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SUPPORTING INFORMATION

Mechanical bonding activation in rotaxane-based organocatalysts

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1. General Experimental Section

Unless stated otherwise, all reagents were purchased from Aldrich Chemicals and used without further purification. HPLC grade solvents (Scharlab) were nitrogen saturated and were dried and deoxygenated using an Innovative Technology Inc. Pure-Solv 400 Solvent Purification System. Column chromatography was carried out using silica gel (60 Å, 70-200 µm, SDS) as stationary phase, and TLC was performed on precoated silica gel on aluminium cards (0.25 mm thick, with fluorescent indicator 254 nm, Fluka) and observed under UV light. All melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker Avance 300, 400 and 600 MHz instruments. ^{1}H NMR chemical shifts are reported relative to Me_4Si and were referenced via residual proton resonances of the corresponding deuterated solvent, whereas ^{13}C NMR spectra are reported relative to Me_4Si using the carbon signals of the deuterated solvent. Signals in the ^{1}H and ^{13}C NMR spectra of the synthesized compounds were assigned with the aid of DEPT, APT, or two-dimensional NMR experiments (COSY, HMQC and HMBC). Abbreviations of coupling patterns are as follows: br, broad; s, singlet; d, doublet; t, triplet; q, quadruplet; qui, quintuplet; m, multiplet. The deuterated solvent $CDCl_3$ was dried over $CaCl_2$ and stored with molecular sieves prior to use. Coupling constants (*J*) are expressed in Hz. High-resolution mass spectra (HRMS) were obtained using a time-of-flight (TOF) instrument equipped with electrospray ionization (ESI).

Abbreviation list:

$(Boc)_2O$: Di-*tert*-butyl dicarbonate

EDCI·HCl: *N*-(3-dimethylaminopropyl)-*N*'-ethylcarbodiimide hydrochloride

DIPEA: *N*,*N*-diisopropylethylamine

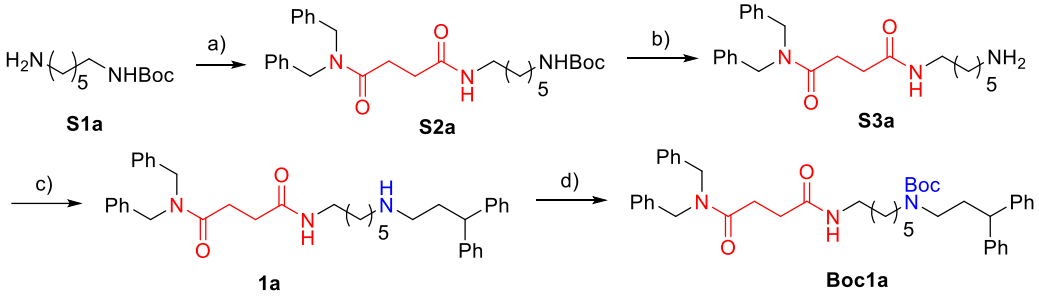
DMAP: dimethylaminopyridine

HOBt: hydroxybenzotriazole

TFA: trifluoroacetic acid

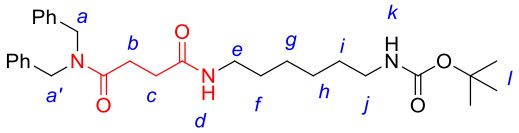
TLC: thin layer chromatography

2. Synthesis of thread 1a and thread Boc1a



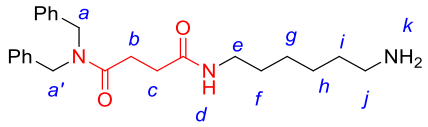
Scheme S2. *Reactions conditions*: a) 4-(dibenzylamino)-4-oxobutanoic acid, HOBt, EDCI·HCl, DIPEA, CH_2Cl_2, 0 ºC to 25 °C, 24 h; b) TFA, CH_2Cl_2, 25 °C, overnight; c) 3,3-diphenylpropanal, $NaBH(OAc)_3$, CH_2Cl_2, 0ºC to 25 °C, 12 h; d) $(Boc)_2O$, DMAP, CH_2Cl_2, 25 °C, overnight.

Synthesis of tert-butyl (6-(4-(dibenzylamino)-4-oxobutanamido)hexyl)carbamate (S2a)



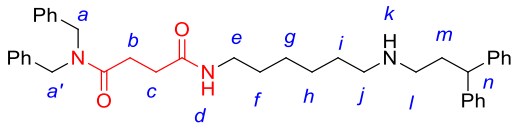
To a solution of 4-(dibenzylamino)-4-oxobutanoic acid (5.1 g, 17.3 mmol) in CH_2Cl_2 (90 mL) under N_2 atmosphere, cooled to 5 °C, was added HOBt (2.8 g, 20.8 mmol), EDCI·HCl (3.2 g, 20.8 mmol) and DIPEA (2.7 g, 20.8 mmol), and the mixture was stirred at room temperature for 30 min. After this time, a solution of **S1a** (4.5 g, 20.8 mmol) in CH_2Cl_2 (20 mL) was added dropwise and the mixture was stirred overnight. After this time the reaction mixture was washed with HCl 1M (2 × 50 mL), saturated $NaHCO_3$ (2 × 50 mL) and brine (2 × 50 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered and concentrated to dryness. The resulting residue was subjected to column chromatography on silica gel using a hexane/AcOEt (1/1) solution as eluent, to give compound **S2a** as a white solid (3.16 g, 37 %); mp 105-107 ºC; **^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) δ:** 7.37 – 7.24 (m, 6H, H_{Ph}), 7.18 – 7.13 (m, 4H, H_{Ph}), 6.37 (bs, 1H, H_d), 4.61 (bs, 1H, H_k), 4.58 (s, 2H, H_a), 4.48 (s, 2H, $H_{a'}$), 3.20 (m, 2H, H_e), 3.06 (m, 2H, H_j), 2.77 (t, J = 6.4 Hz, 2H, H_c), 2.57 (t, J = 6.4 Hz, 2H, H_b), 1.49 – 1.39 (m, 4H, H_{f+i}), 1.42 (s, 9H, H_l), 1.31 – 1.27 (m, 4H, H_{g+h}) ppm; **^{13}C-NMR (75 MHz, $CDCl_3$, 298 K) δ:** 172.8 (C=O), 172.3 (C=O), 156.1 (C=O), 137.1 (C), 136.3 (C), 129.0 (CH), 128.7 (CH), 128.1 (CH), 127.7 (CH), 127.5 (CH), 126.6 (CH), 79.0 (C), 50.1 (CH_2), 48.5 (CH_2), 40.4 (CH_2), 39.4 (CH_2), 31.7 (CH_2), 30.0 (CH_2), 29.5 (CH_2), 29.0 (CH_2), 28.5 (CH_3), 26.5 (CH_2), 26.4 (CH_2) ppm; **HRMS (ESI)** calcd. for $C_{29}H_{42}N_3O_4$ $[M + H]^+$ 496.3170, found 496.3162; **IR (neat) ν:** 3345.9, 2926.5, 1679.7, 1669.1, 1626.7, 1166.7, 698.1 cm^{-1}.

Synthesis of N^1-(6-aminohexyl)-N^4,N^4-dibenzylsuccinamide (S3a)



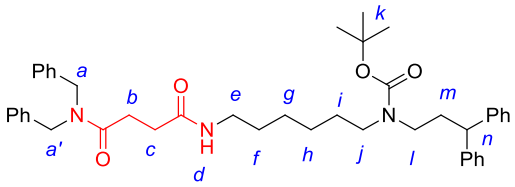
To a solution of compound **S2a** (3.20 g, 6.46 mmol) in CH_2Cl_2 (50 mL) was added TFA (5 mL, 64.6 mmol). The reaction was stirred at room temperature overnight. After this time the solvent and excess of TFA were removed under vacuum. The resulting residue was diluted CH_2Cl_2 (50 mL) and washed with a saturated solution of aqueous $NaHCO_3$ (2 x 40 mL) and brine (2 x 40 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure, to give the title product **S3a** as a yellow oil, which was subjected to the next reaction step without further purification (2.53 g, 99 %).

Synthesis of N^1-(6-aminohexyl)-N^4,N^4-dibenzylsuccinamide (1a)



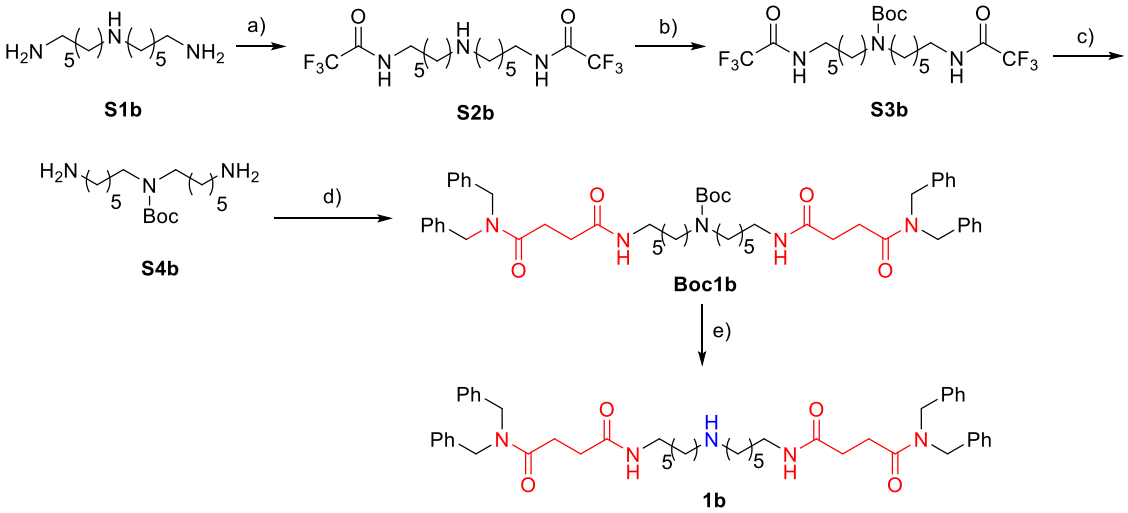
To a solution of amine **S3a** (0.50 g, 1.27 mmol) and 3,3-diphenylpropanal (0.27 g, 1.27 mmol) in dichloroethane (25 mL) was added $NaBH(OAc)_3$ (0.38, 1.78 mmol). The reaction was stirred at room temperature overnight. After this time a saturated solution of $NaHCO_3$ (40 mL) was added and the aqueous phase washed with $CHCl_3$ (2 x 20 mL). The combined organic phase was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The resulting residue was subjected to column chromatography on silica gel using a $CHCl_3$/MeOH (10/1) solution as eluent, to give compound **1a** as a yellow oil (187 mg, 25 %); **^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ:** 7.35 – 7.15 (m, 20H, H_{Ph}), 6.83 (t, J = 5.5 Hz, 1H, H_d), 4.54 (s, 2H, H_a), 4.51 (s, 2H, $H_{a'}$), 4.00 (t, J = 7.9 Hz, 1H, H_n), 3.18 (m, 2H, H_e), 2.77 – 2.70 (m, 6H, H_{c+j+l}), 2.62 – 2.58 (m, 4H, H_{b+m}), 1.66 (m, 2H, H_f), 1.44 (m, 2H, H_i), 1.26 – 1.24 (m, 5H, H_{g+h+k}) ppm; **^{13}C-NMR (100 MHz, $CDCl_3$, 298 K) δ:** 174.0 (C=O), 173.1 (C=O), 144.0 (C), 137.8 (C), 137.0 (C), 129.9 (CH), 129.6 (CH), 129.5 (CH), 128.6 (CH), 128.5 (CH), 128.3 (CH), 127.5 (CH), 127.4 (CH), 51.2 (CH_2), 49.5 (CH), 49.4 (CH_2), 48.6 (CH_2), 47.8 (CH_2), 40.1 (CH_2), 32.6 (CH_2), 32.3 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 26.9 (CH_2), 26.7 (CH_2), 26.7 (CH_2) ppm; **HRMS (ESI)** calcd. for $C_{39}H_{48}N_3O_2$ $[M + H]^+$ 590.3741, found 590.3734; **IR (neat) ν:** 3307.3, 2930.3, 1631.5, 698.1 cm^{-1}.

Synthesis of N^1-(6-aminohexyl)-N^4,N^4-dibenzylsuccinamide (Boc1a)



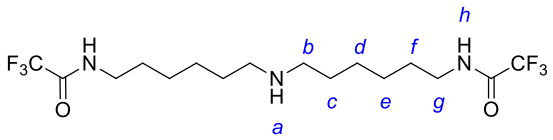
To a solution of thread **1a** (0.10 g, 0.17 mmol) in CH_2Cl_2 (7 mL) was added DMAP (20 mg, 0.17 mmol) and $(Boc)_2O$ (190 mg, 0.85 mmol). The reaction was stirred at room temperature for 24 h. After this time the solvent was removed under reduced pressure. The resulting residue was subjected to column chromatography on silica gel using a $CHCl_3$/MeOH (10/1) solution as eluent, to give compound **Boc1a** as a yellow oil (107 mg, 92 %); **^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) δ:** 7.38 – 7.15 (m, 20H, H_{Ph}), 6.31 (bs, 1H, H_d), 4.61 (s, 2H, H_a), 4.49 (s, 2H, $H_{a'}$), 3.89 (t, J = 6.1 Hz, 1H, H_n), 3.21 (m, 2H, H_e), 3.10 (m, 4H, H_{j+l}), 2.79 (t, J = 6.5 Hz, 2H, H_c), 2.59 (t, J = 6.5 Hz, 2H, H_b), 2.28 (m, 2H, H_m), 1.48 – 1.42 (m, 4H, H_{i+f}), 1.42 (s, 9H, H_k), 1.32 – 1.21 (m, 4H, H_{g+h}) ppm; **^{13}C-NMR (75 MHz, $CDCl_3$, 298 K) δ:** 172.8 (C=O), 172.3 (C=O), 155.6 (C=O), 144.5 (C), 137.2 (C), 136.3 (C), 129.0 (CH), 128.7 (CH), 128.6 (CH), 128.1 (CH), 127.8 (CH), 127.7 (CH), 127.5 (CH), 126.6 (CH), 126.3 (CH), 79.2 (C), 50.0 (CH_2), 49.2 (CH), 48.5 (CH_2), 46.8 (CH_2), 46.2 (CH_2), 39.4 (CH_2), 34.3 (CH_2), 31.7 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.1 (CH_2), 28.6 (CH_3), 28.2 (CH_2), 26.5 (CH_2) ppm; **HRMS (ESI)** calcd. for $C_{44}H_{56}N_3O_4$ [M + H]$^+$ 690.4265, found 690.4267; **IR (neat) ν:** 3333.4, 2926.5, 1679.7, 1642.1, 1162.9, 698.1 cm^{-1}.

3. Synthesis of thread Boc1b and thread 1b



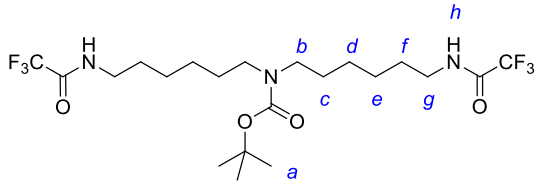
Scheme S1. *Reactions conditions*: a) CF_3CO_2Et, H_2O, CH_3CN, 10 °C to 25 °C, overnight; b) $(Boc)_2O$, THF, 0 °C to 25 °C, overnight; c) NaOH, H_2O, MeOH, 10 °C to 25 °C; d) 4-(dibenzylamino)-4-oxobutanoic acid, EDCI·HCl, DIPEA, HOBt, CH_2Cl_2, 0 °C to 25 °C, overnight; e) TFA, CH_2Cl_2, 25 °C, overnight.

Synthesis of bis(trifluoroacetamidohexyl)amine (S2b)



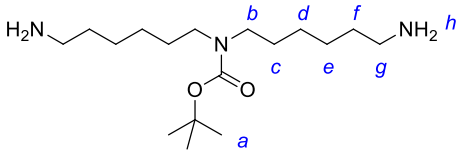
To a stirred solution of bis(hexamethylene)triamine **S1b** (2.81 g, 13 mmol) in acetonitrile (30 mL) was added ethyl trifluoroacetate (5.41 mL, 45.5 mmol) and water (0.30 mL). After the addition, the mixture was refluxed for 20 h. The solvents were removed by evaporation, affording the titled compound **S2b** as a yellow oil, which was subjected to the next reaction step without further purification; **^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) δ:** 6.56 (s, 2H, H_h), 3.39-3.33 (m, 4H, H_g), 2.61 (t, *J* = 7.12 Hz, 4H, H_b), 1.64 – 1.47 (m, 8H, H_{c+f}), 1.40 – 1.31 (m, 8H, H_{d+e}), 1.25 (s, 1H, H_a) ppm; **^{13}C-NMR (75 MHz, $CDCl_3$, 298 K) δ:** 158.3 (q, *J* = 36.8 Hz, C=O), 114.3 (q, *J* = 288.0 Hz, CF_3), 49.6 (CH_2), 39.9 (CH_2), 29.6 (CH_2), 28.9 (CH_2), 26.7 (CH_2), 26.5 (CH_2) ppm; **^{19}F-NMR (282 MHz, $CDCl_3$, 298 K): δ** = - 75.91 ppm; **HRMS (ESI)** calcd. for $C_{16}H_{28}F_6N_3O_2$ $[M + H]^+$ 408.2085, found 408.2071; **IR (neat) ν:** 3196.4, 3075.9, 1669.1, 1149.4 cm^{-1}.

Synthesis of tert-butoxycarbonyl-bis(trifluoroacetamidohexyl)amine (S3b)



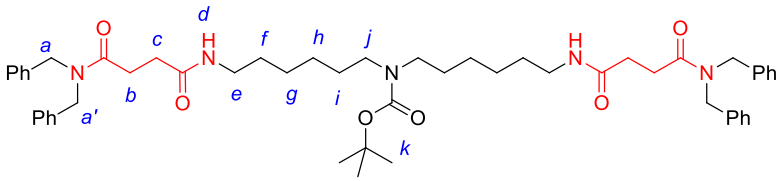
Under nitrogen atmosphere, the crude residue of **S2b** (5.29 g, 13 mmol) in triethylamine (36 mL) was cooled to 0 °C, and a solution of $(Boc)_2O$ (3.12 g, 14.3 mmol) in THF (6.5 mL) was added. The reaction was stirred overnight at room temperature. After this time, the solution was quenched in water (80 mL) and extracted with AcOEt (3 × 50 mL). The combined organic extracts were washed with water and dried over anhydrous $MgSO_4$, filtered and the solvent removed under vacuum. The resulting residue was subjected to column chromatography on silica gel using a $CHCl_3$/MeOH (97:3) solution as eluent, to give the compound **S3b** as a yellow oil (4.94 g, 75 %; for 2 reaction steps); **^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ** 6.61 (bs, 2H, H_h), 3.36 - 3.31 (m, 4H, H_g), 3.14 (bs, 4H, H_b), 1.58 (qui, *J* = 6.9 Hz, 4H, H_f), 1.51 (qui, *J* = 7.2 Hz, 4H, H_c), 1.43 (s, 9H, H_a), 1.41 - 1.34 (m, 4H, H_e), 1.33 - 1.25 (m, 4H, H_d) ppm; **^{13}C-NMR (100 MHz, $CDCl_3$, 298 K) δ**: 158.3 (q, *J* = 36.8 Hz, C=O), 156.7 (C=O), 116.8 (q, *J* = 287.6 Hz, CF_3), 80.1 (C), 47.7 (CH_2), 46.9 (CH_2), 40.7 (CH_2), 40.1 (CH_2), 29.18 (CH_3), 27.2 (CH_2), 26.3 (CH_2) ppm; **^{19}F-NMR (188 MHz, $CDCl_3$, 298K) δ**: -75.92 (s) ppm; **HRMS (ESI)** calcd. for $C_{21}H_{36}F_6N_3O_4$ $[M + H]^+$ 508.2610, found 508.2615; **IR (neat) ν:** 3185.8, 1675.8, 1569.8, 1128.2 cm^{-1}.

Synthesis of *tert*-butoxycarbonyl-bis(6-aminohexyl)amine (S4b)



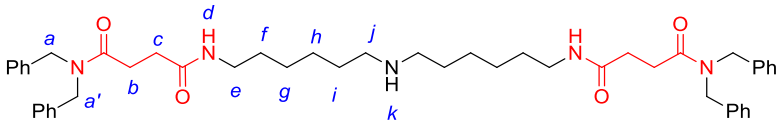
To a solution of **S3b** (4.57 g, 9 mmol) in MeOH (120 mL) at 0 °C was added dropwise a 0.2 N NaOH solution (100 mL, 20 mmol), and the mixture was warmed to room temperature while stirred overnight. After removal of MeOH in vacuo, the aqueous suspension was extracted with a mixture of $CHCl_3$/MeOH (9/1; 5 × 30 mL). The combined organic extracts were dried over anhydrous $MgSO_4$, filtered and concentrated to dryness, affording **S4b** as a colourless oil (2.69 g, 95%); **^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ**: 3.11 (bs, 4H, H_b), 2.66 (t, *J* = 7.01 Hz, 4H, H_g), 1.75 (s, 4H, H_h), 1.42 (s, 9H, H_a), 1.51 - 1.39 (m, 8H, H_{c+f}), 1.35 - 1.22 (m, 8H, H_{d+e}) ppm; **^{13}C-NMR (100 MHz, $CDCl_3$, 298 K) δ**: 156.5 (C=O), 79.8 (C), 47.8 (CH_2), 42.9 (CH_2), 34.4 (CH_2), 29.3 (CH_3), 29.1 (CH_2), 27.6 (CH_2), 27.5 (CH_2) ppm; **HRMS (ESI)** calcd. for $C_{17}H_{38}N_3O_2$ $[M + H]^+$ 316.2964, found 316.2960; **IR (neat) ν:** 3367.1, 1679.7 cm^{-1}.

Synthesis of thread Boc1b



To a solution of 4-(dibenzylamino)-4-oxobutanoic acid[1] (3.92 g, 13.2 mmol) in CH_2Cl_2 (20 mL), cooled to 5 °C, was added HOBt (1.82 g, 13.2 mmol), EDCI·HCl (2.05 g, 13.2 mmol) and DIPEA (2.05 g, 13.2 mmol), and the mixture was stirred at room temperature for 30 min. After this time, a solution of **S4b** (1.89 g, 6 mmol) in CH_2Cl_2 (8 mL) was added dropwise and the mixture was stirred overnight. The reaction mixture was diluted with CH_2Cl_2 (20 mL) and washed with HCl 1M (1 × 15 mL), saturated $NaHCO_3$ (1 × 15 mL) and brine (1 × 15 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered and concentrated to dryness. The resulting residue was subjected to column chromatography on silica gel using a $CHCl_3$/MeOH (40/1 to 20/1) solution as eluent, to give compound **Boc1b** as a yellow oil (3.72 g, 71 %); **^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ:** 7.40 - 7.29 (m, 12H, H_{Ph}), 7.23 - 7.11 (m, 8H, H_{Ph}), 6.30 (bs, 2H, H_d), 4.60 (s, 4H, H_a), 4.49 (s, 4H, $H_{a'}$), 3.25 - 3.20 (m, 4H, H_e), 3.17 – 3.05 (m, 4H, H_j), 2.79 (t, *J*= 6.5 Hz, 4H, H_b), 2.59 (t, *J*= 6.5 Hz, H_c), 1.56 - 1.40 (m, 8H, H_{f+i}), 1.44 (s, 9H, H_k), 1.39 - 1.20 (m, 8H, H_{g+h}) ppm; **^{13}C-NMR (100 MHz, $CDCl_3$, 298 K) δ:** 173.6 (C=O), 173.1 (C=O), 156.5 (C=O), 137.9 (C), 137.1 (C), 129.8 (CH), 129.5 (CH), 128.9 (CH), 128.5 (CH), 128.3 (CH), 127.4 (CH), 79.8 (C), 50.8 (CH_2), 49.3 (CH_2), 47.9 (CH_2), 47.6 (CH_2), 40.3 (CH_2), 32.5 (CH_2), 30.4 (CH_2), 29.8 (CH_2), 29.4 (CH_3), 29.0 (CH_2), 27.4 (CH_2) ppm; **HRMS (ESI)** calcd. for $C_{53}H_{72}N_5O_6$ $[M + H]^+$ 874.5482, found 874.5501; **IR (neat) ν:** 3314.1, 2924.5, 1635.3, 1545.7, 1420.3 cm^{-1}.

Synthesis of thread 1b



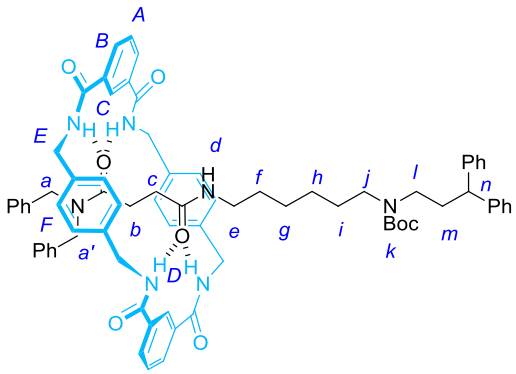
A solution of thread **Boc1b** (95 mg, 0.11 mmol) and TFA (114 mg, 1 mmol) in CH_2Cl_2 (2.5 mL) were stirred overnight at room temperature. The reaction mixture was washed with saturated $NaHCO_3$, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure, to give the compound **1b** as a yellow oil (70 mg, 80 %); **^{1}H-NMR (400 MHz, $CDCl_3$, 294 K) δ:** 7.39 - 7.27 (m, 12H, H_{Ph}), 7.20 - 7.13 (m, 8H, H_{Ph}), 6.54 (t, *J* = 6.54 Hz, 2H, H_d), 4.58 (s, 4H, H_a), 4.51 (s, 4H, $H_{a'}$), 3.27 - 3.18 (m, 4H, H_e), 2.78 (t, *J* = 6.4 Hz, 4H, H_c), 2.68 (t, *J* = 7.3 Hz, 4H, H_j), 2.58 (t, *J* = 6.4 Hz, 4H, H_b), 1.60 - 1.43 (m, 9H, H_{f+i+k}), 1.37 - 1.28 (m, 8H, H_{g+h}) ppm; **^{13}C-NMR (100 MHz, $CDCl_3$, 295 K) δ:** 173.8 (C=O), 173.1 (C=O), 137.9 (C), 137.0 (C), 129.9 (CH), 129.5 (CH), 128.8 (CH), 128.6 (CH), 128.3 (CH), 127.4 (CH), 51.0 (CH_2), 49.8 (CH_2), 49.4 (CH_2), 40.3 (CH_2), 32.3 (CH_2), 29.9 (CH_2), 29.7 (CH_2), 28.7 (CH_2), 27.4 (CH_2), 27.3 (CH_2) ppm; **HRMS (ESI)** calcd for $C_{48}H_{64}N_5O_4$ $[M + H]^+$ 774.4958, found 774.4961; **IR (neat) ν:** 3452.3, 3284.2, 1626.7, 1545.7, 1441.5 cm^{-1}.

4. General procedure for the preparation of the rotaxanes

Rotaxane formation: Thread **Boc1** (1 equiv.) and Et_3N (16 equiv.) in anhydrous $CHCl_3$ (300 mL) were stirred vigorously whilst solutions of *p*-xylylenediamine (4 equiv.) in anhydrous $CHCl_3$ (20 mL) and the corresponding acid dichloride (4 equiv.) in anhydrous $CHCl_3$ (20 mL) were simultaneously added for 4 h using motor-driven syringe pumps. After a further 4 h, the resulting suspension was filtered through a Celite® pad, washed with water (2 x 50 mL), an aqueous solution of HCl 1N (2 x 50 mL), a saturated solution of $NaHCO_3$ (2 x 50 mL) and brine (2 x 50 mL). The organic phase was dried over $MgSO_4$ and the solvent removed under reduced pressure. The resulting solid was subjected to column chromatography (silica gel) to yield unconsumed thread **Boc1**, the [2]rotaxane **Boc2** and, in some cases, the [3]rotaxane **Boc3**.

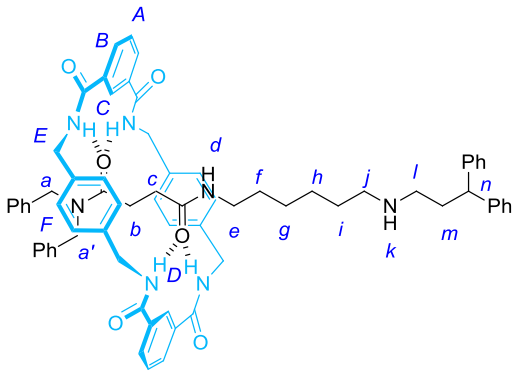
Rotaxane deprotection: Solution of the corresponding rotaxane **Boc2** or **Boc3** (1 equiv.) in CH_2Cl_2 was reacted in the presence of TFA (10 equiv.) at room temperature for 12 h. After this time the solution was diluted with CH_2Cl_2 (20 mL) and extract with a saturated solution of $NaHCO_3$ (3 x 20 mL). The organic phase was dried over $MgSO_4$, filtered and the solvent removed under reduced pressure, to afford the desired unprotected rotaxane **2** or **3**.

Synthesis of [2]rotaxane Boc2a



Rotaxane **Boc2a** was obtained following the described method from thread **Boc1a** (320 mg, 0.46 mmol), *p*-xylylendiamine (0.5 g, 3.71 mmol) and isophthaloyl dichloride (0.75 g, 3.71 mmol). The solid crude was subjected to column chromatography on silica gel using a $CHCl_3$/acetone (9/1) mixture as eluent to give the title product as a white solid (**Boc2a**, 74 mg, 13 %); mp 105-107 ºC. **^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) δ:** 8.45 (s, 2H, H_C), 8.21 (dd, *J* = 7.8 Hz, *J* = 1.3 Hz, 4H, H_B), 7.56 (t, *J* = 7.8 Hz, 2H, H_A), 7.52 – 7.48 (m, 4H, H_D), 7.33 – 7.04 (m, 18H, H_{Ph}), 6.96 (s, 8H, H_F), 6.75 – 6.65 (m, 3H, H_{Ph+d}), 4.41 (m, 9H, H_{E+a}), 4.13 (s, 2H, $H_{a'}$), 3.83 (m, 1H, H_n), 3.11 – 3.05 (m, 6H, H_{e+j+l}), 2.27 – 2.19 (m, 2H, H_m), 1.48 – 1.18 (m, 8H, $H_{f+g+h+i}$), 1.34 (s, 9H, H_k), 1.12 – 0.97 (m, 4H, H_{b+c}) ppm; **^{13}C-NMR (75 MHz, $CDCl_3$, 298 K) δ:** 173.5 (C=O), 173.3 (C=O), 166.0 (C=O), 155.7 (C=O), 144.4 (C), 138.0 (C), 136.7 (C), 135.0 (C), 133.6 (C), 131.9 (CH), 129.3 (CH), 129.2 (CH), 129.1 (CH), 129.0 (CH), 128.9 (CH), 128.6 (CH), 128.4 (CH), 128.1 (CH), 127.7 (CH), 126.4 (CH), 125.7 (CH), 123.4 (CH), 79.3 (C), 53.9 (CH_2), 51.6 (CH_2), 51.3 (CH_2), 49.1 (CH), 46.1 (CH_2), 43.7 (CH_2), 39.4 (CH_2), 34.2 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 29.1 (CH_2), 28.5 (CH_3), 28.0 (CH_2), 26.0 (CH_2), 25.6 (CH_2) ppm; **HRMS (ESI):** calcd. for $C_{76}H_{84}N_7O_8$ $[M+H]^+$ 1222.6376; found 1222.6380; **IR (neat) ν:** 2926.5, 1661.4, 1612.2, 1526.4, 1162.8, 698.1 cm^{-1}.

