Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Aggregation induced emission and mechanochromism in pyrenoimidazoles

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Table of Contents

I. Crystallographic data

II. Photophysical properties

III. Mechanochromism

IV. Copies of ^{1}H NMR, ^{13}C NMR and HRMS spectra of the new compounds

V. DFT calculations

Crystallographic data

A single crystal X-ray structural study of **3a** was performed on a CCD Agilent Technologies (Oxford Diffraction) SUPER NOVA diffractometer. Data were collected at 150(2) K using graphite-monochromated Mo Kα radiation (λ_α = 0.71073 Å). The strategy for the data collection was evaluated by using the CrysAlisPro CCD software. The data were collected by the standard 'phi-omega scan techniques, and were scaled and reduced using CrysAlisPro RED software. The structures were solved by direct methods using SHELXS-97, and refined by full matrix least-squares with SHELXL-97, refining on F^2. The positions of all the atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropically. The remaining hydrogen atoms were placed in geometrically constrained positions, and refined with isotropic temperature factors, generally 1.2U_{eq} of their parent atoms. The crystal, and refinement data are summarized in Table 1. The CCDC number 1409647 contains the supplementary crystallographic data for **3a**. These data can be obtained free of charge via www.ccdc.cam.ac.uk (or from the Cambridge Crystallographic Data Centre, 12 union Road, Cambridge CB21 EZ, UK; Fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Table S1. Crystal data and structure refinement for 3a.

Parameter	**3a**
Identification code	rm172
Empirical formula	C_{11} $H_{7.20}$ $N_{0.40}$
Formula weight	144.97
Temperature	150(2) K
Wavelength(A)	1.5418
Crystal system, space group	Triclinic, P -1
***a*/ (Å)**	9.4209(6)
***b*/ (Å)**	12.0079(11)

***c*/ (Å)**	21.6114(18)
***α*/(°)**	75.523(8)
***β*/ (°)**	85.392(6)
***γ*/ (°)**	73.484(7)
Volume	2269.4(3) $Å^3$
Z, Calculated density (mg m^{-3})	10, 1.061
Absorption coefficient /(mm^{-1})	0.468
F(000)	760
Crystal size	0.230 x 0.190 x 0.130 mm
***θ* range for data collection/(°)**	3.953 to 49.989
Reflections collected / unique	9573 / 4648 [R(int) = 0.0408]
Completeness to theta	θ = 49.989; 99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.85897
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4648 / 0 / 516
Goodness-of-fit on F^2	1.153
Final R indices [I>2sigma(I)]	R1 = 0.1041, wR2 = 0.3147
R indices (all data)	R1 = 0.1268, wR2 = 0.3349
Largest diff. peak and hole (e$Å^{-3}$)	0.348 and -0.253

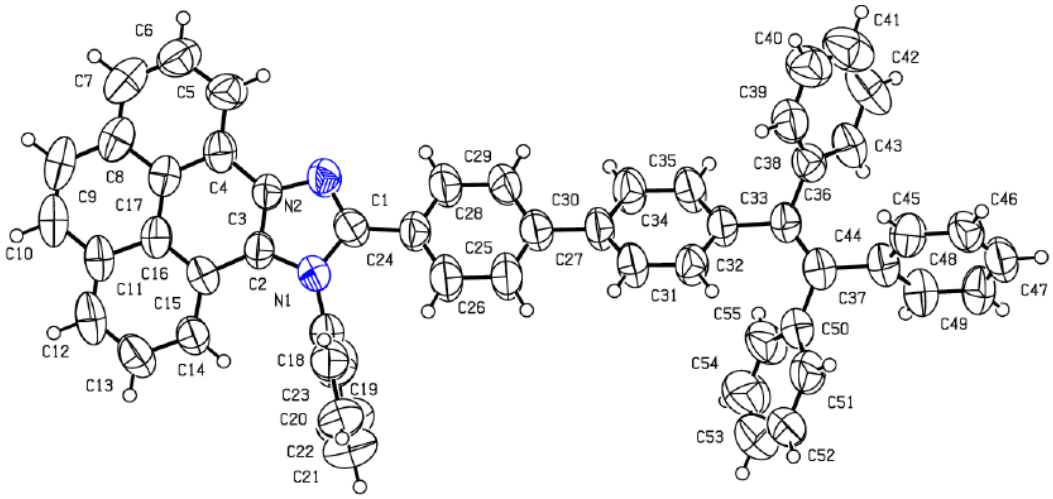


Fig. S1 Crystal structure of **3a.**

Photophysical properties

Table S2. Photophysical, and thermal properties of the 3a and 3b.

Compounds	λ_{max}[nm] (ε[Lmol^{-1}cm^{-1}]) [a]	$\lambda_{em.}$(nm)	Φ_f [b]	Optical band gap (eV)	Theoretical band gap (eV) [c]	T_d (°C)
3a	245 (71366) 292 (40354) 344 (49592) 386 (26260)	438	0.0017	3.06	3.48	404
3b	245 (75325) 293 (42756) 355 (46715) 387 (32859)	387, 409, 432	0.0043	2.95	3.01	412

[a] Measured in tetrahydrofuran. [b] The fluorescence quantum yields using 9, 10-diphenylanthracence as a standard in ethanol solution were performed. [c] Theoretical values at B3LYP/6-31G(d) level.

Table S3. Photophysical properties of 3a and 3b in different solvents.

Compounds	Solvents	$\lambda_{abs.}$(nm)	$\lambda_{em.}$(nm)
3a	Toluene	349, 387	442
	Chloroform	352, 385	436
	Dichloromethane	347, 385	436
	Tetrahydrofuran	345, 386	436
3b	Toluene	355, 388	388, 410, 432
	Chloroform	353, 386	388, 410, 432
	Dichloromethane	353, 386	388, 410, 432
	Tetrahydrofuran	354, 387	387, 410, 432

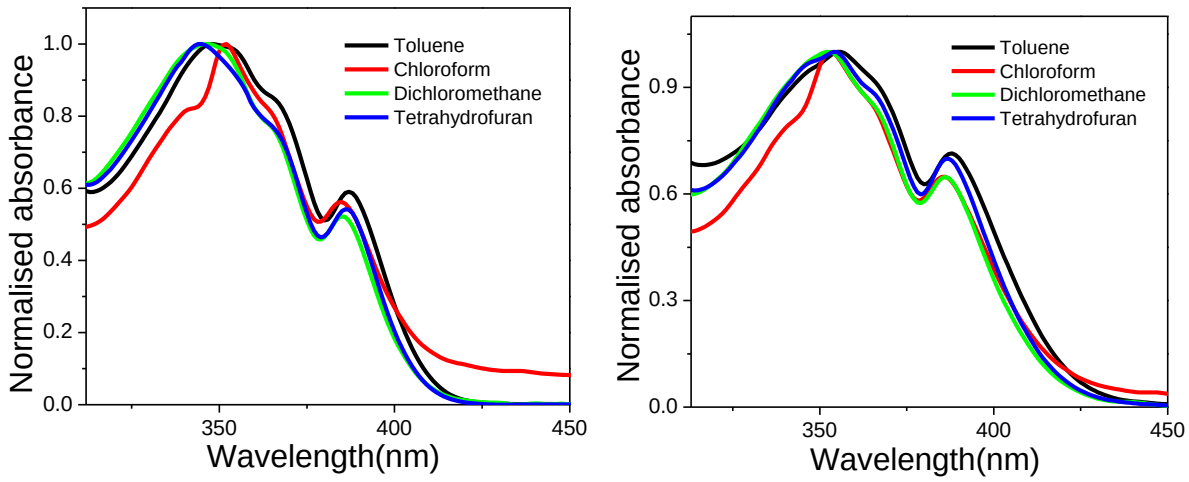


Fig. S2 Absorption spectra of **3a** (left) and **3b** (right) in different solvents with varying polarities

