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

Supporting Information Contents

Heterotriangulene-based unsymmetrical squaraine dyes: synergistic effects of donor moiety and out-of-plane branched alkyl chains on dye cell performance

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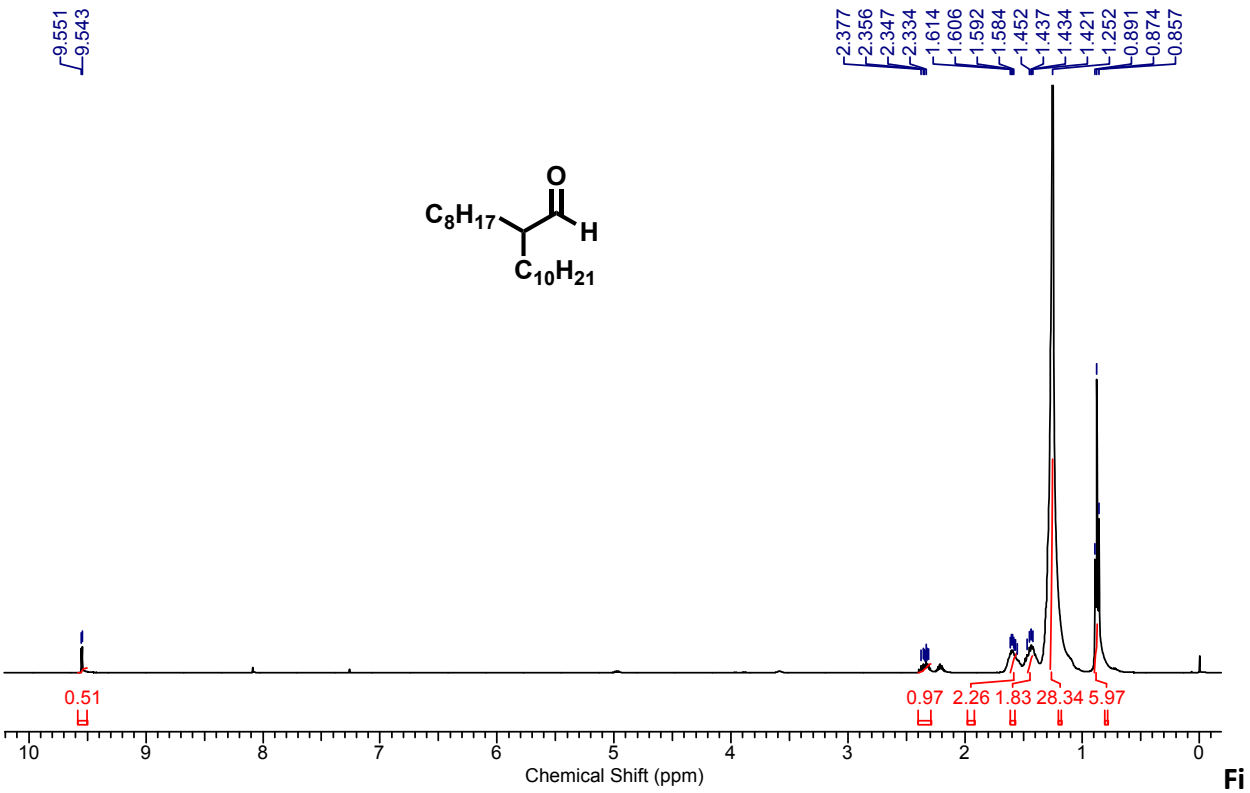


