Supporting Information for: Poly(ester amide)s with Pendant Azobenzenes: Multi-Responsive Self-immolative Moieties for Modulating Polymer Assemblies

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Table of Contents

Procedures for the Synthesis of Compounds **3**-**8**, **10**-**12**

Synthesis of (*E*)-(4-((4-chlorophenyl)diazenyl)phenyl)methanol (Compound 3)

The same procedure described for the preparation of azobenzene **2** was used except that the starting aniline was 4-chloroaniline (1.00 g, 7.84 mmol). The collected solid was then purified by column chromatography (EtOAc/Hex 40:60) to generate compound **3**, as an orange solid (1.32 g, 68%). ^{1}H NMR (600 MHz, DMSO-d_6): [cis] δ = [4.44 (d, J = 5.6 Hz, 2H)], 4.61 (d, J = 5.6 Hz, 2H), [5.22 (t, J = 5.6 Hz, 1H)], 5.38 (t, J = 5.6 Hz, 1H), [6.82-6.83 (m, 2H)], [6.87-6.88 (m, 2H)], [7.25-7.27 (m, 2H)], [7.37-7.39 (m, 2H)], 7.53-7.55 (m, 2H), 7.65-767 (m, 2H), 7.87-7.88 (m, 2H), 7.89-7.91 (m, 2H). ^{13}C NMR (150 MHz): [cis] δ = [152.3], [151.8], 150.7, [150.5], 146.8, [142.1], 135.78, [131.3], 129.6, [128.9], 127.1, [126.7], 124.1, 122.6, 121.7, [120.0], 62.4, [62.2]. FT-IR (NaCl, thin film, ν_{max}/cm^{-1}): 3398 (O-H), 1261 (N=N), 1080 (C–O, alcohol). HRMS (EI): calc. for $[C_{13}H_{11}ClN_2O]^+$ $[M]^+$: 246.0560, found 246.0558.

Synthesis of (*E*)-(4-((3-chlorophenyl)diazenyl)phenyl)methanol (Compound 4)

The same procedure described for the preparation of azobenzene **2** was used except that the starting aniline was 3-chloroaniline (2.00 g, 15.6 mmol). The collected solid was then purified by column chromatography (EtOAc/Hex 40:60) to generate compound **4**, as an orange solid (3.43 g, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.81 (s, 2H), 7.44-7.50 (m, 2H), 7.53-7.55 (m, 2H), 7.83-7.86 (m, 1H), 7.91-7.95 (m, 3H). ^{13}C NMR (100 MHz): δ = 153.4, 151.8, 144.4, 135.1, 130. 7, 130.1, 127.4, 123.3, 122.4, 121.8, 64.8. FT-IR (NaCl, thin film, ν_{max}/cm^{-1}): 3323 (O-H), 1211 (N=N), 1028 (C–O, alcohol). HRMS (EI): calc. for $[C_{13}H_{11}ClN_2O]^+$ $[M]^+$: 246.0560, found 246.0565.

Synthesis of (*E*)-4-((4-(hydroxymethyl)phenyl)diazenyl)benzonitrile (Compound 5)

The same procedure described for the preparation of azobenzene **2** was used except that the starting aniline was 4-aminobenzonitrile (1.00 g, 8.46 mmol). The collected solid was then purified by column

chromatography (EtOAc/Hex 40:60) to generate compound **5**, as an orange solid (1.43 g, 71%). ^{1}H NMR (600 MHz, DMSO-d_6): δ = 4.62 (d, J = 5.1 Hz, 2H), 5.42 (t, J = 5.1 Hz, 1H), 7.54-7.56 (m, 2H), 7.91-7.93 (m, 2H), 7.99-8.01 (m, 2H), 8.06-8.08 (m, 2H). ^{13}C NMR (150 MHz): [cis] δ = [157.3], 154.0, [151.6], 150.7, 147.7, [142.7], 133.8, [133.3], 127.2, [126.7], 123.1, [122.9], 120.4, [120.3], 118.4, [118.3], 113.1, [109.2], 62.4, [62.2]. FT-IR (NaCl, thin film, ν_{max}/cm^{-1}): 3366 (O-H), 2359 (C≡N), 1219 (N=N), 1030 (C–O, alcohol). HRMS (EI): calc. for $[C_{14}H_{11}N_3O]^+$ $[M]^+$: 237.0902, found 237.0906.

Synthesis of (*E*)-(4-((2-(trifluoromethyl)phenyl)diazenyl)phenyl) methanol (Compound 6)

The same procedure described for the preparation of azobenzene **2** was used except that the starting aniline was 2-(trifluoromethyl)aniline (1.00 g, 6.21 mmol). The collected solid was then purified by column chromatography (EtOAc/Hex 40:60) to generate compound **6**, as an orange solid (1.56 g, 90%). ^{1}H NMR (600 MHz, DMSO-d_6): δ = 4.63 (d, J = 5.9 Hz, 2H), 5.41 (t, J = 5.9 Hz, 1H), 7.57-7.59 (m, 2H), 7.73-7.76 (m, 1H), 7.80-7.81 (m, 1H), 7.83-7.86 (m, 1H), 7.89-7.90 (m, 2H), 7.96-7.97 (m, 1H). ^{13}C NMR (150 MHz): δ = 151.7, 149.6, 148.4, 134.5, 132.1, 128.0, 127.4, 124.8 (q, $^{1}J_{C-F}$ = 274 Hz), 123.7, 122.1, 117.0, 63.2. FT-IR (NaCl, thin film, ν_{max}/cm^{-1}): 3365 (O-H), 1219 (N=N), 1052 (C–O, alcohol). HRMS (EI): calc. for $[C_{14}H_{11}F_3N_2O]^+$ $[M]^+$: 280.0823, found 280.0817.

Synthesis of (*E*)-(4-((4-(trifluoromethyl)phenyl)diazenyl)phenyl) methanol (Compound 7)

The same procedure described for the preparation of azobenzene **2** was used except that the starting aniline was 4-(trifluoromethyl)aniline (1.00 g, 6.21 mmol). The collected solid was then purified by column chromatography (EtOAc/Hex 40:60) to generate compound **7**, as an orange solid (1.10 g, 63%). ^{1}H NMR (600 MHz, DMSO-d_6): [cis] δ = [4.44 (d, J = 5.87 Hz, 2H)], 4.63 (d, J = 5.87 Hz, 2H), [5.22 (t, J = 5.87 Hz, 1H)], 5.41 (t, J = 5.87 Hz, 1H), [6.85-6.87 (m, 2H)], [7.05-7.07 (m, 2H)], [7.25-7.27 (m, 2H)], 7.55-7.77 (m, 2H), [7.69-7.70 (m, 2H)], 7.92-7.93 (m, 2H), 7.96-7.97 (m, 2H), 8.04-8.06 (m, 2H). ^{13}C NMR (150 MHz): [cis] δ = [156.9], [154.1], [151.6], 150.7, 147.5, 142.5, 130.6, 127.1, [127.0],

126.9, [126.2], 124.9, [124.8], 123.0, [122.8], 120.3, [120.2], [109.7], 62.4, [62.2]. FT-IR (NaCl, thin film, ν_{max}/cm^{-1}): 3366 (O-H), 1219 (N=N), 1044 (C–O, alcohol). HRMS (EI): calc. for $[C_{14}H_{11}F_3N_2O]^+$ $[M]^+$: 280.0823, found 280.0820.

Synthesis of (*E*)-prop-2-yn-1-yl 4-((4-(hydroxymethyl)phenyl)diazenyl) benzoate (Compound 8)

The same procedure described for the preparation of azobenzene **2** was used except that the starting aniline was prop-2-yn-1-yl 4-aminobenzoate (1.00 g, 5.71 mmol). The collected solid was then purified by column chromatography (EtOAc/Hex 40:60) to generate compound **8**, as an orange solid (1.23 g, 73%). ^{1}H NMR (600 MHz, DMSO-*d*$_6$): δ = 3.65 (t, J = 2.3 Hz, 1H) 4.62 (d, J = 5.3 Hz, 2H) 5.4 (m, 1H) 7.57 (m, 2H) 7.93 (m, 4H) 8.00 (m, 2H) 8.18 (m, 2H). ^{13}C NMR (150 MHz): δ = 164.4, 154.7, 150.8, 148.4, 130.7, 127.2, 122.8, 122.7, 120.4, 119.7, 78.1, 62.4, 52.8. FT-IR (ATR, ν_{max}/cm^{-1}): 3400-3000 (br, OH), 3266, 2125, 1722 (C=O), 1370, 1262, 1224, 1095, 1034, 1007. HRMS (EI): calc. for $[C_{17}H_{14}N_2O_3]^+$ $[M]^+$: 294.1004, found 294.1010.

Synthesis of (*E*)-(4-((2-bromophenyl)diazenyl)phenyl)methanol (Compound 10)

The same procedure described for the preparation of azobenzene **2** was used except that the starting aniline was 2-bromoaniline (2.00 g, 11.63 mmol). The collected solid was then purified by column chromatography (EtOAc/Hex 40:60) to generate compound **10**, as an orange solid (3.08 g, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.81 (s, 2H), 7.31-7.35 (m, 1H), 7.39-7.7.43 (m, 1H), 7.53-7.7.55 (m, 2H), 7.68-7.70 (m, 1H), 7.76-7.78 (m, 1H), 7.98-8.00 (m, 2H). ^{13}C NMR (100 MHz): δ = 152.1, 149.7, 144.5, 133.7, 131.8, 128.0, 127.4, 125.7, 123.6, 117.8, 64.8. FT-IR (NaCl, thin film, ν_{max}/cm^{-1}): 3304 (O-H), 1219 (N=N), 1029 (C–O, alcohol). HRMS (EI): calc. for $[C_{13}H_{11}BrN_2O]^+$ $[M]^+$: 290.0055, found 290.0044.

Synthesis of (*E*)-(4-((2-fluorophenyl)diazenyl)phenyl)methanol (Compound 11)

The same procedure described for the preparation of azobenzene **2** was used except that the starting aniline was 2-fluoroaniline (1.00 g, 9.00 mmol). The collected solid was then purified by column chromatography (EtOAc/Hex 40:60) to generate compound **11**, as an orange solid (1.23 g, 62%). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 4.80 (s, 2H), 7.22-7.25 (m, 1H), 7.28-7.30 (m, 1H), 7.44-7.48 (m, 1H), 7.52-7.53 (m, 2H), 7.76-7.78 (m, 1H), 7.95-7.97 (m, 2H). ^{13}C NMR (100 MHz): δ = 160.1 (d, $^{1}J_{C\text{-}F}$ = 256 Hz), 152.2, 144.3, 140.6 (d, $^{3}J_{C\text{-}F}$ = 7 Hz), 132.5 (d, $^{2}J_{C\text{-}F}$ = 8 Hz), 127.4, 124.3 (d, $^{3}J_{C\text{-}F}$ = 4 Hz), 123.4, 117.7, 117.0 (d, $^{2}J_{C\text{-}F}$ = 20 Hz), 64.8. FT-IR (NaCl, thin film, ν_{max}/cm^{-1}): 3302 (O-H), 1219 (N=N), 1035 (C–O, alcohol). HRMS (EI): calc. for $[C_{13}H_{11}FN_2O]^+$ $[M]^+$: 230.0855, found 230.0858.

Synthesis of (*E*)-(4-((perfluorophenyl)diazenyl)phenyl)methanol (Compound 12)

The same procedure described for the preparation of azobenzene **2** was used except that the starting aniline was 2,3,4,5,6-pentafluoroaniline (1.00 g, 5.46 mmol). The collected solid was then purified by column chromatography (EtOAc/Hex 40:60) to generate compound **12**, as an orange solid (0.66 g, 40%). ^{1}H NMR (600 MHz, DMSO-d_6): [cis] δ = [4.51 (s, 2H)], 4.63 (s, 2H), [7.10-7.11 (m, 2H)], [7.38-7.39 (m, 2H)], 7.57-7.58 (m, 2H), 7.87-7.88 (m, 2H). ^{13}C NMR (150 MHz): [cis] δ = [151.9], 151.1, 148.7, [145.2], [141.6], 141.3, [139.9], 139.7, 138.3, 136.6, [127.4], 127.1, [126.9], 122.7, [119.3], 62.2, [62.0]. FT-IR (NaCl, thin film, ν_{max}/cm^{-1}): 3325 (O-H), 1219 (N=N), 1020 (C–O, alcohol). HRMS (EI): calc. for $[C_{13}H_7F_5N_2O]^+$ [M]+: 302.0479, found 302.0486.

Synthesis of (*E*)-1-(4-(bromomethyl)phenyl)-2-(2-chlorophenyl)diazene (Compound 13)

Compound **2** (4.00 g, 16.2 mmol) was dissolved in CH_2Cl_2 (200 mL). CBr_4 (6.45 g, 19.4 mmol) was added and the solution was cooled to 0 °C. PPh_3 (6.38 g, 24.3 mmol) was added to the solution. The mixture was allowed to warm to room temperature and stirred for 1 hour. The solution was then concentrated *in vacuo*, yielding an orange solid. The collected solid was then purified by column chromatography (EtOAc/Hex 5:95) to provide compound **13** (4.91 g, 98%). ^{1}H NMR (600 MHz,

$CDCl_3$): δ = 4.57 (s, 2H), 7.35-7.37 (m, 1H), 7.40-7.43 (m, 1H), 7.55-7.59 (m, 3H), 7.70-7.71 (m, 1H), 7.95-7.96 (m, 2H). ^{13}C NMR (100 MHz): [cis] δ = 152.4, [152.0], 148.6, 141.1, [140.7], [138.1], [136.1], 135.5, 131.9, 130.7, 129.9, [129.4], [129.2], 127.3, 123.73, [123.65], [123.4], 117.5, [117.4], [91.3], [45.6], 32.6. FT-IR (ATR, ν_{max}/cm^{-1}): 1580, 1459, 1427, 1225 (N=N), 1197, 1144, 1088, 1057. HRMS (EI): calc. for $[C_{13}H_{10}BrClN_2]^+$ $[M]^+$: 307.9716, found 307.9727.

Synthesis of Compound 15

In a flame-dried round bottom flask, compound **13** (2.48 g, 7.99 mmol) was dissolved in THF (50 mL), and compound **14**[1] (1.00 g, 6.66 mmol) was dissolved separately in THF (20 mL). The solution of compound **14** was then transferred by cannula into the solution of compound **13**. The solution was then cooled to 0 °C and DIPEA (2.60 mL, 14.6 mmol) was added. The reaction mixture was stirred for 1 hour and then was heated to 40 °C and stirred 24 hours. The solution was then diluted with H_2O (100 mL) and extracted with CH_2Cl_2 (3 × 100 mL). The organic phase was washed with 1M HCl (200 mL), saturated $NaHCO_3$ (200 mL), and saturated NaCl (200 mL), and then dried on $MgSO_4$, filtered and concentrated *in vacuo*. The collected solid was then purified by column chromatography (EtOAc/Hex/PhMe 15:50:35) to provide compound **15** (1.26 g, 51%). ^1H NMR (600 MHz, $CDCl_3$): δ = 5.28 (s, 2H), 7.36-7.38 (m, 1H), 7.41-7.44 (m, 1H), 7.43-7.46 (m, 1H), 7.55-7.56 (m, 2H), 7.58-7.59 (m, 1H), 7.72-7.74 (m, 1H), 8.01-8.02 (m, 2H), 8.14-8.15 (m, 2H), 10.36 (s, 2H). ^{13}C NMR (150 MHz): δ = 188.4, 163.3, 152.9, 148.6, 137.9, 135.6, 135.5, 132.0, 130.8, 130.3, 129.3, 127.3, 125.2, 123.9, 117.5, 80.7. FT-IR (NaCl, thin film, ν_{max}/cm^{-1}): 3398 (C-H, H-CO), 1678 (C=O), 1219 (N=N), 1057 (C–O, ether). HRMS (EI): calc. for $[C_{21}H_{15}ClN_2O_3]^+$ $[M]^+$: 378.0771, found 378.0767.

Synthesis of Compound 16

Compound **15** (500 mg, 1.32 mmol) was dissolved in MeOH (50 mL) and cooled to 0 °C. $NaBH_4$ (110 mg, 2.90 mmol) was then added to the solution and the reaction mixture was stirred for 1 hour, then warmed to room temperature. The solution was then neutralized to pH 5-6 with NH_4Cl and extracted

with ethyl acetate (3 × 50 mL), and the collected organic phase was then extracted with saturated $NaHCO_3$ (100 mL), and saturated NaCl (100 mL). The organic phase was then dried on $MgSO_4$, filtered and concentrated *in vacuo*. The collected solid was then purified by column chromatography (EtOAc/Hex 20:80) to give compound **16** (330 mg, 65%). ^{1}H NMR (600 MHz, DMSO-d_6): [cis] δ = [4.51 (d, J = 5.3 Hz, 4H)], 4.59 (d, J = 5.3 Hz, 4H), [4.80 (s, 2H)], 5.01 (s, 2H), [5.08 (t, J = 5.3 Hz, 2H)], 5.15 (t, J = 5.3 Hz, 2H), [6.64-6.66 (m, 1H)], [6.95-6.96 (m, 2H)], [7.12-7.14 (m, 1H)], [7.13-7.14 (m, 1H)], 7.16-7.18 (m, 1H), [7.33-7.34 (m, 2H)], 7.37-7.38 (m, 2H), [7.44-7.45 (m, 2H)], 7.49-7.53 (m, 1H), [7.51-7.73 (m, 1H)], 7.57-7.60 (m, 1H), 7.70-7.71 (m, 1H), [7.73-7.74 (m, 2H)], 7.73-7.74 (m, 2H), 7.97-7.99 (m, 2H). ^{13}C NMR (150 MHz): [cis] δ = 153.2, [153.0], [152.9], 151.6, [151.1], 147.9, 141.9, [137.6], 135.1, [135.0], 134.0, [132.7], 130.8, [129.9], 128.6, [128.5], 128.3, 128.1, [128.1], [127.8], 127.3, [124.0], [123.9], [123.8], 123.0, 119.6, [119.6], 117.6, 74.7, [74.6], 58.0, [57.9]. FT-IR (NaCl, thin film, ν_{max}/cm^{-1}): 3377 (O-H), 1219 (N=N), 1057 (C–O, ether) 1021 (C–O, alcohol). HRMS (EI): calc. for $[C_{21}H_{19}ClN_2O_3]^+$ $[M]^+$: 382.1084, found 382.1072.

