Electronic Supporting Information for

Solvent Dependent Isomerization of Photochromic Dithienylethenes: Synthesis, Photochromism, and Self-assembly

Choong Ping Sen and Suresh Valiyaveettil*

Department of Chemistry, National University of Singapore.
3 Science Drive 2, Singapore 117543.
E-mail: chmsv@nus.edu.sg

Content

1. ^{1}H and ^{13}C NMR of intermediate and DTEs.

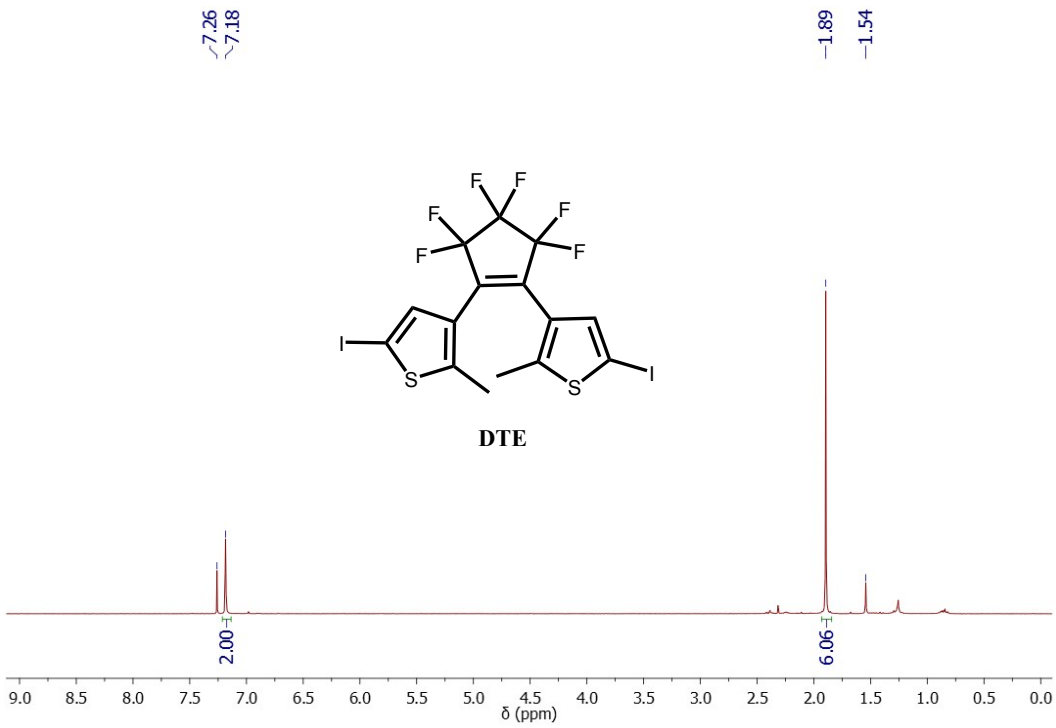


Figure S1. ^{1}H NMR spectrum of compound **DTE** in $CDCl_3$.

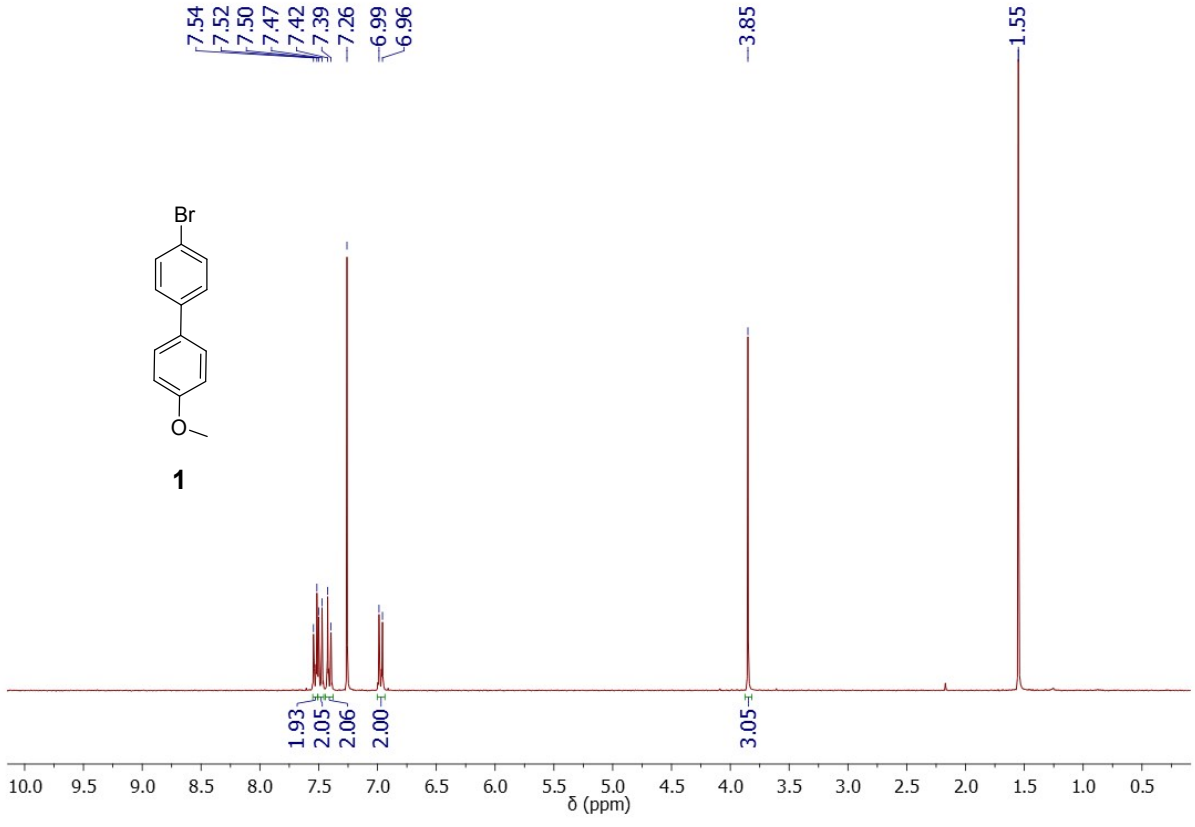


Figure S2. ^{1}H NMR spectrum of **1** in $CDCl_3$.

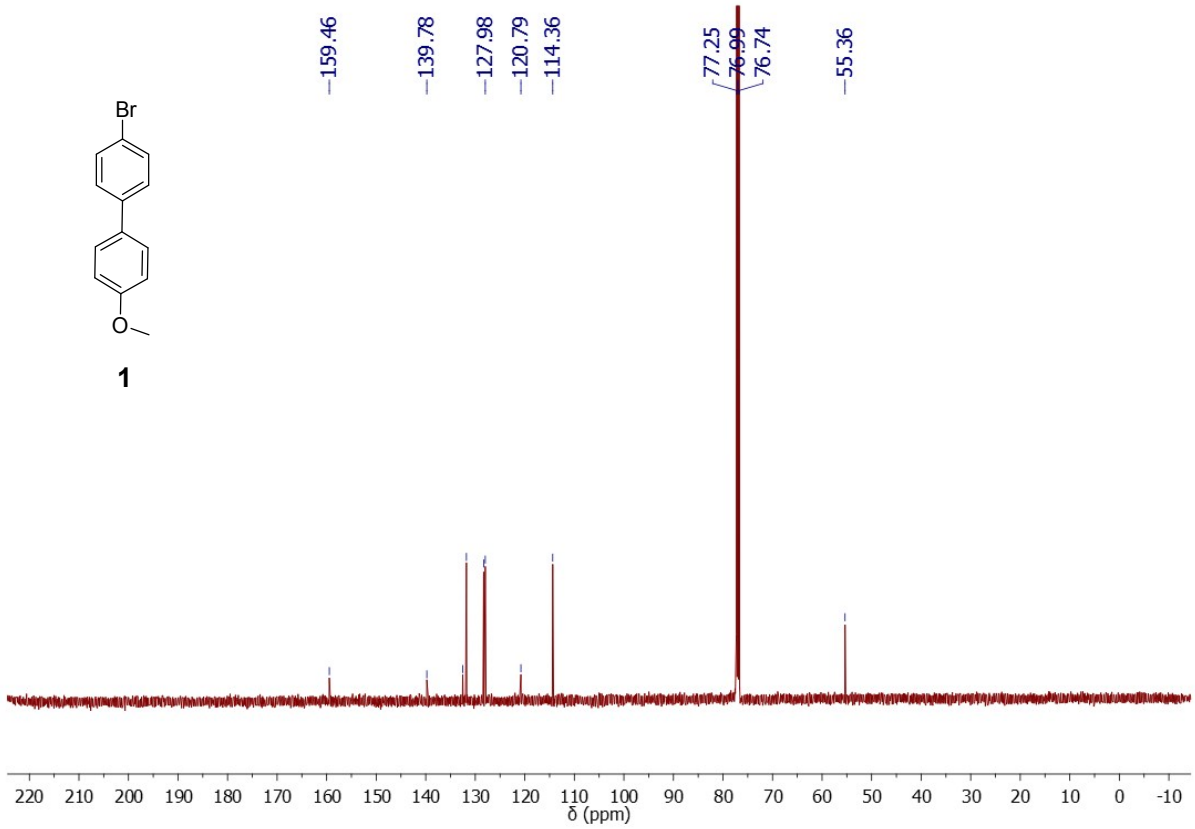


Figure S3. ^{13}C NMR spectrum of **1** in $CDCl_3$.

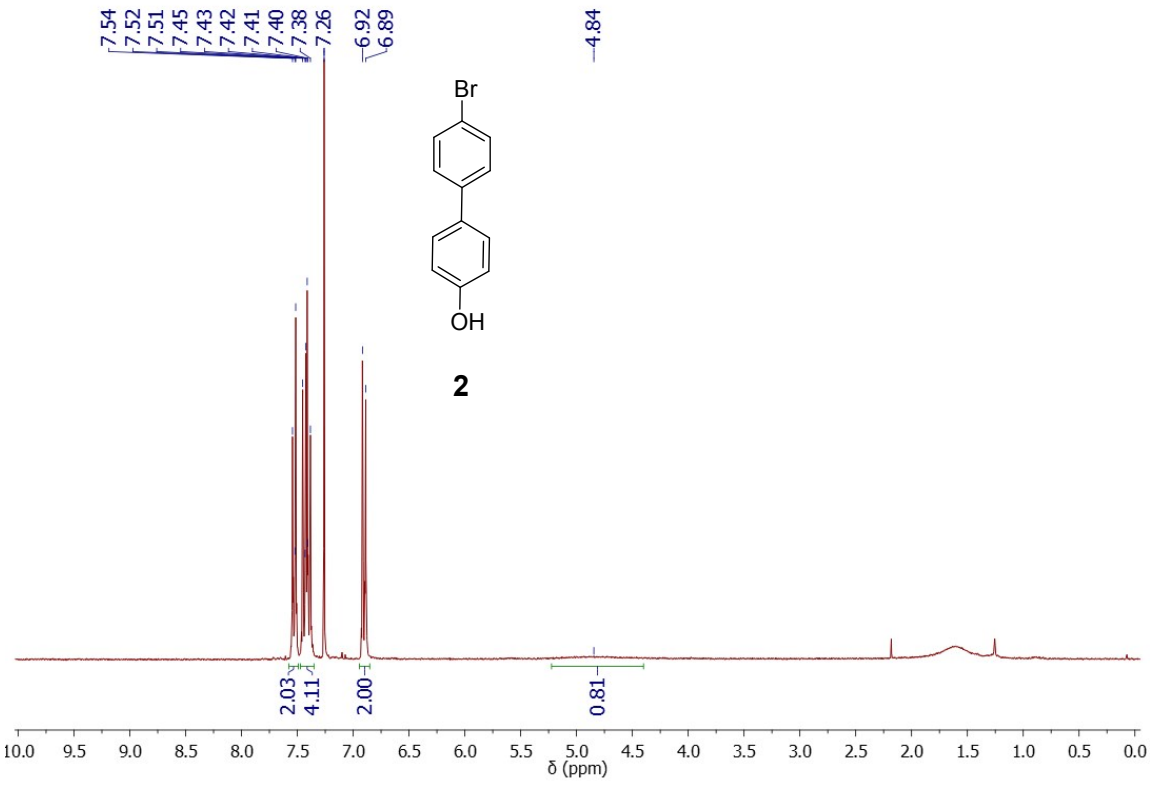


Figure S4. ^{1}H NMR spectrum of **2** in $CDCl_3$.

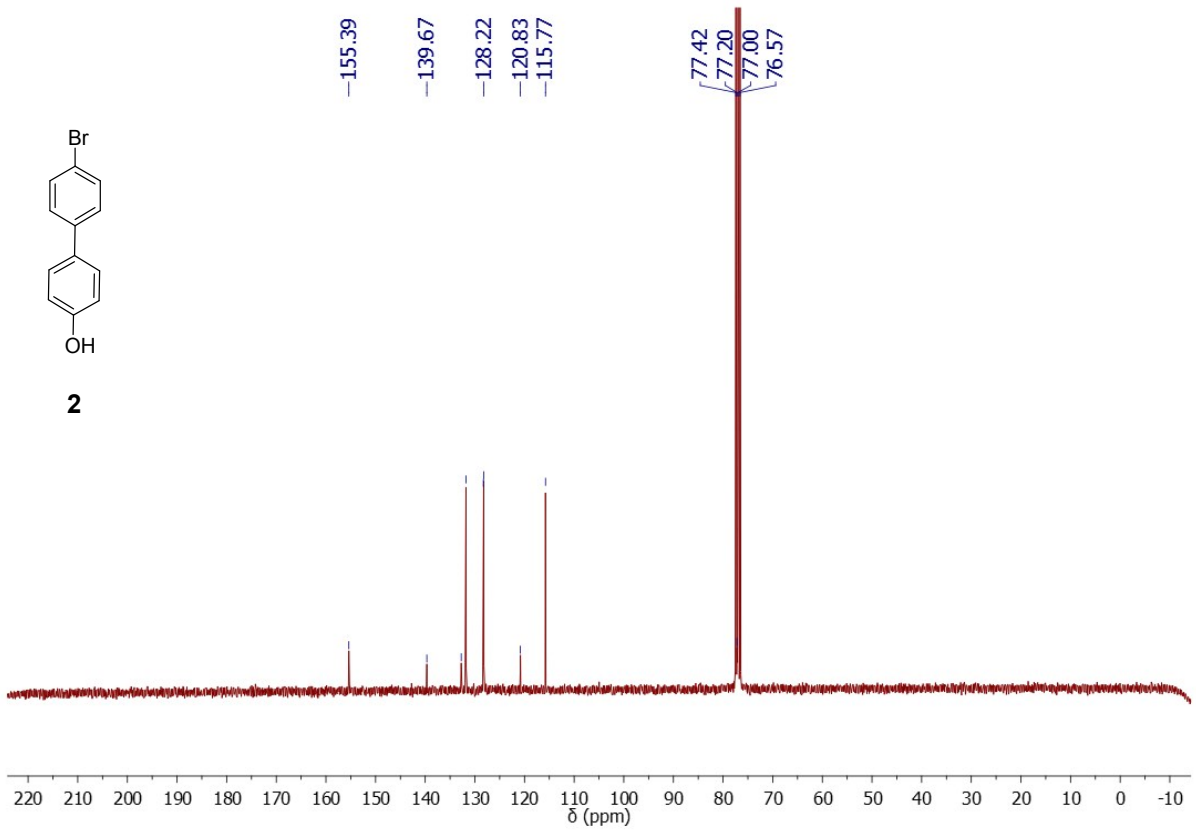


Figure S5. ^{13}C NMR spectrum of **2** in $CDCl_3$.

