Supporting Information

A new route to π-extended polycyclic aromatic hydrocarbons via Cross-Dehydrogenative Coupling

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Contents

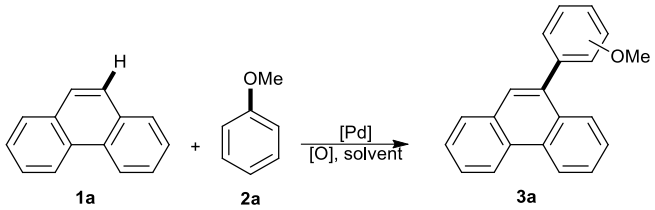
1 General remarks

The following includes general experimental procedures, specific details for representative reactions and spectroscopic information for new compounds. Palladium catalysts and ligands were commercially available and used as received. The reactions were carried out in oil bath using microwave vials (2-5 mL). ^{1}H NMR spectra were recorded at room temperature on 400, 300 and 250 MHz spectrometers, using $CDCl_3$ and DMSO-d_6 as the NMR solvents. ^{1}H NMR spectra are referenced to tetramethylsilane (0.00 ppm) and ^{13}C NMR spectra are referenced from the solvent central peak (77.23 and 39.51 ppm for $CDCl_3$ and DMSO-d_6 respectively). Chemical shifts are given in ppm.

2 Regioselective arylation of phenanthrene

2-1 Screening of reaction conditions

Table S1 Screening of reaction conditions for construction of 9-arylphenanthrene **3a**



1a **2a** **3a**

Entry[a]	Catalyst	[O]	Solvent	Yield (%)[b]
1	$Pd(OAc)_2$	$K_2S_2O_8$	1-propanol	0%
2	$Pd(OAc)_2$	$K_2S_2O_8$	2-propanol	0%
3	$Pd(OAc)_2$	$K_2S_2O_8$	^{t}-Butanol	0%
4	$Pd(OAc)_2$	$K_2S_2O_8$	TFE	25%
5	$Pd(OAc)_2$	$K_2S_2O_8$	AcOH	10%
6	$Pd(OAc)_2$	$K_2S_2O_8$	PivOH	20%
7	$Pd(OAc)_2$	$K_2S_2O_8$	TFAA	28%
8	$Pd(OAc)_2$	$K_2S_2O_8$	TCA	36%
9	$Pd(OAc)_2$	$K_2S_2O_8$	CH_3SO_3H	27%
10	$Pd(OAc)_2$	$K_2S_2O_8$	CF_3SO_3OH	30%
11	$PdCl_2$	$K_2S_2O_8$	TFA	15%
12	$Pd(acac)_2$	$K_2S_2O_8$	TFA	28%
13	$Pd(dba)_2$	$K_2S_2O_8$	TFA	12%
14	$Pd(OAc)_2$	$K_2S_2O_8$	TFA	62%
15	**$Pd(OAc)_2$**	**$Na_2S_2O_8$**	**TFA**	**75%**
16	$Pd(OAc)_2$	$(NH_4)_2S_2O_8$	TFA	60%
17	$Pd(OAc)_2$	AgOAc	TFA	40%
18	$Pd(OAc)_2$	DDQ	TFA	40%
19	$Pd(OAc)_2$	BQ	TFA	20%
20	$Pd(OAc)_2$	BP	TFA	50%
21	$Pd(OAc)_2$	DTBP	TFA	64%
22	$Pd(OAc)_2$	TBHP	TFA	50%

[a]All reactions were run under the following conditions: Phenanthrene (0.1 mmol, 1.0 equiv), Arene (5 equiv), Pd catalyst (10 mol %), Oxidant (1equiv), Solvent (10 equiv), 80 °C, 12 h.

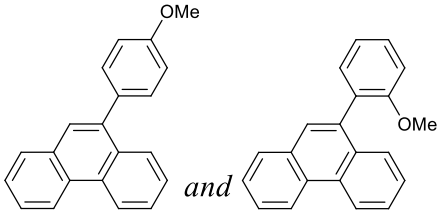
BQ= Benzoquinone, BP= Benzoyl peroxide, DTBP= Di-^{t}-Butyl peroxide, TBHP= ^{t}-Butyl hydrogen peroxide, TFE= Trifluoroethanol, PivOH= Pivalic acid, TFAA= Trifluoroacetic anhydride, TCA= Trichloroacetic acid, TFA= Trifluoroacetic acid.

2-2 General experimental procedure for direct arylation of phenanthrene

A vial equipped with a stir bar was charged with phenanthrene (0.1 mmol, 1 equiv), arene (5 equiv), $Pd(OAc)_2$ (10 mol %), $Na_2S_2O_8$ (1 equiv), TFA (10 eqiuv) and capped. The resulting mixture was heated in an oil bath at 80 °C for 12 h, cooled then filtered through a short plug of silica. Removal of the solvent gave a crude mixture which was purified by column chromatography (n-hexane and n-hexane/EtOAc gradient).

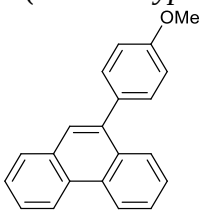
2-3 Experimental characterization data

Mixture of 9-(4-methoxyphenyl)phenanthreneand 9-(2-methoxyphenyl)phenanthrene (**3a**-mixture**)**



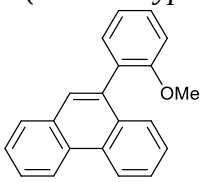
Light yellow solid, as an isomeric mixture of regioisomers. The isomeric ratio was found to be 1/3.8 (*o/p*) as per NMR, 53 mg (75% combined yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (isomeric mixture) 8.80-8.73 (m, 4H), 7.97-7.89 (m, 4H), 7.70-7.46 (m, 14H), 7.14-7.07 (m, 4H), 3.93 (s, 3H, *p*-isomer), 3.71 (s, 3H, *o*-isomer); ^{13}C NMR (100 MHz, $CDCl_3$) δ (isomeric mixture) 157.9, 156.4, 137.3, 132.0, 130.8, 130.6, 130.3, 130.0, 129.6, 128.8, 128.1, 127.5, 126.7, 126.4, 126.1, 125.9, 125.7, 125.5, 125.4, 125.1, 121.8, 121.6, 121.4, 119.6, 112.7, 109.8, 54.5, 54.3.

9-(4-methoxyphenyl)phenanthrene (**3a**-*para isomer*)



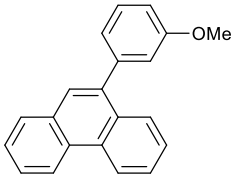
White solid, mp 156-157 °C (157-159 °C)[1]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.79 (d, *J* = 8.2 Hz, 1H), 8.74 (d, *J* = 8.1 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.91 (d, *J* = 7.5 Hz, 1H), 7.71-7.49 (m, 7H), 7.08 (d, *J* = 8.1 Hz, 2H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 137.3, 132.1, 130.6, 130.3, 130.2, 130.01, 129.6, 128.9, 127.5, 126.4, 125.9, 125.8, 125.4, 125.3, 121.8, 121.5, 112.7, 54.3. Anal. Calcd (%) for $C_{21}H_{16}O$: C, 88.70; H, 5.67. Found: C, 88.98; H, 5.83.

9-(2-methoxyphenyl)phenanthrene (**3a**-*ortho isomer*)



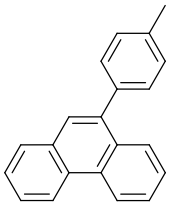
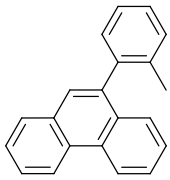
Oil[2], ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.3 Hz, 1H), 8.63 (d, *J* = 8.3 Hz, 1H), 7.79 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.59 (s, 1H), 7.58–7.50 (m, 4H), 7.42–7.35 (m, 2H), 7.27 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.02 (td, *J* = 7.4, 1.2 Hz, 1H), 6.98 (dd, *J* = 8.3, 0.9 Hz, 1H), 3.60 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.4, 134.8, 130.8 130.7, 130.4, 129.2, 129.1, 128.5, 128.1, 127.6, 126.8, 126.1, 125.5, 125.4, 125.2, 125.1, 121.7, 121.5, 119.7, 109.9, 54.5. Anal. Calcd (%) for $C_{21}H_{16}O$: C, 88.70; H, 5.67. Found: C, 88.95; H, 5.79.

9-(3-methoxyphenyl)phenanthrene (**3a**-*meta isomer*)

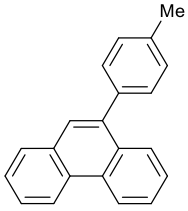


White solid, mp 91-92 °C (92-94 °C)[1]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.82 (d, *J* = 8.1 Hz, 1H), 8.76 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.78−7.59 (m, 5H), 7.50−7.47 (m, 1H), 7.22−7.18 (m, 2H), 7.07 (d, *J* = 8.0 Hz, 1H), 3.91 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.6, 142.3, 138.7, 131.6, 131.1, 130.7, 130.0, 129.4, 128.7, 127.4, 127.0, 126.9, 126.7, 126.6, 126.5, 122.9, 122.6, 122.6, 115.7, 113.1, 55.4. Anal. Calcd (%) for $C_{21}H_{16}O$: C, 88.70; H, 5.67. Found: C, 89.01; H, 5.81.

Mixture of 9-(4-methylphenyl)phenanthrene and 9-(2-methylphenyl)phenanthrene (**3b**-*mixture*)

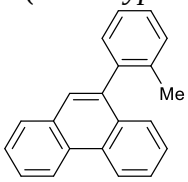
 *and*  Light yellow solid, as an isomeric mixture of regioisomers. The isomeric ratio was found to be 1/2 (*o/p*) as per NMR, 54 mg (80% combined yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ (isomeric mixture) 8.82-8.76 (m, 4H), 7.99-7.90 (m, 3H), 7.77-7.35 (m, 19H), 2.51 (s, 3H, *p*-isomer), 2.10 (s, 3H, *o*-isomer); ^{13}C NMR (100 MHz, $CDCl_3$) δ (isomeric mixture) 137.7, 136.8, 136.0, 131.4, 130.6, 130.2, 129.8, 128.9, 127.9, 127.7, 127.5, 127.1, 127.0, 126.6, 126.3, 125.9, 125.7, 125.5, 125.4, 125.4, 125.3, 124.6, 121.8, 121.5, 121.4, 22.7, 21.9.

9-(4-methyphenyl)phenanthrene (**3b**-*para isomer*)



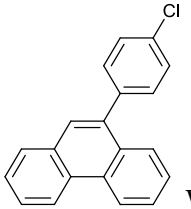
White solid, mp 89−91 °C (90−92 °C)[1]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 8.4 Hz, 1H), 8.60 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.77 (dd, *J* = 7.8, 0.8 Hz, 1H), 7.57-7.53 (m, 3H), 7.59-7.41 (m, 1H), 7.44-7.40 (m, 1H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 136.8, 136.0, 130.6, 130.2, 129.6, 128.9, 128.8, 127.9, 127.6, 126.4, 125.9, 125.7, 125.4, 125.4, 125.3, 121.8, 121.5, 20.2. Anal. Calcd (%) for $C_{21}H_{16}$: C, 93.99; H, 6.01. Found: C, 93.71; H, 5.85.

9-(2-methyphenyl)phenanthrene (**3b**-*ortho isomer*)



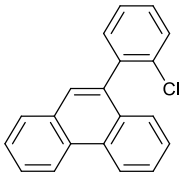
Oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.4 Hz, 1H), 8.62 (d, *J* = 8.2 Hz, 1H), 7.77 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.59-7.50 (m, 4H), 7.42-7.36 (m, 2H), 7.30-7.21 (m, 4H), 1.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 137.3, 135.9, 130.6, 130.3, 129.3, 129.3, 128.9, 128.8, 127.5, 126.6, 126.1, 125.8, 125.7, 125.6, 125.4, 125.3, 124.7, 121.8, 121.5, 19.0. Anal. Calcd (%) for $C_{21}H_{16}$: C, 93.99; H, 6.01. Found: C, 93.68; H, 5.83.

9-(4-chlorophenyl)phenanthrene (**3c**-*para isomer*)



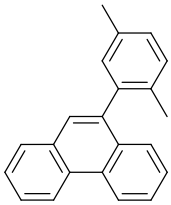
White solid, mp 122-124 °C (131-133 °C)[3]; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.81 (d, *J* = 8.2 Hz, 1H), 8.76 (d, *J* = 8.1 Hz, 1H), 7.94-7.87 (m, 2H), 7.77-7.58 (m, 6H), 7.51-7.47 (m, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 139.2, 137.5, 131.4, 130.1, 128.7, 128.7, 128.5, 128.3, 127.7, 127.6, 127.5, 127.0, 126.8, 126.6, 126.6, 123.0, 122.7, 122.6. Anal. Calcd (%) for $C_{20}H_{13}Cl$: C, 83.19; H, 4.54. Found: C, 83.60; H, 4.72.

9-(2-chlorophenyl)phenanthrene (**3c**-*ortho isomer*)



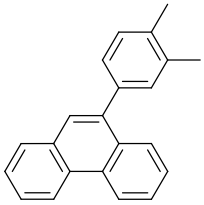
White solid, mp 108-110 ºC (118.9-120.1 ºC)[4]; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.83-8.76 (m, 2H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.81-7.65 (m, 5H), 7.62-7.54 (m, 3H), 7.47-7.44 (m, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 139.4, 136.2, 132.1, 131.4, 130.8, 130.3, 129.6, 129.1, 128.8, 127.9, 126.9, 126.9, 126.8, 126.7, 126.7, 126.6, 122.9, 122.6. Anal. Calcd (%) for $C_{20}H_{13}Cl$: C, 83.19; H, 4.54. Found: C, 82.97; H, 4.40.

9-(2,5-dimethylphenyl)phenanthrene **3d**



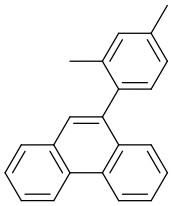
Light yellow oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.75-8.69 (m, 2H), 7.87-7.84 (m, 2H), 7.67-7.46 (m, 6H), 7.21-7.19 (m, 2H), 2.37 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 137.5, 134.0, 132.8, 130.6, 130.4, 130.0, 129.3, 128.9, 128.7, 127.5, 127.3, 126.0, 125.9, 125.7, 125.5, 125.4, 125.3, 121.8, 121.5, 19.9, 18.5; MS *m/z* (%) 282 ($M^{\bullet+}$, 100), 265 (40), 252 (21); IR (KBr) 2919, 2851, 2326, 2160, 2034, 1992, 1685, 1537, 1458, 1076, 799, 725, 683, 629 cm^{-1}. Anal. Calcd (%) for $C_{22}H_{18}$: C, 93.57; H, 6.43. Found: C, 93.81; H, 6.55.

9-(3,4-dimethylphenyl)phenanthrene **3e**



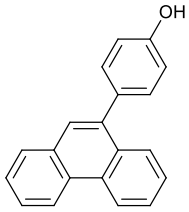
Light orange oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.2 Hz, 1H), 8.60 (d, *J* = 8.5 Hz, 1H), 7.87 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.77 (dd, *J* = 7.7 Hz, 1.4 Hz, 1H), 7.57 (s, 1H), 7.40-7.56 (m, 5H), 7.23 (s, 1H), 7.18 (m, 1H), 2.28 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 137.2, 135.4, 134.6, 130.5, 130.2, 130.1, 129.5, 128.8, 128.4, 127.5, 126.4, 126.2, 126.0, 125.7, 125.3, 125.2, 121.8, 121.4, 18.8, 18.5; MS *m/z* (%) 282 ($M^{\bullet+}$, 100), 267 (48), 252 (40); IR (KBr) 2921, 2316, 2016, 1737, 1496, 1449, 746, 725 cm^{-1}. Anal. Calcd (%) for $C_{22}H_{18}$: C, 93.57; H, 6.43. Found: C, 93.87; H, 6.59.

9-(2,4-dimethylphenyl)phenanthrene **3f**



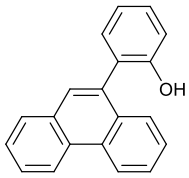
Light yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91-8.85 (m, 2H), 8.03-8.01 (d, *J* = 7.6 Hz, 1H), 7.81-7.73 (m, 5H), 7.66-7.64 (m, 1H), 7.41-7.28 (m, 3H), 2.61 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 136.6, 136.2, 135.6, 130.6, 130.5, 129.6, 129.2, 128.9, 127.9, 127.4, 126.8, 126.2, 125.8, 125.6, 125.4, 125.3, 125.2, 121.7, 121.4, 20.1, 18.9. MS *m/z* (%) 282 ($M^{\bullet+}$, 100), 267 (67), 252 (41); IR (KBr) 2922, 2853, 1600, 1450, 818, 747, 725 cm^{-1}. Anal. Calcd (%) for $C_{22}H_{18}$: C, 93.57; H, 6.43. Found: C, 93.85; H, 6.57.

9-(4-hydroxyphenyl)phenanthrene (**3g**-*para isomer*)



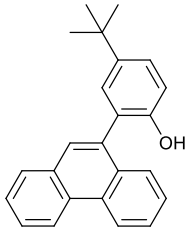
White solid, mp 146-148 °C (150-152 °C)[5]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 8.2 Hz, 1H), 8.64 (d, *J* = 8.2 Hz, 1H), 7.86 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.81 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.61-7.45 (m, 5H), 7.35 (d, *J* = 8.5 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 2H), 4.85 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 138.3, 133.3, 131.6, 131.3, 129.8, 128.5, 127.4, 126.9, 126.8, 126.4, 126.4, 122.9, 122.5, 115.2; MS *m/z* (%) 270 ($M^{\bullet+}$, 100) 252 (15), 239 (25), 149 (15); IR (KBr) 3386, 2922, 2854, 1457, 1148, 1076 cm^{-1}. Anal. Calcd (%) for $C_{20}H_{14}O$: C, 88.86; H, 5.22. Found: C, 89.13; H, 5.37.

9-(2-hydroxyphenyl)phenanthrene (**3g**-*ortho isomer*)



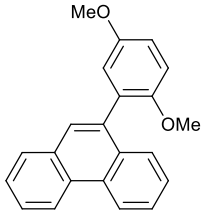
Yellowish oil[6], ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 8.4 Hz, 1H), 8.75 (d, *J* = 8.2 Hz, 1H), 7.92-7.90 (m, 1H), 7.79 (s, 1H), 7.74-7.63 (m, **4**H), 7.58-7.55 (m, 1H), 7.45-7.39 (m, 1H), 7.35-7.33 (m, 1H), 7.14-7.07 (m, 2H), 4.89 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 131.6, 130.4, 130.2, 129.9, 129.7, 129.4, 128.6, 128.2, 127.8, 126.2, 126.1, 126.0, 125.5, 125.2, 122.0, 121.6, 119.6, 114.6; MS *m/z* (%) 270 ($M^{\bullet+}$, 30), 239 (25), 167 (27), 149 (43), 97 (48), 83 (52), 71 (73), 57 (100); Anal. Calcd (%) for $C_{20}H_{14}O$: C, 88.86; H, 5.22. Found: C, 89.18; H, 5.41.

4-(tert-butyl)-2-(phenanthrene-9-yl)phenol **3h**



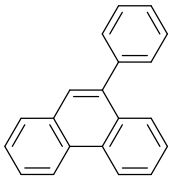
Yellowish solid, mp 158-160 ºC; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.82 (d, *J* = 8.2 Hz, 1H), 8.76 (d, *J* = 8.2 Hz, 1H), 7.95 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.83-7.60 (m, 6H), 7.46 (dd, *J* = 8.3, 2.5 Hz, 1H), 7.38 (d, *J* = 2.5 Hz, 1H), 7.07 (d, *J* = 8.5, 1H), 4.62 (bs, 1H), 1.39 (s, 9H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 151.0, 143.4, 133.4, 131.5, 130.9, 130.9, 129.1, 128.8, 128.1, 127.2, 127.1, 127.1, 126.7, 126.5, 125.6, 123.1, 122.6, 115.1, 31.6; MS *m/z* (%) 326 ($M^{\bullet+}$, 77), 311 (100), 295 (10), 281 (18); IR (KBr) 3749, 3499, 2923, 2277, 2176, 2047, 1984, 1683, 1602, 1446, 1201, 1140, 803, 753 cm^{-1}. Anal. Calcd (%) for $C_{24}H_{22}O$: C, 88.31; H, 6.79. Found: C, 88.05; H, 6.60.

9-(2,5-dimethoxyphenyl)phenanthrene **3i**



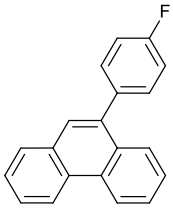
Light yellow solid, mp 150-152 ºC; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.79-8.72 (m, 2H), 7.90 (d, *J* = 7.5 Hz, 2H), 7.77-7.48 (m, 5H), 7.01-7.00 (m, 2H), 6.97 (d, *J* = 1.8 Hz, 1H), 3.81 (s, 3H), 3.65 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 135.7, 151.8, 135.7, 131.7, 131.3, 130.2, 130.2, 128.8, 128.7, 127.7, 127.2, 126.6, 126.5, 126.3, 126.3, 122.7, 122.6, 117.6, 113.8, 112.4, 56.4, 55.9; MS *m/z* (%) 314 ($M^{\bullet+}$, 100), 299 (22), 284 (15), 271 (37) 255 (18) 239 (19); IR (KBr) 3060, 2934, 2829, 1491, 1455, 1420, 1216, 1046, 1020, 798, 749, 721 cm^{-1}. Anal. Calcd (%) for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 84.29; H, 5.88.

9-phenylphenanthrene **3j**



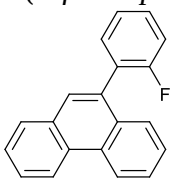
Light yellow solid, mp 101-102 ºC (100-102 ºC)[1]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.2 Hz, 1H), 8.57 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H) 7.57-7.50 (m, 1H), 7.42-7.32 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7, 137.7, 130.5, 130.0, 129.5, 129.0, 128.8, 127.6, 127.2, 126.4, 126.2, 125.8, 125.7, 125.5, 125.4, 125.3, 121.8, 121.4. Anal. Calcd (%) for $C_{20}H_{14}$: C, 94.45; H, 5.55. Found: C, 94.74; H, 5.68.

9-(4-fluorophenyl)phenanthrene (**3k**-*para isomer*)



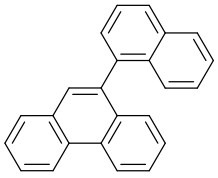
Yellow solid, mp 147-149 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (d, *J* = 8.2 Hz, 1H), 8.72 (d, *J* = 8.2 Hz, 1H), 7.81 (m, 2H), 7.62-7.45 (m, 5H), 7.35 (d, *J* = 8.5 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.3 (d, $J_{C\text{-}F}$ = 244.8 Hz), 137.7, 136.7 (d, $J_{C\text{-}F}$ = 3.4 Hz), 131.6 (d, $J_{C\text{-}F}$ = 7.8 Hz), 131.5, 131.1, 130.7, 130.0, 128.6, 127.6, 126.9, 126.7, 126.7, 126.6, 126.5, 122.9, 122.5, 115.2 (d, $J_{C\text{-}F}$ = 21.2 Hz). Anal. Calcd (%) for $C_{20}H_{13}F$: C, 88.21; H, 4.81. Found: C, 87.97; H, 4.66.

9-(2-fluorophenyl)phenanthrene (**3k**-*ortho isomer*)



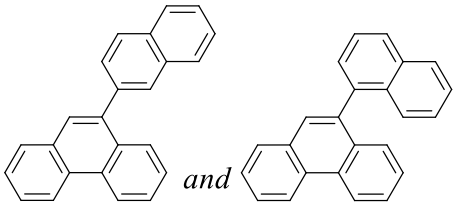
Light yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 8.3 Hz, 1H), 8.65 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.64 (s, 1H), 7.63-7.51 (m, 4H), 7.49-7.43 (m, 1H), 7.41-7.35 (m, 2H), 7.23-7.13 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 159.3 (d, $J_{C\text{-}F}$ = 245.2 Hz), 131.7, 131.3 (d, $J_{C\text{-}F}$ = 2.7 Hz), 130.3, 129.8, 129.3, 128.5, 128.5, 127.8, 127.7, 127.4, 125.8, 125.8, 125.6, 125.5, 123.1, 121.8, 121.5, 114.6 (d, $J_{C\text{-}F}$ = 22.1 Hz); MS *m/z* (%) 272 ($M^{\bullet+}$, 40), 239 (12), 167 (20), 149 (50), 97 (48), 57 (100); IR (KBr) 2923, 1456, 1375, 1278, 1125, 1072cm^{-1}. Anal. Calcd (%) for $C_{20}H_{13}F$: C, 88.21; H, 4.81. Found: C, 87.92; H, 4.64.

9-(naphthalen-1-yl)phenanthrene **3l**



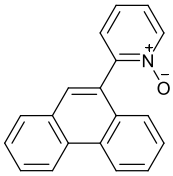
White solid, mp 124-126 ºC (126-127 ºC)[7]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (t, *J* = 8.0 Hz, 2H), 7.88 (t, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 7.7 Hz, 1H), 7.69 (s, 1H), 7.65-7.61 (m, 1H), 7.57-7.47 (m, 4H), 7.40-7.28 (m, 4H), 7.20-7.18 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 136.1, 132.5, 131.9, 131.1, 130.6, 129.3, 129.2, 127.6, 127.4, 127.1, 126.9, 126.8, 126.4, 125.8, 125.7, 125.6, 125.5, 125.4, 125.0, 124.8, 124.4, 121.7, 121.6. Anal. Calcd (%) for $C_{24}H_{16}$: C 94.70, H 5.30. Found: C 95.02, H 5.48.

