

Beta-Thiophene-Fused BF₂-Azadipyrromethenes as Near-Infrared Dyes

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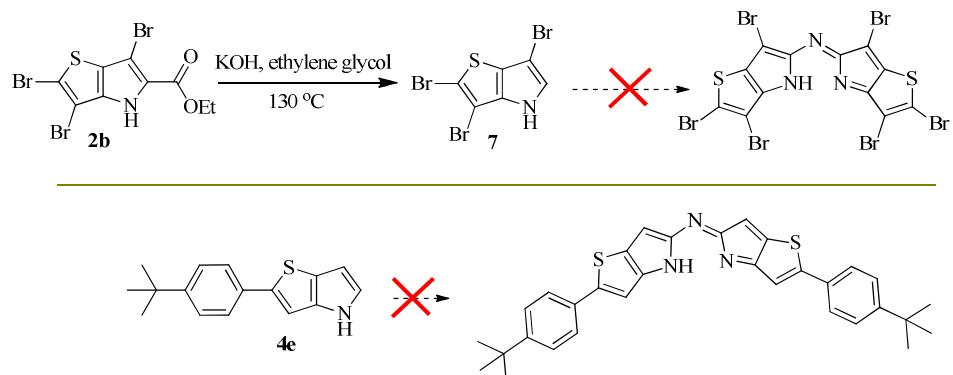
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1. Supporting Schemes, Tables and Figures



Scheme S1. Failed condensation attempts to synthesize corresponding aza-dipyrromethenes.

Table S1. Selected Geometrical Parameters of aza-BDTPs **5c**, **5d**, and thienopyrroles **3a** and **3c** obtained from crystallography

	5c	5d	3a	3c
the B-N bond distances (Å)	1.5723(59), 1.5591(53)	1.5773(50), 1.5669(50)		
dihedral angles of two thiophene rings (deg)	5.165(121)	1.672(109)		
dihedral angles of two pyrrole rings (deg)	5.601(156)	3.200(116)		
dihedral angles between thiophene ring and phenyl ring Pa (deg)	35.182(123), 28.986(110)	24.344(133), 32.832(124)	5.286(60)	31.469(72)
dihedral angles between thiophene ring and phenyl ring Pb (deg)	70.574(111), 61.951(132)	67.559(158), 61.972(130)		57.600(95)
dihedral angles between pyrrole ring and phenyl ring Pc (deg)	19.964(115), 29.339(142)	29.274(138), 34.233(135)	44.240(62)	46.205(102)

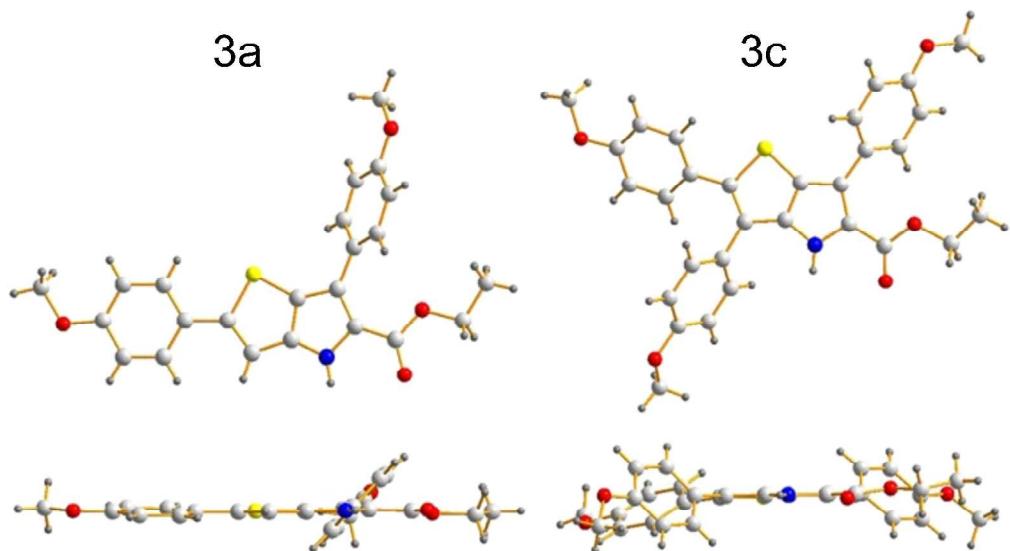


Figure S1. X-ray structures of compounds **3a** and **3c**. C, light gray; H, gray; N, blue; S, yellow; O, red.

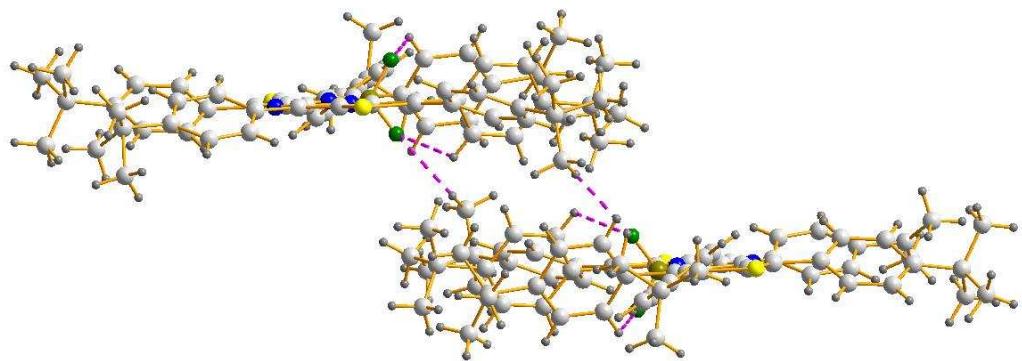


Figure S2. Intermolecular crystal packing of aza-BDTP **5d** through H-bonding.

Table S2. Effects of the solvent polarity on the absorption and emission of aza-BDTP **5c** at room temperature.

	cyclohexane	toluene	chloroform	acetonitrile	DMSO
$\lambda_{\text{abs max}}$ (fwhm) ^a /nm	773 (53)	785 (56)	784 (57)	777 (68)	799 (66)
$\lambda_{\text{em max}}$ (fwhm) ^a /nm	805 (47)	813 (41)	816 (40)	816 (42)	827 (41)
ϕ^b	0.03	0.05	0.04	0.02	0.02

^aFull width at half-maximum height. ^bfluorescence quantum yield was obtained using Indocyanine Green as reference compound ($\phi = 0.12$ in DMSO), excited at 720 nm, the standard errors are less than 5%.

Table S3. Photophysical properties of aza-BDTPs **5a**, **5b** and **5d** in different solvents.

Dyes	solvent	λ_{abs} (nm)	λ_{ems}^a (nm)	SS (cm^{-1}) ^b	$\phi_f^{a,c}$
5a	toluene	788	812	375	0.08
	DMSO	804	825	317	0.05
5b	cyclohexane	754	776	376	0.08
	toluene	769	794	409	0.11
	DMSO	775	807	512	0.09
5d	acetonitrile	759	786	453	0.08
	cyclohexane	753	793	670	0.03
	toluene	765	807	680	0.06
	DMSO	769	712	689	0.04
	acetonitrile	753	801	796	0.04

^aexcited at 720 nm, ^bSS: Stock shift, ^c fluorescence quantum yield was obtained using Indocyanine Green as reference compound ($\phi = 0.12$ in DMSO), excited at 720 nm, the standard errors are less than 5%.

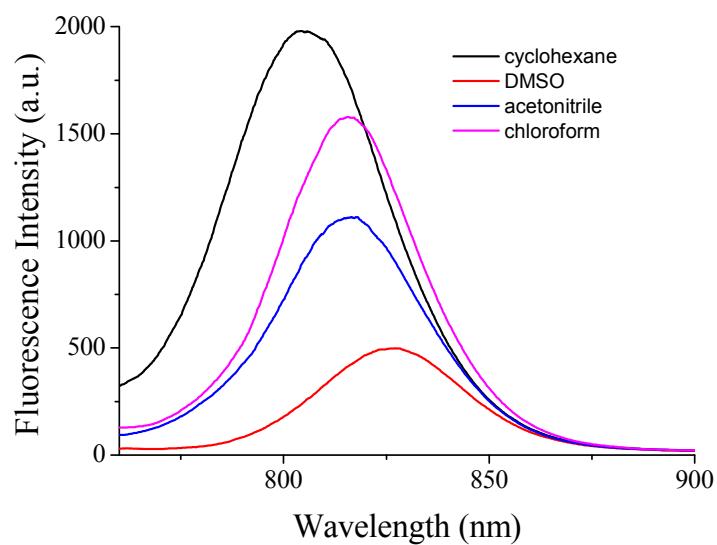
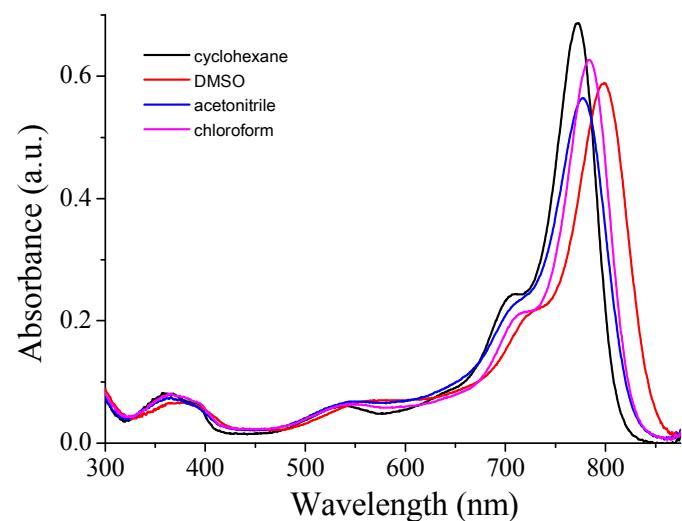


Figure S3. UV-vis (top) and fluorescence spectra (bottom) of aza-BDTP **5c** in different solvents.

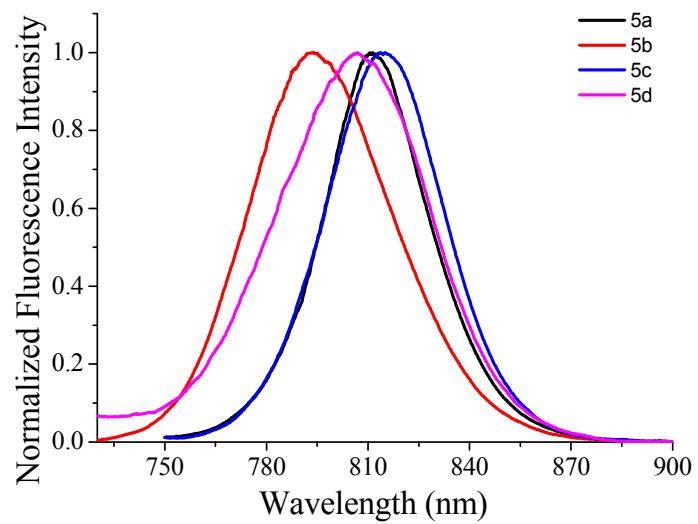
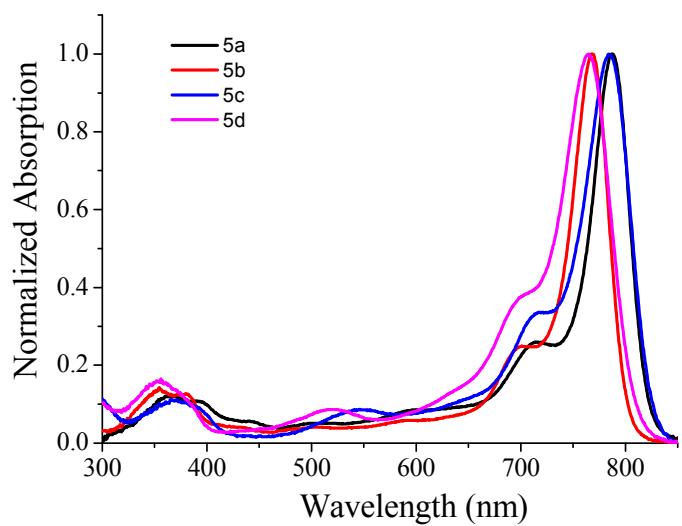


Figure S4. Normalized UV-vis (top) and fluorescence spectra (bottom) of aza-BDTPs **5a** (black), **5b** (red), **5c** (blue), **5d** (magenta) in toluene.

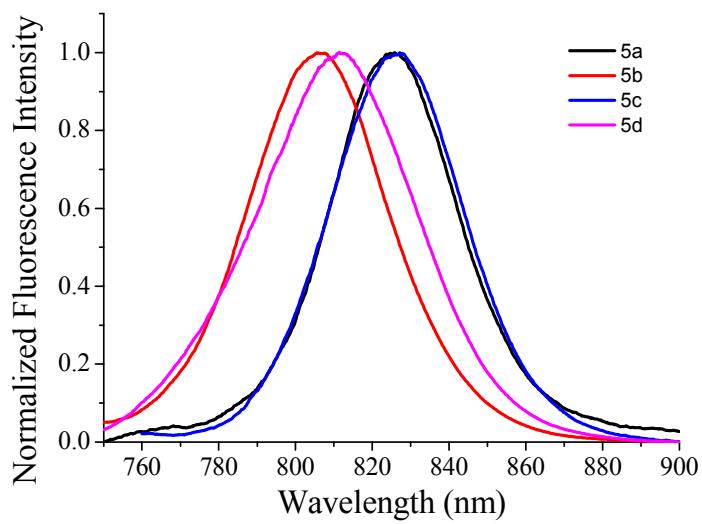
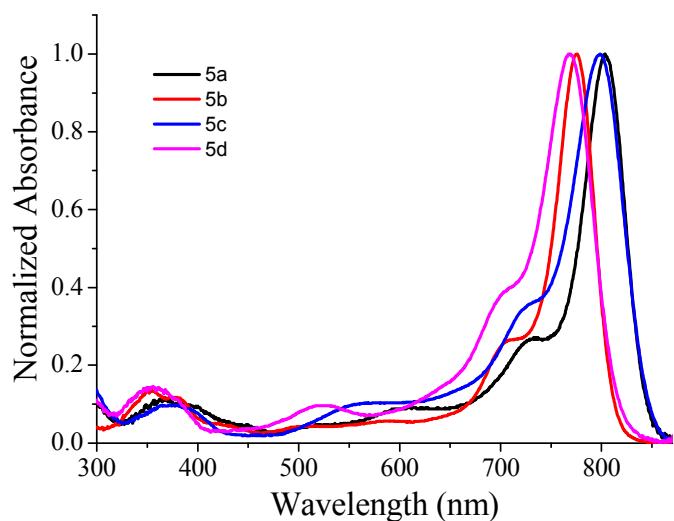


Figure S5. Normalized UV-vis (top) and fluorescence spectra (bottom) of aza-BDTPs **5a** (black), **5b** (red), **5c** (blue), **5d** (magenta) in DMSO.

2. Solvatochromism of **5c**

Solvent-dependent spectral shifts of **5c** are interpreted in terms of the Lippert–Mataga equation, which describes the solvatochromic Stokes shift $\Delta\nu$ (expressed in wavenumbers) as a function of the change of the dipole moment $\Delta\mu_{ge} = \mu_e - \mu_g$ of the dye upon excitation.

The validity of the Lippert–Mataga equation was checked by using various solvents (Table S4) with different dielectric constants (ϵ) and refractive indices (n) and by plotting $\Delta\nu$ as a function of $\Delta f = f(\epsilon) - f(n^2)$.^{1,2}

Figure S6 represents the Lippert–Mataga plot for **5c** in the solvents listed in Table S4. As is evident from Figure S6, the little dependence of the small Stokes shift $\Delta\nu$ as a function of Δf and unsatisfactory correlation coefficient indicate that the dye's permanent dipole moments are similar in the ground and excited states.^{1,2}

Table S4. Spectroscopic properties of **5c** in several solvents.

Solvent	λ_{abs}	λ_{em}	Stokes-shift (cm ⁻¹)	ϵ	n	$\Delta\nu$	Δf
hexane	770	804	549	1.58	1.37510	549.20204	-0.046887519
cyclohexane (C-Hex)	773	805	514	2.02	1.42800	514.25036	-0.002248566
toluene	785	813	529	2.37	1.49610	528.84129	0.012566998
chloroform (TCM)	784	816	500	4.81	1.44590	500.20008	0.148262288
EtOAc	777	816	615	6.02	1.37230	615.11091	0.199671283
THF	783	819	561	7.58	1.40500	561.37987	0.210327943
dichloromethane (DCM)	784	821	575	8.93	1.42420	574.83407	0.217103254
DMSO	799	827	424	48.90	1.47830	423.74613	0.264108843
DMF	791	826	536	37.60	1.43050	535.6875	0.274856488
Acetone	780	820	625	20.70	1.35880	625.39087	0.284269759
MeCN	777	816	615	37.50	1.34423	615.11091	0.305367128
MeOH	779	816	582	33.60	1.33010	582.06851	0.308523772

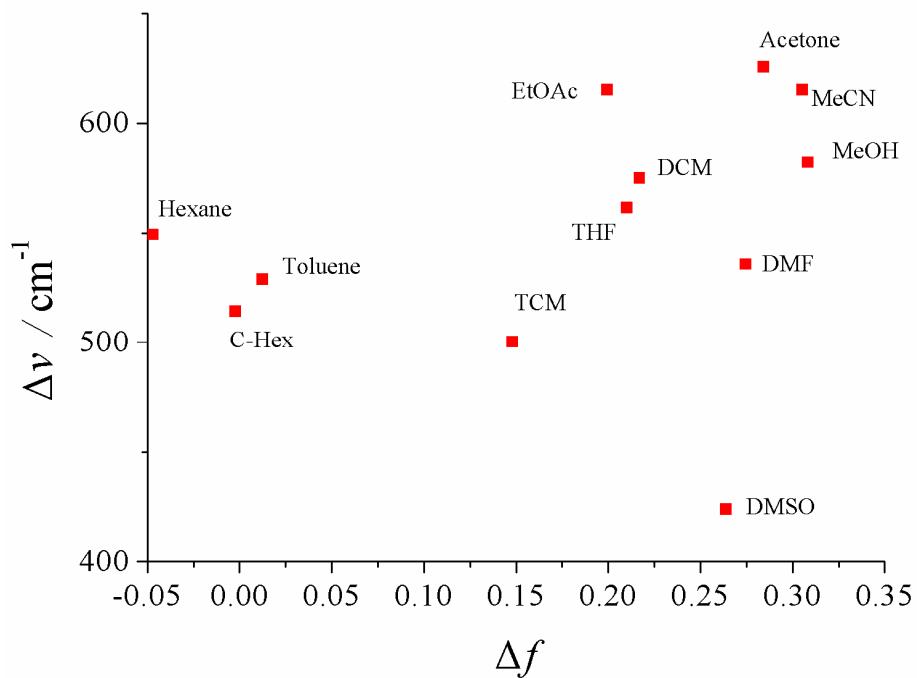


Figure S6. Stokes shift Δv of **5c** versus Δf . The numbers refer to the solvents in Table S4.

3. DFT calculation

3.1 The calculation method: Geometric parameter from X-ray diffraction analysis was used for the calculation. The ground state geometry was optimized by using DFT method at B3LYP/6-31G level in vacuum and solvents in their C1 symmetry. The same method was used for vibrational analysis to verify that the optimized structures correspond to local minima on the energy surface. TD-DFT computations were used to obtain the vertical excitation energies and oscillator strengths at the optimized ground state equilibrium geometries under the same theoretical level. The geometry optimizations of all the molecules in different solvent environments were done using the Self-Consistent Reaction Field (SCRF) method and the Polarizable Continuum Model (PCM). All of the calculations were carried out by the methods implemented in Gaussian 09 package.³

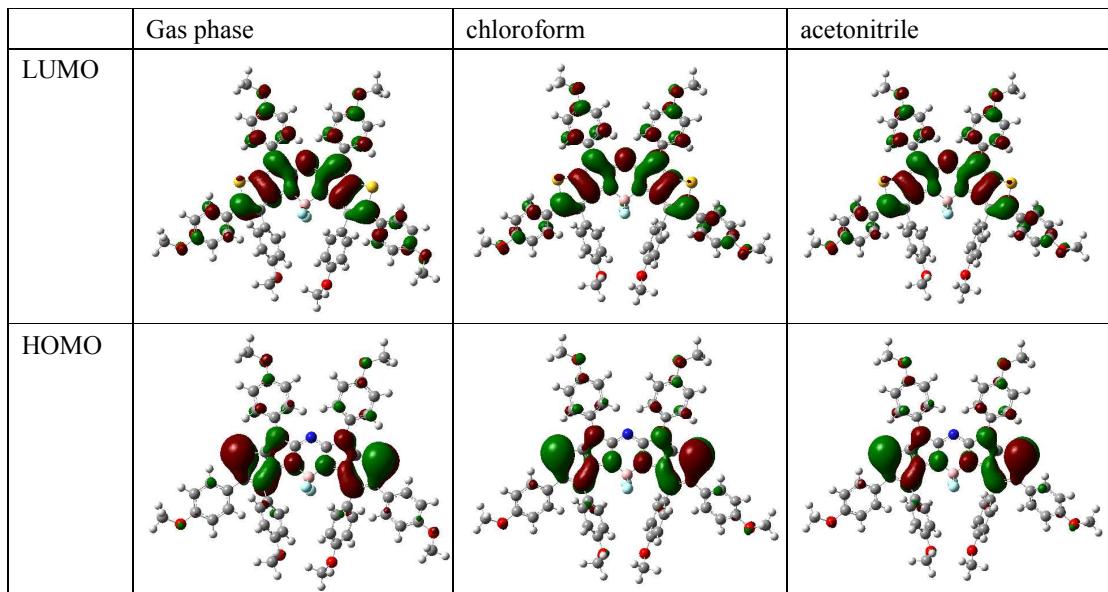
Table S5. The DFT calculated parameter of **5c**.

	ϵ	E (a.u.)	HOMO/LUMO (eV)	λ_{abs}/f	%($\text{H} \rightarrow \text{L}$)
Gas phase		-3718.8595	-4.934/-3.125	710.70/0.6903	79.1
cyclohexane	2.023	-3718.8719	-5.044/-3.256	755.63/1.0619	93.0
toluene	2.374	-3718.8744	-5.072/-3.286	761.36/1.1044	93.9
chloroform	4.90	-3718.8832	-5.165/-3.389	760.21/1.1147	95.5
acetonitrile	36.64	-3718.8944	-5.281/-3.513	751.33/1.1347	94.1
DMSO	46.826	-3718.8949	-5.287/-3.518	757.32/1.1749	94.77

ϵ : dielectric constants; λ_{abs} : the absorption wavelength in nm; f : the oscillator strength;

%($\text{H} \rightarrow \text{L}$): The percentage of the $\text{H} \rightarrow \text{L}$ excitation contribution to the first excited state absorption excitation)

Table S6. Frontier orbitals for **5c** in gas phase, chloroform and acetonitrile. Noted all the first excited state is mainly of the HOMO and LUMO excitation.



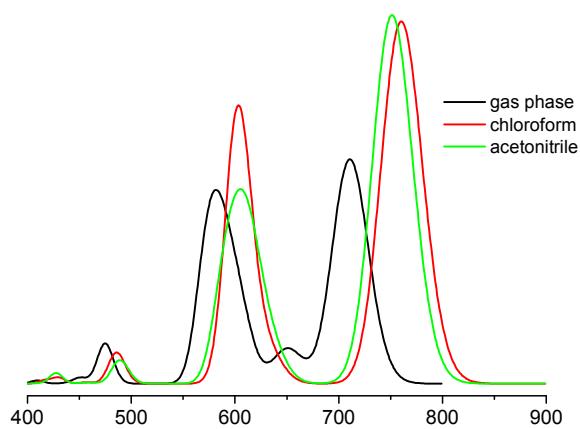


Figure S7. DFT calculated absorption spectra of **5c** in gas phase, chloroform and acetonitrile.

