

# Electronic Supporting Information for the article entitled

## Bathochromic Shift of Fluorescence Peak in Dipyrrolo[1,2-*a*:2',1'-*c*]quinoxaline by Introducing Each of Electron-Donating and Electron-Withdrawing Substituent

Shoji Matsumoto,\* Makoto Takamori, and Motohiro Akazome

Department of Applied Chemistry and Biotechnology, Graduate School of Engineering, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

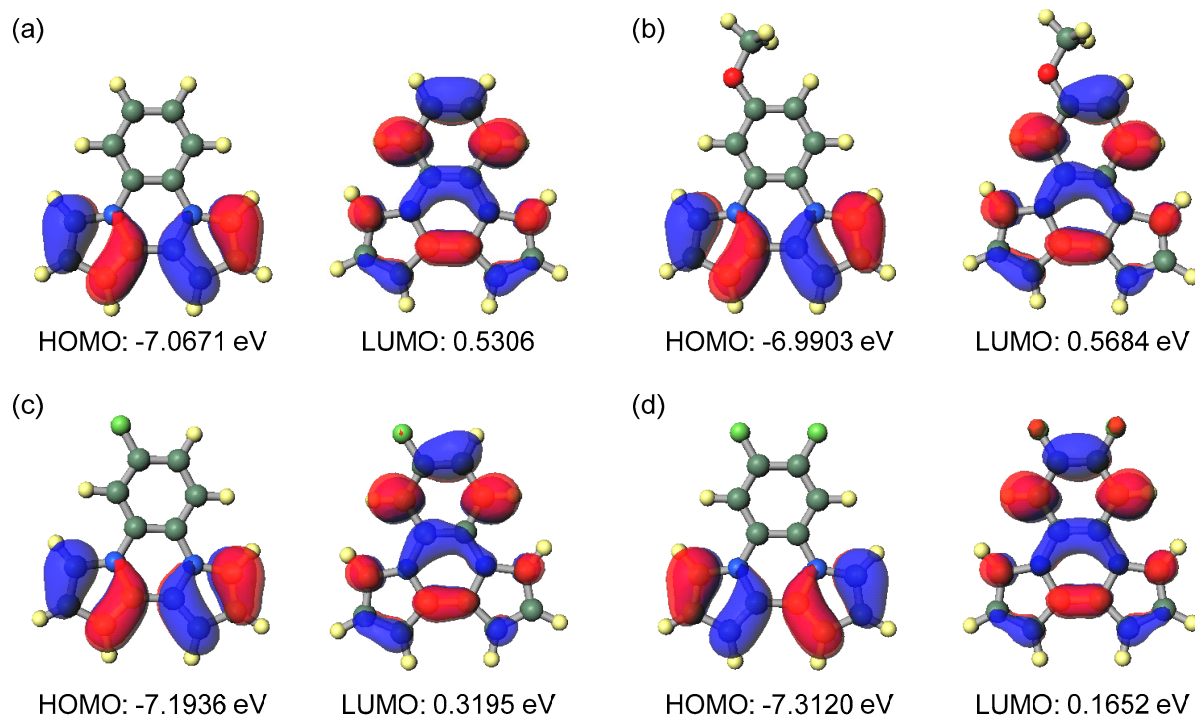
E-mail address: smatsumo@faculty.chiba-u.jp

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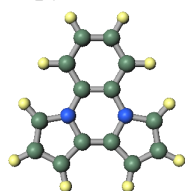
**Table S1.** Computed three longest transition peaks of **1a-d** in the excited singlet state calculated by TDDFT (nstate = 10) using optimized structure (TDDFT (nstate = 1) for the excited state) at TDDFT/ $\omega$ B97XD/6-31+G(d,p) level

Compound	Transition	Band gap (eV)	Wavelength (nm)	Oscillator strength
<b>1a</b>	HOMO $\rightarrow$ LUMO (0.69563)	3.4559	358.76	0.1507
	HOMO-1 $\rightarrow$ LUMO (0.20414)	4.1183	301.06	0.0015
	HOMO $\rightarrow$ LUMO+1 (0.66320)			
	HOMO-2 $\rightarrow$ LUMO+1 (-0.15826)	4.5444	272.83	0.2249
	HOMO-1 $\rightarrow$ LUMO (0.62692)			
	HOMO $\rightarrow$ LUMO+1 (-0.21684)			
<b>1b</b>	HOMO $\rightarrow$ LUMO (0.69702)	3.4219	362.32	0.1426
	HOMO-1 $\rightarrow$ LUMO (0.50409)	4.2142	294.21	0.0478
	HOMO $\rightarrow$ LUMO+1 (-0.45588)			
	HOMO-2 $\rightarrow$ LUMO+1 (-0.11140)	4.4677	277.51	0.2229
	HOMO-1 $\rightarrow$ LUMO (0.43801)			
	HOMO $\rightarrow$ LUMO+1 (0.51652)			
<b>1c</b>	HOMO $\rightarrow$ LUMO (0.69829)	3.3497	370.13	0.1234
	HOMO-1 $\rightarrow$ LUMO (0.27068)	4.1404	299.45	0.0089
	HOMO $\rightarrow$ LUMO+1 (0.63558)			
	HOMO-2 $\rightarrow$ LUMO+1 (0.13571)	4.4839	276.51	0.2385
	HOMO-1 $\rightarrow$ LUMO (0.60629)			
	HOMO $\rightarrow$ LUMO+1 (-0.28423)			
<b>1d</b>	HOMO 62 $\rightarrow$ LUMO 63 (0.69979)	3.2895	376.91	0.1122
	HOMO-1 $\rightarrow$ LUMO (-0.30893)	4.1387	299.57	0.0029
	HOMO $\rightarrow$ LUMO+1 (0.62104)			
	HOMO-2 $\rightarrow$ LUMO+1 (-0.12028)	4.4321	279.74	0.2516
	HOMO-1 $\rightarrow$ LUMO (0.59214)			
	HOMO $\rightarrow$ LUMO+1 (0.32296)			



**Figure S1.** Shape and energies of HOMO and LUMO of (a) **1a**, (b) **1b**, (c) **1c**, and (d) **1d** calculated by DFT/ $\omega$ B97XD/6-31+G(d,p) level of theory. Optimized structure was estimated by DFT/ $\omega$ B97XD/6-31+G(d,p) level of theory.

### Dipyrrolo[1,2-*a*:2',1'-*c*]quinoxaline (1a) optimized by TDDFT calculation

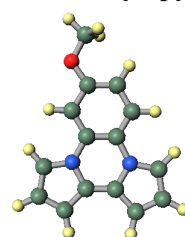


Total energy: -648.812490362 A.U.

Cartesian coordinates:

C1	1.490552	-0.689215	-0.000005	C12	-2.185345	-1.415488	0.000027
N1	0.261564	-1.356826	0.000008	H1	-0.299057	3.416155	-0.000018
C2	-0.978993	-0.700576	0.000011	H2	2.368202	3.876852	-0.000034
C3	-0.978975	0.700582	0.000001	H3	2.368183	-3.876862	0.000005
N2	0.261564	1.356824	-0.000010	H4	-0.299073	-3.416151	0.000024
C4	1.490561	0.689208	-0.000013	C13	-3.401351	-0.687831	0.000028
C5	0.500779	2.694910	-0.000019	H5	-2.197506	-2.496838	0.000036
C6	1.894973	2.905813	-0.000027	H6	-2.197507	2.496849	-0.000010
C7	2.522044	1.675816	-0.000025	C14	-3.401338	0.687843	0.000014
C8	2.522031	-1.675824	-0.000008	H7	-4.339899	-1.232372	0.000040
C9	1.894957	-2.905822	0.000004	H8	-4.339885	1.232389	0.000015
C10	0.500770	-2.694914	0.000014	H9	3.581376	1.467424	-0.000030
C11	-2.185348	1.415499	0.000000	H10	3.581363	-1.467432	-0.000017

