Supplementary Information

Facile Synthesis of Annulated Heterocyclic Benzo[*kl*]acridine Derivatives via One-pot N-H/C-H Coupling

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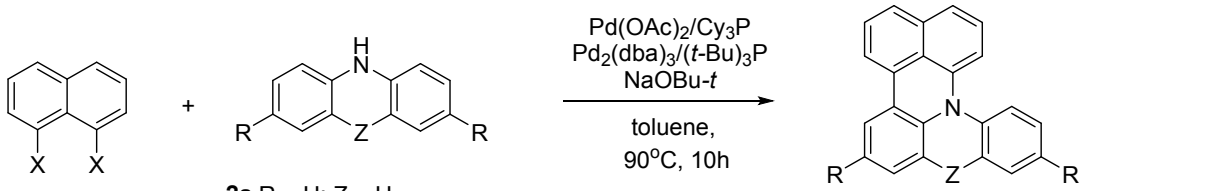
Materials and Methods

^{1}H and ^{13}C NMR spectra were recorded on Bruker AC300 NMR spectrometers using the residual proton or the carbon signal of the deuterated solvent as an internal standard. Chemical shifts are reported in parts per million. FD mass spectra were performed with a VG-Instrument ZAB 2-SE-FDP. The elemental analyses were carried out by the Microanalytical Laboratory of Johannes Gutenberg University. All chemicals and solvents were purchased from commercial suppliers and used without further purification unless otherwise specified. Column chromatography was performed with dichloromethane (Fisher Scientific), methanol, tetrahydrofuran, hexane or acetone (Sigma-Aldrich) on silica gel (Macherey-Nagel, Si60). All reported yields of compounds **3a-3e** are isolated yields.

Experimental Section

General Procedure for 3a-3e: A mixture of dibromoaryl compound (3.5 mmol), diarylamine (3 mmol), sodium *tert*-butoxyde (7 mmol, 0.67 g), $Pd(OAc)_2$ (3 mol%, 0.09 mmol, 0.02 g), $Pd_2(dba)_3$ (3 mol%, 0.09 mmol, 0.082 g), tricyclohexylphosphine (7 mol%, 0.21 mmol, 0.06 g) and tri-*tert*-butylphosphine (7 mol%, 0.21 mmol, 0.043 g) in 50 ml dry toluene was stirred at 90°C for 10 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography using hexane/dichloromethane as eluent on silica.



1a X= Br
1b X= I

2a R = H; Z = H
2b R = 2,4,4-trimethylpentan-2-yl; Z = H
2c R = H; Z= -CH=CH-
2d R = H; Z = S
2e R = H; Z = O

3a R = H; Z = H
3b R = 2,4,4-trimethylpentan-2-yl; Z = H
3c R = H; Z= -CH=CH-
3d R = H; Z = S
3e R = H; Z = O

7-Phenyl-7*H*-benzo[*kl*]acridine (*3a*):

Yield from 1,8-dibromonaphthalene 0.80 g (91%) and from 1,2-diiodonaphthalene 0.84 g (95%).

^{1}H-NMR (δ (ppm), CD_2Cl_2): 5.75 (dd, 1H, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 2.0 Hz); 6.21 (dd, 1H, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.0 Hz); 6.89-7.06 (m, 4H); 7.33-7.46 (m, 4H); 7.55-7.64 (m, 2H); 7.68-7.73 (m, 2H); 7.91 (dd, 1H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.4 Hz).

^{13}C-NMR (δ (ppm), CD_2Cl_2): 105.34; 113.76; 115.92; 117.14; 121.41;, 123.43; 124.60; 124.88; 127.62; 127.81; 129.29; 129.64; 131.10; 131.15; 132.18; 136.41; 140.84; 142.20; 142.56.

MS (FD, 8 kV): m/z (%) calcd for 293.37; found: 293.8 (100) $[M]^+$

Elemental analysis calcd (%) for $C_{22}H_{15}N$: C, 90.07; H, 5.15; N, 4.77; found: C, 90.10; H, 5.02; N, 4.68.

10-(2,4,4-Trimethylpentan-2-yl)-7-(4-(2,4,4-trimethylpentan-2-yl)phenyl)-7*H*-benzo[*kl*]acridine (*3b*):

Yield from 1,8-dibromonaphthalene 1.31 g (84%) and from 1,2-diiodonaphthalene 1.48 g (95%).

^{1}H-NMR (δ (ppm), CD_2Cl_2): 0.78 (s, 9H, CH_3); 0.83 (s, 9H, CH_3); 1.39 (s, 6H, CH_3); 1.48 (s, 6H, CH_3); 1.75 (s, 2H, CH_2); 1.86 (s, 2H, CH_2); 5.74-5.80 (m, 1H); 6.18 (d, 1H, $^3J_{HH}$ = 8.8 Hz); 6.98 (d, 1H, $^4J_{HH}$ = 1.5 Hz); 7.00 (s, 3H); 7.04 (dd, 1H, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 2.2 Hz); 7.23 (d, 2H, $^3J_{HH}$ = 8.4 Hz);7.34-7.43 (m, 2H); 7.64 (dd, 1H, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 1.7 Hz); 7.70 (d, 2H, $^3J_{HH}$ = 8.5 Hz); 7.90 (d, 1H, $^4J_{HH}$ = 2.2 Hz).

^{13}C-NMR (δ (ppm), CD_2Cl_2): 31.93; 32.14; 32.20; 32.83; 32.95; 38.62; 39.25; 57.22; 57.62; 104.94; 113.23; 115.41; 116.60; 120.37; 120.70; 124.52; 124.67; 127.61; 130.03; 130.14; 131.66; 136.54; 137.89; 139.90; 142.69; 143.04; 151.47.

MS (FD, 8 kV): m/z (%) calcd for 517.80; found: 516.7 (100) $[M]^+$

Elemental analysis calcd (%) for $C_{38}H_{47}N$: C, 88.15; H, 9.15; N, 2.71; found: C, 87.90; H, 9.70; N, 2.41.

