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

Electronic Supplementary Information for: Effect of head group size on the photoswitching applications of azobenzene disperse-red 1 analogues

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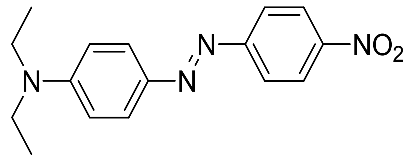
Material Syntheses

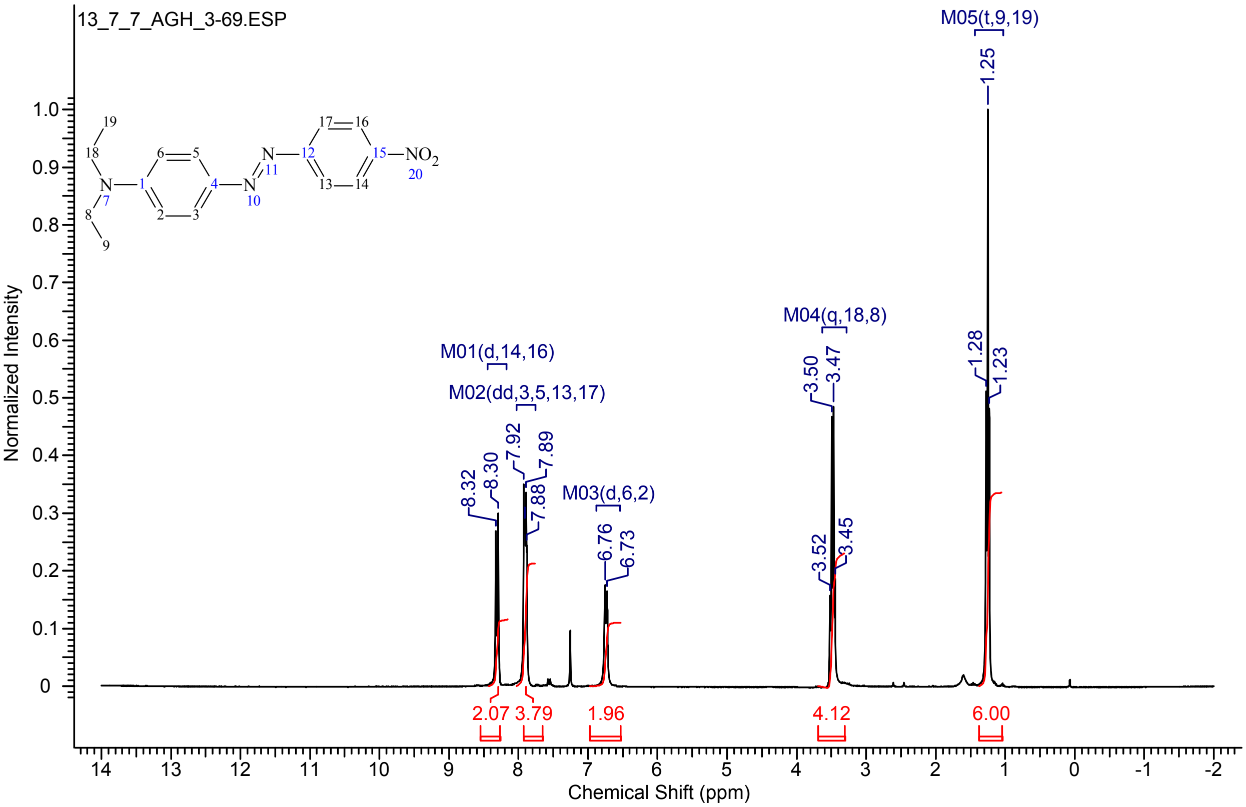
With the goal of keeping these syntheses as facile as possible in the mildest conditions allowable, all reactions except for Sonogashira couplings (dry solvent, nitrogen atmosphere) were conducted under atmospheric conditions at room temperature. ^{1}H NMR spectra were acquired at 300 K, on a Varian-Mercury 300 MHz or 400 MHz spectrometer while ^{13}C NMR spectra were acquired on a Varian-Mercury 300 MHz NMR. Chemical shifts are reported in ppm on the δ-scale using either the solvent signal for reference or internal TMS standard. High resolution mass spectrometry (HR-MS) was acquired on a Thermo Scientific Exactive Plus Orbitrap. Samples were ionized using either atmospheric-pressure chemical ionization (APCI) or electrospray ionization (ESI). All observed ions in positive and negative ionization modes are reported. All chemicals were obtained from Sigma-Aldrich corporation (St. Louis, MO, USA), with the exception of trimethylsilylacetylene which was obtained from Oakwood Chemicals (West Columbia, SC, USA).

Synthesis of N,N-diethyl-4-((4-nitrophenyl)diazenyl)aniline (Compound 2)

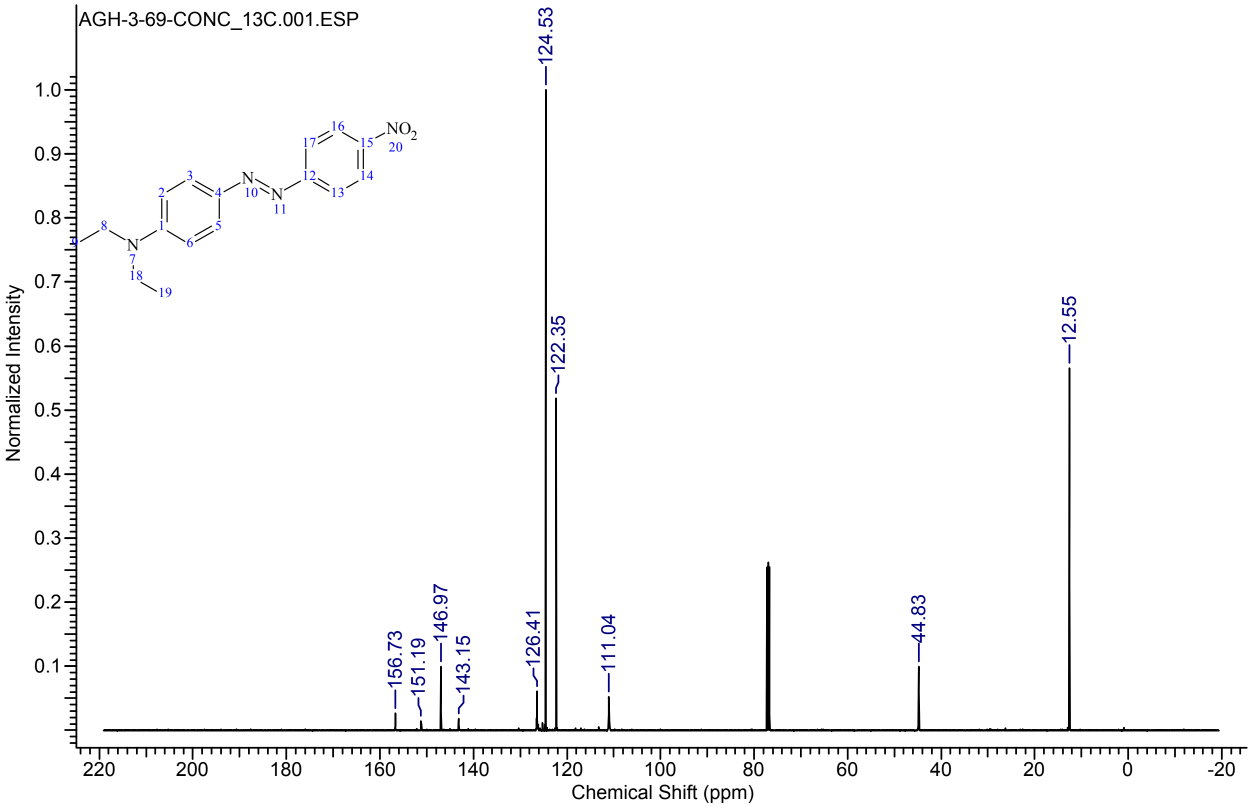


In a 250 mL round-bottom flask containing a stir bar, 100 mL water and 50 mL acetone was set to cool in an ice bath. Once the solvent temperature was below 5 °C, 1.38 g of *p*-nitroaniline (10 mmol, 1 eq.) was added and dissolved, forming an orange/brown solution after which 0.69 g of sodium nitrite (10 mmol, 1.2 eq.) and 1.8 mL concentrated HCl (20 mmol, 2 eq.) were added. This solution was stirred to form the reactive diazonium intermediate for 30 minutes after which 1.6 mL of N,N-diethylaniline was added (10 mmol, 1 eq.). The solution rapidly turned red and was left to react for 2 hours, after which the acetone was removed under reduced pressure and the aqueous solution was extracted with 150 mL ethyl acetate. The organic phase was washed oncewith 100 mL water then once with 100 mL brine, dried with $MgSO_4$, filtered, and evaporated. No further purification was necessary. Yield: 2.2 g, 74%.

^{1}H NMR (300 MHz, chloroform-*d*) δ ppm 1.25 (t, *J*=7.03 Hz, 6 H), 3.48 (q, *J*=7.03 Hz, 4 H), 6.74 (d, *J*=8.50 Hz, 2 H), 7.90 (m, *J*=8.79, 8.50 Hz, 4 H), 8.31 (d, *J*=8.79 Hz, 2 H).

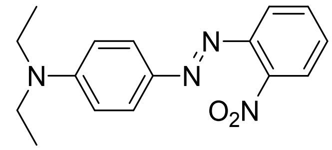


^{13}C NMR (300 MHz, chloroform-*d*) δ ppm 156.7, 151.2, 147.0, 143.2, 126.4, 124.5, 122.4, 111.0, 44.8, 12.6.



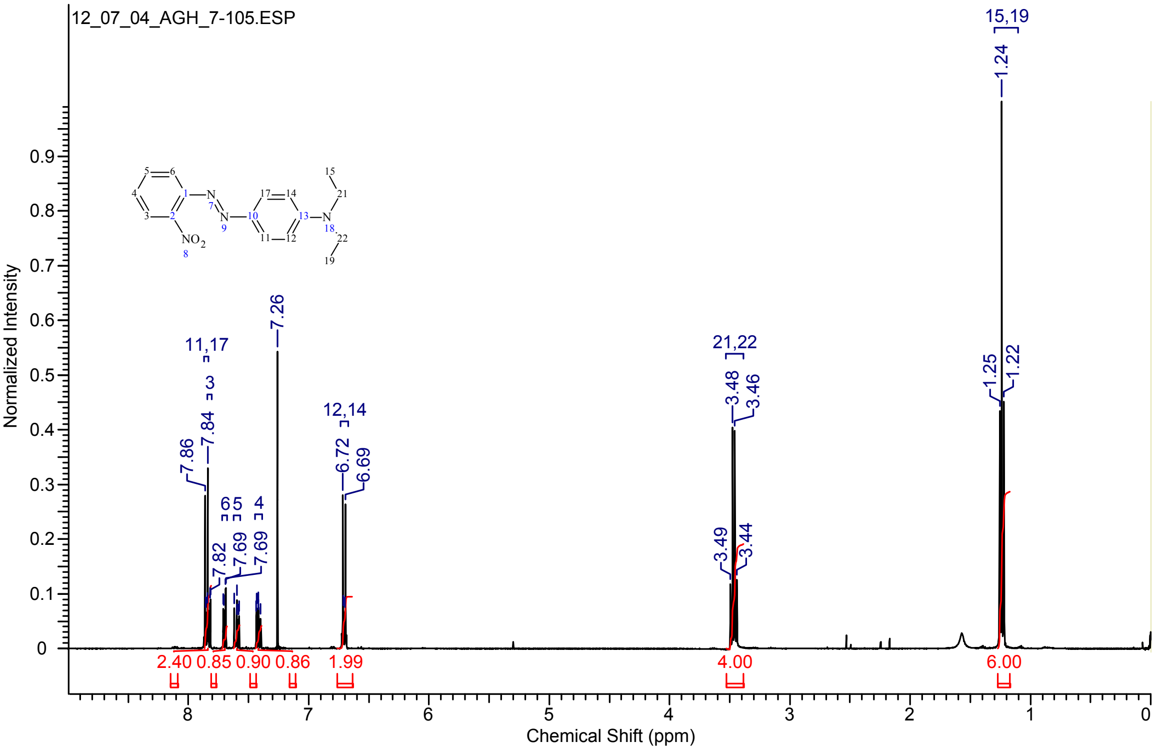
HR-MS (APCI, 4 kV): *m/z* Calculated for $C_{16}H_{19}N_4O_2$ $[M+H]^+$: 299.1503, found: 299.1502.

Synthesis of N,N-diethyl-4-((2-nitrophenyl)diazenyl)aniline (Compound 3)

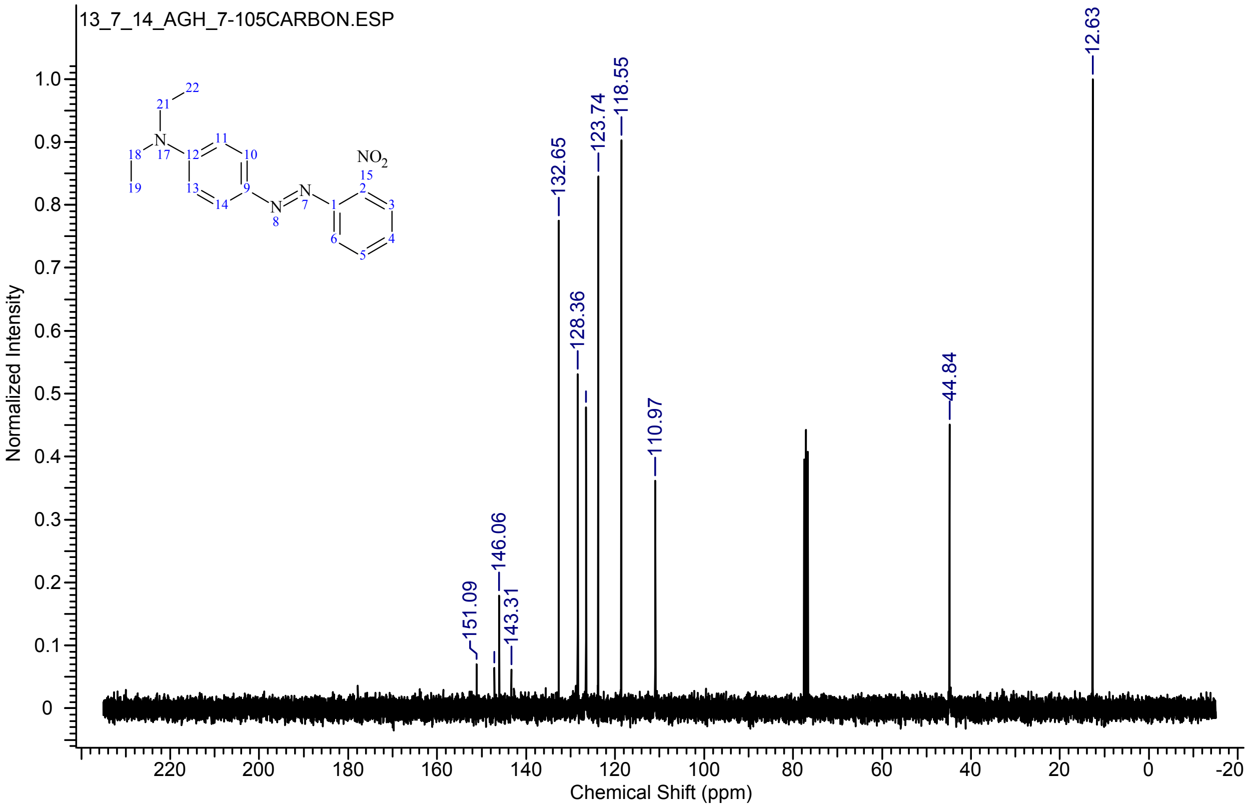


In a 250 mL round-bottom flask containing a stir bar, 1.38 g of 2-nitroaniline (10 mmol, 1 eq.) was dissolved in 100 mL water and 50 mL acetone to form a red solution. 0.69 g of sodium nitrite (10 mmol, 1 eq.) and 1.7 mL concentrated HCl (20 mmol, 2 eq.) were then added. This solution was stirred for 30 minutes to form the reactive diazonium intermediate after which 1.6 mL of N,N-diethylaniline was added (10 mmol, 1 eq.). The solution rapidly turned deep red and was left to react for 2 hours, after which the acetone was removed under reduced pressure, and the aqueous solution was extracted with 100 mL ethyl acetate. The organic phase was washed twice with 100 mL water then 100 mL brine, dried with $MgSO_4$, filtered, and evaporated. No further purification was necessary. Yield: 2.51 g, 84%.

^{1}H NMR (400 MHz, chloroform-*d*) δ ppm 7.81–7.87 (m, 3 H), 7.70 (dd, *J*=8.01, 1.37 Hz, 1 H), 7.60 (ddd, *J*=8.21, 7.23, 1.37 Hz, 1 H), 7.39–7.44 (m, 1 H), 6.64–6.76 (m, 2 H), 3.47 (q, *J*=7.29 Hz, 4 H), 1.24 (t, *J*=7.03 Hz, 6 H).

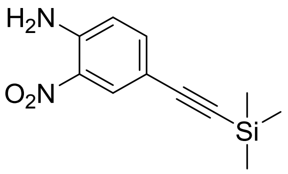


^{13}C NMR (300 MHz, chloroform-*d*) δ ppm 151.1, 147.1, 146.1, 143.3, 132.7, 128.4, 126.5, 123.7, 118.6, 111.0, 44.8, 12.6.



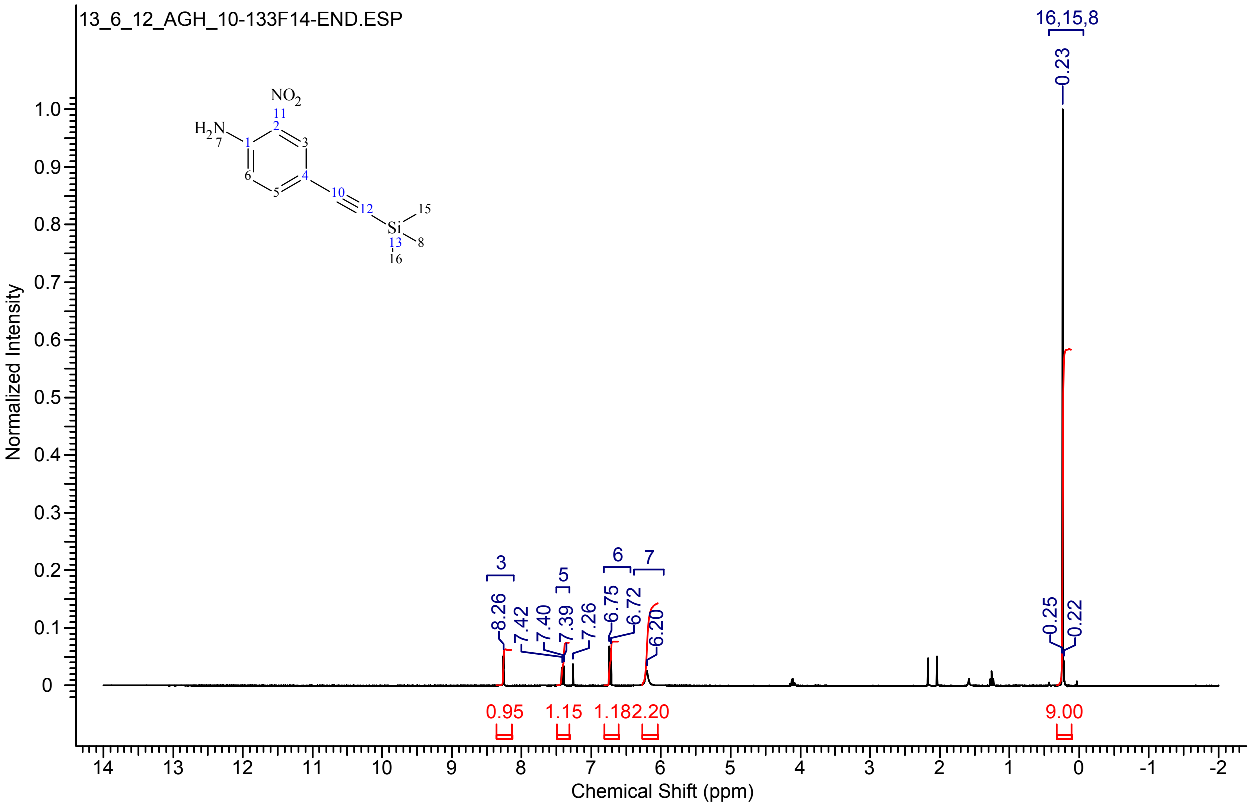
HR-MS (APCI, 4 kV): *m/z* Calculated for $C_{16}H_{18}N_4O_2$ $[M+H]^+$: 299.1503; found: 299.1501. Calculated for $C_{16}H_{19}N_4O_2$ $[M]^-$: 298.1408; found: 298.1420.