### 6-Methoxydipyrrolo[1,2-*a*:2',1'-*c*]quinoxaline (1b) optimized by TDDFT calculation

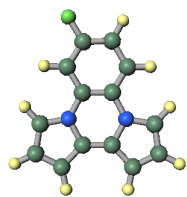


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Cartesian coordinates:

C1	2.278960	-0.462446	-0.000026	H2	2.388823	4.186398	-0.000117
N1	1.186228	-1.327532	0.000006	H3	3.684304	-3.455790	0.000009
C2	-0.155160	-0.886655	0.000020	H4	0.975929	-3.448476	0.000044
C3	-0.380577	0.498634	-0.000008	C13	-2.556442	-1.271114	0.000068
N2	0.726140	1.351185	-0.000041	H5	-1.062580	-2.845918	0.000079
C4	2.050825	0.898606	-0.000054	H6	-1.907532	2.066089	-0.000037
C5	0.741489	2.709818	-0.000063	C14	-2.768141	0.092819	0.000037
C6	2.084111	3.150071	-0.000093	H7	-3.377866	-1.975212	0.000093
C7	2.905581	2.042335	-0.000088	O1	-3.995820	0.684091	0.000039
C8	3.461828	-1.259084	-0.000034	H8	3.984782	2.011777	-0.000108
C9	3.053677	-2.578920	0.000001	H9	4.470136	-0.873185	-0.000057
C10	1.644639	-2.603908	0.000021	C15	-5.130924	-0.150827	0.000111
C11	-1.689875	1.007740	-0.000001	H10	-5.160205	-0.785627	-0.894715
C12	-1.222063	-1.776023	0.000059	H11	-5.160125	-0.785581	0.894970
H1	-0.168029	3.287114	-0.000053	H12	-5.995227	0.513815	0.000132

### 6-Fluorodipyrrolo[1,2-*a*:2',1'-*c*]quinoxaline (1c) optimized by TDDFT calculation

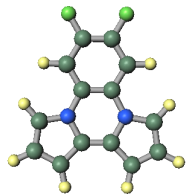


Total energy: -748.024120848 A.U.

Cartesian coordinates:

C1	1.920221	-0.408349	-0.000001	C12	-1.527719	-1.854140	0.000001
N1	0.859505	-1.309649	0.000000	H1	-0.653885	3.252424	0.000001
C2	-0.498585	-0.916542	0.000000	H2	1.869986	4.241547	-0.000002
C3	-0.766544	0.458402	0.000001	H3	3.428159	-3.350688	0.000000
N2	0.307896	1.350248	0.000000	H4	0.721286	-3.436048	0.000000
C4	1.646351	0.944953	-0.000002	C13	-2.878697	-1.394312	0.000001
C5	0.275096	2.707116	0.000000	H5	-1.325745	-2.916020	0.000001
C6	1.601945	3.195235	-0.000002	H6	-2.360323	1.976468	0.000002
C7	2.460727	2.117197	-0.000001	C14	-3.109464	-0.045723	0.000001
C8	3.129152	-1.163192	-0.000001	H7	-3.707893	-2.090044	0.000001
C9	2.767480	-2.496349	0.000000	F1	-4.387810	0.403786	0.000001
C10	1.360635	-2.569238	-0.000001	H8	3.540334	2.124534	-0.000002
C11	-2.100107	0.928680	0.000002	H9	4.123616	-0.742860	-0.000002

### 6,7-Difluorodipyrrolo[1,2-*a*:2',1'-*c*]quinoxaline (1d) optimized by TDDFT calculation

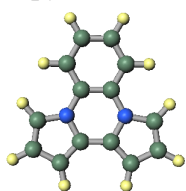


Total energy: -847.228319917 A.U.

Cartesian coordinates:

C1	2.076449	0.690334	0.000000	C12	-1.590351	1.425033	0.000002
N1	0.851927	1.357547	0.000000	H1	0.288498	-3.412724	0.000000
C2	-0.389307	0.698497	0.000001	H2	2.957724	-3.875244	-0.000002
C3	-0.389315	-0.698496	0.000001	H3	2.957715	3.875248	0.000000
N2	0.851930	-1.357549	0.000001	H4	0.288489	3.412718	0.000000
C4	2.076447	-0.690334	0.000000	C13	-2.795470	0.682257	0.000000
C5	1.088941	-2.692026	0.000000	H5	-1.637676	2.503218	0.000002
C6	2.484344	-2.904520	-0.000001	H6	-1.637671	-2.503217	-0.000001
C7	3.108333	-1.674353	0.000000	C14	-2.795474	-0.682257	-0.000001
C8	3.108333	1.674357	0.000000	F1	-3.959660	1.362413	0.000000
C9	2.484342	2.904520	0.000000	F2	-3.959663	-1.362415	-0.000003
C10	1.088937	2.692025	0.000000	H7	4.167329	-1.464301	0.000000
C11	-1.590348	-1.425033	0.000000	H8	4.167329	1.464302	0.000000

### Dipyrrolo[1,2-*a*:2',1'-*c*]quinoxaline (1a) optimized by DFT calculation

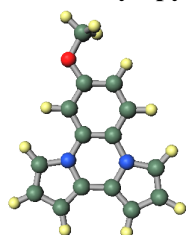


Total energy: -648.825408476 A.U.

Cartesian coordinates:

C1	1.487997	0.718509	0.000006	C12	-2.175009	1.389537	-0.000029
N1	0.270025	1.380690	-0.000013	H1	-0.300890	-3.457162	0.000019
C2	-0.958883	0.703721	-0.000015	H2	2.354032	-3.898327	0.000028
C3	-0.959146	-0.703394	0.000000	H3	2.356337	3.897185	-0.000004
N2	0.269328	-1.380678	0.000013	H4	-0.298503	3.457629	-0.000029
C4	1.487760	-0.719189	0.000015	C13	-3.377565	0.697663	-0.000028
C5	0.503858	-2.740873	0.000020	H5	-2.181753	2.472721	-0.000042
C6	1.861965	-2.936509	0.000023	H6	-2.183789	-2.471825	0.000016
C7	2.489923	-1.662809	0.000022	C14	-3.377803	-0.695803	-0.000012
C8	2.490879	1.661620	0.000014	H7	-4.312115	1.247826	-0.000040
C9	1.863791	2.935587	-0.000003	H8	-4.312839	-1.245397	-0.000009
C10	0.505423	2.740425	-0.000015	H9	3.549705	-1.455864	0.000026
C11	-2.175888	-1.388625	0.000002	H10	3.550528	1.453959	0.000028

### 6-Methoxydipyrrolo[1,2-*a*:2',1'-*c*]quinoxaline (1b) optimized by DFT calculation

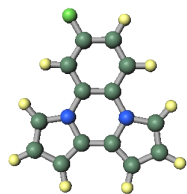


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Cartesian coordinates:

C1	-2.285285	-0.480698	0.000079	H2	-2.344553	4.217374	-0.000254
N1	-1.201405	-1.341853	0.000005	H3	-3.689099	-3.461865	0.000295
C2	0.127669	-0.884087	-0.000095	H4	-0.996234	-3.483724	0.000163
C3	0.371619	0.503786	0.000024	C13	2.521030	-1.285708	-0.000238
N2	-0.722629	1.379824	-0.000002	H5	1.043358	-2.824625	-0.000625
C4	-2.036908	0.935954	0.000023	H6	1.893952	2.037076	0.000372
C5	-0.720265	2.760228	-0.000033	C14	2.754260	0.090749	0.000168
C6	-2.024383	3.185493	-0.000162	H7	3.334595	-1.999817	-0.000773
C7	-2.861576	2.037697	-0.000143	O1	3.984626	0.665167	0.000453
C8	-3.437069	-1.237228	0.000081	H8	-3.941169	2.015497	-0.000212
C9	-3.038888	-2.599041	0.000182	H9	-4.444932	-0.849607	0.000096
C10	-1.665761	-2.639406	0.000095	C15	5.116640	-0.179881	-0.000144
C11	1.678899	0.976333	0.000186	H10	5.143460	-0.812581	0.895525
C12	1.211617	-1.754482	-0.000352	H11	5.143429	-0.811350	-0.896625
H1	0.195845	3.327268	-0.000082	H12	5.982982	0.480975	0.000451