Benzo[*kl*]benzo[6,7]azepino[3,2,1-*de*]acridine (*3c*):

Yield from 1,8-dibromonaphthalene 0.75 g (79%) and from 1,2-diiodonaphthalene 0.79 g (83%).

^{1}H-NMR (δ (ppm), CD_2Cl_2): 6.46-6.49 (m, 1H); 6.77 (d, 1H, $^3J_{HH}$ = 11.4 Hz); 6.86-6.93 (m, 2H); 7.03-7.18 (m, 5H); 7.28-7.33 (m, 1H); 7.43-7.52 (m, 2H); 7.69 (d, 1H, $^3J_{HH}$ = 8.1 Hz); 7.76-7.81 (m, 2H).

^{13}C-NMR (δ (ppm), CD_2Cl_2): 116.25; 116.55; 121.17; 125.03; 125.31; 126.63; 127.24; 127.47; 127.47; 127.69; 128.58; 129.22; 129.84; 130.31; 130.74; 131.71; 132.33; 133.60; 134.97; 135.55; 143.89; 147.26; 153.12.

MS (FD, 8 kV): m/z (%) calcd for 317.39; found: 317.8 (100) $[M]^+$

Elemental analysis calcd (%) for $C_{24}H_{15}N$: C, 90.82; H, 4.76; N, 4.41; found: C, 90.75; H, 4.66; N, 4.28.

Benzo[4,5]quinolino[3,2,1-*kl*]phenothiazine (*3d*):

Yield from 1,8-dibromonaphthalene 0.82 g (85%) and from 1,2-diiodonaphthalene 0.86 g (89%).

^{1}H-NMR (δ (ppm), CD_2Cl_2): 7.06-7.18 (m, 4H); 7.27-7.52 (m, 6H); 7.61-7.72 (m, 3H).

^{13}C-NMR (δ (ppm), CD_2Cl_2): 113.94; 116.54; 118.61; 121.28; 122.49; 124.93; 125.07; 125.39; 125.53; 126.56; 126.89; 127.37; 127.64; 127.96; 128.09; 129.23; 129.30; 135.72; 138.25; 141.07; 144.50.

MS (FD, 8 kV): m/z (%) calcd for 323.41; found: 323.7 (100) $[M]^+$

Elemental analysis calcd (%) for $C_{22}H_{13}NS$: C, 81.70; H, 4.05; N, 4.33; S, 9.91, found: C, 81.72; H, 4.00; N, 4.03; S, 10.69.

Benzo[4,5]quinolino[3,2,1-*kl*]phenoxazine (*3e*):

Yield from 1,8-dibromonaphthalene 0.71 g (77%) and from 1,2-diiodonaphthalene 0.75 g (81%).

^{1}H-NMR (δ (ppm), CD_2Cl_2): 6.84 (dd, $^{3}J_{HH}$ = 7.9, $^{4}J_{HH}$ = 1.2 Hz, 1H), 6.91-7.06 (m, 4H), 7.25-7.36 (m, 2H), 7.37-7.48 (m, 3H), 6.91-7.06 (m, 4H), 7.57 (d, $^{3}J_{HH}$ = 14.2 Hz, $^{4}J_{HH}$ = 0.7 Hz 1H), 7.60 (dd, $^{3}J_{HH}$ = 14.1, $^{4}J_{HH}$ = 0.7 Hz, 1H) (d, $^{3}J_{HH}$ = 7.1 Hz, 1H).

^{13}C-NMR (δ (ppm), CD_2Cl_2): 109.64, 114.69, 115.75, 115.81, 118.04, 118.54, 120.04, 123.96, 124.00, 124.35, 125.17, 126.19, 126.65, 126.75, 127.58, 129.08, 130.71, 131.83, 135.51, 136.09, 147.20, 149.04.

MS (FD, 8 kV): m/z (%) calcd for 307.35; found: 307.7 (100) $[M]^+$

Elemental analysis calcd (%) for $C_{22}H_{13}NO$: C, 85.97; H, 4.26; N, 4.56; found: C, 85.74; H, 4.24; N, 4.54.

Optical and Electrochemical Properties

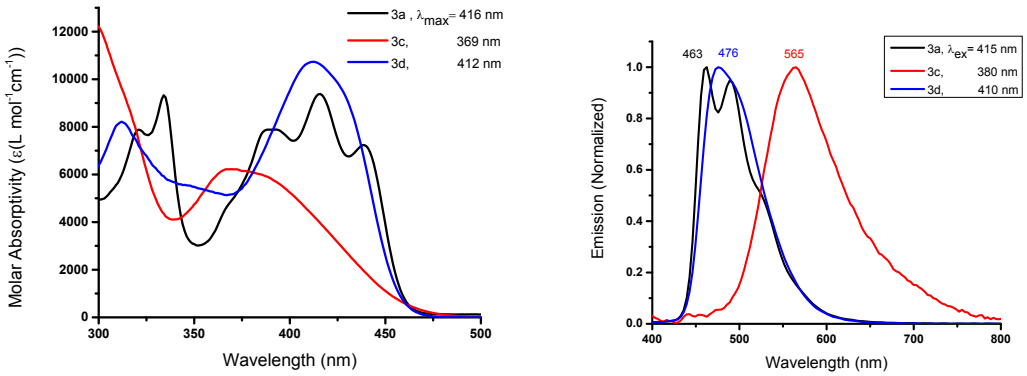


Figure S1. Absorption (left) and emission (right) spectra of compounds 3a, 3c and 3d