Synthesis of Compound 17

Boc-Gly-OH (332 mg, 1.90 mmol) was dissolved in CH_2Cl_2 (20 mL). Carbonyl diimidazole (350 mg, 2.16 mmol) was then added and the resulting reaction mixture was stirred for 30 min. Compound **16** (330 mg, 0.86 mmol) was added and the reaction mixture was stirred for 3 hours. The solution was quenched with 1M HCl (20 mL) and the organic and aqueous phases were separated. The organic phase was washed with saturated $NaHCO_3$ (20 mL), and saturated NaCl (20 mL), then dried on $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting solid was then purified by column chromatography (EtOAc/Hex 30:70) to give compound **17** (225 mg, 37%). ^{1}H NMR (600 MHz, DMSO-d_6, 50 °C (note: elevated temperature was used to eliminate the complicating effects of *cis-trans* isomers)): δ = 1.38 (s, 18H), 3.75-3.81 (m, 4H), 5.07 (s, 2H), 5.25 (s, 4H), 7.14 (br s, 2H), 7.22-7.24 (m, 1H), 7.46-7.47 (m, 2H), 7.47-7.50 (m, 1H), 7.54-7.57 (m, 1H), 7.68-7.70 (m, 2H), 7.74-7.75

(m, 2H), 7.98-8.00 (m, 2H). ^{13}C NMR (150 MHz, 50 °C): δ = 170.01, 169.95, 155.7, 155.1, 151.7, 147.9, 140.8, 133.9, 132.3, 130.4, 129.3, 128.6, 127.7, 124.3, 122.9, 117.3, 78.1, 75.7, 61.0, 42.0, 27.9. FT-IR (ATR, ν_{max}/cm^{-1}): 3340, 2978, 2930, 1684, 1529, 1390, 1366, 1292, 1249, 1156, 1056, 1031. HRMS (EI): calc. for $[C_{35}H_{41}ClN_4O_9]^+$ $[M]^+$: 696.2562, found 696.2594.

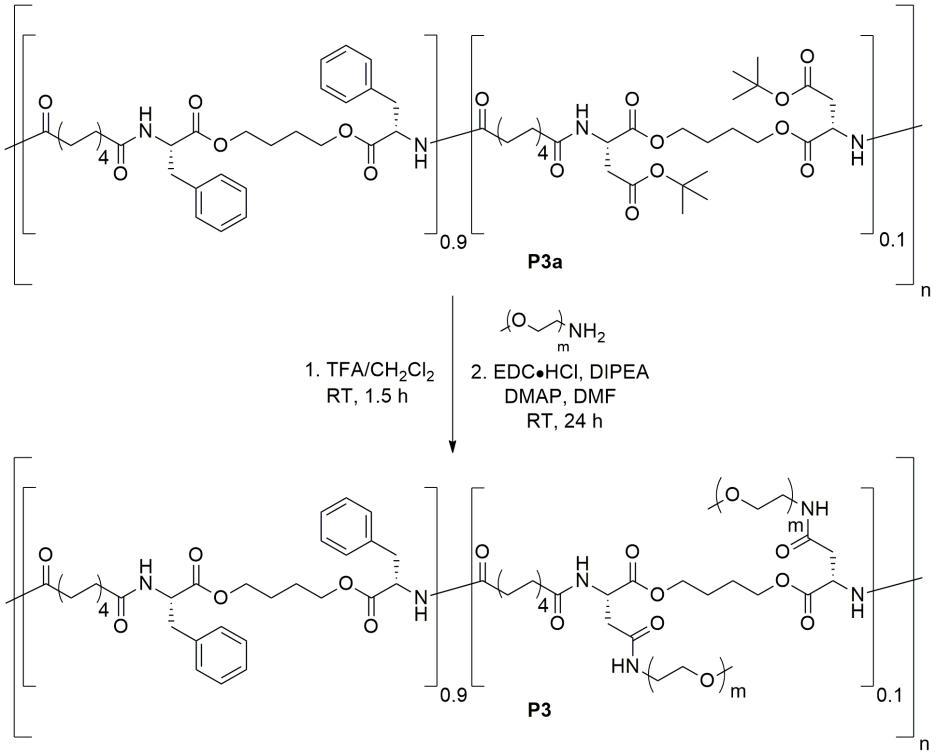
Synthesis of Compound 18

Compound **17** (225 mg, 0.323 mmol) was dissolved in CH_2Cl_2 (5 mL) at room temperature. TFA (5 mL) was then added and the reaction mixture was stirred for 2 hours. The solution was then concentrated *in vacuo* to give compound **18** (160 mg, 98%). This compound was prepared directly before polymerization, removal of the Boc group was confirmed by ^{1}H NMR, and the compound was used immediately as the TFA salt without further purification. ^{1}H NMR (600 MHz, DMSO-d_6): δ = 3.91-3.92 (m, 4H), 5.09 (s, 2H), 5.34 (s, 4H), 7.28-7.31 (m, 1H), 7.52-7.54 (m, 3H), 7.60-7.63 (m, 1H), 7.70-7.72 (m, 1H), 7.74-7.77 (m, 3H), 8.00-8.02 (m, 2H), 8.25 (br s, 6H).

Synthesis of Polymer P3

Poly(ester amide) **P3a** was prepared as previously reported[2] (Scheme S1, M_w = 16500 g mol^{-1}, $Đ$ = 1.55). **P3a** (57 mg) was then dissolved in CH_2Cl_2 (5 mL) and TFA (5 mL) was added. The solution was stirred for 1.5 h, and then the solvents were removed *in vacuo*. This material was then dissolved in DMF (1 mL) at room temperature. EDC·HCl (5 mg, 25.8 μmol) was added, followed by PEO-NH_2 (2000 g mol^{-1}, 51.66 mg, 25.8 μmol) and the reaction mixture was stirred for 10 min. DIPEA (6.7 mg, 52 μL) and DMAP (cat.) were introduced and the solution was stirred for 24 hours. The solution was then dialysed in 50 kg mol^{-1} MWCO dialysis membrane in DMF (50 mL) and then water (50 mL). The precipitated polymer solution was lyophilized to give polymer **P3** as a white solid (35 mg, 38%). ^{1}H NMR (600 MHz, DMSO-d_6): δ = 1.07-1.21 (m, 9.1H), 1.35-1.49 (m, 9.1H), 1.57-1.59 (m, 0.4H), 2.01-2.05 (m, 4.0H), 2.66-2.70 (m, 0.1H), 2.86-2.90 (m, 1.9H), 2.98-3.01 (m, 1.9H), 3.24 (s, 0.2H), 3.40-

3.60 (m, 12.6H), 3.94-3.98 (m, 4.0H), 4.43-4.47 (m, 1.9H), 4.57-4.58 (m, 0.1H), 7.17-7.27 (m, 9.1H), 8.22-8.23 (m, 2.0H). SEC: M_W = 18200 g mol^{-1}, $Đ$ = 1.58.



Scheme S1. Synthesis of control polymer **P3** with no azobenzenes. **P3a** was prepared as previously reported.[2]

Reduction kinetics analysis

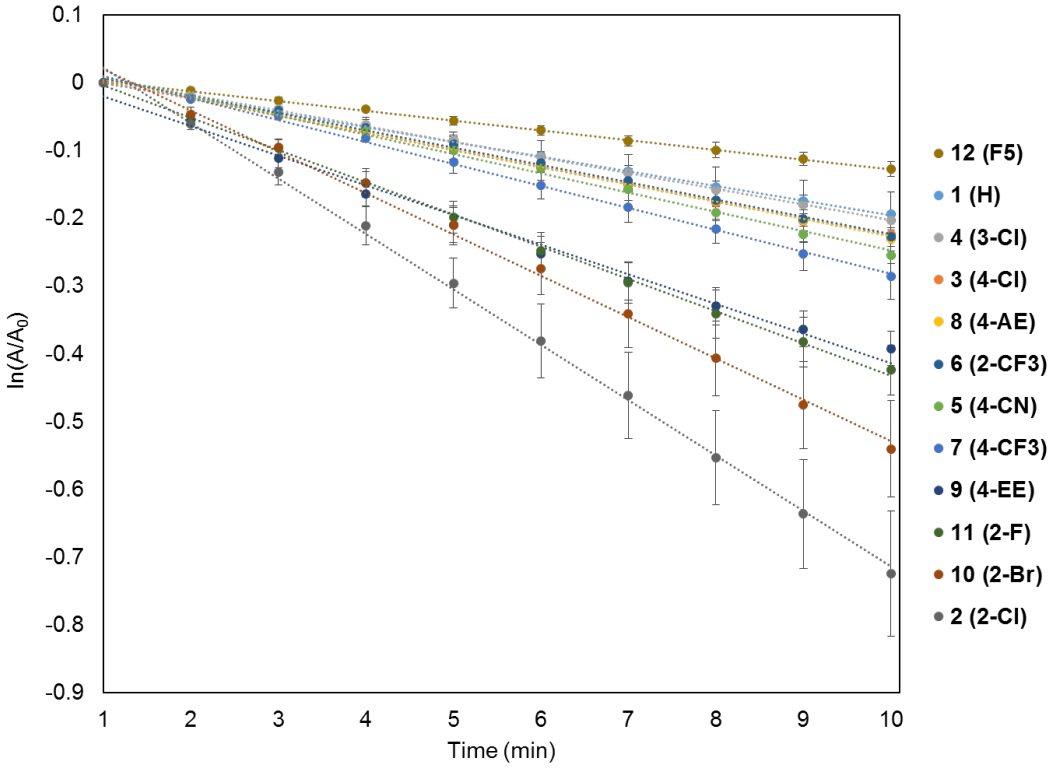


Figure S 1: Plot of $\ln(A/A_0)$ versus time (where A = absorbance) for each of 12 synthesized azobenzenes over time, after the addition of hydrazine.

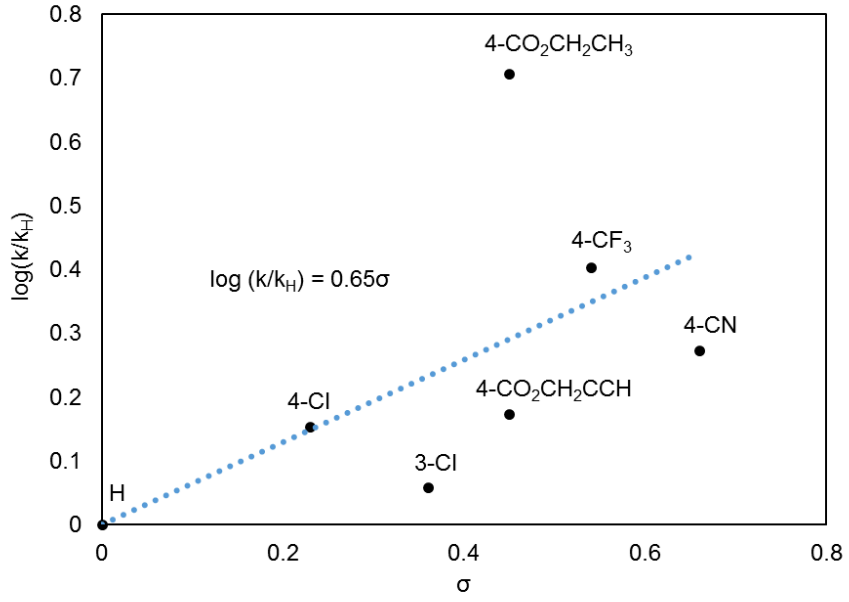


Figure S 2: Hammett plot of 3- and 4-substituted azobenzenes demonstrating poor correlation between σ for the substituents and rate of reduction.

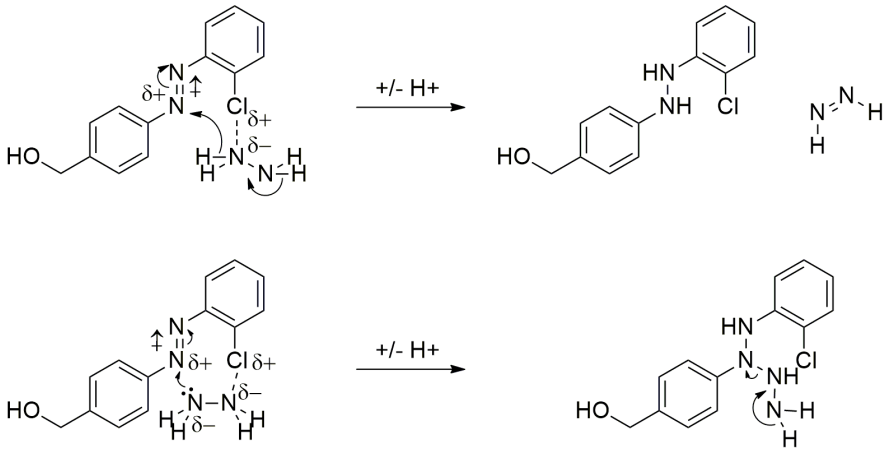


Figure S 3: Possible mechanisms of pre-association and subsequent reduction of ortho-halogen-substituted azobenzenes by hydrazine.

^{1}H NMR Spectra

Compound 2

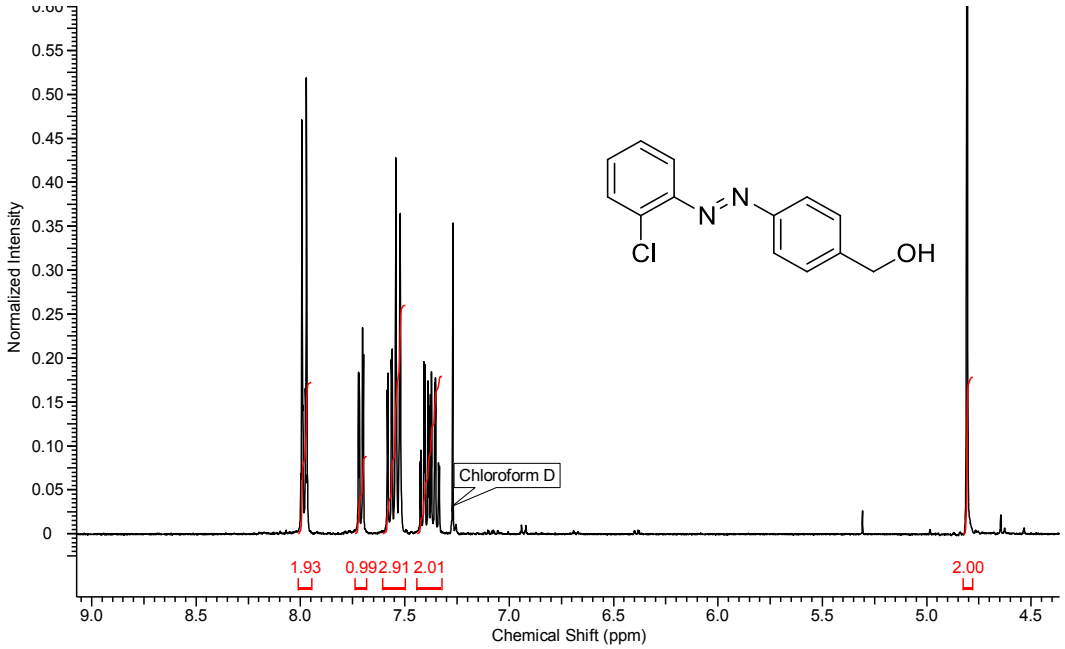


Figure S 4: ^{1}H NMR spectrum of compound **2** (400 MHz, $CDCl_3$).