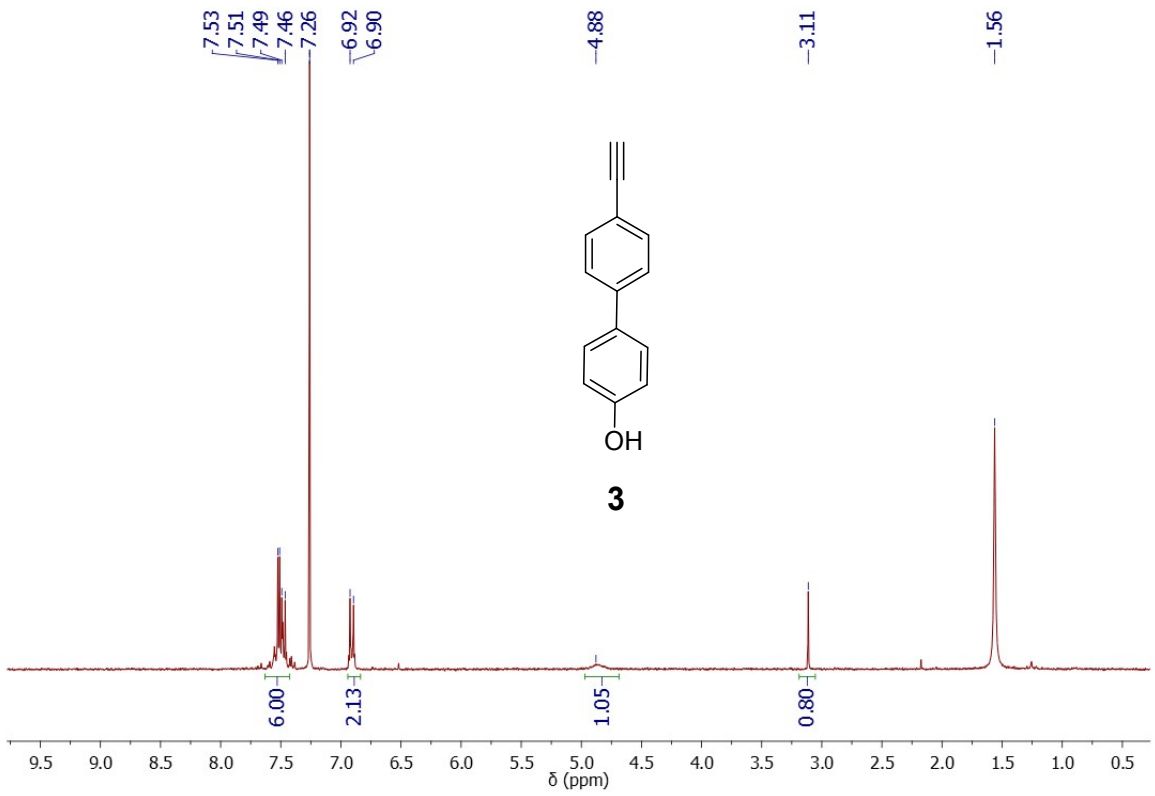


Figure S6. ^{1}H NMR spectrum of **3** in $CDCl_3$.

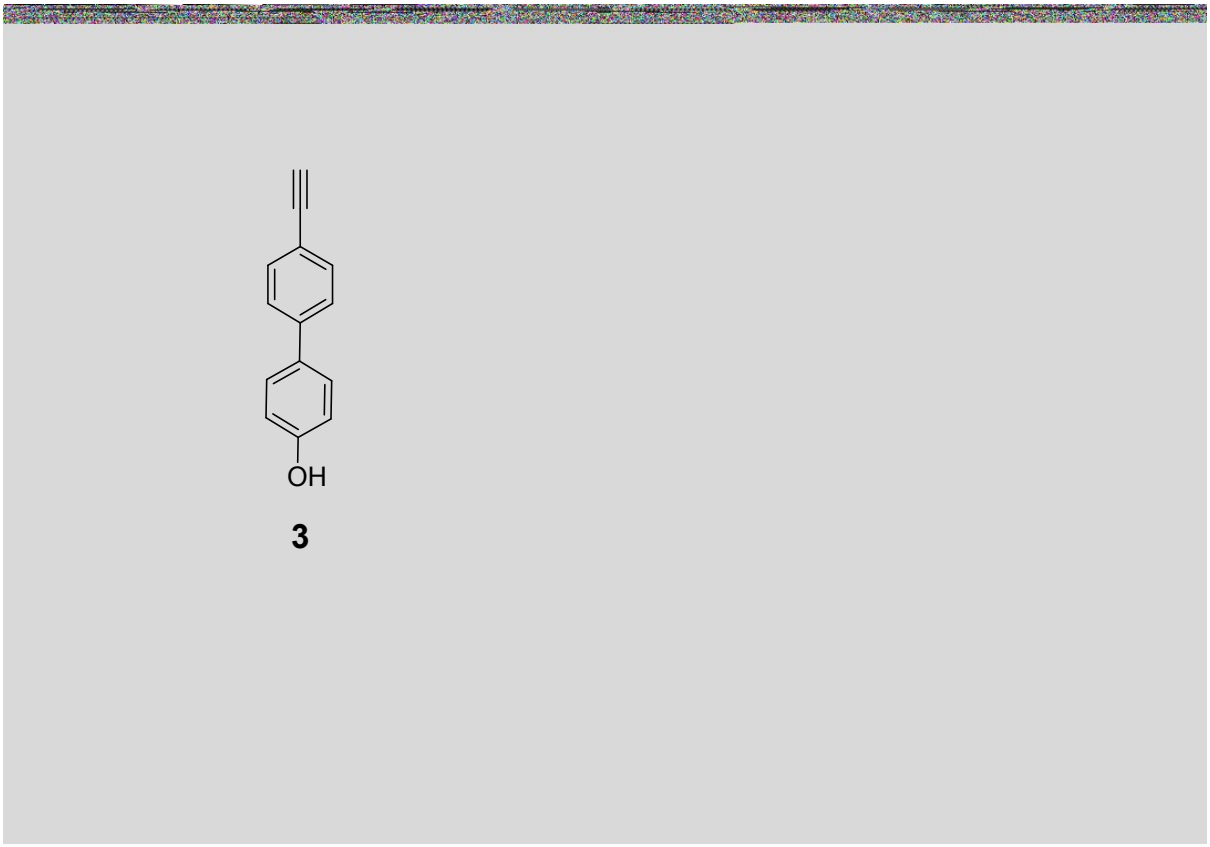


Figure S7. ^{13}C NMR spectrum of **3** in $CDCl_3$.

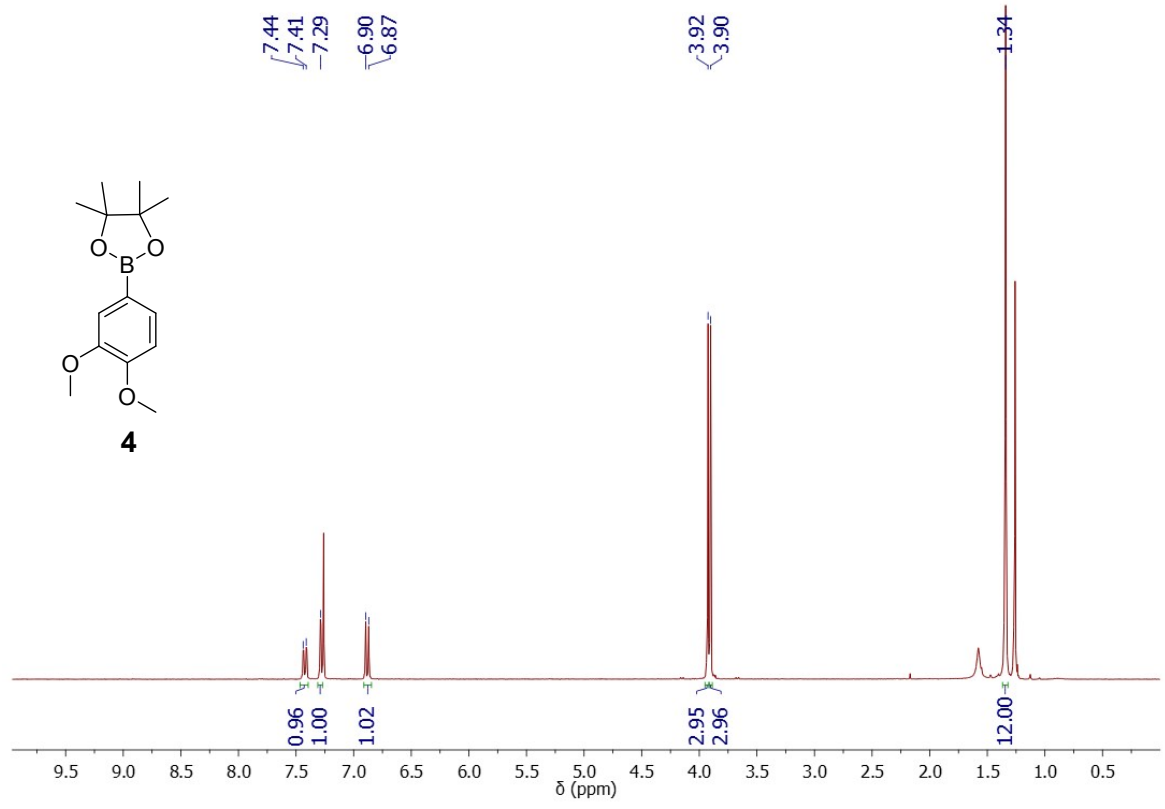


Figure S8. ^{1}H NMR spectrum of **4** in $CDCl_3$.

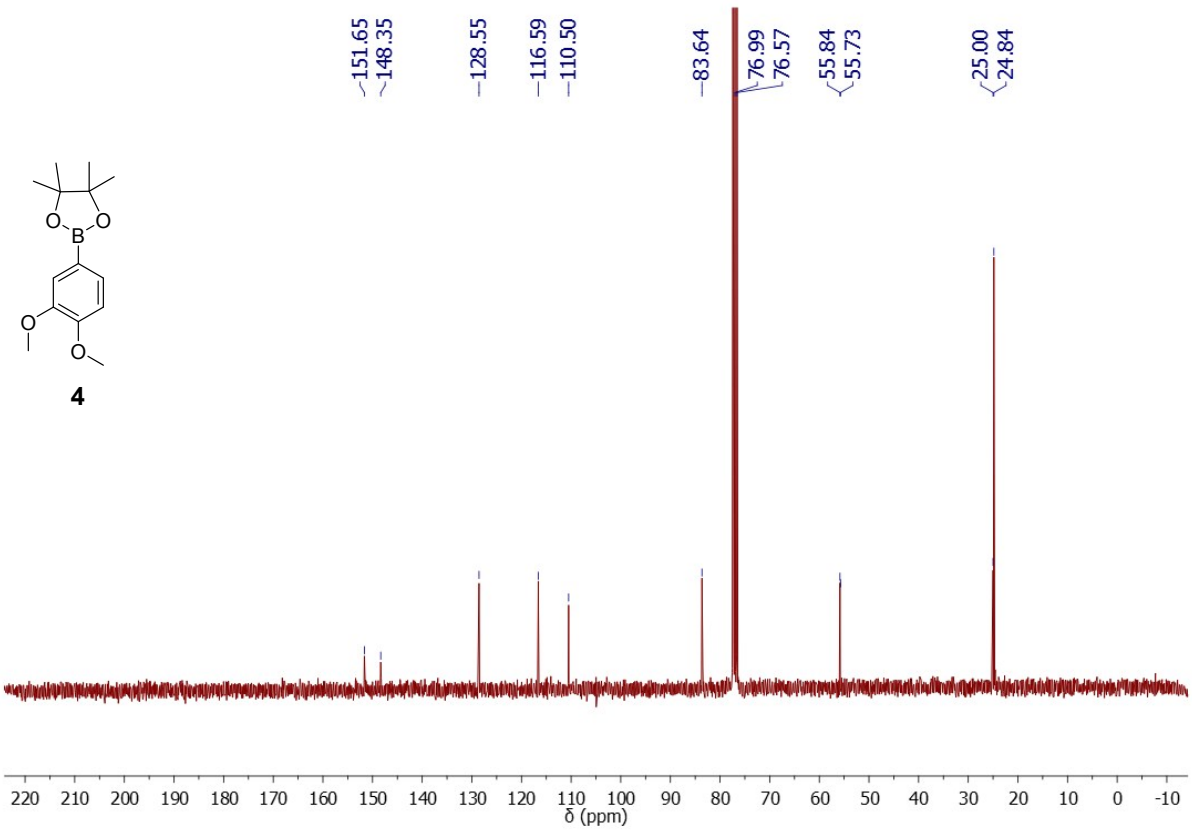


Figure S9. ^{13}C NMR spectrum of **4** in $CDCl_3$.

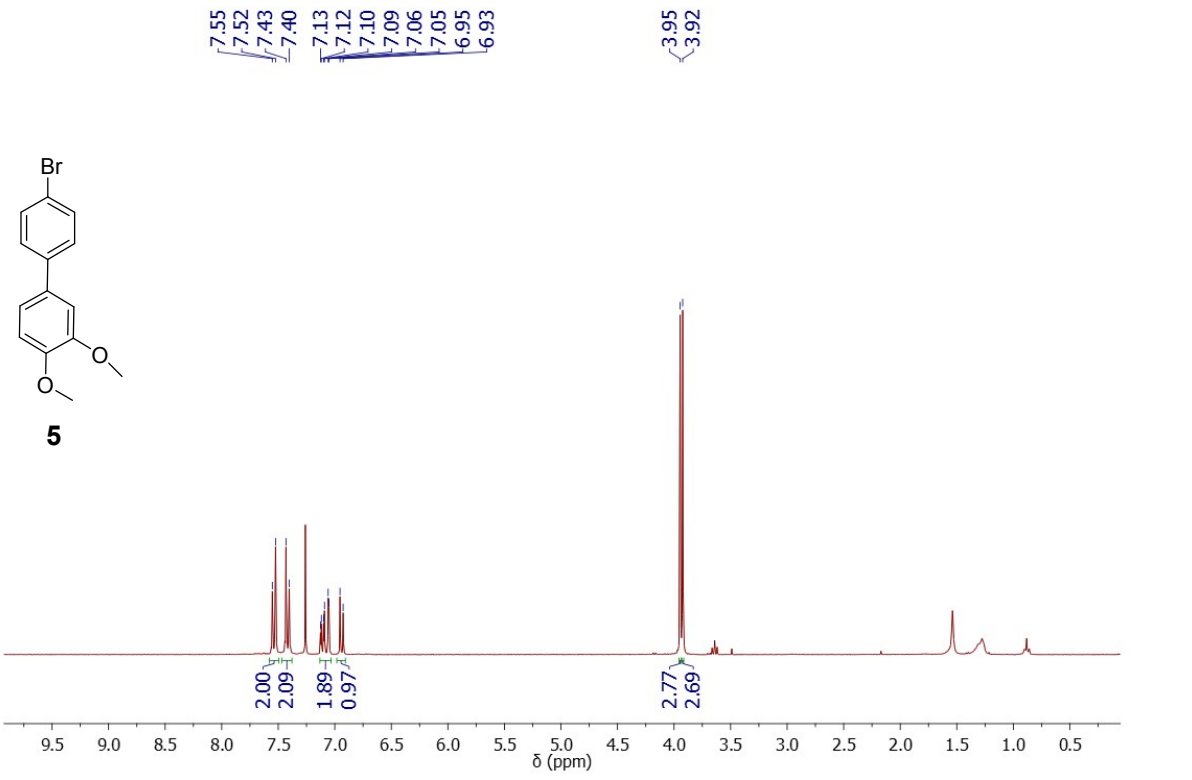


Figure S10. ^{1}H NMR spectrum of **5** in $CDCl_3$.

