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Synthesis of an antimony rhodamine analog

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N-(7-Dimethylamino-5-phenyl-10-(*o*-tolyl)dibenzo[*b*,*e*]stibinin-3(5*H*)-ylidene)-*N*-methylmethanaminium trifluoroacetate ([**6**][TFA]):

Compound **5** (0.500 g, 0.995 mmol) was dissolved in dry THF (100 ml) in a Schlenk flask under an atmosphere of purified nitrogen. After adding *n*-BuLi (1.5 M solution in hexanes, 1.9 mmol, 1.27 ml) at -78 °C, the mixture was slowly warmed to 0 °C. After stirring at this temperature for 2.5 hours, the mixture was cooled to -78 °C. A solution of $PhSbCl_2$ (0.260 g, 0.995 mmol) in THF (2 ml) was added very slowly over the course of 30 min. Once this addition completed, the mixture was allowed to warm to room temperature. It was kept at room temperature for 6 h and then refluxed under nitrogen for 4 h. All the volatiles were then removed under vacuum to afford a residue that was washed thoroughly with water (100 ml). This residue was dissolved in DCM (10 ml) before treated at 0 °C with *p*-chloroanil (0.230 g, 0.995 mmol) solution in DCM (20 ml). The reaction mixture was stirred at this temperature for 1 h. After evaporating the solvents, a crude dark blue solid was obtained. Subjecting this solid to column chromatography over neutral alumina (Methanol/DCM 95/5 (v/v) with 0.1 % TFAH) afforded [**6**][TFA] as a purple solid (35 mg, yield 5.4 %). ^{1}H NMR ($CDCl_3$): 7.59 (d, ^{4}J = 2.9Hz, 2H), 7.47-7.49 (m, 2H), 7.42(t, ^{3}J = 7.6 Hz, 1H), 7.34 (t, ^{3}J = 7.6 Hz, 1H), 7.31 (d, ^{3}J = 7.6 Hz, 1H), 7.22-7.25(m, 3H), 7.18 (d, ^{3}J = 9.7Hz, 2H), 7.08 (d, J = 7.6 Hz, 1H), 6.58 (dd, ^{3}J = 9.7 Hz, ^{4}J = 2.9 Hz, 2H), 3.37 (s, 12H), 1.86 (s, 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): 171.0, 153.4, 152.1, 142.5, 140.5, 139.4, 135.6, 135.0, 130.3, 129.2, 129.1, 128.9, 128.8, 125.7, 125.1, 124.5, 113.9, 41.1, 19.2. HRMS (M^+) Calculated: 539.1442, Observed: 539.1441.

N-(7-Dimethylamino-5-phenyl-10-(*o*-tolyl)dibenzo[*b,e*]stibinin-3(5*H*)-ylidene)-*N*-methylmethanaminium hexafluorophosphate **(**[**6**][PF_6]):

Salt [**6**][TFA] (100 mg) was dissolved in methanol (10 ml) and combined with an excess of KPF_6 (280 mg). After stirring for 2 h, the solvent was evaporated, and the residue was washed with water (100 ml). This procedure afforded [**6**][PF_6] as a purple solid (100 mg, 96% Yield).

