Electronic Supplementary Material (ESI) for Materials Advances.
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Supporting Information for: Modular Synthesis of Zwitterionic, Xanthene Bridged, Low Twist Angle Chromophores with High Hyperpolarizability

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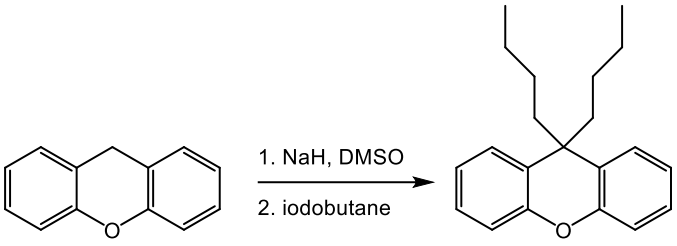
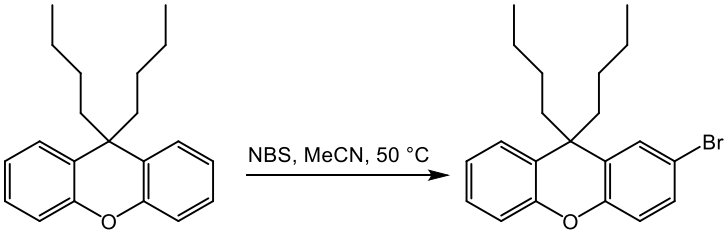
Synthesis of **E1** and **E2a-b**:



1

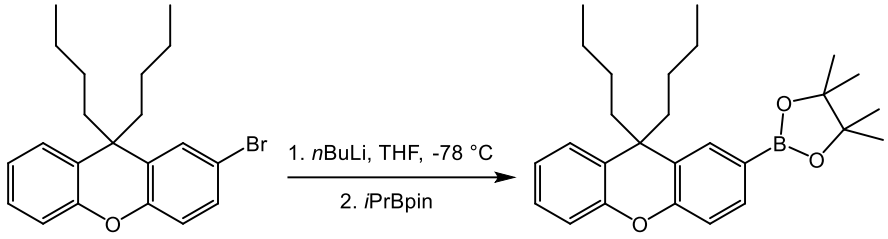
9,9-dibutylxanthene (1)[1]: Sodium hydride (18.5 g, 60 wt% disp, 465 mmol) was loaded into an oven-dried 1 L Schlenk flask equipped with a magnetic stir bar under anhydrous conditions. Dimethylsulfoxide (300 mL) was injected via syringe and the suspension was heated to 60 °C, resulting in the evolution of hydrogen gas. The flask was heated in this manner for 2 h, resulting in a light brown solution. Separately, xanthene (10.0 g, 54.9 mmol) was added to a 250 mL Schlenk flask equipped with a magnetic stir bar, similarly under anhydrous conditions. The solid was dissolved in anhydrous dimethylsulfoxide (150 mL) (Note: this usually requires the application of mild heating) and the resulting solution was added dropwise to the flask containing sodium hydride at 0° C, causing the reaction mixture to turn a deep red. The solution was allowed to warm to RT for 2 h before again being cooled to 0 °C. 1-Bromobutane (23.7 mL, 220 mmol) was then added dropwise over the course of 30 minutes (Note: this process is extremely exothermic, caution should be exercised) causing the solution to turn a pale red before being allowed to warm to RT for 12 h. The reaction was monitored by TLC until the starting material was no longer observed. The reaction products were then poured over ice-water (250 mL) and extracted with hexanes (3 × 150 mL). The combined organic phase was rinsed with cold water (3 × 100 mL), brine (100 mL), dried over sodium sulfate, and filtered before the solvent was removed under reduced pressure. The resulting crude material was purified via column chromatography (SiO_2, Hexanes) yielding compound **1** (12.5 g, 77%) as a colorless oil that crystallizes upon standing. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.29 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.22 – 7.15 (m, 2H), 7.06 (td, *J* = 7.6, 1.4 Hz, 2H), 7.00 (dd, *J* = 8.1, 1.3 Hz, 2H), 2.00 – 1.87 (m, 4H), 1.11 (p, *J* = 7.2 Hz, 4H), 0.84 (dtd, *J* = 12.0, 9.2, 8.7, 5.6 Hz, 4H), 0.70 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 151.88 (2C), 127.28 (2C), 126.37 (2C), 125.78 (2C), 123.11 (2C), 116.11 (2C), 45.31 (2C), 42.23, 27.13 (2C), 23.14 (2C), 14.00 (2C). HRMS (ESI-TOF) m/z: $[M]^+$ Calculated for $C_{21}H_{26}O$ 294.1978; Found 294.1940.



1 **2**

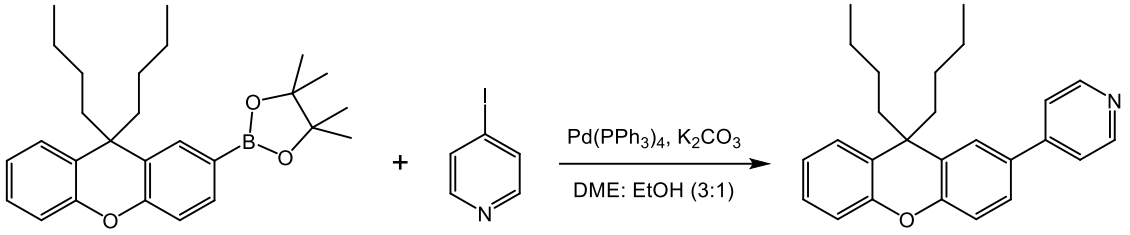
9,9-dibutyl-2-bromoxanthene (2): Compound **1** (12.5 g, 42.3 mmol) and acetonitrile (200 mL) were added to a 500 mL round-bottom flask equipped with a magnetic stir bar under atmospheric conditions. The mixture was lightly heated until homogenous and subsequently cooled to 0 °C. Solid *N*-bromosuccinimide was added portion-wise and the reaction was stirred at 0 °C for another 30 minutes. The mixture was then heated to 50 °C for 2 h, monitored by TLC, and subsequently

cooled to RT. Sodium bisulfite (10 wt%, 100 mL) was added and the resulting mixture was extracted with hexanes (3 × 100 mL). The combined organic phases were washed with 1 M NaOH (100 mL), de-ionized water (100 mL), brine (100 mL), dried over sodium sulfate, and filtered. The solvent was removed under reduced pressure and the resulting crude material was passed through a short hexanes silica plug resulting in 12.5 g (88% yield) of an inseparable mixture comprised of compound **1** (5 mol%), compound **2** (85 mol%), and 2,7-dibromoxanthene (10 mol%), manifested as a colorless oil. These estimated percentages were calculated based on integration peaks of the ^{1}H NMR (not shown). The mixture was used in the subsequent step without further purification.



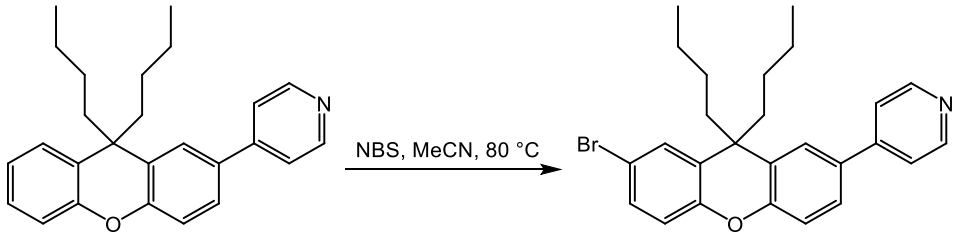
2 **3**

9,9-Dimethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-xanthene (3): A mixture containing mostly compound **2** (4.00 g, 10.1 mmol) and anhydrous THF (50 mL) were added to an oven-dried 200 mL Schlenk flask equipped with a magnetic stirbar under anhydrous conditions. The flask cooled to -78 °C for 20 minutes before *n*-BuLi (6.0 mL, 15.0 mmol, 2.5 M in Hexanes) was added dropwise and the reaction was left to stir at this temperature for 1 h. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.17 mL, 15.5 mmol) was added dropwise at -78 °C after which the reaction was warmed to RT for 12 h. The reaction was monitored via TLC until the starting material was no longer observed. The flask was then cooled to 0 °C in an ice-water bath, water (50 mL) was added and the mixture was stirred at room temperature for 30 min before being extracted with chloroform (3 × 75 mL). The combined organic phase was washed with water (2 × 50 mL), brine (50 mL), dried over Na_2SO_4, and filtered. The solvent was removed under reduced pressure and the resulting crude material was purified via column chromatography (SiO_2: 2.5% EtOAc in Hexanes) yielding compound **3** (3.55 g, 79%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.71 (d, *J* = 1.5 Hz, 1H), 7.63 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.28 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.18 (ddd, *J* = 8.1, 7.1, 1.6 Hz, 1H), 7.09 – 7.04 (m, 1H), 7.02 – 6.96 (m, 2H), 1.95 (dddd, *J* = 44.0, 13.6, 9.7, 6.5 Hz, 4H), 1.36 (s, 12H), 1.10 (dtd, *J* = 14.1, 7.2, 2.8 Hz, 4H), 0.87 – 0.76 (m, 4H), 0.69 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 154.35, 151.67, 134.14, 133.52, 127.24, 126.43, 126.14, 125.16, 123.29, 116.11, 115.56, 83.76, 45.31 (2C), 42.21, 27.17 (2C), 25.07 (4C), 24.97 (2C), 23.09 (2C), 13.99 (2C). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calculated for $C_{27}H_{38}BO_3$ 421.2909; Found 421.2910.



3 **4**

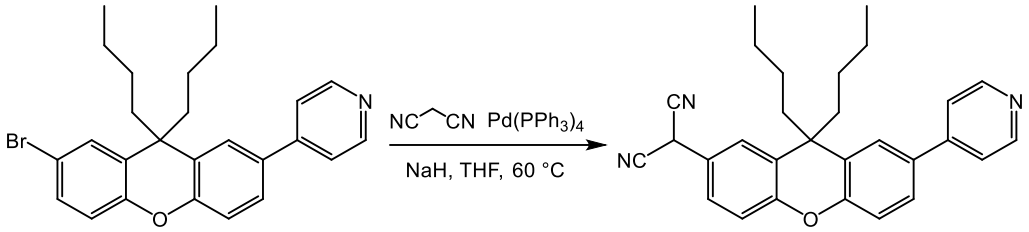
4-(9,9-dibutyl-9H-xanthen-2-yl)pyridine (4): Compound **3** (2.58 g, 6.19 mmol), freshly sublimated 4-iodopyridine (1.15 g, 5.62 mmol), potassium carbonate (2.57 g, 18.6 mmol), and $Pd(PPh_3)_4$ (710 mg, 0.62 mmol) were added to an oven-dried 200 mL Schlenk flask equipped with a magnetic stirbar and reflux condenser. The flask was placed under N_2 before de-oxygenated 1,2 dimethoxyethane (20 mL) and EtOH (7 mL) were added via syringe under positive N_2 flow and the reaction was then heated to 90 °C for 12 h, monitored by TLC until the starting materials were no longer observed. The flask was then cooled to RT before water (50 mL) was added and the mixture was extracted with chloroform (3 × 50 mL). The combined organic phase was washed with water (2 × 50 mL), brine (50 mL), dried over Na_2SO_4, and filtered. The solvent was removed under reduced pressure and the resulting crude material was purified via column chromatography (SiO_2: gradient 20-40% EtOAc in Hexanes) yielding compound **4** (2.00 g, 87%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.84 – 8.38 (m, 2H), 7.50 (d, *J* = 2.3 Hz, 1H), 7.49 – 7.45 (m, 2H), 7.43 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.24 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.14 (ddd, *J* = 8.1, 7.2, 1.6 Hz, 1H), 7.08 – 7.00 (m, 2H), 6.96 (dd, *J* = 8.1, 1.3 Hz, 1H), 2.01 – 1.72 (m, 4H), 1.07 (h, *J* = 7.2 Hz, 4H), 0.91 – 0.71 (m, 4H), 0.64 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 153.05, 151.51, 149.52 (2C), 148.97, 132.50, 127.55, 126.80, 126.37, 126.24, 125.35, 125.17, 123.65, 121.51 (2C), 117.15, 116.26, 45.42 (2C), 42.53, 27.15 (2C), 23.08 (2C), 13.99 (2C). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calculated for $C_{26}H_{30}NO$ 372.2322; Found 372.2326.



4 **5**

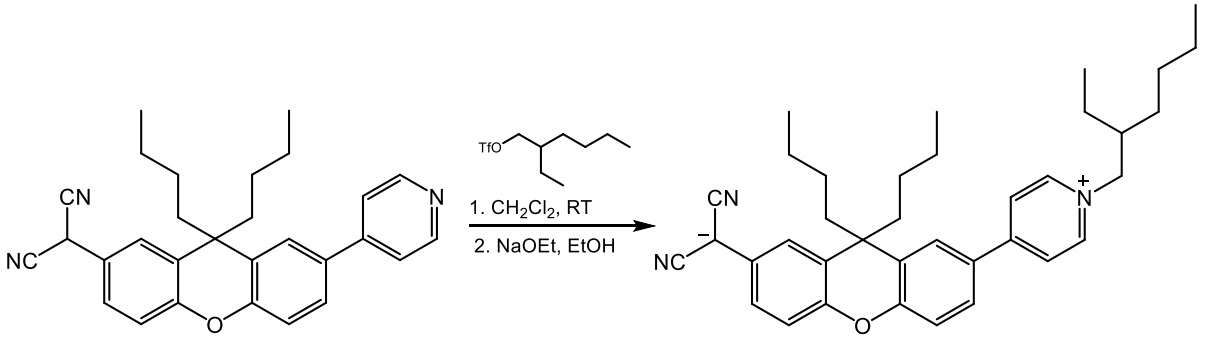
4-(7-bromo-9,9-dibutyl-9H-xanthen-2-yl)pyridine (5): Compound **4** (2.00 g, 5.38 mmol) was added to a 100 mL round bottom flask equipped with a magnetic stirbar under air-free conditions. Anhydrous acetonitrile (30 mL) was injected under positive N_2 flow and the flask was stirred at RT until compound **4** completely dissolved. An air-free solution of *N*-bromosuccinimide (1.92 g, 10.76 mmol) in anhydrous acetonitrile (20 mL) was added dropwise to the reaction vessel and the mixture was heated to 80 °C for 12 h, monitored by TLC (Note: The starting material and product of this reaction look nearly identical on TLC, it was used but is not particularly helpful for checking the reaction progress in this instance). The reaction was then cooled to RT and poured into a 10 wt% solution of sodium bisulfite. This biphasic mixture was mixed vigorously at RT for

approximately 2 h before extracting with chloroform (40 × mL). The combined organic phase was washed with de-ionized water (3 × 50 mL), brine (50 mL), dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the resulting crude mixture was purified via column chromatography (SiO_2: gradient 20-40% EtOAc in hexanes) yielding compound **5** (1.81 g, 75%) as an orange oil that crystallizes upon standing. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.62 – 8.57 (m, 2H), 7.63 – 7.59 (m, 2H), 7.55 (d, *J* = 2.3 Hz, 1H), 7.52 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.40 (d, *J* = 2.3 Hz, 1H), 7.32 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 6.93 (d, *J* = 8.7 Hz, 1H), 2.03 – 1.84 (m, 4H), 1.22 – 1.05 (m, 4H), 0.95 – 0.76 (m, 4H), 0.72 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 153.21, 150.87, 150.47, 147.31 (2C), 131.73, 130.79, 129.16, 127.65, 126.67, 126.52, 125.38, 122.57 (2C), 118.23, 117.54, 116.16, 45.48 (2C), 42.90, 27.14 (2C), 22.99 (2C), 13.99 (2C). HRMS (ESI-TOF) m/z: [Calculated for $C_{26}H_{29}BrNO$ 450.1427; Found 450.1439.