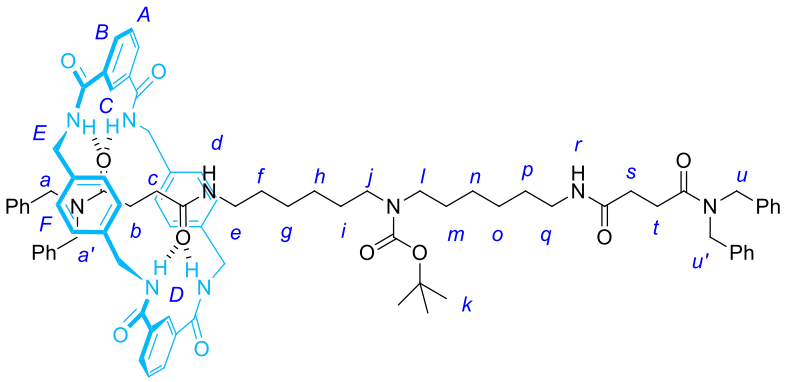
Synthesis of [2]rotaxane 2a



To a solution of Boc-protected rotaxane **Boc2a** (70 mg, 0.06 mmol) in CH_2Cl_2 (5 mL) was added TFA (53 µL, 0.68 mmol). The reaction was stirred at room temperature overnight. After this time the reaction mixture was diluted chloroform (20 mL) and washed with a saturated solution of aqueous $NaHCO_3$ (2 x

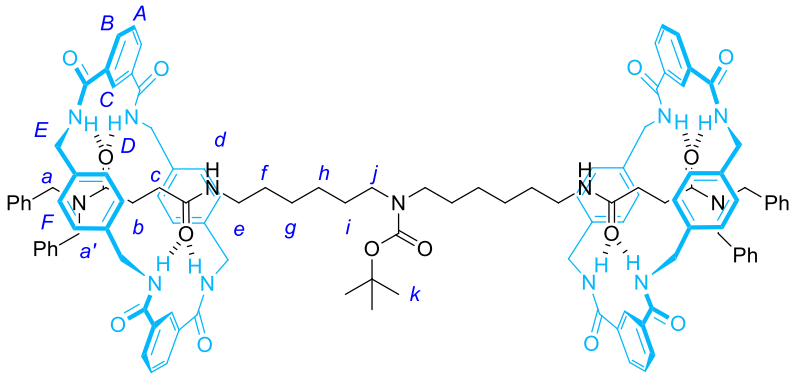
20 mL) and brine (2 x 20 mL). The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure, to give the title product as a white solid (**2a**, 56 mg, 84 %); mp 91-93 ºC; **^{1}H-NMR (400 MHz, $CDCl_3$) δ:** 8.43 (s, 2H, H_C), 8.18 (dd, *J* = 7.8 Hz, *J* = 1.5 Hz, 4H, H_B), 7.58 – 7.51 (m, 6H, H_{A+D}), 7.32 – 7.07 (m, 20H, H_{Ph}), 6.97 (s, 8H, H_F), 6.76 (t, *J* = 5.0 Hz, 1H, H_d), 6.72 (d, *J* = 7.3 Hz, 2H, Ph), 4.43 – 4.39 (m, 10H, H_{E+a}), 4.14 (s, 2H, $H_{a'}$), 3.95 (t, *J* = 7.8 Hz, 1H, H_n), 3.05 (m, 2H, H_e), 2.54 (m, 4H, H_{j+l}), 2.24 (dt, *J* = 7.8 Hz, *J* = 7.6 Hz, 2H, H_m), 1.43 – 1.37 (m, 4H, H_{f+i}), 1.25 – 1.23 (m, 5H, H_{g+h+k}), 1.14 (m, 2H, H_c), 1.03 (m, 2H, H_b) ppm; **^{13}C-NMR (100 MHz, $CDCl_3$) δ:** 173.4 (C=O), 173.3 (C=O), 166.1 (C=O), 144.5 (C), 138.0 (C), 136.8 (C), 135.1 (C), 133.7 (C), 131.8 (CH), 129.3 (CH), 129.2 (CH), 129.1 (CH), 129.0 (CH), 128.9 (CH), 128.6 (CH), 128.3 (CH), 128.1 (CH), 127.8 (CH), 126.4 (CH), 125.7 (CH), 123.5 (CH), 51.5 (CH_2), 51.2 (CH_2), 49.3 (CH_2), 49.2 (CH), 48.2 (CH_2), 43.7 (CH_2), 39.8 (CH_2), 35.1 (CH_2), 29.6 (CH_2), 29.2 (CH_2), 29.0 (CH_2), 27.9 (CH_2), 26.7 (CH_2), 26.6 (CH_2); **HRMS (ESI):** calcd. for $C_{71}H_{76}N_7O_6$ $[M+H]^+$ 1122.5852; found 1122.5846; **IR (neat) ν:** 3292.9, 2926.5, 1645.9, 1624.7, 1529.3, 695.2 cm^{-1}.

Synthesis of [2]rotaxane Boc2b and [3]rotaxane Boc3b



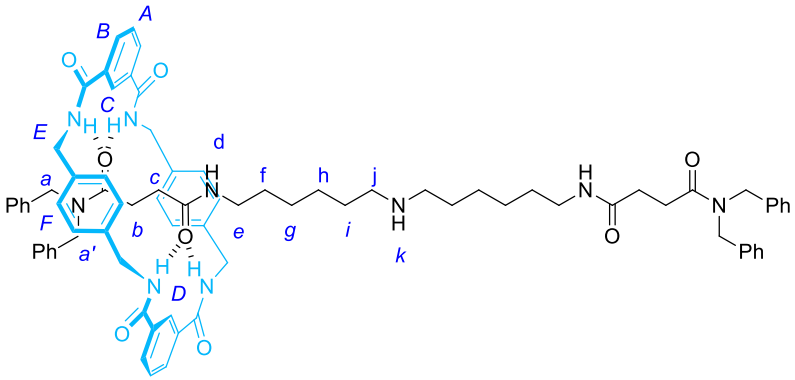
Rotaxane **Boc2b** was obtained following the described method from thread **Boc1b** (0.874 g, 1 mmol), *p*-xylylendiamine (0.544 g, 4 mmol) and isophthaloyl chloride (0.812 g, 4 mmol). The resulting solid was purified by column chromatography (silica gel) using $CHCl_3$/MeOH (20:1) as eluent to give a mixture of thread **Boc1b**, [2]rotaxane **Boc2b** and [3]rotaxane **Boc3b**. Portions of 70 mg of this mixture were separated by preparative TLC using a mixture of $CHCl_3$/MeOH (40:1) as eluent, to give the title product **Boc2b** as a white solid (562 mg, 40%); mp 105-107 ºC; **^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ:** 8.48 (s, 2H, H_C), 8.22 (dd, *J* = 7.7 Hz; *J* = 1.5 Hz, 4H, H_B), 7.61 - 7.49 (m, 6H, H_{A+D}), 7.38 - 7.23 (m, 8H, H_{Ph}), 7.22 - 7.02 (m, 10H, H_{Ph}), 6.95 (s, 8H, H_F), 6.71 (d, *J* = 7.3 Hz, 2H, H_{Ph}), 6.50 (bs, 1H, H_d), 6.42 (bs, 1H, H_r), 4.57 (s, 2H, H_u), 4.46 (s, 2H, $H_{u'}$), 4.45 - 4.35 (m, 10H, H_{E+a}), 4.13 (s, 2H, $H_{a'}$), 3.23 - 3.04 (m, 8H, $H_{e+j+l+q}$), 2.77 - 2.67 (m, 2H, H_s), 2.52 - 2.49 (m, 2H, H_t), 1.55 - 1.35 (m, 8H, $H_{f+i+m+p}$), 1.35 (s, 9H, H_k), 1.34 - 1.19 (m, 8H, $H_{g+h+n+o}$), 1.14 - 1.05 (m, 2H, H_b), 1.04 - 0.94 (m, 2H, H_c) ppm; **^{13}C-NMR (100 MHz, $CDCl_3$, 298 K) δ:** 173.5 (C=O), 173.3 (C=O), 172.9 (C=O), 172.4 (C=O), 166.0 (C=O), 155.8 (C=O), 138.1 (C), 137.1 (C), 136.8 (C), 136.2 (C), 135.1 (C), 133.7 (C), 131.9 (CH), 129.3

(CH), 129.2 (CH), 129.1 (CH), 128.7 (CH), 128.4 (CH), 128.1 (CH), 127.8 (CH), 127.5 (CH), 127.5 (CH), 126.6 (CH), 125.7 (CH), 123.4 (CH), 79.2 (C), 51.6 (CH_2), 51.3 (CH_2), 50.1 (CH_2), 48.6 (CH_2), 47.1 (CH_2), 46.3 (CH_2), 43.7 (CH_2), 39.5 (CH_2), 31.7 (CH_2), 29.6 (CH_2), 29.1 (CH_2), 28.6 (CH_3), 28.0 (CH_2), 26.7 (CH_2), 26.3 (CH_2), 25.8 (CH_2) ppm; **HRMS (ESI)** calcd for $C_{85}H_{100}N_9O_{10}$ $[M + H]^+$ 1406.7593, found 1406.7582; **IR (neat) ν:** 3310.2, 2930.3, 1644.0, 1529.3 cm^{-1}.



White solid (**Boc3b**, 135 mg, 7 %); mp 137-138 ºC; **^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ**: 8.45 (s, 4H, H_C), 8.18 (d, *J* = 7.8 Hz, 8H, H_B), 7.64 - 7.43 (m, 12H, H_{A+D}), 7.41 - 7.25 (m, 6H, H_{Ph}), 7.22 - 7.11 (m, 6H, H_{Ph+d}), 7.07 (t, *J* = 7.6 Hz, 4H, H_{Ph}), 7.15 (d, *J* = 7.4 Hz, 2H, H_{Ph}), 6.97 (s, 16H, H_F), 6.82 - 6.59 (m, 4H, H_{Ph}), 4.44 (s, 4H, H_a), 4.40 (s, 16H, H_E), 4.15 (s, 4H, $H_{a'}$), 3.08 (s, 8H, H_{e+j}), 1.45 – 1.37 (m, 8H, H_{f+i}), 1.33 (s, 9H, H_k), 1.29 - 1.17 (m, 8H, H_{g+h}), 1.14 - 1.05 (m, 4H, H_b), 1.05 – 0.96 (m, 4H, H_c); **^{13}C-NMR (100 MHz, $CDCl_3$, 298 K) δ**: 173.4 (C=O), 173.3 (C=O), 166.1 (C=O), 155.9 (C=O), 138.1 (C), 136.8 (C), 135.1 (C), 133.7 (C), 132.0 (CH), 129.4 (CH), 129.2 (CH), 129.1 (CH), 129.0 (CH), 128.8 (CH), 128.1 (CH), 127.9 (CH), 127.7 (CH), 126.6 (CH), 125.7 (CH), 123.6 (CH), 79.2 (C), 51.6 (CH_2), 51.3 (CH_2), 50.3 (CH_2), 48.8 (CH_2), 47.1 (CH_2), 43.7 (CH_2), 39.7 (CH_2), 31.5 (CH_2), 29.6 (CH_2), 29.0 (CH_2), 28.6 (CH_3), 28.0 (CH_2); **HRMS (ESI)** calcd for $C_{117}H_{128}N_{13}O_{14}$ $[M + H]^+$ 1938.9698, found 1938.9681; **IR (neat) ν:** 3303.5, 2926.5, 1645.9, 1529.3 cm^{-1}.

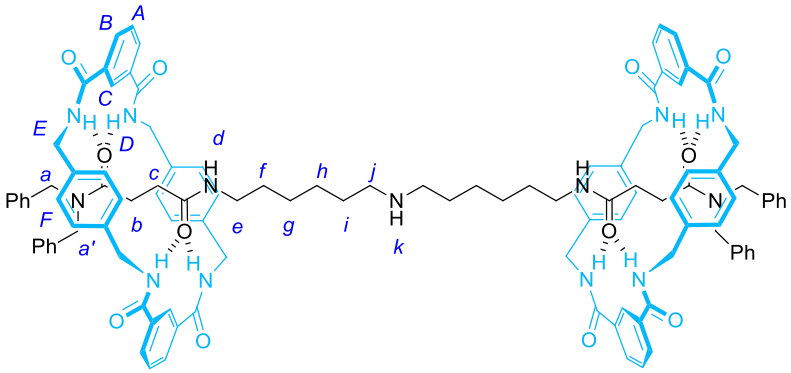
Synthesis of [2]rotaxane 2b



To a solution of Boc-protected rotaxane **Boc2b** (41 mg, 0.029 mmol) in CH_2Cl_2 (1 mL) was added TFA (40 µL , 0.52 mmol) and the reaction stirred at room temperature overnight. After this time the reaction

mixture was diluted chloroform (20 mL) and washed with a saturated solution of aqueous $NaHCO_3$ (2 x 20 mL) and brine (2 x 20 mL). The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure, to give the title product as a white solid (**2b**, 28 mg, 75%); mp 86-88 ºC; **^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ:** 8.48 (s, 2H, H_C), 8.19 (dd, *J* = 7.7 Hz, *J* = 1.5 Hz, 4H, H_B), 7.65 (t, *J* = 5.1 Hz, 4H, H_D), 7.55 (t, *J* = 7.8 Hz, 2H, H_A), 7.36 - 7.27 (m, 7H, H_{Ph}), 7.25 - 7.19 (m, 6H, H_{Ph}), 7.18 – 7.11 (m, 4H, H_{Ph}), 6.93 – 6.89 (m, 3H, H_{Ph}), 6.95 (s, 8H, H_F), 6.76 (bs, 2H, H_d), 4.49 (s, 2H, H_a), 4.40 (d, *J*= 4.9 Hz, 8H, H_E), 4.31 (s, 4H, $H_{a'}$), 3.15 - 3.08 (m, 4H, H_e), 2.59 (t, *J* = 7.2 Hz, 4H, H_j), 2.08 – 1.58 (m, 8H, H_{b+c}), 1.55 – 1.40 (m, 8H, H_{f+i}), 1.35 - 1.21 (m, 9H, H_{g+h+k}) ppm; **^{13}C-NMR (100 MHz, $CDCl_3$, 298 K) δ:** 173.2 (C=O), 172.9 (C=O), 166.2 (C=O), 138.0 (C), 137.0 (C), 135.7 (C), 133.7 (C), 131.8 (C), 129.3 (CH), 129.2 (CH), 129.1 (CH), 128.8 (CH), 128.4 (CH), 128.0 (CH), 126.1 (CH), 123.7 (CH), 50.8 (CH_2), 49.9 (CH_2), 48.9 (CH_2), 43.7 (CH_2), 39.5 (CH_2), 30.6 (CH_2), 29.8 (CH_2), 29.1 (CH_2), 28.5 (CH_3), 28.3 (CH_2), 26.4 (CH_2) ppm; **HRMS (ESI)** calcd for $C_{80}H_{92}N_9O_8$ $[M + H]^+$ 1306.7068, found 1306.7039; **IR (neat) ν:** 3294.8, 3062.4, 2924.5, 1637.3, 1529.3 cm^{-1}.

Synthesis of [3]rotaxane 3b



To a solution of Boc-protected rotaxane **Boc3b** (20 mg, 0.010 mmol) in dichloromethane (1 mL) was added TFA (9 µL, 0.11 mmol). The reaction was stirred at room temperature overnight. After this time the reaction mixture was diluted chloroform (10 mL) and washed with a saturated solution of aqueous $NaHCO_3$ (2 x 10 mL) and brine (2 x 10 mL). The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure, to give the title product as a white solid (**3b**, 12 mg, 66 %); mp 123-128 ºC; **^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ:** 8.46 (s, 4H, H_C), 8.16 (dd, *J* = 7.6 Hz; *J* = 1.6 Hz, 8H, H_B), 7.63 (s, 8H, H_D), 7.55 - 7.46 (m, 6H, H_{A+d}), 7.34 - 7.29 (m, 6H, H_{Ph}), 7.22 - 7.08 (m, 10H, H_{Ph}), 6.98 (s, 16H, H_F), 6.79 - 6.69 (m, 4H, H_{Ph}), 4.44 (s, 4H, H_a), 4.41 (d, *J* = 4.4 Hz, 16H, H_E), 4.16 (s, 4H, $H_{a'}$), 3.04 - 2.99 (m, 4H, H_e), 2.57 - 2.53 (m, 4H, H_j), 1.45 -1.14 (m, 25H, $H_{b+c+f+g+h+i+k}$); **^{13}C-NMR (100 MHz, $CDCl_3$, 298 K) δ**: 173.4 (C=O), 173.3 (C=O), 166.3 (CO), 138.0 (C), 136.9 (C), 135.4 (C), 133.8 (C), 131.8 (CH), 129.3 (CH), 129.1 (CH), 128.9 (CH), 128.8 (CH), 128.3 (CH), 128.1 (CH), 125.8 (CH), 123.8 (CH), 123.4 (CH), 51.4 (CH_2), 51.1 (CH_2), 48.3 (CH_2), 43.8 (CH_2), 43.7 (CH_2), 39.5 (CH_2), 29.8

(CH_2), 29.7 (CH_2), 28.7 (CH_2), 28.0 (CH_2), 26.1 (CH_2); **HRMS (ESI)** calcd for $C_{112}H_{120}N_{13}O_{12}$ $[M + H]^+$ 1838.9179, found 1838.9236; **IR (neat) ν:** 3288.0, 2924.5, 1633.4, 1531.2 cm^{-1}.

5. VT-NMR experiment for rotaxane 2b

Variation temperature ^1H NMR experiments were performed for rotaxane **2b** in order to get valuable information about the translational motion of the polyamide macrocycle along the two binding-sites thread, estimating the relative strength of the intercomponent interactions. The free energies of activation for the translation of the macrocycle were calculated using the Eyring equation, $\Delta G_c^{\neq} = -RT_c \cdot ln(k_c h/k_b T_c)$, where $k_c = \pi\sqrt{(\Delta v^2 + 6J^2)}/\sqrt{2}$ and R, h and k_b are the gas, Planck and Boltzmann constants, respectively. The temperature dependence of the ^1H NMR spectrum of the systems was studied in $CDCl_3$ (from 343K to 233K).

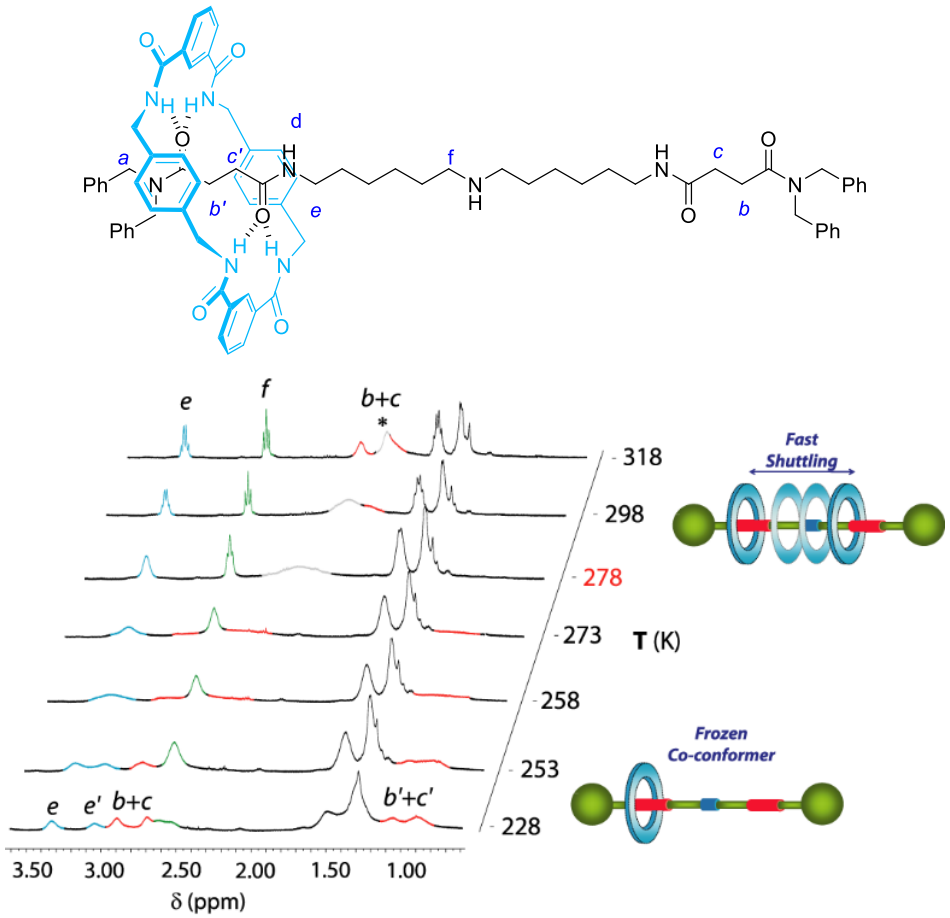


Figure S1. Variable temperature ^1H NMR spectra (400 MHz) of **2b** in $CDCl_3$ at 228–318 K. (* H_2O in grey).

Table S1 Kinetic and thermodynamic parameters for macrocycle shuttling obtained from VT-^1H NMR spectra of the degenerate [2]rotaxane **2b**.

Δv (Hz)	k_c (s^{-1})	T_c (K)[a]	ΔG (Kcal mol^{-1})[b]
712	1581,7	278	12.17

6. Stacked ^{1}H NMR spectra of thread 1a and rotaxane 2a

The comparison of the ^{1}H NMR spectra of thread **1a** and rotaxane **2a** revealed that the macrocycle is predominantly located over the succinamide binding site, which their related signals suffered a variation of the chemical shift of Δδ= 1.58 ppm, similar to that experienced for the same signals between thread **Boc1a** and rotaxane **Boc2a** (Δδ= 1.59 ppm).

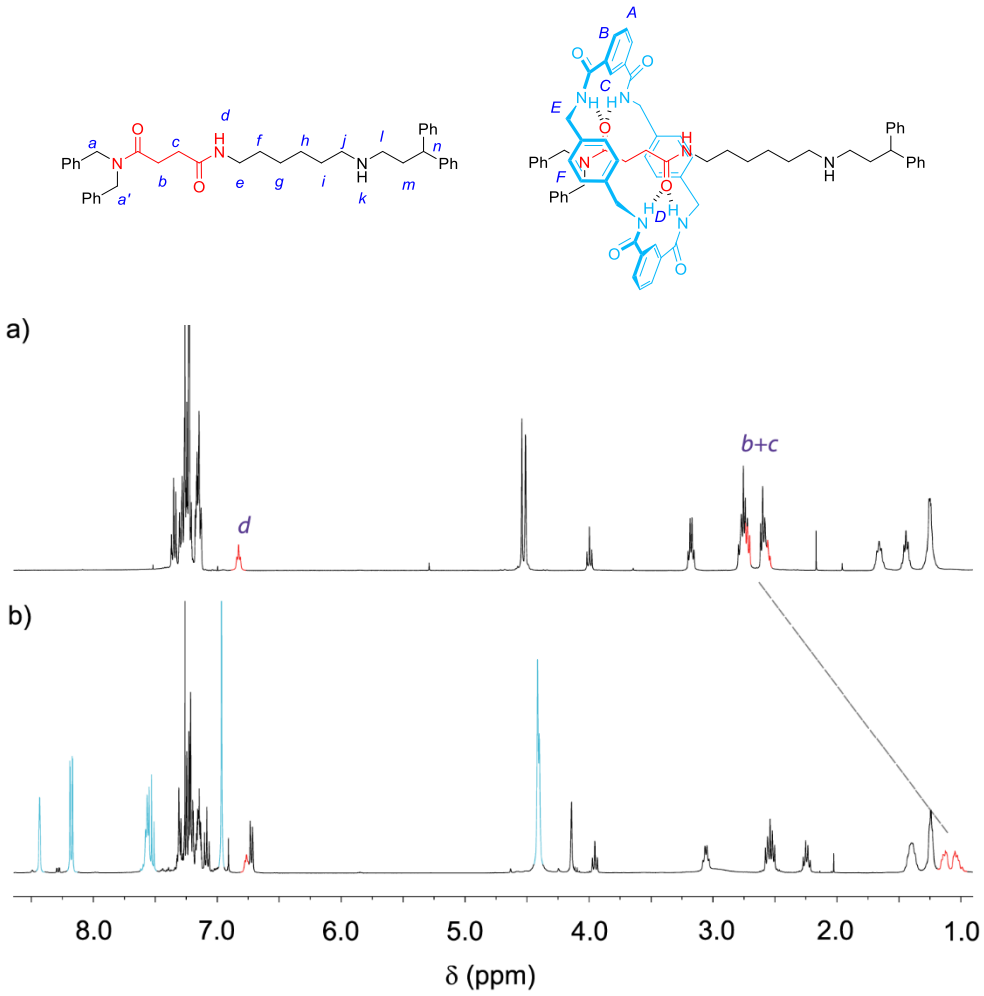
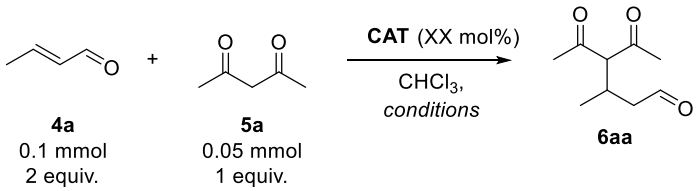


Figure S2. ^{1}H NMR spectra (400MHz, $CDCl_3$, 298K) of: a) thread **1a** and b) rotaxane **2a.**

7. Optimization of the Michael addition of acetylacetone to crotonaldehyde catalysed by thread 1a

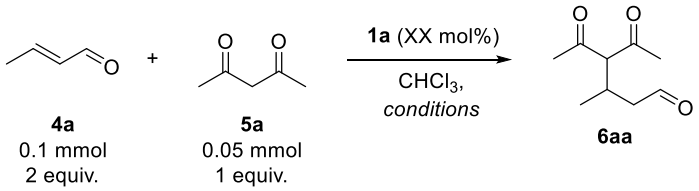
We optimized the reactions conditions of the Michael addition of acetylacetone **5a** to crotonaldehyde **4a** catalysed by the secondary amine thread **1a**. We selected $CHCl_3$ as solvent since it is known that not disrupt the intercomponent hydrogen-bonding interactions in polyamide-based rotaxanes. We tested concentrations, catalyst loadings, reaction times, additives towards the formation of adduct **6aa**[2] (Table S2).

Table S2. Optimization of the reaction conditions for the Michael addition of acetylacetone **5a** to crotonaldehyde **4a**.



entry	CAT	CAT loading (xx mol%)	Additive	Time (h)	Conversion[a] (%)
1	-	-	-	72	0
2	Et_3N	100	-	72	0
3	**1a**	20	-	24	94
[a]Conversion calculated by ^1H NMR using CH_2Br_2 as internal standard.					

Table S3. Optimization of the reaction conditions for the Michael addition of acetylacetone **5a** to crotonaldehyde **4a** catalysed by thread **1a**.

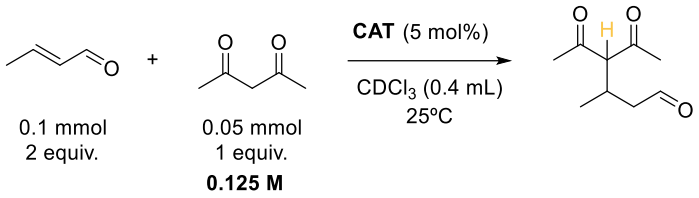


entry	1a loading (xx mol%)	Concentration of 5 (M)	Additive (10 mol%)	Time (h)	Conversion[a] (%)
1	20	0.4	-	6	92
2	5	0.4	-	6	99
3	5	0.4	NaOAc	6	78
4	5	0.125	-	12	70
[a]Conversion calculated by ^1H NMR using CH_2Br_2 as internal standard.					

8. Kinetic studies for the Michael addition of acetylacetone to crotonaldehyde

The Michael addition of acetylacetone **5a** to crotonaldehyde **4a** catalysed by the secondary amines **1, 2** and **3** were carried out inside an NMR spectrometer. We followed the conversion towards adduct **6aa** overtime at room temperature under the same conditions (concentration, solvent and temperature). For comparison, the reaction catalysed with **dibutylamine** was also monitored. The experiments were run on duplicated.

Procedure: A solution of freshly distilled *trans*-crotonaldehyde **4a** (with traces of the *cis* isomer) (7 mg, 0.1 mmol, 2 equiv.), acetylacetone **5a** (5 mg, 0.05 mmol, 1 equiv.) and CH_2Br_2 (8.6 mg, 0.05 mmol, 1 equiv., as internal standard) in $CDCl_3$ (0.4 mL, 0.125 M in acetylacetone) were placed in an NMR tube in the presence of the corresponding catalyst (5 mol%). The formation of adduct **6aa** was followed overtime at 298K (the appearance of the signal related to CH at 3.70 ppm was followed, marked in yellow).



Thread 1a as catalyst

Run 1

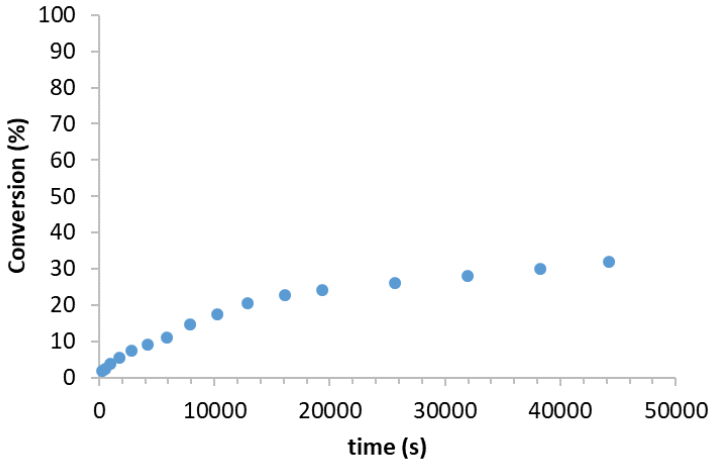


Figure S3. Plot of the conversion (%) versus time of the Michael addition between crotonaldehyde and acetylacetone catalysed by thread **1a** (•). The conversion was determined during time by ^1H NMR using CH_2Br_2 as internal standard.