Mixture of 9-(naphthalene-2-yl)phenanthrene and 9-(naphthalen-1-yl)phenanthrene (**3l**-*mixture*)



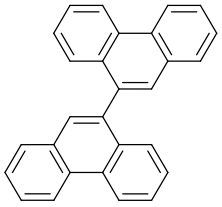
White solid, as an isomeric mixture of regioisomers. The isomeric ratio was found to be 1/4.3 (*α/β*) as per NMR, ^{1}H NMR (400 MHz, $CDCl_3$) δ (isomeric mixture) 8.74-8.71 (m, 2H, *β*-isomer), 8.69-8.67 (m, 2H, *α*-isomer), 7.96-7.81 (m, 5H), 7.78-7.70 (m, 2H), 7.68-7.52 (m, 4H), 7.50-7.28 (m, 4H), 7.24-7.17 (m, 1H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ (isomeric mixture) 138.5, 133.5, 131.6, 128.9, 128.7, 128.5, 128.2, 128.1, 128.0, 127.9, 127.8, 127.5, 126.9, 126.7, 126.6, 126.6, 126.5, 126.0, 125.9, 125.5, 122.8, 122.6; MS *m/z* (%) 304 ($M^{\bullet+}$, 100), 289 (14), 268 (13), 254 (84) 151 (32); IR (KBr) 3369, 2923, 1636, 1473, 1202, 1142, 853, 801, 724, 633 cm^{-1}.

2-(phenanthrene-9-yl)pyridine1-oxide **3m**



Brownish orange solid, mp 143-145 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.97-8.92 (m, 2H), 8.52-8.45 (m, 1H), 8.24-8.16 (m, 1H), 8.12-8.06 (m, 2H), 7.97-7.93 (m, 2H), 7.79-7.72 (m, 4H), 7.55-7.52 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.9, 147.8, 140.1, 140.0, 131.5, 131.1, 129.3, 128.6, 128.5, 128.1, 127.7, 127.4, 127.0, 126.9, 126.3, 125.5, 123.9, 123.0, 122.4; MS *m/z* (%) 271 ($M^{\bullet+}$, 13), 255 (95), 225 (35), 127 (45), 69 (83), 57 (100); IR (KBr) 3408, 2923, 1675, 1456, 1294, 1138 cm^{-1}. Anal. Calcd (%) for $C_{19}H_{13}NO$: C, 84.11; H, 4.83; N, 5.16. Found: C, 84.43; H, 5.01; N, 5.39.

9,9`-biphenanthrene **3n**



Colorless solid, 75 mg (85%); mp 176-178 °C (186-187 °C)[7];^{1}H NMR(400 MHz, $CDCl_3$) δ 8.76-8.72 (m, 4H), 7.85-7.83 (m, 2H), 7.78-7.73 (m, 2H), 7.67-7.62 (m, 2H), 7.61-7.55 (m, 4H), 7.45-7.41 (m, 2H), 7.33-7.28 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.1, 131.1, 130.6, 129.3, 129.2, 127.6, 127.5, 126.5, 125.9, 125.8, 125.6, 125.5, 121.7, 121.6. MS *m/z* (%) 354 ($M^{\bullet+}$, 100), 339 (8), 281 (9), 221 (9), 176 (12). Anal. Calcd (%) for $C_{28}H_{18}$: C, 94.88; H, 5.12. Found: C, 95.14; H, 5.26.

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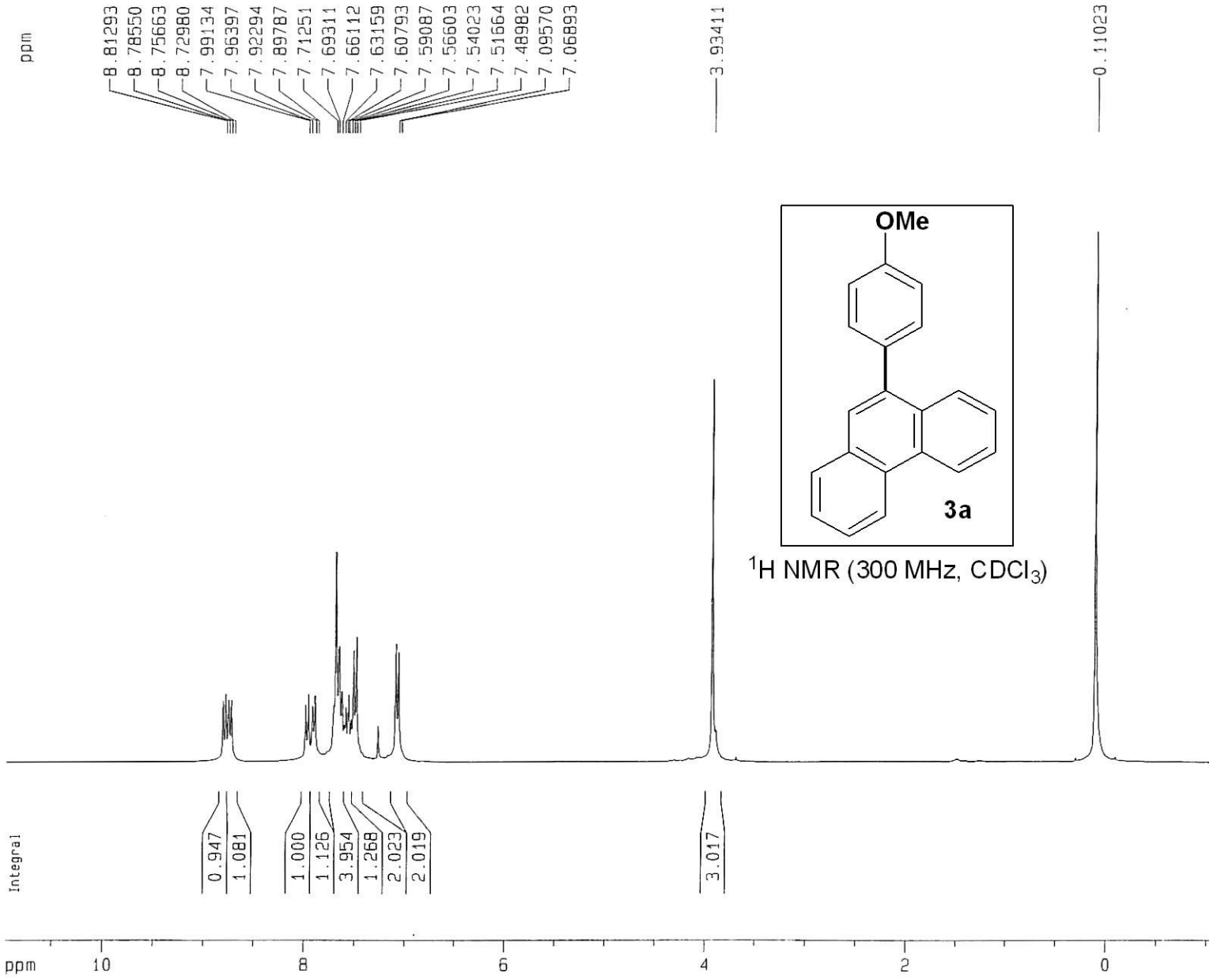
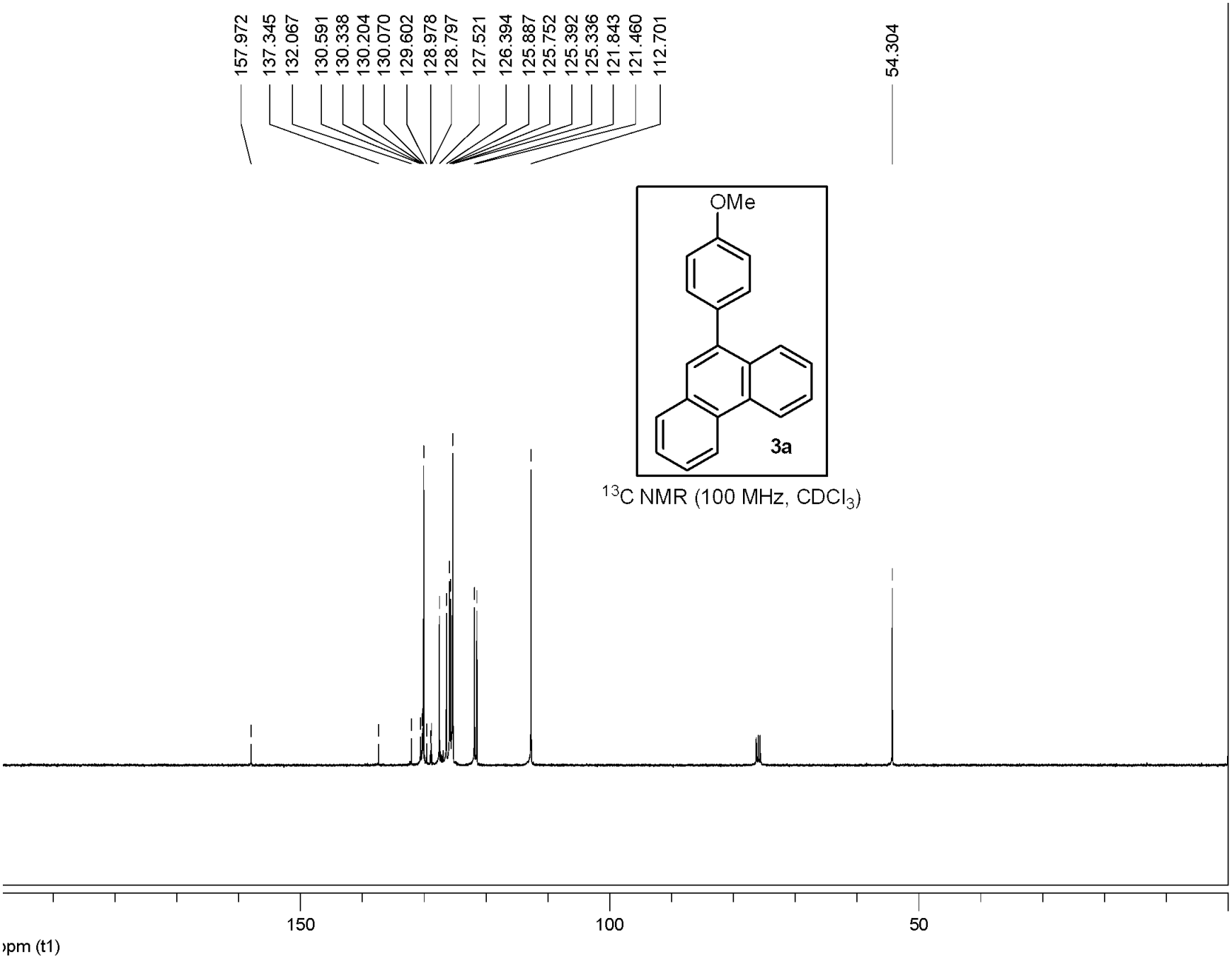
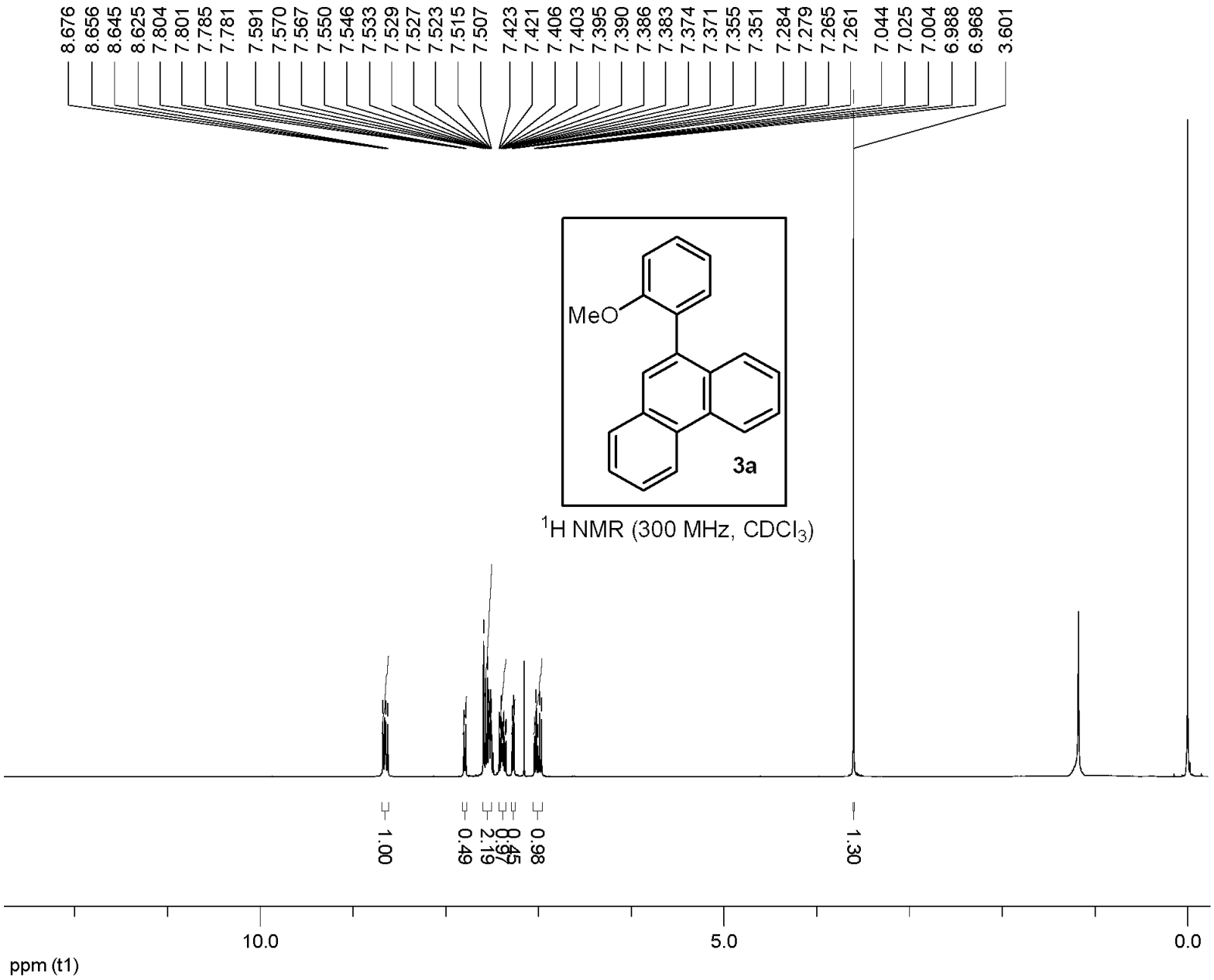
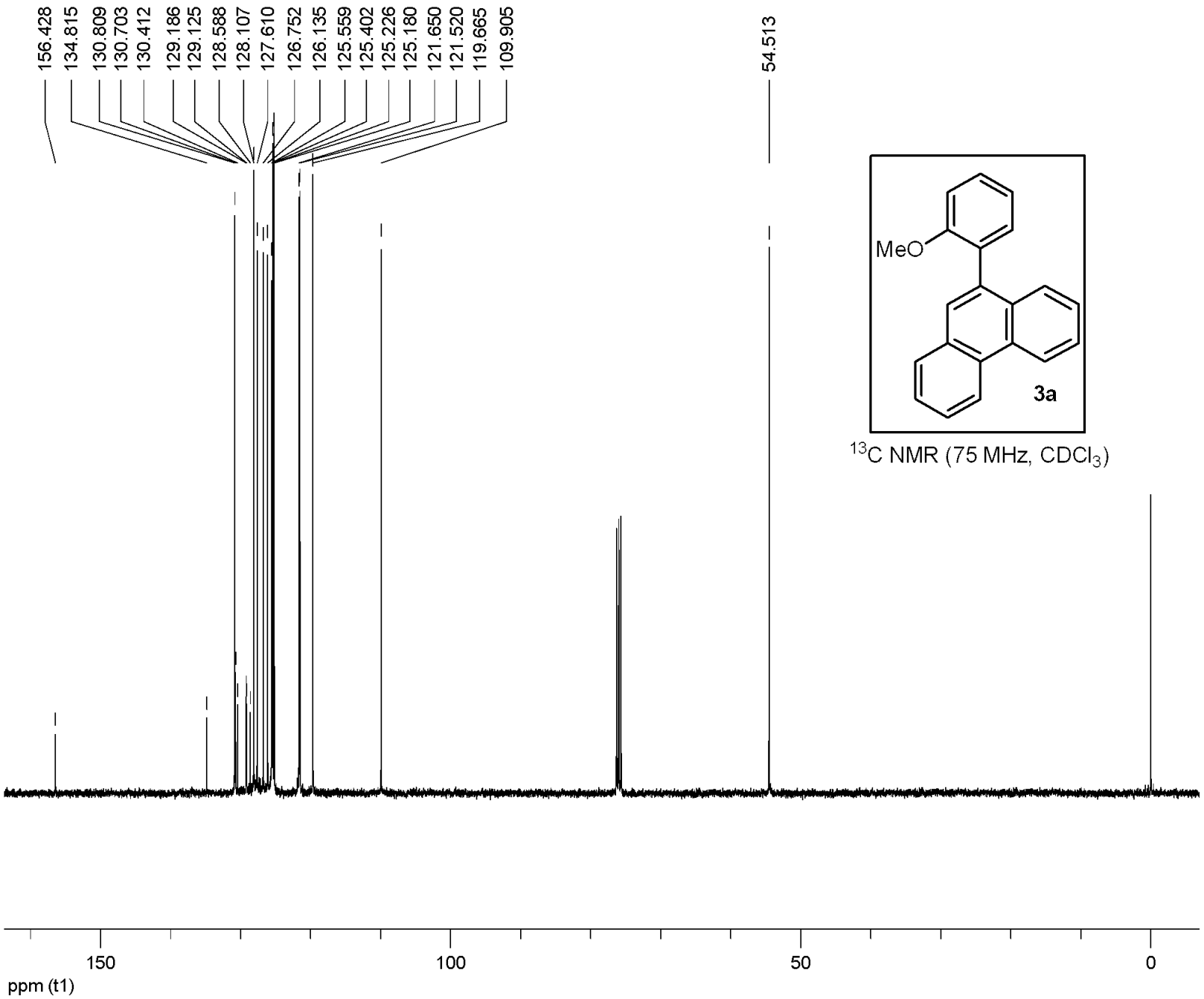
4 Copies of ^{1}H and ^{13}C NMR Spectra





^{13}C NMR (100 MHz, $CDCl_3$)


8.676
8.656
8.645
8.625
7.804
7.801
7.785
7.781
7.591
7.570
7.567
7.550
7.546
7.533
7.529
7.527
7.523
7.515
7.507
7.423
7.421
7.406
7.403
7.395
7.390
7.386
7.383
7.374
7.371
7.355
7.351
7.284
7.279
7.265
7.261
7.044
7.025
7.004
6.988
6.968
3.601
MeO
3a
1H NMR (300 MHz, CDCl3)
1.00
0.49
2.19
0.97
0.45
0.98
1.30
10.0
5.0
0.0
ppm (t1)



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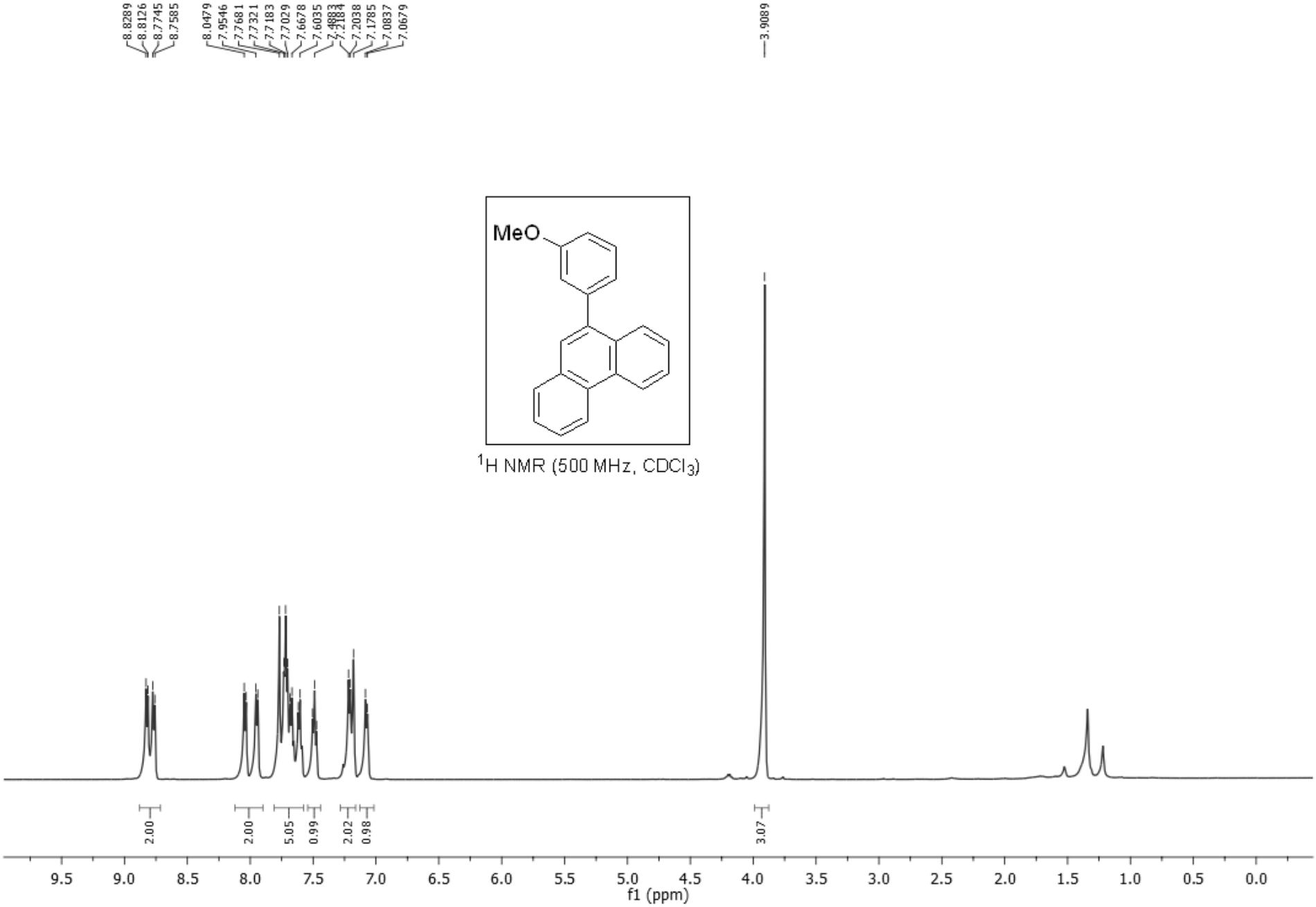
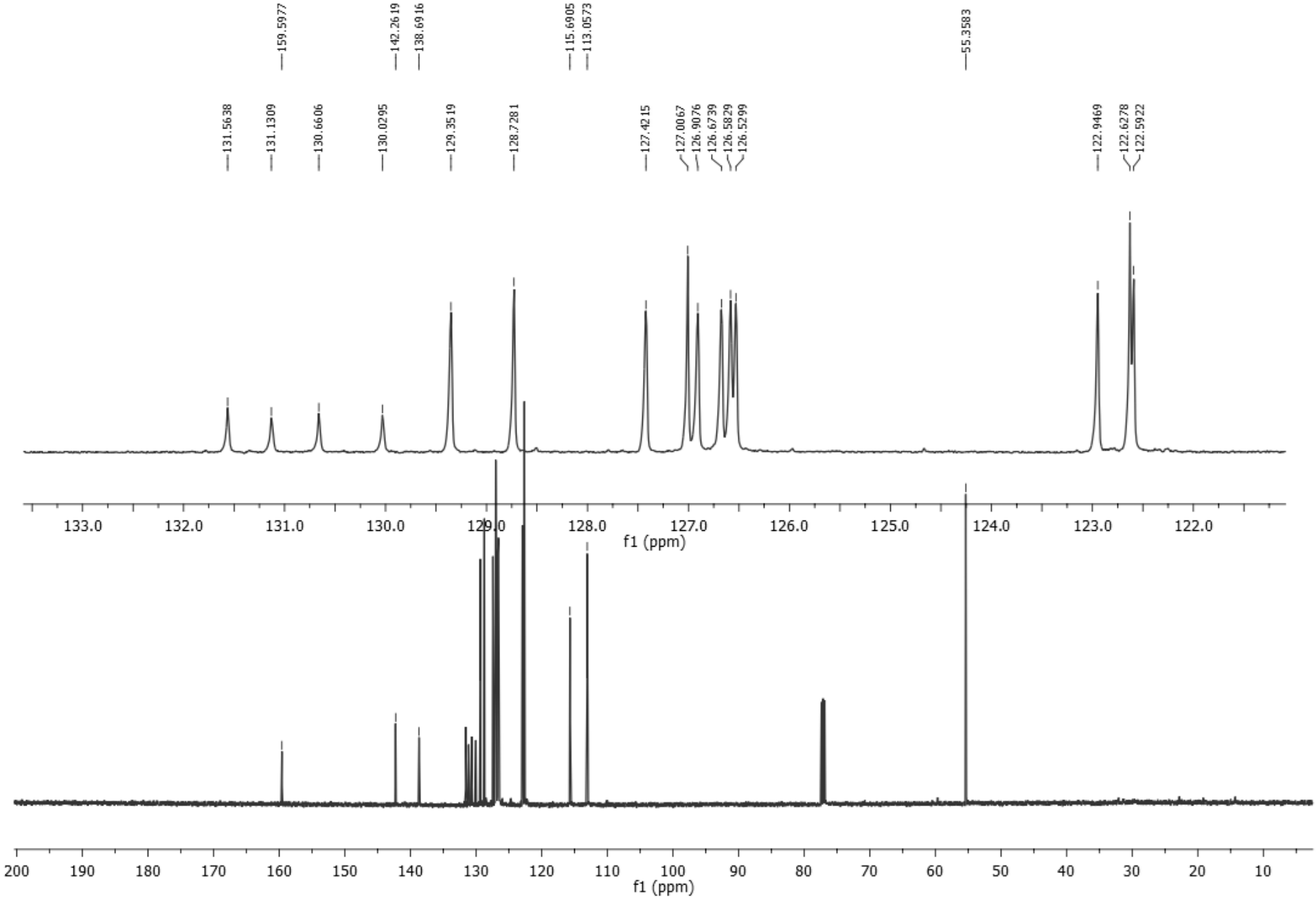


