Supporting Information

Reversible mechanochromism and enhanced AIE in tetraphenylethene substituted phenanthroimidazoles

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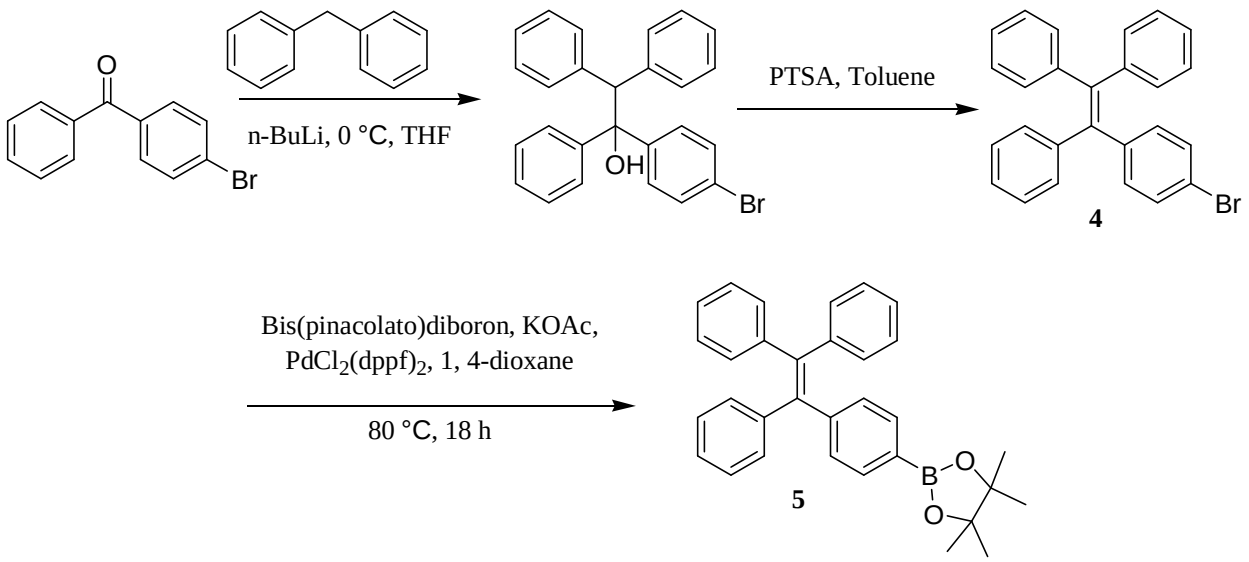
Experimental section

General methods

Chemicals were used as received unless otherwise indicated. All oxygen or moisture sensitive reactions were performed under nitrogen/argon atmosphere. ^{1}H NMR (400 MHz), and ^{13}C NMR (100MHz) spectra were recorded on on the Bruker Avance (III) 400 MHz instrument by using $CDCl_3$. ^{1}H NMR chemical shifts are reported in parts per million (ppm) relative to the solvent residual peak ($CDCl_3$, 7.26 ppm). Multiplicities are given as: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), dt (doublet of triplets), m (multiplet), and the coupling constants, *J*, are given in Hz. ^{13}C NMR chemical shifts are reported relative to the solvent residual peak ($CDCl_3$, 77.36 ppm. Thermogravimetric analyses were performed on the Metler Toledo Thermal Analysis system. UV-visible absorption spectra were recorded on a Carry-100 Bio UV-visible Spectrophotometer. Emission spectra were taken in a fluoromax-4p fluorimeter from HoribaYovin (model: FM-100). The excitation and emission slits were 2/2 nm for the emission measurements. All of the measurements were done at 25°C. HRMS was recorded on Brucker-Daltonics, micrOTOF-Q II mass spectrometer. The density functional theory (DFT) calculation were carried out at the B3LYP/6-31G(d) level in the Gaussian 09 program.[1] TD-DFT calculations was performed at the B3LYP/6-31 G(d) level in dichloromethane solvent using IEFPCM formulation for solvent effect.[2]

Synthesis



Scheme S1. Synthetic route to intermediate **5**.

Compound **4** was prepared according to the synthetic route shown in Scheme S1. Details can be found in the previous publication.[3]

Synthesis and Characterization of intermediates 5 and 2b:

5: Pd(dppf)Cl_2(0.12 mmol) was added to a well degassed solution of bromo-tetraphenylethene (2.4 mmol), bis(pinacolato)diboron (3.84 mmol) and KOAc (7.2 mmol) in anhydrous 1,4-dioxane (20 mL). The resulting mixture was stirred at 90 ºC for 16 h under argon atmosphere. After cooling, the mixture was evaporated to dryness and taken up with CH_2Cl_2. The organic layer was washed with H_2O, dried over $MgSO_4$, filtered and evaporated to dryness. Column chromatography (SiO_2, Hexane/CH_2Cl_2 95:5) gave compound **5** as a colorless solid in 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.53–7.55 (m, 2H), 7.07–7.10 (m, 9H), 6.98-7.04 (m, 8H),1.31 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 146.8, 143.7, 143.6, 143.5, 141.4, 140.9, 134.1, 131.4, 131.3, 131.3, 130.7, 127.7, 127.6, 126.5, 126.5, 126.4, 83.7, 24.9, 0.0 ppm; HRMS (ESI): calcd. for $C_{32}H_{31}BO_2$: 459.2495 $(M+H)^+$, found 459.2491.

2b: The 9,10-phenanthrenequinone (9.6 mmol), 4-bromobenzaldehyde (9.6 mmol), 4-aminobenzonitrile (14.4 mmol), and ammonium acetate (96.1 mmol) in glacial acetic acid (50 mL) refluxed for 4 h under an argon atmosphere. After cooling to room temperature, a pale yellow mixture was obtained and poured into a methanol solution under stirring. The separated solid was filtered off, washed with 30ml water, and dried to gave compound **2b** as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.82 (dd, 1H, *J*=1.6, 8 Hz), 8.79 (d, 1H, *J*=8 Hz), 8.71 (d, 1H, *J*=8 Hz), 7.92 (dt, 2H, *J*=2, 8 Hz), 7.74-7.78 (m, 1H), 7.63-7.71 (m, 3H), 7.54-7.58 (m, 1H), 7.47 (dt, 2H, *J*=2.4, 8 Hz), 7.29-7.37 (m, 3H), 7.09 (dd, 1H, *J*=0.8, 8 Hz) ppm; HRMS (ESI): calcd. for $C_{28}H_{16}BrN_3$: 474.0600 $(M+H)^+$, found 474.0593.

Synthesis and Characterization of 3a-3b:

3a: $Pd(PPh_3)_4$ (0.004 mmol) was added to a well degassed solution of 2-(4-Bromo-phenyl)-1-phenyl-1H-phenanthro[9,10-d]imidazole (**2a**) (0.4 mmol), **5** (0.48 mmol), K_2CO_3(1.2 mmol) in a mixture of toluene (12 mL)/ ethanol (4.0 mL)/ H_2O (1.0 mL). The resulting mixture was stirred at 80 ºC for 24 h under argon atmosphere. After cooling, the mixture was evaporated to dryness and the residue subjected to column chromatography on silica (Hexane-DCM 80:20 in vol.) to yield the desired product **3a** as colorless powder. The compound was recrystalized from DCM:ethanol (8:2) mixtures as colorless niddle like crystals. Yield: 67.0%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.89 (dd, 4H, *J*=0.8, 8 Hz), 8.78 (d, 1H, *J*=8 Hz), 8.71 (d, 1H, *J*=8 Hz), 7.73-7.77 (m, 1H), 7.59-7.68 (m, 6H), 7.47-7.55 (m, 5H), 7.34 (dt, 2H, *J*=2, 8 Hz) 7.24-7.29 (m, 1H), 7.18 (dd, 1H, *J*=0.8, 8 Hz) 7.02-7.14 (m, 17H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 150.6, 143.7, 143.7, 143.6, 143.6, 143.2, 141.2, 140.7, 140.4, 138.8, 137.8, 137.5, 131.8, 131.4, 131.3, 130.2, 129.8, 129.6, 129.2, 129.2, 129.1, 128.2, 128.2, 127.8, 127.7, 127.6, 127.3, 127.2, 126.5, 126.5, 126.4, 126.4, 126.1, 125.6, 124.8, 124.1, 123.1, 123.0, 122.7, 120.8, 0.0 ppm; HRMS (ESI): calcd. for $C_{53}H_{36}N_2$: 701.2951 $(M+H)^+$, found 701.2953.

3b: $Pd(PPh_3)_4$ (0.004 mmol) was added to a well degassed solution of 4-[2-(4-Bromo-phenyl)-phenanthro [9,10-d]imidazol-1-yl]-benzonitrile (**2b**) (0.4 mmol), **5** (0.48 mmol), K_2CO_3(1.2 mmol) in a mixture of toluene (12 mL)/ ethanol (4.0 mL)/ H2O (1.0 mL). The resulting mixture was stirred at 80 ºC for 24 h under argon atmosphere. After cooling, the mixture was evaporated to dryness and the residue subjected to column chromatography on silica (Hexane-DCM 70:30 in vol.) to yield the desired product **3b** as colorless powder. The compound was recrystalized from DCM:ethanol (8:2) mixtures as colorless niddle like crystals. Yield: 78.0%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.86 (dd, 1H, *J*=1.2, 8 Hz), 8.80 (d, 1H, *J*=8 Hz) 8.72 (d, 1H, *J*=8 Hz), 7.91 (dt, 2H, *J*=2, 8.8 Hz) 7.74-7.78 (m, 1H), 7.66-7.70 (m, 3H), 7.49-7.57 (m, 5H), 7.30-7.36 (m, 3H) 7.02-7.15 (m, 18H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 150.5, 143.6, 143.6, 143.5, 142.8, 141.3, 141.3, 140.3, 137.9, 137.5, 134.0, 131.9, 131.4, 131.3, 131.3, 130.2, 129.7, 129.4, 128.4, 128.3, 127.8, 127.7, 127.6, 127.5, 126.9, 126.7, 126.5, 126.5, 126.5, 126.1, 126.0, 125.2, 124.4, 123.1, 122.8, 122.4, 120.4, 117.7, 113.8, 0.0 ppm; HRMS (ESI): calcd. for $C_{54}H_{35}N_3$: 726.2904 $(M+H)^+$, found 726.2923.

Crystallographic data

A single crystal X-ray structural study of **3a** and **3b** 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 997623 and 997624 contain the supplementary crystallographic data for **3a** and **3b**. 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 and 3b.

