Supporting Information

Water-soluble BDPA radicals with improved persistence

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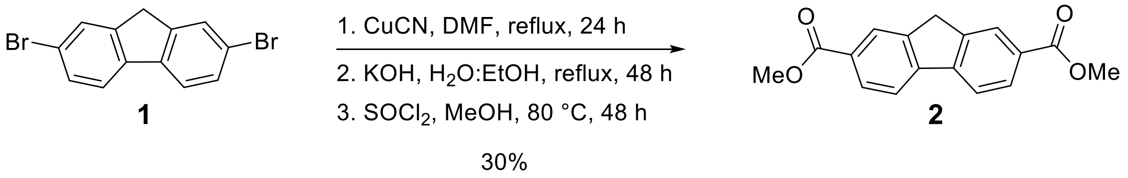
List of abbreviations

BDPA	1,3- Bisdiphenylene-2- phenylallyl
Calcd	Calculated
CMPI	2-Chloro-1-methylpyridinium iodide
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
EPR	Electron paramagnetic resonance
ESI	Electrospray ionization
HPLC	High-performance liquid chromatography
HRMS	High resolution mass spectrometry
NMR	Nuclear magnetic resonance
Pet ether	Petroleum ether
RP	Reverse phase
Satd.	Saturated
TEMPO	2,2,6,6-Tetramethylpiperidine 1-oxyl
TFA	Trifluoroacetic acid
TLC	Thin layer chromatography

Synthetic procedures

General materials and methods

Chemicals were purchased from Sigma-Aldrich Co. or ChemGenes and were used without further purification. All moisture sensitive reactions were carried out in oven-dried glassware under an inert atmosphere of Ar. CH_2Cl_2 was dried over calcium hydride and freshly distilled before use. DMSO and DMF were dried over molecular sieves (3 Å). Thin layer chromatography (TLC) was carried out using glass plates pre-coated with silica gel (Kieselgel 60 F_{254}, 0.2 mm, Silicycle), using UV light for visualization. Silica gel for flash chromatography (230-400 mesh, 60 Å) was purchased from Silicycle. ^{1}H- and ^{13}C-NMR spectra were recorded at the frequencies stated, using deuterated solvents as internal standards on a Bruker Avance 400 spectrometer. Radicals show broadening and loss of NMR signals due to their paramagnetic nature and therefore, those NMR spectra are not shown. Mass spectrometric analyses of all organic compounds were performed on an ESI-HRMS (Bruker, MicrOTOF-Q). EPR spectra were recorded on a MiniScope MS200 with following experimental parameters: 9.43 GHz, microwave power 1 mW, sweep width 12 mT, modulation 0.2 mT, 23 °C. HPLC chromatograms were recorded on a Beckman Coulter Gold HPLC system using a NUCLEODUR C18 Pyramid 4.6 x 150 mm analytical column with UV detection at 254 nm. Solvent gradients for analytical RP-HPLC were run at 1.0 mL/min using the following gradient: solvent A, 0.1% TFA in H_2O; solvent B, CH_3CN; 0-2 min isocratic 0% B, 2-12 min linear gradient 0-100% B, 12-14 min linear gradient 100-0% B, 14-16 min isocratic 0% B.



Dimethyl-9*H*-fluorene-2,7-dicarboxylate (2). To a solution of 2,7-dibromo-9*H*-fluorene (**1**) (6 g, 18.52 mmol) in DMF (50 mL) was added CuCN (3.7 g, 40.74) and the resulting solution heated at 160 °C for 24 h under Ar atmosphere.[1] The reaction mixture was cooled to 60 °C and poured into aq. solution of $FeCl_3.6H_2O$ (11 g, 40.74 mmol) containing HCl (6 mL). The yellow precipitate formed was filtered, washed with H_2O and dried. The precipitate was redissolved in H_2O:EtOH (50:50, 200 mL), KOH (10.4 g, 185.2 mmol) added and the resulting solution refluxed for 48 h. The reaction mixture was cooled to 23 °C, filtered and the filtrate was acidified with HCl (15 mL). The precipitate formed was filtered, washed with H_2O and dried.[1] The precipitate was redissolved in MeOH (50 mL), $SOCl_2$ (1.7 mL, 40.74 mmol) was added drop-wise and the resulting solution heated at 80 °C for 48 h. The reaction mixture was cooled and poured into H_2O (300 mL). The precipitate formed was filtered and purified by flash-column chromatography using a gradient elution (pet ether:EtOAc; 85:15 to 80:20) to give **2** (1.6 g, 30%) as a yellowish solid.

TLC (Silica gel, pet ether:EtOAc, 80:20): R_f (**2**) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (s, 2H), 8.12 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.89 (d, *J* = 8.0 Hz, 2H), 4.01 (s, 2H), 3.96 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 167.26, 145.07, 144.26, 129.49, 128.93, 126.51, 120.57, 52.31, 36.90 ppm.

HRMS (ESI): *m/z* calcd for $C_{17}H_{14}O_4+Na^+$: 305.0784 [*M*+Na]$^+$; found 305.0781.

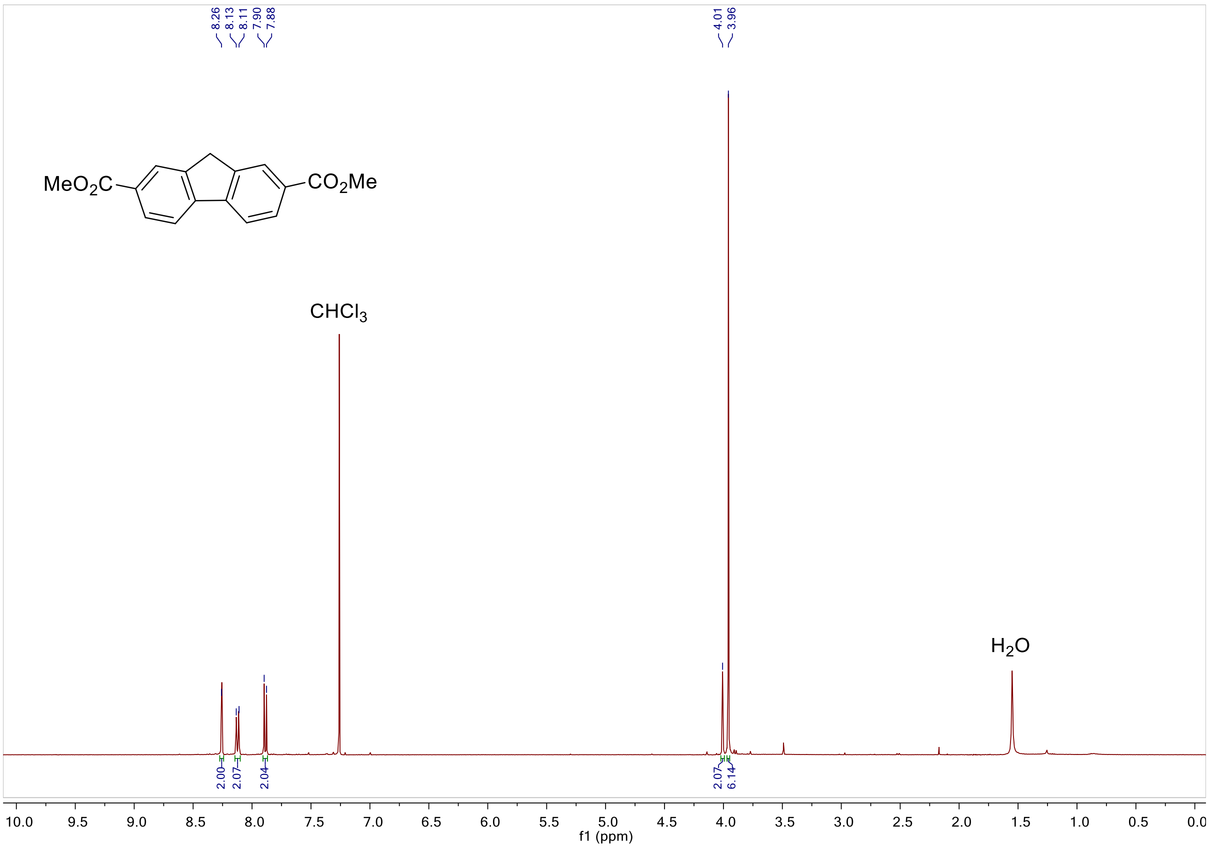


Figure S1. ^{1}H-NMR spectrum of compound **2**.

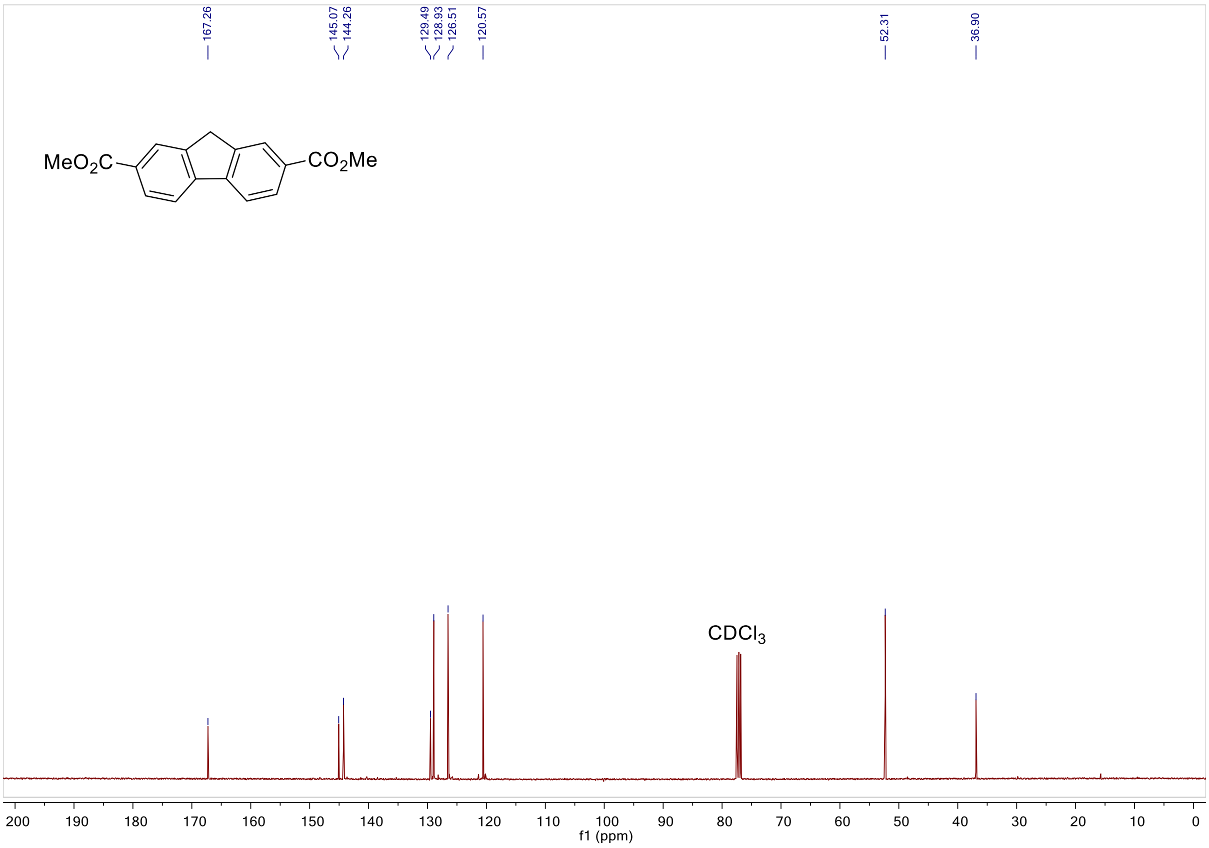
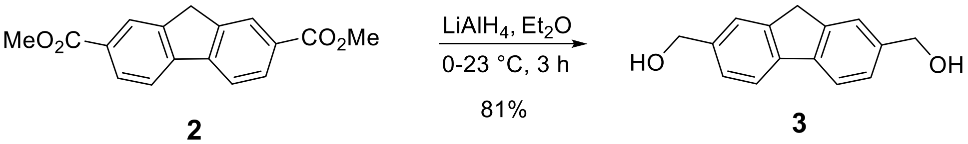


Figure S2. ^{13}C-NMR spectrum of compound **2**.



(9*H*-Fluorene-2,7-diyl)dimethanol (3). To a solution of dimethyl-9*H*-fluorene-2,7-dicarboxylate (**2**) (2.0 g, 7.08 mmol) in Et_2O (50 mL) at 0 °C, $LiAlH_4$ solution (14.2 mL, 14.17 mmol, 1 M in THF) was added and the resulting solution stirred at 23 °C for 3 h. The reaction was quenched by drop-wise addition of EtOH until the effervescence ceased and satd. aq. NH_4Cl (10 mL) added. The mixture was filtered through celite and concentrated *in vacuo*. The crude product was purified by flash-column chromatography using a gradient elution (CH_2Cl_2:MeOH; 97:03 to 95:05) to give **3** (1.3 g, 81%) as a yellowish solid.

TLC (Silica gel, CH_2Cl_2:MeOH; 97:03): R_f (**2**) = 0.9, R_f (**3**) = 0.3

^{1}H NMR (400 MHz, DMSO-d_6): δ 7.80 (d, *J* = 7.8 Hz, 2H), 7.52 (s, 2H), 7.31 (d, *J* = 7.6 Hz, 2H), 5.18 (t, *J* = 5.7 Hz, 2H), 4.56 (d, *J* = 5.7 Hz, 4H), 3.88 (s, 2H) ppm.

^{13}C NMR (101 MHz, DMSO-d_6): δ 143.03, 141.07, 139.75, 125.21, 123.37, 119.39, 63.17, 36.27 ppm.

HRMS (ESI): *m/z* calcd for $C_{15}H_{14}O_2$+Na^+: 249.0886 [*M*+Na]$^+$; found 249.0885.

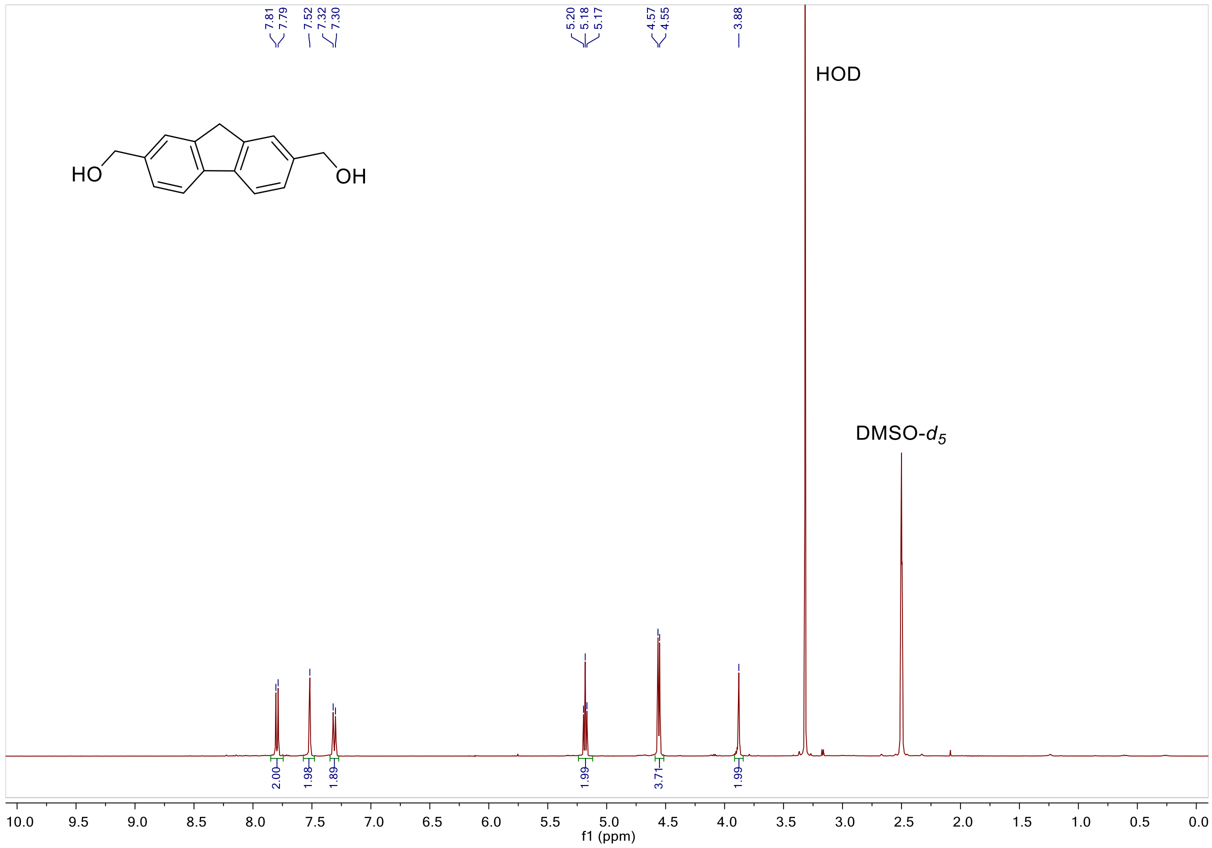


Figure S3. ^{1}H-NMR spectrum of compound **3**.

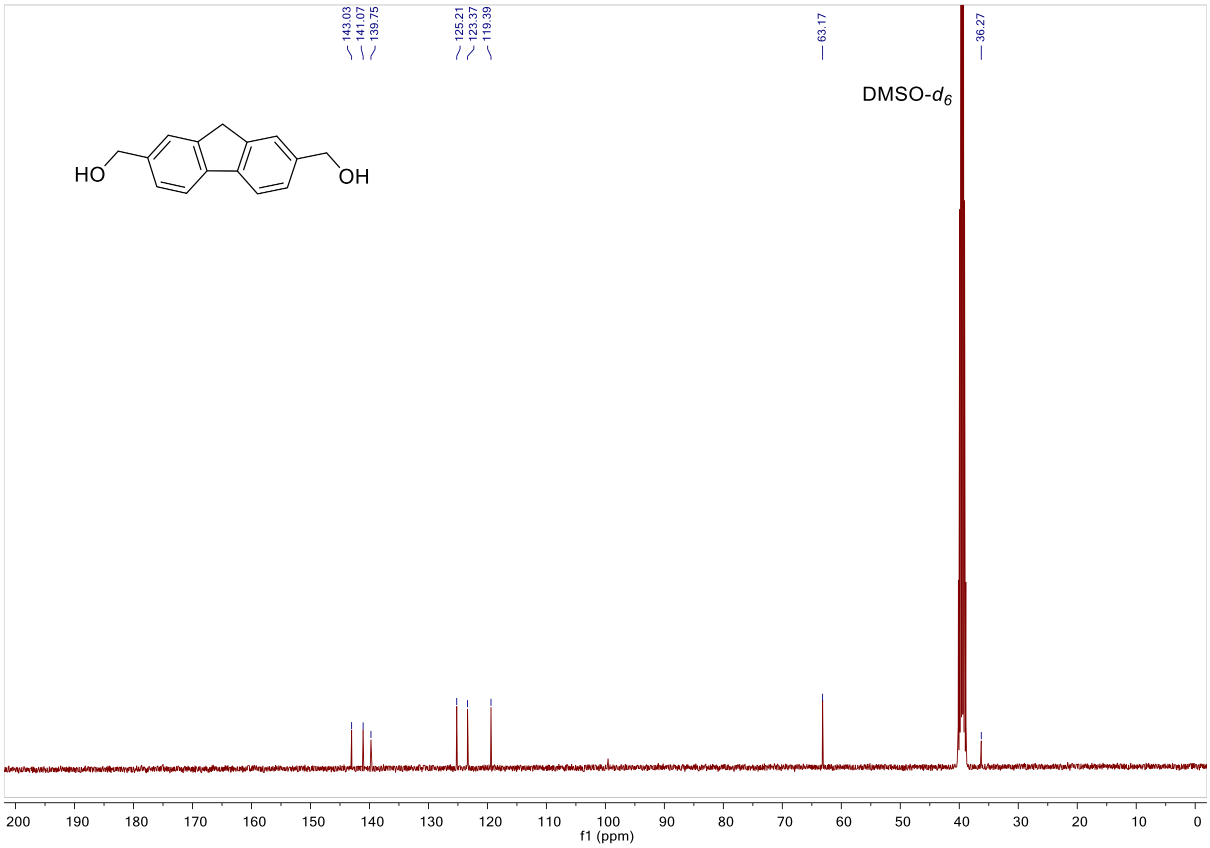
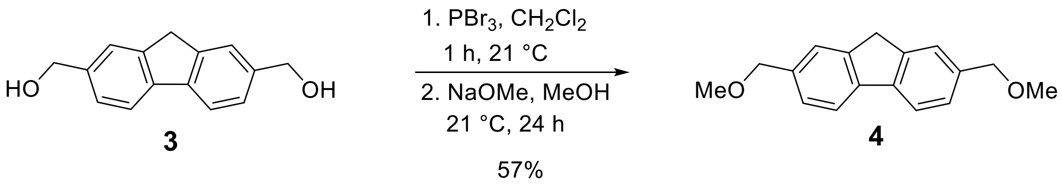


Figure S4. ^{13}C-NMR spectrum of compound **3**.



