

Energy levels tuning of 'Z'- shaped small molecular non-fullerene electron acceptors based on dipyrrolo[2,3-*b*:2',3'-*e*]pyrazine-2,6(1*H*,5*H*)-dione acceptor unit for Organic Photovoltaic Applications: A joint experimental and DFT investigation on the effect of fluorination

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Figure captions:

Fig. S1 Schematic representation showing the impact of fragments on the energy level regulation of the dyes obtained from B3LYP/6-311G(d, p) level of theory.

Fig. S2 Mulliken charge population analysis of the dyes in the ground state.

Fig. S3 Electrostatic potential surface of the dyes.

Fig. S4 Optimized geometry, Isodensity surface and TDDFT of reference acceptor dye

Fig. S5 Geometrical coordinates of the dyes

Fig. S6 ¹H NMR spectrum of compound **1CFPzDP**

Fig. S7 ¹³C NMR spectrum of compound **1CFPzDP**

Fig. S8 MALDI-TOF Mass spectrum of compound **1CFPzDP**

Fig. S9 ¹H NMR spectrum of compound **2CFPzDP**

Fig. S10 ¹³C NMR spectrum of compound **2CFPzDP**

Fig. S11 MALDI-TOF Mass spectrum of compound **2CFPzDP**

Fig. S12 ¹H NMR spectrum of compound **3FPzDP**

Fig. S13 ¹³C NMR spectrum of compound **3FPzDP**

Fig. S14 MALDI-TOF Mass spectrum of compound **3FPzDP**

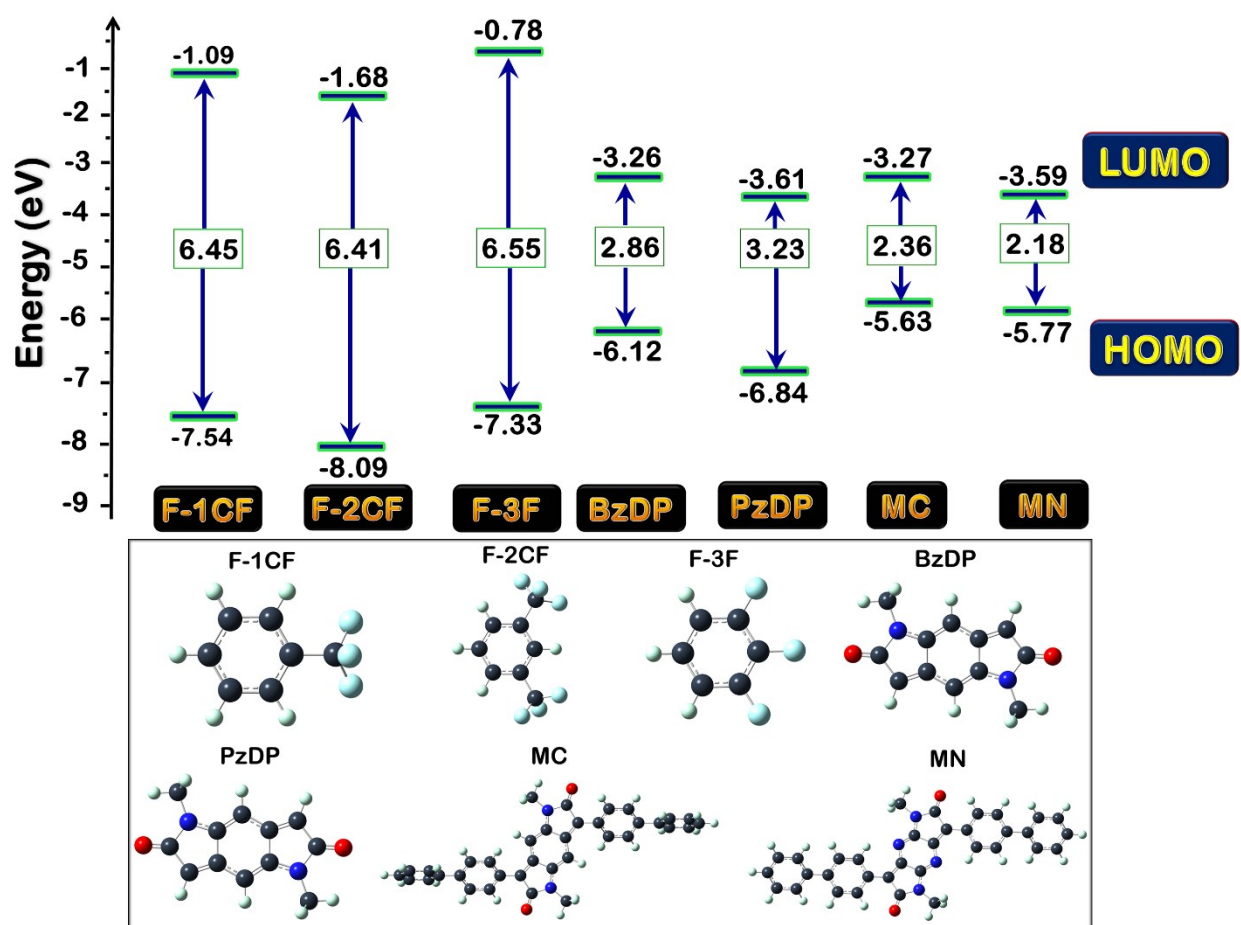


Fig. S1 Schematic representation showing the impact of fragments on the energy level regulation of the dyes obtained from B3LYP/6-311G(d, p) level of theory.