Parameter	3a	3b
Identification code	rm104	rm121a
Empirical formula	C_{53} H_{36} N_2	C_{54} H_{35} N_3
Formula weight	700.84	725.85
Temperature	150(2) K	150(2) K
Wavelength(A)	1.5418	0.71073
Crystal system, space group	Triclinic, P -1	Monoclinic, P 21/n
***a*/ (Å)**	9.4287(9)	9.0367(4)
***b*/ (Å)**	12.0253(11)	11.5650(8)
***c*/ (Å)**	21.1903(15)	38.221(2)
α/(°)	75.864(7)	90
β/ (°)	86.937(7)	94.875(4)
γ/ (°)	74.600(8)	90
Volume	2246.0(3) Å^3	3980.0(4) Å^3

Z, Calculated density (mg m^{-3})	2, 1.036	4, 1.211
Absorption coefficient /(mm^{-1})	0.457	0.071
F(000)	736	1520
Crystal size	0.23 x 0.18 x 0.13 mm	0.21 x 0.17 x 0.13 mm
θ range for data collection/(°)	3.93 to 74.82	2.95 to 25.00
Reflections collected / unique	16015 / 8638 [R(int) = 0.0333]	32887 / 7009 [R(int) = 0.1083]
Completeness to theta	θ = 74.82; 93.4 %	θ = 25.00; 99.8 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9430 and 0.9021	0.9909 and 0.9853
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	8638 / 0 / 497	7009 / 0 / 514
Goodness-of-fit on F^2	0.980	1.005
Final R indices [I>2sigma(I)]	R1 = 0.1095, wR2 = 0.3502	R1 = 0.0652, wR2 = 0.1371
R indices (all data)	R1 = 0.1834, wR2 = 0.3960	R1 = 0.1526, wR2 = 0.1803
Largest diff. peak and hole (eÅ^{-3})	0.253 and -0.279	0.297 and -0.163

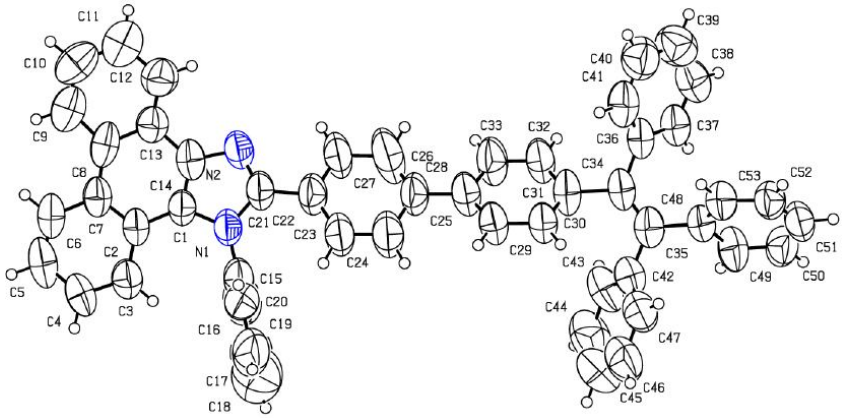


Fig. S1 Crystal structure of **3a.**

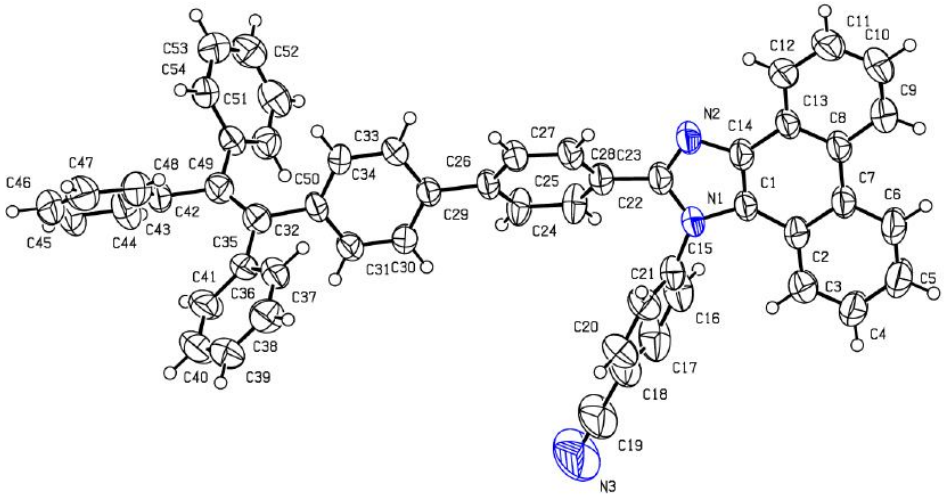


Fig. S2 Crystal structure of **3b**.

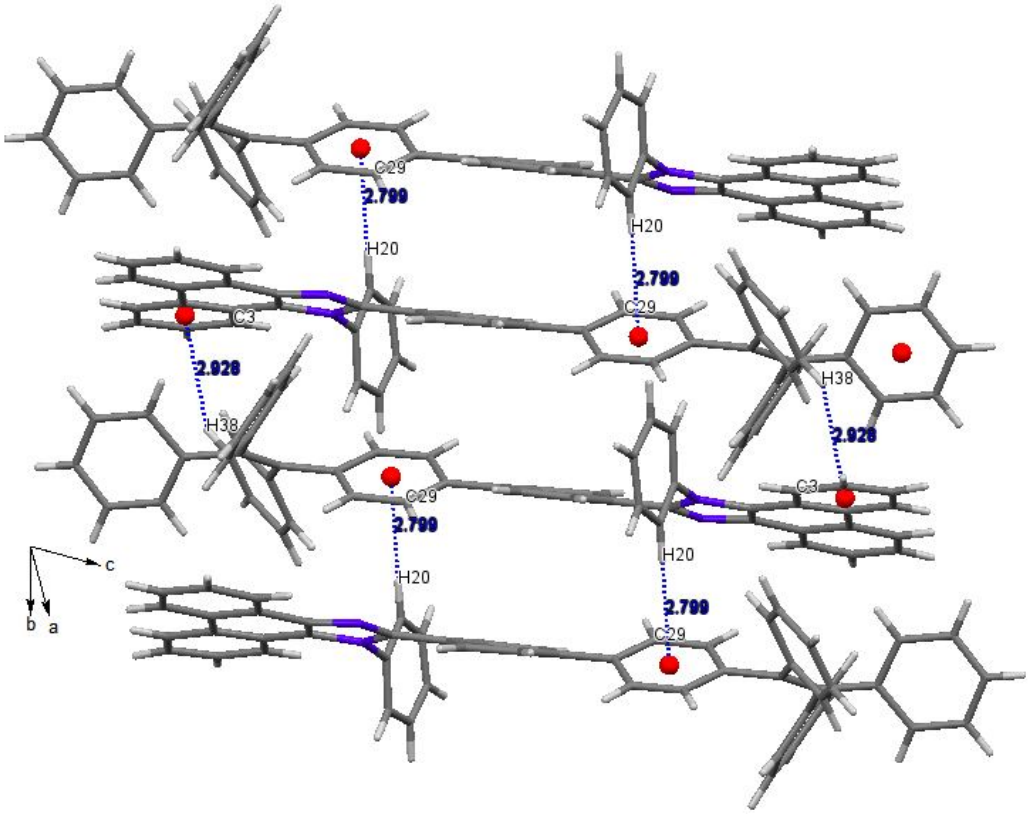


Fig. S3 Crystal packing structure of **3a.**

Thermogravimetric analysis

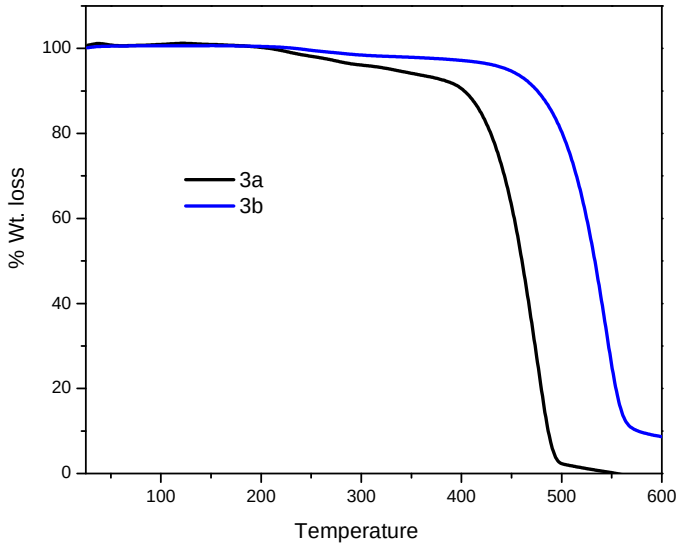


Fig. S4 Thermogravimetric analysis of **3a** and **3b**, measured at a heating rate of 10 $^{\circ}$C/ min under nitrogen atmosphere.

Photophysical properties

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

Compounds	λ_{max}[nm] (ε[Lmol^{-1}cm^{-1}]) [a]	λ_{em} (nm)	Φ_f [b]	Optical band gap (eV)	Theoretical band gap (eV) [c]	T_d (°C)
	260 (52389)					
3a	344 (33215)	415	0.009	3.12	4.08	330
	363 (29321)					
	257 (51452)					
3b	346 (28593)	458	0.004	3.04	3.31	445
	360 (27064)					

[a] Measured in dichloromethane. [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.

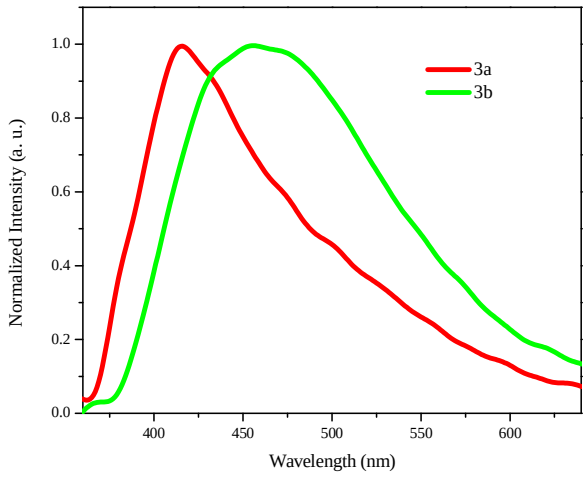


Fig. S5 Fluorescence spectra of **3a** and **3b** recorded in dichloromethane (concentration = 3×10^{-6} M)**.**

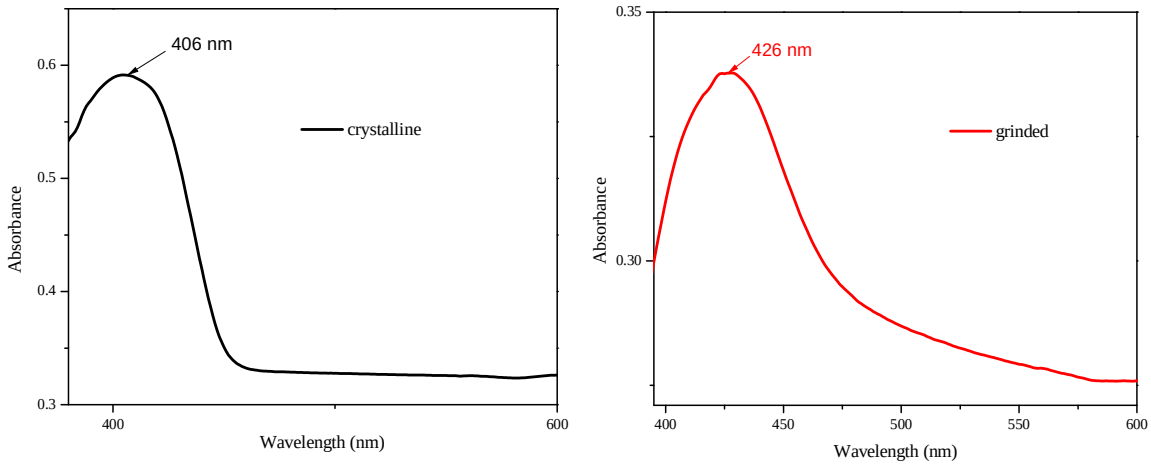


Fig. S6 Solid state absorption spectra of **3a** in crystalline and its grinded form.