Compound 3

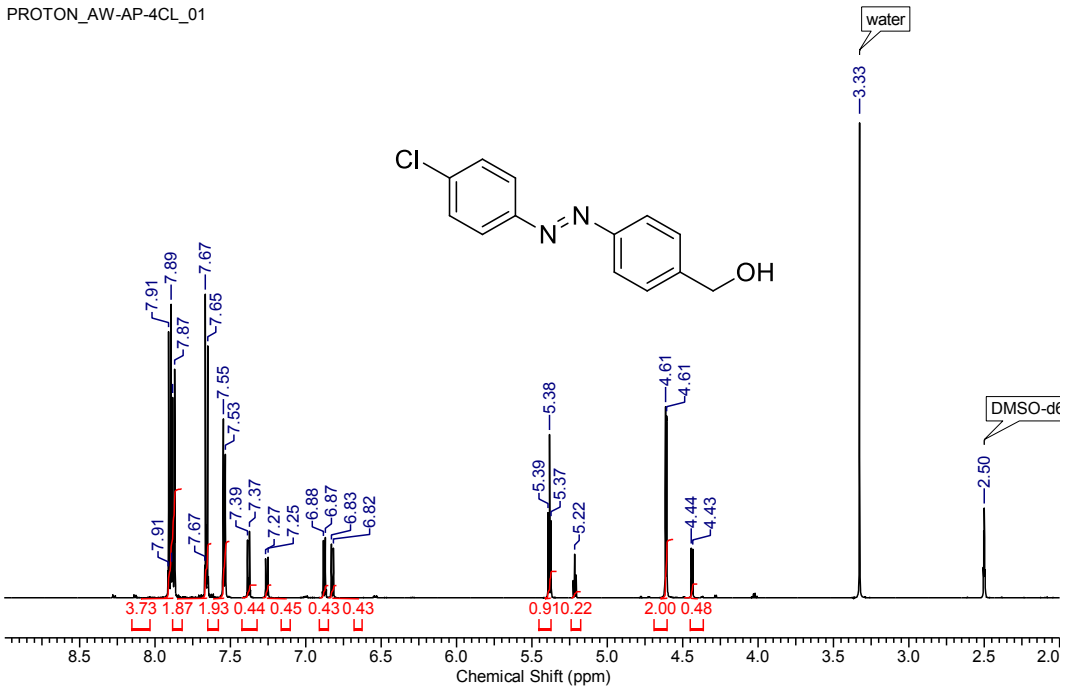


Figure S 5: ^{1}H NMR spectrum of compound **3** (600 MHz, DMSO-d_6). Small peaks correspond to the *cis* isomer.

Compound 4

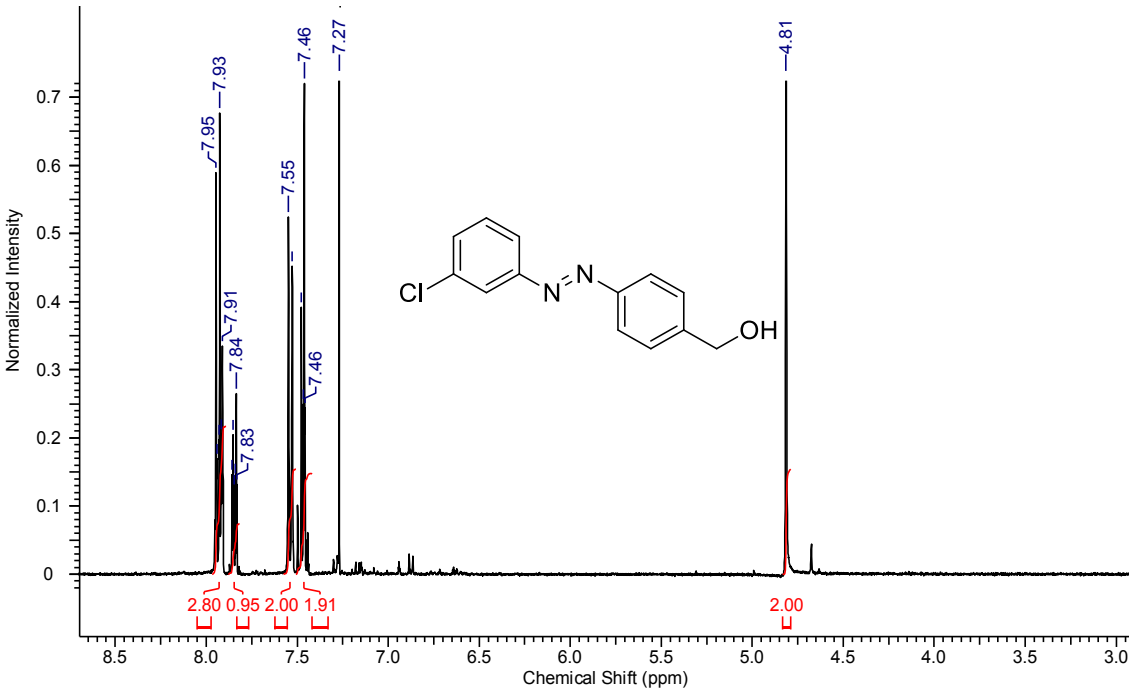


Figure S 6: ^{1}H NMR spectrum of compound **4** (400 MHz, $CDCl_3$). Small peaks correspond to the *cis* isomer.

Compound 5

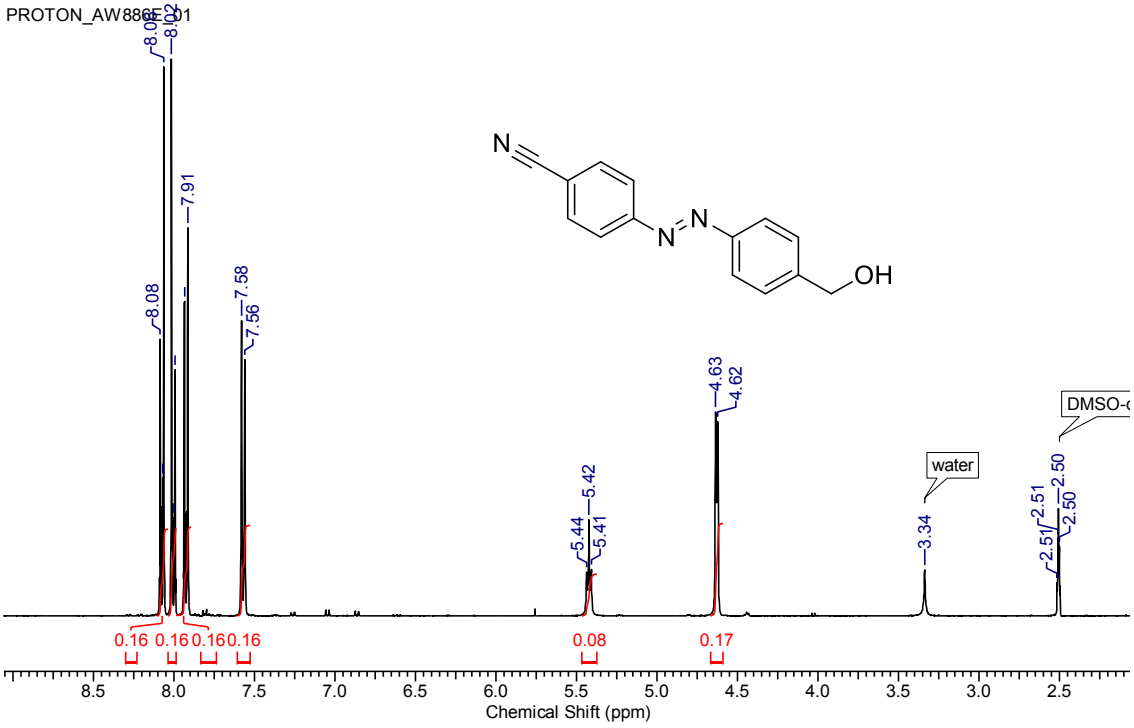


Figure S 7: ^{1}H NMR spectrum of compound **5** (600 MHz, DMSO-d_6).

Compound 6

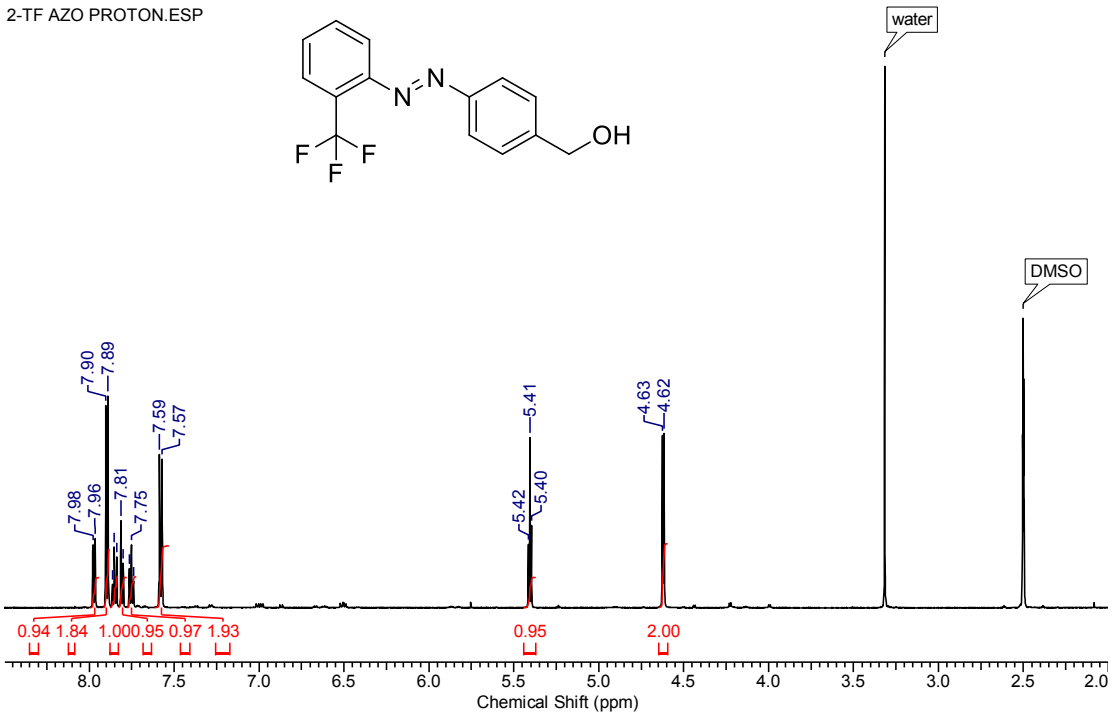


Figure S 8: ^{1}H NMR spectrum of compound **6** (600 MHz, $CDCl_3$).

Compound 7

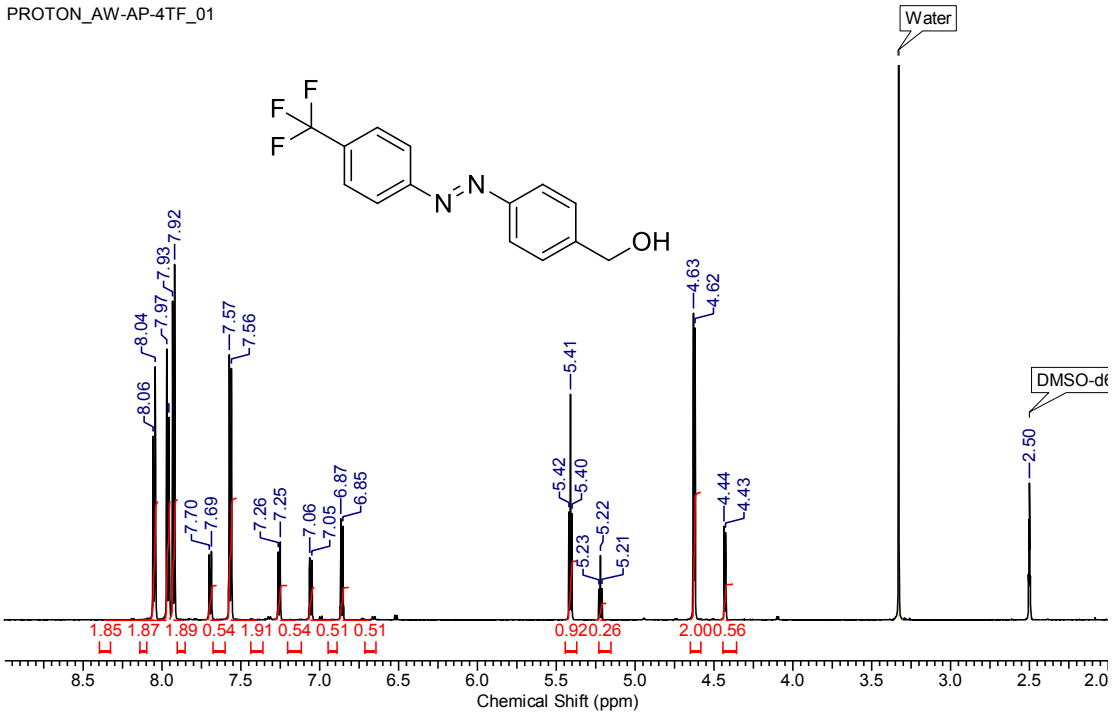


Figure S 9: ^{1}H NMR spectrum of compound **7** (600 MHz, DMSO-d_6). Small peaks correspond to the *cis* isomer.

Compound 8

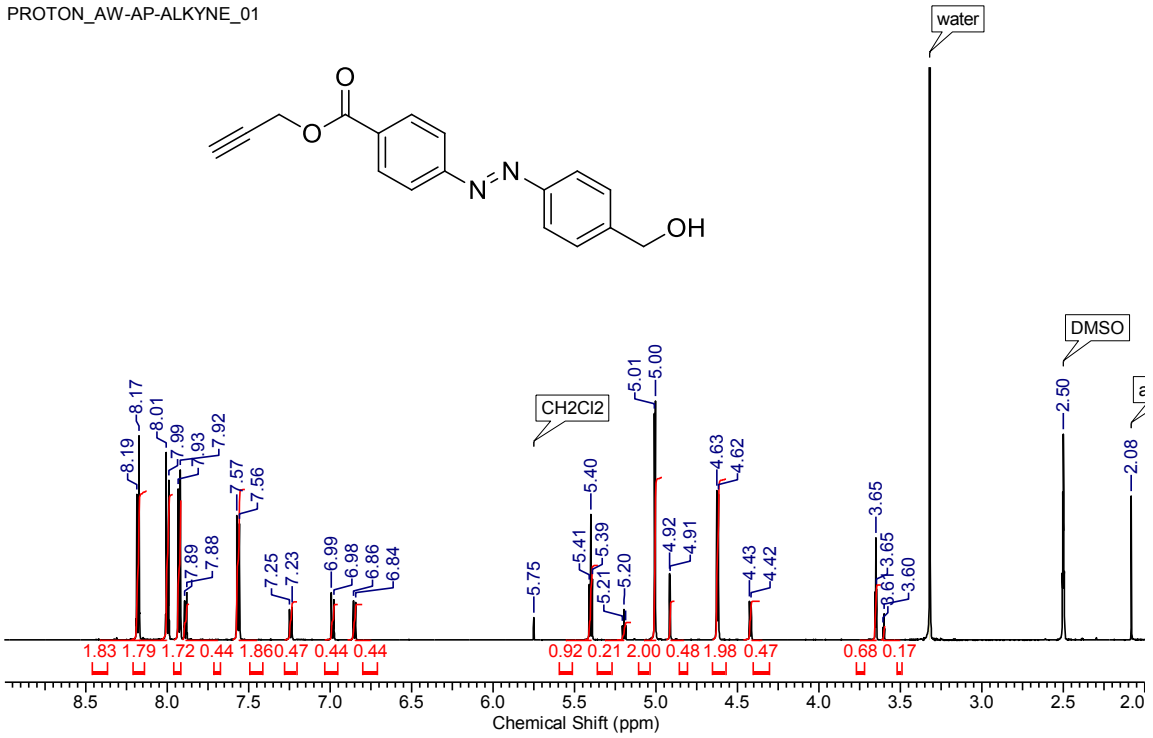


Figure S 10: ^{1}H NMR spectrum of compound **8** (600 MHz, DMSO-d_6). Small peaks correspond to the *cis* isomer.

Compound 10

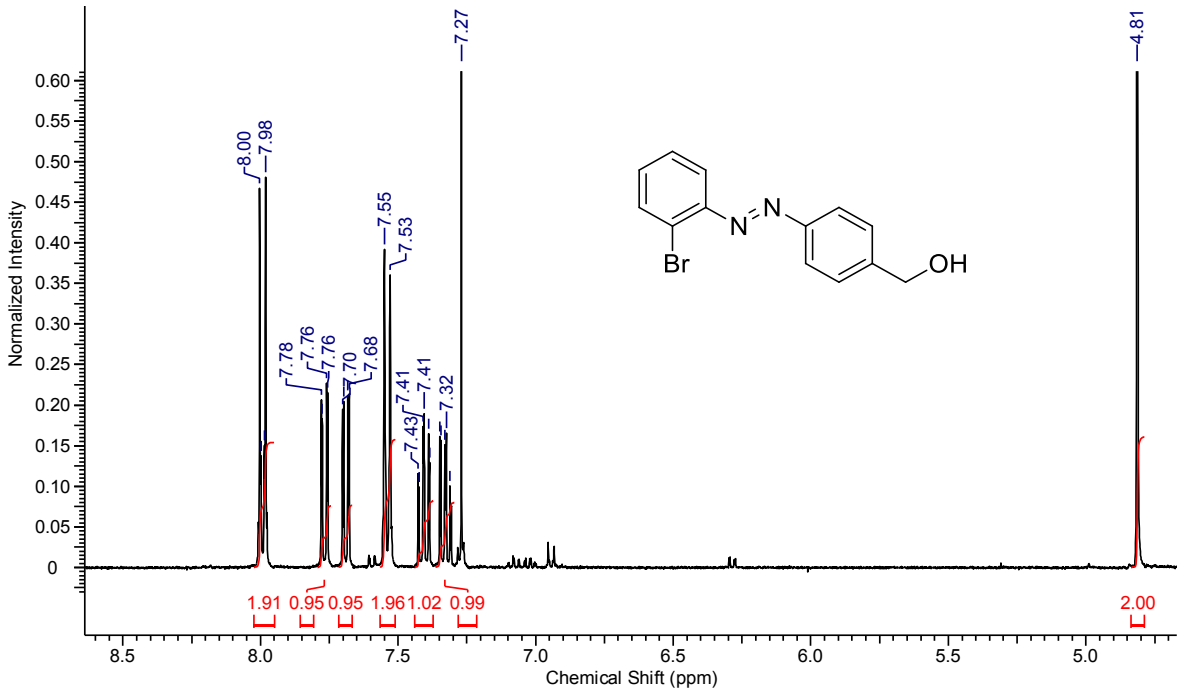


Figure S 11: ^{1}H NMR spectrum of compound **10** (400 MHz, $CDCl_3$). Small peaks correspond to the *cis* isomer.