Run 2

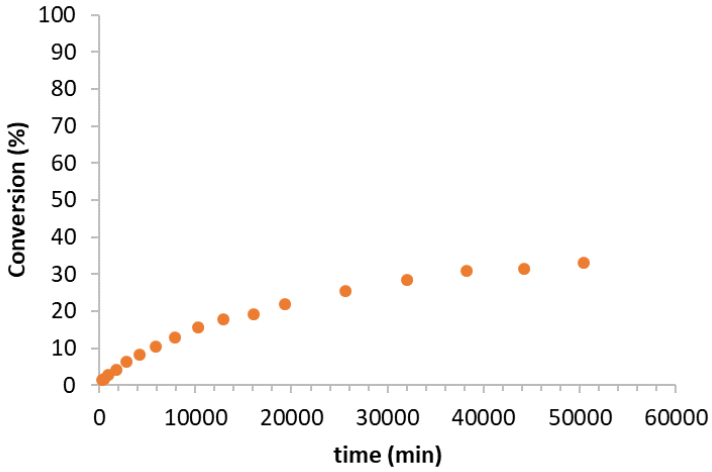


Figure S4. Plot of the conversion (%) versus time of the Michael addition between crotonaldehyde and acetylacetone catalysed by thread **1a** (•). The conversion was determined during time by ^{1}H NMR using CH_2Br_2 as internal standard.

Average between Run 1 and Run 2

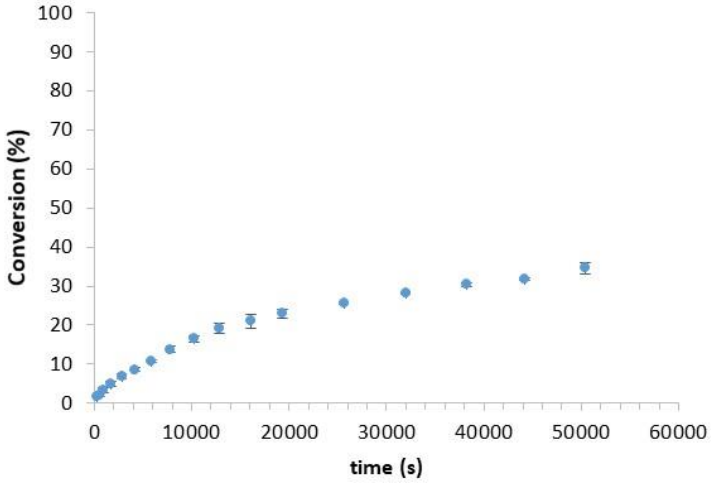


Figure S5. Plot of the conversion (%) versus time of the Michael addition between crotonaldehyde and acetylacetone catalysed by thread **1a**. The conversion was determined during time by ^{1}H NMR using CH_2Br_2 as internal standard.

Thread 1b as catalyst

Run 1

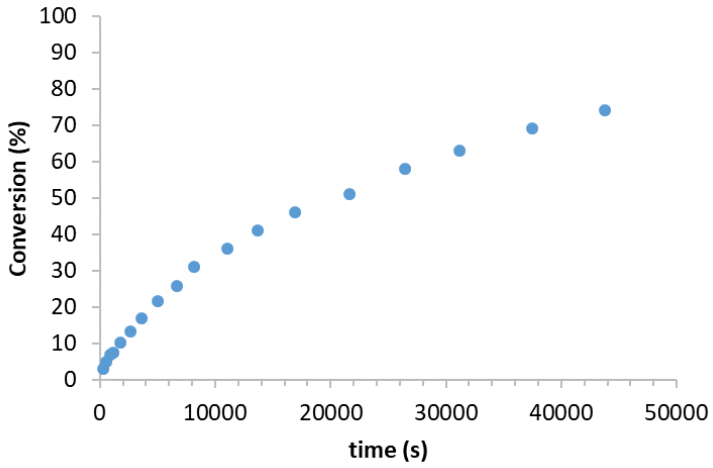


Figure S6. Plot of the conversion (%) versus time of the Michael addition between crotonaldehyde and acetylacetone catalysed by thread **1b** (•). The conversion was determined during time by ^{1}H NMR using CH_2Br_2 as internal standard.

Run 2

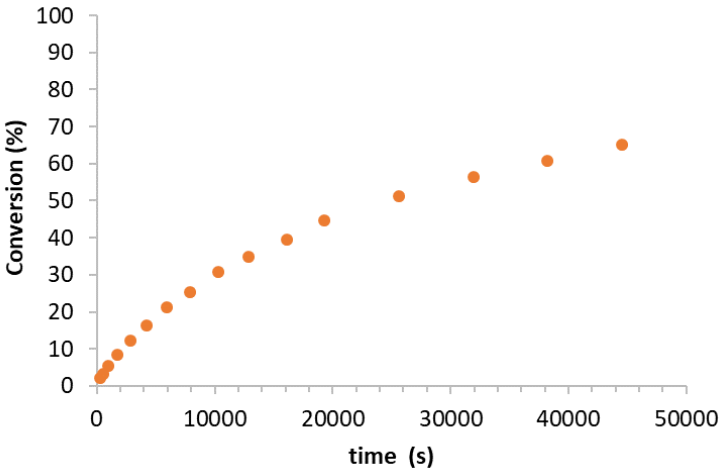


Figure S7. Plot of the conversion (%) versus time of the Michael addition between crotonaldehyde and acetylacetone catalysed by thread **1b** (•). The conversion was determined during time by ^{1}H NMR using CH_2Br_2 as internal standard.

Average between Run 1 and Run 2

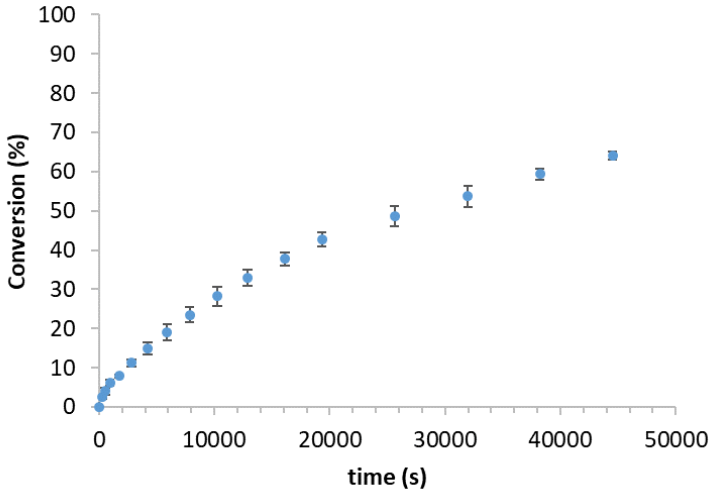


Figure S8. Plot of the conversion (%) versus time of the Michael addition between crotonaldehyde and acetylacetone catalysed by thread **1b**. The conversion was determined during time by ^{1}H NMR using CH_2Br_2 as internal standard.

Rotaxane 2a as catalyst

Run 1

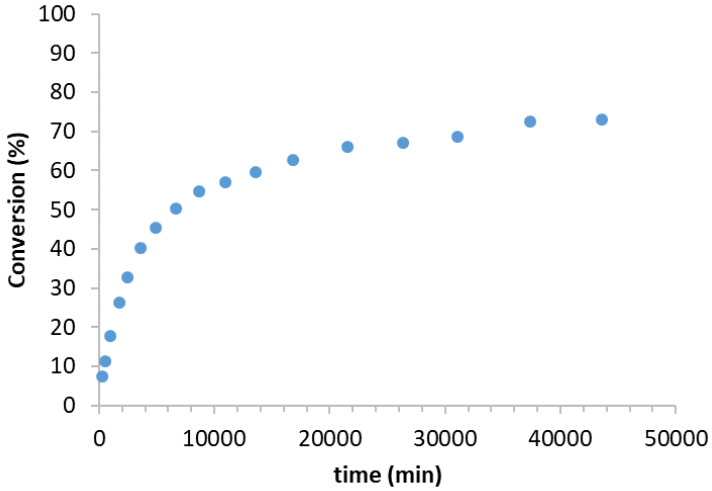


Figure S9. Plot of the conversion (%) versus time of the Michael addition between crotonaldehyde and acetylacetone catalysed by rotaxane **2a** (•). The conversion was determined during time by ^{1}H NMR using CH_2Br_2 as internal standard.

Run 2

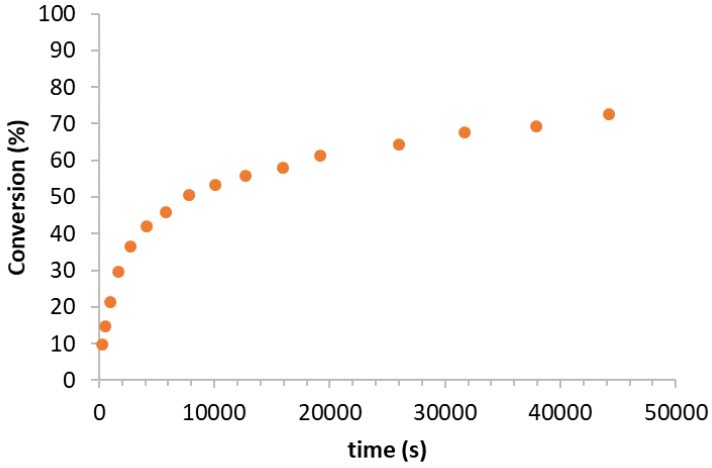


Figure S10. Plot of the conversion (%) versus time of the Michael addition between crotonaldehyde and acetylacetone catalysed by rotaxane **2a** (•). The conversion was determined during time by ^{1}H NMR using CH_2Br_2 as internal standard.

Average between Run 1 and Run 2

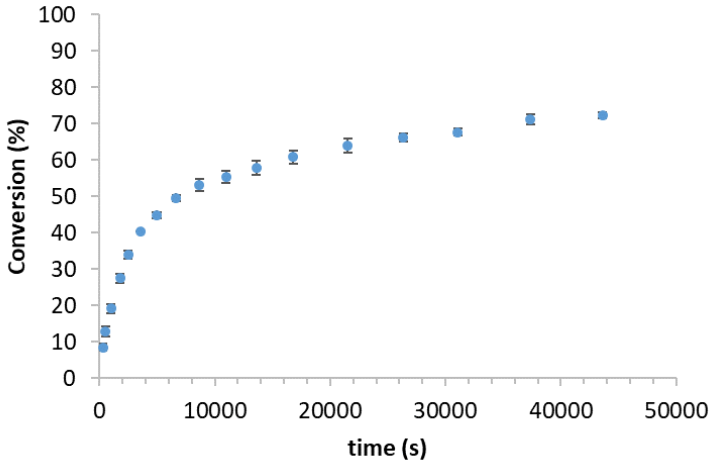


Figure S11. Plot of the conversion (%) versus time of the Michael addition between crotonaldehyde and acetylacetone catalysed by rotaxane **2a.** The conversion was determined during time by ^{1}H NMR using CH_2Br_2 as internal standard.

Rotaxane 2b as catalyst

Run 1

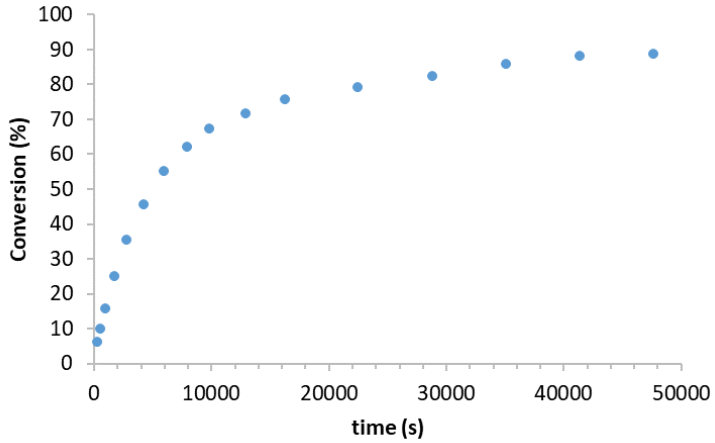


Figure S12. Plot of the conversion (%) versus time of the Michael addition between crotonaldehyde and acetylacetone catalysed by rotaxane **2b** (•). The conversion was determined during time by ^{1}H NMR using CH_2Br_2 as internal standard.

Run 2

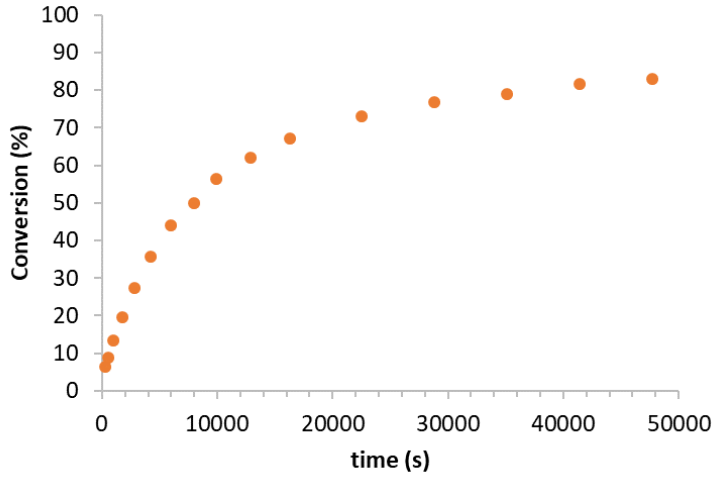


Figure S13. Plot of the conversion (%) versus time of the Michael addition between crotonaldehyde and acetylacetone catalysed by rotaxane **2b** (•). The conversion was determined during time by ^{1}H NMR using CH_2Br_2 as internal standard.

Average between Run 1 and Run 2

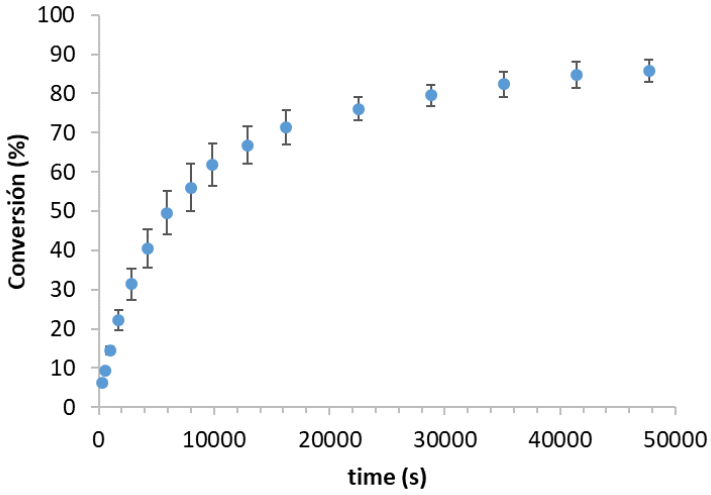


Figure S14. Plot of the conversion (%) versus time of the Michael addition between crotonaldehyde and acetylacetone catalysed by rotaxane **2b.** The conversion was determined during time by ^{1}H NMR using CH_2Br_2 as internal standard.

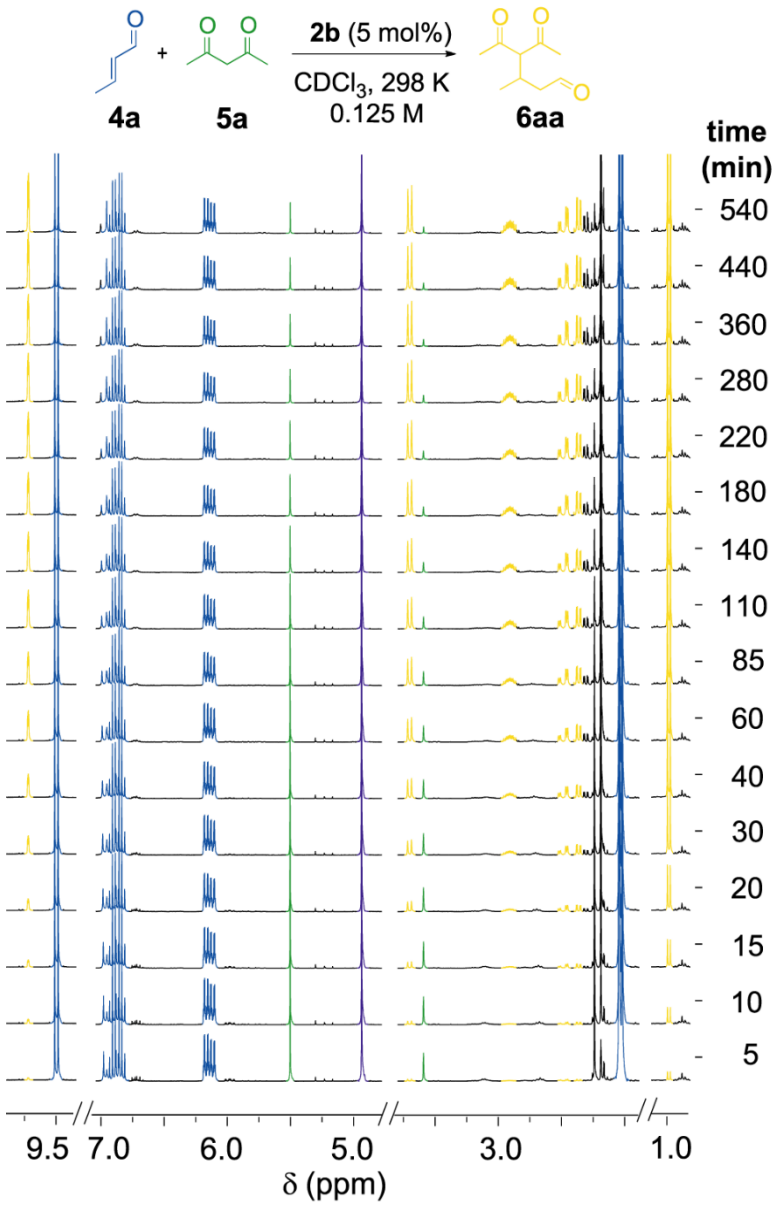


Figure S15. ^{1}H NMR kinetic experiment (400 MHz, $CDCl_3$, 298 K) for the Michael addition of acetylacetone **5a** (green colour) to crotonaldehyde **4a** (dark blue colour) towards the formation of adduct **6aa** (yellow colour) catalysed by rotaxane **2b** (5 mol%) followed over time. Signal referred to the CH_2Br_2 used as an internal standard is highlighted in purple.

[3]Rotaxane 3b as catalyst

Run1

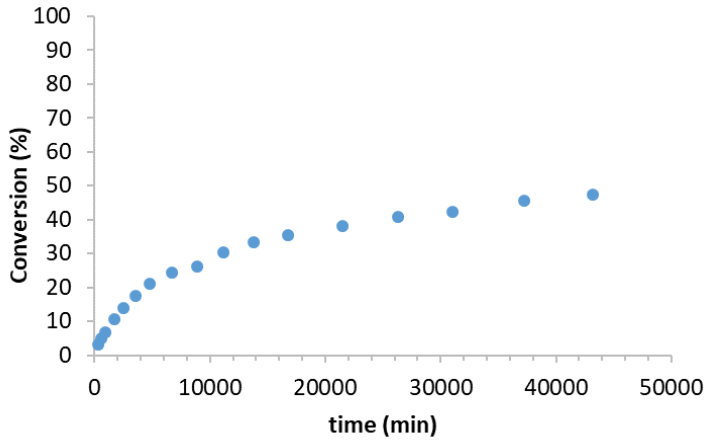


Figure S16. Plot of the conversion (%) versus time of the Michael addition between crotonaldehyde and acetylacetone catalysed by [3]rotaxane **3b** (•). The conversion was determined during time by ^{1}H NMR using CH_2Br_2 as internal standard.

Run 2

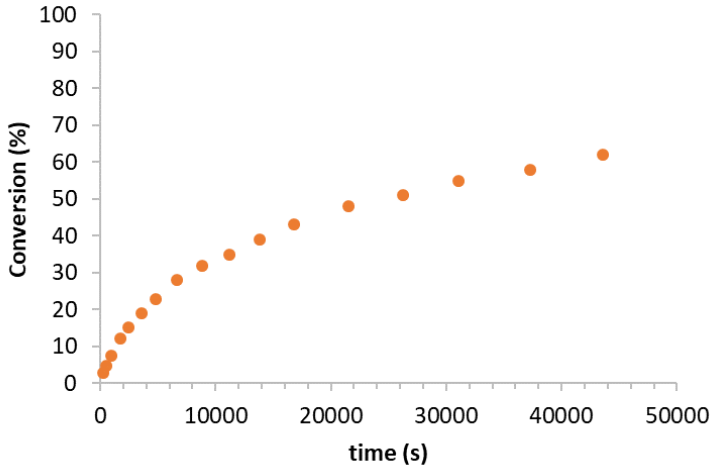


Figure S17. Plot of the conversion (%) versus time of the Michael addition between crotonaldehyde and acetylacetone catalysed by [3]rotaxane **3b** (•). The conversion was determined during time by ^{1}H NMR using CH_2Br_2 as internal standard.

Average between Run 1 and Run 2

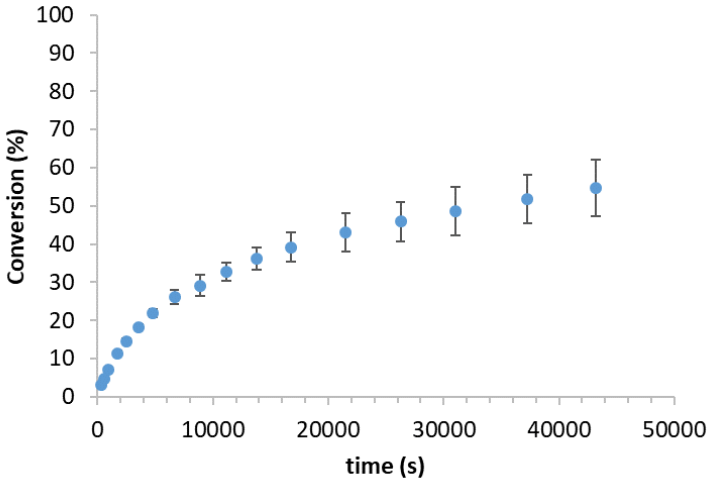


Figure S18. Plot of the conversion (%) versus time of the Michael addition between crotonaldehyde and acetylacetone catalysed by [3]rotaxane **3b**. The conversion was determined during time by ^{1}H NMR using CH_2Br_2 as internal standard.

Dibutylamine as catalyst

Run 1

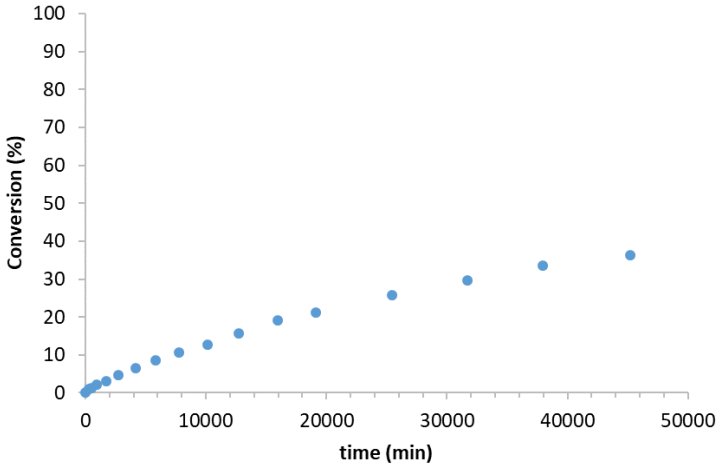


Figure S19. Plot of the conversion (%) versus time of the Michael addition between crotonaldehyde and acetylacetone catalysed by **dibutylamine** (•). The conversion was determined during time by ^{1}H NMR using CH_2Br_2 as internal standard.

Run 2

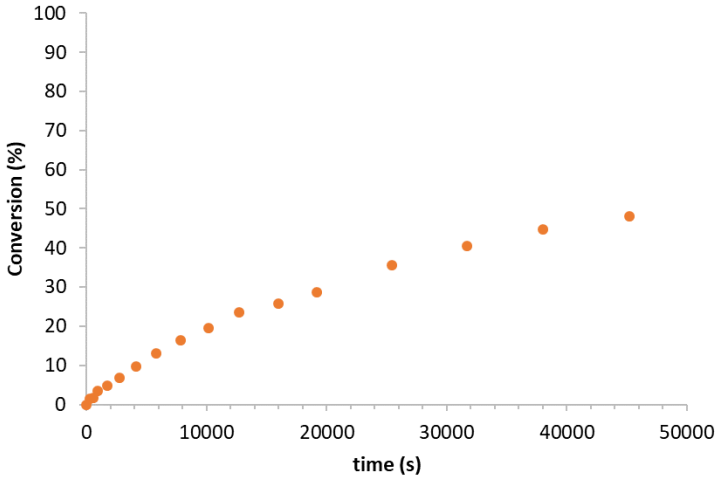


Figure S20. Plot of the conversion (%) versus time of the Michael addition between crotonaldehyde and acetylacetone catalysed by **dibutylamine** (•). The conversion was determined during time by ^{1}H NMR using CH_2Br_2 as internal standard.

Average between Run 1 and Run 2

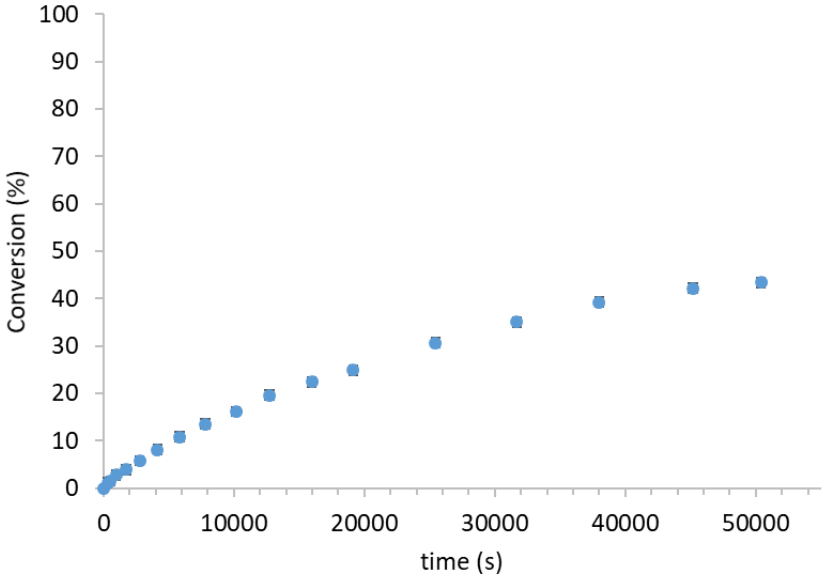


Figure S21. Plot of the conversion (%) versus time of the Michael addition between crotonaldehyde and acetylacetone catalysed by **dibutylamine**. The conversion was determined during time by ^{1}H NMR using CH_2Br_2 as internal standard.

9. Comparison of the reactivity between rotaxanes 2b and 3b

Figure S22 shows the conversion towards adduct **6aa** of the reactions between crotonaldehyde and acetylacetone catalysed by rotaxane **2b** and **3b** followed over time at room temperature under similar conditions (concentration, solvent and temperature).

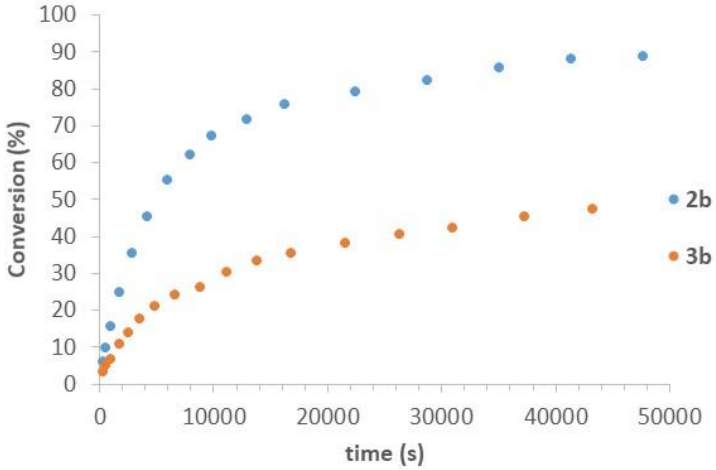
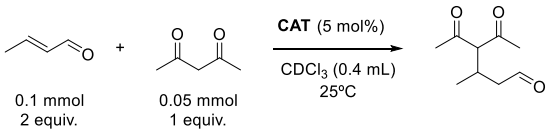
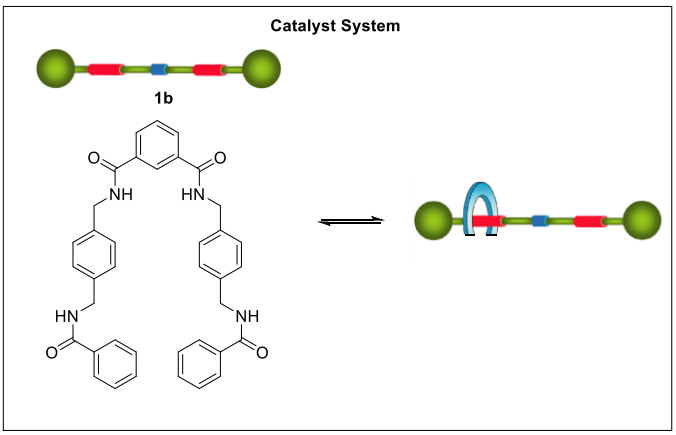


Figure S22. Plot of the conversion (%) versus time of the Michael addition between crotonaldehyde and acetylacetone catalysed by: rotaxane **2b** (•), [3]rotaxane **3b** (•). The conversion was determined during time by ^{1}H NMR using CH_2Br_2 as internal standard.

10. Kinetic studies for the Michael addition of acetylacetone to crotonaldehyde catalysed with thread 1b in the presence of an acyclic tetraamide

The Michael addition of acetylacetone to crotonaldehyde catalysed by the secondary amine **1b** in the presence of a "U" shape tetraamide derivative[3] was carried out inside an NMR spectrometer. We followed the conversion towards adduct **6aa** during time at room temperature and the data were compared with those obtained when **1b** or **2b** were employed as catalysts, under the same reaction conditions.





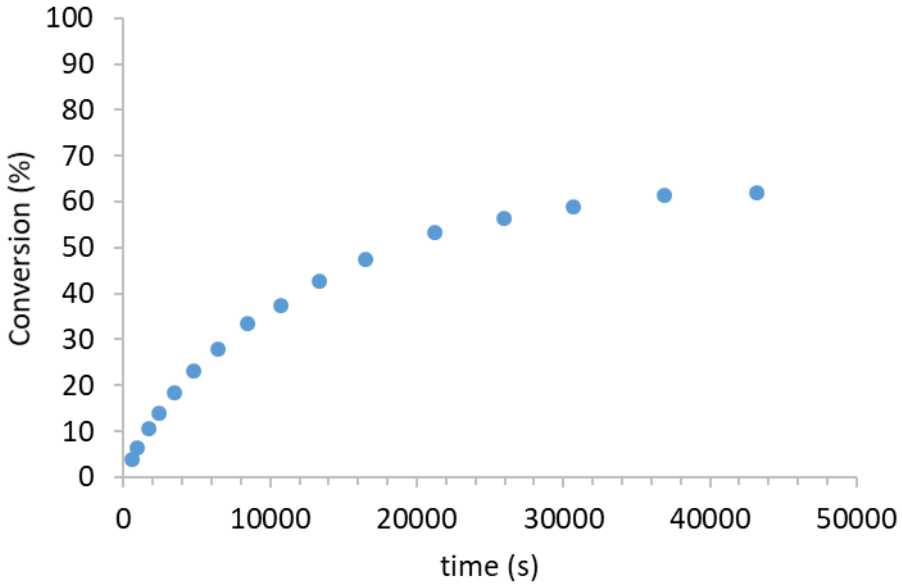


Figure S23. Plot of the conversion (%) versus time of the Michael addition between crotonaldehyde and acetylacetone catalysed by the mixture thread **1b** and tetraamide (•). The conversion was determined during time by ^{1}H NMR using CH_2Br_2 as internal standard.

