Synthesis, Structure and Properties of Thiophene-fused BODIPYs and AzaBODIPYs as Near-infrared Agents

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1. Crystal Structure

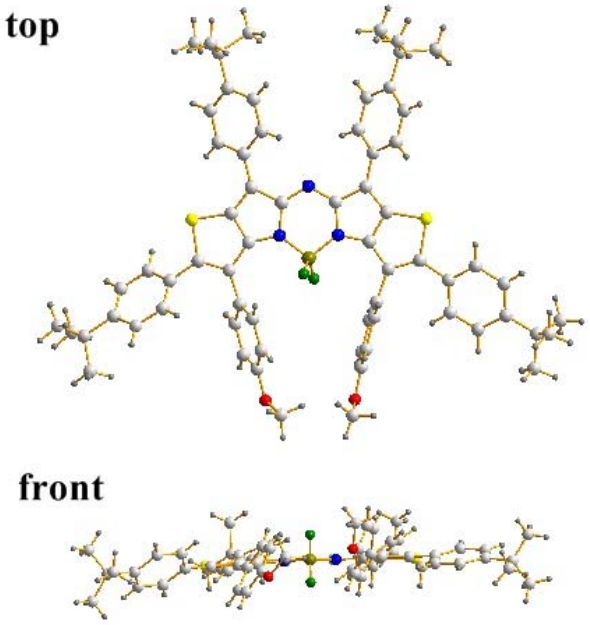


Figure S1: X-ray structures of **1f**. C, light gray; H, gray; N, blue; B, dark yellow; F, light green; S, yellow; O, red.

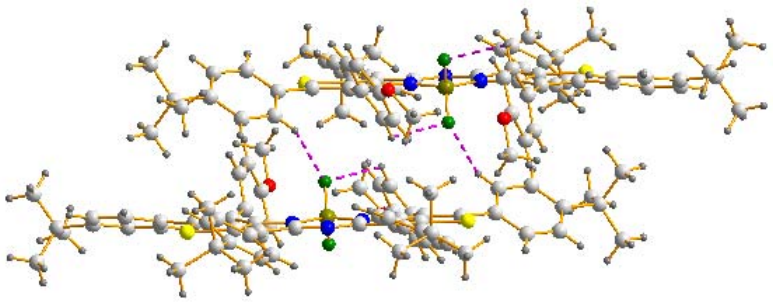


Figure S2: Intermolecular crystal packing of **1f** through H-bonding (dotted line). C, light gray; H, gray; N, blue; B, dark yellow; F, light green; S, yellow; O, red.

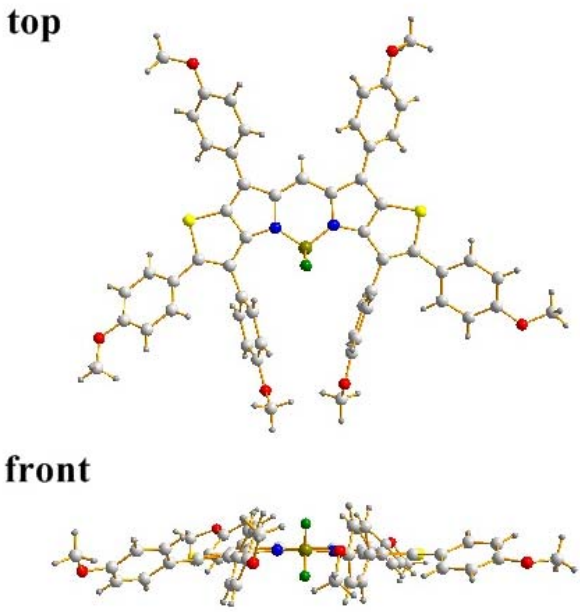


Figure S3: X-ray structures of **2b**. C, light gray; H, gray; N, blue; B, dark yellow; F, light green; S, yellow; O, red.

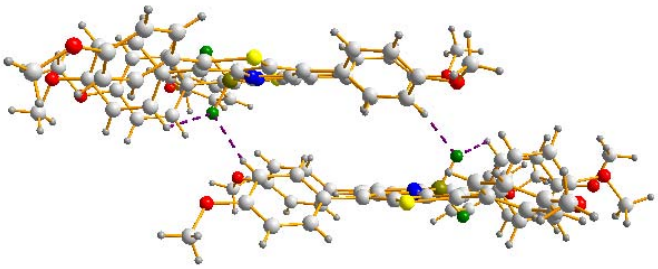
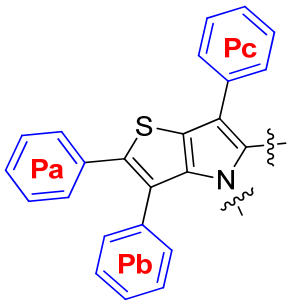


Figure S4: Intermolecular crystal packing of **2b** through H-bonding (dotted line). C, light gray; H, gray; N, blue; B, dark yellow; F, light green; S, yellow; O, red.

Table S1. Selected geometrical parameters of compound 1e and 2b obtained from crystallography



	1f	**2b**
the B-N bond distances (A)	1.5655(74) 1.5684(84)	1.5500(43) 1.5578(78)
the intramolecular F-H Hydrogen bond distances (Å)	2.4463(34)	2.6514(23)
the intermolecular F-H Hydrogen bond distances (Å)	2.7922(35)	2.5344(17) 2.8216(19)
dihedral angles of two thiophene rings (deg)	5.278(178)	7.958(85)
dihedral angles of two pyrrole rings (deg)	2.634(220)	8.943(116)
dihedral angles between thiophene ring and phenyl ring **Pa** (deg)	18.799(210) 38.981(170)	27.547(109) 32.340(87)
dihedral angles between thiophene ring and phenyl ring **Pb** (deg)	57.820(174) 75.174(182)	64.115(141) 88.247(140)
dihedral angles between pyrrole ring and phenyl ring **Pc** (deg)	24.564(222) 33.697(191)	34.699(104) 40.286(117)

2. Photophysical Properties

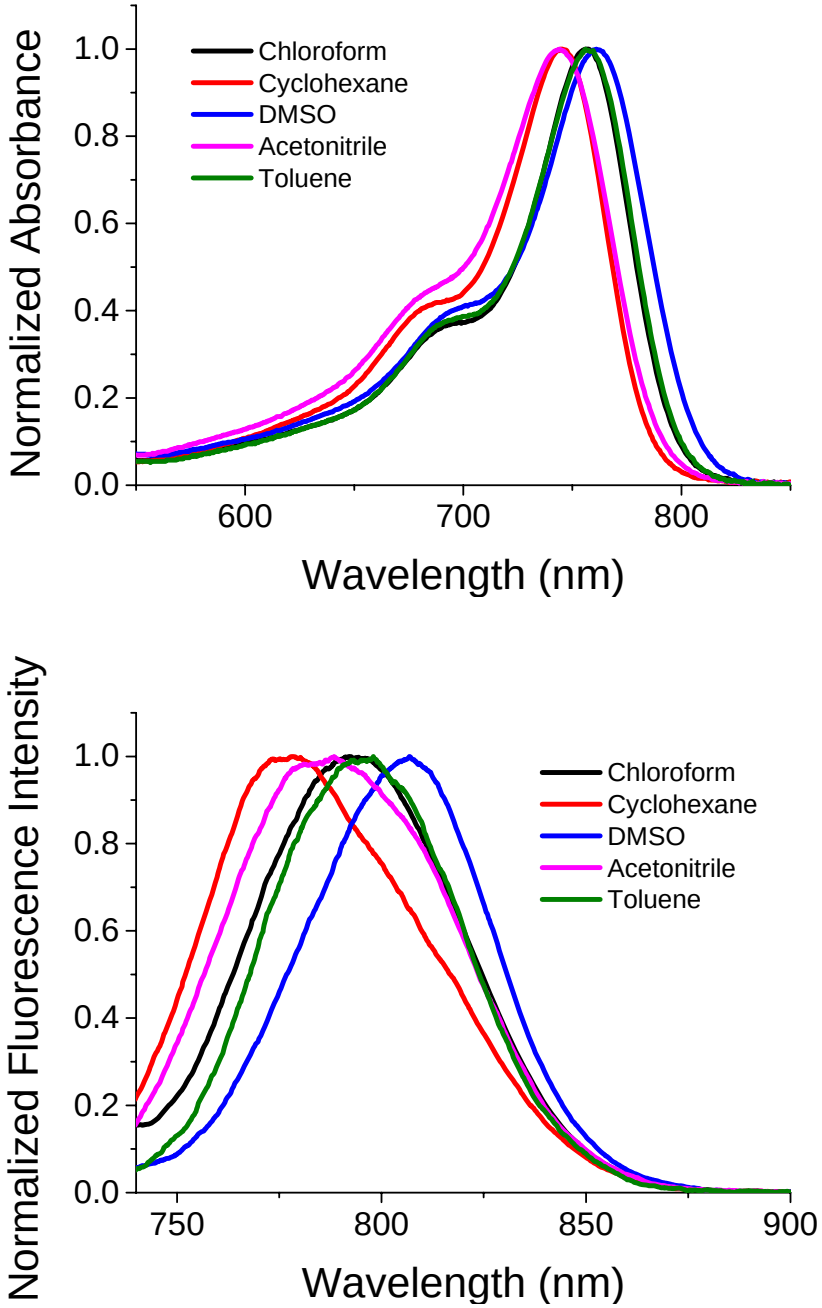


Figure S5: Absorption (top) and emission (bottom) spectra of compound **1e** recorded in different solvents. Excited at 720 nm.

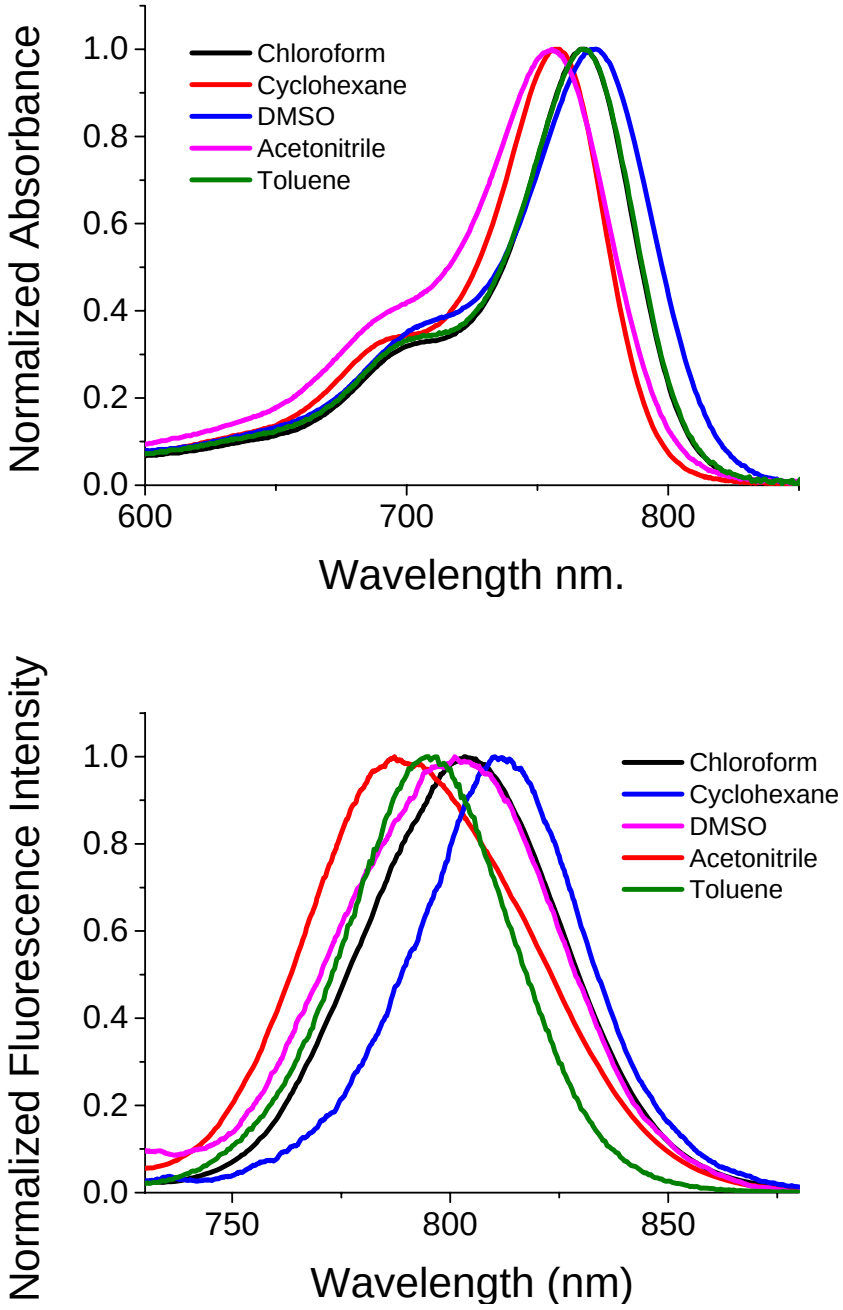


Figure S6: Absorption (top) and emission (bottom) spectra of compound **1f** recorded in different solvents. Excited at 720 nm.

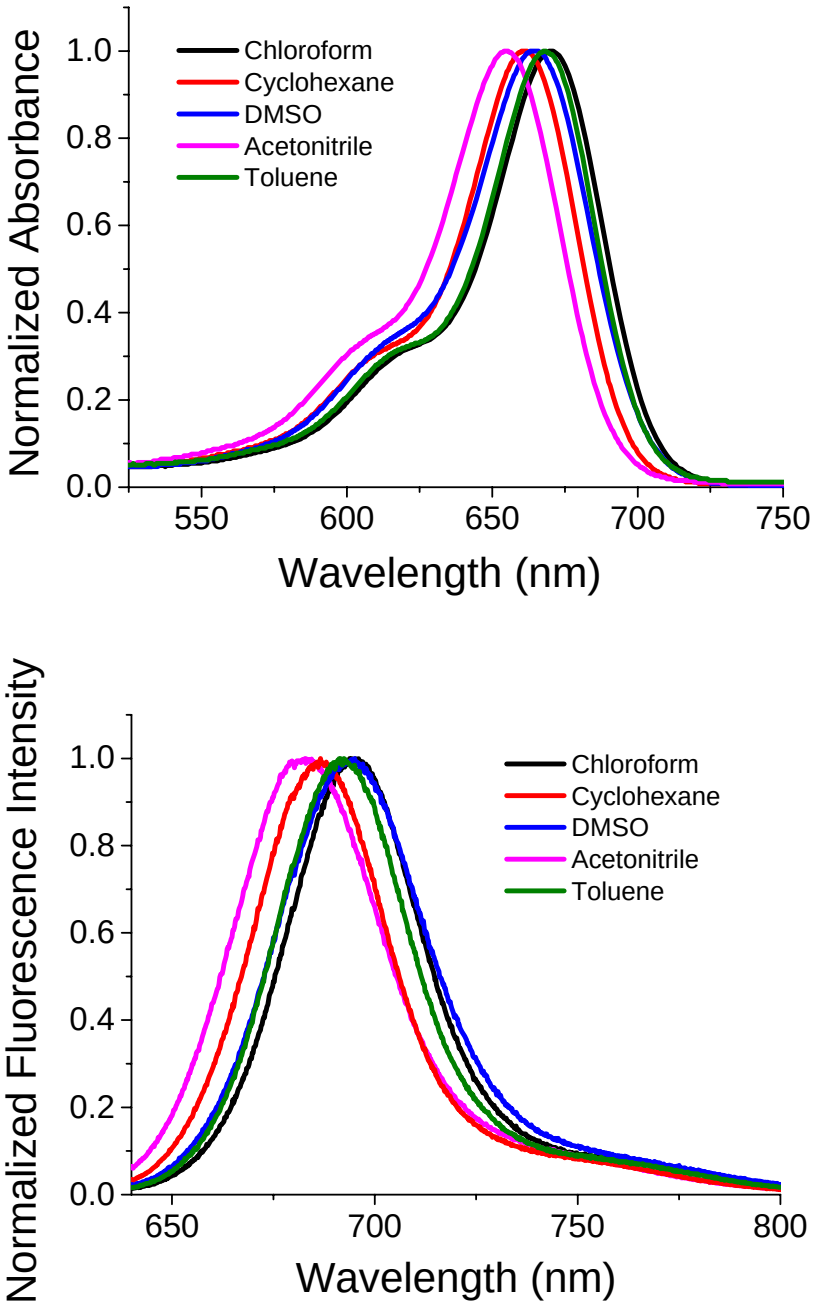


Figure S7: Absorption (top) and emission (bottom) spectra of compound **2a** recorded in different solvents. Excited at 630 nm

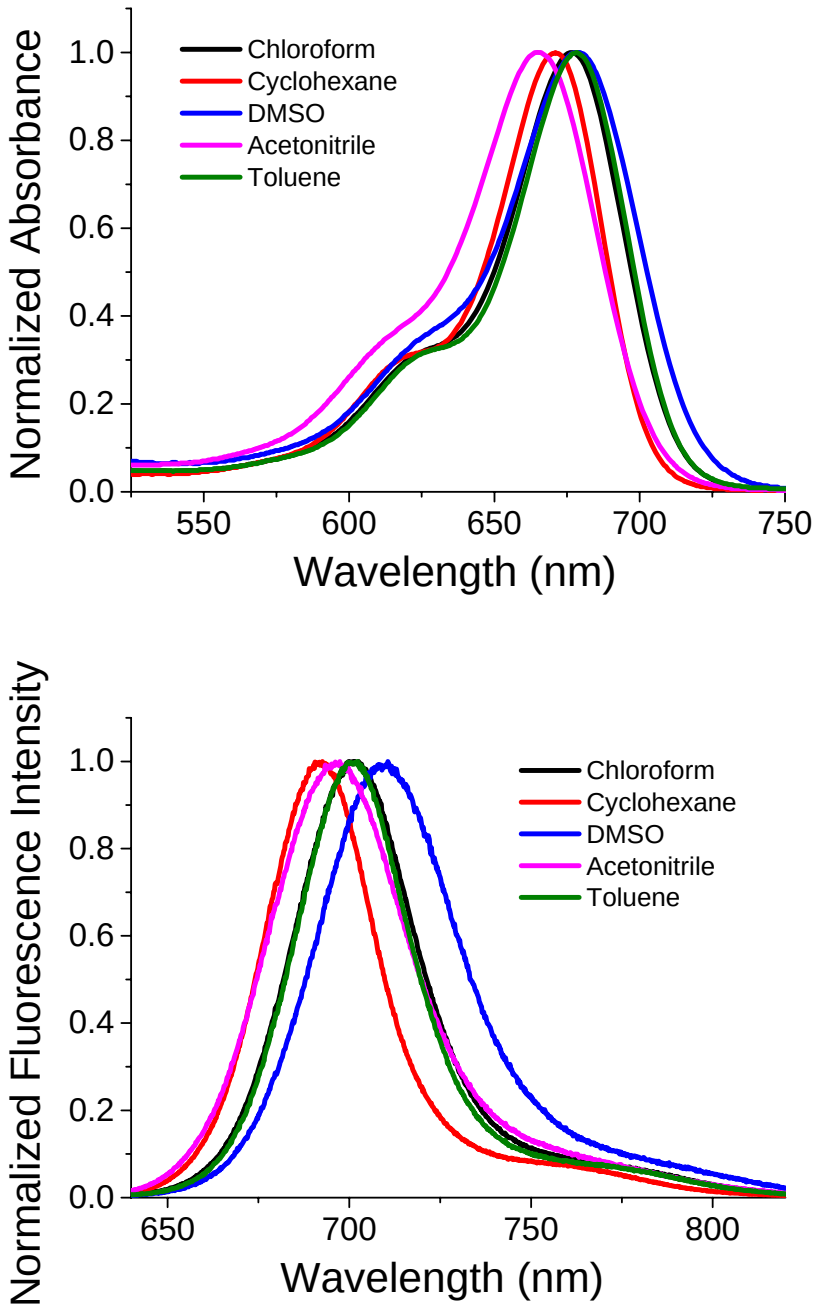


Figure S8: Absorption (top) and emission (bottom) spectra of compound **2b** recorded in different solvents. Excited at 630 nm

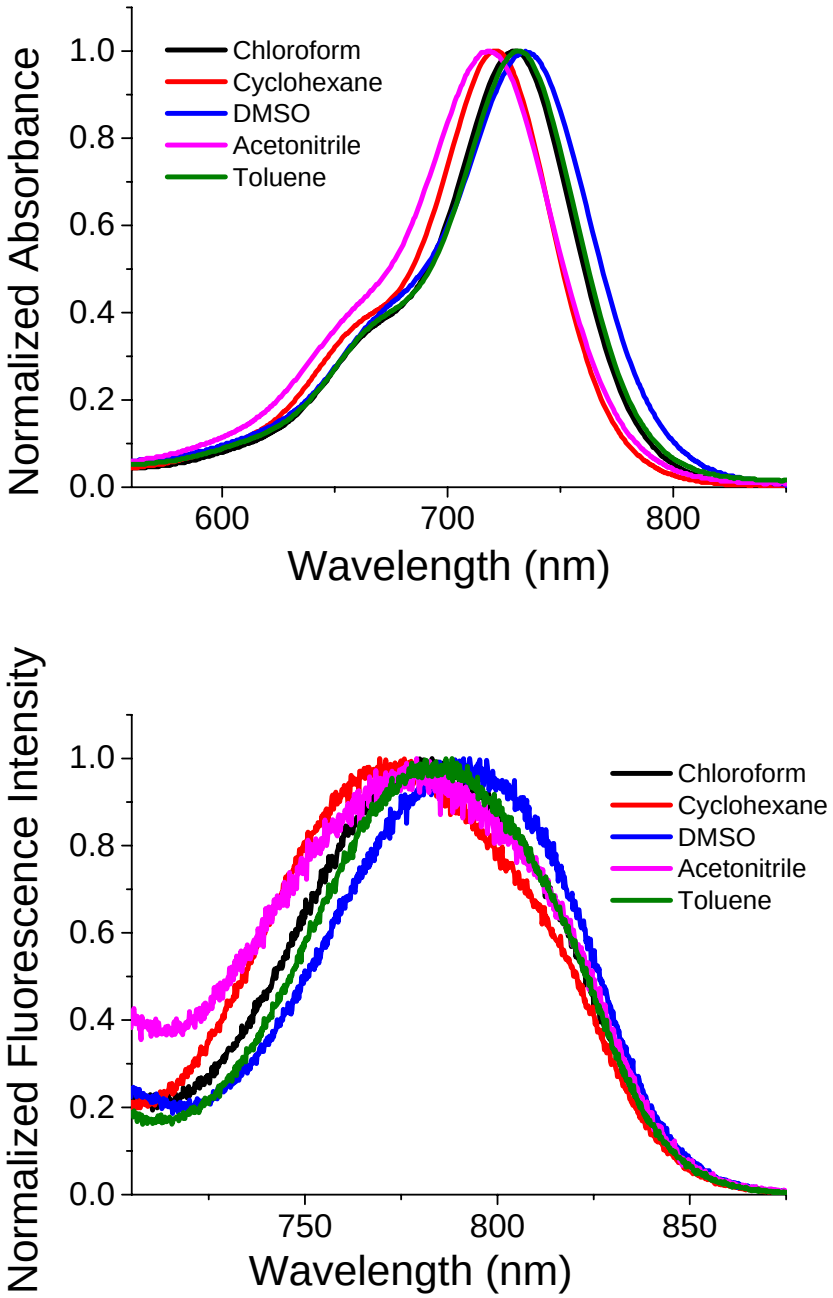


Figure S9: Absorption (top) and emission (bottom) spectra of compound **2c** recorded in different solvents. Excited at 660 nm.

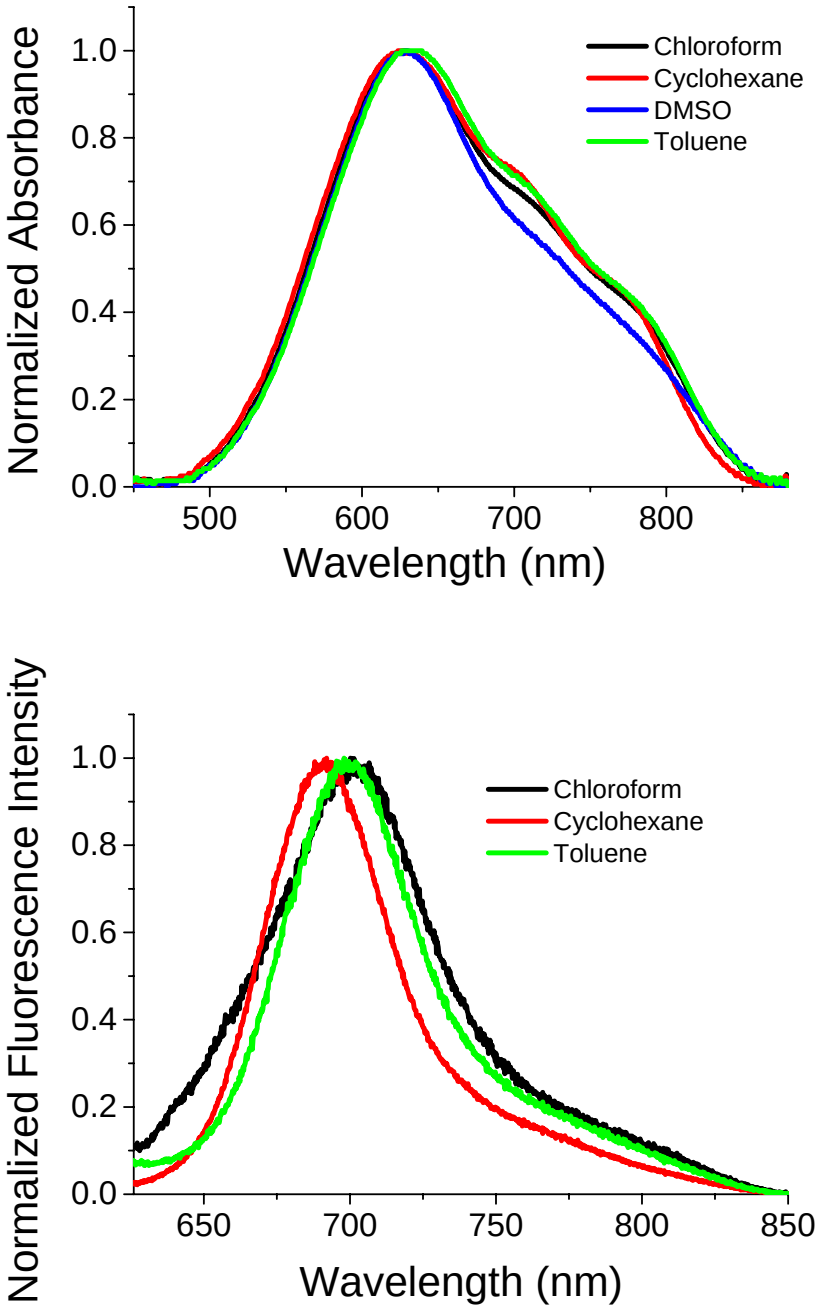


Figure S10: Absorption (top) and emission (bottom) spectra of compound **3a** recorded in different solvents. Excited at 610 nm.