2,7-Bis(methoxymethyl)-9*H*-fluorene (4). To a solution of (9*H*-fluorene-2,7-diyl)dimethanol (**3**) (1.32 g, 5.83 mmol) in CH_2Cl_2 (50 mL), PBr_3 (0.6 mL, 5.83 mmol) was added and the resulting solution stirred at 21 °C for 1 h. The solvent was removed *in vacuo* and the residue treated with a freshly made NaOMe solution, prepared by slowly dissolving Na metal (1.34 g, 58.30 mmol) in MeOH (50 mL). The resulting mixture was stirred at 21 °C for 24 h and extracted with EtOAc (3 x 50 mL). The combined organic layers were washed with brine (2 x 100 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by flash-column chromatography using a gradient elution (pet ether:EtOAc; 90:10 to 85:15) to give **4** (0.85 g, 57%) as a white solid.

TLC (Silica gel, pet ether:EtOAc; 70:30): R_f (**3**) = 0.1, R_f (**4**) = 0.6

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 7.8 Hz, 2H), 7.53 (s, 2H), 7.34 (d, *J* = 7.8, 2H), 4.53 (s, 4H), 3.89 (s, 2H), 3.42 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 143.85, 141.23, 136.93, 126.75, 124.74, 119.88, 75.14, 58.26, 36.90 ppm.

HRMS (ESI): *m/z* calcd for $C_{17}H_{18}O_2$+Na^+: 277.1199 [*M*+Na]$^+$; found 277.1191.

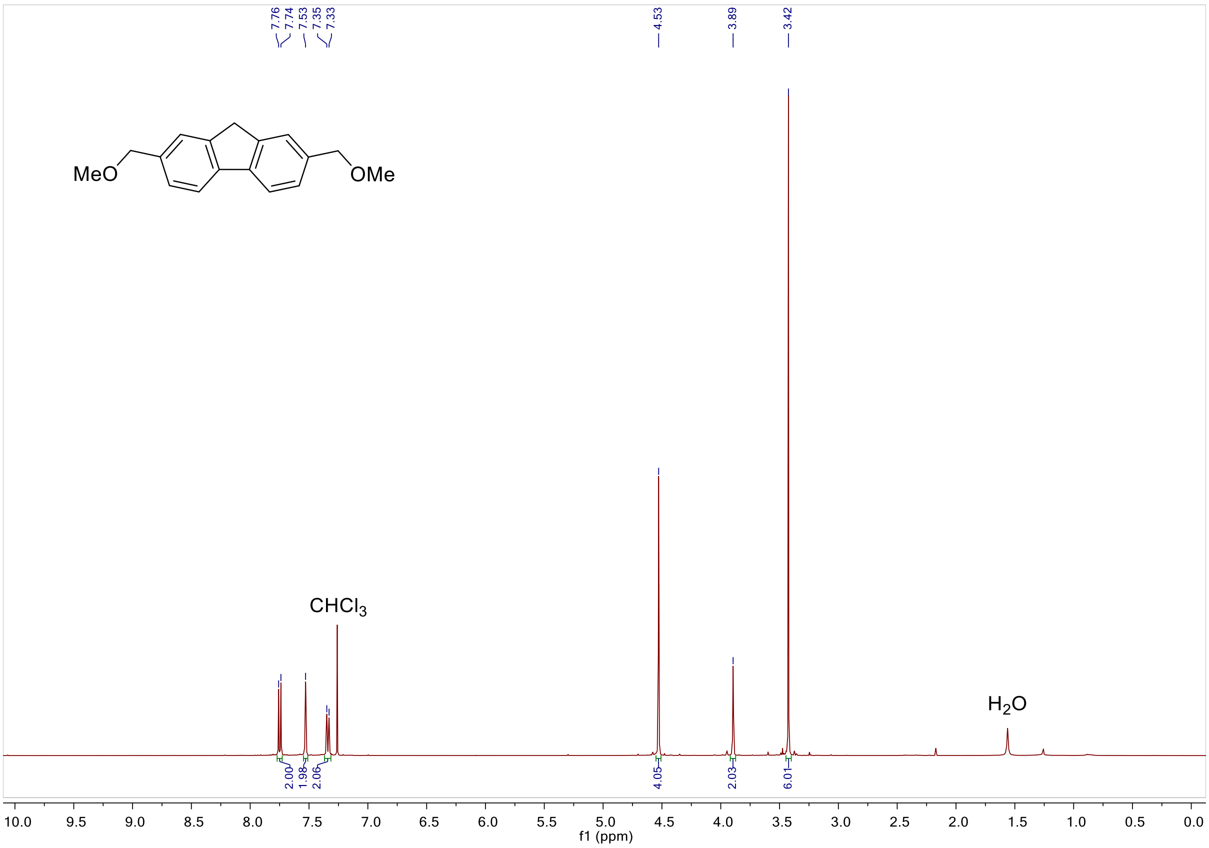


Figure S5. ^{1}H-NMR spectrum of compound **4**.

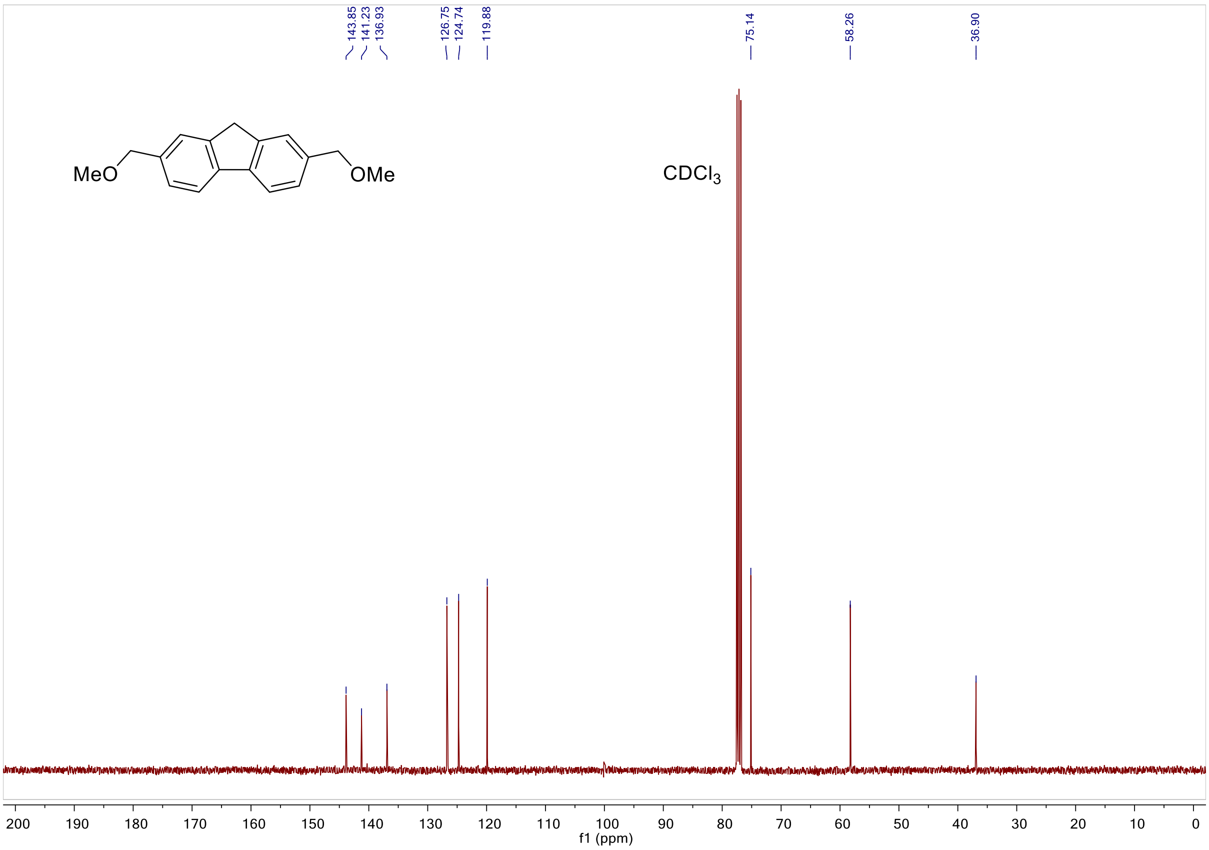
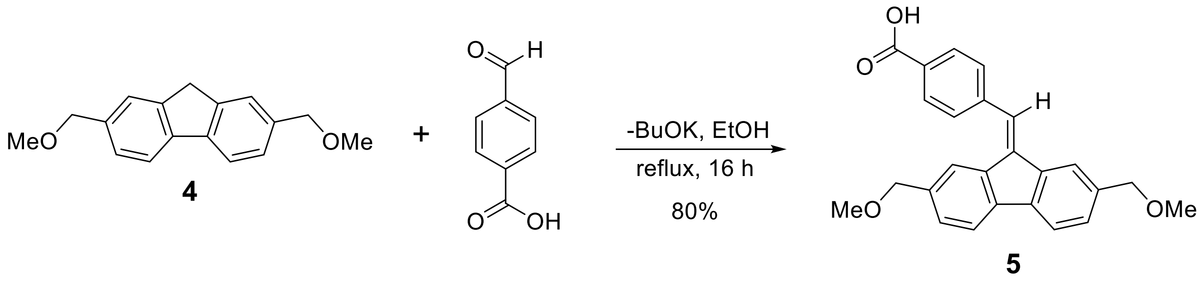


Figure S6. ^{13}C-NMR spectrum of compound **4**.



Compound 5. To a solution of 2,7-bis(methoxymethyl)-9*H*-fluorene (**4**) (400 mg, 7.08 mmol) in EtOH (25 mL), 4-formylbenzoic acid (354 mg, 2.36 mmol) and *t*-BuOK (528 mg, 4.71 mmol) were added and the resulting solution refluxed for 16 h. The solution was cooled, acidified with aq. HCl (1 M, 25 mL) and extracted with EtOAc (3 x 30 mL). The combined organic layers were washed with brine (3 x 50 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by flash-column chromatography using a gradient elution (CH_2Cl_2:MeOH; 100:0 to 97:03) to give **5** (490 mg, 80%) as a yellow solid.

TLC (Silica gel, CH_2Cl_2:MeOH; 97:03): R_f (**4**) = 0.9, R_f (**5**) = 0.3

^{1}H NMR (400 MHz, DMSO-d_6): δ 8.06 (d, *J* = 8.3 Hz, 2H), 7.95 (s, 1H), 7.93 (s, 1H), 7.84 (d, *J* = 5.0 Hz, 1H), 7.82 (d, *J* = 4.9 Hz, 1H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.46 (s, 1H), 7.37 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.31 (dd, *J* = 7.8, 1.4 Hz, 1H), 4.51 (s, 2H), 4.28 (s, 2H), 3.34 (s, 3H), 3.20 (s, 3H) ppm.

^{13}C NMR (101 MHz, DMSO-d_6): δ 167.04, 140.62, 140.05, 139.11, 137.73, 137.53, 137.06, 136.22, 135.76, 130.70, 129.50, 129.36, 128.54, 128.27, 127.44, 122.93, 120.33, 120.03, 119.66, 73.84, 73.53, 57.49, 57.33 ppm.

HRMS (ESI): *m/z* calcd for $C_{25}H_{21}O_4$-H$^-$: 385.1445 [*M*-H]$^-$; found 385.1447.

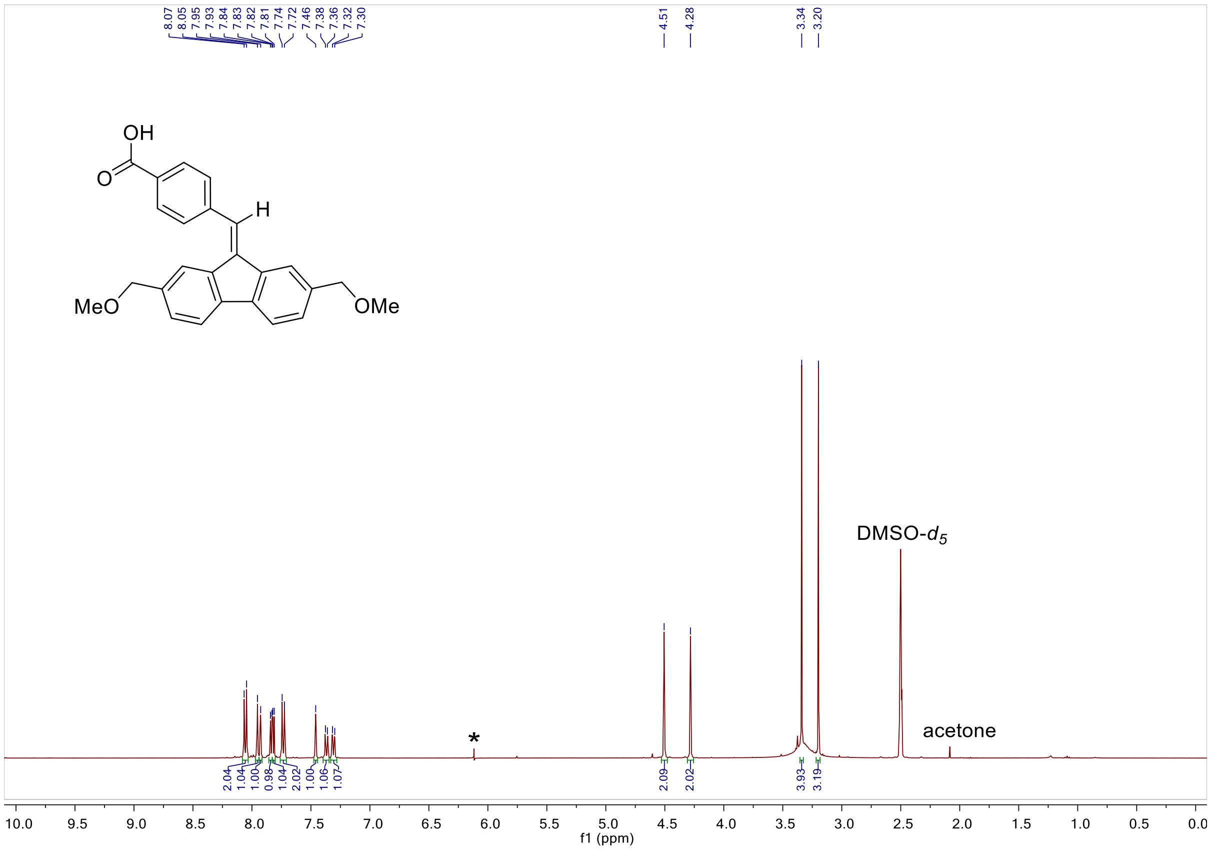


Figure S7. ^{1}H-NMR spectrum of compound **5**. The asterisk indicates an instrumental glitch.

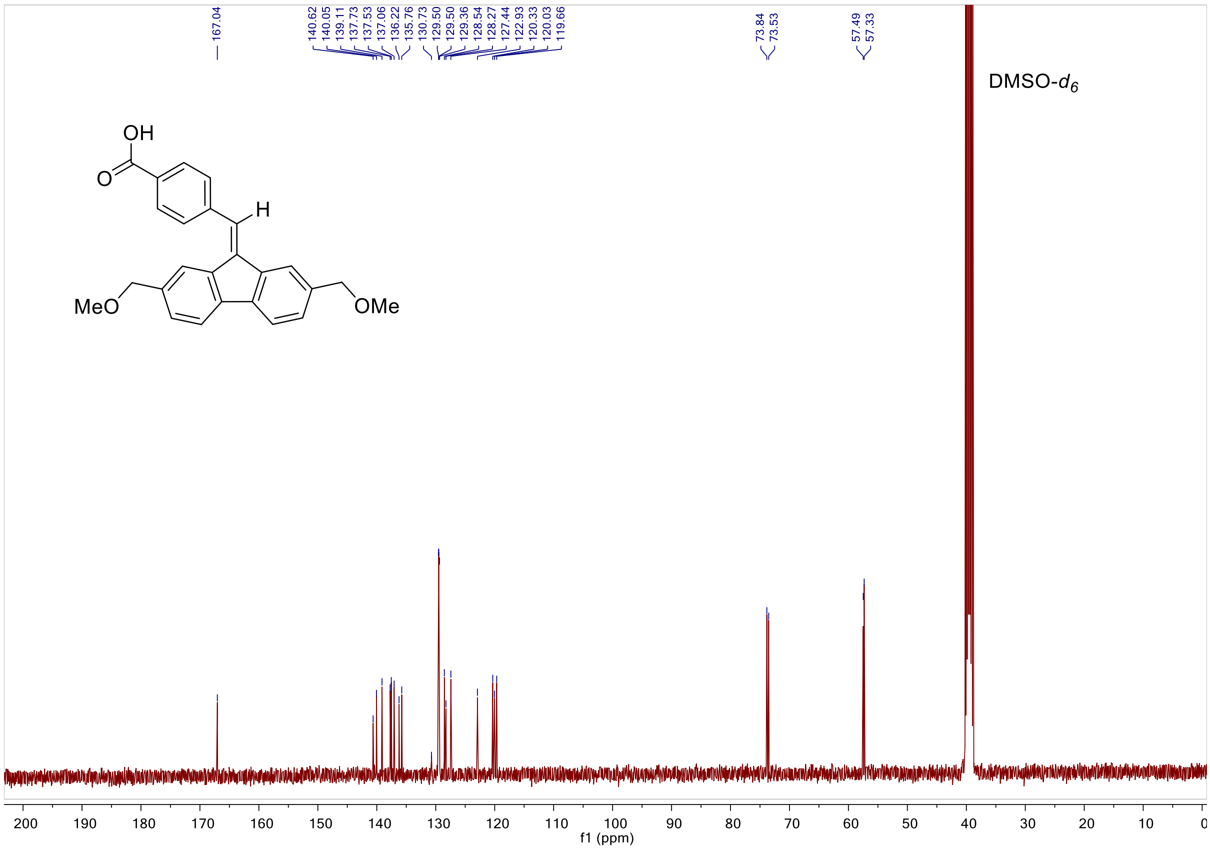
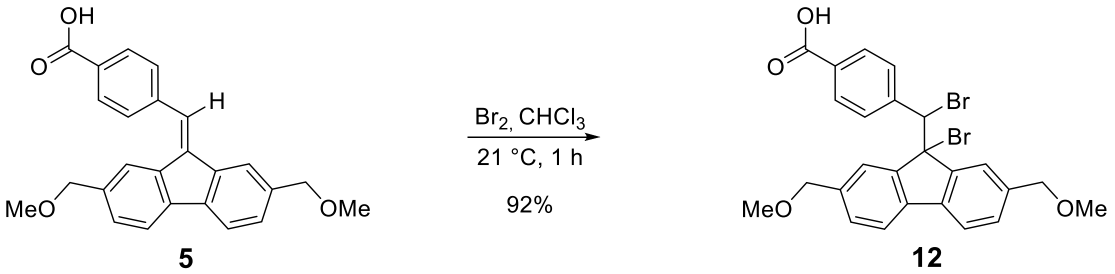


Figure S8. ^{13}C-NMR spectrum of compound **5**.