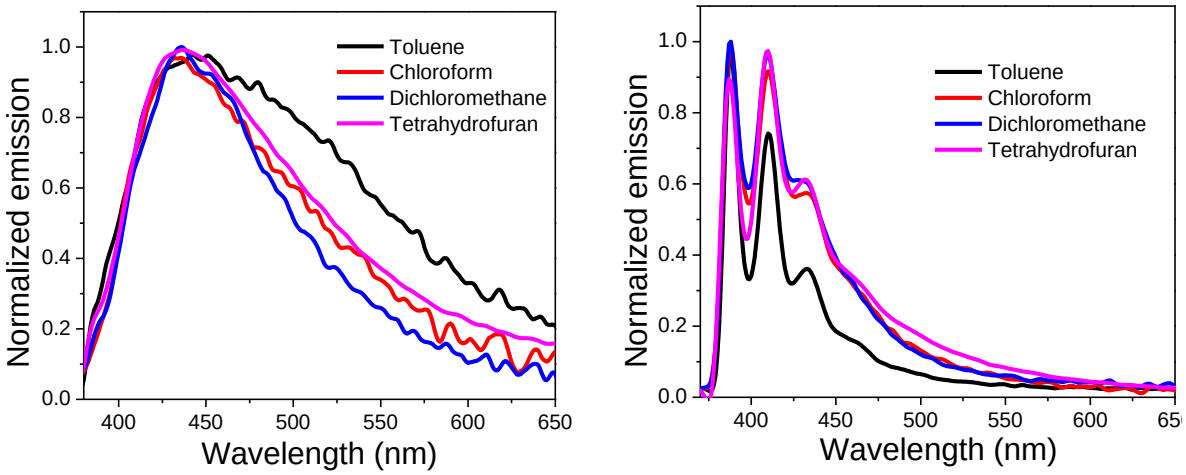


Fig. S3 Photoluminescence spectra of **3a** (left) and **3b** (right) in different solvents with varying polarities (excitation wavelength or λ_{ex} = 340 nm).

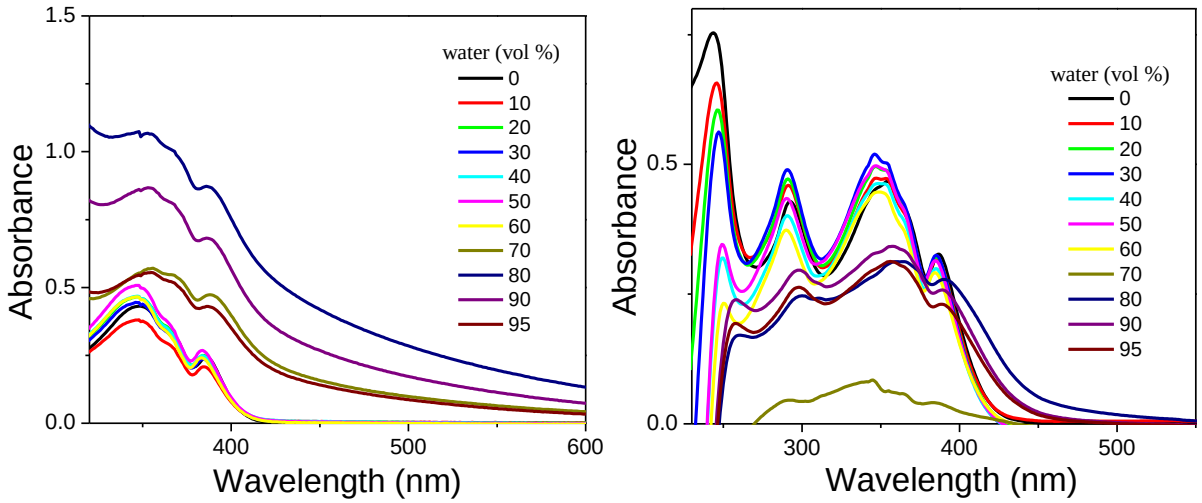


Fig. S4 UV-vis absorption spectra of **3a** (left) and **3b** (right) in THF–water mixtures with different water fractions; Luminogen concentration: 10 μM.

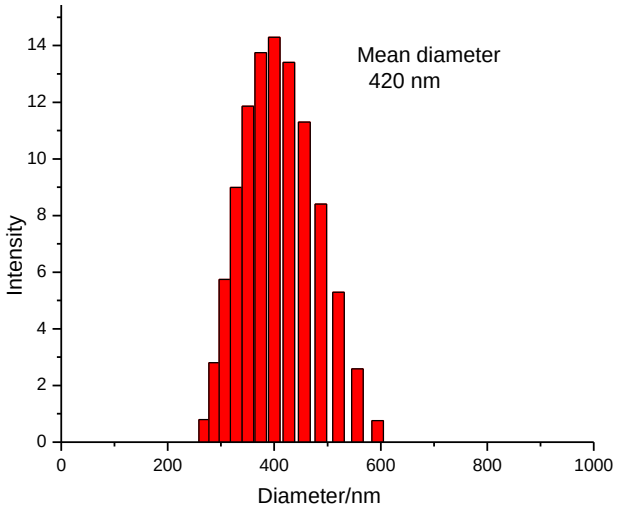


Fig. S5 The particle size distributions of **3a** in THF–water mixture at 90% (f_w).

