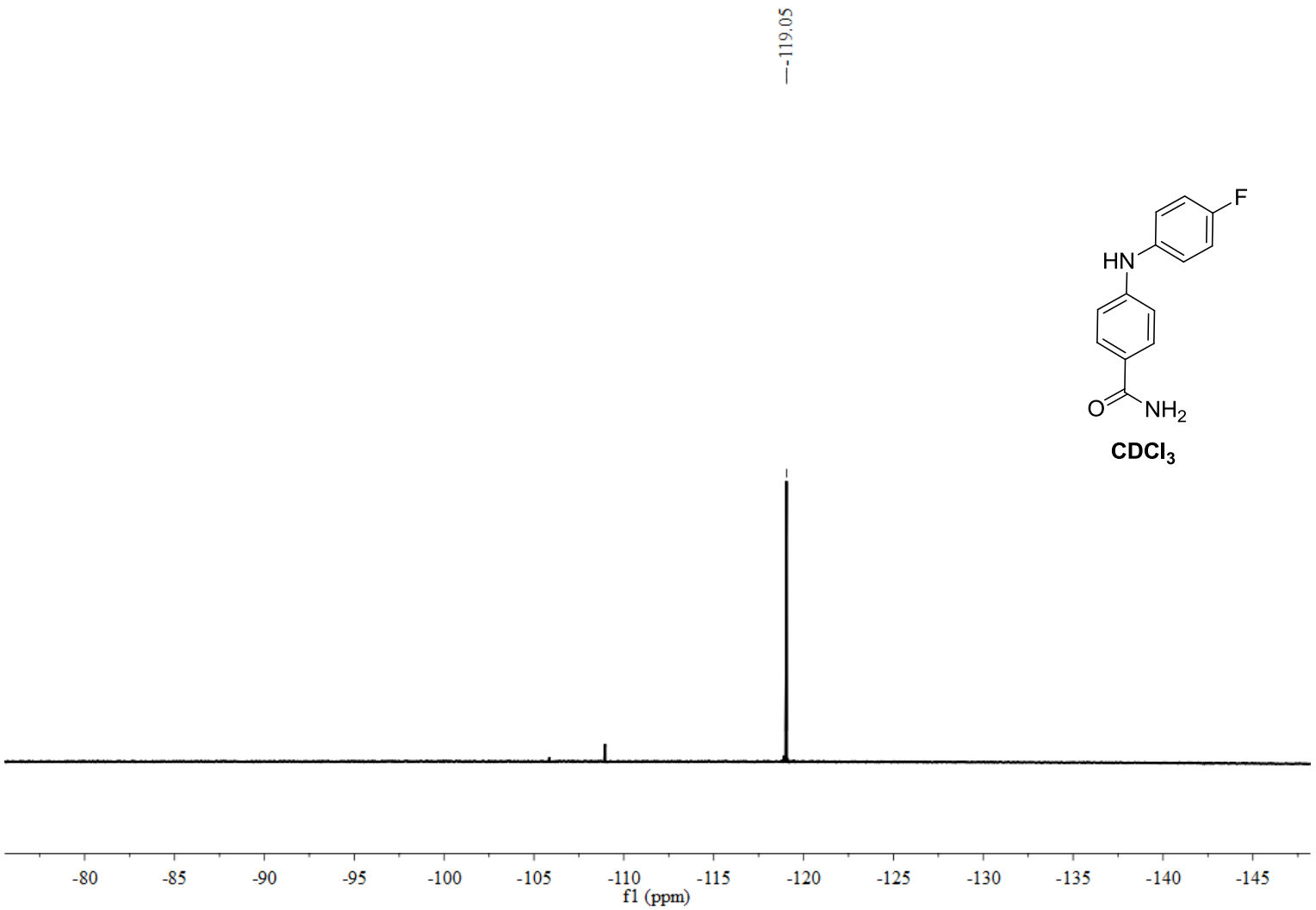
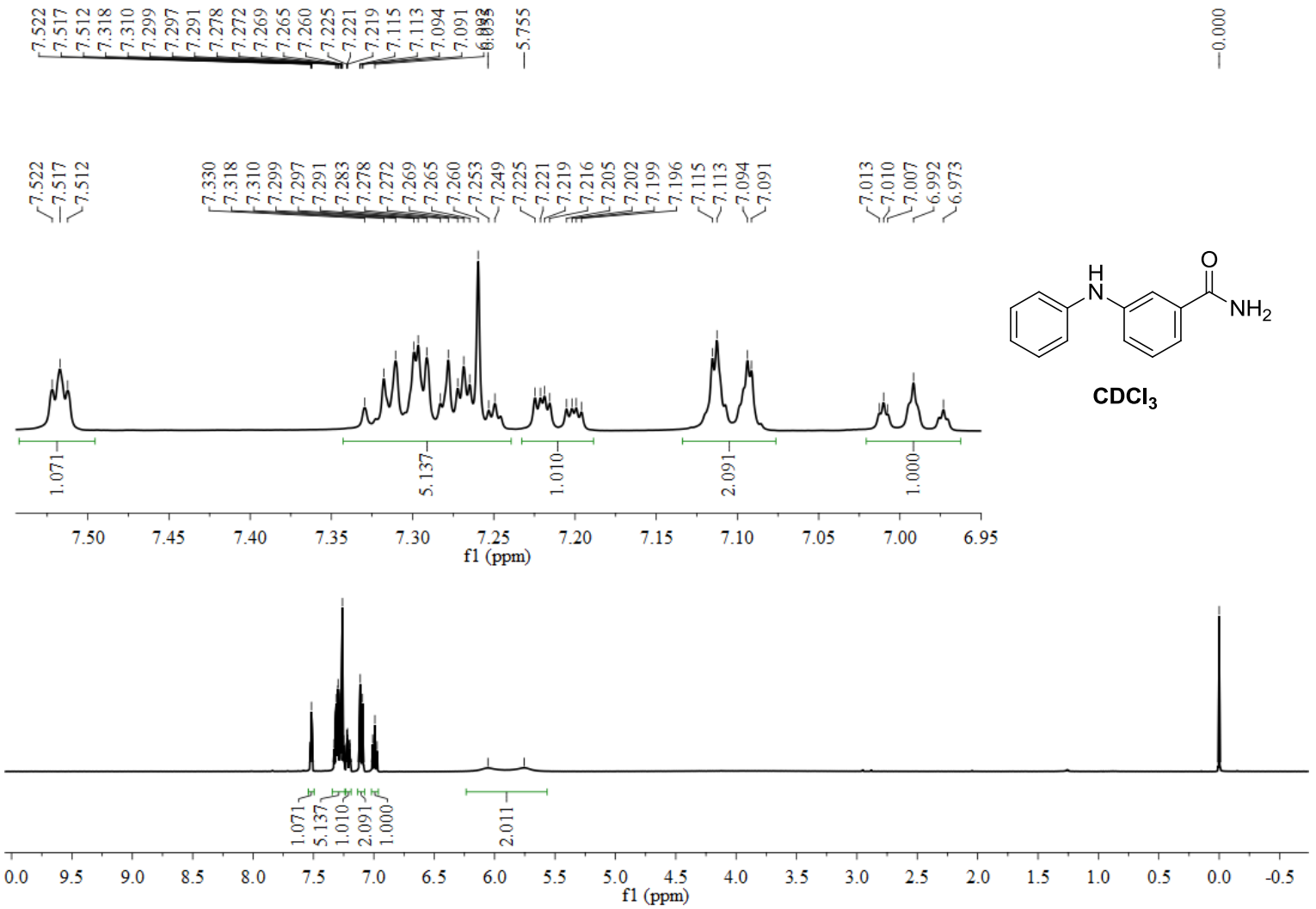
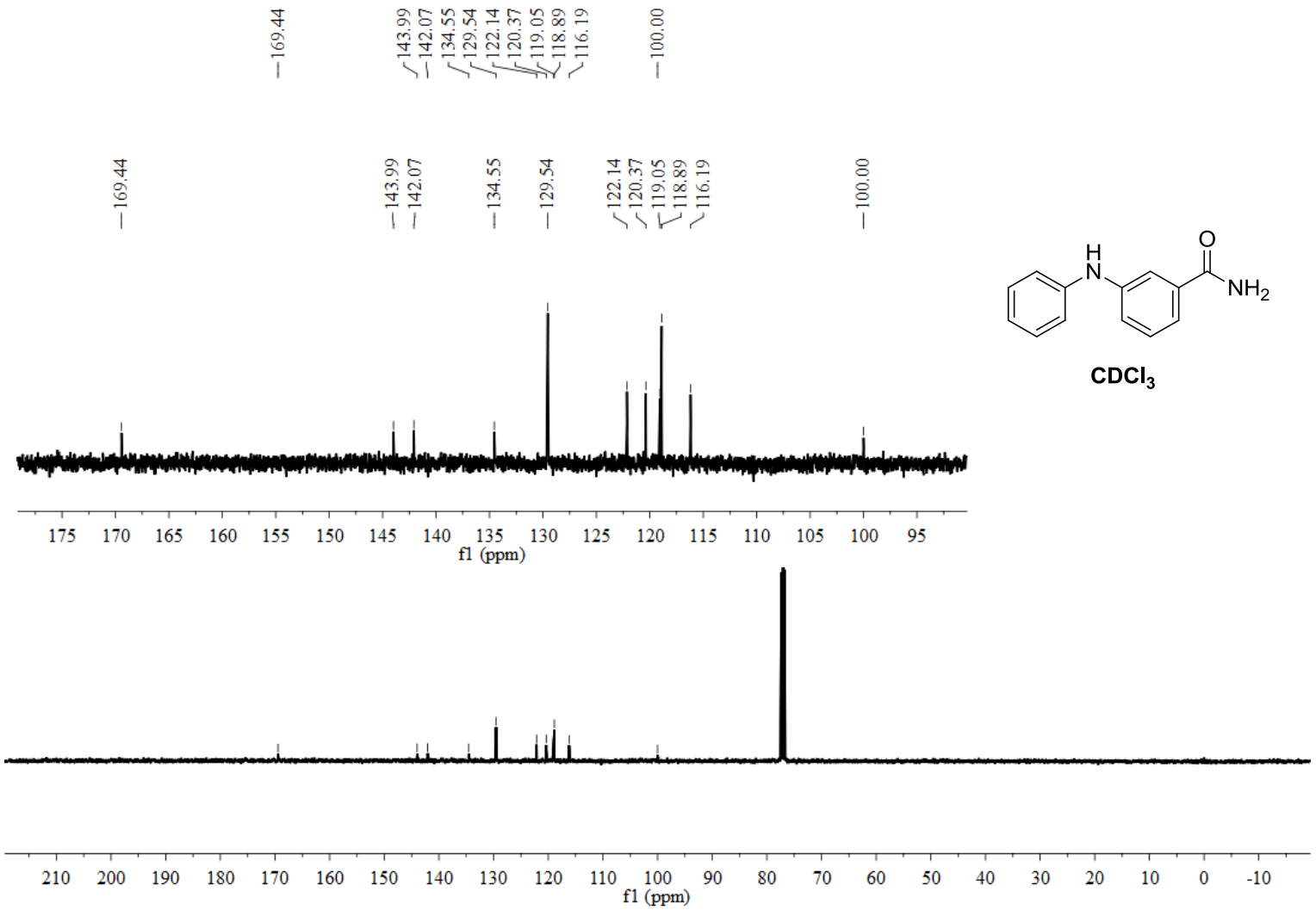
160.35
157.94
148.09
136.85
129.30
123.82
123.19
123.11
116.38
116.15
114.32
136.87
136.85
129.30
123.82
123.19
123.11
116.38
116.15
114.32
137
135
133
131
129
127
125
123
121
119
117
115
f1 (ppm)
F
HN
O
NH2
CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
f1 (ppm)


-119.05
F
HN
O
NH2
CDCl3
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
f1 (ppm)