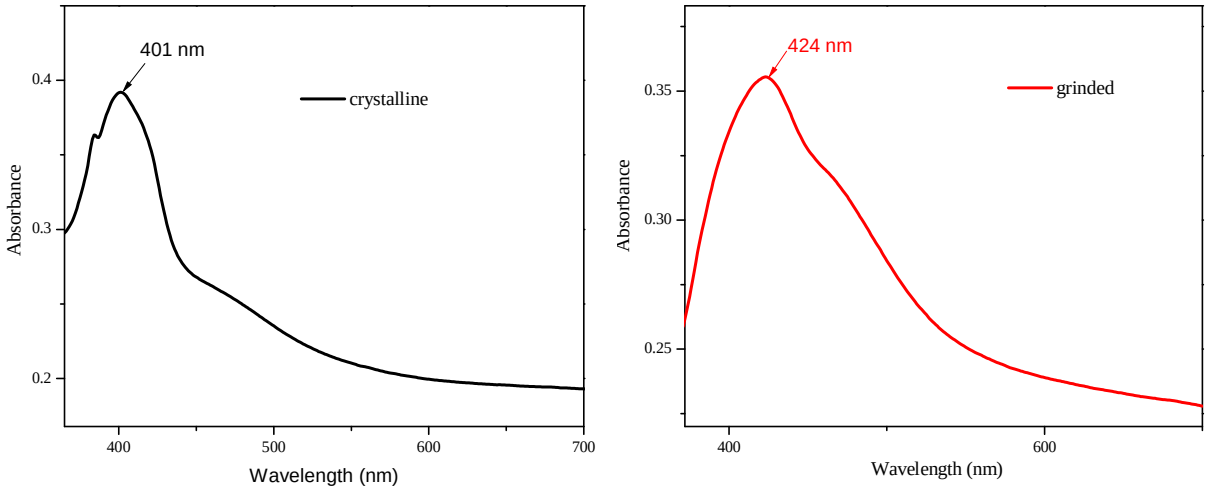


Fig. S7 Solid state absorption spectra of **3b** in crystalline and its grinded form.

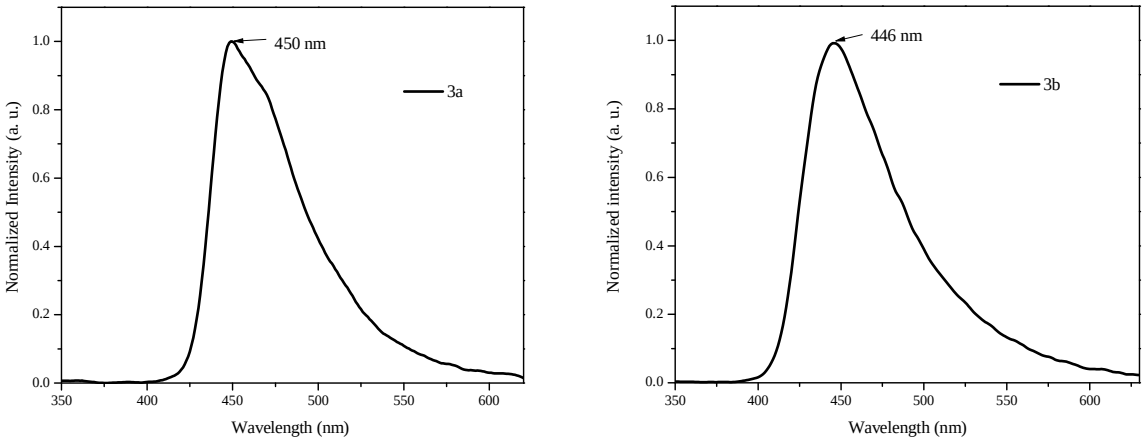


Fig. S8 Fluorescence spectra of single crystals of **3a** and **3b**.

Mechanochromism

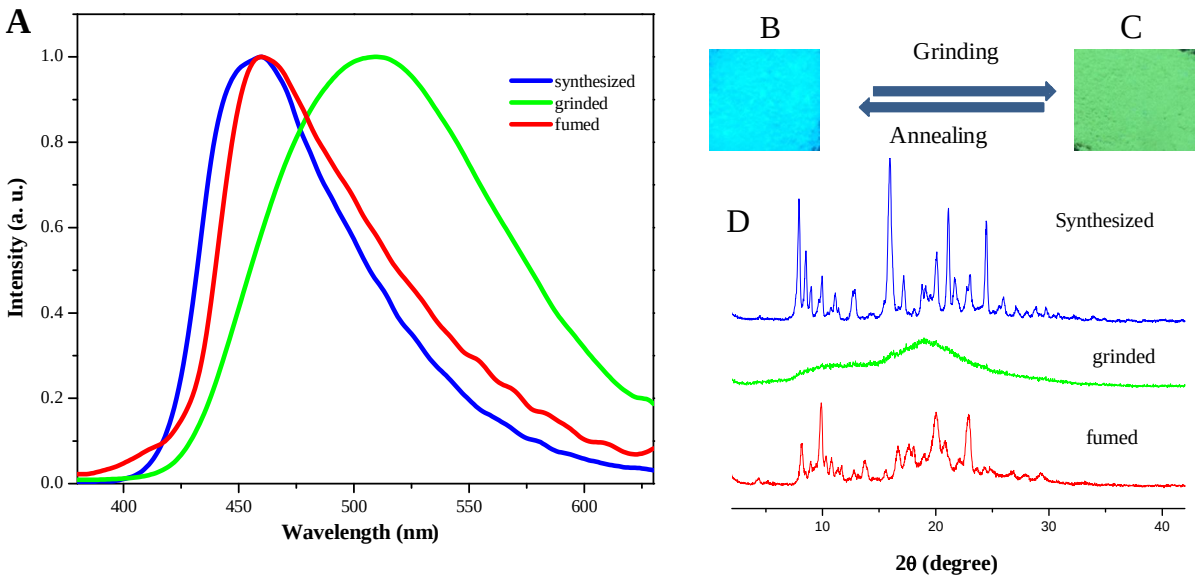


Fig. S9 (A) Emission spectra of **3a** as synthesized, grinded and heated solids and their photographs (B and C) taken under UV illumination and XRD patterns (D).

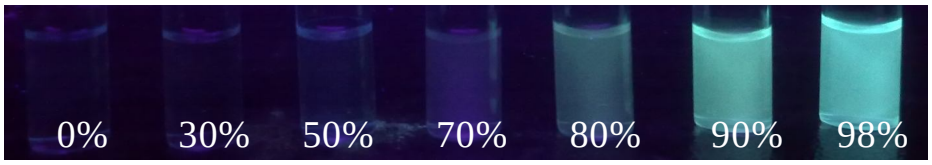


Fig. S10 Fluorescence pictures of **3b** solutions with different water fractions under UV (365 nm) light.

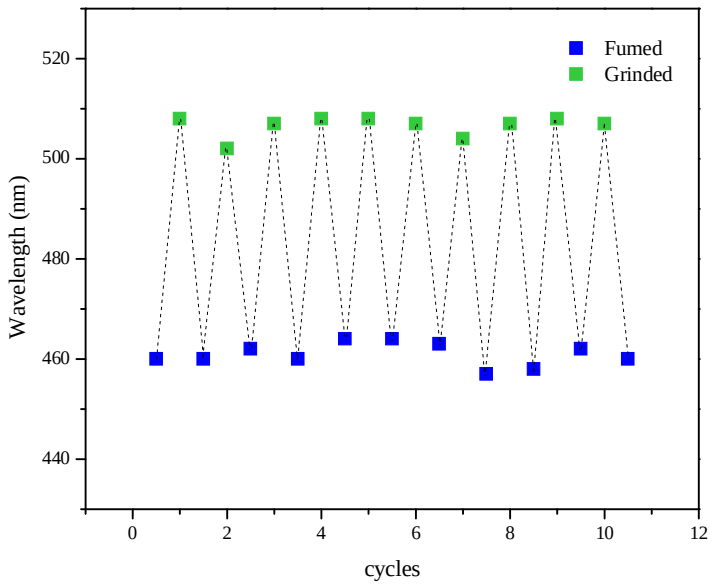


Fig. S11 Repeated switching of the solid-state fluorescence of **3a** by repeated grinding and fuming cycles.

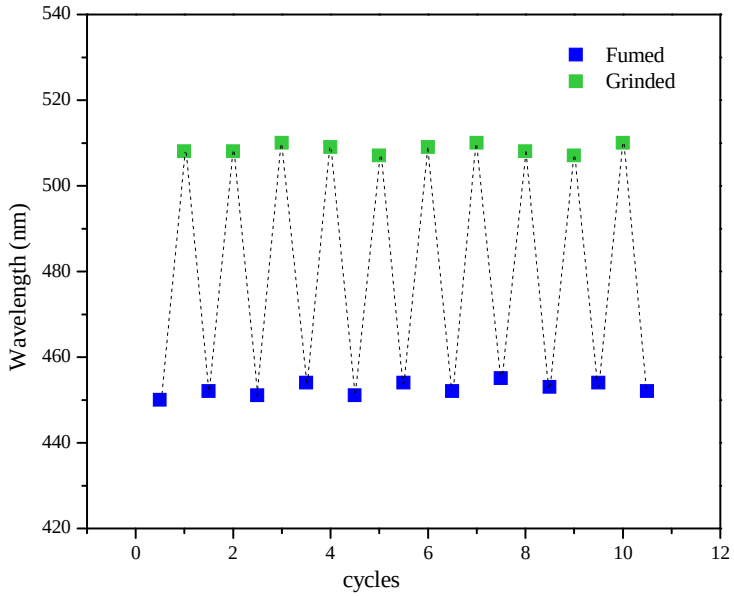


Fig. S12 Repeated switching of the solid-state fluorescence of **3b** by repeated grinding and fuming cycles.

DFT calculations.

TD-DFT data:

Table S3. Computed vertical transitions and their oscillator strengths and configurations.

Compound	DCM		
	λ_{max}[nm]	*F*	Configuration
3b	436.39	1.9068	HOMO→LUMO+1 (-0.69633)
	375.67	0.1205	HOMO-1→LUMO+1 (0.68106) HOMO→LUMO+2 (0.14759)
	356.25	0.1155	HOMO→LUMO+3 (0.64780) HOMO→LUMO+4 (-0.16147) HOMO-1→LUMO+2 (-0.15729)

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 2.3852 eV 519.81 nm f=0.0010 <S**2>=0.000
189 ->191 -0.15508
190 ->191 0.68867
This state for optimization and/or second-order correction.
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 2.8412 eV 436.39 nm f=1.9068 <S**2>=0.000
190 ->192 -0.69633

Excited State 3: Singlet-A 2.9757 eV 416.66 nm f=0.0003 <S**2>=0.000
189 ->191 -0.68680
190 ->191 -0.15596

Excited State 4: Singlet-A 3.3003 eV 375.67 nm f=0.1205 <S**2>=0.000
189 ->192 0.68106
190 ->193 0.14759

Excited State 5: Singlet-A 3.4486 eV 359.52 nm f=0.0005 <S**2>=0.000
188 ->191 0.70238

Excited State 6: Singlet-A 3.4802 eV 356.25 nm f=0.1155 <S**2>=0.000
189 ->192 -0.15729
190 ->193 0.64780
190 ->194 -0.16147

Excited State 7: Singlet-A 3.5677 eV 347.52 nm f=0.0931 <S**2>=0.000
189 ->193 -0.11273
189 ->194 0.15552

190 ->193 -0.17345
190 ->194 -0.63538

Excited State 8: Singlet-A 3.6991 eV 335.18 nm f=0.0260 <S**2>=0.000
188 ->192 -0.18546
189 ->195 -0.16218
190 ->194 0.12250
190 ->195 0.61728
190 ->196 -0.13686

Excited State 9: Singlet-A 3.8108 eV 325.35 nm f=0.0067 <S**2>=0.000
188 ->192 -0.19746
189 ->193 0.34844
190 ->196 0.54380

Excited State 10: Singlet-A 3.8250 eV 324.14 nm f=0.0002 <S**2>=0.000
186 ->191 0.10513
187 ->191 0.68827
SavETr: write IOETrn= 770 NScale= 10 NData= 16 NLR=1 LETran= 180.