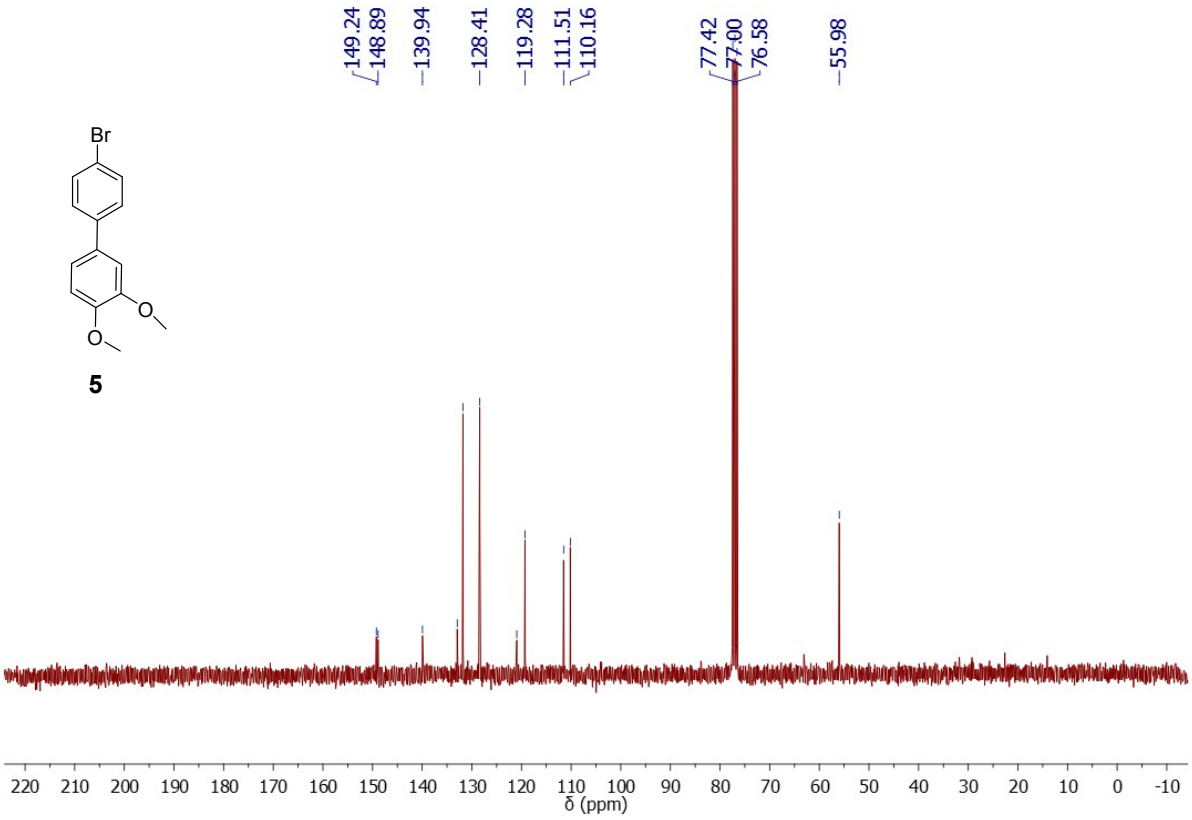


Figure S11. ^{13}C NMR spectrum of **5** in $CDCl_3$.

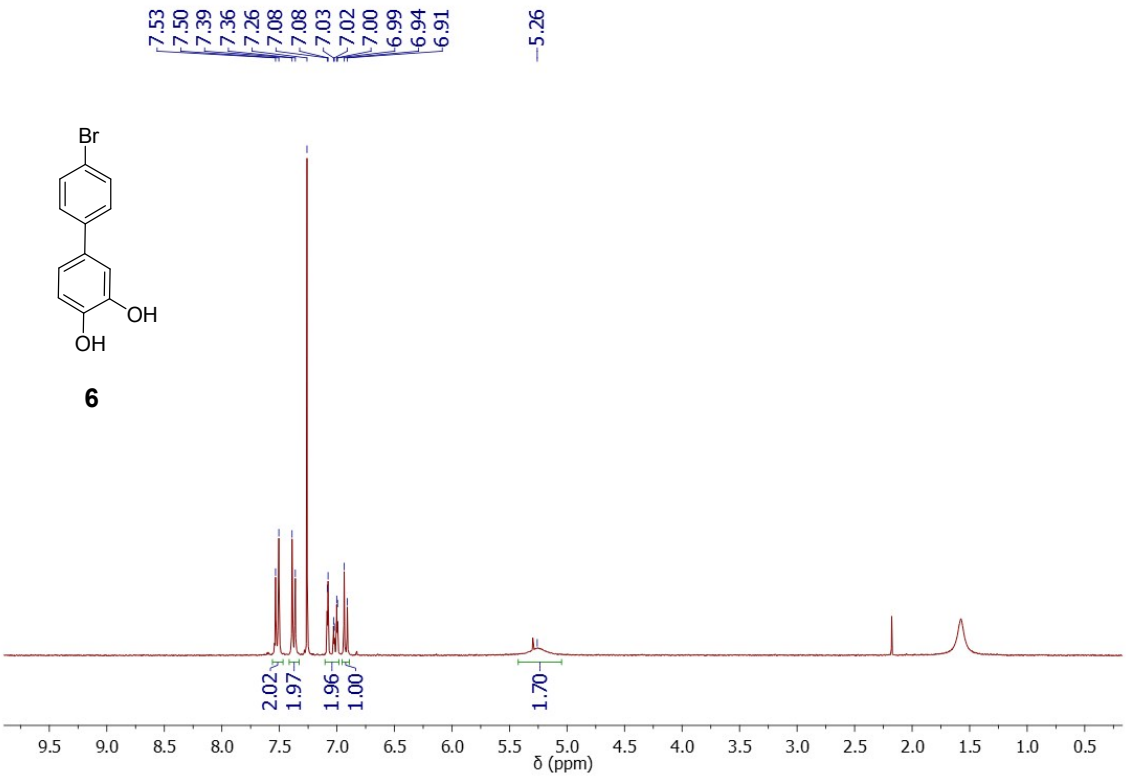


Figure S12. ^{1}H NMR spectrum of **6** in $CDCl_3$.

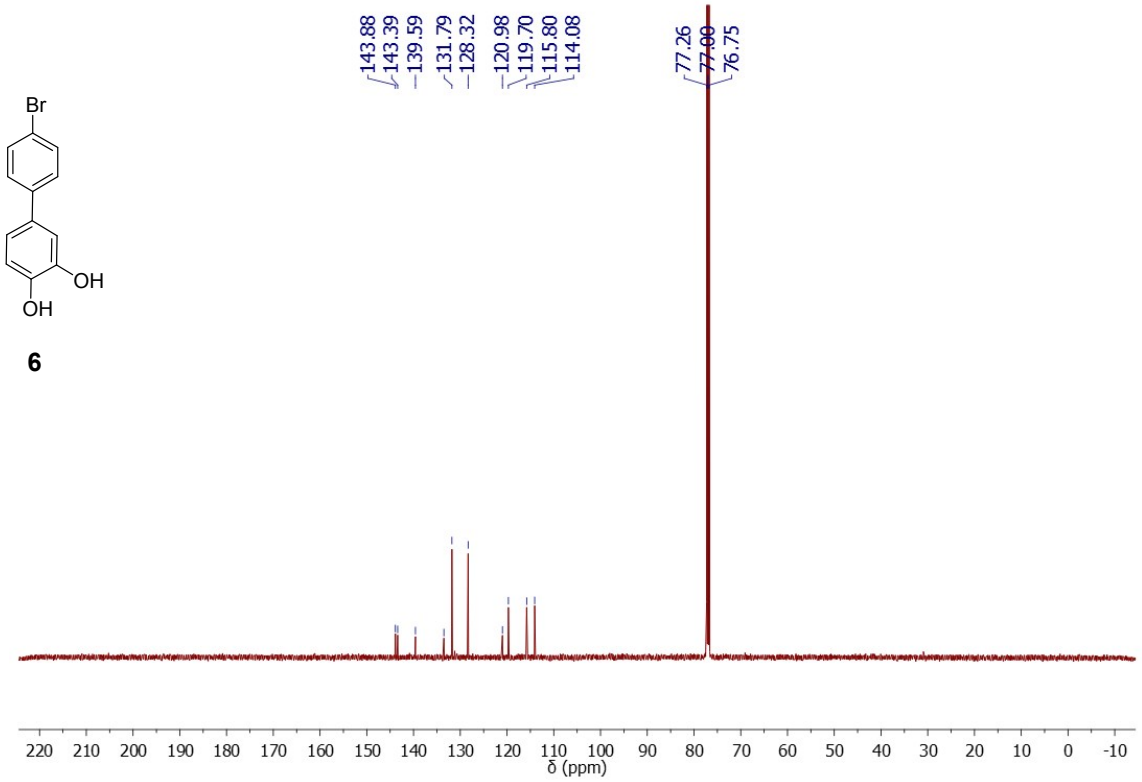


Figure S13. ^{13}C NMR spectrum of **6** in $CDCl_3$.

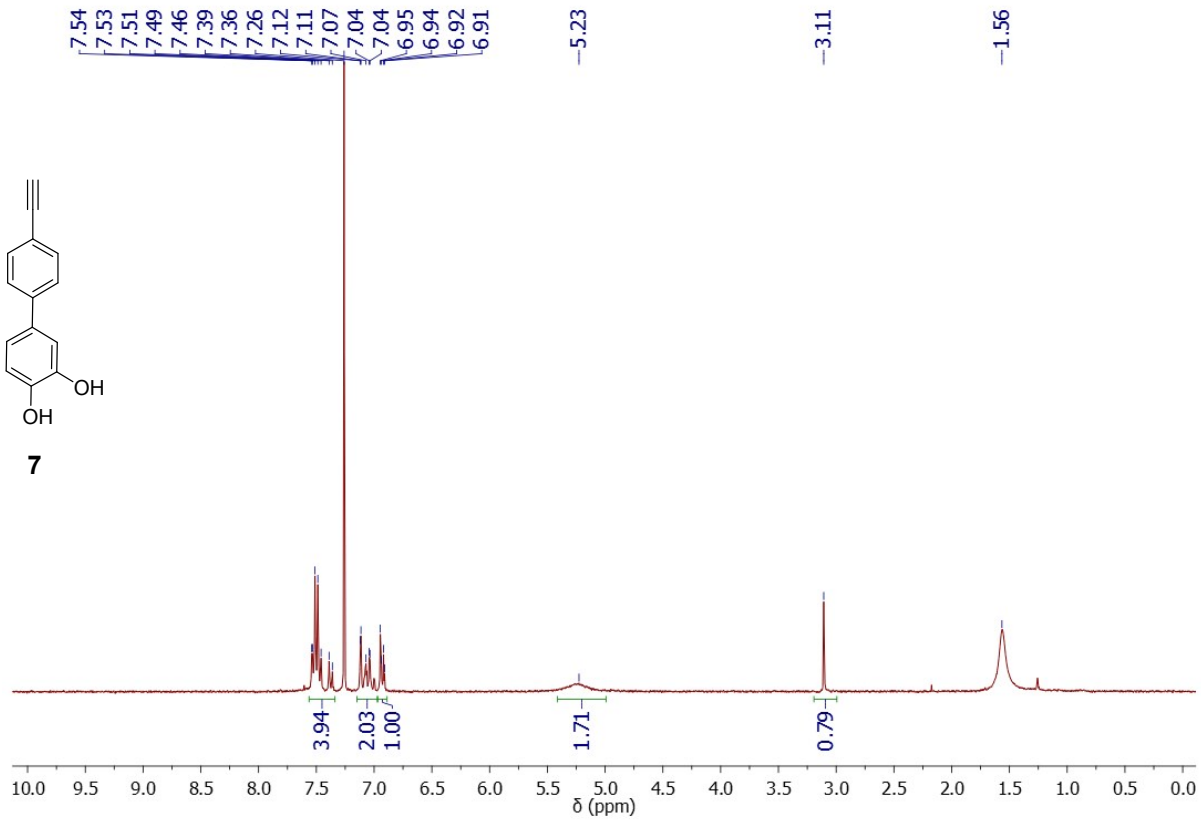


Figure S14. ^{1}H NMR spectrum of **7** in $CDCl_3$.