^{1}H NMR (500 MHz, $CDCl_3$)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115.6905
113.0573
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131.5638
131.1309
130.6606
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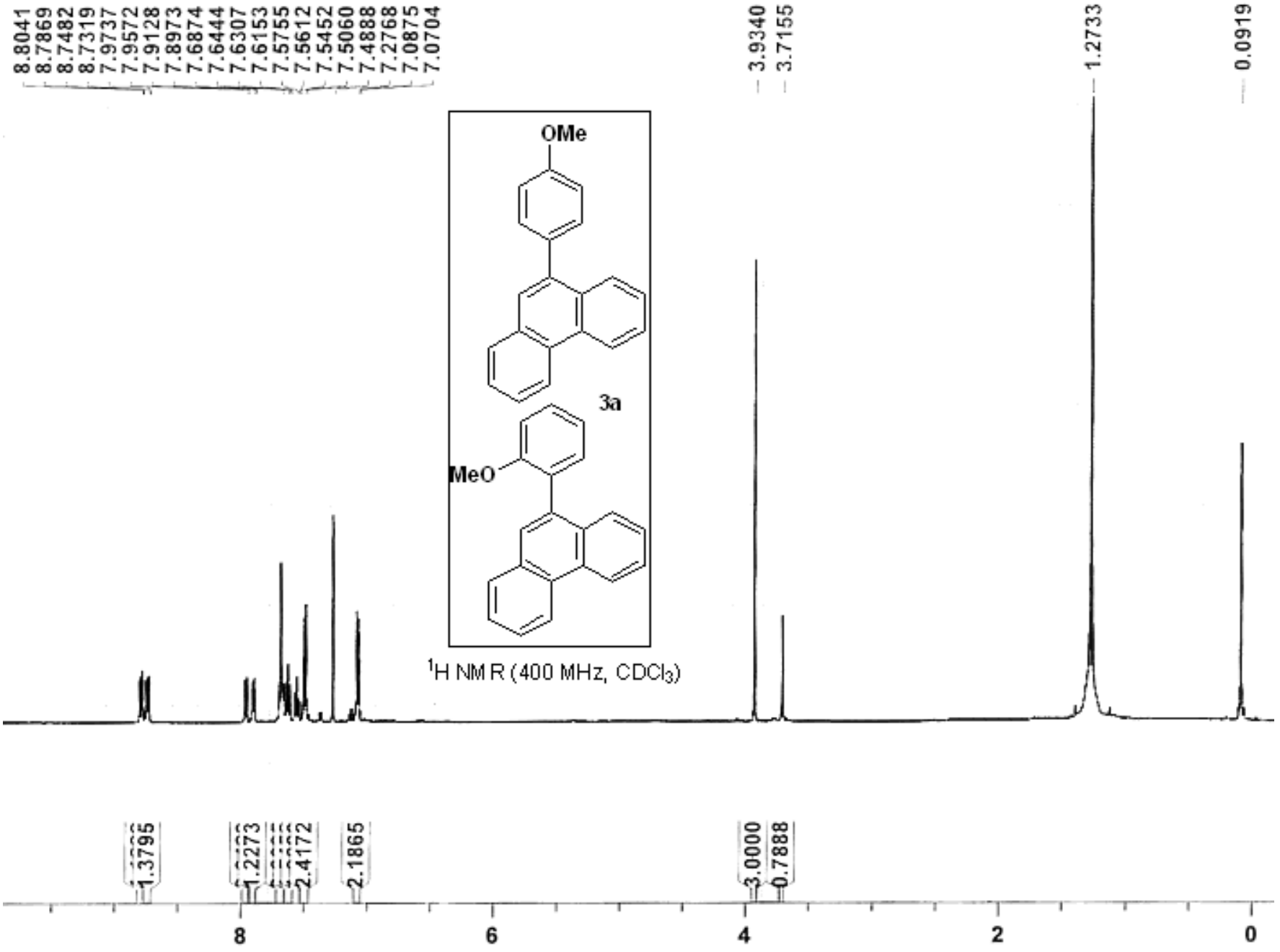
129.3519
128.7281
127.4215
127.0067
126.9076
126.6739
126.5829
126.5299
122.9469
122.6278
122.5922
133.0
132.0
131.0
130.0
129.0
128.0
127.0
126.0
125.0
124.0
123.0
122.0
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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7.6874
7.6444
7.6307
7.6153
7.5755
7.5612
7.5452
7.5060
7.4888
7.2768
7.0875
7.0704
3.9340
3.7155
1.2733
0.0919
OMe
MeO
3a
1H NMR (400 MHz, CDCl3)
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1.2273
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3.0000
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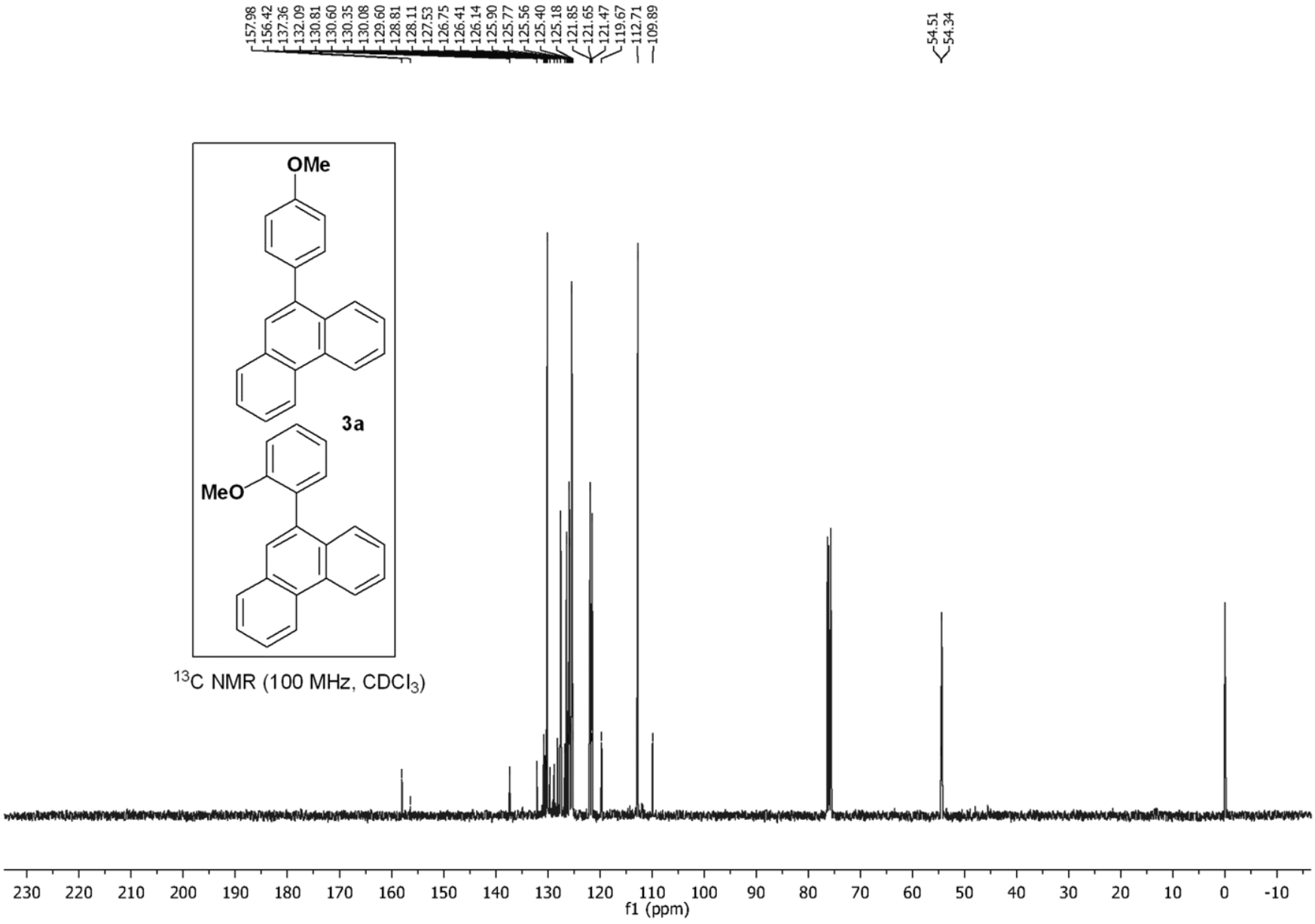
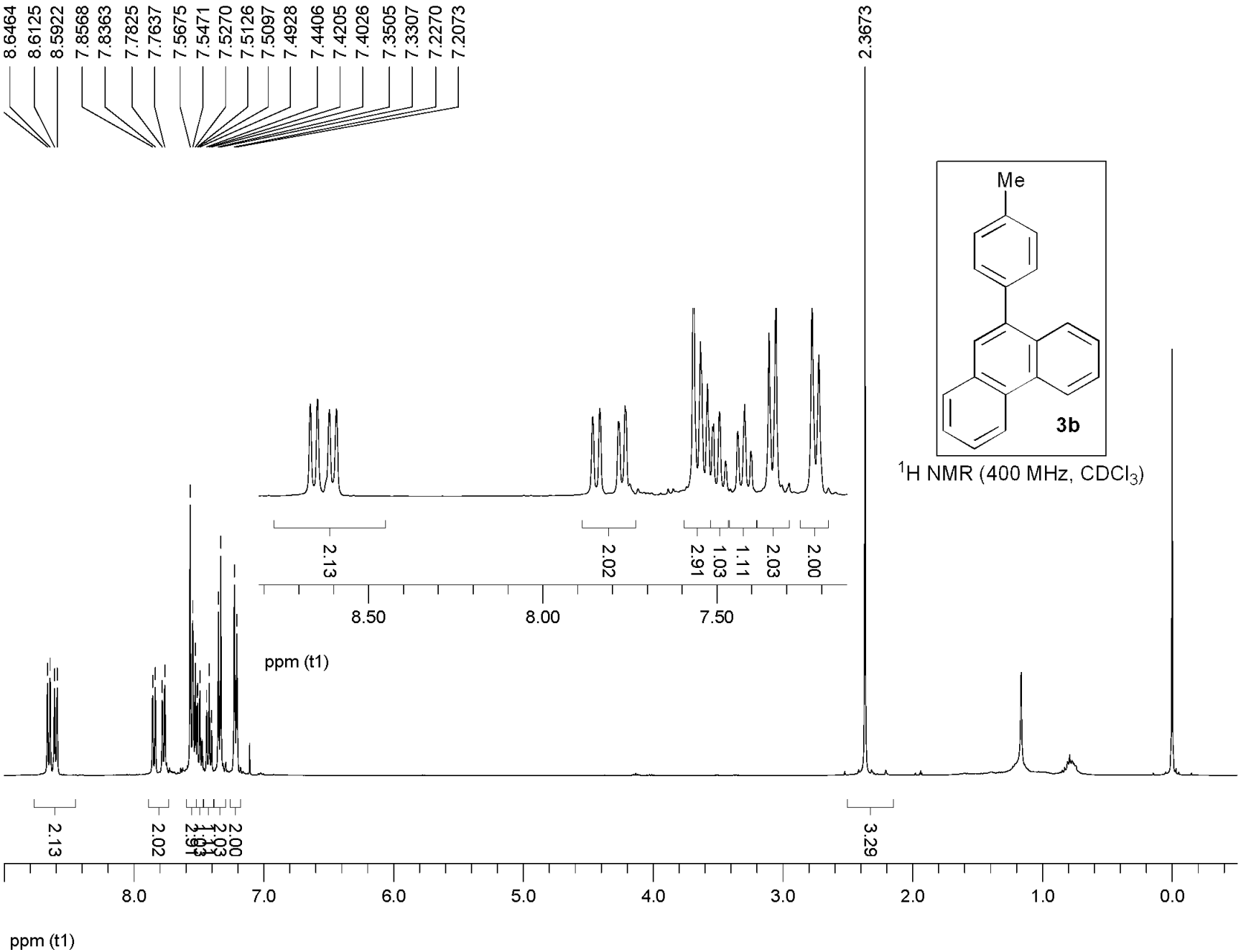
8
6
4
2
0



^{13}C NMR (100 MHz, $CDCl_3$)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7.5097
7.4928
7.4406
7.4205
7.4026
7.3505
7.3307
7.2270
7.2073
2.3673
Me
3b
1H NMR (400 MHz, CDCl3)
2.13
2.02
2.91
1.03
1.11
2.03
2.00
8.50
8.00
7.50
ppm (t1)
2.13
2.02
2.91
1.03
1.11
2.03
2.00
3.29
8.0
7.0
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5.0
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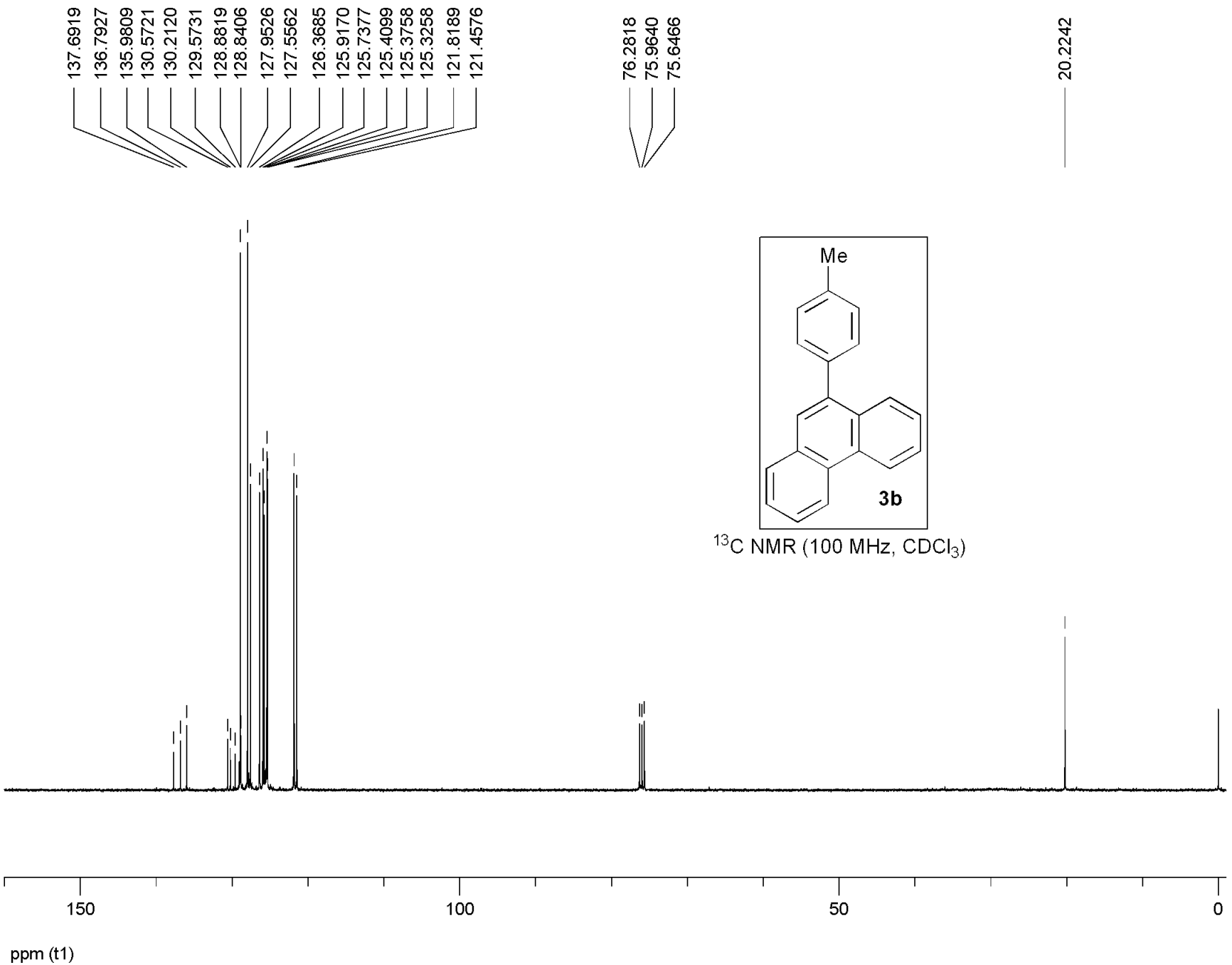
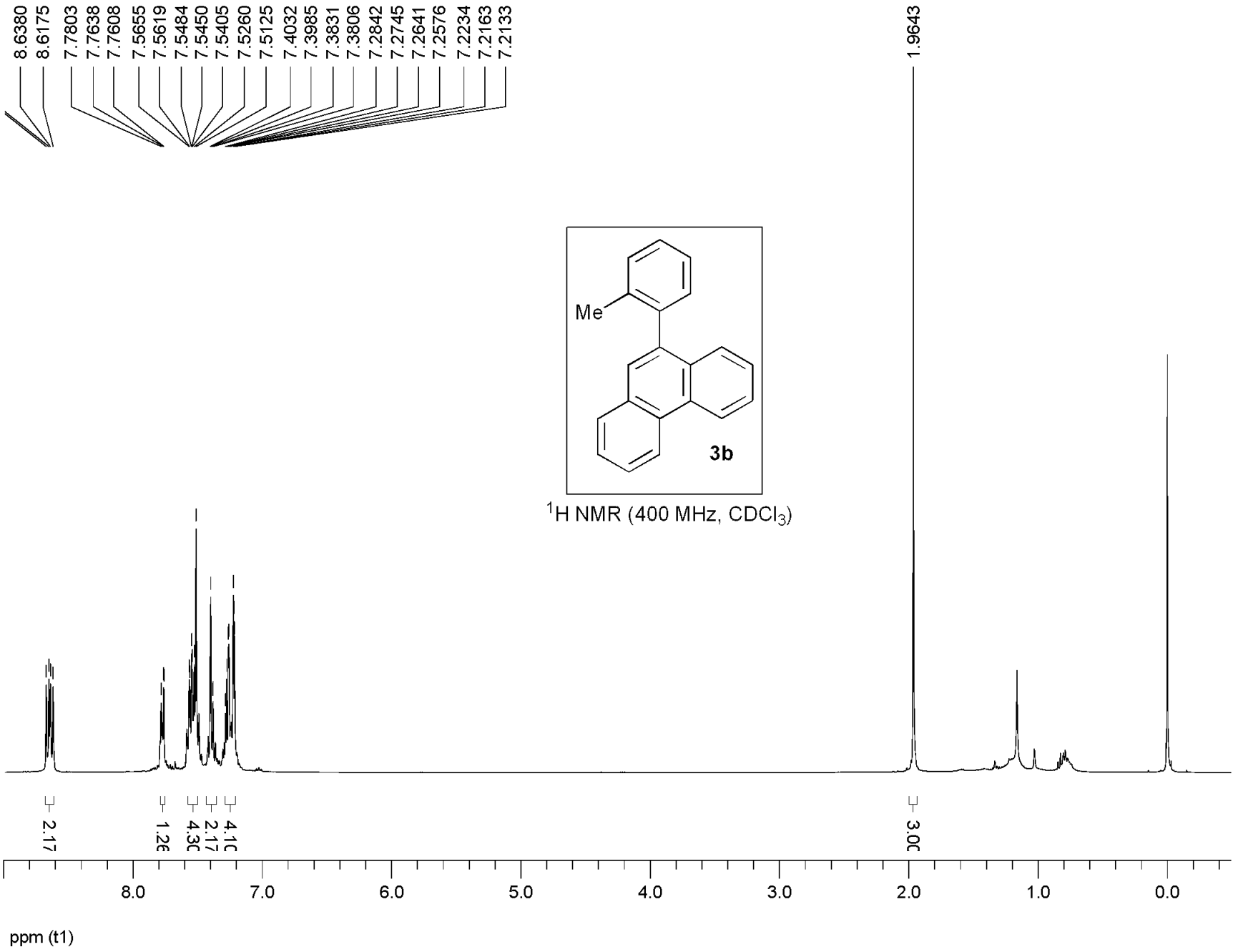
3.0
2.0
1.0
0.0
ppm (t1)



^{13}C NMR (100 MHz, $CDCl_3$)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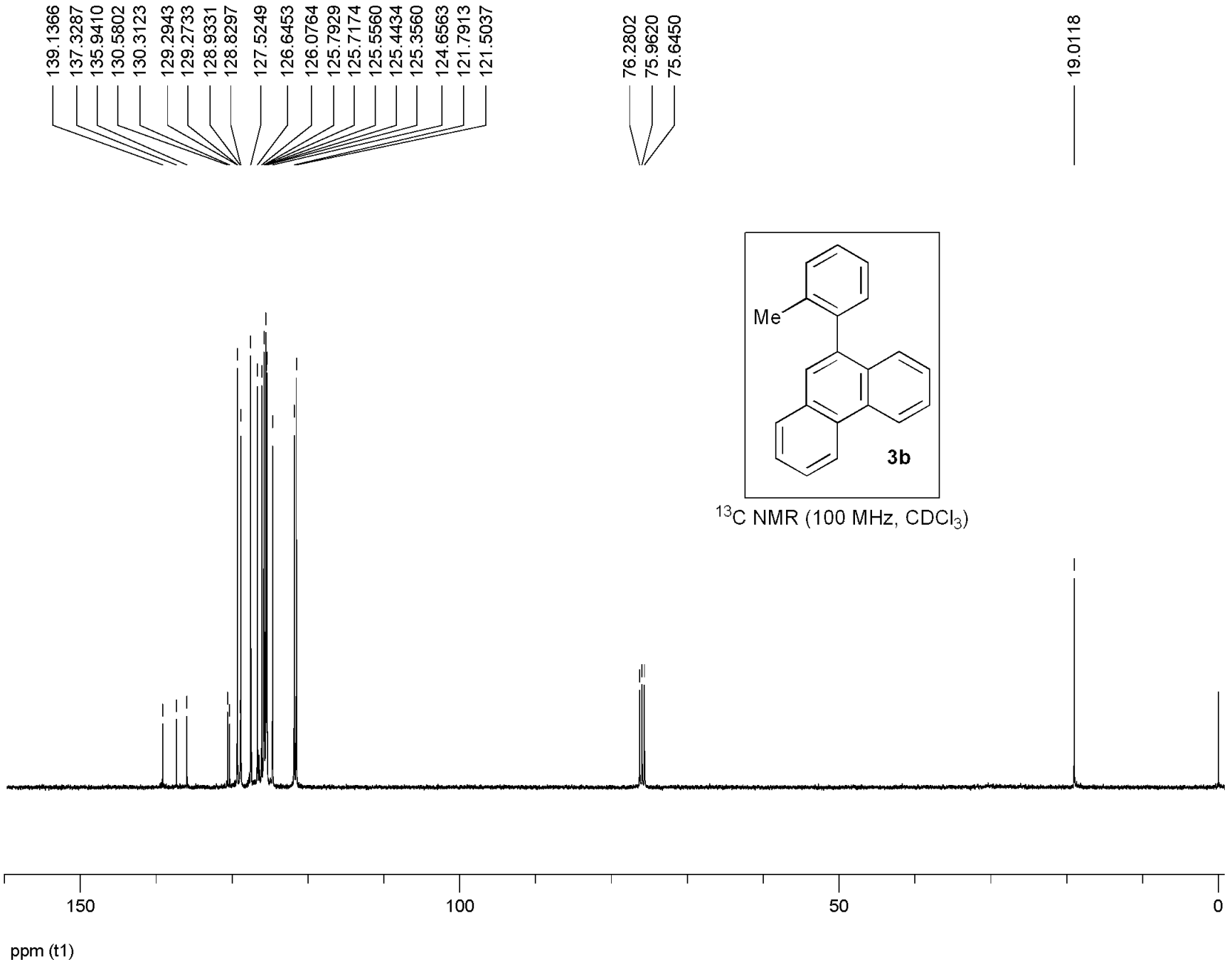
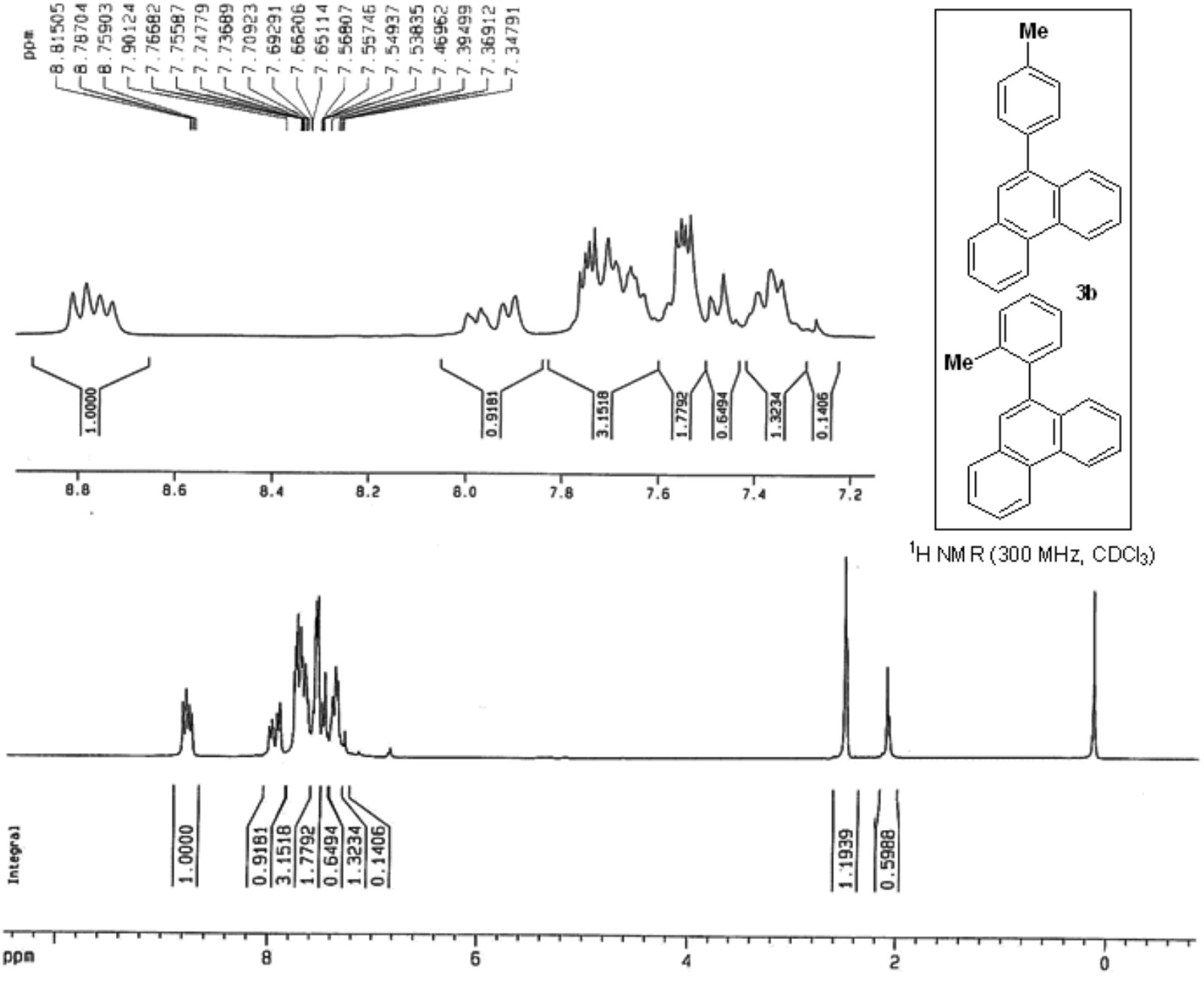
7.3806
7.2842
7.2745
7.2641
7.2576
7.2234
7.2163
7.2133
1.9643
Me
3b
^{1}H NMR (400 MHz, $CDCl_3$)
2.17
1.28
4.30
2.17
4.10
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)



