

Electrofluorochromic Switching of Heat-induced Cross-linkable Multi Styryl-terminated Triphenylamine and Tetraphenylethylene Derivatives

Kang Le Osmund Chin,^a Pin Jin Ong,^b Qiang Zhu,^{a, b} Jianwei Xu,^{*, a, c} Ming Hui Chua^{*, a}

a. Institute of Sustainability for Chemicals, Energy and Environment (ISCE²), Agency for Science, Technology and Research (A*STAR), Singapore. 1 Pesek Road, Jurong Island, Singapore 627833

b. Institute of Materials Research and Engineering (IMRE), Agency for Science, Technology and Research (A*STAR), Singapore. 2 Fusionopolis Way, Innovis, #08-03, Singapore 138634

c. Department of Chemistry, National University of Singapore (NUS), Singapore. 3 Science Drive 3, Singapore 117543

* Corresponding: M. H. Chua (chua_ming_hui@isce2.a-star.edu.sg); J. Xu (xu_jianwei@isce2.a-star.edu.sg)

CONTENT

Figure	Figure Caption	Page
S1	FTIR spectra of M1 – M4 before and after heating	2
S2	Normalized absorption and fluorescence spectra of M1 – M4 in chloroform solutions	2
S3	Cyclic voltammograms of M1 – M4 in solution and in device forms.	3
S4	Normalized absorption spectra of M1 – M4 thin films before and after heating	3
S5	Chronoabsorptometry studies: Transmittance changes of heated M1 – M4 at 715, 930, 505, and 875 nm, successively, recorded upon switching at ± 2.0 V at different time intervals (Δt)	4
S6	EC switching stability studies of M2 at applied voltages of ± 2.0 V and Δt of 30 s	4
S7	EC switching stability studies of M3 at applied voltages of ± 2.0 V and Δt of 30 s	5
S8	EC switching stability studies of M4 at applied voltages of ± 2.0 V and Δt of 30 s	5
S9	Fluorescence intensity changes of heated (a) M1 , (b) M2 , (c) M3 , and (d) M4 at 500, 500, 510, and 535 nm, respectively, with applied voltages of ± 2.0 V at Δt of 30 s	6
S10	Fluorescence intensity changes of heated M2 at 500 nm with applied voltages of ± 2.0 V at different Δt s	6
S11	Fluorescence intensity changes of heated (a) M3 and (b) M4 at 510 and 535 nm, respectively, with applied voltages of -2.2 / +1.6 and -2.2 / +1.8 V, at Δt of 30 s	7
Table	Table Caption	
S1	Fluorescence quantum yield (Φ_{FL}) of EFC devices	7
ANNEX 1: NMR Spectroscopy		8
ANNEX 2: High Resolution Mass Spectrometry (HRMS)		14

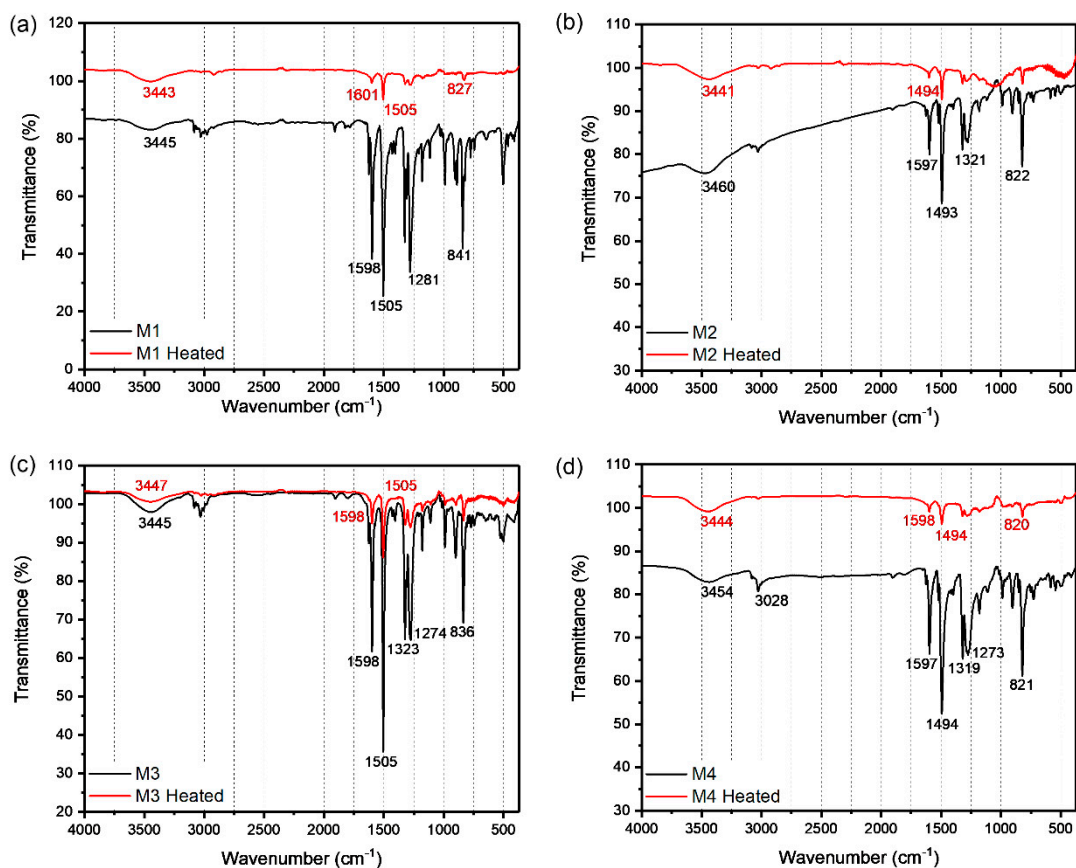


Figure S1. FTIR spectra of **M1** – **M4** before and after heating.

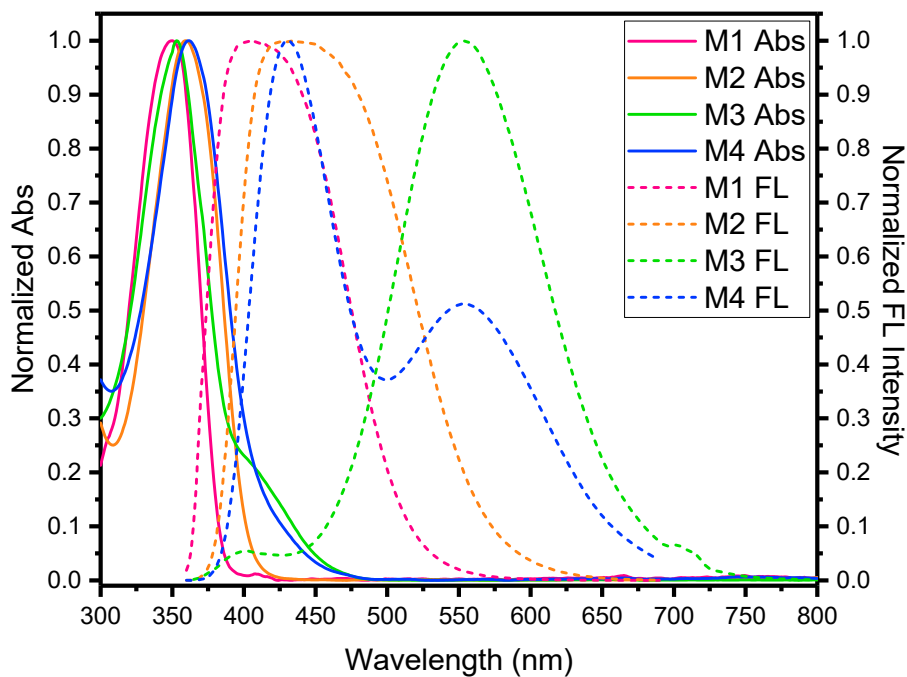


Figure S2. Normalized absorption and fluorescence spectra of **M1** – **M4** in chloroform solutions.

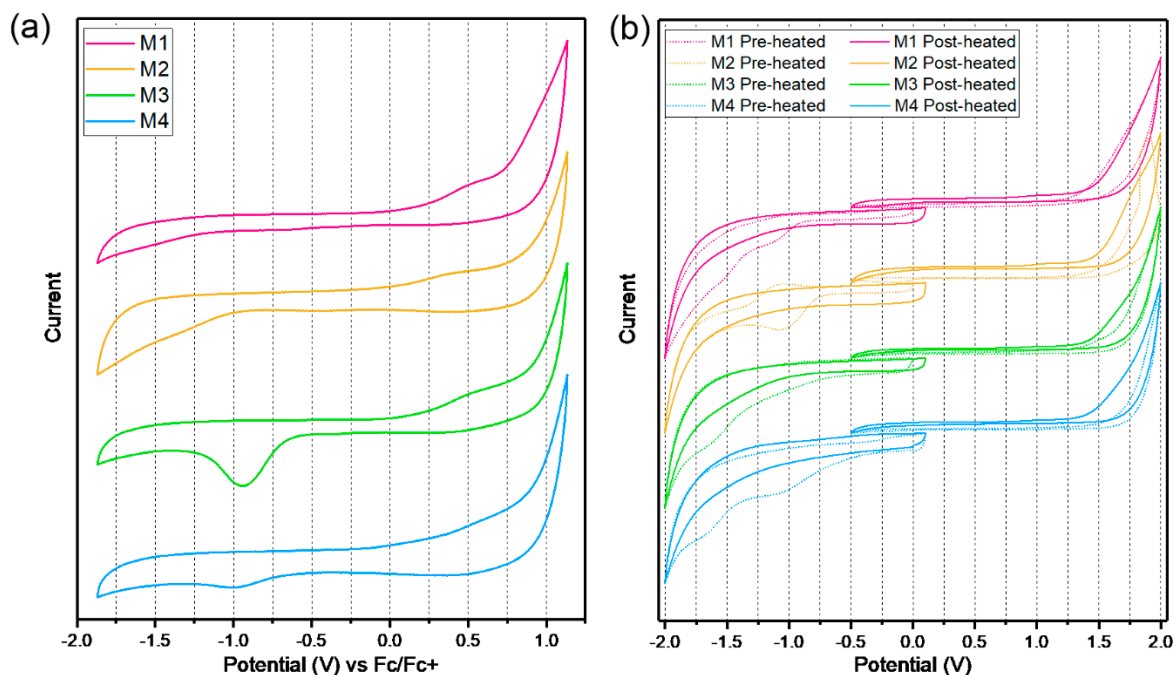


Figure S3. (a) Cyclic voltammograms of **M1** – **M4** in solution containing tetrabutylammonium hexafluorophosphate electrolyte (~0.1 M in DCM) calibrated against ferrocene reference. (b) Cyclic voltammograms of electrochromic devices (ECDs) containing pre- and post-heated **M1** – **M4**.

