Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Dual-stimuli pseudorotaxane switches under kinetic control

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1. Experimental details

1.1. General methods

All reagents and solvents were obtained from commercial sources and used without further purification. Dry solvents were purchased from Acros Organics (Geel, Belgium) and either directly used or treated with the M. Braun solvent purification system SPS 800. **TTFC8**,[1] 2,6-dimethoxybenzonitrile oxide stopper **St1**,[2] (2,6-dimethylphenyl)methanaminium chloride,[3] (3,5-di-*tert*-butylphenyl)methanamine **1**,[4] 5-hexynyl tosylate **4**,[5] 4-(hex-5-yn-1-yloxyl)benzonitrile **S2**,[6] were synthesised according to literature procedures, naphthalen-2-ylmethanaminium hydrochloride was bought at Fluorochem (Hadfield, U.K.), 3,5-di-*tert*-butylbenzaldehyde, 2-methylbenzylamine hydrochloride, 3-methylbenzylamine hydrochloride, (3-phenylphenyl)methanamine hydrochloride, 2-naphthylmethanamine hydrochloride, 2,3-dimethylbenzylamine, 2,5-dimethylbenzylamine, 2-nitrobenzylamine hydrochloride, 2-ethylbenzylamine hydrochloride, sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($NaBArF_{24}$), 6-hydroxy-1-naphthoic acid **2**, benzotriazol-1-ol (HOBT), 3-(ethyliminomethyleneamino)-*N*,*N*-dimethylpropan-1-amine hydrochloride (EDC·HCl), *N*-ethyl-*N*-(propan-2-yl)propan-2-amine (DIPEA) and polystyrene-immobilized phosphazene base P2 were bought at Sigma Aldrich (Taufkirchen, Germany) or TCI Chemicals (Eschborn, Germany). Thin-layer chromatography was performed on silica gel-coated plates with fluorescent indicator F254 (Merck KGaA, Darmstadt, Germany). For column chromatography, silica gel (0.04-0.063 mm, Merck), or Biotage (Uppsala, Sweden) SNAP and SNAP Ultra Cartridges were used on a Biotage Isolera One.

^{1}H and ^{13}C NMR experiments were performed on JEOL ECX 400, JEOL ECZ 600, Bruker AVANCE 500 or Bruker AVANCE 700 instruments. Residual solvent signals were used as the internal standards. All shifts are reported in ppm and NMR multiplicities are abbreviated as s (singlet), d (doublet), t (triplet), m (multiplet) and br (broad). Coupling constants *J* are reported in Hertz. Compounds containing the tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($BArF_{24}^{-}$) anion show ^{13}C NMR spectra with ^{19}F, ^{10}B and ^{11}B couplings. These signals are denoted as one signal.

Melting points were determined on a SMP 30 (Stuart) instrument and are uncorrected.

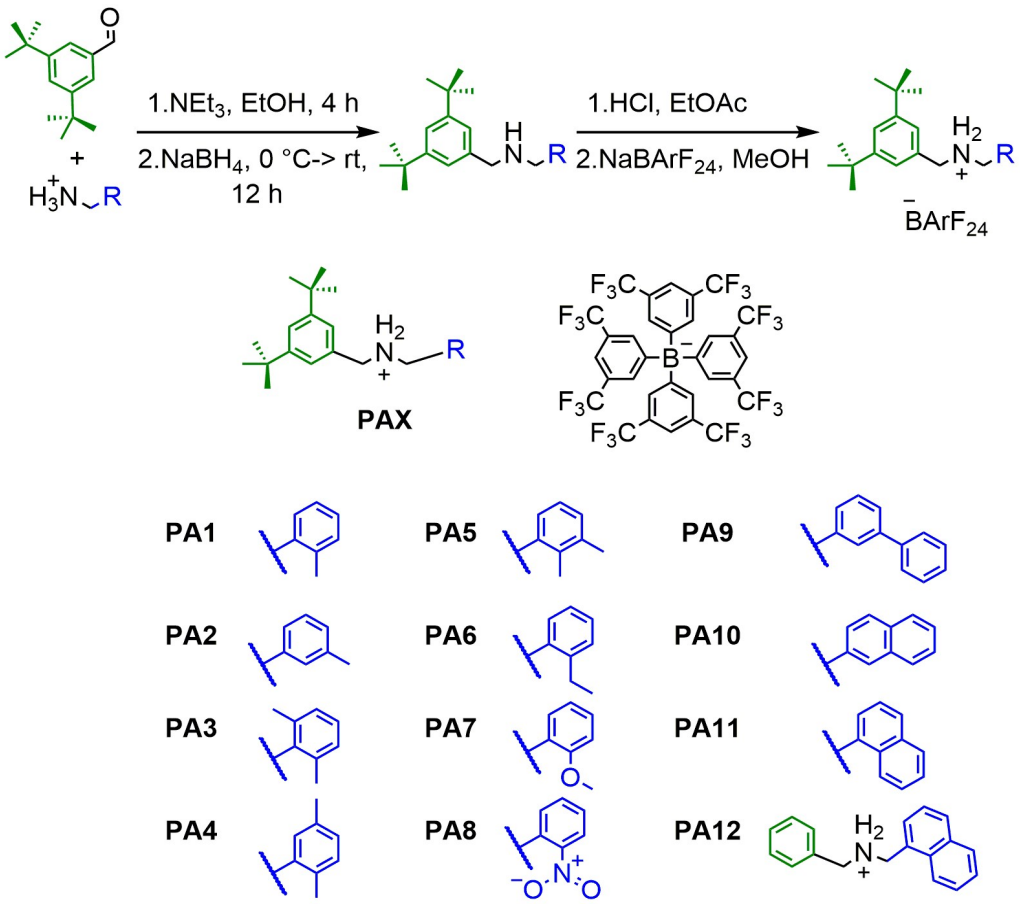
High-resolution ESI mass spectra were measured on an Agilent 6210 ESI-TOF device. CID experiments were performed on a Synapt G2-S HDMS (Waters Co., Milford, MA, USA) mass spectrometer. HPLC grade solvents were used for sample preparation.

UV/Vis spectra were recorded with a Varian Cary 50 Bio spectrometer equipped with a xenon lamp. Solvents with HPLC grade and Suprasil glass cuvettes with a path-length of 1 cm were used.

CV measurements were carried out with an Autolab PGSTAT302N potentiostat in a 2 mL measuring cell in dichloroethane with 0.1 M n-Bu_4NBArF_{24} as the conducting salt. The working electrode was made of glassy carbon, the reference Ag electrode was etched with conc. aq. HCl. A Pt wire worked as the counter electrode. The cyclic voltammograms were recorded with 10, 25, 50, 100, 250, 500, 1000 and 2500 mV/s scan rates, to ensure that the observed processes are reversible and diffusion-limited. In order to obtain the correct half-wave potentials, $FeCp_2^{*0}/FeCp_2^{*+}$ was used as the pseudo reference. These values were afterwards referenced to $FeCp_2/FeCp_2^{+}$ as described in the literature.[7] The raw data were treated with Nova 1.5 by Metrohm and the plots were made with Origin 2020 by OriginLab.

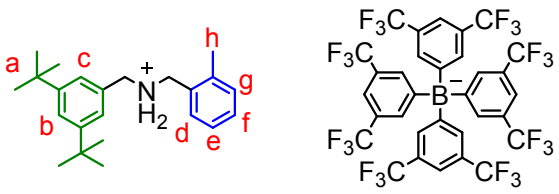
Bulk electrolysis experiments were conducted in a five-neck cell with a four-electrode set-up (see Figure S54 for a photograph) connected to an Autolab PGSTAT302N MBA potentiostat in bipotentiostat mode, using dry and degassed CH_2Cl_2 as the solvent and n-Bu_4NBArF_{24} as the supporting electrolyte. Electrolysis was performed with a cylindrical GC rod (3 mm diameter) at a potential of 1 V vs. the pseudo-reference. A silver wire was used as the pseudo-reference, a coiled Pt wire as the counter electrode. An additional GC disk electrode was employed to perform CV and DPV measurements every 30 minutes to determine the effect of electrolysis on the electrochemical response. The counter electrode was separated from the rest of the cell by glass wool soaked in analyte solution to suppress diffusion towards the working electrodes. Cyclic voltammograms were recorded at a scan rate of 100 mV/s. Differential pulse voltammograms were recorded with a step size of 0.005 V, a modulation amplitude of 0.025 V and modulation and interval times of 0.05 and 0.5 s, respectively. Measurements and treatment of raw data were performed within the Nova 2.1 software by Metrohm, while plots were made using Origin 2020 by OriginLab. The half-wave and peak potentials in CV and DPV experiments drifted between different measurements when recorded during electrolysis, but the diagnostic potential differences between the characteristic oxidation events remained constant. Potentials were afterwards normalized to the values obtained in regular CV measurements.

1.2. Synthesis of axles PA*n*



Scheme S1 Synthesis of axles **PA1-12**.

N-(3,5-di-tert-butylbenzyl)-1-(o-tolyl)methanaminium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate



PA1

A solution of 190 mg (1.21 mmol, 1.0 equiv.) 2-methylbenzylamine hydrochloride, 263 mg (1.21 mmol, 1.0 equiv.) 3,5-di-*tert*-butylbenzaldehyde and 150 µL (1.08 mmol, 0.9 equiv.) NEt_3, in dry EtOH (30 mL) were refluxed under argon atmosphere for 4 h. Afterwards, the solution was cooled to 0 °C and 228 mg (6.03 mmol, 5.0 equiv.) $NaBH_4$ were slowly added. The mixture was stirred under argon atmosphere overnight in the thawing ice bath. The reaction was then quenched by slow addition of sat. $NaHCO_3$ solution and filtered. The solvent was removed from the filtrate under reduced pressure and the residue was dissolved in CH_2Cl_2 and then washed with sat. $NaHCO_3$ solution and brine. The organic phase was dried with $MgSO_4$ and the solvent removed again. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH = 100:1 -> 50:1, R_f ~ 0.3 in CH_2Cl_2/MeOH (100:1)) to obtain a yellowish oil. The oil was dissolved in EtOAc (5 ml) and acidified with HCl (conc.) until the solution reached pH = 1. The mixture was stirred for 1 h and afterwards the solvent was removed under reduced pressure. The residue was dissolved in MeOH (5 ml) and 195 mg (0.22 mmol, 1.0 equiv.) $NaBArF_{24}$ was added. The solution was left stirring overnight at room temperature, then the solvent was removed. The residue was taken up in CH_2Cl_2, washed with brine/water and dried over $MgSO_4$. The product **PA1** (222 mg, 0.19 mmol, 16 % overall) was obtained as off-white sticky solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.31 (s, 18H, a), 2.14 (s, 3H, h), 4.26-4.32 (m, 4H, $C\underline{H_2}$-NH_2), 6.24 (s, 2H, $N\underline{H_2}$), 7.09-7.12 (m, 1H, d), 7.14 (d, *J*=1.7 Hz, 2H, c), 7.17-7.27(m, 2H, g), 7.33-7.37 (m, 1H, e), 7.55 (s_{br}, 4H, $BArF_{24}$), 7.66 (t, *J*=1.7Hz, 1H, b), 7.75 (s_{br}, 8H, $BArF_{24}$) ppm. **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 18.4 31.1, 31.2, 31.4, 31.5, 35.2, 50.7, 54.4, 117.7, 117.8, 121.5, 123.3, 123.7, 125.9, 126.2, 126.3, 127.2, 128.1, 129.2, 130.0, 132.1, 132.4, 135.0, 154.3, 161.3, 161.7, 162.1, 162.5 ppm. **HRMS** (MeOH): *m/z* calcd. for $[C_{23}H_{34}N]^+$: 324.2686 $[M]^+$, found: 324.2704.

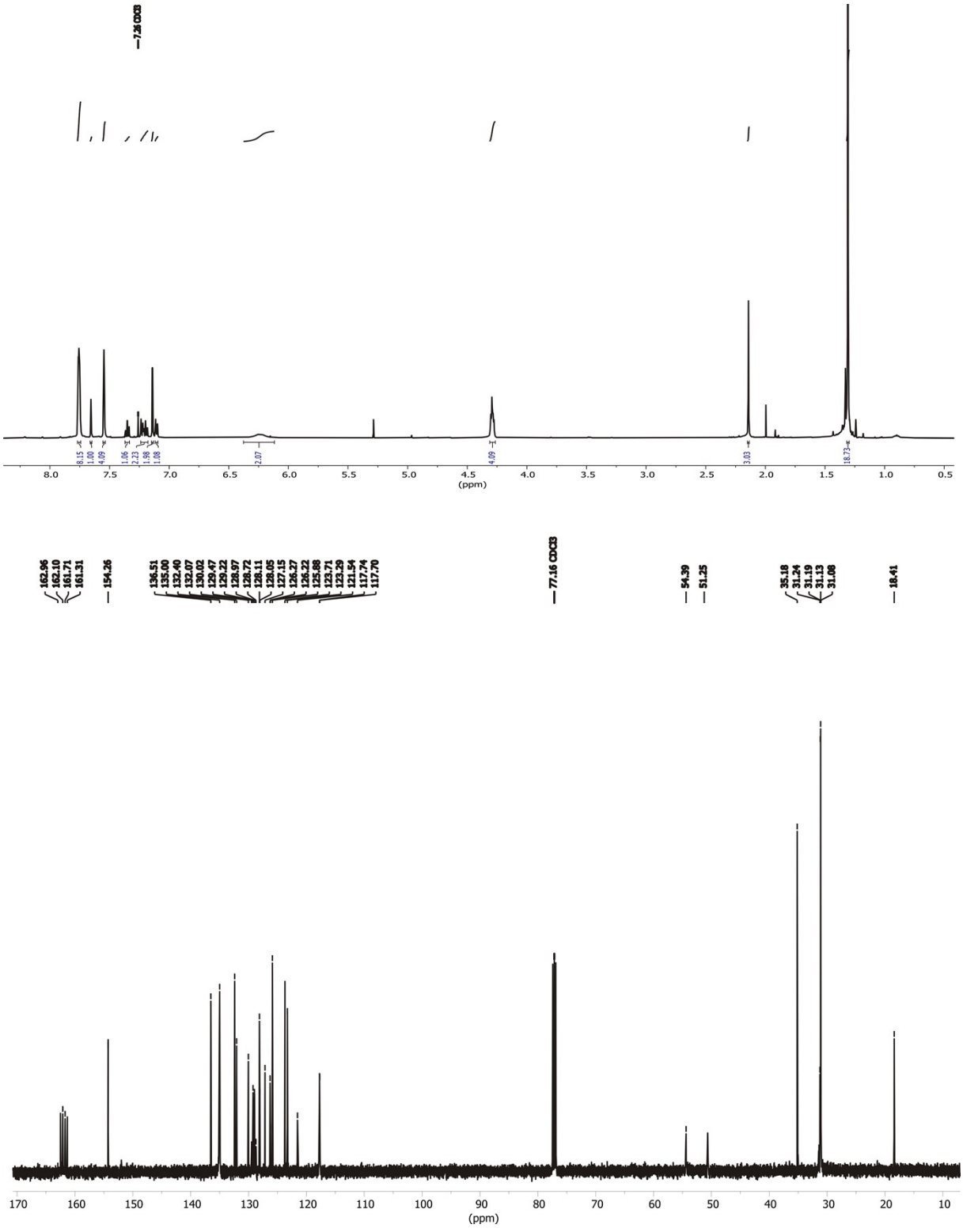
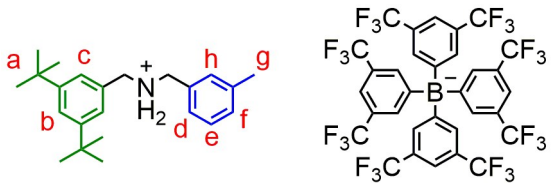


Fig. S1 ^{1}H (top) and ^{13}C (bottom) NMR spectra (500/176 MHz, $CDCl_3$, 298 K) of **PA1**.

N-(3,5-di-tert-butylbenzyl)-1-(*m*-tolyl)methanaminium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate



PA2

A solution of 53 mg (0.34 mmol, 1.0 equiv.) 3-methylbenzylamine hydrochloride, 73 mg (0.34 mmol, 1.0 equiv.) 3,5-di-*tert*-butylbenzaldehyde and 31 µL (0.30 mmol, 0.9 equiv.) NEt_3, in dry EtOH (20 mL) were refluxed under argon atmosphere for 4 h. Afterwards, the solution was cooled to 0 °C and 64 mg (1.7 mmol, 5.0 equiv.) $NaBH_4$ was slowly added. The mixture was left stirring under argon atmosphere overnight in the thawing ice bath. The reaction was quenched by slow addition of sat. $NaHCO_3$ solution and then filtered. The solvent was removed under reduced pressure from the filtrate and the residue was dissolved in CH_2Cl_2 and then washed with sat. $NaHCO_3$ solution and brine. The organic phase was dried with $MgSO_4$ and the solvent removed again. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH = 100:1 -> 50:1, R_f ~ 0.3 in CH_2Cl_2/MeOH (100:1)) to obtain a yellowish oil. The oil was dissolved in EtOAc (5 ml) and acidified with HCl (conc.) until the solution reached pH = 1. The mixture was stirred for 1 h and afterwards the solvent was removed under reduced pressure. The residue was dissolved in MeOH (5 ml) and 150 mg (0.17 mmol, 1.0 equiv.) $NaBArF_{24}$ was added. The solution was left stirring overnight at room temperature, then the solvent was removed. The residue was taken up in CH_2Cl_2, washed with brine/water and dried over $MgSO_4$. The product **PA2** (200 mg, 0.16 mmol, 47 % overall) was obtained as off-white sticky solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.30 (s, 18H, a), 2.32 (s, 3H, g), 4.09-4.19 (m, 4H, C$\underline{H_2}$-NH_2), 7.00-7.05 (m, 2H, f,h), 7.09-7.12 (m, 2H, d,e), 7.19 (s, 2H, N$\underline{H_2}$), 7.28-7.30 (m, 2H, c), 7.52 (s_{br}, 4H, $BArF_{24}$), 7.57-7.58 (m, 1H, b), 7.70 (s_{br}, 8H, $BArF_{24}$) ppm. **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 31.3, 35.8, 52.6, 53.3, 117.7, 123.4, 123.7, 125.6, 125.8, 126.2, 127.7, 128.0, 128.3, 129.1, 129.9, 130.2, 132.2, 135.0, 140.7, 153.7 161.8 ppm. **HRMS** (MeOH): *m/z* calcd. for $[C_{23}H_{34}N]^+$: 324.2686 $[M]^+$, found: 324.2708.

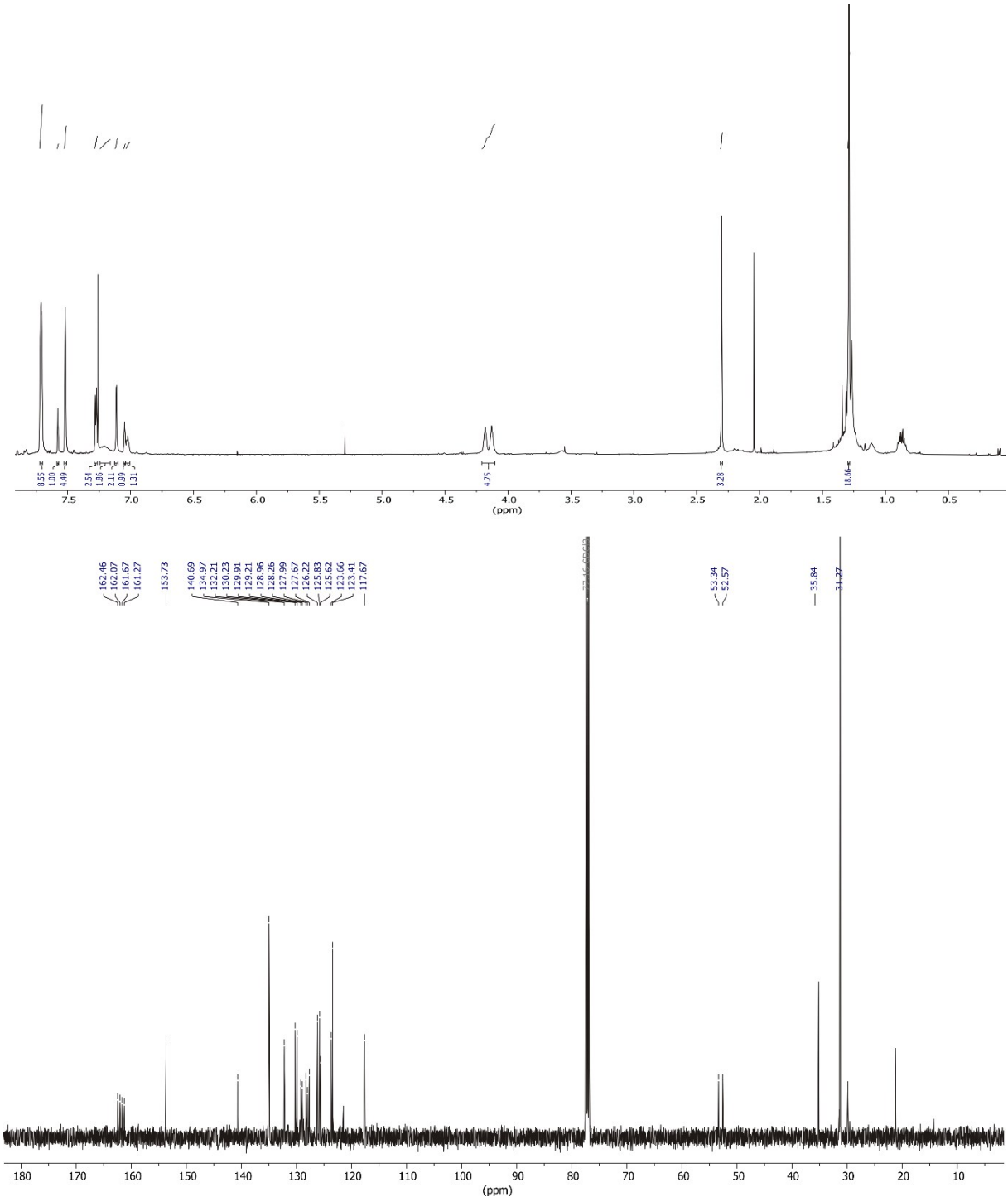
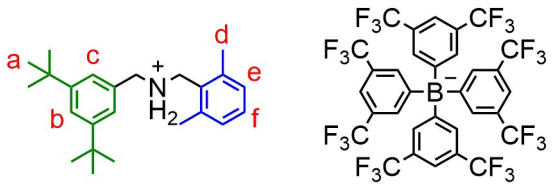


Fig. S2 ^{1}H (top) and ^{13}C (bottom) NMR spectra (500/176 MHz, $CDCl_3$, 298 K) of **PA2**.

N-(3,5-di-tert-butylbenzyl)-1-(2,6-dimethylphenyl)methanaminium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate



PA3

A solution of 433 mg (2.53 mmol, 1.0 equiv.) (2,6-dimethylphenyl)methanaminium chloride[3], 552 mg (2.53 mmol, 1.0 equiv.) 3,5-di-*tert*-butylbenzaldehyde and 310 µL (2.24 mmol, 0.9 equiv.) NEt_3, in dry EtOH (30 mL) were refluxed under argon atmosphere for 4 h. Afterwards, the solution was cooled to 0 °C and 479 mg (12.65 mmol, 5.0 equiv.) $NaBH_4$ was slowly added. The mixture was left stirring under argon atmosphere overnight in the thawing ice bath. The reaction was quenched by slow addition of sat. $NaHCO_3$ solution and then filtered. The solvent was removed under reduced pressure from the filtrate and the residue was dissolved in CH_2Cl_2 and then washed with sat. $NaHCO_3$ solution and brine. The organic phase was dried with $MgSO_4$ and the solvent removed again. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH = 100:1 -> 50:1, R_f ~ 0.3 in CH_2Cl_2/MeOH (100:1)) to obtain a yellowish oil. The oil was dissolved in EtOAc (15 ml) and acidified with HCl (conc.) until the solution reached pH = 1. The mixture was stirred for 1 h and afterwards the solvent was removed under reduced pressure. The residue was dissolved in MeOH (5 ml) and 1.15 g (1.24 mmol, 1.0 equiv.) $NaBArF_{24}$ was added. The solution was left stirring overnight at room temperature, then the solvent was removed. The residue was taken up in CH_2Cl_2, washed with brine/water and dried over $MgSO_4$. The product **PA3** (1.18 g, 0.98 mmol, 39 % overall) was obtained as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.31 (s, 18H, a), 2.11 (s, 6H, d), 4.24-4.34 (m, 4H, C$\underline{H_2}$-NH_2), 6.55 (s, 2H, N$\underline{H_2}$), 7.05-7.08 (m, 2H, e), 7.15 (d, J = 1.7 Hz, 2H, c), 7.21-7.25 (m, 1H, f), 7.52 (s_{br}, 4H, $BArF_{24}$), 7.63 (t, J = 1.7 Hz, 1H, b), 7.70 (s_{br}, 8H, $BArF_{24}$) ppm. **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 31.3, 35.2, 45.2, 54.3, 117.7, 122.4, 123.5, 123.6, 123.9, 125.4, 125.5, 125.9, 126.0, 129.0, 130.1, 132.2, 131.2, 134.9, 137.2, 153.1 161.8 ppm. **HRMS** (MeOH): *m/z* calcd. for $[C_{24}H_{36}N]^+$: 338.2842 $[M]^+$, found: 338.2871.

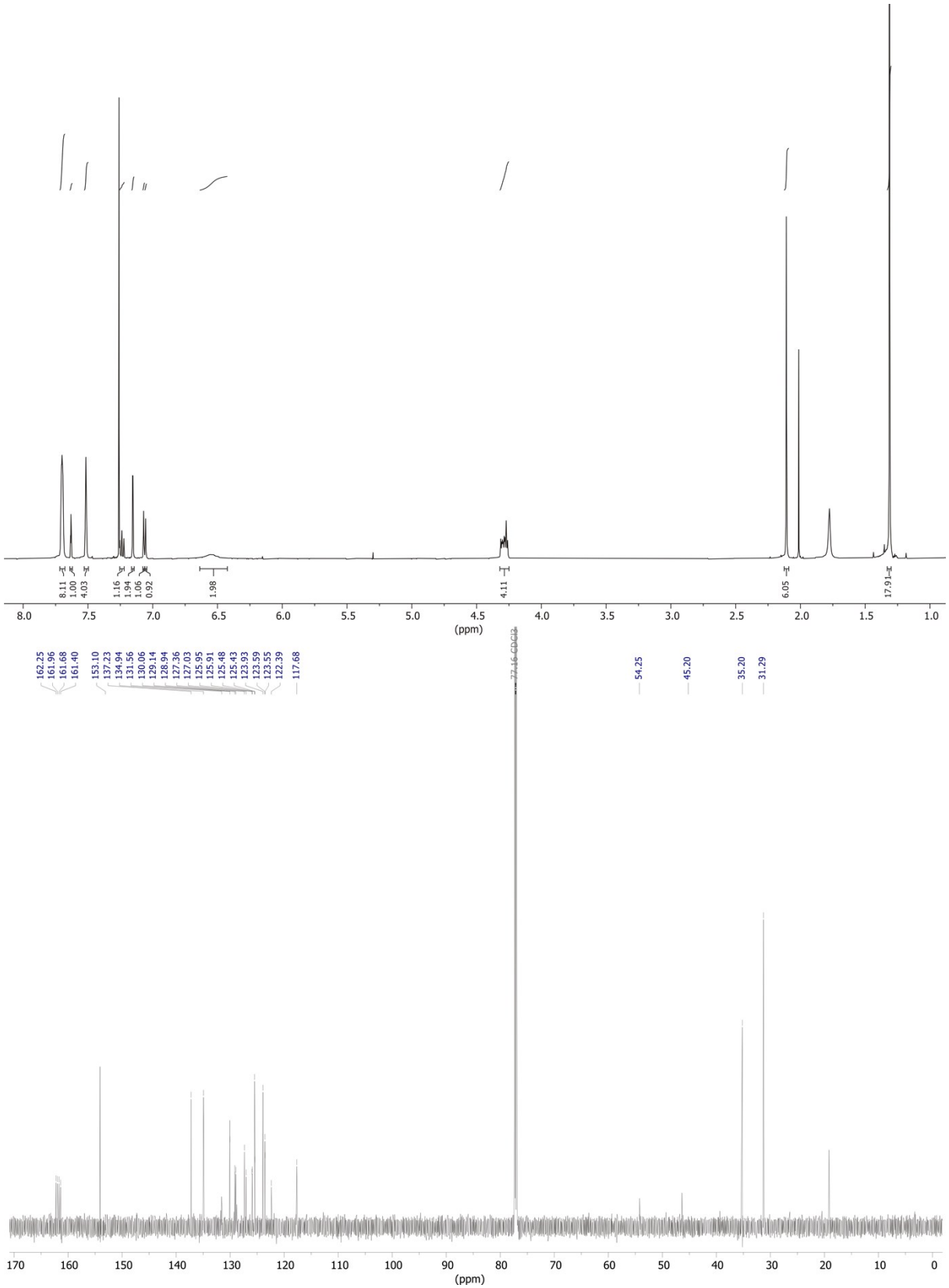
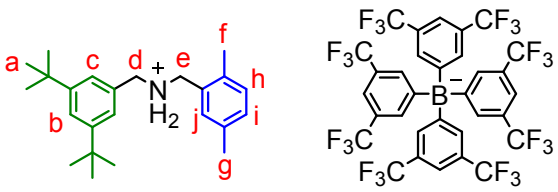


Fig. S3 ^{1}H (top) and ^{13}C (bottom) NMR spectra (500/176 MHz, $CDCl_3$, 298 K) of **PA3**.

N-(3,5-di-tert-butylbenzyl)-1-(2,5-dimethylphenyl)methanaminium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate



PA4

A solution of 250 mg (1.5 mmol, 1.0 equiv.) (2,5-dimethylphenyl)methanaminium chloride, 319 mg (1.5 mmol, 1.0 equiv.) 3,5-di-*tert*-butylbenzaldehyde and 180 µL (1.3 mmol, 0.9 equiv.) NEt_3, in dry EtOH (60 mL) were refluxed under argon atmosphere for 4 h. Afterwards, the solution was cooled to 0 °C and 275 mg (7.3 mmol, 5.0 equiv.) $NaBH_4$ was slowly added. The mixture was left stirring under argon atmosphere overnight in the thawing ice bath. The reaction was quenched by slow addition of sat. $NaHCO_3$ solution and then filtered. The solvent was removed under reduced pressure from the filtrate and the residue was dissolved in CH_2Cl_2 and then washed with sat. $NaHCO_3$ solution and brine. The organic phase was dried with $MgSO_4$ and the solvent removed again. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH = 100:1 -> 50:1, R_f ~ 0.7 in CH_2Cl_2/MeOH (50:1)) to obtain a yellowish oil. The oil was dissolved in Et_2O (15 ml) and acidified with HCl (conc.) until the solution reached pH = 1. The mixture was stirred for 3 h and afterwards the solvent was removed under reduced pressure. A fraction of the residue was dissolved in MeOH (10 ml) and 247 mg (0.27 mmol, 1.0 equiv.) $NaBArF_{24}$ was added. The solution was left stirring overnight at room temperature, then the solvent was removed. The residue was taken up in CH_2Cl_2, washed with brine/water and dried over $MgSO_4$. The product **PA4** (315 mg, 0.26 mmol, 88 % overall) was obtained as colorless oil.

^{1}H NMR (700 MHz, $CDCl_3$): δ = 1.33 (s, 18H, a), 2.12 (s, 3H, f), 2.27 (s, 3H, g), 4.16 - 4.24 (m, 4H, d,e), 6.95 – 6.98 (m, 1H, j), 7.13 - 7.16 (m, 2H, c,h), 7.19 – 7.22 (m, 1H, i), 7.54 (s_{br}, 4H, $BArF_{24}$), 7.62 (t, J = 1.7 Hz, 1H, b), 7.73 (s_{br}, 8H, $BArF_{24}$) ppm. **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 18.1, 20.7, 31.3, 35.2, 49.9, 53.6, 117.7, 122.4, 123.4, 123.9, 125.5, 125.7, 126.6, 127.0, 127.6, 128.8, 129.0, 129.1, 129.3, 130.6, 132.2, 132.5, 133.4, 138.0, 153.9 161.9 ppm. **HRMS** (MeOH): *m/z* calcd. for $[C_{24}H_{36}N]^+$: 338.2842 $[M]^+$, found: 338.2858.

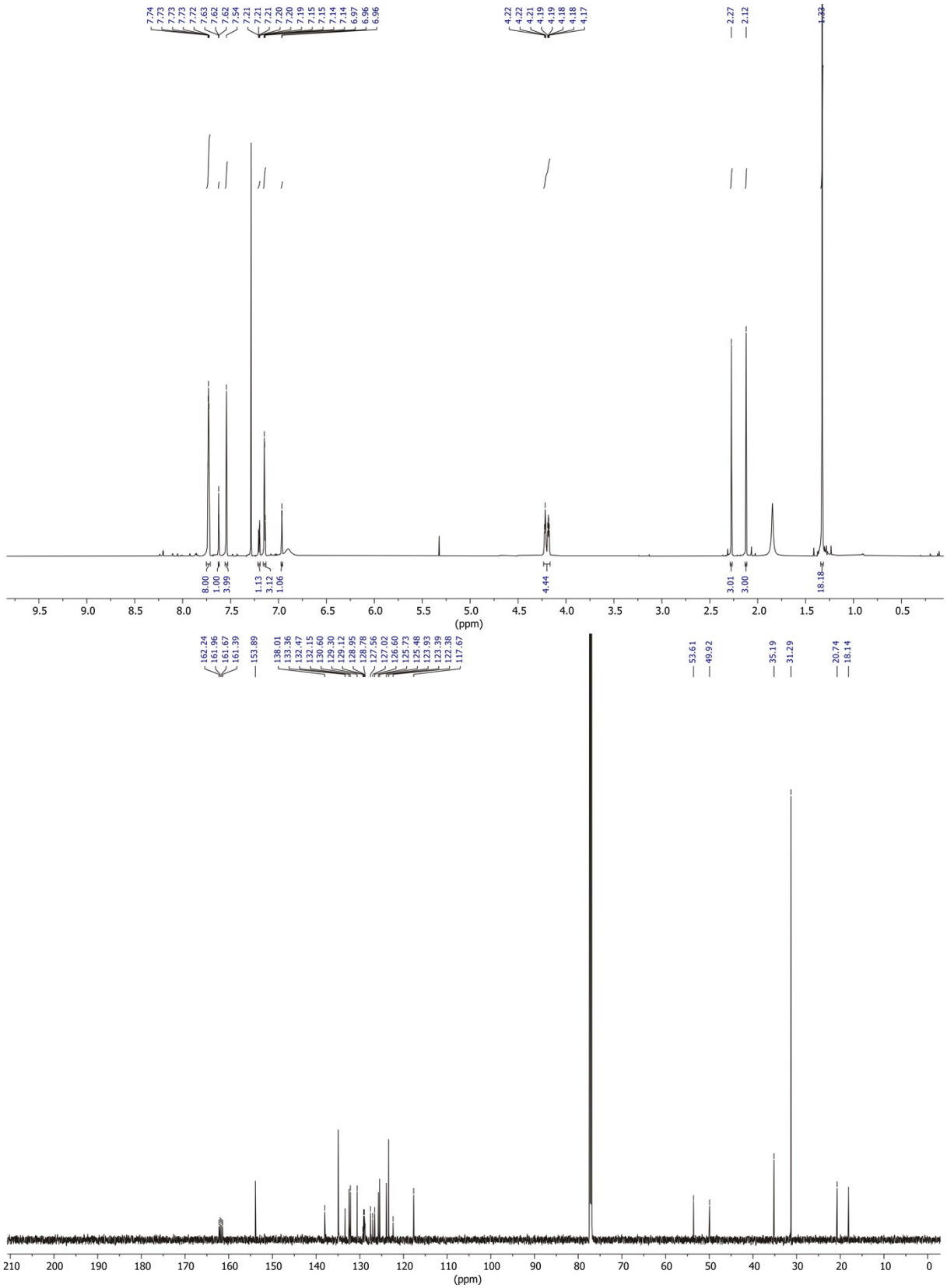
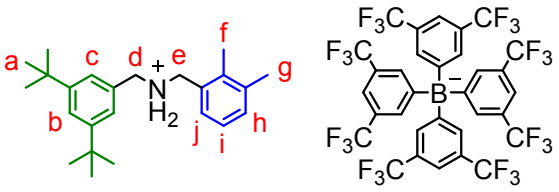


Fig. S4 ^{1}H (top) and ^{13}C (bottom) NMR spectra (700/176 MHz, $CDCl_3$, 298 K) of **PA4**.