Comparison of reactivity between 1b, 2b and the mixture 1b+"U" derivative

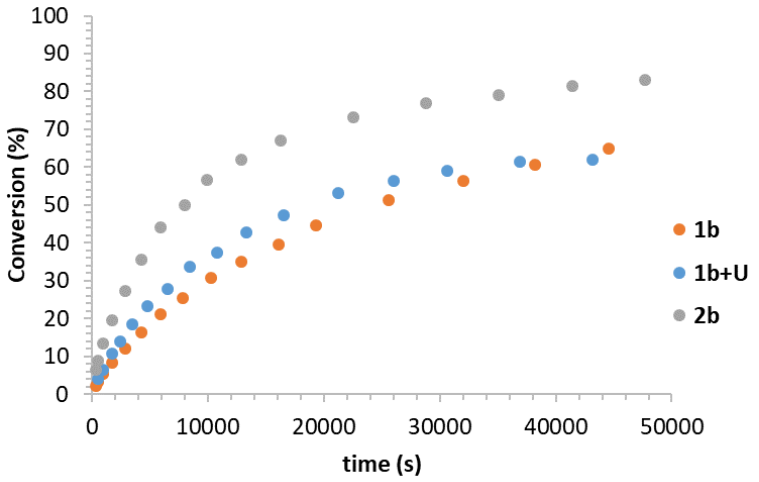


Figure S24. Plot of the conversion (%) versus time of the Michael addition between crotonaldehyde and acetylacetone catalysed by: thread **1b** (•), rotaxane **2b** (•), and the mixture **1b** + **U** (•). The conversion was determined during time by ^{1}H NMR using CH_2Br_2 as internal standard.

11. Reactivity between dibutylamine and crotonaldehyde 4a

The reaction between dibutylamine and crotonaldehyde **4a** towards the formation of the corresponding iminium salt was monitored by ^{1}H NMR spectroscopy: before and after addition of 4 equivalents of crotonaldehyde, in $CDCl_3$ at 298 K. After 24 hours the NMR spectra signals did not change. The addition of TFA triggered the formation of the iminium intermediate between dibutylamine and the aldehyde, identified by ^{1}H-, ^{13}C NMR and bidimensional experiments.

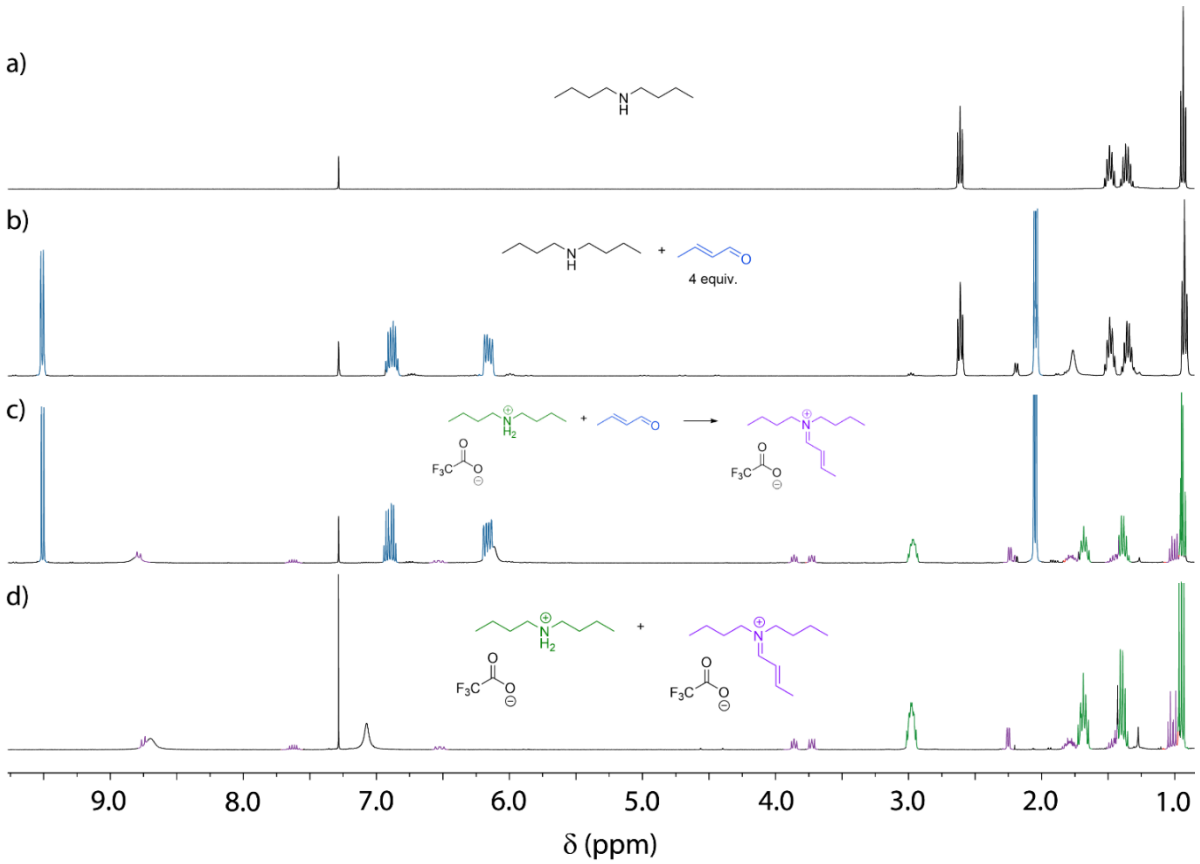


Figure S25. ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of: a) **dibutylamine** and, b) mixture of **Bu_2NH** and crotonaldehyde **4a** (**Bu_2NH**:**4a**; 1:4) after 48 h; c) mixture of **Bu_2NH** and crotonaldehyde **4a** (**Bu_2NH**:**4a**; 1:4) in the presence of TFA after 24 h; c) mixture in c) after removing of the solvent and excess of aldehyde.

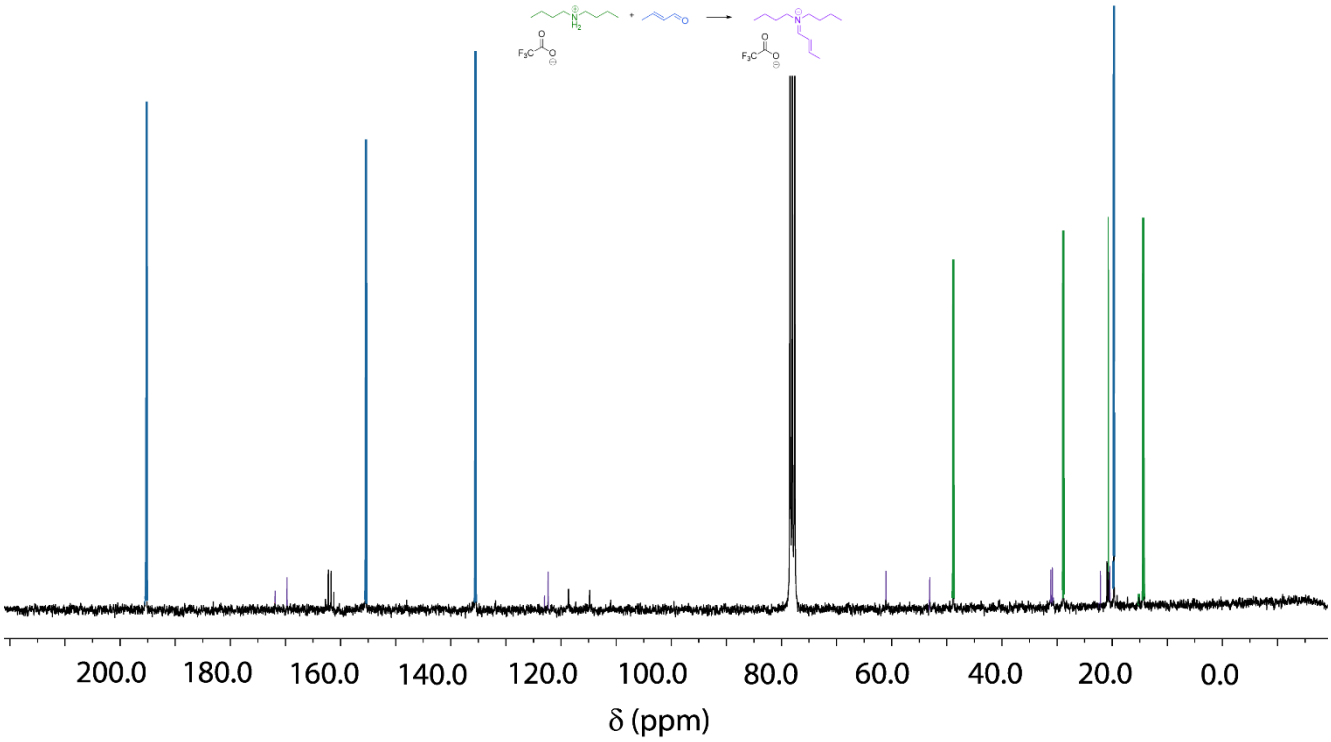


Figure S26. ^{13}C NMR spectra (100 MHz, $CDCl_3$, 298 K) of a mixture of **Bu_2NH·TFA** salt and crotonaldehyde **4a** (**salt**:**4a**; 1:4) after 24 h.

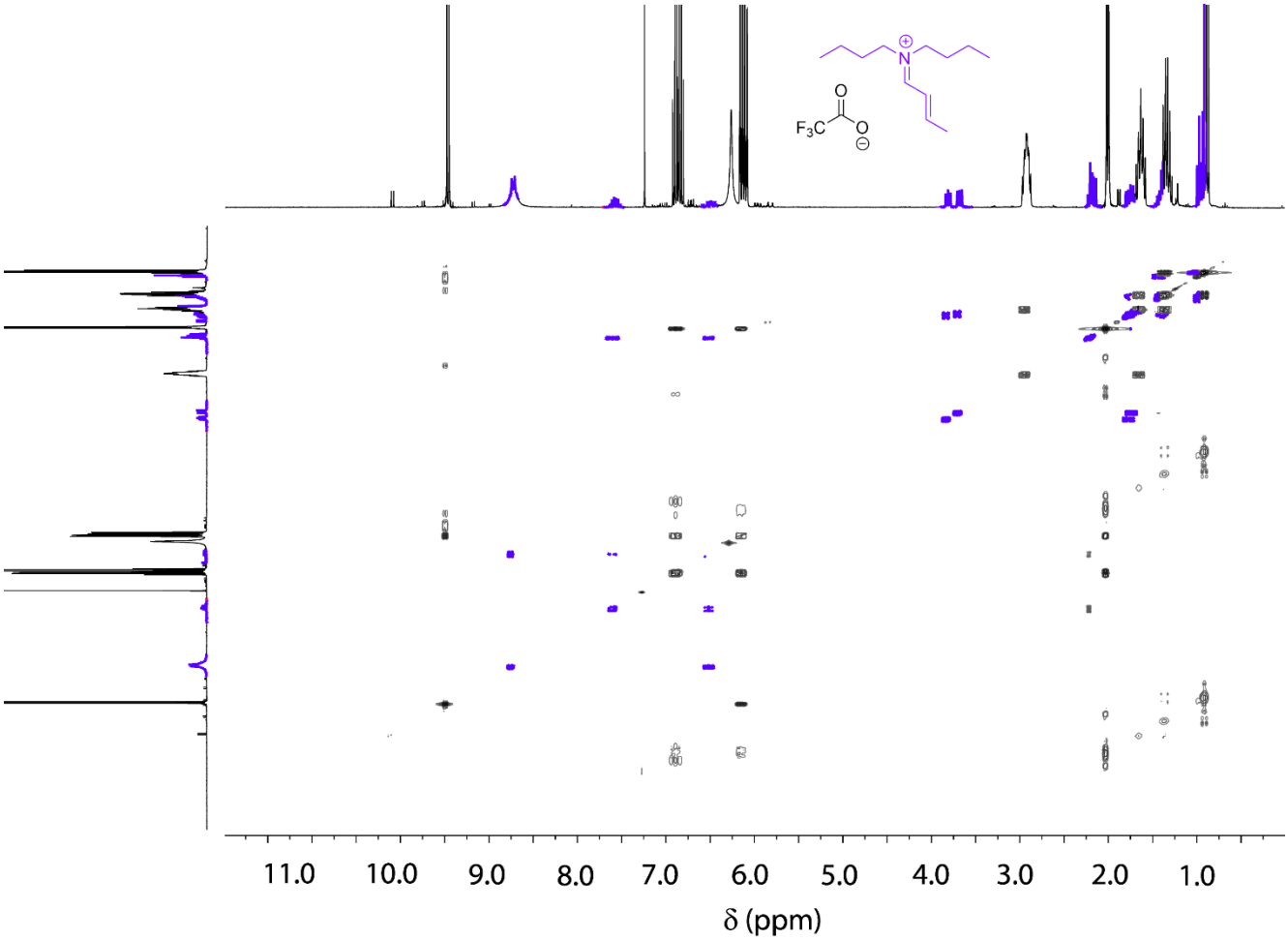


Figure S27. ^{1}H,^{1}H-COSY spectrum crosspeaks for the mixture of **Bu_2NH** and crotonaldehyde **4a** (Bu_2N:**4a**; 1:4) in the presence of TFA after 24 h. Signals related to the iminium intermediate are highlighted in purple.

12. Reactivity between thread 1b and crotonaldehyde 4a

The reaction between thread **1b** and crotonaldehyde **4a** towards the formation of the corresponding iminium salt was monitored by ^{1}H NMR spectroscopy. The equimolecular mixture of both systems in $CDCl_3$ at 298 K for 24 hours did not afford new signals potentially attributable to an iminium intermediate. After 48 h, new signals related to the iminium salt started to arise.

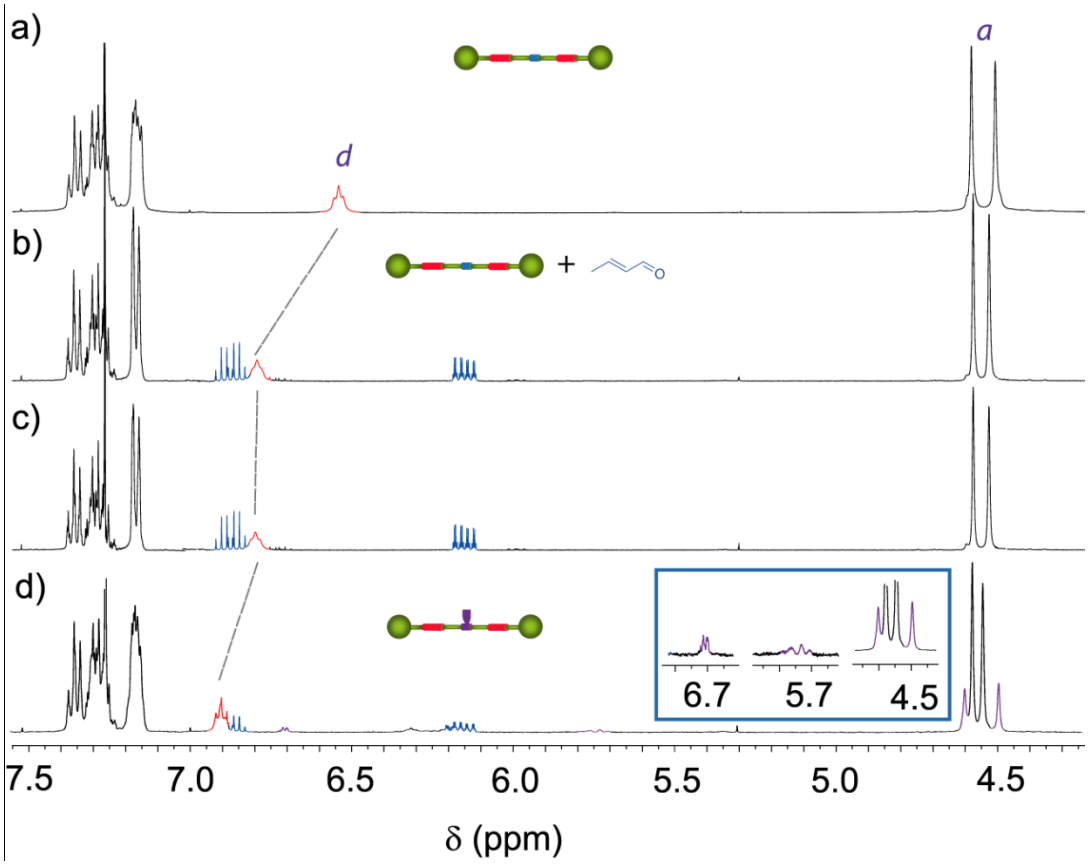


Figure S28. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of: a) **1b**; b) equimolecular mixture of **1b** and crotonaldehyde **4a** after 3 min; c) equimolecular mixture of **1b** and crotonaldehyde **4a** after 24 h; d) equimolecular mixture of **1b** and crotonaldehyde **4a** after 48 h. The assignments correspond to the lettering shown in Scheme 1. The succinamide station is coloured in red. The crotonaldehyde is coloured in dark blue. The new signals attributable to the iminium intermediate is coloured in purple. *Inset:* Amplification of the signals assigned to the iminium salt.

13. Reactivity between rotaxane 2b and crotonaldehyde 4a

The reaction between rotaxane **2b** and crotonaldehyde **4a** towards the formation of the corresponding iminium salt was monitored by ^{13}C NMR spectroscopy: before and after addition of 2 equivalents of crotonaldehyde, in $CDCl_3$ at 298 K. After 24 hours the NMR spectra signals, a complex NMR was recorded, clearly indicating a compartmentalization of the rotaxane **2b** upon formation of the corresponding iminium intermediate **7b** (due to the complexity of the spectra we did not assigned the signals referred to the intermediate **7b**). Selected regions have been amplified.

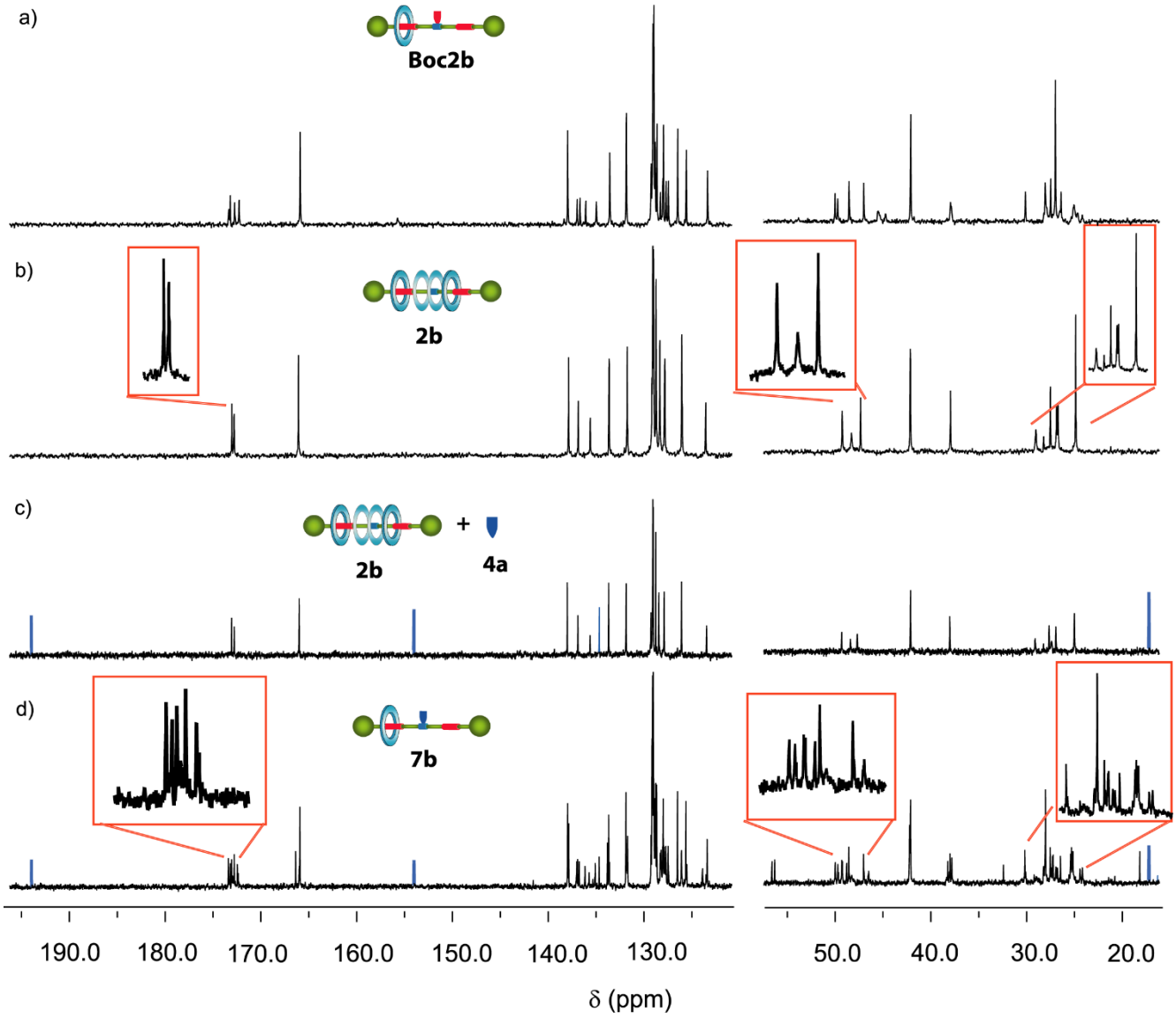


Figure S29. Partial ^{13}C NMR spectra (101 MHz, $CDCl_3$, 298 K) of: a) **Boc2b**; b) **2b**; c) mixture of **2b** and crotonaldehyde **4a** (2 equiv.) after 3 min; d) mixture of **2b** and crotonaldehyde **4a** (2 equiv.) after 3 min after 24 h. The crotonaldehyde is coloured in dark blue. *Insets:* Amplification of the selected signals.

14. Reactivity between rotaxane 2b and TBAH

The reaction between rotaxane **2b** and tetrabutylammonium hydroxide (**TBAH**) towards the formation of the corresponding imidate salt was monitored by ^{1}H NMR spectroscopy: a) before; and b) after addition of 1 equivalent of **TBAH**, in $CDCl_3$ at 298 K. It is observed.

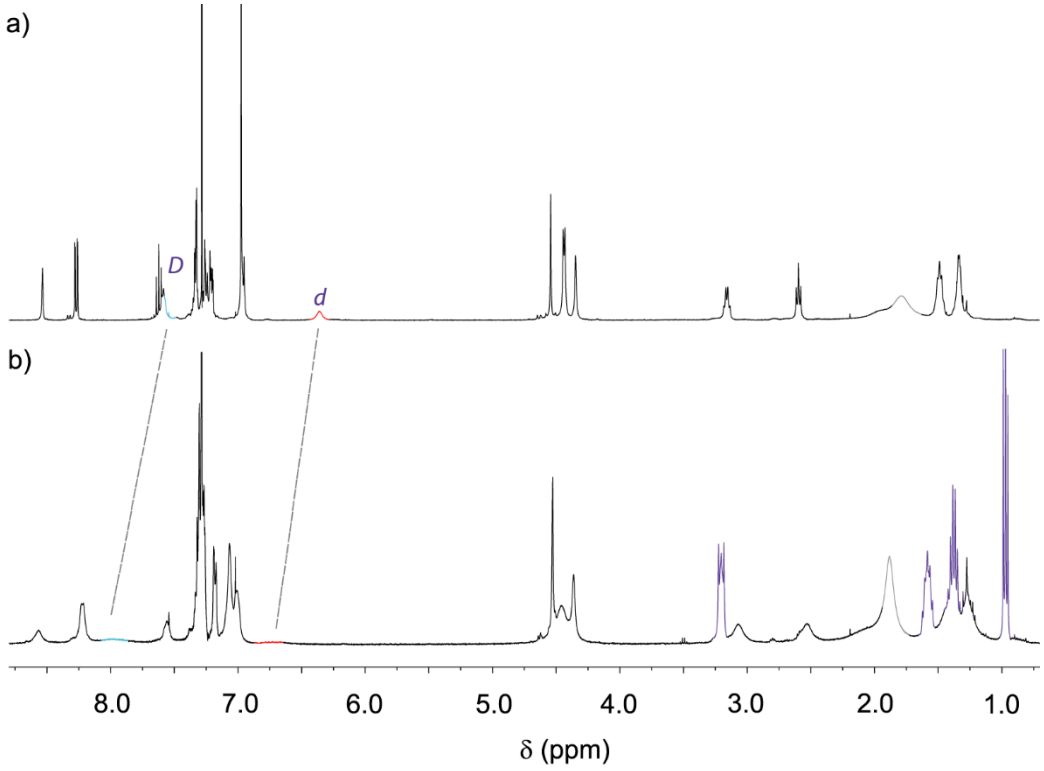


Figure S30. ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of: a) **2b**; b) equimolecular mixture of **2b** and tetrabutylammonium hydroxide (**TBAH**); The **TBAH** is coloured in purple.

15. DOSY NMR experiments for rotaxanes 2b, crotonaldehyde 4a and the mixture 2b:4a

The PGSE NMR diffusion measurements were performed on a 600 MHz Bruker AVANCE spectrometer, equipped with a microprocessor-controlled gradient unit and a multinuclear inverse probe with an actively shielded Z-gradient coil. The sample was not spin and the airflow was disconnected. The shape of the gradient pulse was rectangular, and its strength varied automatically during the course of the experiments. The D-values were determined from the slope of the regression line ln(I/Io) vs G2, according to Eq. 1.

$$\ln(I/I_o) = -(\gamma\delta)^2 G^2 (\Delta - \delta/3) D \quad (1)$$

I/I_o = observed spin echo intensity/intensity without gradients, G = gradient strength, Δ = delay between the midpoints of the gradients, D = diffusion coefficient, δ = gradient length.

The values reported are the average of three different measurements at Δ = 0.05, 0.15 and 0.40 s, which yielded D-values within max. ± 2.6% of the reported one. All the measurements were carried out using the ^{1}H resonances. The gradient length was set in the range of 0.8 and 4.6 ms. The number of scans was 32 and the experimental time was ca. 90 min. The observed data leading to the reported D-values for pure crotonaldehyde and rotaxane afforded lines whose correlation coefficients were above 0.999. The data leading to the D-values for the resonances in the 1:1 and 1:10 **2b**/**Crotonaldehyde** mixtures afforded lines whose correlations coefficients were above 0.99.

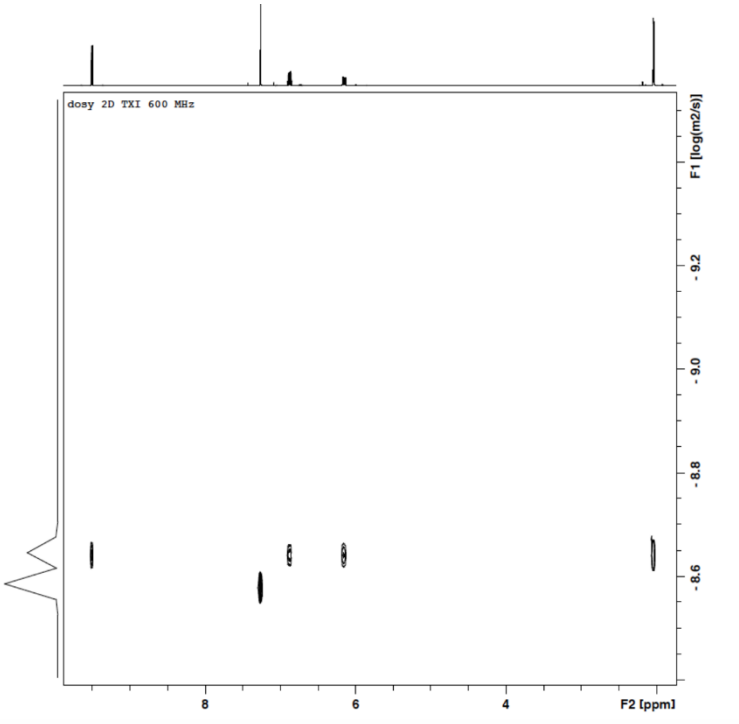


Figure S31. DOSY 2D of crotonaldehyde **4a** (2 mM, 600 MHz, $CDCl_3$, 298 K).

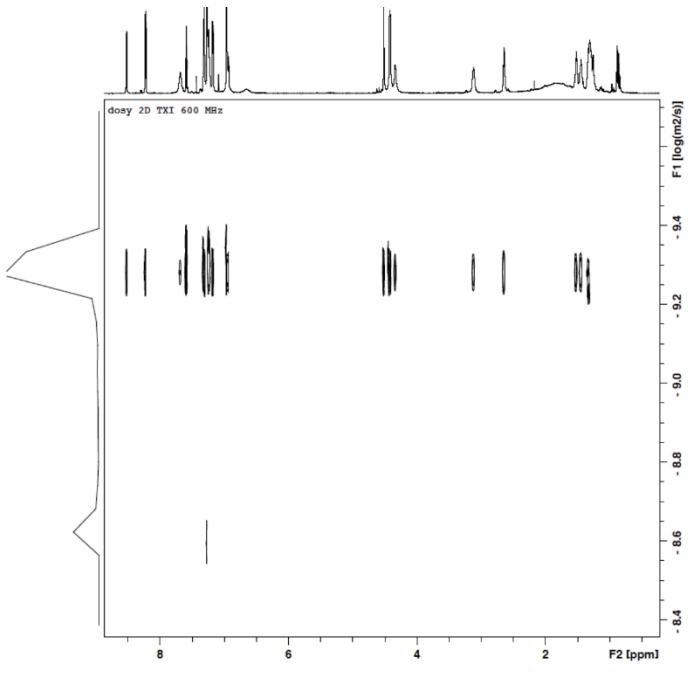


Figure S32. DOSY 2D of rotaxane **2b** (2 mM, 600 MHz, $CDCl_3$, 298 K).