Mechanochromism

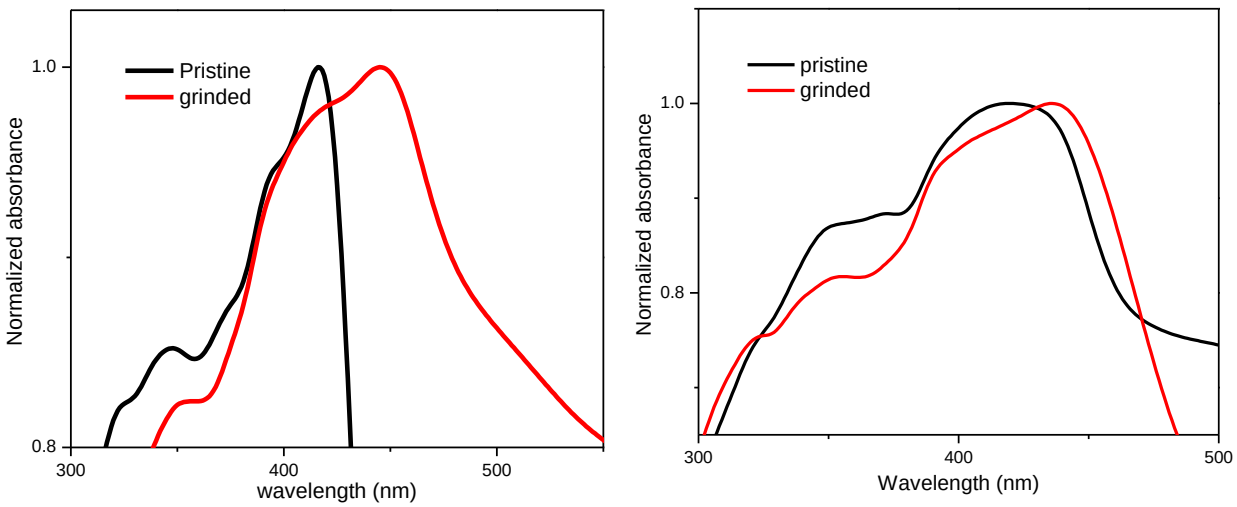
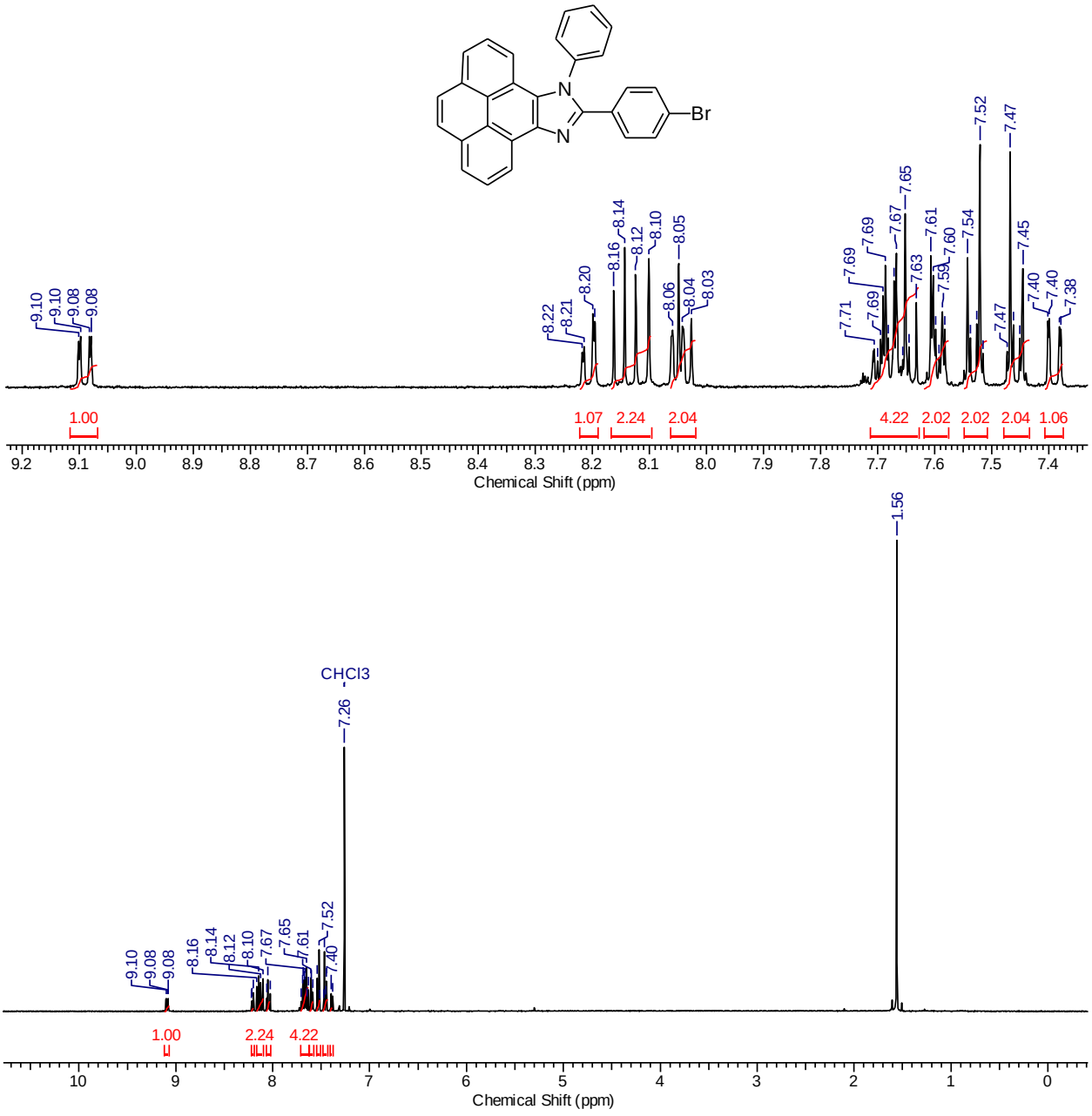


Fig. S6 Solid state absorption spectra of **3a** (left) and **3b** (right) in crystalline and its grinded form.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9.08
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8.10
8.06
8.05
8.04
8.03
7.71
7.69
7.69
7.69
7.67
7.65
7.63
7.61
7.60
7.59
7.54
7.52
7.47
7.47
7.45
7.40
7.40
7.38
1.00
1.07
2.24
2.04
4.22
2.02
2.02
2.04
1.06
9.2
9.1
9.0
8.9
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
Chemical Shift (ppm)
1.56
CHCl3
7.26
9.10
9.08
9.08
8.16
8.14
8.12
8.10
7.67
7.65
7.61
7.52
7.40
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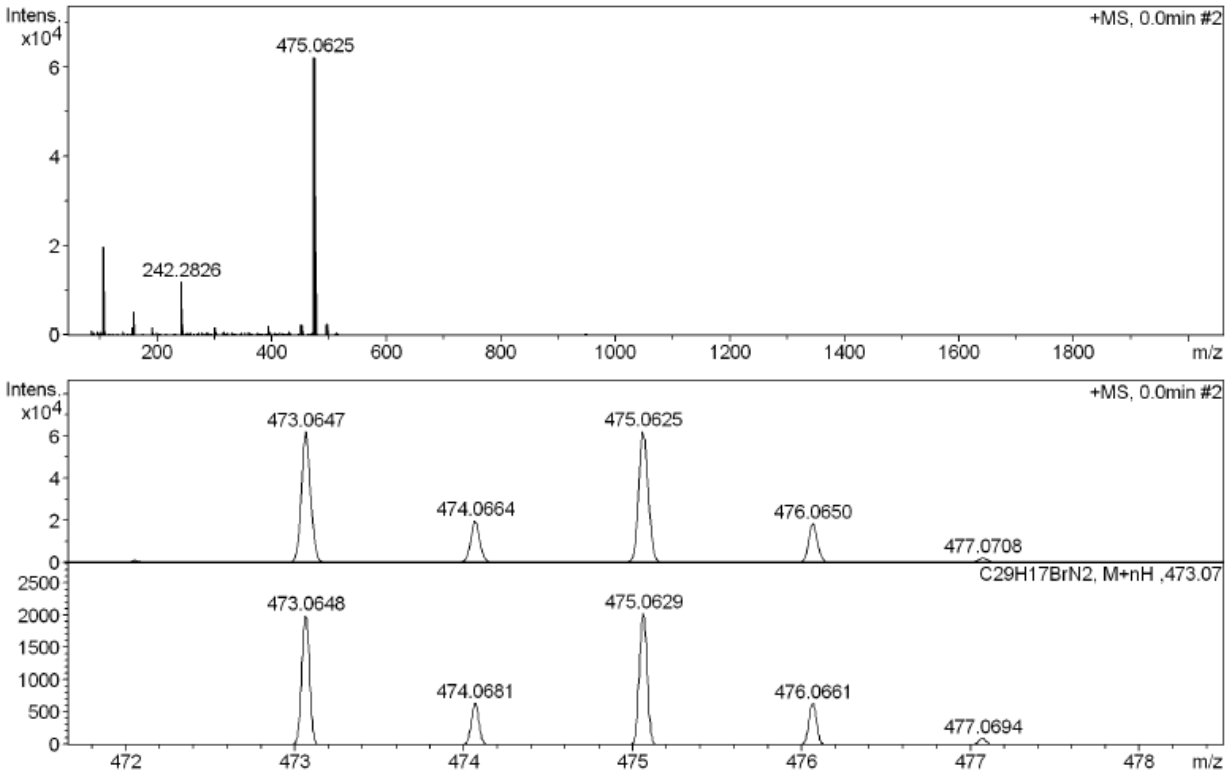
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

