Electronic Supplementary information

Synthesis and characterisation of push-pull flavin-based dyes with efficient second harmonic generation (SHG) properties.

Nabeel Mohammed,[a‡] Alan A. Wiles,[a‡] Michael Belsley,[b‡] Sara S. M. Fernandes,[c] Michele Cariello,[a] Vincent M. Rotello,[d] Manuela M. Raposo,[c*] and Graeme Cooke[a*]

a. *Glasgow Centre for Physical Organic Chemistry (GCPOC), WestCHEM, School of Chemistry, University of Glasgow, Glasgow, G12 8QQ, U.K.*

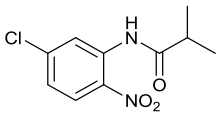
b. *Center of Physics, University of Minho, Campus de Gualtar, 4710-057 Braga Portugal.*

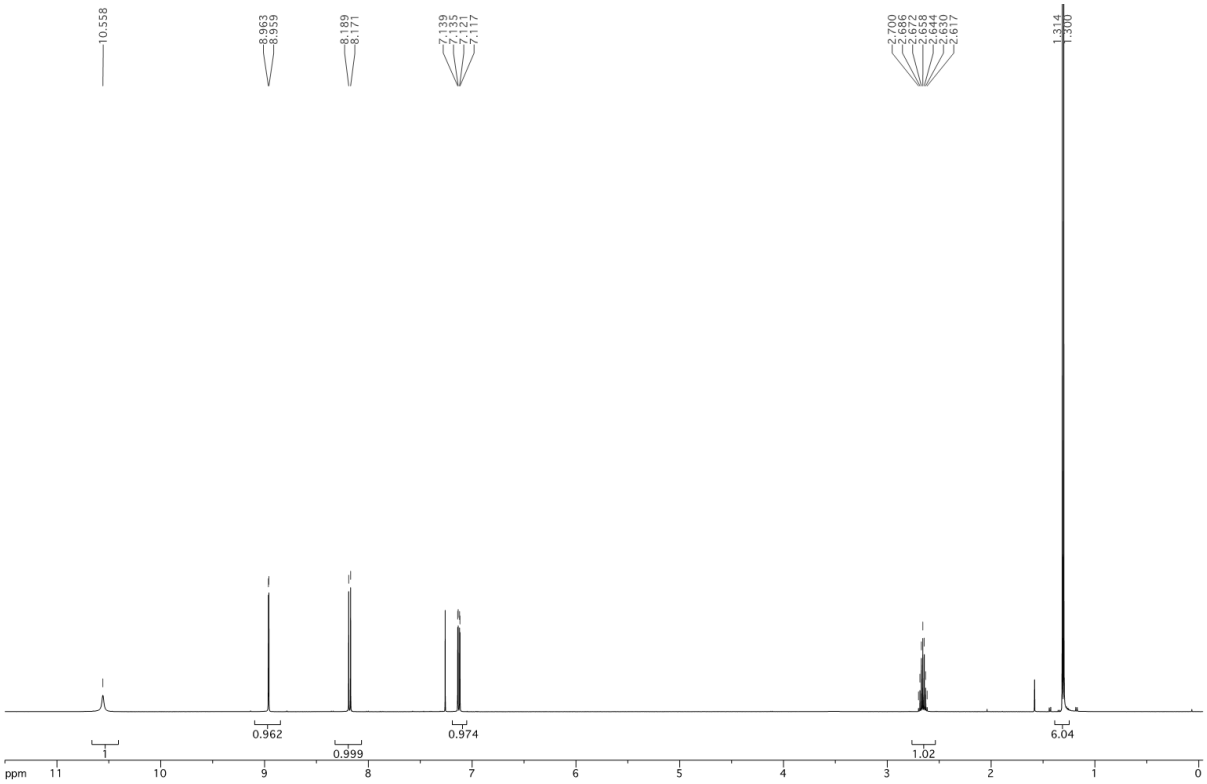
c. *Center of Chemistry, University of Minho, Campus de Gualtar, 4710-057 Braga Portugal.*

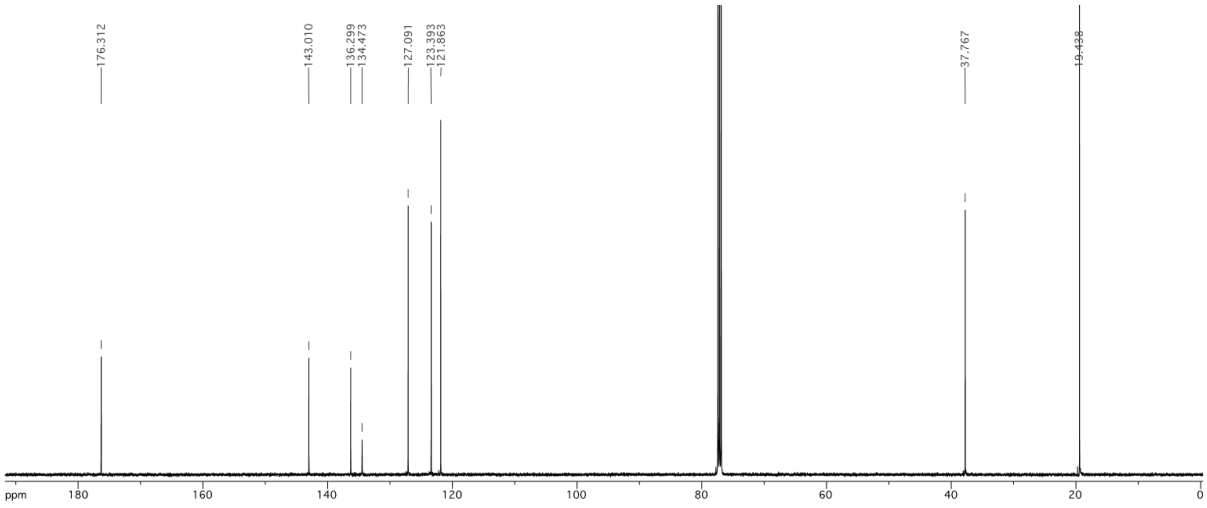
d. Department of Chemistry, University of Massachusetts, Amherst, MA 01003, USA