7.522
7.517
7.512
7.318
7.310
7.299
7.297
7.291
7.278
7.272
7.269
7.265
7.260
7.225
7.221
7.219
7.115
7.113
7.094
7.091
5.755
0.000
7.330
7.318
7.310
7.299
7.297
7.291
7.283
7.278
7.272
7.269
7.265
7.260
7.253
7.249
7.225
7.221
7.219
7.216
7.205
7.202
7.199
7.196
7.115
7.113
7.094
7.091
7.013
7.010
7.007
6.992
6.973
1.071
5.137
1.010
2.091
1.000
7.50
7.45
7.40
7.35
7.30
7.25
7.20
7.15
7.10
7.05
7.00
6.95
f1 (ppm)
H
N
O
NH2
CDCl3
1.071
5.137
1.010
2.091
1.000
2.011
0.0
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
0.0
-0.5
f1 (ppm)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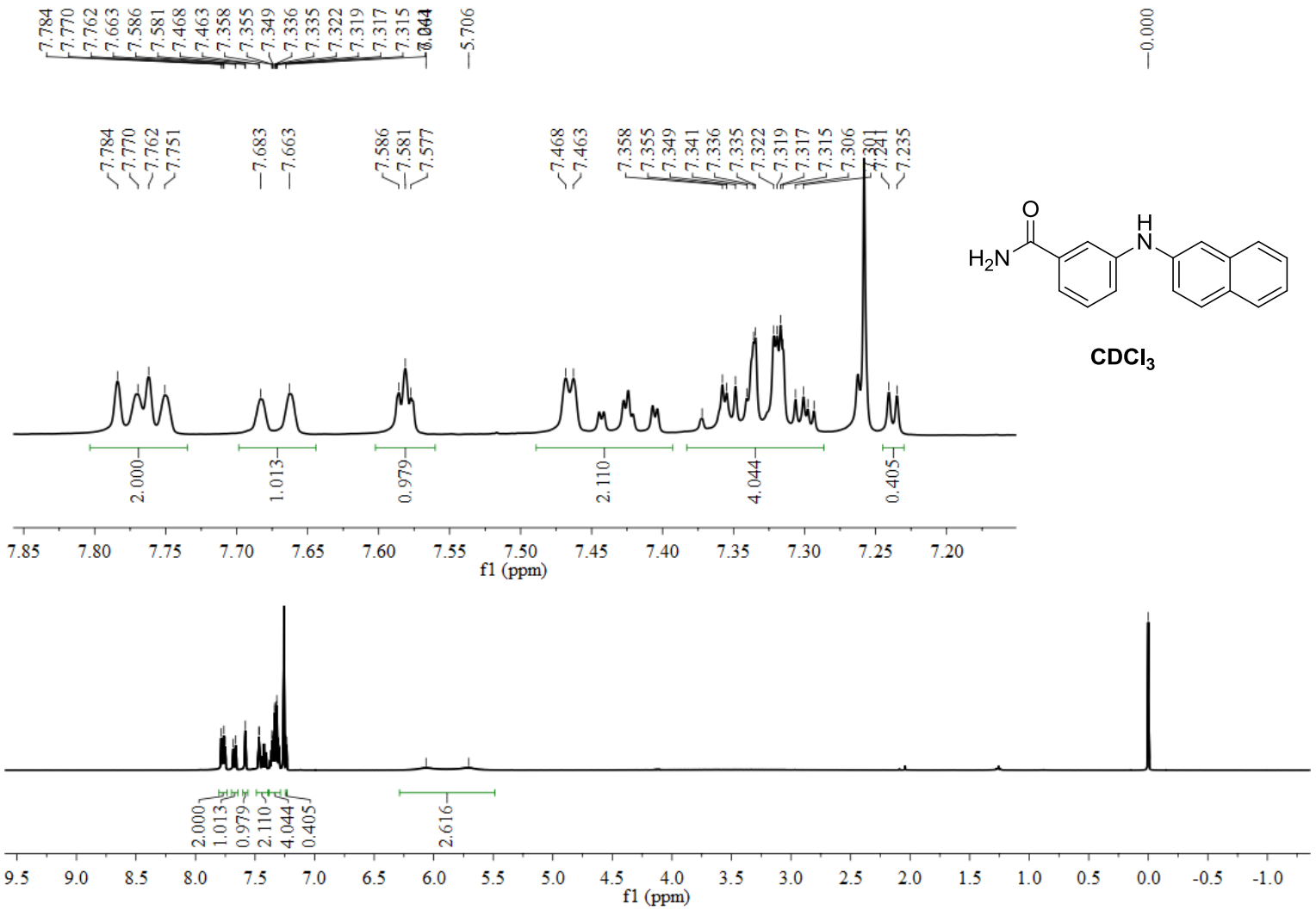
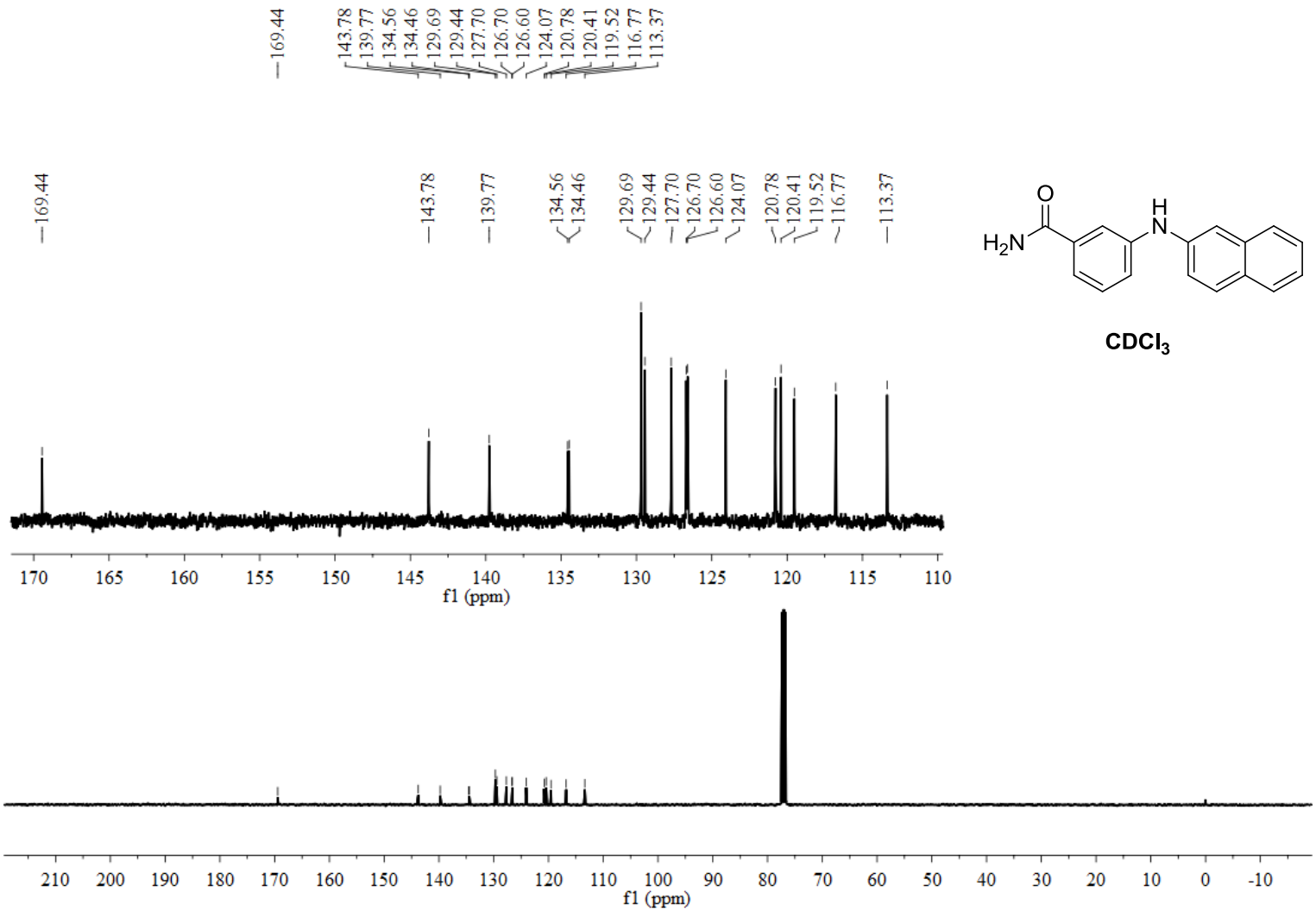
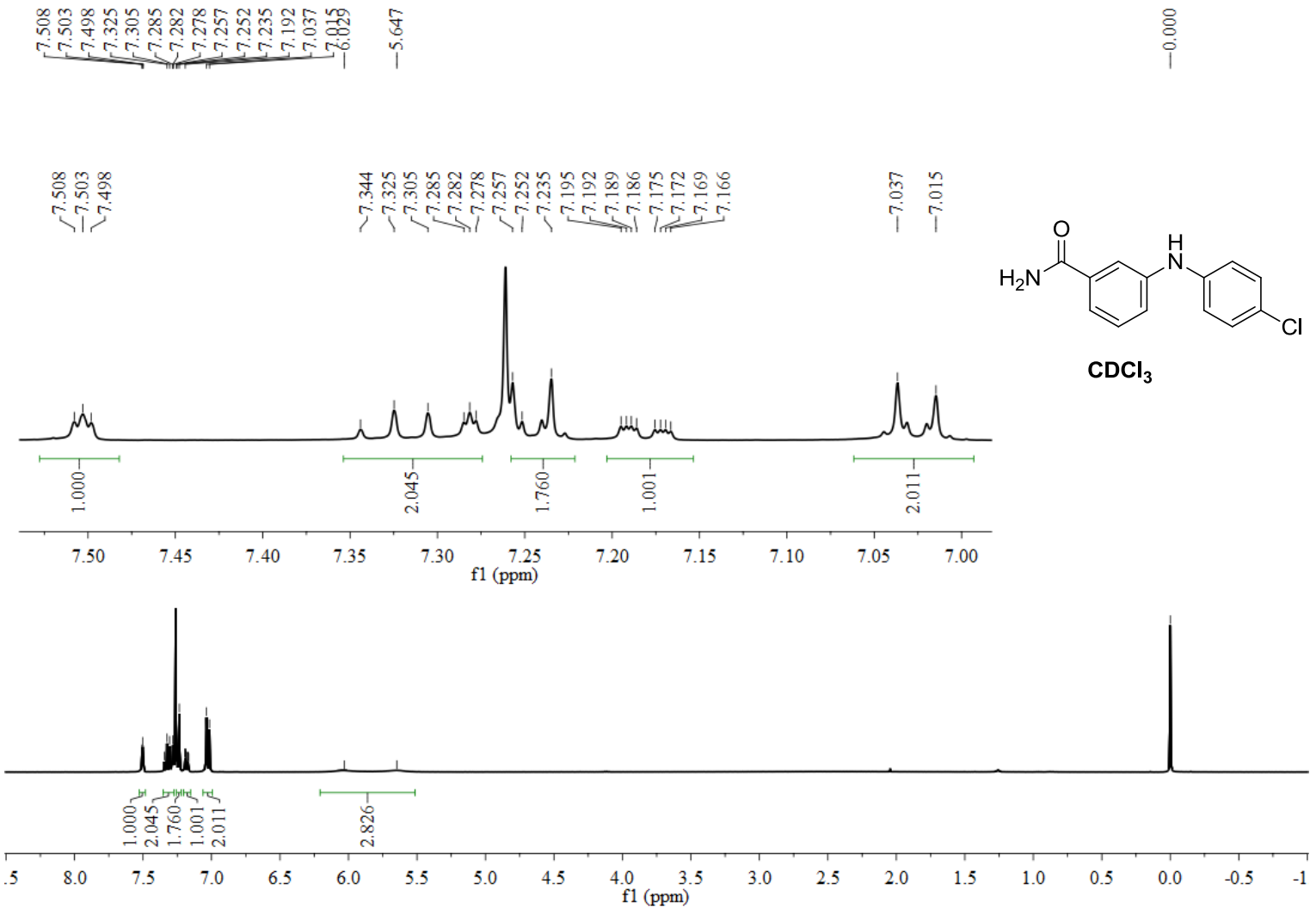
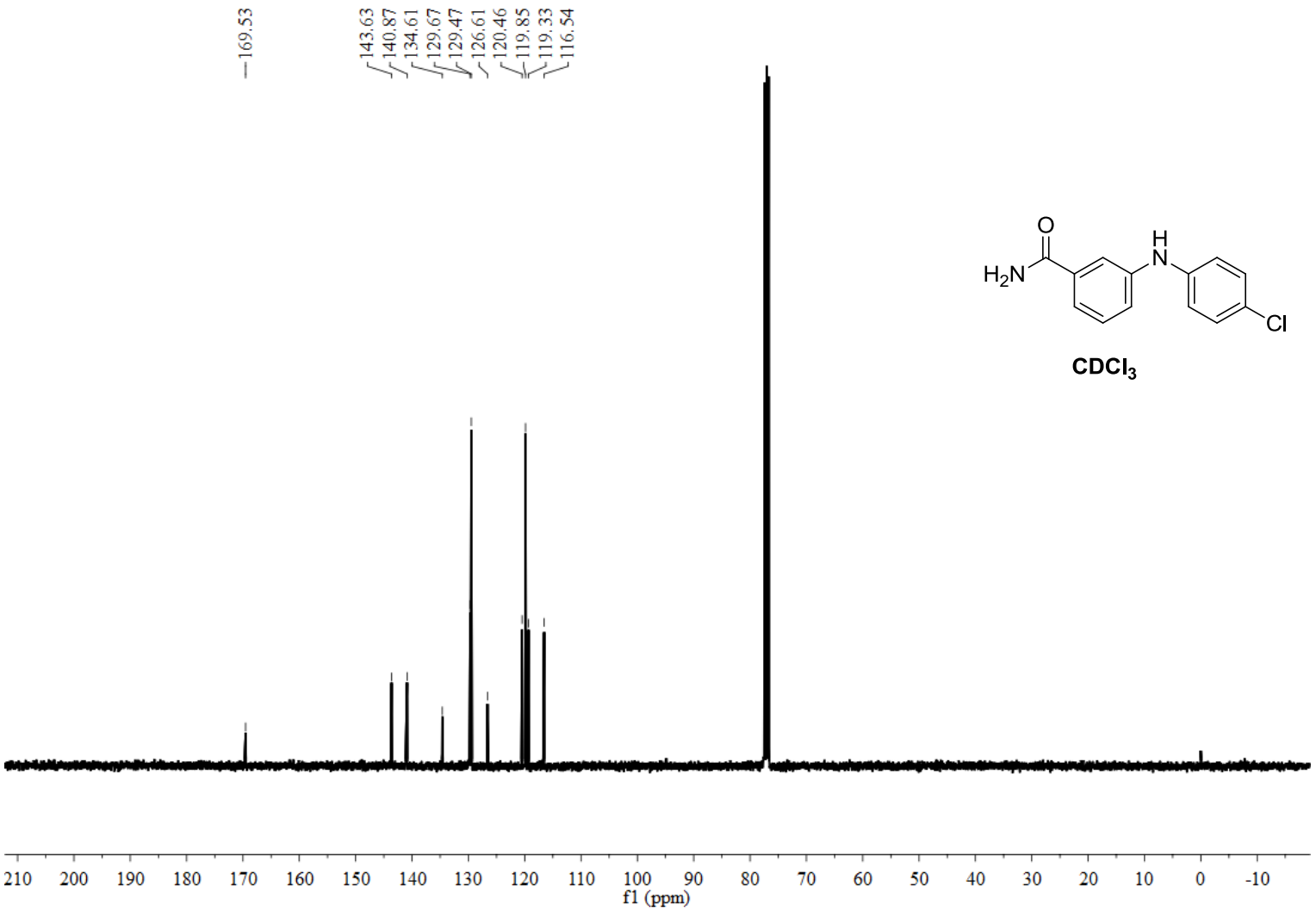
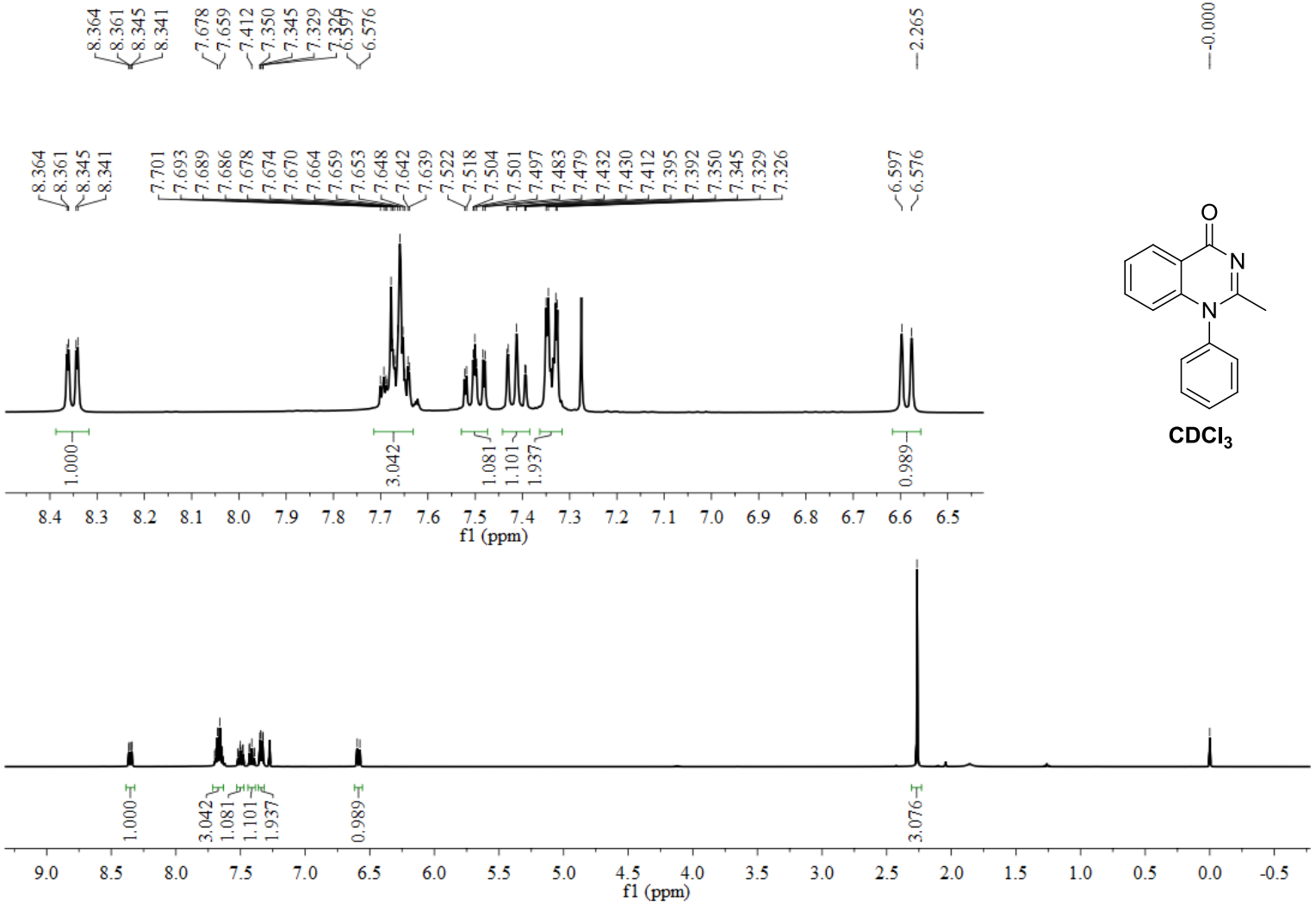
143.99
142.07
134.55
129.54
122.14
120.37
119.05
118.89
116.19
100.00
169.44
143.99
142.07
134.55
129.54
122.14
120.37
119.05
118.89
116.19
100.00
H
N
O
NH2
CDCl3
175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