gure S1. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1a.**

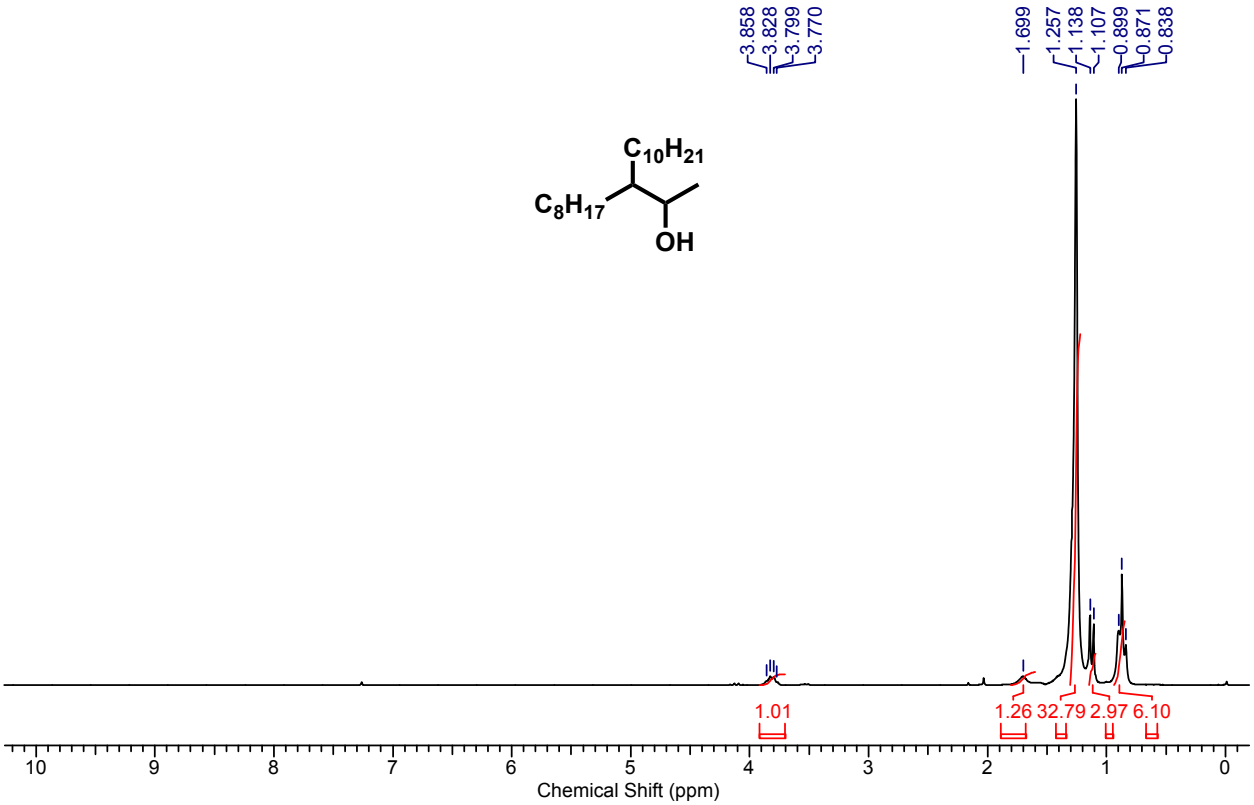


Figure S2. ^{1}H NMR (200 MHz, $CDCl_3$) spectrum of compound **1b.**

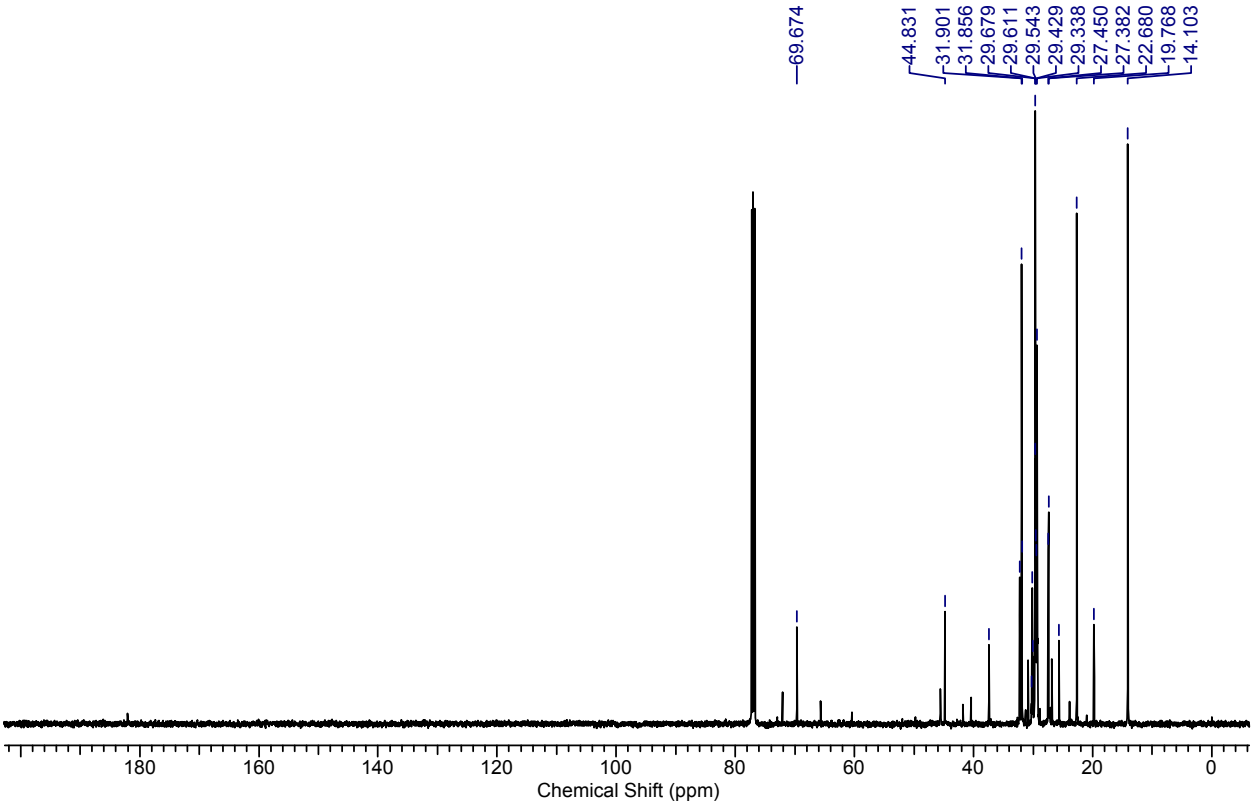


Figure S3. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **1b.**

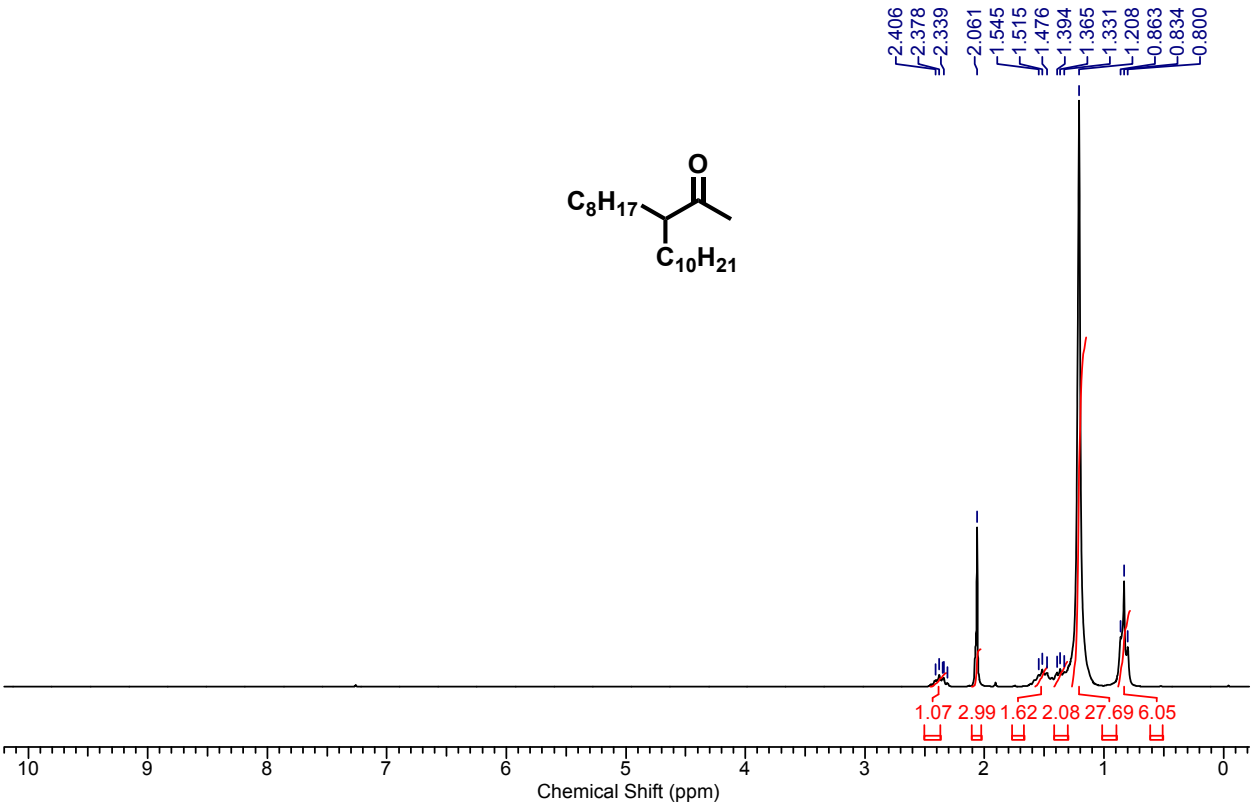


Figure S4. ^{1}H NMR (200 MHz, $CDCl_3$) spectrum of compound **1c.**

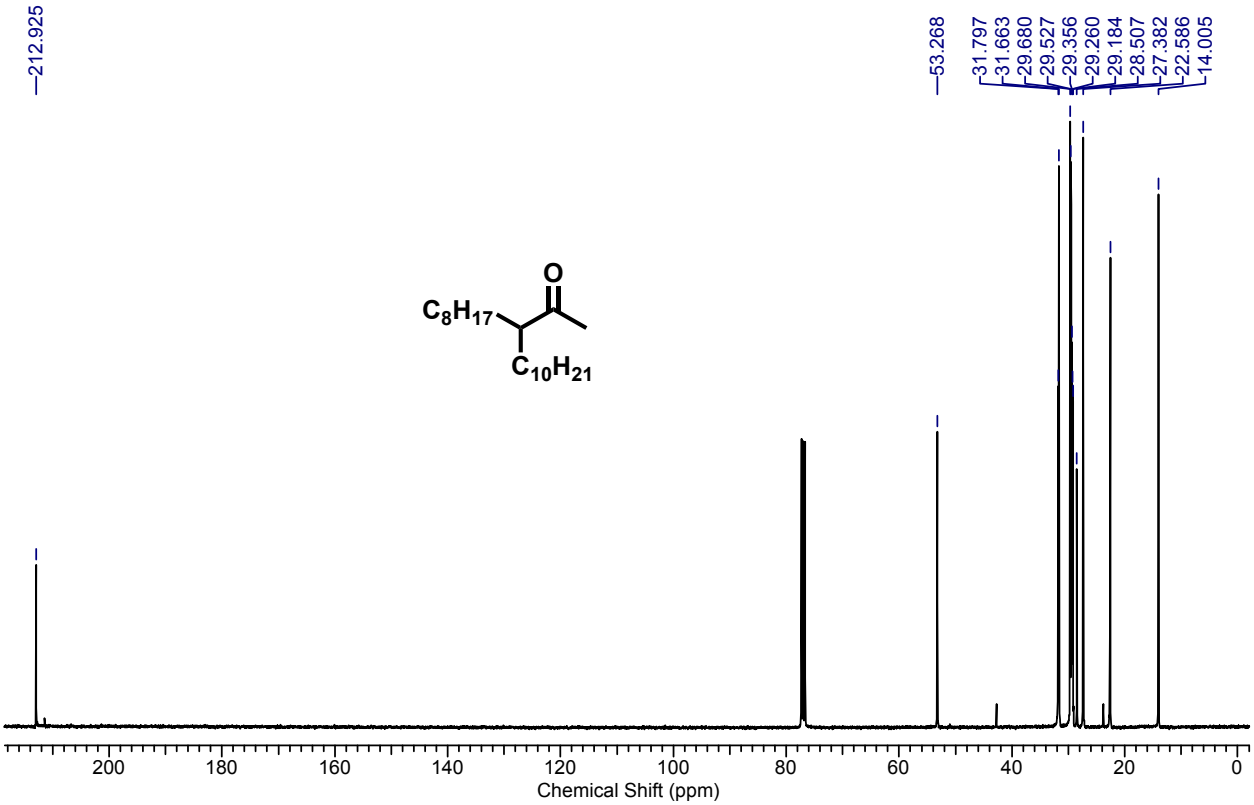


Figure S5. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **1c.**

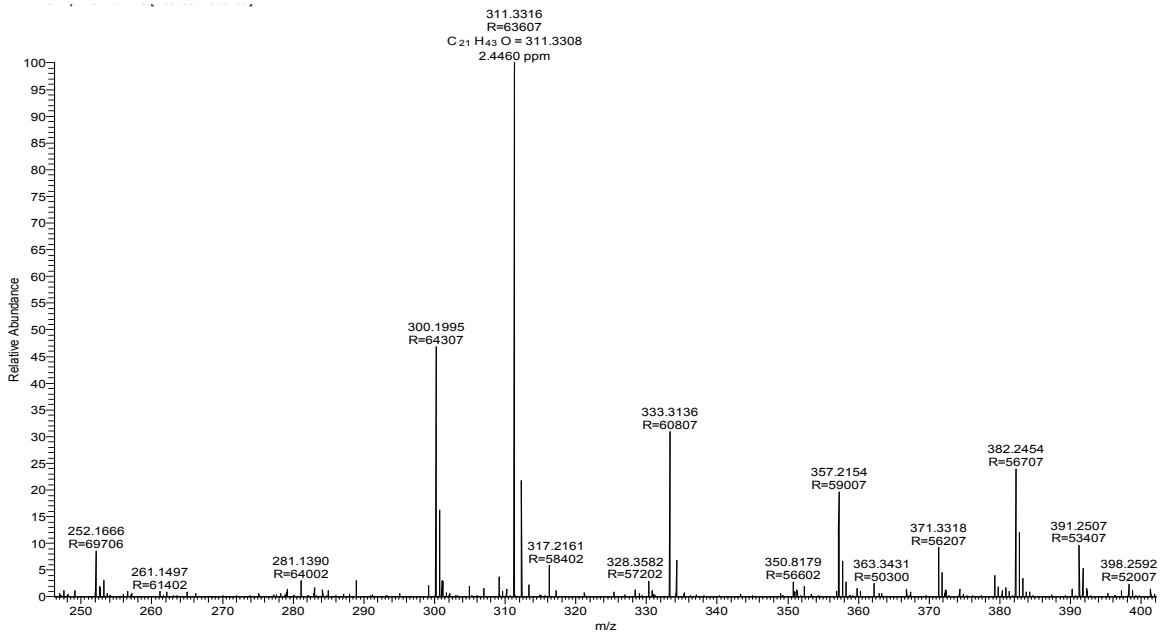


Figure S6. HRMS spectrum of **1c.**

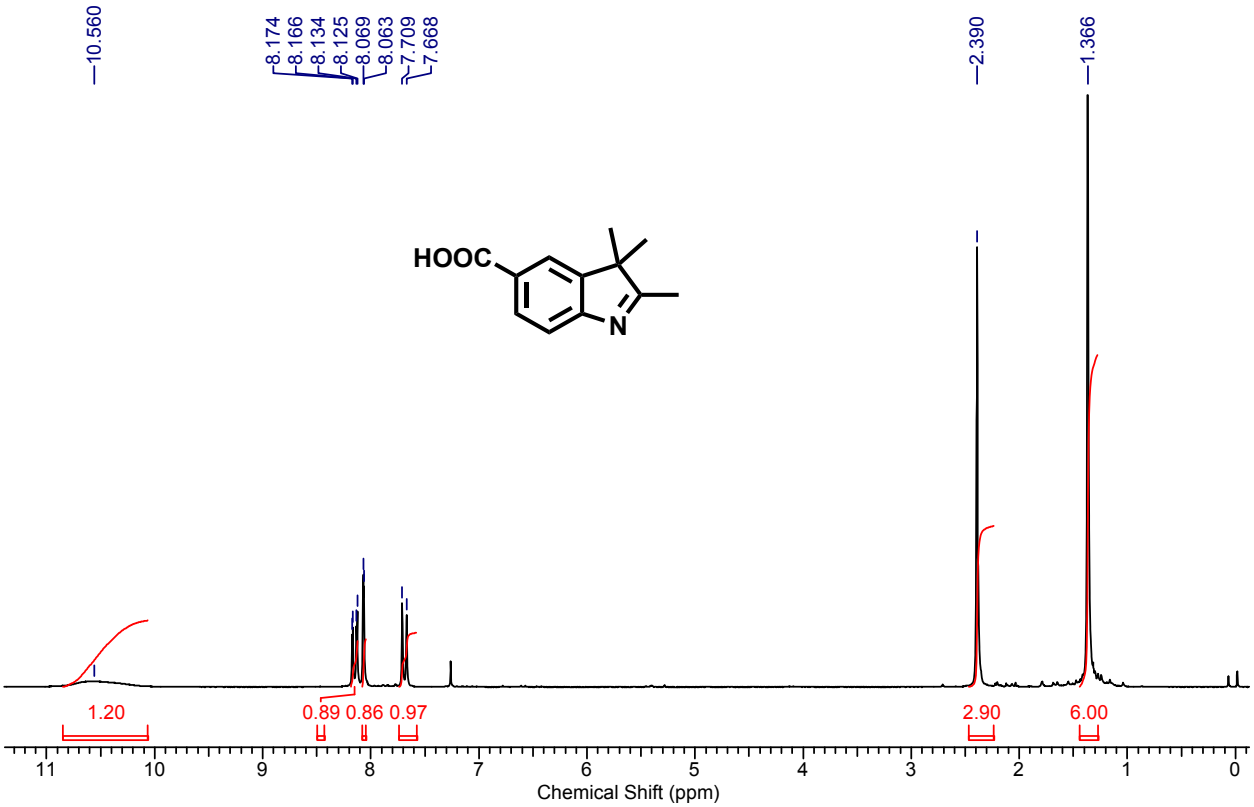


Figure S7. ^{1}H NMR (200 MHz, $CDCl_3$) spectrum of compound **2a.**

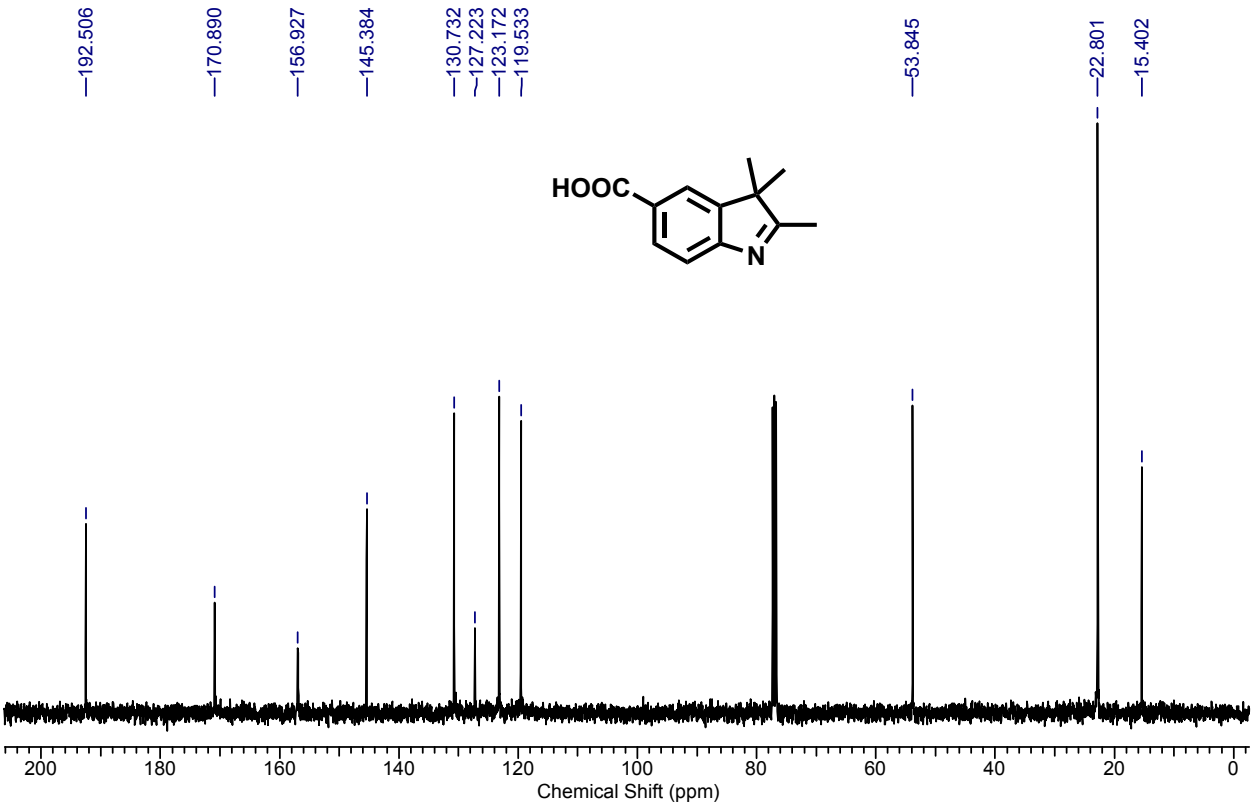


Figure S8. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **2a.**

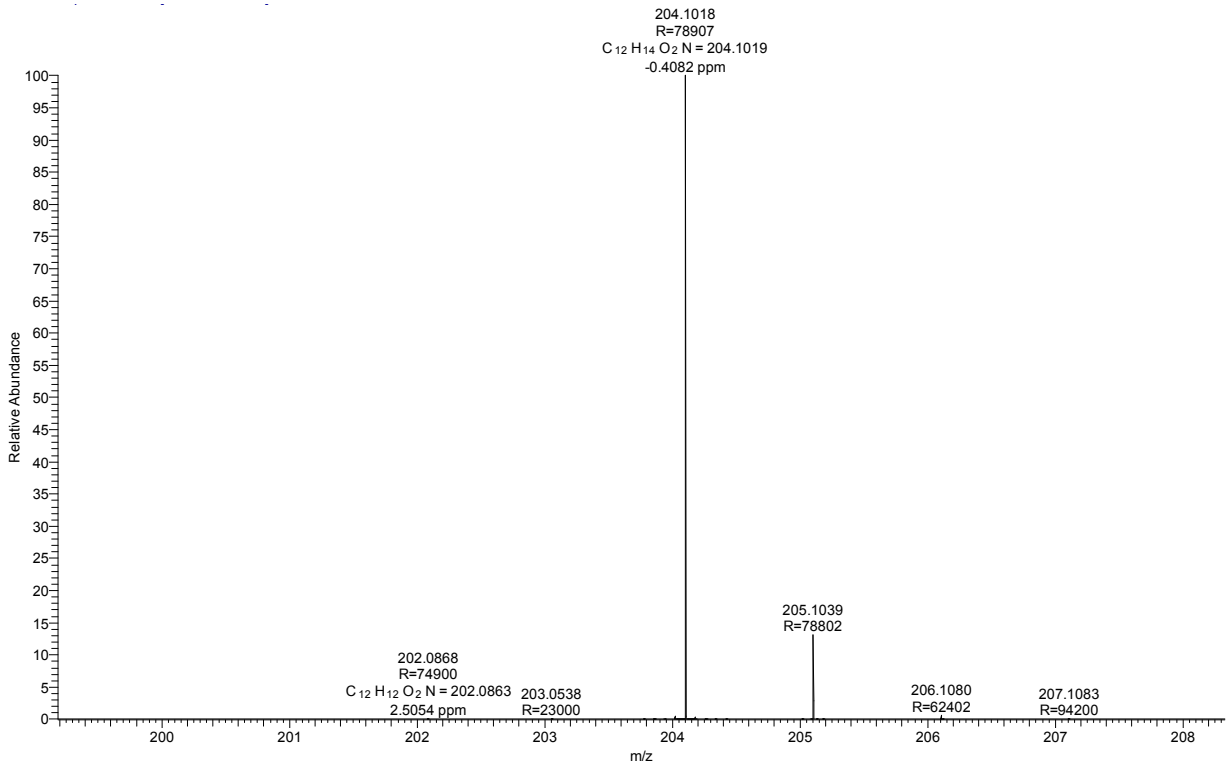


Figure S9. HRMS spectrum of **2a.**

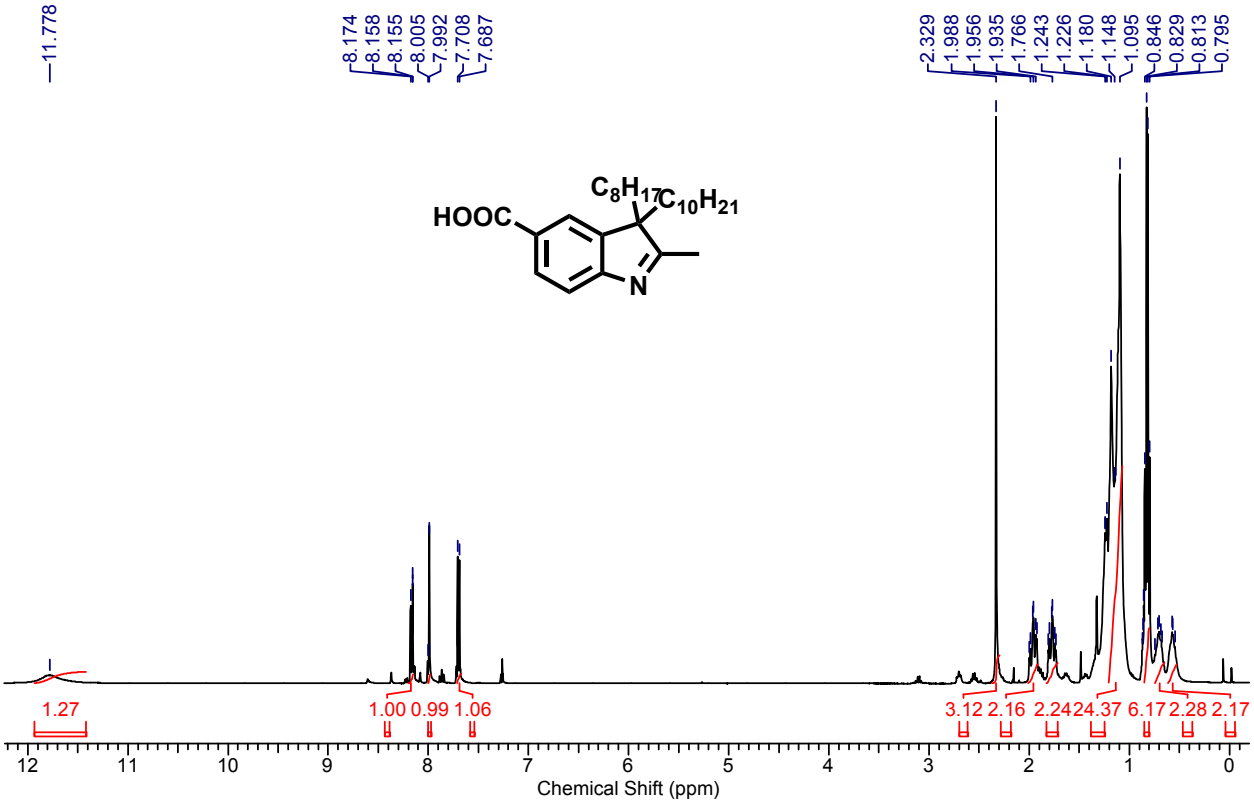
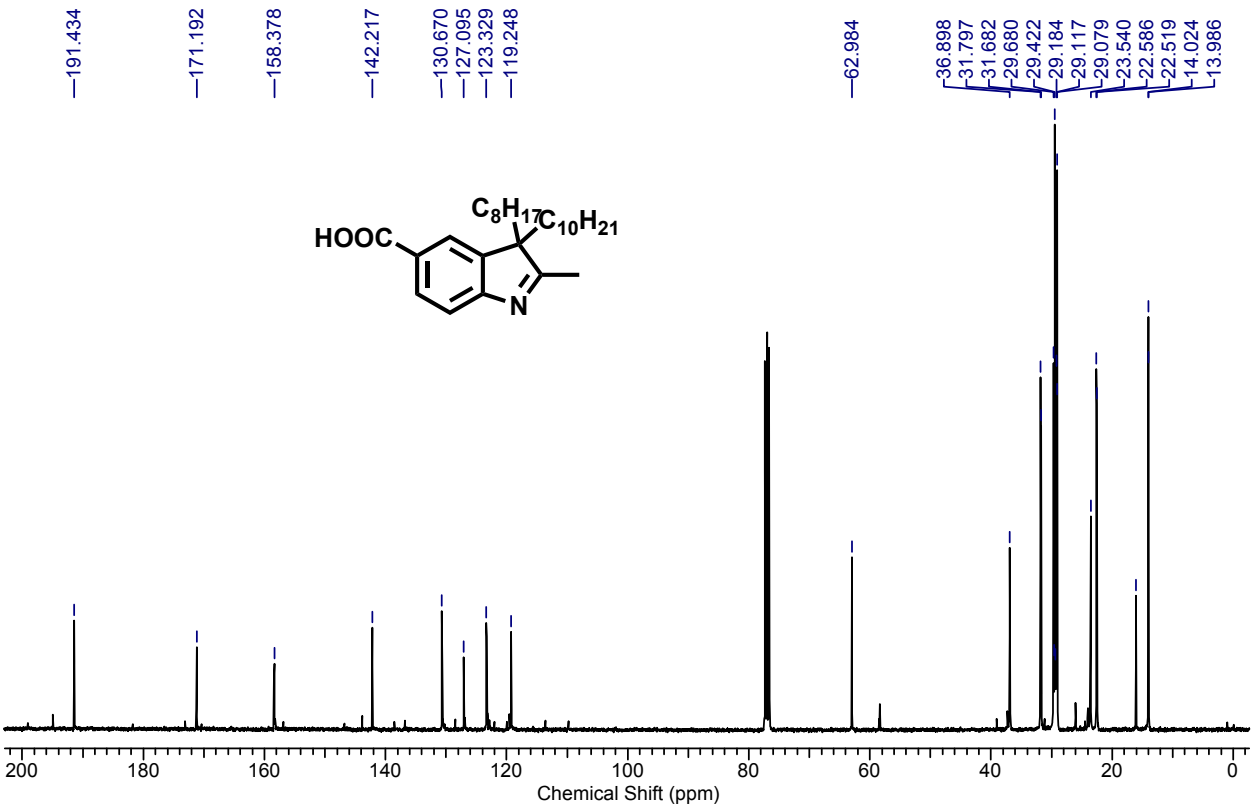


Figure S10. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **2b.**



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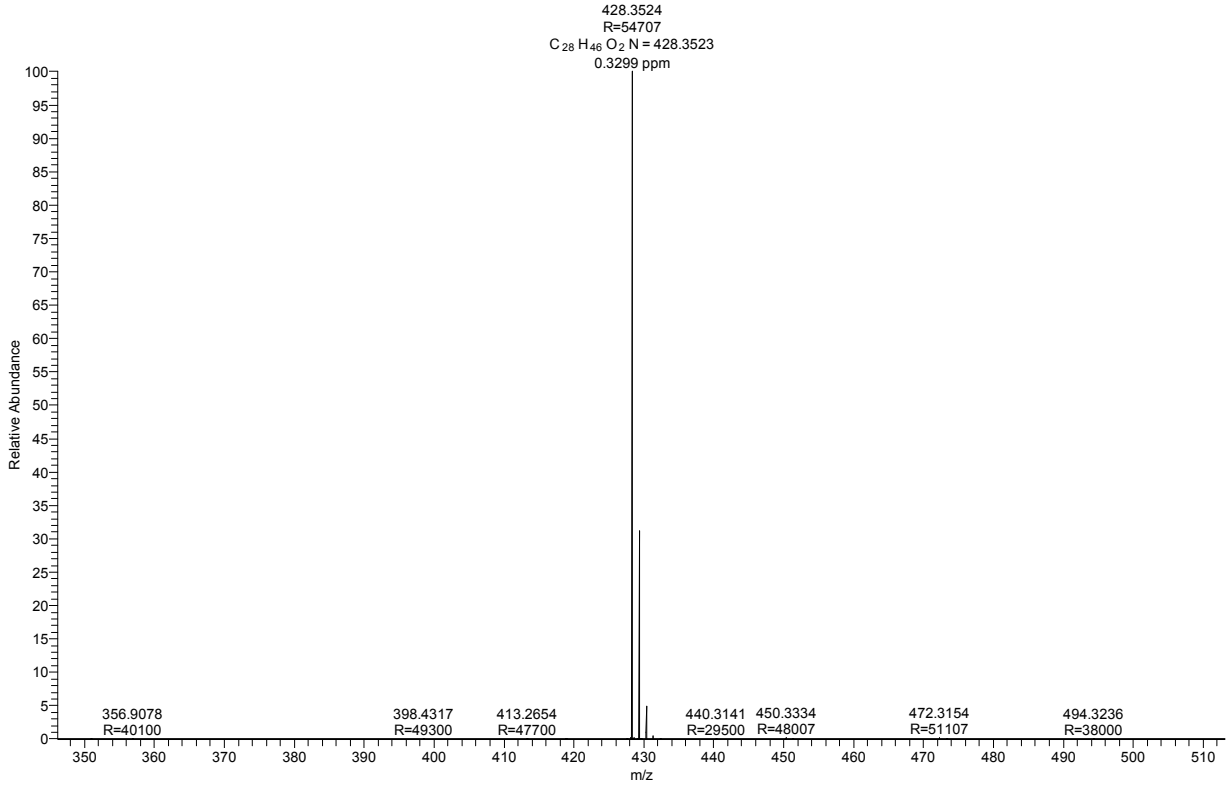