1. ^{1}H and ^{13}C NMR data

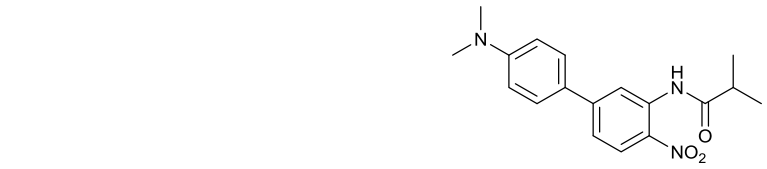
Compound **2**

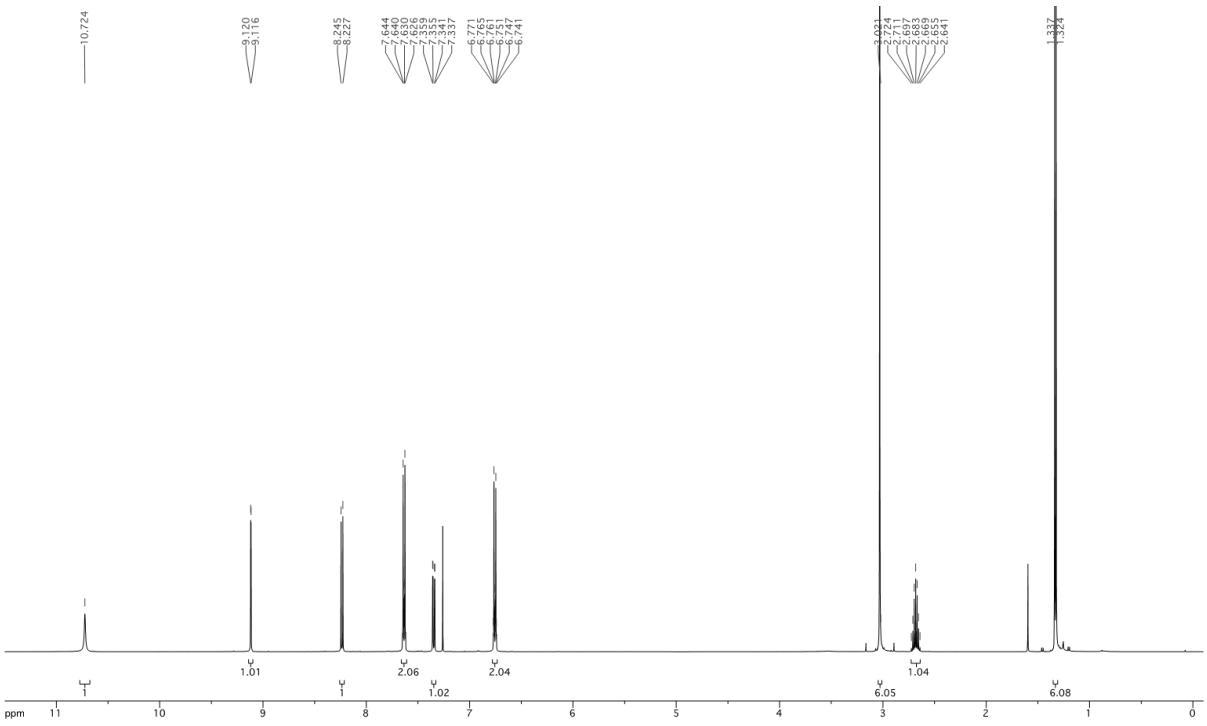






Compound **3a**

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9.116
8.245
8.227
7.644
7.640
7.630
7.626
7.359
7.355
7.341
7.337
6.771
6.765
6.761
6.751
6.747
6.741
3.021
2.724
2.711
2.697
2.683
2.669
2.655
2.641
1.337
1.324
1.01
2.06
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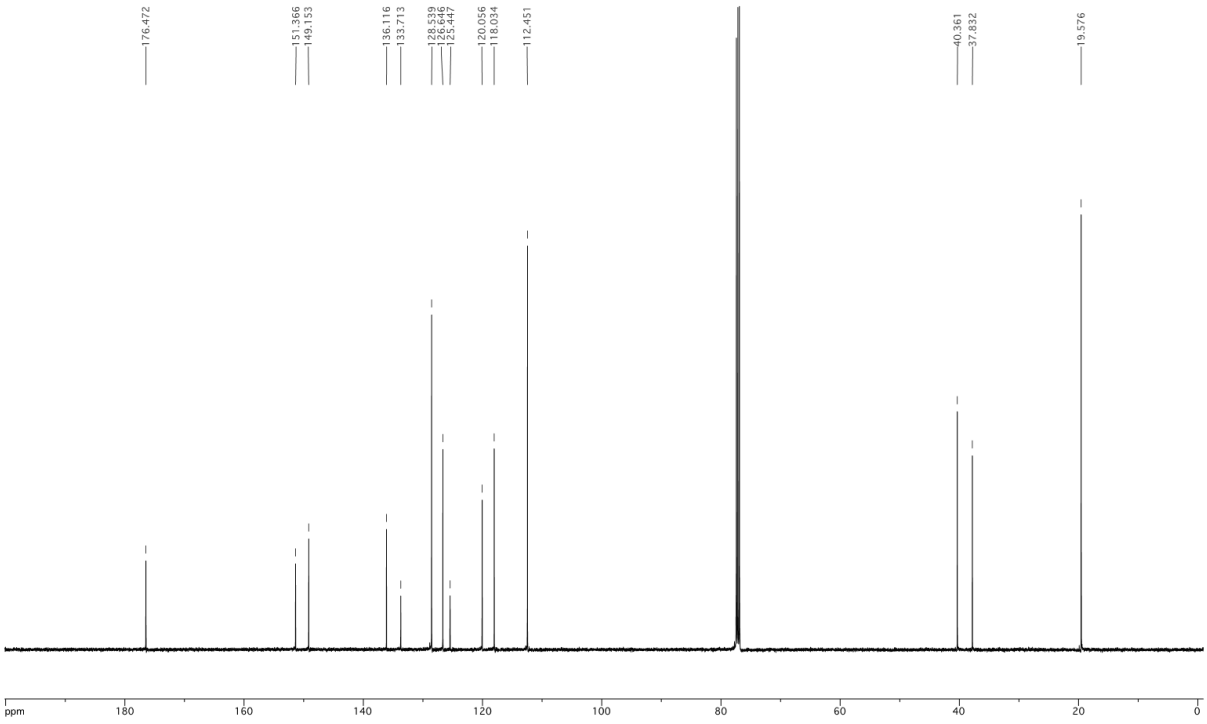
1.04
1
1
1.02
6.05
6.08
ppm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149.153
136.116
133.713
128.539
128.446
125.447
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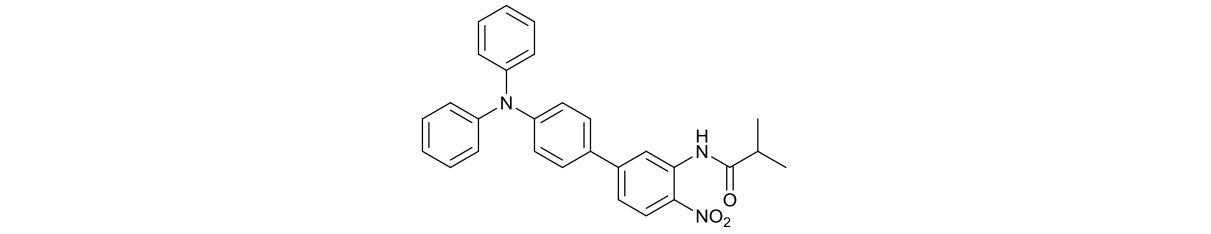
118.034
112.451
40.361
37.832
19.576
ppm