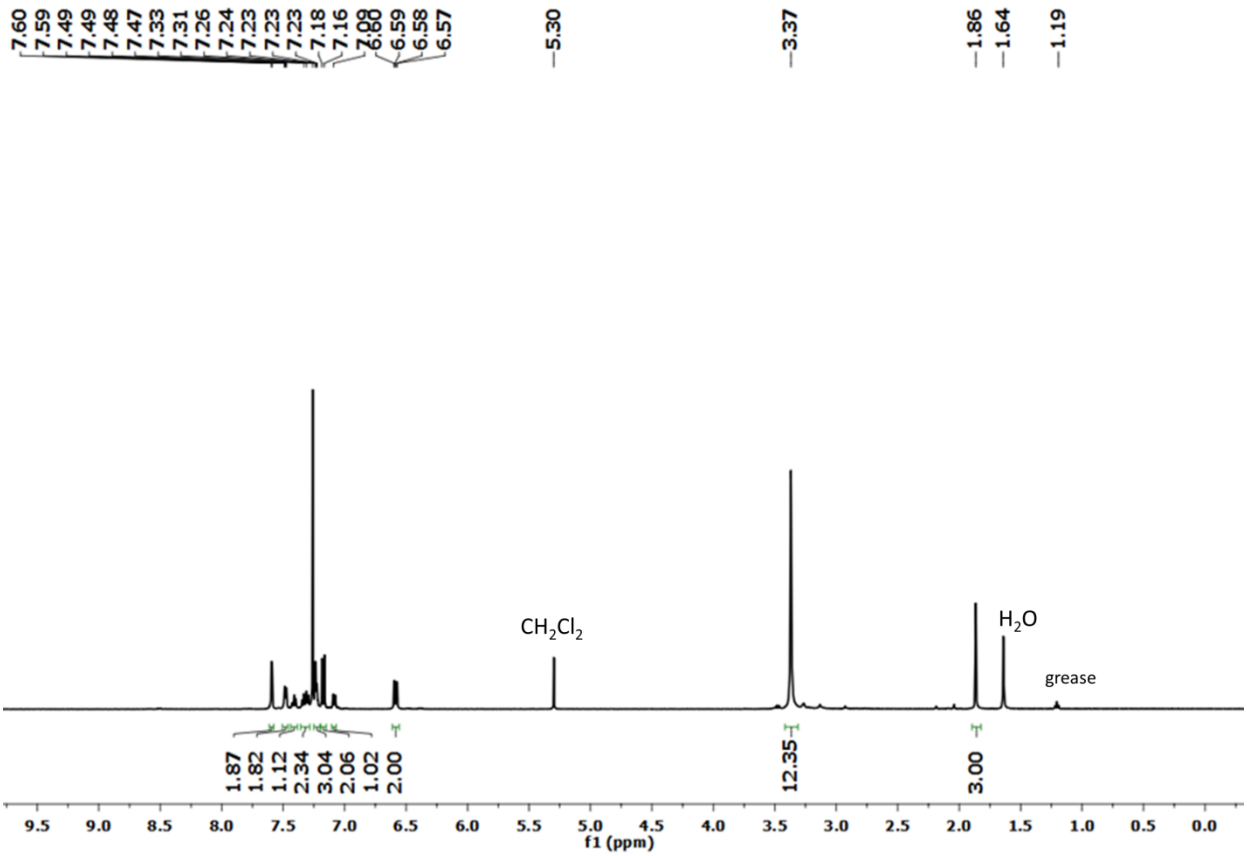

Figure S1: ^{1}H NMR spectrum of [**6**][TFA] in $CDCl_3$