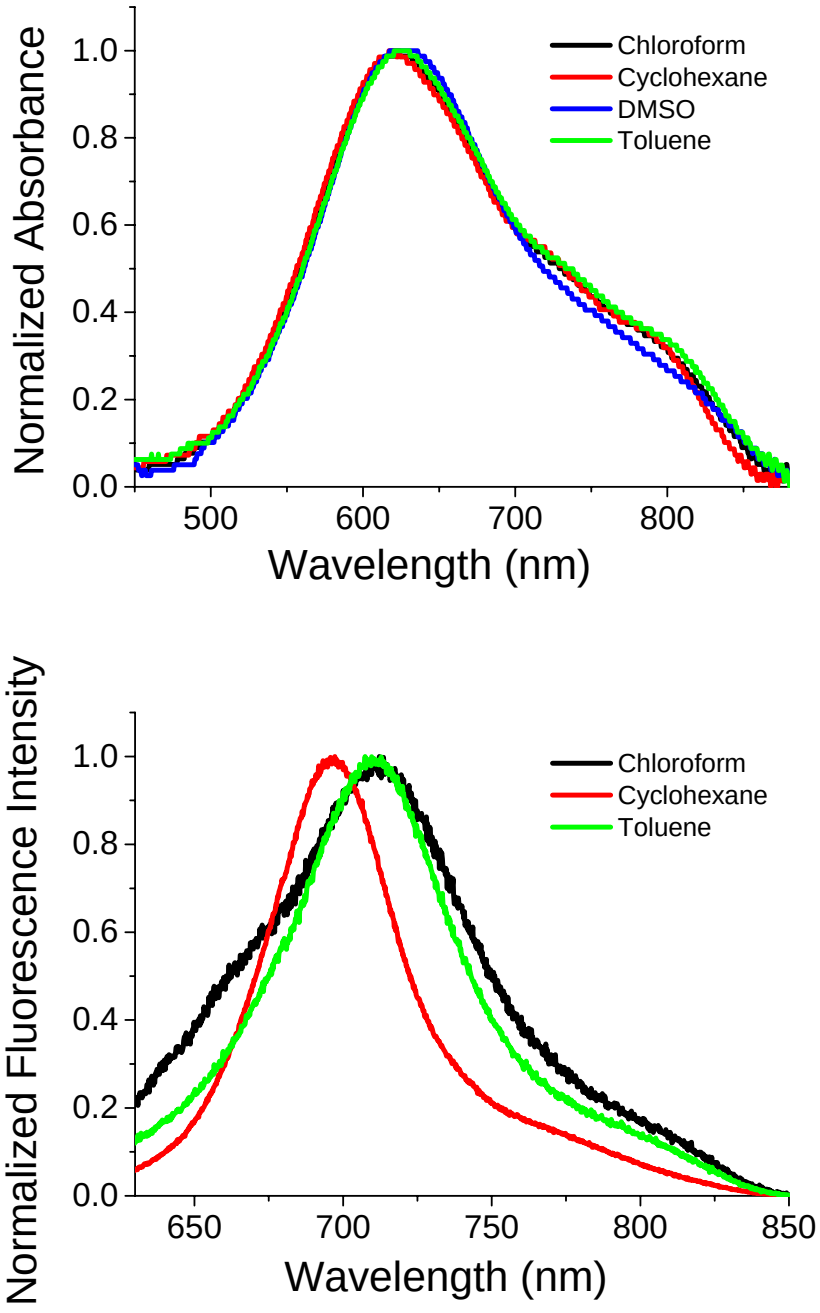


Figure S11: Absorption (top) and emission (bottom) spectra of compound **3b** recorded in different solvents. Excited at 610 nm.

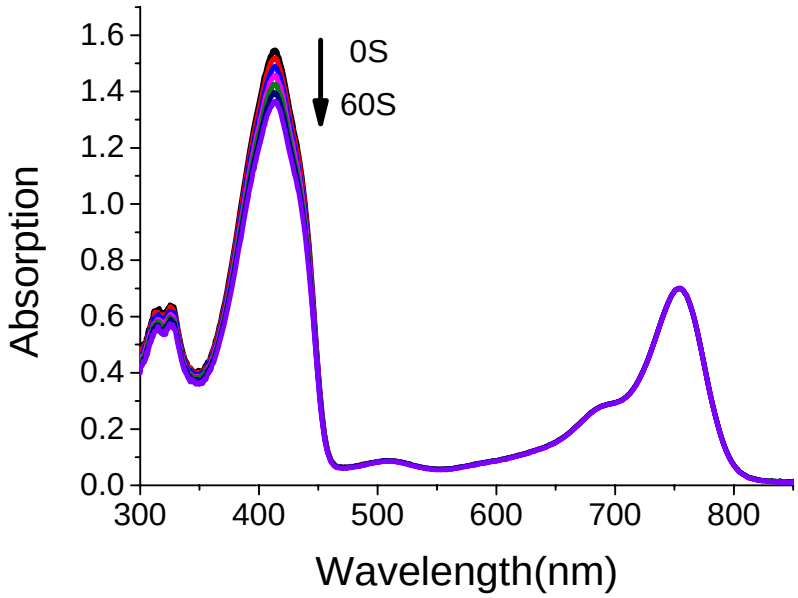


Figure S12. Absorption spectra of DPBF (5×10^{-5} mol/ L) upon irradiation in the presence of **1e** (5×10^{-6} mol/ L) for 60s. (a) 0 s to (b) 60s (recorded at 10s interval) under broad band light (>590 nm) in chloroform.

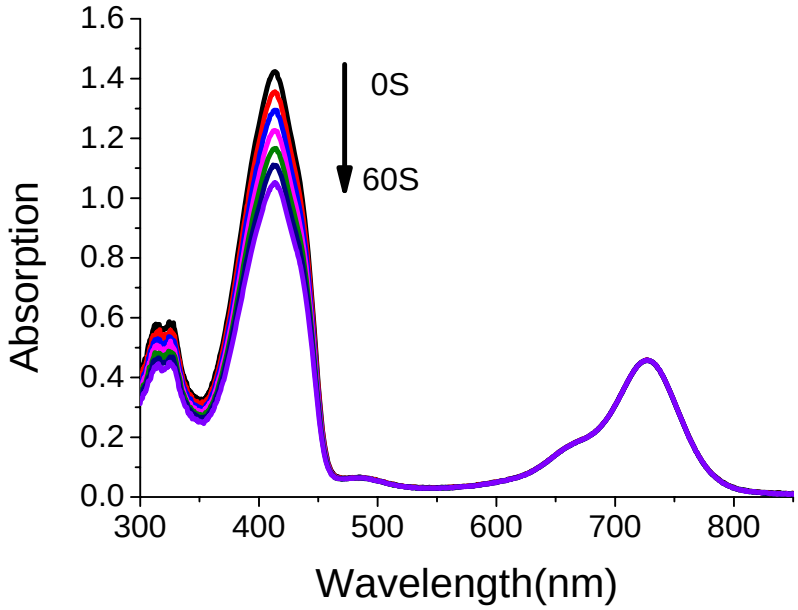


Figure S13. Absorption spectra of DPBF (5×10^{-5} mol/ L) upon irradiation in the presence of **2c** (5×10^{-6} mol/ L) for 60 s. (a) 0 s to (b) 60 s (recorded at 10 s interval) under broad band light (>590 nm) in chloroform.

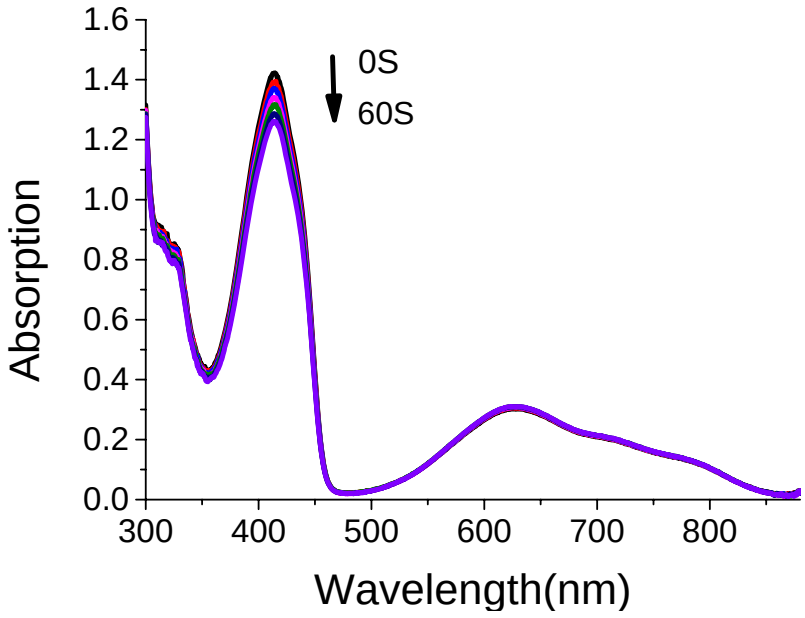


Figure S14. Absorption spectra of DPBF (5×10^{-5} mol/ L) upon irradiation in the presence of **3a** (5×10^{-6} mol/ L) for 60 s. (a) 0 s to (b) 60 s (recorded at 10 s interval) under broad band light (>590 nm) in chloroform.

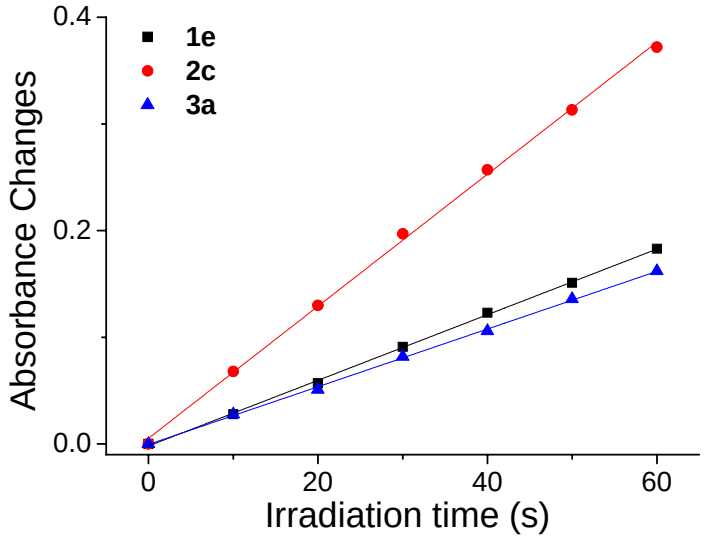


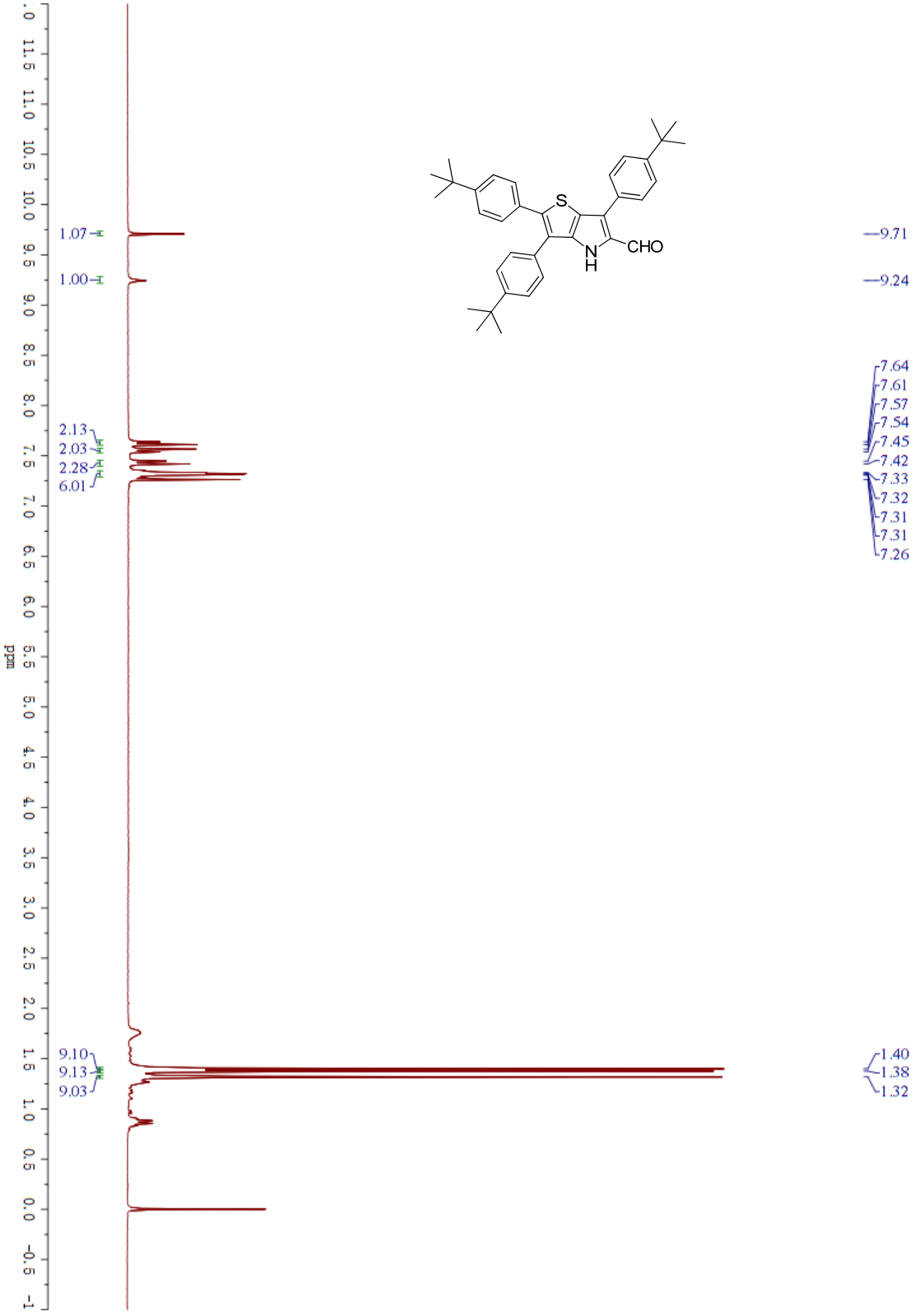
Figure S15. Comparative DPBF (initial concentration at 4×10^{-5} M) degradation profiles (absorption changes at 415 nm) in chloroform by **1e** (black), **2c** (red) and **3a** (blue) (5×10^{-6} M). Filtered light > 590 nm was used.

3. Table S2: Photophysical properties of 1e-f, 2a-c and 3a-b in different solvents at room temperature (DMSO: Dimethyl sulfoxide).

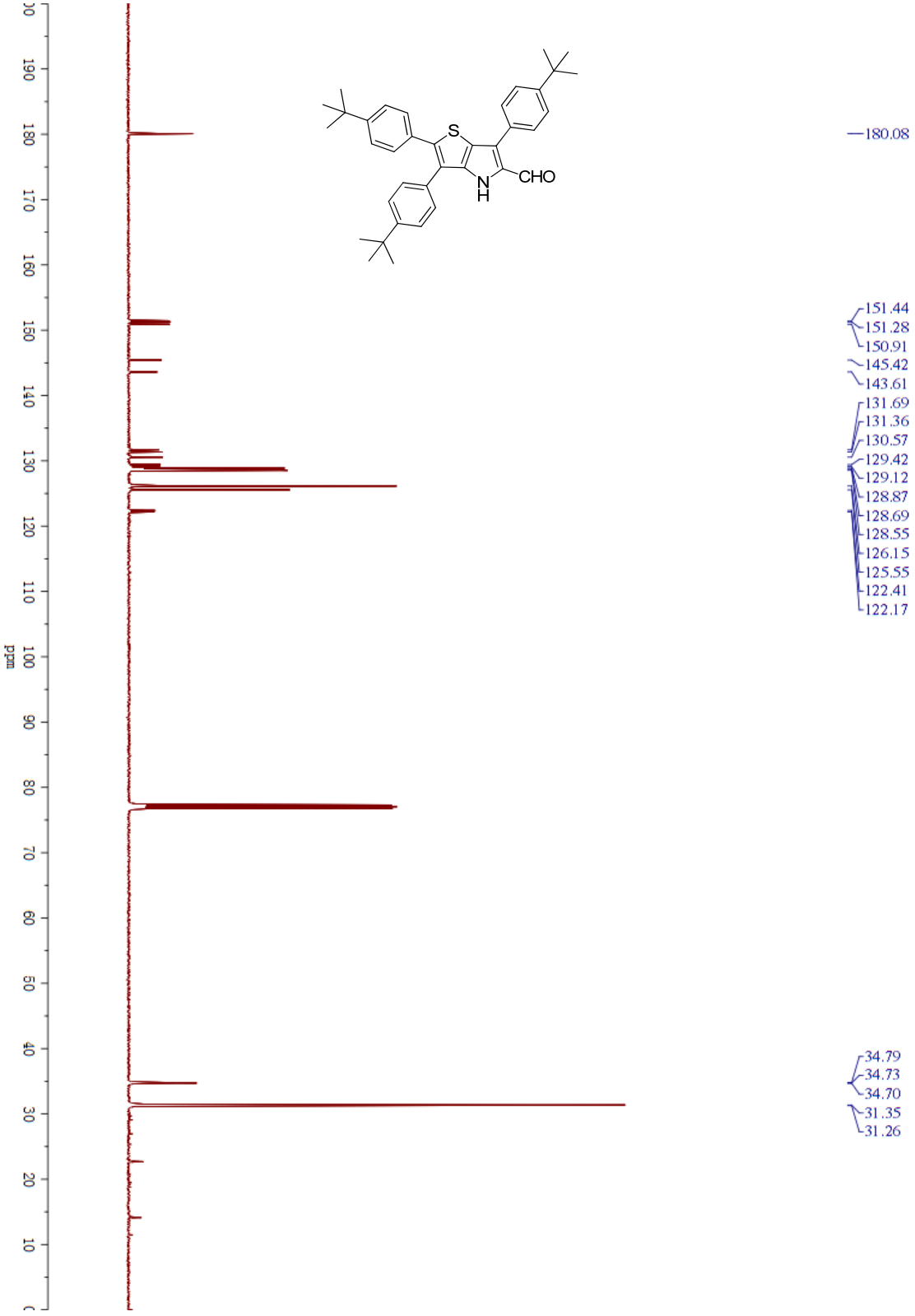
BODIPYs	solvents	λ_{abs}^{max} (nm)	λ_{em}^{max} (nm)	$\log\varepsilon_{max}$ [a]	ϕ [c]	Stokes Shift (cm^{-1})
1e	cyclohexane	746	778	5.22	0.02	551
	toluene	757	798	4.97	0.02	679
	chloromethane	757	796	5.22	0.02	647
	DMSO	761	806	5.19	0.01	734
	acetonitrile	745	788	5.18	0.01	732
1f	cyclohexane	757	792	5.21	0.05	584
	toluene	767	795	5.18	0.07	459
	chloromethane	767	803	5.21	0.05	585
	DMSO	756	812	5.14	0.01	912
	acetonitrile	771	802	5.14	0.01	501
2a	cyclohexane	661	687	5.19	0.86	573
	toluene	668	692	5.15	0.76	519
	chloromethane	670	694	5.20	0.85	516
	DMSO	664	695	5.08	0.61	672
	acetonitrile	655	683	5.18	0.68	626
2b	cyclohexane	671	694	5.17	0.85	494
	toluene	678	702	5.17	0.76	504
	chloromethane	677	700	5.26	0.82	485
	DMSO	679	710	5.10	0.52	643
	acetonitrile	665	697	5.16	0.56	690
2c	cyclohexane	735	769	5.07	0.001	602
	toluene	718	788	5.10	0.002	1237
	chloromethane	730	783	5.08	0.002	927
	DMSO	732	793	5.01	0.001	1051
	acetonitrile	721	779	5.09	0.001	1033
3a	cyclohexane	626	692	4.76	0.002	1524
	toluene	635	693	4.73	0.001	1318
	chloromethane	628	709	4.73	0.001	1819
	DMSO	630	-[c]	4.68	-	-
	acetonitrile	-	-	-	-	-
3b	cyclohexane	618	697	4.70	0.01	1834
	toluene	623	708	4.71	0.004	1927
	cyclohexane	618	697	4.70	0.01	1834
	DMSO	626	-	4.65	-	-
	acetonitrile	-	-	-	-	-

[a]Molar extinction coefficients are in the maximum of the highest peak. [b]Fluorescence quantum yields of **1e-f** were calculated using ICG (ϕ = 0.12 in DMSO), **2a-c** were calculated using 1,7-diphenyl-3,5- di(*p*-methoxyphenyl)-azadipyrromethene (ϕ = 0.36 in chloroform), **3a-b** were calculated using 1,3,5,7-tetraphenyl-azadipyrromethene (ϕ = 0.34 in chloroform). [c]"-" means no data available due to poor solubility or very low emission.

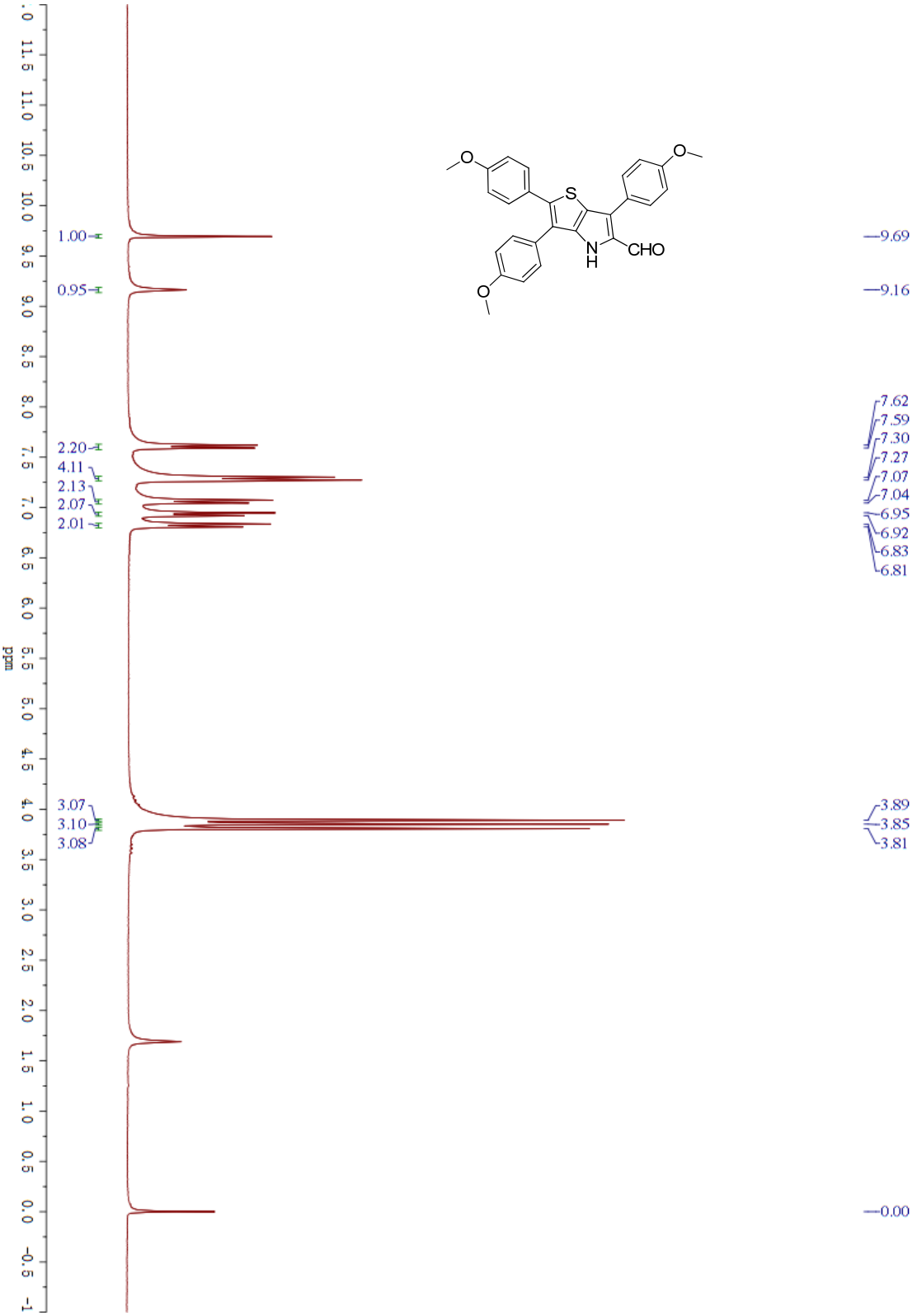
4. Copies of ^{1}H NMR and ^{13}C NMR spectra



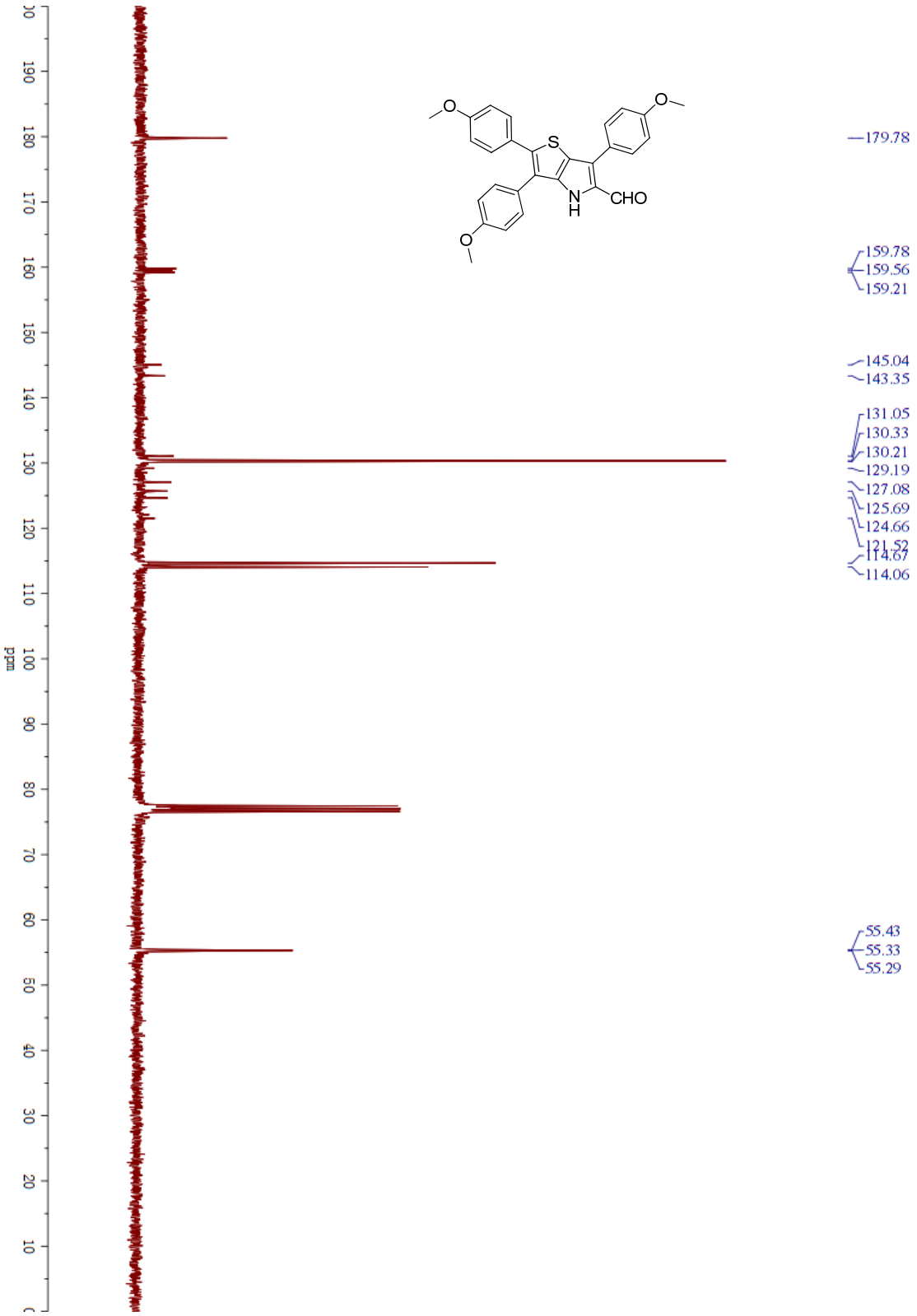
^{1}H NMR spectrum of **Compound 8a** in $CDCl_3$ solution.