Compound **3b**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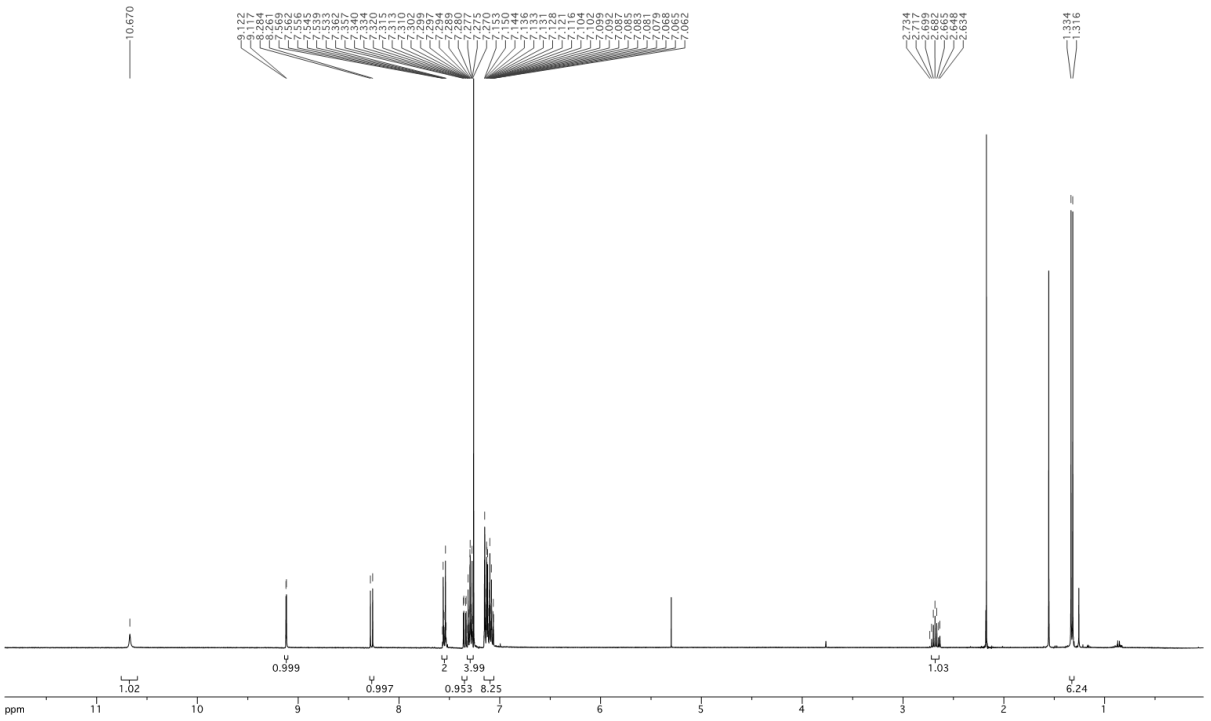
H
N
O
NO2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7.562
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7.357
7.340
7.334
7.320
7.315
7.313
7.310
7.302
7.299
7.297
7.294
7.289
7.280
7.277
7.275
7.270
7.153
7.144
7.135
7.131
7.128
7.116
7.104
7.102
7.099
7.092
7.087
7.085
7.083
7.081
7.079
7.068
7.065
7.062
2.734
2.717
2.699
2.682
2.665
2.648
2.634
1.334
1.316
0.999
2
3.99
1.03
1.02
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6.24
ppm
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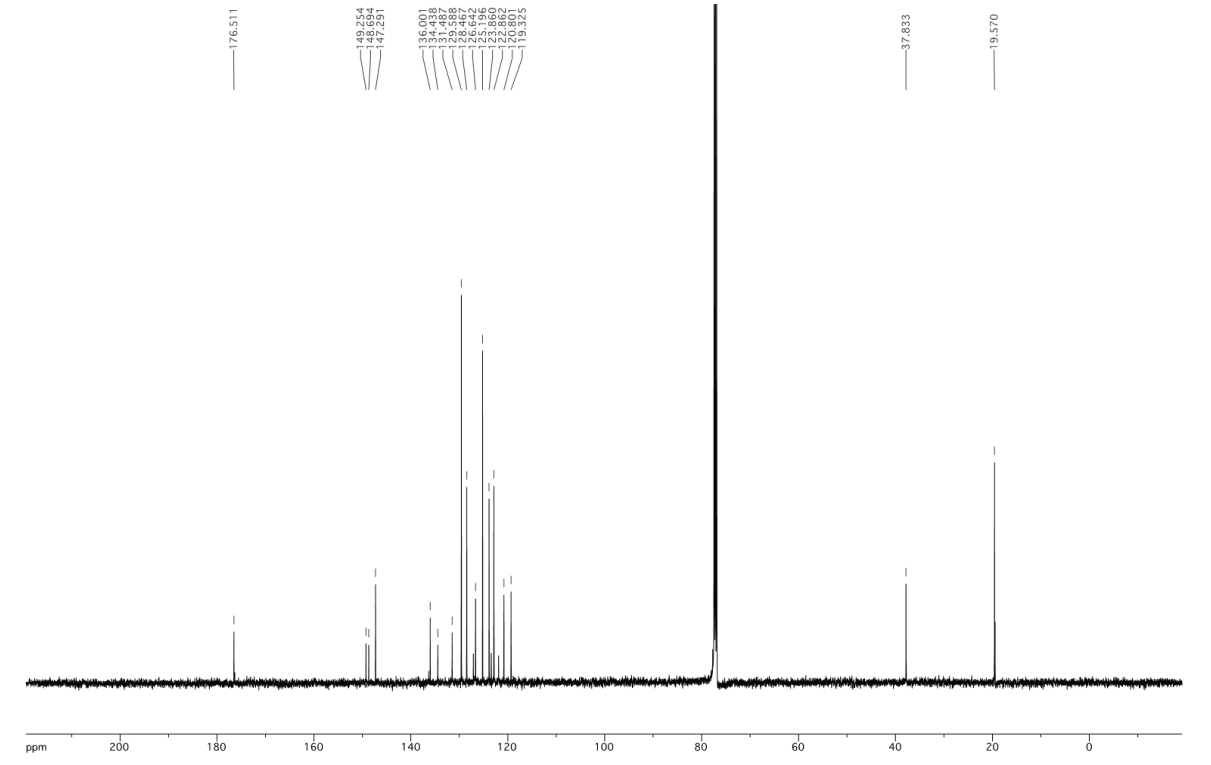
10
9
8
7
6
5
4
3
2
1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147.291
136.001
134.438
131.487
131.188
128.467
126.642
126.596
123.866
122.862
120.801
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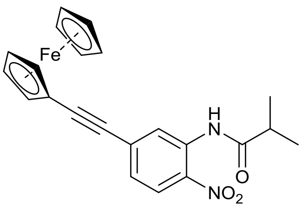
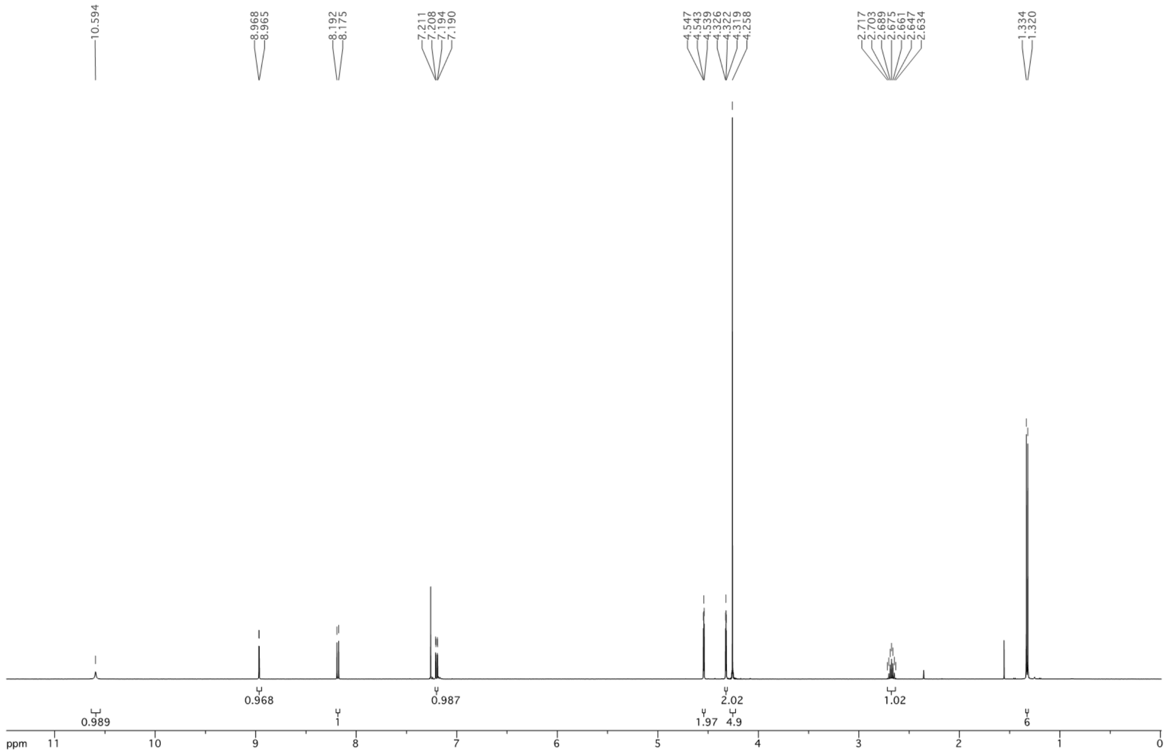
19.570
ppm
200
180
160
140
120
100
80
60
40
20
0