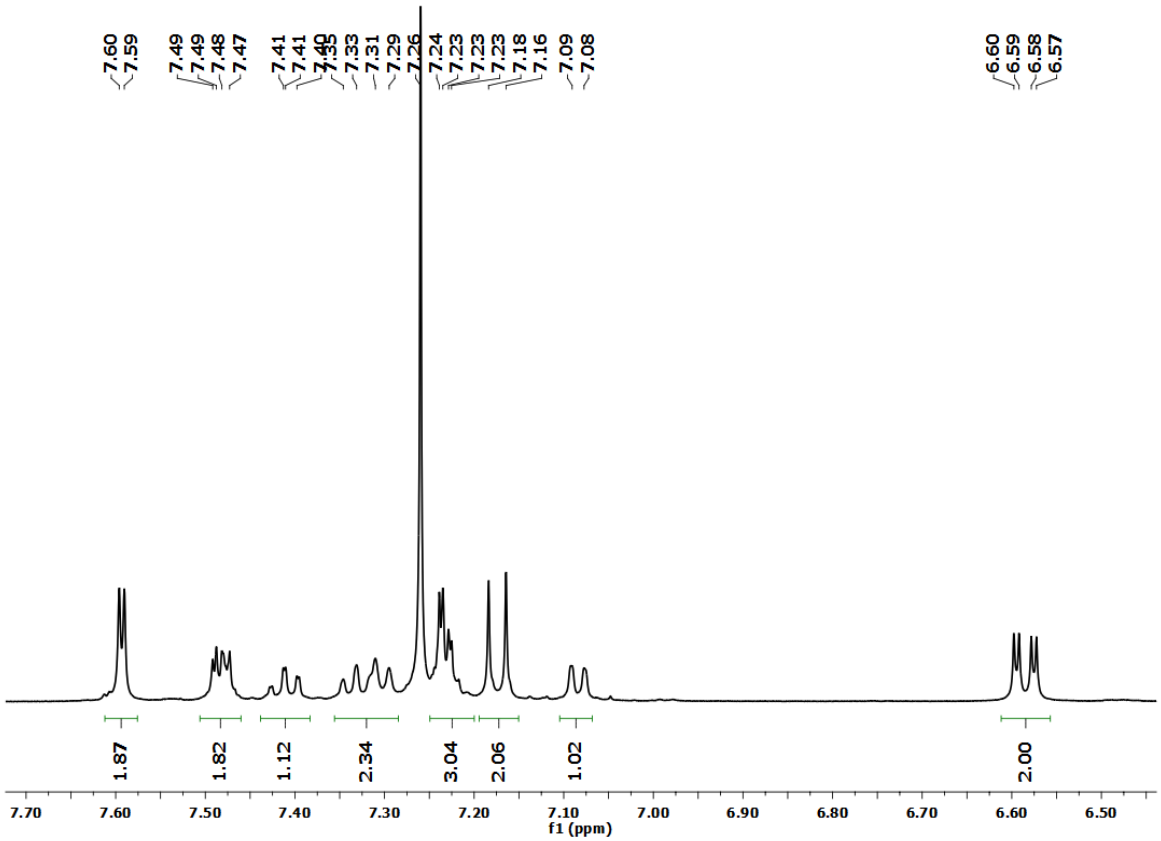

Figure S2: ^{1}H NMR spectrum of [**6**][TFA] in $CDCl_3$ (aromatic region expanded)

