

Supporting Information

Luminescent Organoboron Ladder Compounds via Directed Electrophilic Aromatic C-H Borylation

Mayyadah Yusuf,^a Kanglei Liu,^a Fang Guo,^a Roger A. Lalancette,^a and Frieder Jäkle^{a}*

^aDepartment of Chemistry, Rutgers University-Newark, 73 Warren Street, Newark, NJ 07102,
USA.

* E-mail: fjaekle@rutgers.edu

Synthesis of Precursors

Synthesis of 2,7-Dibromo-9,9-dihexylfluorene.¹ Under N₂ atmosphere, to a solution of 2,7-dibromo-9H-fluorene (12.86 g, 39.70 mmol) in THF (100 mL) was added 1-bromohexane (24.9 g, 150.9 mmol, 3.8 equiv) via syringe. The reaction mixture was kept stirring for 10 min at room temperature and then placed in an ice bath (0 °C). A solution of potassium *tert*-butoxide (10.24 g, 91.3 mmol, 2.3 equiv) in THF (240 mL) was then added. The resulting solution was stirred for 3 hours and the temperature was slowly raised to 25 °C. After overnight stirring, 400 mL of saturated NH₄Cl were added and the mixture was extracted with hexanes (4 × 60 mL). The combined organic layers were dried over magnesium sulfate and concentrated. The residue was taken back up in hot ethanol and crystallization occurred at room temperature to give light brown crystals. Yield: 14.4 g (74%). ¹H-NMR (499.9 MHz, CDCl₃, 25 °C): δ = 7.52 (d, J = 8.5 Hz, 2H; Fl), 7.47 (d, J = 2.0 Hz, 2H; Fl), 7.45 (s, 2H; Fl), 1.92 (m, 4H; hexyl), 1.14 (m, 4H; hexyl), 1.06 (m, 8H; hexyl), 0.79 (t, J = 7.5 Hz, 6H; hexyl), 0.60 (m, 4H; hexyl). GC-MS: m/z 492 ([M]⁺, 100%).

Synthesis of (9,9-Dihexylfluorene-2,7-diyl)diboronic acid.² To a pre-cooled (−78 °C) solution of 2,7-dibromo-9,9-dihexylfluorene (6.94 g, 14.1 mmol) in THF (200 mL) was added n-butyl lithium (1.60 M in hexanes, 19.5 mL, 31.0 mmol, 2.2 equiv) dropwise and the mixture was stirred for 4 hours. A solution of B(*i*PrO)₃ (10.0 mL, 33.9 mmol, 2.4 equiv) was then added and the mixture was allowed to warm up and stirred overnight at 25 °C. After the addition of 150 mL of distilled water, the mixture was stirred for half an hour and a diluted HCl solution (60 mL, 0.1 M) was then added dropwise via syringe until a pH=4 was reached. The acidity of the solution was tested by pH indicator. The mixture was extracted with diethyl ether (3 × 100 mL). The combined organic layers were dried over magnesium sulfate and concentrated. The residue was dissolved in acetone and a diluted HCl solution was added (0.34 M, 46 mL) to form a beige powder. To further purify the product, the crude product was dissolved in acetone and precipitated by addition of hexanes (1:3 ratio) to give a white precipitate that was dried at high vacuum. Yield: 3.23 g (54%). ¹H-NMR (400 MHz, acetone-d₆, 25 °C): δ = 8.00 (s, 2H; Fl), 8.90 (d, J = 7.5 Hz, 2H; Fl), 7.81 (d, J = 7.5 Hz, 2H; Fl), 7.15 (s, 4H; OH), 2.07 (m, 4H; hexyl), 1.05 (m, 12; hexyl), 0.75 (t, 6H; hexyl), 0.61 (m, 4H; hexyl).

Synthesis of 2,7-Bis(trimethylstannyl)-9,9-dihexylfluorene.³ To a pre-cooled (−78 °C) solution of 2,7-dibromo-9,9-dihexylfluorene (7.32 g, 14.9 mmol) in THF (230 mL) was added n-butyl lithium (1.60 M in hexanes, 20.5 mL, 32.7 mmol, 2.2 equiv) dropwise and the mixture was stirred for 4 hours. A solution of Me₃SnCl (6.92 g, 35.7 mmol, 2.4 equiv) in THF (10 mL) was then added and the mixture was allowed to warm up and stirred overnight at room temperature. The mixture was extracted with sodium bicarbonate and diethyl ether (3 × 100 mL). The combined organic layers were washed with distilled water, dried over sodium sulfate and concentrated. The residue was taken up in hot ethanol forming beige crystals at room temperature. Yield: 5.31 g (54%). ¹H-NMR (499.9 MHz, CDCl₃, 25 °C): δ = 7.67 (d, J = 8.0 Hz, 2H; Fl), 7.44 (d, J = 7.5 Hz, 2H; Fl), 7.42 (s, 2H; Fl), 1.96 (m, 4H; hexyl), 1.11 (m, 4H; hexyl), 1.10 (m, 8H; hexyl), 0.78 (t, J = 7.0 Hz, 6H; hexyl), 0.67 (m, 4H; hexyl), 0.32 (s, 18H; Sn-Me).

Synthesis of Bis(pivaloyloxy)zinc. To a pre-cooled (0 °C) solution of pivalic acid (30.1 g, 0.295 mol, 2 equiv) in THF (150 mL) was added a solution of diethyl zinc (18.0 g, 0.146 mol, 1 equiv) in THF (150 mL) dropwise over a period of 60 min (gas formation and precipitation of the product were observed). After stirring at room temperature overnight, the solvent was removed under reduced pressure and Zn(OPiv)₂ was obtained as a white solid that was stored inside a glove box. Yield: 36.9 g (95%). ¹H-NMR (499.9 MHz, CDCl₃, 25 °C): δ = 1.2 (s, 18H; *t*-Bu).

Synthesis of 6-Methylpyridin-2-yl(pivaloyloxy)zinc.⁴ To a pre-cooled (−78 °C) solution of 2-bromo-6-methylpyridine (11.6 g, 0.0674 mol, 1 equiv) in dry THF (150 mL) was added n-butyl lithium (1.60 M in hexanes, 42.1 mL, 0.0674 mol, 1 equiv) dropwise and the mixture was allowed to stirred at −78 °C for another 30 min. Under a flow of N₂, Zn(OPiv)₂ (18.0 g, 0.0674 mol, 1 equiv) was added and the mixture was slowly warmed up to 25 °C. The solvent was removed under high vacuum to give (6-methylpyridin-2-yl)(pivaloyloxy)zinc as a beige solid. Yield: 17.7 g (49%). The content of active zinc species was determined by titrating 90 mg of the reagent with a stock solution of iodine (1.00 M in THF). A concentration of 1.67 mol/g was determined which corresponds to 69% of active species. ¹H-NMR (499.9 MHz, CDCl₃, 25 °C): δ = 7.58 (d, J = 6.0 Hz, 1H; Py), 7.34 (pst, J = 6.5 Hz, 1H; Py), 6.93 (d, J = 7.0 Hz, 1H; Py), 2.85 (s, 3H; Me), 1.08 (s, 9H; *t*-Bu).

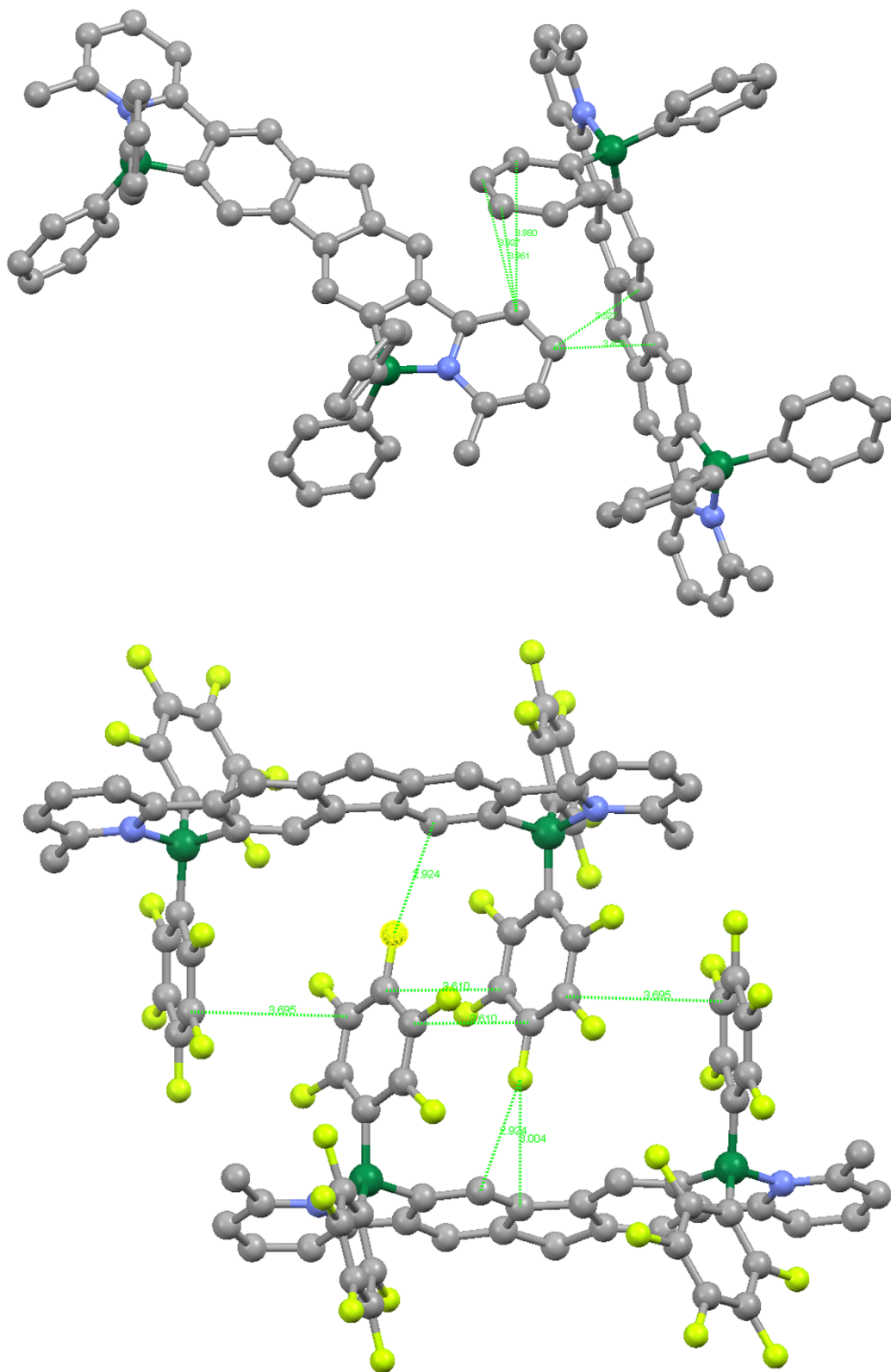


Figure S1. Illustration of CH- π , CF- π and π - π stacking interactions in the extended structures of 2-Ph (top) and 2-Pf (bottom). Hexyl groups are omitted for clarity.

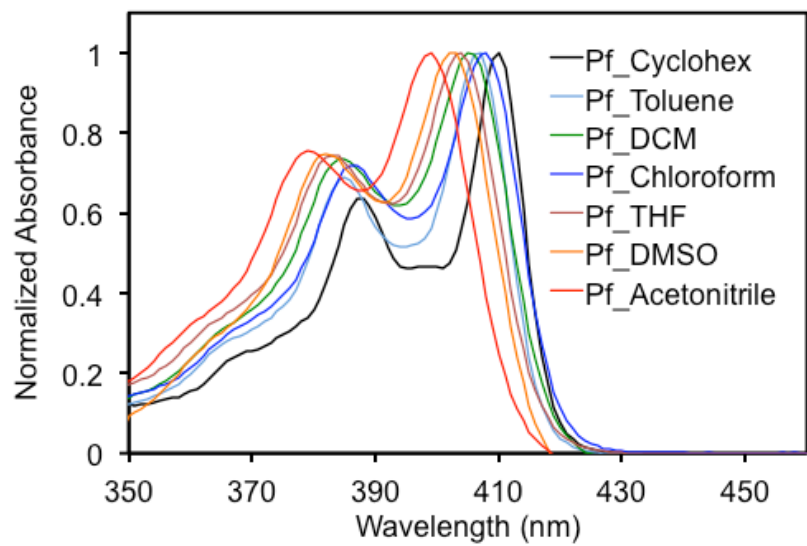


Figure S2a. UV-Vis spectra of **2-Pf** in different solvents.

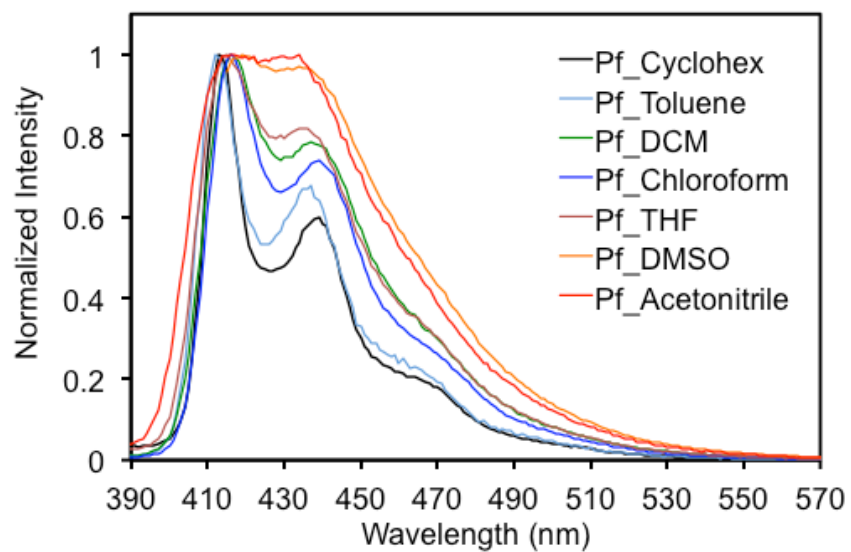


Figure S2b. Fluorescence spectra of **2-Pf** in different solvents.