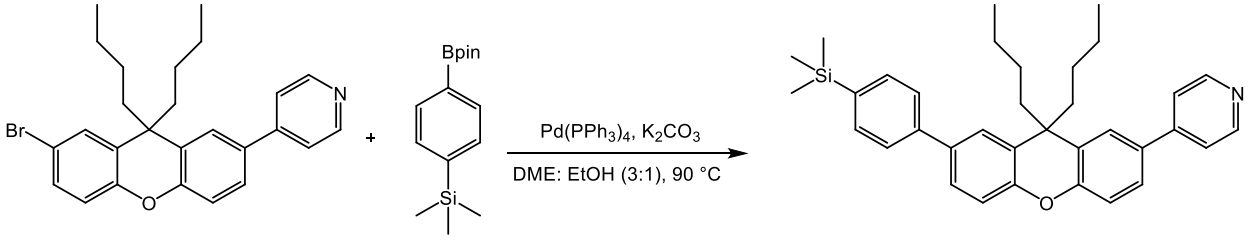
5 **6**

2-(9,9-Dibutyl-7-(pyridin-4-yl)-9H-xanthen-2-yl)malononitrile (6): Sodium hydride (235 mg, 5.88 mmol, 60 wt% in oil) was added to an oven-dried 100 mL Schlenk flask under air-free conditions and was dispersed in anhydrous THF (2 mL). The flask was cooled to 0 °C before a solution of malonitrile (0.5 mL, 1.83 mmol, 3.66 M in THF) was added dropwise causing the evolution of hydrogen gas. The reaction mixture was then warmed to RT and stirred for 2 h. Separately, compound **5** (660 mg, 1.47 mmol) and $Pd(PPh_3)_4$ 7(170 mg, 0.15 mmol) were added to a 50 mL Schlenk flask, dissolved in anhydrous THF (3 mL), and slowly injected via syringe to the sodium hydride/malonitrile mixture. The reaction was then heated to 80 °C for 12 h, monitored by TLC until the starting material was no longer present. The flask was then cooled to RT before de-ionized water was added slowly causing the evolution of more hydrogen gas. The resulting mixture was then carefully neutralized using 1 M hydrochloric acid until a pH of approximately 7.0 had been achieved. This mixture was then extracted with chloroform (3 × 30 mL) resulting in a solution that was visibly blue or purple in appearance. The combined organic phase was washed with de-ionized water (3 × 30 mL), brine (30 mL), dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the resulting crude material was purified via flash chromatography (SiO_2: gradient 30-45% EtOAc: Hexanes) yielding compound **6** (407 mg, 65%) as a dark-colored oil that crystallizes to a light blue solid upon standing (Note: This product does not appear to be particularly stable for extended periods of time, it is recommended to move on to the next step as soon as possible). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.70 – 8.63 (m, 2H), 7.56 (d, *J* = 2.2 Hz, 1H), 7.54 – 7.48 (m, 3H), 7.42 (d, *J* = 2.4 Hz, 1H), 7.35 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.16 (d, *J* = 5.1 Hz, 1H), 7.14 (d, *J* = 5.0 Hz, 1H), 5.12 (s, 1H), 2.12 – 1.88 (m, 4H), 1.16 (h, *J* = 7.3 Hz, 4H), 0.93 – 0.77 (m, 4H), 0.73 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 152.91, 152.09, 150.26 (2C), 148.02, 133.74, 127.81, 126.62, 126.57, 125.84, 125.53, 124.98, 121.45 (2C), 120.92, 118.19, 117.24, 112.01, 45.36 (2C), 42.98, 27.97, 27.14 (2C), 22.91 (2C), 13.93 (2C). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calculated for $C_{29}H_{30}N_3O$ 436.2383; Found 436.2398.



6 **E1**

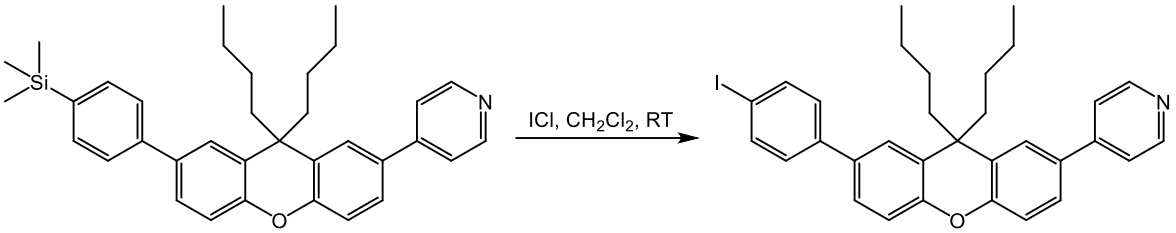
Dicyano(9,9-dibutyl-7-(1-(2-ethylhexyl)pyridin-1-ium-4-yl)-9H-xanthen-2-yl)methanide (E1): Compound **6** (430 mg, 0.99 mmol) was added to a 50 mL Schlenk flask equipped with a magnetic stirbar under air-free conditions. Anhydrous CH_2Cl_2 (24 mL) was injected under positive N_2 flow and left to stir at RT for approximately 30 minutes. Freshly prepared 2-ethyl hexyl triflate[2] (288 mg, 1.11 mmol) was added dropwise and the reaction was left at RT for an additional 12 h. The reaction was monitored by TLC until the starting material was no longer observed. Sodium ethoxide (1.0 ml, 2.5 mmol, 21 wt% in ethanol) was added dropwise and the reaction was left stirring for approximately 30 min. The solvent was removed under reduced pressure and the resulting crude was purified dispersed by water and filtered. The solid crude was purified via column chromatography (SiO_2: gradient 0 to 5% MeOH in CH_2Cl_2) resulting in compound **E1** (400 mg, 55%) as a dark purple solid. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ 8.99 (d, J = 6.8 Hz, 2H), 8.61 – 8.55 (m, 2H), 8.23 (d, J = 2.4 Hz, 1H), 8.00 (dd, J = 8.7, 2.3 Hz, 1H), 7.19 (d, J = 8.6 Hz, 1H), 6.82 (d, J = 8.5 Hz, 1H), 6.72 (s, 1H), 6.67 – 6.57 (m, 1H), 4.48 (d, J = 7.6 Hz, 2H), 2.18 (td, J = 12.9, 12.5, 4.5 Hz, 2H), 2.01 (d, J = 10.6 Hz, 1H), 1.90 (td, J = 12.9, 4.4 Hz, 2H), 1.38 – 1.17 (m, 6H), 1.10 (q, J = 7.4 Hz, 4H), 0.93 – 0.80 (m, 7H), 0.67 (t, J = 7.3 Hz, 9H). ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ 154.80, 153.84, 144.56 (2C), 142.86, 137.25, 127.58, 127.40, 127.17, 126.88, 126.59, 124.41, 123.31 (2C), 117.81, 116.97, 115.75, 114.03, 62.80, 44.16 (2C), 42.26, 28.92, 27.53, 26.94 (2C), 26.41, 22.36 (4C), 22.20, 13.87, 13.80, 13.74 (2C), 9.97. ^{19}F NMR (376 MHz, DMSO-d_6, 25 °C) δ -80.1 ppm. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calculated for $C_{37}H_{46}N_3O$ 548.3633; Found 548.3662. m.p. 154 – 180 °C. *While this is a broader melting temperature than expected, it is the range we observed. It is possible some degradation occurred/was occurring at those high temperatures in the melting point apparatus.



5 **7**

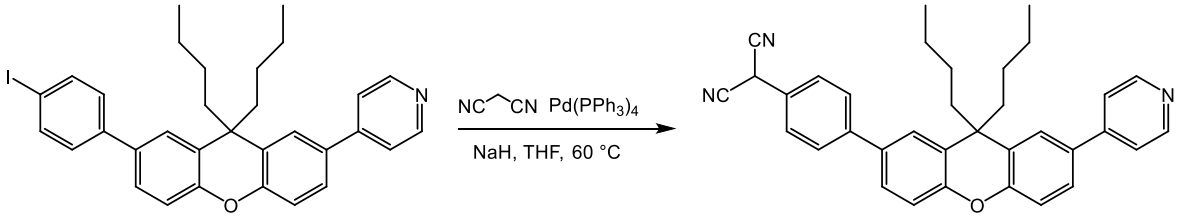
4-(9,9-Dibutyl-7-(4-(trimethylsilyl)phenyl)-9H-xanthen-2-yl)pyridine (7): Compound **5** (1.75 g, 3.88 mmol), tetramethyl-2-[4-(trimethylsilyl)phenyl]-1,3,2-dioxaborolane (1.22 g, 4.66 mmol), $Pd(PPh_3)_4$ (448 mg, 0.39 mmol), and K_2CO_3 (1.61g, 11.64 mmol) were added to a 100 mL Schlenk

flask under air-free conditions. De-oxygenated 1,2 dimethoxyethane (12 mL) and ethanol (4 mL) were injected via syringed under positive N_2 flow and the reaction was heated to 90 °C for 12 h, observed by TLC (Note: As before, retention factor of starting material and product are extremely similar, there is a difference in fluorescence at 254 nm between **5** and **7** which was the primary method of verification for this reaction). The reaction was then cooled to RT, de-ionized water (20 mL) was added, and the mixture was then extracted with chloroform (3 × 50 mL). The combined organic phase was washed with water (3 × 50 mL), brine (50 mL), dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the resulting crude was purified via flash chromatography (SiO_2: gradient 20-40% EtOAc: Hexanes) yielding compound **7** (1.59 g, 79%) as a colorless oil that crystallizes upon standing. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.67 (d, *J* = 6.3 Hz, 2H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.60 – 7.56 (m, 3H), 7.55 – 7.50 (m, 4H), 7.46 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 7.11 (d, *J* = 8.4 Hz, 1H), 2.03 (dt, *J* = 8.8, 6.0 Hz, 4H), 1.15 (q, *J* = 7.3 Hz, 4H), 0.92 (q, *J* = 7.4, 6.7 Hz, 5H), 0.72 (t, *J* = 7.3 Hz, 6H), 0.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C C) δ 152.92, 151.18, 149.79 (2C), 148.72, 141.40, 139.16, 136.54, 134.04 (2C), 132.74, 126.65, 126.44, 126.31 (2C), 126.28, 125.62, 125.18, 125.06, 121.49 (2C), 117.19, 116.66, 45.48 (2C), 42.77, 27.19 (2C), 23.08 (2C), 14.02 (2C), -0.92 (3C). HRMS (ESI-TOF) m/z: $[M]^+$ Calculated for $C_{35}H_{41}SiNO$ 519.2952; Found 519.3030.



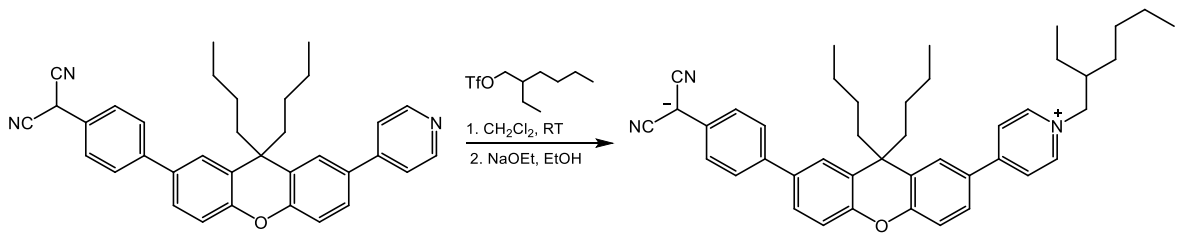
7 **8**

4-(9,9-Dibutyl-7-(4-iodophenyl)-9H-xanthen-2-yl)pyridine (8): Compound **7** (1.55 g, 2.88 mmol) was added to an oven-dried 100 mL Schlenk flask under air-free conditions. Anhydrous CH_2Cl_2 (15 mL) was injected via syringe under positive N_2 flow and the solution was cooled to 0 °C in an ice-water bath for 20 minutes. A solution of iodine monochloride (5.76 mL, 1.0 M in CH_2Cl_2) was added dropwise and the flask was warmed to RT and stirred for 4 hours, monitored by TLC (Note: As in the previous examples, retention factor is not helpful. The disparity in visible fluorescence at 254 nm between **7** and **8** is the best metric available for benchtop analysis). A solution of 10 wt% sodium bisulfite (20 mL) was then added and the biphasic mixture was mixed vigorously for 2 hours before the aqueous portion was partitioned and extracted with CH_2Cl_2 (2 × 30 mL). The combined organic phase was washed with de-ionized water (2 × 50 mL), brine (50 mL), dried over Na_2SO_4, and filtered. The solvent was removed under reduced pressure and the resulting crude material was purified via a short silica plug resulting in compound **8** (1.45 g, 89%) as an off-white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.74 – 8.65 (m, 2H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.59 (s, 1H), 7.56 – 7.50 (m, 3H), 7.47 (d, *J* = 2.2 Hz, 1H), 7.41 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.35 – 7.29 (m, 2H), 7.15 (d, *J* = 8.5 Hz, 1H), 7.11 (d, *J* = 8.4 Hz, 1H), 2.16 – 1.95 (m, 4H), 1.15 (p, *J* = 7.3 Hz, 4H), 0.91 (ddd, *J* = 12.9, 7.7, 5.2 Hz, 4H), 0.72 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C δ 152.81, 151.41, 149.80 (2C), 148.67, 140.52, 138.02 (2C), 135.48, 132.87, 128.84 (2C), 126.52, 126.35, 126.25, 125.89, 125.17, 124.77, 121.50 (2C), 117.21, 116.86, 92.70, 45.47 (2C), 42.79, 27.18 (2C), 23.06 (2C), 14.01 (2C). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calculated for $C_{32}H_{33}INO$ 574.1601; Found 574.1627.