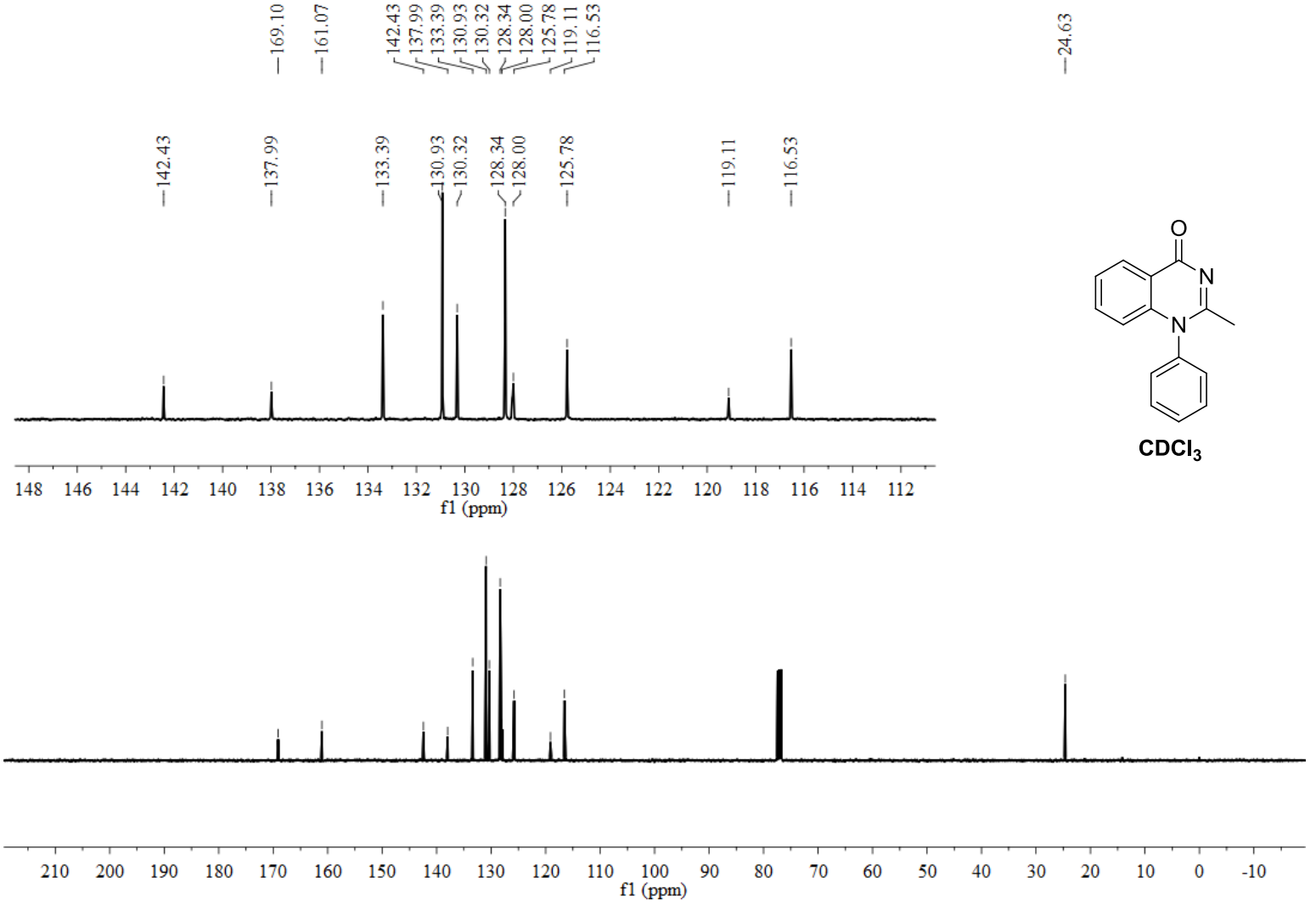

7.784
7.770
7.762
7.751
7.683
7.663
7.586
7.581
7.577
7.468
7.463
7.358
7.355
7.349
7.341
7.336
7.335
7.322
7.319
7.317
7.315
7.306
7.301
7.241
7.235
5.706
0.000
2.000
1.013
0.979
2.110
4.044
0.405
2.616
f1 (ppm)
O
H
N
H2N
CDCl3