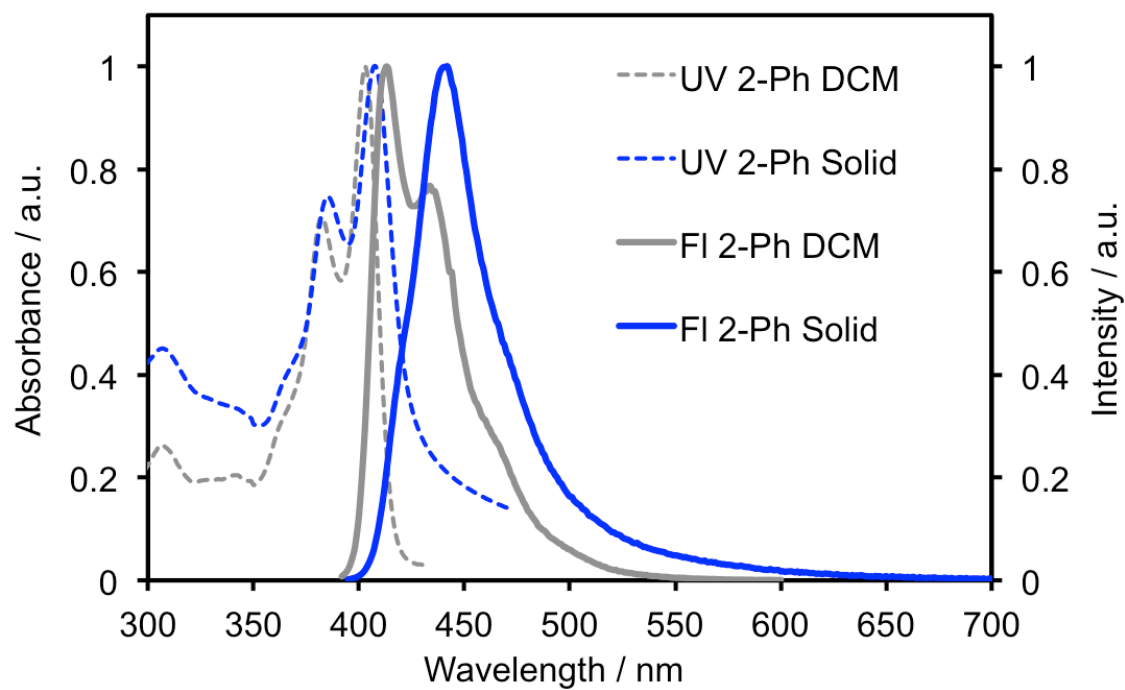


Figure S3a. Absorption and fluorescence spectra of **2-Ph** in DCM and in the solid state.

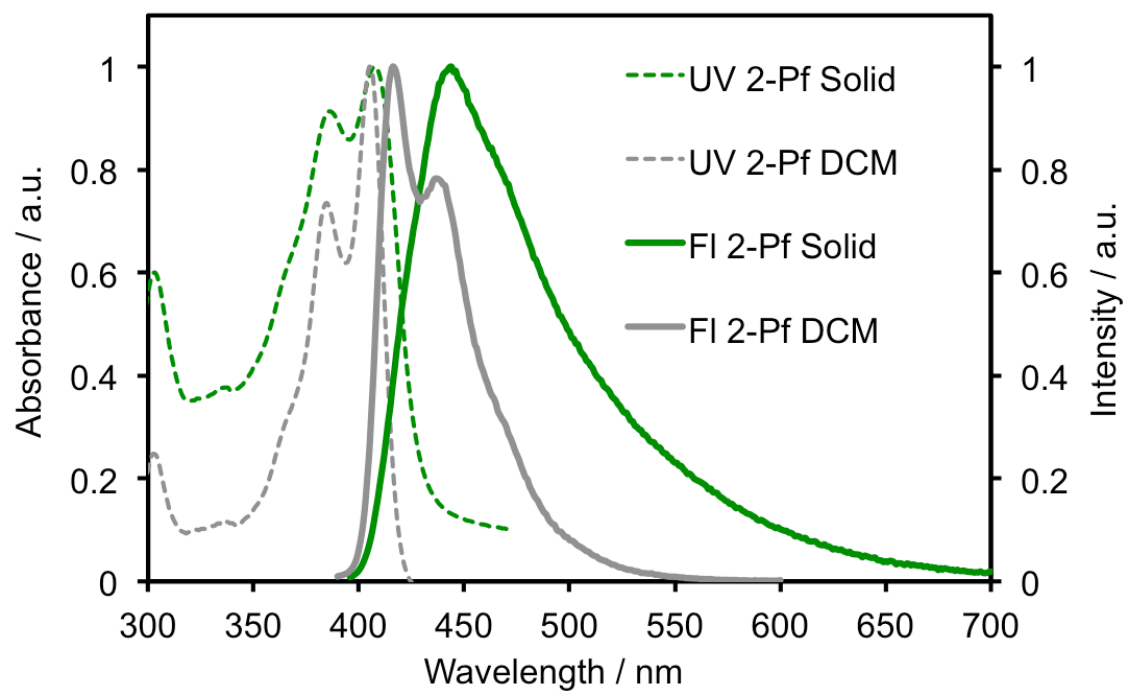


Figure S3b. Absorption and fluorescence spectra of **2-Pf** in DCM and in the solid state.

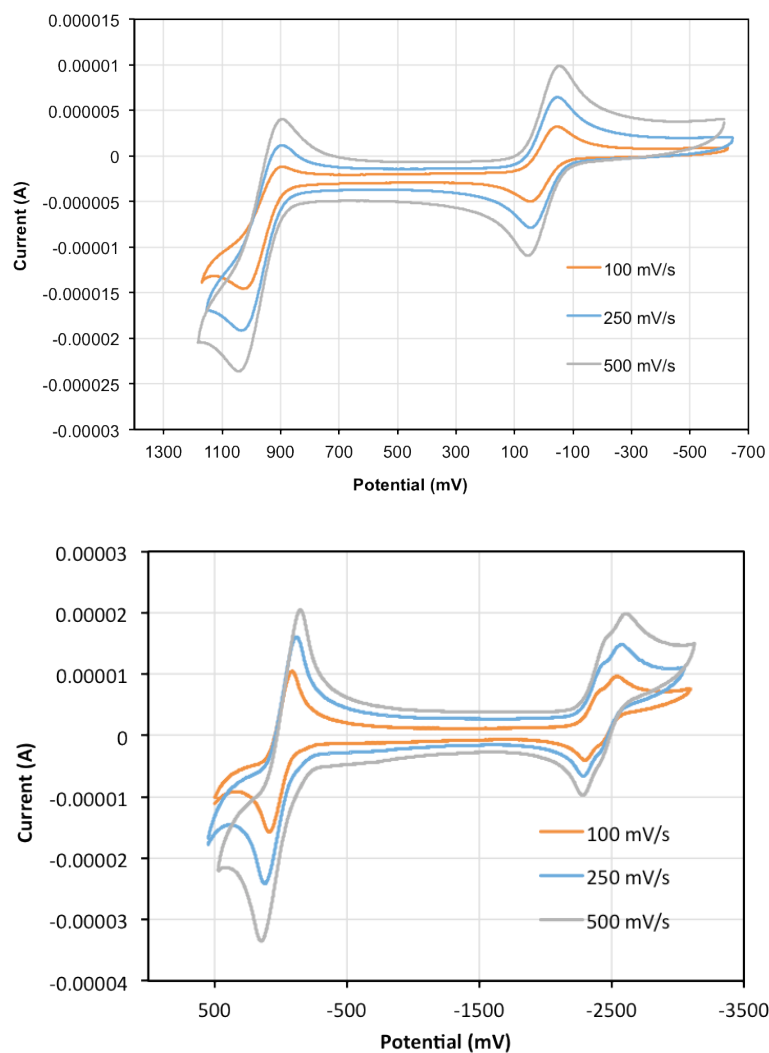


Figure S4a. Cyclic Voltammetry Data for **2-Ph** at Different Scan Rates (Reported vs $\text{Cp}_2\text{Fe}^{0/+}$). Oxidation in DCM, reduction in THF containing 0.1 M $\text{Bu}_4\text{N}[\text{PF}_6]$.

Table S1. Data from cyclic voltammetry experiments at different scan rates.

First Reduction Process for Compound 2-Ph

ν	$\nu^{1/2}$	I_{pa}	E_{pa}	E_{pc}	ΔE_p
100	10	-0.000003752	-2300	-2408	108
250	15.81	-5.5771E-06	-2288	-2442	154
500	22.36	-0.000007761	-2281	-2477	196

Oxidation Process for Compound 2-Ph

ν	$\nu^{1/2}$	I_{pa}	E_{pa}	E_{pc}	ΔE_p
100	10	-0.000011111	1025.5	896.5	129
250	15.81	-0.00001527	1033.5	895.5	138
500	22.36	-0.000018855	1043.25	894.25	149

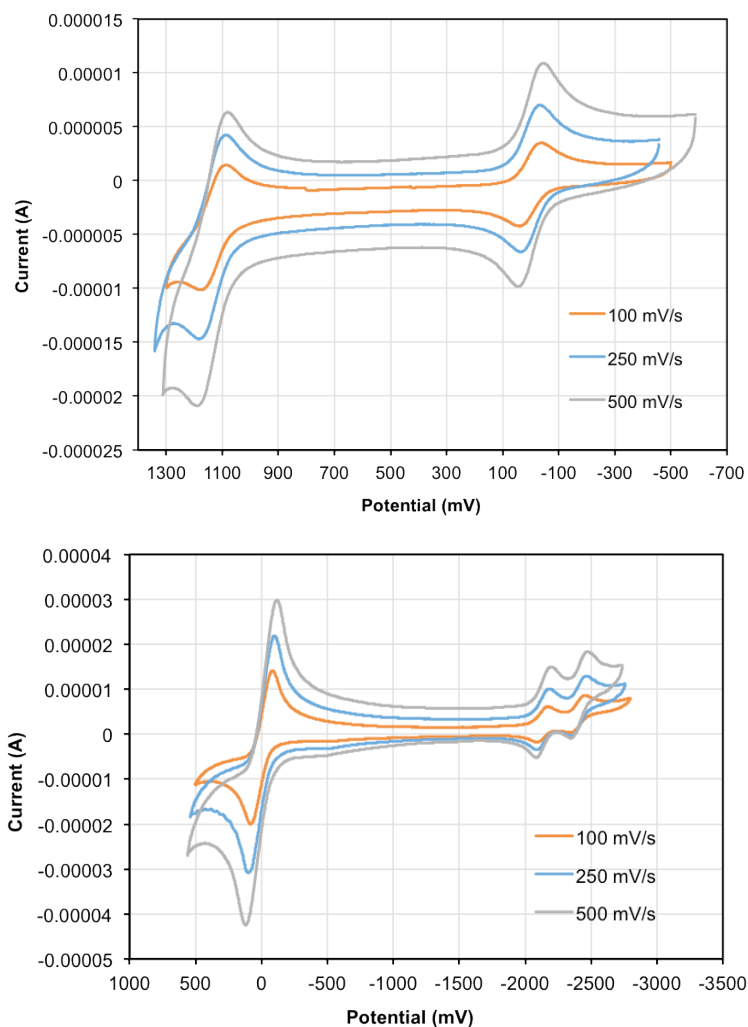


Figure S4b. Cyclic Voltammetry Data for **2-Pf** at Different Scan Rates (Reported vs $\text{Cp}_2\text{Fe}^{0/+}$). Oxidation in DCM, reduction in THF containing 0.1 M $\text{Bu}_4\text{N}[\text{PF}_6]$.

Table S2. Data from cyclic voltammetry experiments at different scan rates.

First Reduction Process for Compound 2-Pf

ν	$\nu^{1/2}$	I_{pa}	E_{pa}	E_{pc}	ΔE_p
100	10	-0.000001532	-2088.5	-2172.5	84
250	15.81	-2.8843E-06	-2088	-2188	100
500	22.36	-0.000004445	-2080	-2198	118

Oxidation Process for Compound 2-Pf

ν	$\nu^{1/2}$	I_{pa}	E_{pa}	E_{pc}	ΔE_p
100	10	-0.000006314	1175	1085	90
250	15.81	-0.000009367	1182.5	1086.5	96
500	22.36	-1.32854E-05	1187.75	1081.75	106

Table S3. Kohn-Sham Orbital Representations for **2-Ph'** and **2-Pf'** (B3LYP/6-31G(d), 75%)⁵

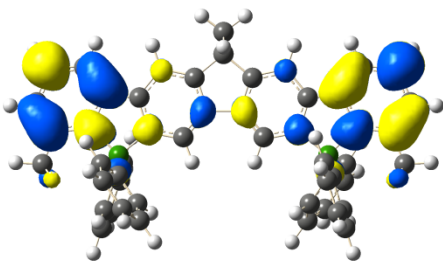
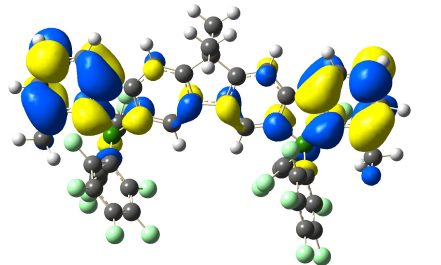
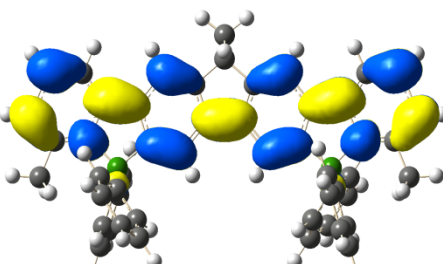
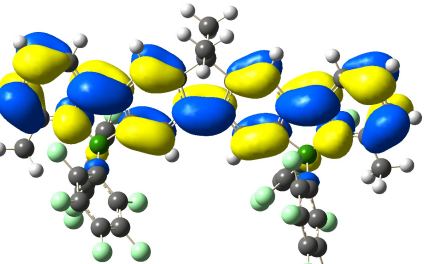
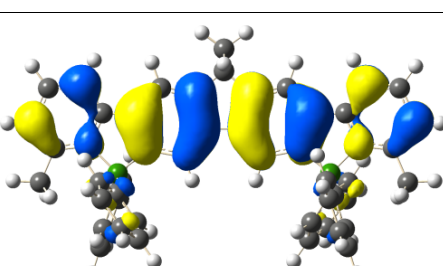
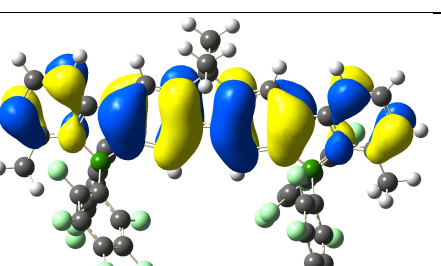
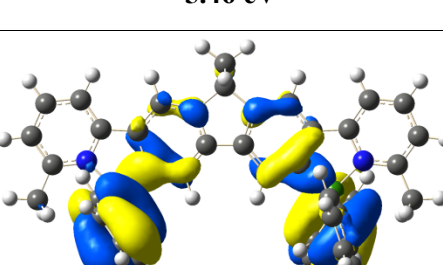
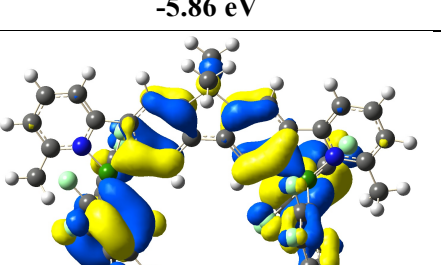
	2-Ph'	2-Pf'
LUMO+1	 -1.55 eV	 -1.99 eV
LUMO	 -1.99 eV	 -2.42 eV
HOMO	 -5.46 eV	 -5.86 eV
HOMO-1	 -5.76 eV	 -6.40 eV

Table S4. Results from TD-DFT Calculations (B3LYP/6-31G(d))⁵

Compound	Transition	Wavelength / nm (eV)	Oscillator Strength, <i>f</i>	Orbital Contributions
2-Ph'	S₀ → S₁	404.1 (3.068)	0.7849	HOMO → LUMO, 0.68582
	S ₀ → S ₂	383.4 (3.234)	0.0051	HOMO-2 → LUMO+1, -0.18121 HOMO-1 → LUMO, 0.66619 HOMO → LUMO+1, -0.11393
	S ₀ → S ₃	380.5 (3.259)	0.0631	HOMO-2 → LUMO, 0.66675 HOMO-1 → LUMO+1, -0.17637
2-Pf'	S₀ → S₁	404.9 (3.064)	0.9098	HOMO → LUMO, 0.69599
	S ₀ → S ₂	364.9 (3.398)	0.0004	HOMO-1 → LUMO, -0.12319 HOMO → LUMO+1, 0.68053
	S ₀ → S ₃	354.7 (3.495)	0.0192	HOMO-3 → LUMO, 0.14589 HOMO-2 → LUMO+1, -0.12645 HOMO-1 → LUMO, 0.65450 HOMO → LUMO+1, 0.14037

