- Supporting Information -

Pyridyl-Acyl Hydrazone Rotaxanes and Molecular Shuttles

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Table of Contents

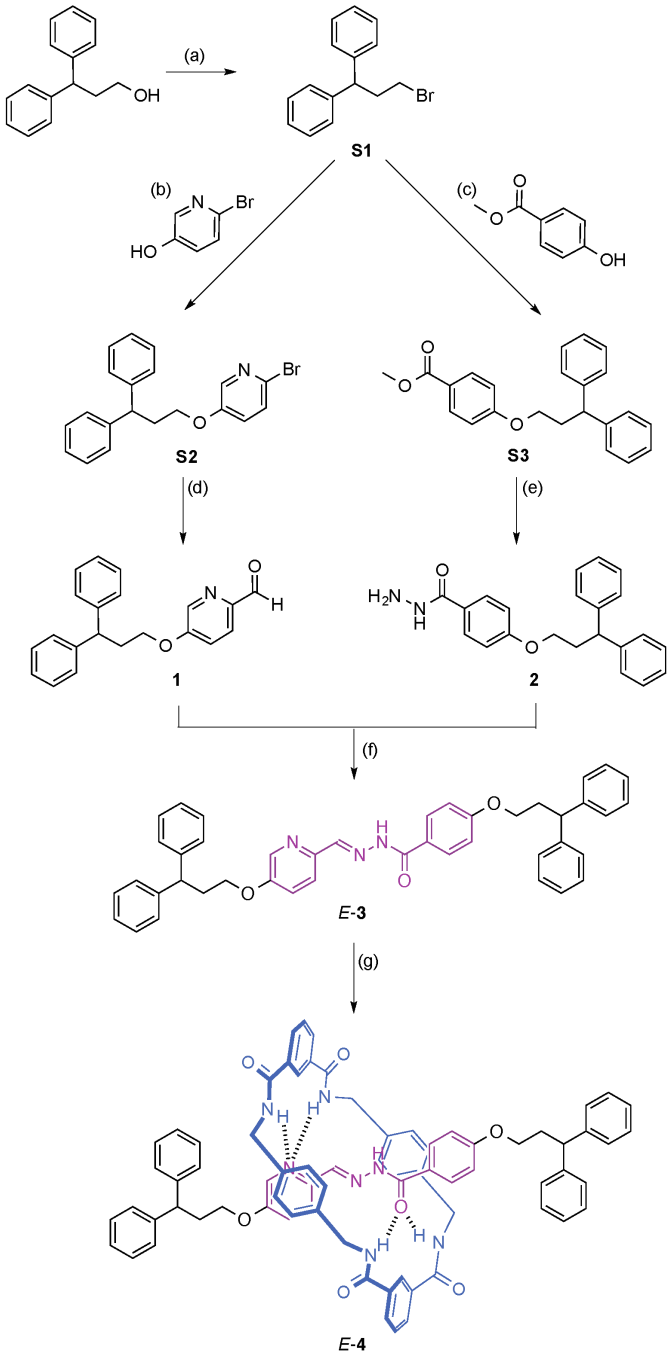
1. Experimental Section

1.1. General Methods

Unless stated otherwise, all reagents and solvents were purchased from Sigma-Aldrich Chemicals and used without further purification. Compound *E*-**4** and *E*-**6** were prepared according to the modified literature procedure.[S1] Dry THF, DMF, CH_2Cl_2, and CH_3CN were obtained by passing the solvent (HPLC grade) through an activated alumina column on a Phoenix SDS solvent drying system (JC Meyer Solvent Systems, CA, USA). Anhydrous MeOH was purchased from Sigma-Aldrich. Column chromatography was carried out using Aldrich Si 60 (particle size 40-63μm) as the stationary phase, and TLC was performed on precoated silica gel plates (0.25 mm thick, 60 F_{254}, Merck, Germany) and observed under UV light. Preparative TLC was carried out on Merck preparative plates (SiO_2, 2000 μm) and observed under UV light. NMR spectra were recorded on a Bruker Avance III (equipped with a cryoprobe) instrument with an Oxford AS600 magnet. Chemical shifts are reported in parts per million (ppm) from high to low frequency and referenced to the residual solvent resonance. Coupling constants (*J*) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, br = broad. ^{1}H assignments were made using 2D NMR methods (COSY, HSQC, HMBC). Low resolution ESI mass spectrometry was performed with a Thermo Scientific LCQ Fleet or an Agilent Technologies 1200 LC system with 6130 single quadrupole MS detector mass spectrometer. High resolution ESI (electrospray ionization) and EI (electron ionization) mass spectrometry were carried out by the EPSRC National Mass Spectrometry Service Centre (Swansea, UK).

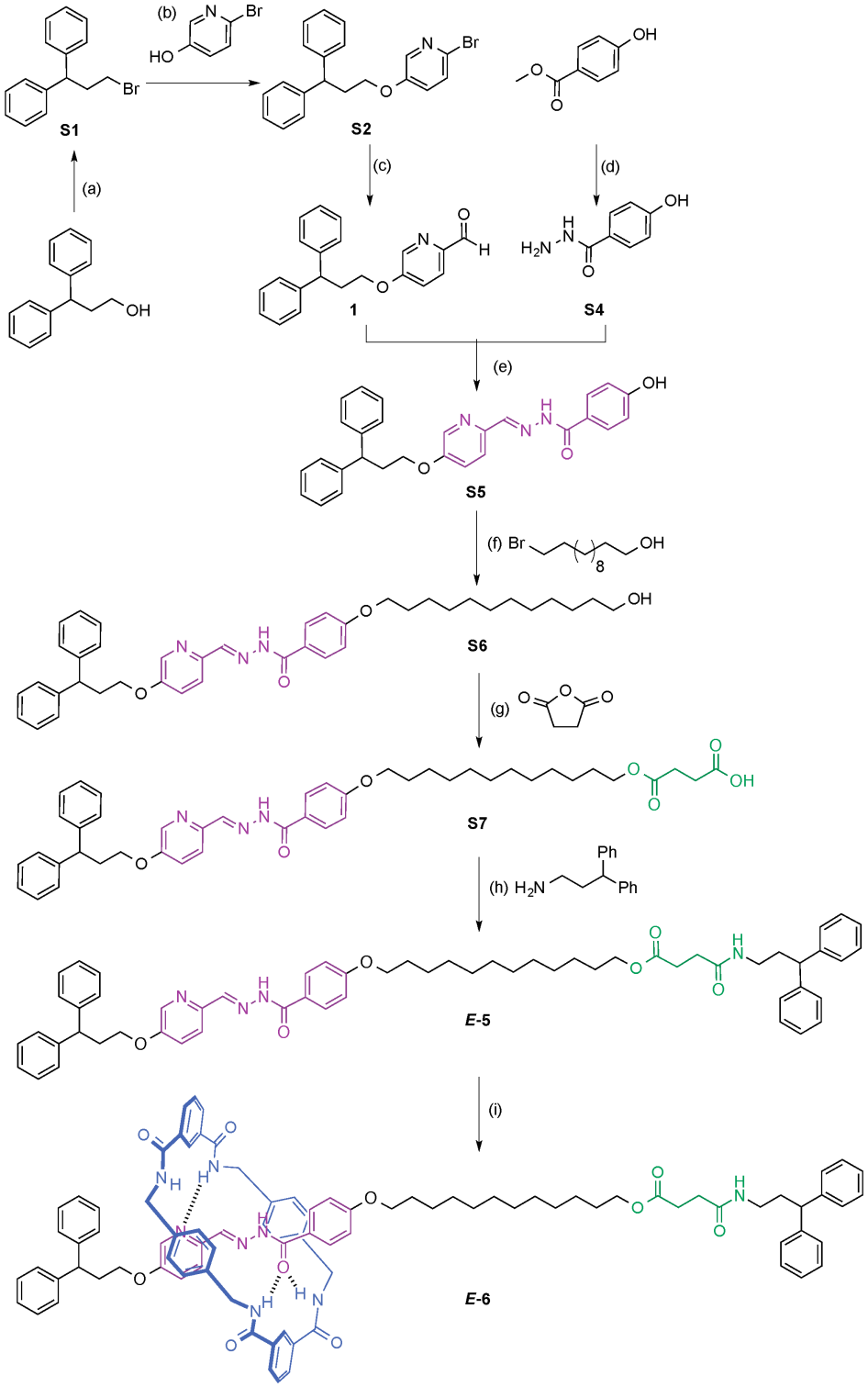
1.2. Synthetic Overview

1.2.1. Synthetic overview of *E*-4 rotaxane



Scheme S1: Synthesis of one-station [2]rotaxane (*E*-**4**). Reagents and conditions: (a) CBr_4, PPh_3, RT, 4 h, quantitative; (b) 2-Bromo-5-hydroxypyridine, Cs_2CO_3, MeCN, reflux, 18 h, 92 %; (c) Methyl 4-hydroxybenzoate, Cs_2CO_3, MeCN, reflux, 18 h, 90 %; (d) *n*BuLi, THF, DMF, -78 °C, 18 h, 70 %; (e) $N_2H_4{\cdot}H_2O$, reflux, 18 h, 99 %; (f) AcOH (cat.), EtOH, RT, 18 h, 80 %; (g) *p*-xylylenediamine, isophthaloyl dichloride, Et_3N, $CHCl_3$, RT, 18 h, 85 %.

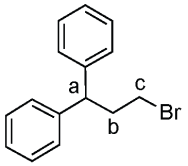
1.2.2. Synthetic overview of *E*-6 molecular shuttle



Scheme S2: Synthesis of Molecular Shuttle (*E*-**6**). Reagents and conditions: (a) CBr_4, PPh_3, CH_2Cl_2, RT, 4 h, quantitative; (b) **S2**, Cs_2CO_3, MeCN, reflux, 18 h, 92 %; (c) *n*BuLi, THF, DMF, -78 °C, 18 h, 70 %; (d) $N_2H_4{\cdot}H_2O$, reflux, 18 h, 99 %; (e) AcOH (cat.), EtOH, RT, 18 h, 80 %; (f) 12-Bromo-1-dodecanol, K_2CO_3, DMF, 60 °C, 18 h, 48 %; (g) Succinimide, Et_3N, CH_2Cl_2, RT, 18 h, quantitative; (h) 3,3-Diphenylpropylamine, 4-DMAP, EDCI.HCl, CH_2Cl_2, RT, 18 h, 88 %; (i) *p*-xylylenediamine, isophthaloyl dichloride, Et_3N, $CHCl_3$, RT, 18 h, 70 %.

1.3 Synthetic Procedures and Characterization Details

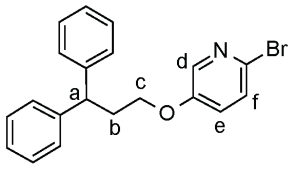
Synthesis of S1



A solution of 3,3-diphenyl-1-propanol (4.70 g, 22.13 mmol, 1.00 eq) and carbon tetrabromide (8.81 g, 26.55 mmol, 1.20 eq) in CH_2Cl_2 (60 mL) was cooled to 0 °C, and triphenylphosphine (6.96 g, 26.55 mmol, 1.20 eq) was added. The resulting mixture was stirred at room temperature for 4 h and then the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO_2, Et_2O/Petroleum ether 0:100 → 20:80) to afford compound **S1** (6.09 g, 22.13 mmol, quantitative) as colourless oil

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.37 – 7.19 (m, 10H, H_{Ar}), 4.23 (t, J = 7.7 Hz, 1H, H_a), 3.35 (t, J = 6.7 Hz, 2H, H_c), 2.61 (q, J = 7.0 Hz, 2H, H_b). ^{13}C NMR (151 MHz, $CDCl_3$): δ = 143.55, 128.78, 128.00, 126.69, 49.23, 38.41, 32.20. HRMS (ESI^+): *m/z* = 274.0365 $[M]^+$ (calcd. 274.0357 for $C_{15}H_{15}Br$).

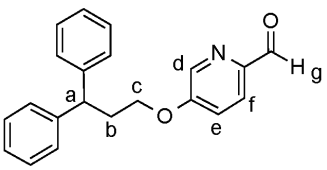
Synthesis of S2



A solution of **S1** (6.11 g, 22.20 mmol, 1.00 eq) in MeCN (40 mL) was added to a solution of 2-bromo-5-hydroxypyridine (3.86 g, 22.20 mmol, 1 eq) and Cs_2CO_3 (8.68 g, 26.64 mmol, 1.20 eq) in MeCN (80 mL). The resulting mixture was refluxed overnight under a N_2 atmosphere and then concentrated under reduced pressure. The mixture was diluted with CH_2Cl_2 (3 x 200 mL) and washed with H_2O (3 × 200 mL) and brine (3 × 200 mL). The organic layer was dried over $MgSO_4$ and concentrated under vacuum to afford **S2** (7.53 g, 20.44 mmol, 92 %) as a light brown solid.

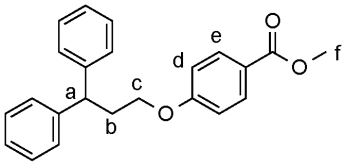
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.01 (d, J = 3.2 Hz, 1H, H_d), 7.34 (d, J = 8.8 Hz, 1H, H_f), 7.33 – 7.20 (m, 10H, H_{Ar}), 7.02 (dd, J = 8.8, 3.2 Hz, 1H, H_e), 4.24 (t, J = 7.9 Hz, 1H, H_a), 3.93 (t, J = 6.3 Hz, 2H, H_c), 2.56 (dt, J = 7.9, 6.3 Hz, 2H, H_b).^{13}C NMR (151 MHz, $CDCl_3$): δ= 154.78, 143.83, 137.61, 132.05, 128.67, 128.09, 127.83, 126.55, 124.75, 66.74, 47.09, 34.70. HRMS (ESI^+): *m/z* = 368.0647 $[M+H]^+$ (calcd. 368.0645 for $C_{20}H_{18}BrNO$).

Synthesis of 1



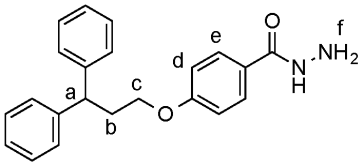
*n*BuLi (0.51 mL, 1.6 M in hexanes, 0.81 mmol, 1.20 eq) was slowly added to a stirring solution of **S2** (250 mg, 0.67 mmol, 1.00 eq) in dry THF (10 mL) at -78 ºC under inert atmosphere. After 2 h, DMF (0.5 mL) was added and then the mixture was stirred at room temperature for 18 h. The mixture was quenched by addition of NH_4Cl_{aq} (10 mL) and extracted with Et_2O (3 × 30 mL). The combined organic layers were dried over $MgSO_4$, and the solvent removed under reduced pressure. The residue was purified by column chromatography (SiO_2, EtOAc/ hexane 20:80) to afford **1** (148 mg, 0.47 mmol, 70%) as brown oil.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 10.01 (s, 1H, H_g), 8.40 (d, *J* = 2.8 Hz, 1H, H_d), 7.94 (d, *J* = 8.6 Hz, 1H, H_f), 7.35 – 7.19 (m, 11H, H_{Ar+e}), 4.27 (t, *J* = 8.0 Hz, 1H, H_a), 4.05 (t, *J* = 6.3 Hz, 2H, H_c), 2.62 (dt, *J* = 8.0, 6.3 Hz, 2H, H_b). ^{13}C NMR (151 MHz, $CDCl_3$): δ= 191.98, 158.39, 146.15, 143.68, 138.79, 128.72, 127.80, 126.63, 123.41, 120.49, 66.86, 47.13, 34.58. HRMS (ESI^+): *m/z* = 318.1484 $[M+H]^+$ (calcd. 318.1489 for $C_{21}H_{19}NO_2$).

Synthesis of S3



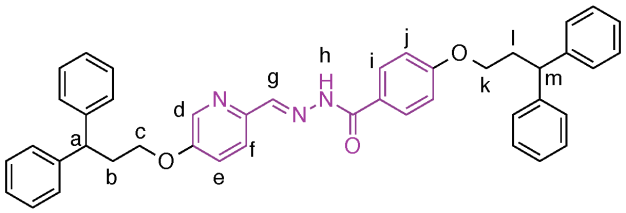
A solution of **S1** (1.00 g, 3.63 mmol, 1.00 eq) in MeCN (80 mL) was added to a degassed solution of methyl-4-hydroxybenzoate (552 mg, 3.63 mmol, 1.00 eq) and Cs_2CO_3 (1.42 g, 4.36 mmol, 1.20 eq) in MeCN (40 mL). The resulting mixture was refluxed overnight under a N_2 atmosphere and then the solvent removed under reduced pressure. The mixture was diluted with CH_2Cl_2 (3 x 200 mL) and washed with H_2O (3 × 200 mL) and brine (3 × 200 mL). The organic layer was dried over $MgSO_4$ and concentrated under vacuum to afford **S3** (1.13 g, 3.26 mmol, 90 %) as a light brown solid.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.8 Hz, 2H, H_e), 7.42 – 7.17 (m, 10H, H_{Ar}), 6.87 (d, *J* = 8.8 Hz, 2H, H_d), 4.27 (t, *J* = 7.8 Hz, 1H, H_a), 3.97 (t, *J* = 6.3 Hz, 2H, H_c), 3.91 (s, 3H, H_f), 2.58 (dt, *J* = 7.8, 6.3 Hz, 2H, H_b). ^{13}C NMR (151 MHz, $CDCl_3$): δ= 166.90, 162.70, 144.06, 131.57, 128.63, 127.89, 126.46, 122.50, 114.11, 66.07, 51.89, 47.18, 34.78. HRMS (ESI^+): *m/z* = 347.1641 $[M+H]^+$ (calcd. 347.1642 for $C_{23}H_{23}O_3$).

Synthesis of 2



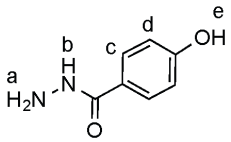
Under N_2 atmosphere, **S3** (500 mg, 1.44 mmol, 1.00 eq) was dissolved in dry MeOH (20 mL) and hydrazine hydrate (360 µL, 11.55 mmol, 8.00 eq) was added. The reaction mixture was refluxed overnight and then the solvent removed under reduced pressure.. The mixture was diluted with CH_2Cl_2 (50 mL) and washed with H_2O (50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$ and concentrated under vacuum to afford **2** (493 mg, 1.42 mmol, 99%) as a colourless solid.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 8.8 Hz, 2H, H_e), 7.34 – 7.20 (m, 10H, H_{Ar}), 6.89 – 6.86 (m, 2H, H_d), 4.26 (t, *J* = 7.8 Hz, 1H, H_a), 4.08 (brs, 2H, H_f), 3.95 (t, *J* = 6.4 Hz, 2H, H_c), 2.57 (dt, *J* = 7.8, 6.4 Hz, 2H, H_b). ^{13}C NMR (151 MHz, $CDCl_3$): δ= 168.36, 161.86, 144.04, 128.62, 128.58, 127.87, 126.46, 124.76, 114.49, 66.08, 47.17, 34.76. HRMS (ESI^+): *m/z* = 347.1755 $[M+H]^+$ (calcd. 347.1754 for $C_{22}H_{23}O_2N_2$).

Synthesis of *E*-3



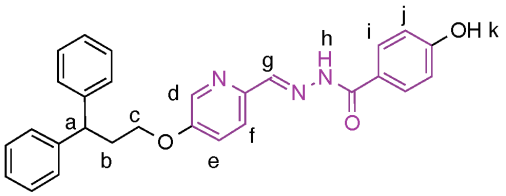
Aldehyde **1** (100 mg, 0.31 mmol, 1.00 eq) and hydrazine **2** (110 mg, 0.31 mmol, 1.00 eq) were combined in EtOH (5 mL) and catalytic amount of acetic acid was added and the mixture was stirred at room temperature overnight. Evaporation of solvent and recrystallization in EtOH afforded the product (163 mg, 0.25 mmol, 80 %, *E/Z* = 98 %) as a brown solid.
^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.11 (s, 1H, H_h), 8.24 (d, *J* = 2.8 Hz, 1H, H_d), 8.03 – 7.94 (brs, 1H, H_f), 7.78 (brs, 2H, H_i), 7.29 (m, 17H, H_{Ar+g}), 7.19 (m, 5H, H_{Ar+e}), 6.92 (d, *J* = 8.8 Hz, 2H, H_j), 4.27 (td, *J* = 8.0, 4.0 Hz, 2H, H_{a+m}), 3.99 (dt, *J* = 12.7, 6.3 Hz, 4H, H_{c+k}), 2.58 (dtd, *J* = 8.7, 6.4, 2.3 Hz, 4H, H_{b+l}). ^{13}C NMR (151 MHz, CD_2Cl_2): δ = 167.71, 163.69, 162.14, 155.09, 145.57, 144.46, 144.18, 137.93, 136.51, 129.46, 128.80, 128.71, 127.95, 127.87, 126.65, 122.11, 114.56, 66.97, 66.31, 47.40, 47.31, 34.74, 34.61. HRMS (ESI$^+$): *m/z* = 646.3051 $[M+H]^+$ (calcd. 646.3064 for $C_{43}H_{40}N_3O_3$).

Synthesis of S4



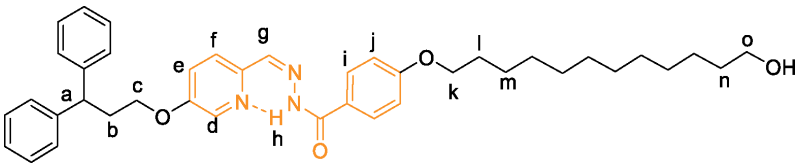
Hydrazine hydrate (8.2 mL, 263 mmol, 8.00 eq) was added to methyl 4-hydroxy benzoate (5 g, 32.88 mmol, 1.00 eq) and the mixture refluxed overnight. The solid obtained was washed with hexane to afford the **S4** (4.94 g, 32.47 mmol, 99 %) as a light brown solid.
^{1}H NMR (600 MHz, DMSO-d_6): δ= 9.80 (brs, 1H, H_e), 9.49 (s, 1H, H_b), 7.68 (d, *J* = 8.6 Hz, 2H, H_c), 6.77 (d, *J* = 8.6 Hz, 2H, H_d), 4.38 (brs, 2H, H_a). ^{13}C NMR (151 MHz, DMSO-d_6): δ= 166.36, 160.44, 129.27, 124.41, 115.27. HRMS (ESI$^+$): *m/z* = 153.0655 $[M+H]^+$ (calcd. 153.0659 for $C_7H_9N_2O_2$).