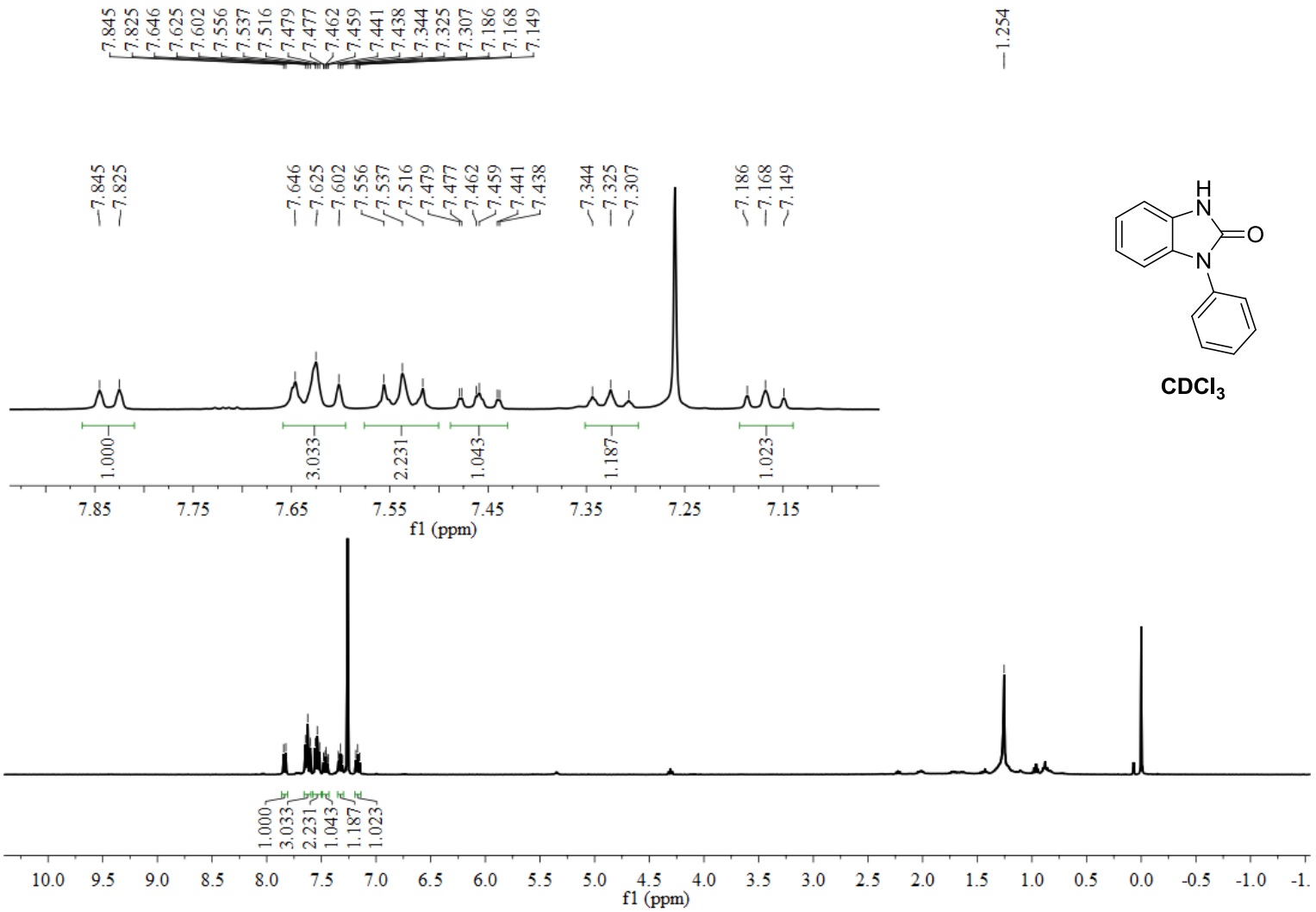

169.44
143.78
139.77
134.56
134.46
129.69
129.44
127.70
126.70
126.60
124.07
120.78
120.41
119.52
116.77
113.37
O
H2N
H
N
CDCl3
f1 (ppm)
f1 (ppm)


7.508
7.503
7.498
7.325
7.305
7.285
7.282
7.278
7.257
7.252
7.235
7.192
7.037
7.015
6.029
5.647
0.000
7.344
7.189
7.186
7.175
7.172
7.169
7.166
1.000
2.045
1.760
1.001
2.011
2.826
f1 (ppm)
O
H
N
H2N
Cl
CDCl3


169.53
143.63
140.87
134.61
129.67
129.47
126.61
120.46
119.85
119.33
116.54
O
H
N
H_2N
Cl
$CDCl_3$
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)


8.364
8.361
8.345
8.341
7.678
7.659
7.412
7.350
7.345
7.329
6.576
2.265
0.000
7.701
7.693
7.689
7.686
7.678
7.674
7.670
7.664
7.659
7.653
7.648
7.642
7.639
7.522
7.518
7.504
7.501
7.497
7.483
7.479
7.432
7.430
7.412
7.395
7.392
7.350
7.345
7.329
7.326
6.597
6.576
1.000
3.042
1.081
1.101
1.937
0.989
f1 (ppm)
O
N
N
CDCl3
1.000
3.042
1.081
1.101
1.937
0.989
3.076
f1 (ppm)


169.10
161.07
142.43
137.99
133.39
130.93
130.32
128.34
128.00
125.78
119.11
116.53
24.63
142.43
137.99
133.39
130.93
130.32
128.34
128.00
125.78
119.11
116.53
148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114 112
f1 (ppm)
O
N
N
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)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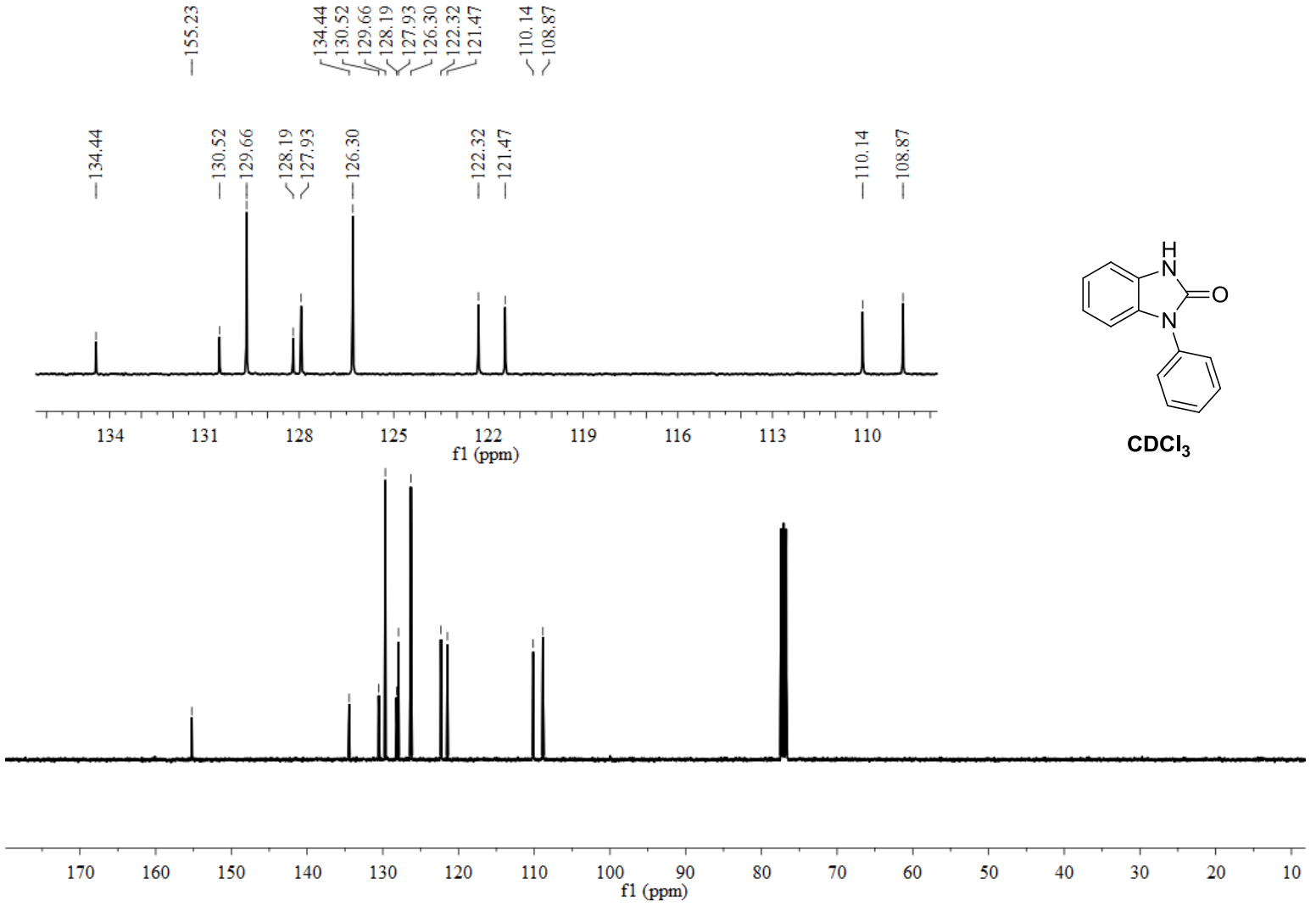
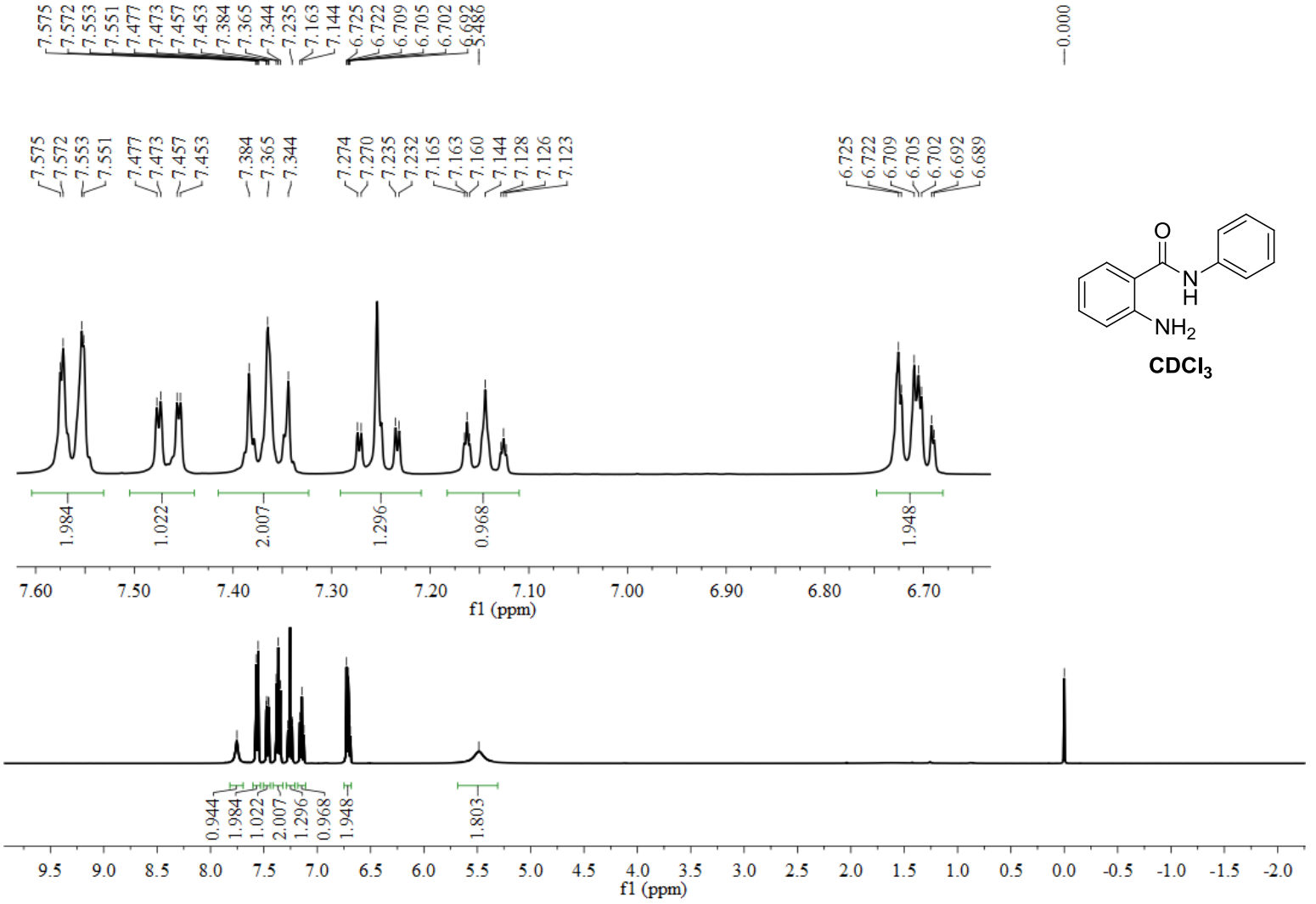
7.825
7.646
7.625
7.602
7.556
7.537
7.516
7.479
7.477
7.462
7.459
7.441
7.438
7.344
7.325
7.307
7.186
7.168
7.149
1.254
1.000
3.033
2.231
1.043
1.187
1.023
f1 (ppm)
CDCl3