Table S5. Coordinated for Optimized Structure of **2-Ph'**

opt b3lyp/6-31g(d) geom=connectivity

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.179996	2.627318	-0.002804
2	6	0	2.534140	2.911409	-0.005586
3	6	0	3.431296	1.827650	-0.005677
4	6	0	3.008524	0.481393	-0.005561
5	6	0	1.636865	0.216699	-0.004387
6	6	0	0.732925	1.282429	-0.002002
7	6	0	-2.534132	2.911412	0.005592
8	6	0	-1.179988	2.627320	0.002813
9	6	0	-0.732919	1.282430	0.002011
10	6	0	-1.636860	0.216700	0.004395
11	6	0	-3.008519	0.481397	0.005567
12	6	0	-3.431289	1.827654	0.005682
13	6	0	-7.061274	2.908286	-0.035755
14	6	0	-5.681781	3.050452	-0.021321
15	6	0	-4.884490	1.902597	-0.000209
16	7	0	-5.450228	0.655106	0.009703
17	6	0	-6.796870	0.502720	-0.008211
18	6	0	-7.620102	1.630130	-0.029604
19	6	0	5.681788	3.050448	0.021304
20	6	0	7.061280	2.908283	0.035718
21	6	0	7.620109	1.630128	0.029560
22	6	0	6.796879	0.502717	0.008181
23	7	0	5.450235	0.655101	-0.009711
24	6	0	4.884498	1.902592	0.000204
25	6	0	-7.385266	-0.878016	-0.011558
26	6	0	7.385280	-0.878017	0.011509
27	6	0	0.000004	3.598726	0.000004
28	6	0	0.002749	4.485779	1.265178
29	6	0	-0.002739	4.485782	-1.265167
30	5	0	4.276569	-0.523235	-0.029739
31	5	0	-4.276564	-0.523230	0.029745
32	6	0	4.847958	-2.748776	1.357751
33	6	0	4.965573	-3.472643	2.548093
34	6	0	4.655493	-2.871005	3.767723
35	6	0	4.226360	-1.542289	3.781106
36	6	0	4.107469	-0.834171	2.584663
37	6	0	4.414984	-1.410220	1.336254
38	6	0	4.993034	-0.884500	-2.589270
39	6	0	4.911904	-1.553921	-3.813206
40	6	0	4.126895	-2.700263	-3.934531
41	6	0	3.424970	-3.161812	-2.819699
42	6	0	3.519320	-2.487006	-1.601433
43	6	0	4.310670	-1.331501	-1.442769
44	6	0	-3.519323	-2.486990	1.601457
45	6	0	-3.424982	-3.161788	2.819727
46	6	0	-4.126920	-2.700236	3.934550
47	6	0	-4.911933	-1.553898	3.813210
48	6	0	-4.993054	-0.884484	2.589269

49	6	0	-4.310676	-1.331488	1.442778	
50	6	0	-4.107410	-0.834191	-2.584650	
51	6	0	-4.226304	-1.542311	-3.781092	
52	6	0	-4.655499	-2.871007	-3.767711	
53	6	0	-4.965639	-3.472622	-2.548086	
54	6	0	-4.848020	-2.748753	-1.357745	
55	6	0	-4.414982	-1.410218	-1.336245	
56	1	0	2.889666	3.939966	-0.006880	
57	1	0	1.275303	-0.808792	-0.007507	
58	1	0	-2.889657	3.939969	0.006886	
59	1	0	-1.275299	-0.808791	0.007518	
60	1	0	-7.703251	3.784669	-0.052312	
61	1	0	-5.215639	4.029159	-0.027109	
62	1	0	-8.695683	1.492944	-0.041409	
63	1	0	5.215644	4.029154	0.027094	
64	1	0	7.703257	3.784666	0.052264	
65	1	0	8.695690	1.492943	0.041347	
66	1	0	-7.132675	-1.402959	-0.937873	
67	1	0	-6.987380	-1.475971	0.812992	
68	1	0	-8.472970	-0.822319	0.079922	
69	1	0	6.987401	-1.475959	-0.813053	
70	1	0	8.472983	-0.822314	-0.079965	
71	1	0	7.132686	-1.402976	0.937814	
72	1	0	0.003919	3.875416	2.173772	
73	1	0	0.888725	5.131509	1.284714	
74	1	0	-0.882694	5.132099	1.288049	
75	1	0	0.882705	5.132101	-1.288036	
76	1	0	-0.003909	3.875421	-2.173762	
77	1	0	-0.888714	5.131513	-1.284702	
78	1	0	5.097997	-3.241448	0.421583	
79	1	0	5.299501	-4.507670	2.519873	
80	1	0	4.743397	-3.430339	4.696076	
81	1	0	3.976103	-1.060007	4.723572	
82	1	0	3.757674	0.195608	2.622319	
83	1	0	5.600949	0.017041	-2.537542	
84	1	0	5.459743	-1.174648	-4.673287	
85	1	0	4.059176	-3.224479	-4.884590	
86	1	0	2.802197	-4.050250	-2.897477	
87	1	0	2.962042	-2.870129	-0.749713	
88	1	0	-2.962034	-2.870116	0.749745	
89	1	0	-2.802206	-4.050223	2.897517	
90	1	0	-4.059207	-3.224446	4.884612	
91	1	0	-5.459781	-1.174622	4.673284	
92	1	0	-5.600973	0.017054	2.537530	
93	1	0	-3.757567	0.195573	-2.622305	
94	1	0	-3.976000	-1.060046	-4.723554	
95	1	0	-4.743405	-3.430342	-4.696063	
96	1	0	-5.299617	-4.507633	-2.519867	
97	1	0	-5.098110	-3.241406	-0.421580	

Sum of electronic and thermal Free Energies=				-2127.377345		
Total E (Thermal) 526.220 kcal/mol						
Low frequencies	-4.7400	-3.3006	-2.3451	-0.0048	-0.0025	0.0011
Low frequencies	11.8026	11.9883	25.5713			

Table S6. Coordinated for Optimized Structure of **2-Pf'**

opt b3lyp/6-31g(d) geom=connectivity

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.179077	-0.013882	3.342363
2	6	0	2.534129	-0.030767	3.626308
3	6	0	3.429295	-0.044430	2.543930
4	6	0	3.003504	-0.036385	1.198906
5	6	0	1.634494	-0.012990	0.930059
6	6	0	0.732472	-0.007668	1.999131
7	6	0	-2.534236	0.029734	3.626282
8	6	0	-1.179179	0.012952	3.342349
9	6	0	-0.732553	0.007171	1.999123
10	6	0	-1.634560	0.012827	0.930039
11	6	0	-3.003573	0.036129	1.198877
12	6	0	-3.429387	0.043729	2.543896
13	6	0	-7.058223	0.220279	3.611638
14	6	0	-5.680545	0.159613	3.760420
15	6	0	-4.880990	0.092815	2.617836
16	7	0	-5.446468	0.081465	1.370589
17	6	0	-6.790005	0.138728	1.209860
18	6	0	-7.613806	0.211043	2.332185
19	6	0	5.680430	-0.160650	3.760463
20	6	0	7.058115	-0.221187	3.611693
21	6	0	7.613726	-0.211472	2.332256
22	6	0	6.789944	-0.138837	1.209937
23	7	0	5.446399	-0.081750	1.370652
24	6	0	4.880896	-0.093525	2.617883
25	6	0	-7.379181	0.142331	-0.171672
26	6	0	7.379155	-0.141868	-0.171581
27	6	0	-0.000058	-0.000617	4.313992
28	6	0	-0.014252	-1.266467	5.200318
29	6	0	0.014122	1.264956	5.200715
30	5	0	4.288755	0.001108	0.215240
31	5	0	-4.288801	-0.001127	0.215181
32	6	0	4.849354	-1.315175	-2.086144
33	6	0	4.924543	-2.458343	-2.880234
34	6	0	4.595980	-3.694460	-2.334820
35	6	0	4.208551	-3.763475	-1.000772
36	6	0	4.146013	-2.594404	-0.246327
37	6	0	4.441139	-1.321046	-0.748595
38	9	0	5.234599	-0.167330	-2.686004
39	9	0	5.325233	-2.376452	-4.156717
40	9	0	4.668617	-4.804091	-3.077559
41	9	0	3.908471	-4.949083	-0.451624
42	9	0	3.792393	-2.747349	1.047519
43	6	0	5.013534	2.592967	-0.173392
44	6	0	4.879198	3.837502	-0.790377
45	6	0	3.968561	3.995291	-1.826793
46	6	0	3.206447	2.900991	-2.228117
47	6	0	3.376986	1.681894	-1.583065
48	6	0	4.287628	1.459912	-0.544089
49	9	0	5.918658	2.543360	0.835096

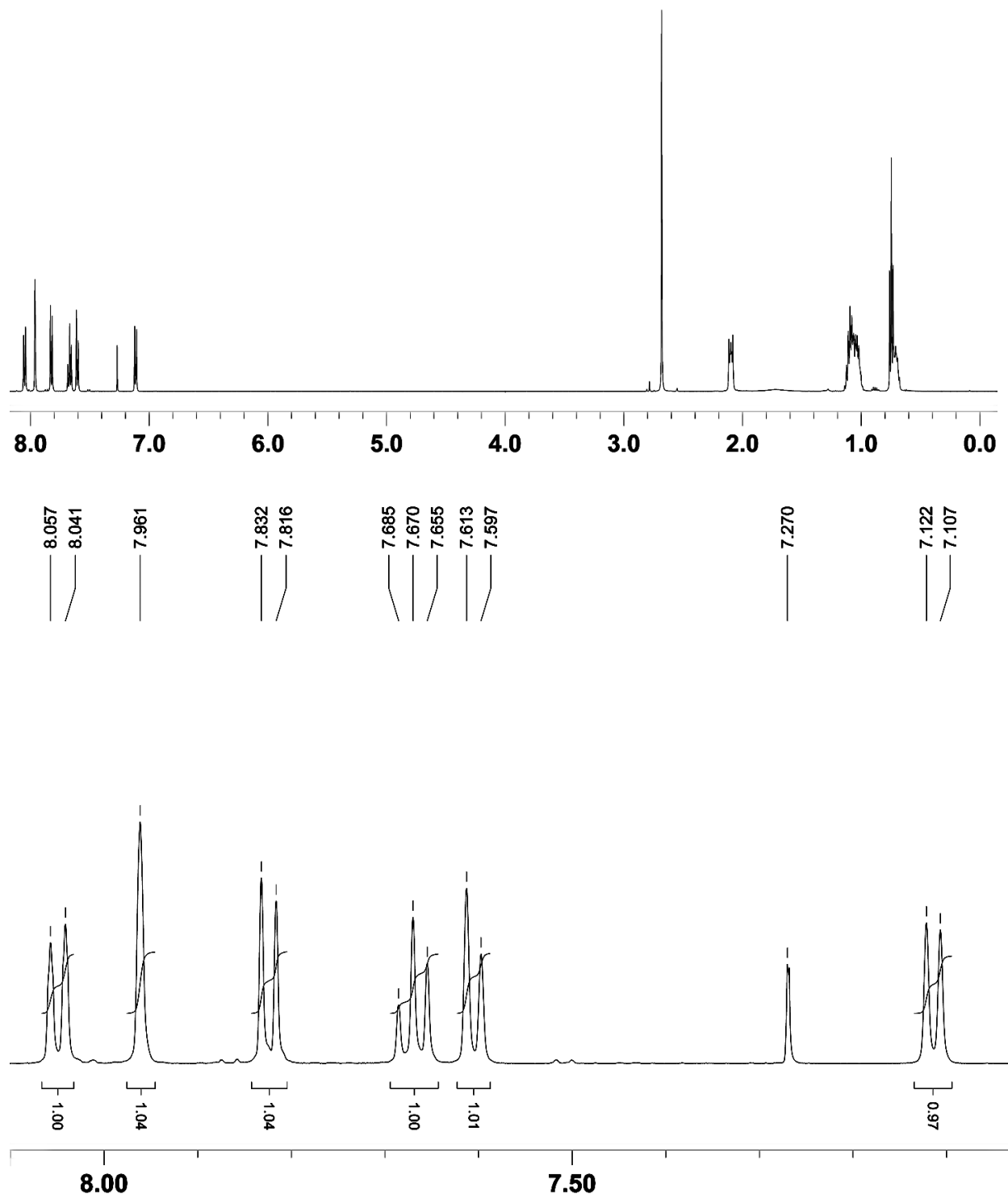
50	9	0	5.620536	4.879115	-0.384451
51	9	0	3.823406	5.180616	-2.429904
52	9	0	2.318167	3.033673	-3.221898
53	9	0	2.594996	0.664187	-2.012279
54	6	0	-3.376815	-1.681501	-1.583390
55	6	0	-3.206176	-2.900453	-2.228691
56	6	0	-3.968325	-3.994852	-1.827707
57	6	0	-4.879080	-3.837311	-0.791357
58	6	0	-5.013508	-2.592917	-0.174108
59	6	0	-4.287600	-1.459756	-0.544488
60	9	0	-2.594733	-0.663707	-2.012229
61	9	0	-2.317753	-3.032907	-3.222375
62	9	0	-3.823071	-5.180043	-2.431056
63	9	0	-5.620428	-4.879034	-0.385734
64	9	0	-5.918715	-2.543572	0.834317
65	6	0	-4.146293	2.594529	-0.245748
66	6	0	-4.208857	3.763767	-0.999933
67	6	0	-4.596066	3.695014	-2.334059
68	6	0	-4.924390	2.458983	-2.879810
69	6	0	-4.849188	1.315640	-2.085973
70	6	0	-4.441178	1.321249	-0.748359
71	9	0	-3.792914	2.747231	1.048192
72	9	0	-3.909017	4.949286	-0.450461
73	9	0	-4.668723	4.804808	-3.076552
74	9	0	-5.324866	2.377338	-4.156376
75	9	0	-5.234181	0.167883	-2.686163
76	1	0	2.890528	-0.034729	4.654133
77	1	0	1.274287	0.002081	-0.094170
78	1	0	-2.890649	0.033369	4.654103
79	1	0	-1.274343	-0.001930	-0.094192
80	1	0	-7.701996	0.273359	4.484971
81	1	0	-5.218213	0.166958	4.740609
82	1	0	-8.688167	0.252350	2.191809
83	1	0	5.218076	-0.168327	4.740640
84	1	0	7.701872	-0.274506	4.485023
85	1	0	8.688093	-0.252638	2.191890
86	1	0	-7.363590	1.155227	-0.590545
87	1	0	-6.830695	-0.501826	-0.859457
88	1	0	-8.419868	-0.189155	-0.131356
89	1	0	7.363707	-1.154616	-0.590817
90	1	0	6.830607	0.502469	-0.859149
91	1	0	8.419798	0.189738	-0.131118
92	1	0	-0.022941	-2.175288	4.590479
93	1	0	0.870339	-1.296383	5.847163
94	1	0	-0.900424	-1.277813	5.845619
95	1	0	0.900283	1.276096	5.846033
96	1	0	0.022823	2.173968	4.591161
97	1	0	-0.870481	1.294670	5.847553