2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242.2826
m/z
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474.0664
475.0625
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C29H17BrN2, M+nH ,473.07
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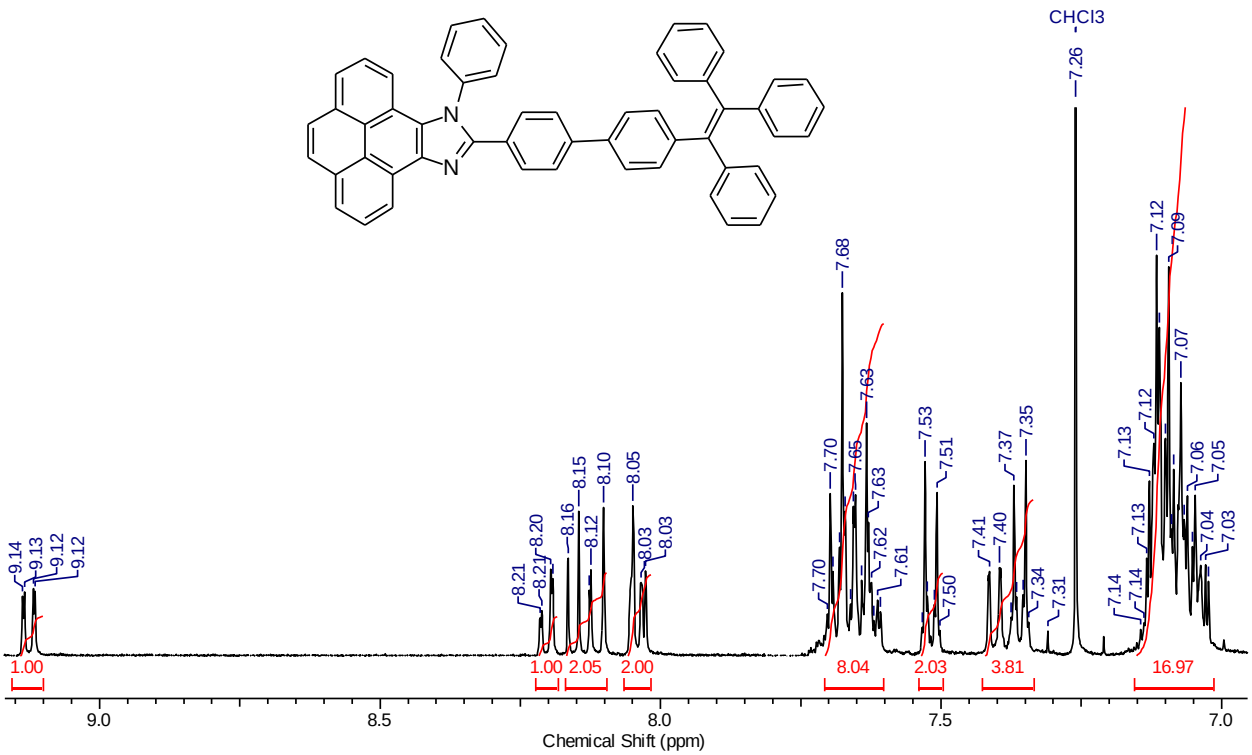
474.0681
475.0629
476.0661
477.0694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9.13
9.12
9.12
8.21
8.21
8.20
8.16
8.15
8.12
8.10
8.05
8.03
8.03
7.70
7.70
7.68
7.65
7.63
7.63
7.62
7.61
7.53
7.51
7.50
7.41
7.40
7.37
7.35
7.34
7.31
7.14
7.13
7.13
7.12
7.12
7.09
7.07
7.06
7.05
7.04
7.03
1.00
1.00
2.05
2.00
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2.03
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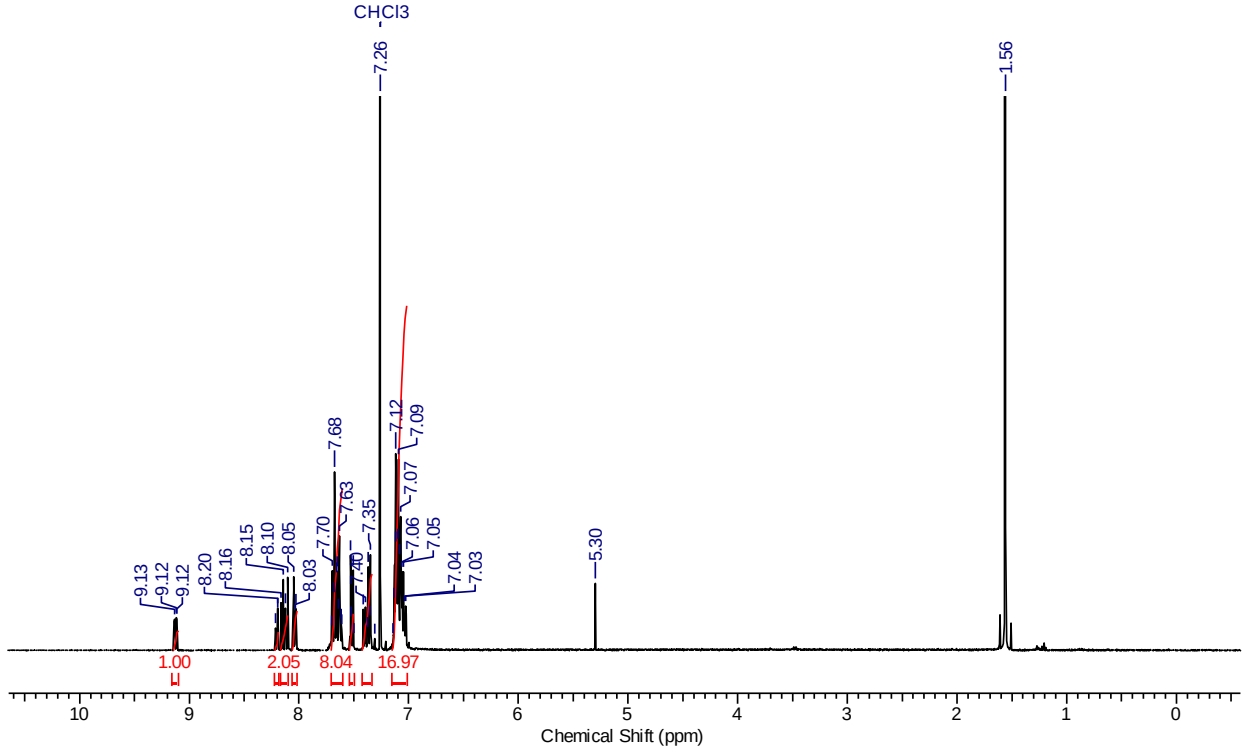
8.5
8.0
7.5
7.0
Chemical Shift (ppm)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9.12
9.12
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8.10
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8.03
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7.35
7.12
7.09
7.07
7.06
7.05
7.04
7.03
5.30
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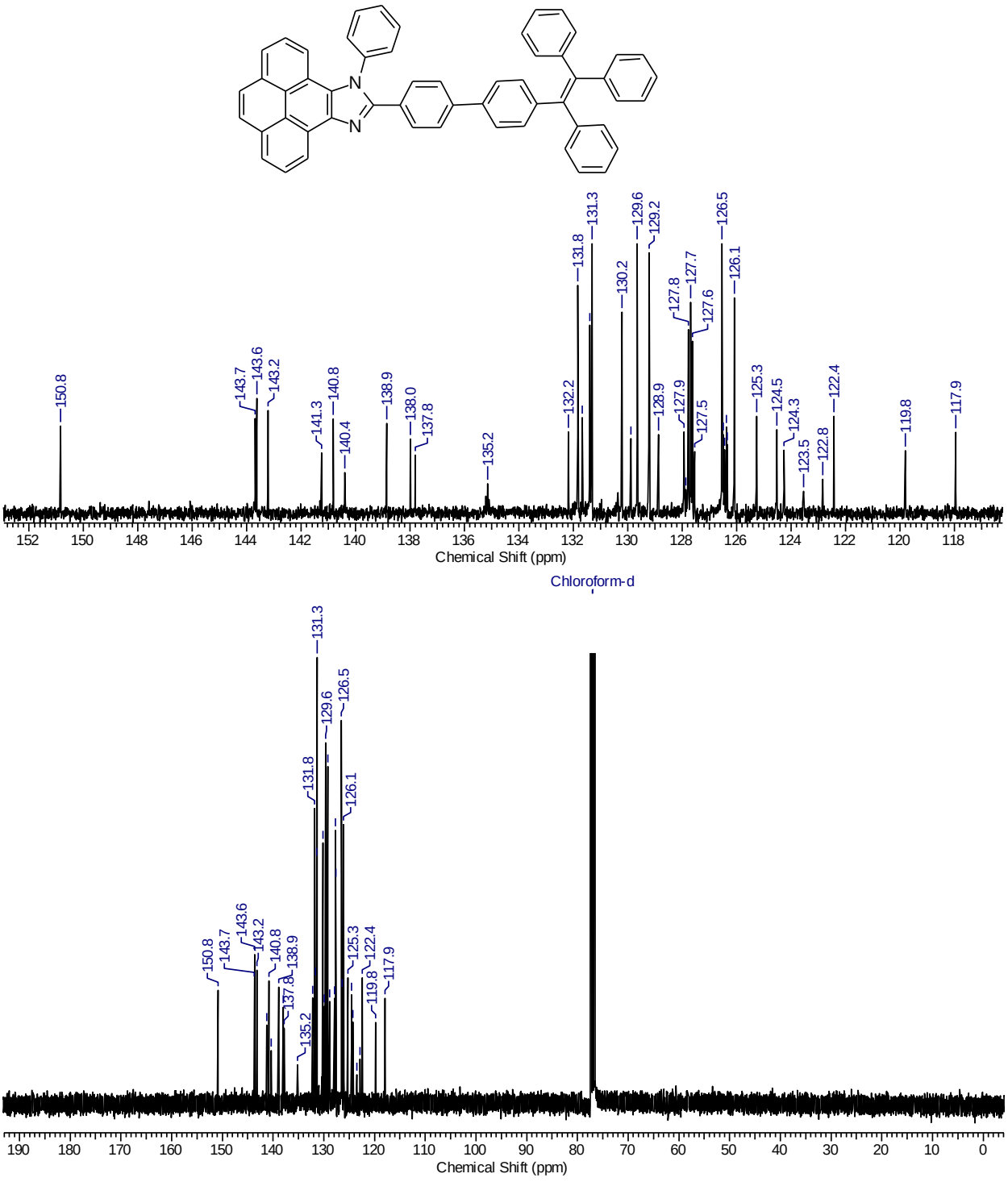
16.97
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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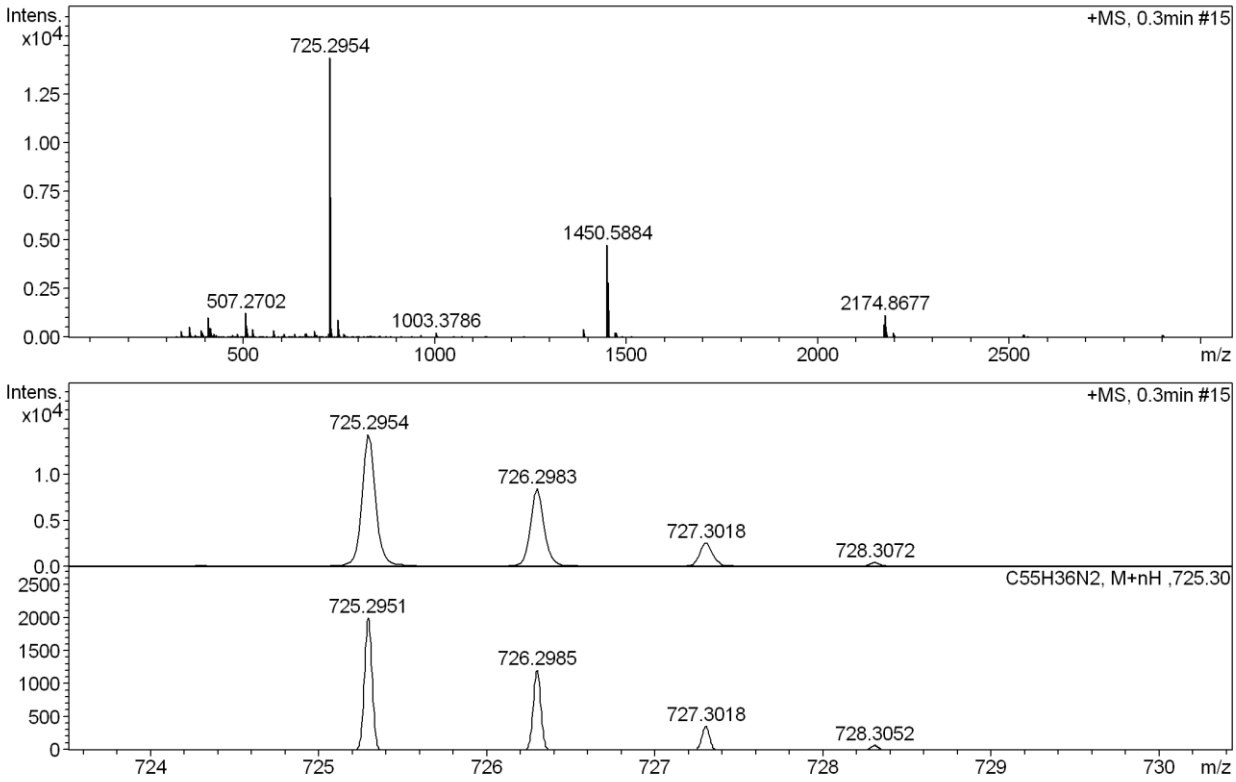
132.2
131.8
131.3
130.2
129.6
129.2
128.9
127.9
127.8
127.7
127.6
127.5
126.5
126.1
125.3
124.5
124.3
123.5
122.8
122.4
119.8
117.9
Chemical Shift (ppm)
Chloroform-d
150.8
143.7
143.6
143.2
140.8
138.9
137.8
135.2
131.8
131.3
129.6
126.5
126.1
125.3
122.4
119.8
117.9
Chemical Shift (ppm)