N-(3,5-di-tert-butylbenzyl)-1-(2,3-dimethylphenyl)methanaminium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate



PA5

A solution of 250 mg (1.5 mmol, 1.0 equiv.) (2,3-dimethylphenyl)methanaminium chloride, 319 mg (1.5 mmol, 1.0 equiv.) 3,5-di-*tert*-butylbenzaldehyde and 180 µL (1.3 mmol, 0.9 equiv.) NEt_3, in dry EtOH (60 mL) were refluxed under argon atmosphere for 4 h. Afterwards, the solution was cooled to 0 °C and 275 mg (7.3 mmol, 5.0 equiv.) $NaBH_4$ was slowly added. The mixture was left stirring under argon atmosphere overnight in the thawing ice bath. The reaction was quenched by slow addition of sat. $NaHCO_3$ solution and then filtered. The solvent was removed under reduced pressure from the filtrate and the residue was dissolved in CH_2Cl_2 and then washed with sat. $NaHCO_3$ solution and brine. The organic phase was dried with $MgSO_4$ and the solvent removed again. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2 -> CH_2Cl_2/MeOH = 50:1, R_f ~ 0.7 in CH_2Cl_2/MeOH (50:1)) to obtain a yellowish oil. The oil was dissolved in EtOAc (10 ml) and acidified with HCl (conc.) until the solution reached pH = 1. The mixture was stirred for 3 h and afterwards the solvent was removed under reduced pressure. A fraction of the residue was dissolved in MeOH (5 ml) and 247 mg (0.27 mmol, 1.0 equiv.) $NaBArF_{24}$ was added. The solution was left stirring overnight at room temperature, then the solvent was removed. The residue was taken up in CH_2Cl_2, washed with brine/water and dried over $MgSO_4$. The product **PA5** (324 mg, 0.27 mmol, 58 % overall) was obtained as colorless oil.

^{1}H NMR (700 MHz, $CDCl_3$): δ = 1.30 (s, 18H, a), 2.01 (s, 3H, f), 2.20 (s, 3H, g), 4.11-4.17 (m, 4H, d,e), 6.98 (d, J = 7.6 Hz, 1H, h), 7.08 (t, J = 7.6 Hz, 1H, i), 7.14 (d, J=1.8 Hz, 2H, c), 7.22 (d, J = 7.6 Hz, 1H, j), 7.51 (s_{br}, 4H, $BArF_{24}$), 7.58 (t, J = 1.5 Hz, 1H, b), 7.70 (s_{br}, 8H, $BArF_{24}$) ppm. **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 14.9, 20.5, 31.3, 35.2, 50.0, 53.2, 117.6, 117.6, 117.7, 122.4, 123.5, 123.9, 125.4, 125.5, 127.0, 127.1, 127.9, 128.1, 128.8, 129.0, 129.1, 129.3, 133.0, 134.9, 135.2, 139.4, 153.7 161.9 ppm. **HRMS** (MeOH): *m/z* calcd. for $[C_{24}H_{36}N]^+$: 338.2842 $[M]^+$, found: 338.2847.

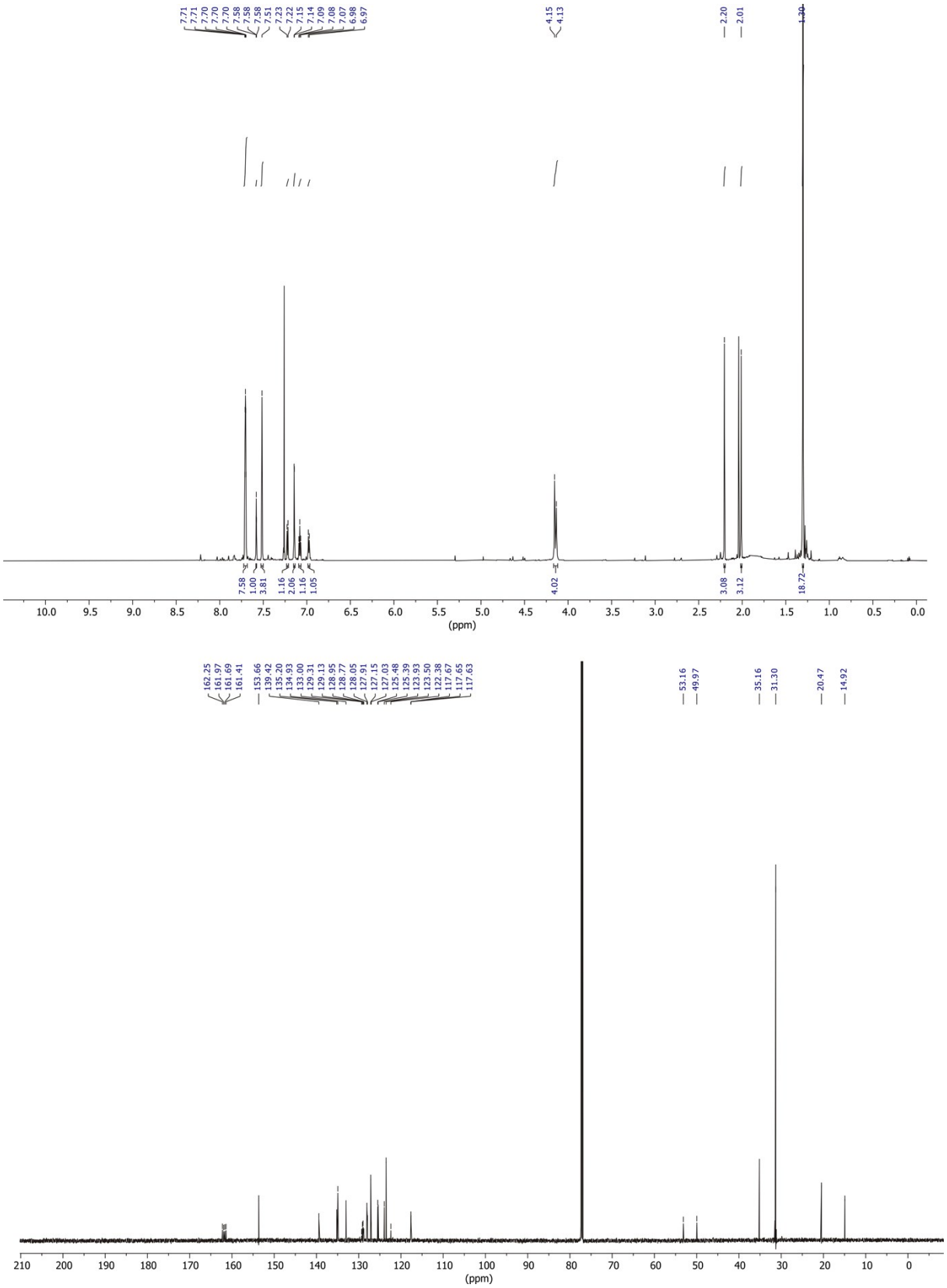
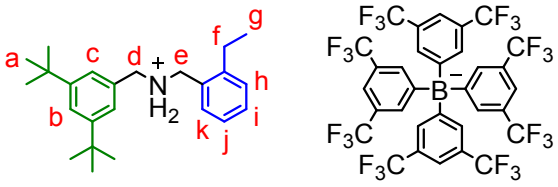


Fig. S5 ^{1}H (top) and ^{13}C (bottom) NMR spectra (700/176 MHz, $CDCl_3$, 298 K) of **PA5**.

N-(3,5-di-tert-butylbenzyl)-1-(2-ethylphenyl)methanaminium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate



PA6

A solution of 250 mg (1.5 mmol, 1.0 equiv.) (2-ethylphenyl)methanaminium chloride[8], 319 mg (1.5 mmol, 1.0 equiv.) 3,5-di-*tert*-butylbenzaldehyde and 180 µL (1.08 mmol, 0.9 equiv.) NEt_3, in dry EtOH (60 mL) were refluxed under argon atmosphere for 4 h. Afterwards, the solution was cooled to 0 °C and 273 mg (7.3 mmol, 5.0 equiv.) $NaBH_4$ was slowly added. The mixture was left stirring under argon atmosphere overnight in the thawing ice bath. The reaction was quenched by slow addition of sat. $NaHCO_3$ solution and then filtered. The solvent was removed under reduced pressure from the filtrate and the residue was dissolved in CH_2Cl_2 and then washed with sat. $NaHCO_3$ solution and brine. The organic phase was dried with $MgSO_4$ and the solvent removed again. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2 -> CH_2Cl_2/MeOH = 100:1, R_f ~ 0.3 in CH_2Cl_2/MeOH (100:1)) to obtain a yellowish oil. The oil was dissolved in EtOAc (10 ml) and acidified with HCl (conc.) until the solution reached pH = 1. The mixture was stirred for 1 h and afterwards the solvent was removed under reduced pressure. A fraction of the residue was dissolved in MeOH (10 ml) and 239 mg (0.27 mmol, 1.0 equiv.) $NaBArF_{24}$ was added. The solution was left stirring overnight at room temperature, then the solvent was removed. The residue was taken up in CH_2Cl_2, washed with brine/water and dried over $MgSO_4$. The product **PA6** (325 mg, 0.27 mmol, 58 % overall) was obtained as colorless oil.

^{1}H NMR (700 MHz, $CDCl_3$): δ = 1.04 (t, J = 7.6 Hz, 3H, g), 1.31 (s, 18H, a), 2.36 (q, J = 7.5 Hz, 2H, f), 4.13 - 4.22 (m, 4H, d,e), 7.15 - 7.17 (m, 3H, c,i), 7.17 - 7.20 (m, 1H, h), 7.21 - 7.30 (m, 1H, j), 7.36 - 7.39 (m, 1H, k), 7.45 - 7.50 (m, 1H, h), 7.52 (s_{br}, 4H, $BArF_{24}$), 7.59 – 7.60 (m, 1H, b), 7.70 (s_{br}, 8H, $BArF_{24}$) ppm. **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 15.4, 25.5, 31.3, 35.2, 48.7, 53.4, 117.7, 122.4, 123.6, 123.9, 125.5, 125.5, 126.5, 127.0, 127.7, 127.8, 129.0, 129.1, 130.2, 130.3, 131.7, 134.9, 142.9, 153.8, 161.8 ppm. **HRMS** (MeOH): *m/z* calcd. for $[C_{24}H_{36}N]^+$: 338.2842 $[M]^+$, found: 338.2854.

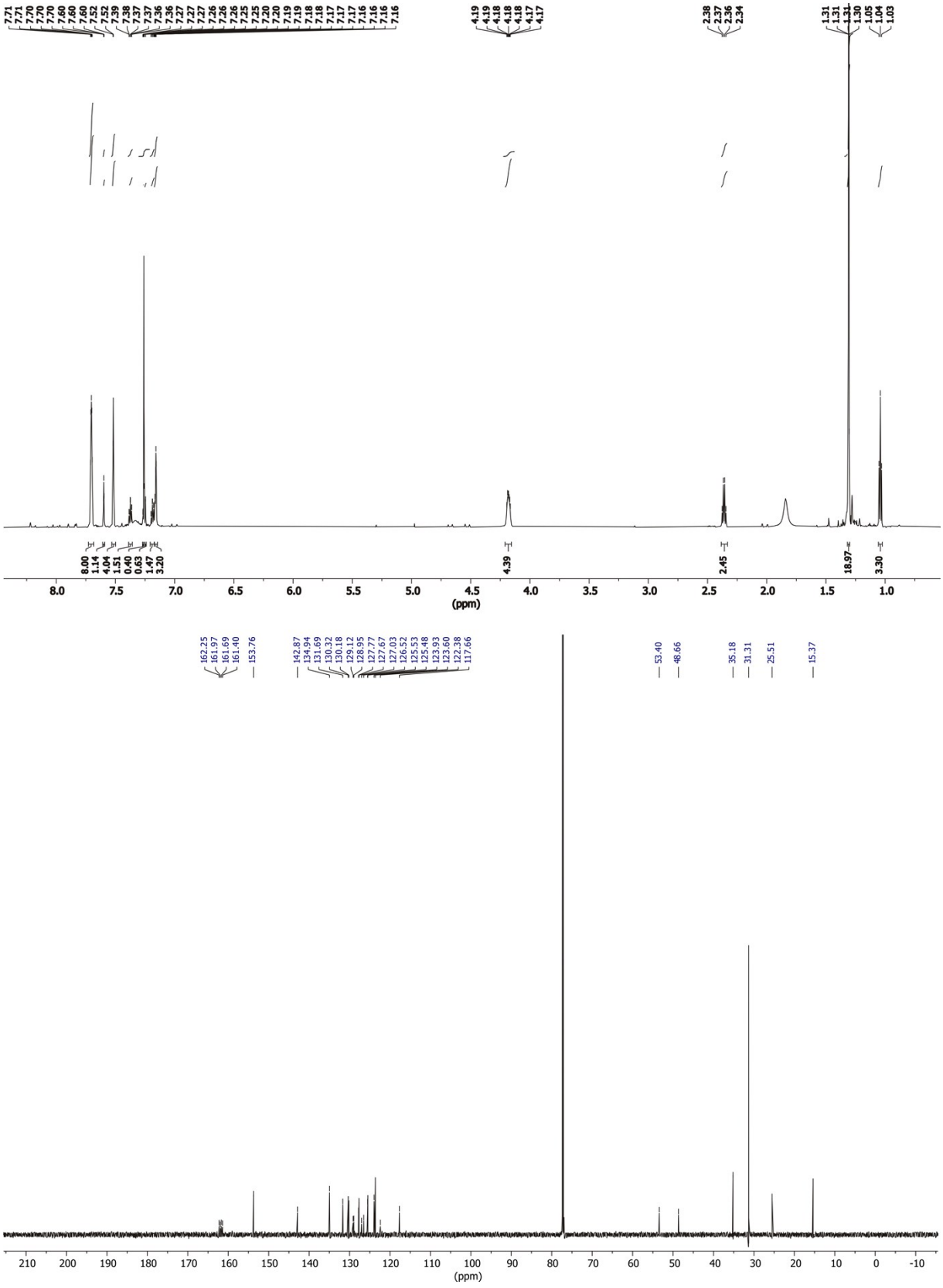
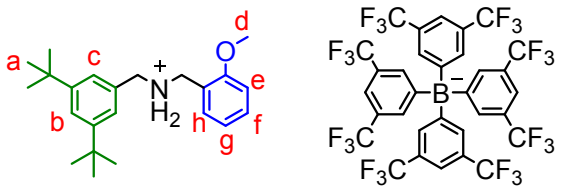


Fig. S6 ^{1}H (top) and ^{13}C (bottom) NMR spectra (700/176 MHz, $CDCl_3$, 298 K) of **PA6**.

N-(3,5-di-tert-butylbenzyl)-1-(2-methoxyphenyl)methanaminium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate



PA7

A solution of 190 mg (1.1 mmol, 1.0 equiv.) (2-methoxyphenyl)methanaminium chloride[8], 240 mg (1.1 mmol, 1.0 equiv.) 3,5-di-*tert*-butylbenzaldehyde and 150 µL (1.08 mmol, 0.9 equiv.) NEt_3, in dry EtOH (30 mL) were refluxed under argon atmosphere for 4 h. Afterwards, the solution was cooled to 0 °C and 207 mg (5.5 mmol, 5.0 equiv.) $NaBH_4$ was slowly added. The mixture was left stirring under argon atmosphere overnight in the thawing ice bath. The reaction was quenched by slow addition of sat. $NaHCO_3$ solution and then filtered. The solvent was removed under reduced pressure from the filtrate and the residue was dissolved in CH_2Cl_2 and then washed with sat. $NaHCO_3$ solution and brine. The organic phase was dried with $MgSO_4$ and the solvent removed again. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH = 100:1 -> 50:1, R_f ~ 0.3 in CH_2Cl_2/MeOH (100:1)) to obtain a yellowish oil. The oil was dissolved in EtOAc (10 ml) and acidified with HCl (conc.) until the solution reached pH = 1. The mixture was stirred for 1 h and afterwards the solvent was removed under reduced pressure. The residue was dissolved in MeOH (5 ml) and 478 mg (0.54 mmol, 1.0 equiv.) $NaBArF_{24}$ was added. The solution was left stirring overnight at room temperature, then the solvent was removed. The residue was taken up in CH_2Cl_2, washed with brine/water and dried over $MgSO_4$. The product **PA7** (603 mg, 0.50 mmol, 45 % overall) was obtained as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.30 (s, 18H, a), 3.84 (s, 3H, d), 4.11-4.22 (m, 4H, C$\underline{H_2}$-NH_2), 6.84 (s, 2H, N$\underline{H_2}$), 6.95-7.04 (m, 2H, e,f), 7.06 (d, *J*=1.7 Hz, 2H, c), 7.07-7.11 (m, 1H, g), 7.45-7.50 (m, 1H, h), 7.52 (s_{br}, 4H, $BArF_{24}$), 7.59 (t, *J* = 1.7 Hz, 1H, b), 7.70 (s_{br}, 8H, $BArF_{24}$) ppm.

^{13}C NMR (176 MHz, $CDCl_3$): δ = 31.3, 35.2, 50.5, 53.3, 56.3, 111.8, 115.3, 117.7, 122.4, 122.9, 123.1, 123.9, 125.5, 126.0, 127.0, 127.4, 129.1, 131.2, 133.5, 134.9, 154.0, 157.0, 161.8 ppm.

HRMS (MeOH): *m/z* calcd. for $[C_{23}H_{34}NO]^+$: 340.2635 $[M]^+$, found: 340.2643.

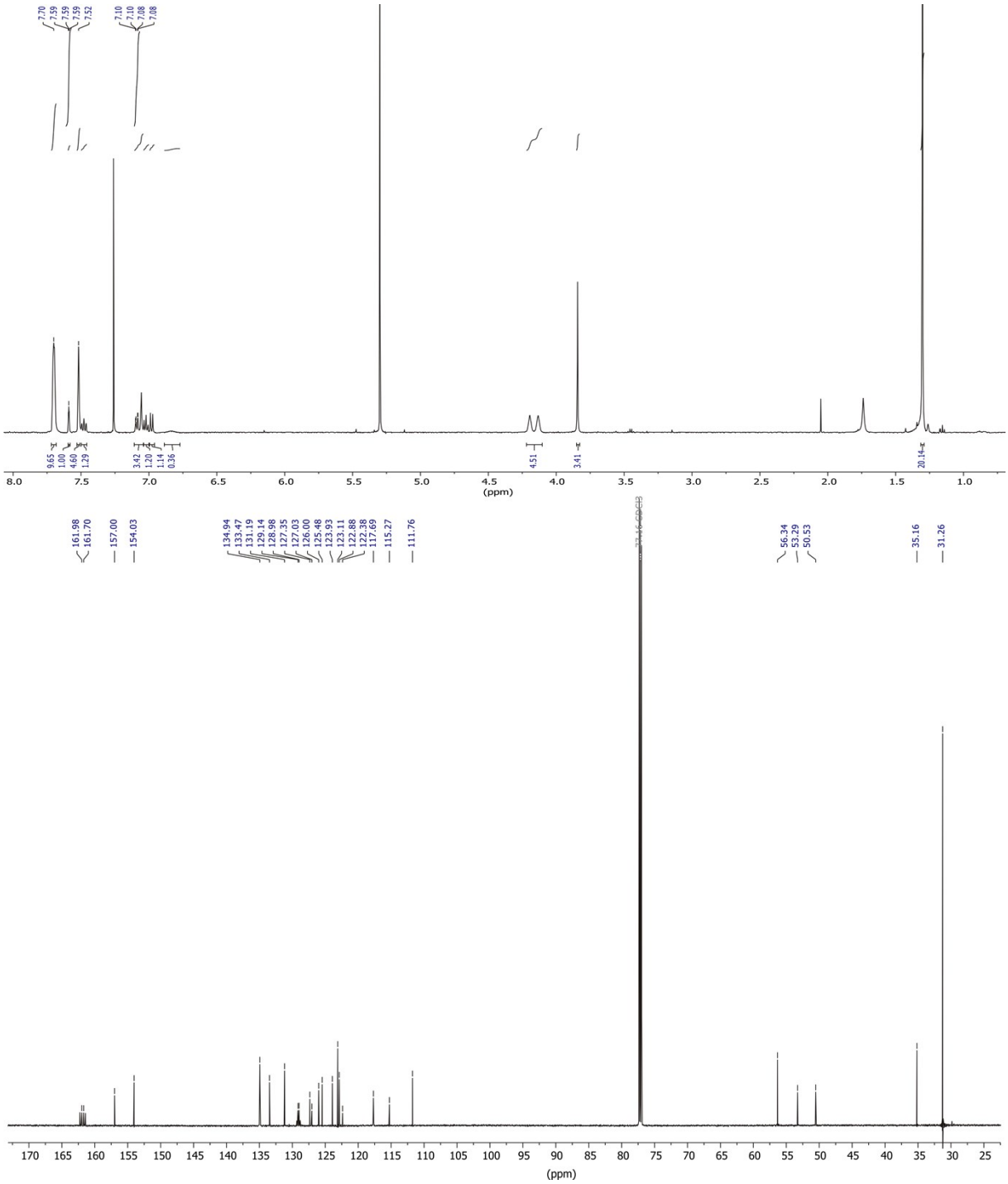
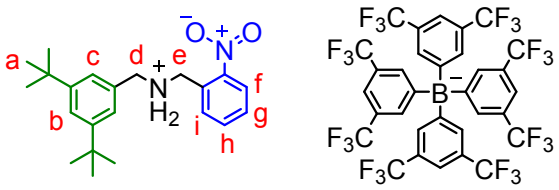


Fig. S7 ^{1}H (top) and ^{13}C (bottom) NMR spectra (500/176 MHz, $CDCl_3$, 298 K) of **PA7**.

N-(3,5-di-tert-butylbenzyl)-1-(2-nitrophenyl)methanaminium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate



PA8

A solution of 250 mg (1.3 mmol, 1.0 equiv.) (2-nitrophenyl)methanaminium hydrochloride, 290 g (1.3 mmol, 1.0 equiv.) 3,5-di-*tert*-butylbenzaldehyde and 170 µL (0.9 mmol, 0.9 equiv.) dry NEt_3 in dry EtOH (60 mL) was left refluxing under argon atmosphere for 4 h. Afterwards, the solution was cooled to 0 °C in an ice bath and 252 mg (6.7 mmol, 5.0 equiv.) $NaBH_4$ was added. The mixture was left stirring under argon atmosphere in the thawing ice bath overnight. Then, the reaction was stopped by slow addition of sat. $NaHCO_3$ solution until no additional gas development occurred. The solvent was removed under reduced pressure and the residue was taken up in CH_2Cl_2. After washing with water, the organic phase was dried over $MgSO_4$. The crude product was then purified by column chromatography (SiO_2, CH_2Cl_2 → CH_2Cl_2/MeOH = 100:1, R_f ~ 0.2 in CH_2Cl_2/MeOH = 100:1) to get the desired oil, which was directly dissolved in Et_2O (10 mL) and acidified with conc. HCl, until the solution reached pH = 1. Afterwards, the solution was left stirring at r.t. for 3 h, then the solvent was removed under reduced pressure. A fraction of the yellow oil was dissolved in MeOH (10 mL) and 227 mg (0.26 mmol, 1.0 equiv.) $NaBArF_{24}$ was added. The solution was left stirring at r.t. overnight, then the solvent was removed under reduced pressure. Afterwards, the residue was taken up in CH_2Cl_2 and washed with water and dried over $MgSO_4$ to obtain the desired product **PA8** as yellow oil in a combined yield of 80% (327 mg, 0.26 mmol).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.30 (s, 18H, a), 4.29 – 4.39 (m, 4H, d,e), 7.20 (d, J = 1.7 Hz, 2H, c), 7.21 – 7.30 (m, 1H, i), 7.34 (s_{br}, 2H, NH_2), 7.51 (s_{br}, 4H, $BArF_{24}$), 7.52 - 7.55 (m, 1H, h), 7.60 (t, J = 1.8 Hz, 1H, b), 7.62 - 7.66 (m, 1H, g), 7.71 (s_{br}, 8H, $BArF_{24}$), 8.13 – 8.16 (m, 1H, f). ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ [ppm] 31.5, 35.2, 50.9, 54.6, 117.7, 121.4, 123.3, 123.4, 123.6, 125.8, 126.0, 127.0, 127.1, 127.9, 128.9, 129.2, 133.4, 134.1, 134.9, 136.0, 149.1, 154.0, 161.9. **HRMS (MeOH):**m/z calcd. for $[C_{22}H_{31}N_2O_2]^+$: 355.2380 $[M]^+$, found: 355.2379.

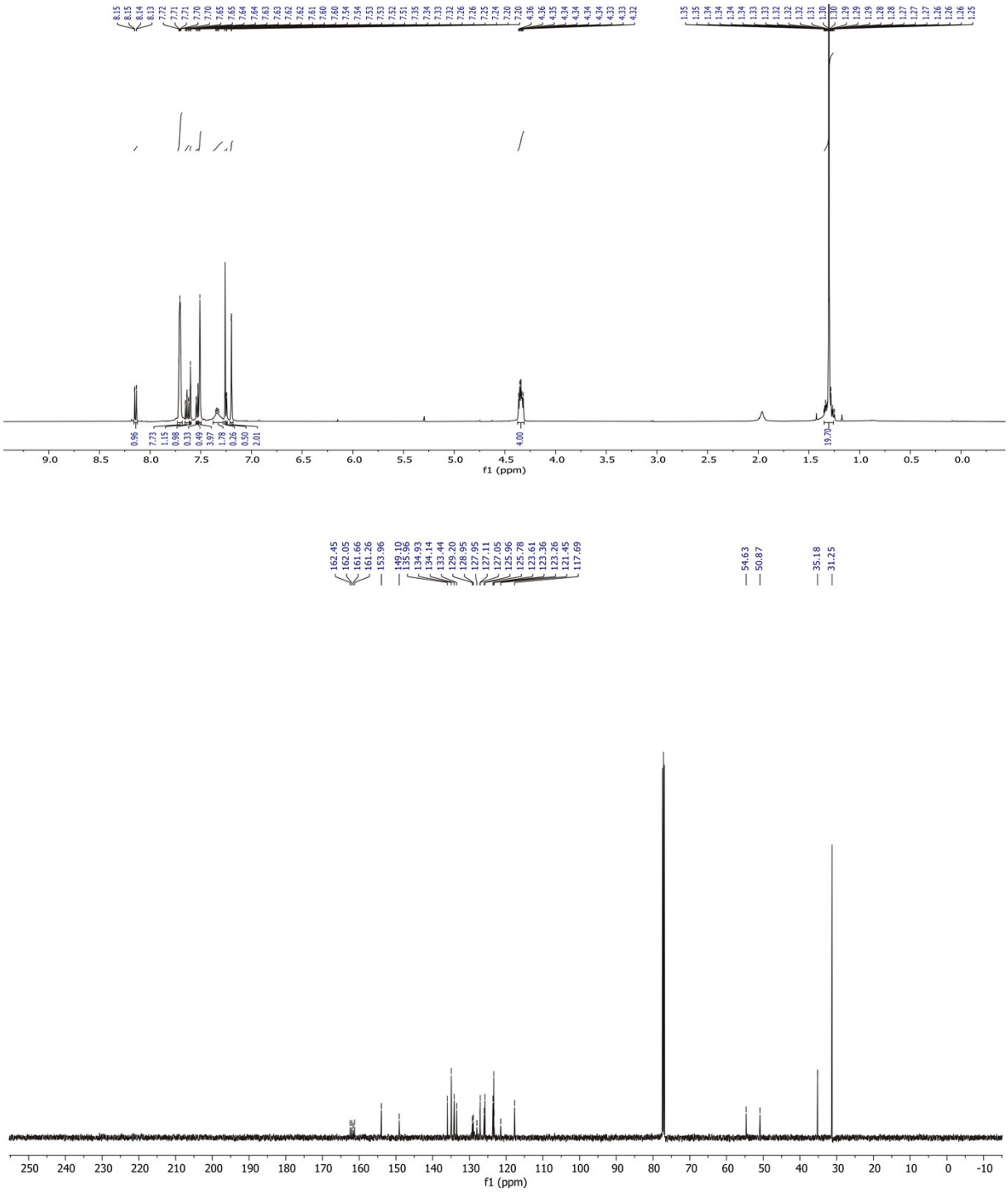
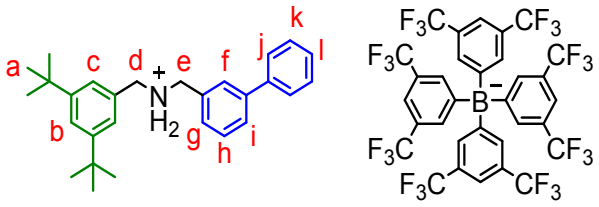


Fig. S8 ^{1}H (top) and ^{13}C (bottom) NMR spectra (500/126 MHz, $CDCl_3$, 298 K) of **PA8**.

1-([1,1'-biphenyl]-3-yl)-N-(3,5-di-tert-butylbenzyl)methanaminiumtetrakis(3,5-bis(trifluoromethyl)phenyl)borate



PA9

A solution of 200 mg (0.9 mmol, 1.0 equiv.) (3-Phenylphenyl)methanamine hydrochloride, 218 mg (0.9 mmol, 1.0 equiv.) 3,5-di-*tert*-butylbenzaldehyde and 115 µL (0.8 mmol, 0.9 equiv.) dry NEt_3 in dry EtOH (50 mL) was refluxed under argon atmosphere for 4 h. Afterwards, the solution was cooled to 0 °C in an ice bath and 172 mg (4.6 mmol, 5.0 equiv.) $NaBH_4$ was added. The mixture was left stirring under argon atmosphere in the thawing ice bath overnight. Then, the reaction was stopped by slow addition of sat. $NaHCO_3$ solution until no additional gas development occurred. The solvent was removed under reduced pressure and the residue was taken up in CH_2Cl_2. After washing with water, the organic phase was dried over $MgSO_4$. The crude product was then purified by column chromatography (SiO_2, CH_2Cl_2 → CH_2Cl_2/MeOH = 50:1, R_f ~ 0.2 in CH_2Cl_2/MeOH = 100:1) to obtain a yellowish oil, which was directly dissolved in EtOAc (10 mL) and acidified with conc. HCl, until the solution reached pH = 1. Afterwards, the solution was left stirring at r.t. for 3 h, then the solvent was removed under reduced pressure. The yellow solid was dissolved in MeOH (10 mL) and 361 mg (0.4 mmol, 1.0 equiv.) $NaBArF_{24}$ was added. The solution was left stirring at r.t. overnight, then the solvent was removed under reduced pressure. Afterwards, the residue was taken up in CH_2Cl_2 and washed with water and dried over $MgSO_4$ to obtain the desired product **PA9** as colorless oil in a combined yield of 43% (484 mg, 0.4 mmol).

^{1}H NMR (700 MHz, $CDCl_3$): δ = 1.29 (s, 18H, a), 4.17 - 4.22 (m, 4H, d,e), 7.17 (d, J = 1.8 Hz, 2H, c), 7.17 – 7.19 (m, 1H, j), 7.37 – 7.39 (m, 2H, g,i), 7.43 (t, J = 7.7 Hz, 1H, l), 7.45 - 7.47 (m, 2H, k), 7.52 (s_{br}, 4H, $BArF_{24}$), 7.55 (t, J = 1.9 Hz, 1H, f), 7.57 (t, J = 1.8 Hz, 1H, b), 7.68 (ddd, J = 1.0, 1.8, 7.8 Hz, 1H, h), 7.73 (s_{br}, 8H, $BArF_{24}$) ppm. **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 31.3, 35.2,.1, 52.3, 53.3, 117.6, 117.7, 117.7, 117.7, 117.7, 122.4, 123.6, 124.0, 125.5, 127.1, 127.7, 128.0, 128.3, 128.6, 128.9, 128.9, 129.0, 129.0, 129.1, 129.1, 129.1, 129.1, 129.2, 129.3, 129.8, 129.9, 130.7, 135.0, 139.3, 143.4, 153.6, 161.8 ppm. **HRMS** (MeOH): *m/z* calcd. for $[C_{28}H_{36}N]^+$: 386.2842 $[M]^+$, found: 386.2848.

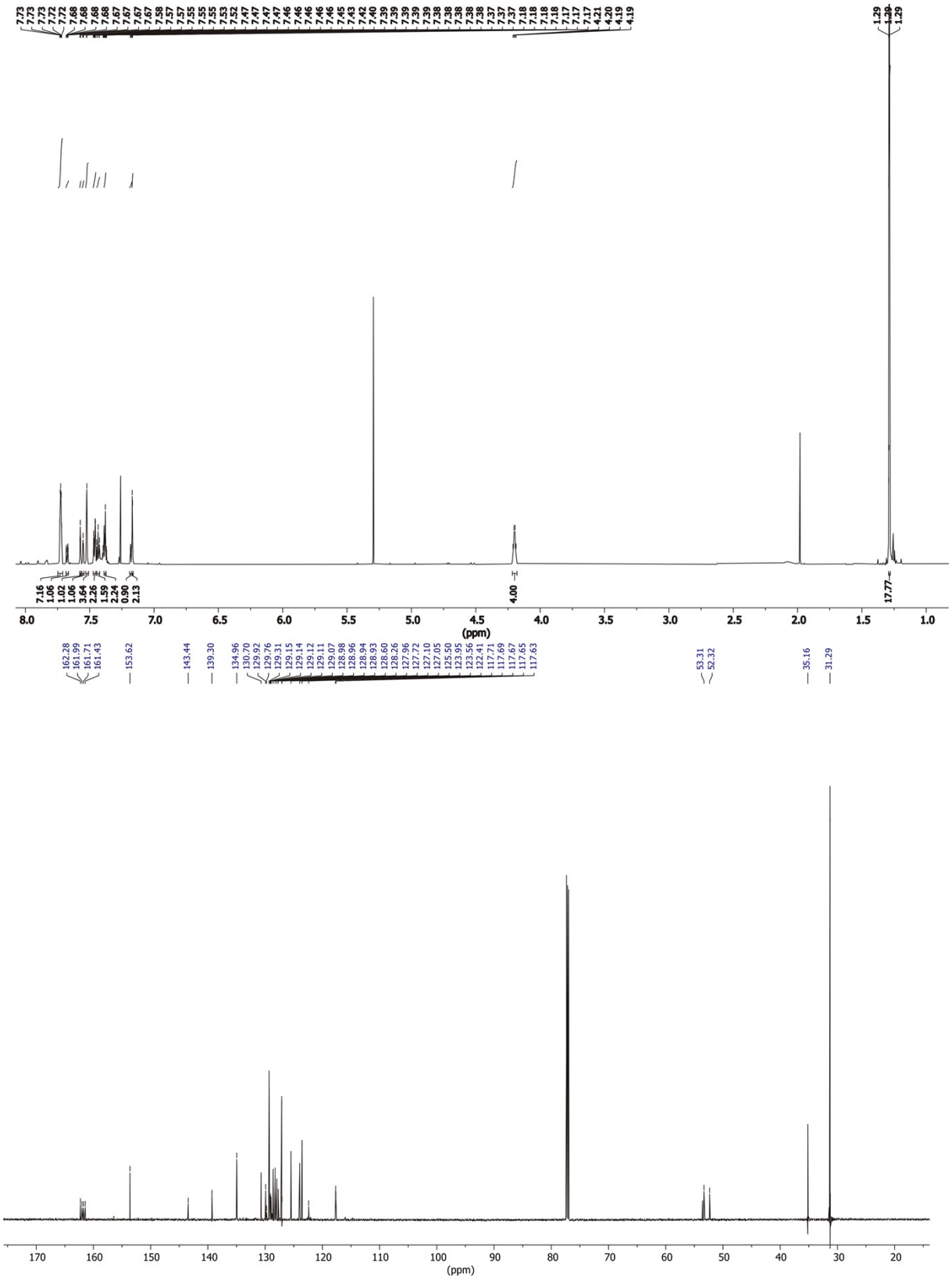
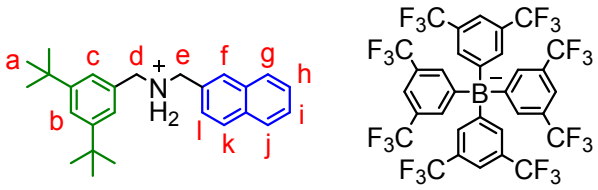


Fig. S9 ^{1}H (top) and ^{13}C (bottom) NMR spectra (700/176 MHz, $CDCl_3$, 298 K) of **PA9**.

N-(3,5-di-tert-butylbenzyl)-1-(naphthalen-2-yl)methanaminiumtetrakis(3,5-bis(trifluoromethyl)phenyl)borate



PA10

A solution of 200 mg (1.0 mmol, 1.0 equiv.) naphthalen-2-ylmethanaminium hydrochloride, 226 g (1.0 mmol, 1.0 equiv.) 3,5-di-*tert*-butylbenzaldehyde and 130 µL (0.9 mmol, 0.9 equiv.) dry NEt_3 in dry EtOH (50 mL) was left refluxing under argon atmosphere for 4 h. Afterwards, the solution was cooled to 0 °C in an ice bath and 200 mg (5.2 mmol, 5.0 equiv.) $NaBH_4$ was added. The mixture was left stirring under argon atmosphere in the thawing ice bath overnight. Then, the reaction was stopped by slow addition of sat. $NaHCO_3$ solution until no additional gas development occurred. The solvent was removed under reduced pressure and the residue was taken up in CH_2Cl_2. After washing with water, the organic phase was dried over $MgSO_4$. The crude product was then purified by column chromatography (SiO_2, CH_2Cl_2 → CH_2Cl_2/MeOH = 100:1, R_f ~ 0.2 in CH_2Cl_2/MeOH = 100:1) to get the desired oil, which was directly dissolved in EtOAc (10 mL) and acidified with conc. HCl, until the solution reached pH = 1. Afterwards, the solution was left stirring at r.t. for 3 h, then the solvent was removed under reduced pressure. The yellow solid was dissolved in MeOH (10 mL) and 599 mg (0.7 mmol, 1.0 equiv.) $NaBArF_{24}$ was added. The solution was left stirring at r.t. overnight, then the solvent was removed under reduced pressure. Afterwards, the residue was taken up in CH_2Cl_2 and washed with water and dried over $MgSO_4$ to obtain the desired product **PA10** as yellow oil in a combined yield of 61% (751 mg, 0.6 mmol).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.29 (s, 18H, a), 4.19 – 4.25 (m, 2H, d), 4.29 – 4.38 (m, 2H, e), 7.12 (d, J = 1.8 Hz, 2H, c), 7.23 (dd, J = 8.5, 1.8 Hz, 1H, f), 7.52 (s_{br}, 4H, $BArF_{24}$), 7.56 - 7.60 (m, 2H, h, i), 7.60 – 7.64 (m, 1H, b), 7.73 (s_{br}, 8H, $BArF_{24}$), 7.74 – 7.77 (m, 2H, g, j), 7.84 – 7.91 (m, 2H, l, k) ppm.**^{13}C NMR** (176 MHz, $CDCl_3$) δ [ppm] 31.5, 35.2, 49.3, 50.1, 114.5, 116.0, 122.4, 122.8, 123.9, 124.0, 124.3, 125.5, 126.5, 127.1, 127.2, 127.5, 127.7, 127.9, 128.1, 128.7, 129.5, 129.8, 130.2, 132.9, 133.0, 133.1, 133.2, 133.2, 133.3, 133.6, 134.0, 135.0, 140.6, 152.5, 156.7.**HRMS (MeOH):**m/z calcd. for $[C_{26}H_{34}N]^+$: 360.2686 $[M]^+$, found: 360.2677.