Compound **3c**



Fe
H
N
O
NO2



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8.192
8.175
7.211
7.208
7.194
7.190
4.547
4.543
4.539
4.326
4.322
4.319
4.258
2.717
2.703
2.689
2.675
2.661
2.647
2.634
1.334
1.320
0.968
0.987
2.02
1.02
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1
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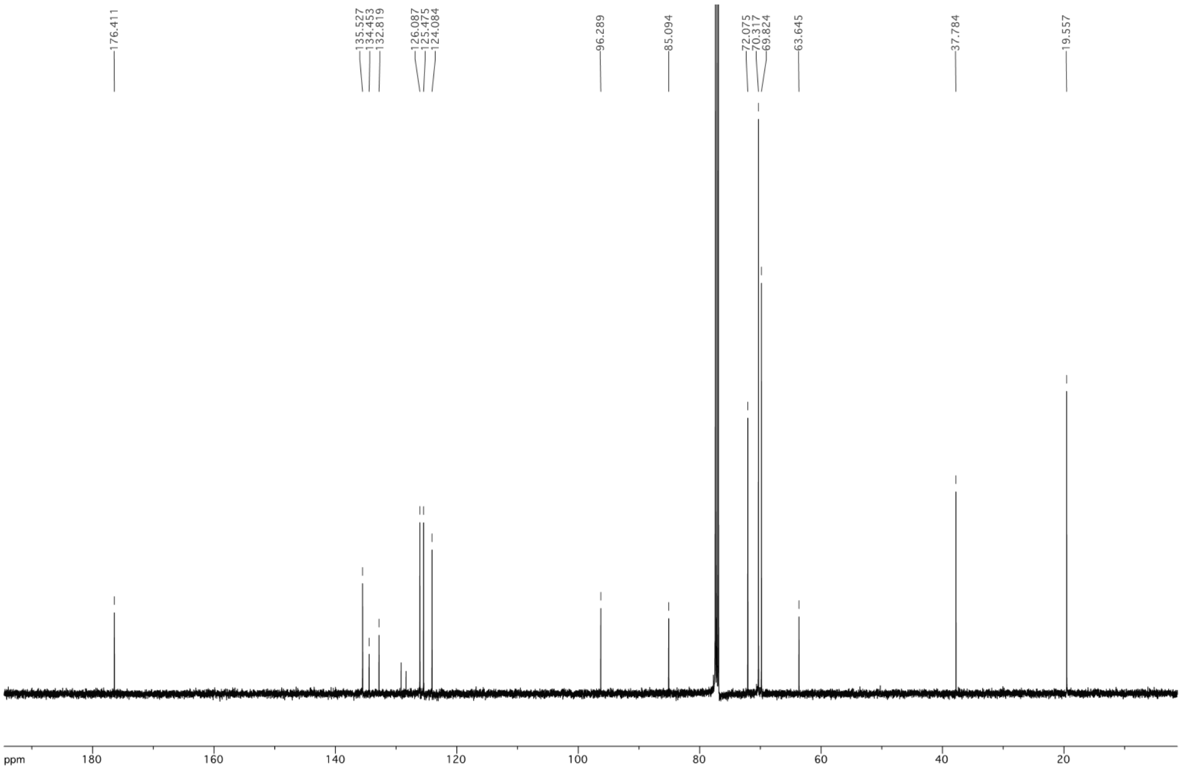
4.9
6
ppm
11
10
9
8
7
6
5
4
3
2
1
0



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126.087
125.475
124.084
96.289
85.094
72.075
70.317
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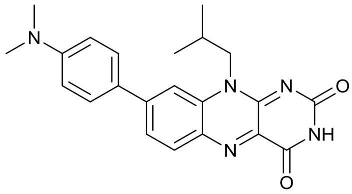
37.784
19.557
ppm
180
160
140
120
100
80
60
40
20

FLA-A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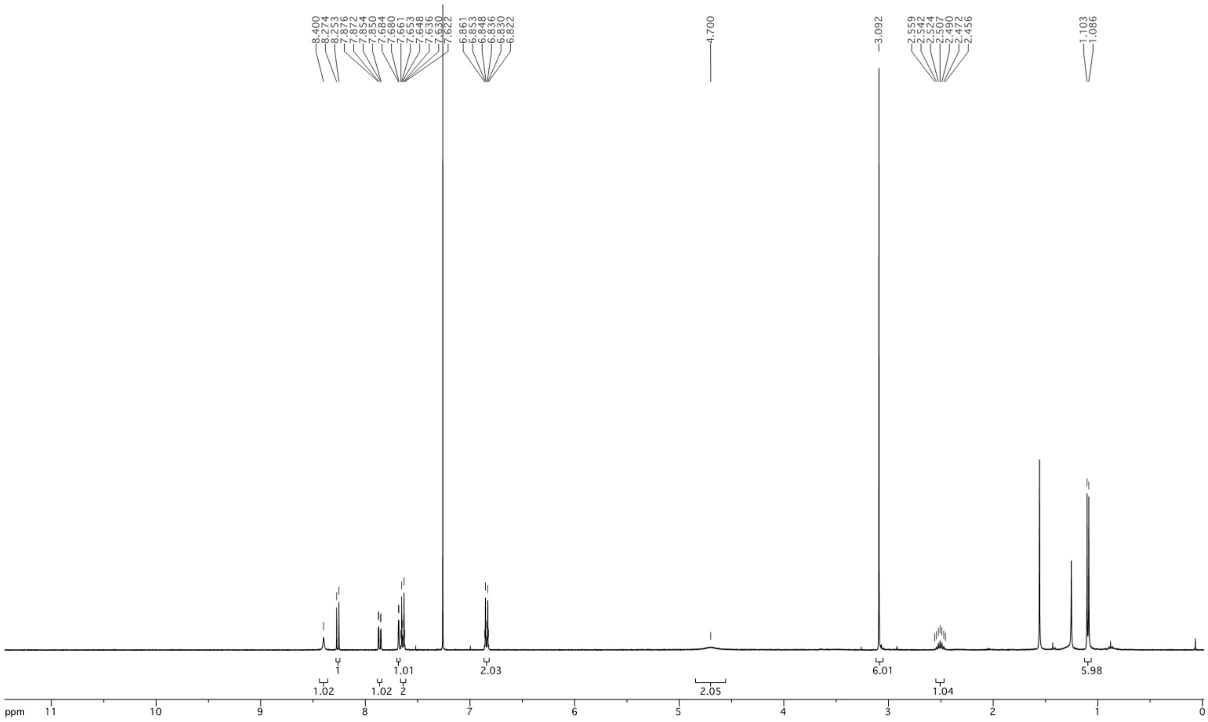
N
O
NH
N
O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7.630
7.622
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6.853
6.848
6.836
6.830
6.822
4.700
3.092
2.559
2.542
2.524
2.507
2.490
2.472
2.456
1.103
1.086
1.02
1
1.02
1.01
2
2.03
2.05
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1.04
5.98
ppm
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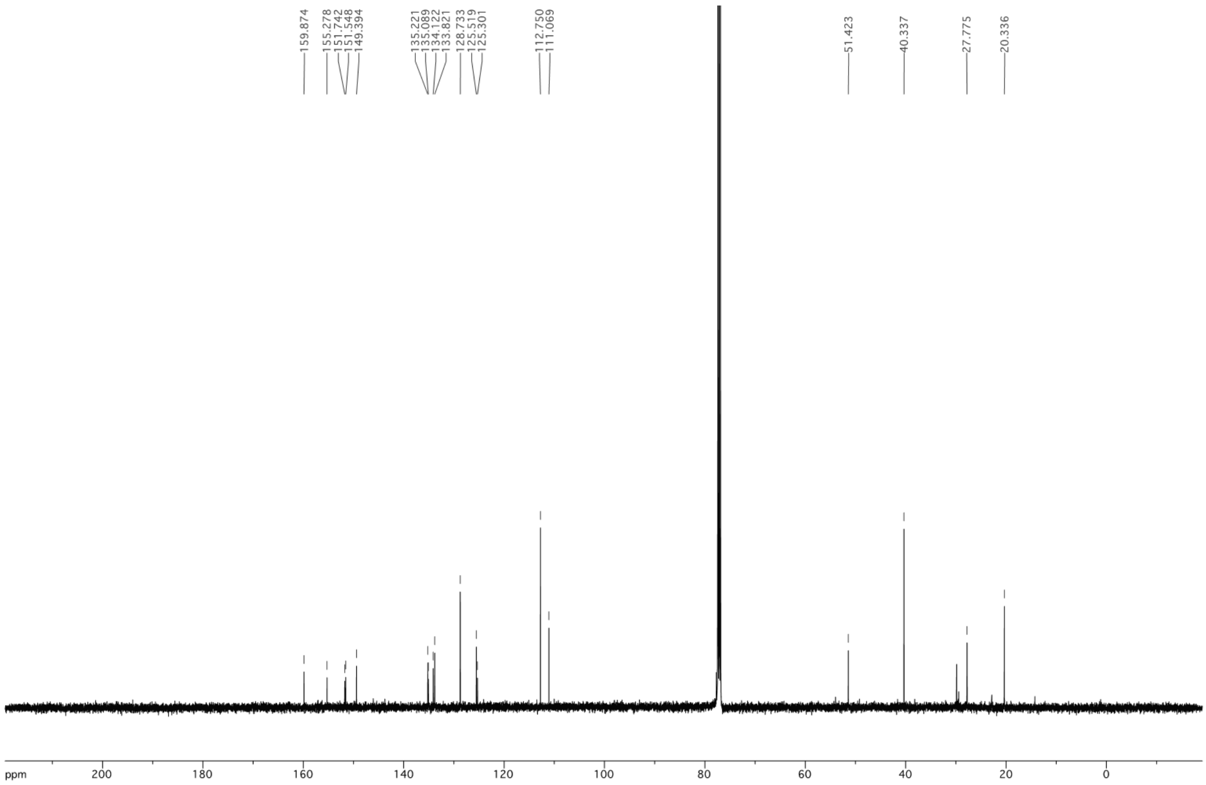
10
9
8
7
6
5
4
3
2
1
0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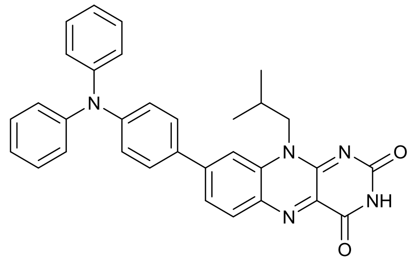
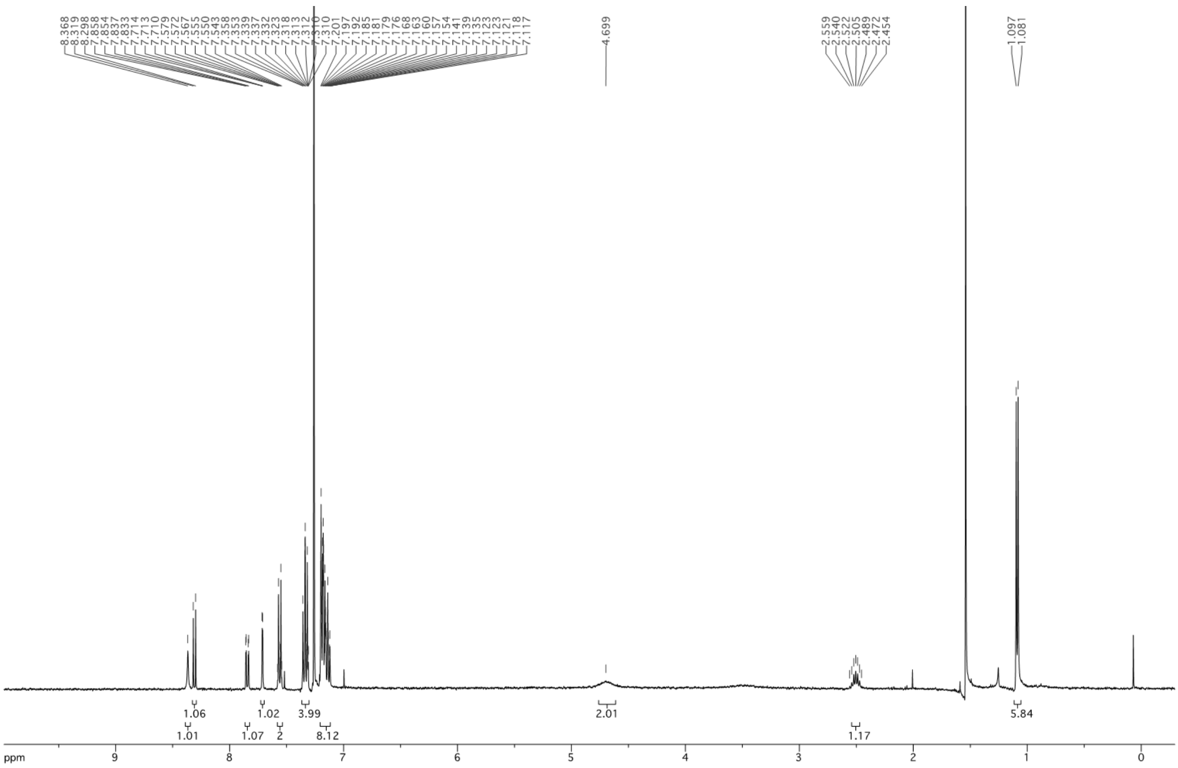
151.548
149.394
135.221
135.089
134.122
133.821
128.733
125.519
125.301
112.750
111.069
51.423
40.337
27.775
20.336
ppm
200
180
160
140
120
100
80
60
40
20
0