Figure S12. HRMS spectrum of **2b.**

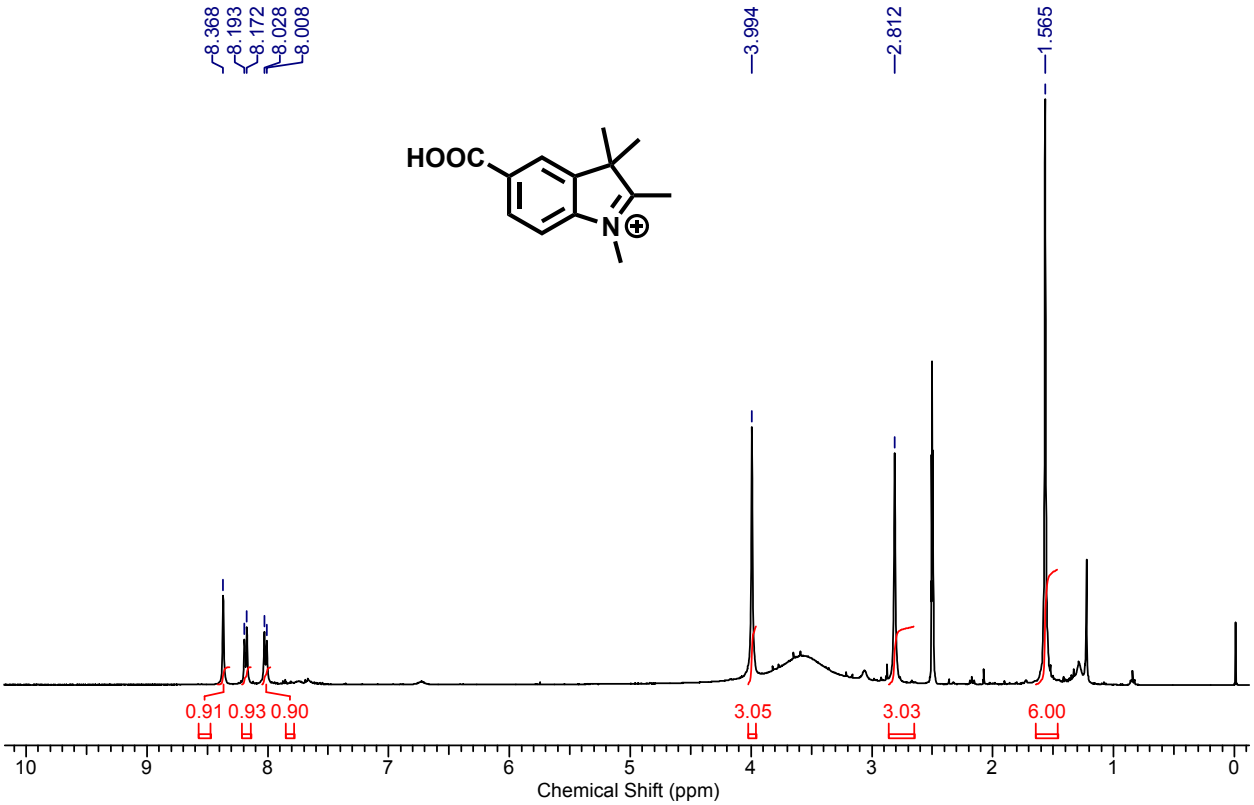


Figure S13. ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound **3a.**

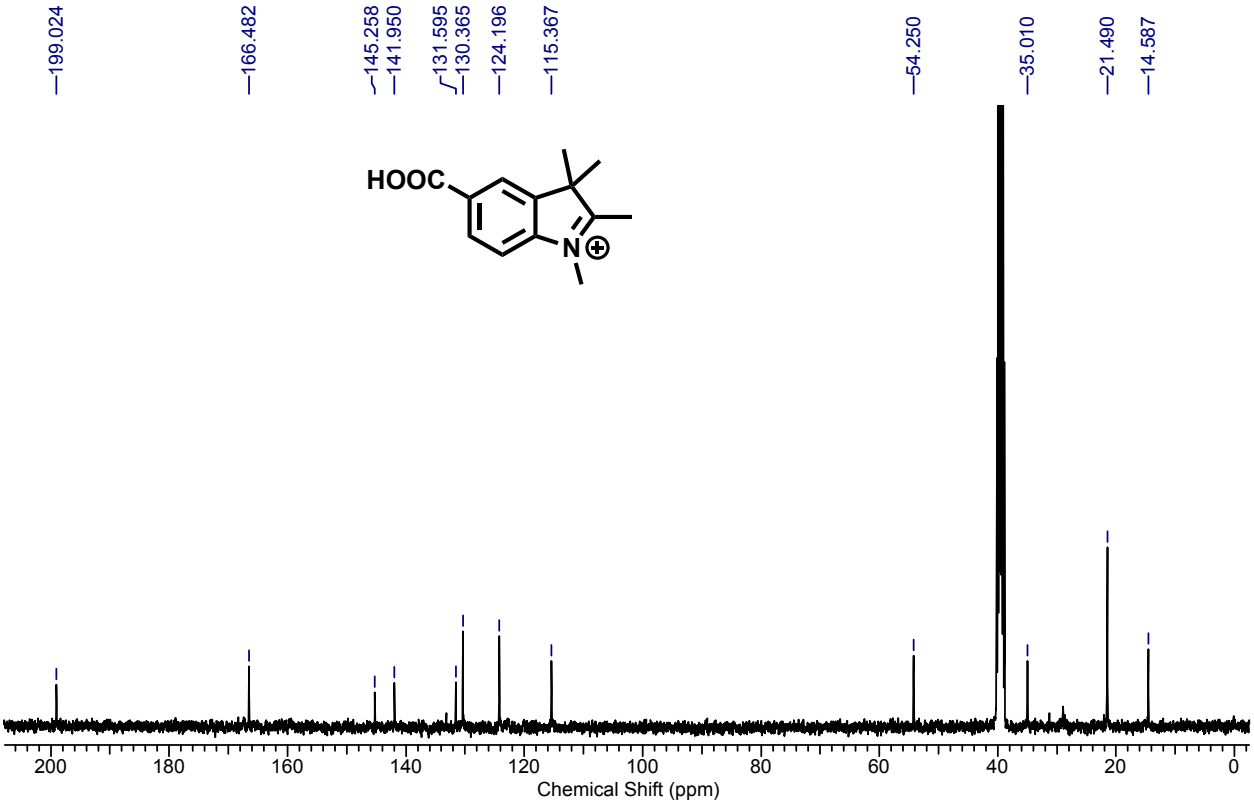
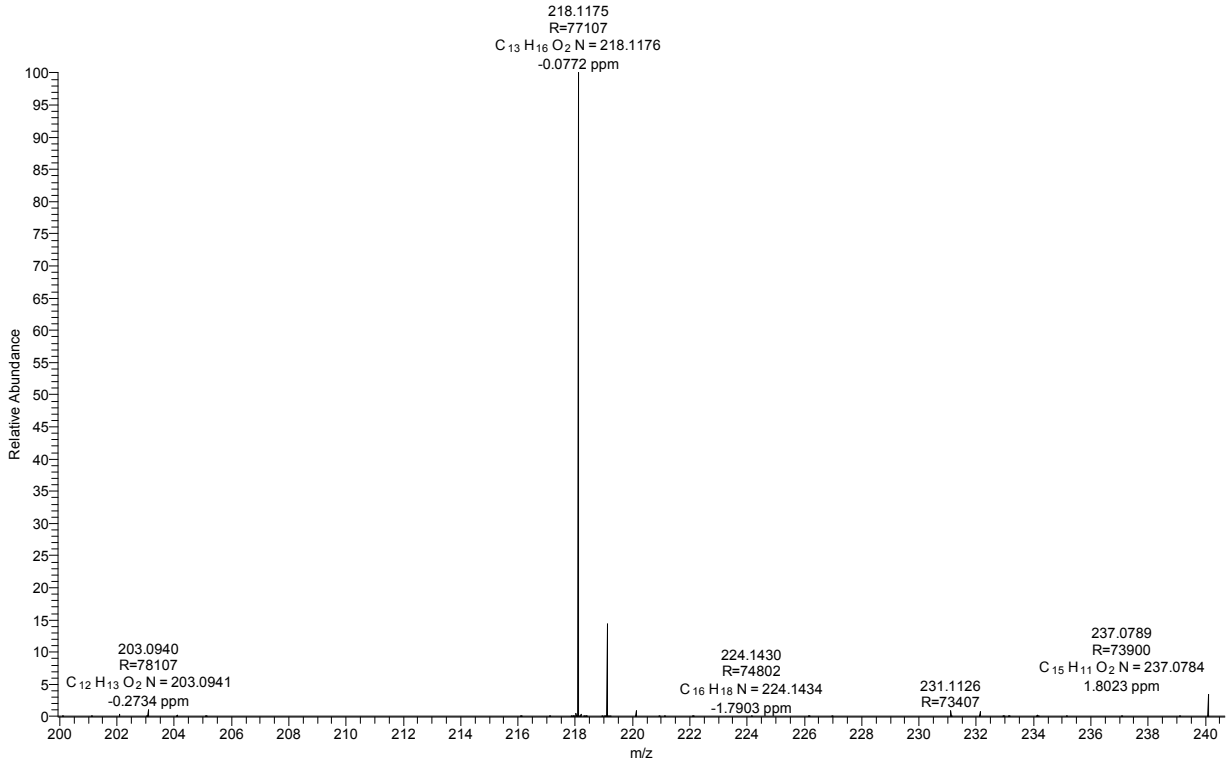


Figure S14. ^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound **3a.**



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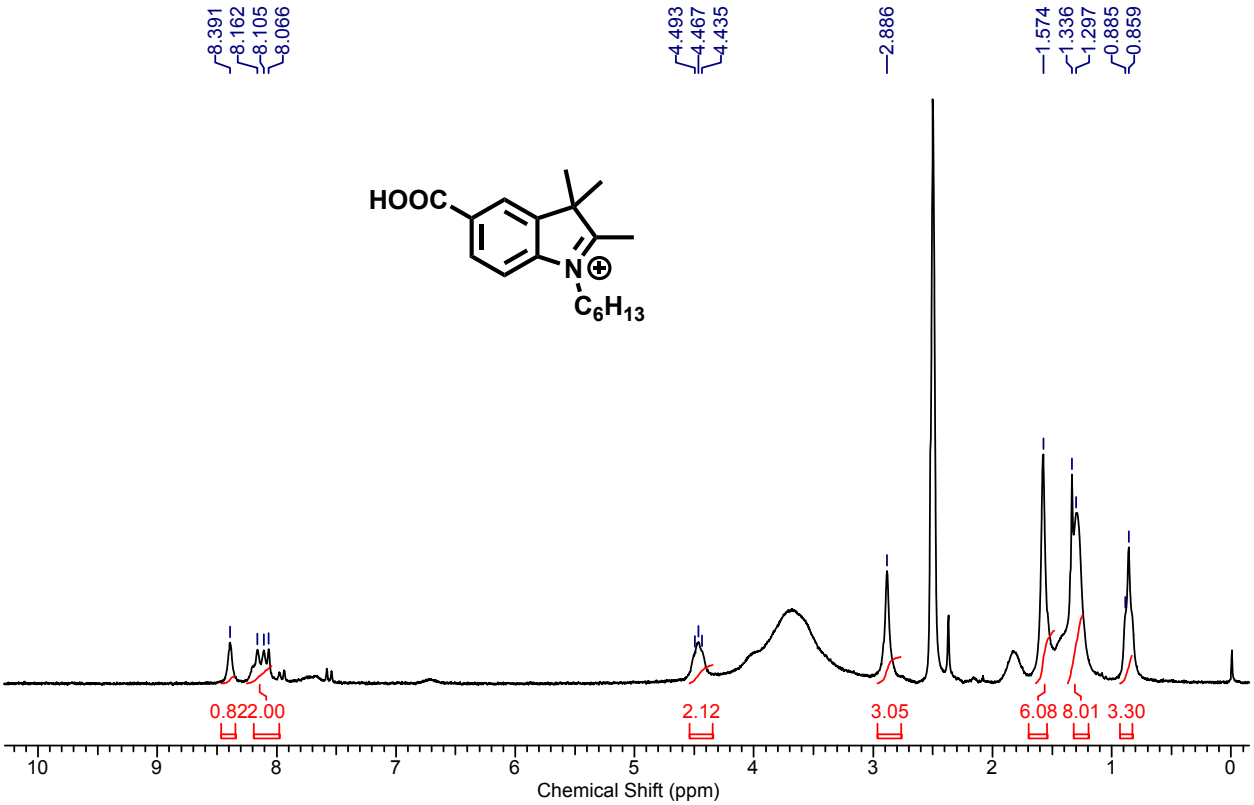

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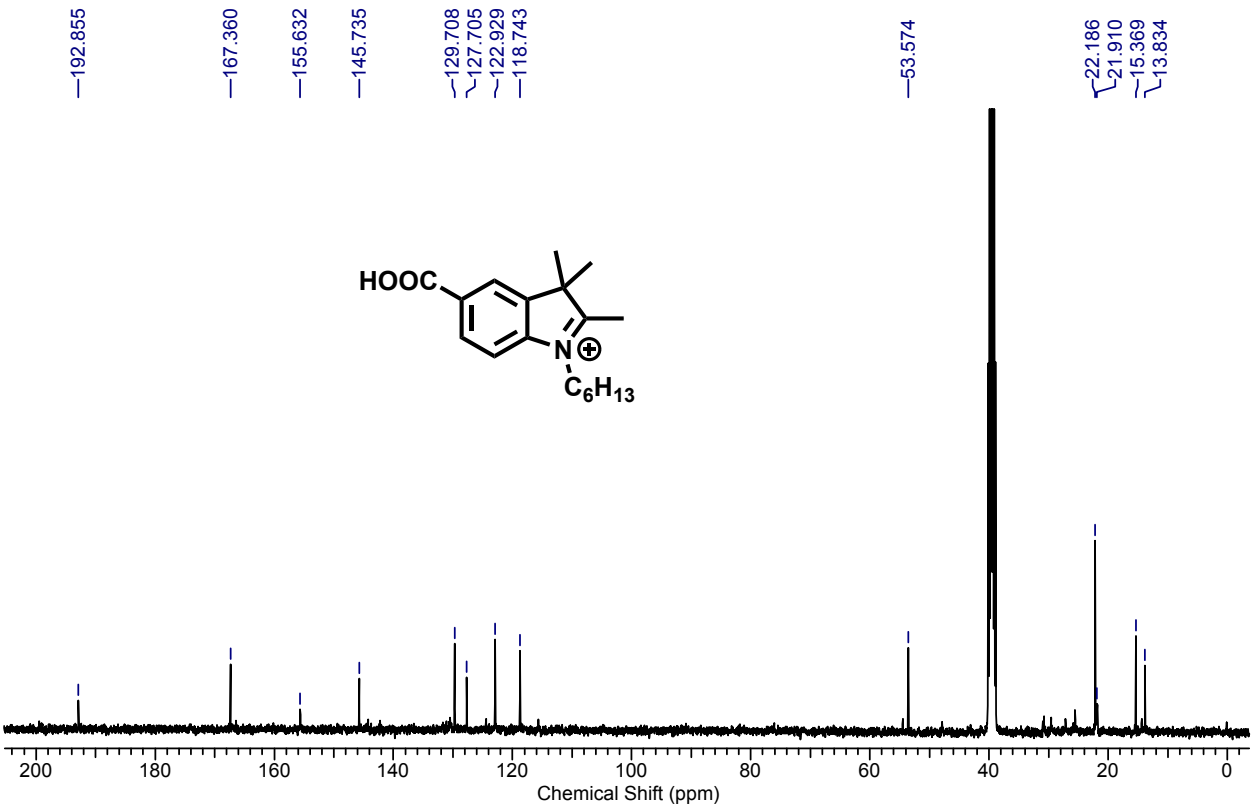

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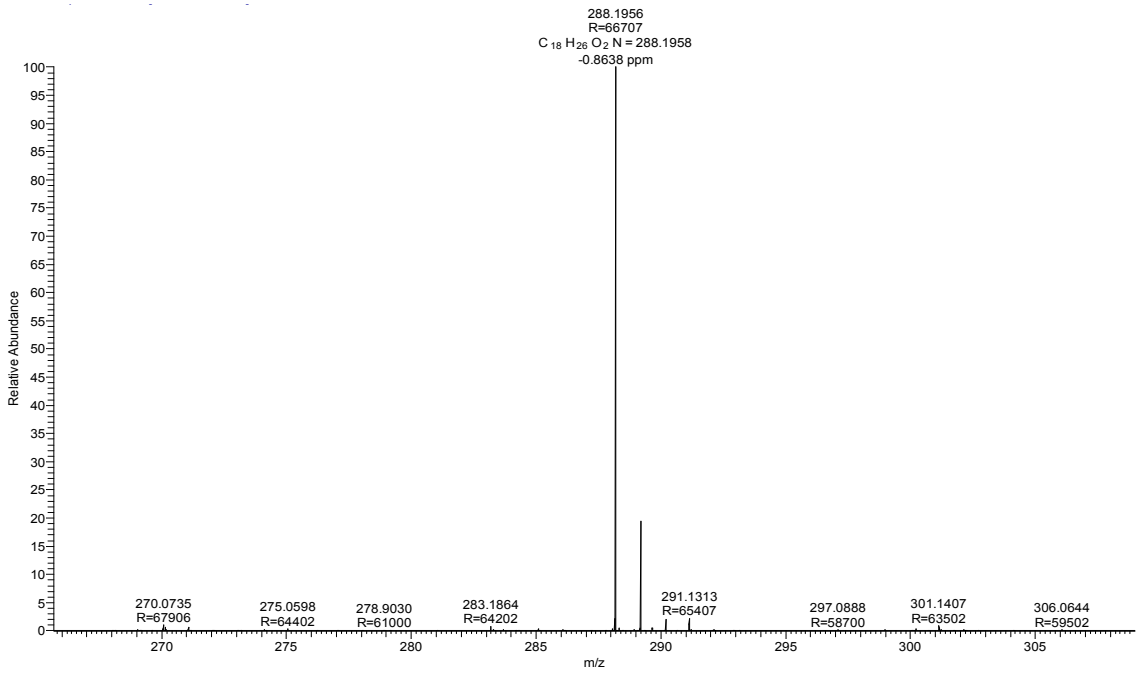


Figure S18. HRMS spectrum of **3b**.

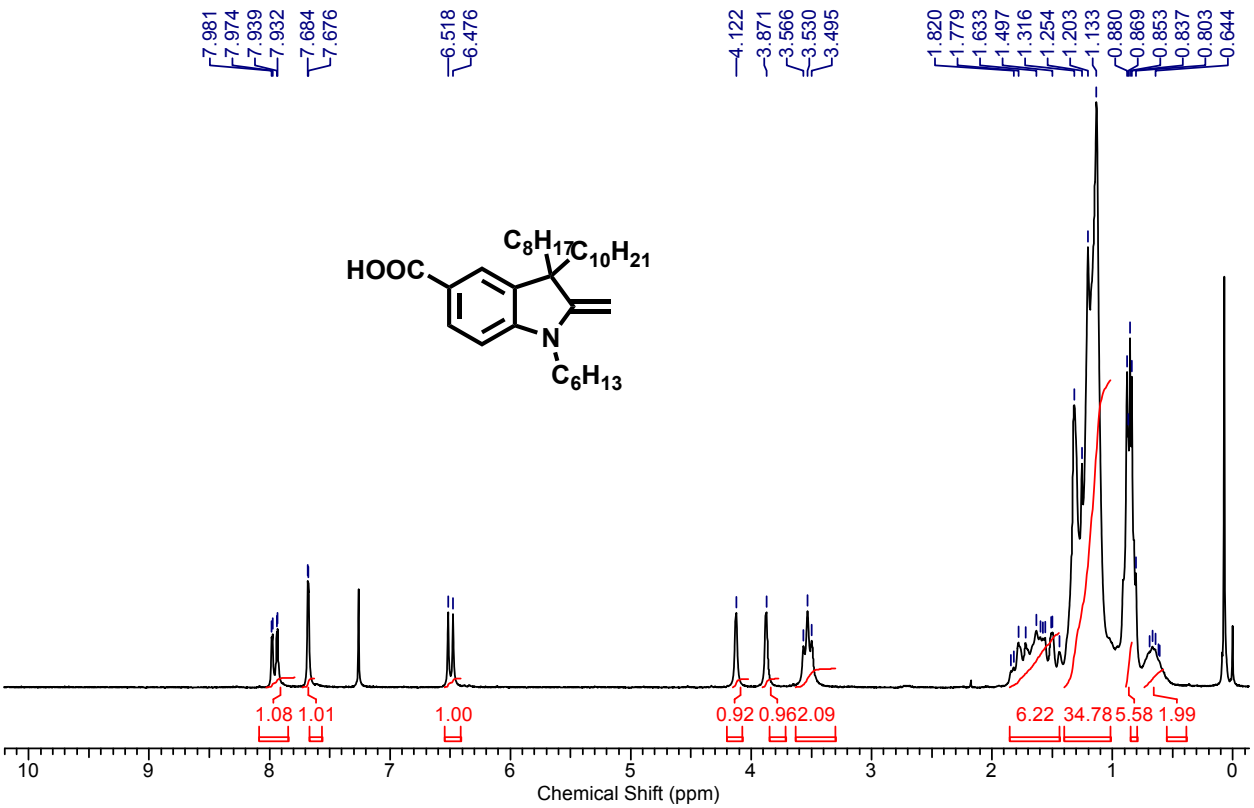


Figure S19. ^{1}H NMR(200 MHz, $CDCl_3$) spectrum of compound 3-decyl-1-hexyl-3-methyl-2-methyleneindoline-5-carboxylic acid.