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	-6.408157	0.029202	-0.048620
2	6	0	-7.713821	0.621892	0.079123
3	6	0	-7.950879	1.990971	0.344691
4	1	0	-7.114415	2.664506	0.472428
5	6	0	-9.235781	2.490410	0.456467
6	1	0	-9.387729	3.546526	0.662380
7	6	0	-10.334339	1.632164	0.308674
8	1	0	-11.346983	2.016644	0.394167
9	6	0	-10.126930	0.286287	0.062042
10	1	0	-10.994471	-0.356310	-0.034210
11	6	0	-8.833464	-0.268663	-0.056503
12	6	0	-8.639485	-1.705277	-0.294093
13	6	0	-9.716208	-2.609350	-0.449543
14	1	0	-10.738928	-2.251475	-0.410265
15	6	0	-9.503611	-3.961735	-0.657589
16	1	0	-10.355493	-4.626519	-0.773486
17	6	0	-8.196850	-4.476091	-0.720220
18	1	0	-8.035551	-5.538289	-0.883626
19	6	0	-7.119449	-3.622179	-0.576454
20	1	0	-6.098343	-3.986794	-0.625294
21	6	0	-7.324274	-2.243732	-0.366741

22	6	0	-6.221292	-1.336515	-0.229372
23	6	0	-4.749479	1.927440	0.235723
24	6	0	-4.292659	2.320720	1.495532
25	1	0	-4.227596	1.585869	2.291693
26	6	0	-3.924978	3.649443	1.712413
27	1	0	-3.567877	3.954761	2.691787
28	6	0	-4.018184	4.581872	0.677540
29	1	0	-3.732790	5.615792	0.849820
30	6	0	-4.478383	4.184289	-0.580626
31	1	0	-4.551960	4.906620	-1.388668
32	6	0	-4.841596	2.856582	-0.806046
33	1	0	-5.199818	2.532131	-1.778427
34	6	0	-4.238657	-0.517823	-0.127236
35	6	0	-2.768150	-0.451632	-0.099648
36	6	0	-2.008732	0.638525	-0.556263
37	1	0	-2.495855	1.521671	-0.951100
38	6	0	-0.617845	0.599816	-0.523021
39	1	0	-0.058808	1.466842	-0.863285
40	6	0	0.074685	-0.521554	-0.038070
41	6	0	-0.690873	-1.615883	0.404063
42	1	0	-0.189129	-2.513203	0.755122
43	6	0	-2.078533	-1.584427	0.371870
44	1	0	-2.655676	-2.442358	0.699371
45	6	0	1.555808	-0.549897	0.001524
46	6	0	2.323352	0.049802	-1.012184
47	1	0	1.823361	0.509712	-1.860049
48	6	0	3.713156	0.029714	-0.972727
49	1	0	4.276980	0.490748	-1.777409
50	6	0	4.403126	-0.590336	0.083491
51	6	0	3.635465	-1.210638	1.085125
52	1	0	4.139022	-1.708825	1.908662
53	6	0	2.245170	-1.182048	1.050744
54	1	0	1.683935	-1.636905	1.862272
55	6	0	5.894443	-0.649540	0.117478
56	6	0	6.684033	0.440860	-0.120945
57	6	0	6.459340	-1.996960	0.437239
58	6	0	7.424438	-2.160228	1.445342
59	1	0	7.784634	-1.286927	1.980328
60	6	0	7.919155	-3.423731	1.765205
61	1	0	8.661665	-3.526456	2.552354
62	6	0	7.461134	-4.552213	1.082505
63	1	0	7.848349	-5.536898	1.330621
64	6	0	6.495019	-4.407270	0.084527
65	1	0	6.128352	-5.279527	-0.450512
66	6	0	5.991627	-3.144989	-0.226145
67	1	0	5.230920	-3.041354	-0.994955
68	6	0	6.143446	1.834138	-0.164957
69	6	0	5.324935	2.330770	0.863776
70	1	0	5.060046	1.679130	1.690630
71	6	0	4.855611	3.643095	0.835343
72	1	0	4.228416	4.006848	1.645190
73	6	0	5.193280	4.488484	-0.223404
74	1	0	4.826416	5.511272	-0.246005
75	6	0	6.014508	4.012962	-1.247963

76	1	0	6.287621	4.663870	-2.074603
77	6	0	6.493537	2.704371	-1.212599
78	1	0	7.142796	2.345444	-2.006268
79	6	0	8.156963	0.335430	-0.353356
80	6	0	9.048074	1.200925	0.305839
81	1	0	8.656544	1.933244	1.006273
82	6	0	10.421173	1.126656	0.077533
83	1	0	11.091931	1.797308	0.608481
84	6	0	10.932973	0.199565	-0.832798
85	1	0	12.002726	0.146037	-1.016887
86	6	0	10.058770	-0.651499	-1.511636
87	1	0	10.444688	-1.367824	-2.232327
88	6	0	8.686830	-0.584495	-1.274377
89	1	0	8.013623	-1.247944	-1.807987
90	7	0	-5.115731	0.560933	0.006595
91	7	0	-4.890735	-1.657140	-0.268060

Total Energy (HF) = -2150.8798851 Hartree

Data for **3b**:

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-6.298206	-0.294730	-0.072086
2	6	0	-7.609624	0.285073	0.054773
3	6	0	-7.861998	1.648607	0.333392
4	1	0	-7.034288	2.329226	0.479646
5	6	0	-9.151980	2.135507	0.441525
6	1	0	-9.315203	3.187520	0.658742
7	6	0	-10.240927	1.268224	0.277195
8	1	0	-11.257600	1.642418	0.358582
9	6	0	-10.018890	-0.073977	0.023553
10	1	0	-10.879458	-0.724549	-0.080219
11	6	0	-8.719524	-0.616157	-0.089467
12	6	0	-8.510070	-2.050947	-0.323586
13	6	0	-9.576889	-2.964801	-0.489327
14	1	0	-10.603074	-2.615773	-0.466023
15	6	0	-9.349339	-4.316107	-0.687897
16	1	0	-10.193638	-4.988840	-0.812289
17	6	0	-8.037551	-4.819597	-0.729999
18	1	0	-7.865123	-5.881077	-0.885822
19	6	0	-6.969400	-3.955831	-0.576703
20	1	0	-5.944769	-4.311970	-0.611181
21	6	0	-7.189563	-2.578270	-0.377544
22	6	0	-6.096595	-1.659593	-0.237130
23	6	0	-4.647685	1.617485	0.175857
24	6	0	-4.094933	2.030007	1.391970
25	1	0	-3.958403	1.306414	2.188559
26	6	0	-3.723395	3.358843	1.571451

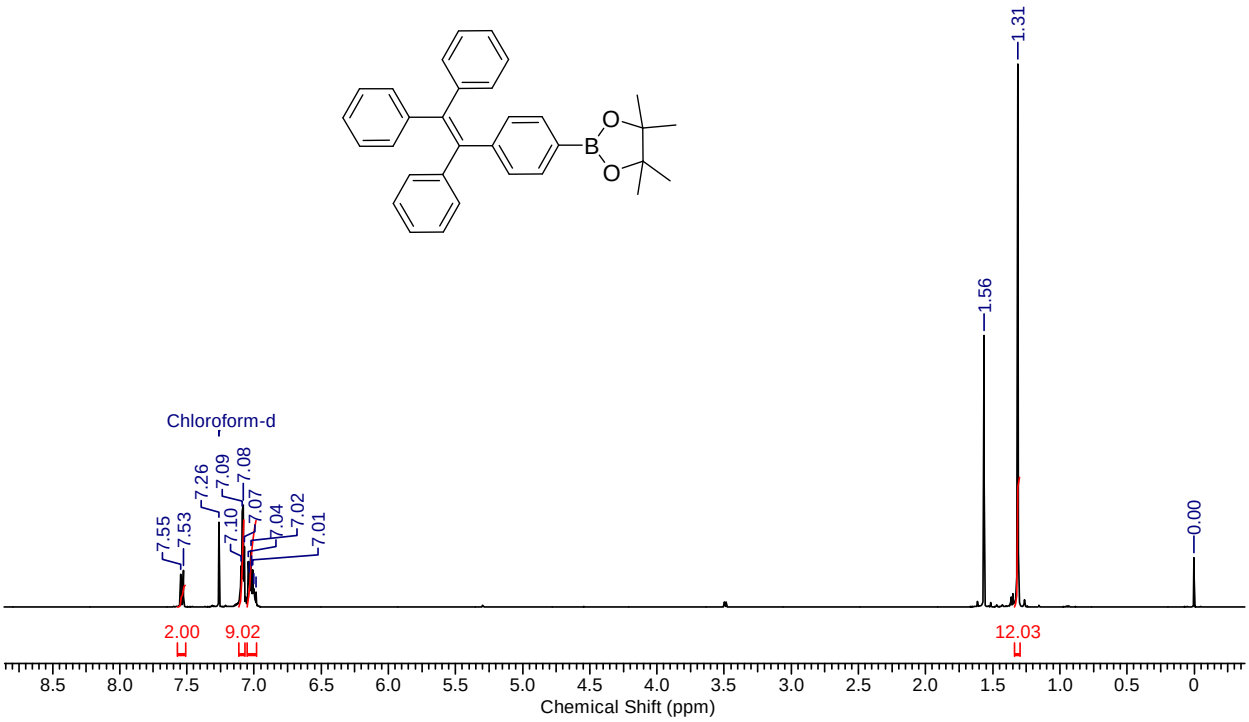
27	1	0	-3.293283	3.685164	2.512449
28	6	0	-3.909486	4.285596	0.532462
29	6	0	-4.468525	3.867533	-0.688017
30	1	0	-4.609000	4.585508	-1.489218
31	6	0	-4.831362	2.536930	-0.864414
32	1	0	-5.260998	2.201309	-1.802813
33	6	0	-4.119488	-0.826427	-0.130291
34	6	0	-2.650462	-0.738033	-0.104720
35	6	0	-1.911473	0.330479	-0.638829
36	1	0	-2.415386	1.172449	-1.099010
37	6	0	-0.520364	0.320080	-0.604616
38	1	0	0.023429	1.170217	-1.006084
39	6	0	0.191538	-0.752749	-0.042971
40	6	0	-0.554120	-1.827801	0.474293
41	1	0	-0.035775	-2.689108	0.885832
42	6	0	-1.942413	-1.823829	0.442190
43	1	0	-2.503600	-2.667792	0.828900
44	6	0	1.672880	-0.750469	-0.001581
45	6	0	2.429747	-0.198800	-1.049877
46	1	0	1.923212	0.196866	-1.925801
47	6	0	3.819425	-0.185933	-1.006722
48	1	0	4.375579	0.237189	-1.837028
49	6	0	4.519344	-0.722765	0.087678
50	6	0	3.762750	-1.298348	1.123743
51	1	0	4.274843	-1.733638	1.977063
52	6	0	2.372282	-1.302900	1.085285
53	1	0	1.818937	-1.719346	1.922494
54	6	0	6.011780	-0.742037	0.129757
55	6	0	6.772525	0.354751	-0.166286
56	6	0	6.609067	-2.054931	0.525022
57	6	0	7.577689	-2.138396	1.539468
58	1	0	7.917053	-1.228186	2.024107
59	6	0	8.102752	-3.369803	1.928561
60	1	0	8.847666	-3.410460	2.719049
61	6	0	7.671931	-4.545451	1.310771
62	1	0	8.082873	-5.505083	1.612946
63	6	0	6.702621	-4.479819	0.307594
64	1	0	6.357229	-5.389133	-0.177583
65	6	0	6.169291	-3.249253	-0.072618
66	1	0	5.406706	-3.207056	-0.845440
67	6	0	6.193424	1.727442	-0.291450
68	6	0	5.356062	2.258905	0.704140
69	1	0	5.106791	1.649372	1.567246
70	6	0	4.847723	3.552580	0.597113
71	1	0	4.206491	3.944621	1.382334
72	6	0	5.164549	4.343865	-0.508785
73	1	0	4.767123	5.351864	-0.592569
74	6	0	6.004479	3.833880	-1.501153
75	1	0	6.261739	4.443089	-2.363842
76	6	0	6.522462	2.544740	-1.387460
77	1	0	7.185668	2.159714	-2.157052
78	6	0	8.248994	0.277670	-0.385921
79	6	0	9.111345	1.202699	0.229088
80	1	0	8.695216	1.960965	0.886432