FLA-B


N
N
N
N
O
NH
O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1.081
1.06
1.01
1.02
1.07
2
3.99
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2.01
1.17
5.84
ppm
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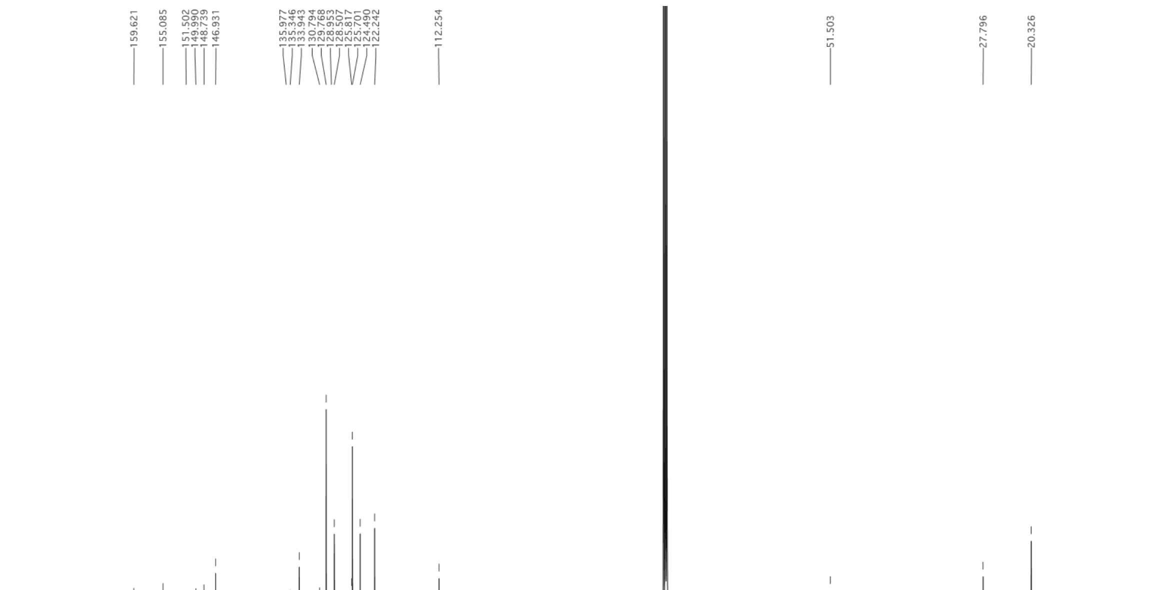
8
7
6
5
4
3
2
1
0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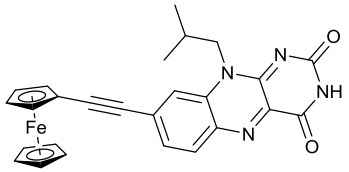
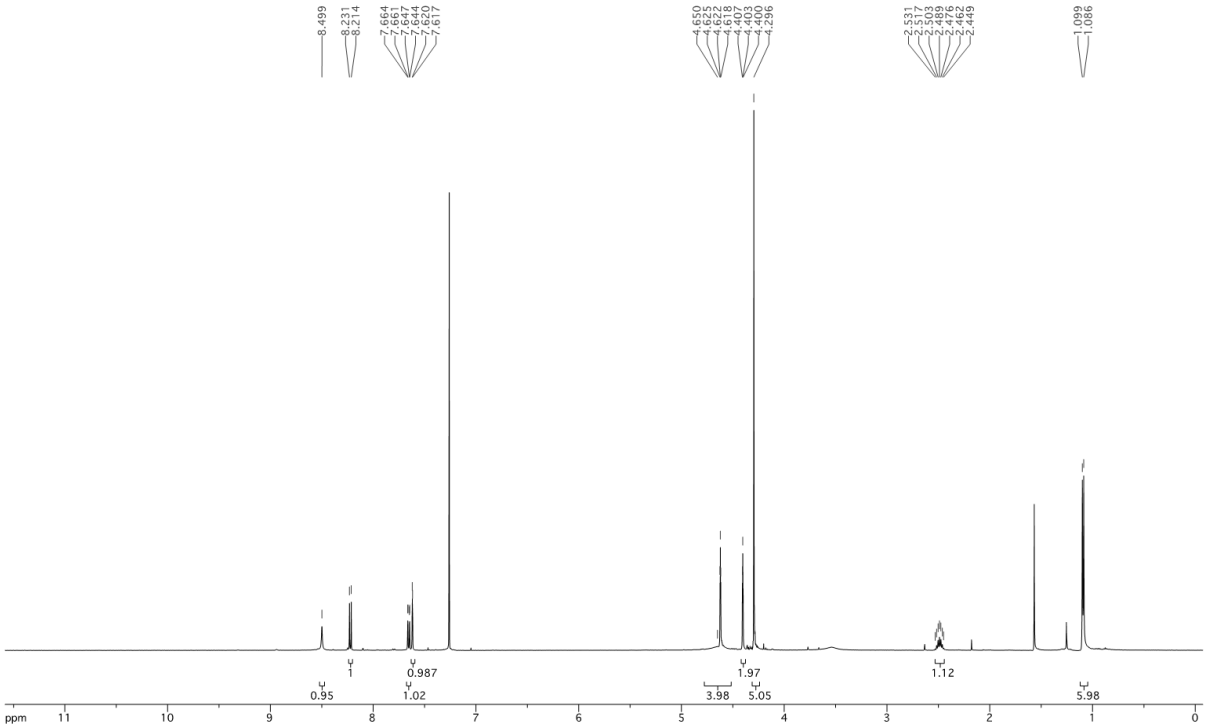
146.931
135.977
112.254
51.503
27.796
20.326
ppm
160
140
120
100
80
60
40
20
0