^{13}C NMR (100 MHz, $CDCl_3$)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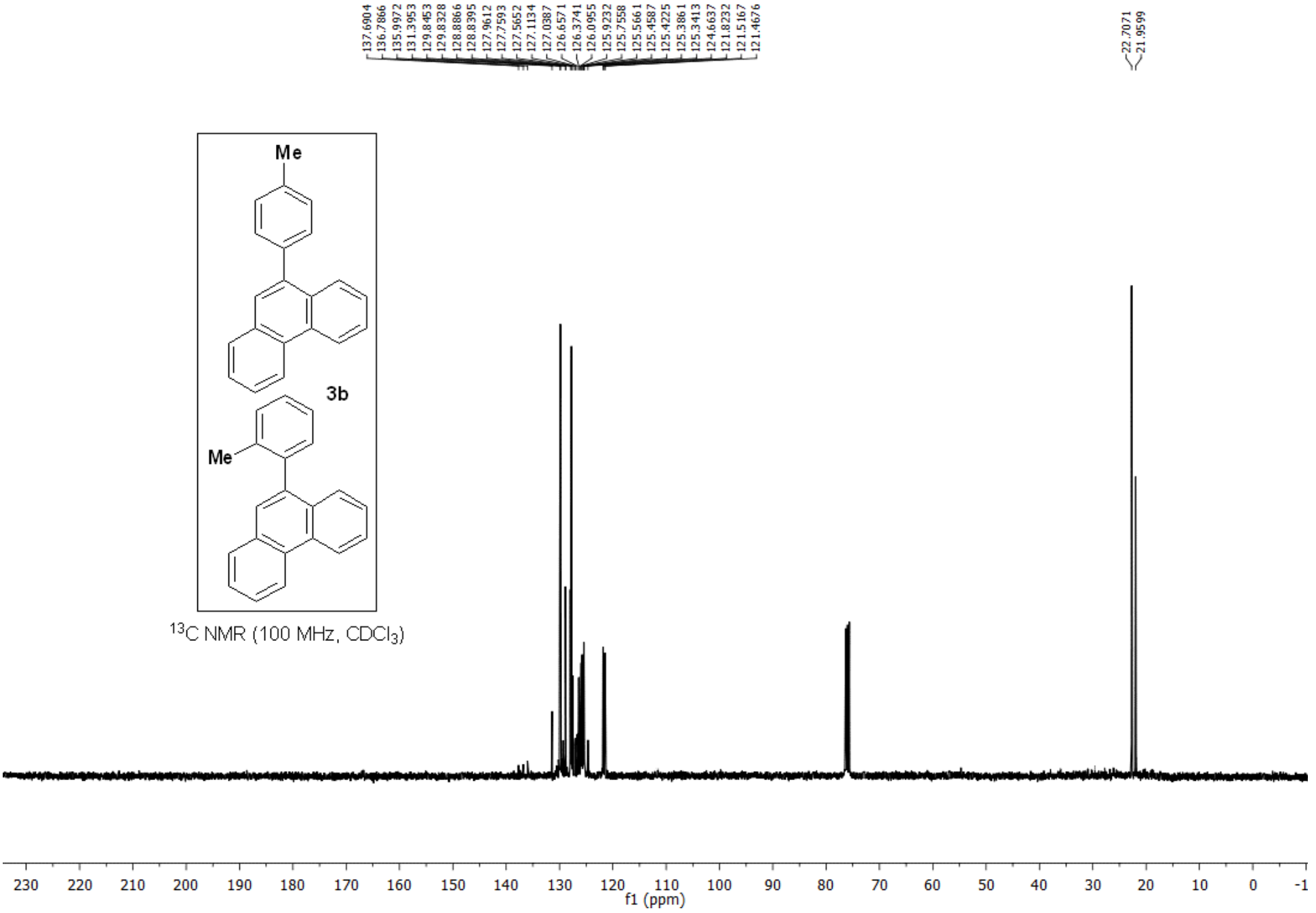
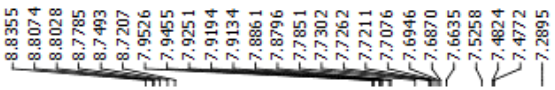
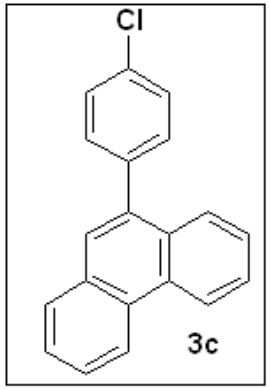
3.1518
1.7792
0.6494
1.3234
0.1406
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
Me
3b
Me
1H NMR (300 MHz, CDCl3)
Integral
1.0000
0.9181
3.1518
1.7792
0.6494
1.3234
0.1406
1.1939
0.5988
ppm
8
6
4
2
0

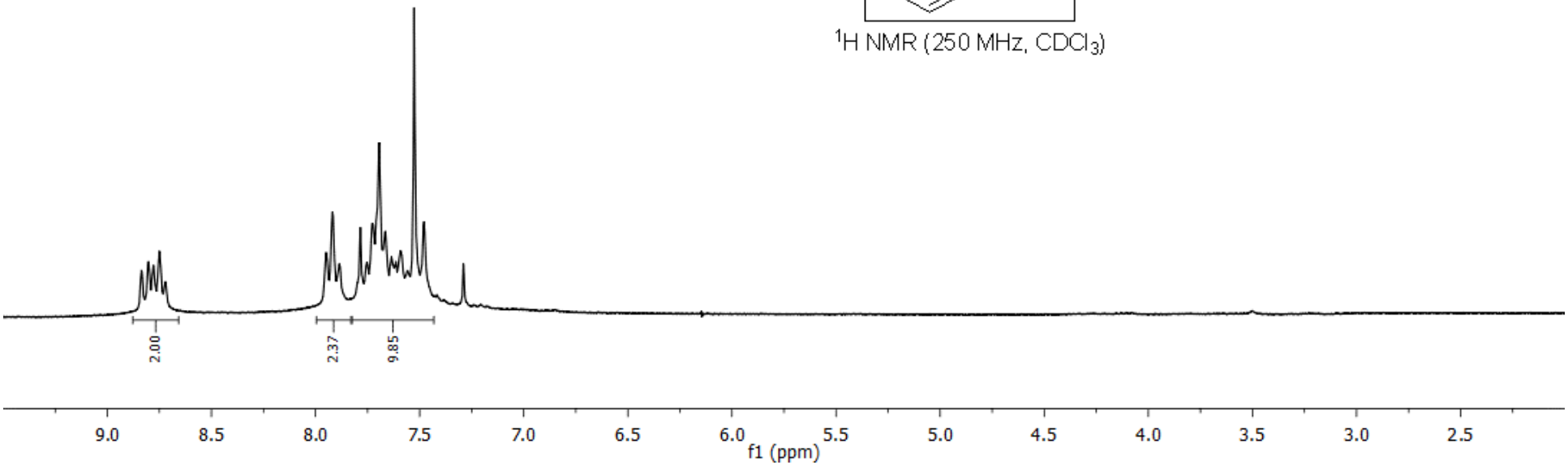


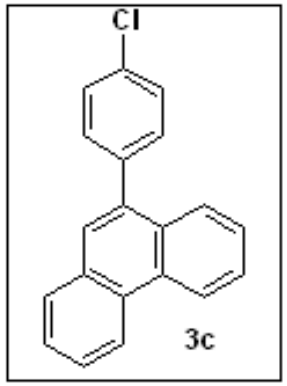
^{13}C NMR (100 MHz, $CDCl_3$)



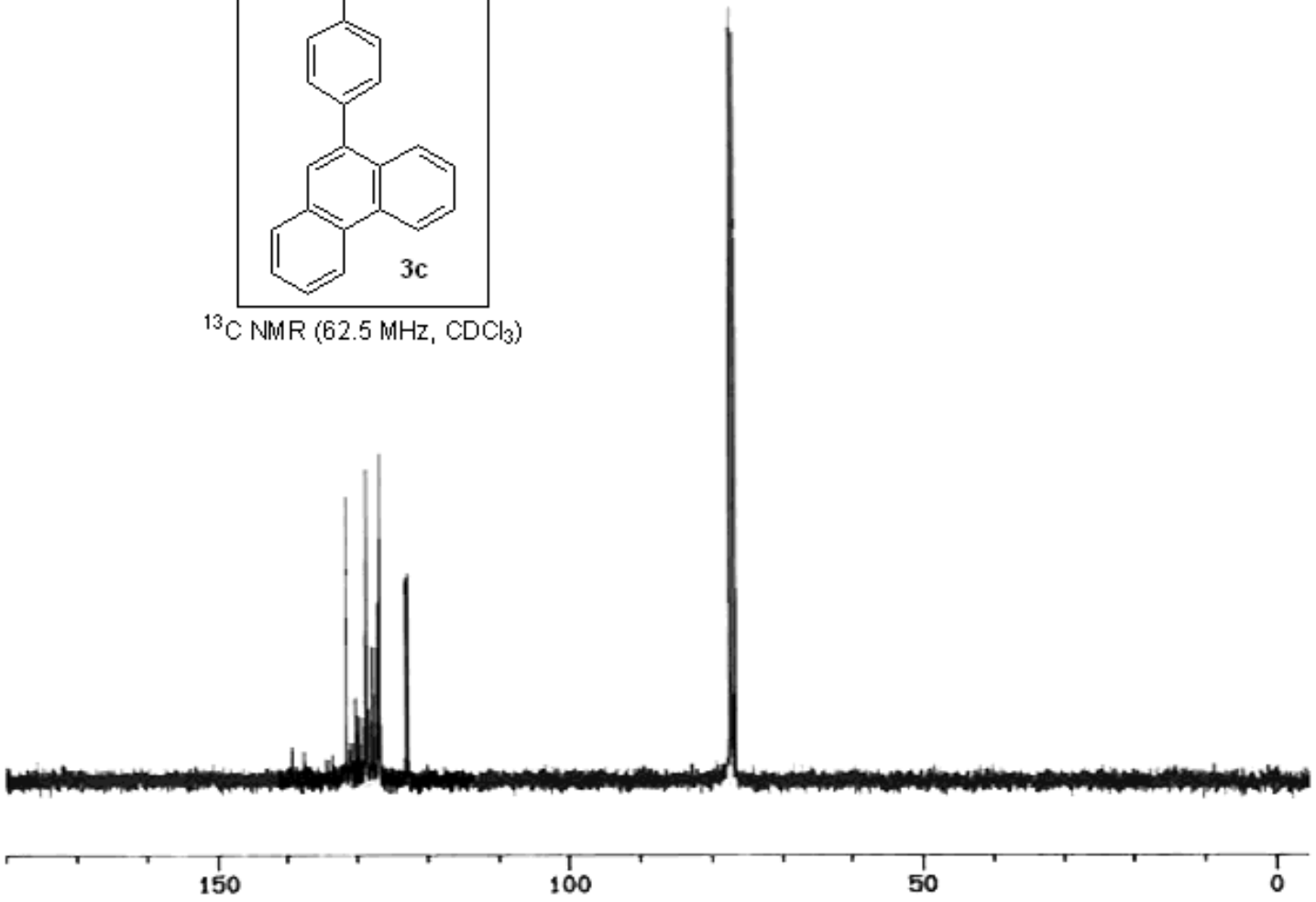


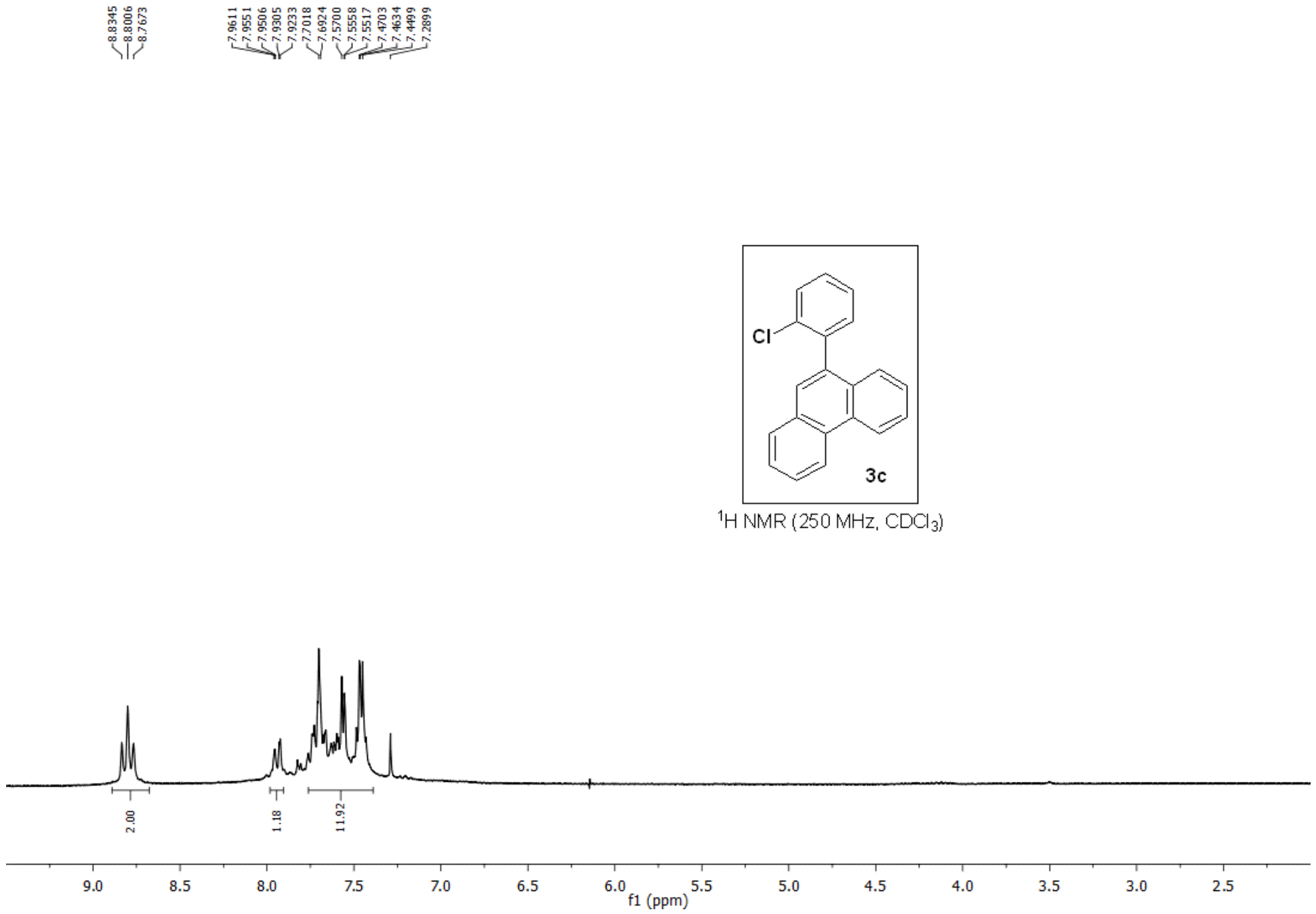
^{1}H NMR (250 MHz, $CDCl_3$)



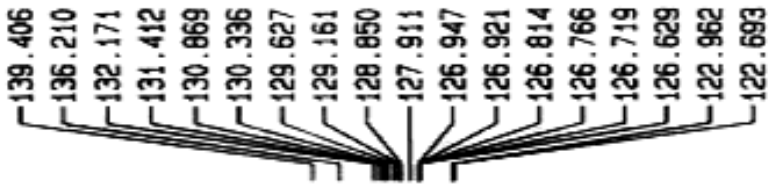


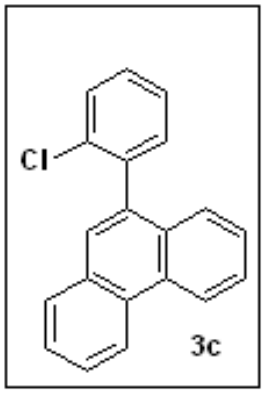
^{13}C NMR (62.5 MHz, $CDCl_3$)



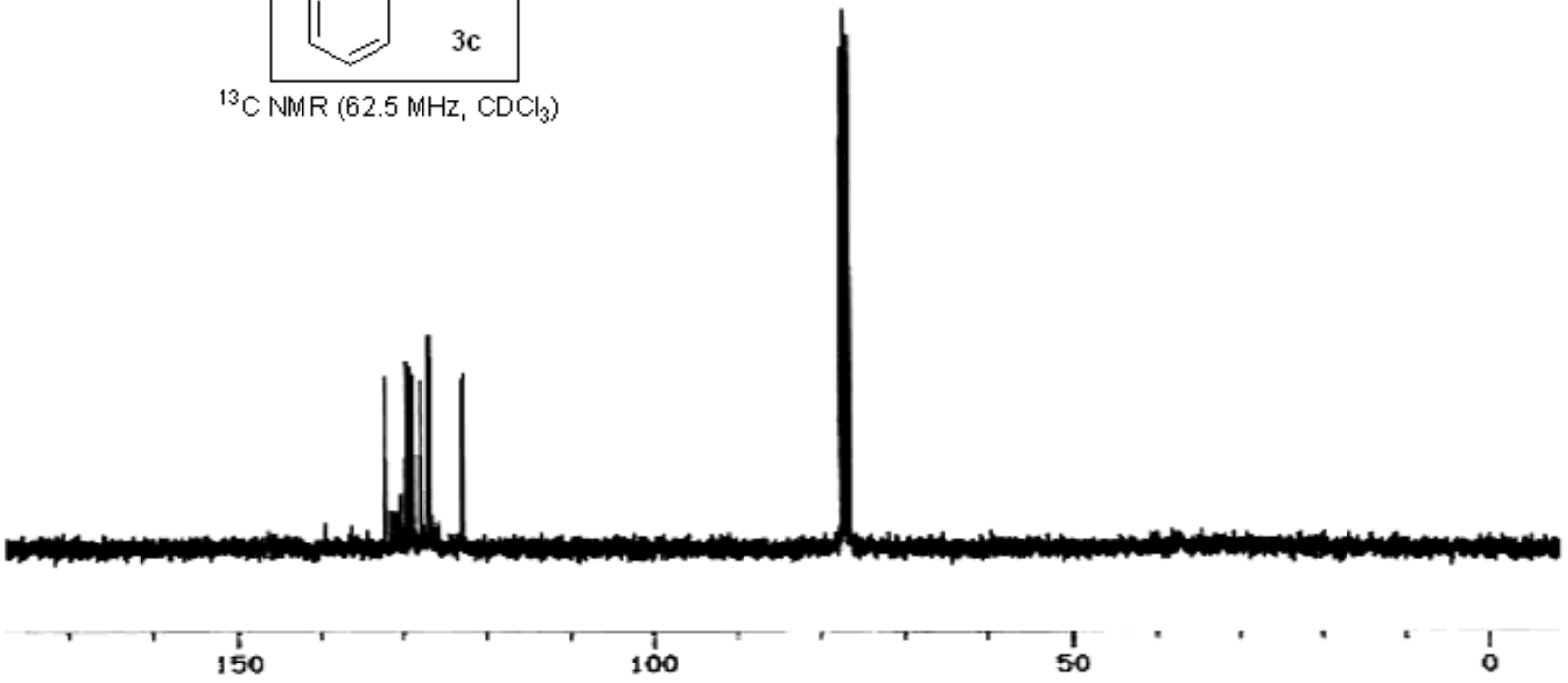


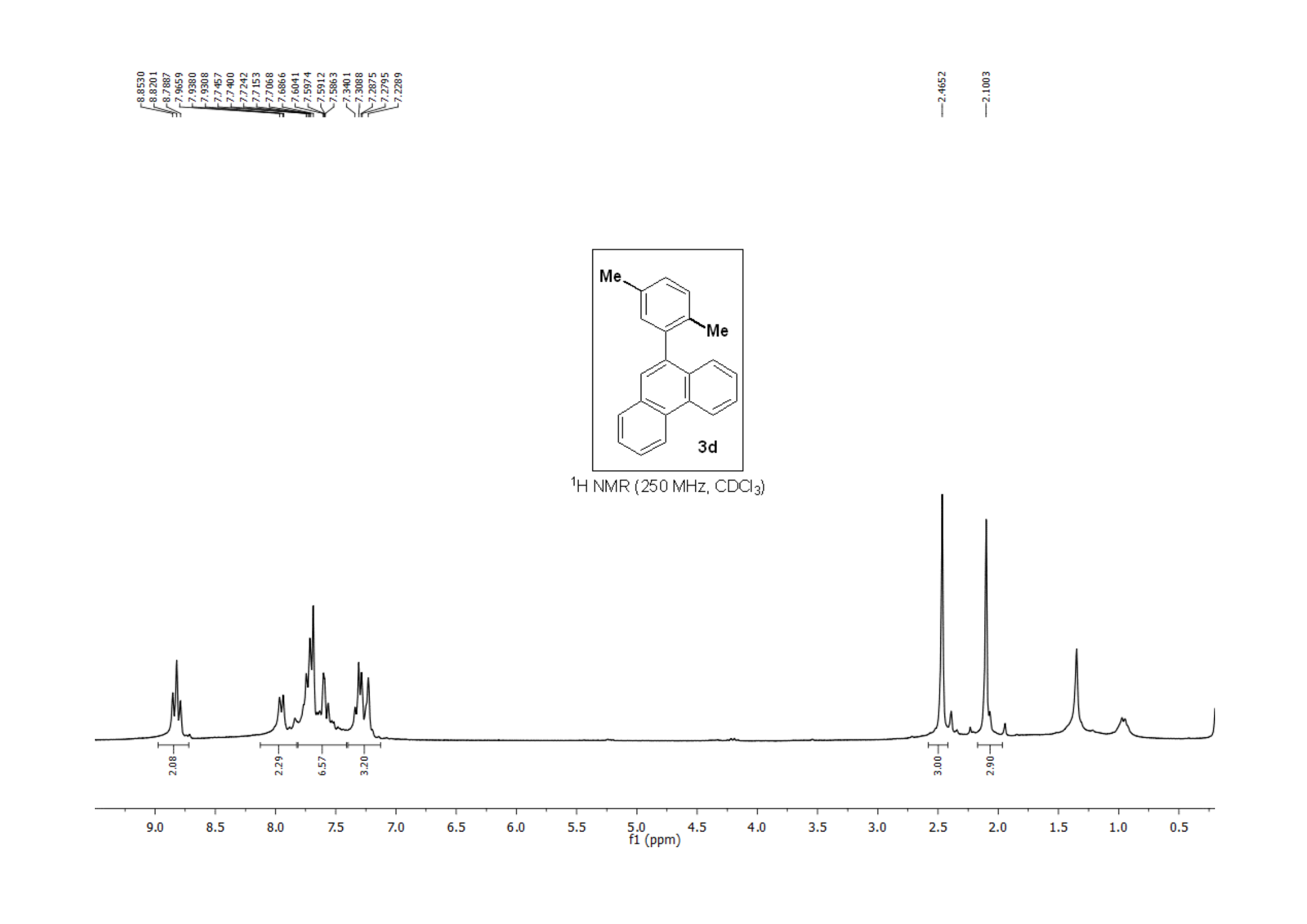
^{1}H NMR (250 MHz, $CDCl_3$)