Synthesis of S5



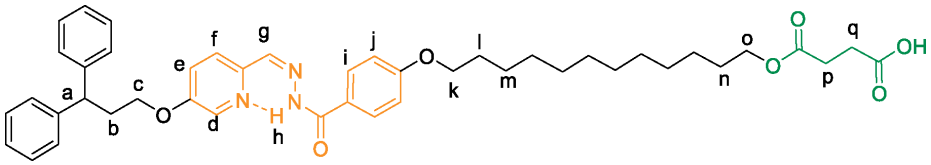
Aldehyde **1** (398 mg, 1.25 mmol, 1 eq) and hydrazide **S4** (190 mg, 1.25 mmol, 1 eq) were combined in EtOH (5 mL) and catalytic amount of acetic acid was added. The reaction mixture was stirred at room temperature overnight. Evaporation of solvent and recrystallization in EtOH afforded the **S5** (451 mg, 1.00 mmol, 80%) as a brown solid.
^{1}H NMR (600 MHz, DMSO-d_6): δ = 11.70 (s, 1H, H_h), 10.20 (br s, 1H, H_k), 8.39 (s, 1H, H_d), 8.26 (d, *J* = 2.8 Hz, 1H, H_f), 7.87 (d, *J* = 8.2 Hz, 1H, H_e), 7.80 (d, *J* = 8.3 Hz, 2H, H_i), 7.41 (dd, *J* = 8.8, 2.8 Hz, 1H, H_g), 7.37 (d, *J* = 7.6 Hz, 4H, H_{Ar}), 7.30 (t, *J* = 7.6 Hz, 4H, H_{Ar}), 7.18 (t, *J* = 7.3 Hz, 2H, H_{Ar}), 6.86 (d, *J* = 8.2 Hz, 2H, H_j), 4.24 (t, *J* = 8.0 Hz, 1H, H_a), 3.99 (t, *J* = 6.4 Hz, 2H, H_c), 2.54 (q, *J* = 6.9 Hz, 2H, H_b). ^{13}C NMR (151 MHz, DMSO-d_6): δ= 162.90, 161.47, 155.19, 145.44, 144.743, 138.33, 137.12, 129.73, 129.02, 128.29, 128.07, 126.77, 123.12, 116.17, 66.16, 47.14, 34.22. HRMS (ESI$^+$): *m/z* = 452.1962 $[M+H]^+$ (calcd. 452.1969 for $C_{28}H_{26}N_3O_3$).

Synthesis of S6



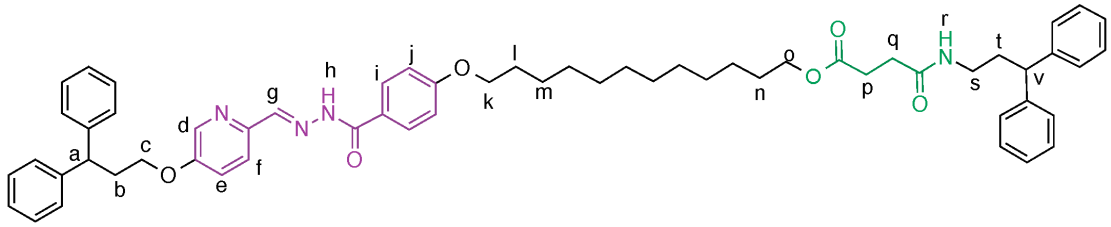
12-bromo-1-dodecanol (210 mg, 0.79 mmol, 2 eq) was added to a solution of **S5** (179 mg, 0.39 mmol, 1 eq) and K_2CO_3 (110 mg, 0.79 mmol, 2 eq) in dry DMF (10 mL). The resulting mixture was stirred at 60 °C overnight under a N_2 atmosphere and then concentrated under reduced pressure. The residue was purified by a flash column chromatography (SiO_2, MeOH/CH_2Cl_2 0:100 → 5:95) to afford **S6** (121 mg, 0.19 mmol, 48%) as a colourless oil.
^{1}H NMR (600 MHz, CD_2Cl_2): δ = 15.12 (s, 1H, H_h), 8.38 (d, *J* = 2.9 Hz, 1H, H_d), 7.92 (d, *J* = 8.8 Hz, 2H, H_i), 7.44 (d, *J* = 8.8 Hz, 1H, H_f), 7.41 (s, 1H, H_g), 7.33 – 7.18 (m, 11H, H_{Ar+e}), 7.00 (d, *J* = 8.4 Hz, 2H, H_j), 4.26 (t, *J* = 7.9 Hz, 1H, H_a), 4.04 (t, *J* = 6.4 Hz, 4H, H_{c+k}), 3.58 (t, *J* = 6.6 Hz, 2H, H_o), 2.60 (dt, *J* = 8.0, 6.2 Hz, 2H, H_b), 1.81 (dt, *J* = 14.7, 6.9 Hz, 2H, H_l), 1.55 – 1.50 (m, 2H, H_n), 1.49 – 1.43 (m, 2H, H_m), 1.41 – 1.22 (m, 14H, $H_{aliphatic}$). ^{13}C NMR (151 MHz, CD_2Cl_2): δ= 155.48, 146.03, 144.71, 144.59, 136.94, 129.88, 129.19, 129.15, 128.29, 128.28, 127.58, 127.05, 126.98, 122.50, 114.94, 68.85, 67.38, 67.14, 63.36, 47.73, 35.10, 35.03, 33.43, 30.24, 30.17, 30.14, 30.11, 30.07, 30.04, 29.99, 29.90, 29.80, 29.67, 29.60, 26.50, 26.43, 26.31. HRMS (ESI$^+$): *m/z* = 636.3783 $[M+H]^+$ (calcd. 636.3796 for $C_{40}H_{50}N_3O_4$).

Synthesis of S7



To a stirred solution of **S6** (1.21 g, 1.90 mmol, 1 eq) in CH_2Cl_2 (150 mL), Et_3N (270 µL, 1.93 mmol, 1 eq) and a solution of succinic anhydride (190 mg, 1.99 mmol, 1 eq) in CH_2Cl_2 (20 mL) were added. The reaction mixture was stirred at room temperature for 16h and then concentrated under reduced pressure. The residue was purified by a flash column chromatography (SiO_2, MeOH/CH_2Cl_2 0:100 → 10:90) to afford **S7** (1.40 g, 1.90 mmol, 100 %) as a colourless oil.
^{1}H NMR (600 MHz, CD_2Cl_2): δ = 15.21 (s, 1H, H_h), 8.42 (d, *J* = 2.9 Hz, 1H, H_d), 7.96 (d, *J* = 8.7 Hz, 2H, H_i), 7.50 (s, 1H, H_f), 7.48 (s, 1H, H_g), 7.38 – 7.24 (m, 11H, H_{Ar+e}), 7.04 (d, *J* = 8.4 Hz, 2H, H_j), 4.30 (t, *J* = 7.9 Hz, 1H, H_a), 4.14 – 4.03 (m, 6H, H_{c+k+o}), 2.67 – 2.59 (m, 6H, H_{b+q+p}), 1.85 (quin, *J* = 6.8 Hz, 2H, H_l), 1.62 (q, *J* = 6.7 Hz, 2H, H_n), 1.51 (quin, *J* = 7.8 Hz, 2H, H_m), 1.42 – 1.25 (m, 14H, $H_{aliphatic}$). ^{13}C NMR (151 MHz, CD_2Cl_2): δ= 172.36, 172.30, 162.37, 155.02, 144.09, 144.03, 136.46, 129.41, 128.64, 128.58, 127.73, 126.51, 126.42, 121.93, 114.46, 68.26, 66.85, 64.88, 47.18, 34.47, 29.44, 29.41, 29.31, 29.20, 29.17, 29.09, 29.00, 28.95, 28.55, 28.49, 28.47, 25.83, 25.81. HRMS (ESI$^+$): *m/z* = 734.3793 $[M-H]^-$ (calcd. 734.3811 for $C_{44}H_{52}N_3O_7$).

Synthesis of *E*-5

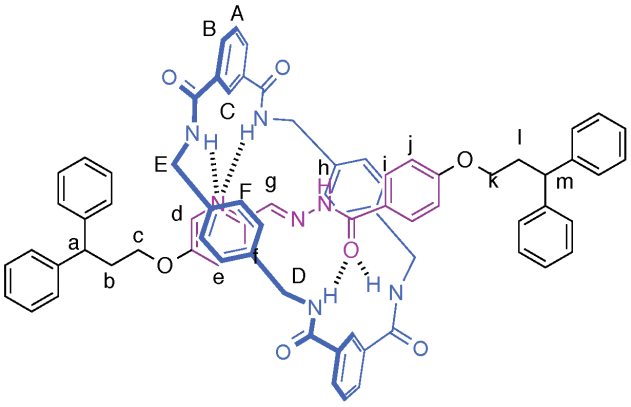


To a stirring solution of **S7** (64.0 mg, 0.09 mmol, 1.00 eq), 3,3-diphenylpropyl amine (18.4 mg, 0.09 mmol, 1.00 eq) and 4-DMAP (13.4 mg, 0.11 mmol, 1.23 eq) in anhydrous CH_2Cl_2 (13 mL) at 0 °C was added EDCI·HCl (18.7 mg, 0.10 mmol, 1.15 eq) and stirred at room temperature for 16 h. The reaction mixture was washed with a saturated solution of citric acid (3 x 50 mL) and H_2O (3 x 50 mL). The organic layer was dried over anhydrous $MgSO_4$, filtrated and evaporated under reduced pressure and charged in a flash column chromatography (SiO_2, MeOH/CH_2Cl_2 0:100 → 15:85) to give the **S7** (71.3 mg, 0.08 mmol, 88 %, 77:23 *E/Z* ratio) as a colourless oil.
^{1}H NMR (600 MHz, CD_2Cl_2, major isomer (*E*)): δ = 11.20 (s, 1H, H_h), 8.47 (s, 1H, H_d), 7.88 (s, 2H, H_i), 7.40 (d, *J* = 8.7 Hz, 1H, H_f), 7.35 – 7.16 (m, 22H, H_{Ar+e+g}), 6.95 (d, *J* = 8.3 Hz, 2H, H_j), 5.86 (s, 1H, H_r), 4.09 – 3.95 (m, 6H, H_{c+k+o}), 3.80 (m, 1H, H_a), 3.62 (t, *J* = 7.8 Hz, 1H, H_v), 3.15 – 3.12 (m, 2H, H_s), 2.64 – 2.56 (m, 4H, H_{b+p}), 2.38 (t, *J* = 6.8 Hz, 2H, H_q), 2.37 (t, *J* = 6.8 Hz, 2H, H_t), 2.25 (q, *J* = 7.4 Hz, 2H, H_l), 1.81 (m, 2H, H_n), 1.40 (m, 2H, H_m), 1.39 – 1.27 (m, 14H, $H_{aliphatic}$). ^{13}C NMR (151 MHz, CD_2Cl_2): δ= 173.47, 171.59, 164.09, 162.82, 155.47, 146.03, 145.10, 144.59, 138.22, 136.94, 129.89, 129.19, 129.08, 128.28, 128.21, 127.58, 127.05, 126.86, 126.02, 122.51, 114.94, 112.52, 68.85, 67.37, 65.28, 49.49, 47.72, 38.84, 35.61, 35.03, 31.42, 30.09, 30.06, 30.05, 29.90, 29.80, 29.68, 29.15, 26.50, 26.42, 16.75. HRMS (ESI$^+$): *m/z* = 929.5204 $[M+H]^+$ (calcd. 929.5212 for $C_{59}H_{69}N_4O_6$).

General procedure for the preparation of benzylic amide macrocycle rotaxanes. [S1]

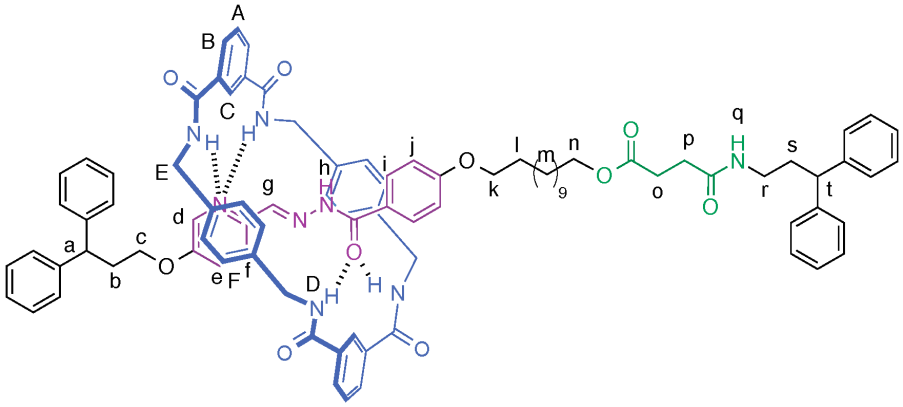
The corresponding thread (1.00 eq) and triethylamine (16.00 eq) were dissolved in anhydrous chloroform (ethanol-free, stabilized with amylenes, 100 mL) and stirred vigorously whilst solutions of p-xylylenediamine (8.00 eq) in anhydrous chloroform (40 mL) and isophthaloyl dichloride (8.00 eq.) in anhydrous chloroform (40 mL) were simultaneously added over a period of 2 h using motor driven syringe pumps. After further 18 h of stirring the resulting suspension was filtered through a pad of celite and the filtrate was concentrated under reduced pressure to afford the rotaxane product as a crude mixture that was purified using column chromatography (See Supporting Information, Section 3.1).

Synthesis of *E*-4



Rotaxane *E*-**4** was prepared from thread *E*-**3** (500 mg, 0.78 mmol, 1.00 eq) according to the general procedure for the preparation of benzylic amide macrocycle [2]rotaxanes. The crude material was purified through a flash column chromatography (SiO_2, $MeOH/CH_2Cl_2$ 0:100 → 2:98) to obtain the desired compound (775 mg, 0.66 mmol, 85%, *E*/*Z* = 98 %) as a colourless solid.
^{1}H NMR (600 MHz, CD_2Cl_2): δ = 10.18 (s, 1H, H_h), 8.78 (s, 2H, H_C), 8.19 (d, *J* = 7.8 Hz, 4H, H_B), 7.97 (d, *J* = 8.5 Hz, 2H, H_i), 7.84 (s, 4H, H_D), 7.82 (s, 1H, H_d), 7.67 (t, *J* = 7.8 Hz, 2H, H_A), 7.37 (s, 1H, H_g), 7.33 – 7.21 (m, 20H, H_{Ar}), 7.11 (d, *J* = 8.8 Hz, 1H, H_f), 6.97 (d, *J* = 8.5 Hz, 2H, H_j), 6.81 (s, 8H, H_F), 6.74 (d, *J* = 7.2 Hz, 1H, H_e), 4.53 (m, 4H, H_E), 4.27 (m, 5H, H_{E+a}), 4.22 (t, *J* = 7.9 Hz, 1H, H_m), 4.04 (t, *J* = 6.6 Hz, 2H, H_c), 3.89 (t, *J* = 6.5 Hz, 2H, H_k), 2.63 (q, *J* = 6.6 Hz, 2H, H_b), 2.54 (q, *J* = 6.5 Hz, 2H, H_l).^{13}C NMR (151 MHz, CD_2Cl_2): δ= 166.30, 164.68, 162.60, 156.15, 144.27, 143.97, 137.37, 134.40, 130.84, 129.98, 129.23, 128.63, 128.60, 127.93, 127.78, 127.69, 126.50, 126.44, 125.70, 114.23, 66.79, 66.32, 47.27, 47.10, 43.87, 34.58, 34.31. HRMS (ESI^+): *m/z* = 1178.5156 $[M+H]^+$ (calcd. 1178.5175 for $C_{75}H_{68}N_7O_7$).

Synthesis of *E*-6



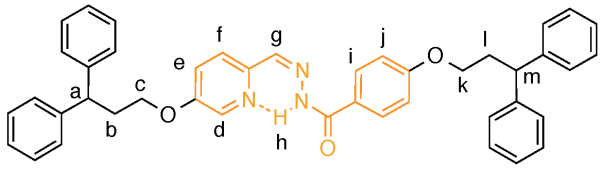
Rotaxane ***E*-6** was prepared from thread **5** (20 mg, 0.02 mmol, 1.00 eq) according to the general procedure for the preparation of benzylic amide macrocycle [2]rotaxanes. The crude material was purified through a flash column chromatography (SiO_2, $MeOH/CH_2Cl_2$ 0:100 → 10:80) to obtain the desired compound (24 mg, 0.016 mmol, 70%, > 95 %, *E*/*Z* = 98 %) as a colourless oil. The reported yield of *E*-**6** was calculated on basis of the E/Z mixture (77:23) of thread **5**.
^{1}H NMR (600 MHz, CD_2Cl_2): δ = 10.26 (s, 1H, H_h), 8.80 (s, 2H, H_C), 8.20 (d, *J* = 7.6 Hz, 4H, H_B), 8.01 (d, *J* = 7.8 Hz, 2H, H_i), 7.91 (s, 1H, H_d), 7.90 (s, 4H, H_D), 7.67 (t, *J* = 7.7 Hz, 2H, H_A), 7.45 (s, 1H, H_g), 7.31 – 7.18 (m, 21H, H_{Ar+e}), 7.03 (d, *J* = 8.0 Hz, 2H, H_j), 6.82 (s, 8H, H_F), 6.77 (d, *J* = 8.0 Hz, 1H, H_f), 5.76 (brs, 1H, H_p), 4.53 (m, 4H, H_E), 4.28 (m, 4H, H_E), 4.22 (t, *J* = 7.8 Hz, 1H, H_a), 4.10 (t, *J* = 6.3 Hz, 2H, H_k), 4.05 (dt, *J* = 29.7, 6.3 Hz, 2H, H_m), 3.95 (t, *J* = 7.8 Hz, 1H, H_s), 3.90 (t, *J* = 7.8 Hz, 2H, H_c), 3.16 (m, 2H, H_q), 2.55 (m, 4H, H_{b+n}), 2.33 (m, 2H, H_o), 2.25 (q, *J* = 7.5 Hz, 1H, H_r), 1.86 (q, *J* = 7.1 Hz, 2H, H_l), 1.62 (q, *J* = 7.0 Hz, 2H, H_m), 1.40 – 1.22 (m, 16H, $H_{aliphatic}$). ^{13}C NMR (151 MHz, CD_2Cl_2): δ= 172.97, 171.30, 166.30, 164.72, 162.87, 156.11, 155.00, 144.46, 143.99, 143.99, 137.41, 134.42, 130.88, 130.04, 129.20, 128.88, 128.65, 128.54, 127.99, 127.74, 127.69, 127.63, 126.49, 126.34, 114.19, 68.35, 66.86, 64.79, 53.82, 53.64, 53.45, 53.27, 53.10, 48.93, 47.10, 43.86, 38.36, 34.99, 34.33, 30.82, 29.39, 29.14, 29.01, 28.56, 25.87, 25.82. HRMS (ESI^+): *m/z* = 1461.7299 $[M+H]^+$ (calcd. 1461.7322 for $C_{91}H_{97}N_8O_{10}$).

1.4. Isomerization studies of threads and rotaxanes

1.4.1. General procedure for the photochemical isomerization

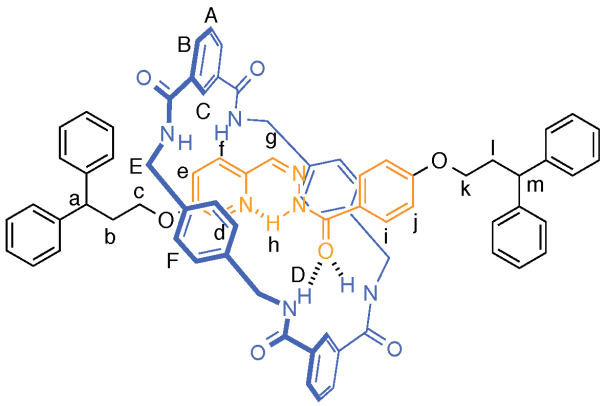
Irradiations were carried out in a photoreactor (Photochemical Reactors Ltd.) fitted with 6× 15 W gas discharge bulbs (Vilber-Lourmat T-15M, emission centred at 312 nm). The samples were irradiated in quartz NMR tubes and NMR spectra were recorded immediately after irradiation. The photochemical isomerizations were followed by ^{1}H NMR (See Supporting Information, section 3.2).

Synthesis of *Z*-3



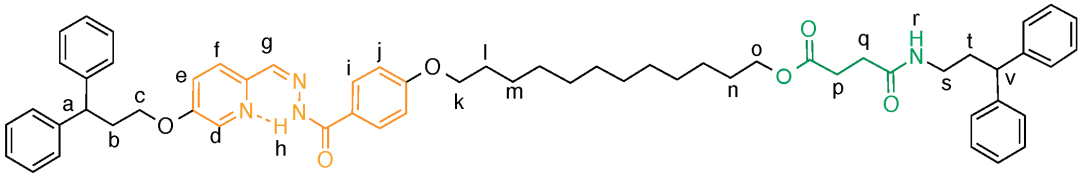
A solution of *E*-**3** (1.0 mg, 1.55 µmol, 1.00 eq.) in degassed CD_2Cl_2 (0.4 mL) was irradiated for 30 min using the method described above, affording *Z*-**3** (91 %).
^{1}H NMR (600 MHz, $CDCl_3$): δ = 15.17 (s, 1H, H_h), 8.41 (d, *J* = 2.8 Hz, 1H, H_d), 7.93(d, *J* = 8.7 Hz, 2H, H_i), 7.48 – 7.31 (m, 19H, $H_{Ar+e+f+g}$), 7.27 – 7.18 (m, 4H, H_{Ar}), 6.99 (d, *J* = 8.5 Hz, 2H, H_j), 4.31 (td, *J* = 7.9, 3.2 Hz, 2H, H_{a+m}), 4.08 (t, *J* = 6.3 Hz, 2H, H_c), 4.02 (t, *J* = 6.3 Hz, 2H, H_k), 2.63 (m, 4H, H_{b+l}).
^{13}C NMR (151 MHz, CD_2Cl_2): δ = 167.71, 163.69, 162.14, 155.09, 145.57, 144.46, 144.18, 137.93, 136.51, 129.46, 128.80, 128.71, 127.95, 127.87, 126.65, 122.11, 114.56, 66.97, 66.31, 47.40, 47.31, 34.74, 34.61.

Synthesis of *Z*-4



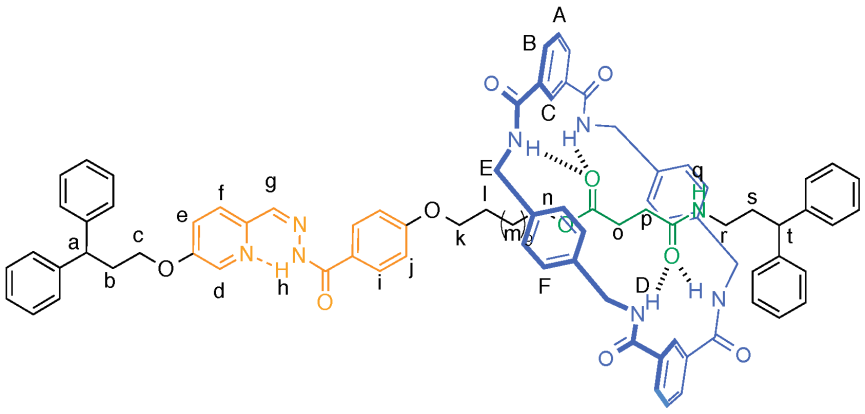
A solution of *E*-**4** (1.0 mg, 0.85 µmol, 1.00 eq.) in degassed CD_2Cl_2 (0.4 mL) was irradiated for 1 h using the method described above, affording *Z*-**4** (98 %).
^{1}H NMR (600 MHz, $CDCl_3$): δ = 13.94, 12.74 (s, 1H, H_h), 8.54, 8.33 (s, 2H, H_C), 8.23 (d, *J* = 7.8 Hz, 4H, H_B), 7.92 (s, 1H, H_d), 7.65, 7.57 (t, *J* = 7.8 Hz, 2H, H_A), 7.48 (d, *J* = 8.7 Hz, 1H, H_f), 7.39 (s, 1H, H_g), 7.36 – 7.22 (m, 26H, H_{Ar+D+i}), 6.97 (d, *J* = 8.5 Hz, 2H, H_j), 6.93, 6.90 (s, 8H, H_F), 6.53, 6.35 (d, *J* = 8.7 Hz, 1H, H_e), 4.64 (m, 2H, H_E), 4.49 (m, 2H, H_E), 4.27 – 3.93 (m, 8H, $H_{E+m+a+c}$), 3.75 – 3.64 (m, 2H, H_k), 2.63 – 2.61 (m, 2H, H_b), 2.63 – 2.61 (m, 2H, H_l).