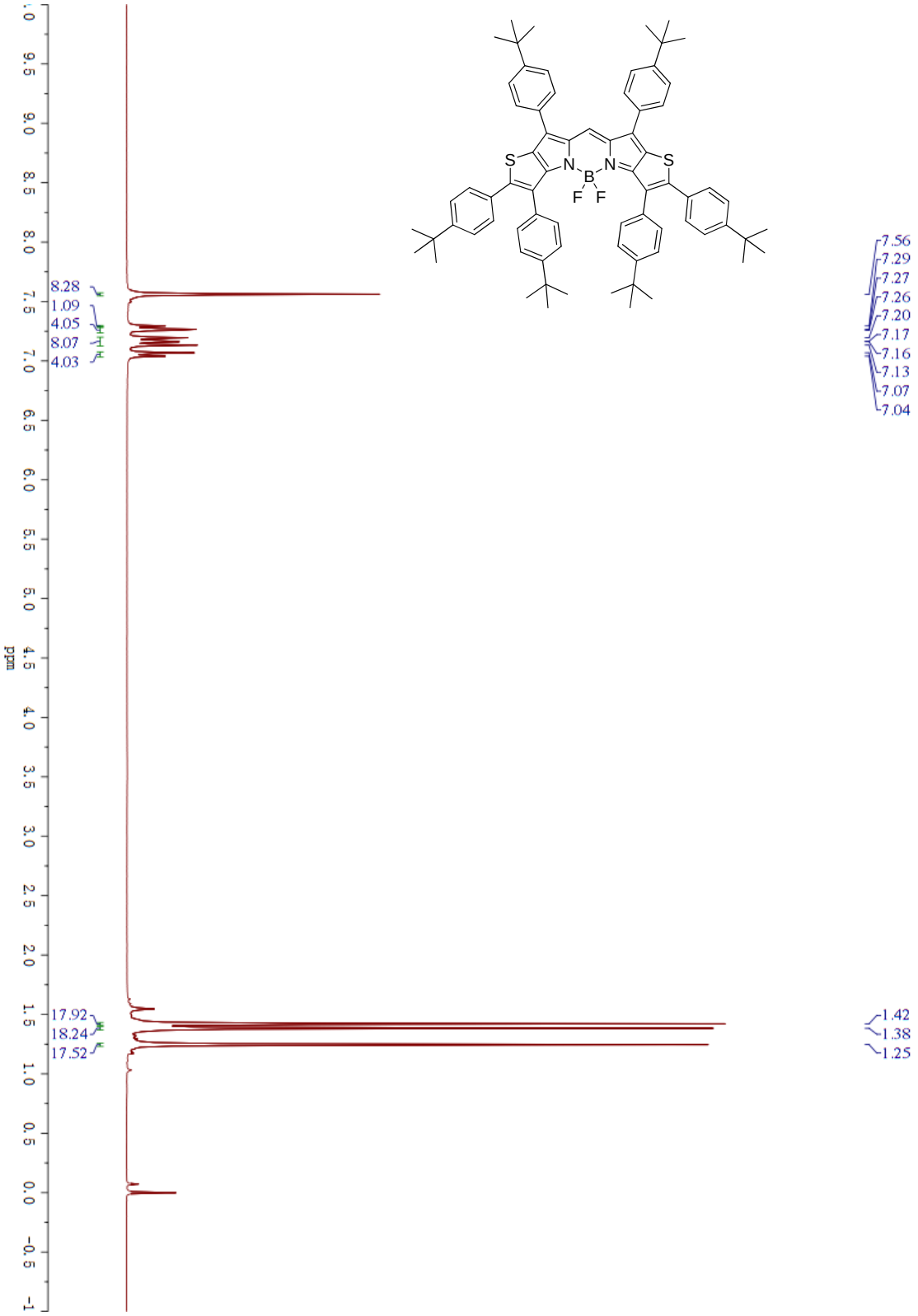
^{13}C NMR spectrum of **Compound 8a** in $CDCl_3$ solution.



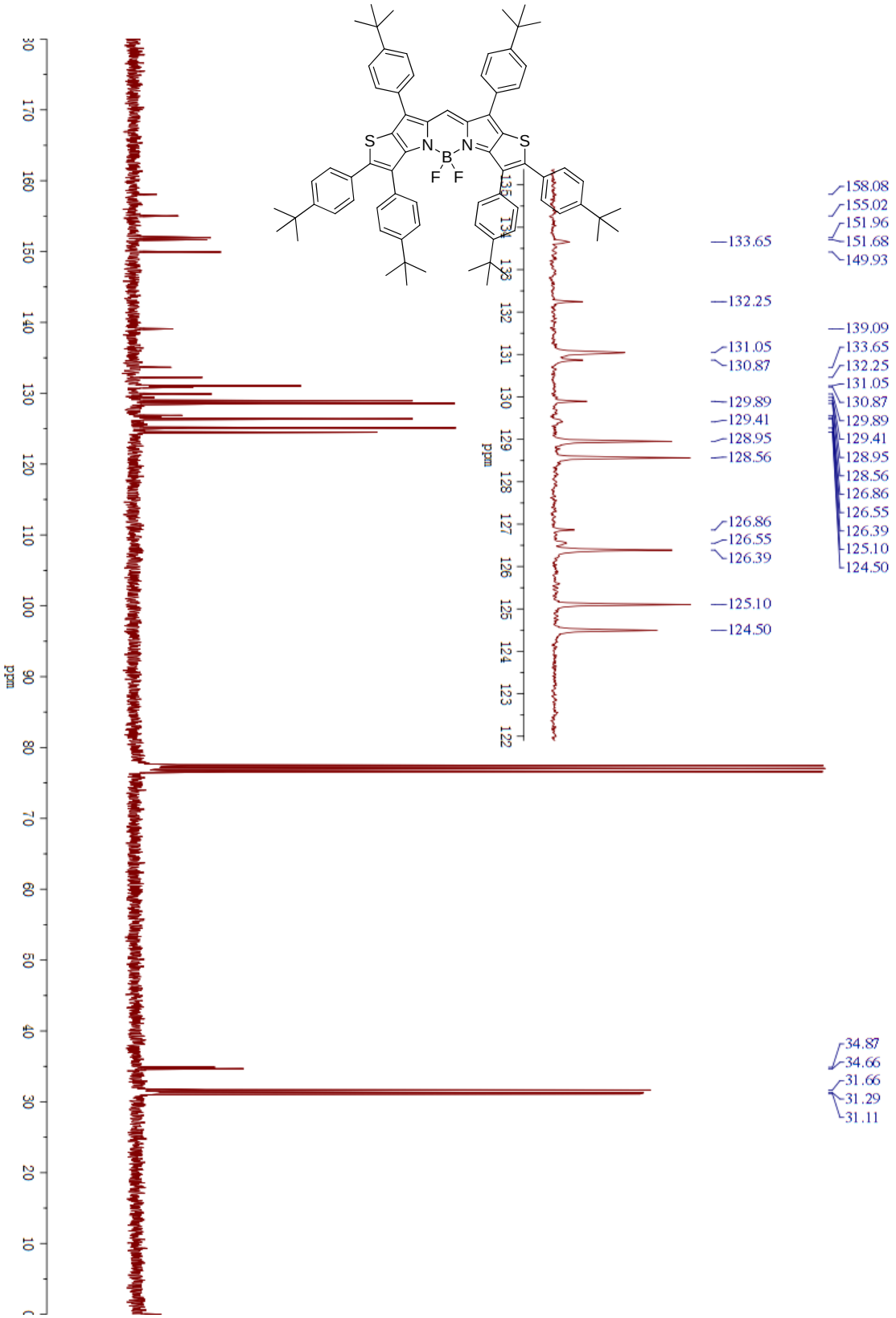
^{1}H NMR spectrum of **Compound 8b** in $CDCl_3$ solution.



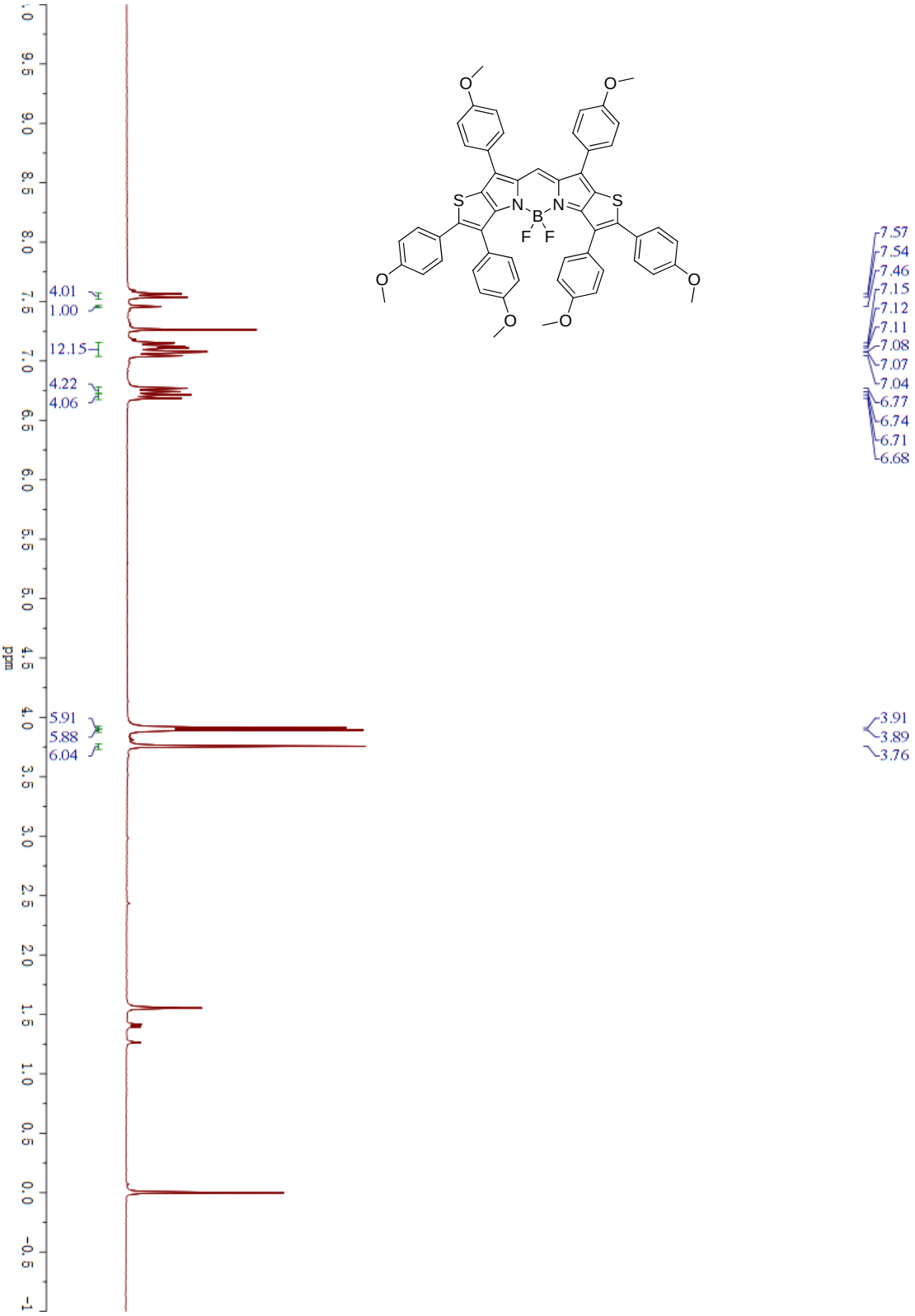
^{13}C NMR spectrum of **Compound 8b** in $CDCl_3$ solution.



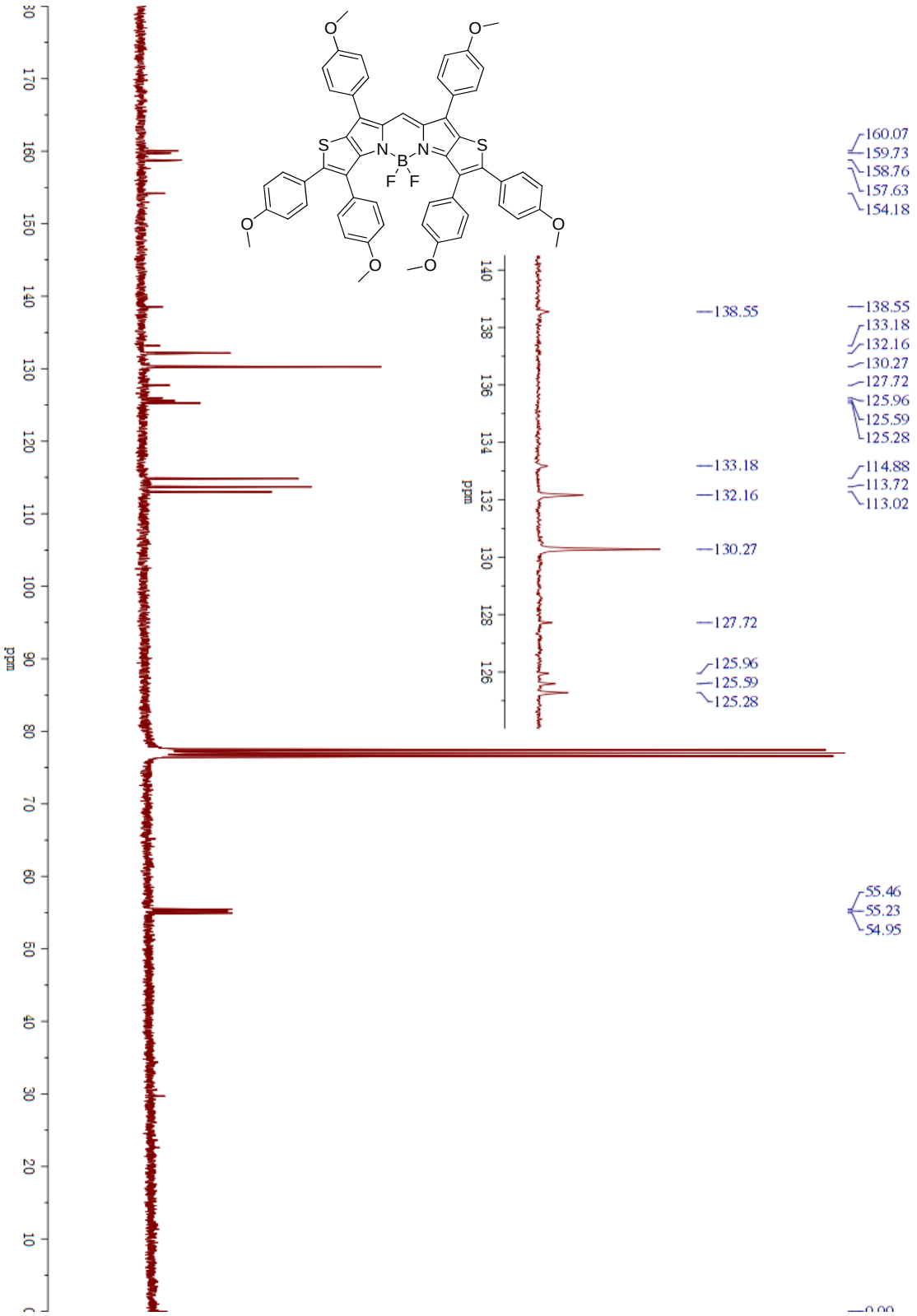
^{1}H NMR spectrum of **Compound 2a** in $CDCl_3$ solution.



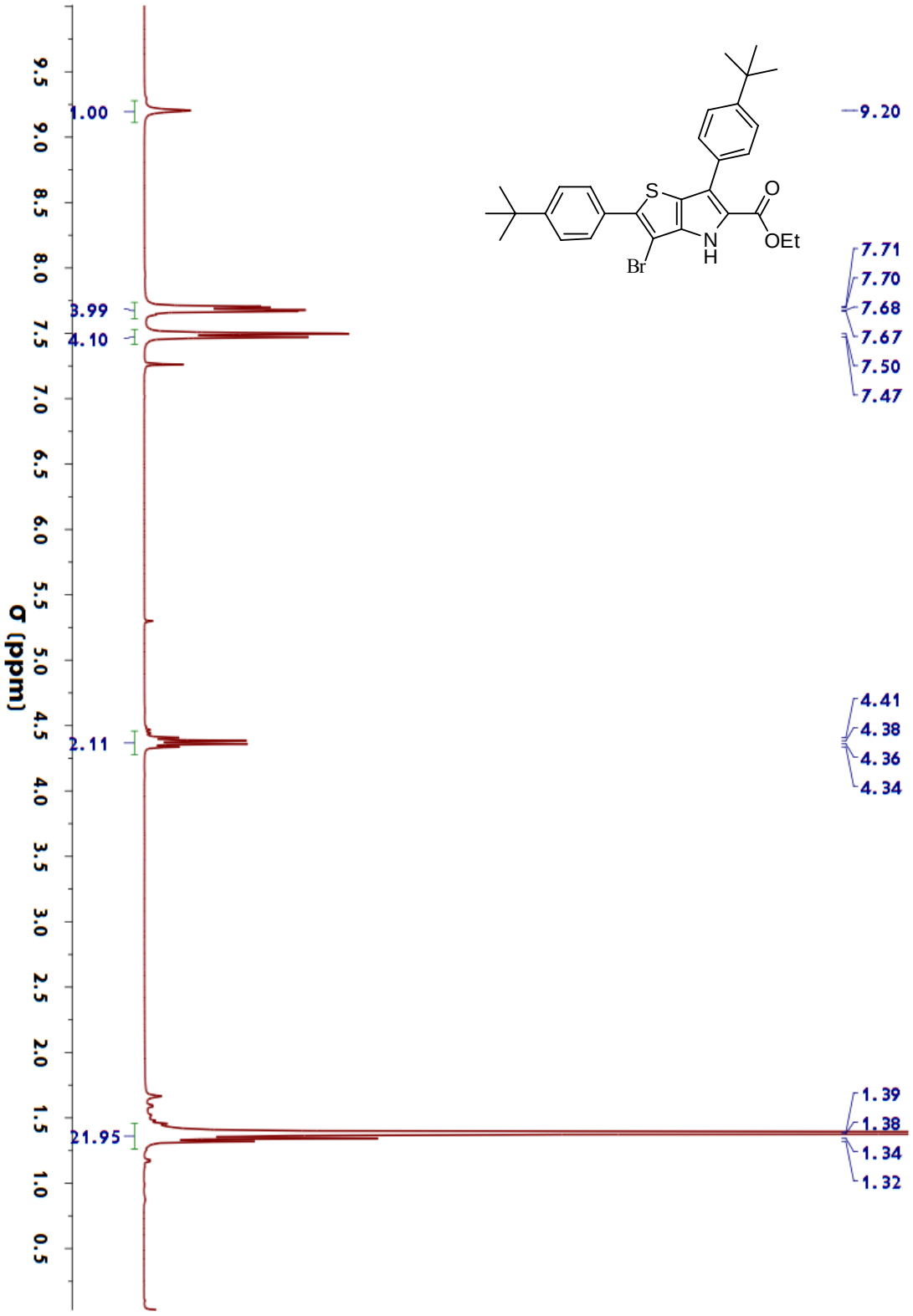
^{13}C NMR spectrum of **Compound 2a** in $CDCl_3$ solution.



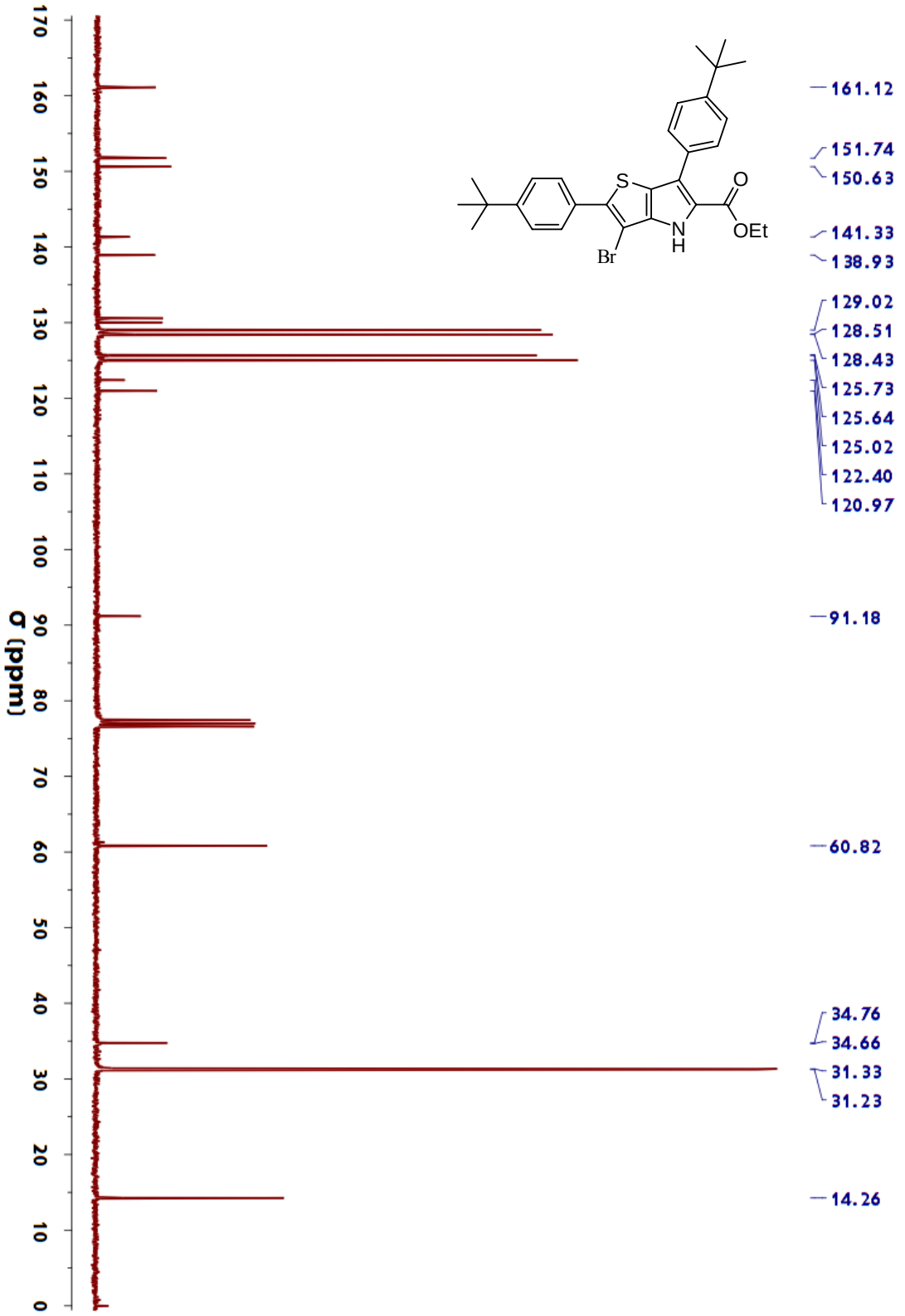
^{1}H NMR spectrum of **Compound 2b** in $CDCl_3$ solution.



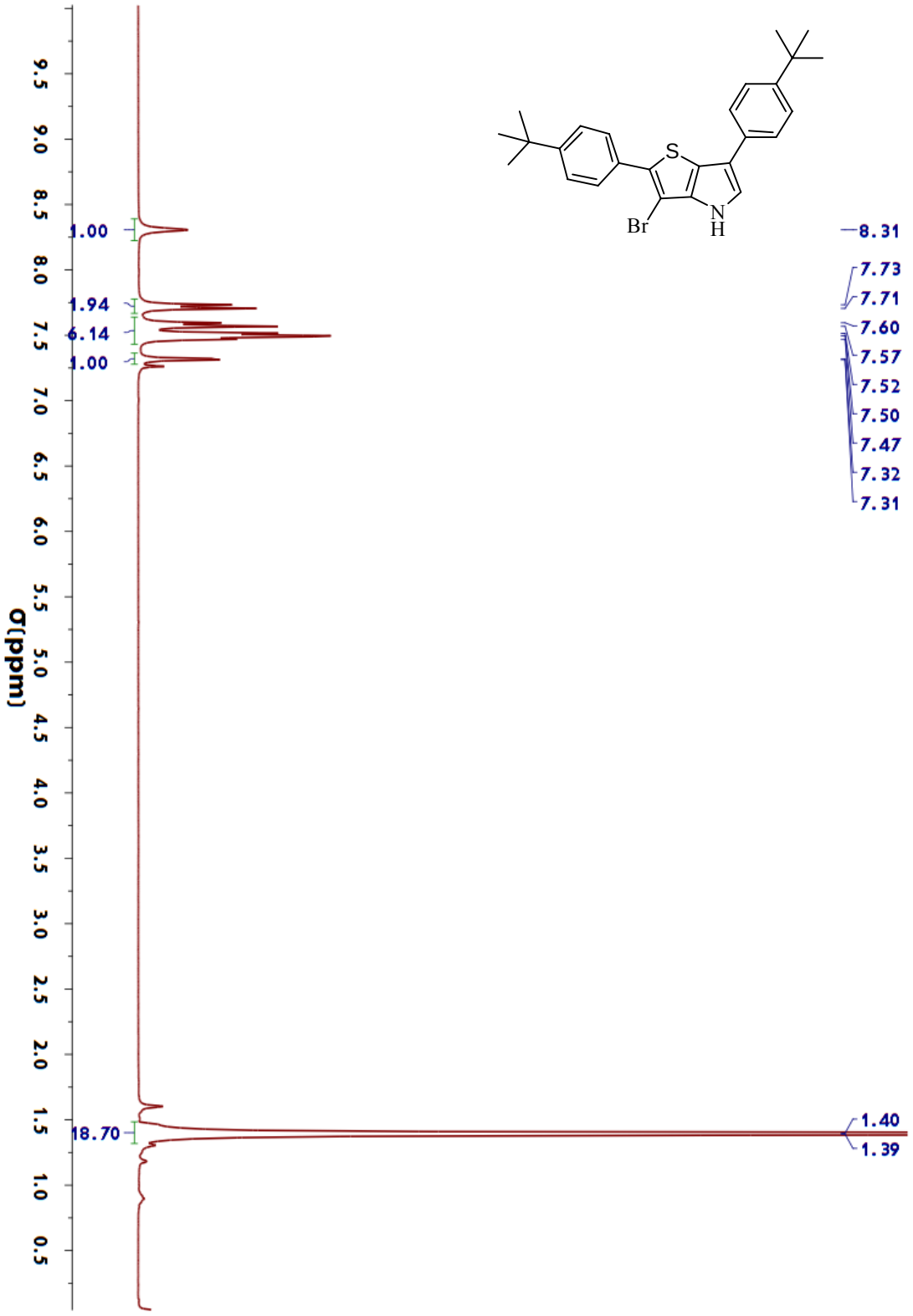
^{13}C NMR spectrum of **Compound 2b** in $CDCl_3$ solution.



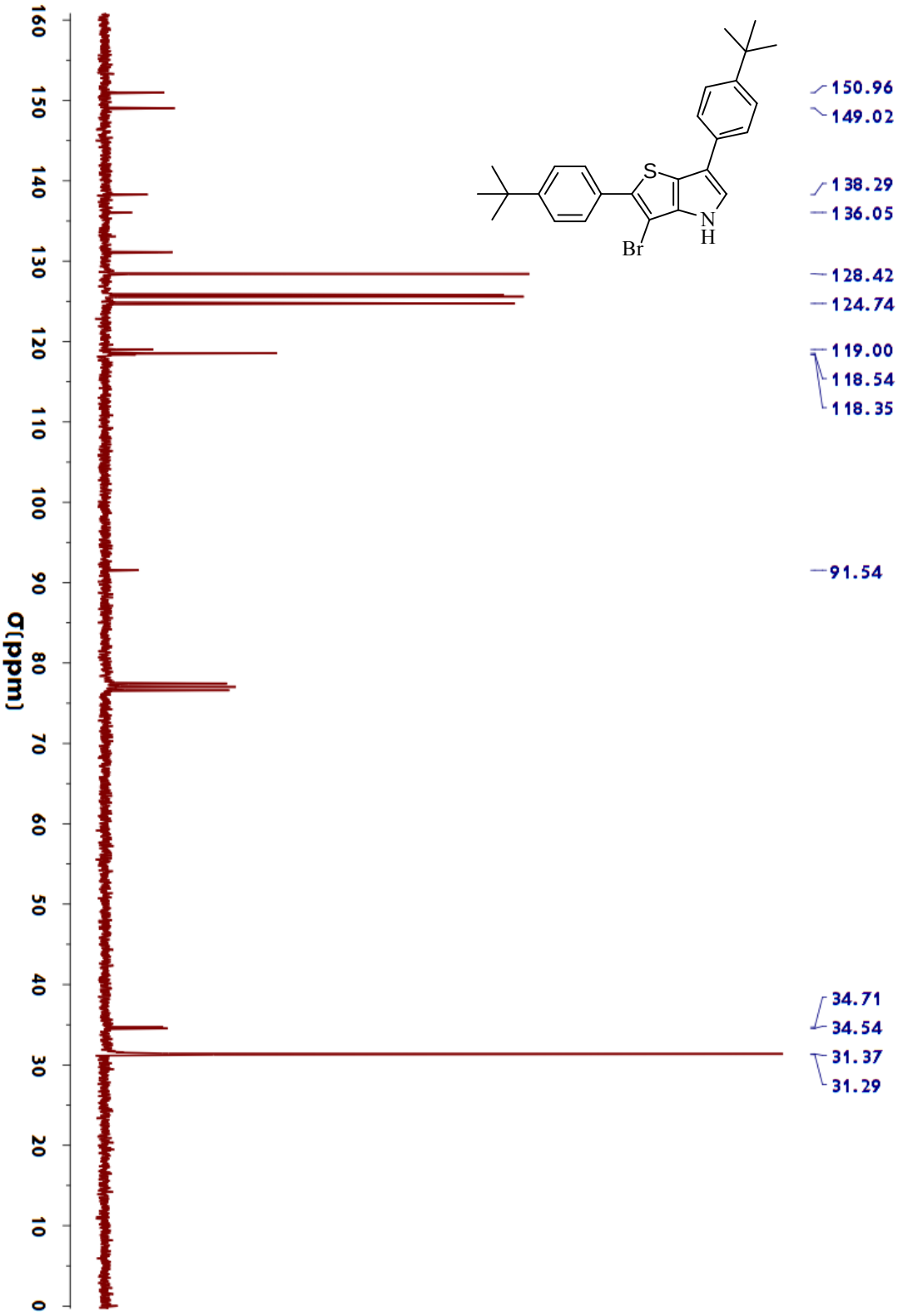
^{1}H NMR spectrum of **Compound 6e** in $CDCl_3$ solution.