155.23
134.44
130.52
129.66
128.19
127.93
126.30
122.32
121.47
110.14
108.87
f1 (ppm)
H
N
O
N
CDCl3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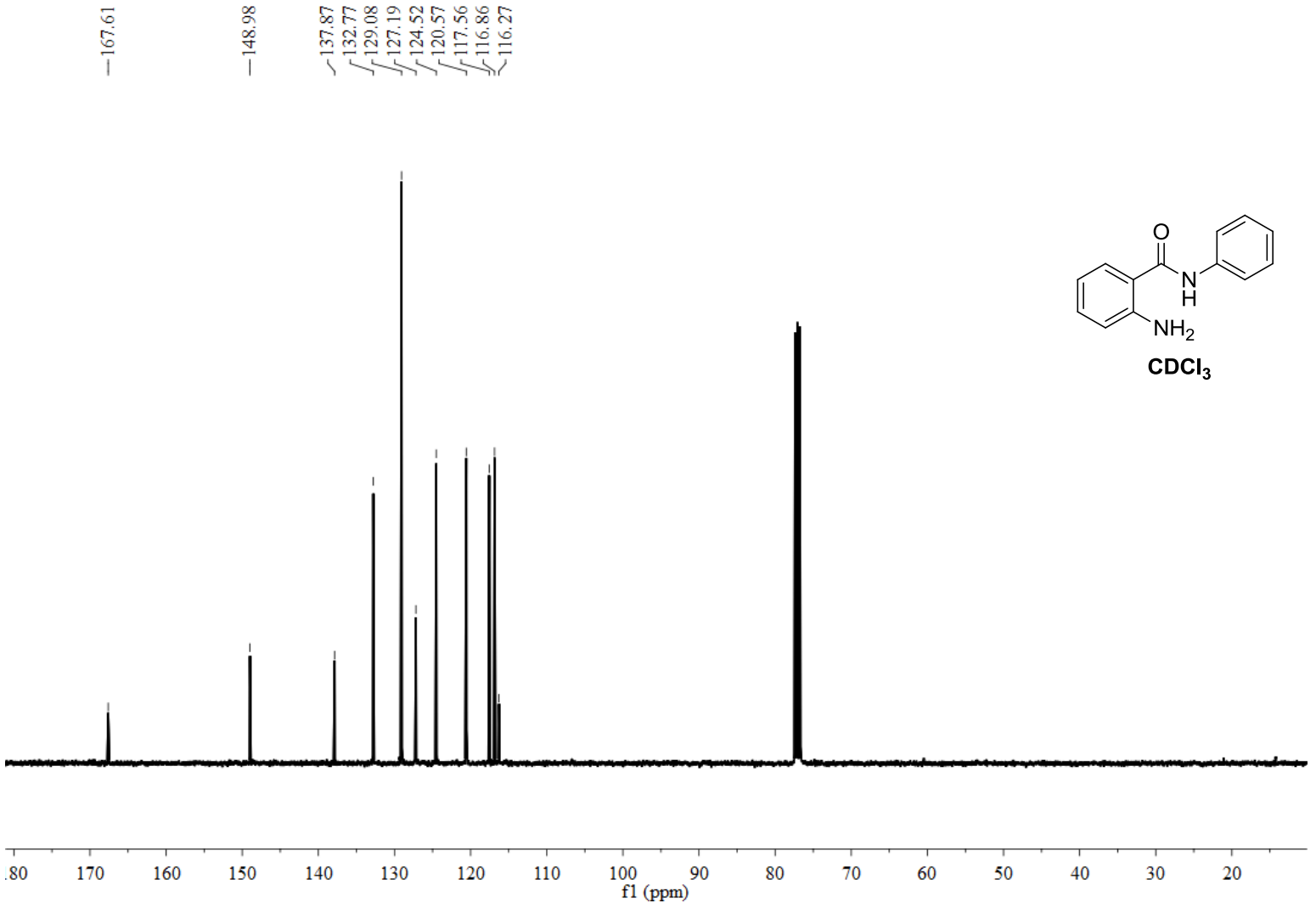
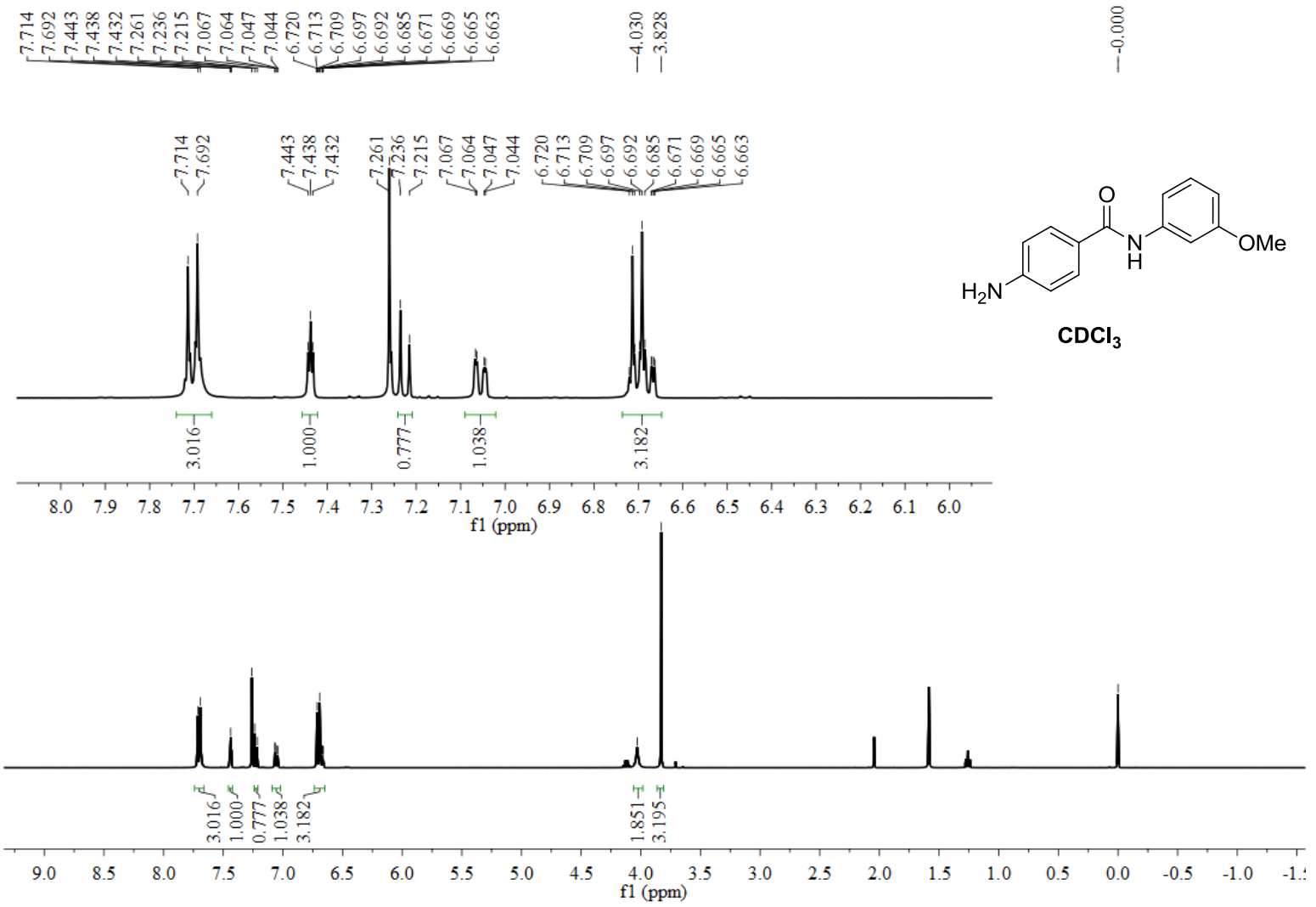
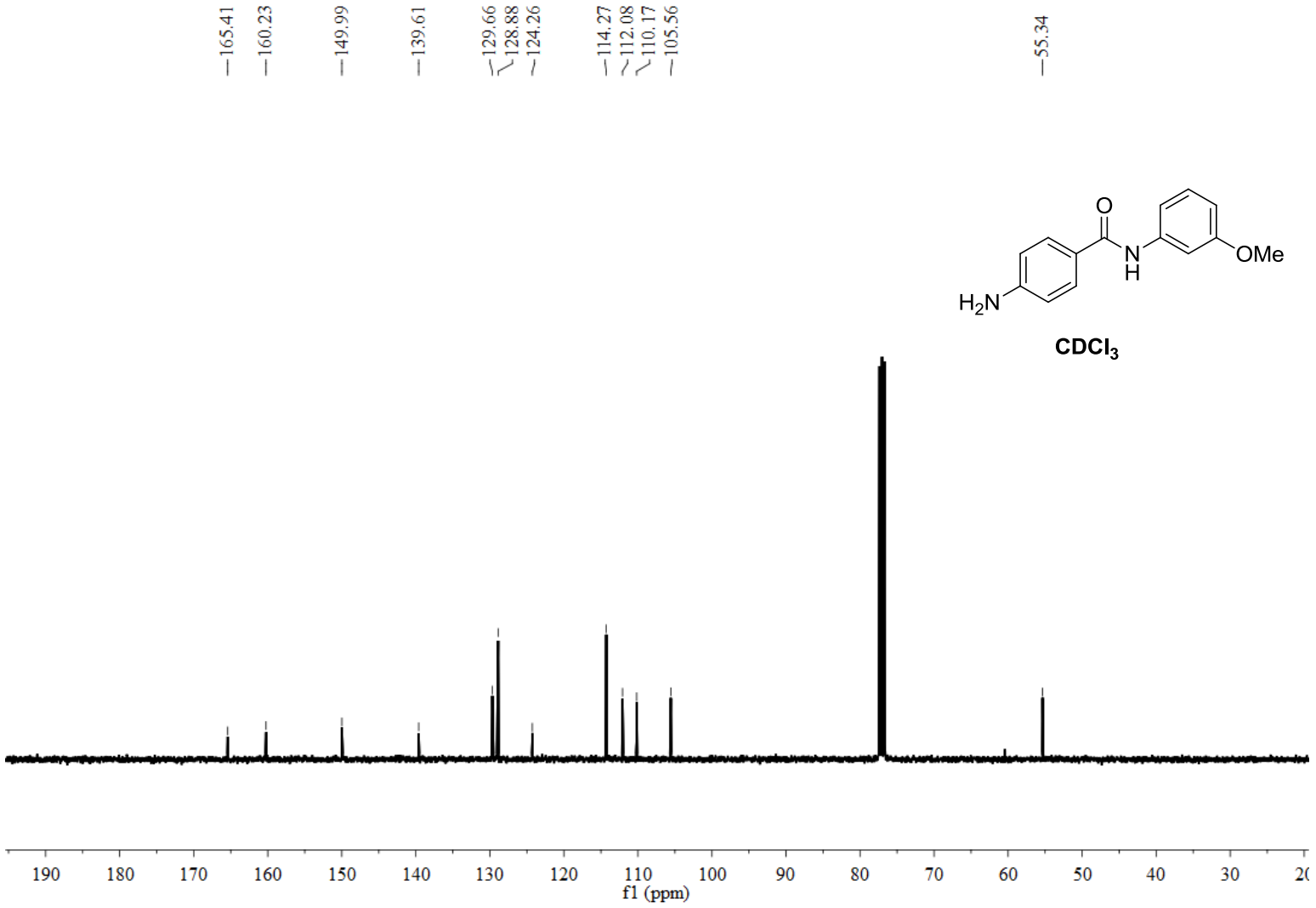
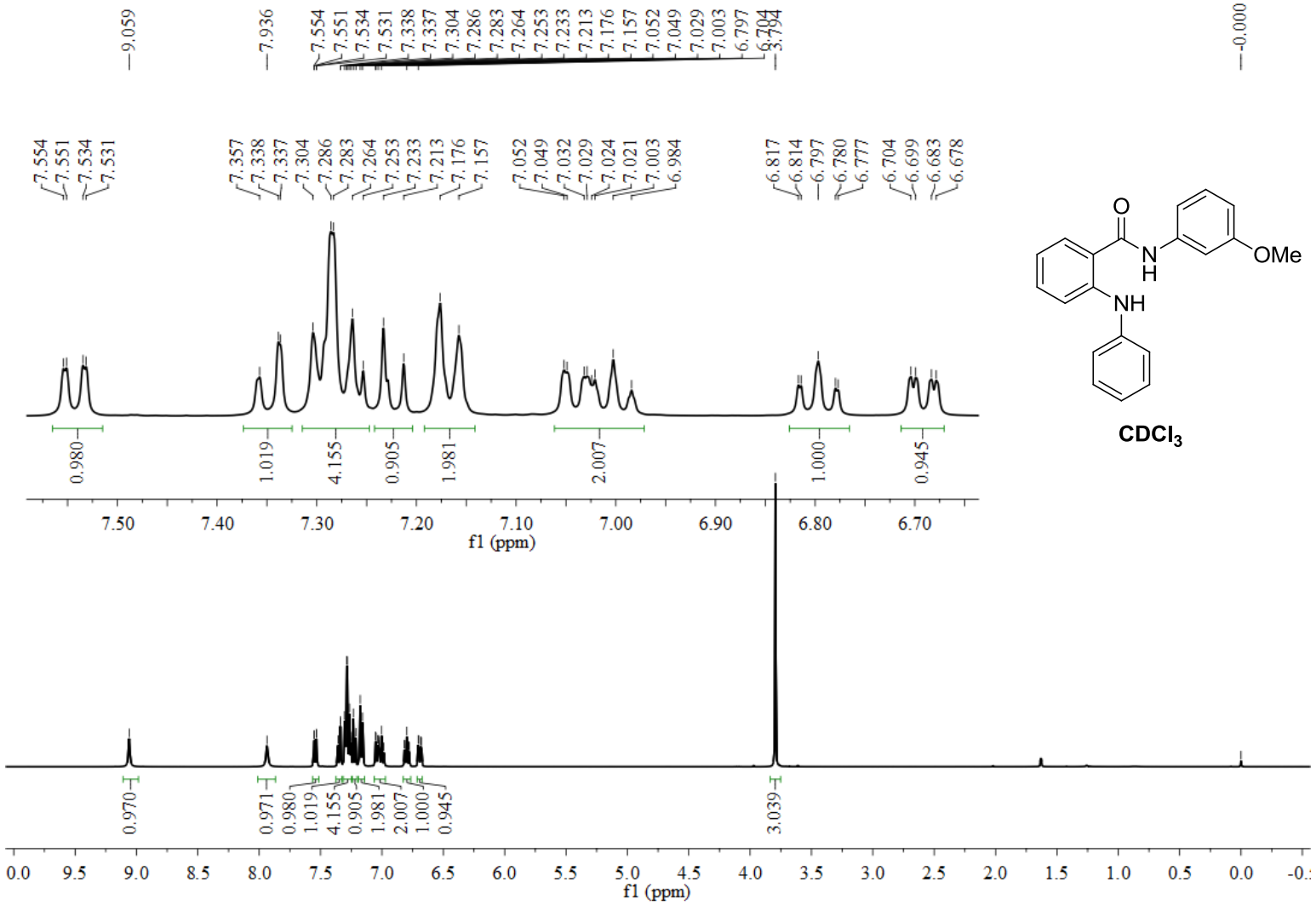
7.572
7.553
7.551
7.477
7.473
7.457
7.453
7.384
7.365
7.344
7.235
7.163
7.144
6.725
6.722
6.709
6.705
6.702
6.692
6.689
5.486
0.000
7.274
7.270
7.232
7.165
7.160
7.128
7.126
7.123
1.984
1.022
2.007
1.296
0.968
1.948
1.803
0.944
f1 (ppm)
O
N
H
NH2
CDCl3