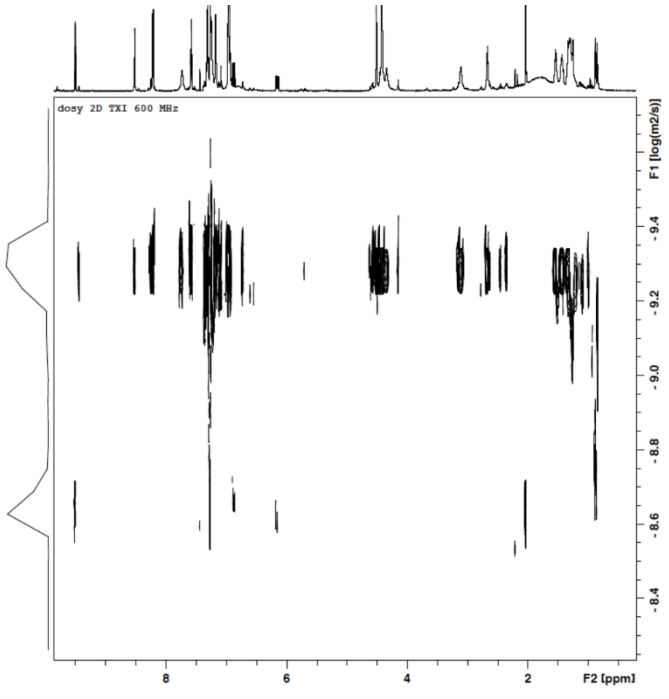


Figure S33. DOSY 2D of the 1:1 mixture of rotaxane **2b** and crotonaldehyde **4a** (2 mM, 600 MHz, $CDCl_3$, 298 K).

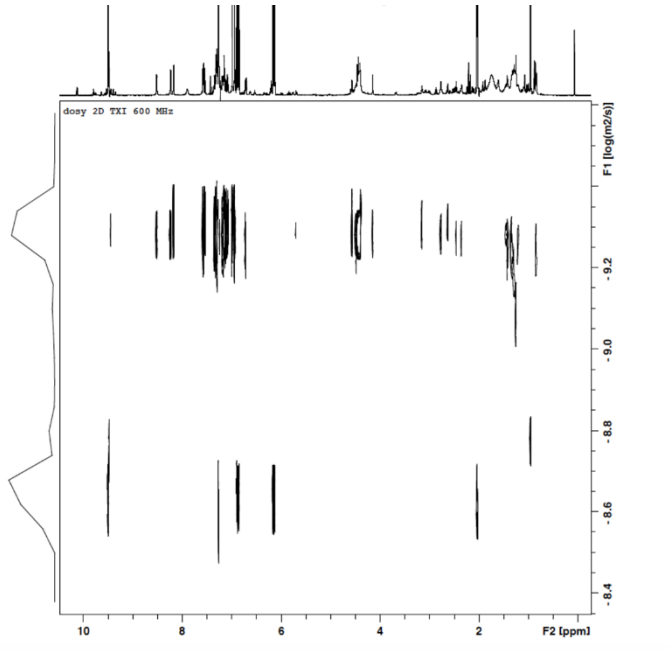
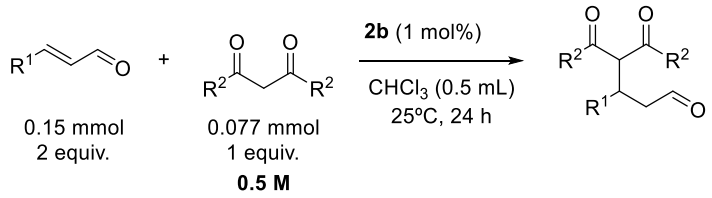


Figure S34. DOSY 2D of the 1:10 mixture of rotaxane **2b** and crotonaldehyde **4a** (2 mM, 600 MHz, $CDCl_3$, 298 K).

16. Scope of the Michael addition catalysed by 2b



Procedure: A solution of the corresponding freshly distilled aldehyde **4** (0.15 mmol), diketone **5** (0.077 mmol) and rotaxane **2b** (1 mg, 0.00077 mmol, 1 mol%) in $CHCl_3$ (0.15 mL, 0.5 M in **5**) were placed in vial and stirred at room temperature during 24 hours. After this time the ^1H NMR spectrum was recorded to calculate the conversion by integrating the remained signals of the diketone **5** and the formed adduct **6**.[2,4,5]

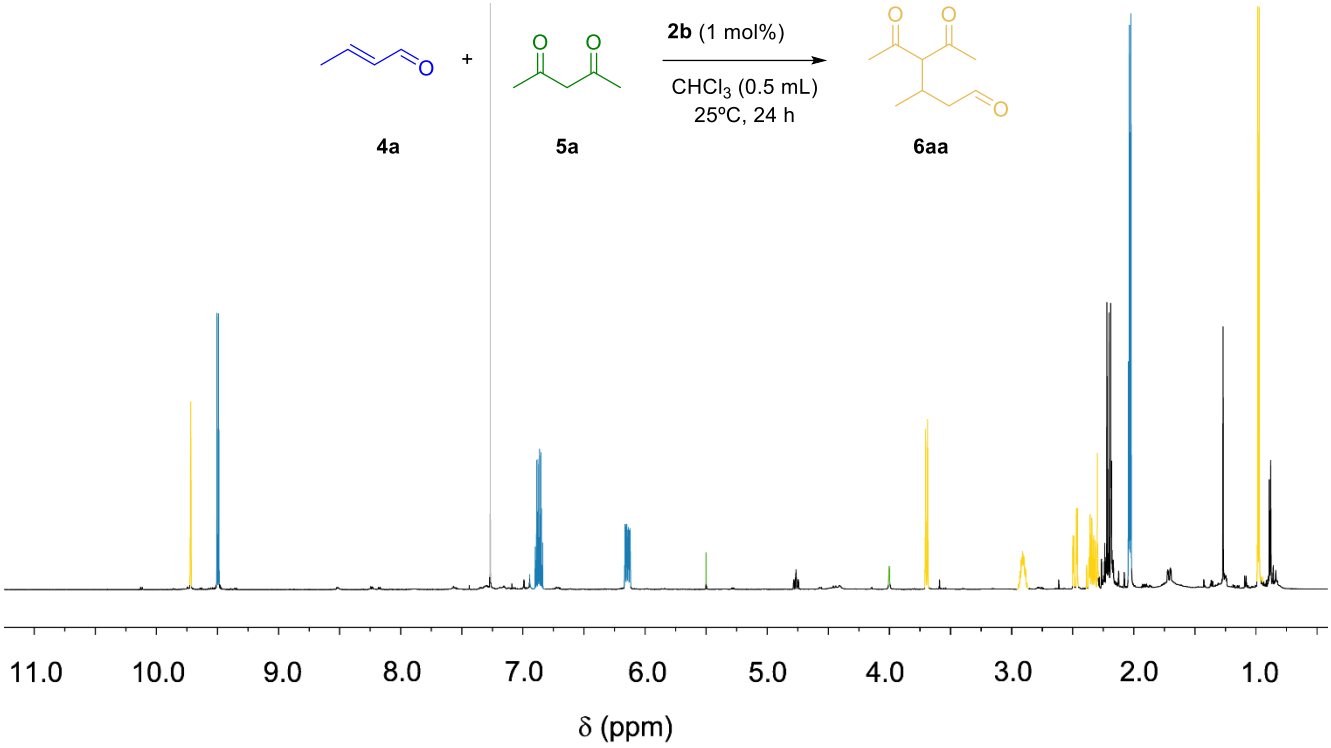


Figure S35. ^1H NMR spectra (400MHz, $CDCl_3$, 298K) of the reaction between crotonaldehyde **4a** (blue) and acetylacetone **5a** (green) to the formation of adduct **6aa**[2] (yellow).

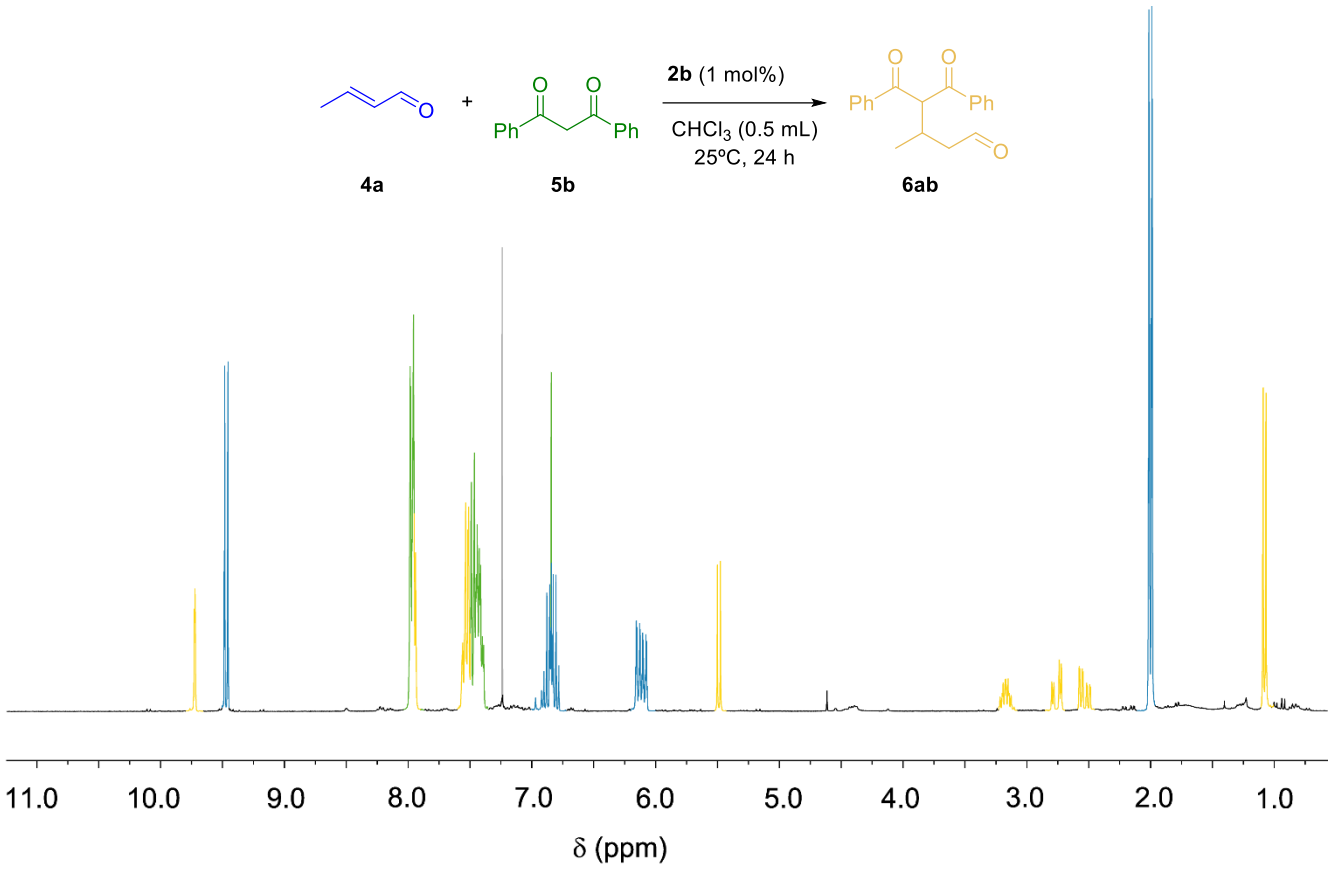


Figure S36. ^{1}H NMR spectra (400MHz, $CDCl_3$, 298K) of the reaction between crotonaldehyde **4a** (blue) and 1,3-diphenyl-1,3-propanedione **5b** (green) to the formation of adduct **6ab**[4] (yellow).

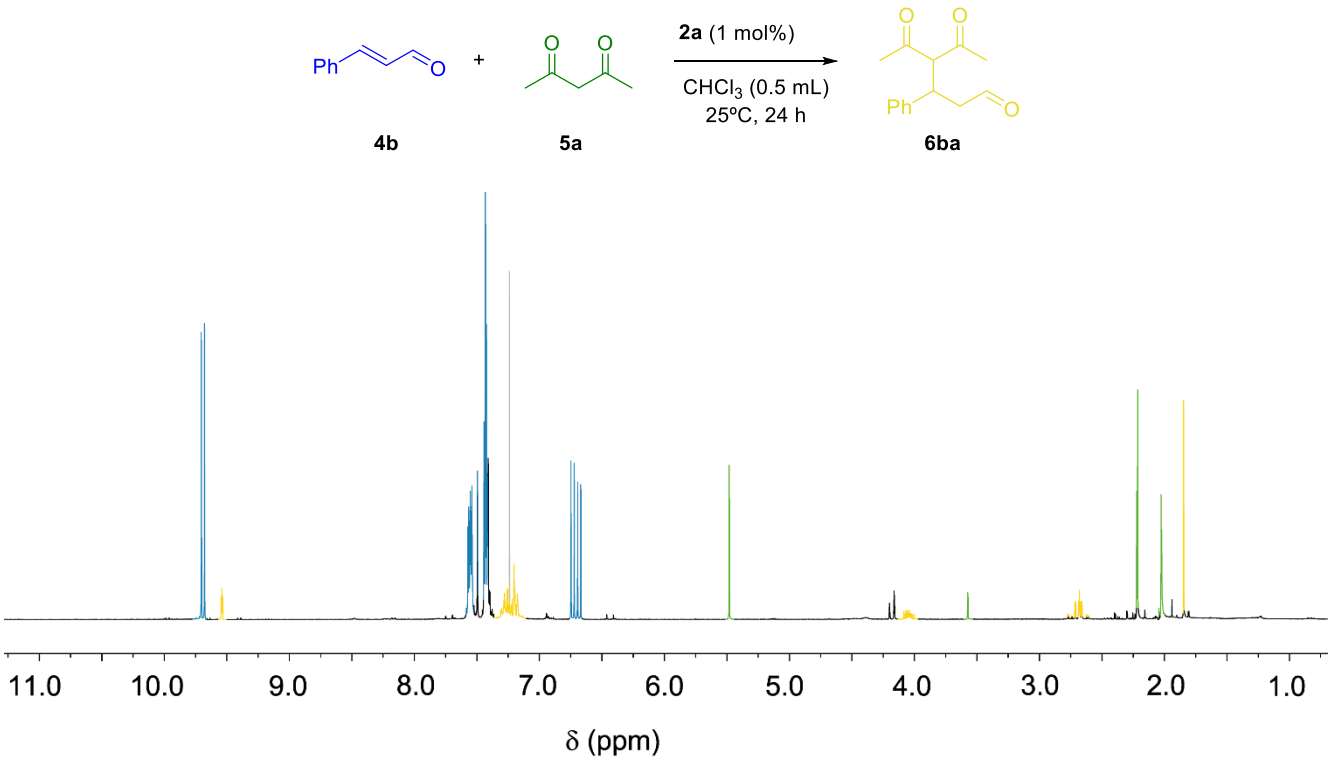
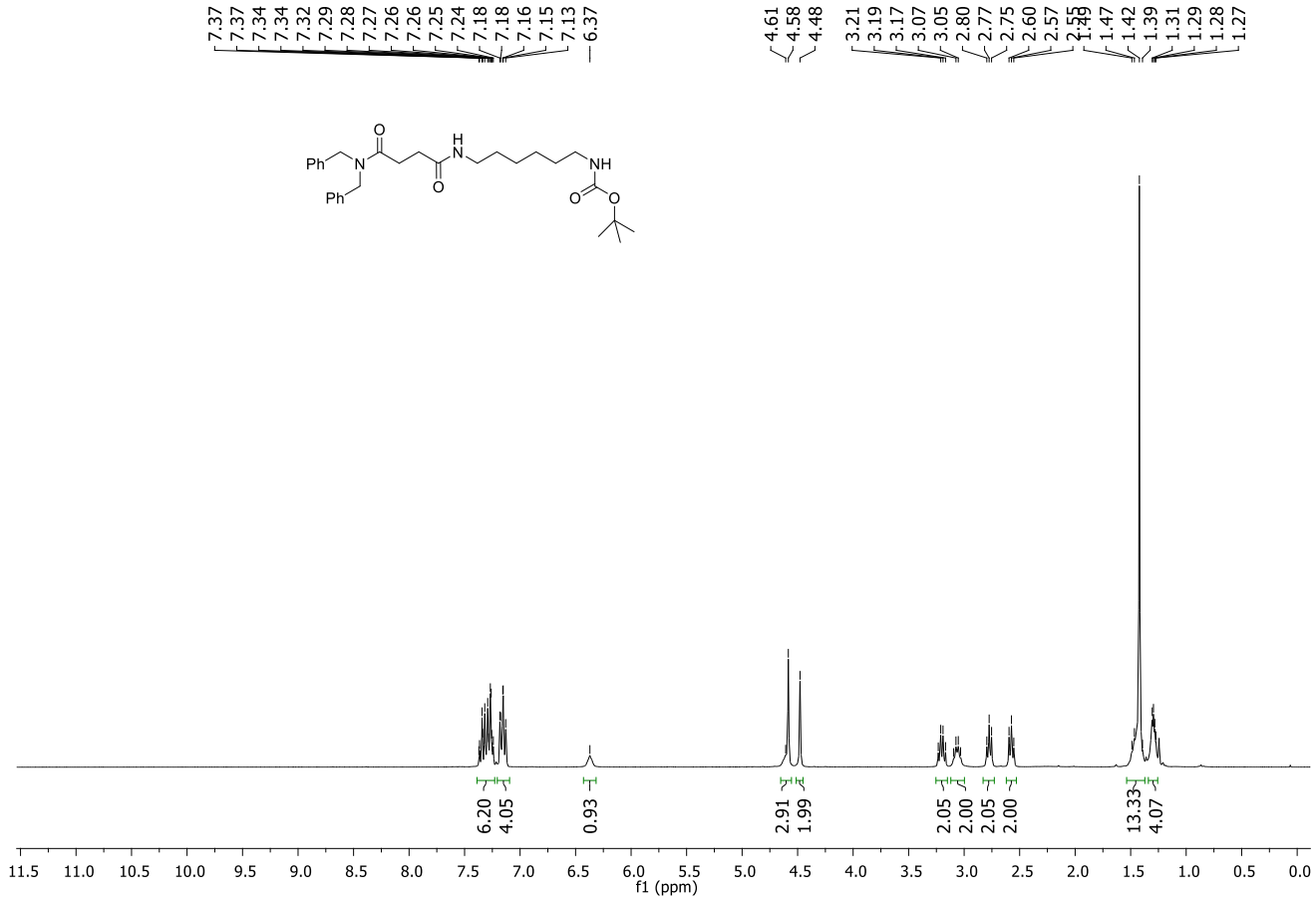


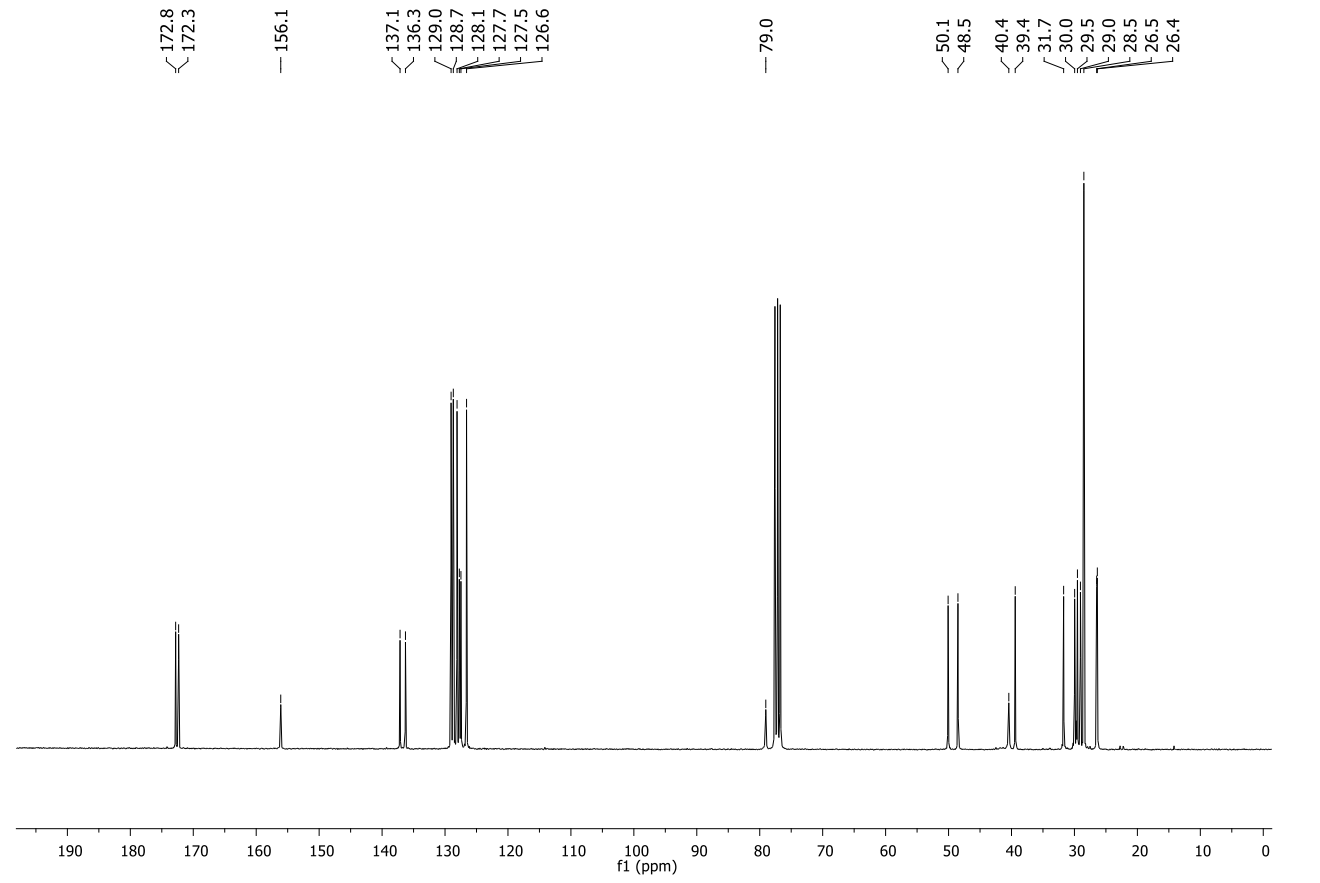
Figure S37. ^{1}H NMR spectra (400MHz, $CDCl_3$, 298K) of the reaction between cinnamaldehyde **4b** (blue) and acetylacetone **5a** (green) to the formation of adduct **6ba**[5] (yellow).

17. ^{1}H and ^{13}C NMR Spectra of synthesized compounds

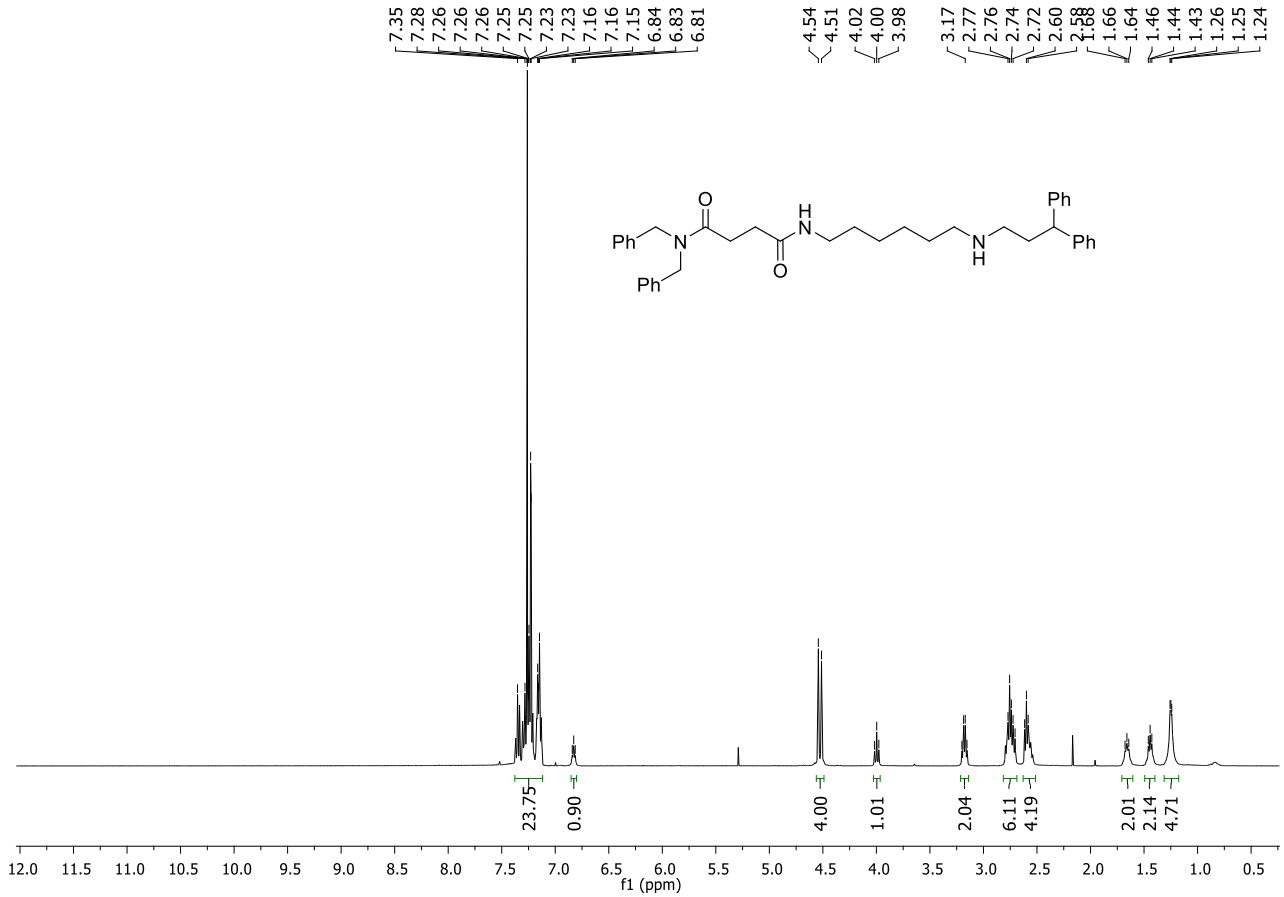
S2a (^{1}H NMR, 300 MHz, $CDCl_3$, 298 K)



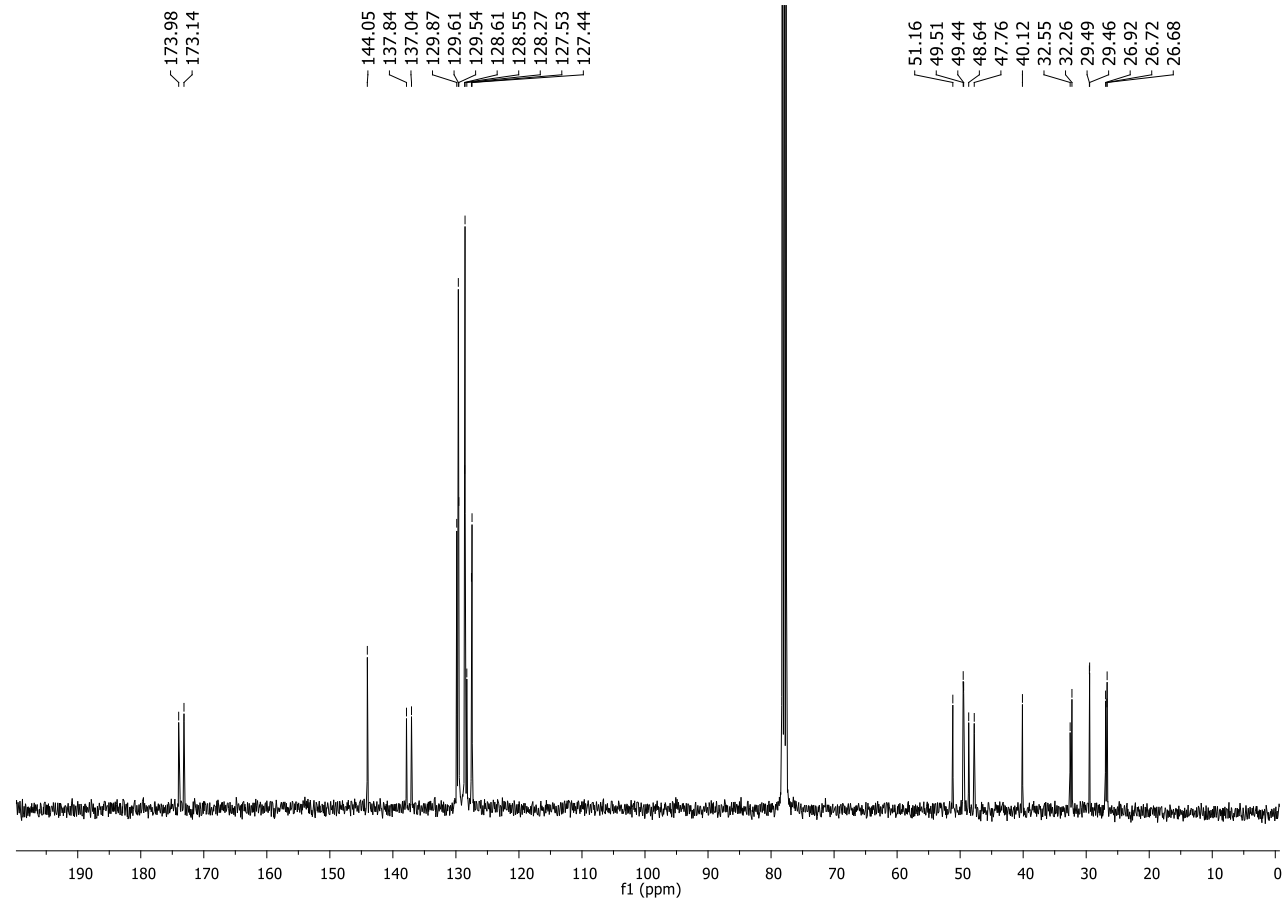
S2a (^{13}C NMR, 75 MHz, $CDCl_3$, 298 K)