Synthesis of *Z*-5



A solution of *E*-**5** (1.0 mg, 1.08 µmol, 1.00 eq.) in degassed CD_2Cl_2 (0.4 mL) was irradiated for 1 h using the method described above, affording *Z*-**5** (91 %).
^{1}H NMR (600 MHz, CD_2Cl_2): δ = 15.12 (s, 1H, H_h), 8.38 (d, *J* = 2.8 Hz, 1H, H_d), 7.92 (d, *J* = 8.7 Hz, 2H, H_i), 7.43 (d, *J* = 8.7 Hz, 1H, H_f), 7.40 (s, 1H, H_g), 7.33 – 7.21 (m, 17H, H_{Ar+e}), 7.21 – 7.15 (m, 4H, H_{Ar}), 7.00 (d, *J* = 8.3 Hz, 2H, H_j), 5.63 (s, *J* = 5.7 Hz, 1H, H_r), 4.26 (t, *J* = 8.0 Hz, 1H, H_a), 4.04 (td, *J* = 6.5, 4.5 Hz, 6H, H_{c+k+o}), 3.95 (t, *J* = 7.8 Hz, 1H, H_v), 3.19 – 3.12 (m, 2H, H_s), 2.60 (dt, *J* = 8.0, 6.5 Hz, 2H, H_b), 2.56 (t, *J* = 6.8 Hz, 2H, H_p), 2.34 (t, *J* = 6.8 Hz, 2H, H_q), 2.25 (q, *J* = 7.4 Hz, 2H, H_t), 1.81 (m, 2H, H_l), 1.60 (m, 2H, H_n), 1.51 – 1.43 (m, 2H, H_m), 1.40 – 1.22 (m, 14H, $H_{aliphatic}$). ^{13}C NMR (151 MHz, CD_2Cl_2): δ= 173.47, 171.59, 164.09, 162.82, 155.47, 146.03, 145.10, 144.59, 138.22, 136.94, 129.89, 129.19, 129.08, 128.28, 128.21, 127.58, 127.05, 126.86, 126.02, 122.51, 114.94, 112.52, 68.85, 67.37, 65.28, 49.49, 47.72, 38.84, 35.61, 35.03, 31.42, 30.09, 30.06, 30.05, 29.90, 29.80, 29.68, 29.15, 26.50, 26.42, 16.75.

Synthesis of *Z*-6

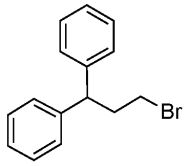


A solution of *E*-**6** (1.0 mg, 0.68 µmol, 1.00 eq.) in degassed CD_2Cl_2 (0.4 mL) was irradiated for 2 h using the method described above, affording *Z*-**6** (> 95 %, *Z*/*E* = 91 %).
^{1}H NMR (600 MHz, CD_2Cl_2): δ = 15.16 (s, 1H, H_h), 8.40 (s, 1H, H_d), 8.38 (s, 2H, H_C), 8.23 (d, *J* = 7.8 Hz, 4H, H_B), 7.92 (d, *J* = 8.3 Hz, 2H, H_i), 7.60 (t, *J* = 7.8 Hz, 2H, H_A), 7.46 (d, *J* = 8.7 Hz, 1H, H_f), 7.40 (s, 1H, H_g), 7.38 (s, 4H, H_D), 7.36 – 7.12 (m, 21H, H_{Ar+e}), 7.01 (s, 8H, H_F), 6.98 (d, *J* = 8.3 Hz, 2H, H_j), 6.43 (s, 1H, H_q), 4.49 – 4.41 (m, 8H, H_E), 4.25 (t, *J* = 8.2 Hz, 1H, H_a), 4.04 – 4.02 (m, 4H, H_{c+k}), 3.87 (t, *J* = 8.0 Hz, 2H, H_n), 3.75 (t, *J* = 7.8 Hz, 1H, H_t), 2.74 – 2.70 (m, 2H, H_r), 2.59 (dt, *J* = 8.2, 6.3 Hz, 2H, H_b), 2.02– 2.00 (m, 2H, H_s), 1.82– 1.78 (m, 2H, H_l), 1.60 – 1.19 (m, 22H, $H_{m+o+p+aliphatic}$). ^{13}C NMR (151 MHz, CD_2Cl_2): δ= 173.47, 171.59, 164.09, 162.82, 155.47, 146.03, 145.10, 144.59, 138.22, 136.94, 129.89, 129.19, 129.08, 128.28, 128.21, 127.58, 127.05, 126.86, 126.02, 122.51, 114.94, 112.52, 68.85, 67.37, 65.28, 49.49, 47.72, 38.84, 35.61, 35.03, 31.42, 30.09, 30.06, 30.05, 29.90, 29.80, 29.68, 29.15, 26.50, 26.42, 16.75.

1.4.2. General procedure for the thermal isomerization

In a NMR tube, a solution of the corresponding *Z*-thread (*Z*-**3** and *Z*-**5**) or rotaxane (*Z*-**4** and *Z*-**6**) (1.0 mg, 1.00 eq.) in degassed CD_2Cl_2 (0.4 mL) was heated at 40 ºC with catalytic amount of trifluoroacetic acid (TFA) for 2 hours followed by neutralization with K_2CO_3. The thermal isomerizations were followed by ^{1}H NMR (See Supporting Information, Section 3.2).

2. ^{1}H and ^{13}C NMR spectra for new compounds



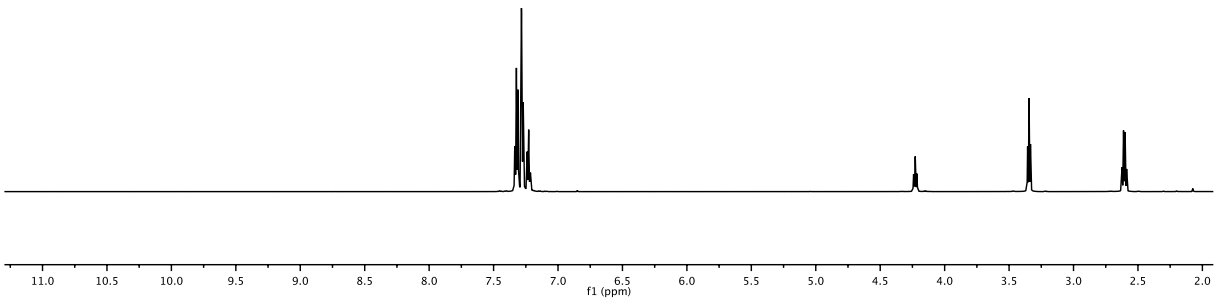


Figure S1: ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **S1**.

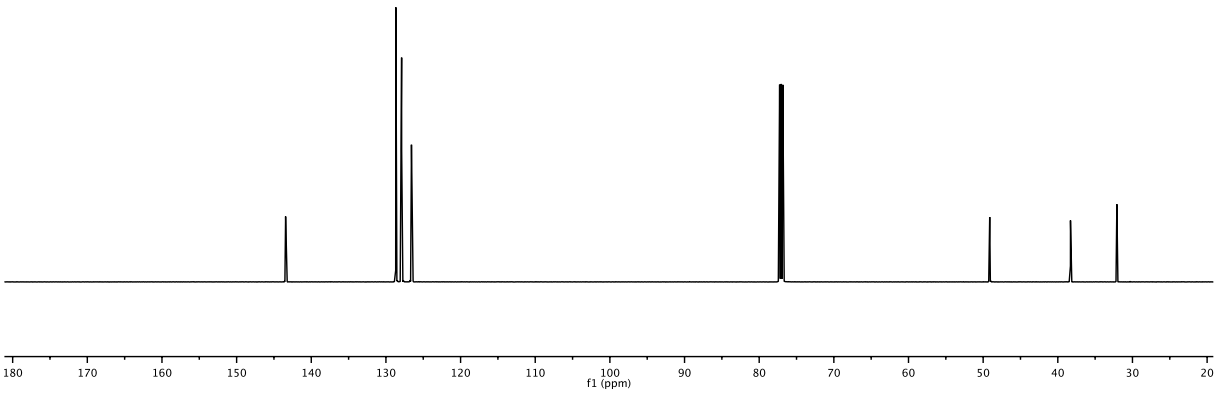
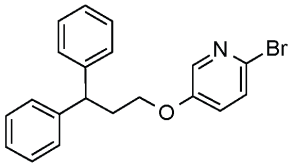


Figure S2: ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **S1**.



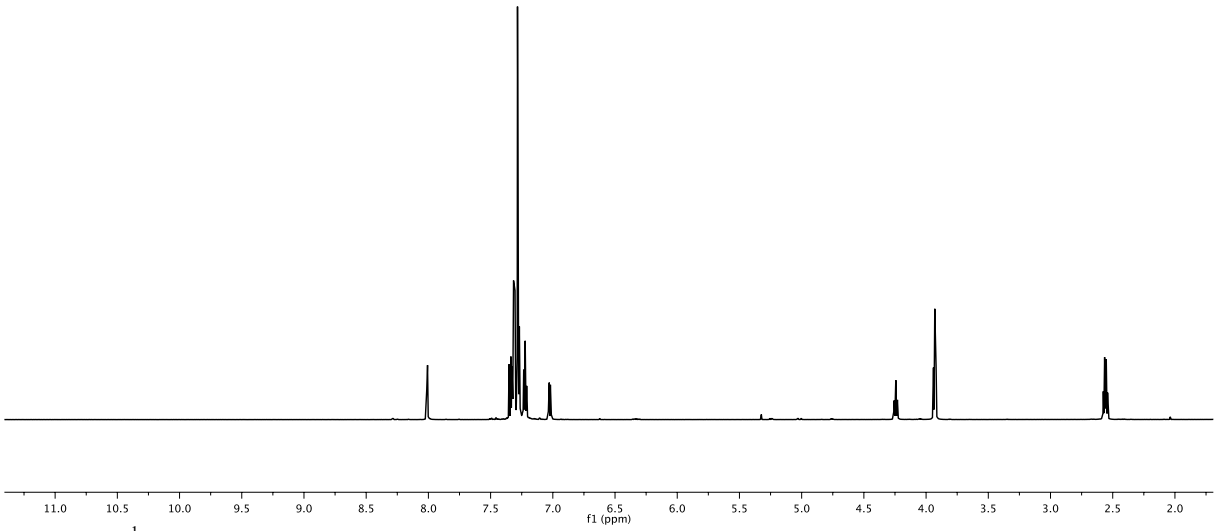


Figure S3: ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **S2**.

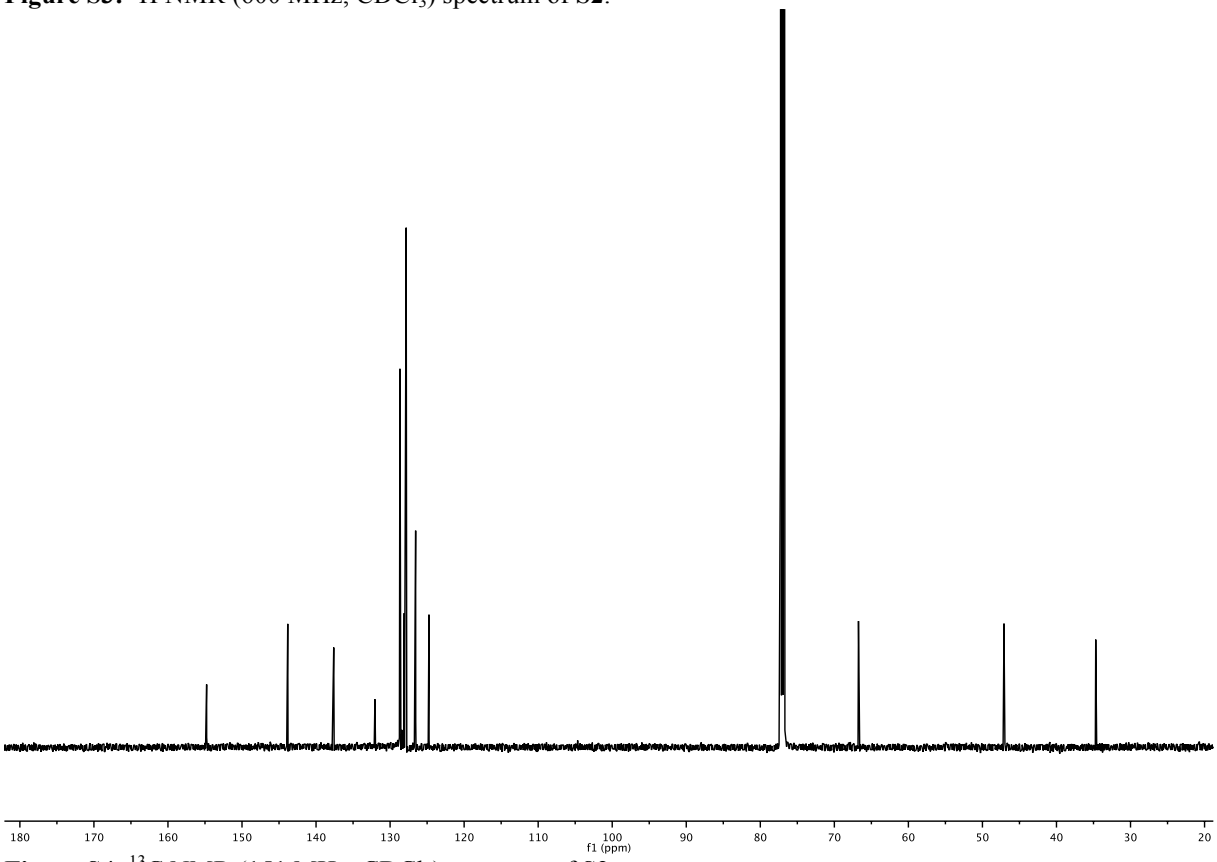
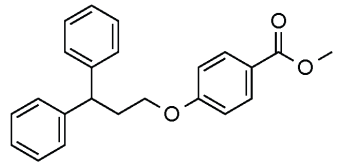


Figure S4: ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **S2.**



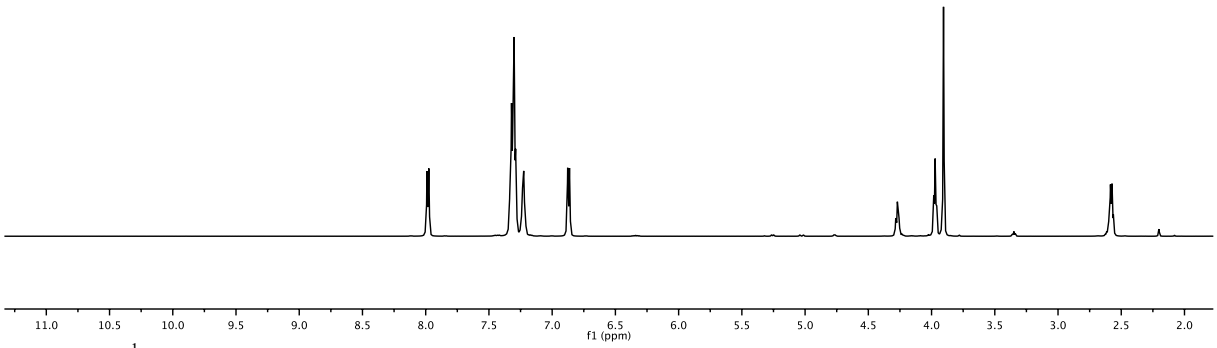


Figure S5: ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **S3**.

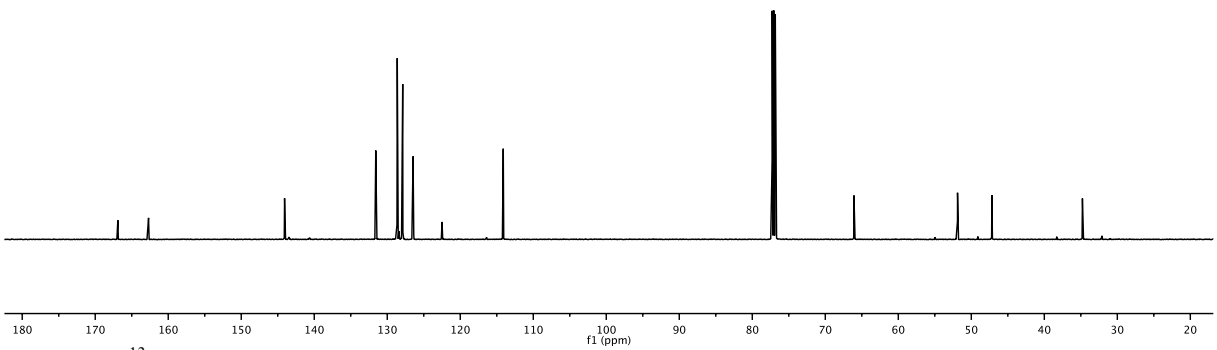


Figure S6: ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **S3.**

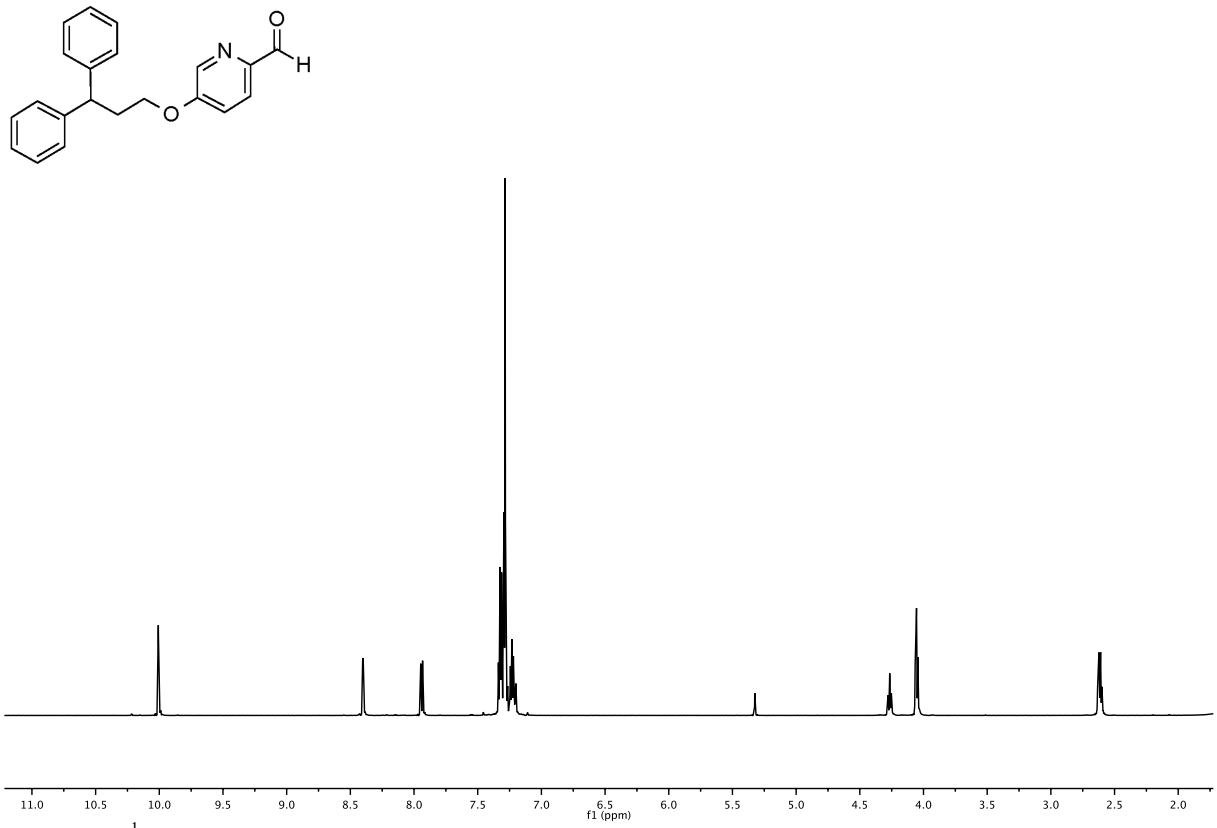


Figure S7: ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **1**.

Chem. Sci. 2016, DOI: 10.1039/C6SC00783J.