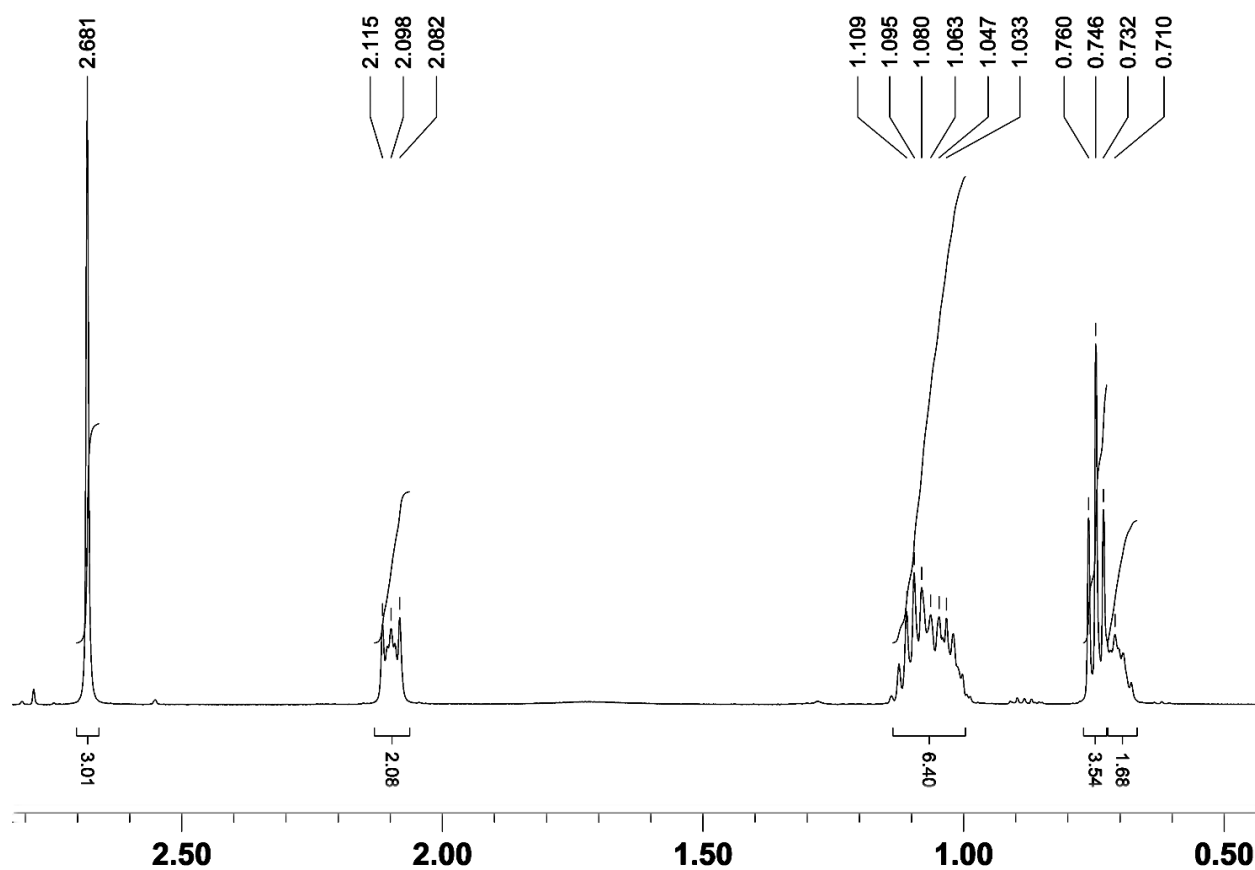
Sum of electronic and thermal Free Energies= -4112.131866
Total E (Thermal) 434.483 kcal/mol

Low frequencies -4.1737 -3.6394 -1.3814 -0.0078 -0.0076 -0.0059
Low frequencies 6.8013 8.7437 17.6894

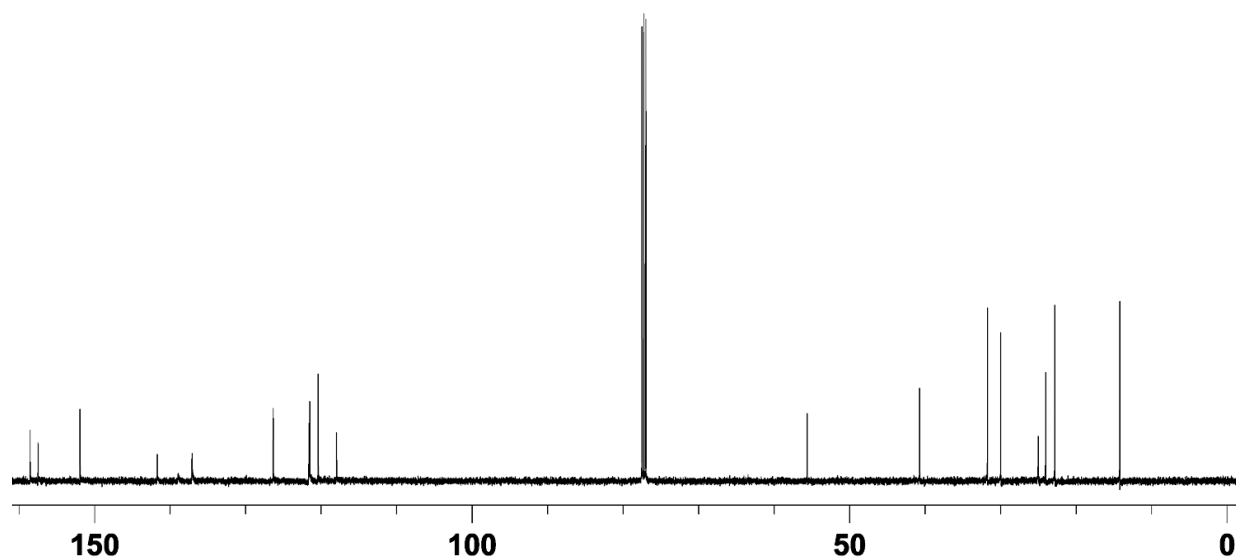
Spectral Data

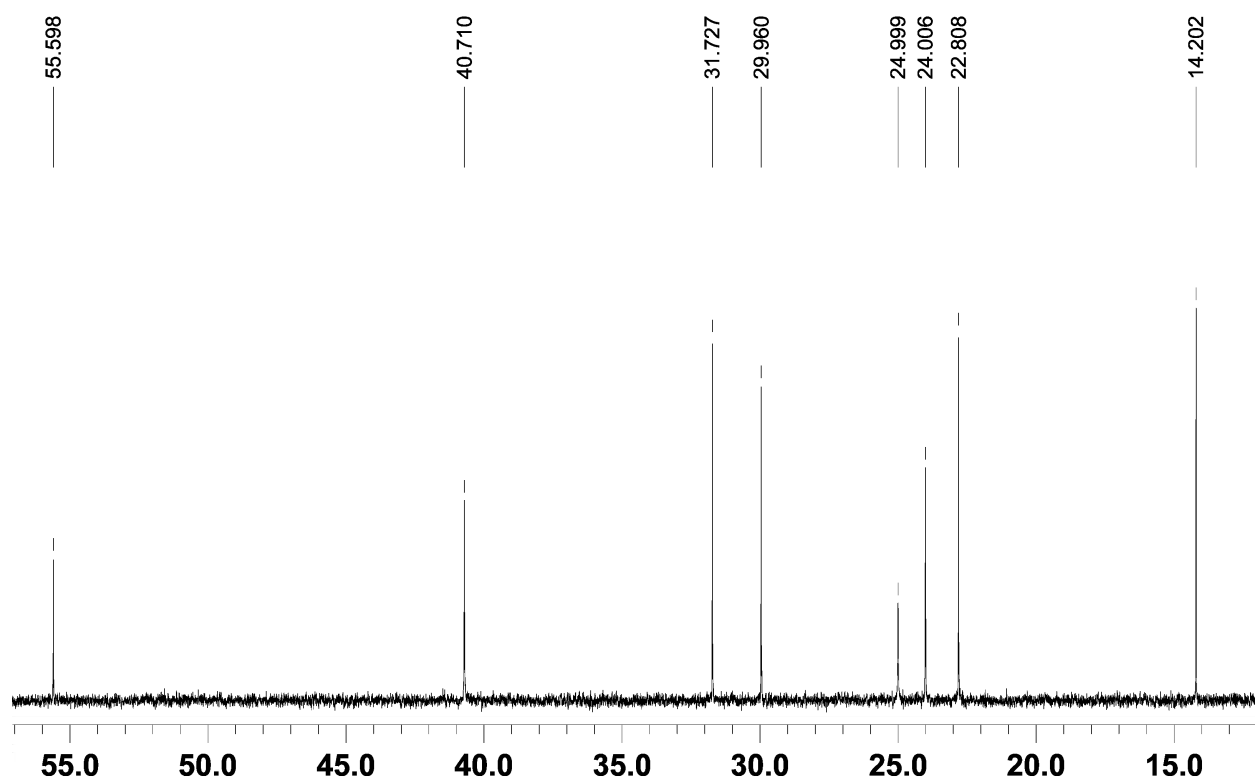
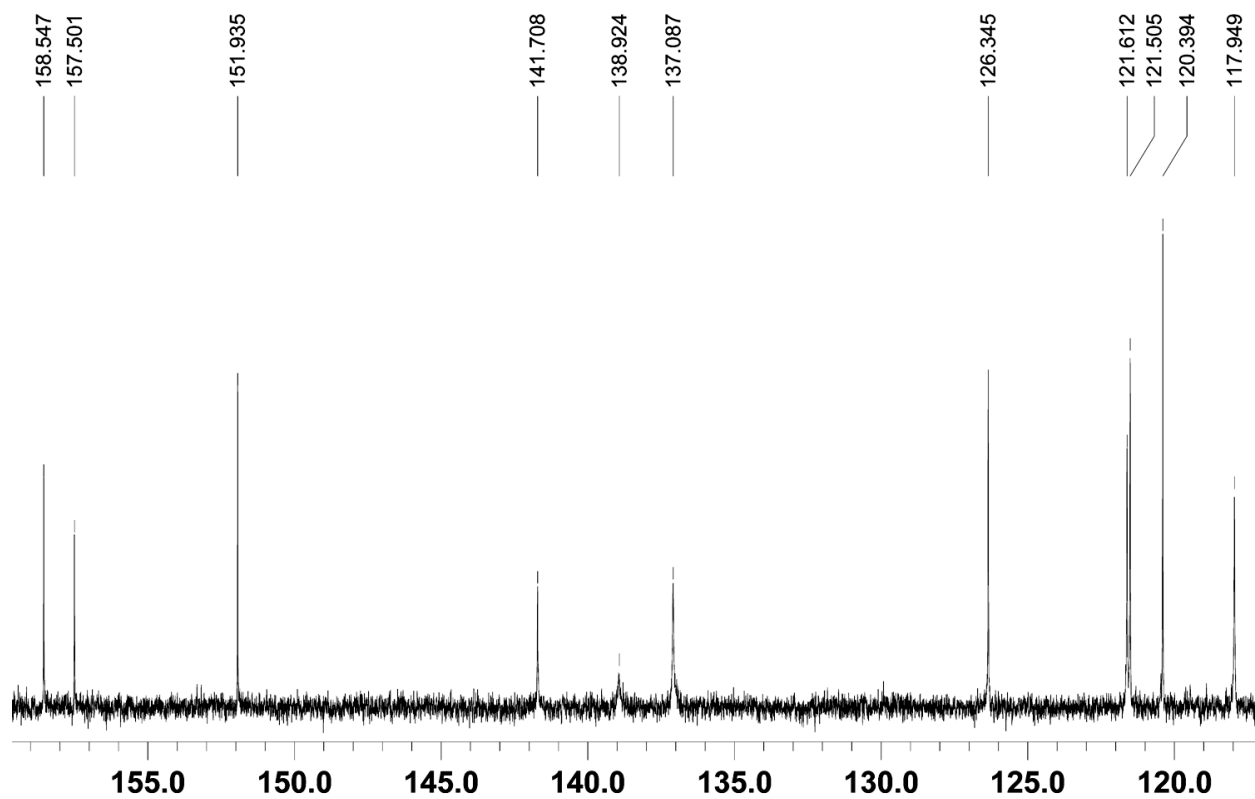
^1H -NMR spectrum of **1** in CDCl_3 (δ , ppm)



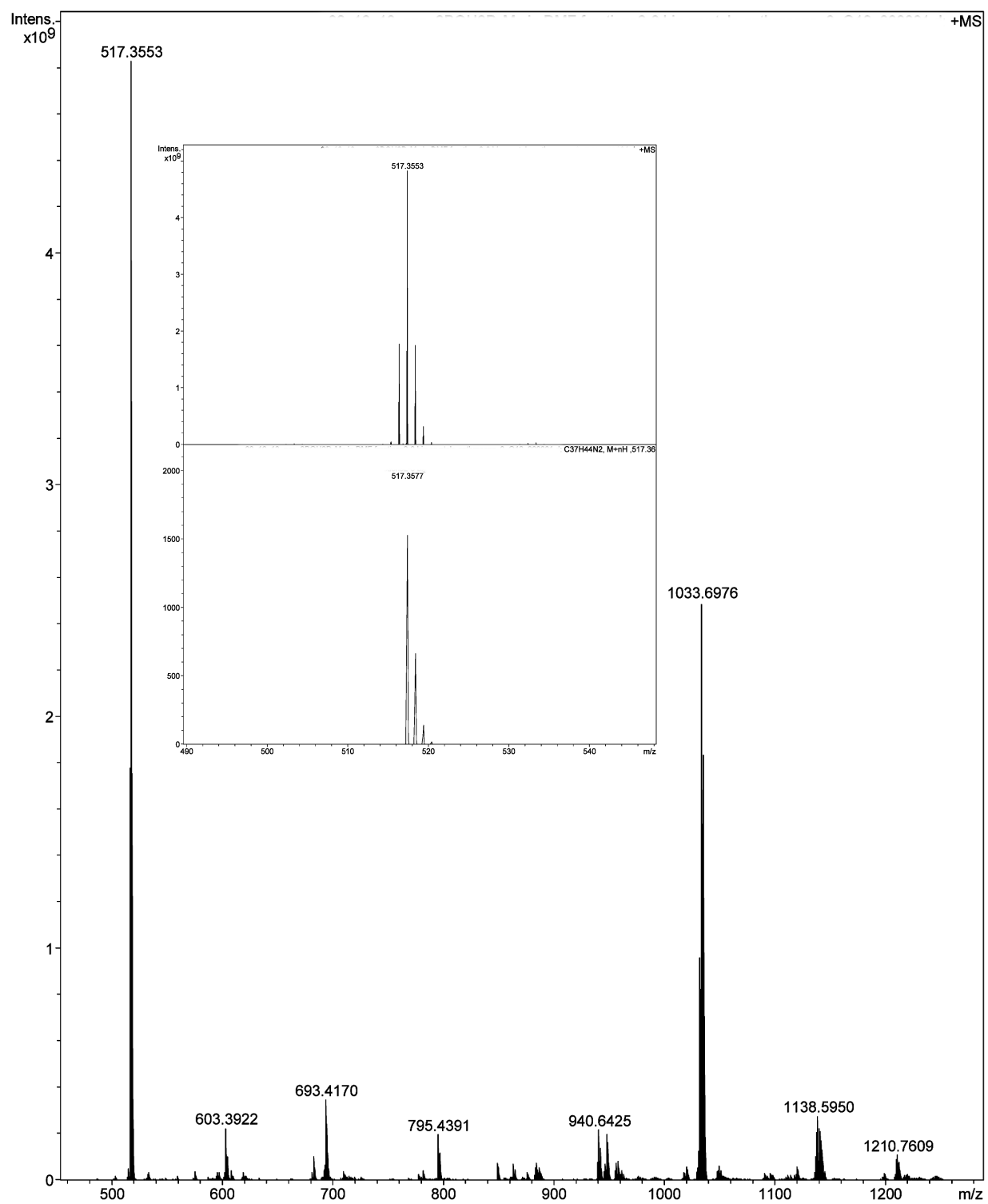


^{13}C -NMR spectrum of **1** in CDCl_3 (δ , ppm)