8 **9**

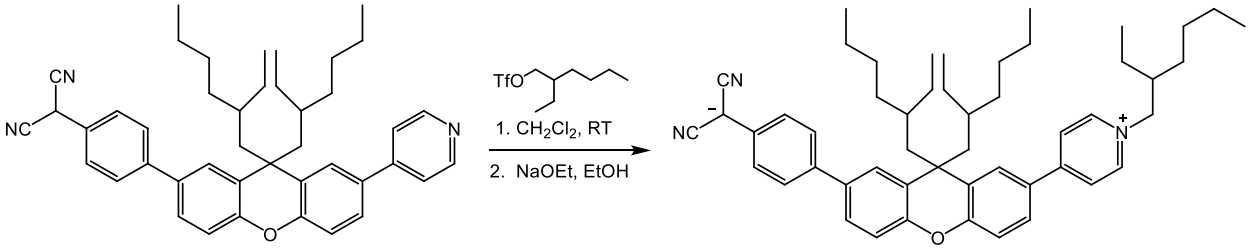
2-(4-(9,9-Dibutyl-7-(pyridin-4-yl)-9H-xanthen-2-yl)phenyl)malononitrile (8): Sodium hydride (139 mg, 3.48 mmol, 60 wt% in oil) was added to an oven-dried 100 mL Schlenk flask under air-free conditions and was dispersed in anhydrous THF (2 mL). The flask was cooled to 0 °C before a solution of malonitrile (0.5 mL, 1.08 mmol, 2.18 M in THF) was added dropwise causing the evolution of hydrogen gas. The reaction mixture was then warmed to RT and stirred for 2 h. Separately, compound **7** (500 mg, 0.87 mmol) and $Pd(PPh_3)_4$ (50 mg, 0.04 mmol) were added to a 50 mL Schlenk flask and dissolved in anhydrous THF (3 mL) and slowly injected via syringe to the sodium hydride/malonitrile mixture. The reaction was then heated to 60 °C for 6 h, monitored by TLC until the starting material was no longer present. The flask was then cooled to RT before de-ionized water was added slowly causing the evolution of more hydrogen gas. The resulting mixture was then carefully neutralized using 1 M hydrochloric acid until a pH of approximately 7.0 had been achieved. This mixture was then extracted with chloroform (3 × 30 mL) resulting in a solution that was visibly blue or purple in appearance. The combined organic phase was washed with de-ionized water (3 × 30 mL), brine (30 mL), dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the resulting crude material was purified via flash chromatography (SiO_2: gradient 30-45% EtOAc: Hexanes) yielding compound **8** (262 mg, 59%) as a dark-colored oil that crystallizes upon standing (Note: This product does not appear to be particularly stable for extended periods of time, it is recommended to move on to the next step as soon as possible). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.73 – 8.64 (m, 2H), 7.72 – 7.66 (m, 2H), 7.62 – 7.58 (m, 3H), 7.55 – 7.50 (m, 4H), 7.45 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.16 (d, *J* = 6.3 Hz, 1H), 7.14 (d, *J* = 6.2 Hz, 1H), 5.14 (s, 1H), 2.17 – 1.95 (m, 4H), 1.17 (h, *J* = 7.3 Hz, 4H), 0.99 – 0.86 (m, 4H), 0.73 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 152.69, 151.83, 149.91 (2C), 148.54, 143.30, 134.76, 133.06, 128.47 (2C), 127.86 (2C), 126.54, 126.41, 126.14, 125.14 (2C), 124.78, 121.49 (3C), 117.23, 117.06, 111.87, 100.13, 45.47 (2C), 42.82 (2C), 28.02, 27.19 (2C), 23.05 (2C), 14.01 (2C). HRMS (ESI-TOF) m/z: $[M]^+$ Calculated for $C_{35}H_{33}N_3O$ 511.2624; Found 511.2619.



9 **E2a**

Dicyano(4-(9,9-dibutyl-7-(1-(2-ethylhexyl)pyridin-1-ium-4-yl)-9H-xanthen-2-yl)phenyl) methanide (E2a): Compound **8** (250 mg, 0.49 mmol) was added to an oven-dried 50 mL Schlenk flask under air-free conditions. Anhydrous CH_2Cl_2 (10 mL) was injected via syringe and the reaction mixture was left to stir at RT for 20 minutes. Freshly prepared 2-ethylhexyl triflate[2] was injected via syringe and the reaction was left to stir at RT for 12 h, monitored by TLC until the starting material was no longer present. Sodium ethoxide (0.25 mL, 21 wt%) was then added dropwise causing the solution to turn a dark shade of red. The reaction was left to stir at RT for approximately 30 minutes before water (10 mL) was added. The resulting biphasic mixture was separated and the aqueous phase was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic phase was washed with water (20 mL), brine (20 mL), dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure resulting crude was washed with 1:1 hexanes: CH_2Cl_2 yielding **E2a** (226 mg, 73%) as a bright red solid. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ 9.02 (d, J = 6.6 Hz, 2H), 8.64 – 8.56 (m, 2H), 8.29 (d, J = 2.3 Hz, 1H), 8.04 (dd, J = 8.7, 2.2 Hz, 1H), 7.63 (d, J = 2.2 Hz, 1H), 7.45 (dd, J = 8.5, 2.1 Hz, 1H), 7.39 (d, J = 8.5 Hz, 2H), 7.27 (d, J = 8.7 Hz, 1H), 7.07 (d, J = 8.5 Hz, 1H), 6.81 (d, J = 8.4 Hz, 2H), 4.48 (d, J = 7.6 Hz, 2H), 2.32 – 2.10 (m, 4H), 2.09 – 1.94 (m, 1H), 1.36 – 1.18 (m, 8H), 1.10 (q, J = 7.4 Hz, 4H), 0.90 – 0.83 (m, 6H), 0.76 – 0.60 (m, 10H). ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ 154.26, 153.77, 148.71, 144.65 (2C), 140.90, 136.75, 128.02, 127.91, 127.83, 127.39, 127.09, 126.22 (2C), 125.94, 125.06, 124.77, 123.53 (2C), 122.83, 118.45 (2C), 117.13, 116.05, 62.89, 44.07 (2C), 42.51, 28.92, 27.89, 27.53, 27.04 (2C), 22.36 (2C), 22.26 (2C), 13.86, 13.78 (3C), 9.96. ^{19}F NMR (376 MHz, DMSO-d_6, 25 °C) δ -80.1 ppm. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calculated for $C_{43}H_{50}N_3O_3$ 624.3948; Found 624.3923. mp 199-203 °C.

Precursor compounds leading to chromophore **E2b** (compounds **E2b-1**, **E2b-2**, **E2b-3**, **E2b-4**, **E2b-5**, **E2b-7**, **E2b-8**, and **E2b-9**) were synthesized identically to those of the butylated precursors leading to chromophore **E2a** (compounds **1-5**,**7-9**). The yields for each reaction are as follows: **E2b-1:** 74% (11.87 g); **E2b-2:** 96% (10.64 g); **Eb2-3:** 59% (6.89 g); **E2b-4:** 83% (750 mg; small scale example, large scale yields similar result); **E2b-5:** 75% (3.71 g); **E2b-7:** 72% (3.21 g); **E2b-8:** 77% (2.87 g); **E2b9:** 85% (1.27 g).



E2b-9 **E2b**

Dicyano(4-(9,9-di(2-ethylhexyl)l-7-(1-(2-ethylhexyl)pyridin-1-ium-4-yl)-9H-xanthen-2-yl)phenyl) methanide (E2b): Chromophore **E2b** was synthesized identically to Chromophore **E1** from compound **E2b-9**, yielding a soft orange solid. Yield: 11.87 g, 74%. Mp 73-76.

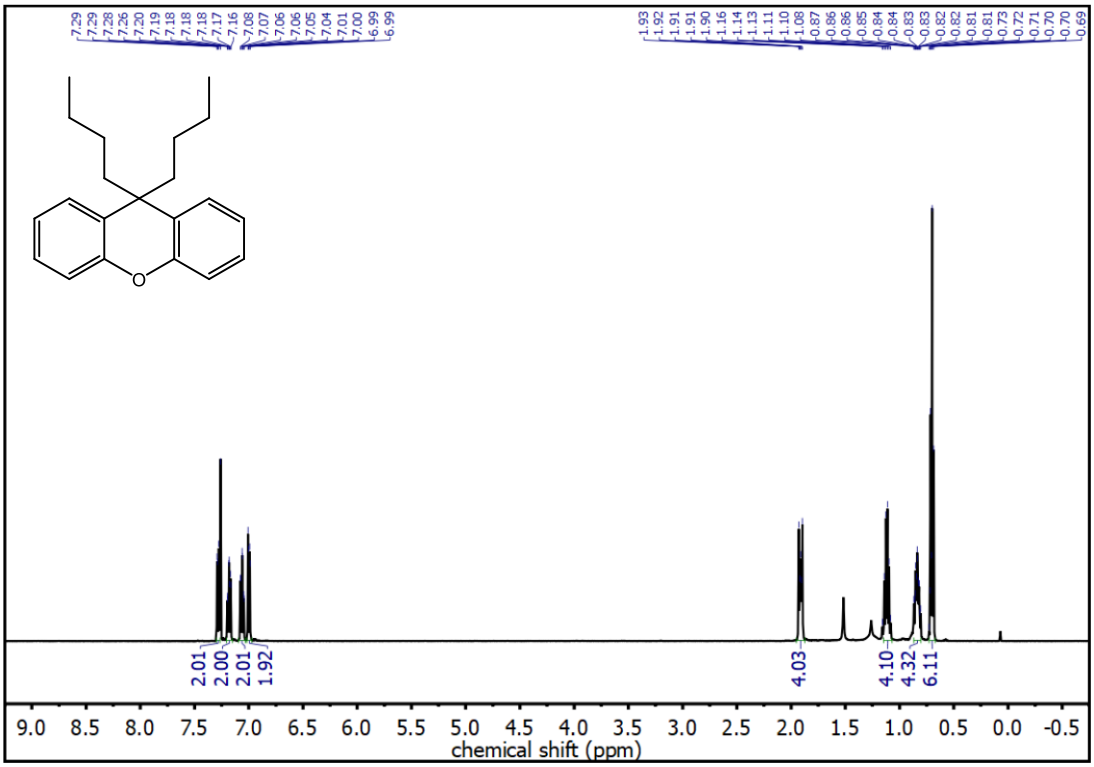


Figure S1. ^{1}H NMR Spectrum of Compound 1.

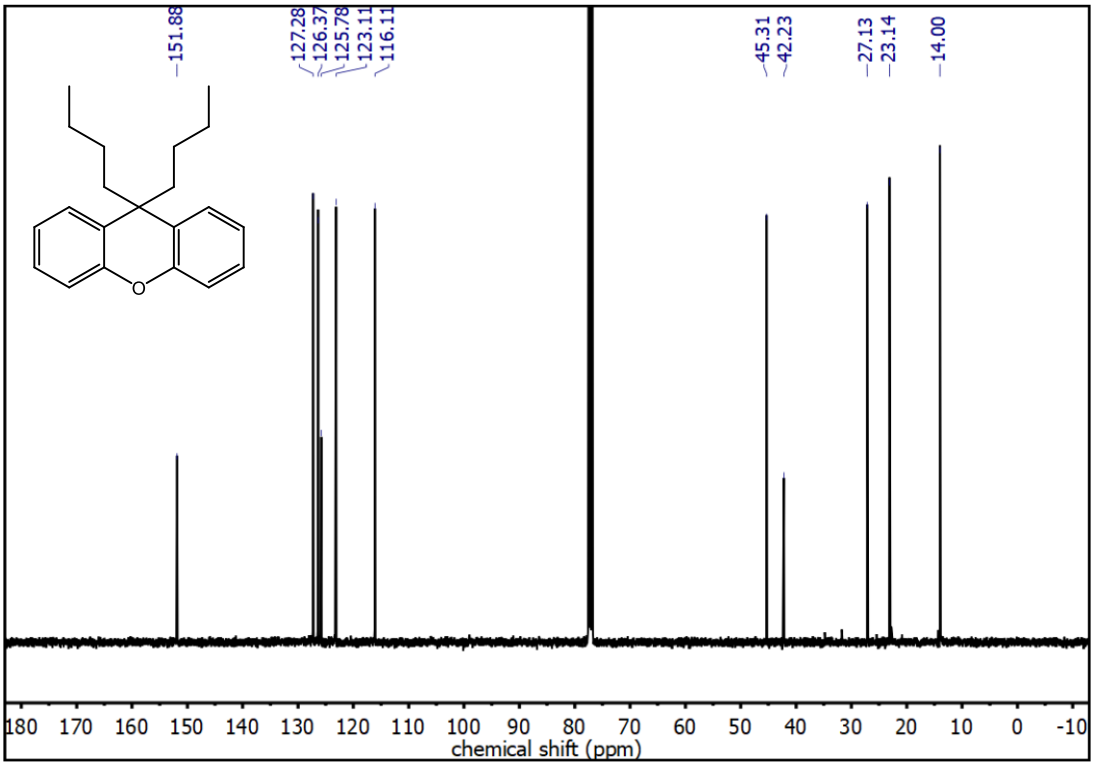


Figure S2. ^{13}C NMR spectrum of compound 1.

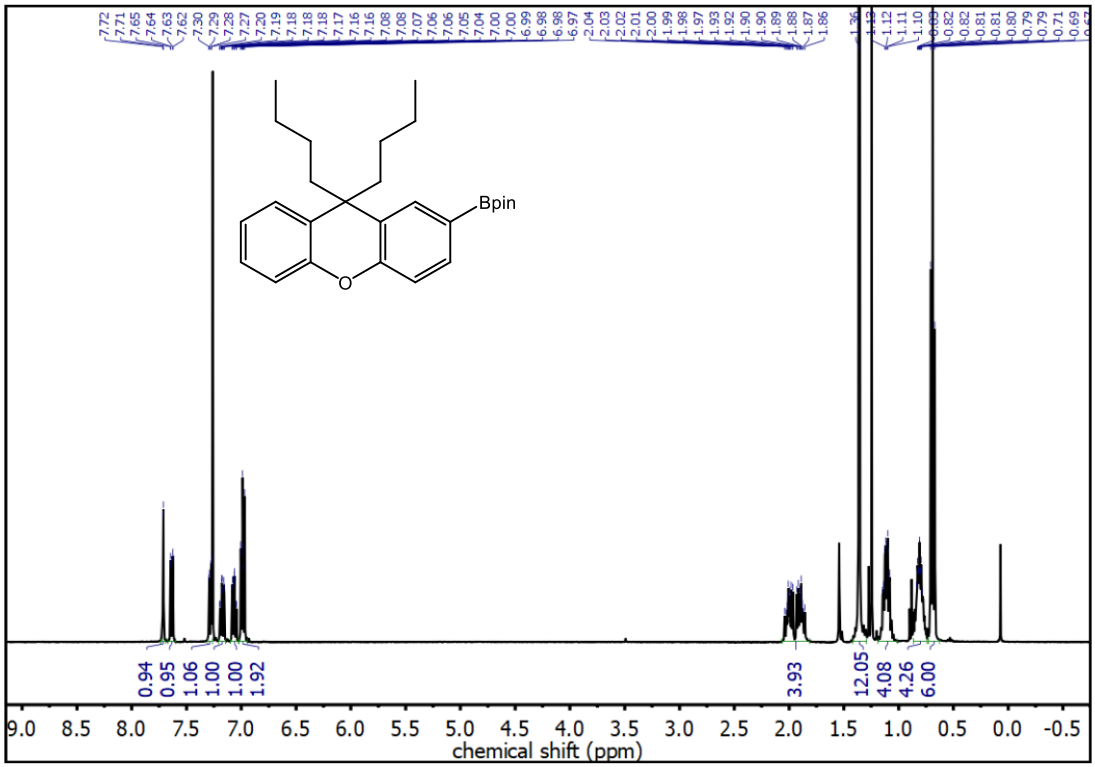


Figure S3. ^{1}H NMR Spectrum of Compound 3.