3a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1003.3786
2174.8677
m/z
Intens.
x10^4
+MS, 0.3min #15
725.2954
726.2983
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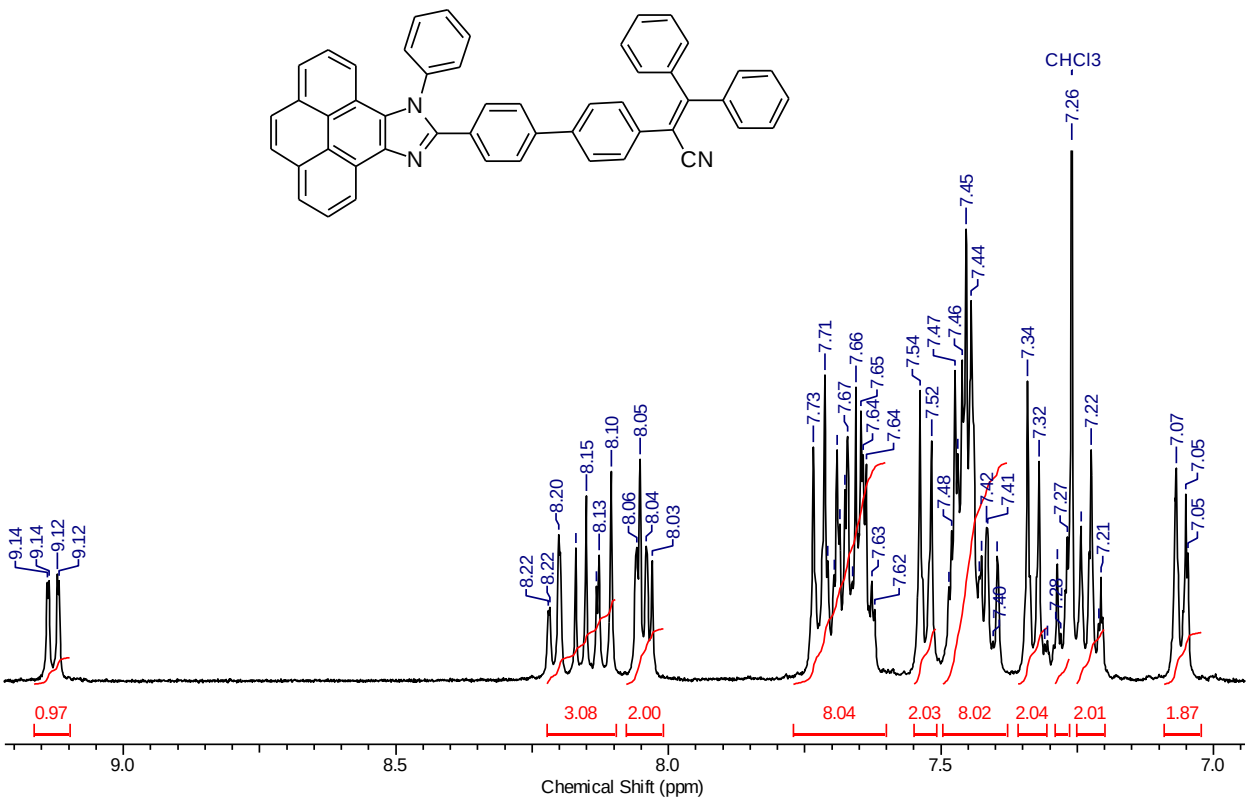
728.3072
C55H36N2, M+nH ,725.30
725.2951
726.2985
727.3018
728.3052
m/z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CN
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7.73
7.67
7.64
7.64
7.52
7.32
7.22
7.07
7.05
7.05
7.48
7.42
7.41
7.27
7.21
8.20
8.15
8.10
8.05
8.06
8.04
8.03
8.22
8.22
9.14
9.14
9.12
9.12
7.63
7.62
7.40
7.29
0.97
3.08
2.00
8.04
2.03
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2.04
2.01
1.87
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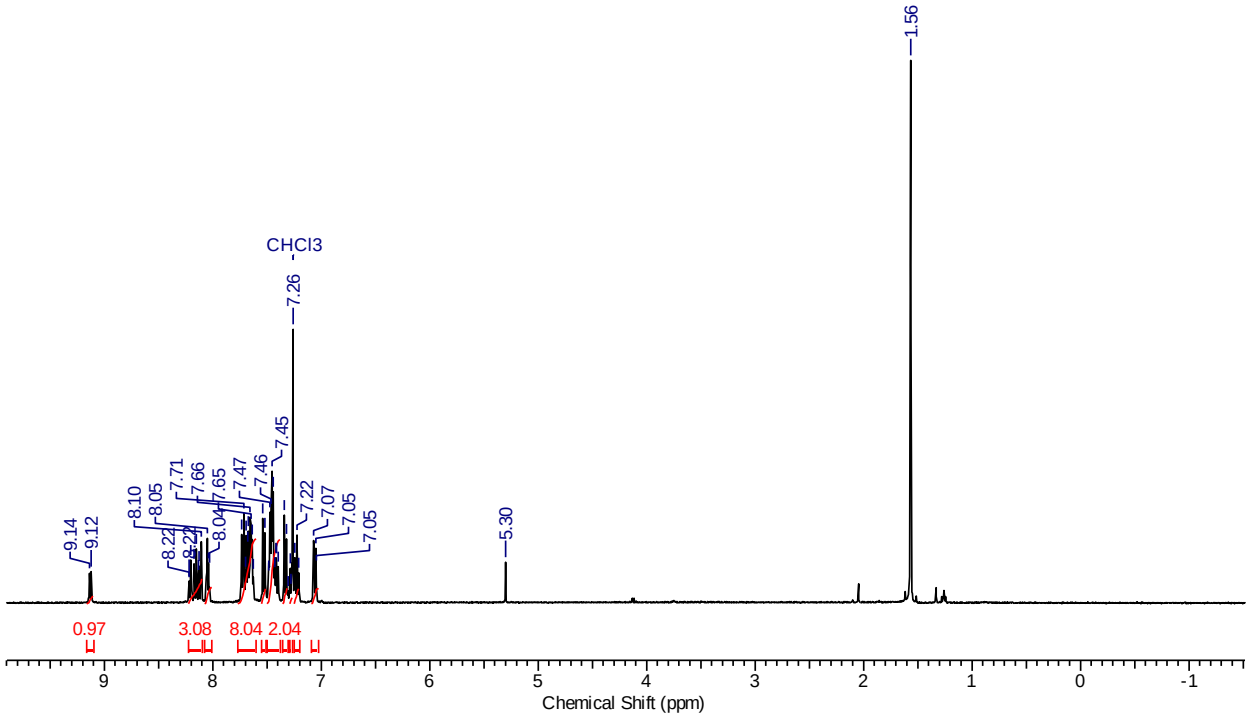
8.0
7.5
7.0