81	6	0	10.487387	1.154563	0.011807
82	1	0	11.135846	1.871874	0.508300
83	6	0	11.030382	0.193937	-0.844023
84	1	0	12.102304	0.160610	-1.019972
85	6	0	10.184482	-0.717209	-1.479375
86	1	0	10.594678	-1.460591	-2.158019
87	6	0	8.809766	-0.676173	-1.252409
88	1	0	8.158595	-1.386676	-1.751782
89	7	0	-5.008156	0.248794	-0.012387
90	7	0	-4.761682	-1.969466	-0.262814
91	6	0	-3.530076	5.656464	0.715498
92	7	0	-3.222508	6.768463	0.863126

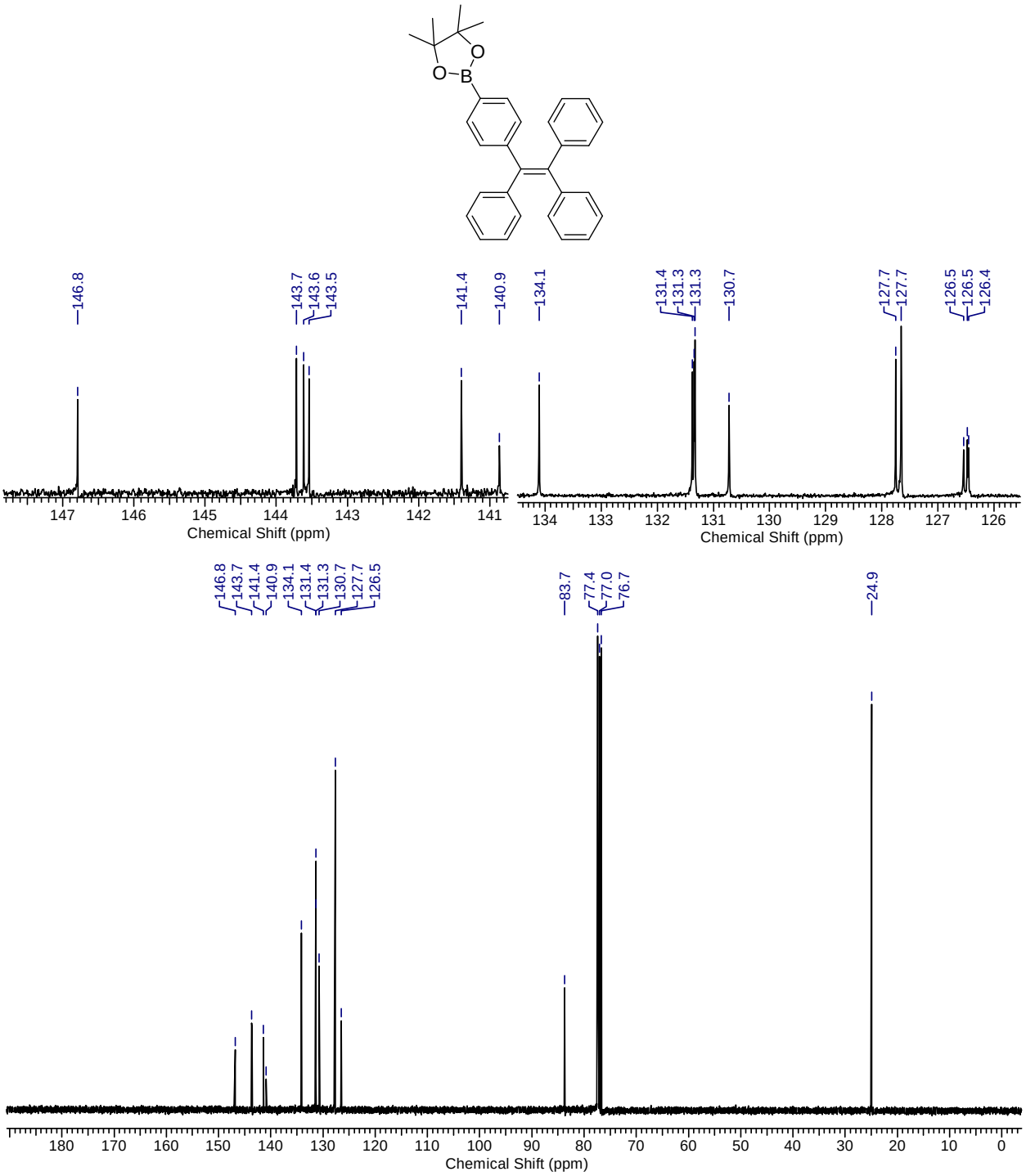
Total Energy (HF) = -2243.1205288 Hartree

Copies of NMR and HRMS spectra of the new compounds:

^{1}H NMR of **5**



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


O
O
B
146.8
143.7
143.6
143.5
141.4
140.9
134.1
131.4
131.3
131.3
130.7
127.7
127.7
126.5
126.5
126.4
147
146
145
144
143
142
141
Chemical Shift (ppm)
134
133
132
131
130
129
128
127
126
Chemical Shift (ppm)
146.8
143.7
141.4
140.9
134.1
131.4
131.3
130.7
127.7
126.5
83.7
77.4
77.0
76.7
24.9
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

HRMS of **5**

Display Report

Analysis Info

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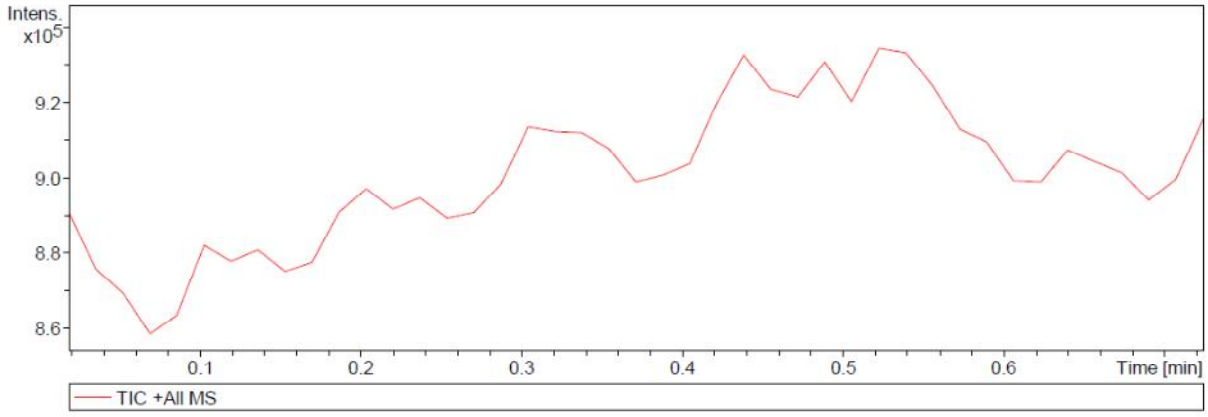
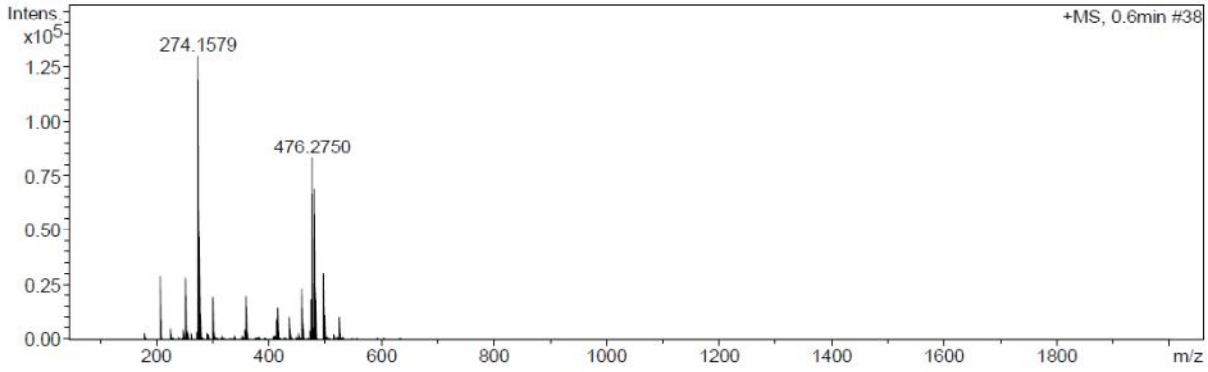
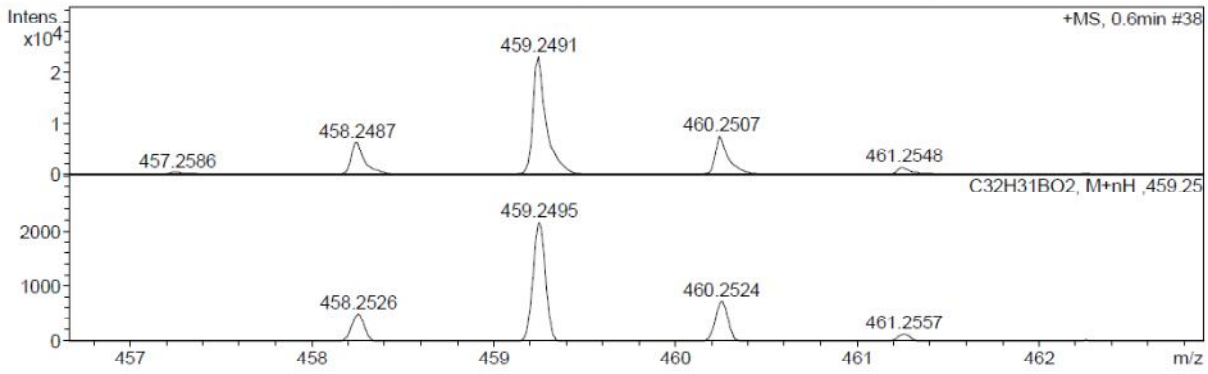
Method	tune_low.m	Operator	Ghanashyam Bhavsar
Sample Name	rm-tj-03-111__	Instrument	micrOTOF-Q II 10348
Comment			