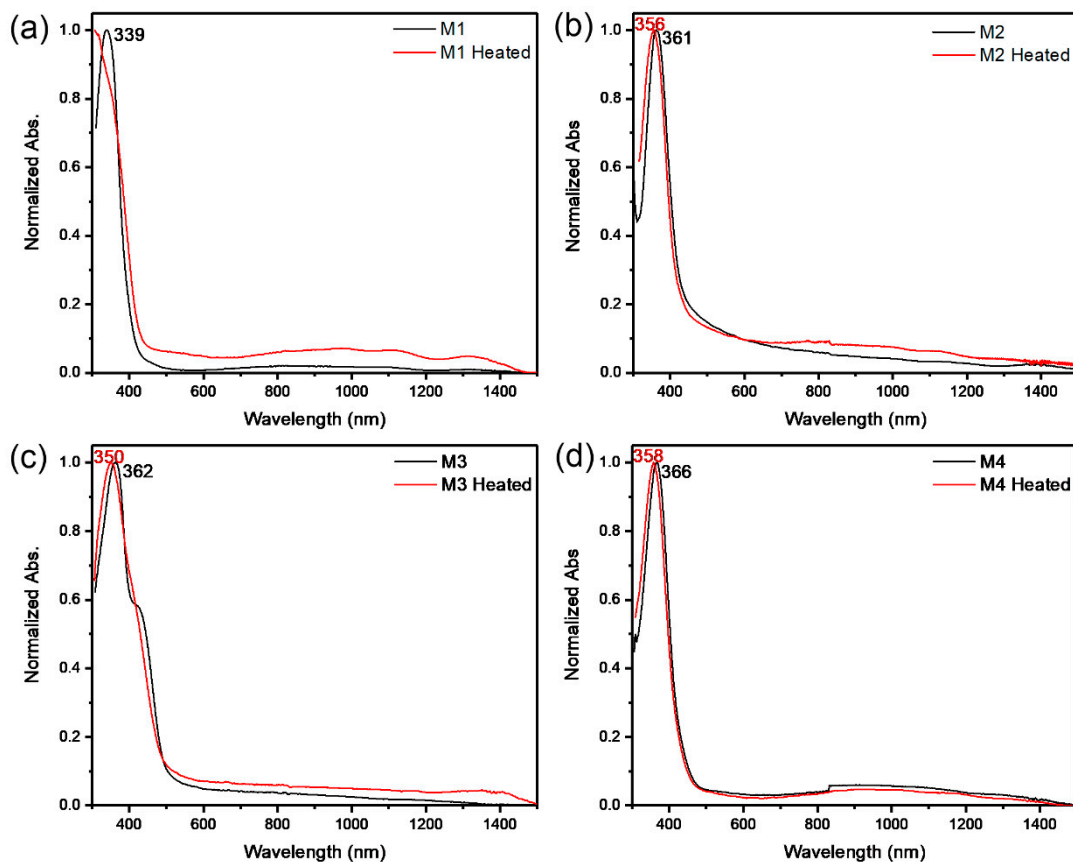


Figure S4. Normalized absorption spectra of **M1** – **M4** thin films before and after heating.

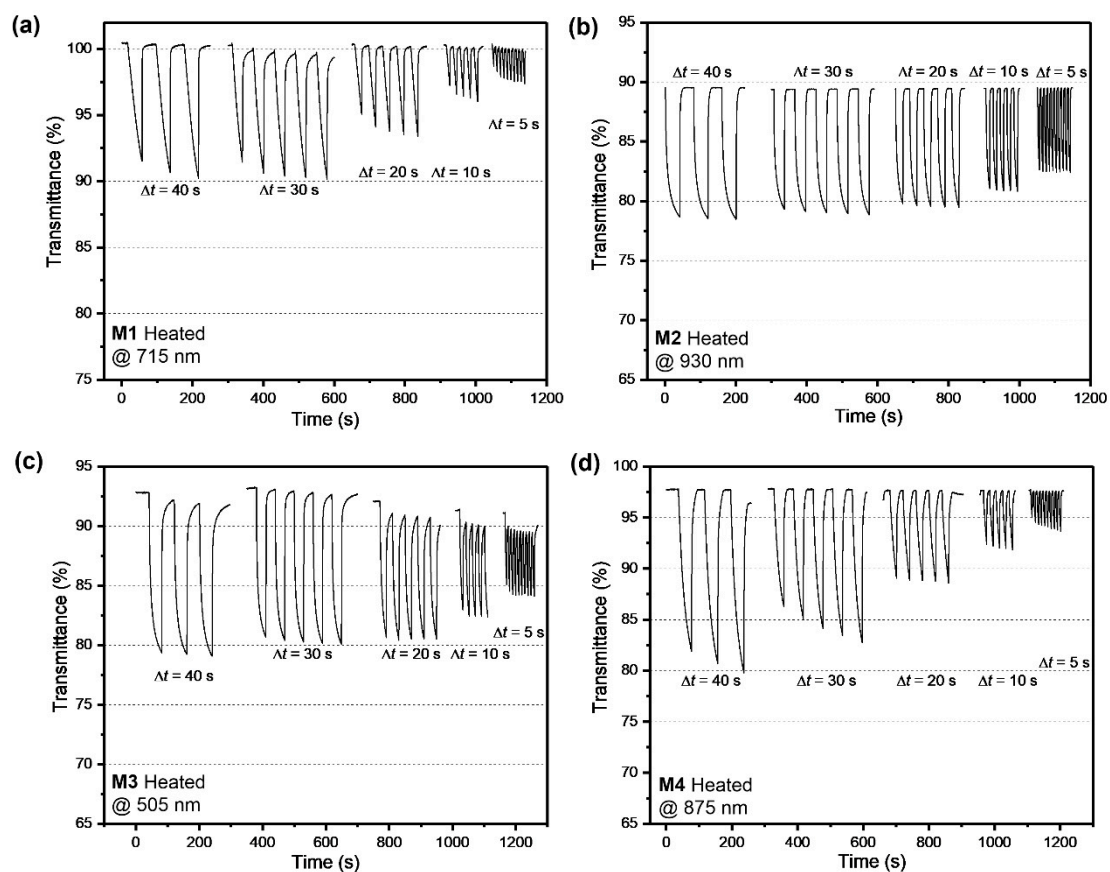


Figure S5. Chronoabsorptometry studies: Transmittance changes of heated **M1** – **M4** at 715, 930, 505, and 875 nm, successively, recorded upon switching at ± 2.0 V at different time intervals (Δt).

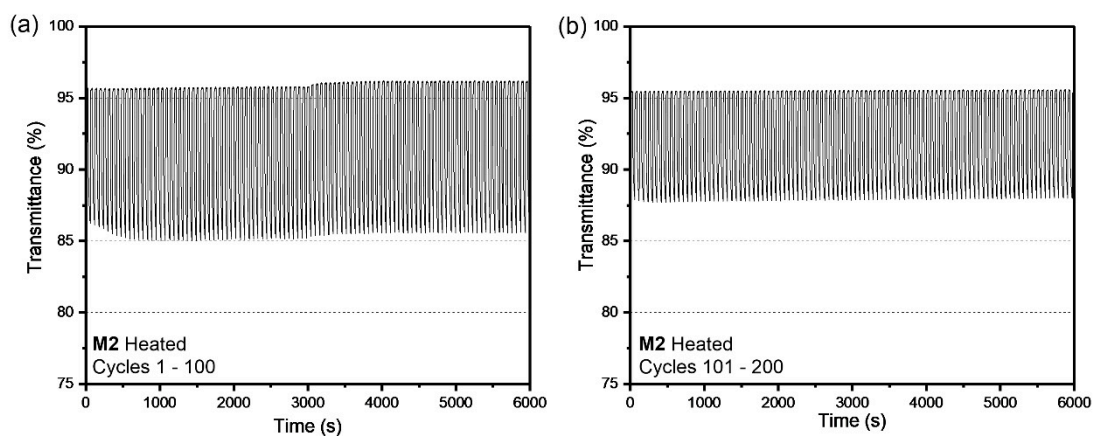


Figure S6. EC switching stability studies of **M2** at applied voltages of ± 2.0 V and Δt of 30 s.

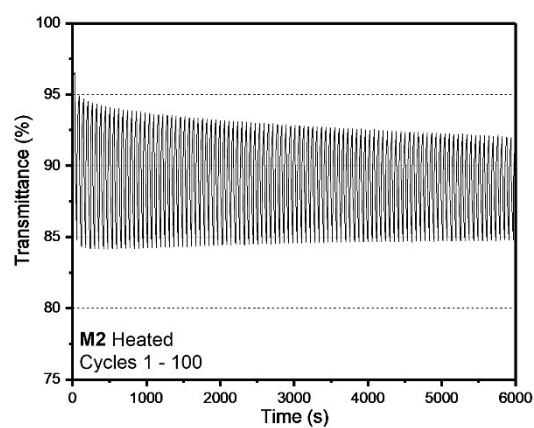


Figure S7. EC switching stability studies of **M3** at applied voltages of ± 2.0 V and Δt of 30 s.