Synthesis of 2-nitro-4-((trimethylsilyl)ethynyl)aniline (Compound 4a)

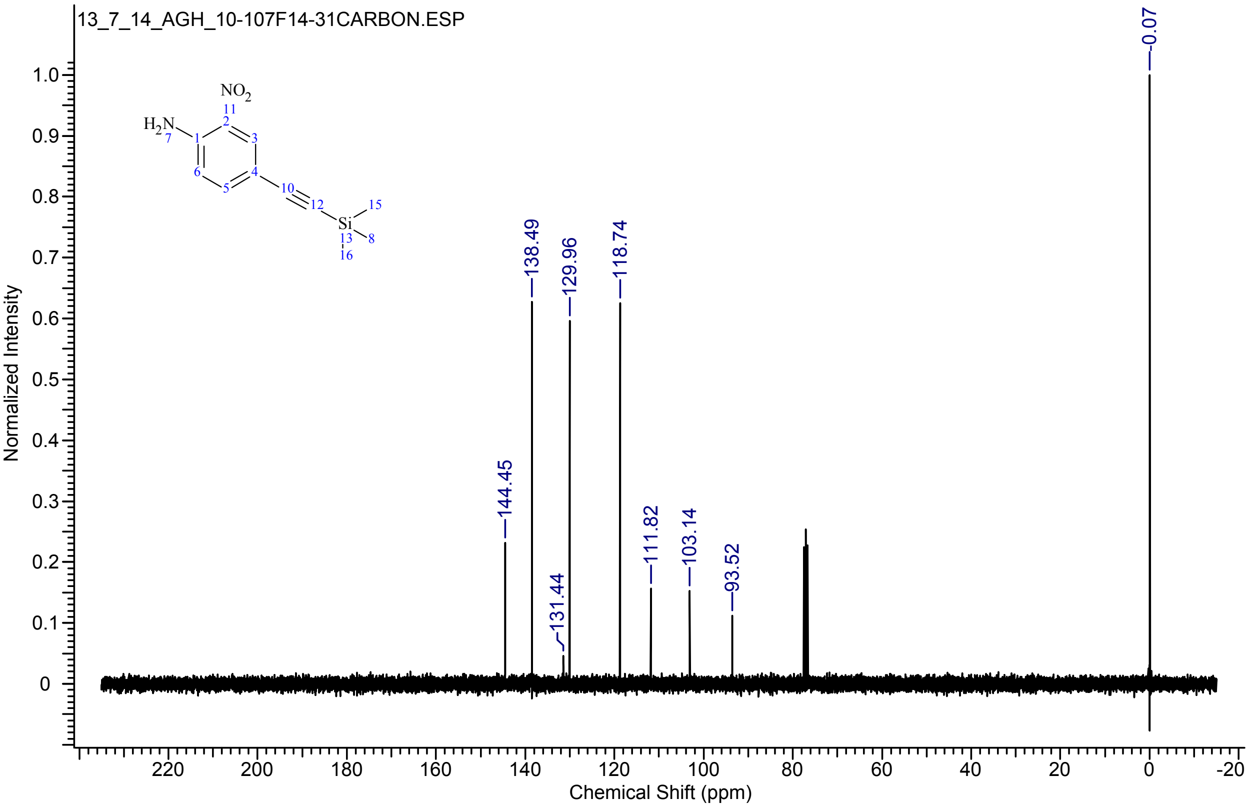


In a 250 mL round-bottom flask containing a stir bar, 2.64 g of 4-iodo-2-nitroaniline (10 mmol, 1 eq.), 0.351 g $PdCl_2(PPh_3)_2$ (0.05 mmol, 0.005 eq.) and 9 mg CuI (0.05 mmol, 0.005 eq.) were dissolved in 80 mL dry THF and 40 mL dry triethylamine, forming a brown solution. The flask was capped with a septum and the solution purged with nitrogen for 30 minutes. Under a blanket of nitrogen, 2.2 mL trimethylsilylacetylene (12 mmol, 1.2 eq.) was injected. The solution was left to stir for 16 hours, at which point it was a dark solution with grey precipitate. The solution was filtered through a celite plug, rinsed with ethyl acetate and concentrated under reduced pressure to ~60 mL. The concentrate was transferred to a separatory funnel and washed twice with 150 mL water, once with saturated 100 mL NH_4Cl solution, once with 150 mL brine, dried with Na_2SO_4, filtered, and the solvent removed under reduced pressure. The crude product was purified by silica gel chromatography, 0 to 60% ethyl acetate in hexane. Yield: 1.92 g, 82%.

^{1}H NMR (300 MHz, chloroform-*d*) δ ppm 8.26 (d, *J*=1.76 Hz, 1 H), 7.41 (dd, *J*=8.64, 1.90 Hz, 1 H), 6.73 (d, *J*=8.50 Hz, 1 H), 6.20 (br. s., 2 H), 0.23 (s, 9 H).

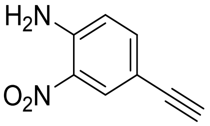


^{13}C NMR (300 MHz, chloroform-*d*) δ ppm 144.5, 138.5, 131.4, 130.0, 118.7, 111.8, 103.1, 93.5, -0.1.



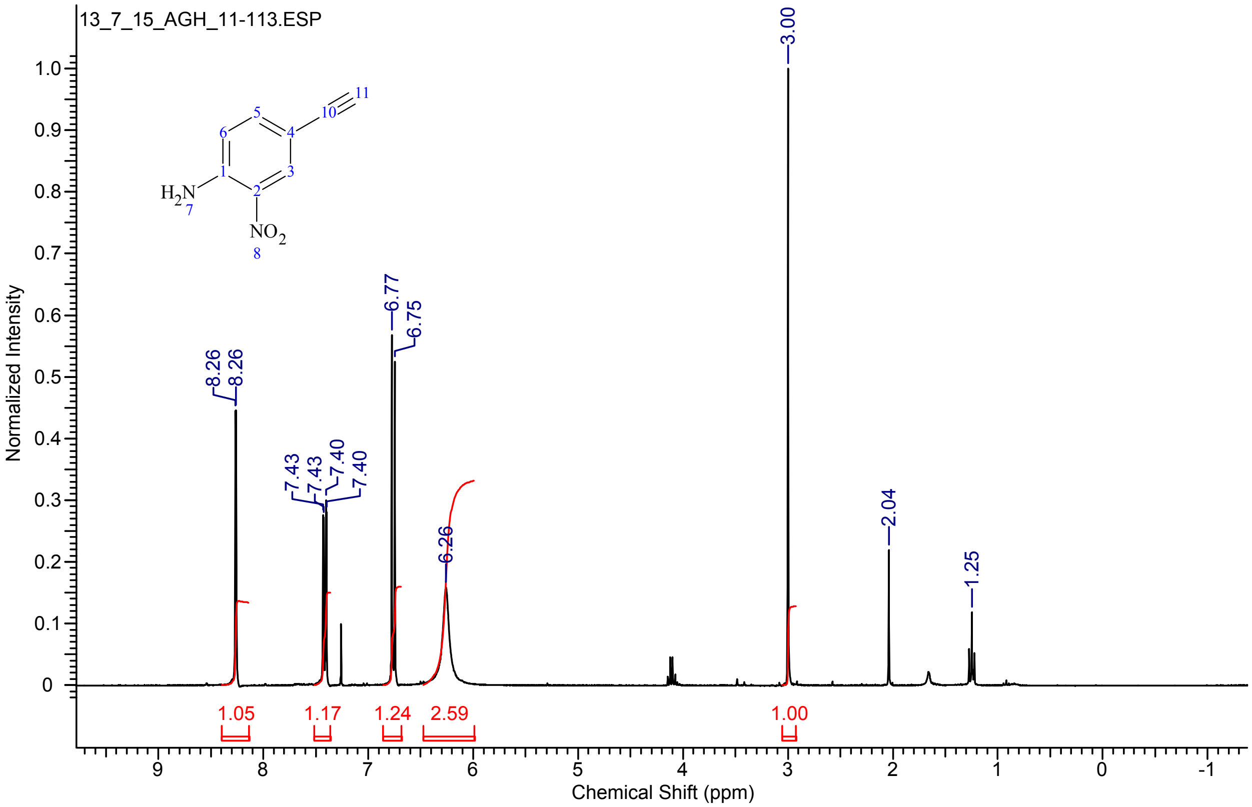
HR-MS (APCI, 4 kV): *m/z* Calculated for $C_{11}H_{13}N_2O_2Si$ $[M-H]^-$: 233.0752; found: 233.0748.

Synthesis of 2-nitro-4-((trimethylsilyl)ethynyl)aniline (Compound 4b)

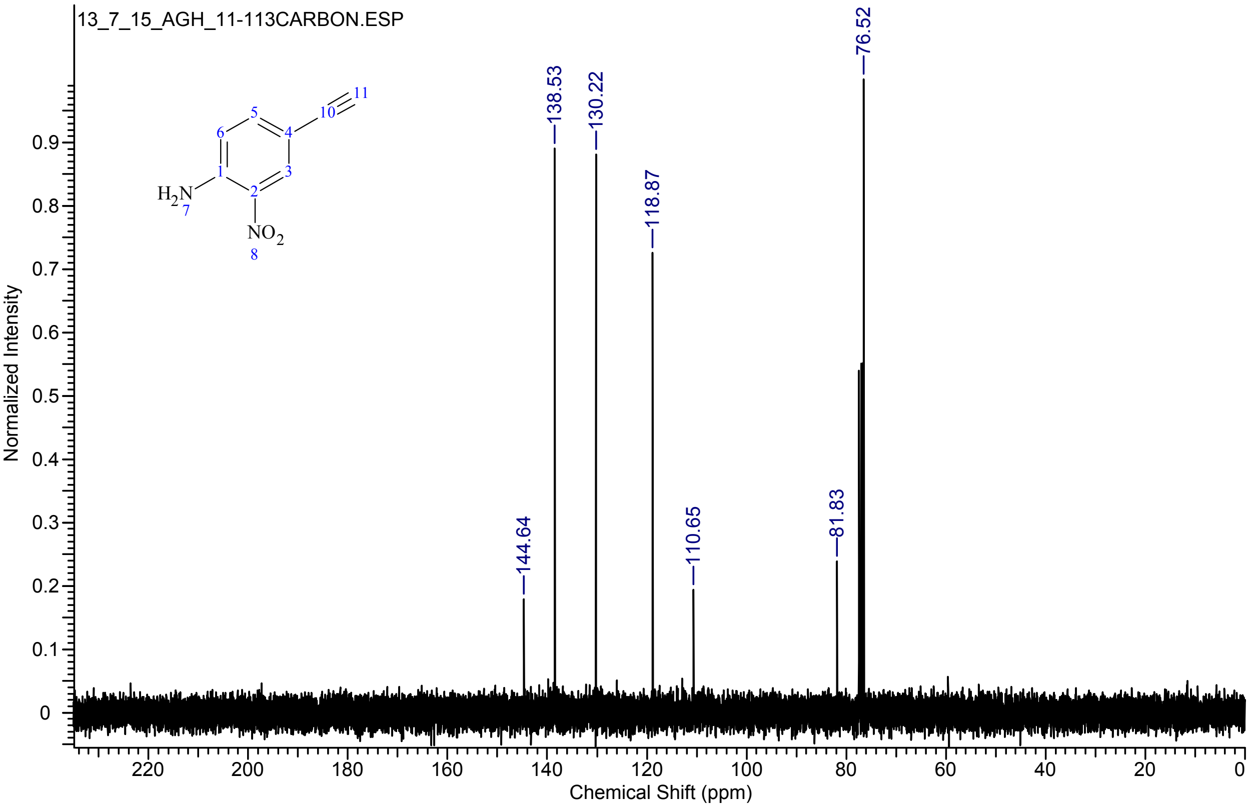


In a 100 mL round-bottom flask containing a stir bar, 0.384 g of 2-nitro-4-((trimethylsilyl)ethynyl)aniline (Compound **4a**, 1.64 mmol, 1 eq.) was dissolved in 30 mL CH_2Cl_2 and 20 mL methanol, followed by the addition of 1.13 g K_2CO_3 (8.2 mmol, 5 eq.). The solution was left to stir 16 hours after which it was filtered on a plug of celite, rinsed with ethyl acetate and concentrated under reduced pressure. The concentrated product was dissolved in 50 mL ethyl acetate and washed twice with 50 mL water and once with 50 mL brine, after which the organic phase was dried with Na_2SO_4, and filtered. Once the solvent was evaporated, the product was pure for further use. Yield: 0.26 g, 96%.

^{1}H NMR (300 MHz, chloroform-*d*) δ ppm 8.29 (d, *J*=1.76 Hz, 1 H), 7.43 (dd, *J*=8.79, 1.76 Hz, 1 H), 6.76 (d, *J*=8.79 Hz, 1 H), 6.21 (br. s., 2 H), 3.00 (s, 1 H).

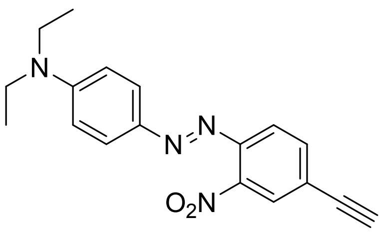


^{13}C NMR (300 MHz, chloroform-*d*) δ ppm 144.6, 138.5, 130.2, 118.9, 110.7, 81.8, 76.5.



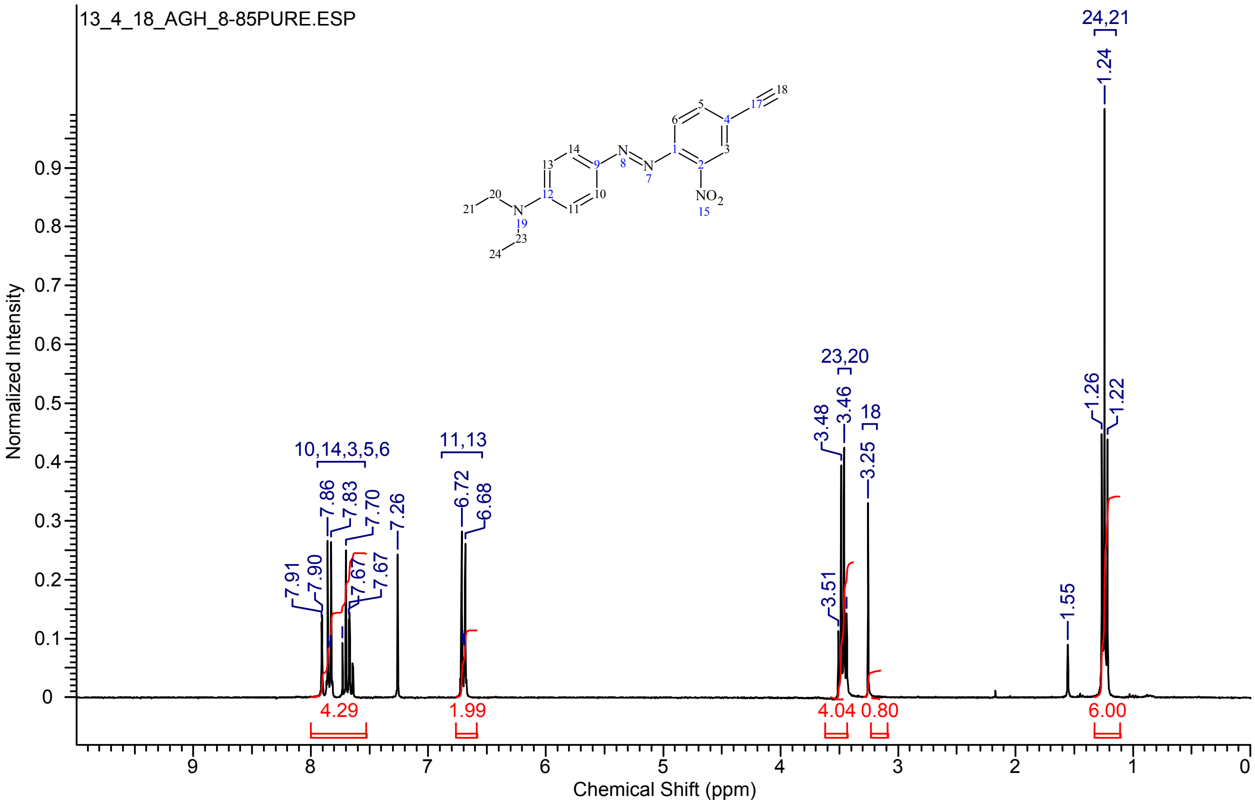
HR-MS (ESI, 4 kV): *m/z* Calculated for $C_8H_7N_6O_2$ $[M+H]^+$:163.0502; found: 163.0501. Calculated for $C_8H_5N_2O_2$ $[M-H]^-$:161.0357; found: 161.0348.

Synthesis of N,N-diethyl-4-((4-ethynyl-2-nitrophenyl)diazenyl)aniline (Compound 4)



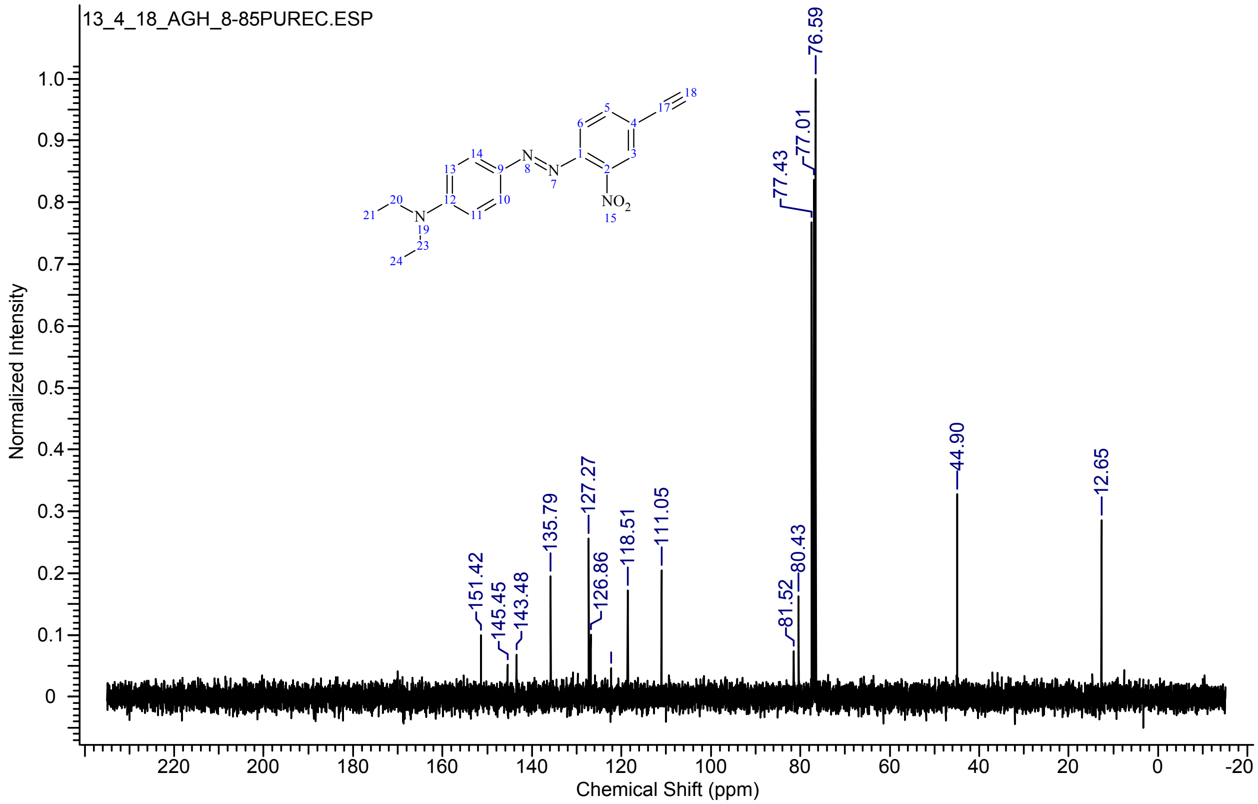
In a 250 mL round-bottom flask containing a stir bar, 40 mL acetone and 80 ml water was set to cool in an ice bath. Once the solvent temperature was below 5 °C, 0.056 g of 2-nitro-4-((trimethylsilyl)ethynyl)aniline (Compound **4b**, 0.34 mmol, 1 eq.) was added, forming a deep red solution, after which 26 mg of sodium nitrite (0.38 mmol, 1.2 eq.) and 750 µL 1 M HCl (0.75 mmol, 2.4 eq.) were added. This solution was stirred to form the reactive diazonium intermediate for 30 minutes after which 60 µL of N,N-diethylaniline was added (0.37 mmol, 1.2 eq.). The solution rapidly turned red and was left to react for 2 hours. The acetone was removed under reduced pressure and the product extracted from the aqueous solution with 50 mL ethyl acetate. The organic phase was washed twice with 100 mL water, once with 100 mL brine, dried with $MgSO_4$, filtered, and evaporated. The crude product was purified by silica gel chromatography, 0 to 60% ethyl acetate in hexane. The azo product co-elutes with unreacted 2-nitro-4-((trimethylsilyl)ethynyl)aniline which was removed by dissolving the crude in 20 mL THF with a trace of DMAP and adding an excess of di-*tert*-butyl dicarbonate until the reaction was complete by TLC. The solvent was removed and the product purified on a short silica column, 0 to 60% ethyl acetate in hexane. Yield: 0.054 g, 49%.

^{1}H NMR (300 MHz, chloroform-*d*) δ ppm 7.91 (d, *J*=1.76 Hz, 1 H), 7.80–7.87 (m, 2 H), 7.53–7.78 (m, 2 H), 6.70 (d, *J*=9.38 Hz, 2 H), 3.47 (q, *J*=7.23 Hz, 4 H), 3.25 (s, 1 H), 1.24 (t, *J*=7.03 Hz, 6 H).



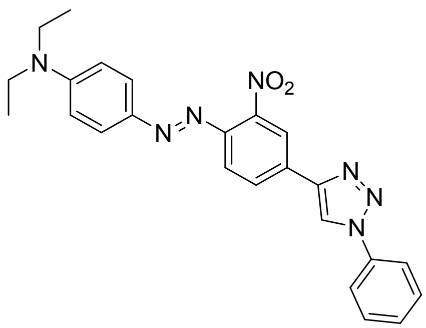
^{13}C NMR (300 MHz, chloroform-*d*) δ ppm 151.4, 147.1, 145.5, 143.5, 135.8, 127.3, 126.9, 122.3, 118.5, 111.1, 81.5, 80.4, 44.9, 12.7.