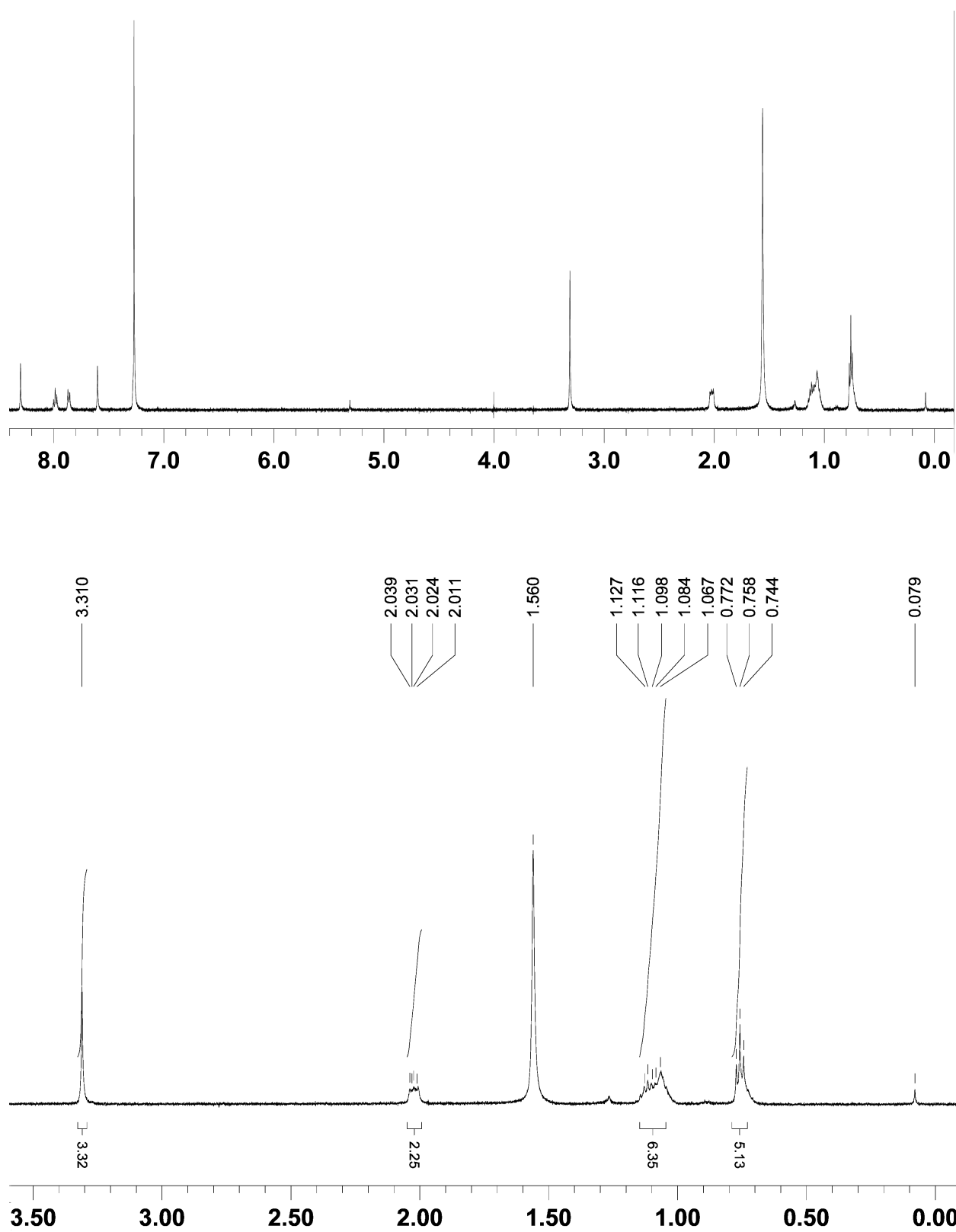


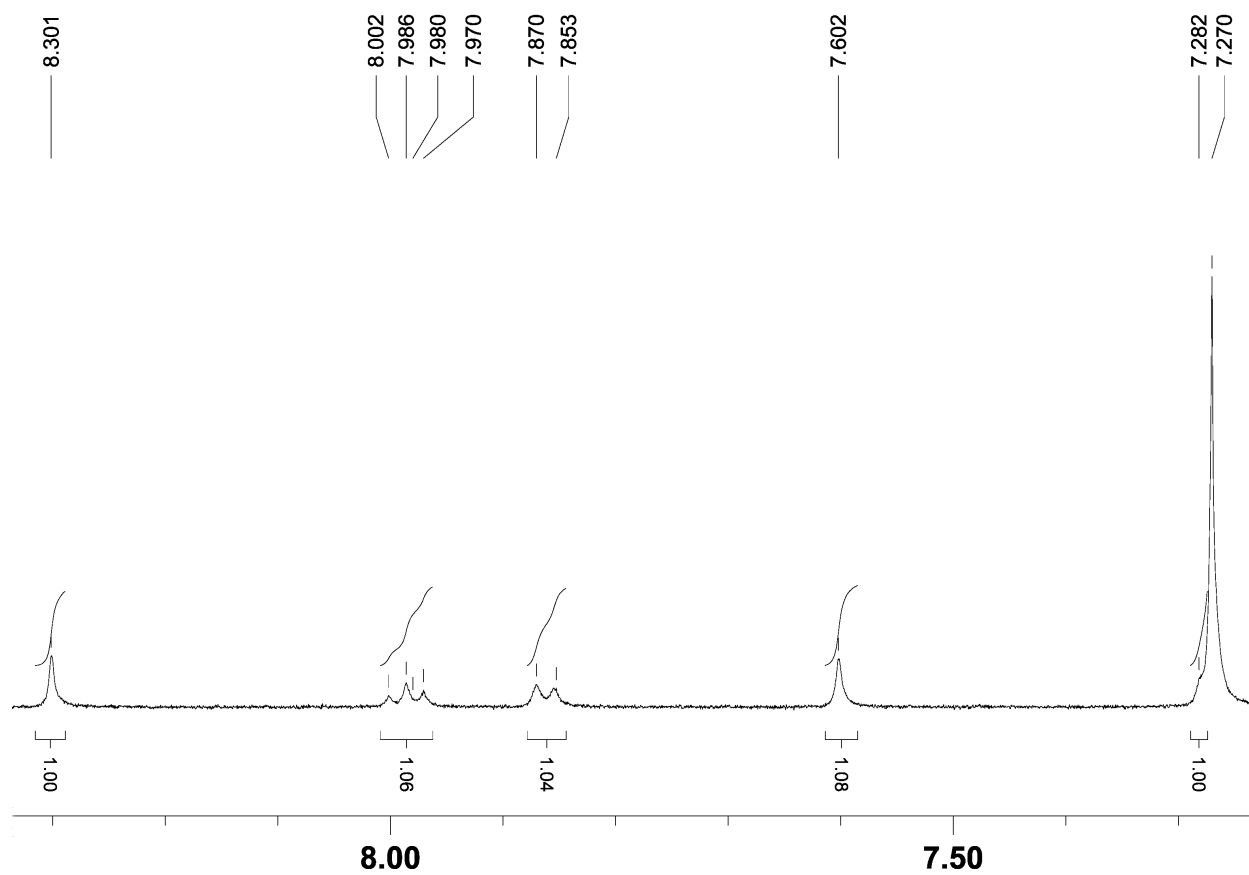


High-resolution MALDI-MS of **1** (anthracene, pos. mode)

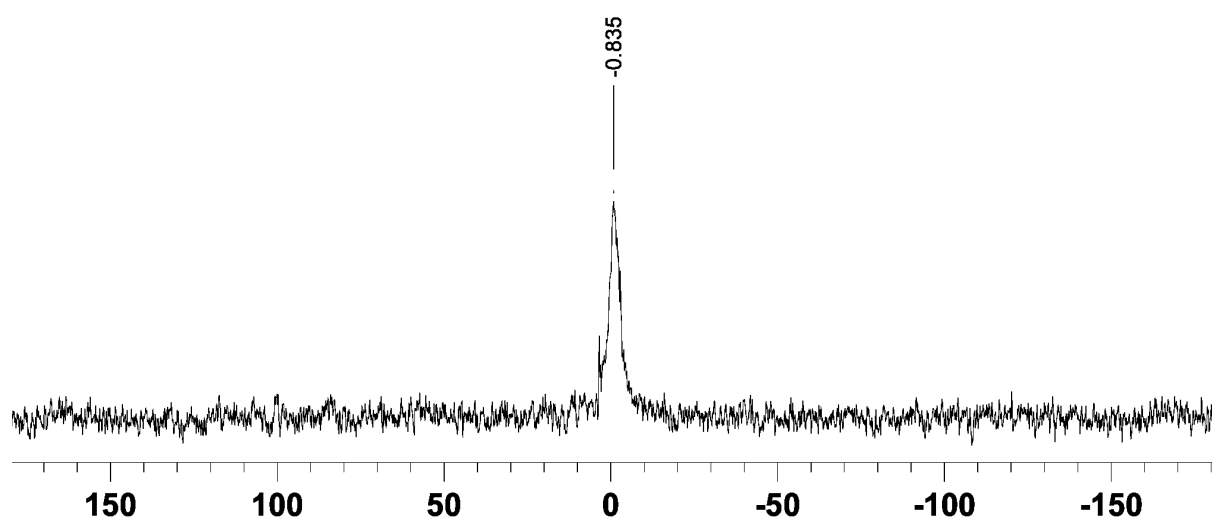


^1H -NMR spectrum of **2-Br** in CDCl_3 (δ , ppm)