Compound 12. To a solution of compound **5** (500 mg, 1.29 mmol) in $CHCl_3$ (5 mL), Br_2 (66 μL, 1.29 mmol) was added and the resulting solution was stirred at 21 °C for 1 h. Satd. aq. $Na_2S_2O_3$ (10 mL) was added and the mixture extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were washed with brine (2 x 30 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by flash-column chromatography using a gradient elution (CH_2Cl_2:MeOH; 100:0 to 97:03) to give **12** (645 mg, 92%) as a yellow solid.

TLC (Silica gel, CH_2Cl_2:MeOH; 97:03): R_f (**5**) = 0.3, R_f (**12**) = 0.3

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (s, 1H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.53 (s, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.42 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.38 (d, *J* = 7.7 Hz, 1H), 7.22 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.01 (d, *J* = 8.1 Hz, 2H), 5.81 (s, 1H), 4.60 (d, *J* = 2.5 Hz, 2H), 4.56 – 4.42 (m, 2H), 3.48 (s, 3H), 3.41 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.56, 145.34, 145.02, 142.12, 138.78, 138.36, 138.29, 138.24, 129.63, 129.54, 129.26, 129.11, 129.09, 125.89, 125.08, 120.07, 74.57, 74.34, 65.15, 61.05, 58.22, 58.10 ppm.

HRMS (ESI): *m/z* calcd for $C_{25}H_{21}Br_2O_4$-H^-: 542.9812 [*M*-H]$^-$; found 542.9834.

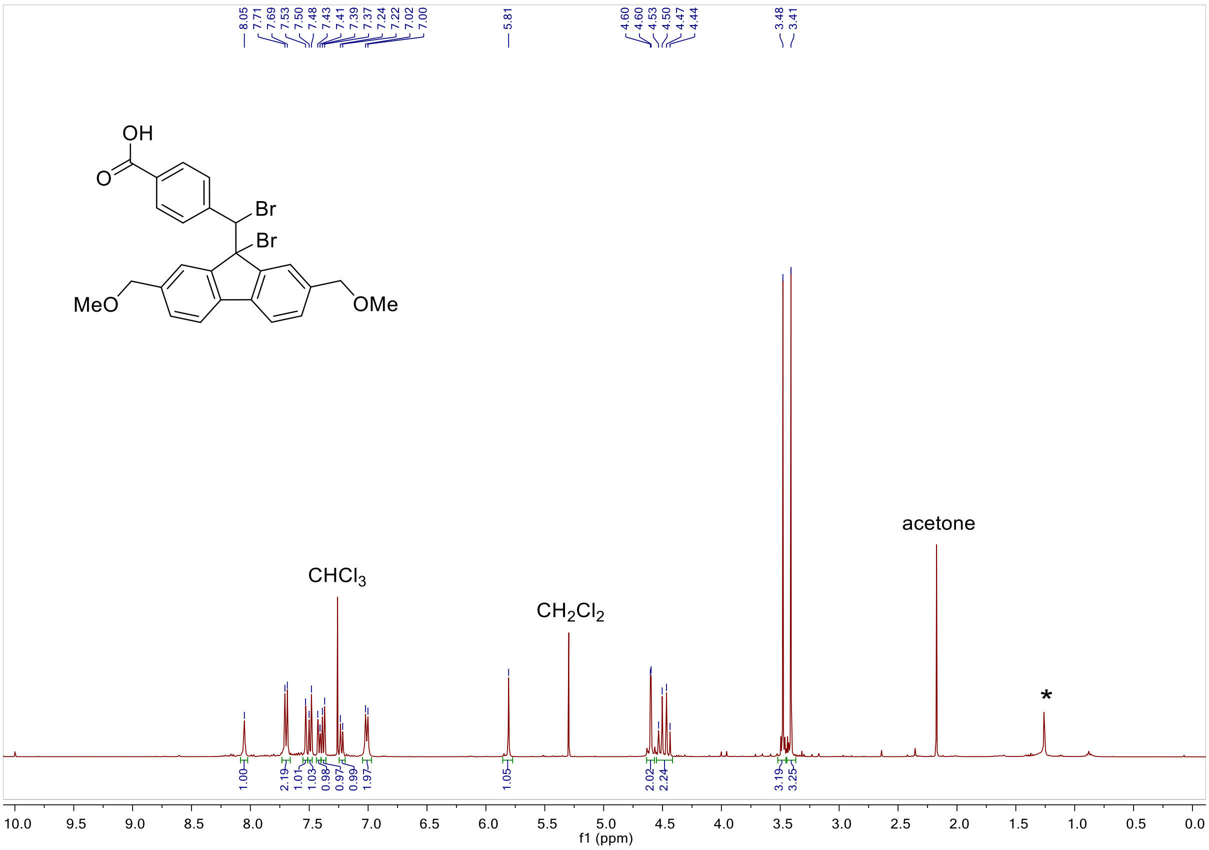


Figure S9. ^{1}H-NMR spectrum of compound **12**. The asterisk indicates an impurity from a preparatory TLC.

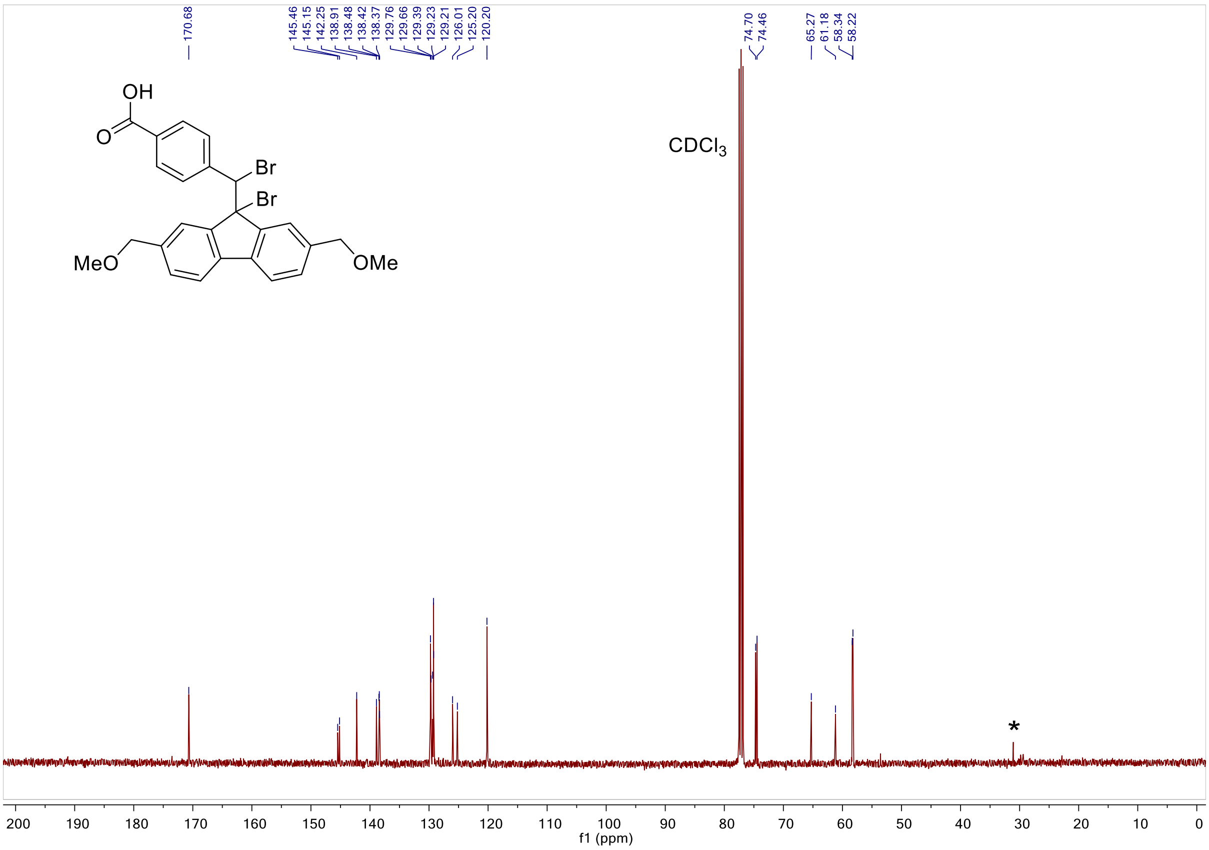
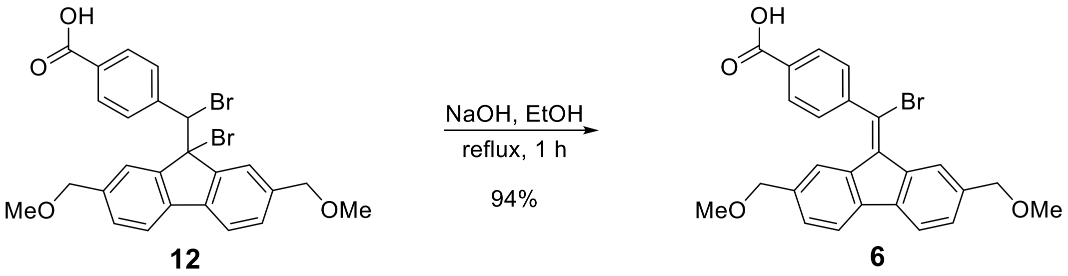


Figure S10. ^{13}C-NMR spectrum of compound **12**. The asterisk indicates an impurity from a preparatory TLC.



Compound 6. To a solution of compound **12** (645 mg, 1.18 mmol) in EtOH (30 mL), NaOH (189 mg, 4.72 mmol) was added and the resulting solution refluxed for 1 h. The solution was cooled to 23 °C, acidified with aq. HCl (1 N, 50 mL) and extracted with EtOAc (3 x 50 mL). The combined organic layers were washed with brine (2 x 100 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by flash-column chromatography using a gradient elution (CH_2Cl_2:MeOH; 100:0 to 97:03) to give **6** (520 mg, 94%) as an orange solid.

TLC (Silica gel, CH_2Cl_2:MeOH; 97:03): R_f (**12**) = 0.3, R_f (**6**) = 0.3

^{1}H NMR (400 MHz, DMSO-d_6): δ 8.73 (s, 1H), 8.13 (d, *J* = 8.4 Hz, 2H), 7.88 (d, *J* = 7.7 Hz, 1H), 7.79 (d, *J* = 7.7 Hz, 1H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.47 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.19 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.00 (s, 1H), 4.54 (s, 2H), 4.06 (s, 2H), 3.35 (s, 3H), 3.02 (s, 3H) ppm.

^{13}C NMR (101 MHz, DMSO-d_6): δ 166.68, 145.93, 139.95, 138.33, 137.59, 137.33, 137.23, 137.14, 135.39, 131.50, 130.44, 129.25, 128.54, 127.83, 124.76, 123.15, 123.10, 119.98, 119.71, 73.92, 73.19, 57.55, 57.30 ppm.

HRMS (ESI): *m/z* calcd for $C_{25}H_{21}BrO_4$-H^-: 463.0550 [*M*-H]$^-$; found 463.0541.

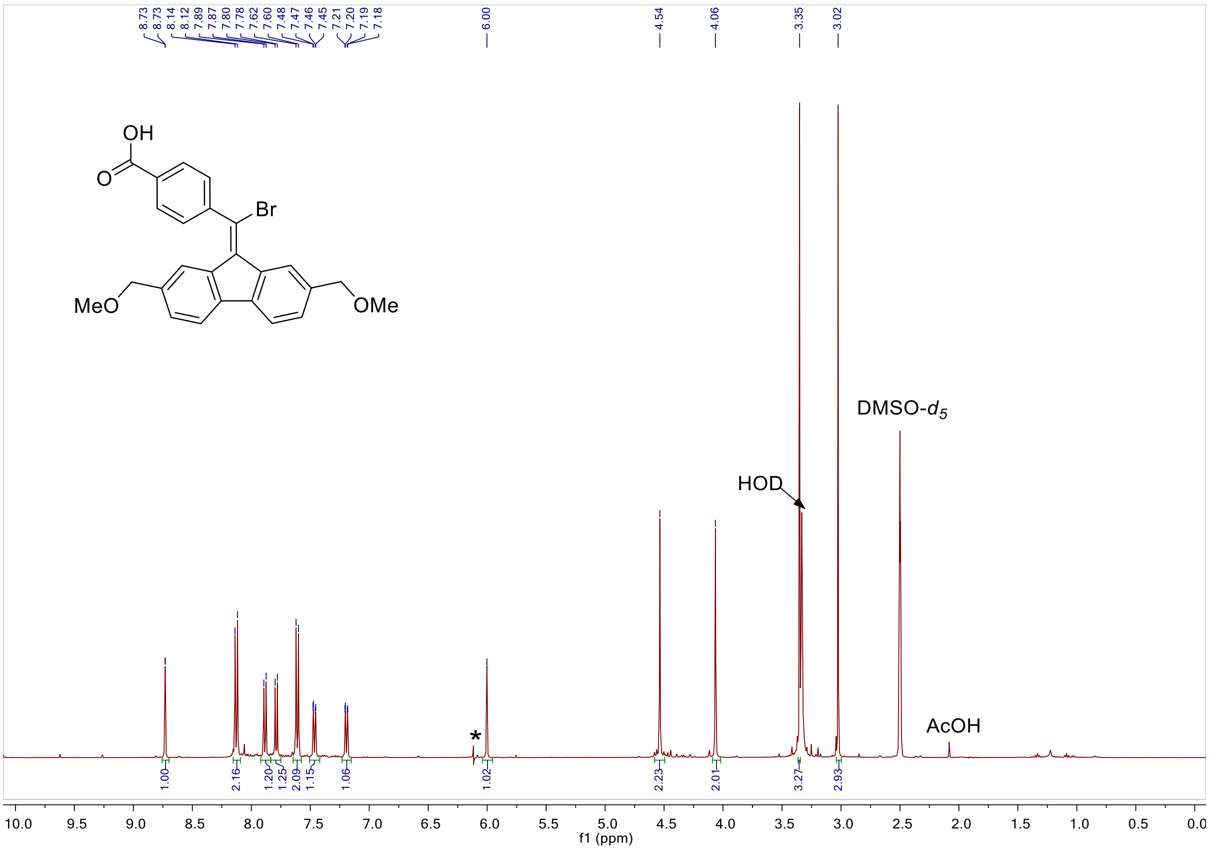


Figure S11. ^{1}H-NMR spectrum of compound **6**. The asterisk indicates an instrumental glitch.

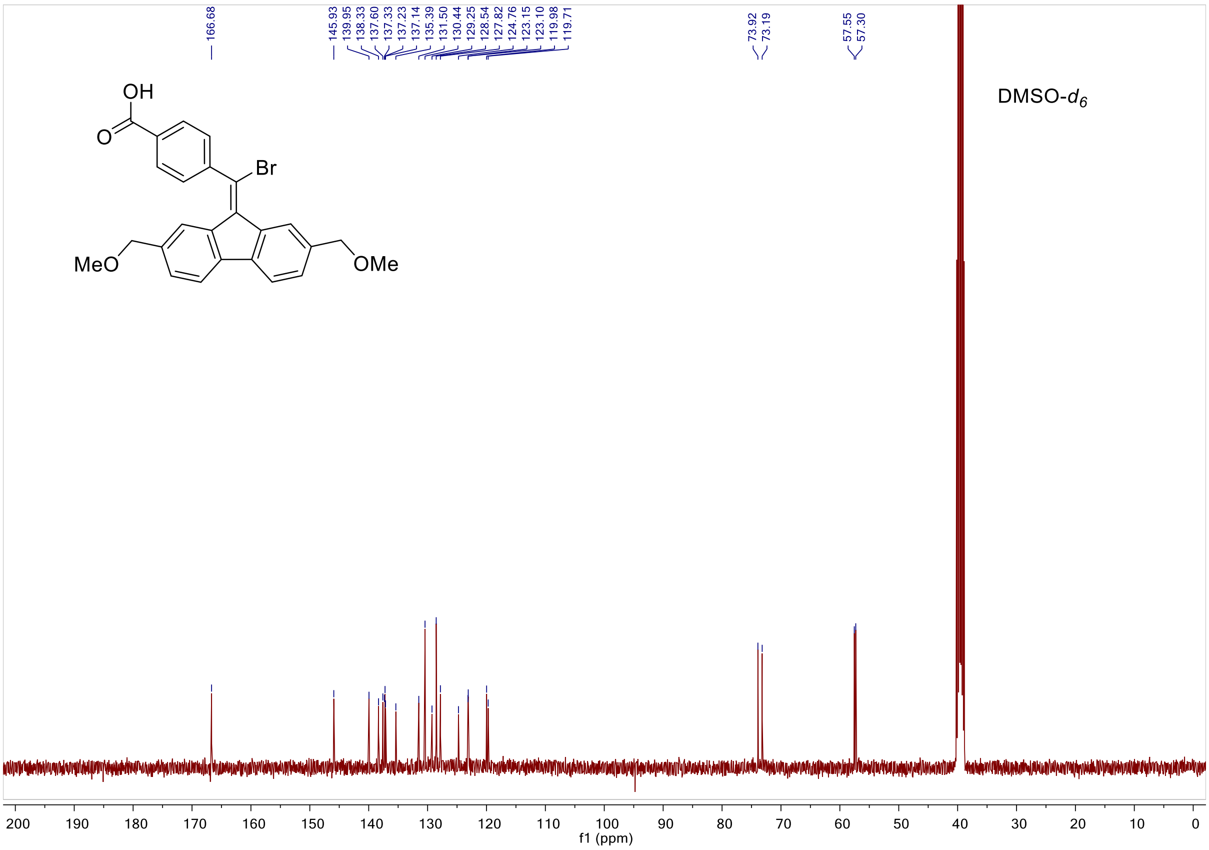
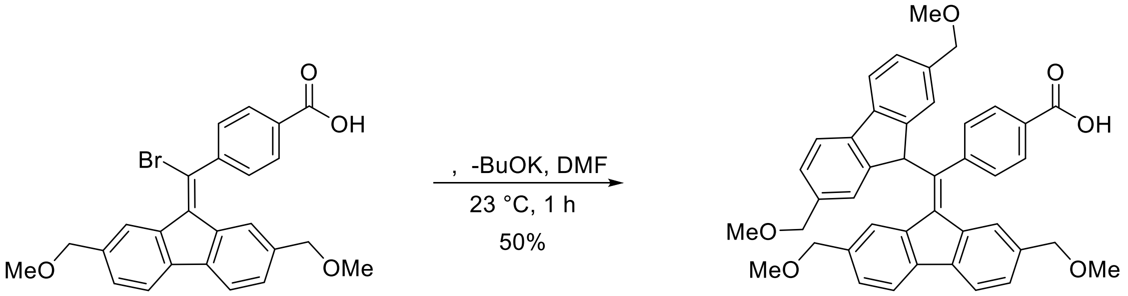


Figure S12. ^{13}C-NMR spectrum of compound **6**.