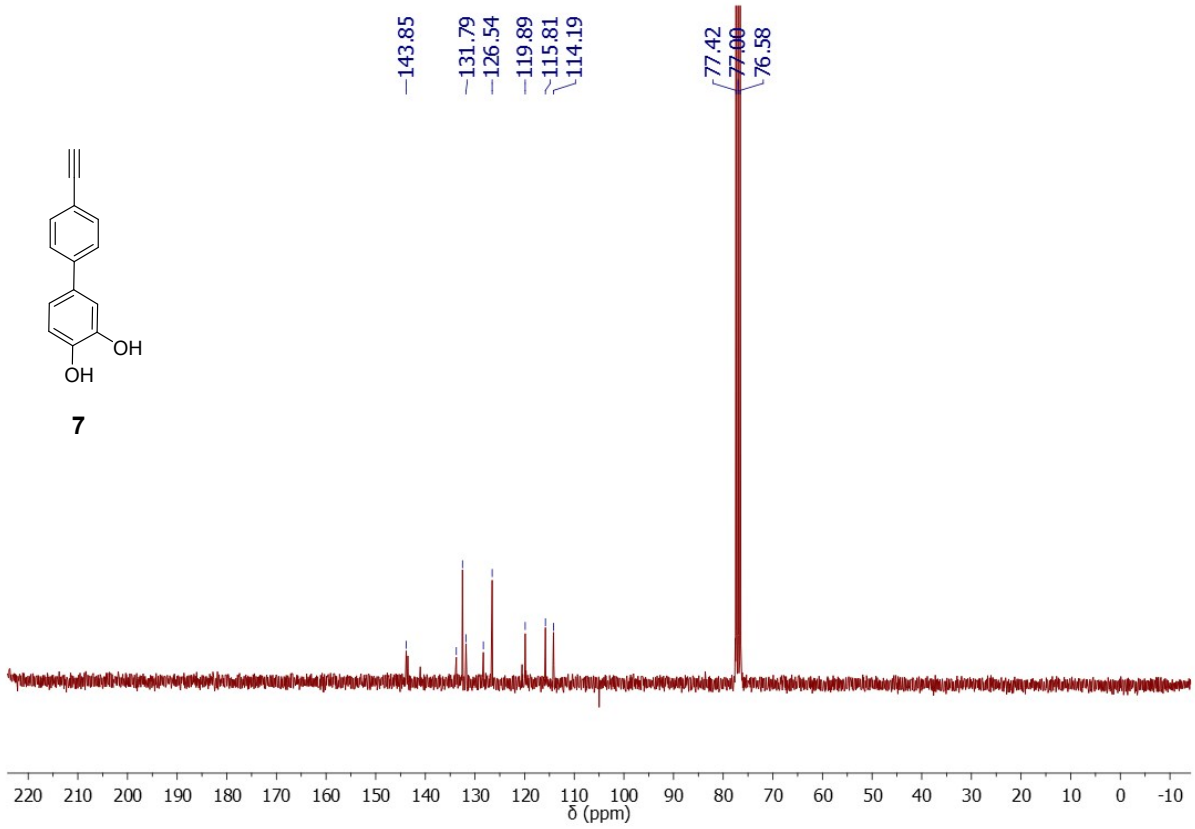


Figure S15. ^{13}C NMR spectrum of **7** in $CDCl_3$.

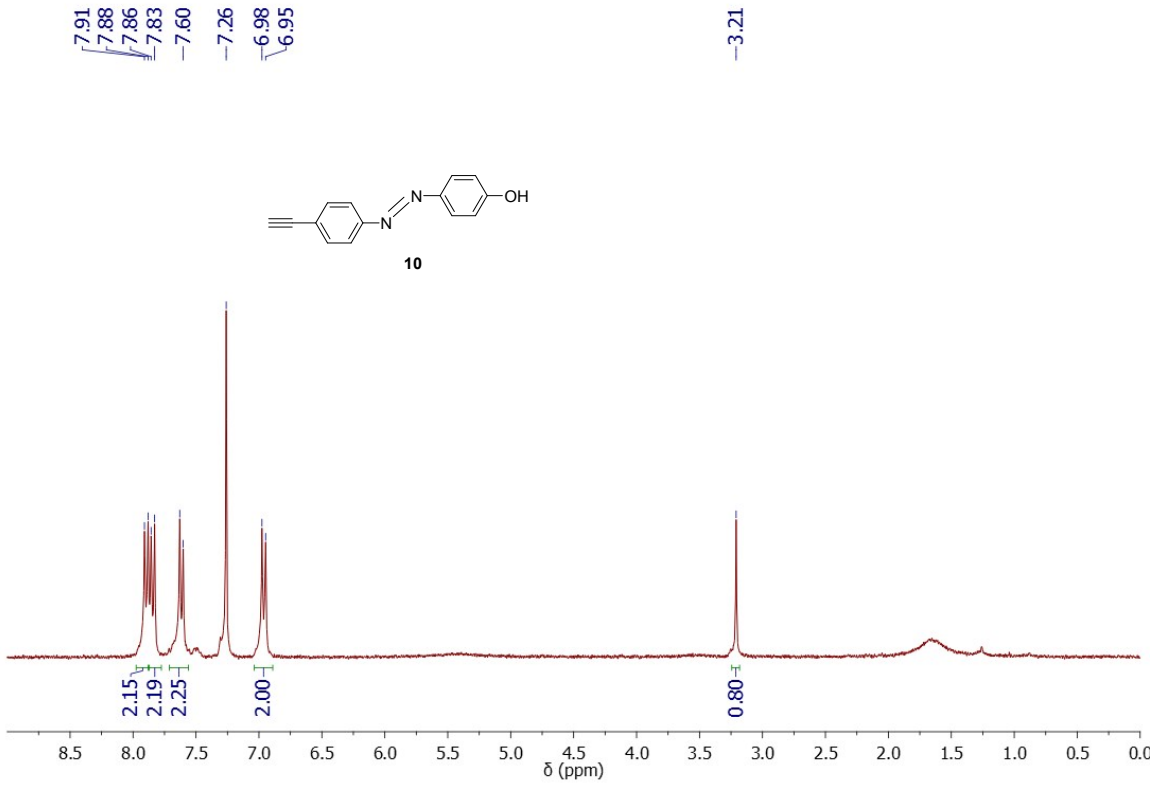


Figure S16. ^{1}H NMR spectrum of **10** in $CDCl_3$.

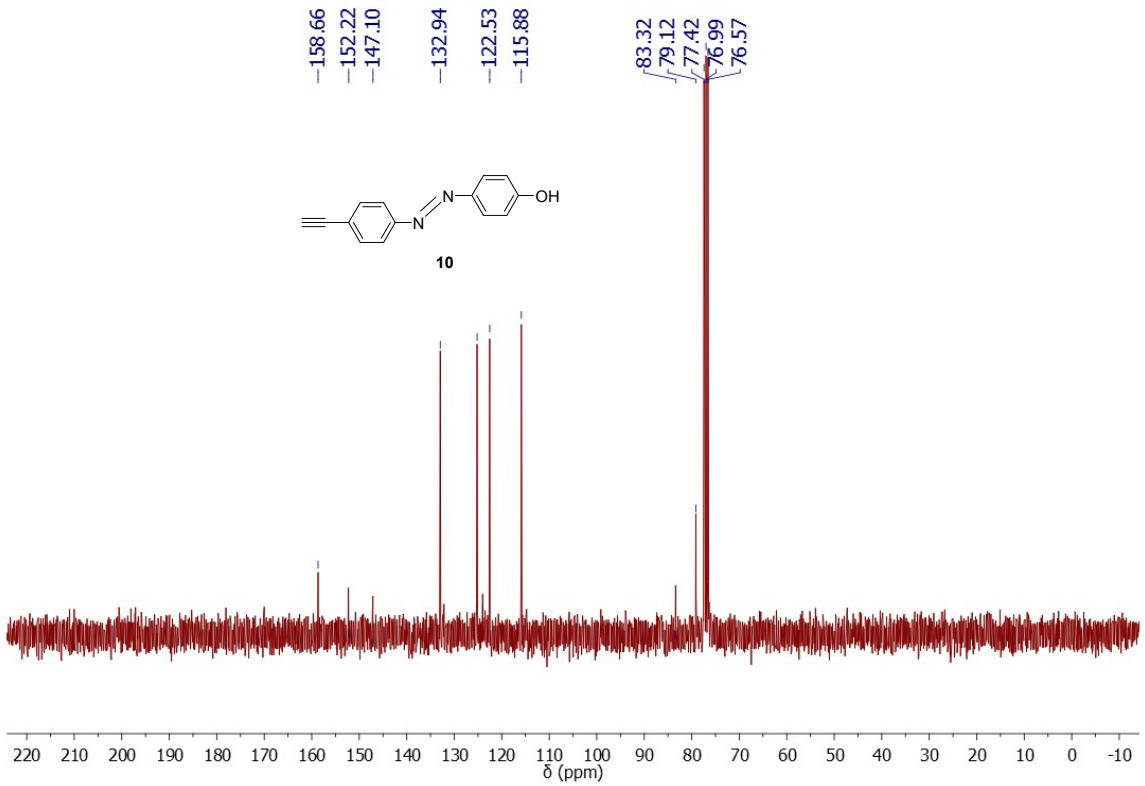


Figure S17. ^{13}C NMR spectrum of **10** in $CDCl_3$.

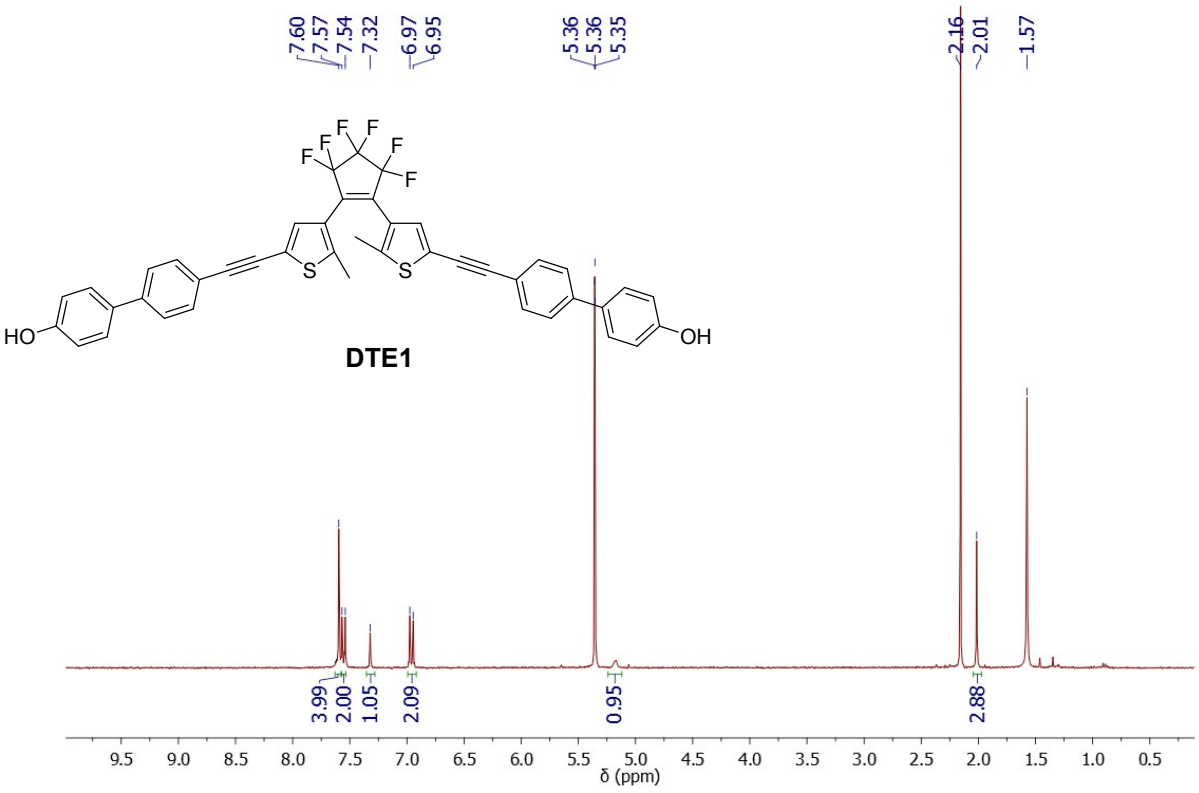


Figure S18. ^{1}H NMR spectrum of **DTE1** in CD_2Cl_2.

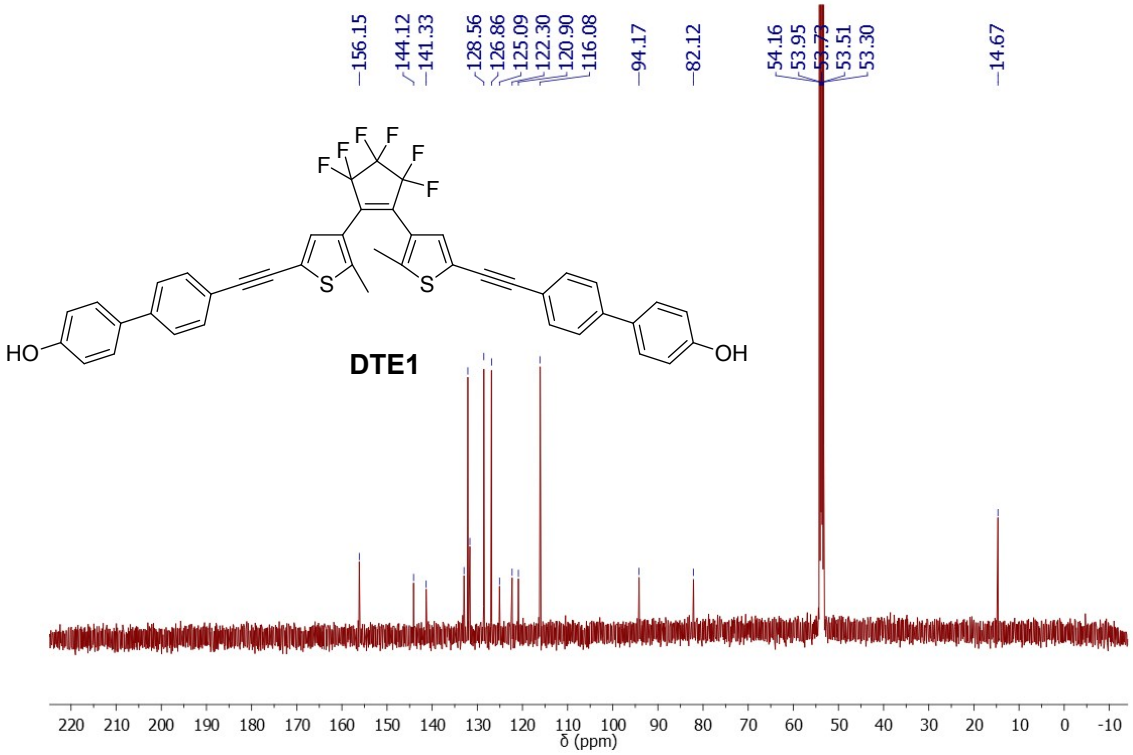


Figure S19. ^{13}C NMR spectrum of **DTE1** in CD_2Cl_2.

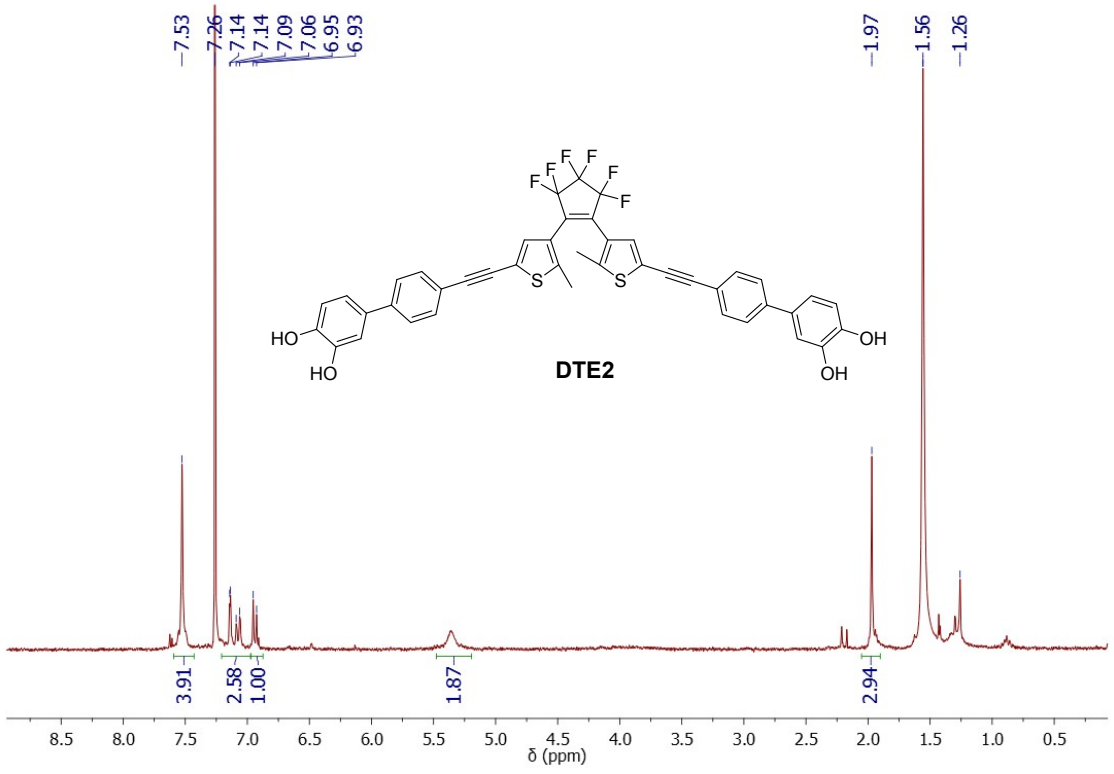


Figure S20. ^{1}H NMR spectrum of **DTE2** in $CDCl_3$.