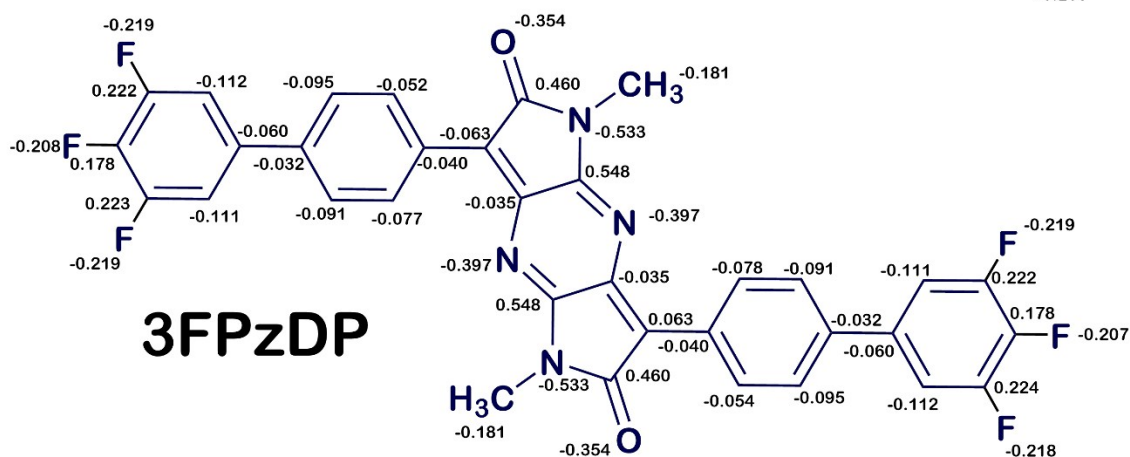
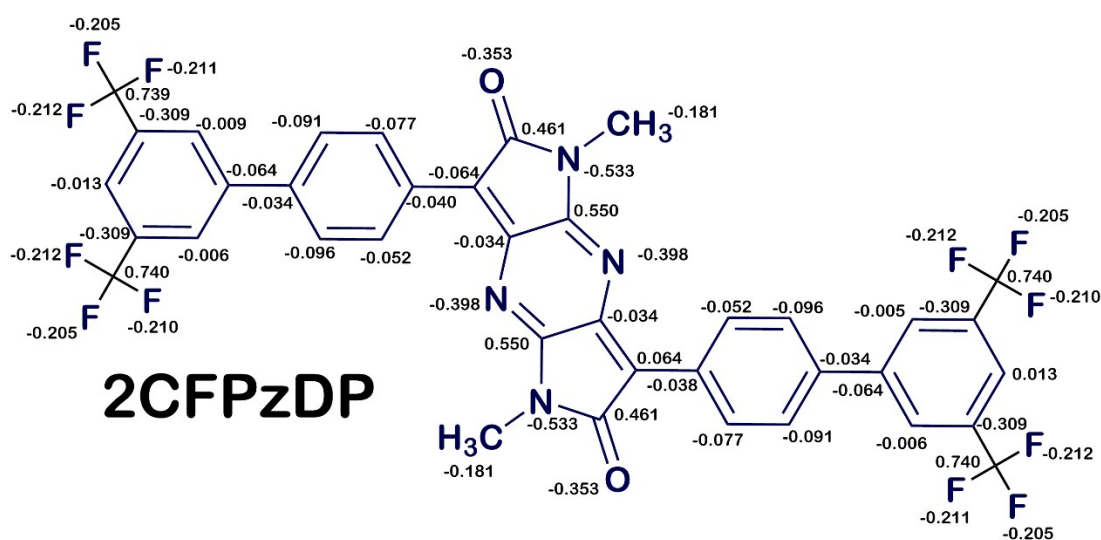
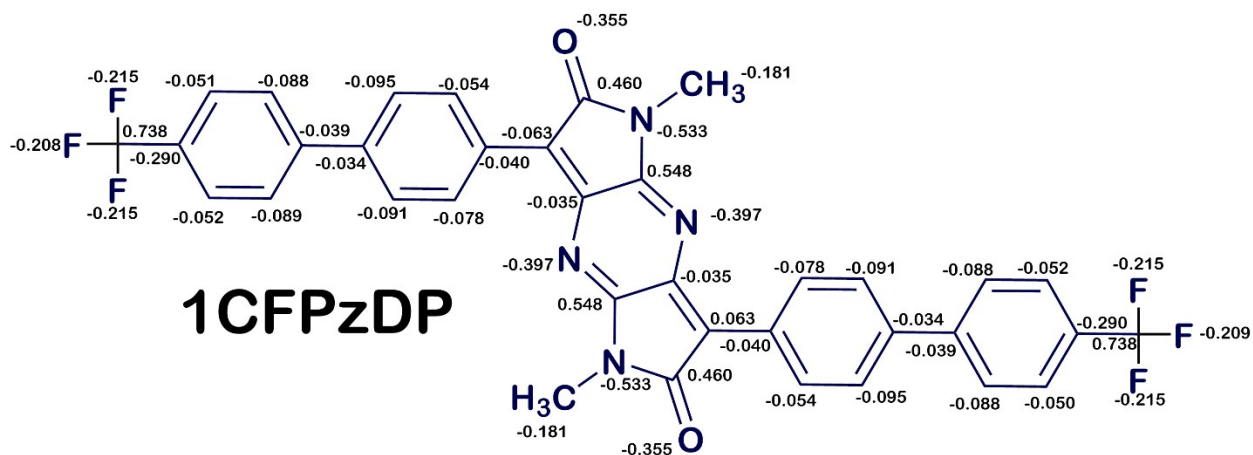


Fig. S2 Mulliken charge population analysis of the dyes in the ground state.

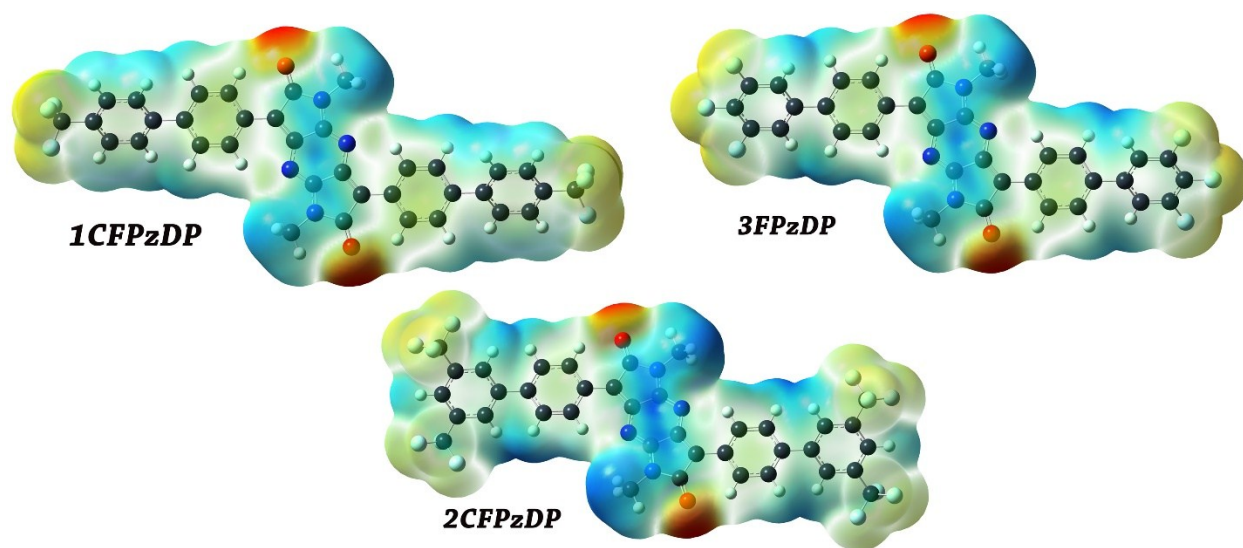


Fig. S3 Electrostatic potential surface of the dyes.