Table S7. The DFT calculated standard ordinations of **5c** in gas phase, chloroform and acetonitrile.

a. in gas phase

C	-4.78251	-0.41097	0.02242
C	-3.43109	-0.73291	0.10664
C	-2.60416	0.43405	-0.01622
C	-3.31052	1.6647	-0.14841
C	-1.1183	2.10634	-0.10135
C	-2.42201	2.73539	-0.20947
S	-5.08469	1.39816	-0.19884
N	-1.25522	0.70634	-0.00499
C	-5.9691	-1.26588	0.05947
C	-5.96058	-2.57376	-0.47104
C	-7.18862	-0.78528	0.59881
C	-7.10602	-3.37086	-0.45935
H	-5.05145	-2.9688	-0.90465
C	-8.33164	-1.57272	0.61745
H	-7.22796	0.21057	1.02666
C	-8.29646	-2.87278	0.08868
H	-7.05797	-4.36725	-0.88059
H	-9.26086	-1.20934	1.0398
C	-2.97721	-2.1199	0.41764
C	-3.28936	-2.67668	1.67479
C	-2.32195	-2.92434	-0.52604
C	-2.97801	-3.99893	1.97096
H	-3.78779	-2.06379	2.41833
C	-2.01177	-4.26018	-0.24203
H	-2.02877	-2.50361	-1.4795
C	-2.34939	-4.8001	1.00579
H	-3.21576	-4.43546	2.93389

H	-1.49103	-4.85387	-0.98272
C	-2.70556	4.16092	-0.33445
C	-3.97698	4.66966	0.00555
C	-1.73676	5.07942	-0.81243
C	-4.28113	6.02618	-0.11693
H	-4.73662	4.00385	0.39906
C	-2.03126	6.43026	-0.9377
H	-0.75347	4.71808	-1.08047
C	-3.30443	6.91237	-0.59241
H	-5.26708	6.37581	0.16301
H	-1.2949	7.13349	-1.30852
C	4.6942	-0.69484	0.13389
C	3.32954	-0.9379	0.02956
C	2.56963	0.28047	0.09086
C	3.34671	1.46978	0.18372
C	1.18684	2.04039	0.08606
C	2.52267	2.59424	0.18577
S	5.10077	1.09987	0.28511
N	1.23912	0.63173	0.04795
C	5.82354	-1.62528	0.16944
C	7.07102	-1.26631	-0.38157
C	5.721	-2.89413	0.79332
C	8.17023	-2.12642	-0.33182
H	7.18008	-0.30632	-0.87501
C	6.80905	-3.75388	0.84989
H	4.78359	-3.19435	1.24291
C	8.03932	-3.37717	0.28597
H	9.10773	-1.81498	-0.77549
H	6.736	-4.72072	1.33345
C	2.79571	-2.30065	-0.25586
C	2.00071	-3.00697	0.66688
C	3.1387	-2.92713	-1.46401
C	1.57403	-4.30274	0.38833
H	1.68762	-2.52905	1.58534
C	2.7113	-4.22563	-1.75735
H	3.74712	-2.39297	-2.18611
C	1.92866	-4.91198	-0.82282
H	0.95521	-4.84734	1.09102
H	2.98743	-4.67622	-2.70262
C	2.89133	4.00414	0.25867
C	4.19606	4.42092	-0.07977
C	1.97435	4.9981	0.68511
C	4.58162	5.76028	-0.0038
H	4.91872	3.69503	-0.43507

C	2.34954	6.33236	0.7633
H	0.96729	4.70805	0.95145
C	3.65478	6.72212	0.42156
H	5.59119	6.03795	-0.28041
H	1.65275	7.09295	1.09534
N	0.05306	2.72702	-0.02273
B	-0.03777	-0.25914	0.05182
F	-0.09516	-1.03363	1.25549
F	-0.0324	-1.12087	-1.09124
O	-3.49686	8.2759	-0.75744
O	3.92831	8.07699	0.53855
O	9.05995	-4.30973	0.39519
O	1.44026	-6.20851	-1.01816
O	-2.10292	-6.11435	1.38871
O	-9.48675	-3.58027	0.15404
C	-4.78967	8.8496	-0.42555
H	-5.02678	8.70586	0.63499
H	-4.69233	9.91291	-0.64037
H	-5.58576	8.41769	-1.04305
C	5.26075	8.55665	0.21566
H	6.01573	8.0988	0.86532
H	5.50989	8.36047	-0.83374
H	5.22637	9.63106	0.39107
C	-9.5281	-4.93848	-0.36139
H	-10.54937	-5.27595	-0.19025
H	-9.30459	-4.96216	-1.43422
H	-8.82743	-5.58759	0.17614
C	-1.59518	-7.05304	0.39754
H	-2.27765	-7.12095	-0.45929
H	-0.59415	-6.77661	0.05267
H	-1.5594	-8.01225	0.91422
C	1.82073	-6.92003	-2.22518
H	1.44977	-6.41073	-3.12233
H	2.90901	-7.03297	-2.29142
H	1.35426	-7.90112	-2.14003
C	10.36845	-3.98847	-0.14819
H	10.98679	-4.85897	0.0665
H	10.31974	-3.82675	-1.23136
H	10.79333	-3.10278	0.33822

b. in chloroform

C	-4.73818	-0.69038	0.06055
C	-3.37849	-0.91949	0.23779
C	-2.62417	0.2976	0.17135

C	-3.38945	1.48084	-0.01719
C	-1.22413	2.0435	0.0789
C	-2.55581	2.59788	-0.07949
S	-5.13827	1.10009	-0.17939
N	-1.2902	0.64014	0.20929
C	-5.87212	-1.61377	0.07339
C	-7.00004	-1.37214	-0.74061
C	-5.90336	-2.75157	0.91925
C	-8.10749	-2.22144	-0.73202
H	-7.005	-0.51824	-1.40972
C	-7.00297	-3.59908	0.93721
H	-5.06756	-2.95725	1.57434
C	-8.11059	-3.34254	0.11046
H	-8.94673	-2.00439	-1.38045
H	-7.03077	-4.46296	1.59088
C	-2.8077	-2.27491	0.47797
C	-2.31934	-2.61991	1.75394
C	-2.78898	-3.24676	-0.53246
C	-1.84318	-3.90141	2.01159
H	-2.30663	-1.87659	2.54206
C	-2.30521	-4.53754	-0.28797
H	-3.15256	-2.99552	-1.52336
C	-1.83822	-4.86551	0.9917
H	-1.46861	-4.17556	2.99111
H	-2.29184	-5.26285	-1.09161
C	-2.91612	3.99902	-0.26243
C	-4.22823	4.43994	0.01689
C	-1.98718	4.95988	-0.73687
C	-4.60944	5.77028	-0.16149
H	-4.96043	3.74351	0.40963
C	-2.35814	6.28557	-0.91784
H	-0.97472	4.65211	-0.95967
C	-3.67084	6.7	-0.63336
H	-5.62337	6.06755	0.07419
H	-1.65029	7.01869	-1.28673
C	4.71424	-0.49642	0.08364
C	3.35763	-0.8028	0.02277
C	2.54675	0.37996	0.12135
C	3.27197	1.60319	0.18605
C	1.08657	2.08158	0.18502
C	2.40089	2.69125	0.22585
S	5.04375	1.31488	0.218
N	1.19891	0.67406	0.13785
C	5.88398	-1.37401	0.08907

C	7.09927	-0.96402	-0.49938
C	5.85454	-2.64108	0.72506
C	8.23594	-1.77443	-0.47553
H	7.15416	-0.00492	-1.00339
C	6.98104	-3.45122	0.75786
H	4.94478	-2.97867	1.20436
C	8.17813	-3.0255	0.15516
H	9.14508	-1.42588	-0.94872
H	6.96143	-4.41557	1.25179
C	2.88758	-2.18514	-0.28345
C	2.11146	-2.94685	0.612
C	3.27158	-2.77207	-1.50077
C	1.75012	-4.25604	0.30184
H	1.76507	-2.50266	1.53651
C	2.90907	-4.08267	-1.82654
H	3.86349	-2.19738	-2.20542
C	2.1501	-4.82718	-0.91576
H	1.14654	-4.84625	0.98128
H	3.21804	-4.49969	-2.77672
C	2.7113	4.11537	0.28057
C	3.97397	4.58972	-0.13675
C	1.77896	5.06762	0.76546
C	4.30417	5.94435	-0.08214
H	4.705	3.89769	-0.53921
C	2.09939	6.41739	0.82429
H	0.80424	4.73448	1.09456
C	3.36334	6.86514	0.40278
H	5.28046	6.26651	-0.42141
H	1.39002	7.14434	1.20237
N	-0.07928	2.71795	0.11962
B	-0.02996	-0.25484	0.32152
F	0.03848	-0.85938	1.63338
F	-0.0654	-1.27562	-0.67557
O	-3.93993	8.04117	-0.85004
O	3.58497	8.22835	0.50541
O	9.24098	-3.90866	0.24001
O	1.73782	-6.14133	-1.1376
O	-1.34245	-6.11475	1.35212
O	-9.15288	-4.24915	0.20177
C	-5.28157	8.54725	-0.57933
H	-5.54331	8.41918	0.47608
H	-5.23982	9.6072	-0.82428
H	-6.02421	8.04819	-1.21047
C	4.87833	8.76853	0.09993

H	5.68794	8.33987	0.69962
H	5.06457	8.58431	-0.96323
H	4.80868	9.83943	0.28312
C	-10.34275	-4.04554	-0.61843
H	-11.00375	-4.87399	-0.36967
H	-10.82868	-3.09514	-0.37477
H	-10.09416	-4.07468	-1.68434
C	-1.27876	-7.16479	0.33924
H	-2.27125	-7.36865	-0.07709
H	-0.5757	-6.89256	-0.45298
H	-0.91526	-8.04481	0.86875
C	2.14319	-6.80082	-2.37243
H	1.73665	-6.28389	-3.2483
H	3.23435	-6.85582	-2.44917
H	1.72664	-7.80519	-2.31071
C	10.51982	-3.5387	-0.35759
H	11.18008	-4.38107	-0.15838
H	10.41988	-3.39171	-1.43802
H	10.92256	-2.63239	0.10637

c. in acetonitrile

C	-4.74024	-0.64671	0.06624
C	-3.38268	-0.88876	0.24905
C	-2.6162	0.32057	0.18154
C	-3.37026	1.51046	-0.0073
C	-1.20012	2.05582	0.08406
C	-2.52713	2.62087	-0.07168
S	-5.12205	1.14678	-0.17162
N	-1.27734	0.65209	0.21545
C	-5.88263	-1.55929	0.06507
C	-6.9969	-1.30603	-0.76512
C	-5.93651	-2.6978	0.90889
C	-8.11126	-2.14563	-0.7751
H	-6.98534	-0.45137	-1.433
C	-7.0439	-3.53569	0.90893
H	-5.11377	-2.91167	1.57777
C	-8.13676	-3.26855	0.06524
H	-8.93832	-1.92025	-1.43588
H	-7.08838	-4.39955	1.56186
C	-2.8308	-2.25181	0.49509
C	-2.38304	-2.6129	1.78192
C	-2.79864	-3.21857	-0.52026
C	-1.93377	-3.90375	2.04481
H	-2.38917	-1.87695	2.57746

C	-2.3401	-4.5183	-0.27145
H	-3.13522	-2.95826	-1.51846
C	-1.9137	-4.86207	1.01864
H	-1.59538	-4.18971	3.03419
H	-2.32099	-5.23981	-1.07841
C	-2.87666	4.02447	-0.25521
C	-4.18585	4.47588	0.02398
C	-1.94049	4.97819	-0.73046
C	-4.55712	5.80876	-0.15469
H	-4.92432	3.78626	0.41669
C	-2.30141	6.30667	-0.91171
H	-0.93053	4.66329	-0.95445
C	-3.61123	6.73158	-0.62681
H	-5.56876	6.11348	0.08058
H	-1.58717	7.03325	-1.28148
C	4.71934	-0.53229	0.07017
C	3.35943	-0.82736	0.02183
C	2.55864	0.36131	0.11863
C	3.29305	1.57836	0.17871
C	1.11115	2.07547	0.18561
C	2.43055	2.67392	0.22296
S	5.06278	1.27612	0.19849
N	1.21146	0.66612	0.13826
C	5.88152	-1.4191	0.06436
C	7.09252	-1.02062	-0.54205
C	5.85029	-2.68367	0.70537
C	8.22243	-1.84017	-0.53119
H	7.14915	-0.06421	-1.05071
C	6.97073	-3.50287	0.72574
H	4.94579	-3.01209	1.20067
C	8.16318	-3.08901	0.10486
H	9.1273	-1.50087	-1.01861
H	6.94926	-4.46475	1.22458
C	2.87295	-2.20864	-0.26321
C	2.13543	-2.96313	0.66991
C	3.20415	-2.80475	-1.4917
C	1.75429	-4.27241	0.38299
H	1.83832	-2.51413	1.60904
C	2.8228	-4.11626	-1.7941
H	3.77001	-2.23787	-2.22361
C	2.09947	-4.85312	-0.84783
H	1.17993	-4.85711	1.09228
H	3.09201	-4.54103	-2.75283
C	2.75385	4.09477	0.28178

C	4.02165	4.55904	-0.13328
C	1.83063	5.05399	0.77093
C	4.36542	5.90976	-0.07196
H	4.74676	3.86306	-0.53932
C	2.16454	6.40024	0.83655
H	0.85254	4.72965	1.09879
C	3.43353	6.83775	0.4177
H	5.34482	6.22354	-0.40954
H	1.46147	7.13152	1.21828
N	-0.04976	2.72096	0.12272
B	-0.02477	-0.2517	0.30616
F	0.03977	-0.89322	1.60109
F	-0.07186	-1.2542	-0.71518
O	-3.87019	8.07375	-0.84295
O	3.66925	8.19698	0.52762
O	9.21957	-3.97932	0.17835
O	1.673	-6.16504	-1.04205
O	-1.44809	-6.121	1.38275
O	-9.18753	-4.16552	0.13759
C	-5.2108	8.59119	-0.57415
H	-5.47387	8.46467	0.48062
H	-5.16013	9.65053	-0.81944
H	-5.95462	8.09675	-1.20663
C	4.97054	8.72752	0.12501
H	5.77395	8.28732	0.72374
H	5.15452	8.54573	-0.93843
H	4.91081	9.79797	0.3134
C	-10.36366	-3.95077	-0.7041
H	-11.03486	-4.77461	-0.46831
H	-10.84502	-2.99719	-0.46612
H	-10.09537	-3.9798	-1.7647
C	-1.40261	-7.17463	0.36954
H	-2.39648	-7.3536	-0.05333
H	-0.68922	-6.91896	-0.41865
H	-1.06384	-8.06284	0.9014
C	2.01689	-6.83696	-2.29214
H	1.57576	-6.32023	-3.15052
H	3.10266	-6.90205	-2.41592
H	1.59319	-7.83607	-2.20478
C	10.49582	-3.62083	-0.43804
H	11.15154	-4.46785	-0.24447
H	10.38147	-3.47664	-1.51686
H	10.90997	-2.71646	0.01842

4. Experimental Section

General. The NMR experiments were obtained on a 300 MHz NMR spectrometer at room temperature. Chemical shifts (δ) are given in ppm relative to TMS. High-resolution mass spectra were obtained using APCI-TOF in positive mode. UV-visible absorption spectra and fluorescence emission spectra were recorded on a commercial spectrophotometer (190-900 nm scan range). The slit width was set at 2.5 nm for excitation and 5.0 nm for emission. Relative fluorescence quantum yields were calculated using ICG in DMSO ($\phi = 0.12$) as the standard.^{5a} Non-degassed, spectroscopic grade solvents and a 10 mm quartz cuvette were used. Dilute solutions (0.01 < A < 0.05) were used to minimize the reabsorption effects. Quantum yields were determined using the following equation^{5b}:

$$\Phi_X = \Phi_S (I_X/I_S) (A_S/A_X) (\eta_X/\eta_S)^2$$

Where Φ_S stands for the reported quantum yield of the standard, I stands for the integrated emission spectra, A stands for the absorbance at the excitation wavelength and η stands for the refractive index of the solvent being used ($\eta = 1$ when the same solvent was used for both the test sample and the standard). X subscript stands for the test sample, and S subscript stands for the standard.

Fluorescence lifetime was measured in chloroform by time-correlated single photon counting method (Edinburgh FLS920 spectrophotometer). The compounds were excited at 370 nm and the emission was monitored at the maximum emission wavelength. Details of the instrumentation and experimental procedures used have been described elsewhere⁶. When the fluorescence decays were monoexponential, the rate constants of radiative (k_f) and nonradiative (k_{nr}) deactivation were calculated from the measured fluorescence quantum yield and fluorescence lifetime according to eqs below: $k_f = \Phi/\tau$ and $k_{nr} = (1 - \Phi)/\tau$.

Crystals of compoundss **3a**, **3c**, **5c** and **5d** suitable for X-ray analysis were obtained by slow evaporation of their dichloromethane solutions. The vial containing this solution was placed, loosely capped, to promote the crystallization. A suitable crystal was chosen and mounted on a glass fiber using grease. Data were collected using a diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection at room temperature. Cell

parameters were retrieved using SMART⁷ software and refined using SAINT on all observed reflections. The determination of unit cell parameters and data collections were performed with Mo K α radiation (λ) at 0.71073 Å. Data reduction was performed using the SAINT software,⁸ which corrects for Lp and decay. The structure was solved by the direct method using the SHELXS-974 program and refined by least squares method on F², SHELXL-97,⁹ incorporated in SHELXTL V5.10.¹⁰

Synthesis and characterizations:

Pyrrole **1** was synthesized using a modified method according to the literature⁴: to EtONa (12.8 g, 188 mmol, 4.4 eq) in 80 mL of ethanol was dropwisely added a mixture of 2-thenaldehyde (4.8 g, 43 mmol) and ethyl 2-azidoacetate (20.4 g, 188 mmol, 4.4 eq) in round 20 mL ethanol over 40 mins at 0 °C. The mixture was stirred for 3 h at room temperature, quenched by addition of saturated NH₄Cl solution. The precipitate was filtrated to give **6** as yellow solid in 48% yield (4.58 g). A solution of **6** (7.6 g, 34.1 mmol) in 180 mL of dry toluene was heated to reflux for 2 h. Solvent was removed under vacuum, and the residue was recrystallized twice from ethanol to generate **1** as a white solid in 93% yield (6.18 g). ¹H NMR (300 MHz, CDCl₃) δ: 9.52 (s, 1H), 7.32 (d, *J* = 4.8 Hz, 1H), 7.15 (s, 1H), 6.96 (d, *J* = 4.8 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ: 162.0, 141.5, 129.5, 127.0, 124.7, 111.2, 107.6, 60.8, 14.5.

General procedure for the preparation of 2: to 1 (195 mg, 1.0 mmol) in 80 mL dichloromethane was dropwisely added the dichloromethane (30 mL) solution of bromine (160 mg, 2.0 mmol, 2 eq). The solution was stirred for 1 h. The evolution of hydrogen bromide was shown by a test with a piece of moistened litmus paper. After the reaction, the reaction mixture was evaporated to dryness under vacuum. The solid residue was obtained and was recrystallized from an ethanol/water mixture to give **2a** as a white solid in 96% yield (339 mg). ¹H NMR (300 MHz, CDCl₃) δ: 9.44 (s, 1H), 87.01 (s, 1H), 4.40 (q, *J* = 6.0 Hz, 2H), 1.42 (t, *J* = 6.0 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ: 160.8, 137.6, 127.4, 122.9, 117.1, 114.9, 114.4, 61.3, 14.4. HRMS (APCI) Calcd. for C₉H₇Br₂NO₂S [M + H]⁺ 351.8637, found 351.8642.

2b was prepared as a white solid in 87% yield (375 mg) from the bromination of **1** (195 mg, 1.0 mmol) with 3 eq of bromine (240 mg, 3.0 mmol). ¹H NMR (300 MHz, CDCl₃) δ: 9.24 (s, 1H),

4.46 (q, $J = 7.0$ Hz, 2H), 1.46 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR was not available due to poor solubility. HRMS (APCI) Calcd. for $\text{C}_9\text{H}_6\text{Br}_3\text{NO}_2\text{S} [\text{M} + \text{H}]^+$ 429.7742, found 429.7741.

General procedure for the preparation of 3: to **2a** (366 mg, 1.2 mmol), palladium(0)tetrakis(triphenylphosphine) (24 mg, 0.02 mmol), and 4-methoxyphenylboronic acid (435 mg, 3.6 mmol, 3eq) in Schlenk flask was added Na_2CO_3 (1 mol/L in 5 mL dry toluene). The mixture was then degassed via three freeze-pump-thaw cycles before purging with argon again. The Schlenk flask was sealed and heated to 90 °C for 12 h. After cooling down to room temperature, the reaction mixture was washed with brine. Organic layers were combined, dried over anhydrous Na_2SO_4 , and evaporated to dryness under vacuum. The residue was column chromatographed (silica, hexane: dichloromethane = 1:2, v/v) to afford compound **3a** in 83% yield (297 mg). ^1H NMR (300 MHz, CDCl_3) δ: 9.23 (s, 1H), 7.74 (d, $J = 4.8$ Hz, 2H), 7.56 (d, $J = 4.8$ Hz, 2H), 7.06 (s, 1H), 7.02 (d, $J = 6.8$ Hz, 2H), 6.94 (d, $J = 6.8$ Hz, 2H), 4.35 (q, $J = 7.1$ Hz, 2H), 3.90 (s, 3H), 3.86 (s, 3H), 1.34 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ: 161.5, 159.6, 158.9, 148.3, 140.0, 130.6, 127.8, 127.1, 126.0, 124.6, 124.4, 120.3, 114.3, 113.4, 106.1, 60.5, 55.4, 55.3, 14.3. HRMS (APCI) Calcd. for $\text{C}_{23}\text{H}_{22}\text{NO}_4\text{S} [\text{M} + \text{H}]^+$ 408.1264, found 408.1262. HRMS (APCI) Calcd. for $\text{C}_9\text{H}_6\text{Br}_3\text{NO}_2\text{S} [\text{M} + \text{H}]^+$ 429.7742, found 429.7741.

3b was prepared in 85% yield (545 mg) from **2a** (433 mg, 1.42 mmol) and 4-butylphenylboronic acid (758 mg, 4.3 mmol, 3eq). ^1H NMR (300 MHz, CDCl_3) δ: 9.21 (s, 1H), 7.76 (d, $J = 8.3$ Hz, 2H), 7.60 (d, $J = 8.3$ Hz, 2H), 7.52-7.44 (m, 4H), 7.19 (s, 1H), 4.37 (q, $J = 7.1$ Hz, 2H), 1.45 (s, 9H), 1.38 (s, 9H), 1.32 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ: 161.3, 151.3, 150.3, 148.5, 139.9, 132.2, 130.5, 129.0, 125.9, 125.5, 125.2, 124.9, 124.6, 120.8, 106.6, 60.5, 34.7, 31.4, 31.3, 14.3. HRMS (APCI) Calcd. for $\text{C}_{29}\text{H}_{33}\text{NO}_2\text{S} [\text{M} + \text{H}]^+$ 460.2305, found 460.2309.

3c was prepared in 87% yield (446 mg) from **2b** (430 mg, 1 mmol) and 4-methoxyphenylboronic acid (760 mg, 5 mmol, 5eq). ^1H NMR (300 MHz, CDCl_3) δ: 9.12 (s, 1H), 7.72 (d, $J = 8.6$ Hz, 2H), 7.31-7.25 (m, 4H), 7.00 (d, $J = 8.7$ Hz, 2H), 6.93 (d, $J = 8.5$ Hz, 2H), 6.81 (d, $J = 8.7$ Hz, 2H), 4.29 (q, $J = 7.1$ Hz, 2H), 3.88 (s, 3H), 3.83 (s, 3H), 3.80 (s, 3H), 1.29 (t, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ: 161.6, 159.2, 159.0, 141.9, 140.3, 130.8, 130.3, 130.3, 127.4, 126.3, 126.1, 124.5, 123.1, 121.6, 120.2, 114.6, 114.0, 113.4, 60.6, 55.3, 55.2, 53.5, 14.3. HRMS (APCI) Calcd. for $\text{C}_{30}\text{H}_{27}\text{NO}_5\text{S} [\text{M} + \text{H}]^+$ 514.1683, found 514.1675.

3d was prepared in 75% yield (442 mg) from **2b** (430 mg, 1 mmol) and 4-butylphenylboronic acid (900 mg, 5 mmol, 5 eq). ¹H NMR (300 MHz, CDCl₃) δ: 9.08 (s, 1H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.52-7.45 (m, 4H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.31-7.26 (m, 4H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.42 (s, 9H), 1.41 (s, 9H), 1.34 (s, 9H), 1.32 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ: 161.3, 151.3, 150.3, 148.5, 139.9, 132.2, 130.5, 129.0, 125.9, 125.5, 125.2, 124.9, 124.6, 120.8, 106.6, 60.5, 34.7, 31.4, 31.2, 14.3. HRMS (APCI) Calcd. for C₃₉H₄₅NO₂S [M + H]⁺ 592.3244, found 592.3247.

General procedure for the preparation of 4: the mixture of **3a** (610 mg, 1.5 mmol) and KOH (3.9 g, 46.4 mmol, 46 eq) in ethylene glycol (30 mL) was heated at 130 °C under Ar for 2h. After cooling down to room temperate, the reaction mixture was quenched with water, extracted with diethyl ether, and dried over anhydrous Na₂SO₄. Solvent was removed under vacuum. The residue was column chromatographed (silica, hexane: DCM = 1:1, v/v) to generate **4a** as a white solid in 91% yield (453 mg). ¹H NMR (300 MHz, CDCl₃) δ: 8.27 (s, 1H), 7.63-7.58 (m, 4H), 7.25 (s, 1H), 7.15 (s, 1H), 7.02-6.94 (m, 4H), 3.88 (s, 3H), 3.87 (s, 3H). ¹³C NMR was not available due to poor solubility. HRMS (APCI) Calcd. for C₂₀H₁₇NO₂S [M + H]⁺ 336.1053, found 336.1054.

4b was prepared as a white solid in 89% yield (348 mg) from **3b** (500 mg, 1.1 mmol) and KOH (2.6 g, 46.4 mmol, 43 eq). ¹H NMR (300 MHz, CDCl₃) δ: 8.39 (s, 1H), 7.58 (d, *J* = 8.0 Hz, 4H), 7.47-7.39 (m, 5H), 7.18 (s, 1H), 1.37 (s, 9H), 1.35 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ: 151.2, 148.6, 143.0, 139.1, 132.9, 131.5, 129.5, 126.2, 125.8, 125.7, 125.2, 124.7, 118.5, 107.1, 34.6, 34.5, 31.4, 31.3. HRMS (APCI) Calcd. for C₂₆H₂₉NS [M + H]⁺ 388.2093, found 388.2095.

4c was prepared as a white solid in 84% yield (741 mg) from **3c** (1.0 g, 2 mmol) and KOH (5 g, 90 mmol, 46 eq). ¹H NMR (300 MHz, CDCl₃) δ: 8.25 (s, 1H), 7.60 (d, *J* = 7.0 Hz, 2H), 7.31-7.21 (m, 5H), 6.99 (d, *J* = 7.2 Hz, 2H), 6.92 (d, *J* = 7.7 Hz, 2H), 6.82 (d, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 3.84 (s, 3H), 3.82 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ: 158.8, 158.7, 157.8, 139.5, 136.7, 132.6, 130.3, 130.2, 128.0, 127.3, 127.1, 126.2, 121.8, 118.3, 117.3, 114.5, 114.3, 113.9, 55.4, 55.3, 55.3. HRMS (APCI) Calcd. for C₂₇H₂₃NO₃S [M + H]⁺ 442.1471, found 442.1465.