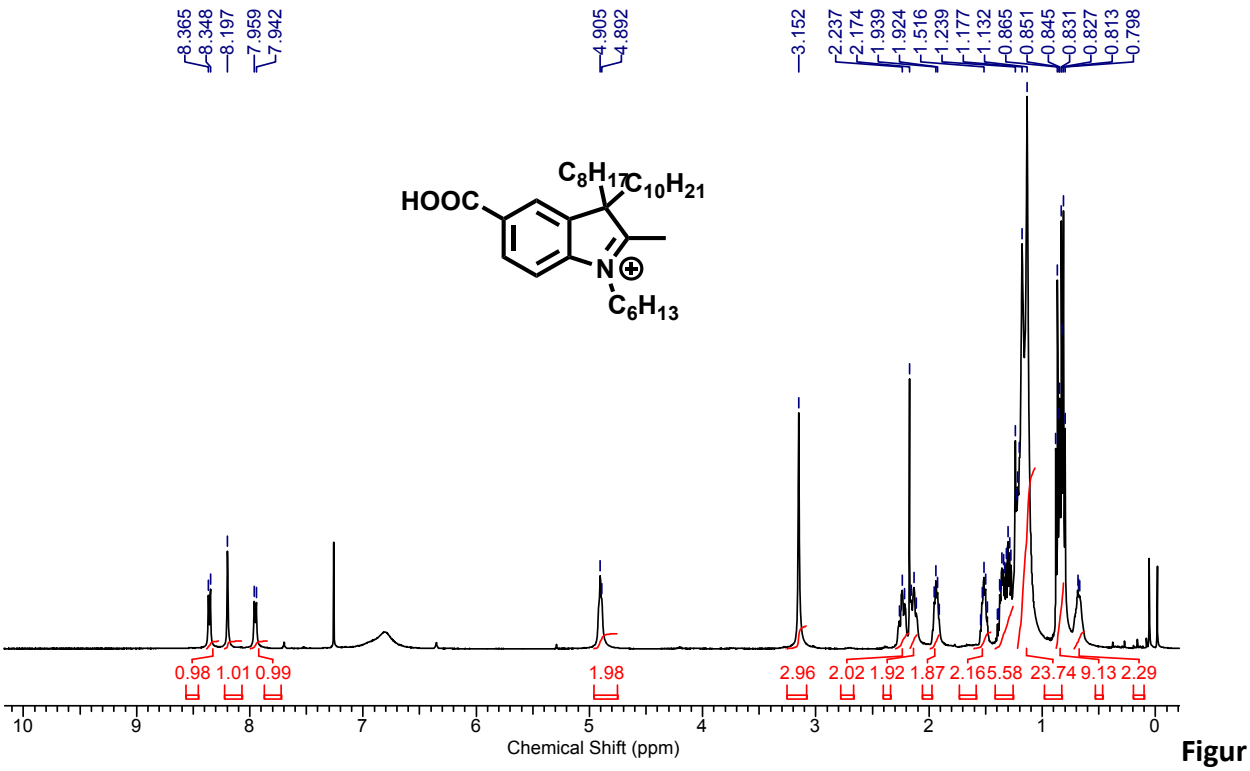
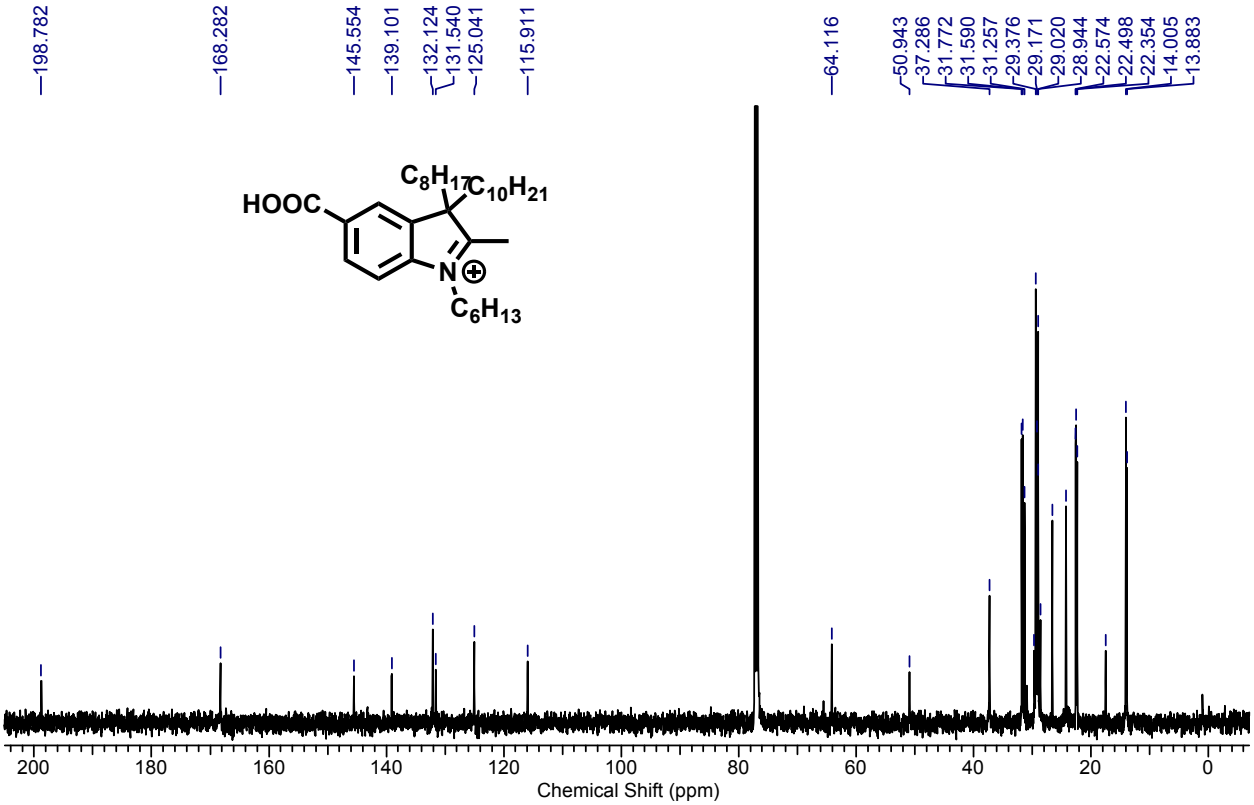


Figure S20. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3c.**



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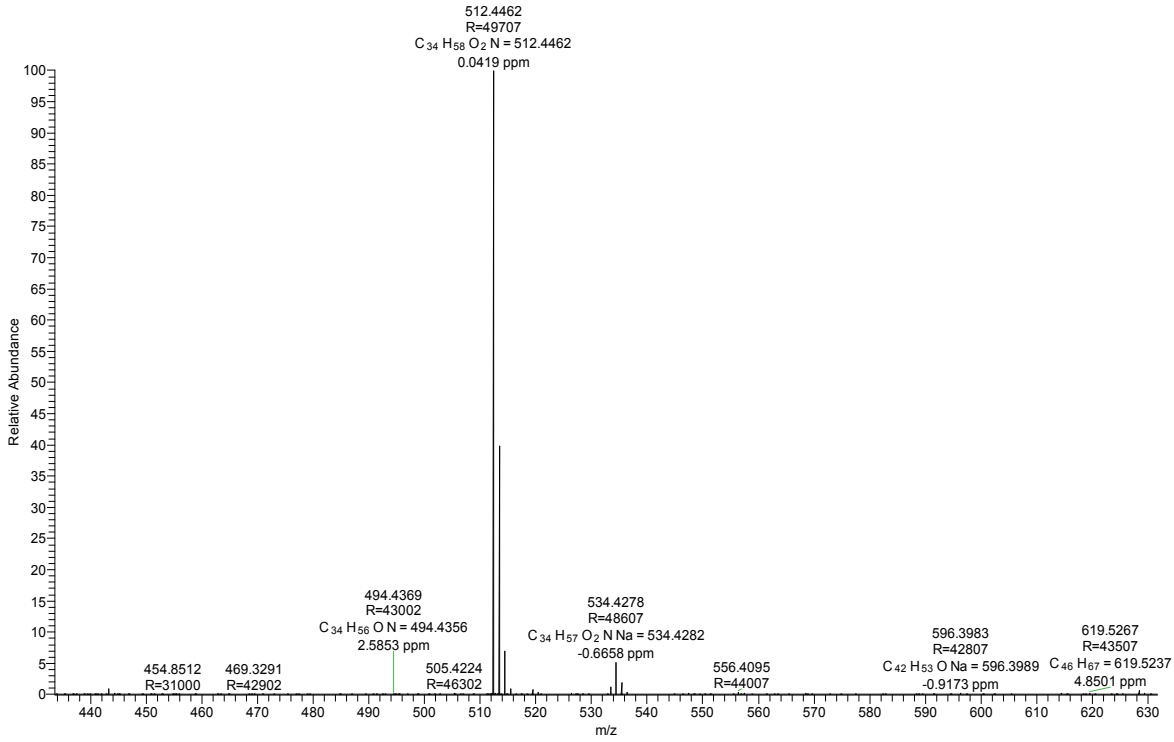


Figure S22. HRMS spectrum of **3c.**

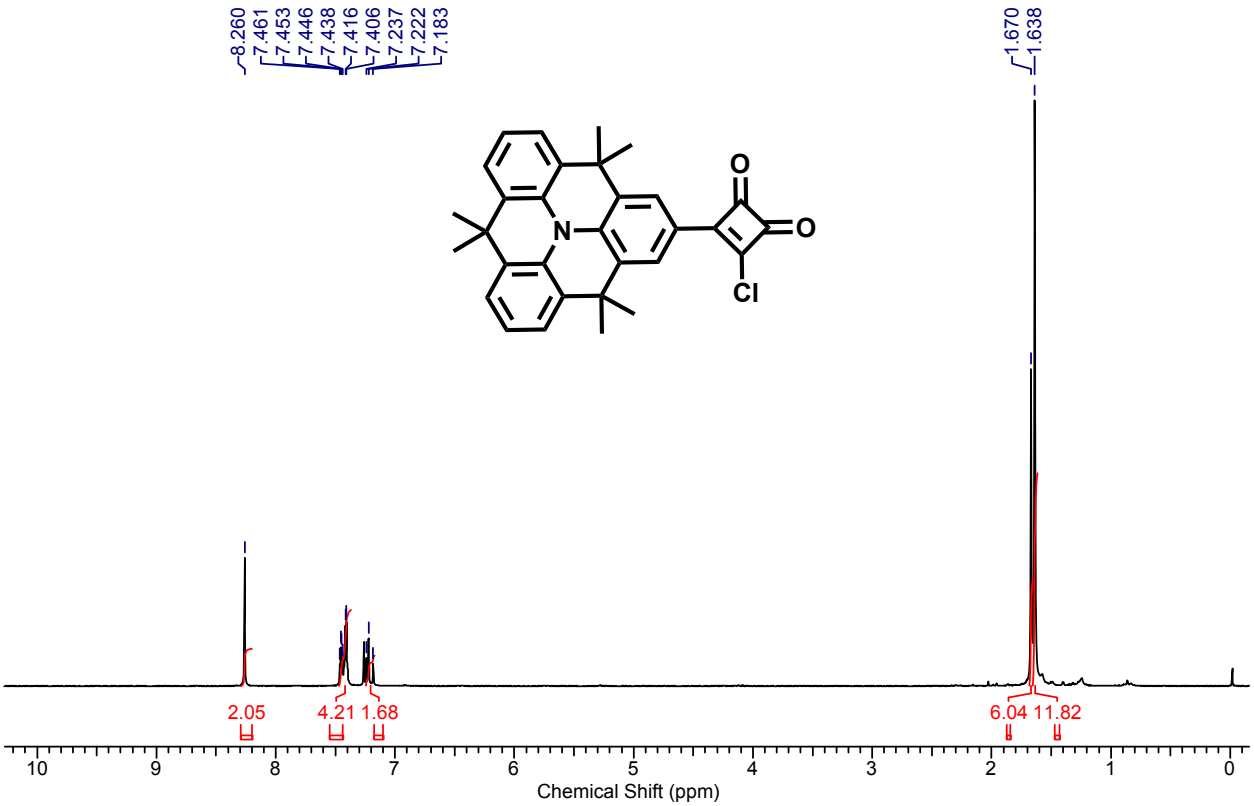
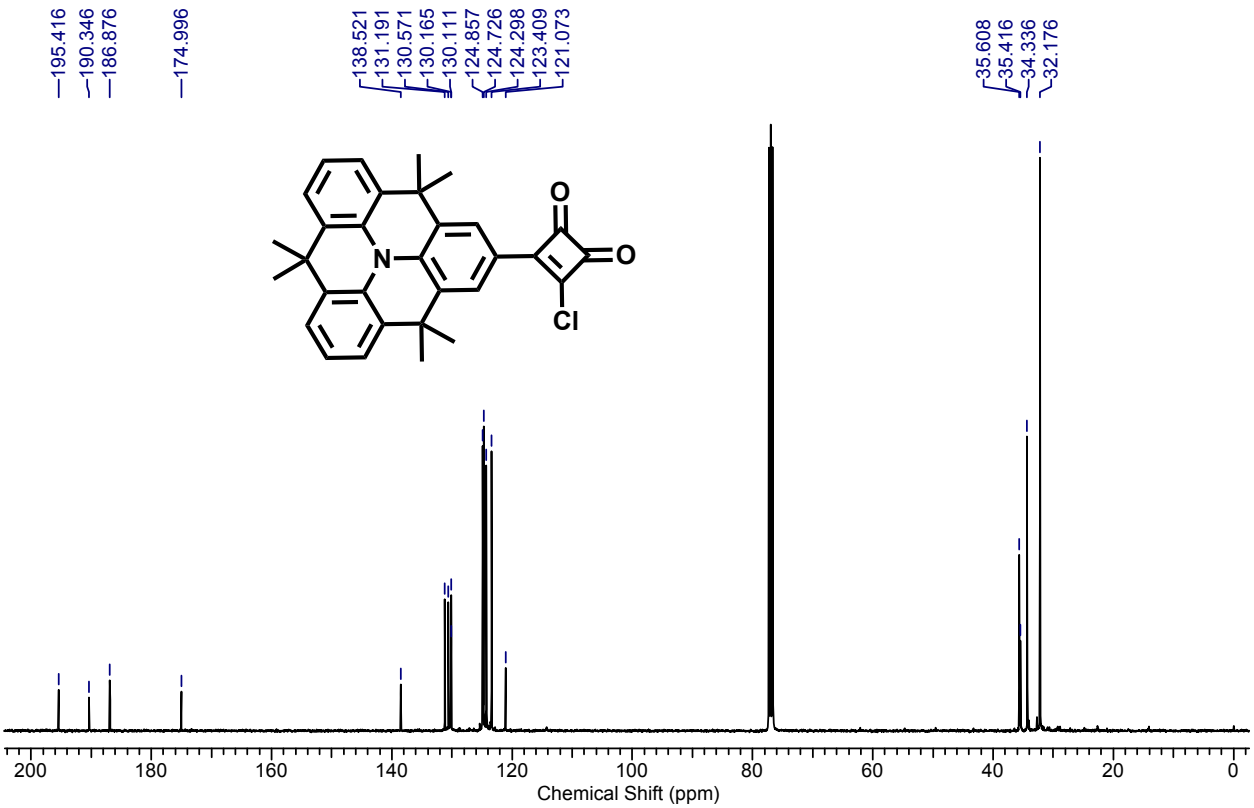


Figure S23.[1]H NMR (200 MHz, $CDCl_3$) spectrum of compound **4b.**



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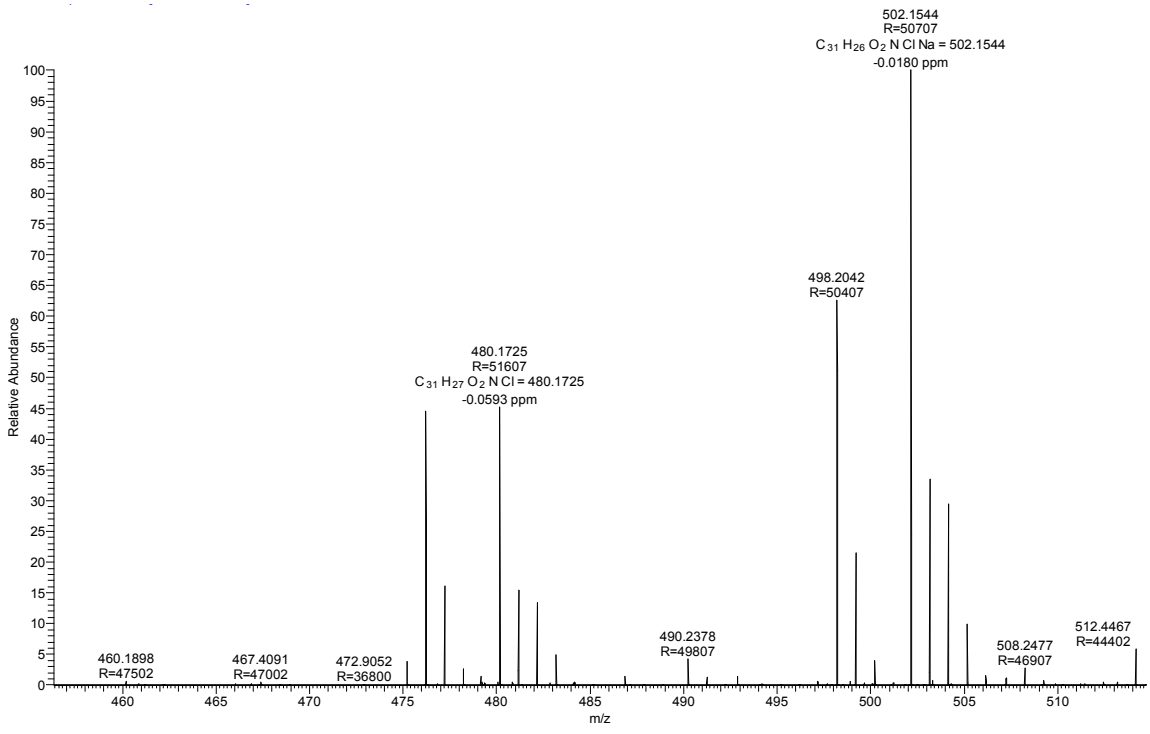