Chemical Shift (ppm)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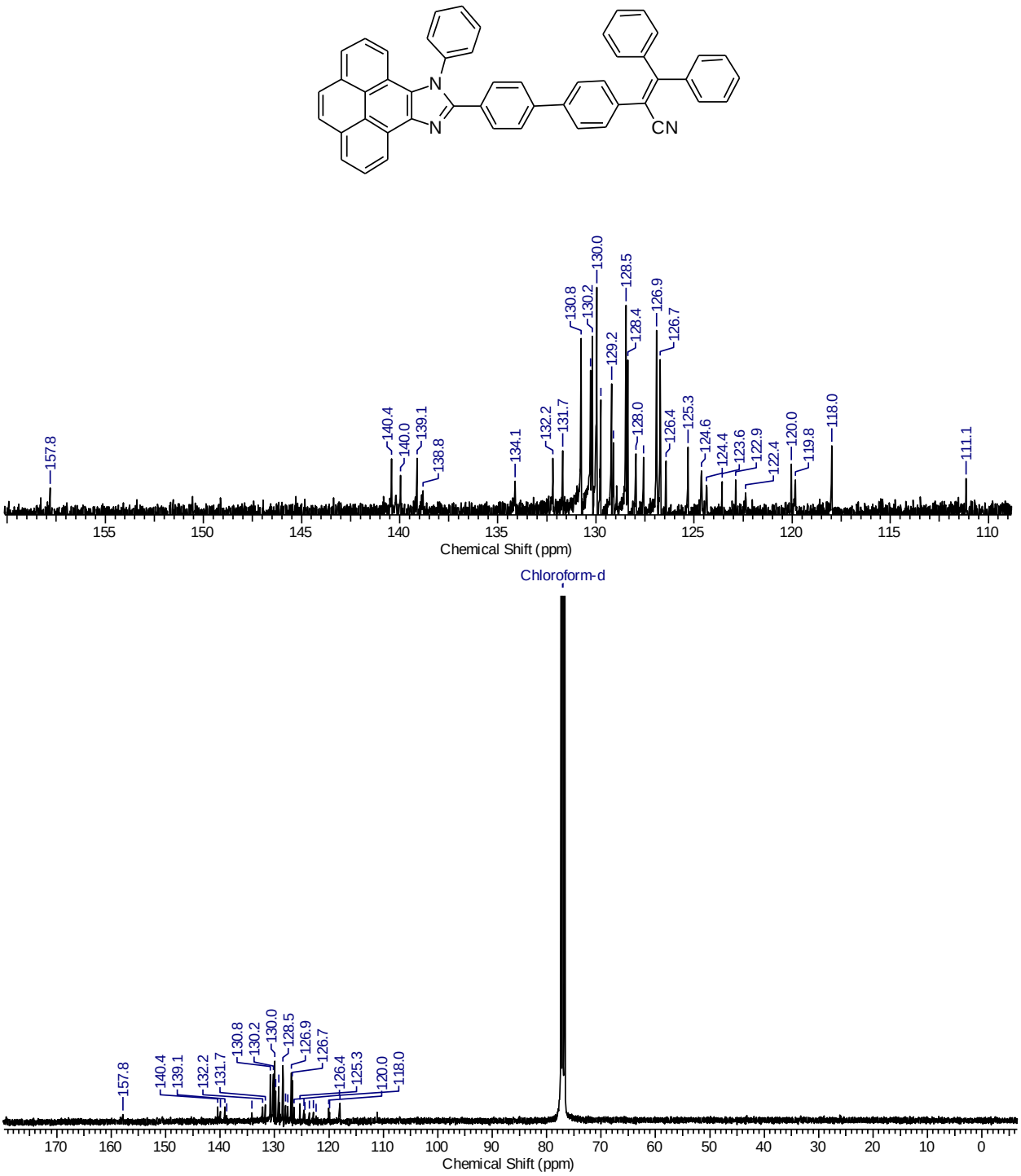
7.22
7.07
7.05
7.05
8.10
8.05
8.04
5.30
9.14
9.12
8.22
8.22
0.97
3.08
8.04
2.04
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)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N
CN
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140.4
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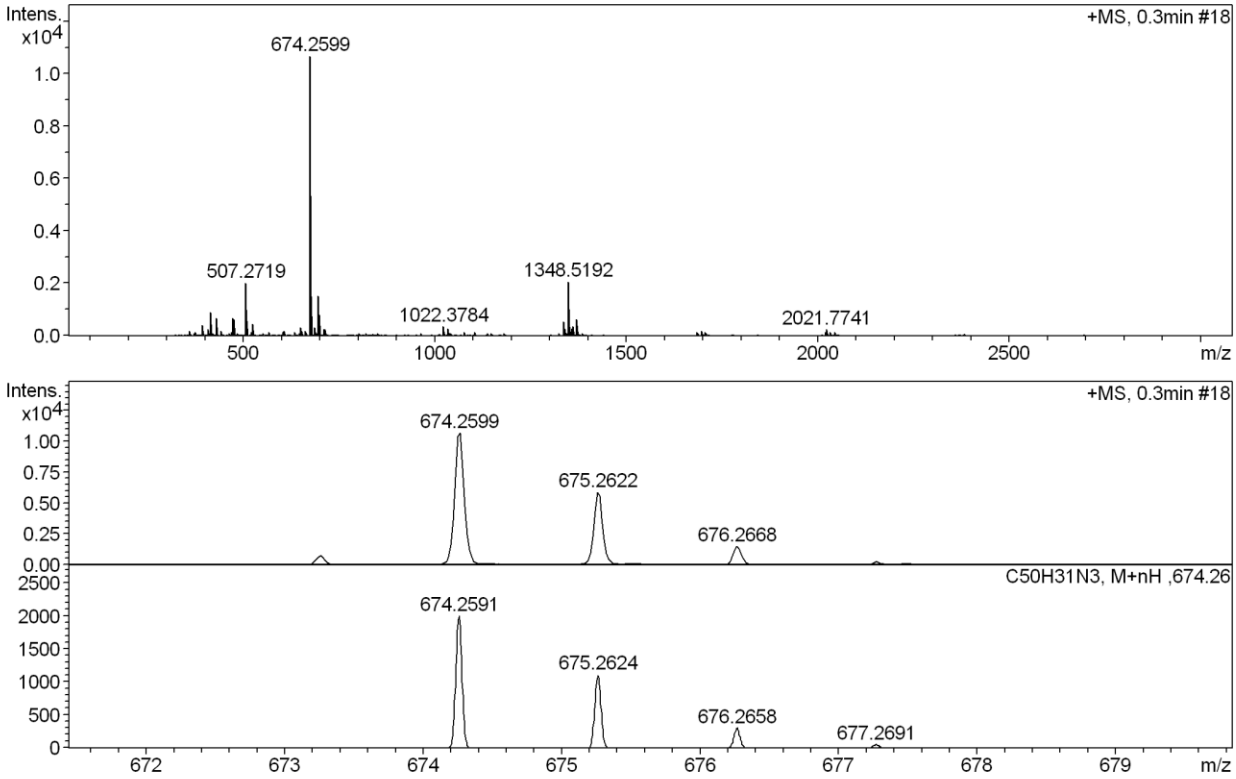
139.1
138.8
134.1
132.2
131.7
130.8
130.2
130.0
129.2
128.5
128.4
128.0
126.9
126.7
126.4
125.3
124.6
124.4
123.6
122.9
122.4
120.0
119.8
118.0
111.1
155
150
145
140
135
130
125
120
115
110
Chemical Shift (ppm)
Chloroform-d
157.8
140.4
139.1
132.2
131.7
130.8
130.2
130.0
128.5
126.9
126.7
126.4
125.3
120.0
118.0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