^{13}C NMR (300 MHz, chloroform-*d*) δ ppm 151.4, 145.5, 143.5, 135.8, 127.3, 126.9, 122.3, 118.5, 111.1, 81.5, 80.4, 44.9, 12.7.



HR-MS (APCI, 4 kV): *m/z* Calculated for $C_{18}H_{19}N_4O_2$ $[M+H]^+$: 323.1503; found: 323.1511.

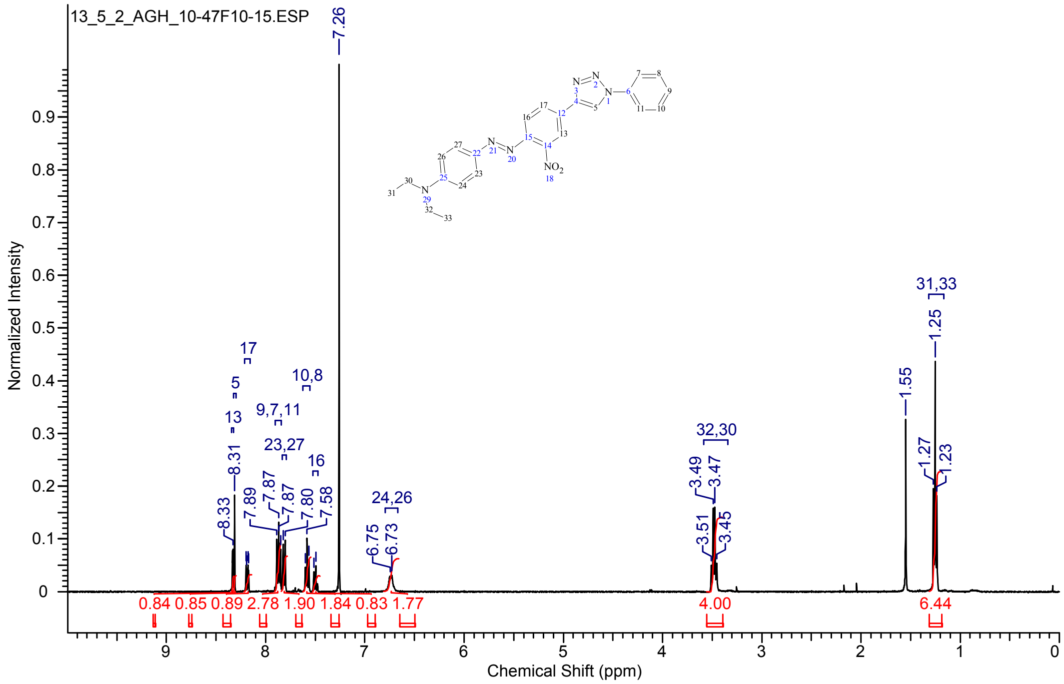
Synthesis of N,N-diethyl-4-((2-nitro-4-(1-phenyl-1H-1,2,3-triazol-4-yl)phenyl)diazenyl)aniline (Compound 5)



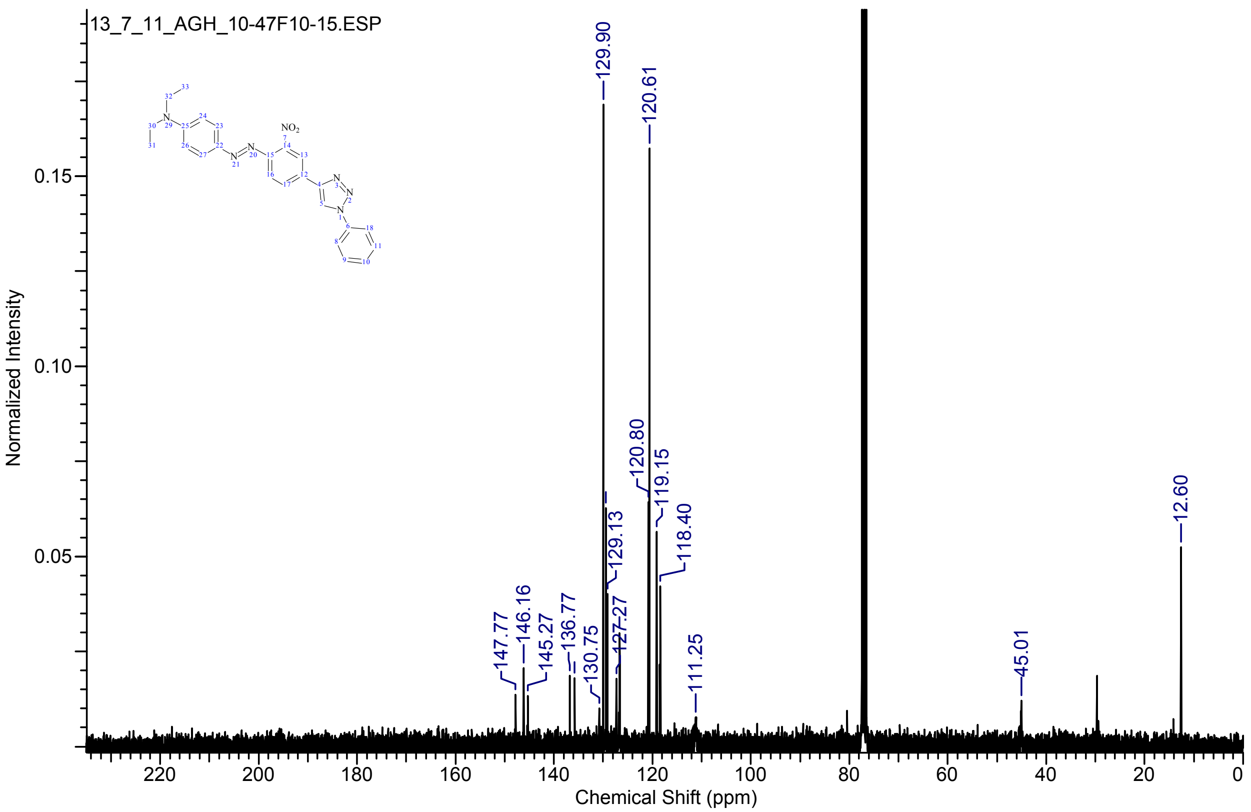
In a 100 mL round-bottom flask containing a stir bar, 0.096 g N,N-diethyl-4-((4-ethynyl-2-nitrophenyl)diazenyl)aniline (Compound **4**, 0.29 mmol, 1 eq.), 41 mg CuBr (0.29 mmol, 1 eq.), 114 mg sodium ascorbate (0.58 mmol, 2 eq.) and 60 µL *N*,*N*,*N*′,*N*′,*N*″-

pentamethyldiethylenetriamine (PMDTA) (0.29 mmol, 1 eq.) were dissolved in 20 mL DMF. After the reactants were dissolved, 103 mg phenyl azide (0.87 mmol, 3 eq.) was added and the solution was left to stir 16 hours. The red solution was concentrated to ~10 mL, added to a separatory funnel with 60 mL water and extracted twice with 50 mL ethyl acetate. The red organic extractions were combined and washed in sequence with 80 mL water, 80 mL saturated NH_4Cl, and 80 mL brine. The organic phase was dried with magnesium sulfate, filtered, and evaporated. The crude product was purified by silica gel chromatography, 0 to 100% ethyl acetate in hexane. Yield: 0.081 g, 64%.

^{1}H NMR (400 MHz, chloroform-*d*) δ ppm 8.33 (d, *J*=1.56 Hz, 1 H), 8.31 (s, 1 H), 8.19 (dd, *J*=8.40, 1.76 Hz, 1 H), 7.84–7.91 (m, 3 H), 7.81 (d, *J*=7.42 Hz, 2 H), 7.54–7.63 (m, 2 H), 7.50 (d, *J*=7.03 Hz, 1 H), 6.74 (d, *J*=7.42 Hz, 2 H), 3.48 (q, *J*=7.03 Hz, 4 H), 1.25 (t, *J*=7.03 Hz, 6 H).

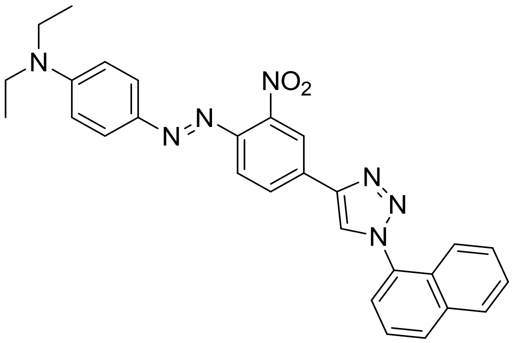


^{13}C NMR (300 MHz, chloroform-*d*) δ ppm 147.8, 146.2, 145.3, 136.8, 135.8, 130.8, 129.9, 129.4, 129.1, 127.3, 126.7, 120.8, 120.6, 119.2, 118.4, 111.3, 45.0, 12.6.



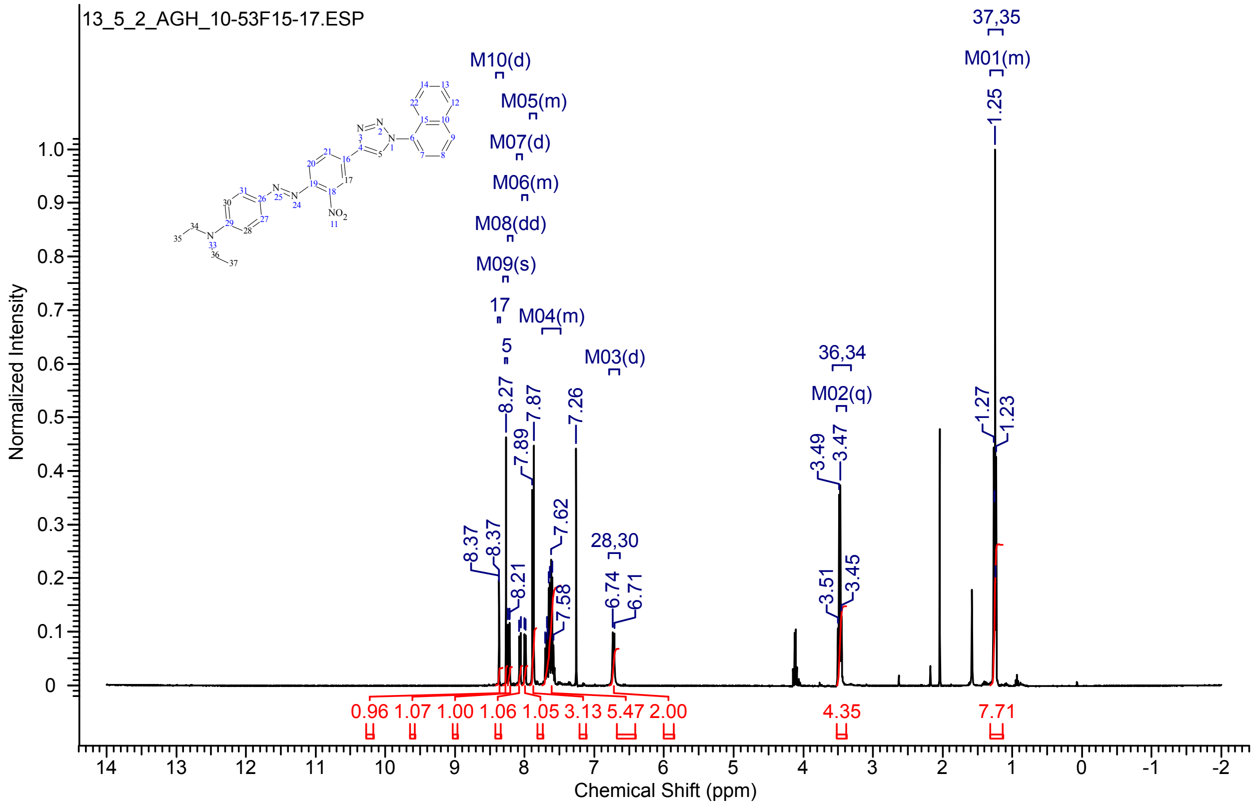
HR-MS (APCI, 4 kV): *m/z* Calculated for $C_{24}H_{24}N_7O_2$ $[M+H]^+$: 442.1986; found: 442.1990. Calculated for $C_{24}H_{24}N_7O_2$ $[M]^-$: 441.1908; found: 441.1907.

Synthesis of N,N-diethyl-4-((4-(1-(naphthalen-1-yl)-1H-1,2,3-triazol-4-yl)-2-nitrophenyl)diazenyl)aniline (Compound 6)

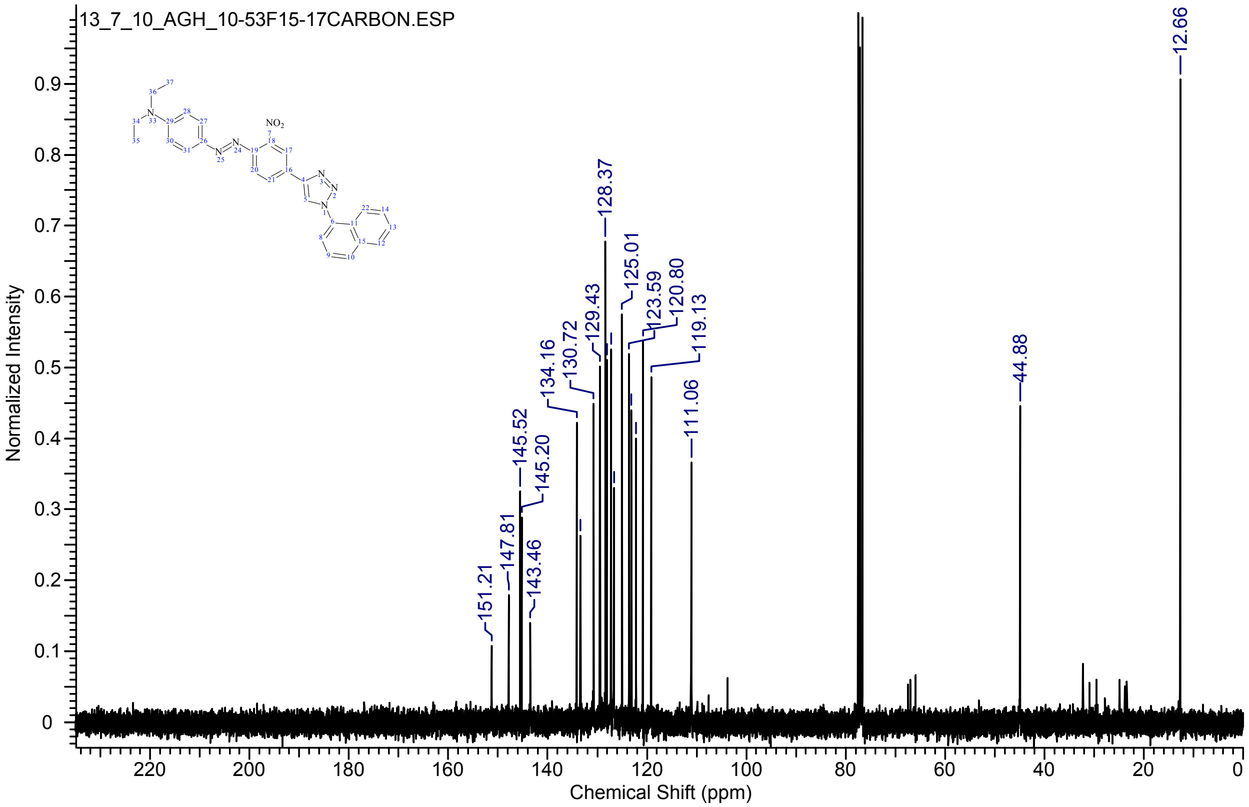


In a 100 mL round-bottom flask containing a stir bar, 0.096 g N,N-diethyl-4-((4-ethynyl-2-nitrophenyl)diazenyl)aniline (Compound **4**, 0.29 mmol, 1 eq.), 41 mg CuBr (0.29 mmol, 1 eq.), 114 mg sodium ascorbate (0.58 mmol, 2 eq.) and 60 µL PMDTA (0.29 mmol, 1 eq.) were dissolved in 20 mL DMF. After the reactants were dissolved, 147 mg 1-azido-naphtalene (0.87 mmol, 3 eq.) was added and the solution was left to stir 16 hours. The red DMF solution was concentrated to ~10 mL, added to a separatory funnel with 60 mL water and extracted twice with 50 mL ethyl acetate. The red organic extractions were combined and washed in sequence with 80 mL water, 80 mL saturated NH_4Cl, and 80 mL brine. The organic phase was dried with magnesium sulfate, filtered, and evaporated. The crude product was purified by silica gel chromatography, 0 to 100% ethyl acetate in hexane. Yield: 0.081 g, 57%.

^{1}H NMR (400 MHz, chloroform-*d*) δ ppm 8.37 (d, *J*=1.95 Hz, 1 H), 8.27 (s, 1 H), 8.23 (dd, *J*=8.40, 1.76 Hz, 1 H), 8.07 (d, *J*=7.82 Hz, 1 H), 7.96–8.04 (m, 1 H), 7.88 (m, *J*=8.60 Hz, 3 H), 7.48–7.75 (m, 5 H), 6.73 (d, *J*=8.99 Hz, 2 H), 3.48 (q, *J*=7.16 Hz, 4 H), 1.14–1.32 (m, 6 H).

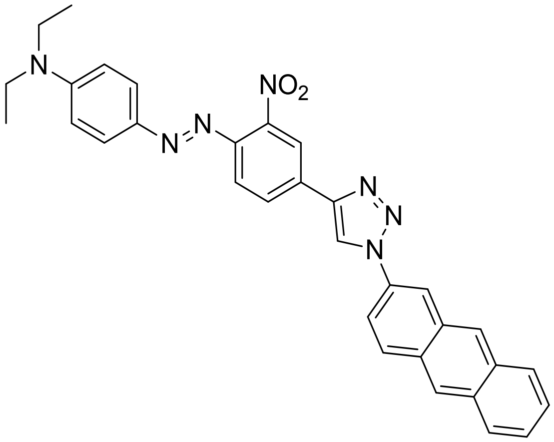


^{13}C NMR (300 MHz, chloroform-*d*) δ ppm 151.2, 147.8, 145.5, 145.2, 143.5, 134.2, 133.3, 130.7, 129.4, 128.4, 128.1, 127.2, 126.7, 125.0, 123.6, 123.1, 122.2, 120.8, 119.1, 111.1, 44.9, 12.7.



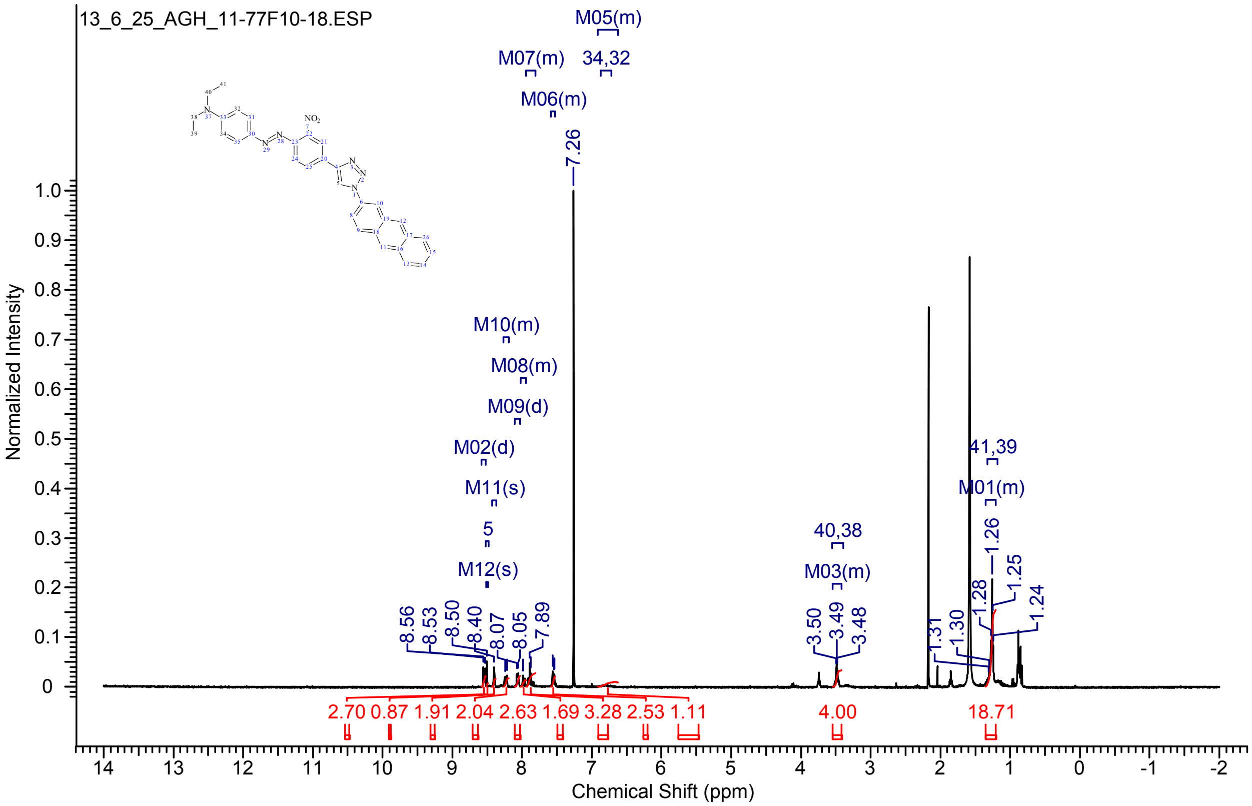
HR-MS (APCI, 4 kV): *m/z* Calculated for $C_{28}H_{26}N_7O_2$ $[M+H]^+$: 492.2154; found: 492.2148. Calculated for $C_{28}H_{25}N_7O_2$ $[M]^-$: 491.2075; found: 491.2056.