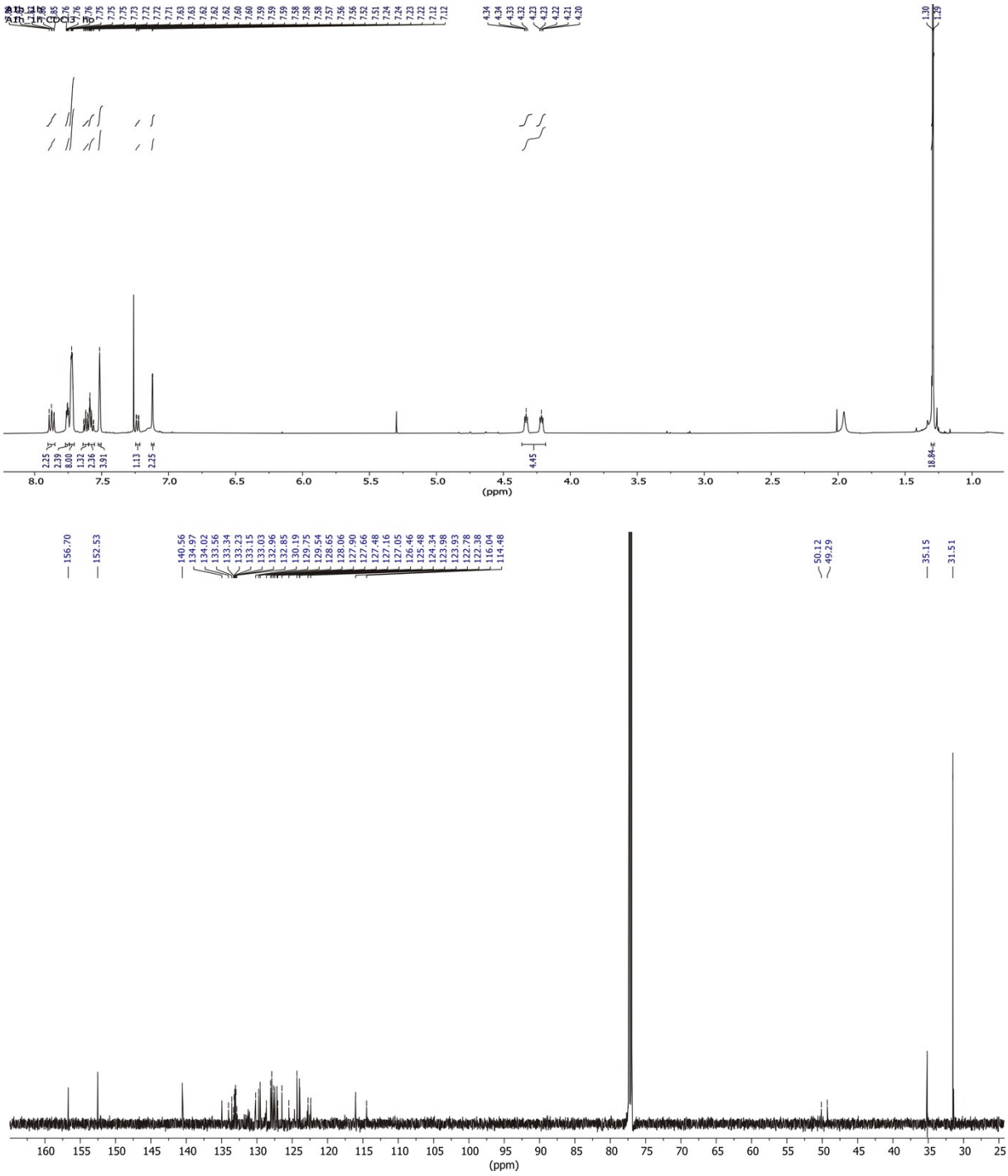
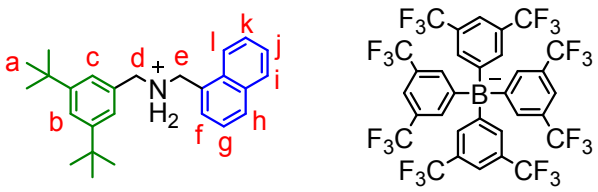


Fig. S10 ^{1}H (top) and ^{13}C (bottom) NMR spectra (500/176 MHz, $CDCl_3$, 298 K) of **PA10**.

N-(3,5-di-tert-butylbenzyl)-1-(naphthalen-1-yl)methanaminiumtetrakis(3,5-bis(trifluoromethyl)phenyl)borate



PA11

A solution of 200 mg (1.0 mmol, 1.0 equiv.) naphthalen-1-ylmethanaminium hydrochloride[9], 226 mg (1.0 mmol, 1.0 equiv.) 3,5-di-*tert*-butylbenzaldehyde and 130 µL (0.9 mmol, 0.9 equiv.) dry NEt_3 in dry EtOH (50 mL) was refluxed under argon atmosphere for 4 h. Afterwards, the solution was cooled to 0 °C in an ice bath and 195 mg (5.2 mmol, 5.0 equiv.) $NaBH_4$ was added. The mixture was left stirring under argon atmosphere in the thawing ice bath overnight. Then, the reaction was stopped by slow addition of sat. $NaHCO_3$ solution until no additional gas development occurred. The solvent was removed under reduced pressure and the residue was taken up in CH_2Cl_2. After washing with water, the organic phase was dried over $MgSO_4$. The crude product was then purified by column chromatography (SiO_2, CH_2Cl_2 → CH_2Cl_2/MeOH = 100:1, R_f ~ 0.2 in CH_2Cl_2/MeOH = 100:1) to obtain a yellowish oil, which was directly dissolved in EtOAc (10 mL) and acidified with conc. HCl, until the solution reached pH = 1. Afterwards, the solution was left stirring at r.t. for 3 h, then the solvent was removed under reduced pressure. The yellow solid was dissolved in MeOH (10 mL) and 599 mg (0.7 mmol, 1.0 equiv.) $NaBArF_{24}$ was added. The solution was left stirring at r.t. overnight, then the solvent was removed under reduced pressure. Afterwards, the residue was taken up in CH_2Cl_2 and washed with water and dried over $MgSO_4$ to obtain the desired product **PA11** as reddish oil in a combined yield of 63% (773 mg, 0.6 mmol).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.30 (s, 18H, a), 4.20 (s, 2H, d), 4.31 (s, 2H, e), 7.12 (d, J = 1.7 Hz, 2H, c), 7.21 – 7.25 (m, 1H, f), 7.51 (s_{br}, 4H, $BArF_{24}$), 7.56 - 7.64 (m, 3H, b, g, k), 7.72 (s_{br}, 8H, $BArF_{24}$), 7.74 – 7.78 (m, 2H, h, j), 7.86 – 7.91 (m, 2H, l, i). **^{13}C NMR** (176 MHz, $CDCl_3$): δ = 31.5, 31.6, 35.1, 46.1, 51.0, 114.3, 116.0, 116.1, 116.1, 116.1, 121.7, 121.9, 122.4, 122.5, 122.6, 122.8, 122.9, 123.9, 124.0, 124.1, 124.3, 125.5, 125.8, 126.7, 127.6, 127.7, 127.7, 128.9, 129.4, 129.8, 130.0, 130.8, 130.9, 131.0, 131.1, 133.0, 133.8, 134.1, 135.0, 140.6, 152.7, 156.9 ppm. **HRMS** (MeOH): *m/z* calcd. for $[C_{26}H_{34}N]^+$: 360.2686 $[M]^+$, found: 360.2688.

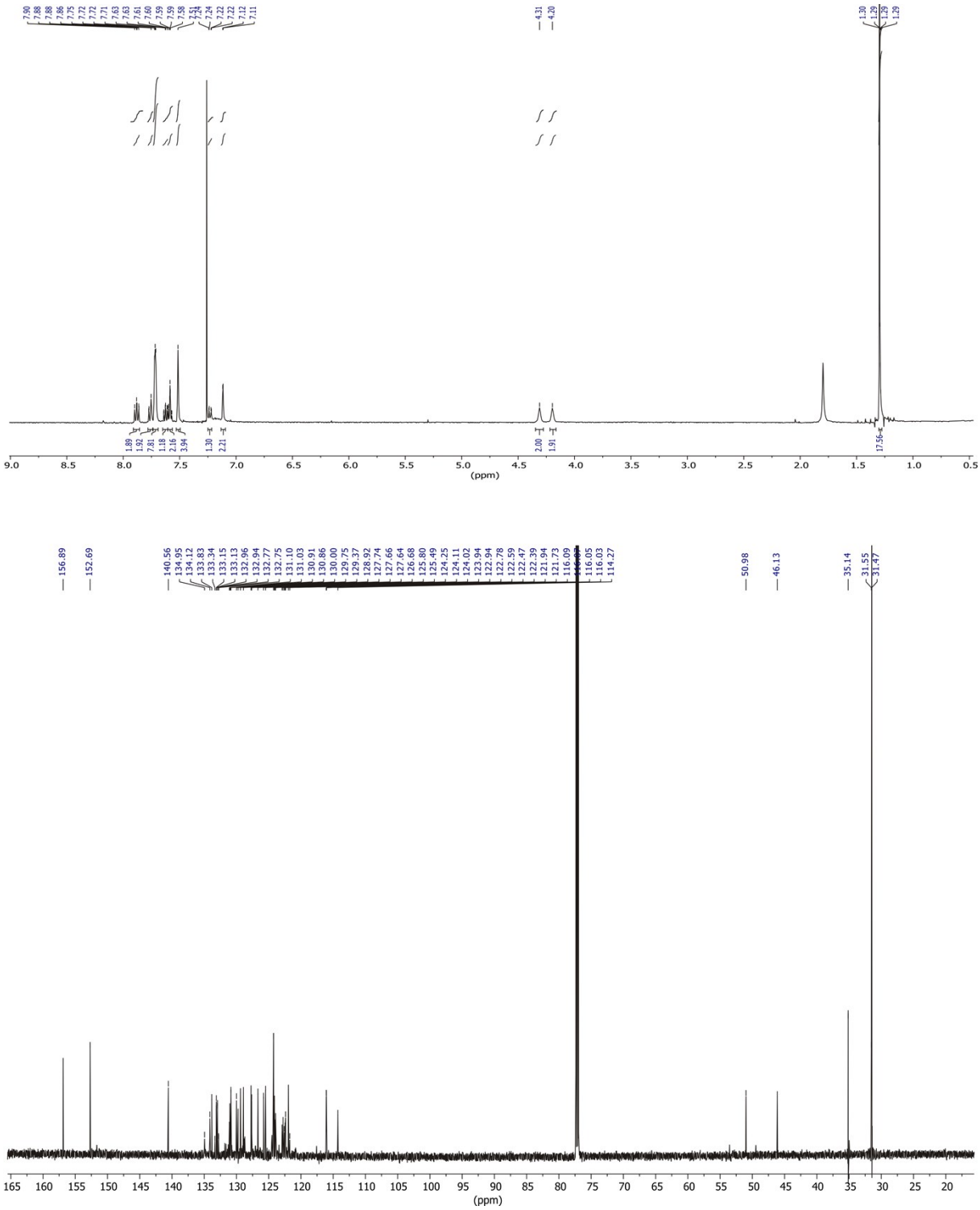
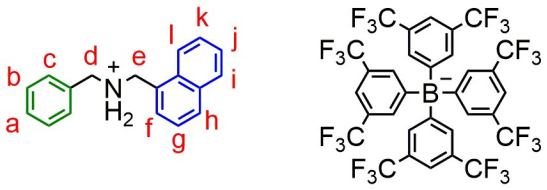


Fig. S11 ^{1}H (top) and ^{13}C (bottom) NMR spectra (500/176 MHz, $CDCl_3$, 298 K) of **PA11**.

N-benzyl-1-(naphthalen-1-yl)methanaminiumtetrakis(3,5-bis(trifluoromethyl)phenyl)borate



PA12

A solution of 52 mg (0.27 mmol, 1.0 equiv.) naphthalen-1-ylmethanaminium hydrochloride[9], 27 µL (0.27 mmol, 1.0 equiv.) benzaldehyde and 32 µL (0.24 mmol, 0.9 equiv.) dry NEt_3 in dry EtOH (15 mL) was refluxed under argon atmosphere for 4 h. Afterwards, the solution was cooled to 0 °C in an ice bath and 52 mg (1.3 mmol, 5.0 equiv.) $NaBH_4$ was added. The mixture was left stirring under argon atmosphere in the thawing ice bath overnight. Then, the reaction was stopped by slow addition of sat. $NaHCO_3$ solution until no additional gas development occurred. The solvent was removed under reduced pressure and the residue was taken up in CH_2Cl_2. After washing with water, the organic phase was dried over $MgSO_4$. The crude product was then purified by flash column chromatography (spherical SiO_2, CH_2Cl_2 → CH_2Cl_2/MeOH = 6%, R_f ~ 0.3 in CH_2Cl_2/MeOH = 1%) to obtain a yellow oil, which was directly dissolved in EtOAc (10 mL) and acidified with conc. HCl, until the solution reached pH = 1. Afterwards, the solution was left stirring at r.t. for 3 h, then the solvent was removed under reduced pressure. A fraction of the brown oil was dissolved in MeOH (5 mL) and 62 mg (70 µmol, 1.0 equiv.) $NaBArF_{24}$ was added. The solution was left stirring at r.t. overnight, then the solvent was removed under reduced pressure. Afterwards, the residue was taken up in CH_2Cl_2 and washed with water and dried over $MgSO_4$ to obtain the desired product **PA12** as brown oil in a combined yield of 54% (52 mg, 46 µmol).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 4.20 (s, 2H, d), 4.41 (s, 2H, e), 7.08 – 7.11 (m, 2H, c), 7.23 (dd, J = 7.0, 1.2 Hz, 1H, f), 7.33 – 7.39 (m, 4H, g,k,b), 7.42 – 7.46 (m, 1H, a), 7.48 – 7.50 (m, 1H, h), 7.49 – 7.52 (s_{br}, 4H, $BArF_{24}$), 7.57 (m, 1H, j), 7.72 (s_{br}, 8H, $BArF_{24}$), 7.93 – 7.97 (m, 1H, i,l). **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 49.79, 52.99, 117.68, 120.22, 122.01, 123.82, 125.62, 127.46, 128.67, 129.04, 129.34, 130.33, 130.47, 131.19, 132.15, 134.33, 134.95, 161.38, 161.70, 162.04, 162.36 ppm. **HRMS** (MeOH): *m/z* calcd. for $[C_{18}H_{18}N]^+$: 248.1434 $[M]^+$, found: 248.1431.

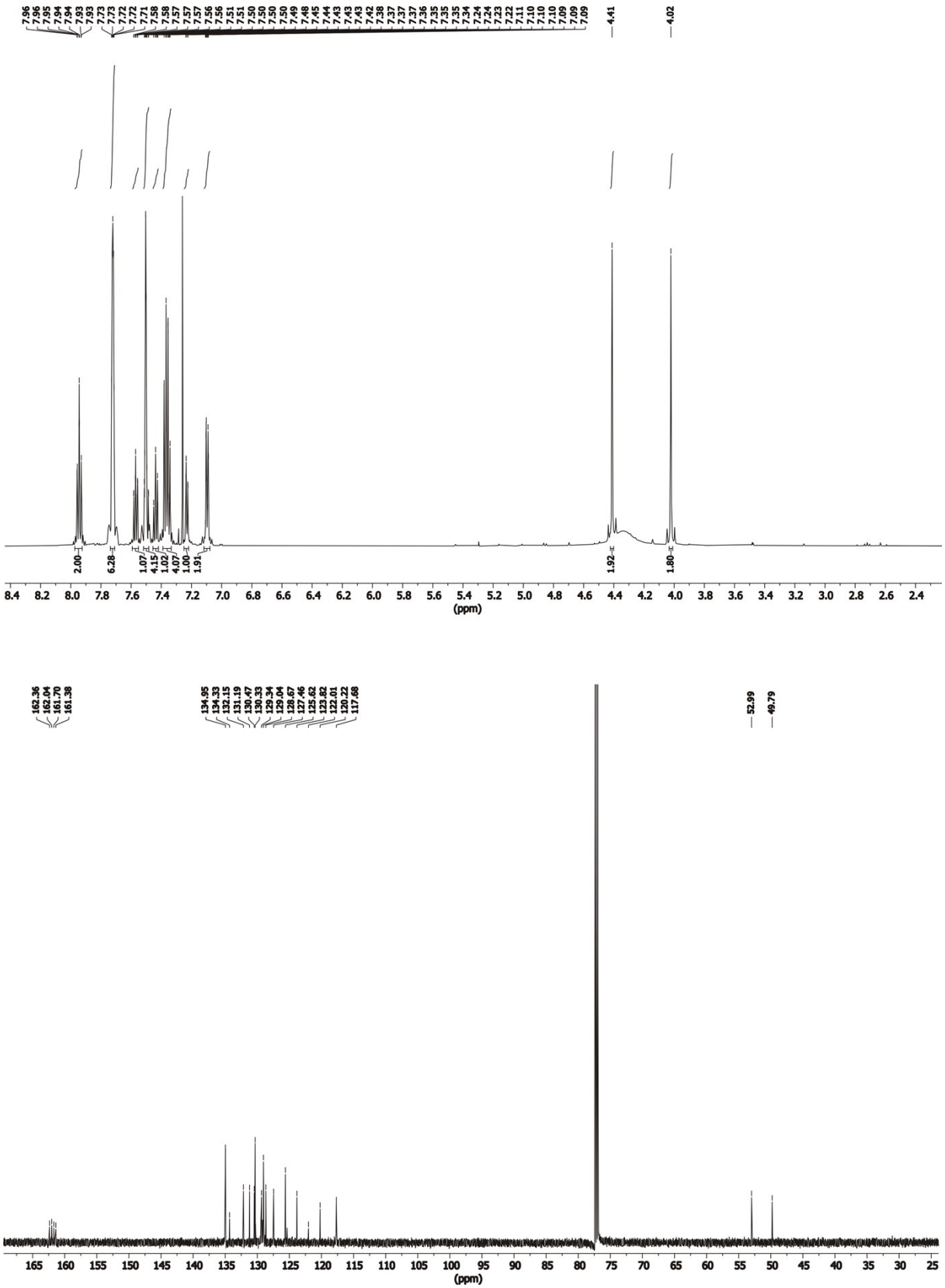
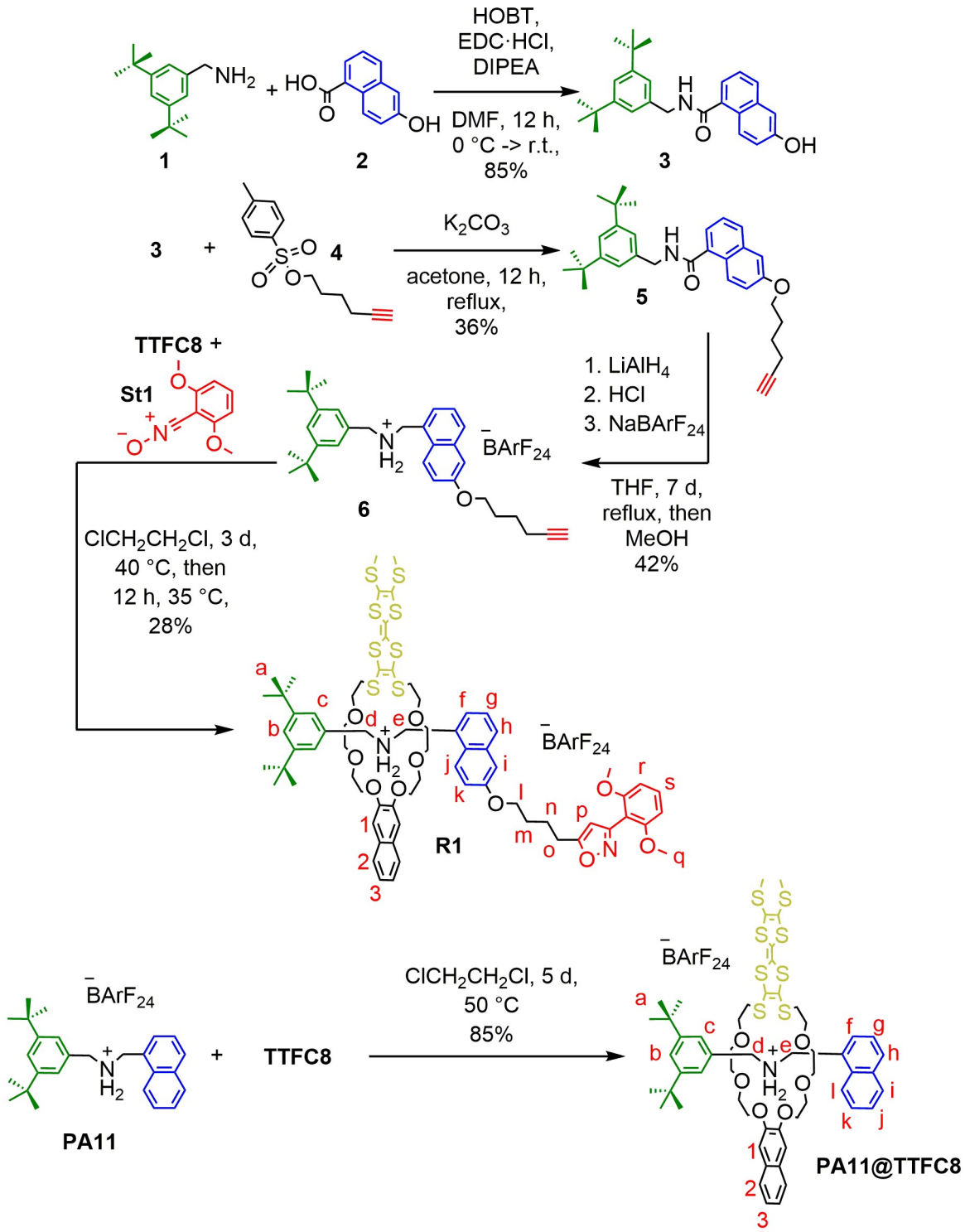


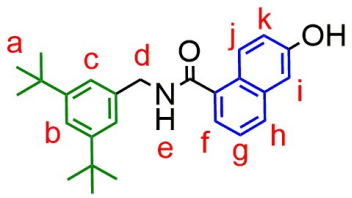
Fig. S12 ^{1}H (top) and ^{13}C (bottom) NMR spectra (600/151 MHz, $CDCl_3$, 298 K) of **PA12**.

1.3. Synthesis of [2]rotaxane R1, R2 and PA11@TTFC8



Scheme S2 Synthesis of **R1** and **PA11@TTFC8**.

N-(3,5-di-tert-butylbenzyl)-6-hydroxy-1-naphthamide 3



3

A solution of 58 mg (0.27 mmol, 1.0 equiv.) (3,5-di-*tert*-butylphenyl)methanamine **1**, 50 mg (0.27 mmol, 1.0 equiv.) 6-hydroxy-1-naphthoic acid **2** were dissolved in dry DMF (5 mL). In an ice bath 22 mg (0.16 mmol, 0.6 equiv.) HOBT, 66 mg (0.35 mmol, 1.3 equiv.) EDC·HCl and 72 µL (0.43 mmol, 1.6 equiv.) DIPEA were added. The mixture was stirred under argon atmosphere in the thawing ice bath overnight. Then, the mixture was diluted with 30 mL EtOAc and washed with water and brine. After drying over $MgSO_4$, the solvent was removed. Afterwards, the crude product was purified by column chromatography (SiO_2, CH_2Cl_2 -> CH_2Cl_2/MeOH 50:1, R_f ~ 0.4 in CH_2Cl_2/MeOH = 50:1) to get the desired product **3** as yellow sticky solid in 85% yield (85.7 mg, 0.22 µmol).

^{1}H NMR (500 MHz, acetone-d_6) δ = 1.33 (s, 18H, a), 4.68 (d, J = 6.2 Hz, 2H, d), 7.16 (dd, J = 9.1, 2.5 Hz, 1H, k), 7.23 (d, J = 2.5 Hz, 1H, i), 7.35 (d, J = 1.8 Hz, 2H, c), 7.37 – 7.42 (m, 2H, b, h), 7.46 (dd, J = 7.0, 1.3 Hz, 1H, g), 7.72 – 7.76 (m, 1H, f), 8.02 – 8.09 (s_{br}, 1H, e), 8.28 (d, J = 9.2 Hz, 1H, j), 8.83 (s_{br}, 1H, OH) ppm. **^{13}C NMR** (126 MHz, Acetone-d_6) δ = 31.8, 35.4, 44.3, 110.2, 119.8, 121.6, 122.5, 122.8, 126.1, 126.1, 128.4, 129.1, 136.2, 136.4, 139.8, 151.5, 156.4, 169.9 ppm. **HRMS** (CH_2Cl_2/MeOH): m/z calcd. for $[C_{26}H_{31}NO_2]$: 412.2247 $[M+Na]^+$, found: 412.2263.

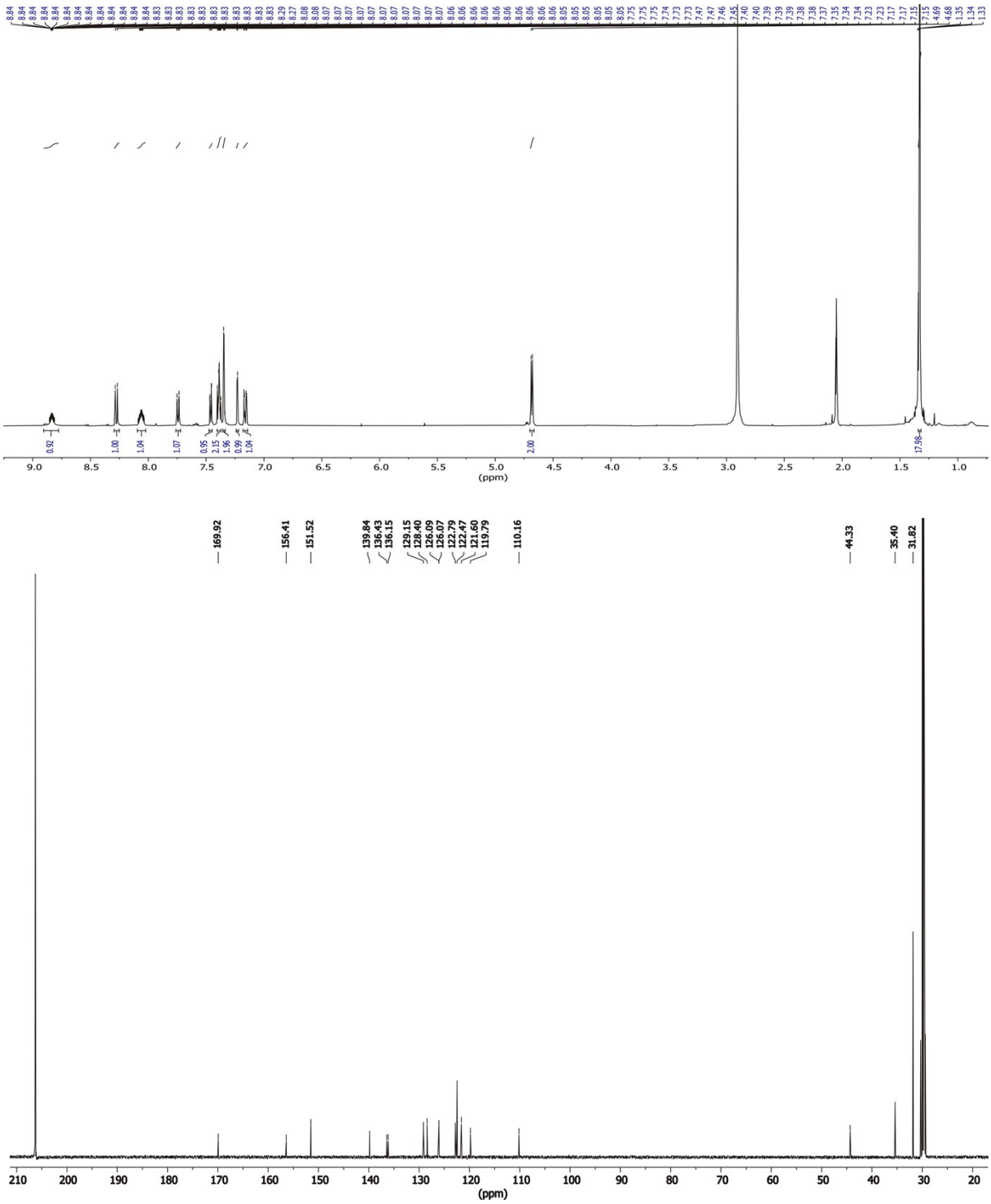
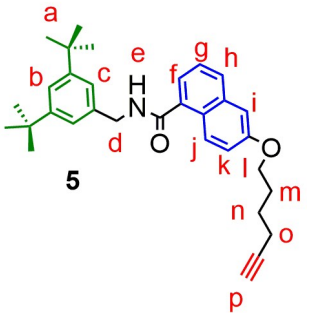


Fig. S13 ^{1}H (top) and ^{13}C (bottom) NMR spectra (500/126 MHz, Acetone-d_6, 298 K) of **3**.

N-(3,5-di-tert-butylbenzyl)-6-(hex-5-yn-1-yloxy)-1-naphthamide 5



5

A solution of 194 mg (0.77 mmol, 1.2 equiv.) tosylate **4**, 250 mg (0.64 mmol, 1.0 equiv.) amide **3** and 177 mg (1.28 mmol, 2.0 equiv.) K_2CO_3 in acetone (10 mL) was refluxed for 12 h. Then, the mixture was filtered and the solvent was removed, the crude product was dissolved in CH_2Cl_2 and washed with water and brine. After drying over $MgSO_4$, the solvent was removed. Afterwards, the crude product was purified by column chromatography (SiO_2, CH_2Cl_2 -> CH_2Cl_2/MeOH 100:1, R_f ~ 0.8 in CH_2Cl_2/MeOH = 100:1) to get the desired product **5** as yellow sticky solid in 36% yield (108 mg, 0.23 mmol).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.34 (s, 18H, a), 1.73 – 1.82 (m, 2H, n), 1.95 – 2.05 (m, 3H, m, p), 2.31 (td, *J* = 7.0, 2.7 Hz, 2H, o), 4.11 (t, *J* = 6.3 Hz, 2H, l), 4.72 (d, *J* = 5.7 Hz, 2H, d), 6.24 (t, *J* = 5.7 Hz, 1H, e), 7.14 (d, *J* = 2.6 Hz, 1H, i), 7.20 (dd, *J* = 9.2, 2.6 Hz, 1H, k), 7.25 (d, *J* = 1.9 Hz, 2H, c), 7.37 – 7.42 (m, 2H, b, g), 7.47 (dd, *J* = 7.1, 1.3 Hz, 1H, h), 7.75 – 7.79 (m, 1H, f), 8.30 (dt, *J* = 9.2, 0.6 Hz, 1H, j) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 18.3, 25.2, 28.3, 31.6, 35.0, 44.9, 67.5, 68.9, 84.2, 107.1, 120.2, 121.9, 122.3, 122.6, 125.4, 125.7, 127.2, 129.5, 134.6, 135.3, 137.3, 151.6, 157.4, 169.6 ppm. **HRMS (CH_2Cl_2/MeOH):** m/z calcd. for $[C_{32}H_{39}NO_2]$: 470.3059 $[M+H]^+$, found: 470.3028; 492.2879 $[M+Na]^+$, found: 492.2848; 508.2618 $[M+K]^+$, found: 508.2585.

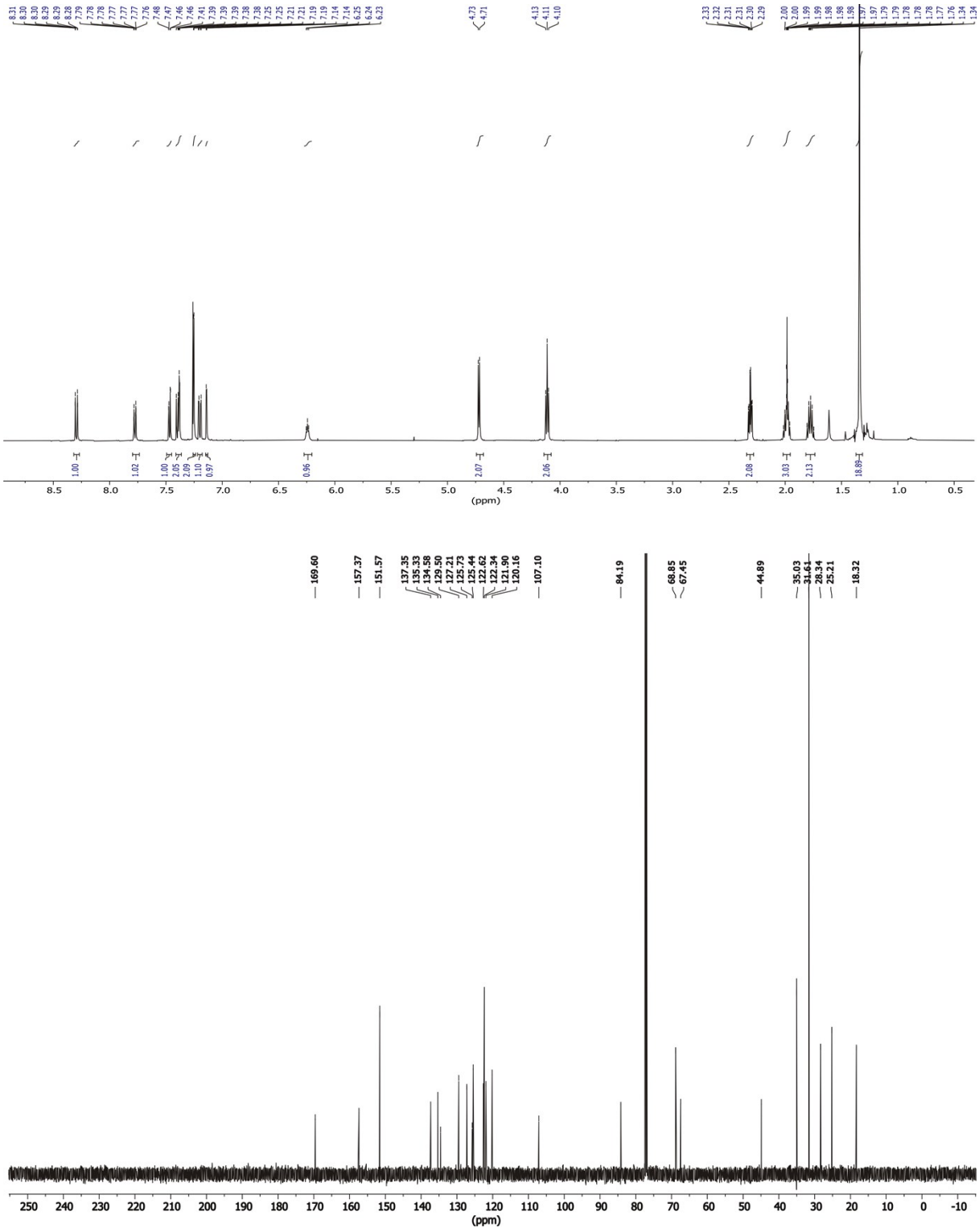
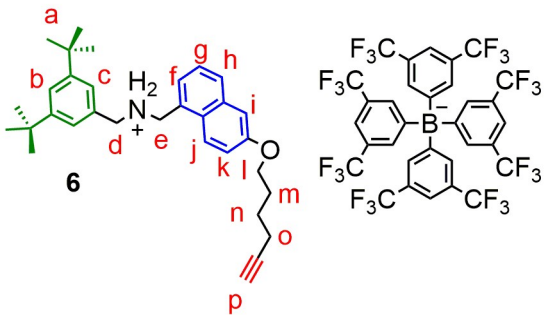


Fig. S14 ^{1}H (top) and ^{13}C (bottom) NMR spectra (500/126 MHz, $CDCl_3$, 298 K) of **5**.