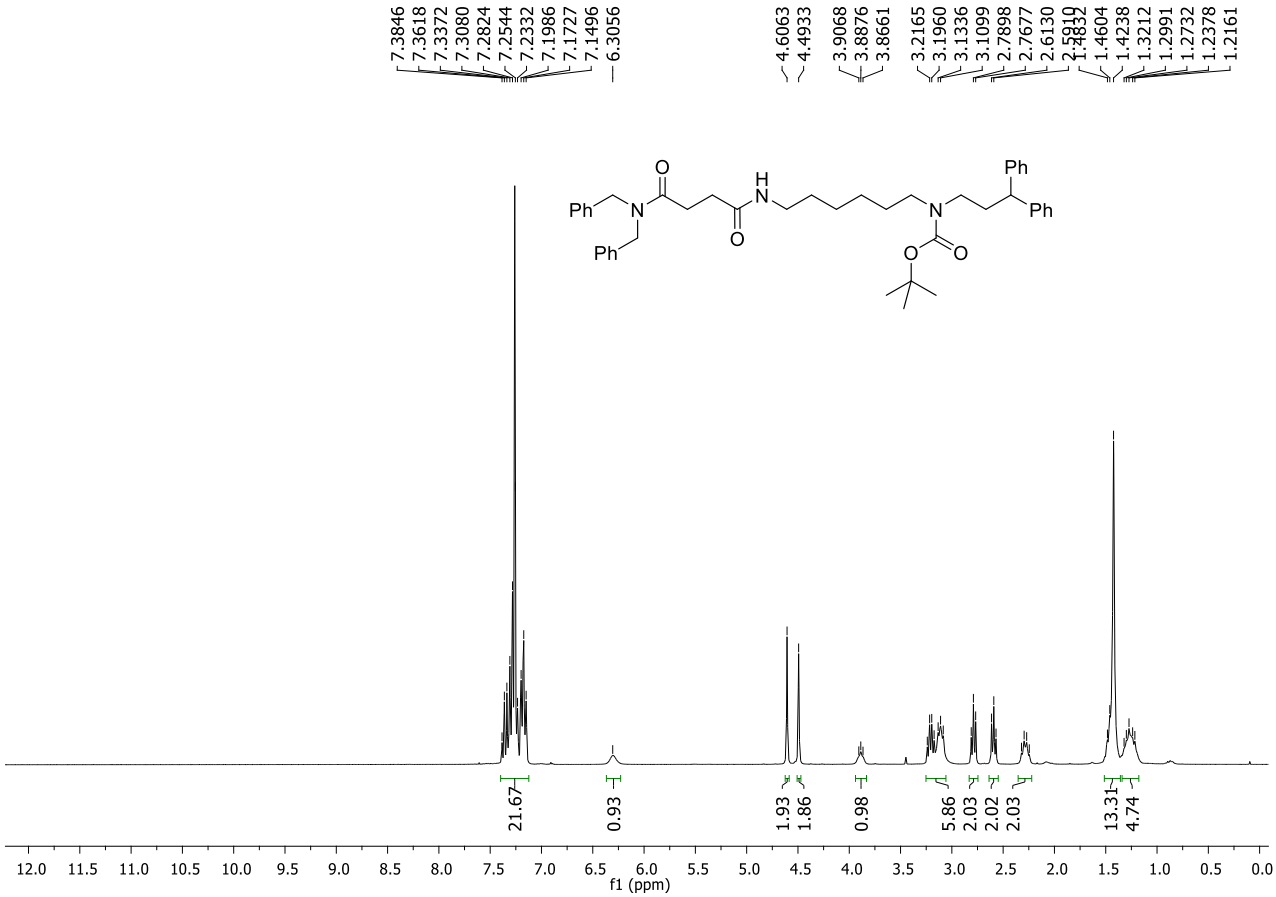
1a (^{1}H NMR, 400 MHz, $CDCl_3$, 298 K)



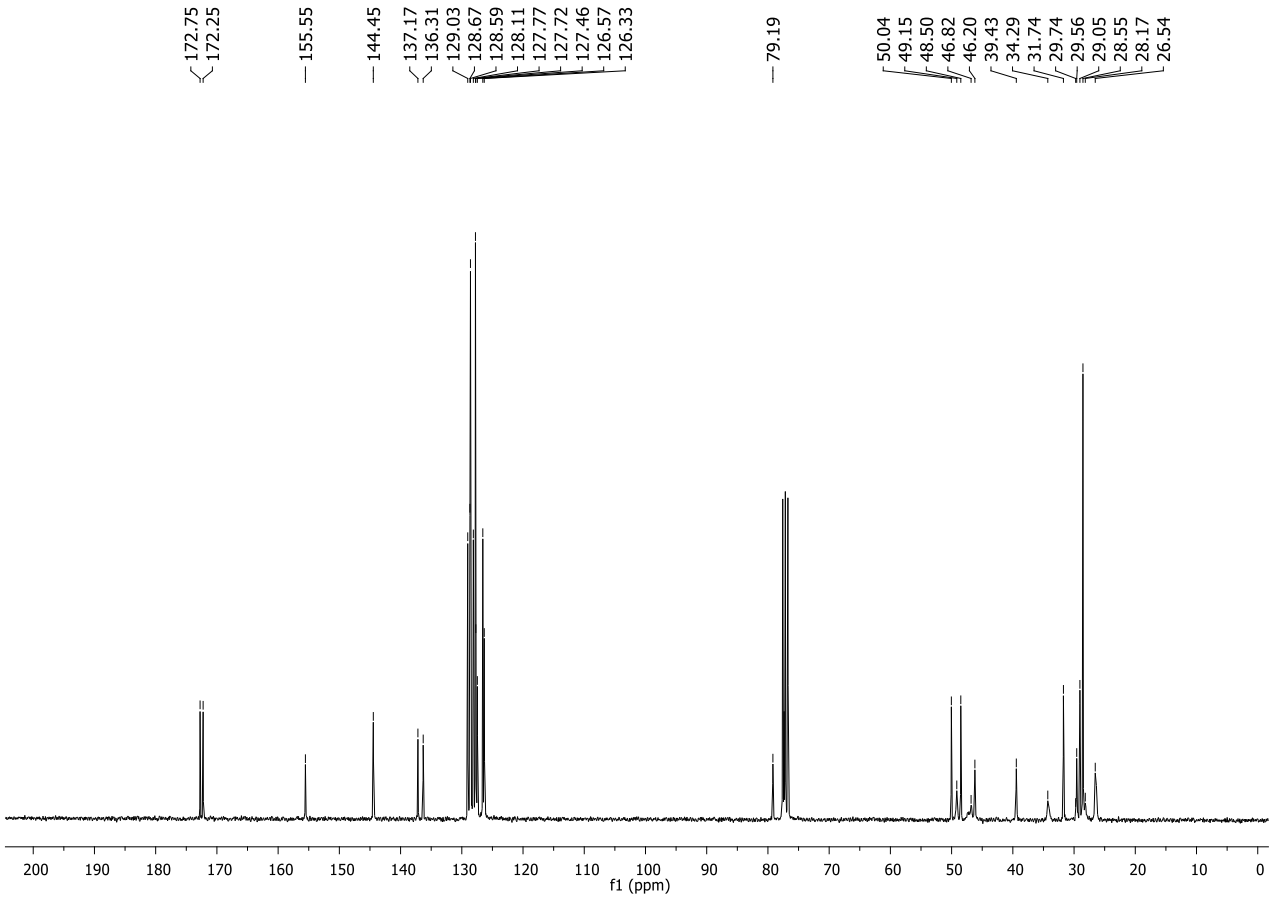
1a (^{13}C NMR, 100 MHz, $CDCl_3$, 298 K)



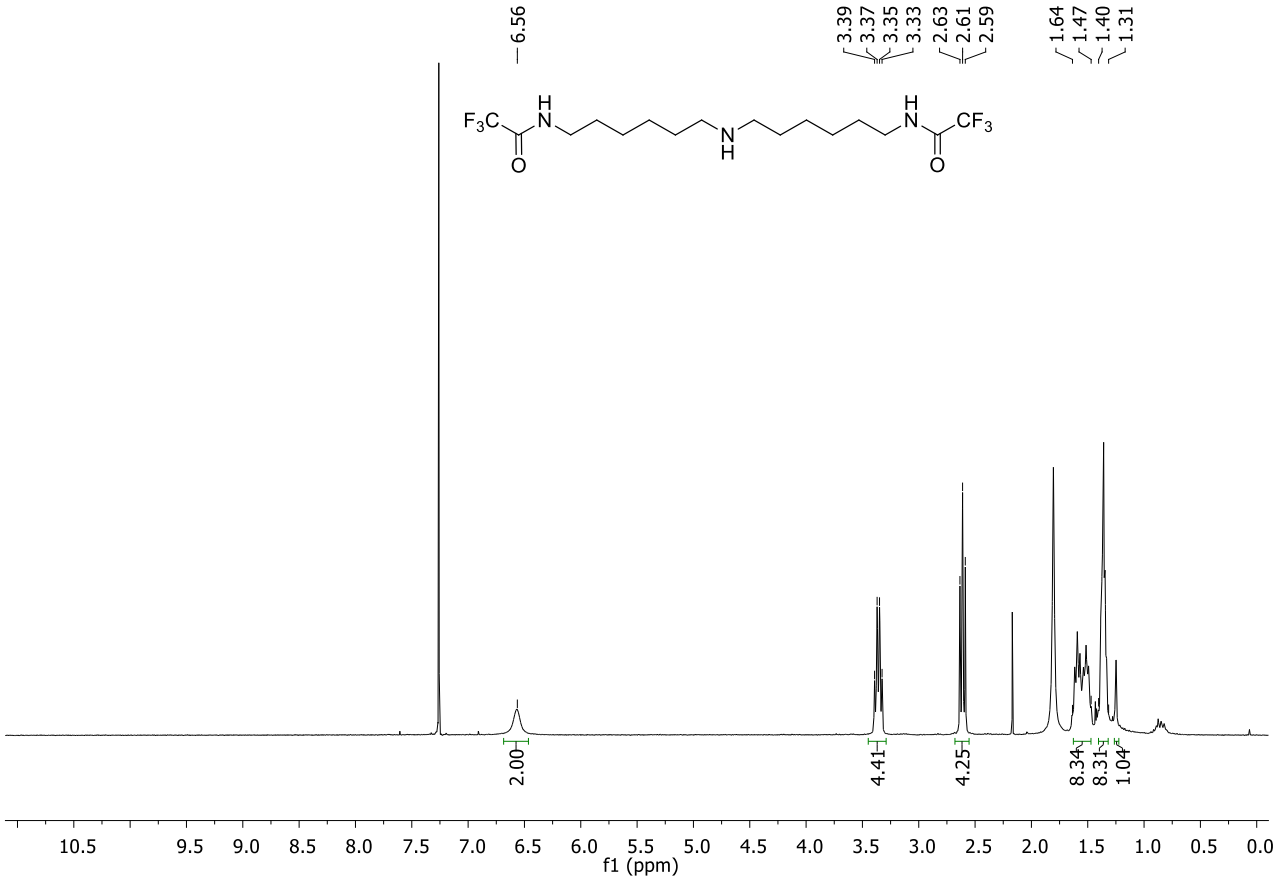
Boc1a (^{1}H NMR, 300 MHz, $CDCl_3$, 298 K)



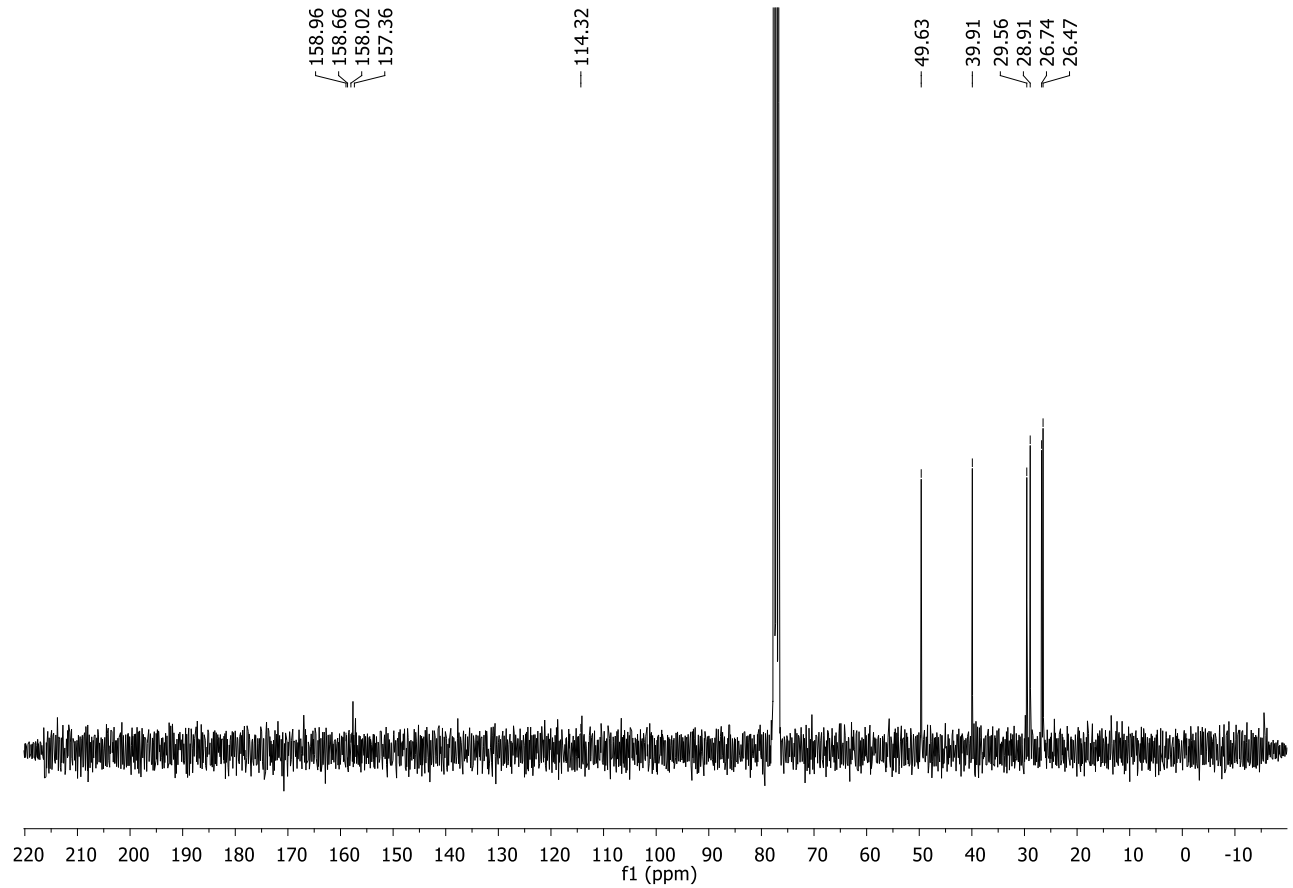
Boc1a (^{13}C NMR, 75 MHz, $CDCl_3$, 298 K)



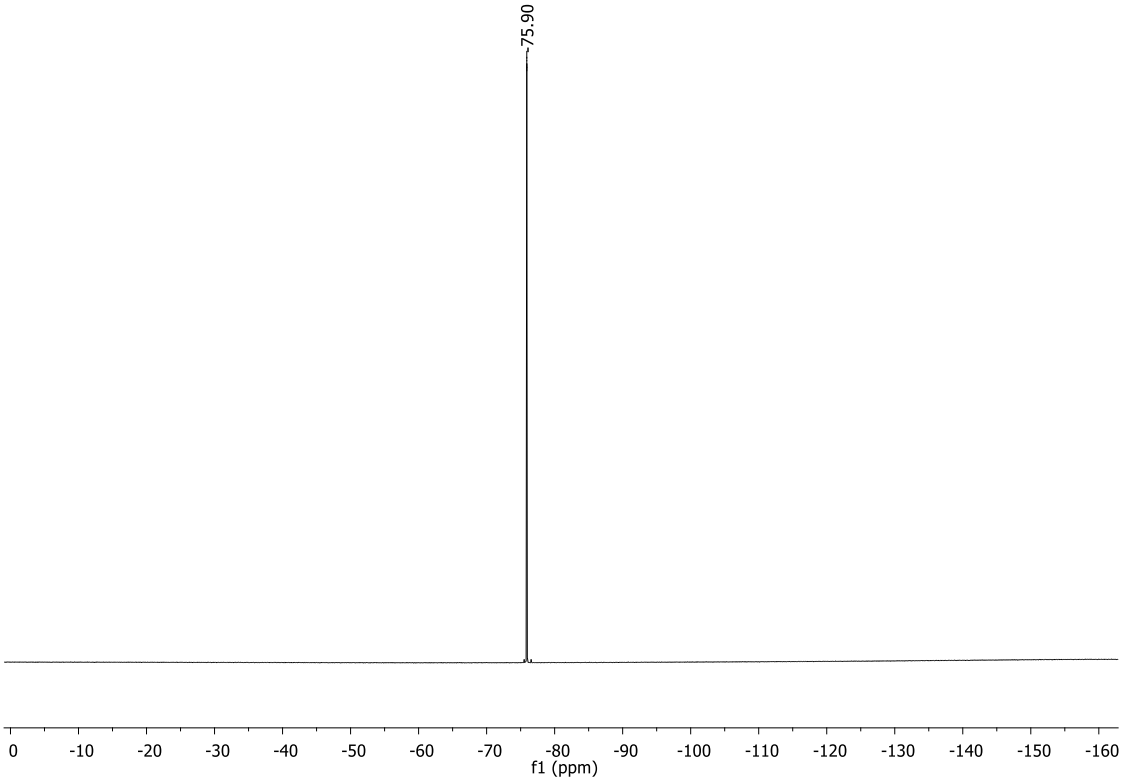
S2b (^{1}H NMR, 300 MHz, $CDCl_3$, 298 K)



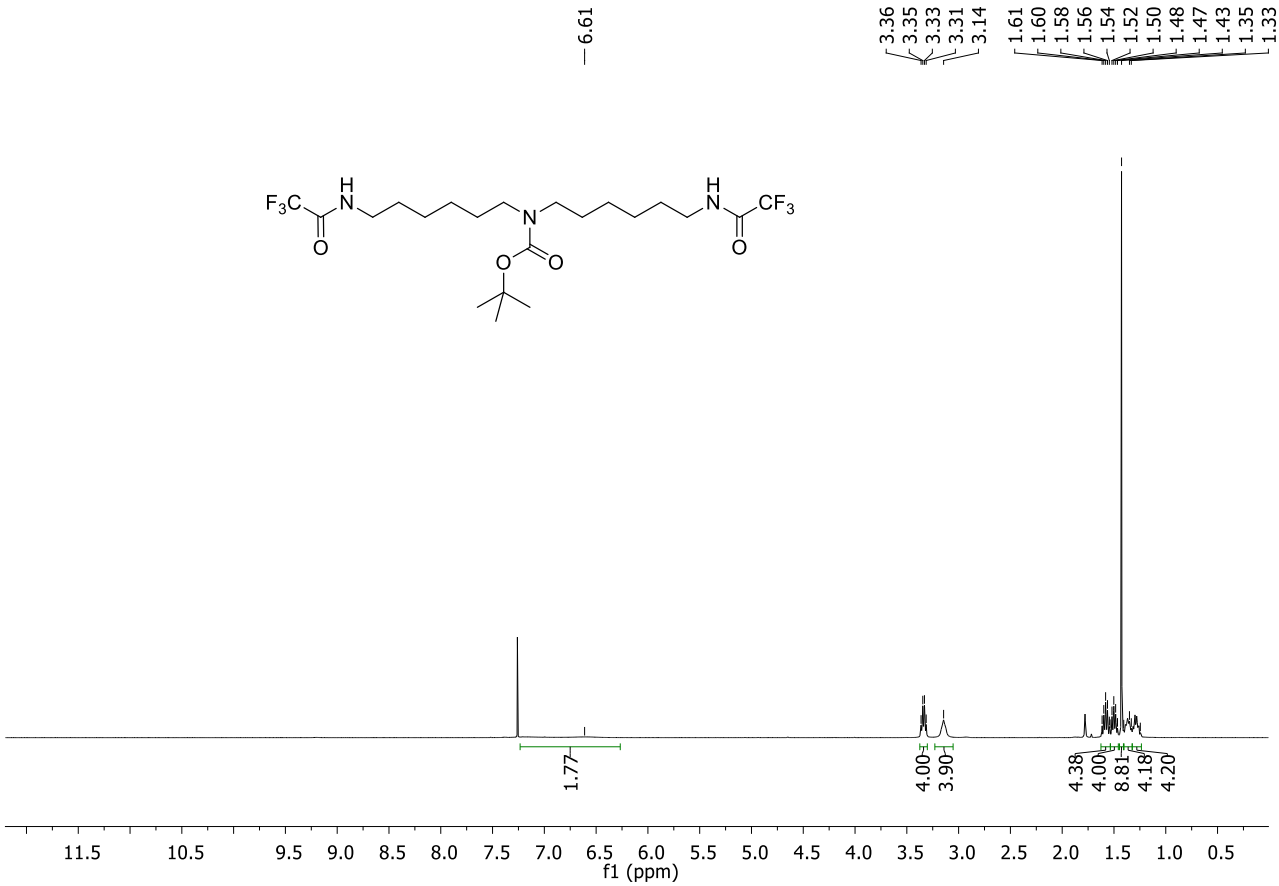
S2b (^{13}C NMR, 75 MHz, $CDCl_3$, 298 K)



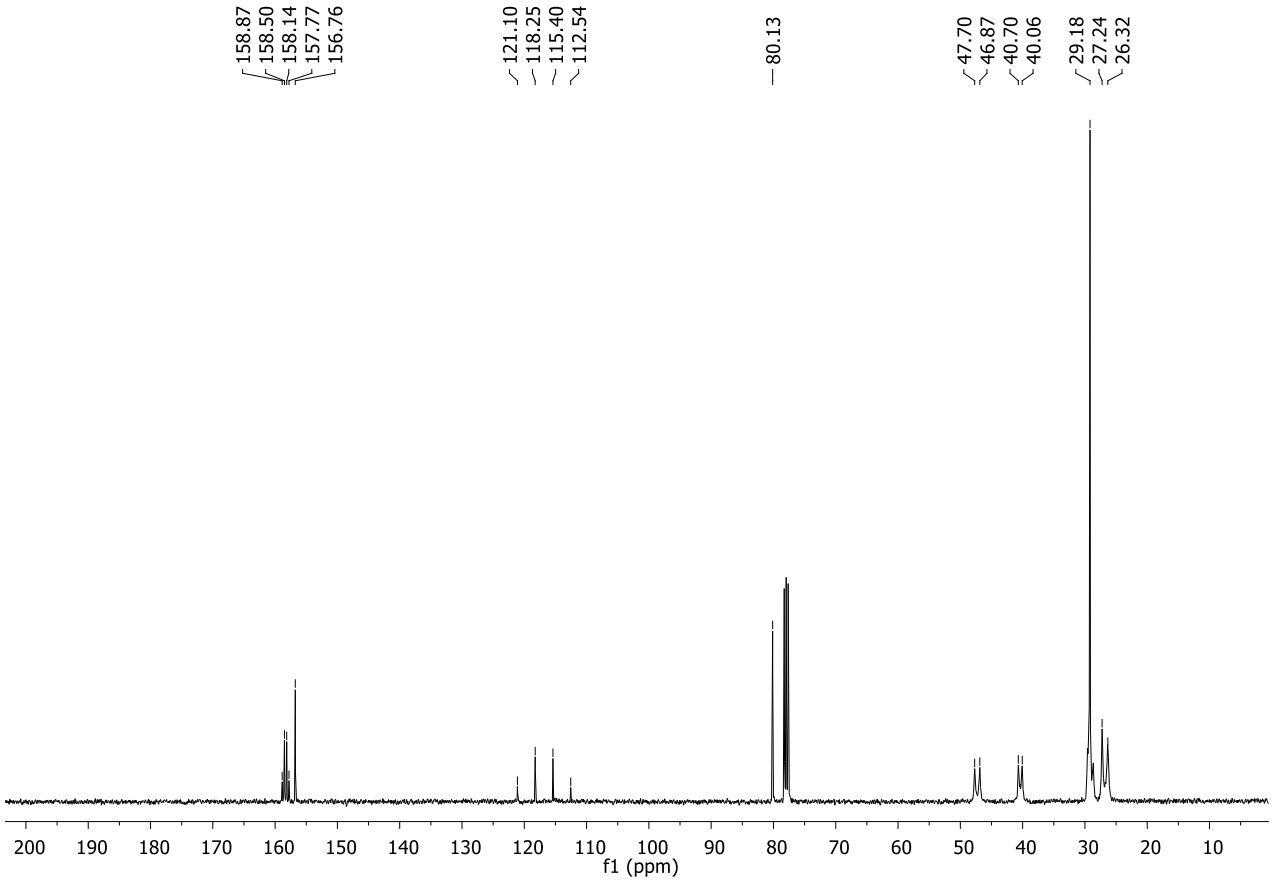
S2b (^{19}F NMR, 282 MHz, $CDCl_3$, 298 K)


-75.90
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

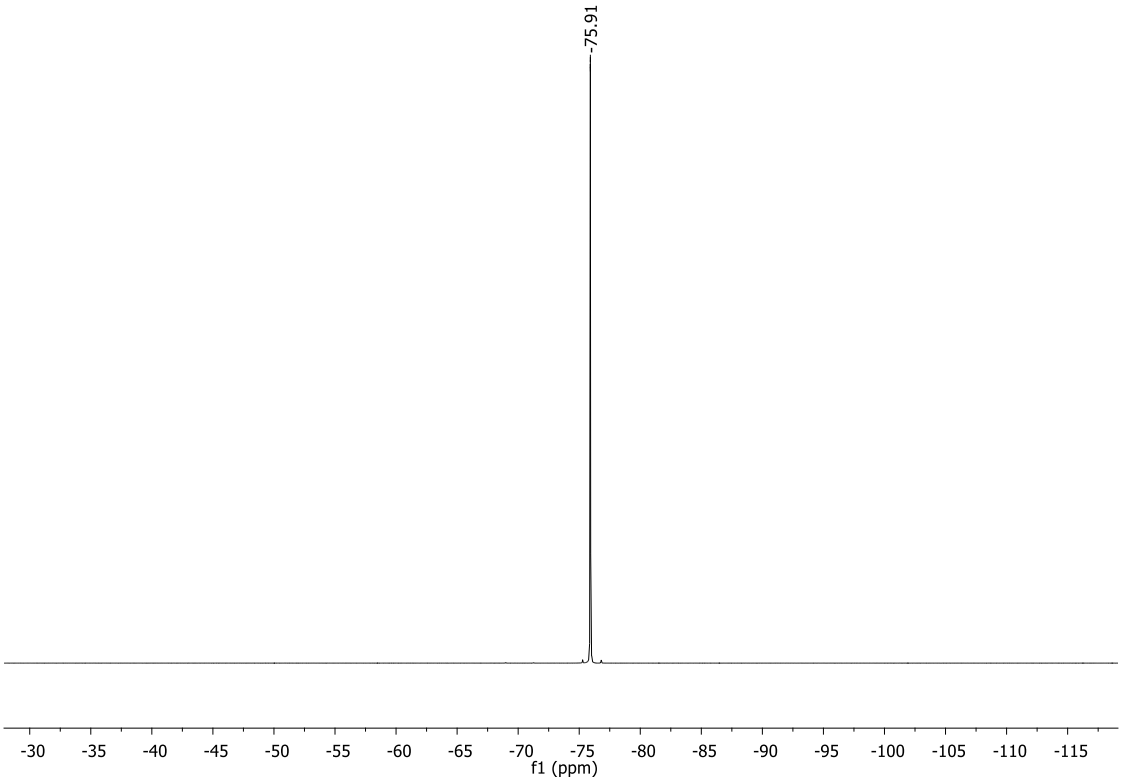
S3b (^{1}H NMR, 300 MHz, $CDCl_3$, 298 K)



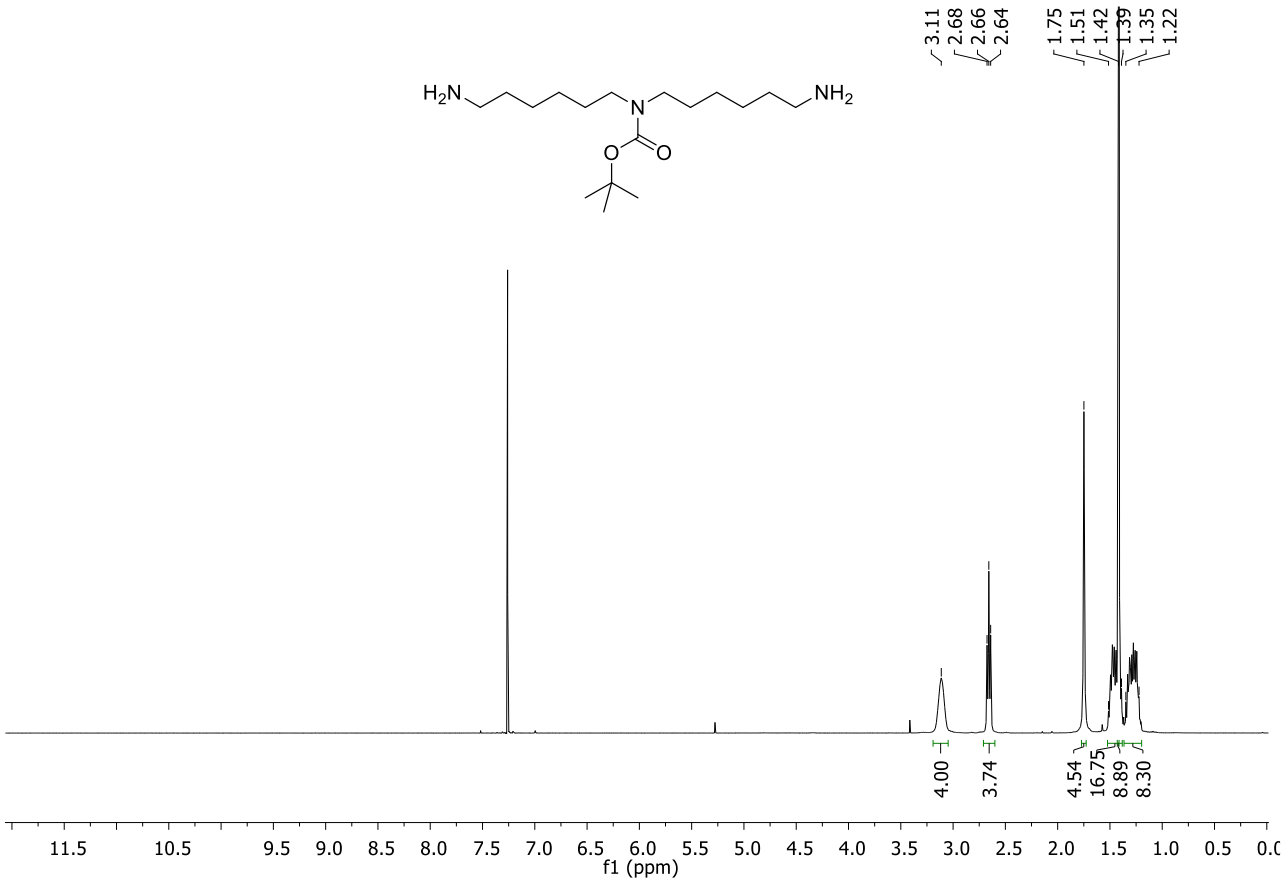
S3b (^{13}C NMR, 75 MHz, $CDCl_3$, 298 K)