FLA-C


O
N
NH
O
N
N
Fe


8.499
8.231
8.214
7.664
7.661
7.647
7.644
7.620
7.617
4.650
4.625
4.622
4.618
4.407
4.403
4.400
4.296
2.531
2.517
2.503
2.489
2.476
2.462
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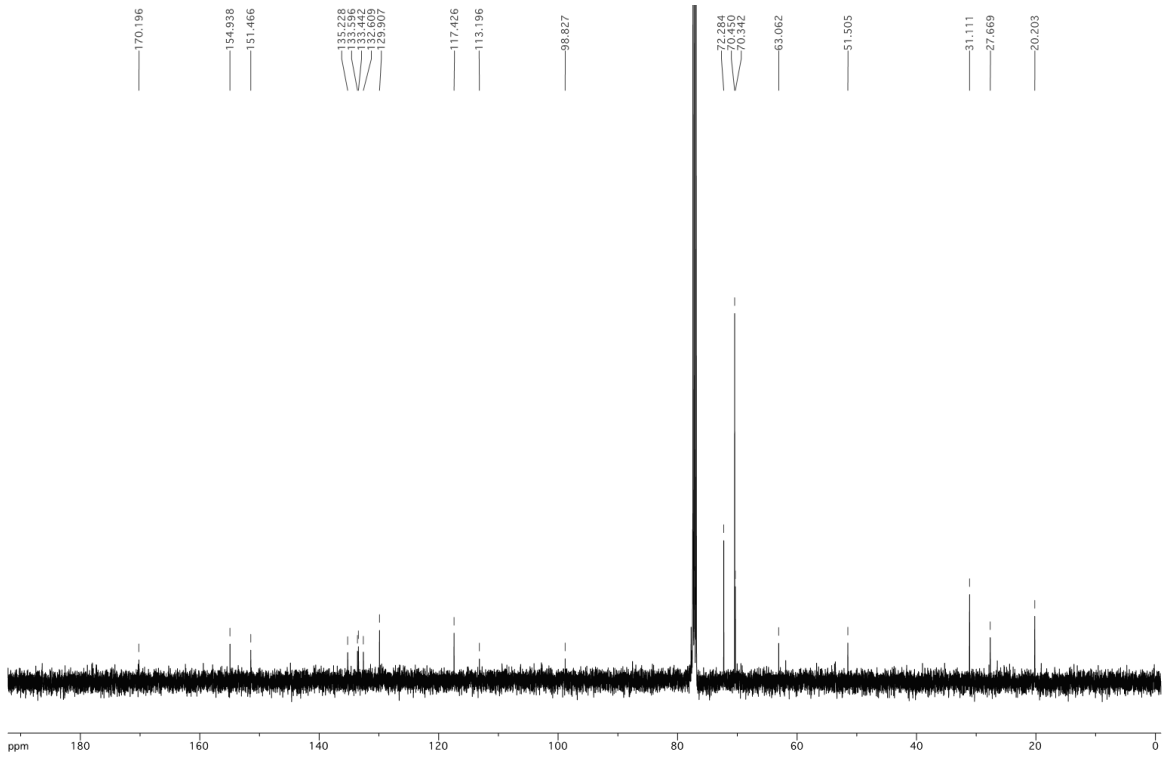
1.099
1.086
1
0.987
1.97
1.12
0.95
1.02
3.98
5.05
5.98
ppm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135.228
133.566
133.442
132.609
129.907
117.426
113.196
98.827
72.284
70.450
70.403
70.342
63.062
51.505
31.111
27.669
20.203
ppm

2. TGA and DSC data

FLA-A

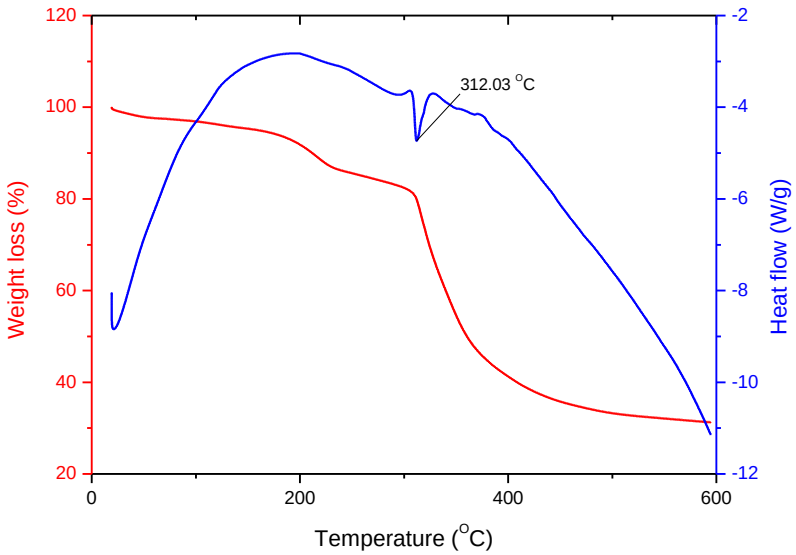

Figure S1 – Thermal analysis data for compound **FLA-A** recorded under a nitrogen atmosphere, measured at a heating rate of 10 °C min^{-1}.