N-(3,5-di-tert-butylbenzyl)-1-(6-(hex-5-yn-1-yloxy)naphthalen-1-yl)methanaminium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate 6



6

Amide **5** (382 mg, 0.813 mmol, 1 equiv.) and $LiAlH_4$ (124 mg, 3.25 mmol, 4 equiv.) were dissolved in 60 mL dry THF and refluxed for 7 days. Afterwards, the reaction was quenched with saturated aq. Na_2SO_4 solution. The white precipitate was filtered off and the solvent was removed. The residue was dissolved in CH_2Cl_2 (50 mL) and washed with brine (3x70 mL). The organic phase was dried over $MgSO_4$ and the solvent was removed. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2 -> CH_2Cl_2/MeOH 100:1, R_f ~ 0.2 in CH_2Cl_2/MeOH = 100:1) to get the desired amine as a yellow oil, which was dissolved in diethylether (20 mL) and protonated with HCl conc. under cooling in an ice bath. The solvent was removed, 100 mg (0.2 mmol) of the brown sticky oil were dissolved in MeOH (10 mL) and $NaBArF_{24}$ (180 mg, 0.2 mmol, 1.0 equiv.) was added. After stirring overnight at room temperature, the solvent was removed, the residue was taken up in CH_2Cl_2 and washed with water (3x50 mL). The organic phase was dried over $MgSO_4$ and the solvent was removed. The crude salt was purified via column chromatography (SiO_2, CH_2Cl_2 -> CH_2Cl_2/acetone 10:1, R_f ~ 0.4 in CH_2Cl_2/acetone = 50:1) to get the desired axle **6** as brown oil in 42% overall yield (112.4 mg, 0.85 µmol).

^{1}H NMR (700 MHz, $CDCl_3$) δ = 1.33 (s, 18H, a), 1.74 – 1.79 (m, 2H, n), 1.97 – 2.02 (m, 3H, m,p), 2.31 (td, *J* = 7.0, 2.7 Hz, 2H, o), 4.10 (t, *J* = 6.3 Hz, 2H, l), 4.14 (s, 2H, d), 4.37 (s, 2H, e), 7.06 – 7.10 (m, 2H, j, f), 7.15 (d, *J* = 1.7 Hz, 2H, c), 7.17 – 7.20 (m, 2H, k, i), 7.26 – 7.29 (m, 1H, g), 7.52 (s, 4H, $BArF_{24}$), 7.61 (d, *J* = 1.8 Hz, 1H, b), 7.71 – 7.74 (m, 8H, $BArF_{24}$), 7.75 (d, *J* = 8.4 Hz, 1H, h) ppm.**^{13}C NMR** (176 MHz, $CDCl_3$) δ = 18.3, 25.1, 28.2, 31.0, 31.4, 35.2, 49.1, 53.5, 67.8, 68.9, 84.0, 108.5, 117.6, 121.4, 122.0, 122.4, 123.40, 123.9, 125.2, 125.5, 125.5, 126.2, 127.0, 129.1, 130.6, 135.0, 153.6, 157.8, 161.9, 212.8 ppm. **HRMS (MeOH):** m/z calcd. for $[C_{32}H_{42}NO]^+$: 456.3261 $[M]^+$, found: 456.3283

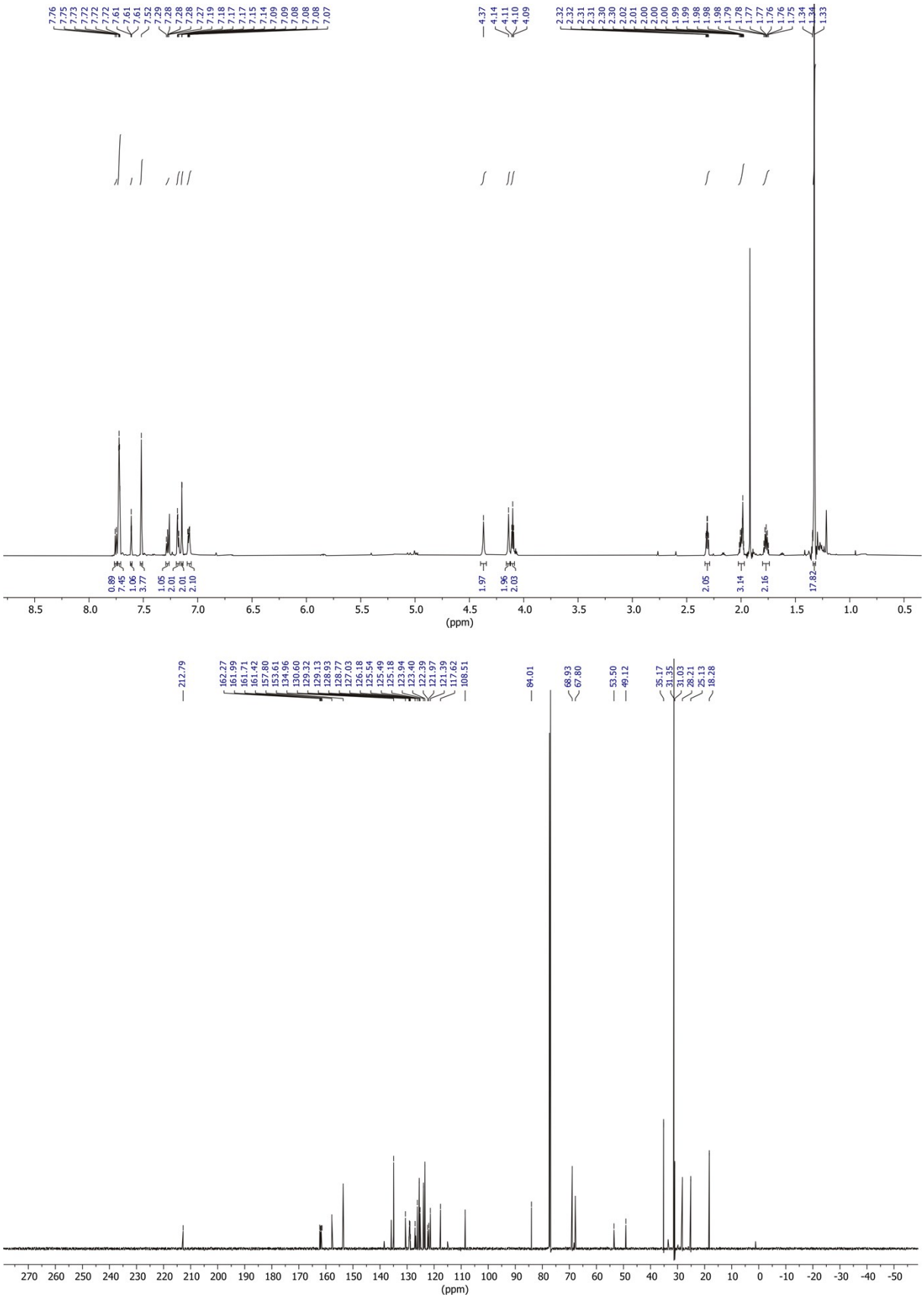
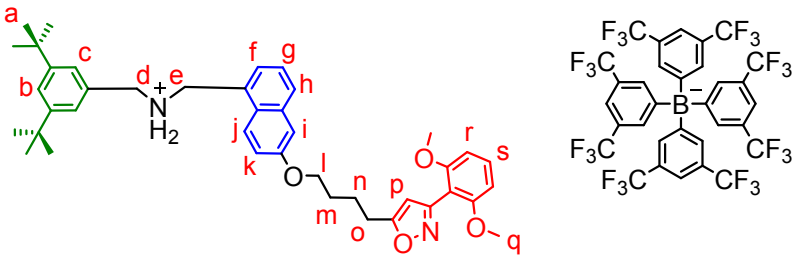


Fig. S15 ^{1}H (top) and ^{13}C (bottom) NMR spectra (700/176 MHz, $CDCl_3$, 298 K) of **6**.

N-(3,5-di-tert-butylbenzyl)-1-(6-(4-(3-(2,6-dimethoxyphenyl)isoxazol-5-yl)butoxy)naphthalen-1-yl)methanaminium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate 7



7

The axle **6** (20 mg, 15 µmol, 1.0 equiv.) and stopper **St1** (4 mg, 20 µmol, 1.3 equiv.) was added and the mixture heated to 35°C for 2 days. Then, the mixture was purified by column chromatography (SiO_2, CH_2Cl_2 + EtOH 3%, R_f ~ 0.3 in CH_2Cl_2) to obtain the desired product **7** (8 mg, 5 µmol, 30%) as an brown oil.

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 1.28 (s, 18H, a), 1.80 – 1.92 (m, 4H, m,n), 2.82 (t, J = 7.0 Hz, 2H, o), 3.66 (s, 6H, q), 4.15 (t, J = 5.7 Hz, 2H, l), 4.29 (s, 2H, d,e), 4.59 (s, 2H, d,e), 6.46 (s, 1H, p), 6.65 – 6.69 (d, J = 8.5 Hz, 2H, r), 7.13 – 7.19 (m, 1H, j), 7.20 – 7.25 (m, 4H, c,f,i), 7.29 – 7.35 (m, 1H, g), 7.40 – 7.49 (m, 2H, s,k), 7.55 (s_{br}, 4H, $BArF_{24}$), 7.59 (t, J = 1.8 Hz, 1H, b), 7.71 (s_{br}, 8H, $BArF_{24}$), 7.77 (d, J = 8.3 Hz, 1H, h), 7.97 – 8.05 (s_{br}, 2H, NH_2) ppm. **^{13}C NMR** (176 MHz, CD_2Cl_2) δ = 24.2, 26.7, 28.5, 29.3, 30.1, 31.4, 35.3, 47.2, 49.3, 57.0, 67.9, 105.9, 106.0, 109.4, 117.9, 121.3, 122.7, 123.1, 124.2, 124.2, 125.4, 125.5, 125.8, 126.3, 126.4, 127.3, 127.5, 129.3, 130.7, 135.2, 153.6, 156.5, 157.5, 159.3, 162.2, 173.9 ppm. **HRMS (MeOH):**m/z calcd. for $[C_{41}H_{51}N_2O_4]^+$: 635.3849 $[M]^+$, found: 635.3868.

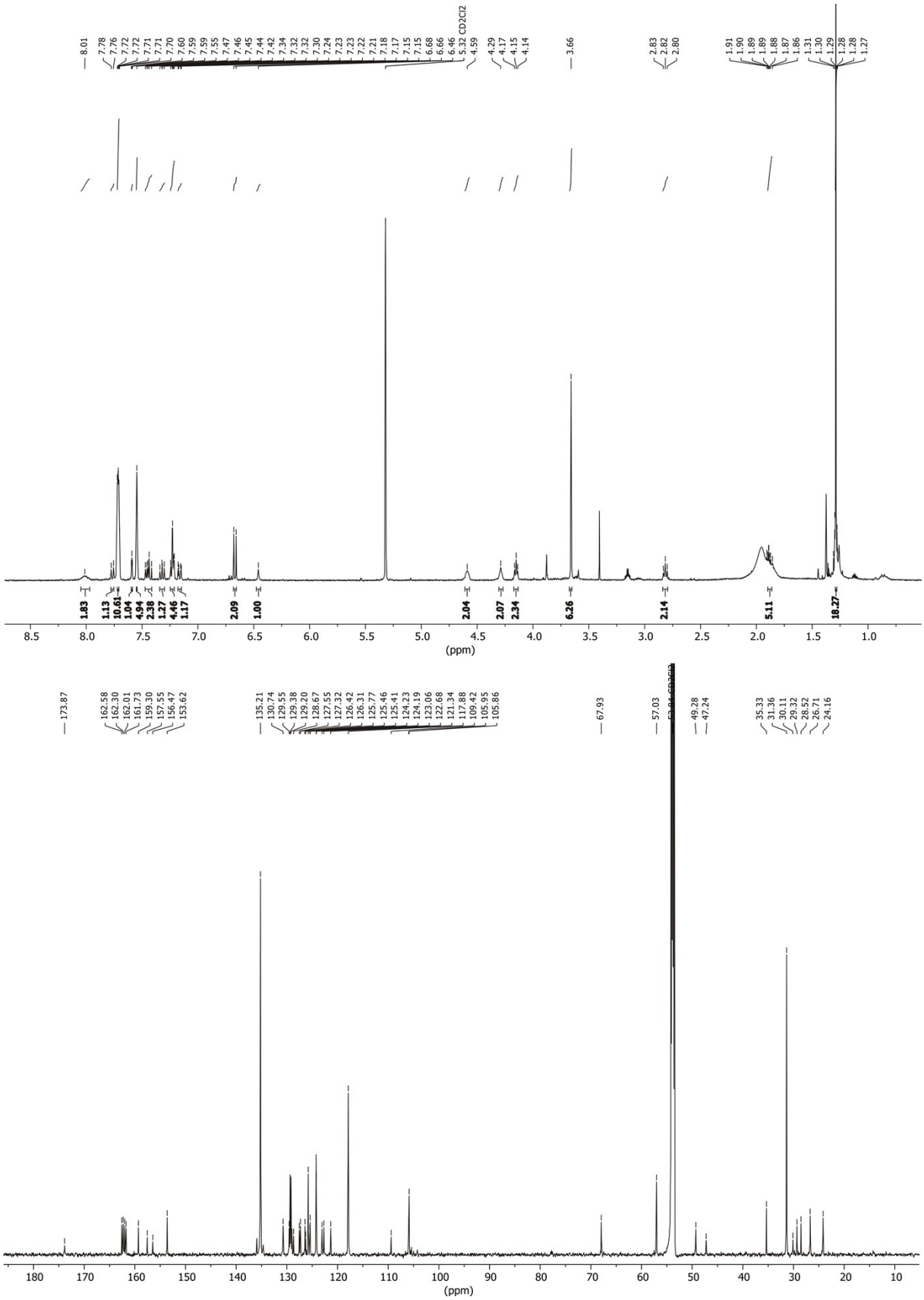
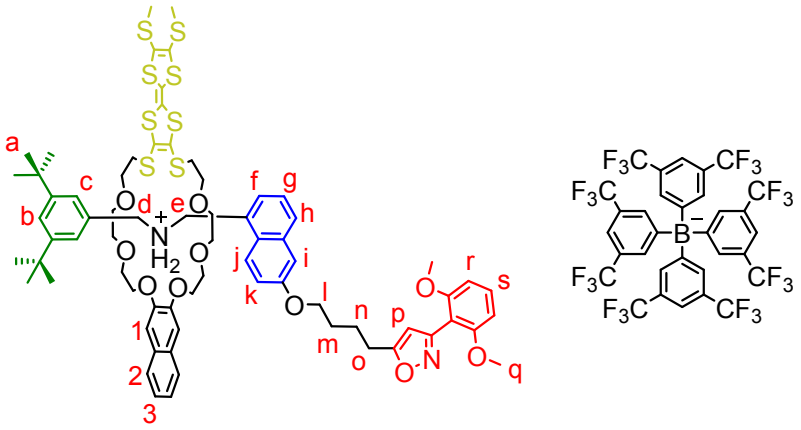


Fig. S16 ^{1}H (top) and ^{13}C (bottom) NMR spectra (400/176 MHz, CD_2Cl_2, 298 K) of **7**.

[2]Rotaxane R1



R1

The axle **6** (38 mg, 29 µmol, 1.0 equiv.) and macrocycle **TTFC8** (24 mg, 32 µmol, 1.1 equiv.) were dissolved in $ClCH_2CH_2Cl$ (2 mL) and stirred at 40 °C. for 3 days. Afterwards, the mixture was allowed to cool to room temperature, stopper **St1** (7 mg, 37 µmol, 1.3 equiv.) was added and the mixture heated to 35°C for 2 days. Then, the mixture was purified by column chromatography (SiO_2, CH_2Cl_2/hexane 8:2 -> CH_2Cl_2, R_f ~ 0.5 in CH_2Cl_2) to obtain the desired product **R1** (15 mg, 7 µmol, 23%) as an orange oil.

^{1}H NMR (700 MHz, CD_2Cl_2) δ = 1.28 (s, 18H, a), 1.90 – 1.95 (m, 2H, m), 1.97 – 2.03 (m, 2H, n), 2.40 (s, 6H, S-CH_3), 2.93 – 2.96 (m, 2H, o), 3.17 – 3.25 (m, 4H, S-CH_2-CH_2), 3.42 – 3.49 (m, 5H, O-CH_2-CH_2), 3.55 – 3.59 (m, 3H, O-CH_2-CH_2), 3.60 – 3.68 (m, 5H, O-CH_2-CH_2), 3.75 – 3.77 (m, 2H, l), 3.78 (s, 6H, q), 3.82 – 3.89 (m, 6H, O-CH_2-CH_2), 3.92 – 4.01 (m, 6H, O-CH_2-CH_2), 5.00 – 5.04 (m, 2H, d), 5.06 – 5.11 (m, 2H, e), 6.14 (t, *J* = 0.7 Hz, 1H, p), 6.38 (d, *J* = 2.6 Hz, 1H, j), 6.53 (s, 2H, 1), 6.67 (d, *J* = 8.4 Hz, 2H, r), 7.11 – 7.14 (m, 3H, g,k,i), 7.36 – 7.39 (m, 4H, 2,f,s), 7.50 (t, *J* = 1.7 Hz, 1H, b), 7.52 – 7.54 (m, 4H, 3, c), 7.55 – 7.57 (s_{br}, 4H, $BArF_{24}$), 7.70 – 7.74 (s_{br}, 8H, $BArF_{24}$), 7.98 – 8.01 (d, *J* = 9.2 Hz, 1H, h) ppm. **^{13}C NMR** (176 MHz, CD_2Cl_2) δ = 19.5, 25.0, 27.2, 29.3, 30.3, 31.7, 35.6, 39.1, 51.0, 56.5, 67.8, 68.8, 70.6, 71.2, 71.3, 72.8, 104.2, 104.7, 107.4, 108.0, 108.2, 109.2, 113.9, 118.0, 120.5, 122.8, 122.8, 123.4, 124.4, 124.5, 125.4, 125.8, 125.9, 126.6, 126.7, 127.0, 127.2, 127.5, 128.1, 128.9, 129.4, 129.5, 129.8, 130.1, 131.6, 135.4, 135.5, 147.5, 153.4, 157.4, 157.6, 159.2, 162.3, 173.1 ppm. **HRMS (MeOH):**m/z calcd. for $[C_{71}H_{87}N_2O_{10}S_8]^+$: 1383.4121 $[M]^+$, found: 1383.4156

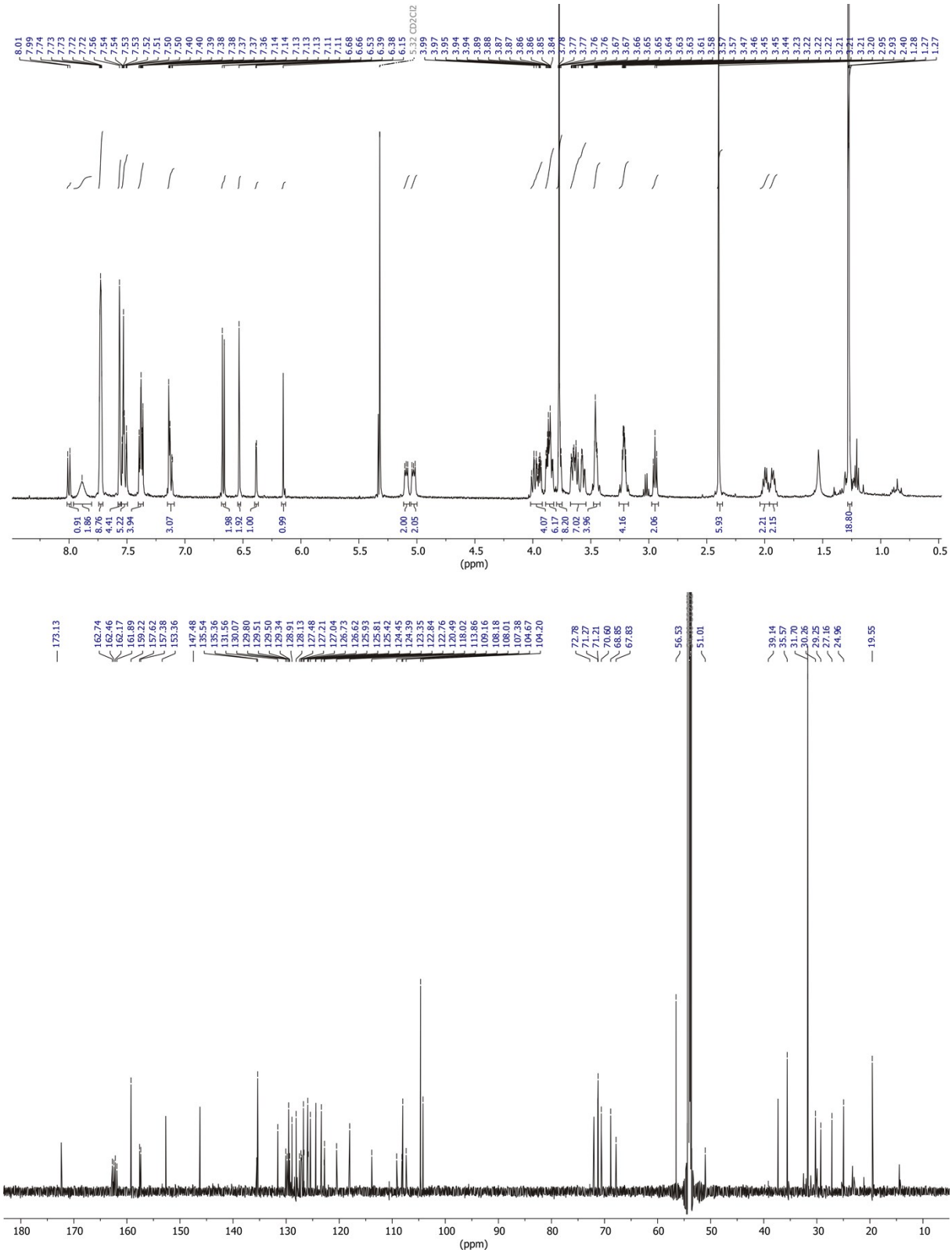


Fig. S17 ^{1}H (top) and ^{13}C (bottom) NMR spectra (700/176 MHz, CD_2Cl_2, 298 K) of **R1**.

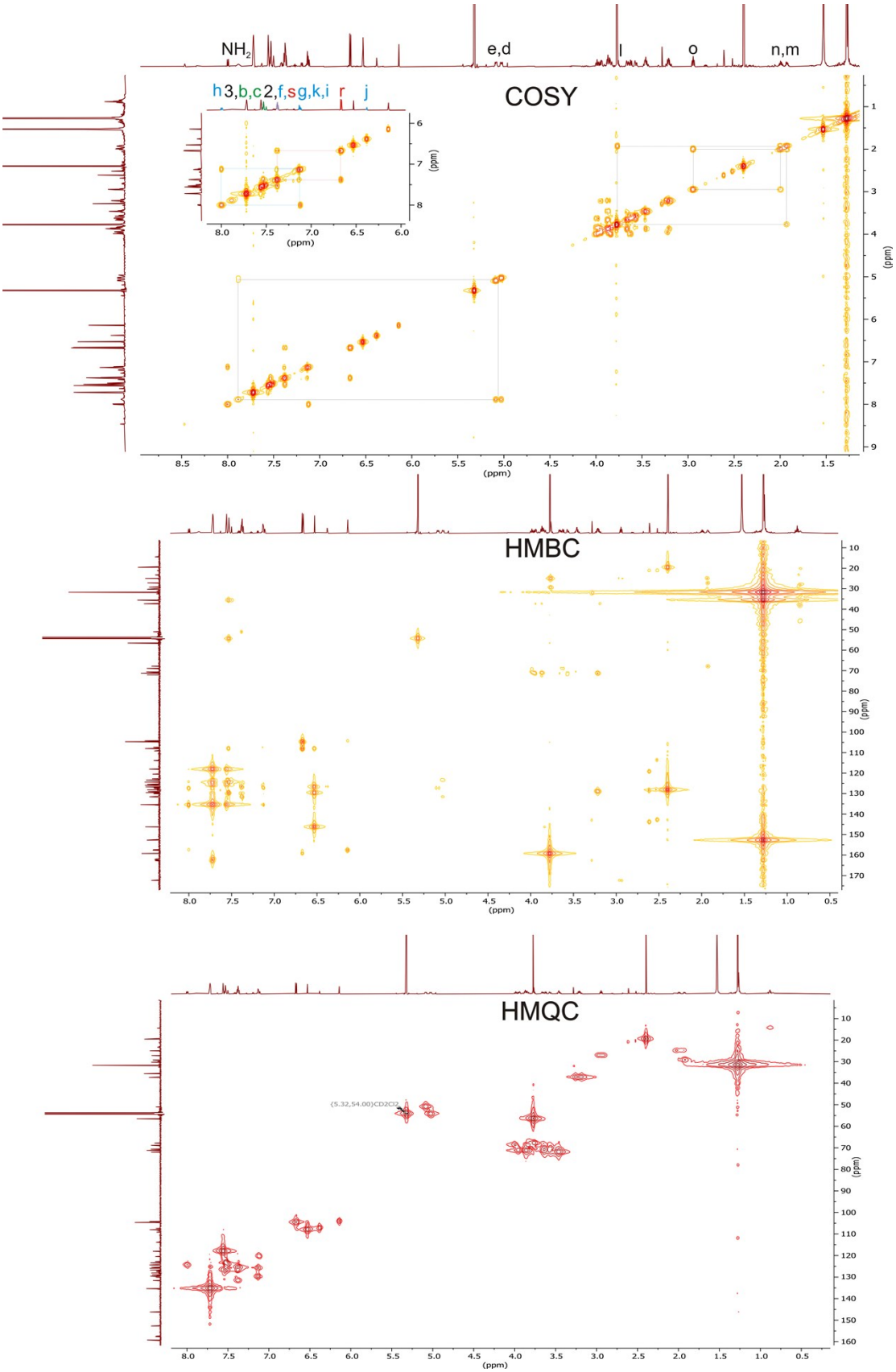


Fig. S18 COSY (top), HMBC (center) and HMQC (bottom) NMR spectra (700/176 MHz, CD_2Cl_2, 298 K) of **R1**.

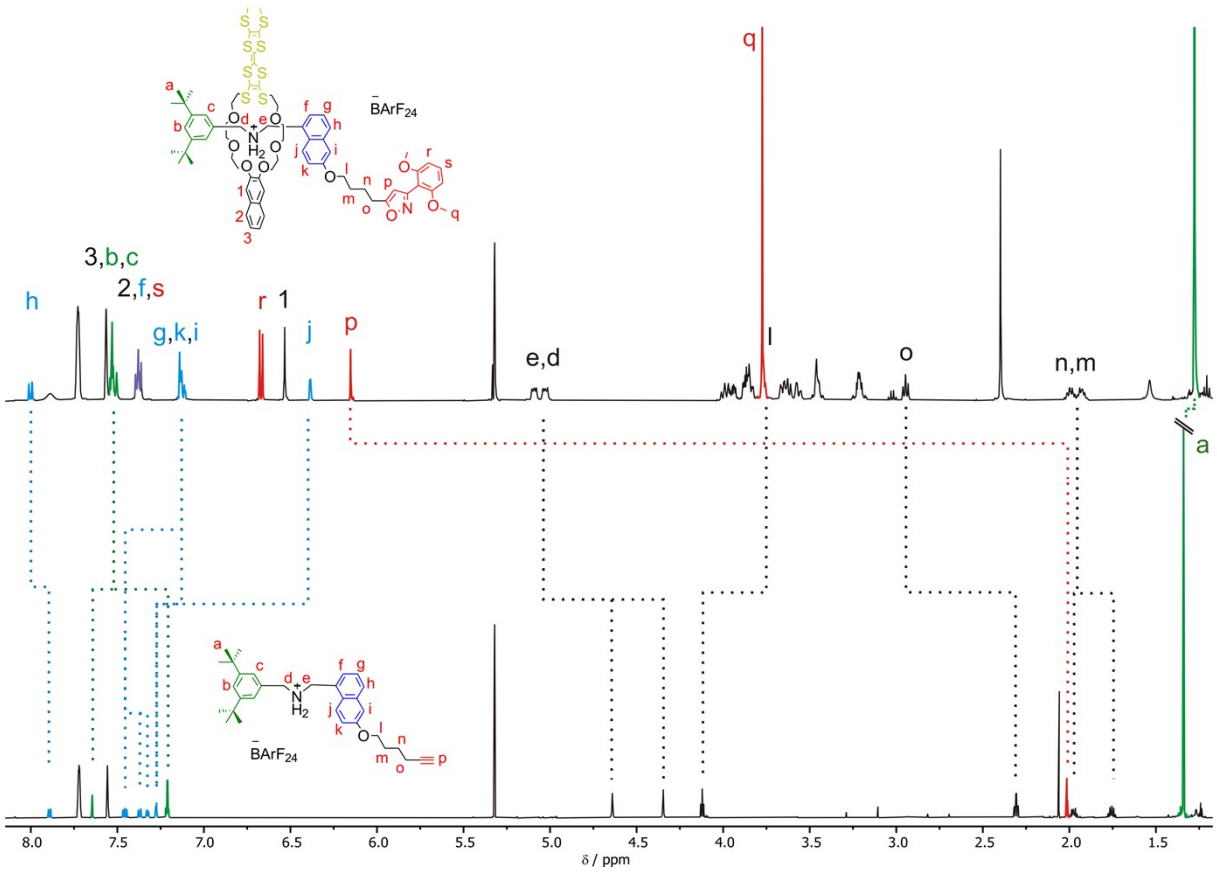
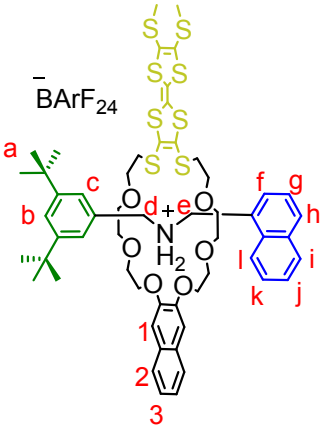


Fig. S19 [2]rotaxane **R1** (top) and axle **6** (bottom) NMR spectra (500 MHz, CD_2Cl_2, 298 K).

Pseudorotaxane PA11@TTFC8



PA11@TTFC8

Axle **PA11** (50 mg, 41 µmol, 1.0 equiv.) and macrocycle **TTFC8** (31 mg, 41 µmol, 1.0 equiv.) were dissolved in $ClCH_2CH_2Cl$ (2 mL) and stirred at 50 °C for 5 days. The mixture was purified by column chromatography (SiO_2, CH_2Cl_2, R_f ~ 0.5 in CH_2Cl_2) to obtain the desired product **PA11@TTFC8** (65.2 mg, 33 µmol, 85%) as an orange sticky solid.

^{1}H NMR (700 MHz, CD_2Cl_2) δ = 1.27 (s, 18H, b), 2.40 (s, 6H, S-Me), 3.16 – 3.24 (m, 4H, S-$C\underline{H}_2$-CH_2), 3.43 – 3.45 (m, 4H, O-CH_2), 3.55 – 3.58 (m, 4H, O-CH_2), 3.61 – 3.68 (m, 4H, O-CH_2), 3.81 – 3.88 (m, 6H, O-CH_2), 3.90 – 3.97 (m, 4H, O-CH_2), 5.02 – 5.06 (m, 2H, d), 5.13 – 5.17 (m, 2H, e), 6.52 (s, 2H, 1), 7.08 (dd, J = 8.2, 7.0 Hz, 1H, j), 7.18 – 7.21 (m, 1H, k), 7.27 – 7.29 (m, 1H, f), 7.30 – 7.33 (m, 1H, l), 7.36 – 7.40 (m, 1H, 2), 7.49 (t, J = 1.8 Hz, 1H, a), 7.47 – 7.56 (m, 6H, 3, c, g, i), 7.55 – 7.57 (m, 4H, $BArF_{24}$), 7.71 – 7.74 (m, 8H, $BArF_{24}$), 7.91 (s_{br}, 2H, NH_2), 8.10 (d, J = 8.5, 0.9 Hz, 1H, h) ppm. **^{13}C-NMR** (176 MHz, CD_2Cl_2) δ = 19.6, 31.7, 35.5, 37.3, 44.5, 50.9, 54.2, 68.8, 70.6, 71.2, 71.3, 72.0, 108.1, 118.0, 122.9, 123.1, 123.4, 124.4, 124.5, 125.2, 125.5, 125.9, 126.7, 126.8, 127.2, 127.5, 127.5, 128.1, 128.8, 129.1, 129.4, 129.5, 130.9, 131.2, 131.5, 134.0, 135.4, 146.2, 152.7, 162.3 ppm. **HRMS (CH_2Cl_2):** m/z calcd. for $[C_{56}H_{70}NO_6S_8]^+$:1108.2963 $[M]^+$, found: 1108.2948

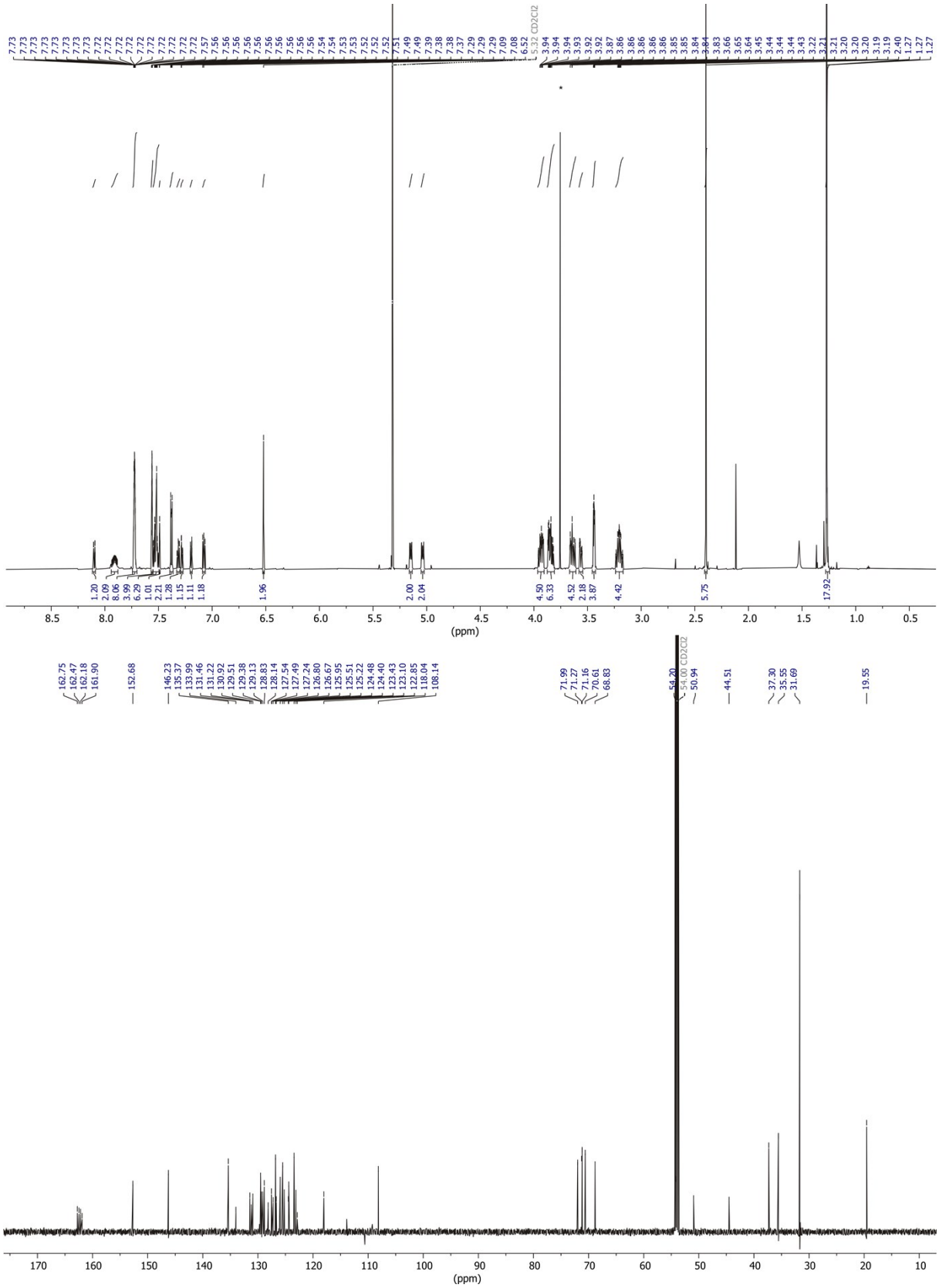


Fig. S20 ^{1}H (top) and ^{13}C (bottom) NMR spectra (700/176 MHz, CD_2Cl_2, 298 K) of **PA11@TTFC8**.