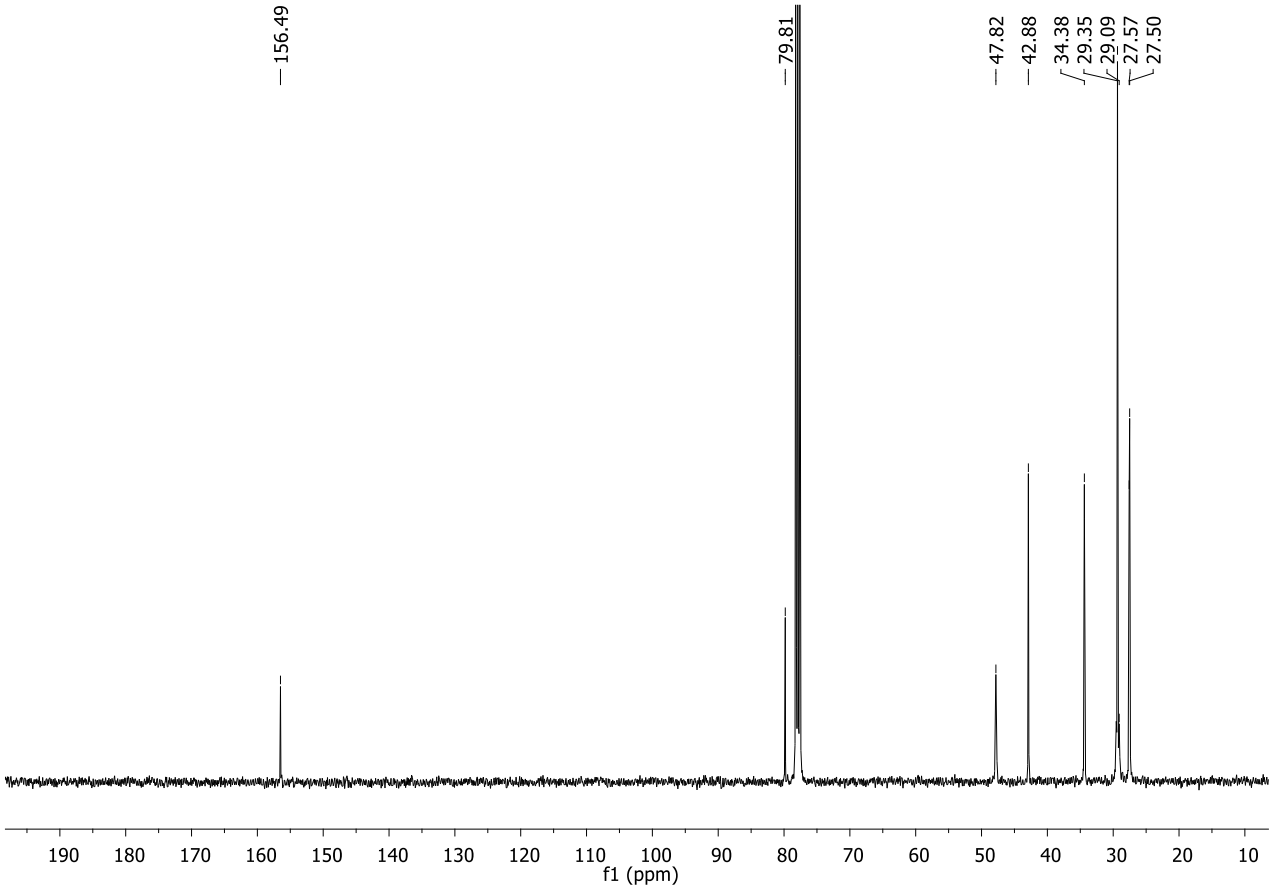
S3b (^{19}F NMR, 282 MHz, $CDCl_3$, 298 K)



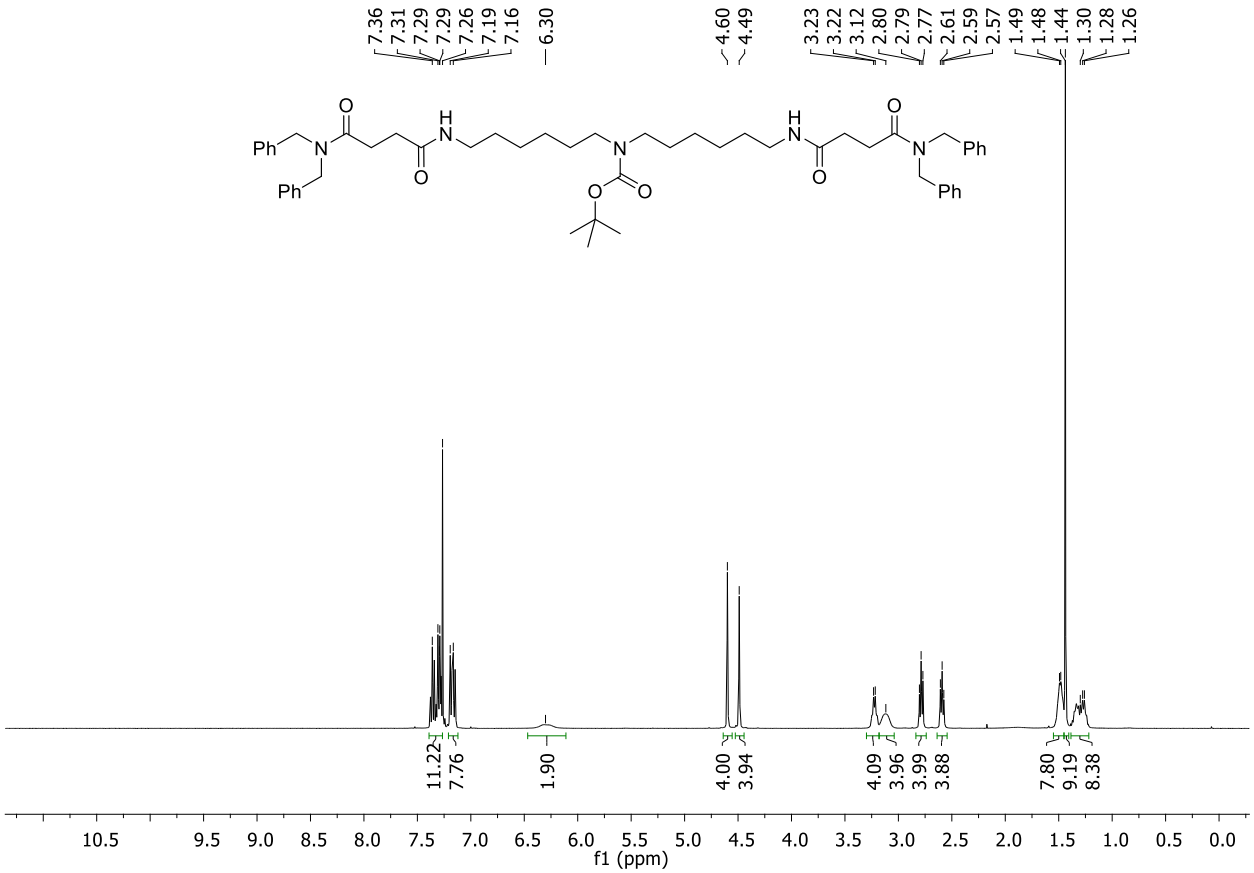
S4b (^{1}H NMR, 400 MHz, $CDCl_3$, 298 K)



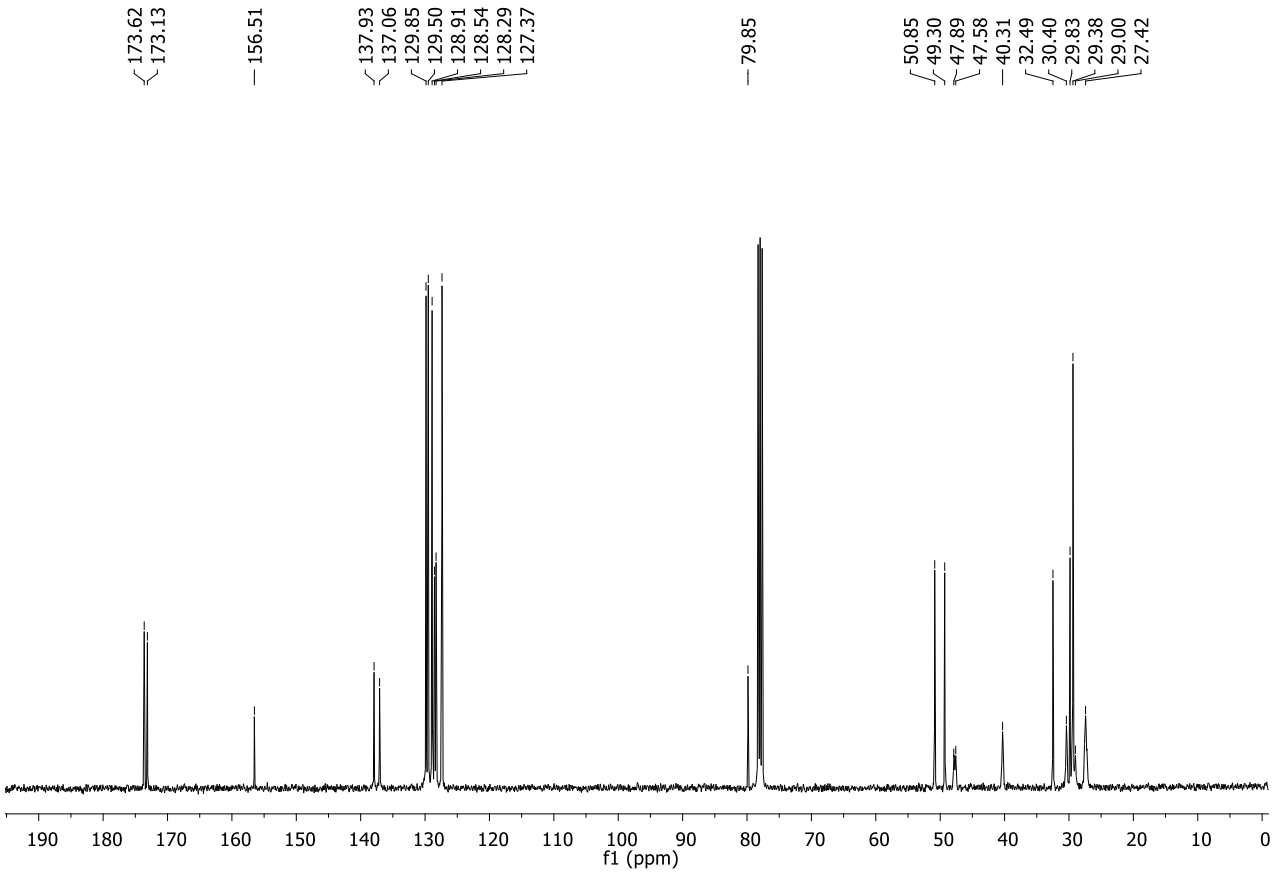
S4b (^{13}C NMR, 100 MHz, $CDCl_3$, 298 K)



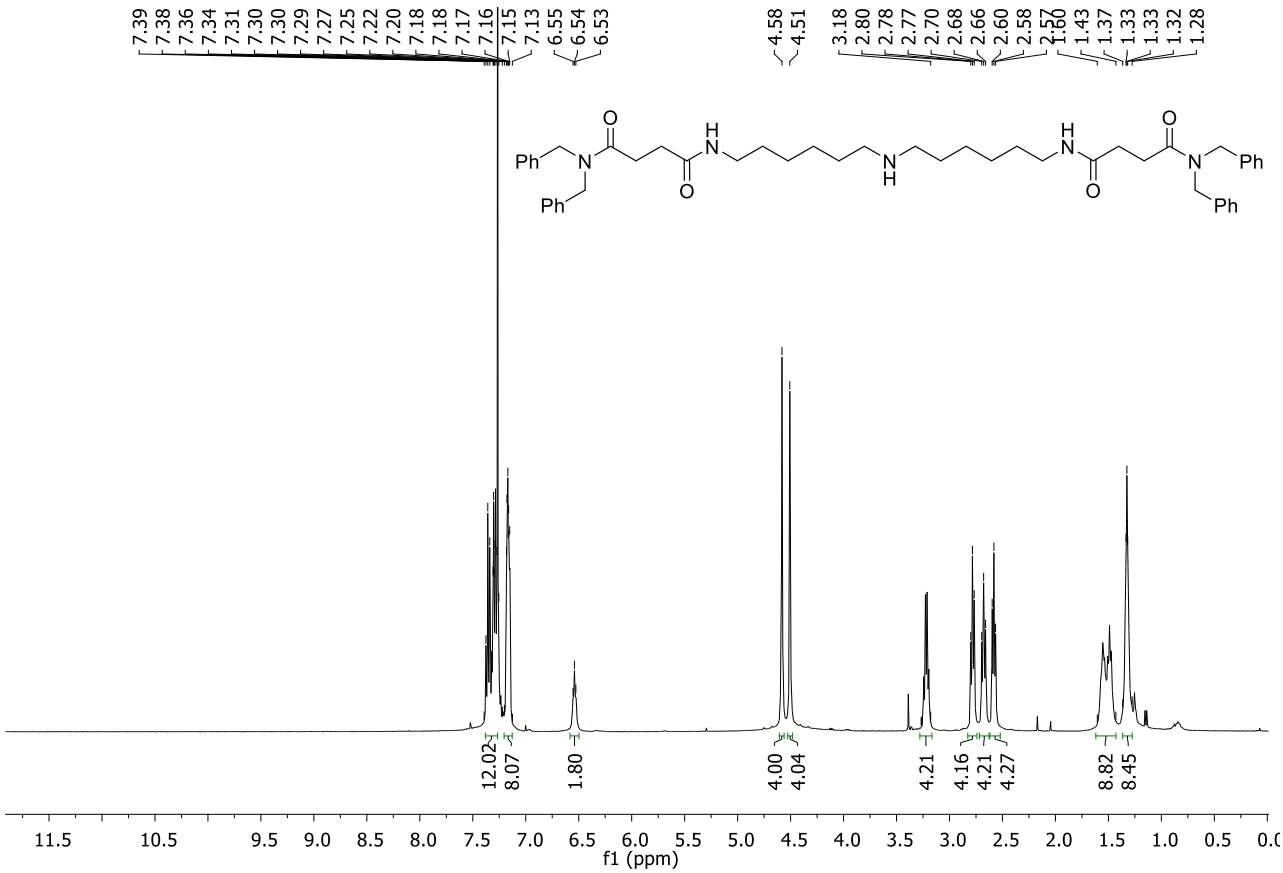
Boc1b (^{1}H NMR, 400 MHz, $CDCl_3$, 298 K)



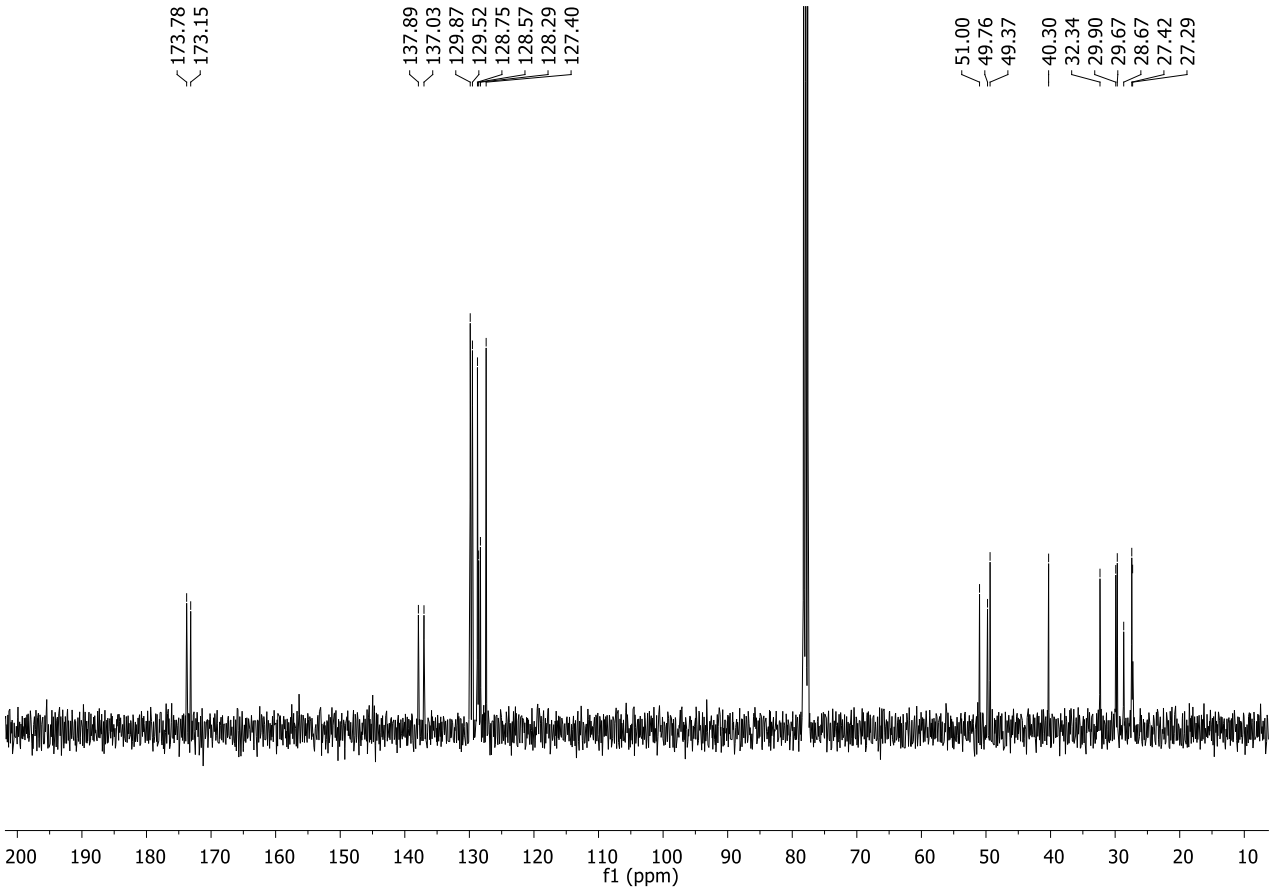
Boc1b (^{13}C NMR, 100 MHz, $CDCl_3$, 298 K)



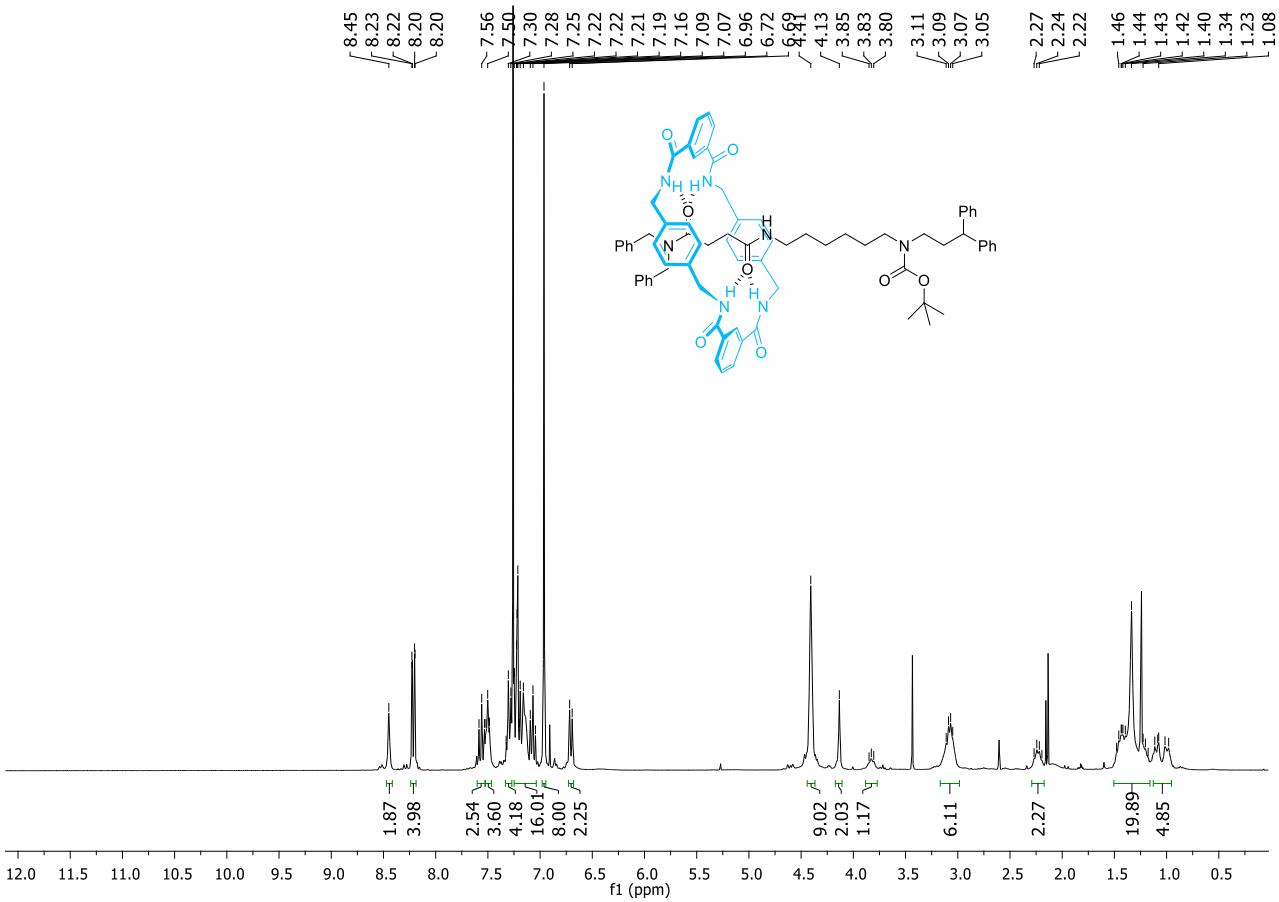
1b (^{1}H NMR, 400 MHz, $CDCl_3$, 298 K)



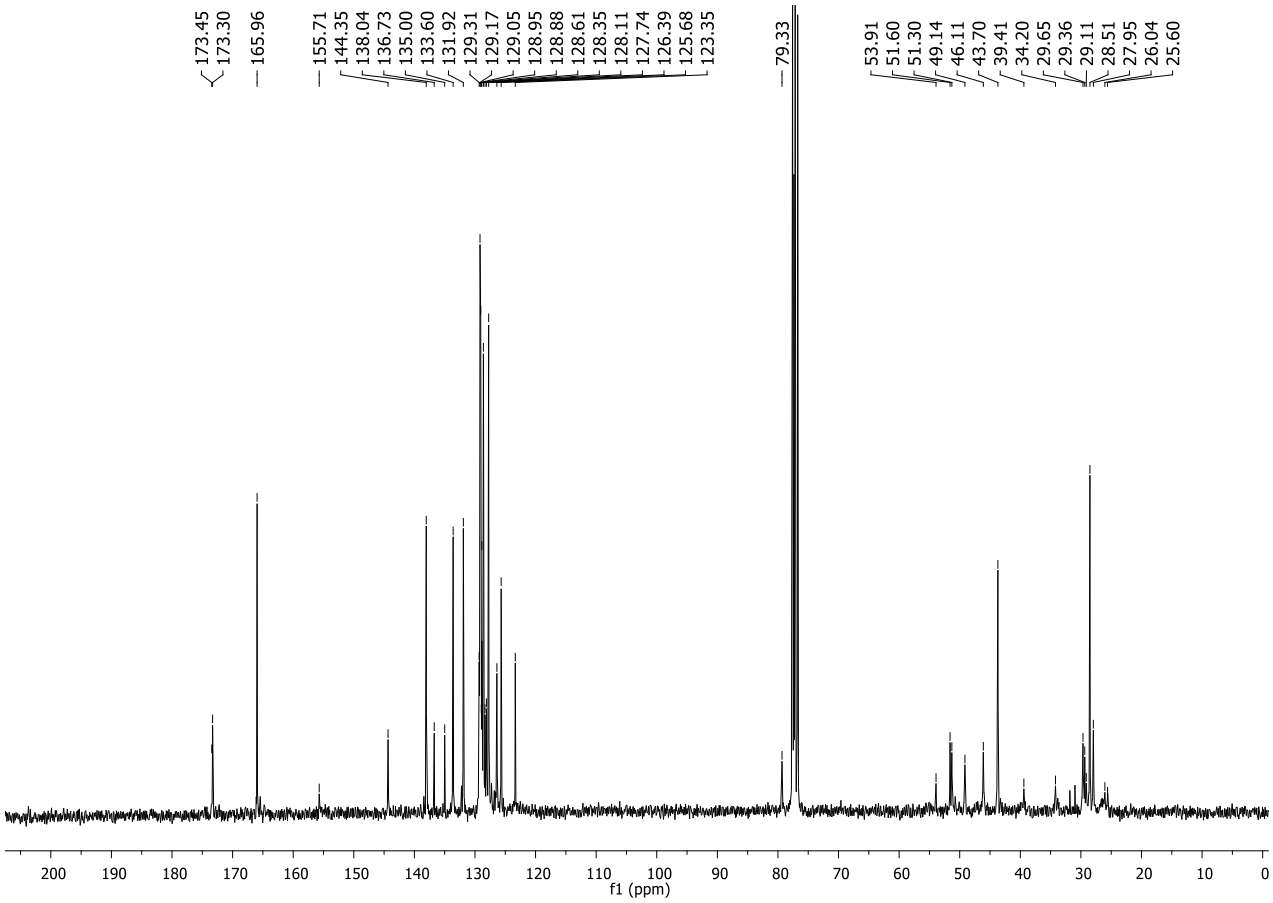
1b (^{13}C NMR, 100 MHz, $CDCl_3$, 298 K)



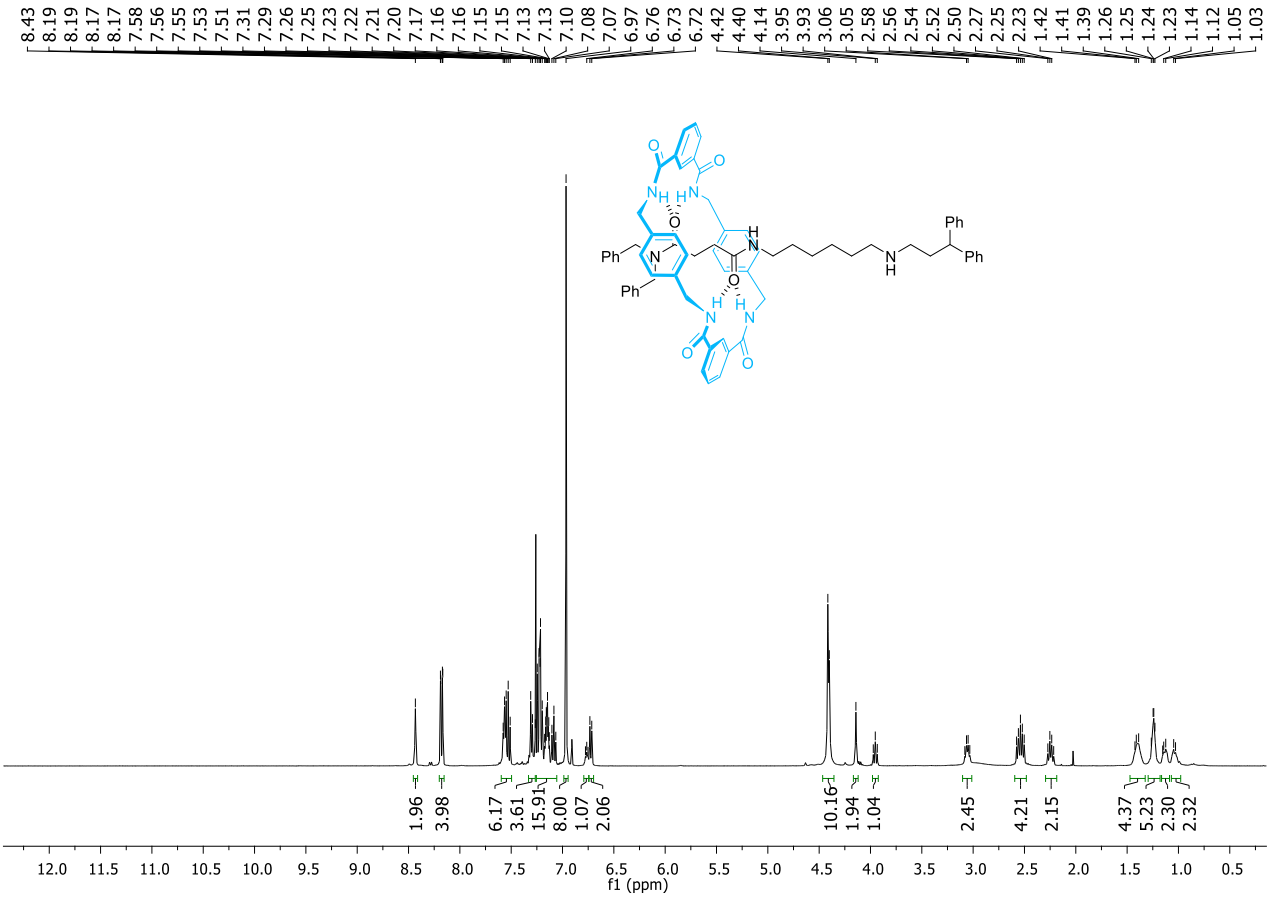
Boc2a (^{1}H NMR, 300 MHz, $CDCl_3$, 298 K)



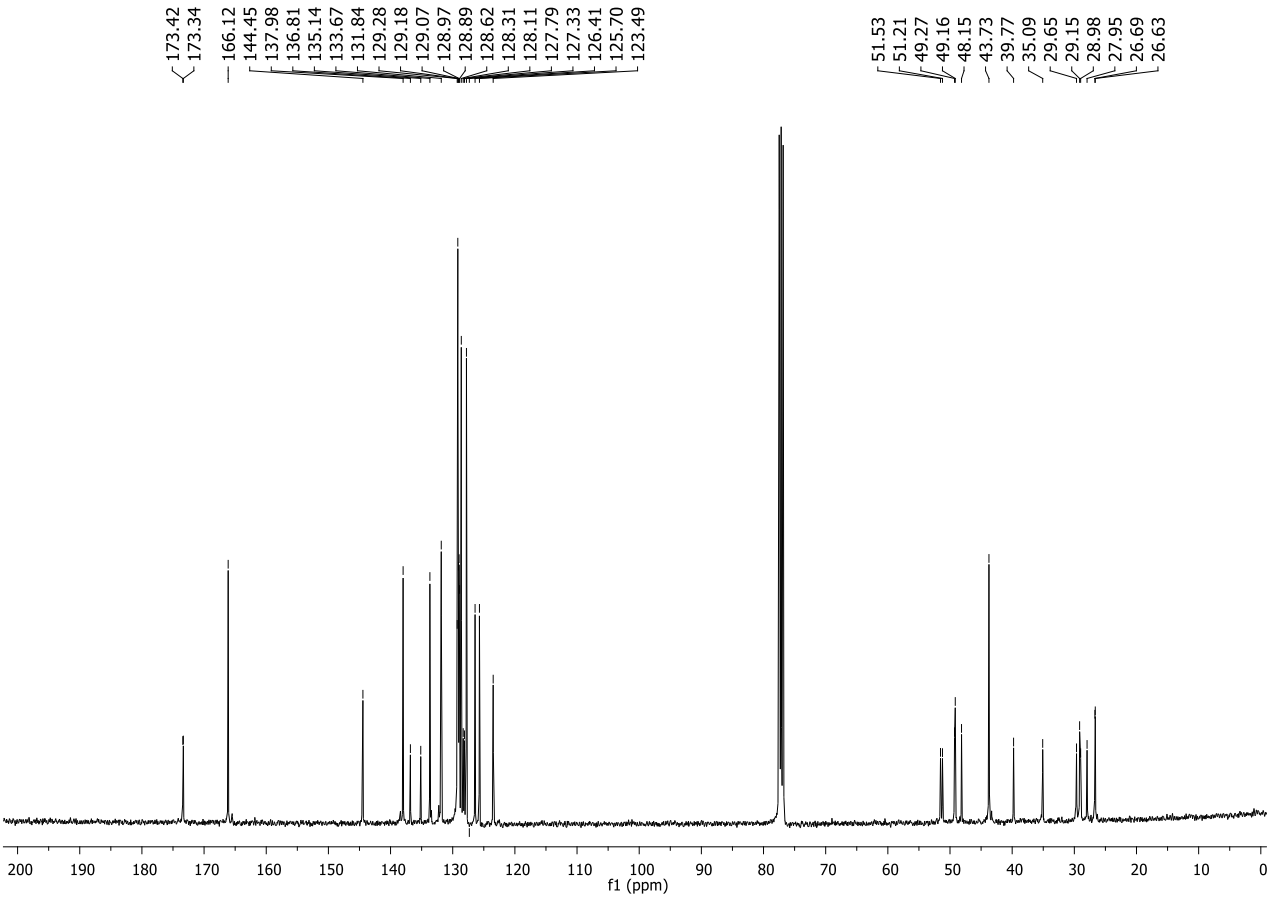
Boc2a (^{13}C NMR, 75 MHz, $CDCl_3$, 298 K)