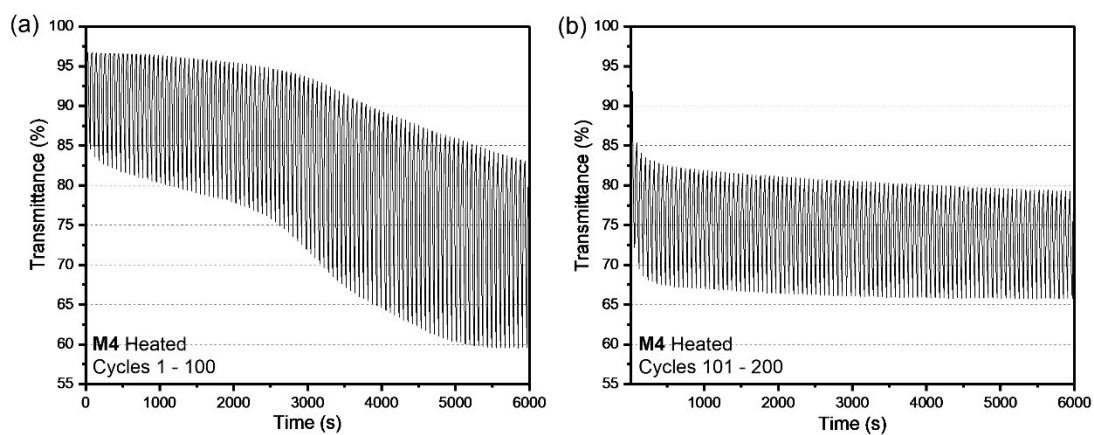


Figure S8. EC switching stability studies of **M4** at applied voltages of ± 2.0 V and Δt of 30 s.

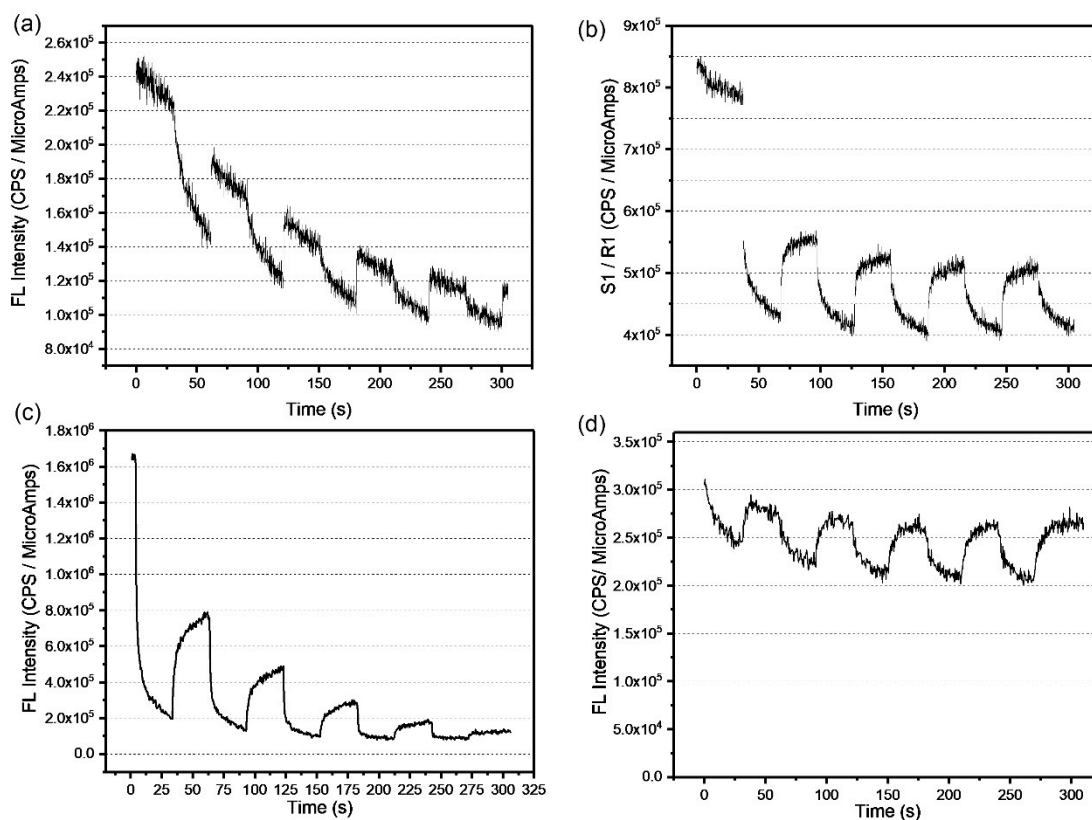


Figure S9. Fluorescence intensity changes of heated (a) **M1**, (b) **M2**, (c) **M3**, and (d) **M4** at 500, 500, 510, and 535 nm, respectively, with applied voltages of ± 2.0 V at Δt of 30 s.

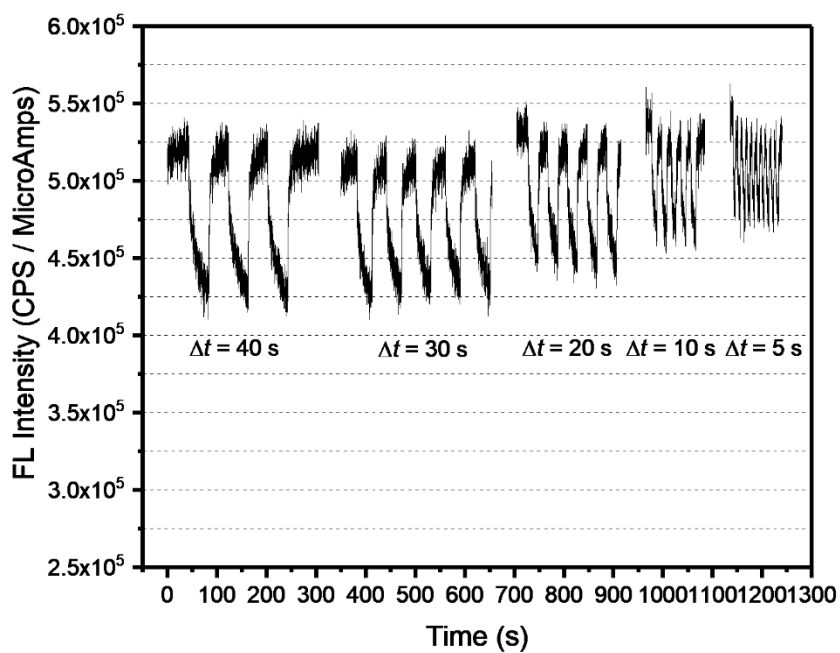


Figure S10. Fluorescence intensity changes of heated **M2** at 500 nm with applied voltages of ± 2.0 V at different Δt s.

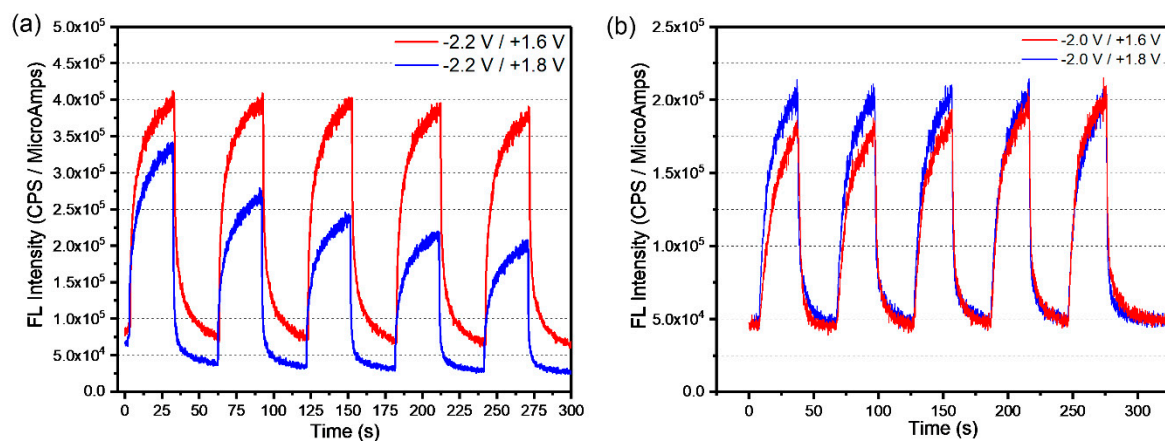


Figure S11. Fluorescence intensity changes of heated (a) **M3** and (b) **M4** at 510 and 535 nm, respectively, with applied voltages of -2.2 / +1.6 and -2.2 / +1.8 V, at Δt of 30 s.

Table S1. Fluorescence quantum yield (Φ_{FL}) of EFC devices

Compound	Treatment of coated substrate	λ_{FL} (nm)	Φ_{FL} at 0.0 V (%)	Φ_{FL} at +2.0 V (%)
M1	Without Heating	438	5.08	0.92
	With Heating	503	3.25	0.12
M2	Without Heating	467	2.08	1.57
	With Heating	500	5.13	3.43
M3	Without Heating	510	3.34	2.39
	With Heating	525	1.39	0.03
M4	Without Heating	534	6.29	0.94
	With Heating	535	4.51	0.37