Compound 11

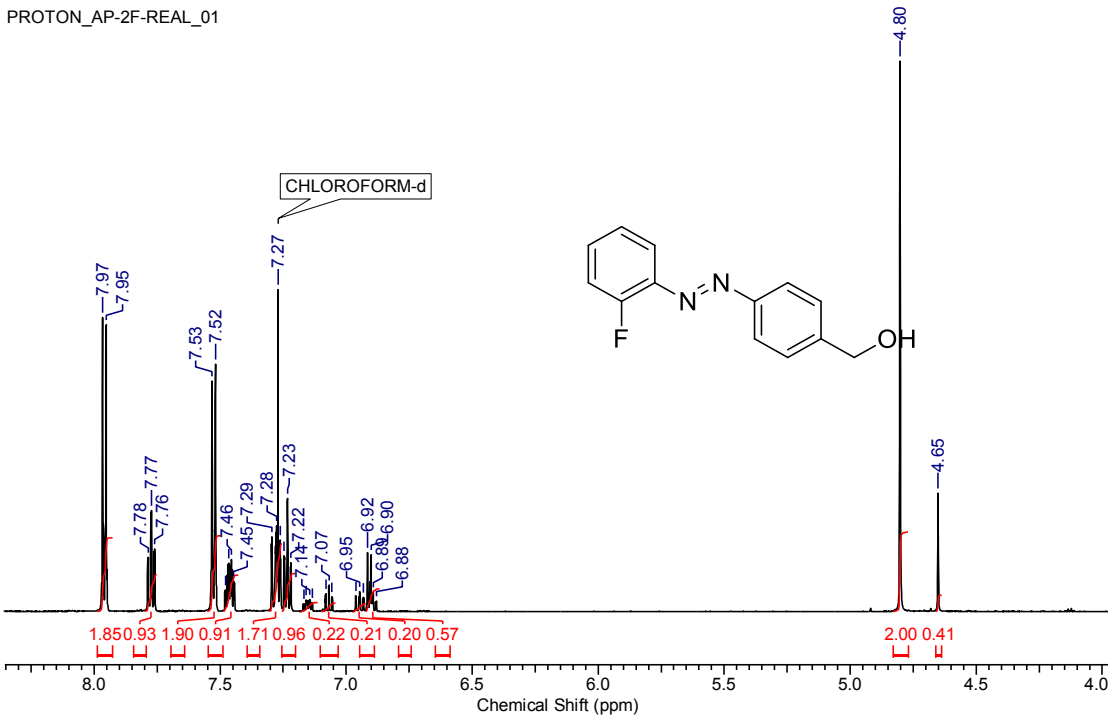


Figure S 12: ^{1}H NMR spectrum of compound **11** (400 MHz, $CDCl_3$). Small peaks correspond to the *cis* isomer.

Compound 12

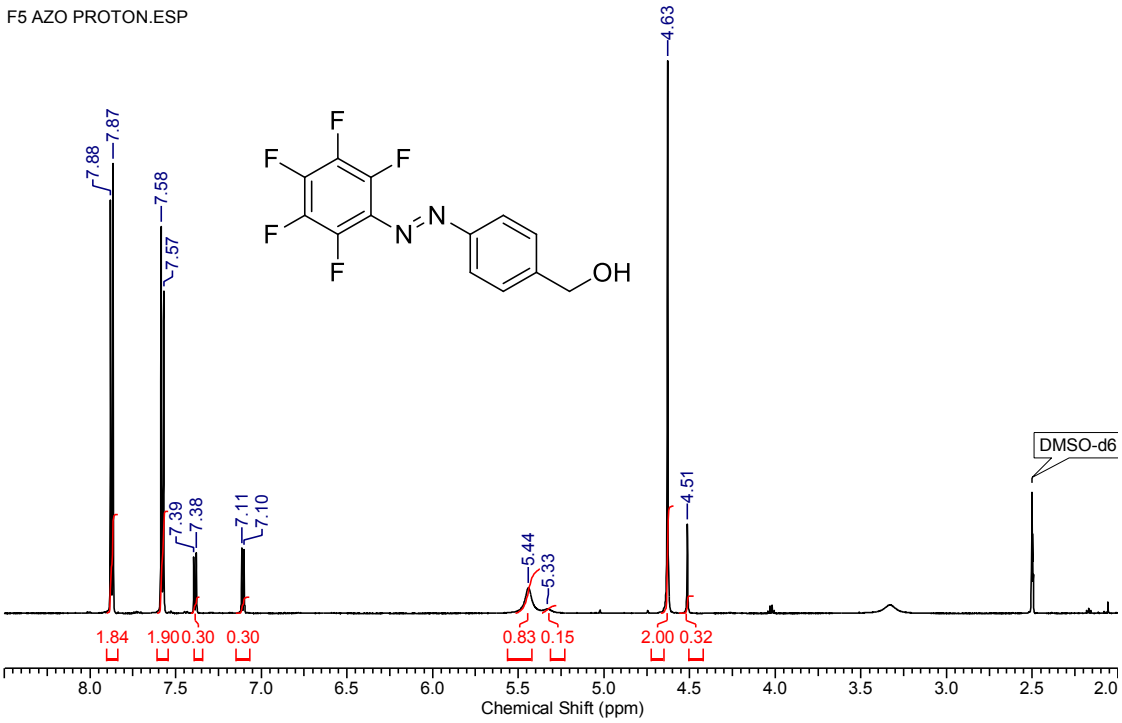


Figure S 13: ^{1}H NMR spectrum of compound **12** (600 MHz, DMSO-d_6). Small peaks correspond to the *cis* isomer.

Compound 13

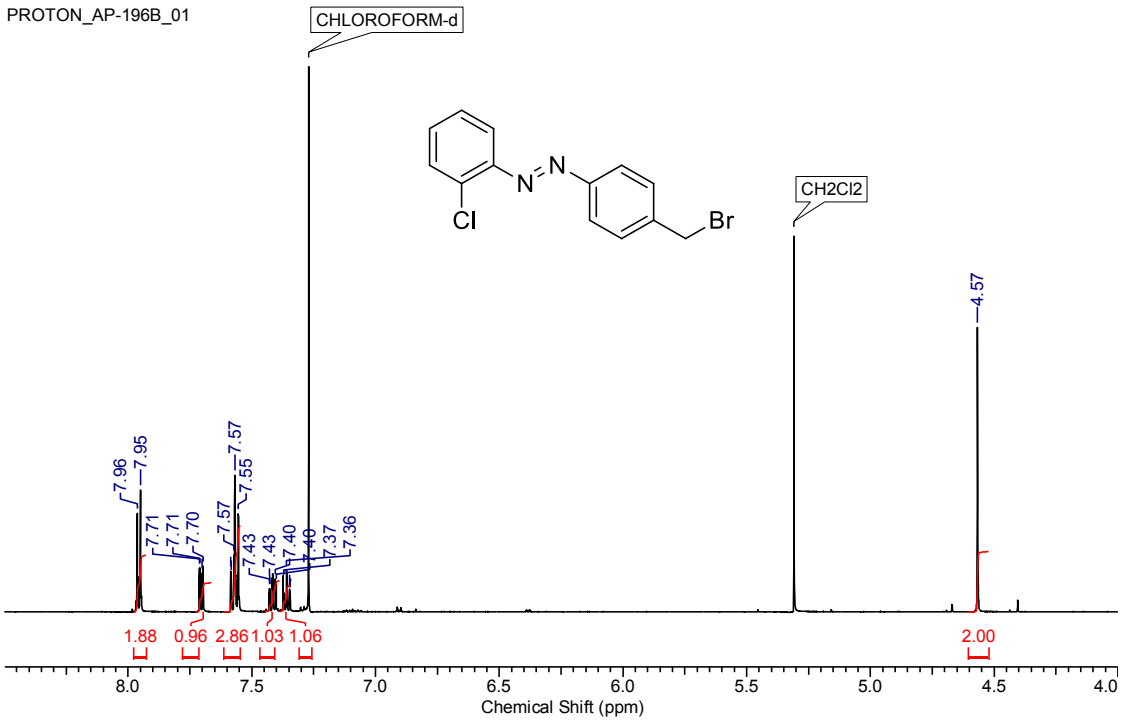


Figure S 14: ^{1}H NMR spectrum of compound **13** (600 MHz, $CDCl_3$).

Compound 15

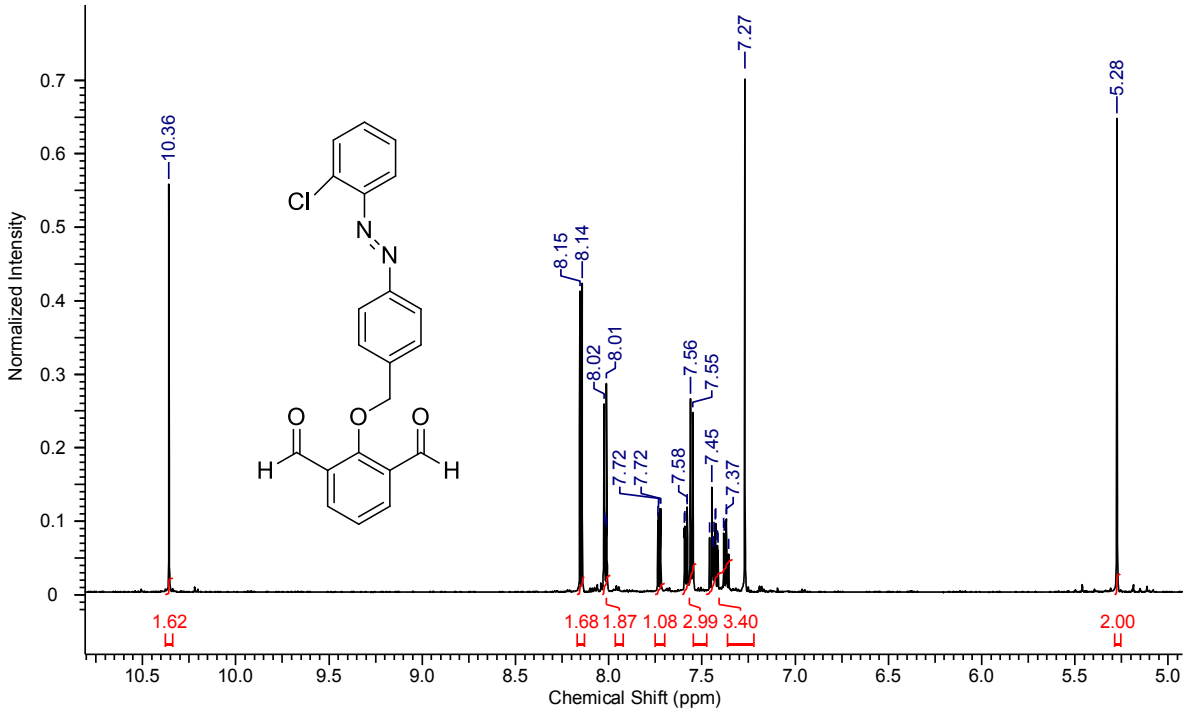


Figure S 15: ^{1}H NMR spectrum of compound **15** (600 MHz, $CDCl_3$).

Compound 16

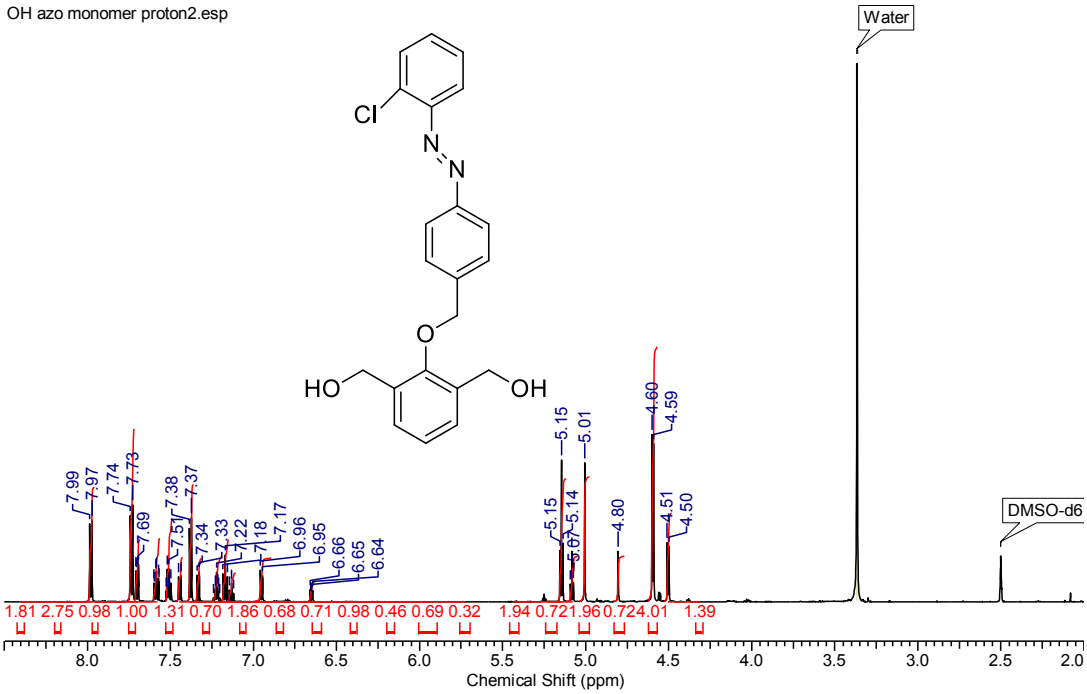


Figure S 16: ^{1}H NMR spectrum of compound **16** (600 MHz, DMSO-d_6). Small peaks correspond to the *cis* isomer.

Compound 17

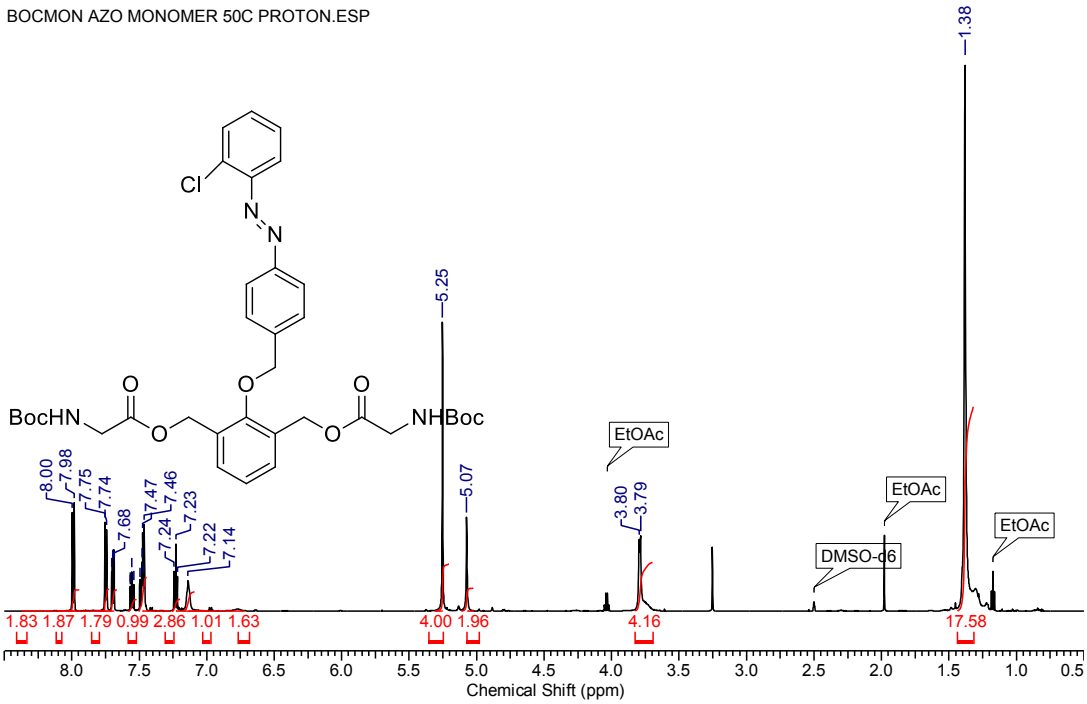


Figure S 17: ^{1}H NMR spectrum of compound **17** (600 MHz, DMSO-d_6, 50 °C). Elevated temperature was used to reduce the signal intensity of the *cis* isomer and identify peaks.