### 6-Fluorodipyrrolo[1,2-*a*:2',1'-*c*]quinoxaline (1c) optimized by DFT calculation

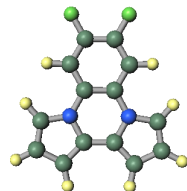


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Cartesian coordinates:

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N1	-0.883246	-1.319280	-0.000004	H1	0.706061	3.287511	-0.000009
C2	0.461843	-0.918082	-0.000002	H2	-1.793582	4.282864	0.000003
C3	0.759665	0.458009	0.000001	H3	-3.456404	-3.334760	0.000005
N2	-0.293670	1.379113	0.000001	H4	-0.769296	-3.469489	-0.000005
C4	-1.626209	0.991323	0.000000	C13	2.831449	-1.431598	-0.000002
C5	-0.232815	2.758933	-0.000005	H5	1.287547	-2.903900	-0.000007
C6	-1.517457	3.238388	0.000001	H6	2.356673	1.927047	0.000006
C7	-2.402894	2.127067	-0.000001	C14	3.093612	-0.070770	0.000001
C8	-3.113204	-1.121963	0.000005	H7	3.645898	-2.145539	-0.000003
C9	-2.771177	-2.499519	0.000003	F1	4.374662	0.349480	0.000004
C10	-1.402016	-2.597413	0.000000	H8	-3.482367	2.151349	0.000000
C11	2.091198	0.878194	0.000003	H9	-4.104482	-0.693892	0.000008

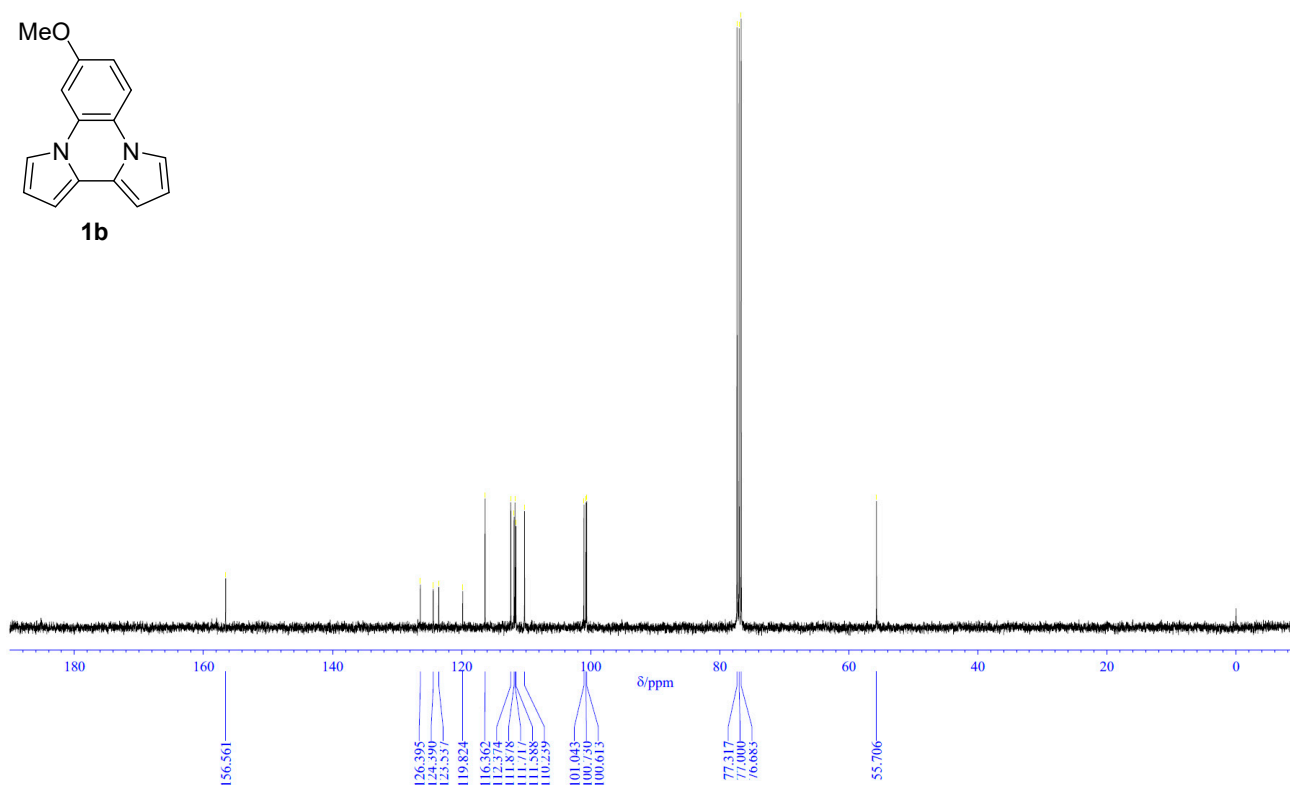
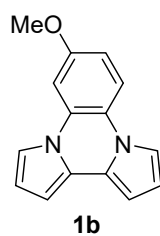
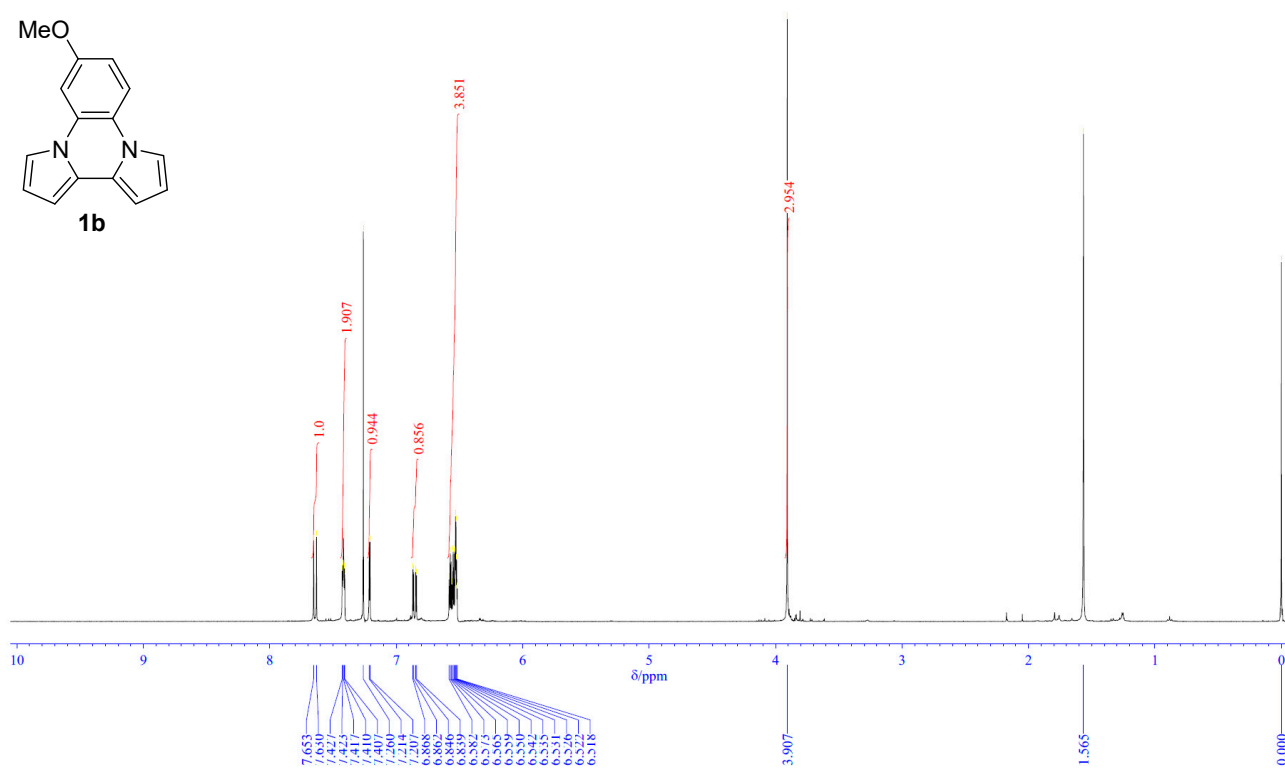
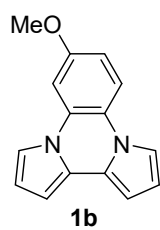
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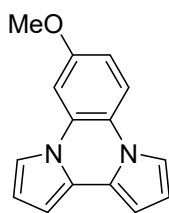
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Cartesian coordinates:

C1	2.073781	0.718967	0.000000	C12	-1.584127	1.393318	-0.000003
N1	0.854722	1.381416	-0.000002	H1	0.284209	-3.458908	0.000005
C2	-0.370218	0.703711	-0.000002	H2	2.938860	-3.898603	-0.000012
C3	-0.370121	-0.703705	0.000000	H3	2.937748	3.899123	0.000003
N2	0.854955	-1.381435	0.000001	H4	0.283523	3.458886	-0.000002
C4	2.074079	-0.718841	0.000001	C13	-2.774103	0.694409	-0.000002
C5	1.088862	-2.742175	0.000003	H5	-1.622768	2.474672	-0.000005
C6	2.446550	-2.937022	-0.000007	H6	-1.622180	-2.474506	0.000005
C7	3.074794	-1.663169	0.000000	C14	-2.774625	-0.694873	0.000001
C8	3.074320	1.663621	0.000004	F1	-3.938440	1.357114	-0.000002
C9	2.445888	2.937303	0.000002	F2	-3.938484	-1.357643	0.000003
C10	1.088159	2.742104	0.000000	H7	4.134672	-1.457109	-0.000001
C11	-1.583854	-1.393021	0.000002	H8	4.134200	1.457583	0.000006





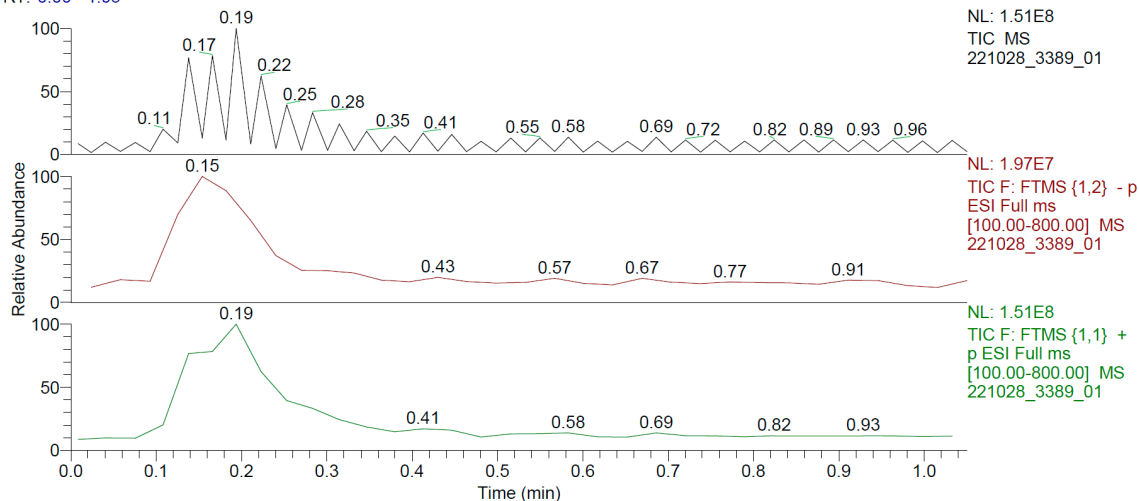


**1b**

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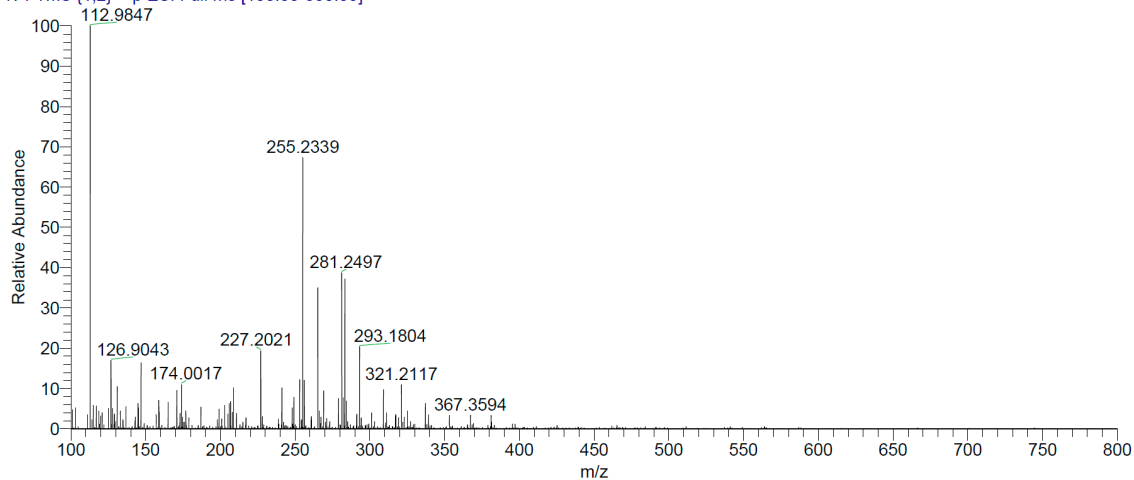
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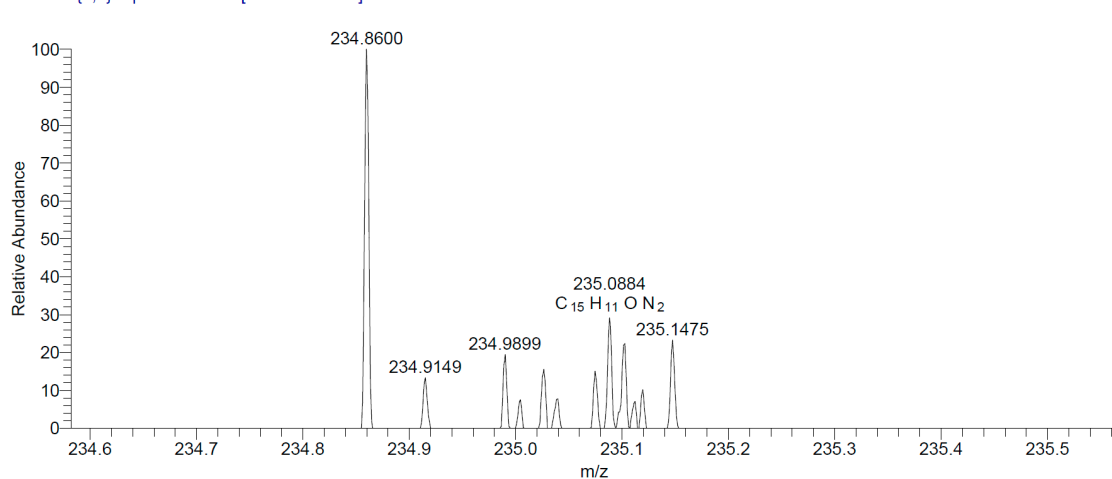
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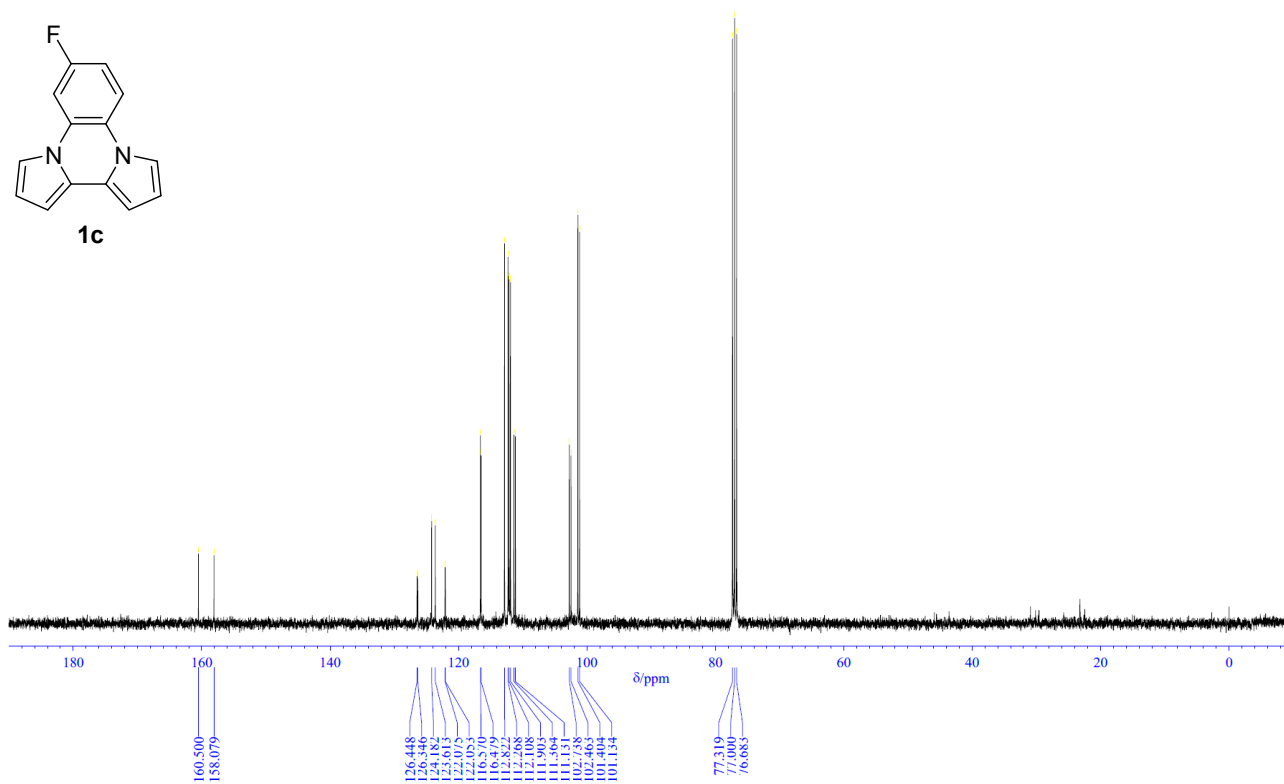
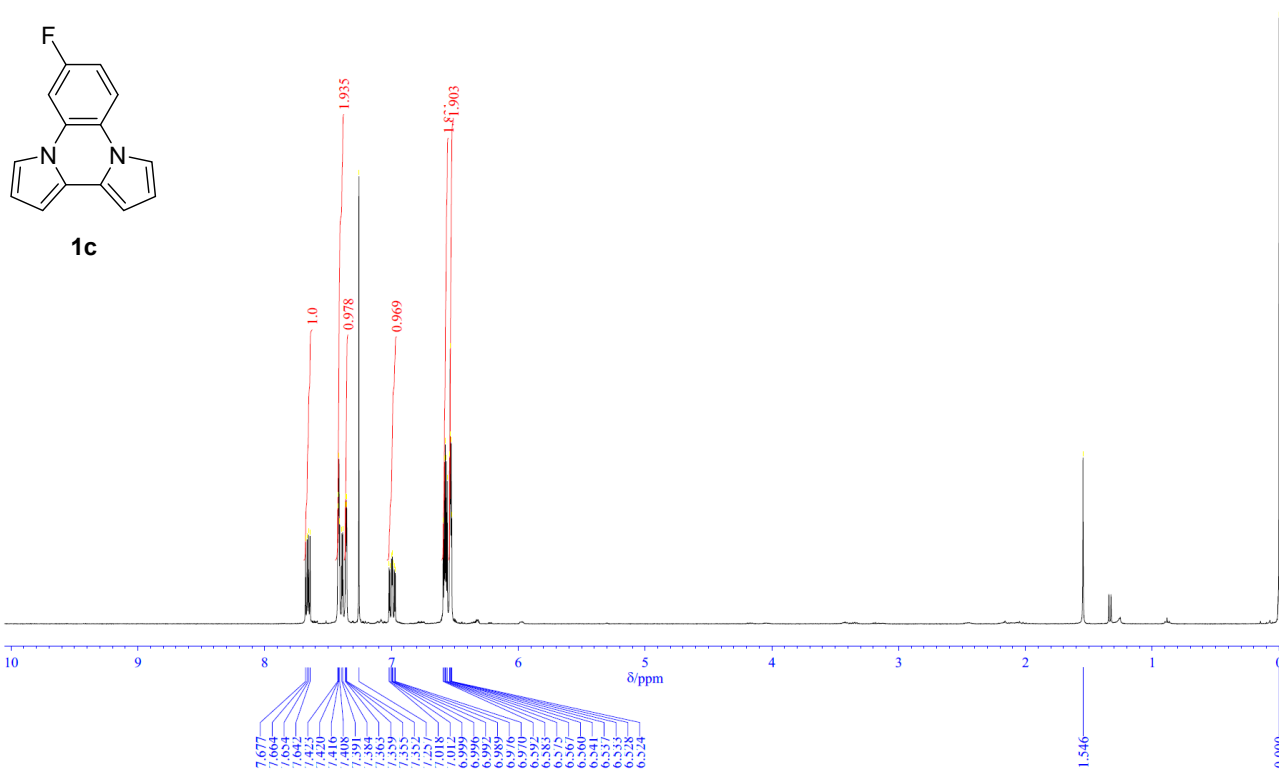
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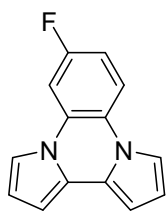


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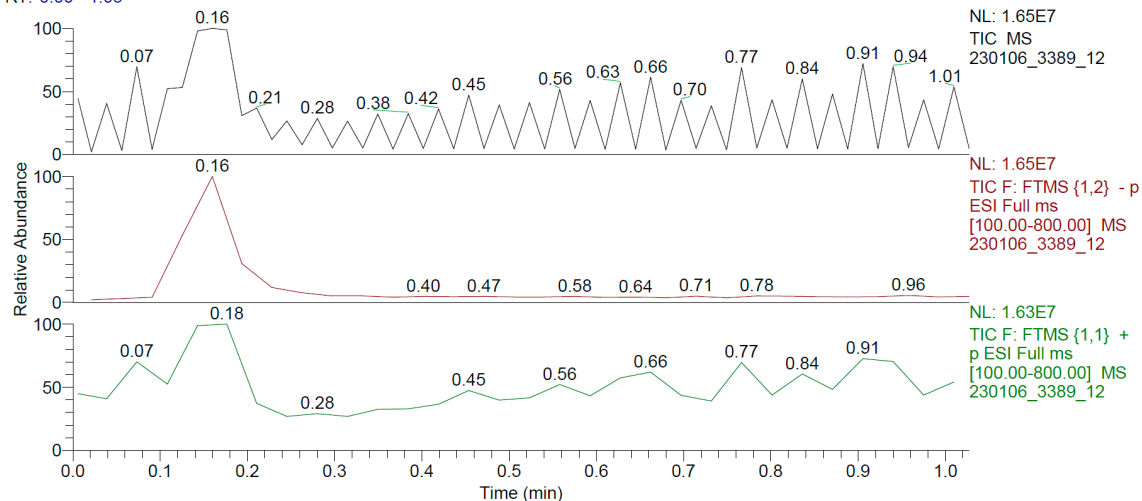