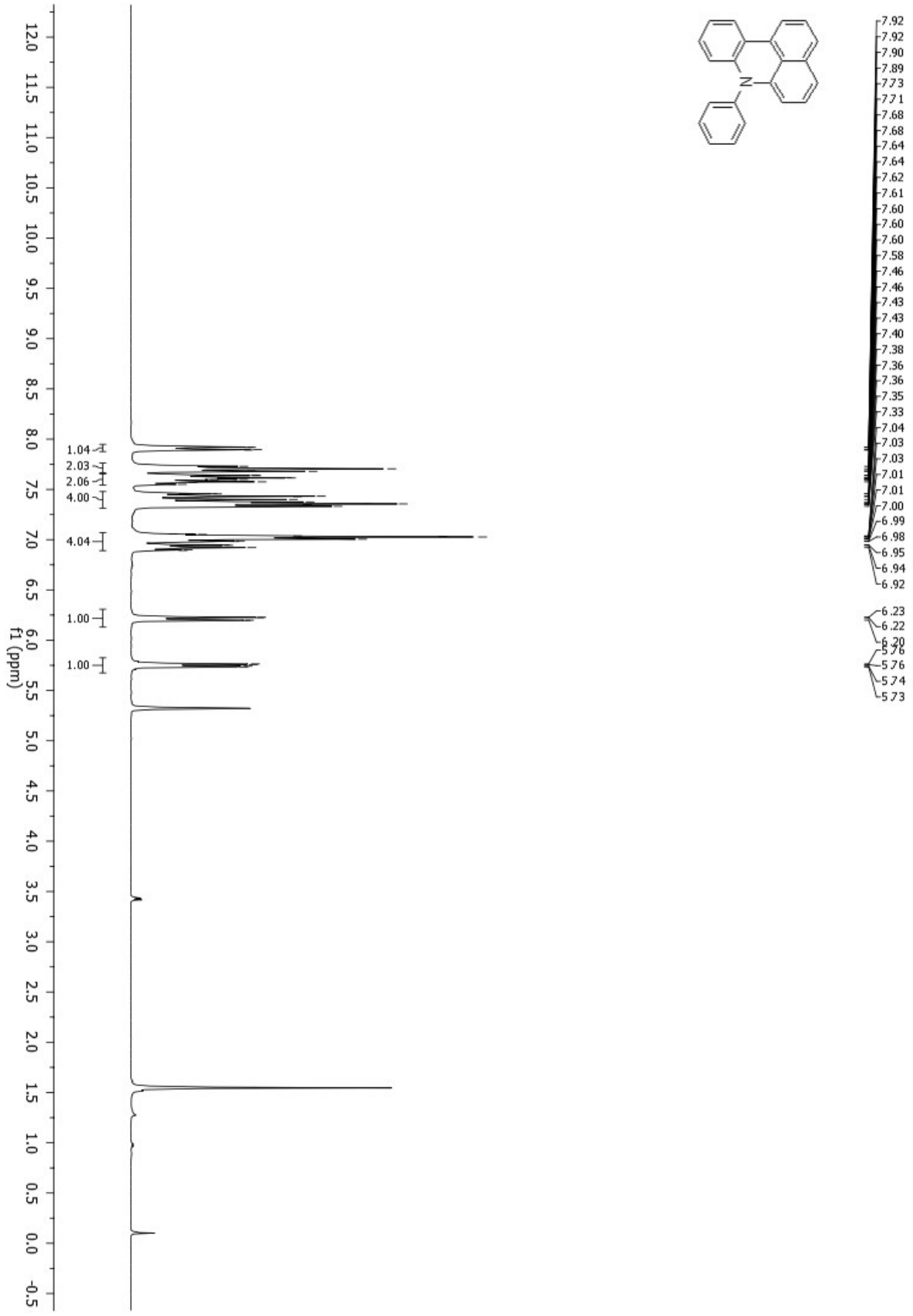
Table S1. Summary of final products' (3a, 3c and 3d) optical and electrochemical properties.

Compound	ε_0[a]	λ_{max}	$\lambda_{max,PL}$	E_{ox}[b]	HOMO[c]	LUMO[d]	HOMO[d]
	(L mol^{-1}cm^{-1})	(nm)	(nm)	(V)	(eV)	(eV)	(eV)
3a	9400	416	463	0.156	-4.96	-1.75	-5.00
3c	6200	369	565	0.340	-5.14	-2.00	-5.21
3d	10700	412	476	0.324	-5.12	-2.00	-5.18