Compound 18

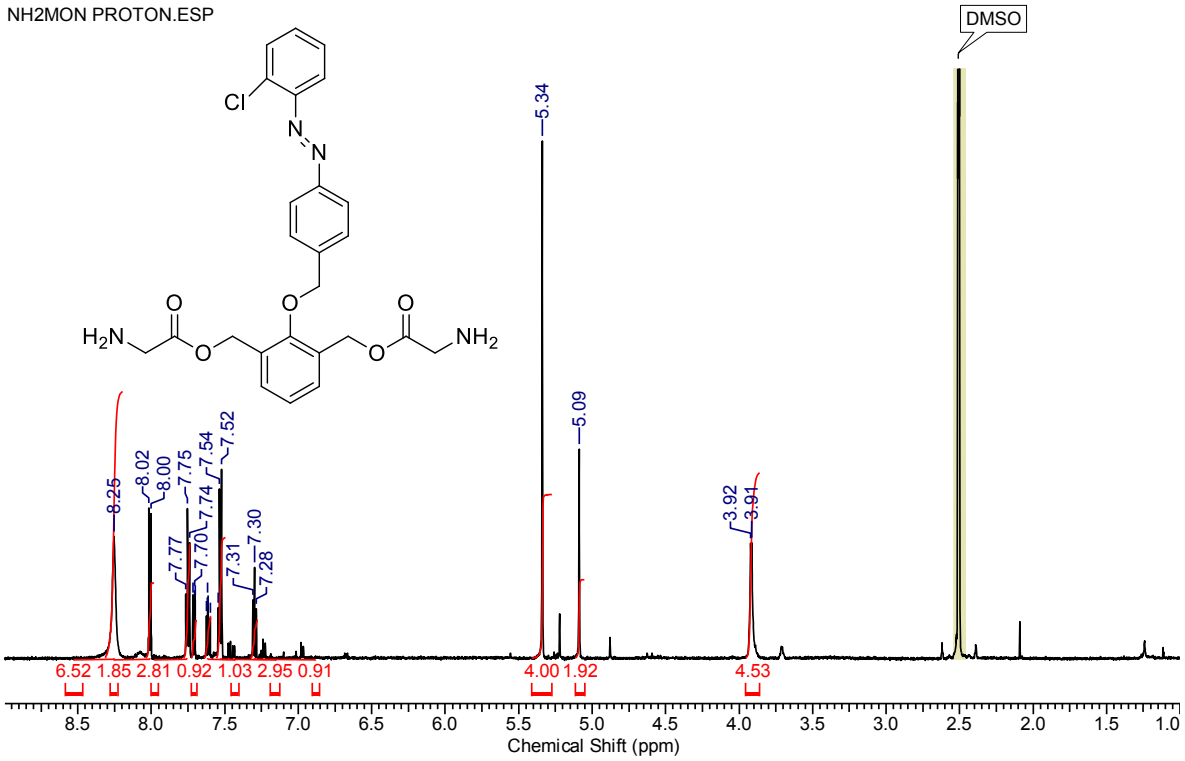


Figure S 18: ^{1}H NMR spectrum of compound **18** (600 MHz, DMSO-d_6). Small peaks correspond to the *cis* isomer.

Polymer P1

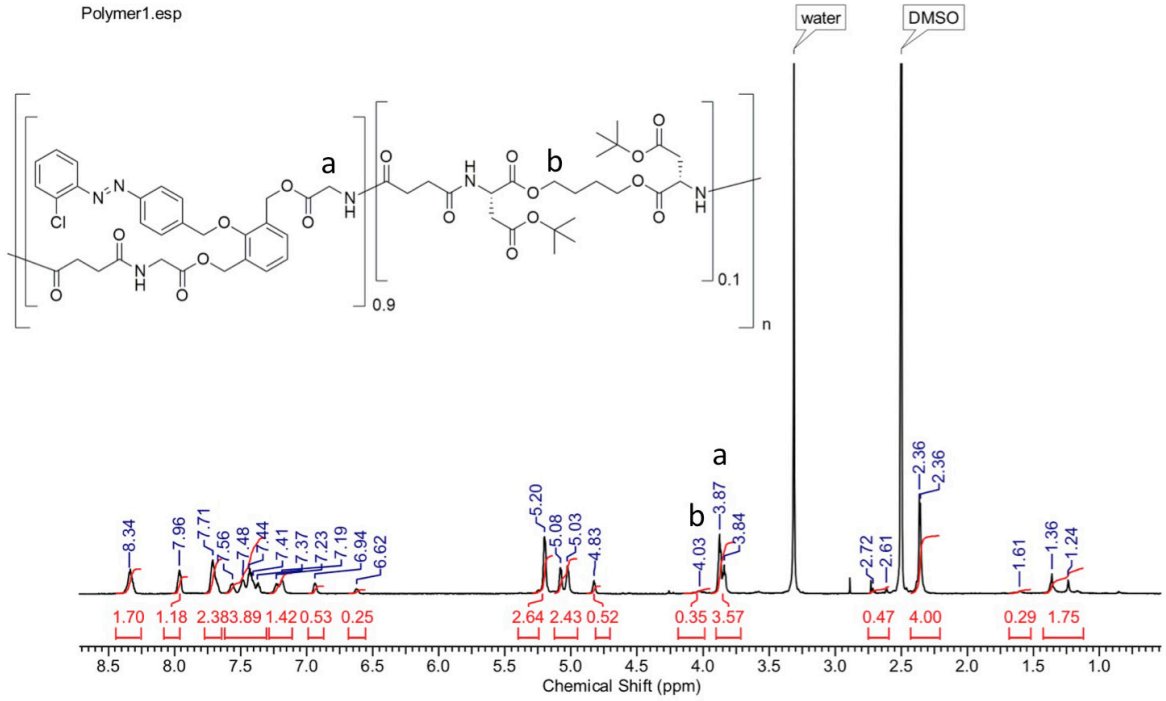


Figure S 19: ^{1}H NMR spectrum of polymer **P1** (600 MHz, DMSO-d_6). Note a mixture of *trans* and *cis* isomers was observed in this NMR solvent. An approximate 9:1 ratio of monomers **18**:**19** as per the feed ratios indicated in Scheme 3 is supported by the relative integrations of the peak at 3.8 ppm corresponding to the α-hydrogens on the glycine of monomer **18** (labeled a) and the peak at 4.0 corresponding to -CH_2-C**H**$_2$O-C(O)- on monomer **19** (labeled b).

Polymer P2

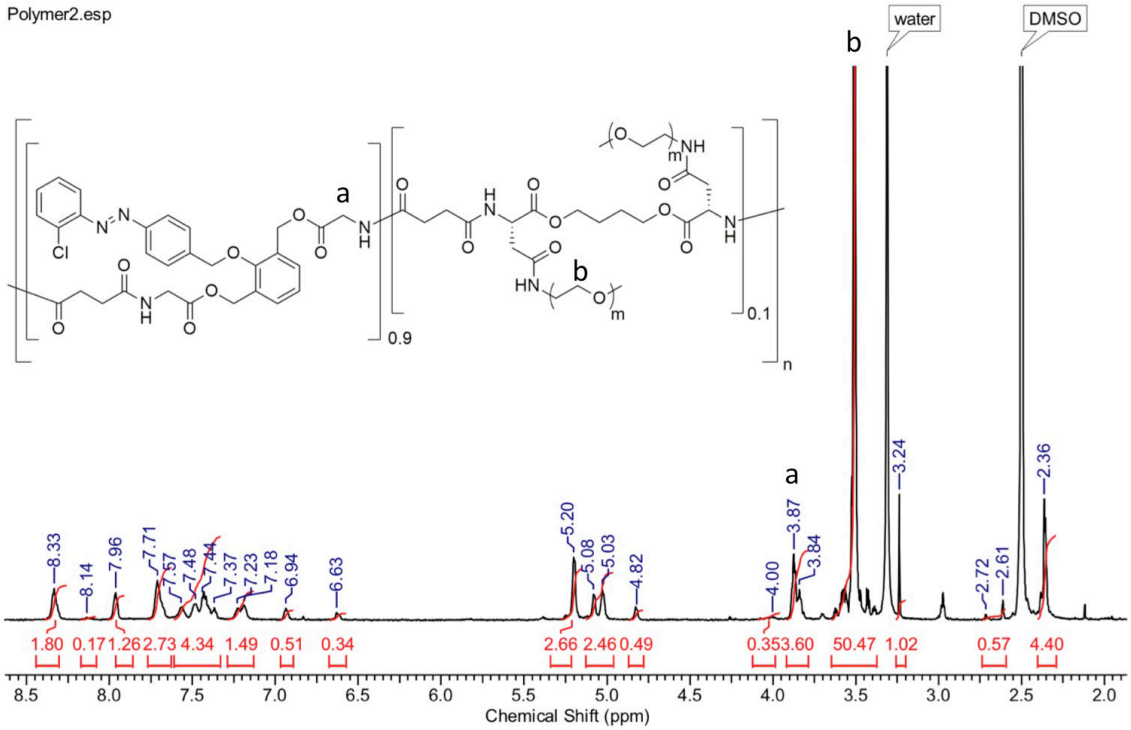


Figure S 20: ^{1}H NMR spectrum of polymer **P2** (600 MHz, DMSO-d_6). Note a mixture of *trans* and *cis* isomers was observed in this NMR solvent. Approximately quantitative coupling of PEO-NH_2 to the carboxylic acids is supported by the relative integrations of the peak at 3.5 ppm corresponding to PEO (labeled b) and the peak at 3.9 ppm corresponding to the α-hydrogens on the glycine of monomer **18** (labeled a).

Polymer P3a

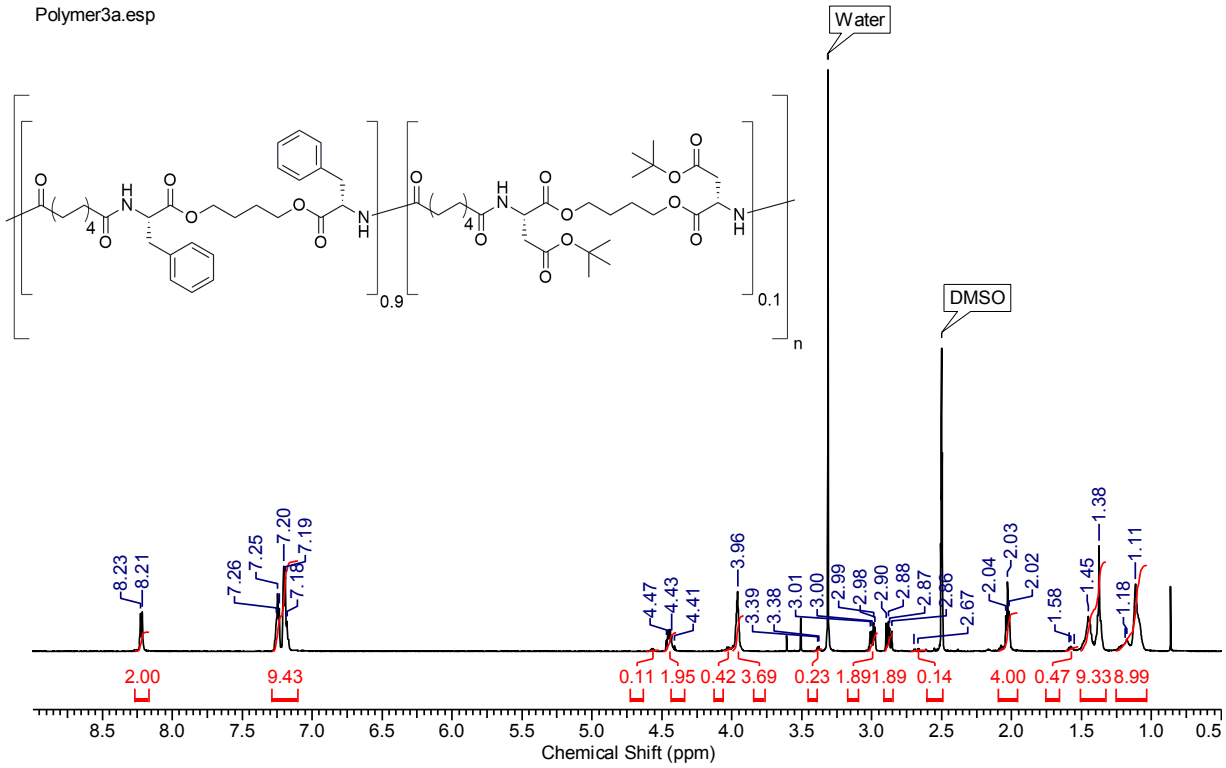


Figure S 21: ^{1}H NMR spectrum of polymer **P3a** (600 MHz, DMSO-d_6). This polymer was previously reported[2] and this spectrum is only included for comparison with **P3**.

Polymer 3

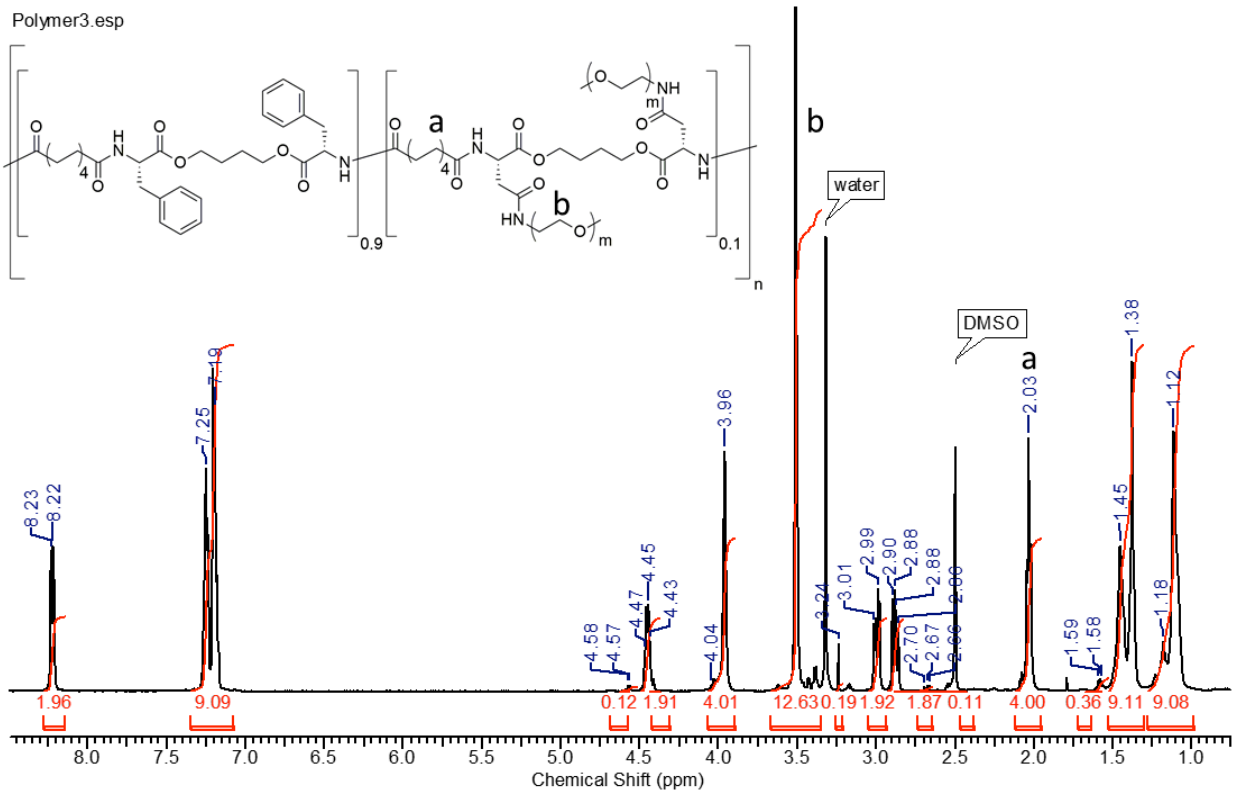


Figure S 22: ^{1}H NMR spectrum of polymer **P3** (600 MHz, DMSO-d_6). Approximately quantitative coupling of PEO-NH_2 to the carboxylic acids is supported by the relative integrations of the peak at 3.5 ppm corresponding to PEO (labeled b) and the peak at 2.0 ppm corresponding to the α-hydrogens of the sebacic acid component (labeled a).

^{13}C NMR Spectra

Compound 2

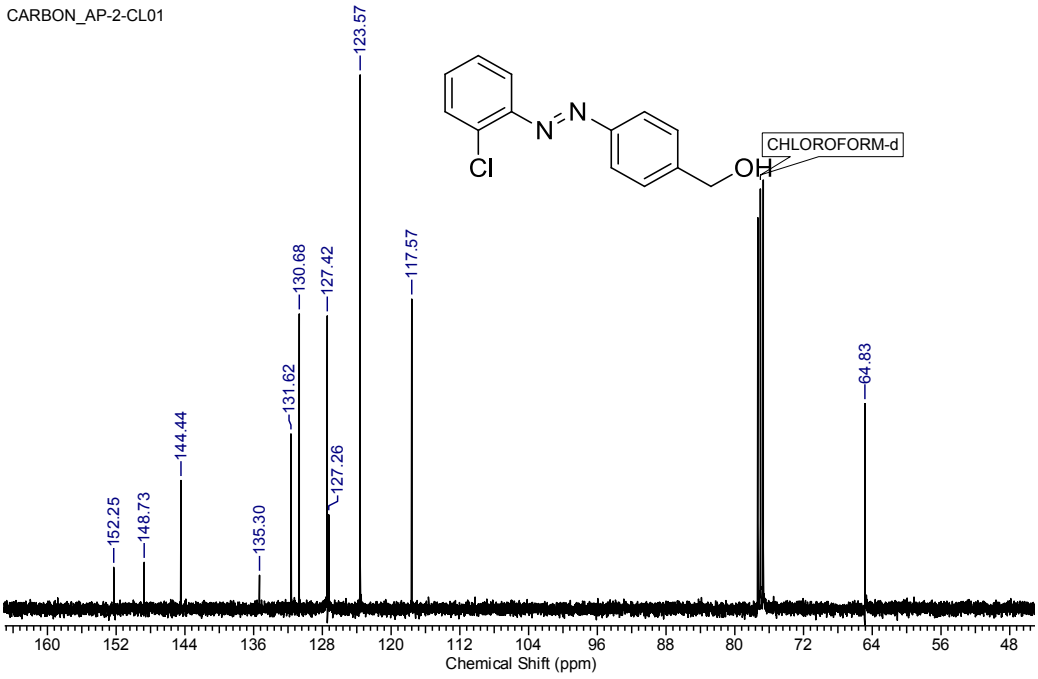


Figure S 23: ^{13}C NMR spectrum of compound **2** (100 MHz, $CDCl_3$).