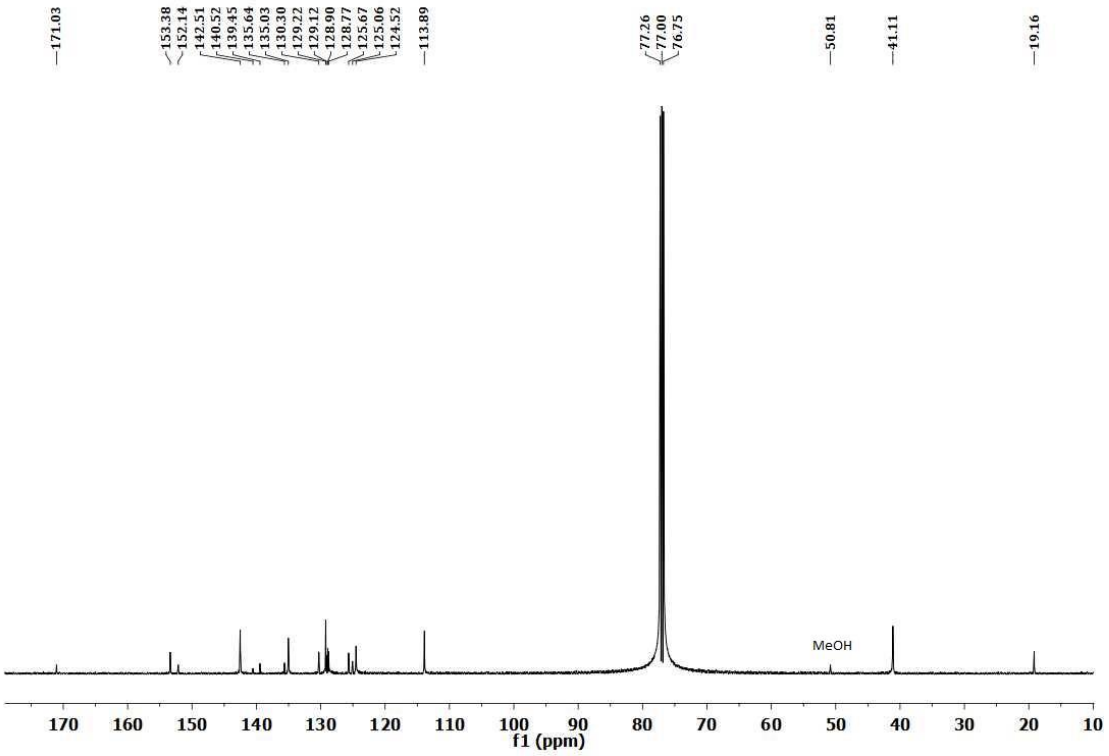

Figure S3: $^{13}C\{^{1}H\}$ NMR spectrum of [**6**][TFA] in $CDCl_3$

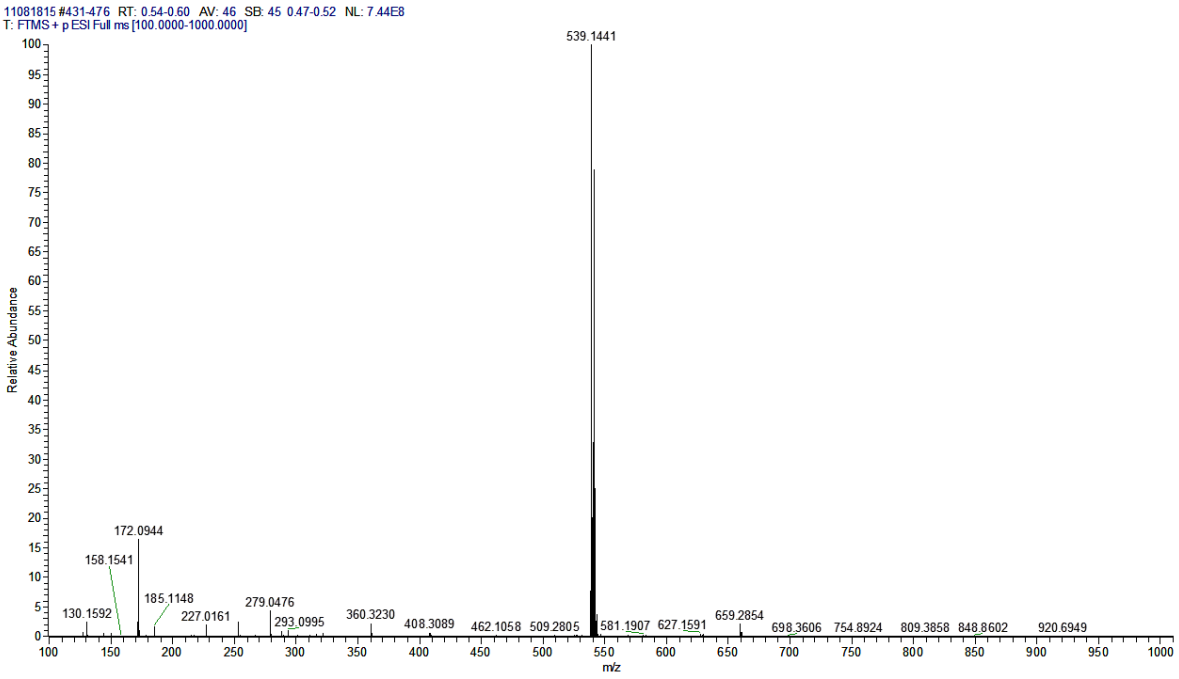

Figure S4: HRMS of [**6**][TFA]

Quantum Yield Measurement:[1]

Fluorescence quantum yields were obtained from gradients of integrated emission (IE) versus absorbance at λ_{exc}(Abs) of series of measurements for [**6**][TFA] and reference (Cresyl Violet), according to the following equation.

$$\Phi_{sample} = \Phi_{std} \times \frac{IE_{sample}}{IE_{std}} \times \frac{Abs_{std}}{Abs_{sample}} \times \left(\frac{\eta_{sample}}{\eta_{std}}\right)^2 = \Phi_{std} \times \frac{Grad_{sample}}{Grad_{std}} \times \left(\frac{\eta_{sample}}{\eta_{std}}\right)^2$$