FLA-B

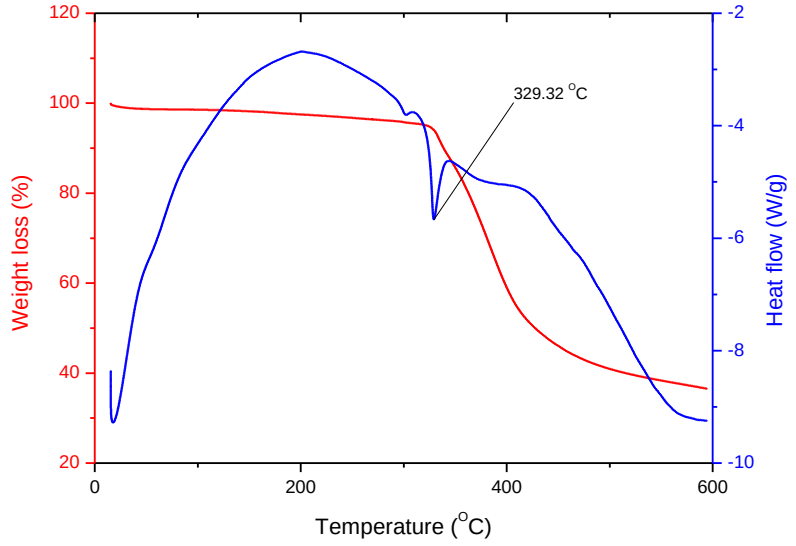

Figure S2 – Thermal analysis data for compound **Fla-B** recorded under a nitrogen atmosphere, measured at a heating rate of 10 °C min^{-1}.

FLA-C

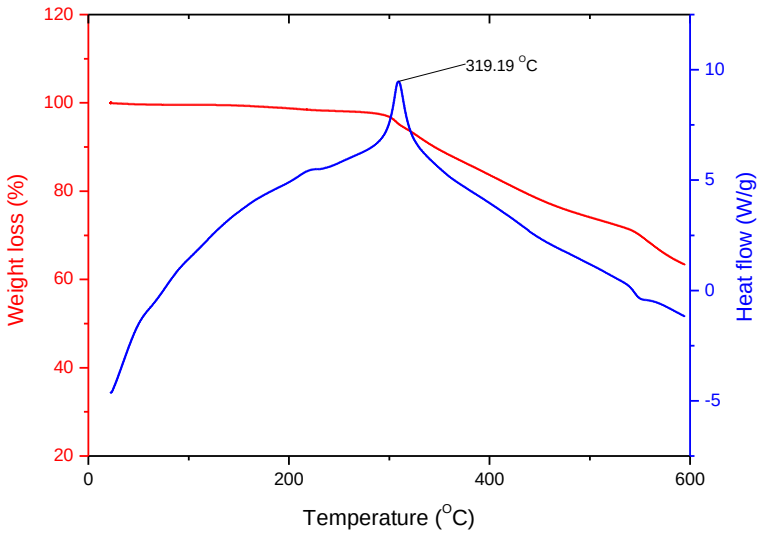

Figure S3 – Thermal analysis data for compound **Fla-C** recorded under a nitrogen atmosphere, measured at a heating rate of 10 °C min^{-1}.

3. Voltammetry data

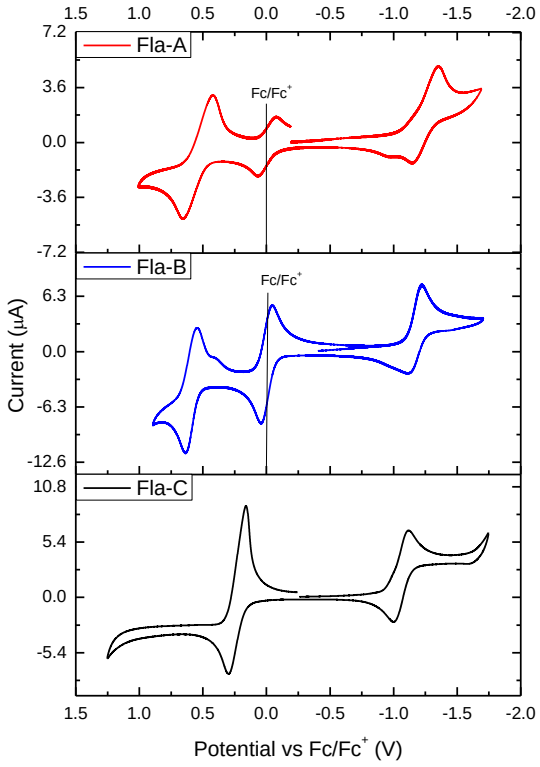

Figure S4 – Cyclic voltammetry plots of **Fla A-C**, in $CHCl_3$ (C = 10^{-3}M). All the experiments were performed using a Pt working electrode, a Pt counter electrode and Ag wire as reference. $TBAPF_6$ (0.1M) was used as supporting electrolyte and the collected data were referenced to the redox potential of Fc/Fc^+ couple.

	E_{OX} (V)	E_{RED} (V)	IP (eV)	EA (eV)	$E_{G,FUND}$ (eV)
FLA-A	0.52	-1.25	-5.32	-3.55	1.77
FLA-B	0.69	-0.92	-5.49	-3.88	1.61
FLA-C	0.19	-1.04	-4.99	-3.76	1.23

Table S1 – Summary of electrochemical properties of **FLA-A – C**. Ionisation potentials (IPs) and electron affinities (EAs) were calculated by applying the empirical equations: IP = –(E_{OX} + 4.80) and EA = –(E_{RED} + 4.80).[S1,S2]

4. Theoretical calculations

Solvent dependence computation was performed at DFT level using the hybrid B3LYP level by employing the 6-31+G** basis set using polarizable continuum model (keyword: scrf=*solvent*). Frequency calculations were performed to insure the absence of negative frequencies.

Flavin A	**μ**	**HOMO**	**LUMO**
1,4-Dioxane	17.0152	-5.6428	-3.1410
Toluene	17.2402	-5.6333	-3.1467
Dichloromethane	20.2001	-5.5245	-3.2142
Dimethylsulfoxide	21.4030	-5.4888	-3.2392
Flavin B	**μ**	**HOMO**	**LUMO**
1,4-Dioxane	14.3034	-5.5658	-3.2420
Toluene	14.4754	-5.5596	-3.2463
Dichloromethane	16.6393	-5.4913	-3.2937
Dimethylsulfoxide	17.4862	-5.4676	-3.3086
Flavin C	**μ**	**HOMO**	**LUMO**
1,4-Dioxane	13.6595	-5.8856	-3.3554
Toluene	13.8190	-5.8782	-3.3592
Dichloromethane	15.7836	-5.7818	-3.3954
Dimethylsulfoxide	16.5851	-5.7593	-3.4061

Table S2 – Summary of calculated solvent dependant properties of **FLA-A – C**.

Gaussian 09 keywords freq=raman, cphf=rdfreq and polar were used to compute the hyperpolarisability. Here the hyperpolarisability β_{tot} is given as the function of the tensor and $\beta_{||}$ is the hyperpolarisability parallel to the ground state CT direction. $\beta_{||}$ is given in the output file whereas β_{tot} is obtained from the different parts of the tensor.

$$\beta_{tot} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$

$$\beta_{tot} = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]^{1/2}$$

Fla-A

#p freq=raman cphf=rdfreq rb3lyp/6-31+g(d,p) scrf=(solvent=1,4-dioxane)
nosymm polar

Title Card Required

0 1

C	0.34186171	-2.77753182	0.27184066
C	1.34547543	-1.79595576	0.09351121
C	0.96029304	-0.43563676	-0.10774755
C	-0.40466016	-0.10934526	-0.13294995
C	-1.39353121	-1.09059509	0.02864838