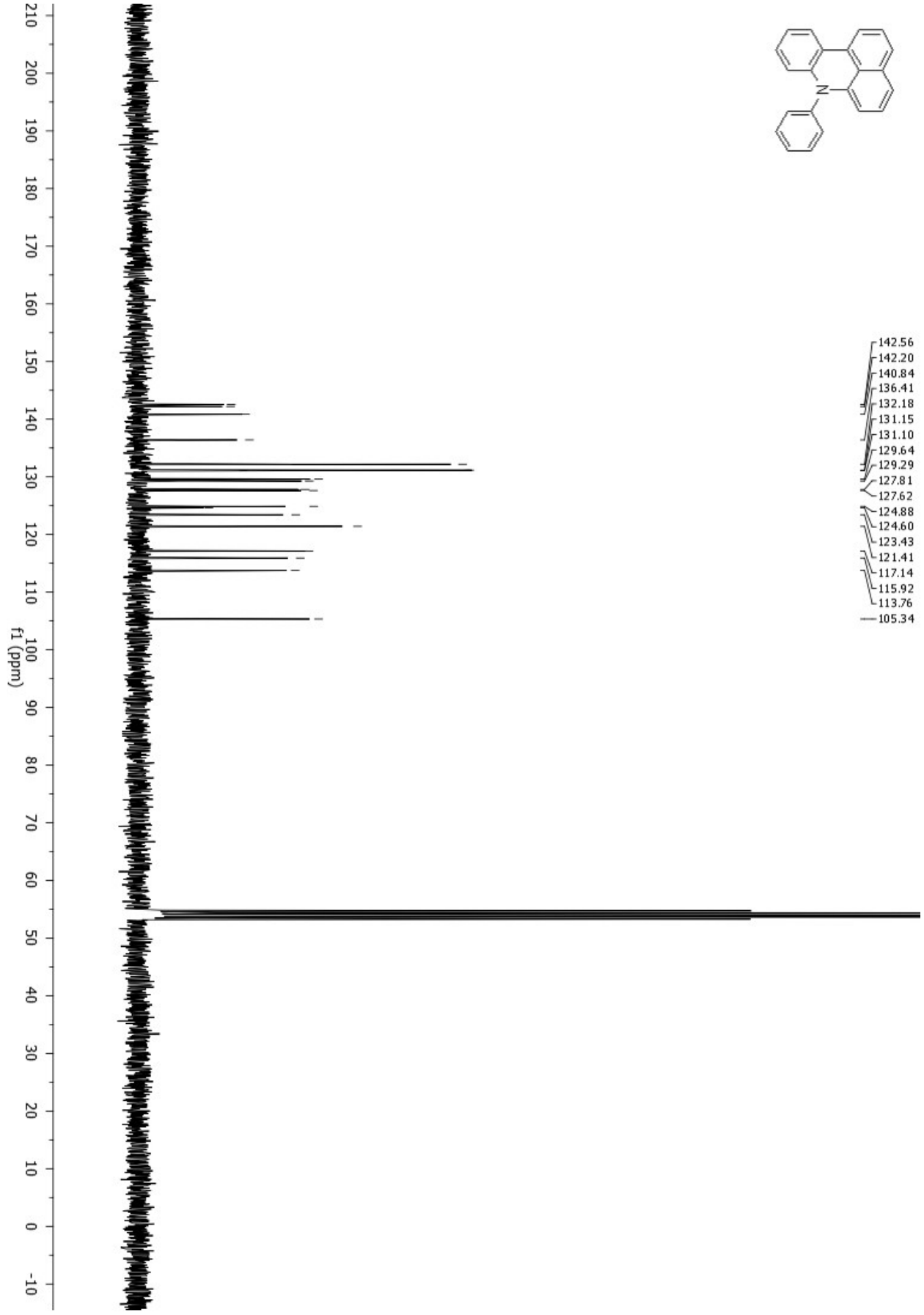
[a]Measured at λ_{max} in CH_2Cl_2 at rt; [b]Onset potentials, determined by cyclic voltammetric measurements in 0.1 M solution of Bu_4NPF_6 in CH_2Cl_2 *vs* Fc^+/Fc; [c]Estimated vs. vacuum level from E_{HOMO} = -4.80 eV - E_{ox1}; [d]the measurements of the HOMO/LUMO values are done: Gaussian 09, function: DFT B3LYP 6-311+G**

^{1}H NMR and ^{13}C NMR Spectra

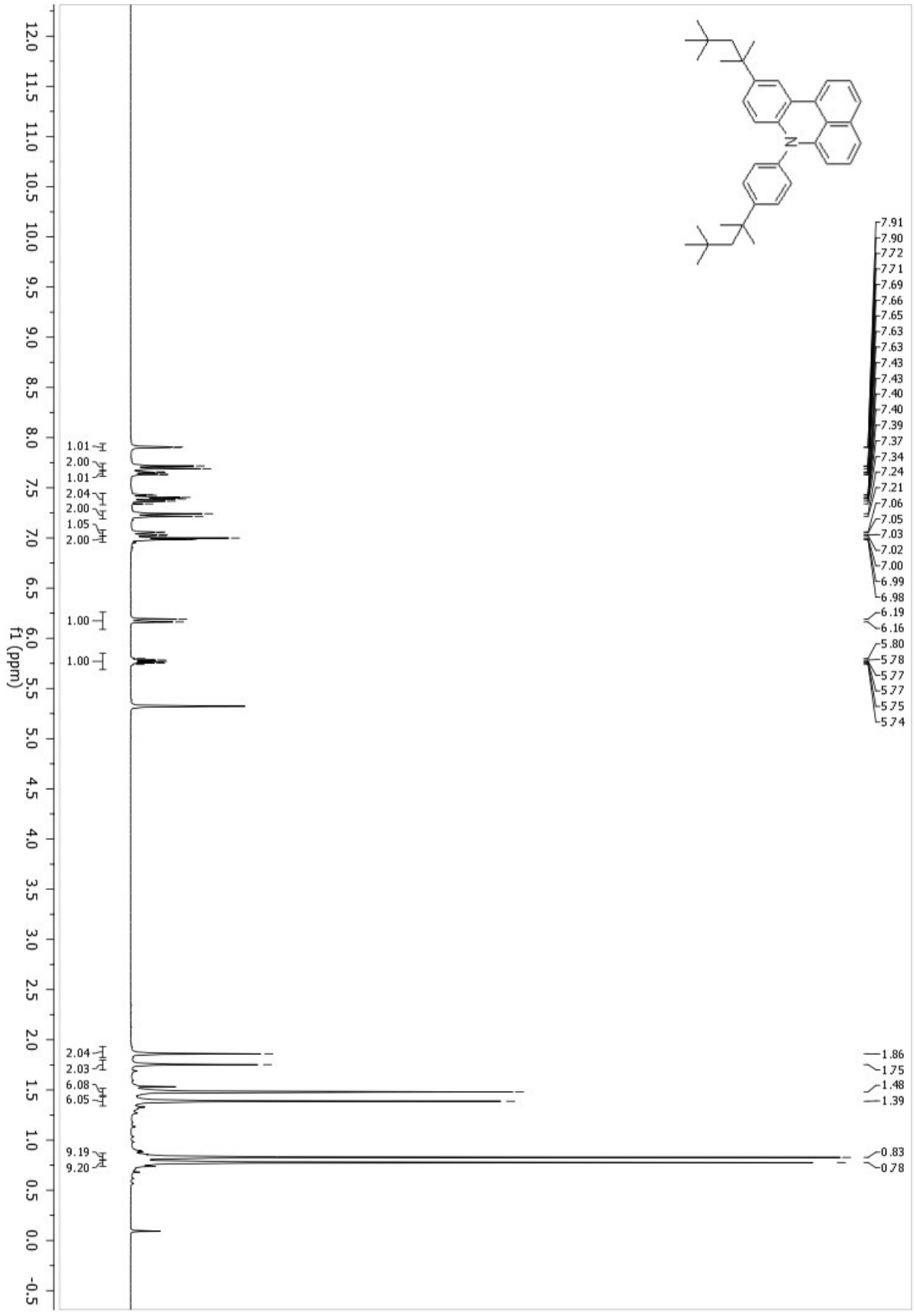
^{1}H-NMR spectrum of compound **3a** in CD_2Cl_2