6 → **13**

Tetra-(methoxymethyl)-BDPA 13. Compound **6** (1.4 g, 3.01 mmol), 2,7-bis(methoxymethyl)-9*H*-fluorene (**4**) (918 mg, 3.61 mmol) and *t*-BuOK (1.69 g, 15.04 mmol) were weighed into a round-bottom flask and DMF (50 mL) was added. The resulting solution was stirred at 23 °C for 1 h, acidified with aq. HCl (1 N, 100 mL) and extracted with EtOAc (3 x 100 mL). The combined organic layers were washed with brine (2 x 200 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by flash-column chromatography using a gradient elution (CH_2Cl_2:MeOH; 100:0 to 98:02) to give **13** (960 mg, 50%) as a yellow solid.

TLC (Silica gel, CH_2Cl_2:MeOH; 97:03): R_f (**6**) = 0.3, R_f (**13**) = 0.35

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (s, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.75 – 7.66 (m, 3H), 7.61 (d, *J* = 7.8 Hz, 2H), 7.57 (s, 2H), 7.48 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.32 (dd, *J* = 7.9, 1.4 Hz, 2H), 7.20 (dd, *J* = 7.7, 1.4 Hz, 1H), 6.77 (d, *J* = 8.4 Hz, 2H), 6.51 (s, 1H), 5.76 (s, 1H), 4.53 (s, 2H), 4.47 (s, 4H), 4.03 (s, 2H), 3.39 (s, 3H), 3.34 (s, 6H), 3.11 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.91, 144.37, 144.34, 143.50, 141.49, 140.98, 139.38, 139.00, 138.90, 137.54, 137.46, 136.63, 136.19, 129.67, 129.11, 128.55, 128.15, 127.76, 127.48, 125.52, 125.21, 124.78, 120.21, 120.10, 119.35, 75.21, 74.81, 74.77, 58.20, 58.02, 57.95, 52.24 ppm.

HRMS (ESI): *m/z* calcd for $C_{42}H_{37}O_6$-H^-: 637.2596 [*M*-H]$^-$; found 637.2589.

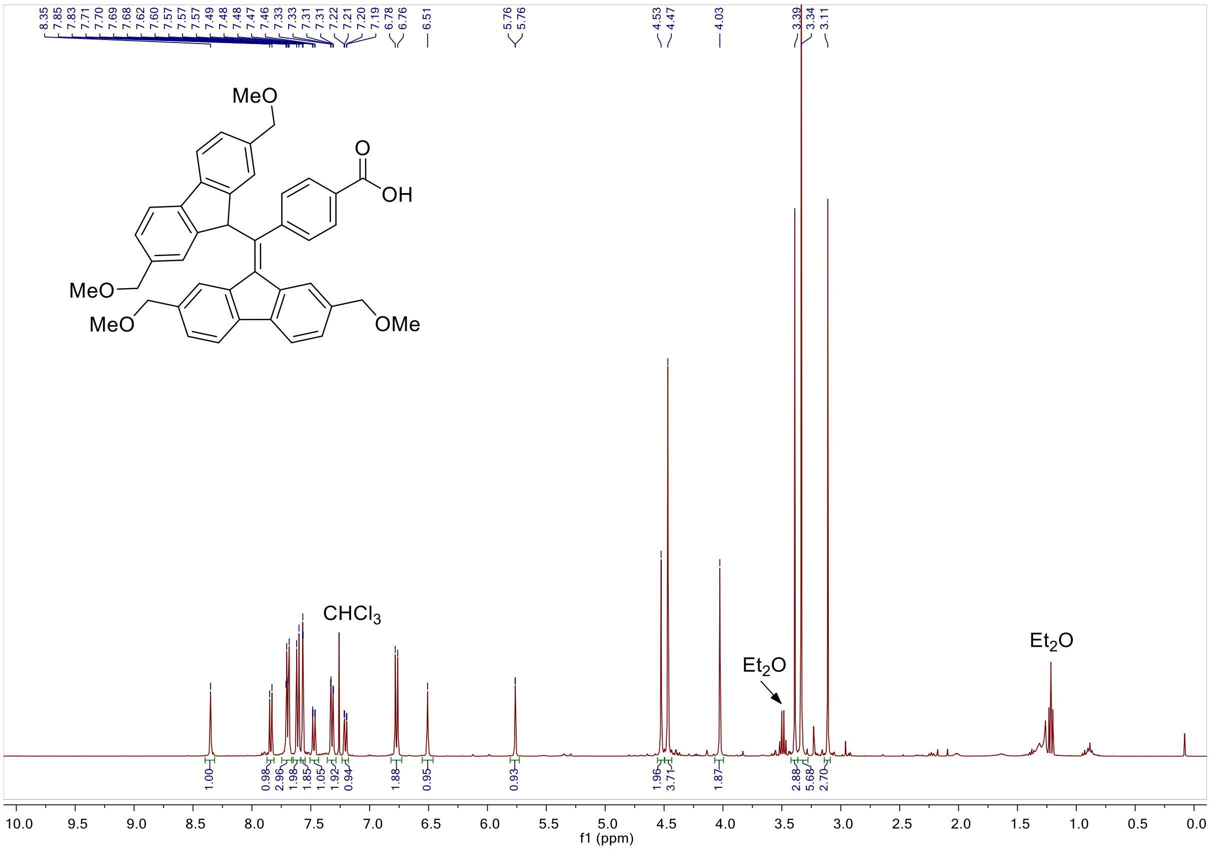


Figure S13. ^{1}H-NMR spectrum of compound **13**.

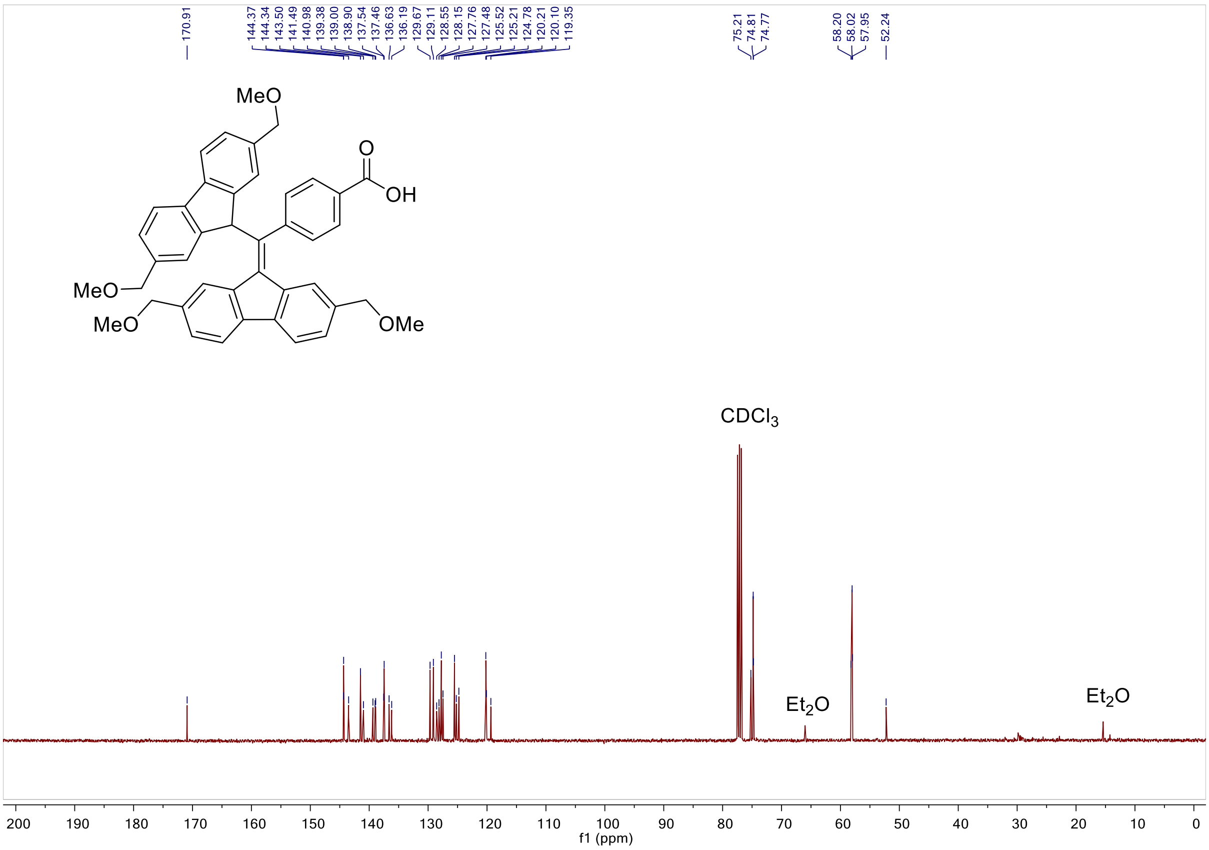
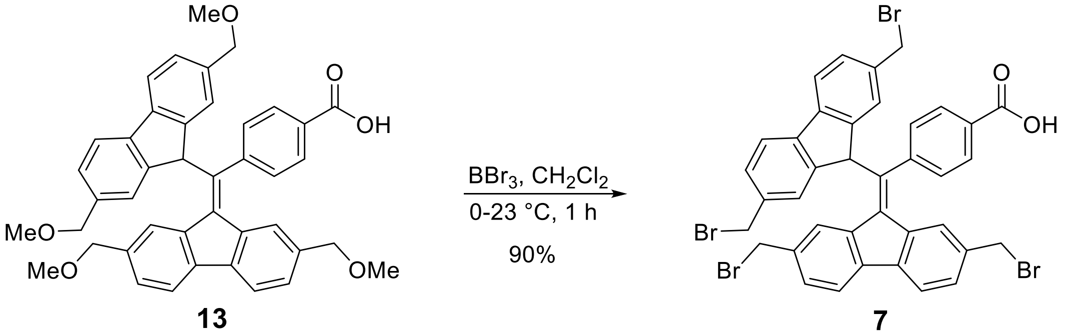


Figure S14. ^{13}C-NMR spectrum of compound **13**.



Tetra-(bromomethyl)-BDPA 7. To a solution of compound **13** (930 mg, 1.45 mmol) in CH_2Cl_2 (30 mL) at 0 °C, BBr_3 (0.6 mL, 5.82 mmol) was added and the resulting solution stirred at 23 °C for 1 h. The reaction was quenched with satd. aq. $NaHCO_3$ (30 mL) and extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by flash-column chromatography using a gradient elution (CH_2Cl_2:MeOH; 100:0 to 98:02) to give **7** (1.08 g, 90%) as an orange solid.

TLC (Silica gel, CH_2Cl_2:MeOH; 97:03): R_f (**13**) = 0.35, R_f (**7**) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (s, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.63 (s, 2H), 7.60 (d, *J* = 7.9 Hz, 2H), 7.55 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.38 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.28 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.77 (d, *J* = 8.4 Hz, 2H), 6.43 (s, 1H), 5.87 (s, 1H), 4.61 (s, 2H), 4.53 (q, *J* = 7.7 Hz, 4H), 4.08 (s, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.91, 144.56, 144.06, 143.59, 141.73, 141.15, 139.56, 139.29, 139.20, 137.55, 137.48, 136.59, 135.74, 130.06, 129.94, 129.26, 128.97, 128.91, 128.46, 126.85, 126.61, 125.94, 120.84, 120.76, 119.83, 52.28, 34.36, 34.14, 33.91 ppm.

HRMS (ESI): *m/z* calcd for $C_{38}H_{25}Br_4O_2$-H^-: 828.8594 [*M*-H]$^-$; found 828.8621.

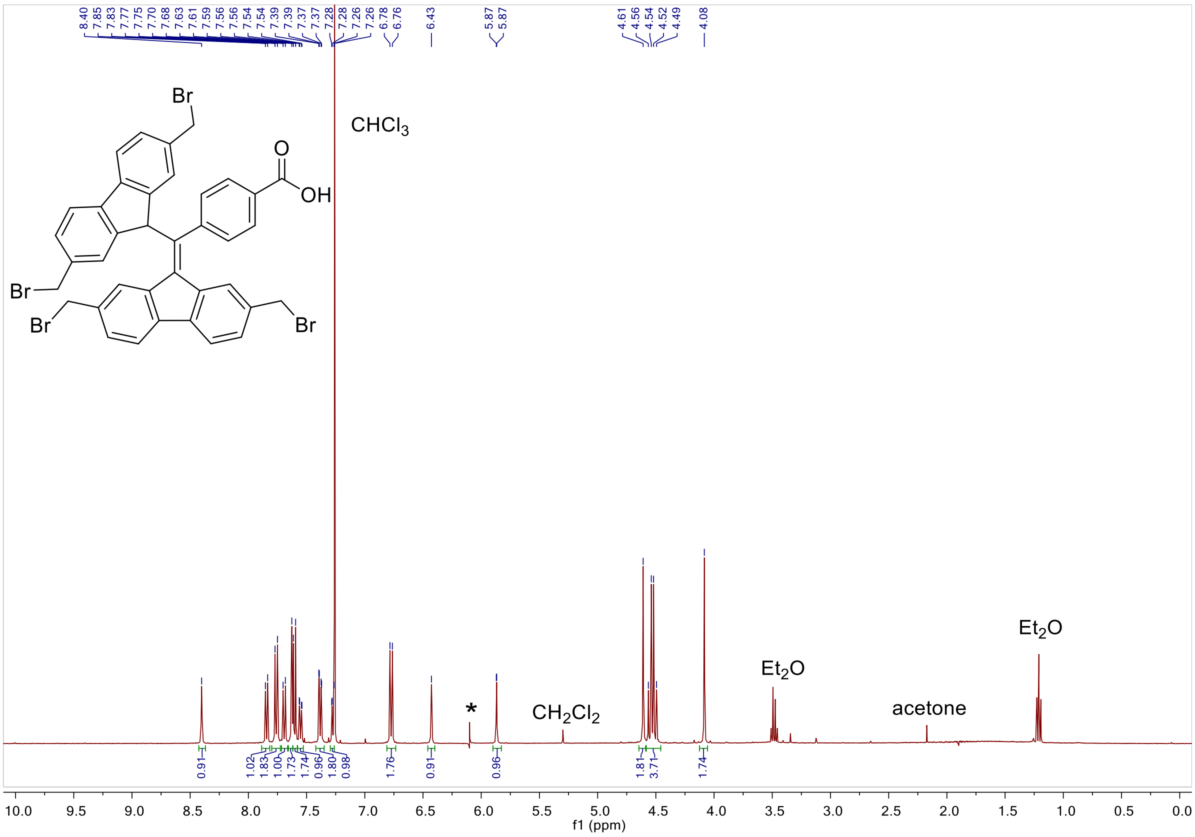


Figure S15. ^{1}H-NMR spectrum of compound **7**. The asterisk indicates an instrumental glitch.

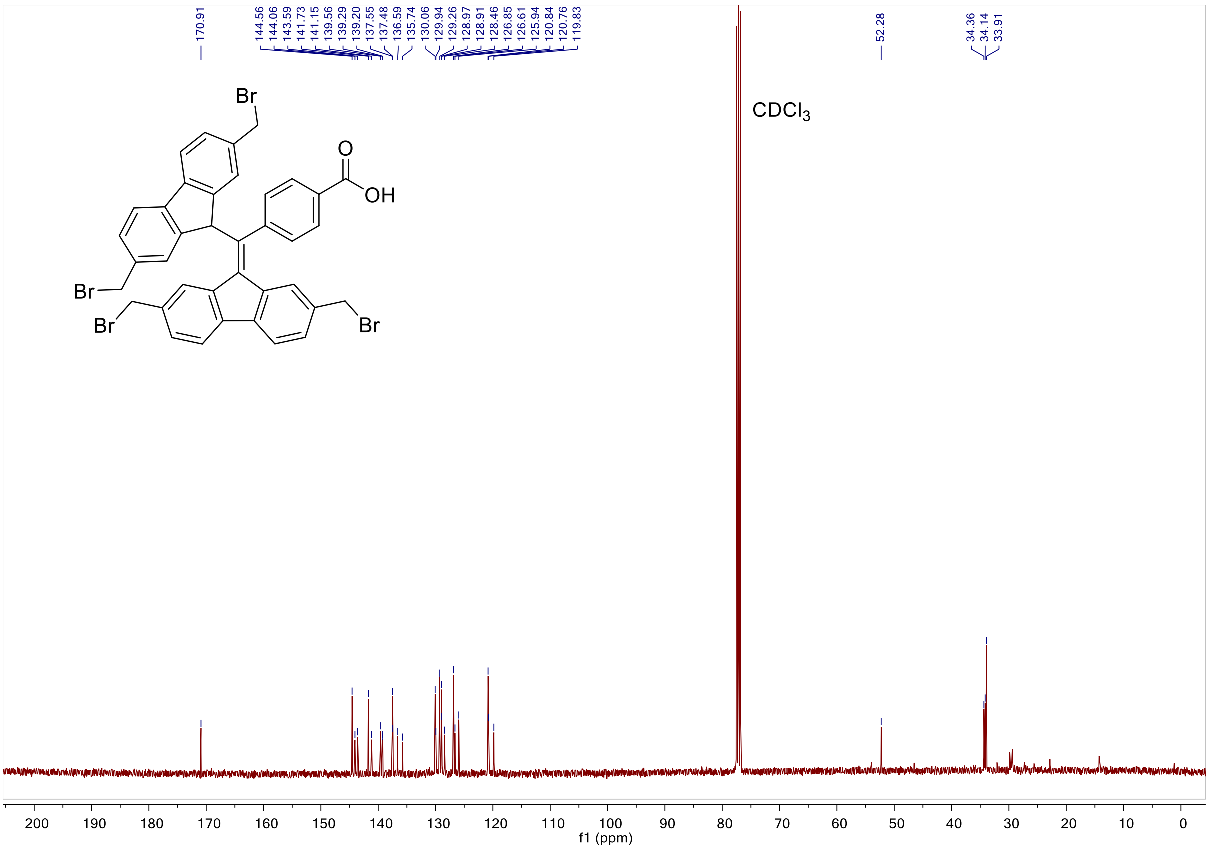
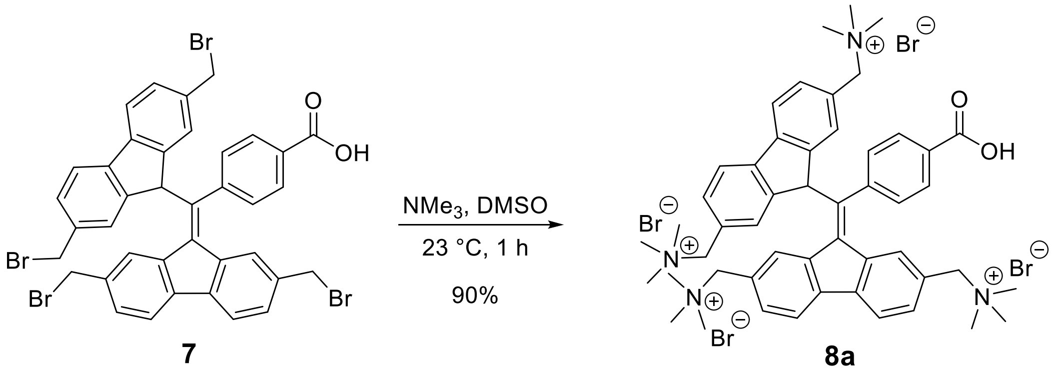


Figure S16. ^{13}C-NMR spectrum of compound **7**.