Synthesis of 4-((4-(1-(anthracen-2-yl)-1H-1,2,3-triazol-4-yl)-2-nitrophenyl)diazenyl)-N,N-diethylaniline (Compound 7)



In a 100 mL round-bottom flask containing a stir bar, 0.096 g N,N-diethyl-4-((4-ethynyl-2-nitrophenyl)diazenyl)aniline (Compound **4**, 0.29 mmol, 1 eq.), 41 mg CuBr (0.29 mmol, 1 eq.), 114 mg sodium ascorbate (0.58 mmol, 2 eq.) and 60 µL PMDTA (0.29 mmol, 1 eq.) were dissolved in 20 mL DMF. After the reactants were dissolved, 190 mg 2-azido-anthracene (0.87 mmol, 3 eq.) was added and the solution was left to stir 16 hours. The red DMF solution was concentrated to ~10 mL, added to a separatory funnel with 60 mL water and extracted twice with 50 mL ethyl acetate. The red organic extractions were combined and washed in sequence with 80 mL water, 80 mL saturated NH_4Cl, and 80 mL brine. The organic phase was dried with magnesium sulfate, filtered, and evaporated. The crude product was purified by silica gel chromatography, 0 to 100% ethyl acetate in hexane. Yield: 0.021 g, 18%.

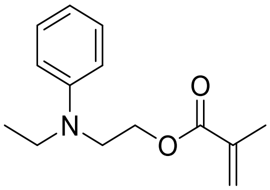
^1H NMR (400 MHz, chloroform-*d*) δ ppm 8.55 (d, *J*=10.55 Hz, 1 H), 8.50 (s, 1 H), 8.40 (s, 2 H), 8.19–8.27 (m, 2 H), 8.06 (d, *J*=9.38 Hz, 2 H), 7.94–8.02 (m, 2 H), 7.81–7.94 (m, 3 H), 7.52–7.59 (m, 2 H), 6.62–6.91 (m, 2 H), 3.42–3.55 (m, 4 H), 1.21–1.35 (m, 6 H).



Due to insufficient solubility, a ^{13}C NMR spectrum was unattainable.

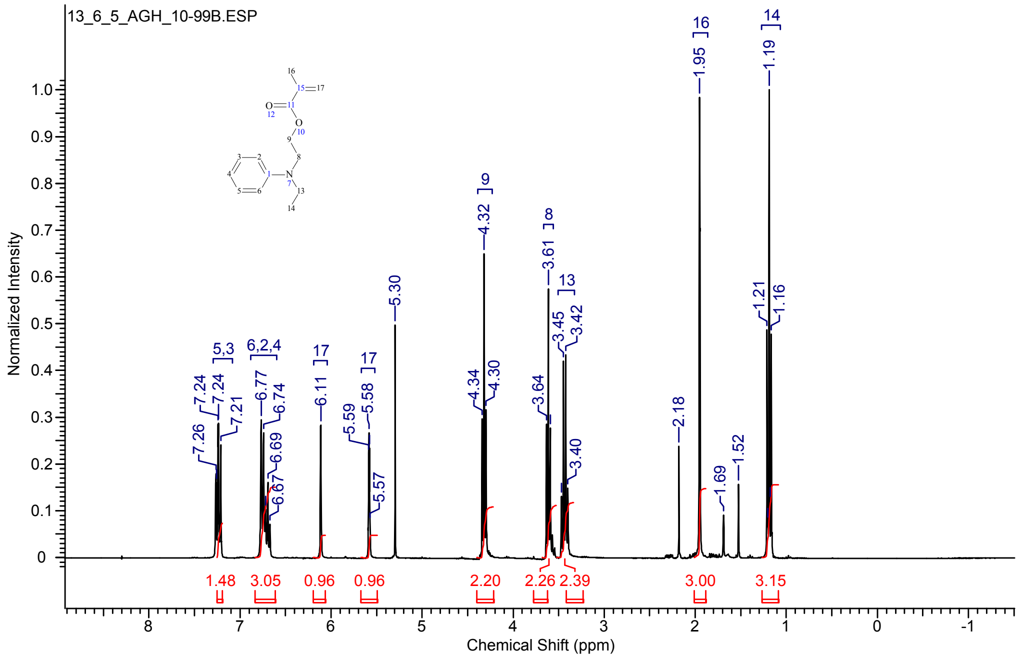
HR-MS (APCI, 4 kV): *m/z* Calculated for $C_{32}H_{28}N_7O_2$ $[M+H]^+$: 542.2305; found: 542.2298. Calculated for $C_{32}H_{27}N_7O_2$ $[M]^-$: 541.2221; found: 541.2206.

Synthesis of 2-(ethyl(phenyl)amino)ethylmethacrylate (Compound 8a)

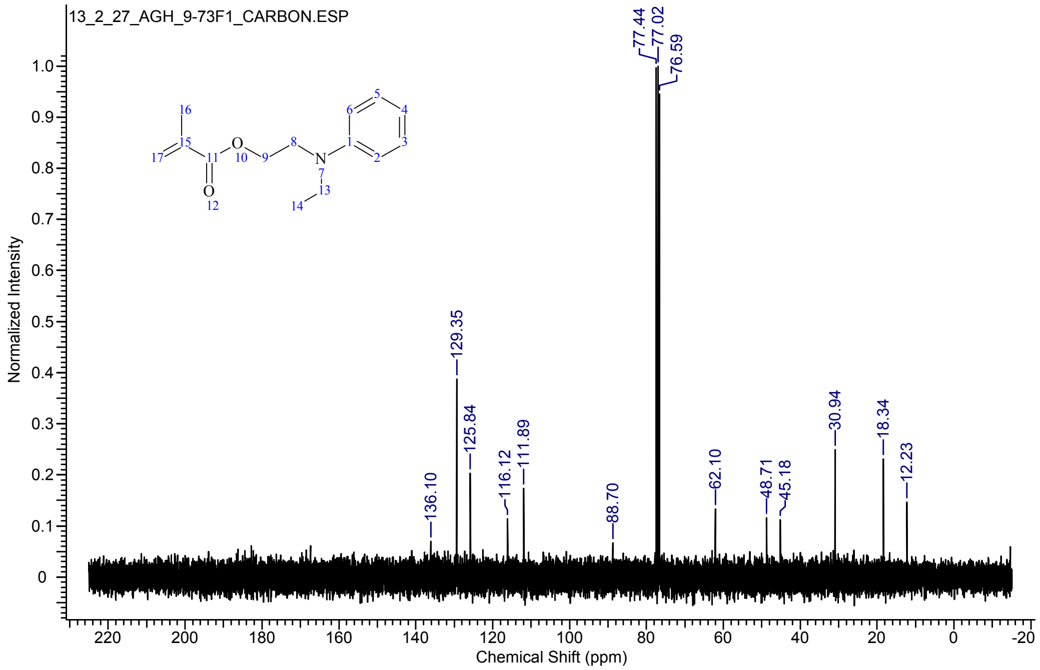


In a 1 L round-bottom flask containing a stir bar, 500 mL CH_2Cl_2 was set to cool in an ice bath. Once cool, 17.9 g of N-ethyl aniline ethanol (108.4 mmol, 1 eq.) was added and dissolved, followed by the addition of 50 mL triethylamine, forming a clear blue solution. In a dropping funnel above the reaction flask, 16.8 mL methacryloyl chloride (173 mmol, 1.6 eq.) was dissolved in 200 mL CH_2Cl_2 and added dropwise to the cooled reaction flask. Within an hour, the solution started turning red. After 3 hours the reaction mixture was concentrated to 200 mL and washed with 200 mL water four times. The organic phase was transferred to a 500 mL round bottom flask and stirred with 100 mL 5 wt% NaOH for one hour, to remove unreacted methacryloyl chloride. The mixture was transferred to a separatory funnel and the aqueous phase discarded. The red organic phase was washed with two portions of 100 mL water and then 100 mL brine, dried with $MgSO_4$, filtered, and evaporated. The pure monomer was separated from starting material by running through a short silica plug with CH_2Cl_2. Yield: 22.1 g, 86%.

^{1}H NMR (300 MHz, chloroform-*d*) δ ppm 7.19–7.25 (m, 2 H), 6.61–6.84 (m, 3 H), 6.11 (s, 1 H), 5.58 (s, 1 H), 4.32 (t, *J*=6.45 Hz, 2 H), 3.61 (t, *J*=6.45 Hz, 2 H), 3.43 (q, *J*=7.03 Hz, 2 H), 1.95 (s, 3 H), 1.19 (t, *J*=7.03 Hz, 3 H).

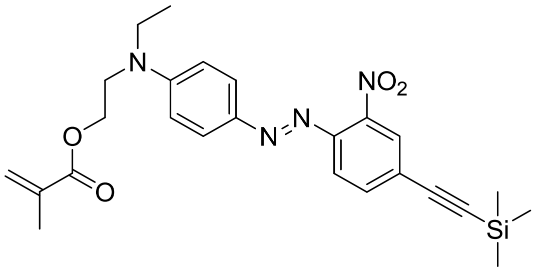


^{13}C NMR (300 MHz, chloroform-*d*) δ ppm 136.1, 129.4, 125.8, 116.1, 111.9, 88.7, 62.1, 48.7, 45.2, 30.9, 18.3, 12.2.



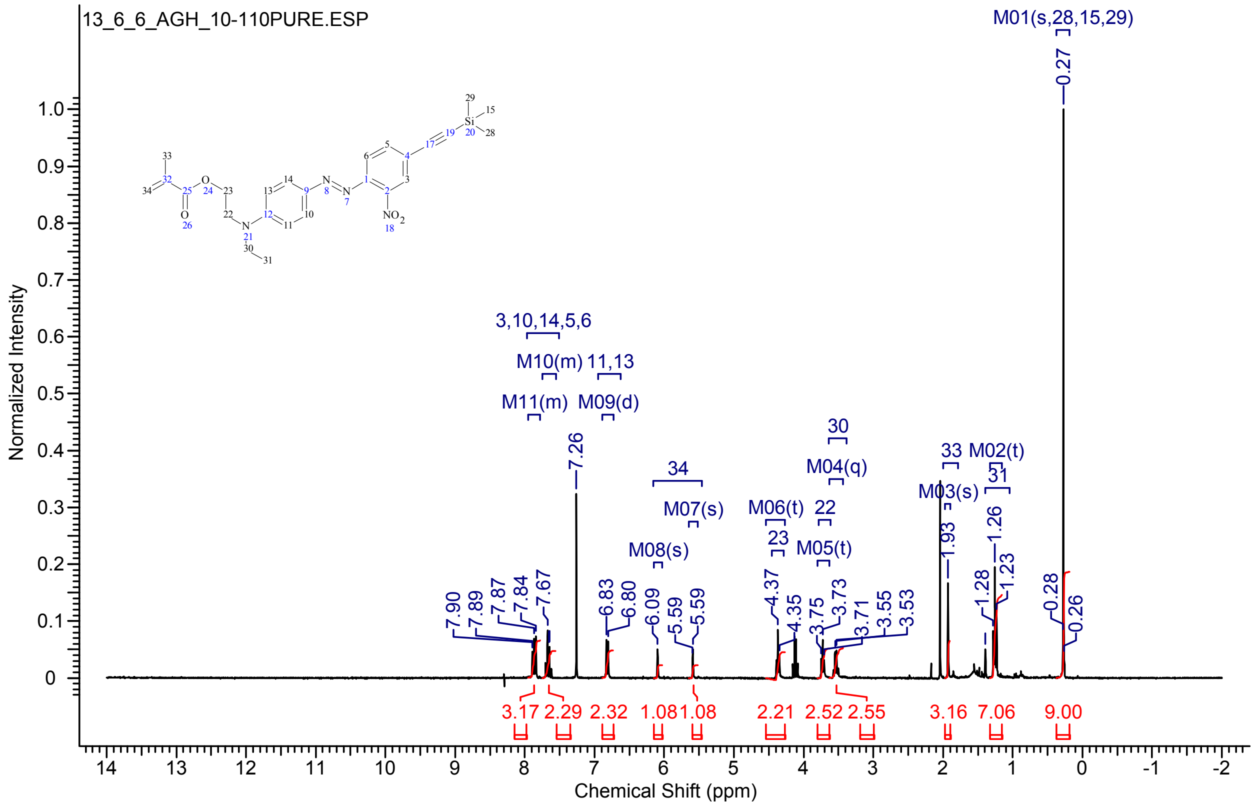
HR-MS (APCI, 4 kV): *m/z* Calculated for $C_{14}H_{20}NO_2$ $[M+H]^+$: 234.1489; found; 234.1486.

Synthesis of 2-(ethyl(4-((2-nitro-4-((trimethylsilyl)ethynyl)phenyl)diazenyl)phenyl)amino)ethylmethacrylate (Compound 8b)

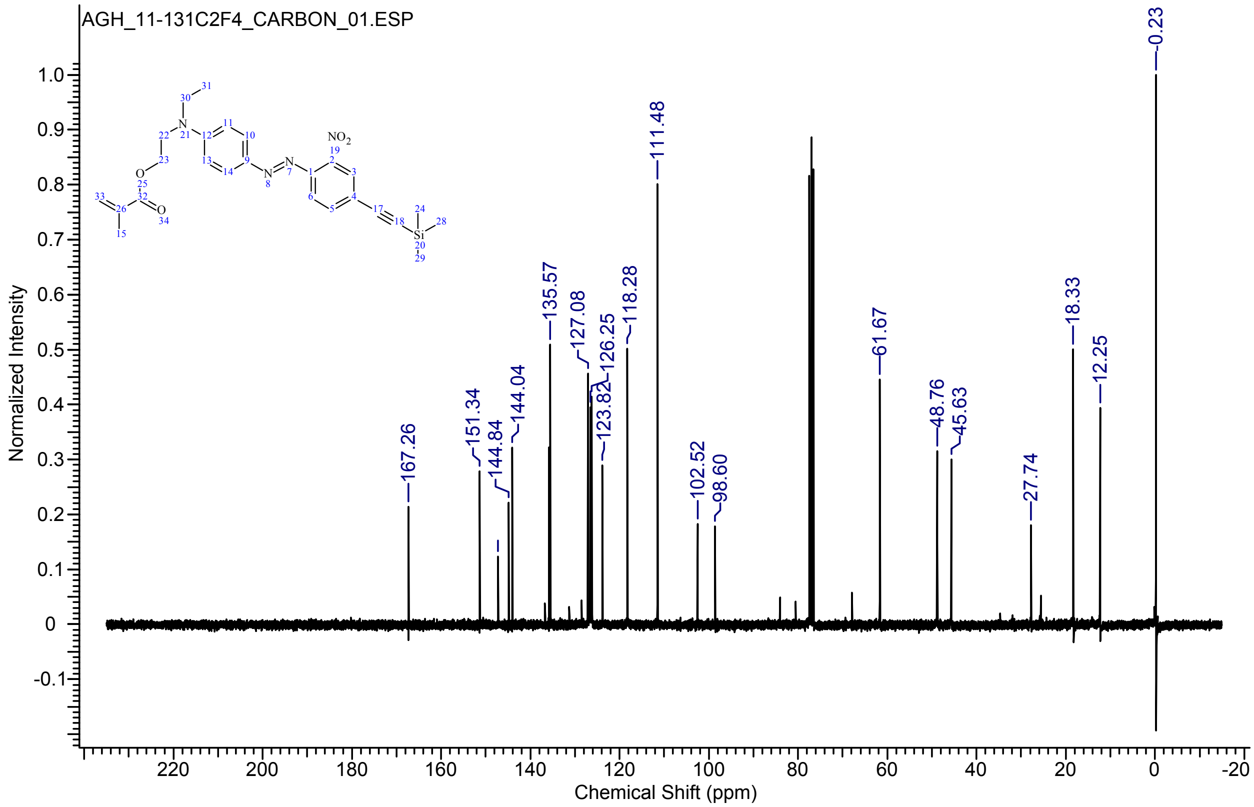


In a 500 mL round-bottom flask containing a stir bar, 250 mL acetone and 150 ml water was set to cool in an ice bath. Once the solvent temperature was below 5 °C, 1.692 g of 2-nitro-4-((trimethylsilyl)ethynyl)aniline (Compound **4a**, 7.2 mmol, 1 eq.) was added and dissolved, forming a deep red solution, after which 0.4 g of sodium nitrite (5.8 mmol, 0.8 eq.) and 12 mL 2 M HCl (24 mmol, 3.3 eq.) was added. This solution was stirred for 30 minutes to form the reactive diazonium intermediate, after which 1.35 g of 2-(ethyl(phenyl)amino)ethylmethacrylate was added (Compound **8a**, 5.78 mmol, 0.8 eq.). The solution rapidly turned red and was left to react for 2 hours after which the acetone was removed under reduced pressure and the aqueous solution was extracted with 100 mL ethyl acetate. The organic phase was washed twice with 150 mL water then 150 mL brine, dried with $MgSO_4$, filtered, and evaporated. The crude product was purified by silica gel chromatography, 0 to 60% ethyl acetate in hexane. The azo product co-elutes with unreacted 2-nitro-4-((trimethylsilyl)ethynyl)aniline which was removed by dissolving the crude in 100 mL THF with a trace of DMAP and adding an excess of di-*tert*-butyl dicarbonate until the reaction was complete by TLC. The solvent was removed and the product purified on a short silica column, 0 to 60% ethyl acetate in hexane. Yield: 1.0 g, 36%.

^{1}H NMR (300 MHz, chloroform-*d*) δ ppm 7.78–7.95 (m, 3 H), 7.55–7.75 (m, 2 H), 6.82 (d, *J*=9.38 Hz, 2 H), 6.09 (s, 1 H), 5.59 (s, 1 H), 4.37 (t, *J*=5.90 Hz, 2 H), 3.73 (t, *J*=6.15 Hz, 2 H), 3.54 (q, *J*=7.03 Hz, 2 H), 1.93 (s, 3 H), 1.26 (t, *J*=8.20 Hz, 3 H), 0.26 (s, 9 H).

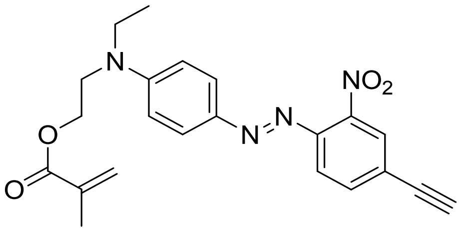


^{13}C NMR (300 MHz, chloroform-*d*) δ ppm 167.3, 151.3, 147.2, 144.8, 144.0, 135.6, 127.1, 126.6, 126.3, 123.8, 118.3, 111.5, 102.5, 98.6, 61.7, 48.8, 45.6, 27.7, 18.3, 12.3, -0.2.



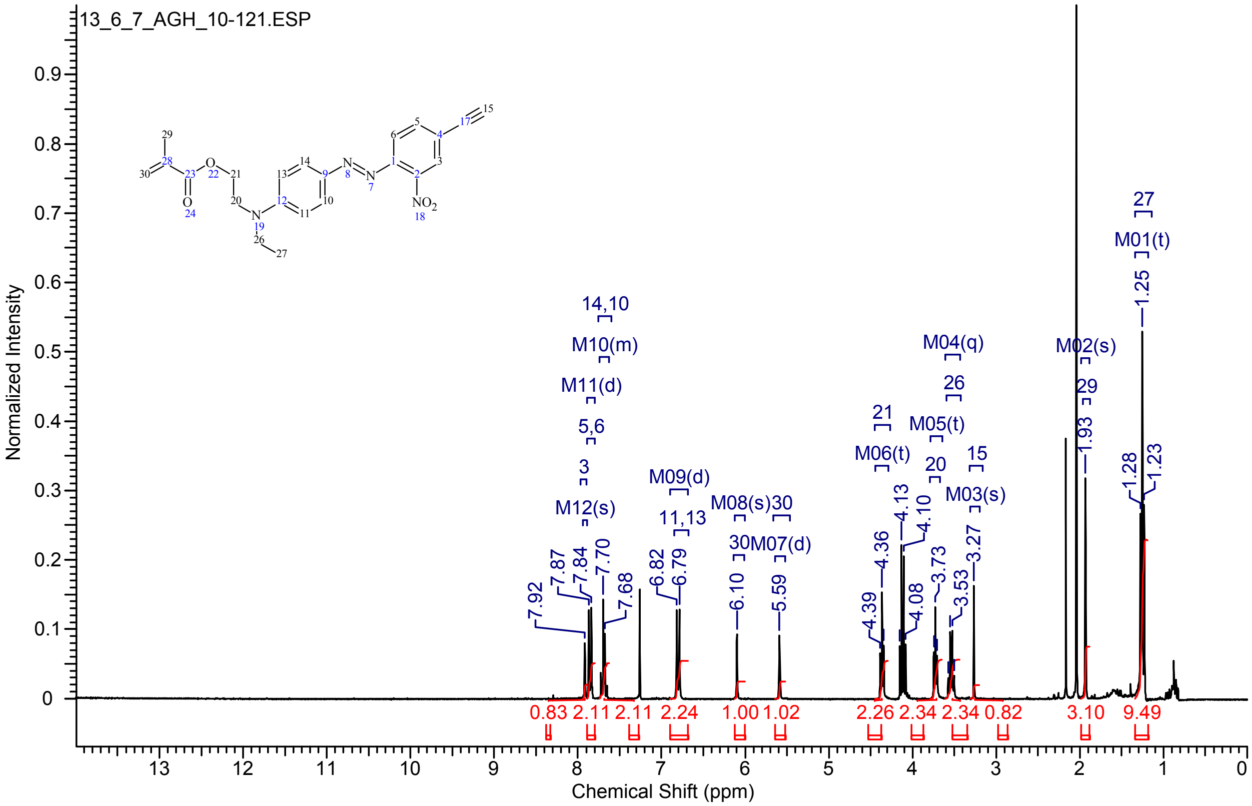
HR-MS (APCI, 4 kV): *m/z* Calculated for $C_{25}H_{31}N_4O_4Si$ $[M+H]^+$: 479.2109; found: 479.2101. Calculated for $C_{25}H_{30}N_4O_4Si$ $[M]^-$: 478.2042; found: 478.2040.