**1c**

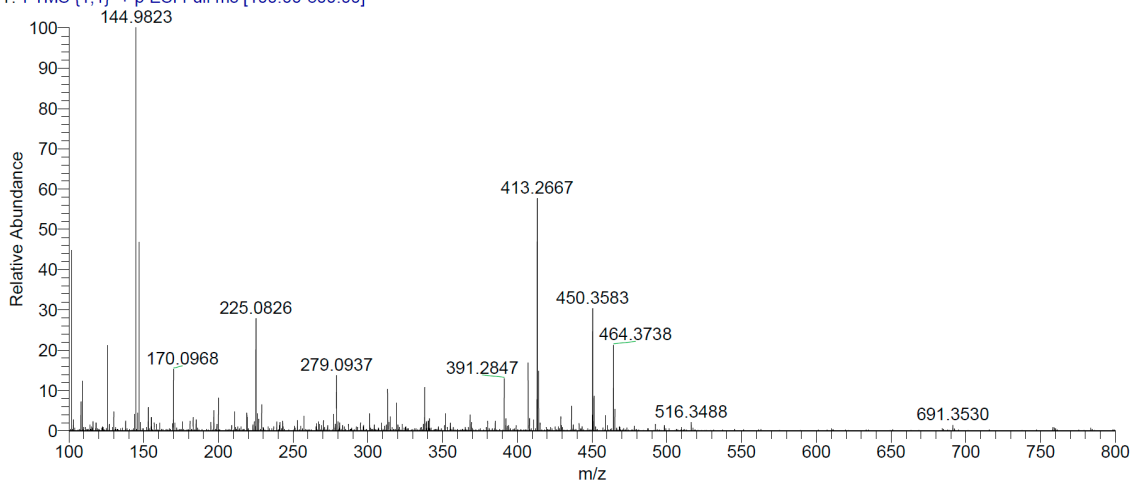
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2023/01/06 12:40:42

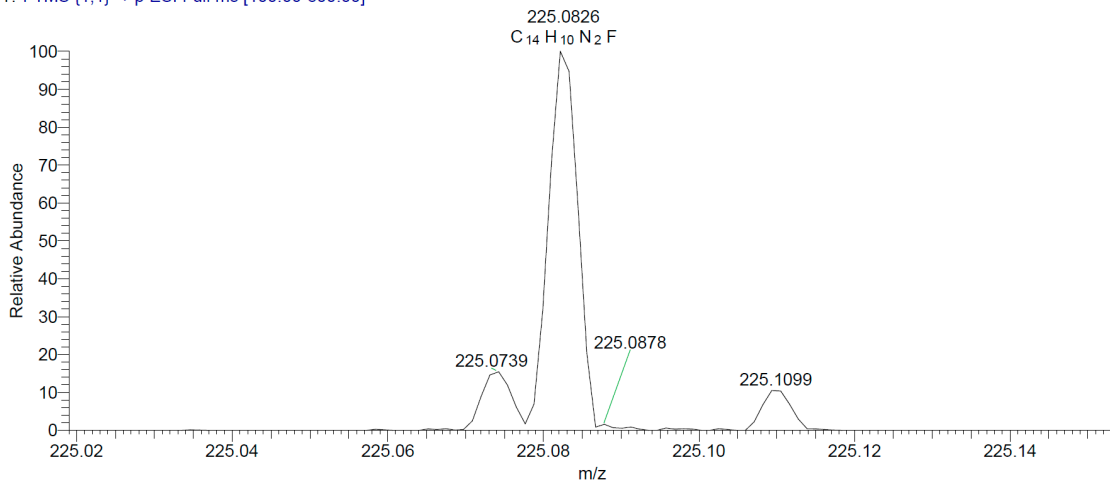
RT: 0.00 - 1.03

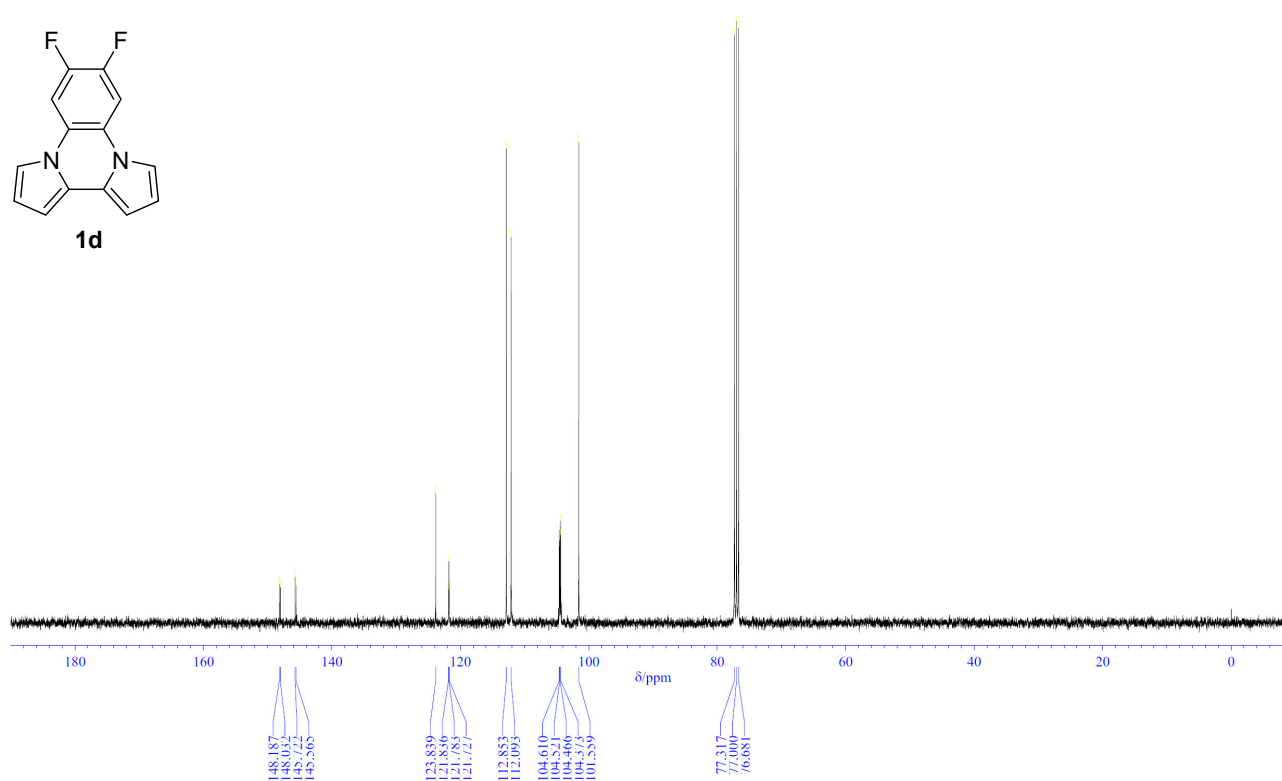
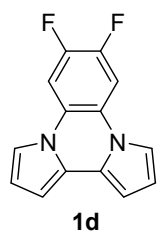
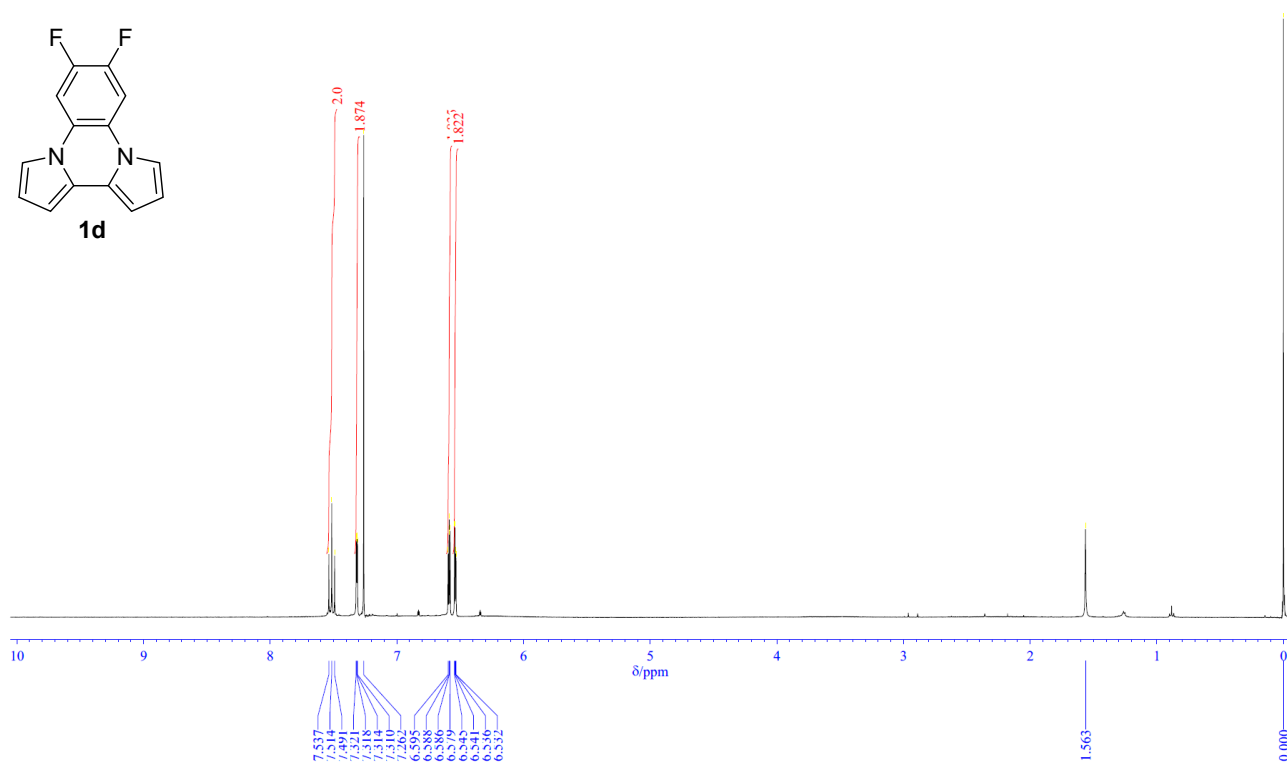
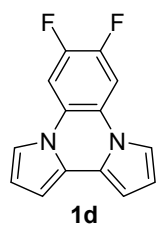