Tetraalkylammonium BDPA 8a. To a solution of tetra-bromo BDPA derivative **7** (20 mg, 0.024 mmol) in DMSO (2 mL), NMe_3 (60 μL, 0.24 mmol, 4 M) was added and the resulting solution stirred at 23 °C for 1 h. The reaction mixture was poured into Et_2O (10 mL), the precipitate collected by centrifugation followed by decantation of the solvent. The precipitate was redissolved in MeOH (2 mL) and reprecipitated by addition of Et_2O (10 mL). This precipitation was repeated to yield **8a** (23 mg, 90%) as a reddish brown solid.

^{1}H NMR (400 MHz, Methanol-*d*$_4$) δ 8.92 (s, 1H), 8.22 (d, *J* = 7.8 Hz, 1H), 8.08 (d, *J* = 7.8 Hz, 1H), 7.99 (d, *J* = 7.9 Hz, 2H), 7.89 (d, *J* = 1.4 Hz, 2H), 7.79 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.70 – 7.58 (m, 4H), 7.53 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 2H), 6.83 (s, 1H), 6.03 (d, *J* = 1.5 Hz, 1H), 4.84 (s, 2H), 4.63 (s, 4H), 4.15 (s, 2H), 3.21 (s, 9H), 3.11 (s, 18H), 2.85 (s, 9H) ppm.

^{13}C NMR (101 MHz, Methanol-*d*$_4$) δ 146.75, 144.78, 143.59, 142.52, 140.84, 140.72, 136.74, 134.73, 134.30, 134.06, 131.77, 131.15, 130.94, 130.57, 129.76, 129.46, 128.90, 127.79, 122.64, 122.55, 121.96, 101.39, 70.72, 70.25, 70.04, 54.05, 53.27, 53.08 ppm.

HRMS (ESI): *m/z* calcd for $C_{50}H_{62}N_4O_2\text{-}H^{3+}$: 249.8259 [*M*-H]$^{3+}$; found 249.8252.

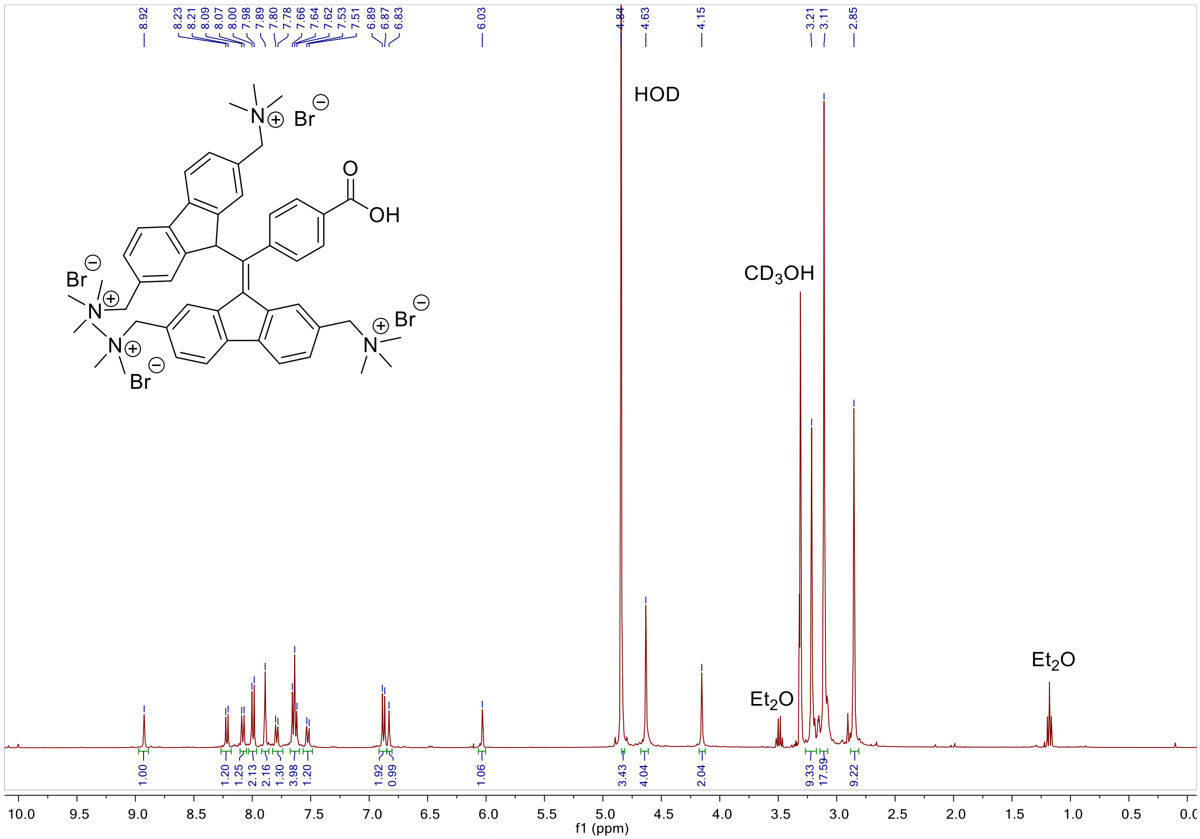


Figure S17. ^{1}H-NMR spectrum of compound **8a**.

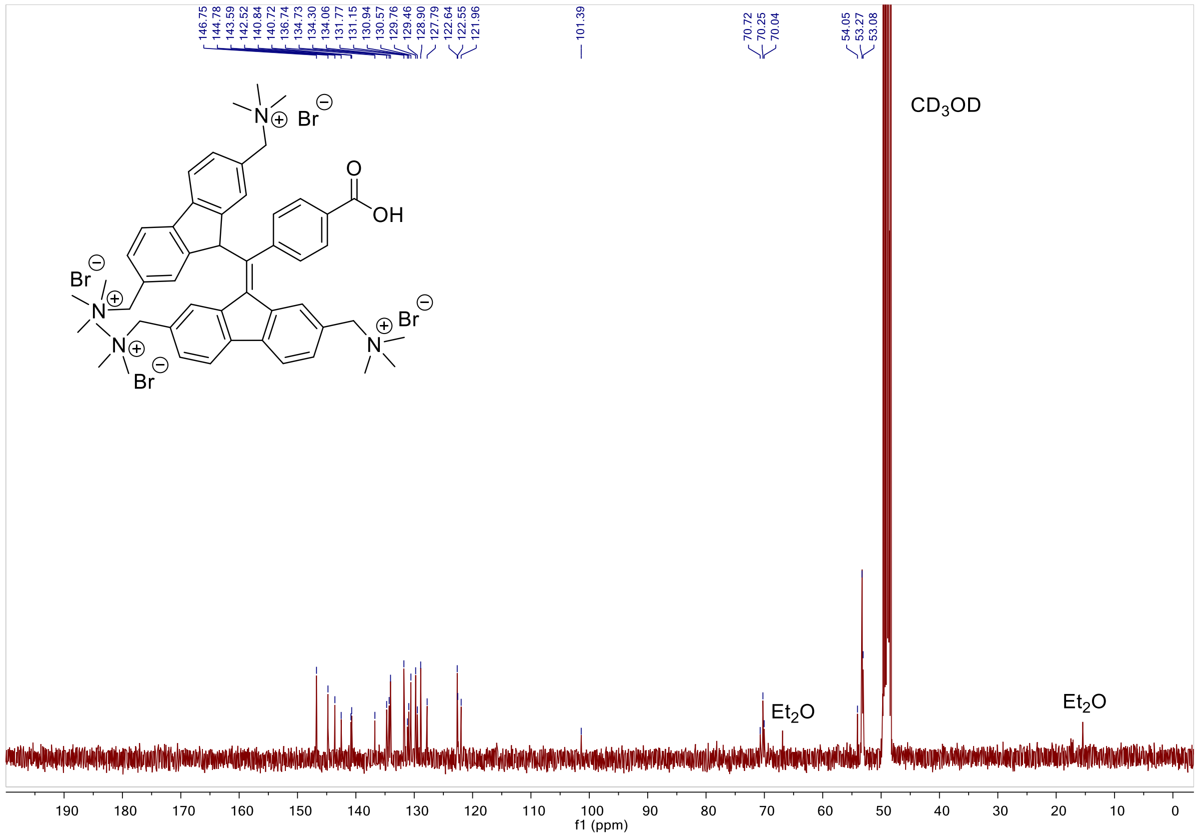
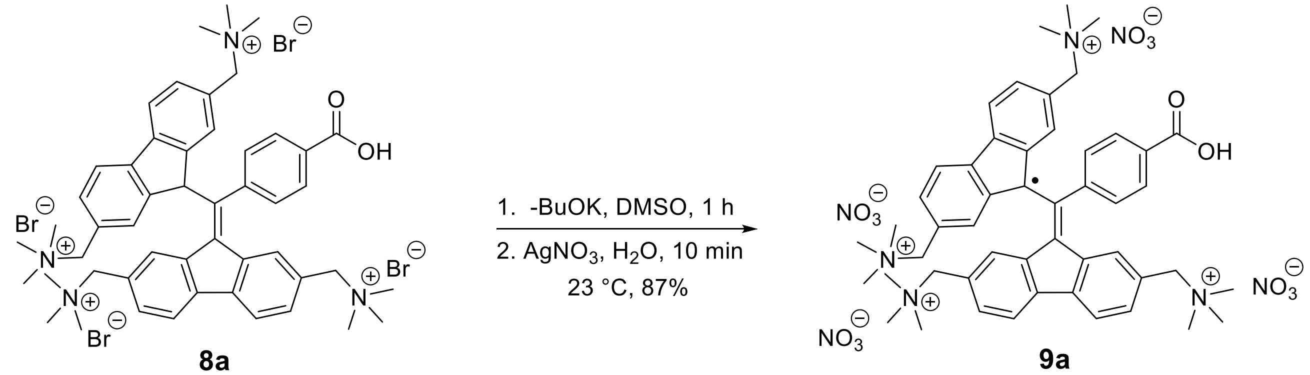


Figure S18. ^{13}C-NMR spectrum of compound **8a**.

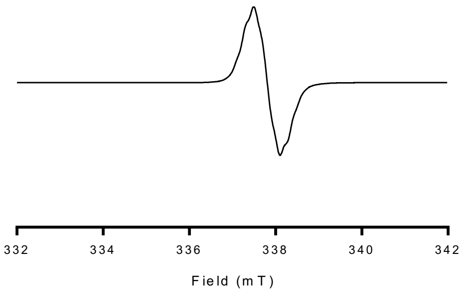


8a **9a**

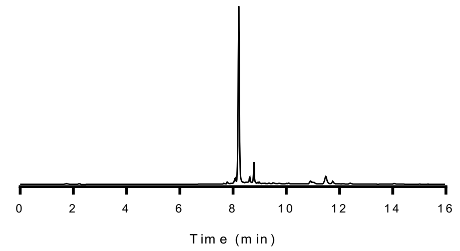
BDPA radical 9a. To a solution of **8a** (13 mg, 0.012 mmol) in DMSO (1 mL) was added a freshly prepared *t*-BuOK solution (96 µL, 0.024 mmol, 0.25 M in DMSO) and the resulting solution stirred at 23 °C for 1 h. A solution of $AgNO_3$ (10 mg, 0.06 mmol) in H_2O (0.2 mL) was added and the brown solution stirred for 10 min. The mixture was centrifuged, the solution was decanted and poured into Et_2O (10 mL). The precipitate formed was collected by centrifugation followed by decantation of the solvent. The precipitate was redissolved in MeOH (2 mL) and reprecipitated by addition of Et_2O (10 mL) twice. The precipitate was redissolved in MeOH (2 mL), filtered through celite and dried to give **9a** (10.5 mg, 87%) as a reddish brown solid.

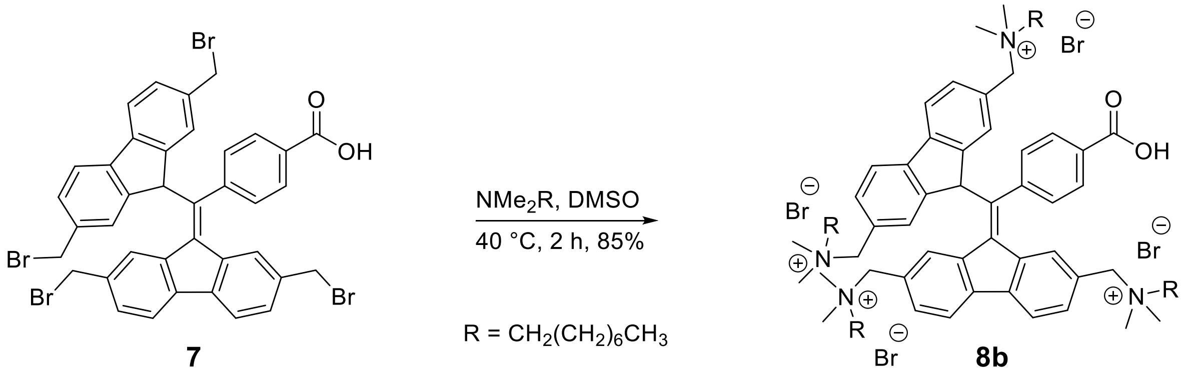
HRMS (ESI): *m/z* calcd for $C_{50}H_{61}N_4O_2+NO_3^{3+}$: 270.4885 $[M+NO_3]^{3+}$; found: 270.4854.

EPR (H_2O):



HPLC:





Tetraalkylammonium BDPA 8b. To a solution of tetra-bromo BDPA derivative **7** (10 mg, 0.012 mmol) in DMSO (1 mL), *N*,*N*-dimethyloctylamine (25 µL, 0.12 mmol) was added and the resulting solution stirred at 40 °C for 2 h. The reaction mixture was poured into Et_2O (10 mL), the precipitate collected by centrifugation followed by decantation of the solvent. The precipitate was redissolved in MeOH (2 mL) and reprecipitated by addition of Et_2O (10 mL). This precipitation was repeated to yield **8b** (15 mg, 85%) as a reddish brown solid.

^{1}H NMR (400 MHz, MeOD) δ 8.88 (s, 1H), 8.21 (d, *J* = 7.9 Hz, 1H), 8.07 (d, *J* = 7.8 Hz, 1H), 7.99 (d, *J* = 7.9 Hz, 2H), 7.88 (s, 2H), 7.77 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.66 – 7.59 (m, 4H), 7.51 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.83 (d, *J* = 8.3 Hz, 2H), 6.79 (s, 1H), 5.97 (s, 1H), 4.81 (s, 2H), 4.67 – 4.55 (m, 4H), 4.12 (s, 2H), 3.47 – 3.40 (m, 2H), 3.40 – 3.32 (m, 4H), 3.15 – 3.12 (m, 8H), 3.00 (s, 12H), 2.71 (s, 6H), 1.85 (bs, 6H), 1.72 (bs, 2H), 1.48 – 1.13 (m, 40H), 0.89 (t, *J* = 6.7 Hz, 12H) ppm.

^{13}C NMR (101 MHz, MeOD) δ 146.68, 144.70, 143.50, 142.51, 140.82, 140.65, 136.76, 134.96, 134.27, 131.81, 131.12, 130.61, 129.77, 129.31, 128.79, 127.55, 122.64, 122.57, 121.96, 69.37, 68.41, 66.03, 65.98, 54.00, 50.55, 50.52, 50.47, 50.18, 32.91, 32.87, 30.27, 30.23, 30.20, 30.19, 30.14, 27.50, 27.43, 23.71, 23.66, 14.44 ppm.

HRMS (ESI): *m/z* calcd for $C_{78}H_{117}N_4O_2$-H^{3+}: 380.6387 [*M*-H] $^{3+}$; found 380.6396.

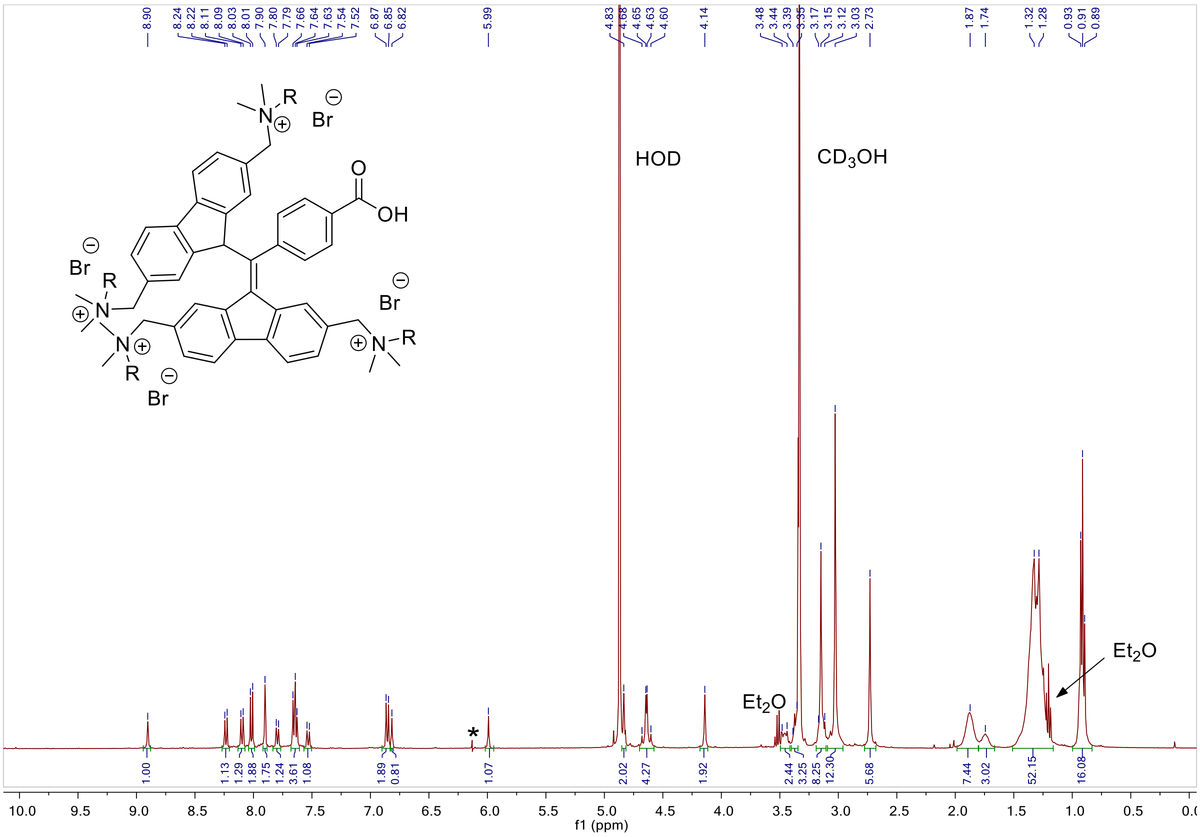


Figure S19. ^{1}H-NMR spectrum of compound **8b**. The asterisk indicates an instrumental glitch.