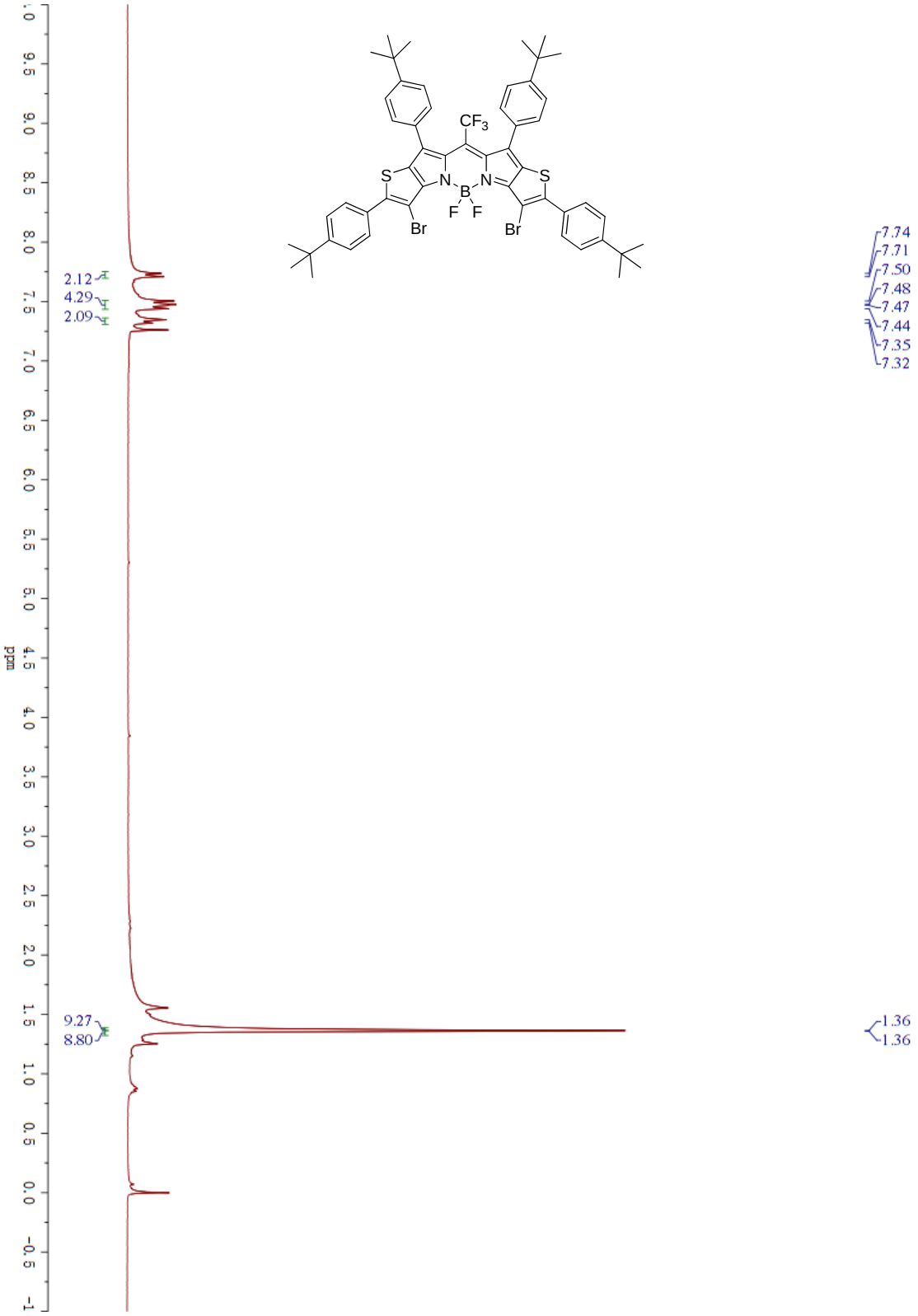
^{13}C NMR spectrum of **Compound 6e** in $CDCl_3$ solution.



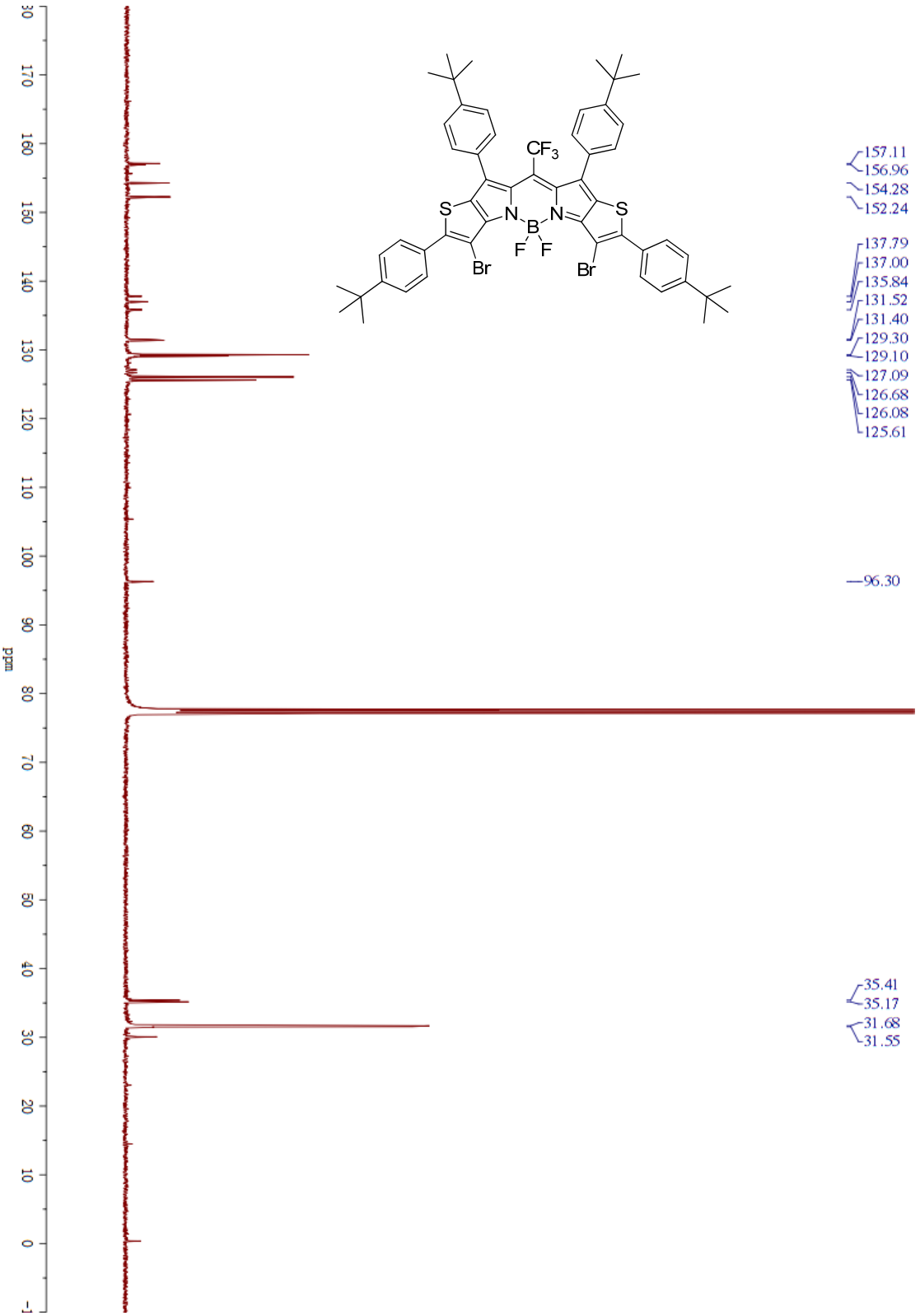
^{1}H NMR spectrum of **Compound 7e** in $CDCl_3$ solution.



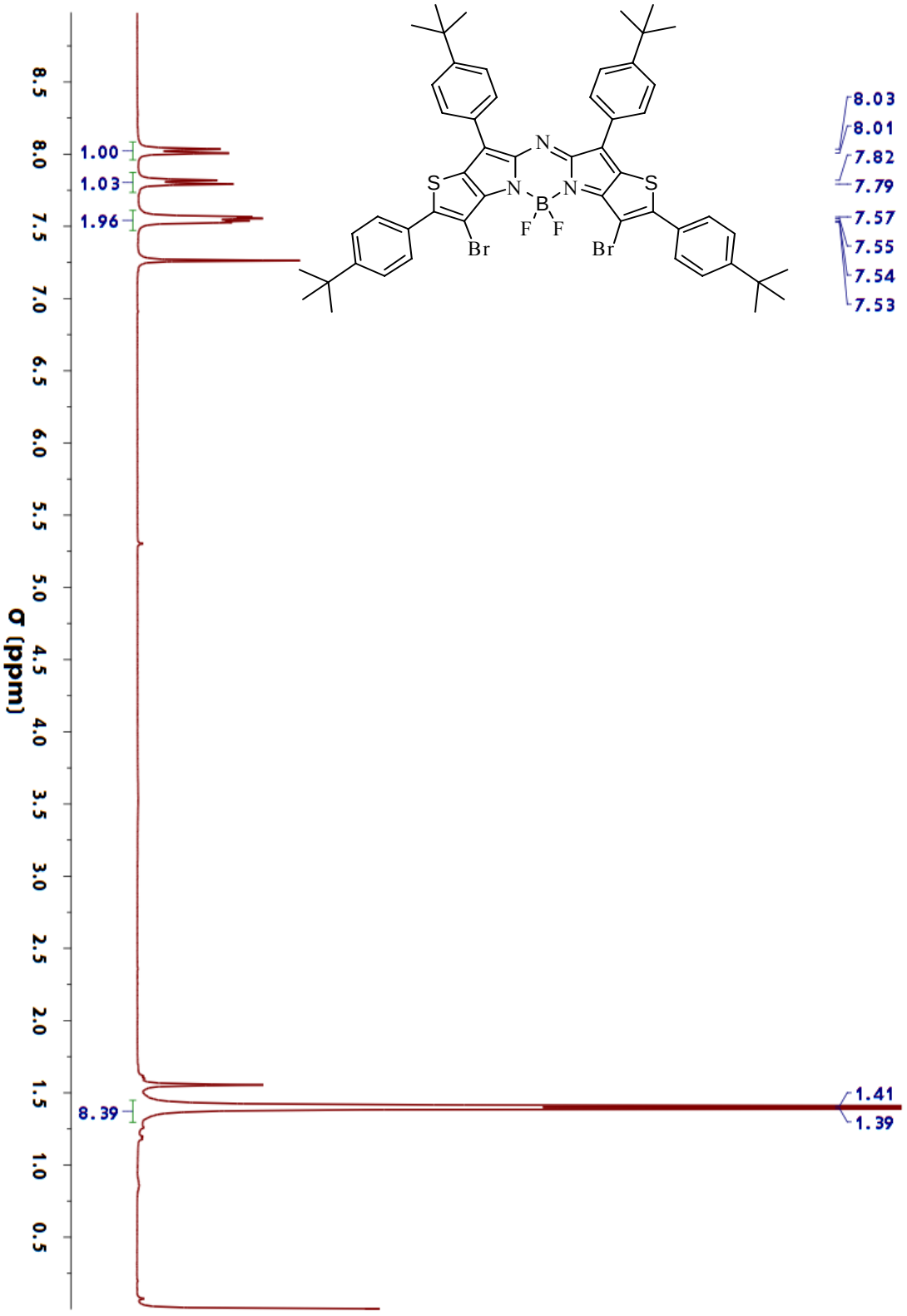
^{13}C NMR spectrum of **Compound 7e** in $CDCl_3$ solution.



^{1}H NMR spectrum of **Compound 2c** in $CDCl_3$ solution.



^{13}C NMR spectrum of **Compound 2c** in $CDCl_3$ solution.



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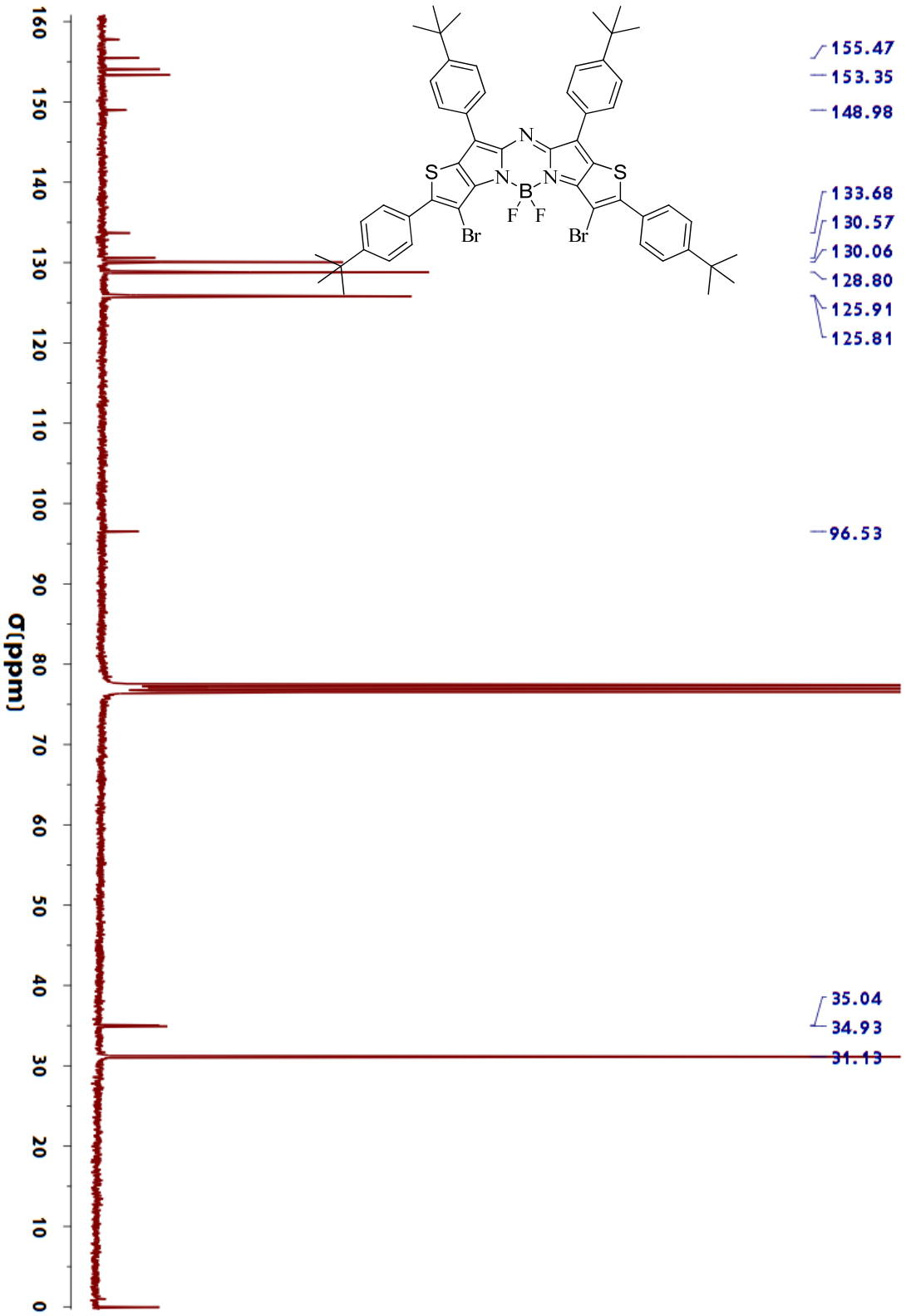

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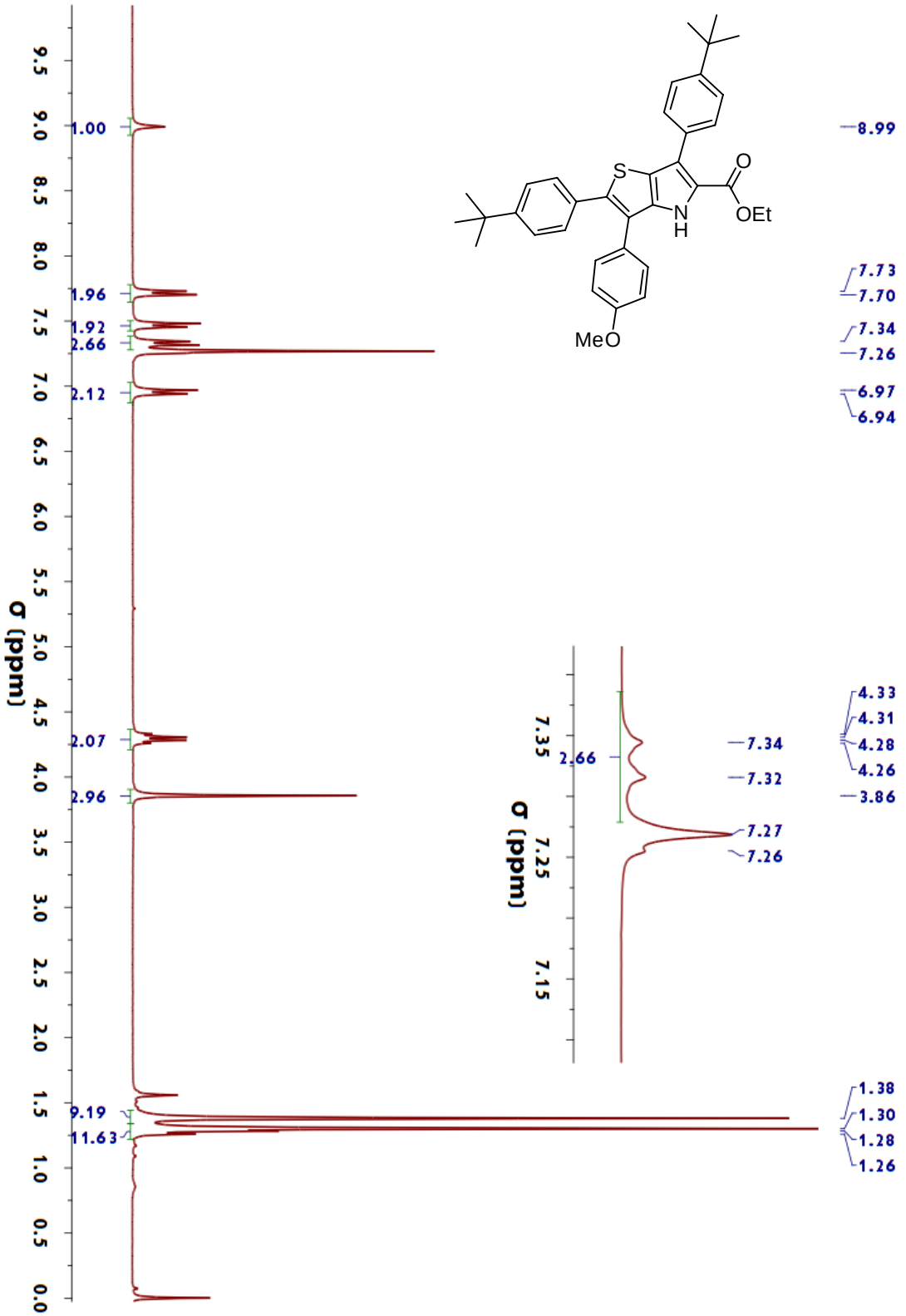

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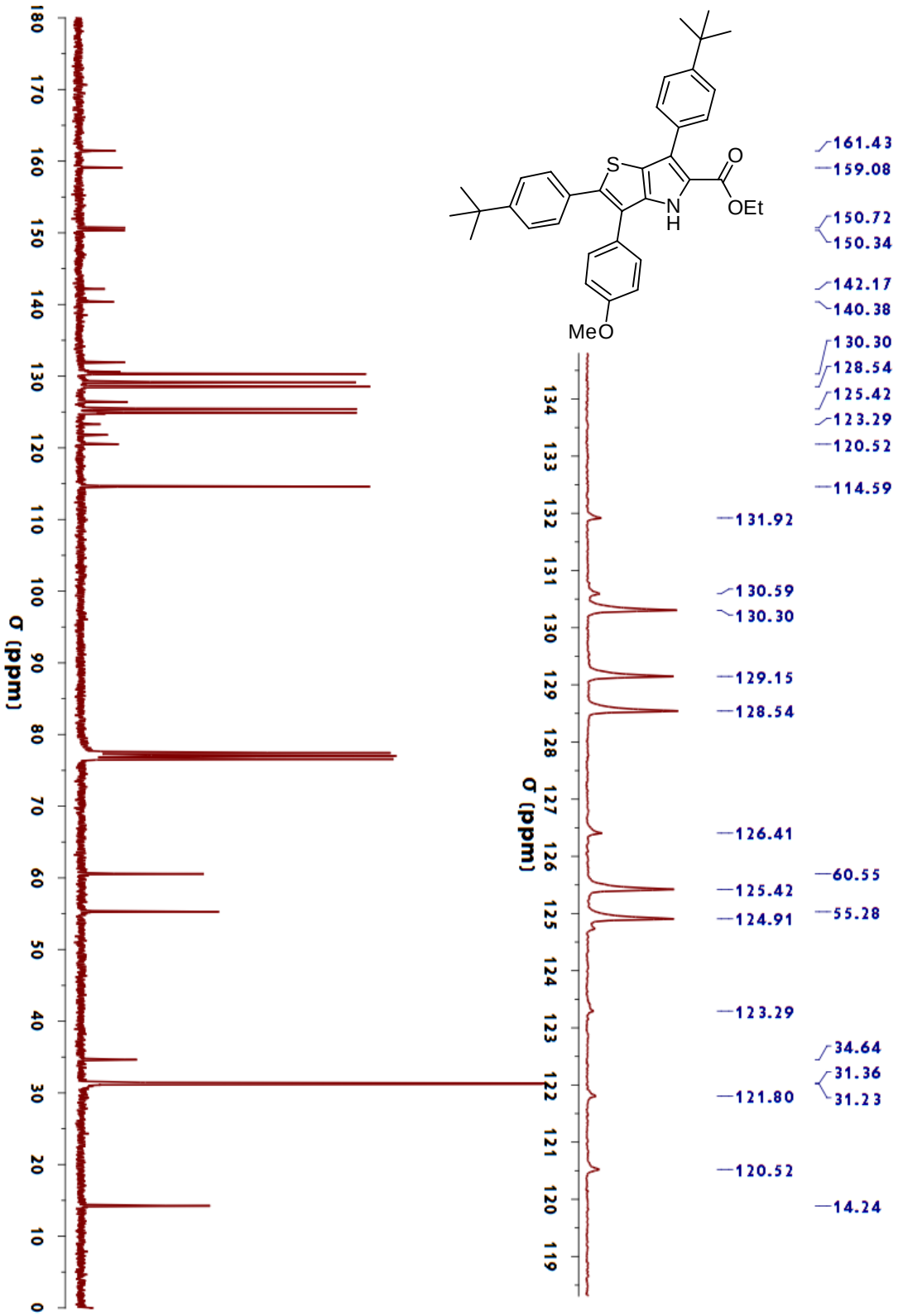