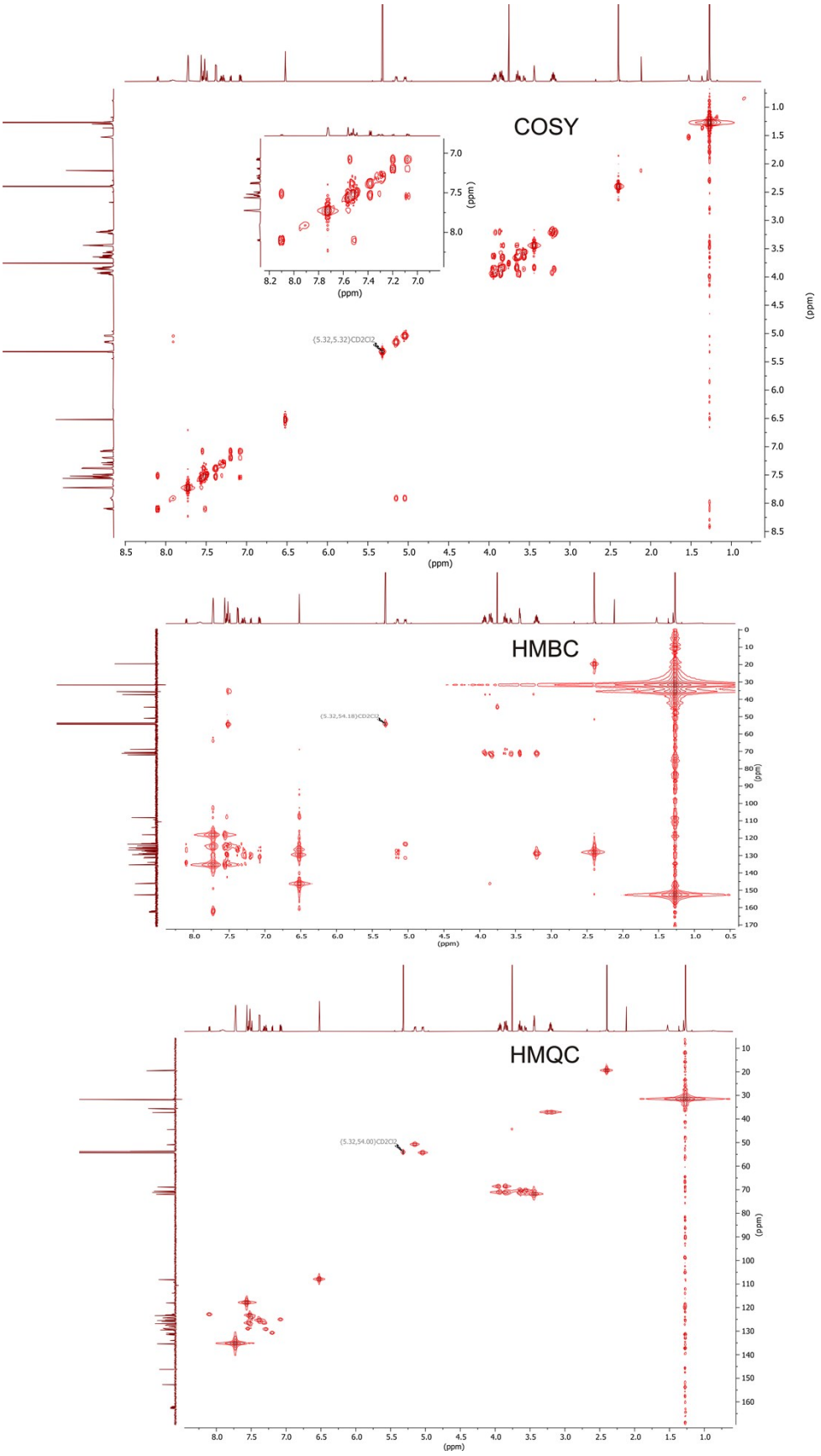
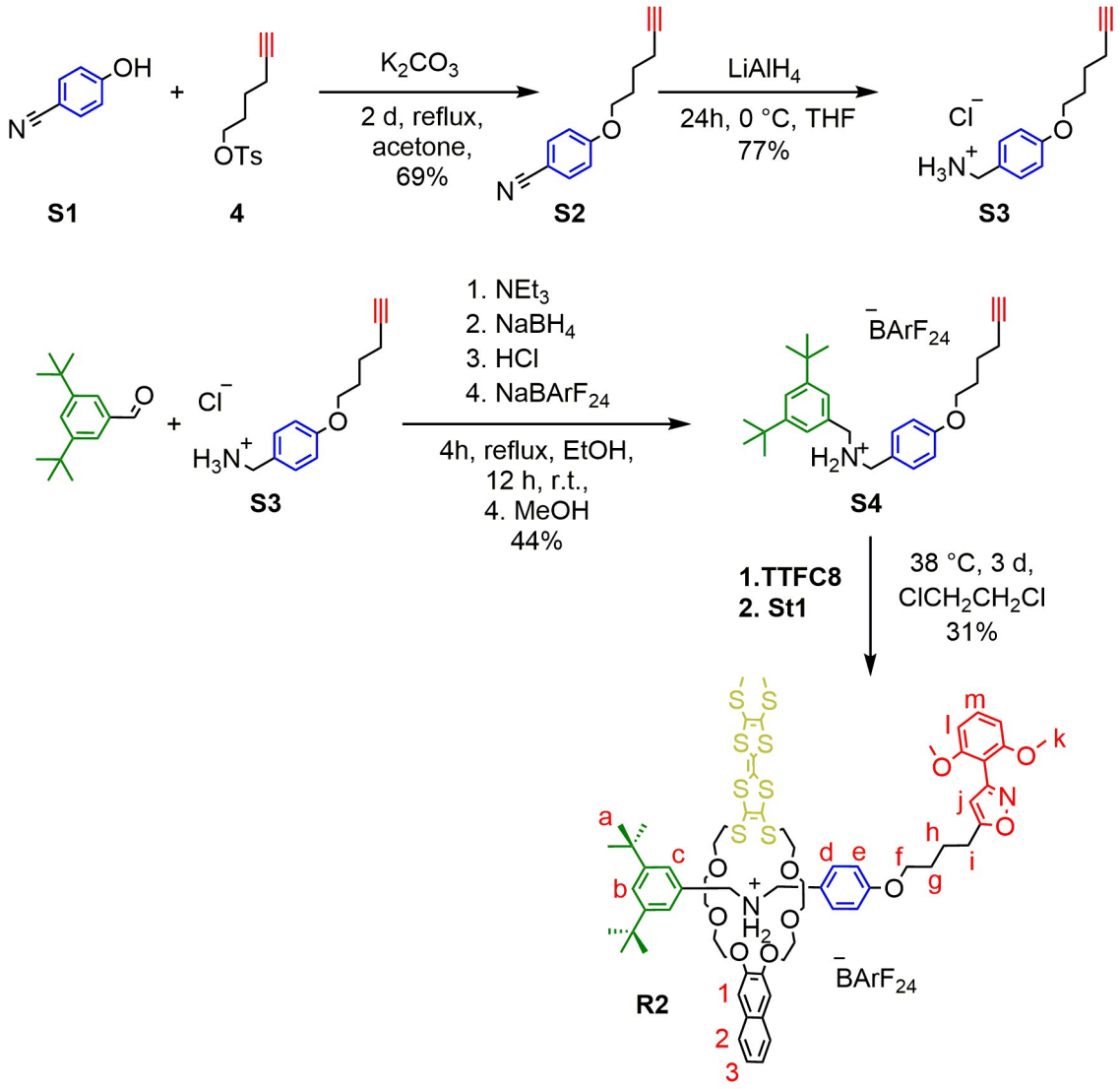
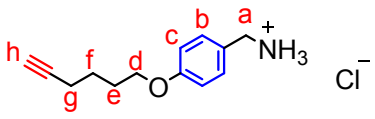


Fig. S21 COSY (top), HMBC (center) and HMQC (bottom) NMR spectra (700/176 MHz, CD_2Cl_2, 298 K) of **PA11@TTFC8**.



Scheme S3 Synthesis of **R2**.

(4-(Hex-5-yn-1-yloxy)phenyl)methanaminium chloride S3



S3

To a solution of 400 mg (2.0 mmol, 1.0 equiv.) 4-(hex-5-yn-1-yloxy)benzonitrile **S2** in dry THF (100 mL), 380 mg (10 mmol, 5.0 equiv.) $LiAlH_4$ was added at 0 °C and stirred for 24 h in the thawing ice bath. The excess $LiAlH_4$ was quenched with saturated Na_2SO_4 solution. The solid parts were filtered off and the solvent was removed under reduced pressure. The oily residue was dissolved in CH_2Cl_2, washed with brine and dried with $MgSO_4$. After removal of the solvent, the crude product was purified by flash column chromatography (SiO_2, CH_2Cl_2 + 1% NEt_3 → CH_2Cl_2 + 1% NEt_3/ 5% EtOH, *Rf* ~ 0.5 in CH_2Cl_2 + 1% NEt_3/ 3% EtOH) to isolate the desired amine, which was dissolved in Et_2O and conc. HCl (aq.) was added until no more solid crushed out. After filtration the white solid was washed with cold acetone. The product is a white sticky solid, which could be isolated in 77% yield (370 mg, 1.5 mmol) over two steps.

^{1}H NMR (700 MHz, DMSO-d_6) δ = 1.55 – 1.61 (m, 2H, f), 1.76 – 1.81 (m, 2H, e), 2.22 (td, *J*=7.1, 2.7 Hz, 2H, g), 2.78 (t, *J*=2.6, 1H, h), 3.92 (s, 2H, a), 3.98 (t, *J*=6.4, 2H, d), 6.92 – 6.98 (m, 2H, c), 7.36 – 7.40 (m, 2H, b), 8.16 – 8.34 (s_{br}, 3H, NH) ppm. **^{13}C NMR** (176 MHz, DMSO-d_6) δ = 17.4, 24.6, 27.7, 41.7, 67.0, 71.4, 84.3, 114.5, 125.8, 130.5, 158.7 ppm. **HRMS (MeOH):** m/z calcd. for $[C_{13}H_{18}NO]$: $[M\text{-}NH_3]^+$, 187.1123 found: 187.1119.

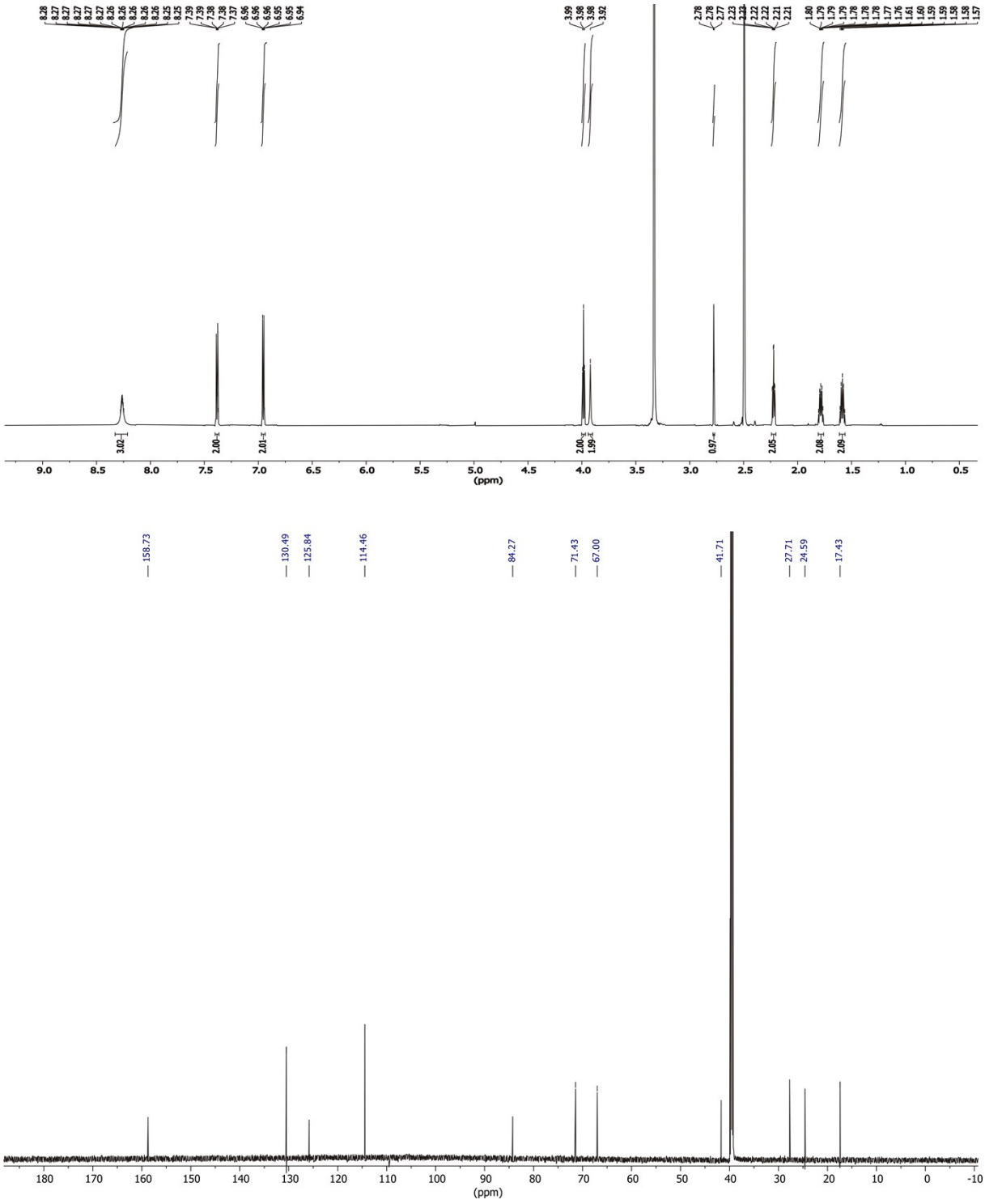
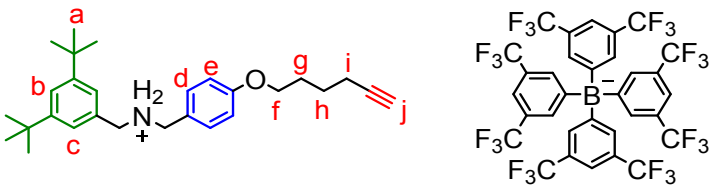


Fig. S22 ^{1}H (top) and ^{13}C (bottom) NMR spectra (700/176 MHz, DMSO-d_6, 298 K) of **S3**.

N-(3,5-di-tert-butylbenzyl)-1-(4-(hex-5-yn-1-yloxy)phenyl)methanaminium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate S4



S4

Ammonium compound **S3** (150 mg, 0.63 mmol, 1 equiv.), 3,5-di-*tert*-butylbenzaldehyde (140.0 mg, 0.63 mmol, 1.0 equiv.) and NEt_3 (90 µL, 0.56 mmol, 0.9 equiv.) were dissolved in 30 mL dry EtOH and refluxed for 5.5 h. Then, the mixture was cooled to 0 °C and $NaBH_4$ (150.0 mg, 3.13 mmol, 5 equiv.) was added. The reaction stirred overnight in the thawing ice bath. Afterwards, the reaction was quenched with saturated aq. $NaHCO_3$ solution. The solvent was removed. The residue was taken up with CH_2Cl_2 (40 mL) and washed with Brine (3x50 mL). The organic phase was dried over $MgSO_4$ and the solvent was removed. The crude product was purified via flash column chromatography (SiO_2, CH_2Cl_2 -> CH_2Cl_2 + 10% EtOH, R_f ~ 0.5 in CH_2Cl_2 + 3% EtOH) to get the desired Amine as yellow oil, which was dissolved in EtOAc (10 mL) and protonated with HCl conc. under cooling in an ice bath. The solvent was removed and 60 mg (0.14 mmol) of the brown sticky oil were dissolved in MeOH (5 mL) and $NaBArF_{24}$ (120 mg, 0.14 mmol, 1.0 equiv.) was added. After stirring overnight at room temperature, the solvent was removed, the residue was taken up in CH_2Cl_2 and washed with water (3x50 mL). The organic phase was dried over $MgSO_4$ and the solvent was removed to get the desired axle **S4** as brown oil in 44% yield overall (160 mg, 0.13 mmol).

^{1}H NMR (700 MHz, CD_2Cl_2) δ = 1.32 (s, 18H, a), 1.68 – 1.73 (m, 2H, h), 1.89 – 1.94 (m, 2H, g), 2.00 (t, J = 2.7 Hz, 1H, j), 2.28 (td, J = 7.1, 2.7 Hz, 2H, i), 4.01 (t, J = 6.3 Hz, 2H, f), 4.22 (s, 2H, N-CH_2), 4.24 (s, 2H, N-CH_2), 6.97 – 7.01 (m, 2H, e), 7.15 (d, J = 1.8 Hz, 2H, c), 7.24 – 7.27 (m, 2H, d), 7.56 (s_{br}, 4H, $BArF_{24}$), 7.60 (t, J = 1.8 Hz, 1H, b), 7.72 (s_{br}, 8H, $BArF_{24}$) ppm. **^{13}C NMR** (176 MHz, CD_2Cl_2) δ = 18.6, 25.6, 28.7, 31.6, 35.5, 53.1, 68.4, 69.0, 84.5, 116.4, 118.0, 121.0, 122.9, 123.9, 124.4, 125.9, 125.9, 127.5, 128.9, 129.4, 131.5, 135.4, 153.9, 161.7, 162.3 ppm. **HRMS (MeOH):** m/z calcd. for $[C_{28}H_{40}NO]^+$: 406.3104 $[M]^+$, found: 406.3109

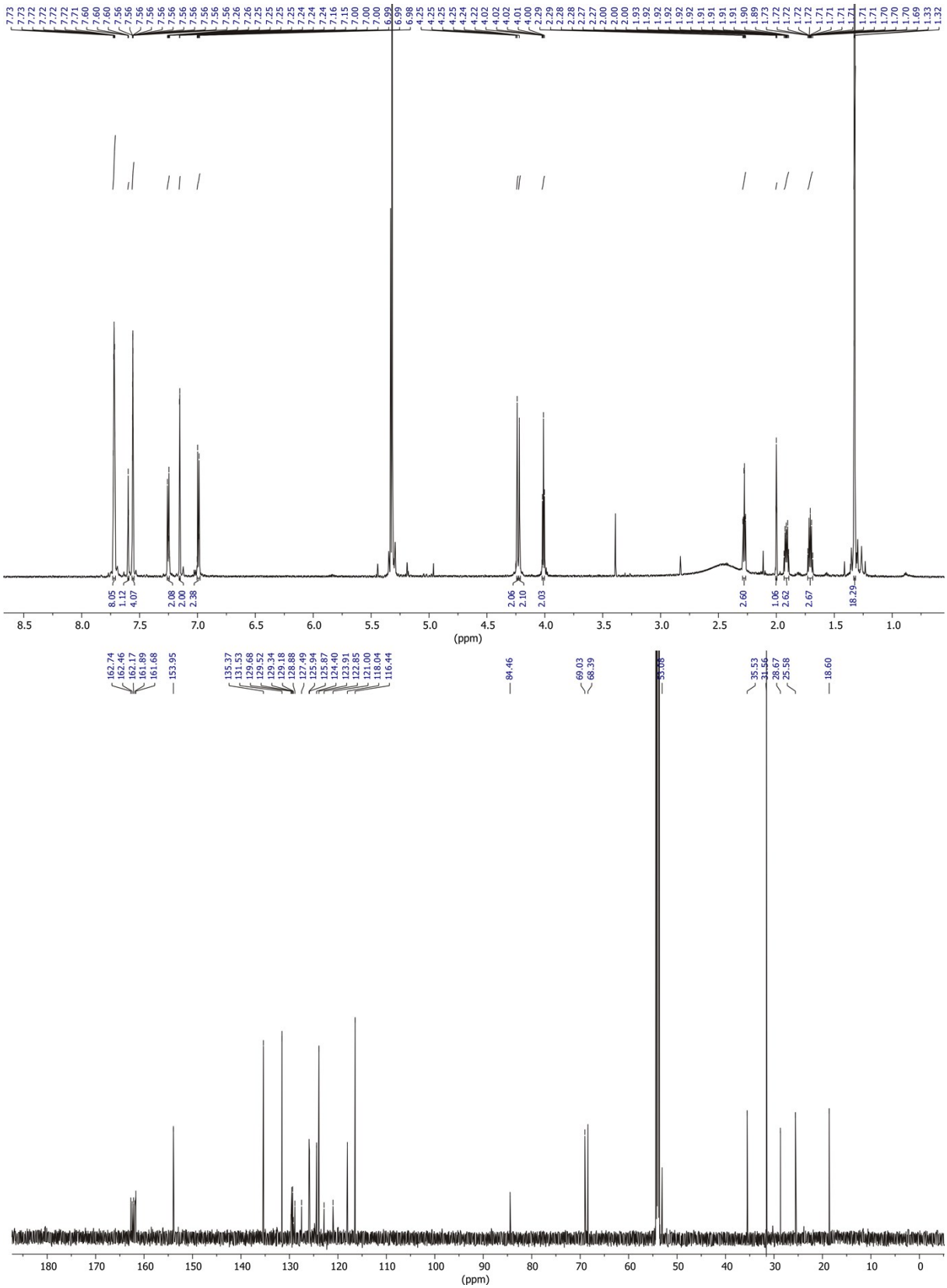
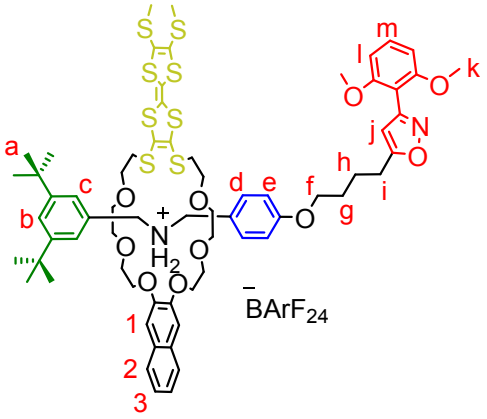


Fig. S23 ^{1}H (top) and ^{13}C (bottom) NMR spectra (700/176 MHz, CD_2Cl_2, 298 K) of **S4**.

[2]Rotaxane R2



R2

A solution of 50 mg (39 µmol, 1.0 equiv.) axle **S4** and 32 mg (43 µmol, 1.1 equiv.) macrocycle **TTFC8** in $ClCH_2CH_2Cl$ (2 mL) was stirred at 38 °C. for 10 min. Afterwards, the mixture was allowed to cool to r.t. and 9 mg (50 µmol, 1.3 equiv.) stopper **St1** was added and the mixture was stirred at 38 °C for 36 h. Then, the mixture was purified by column chromatography (SiO_2, CH_2Cl_2/hexane 8:2-> CH_2Cl_2, R_f ~ 0.6 in CH_2Cl_2) to obtain the desired product **R2** (27 mg, 12 µmol, 31 %) as orange oil.

^{1}H NMR (700 MHz, CD_2Cl_2) δ = 1.27 (s, 18H, a), 1.54 – 1.59 (m, 2H, g), 1.66 – 1.72 (m, 2H, h), 2.41 (s, 6H, S-CH_3), 2.74 – 2.83 (m, 2H, i), 3.10 (t, *J* = 6.5 Hz, 2H, f), 3.18 (m, 4H, S-CH_2-), 3.46 – 3.54 (m, 4H, O-CH_2-), 3.59 – 3.65 (m, 6H, O-CH_2-), 3.73 – 3.78 (m, 8H, k, O-CH_2-), 3.79 – 3.83 (m, 2H, O-CH_2-), 3.84 – 3.90 (m, 2H, O-CH_2-), 4.00 - 4.04 (m, 2H, O-CH_2-), 4.19 – 4.24 (m, 2H, O-CH_2-), 4.55 – 4.60 (m, 2H, N-CH_2-), 4.78 – 4.82 (m, 2H, N-CH_2-), 6.09 (s, 1H, j), 6.32 – 6.35 (m, 2H, e), 6.67 (d, *J* = 8.4 Hz, 2H, l), 6.93 (s, 2H, 1), 7.10 – 7.12 (m, 2H, d), 7.35 – 7.40 (m, 2H, 3, m), 7.49 (dd, *J* = 7.5, 1.8 Hz, 3H, b, c), 7.56 (s_{br}, 4H, $BArF_{24}$), 7.65 (m, 2H, 2), 7.70 (s_{br}, 2H, NH_2), 7.72 (s_{br}, 8H, $BArF_{24}$) ppm.**^{13}C NMR** (176 MHz, CD_2Cl_2) δ = 19.6, 24.6, 27.0, 29.1, 31.7, 35.5, 37.3, 56.5, 67.5, 69.0, 70.4, 71.1, 71.2, 72.1, 104.2, 104.7, 108.1, 108.3, 114.7, 118.0, 122.8, 122.9, 123.7, 124.4, 124.4, 125.7, 125.9, 126.9, 127.5, 128.1, 129.0, 129.4, 129.6, 131.2, 131.5, 131.6, 135.4, 147.1, 152.7, 157.6, 159.2, 160.3, 162.3, 172.4 ppm. **HRMS (MeOH):** m/z calcd. for $[C_{67}H_{85}N_2O_{10}S_8]^+$: 1333.3964 $[M]^+$, found: 1333.3990 m/z.

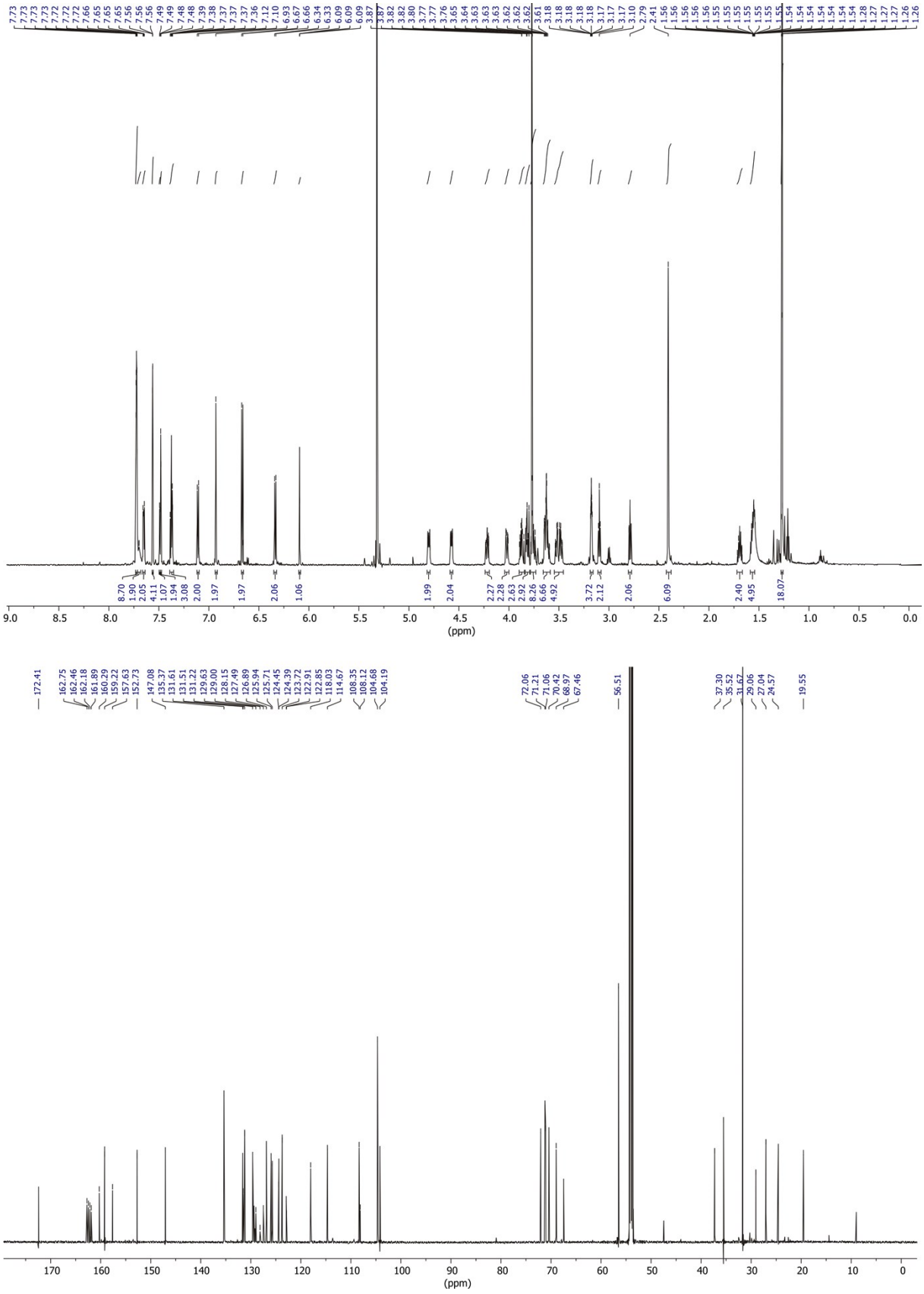


Fig. S24 ^{1}H (top) and ^{13}C (bottom) NMR spectra (700/176 MHz, CD_2Cl_2, 298 K) of **R2**.

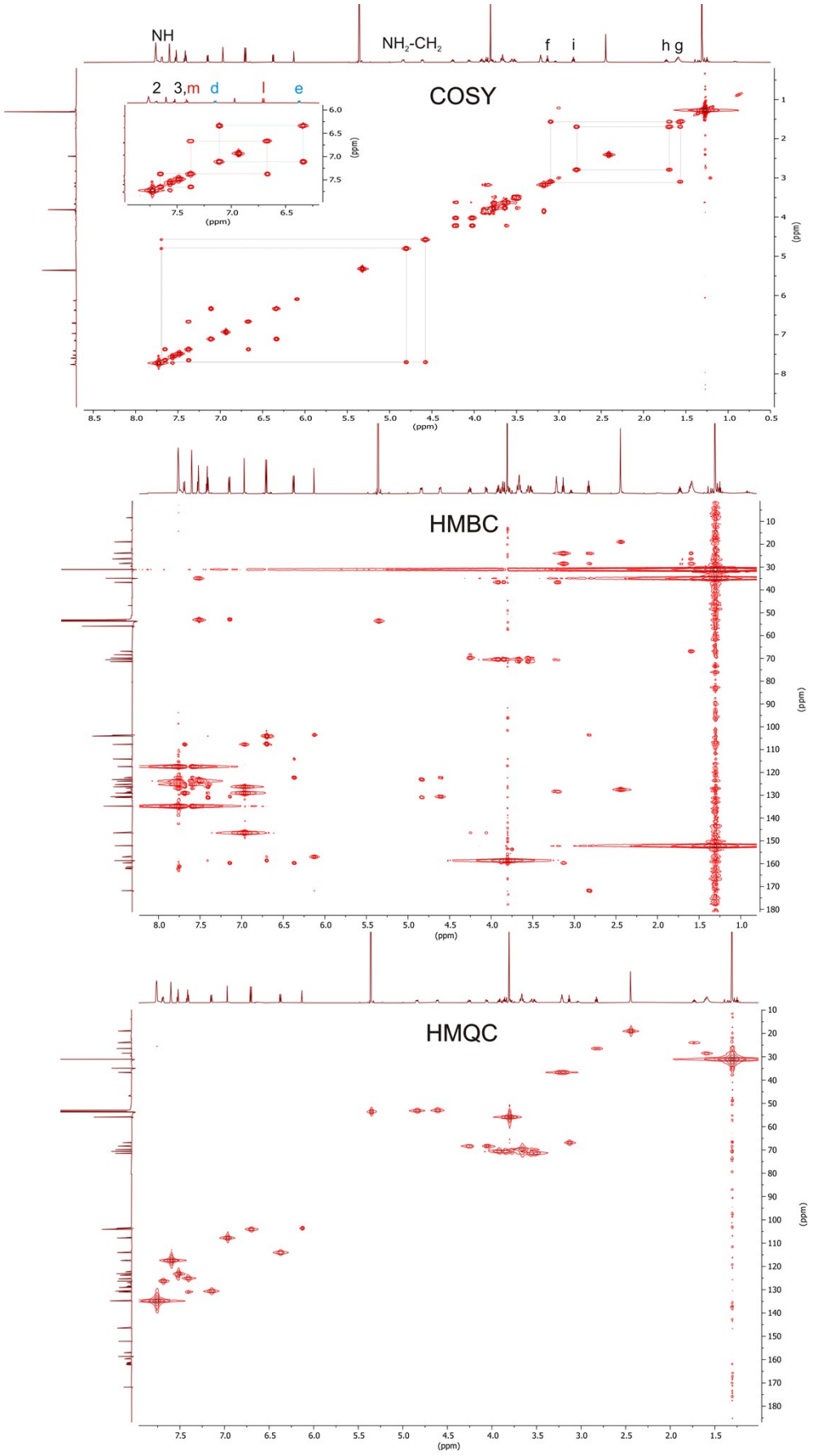


Fig. S25 COSY (top), HMBC (center) and HMQC (bottom) NMR spectra (700/176 MHz, CD_2Cl_2, 298 K) of **R2**.

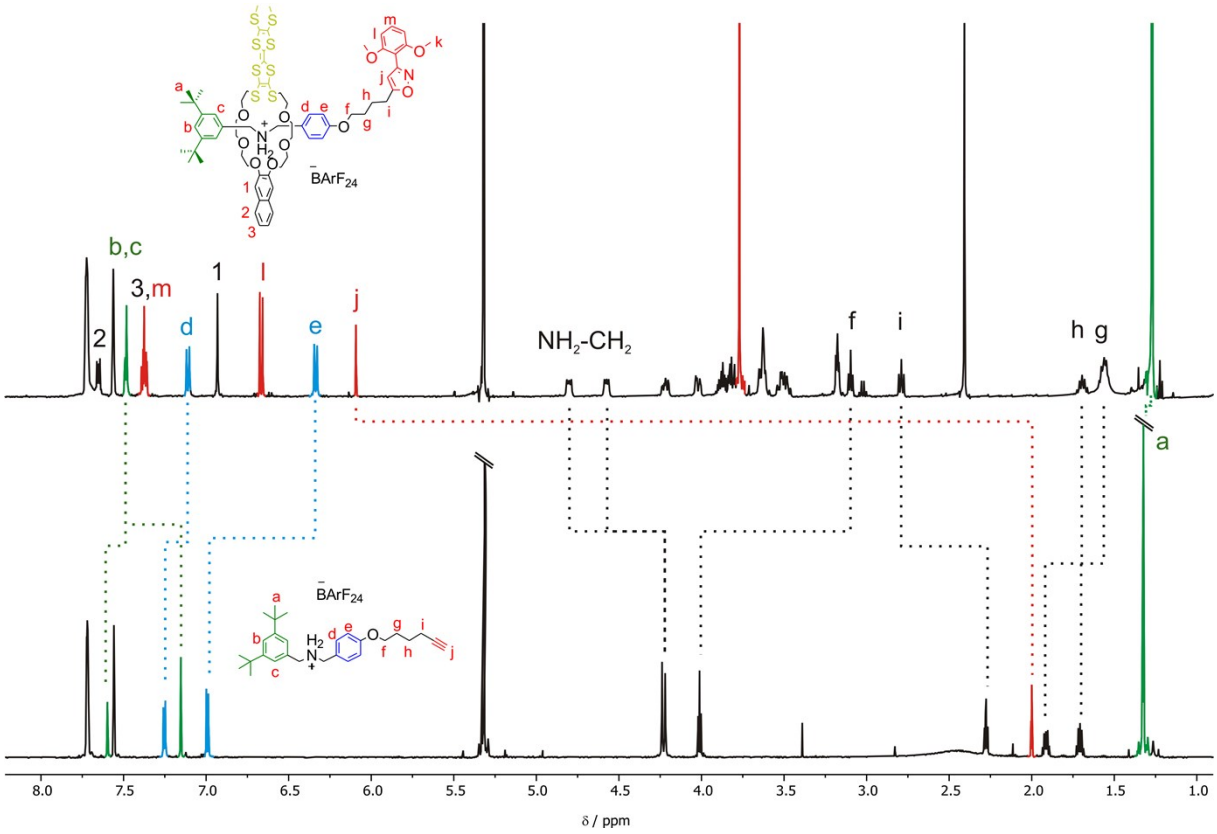


Fig. S26 [2]rotaxane **R2** (top) and axle **S4** (bottom) NMR spectra (500 MHz, CD_2Cl_2, 298 K).

2. Threading and dethreading: ^{1}H NMR experiments

Threading and unthreading experiments were performed at 4 mM concentration, deprotonation/oxidation was performed in dry CD_2Cl_2. Oxidation was performed by adding an excess of $NOSbF_6$ shaking gently, until the solution turned deep blue and subsequent filtration into a J. Young tube under argon atmosphere of residual $NOSbF_6$. Deprotonation was performed by adding an excess of polystyrene-immobilized P2 base, shaking and then filtration into a J. Young tube under argon atmosphere.

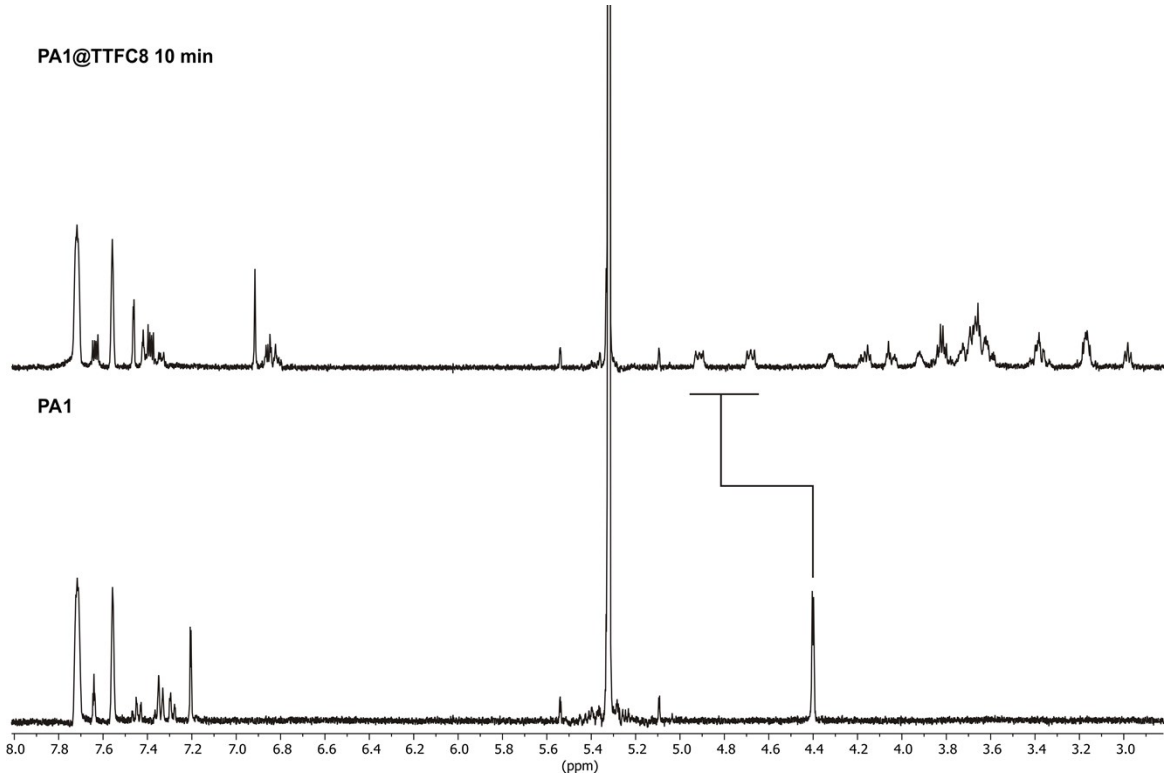


Fig. S27 Partial ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298 K) of **PA1** before (bottom) and after addition of **TTFC8** (top) the highlighted downfield shift and splitting of the methylene protons next to the ammonium is characteristic for a threaded complex.