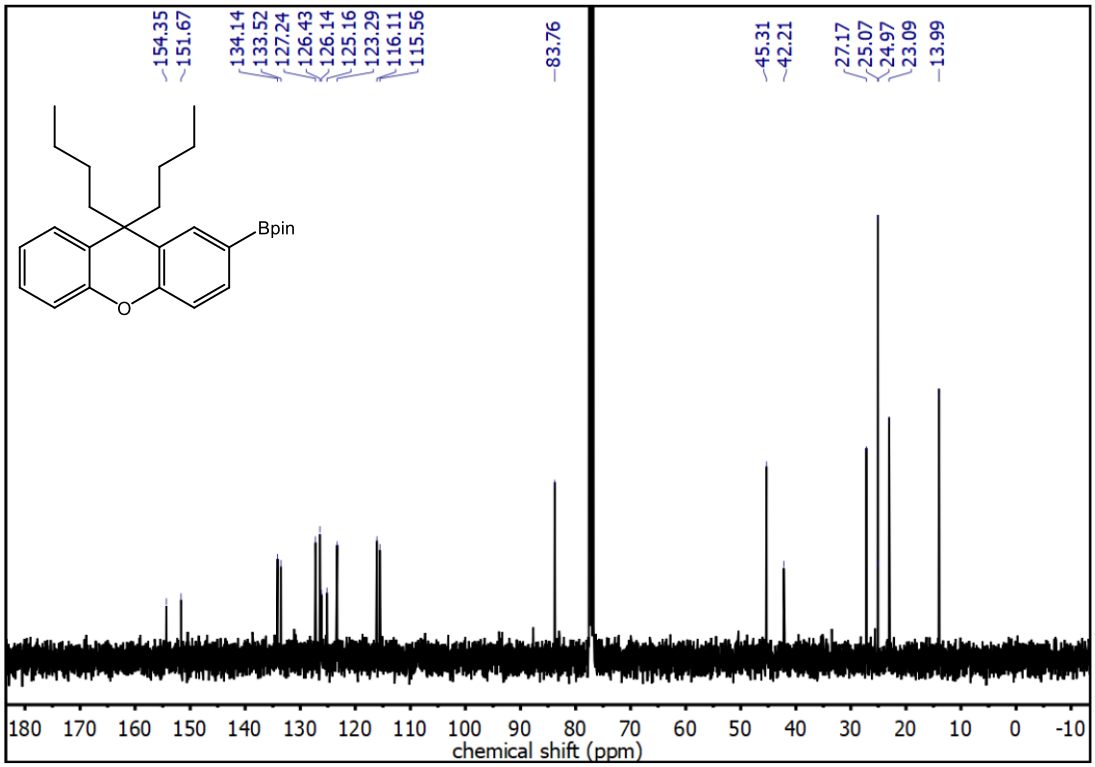


Figure S4. ^{13}C NMR spectrum of compound 3.

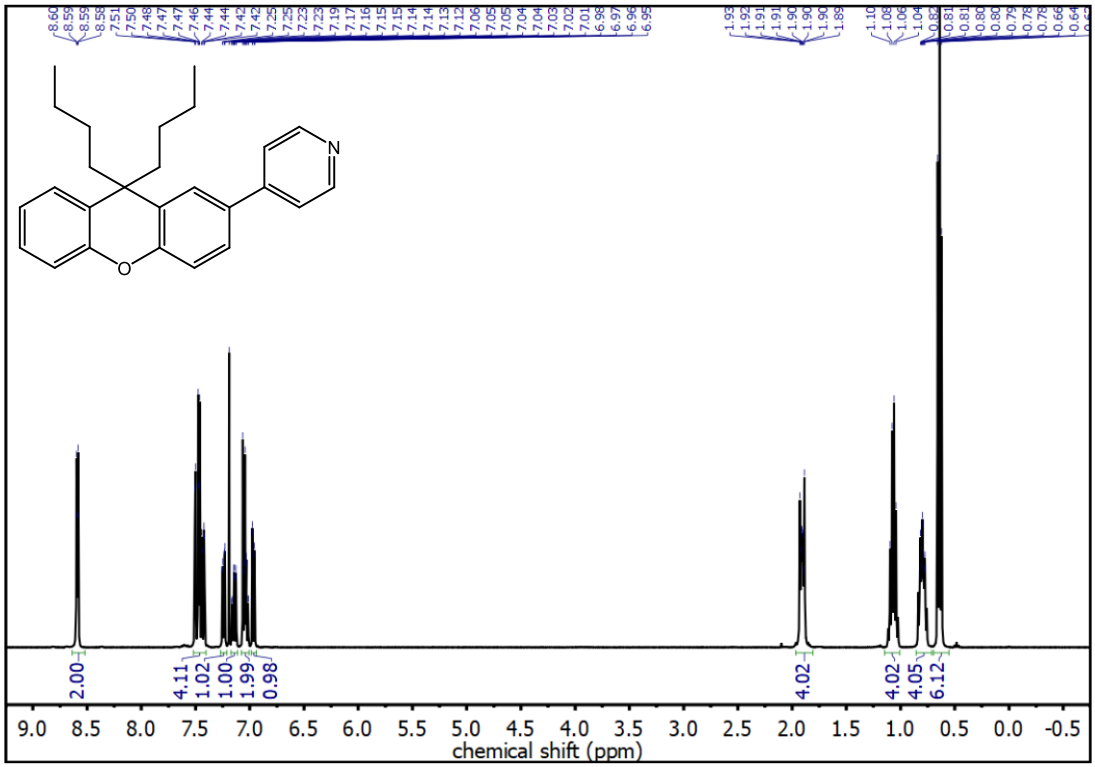


Figure S5. ^{1}H NMR Spectrum of Compound 4.

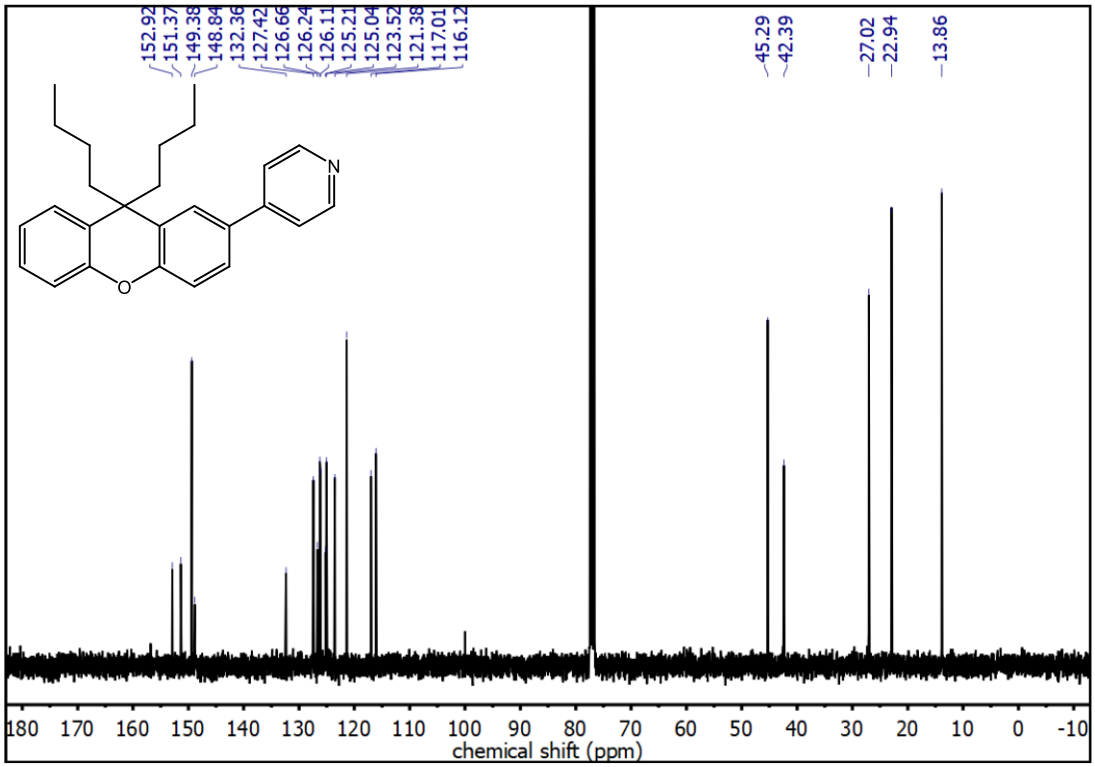


Figure S6. ^{13}C NMR spectrum of compound 4.

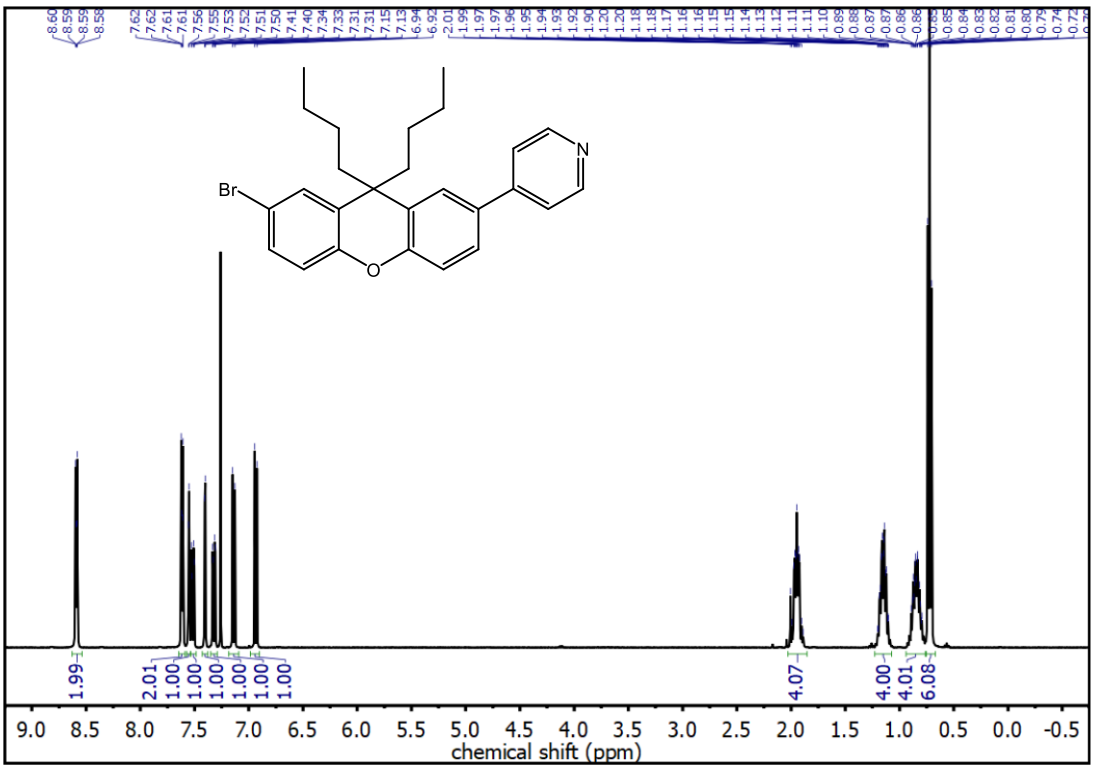


Figure S7. ^{1}H NMR Spectrum of Compound 5.

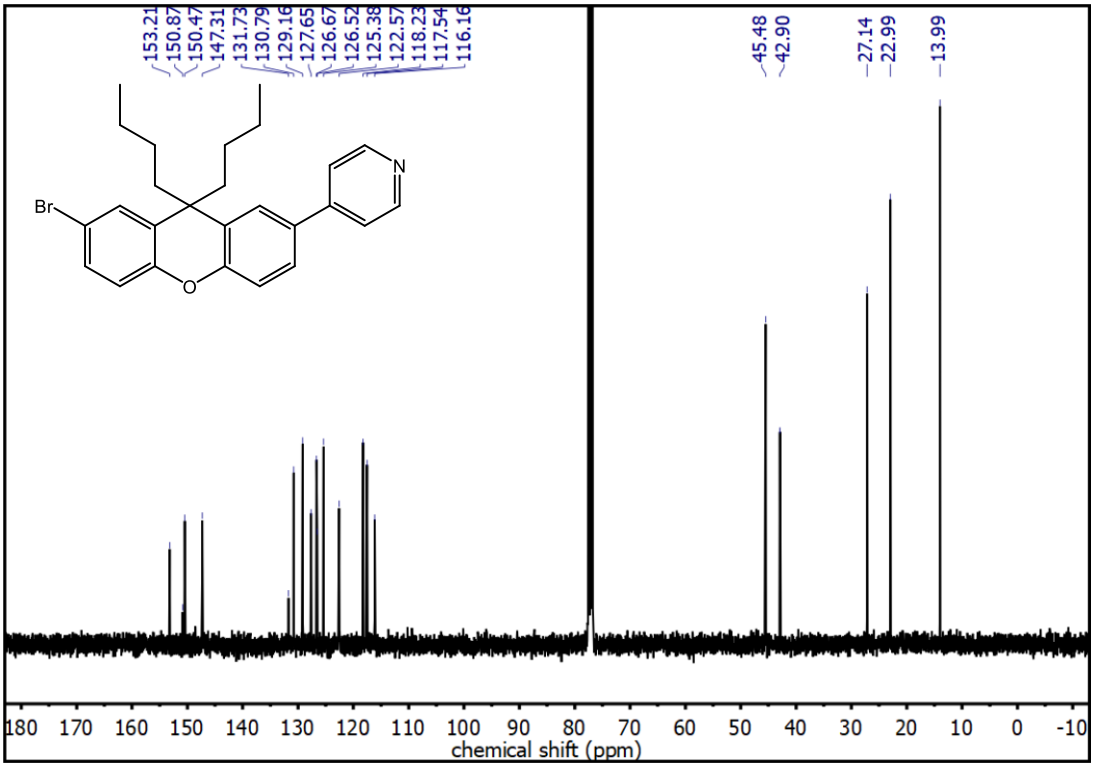


Figure S8. ^{13}C NMR spectrum of compound 5.