Figure S25. HRMS spectrum of **4b.**

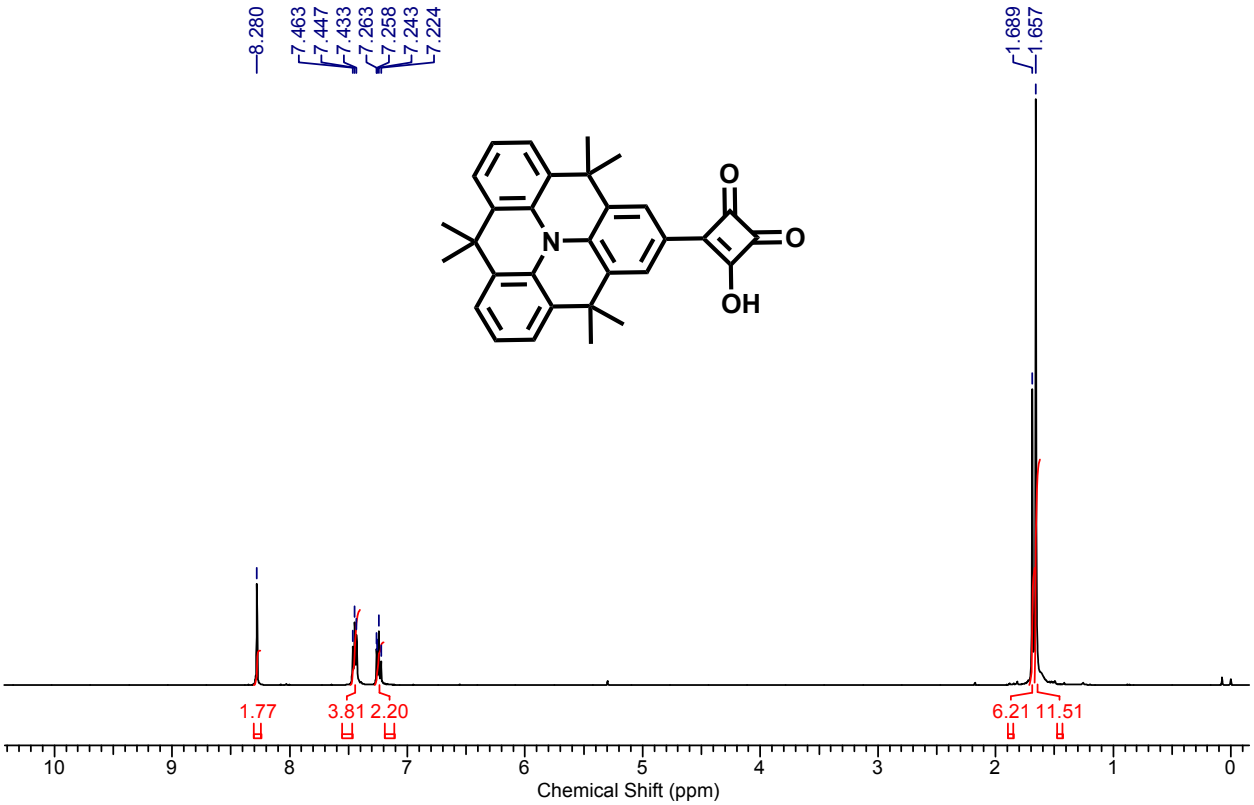


Figure S26. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4c.**

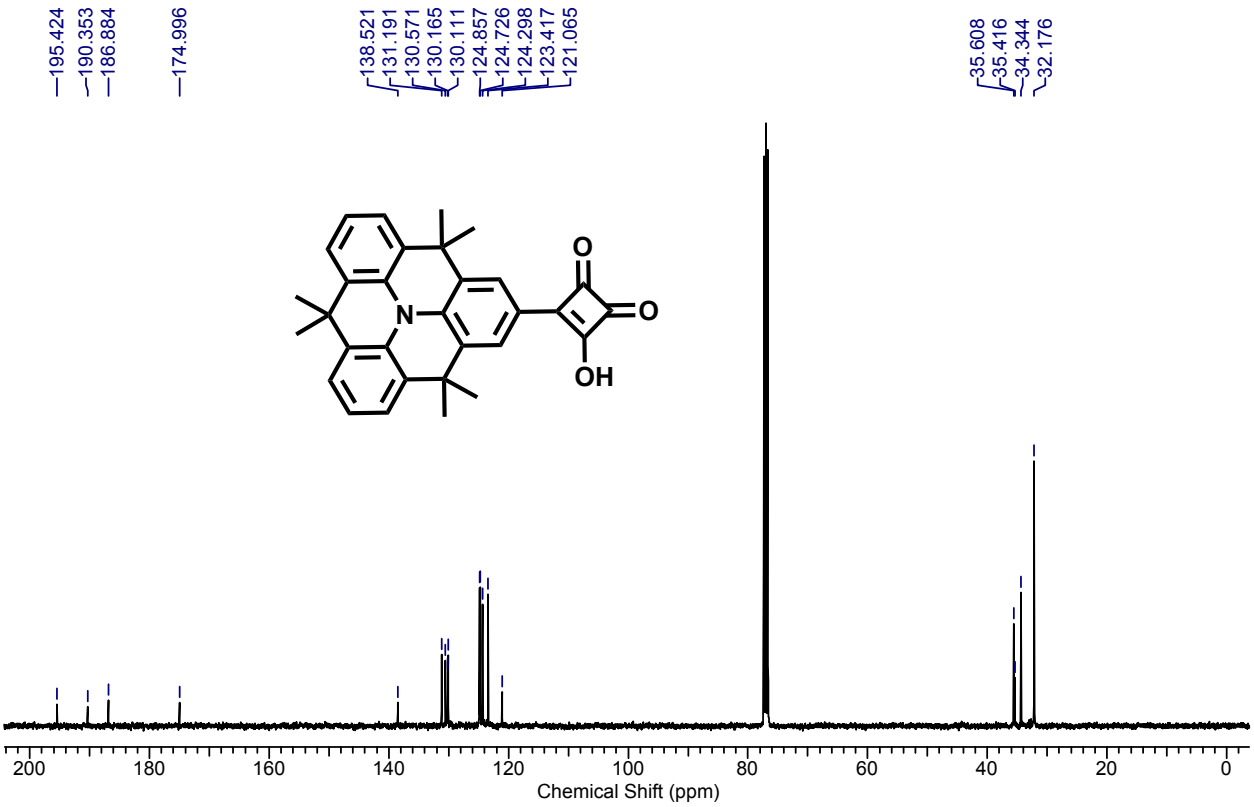


Figure S27. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4c.**

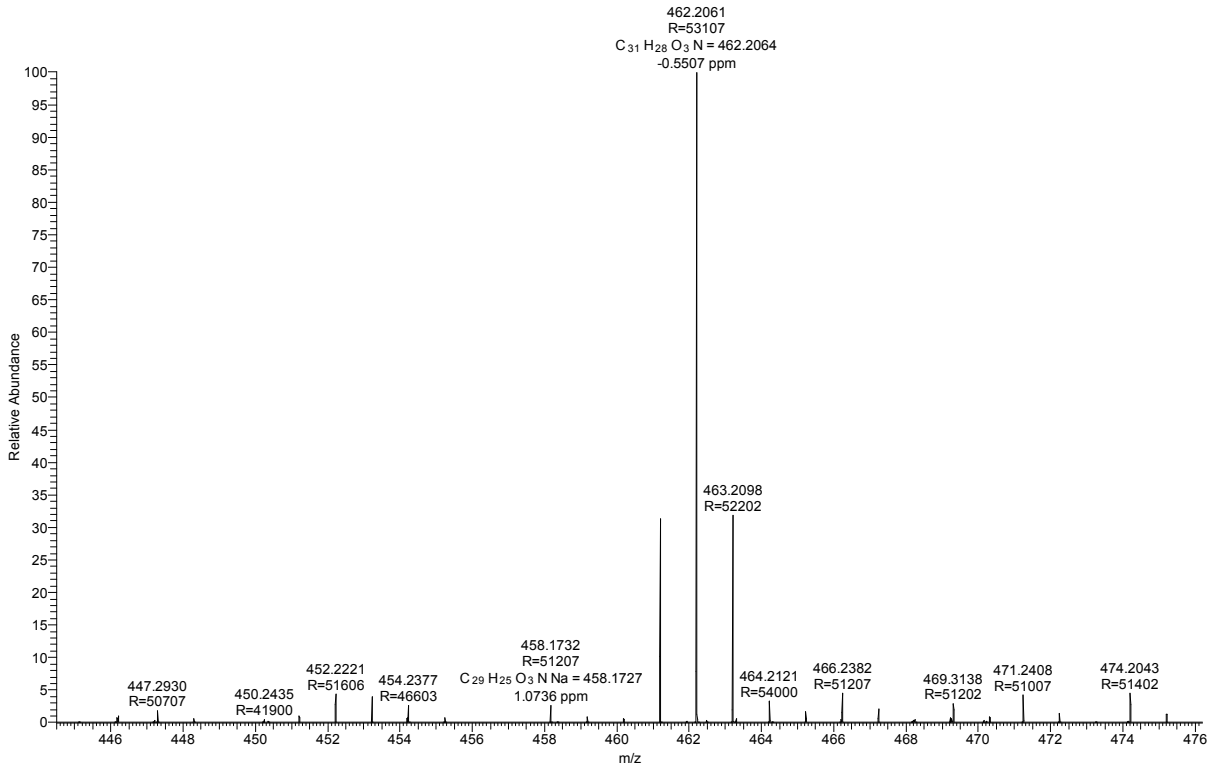


Figure S28. HRMS spectrum of **4c.**

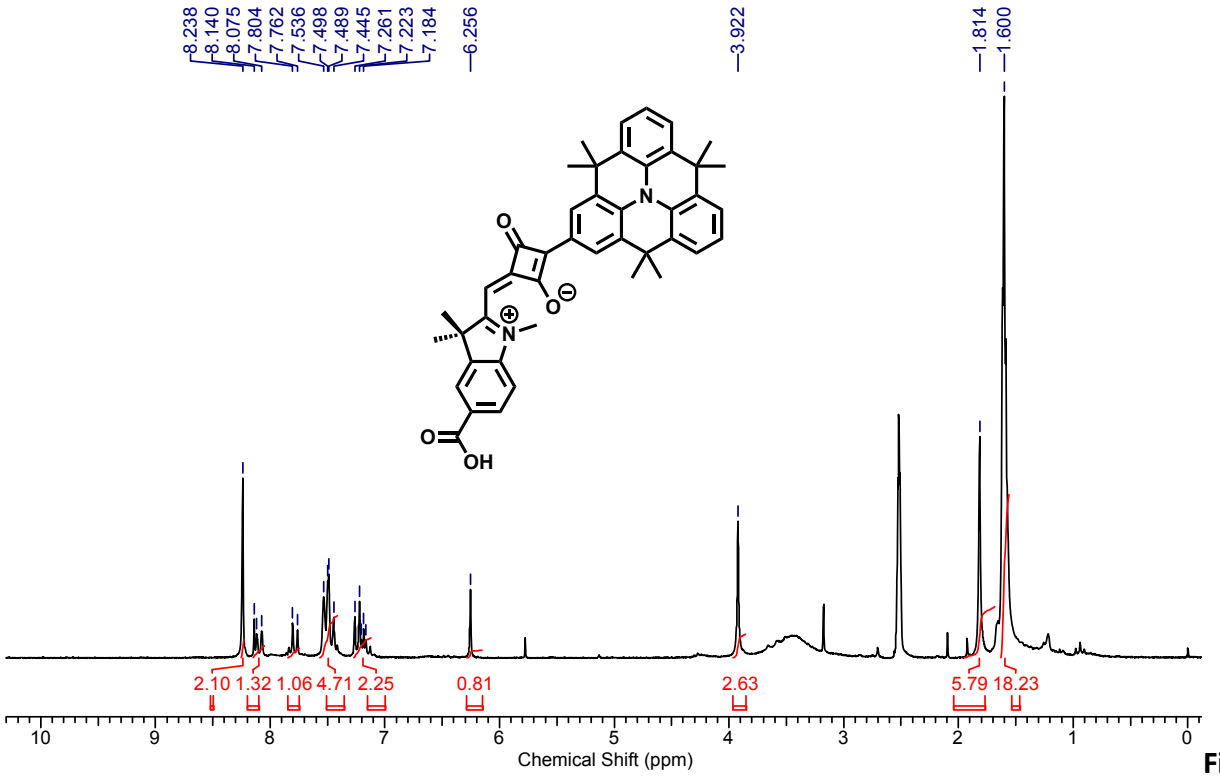


Figure S29. ^{1}H NMR (200 MHz, DMSO-d_6) spectrum of compound **NSQ1.**

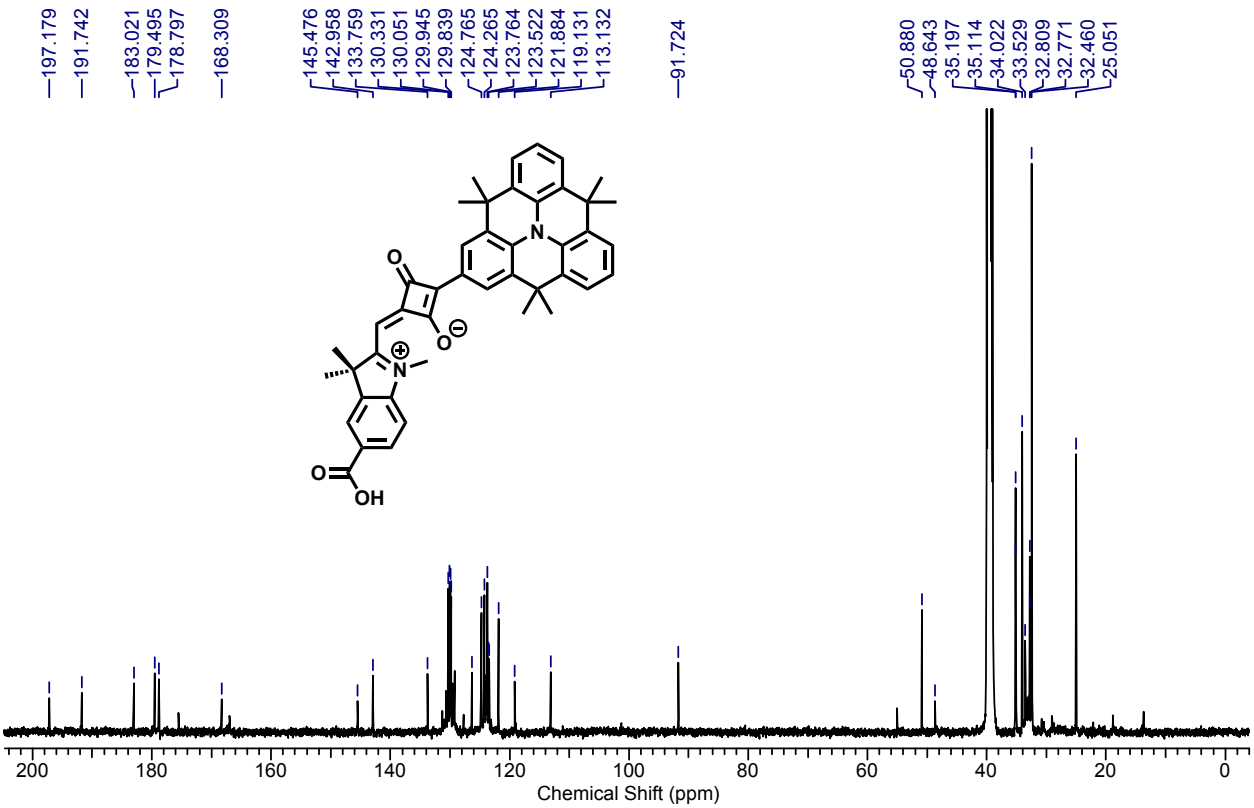


Figure S30. ^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound **NSQ1.**

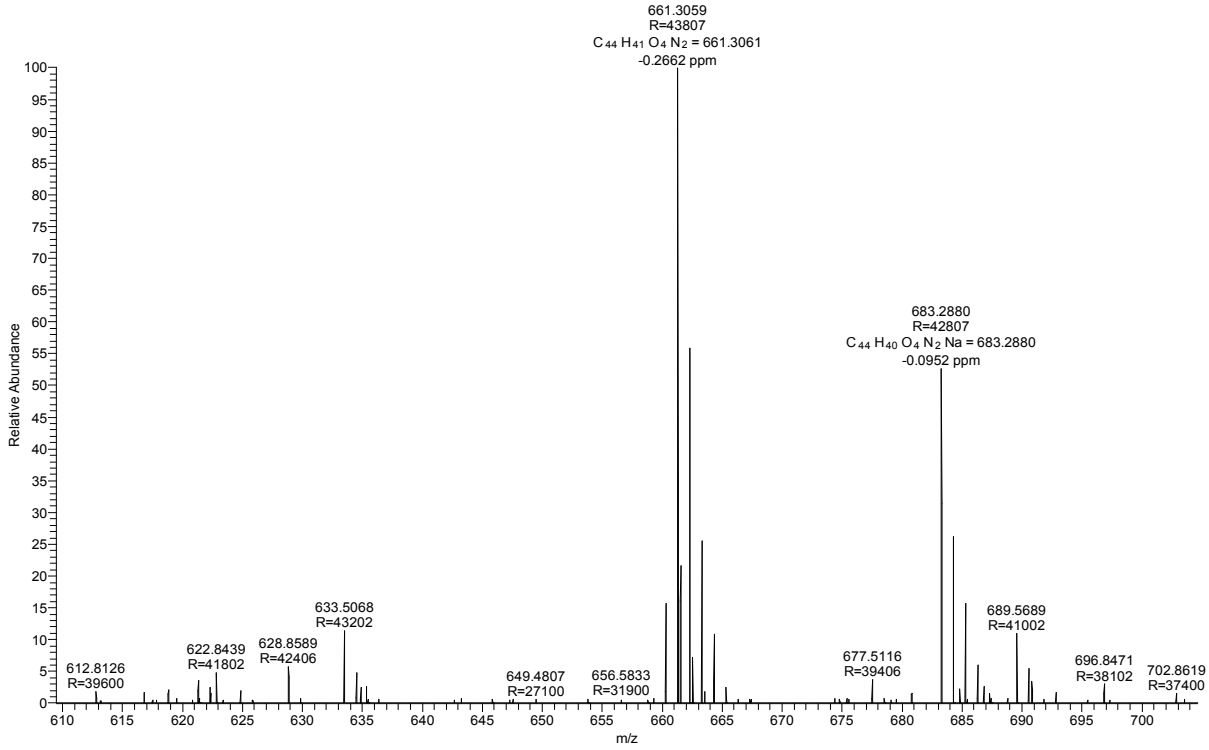


Figure S31. HRMS spectrum of **NSQ1.**

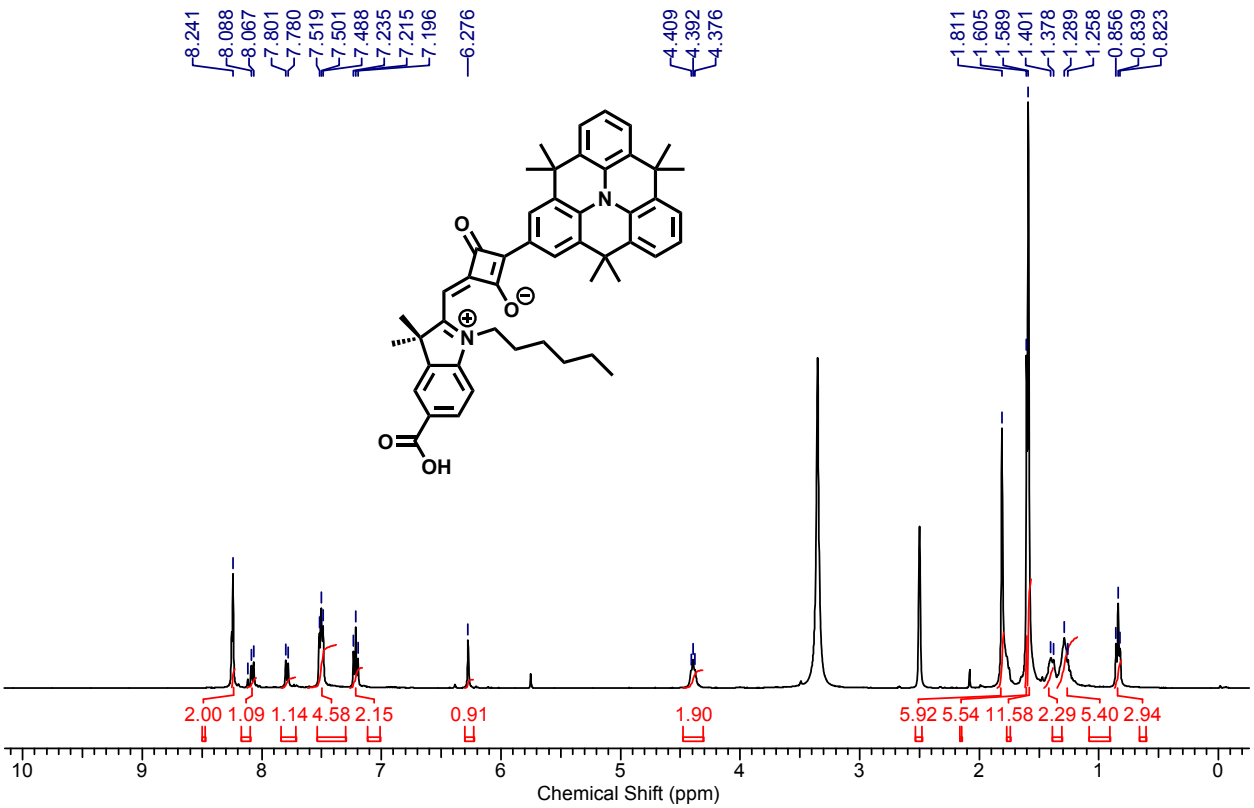


Figure S32. ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound **NSQ2.**

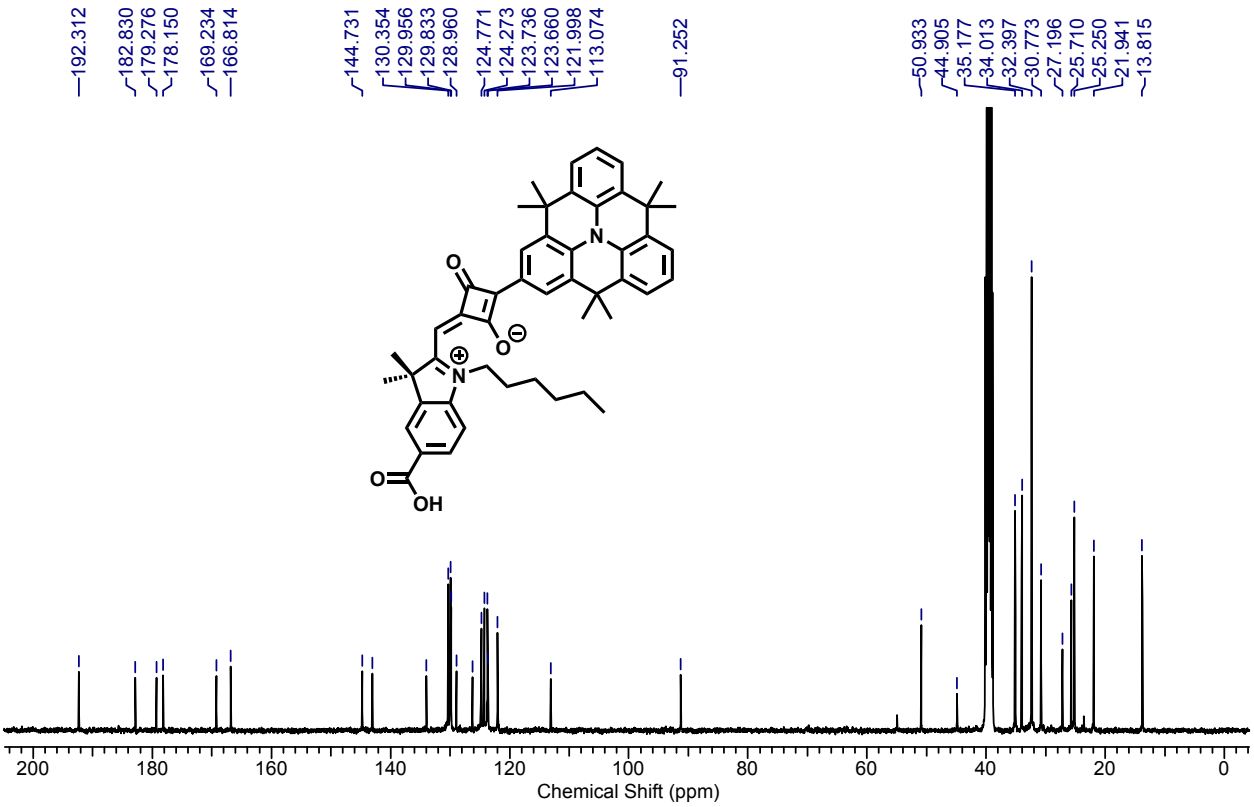


Figure S33. ^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound **NSQ2.**

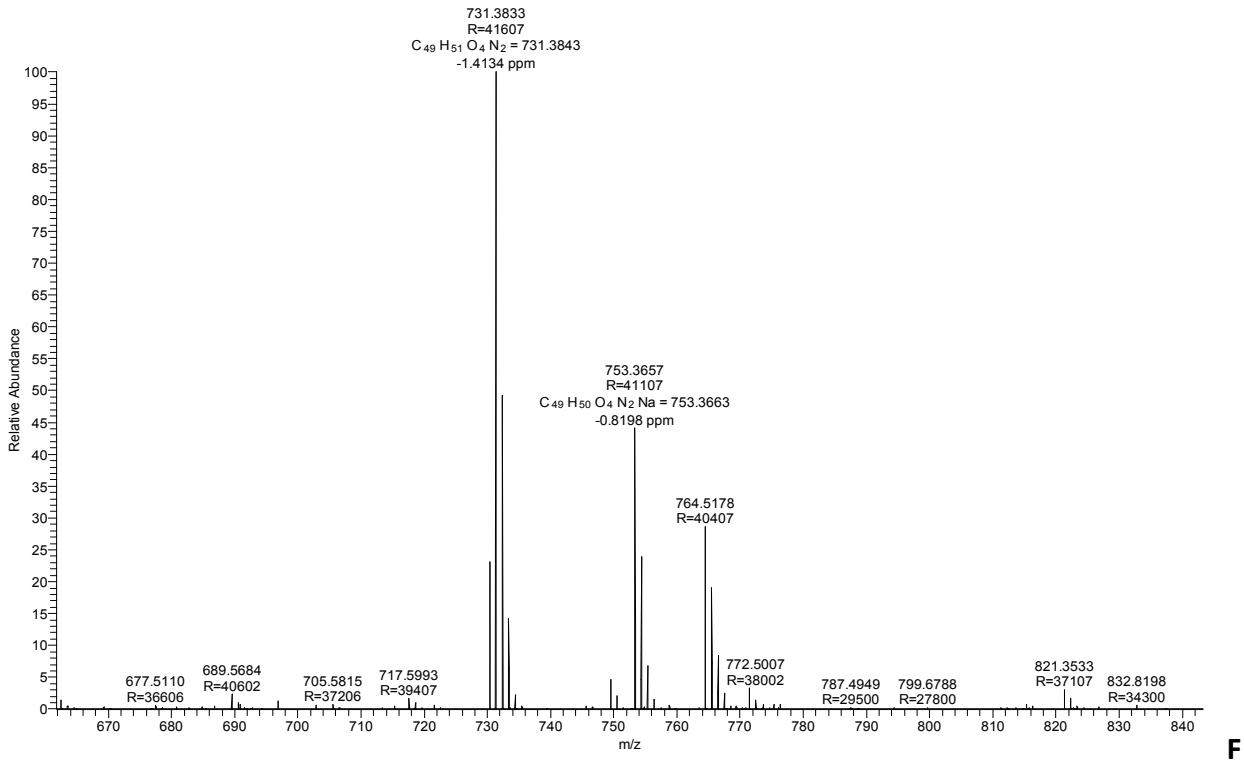


Figure S34. HRMS spectrum of **NSQ2.**

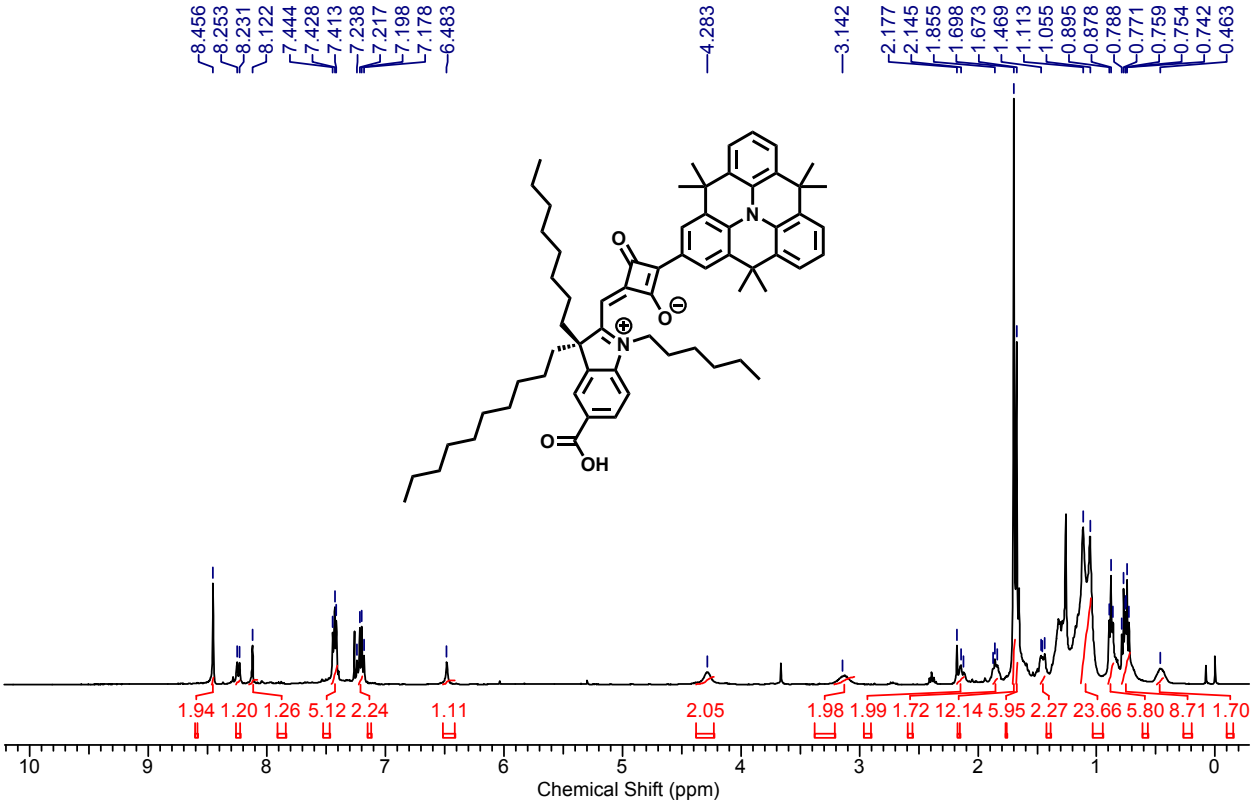


Figure S35. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **NSQ3.**