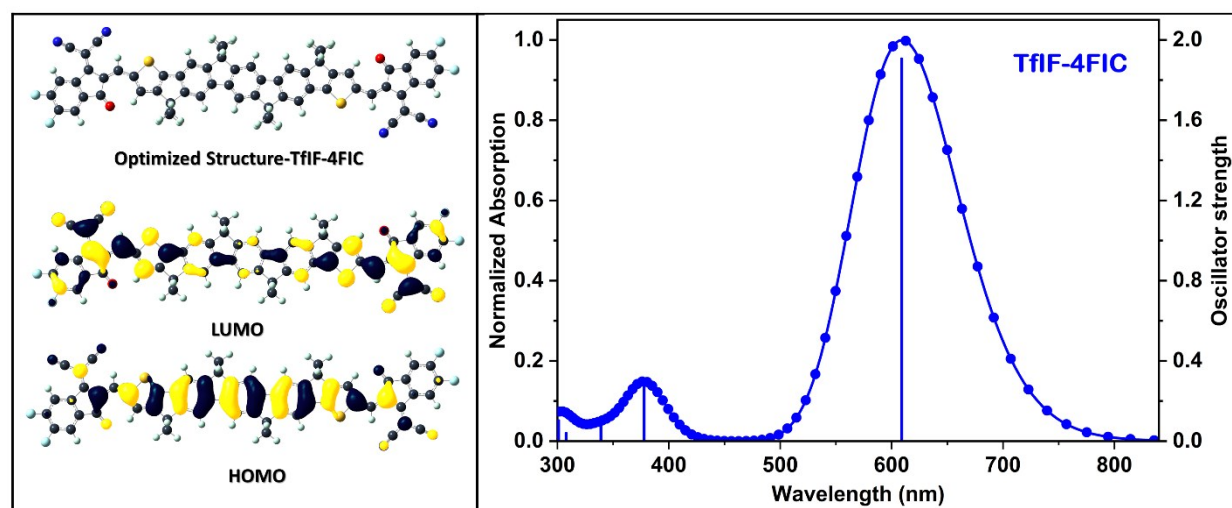
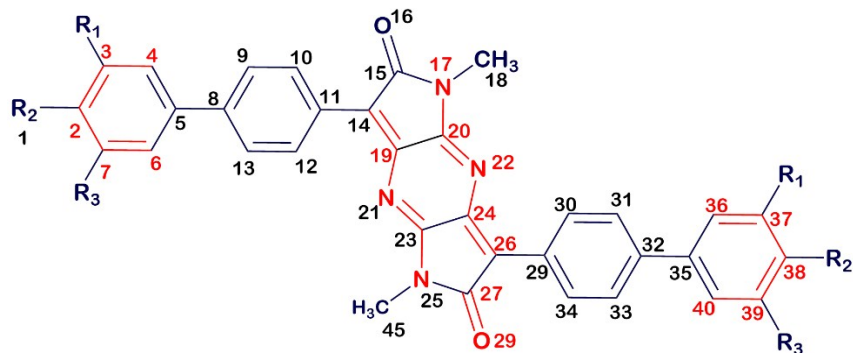


Fig. S4 Optimized geometry, isodensity surfaces and TDDFT simulated absorption of the reference acceptor (TfIF-4FIC) molecule.



	1CFPzDP	2CFPzDP	3FPzDP
C ₁ -C ₂	1.503	1.507	1.391
C ₂ -C ₃	1.394	1.391	1.393
C ₃ -C ₄	1.389	1.393	1.389
C ₄ -C ₅	1.403	1.400	1.402
C ₅ -C ₆	1.404	1.402	1.390
C ₆ -C ₇	1.389	1.390	1.394
C ₂ -C ₇	1.395	1.394	1.393
C ₅ -C ₈	1.401	1.401	1.404
C ₈ -C ₉	1.403	1.404	1.402
C ₈ -C ₁₁	1.386	1.384	1.384
C ₉ -C ₁₀	1.410	1.411	1.411
C ₁₁ -C ₁₂	1.412	1.410	1.410
C ₁₂ -C ₁₃	1.384	1.386	1.386
C ₁₀ -C ₁₃	1.405	1.402	1.402
C ₁₃ -C ₁₄	1.455	1.456	1.456
C ₁₄ -C ₁₅	1.510	1.510	1.510
C ₁₅ -O ₁₆	1.210	1.210	1.210
C ₁₅ -N ₁₇	1.409	1.410	1.410
N ₁₇ -C ₁₈	1.452	1.453	1.453
N ₁₇ -C ₂₀	1.409	1.410	1.410
C ₁₄ -C ₁₉	1.374	1.374	1.374
C ₁₉ -C ₂₀	1.473	1.474	1.473
C ₁₉ -N ₂₁	1.375	1.375	1.375
C ₂₀ -N ₂₂	1.298	1.298	1.298
N ₂₁ -C ₂₃	1.298	1.298	1.298
N ₂₂ -C ₂₄	1.375	1.375	1.375
C ₂₃ -C ₂₄	1.473	1.472	1.474
C ₂₃ -N ₂₅	1.367	1.366	1.366
C ₂₄ -C ₂₆	1.374	1.374	1.375
N ₂₅ -C ₄₅	1.452	1.453	1.453
N ₂₅ -C ₂₆	1.409	1.409	1.410
C ₂₆ -C ₂₇	1.510	1.510	1.510
C ₂₇ -O ₂₉	1.210	1.210	1.210
C ₂₆ -C ₂₉	1.455	1.456	1.456
C ₂₉ -C ₃₀	1.412	1.410	1.410

C ₃₀ -C ₃₁	1.394	1.386	1.386
C ₃₁ -C ₃₂	1.405	1.402	1.402
C ₃₂ -C ₃₃	1.403	1.404	1.404
C ₃₃ -C ₃₄	1.386	1.384	1.384
C ₂₉ -C ₃₄	1.140	1.141	1.141
C ₃₂ -C ₃₅	1.481	1.481	1.481
C ₃₅ -C ₃₆	1.403	1.402	1.402
C ₃₆ -C ₃₇	1.389	1.390	1.390
C ₃₇ -C ₃₈	1.394	1.394	1.394
C ₃₈ -C ₃₉	1.395	1.391	1.391
C ₃₉ -C ₄₀	1.388	1.393	1.393
C ₃₅ -C ₄₀	1.404	1.400	1.400
C ₄₀ -C ₄₁	1.503	1.507	-
C ₄₁ -F ₄₂	1.351	1.351	1.350
C ₄₂ -F ₄₃	1.351	1.355	1.350
C ₄₃ -F ₄₄	1.350	1.351	1.350