4d was prepared as a light yellow solid in 87% yield (453 mg) from **3d** (600 mg, 1 mmol) and KOH (2.6 g, 46.4 mmol, 46 eq). ¹H NMR (300 MHz, CDCl₃) δ: 8.39 (s, 1H), 7.64 (d, *J* = 8.4 Hz,

2H), 7.49 (d, J = 8.4 Hz, 2H), 7.42-7.30 (m, 9H), 1.40 (s, 18H), 1.35 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3) δ : 150.2, 149.9, 148.6, 139.7, 139.3, 137.2, 132.5, 131.9, 131.6, 128.7, 128.5, 126.0, 125.9, 125.7, 125.3, 124.8, 122.2, 118.8, 1118.4, 118.0, 34.6, 34.5, 34.5, 31.4, 31.4, 31.3. HRMS (APCI) Calcd. for, $\text{C}_{36}\text{H}_{41}\text{NS} [\text{M} + \text{H}]^+$ 520.3032, found 520.3029.

General procedure for the preparation of aza-BDTPs 5: to the suspension solution of **4a** (34 mg, 0.1 mmol) in a mixture of acetic acid/acetic anhydride (1 ml/0.5ml) was added sodium nitrite (7 mg, 0.1 mmol) at 0 °C. The mixture was stirred for 15 min. During this period, the color changed from colorless to brown, then green, and finally to brown. Upon addition of pyrrole (34 mg, 0.1 mmol), the mixture immediately turned blue. The mixture was further stirred for 0.5 h at room temperature before raising the temperature to 80 °C. After further stirring at this temperature for 0.5 h, the resultant blue solid was filtered and washed with ethanol. The resultant blue solid was dissolved in dry toluene (30 mL), and triethylamine (1 mL) was added to the solution, followed by dropwisely addition of $\text{BF}_3\text{-Et}_2\text{O}$ (1 mL). The mixture was stirred at 80 °C in oil bath for 0.5 h before cooling down to room temperature. The reaction mixture was concentrated (to around 5 mL) under vacuum to afford reddish brown precipitate. This precipitate was collected, washed with ethanol and recrystallized from the mixture solvent of dichloromethane and hexane (v/v = 1:1) to afford aza-BDTP **5a** as reddish-brown solid in 54% yield (39 mg). ^1H NMR (500 MHz, CDCl_3) δ : 8.12 (brs, 4H), 7.72 (brs, 4H), 7.47 (s, 2H), 7.05 (brs, 4H), 7.00 (brs, 4H), 3.93(s, 6H), 3.90 (s, 6H). ^{13}C NMR was not available due to poor solubility. HRMS (APCI) Calcd. for $\text{C}_{40}\text{H}_{30}\text{BF}_2\text{N}_3\text{O}_4\text{S}_2 [\text{M} + \text{H}]^+$ 730.1812, found 730.1810. Anal. Calcd. (%) for $\text{C}_{40}\text{H}_{30}\text{BF}_2\text{N}_3\text{O}_4\text{S}_2$: C 65.85, H 4.14, N 5.76; found: C 65.49, H 4.51, N 5.38.

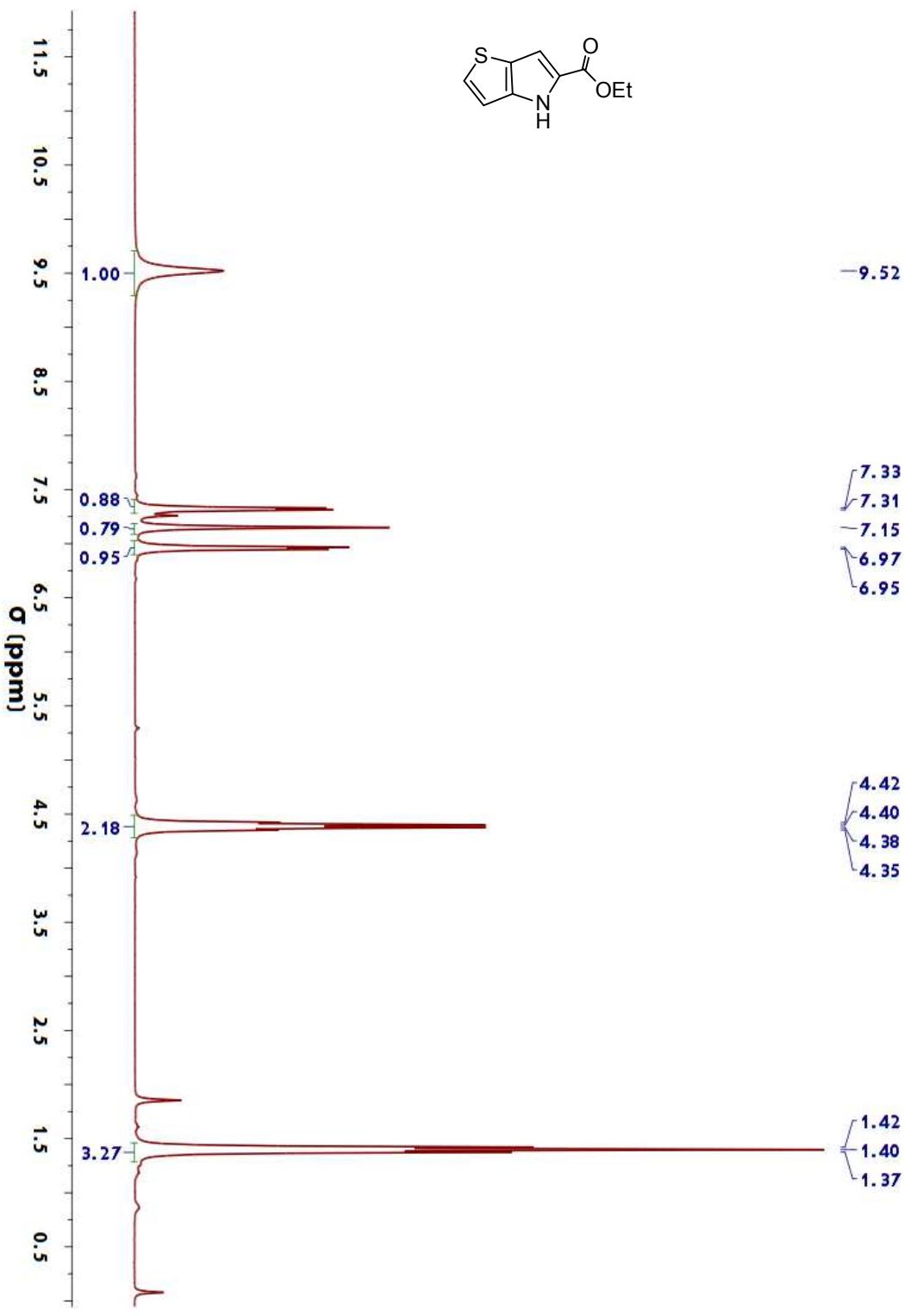
5b was prepared as reddish-brown solid in 58% yield (48 mg) from sodium nitrite (7 mg, 0.1 mmol) and **4b** (39 mg, 0.1 mmol). ^1H NMR (500 MHz, CDCl_3) δ : 8.10 (d, J = 6.5 Hz, 4H), 7.71 (brs, 4H), 7.55 (d, J = 8.0 Hz, 4H), 7.50 (d, J = 7.5 Hz, 4H), 7.40 (s, 2H), 1.41 (s, 18H), 1.37 (s, 18H). ^{13}C NMR (75 MHz, CDCl_3) δ : 161.5, 158.2, 154.4, 152.7, 149.7, 132.7, 131.0, 129.9, 129.8, 129.7, 129.2, 128.8, 126.4, 126.2, 125.8, 109.3, 35.0, 34.9, 31.2, 31.1. HRMS (APCI) Calcd. for $\text{C}_{52}\text{H}_{54}\text{BF}_2\text{N}_3\text{S}_2 [\text{M} + \text{H}]^+$ 834.3893, found 834.3872. Anal. Calcd. (%) for $\text{C}_{52}\text{H}_{54}\text{BF}_2\text{N}_3\text{S}_2$: C 74.89, H 6.53, N 5.04; found: C 74.57, H 6.71, N 4.86.

5c was prepared in 65% yield (62 mg) from sodium nitrite (7 mg, 0.1 mmol) and **4c** (44 mg, 0.1

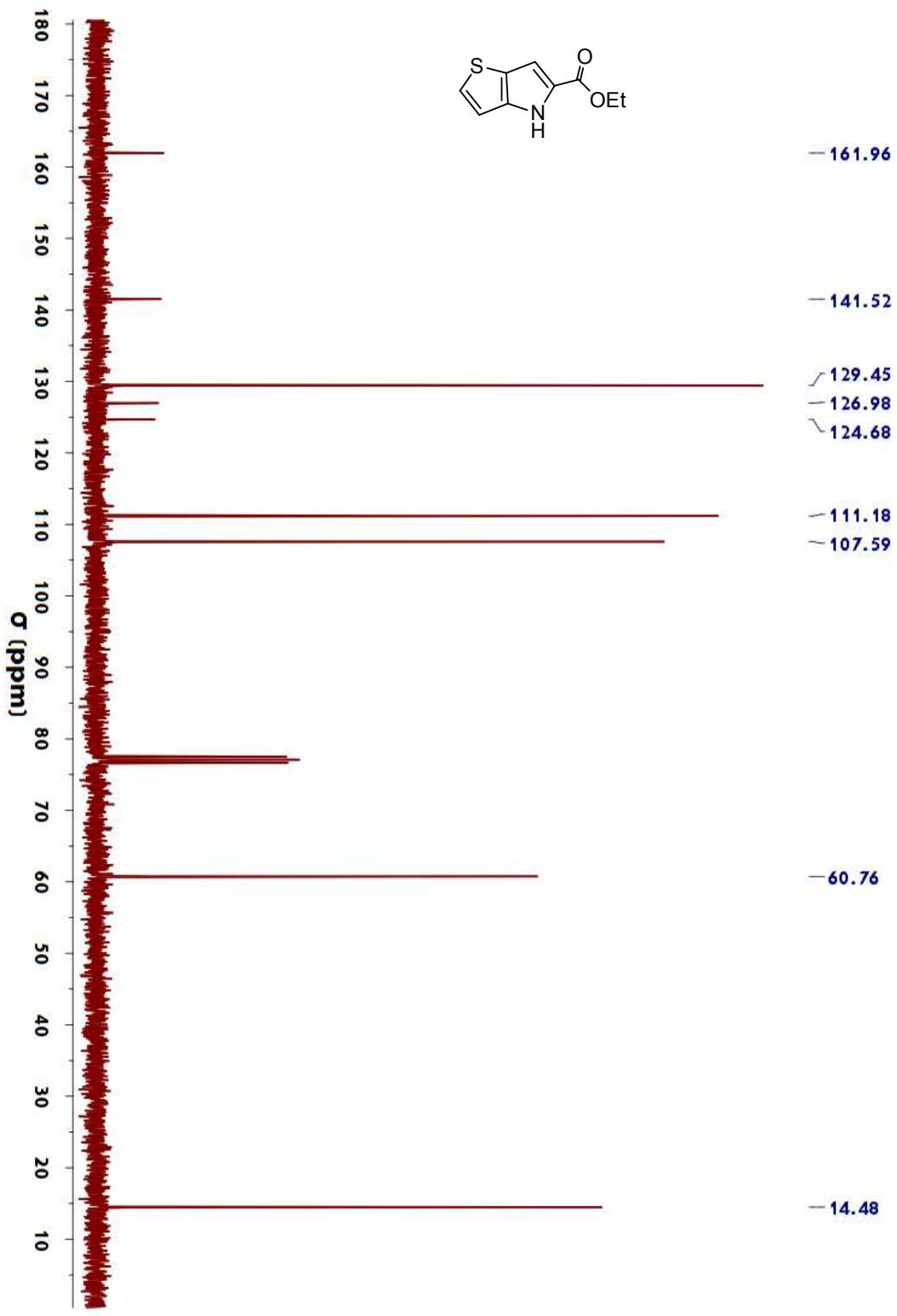
mmol). ^1H NMR (500 MHz, CDCl_3) δ : 8.09 (d, $J = 8.0$ Hz, 4H), 7.16-7.11 (m, 8H), 7.04 (d, $J = 8.5$ Hz, 4H), 6.76 (d, $J = 8.0$ Hz, 4H), 6.71 (d, $J = 8.5$ Hz, 4H), 3.91 (s, 12H), 3.77 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ : 160.4, 160.3, 159.0, 158.1, 156.3, 149.0, 132.1, 131.5, 130.3, 128.0, 127.3, 126.3, 125.2, 125.0, 114.3, 113.9, 113.1, 55.5, 55.3, 55.0. HRMS (APCI) Calcd. for, $\text{C}_{54}\text{H}_{42}\text{BF}_2\text{N}_3\text{O}_6\text{S}_2$ $[\text{M} + \text{H}]^+$ 942.2649, found 942.2654. Anal. Calcd. (%) for $\text{C}_{54}\text{H}_{42}\text{BF}_2\text{N}_3\text{O}_6\text{S}_2$: C 68.86, H 4.49, N 4.46; found: C 68.59, H 4.62, N 4.15.

5d was prepared as reddish brown solid in 65% yield (71 mg) from sodium nitrite (7 mg, 0.1 mmol) and **4d** (52 mg, 0.1 mmol). ^1H NMR (500 MHz, CDCl_3) δ : 8.08 (d, $J = 8.0$ Hz, 4H), 7.55 (d, $J = 7.5$ Hz, 4H), 7.27 (d, $J = 8.5$ Hz, 4H), 7.19 -7.15 (m, 8H), 7.05 (d, $J = 8.0$ Hz, 4H), 1.41 (s, 18H), 1.40 (s, 18H), 1.25 (s, 18H). ^{13}C NMR (75 MHz, CDCl_3) δ : 158.5, 157.6, 152.5, 152.4, 150.3, 149.7, 132.0, 131.8, 130.9, 130.1, 129.9, 129.7, 129.4, 128.5, 127.3, 125.7, 125.5, 125.2, 124.6, 34.9, 34.7, 34.6, 31.6, 31.3, 31.2, 31.0. HRMS (APCI) Calcd. for $\text{C}_{72}\text{H}_{78}\text{BF}_2\text{N}_3\text{S}_2$ $[\text{M} + \text{H}]^+$ 1098.5771, found 1098.5770. Anal. Calcd. (%) for $\text{C}_{72}\text{H}_{78}\text{BF}_2\text{N}_3\text{S}_2$: C 78.73, H 7.16, N 3.83; found: C 78.51, H 7.31, N 3.65.