ANNEX 1: NMR Spectroscopy

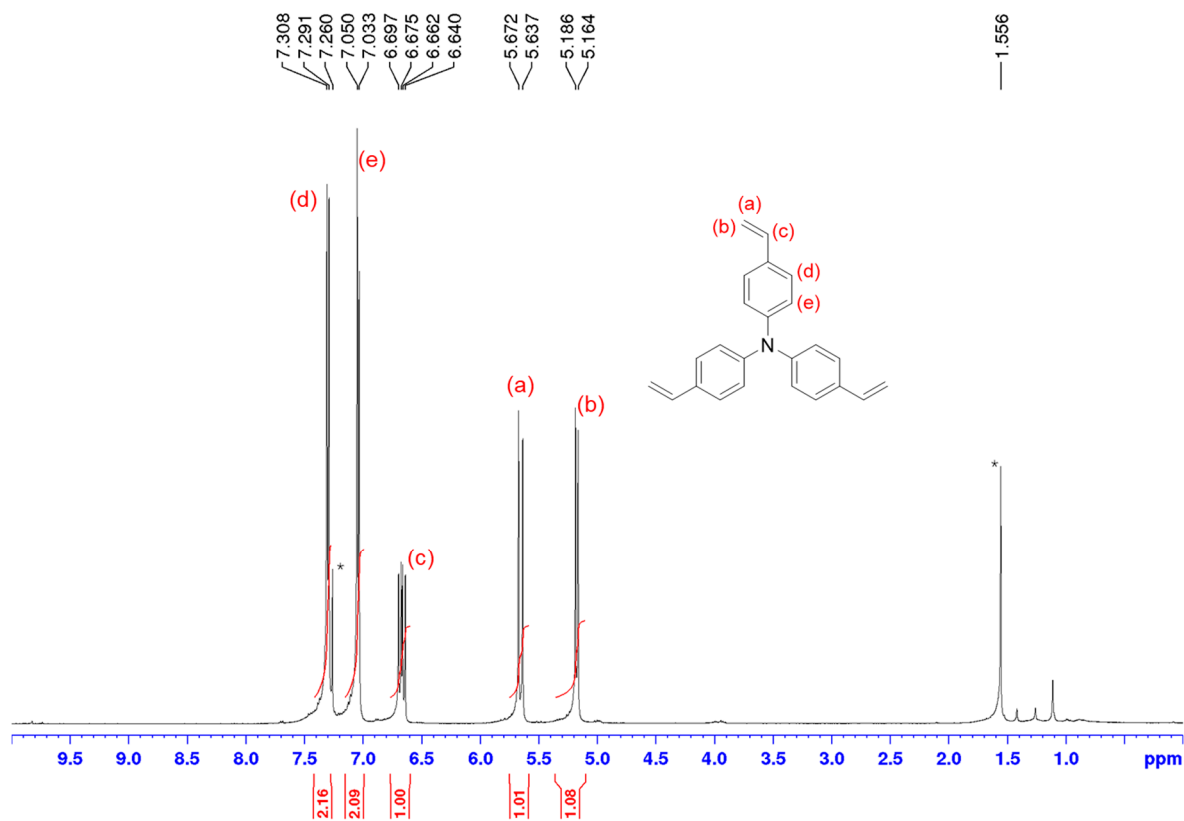


Figure S12. ¹H NMR of **M1** in CDCl₃

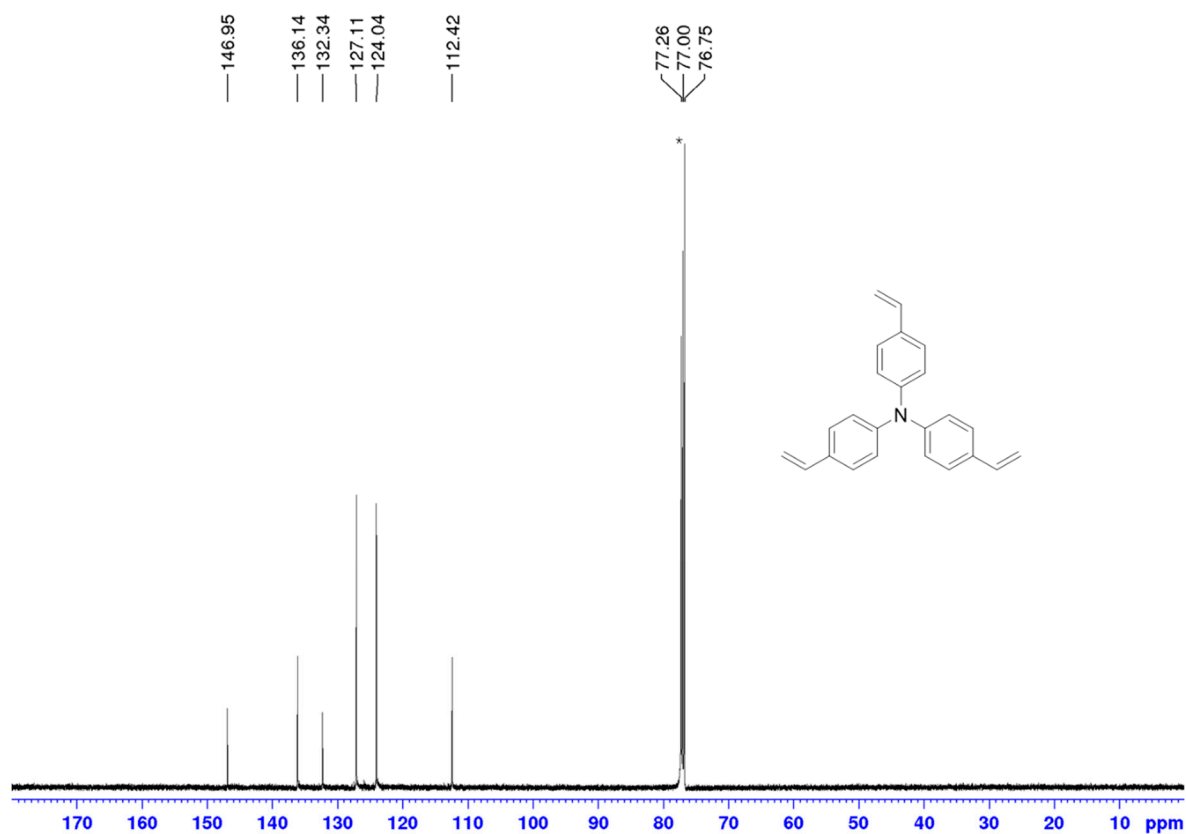


Figure S13. ¹³C NMR of **M1** in CDCl₃