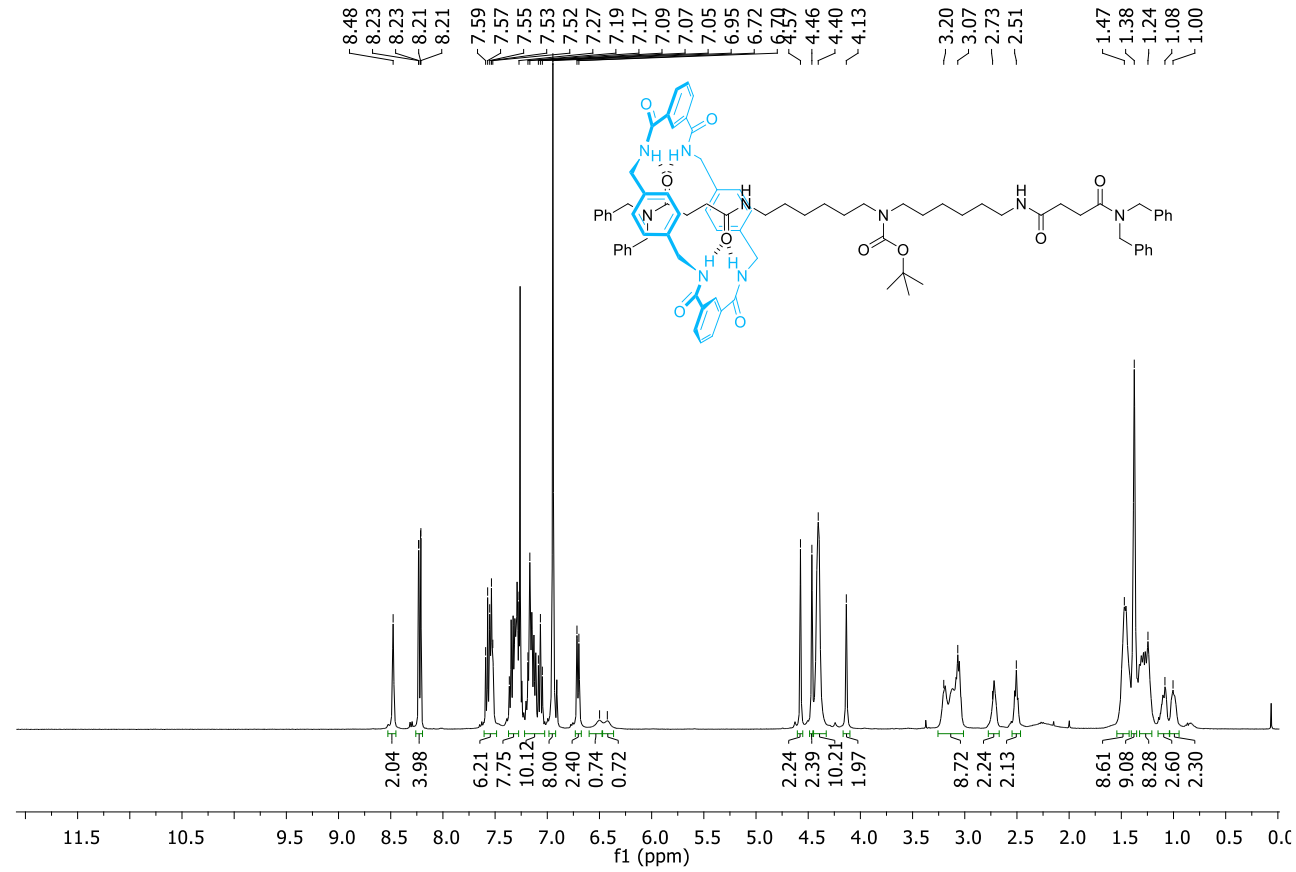
2a (^{1}H NMR, 400 MHz, $CDCl_3$, 298 K)



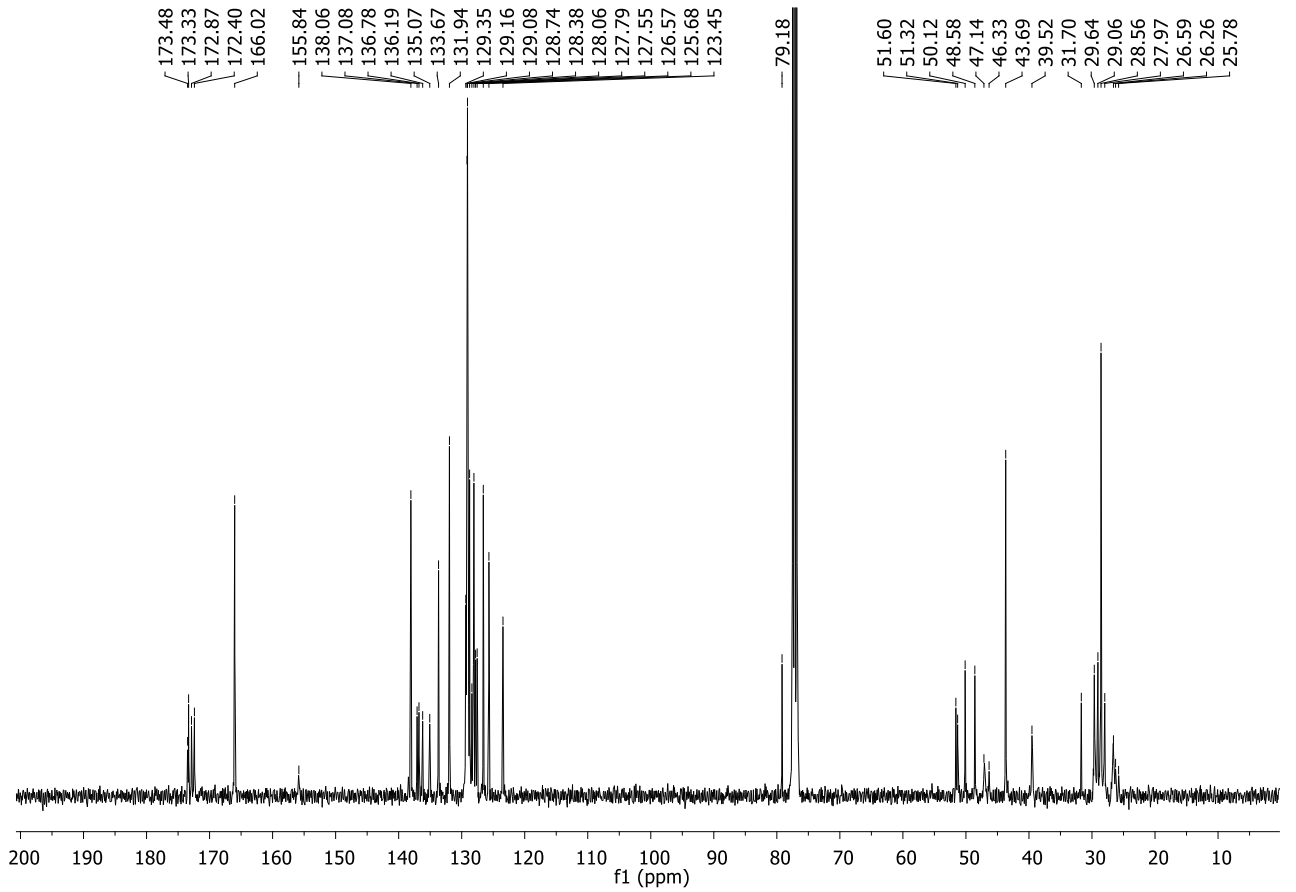
2a (^{13}C NMR, 100 MHz, $CDCl_3$, 298 K)



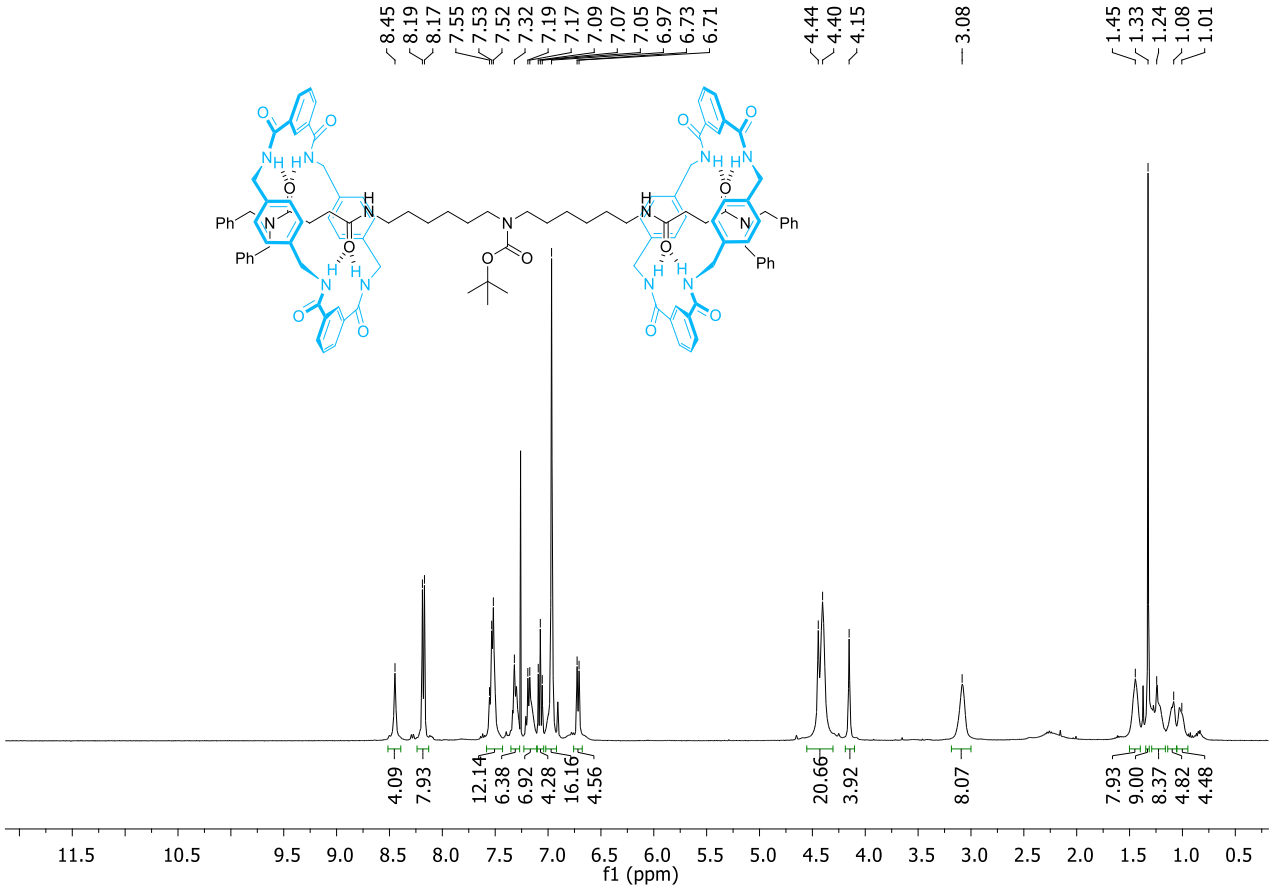
Boc2b (^{1}H NMR, 400 MHz, $CDCl_3$, 298 K)



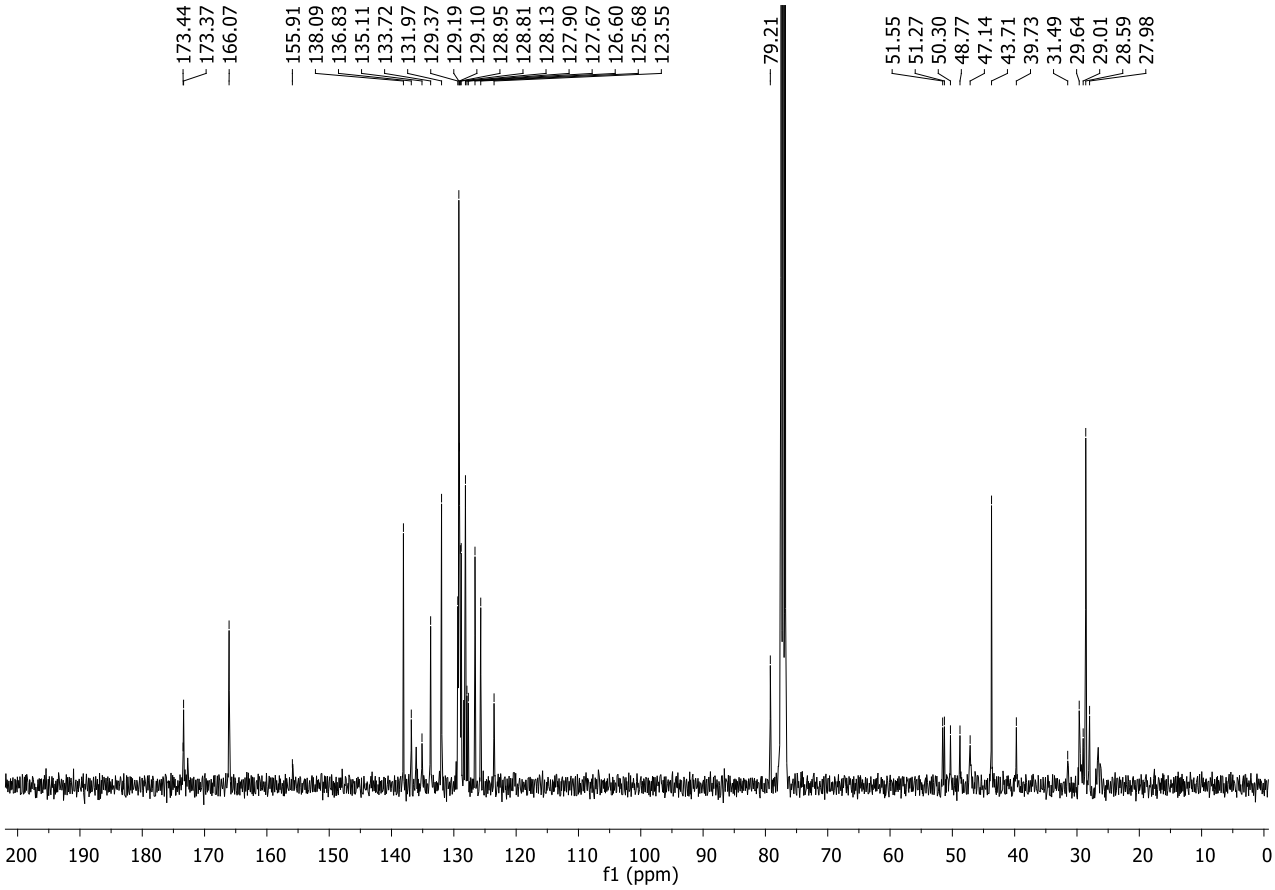
Boc2b (^{13}C NMR, 100 MHz, $CDCl_3$, 298 K)



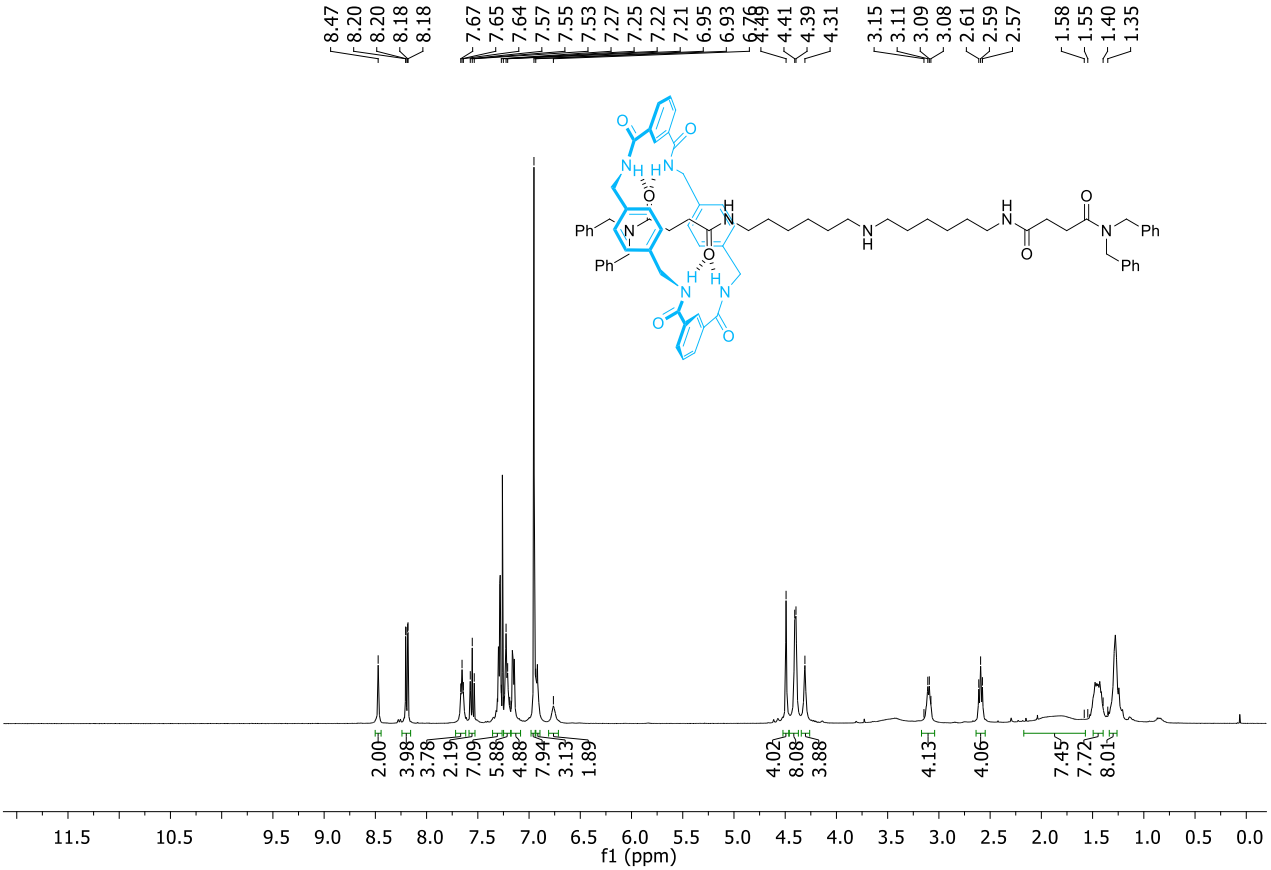
Boc3b (^{1}H NMR, 400 MHz, $CDCl_3$, 298 K)



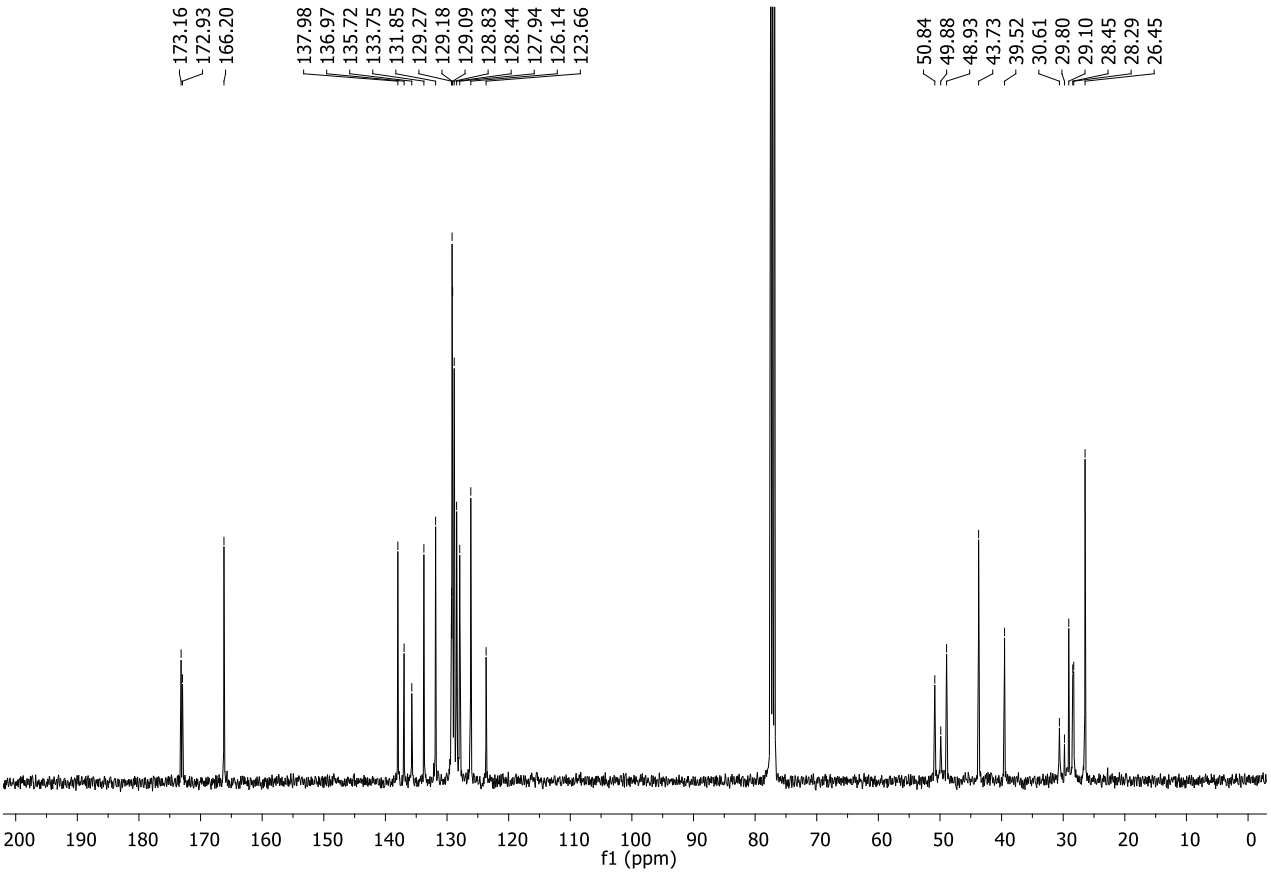
Boc3b (^{13}C NMR, 100 MHz, $CDCl_3$, 298 K)



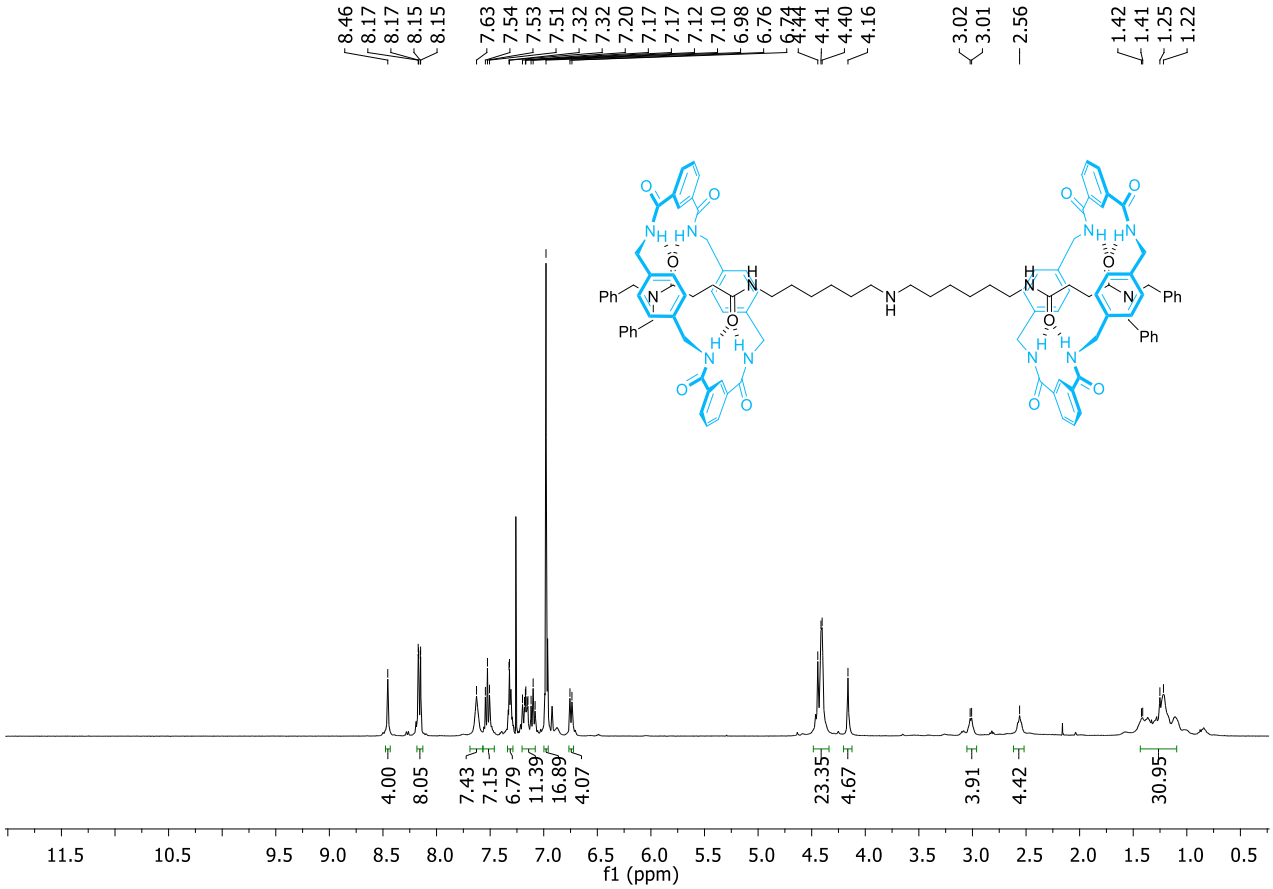
2b (^{1}H NMR, 400 MHz, $CDCl_3$, 298 K)



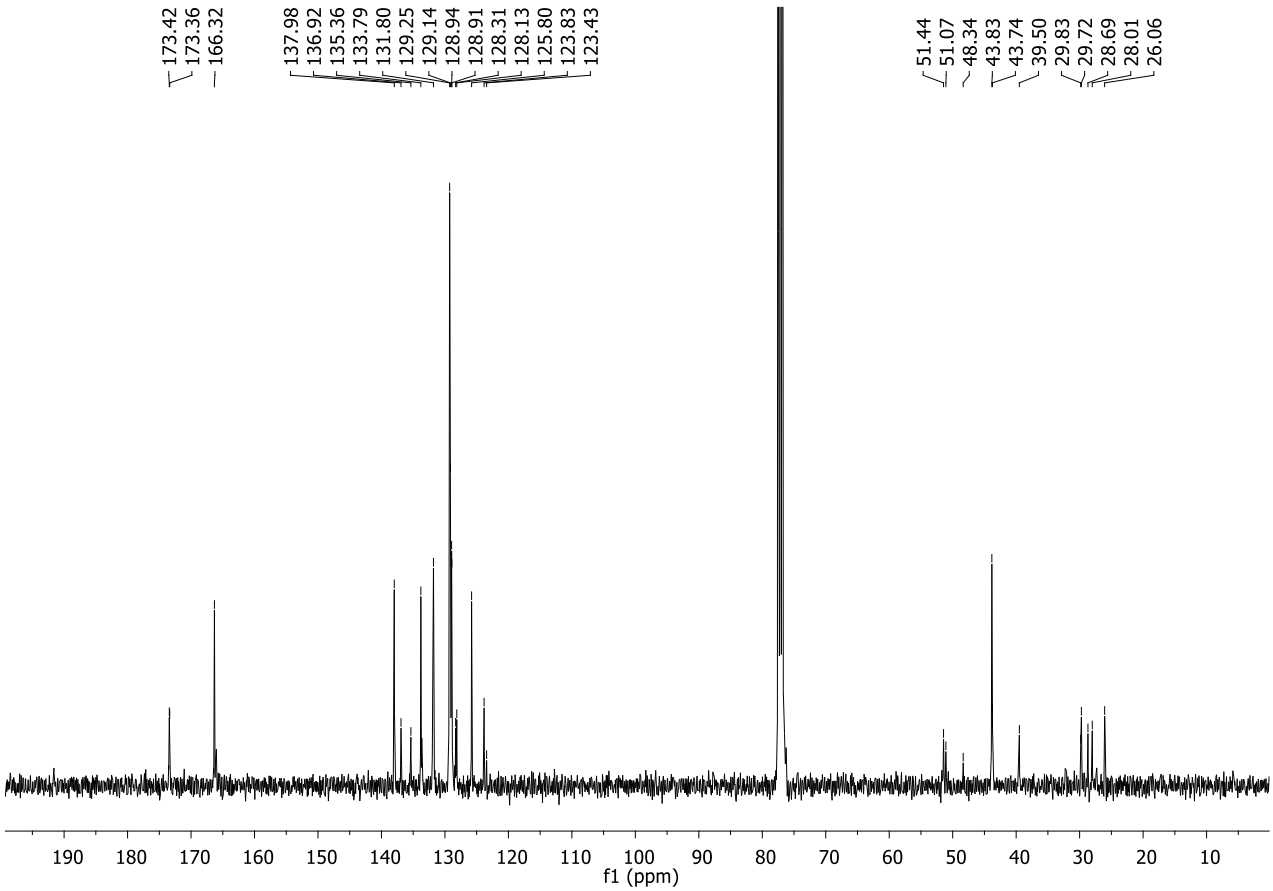
2b (^{13}C NMR, 100 MHz, $CDCl_3$, 298 K)



3b (^{1}H NMR, 400 MHz, $CDCl_3$, 298 K)



3b (^{13}C NMR, 100 MHz, $CDCl_3$, 298 K)



18. References

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[3] A. Martinez-Cuezva, C. Lopez-Leonardo, D. Bautista, M. Alajarin, J. Berna, *J. Am. Chem. Soc*. **2016**, *138*, 8726–8729.

[4] J. Beswick, V. Blanco, G. D. Bo, D. A. Leigh, U. Lewandowska, B. Lewandowski, K. Mishiro, *Chem. Sci.* **2015**, *6*, 140–143.

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