Acquisition Parameter

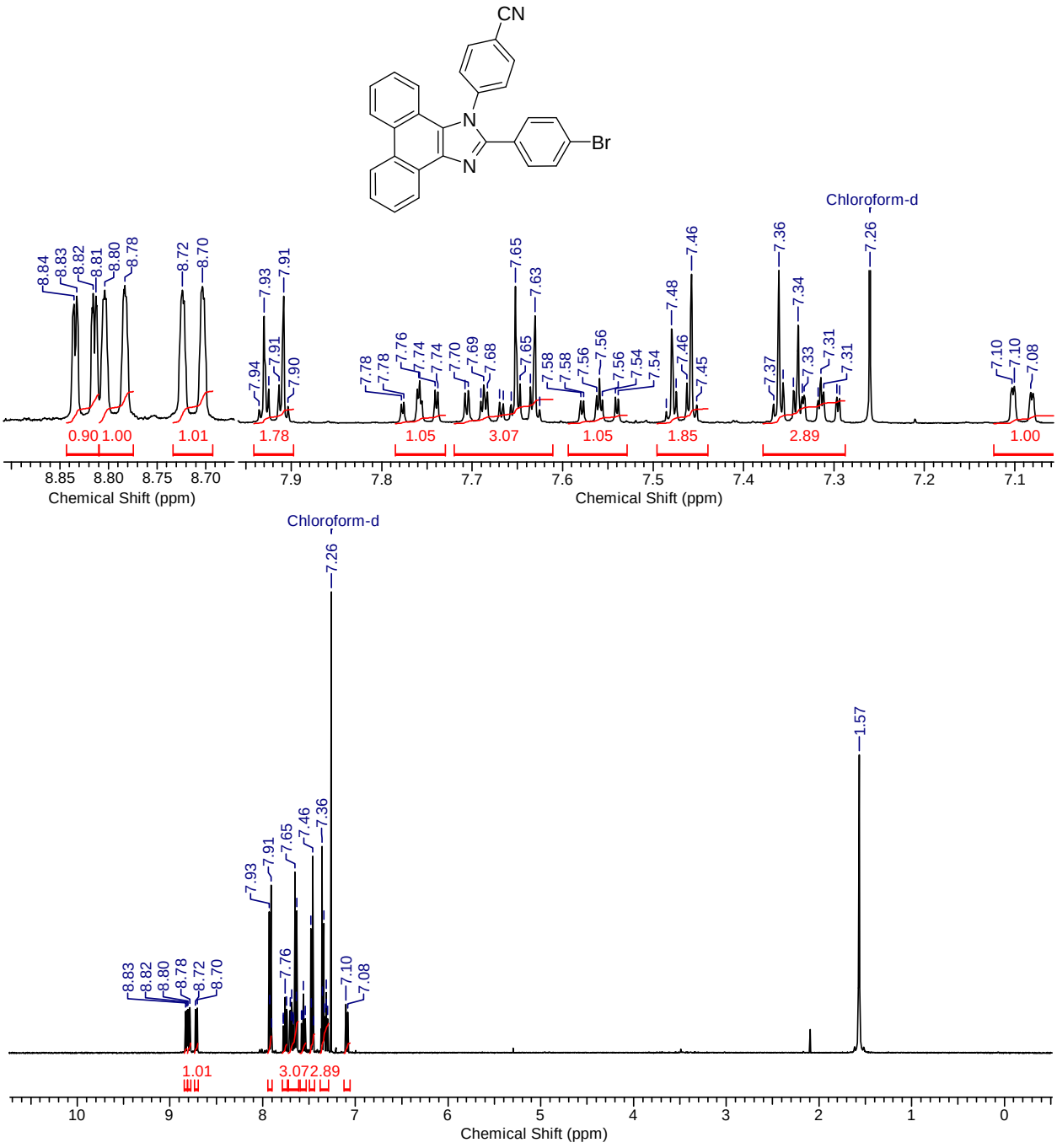
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	2000 m/z	Set Collision Cell RF	300.0 Vpp	Set Divert Valve	Waste



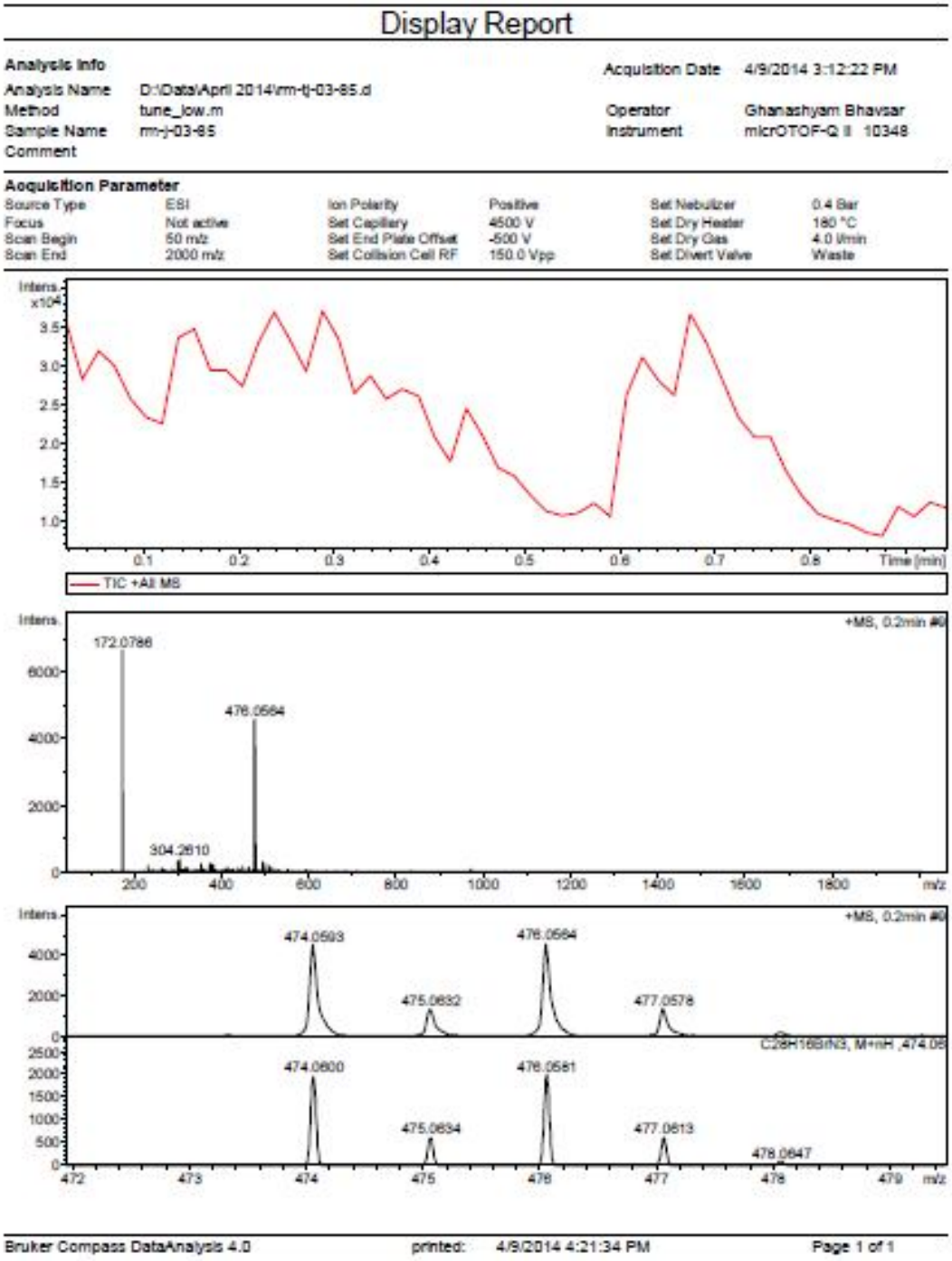




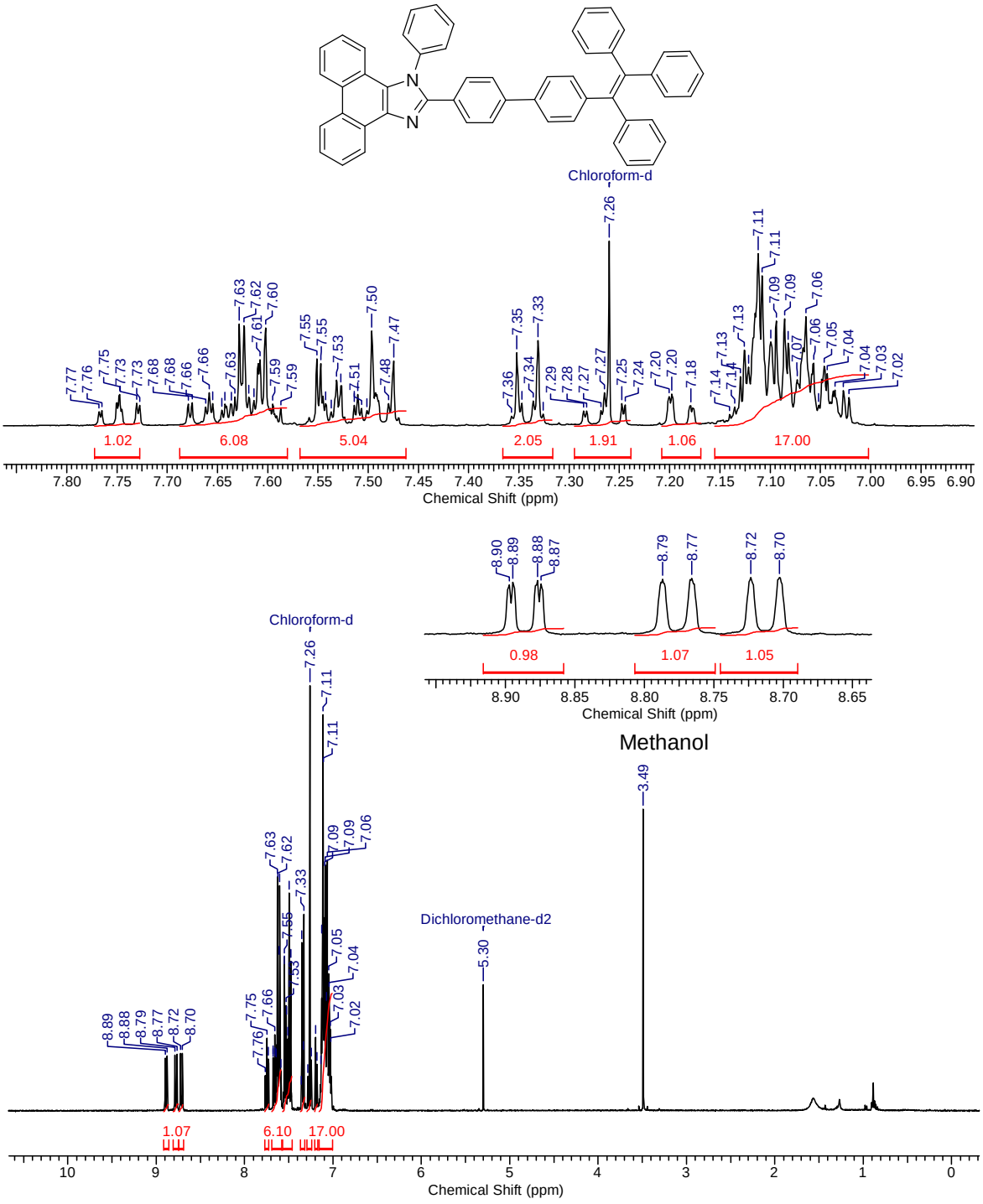
^{1}H NMR of **2b**


CN
N
N
Br
Chloroform-d
8.84
8.83
8.82
8.81
8.80
8.78
8.72
8.70
7.93
7.91
7.94
7.91
7.90
7.78
7.78
7.76
7.74
7.74
7.70
7.69
7.68
7.65
7.63
7.65
7.58
7.58
7.56
7.56
7.56
7.54
7.54
7.48
7.46
7.46
7.45
7.36
7.34
7.37
7.33
7.31
7.31
7.26
7.10
7.10
7.08
0.90 1.00
1.01
1.78
1.05
3.07
1.05
1.85
2.89
1.00
8.85 8.80 8.75 8.70
Chemical Shift (ppm)
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1
Chemical Shift (ppm)
Chloroform-d
7.26
1.57
8.83
8.82
8.80
8.78
8.72
8.70
7.93
7.91
7.65
7.46
7.36
7.76
7.10
7.08
1.01
3.072.89
10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)