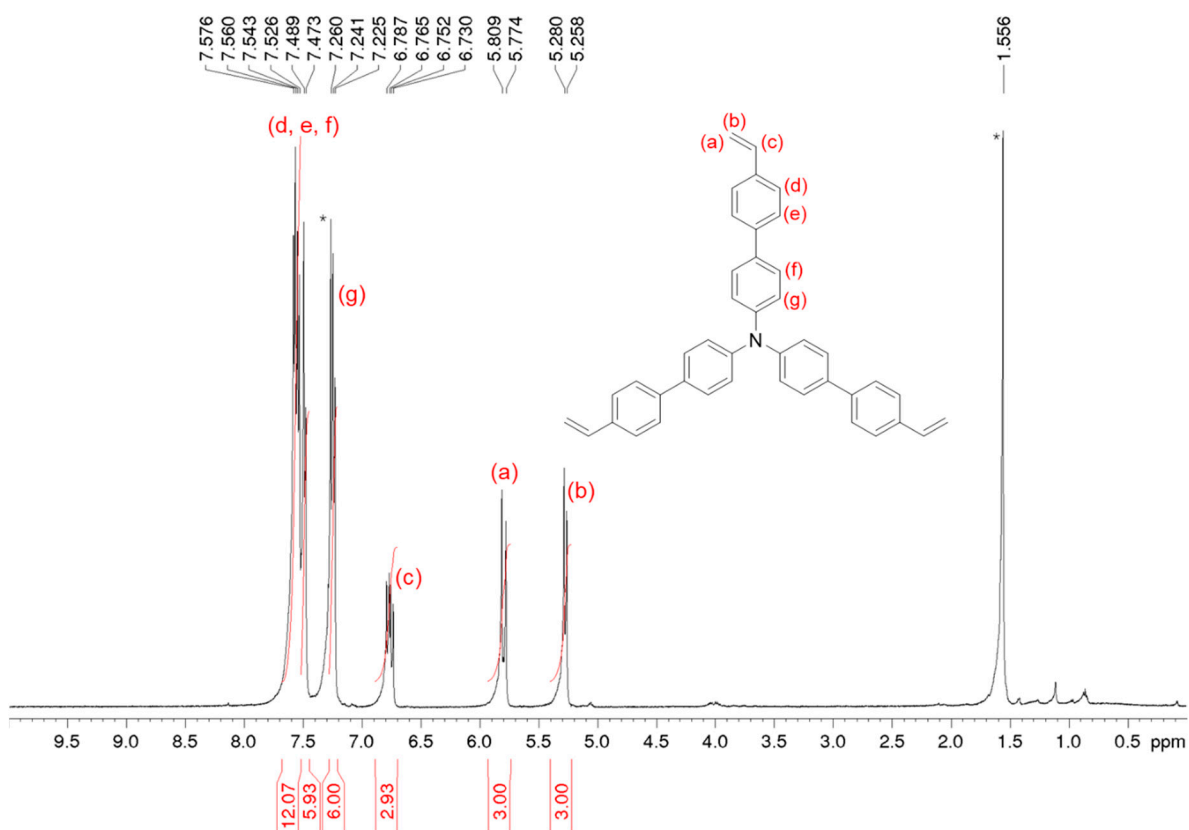


Figure S14. ¹H NMR of **M2** in CDCl₃

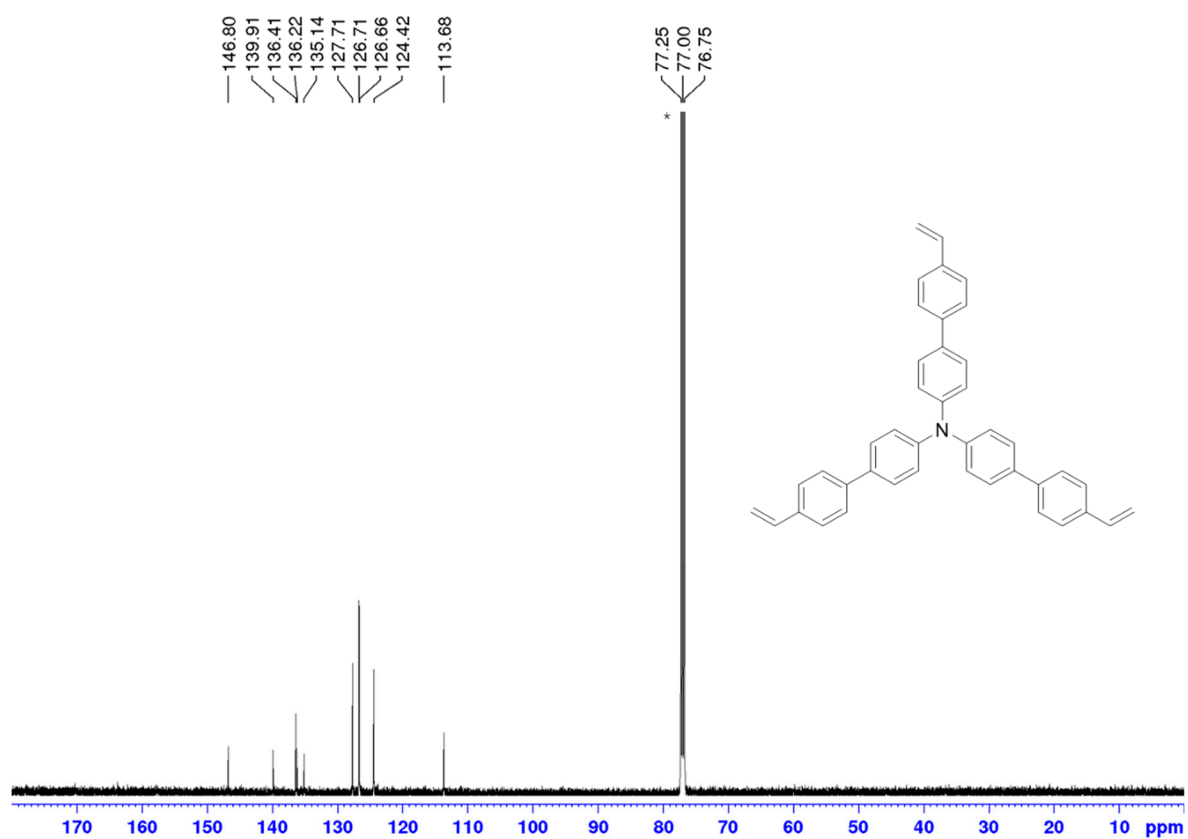
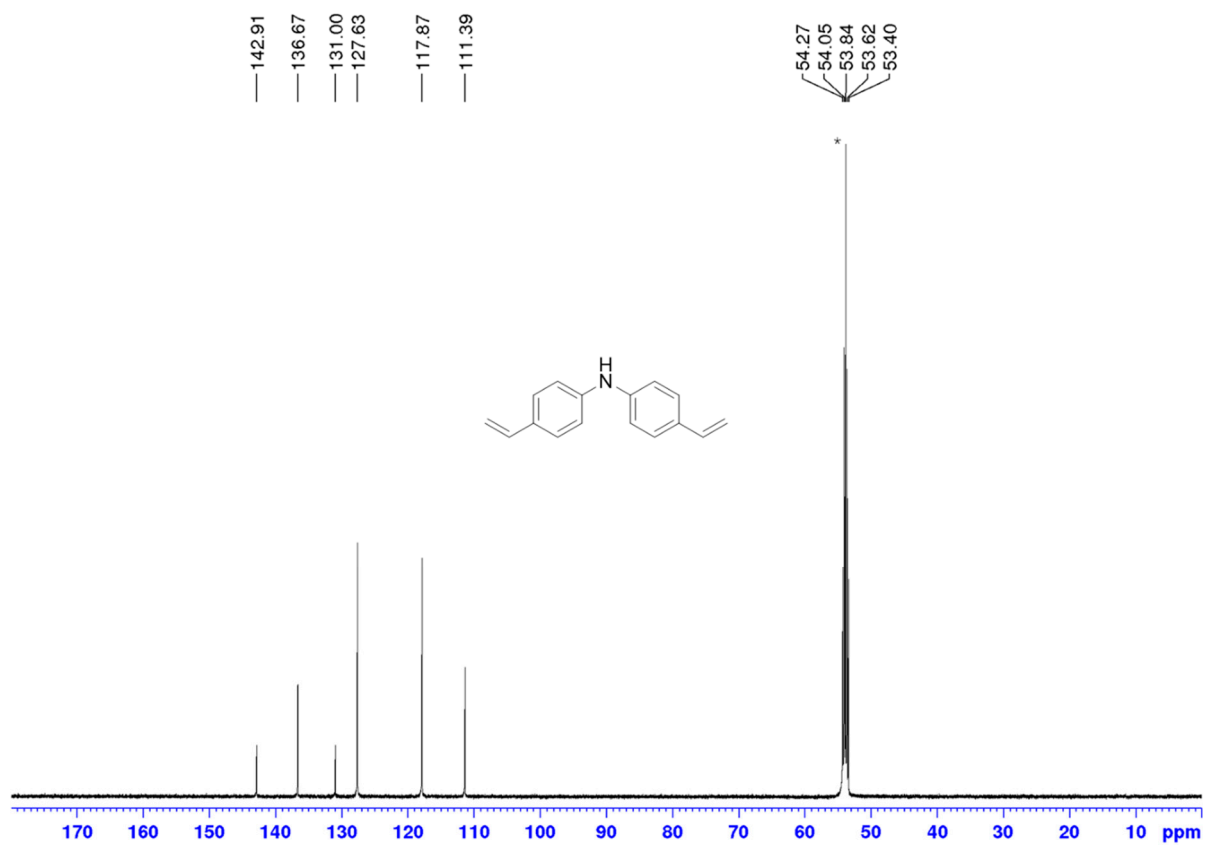
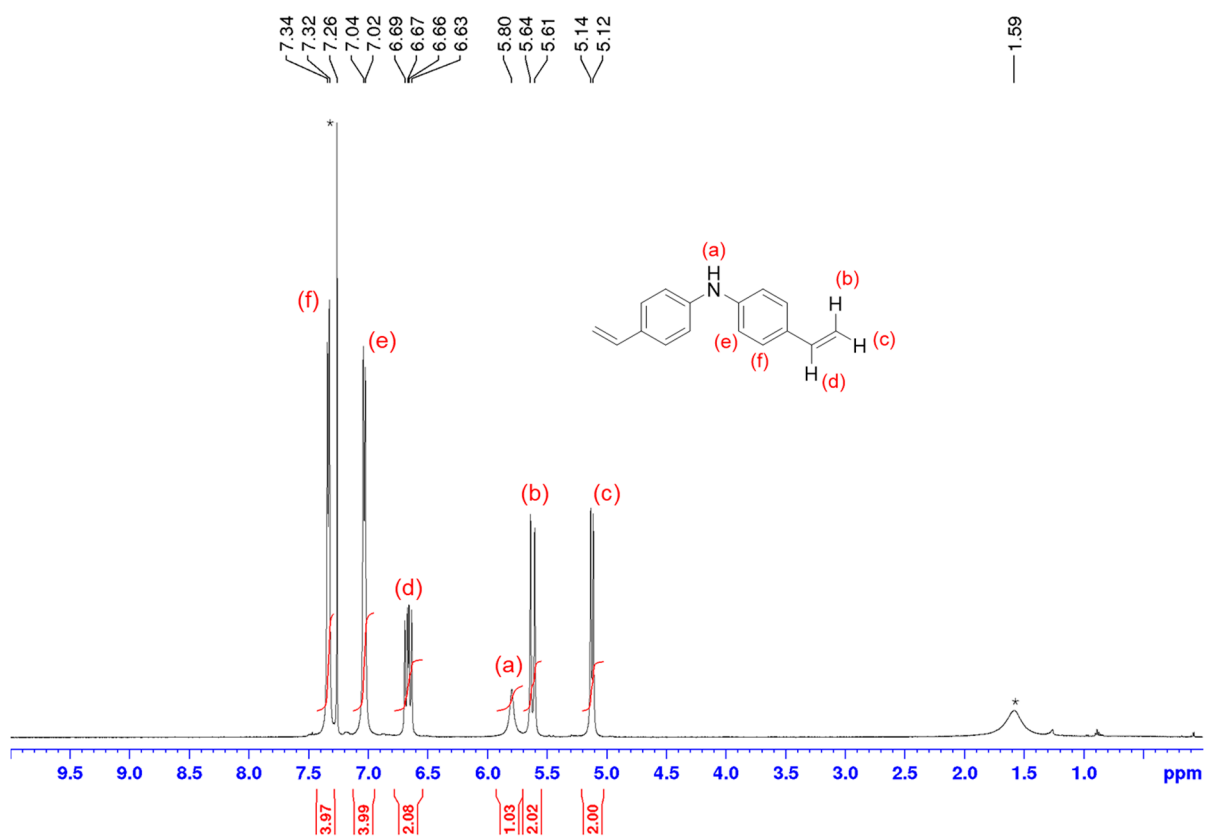