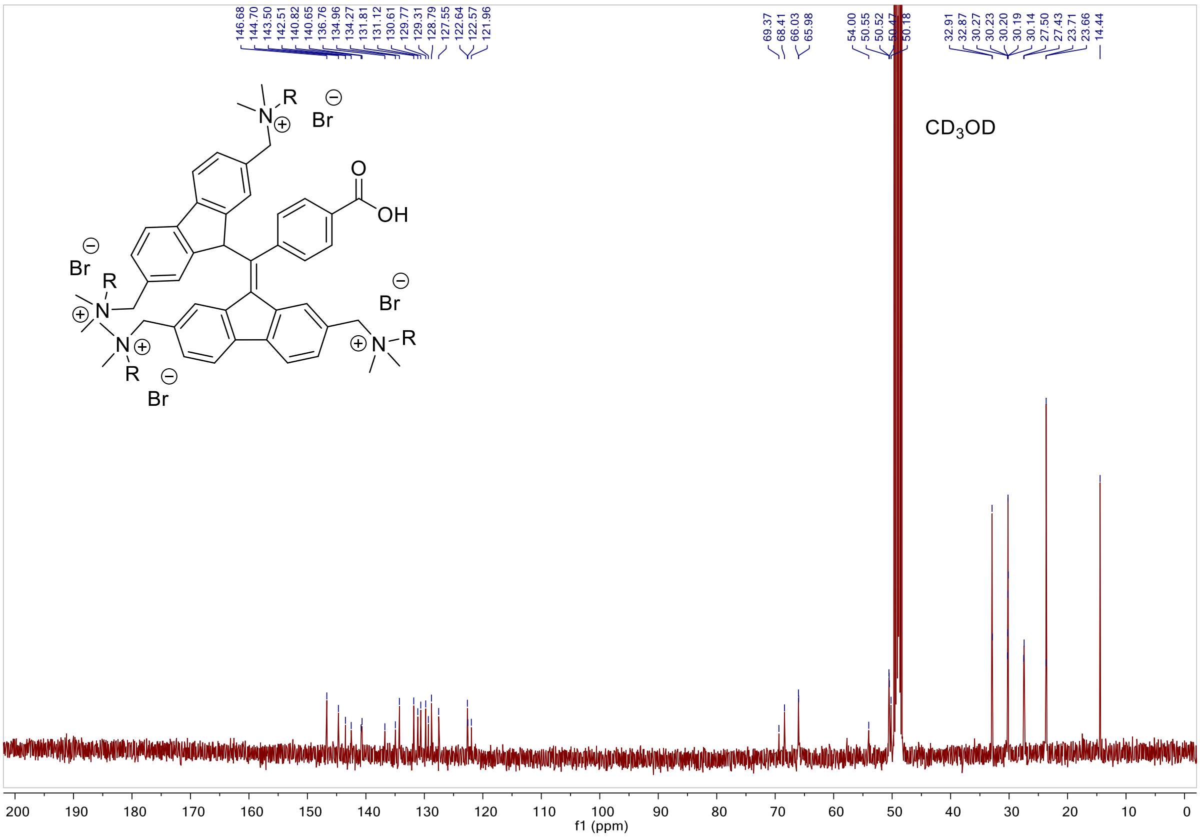
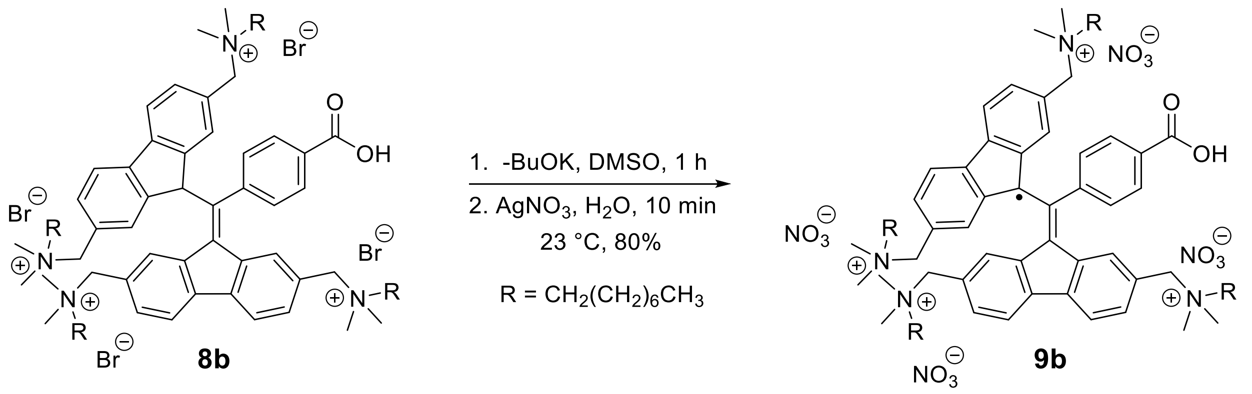


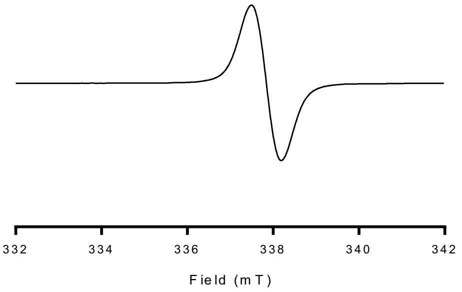
Figure S20. ^{13}C-NMR spectrum of compound **8b**.



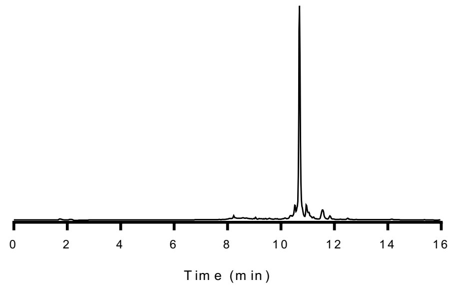
BDPA radical 9b. To a solution of **8b** (8 mg, 0.005 mmol) in DMSO (1 mL) was added a freshly prepared *t*-BuOK solution (40 µL, 0.01 mmol, 0.25 M in DMSO) and the resulting solution stirred at 23 °C for 1 h. A solution of $AgNO_3$ (4 mg, 0.025 mmol) in H_2O (0.2 mL) was added and the brown solution stirred for 10 min. The mixture was centrifuged, the solution was decanted and poured into Et_2O (10 mL). The precipitate formed was collected by centrifugation followed by decantation of the solvent. The precipitate was redissolved in MeOH (2 mL) and reprecipitated by addition of Et_2O (10 mL) twice. The precipitate was redissolved in MeOH (2 mL), filtered through celite and dried to give **9b** (6 mg, 80%) as a reddish brown solid.

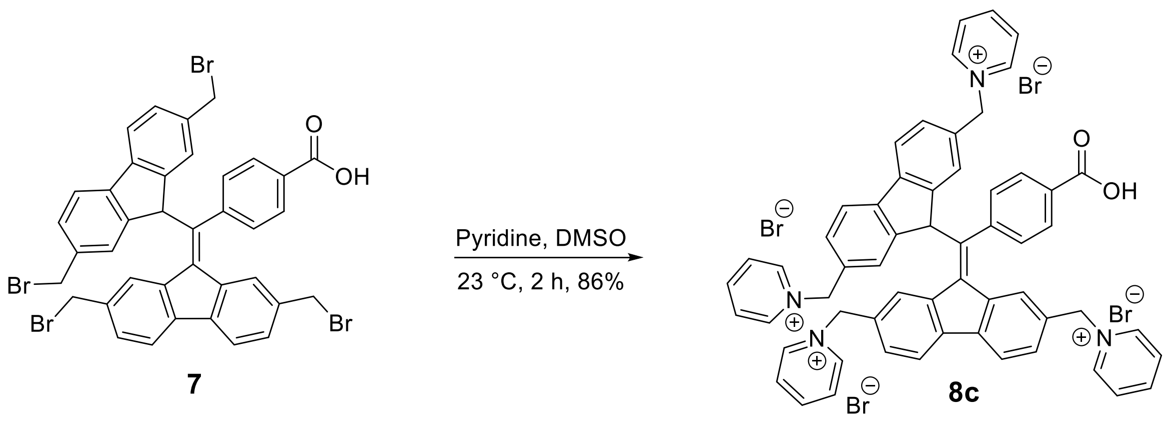
<u>HRMS</u> (ESI): *m/z* calcd for $C_{78}H_{117}N_4O_2^{4+}$: 285.4789 $[M]^{4+}$; found 285.4788.

<u>EPR</u> (MeOH):



<u>HPLC</u>:





Tetrapyridinium BDPA 8c. To a solution of tetra-bromo BDPA derivative **7** (10 mg, 0.012 mmol) in DMSO (1 mL), pyridine (10 μL, 0.12 mmol) was added and the resulting solution stirred at 23 °C for 2 h. The reaction mixture was poured into Et$_2$O (10 mL), the precipitate collected by centrifugation followed by decantation of the solvent. The precipitate was redissolved in MeOH (2 mL) and reprecipitated by addition of Et$_2$O (10 mL). This precipitation was repeated to yield **8c** (12 mg, 86%) as a reddish brown solid.

^{1}H NMR (400 MHz, MeOD) δ 9.25 – 9.16 (m, 2H), 9.14 – 9.04 (m, 4H), 8.77 (s, 1H), 8.71 – 8.53 (m, 6H), 8.15 – 8.11 (m, 7H), 8.07 – 8.02 (m, 2H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.87 (d, *J* = 7.9 Hz, 2H), 7.76 (s, 2H), 7.67 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.53 (dt, *J* = 7.8, 1.9 Hz, 3H), 7.39 (d, *J* = 8.3 Hz, 2H), 6.70 (s, 1H), 6.64 (d, *J* = 8.3 Hz, 2H), 6.05 (s, 2H), 5.92 (s, 4H), 5.75 (s, 1H), 5.55 (s, 2H) ppm.

^{13}C NMR (101 MHz, MeOD) δ 168.79, 147.51, 147.36, 147.32, 146.80, 146.33, 146.16, 146.02, 145.78, 144.23, 143.93, 142.92, 141.70, 141.12, 140.67, 136.57, 134.45, 134.20, 133.46, 131.19, 131.12, 130.61, 130.53, 130.33, 129.73, 129.71, 129.55, 128.25, 127.95, 126.22, 122.83, 121.98, 65.65, 65.60, 65.53, 53.81 ppm.

HRMS (ESI): *m/z* calcd for $C_{58}H_{46}N_4O_2^{4+}$: 207.5900 [*M*]$^{4+}$; found 207.5898.

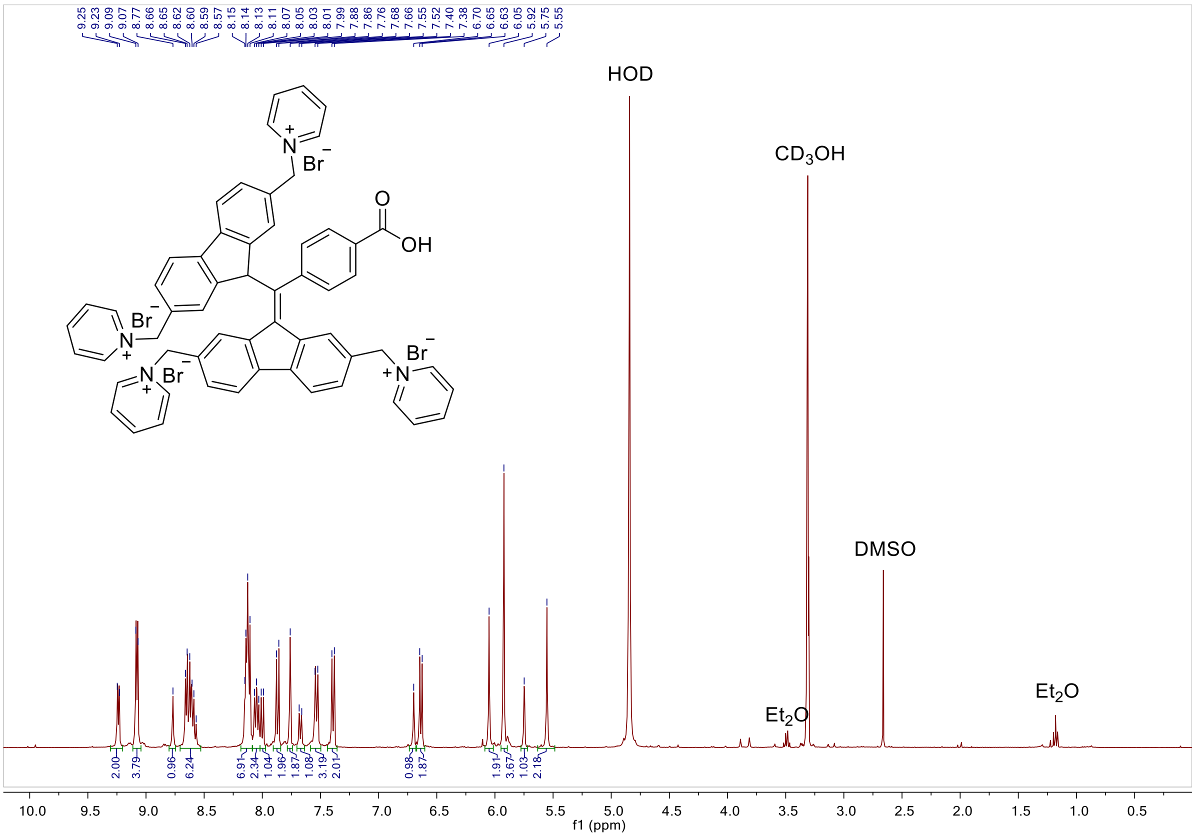


Figure S21. ^{1}H-NMR spectrum of compound **8c**.

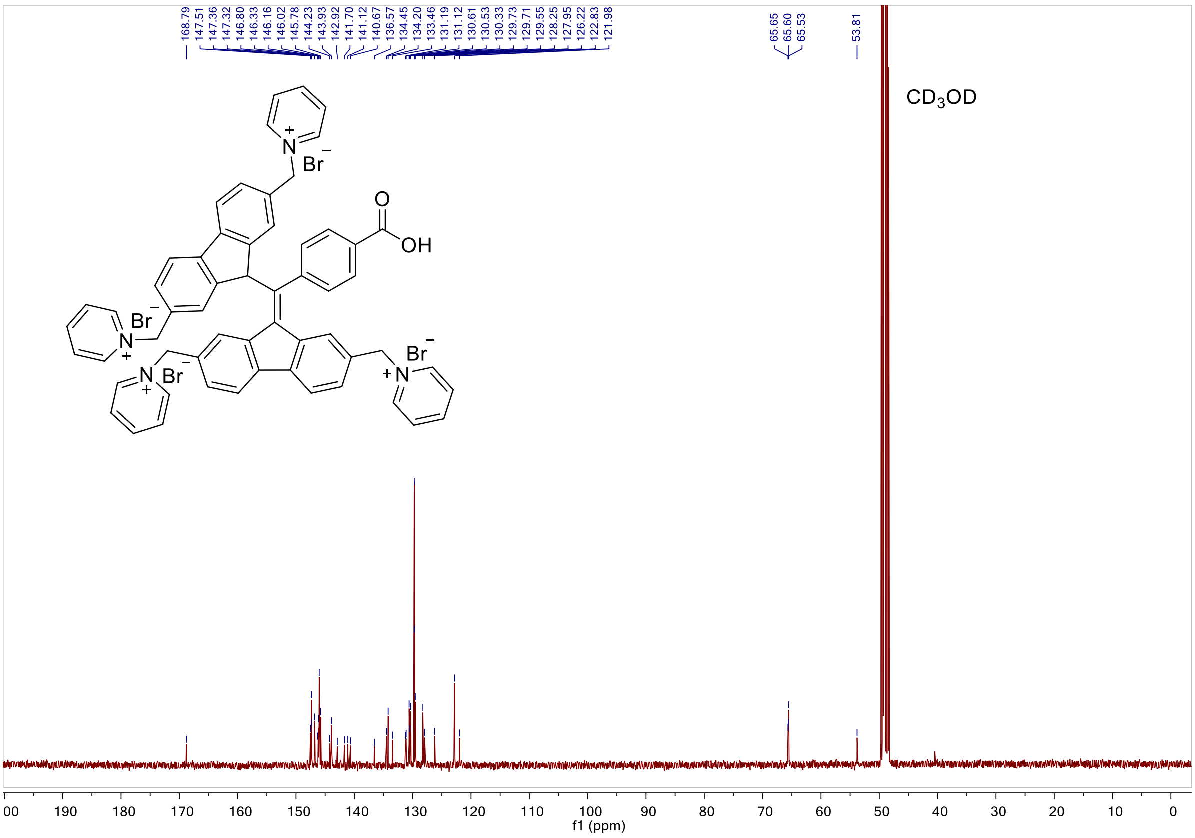
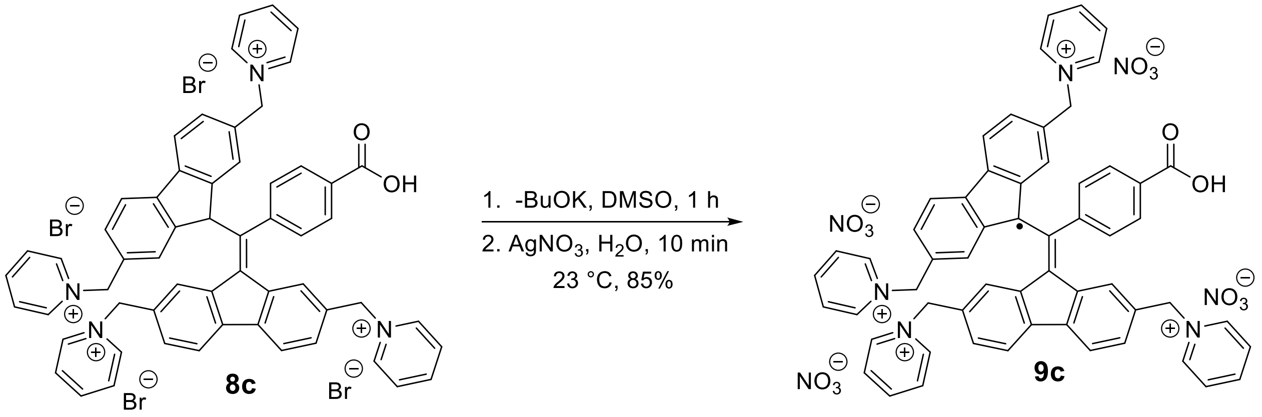


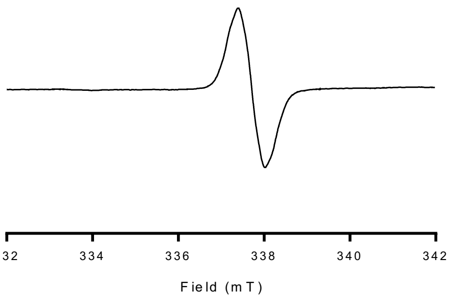
Figure S22. ^{13}C-NMR spectrum of compound **8c**.