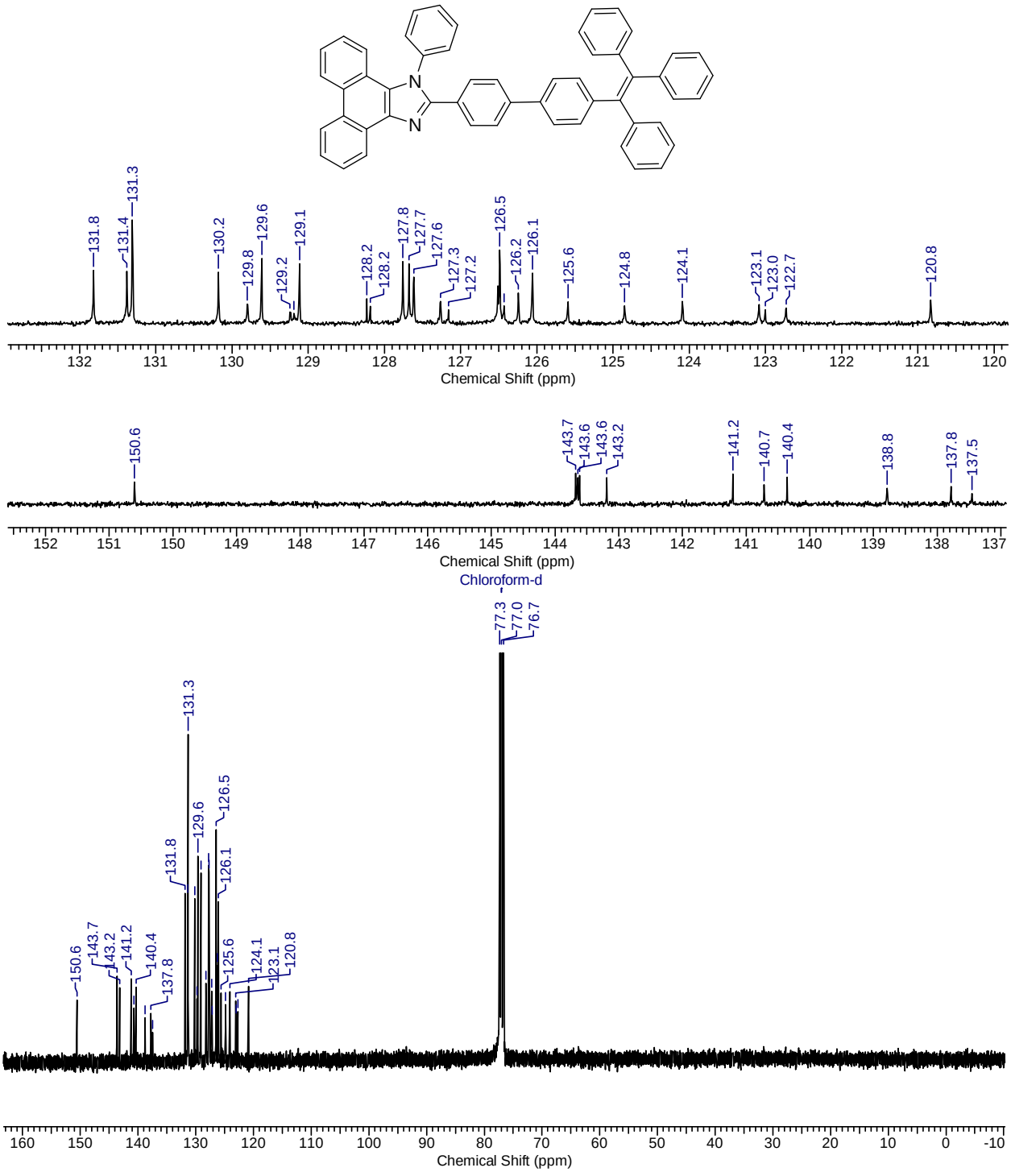
HRMS of **2b**


Display Report
Analysis Info
Analysis Name D:\Data\April 2014\rm-tj-03-85.d
Method tune_low.m
Sample Name rm-j-03-85
Comment
Acquisition Date 4/9/2014 3:12:22 PM
Operator Ghanashyam Bhavsar
Instrument micrOTOF-Q II 10348
Acquisition Parameter
Source Type ESI
Focus Not active
Scan Begin 50 m/z
Scan End 2000 m/z
Ion Polarity Positive
Set Capillary 4500 V
Set End Plate Offset -500 V
Set Collision Cell RF 150.0 Vpp
Set Nebulizer 0.4 Bar
Set Dry Heater 180 °C
Set Dry Gas 4.0 l/min
Set Divert Valve Waste
Intens.
x10^4
Time [min]
TIC +All MS
+MS, 0.2min #9
172.0786
476.0684
304.2610
m/z
474.0593
476.0684
475.0632
477.0578
C28H16BrN3, M+nH, 474.05
474.0600
476.0681
475.0634
477.0613
478.0647
Bruker Compass DataAnalysis 4.0
printed: 4/9/2014 4:21:34 PM
Page 1 of 1

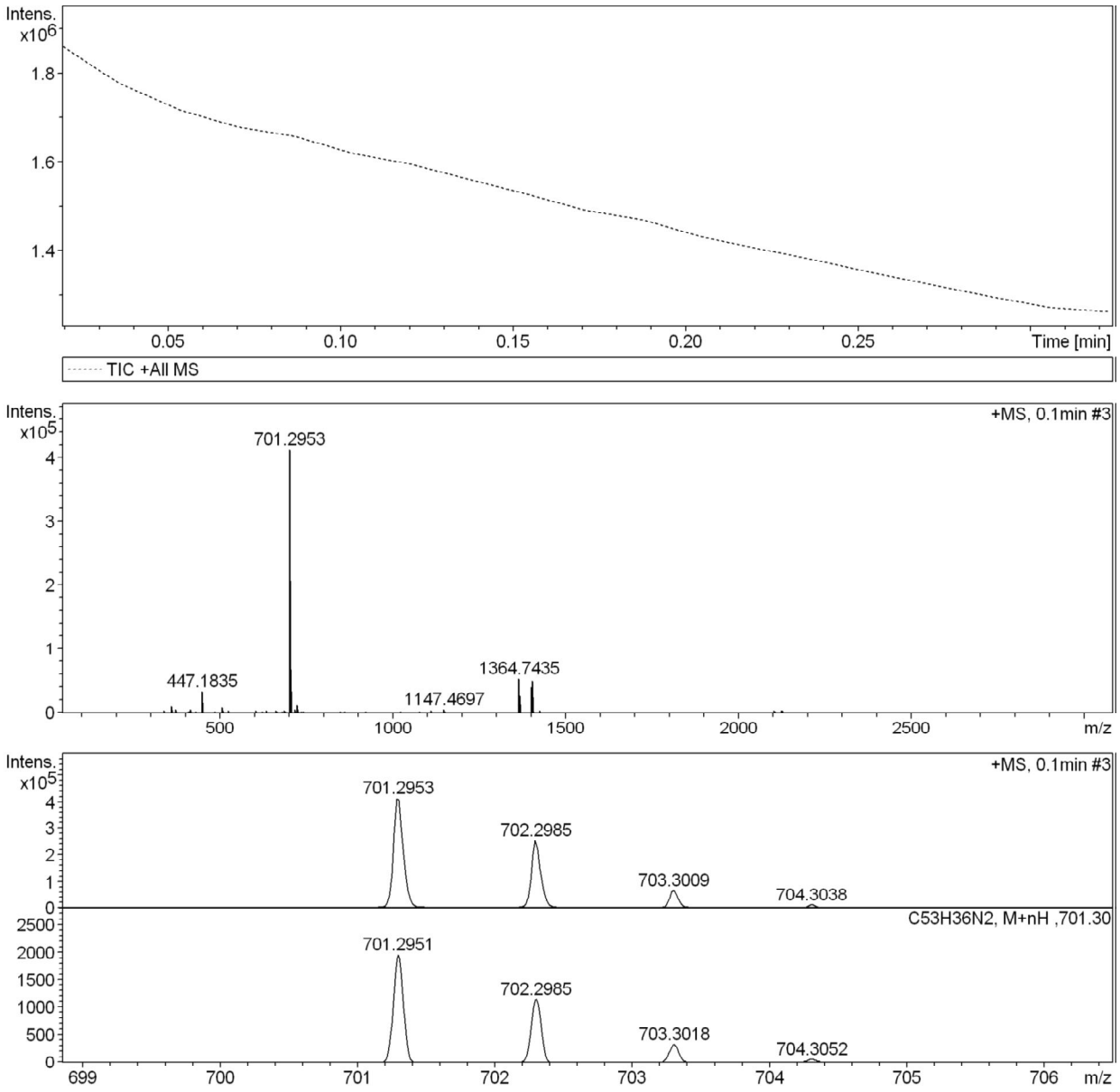
^{1}H NMR of **3a**


Chloroform-d
Chemical Shift (ppm)
Chloroform-d
Methanol
Dichloromethane-d2
Chemical Shift (ppm)

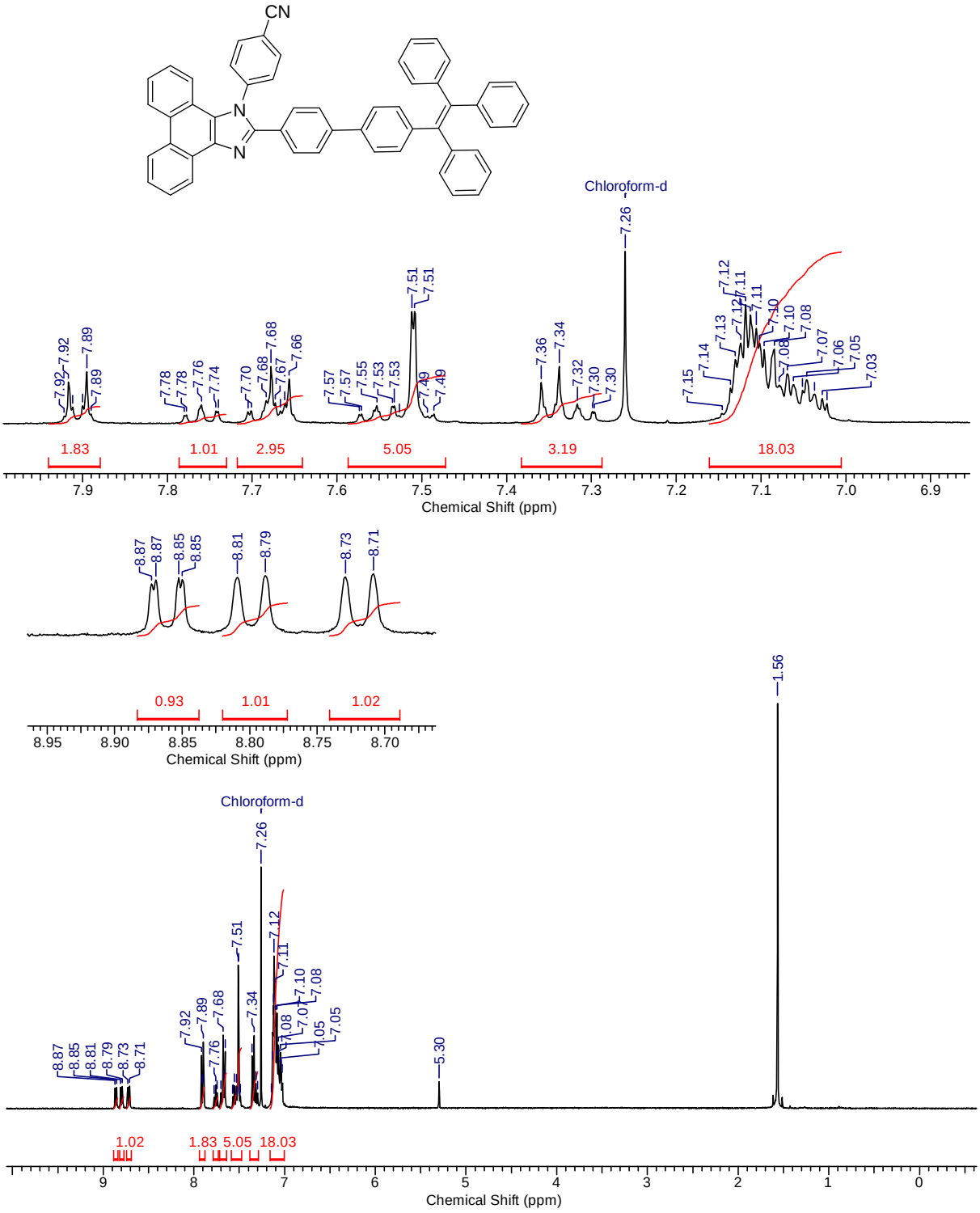
^{13}C NMR of **3a**


N
N
131.8
131.4
131.3
130.2
129.8
129.6
129.2
129.1
128.2
128.2
127.8
127.7
127.6
127.3
127.2
126.5
126.2
126.1
125.6
124.8
124.1
123.1
123.0
122.7
120.8
Chemical Shift (ppm)
150.6
143.7
143.6
143.6
143.2
141.2
140.7
140.4
138.8
137.8
137.5
Chemical Shift (ppm)
Chloroform-d
77.3
77.0
76.7
131.3
129.6
126.5
131.8
126.1
150.6
143.7
143.2
141.2
140.4
137.8
125.6
124.1
123.1
120.8
Chemical Shift (ppm)