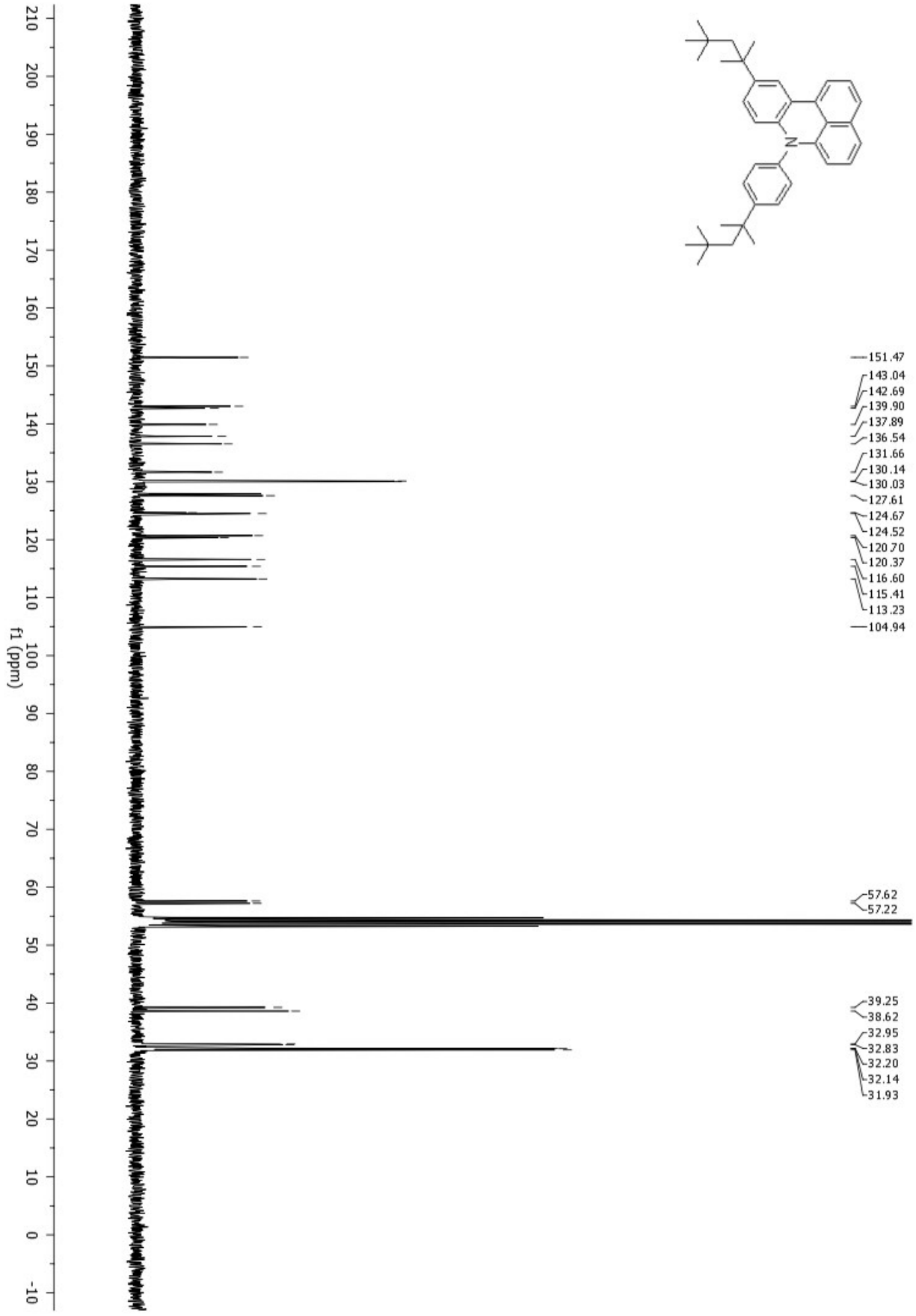
^{13}C-NMR spectrum of compound **3a** in CD_2Cl_2