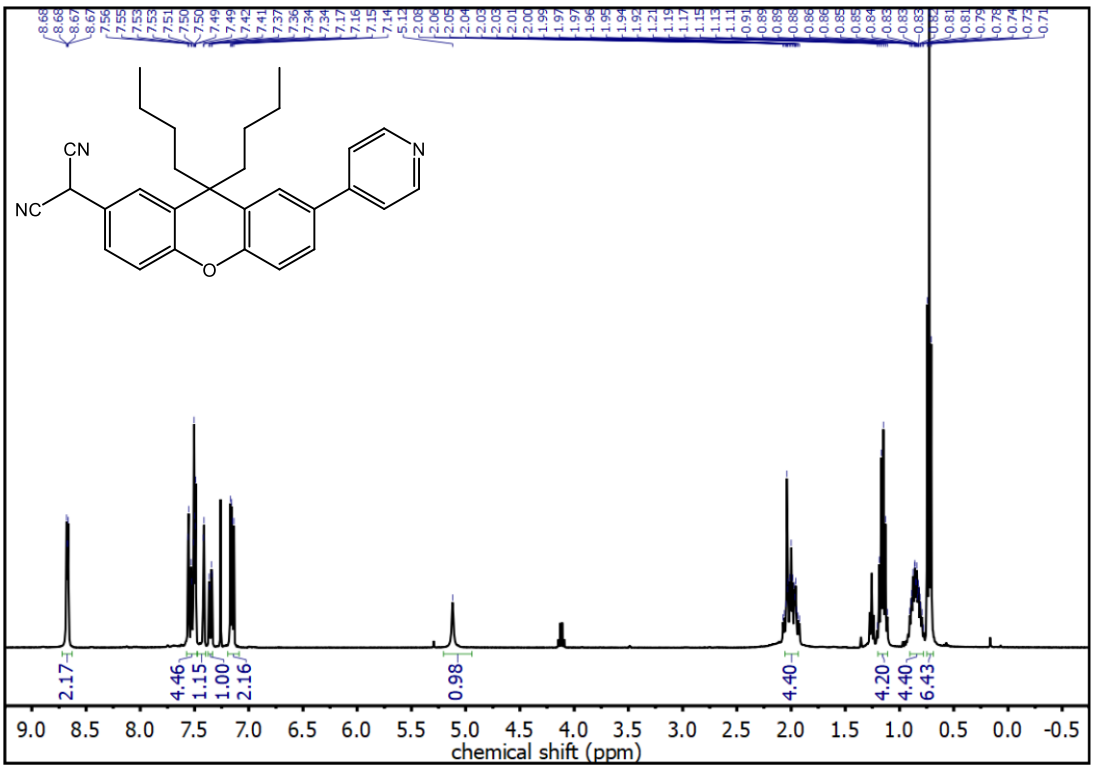


Figure S9. ^{1}H NMR Spectrum of Compound 6.

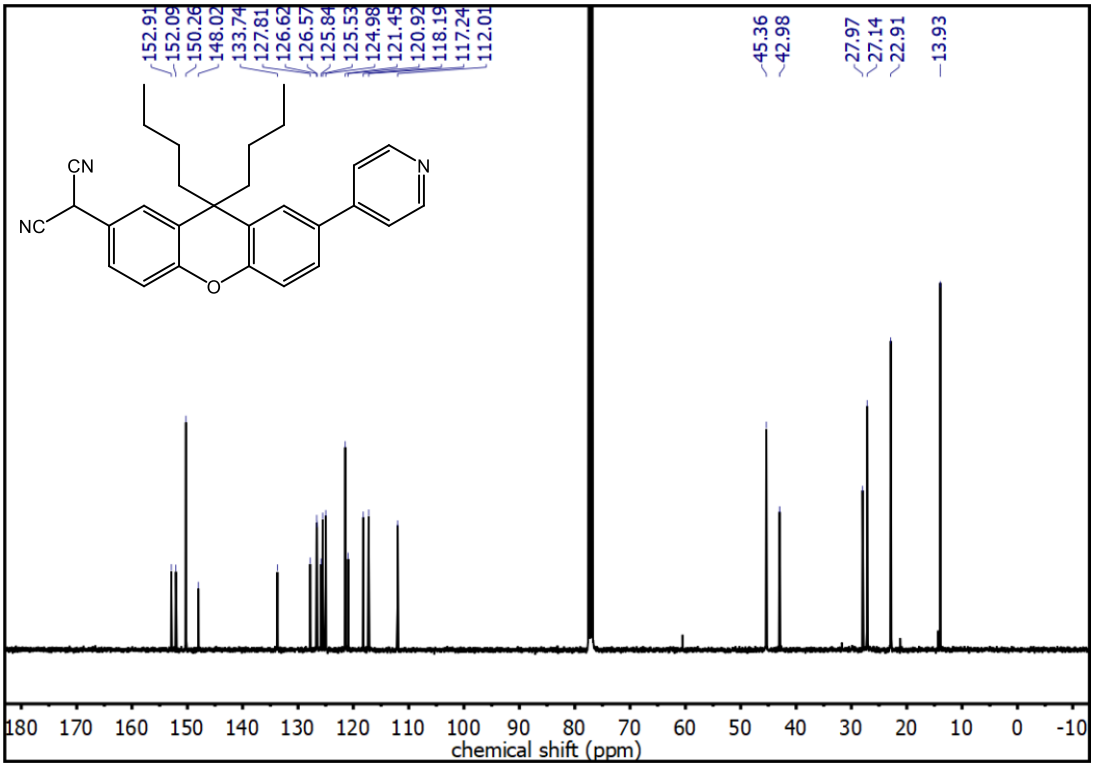


Figure S10. ^{13}C NMR spectrum of compound 6.

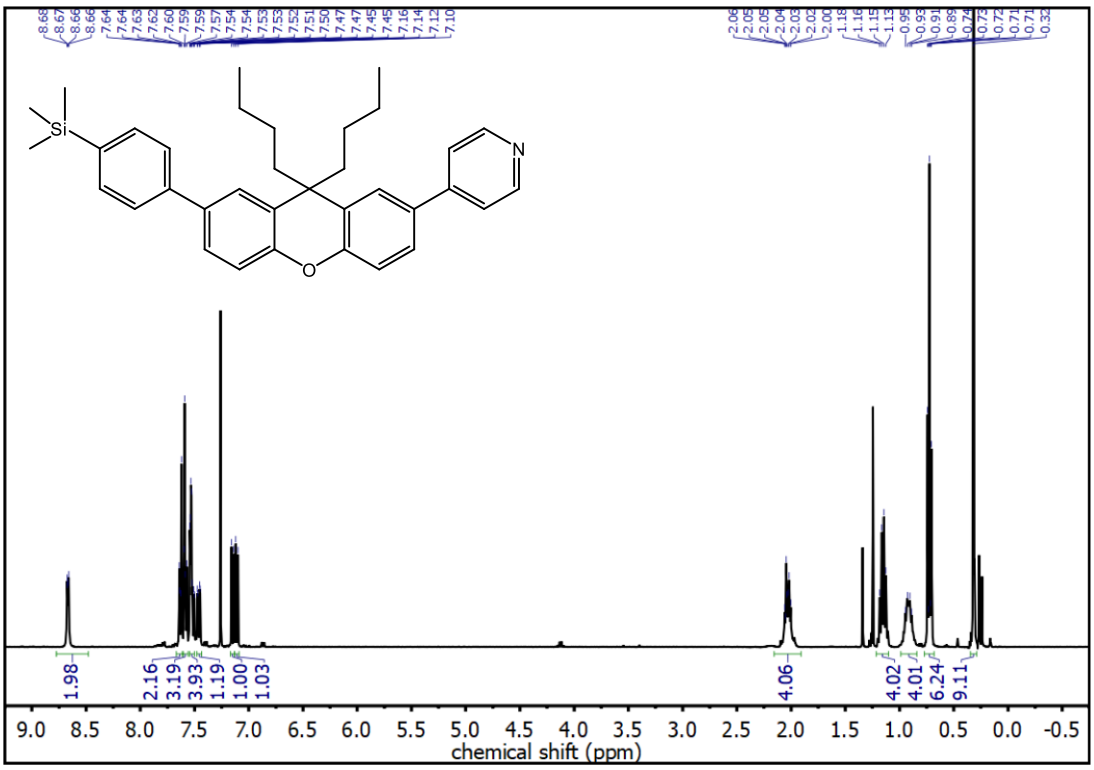


Figure S11. ^{1}H NMR Spectrum of Compound 7.

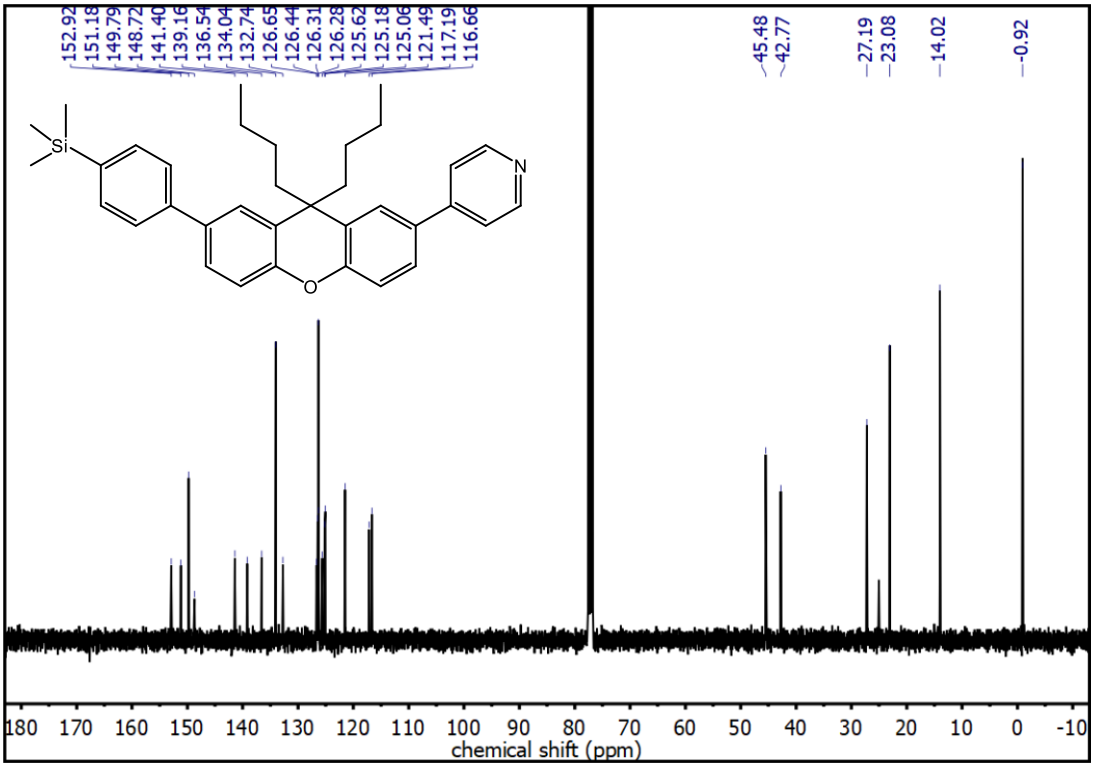


Figure S12. ^{13}C NMR spectrum of compound 7.

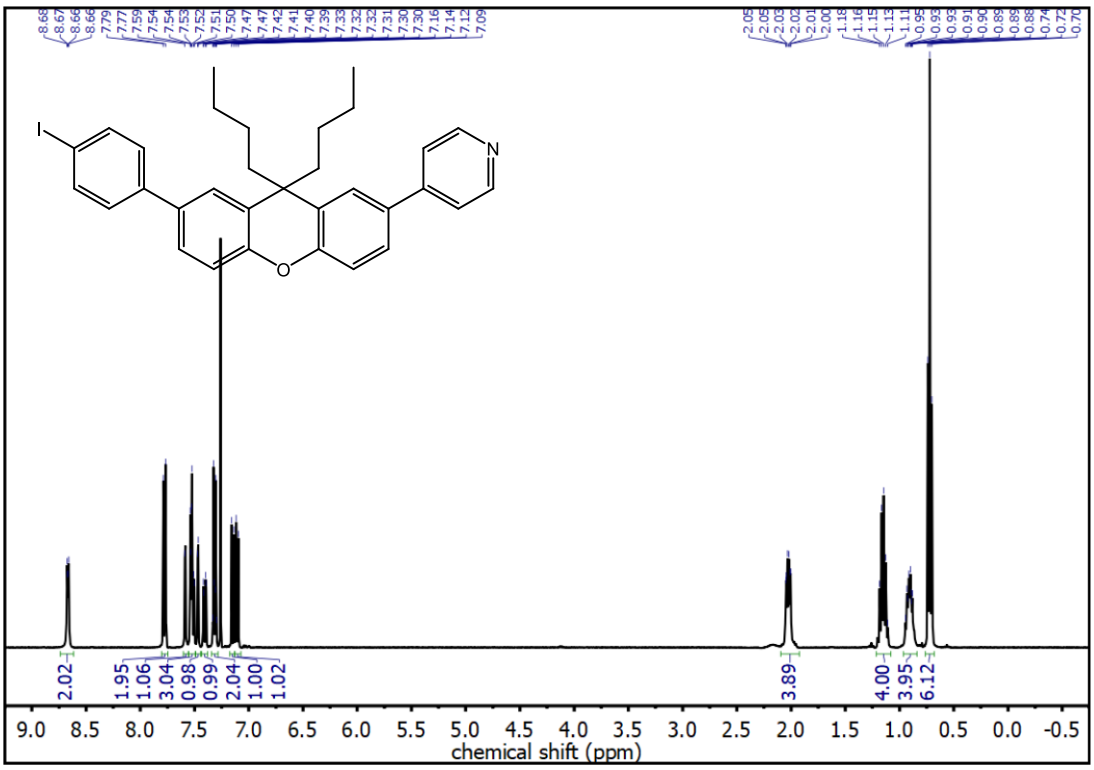


Figure S13. ^{1}H NMR Spectrum of Compound 8.

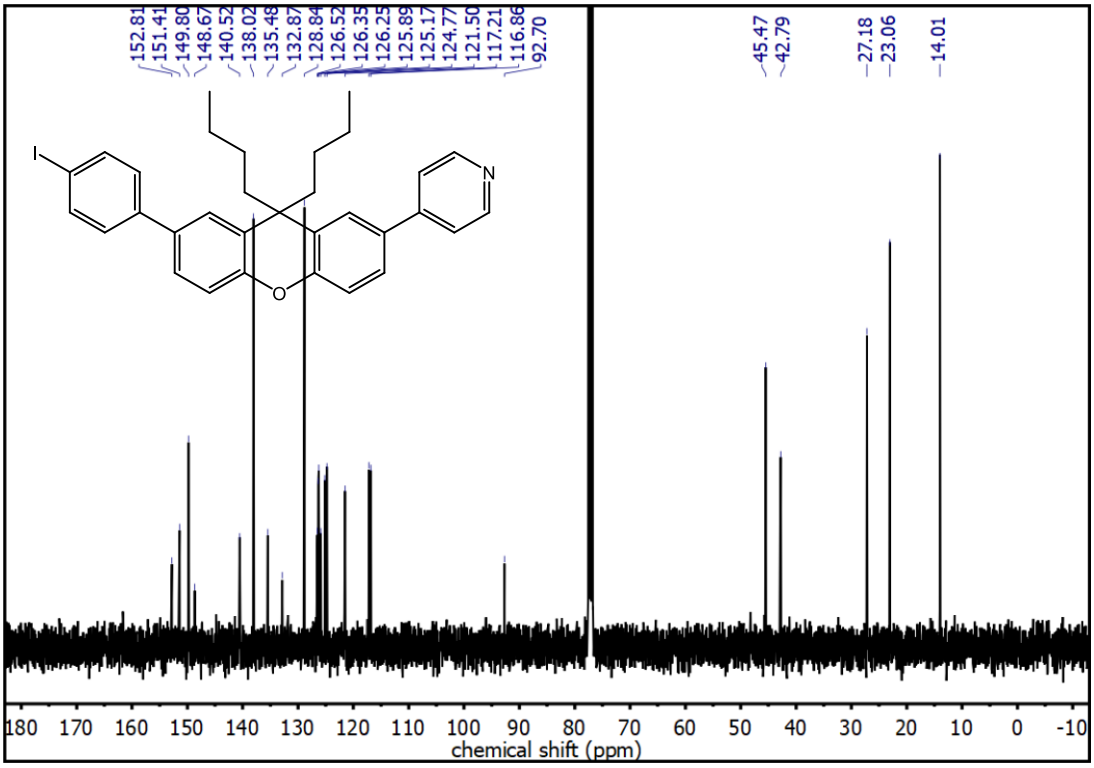


Figure S14. ^{13}C NMR spectrum of compound 8.