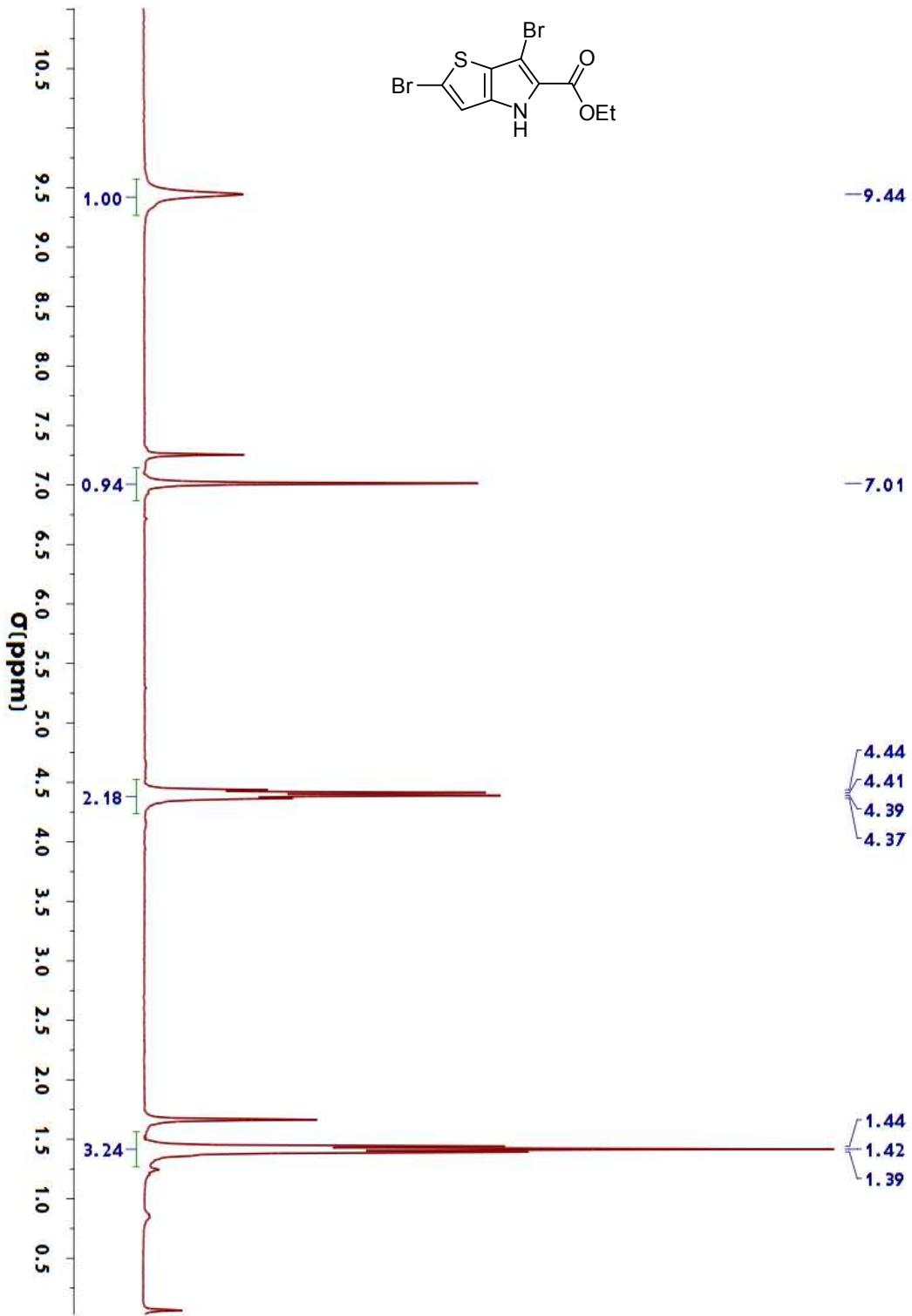
5. Copies of ^1H and ^{13}C NMR spectra

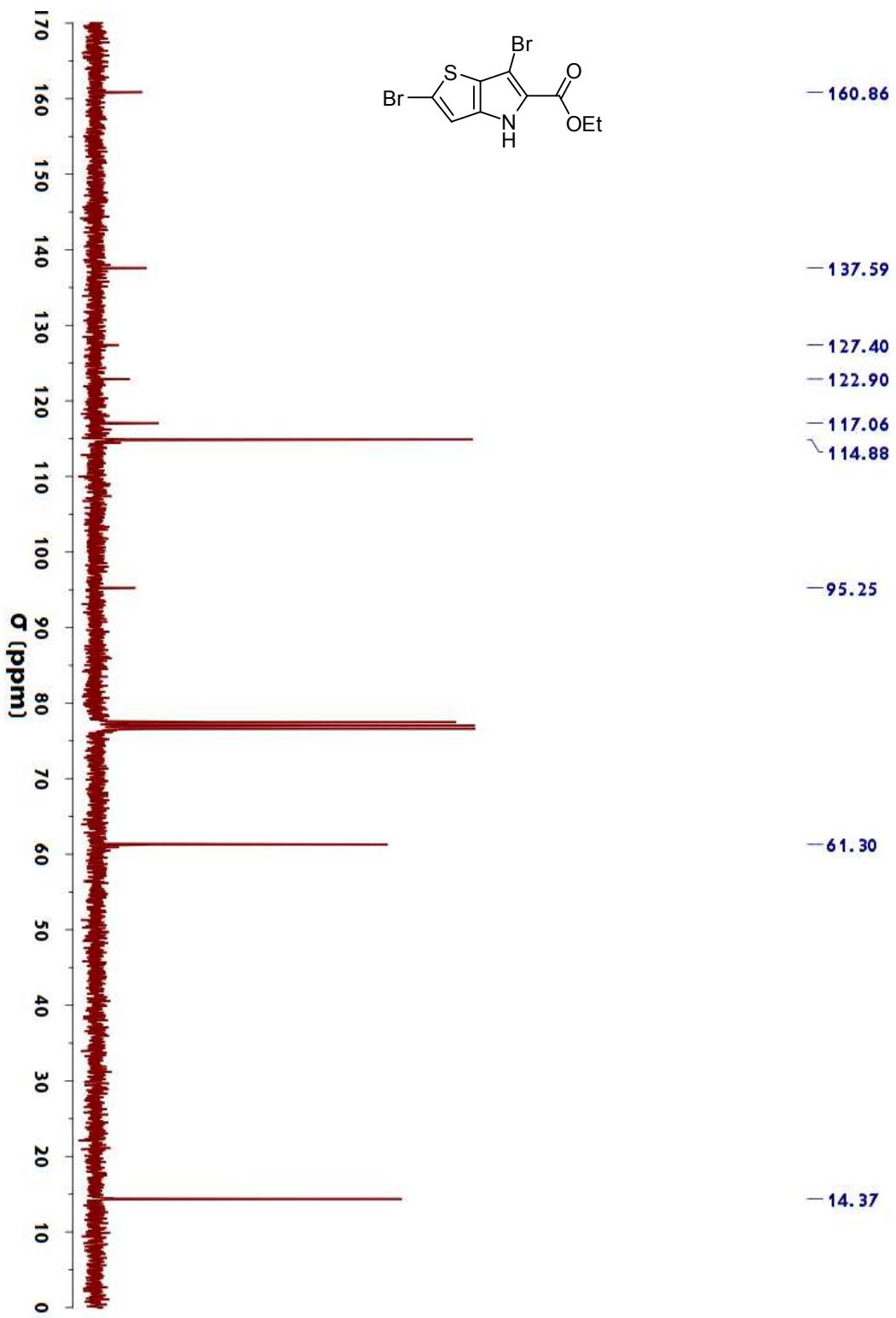


^1H NMR spectrum of **1**

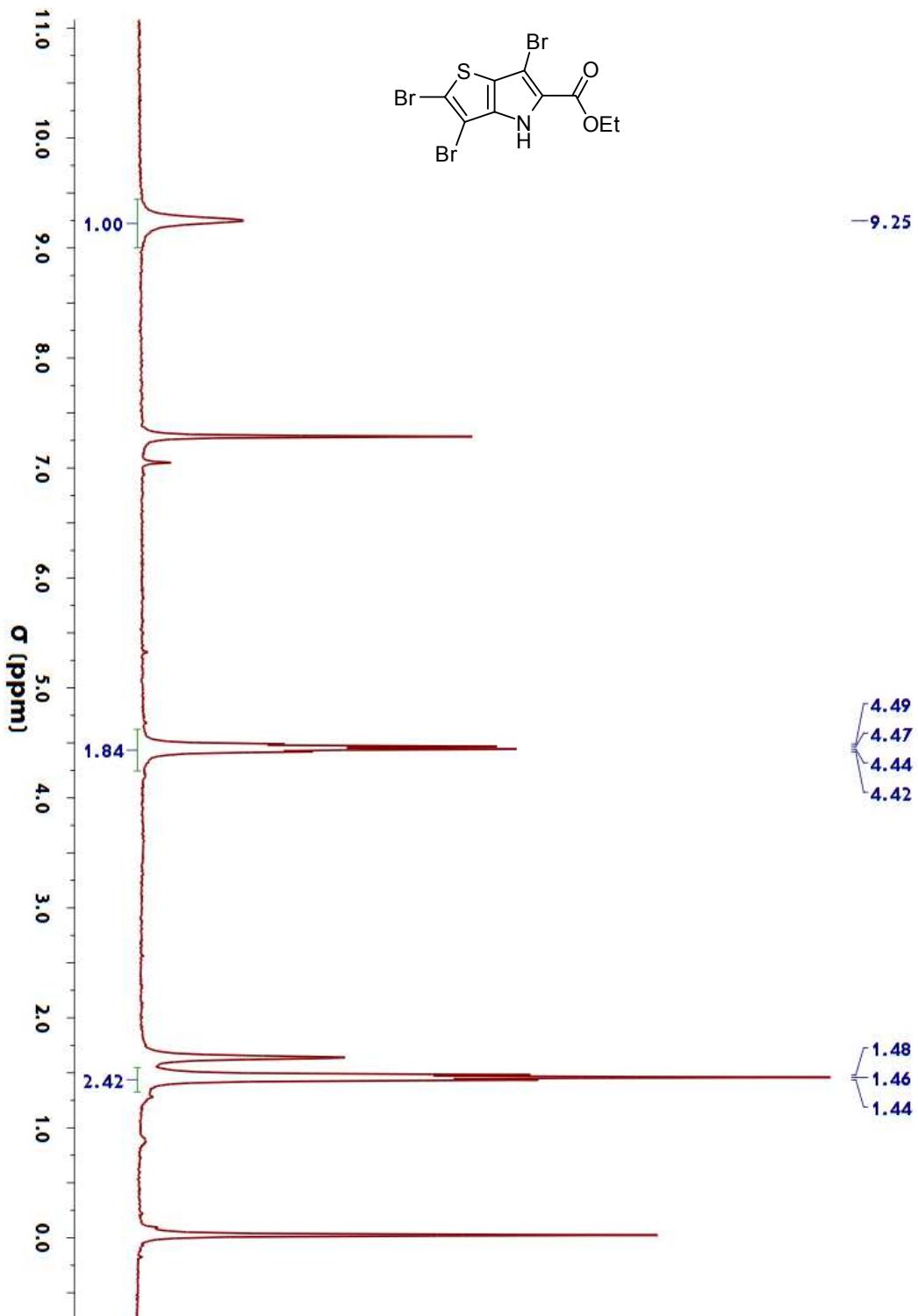


^{13}C NMR spectrum of **1**

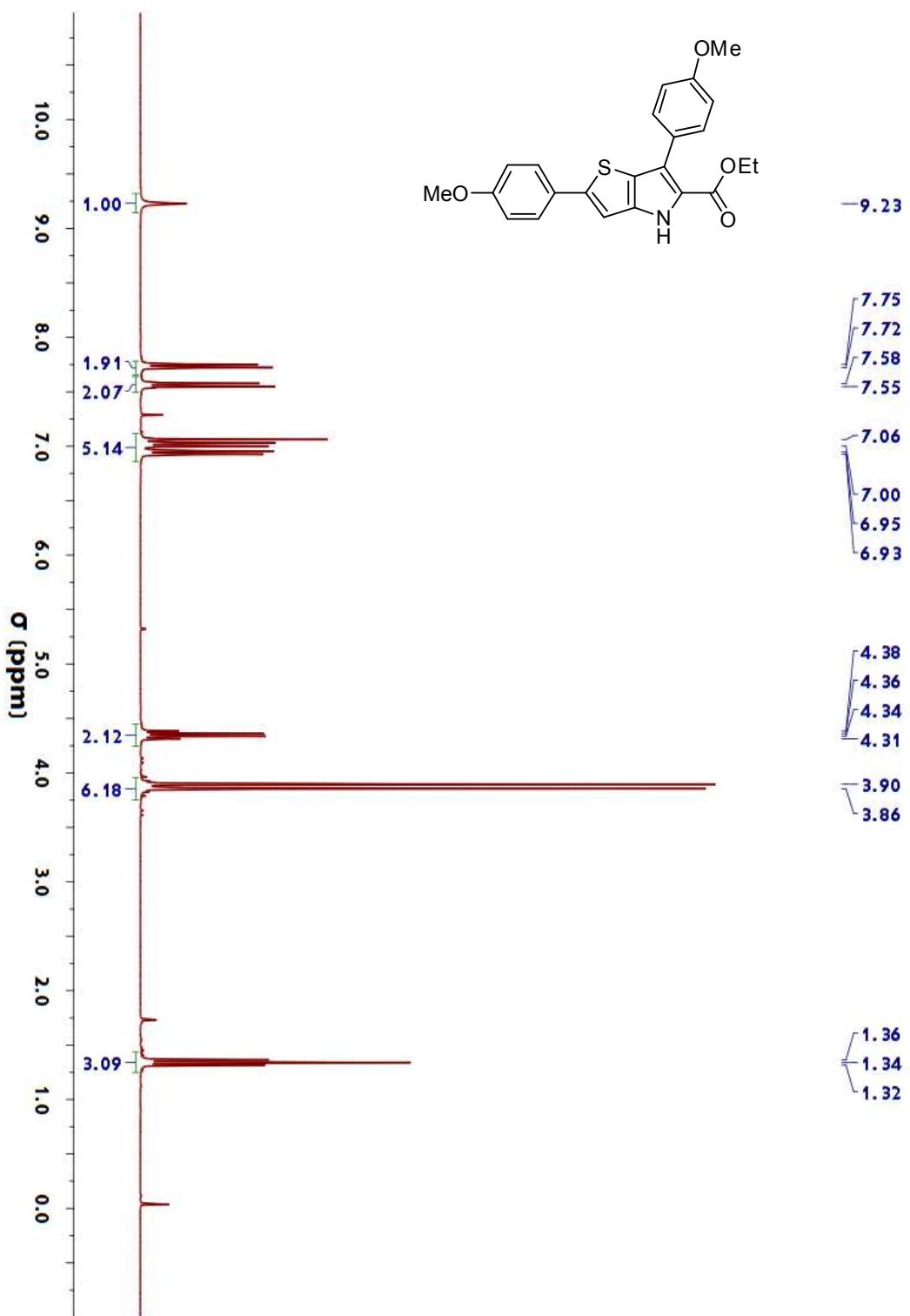




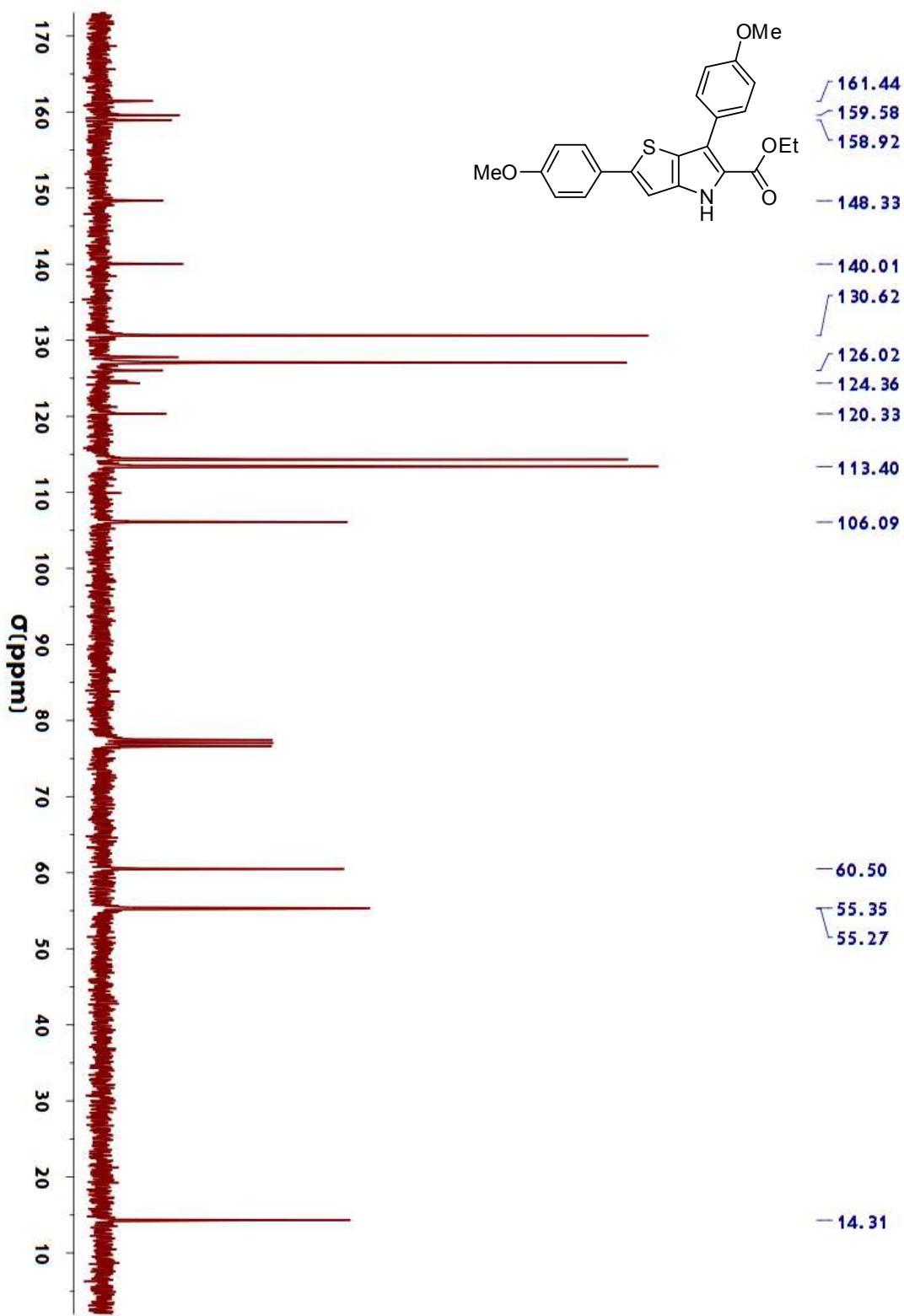
^{13}C NMR spectrum of **2a**



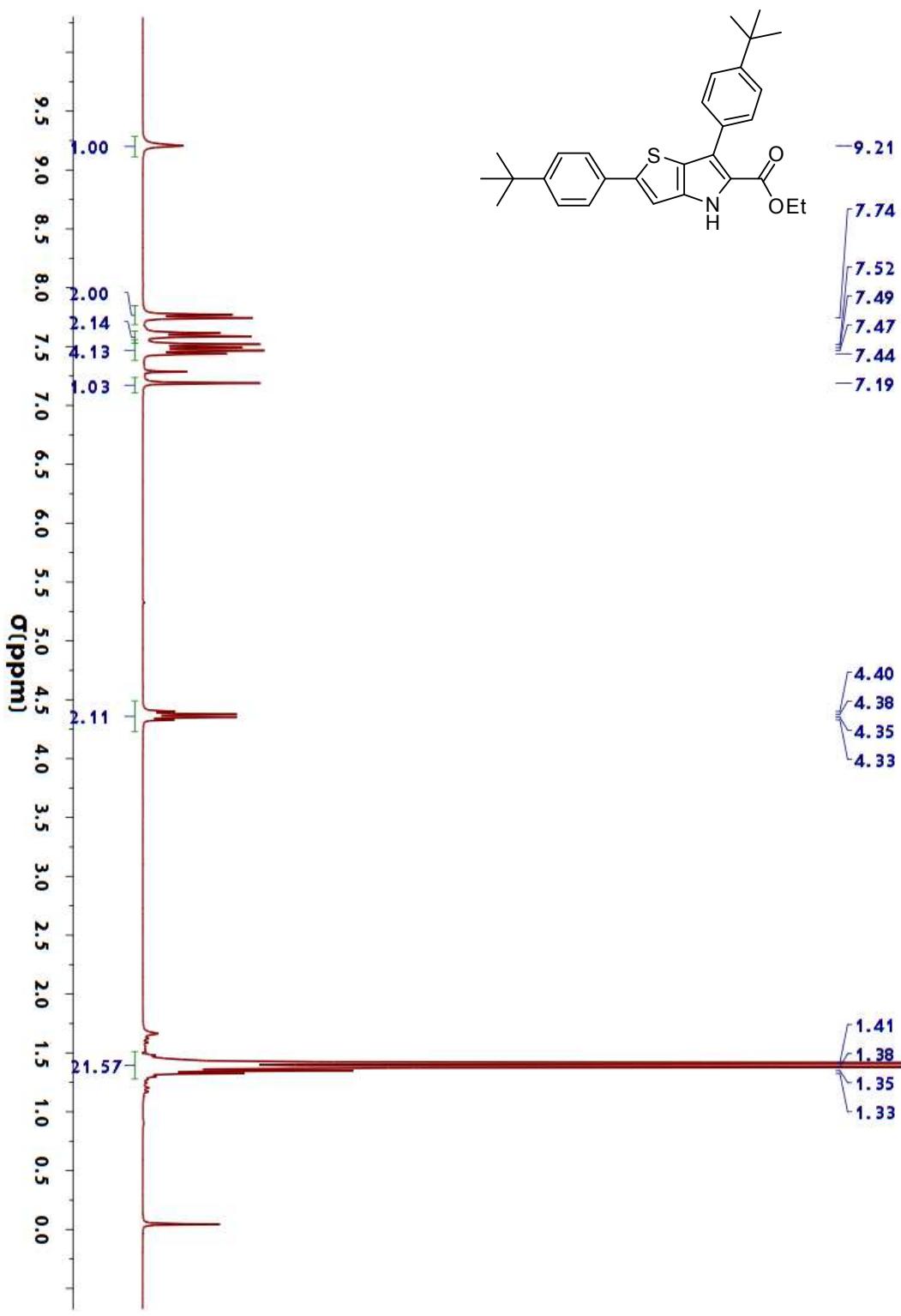
¹H NMR spectrum of **2b**



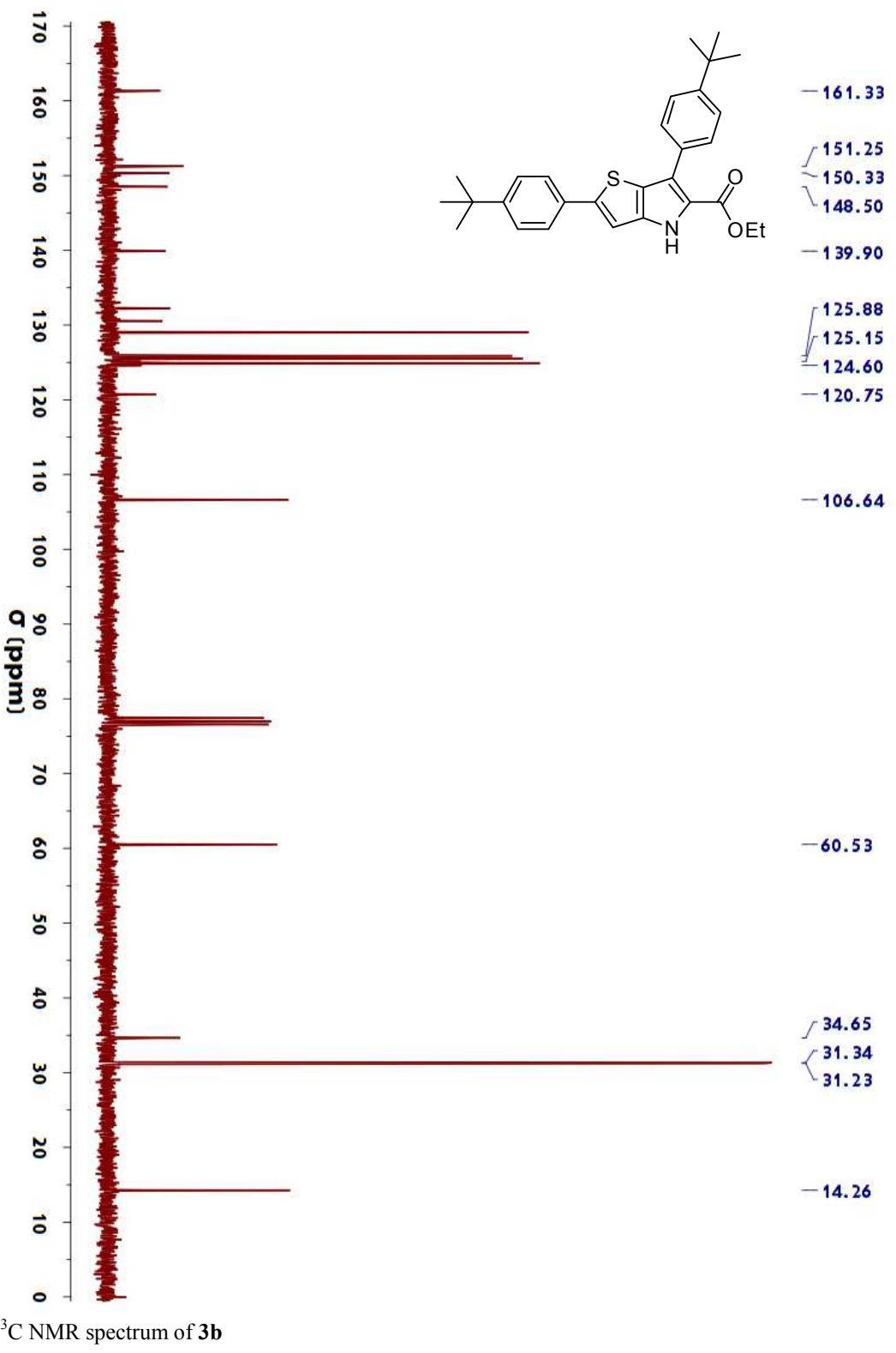
¹H NMR spectrum of 3a



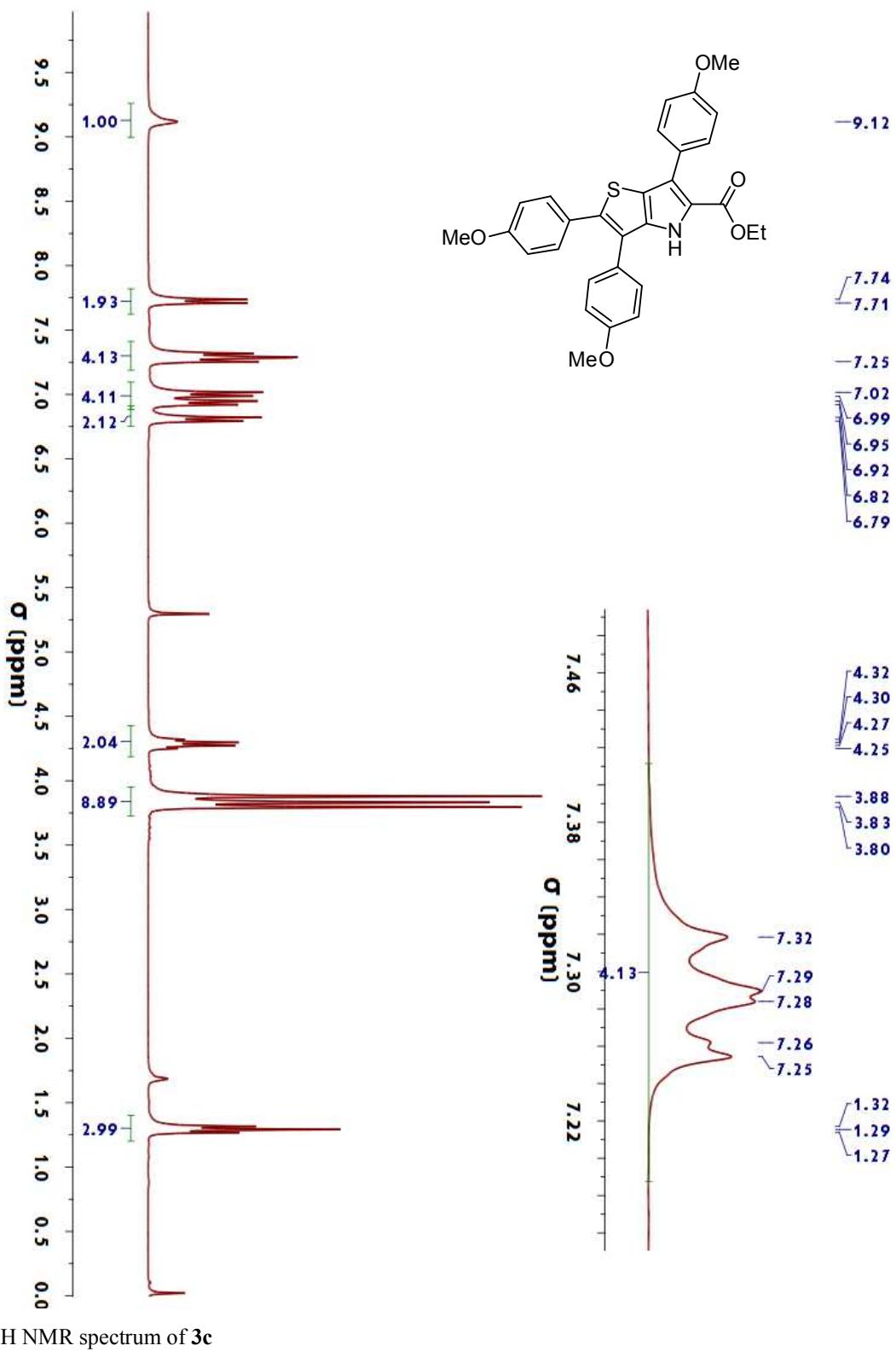
^{13}C NMR spectrum of **3a**

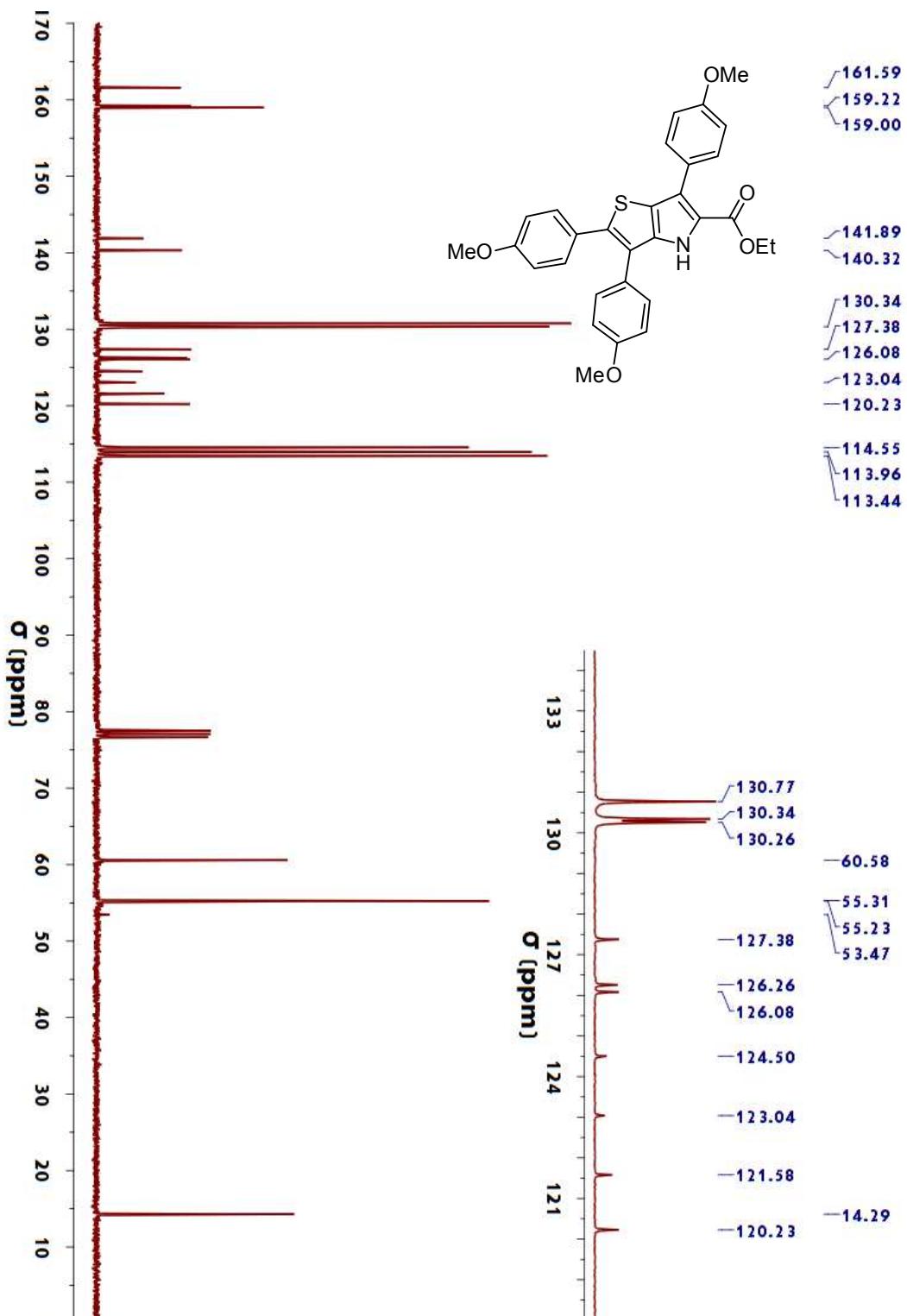


^1H NMR spectrum of **3b**

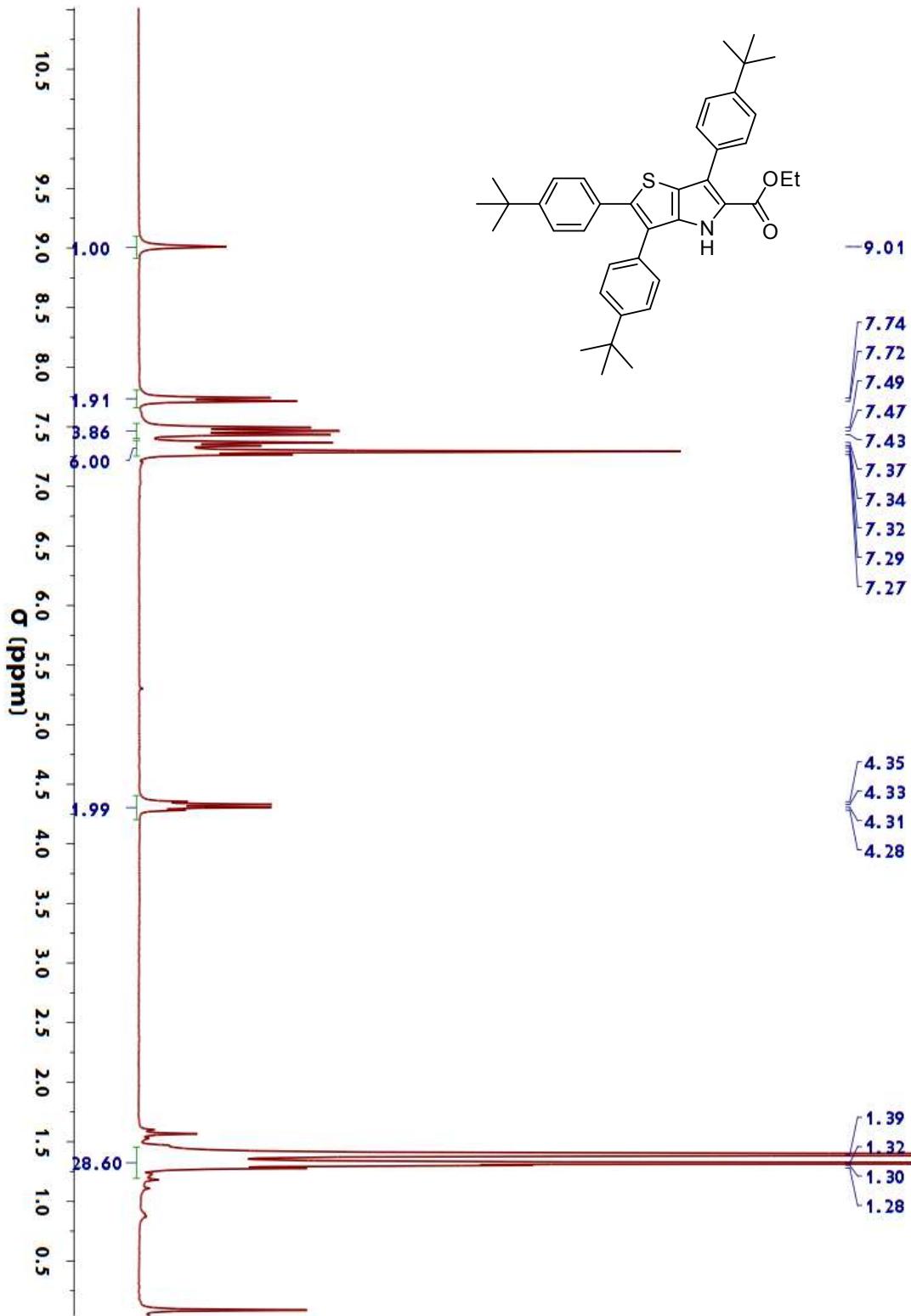


^{13}C NMR spectrum of **3b**