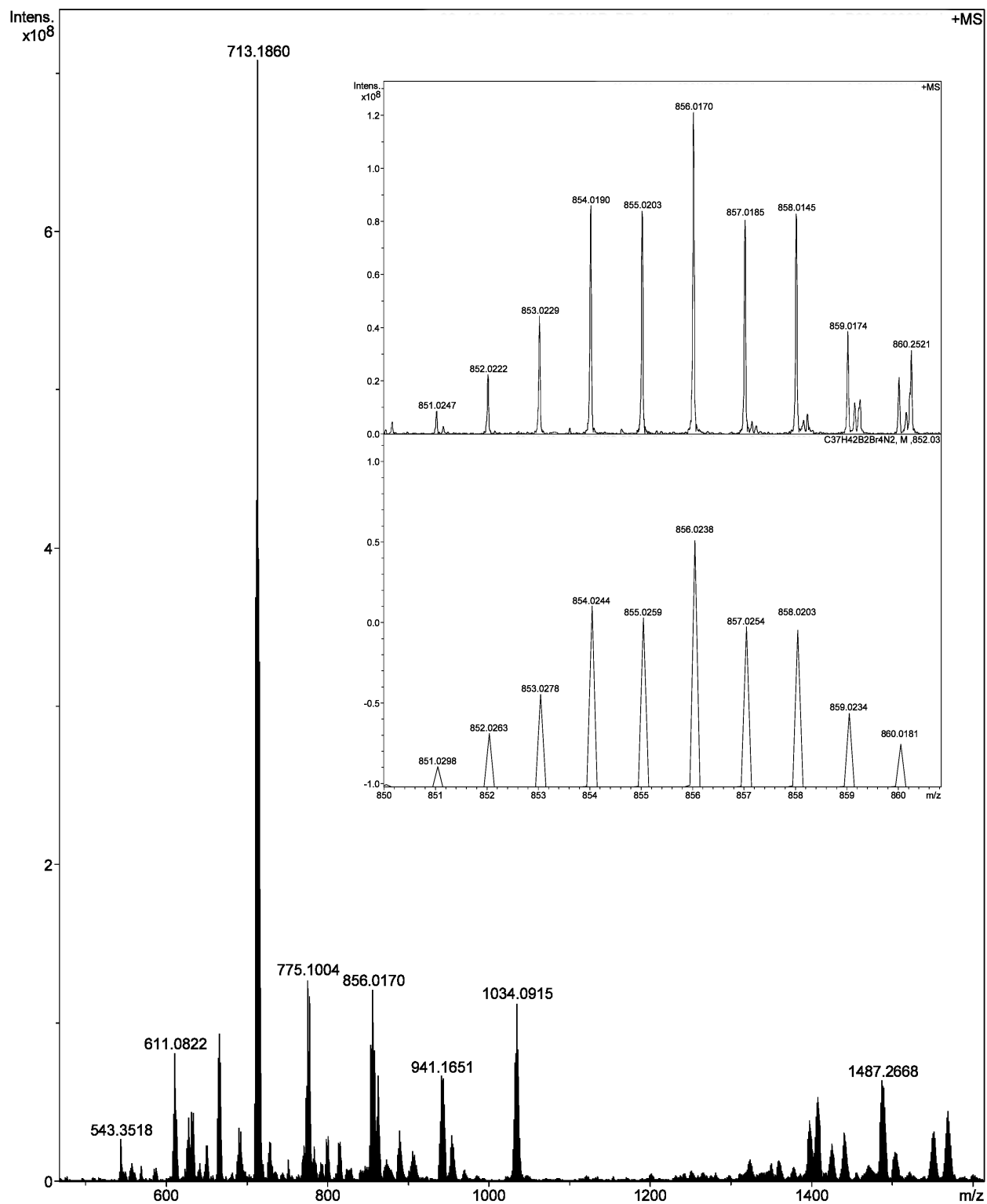




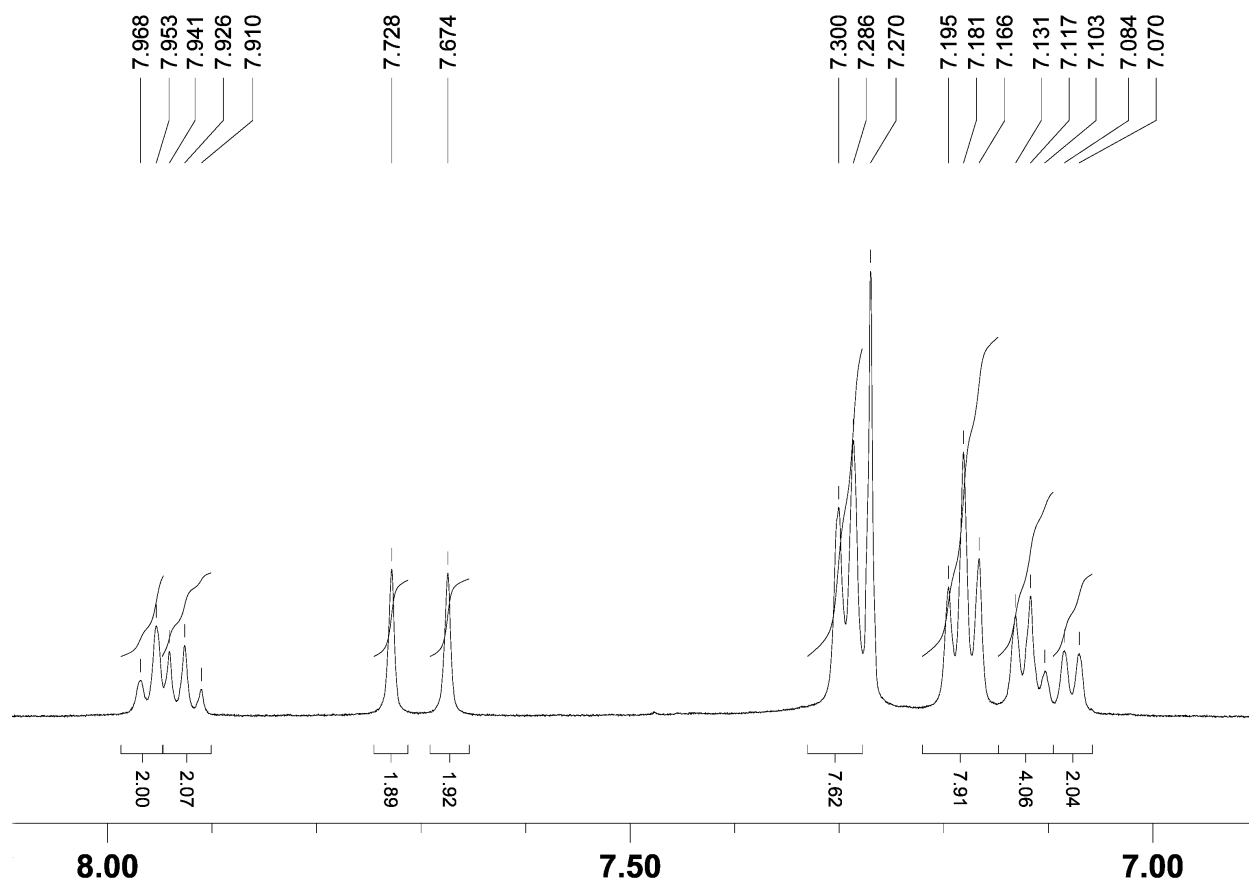
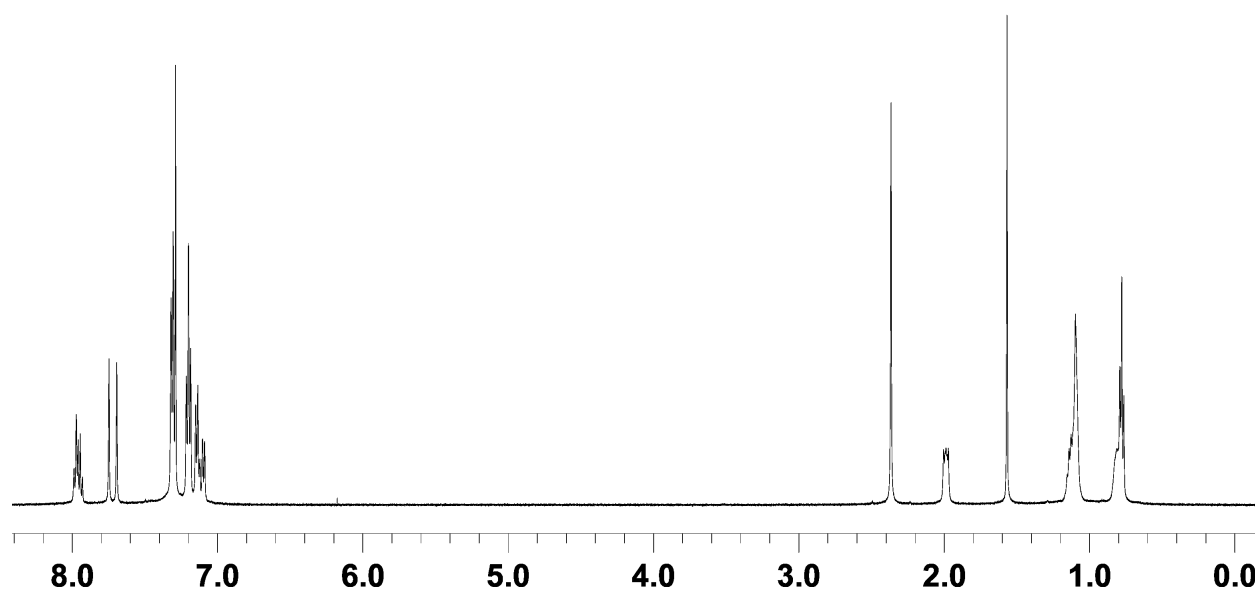
¹¹B-NMR spectrum of **2-Br** in CDCl₃ (δ , ppm)

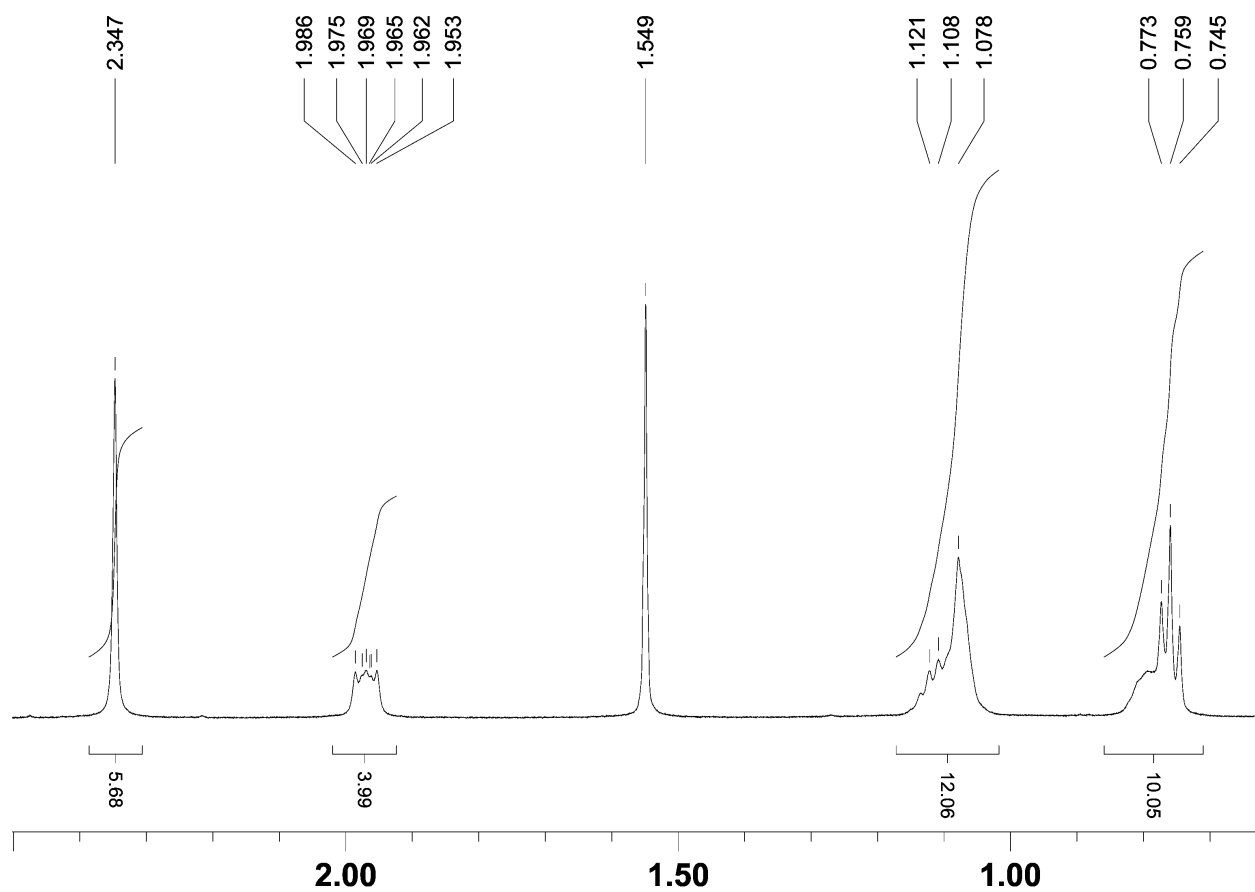


High-resolution MALDI-MS spectrum of **2-Br** (anthracene, pos. mode)

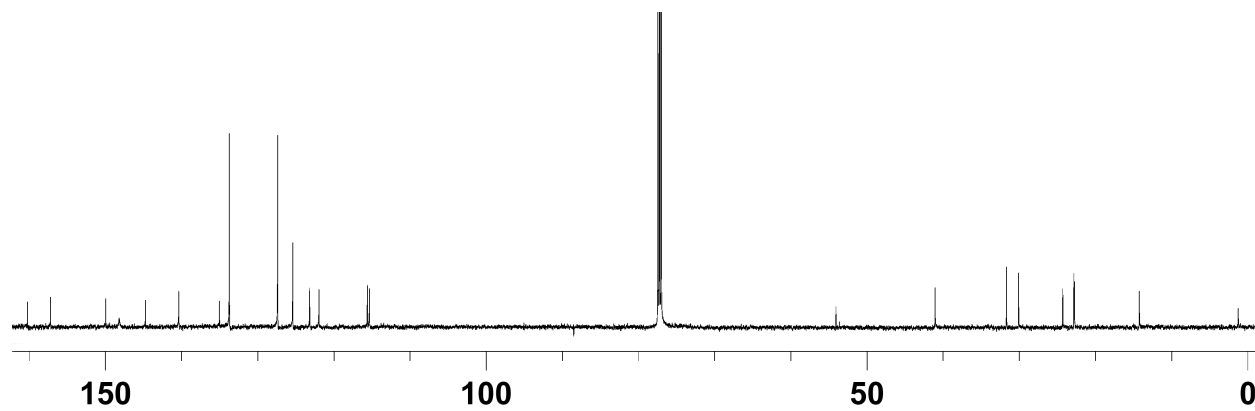


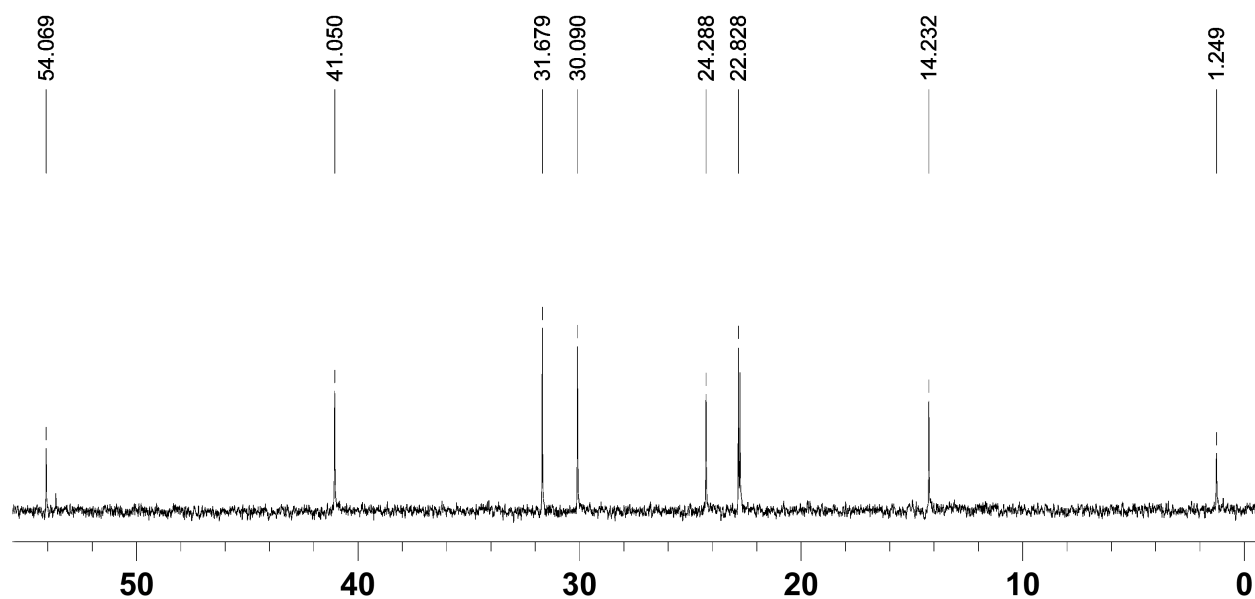
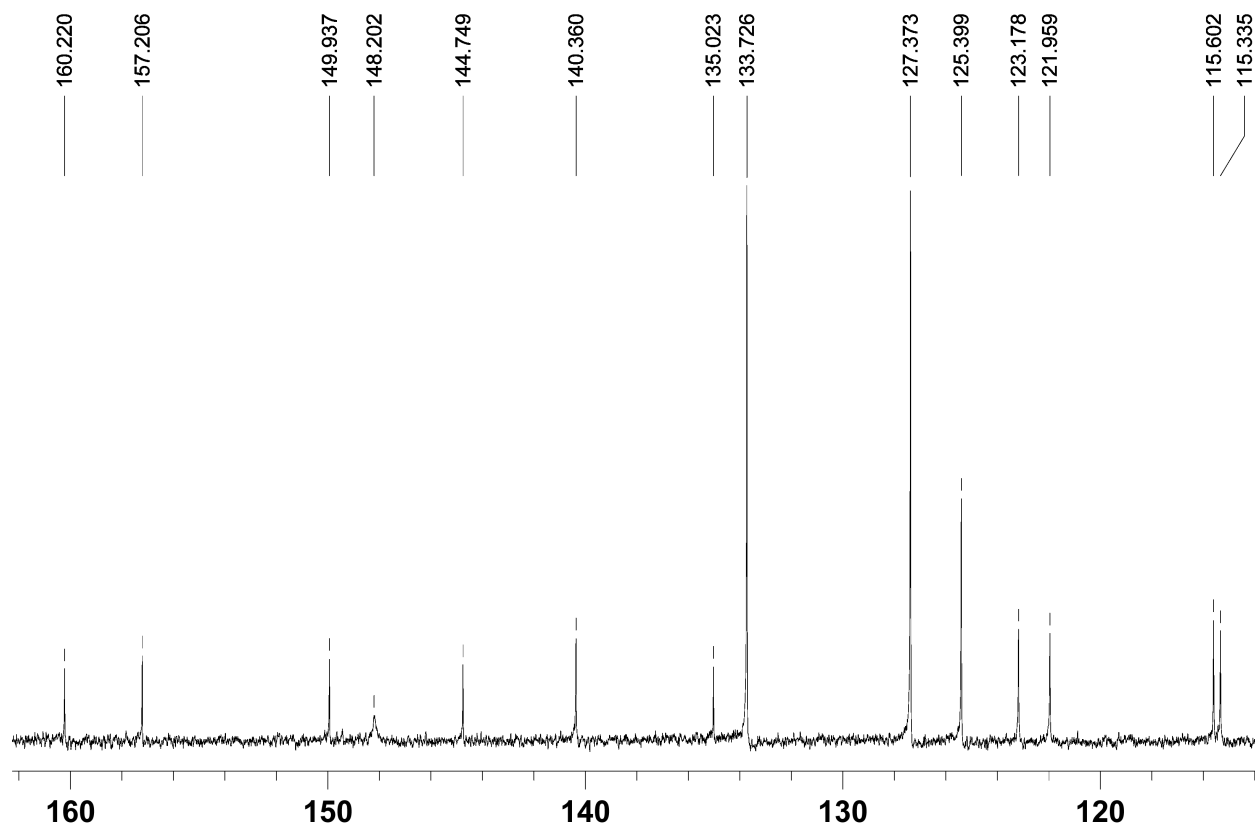
^1H -NMR spectrum of **2-Ph** in CDCl_3 (δ , ppm)