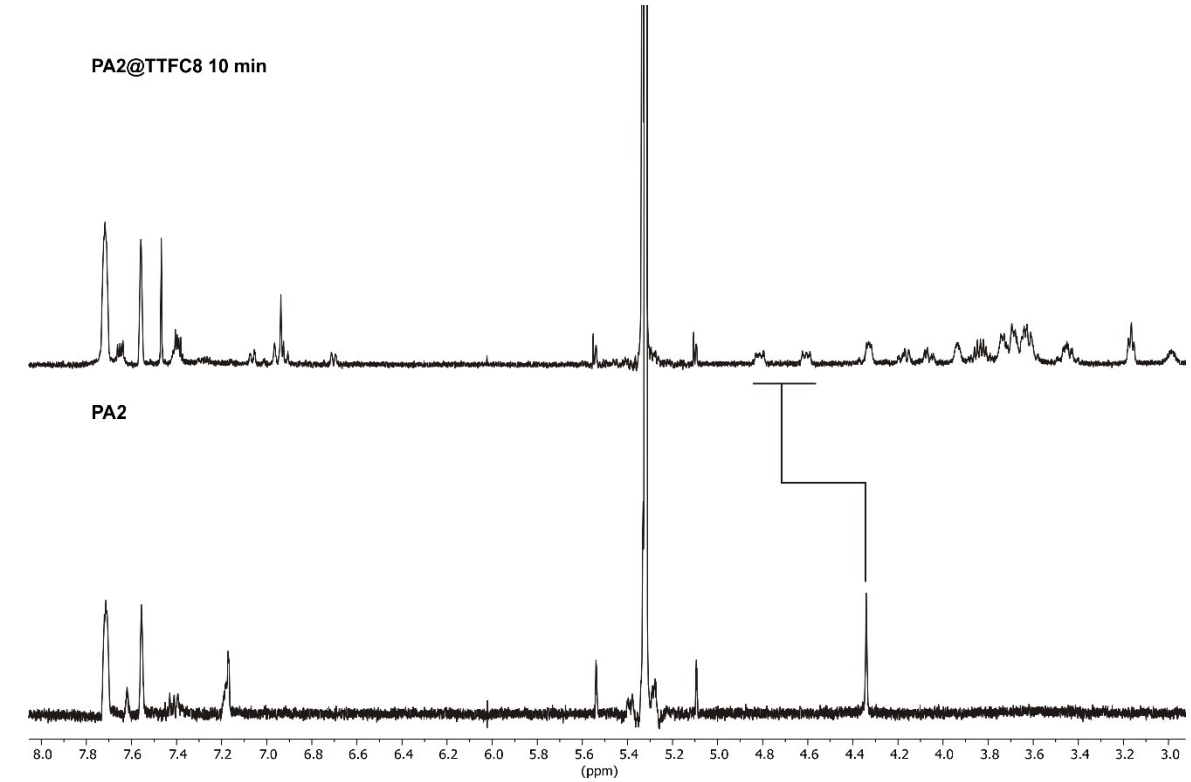


Fig. S28 Partial ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298 K) of **PA2** before (bottom) and after addition of **TTFC8** (top) the highlighted downfield shift and splitting of the methylene protons next to the ammonium is characteristic for a threaded complex.

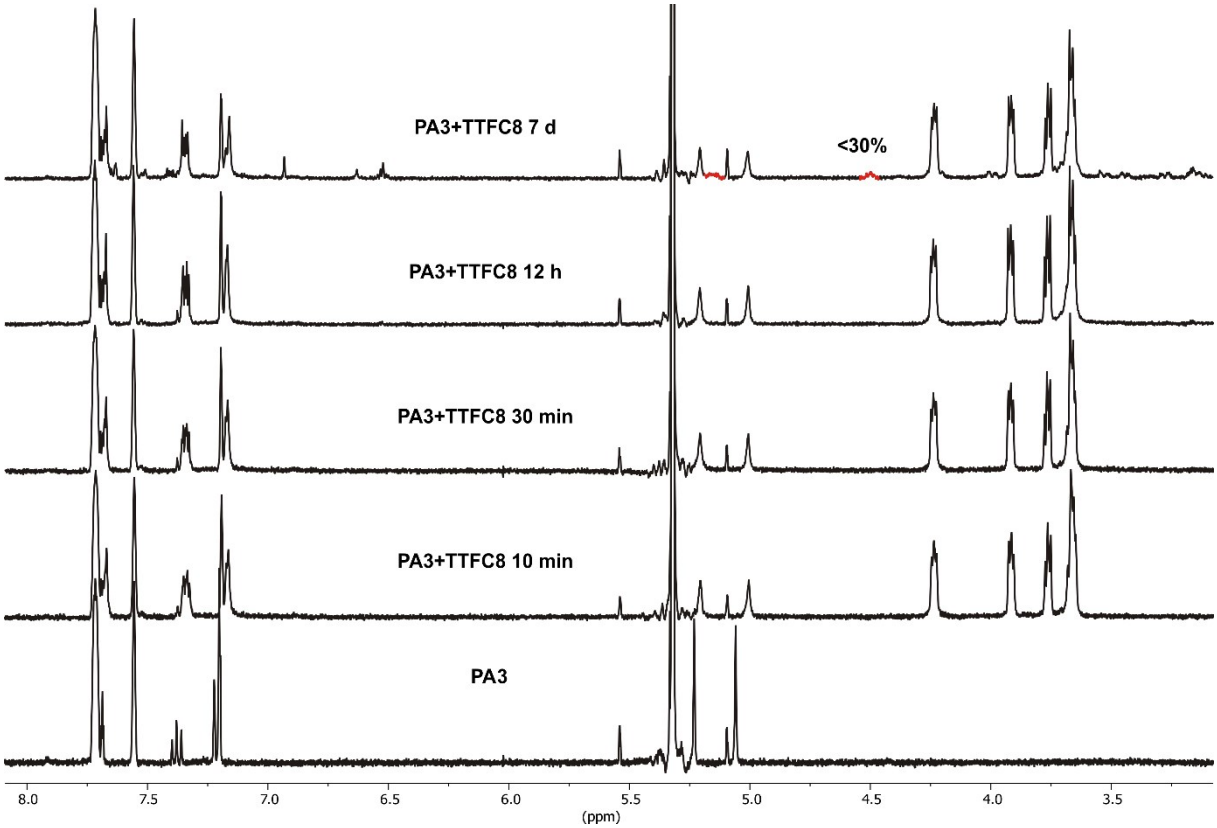


Fig. S29 Partial ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298 K) of **PA3** before (bottom) and after addition of **TTFC8** (top), the emerging peaks (red) correspond to the threaded complex.

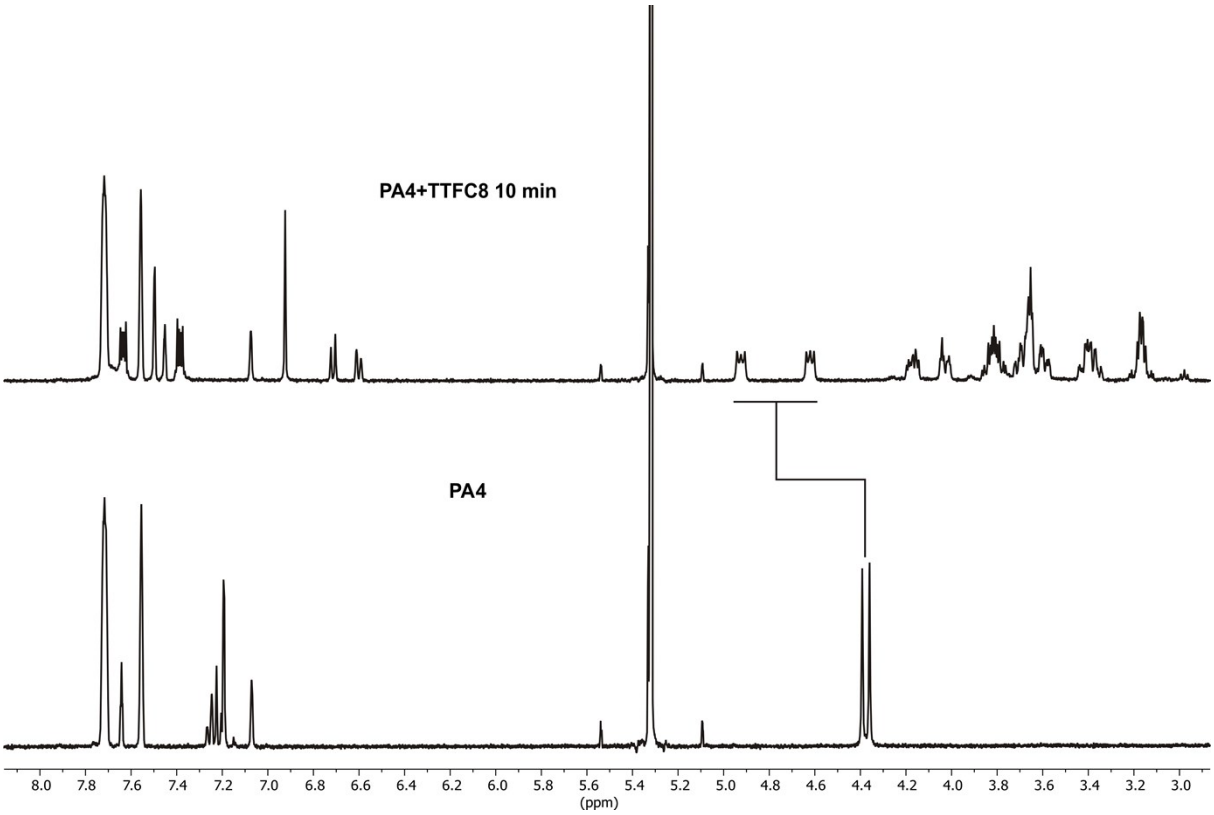


Fig. S30 Partial ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298 K) of **PA4** before (bottom) and after addition of **TTFC8** (top) the highlighted downfield shift and splitting of the methylene protons next to the ammonium is characteristic for a threaded complex.

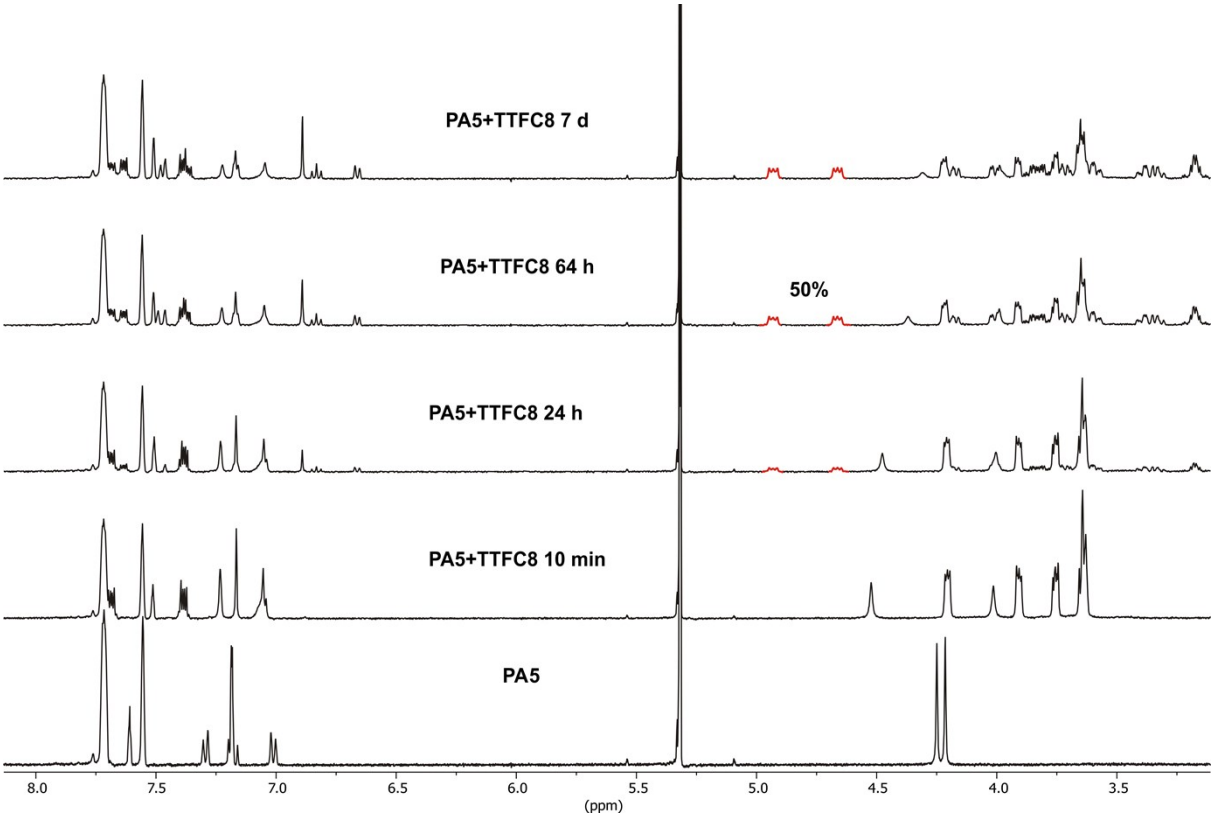


Fig. S31 Partial ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298 K) of **PA5** before (bottom) and after addition of **TTFC8** (top), the emerging peaks (red) correspond to the threaded complex.

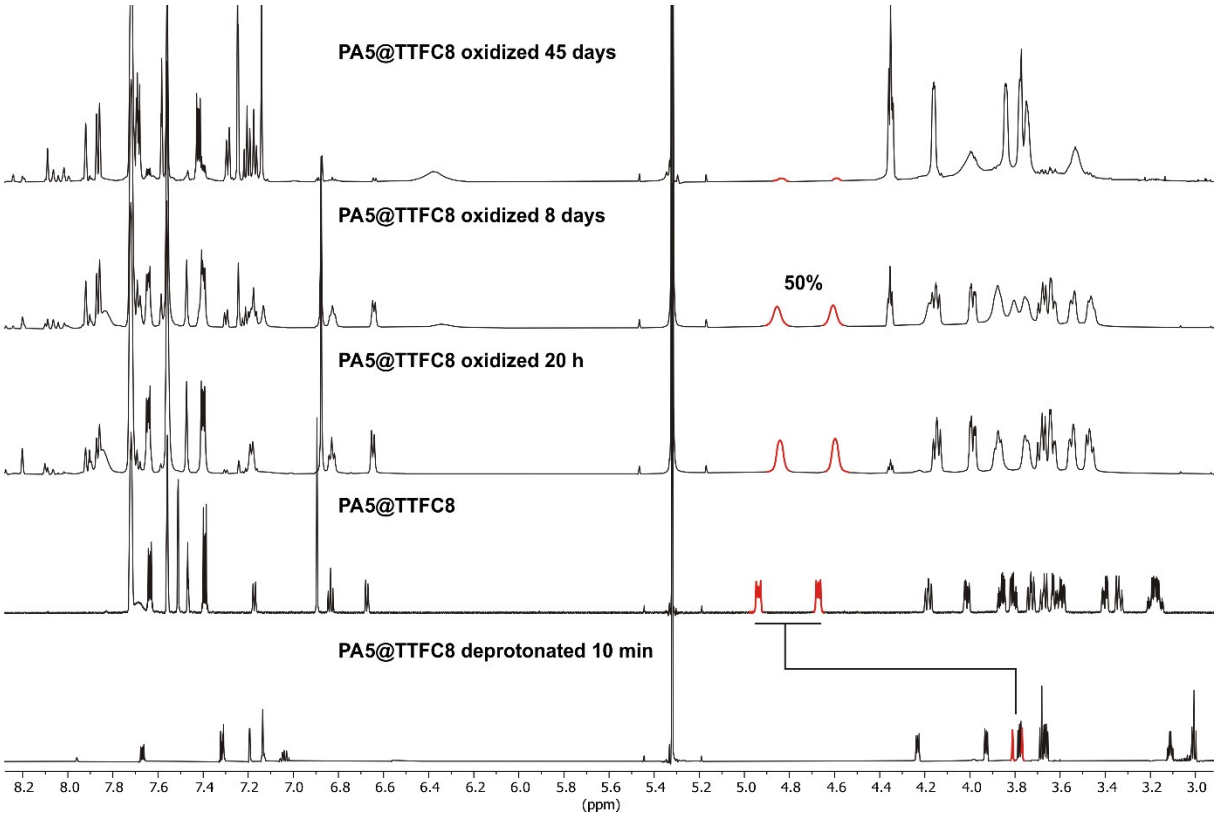


Fig. S32 Partial ^{1}H NMR spectra (700 MHz, CD_2Cl_2, 298 K) of **PA5@TTFC8** (center) after oxidation with $NO^{\cdot+}SbF_6^-$ (top) and after deprotonation with P2 base (bottom). The highlighted peaks in red correspond to the methylene protons next to the nitrogen.

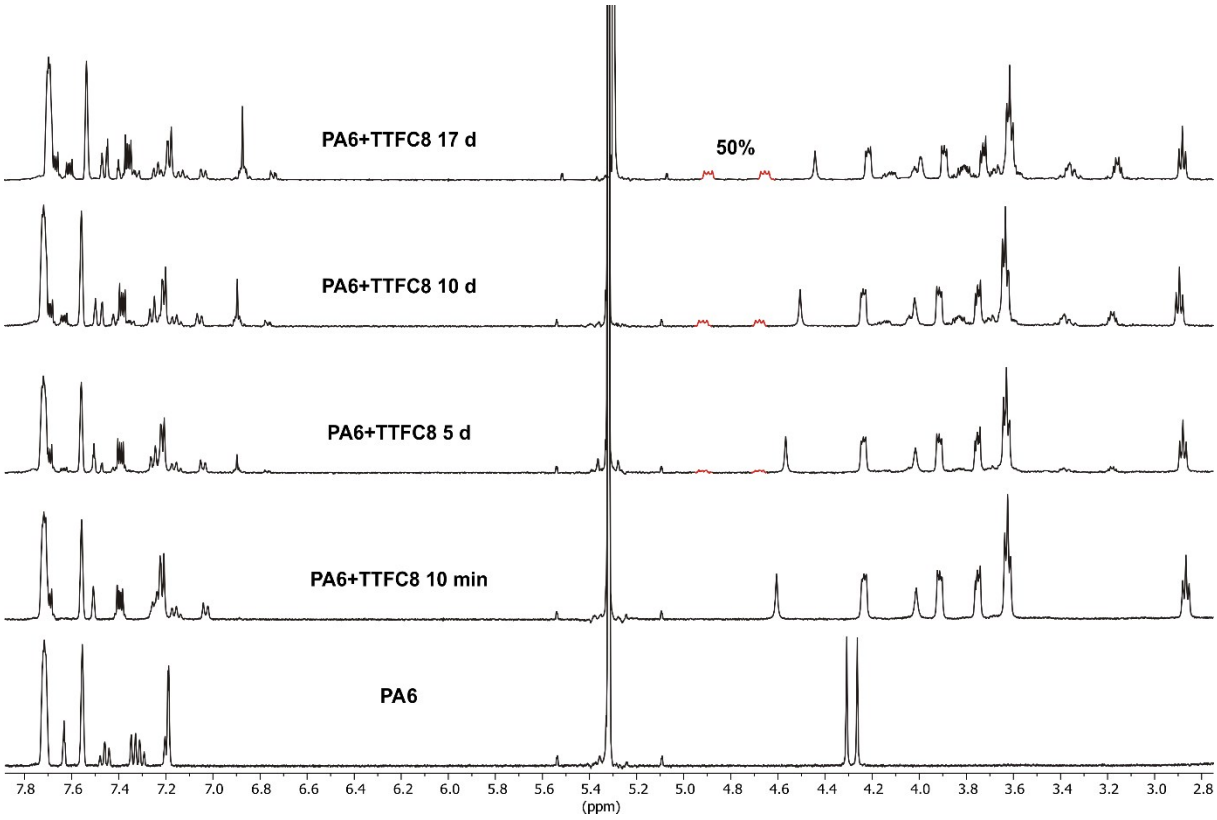


Fig. S33 Partial ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298 K) of **PA6** before (bottom) and after addition of **TTFC8** (top), the emerging peaks (red) correspond to the threaded complex.

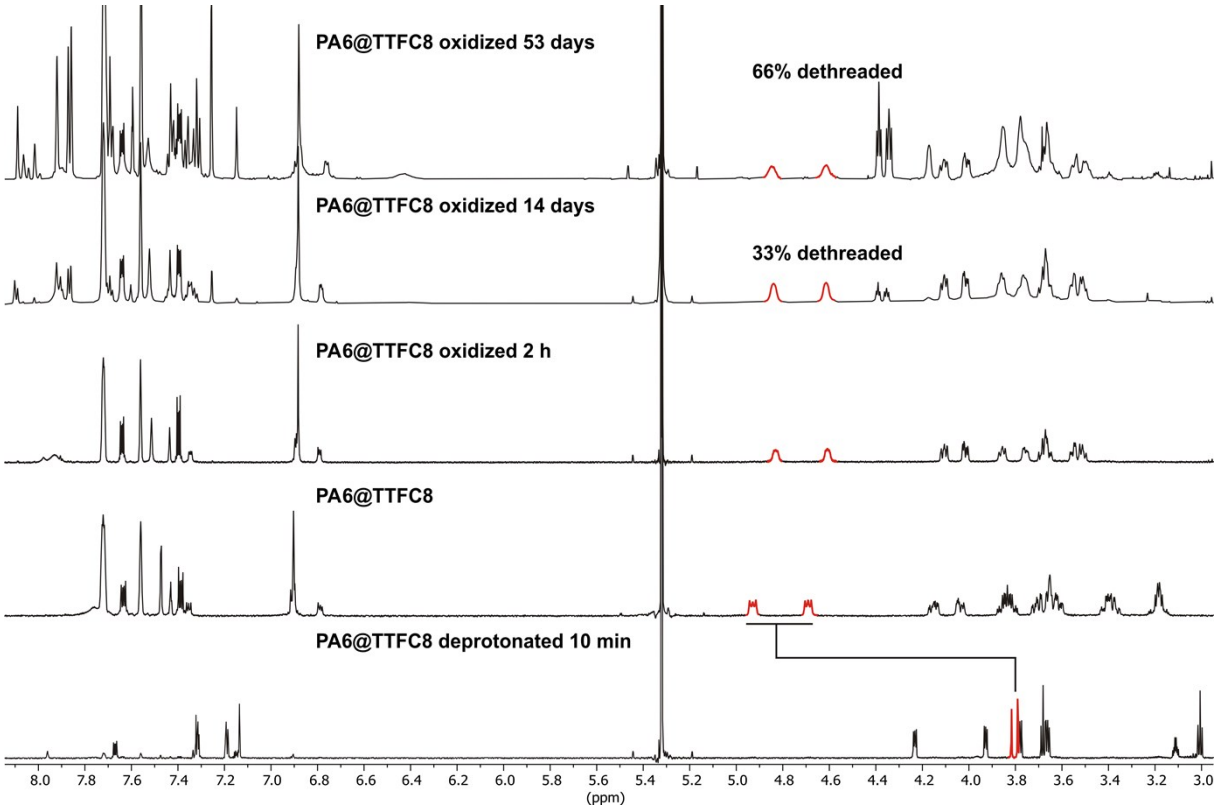


Fig. S34 Partial ^{1}H NMR spectra (700 MHz, CD_2Cl_2, 298 K) of **PA6@TTFC8** (center) after oxidation with $NO^{\cdot+}SbF_6^-$ (top) and after deprotonation with P2 base (bottom). The highlighted peaks in red correspond to the methylene protons next to the nitrogen.

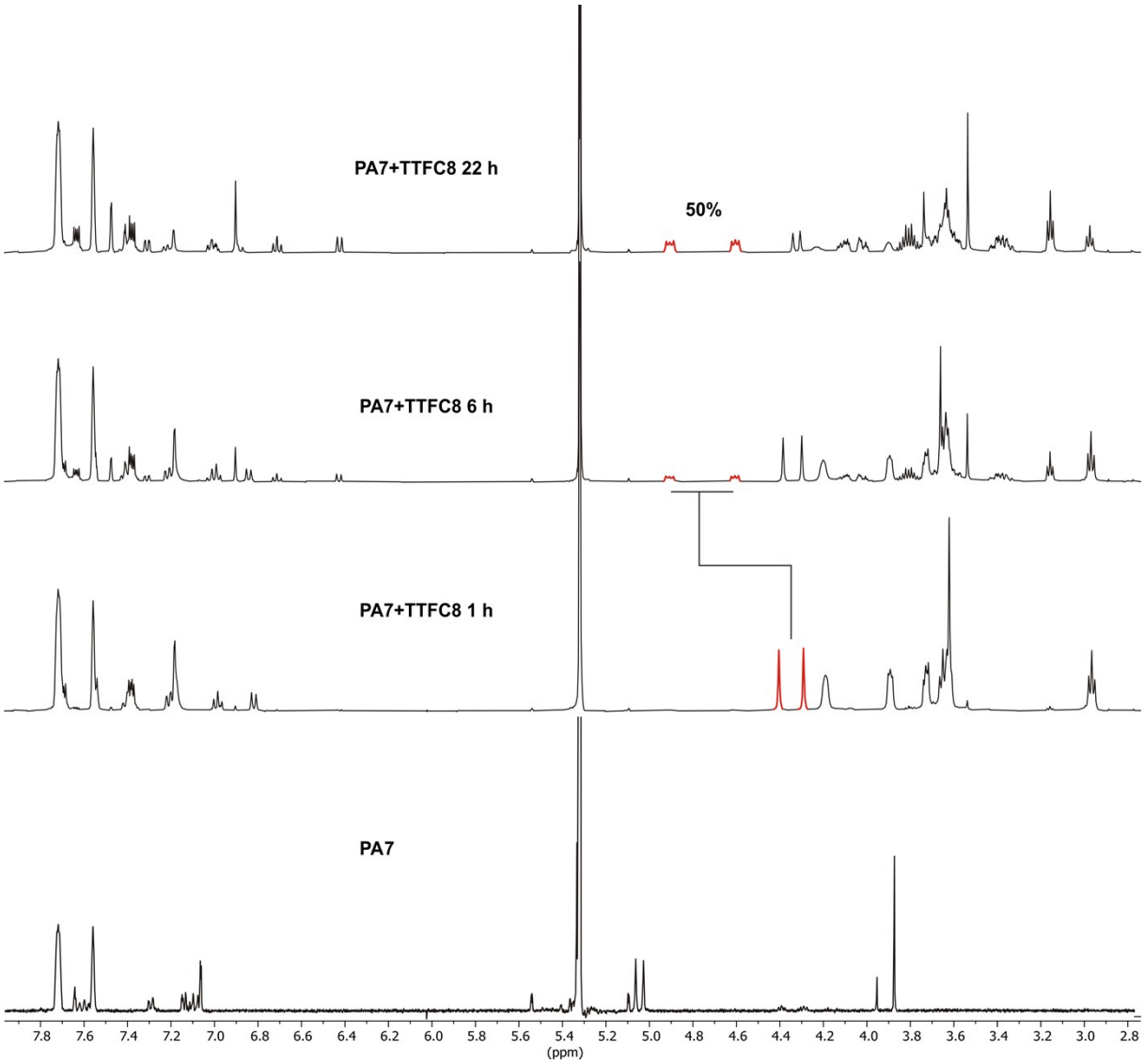


Fig. S35 Partial ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) spectra of **PA7** before (bottom) and after addition of **TTFC8** (top), the emerging peaks (red) correspond to the threaded complex.

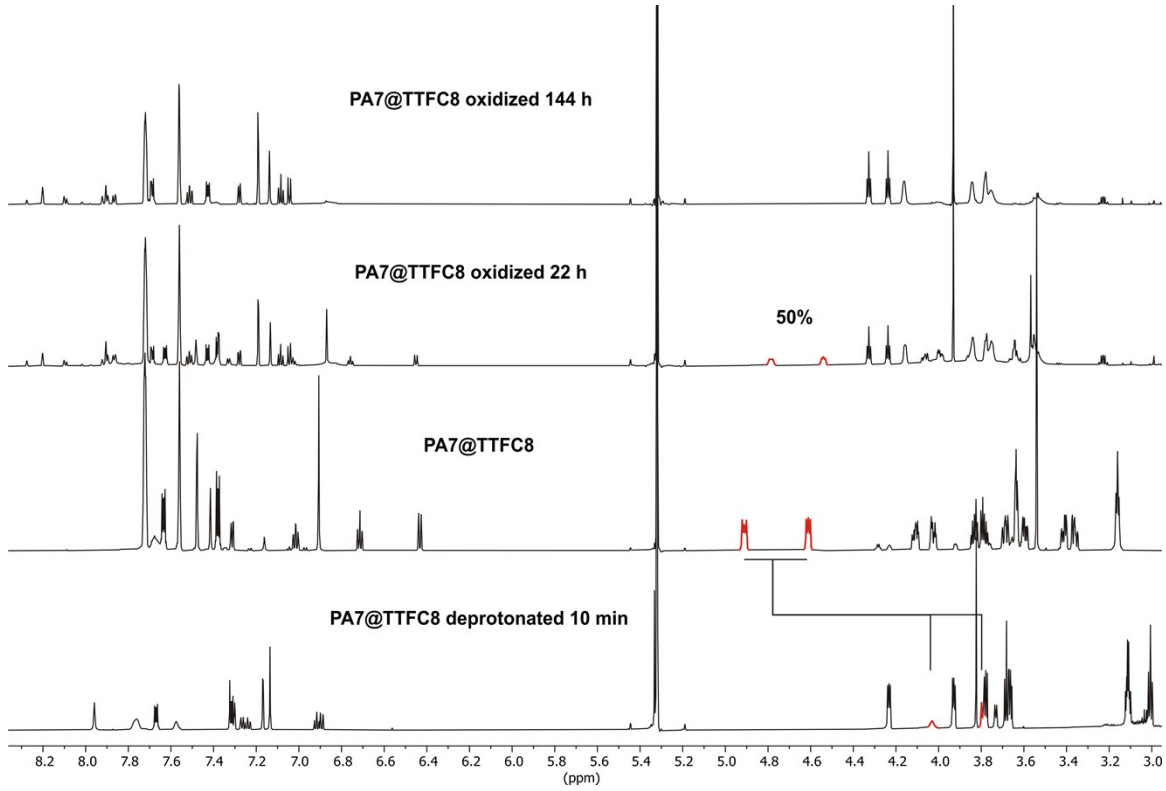


Fig. S36 Partial ^{1}H NMR spectra (700 MHz, CD_2Cl_2, 298 K) of **PA7@TTFC8** (center) after oxidation with $NO^{\cdot+}SbF_6^-$ (top) and after deprotonation with P2 base (bottom). The highlighted peaks in red correspond to the methylene protons next to the nitrogen.

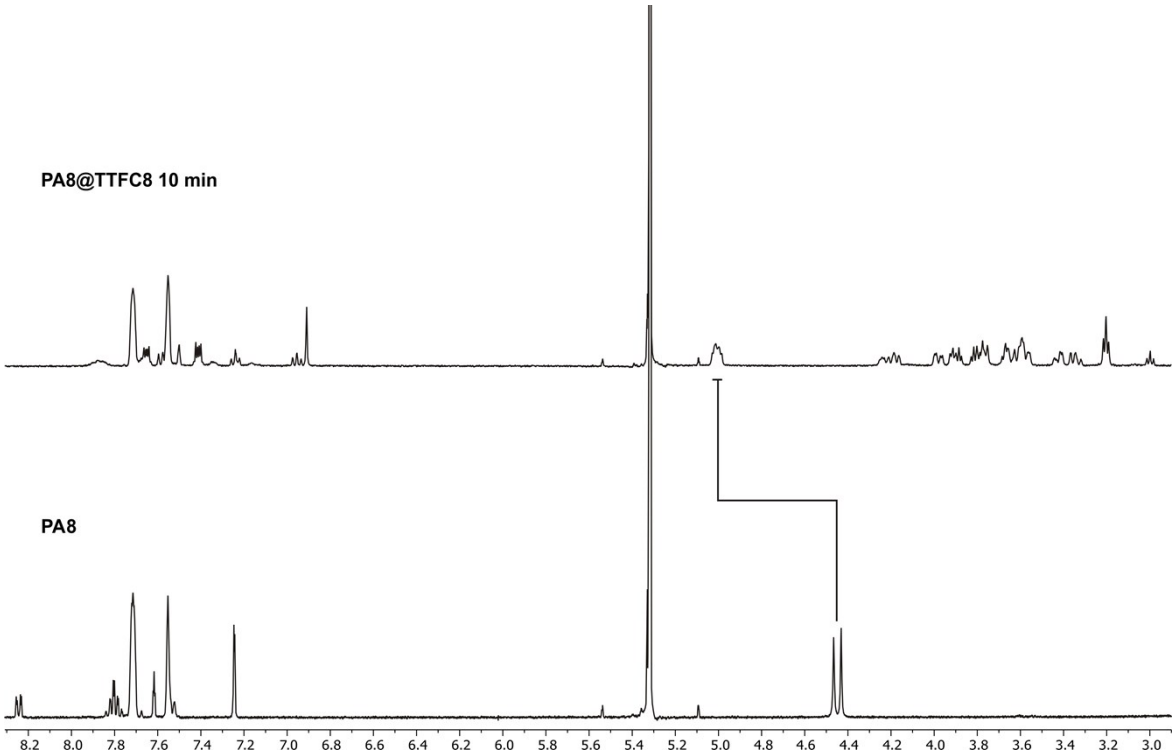


Fig. S37 Partial ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298 K) of **PA8** before (bottom) and after addition of **TTFC8** (top), the highlighted peaks correspond to the threaded complex.

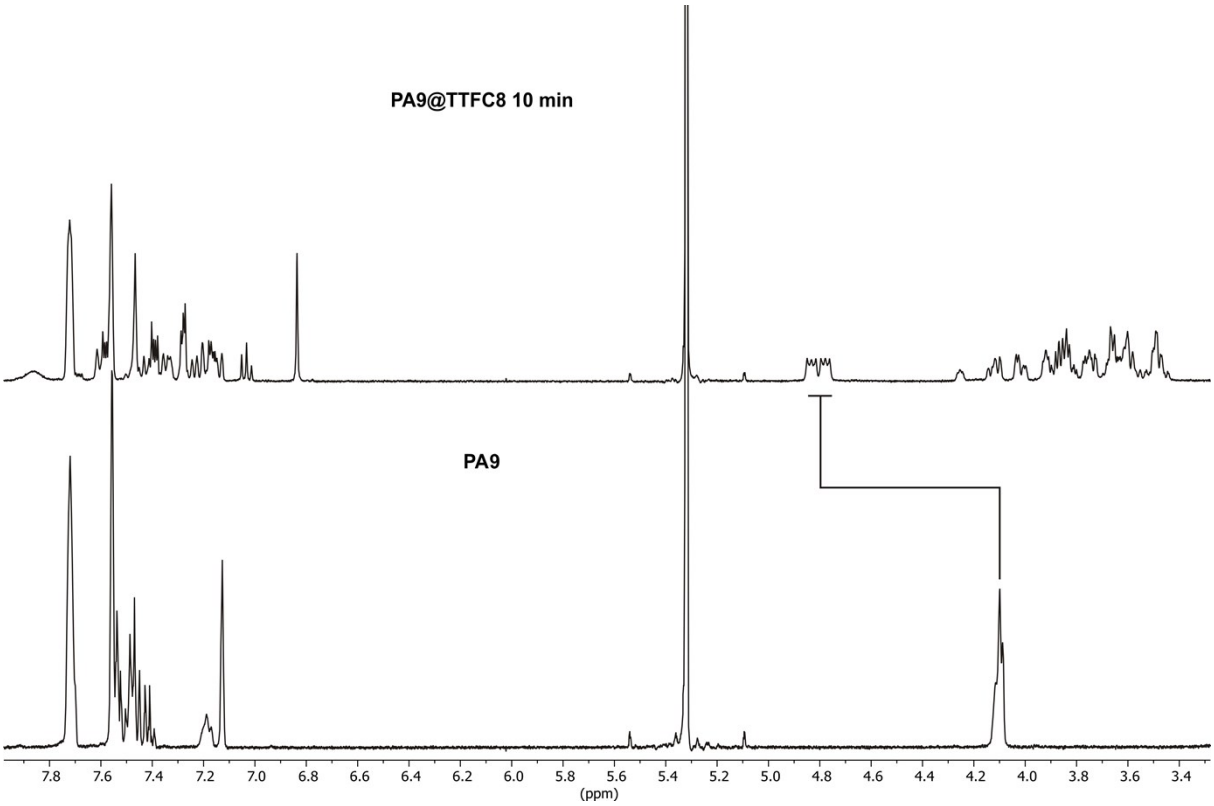


Fig. S38 Partial ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298 K) of **PA9** before (bottom) and after addition of **TTFC8** (top), the highlighted peaks correspond to the threaded complex.