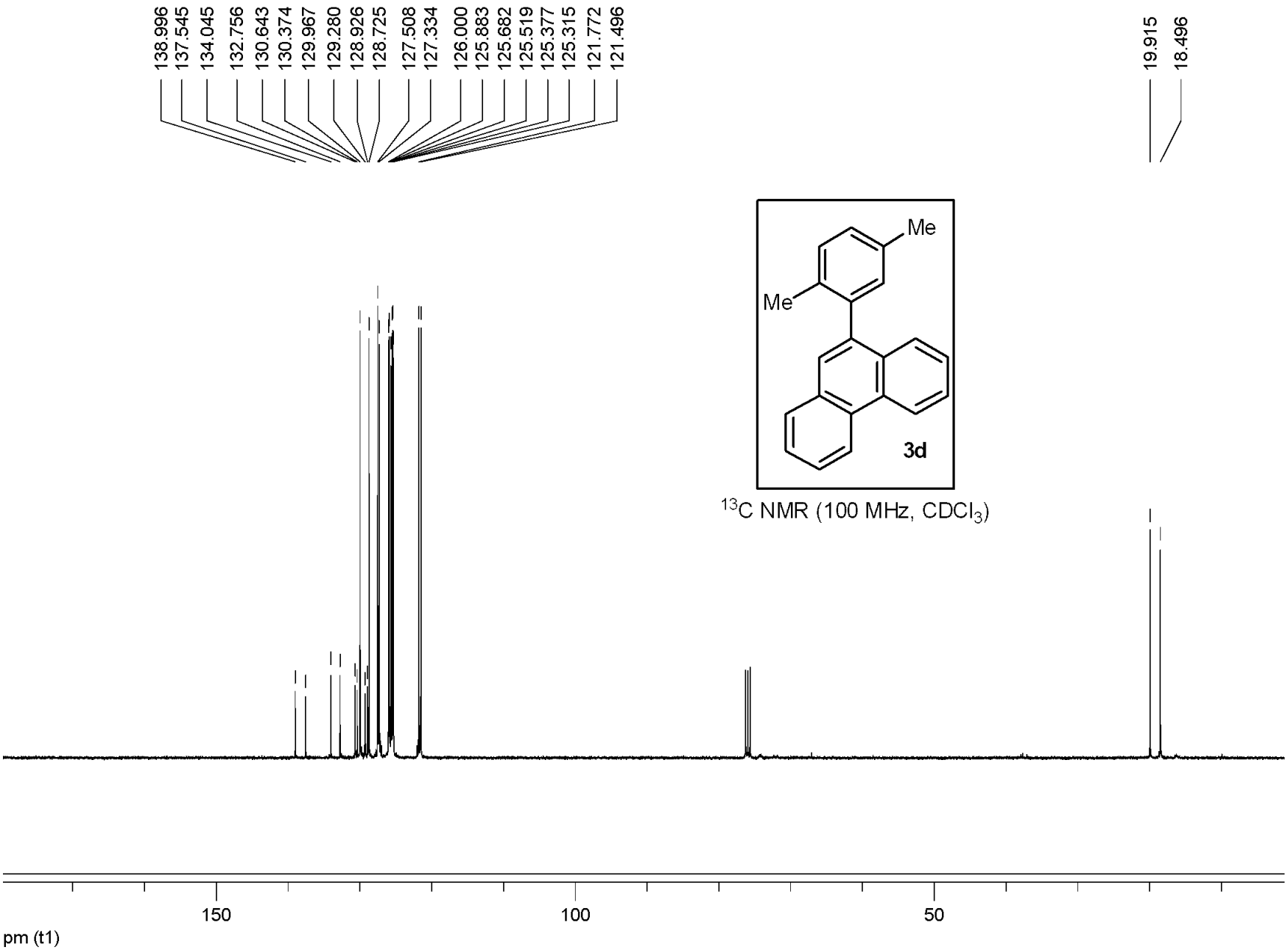


^{13}C NMR (62.5 MHz, $CDCl_3$)

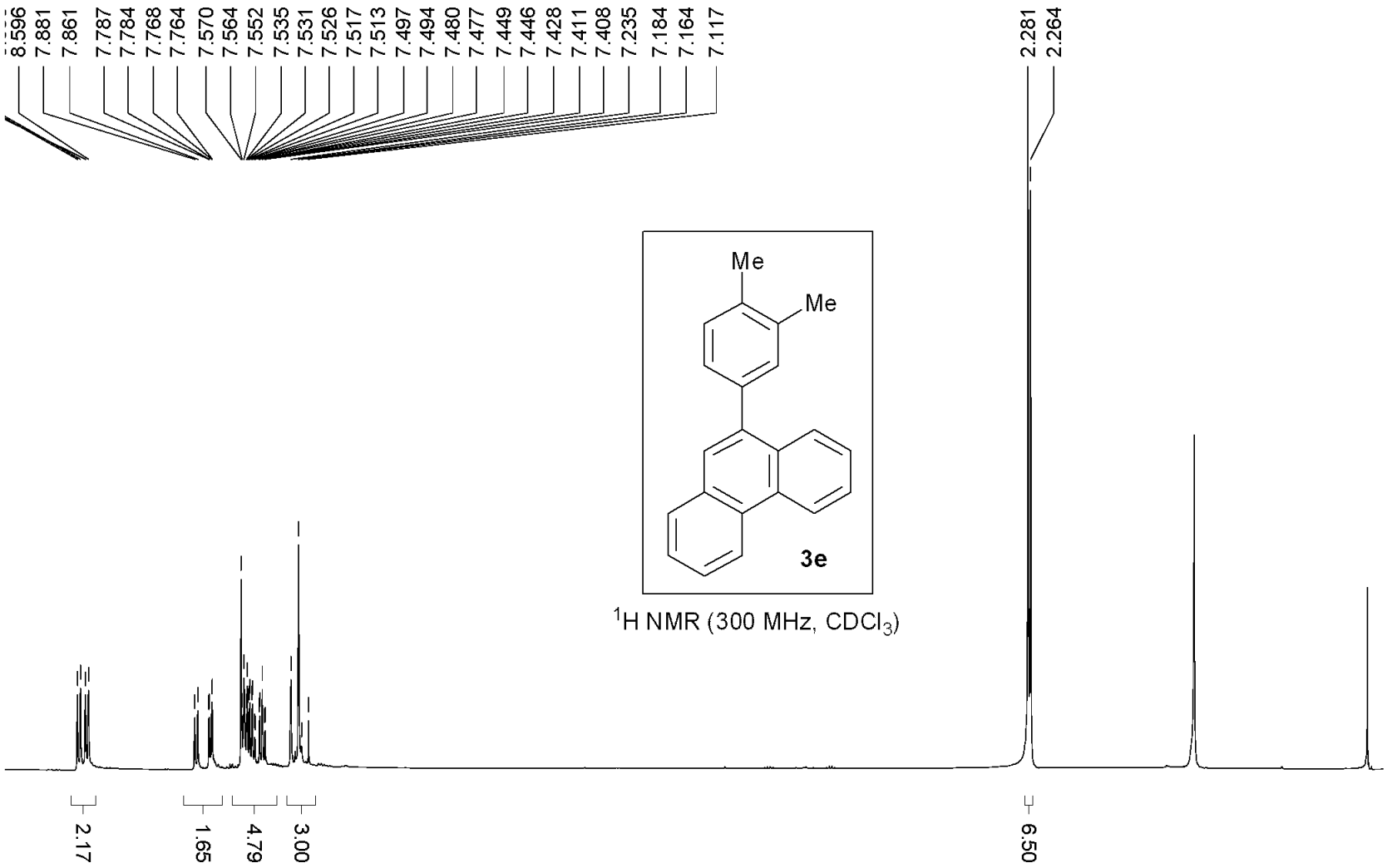




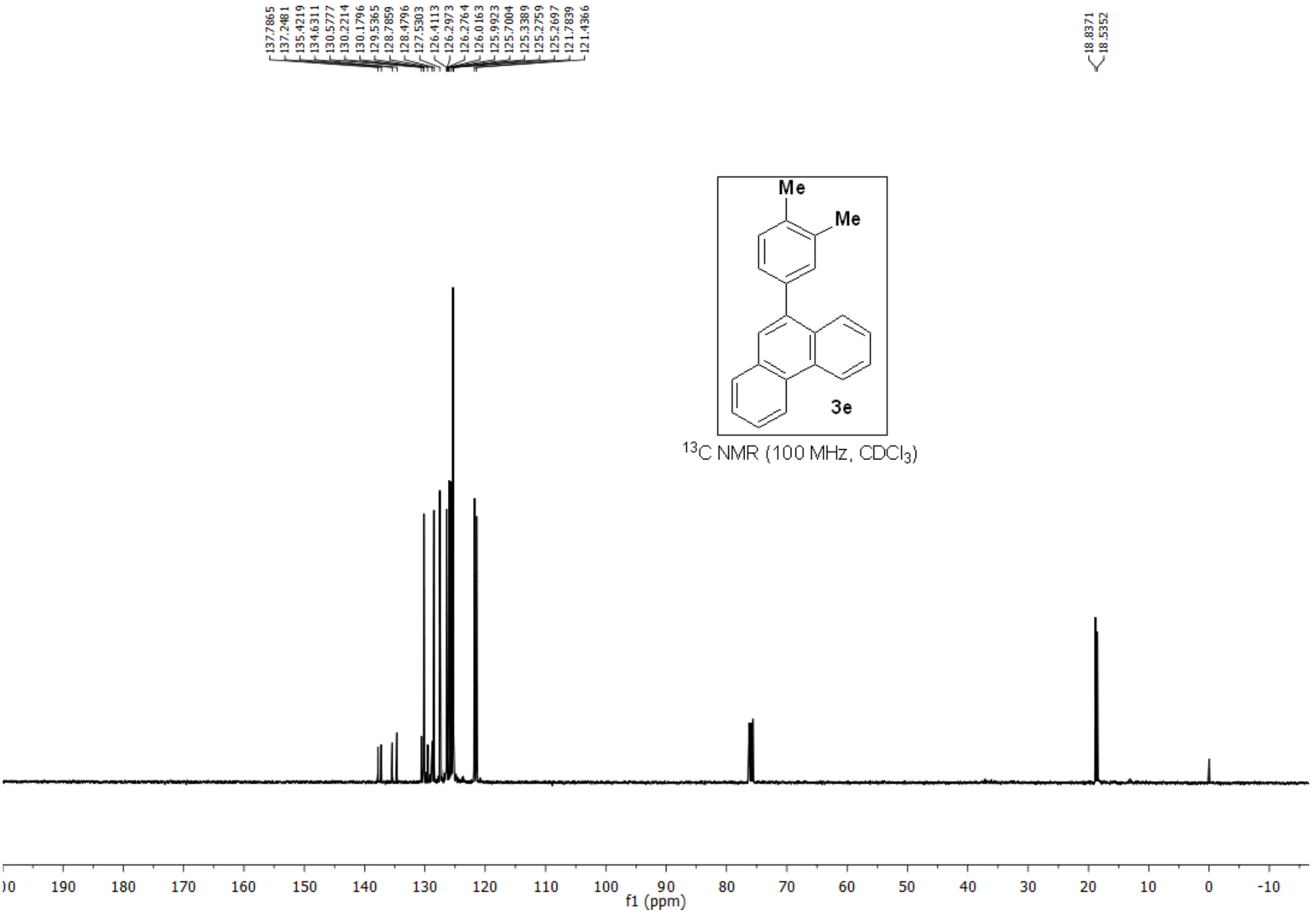
^{1}H NMR (250 MHz, $CDCl_3$)

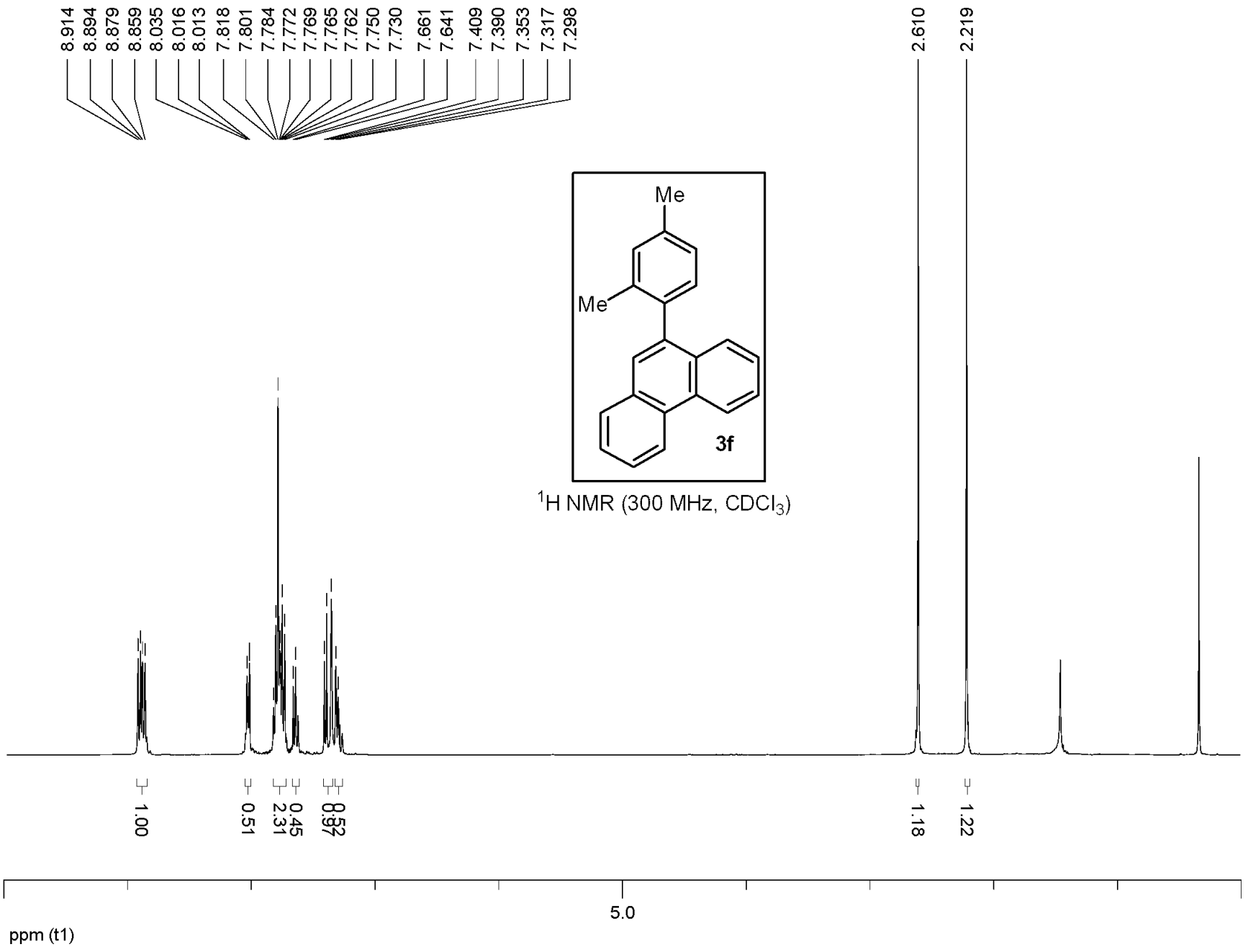


^{13}C NMR (100 MHz, $CDCl_3$)

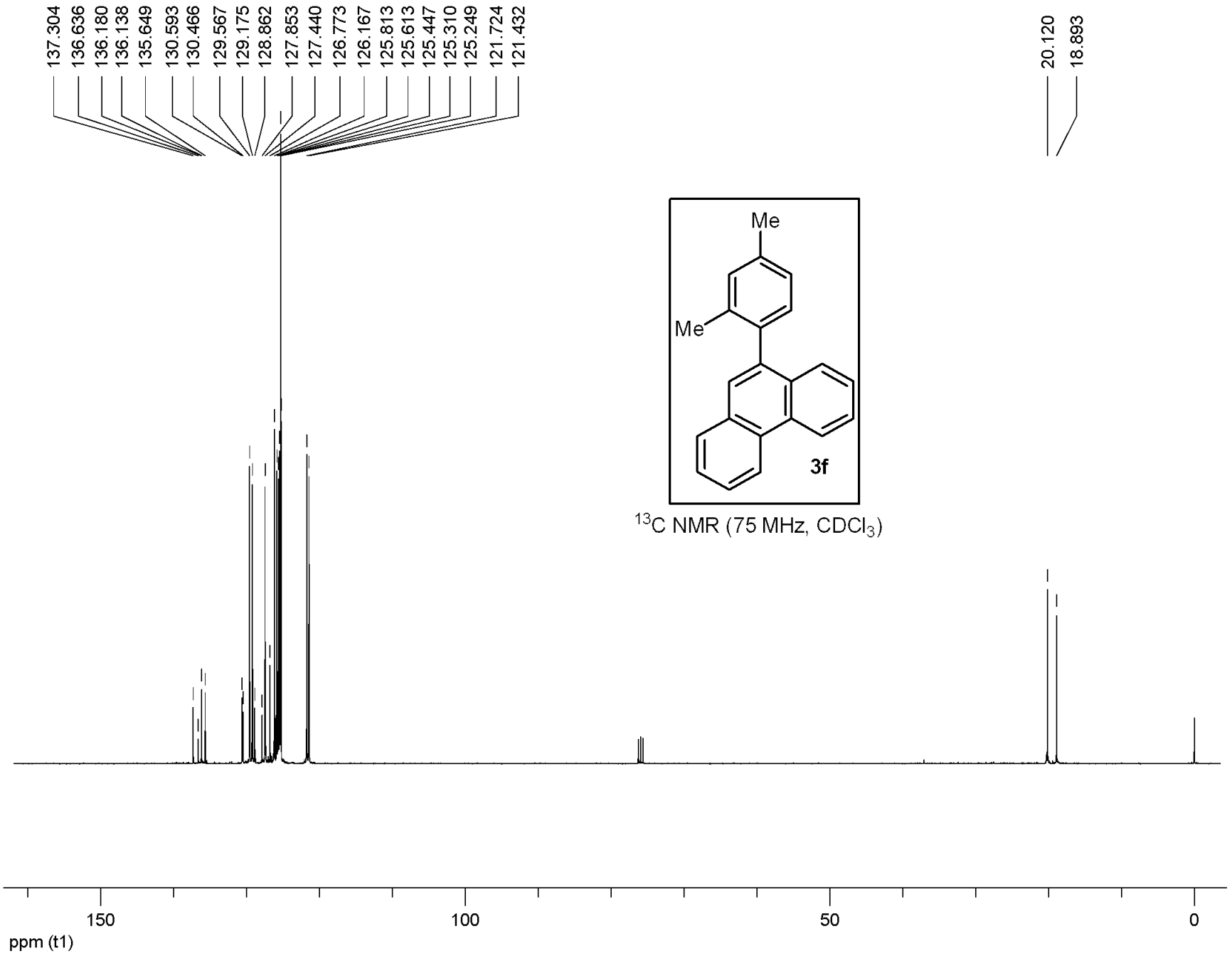


^{1}H NMR (300 MHz, $CDCl_3$)

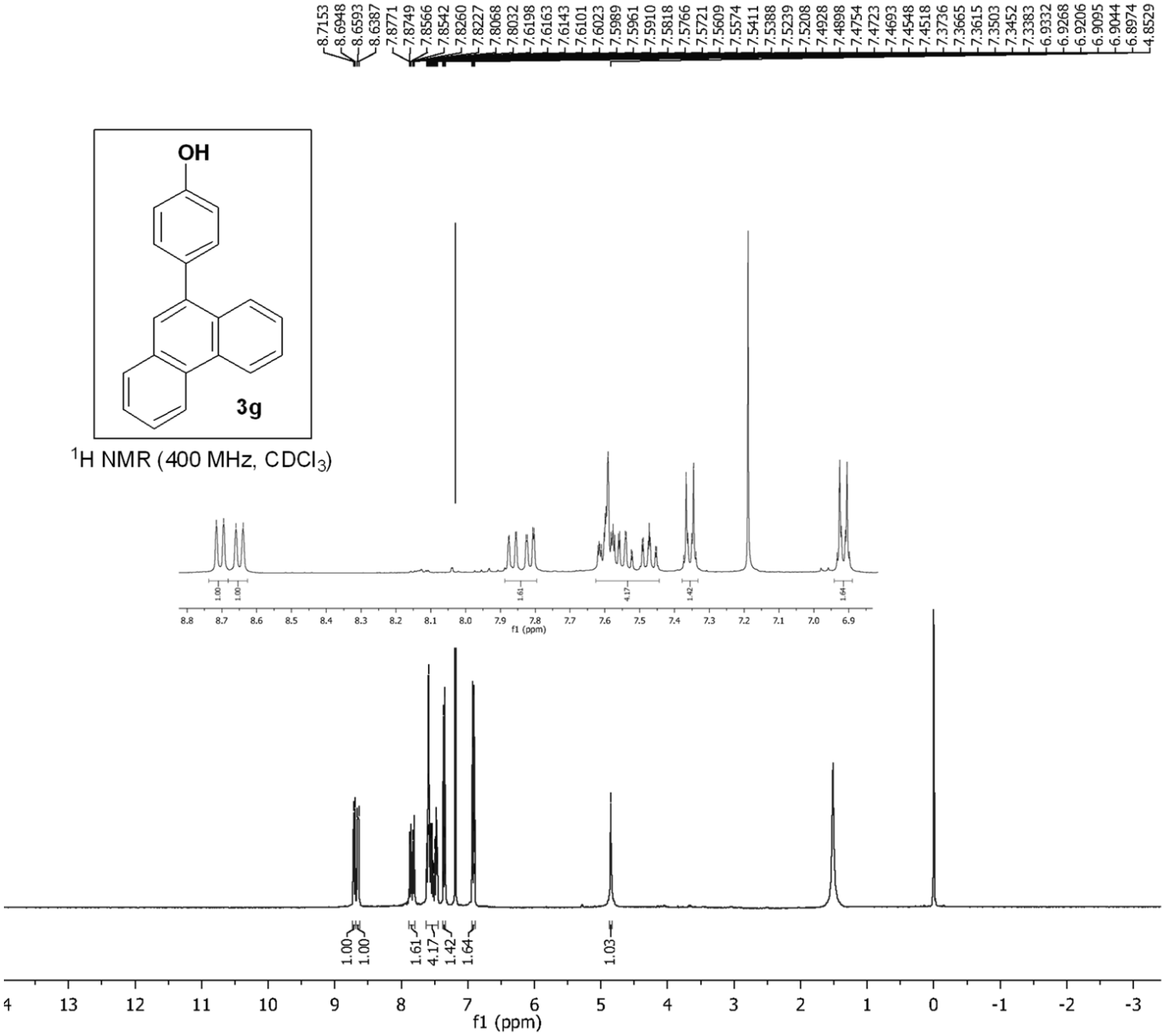

137.7865
137.2481
135.4219
134.6311
130.5777
130.2214
130.1796
129.5365
128.7859
128.4796
127.5303
126.4113
126.2973
126.2764
126.0163
125.9923
125.7004
125.3389
125.2759
125.2697
121.7839
121.4366
18.8371
18.5352
Me
Me
3e
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)

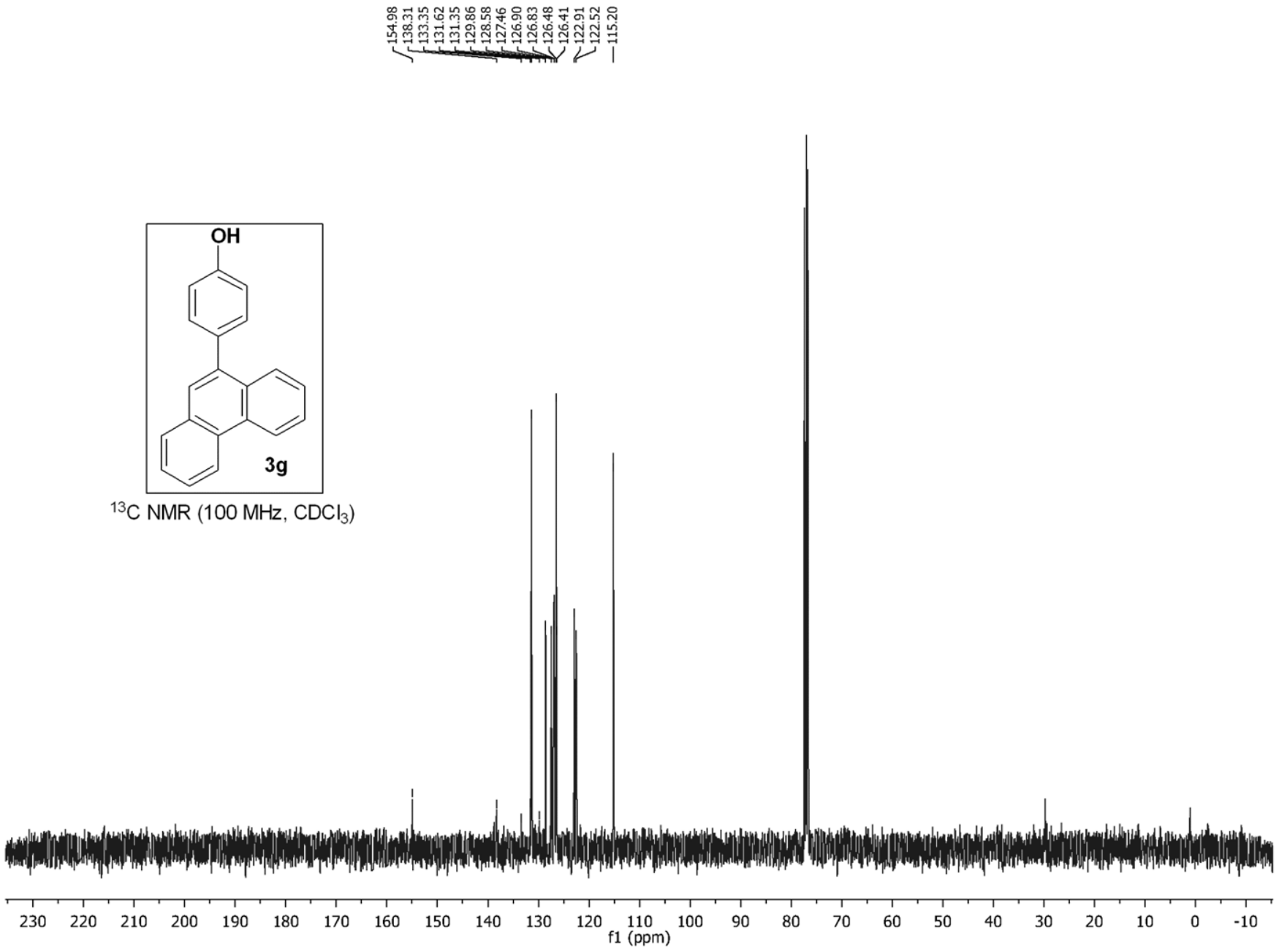


^{1}H NMR (300 MHz, $CDCl_3$)