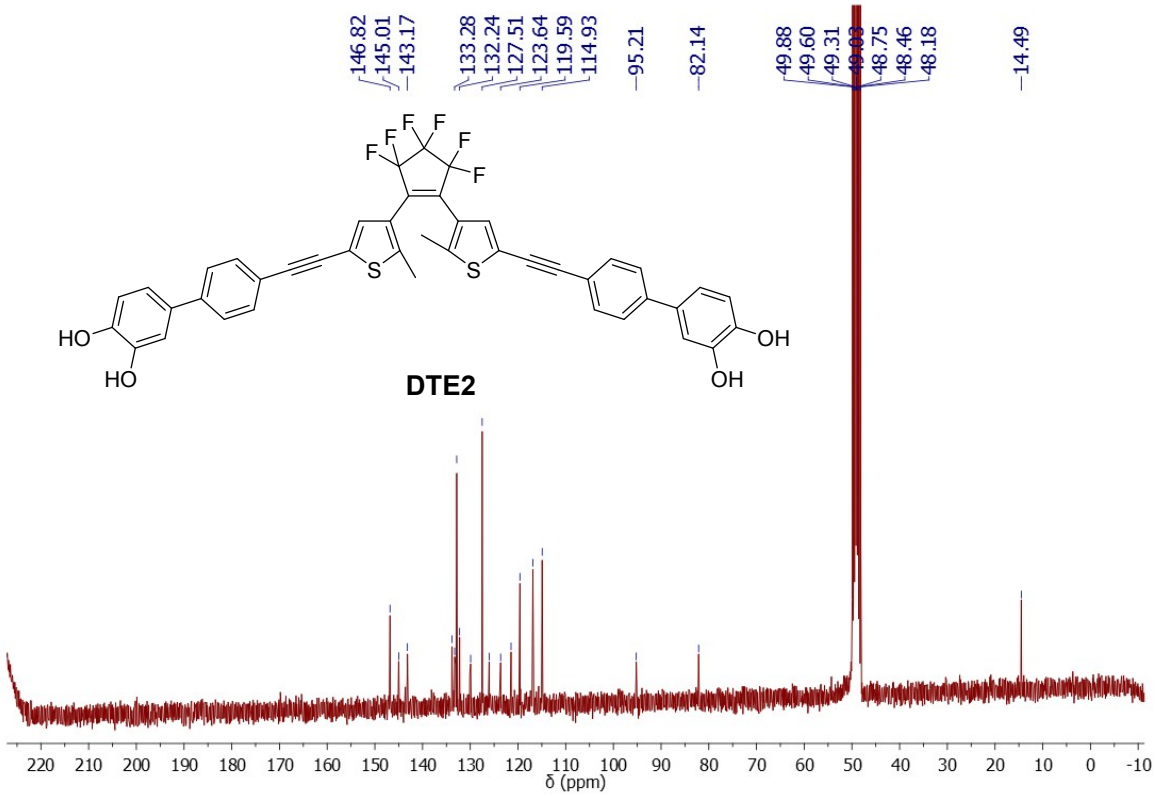


Figure S21. ^{13}C NMR spectrum of **DTE2** in MeOD.

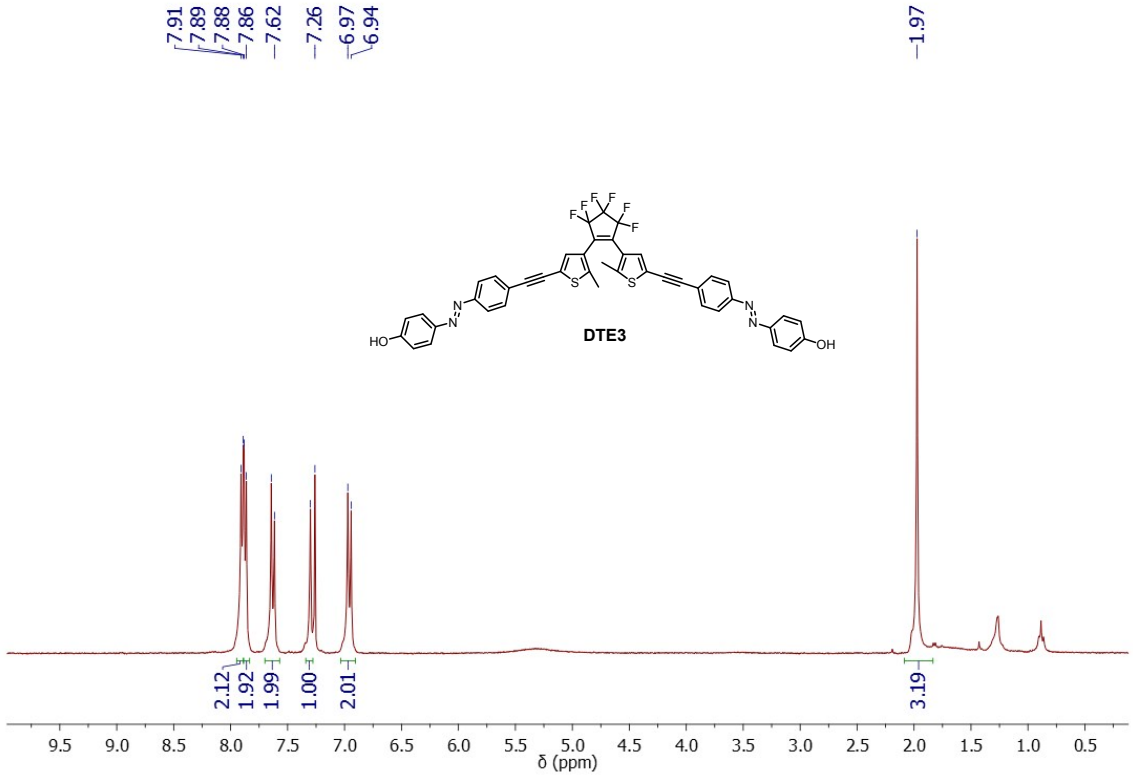


Figure S22. ^{1}H NMR spectrum of **DTE3** in $CDCl_3$.

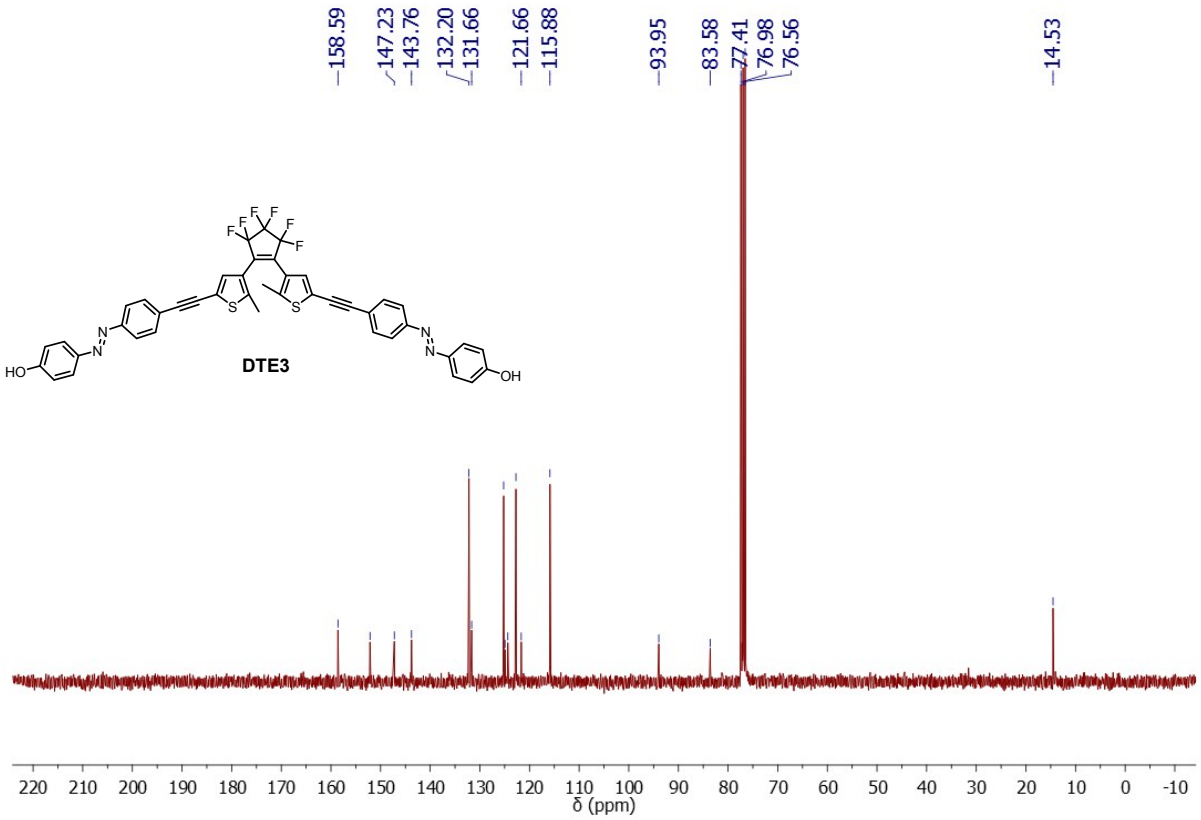
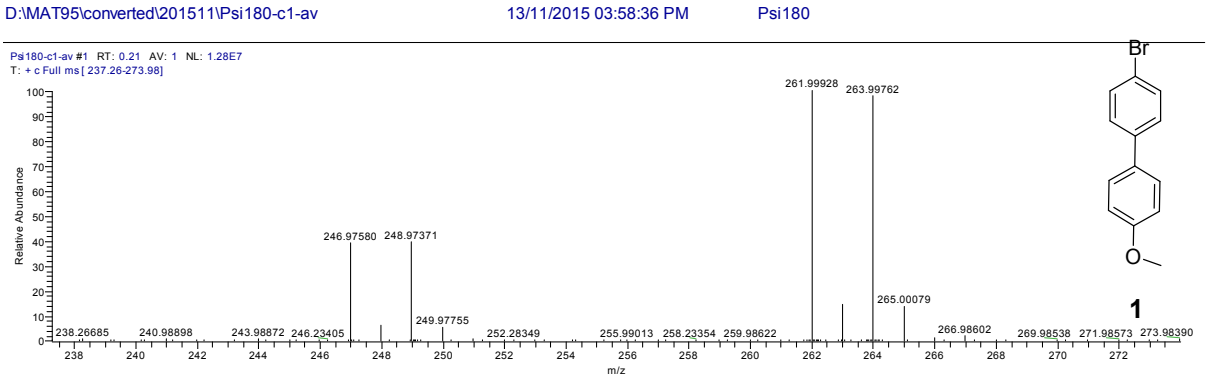


Figure S23. ^{13}C NMR spectrum of **DTE3** in $CDCl_3$.

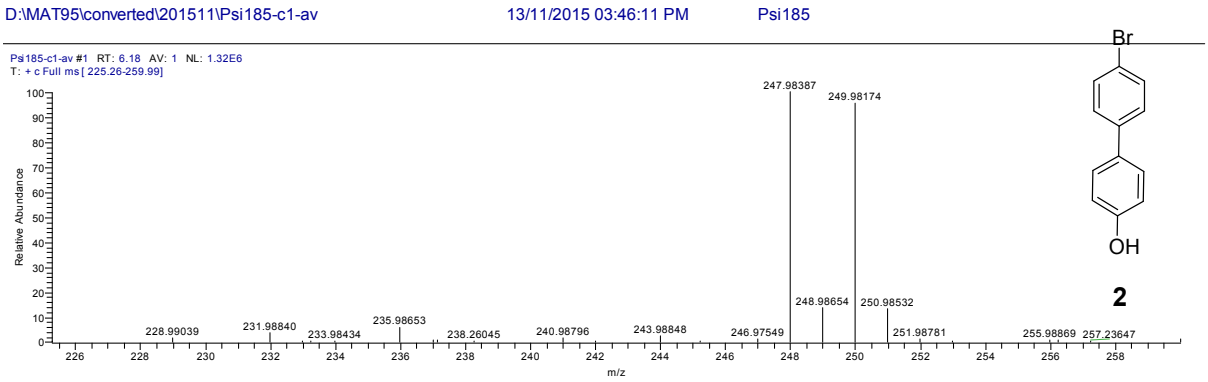
2. High resolution mass spectra of intermediates and DTEs.