3b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m/z
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x10^4
+MS, 0.3min #18
674.2599
675.2622
676.2668
C50H31N3, M+nH ,674.26
674.2591
675.2624
676.2658
677.2691
m/z

DFT calculation data of 3a, and 3b

Calculation method: B3LYP/6-31+G(d) with Gaussian 09

3a

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-6.040414	0.140553	-0.036740
2	6	0	-7.337340	0.755816	0.089622
3	6	0	-7.578586	2.116767	0.337465
4	1	0	-6.750567	2.801689	0.460220
5	6	0	-8.880103	2.609757	0.437625
6	1	0	-9.033939	3.668341	0.629485
7	6	0	-9.971843	1.764450	0.295672
8	1	0	-10.983931	2.154525	0.370556
9	6	0	-9.784682	0.391512	0.061105
10	6	0	-8.460299	-0.137449	-0.039425
11	6	0	-8.286869	-1.547688	-0.257099
12	6	0	-9.425901	-2.402058	-0.382265
13	6	0	-9.235758	-3.779715	-0.588915
14	1	0	-10.107974	-4.422121	-0.683917
15	6	0	-7.955966	-4.319907	-0.669387
16	1	0	-7.828752	-5.387341	-0.829178
17	6	0	-6.833581	-3.500251	-0.546345
18	1	0	-5.830669	-3.910202	-0.608810
19	6	0	-6.984885	-2.124731	-0.343067
20	6	0	-5.869353	-1.229263	-0.215354
21	6	0	-4.366718	2.020473	0.245941
22	6	0	-3.910804	2.409906	1.507232
23	1	0	-3.852390	1.674172	2.303095
24	6	0	-3.535552	3.736193	1.725926
25	1	0	-3.179141	4.038694	2.706416
26	6	0	-3.620390	4.669853	0.691416
27	1	0	-3.329019	5.701865	0.865112
28	6	0	-4.079955	4.276045	-0.568149
29	1	0	-4.147101	4.999377	-1.375850
30	6	0	-4.450997	2.950755	-0.795361
31	1	0	-4.808868	2.629161	-1.768806
32	6	0	-3.877656	-0.431207	-0.118756
33	6	0	-2.406663	-0.380843	-0.093189
34	6	0	-1.636447	0.703460	-0.545664
35	1	0	-2.114776	1.593341	-0.936143
36	6	0	-0.245978	0.650199	-0.513792
37	1	0	0.321807	1.512813	-0.850779
38	6	0	0.435242	-0.480412	-0.034324
39	6	0	-0.341259	-1.568717	0.403608
40	1	0	0.151478	-2.472714	0.750229
41	6	0	-1.728496	-1.522787	0.372832
42	1	0	-2.314269	-2.376033	0.697215