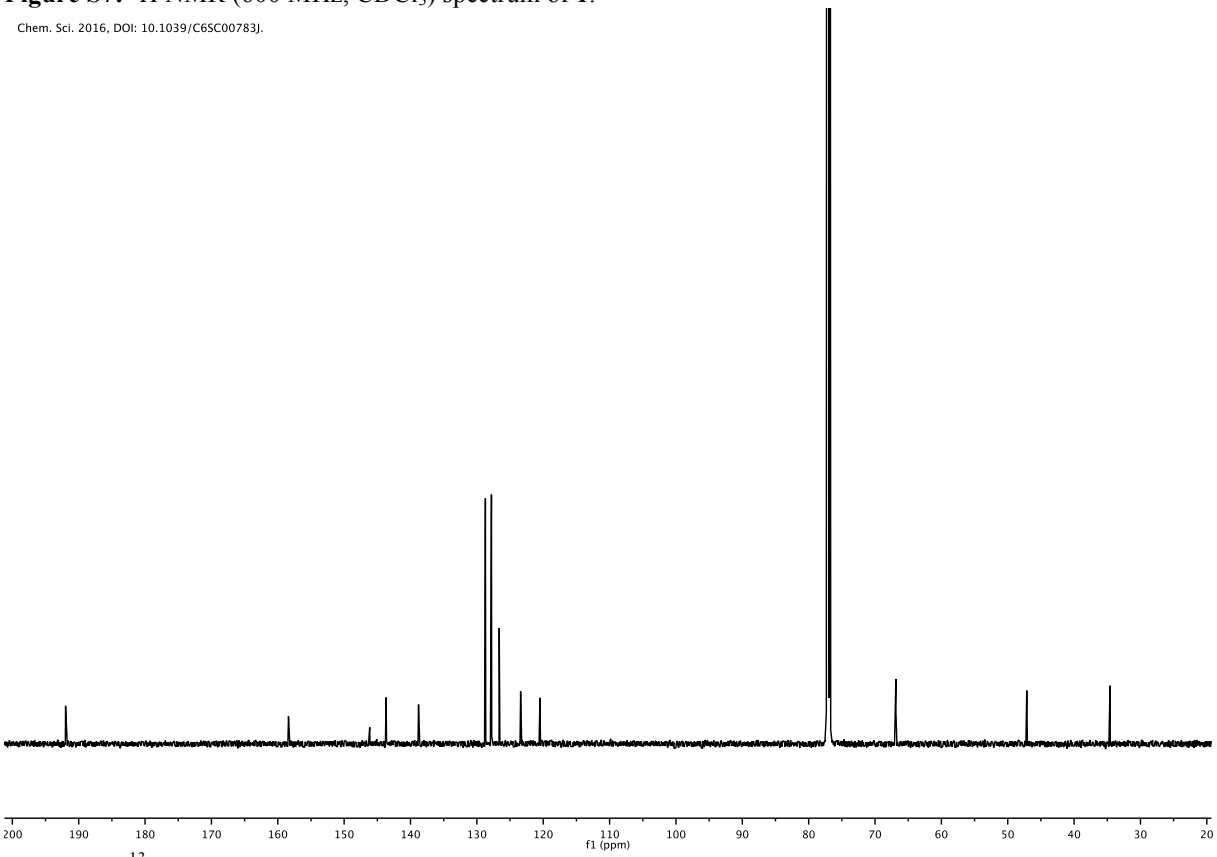


Figure S8: ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **1.**

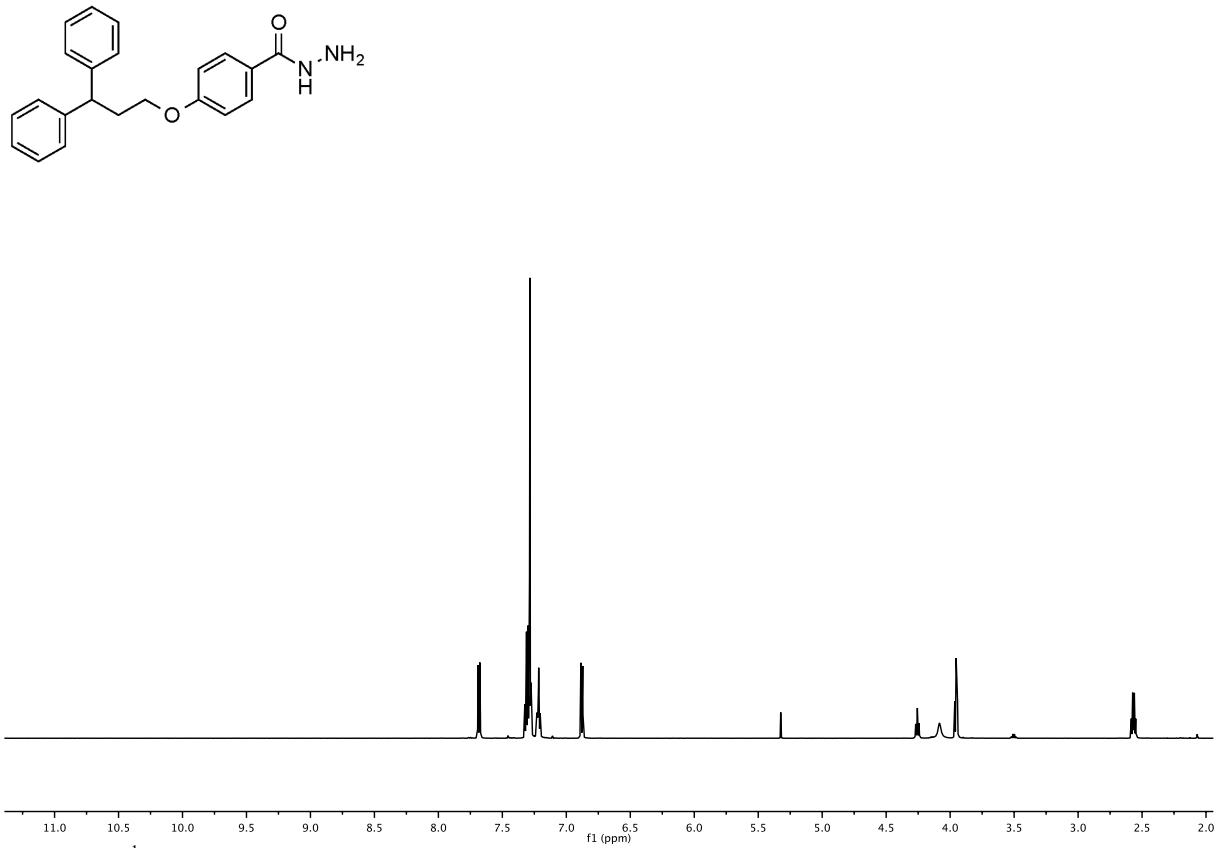


Figure S9: ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2**.

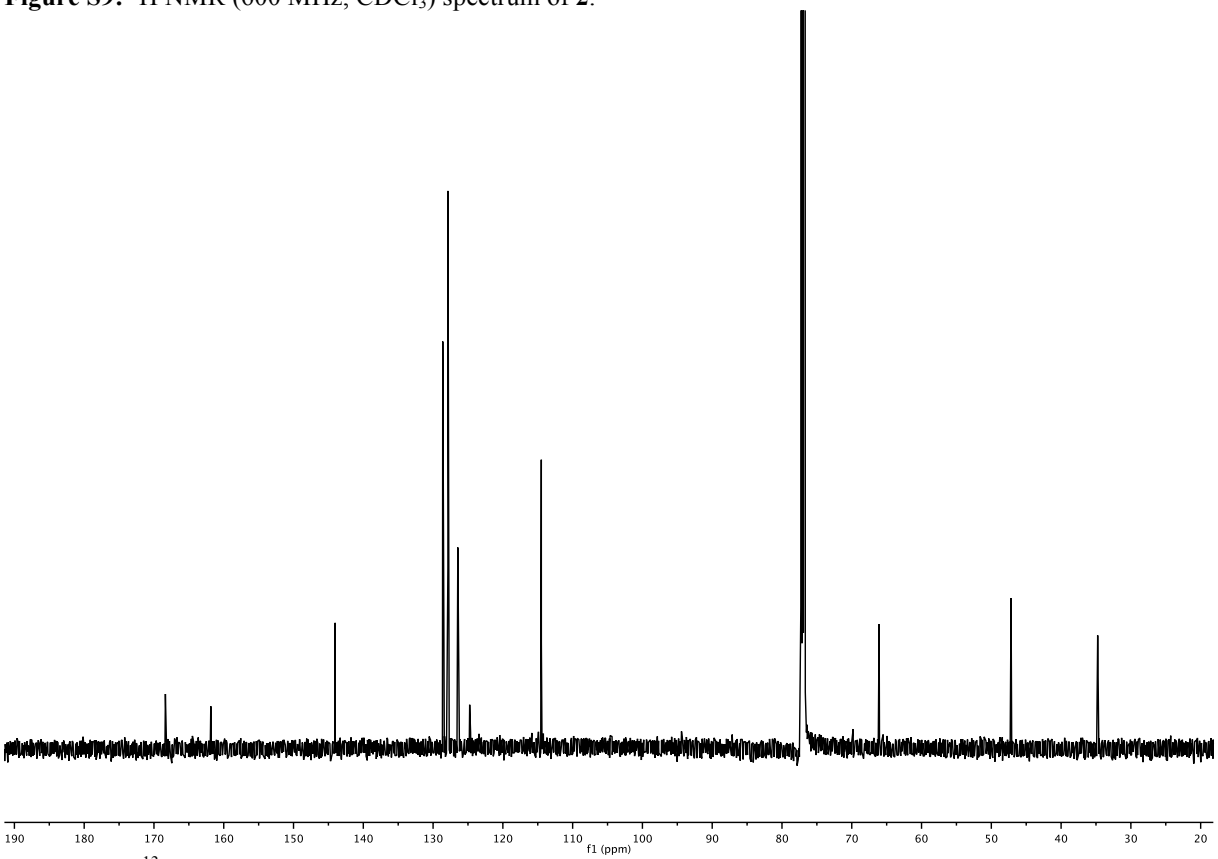


Figure S10: ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2.**

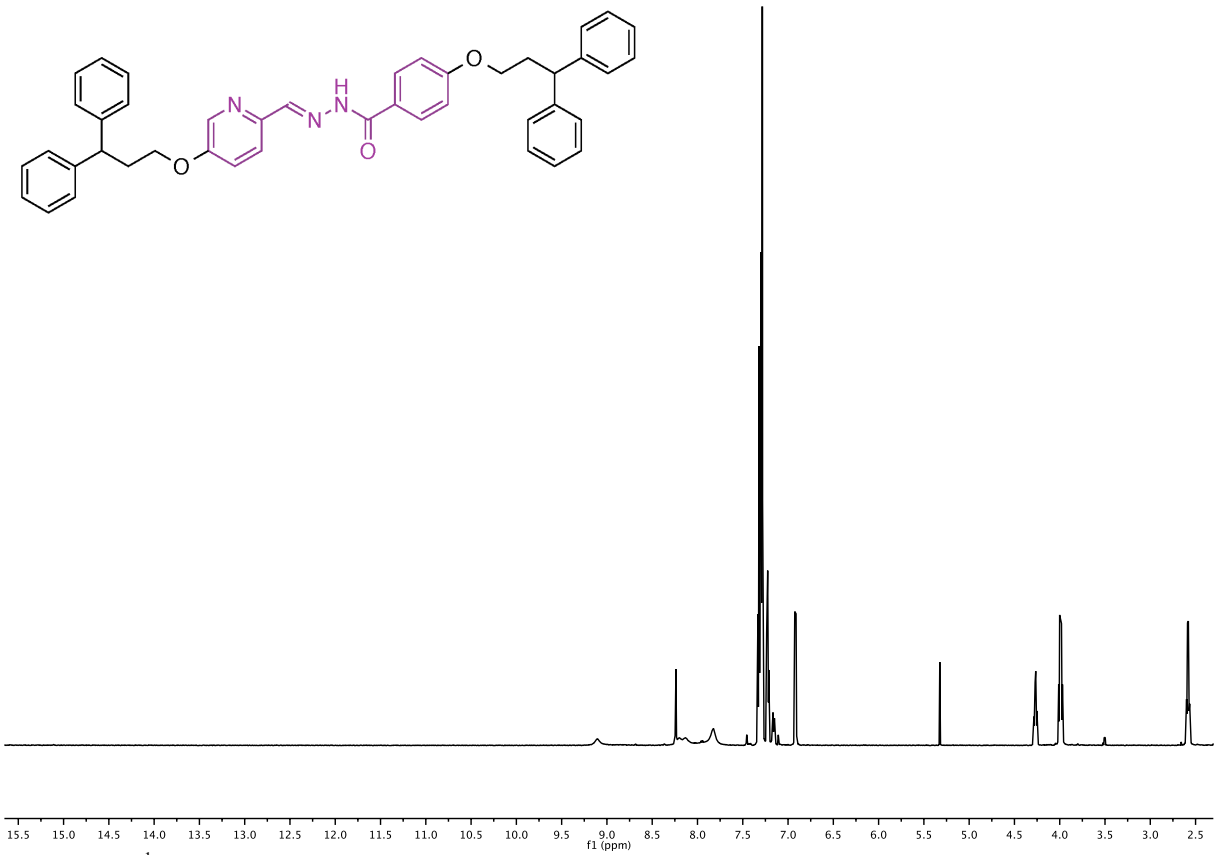


Figure S11: ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of *E*-**3**.

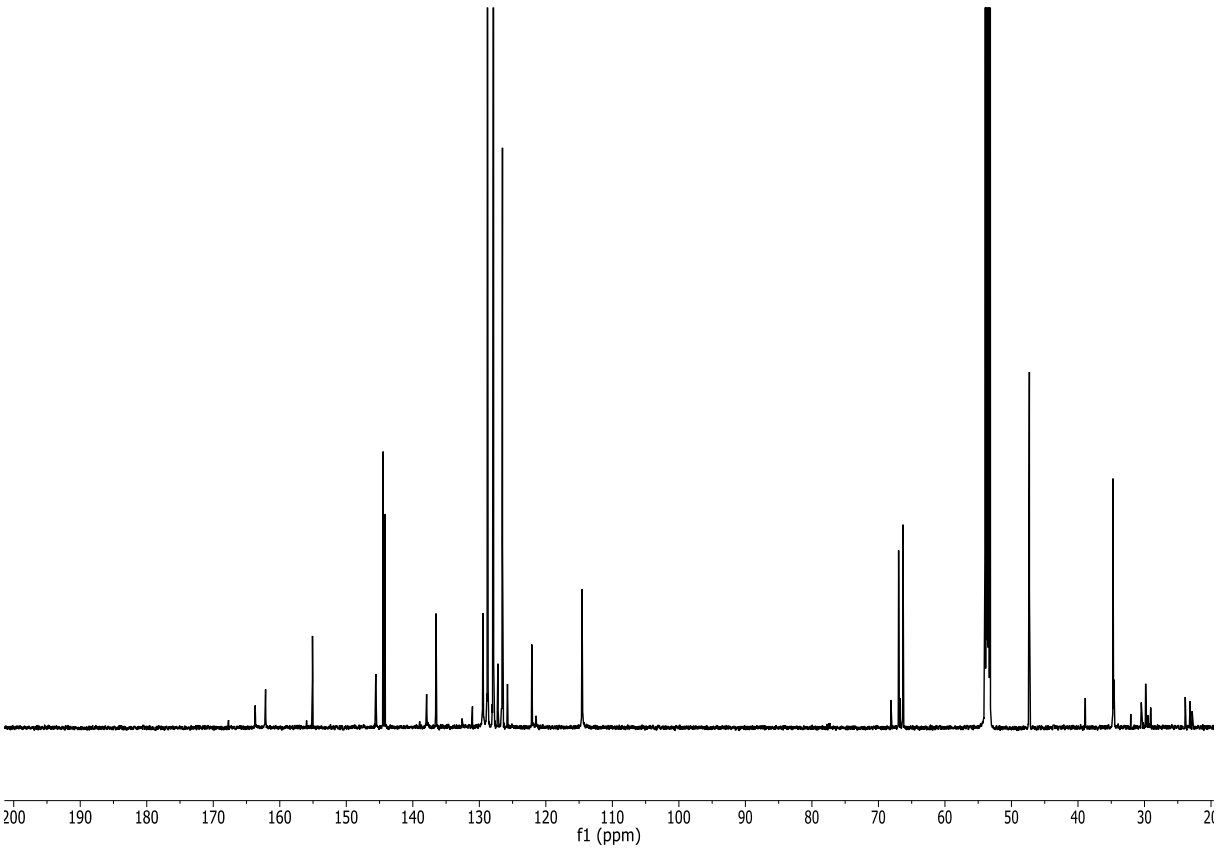


Figure S12: ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of *E*-**3.**

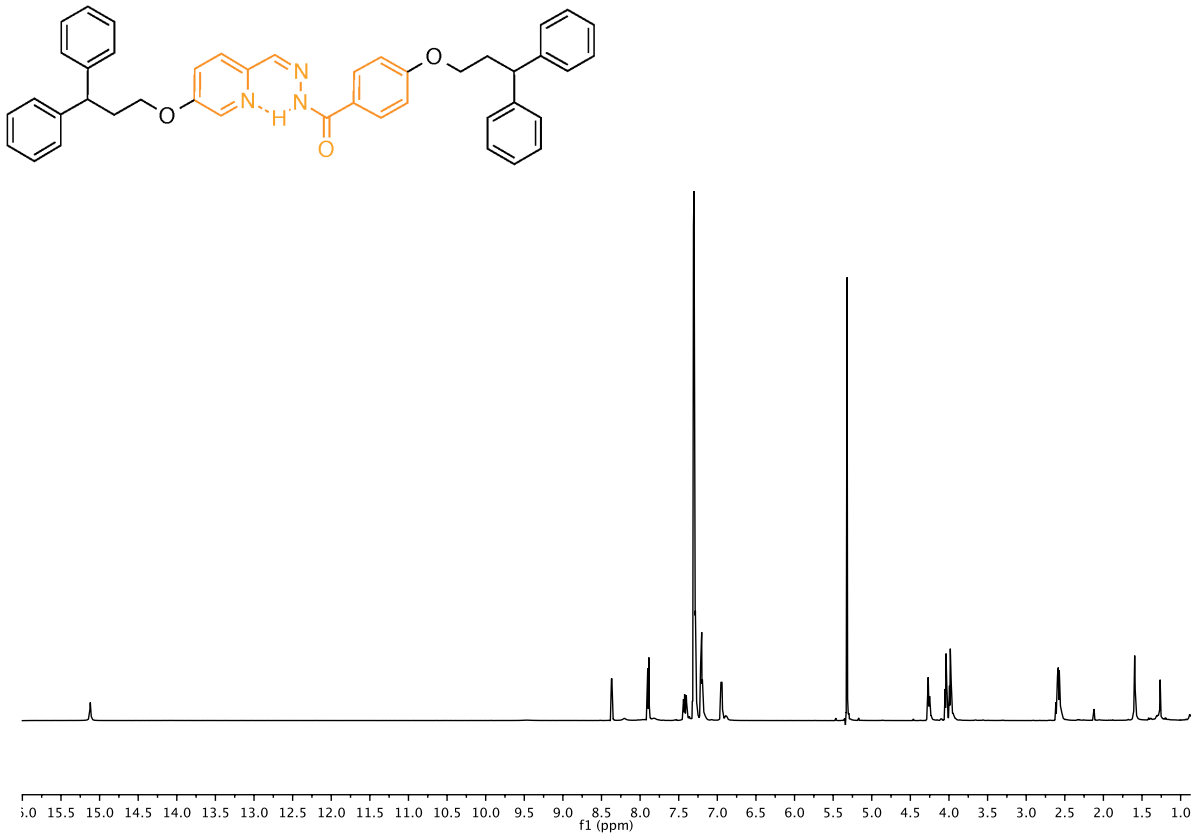


Figure S13: ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of *Z*-**3**.

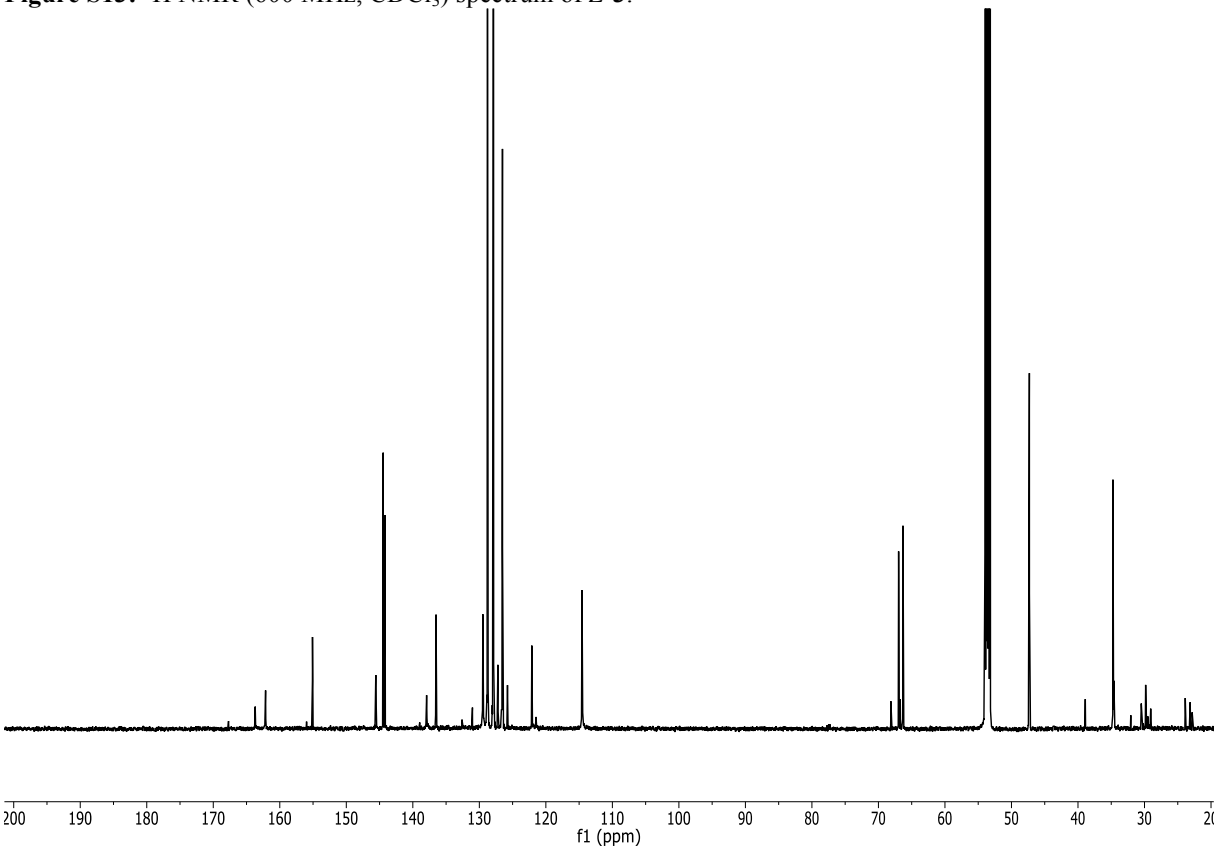
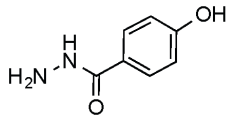


Figure S14: ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of *Z*-**3.**



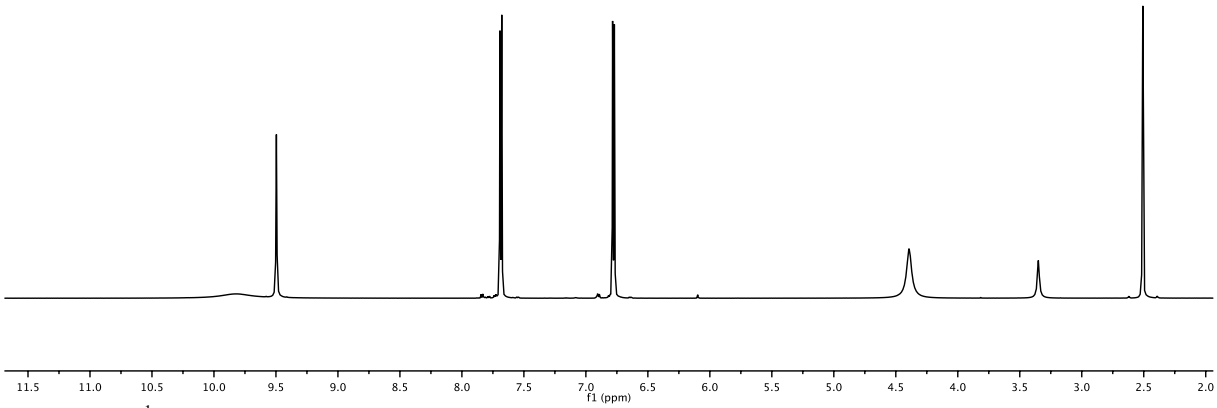


Figure S15: ^{1}H NMR (600 MHz, DMSO-d_6) spectrum of **S4**.

