Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Evaluation of Multivalency as an Organization Principle for the Efficient Synthesis of Doubly and Triply Threaded Amide Rotaxanes

Supporting Information

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1. Experimental Details

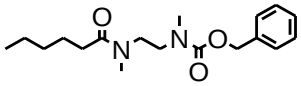
General: Reagents were purchased from Aldrich, ACROS or Fluka and used without further purification. Dry solvents were purchased from ACROS Organics and used as received. Yields refer to chromatographically and spectroscopically homogeneous materials. Thin-layer chromatography (TLC) was performed on precoated silica gel 60/F254 plates (Merck KGaA). Silica gel (0.04-0.063 mm; Merck) was used for column chromatography. TLMs[1], benzyl-methyl(2-(methylamino)ethyl)carbamate[2] and triphenyl acetic acid chloride[3] were synthesized according to literature procedures.

NMR spectroscopy and NMR titrations: ^{1}H (400 MHz) and ^{13}C (101 MHz) spectra were obtained on a Bruker ECX 400 instrument at 298 K. ^{1}H (500 MHz) and ^{13}C (126 MHz) spectra were obtained on JEOL ECP 500 or Bruker AVANCE 500 instruments at 298 K. ^{1}H (700 MHz) and ^{13}C (176 MHz) spectra were obtained on a Bruker AVANCE 700 instrument at 298 K. All chemical shifts are reported in ppm with signals of $CHCl_3$ (7.26 ppm (^{1}H) and 77.2 ppm (^{13}C)) or DMSO (2.50 (^{1}H) and 39.5 (^{13}C)) as internal standards; coupling constants are in Hz. The following abbreviations were used to indicate NMR multiplicities: s (singlet), d (doublet), t (triplet), m (multiplet), br (broad). Titration experiments were carried out in $CDCl_3$ at 25 °C on the Bruker ECX 400 instrument.
As the diamide station in the axle comprises two tertiary amides, an equilibrium between *cis*- and *trans*-amide isomers exists. The *trans, trans*-isomer is the major isomer for the axles under study, but a significant contribution from the *trans, cis*- and a minor amount of the *cis, cis*-isomer are clearly visible in NMR spectra and lead to the corresponding number of sets of signals in the NMR spectra. This complicates the analysis of the NMR spectra, but has been taken into account.

Analytical mass spectrometry: Samples were measured on an Agilent 6210 ESI-TOF, Agilent Technologies, Santa Clara, CA, USA or an Ionspec QFT-7, Agilent Technologies, Santa Clara, CA, USA. In case of the Agilent 6210 ESI-TOF the solvent flow rate was adjusted to 4-15 µL/min and the spray voltage was set to 4 kV. The drying gas flow rate was adjusted to 15 psi (1 bar). All other parameters were optimized for a maximum abundance of the respective $[M+H]^+$, ($[M+Cat]^+$ or $[M-H]^-$) ions. The Ionspec QFT-7 is equipped with a 7 T superconducting magnet and a Micromass Z-spray ESI source, Waters Co., Saint-Quentin, France. The solvent flow rate was adjusted to 4 µL/min and the spray voltage set to 3.8 kV. All other parameters were optimized for a maximum abundance of the respective $[M+H]^+$, ($[M+Cat]^+$ or $[M-H]^-$) ions. Solvents (HPLC gradient grade) were purchased at LGC Promochem. Mass data refer always to the first signal in the isotopic pattern.

Synthesis and analytical data of new compounds:

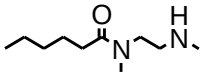
Benzyl-methyl(2-(*N*-methylhexanamido)ethyl)carbamate



Benzyl-methyl(2-(methylamino)ethyl)carbamate (2.0 g, 9.0 mmol) and 5-hexanoic acid (1.4 mL, 12.0 mmol) were dissolved in 50 mL DMF under argon atmosphere and cooled to 0 °C. HOBt (11-18% H_2O; 1.0 g, 6.0 mmol) und EDC (2.2 mL, 12.5 mmol) were added and the reaction mixture was allowed to warm up to rt. After stirring for 20 h, the solvent was removed under reduced pressure and the residue was taken up in EtOAc. The organic layer was washed with sodium bicarbonate solution (3x80 mL) and brine (3x80 mL), dried over $MgSO_4$ and evaporated to dryness. The crude product was purified by column chromatography (SiO_2, EtOAc) and the product was obtained as slightly yellow oil (2.6 g, 8.1 mmol, 91%).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.87 (t, ^3J = 6.5 Hz, 3H, CH_3), 1.28 (m, 4H, CH_2), 1.56 (br, 2H, CH_2), 2.14-2.27 (m, 2H, CH_2), 2.83-2.99 (m, 6H, NCH_3), 3.45 (m, 4H, NCH_2), 5.09 (m, 2H, CH_2), 7.44-7.21 (m, 5H, ArH); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 14.0, 21.1, 22.6, 24.8, 31.7, 35.8, 45.0, 46.3, 60.4, 127.8, 128.6, 137.0, 156.6, 171.2 ppm; HR-MS (ESI, pos. mode, DCM/MeOH): *m/z* calcd. for $[C_{18}H_{29}N_2O_3]^+$: 321.2173 ($[M+H]^+$); found: 321.2177 (Δ = 1.2 ppm); *m/z* calcd. for $[C_{18}H_{28}N_2O_3Na]^+$: 343.1992 ($[M+Na]^+$); found: 343.1992 (Δ = 0 ppm); *m/z* calcd. for $[C_{18}H_{28}N_2O_3K]^+$: 359.1732 ($[M+K]^+$); found: 343.1728 (Δ = 1.1 ppm).