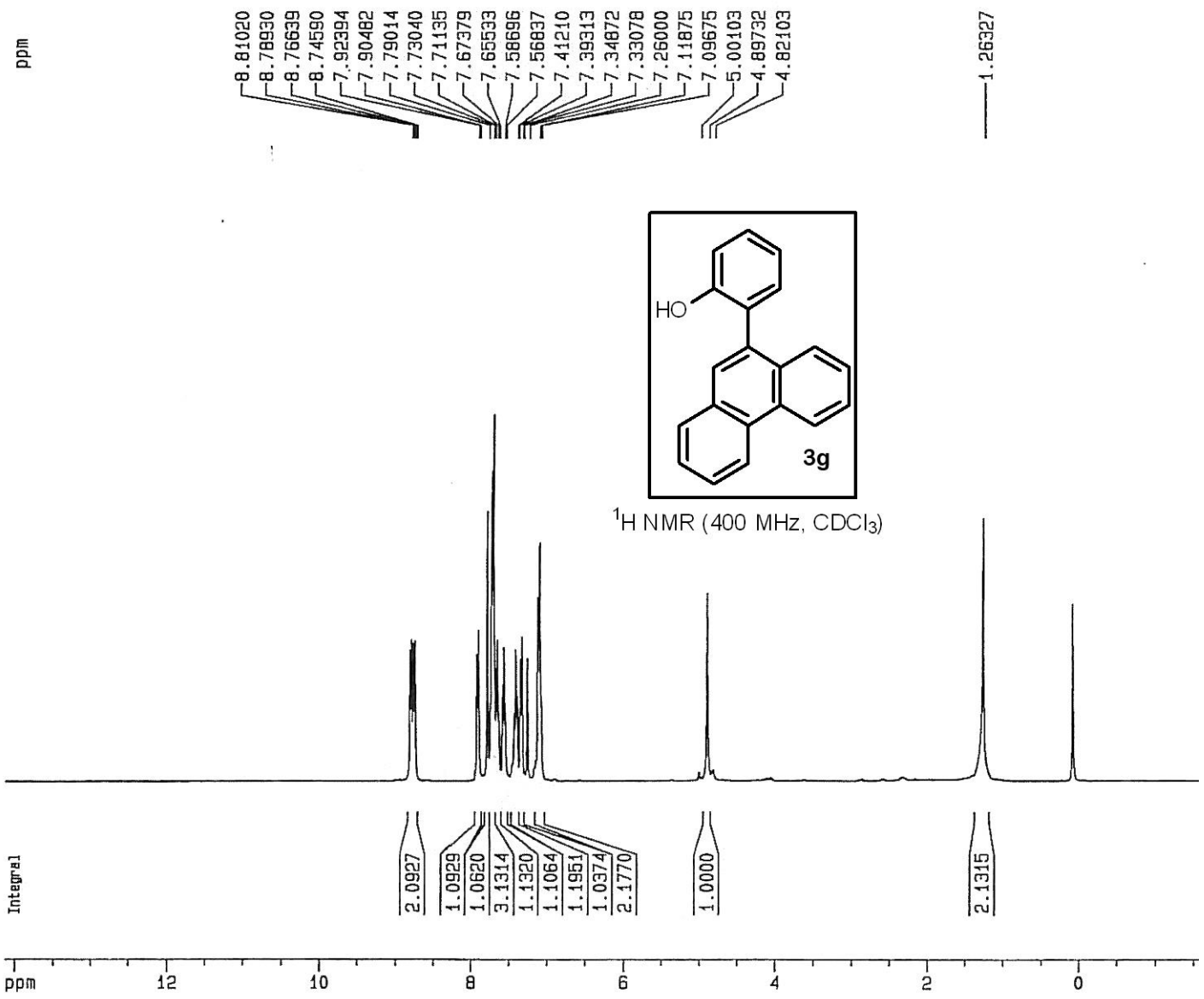


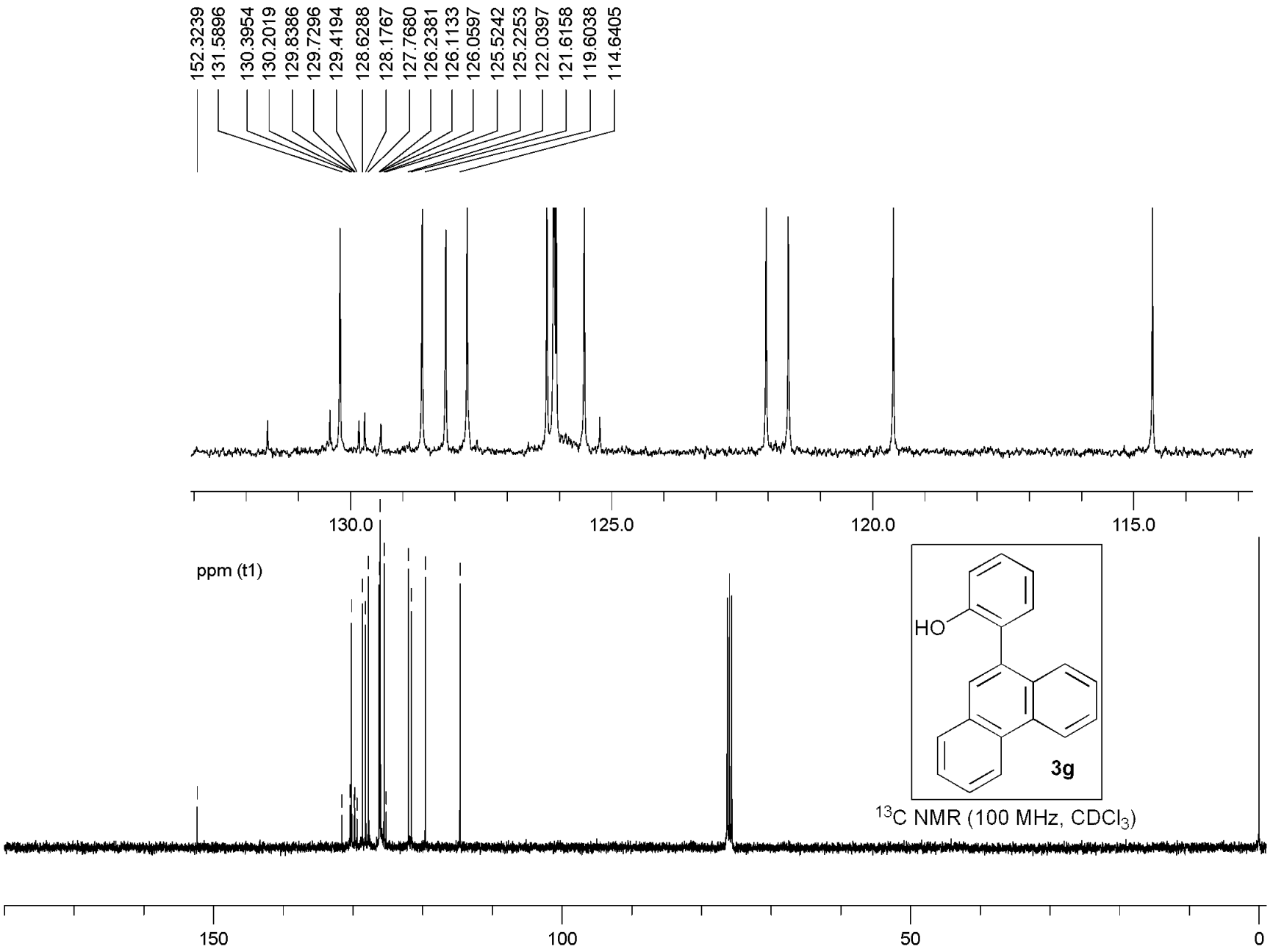
^{13}C NMR (75 MHz, $CDCl_3$)


8.7153
8.6948
8.6593
8.6387
7.8771
7.8749
7.8566
7.8542
7.8260
7.8227
7.8068
7.8032
7.6198
7.6163
7.6143
7.6101
7.6023
7.5989
7.5961
7.5910
7.5818
7.5766
7.5721
7.5609
7.5574
7.5411
7.5388
7.5239
7.5208
7.4928
7.4898
7.4754
7.4723
7.4693
7.4548
7.4518
7.3736
7.3665
7.3615
7.3503
7.3452
7.3383
6.9332
6.9268
6.9206
6.9095
6.9044
6.8974
4.8529
OH
3g
1H NMR (400 MHz, CDCl3)
1.00
1.00
1.61
4.17
1.42
1.64
1.03
f1 (ppm)

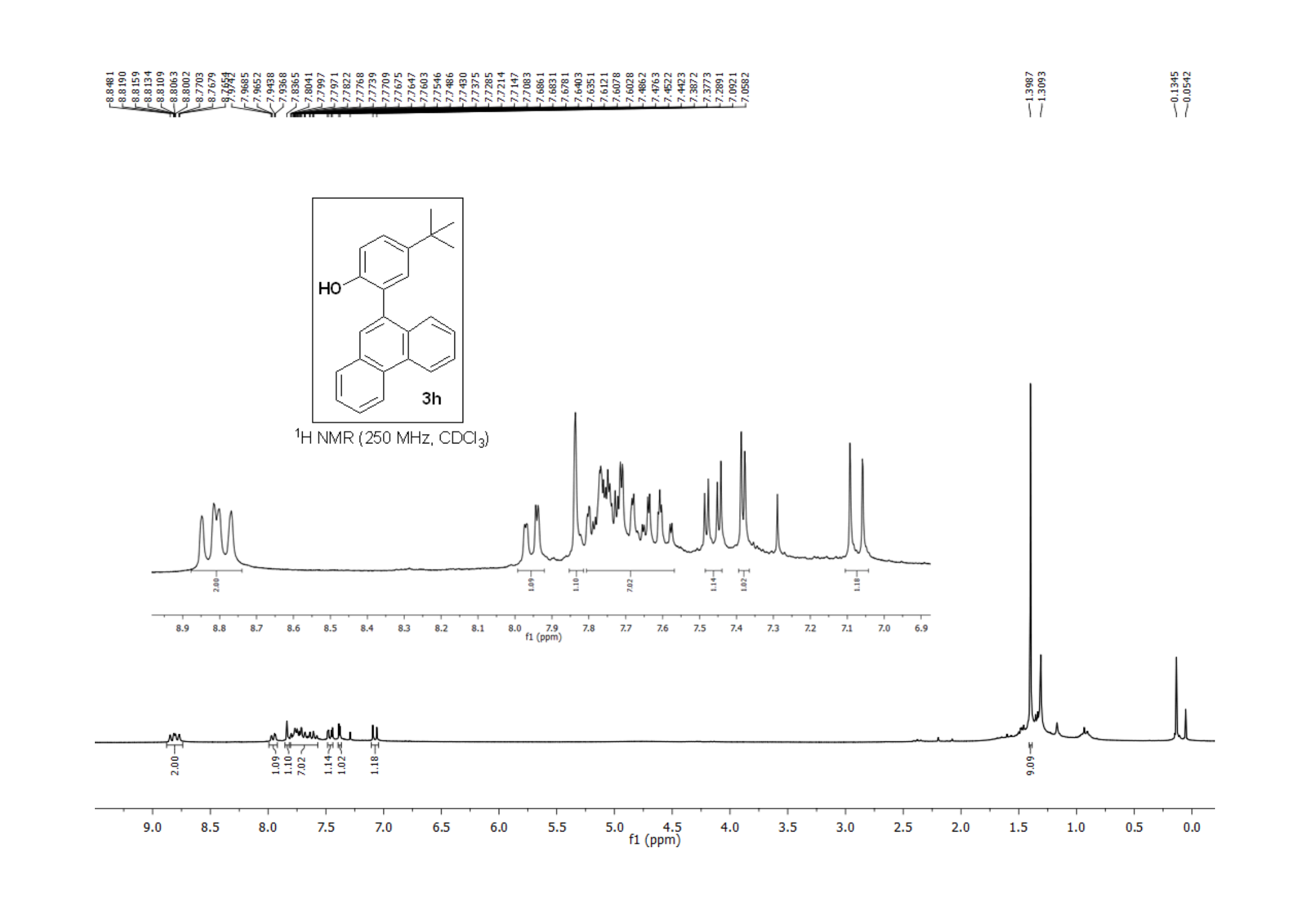


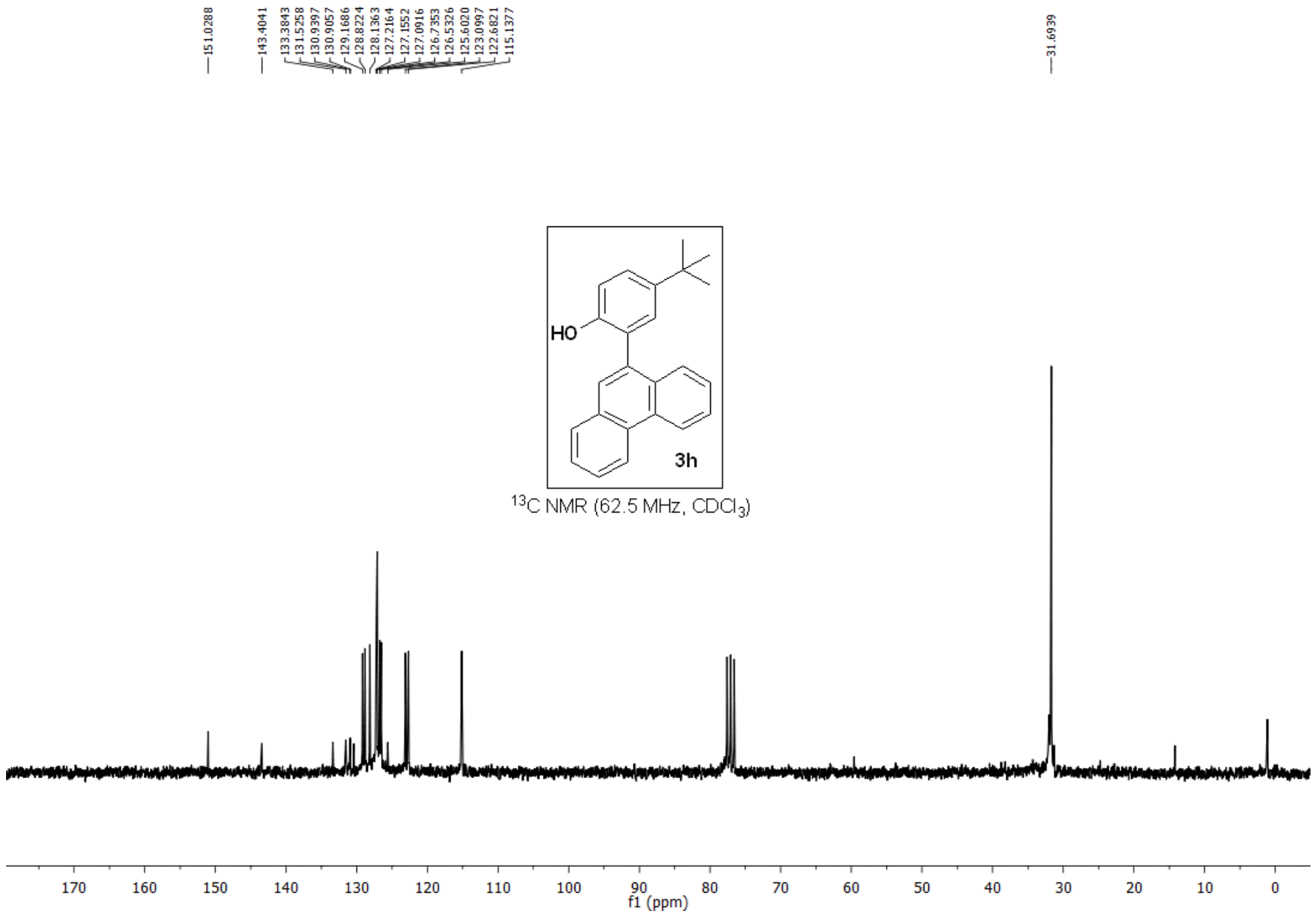
^{13}C NMR (100 MHz, $CDCl_3$)

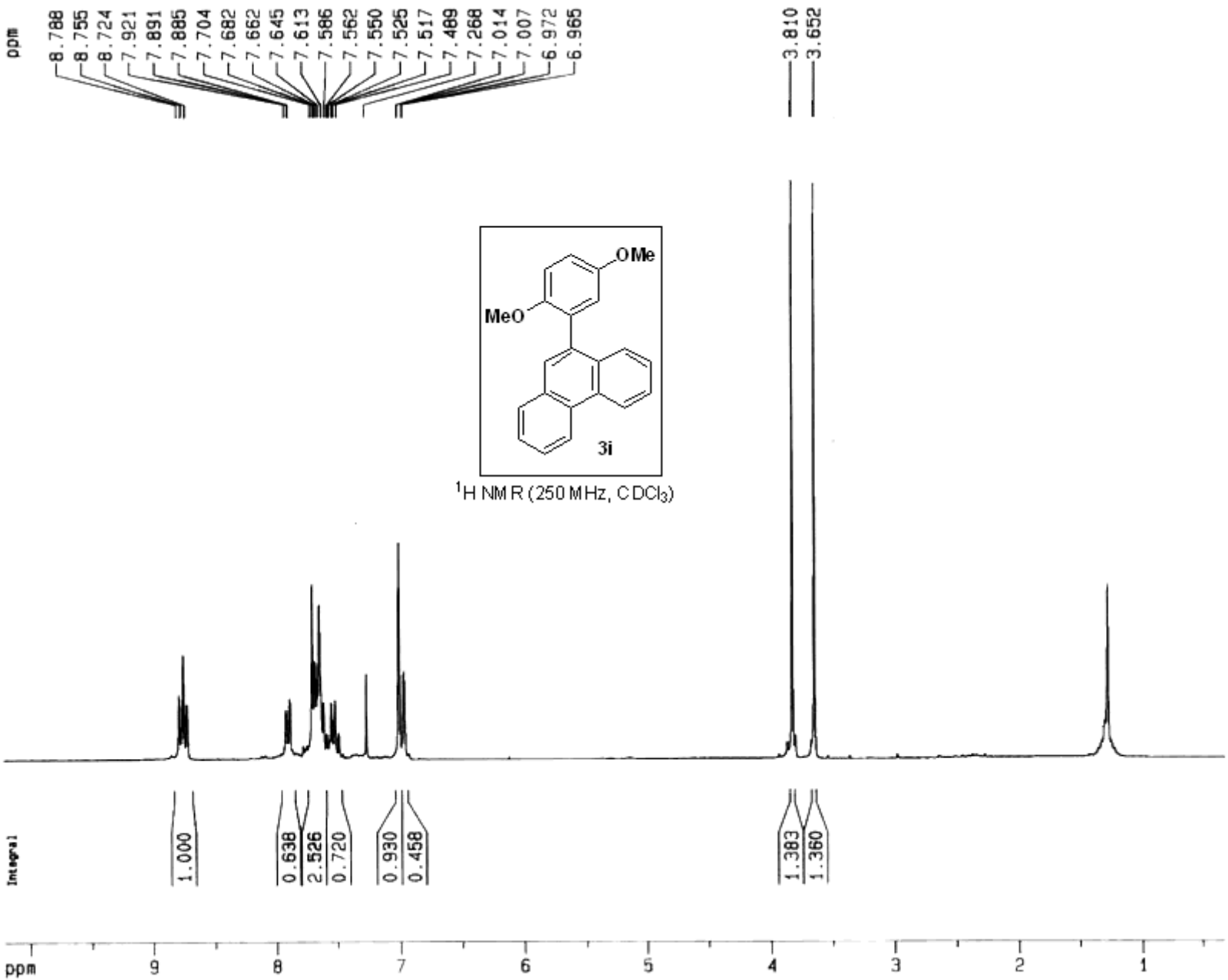

ppm
8.81020
8.78930
8.76639
8.74590
7.92394
7.90482
7.79014
7.73040
7.71135
7.67379
7.65533
7.58696
7.56837
7.41210
7.39313
7.34872
7.33078
7.26000
7.11875
7.09675
5.00103
4.89732
4.82103
1.26327
HO
3g
1H NMR (400 MHz, CDCl3)
Integral
2.0927
1.0929
1.0620
3.1314
1.1320
1.1064
1.1951
1.0374
2.1770
1.0000
2.1315
ppm
12
10
8
6
4
2
0



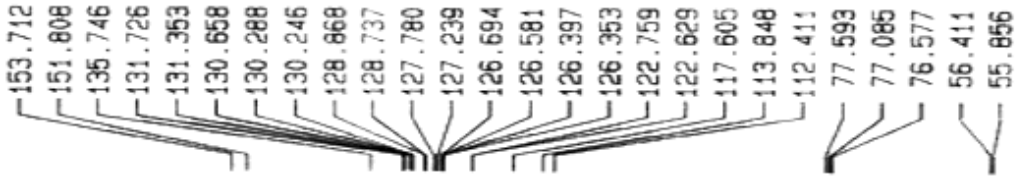
^{13}C NMR (100 MHz, $CDCl_3$)

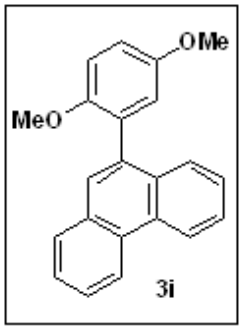

HO
3h
^{1}H NMR (250 MHz, CDCl$_3$)
f1 (ppm)


151.0288
143.4041
133.3843
131.5258
130.9397
130.9057
129.1686
128.8224
128.1363
127.2164
127.1552
127.0916
126.7353
126.5326
125.6020
123.0997
122.6821
115.1377
31.6939
HO
3h
13C NMR (62.5 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

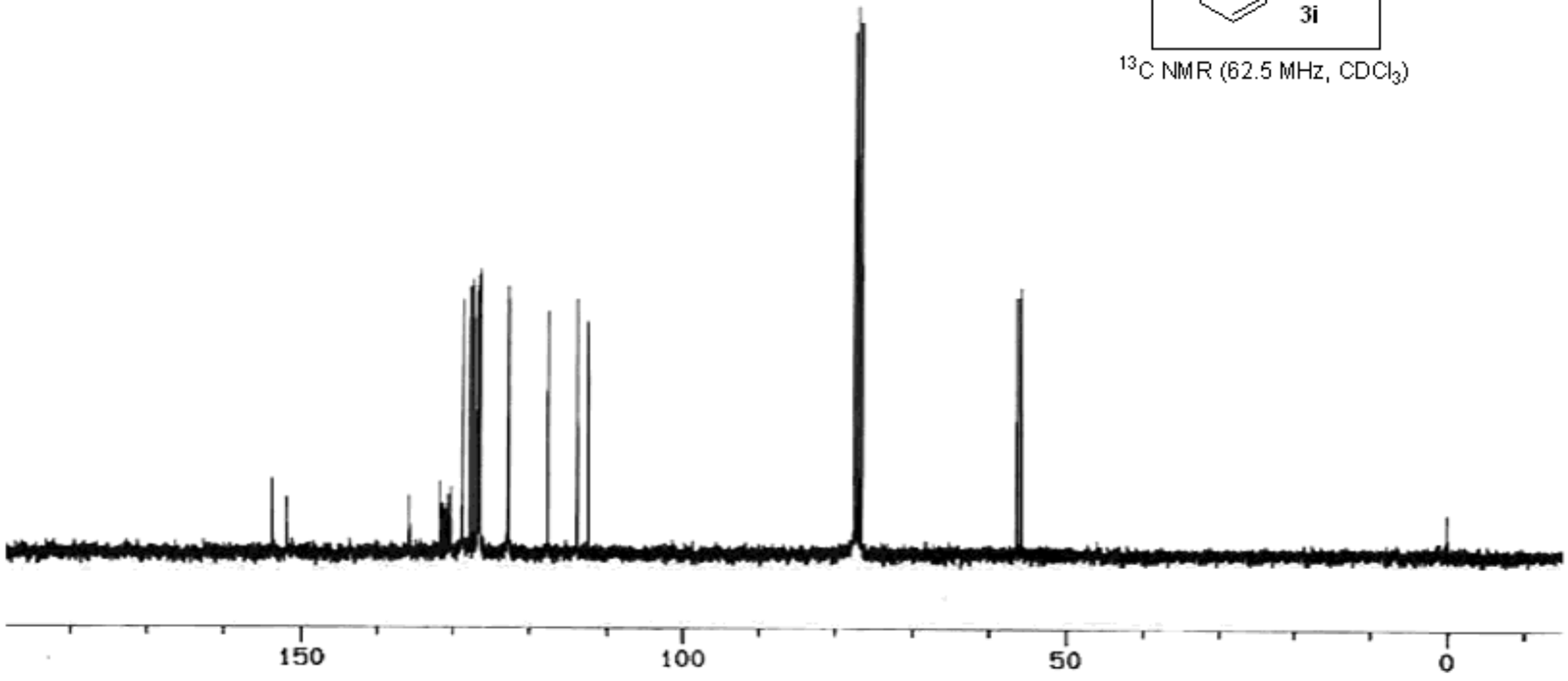


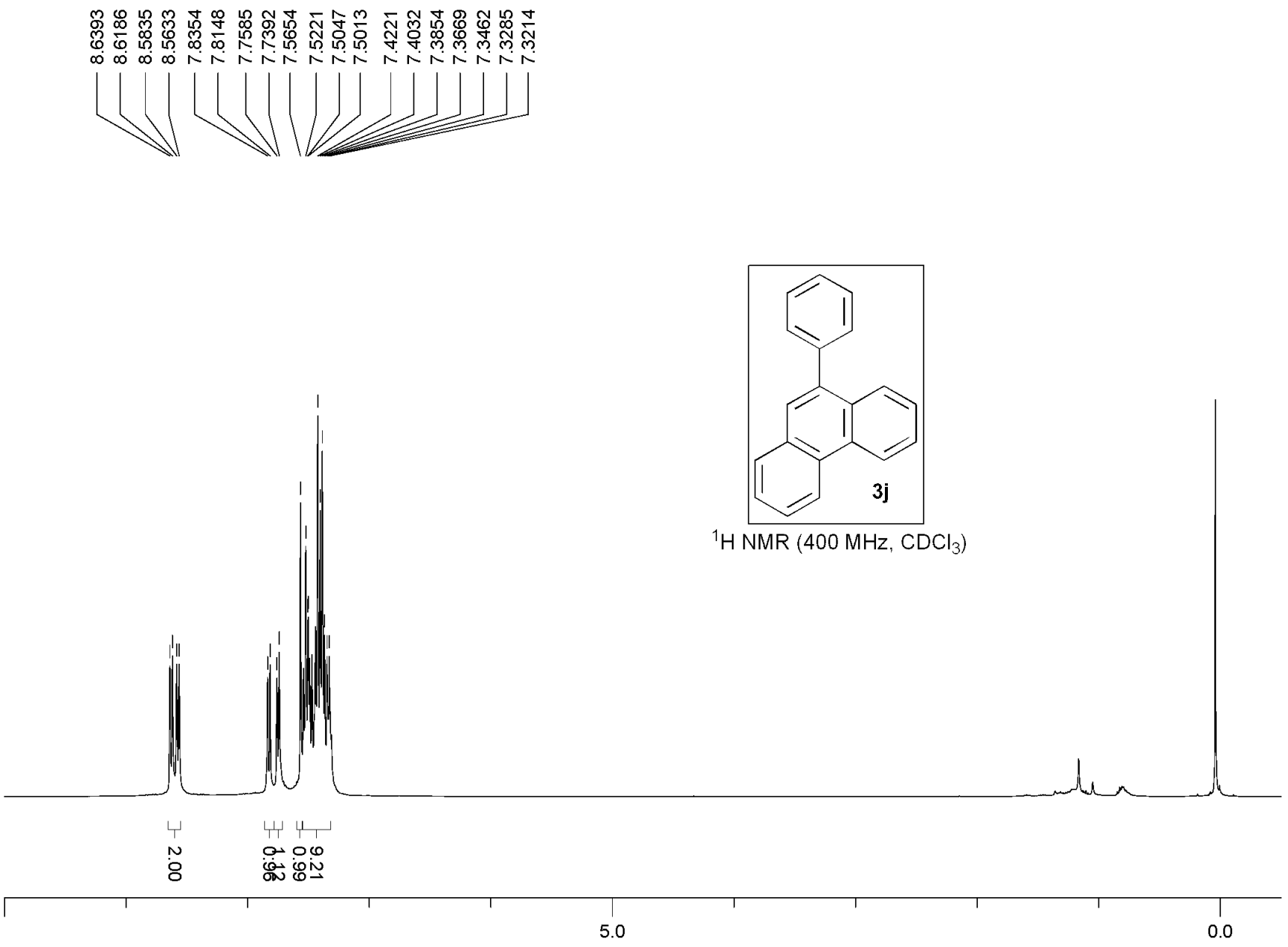
^{1}H NMR (250 MHz, $CDCl_3$)