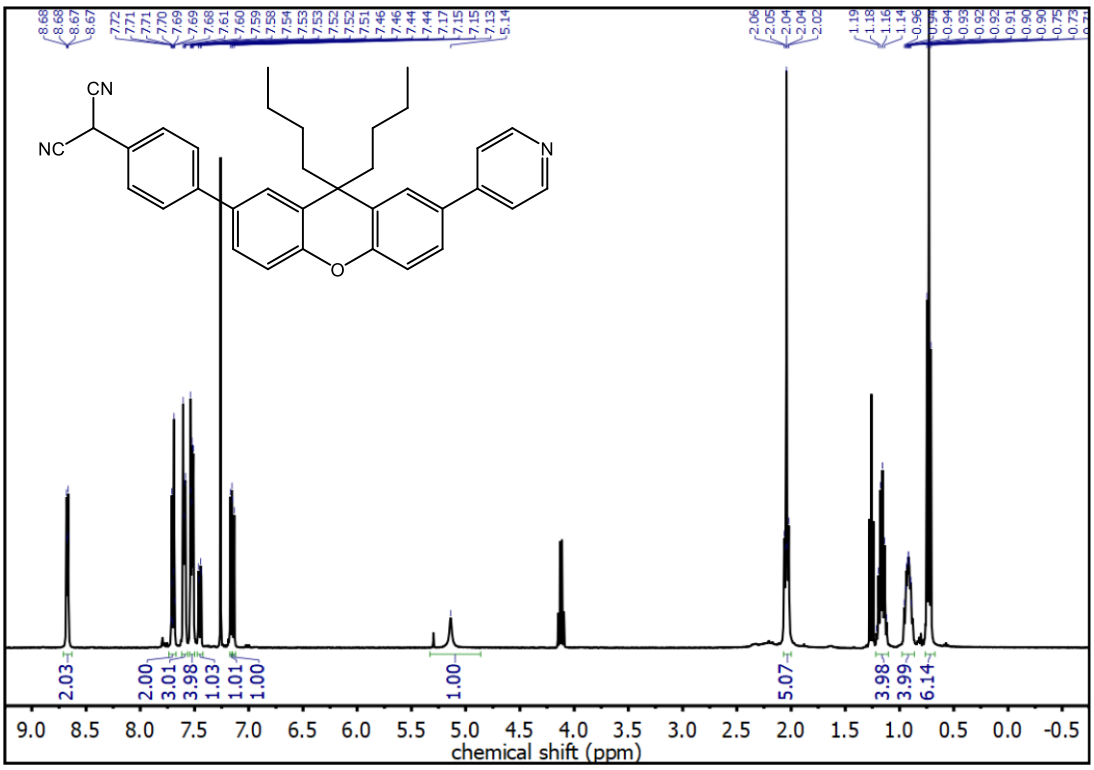


Figure S15. ^{1}H NMR Spectrum of Compound 9.

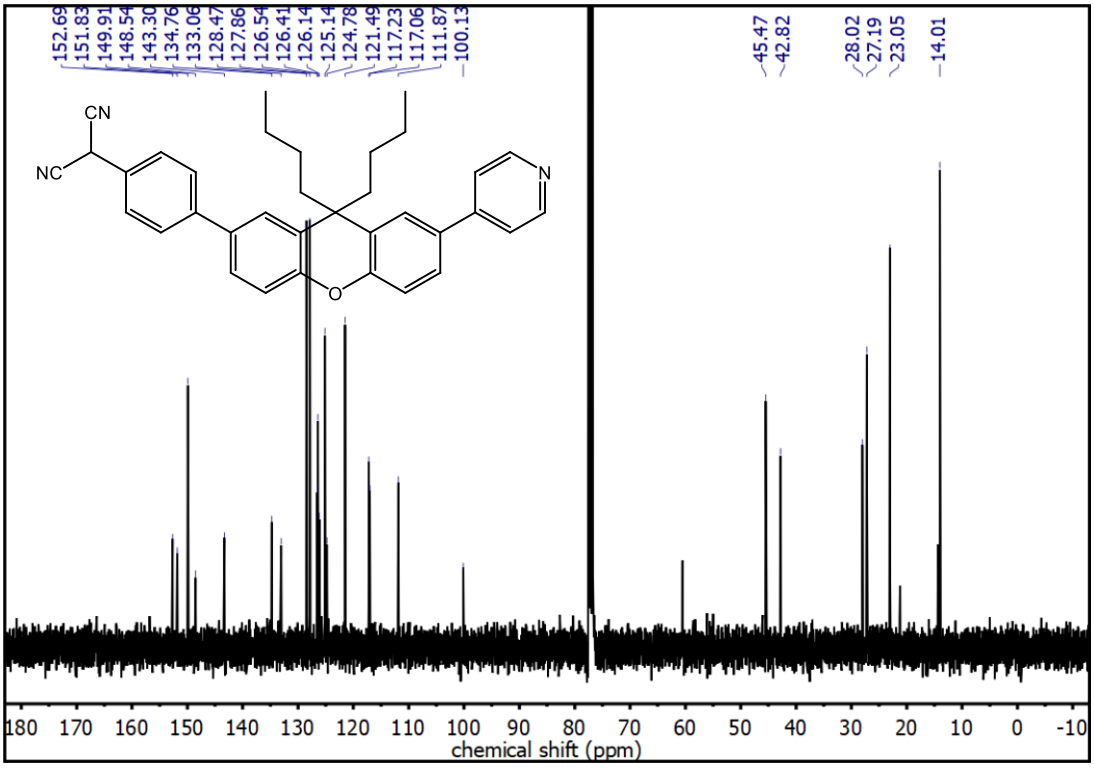


Figure S16. ^{13}C NMR spectrum of compound 9.

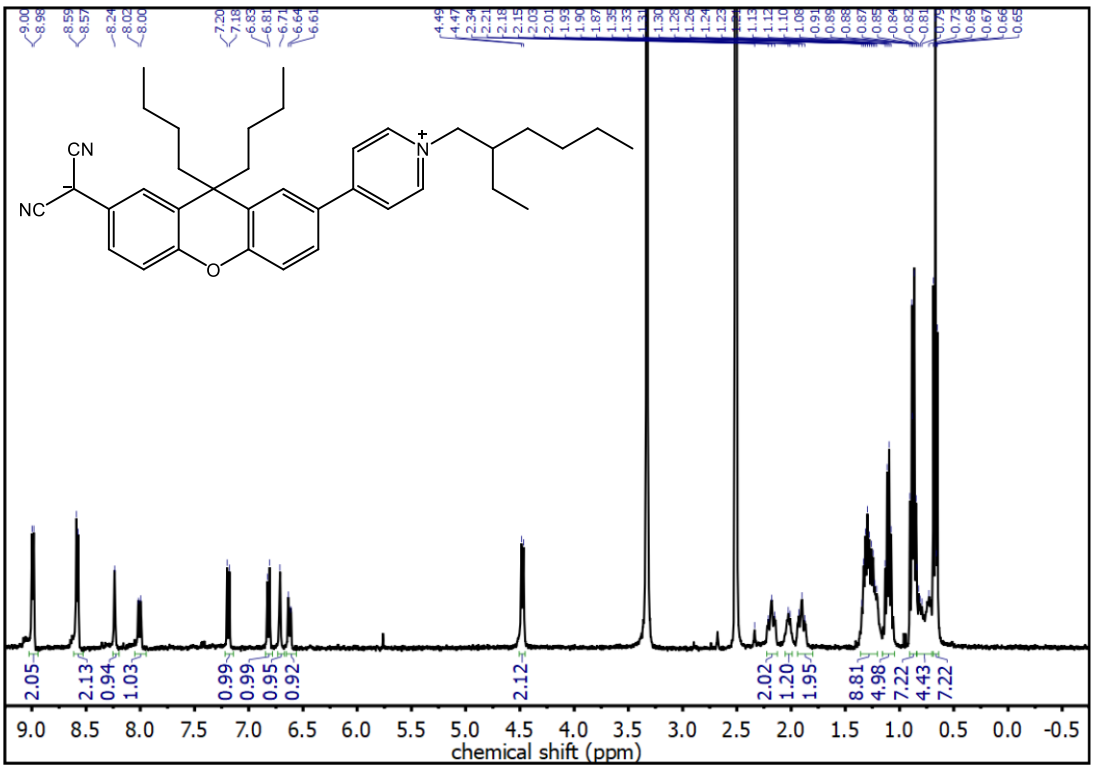


Figure S17. ^{1}H NMR Spectrum of **E1**.

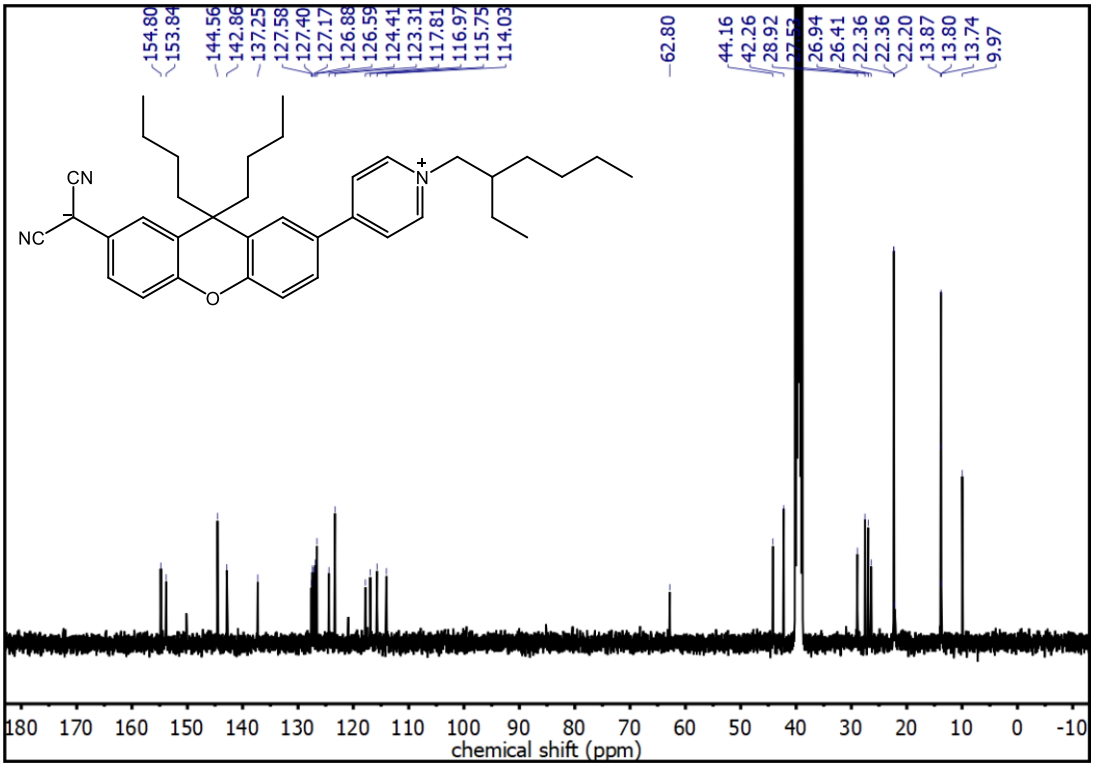


Figure S18. ^{13}C NMR spectrum of **E1**.

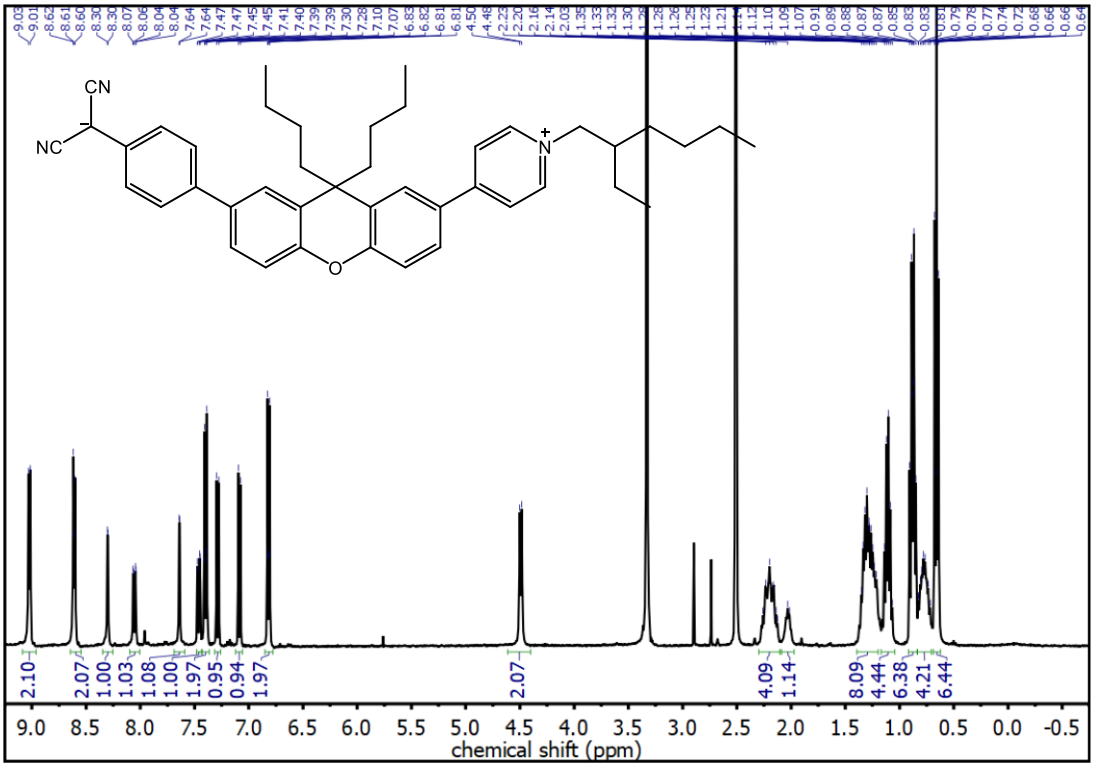


Figure S19. ^{1}H NMR Spectrum of **E2a**.