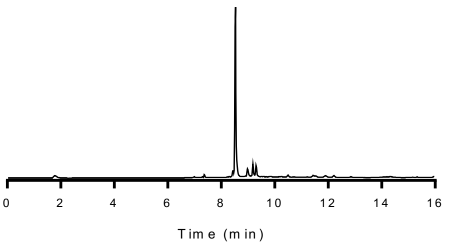
BDPA radical 9c. To a solution of **8c** (12 mg, 0.01 mmol) in DMSO (1 mL) was added a freshly prepared *t*-BuOK solution (80 µL, 0.02 mmol, 0.25 M in DMSO) and the resulting solution stirred at 23 °C for 1 h. A solution of $AgNO_3$ (9 mg, 0.05 mmol) in H_2O (0.2 mL) was added and the brown solution stirred for 10 min. The mixture was centrifuged, the solution was decanted and poured into Et_2O (10 mL). The precipitate formed was collected by centrifugation followed by decantation of the solvent. The precipitate was redissolved in MeOH (2 mL) and reprecipitated by addition of Et_2O (10 mL) twice. The precipitate was redissolved in MeOH (2 mL), filtered through celite and dried to give **9c** (9.5 mg, 85%) as a reddish brown solid.

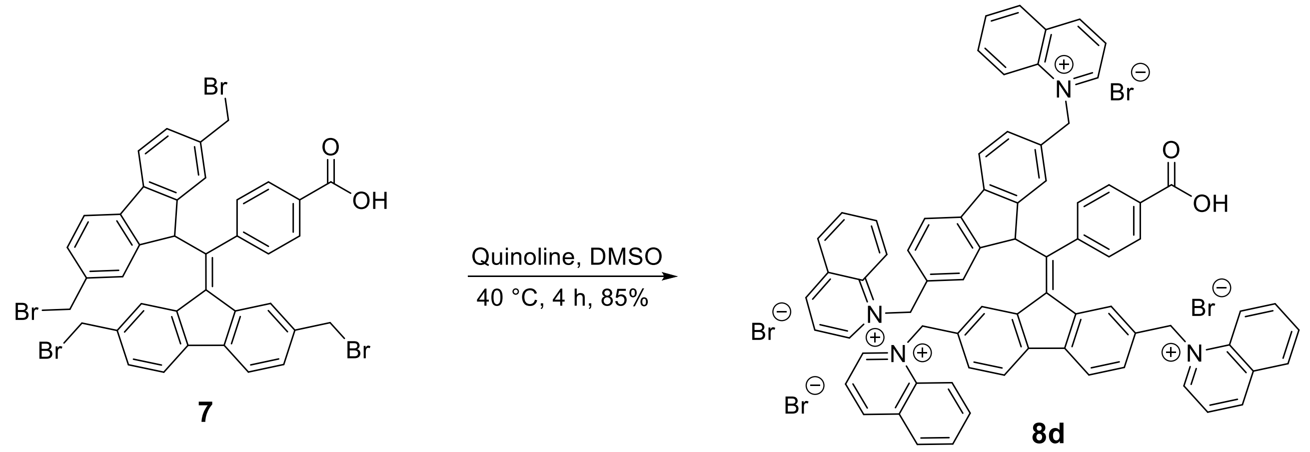
HRMS (ESI): *m/z* calcd for $C_{58}H_{45}N_4O_2$+NO_3^{3+}: 297.1135 [M+NO_3]$^{3+}$; found: 297.1151.

EPR (H_2O):



HPLC:





Tetraquinolinium BDPA 8d. To a solution of tetra-bromo BDPA derivative **7** (10 mg, 0.012 mmol) in DMSO (1 mL), quinoline (14 μL, 0.12 mmol) was added and the resulting solution stirred at 40 °C for 4 h. The reaction mixture was poured into Et_2O (10 mL), the precipitate collected by centrifugation followed by decantation of the solvent. The precipitate was redissolved in MeOH (2 mL) and reprecipitated by addition of Et_2O (10 mL). This precipitation was repeated to yield **8d** (13.5 mg, 85%) as a reddish brown solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.67 (dd, J = 6.0, 1.4 Hz, 1H), 9.60 (dd, J = 5.9, 1.4 Hz, 2H), 9.32 (d, J = 8.6 Hz, 1H), 9.28 (dd, J = 8.5, 3.7 Hz, 3H), 9.24 (dd, J = 6.0, 1.4 Hz, 1H), 8.59 (d, J = 8.4 Hz, 1H), 8.51 (dd, J = 8.2, 1.6 Hz, 1H), 8.49 – 8.45 (m, 2H), 8.44 – 8.39 (m, 2H), 8.38 – 8.32 (m, 2H), 8.22 – 8.11 (m, 4H), 8.11 – 8.07 (m, 1H), 8.07 – 8.03 (m, 3H), 8.00 – 7.97 (m, 2H), 7.95 (dd, J = 7.1, 1.2 Hz, 1H), 7.93 – 7.84 (m, 4H), 7.75 (d, J = 7.5 Hz, 2H), 7.66 (dd, J = 8.0, 1.5 Hz, 1H), 7.47 (dd, J = 8.1, 1.2 Hz, 1H), 7.40 – 7.37 (m, 4H), 6.82 (d, J = 8.4 Hz, 2H), 6.38 – 6.18 (m, 7H), 6.09 (d, J = 8.3 Hz, 2H), 6.06 (s, 2H), 5.28 (d, J = 1.4 Hz, 1H) ppm.

^{13}C NMR (101 MHz, MeOD) δ 168.43, 150.92, 150.78, 149.95, 149.68, 149.58, 146.45, 146.00, 143.60, 143.07, 142.09, 140.99, 140.32, 140.00, 139.74, 139.44, 139.36, 137.47, 137.36, 137.16, 135.53, 134.12, 134.09, 133.63, 132.47, 132.10, 132.06, 131.68, 131.62, 131.57, 131.55, 131.38, 131.36, 130.78, 129.98, 129.45, 129.15, 128.66, 128.41, 126.26, 125.78, 123.46, 123.36, 123.20, 123.00, 122.53, 122.23, 120.51, 120.29, 120.05, 62.29, 61.90, 61.88, 53.47 ppm.

HRMS (ESI): *m/z* calcd for $C_{74}H_{54}N_4O_2^{4+}$: 257.6056 [*M*]$^{4+}$; found 257.6031.

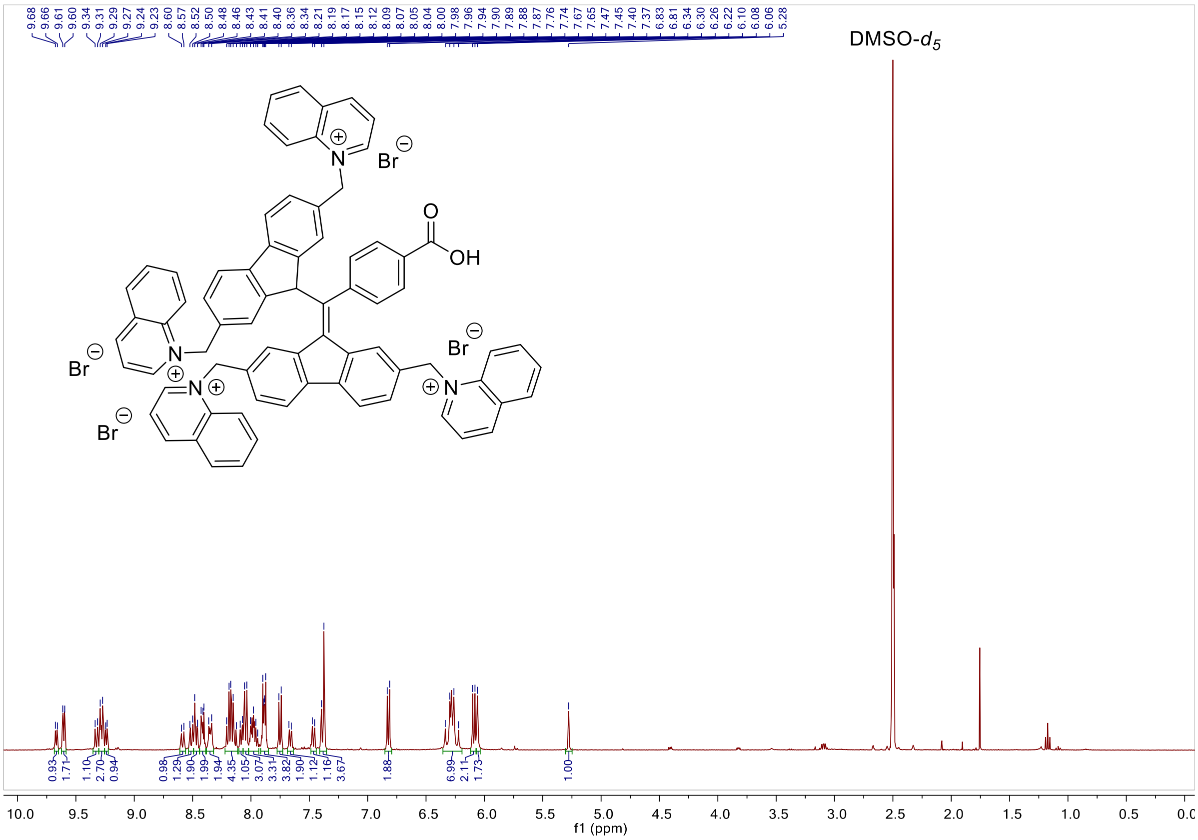


Figure S23. ^{1}H-NMR spectrum of compound **8d**. A water peak at 3.54 ppm was suppressed.

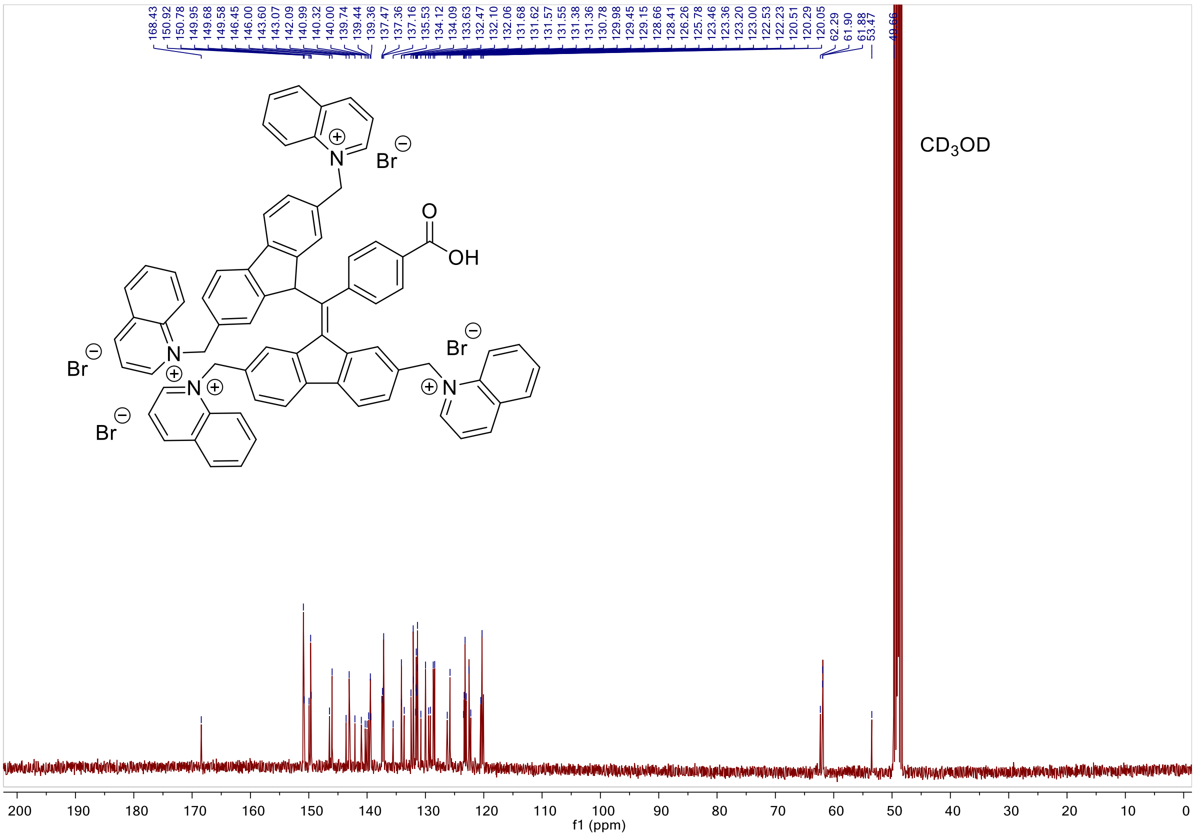
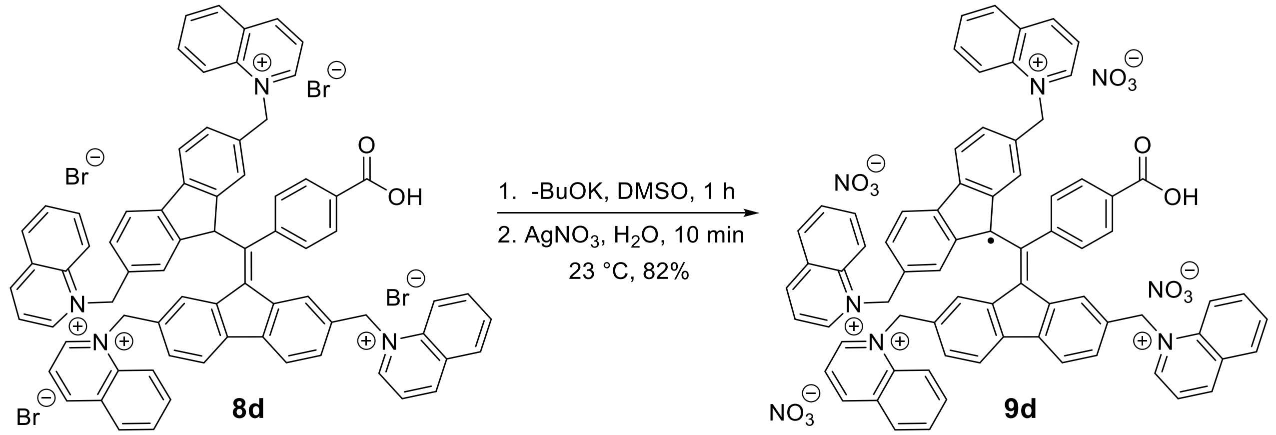


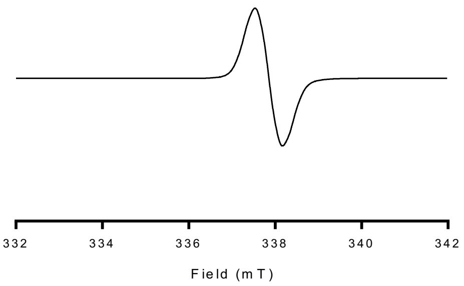
Figure S24. ^{13}C-NMR spectrum of compound **8d**.



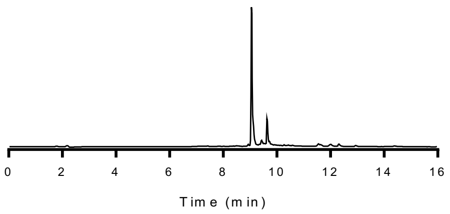
BDPA radical 9d. To a solution of **8d** (13 mg, 0.01 mmol) in DMSO (1 mL) was added a freshly prepared *t*-BuOK solution (80 µL, 0.02 mmol, 0.25 M in DMSO) and the resulting solution stirred at 23 °C for 1 h. A solution of $AgNO_3$ (9 mg, 0.05 mmol) in H_2O (0.2 mL) was added and the brown solution stirred for 10 min. The mixture was centrifuged, the solution was decanted and poured into Et_2O (10 mL). The precipitate formed was collected by centrifugation followed by decantation of the solvent. The precipitate was redissolved in MeOH (2 mL) and reprecipitated by addition of Et_2O (10 mL) twice. The precipitate was redissolved in MeOH (2 mL), filtered through celite and dried to give **9d** (10 mg, 82%) as a reddish brown solid.

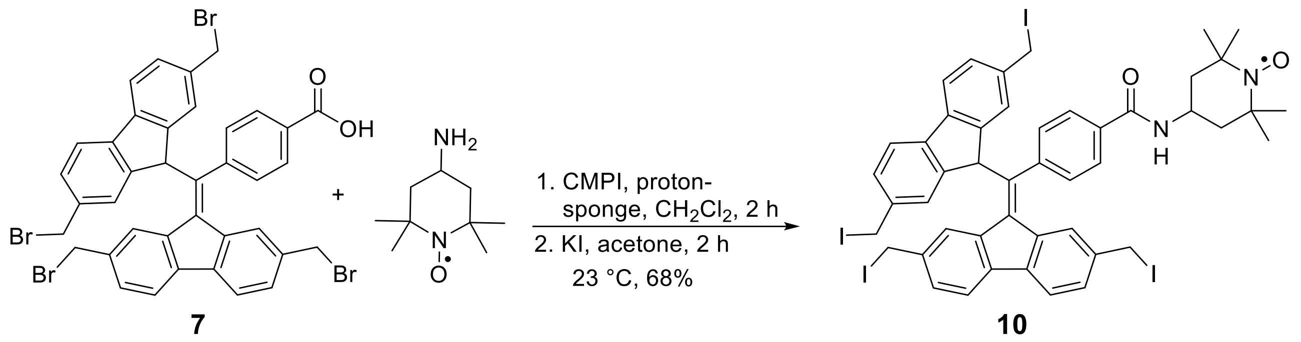
HRMS (ESI): *m/z* calcd for $C_{74}H_{53}N_4O_2^{4+}$: 257.3537 [*M*] $^{4+}$; found 257.3599.

EPR (H_2O):



HPLC:



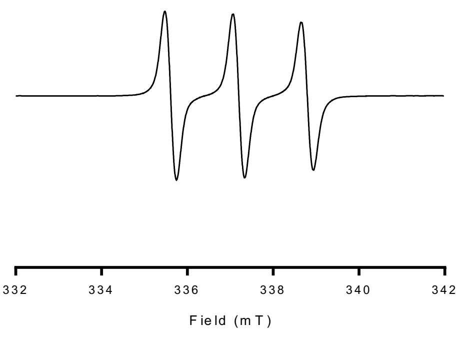


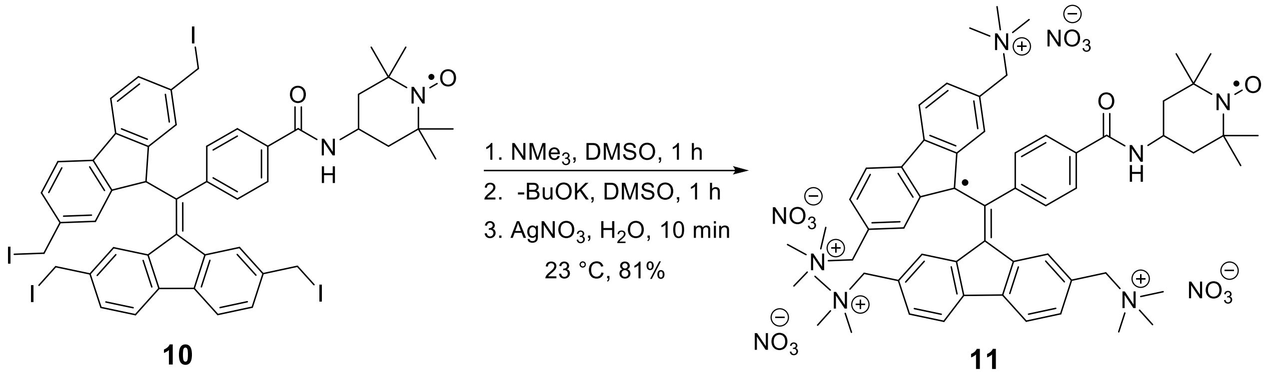
Tetra-(iodomethyl)-BDPA-TEMPO 10. To a solution of BDPA **7** (200 mg, 0.24 mmol) and 2-chloro-1-methylpyridinium iodide (CMPI) (67 mg, 0.26 mmol) in CH_2Cl_2 (10 mL), 4-amino TEMPO (45 mg, 0.26 mmol) and 1,8-bis(dimethylamino)naphthalene (proton-sponge) (103 mg, 0.48 mmol) were added. The resulting solution was stirred at 23 °C for 2 h, aq. HCl (1 N, 20 mL) added and extracted with CH_2Cl_2 (2 x 30 mL). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The residue was redissolved in acetone (10 mL), KI (398 mg, 2.40 mmol) added and the resulting solution stirred at 23 °C for 2 h. H_2O (20 mL) was added and the mixture extracted with CH_2Cl_2 (2 x 30 mL). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash-column chromatography using a gradient elution (pet ether:EtOAc; 80:20 to 70:30) to give **10** (193 mg, 68%) as a reddish solid.