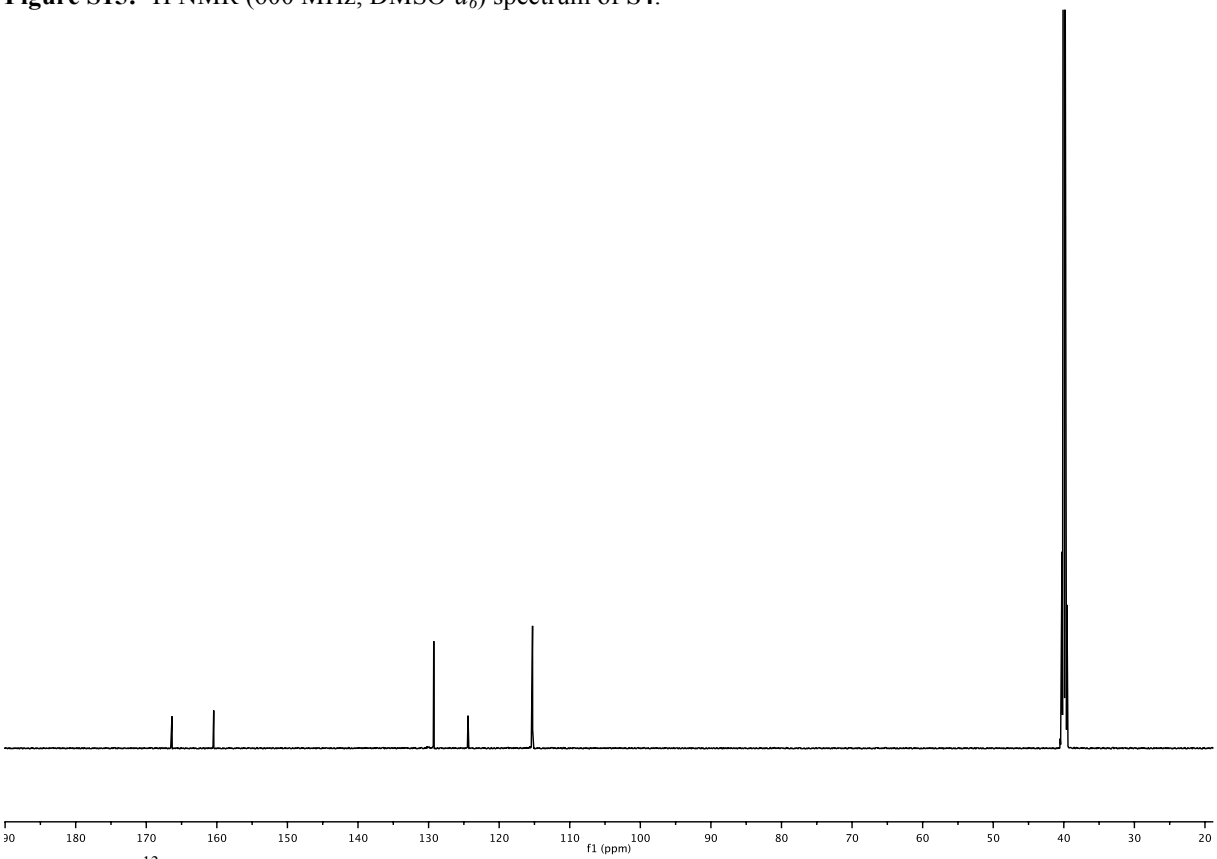


Figure S16: ^{13}C NMR (151 MHz, DMSO-d_6) spectrum of **S4.**

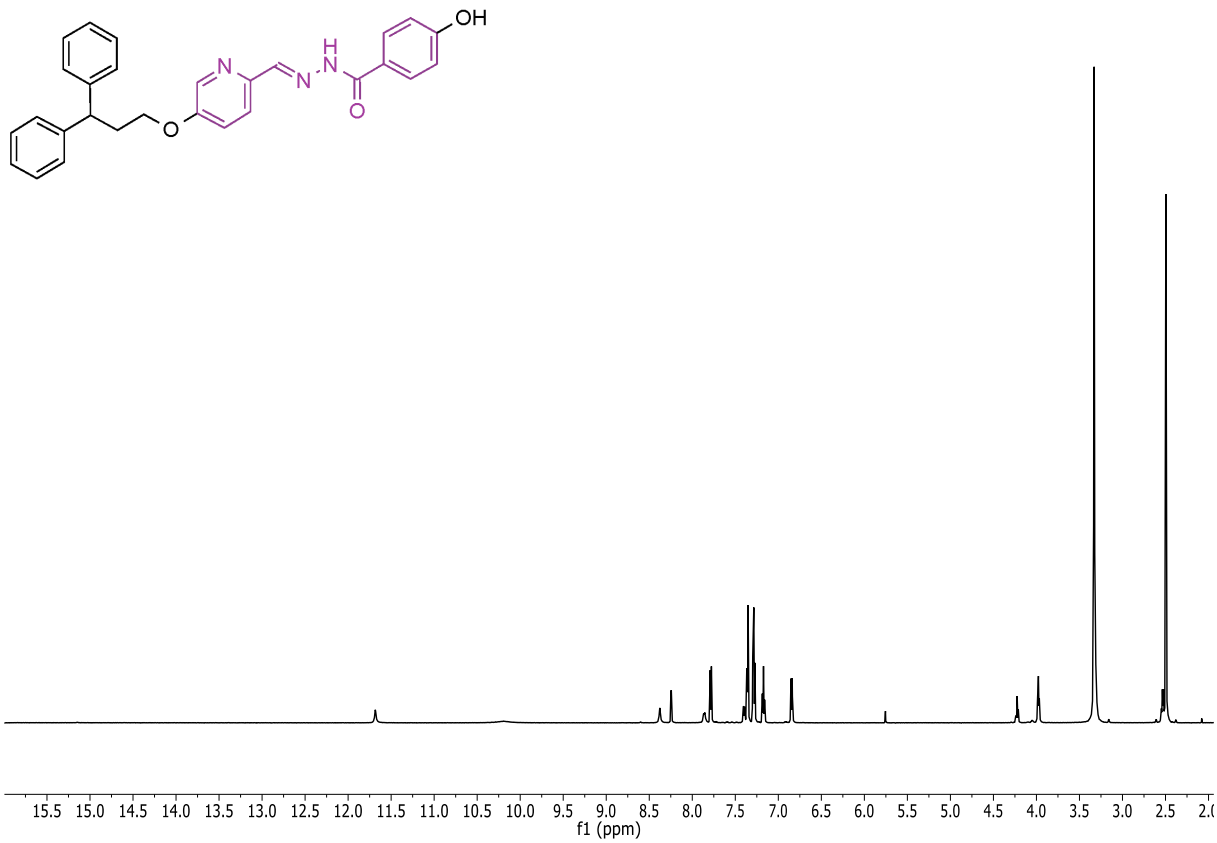


Figure S17: ^{1}H NMR (600 MHz, DMSO-d_6) spectrum of **S5.**

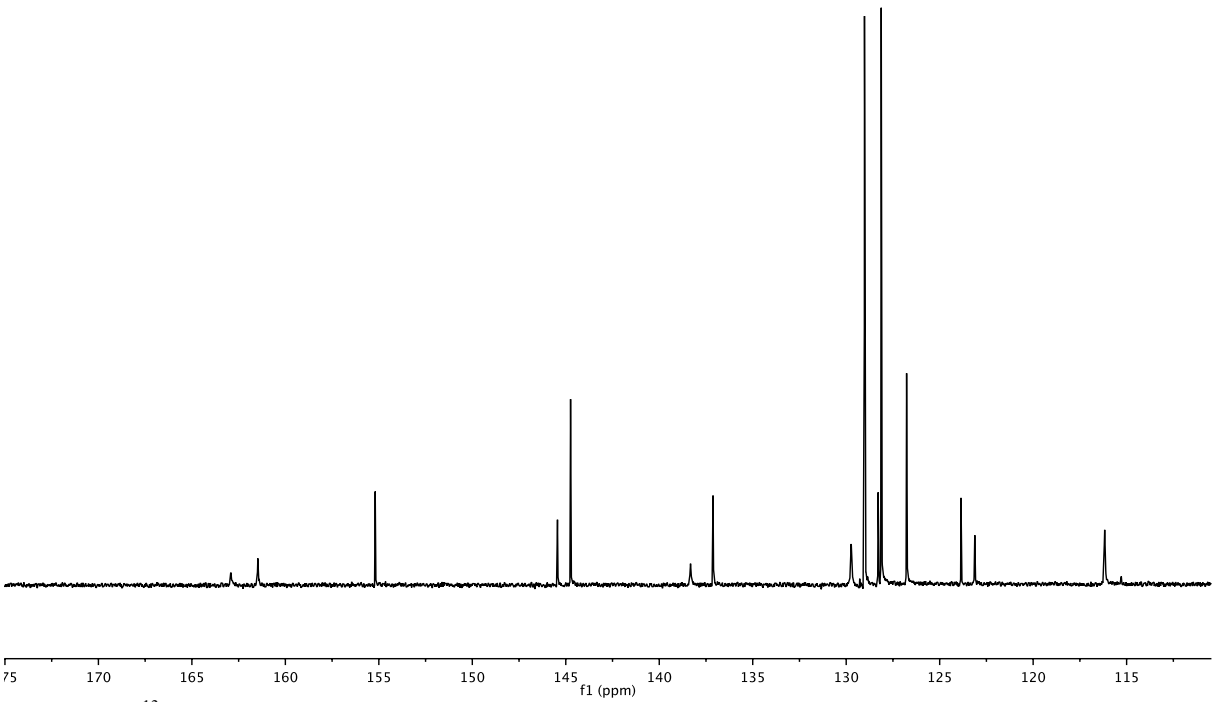


Figure S18: ^{13}C NMR (151 MHz, DMSO-d_6) spectrum of **S5.**

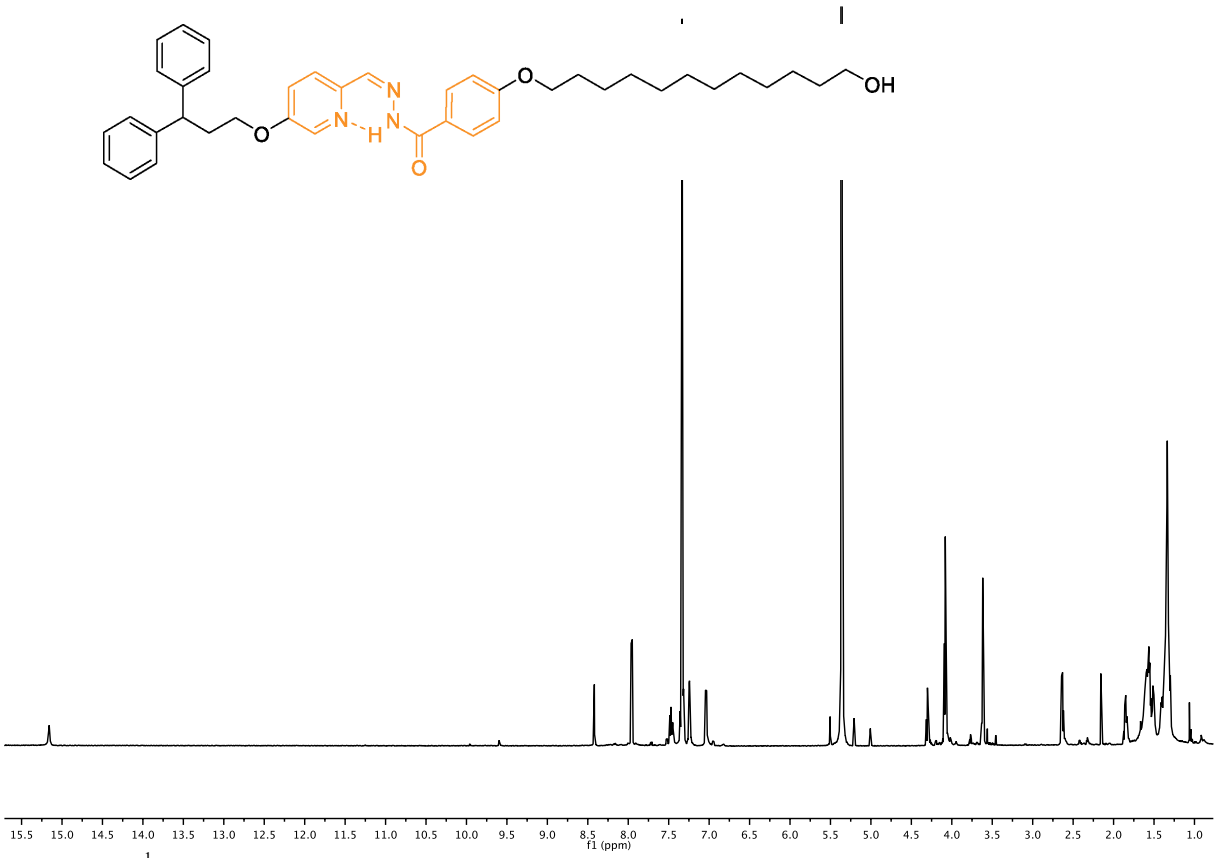


Figure S19: ^{1}H NMR (600 MHz, CD_2Cl_2) spectrum of **S6**.

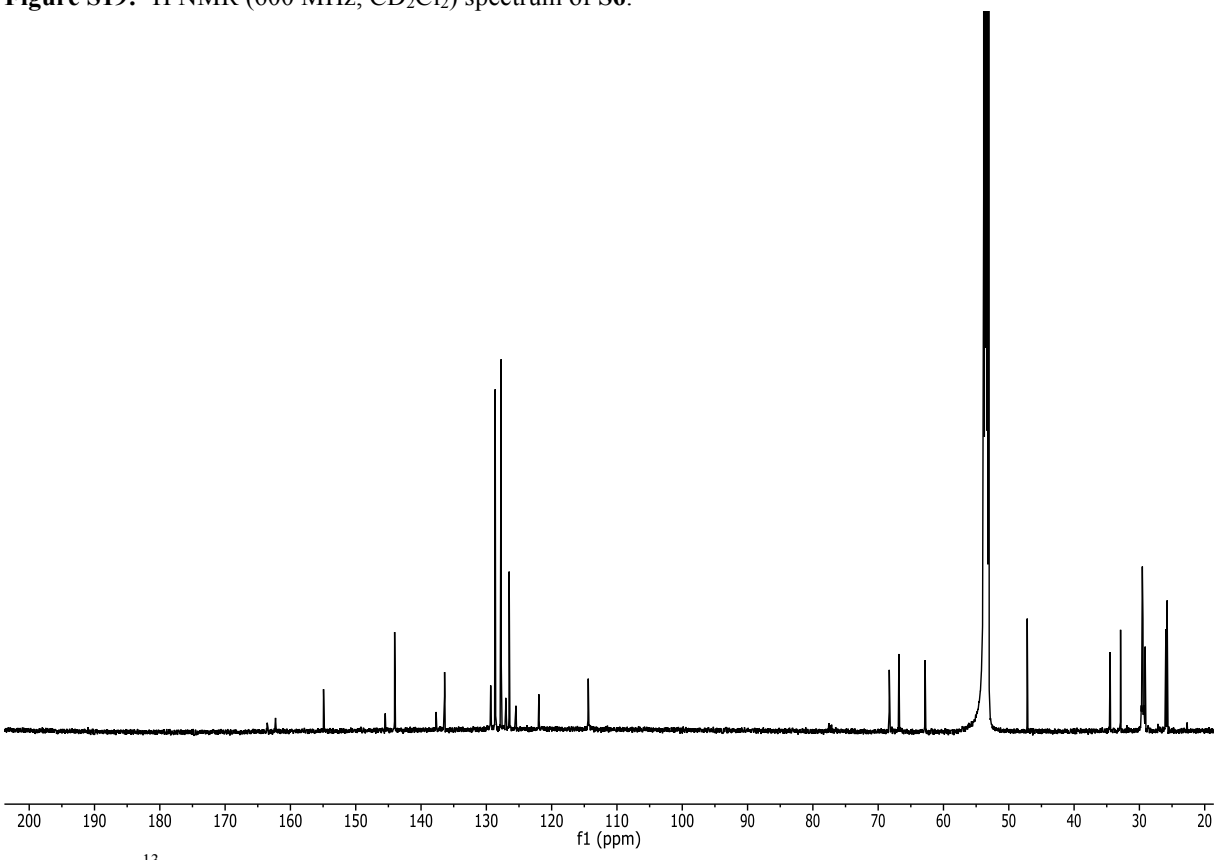


Figure S20: ^{13}C NMR (151 MHz, CD_2Cl_2) spectrum of **S6.**

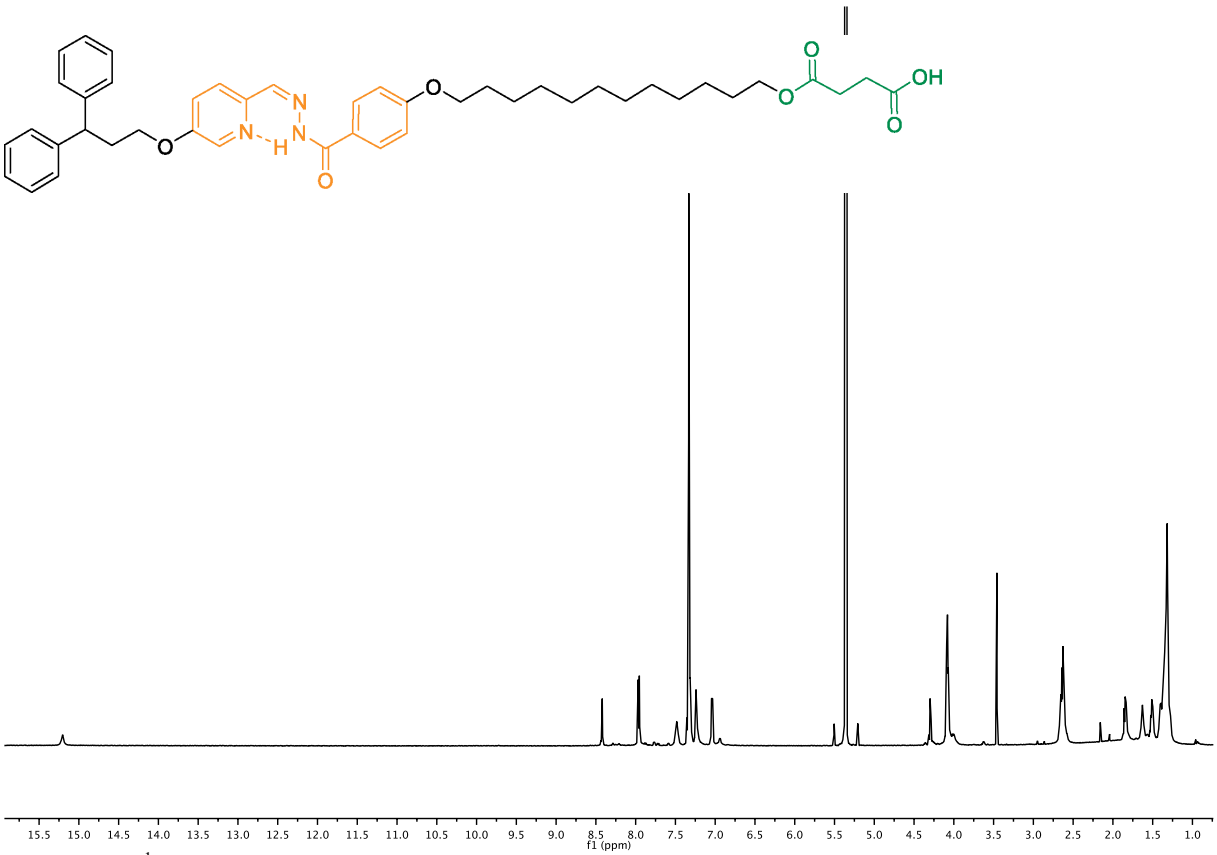


Figure S21: ^{1}H NMR (600 MHz, CD_2Cl_2) spectrum of **S7**.

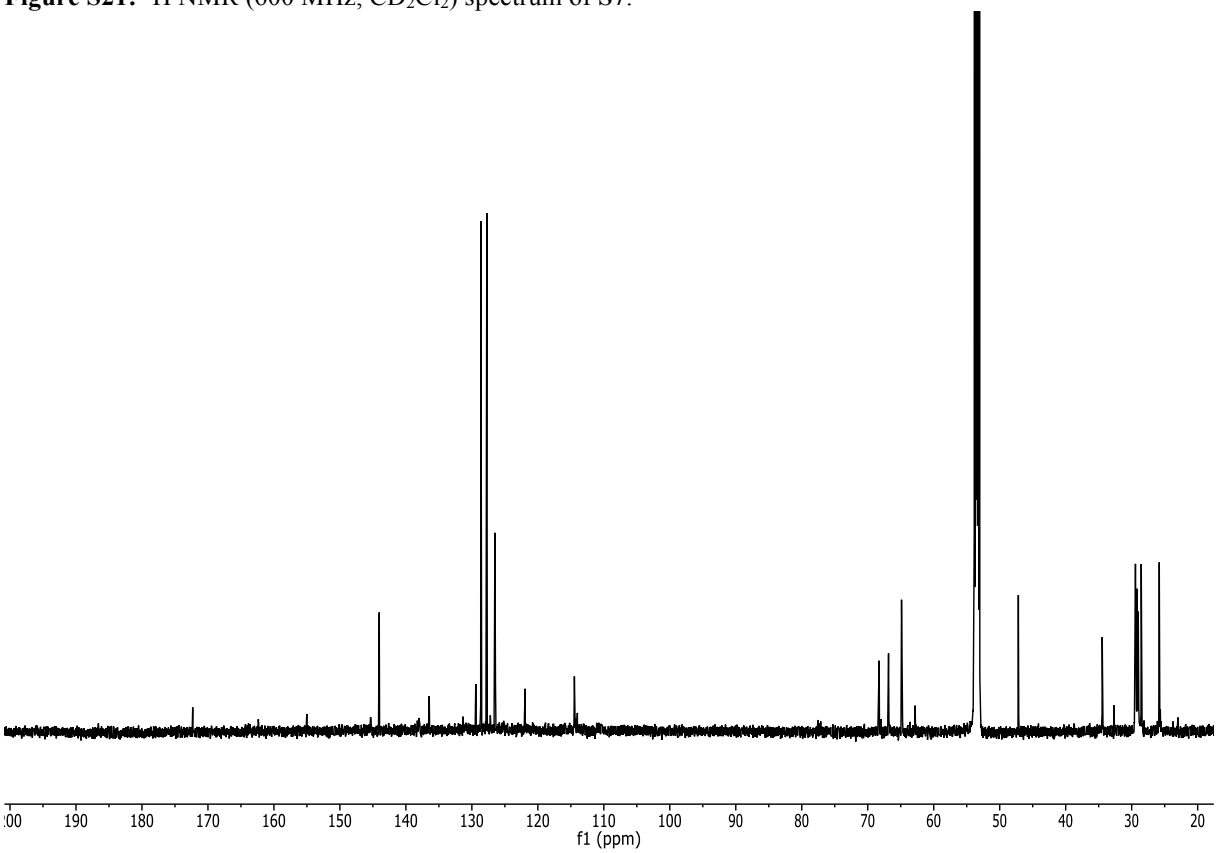


Figure S22: ^{13}C NMR (151 MHz, CD_2Cl_2) spectrum of **S7**

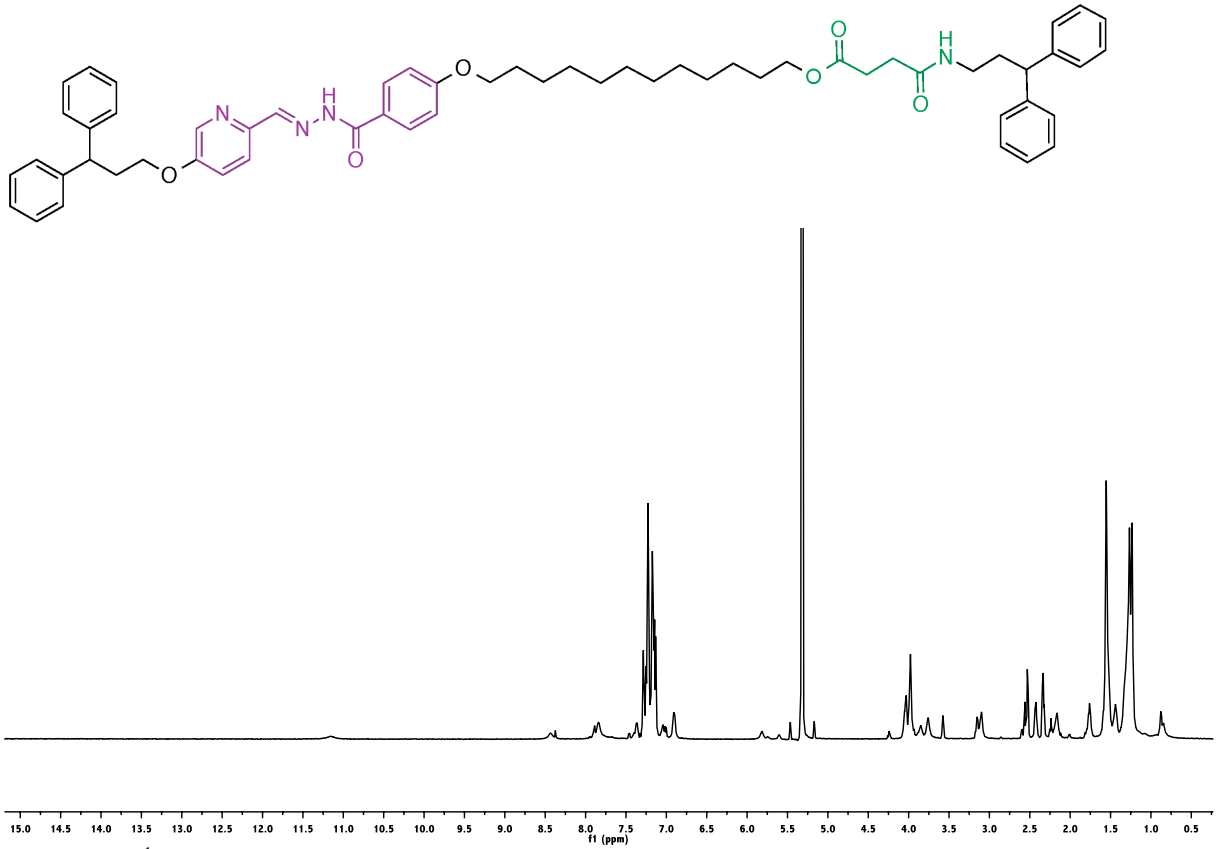


Figure S23: ^{1}H NMR (600 MHz, CD_2Cl_2) spectrum of *E*-**5** (77: 23 *E/Z* mixture).