167.61
148.98
137.87
132.77
129.08
127.19
124.52
120.57
117.56
116.86
116.27
O
N
H
NH2
CDCl3
.80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


7.714
7.692
7.443
7.438
7.432
7.261
7.236
7.215
7.067
7.064
7.047
7.044
6.720
6.713
6.709
6.697
6.692
6.685
6.671
6.669
6.665
6.663
4.030
3.828
0.000
3.016
1.000
0.777
1.038
3.182
1.851
3.195
f1 (ppm)
O
N
H
OMe
H2N
CDCl3


165.41
160.23
149.99
139.61
129.66
128.88
124.26
114.27
112.08
110.17
105.56
55.34
O
N
H
OMe
H2N
CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
f1 (ppm)


9.059
7.936
7.554
7.551
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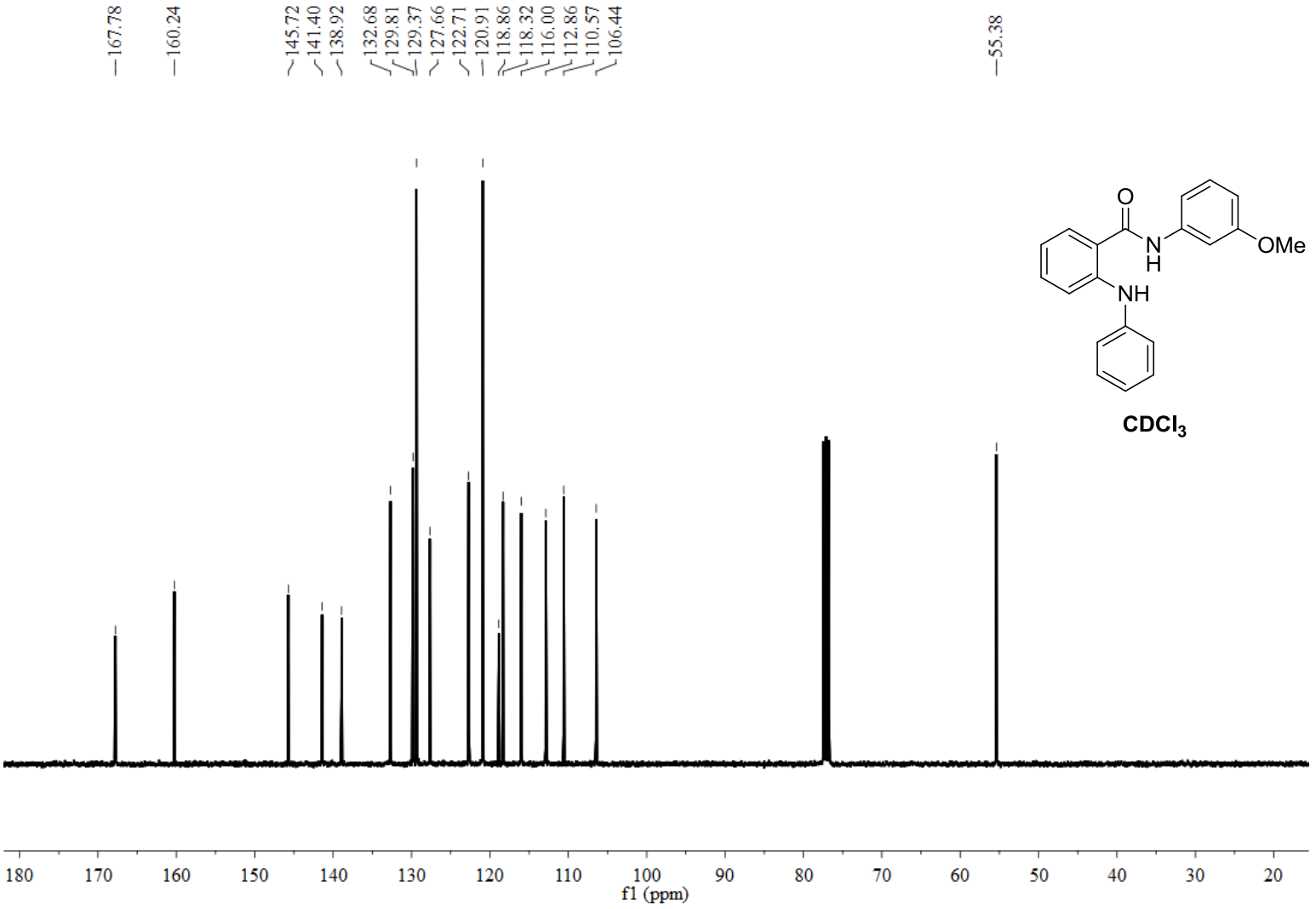
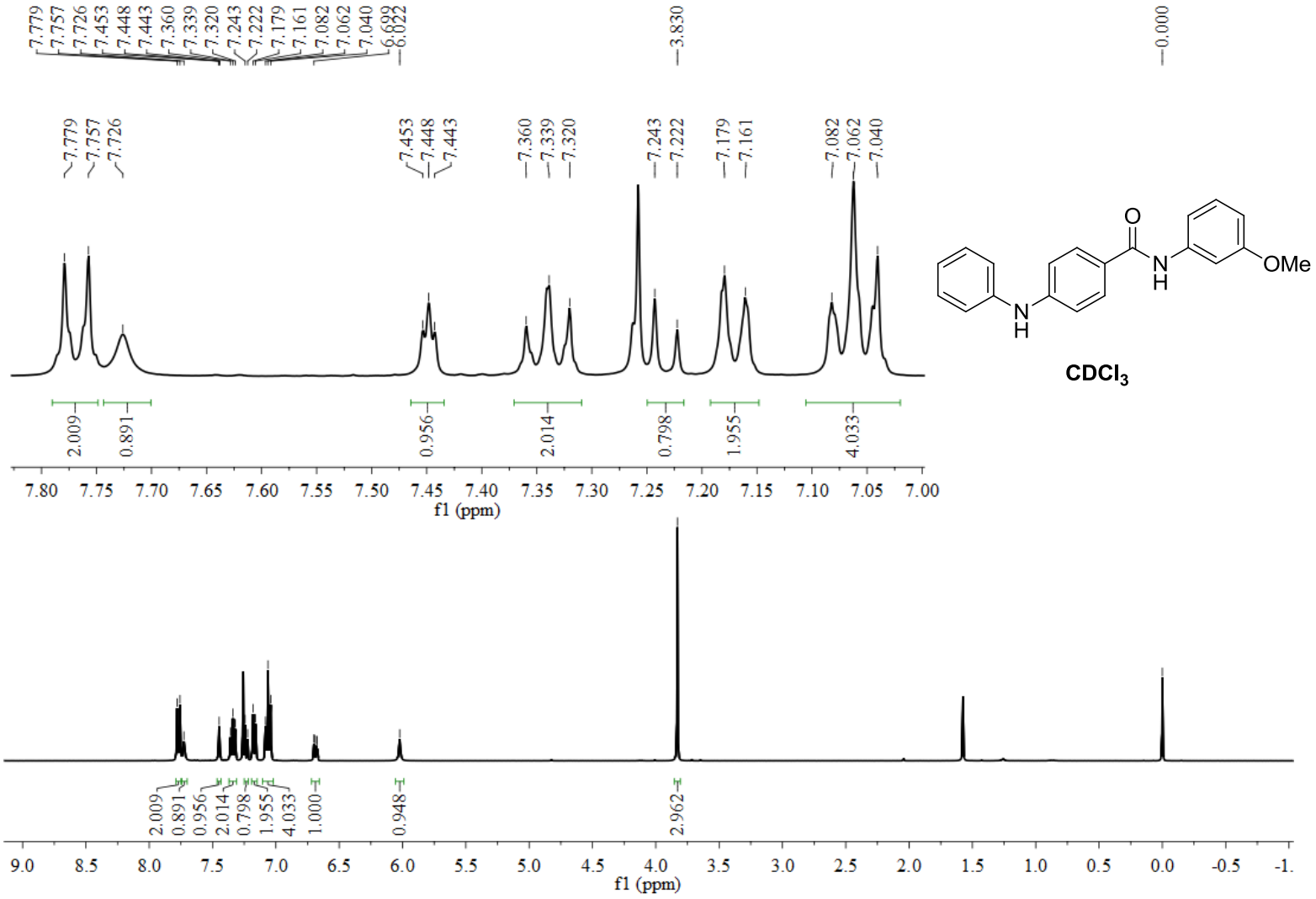
7.531
7.338
7.337
7.304
7.286
7.283
7.264
7.253
7.233
7.213
7.176
7.157
7.052
7.049
7.029
7.003
6.797
6.784
3.794
0.000
7.357
7.338
7.337
7.304
7.286
7.283
7.264
7.253
7.233
7.213
7.176
7.157
7.052
7.049
7.032
7.029
7.024
7.021
7.003
6.984
6.817
6.814
6.797
6.780
6.777
6.704
6.699
6.683
6.678
0.980
1.019
4.155
0.905
1.981
2.007
1.000
0.945
7.50
7.40
7.30
7.20
7.10
7.00
6.90
6.80
6.70
f1 (ppm)
O
N
H
NH
OMe
CDCl3
0.970
0.971
0.980
1.019
4.155
0.905
1.981
2.007
1.000
0.945
3.039
0.0
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
0.0
f1 (ppm)