Fig. S5 Geometrical coordinates of the dyes

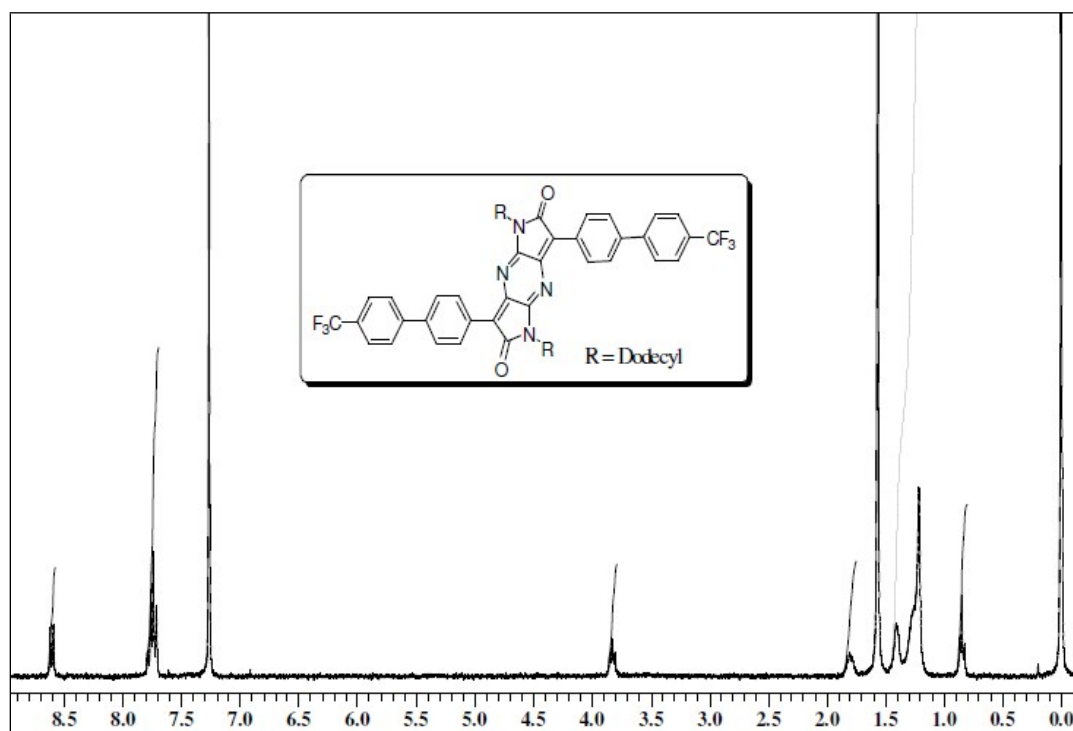


Fig. S6 ¹H NMR spectrum of compound 1CFPzDP

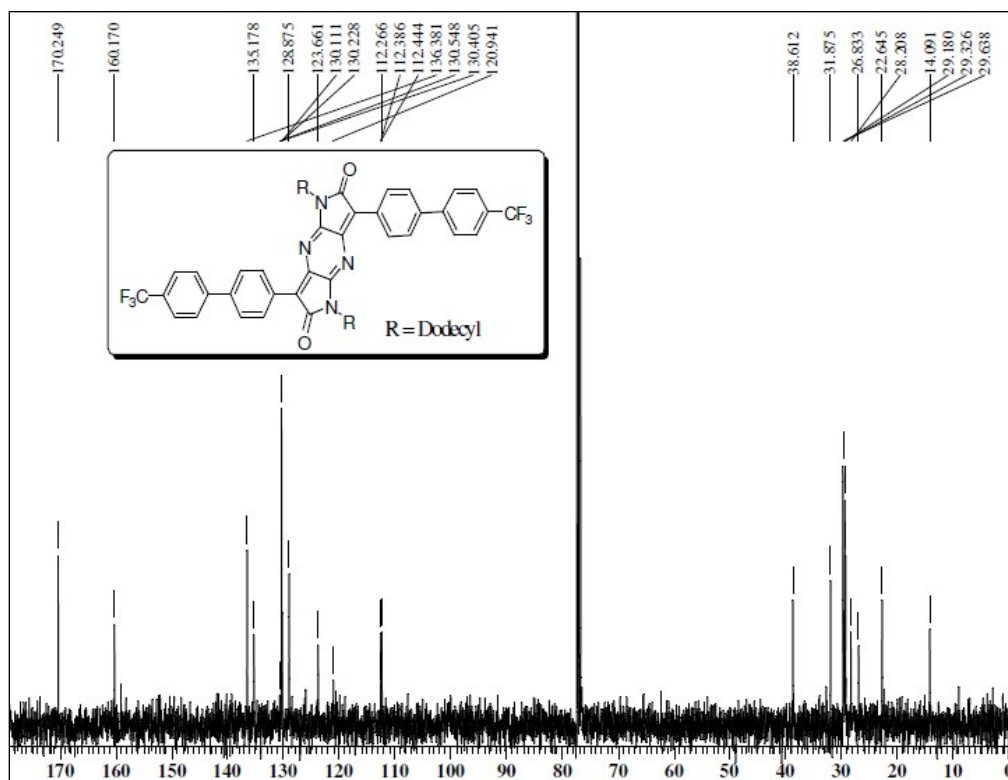


Fig. S7 ^{13}C NMR spectrum of compound 1CFPzDP

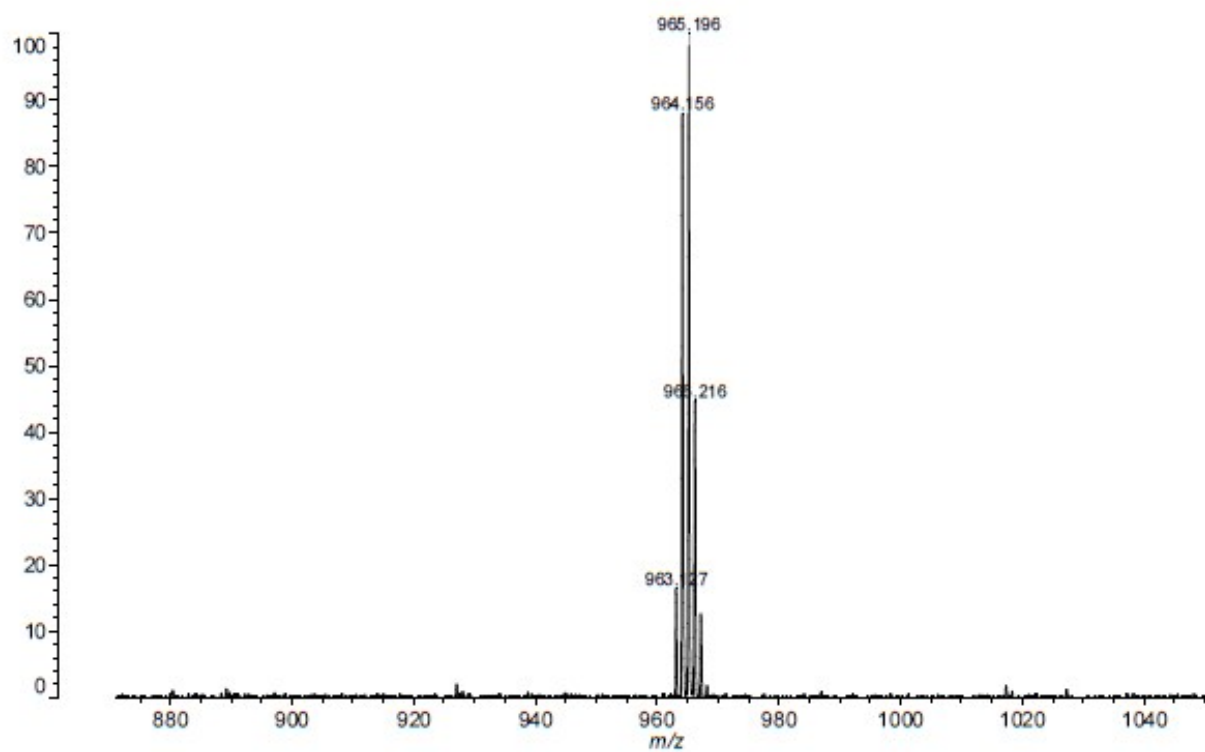


Fig. S8 MALDI-TOF Mass spectrum of compound **1CFPzDP**

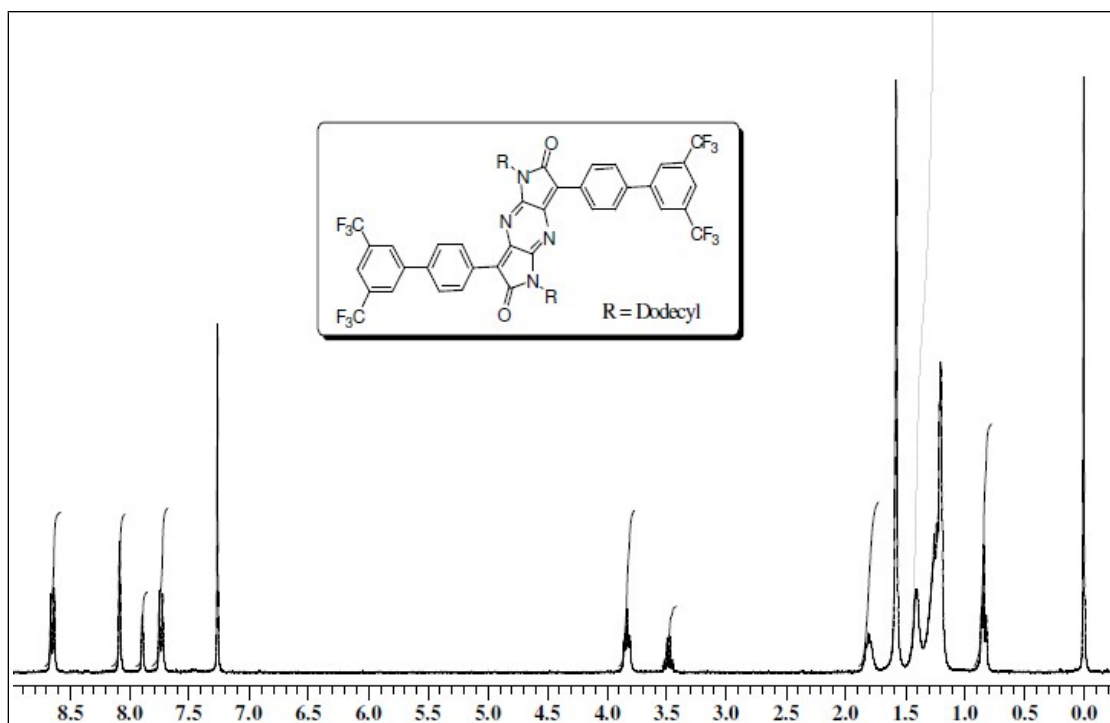


Fig. S9 ¹H NMR spectrum of compound 2CFPzDP

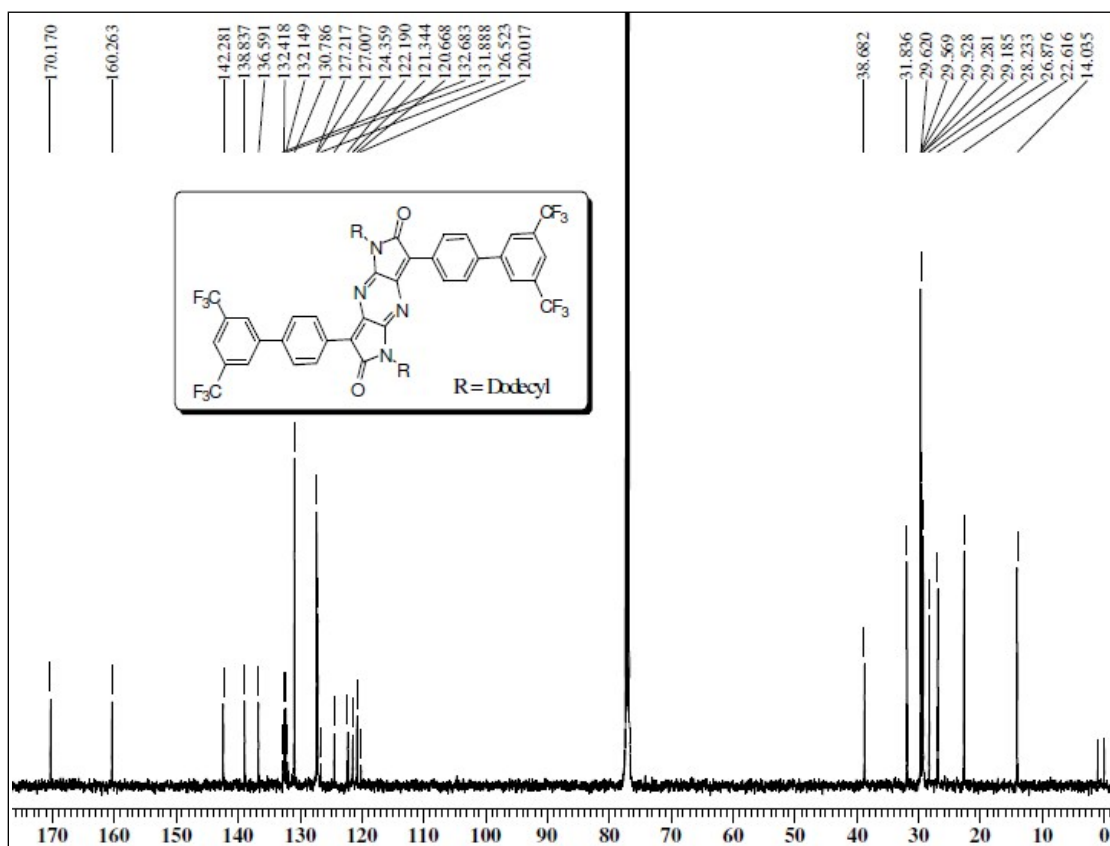


Fig. S10 ¹³C NMR spectrum of compound 2CFPzDP

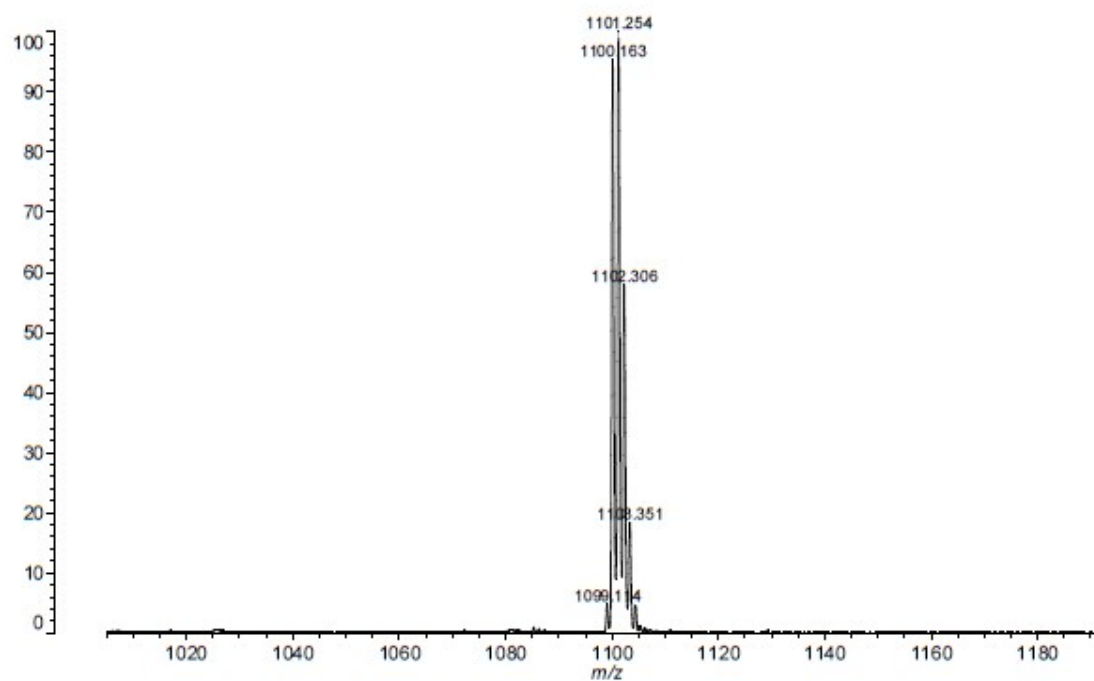


Fig. S11 MALDI-TOF Mass spectrum of compound **2CFPzDP**

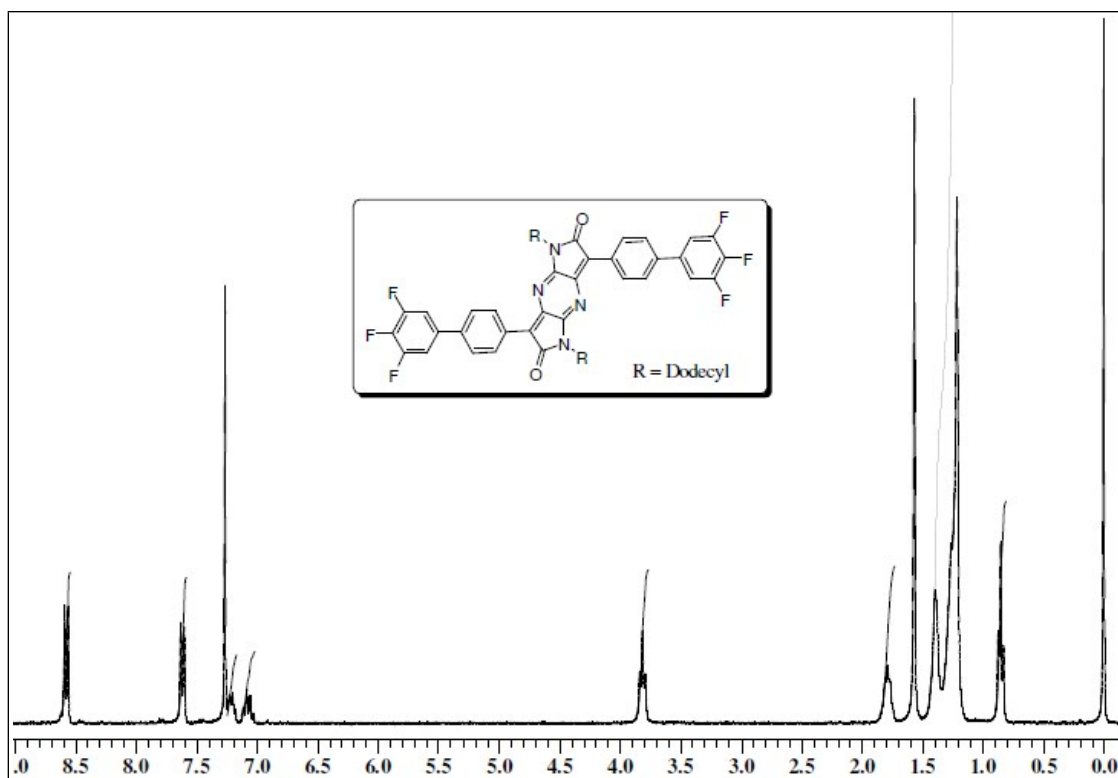


Fig. S12 ^1H NMR spectrum of compound **3FPzDP**

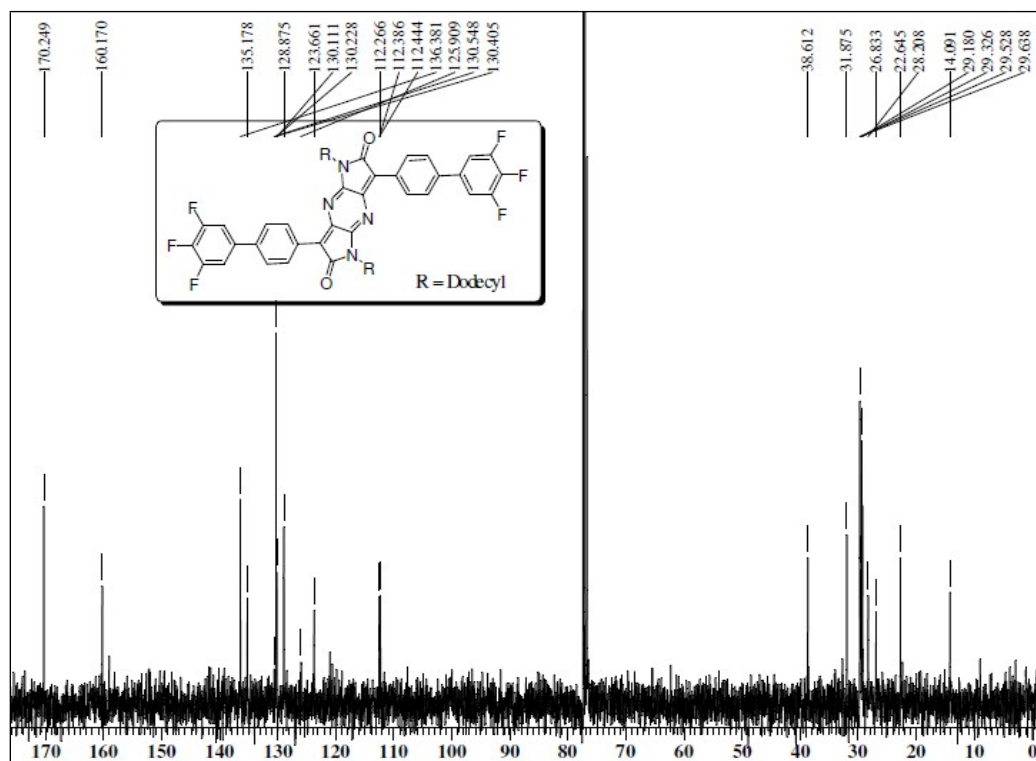


Fig. S13 ^{13}C NMR spectrum of compound **3FPzDP**