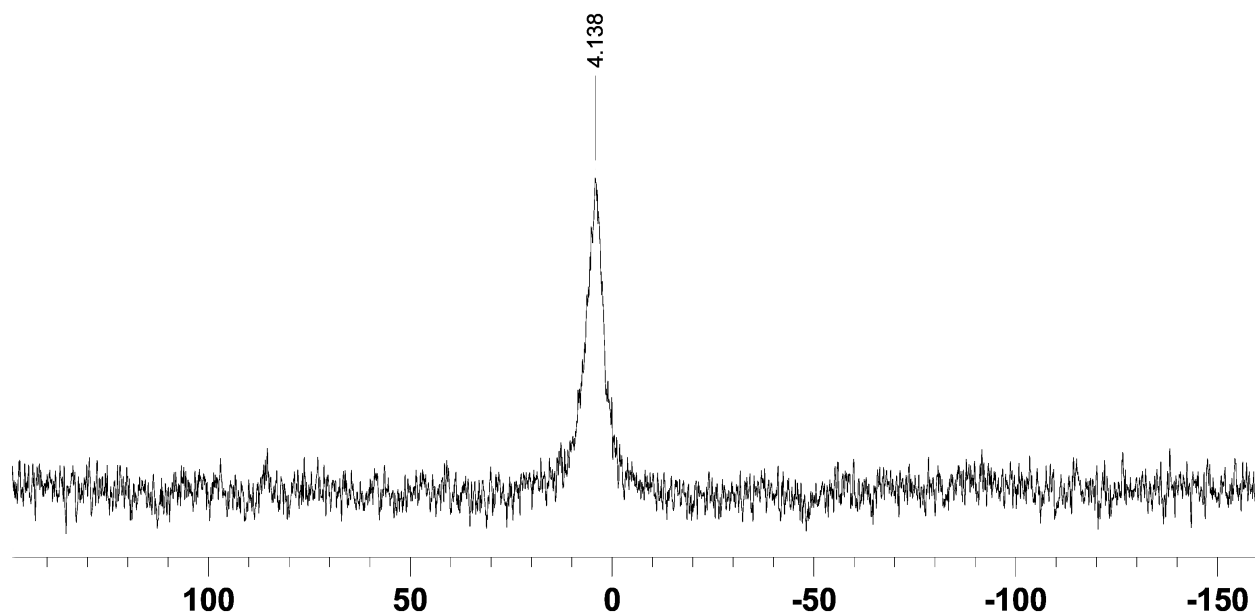


^{13}C -NMR spectrum of **2-Ph** in CDCl_3 (δ , ppm)

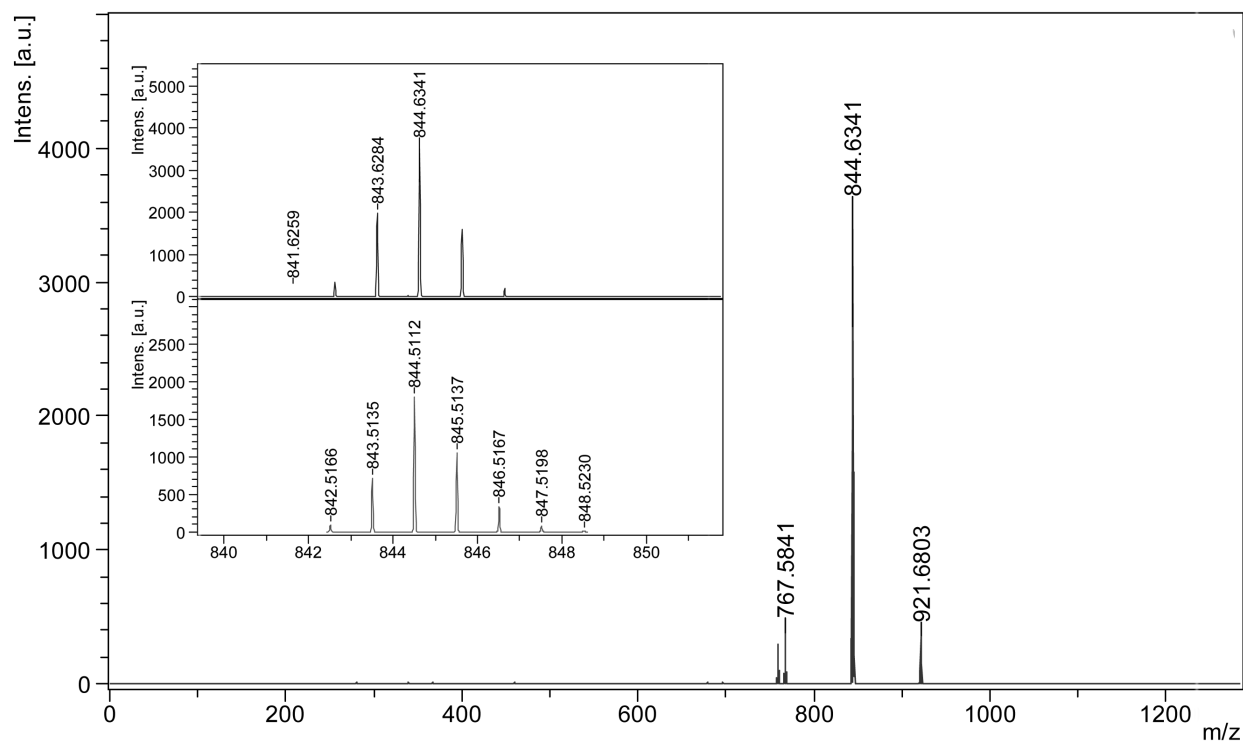




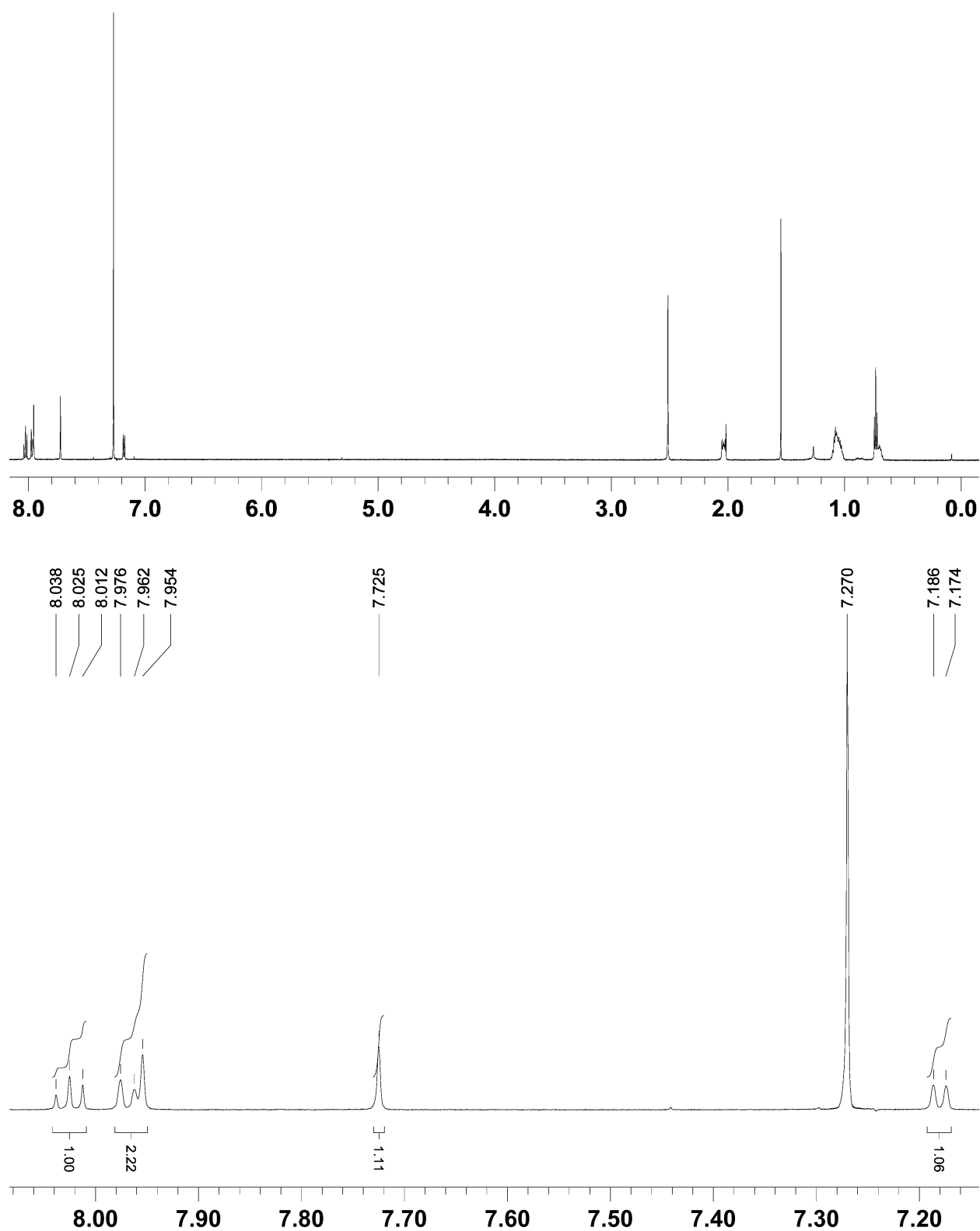
^{11}B -NMR spectrum of **2-Ph** in CDCl_3 (δ , ppm)

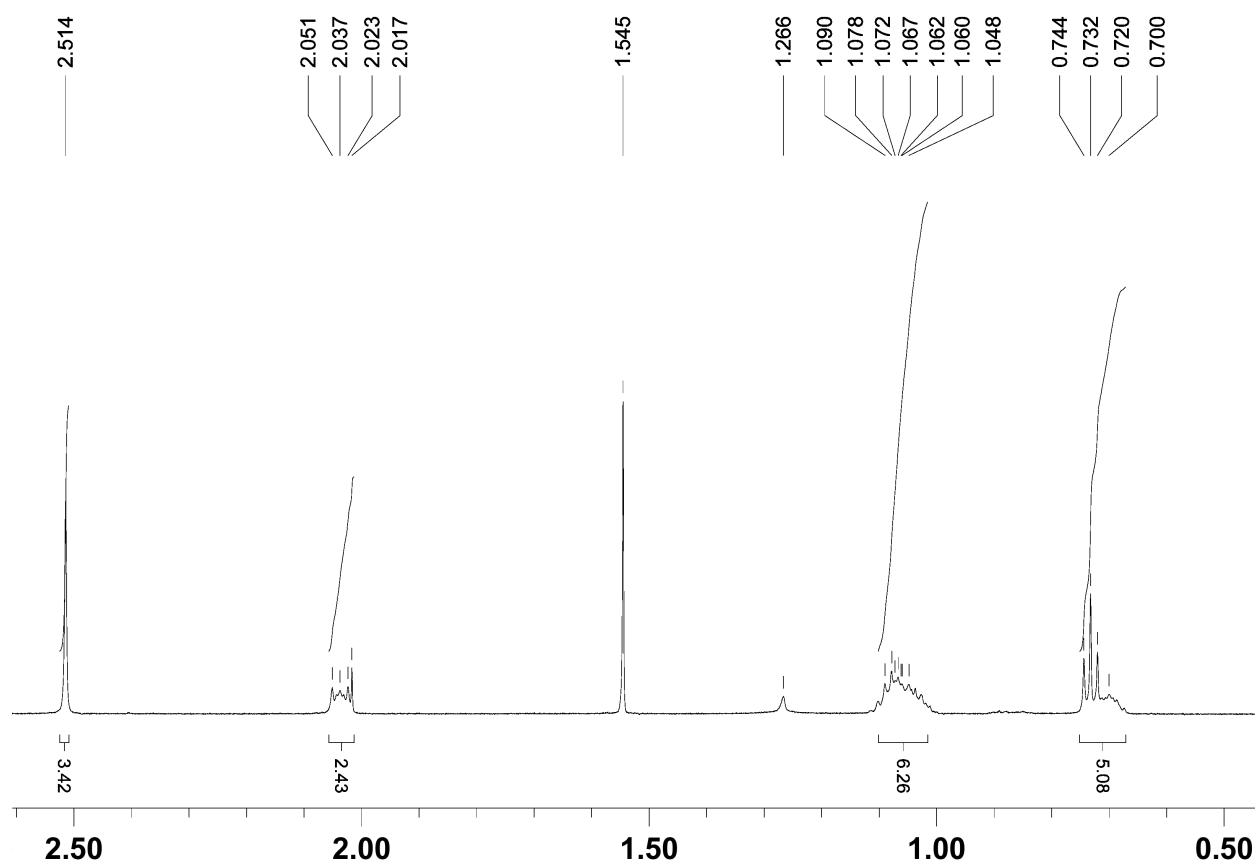


High-resolution MALDI-TOF mass spectrum of **2-Ph** (neg. mode)