167.78
160.24
145.72
141.40
138.92
132.68
129.81
129.37
127.66
122.71
120.91
118.86
118.32
116.00
112.86
110.57
106.44
55.38
O
N
H
OMe
NH
CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)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7.726
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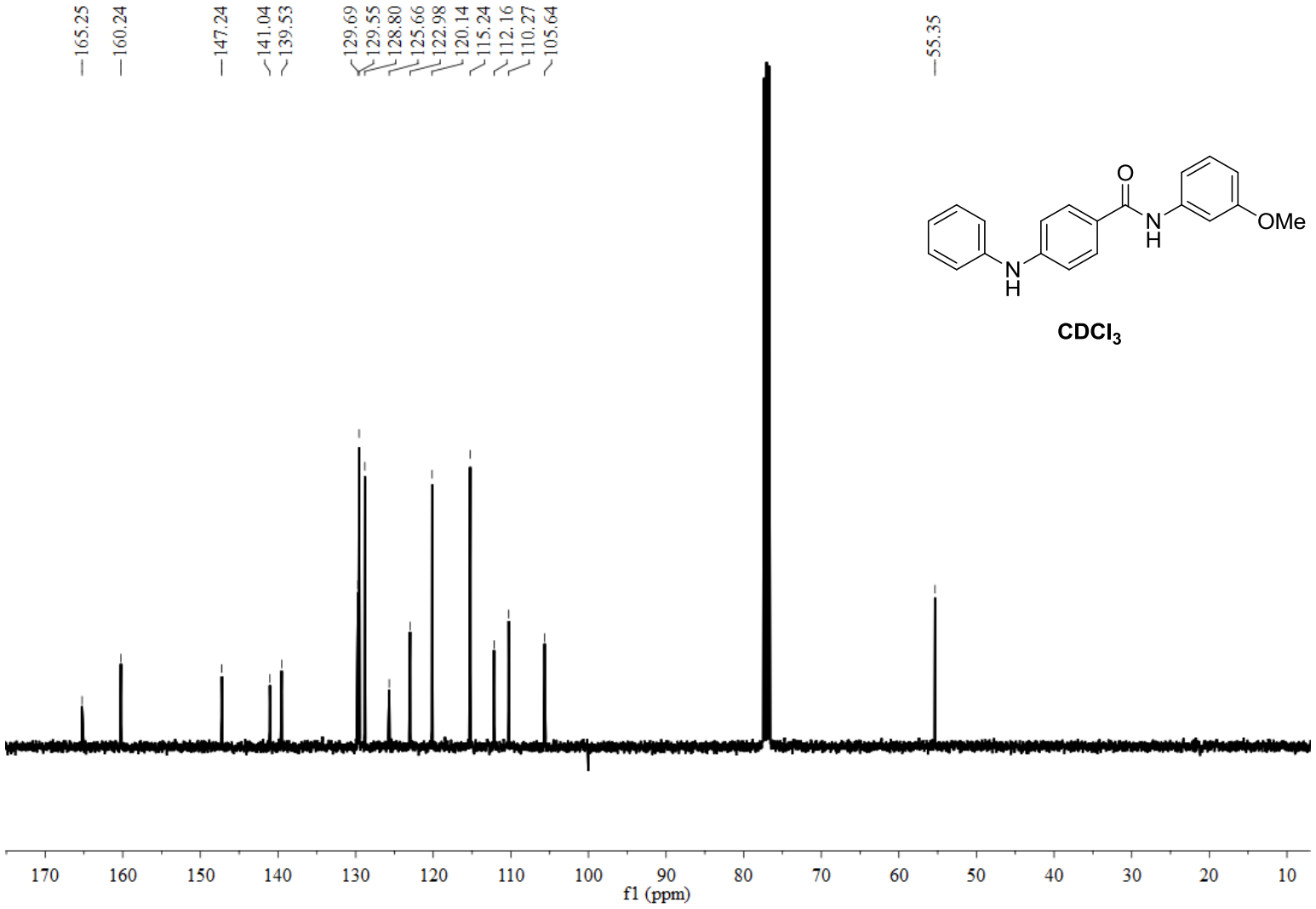
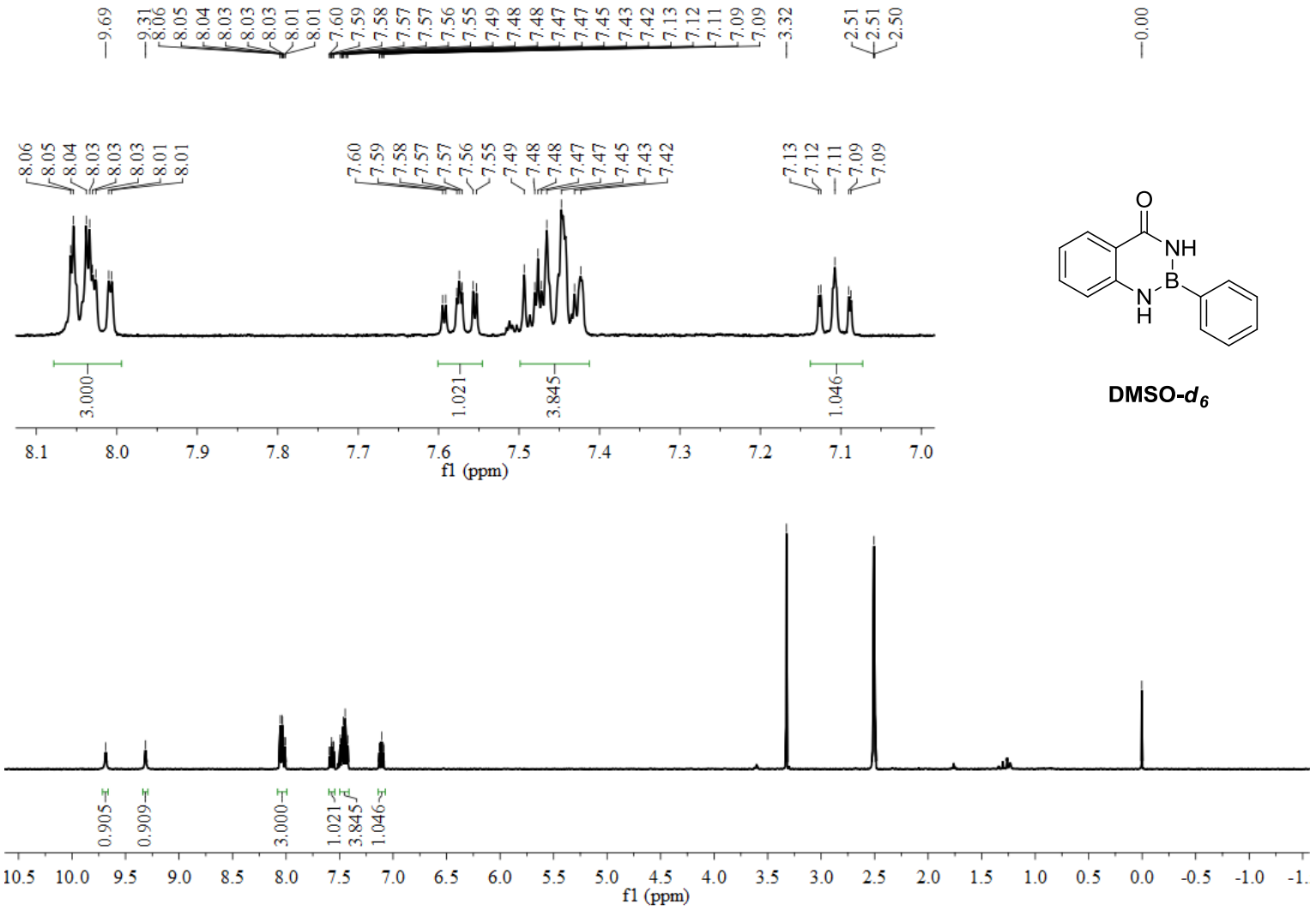
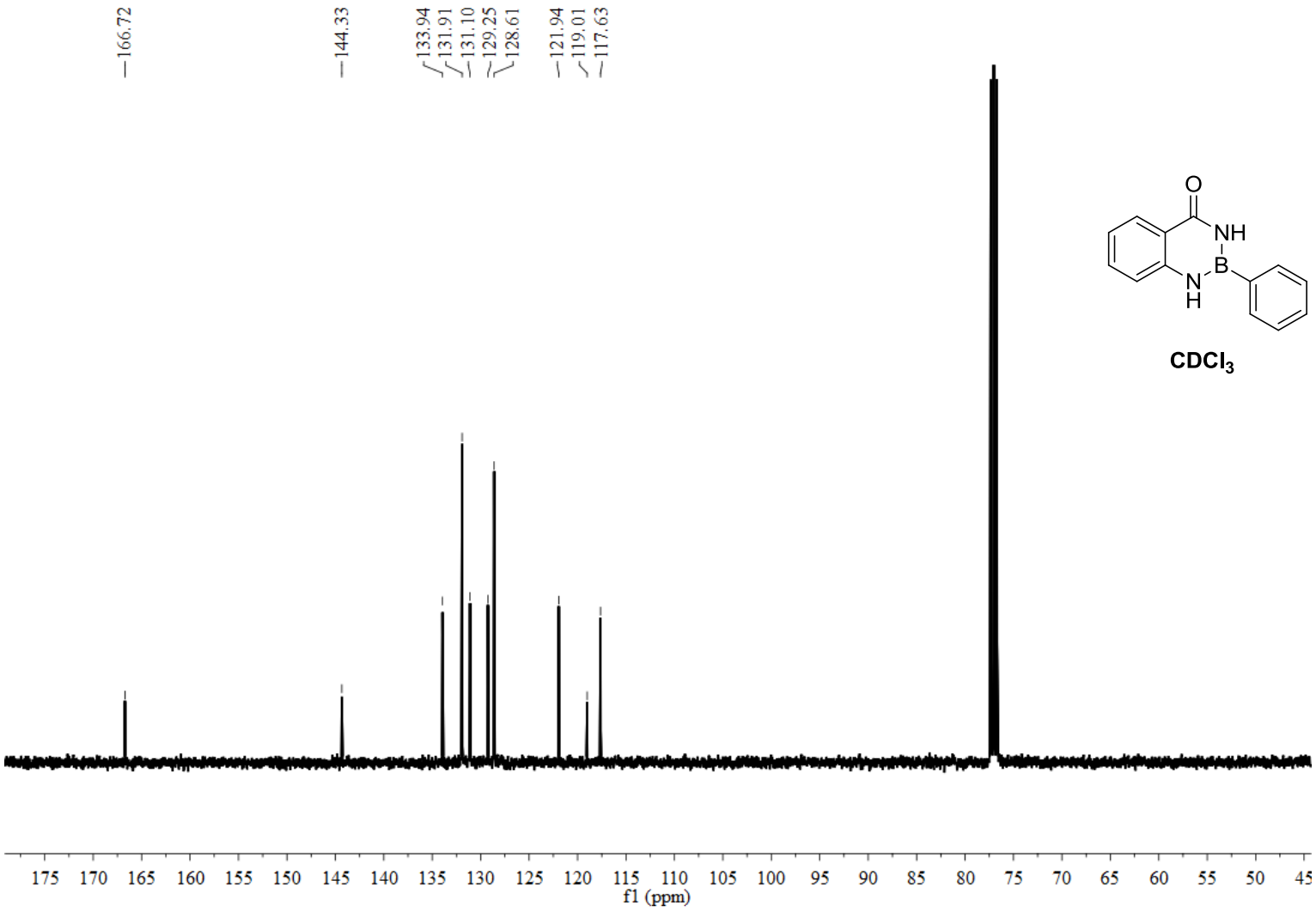
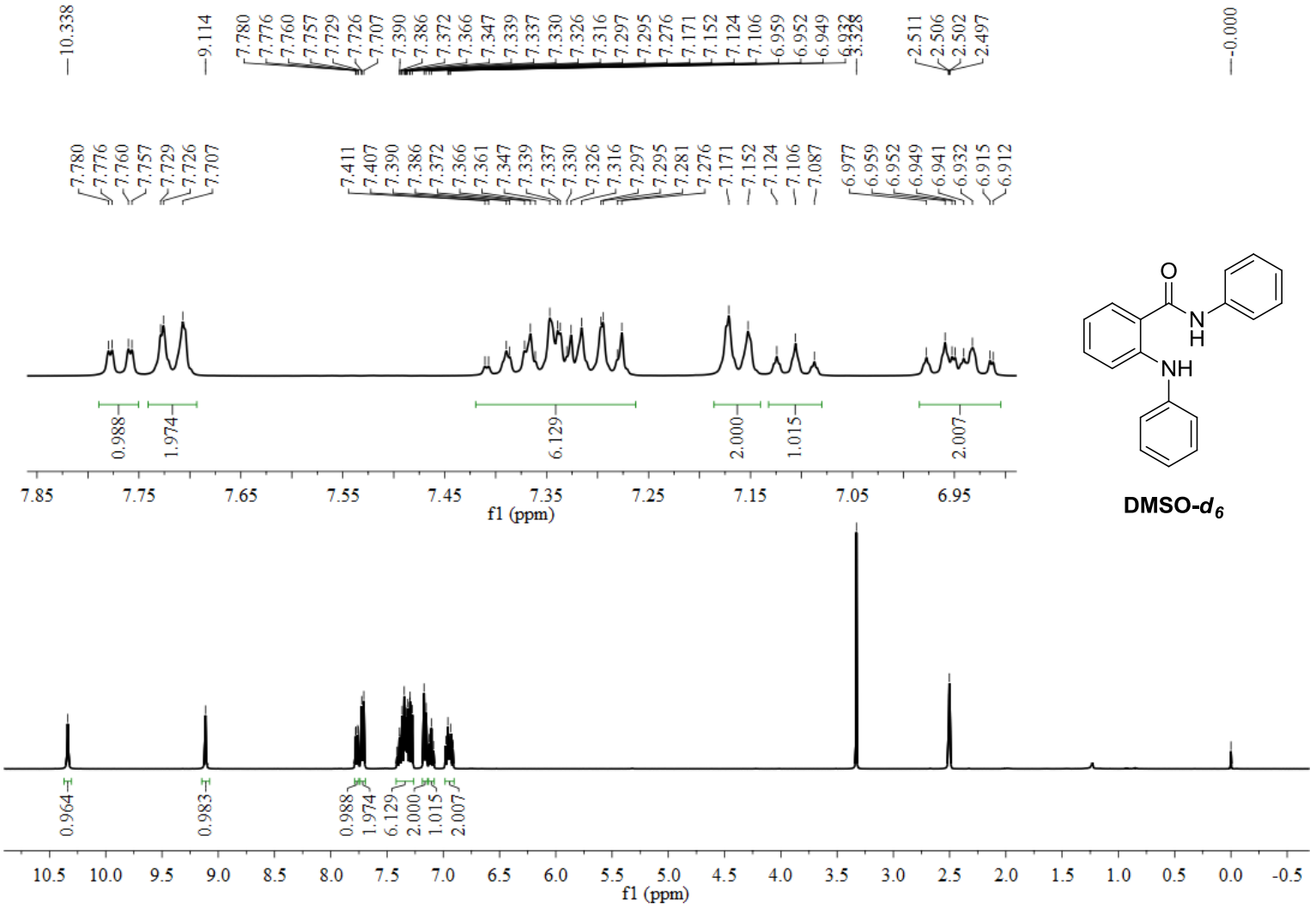
7.448
7.443
7.360
7.339
7.320
7.243
7.222
7.179
7.161
7.082
7.062
7.040
6.822
3.830
0.000
2.009
0.891
0.956
2.014
0.798
1.955
4.033
1.000
0.948
2.962
f1 (ppm)
O
N
H
OMe
CDCl3