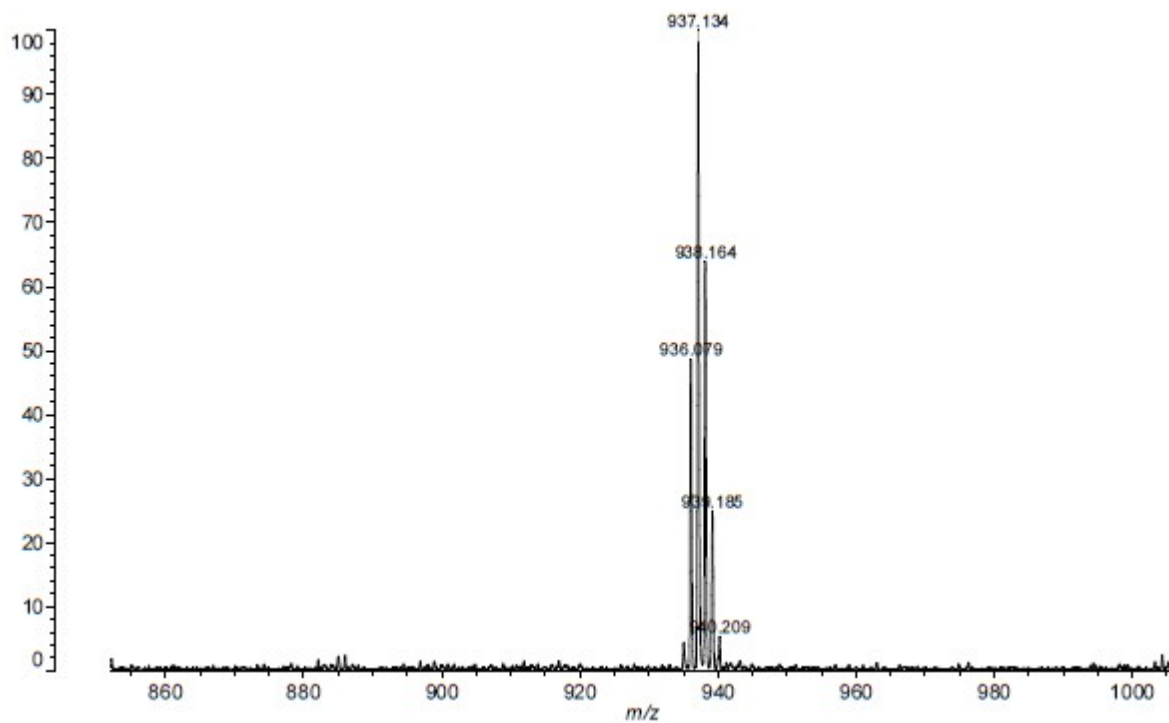


Fig. S14 MALDI-TOF Mass spectrum of compound **3FPzDP**

Cartesian coordinates of the dyes:

1CFPzDP:

N	1.20673600	0.84589900	0.06921000
N	-1.21124900	-0.82618800	-0.01249500
C	0.00031800	1.32360100	0.09752200
C	-1.25060500	0.54628500	0.05936700
C	-0.00484700	-1.30389700	-0.04074500
C	1.24609200	-0.52656700	-0.00333000
N	-0.31949400	2.65022800	0.16720200
O	-2.29175417	3.91801817	0.23302226

C	-1.72096300	2.79801200	0.17510700
C	-2.31686800	1.41236600	0.10408000
C	0.62129200	3.75490500	0.22491900
H	0.04864106	4.65795327	0.26332115
H	1.23639890	3.67929091	1.09717241
H	1.24761065	3.75944149	-0.64260873
N	0.31485300	-2.63049800	-0.11105400
O	2.28694710	-3.89822701	-0.18097741
C	1.71626800	-2.77823500	-0.12170000