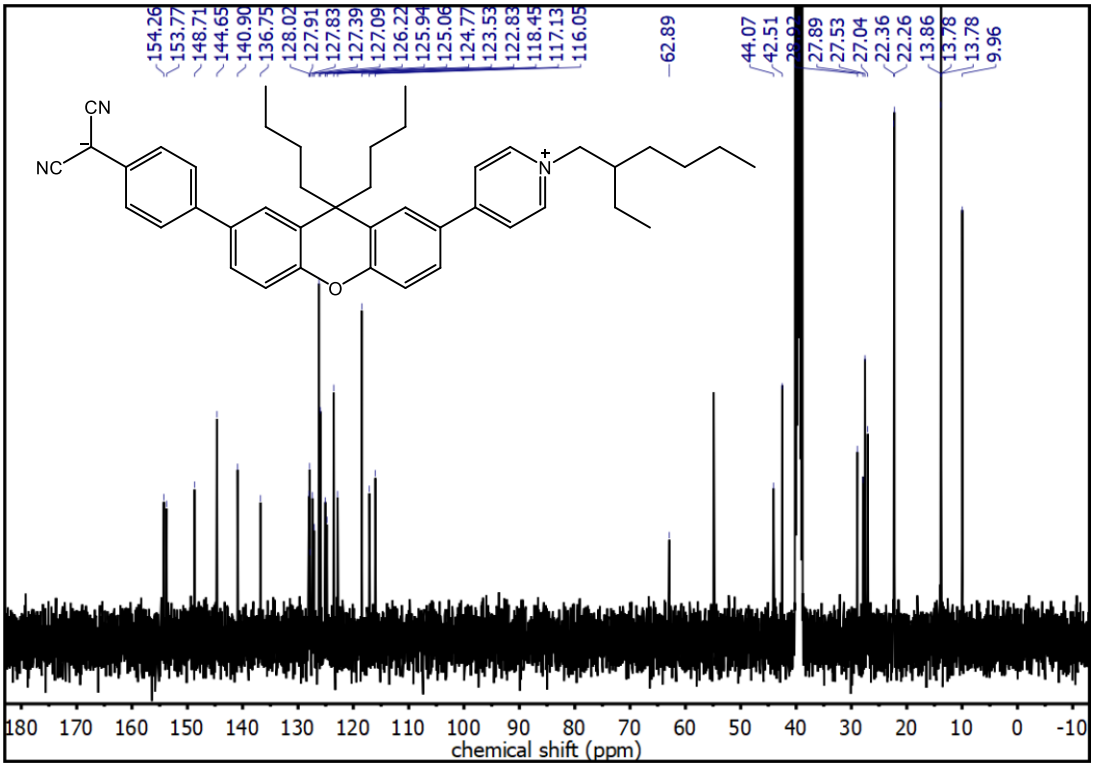


Figure S20. ^{13}C NMR spectrum of **E2a**.

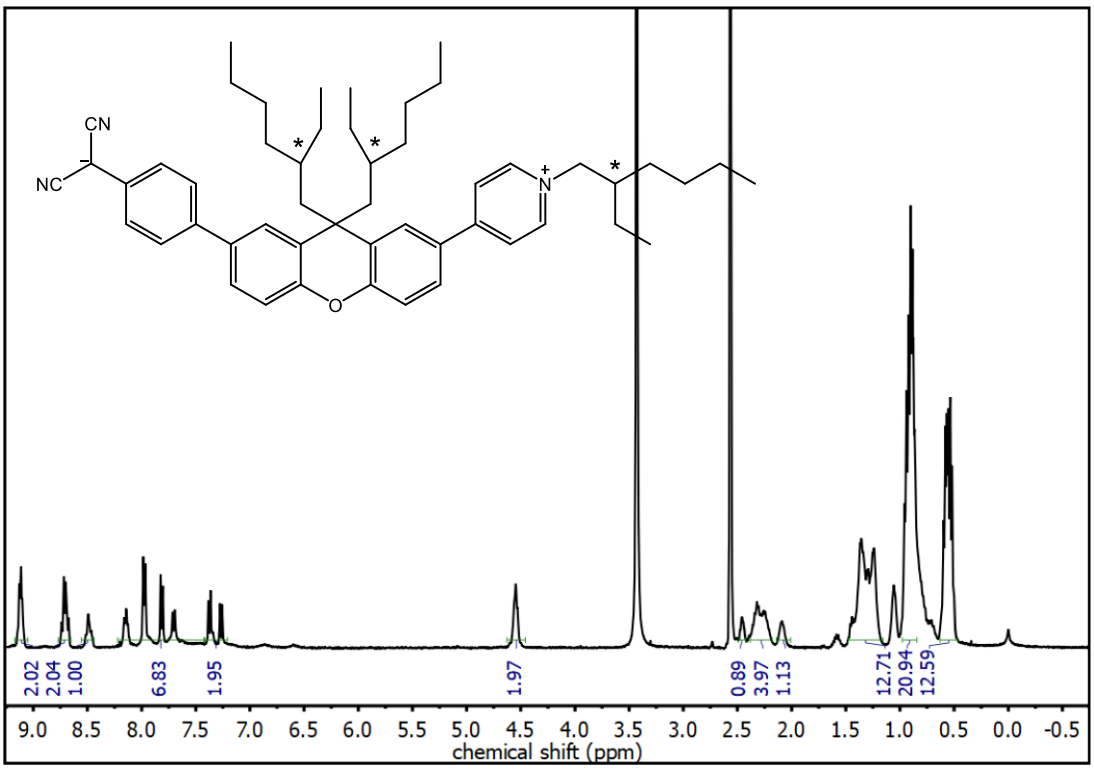


Figure S21. ^{1}H NMR Spectrum of **E2b**.

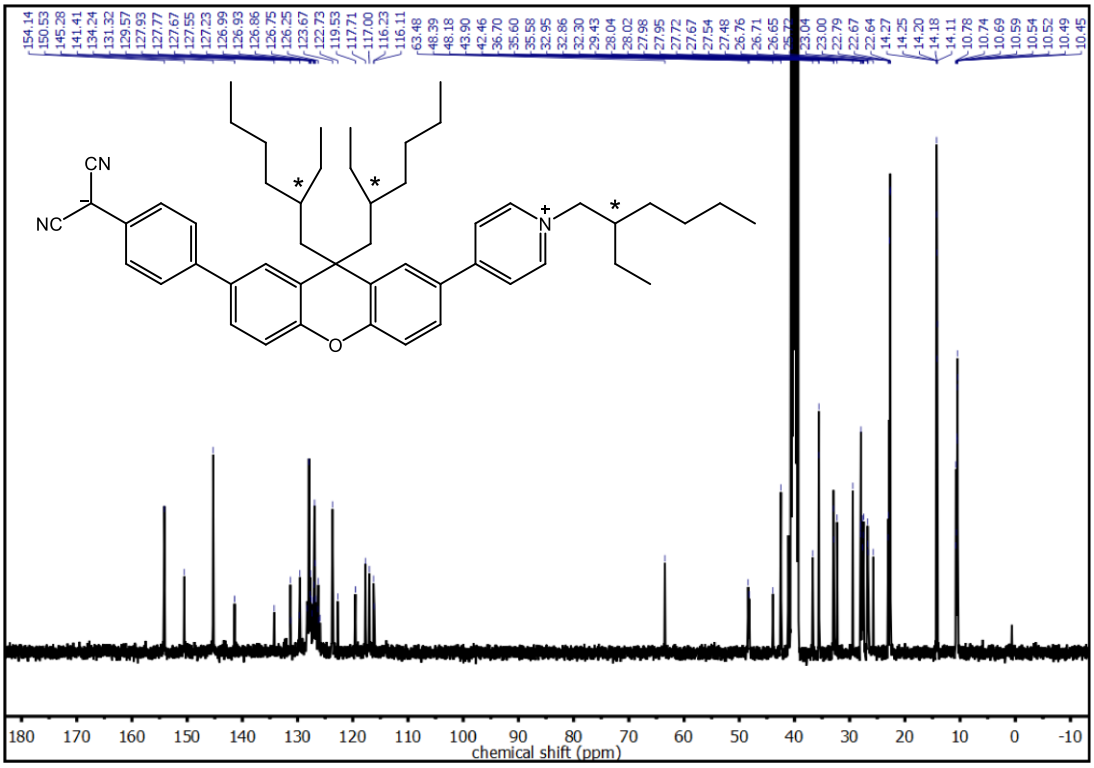


Figure S22. ^{13}C NMR spectrum of **E2b**.

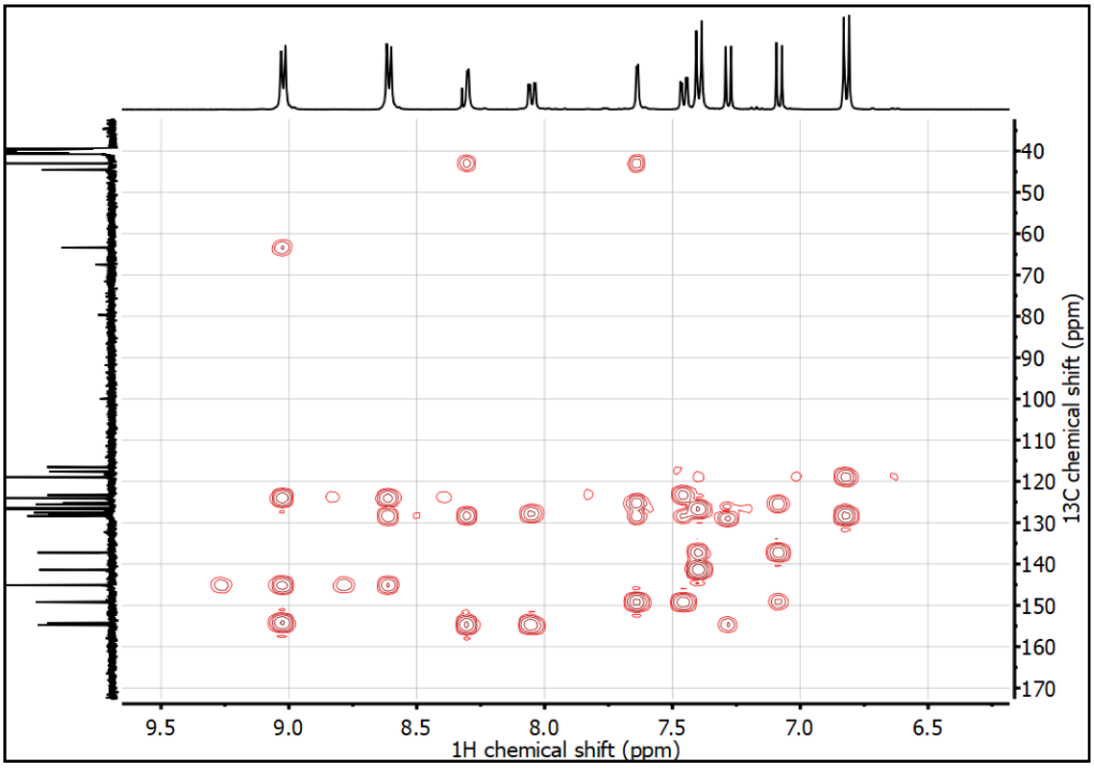


Figure S23. HMBC NMR Spectrum of **E2a**.

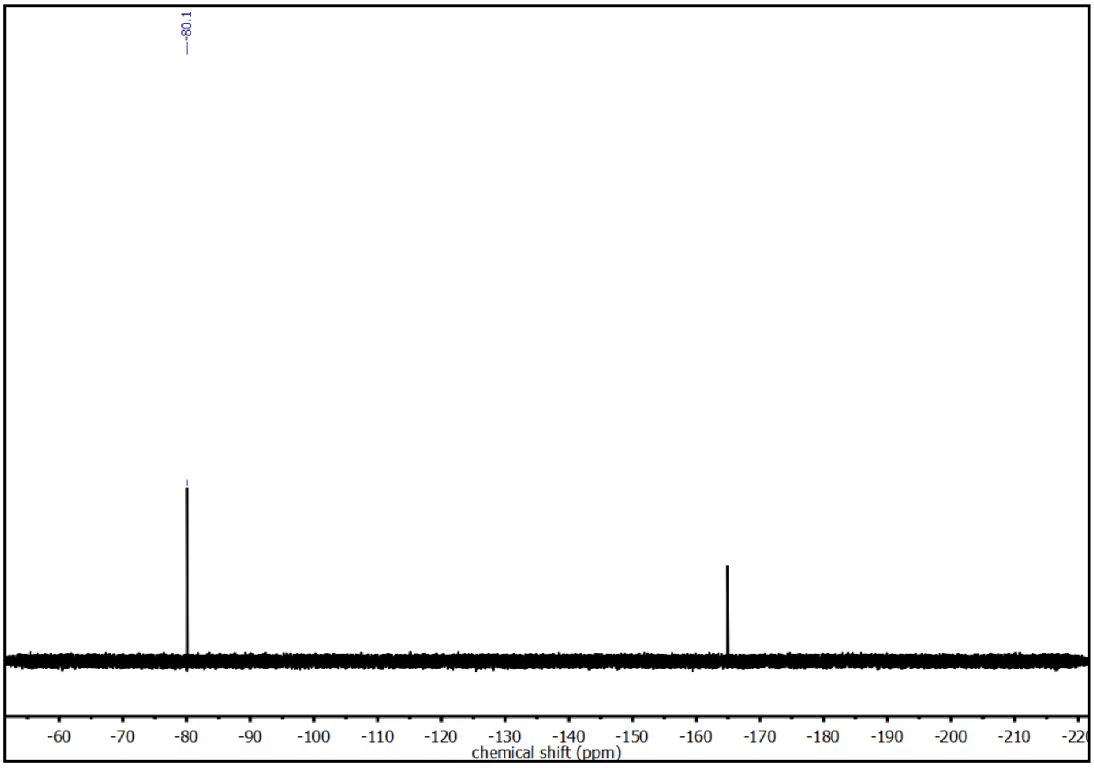


Figure S24. ^{19}F NMR spectrum of **E1**.

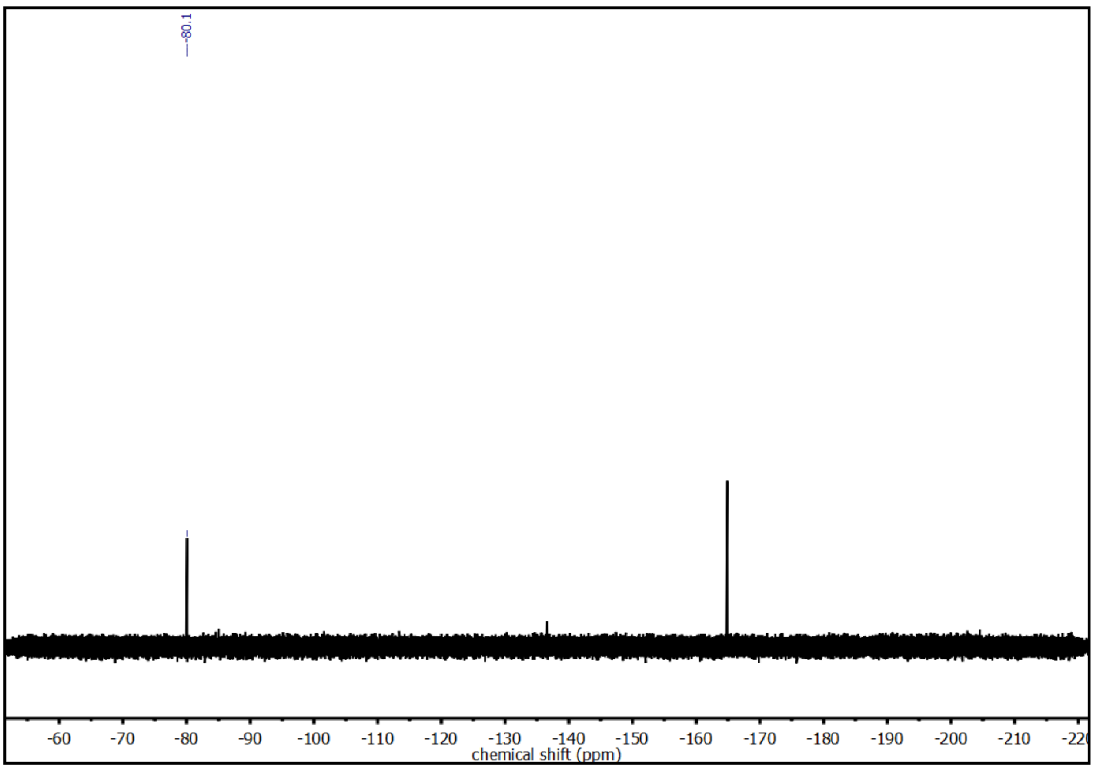


Figure S25. ^{19}F NMR spectrum of **E2a**.