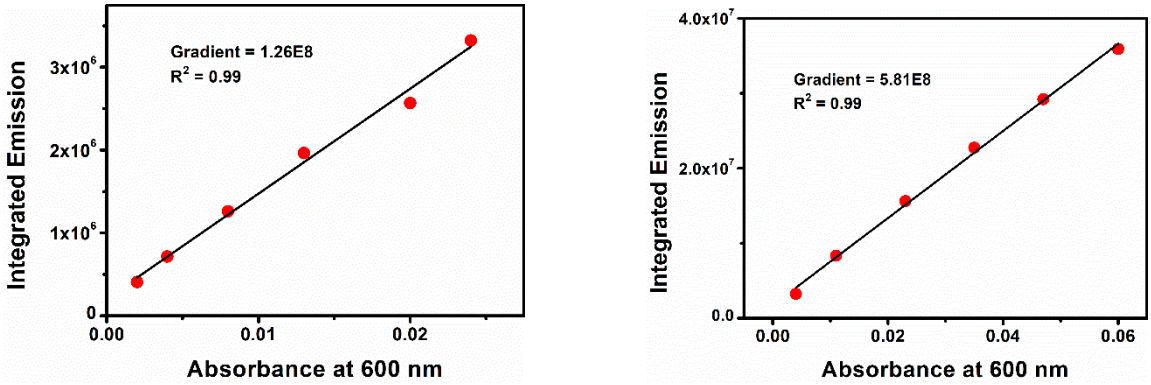

Figure S5: Quantum yield gradient plot of [**6**][TFA] (left) and cresyl violet (right)

Coordinates of $[6]^+$ (gas phase)

Sb	-0.02731825	-2.16211187	-0.28548054
C	2.44293724	1.48836605	-0.72971267
H	2.32664843	2.56324305	-0.65479864
N	5.15253696	-0.90862856	-1.27199182
C	-3.94637267	-0.32763374	-1.02668059
C	-2.43690039	1.53119607	-0.64189200
H	-2.30784676	2.59882704	-0.51139372
C	-0.03820501	-1.55714798	1.78821005
N	-5.18096965	-0.80616503	-1.26160195
C	3.92472456	-0.40416018	-1.05296271
C	0.00538067	1.28010040	-0.51704004
C	-1.25917091	-0.97863606	3.79867348
H	-2.20459793	-0.83748491	4.31312690
C	1.16180548	-1.34240203	2.47063068
H	2.11559772	-1.46748313	1.96173732
C	-1.28642883	0.68294822	-0.62449583
C	0.07472565	5.49198723	0.23415987
H	0.09231444	6.55793966	0.43599231
C	-6.32094339	0.10237410	-1.31732961
H	-6.45745895	0.62027935	-0.36241656
H	-6.18824796	0.84572314	-2.10982387
H	-7.22115221	-0.47096881	-1.52995885
C	0.02793897	2.75564713	-0.25730450
C	1.15170719	-0.94516772	3.80681223
H	2.08949129	-0.77789744	4.32759143
C	-1.54120492	-0.72210310	-0.74373640
C	1.28400414	0.65623906	-0.64881576
C	2.78124555	-1.25451892	-0.93077939
H	2.92218556	-2.32872704	-0.98741723
C	0.15637135	3.20694060	1.06671232
C	0.29074850	2.23244006	2.21003417

H	-0.49098917	1.46384927	2.18783730
H	1.25062788	1.70453813	2.16809740
H	0.23317137	2.74931923	3.17049934
C	-3.70836462	1.06159253	-0.83578731
H	-4.53017636	1.76556126	-0.84841348
C	1.51635794	-0.75376166	-0.73718730
C	5.34985710	-2.34679156	-1.41057699
H	5.07961845	-2.87354094	-0.48912171
H	4.75324309	-2.74543719	-2.23710899
H	6.39974476	-2.54105835	-1.62129590
C	6.30348689	-0.01820052	-1.37226138
H	6.18423151	0.68263071	-2.20484823
H	6.44190326	0.54927381	-0.44632555
H	7.19770966	-0.61306454	-1.54796940
C	-0.05857939	-0.75995356	4.47083336
H	-0.06646519	-0.44974034	5.51070370
C	3.70561025	0.99505379	-0.92314971
H	4.53405205	1.68832308	-0.98769769
C	-5.39940291	-2.23545320	-1.45258096
H	-4.79998743	-2.61342651	-2.28652409
H	-5.14761614	-2.79900209	-0.54776830
H	-6.44973561	-2.40515399	-1.68144536
C	-0.04638186	5.02982499	-1.07342017
H	-0.12259979	5.72864535	-1.89967912
C	-2.81440856	-1.19857006	-0.93873451
H	-2.97298182	-2.26889508	-1.01820741
C	-0.07237663	3.65982954	-1.31641731
H	-0.17031305	3.28328395	-2.33134593
C	0.17277161	4.58619295	1.28670665
H	0.26557501	4.95222220	2.30541942
C	-1.24895991	-1.37649851	2.46296184
H	-2.19551883	-1.52890790	1.94801893