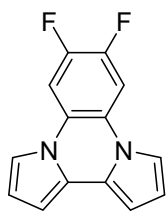
230106\_3389\_12 #11 RT: 0.18 AV: 1 NL: 1.36E6  
T: FTMS {1,1} + p ESI Full ms [100.00-800.00]



230106\_3389\_12 #11 RT: 0.18 AV: 1 NL: 3.79E5  
T: FTMS {1,1} + p ESI Full ms [100.00-800.00]





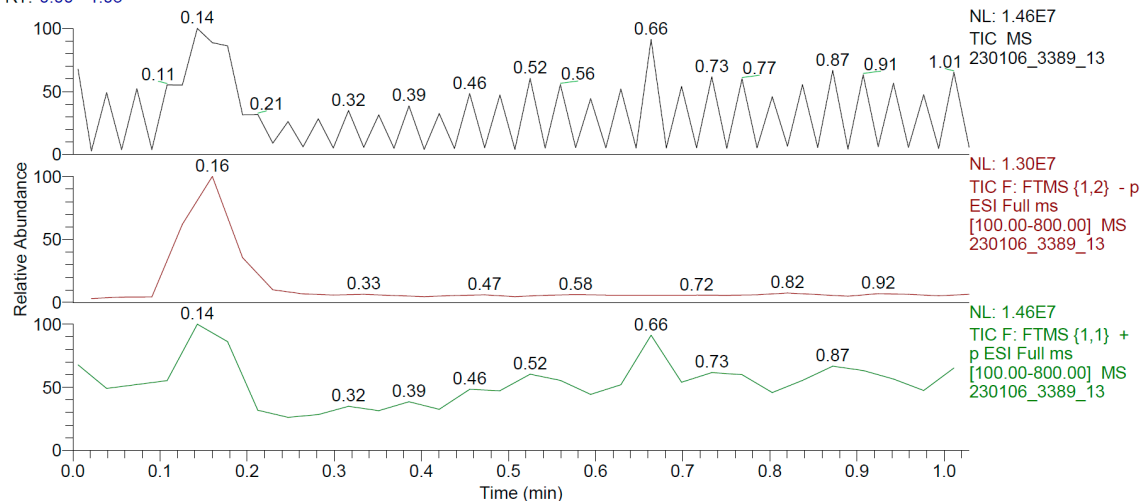


**1d**

\\EXACTIVE-W7\data\...230106\_3389\_13

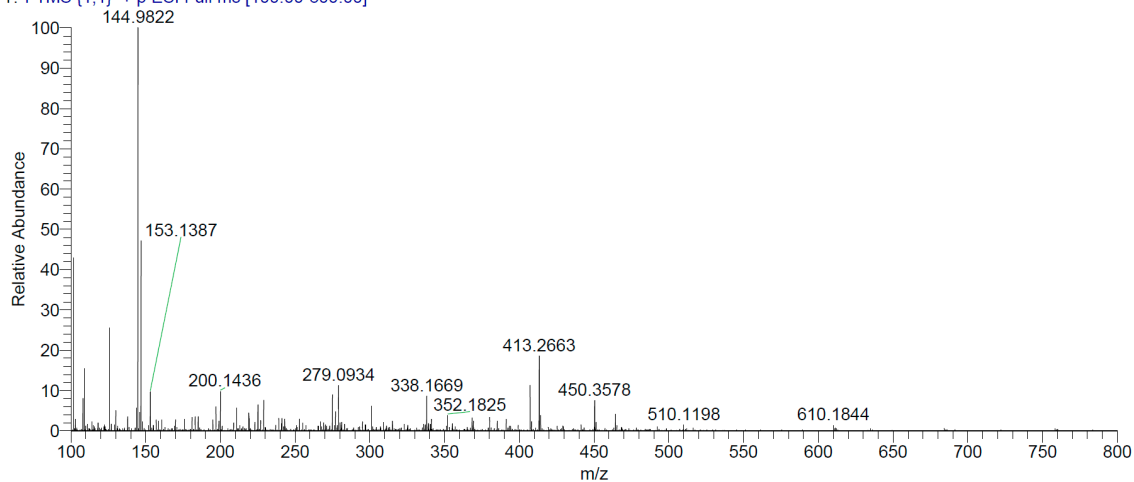
2023/01/06 12:44:20

RT: 0.00 - 1.03



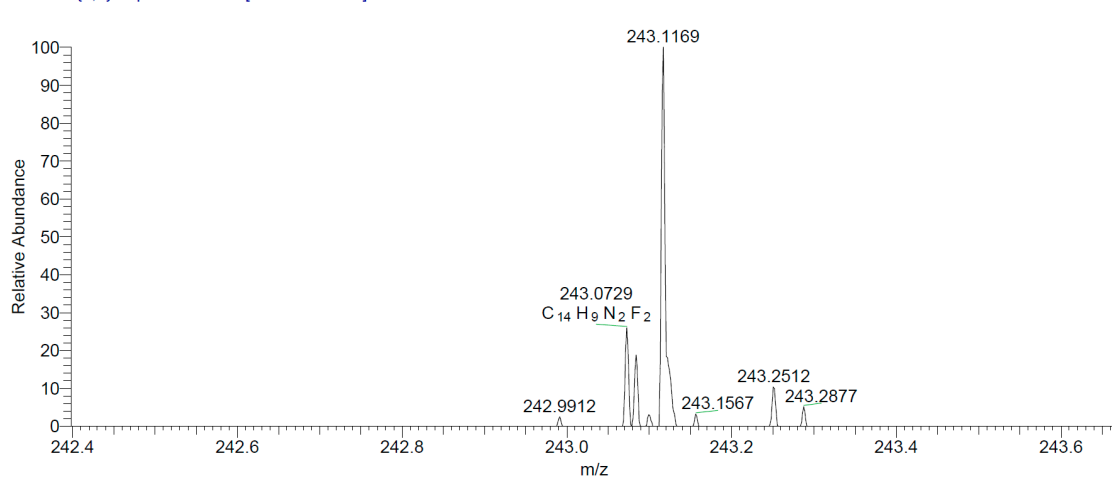
230106\_3389\_13 #11 RT: 0.18 AV: 1 NL: 1.28E6