Figure S15. ¹³C NMR of **M2** in CDCl₃



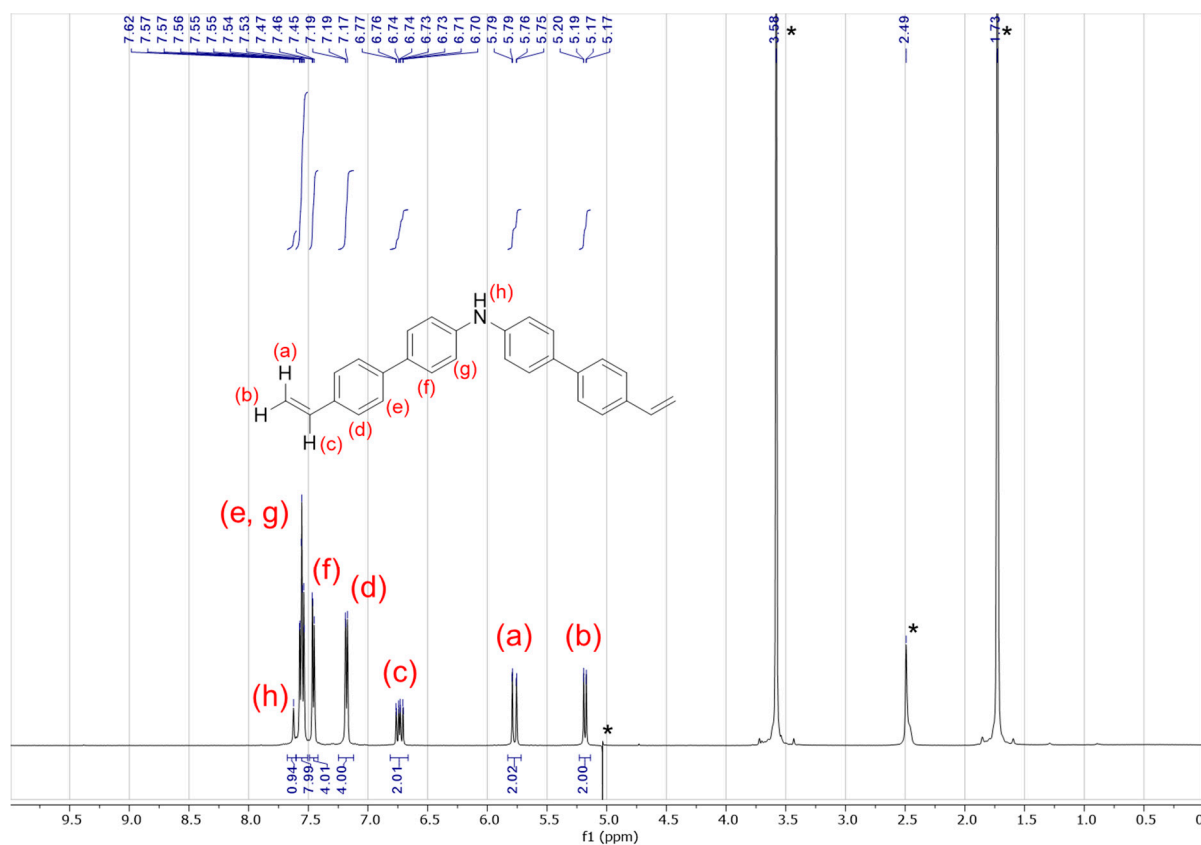


Figure S18. ¹H NMR of compound **2** in THF-d₈

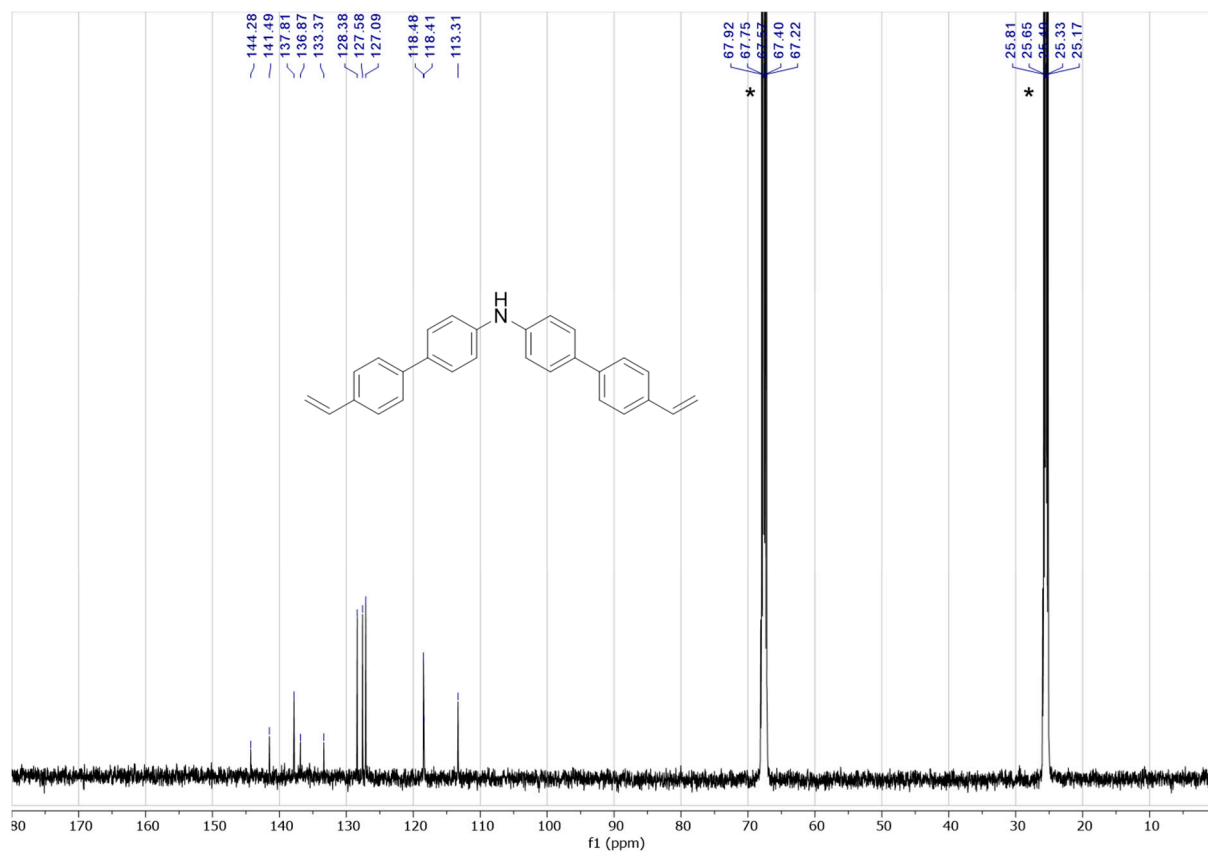


Figure S19. ¹³C NMR of compound **2** in THF-d₈

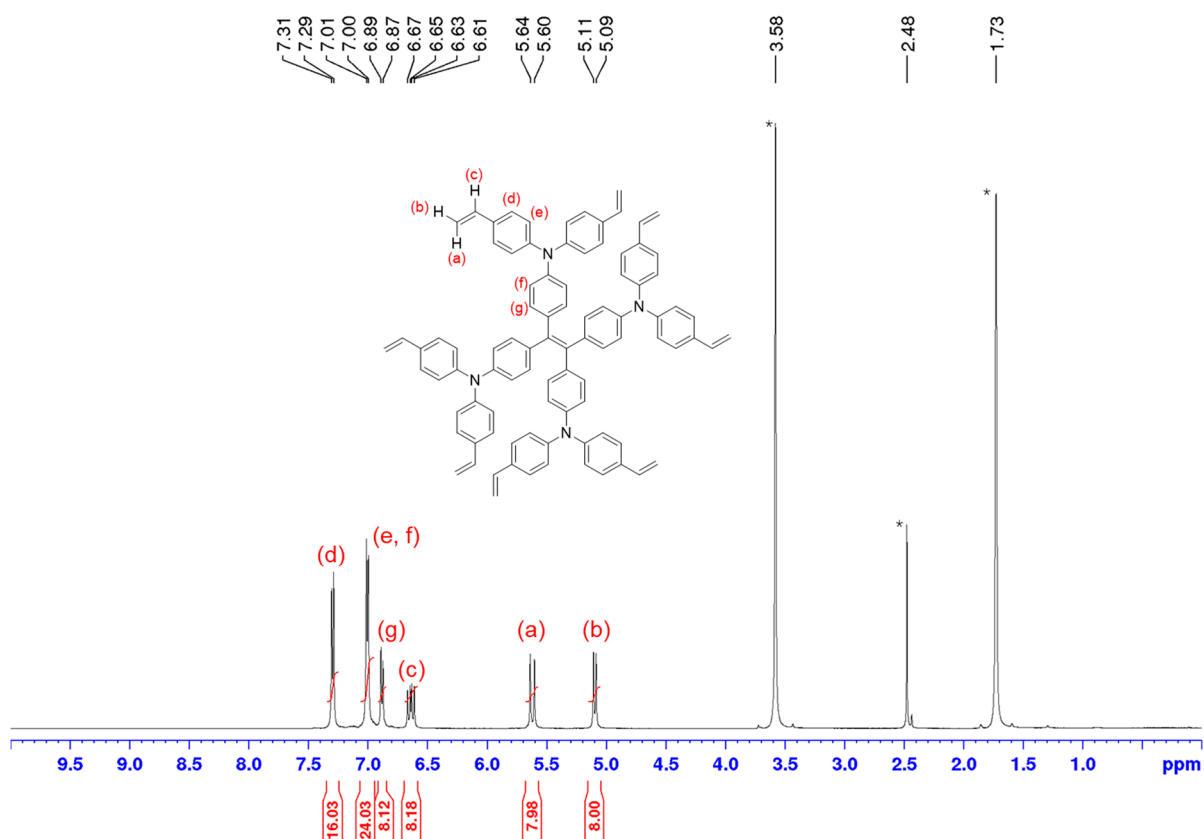


Figure S20. ¹H NMR of M3 in THF-d₈

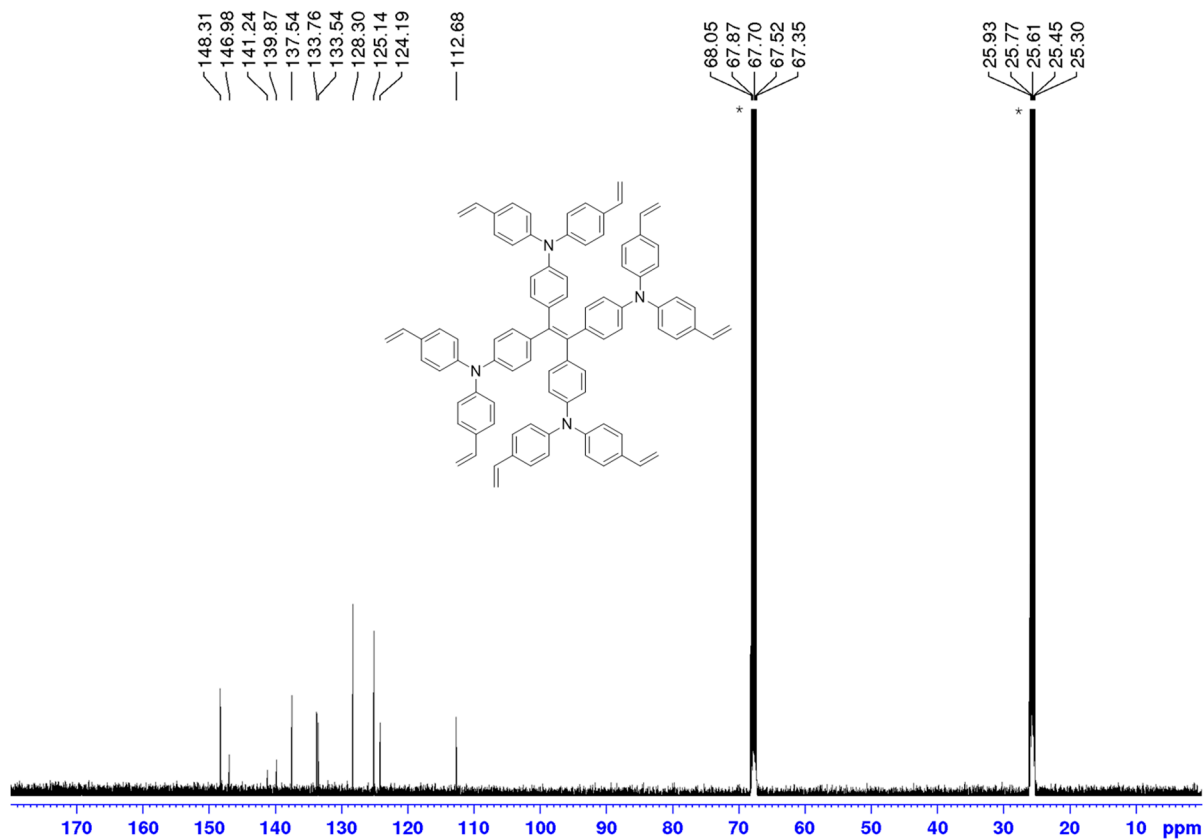


Figure S21. ¹³C NMR of M3 in THF-d₈

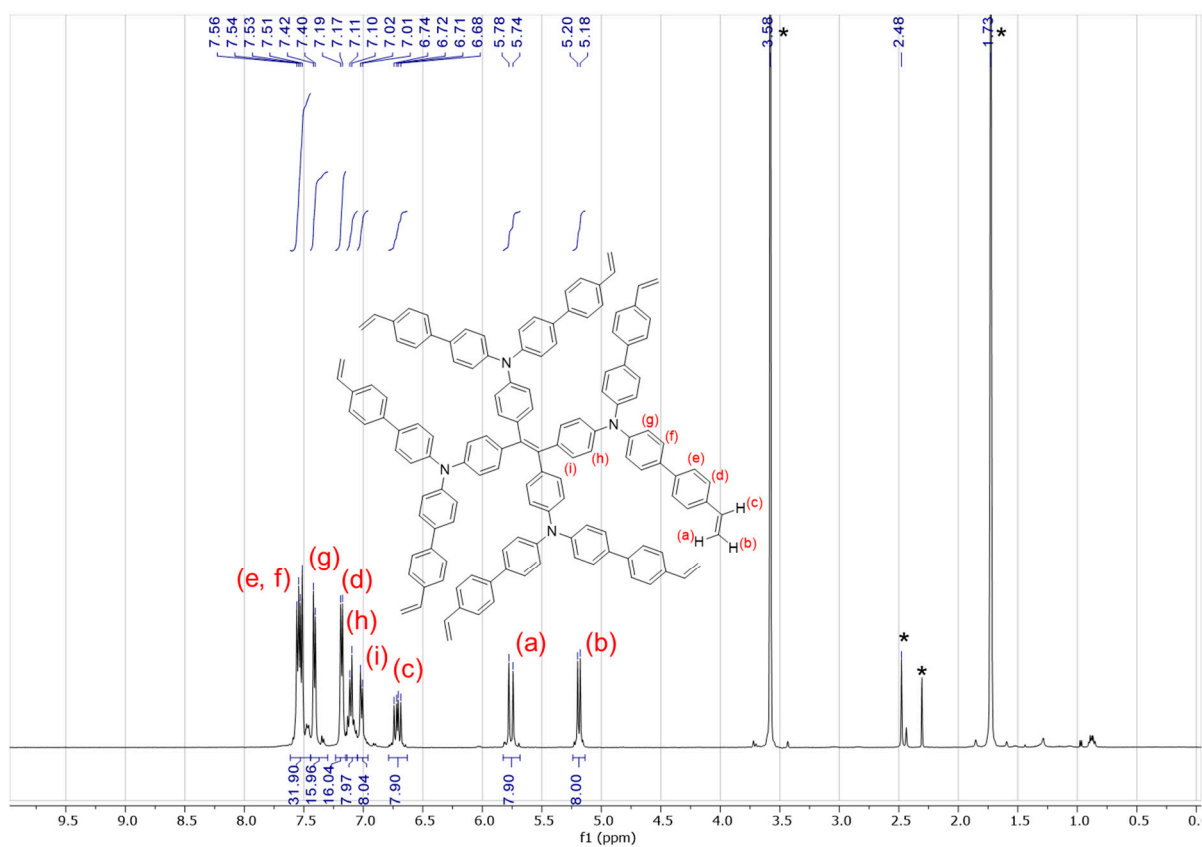


Figure S22. ¹H NMR of M4 in THF-d8

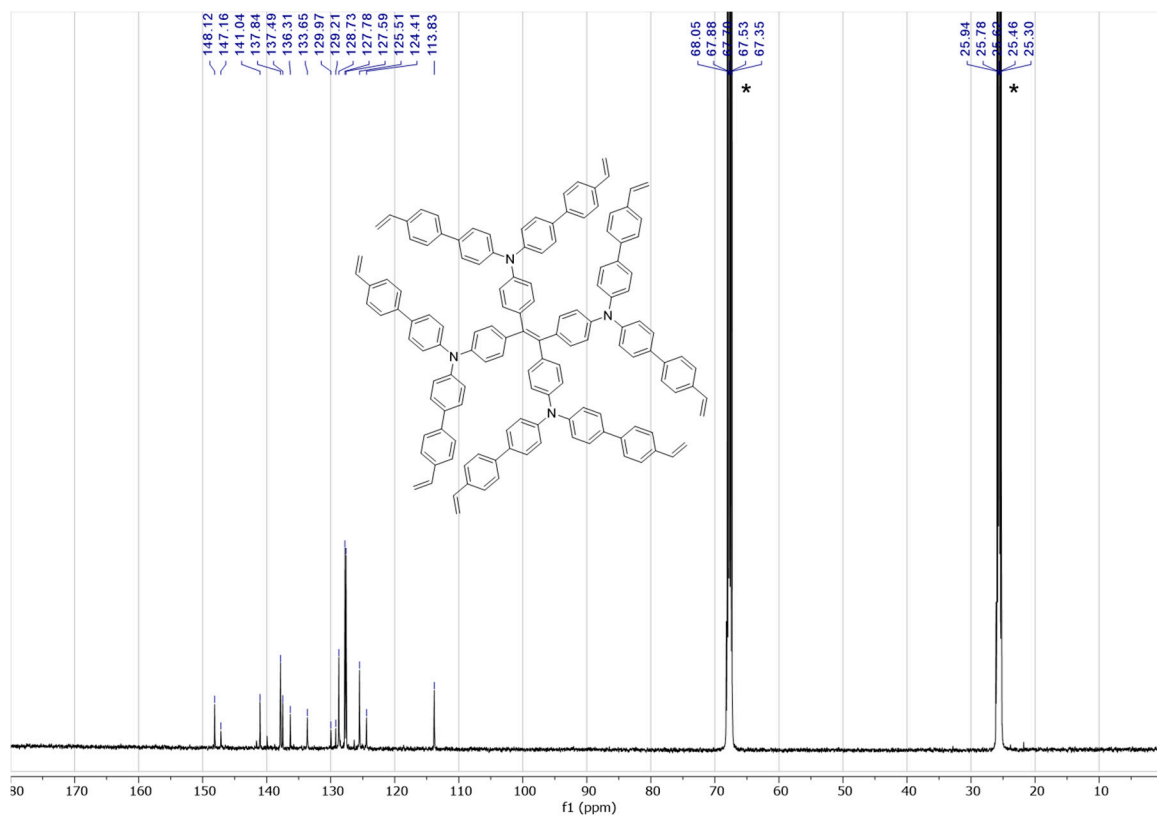


Figure S23. ¹³C NMR of M4 in THF-d8

ANNEX 2: High Resolution Mass Spectrometry (HRMS)

Compound Table

Label	Tgt Score	Mass Error (ppm)	Tgt Formula	Obs. RT	Ref. Mass	Obs. Mass