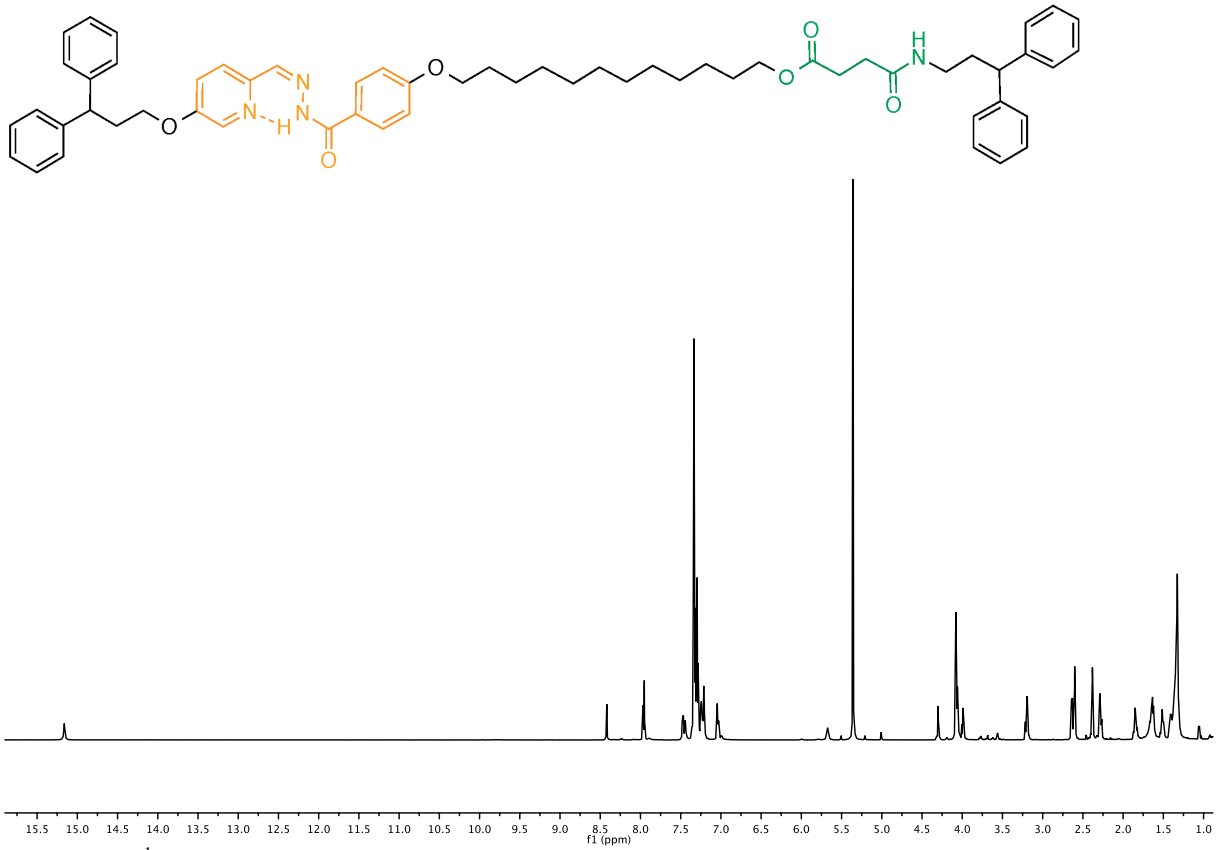


Figure S24: ^{1}H NMR (600 MHz, CD_2Cl_2) spectrum of *Z*-**5**.

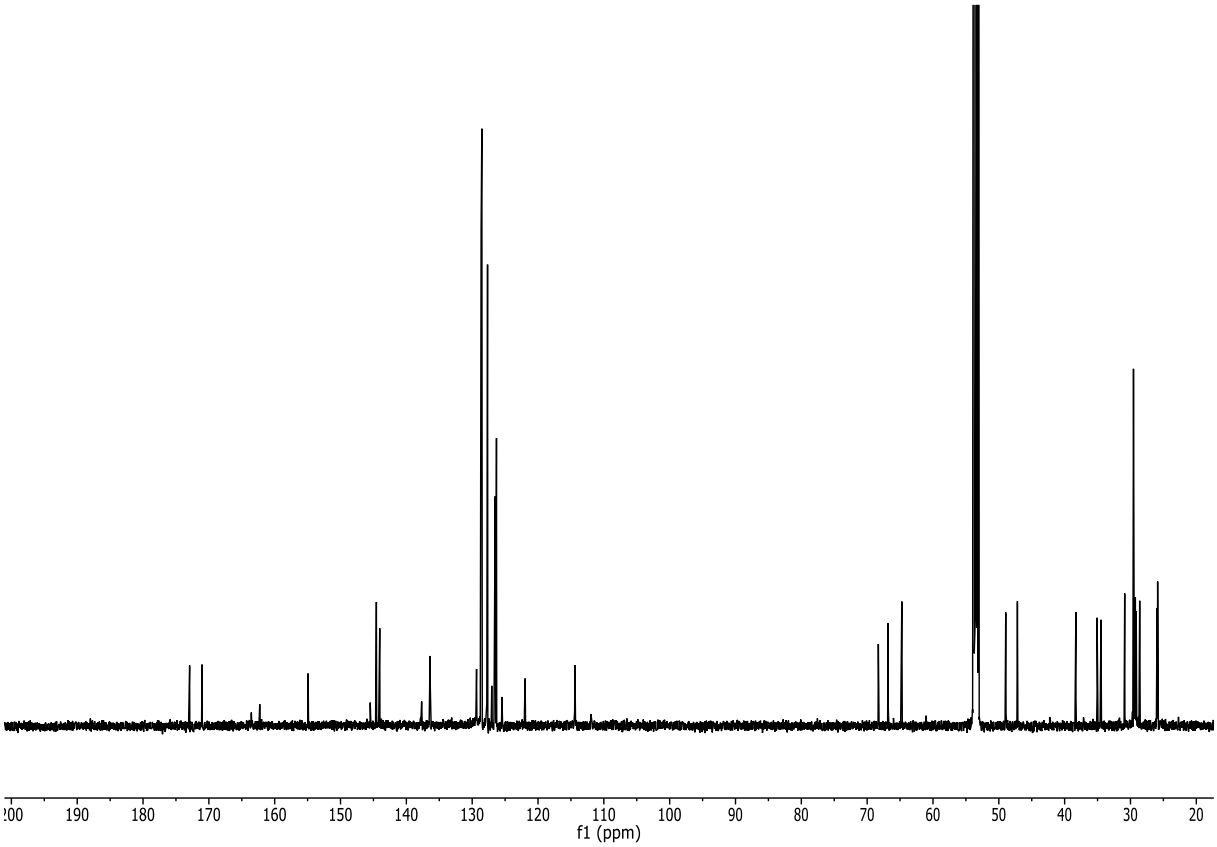


Figure S25: ^{13}C NMR (151 MHz, CD_2Cl_2) spectrum of *Z*-**5**.

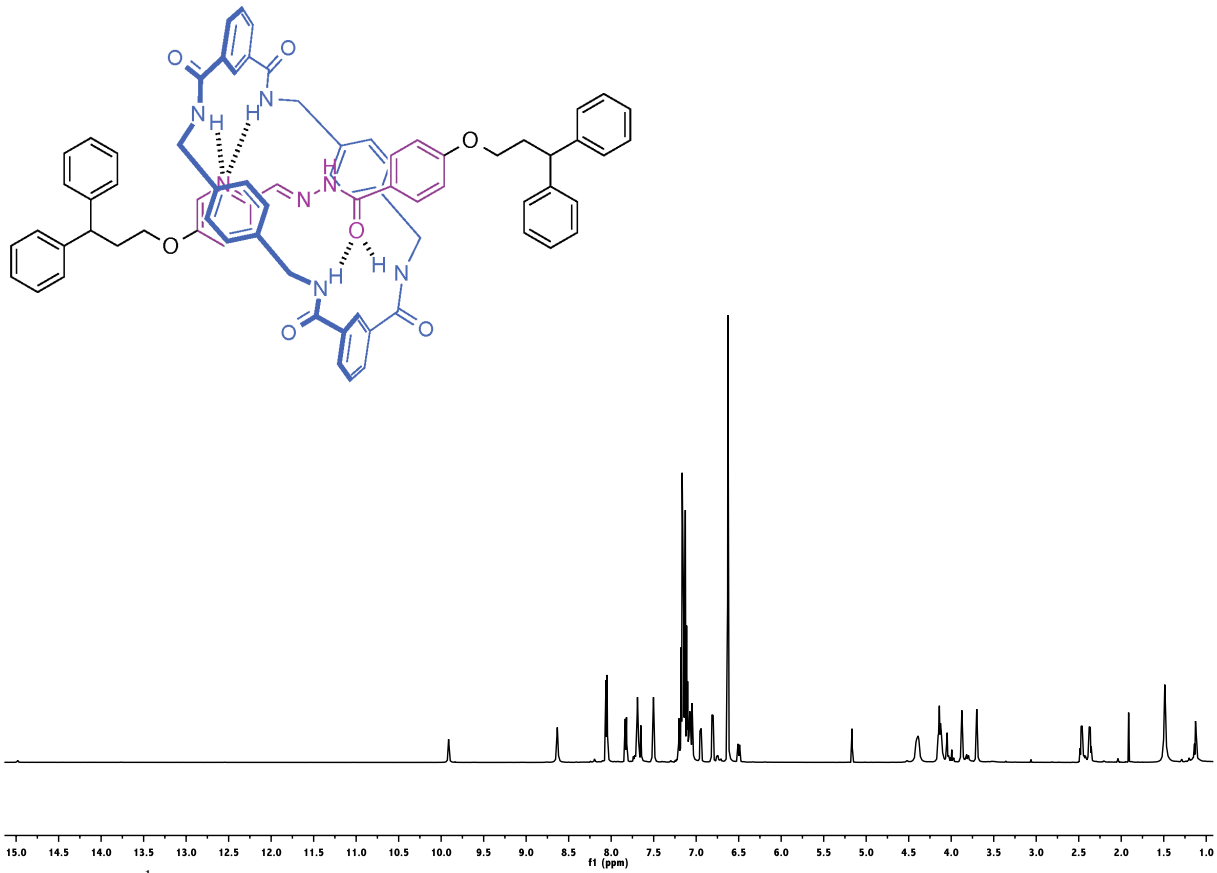


Figure S26: ^{1}H NMR (600 MHz, CD_2Cl_2) spectrum of ***E*-4**

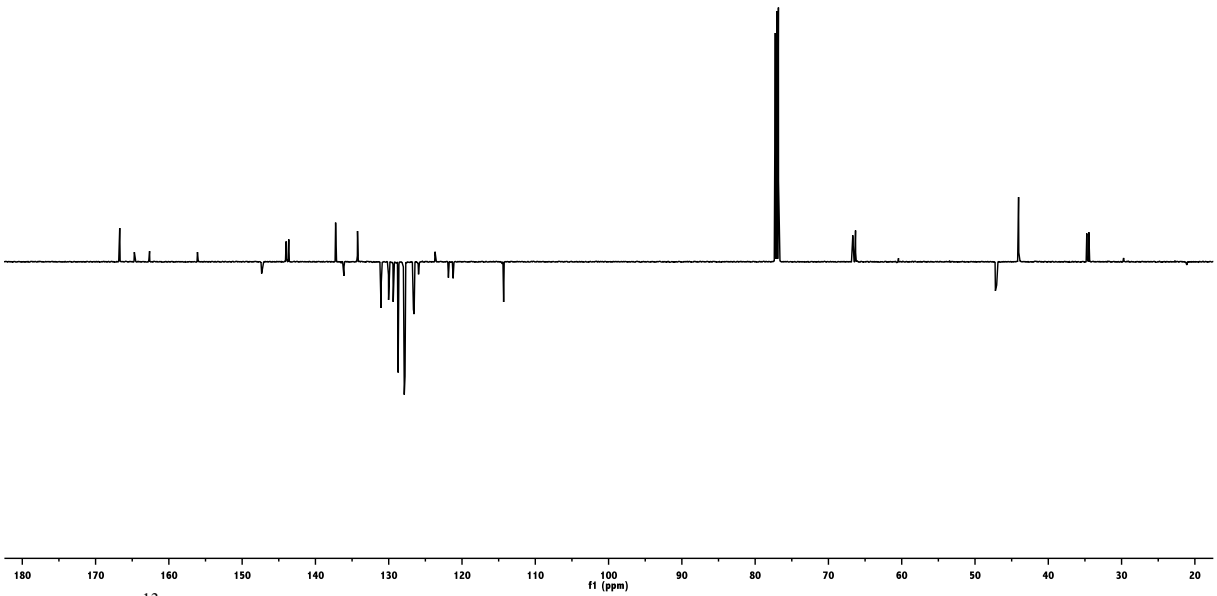


Figure S27: ^{13}C DEPT (151 MHz, CD_2Cl_2) spectrum of ***E*-4.**

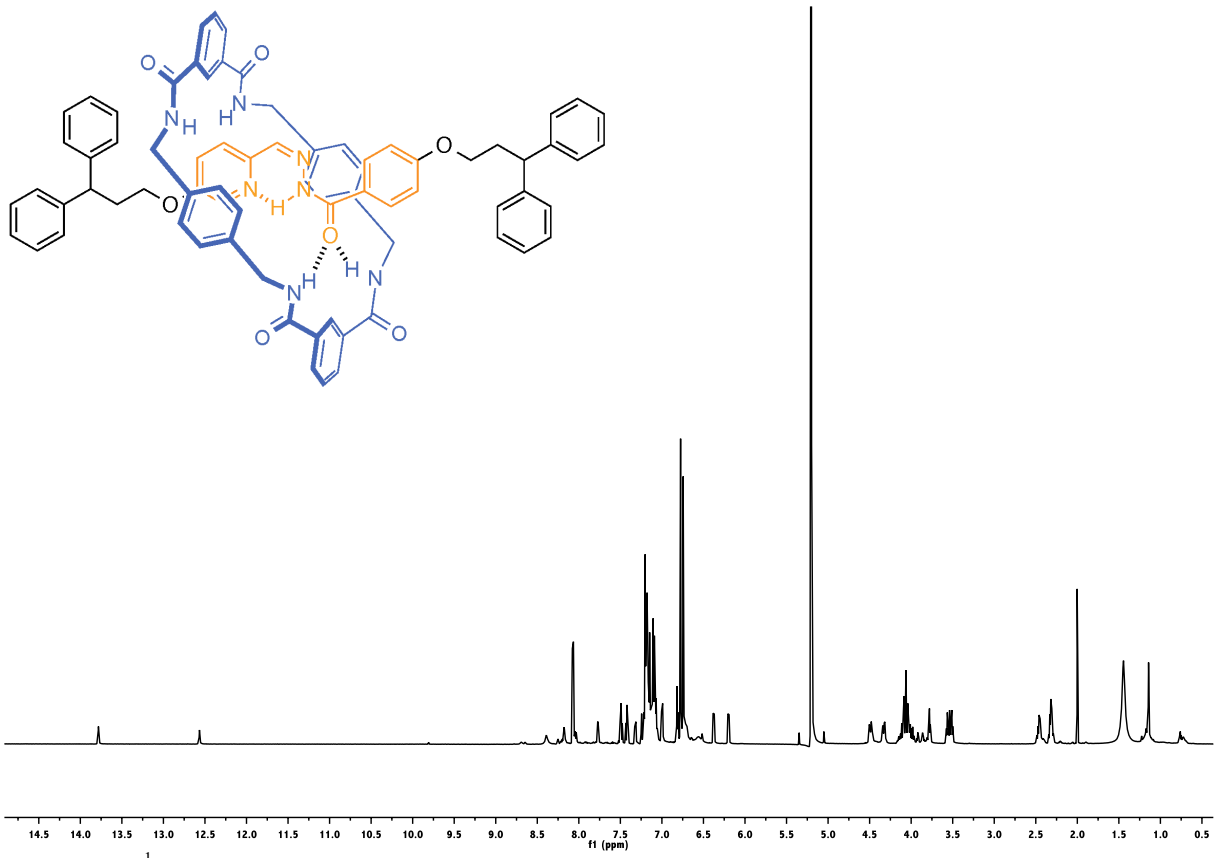


Figure S28: ^{1}H NMR (600 MHz, CD_2Cl_2) spectrum of *Z*-**4**.

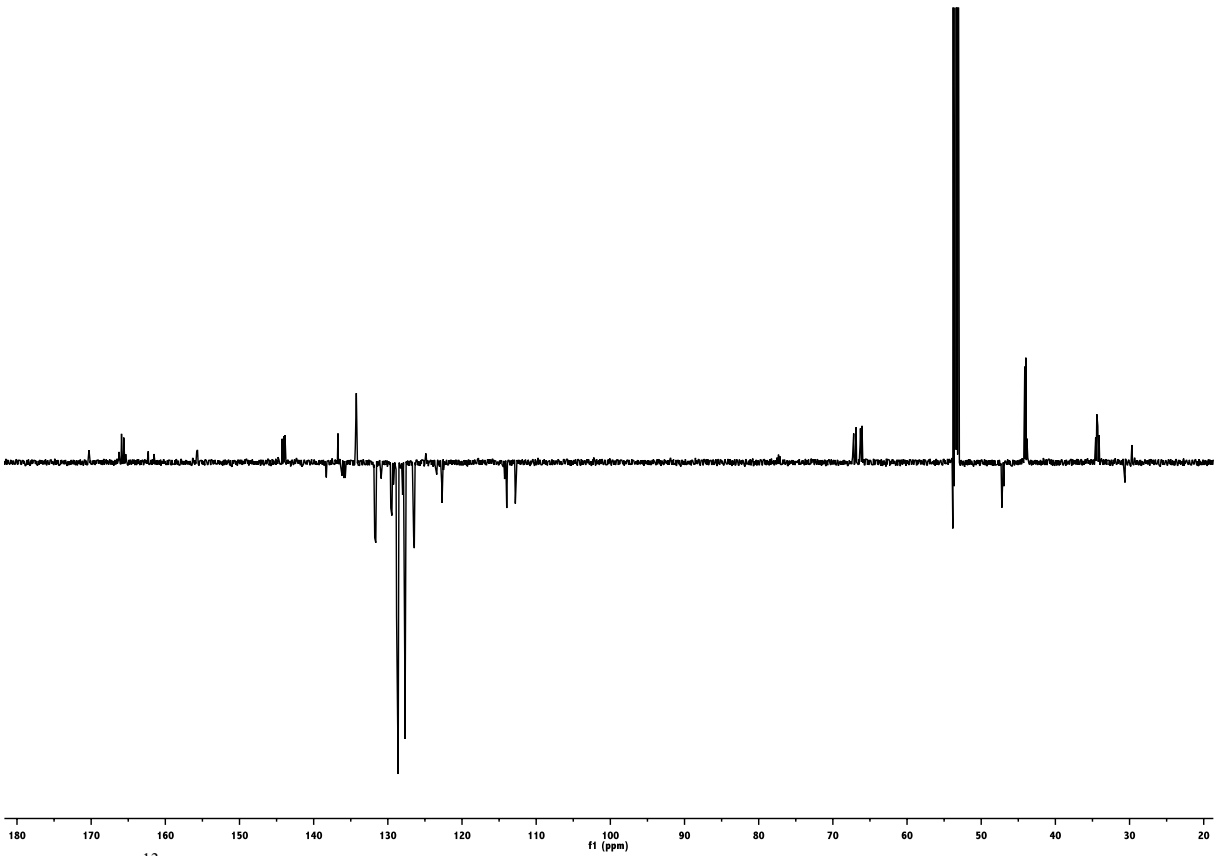


Figure S29: ^{13}C DEPT (151 MHz, CD_2Cl_2) spectrum of *Z*-**4**.