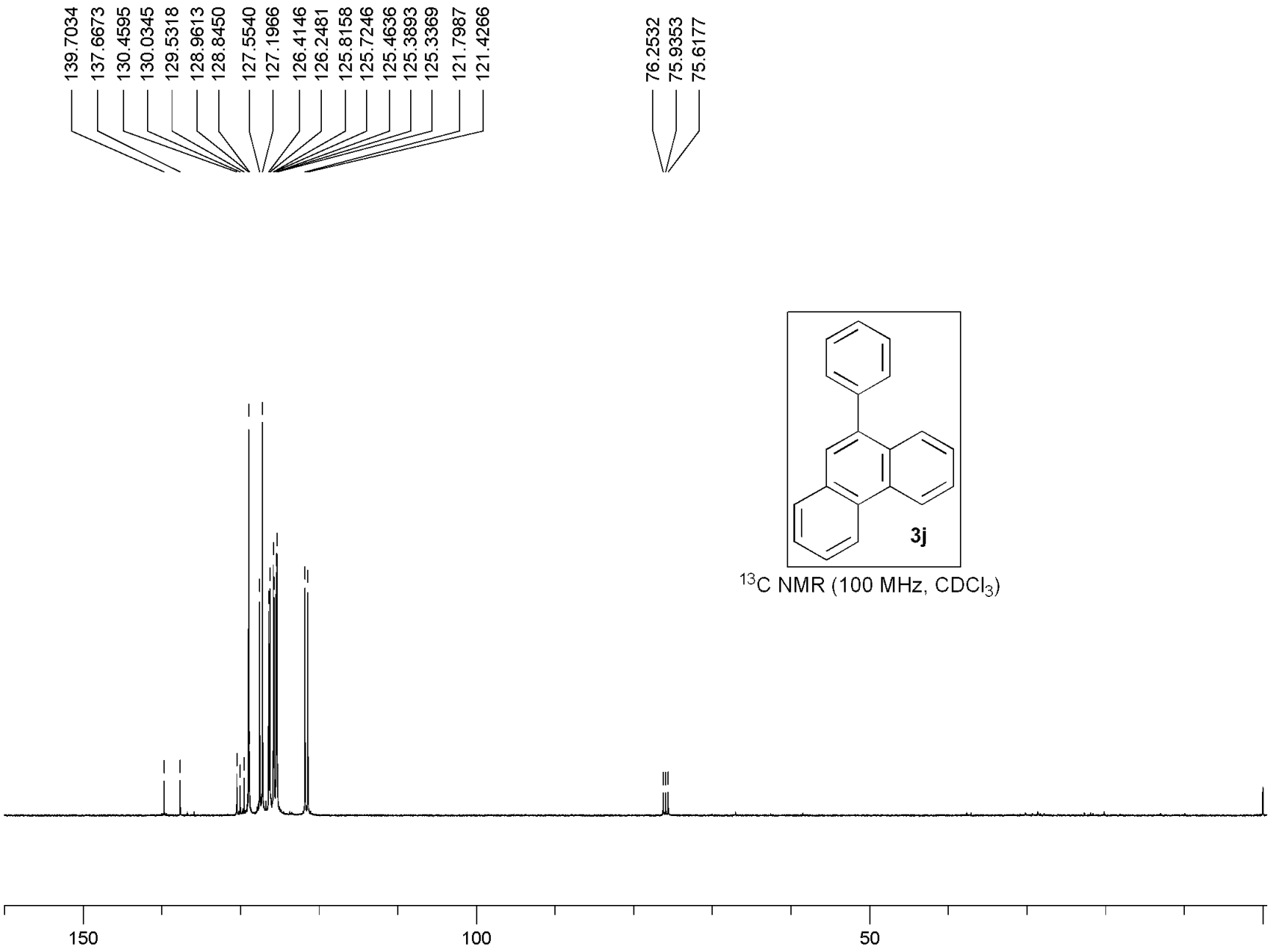




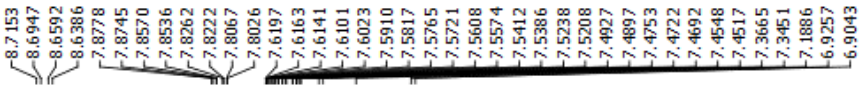
^{13}C NMR (62.5 MHz, $CDCl_3$)

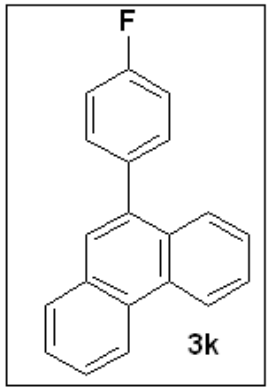



8.6393
8.6186
8.5835
8.5633
7.8354
7.8148
7.7585
7.7392
7.5654
7.5221
7.5047
7.5013
7.4221
7.4032
7.3854
7.3669
7.3462
7.3285
7.3214
3j
^{1}H NMR (400 MHz, $CDCl_3$)
2.00
0.96
1.12
0.99
6.21
5.0
0.0
ppm (t1)

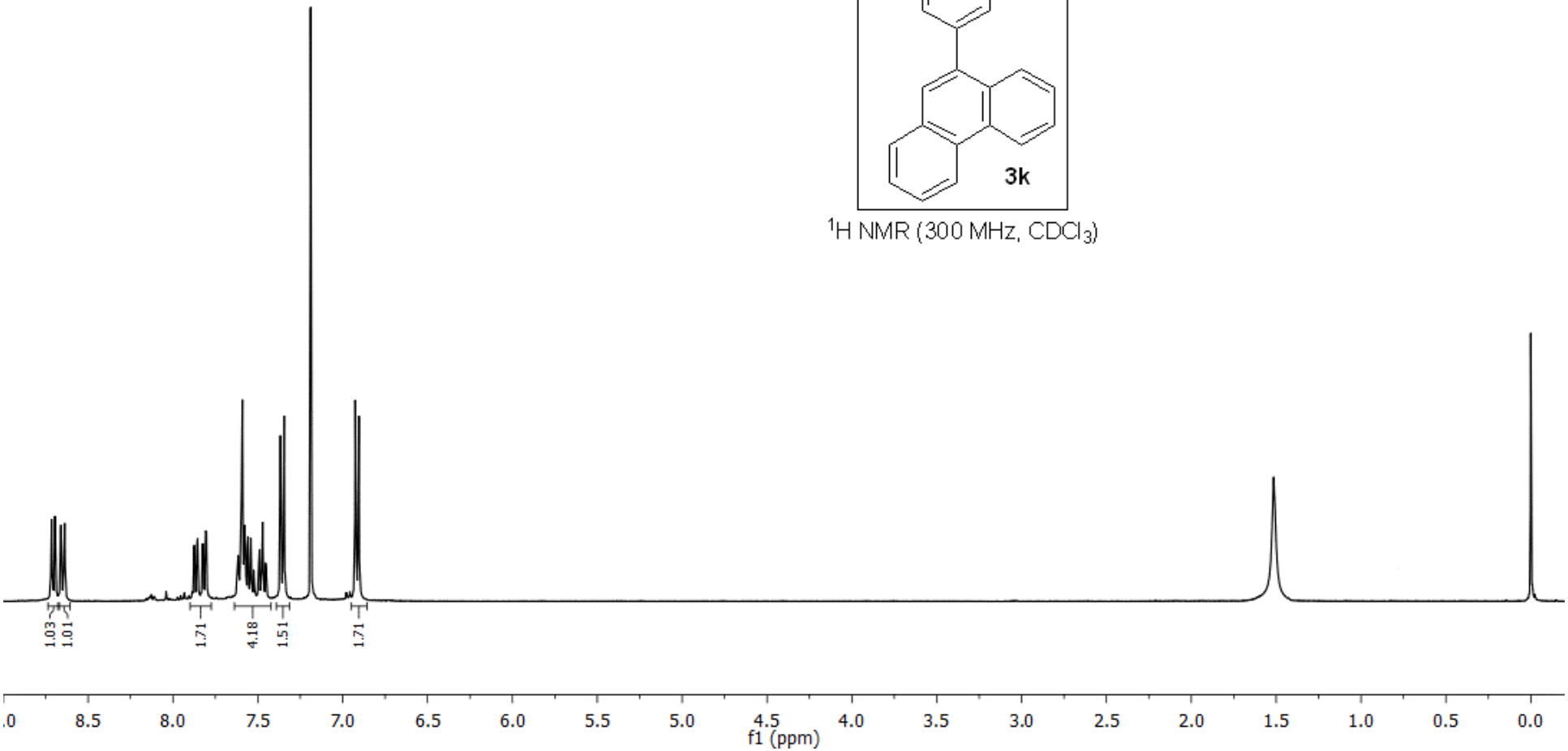


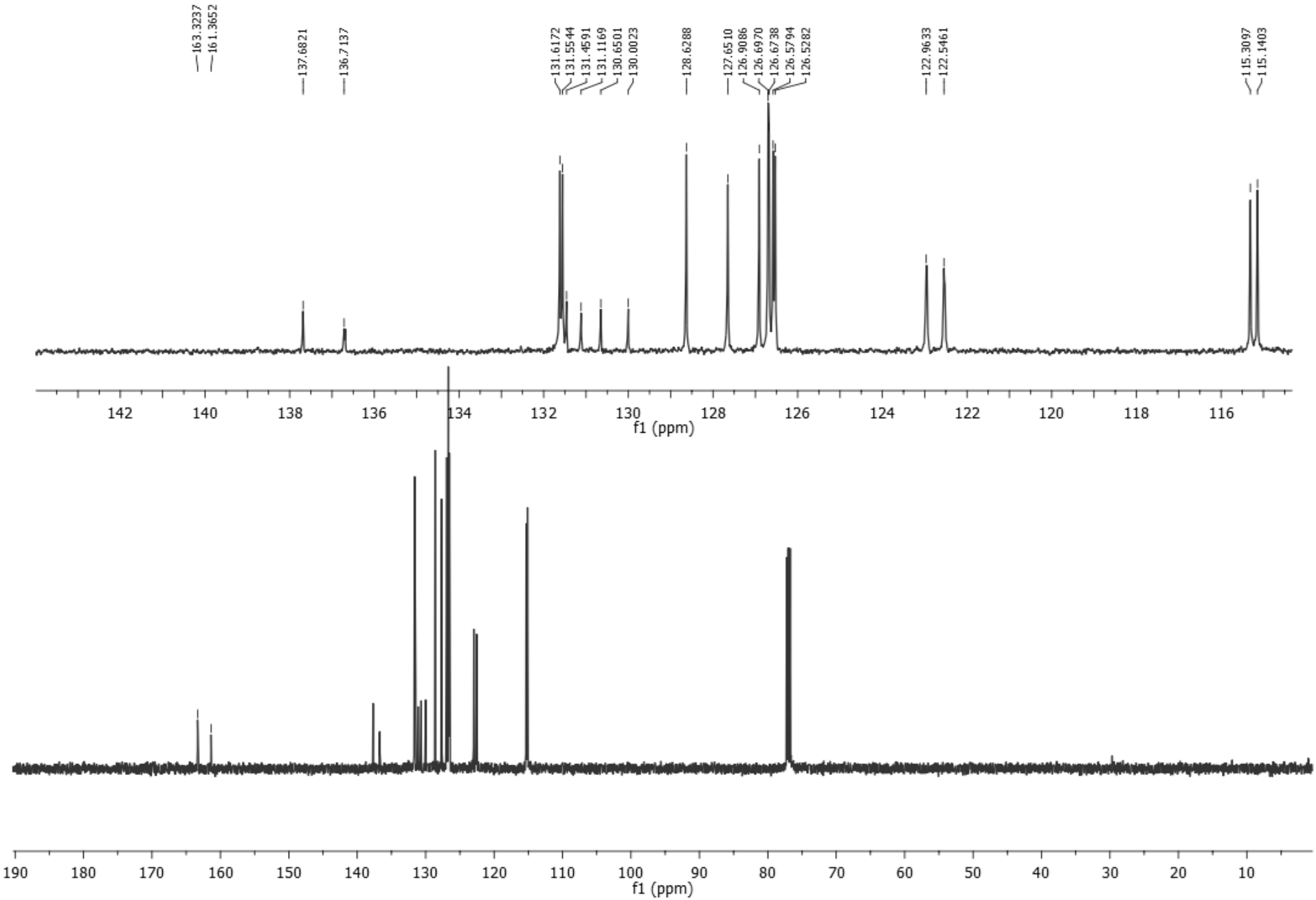
^{13}C NMR (100 MHz, $CDCl_3$)

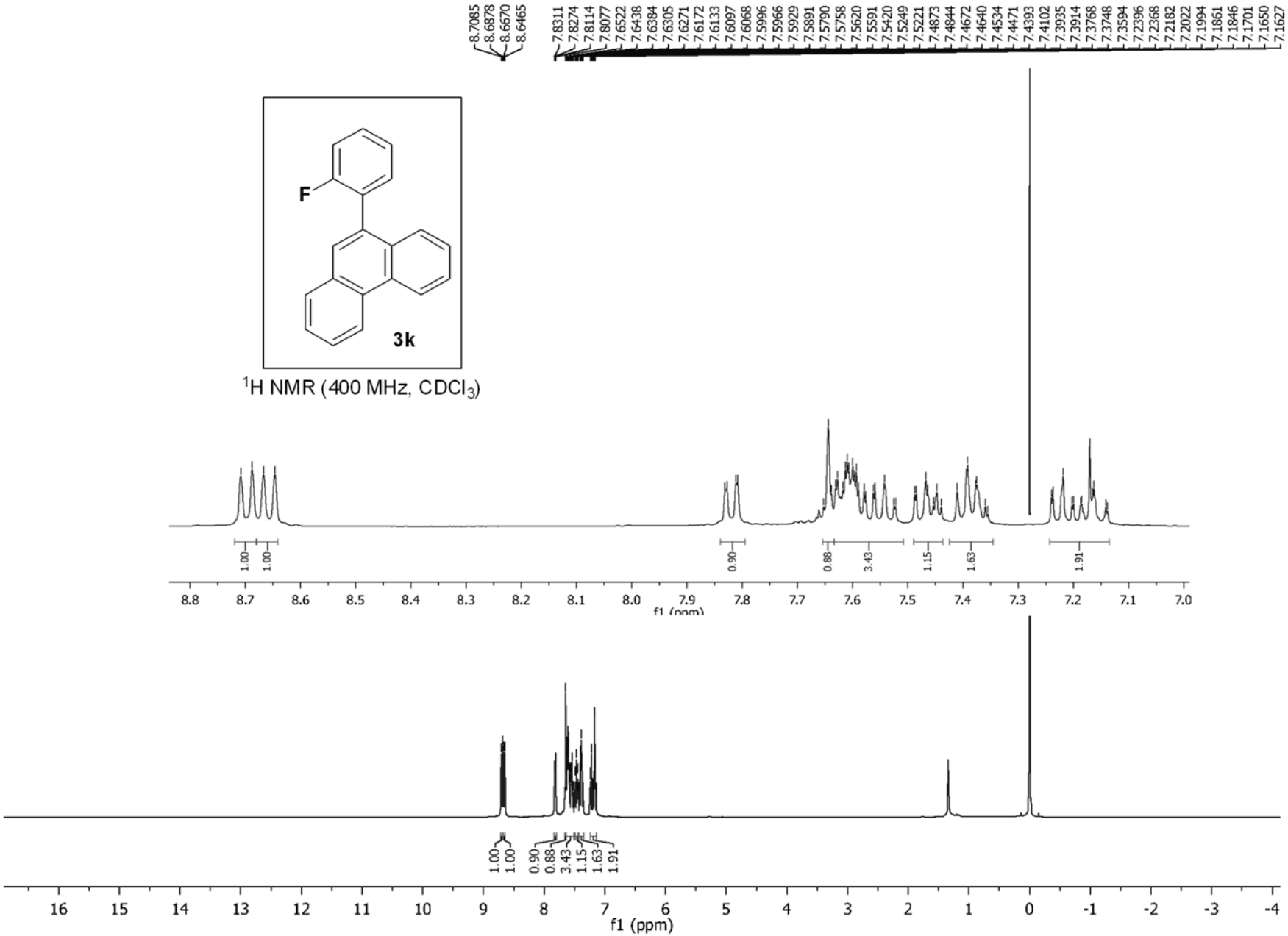




^{1}H NMR (300 MHz, $CDCl_3$)

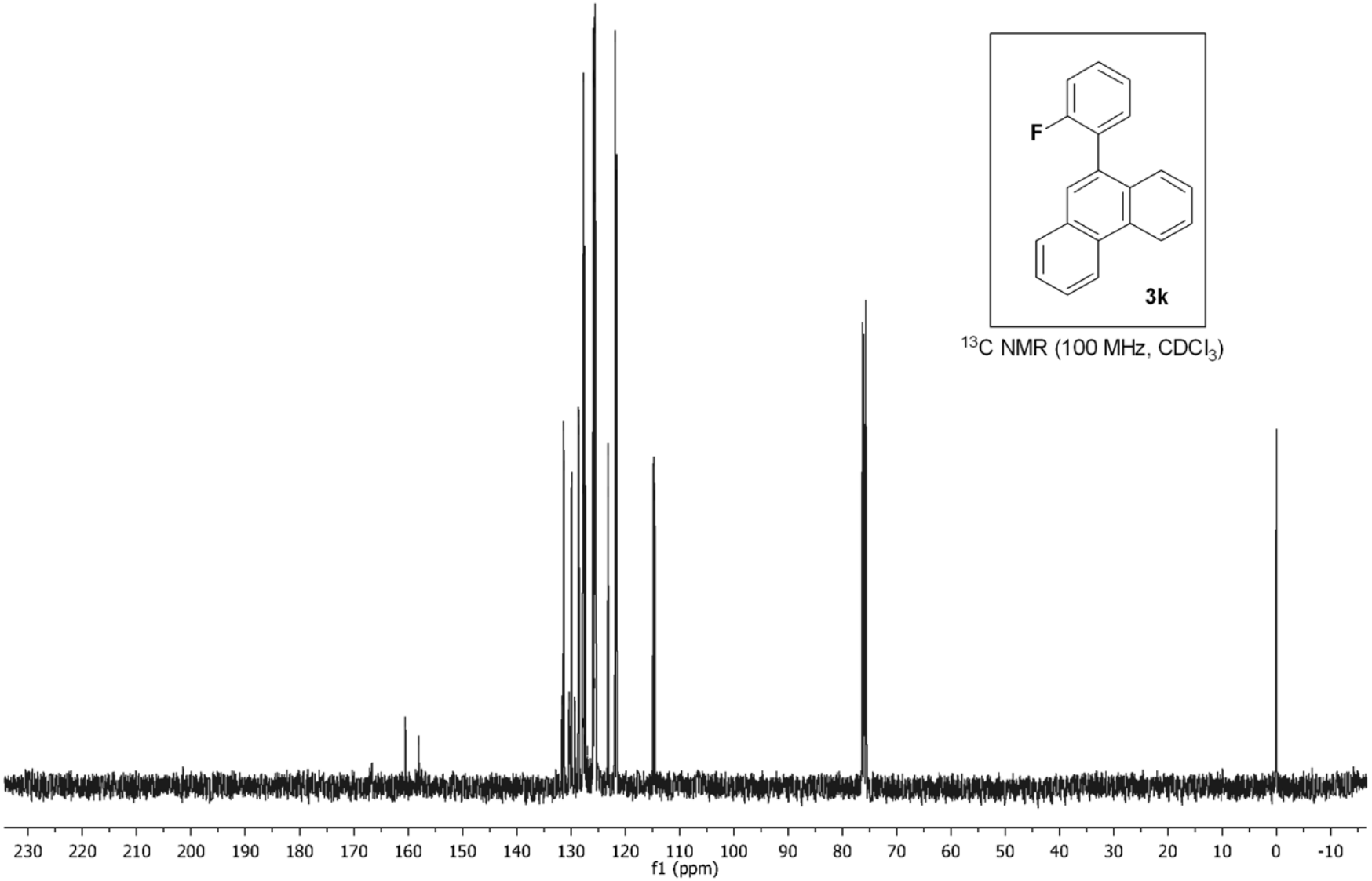


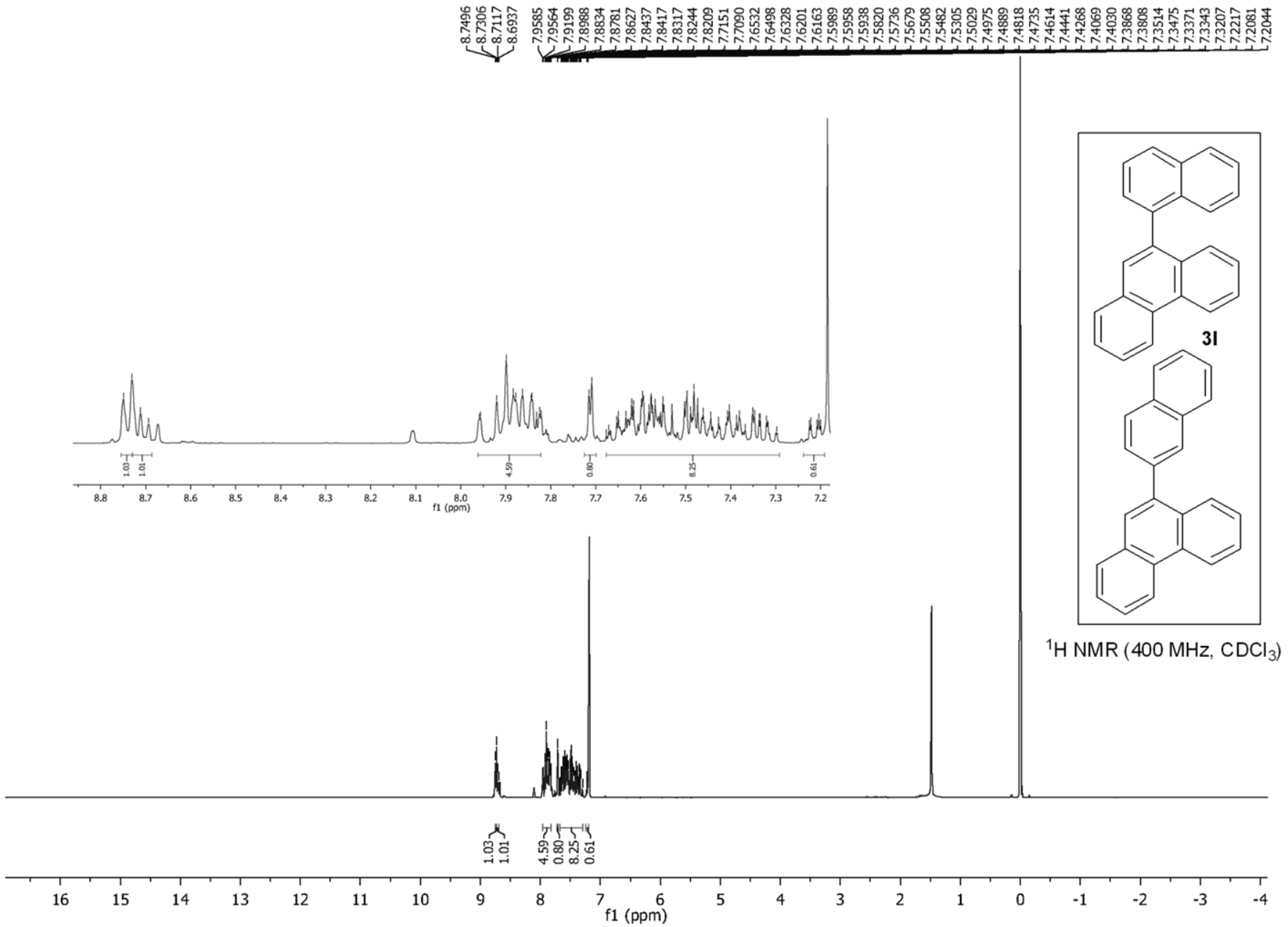

163.3237
161.3652
137.6821
136.7137
131.6172
131.5544
131.4591
131.1169
130.6501
130.0023
128.6288
127.6510
126.9086
126.6970
126.6738
126.5794
126.5282
122.9633
122.5461
115.3097
115.1403
142
140
138
136
134
132
130
128
126
124
122
120
118
116
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