Compound 3

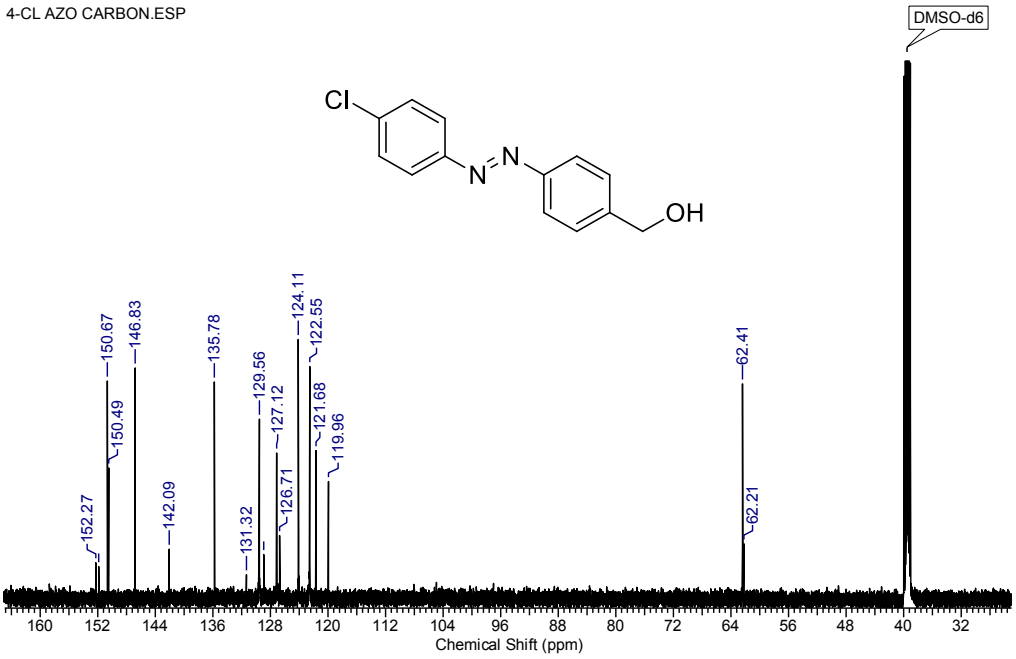


Figure S 24: ^{13}C NMR spectrum of compound **3** (150 MHz, DMSO-d_6). Peaks corresponding to the *cis* isomer are observed.

Compound 4

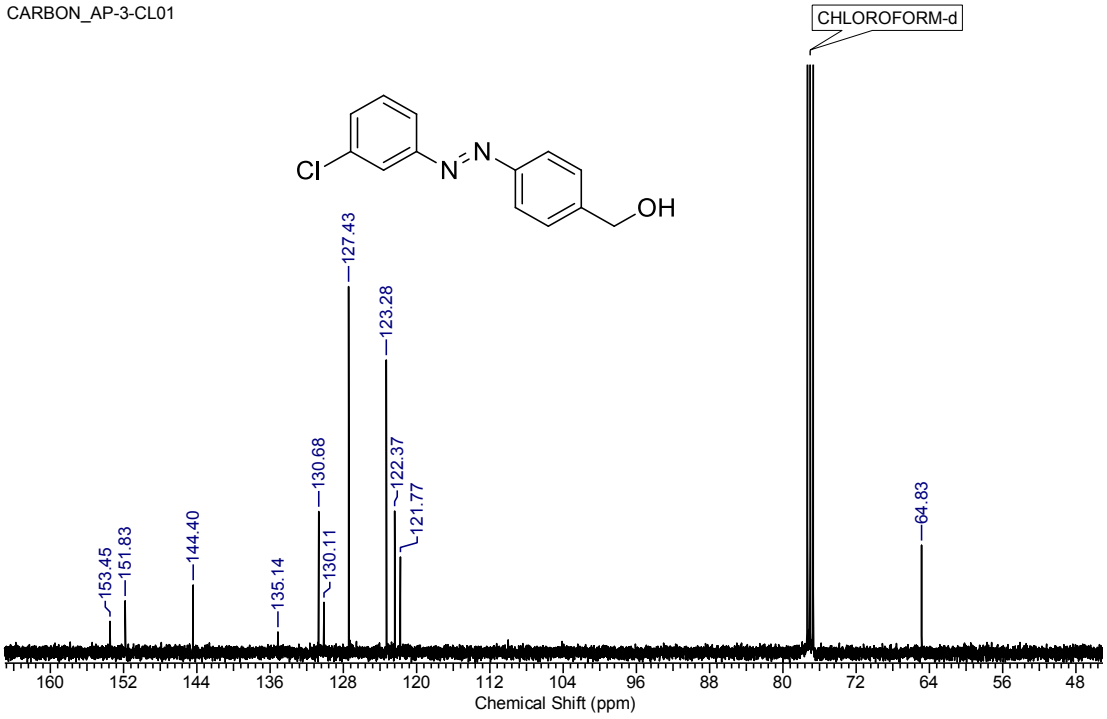


Figure S 25: ^{13}C NMR spectrum of compound **4** (100 MHz, $CDCl_3$).

Compound 5

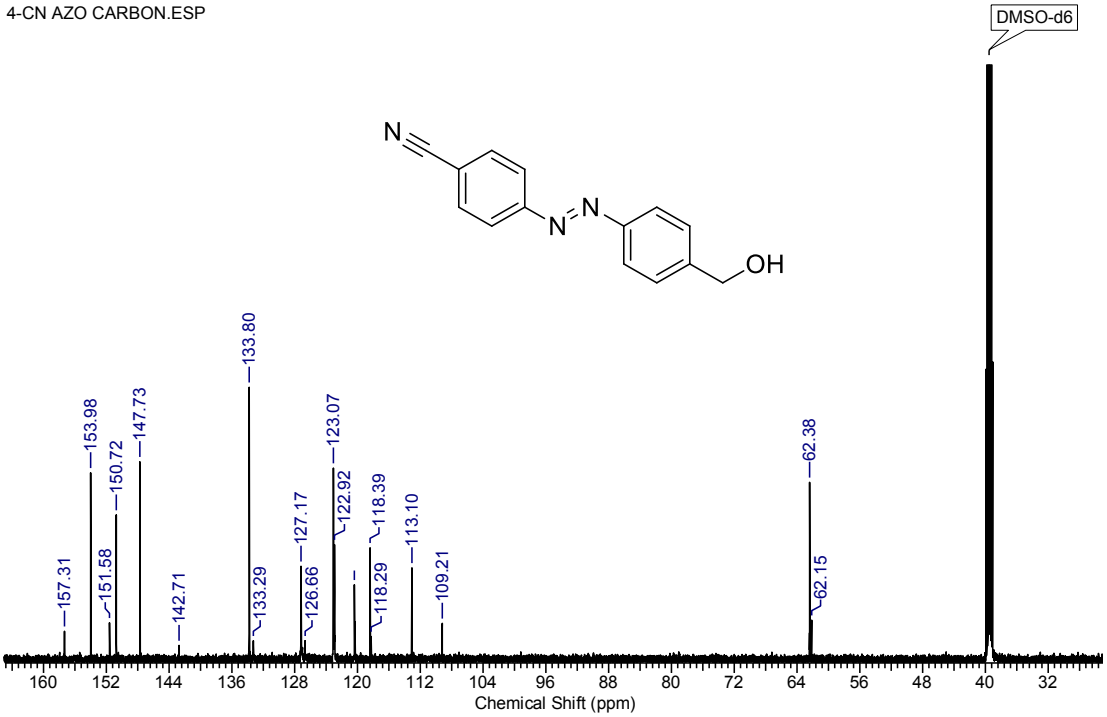


Figure S 26: ^{13}C NMR spectrum of compound **5** (150 MHz, DMSO-d_6). Peaks corresponding to the *cis* isomer are observed.

Compound 6

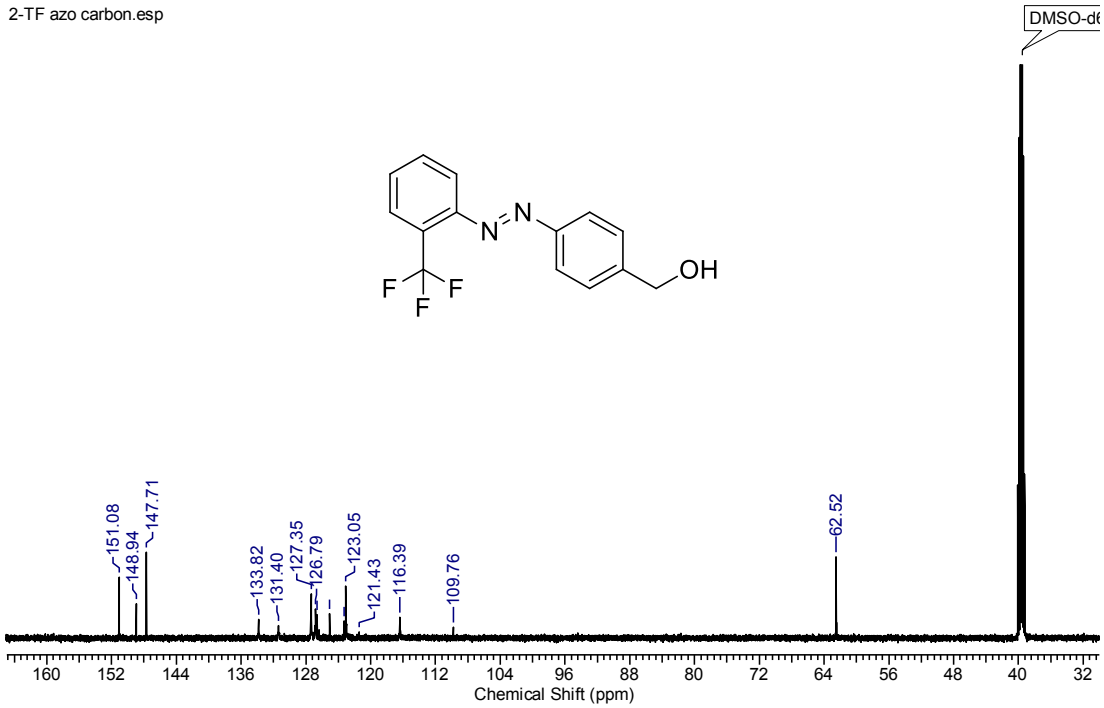


Figure S 27: ^{13}C NMR spectrum of compound **6** (150 MHz, DMSO-d_6).

Compound 7

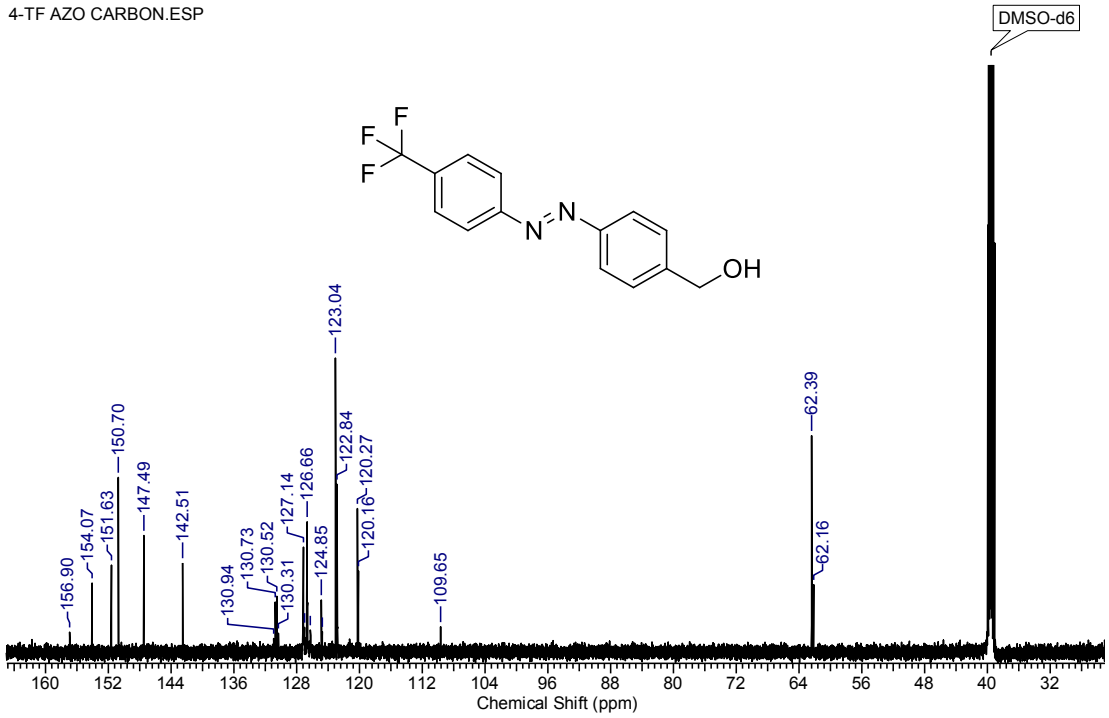


Figure S 28: ^{13}C NMR spectrum of compound **7** (150 MHz, DMSO-d_6). Peaks corresponding to the *cis* isomer are observed.

Compound 8

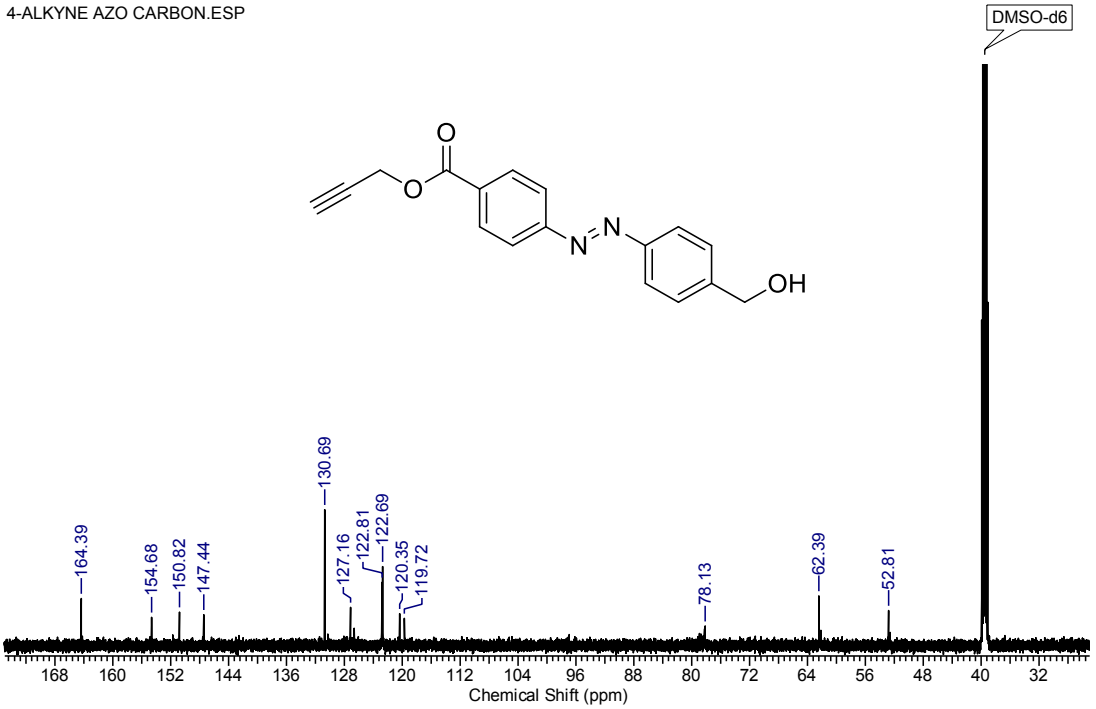


Figure S 29: ^{13}C NMR spectrum of compound **9** (150 MHz, DMSO-d_6).