Synthesis of 2-(ethyl(4-((4-ethynyl-2-nitrophenyl)diazenyl)phenyl)amino)ethylmethacrylate (Compound 8)

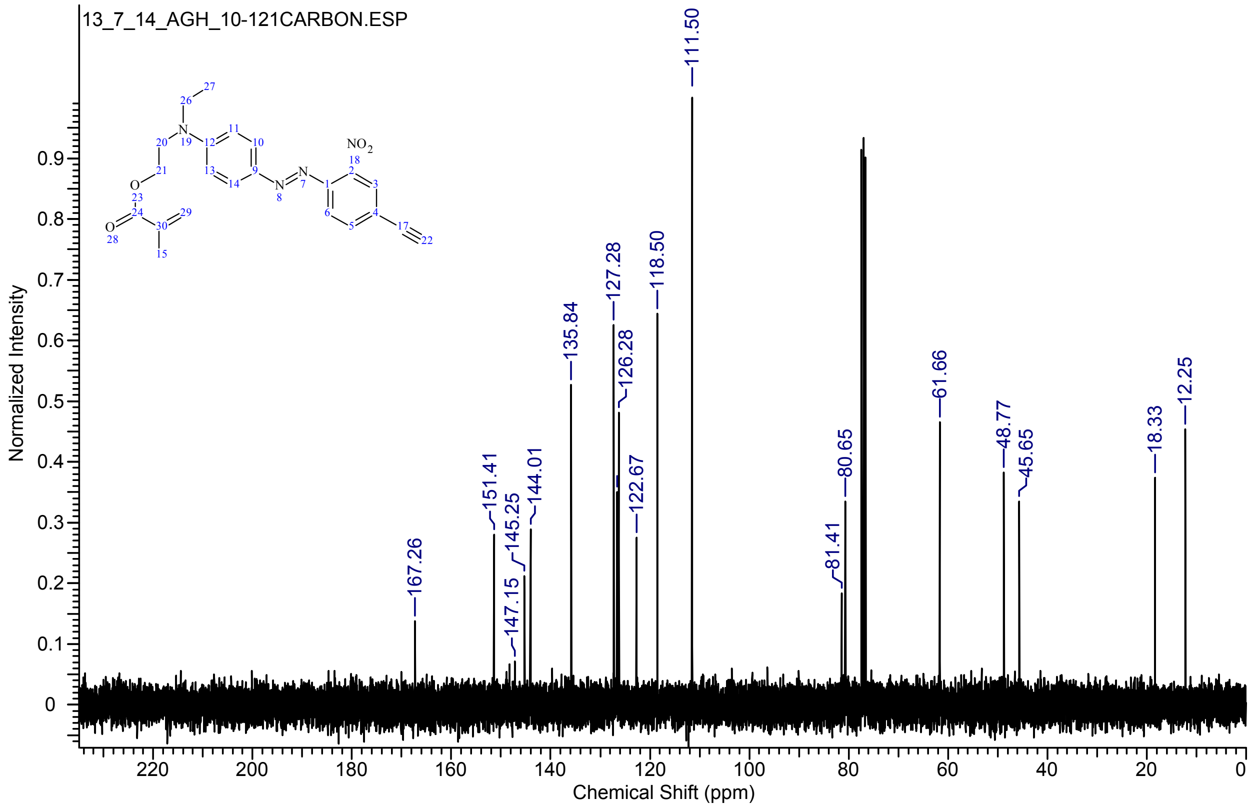


In a 100 mL round-bottom flask containing a stir bar, 2.4 g 2-(ethyl(4-((2-nitro-4-((trimethylsilyl)ethynyl)phenyl)diazenyl)phenyl)amino)ethylmethacrylate (Compound **8b**, 4.0 mmol, 1 eq.) was dissolved in 40 mL THF. To the deep red solution, 4.1 mL 1 M tetra-*n*-butylammonium fluoride (4.1 mmol, 1.02 eq.) was added dropwise over 10 minutes. Once the reaction was complete, as judged by thin layer chromatography, the THF solution was transferred to a separatory funnel with 200 mL water and 200 mL ethyl acetate. The organic phase was washed with 100 mL water, then 100 mL brine, dried with $MgSO_4$, filtered, and evaporated. The crude product was purified by silica gel chromatography, 0 to 50% ethyl acetate in hexane. Yield: 1.66 g, 81%.

^{1}H NMR (300 MHz, chloroform-*d*) δ ppm 7.92 (s, 1 H), 7.85 (d, *J*=9.38 Hz, 2 H), 7.63–7.74 (m, 3 H), 6.80 (d, *J*=9.38 Hz, 2 H), 6.10 (s, 1 H), 5.59 (d, *J*=1.76 Hz, 1 H), 4.36 (t, *J*=6.15 Hz, 2 H), 3.72 (t, *J*=6.15 Hz, 2 H), 3.54 (q, *J*=7.03 Hz, 1 H), 3.27 (s, 1 H), 1.93 (s, 3 H), 1.25 (t, *J*=7.03 Hz, 3 H).

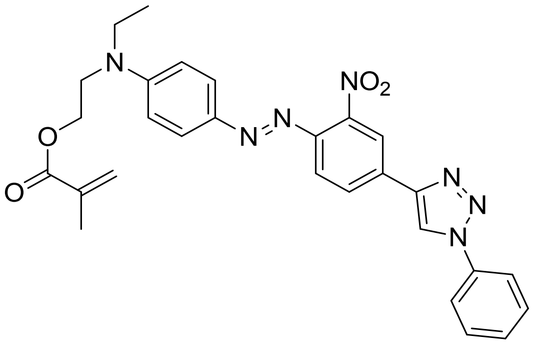


^{13}C NMR (300 MHz, chloroform-*d*) δ ppm 167.3, 151.4, 147.2, 145.3, 144.0, 135.8, 135.8, 127.3, 126.7, 126.3, 122.7, 118.5, 111.5, 81.4, 80.7, 61.7, 48.8, 45.7, 18.3, 12.3.



HR-MS (APCI, 4 kV): *m/z* Calculated for $C_{22}H_{23}N_4O_4$ $[M+H]^+$: 407.1714; found: 407.1729.

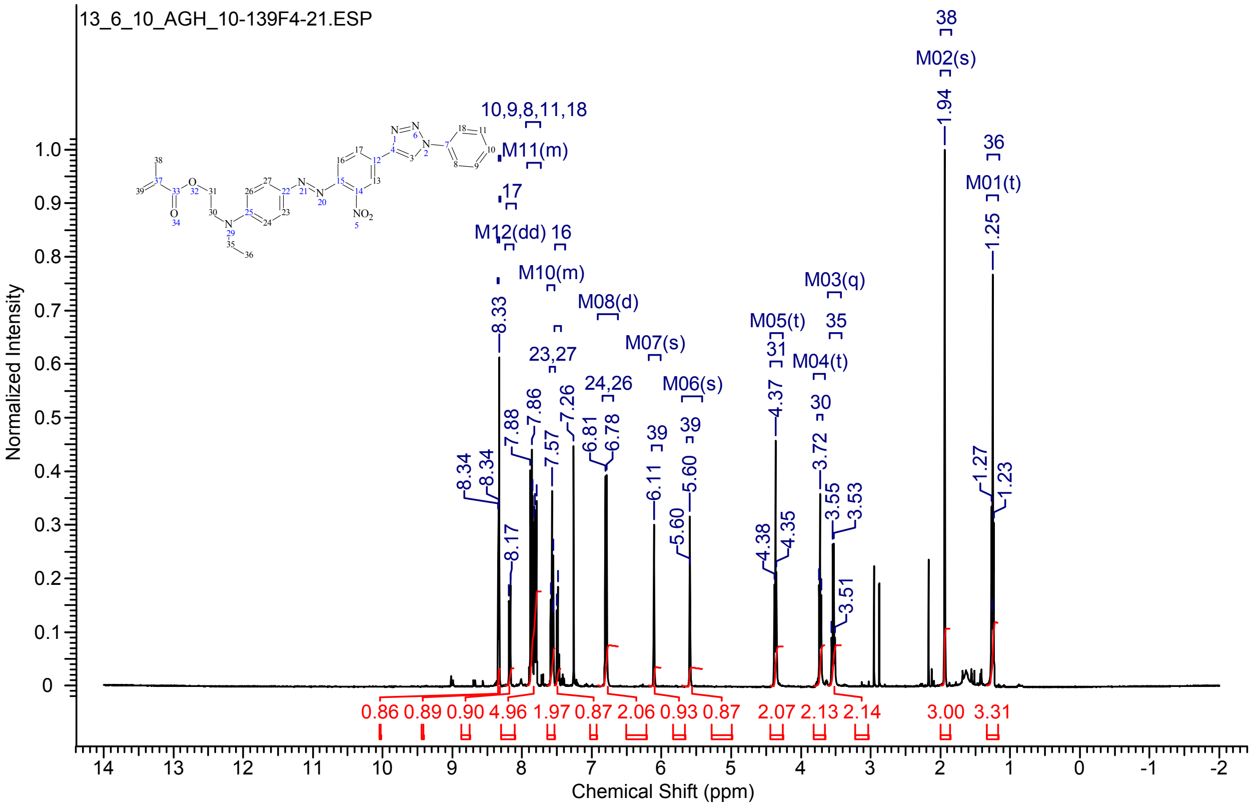
Synthesis of 2-(ethyl(4-((2-nitro-4-(1-phenyl-1H-1,2,3-triazol-4-yl)phenyl)diazenyl)phenyl)amino)ethylmethacrylate (Compound 9)



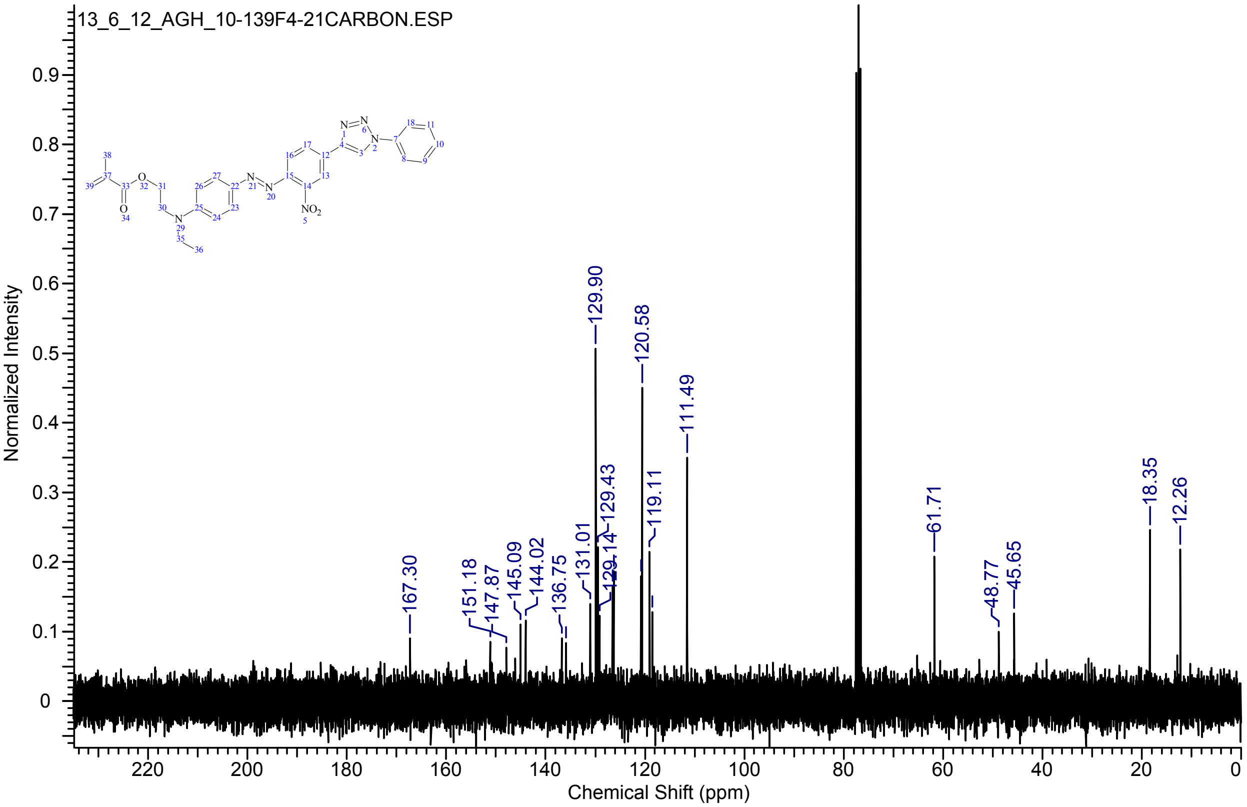
To a 100 mL round-bottom flask containing a stir bar and 30 mL DMF, 0.3 g 2-(ethyl(4-((4-ethynyl-2-nitrophenyl)diazenyl)phenyl)amino)ethylmethacrylate (Compound **8**, 0.74 mmol, 1 eq.), 106 mg CuBr (0.74 mmol, 1 eq.), 293 mg sodium ascorbate (1.48 mmol, 2 eq.) and 154 µL

PMDTA (0.74 mmol, 1 eq.) were added. After the reactants were dissolved, 300 mg phenyl azide (2 mmol, 3 eq.) was added and the solution was left to stir 16 hours. The red solution was added to a separatory funnel with 200 mL water and extracted twice with 50 mL ethyl acetate. The red organic extractions were combined and washed with 80 mL water, 80 mL saturated NH_4Cl, and 80 mL brine. The organic phase was dried with Na_2SO_4, filtered, and evaporated. The crude product was purified by silica gel chromatography, 0 to 100% ethyl acetate in hexane. Yield: 160 mg, 41%.

^{1}H NMR (400 MHz, chloroform-*d*) δ ppm 8.34 (d, *J*=1.95 Hz, 1 H), 8.33 (s, 1 H), 8.18 (dd, *J*=8.40, 1.76 Hz, 1 H), 7.73–7.93 (m, 5 H), 7.54–7.64 (m, 2 H), 7.49 (d, *J*=7.42 Hz, 1 H), 6.79 (d, *J*=8.99 Hz, 2 H), 6.11 (s, 1 H), 5.60 (s, 1 H), 4.37 (t, *J*=6.25 Hz, 2 H), 3.72 (t, *J*=6.25 Hz, 2 H), 3.54 (q, *J*=7.03 Hz, 2 H), 1.94 (s, 3 H), 1.25 (t, *J*=7.03 Hz, 3 H).

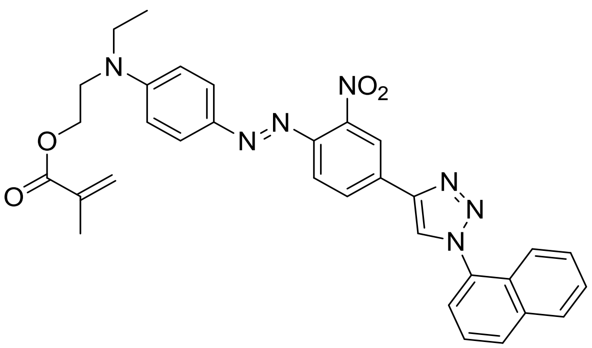


^{13}C NMR (300 MHz, chloroform-*d*) δ ppm 167.3, 151.2, 147.9, 145.1, 144.0, 136.8, 135.8, 131.0, 129.9, 129.4, 129.1, 126.5, 126.3, 120.8, 120.6, 119.1, 118.5, 111.5, 61.7, 48.8, 45.7, 18.4, 12.3.



HR-MS (APCI, 4 kV): *m/z* Calculated for $C_{28}H_{28}N_7O_4$ $[M+H]^+$: 526.2197.; found: 526.2216.

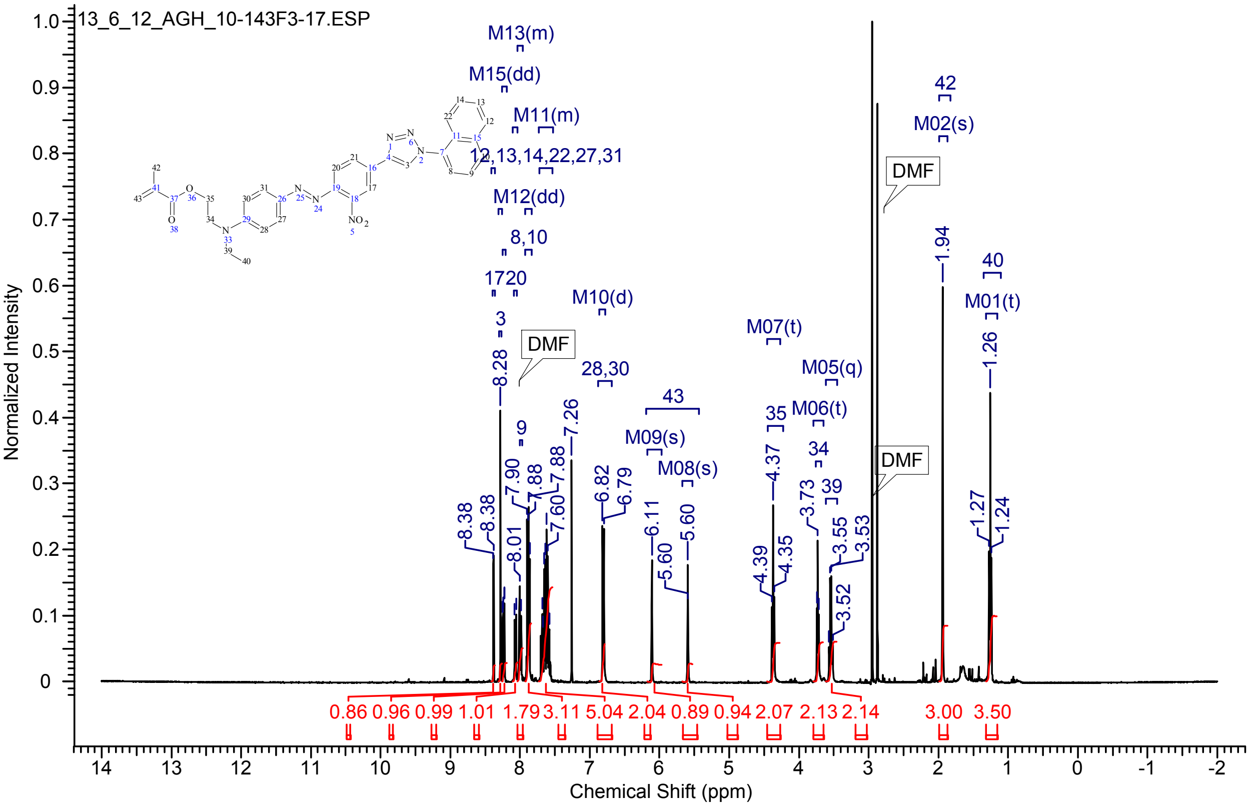
Synthesis of 2-(ethyl(4-((4-(1-(naphthalen-1-yl)-1H-1,2,3-triazol-4-yl)-2-nitrophenyl)diazenyl)phenyl)amino)ethylmethacrylate (Compound 10)



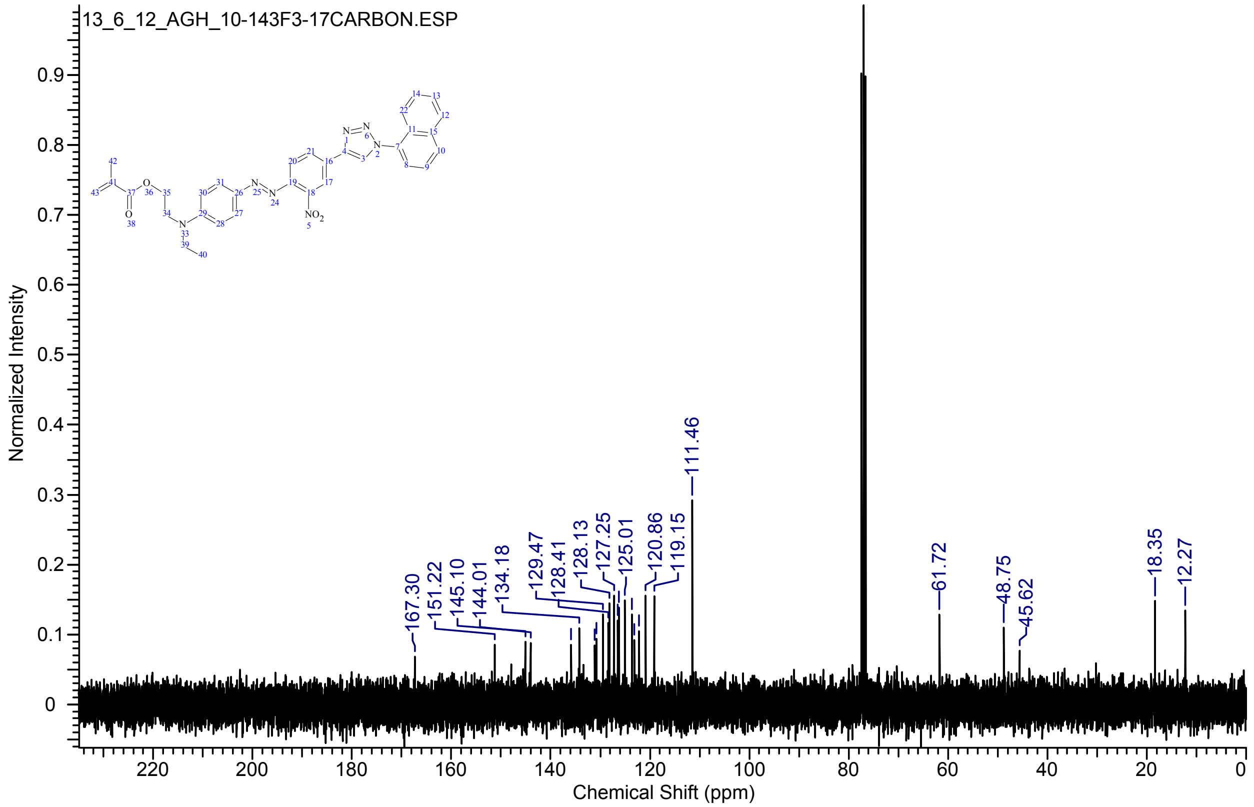
To a 100 mL round-bottom flask containing a stir bar and 30 mL DMF, 0.3 g 2-(ethyl(4-((4-ethynyl-2-nitrophenyl)diazenyl)phenyl)amino)ethylmethacrylate (Compound **8**, 0.74 mmol, 1 eq.), 106 mg CuBr (0.74 mmol, 1 eq.), 293 mg sodium ascorbate (1.48 mmol, 2 eq.) and 154 µL

PMDTA (0.74 mmol, 1 eq.) were added. After the reactants were dissolved, 376 mg 1-azido naphthalene (2 mmol, 3 eq.) was added and the solution was left to stir 16 hours. The red solution was added to a separatory funnel with 200 mL water and extracted twice with 50 mL ethyl acetate. The red organic extractions were combined and washed with 80 mL water, 80 mL saturated NH$_4$Cl, and 80 mL brine. The organic phase was dried with Na$_2$SO$_4$, filtered, and evaporated. The crude product was purified by silica gel chromatography, 0 to 100% ethyl acetate in hexane. Yield: 140 mg, 33%.