43	6	0	1.915994	-0.524866	0.003883
44	6	0	2.689387	0.069592	-1.008473
45	1	0	2.193886	0.538438	-1.854090
46	6	0	4.078930	0.032678	-0.970902
47	1	0	4.647199	0.489792	-1.774698
48	6	0	4.762756	-0.599671	0.082034
49	6	0	3.988930	-1.213779	1.082743
50	1	0	4.487475	-1.720806	1.903919
51	6	0	2.599069	-1.168447	1.050256
52	1	0	2.033517	-1.619315	1.861014
53	6	0	6.253185	-0.678527	0.113402
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55	6	0	6.800507	-2.034071	0.429668
56	6	0	7.763461	-2.212315	1.437281
57	1	0	8.135201	-1.345046	1.974179
58	6	0	8.241453	-3.482967	1.754295
59	1	0	8.982586	-3.597269	2.541145
60	6	0	7.768479	-4.603757	1.069142
61	1	0	8.142617	-5.594031	1.315068
62	6	0	6.804401	-4.443818	0.071476
63	1	0	6.426269	-5.309957	-0.465515
64	6	0	6.317746	-3.174303	-0.236366
65	1	0	5.558503	-3.058888	-1.004943
66	6	0	6.536027	1.802160	-0.164502
67	6	0	5.725002	2.307850	0.865742
68	1	0	5.451436	1.658133	1.691282
69	6	0	5.274071	3.626671	0.840542
70	1	0	4.652422	3.997303	1.651545
71	6	0	5.622993	4.469696	-0.216447
72	1	0	5.270441	5.497557	-0.236527
73	6	0	6.436974	3.985068	-1.242511
74	1	0	6.718746	4.633938	-2.067845
75	6	0	6.897626	2.669810	-1.210396
76	1	0	7.541339	2.303744	-2.005332
77	6	0	8.528274	0.276041	-0.358625
78	6	0	9.432480	1.126738	0.301981
79	1	0	9.052377	1.862511	1.005100
80	6	0	10.804082	1.033505	0.071639
81	1	0	11.485049	1.692835	0.603771
82	6	0	11.301421	0.102035	-0.842247
83	1	0	12.370065	0.033788	-1.027893
84	6	0	10.414266	-0.734269	-1.522601
85	1	0	10.788940	-1.453796	-2.246028
86	6	0	9.043738	-0.648388	-1.283271
87	1	0	8.360398	-1.300392	-1.818108
88	7	0	-4.742681	0.656786	0.015172
89	7	0	-4.542854	-1.563752	-0.256852
90	6	0	-10.907232	-0.495480	-0.075061
91	1	0	-11.905610	-0.071038	-0.000553
92	6	0	-10.737957	-1.827574	-0.288491
93	1	0	-11.598481	-2.484967	-0.387796

Total Energy (HF) = -2227.1155502 Hartree

3b

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.476929	0.155475	-0.043056
2	6	0	-6.744738	0.835264	0.042521
3	6	0	-6.924277	2.215922	0.224596
4	1	0	-6.066289	2.867129	0.321923
5	6	0	-8.202231	2.772236	0.291001
6	1	0	-8.308234	3.844580	0.432042
7	6	0	-9.330876	1.972062	0.179717
8	1	0	-10.324301	2.411103	0.228636
9	6	0	-9.205964	0.582572	0.010089
10	6	0	-7.906858	-0.010604	-0.055340
11	6	0	-7.797649	-1.435866	-0.207540
12	6	0	-8.974267	-2.241810	-0.302027
13	6	0	-8.847019	-3.634808	-0.444046
14	1	0	-9.747577	-4.240003	-0.515658
15	6	0	-7.593302	-4.236469	-0.490373
16	1	0	-7.514737	-5.314839	-0.599938
17	6	0	-6.434843	-3.464419	-0.396914
18	1	0	-5.451820	-3.922810	-0.433191
19	6	0	-6.523460	-2.075618	-0.257517
20	6	0	-5.368483	-1.227337	-0.160718
21	6	0	-3.723523	1.968359	0.173088
22	6	0	-3.278334	2.399844	1.424497
23	1	0	-3.271750	1.703240	2.256872
24	6	0	-2.847953	3.717459	1.586915
25	1	0	-2.500365	4.052823	2.559848
26	6	0	-2.867030	4.600739	0.505868
27	1	0	-2.533396	5.626387	0.635714
28	6	0	-3.316123	4.165069	-0.743686
29	1	0	-3.332863	4.849452	-1.587160
30	6	0	-3.742369	2.847957	-0.914548
31	1	0	-4.093325	2.494283	-1.879338
32	6	0	-3.342318	-0.518318	-0.077900
33	6	0	-1.870965	-0.540268	-0.036688
34	6	0	-1.039529	0.499888	-0.484834
35	1	0	-1.464859	1.410027	-0.889083
36	6	0	0.345875	0.376448	-0.430119
37	1	0	0.960978	1.207641	-0.763048
38	6	0	0.961129	-0.783399	0.067553
39	6	0	0.124007	-1.828468	0.498998
40	1	0	0.563988	-2.754535	0.857799
41	6	0	-1.258072	-1.712006	0.446806
42	1	0	-1.891345	-2.531687	0.767884
43	6	0	2.436624	-0.901747	0.133138
44	6	0	3.258524	-0.341841	-0.861699
45	1	0	2.804011	0.151538	-1.716046

46	6	0	4.642747	-0.447156	-0.799753
47	1	0	5.246099	-0.021424	-1.594605
48	6	0	5.268863	-1.115027	0.266217
49	6	0	4.451341	-1.697198	1.248954
50	1	0	4.907301	-2.238167	2.073214
51	6	0	3.066353	-1.584768	1.187353
52	1	0	2.465074	-2.015497	1.982702
53	6	0	6.751461	-1.265674	0.329984
54	6	0	7.681224	-0.305740	0.022180
55	6	0	7.309273	1.122142	-0.185325
56	6	0	6.495382	1.802722	0.736543
57	1	0	6.111099	1.271049	1.601240
58	6	0	6.188615	3.149672	0.554369
59	1	0	5.565864	3.661913	1.282786
60	6	0	6.681290	3.839648	-0.555572
61	1	0	6.437894	4.889019	-0.698435
62	6	0	7.497027	3.177173	-1.475044
63	1	0	7.889182	3.707656	-2.338548
64	6	0	7.819800	1.834519	-1.284435
65	1	0	8.466184	1.326269	-1.993979
66	6	0	9.131075	-0.622619	-0.082926
67	6	0	10.081776	0.223754	0.517399
68	1	0	9.745423	1.100093	1.063157
69	6	0	11.442179	-0.060987	0.433628
70	1	0	12.160152	0.595367	0.917866
71	6	0	11.882248	-1.183700	-0.271621
72	1	0	12.944376	-1.401693	-0.343145
73	6	0	10.951626	-2.020093	-0.889711
74	1	0	11.285225	-2.889039	-1.450028
75	6	0	9.588551	-1.744255	-0.795772
76	1	0	8.873627	-2.394339	-1.289592
77	7	0	-4.157140	0.613150	0.000243
78	7	0	-4.059113	-1.623551	-0.174567
79	6	0	7.180960	-2.563367	0.776888
80	7	0	7.445133	-3.623924	1.180041
81	6	0	-10.367597	-0.257207	-0.093861
82	1	0	-11.345658	0.215602	-0.046457
83	6	0	-10.258882	-1.604096	-0.244521
84	1	0	-11.148262	-2.225223	-0.319983

Total Energy (HF) = -2088.3069087 Hartree