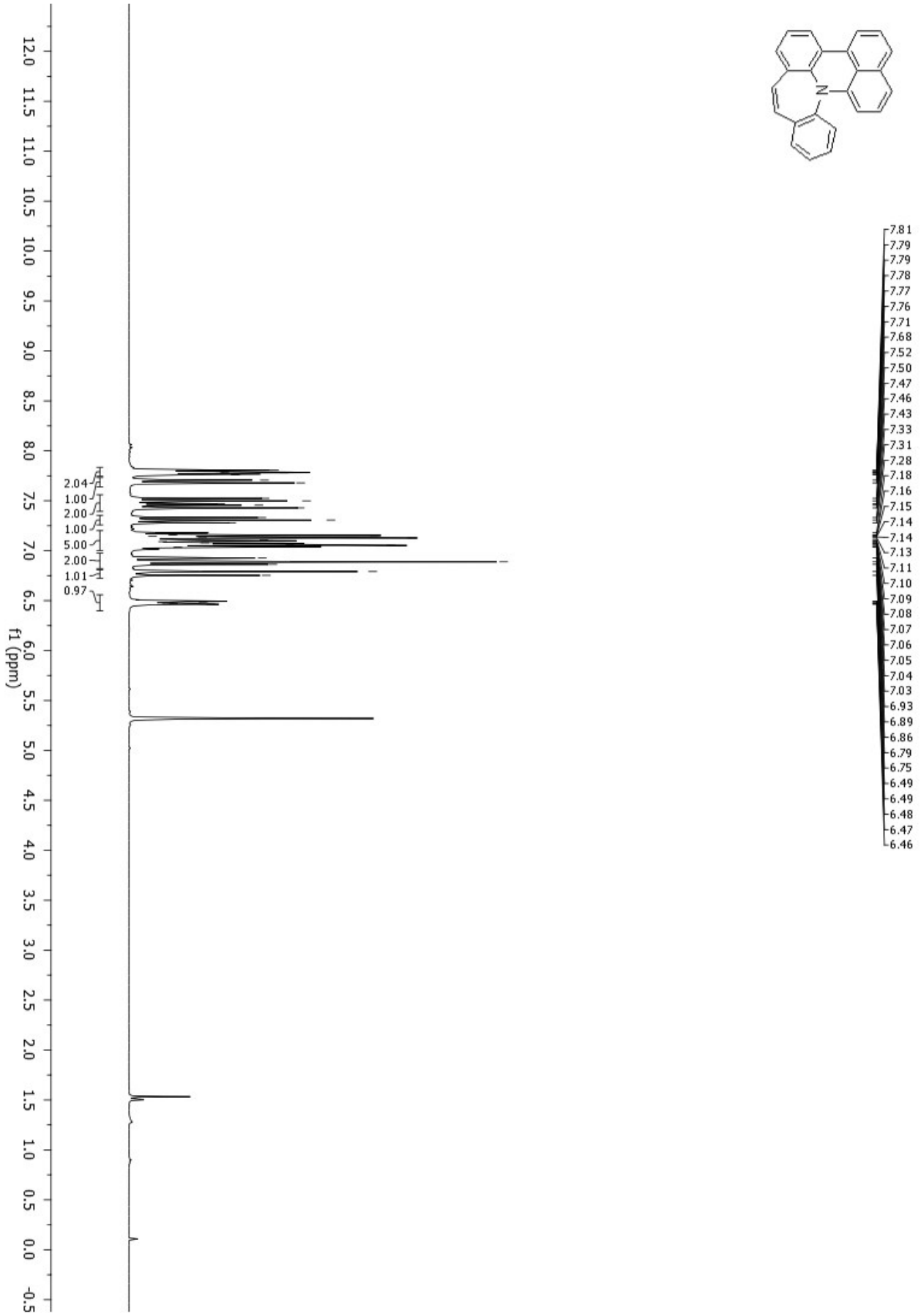
^{1}H-NMR spectrum of compound **3b** in CD_2Cl_2



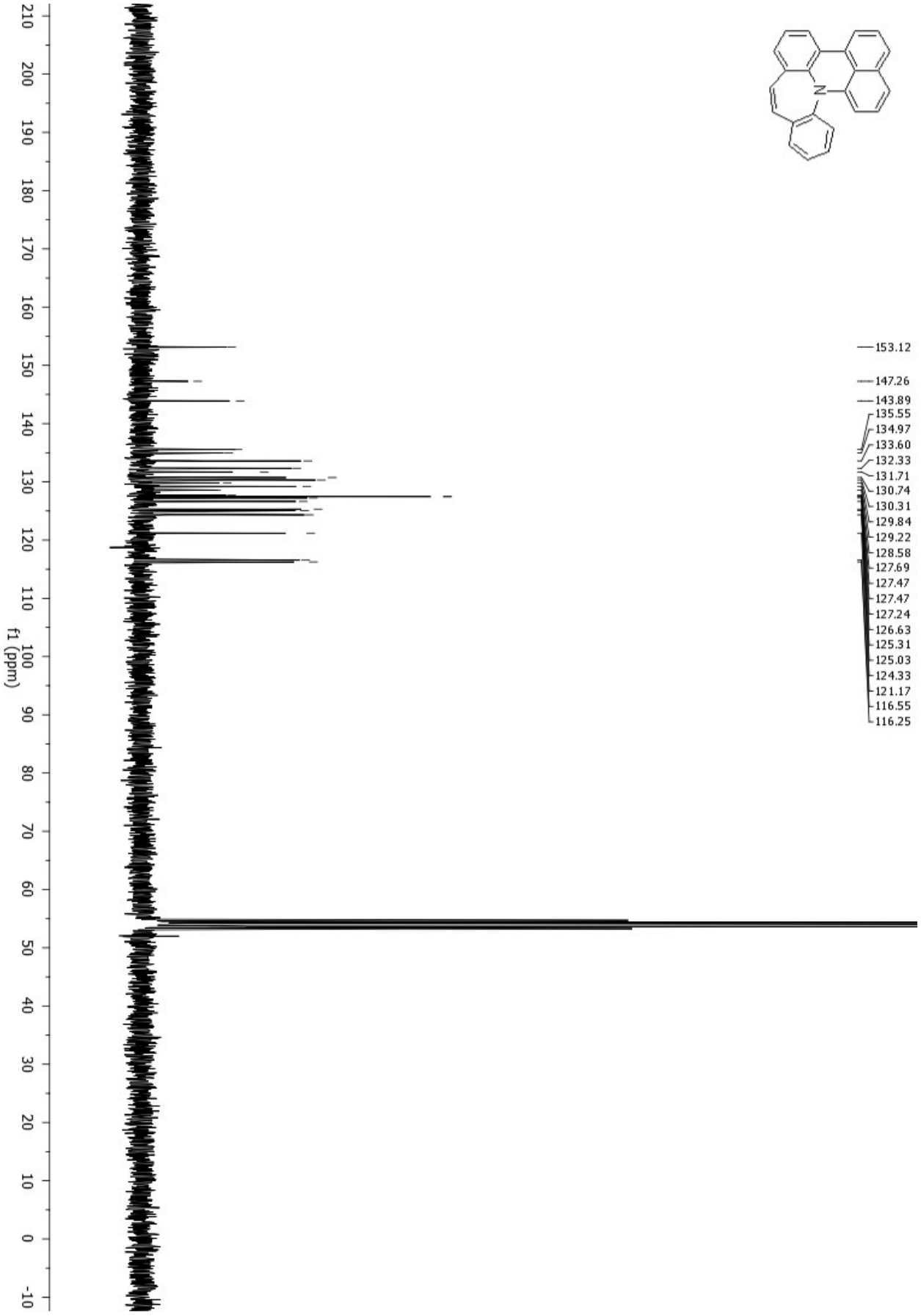
^{13}C-NMR spectrum of compound **3b** in CD_2Cl_2