Compound 10

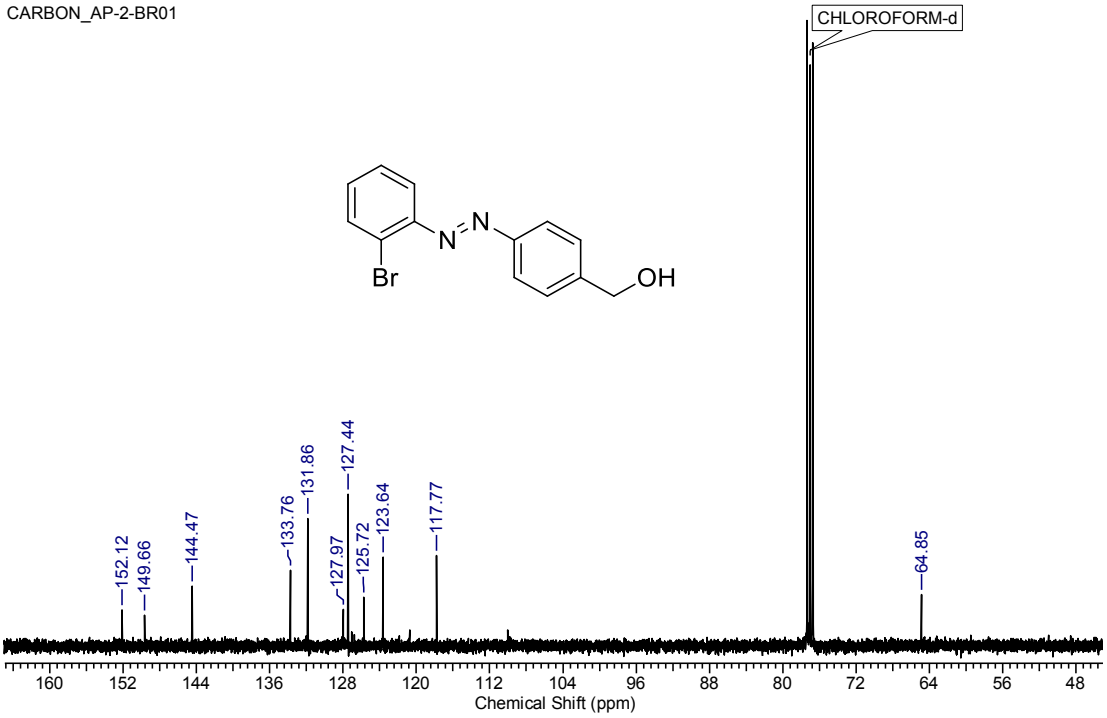


Figure S 30: ^{13}C NMR spectrum of compound **10** (100 MHz, $CDCl_3$).

Compound 11

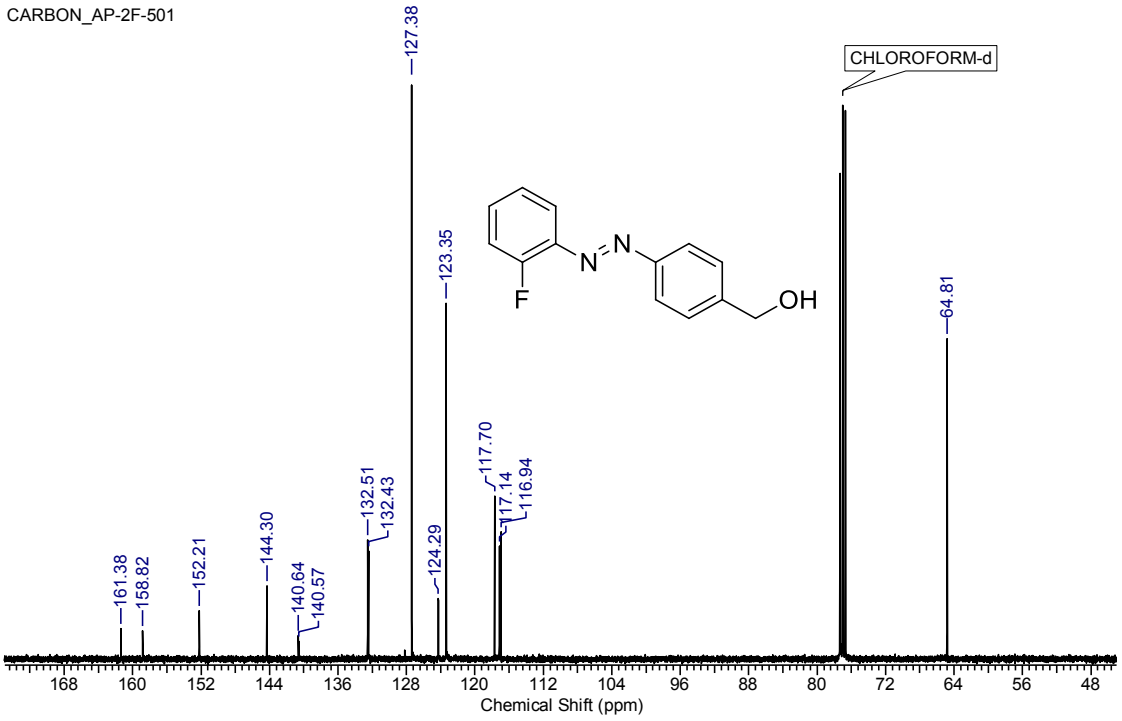


Figure S 31: ^{13}C NMR spectrum of compound **11** (100 MHz, $CDCl_3$).

Compound 12

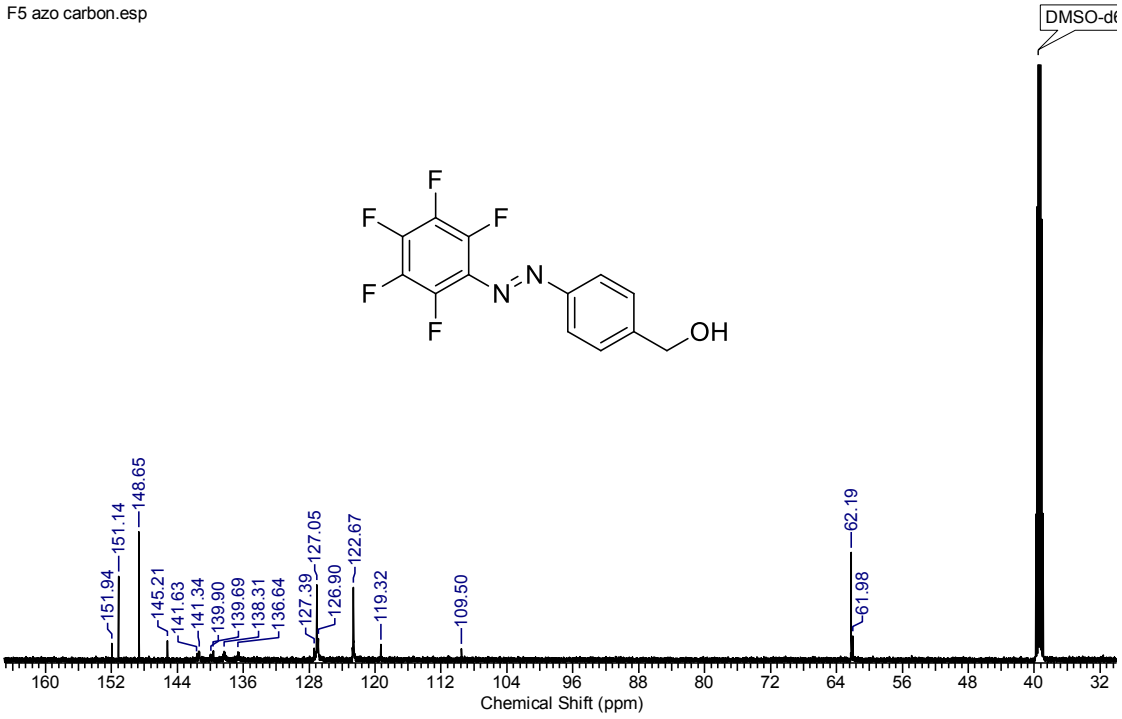


Figure S 32: ^{13}C NMR spectrum of compound **12** (150 MHz, DMSO-d_6). Peaks corresponding to the *cis* isomer are observed.

Compound 13

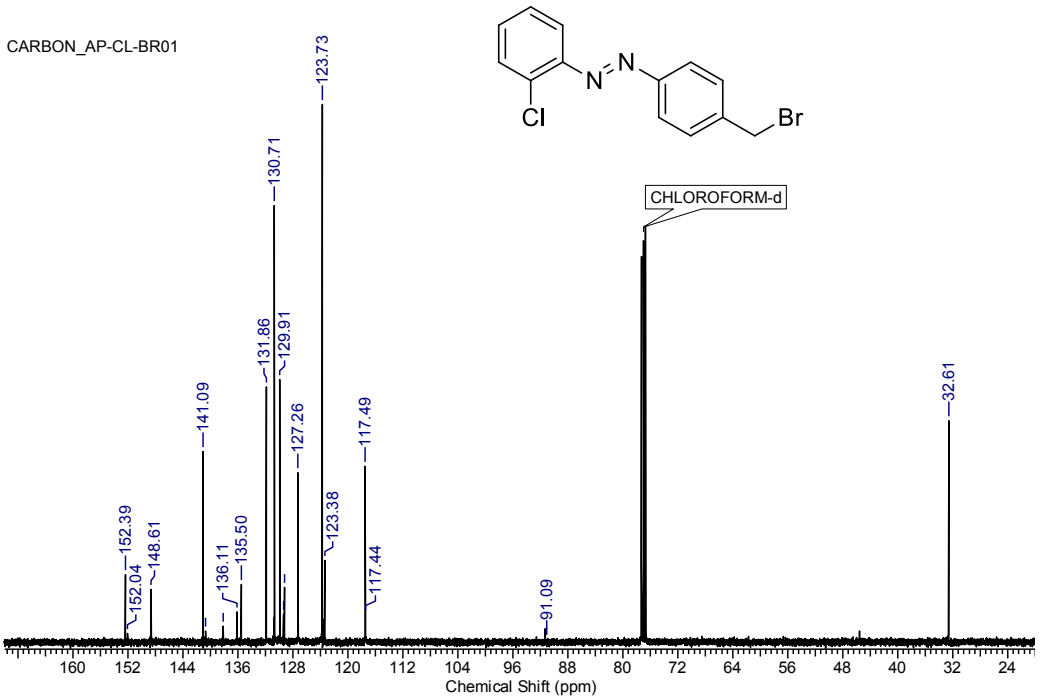


Figure S 33: ^{13}C NMR spectrum of compound **13** (100 MHz, $CDCl_3$). Small peaks belong to the *cis* isomer. Peaks corresponding to the *cis* isomer are observed.

Compound 15

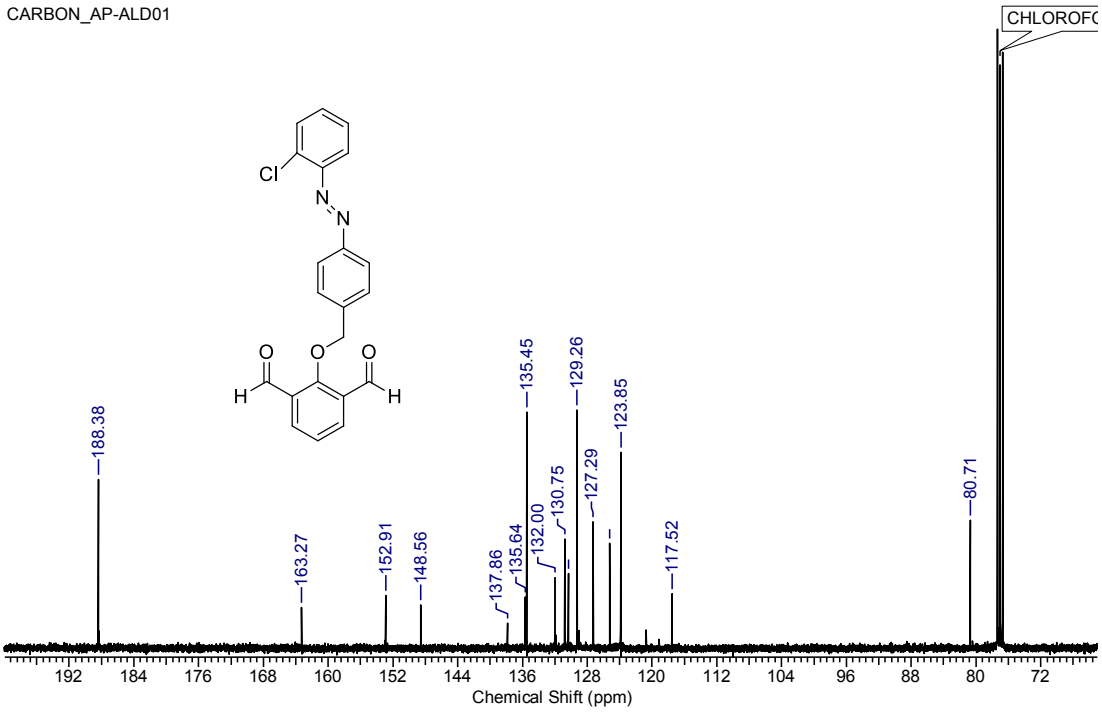


Figure S 34: ^{13}C NMR spectrum of compound **15** (100 MHz, $CDCl_3$).

Compound 16

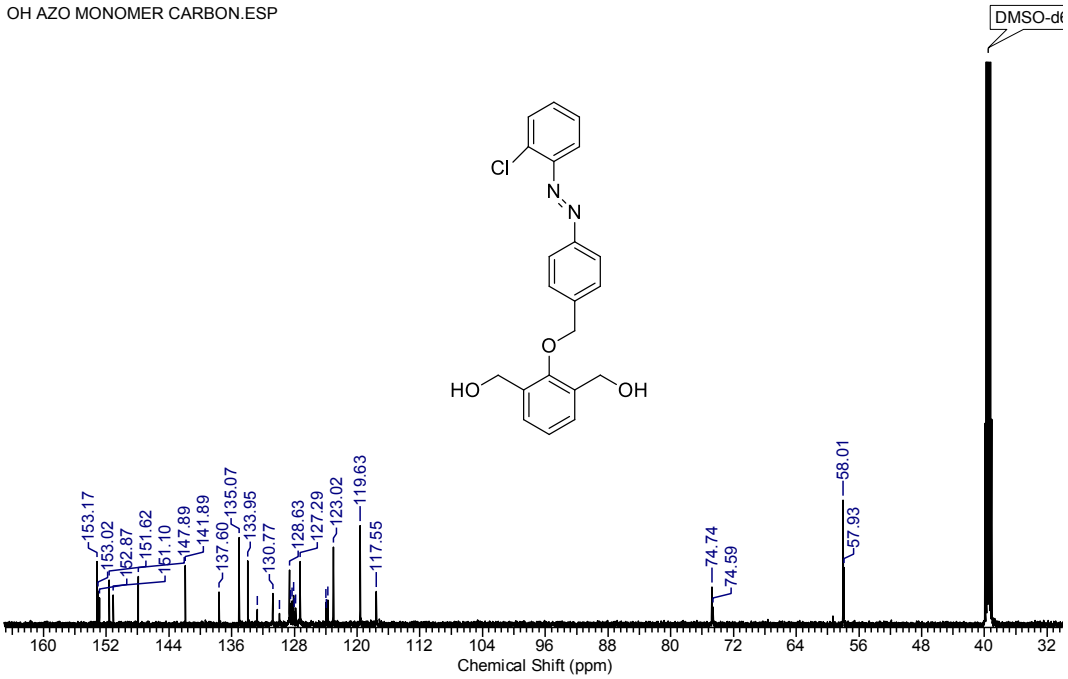


Figure S 35: ^{13}C NMR spectrum of compound **17** (150 MHz, DMSO-d_6). Peaks corresponding to the *cis* isomer are observed.

Compound 17

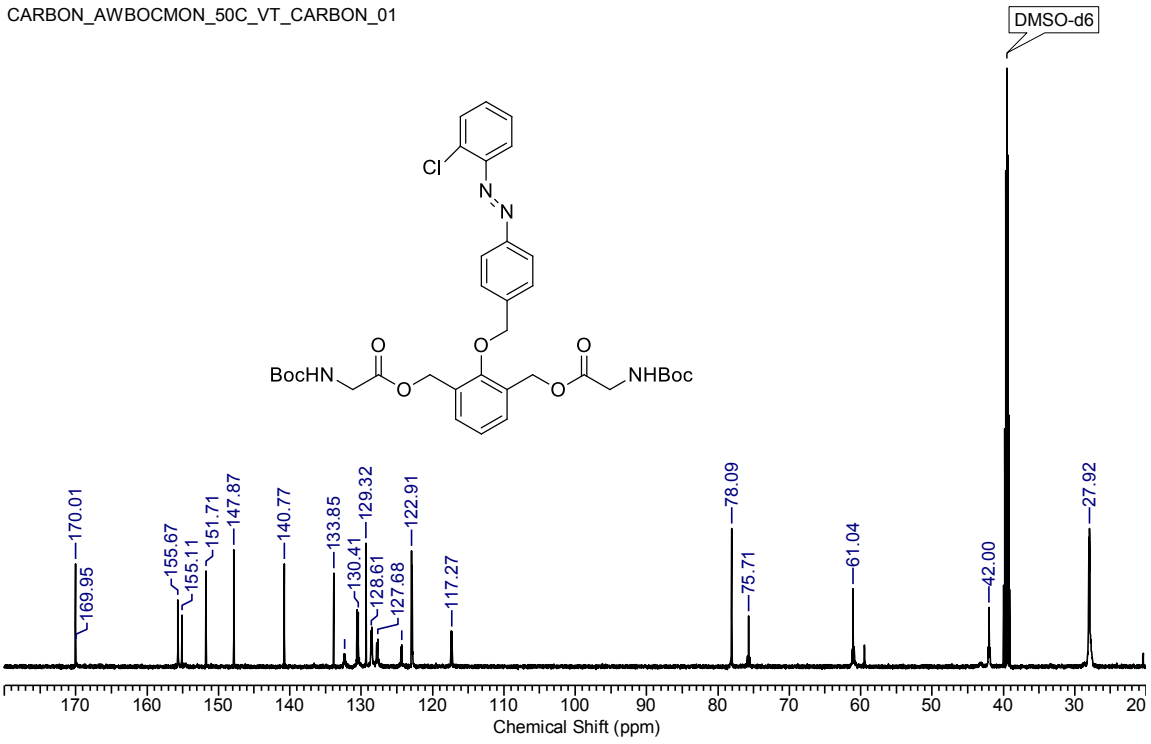


Figure S 36: ^{13}C NMR spectrum of compound **17** (150 MHz, DMSO-d_6, 50 °C).