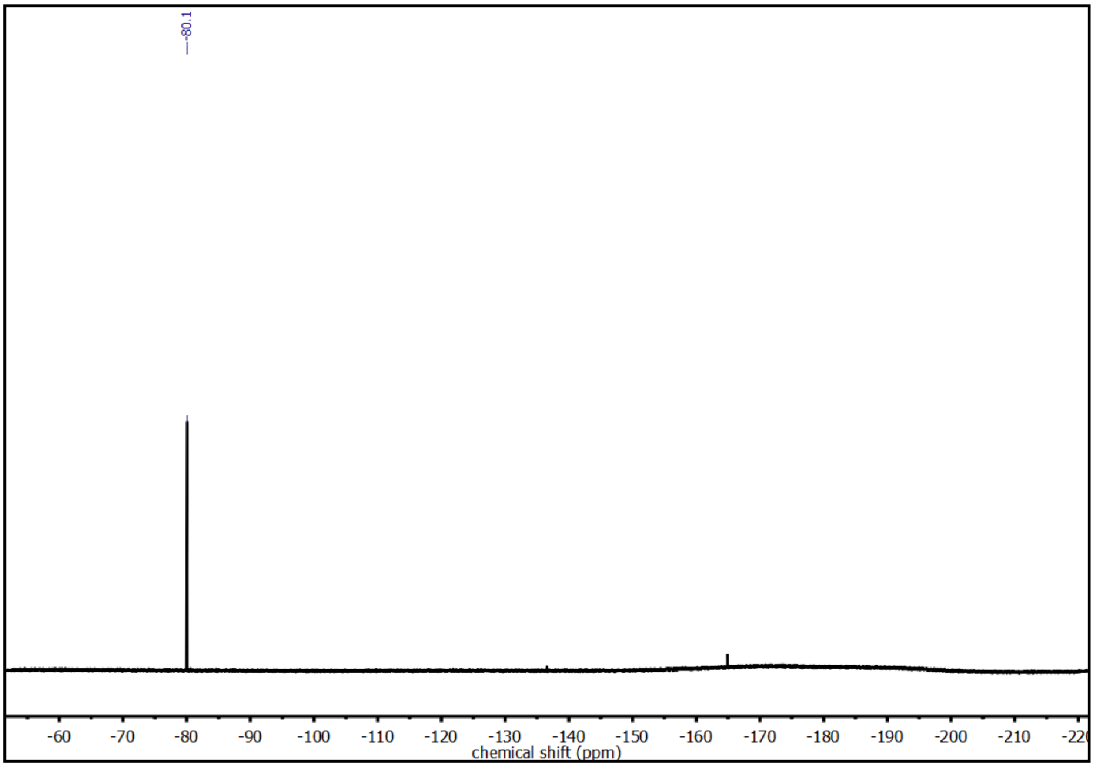


Figure S26. ^{19}F NMR spectrum of **E2b**.

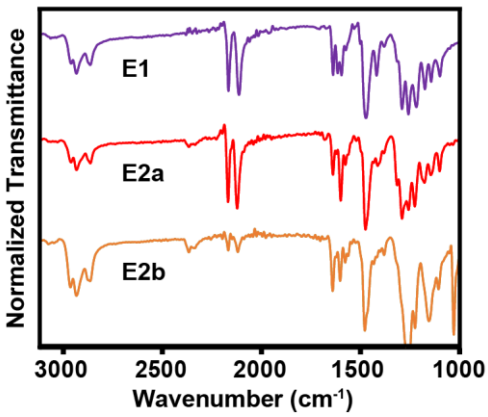


Figure 27. FTIR-ATR of E1 and E2a-b chromophores.

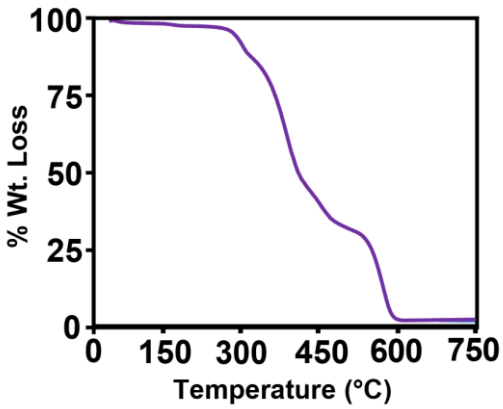


Figure S28. TGA of Chromophore **E1**.

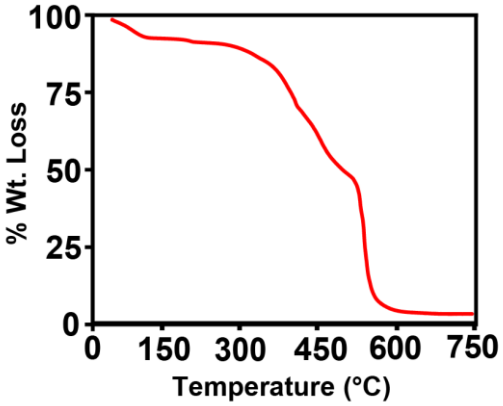


Figure S29. TGA of Chromophore **E2a**.

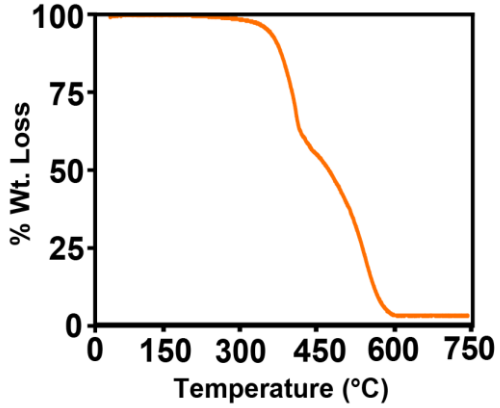


Figure S30. TGA of Chromophore **E2b**.

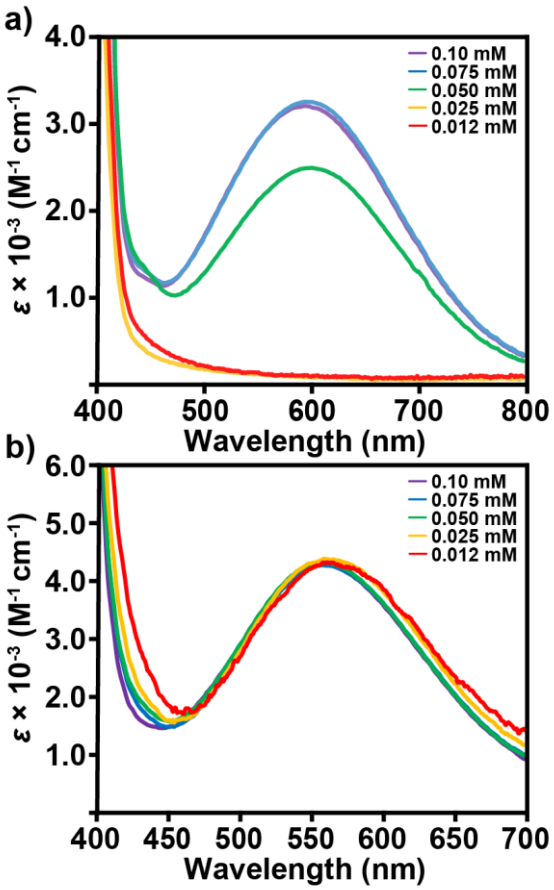


Figure S31. UV-Vis of **E1** in a) CH_2Cl_2 and b) PhCl as a function of concentration.

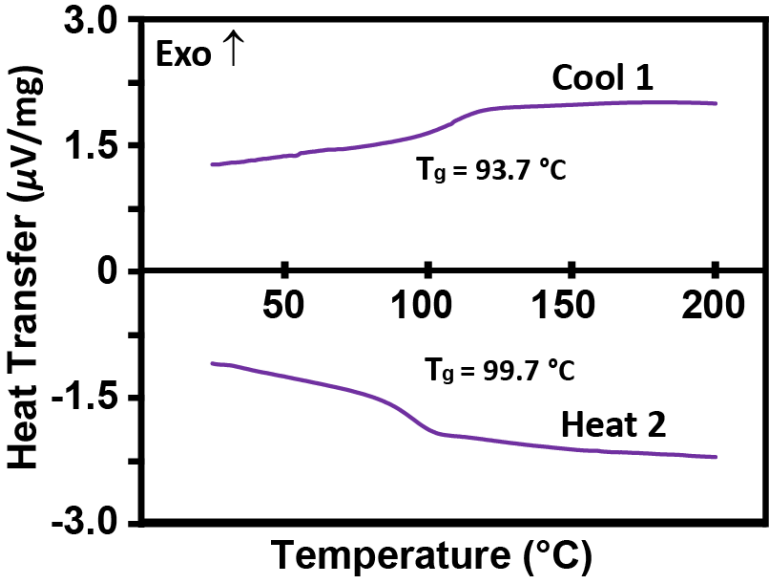


Figure S32. DSC of 5 wt% **E1** in poly(vinyl phenol).

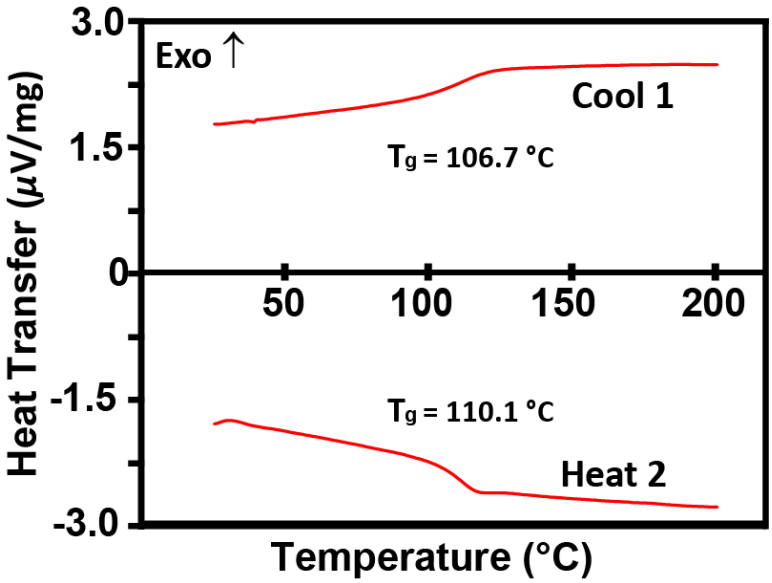


Figure S33. DSC of 5 wt% **E2a** in poly(vinyl phenol)..

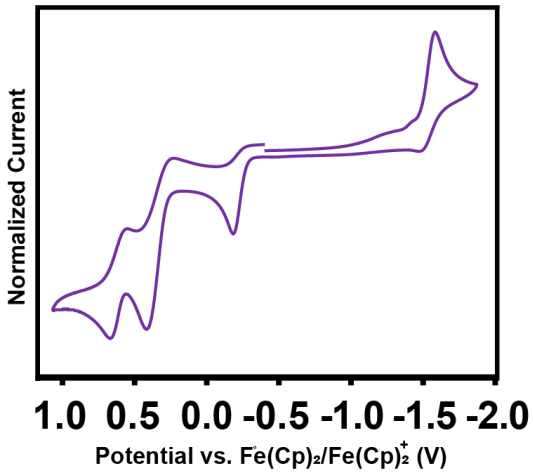


Figure S34. Voltammogram of Chromophore **E1**. Scan rate 100 mV/s and taking $FeCp_2^+$ /$FeCp_2$ taken at 0 V.

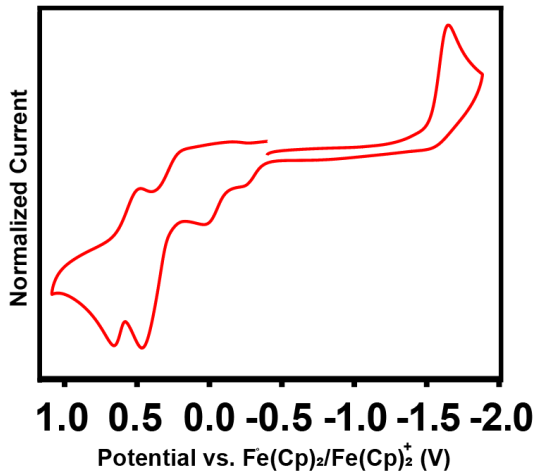


Figure S35. Voltammogram of Chromophore **E2a**. Scan rate 100 mV/s and taking $FeCp_2^+$ /$FeCp_2$ taken at 0 V.

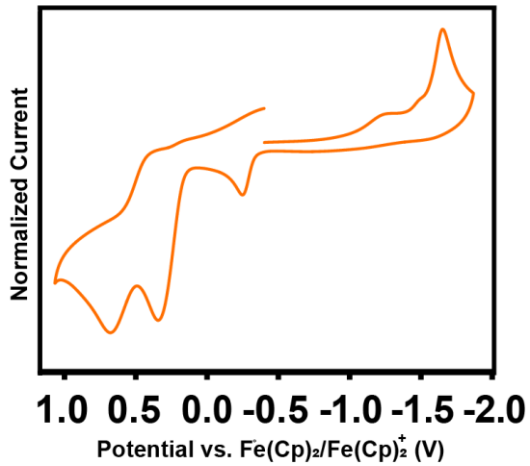


Figure S36. Voltammogram of Chromophore **E2b**. Scan rate 100 mV/s and taking $FeCp_2^+$ /$FeCp_2$ taken at 0 V.

Table S1

TICT Chromophores	$\|\mu\beta$ (x 10^{-48})$\|$	$\|\beta$ (x 10^{-30})$\|$	References
TM-1 (^{t}butl)	-	~70,000[c]	14
TMC-1	24,000 ± 4320[a,16]	518[y]	9, 16
TMC-2	488,000 ± 48,800[a]	-	16
2TTMC	6,000[a]	465[d]	9
4TTMC	-	11,078[d]	9
E1	11,500[g]	59,400[e], 370 ± 10[f]	This work
E2a	79,900[g]	121,000[e], 1,520 ± 50[f]	This work
E2b	86,000[g]	148,000[e]; 1,650 ± 150[f]	This work
Non-TICT			
FTC-1	17,600	635	12
JRD1	-	1,300 ± 50[b]	13
HLD1	-	2,120 ± 50[b]	13
DR1	580[h]	-	12

[a]EFISH CH_2Cl_2 @ 1907 nm; [b]$CHCl_3$ @ 1300 nm; [c]computed (ZINDO); [d]computed (INDO/SCI); [e]computed (M06-2x/D95+*); [f]MeCN @ 900 nm; [g]product of e and f; [h] HRS @ 1900 nm