C	-0.99097286	-2.43916695	0.24154746
H	0.66679497	-3.80307117	0.41242053
H	-0.71424368	0.91908924	-0.24868201
H	-1.74227847	-3.21383308	0.34437730
N	1.96614157	0.51367750	-0.26570923
N	2.64816200	-2.18408358	0.10970711
N	4.21574517	1.05585094	-0.48066142
N	5.87266020	-0.65879481	-0.28688728
H	6.86226325	-0.88177527	-0.30387263
C	3.29677668	0.13658275	-0.28286569
C	3.56936063	-1.27832126	-0.07421452
C	5.54153034	0.69747729	-0.50206120
C	4.99993160	-1.70443568	-0.07124025
O	6.45175977	1.49763939	-0.69611874
O	5.38094891	-2.85490623	0.10005514
C	1.62682974	1.94234839	-0.46578630
H	2.50711358	2.40354399	-0.91153678
H	0.81439367	1.98384344	-1.19607932
C	-3.78798311	-1.44240162	0.71810118
C	-2.82228168	-0.73308162	-0.02360055
C	-3.29443554	0.32924690	-0.82017450
C	-4.63865224	0.67033293	-0.87587494
C	-5.60606292	-0.03418293	-0.11220799
C	-5.13511765	-1.10995294	0.68496022
H	-3.47969688	-2.25803699	1.36504728
H	-2.60116596	0.88261257	-1.44685558
H	-4.93895620	1.47996066	-1.52905580
H	-5.82356366	-1.68517187	1.29101868
N	-6.93805016	0.31074610	-0.14129010
C	-7.40218031	1.35898767	-1.04033884
H	-8.46904398	1.51672788	-0.88289419
H	-6.89113521	2.30790479	-0.84018329
H	-7.24559597	1.09923046	-2.09729534
C	-7.92014561	-0.51070791	0.55459834
H	-8.90858114	-0.07007833	0.42552834
H	-7.94918078	-1.53886473	0.16655090
H	-7.71196406	-0.55528418	1.63027054
C	1.23689033	2.69420131	0.82511649
H	0.37156000	2.19079470	1.27552854
C	2.36553870	2.71147053	1.86573740
H	3.25521768	3.21702577	1.47680166
H	2.03615694	3.23968738	2.76687090
H	2.65934587	1.70046318	2.16539570
C	0.80881236	4.12032272	0.44317292
H	-0.02456223	4.11807427	-0.26898624
H	0.48840398	4.67480861	1.33092884
H	1.64077409	4.67078105	-0.01193454

1064nm

Fla-B

#p freq=raman cphf=rdfreq rb3lyp/6-31+g(d,p) scrf=(solvent=1,4-dioxane)
polar

Title Card Required

0 1

C	2.45963771	-2.88526050	0.17346983
C	3.43251270	-1.86775461	0.03955260
C	3.01035122	-0.51083335	-0.09149787
C	1.63548547	-0.22243983	-0.10008167
C	0.67891074	-1.23808182	0.02507857

C	1.11693442	-2.58304541	0.16768498
H	2.81468053	-3.90434365	0.28484545
H	1.29539479	0.79372718	-0.23889571
H	0.38767521	-3.37439320	0.29895985
N	3.98730915	0.47084713	-0.23011924
N	4.74726991	-2.22132004	0.02396292
N	6.21816828	1.08027216	-0.45705950
N	7.92284389	-0.59631407	-0.36466847
H	8.91732897	-0.79223395	-0.41040513
C	5.32668115	0.13067988	-0.28452639
C	5.63934653	-1.28511328	-0.13829991
C	7.55298344	0.75874620	-0.51419613
C	7.08173226	-1.67309772	-0.18252462
O	8.43781257	1.59090967	-0.68614927
O	7.49339332	-2.82003395	-0.07466107
C	3.60763980	1.89742571	-0.36609027
H	4.47129196	2.40051936	-0.79868625
H	2.78819565	1.94872394	-1.08770345
C	-1.70245683	-1.81659535	-0.53674500
C	-0.76308708	-0.91853611	0.00777635
C	-1.25952471	0.29284959	0.52841593
C	-2.61629653	0.59202012	0.51403273
C	-3.54651610	-0.30931635	-0.04176230
C	-3.05951363	-1.52065286	-0.57169758
H	-1.36472869	-2.74620617	-0.98421960
H	-0.58032363	0.99768597	0.99836189
H	-2.96461469	1.52187185	0.94982725
H	-3.74953083	-2.22444312	-1.02360214
N	-4.92200232	-0.00949136	-0.06430645
C	-4.81973162	2.17196592	-1.19383497
C	-5.26619979	3.48726490	-1.32994616
C	-6.27569170	3.98317946	-0.49846619
C	-6.83173925	3.15023775	0.47742377
C	-6.37956131	1.83842556	0.62981652
C	-5.36971448	1.33846239	-0.20694965
H	-4.04741137	1.78563798	-1.85127380
H	-4.83310700	4.12063020	-2.09884714
H	-6.62601894	5.00452914	-0.61166165
H	-7.61419935	3.52391922	1.13154534
H	-6.80768629	1.19705987	1.39345341
C	-5.77233486	-2.02816651	1.05185603
C	-5.89396472	-1.04872181	0.05336792
C	-6.99134207	-1.09129418	-0.82065687
C	-7.95061262	-2.09751879	-0.69399723
C	-7.82222639	-3.07957500	0.29308344
C	-6.72713286	-3.04009746	1.16216674
H	-4.93228864	-1.99261266	1.73817549
H	-7.08981820	-0.33544697	-1.59321696
H	-8.79476665	-2.11823570	-1.37719697
H	-8.56698161	-3.86412367	0.38552291
H	-6.62089751	-3.79119654	1.93962537
C	3.21024164	2.58094468	0.95964183
H	2.37185567	2.02582735	1.40074648
C	4.35407438	2.59889899	1.98351335
H	5.21670135	3.15503325	1.60257449
H	4.02010583	3.07622084	2.91088449
H	4.69208769	1.58884939	2.23603152
C	2.72278630	4.00411358	0.64358710
H	1.87899115	3.99988815	-0.05612947
H	2.39706312	4.50967500	1.55826486
H	3.52620538	4.60379162	0.19966815

1064nm

Fla-C

#p freq=raman cphf=rdfreq rb3lyp/6-31+g(d,p) scrf=(solvent=1,4-dioxane)
polar

Title Card Required

0 1

C	0.38952884	-2.56401702	0.04425735
C	1.71450198	-2.82900598	0.30083676
C	2.70182498	-1.82864938	0.13580897
C	2.31843716	-0.52224715	-0.29529034
C	0.96406304	-0.25970943	-0.55422164
C	-0.00076540	-1.26628551	-0.39338821
C	4.64069545	0.12102101	-0.23155790
C	4.91409671	-1.24163875	0.20881770
C	6.34179086	-1.60046370	0.46973932
C	6.88001450	0.74351400	-0.21025420
H	-0.36568277	-3.33189761	0.16686339
H	2.04640262	-3.80787373	0.63008522
H	0.63482806	0.71553810	-0.88287807
C	-1.36632273	-0.99390823	-0.66883678
C	-2.54341229	-0.78221887	-0.90797687
C	-3.90351446	-0.54841467	-1.22419777
C	-4.96695090	-1.52402430	-1.18958266
C	-4.48134929	0.70144892	-1.65744963
C	-6.16394899	-0.88475801	-1.61638240
H	-4.85604114	-2.55661380	-0.88892845
C	-5.86579095	0.48373199	-1.90332010
H	-3.94250728	1.63199174	-1.77014579
H	-7.13883345	-1.34856154	-1.68159210
H	-6.57603657	1.23414290	-2.22318802
Fe	-5.40272445	0.05083554	0.07329324
C	-6.84390048	-0.07832334	1.55361761
C	-5.63447630	-0.70334056	1.98884097
C	-6.55479010	1.29076613	1.26573640
H	-7.80345870	-0.56340962	1.43468761
C	-4.59938399	0.28057921	1.96976313
H	-5.51736345	-1.74408614	2.25940323
C	-5.16646091	1.51268408	1.52238177
H	-7.25734195	2.02322103	0.89118823
H	-3.55879429	0.11168254	2.21346630
H	-4.63373457	2.44308946	1.37880839
N	3.31259540	0.43865274	-0.44966683
N	4.00048574	-2.15331035	0.38662754
N	5.55556486	1.04259286	-0.42575087
N	7.20976066	-0.55564922	0.23583744
H	8.19684589	-0.73494266	0.38776684
C	2.96914081	1.81104499	-0.89396446
H	3.89235808	2.24555504	-1.27466937
H	2.26896813	1.71588917	-1.72800951
O	7.78712633	1.55037218	-0.38327743
O	6.71981360	-2.69990545	0.84949358
C	2.38082803	2.71129807	0.21346467
H	1.48029468	2.22779836	0.61435830
C	1.95919662	4.04633662	-0.42104301
H	1.23171878	3.90191789	-1.22807643
H	1.50201413	4.69890057	0.32952421
H	2.82565835	4.57354954	-0.83758759
C	3.35597927	2.93307038	1.37841754
H	3.64114280	1.99134742	1.85810127
H	4.27223628	3.42640223	1.03833385
H	2.88960748	3.56395605	2.14250684

1064nm

5. References

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