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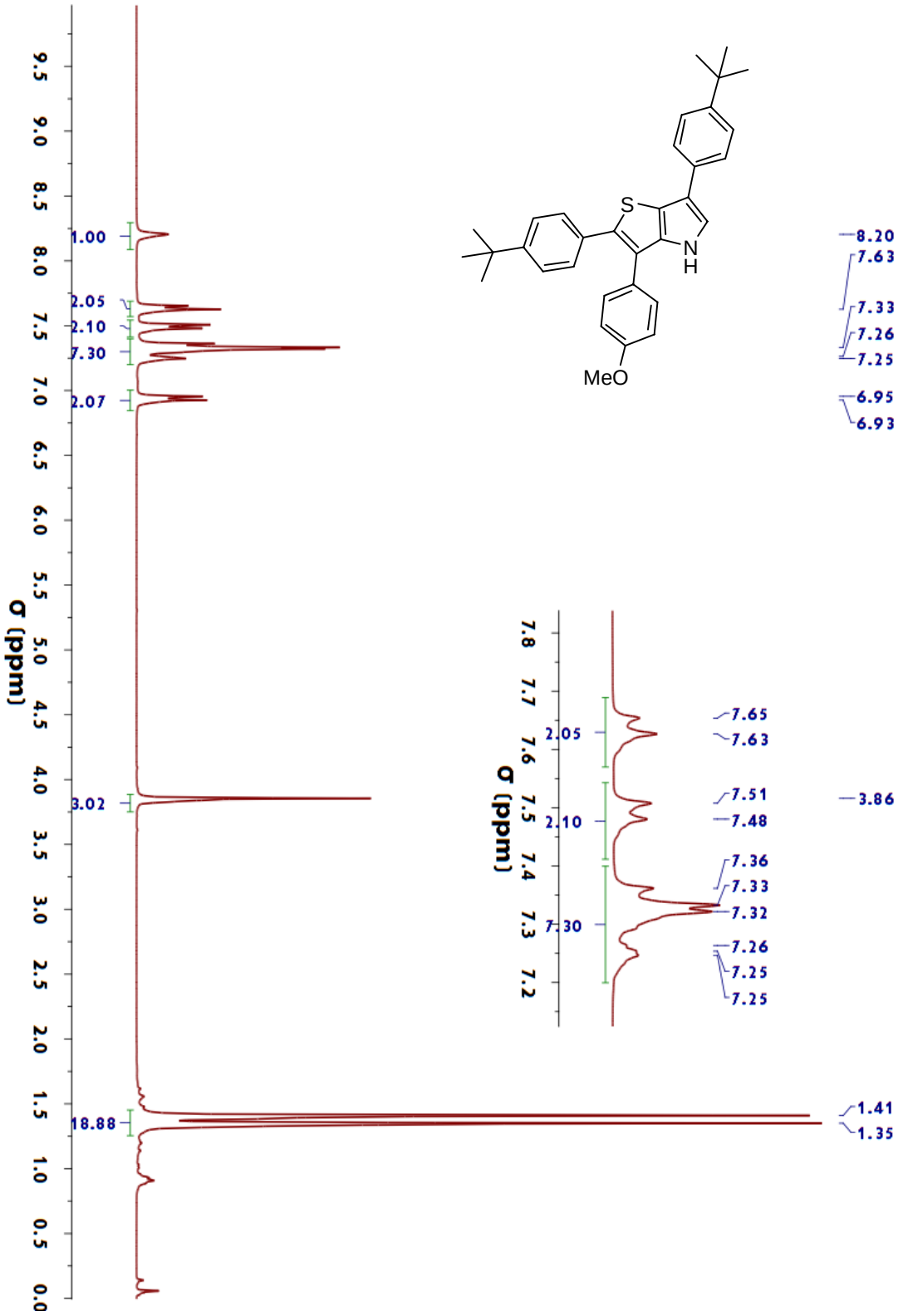
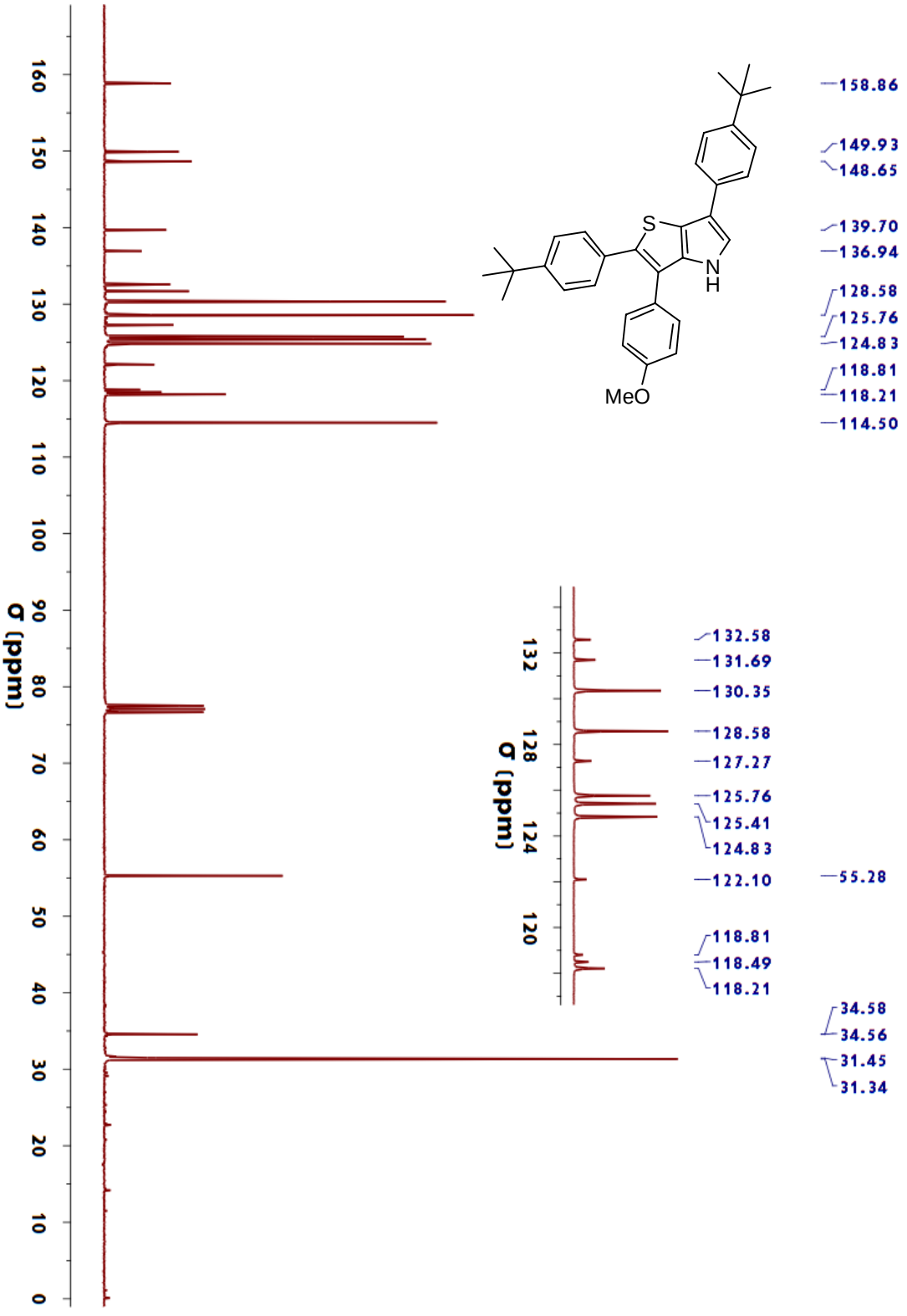
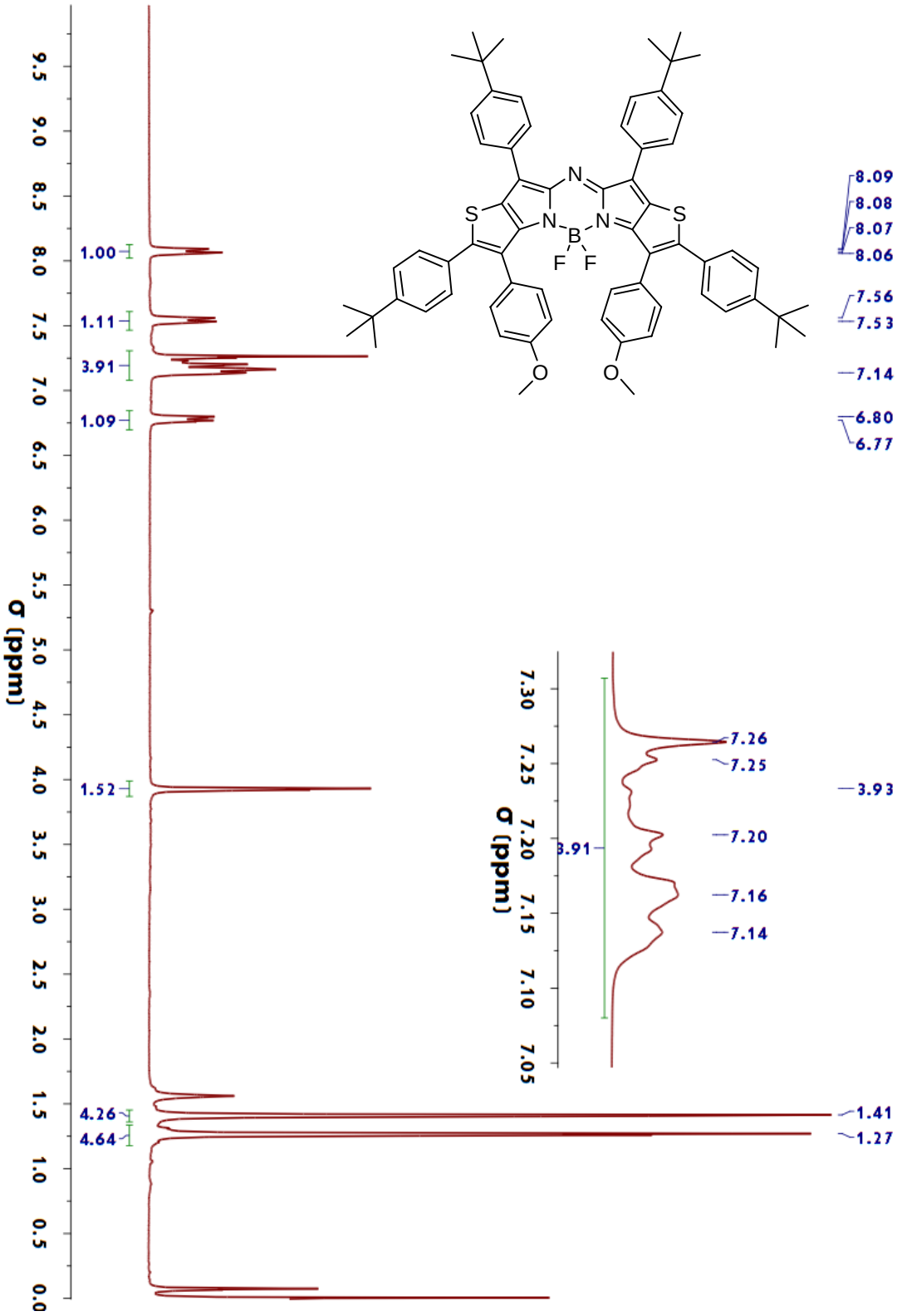


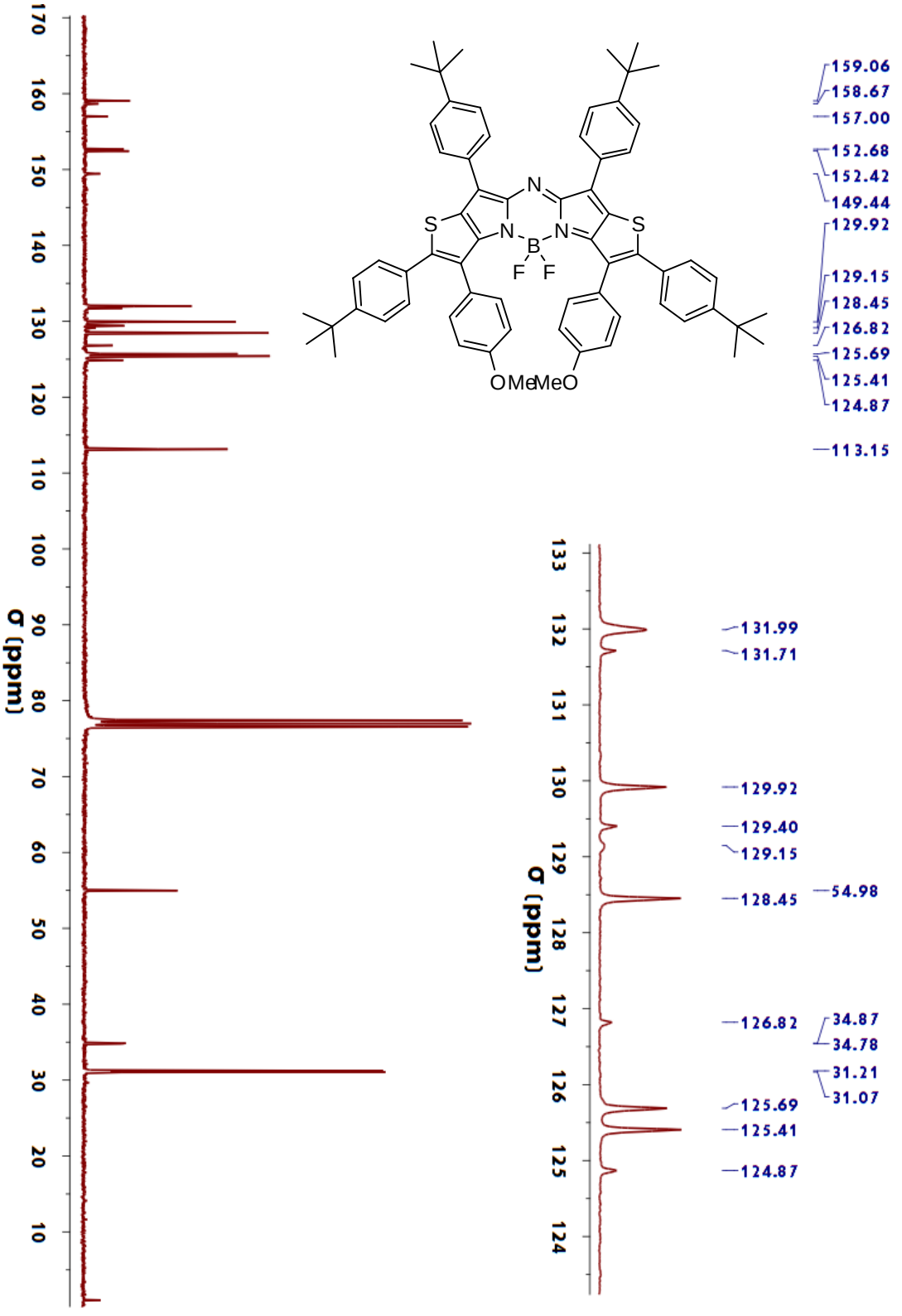
^{1}H NMR spectrum of **Compound 7f** in $CDCl_3$ solution.



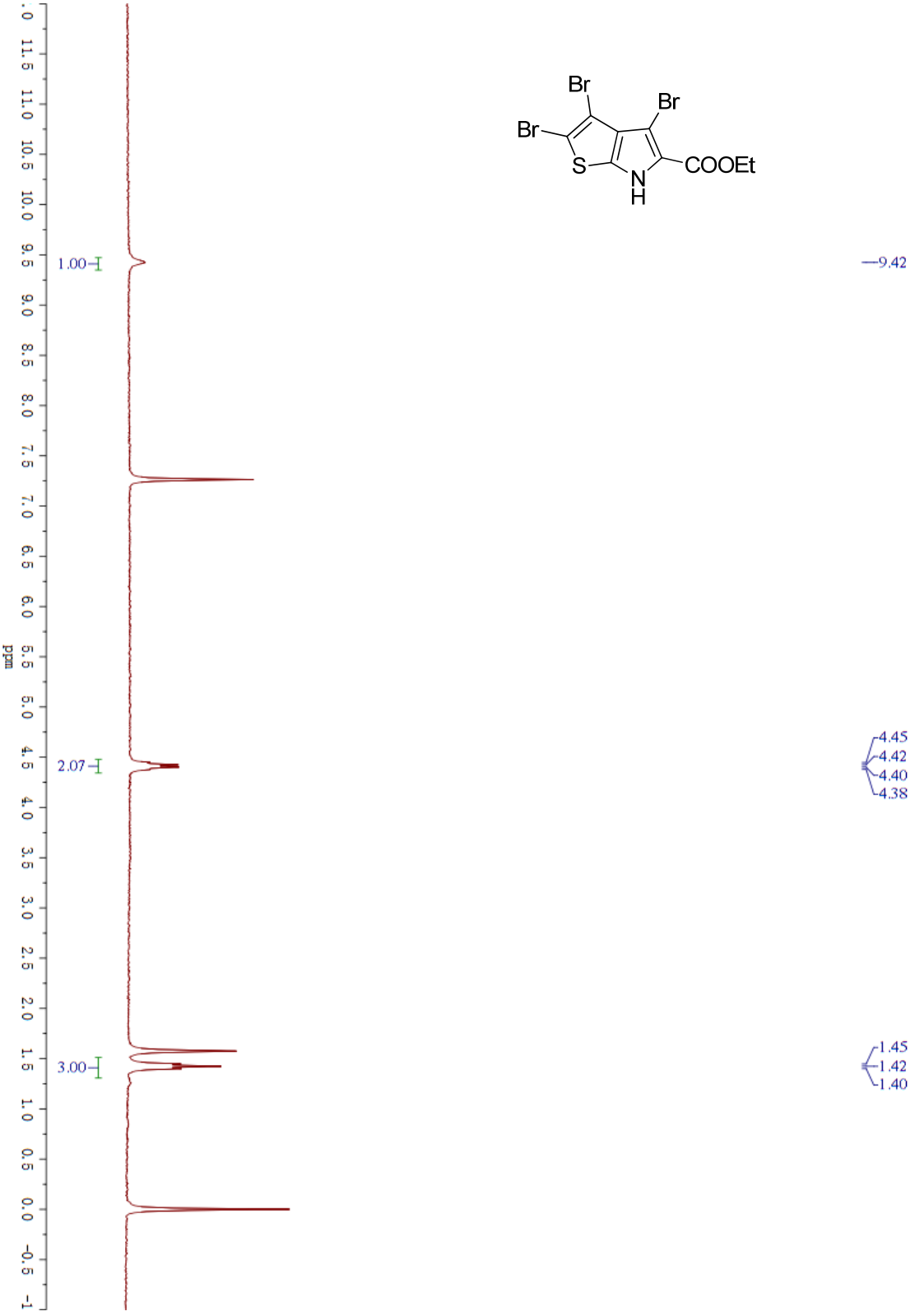
^{13}C NMR spectrum of **Compound 7f** in $CDCl_3$ solution.



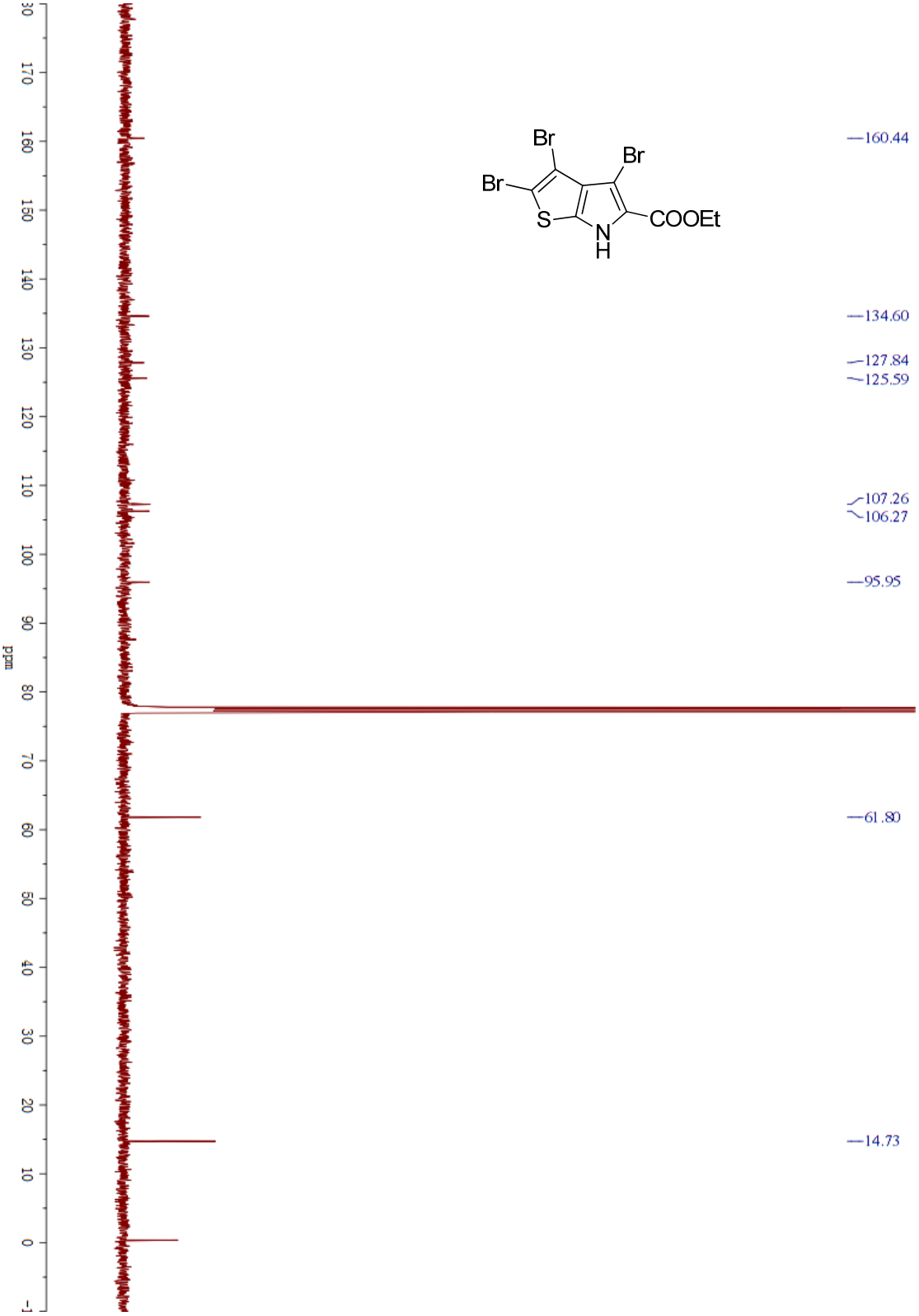
^{1}H NMR spectrum of **Compound 1f** in $CDCl_3$ solution.



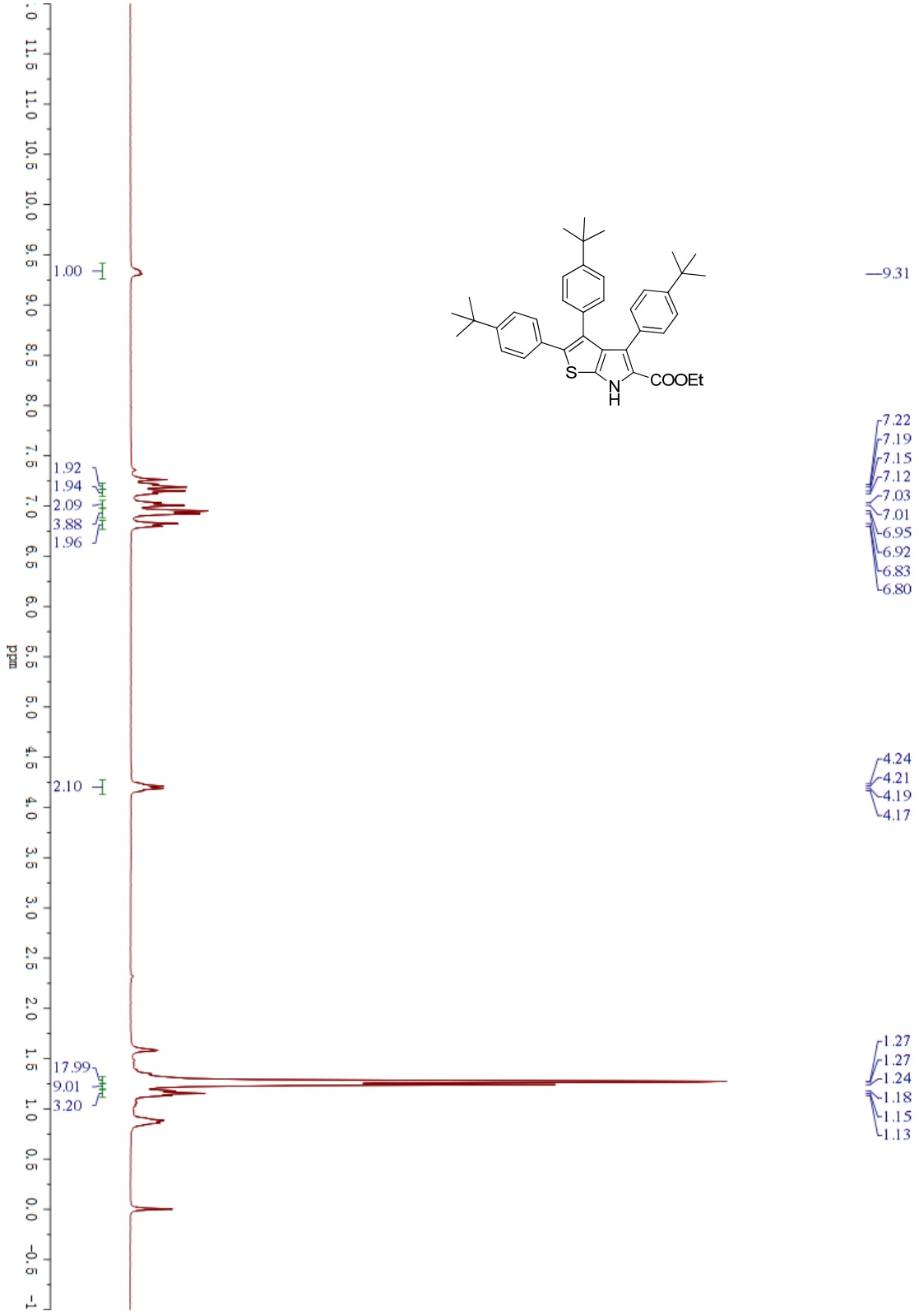
^{13}C NMR spectrum of **Compound 1f** in $CDCl_3$ solution.



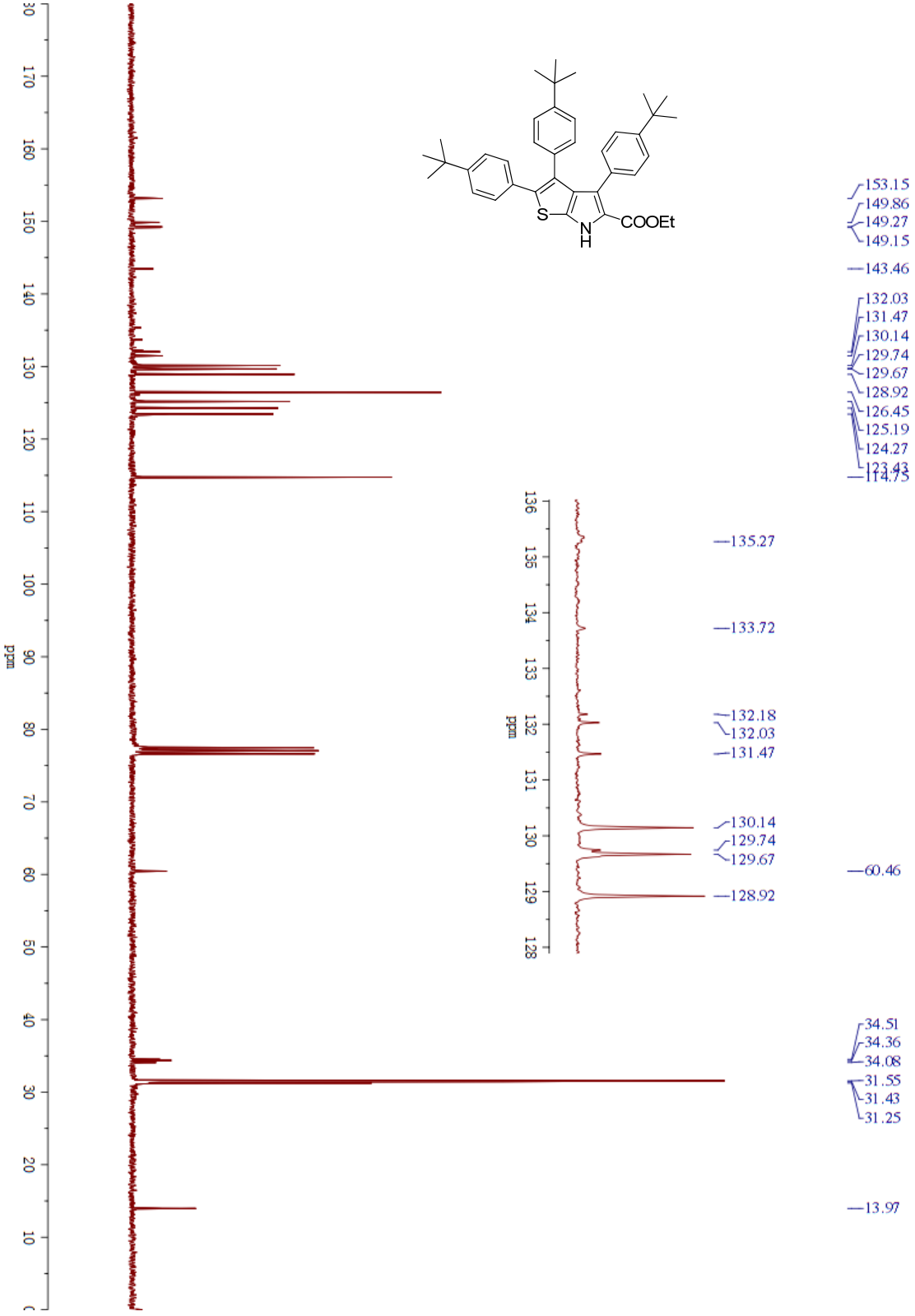
^{1}H NMR spectrum of **Compound 10** in $CDCl_3$ solution.