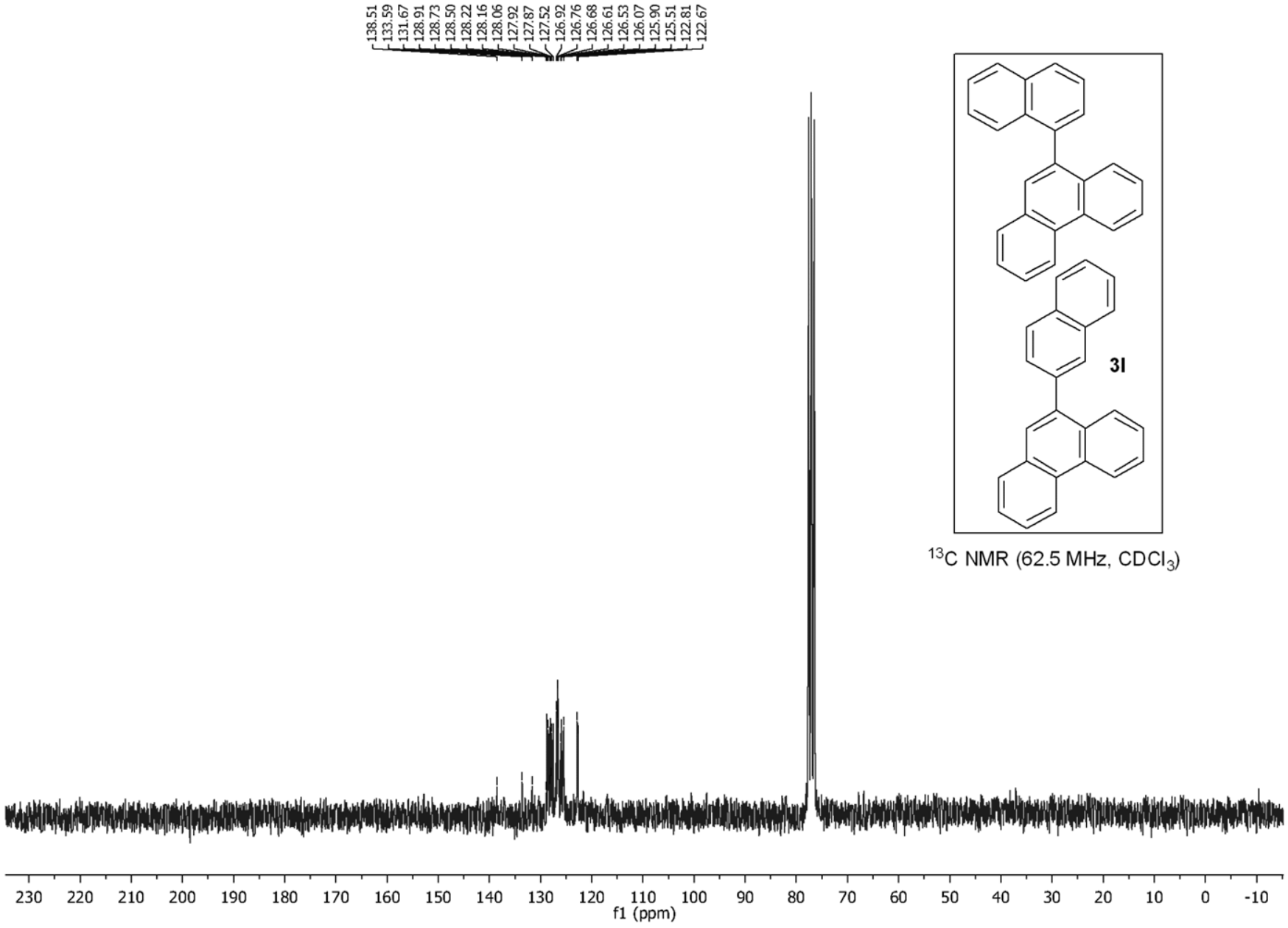

8.7085
8.6878
8.6670
8.6465
7.8311
7.8274
7.8114
7.8077
7.6522
7.6438
7.6384
7.6305
7.6271
7.6172
7.6133
7.6097
7.6068
7.5996
7.5966
7.5929
7.5891
7.5790
7.5758
7.5620
7.5591
7.5420
7.5249
7.5221
7.4873
7.4844
7.4672
7.4640
7.4534
7.4471
7.4393
7.4102
7.3935
7.3914
7.3768
7.3748
7.3594
7.2396
7.2368
7.2182
7.2022
7.1994
7.1861
7.1846
7.1701
7.1650
7.1627
F
3k
1H NMR (400 MHz, CDCl3)
1.00
1.00
0.90
0.88
3.43
1.15
1.63
1.91
f1 (ppm)

Ayobi-Mojgan-EN92031[illegible]
M22
C13c CDCl3 D:\\ Administrator 15

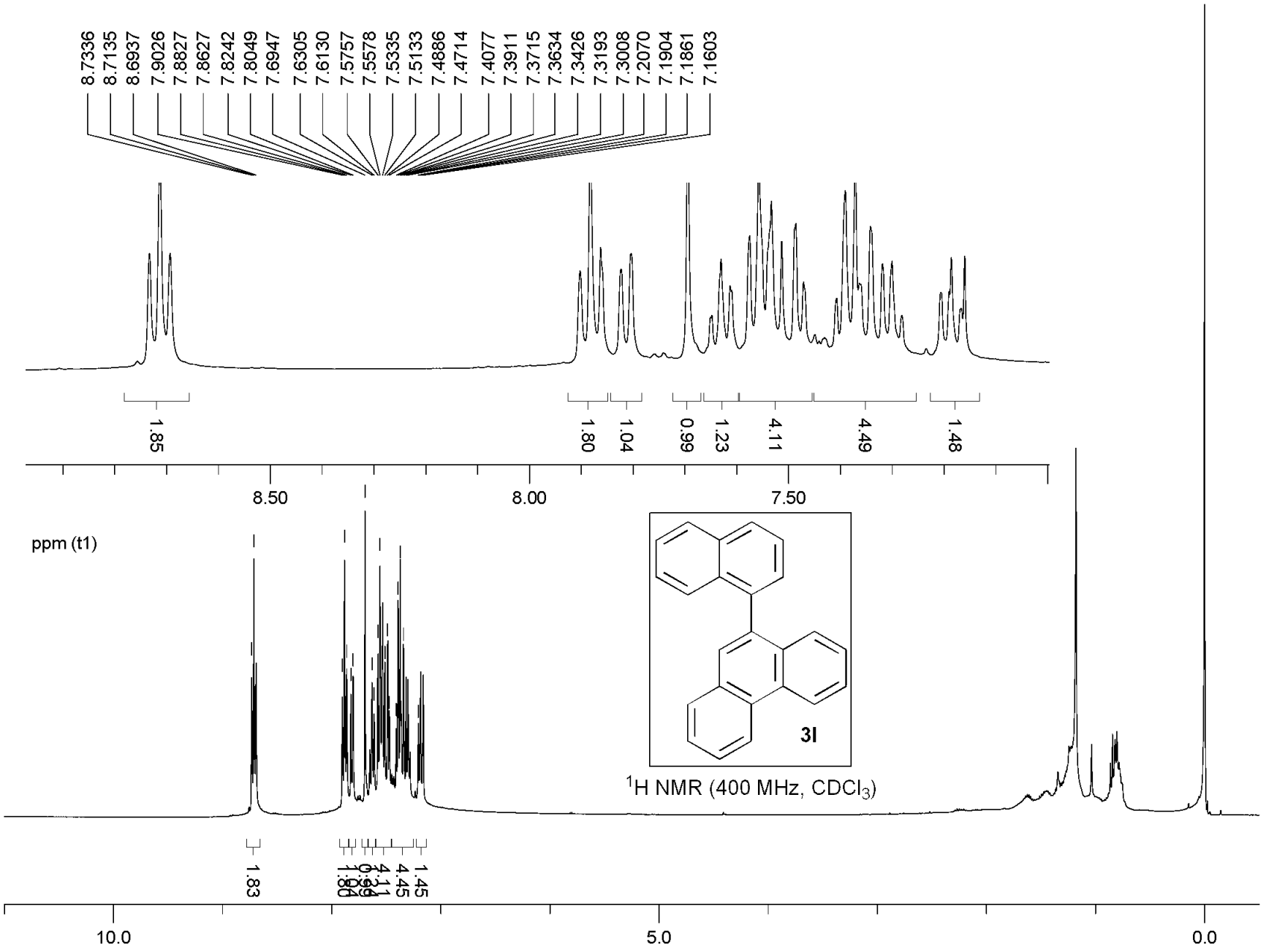
^{13}C NMR (100 MHz, $CDCl_3$)

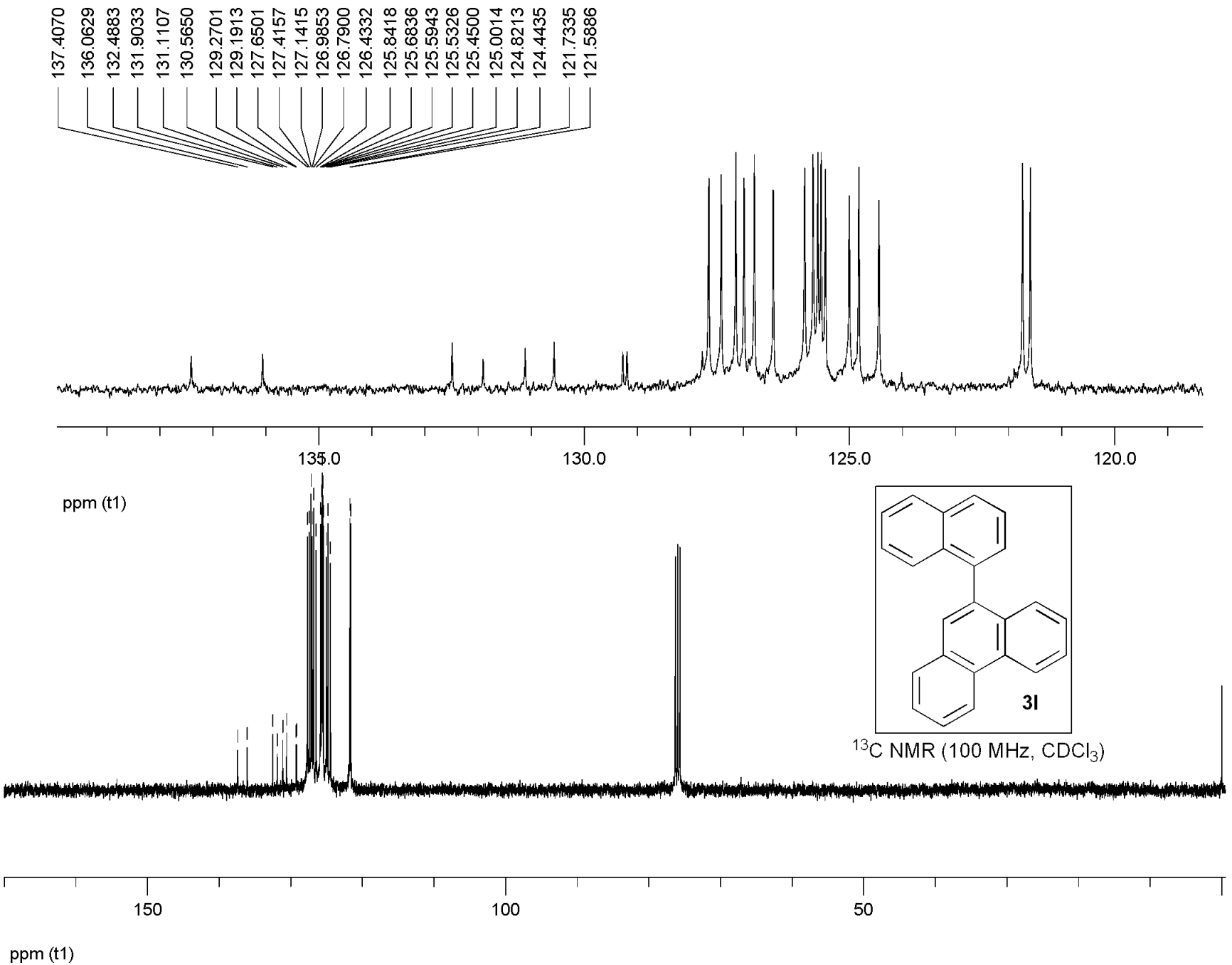


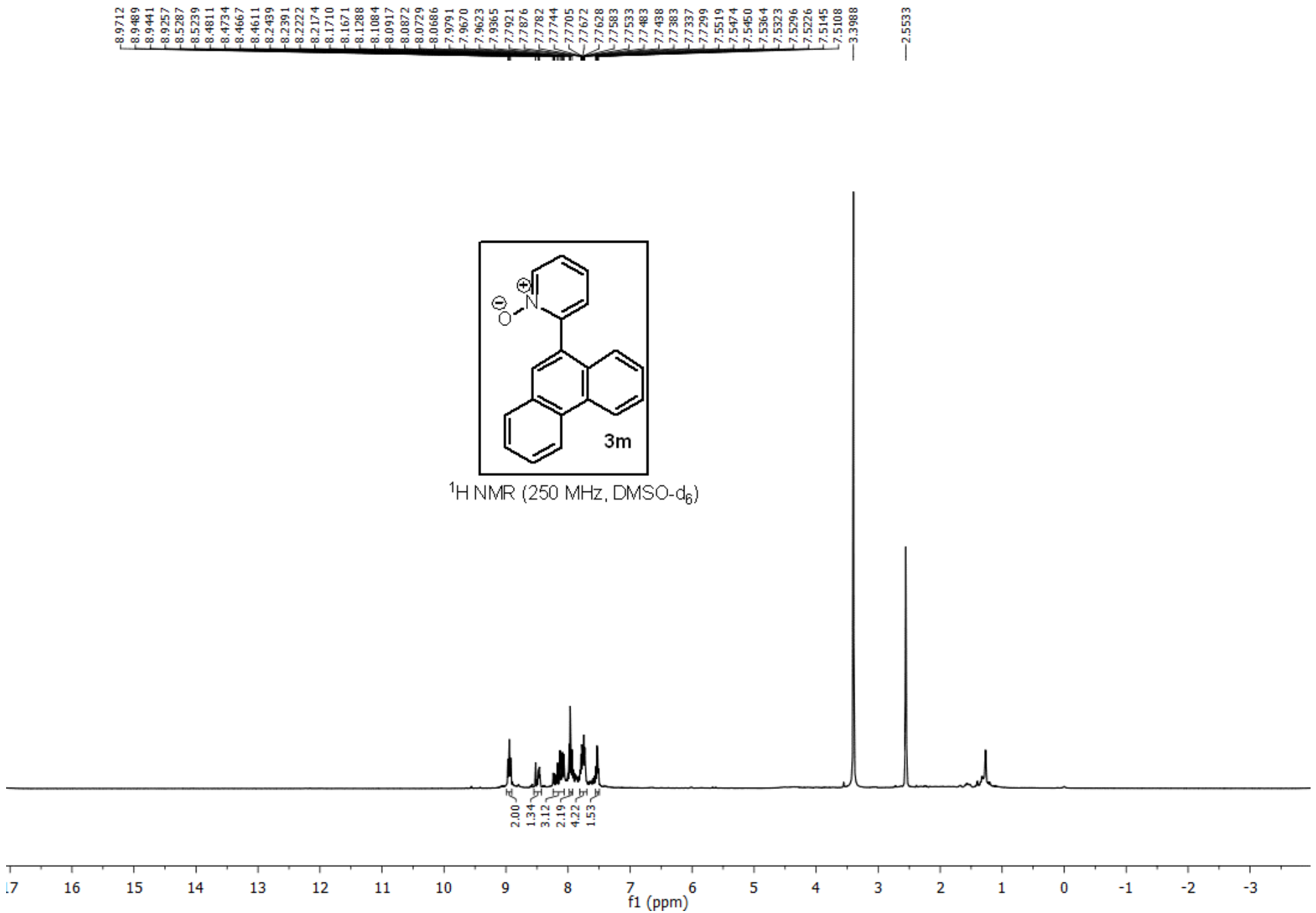

8.7496
8.7306
8.7117
8.6937
7.9585
7.9564
7.9199
7.8988
7.8834
7.8781
7.8627
7.8437
7.8417
7.8317
7.8244
7.8209
7.7151
7.7090
7.6532
7.6498
7.6328
7.6201
7.6163
7.5989
7.5958
7.5938
7.5820
7.5736
7.5679
7.5508
7.5482
7.5305
7.5029
7.4975
7.4889
7.4818
7.4735
7.4614
7.4441
7.4268
7.4069
7.4030
7.3868
7.3808
7.3514
7.3475
7.3371
7.3343
7.3207
7.2217
7.2081
7.2044
1.03
1.01
4.59
0.80
8.25
0.61
f1 (ppm)
3l
^{1}H NMR (400 MHz, $CDCl_3$)



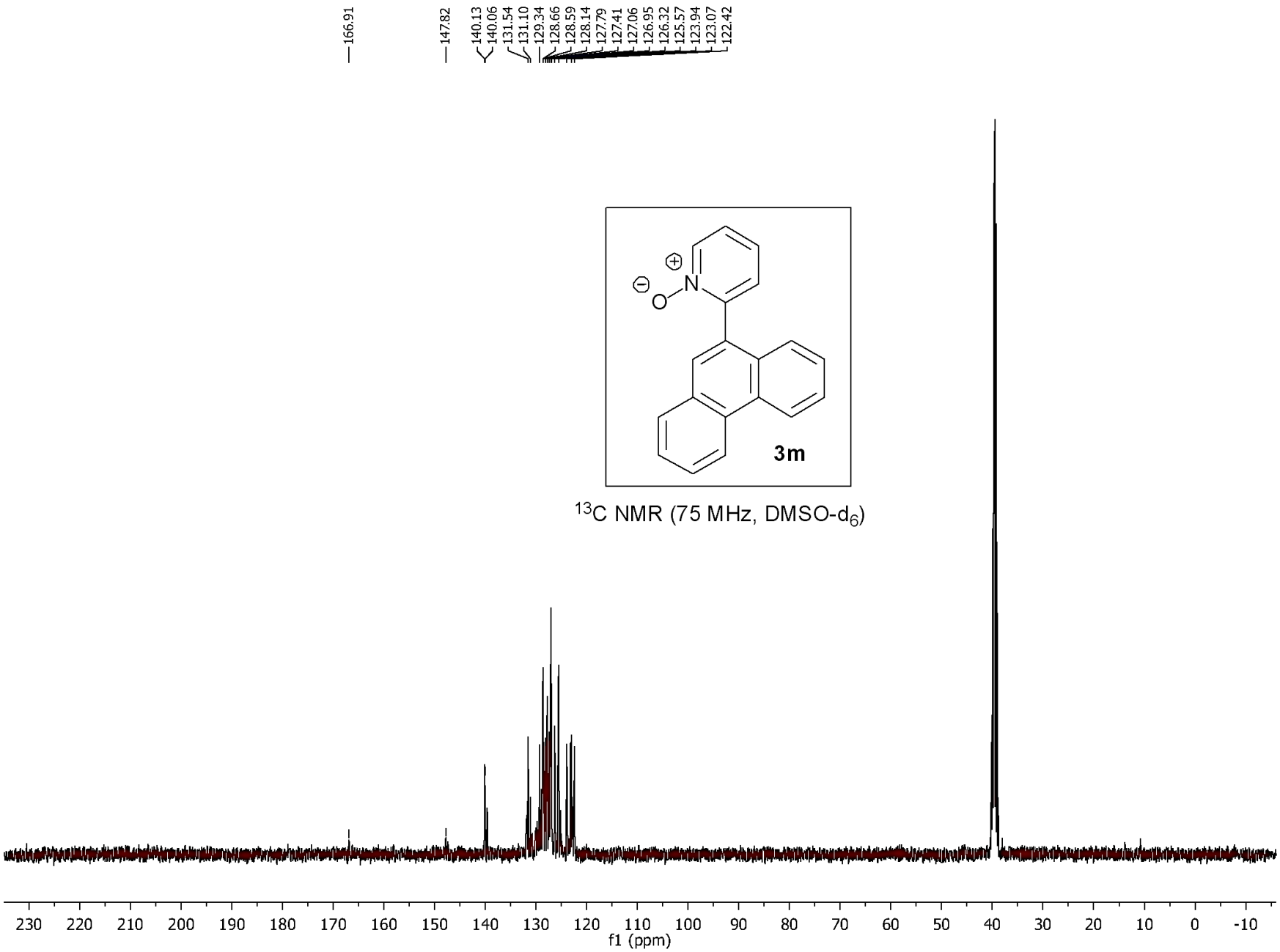
^{13}C NMR (62.5 MHz, $CDCl_3$)


8.7336
8.7135
8.6937
7.9026
7.8827
7.8627
7.8242
7.8049
7.6947
7.6305
7.6130
7.5757
7.5578
7.5335
7.5133
7.4886
7.4714
7.4077
7.3911
7.3715
7.3634
7.3426
7.3193
7.3008
7.2070
7.1904
7.1861
7.1603
1.85
1.80
1.04
0.99
1.23
4.11
4.49
1.48
8.50
8.00
7.50
ppm (t1)
3l
^{1}H NMR (400 MHz, $CDCl_3$)
1.83
1.45
4.45
10.0
5.0
0.0
ppm (t1)

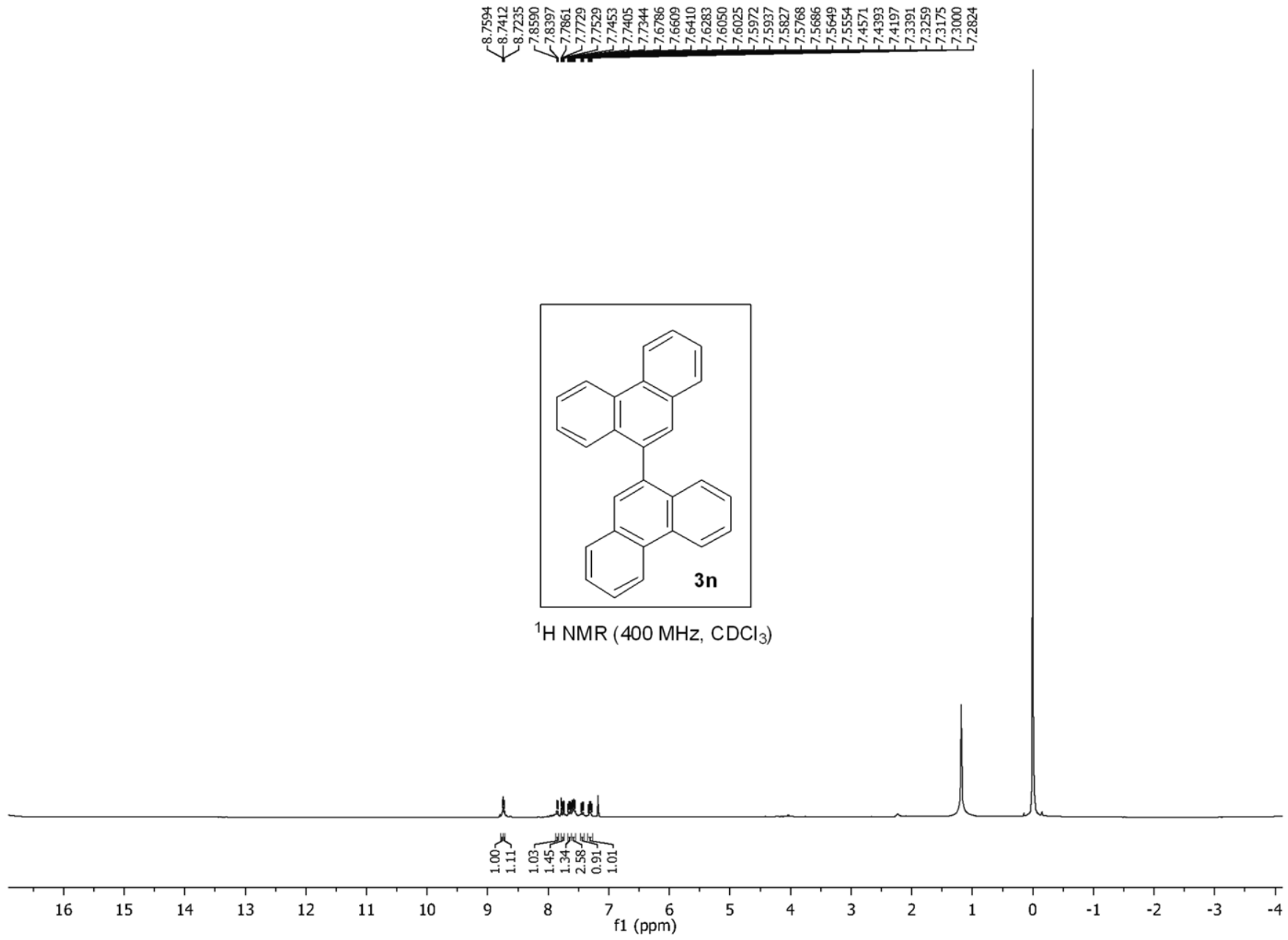

137.4070
136.0629
132.4883
131.9033
131.1107
130.5650
129.2701
129.1913
127.6501
127.4157
127.1415
126.9853
126.7900
126.4332
125.8418
125.6836
125.5943
125.5326
125.4500
125.0014
124.8213
124.4435
121.7335
121.5886
135.0
130.0
125.0
120.0
ppm (t1)
3l
^{13}C NMR (100 MHz, $CDCl_3$)
150
100
50
ppm (t1)



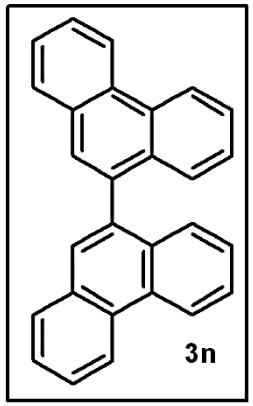
^{1}H NMR (250 MHz, DMSO-d_6)



^{13}C NMR (75 MHz, DMSO-d_6)



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)