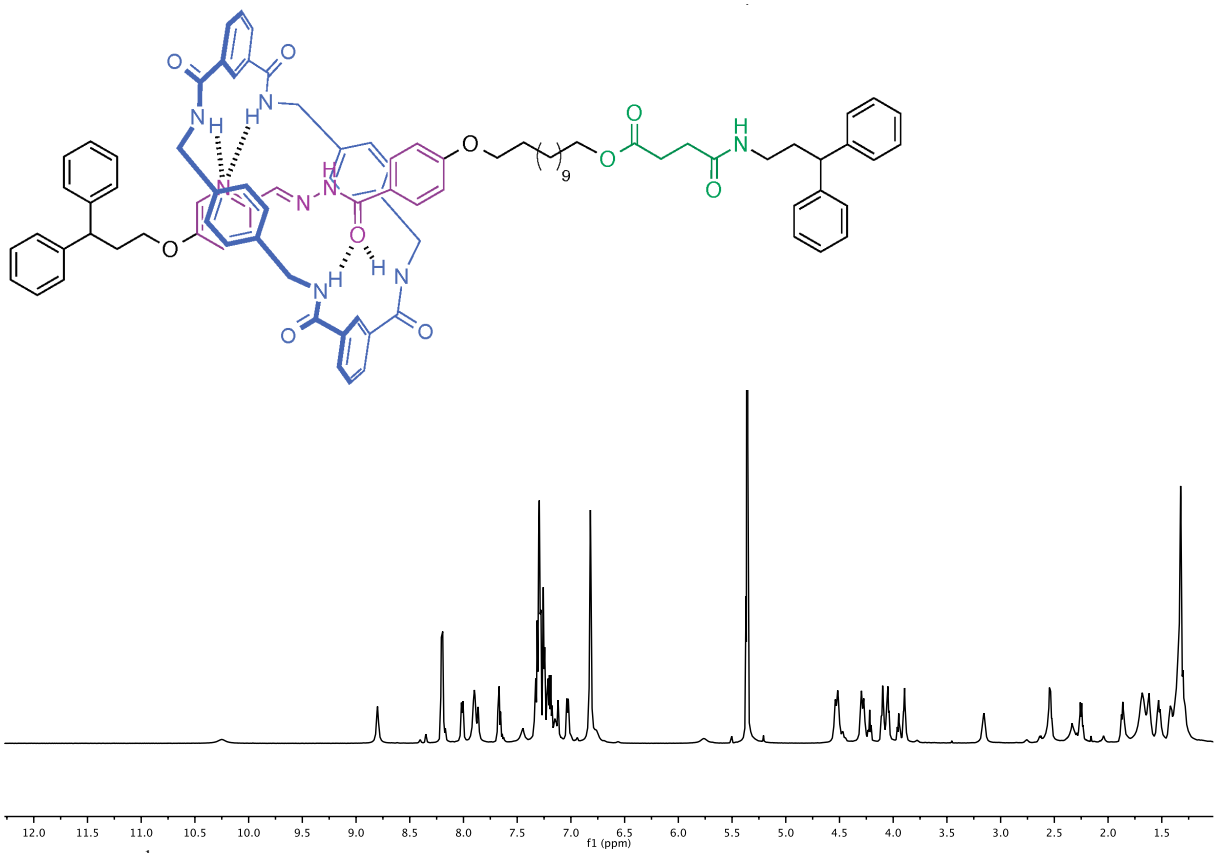


Figure S30: ^{1}H NMR (600 MHz, CD_2Cl_2) spectrum of ***E*-6.**

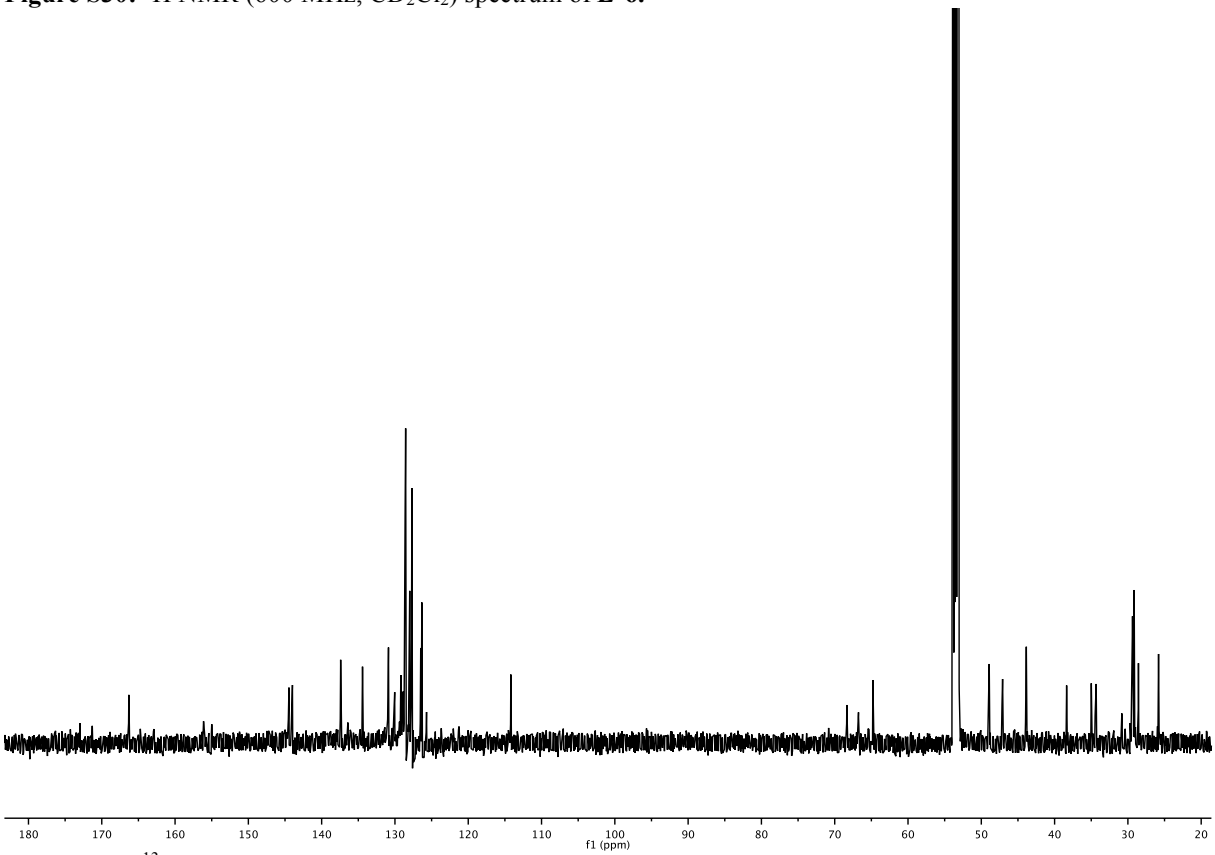
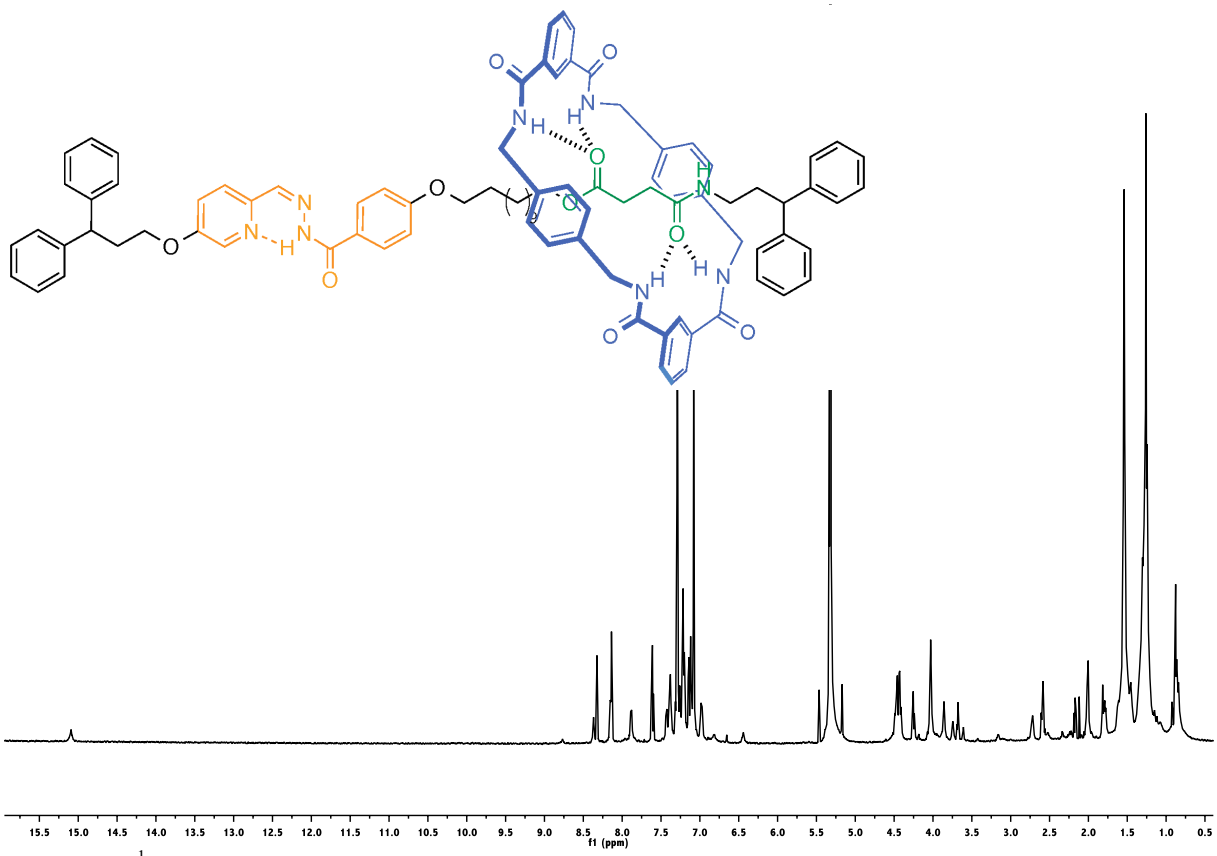


Figure S31: ^{13}C NMR (151 MHz, CD_2Cl_2) spectrum of *E*-**6.**



FigureS32: ^{1}H NMR (600 MHz, CD_2Cl_2) spectrum of *Z*-**6**.

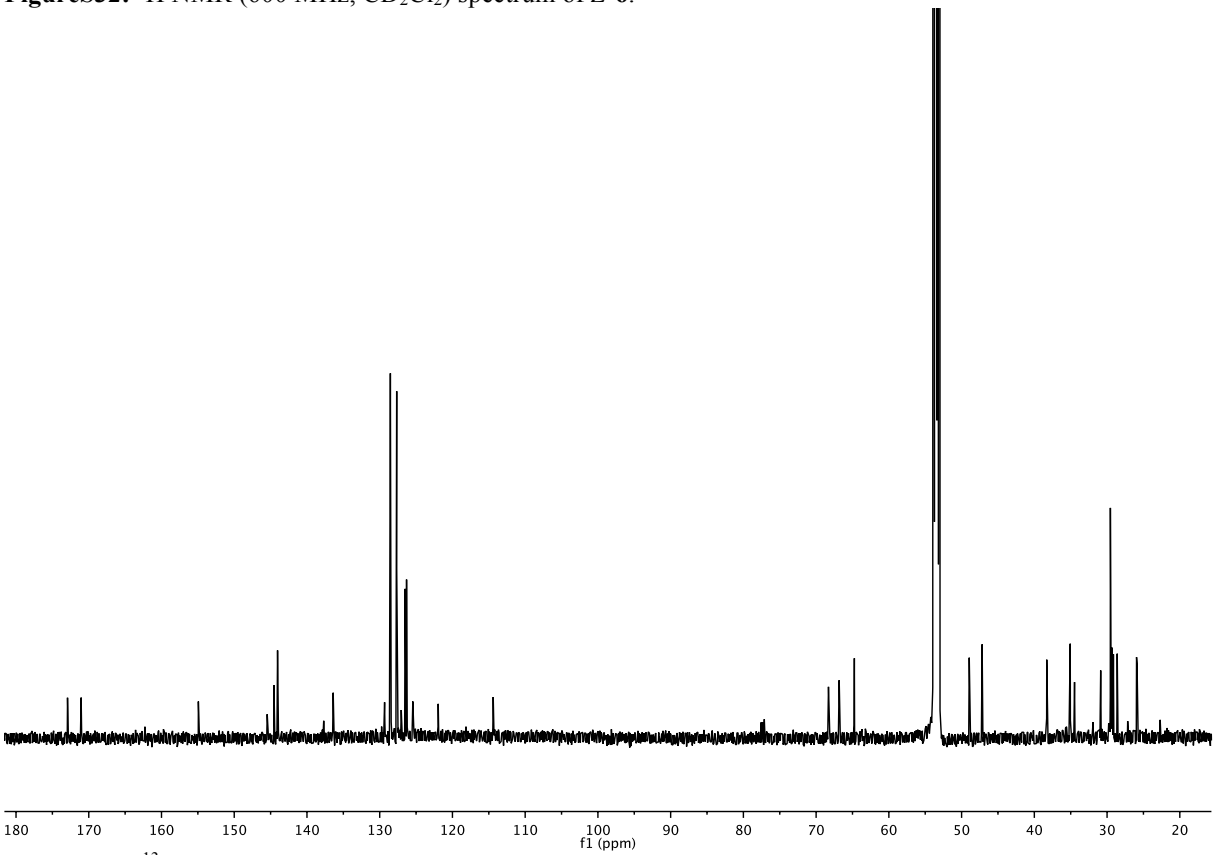


Figure S33: ^{13}C NMR (151 MHz, CD_2Cl_2) spectrum of *Z*-**6**.

3. Stack plot ^{1}H NMR spectra

3.1. Stack Plots for [2]rotaxanes synthesis.

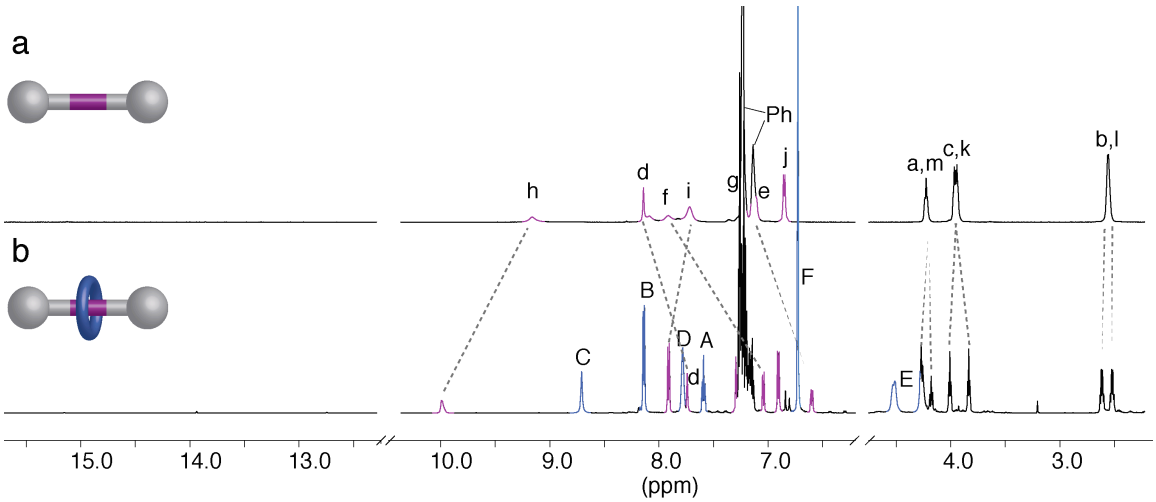


Figure S34: Partial ^{1}H NMR spectra (600 MHz, CD_2Cl_2, 298 K) of: a) Thread *E*-**3**; b) Rotaxane *E*-**4**.

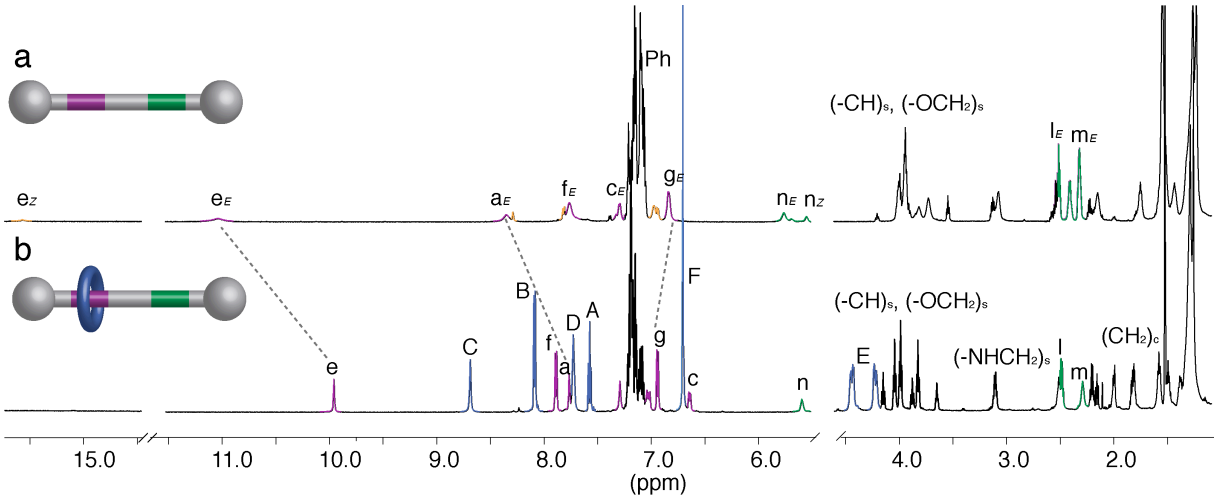


Figure S35: Partial ^{1}H NMR spectra (600 MHz, CD_2Cl_2, 298 K) of: a) Thread *E*-**5**; b) Rotaxane *E*-**6**.

3.2. Stack Plots for isomerization studies.

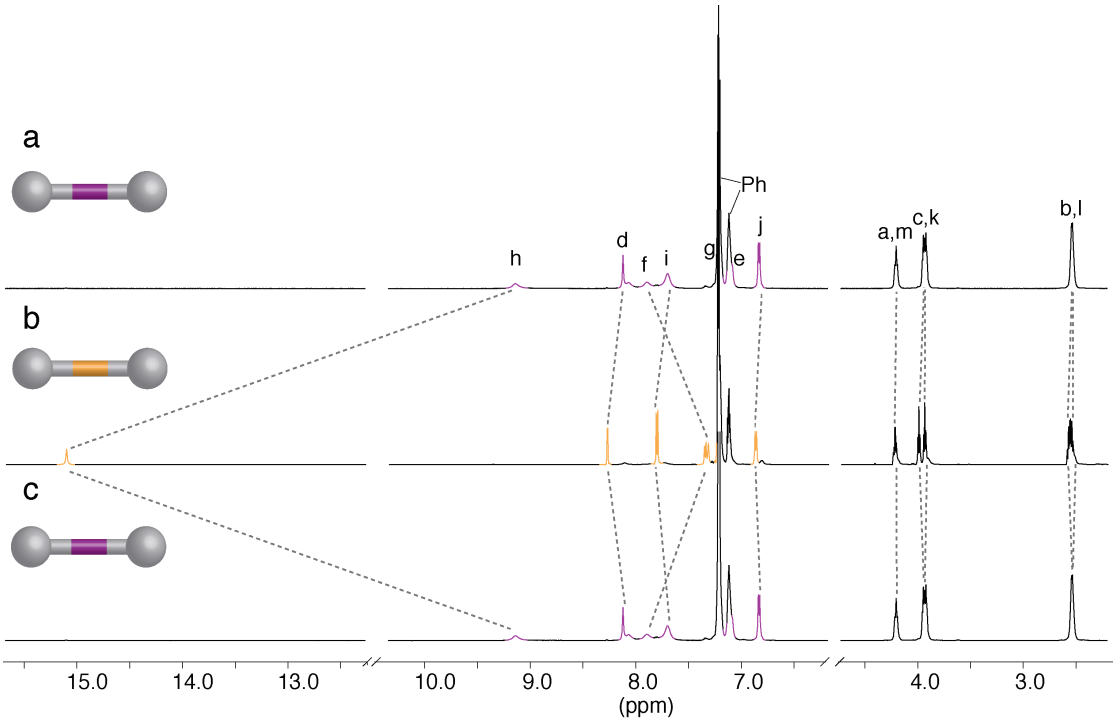


Figure S36: Partial ^{1}H NMR spectra (600 MHz, CD_2Cl_2, 298 K) of: a) Thread *E*-**3**; b) Thread Z-**3** obtained from irradiation of *E*-**3** with 365 nm UV light for 30 min; c) Solution of (b) after 1 h heating at 40 ºC with catalytic amount of TFA (20 mol%), followed by a neutralization with K_2CO_3.

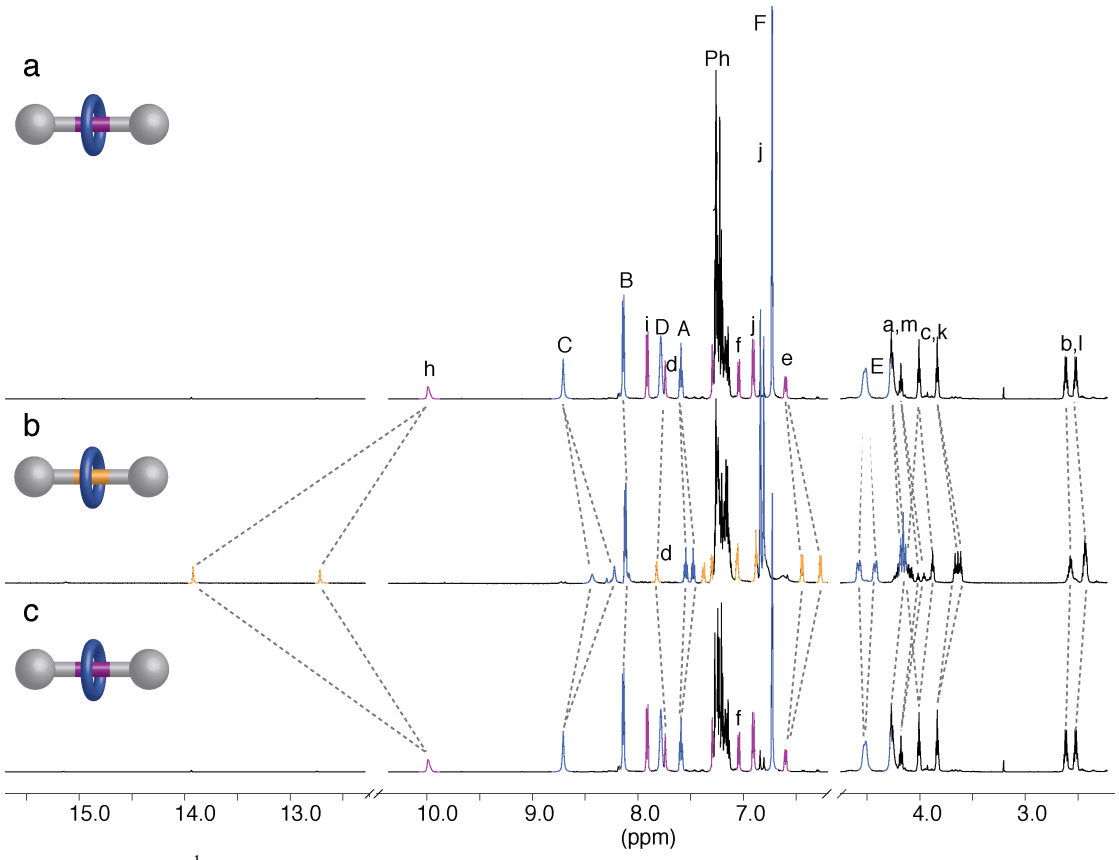


Figure S37: Partial ^{1}H NMR spectra (600 MHz, CD_2Cl_2, 298 K) of: a) Rotaxane *E*-**4**; b) Rotaxane*Z*-**4** obtained from irradiation of *E*-**4** with 365 nm UV light for 1 h; c) Solution of (b) after 2 h heating at 40 ºC with catalytic amount of TFA (20 mol%), followed by a neutralization with K_2CO_3.