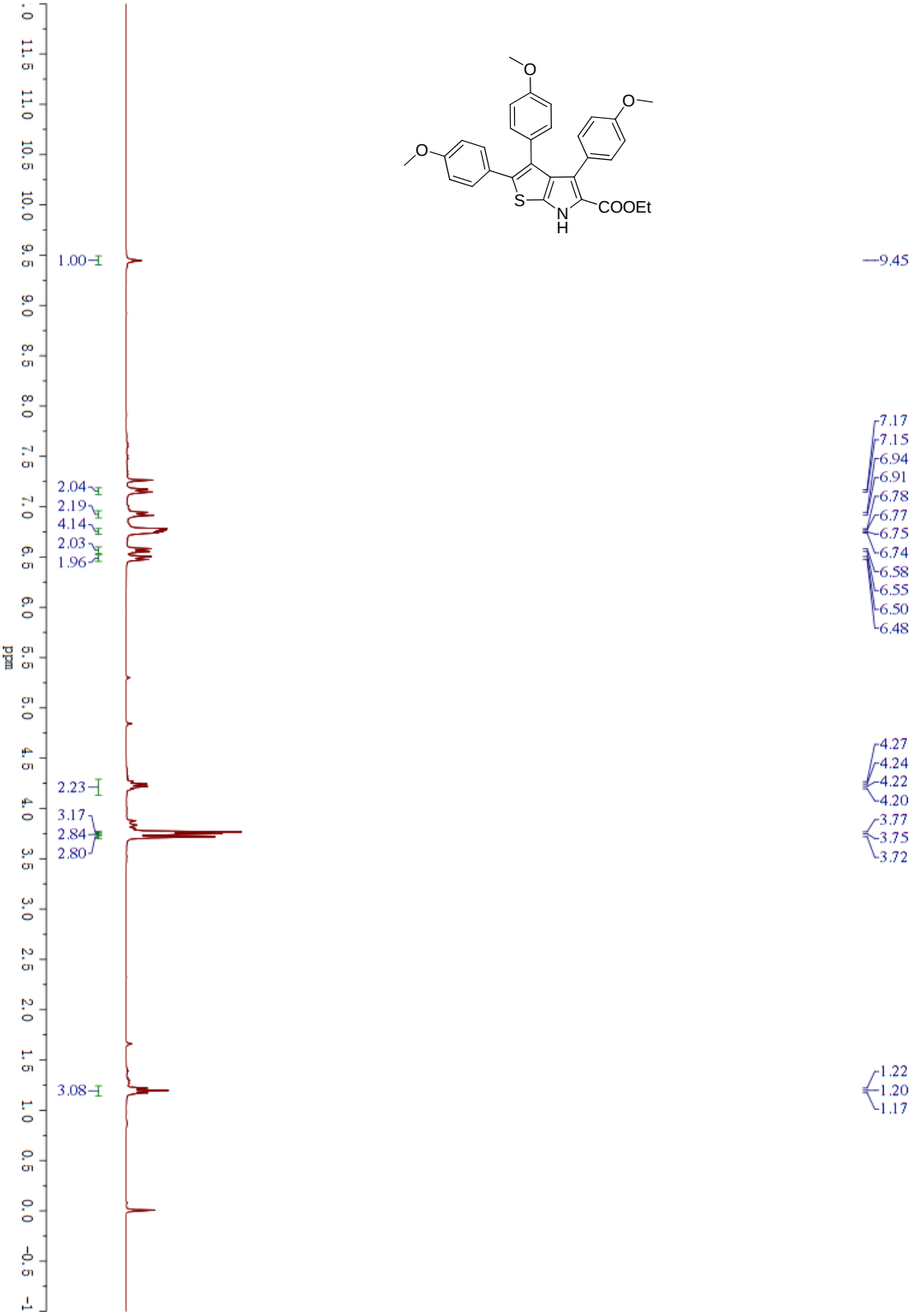
^{13}C NMR spectrum of **Compound 10** in $CDCl_3$ solution



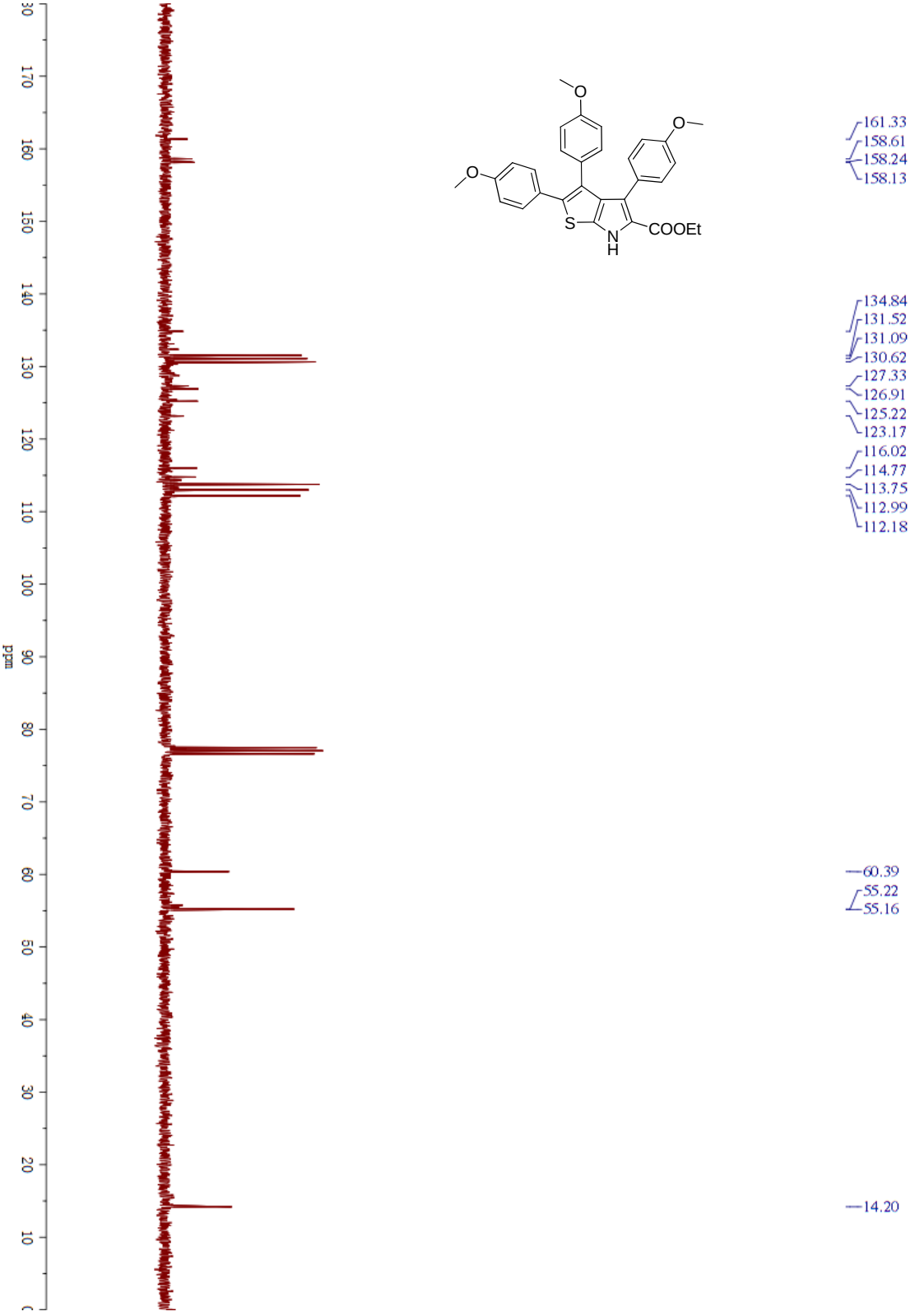
^{1}H NMR spectrum of **Compound 11a** in $CDCl_3$ solution



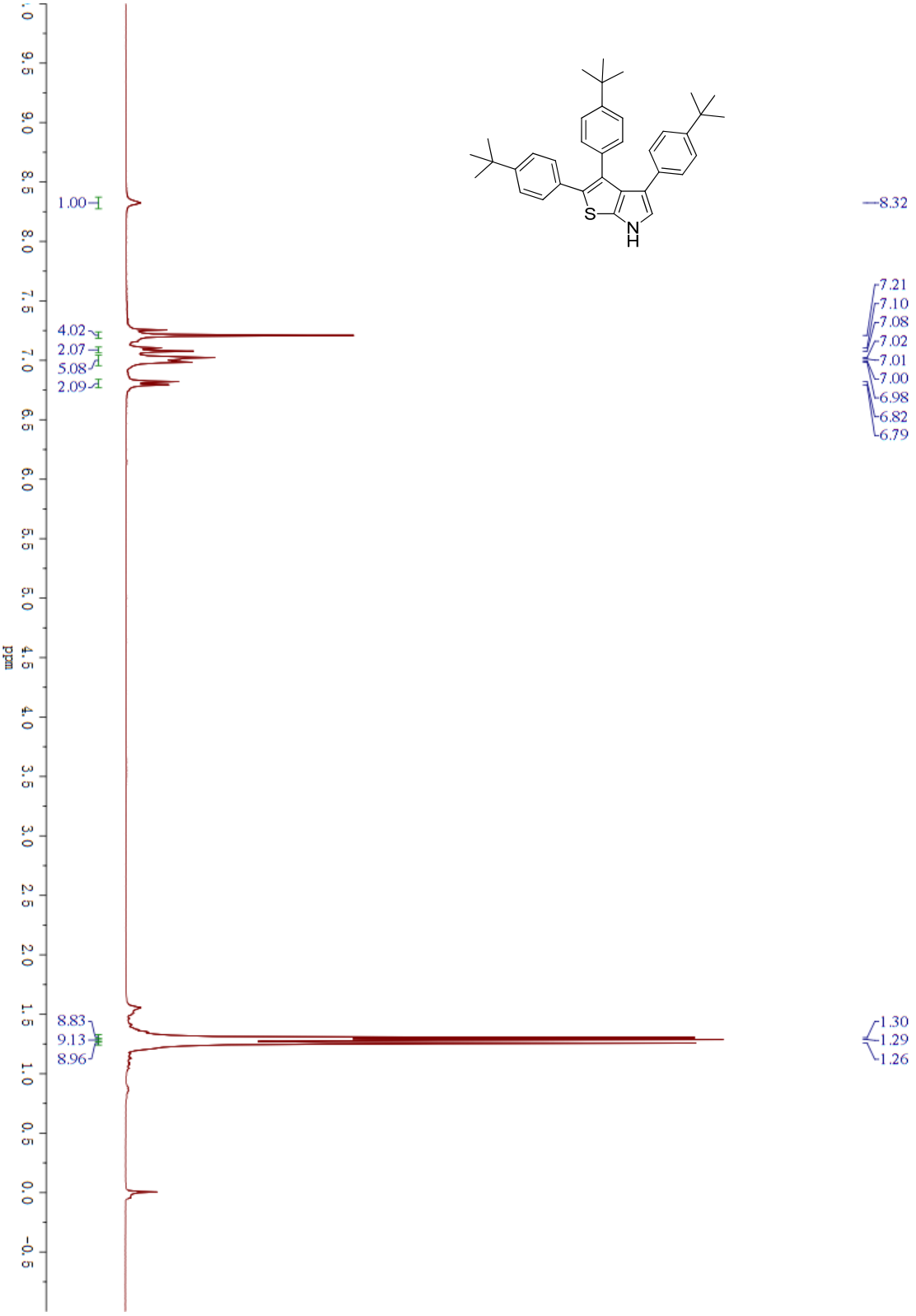
^{13}C NMR spectrum of **Compound 11a** in $CDCl_3$ solution.



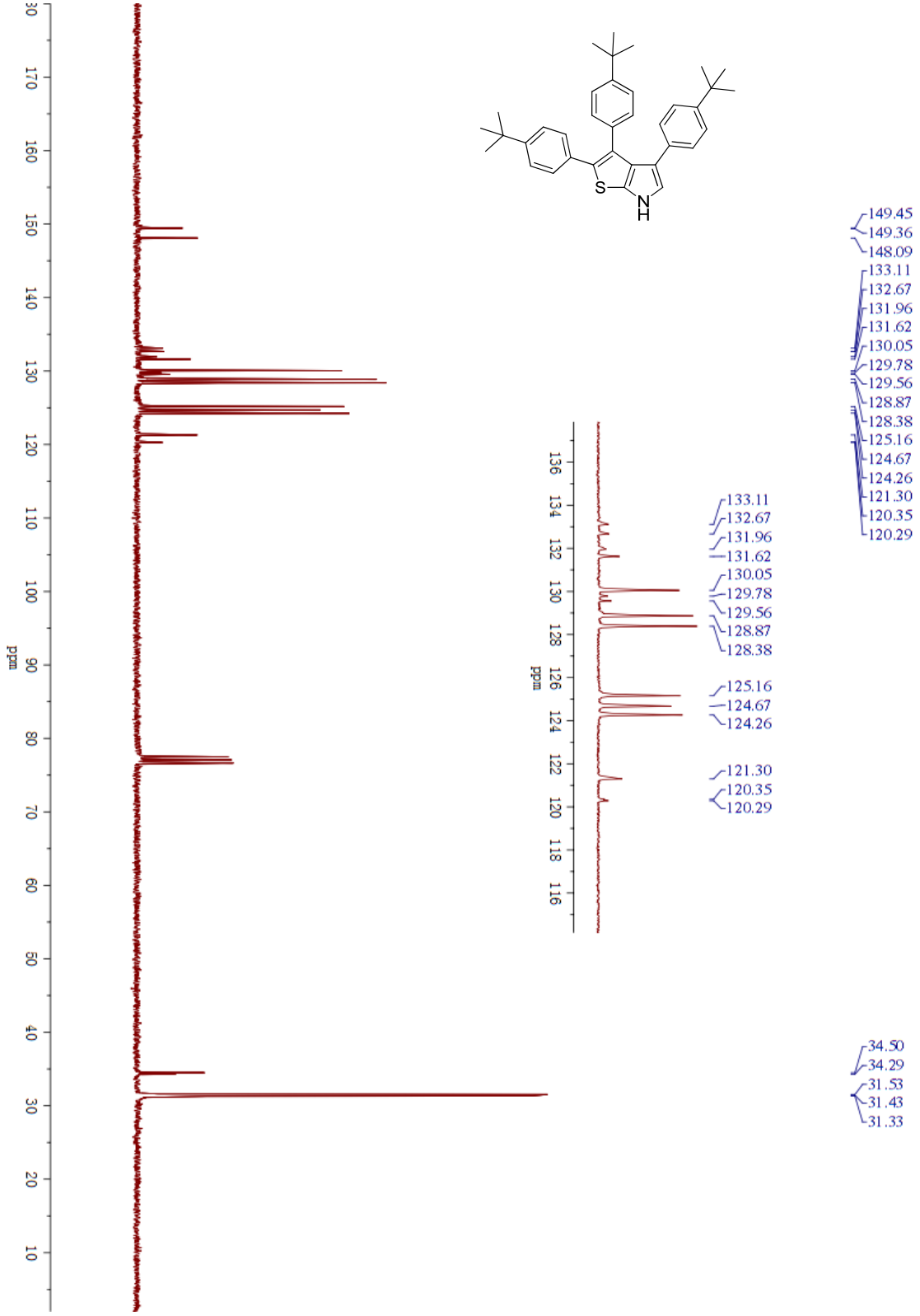
^{1}H NMR spectrum of **Compound 11b** in $CDCl_3$ solution.



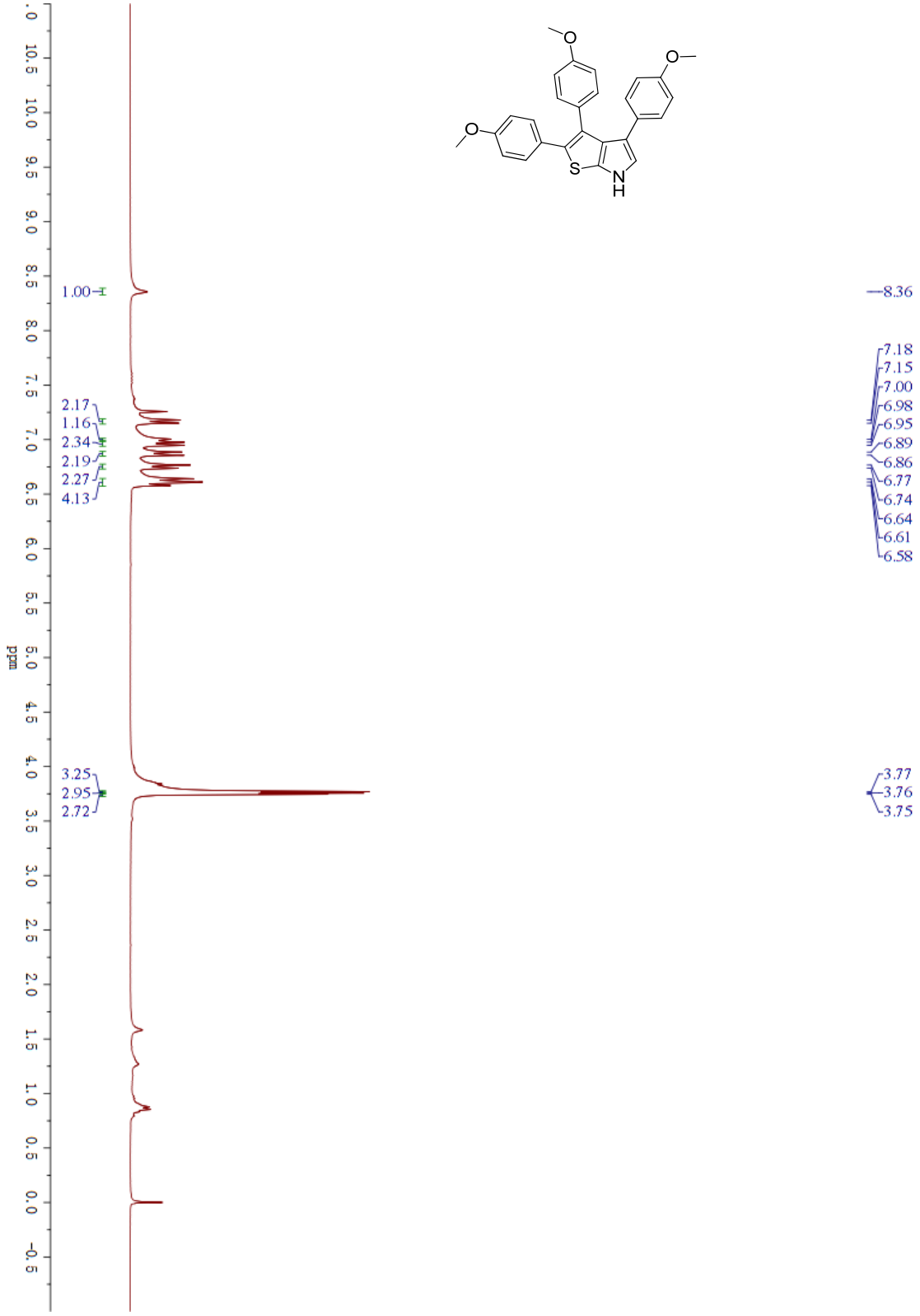
^{13}C NMR spectrum of **Compound 11b** in $CDCl_3$ solution.



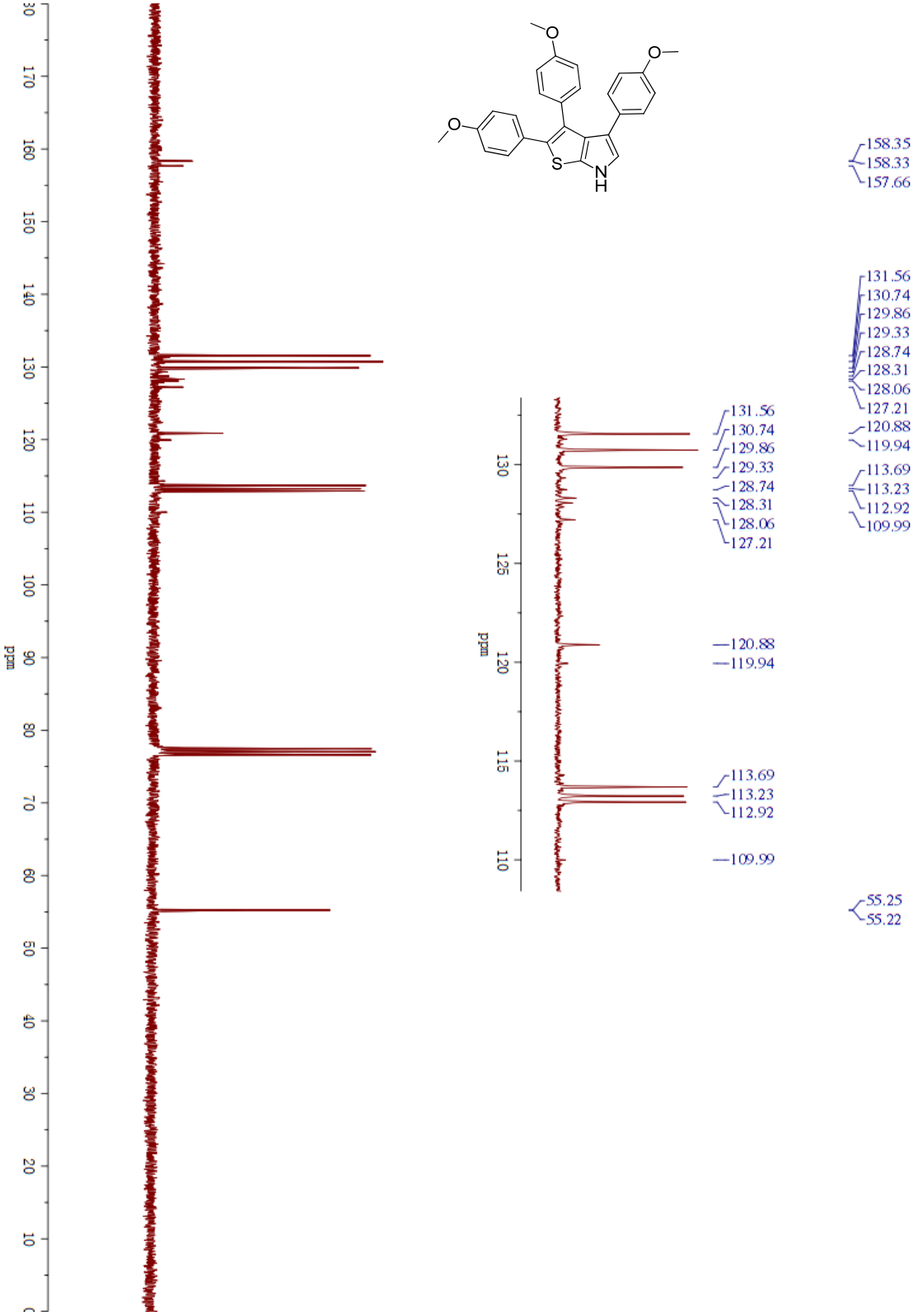
^{1}H NMR spectrum of **Compound 12a** in $CDCl_3$ solution.



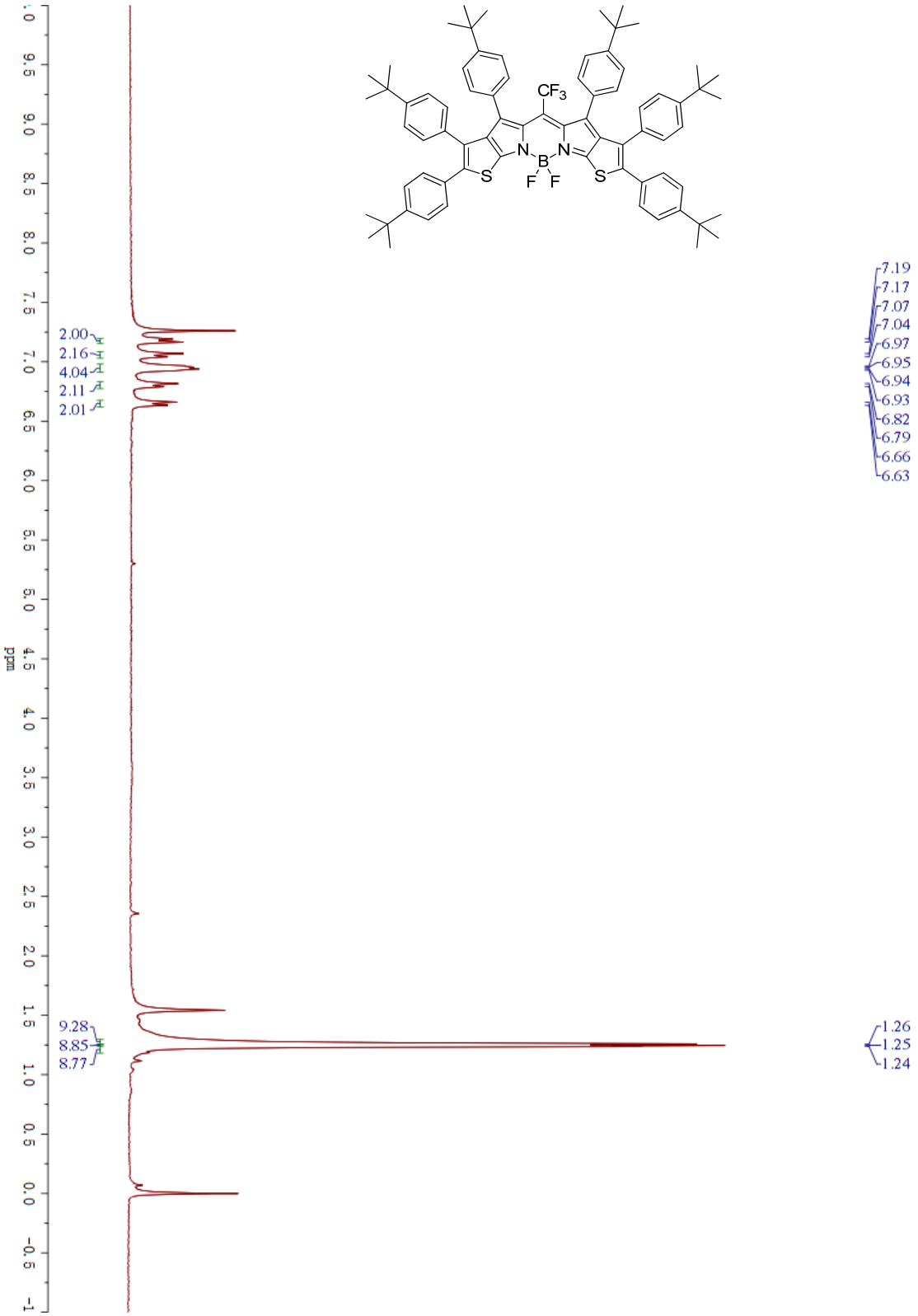
^{13}C NMR spectrum of **Compound 12a** in $CDCl_3$ solution.



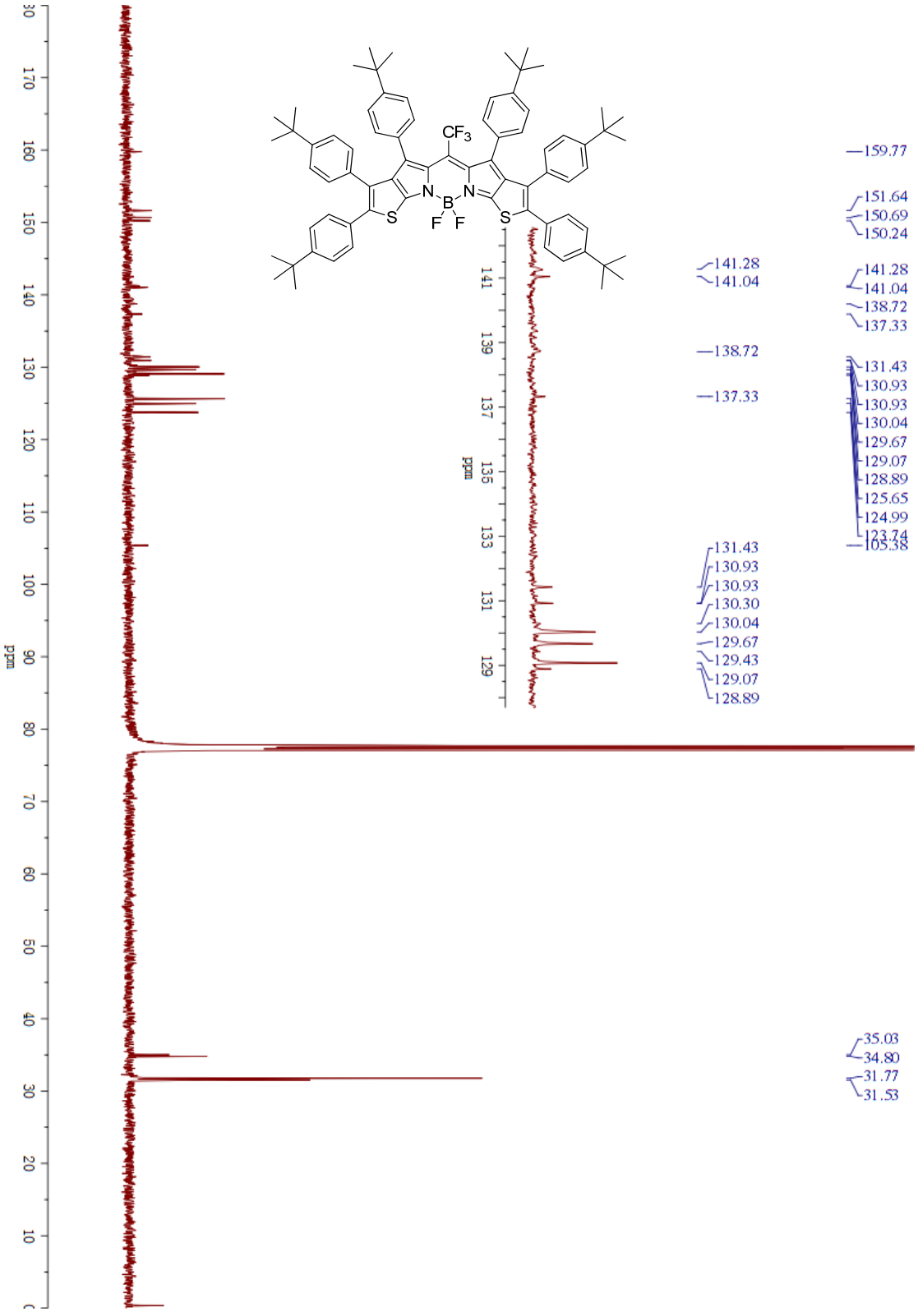
^{1}H NMR spectrum of **Compound 12b** in $CDCl_3$ solution.