Cpd 1: C ₂₄ H ₂₁ N; 0.108	96.78	0.33	C ₂₄ H ₂₁ N	0.108	323.1674	323.16751

Obs. m/z	Obs. RT	Obs. Mass	Tgt Formula	Tgt Mass	Tgt Mass Error (ppm)	Find Cpd Algorithm
324.1748	0.108	323.16751	C ₂₄ H ₂₁ N	323.1674	0.33	Find by Formula

Compound Chromatograms

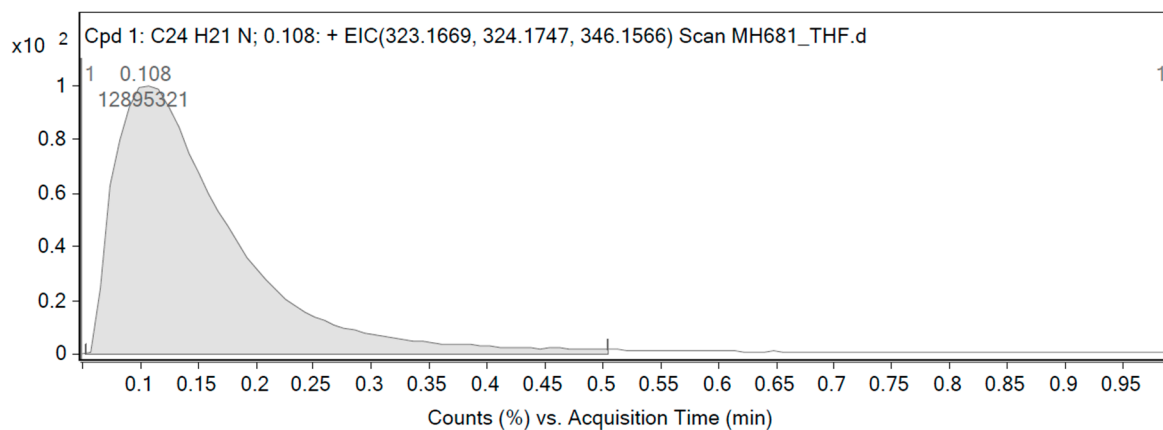


Figure S24. HRMS of M1

Compound Table

Label	Tgt Score	Mass Error (ppm)	Tgt Formula	Obs. RT	Ref. Mass	Obs. Mass
Cpd 1: C ₄₂ H ₃₃ N; 0.888	94.65	0.95	C ₄₂ H ₃₃ N	0.888	551.2613	551.26182

Obs. m/z	Obs. RT	Obs. Mass	Tgt Formula	Tgt Mass	Tgt Mass Error (ppm)	Find Cpd Algorithm
551.2609	0.888	551.26182	C ₄₂ H ₃₃ N	551.2613	0.95	Find by Formula