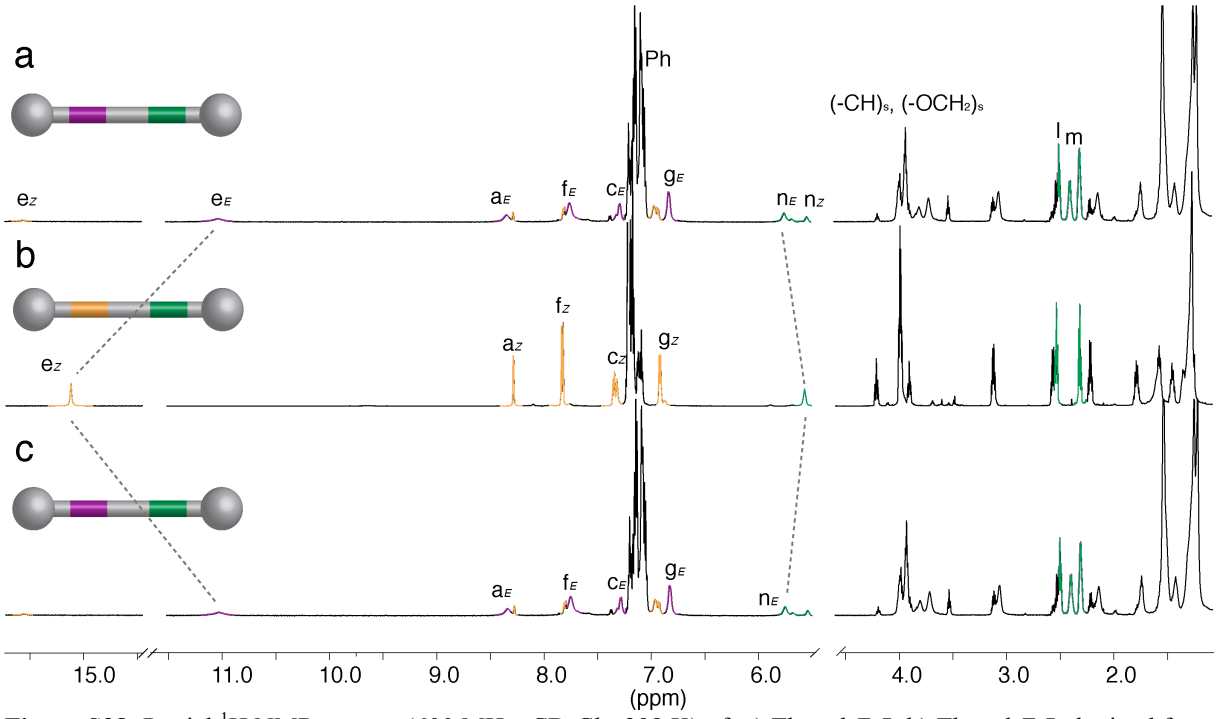


Figure S38: Partial ^{1}H NMR spectra (600 MHz, CD_2Cl_2, 298 K) of: a) Thread *E*-**5**; b) Thread *Z*-**5** obtained from irradiation of *E*-**5** with 365 nm UV light for 1 h; c) Solution of (b) after 2 h heating at 40 ºC with catalytic amount of TFA (20 mol%), followed by a neutralization with K_2CO_3.

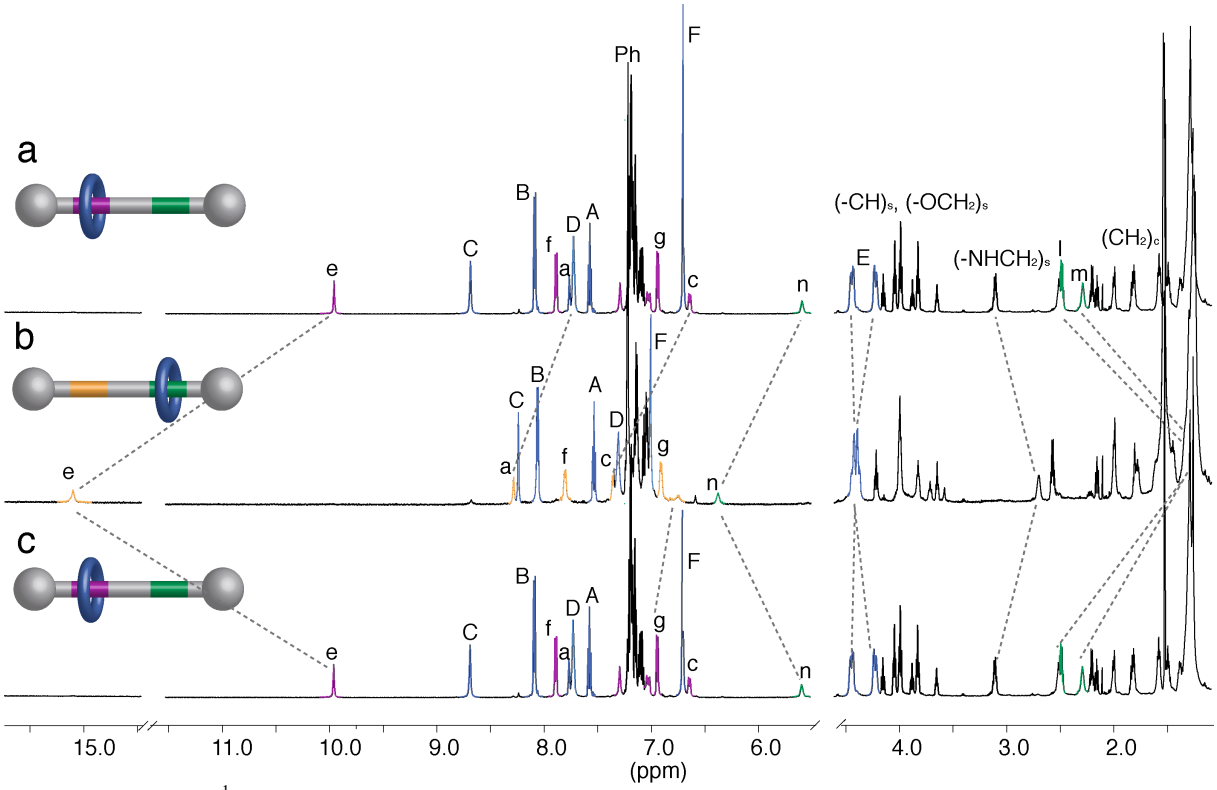


Figure S39: Partial ^{1}H NMR spectra (600 MHz, CD_2Cl_2, 298 K) of: a) Rotaxane *E*-**6**; b) Rotaxane *Z*-**6** obtained from irradiation of *E*-**6** with 365 nm UV light for 2 h; c) Solution of (b) after 2 h heating at 40 ºC with catalytic amount of TFA (20 mol%), followed by a neutralization with K_2CO_3.

3. Mass spectra for rotaxanes (*E*-4 and *E*-6)

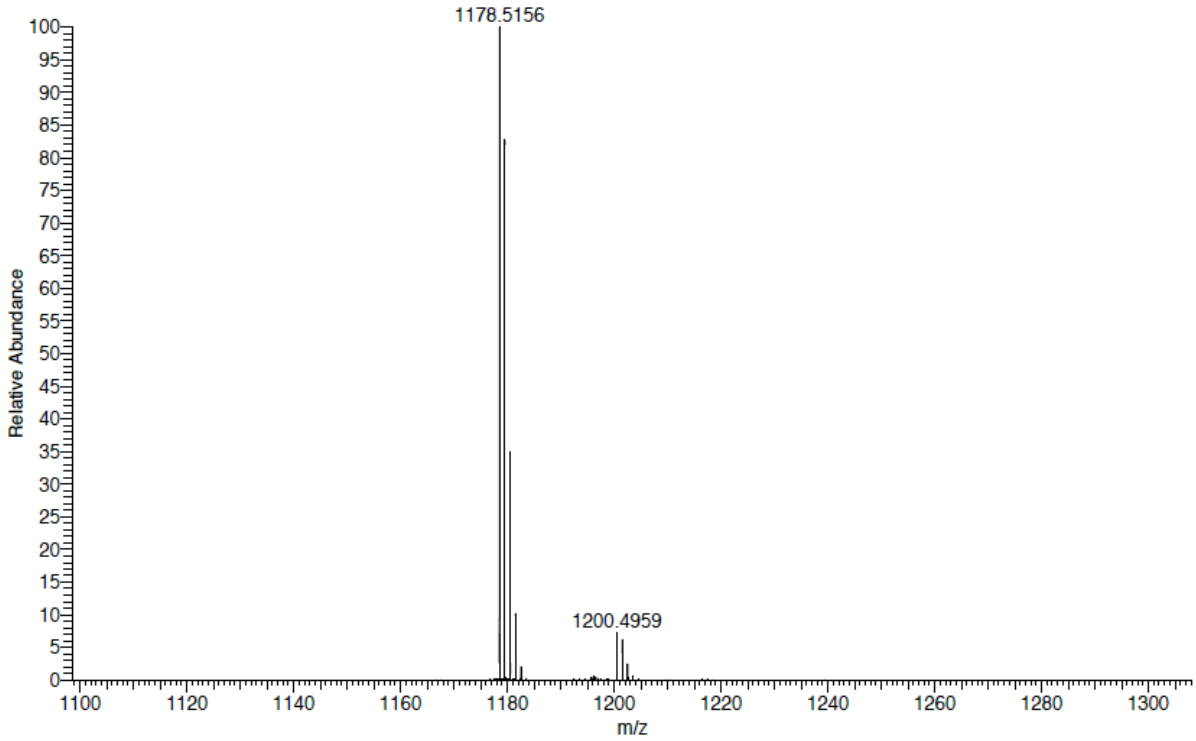


Figure S40: HRMS (ESI$^+$) of *E*-**4**, *m/z* = 1178.5156 $[M+H]^+$ (calcd. 1178.5175 for $C_{75}H_{68}N_7O_7$).

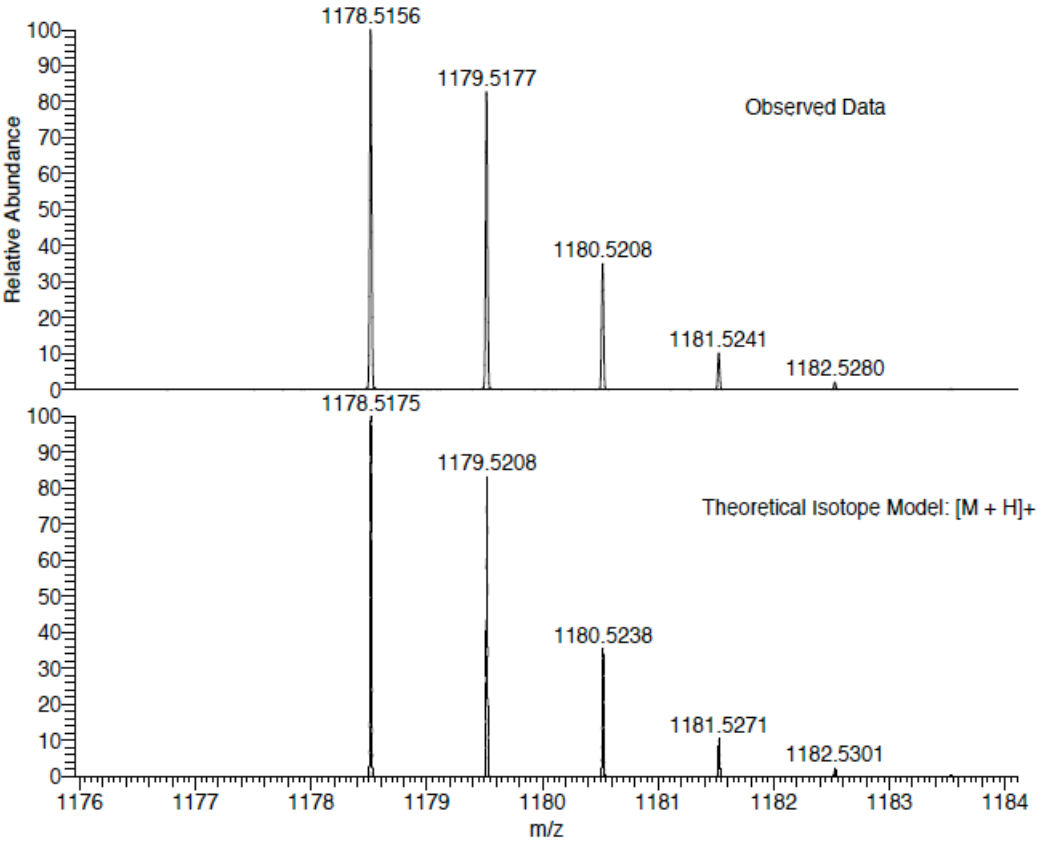


Figure S41: Experimental (top) and theoretical (bottom) isotopic mass distribution for *E*-**4**. HRMS (ESI *m/z* = 1178.5156 $[M+H]^+$ (calcd. 1178.5175 for $C_{75}H_{68}N_7O_7$).

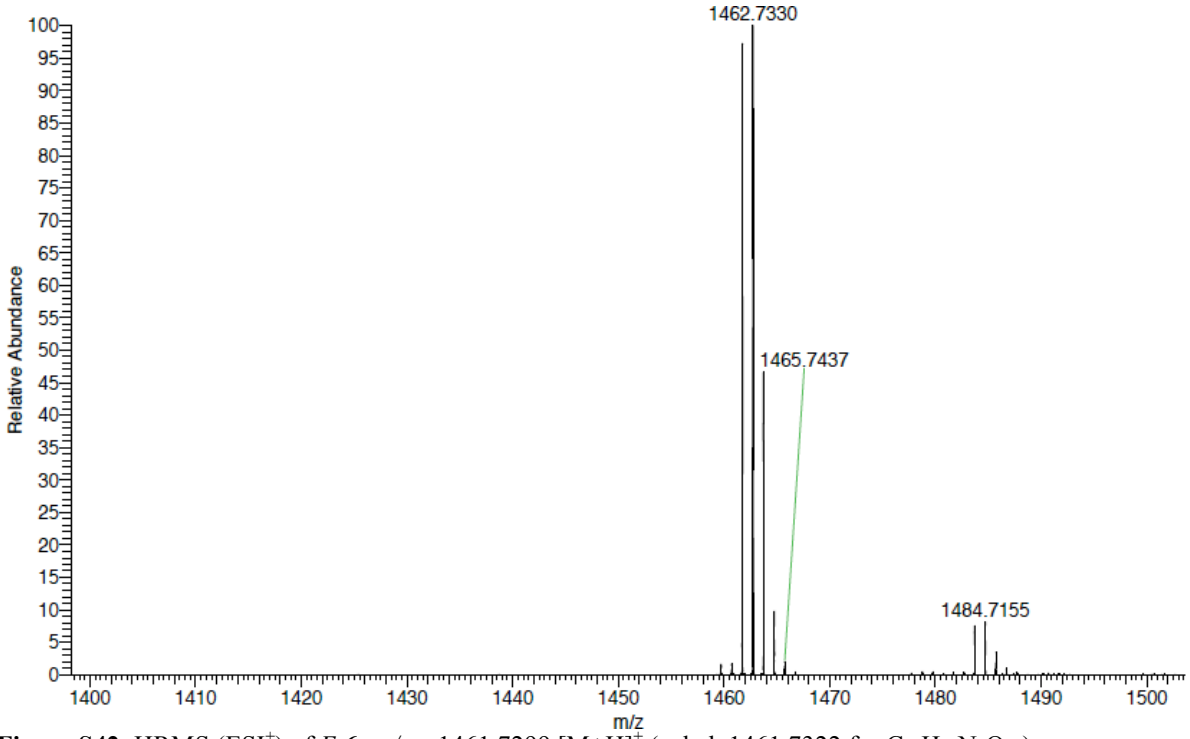


Figure S42: HRMS (ESI$^+$) of *E*-**6**: *m/z* = 1461.7299 $[M+H]^+$ (calcd. 1461.7322 for $C_{91}H_{97}N_8O_{10}$).

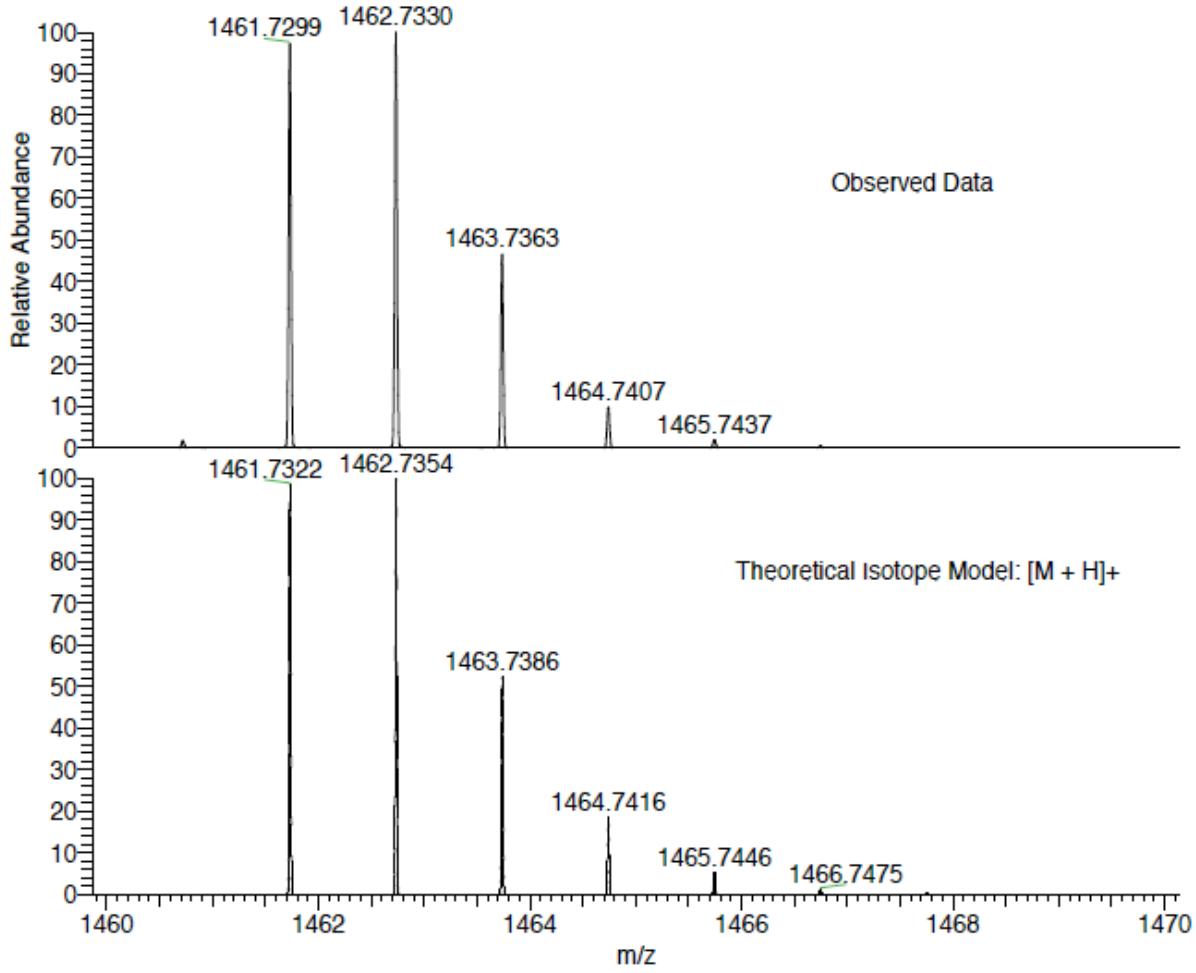


Figure S43: Experimental (top) and theoretical (bottom) isotopic mass distribution for *E*-**6**. HRMS (ESI$^+$): *m/z* = 1461.7299 $[M+H]^+$ (calcd. 1461.7322 for $C_{91}H_{97}N_8O_{10}$).

5. X-Ray Crystal Structure Experimental Details

Single crystals of the *E*- and *Z*-[2]rotaxanes (*E*-**4** and *Z*-**4**) were obtained through slow evaporation of a solution in a mixture of CH_2Cl_2 and acetonitrile. X-ray data for compound *Z*-**4** was collected at a temperature of 150 K on an Agilent Technologies Supernova diffractometer with Mo-Kα radiation, (λ = 0.71073 Å), equipped with an Oxford Cryosystems Cobra nitrogen flow gas system. Data was measured using CrysAlisPro suite of programs. X-ray data for compound *E*-**4** was collected at a temperature of 100 K using a Bruker X8 Prospector diffractometer with Cu-Kα radiation (λ = 1.54184 Å), equipped with an Oxford Cryosystems Cobra nitrogen flow gas system. X-ray data were processed and reduced using CrysAlisPro suite of programs. Absorption correction was performed using empirical methods based upon symmetry-equivalent reflections combined with measurements at different azimuthal angles.[S2] The crystal structures were solved and refined against all F^2 values using SHELXL and Olex 2 suite of programs.[S3] All the atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions refined using idealized geometries (riding model) and assigned fixed isotropic displacement parameters. Hydrogens corresponding to the disordered water and acetonitrile molecules were not included in the model but they were added into the formula. Large parts of the rotaxanes were found disordered and modelled over two positions. Bond distances were restrained using DFIX and SADI command. The atomic displacement parameters (adp) of the ligands, anions and solvent molecules have been restrained using RIGU, EADP and SIMU commands.

Table S1. Crystallographic information for *E*-**4** and *Z*-**4**

	Z-**4**	*E*-**4**
Crystal color	colorless	colorless
Crystal size (mm)	0.3 × 0.15 × 0.15	0.23 × 0.05 × 0.05
Crystal system	Monoclinic	Monoclinic
Space group, *Z*	$P2_1/c$, *4*	C2/c,*8*
a (Å)	10.0686(7)	18.5033(9)
b (Å)	10.337(1)	10.5908(5)
c (Å)	31.789(5)	68.072(2)
α (°)	90	90
β (°)	91.522(6)	91.094(4)
γ (°)	90	90
V (Å^3)	3307.4(5)	13337.2(9)
Density (Mg.m^{-3})	1.270	1.238
Wavelength (Å)	0.71073	1.54184
Temperature (K)	150	100
μ(Mo-Kα) (mm^{-1})	0.083	0.656
2Θ range (°)	6.618 to 50.7	5.194 to 136.494
Reflns collected	13935	53648
Independent reflns (R_{int})	6054 (0.0382)	12116 (0.0605)
L.S. parameters, *p*	603	1042
No. of restraints, *r*	755	753
*R*1 (*F*)[a] *I* > 2.0σ*(I)*	0.1144	0.0921
*wR*2(F^2),[a] all data	0.2836	0.2641
S(F^2),[a] all data	1.106	1.044

[a] $R1(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; [b] $wR^2(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{½}$; [c] $S(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/(n + r - p)]^{½}$

CCDC 1491182 and 1491183 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk

6. Refereces

S1. Altieri, A.; Bottari, G.; Dehez, F.; Leigh, D.; Wong, J.; Zerbetto, F. *Angew. Chem., Int. Ed.* **2013**, *42*, 2296.

S2. (a) Sheldrick, G. M. *SADABS*, empirical absorption correction program based upon the method of Blessing. (b) Krause, L.; Herbst-Irmer, R.; Sheldrick, G. M.; Stalke, D. *J. Appl. Cryst.* **2015**, *48*. (c) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33.

S3. (a) Sheldrick. G. M. *Acta Crystallogr.* **2015**, *C71*, 3. (b) Dolomanov, O. V.; Bourhis, R. J.; Gildea L. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339.