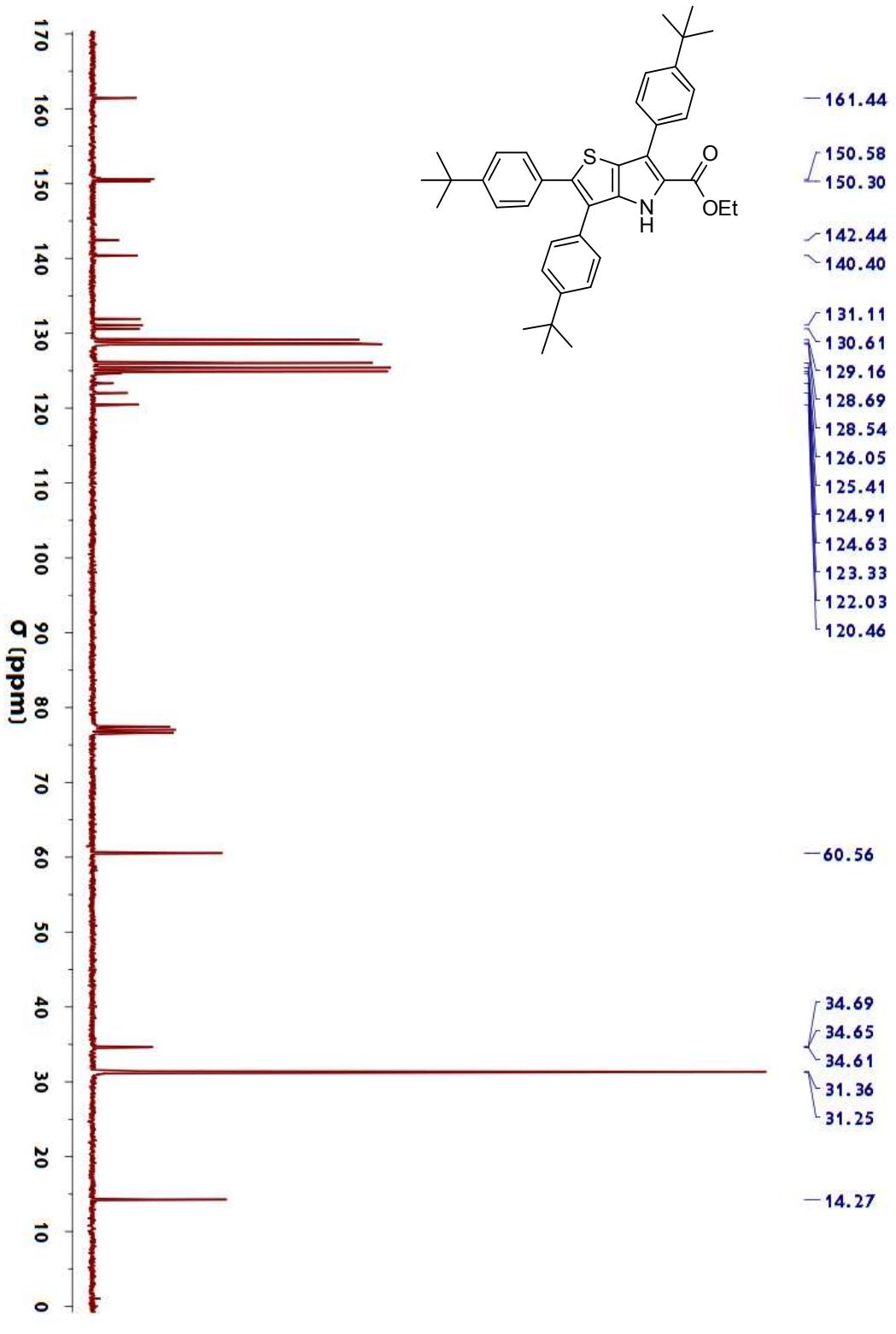




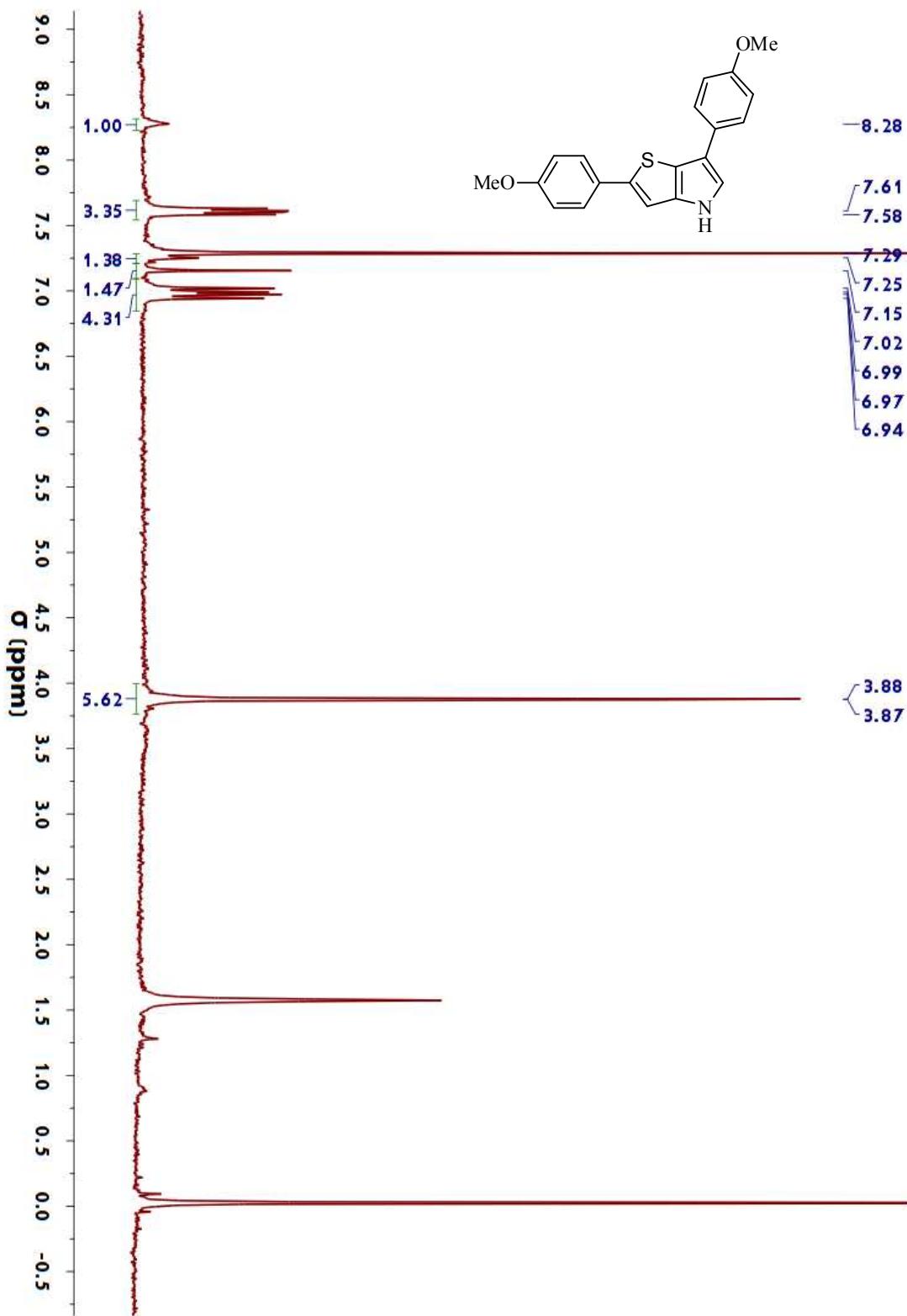
^{13}C NMR spectrum of **3c**



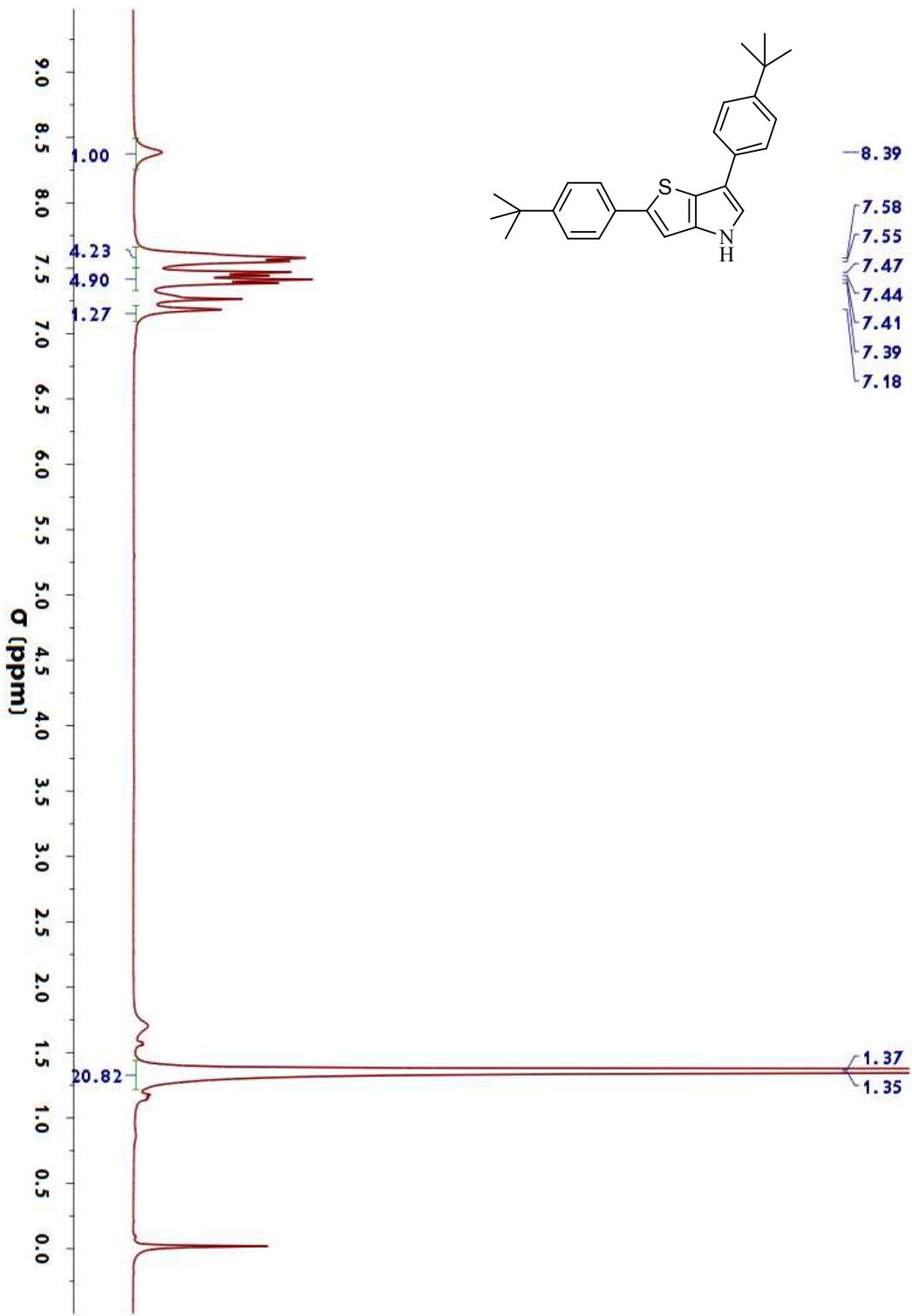
¹H NMR spectrum of 3d



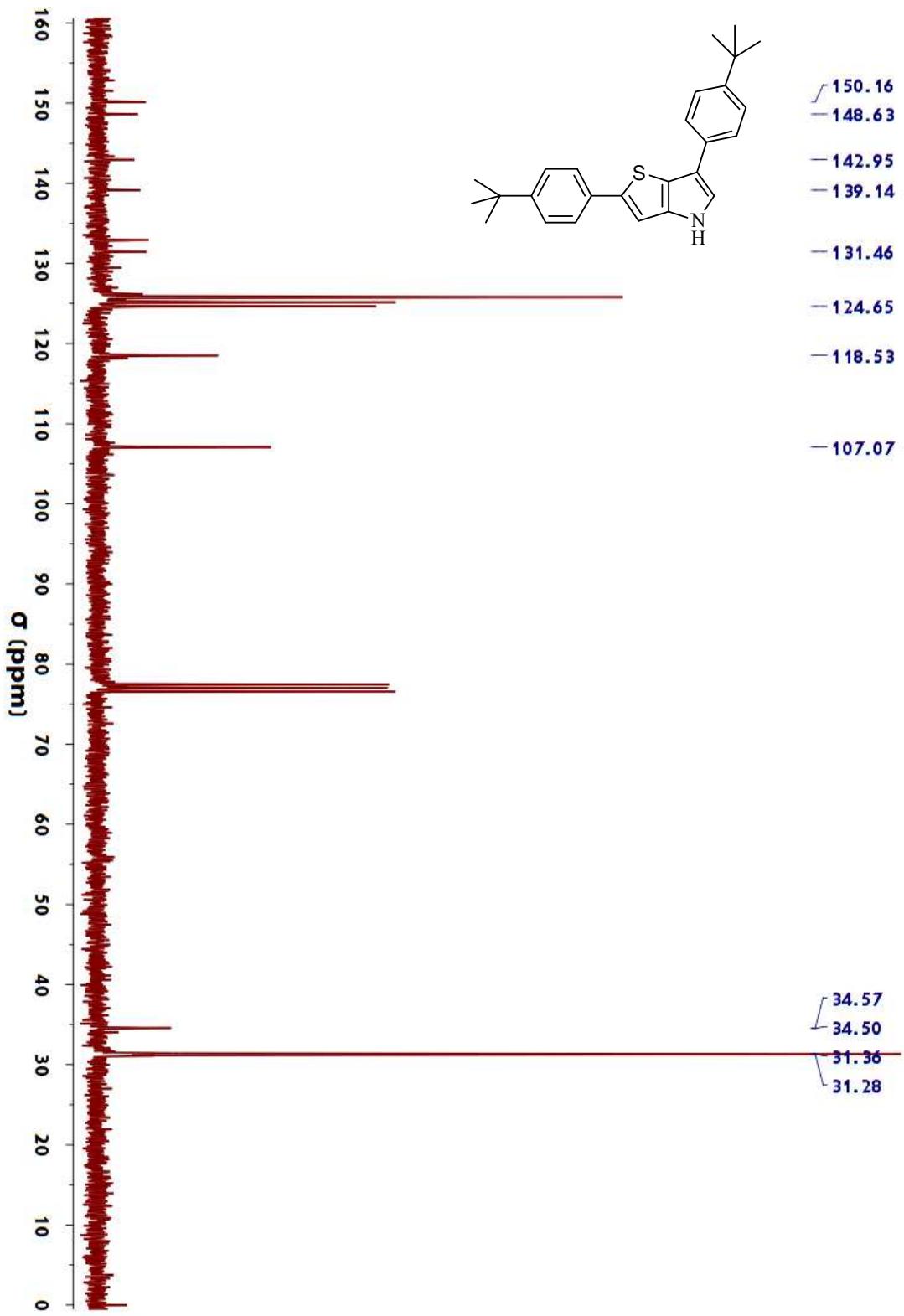
^{13}C NMR spectrum of **3d**



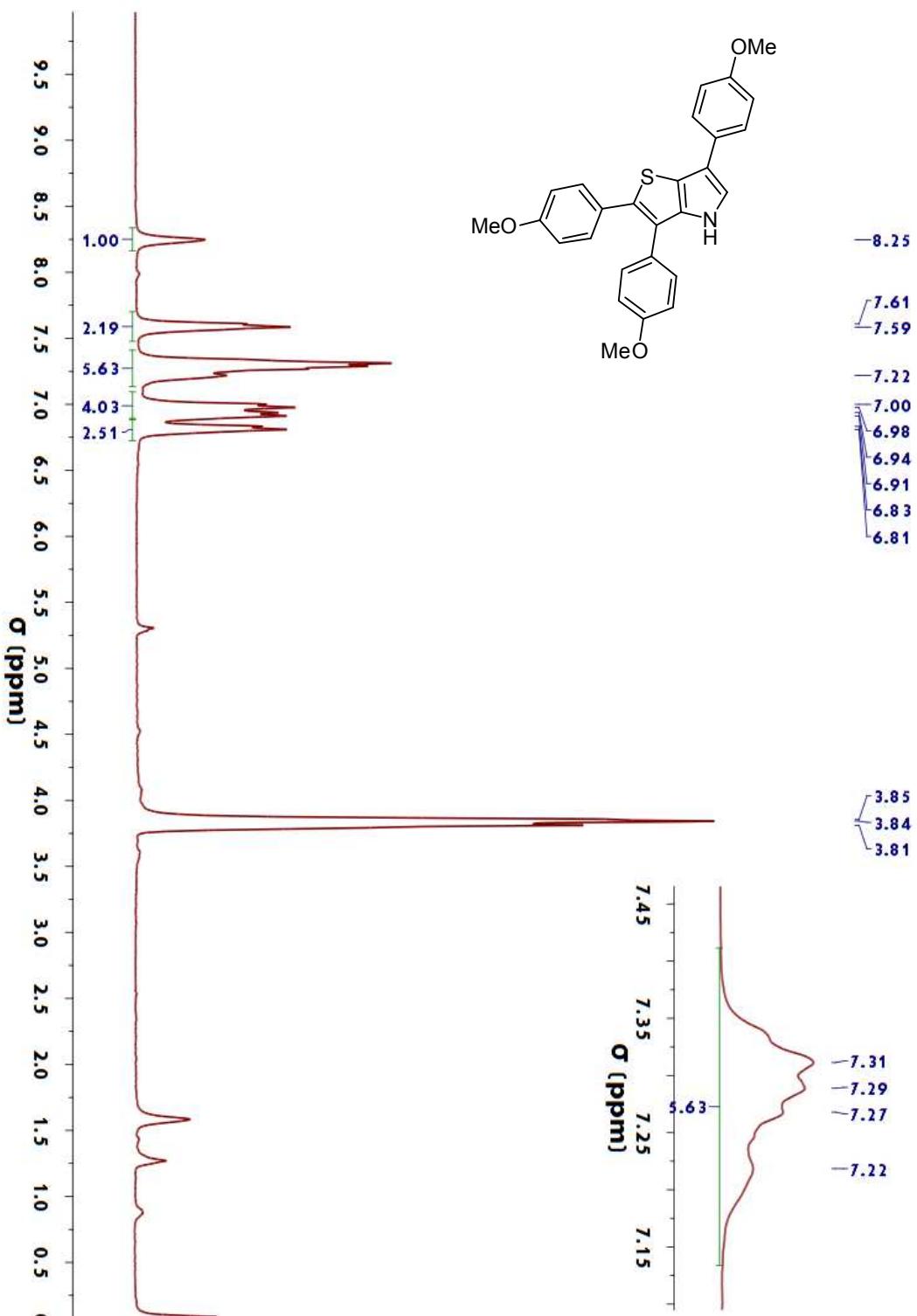
^1H NMR spectrum of **4a**



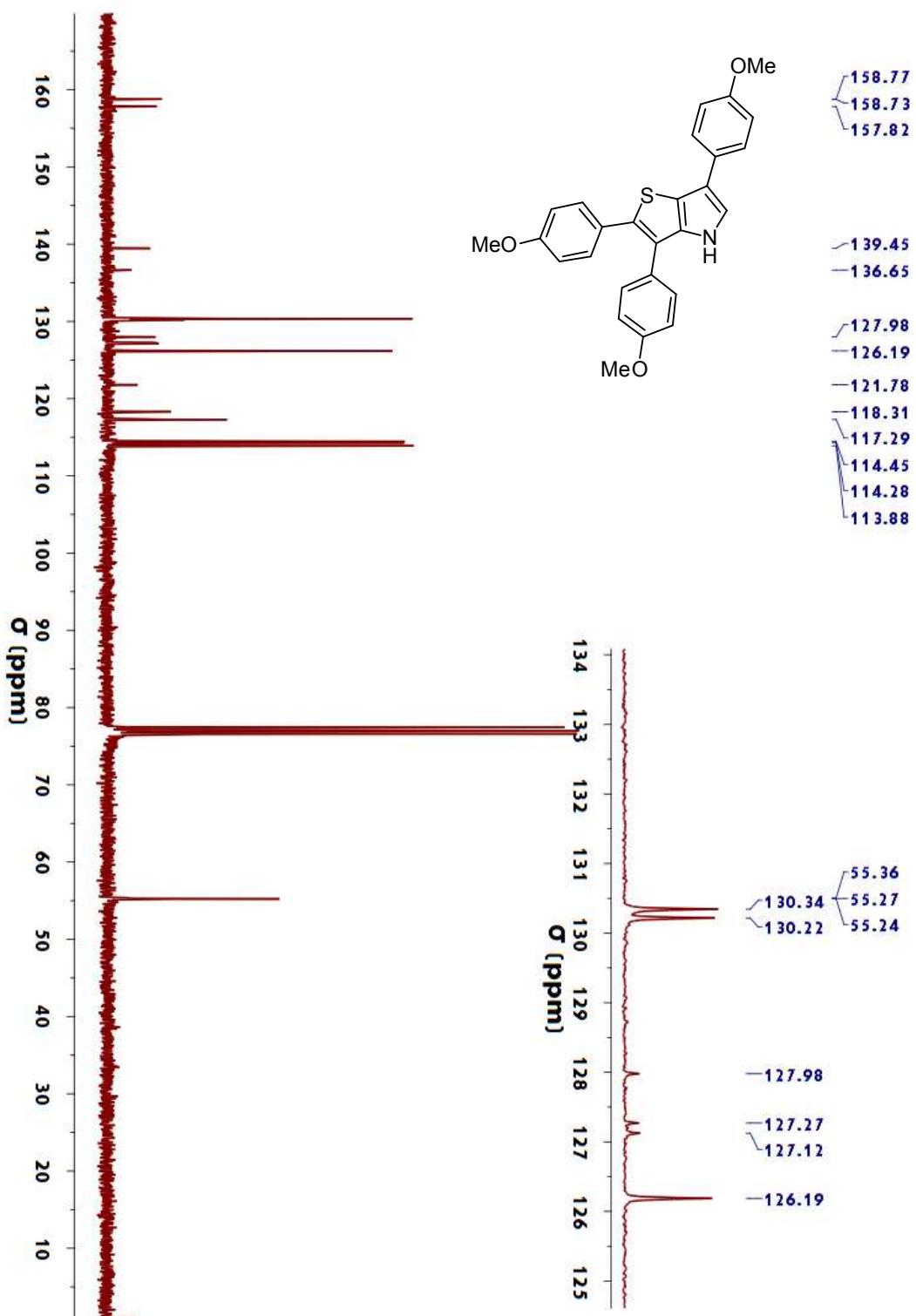
¹H NMR spectrum of **4b**



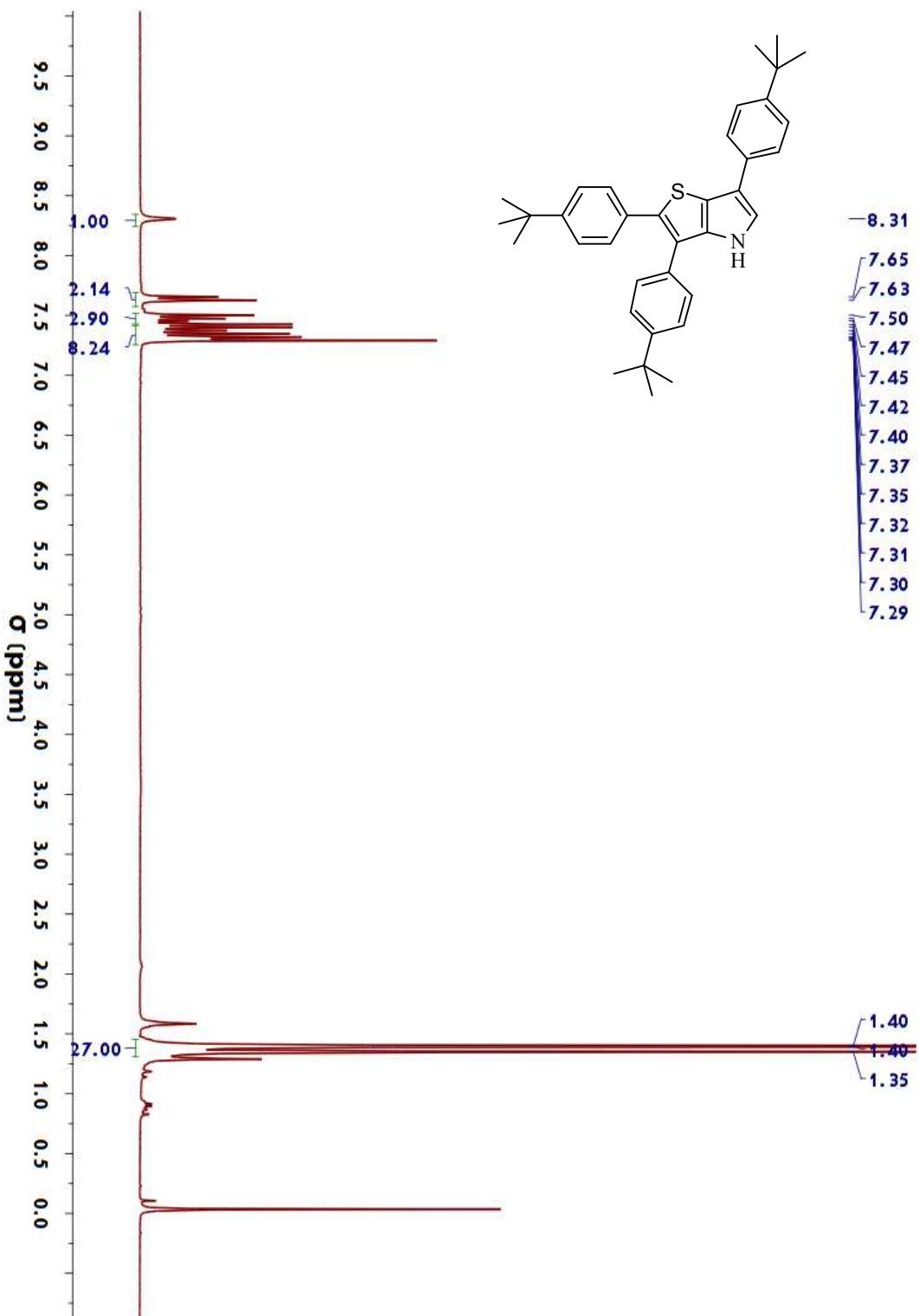
^{13}C NMR spectrum of **4b**



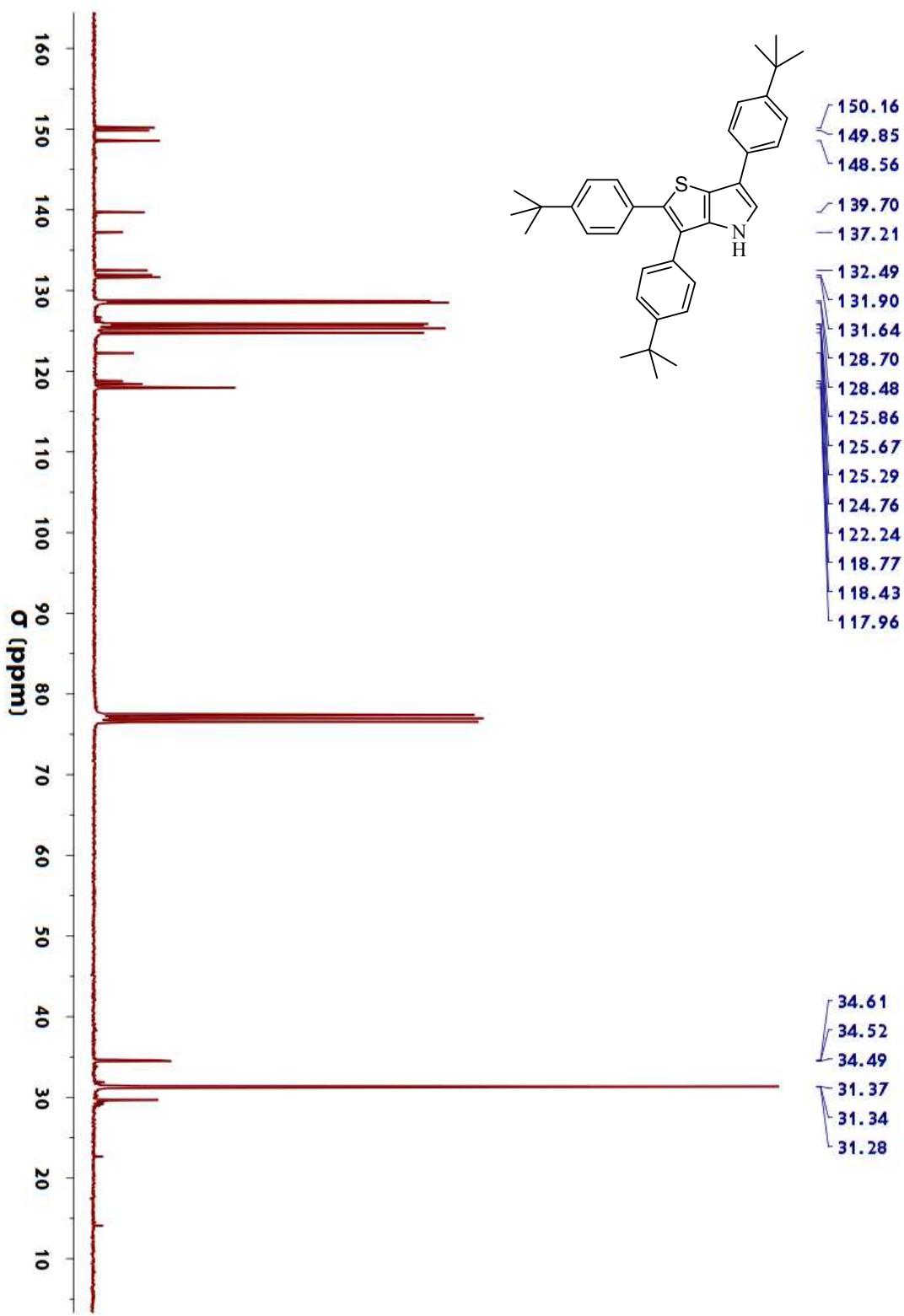
^1H NMR spectrum of **4c**



^{13}C NMR spectrum of **4c**

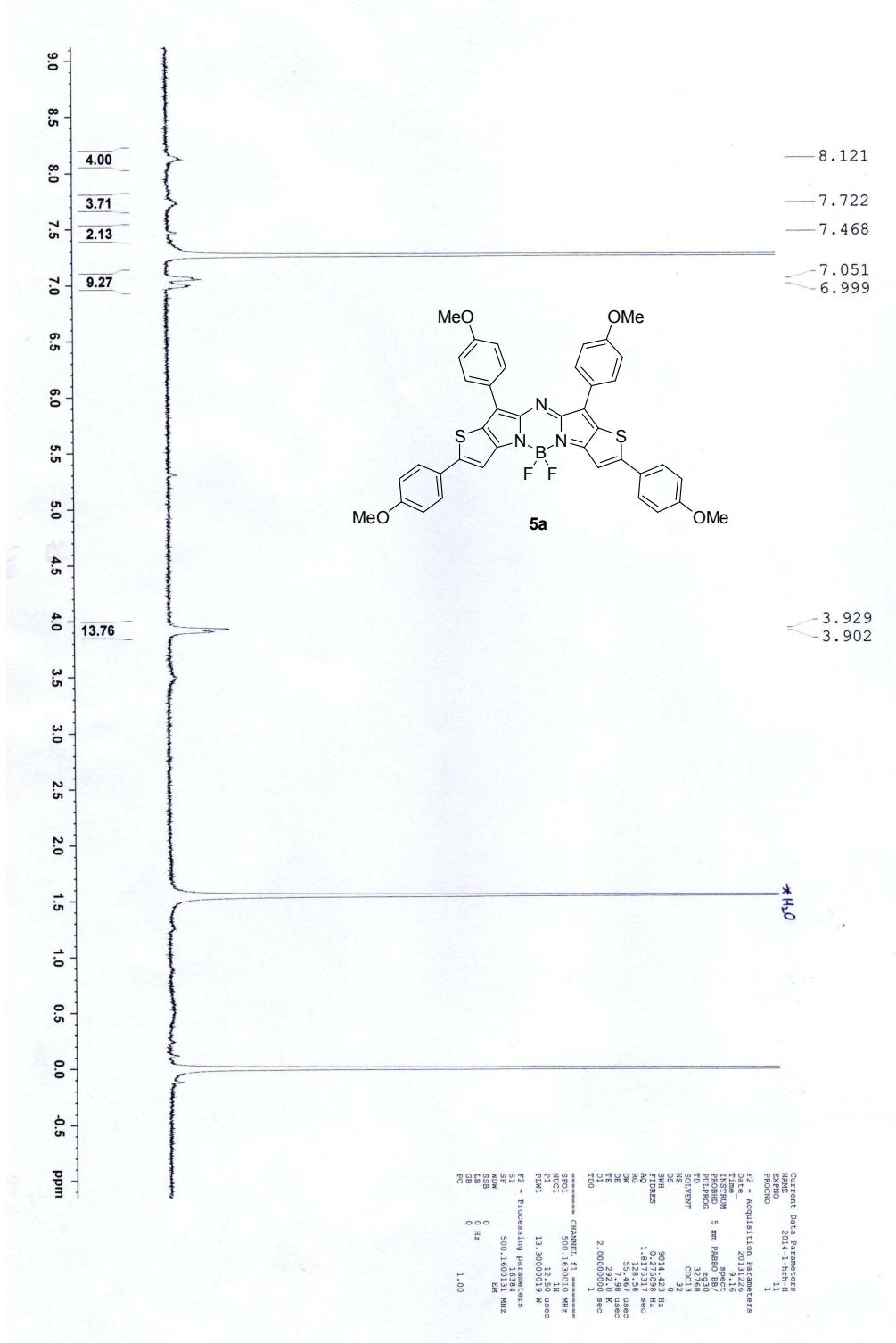


¹H NMR spectrum of **4d**



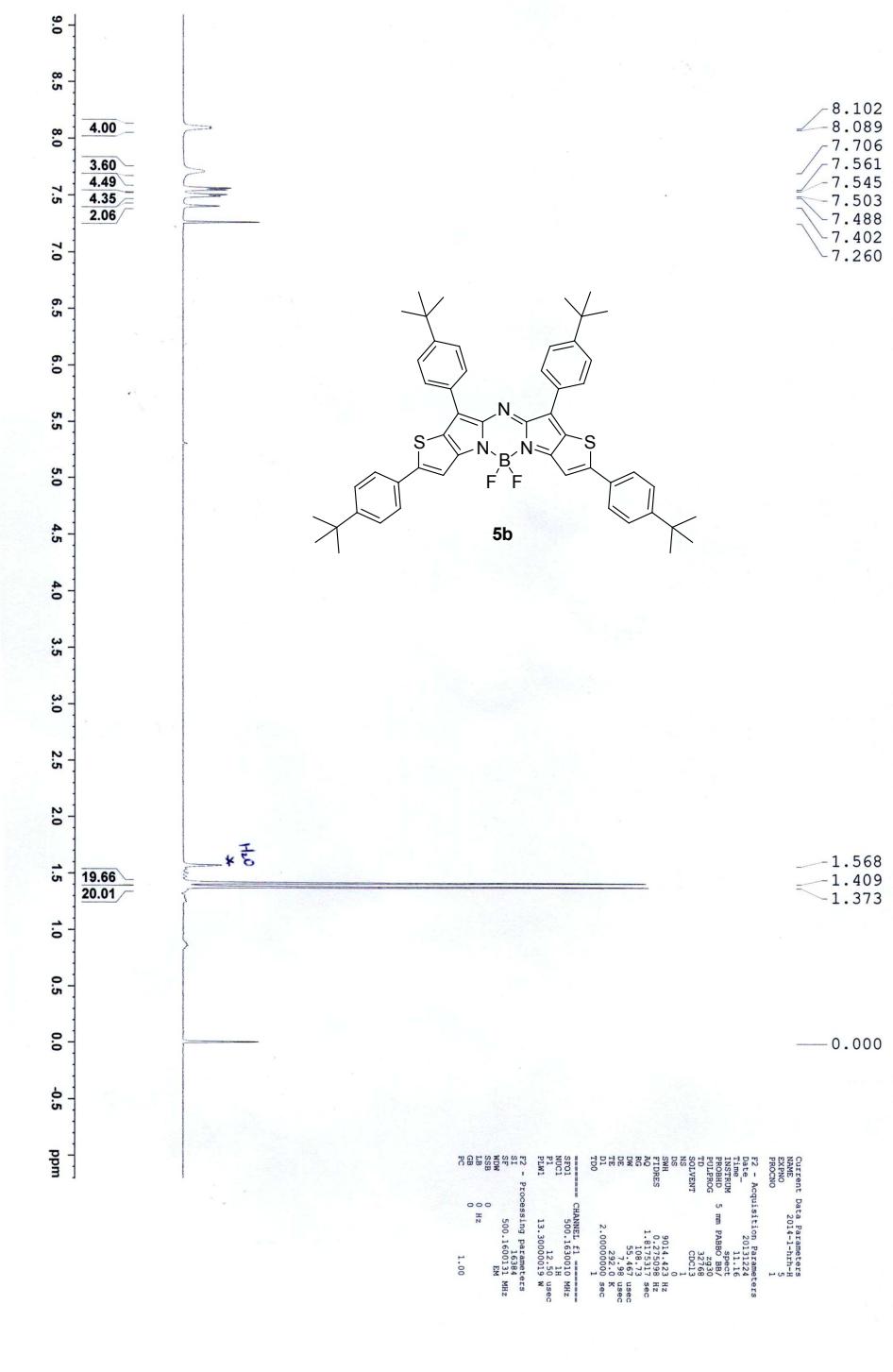