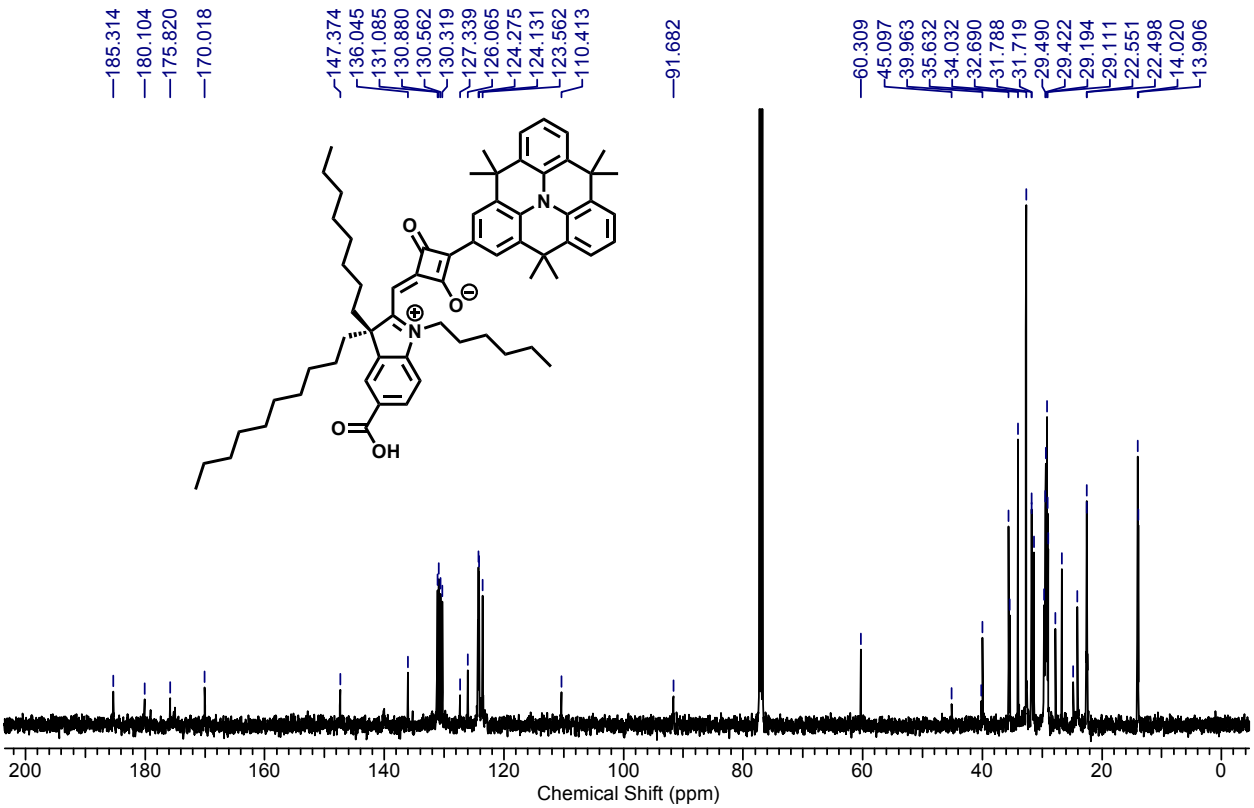


Figure S36. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **NSQ3.**

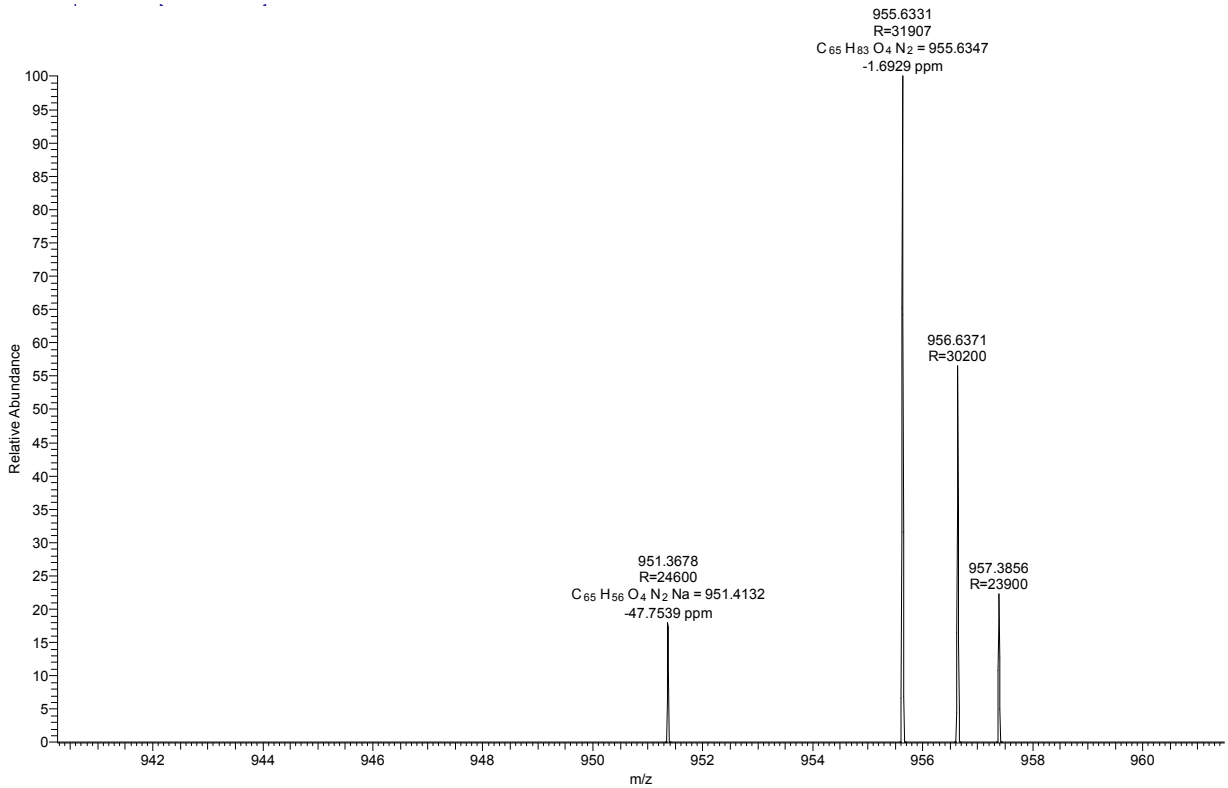


Figure S37. HRMS spectrum of **NSQ3.**

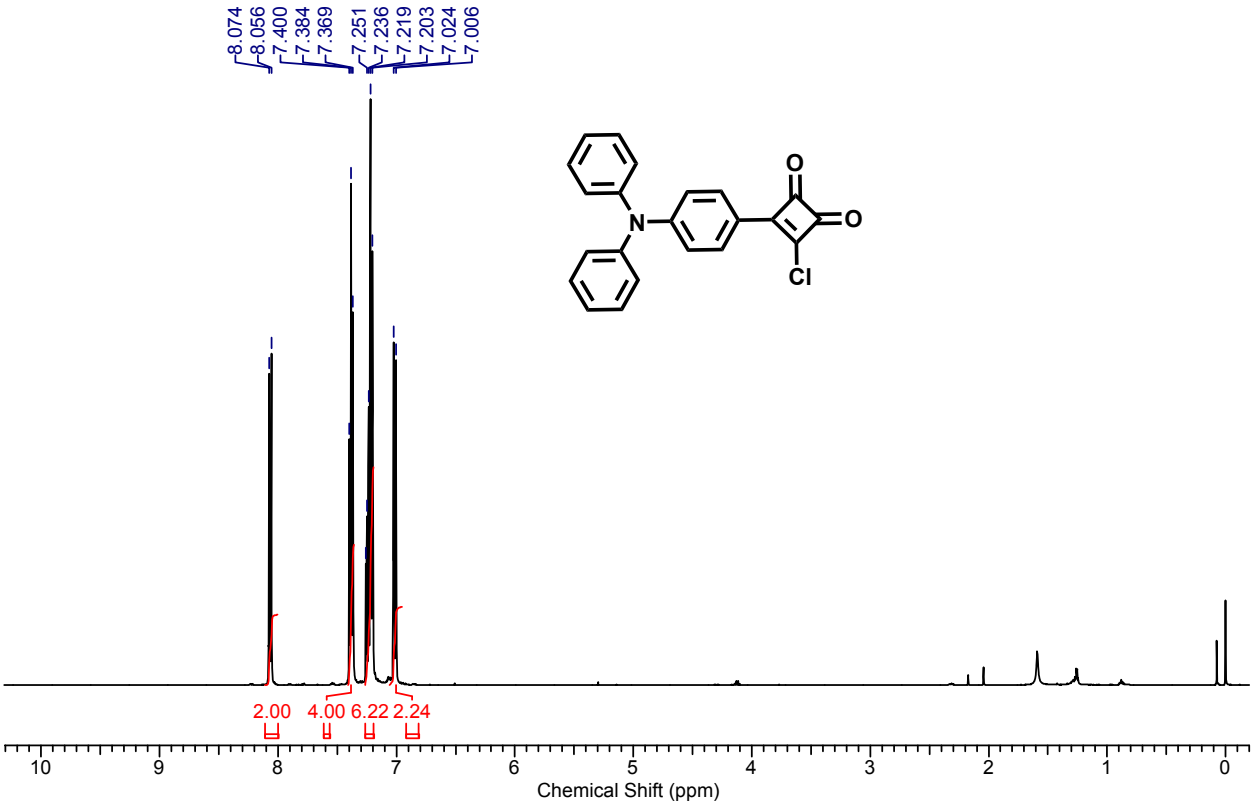


Figure S38. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **5b.**

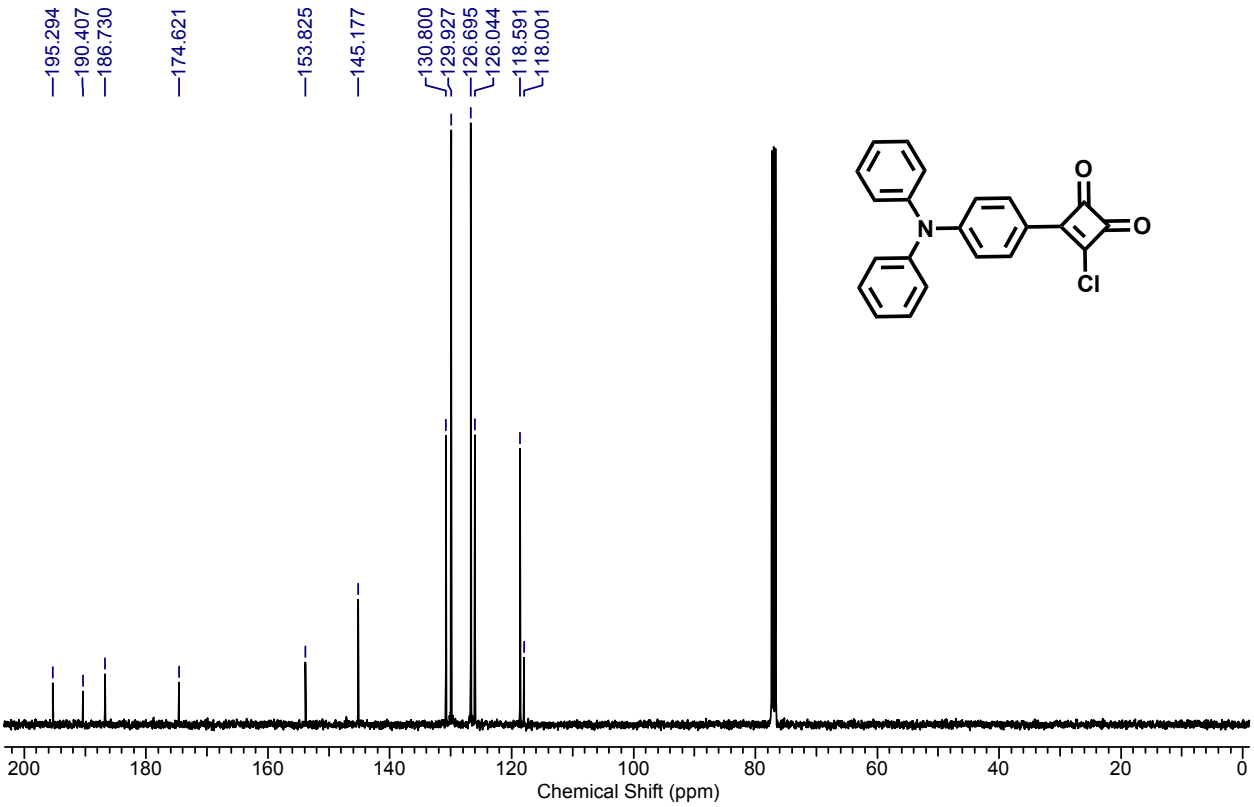


Figure S39. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5b.**

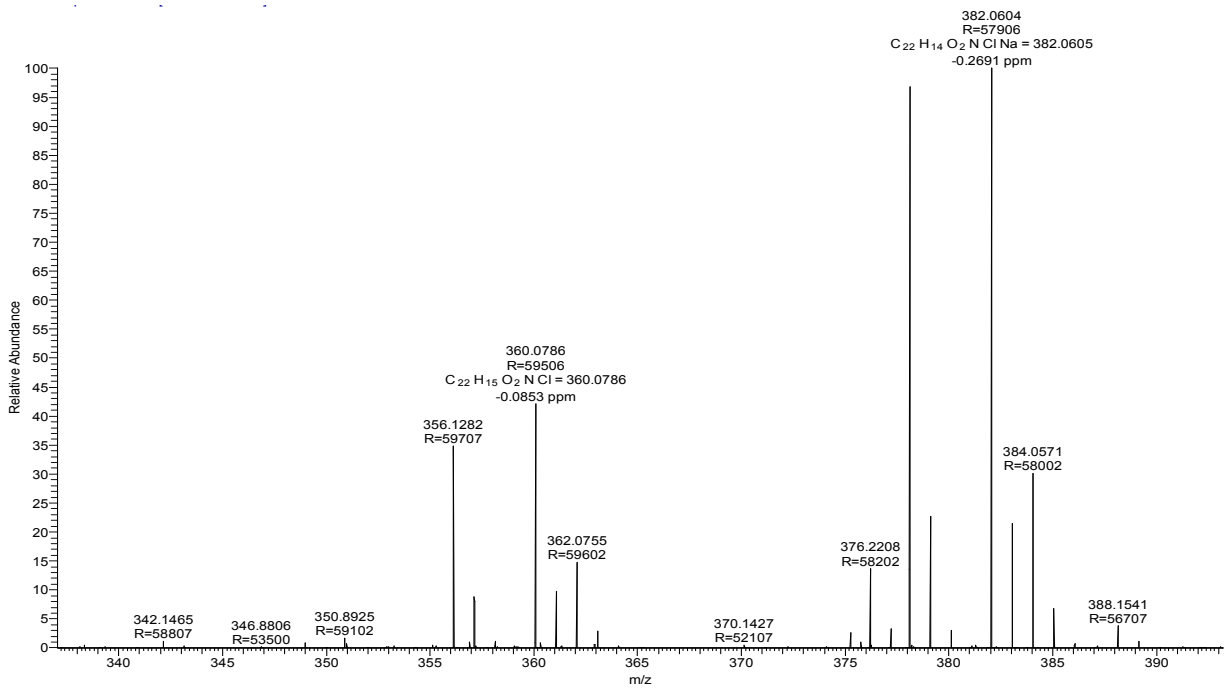


Figure S40. HRMS spectrum of **5b.**

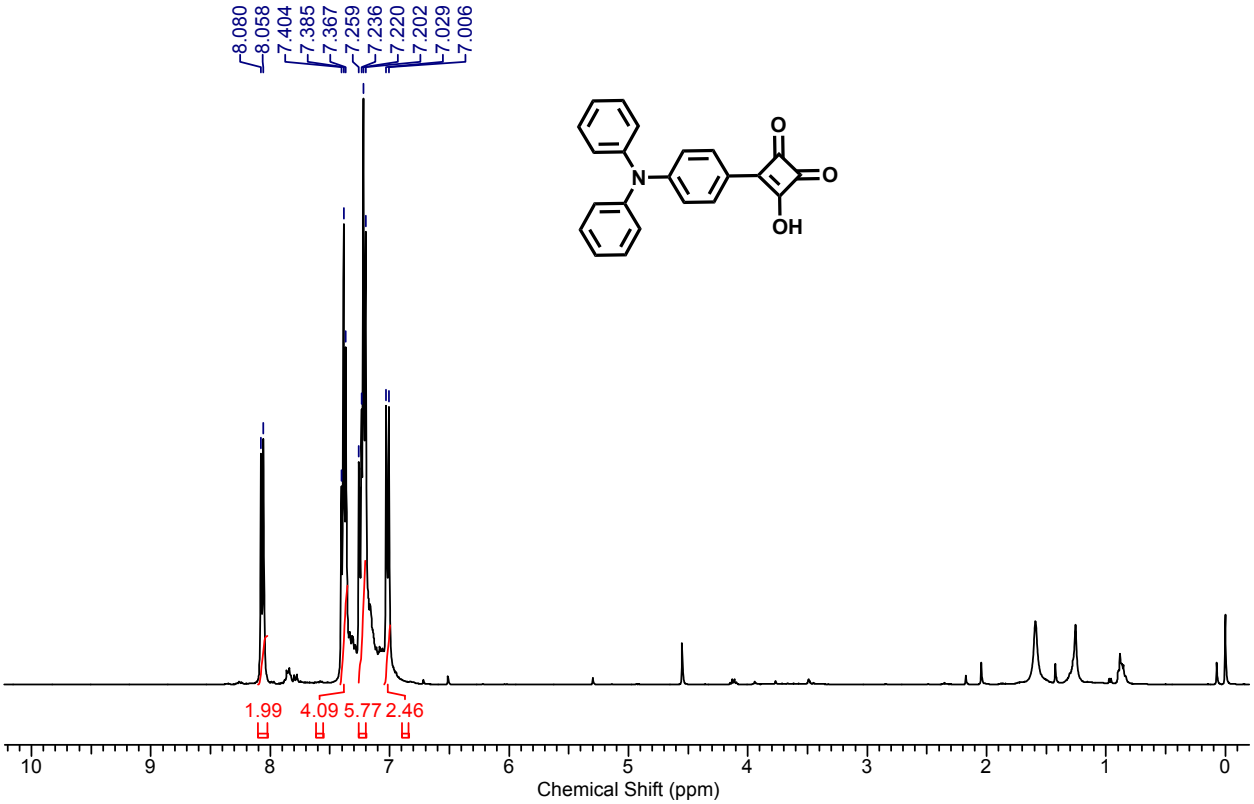


Figure S41. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5c.**

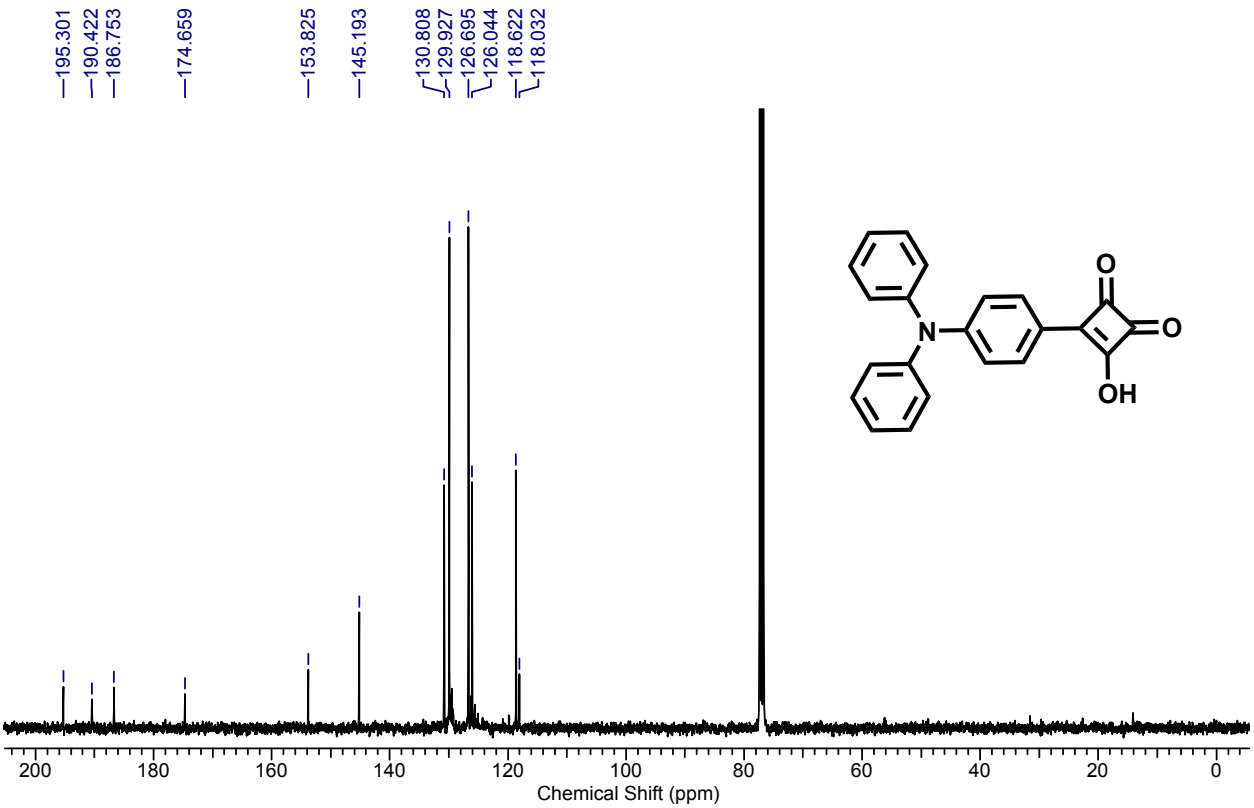


Figure S42. ^{13}C (100 MHz, $CDCl_3$) spectrum of compound **5c.**

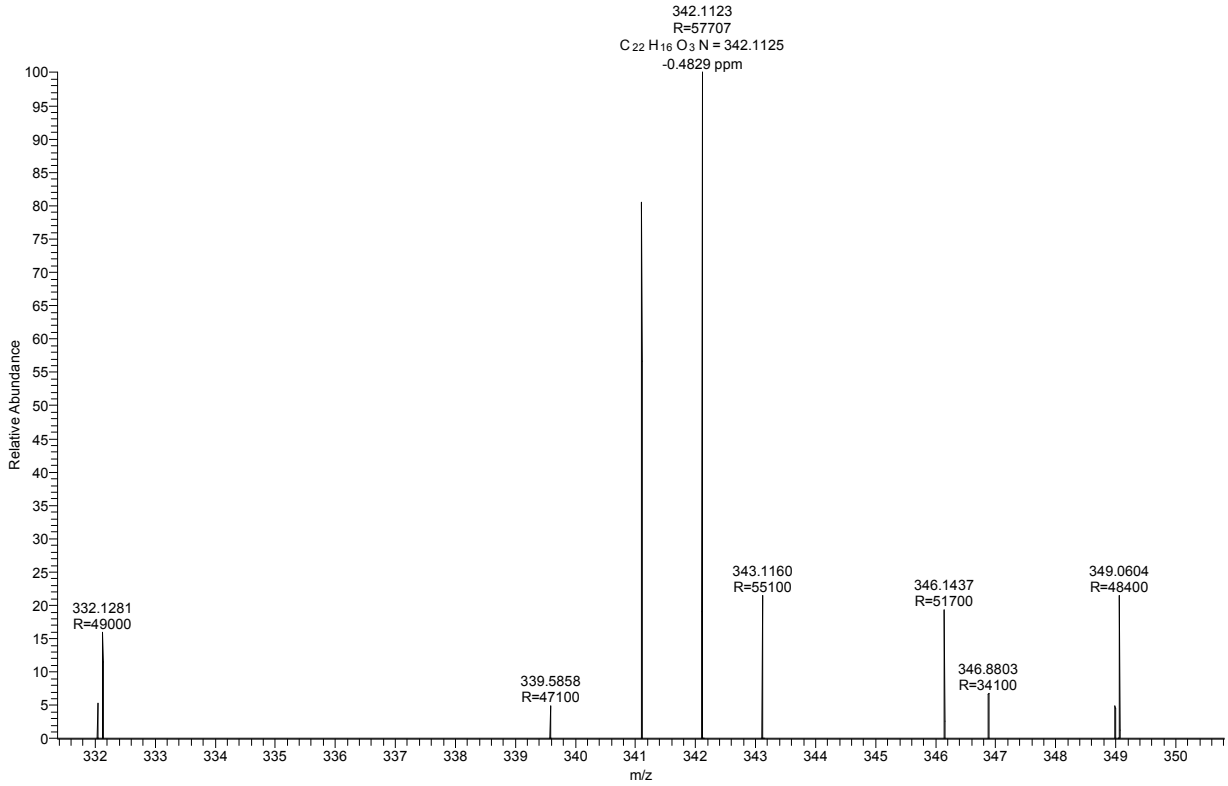


Figure S43. HRMS spectrum of **5c.**

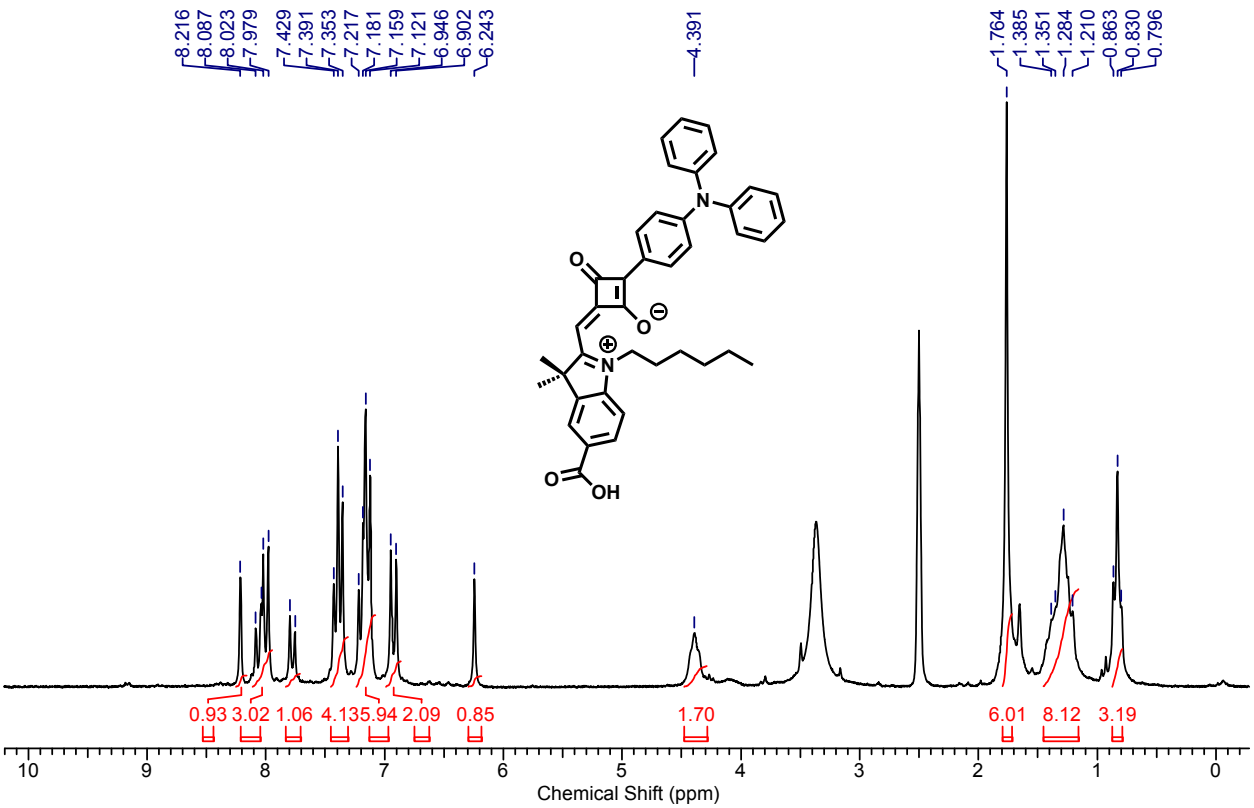


Figure S44. ^{1}H NMR (200 MHz, DMSO-d_6) spectrum of compound **NSQR.**

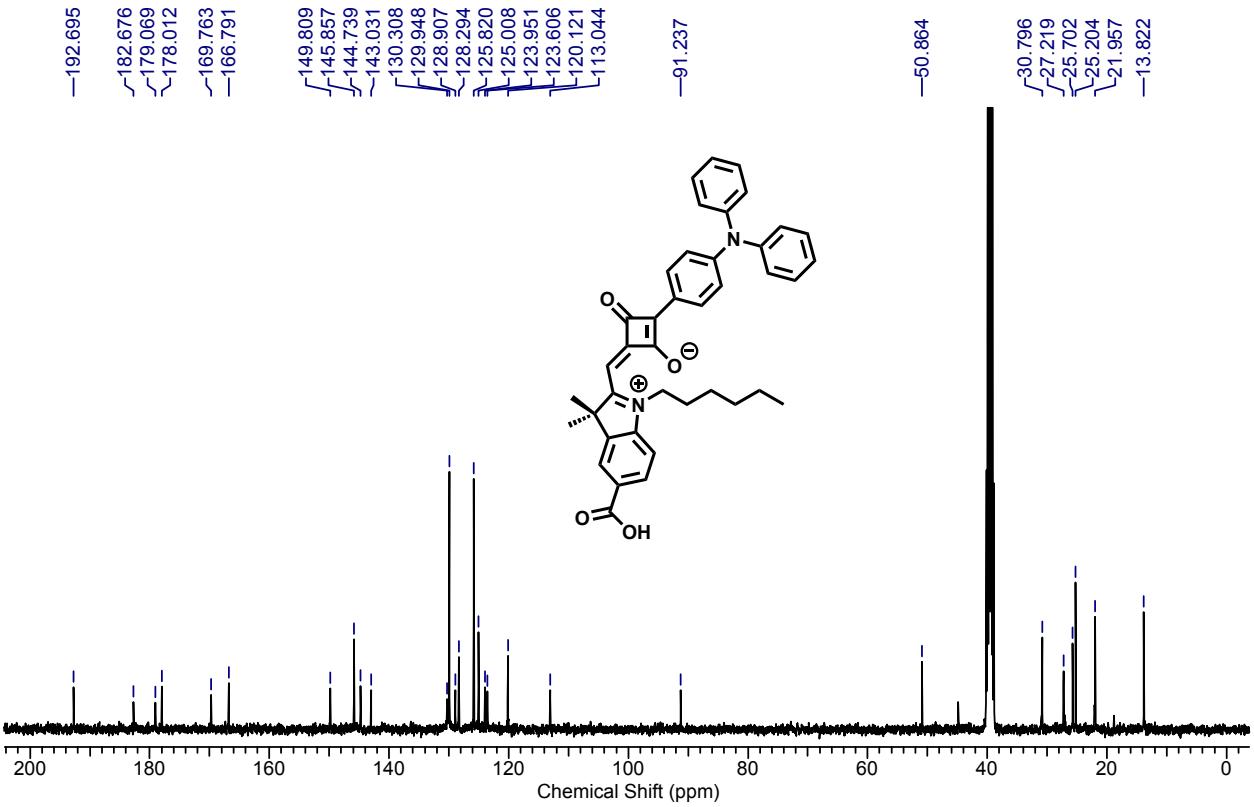


Figure S45. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **NSQR.**

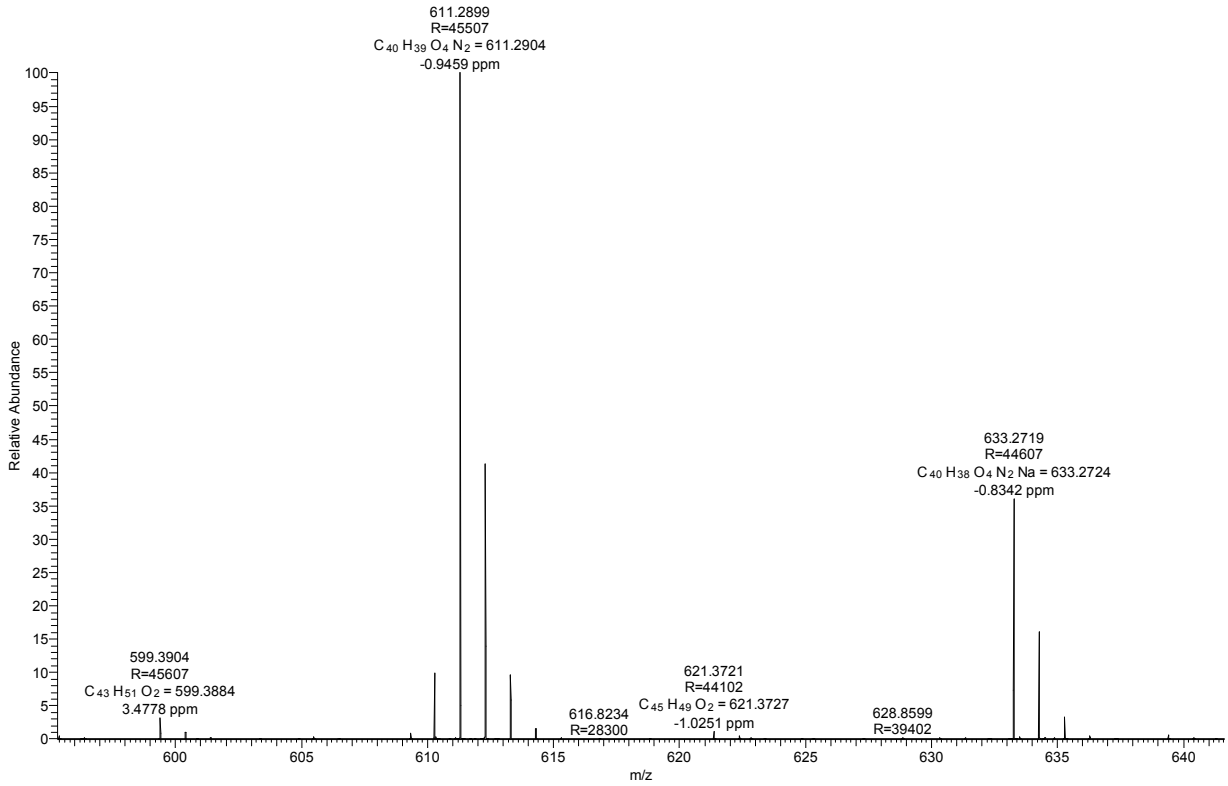


Figure S46. HRMS spectrum of dye **NSQR.**

Theoretical calculations