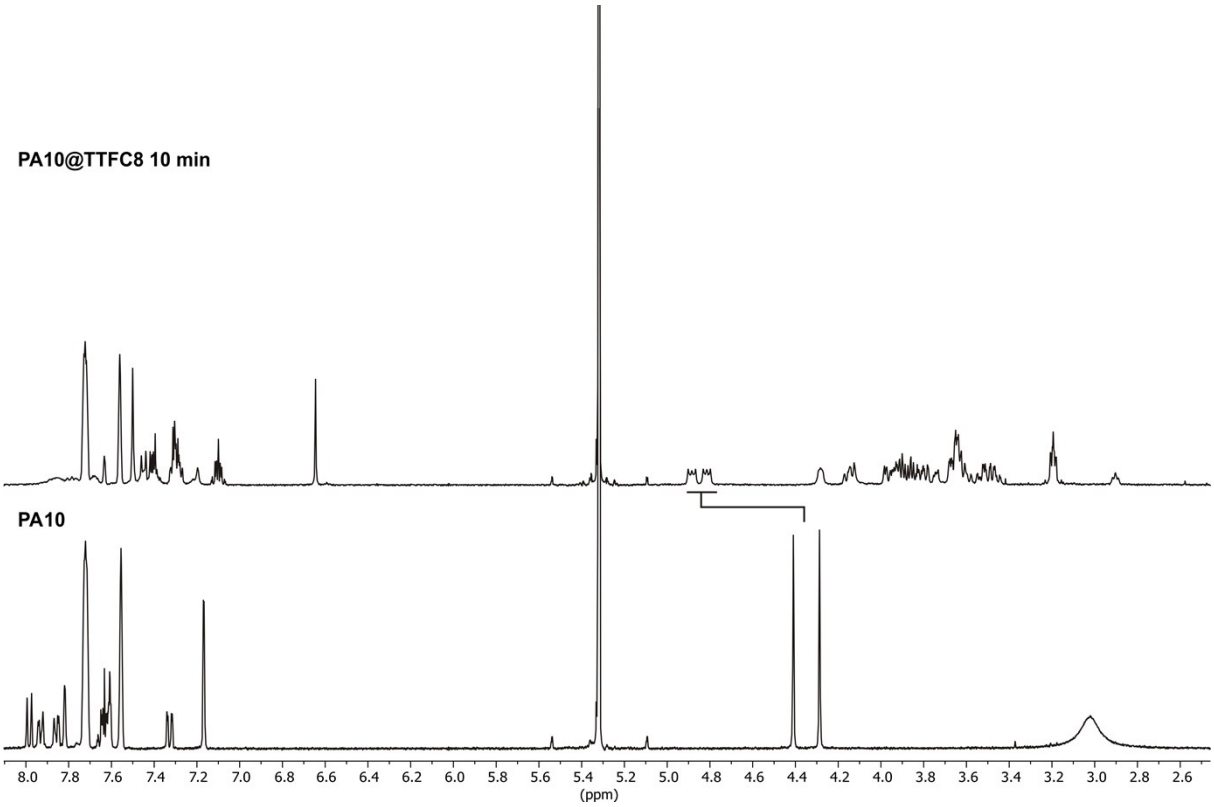


Fig. S39 Partial ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298 K) of **PA10** before (bottom) and after addition of **TTFC8** (top), the highlighted peaks correspond to the threaded complex

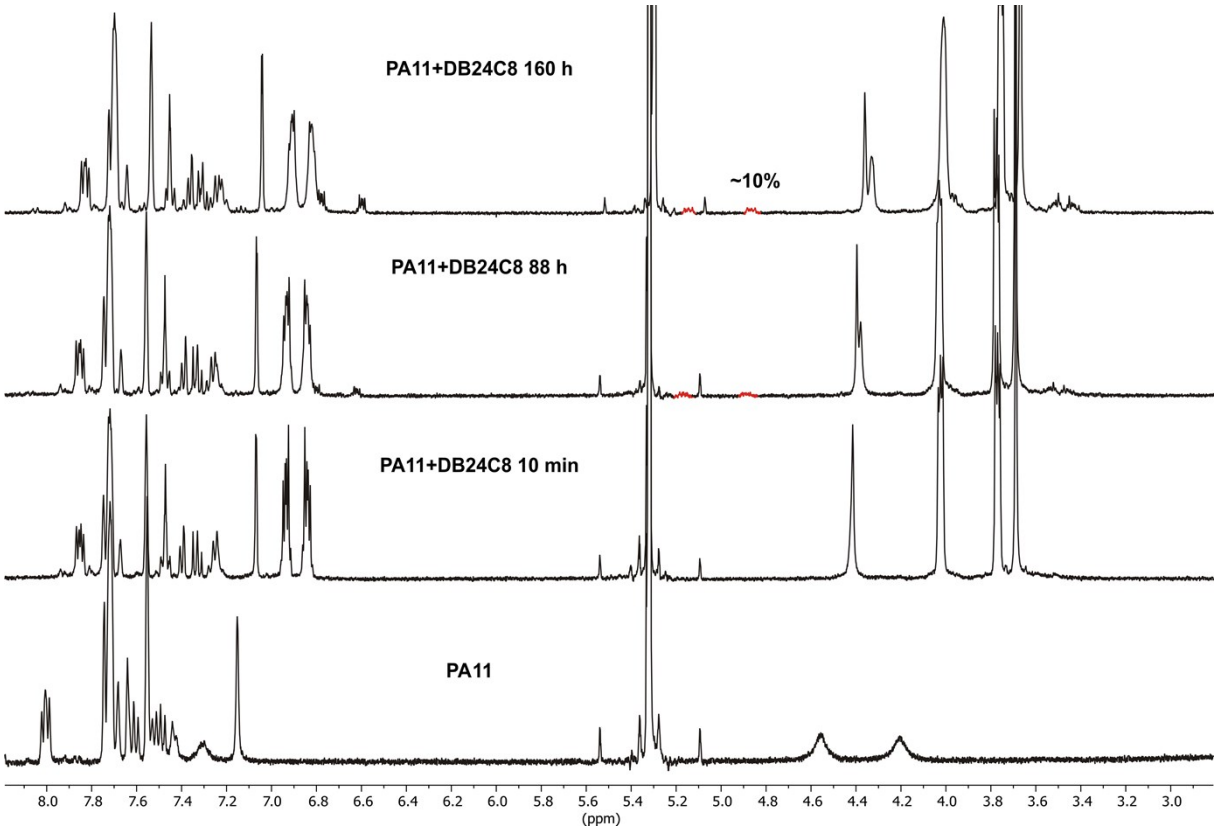


Fig. S40 Partial ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298 K) of **PA11** before (bottom) and after addition of **DB24C8** (top), the highlighted peaks correspond to the threaded complex.

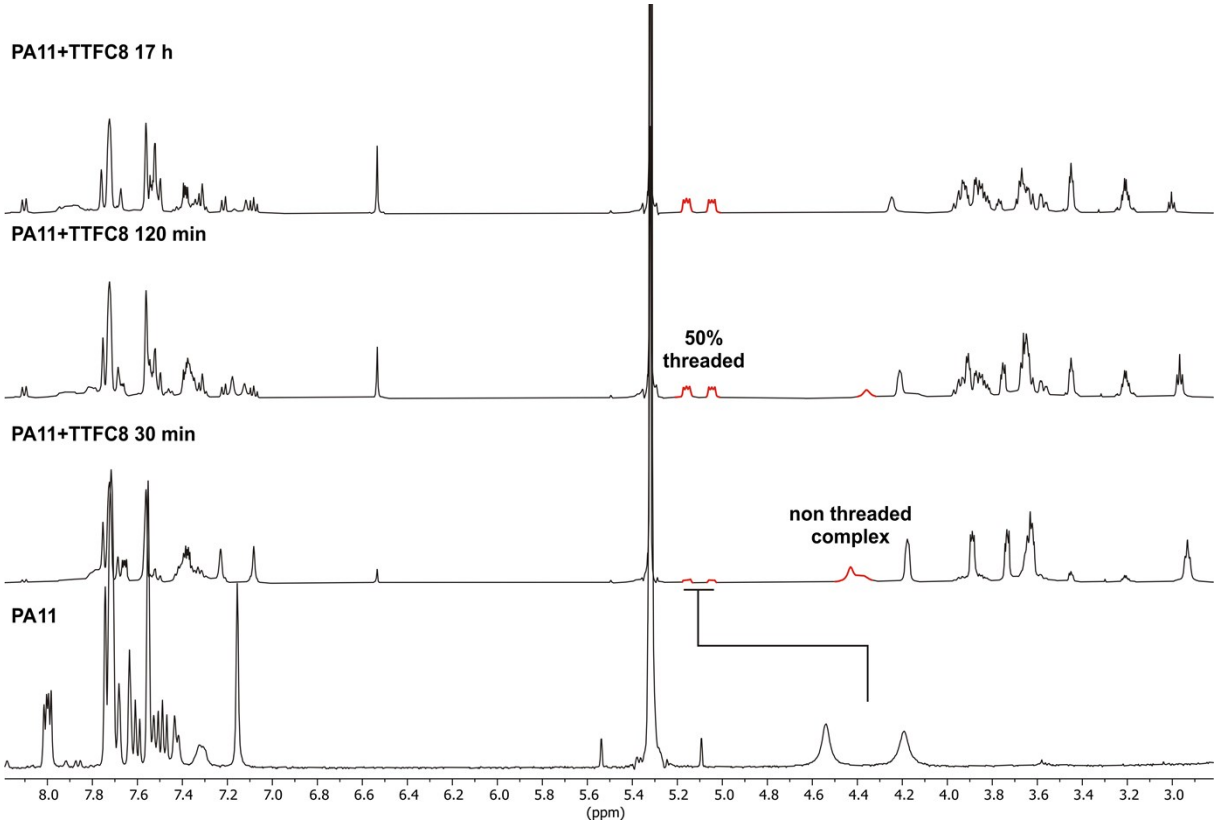


Fig. S41 Partial ^{1}H NMR spectra (500 MHz, CD_2Cl_2, 298 K) of **PA11** before (bottom) and after addition of **TTFC8** (top), the highlighted peaks correspond to the threaded complex.

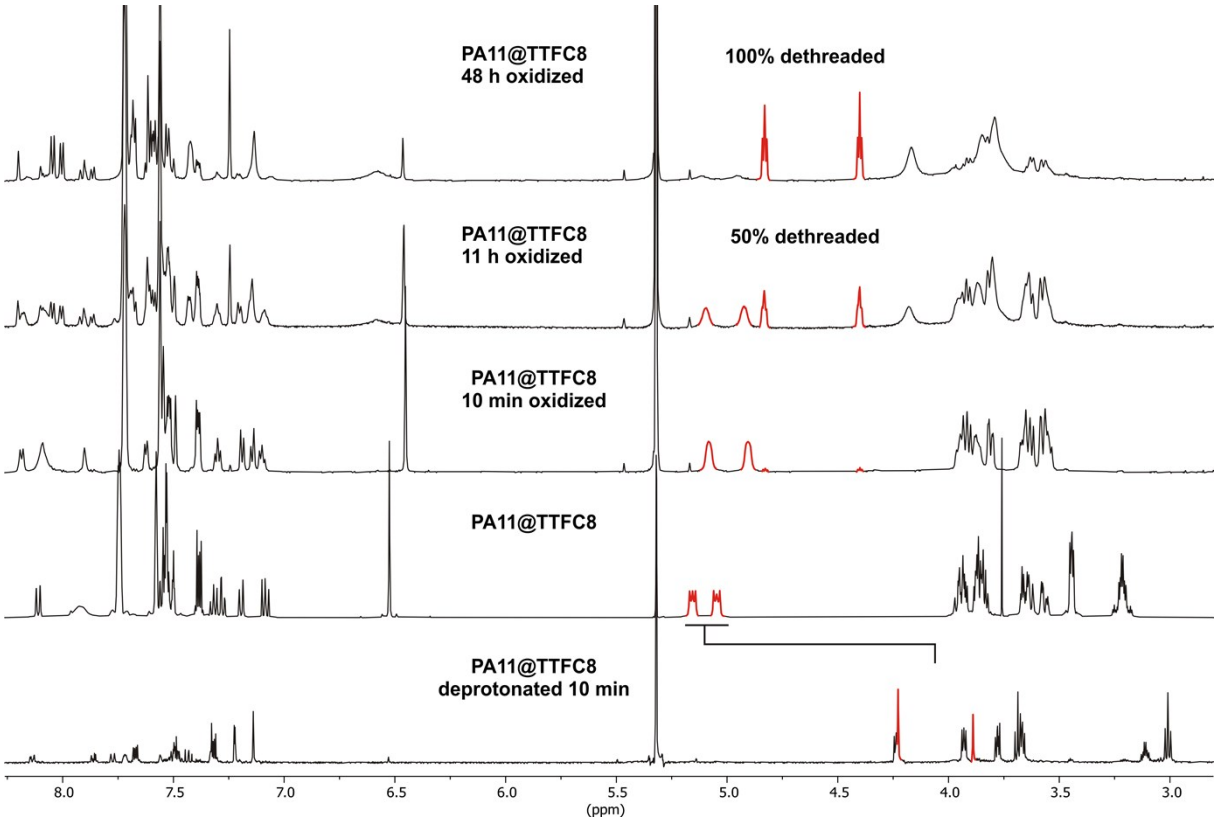


Fig. S42 ^{1}H NMR spectra (600 MHz, CD_2Cl_2, 298 K) of **PA11@TTFC8** (center) after oxidation with $NO^{\cdot+}SbF_6^-$ (top) and after deprotonation with P2 base (bottom). The highlighted peaks in red correspond to the methylene protons next to the nitrogen.

Tab. S1: Dethreading timescales in model pseudo[2]rotaxanes **PA*n*@TTFC8**: $t_{1/2}$, obtained via ^{1}H NMR (2 mM in CD_2Cl_2 400/600/700 MHz at r.t.).

	PA5@TTFC8	**PA6@TTFC8**	**PA7@TTFC8**	**PA11@TTFC8**
deprotonation (P2 base)	< 10 min	< 10 min	< 10 min	< 10 min
oxidation ($NO^{\cdot+}SbF_6^-$)	184 h	> 335 h	22 h	11 h

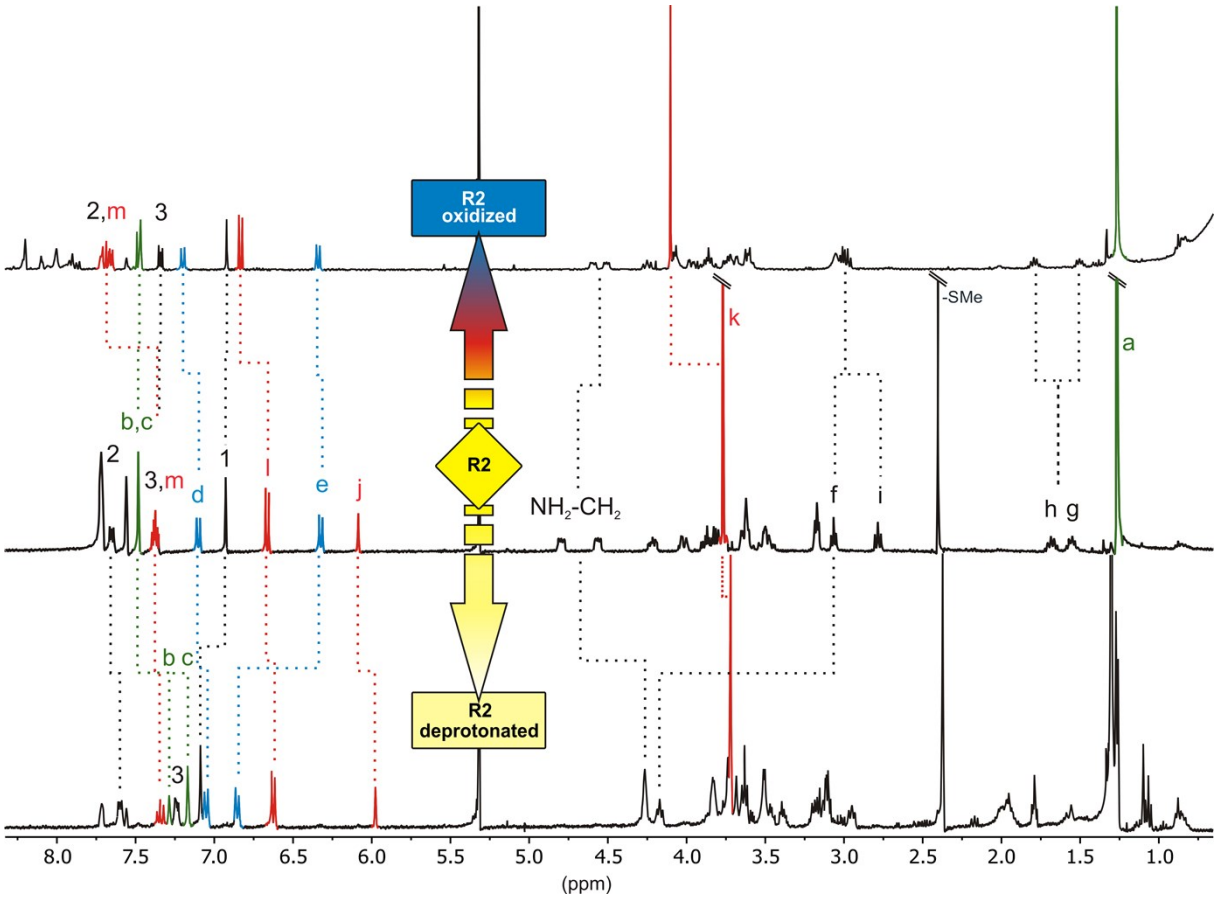


Fig. S43 ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298 K) with selected shifts highlighted of **R2** (center) 10 min after oxidation with $NO^{\cdot+}SbF_6^-$ (top) and 10 min after deprotonation with polystyrene-immobilized P2 base (bottom).

3. Tandem mass spectrometry

A Synapt G2-S HDMS (Waters Co., Milford, MA, USA) instrument with a quadrupole-time-of-flight high resolution mass detector was used to perform electrospray ionization tandem mass spectrometry. Collision-induced dissociation (CID) experiments of mass-selected ions, were performed using the following settings: flow rate 10 µL min^{-1}, capillary voltage 1.5 kV, sample cone voltage 34 V, source offset 54 V, source temperature 100 °C, desolvation temperature 20 °C, nebulizer gas 5 bar, desolvation gas flow 460 L h^{-1}. For CID, N_2 was used as the collision gas. Fragmentation experiments were conducted in the trap cell of the Synapt G2-S HDMS instrument with collision energies of 2 – 72 V. For the column chromatography isolated sample, 4 V steps were used and for the other samples 2 V steps. Data acquisition and processing was carried out using MassLynx™ (version 4.1).

For plotting of the survival yield curves the spectra were centered. For each spectrum at different collision voltages, the intensity of the ion with the selected mass (m/z 1108) was divided by the total ion intensity (only fragments with an intensity above 1% were considered) and then plotted against the collision voltage. Fitting was done by applying a sigmoidal Boltzmann equation using Origin Pro 2020 to obtain the 50%-survival yield voltages of threaded and non-threaded complex.

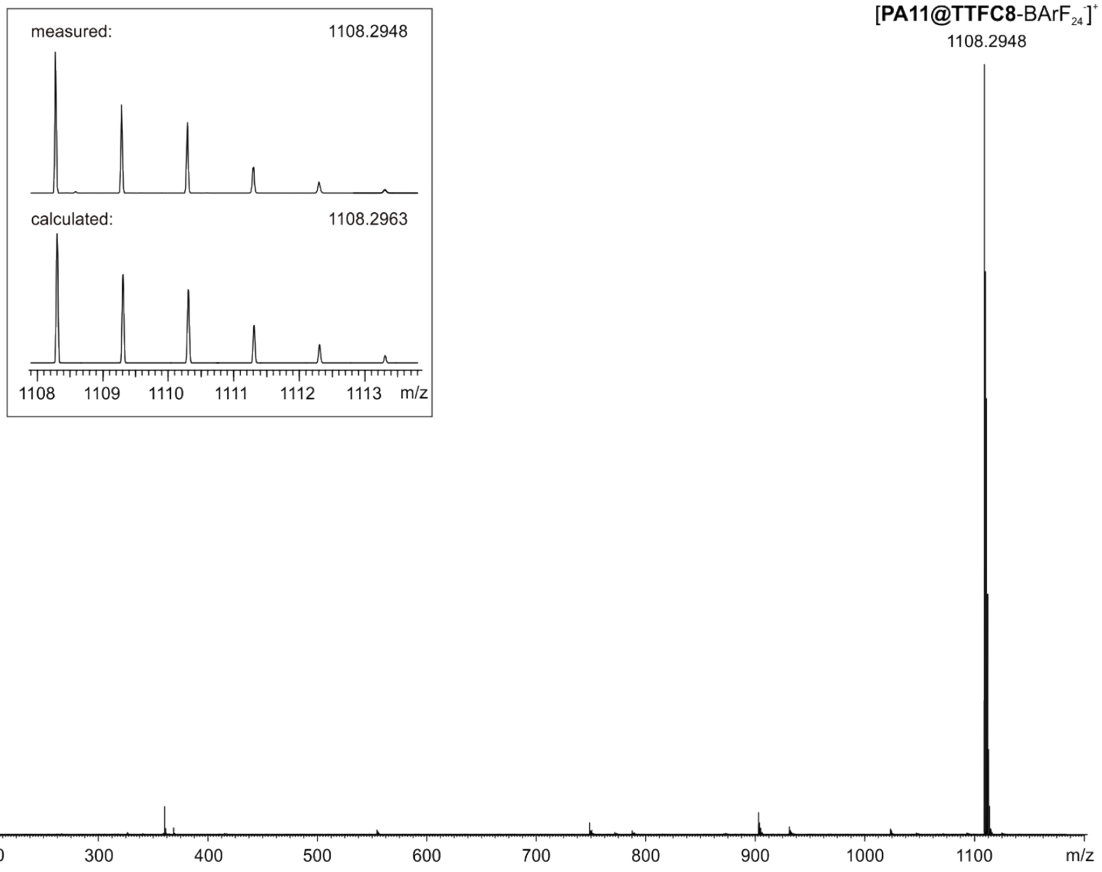


Figure S44 ESI-Q-TOF-HRMS spectrum of **PA11@TTFC8** (5 µM in CH_2Cl_2) isolated after column chromatography; (inset) comparison of measured and calculated isotopic patterns.

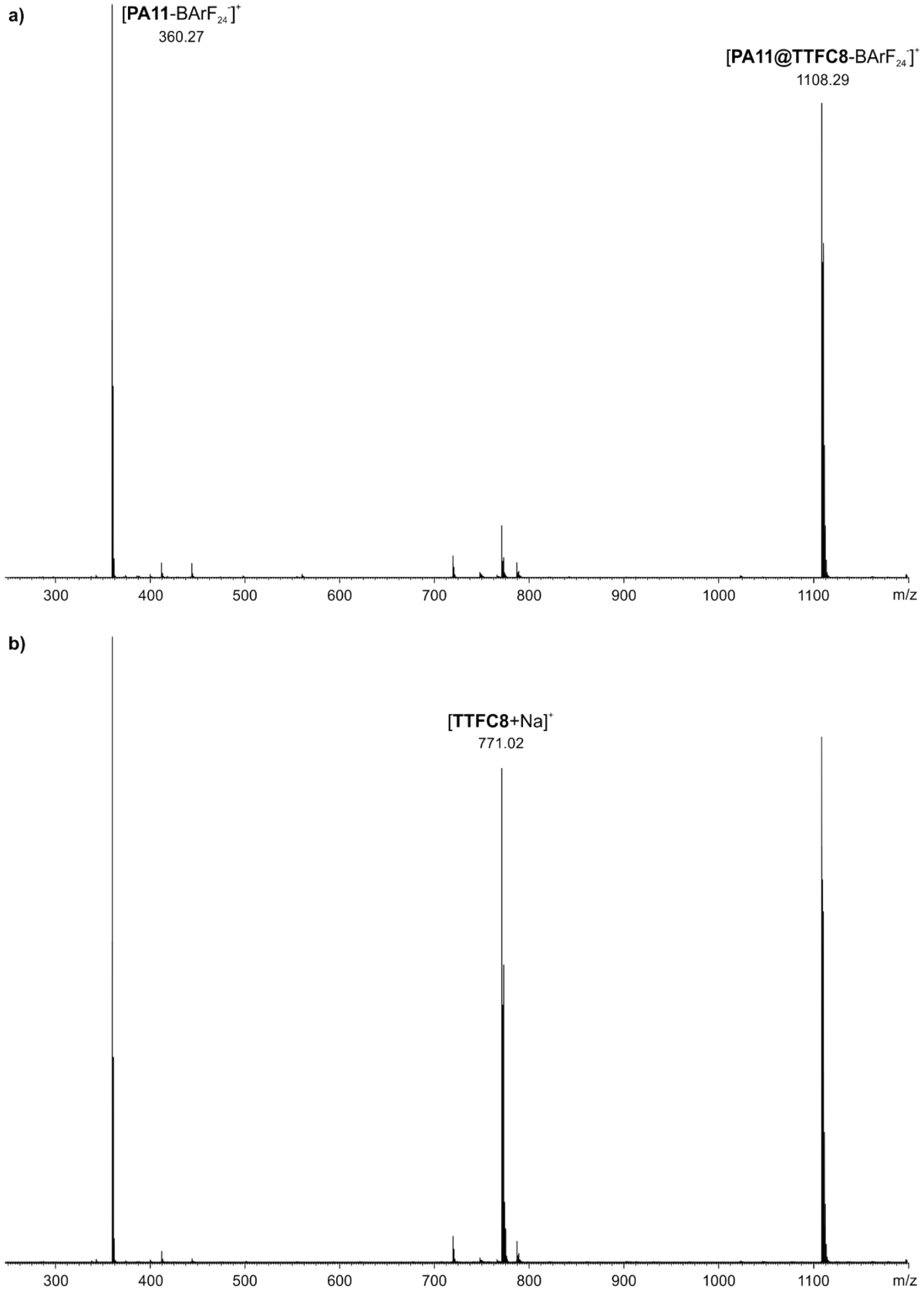


Figure S45 ESI-Q-TOF-HRMS spectrum of a mixture of **PA11** and **TTFC8** (500 µM in CH_2Cl_2), diluted before measuring to 50 µM after 5 min (a) and 135 min (b). Both solutions feature a complex of **TTFC8** and **PA11**, as well as **TTFC8**(+Na) and **PA11** individually. Which indicates that a non-threaded complex is formed within 5 min or during the ionization.

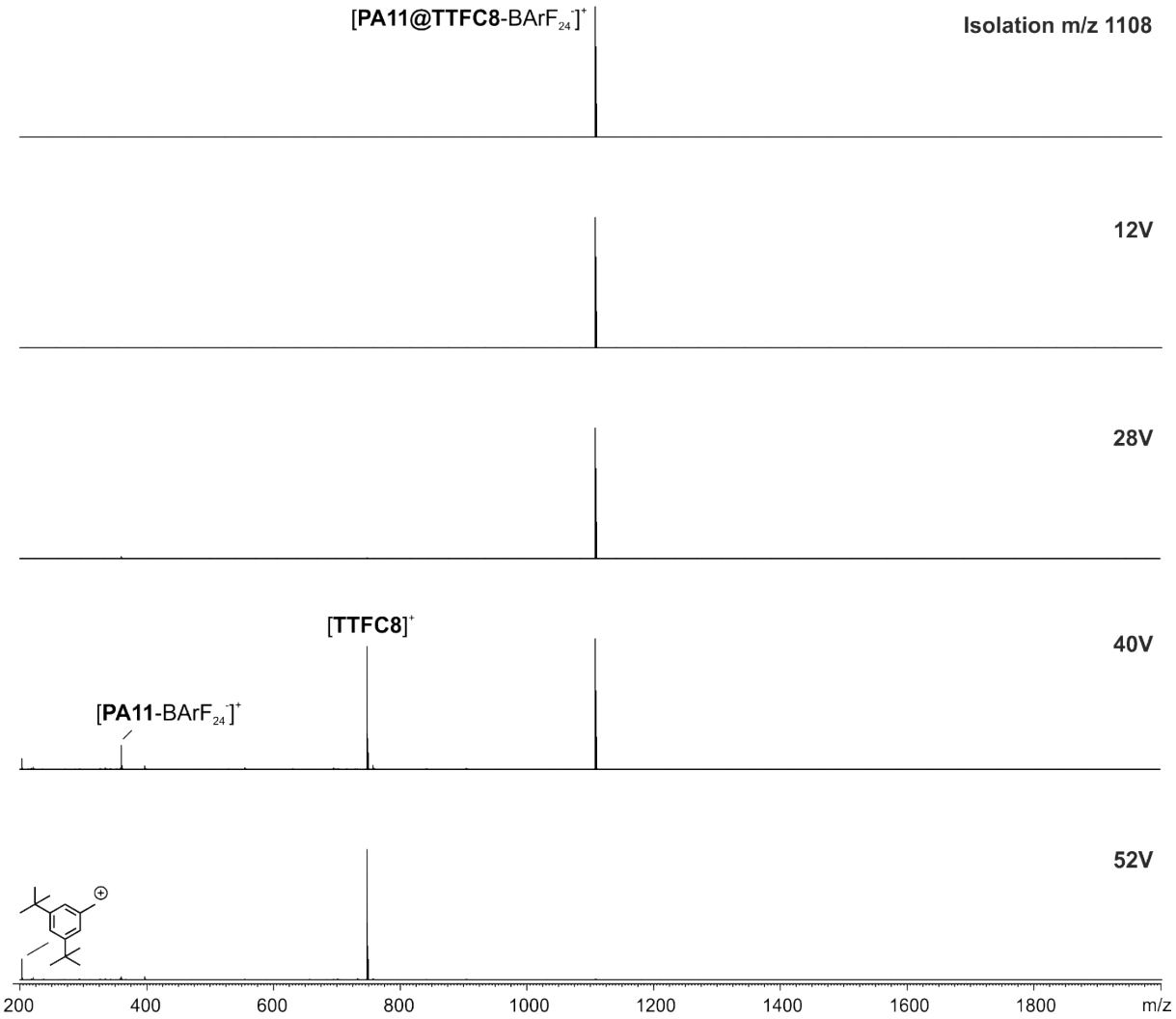


Figure S46 CID experiment with mass-selected ions at *m/z* 1108 obtained from a CH_2Cl_2 solution (50 nM) of **PA11@TTFC8** isolated after column chromatography: (top) after mass-selection; (bottom) after fragmentation at different voltages. Higher voltages are necessary to induce fragmentation and as a major fragment oxidized **TTFC8** is observed. This is diagnostic for a mechanically interlocked structure.[10]

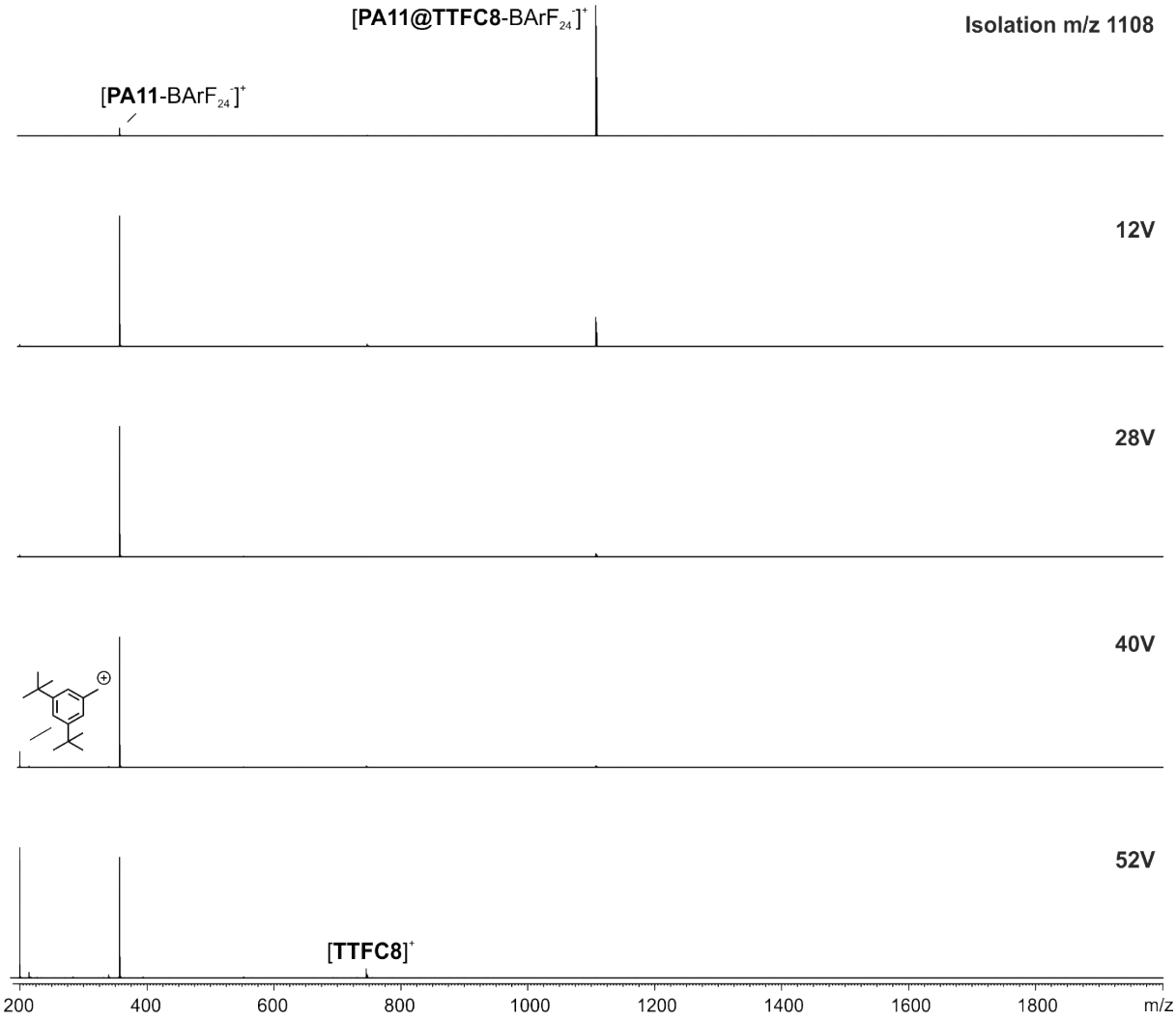


Figure S47 CID experiment with mass-selected ions at *m/z* 1108 obtained from a mixture of **PA11** and **TTFC8** (500 µM in CH_2CCl_2), diluted before measuring to 50 µM after 5 min (top) after mass-selection; (bottom) after fragmentation at different voltages. The complex fragments already appear at low collision voltages, which can be explained by the formation of a non-threaded complex. A minor amount of the complex is still existing at higher voltages (28 and 40 V), which represents the amount of threaded complex.