Psi180-c1-av#1 RT: 0.21
T: + c Full ms [237.26-273.98]
m/z= 261.58278-262.87741

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
261.99928	12769280.0	100.00	261.99933	-0.17	8.0	$C_{13}H_{11}O_1{}^{79}Br_1$

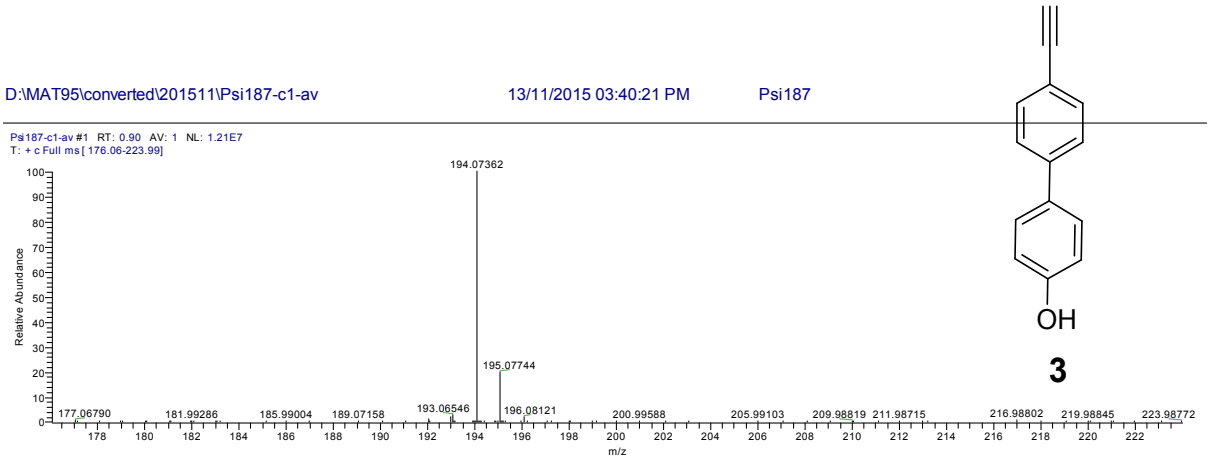
Figure S24. High resolution EI mass spectrum of ***1.***



Psi185-c1-av#1 RT: 6.18
T: + c Full ms [225.26-259.99]
m/z= 247.29475-248.29326

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
247.98387	1318127.0	100.00	247.98368	0.79	8.0	$C_{12}H_9O_1{}^{79}Br_1$

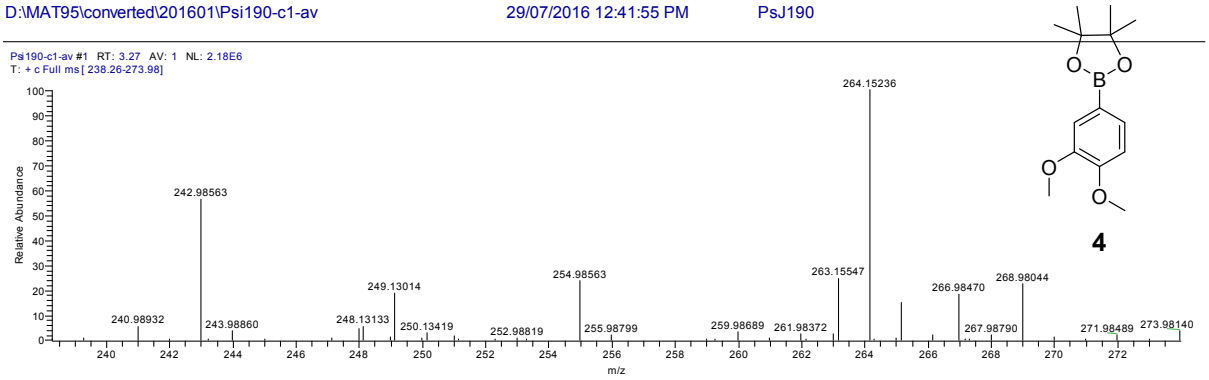
Figure S25. High resolution EI mass spectrum of ***2.***



Psi187-c1-av#1 RT: 0.90
T: + c Full ms [176.06-223.99]
m/z= 193.66778-194.15682

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
194.07362	12082688.0	100.00	194.07317	2.36	10.0	$C_{14}H_{10}O_1$

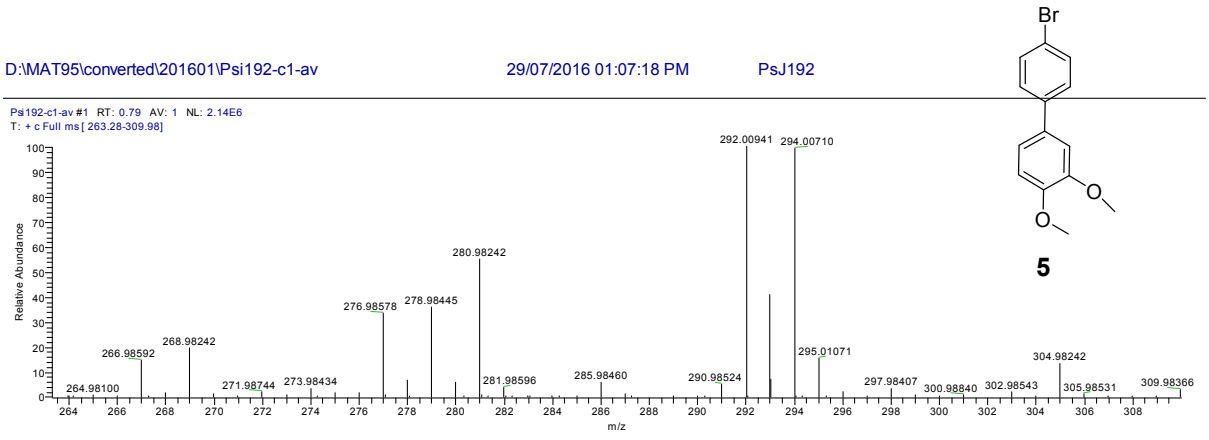
Figure S26. High resolution EI mass spectrum of ***3.***



Psi190-c1-av#1 RT: 3.27
T: + c Full ms [238.26-273.98]

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
264.15236	2177056.0	100.00	264.15329	-3.52	4.5	$C_{14}H_{21}O_4{}^{11}B_1$

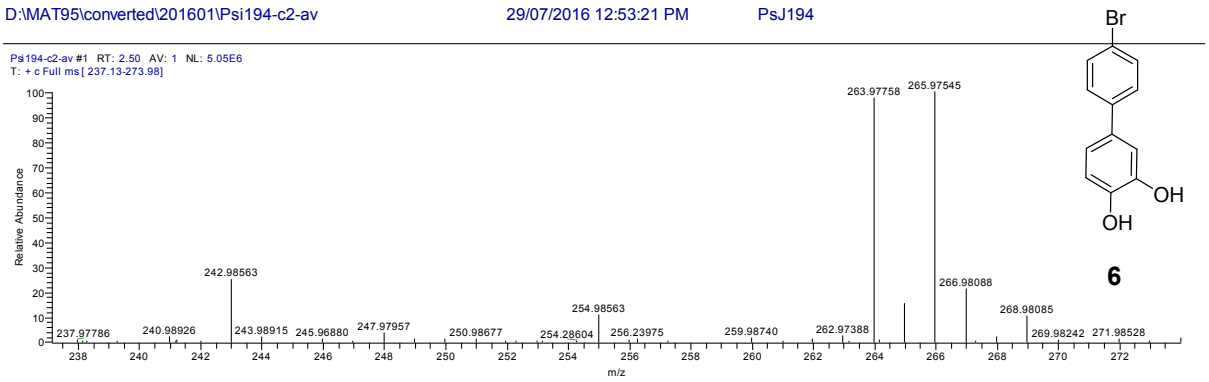
Figure S27. High resolution EI mass spectrum of ***4.***



Psi192-c1-av#1 RT: 0.79
T: + c Full ms [263.28-309.98]
m/z= 291.83166-292.13492

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
292.00941	2143098.0	100.00	292.00989	-1.63	8.0	$C_{14}H_{13}O_2{}^{79}Br_1$

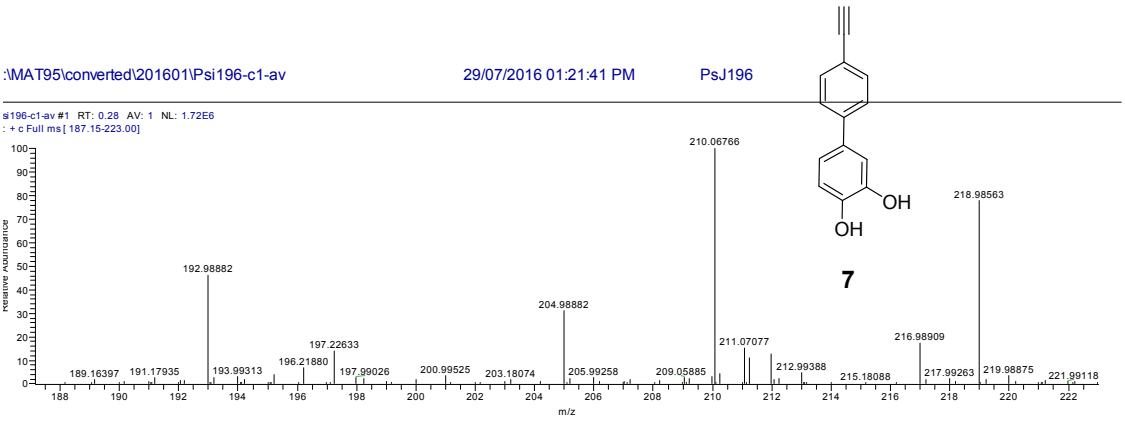
Figure S28. High resolution EI mass spectrum of ***5.***



Psi194-c2-av#1 RT: 2.50
T: + c Full ms [237.13-273.98]
m/z= 263.72617-264.37572

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
263.97758	4943435.0	100.00	263.97859	-3.81	8.0	$C_{12}H_9O_2{}^{79}Br_1$

Figure S29. High resolution EI mass spectrum of ***6.***



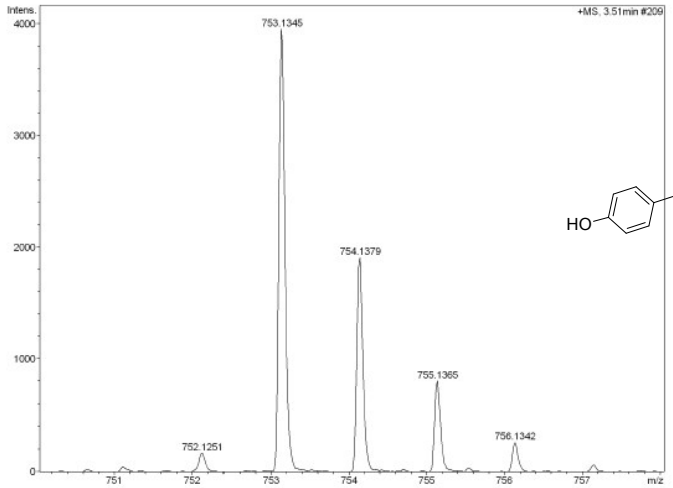
'si196-c1-av#1 RT: 0.28
': + c Full ms [187.15-223.00]
ı/z= 209.76253-210.39434

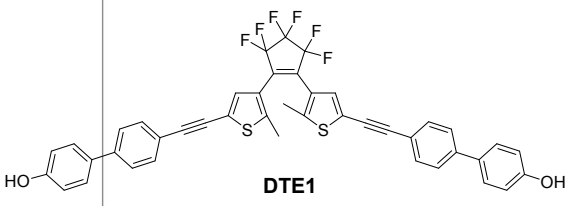
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
210.06766	1715174.0	100.00	210.06808	-2.01	10.0	$C_{14}H_{10}O_2$

Figure S30. High resolution EI mass spectrum of ***7.***

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	3.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	2500 m/z	Set Collision Cell RF	300.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
753.1345	1	C 43 H 27 F 6 O 2 S 2	753.1351	0.8	27.5	even	ok





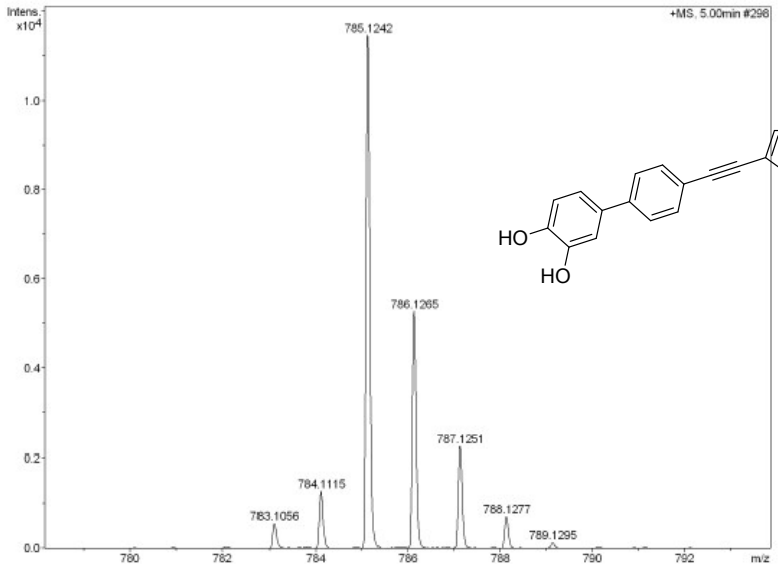
Bruker Compass DataAnalysis 4.0 printed: 1/14/2016 11:05:03 AM Page 1 of 1

Figure S31. High resolution APCI mass spectrum of ***DTE1.***

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	3.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1800 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
785.1242	1	C 43 H 27 F 6 O 4 S 2	785.1249	1.0	27.5	even	ok



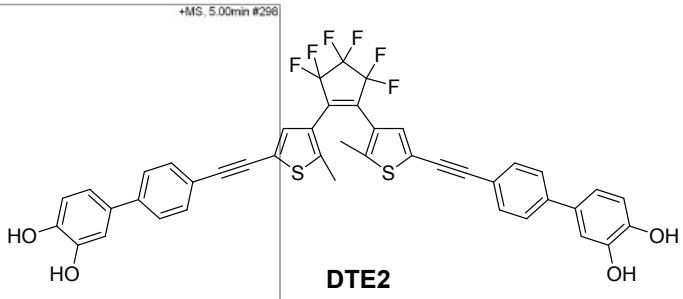


Figure S32. High resolution APCI mass spectrum of ***DTE2.***

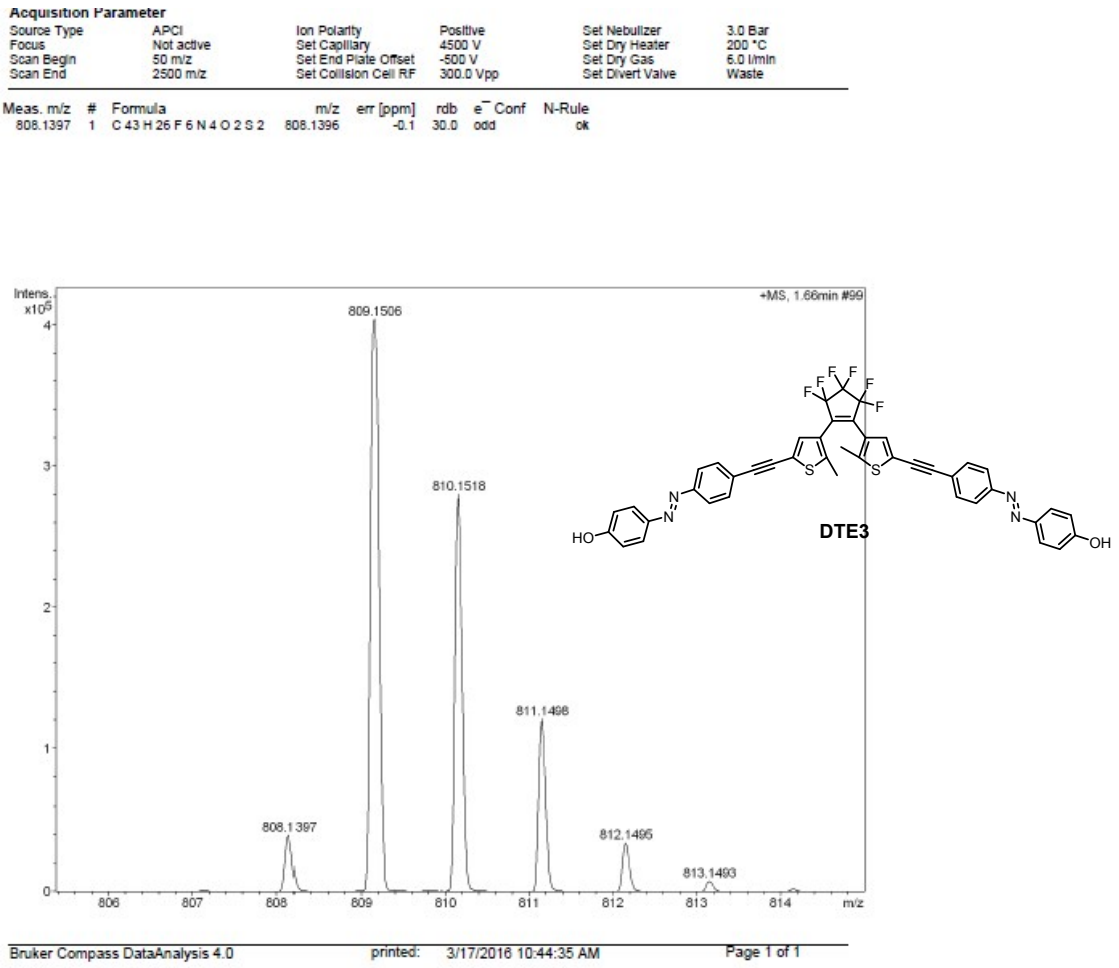


Figure S33. High resolution APCI mass spectrum of ***DTE3.***

3. ^{1}H NMR of DTEs before and after photoirradiation.