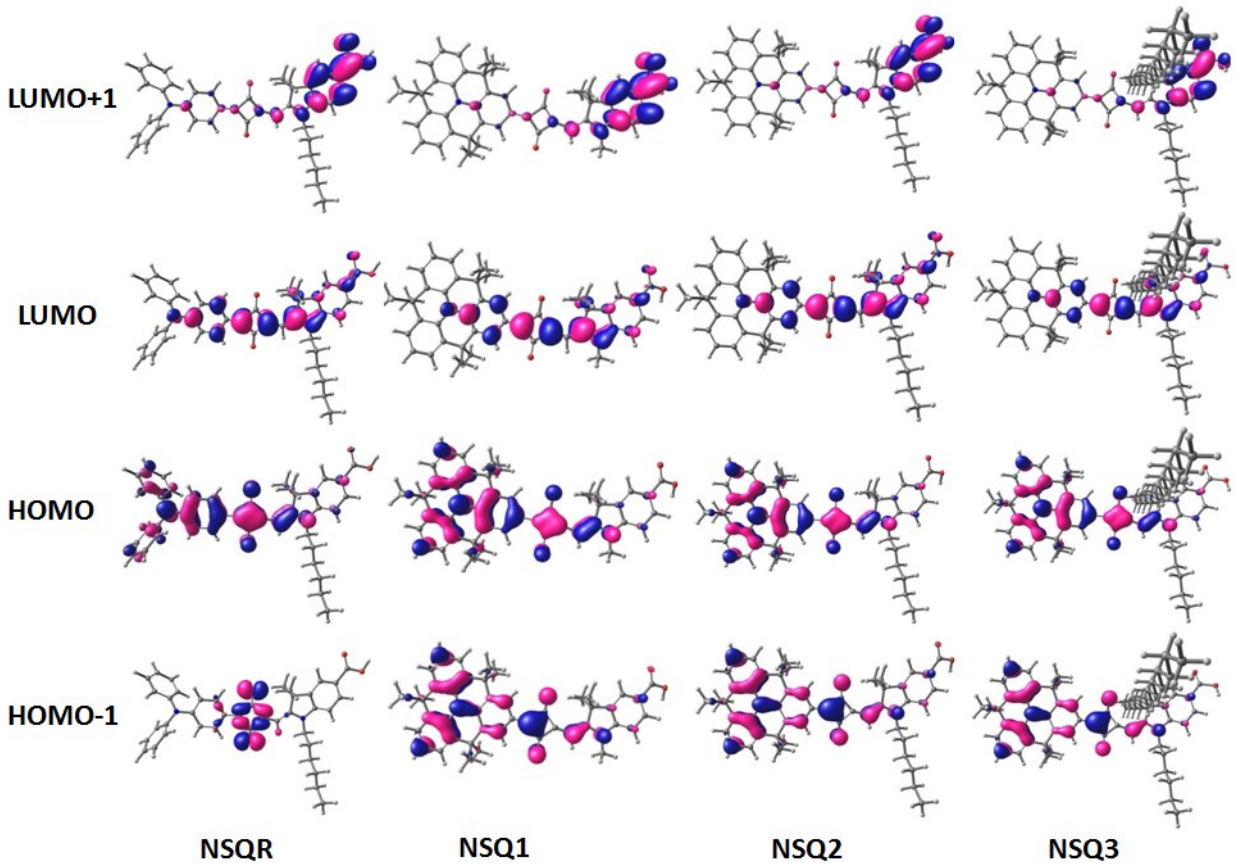


Figure S47. Isodensity surface plots of the HOMO, HOMO-1, LUMO and LUMO+1 of NSQ sensitizers.[S1]

Table S1. Selected dihedral angles of NSQs were calculated from the optimized ground state geometry

NSQ Dyes	**Dihedral angle (degree)**			
	θ_1	θ_2	θ_3	θ_4
NSQR	47.06	-0.33	-178.08	-
NSQ1	-0.05	0.05	-179.6	-
NSQ2	-0.43	0.57	-177.65	-
NSQ3	0.61	-0.24	-178.57	-176.66

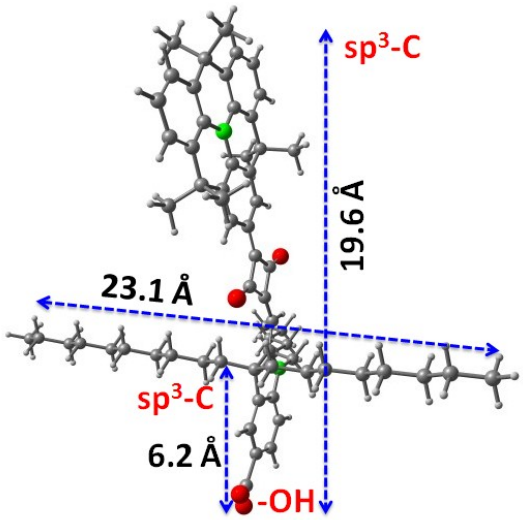
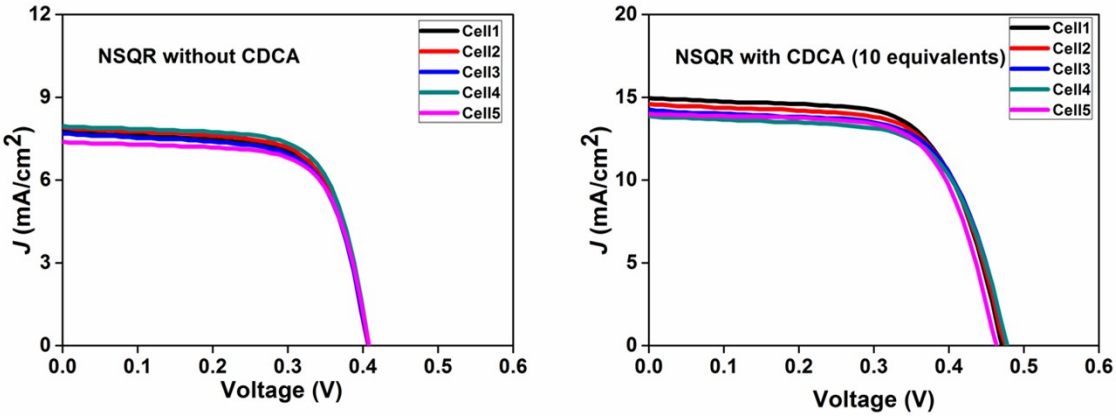


Figure S48. Distance between sp^3-C (methyl group of HT) to –O atom of carboxylic acid, distance between the terminal carbon atomes of sp^3 -branched alkyl chain and sp^3-C (indoline) to –O atom of carboxylic acid of **NSQ3** calculated from the optimized ground state geometry using density functional theory (DFT) at B3LYP/6-31G** level with the Gaussian 09 program.

Supplementary photovoltaic performance



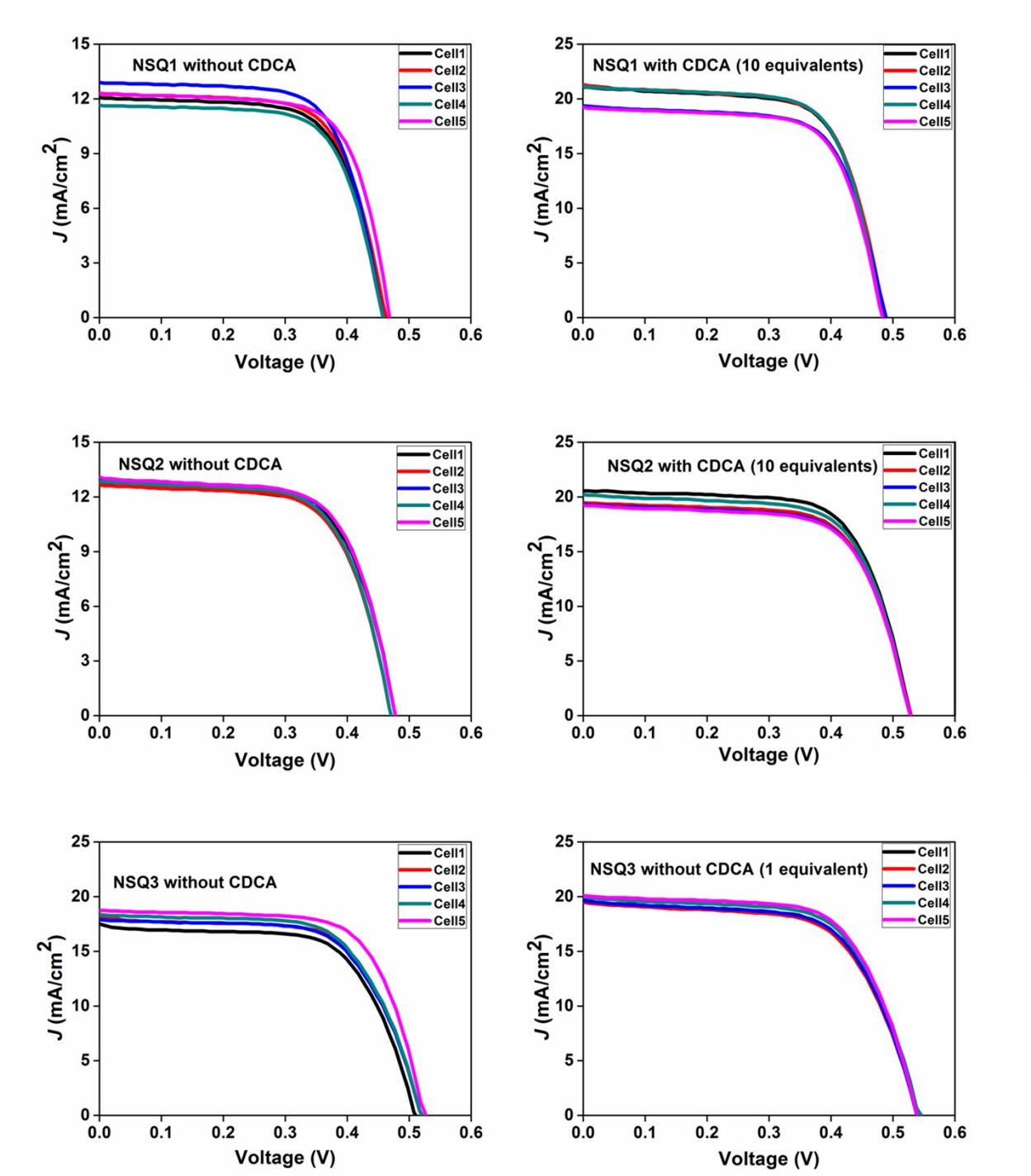


Figure S49. *J*–*V* characteristics of **NSQR** and **NSQ1-3** with deviation of 5 cells measured under simulated AM 1.5 G simulated sunlight (100 mW cm^{-2}).