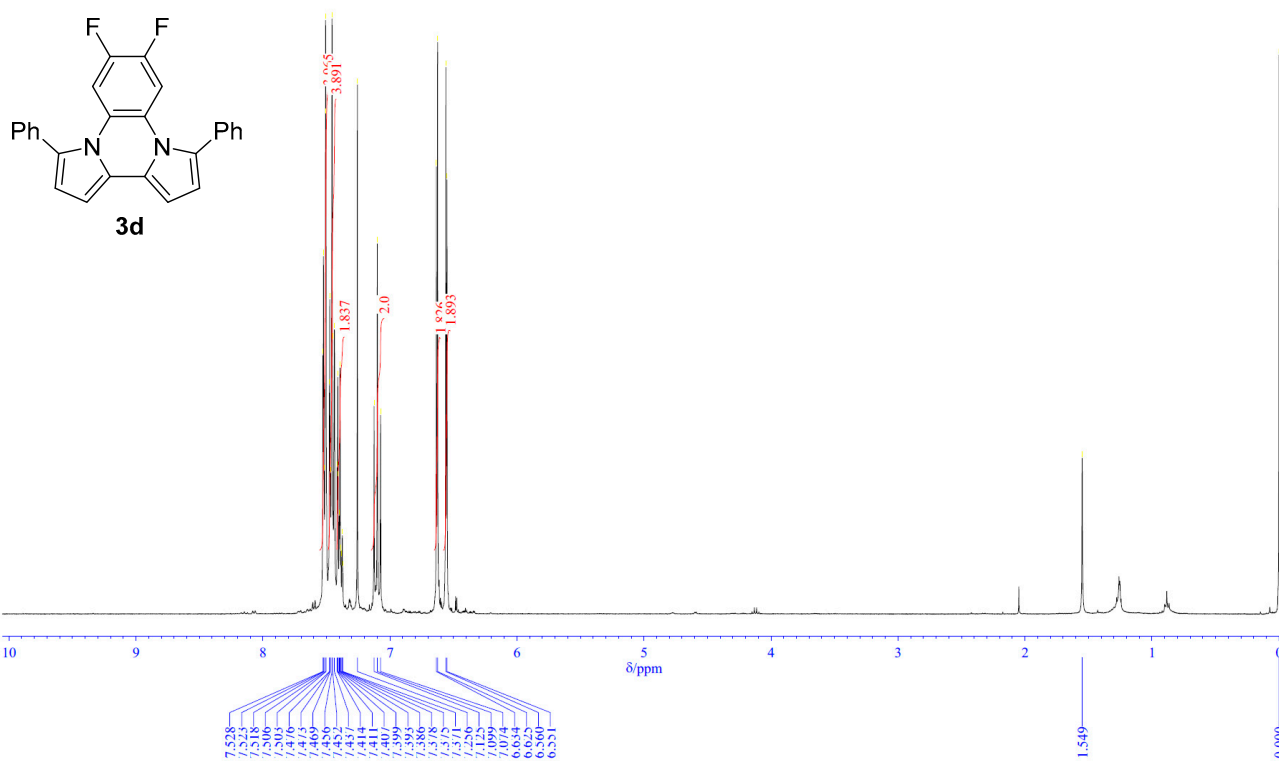
T: FTMS {1,1} + p ESI Full ms [100.00-800.00]

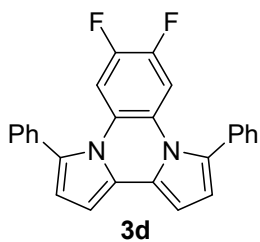


230106\_3389\_13 #9 RT: 0.14 AV: 1 NL: 2.46E4

T: FTMS {1,1} + p ESI Full ms [100.00-800.00]



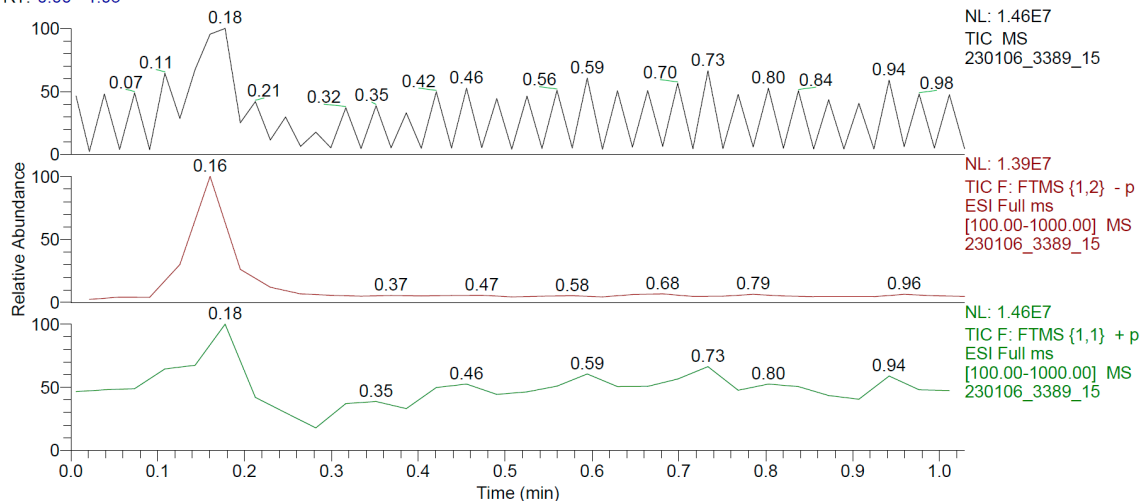




\\EXACTIVE-W7\data\...\230106\_3389\_15

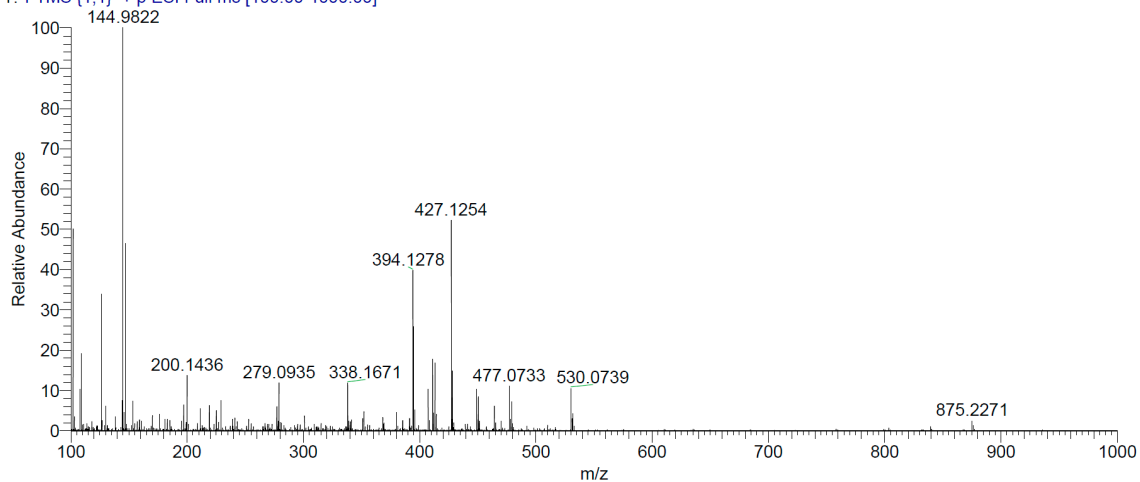
2023/01/06 12:51:43

RT: 0.00 - 1.03



230106\_3389\_15 #11 RT: 0.18 AV: 1 NL: 1.17E6

T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]



230106\_3389\_15 #11 RT: 0.18 AV: 1 NL: 3.03E5

T: FTMS {1,1} + p ESI Full ms [100.00-1000.00]