C	2.31230100	-1.39255900	-0.05127500
C	-0.62603300	-3.73511100	-0.16862500
H	-1.25051580	-3.74118903	0.70021577
H	-0.05344128	-4.63807884	-0.20970773
H	-1.24297777	-3.65797649	-1.03944612
C	3.74120000	-1.11697800	-0.04152800
C	4.22021900	0.20961000	0.02007500
C	5.57832700	0.47746900	0.02773200
C	6.52844300	-0.55590700	-0.02079700
C	6.05282800	-1.87403700	-0.08055900
C	4.69528400	-2.15441600	-0.09288100
H	3.51764948	1.01514534	0.06915529
H	5.90666907	1.49323360	0.10062759
H	6.74839064	-2.68444049	-0.14642844
H	4.36332180	-3.16999512	-0.15032784
C	-4.70013200	2.17461900	0.12157400
C	-3.74572500	1.13671900	0.08909300
C	-4.22424200	-0.19054800	0.03921600
C	-5.58222900	-0.45852900	0.02366200
C	-6.53261200	0.57533700	0.05171500
C	-6.05759900	1.89408500	0.10082900
H	-4.36856826	3.19076403	0.17071418
H	-6.75372537	2.70511427	0.15122347
H	-5.91023933	-1.47502729	-0.03990252
H	-3.52132668	-0.99652397	0.00439080
C	7.98036200	-0.26454100	-0.00992600
C	8.49878000	0.85239500	-0.68371400
C	9.86014800	1.12588400	-0.67703700
C	10.73664200	0.28615500	0.00984800
C	10.24077600	-0.82677700	0.68782500
C	8.87835400	-1.09621100	0.67674600
H	7.83952854	1.49199693	-1.23252807
H	10.23895462	1.98022880	-1.19809411
H	10.90990230	-1.46259884	1.22902790
H	8.50708509	-1.93725677	1.22419592
C	12.21528600	0.55006200	-0.02986300
F	12.49372964	1.86857761	-0.11039695
F	12.79820480	-0.03252597	-1.09911364
F	12.84754926	0.07236233	1.06308997
C	-7.98404300	0.28235000	0.02798100
C	-8.50952000	-0.82394900	0.71408700
C	-9.87014900	-1.09982900	0.69417300
C	-10.73932300	-0.27159700	-0.01594500