^{13}C NMR spectrum of **4d**

1H

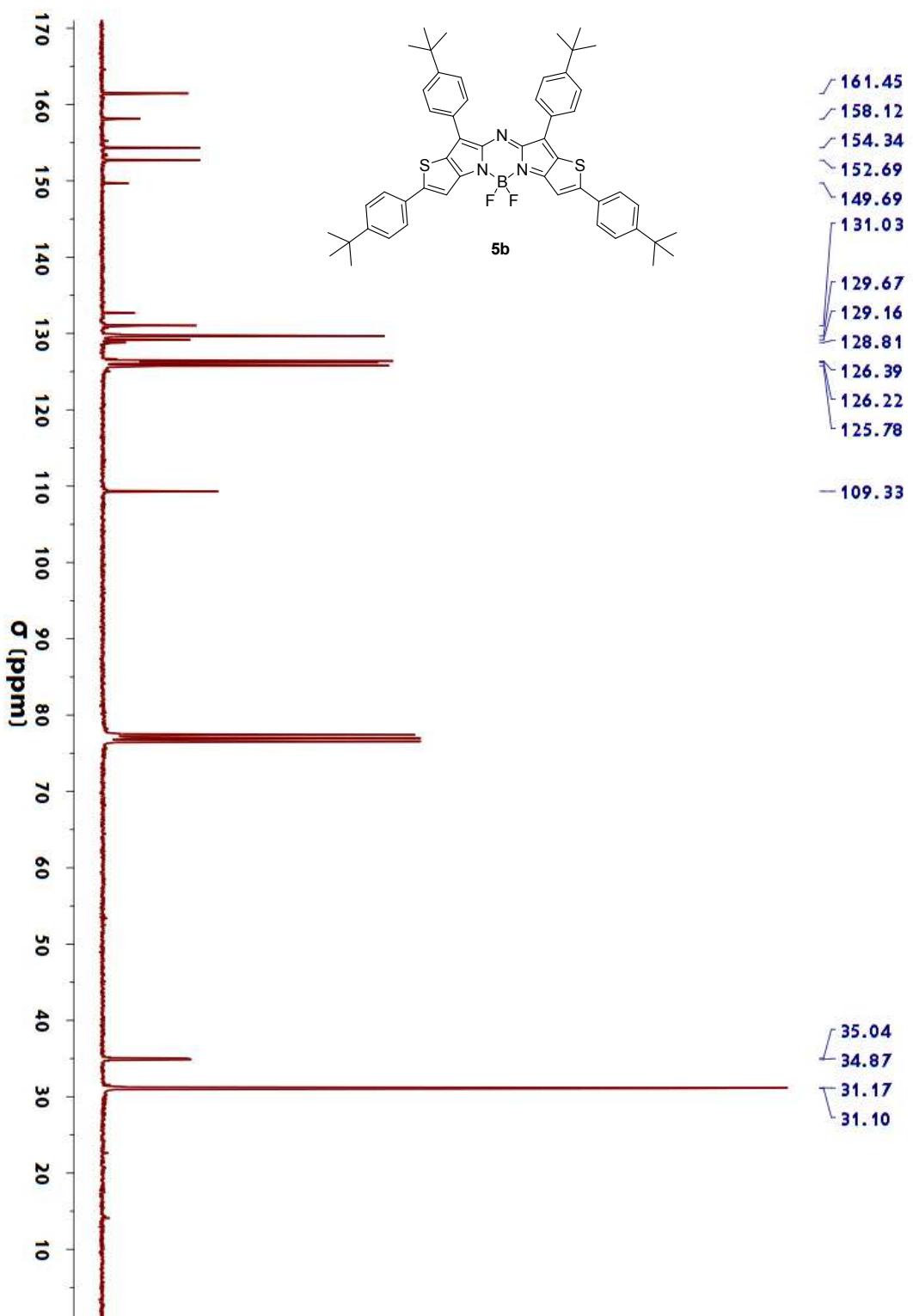


¹H NMR spectrum of **5a**

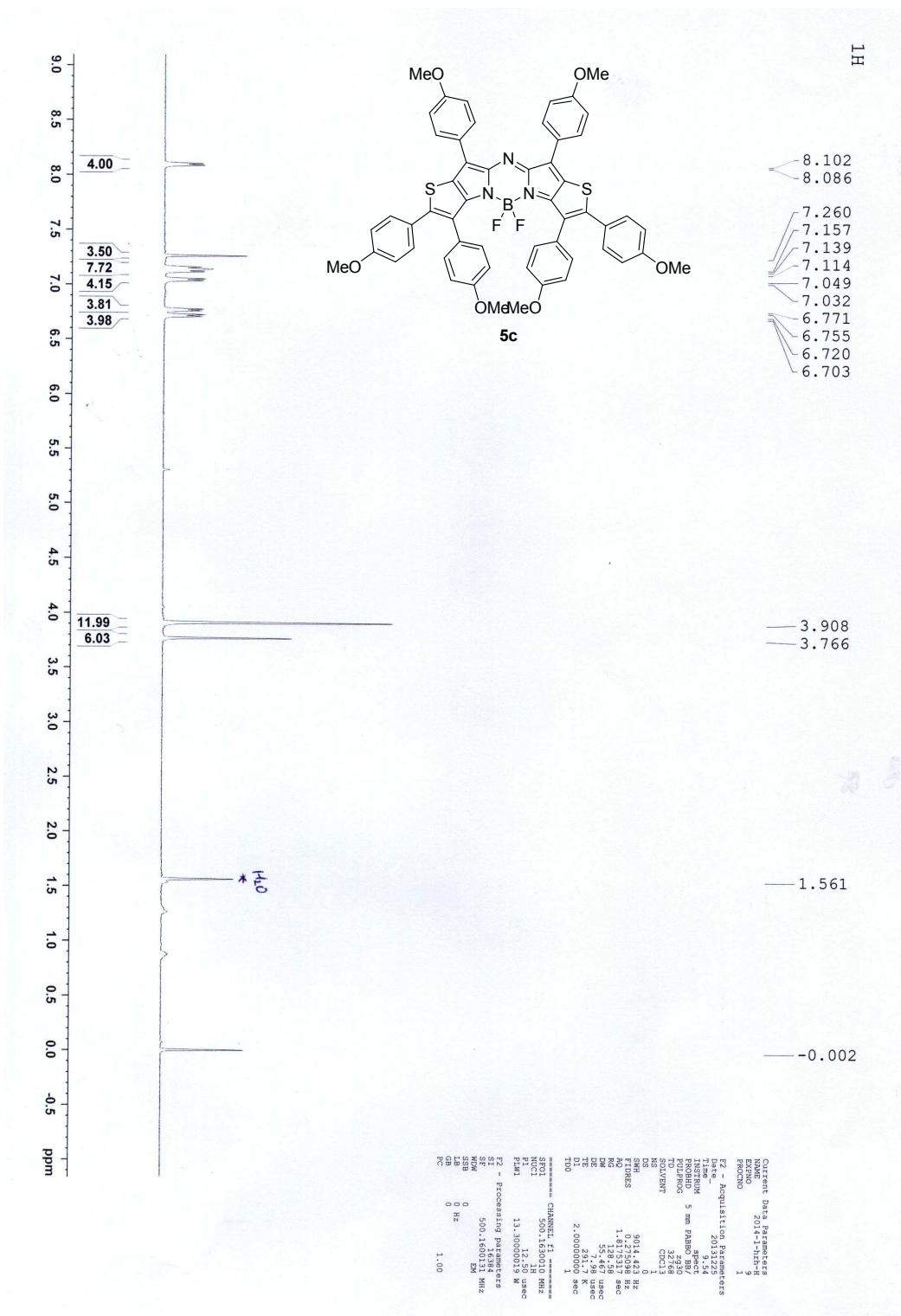
1H



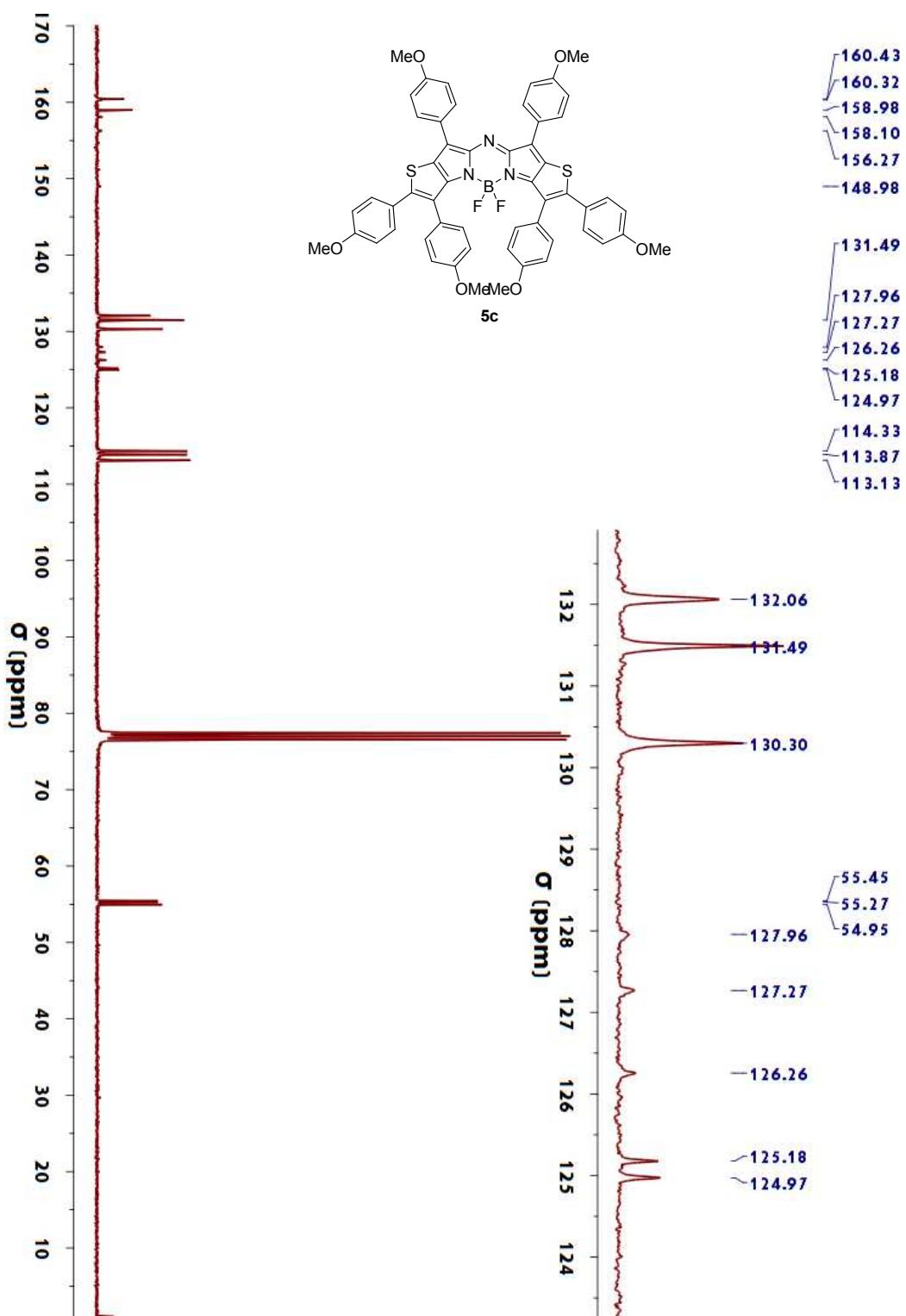
¹H NMR spectrum of **5b**



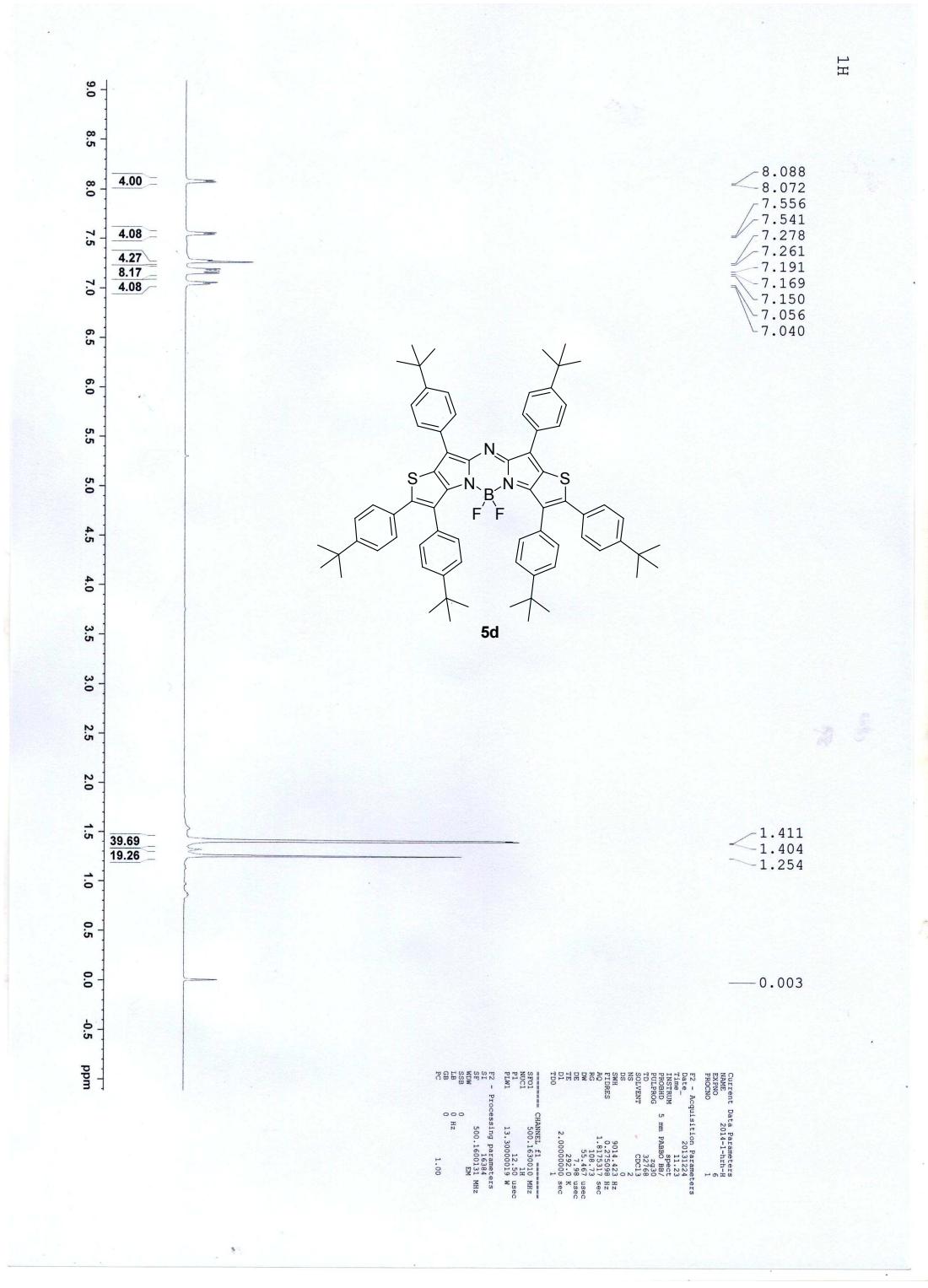
^{13}C NMR spectrum of **5b**



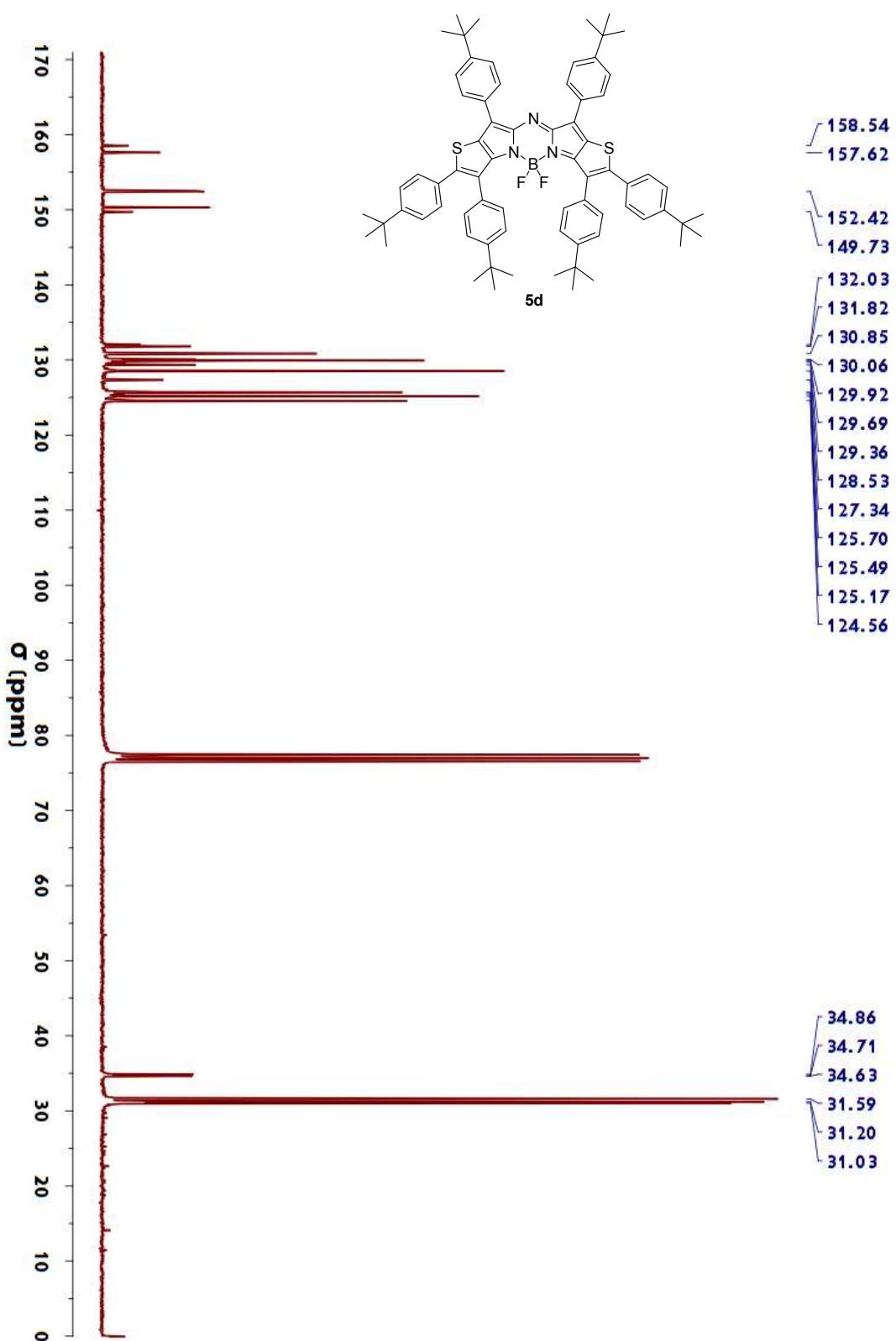
¹H NMR spectrum of **5c**



^{13}C NMR spectrum of **5c**



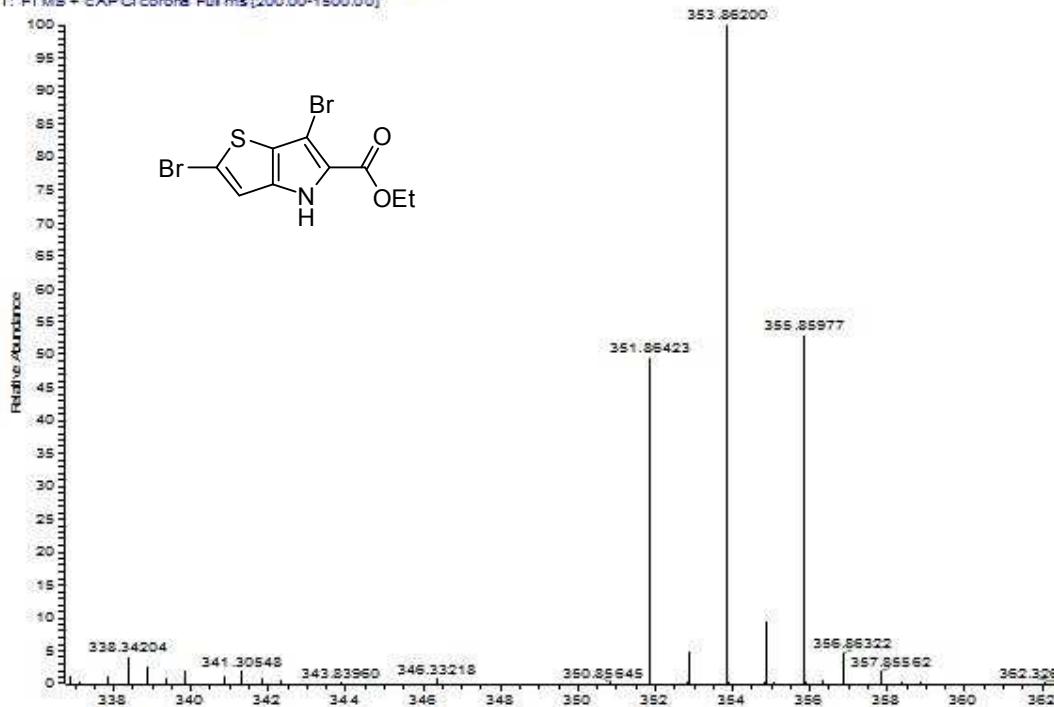
¹H NMR spectrum of **5d**



^{13}C NMR spectrum of **5d**

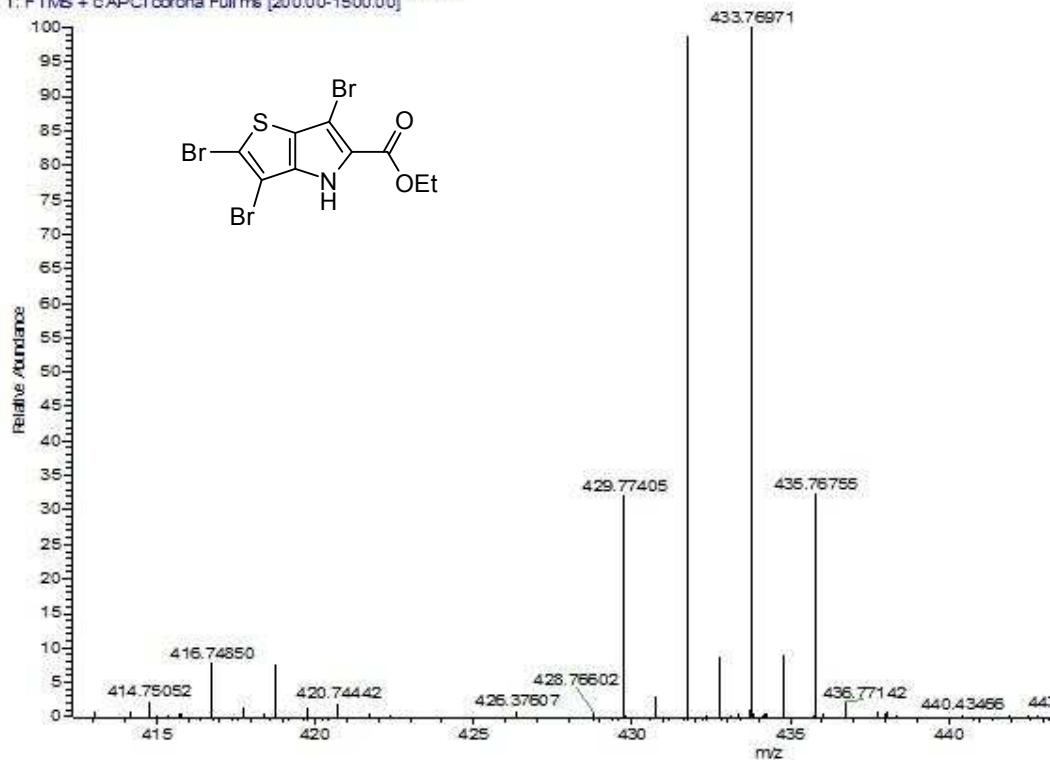
6. High resolution mass spectrosopes for all new compounds

20130607_APCHW14 #10 RT: 0.13 AV: 1 NL: 1.96E8
T: FTMS + cAPCI corona Full ms [200.00-1500.00]