^{1}H NMR (400 MHz, chloroform-*d*) δ ppm 8.38 (d, *J*=1.56 Hz, 1 H), 8.28 (s, 1 H), 8.23 (dd, *J*=8.60, 1.95 Hz, 1 H), 8.07 (d, *J*=7.82 Hz, 1 H), 7.96–8.04 (m, 1 H), 7.88 (dd, *J*=8.79, 5.67 Hz, 3 H), 7.53–7.73 (m, 5 H), 6.81 (d, *J*=9.38 Hz, 2 H), 6.11 (s, 1 H), 5.60 (s, 1 H), 4.37 (t, *J*=6.06 Hz, 2 H), 3.73 (t, *J*=6.06 Hz, 2 H), 3.54 (q, *J*=7.03 Hz, 2 H), 1.94 (s, 3 H), 1.26 (t, *J*=7.03 Hz, 3 H).

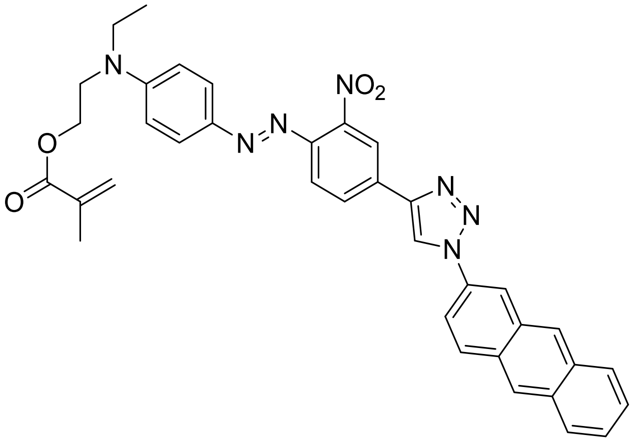


^{13}C NMR (300 MHz, chloroform-*d*) δ ppm 167.3, 151.2, 145.1, 144.0, 135.9, 134.2, 131.1, 130.8, 129.5, 128.4, 128.1, 127.3, 126.5, 126.3, 125.0, 123.6, 123.1, 122.2, 120.9, 119.2, 111.5, 61.7, 48.8, 45.6, 18.4, 12.3.



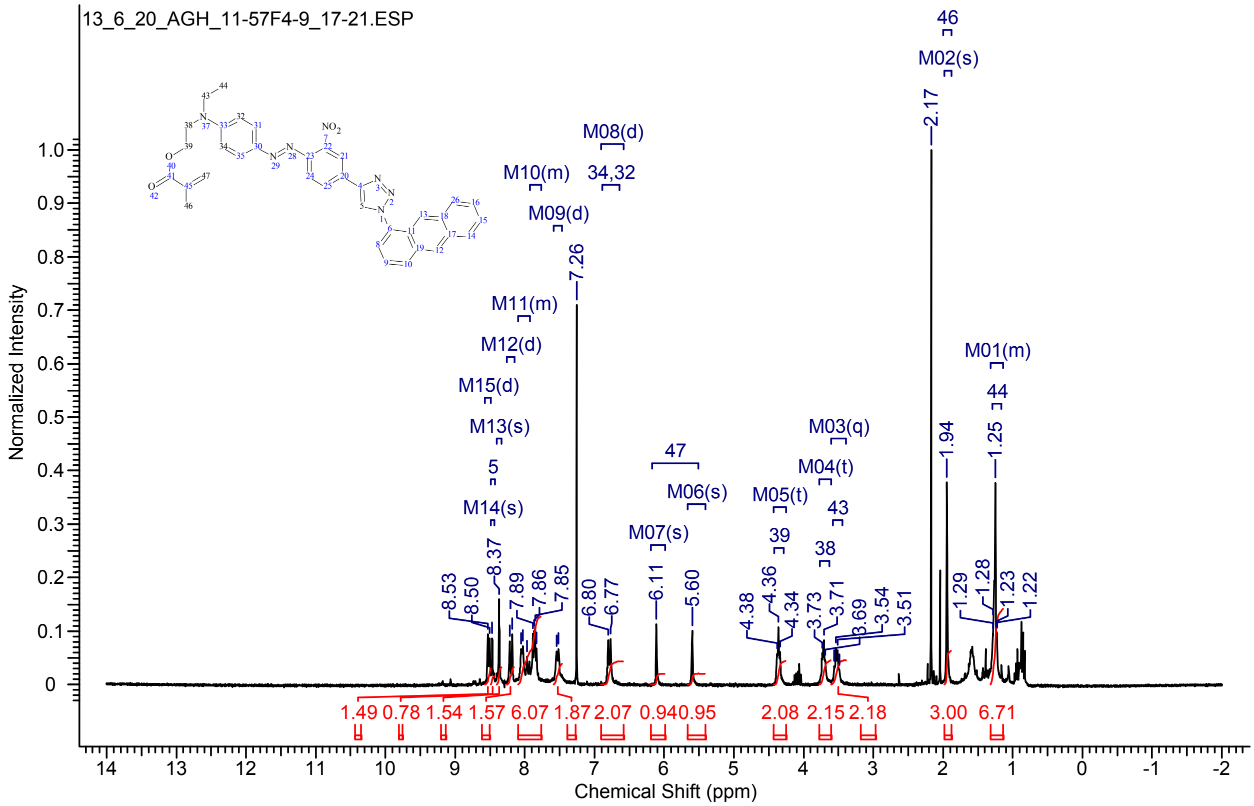
HR-MS (APCI, 4 kV): *m/z* Calculated for $C_{32}H_{30}N_7O_4$ $[M+H]^+$: 576.2354; found: 576.2376.

Synthesis of 2-((4-((4-(1-(anthracen-2-yl)-1H-1,2,3-triazol-4-yl)-2-nitrophenyl)diazenyl)phenyl)(ethyl)amino)ethylmethacrylate (Compound 11)



To a 100 mL round-bottom flask containing a stir bar and 30 mL DMF, 0.3 g 2-(ethyl(4-((4-ethynyl-2-nitrophenyl)diazenyl)phenyl)amino)ethylmethacrylate (Compound **8**, 0.74 mmol, 1 eq.), 106 mg CuBr (0.74 mmol, 1 eq.), 293 mg sodium ascorbate (1.48 mmol, 2 eq.) and 154 µL PMDTA (0.74 mmol, 1 eq.) were added. After the reactants were dissolved, 487 mg 2-azido anthracene (2 mmol, 3 eq.) was added and the solution was left to stir 16 hours. The red solution was added to a separatory funnel with 200 mL water and extracted twice with 50 mL ethyl acetate. The red organic extractions were combined and washed with 80 mL water, 80 mL saturated NH_4Cl, and 80 mL brine. The organic phase was dried with Na_2SO_4, filtered, and evaporated. The crude product was purified by silica gel chromatography, 0 to 100% ethyl acetate in hexane. Yield: 180 mg, 39%.

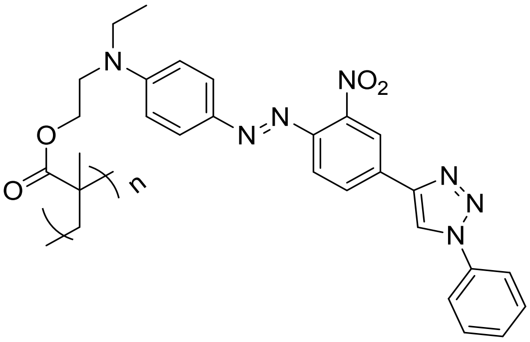
^{1}H NMR (300 MHz, chloroform-*d*) δ ppm 8.52 (d, *J*=7.62 Hz, 1 H), 8.47 (s, 1 H), 8.37 (s, 2 H), 8.20 (d, *J*=10.26 Hz, 2 H), 7.93–8.10 (m, 3 H), 7.77–7.93 (m, 4 H), 7.53 (d, *J*=7.33 Hz, 2 H), 6.79 (d, *J*=9.96 Hz, 2 H), 6.11 (s, 1 H), 5.60 (s, 1 H), 4.36 (t, *J*=5.71 Hz, 2 H), 3.71 (t, *J*=6.30 Hz, 2 H), 3.52 (q, *J*=7.00 Hz, 2 H), 1.94 (s, 3 H), 1.14–1.31 (m, 3 H).



Due to insufficient solubility, a ^{13}C NMR spectrum was unattainable.

HR-MS (APCI, 4 kV): *m/z* Calculated for $C_{36}H_{32}N_7O_4$ $[M+H]^+$: 626.2510; found: 626.2527.

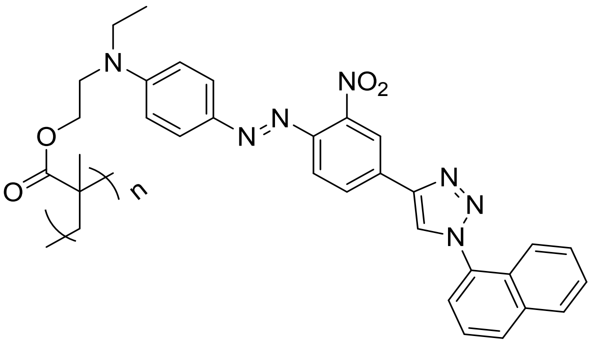
Synthesis of poly(9) Compound 12



In a 25 mL custom-made rota-flo polymerization flask with stir bar, 160 mg 2-(ethyl(4-((2-nitro-4-(1-phenyl-1H-1,2,3-triazol-4-yl)phenyl)diazenyl)phenyl)amino)ethylmethacrylate (Compound **9**, 0.31 mmol, 1 equiv), was dissolved in 6 mL dry THF. This was followed by the addition of 5 mg of freshly recrystallized AIBN (0.031 mmol, 0.1 eq.). Oxygen was removed by four freeze-pump-thaw-backfill cycles in liquid nitrogen with an argon backfill. After deoxygenation, the flask was placed in an oil bath at 80 °C for 36 hours. The flask was then cooled to room temperature and the contents rinsed to a round bottom flask to be concentrated to ~5 mL. This solution was flocculated into ~300 mL methanol. After stirring for 16 hours, the flocculated polymer was filtered on a fine frit. Yield: 50 mg, 31%.

Mw: 3555; Mn: 2277; PDI: 1.56.

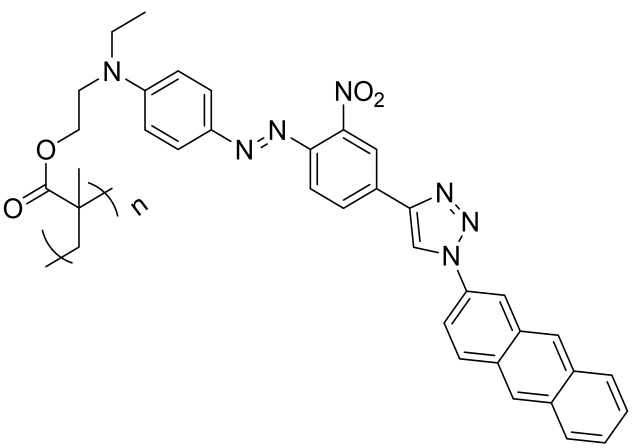
Synthesis of poly(10) Compound 13



In a 25 mL custom-made rota-flo polymerization flask with stir bar, 139 mg 2-(ethyl(4-((4-(1-(naphthalen-1-yl)-1H-1,2,3-triazol-4-yl)-2-nitrophenyl)diazenyl)phenyl)amino)ethylmethacrylate (Compound **10**, 0.31 mmol, 1 equiv), was dissolved in 6 mL dry THF. This was followed by the addition of 5 mg of freshly recrystallized AIBN (0.031 mmol, 0.1 eq.). Oxygen was removed by four freeze-pump-thaw-backfill cycles in liquid nitrogen with an argon backfill. After deoxygenation, the flask was placed in an oil bath at 80 °C for 36 hours. The flask was then cooled to room temperature and the contents rinsed to a round bottom flask to be concentrated to ~5 mL. This solution was flocculated into ~300 mL methanol. After stirring for 16 hours, the flocculated polymer was filtered on a fine frit. Yield: 36 mg, 26%.

Mw: 2485; Mn: 2275; PDI: 1.09.

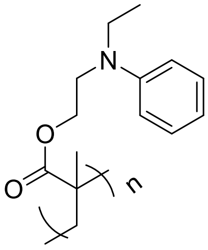
Synthesis of poly(11) Compound 14



In a 25 mL custom-made rota-flo polymerization flask with stir bar, 180 mg 2-((4-((4-(1-(anthracen-1-yl)-1H-1,2,3-triazol-4-yl)-2-nitrophenyl)diazenyl)phenyl)(ethyl)amino)ethylmethacrylate (Compound **11**, 0.31 mmol, 1 equiv), was dissolved in 6 mL dry THF. This was followed by the addition of 5 mg of freshly recrystallized AIBN (0.031 mmol, 0.1 eq.). Oxygen was removed by four freeze-pump-thaw-backfill cycles in liquid nitrogen with an argon backfill. After deoxygenation, the flask was placed in an oil bath at 80 °C for 36 hours. The flask was then cooled to room temperature and the contents rinsed to a round bottom flask to be concentrated to ~5 mL. This solution was flocculated into ~300 mL methanol. After stirring for 16 hours, the flocculated polymer was filtered on a fine frit. Precipitation failed to adequately separate the polymer from starting material. The crude material was dissolved in CH_2Cl_2 and loaded onto a silica plug, ethyl acetate was added to remove the monomer from the plug, once the eluent was clear, THF was added to remove the polymer. The THF portion was concentrated to ~2 mL, flocculated in 100 mL hexanes, and filtered on a fine frit. Yield: 22 mg, 12%.

Mw: 2600; Mn: 1954; PDI: 1.33.

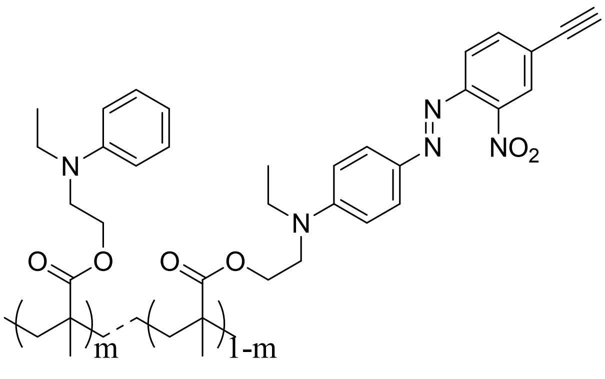
Synthesis of polymer 15a, poly(8a)



In a 100 mL custom-made rota-flo polymerization flask with stir bar 6.0 g 2-(ethyl(phenyl)amino)ethylmethacrylate (Compound **8**, 25.8 mmol, 1 equiv) was dissolved in 60 mL dry THF. This was followed by 300 mg of freshly recrystallized AIBN (1.8 mmol, 0.07 eq.). Oxygen was removed by four freeze-pump-thaw-backfill cycles in liquid nitrogen with an argon backfill. After deoxygenation, the flask was placed in an oil bath at 80 °C for 16 hours. The flask was then cooled to room temperature and the contents transferred to a round bottom flask and concentrated to ~40 mL. This solution was flocculated into 1 L petroleum ether. After stirring for 30 minutes, the flocculated polymer was filtered on a Buchner funnel. Yield: 3 g, 50%.

Mw: 8802; Mn: 3835; PDI: 2.3.

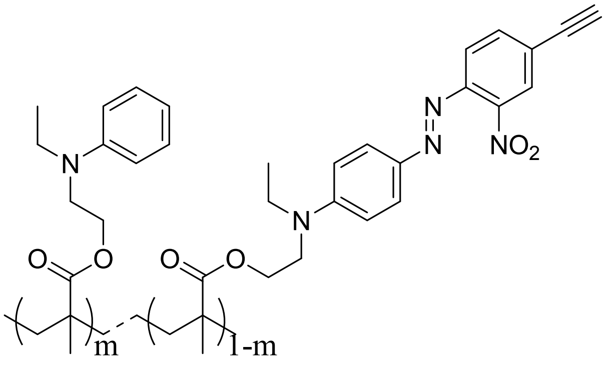
Synthesis of polymer 15



In a 1 L round-bottom flask containing a stir bar, 400 mL of DMF was set to cool in an ice bath. Once cool, 3.3 g poly(**8a**) (Compound **15a**, 14.1 mmol, 1 eq.) was added. In a separate 100 mL round-bottom flask containing a stir bar, 23 mL of acetone and 14 mL of water were added and cooled in an ice bath. Once the acetone/water solvent temperature was below 5 °C, 158 mg of 2-nitro-4-(ethynyl)aniline (0.38 mmol, 0.03 eq.) was added and dissolved, resulting in a yellow solution, followed by adding 19 mg of sodium nitrite (0.28 mmol, 0.02 eq.) and 1 mL 2 M HCl (2 mmol, 0.14 eq.). This solution was stirred for 30 minutes, forming the reactive diazonium intermediate, after which it was added dropwise to the stirring polymer in DMF solution. The solution rapidly turned orange/red and was left to react for 2 hours after which the solvent was removed under reduced pressure, the polymer was dissolved in 40 mL THF, and flocculated into 1.5 L petroleum ether. The crude polymer was redissolved in 30 mL DMF and flocculated in 1 L of rapidly stirring water. Yield: 1.6 g, 48%.

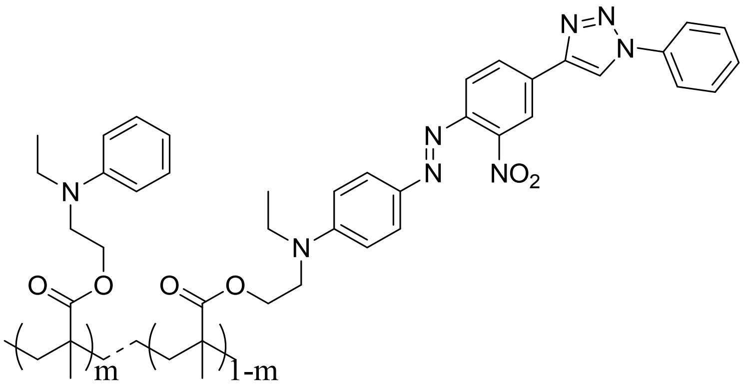
Mw: 10,181; Mn: 4452; PDI: 2.3.

Synthesis of polymer 15b



In a 15 mL round-bottom flask containing a stir bar, 15 mL DMF, 100 mg poly(**8**-*co*-**8a**) (Compound **15**, 0.25 mmol, 1 eq.), 35 mg CuBr (0.25 mmol, 1 eq.), 98 mg sodium ascorbate (0.5 mmol, 2 eq.) and 51 µL PMDTA (0.25 mmol, 1 eq.) were combined. The mixture was set to stir for 16 hours, after which the red DMF solution was concentrated to ~5 mL and flocculated into 250 mL water. The precipitate was filtered and rinsed generously with water, then dried for 16 hours in a vacuum oven at 35 °C. The dry orange filter cake was dissolved in THF, filtered through a fine frit filter and rinsed with THF. The THF filtrate was concentrated to ~5 mL, flocculated into 250 mL hexanes, and filtered. Yield: 88 mg, 88%.