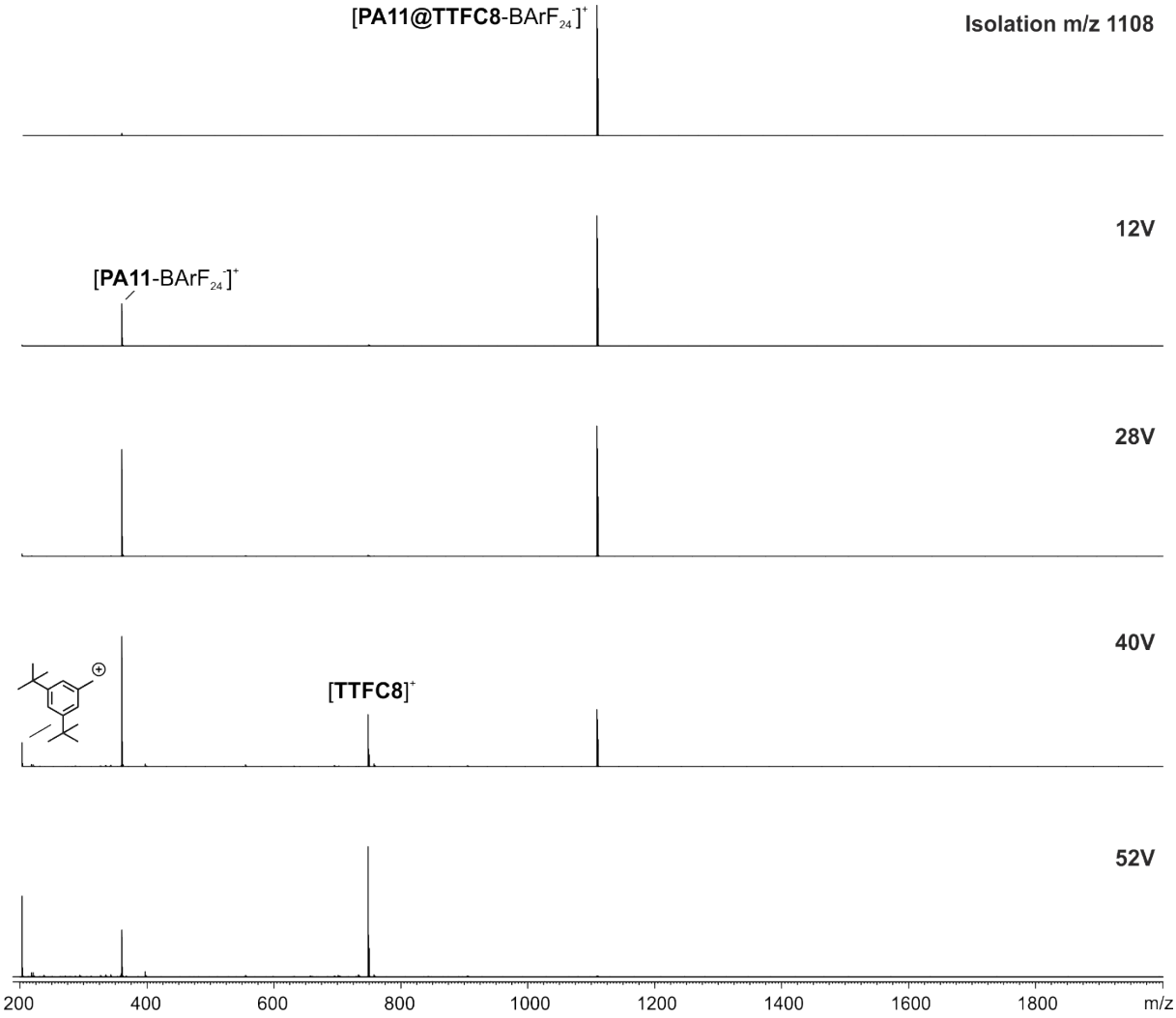


Figure S48 CID experiment with mass-selected ions at *m/z* 1108 obtained from a mixture of **PA11** and **TTFC8** (500 µM in CH_2Cl_2), diluted before measuring to 50 µM after 135 min (top) after mass-selection; (bottom) after fragmentation at different voltages. A fraction of the complex fragments appear already at low collision voltages, which can be explained by the formation of a non-threaded complex. A bigger amount of the complex is still existing at higher voltages (28 and 40 V), which represents the amount of threaded complex.

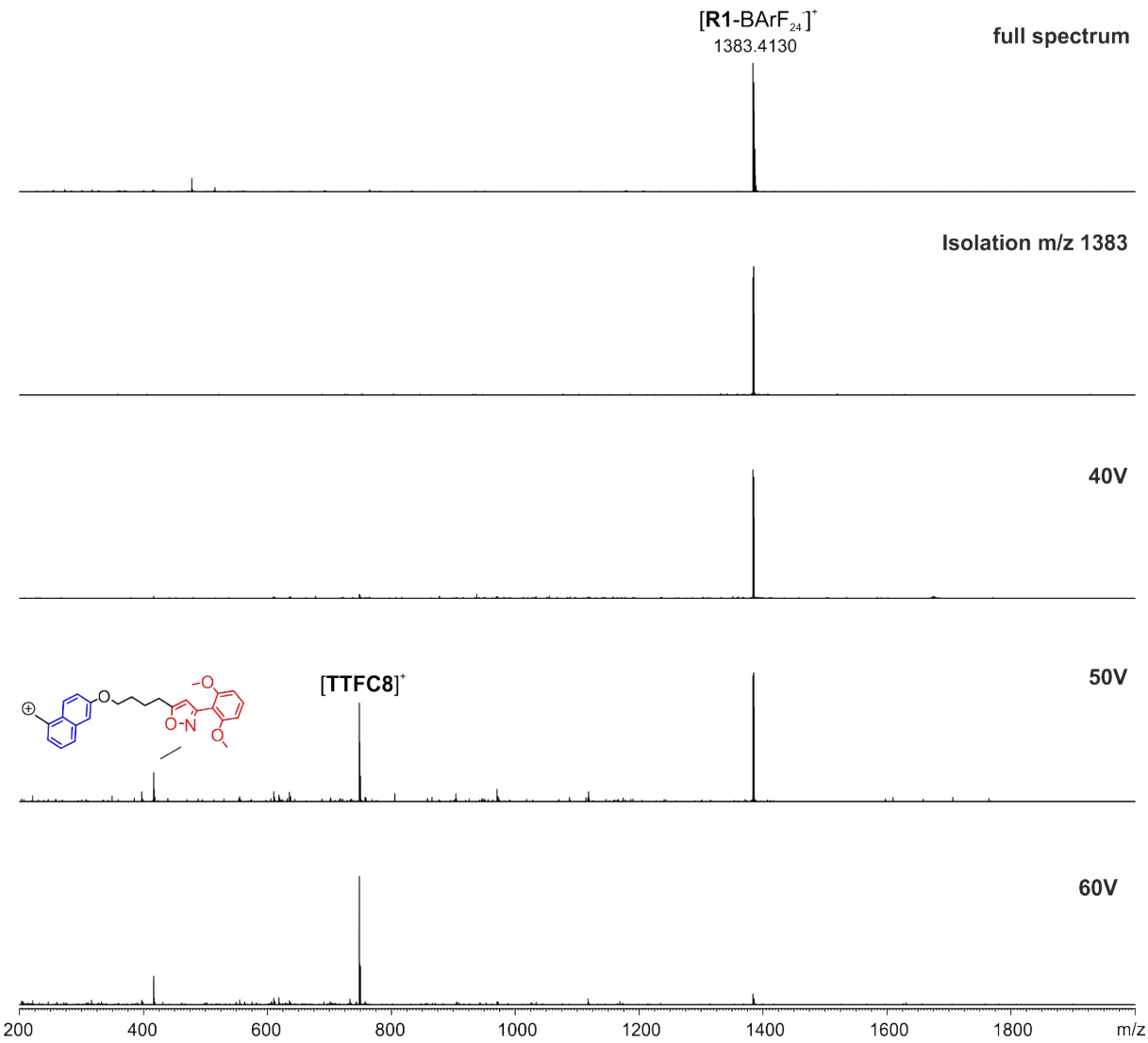


Figure S49 ESI-Q-TOF-HRMS spectrum (top) and CID experiment with mass-selected ions at *m/z* 1383 obtained from solution of **R1** (5 μM in acetonitrile). Higher voltages are necessary to induce fragmentation of **R1** and as major fragments oxidized **TTFC8** and axle fragments are observed. The free axle (m/z 635) is not observed as a fragment. This is diagnostic for a mechanically interlocked structure.[10]

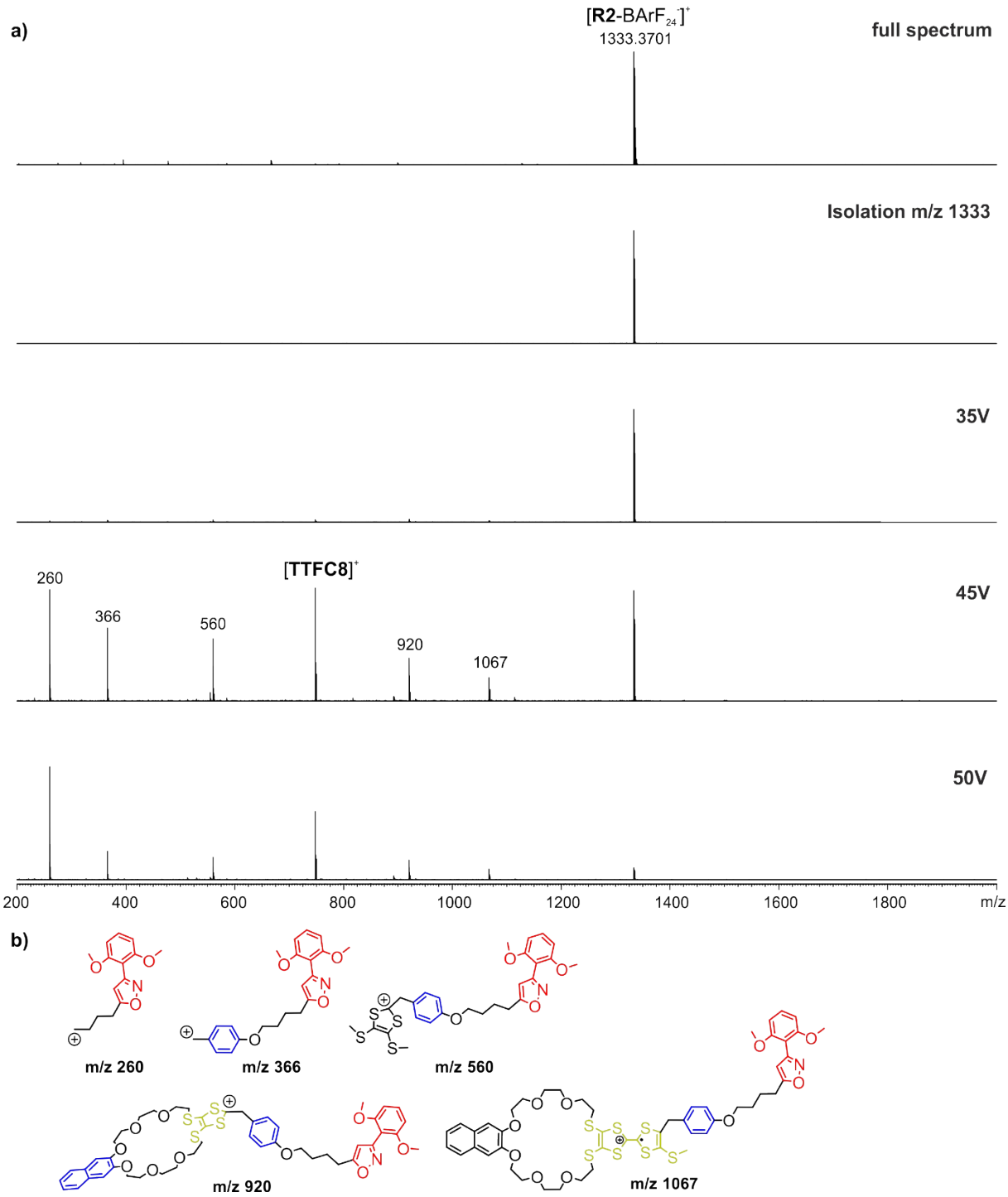


Figure S50 (a) ESI-Q-TOF-HRMS spectrum (top) and CID experiment with mass-selected ions at *m/z* 1333 obtained from solution of **R2** (5 µM in acetonitrile). Higher voltages are necessary to induce fragmentation of **R2** and as major fragments oxidized **TTFC8** and axle fragments are observed. The free axle (m/z 635) is not observed as a fragment. This is diagnostic for a mechanically interlocked structure. (b) Proposed structures for m/z values occurring in the fragmentation spectra. Similar fragments have been observed for other TTF crown/ammonium rotaxane.[10]

4. Variable-temperature ^{1}H NMR spectroscopy

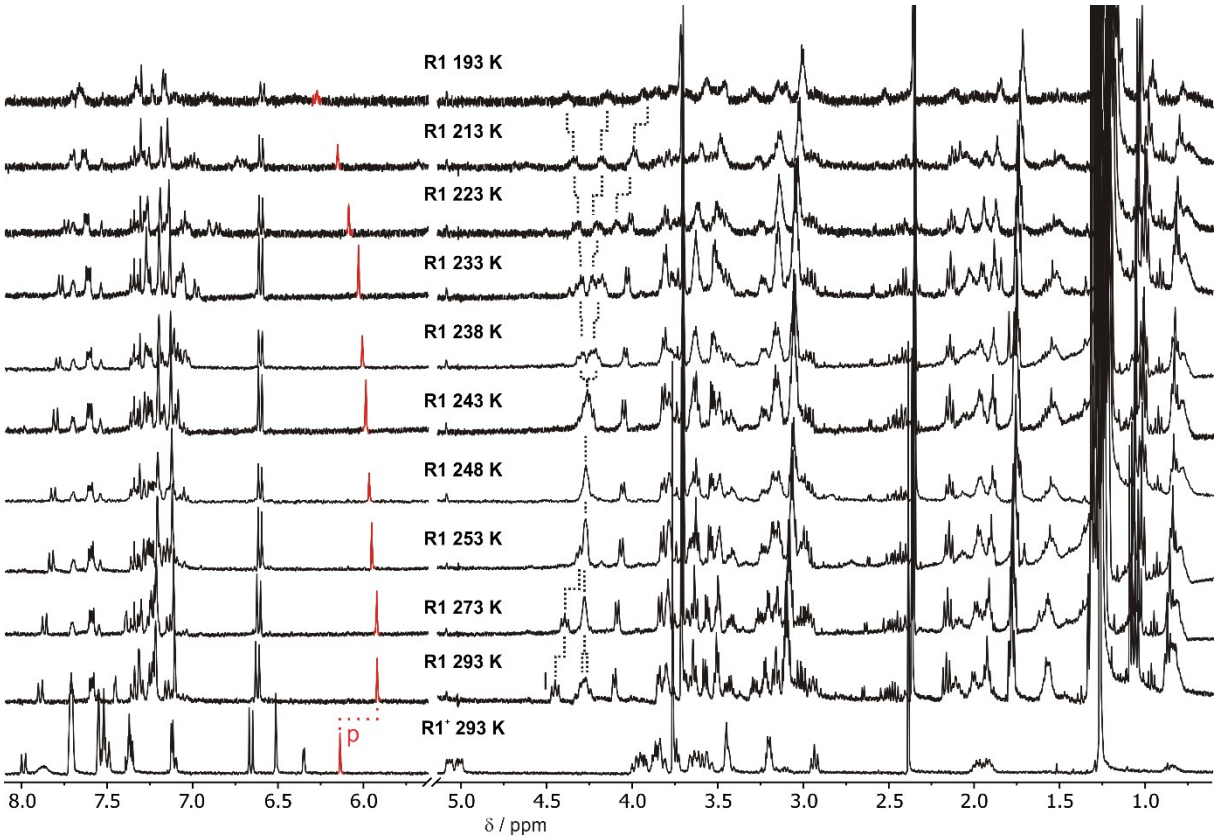


Fig. S51 VT ^{1}H NMR spectra (400 MHz, CD_2Cl_2) of [2]rotaxane **R1** before (bottom) and after deprotonation with P2 base (gradual cooling from 293 to 193 K), showing the shift of H_p (isoxazol).

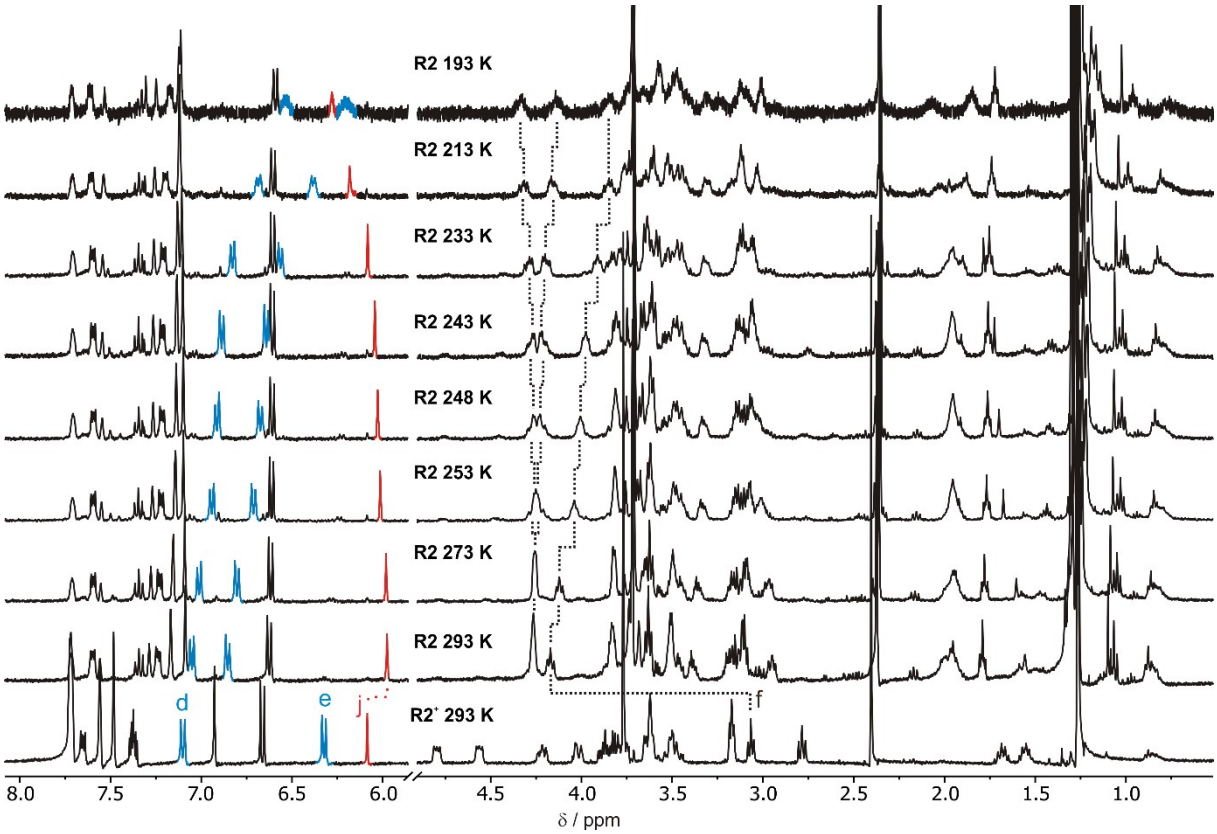


Fig. S52 VT ^{1}H NMR spectra (400 MHz, CD_2Cl_2) of [2]rotaxane **R2** before (bottom) and after deprotonation with P1 base (gradual cooling from 293 to 193 K), showing the shift of H_j (isoxazol), $H_{d,e}$ (phenyl).

5. Isothermal titration calorimetry

ITC experiments were carried out in dry 1,2-dichloroethane at 298 K on a TAM III microcalorimeter (Waters GmbH, TA Instruments, Eschborn, Germany). In a typical experiment, an 800 µL solution of crown ether was placed in the sample cell at a concentration of 1.1 mM, and 250 µL of a solution of the ammonium salt (7.0 mM) were put into the syringe. The titrations consisted of 32 consecutive injections of 8 µL each with a 20 min interval between injections. Heats of dilution were determined by titration of ammonium salt solutions into the sample cell containing blank solvent and were subtracted from each data set. The heat flow generated in the sample cell is measured as a differential signal between sample and reference cell. Hence, an exothermic event results in a positive and an endothermic in a negative heat flow. The data were analysed using the instrument's internal software package and fitted with a 1:1 binding model. Each titration was conducted three times and the measured values for K and ΔH were averaged.

Tab. S2: Thermodynamic data obtained from the ITC experiments.

	K_a /10^4 M^{-1}	ΔG / kJ mol^{-1}	ΔH / kJ mol^{-1}	$T\Delta S$ / kJ mol^{-1}
PA11@TTFC8	1.0 ± 0.3	-22.9 ± 0.6	-28.6 ± 2.0	-5.7 ± 2.6
PA12@TTFC8	39 ± 7	-31.9 ± 0.4	-44.1 ± 1.2	-12.2 ± 1.6
DBA@TTFC8	77 ± 10	-33.6 ± 0.3	-39.8 ± 1.0	-6.2 ± 1.3

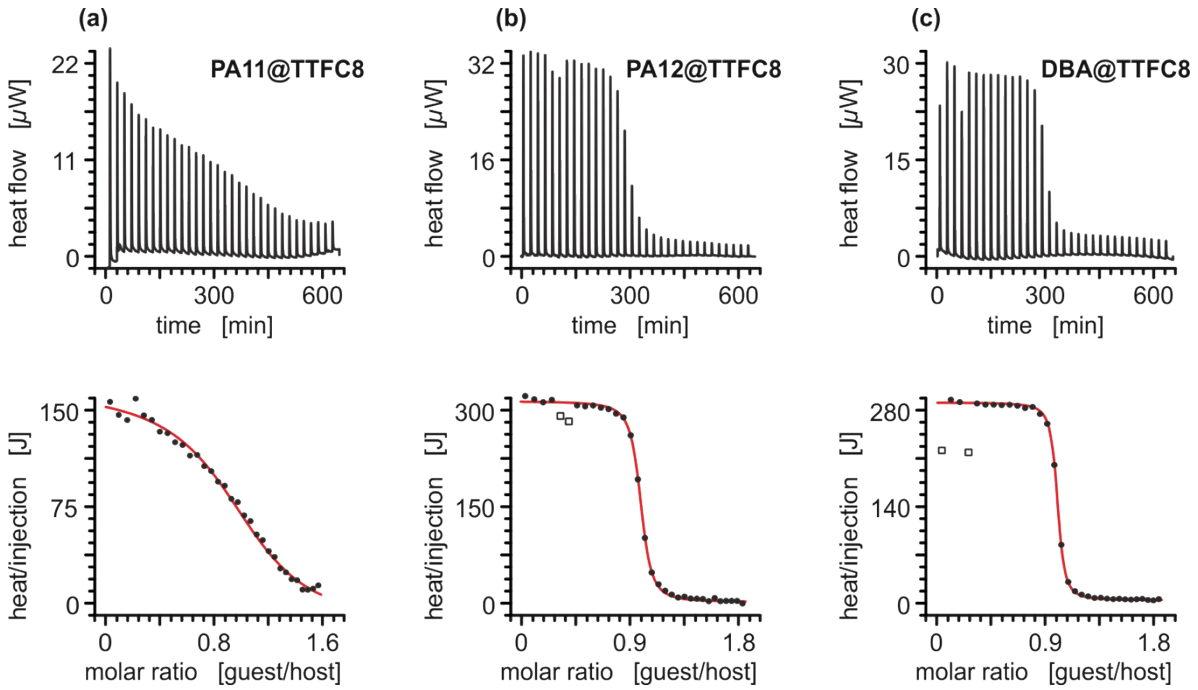


Figure S53. Titration plots (heat flow versus time and heat/volume versus guest/host ratio) obtained from ITC experiments at 298 K in 1,2-dichloroethane**: (a)** vial: **TTFC8**, syringe: axle **PA11**; **(b)** vial: **TTFC8**, syringe: axle **PA12**; **(c)** vial: **TTFC8**, syringe: axle **DBA** (dibenzylammonium $BArF_{24}$). Points marked with non-filled squares were not considered in the fitting process. **PA11@TTFC8** was fitted using a 1:1 binding model. However, for this axle the formation of a threaded complex happens over the course of hours and the formation of a non-threaded complex is observed on a minute timescale. The thermodynamic parameters obtained for this macrocycle/axle combination can therefore be interpreted as a combination of both equilibria (see Figure 3 main text) with the formation of the threaded complex contributing with a less time dependent heat flow. The obtained thermodynamic parameters can therefore be used as an upper limit for the values of K and ΔH of the non-threaded complex.

6. Electrochemical measurements

Redox-potentials reported in this study were obtained by DPV. All measurements were at least conducted twice. Measurements were conducted in CH_2Cl_2 with 0.1 M electrolyte and 2 mM analyte concentration.

Tab. S3 Electrochemical data obtained from DPV measurements (CH_2Cl_2, with n-Bu_4NBArF_{24} as the electrolyte, 298 K).

species	$E^1_{1/2}$ / mV	$E'_{1/2}$ / mV	$E^2_{1/2}$ / mV
TTFC8	594	/	987
PA12@TTFC8	599	987	1294
PA11@TTFC8	695	/	1385
R1	695	/	1380
R2	694	/	1349

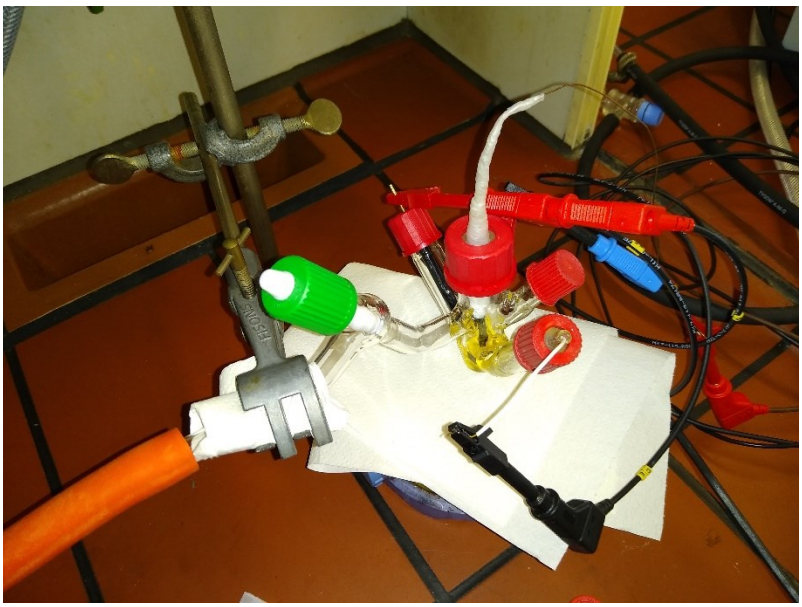


Fig. S54: General set-up for bulk electrolysis experiments.

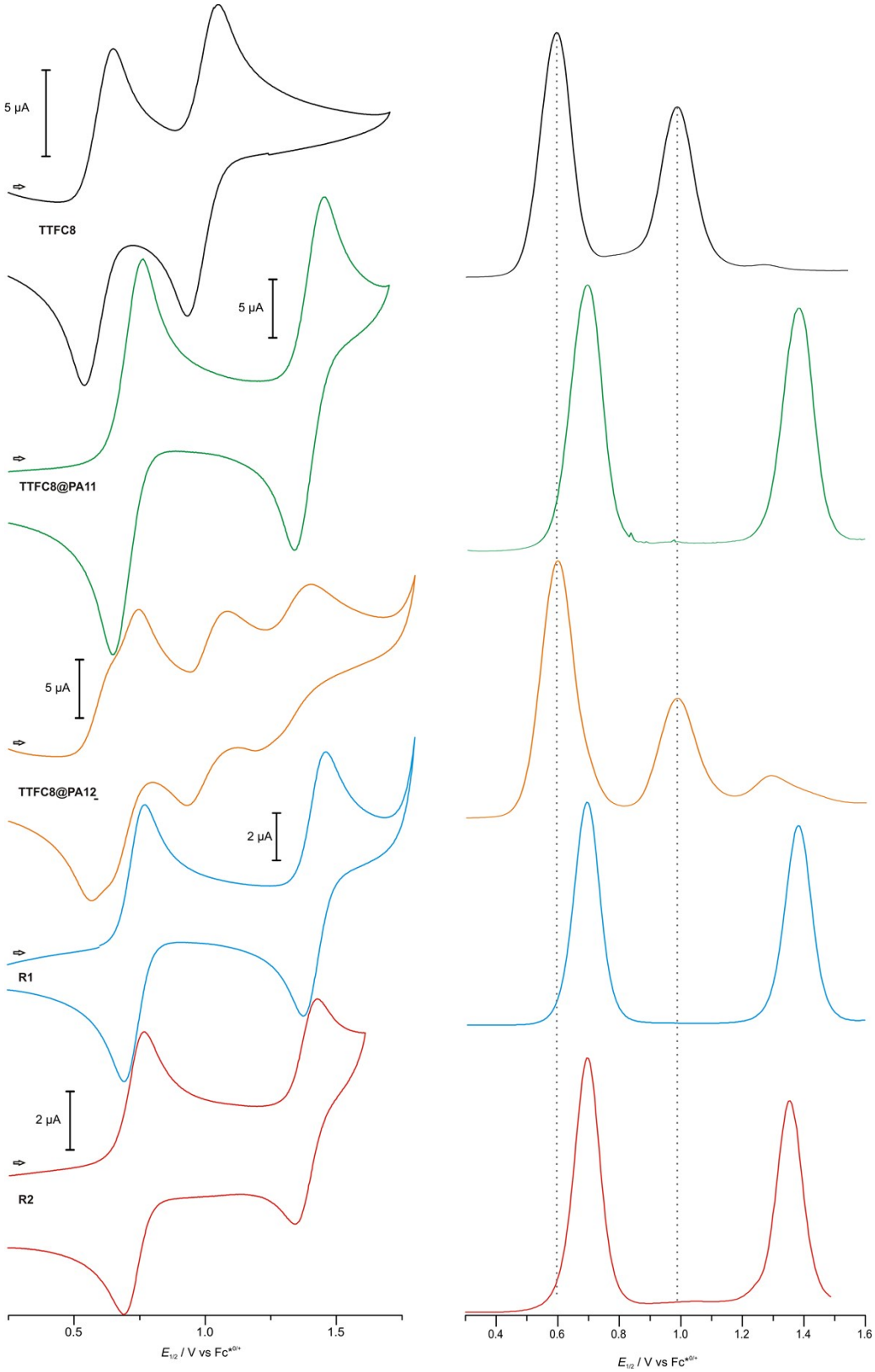


Fig. S55 Stacked cyclic voltammograms (100 mV/s scan rate) with corresponding differential pulse voltammograms (DPV, 10 mV/s scan rate, 25 mV modulation amplitude, 50 ms modulation time, 5 mV step potential, 0.5 s interval time) (CH_2Cl_2, n-Bu_4NBArF_{24}, 298 K) of **TTFC8, PA11@TTFC8, PA12@TTFC8, R1, R2.**

7. UV/Vis experiments

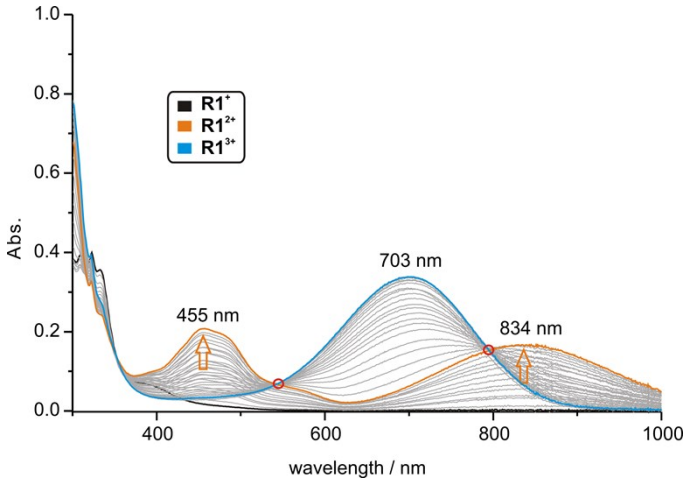


Fig. S56 UV/Vis spectra of **R1** (25 µM in CH_2Cl_2, 298 K, bulk $Fe(ClO_4)_3$ as the oxidant) in the TTF^0 (black), $TTF^{\bullet+}$ (orange) and TTF^{2+} (blue) state. The grey lines correspond to spectra taken in between full conversion to the radical cation or the doubly oxidized species, since the bulk $Fe(ClO_4)_3$ does not dissolve completely in CH_2Cl_2.

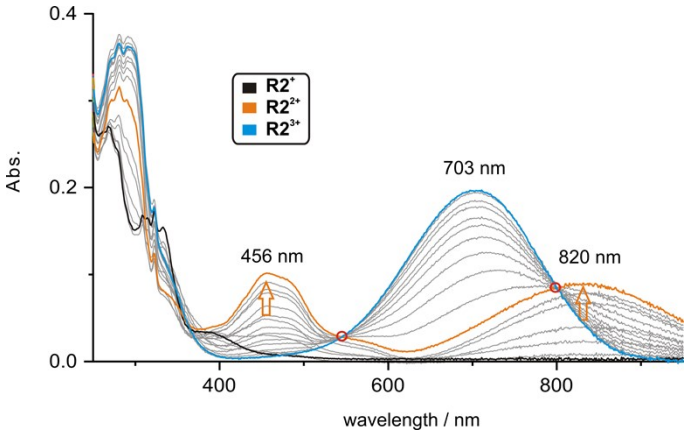


Fig. S57 UV/Vis spectra of **R2** (25 µM in CH_2Cl_2, 298 K, bulk $Fe(ClO_4)_3$ as the oxidant) in the TTF^0 (black), $TTF^{\bullet+}$ (orange) and TTF^{2+} (blue) state. The grey lines correspond to spectra taken in between full conversion to the radical cation or the doubly oxidized species, since the bulk $Fe(ClO_4)_3$ does not dissolve completely in CH_2Cl_2.

8. Crystallographic data

The data for **TTFC8** were collected on an Agilent SuperNova single-source diffractometer equipped with an Eos CCD detector at 123(2) K using mirror-monochromated Mo-Kα (λ = 0.71073 Å) radiation. Data collection (ω scans) and reduction was performed using the program CrysAlisPro. (Version 1.171.38.43, Rigaku Oxford Diffraction 2015) The analytical face-indexing-based absorption correction method was applied. The structure was solved by intrinsic phasing methods (SHELXT[11]) and refined by full-matrix least squares on F^2 using SHELXL-2017/1.[11, 12] Anisotropic displacement parameters were assigned to non-H atoms. All hydrogen atoms were constrained to their idealised positions and refined using riding models with U_{eq}(H) of 1.5U_{eq}(C) for terminal methyl groups and of 1.2U_{eq}(C) for other groups. Moderate geometric and anisotropic restraints were utilized to stabilize the refinement of disordered ethylene group and to make it chemically reasonable. Deposition Number CCDC-2073308 contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

The slow diffusion of diisopropyl ether into a concentrated solution of **TTFC8** in CH_2Cl_2/CH_3CN (1:1) mixture yielded single crystals suitable for X-ray diffraction study (see Fig. 2). The solid state structure shows planar TTF moiety, as well as, typical bond lengths and angles of neutral TTF derivatives, like characteristically short C=C distance of 1.343(5) Å between the 1,3-dithiole rings and a distance range of 1.749(4) to 1.816(3) Å for C-S bonds.[13, 14] Almost orthogonal distortion of naphthalene unit out of TTF plane with 84.65° interplanar angle is resulting in bent boat-shaped conformation of the molecule. In the crystal packing, the molecules are arranged in columnar stacks with naphthalenes and TTFs on top of each other with plane-to-plane distances of 3.247 Å and 3.415 Å, shifted by 3.908 Å and 3.762 Å, respectively. There is a slight disorder in one ethylene group in the crown ether moiety, which is refined by splitting C and H atoms of that ethylene group over two spatial positions with approximately 63/37 ratio (major/minor).

Crystal data of **TTFC8**: $C_{30}H_{36}O_6S_8$, M = 749.07, triclinic, space group *P*-1 (no.2), a = 5.0805(3), b = 14.9091(10), c = 22.3719(14) Å, α = 98.267(5), β = 91.760(5), γ = 96.811(5)°, V = 1663.2(2) Å^3, Z = 2, ρ_{calc} = 1.496 Mgm^{-3}, μ = 0.579 mm^{-1} (T_{max} = 0.974 and T_{min} = 0.943), F(000) = 784, θ range = 3.27-26.50°, 10254 reflections collected, 6834 unique (R_{int} = 0.0328, I>2σ(I) = 4509), which were used in all calculations (418 parameters, 39 restraints), Goodness-of-fit (F^2) = 1.066. The final R indices [I>2σ(I)]: R1 = 0.0551 and wR2 = 0.1023. R indices (all data): R1 = 0.0947 and wR2 = 0.1248. Largest residual electron densities: 0.531 and -0.398 e.Å^{-3}.

9. References

1. H. V. Schröder, S. Sobottka, M. Nössler, H. Hupatz, M. Gaedke, B. Sarkar and C. A. Schalley, *Chem. Sci.*, 2017, **8**, 6300-6306.
2. T. Matsumura, F. Ishiwari, Y. Koyama and T. Takata, *Org. Lett.*, 2010, **12**, 3828-3831.
3. O. P. S. Rossi, F. Selva, *Farmaco. Ed. Sci.*, 1967, **22**, 172-176.
4. S. Grunder, D. Muñoz Torres, C. Marquardt, A. Błaszczyk, R. Krupke and M. Mayor, *Eur. J. Org. Chem.*, 2011, **2011**, 478-496.
5. J. Bucher, T. Wurm, K. S. Nalivela, M. Rudolph, F. Rominger and A. S. Hashmi, *Angew. Chem. Int. Ed.*, 2014, **53**, 3854-3858.
6. D. Y. Wang, Z. K. Yang, C. Wang, A. Zhang and M. Uchiyama, *Angew. Chem. Int. Ed.*, 2018, **57**, 3641-3645.
7. J. R. Aranzaes, M.-C. Daniel and D. Astruc, *Can. J. Chem.*, 2006, **84**, 288-299.
8. C. Bornschein, S. Werkmeister, K. Junge and M. Beller, *New J. Chem.*, 2013, **37**, 2061.
9. A. R. Salimi, M. Azizpoor Fard, H. Eshtiagh-Hosseini, M. A. M and H. R. Khavasi, *Acta Crystallogr Sect E Struct Rep Online*, 2010, **66**, o509.
10. M. Gaedke, F. Witte, J. Anhäuser, H. Hupatz, H. V. Schröder, A. Valkonen, K. Rissanen, A. Lützen, B. Paulus and C. A. Schalley, *Chem. Sci.*, 2019, **10**, 10003-10009.
11. G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.*, 2015, **71**, 3-8.
12. G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 3-8.
13. J. Sun, X. Lu, J. Shao, X. Li, S. Zhang, B. Wang, J. Zhao, Y. Shao, R. Fang, Z. Wang, W. Yu and X. Shao, *Chem. Eur. J.*, 2013, **19**, 12517-12525.
14. H. Kobayashi, R. Kato, T. Mori, A. Kobayashi, Y. Sasaki, G. Saito, T. Enoki and H. Inokuchi, *Mol. Cryst. Liq. Cryst.*, 2011, **107**, 33-43.