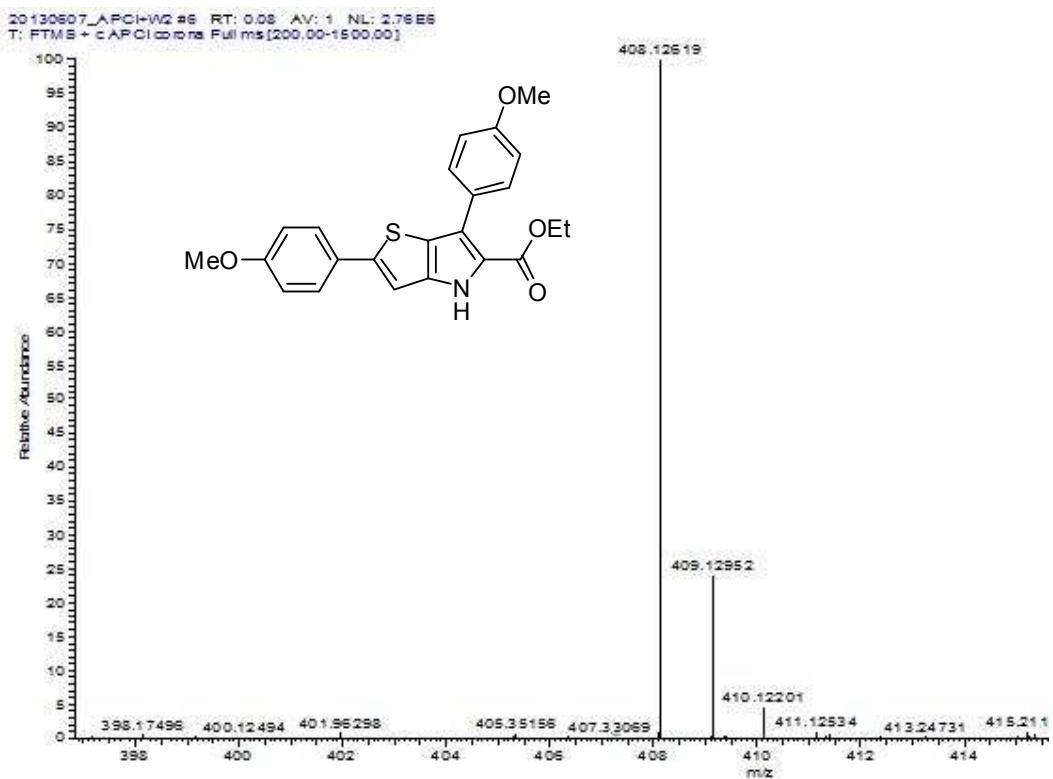


HRMS for 2a

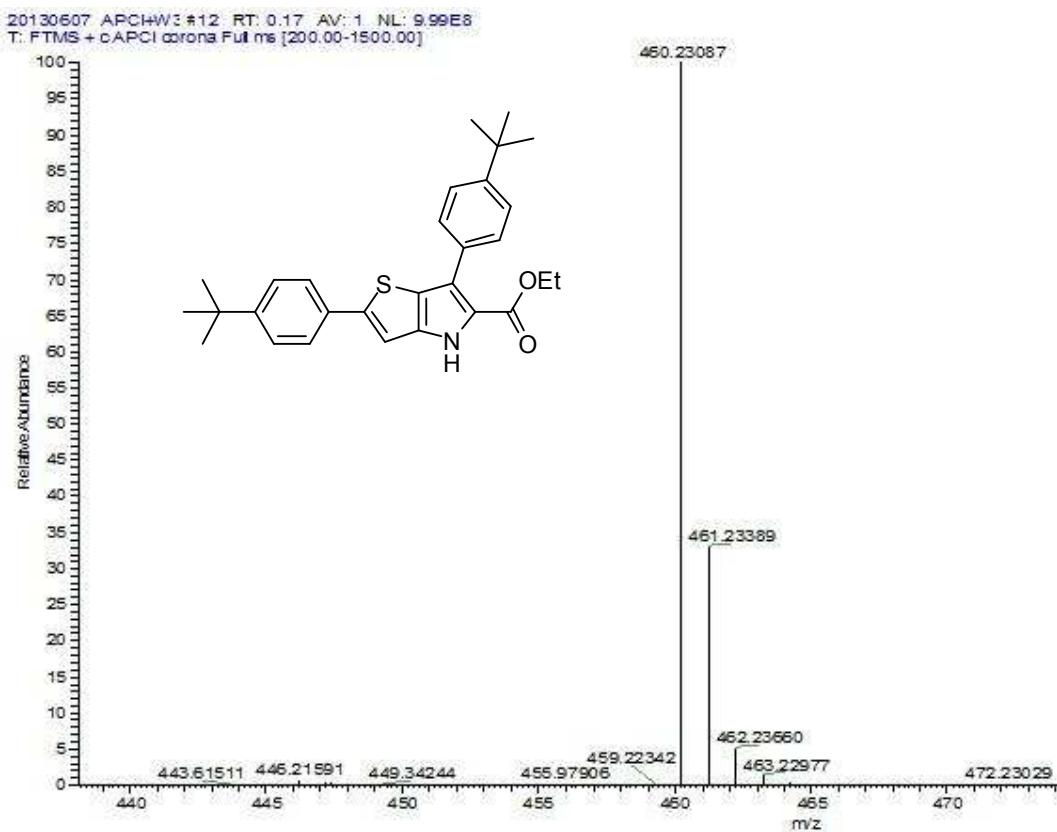
20130607_APCHW15 #11 RT: 0.14 AV: 1 NL: 4.36E7
T: FTMS + cAPCI corona Full ms [200.00-1500.00]



HRMS for 2b

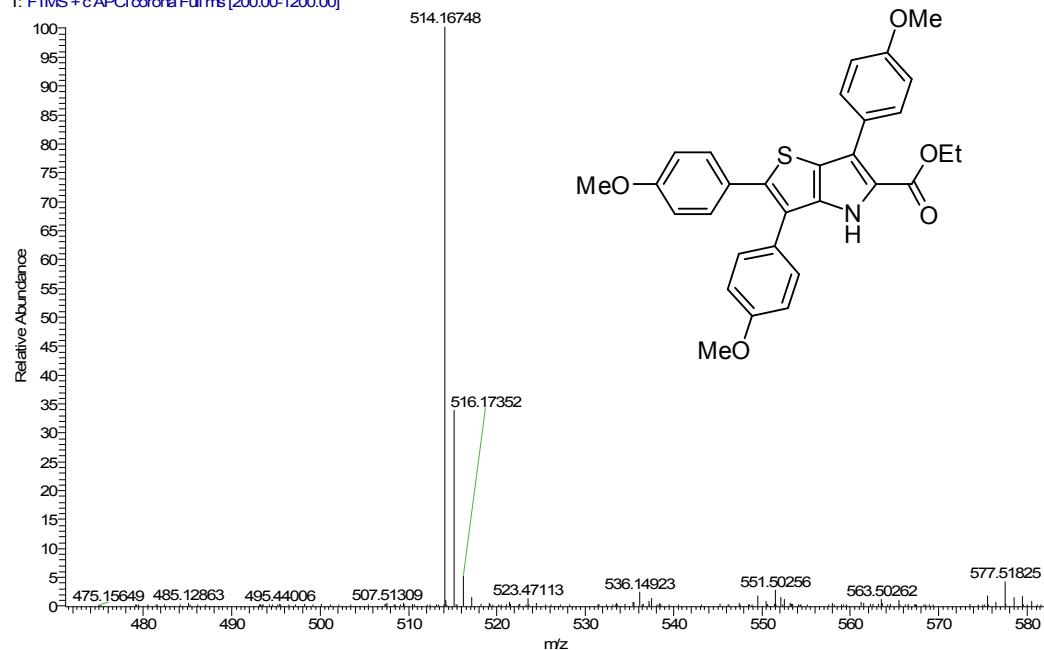


HRMS for 3a



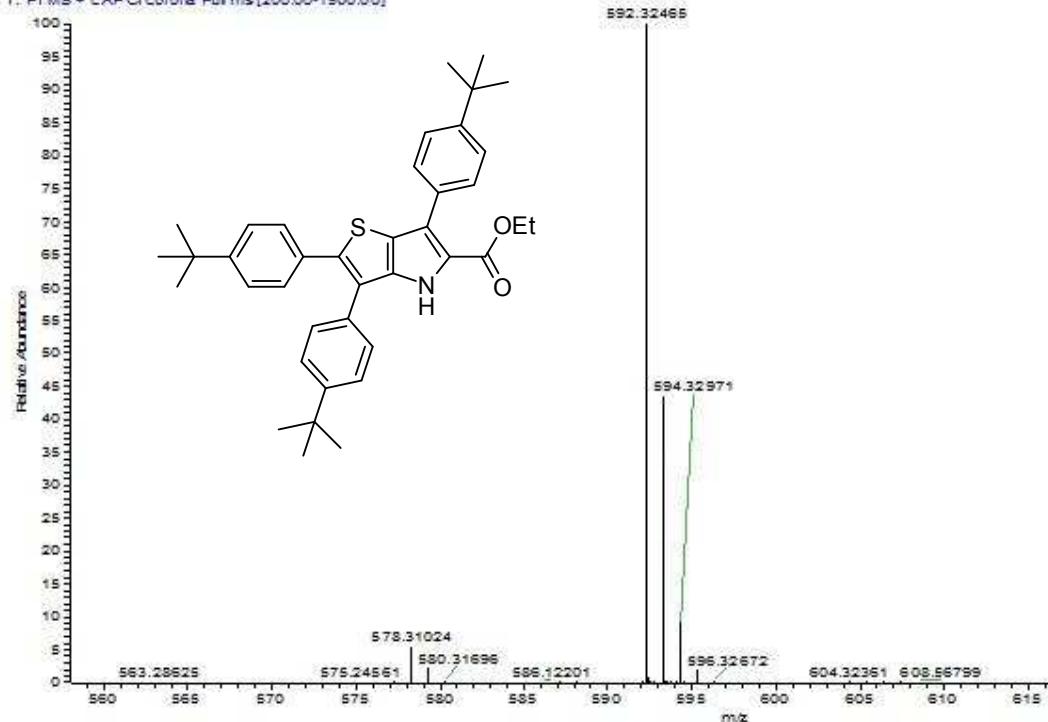
HRMS for 3b

20131015_APCHW8 #10 RT: 0.15 AV: 1 NL: 5.95E6
T: FTMS + cAPCI corona Full ms [200.00-1200.00]



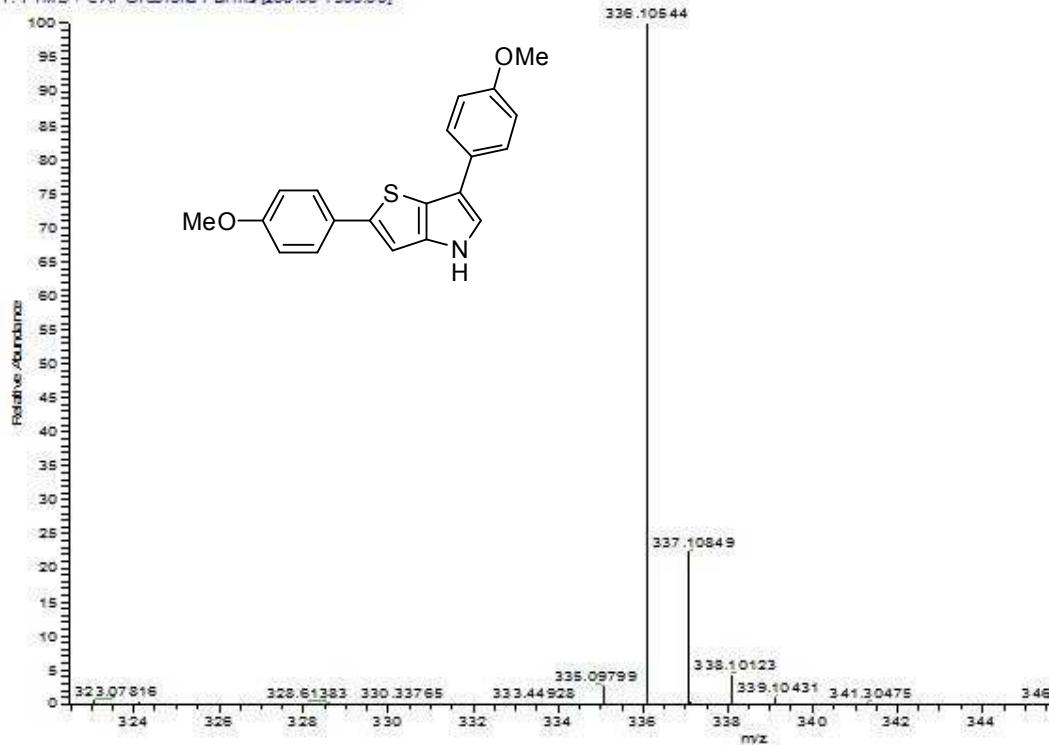
HRMS for 3c

20130607_APCHW4 #14 RT: 0.19 AV: 1 NL: 8.12E9
T: FTMS + cAPCI corona Full ms [200.00-1500.00]



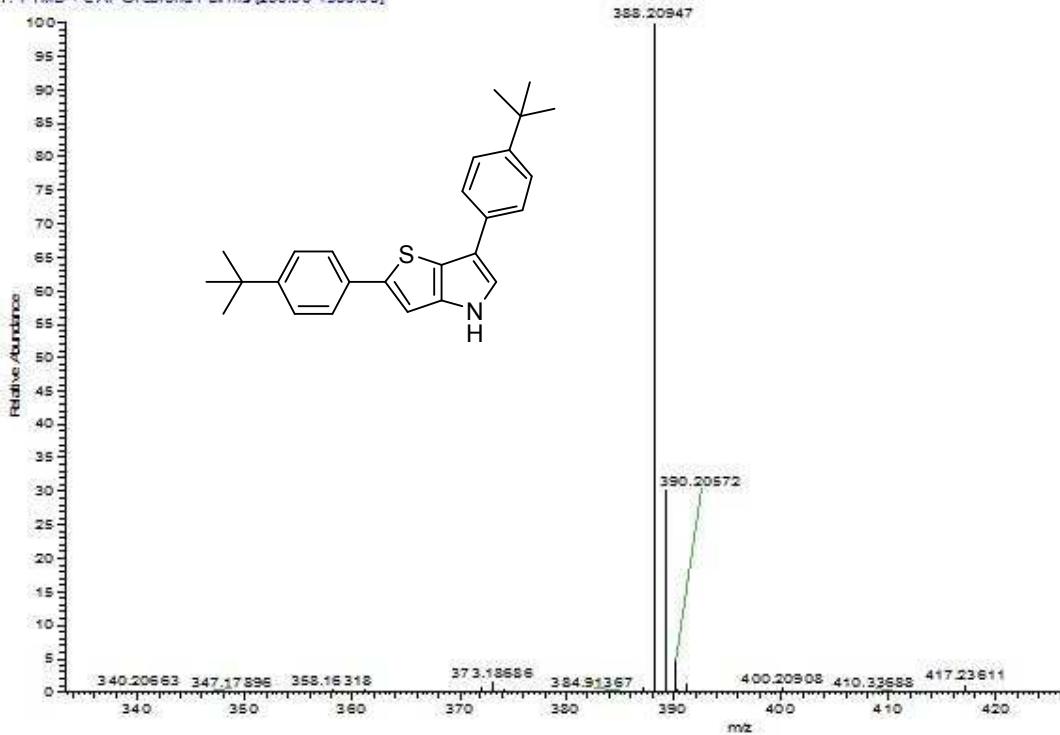
HRMS for 3d

20130607_APCI-HW#11 RT: 0.14 AV: 1 NL: 2.57E9
T: FTMS + cAPCI corona Full ms [200.00-1500.00]