Polymer Characterization

SEC Traces

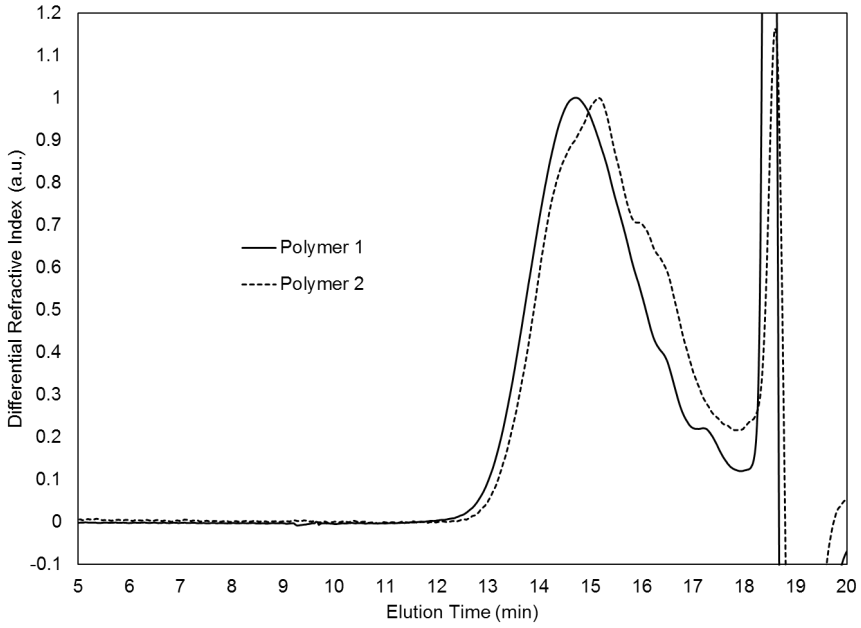


Figure S 37: SEC traces of **P1** and **P2**. The peak at 18.3 min corresponds to the eluent of the system.

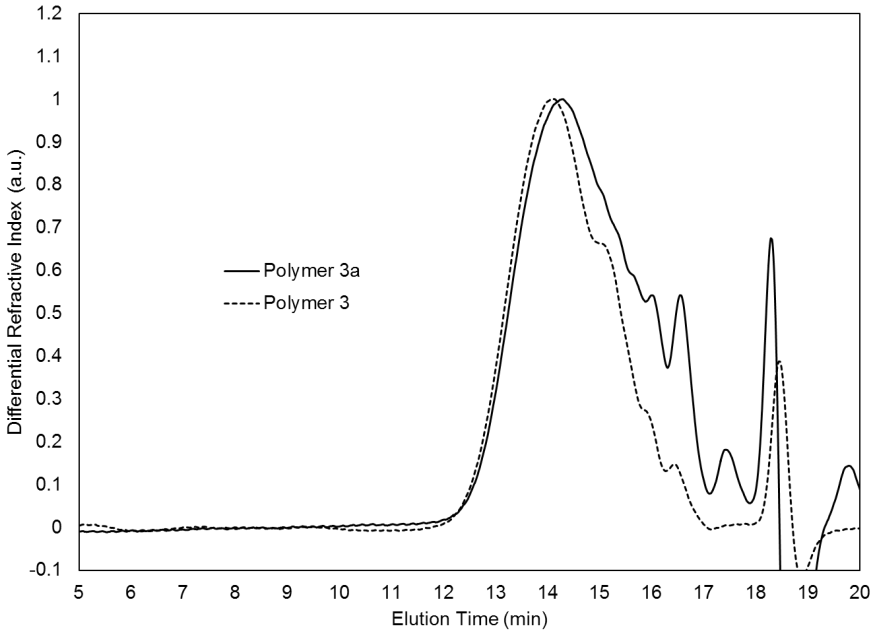


Figure S 38: SEC traces of **P3a** and **P3**. The peak at 18.3 min corresponds to the eluent of the system.

Polymer P3 DLS and TEM

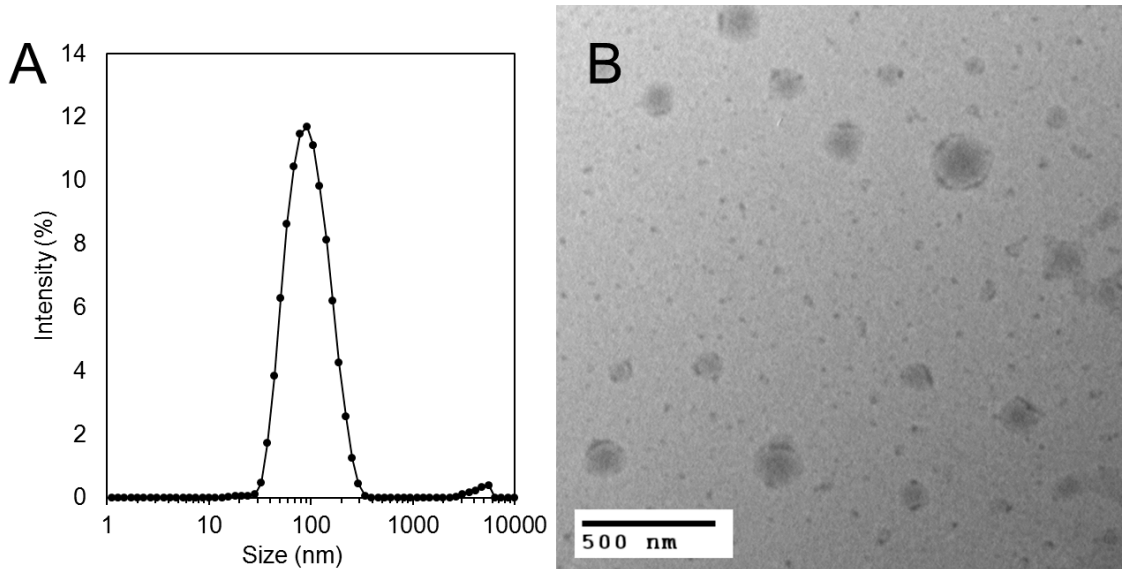


Figure S 39: A) DLS trace of **P3** assemblies. B) TEM image of **P3** assemblies.

Dynamic Light Scattering

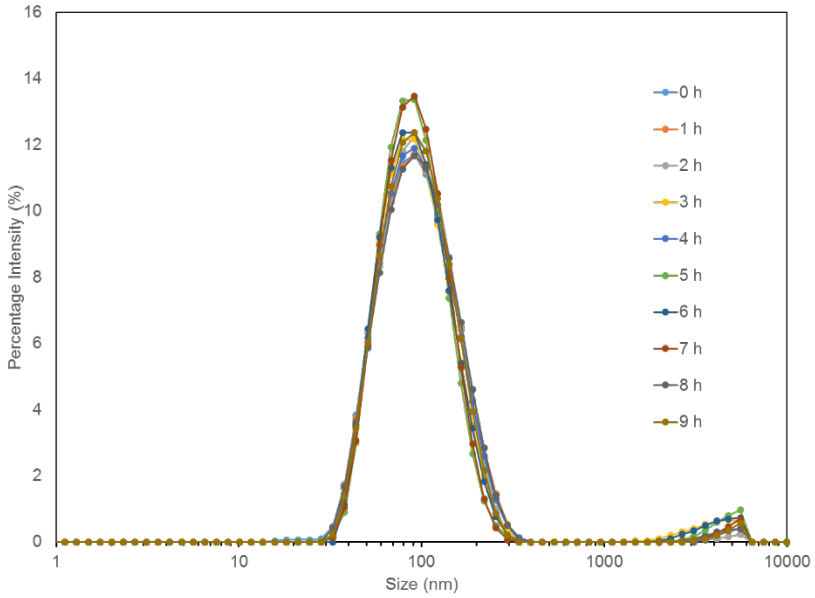


Figure S 40: Size distributions (intensity) for **P3** assemblies exposed to N_2H_4 as measured by DLS.

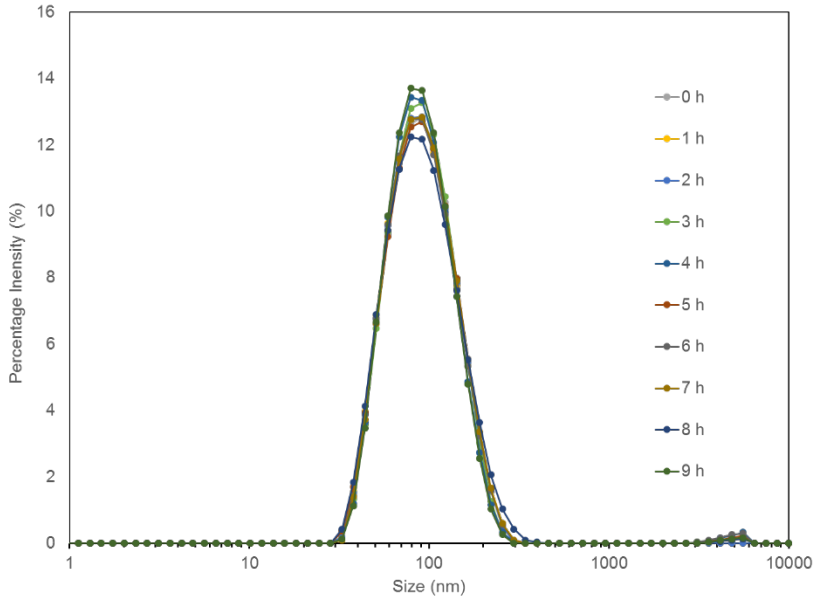


Figure S 41: Size distribution (intensity) for **P3** assemblies exposed to UV irradiation and N_2H_4 as measured by DLS.

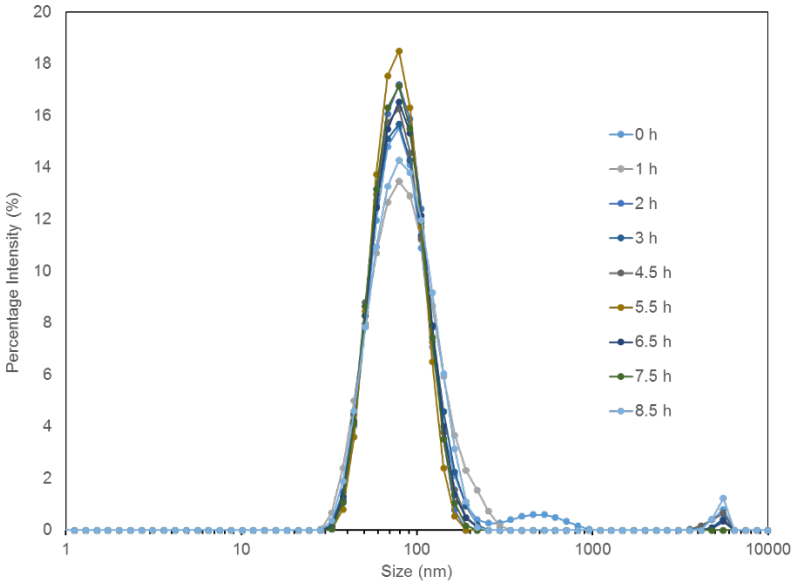


Figure S 42: Size distribution (intensity) for **P2** assemblies exposed to no stimulus as measured by DLS.

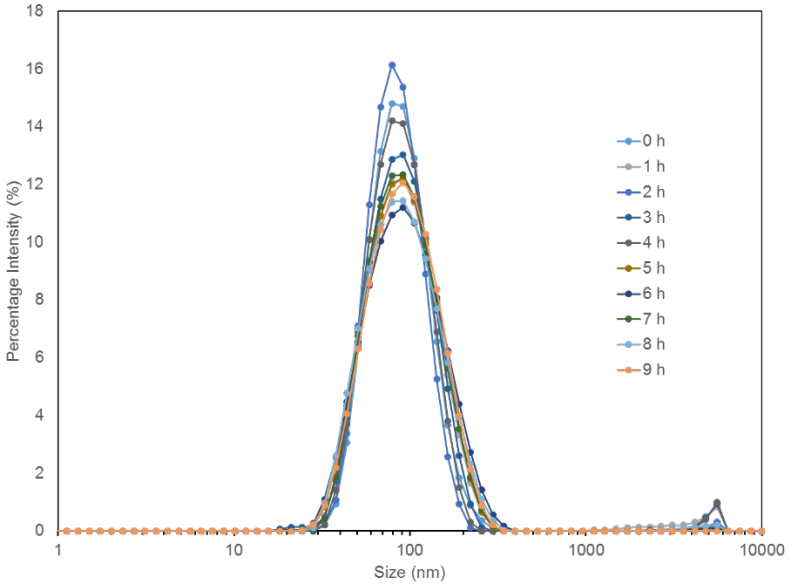


Figure S 43: Size distribution (intensity) for **P2** assemblies exposed to N_2H_4 as measured by DLS.

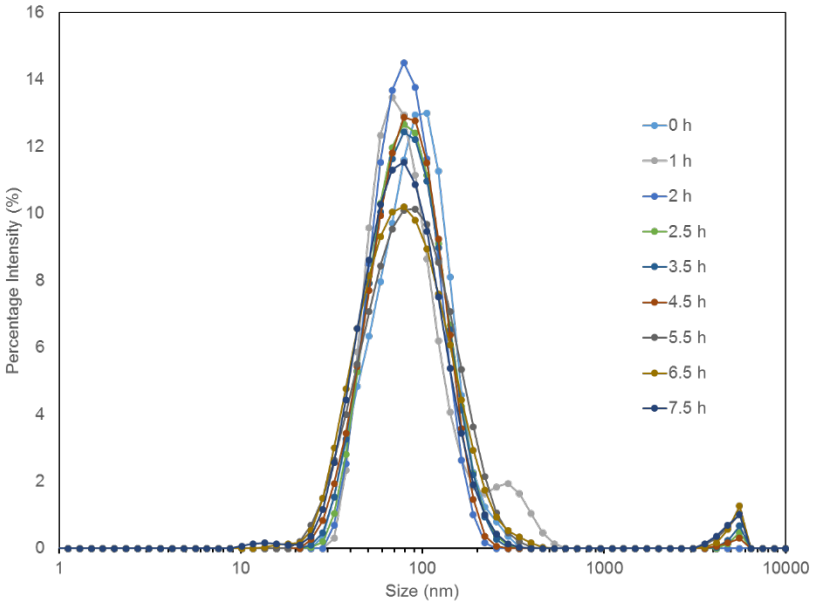


Figure S 44: Size distribution (intensity) for **P2** assemblies exposed to UV irradiation and N_2H_4 as measured by DLS.

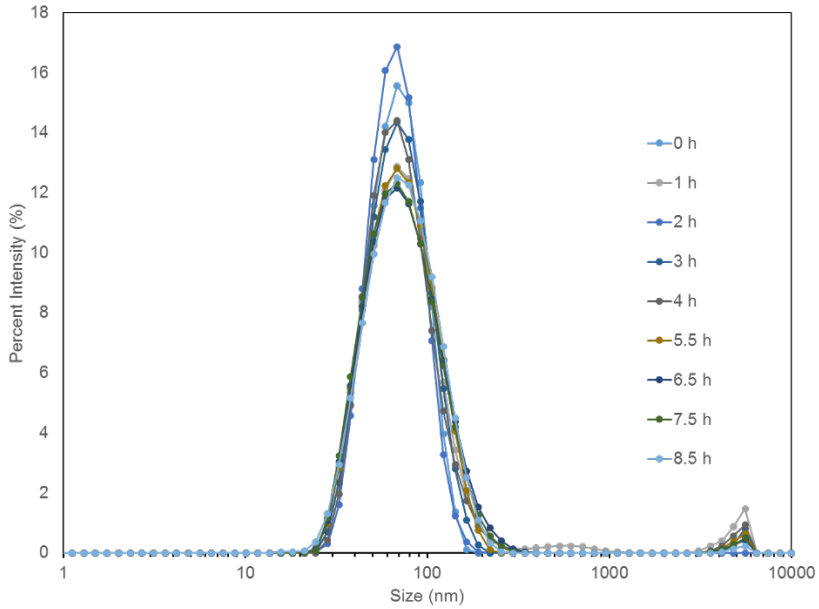


Figure S 45: Size distribution (intensity) for **P2** assemblies exposed to UV irradiation as measured by DLS.

References

1. P.-H. Lin, M. Leclere, J. Long, T. J. Burchell, I. Korobkov, R. Clerac and M. Murugesu, *Dalton Trans.*, 2010, **39**, 5698-5704.
2. D. K. Knight, E. R. Gillies and K. Mequanint, *Acta Biomater*, 2014, **10**, 3484-3496.