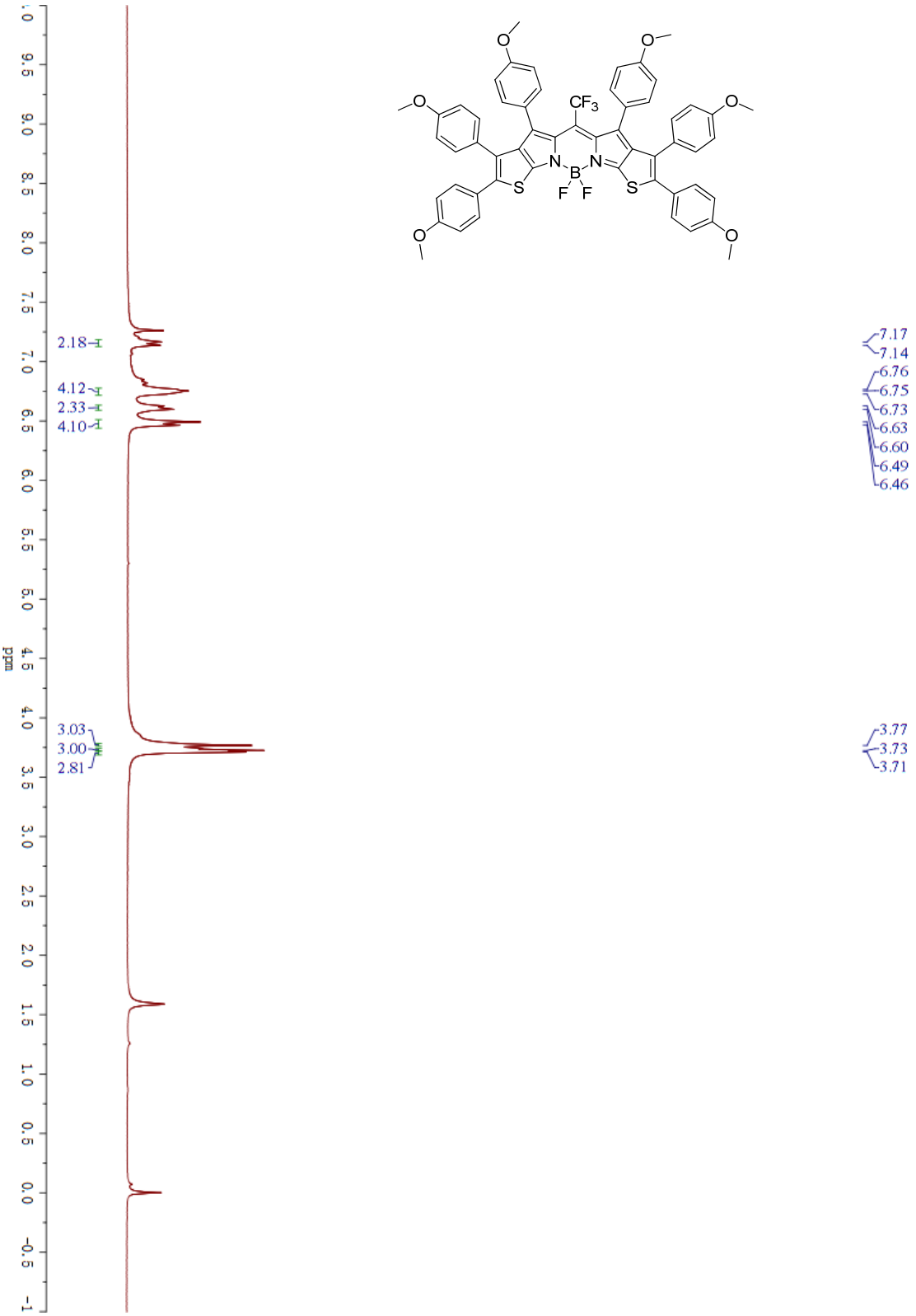
^{13}C NMR spectrum of **Compound 12b** in $CDCl_3$ solution.



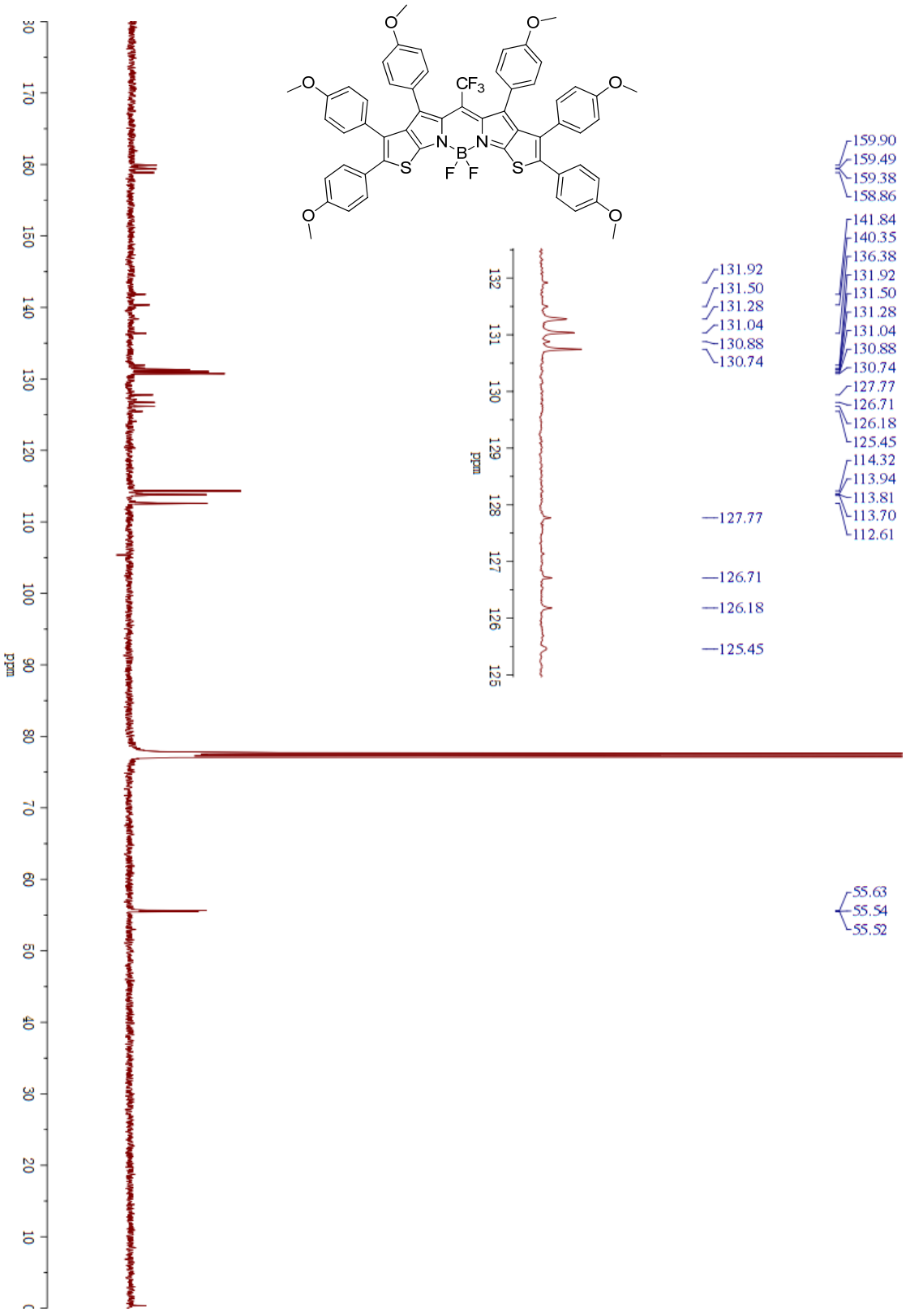
^{1}H NMR spectrum of **Compound 3a** in $CDCl_3$ solution.



^{13}C NMR spectrum of **Compound 3a** in $CDCl_3$ solution.

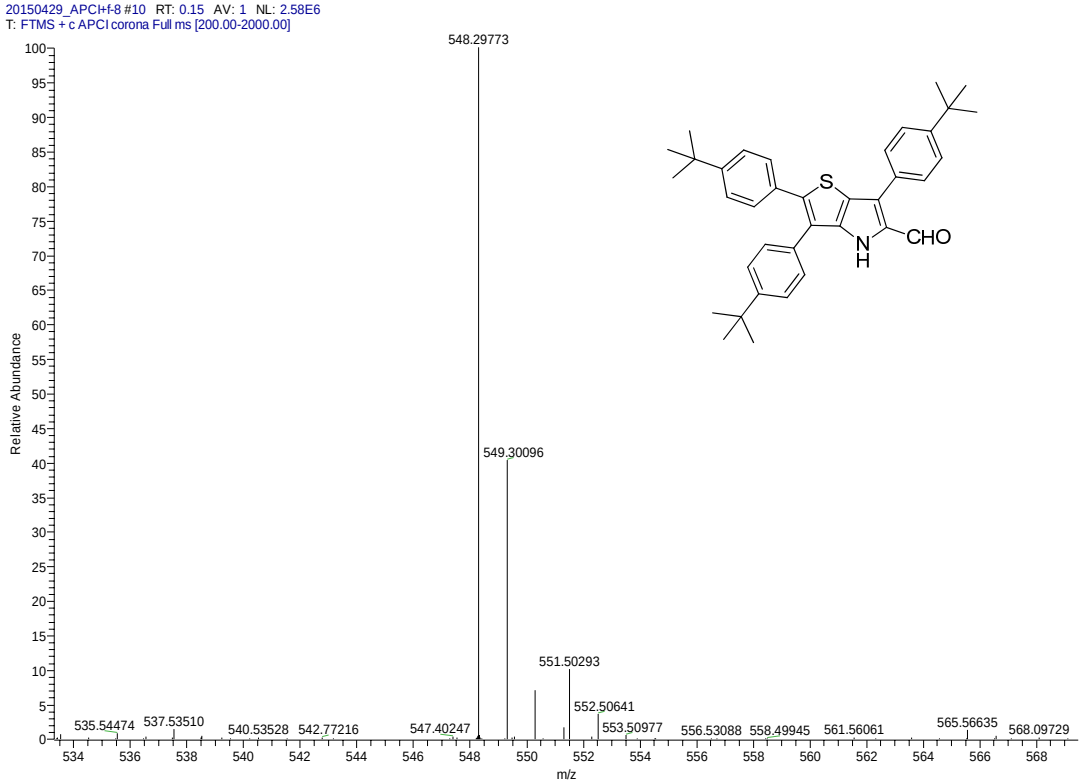


^{1}H NMR spectrum of **Compound 3b** in $CDCl_3$ solution.

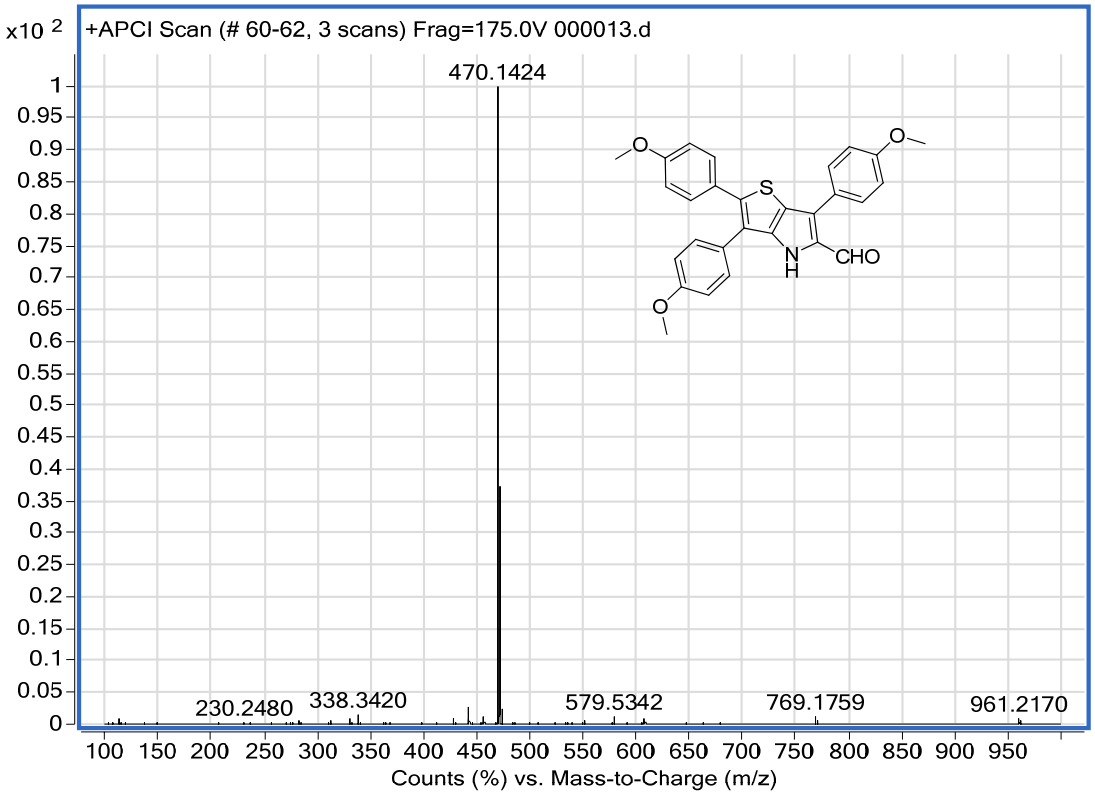


^{13}C NMR spectrum of **Compound 3b** in $CDCl_3$ solution.

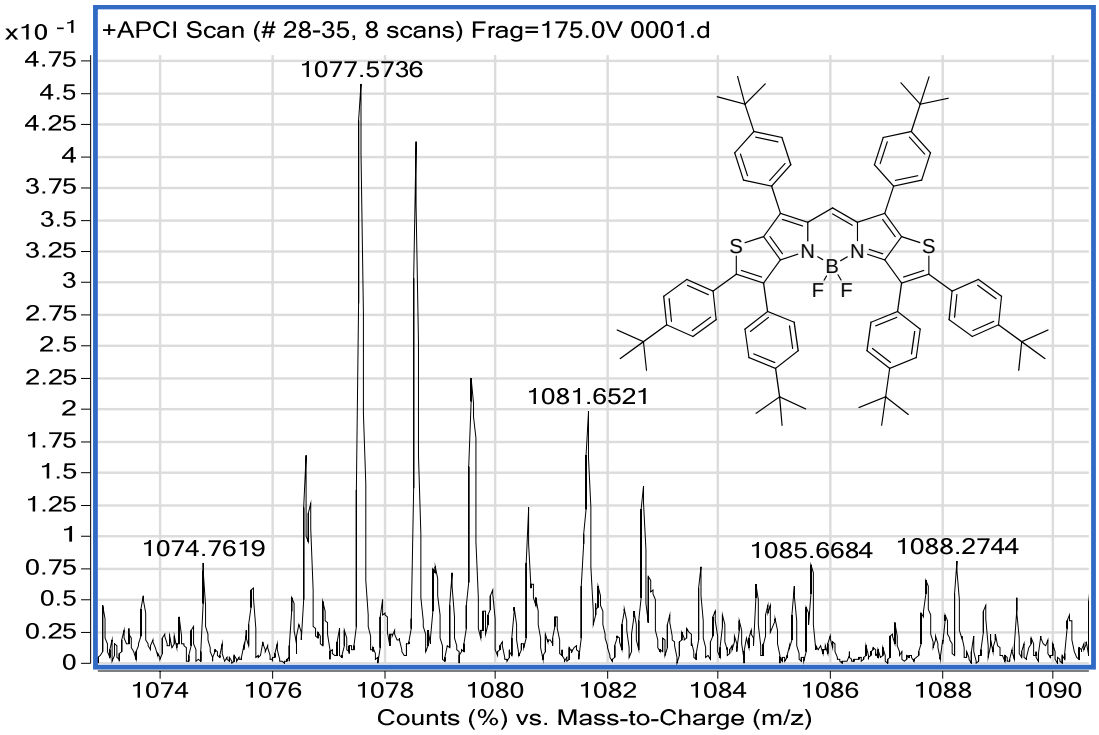
5. High resolution mass spectroscopes for all new compound