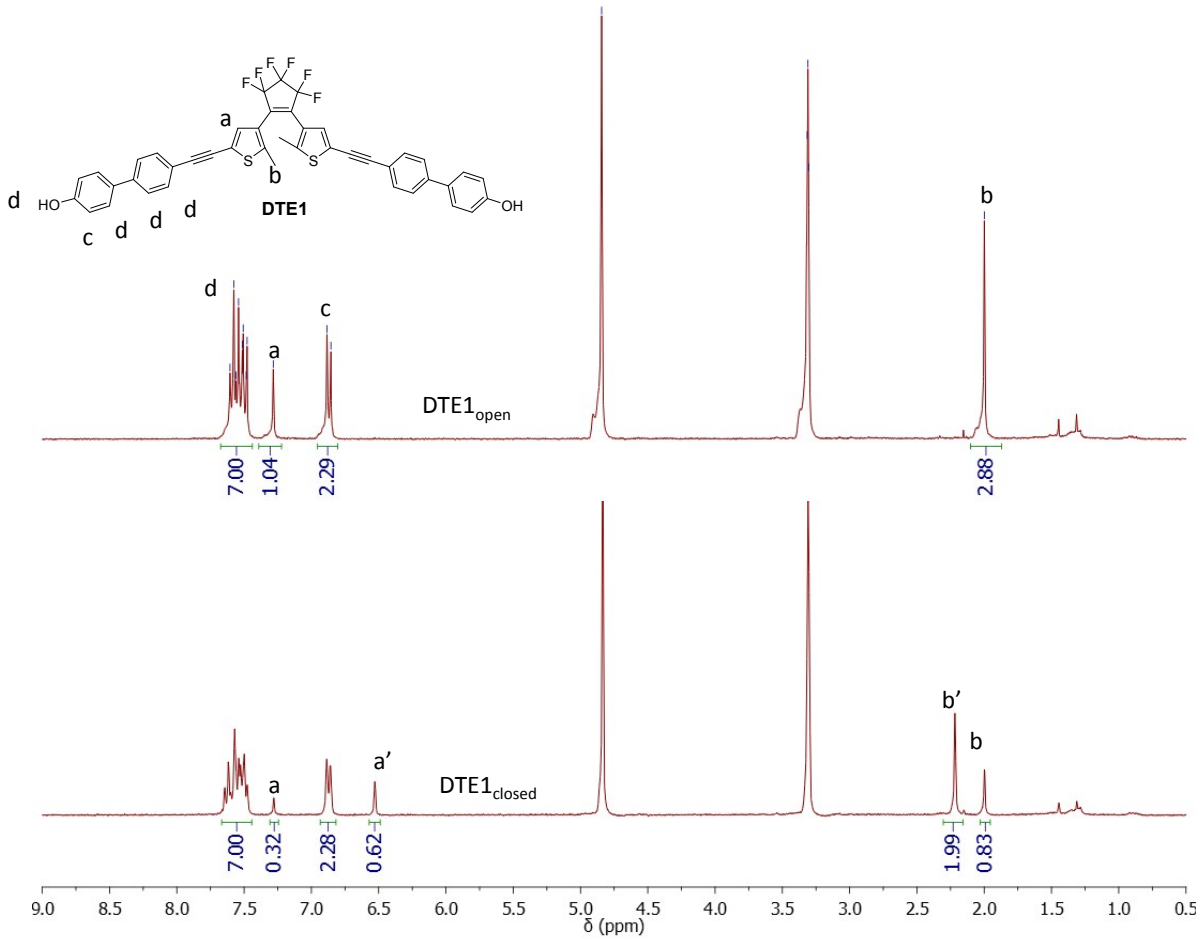


Figure S34. ^{1}H NMR of **DTE1**$_{open}$ and **DTE1**$_{closed}$ (λ = 365 nm, photostationary state) in MeOD.

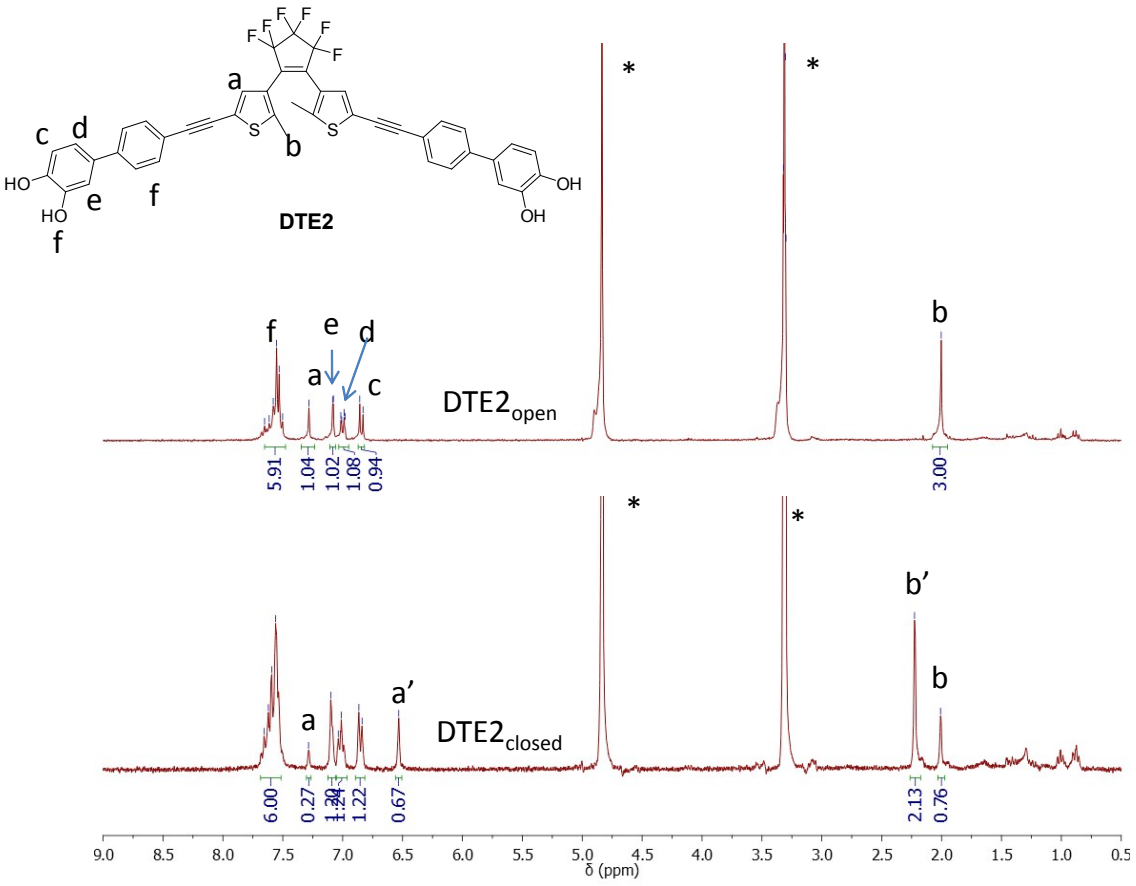


Figure S35. ^{1}H NMR of **DTE2**$_{open}$ and **DTE2**$_{closed}$ (λ = 365 nm, photostationary state) in MeOD.

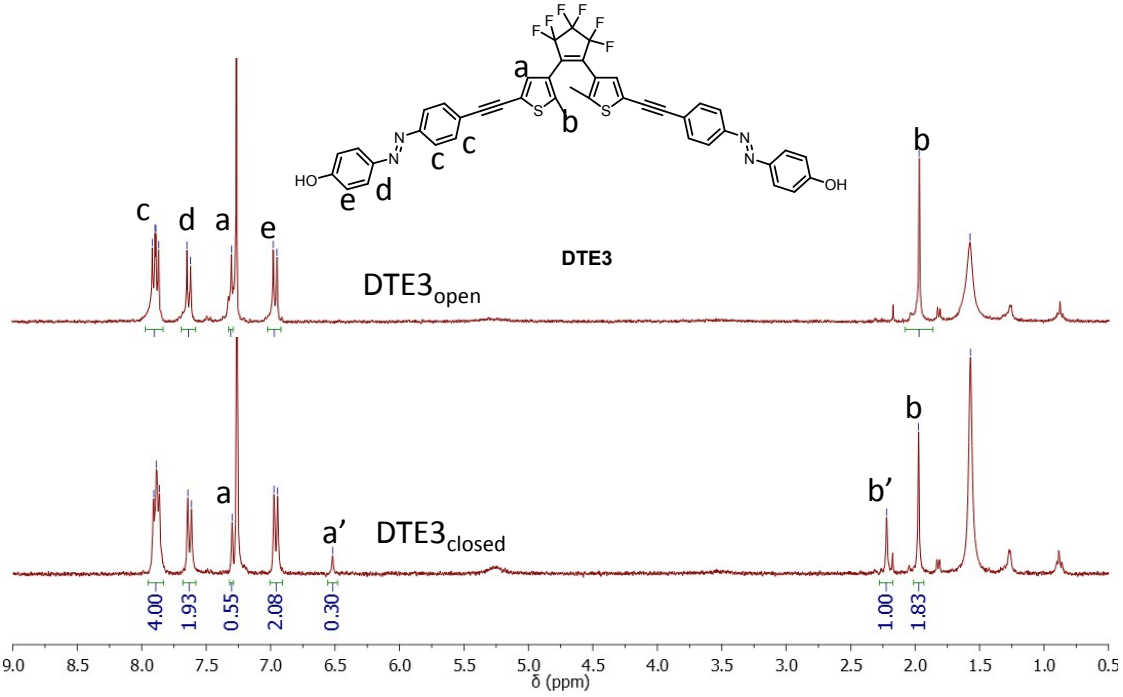


Figure S36. ^{1}H NMR of **DTE3**$_{open}$ and **DTE3**$_{closed}$ (λ = 365 nm, photostationary state) in $CDCl_3$.

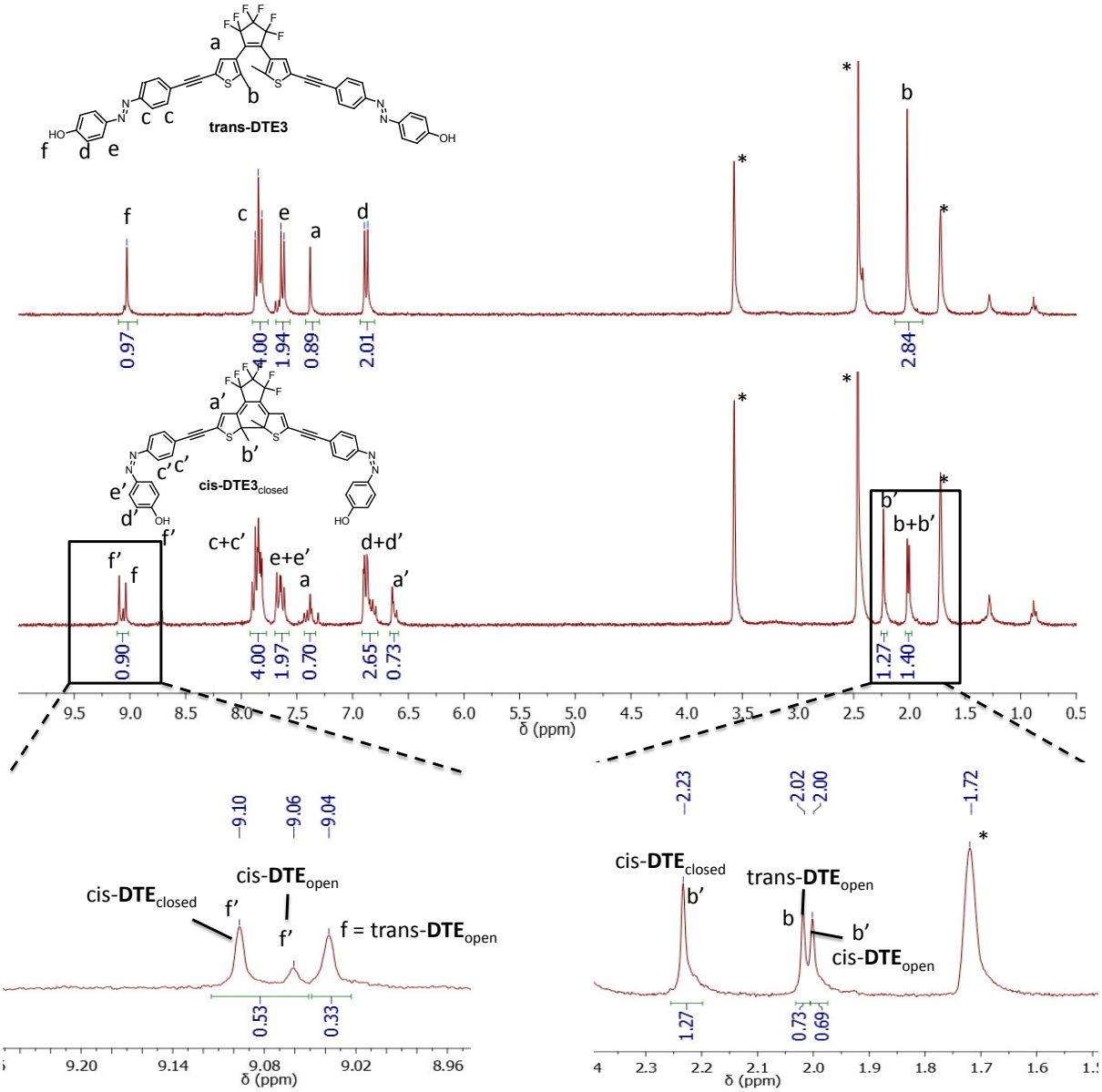


Figure S37. ^{1}H NMR of **DTE3**$_{open}$ and **DTE3**$_{closed}$ (λ = 365 nm, photostationary state) in THF-d8.