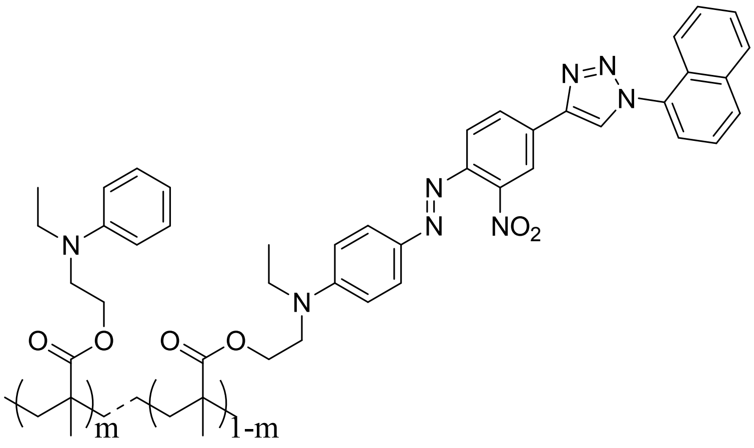
Synthesis of polymer 16



In a 100 mL round-bottom flask containing a stir bar, 30 mL DMF, 0.3 g poly(**8**-*co*-**8a**) (Compound **15**, 1.1 mmol, 1 eq.), 158 mg CuBr (1.1 mmol, 1 eq.), 436 mg sodium ascorbate (2.2 mmol, 2 eq.) and 230 µL PMDTA (1.1 mmol, 1 eq.) were combined. After the reactants dissolved, 142 mg phenyl azide (1.1 mmol, 1 eq.) was added and the solution was left to stir 16 hours. The red DMF solution was concentrated to ~5 mL and flocculated into 250 mL water, filtered and rinsed generously with water, then dried for 16 hours in a vacuum oven at 35 °C. The dry orange filter cake was dissolved in THF, filtered through a fine frit filter and rinsed with THF. The THF filtrate was concentrated to ~5 mL, flocculated into 250 mL hexanes, and filtered. Yield: 218 mg, 73%.

Mw: 9772; Mn: 4828; PDI: 2.02.

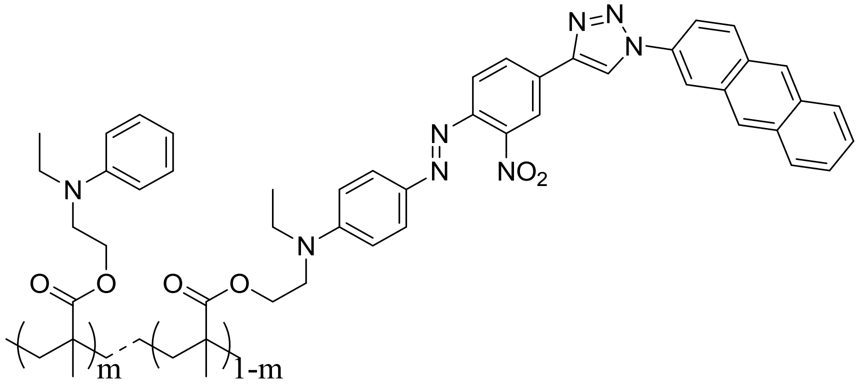
Synthesis of polymer 17



In a 100 mL round-bottom flask containing a stir bar, 30 mL DMF, 0.3 g poly(**8**-*co*-**8a**) (Compound **15**, 1.1 mmol, 1 eq.), 158 mg CuBr (1.1 mmol, 1 eq.), 436 mg sodium ascorbate (2.2 mmol, 2 eq.) and 230 µL PMDTA (1.1 mmol, 1 eq.) were combined. After the reactants dissolved, 186 mg 1-azido naphthalene (1.1 mmol, 1 eq.) was added and the solution was left to stir for 16 hours. The red DMF solution was concentrated to ~5 mL and flocculated into 250 mL water, filtered and rinsed generously with water, then dried for 16 hours in a vacuum oven at 35 °C. The dry orange filter cake was dissolved in THF, filtered through a fine frit filter and rinsed with THF. The THF filtrate was concentrated to ~5 mL, flocculated into 250 mL hexanes, and filtered. Yield: 244 mg, 81%.

Mw: 10,392; Mn: 4670; PDI: 2.22.

Synthesis of polymer 18



In a 100 mL round-bottom flask containing a stir bar, 30 mL DMF, 0.3 g poly(**8**-*co*-**8a**) (Compound **15**, 1.1 mmol, 1 eq.), 158 mg CuBr (1.1 mmol, 1 eq.), 436 mg sodium ascorbate (2.2 mmol, 2 eq.) and 230 μL PMDTA (1.1 mmol, 1 eq.) were combined. After the reactants dissolved, 219 mg 2-azido anthracene (1.1 mmol, 1 eq.) was added and the solution was left to stir for 16 hours. The red DMF solution was concentrated to ~5 mL and flocculated into 250 mL water, filtered and rinsed generously with water, then dried for 16 hours in a vacuum oven at 35 °C. The dry orange filter cake was dissolved in THF, filtered through a fine frit filter and rinsed with THF. The THF filtrate was concentrated to ~5 mL, flocculated into 250 mL hexanes, and filtered. Yield: 258 mg, 86%.

Mw: 9351; Mn: 4568; PDI: 2.05.

Optical Characterization of Materials

All small molecules and polymers were optically characterized in dry spectral grade THF on a Cary Bio 300 UV/vis spectrophotometer to measure the absorbance spectra and λ_{max} values. For the pump-probe laser setup, a Melles Griot Series 43 argon-ion laser was employed. The pump beam was ≈314 mW/cm^2 with a pump cycle of between 5 and 10 seconds to induce isomerization and ensure sample relaxation back to the *trans* state. The pump irradiation time (~100–200 ms) was fast enough to avoid heating the sample, so the kinetic measurements can be considered to have been acquired at room temperature.[1] The probe beam was chopped mechanically at 1410 Hz, attenuated to between 0.21 to 3.16 mW/cm^2 (as needed) and passed through the sample into a photodiode detector, where the intensity was recorded as a function of time.

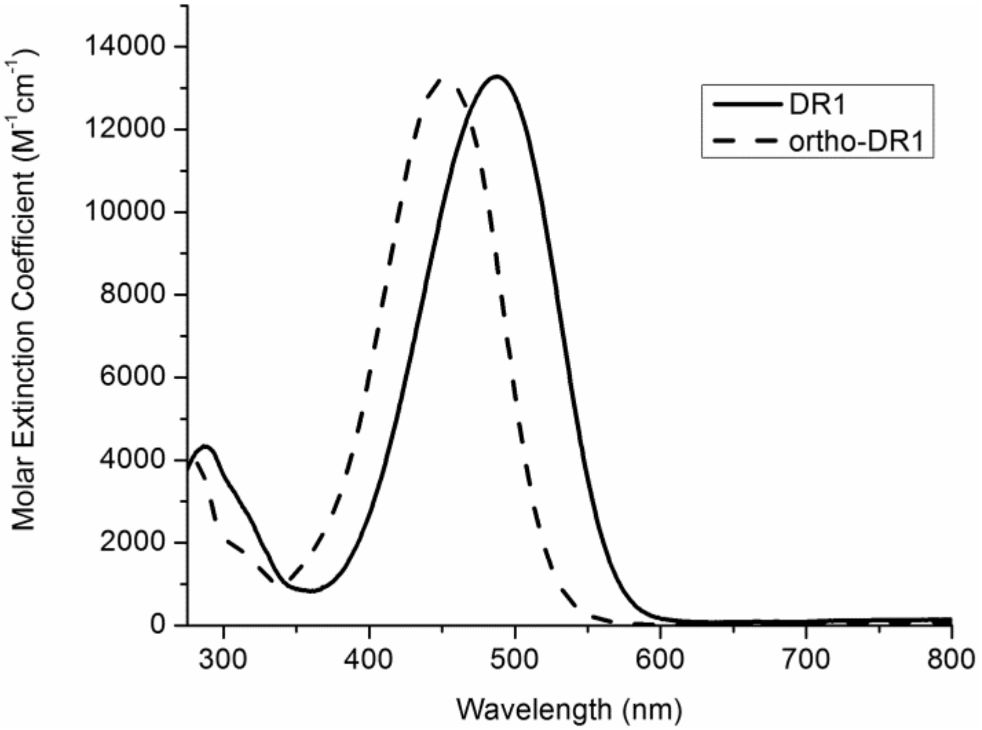


Figure S1. UV-vis absorbance of diethylaniline DR1 (**2**) and *ortho*-DR1 (**3**) dyes in THF.

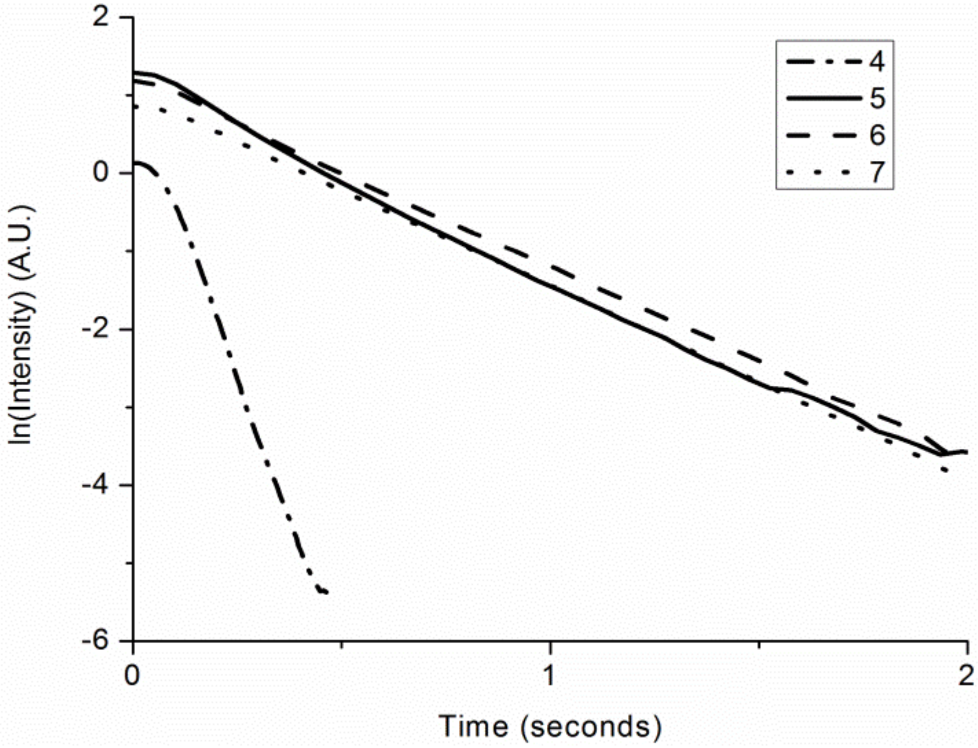


Figure S2. Natural log of the intensity measured from the decay of the *cis* state of the small molecules **4–7** in THF.

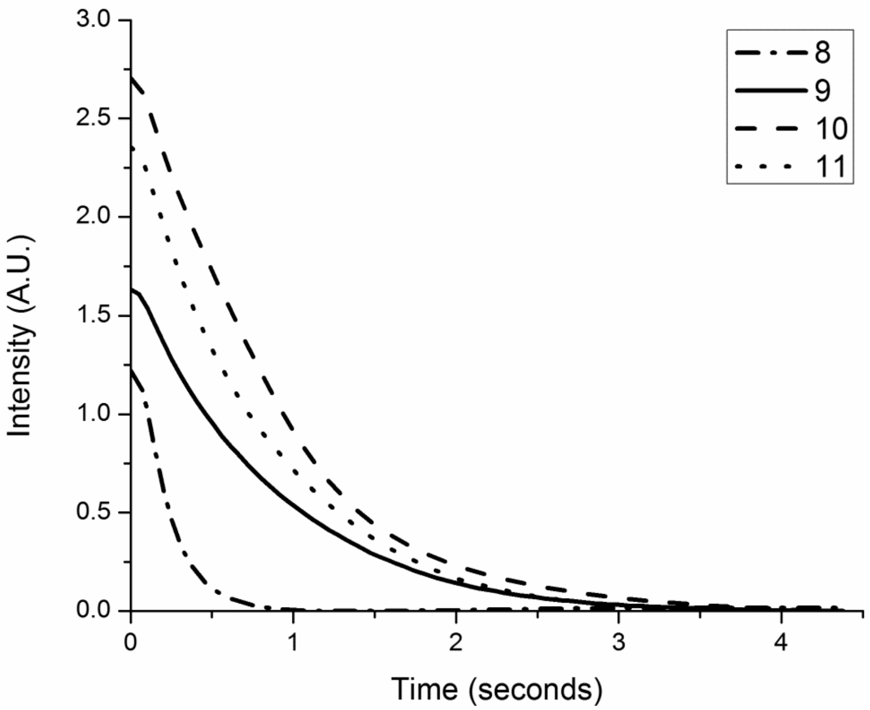


Figure S4. Kinetic decay of the *cis* state of the 4 monomers **8–11** in THF.

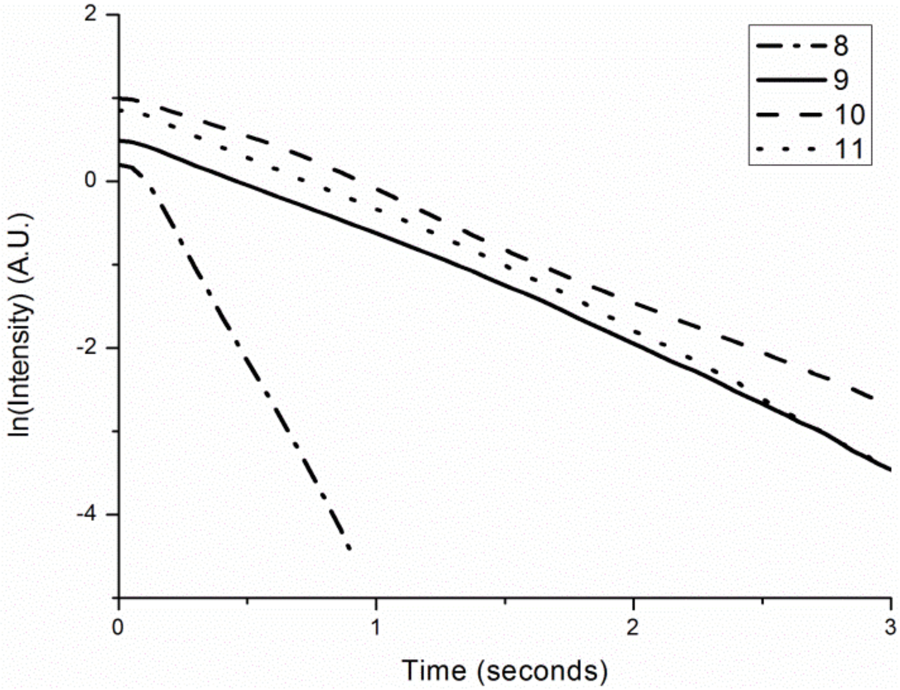


Figure S5. Natural log of the intensity measured from the kinetic decay of the *cis* state of monomers **8–11** in THF.

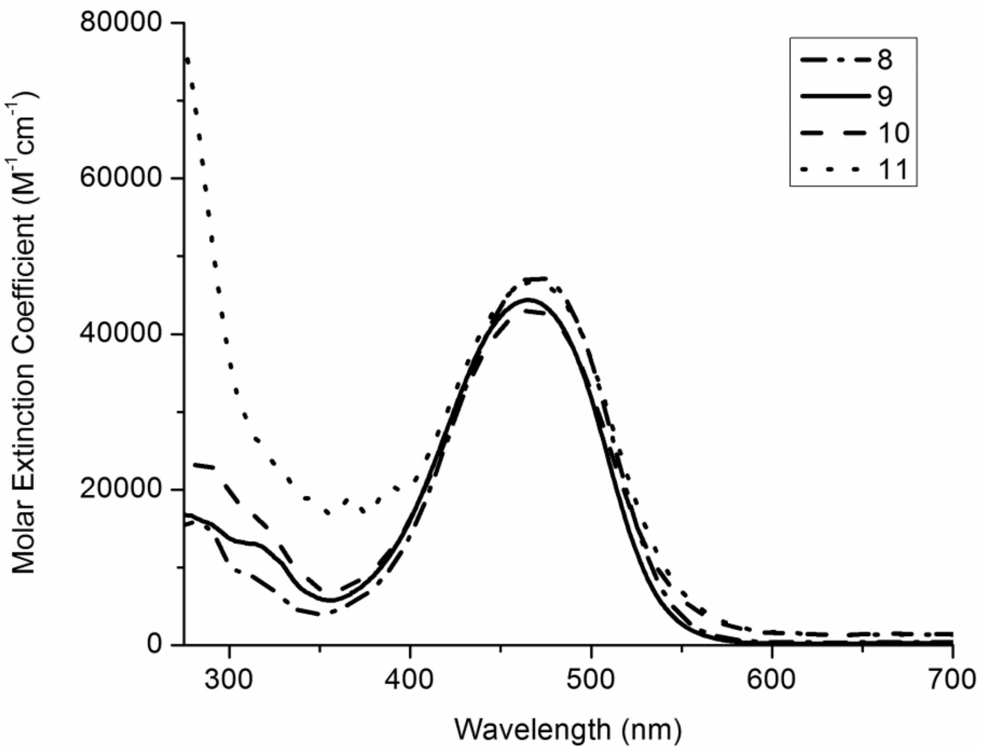


Figure S6. UV-vis spectra of ‘clickable’ and ‘clicked’ monomers **8–11** in THF.

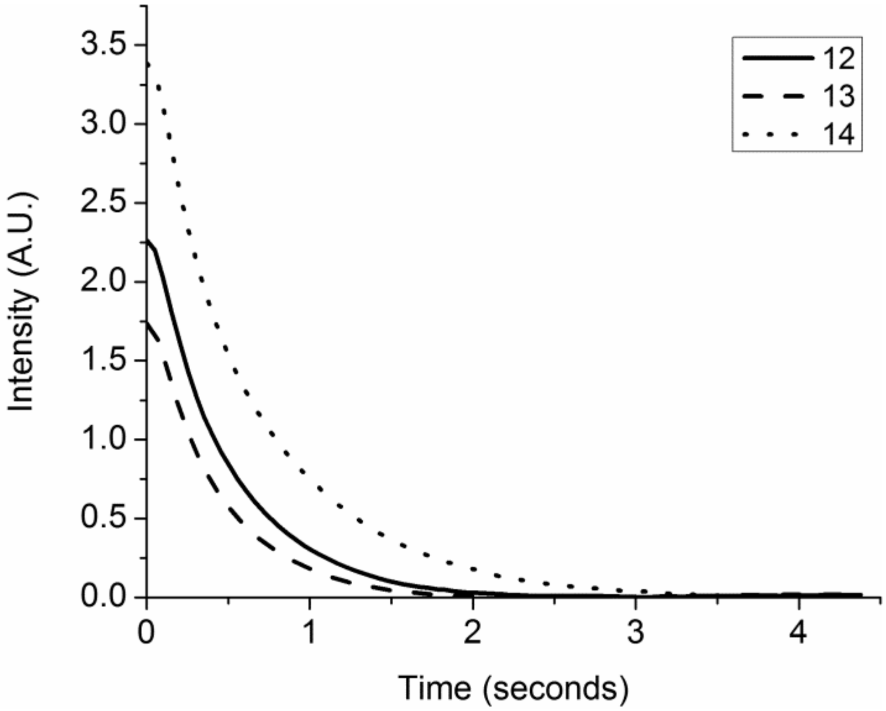


Figure S7. Kinetic decay of the *cis* state of homopolymers, **12–14** in THF.

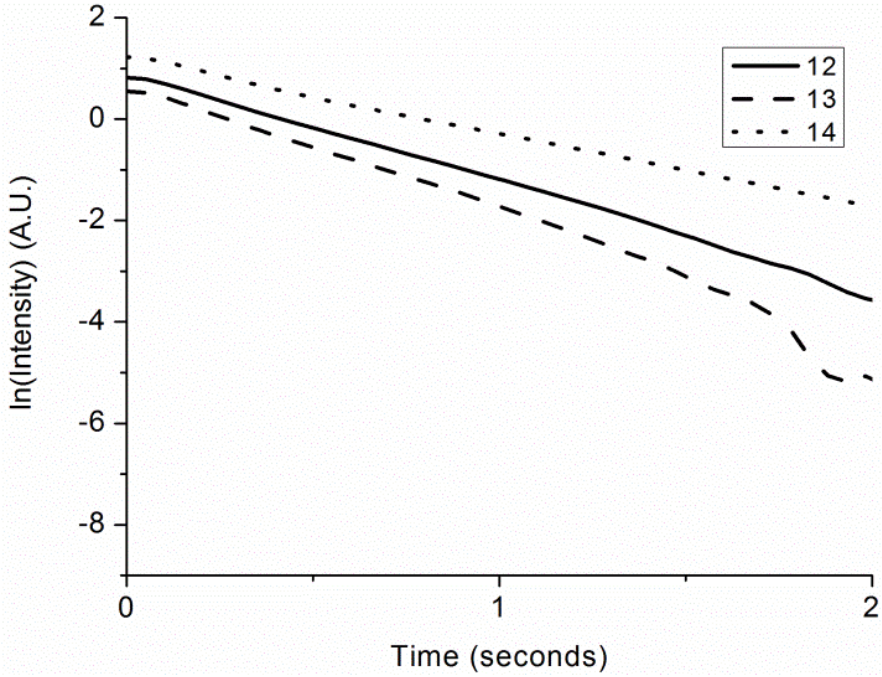


Figure S8. Natural log of the intensity measured from the kinetic decay of the *cis* state of homopolymers **12–14** in THF.