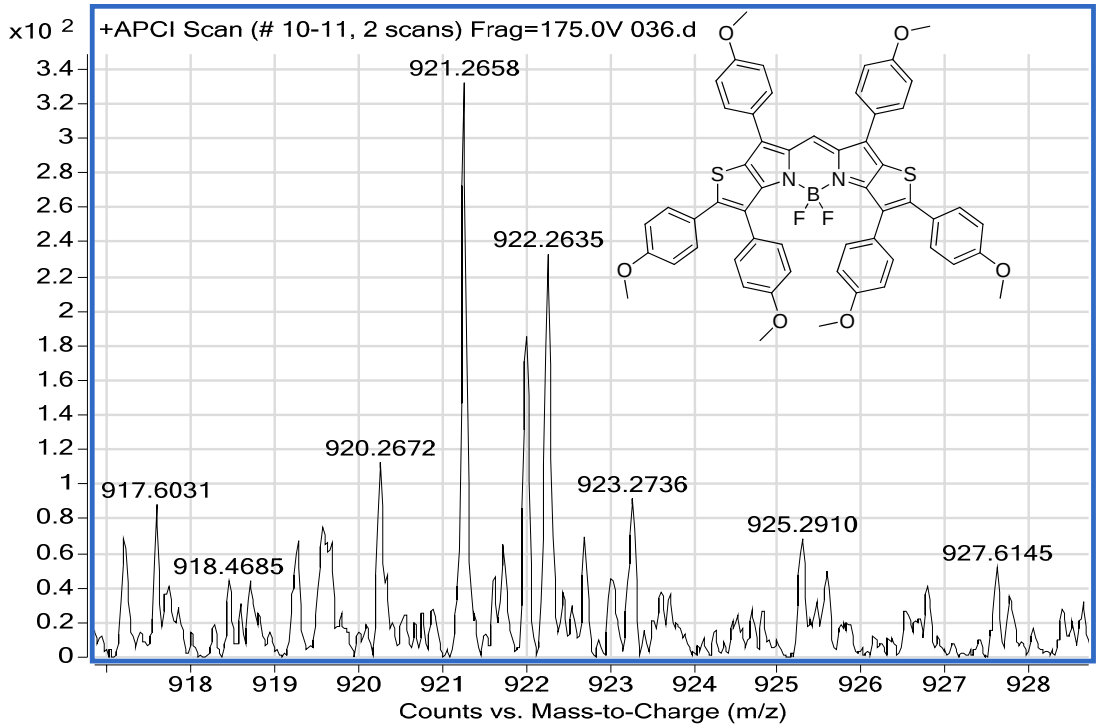
HRMS for **8a**



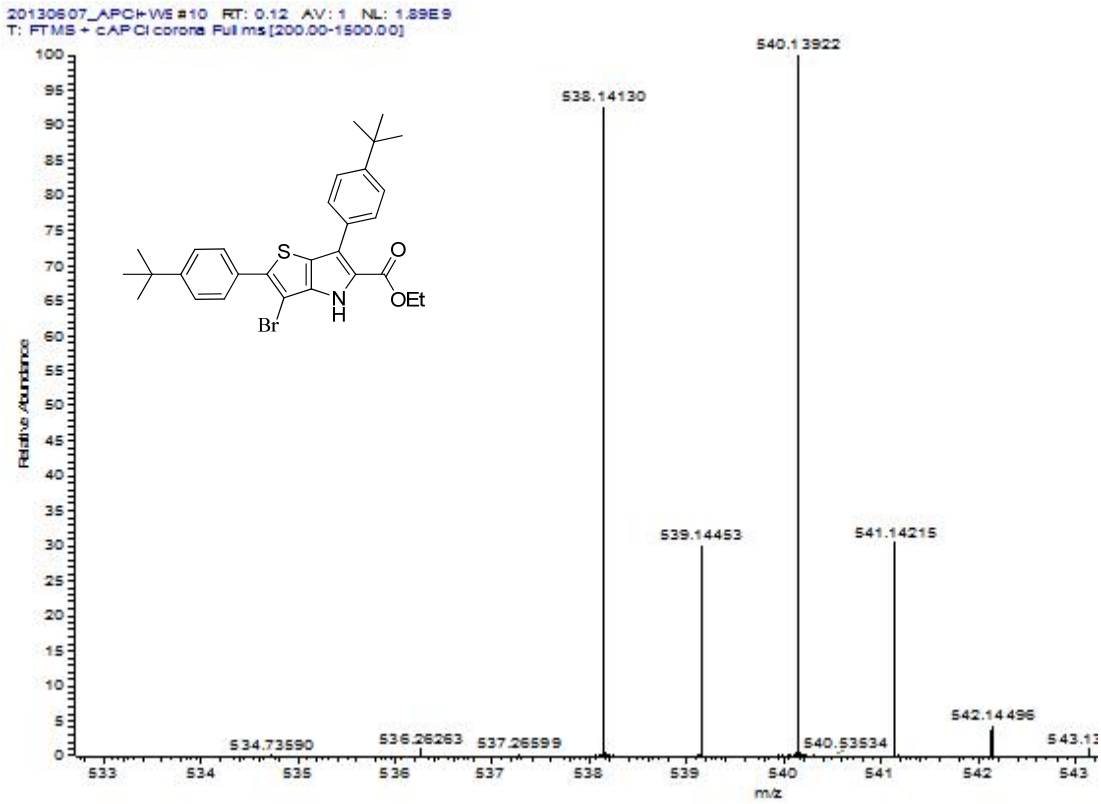
HRMS for **8b**



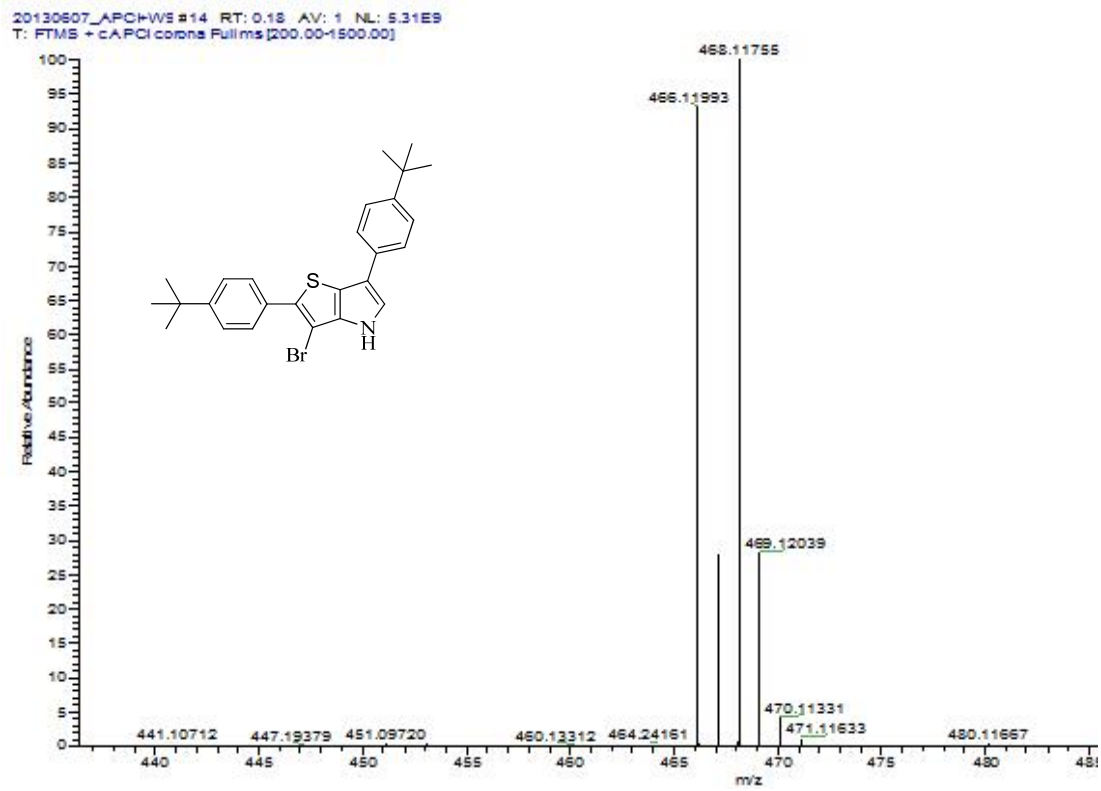
HRMS for **2a**



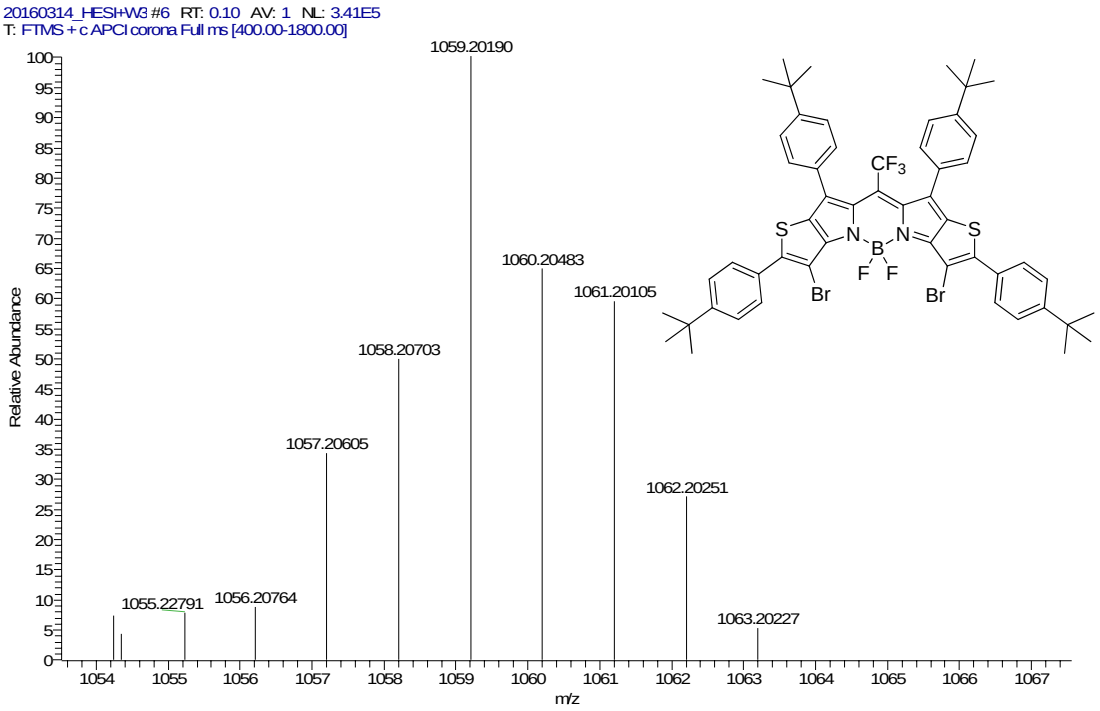
HRMS for **2b**



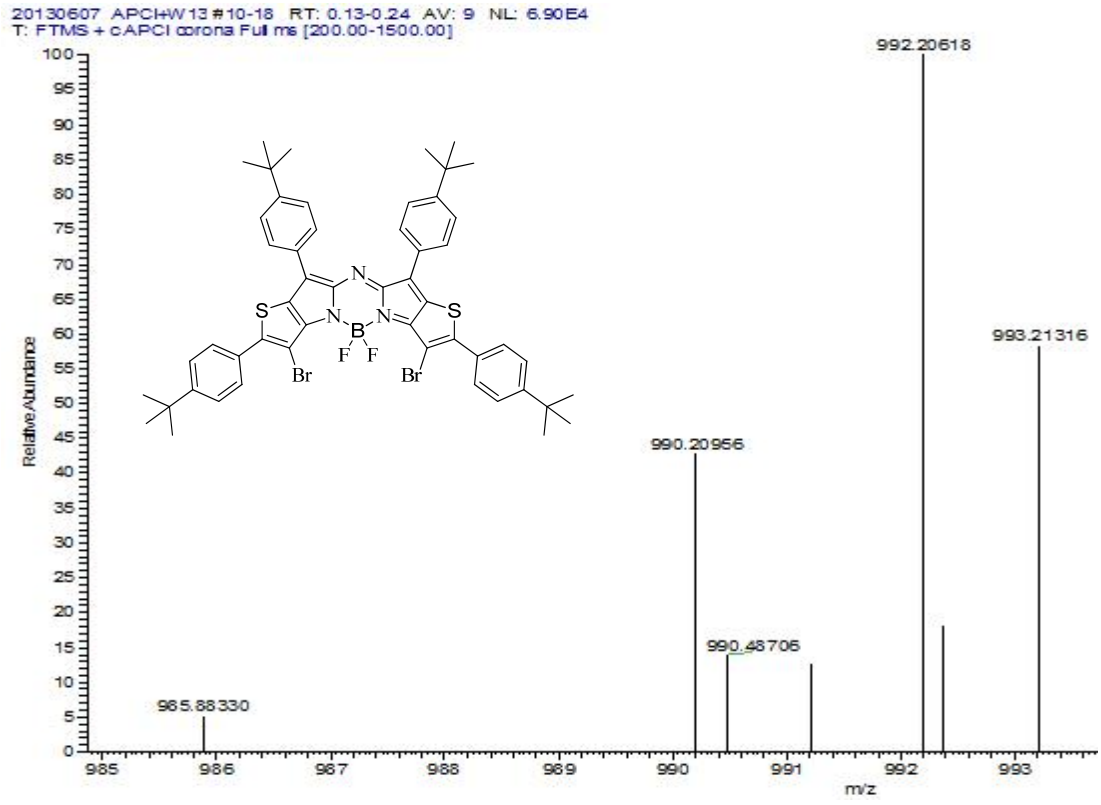
HRMS for **6e**



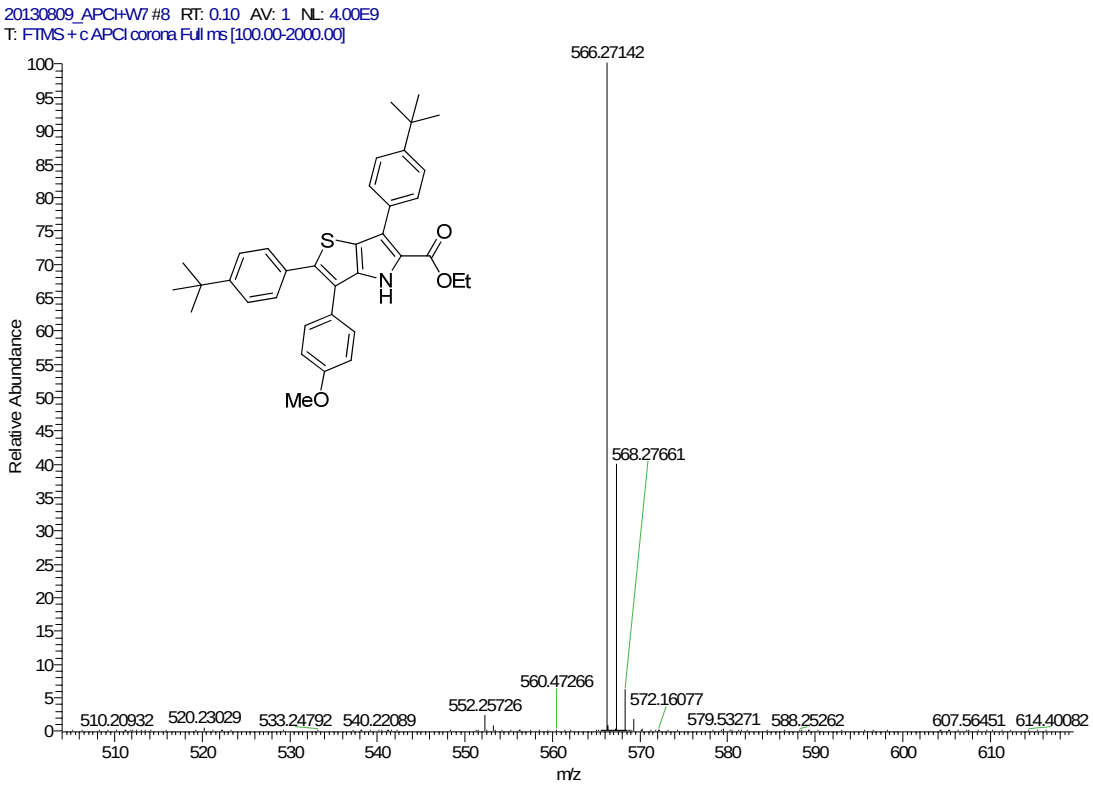
HRMS for **7e**



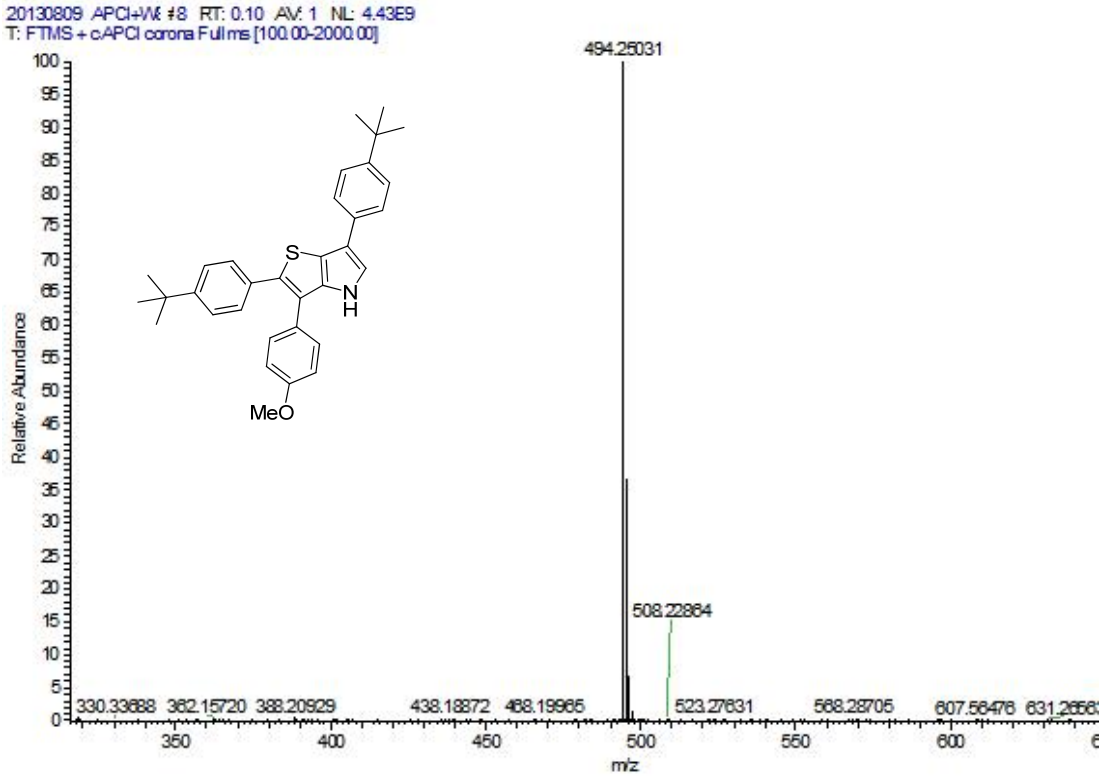
HRMS for 2c



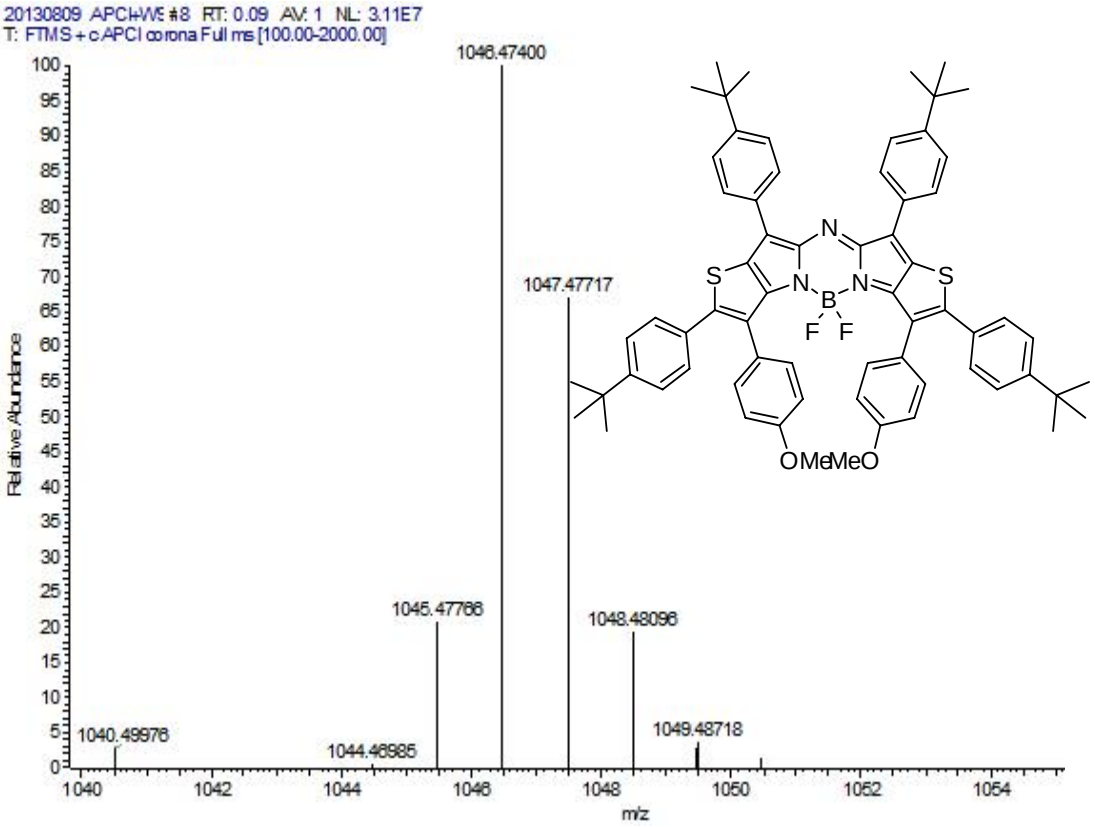
HRMS for **1e**



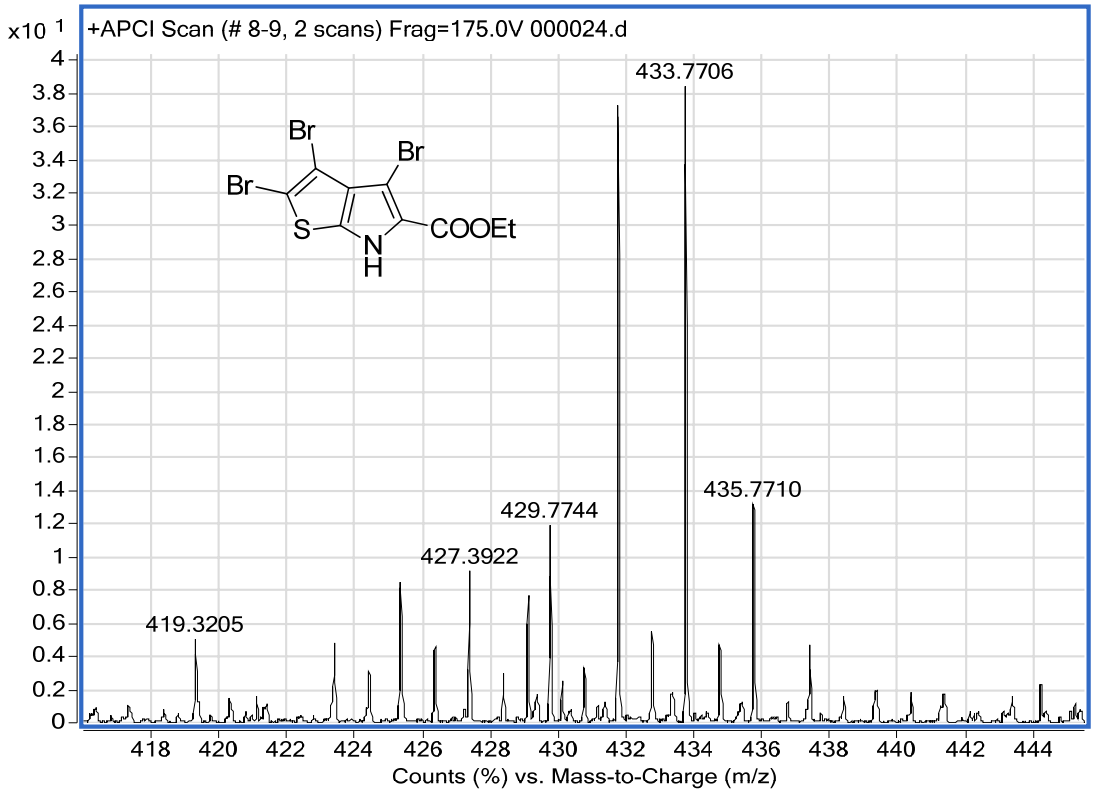
HRMS for **6f**



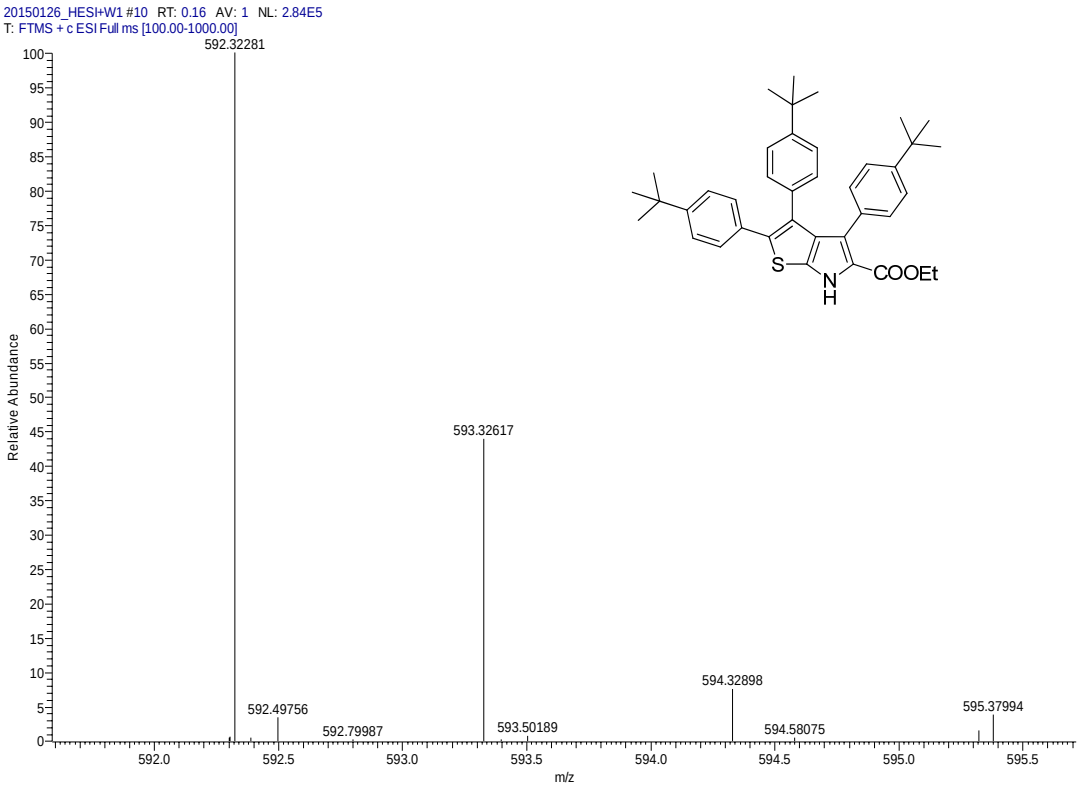
HRMS for **7f**



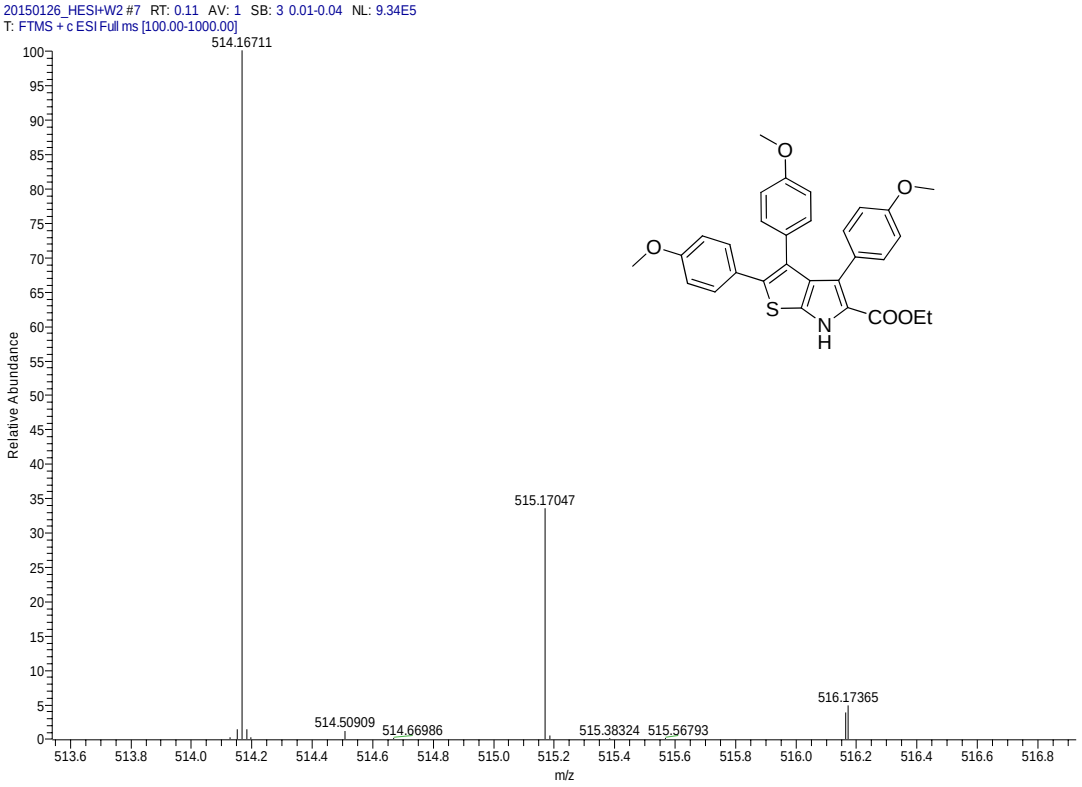
HRMS for **1f**



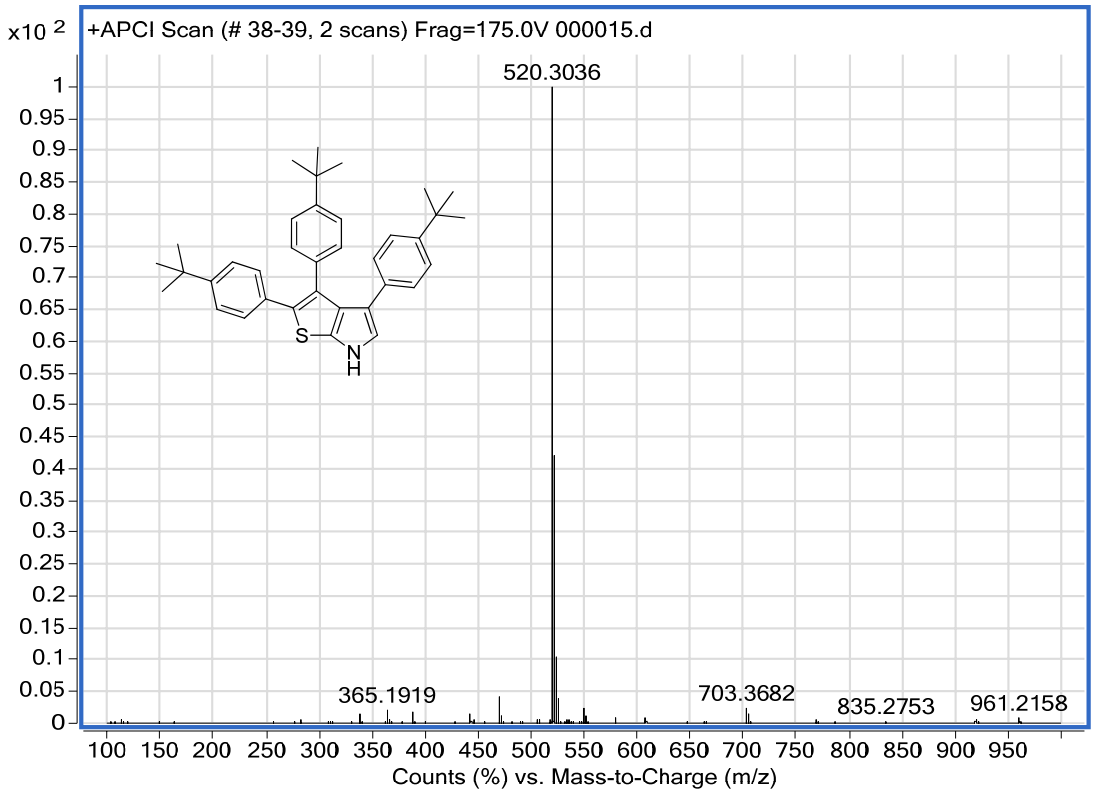
HRMS for **10**



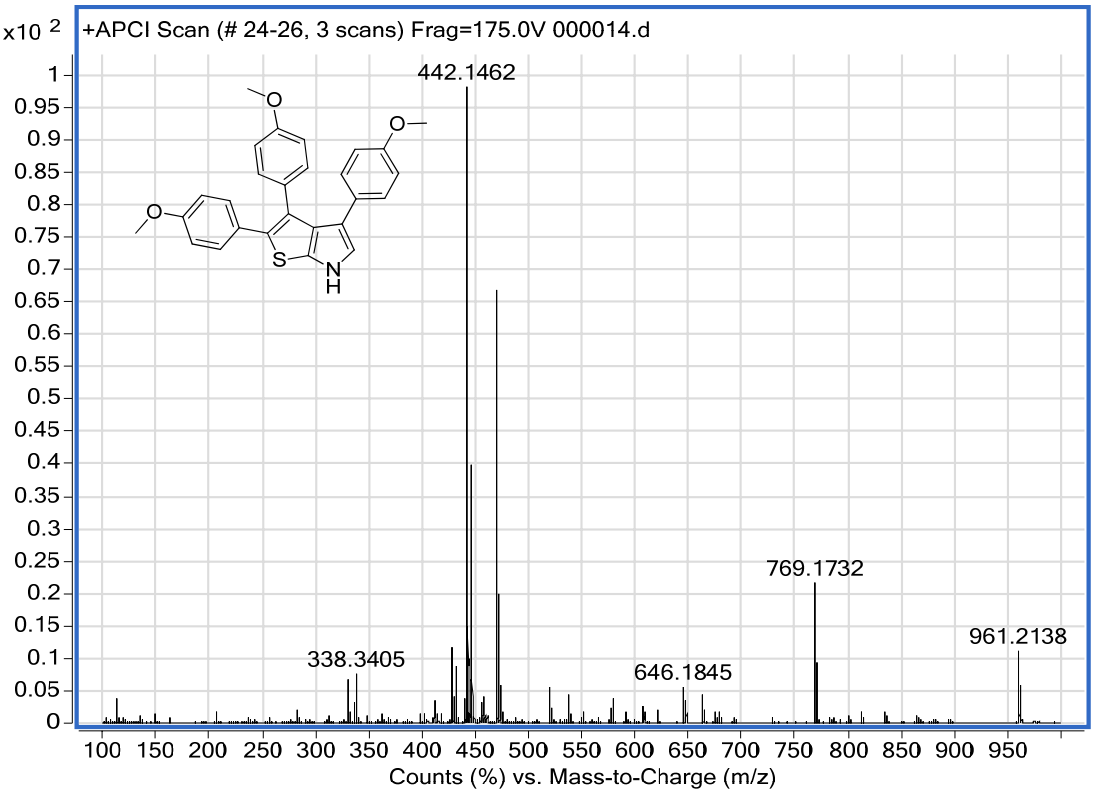
HRMS for **11a**



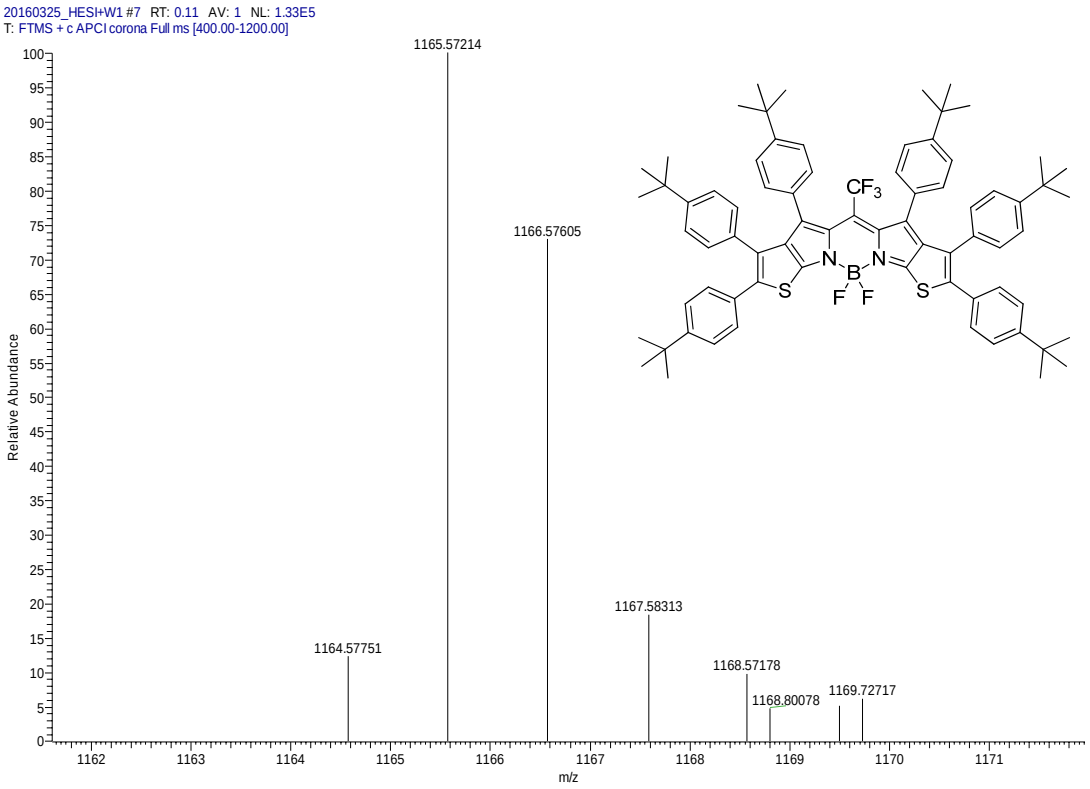
HRMS for **11b**



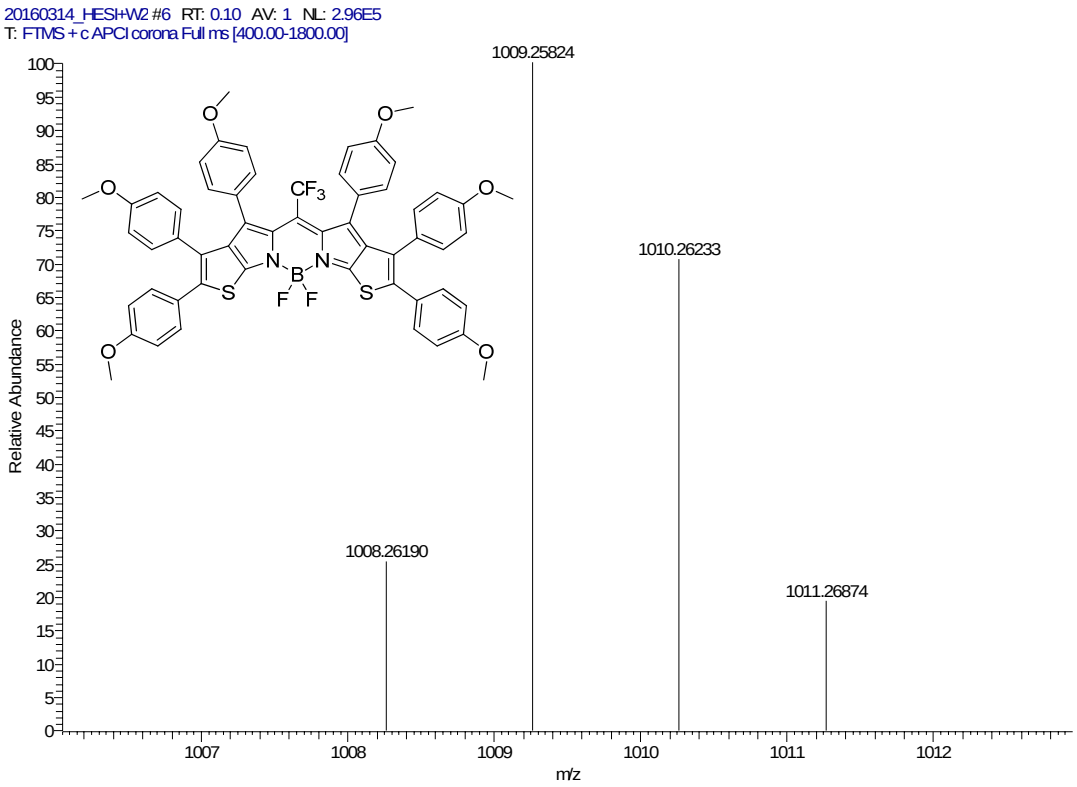
HRMS for **12a**



HRMS for **12b**



HRMS for **3a**



HRMS for **3b**

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