C	-10.23672900	0.83201800	-0.70379600
C	-8.87495100	1.10451800	-0.67862700
H	-10.25638554	-1.93711701	1.23700826
H	-7.85701726	-1.45017259	1.28591232
H	-8.49907357	1.94258453	-1.22749915
H	-10.90191535	1.46769802	-1.24999929
C	-12.20354000	-0.60242600	-0.08148200
F	-12.64498152	-1.17564781	1.05827505
F	-12.47639036	-1.47024466	-1.07895052
F	-12.96384039	0.49124877	-0.30129743

2CFPzDP:

N	1.20358300	-0.79081800	0.29975700
N	-1.20359000	0.79081400	-0.29973900
C	-1.25206800	-0.48965000	0.19806500
C	-0.00601500	-1.22694300	0.47654700
C	0.00600900	1.22693900	-0.47652900
C	1.25206100	0.48964500	-0.19804900
N	-0.33520500	-2.46153000	0.95863000
O	-2.31757646	-3.62660900	1.42439119
C	-1.73803300	-2.58687400	1.01616200
C	-2.32373900	-1.28876900	0.51489700
C	0.59698400	-3.50168800	1.35752700
H	0.01708838	-4.33658286	1.69155041
H	1.20919543	-3.79418096	0.53015463
H	1.22602273	-3.15700866	2.15150838
N	0.33519900	2.46152700	-0.95861000
O	2.31757010	3.62660338	-1.42437575
C	2.32373300	1.28876400	-0.51488500
C	1.73802600	2.58686700	-1.01615100
C	-0.59699000	3.50168100	-1.35751500
H	-0.01709496	4.33657994	-1.69152923
H	-1.20921190	3.79416989	-0.53014894
H	-1.22601890	3.15700168	-2.15150418
C	3.75111000	1.01990000	-0.41658100
C	4.21955700	-0.22235000	0.06272000
C	5.57560100	-0.48373100	0.15793100
C	6.53150200	0.47486800	-0.21448500
C	6.06783300	1.71006400	-0.68875300
C	4.71211800	1.98137700	-0.79149100
H	3.51113122	-0.96598170	0.36279468
H	5.89544162	-1.42640460	0.55031914
H	6.76851354	2.45380717	-1.00623192
H	4.38767313	2.92925443	-1.16720885
C	-4.71212700	-1.98140500	0.79143200
C	-3.75111600	-1.01990400	0.41659200

C	-4.21955900	0.22237300	-0.06264400
C	-5.57560200	0.48375500	-0.15785900
C	-6.53150600	-0.47486700	0.21448700
C	-6.06784100	-1.71009000	0.68869000
H	-6.76852454	-2.45385394	1.00611366
H	-4.38768520	-2.92930198	1.16710318
H	-5.89543946	1.42645073	-0.55019656
H	-3.51113011	0.96602168	-0.36266923
C	7.98136500	0.18878300	-0.11039600
C	8.48490100	-1.08735600	-0.39205000
C	9.84779800	-1.35431100	-0.29298100
C	10.74106800	-0.35762700	0.08643600
C	10.24857900	0.91459300	0.36830800
C	8.88805500	1.18724500	0.27273300
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H	11.78831360	-0.56453419	0.15968945
H	8.53166506	2.16770172	0.51062128
C	10.36089700	-2.72074100	-0.66589100
C	11.19705900	1.98269200	0.84727500
F	10.54415022	-2.83477117	-1.99852575
F	9.49768102	-3.69484532	-0.30745139
F	11.54585652	-2.99477985	-0.07999541
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F	12.41852686	1.85707636	0.28626076
F	11.37321583	1.92430651	2.18445857
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C	-10.74107100	0.35763200	-0.08644500
C	-10.24857300	-0.91457000	-0.36838800
C	-8.88804900	-1.18722100	-0.27281100
H	-8.53165065	-2.16766154	-0.51075333
H	-7.81997129	1.86597114	0.70273955
H	-11.78831672	0.56453822	-0.15969944
C	-10.36091100	2.72070500	0.66602600
C	-11.19703400	-1.98264900	-0.84743500
F	-9.49773688	3.69483331	0.30755078
F	-11.54591486	2.99473914	0.08021788
F	-10.54407132	2.83470120	1.99867643
F	-11.37306323	-1.92427643	-2.18463594
F	-10.74764854	-3.22386678	-0.56471406
F	-12.41855158	-1.85700237	-0.28653596

3FPzDP

N	1.18907300	-0.85766400	0.11606100
N	-1.18907300	0.85766400	-0.11606100

C	0.02826800	1.30233600	-0.18600500
C	1.26051900	0.50156600	-0.07791800
C	-0.02826800	-1.30233600	0.18600500
C	-1.26051900	-0.50156600	0.07791800
N	0.37955600	2.60923400	-0.37395200
O	2.38179661	3.81795533	-0.55298280
C	1.78415000	2.72196800	-0.39423500
C	2.34676300	1.33449500	-0.19922600
C	-0.53434300	3.72668100	-0.53285000
H	0.05994984	4.60612077	-0.66813383
H	-1.14893261	3.83575716	0.33621962
H	-1.16212489	3.57885583	-1.38662843
N	-0.37955600	-2.60923400	0.37395200
O	-2.38179661	-3.81795533	0.55298280
C	-1.78415000	-2.72196800	0.39423500
C	-2.34676300	-1.33449500	0.19922600
C	0.53434300	-3.72668100	0.53285000
H	-0.05994984	-4.60612077	0.66813383
H	1.16212489	-3.57885583	1.38662843
H	1.14893261	-3.83575716	-0.33621962
C	3.76878400	1.02737400	-0.16129600
C	4.74664600	2.03890500	-0.25792100
C	6.09728300	1.72979300	-0.21515600
C	6.54134300	0.40675800	-0.07870600
C	5.56821700	-0.60142100	0.01391600
C	4.21673500	-0.30422500	-0.02368800
H	4.43869279	3.05684910	-0.37562667
H	6.81128655	2.52020498	-0.31688023
H	5.87207318	-1.61888762	0.14557122
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C	8.88902900	0.94235900	0.61143800
C	10.23613500	0.62964600	0.64922400
C	10.72751800	-0.52928700	0.05916000
C	9.82829500	-1.37713400	-0.57740400
C	8.47664500	-1.08664600	-0.62902900
H	7.83287326	-1.75881914	-1.15689378
H	8.56031703	1.83205066	1.10671287
F	11.10639004	1.44779504	1.27834109
F	12.04419785	-0.82404734	0.10355059
F	10.30543566	-2.49658577	-1.16192476
C	-7.98575200	-0.08366600	0.03194400

C	-8.88902900	-0.94235900	-0.61143800
C	-10.23613500	-0.62964600	-0.64922400
C	-10.72751800	0.52928700	-0.05916000
C	-9.82829500	1.37713400	0.57740400
C	-8.47664500	1.08664600	0.62902900
H	-7.83287326	1.75881914	1.15689378
H	-8.56031703	-1.83205066	-1.10671287
F	-11.10639004	-1.44779504	-1.27834109
F	-12.04419785	0.82404734	-0.10355059
F	-10.30543566	2.49658577	1.16192476