4. Absorption spectra of intermediate and DTEs.

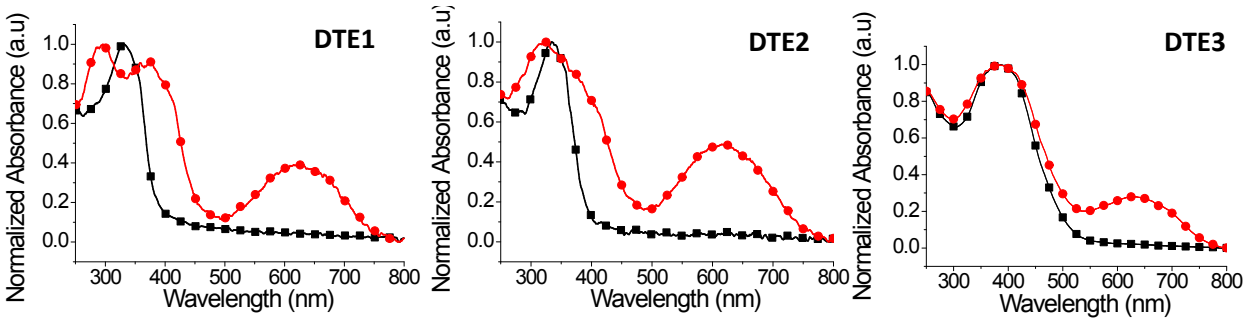


Figure S38. Solid state absorption spectra of **DTE1-3**; open-ring (-■-) and closed-ring (PSS, -●-) isomer upon irradiation at 365 nm for 5 minutes.

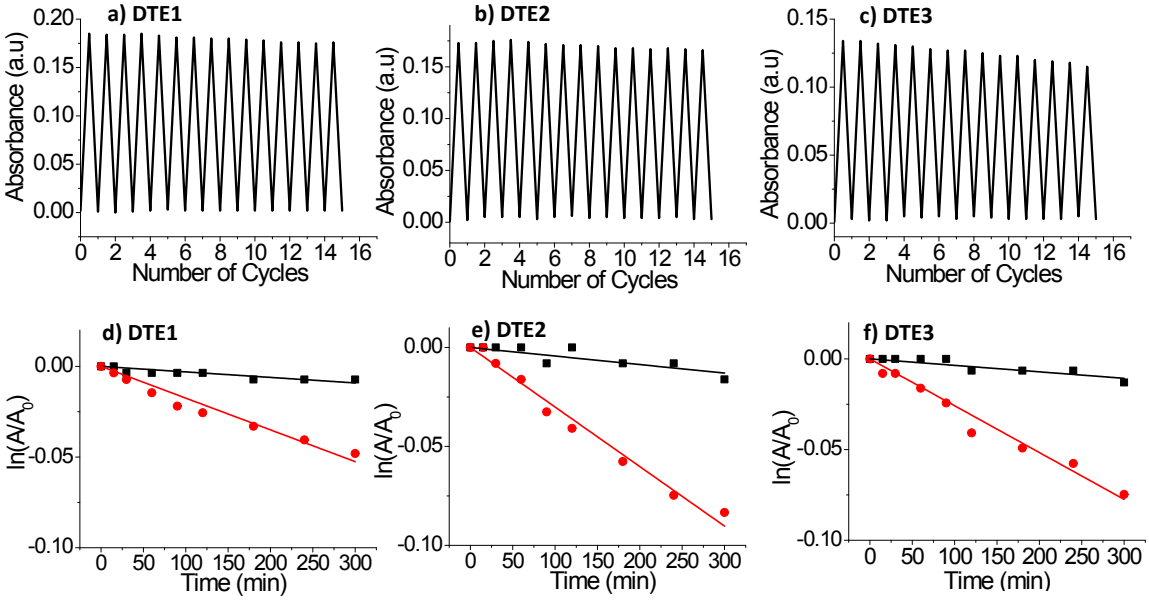


Figure S39. Absorbance changes of **DTEs** (**a** - **c**) at 620 nm (**DTE1** and **DTE2**) and at 630 nm (**DTE3**) by alternate irradiation with UV and visible light over 15 cycles in chloroform at 25 °C; and a plot of $\ln(A/A_0)$ versus time for the absorption changes of **DTEs** (**d** - **f**) at 620 nm (**DTE1** and **DTE2**) and at 630 nm (**DTE3**) at 25 °C (-■-) and 100 °C (-●-) in chlorobenzene solution. A is the absorbance at time t, A_0 is the initial absorbance, and solid lines denote the theoretical linear fits.

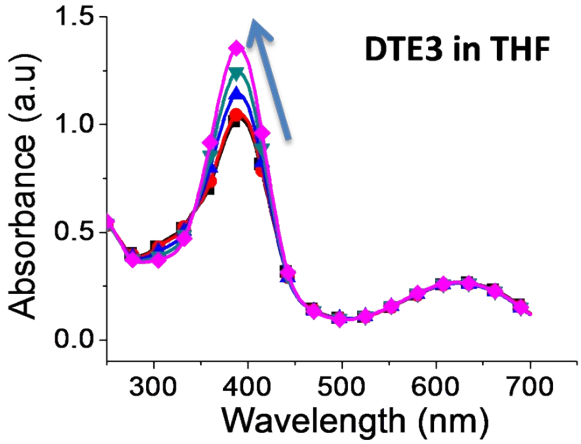


Figure S40. Time-dependent absorption studies on $\mathbf{DTE3}_{closed}$ solution in THF at 50 °C; 0 minute (-■-), 2 minutes (-●-), 5 minutes (-▲-), 15 minutes (-▼-), 30 minutes (-♦-).

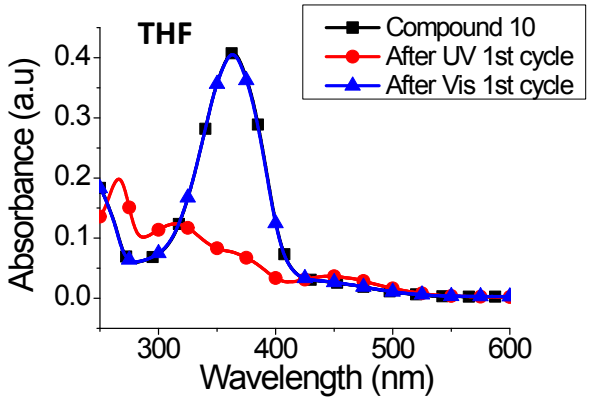


Figure S41. Absorption spectra of compound **10** in THF, trans- (-■-), and cis-isomer (-●-) at the photostationary state upon irradiation at 365 nm, and the reversible formation of trans-isomer (-▲-) upon irradiation with visible light.

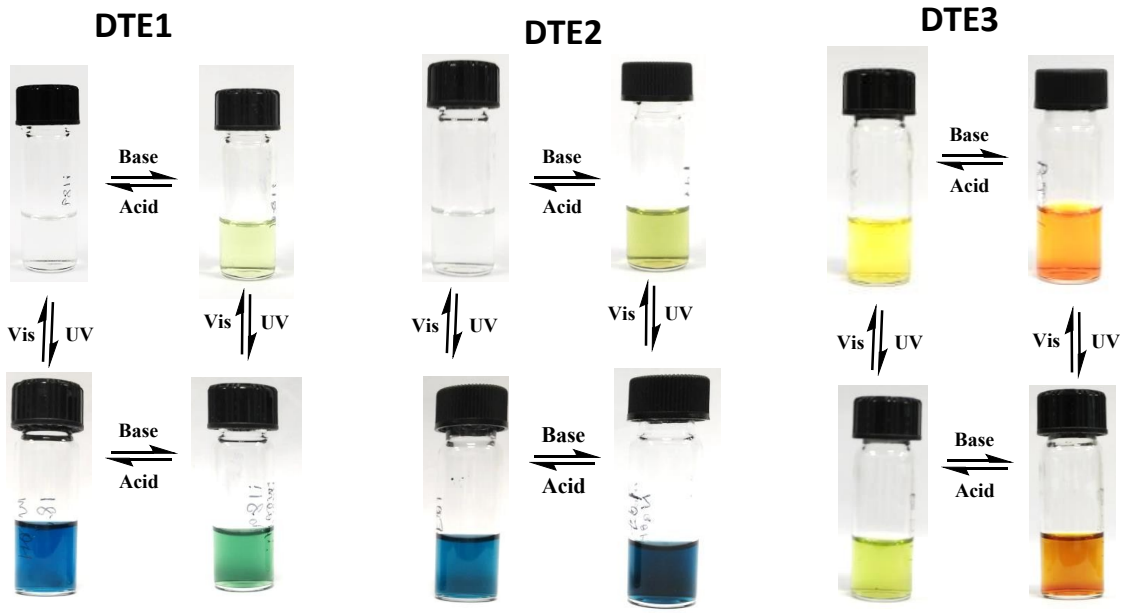


Figure S42. Optical images to show photochromic changes of **DTEs** in different pH.

5. SEM image of deprotonated $DTE2_{closed}$ film cast from MeOH.

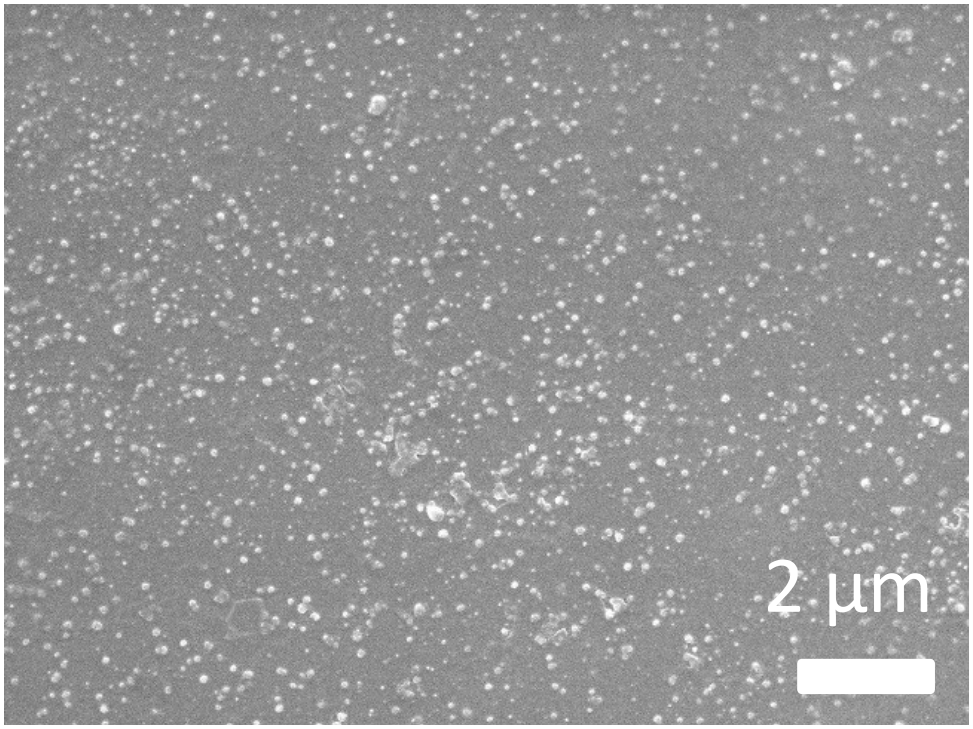


Figure S43. SEM image of **DTE2**$_{closed}$ film dropcasted from MeOH (6.0 x 10^{-4} M) upon deprotonation using aqueous NaOH solution (4 eq).

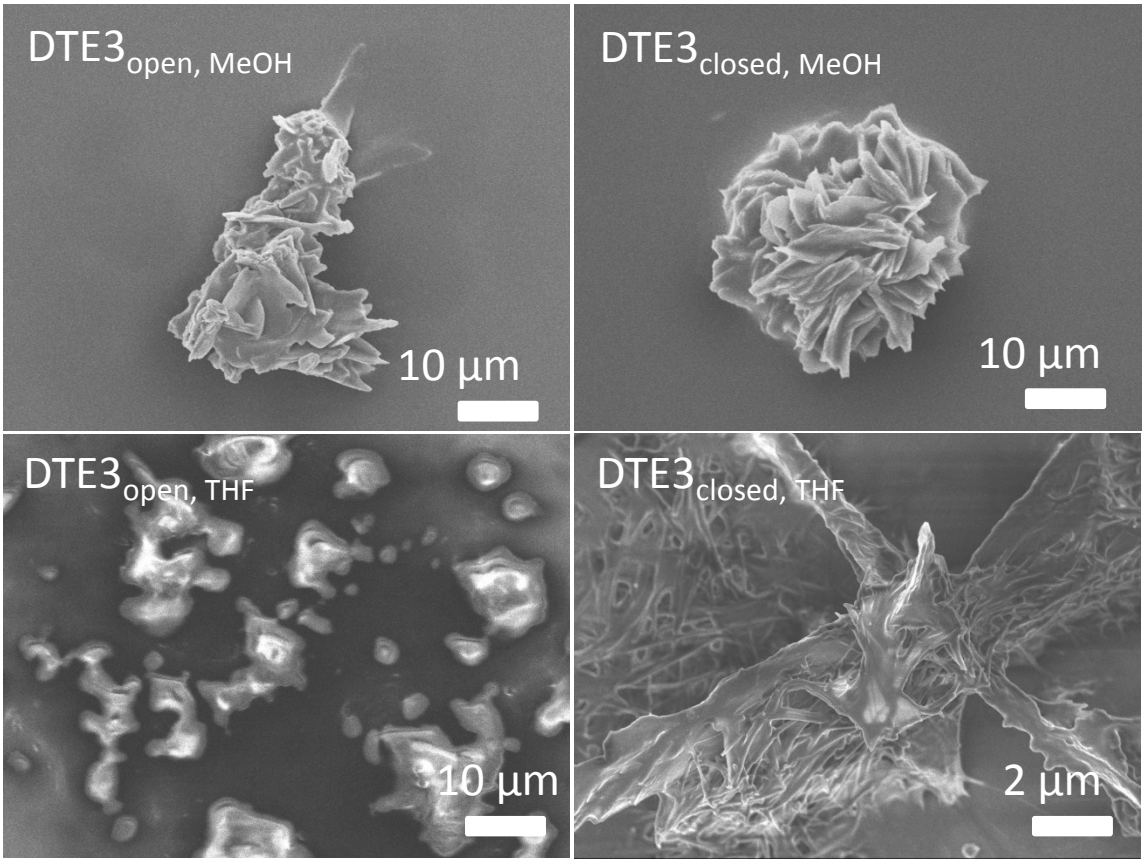


Figure S44. FESEM images of **DTE3** films drop-casted from MeOH or THF solutions (6.0 x 10^{-4} M) on a precleaned glass substrate. The solvent was allowed to evaporate slowly inside a

desiccator at room temperature under darkness. **DTE3**$_{closed}$ films were prepared by first irradiating the solution with UV light (365 nm, 10 minutes) prior to drop casting.