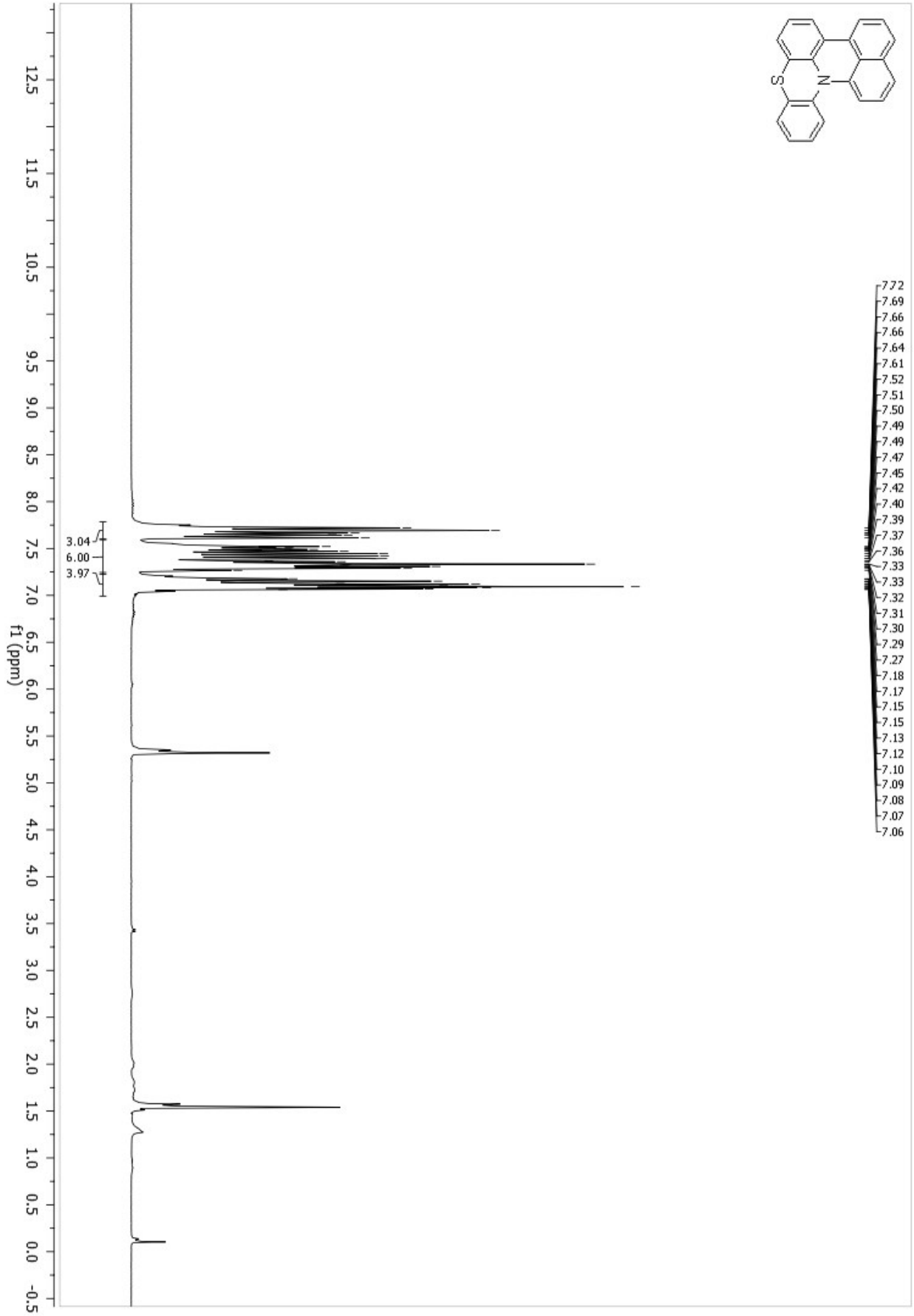
^{1}H-NMR spectrum of compound **3c** in CD_2Cl_2



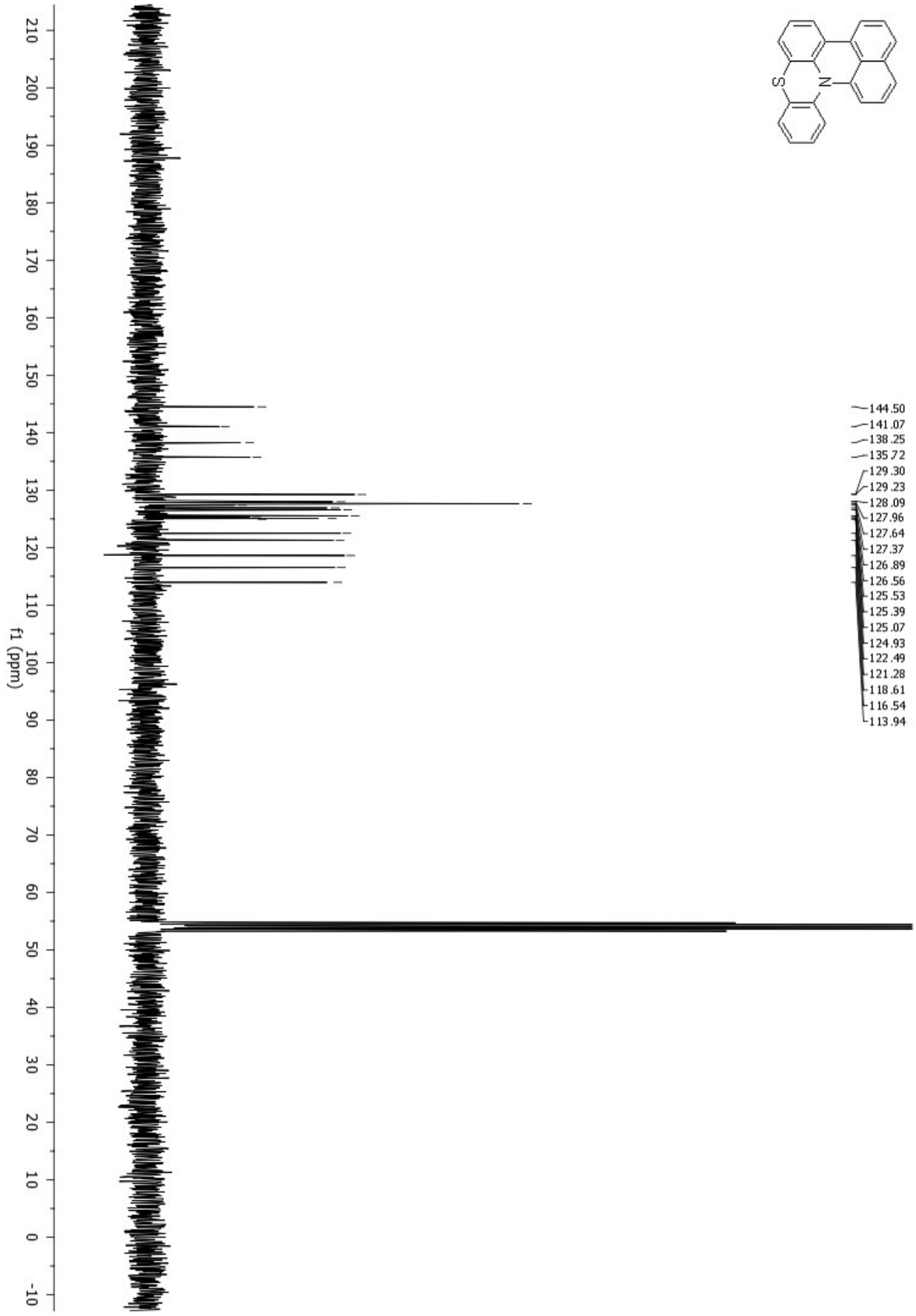
^{13}C-NMR spectrum of compound **3c** in CD_2Cl_2