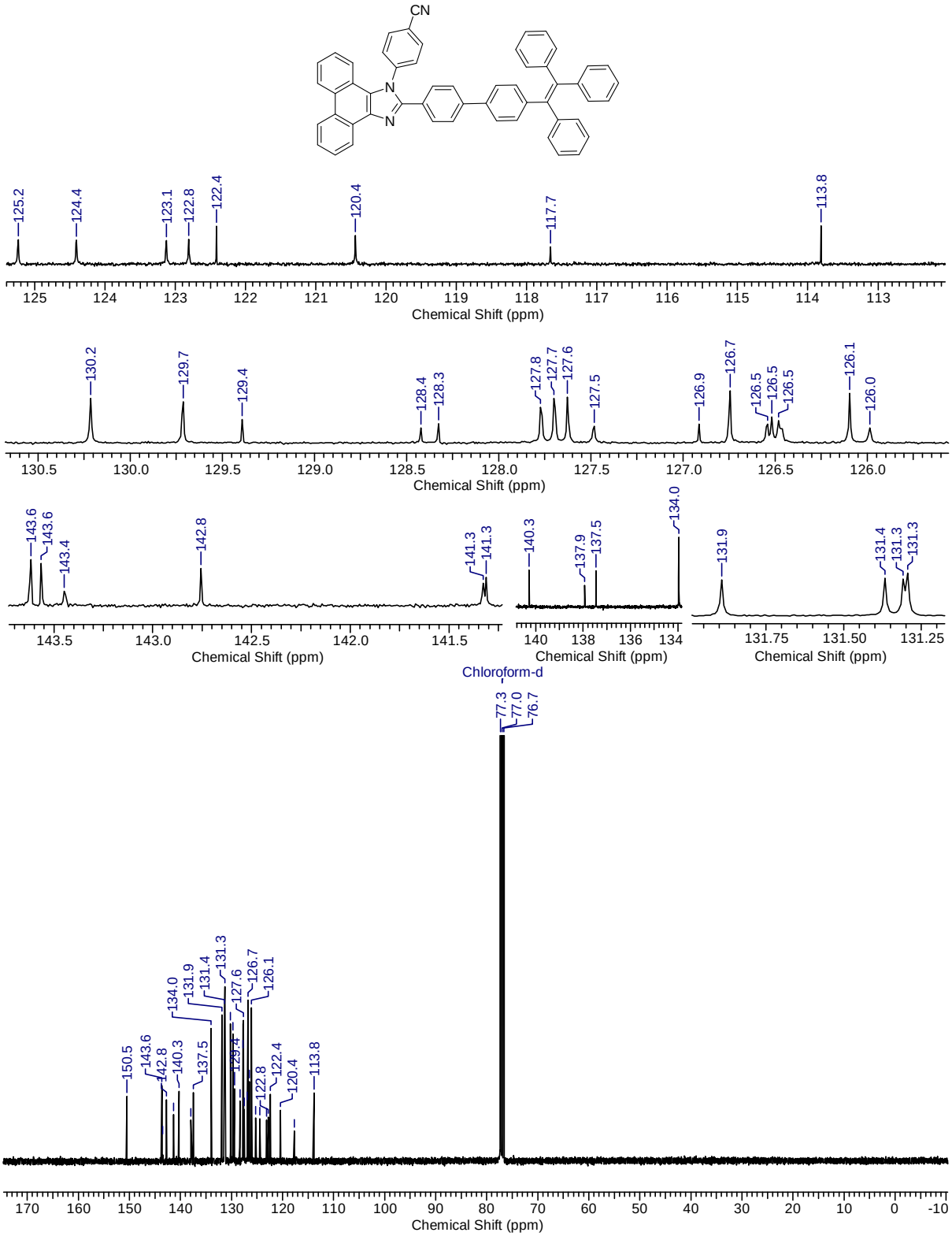
HRMS of **3a**


Intens.
x10^6
1.8
1.6
1.4
0.05
0.10
0.15
0.20
0.25
Time [min]
TIC +All MS
Intens.
x10^5
+MS, 0.1min #3
701.2953
447.1835
1147.4697
1364.7435
500
1000
1500
2000
2500
m/z
Intens.
x10^5
+MS, 0.1min #3
701.2953
702.2985
703.3009
704.3038
C53H36N2, M+nH ,701.30
701.2951
702.2985
703.3018
704.3052
699
700
701
702
703
704
705
706
m/z

^{1}H NMR of **3b**


CN
N
N
Chloroform-d
7.26
7.92
7.89
7.78
7.76
7.74
7.70
7.68
7.67
7.66
7.57
7.55
7.53
7.51
7.49
7.36
7.34
7.32
7.30
7.15
7.14
7.13
7.12
7.11
7.10
7.08
7.07
7.06
7.05
7.03
1.83
1.01
2.95
5.05
3.19
18.03
Chemical Shift (ppm)
8.87
8.85
8.81
8.79
8.73
8.71
0.93
1.01
1.02
Chemical Shift (ppm)
1.56
Chloroform-d
7.26
7.92
7.89
7.68
7.51
7.34
7.12
7.11
7.10
7.08
7.07
7.05
8.87
8.85
8.81
8.79
8.73
8.71
7.76
5.30
1.02
1.83
5.05
18.03
Chemical Shift (ppm)

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


CN
N
N
125.2
124.4
123.1
122.8
122.4
120.4
117.7
113.8
Chemical Shift (ppm)
130.2
129.7
129.4
128.4
128.3
127.8
127.7
127.6
127.5
126.9
126.7
126.5
126.5
126.5
126.1
126.0
Chemical Shift (ppm)
143.6
143.6
143.4
142.8
141.3
141.3
140.3
137.9
137.5
134.0
131.9
131.4
131.3
131.3
Chemical Shift (ppm)
Chemical Shift (ppm)
Chloroform-d
77.3
77.0
76.7
150.5
143.6
142.8
140.3
137.5
134.0
131.9
131.4
131.3
129.4
127.6
126.7
126.1
122.8
122.4
120.4
113.8
Chemical Shift (ppm)

HRMS of **3b**

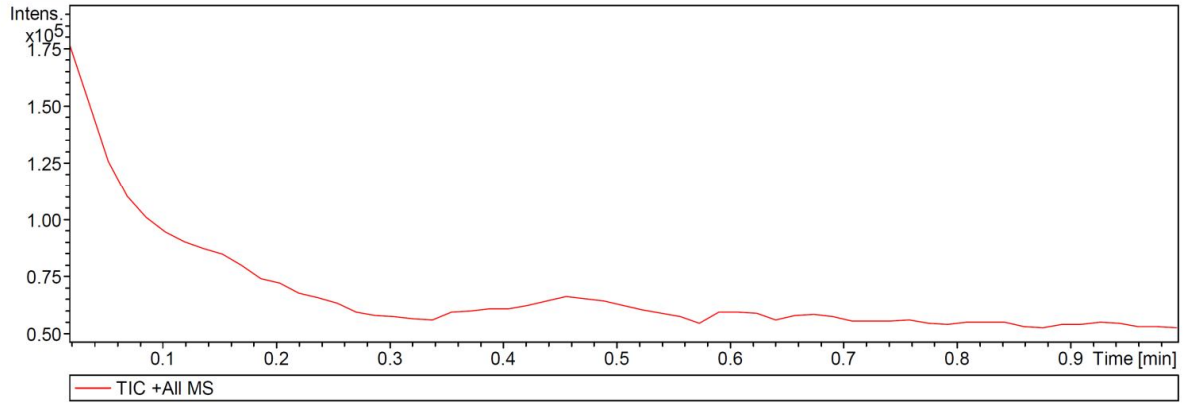
Display Report

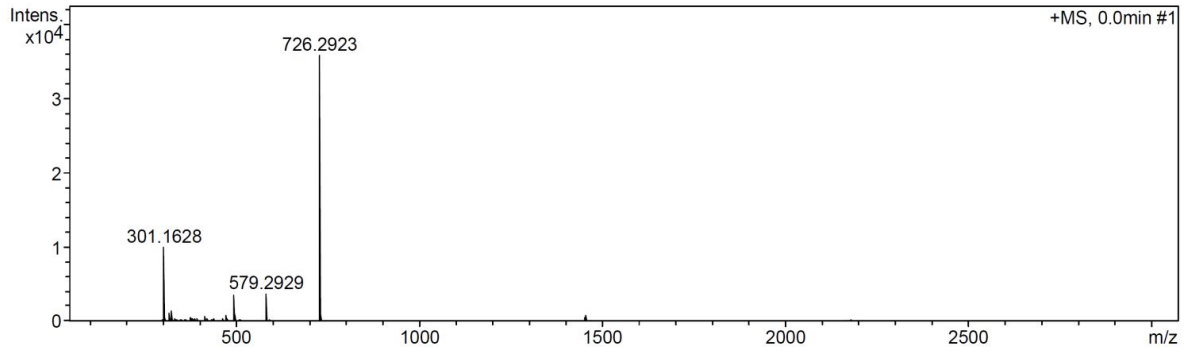
Analysis Info

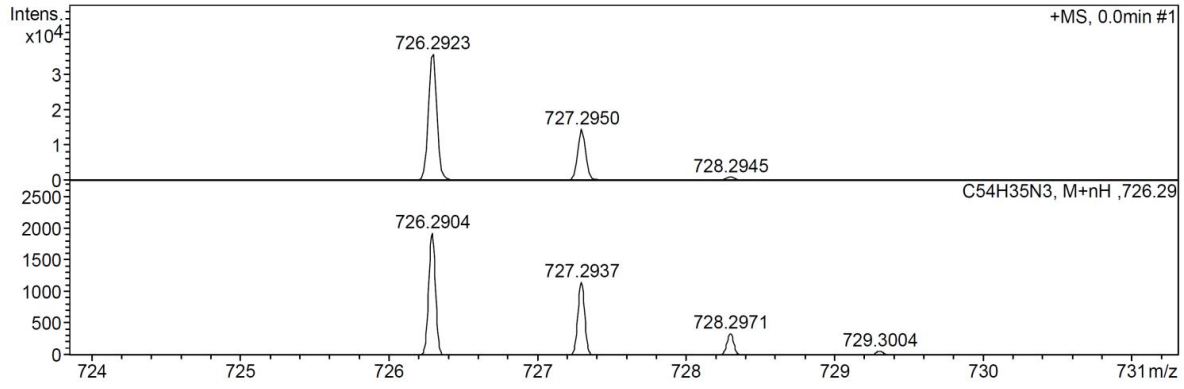
Analysis Name	D:\Data\January 2014\RM-TJ-03-90-1.d	Acquisition Date	1/28/2014 11:42:54 AM
Method	tune_wide.m	Operator	Ghanashyam Bhavsar
Sample Name	0	Instrument	micrOTOF-Q II 10348
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	650.0 Vpp	Set Divert Valve	Waste







References

1 (a) 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. Jr. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. 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, D. J. Fox, Gaussian 09, revision A.02; Gaussian, Inc.: Wallingford, CT, 2009. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B*, 1988, **37**, 785− 789. (c) Becke, A. D. *J. Chem. Phys.*, 1993, **98**, 1372−1377.

2 B. Mennucci, E. Cances and J. Tomasi, *J. Phys. Chem. B*, 1997, **101**, 10506−10517.

3 R. R. Hu, J. L. Maldonado, M. Rodriguez, C. M. Deng, C. K. W. Jim, J. W. Y. Lam, M. M. F. Yuen, G. R. Ortiz and B. Z. Tang, *J. Mater. Chem.*, 2012, **22**, 232–240.