165.25
160.24
147.24
141.04
139.53
129.69
129.55
128.80
125.66
122.98
120.14
115.24
112.16
110.27
105.64
55.35
O
N
H
OMe
N
H
CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


9.69
9.31
8.06
8.05
8.04
8.03
8.03
8.03
8.01
8.01
7.60
7.59
7.58
7.57
7.57
7.56
7.55
7.49
7.48
7.48
7.47
7.47
7.45
7.43
7.42
7.13
7.12
7.11
7.09
7.09
3.32
2.51
2.51
2.50
0.00
3.000
1.021
3.845
1.046
f1 (ppm)
0.905
0.909
3.000
1.021
3.845
1.046
f1 (ppm)
O
NH
B
N
H
DMSO-d6


166.72
144.33
133.94
131.91
131.10
129.25
128.61
121.94
119.01
117.63
O
NH
B
N
H
CDCl3
175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45
f1 (ppm)


10.338
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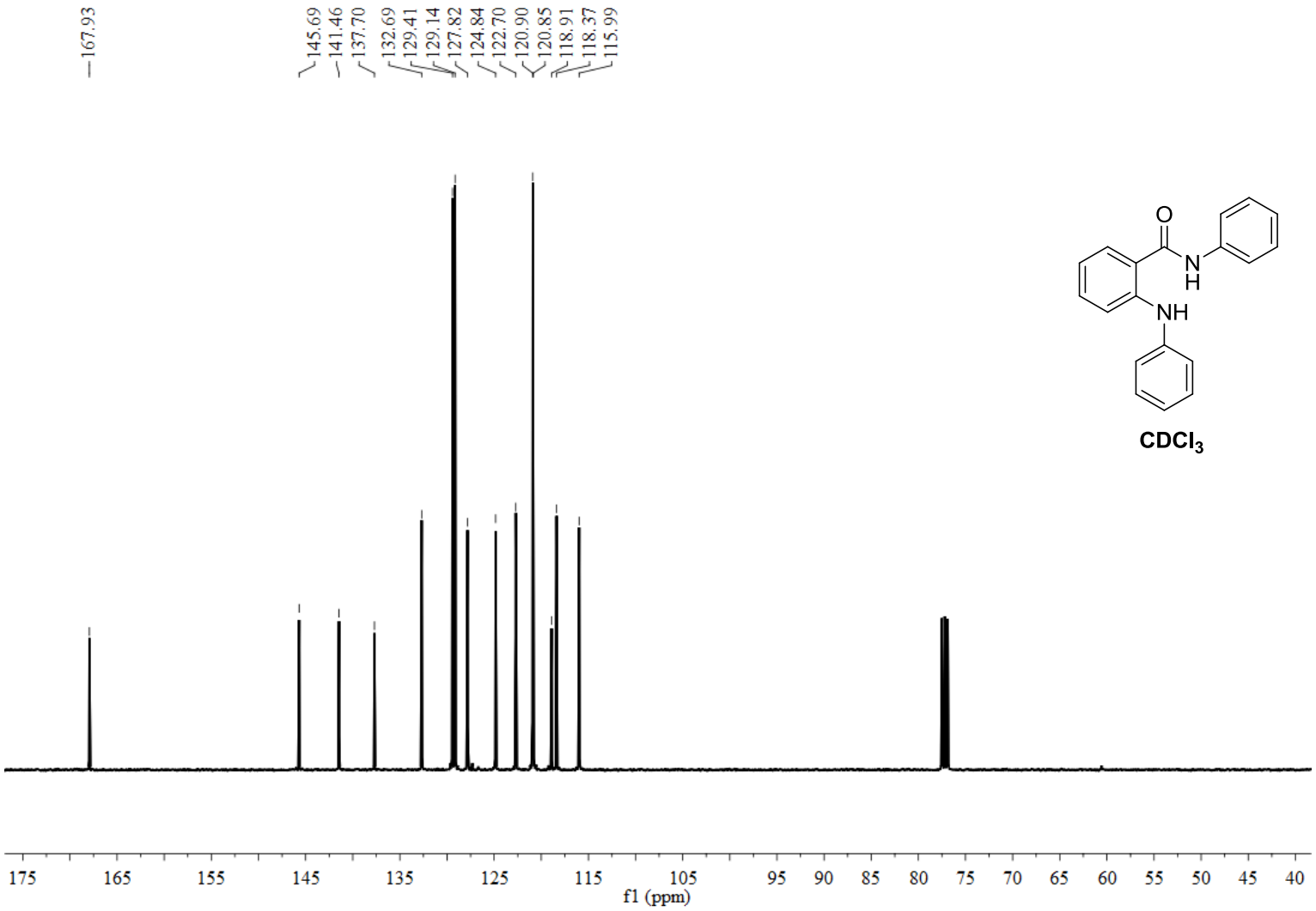
7.780
7.776
7.760
7.757
7.729
7.726
7.707
7.390
7.386
7.372
7.366
7.347
7.339
7.337
7.330
7.326
7.316
7.297
7.295
7.276
7.171
7.152
7.124
7.106
6.959
6.952
6.949
6.932
3.328
2.511
2.506
2.502
2.497
0.000
7.411
7.407
7.361
7.281
7.087
6.977
6.941
6.915
6.912
0.988
1.974
6.129
2.000
1.015
2.007
f1 (ppm)
O
N
H
NH
DMSO-d6
0.964
0.983


167.93
145.69
141.46
137.70
132.69
129.41
129.14
127.82
124.84
122.70
120.90
120.85
118.91
118.37
115.99
O
N
H
NH
CDCl3
175
165
155
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
f1 (ppm)