Table S2. Photovoltaic performance of **NSQ3** with different ratios of CDCA.

Dye	V_{oc} (V)	J_{sc} (mA/cm^2)	*ff* (%)	η (%)	Amount of adsorbed dyes (x 10^{-7} mol cm^{-2})[a]
NSQ3/CDCA (1 eqv.)	0.541	20.11	65.6	7.14	0.94
NSQ3/CDCA (3 eqv.)	0.544	20.01	64.1	6.99	0.76
NSQ3/CDCA (5 eqv.)	0.541	19.51	63.2	6.67	0.64
NSQ3/CDCA (10 eqv.)	0.550	14.28	69.4	5.45	0.32

[a]by dye desorption method, carried out in 2M ethanolic HCl.

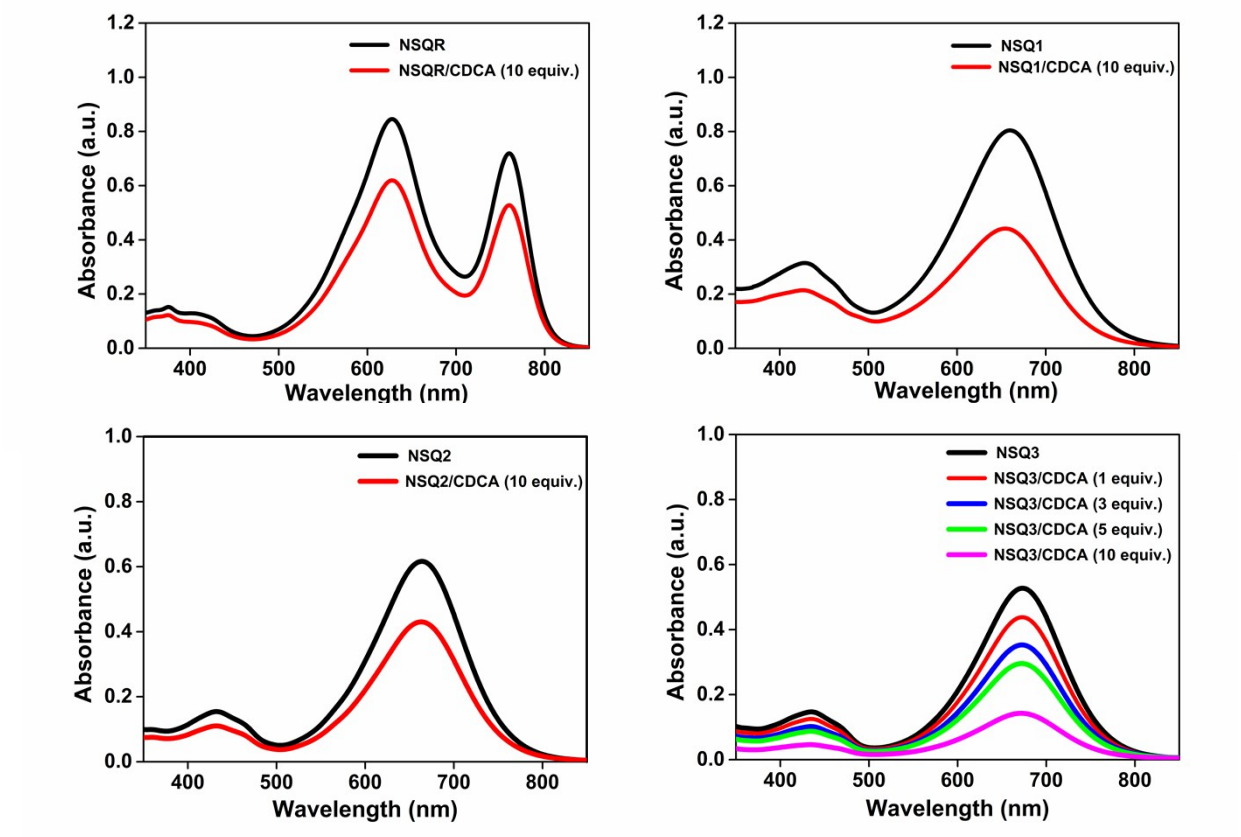


Figure S50. UV-Vis absorption spectra of desorbed **NSQR** and **NSQ1-3** dyes in 2 M HCl in EtOH.

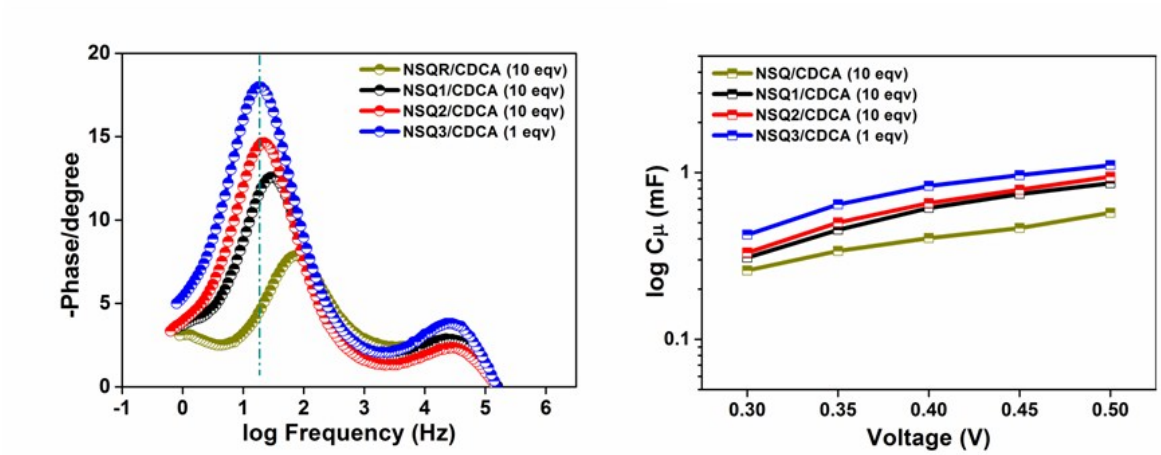


Figure S51. (a) Bode plot of **NSQ** dye cells (with an applied potential of -0.5 V), and (b) C_{μ} as a function of voltage (with an applied potential of -0.3 V).

Supplementary references

S1. Gaussian 09, Revision A. 02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone,V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino,J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi , R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski,V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J.; Gaussian, Inc., Wallingford CT, 2009.