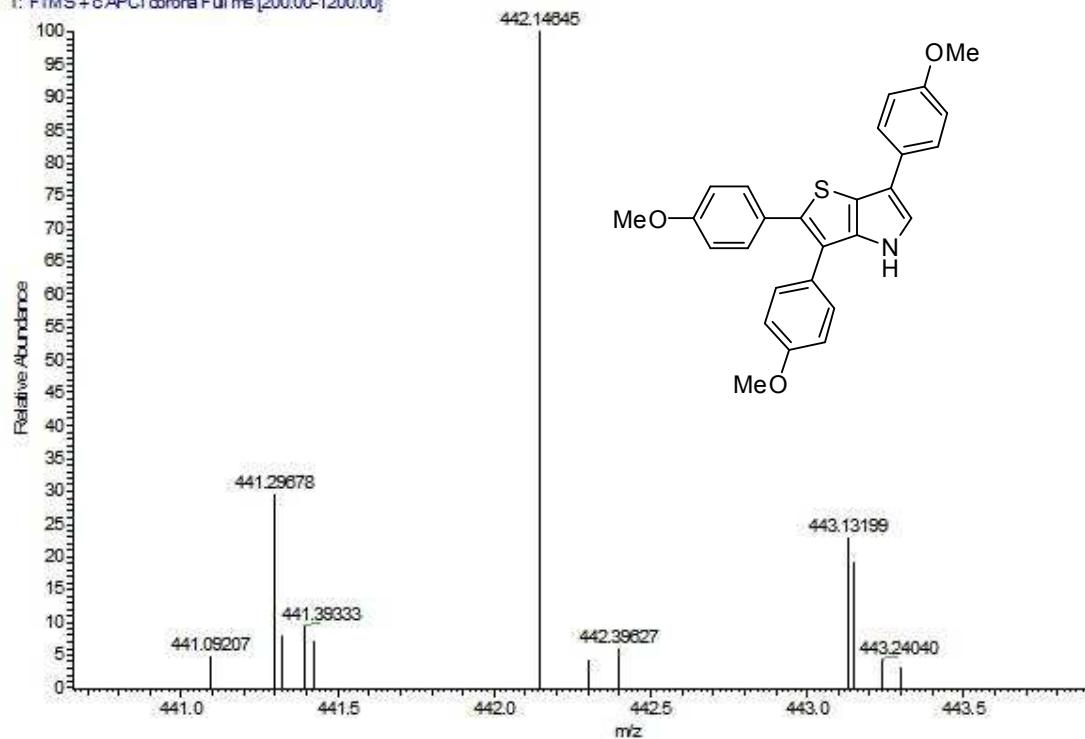
HRMS for 4a

20130607_APCI-HW#11 RT: 0.14 AV: 1 NL: 7.74E9
T: FTMS + cAPCI corona Full ms [200.00-1500.00]



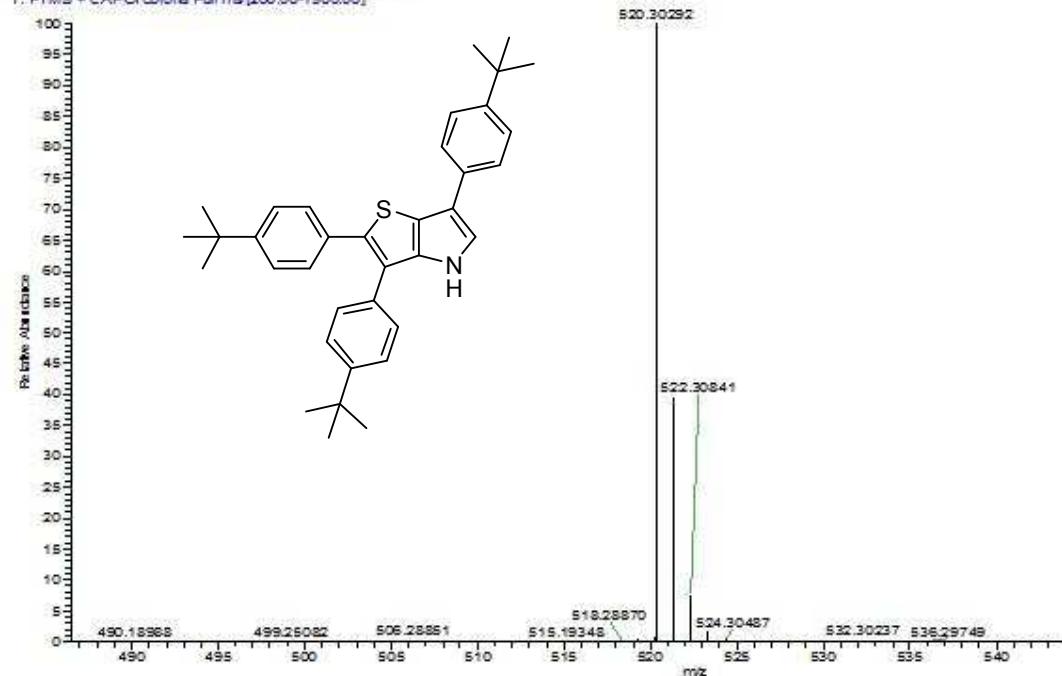
HRMS for 4b

20131015_APCI+W #13 RT: 0.19 AV: 1 SB: 4 0.01-0.05 NL: 7.11E4
T: FTMS + cAPCI corona Full ms [200.00-1200.00]

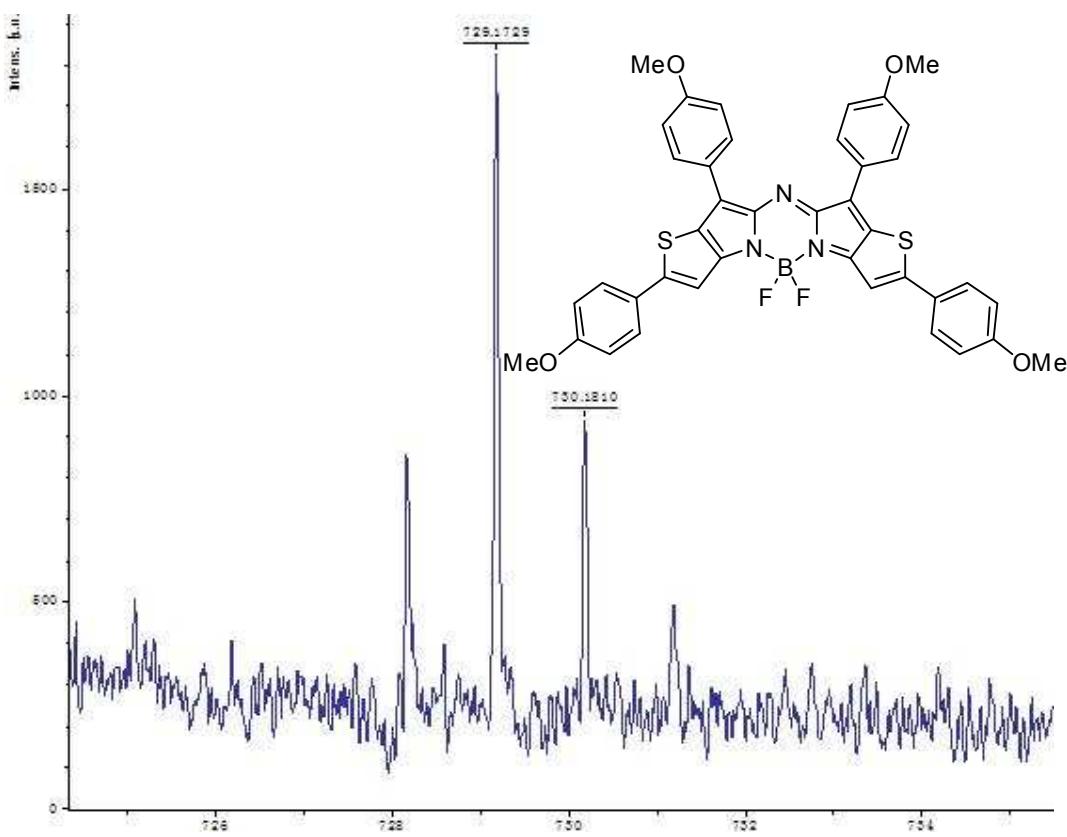


HRMS for 4c

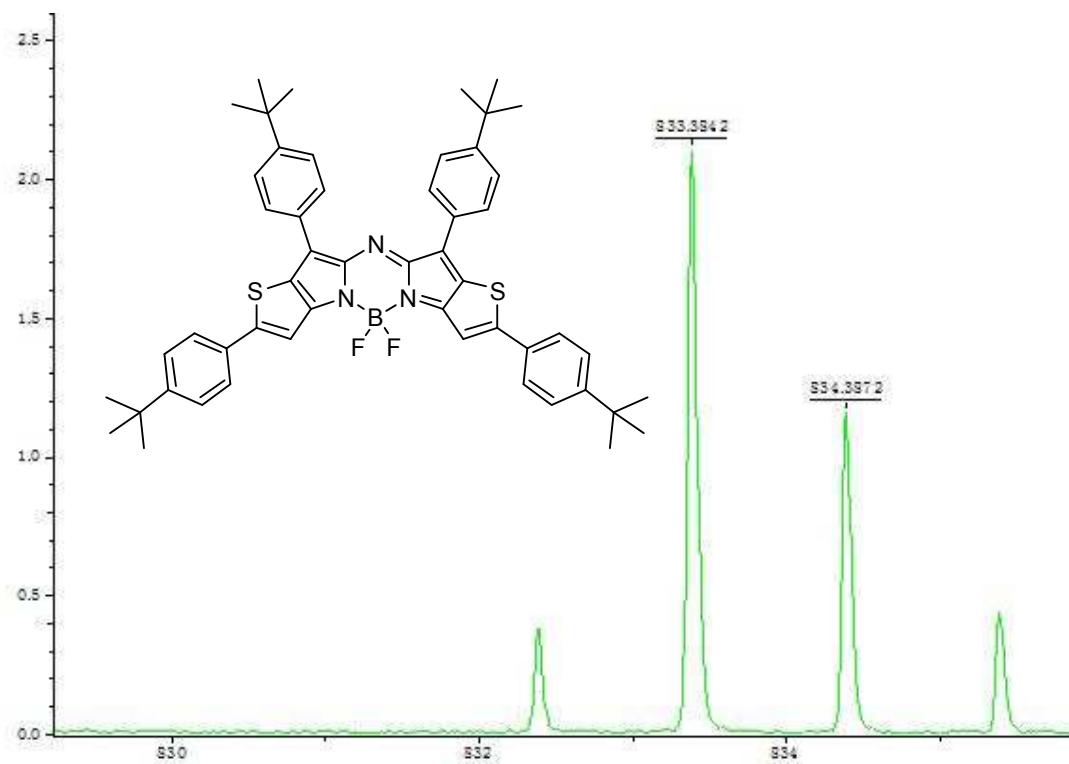
20130607_APCI+WS #11 RT: 0.14 AV: 1 NL: 6.10E3
T: FTMS + cAPCI corona Full ms [200.00-1500.00]



HRMS for 4d

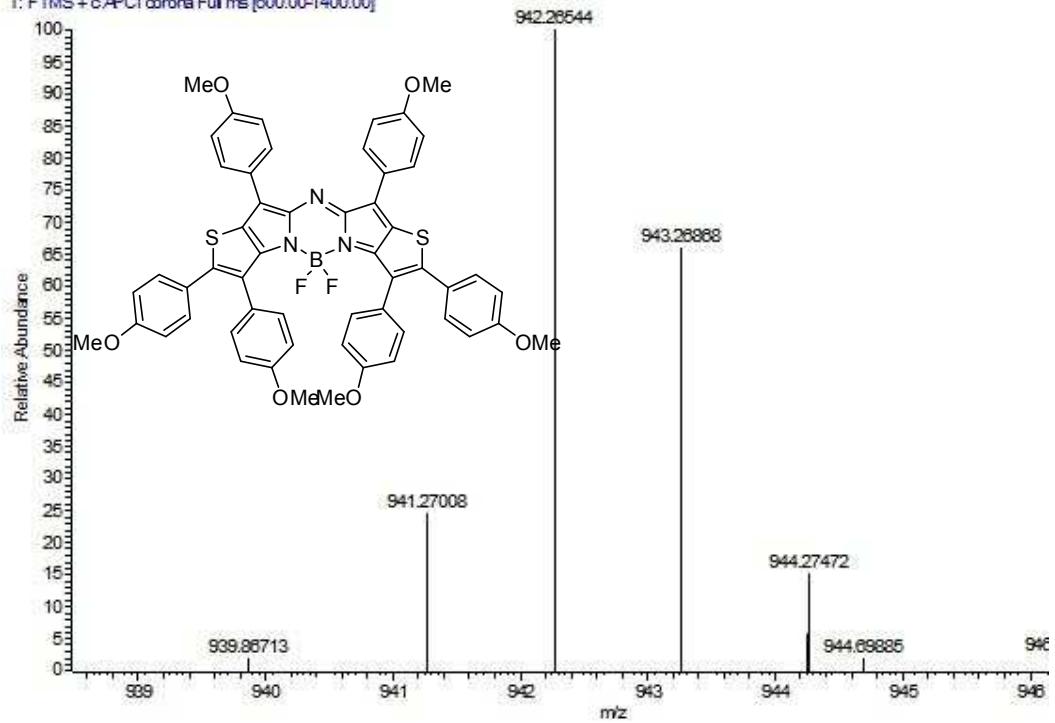


HRMS for **5a**



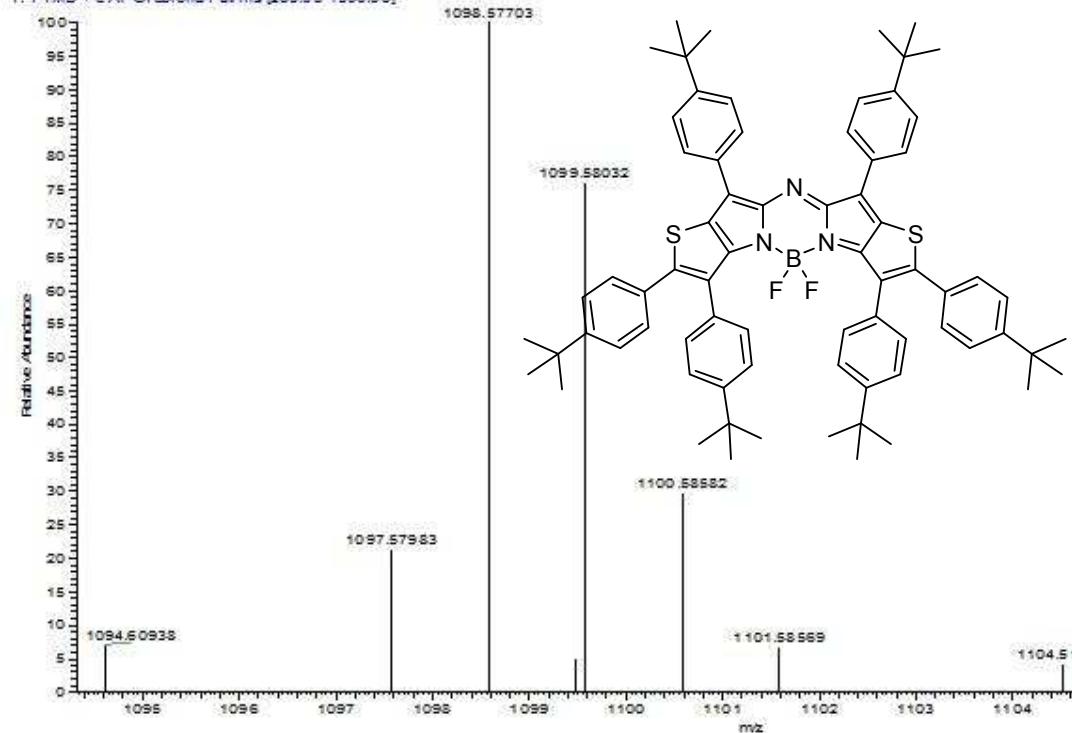
HRMS for **5b**

20131018 APCHW#9 RT: 0.14 AV: 1 NL: 1.49E8
T: FTMS + cAPCI corona Full ms [800.00-1400.00]



HRMS for **5c**

20130607_APCL-W12 #45 RT: 0.63 AV: 1 NL: 6.39E5
T: FTMS + cAPCI corona Full ms [200.00-1500.00]



HRMS for **5d**

7. Fluorescence lifetime decay curves

Fluorescence lifetime was measured in chloroform by time-correlated single photon counting method (Edinburgh FLS920 spectrophotometer). The compounds were excited at 370 nm and the emission was monitored at the maximum emission wavelength.

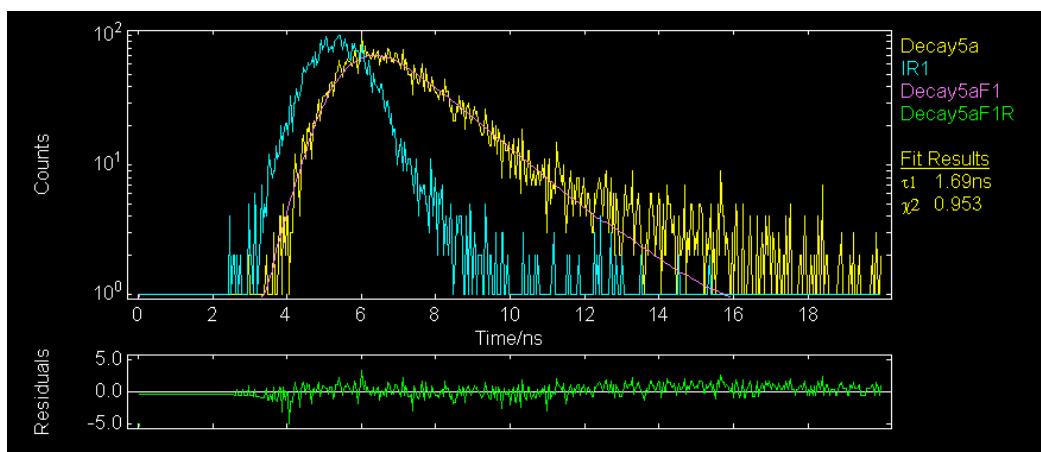


Figure S8. The fluorescence decay of dye **5a** in chloroform measured by single photon counting method with emission was monitored at 813 nm.

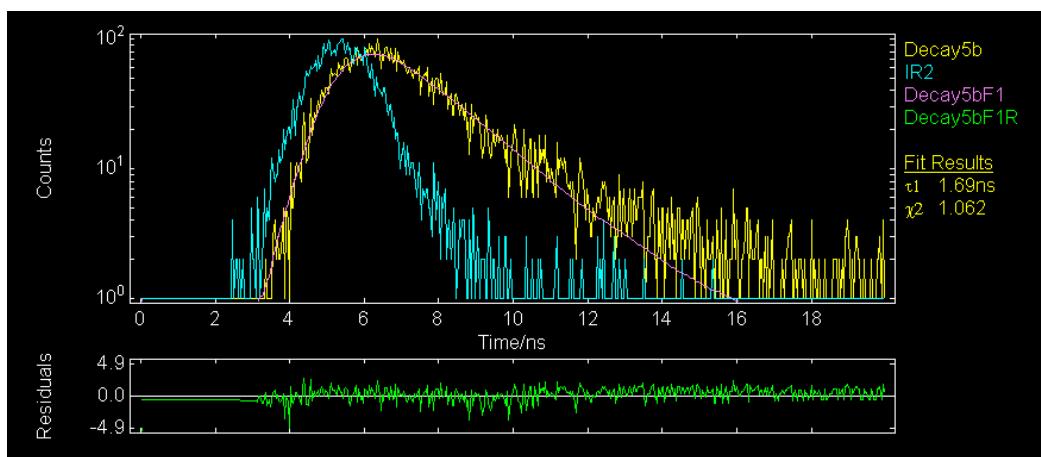


Figure S9. The fluorescence decay of dye **5b** in chloroform measured by single photon counting method with emission was monitored at 813 nm.

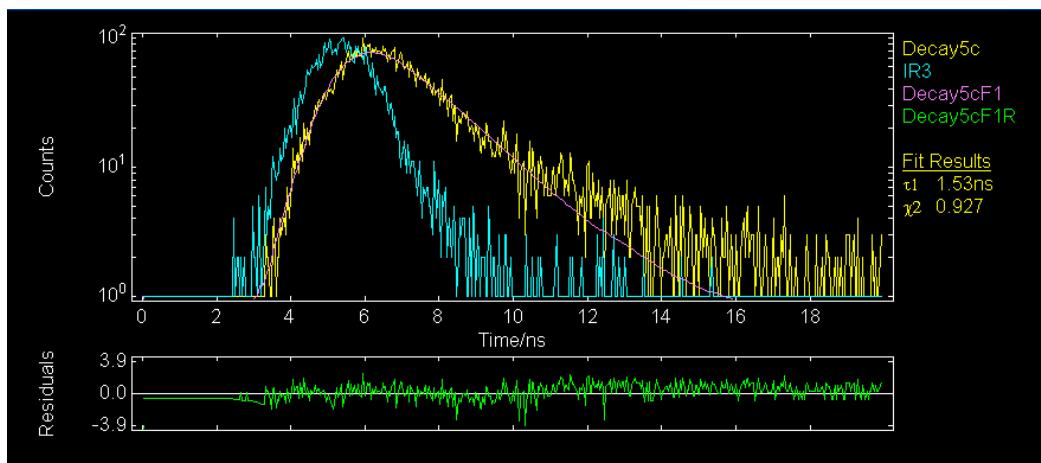


Figure S10. The fluorescence decay of dye **5c** in chloroform measured by single photon counting method with emission was monitored at 817 nm.

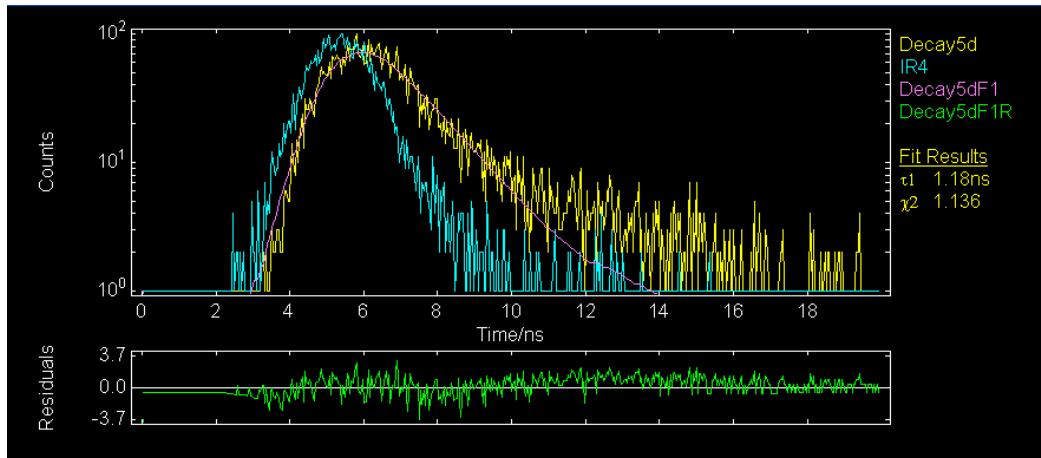


Figure S11. The fluorescence decay of dye **5d** in chloroform measured by single photon counting method with emission was monitored at 817 nm.

Reference:

1. (a) Lippert, E. *Z. Naturforsch., A: Phys. Sci.* **1955**, *10*, 541. (b) Mataga, N.; Kaifu, Y.; Koizumi, M. *Bull. Chem. Soc. Jpn.* **1956**, *29*, 465.
2. Filarowski, A.; Kluba, M.; Cieślik-Boczula, K.; Koll, A.; Kochel, A.; Pandey, L.; De Borggraeve, W. M.; Van der Auweraer, M.; Catalán, J.; Noens, N. *Photochem. Photobiol. Sci.*, **2010**, *9*, 996.
3. Gaussian 09, Revision C.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**.
4. Chang, Y.; Chen, H.; Zhou, Z.; Zhang, Y.; Schutt, C.; Herges, R.; Shen, Z. *Angew. Chem. Int. Ed.* **2012**, *51*, 12801.
5. (a) Benson, R. C.; Kues, H. A. *Phys. Med. Biol.*, **1978**, *23*, 159. (b) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*, 3rd ed.; Springer: New York, **2006**.
6. Pang, W.; Zhang, X.-F.; Zhou, J.; Yu, C.; Hao, E. H.; Jiao, L. J. *Chem. Commun.* **2012**, *48*, 5437.
7. SAINT V 6.01 (NT) *Software for the CCD Detector System*, Bruker Analytical X-ray Systems, Madison, WI (**1999**).
8. Sheldrick, G. M. SHELXS-90, *Program for the Solution of Crystal Structure*, University of Göttingen, Germany, **1990**.
9. SHELXL-97, *Program for the Refinement of Crystal Structure*, University of Göttingen, Germany, **1997**.
10. SHELXTL 5.10 (PC/NT-Version), *Program library for StructureSolution and Molecular Graphics*, Bruker Analytical X-ray Systems, Madison, WI (**1998**).