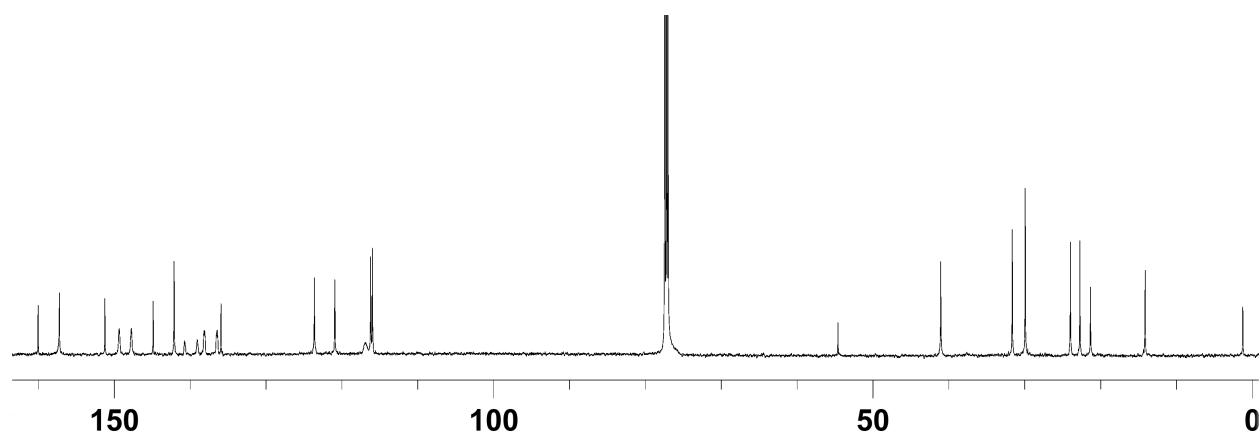


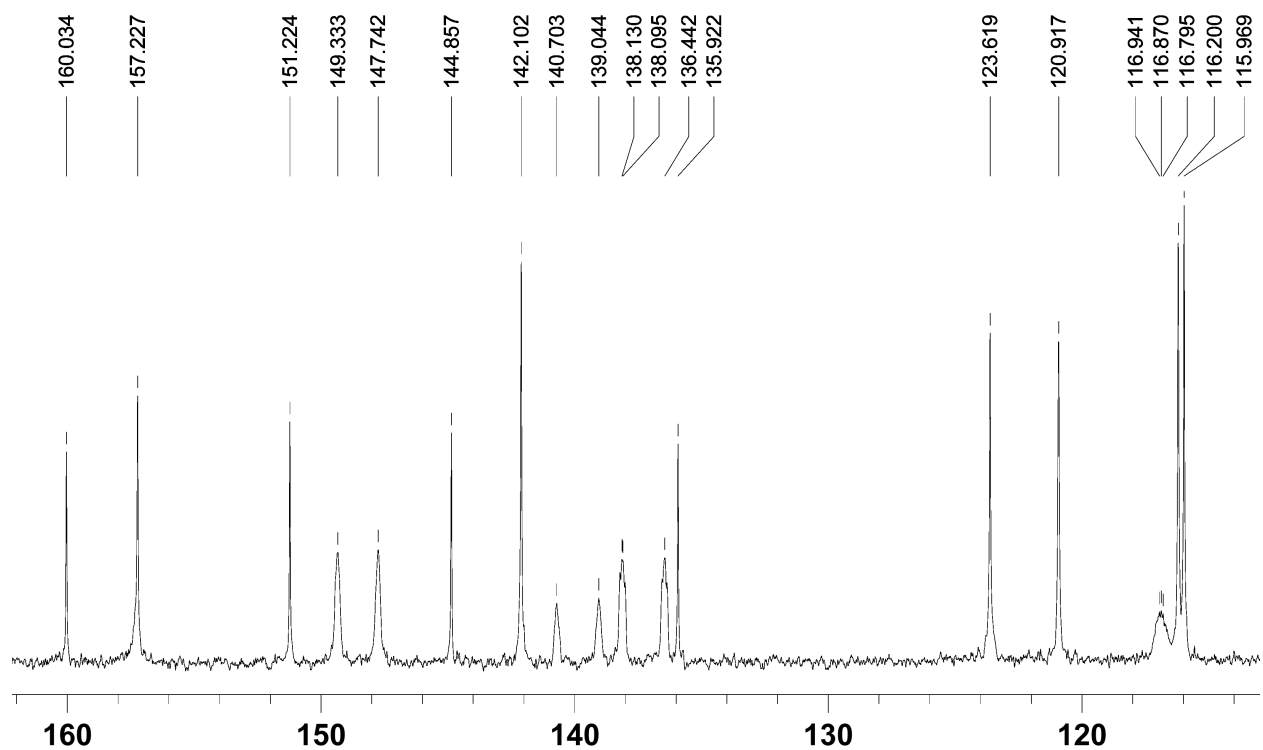
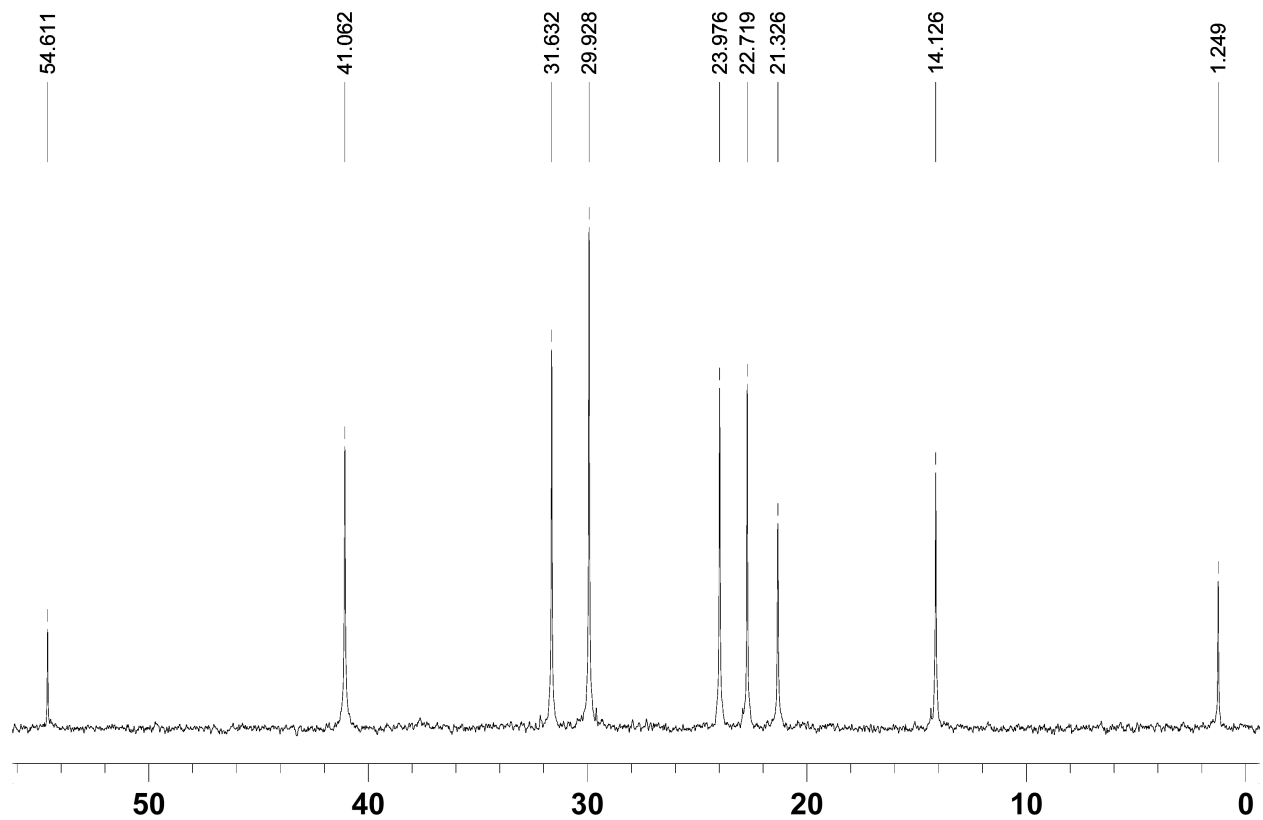
^1H -NMR spectrum of **2-Pf** in CDCl_3 (δ , ppm)



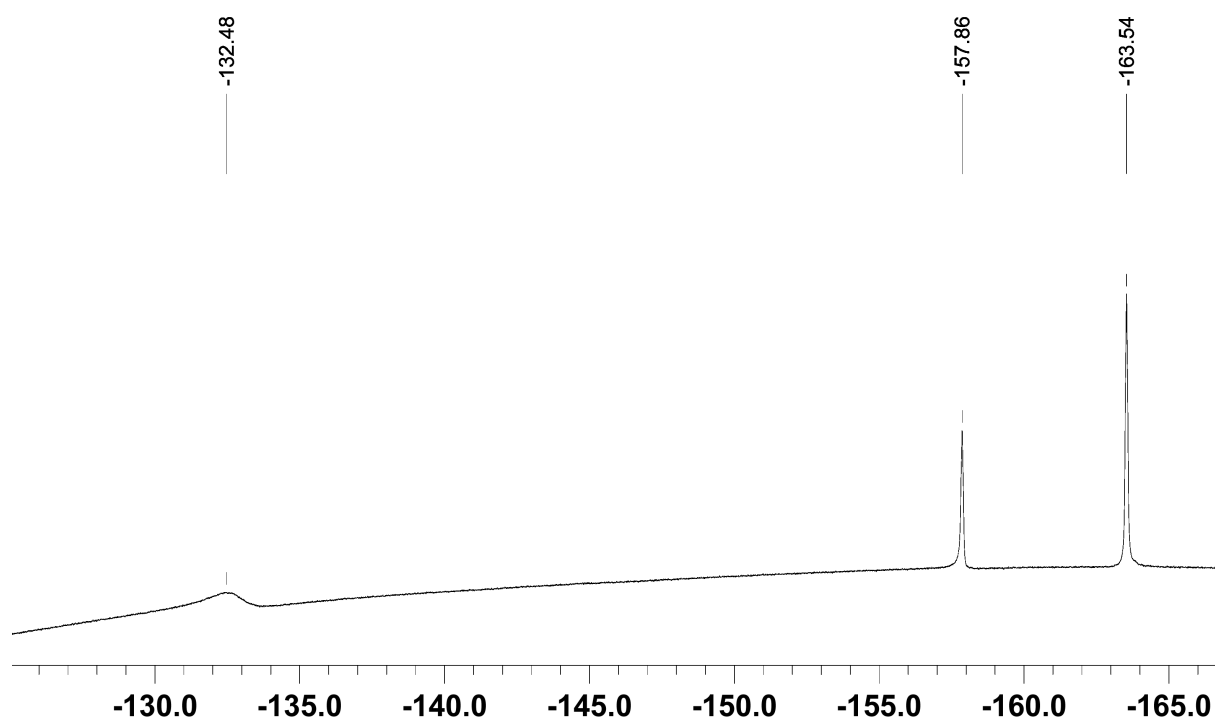


^{13}C -NMR spectrum of **2-Pf** in CDCl_3 (δ , ppm)

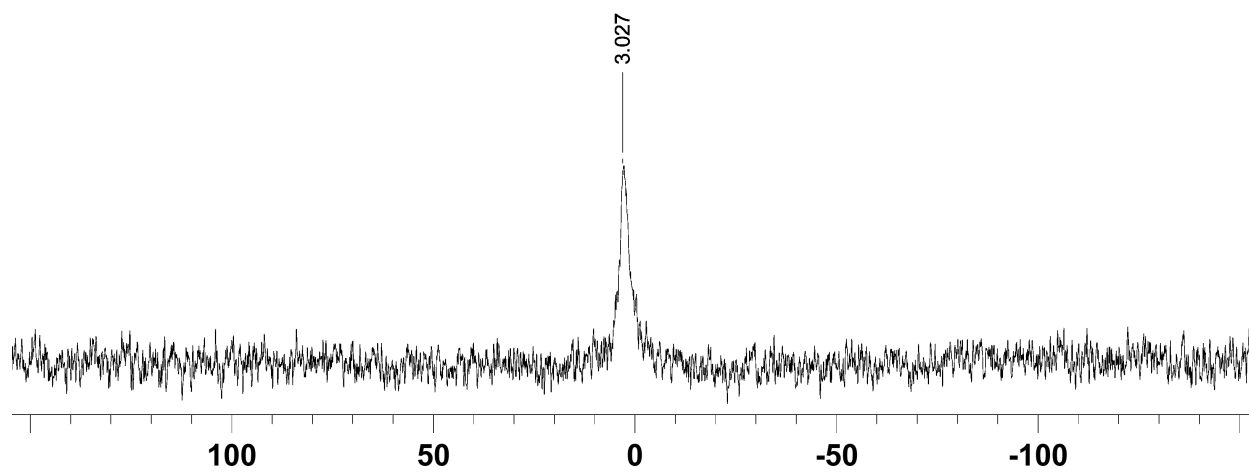




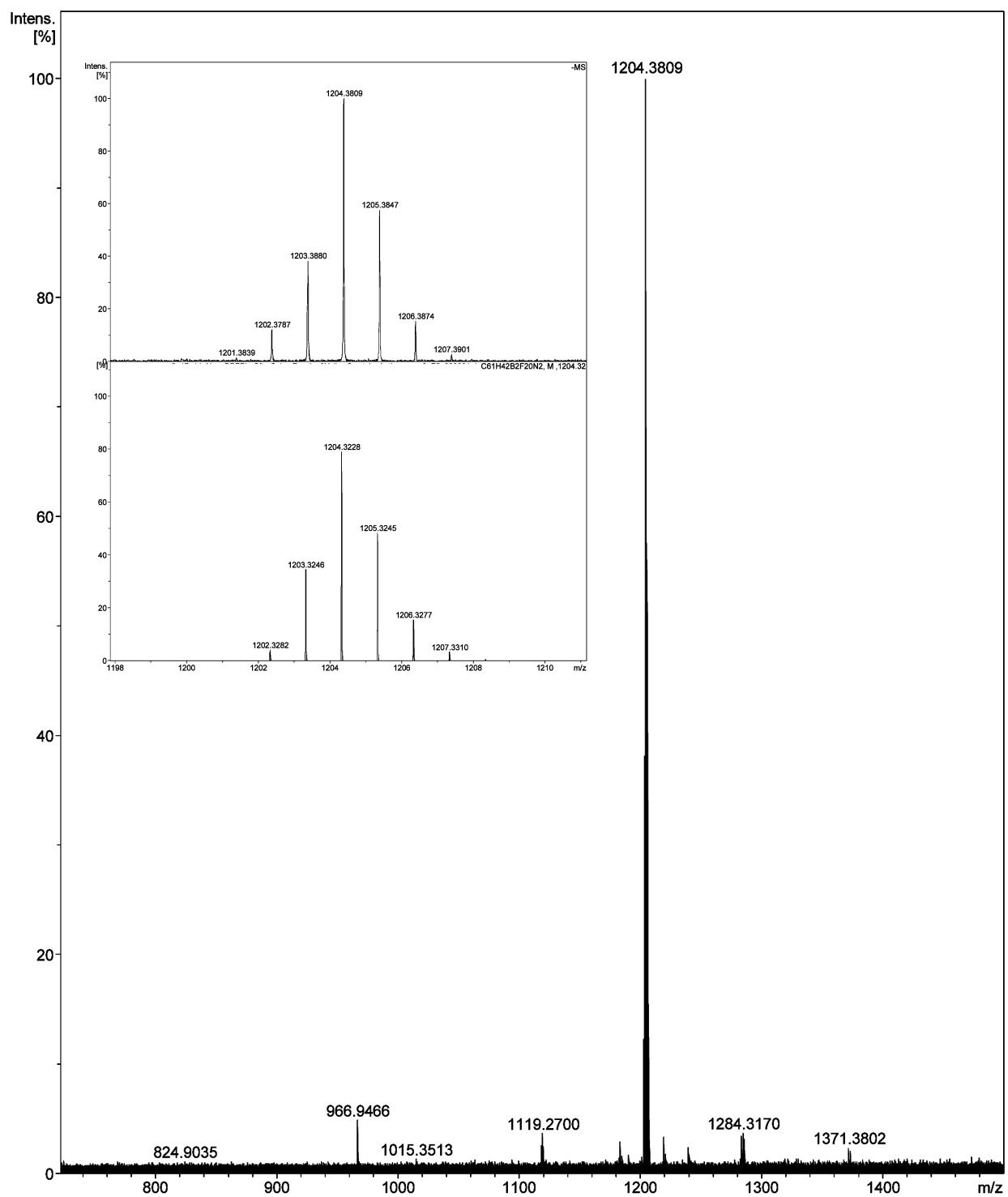
^{19}F -NMR spectrum of **2-Pf** in CDCl_3 (δ , ppm)



^{11}B -NMR spectrum of **2-Pf** in CDCl_3 (δ , ppm)



High-resolution MALDI-MS of **2-Pf** (anthracene, neg. mode)



References

1. Ranger, M.; Rondeau, D.; Leclerc, M., *Macromolecules* **1997**, *30*, 7686-7691.
2. Perepichka, I. I.; Perepichka, I. F.; Bryce, M. R.; Palsson, L. O., *Chem. Commun.* **2005**, 3397-3399.
3. Li, H.; Jäkle, F., *Angew. Chem. Int. Ed.* **2009**, *48*, 2313-2316.
4. Colombe, J. R.; Bernhardt, S.; Stathakis, C.; Buchwald, S. L.; Knochel, P., *Org. Lett.* **2013**, *15*, 5754-5757.
5. Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.