Compound Chromatograms

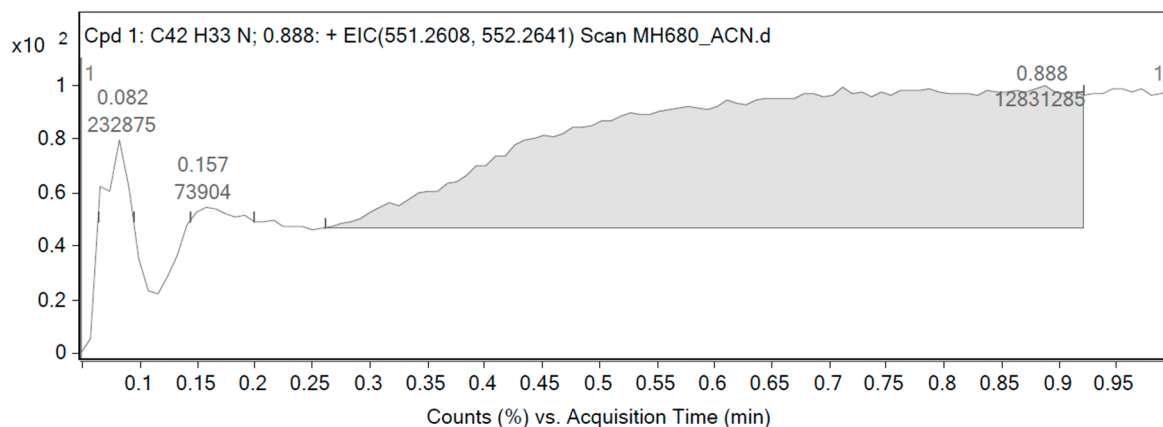


Figure S25. HRMS of M2

Compound Table

Label	Tgt Score	Mass Error (ppm)	Tgt Formula	Obs. RT	Ref. Mass	Obs. Mass
Cpd 1: C16 H15 N; 0.095	98.38	-0.4	C16 H15 N	0.095	221.12045	221.12036

Obs. m/z	Obs. RT	Obs. Mass	Tgt Formula	Tgt Mass	Tgt Mass Error (ppm)	Find Cpd Algorithm
222.1277	0.095	221.12036	C16 H15 N	221.12045	-0.4	Find by Formula

Compound Chromatograms

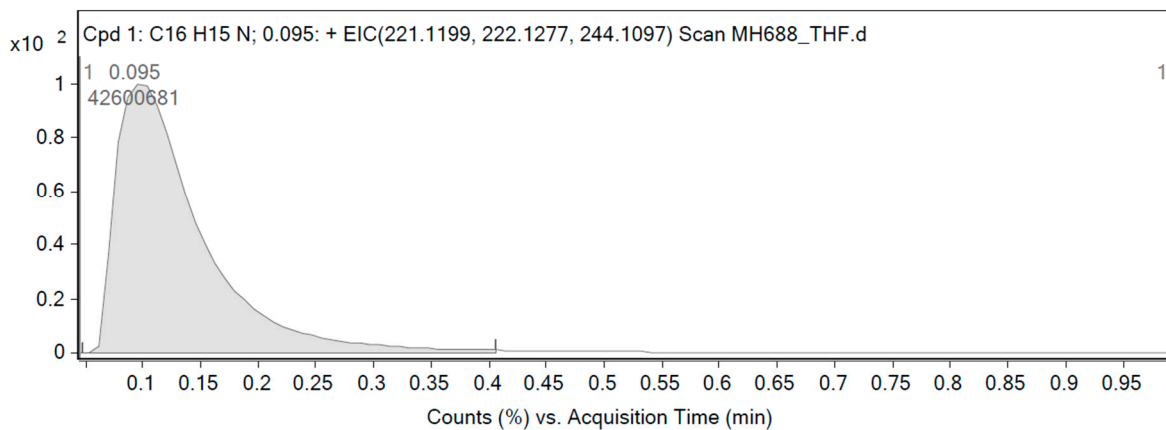


Figure S26. HRMS of compound 1.

Compound Table

Label	Tgt Score	Mass Error (ppm)	Tgt Formula	Obs. RT	Ref. Mass	Obs. Mass
Cpd 1: C28 H23 N; 0.165	97.94	-1.01	C28 H23 N	0.165	373.18305	373.18267

Obs. m/z	Obs. RT	Obs. Mass	Tgt Formula	Tgt Mass	Tgt Mass Error (ppm)	Find Cpd Algorithm
374.19	0.165	373.18267	C28 H23 N	373.18305	-1.01	Find by Formula

Compound Chromatograms

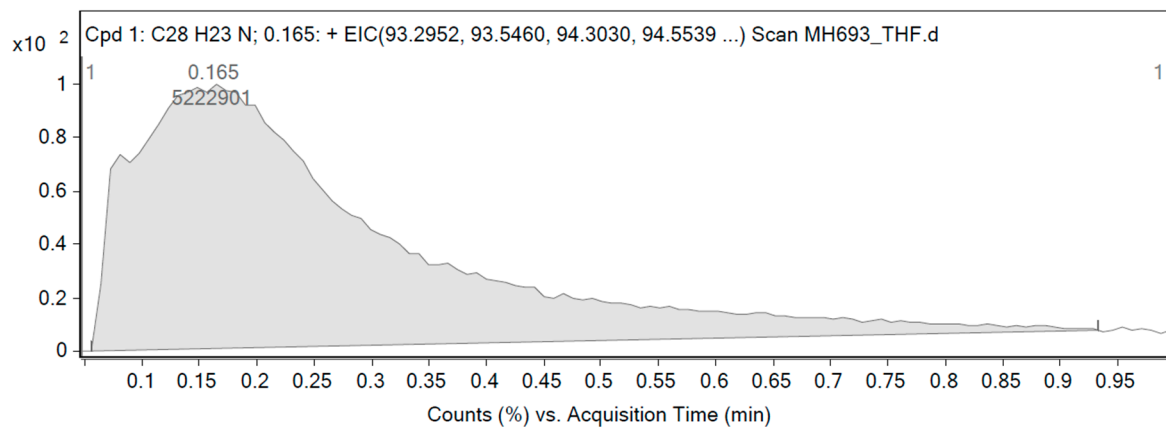


Figure S27. HRMS of compound 2.

Compound Table

Label	Tgt Score	Mass Error (ppm)	Tgt Formula	Obs. RT	Ref. Mass	Obs. Mass
Cpd 1: C90 H72 N4; 0.077	62.46	-4.35	C90 H72 N4	0.077	1208.5757	1208.57044

Obs. m/z	Obs. RT	Obs. Mass	Tgt Formula	Tgt Mass	Tgt Mass Error (ppm)	Find Cpd's Algorithm
1209.5779	0.077	1208.57044	C90 H72 N4	1208.5757	-4.35	Find by Formula

Compound Chromatograms

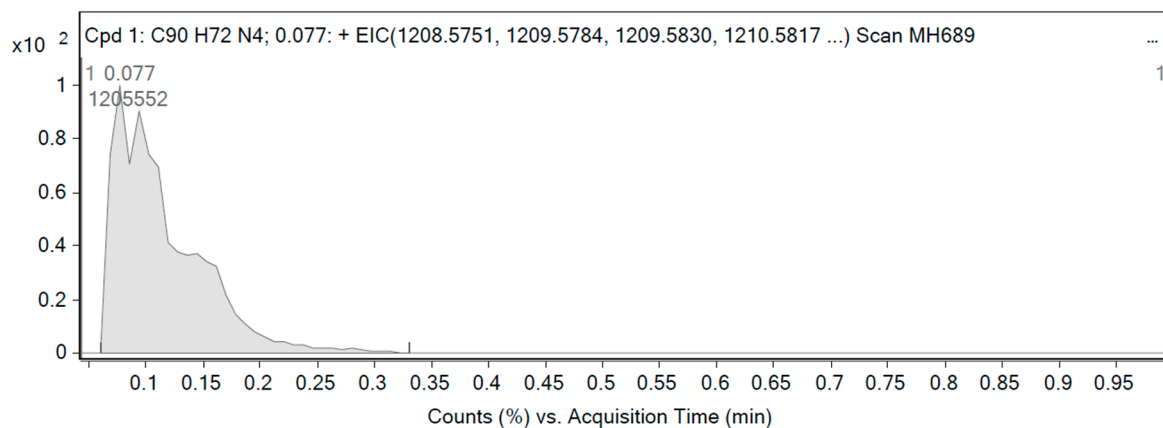


Figure S28. HRMS of M3.

Meas. m/z	#	Formula	Calc. Mass	Err [ppm]
1816.8229	1	C138 H104 N4	1816.8256	1.49

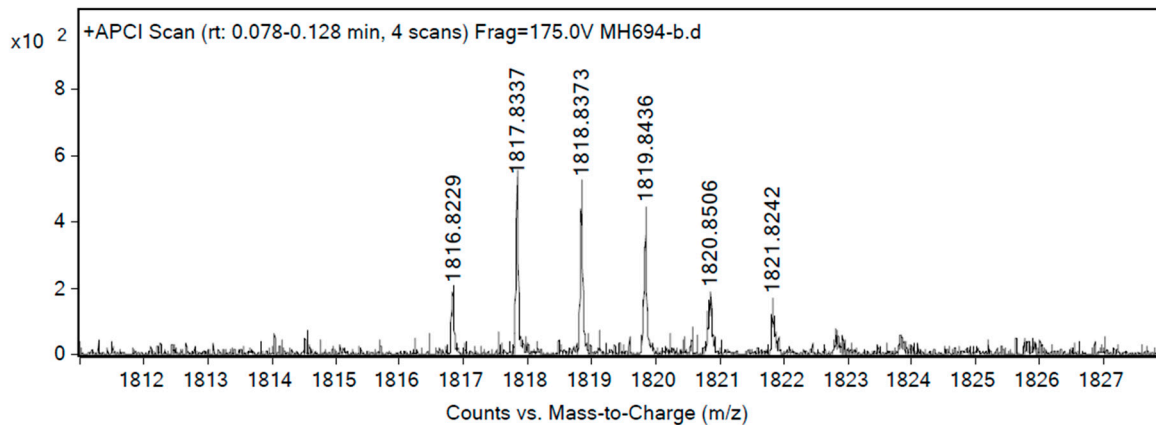


Figure S29. HRMS of M4.