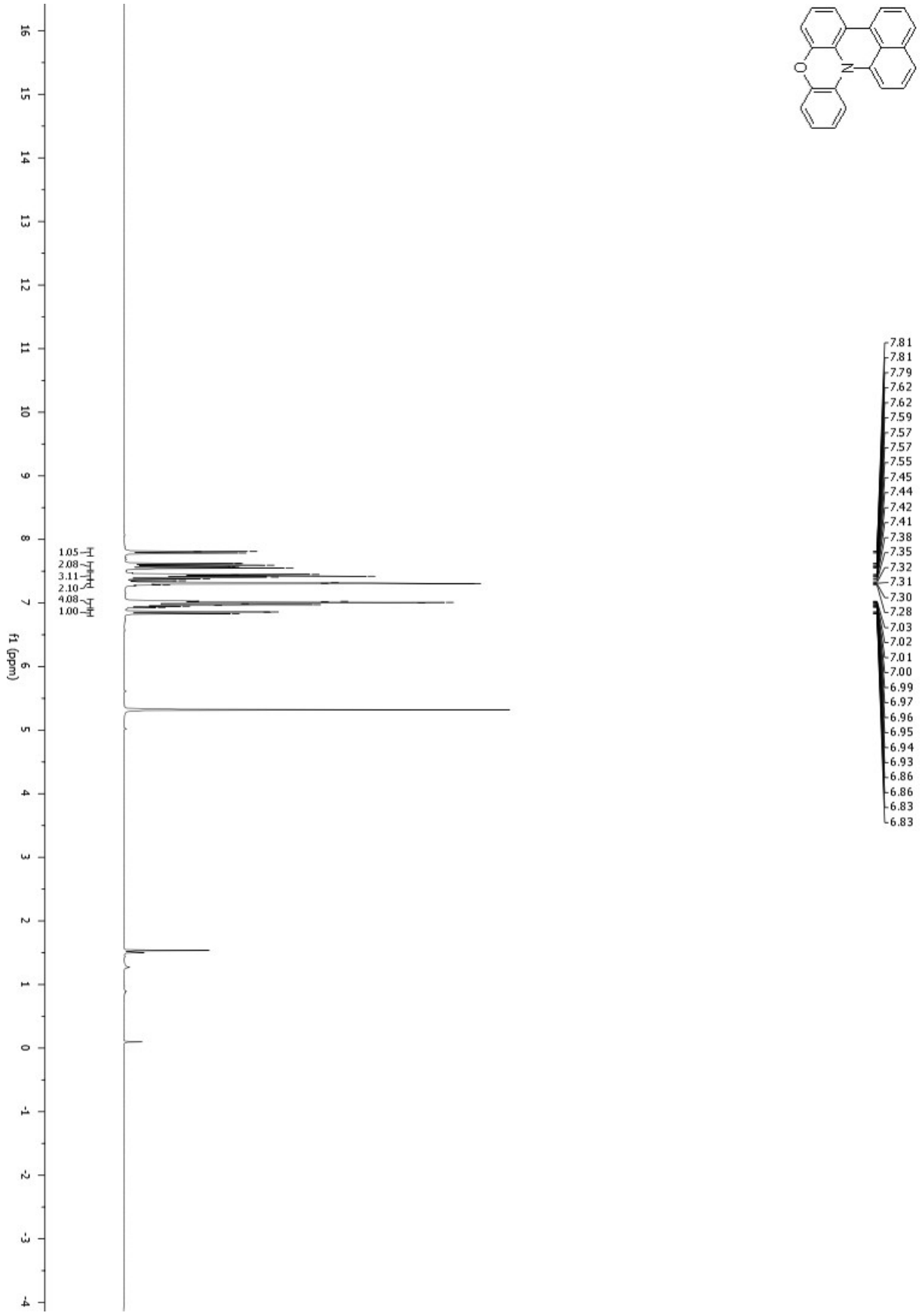
^{1}H-NMR spectrum of compound **3d** in CD_2Cl_2



^{13}C-NMR spectrum of compound **3d** in CD_2Cl_2



[1]H-NMR spectrum of compound **3e** in CD_2Cl_2



^{13}C-NMR spectrum of compound **3e** in CD_2Cl_2