TLC (Silica gel, pet ether:EtOAc, 70:30): R_f (**7**) = 0.2, R_f (**10**) = 0.3

HRMS (ESI): *m/z* calcd for $C_{47}H_{43}I_4N_2O_2$+Na^+: 1197.9396 [*M*+Na]$^+$; found 1197.9402

EPR (CH_2Cl_2):

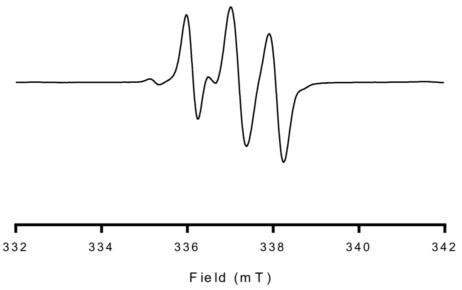




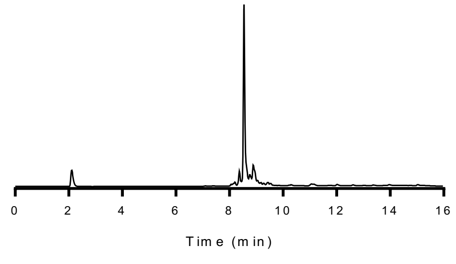
BDPA-TEMPO biradical 11. To a solution of BDPA derivative **10** (10 mg, 0.0085 mmol) in DMSO (1 mL), NMe_3 (21 µL, 0.085 mmol, 4 M) was added and the resulting solution stirred at 23 °C for 1 h. The reaction mixture was poured into Et_2O (10 mL), the precipitate collected by centrifugation followed by decantation of the solvent. The precipitate was redissolved in MeOH (2 mL) and reprecipitated by addition of Et_2O (10 mL) twice and dried. The precipitate was dissolved in DMSO (1 mL), freshly prepared *t*-BuOK solution (70 µL, 0.017 mmol, 0.25 M in DMSO) added and the resulting solution stirred at 23 °C for 1 h. A solution of $AgNO_3$ (7 mg, 0.043 mmol) in H_2O (0.2 mL) was added and the brown solution stirred for 10 min. The mixture was centrifuged, the solution was decanted and poured into Et_2O (10 mL). The precipitate formed was collected by centrifugation followed by decantation of the solvent. The precipitate was redissolved in MeOH (2 mL) and reprecipitated by addition of Et_2O (10 mL) twice. The precipitate was redissolved in MeOH (2 mL), filtered through celite and dried to give **11** (8 mg, 81%) as a reddish brown solid.

HRMS (ESI): *m/z* calcd for $C_{59}H_{78}N_4O_2+NO_3^{3+}$: 321.5349 $[M+NO_3]^{3+}$; found: 321.5420.

EPR (DMSO):



HPLC:



Solubility in DNP juice

The solubility of the tetraalkyl/aryl-ammonium BDPA derivatives **8a-d** in DNP juice (glycerol: H_2O, 6:4) was determined by UV-vis spectroscopy. For each of compounds **8a-d**, solutions were prepared in the glycerol-H_2O mixture at different concentrations. A calibration curve was prepared by recording the UV-vis spectra of these solutions and plotting the absorbance at the wavelength stated, 342 nm (**8a**), 290 nm (**8b**), 324 nm (**8c**) and 336 nm (**8d**) as a function of the concentration. The maximum solubility of compounds **8a-d** was determined from the calibration curve by recording the absorbance of a saturated solution. The values were as follows: >150 mM (**8a**), 20 mM (**8b**), 65 mM (**8c**) and 45 mM (**8d**).

Quantification of BDPA radicals

EPR spectroscopy was used to quantify the amount of tetraalkyl/aryl-ammonium BDPA radicals present in each sample. The EPR spectra of a solution of 4-hydroxy TEMPO (1 mM) and BDPA radicals **9a-d** (1 mM) in DMSO were recorded and double-integrated to obtain the area under the peaks. The percentage of BDPA radicals **9a-d** was determined by comparing these two areas, which was found to be approximately 92% (**9a**), 82% (**9b**), 85% (**9c**) and 80% (**9d**). The amount of the biradical **11** was determined with respect to a nitroxide monoradical impurity present in the sample[2] and found to be ca. 90%.

Persistence of BDPA radicals

Solvent-dependent persistence. The persistence of BDPA radicals was investigated under different conditions by monitoring the absorption of BDPA radicals at 503 nm using UV-vis spectroscopy. The samples were prepared in the following manner: A stock solution of the radicals (10 mM for radical **9a**, 5 mM for biradical **11**, 1 mM for radical **9b** and **9d**) were prepared in MeOH. Aliquots were removed from the stock solutions (200 µL), distributed into microfuge tubes, dried in a vacuum concentrator and the solid was redissolved in the chosen solvent (200 µL). The solutions were kept at 23 °C in the presence of air and UV-vis spectra were recorded at different time intervals by taking out aliquots (2-20 µL) followed by dilution with H_2O (0.5 mL). Commercially purchased solvents were used without further drying and purification for these experiments, except for DMSO which was dried over molecular sieves (3 Å).

Figure S25A shows the UV-vis spectra of BDPA radical **9a** in DNP juice at various times. The peak between 400 – 550 nm arises from the absorption of the BDPA radical and decreases when the radical decomposes. **Figure S25B** shows the persistence of **9a**, as investigated by both UV-vis (left y-axis) and EPR spectroscopy (right y-axis).[2] Both techniques give similar results.

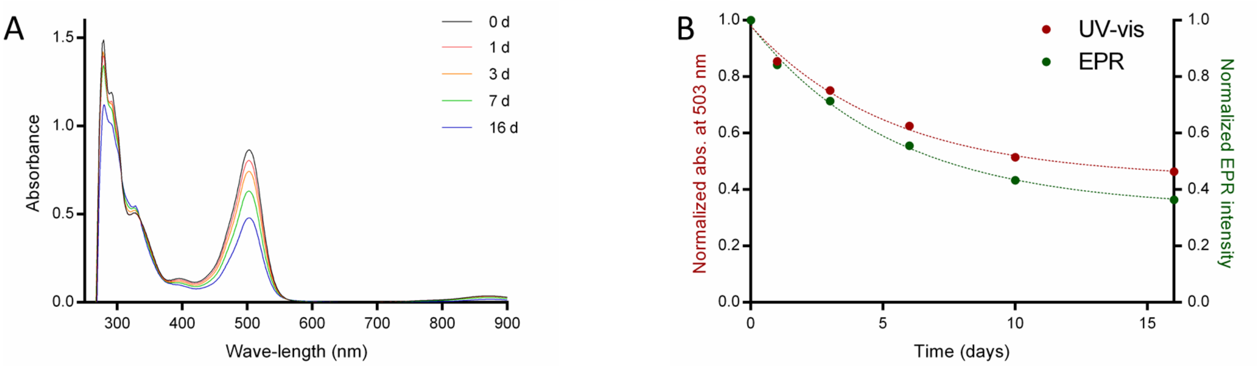


Figure S25. Persistence of BDPA radical **9a** in DNP juice (10 mM) at 23 °C. **A**. The UV-vis absorbance spectra of BDPA radical **9a** at different times. **B**. The normalized absorbance of **9a** at 503 nm (left y-axis) and the normalized EPR intensity of the radical (right y-axis) plotted as a function of time.

The solvent-dependent persistence of radical **9a** at 23 °C is shown in **Figure 2**. The tetraalkylammonium BDPA-TEMPO biradical **11**, which has the same tetraalkylammonium group as radical **9a**, shows a similar solvent-dependency as **9a** (**Figure S26**). The highest persistence of **11** was observed in DMSO, with a decomposition of ca. 10% of the radical after 2 weeks. Ca. 40-50% of the radical was decomposed in DNP juice and MeOH under the same condition. However, similar to what was found for **9a**, a significantly higher degradation was observed in water.

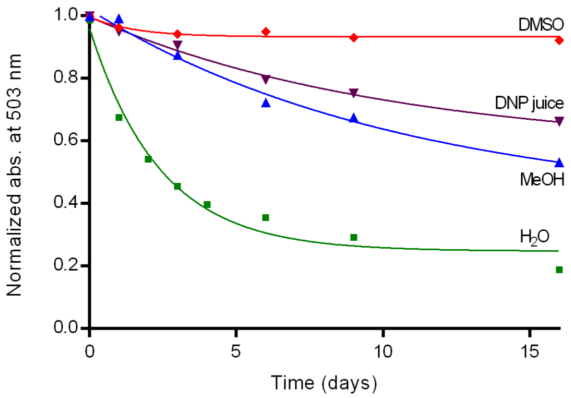


Figure S26. Persistence of BDPA-TEMPO biradical **11** in solution (5 mM) at 23 °C monitored by UV-vis spectroscopy at 503 nm.

Figure S27 shows the persistence of radicals **9b** and **9d** in solution at 23 °C. Due to the limited solubility of these radicals in MeOH in which the stock solutions were prepared for the experiments, persistence for a 1 mM solution is reported. A similar solvent-dependency was observed for these radicals as well.

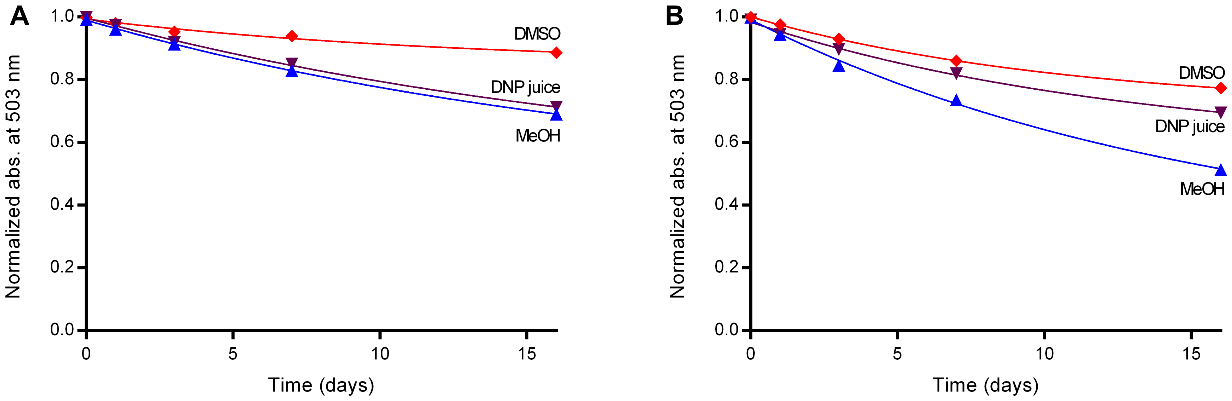


Figure S27. Persistence of radicals **9b** (**A**) and **9d** (**B**) in solution (1 mM) at 23 °C.

Temperature-dependent persistence. We investigated the persistence of radical **9a** at -80 °C in DNP juice by UV-vis spectroscopy (**Figure S28**). Negligible degradation was detected after 30 days, as has been observed with other BDPA radicals.[2]

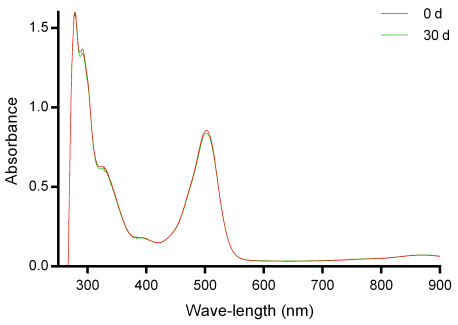


Figure S28. The persistence of radical **9a** at -80 °C in DNP juice (10 mM) investigated by UV-vis spectroscopy.

Concentration-dependent persistence. To determine if dimerization was a major pathway of degradation of the BDPA radicals in water, the rate of decomposition of radical **9a** in water was investigated for solutions of different concentration. The initial rates of degradation were determined[2] and plotted as a function of concentration (**Figure S29**). The rate was found to increase 3-fold with a 2-fold increase in the concentration, with a reaction order of ca. 1.6 with respect to the radical suggesting dimerization in water. A similar result was also obtained for biradical **11** (data not shown).

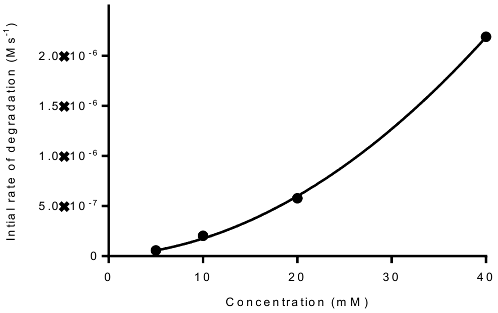


Figure S29. Concentration-dependent initial rates of BDPA radical **9a** in water at 23 °C.

Ionic strength-dependent persistence. In an attempt to reduce aggregation in water by increasing the ionic strength, the persistence of **9a** was determined in presence of varying concentration of NaCl (aq.) (**Figure S30**). However, this data shows that the presence of NaCl is detrimental to the persistence of **9a**.

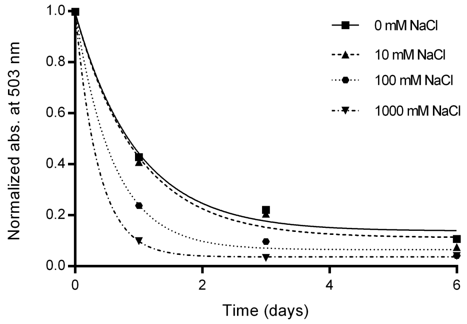


Figure S30. Persistence of BDPA radical **9a** at different concentration of NaCl (aq.) as a function of time.

Analysis of BDPA-decomposition products

To detect dimerization, we investigated the decomposition of **9a** in water by HRMS (ESI). **Figure S31** shows a mass spectrum of **9a** in water at 23 °C after 48 h. Formation of a major peak (m/z 560.6397) was observed which can only originate through dimerization of **9a**. The mass is triply charged, possibly due to the presence of eight ammonium cations and two carboxylate anions in the dimeric structure along with three counter anions (NO_3^-). We speculate that the dimer is formed in a similar fashion as the Gomberg radical through a σ-bond formation between two radicals,[3] followed by oxidation/H_2 elimination. A putative structure of the dimer ($C_{100}H_{118}N_{11}O_{13}^{3+}$; m/z 560.6309) is shown in **Figure S31**.

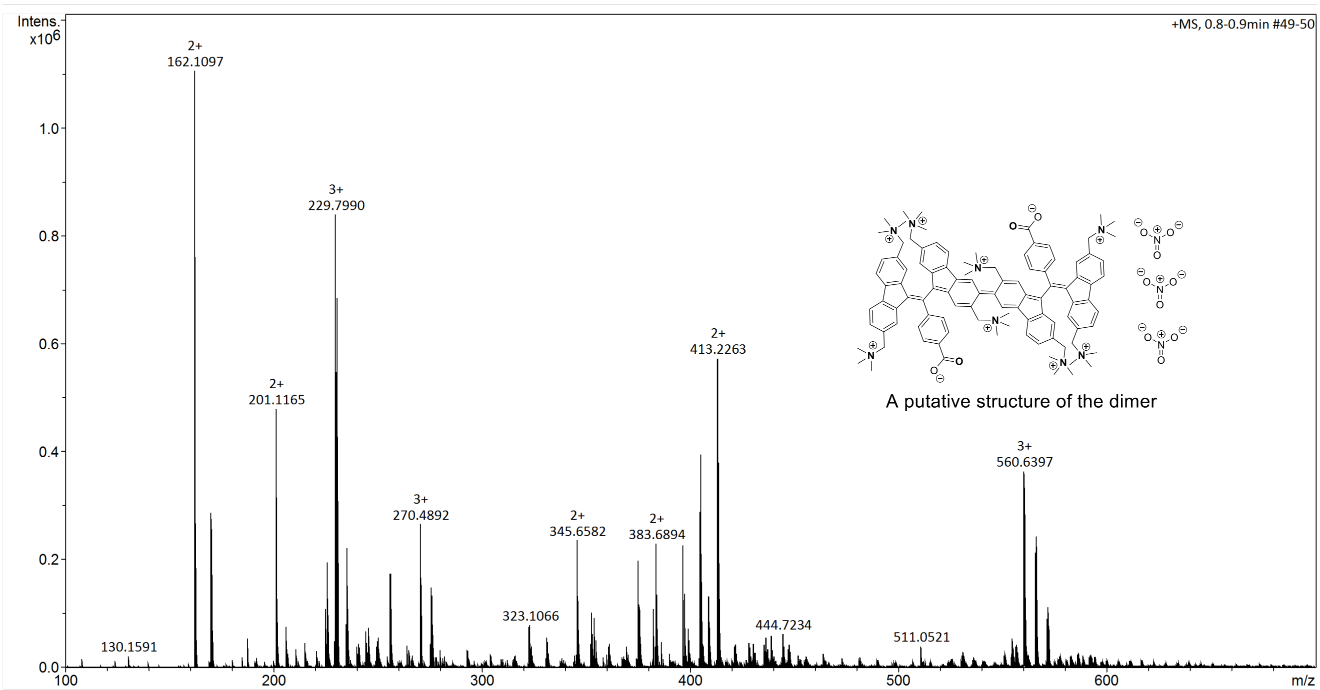


Figure S31. The HRMS (ESI) spectrum of radical **9a** in water (5 mM) kept for 48 h at 23 °C, recorded in a positive-ion mode. All the masses in the spectrum originate from the sample.

References:

1. C. M. G. Henríquez, L. H. Tagle, C. A. Terraza, A. B. González, A. L. Cabrera and U. G. Volkmann, *J. Appl. Polym. Sci.*, 2012, **125**, 477-487.
2. S. Mandal and S. T. Sigurdsson, *Chem. Eur. J.*, 2020, **26**, 7486-7491.
3. H. Lankamp, W. T. Nauta and C. MacLean, *Tetrahedron Lett.*, 1968, **9**, 249-254.