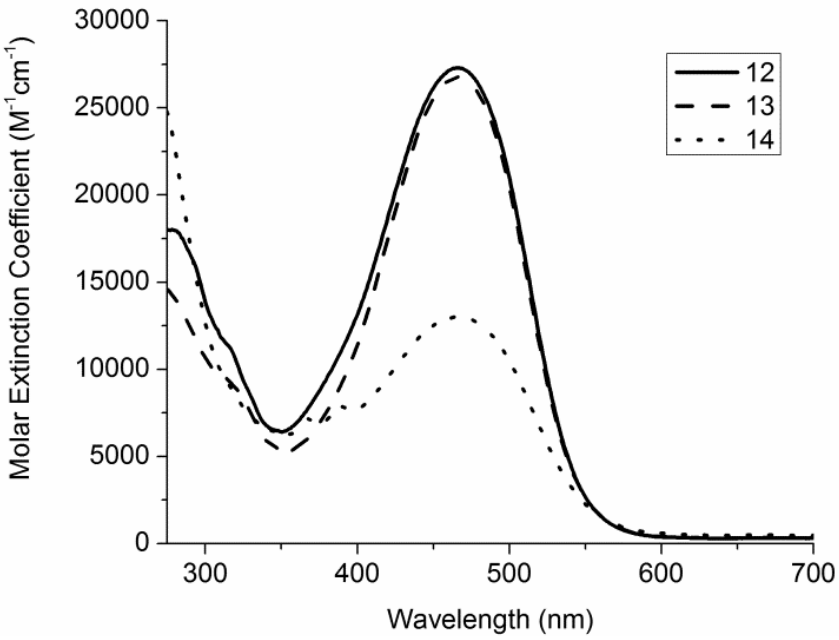


Figure S9. UV-vis spectra of the three homopolymers of 'clicked' phenyl **12**, napthyl **13**, and anthracyl **14**. All show identical λ_{max} to their monomer counterparts at 466 nm.

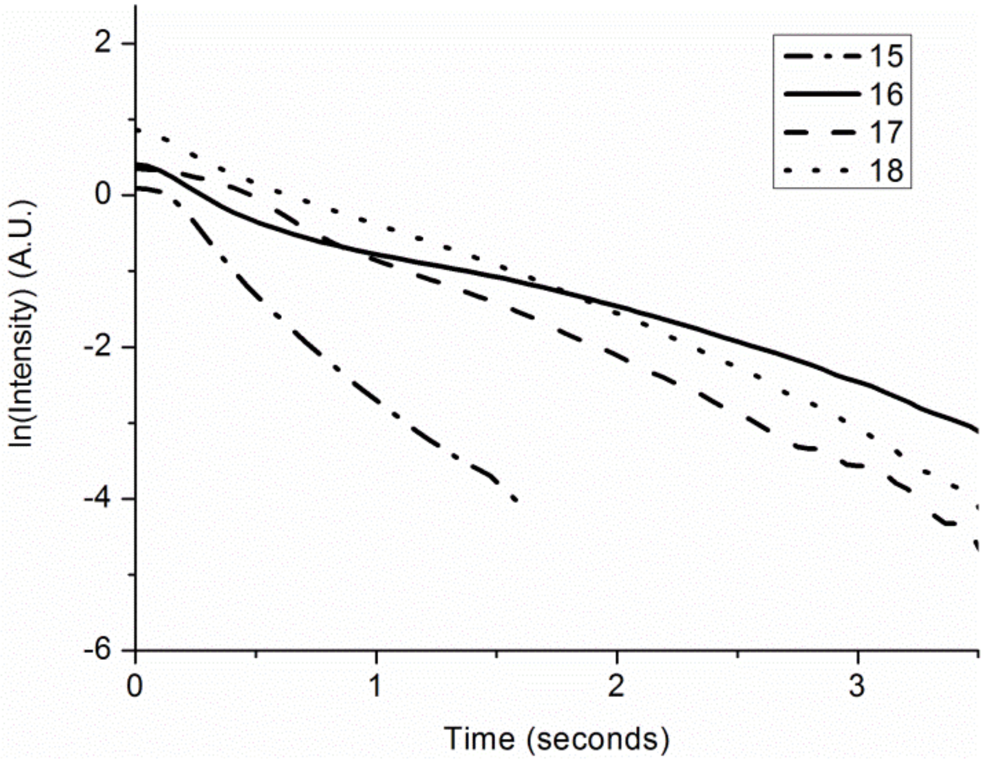


Figure S10. Natural log of the intensity measured from the kinetic decay of the *cis* state in the copolymers **15–18** in THF.

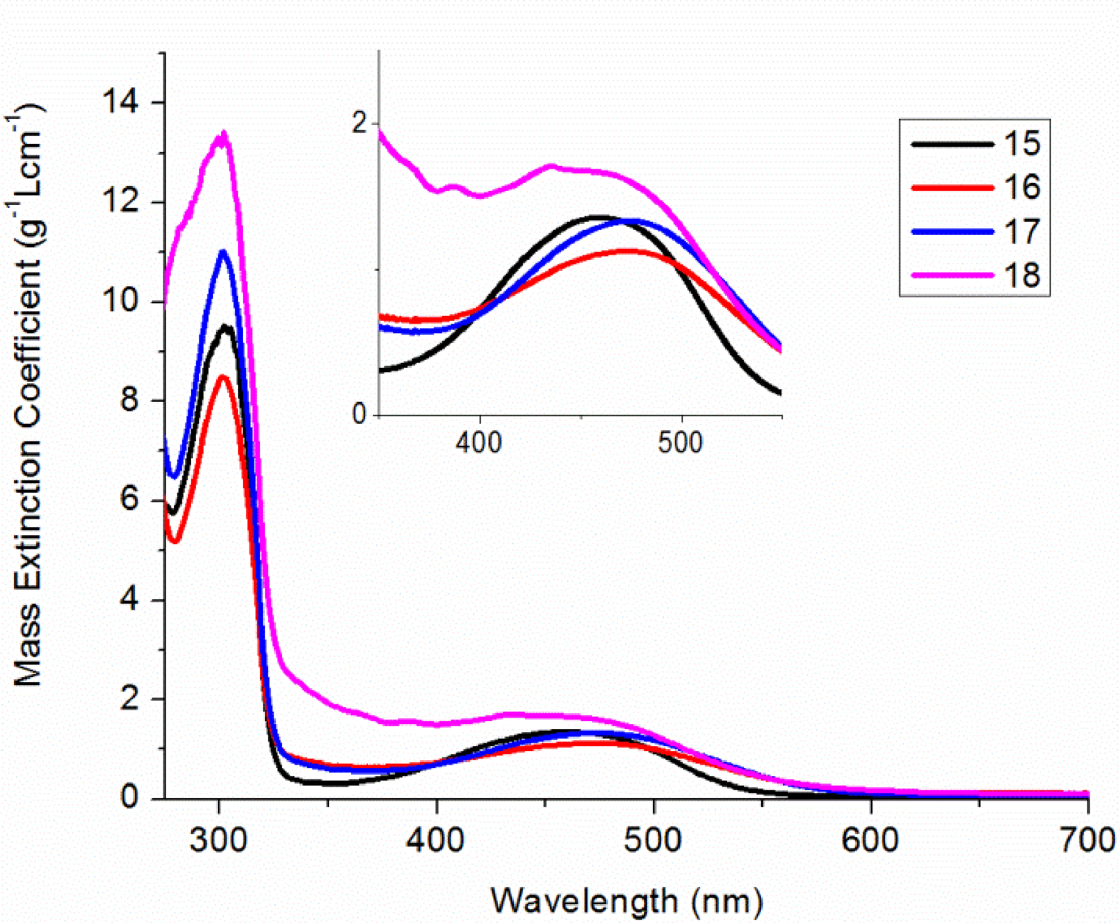


Figure S11**.** UV-vis spectra of ‘unclicked’ and ‘clicked’ copolymers **15–18** in THF, including expanded view of the azobenzene absorbance peak.

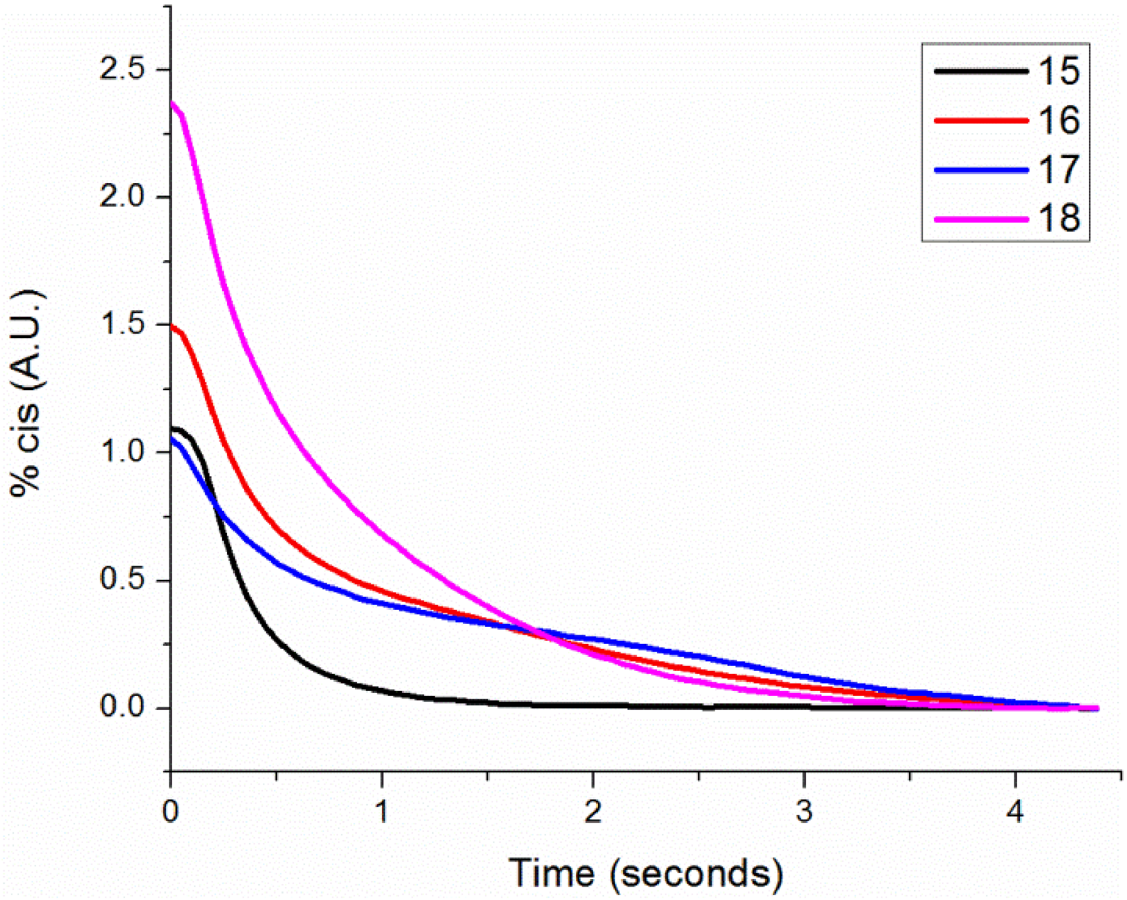


Figure S12. Natural log of the intensity measured from the kinetic decay of the *cis* state of copolymers **15–18** in THF.

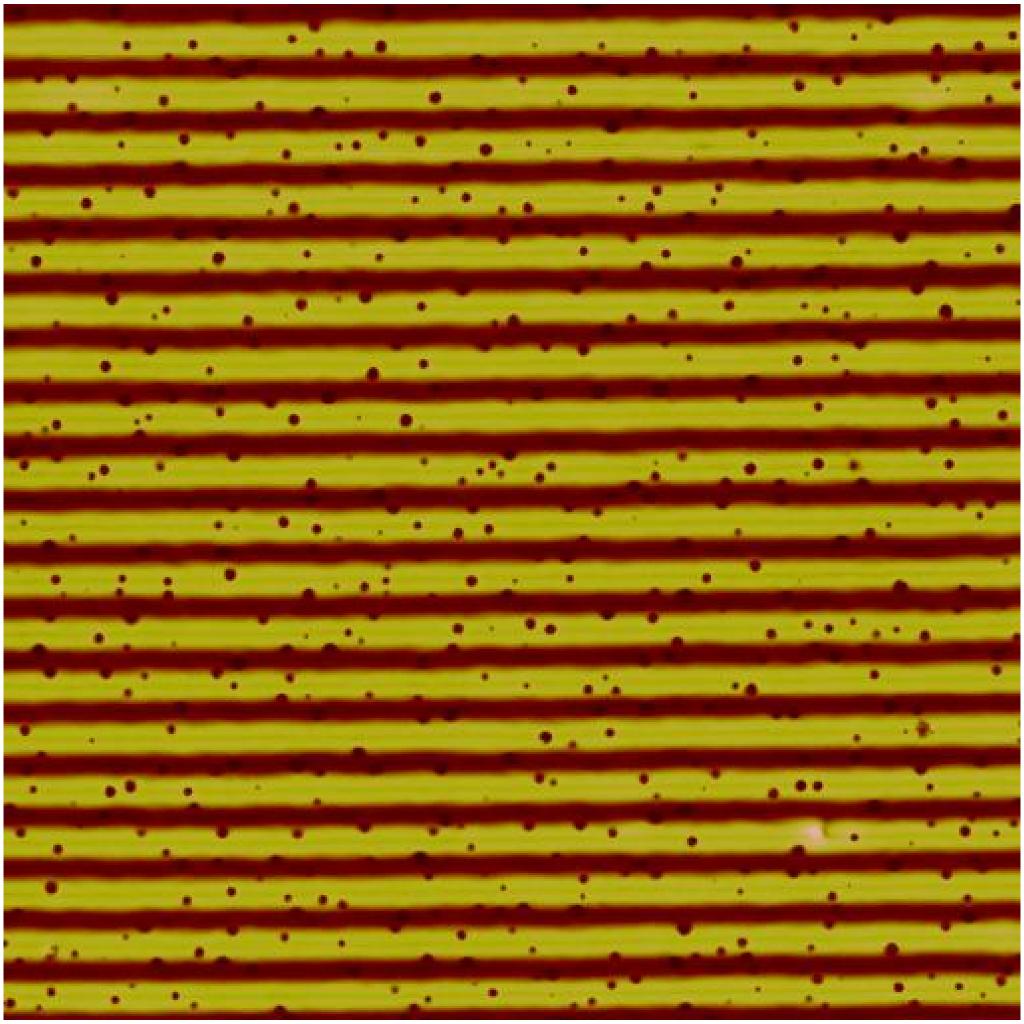


Figure S13. Top down AFM view of an SRG written into a thin film of polymer **13**.

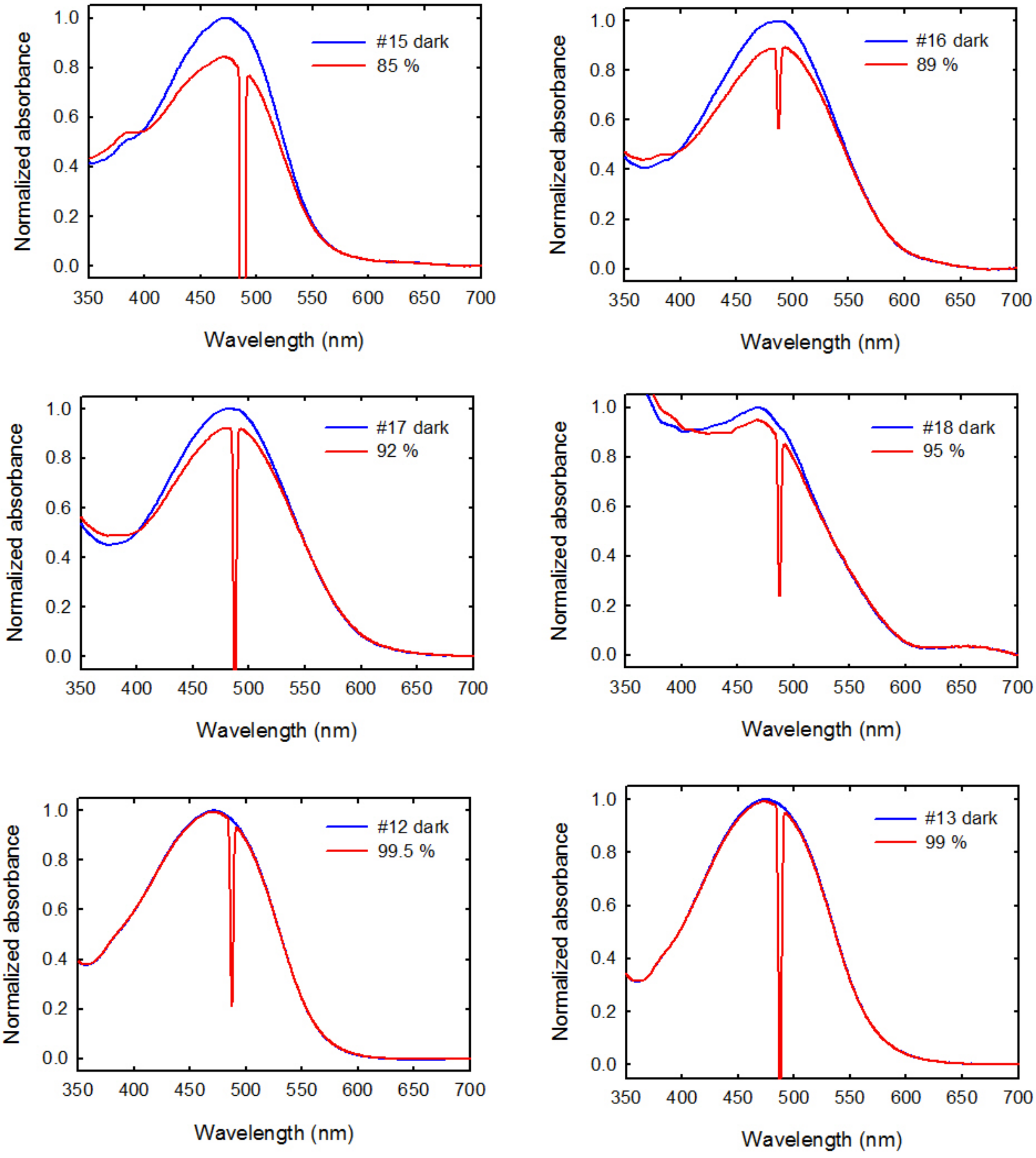


Figure S14. UV/vis traces of isomerization extent in films of polymer **12,13,15–18** spun cast on glass from THF solution, demonstrating an isomerization extent of 15% under irradiation from a 488 nm Ar+ laser at a power of 50 mW/cm^2. The sharp feature at 488nm is due to scattering from the laser light.

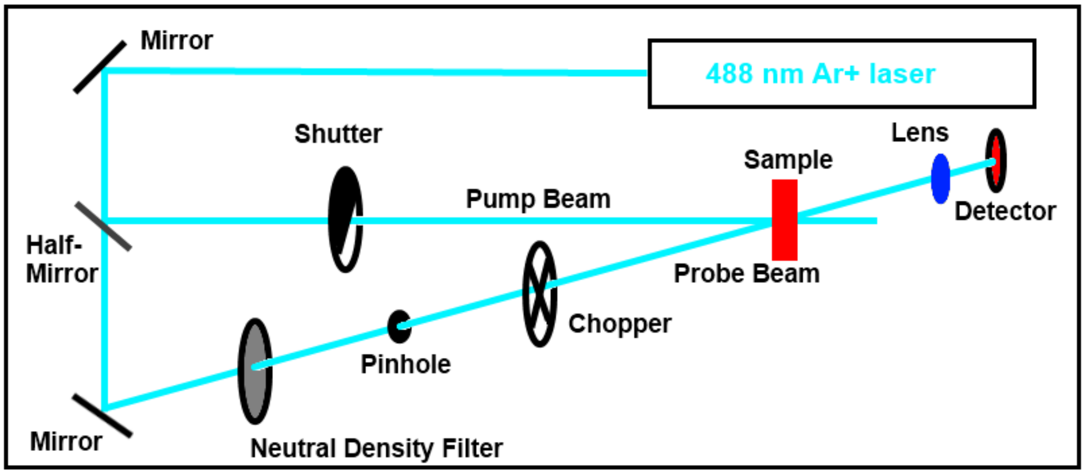


Figure S15. Pump-probe laser set-up to determine kinetics of *cis*-*trans* thermal reconversion.

Table 1. Extinction coefficients of all dyes measured in this study

Compound	ε ($M^{-1}cm^{-1}$)
2	13,280
3	13,220
4	37,430
5	32,120
6	26,360
7	16,910
8	47,430
9	39,920
10	42,320
11	42,090
12	26,050
13	26,770
14	13,660
15	1.37*
15b	1.17*
16	1.15*
17	1.32*
18	1.81*

*** Extinction coefficient measured as ($g^{-1}cm^{-1}L$).**

Table 2. Molecular weight of all polymers used in this study as measured against a polystyrene standard in tetrahydrofuran.

Compound	Mw (g/mol)
12	3,560
13	2,490
14	2,600
15	10,180
16	9,770
17	10,390
18	9,350

References

1. K. G. Yager and C. J. Barrett, *J. Chem. Phys.*, 2004, **120**, 1089–1096.