***N*-Methyl-*N*-(2-(methylamino)ethyl)hexanamide**

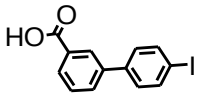


Benzyl-methyl(2-(*N*-methylhexanamido)ethyl)carbamate (1.30 g, 4.1 mmol) and Pd/C (10%; 0.55 g, 5.2 mmol) were dissolved in 100 mL EtOH under argon atmosphere. The reaction mixture was hydrogenated for 5 d under normal pressure and was filtered over celite afterwards to remove the catalyst. The desired product was obtained as colorless oil (0.69 mg, 3.7 mmol, 90%).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.87 (m, 3H, CH_3), 1.29 (m, 4H, CH_2), 1.60 (m, 2H, CH_2), 2.27-2.35 (m, 2H, CH_2), 2.43 (m, 3H, NCH_3), 2.74, (m, 2H, NCH_2), 3.00 (m, 3H, NCH_3), 3.32-3.50 (m, 2H, NCH_2); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 14.1, 22.6, 24.8, 25.3, 31.8, 31.8, 33.1, 33.6, 33.7, 36.1, 36.2, 36.6, 47.4, 49.4, 49.8, 49.9, 173.7 ppm; HR-MS (ESI, pos. mode, DCM/MeOH): *m/z* calcd. for $[C_{10}H_{23}N_2O]^+$: 187.1805 ($[M+H]^+$); found: 187.1804 (Δ = 0.5

ppm); *m/z* calcd. for $[C_{10}H_{22}N_2ONa]^+$: 209.1624 ($[M+Na]^+$); found: 209.1623 (Δ = 0.5 ppm); *m/z* calcd. for $[C_{10}H_{22}N_2OK]^+$: 225.1364 ($[M+K]^+$); found: 225.1363 (Δ = 0.4 ppm).

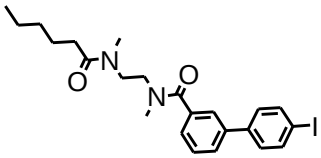
4'-Iodobiphenyl-3-carboxylic acid



Iodine (0.76 g, 3.0 mmol) and [bis(trifluoroacetoxy)iodo]benzene (1.29 g, 3.0 mmol) were dissolved in 20 mL of a 1:1 mixture of glacial acetic acid and acetic anhydride and stirred for 10 min under exclusion of light. Afterwards biphenyl-3-carboxylic acid (850 mg, 4.3 mmol) were added and the reaction mixture was stirred for 3 d. The desired product was obtained by filtration as white solid (0.82 g, 2.5 mmol, 85%).

^{1}H NMR (500 MHz, DMSO-d_6) δ = 7.51 (m, 2H, ArH), 7.60 (m, 1H, ArH), 7.84 (m, 2H, ArH), 7.90 (m, 1H, ArH), 7.96 (m, 1H, ArH), 8.16 (m, 1H, ArH), 13.15 (br, 1H, COOH); ^{13}C NMR (126 MHz, DMSO-d_6) δ = 94.4, 127.1, 128.6, 129.0, 129.5, 130.9, 131.6, 137.8, 138.7, 139.4, 167.13 ppm; HR-MS (ESI, neg. mode, DCM/MeOH): *m/z* calcd. for $[C_{13}H_8IO_2]^-$: 322.9574 ($[M-H]^-$); found: 322.9581 (Δ = 2.2 ppm).

4'-Iodo-*N*-methyl-*N*-(2-(*N*-methylhexanamido)ethyl)-[1,1'-biphenyl]-3-carboxamide (4)

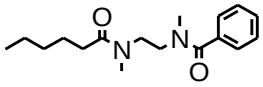


N-Methyl-*N*-(2-(methylamino)ethyl)hexanamide (290 mg, 1.6 mmol) and (360 mg, 1.1 mmol) 4'-iodobiphenyl-3-carboxylic acid were dissolved in 5 mL DMF under argon atmosphere and cooled to 0 °C. HOBt (11-18% H_2O; 107 mg, 0.6 mmol) and EDC (0.3 mL, 1.6 mmol) were added and the reaction was allowed to warm up to rt. After stirring for 3 d the solvent was removed under reduced pressure and the residue was taken up in EtOAc. The organic layer was washed with sodium bicarbonate solution (3x20 mL) and brine (3x20 mL), dried over $MgSO_4$ and evaporated to dryness. The crude product was purified by column chromatography (SiO_2, DCM/MeOH 25:1) and the product was obtained as colorless oil (356 mg, 0.7 mmol, 66%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.85 (m, 3H, CH_3), 1.26 (m, 4H, CH_2), 1.59 (m, 2H, CH_2), 2.29 (m, 2H, CH_2), 3.08 (m, 6H, NCH_3), 3.73 (m, 4H, NCH_2), 7.34 (m, 3H, ArH), 7.44 (m, 1H, ArH), 7.58 (m, 2H, ArH), 7.76 (m, 2H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 13.8, 19.3, 22.3, 31.4, 33.3, 35.3, 37.8, 44.0, 44.4, 53.3, 93.3, 125.2, 125.9, 127.6, 128.7, 136.8, 137.7, 137.8, 139.6, 139.9, 171.1, 173.7 ppm; HR-MS (ESI, pos. mode, DCM/MeOH): *m/z* calcd. for

$[C_{23}H_{30}IN_2O_2]^+$: 493.1347 ($[M+H]^+$); found: 493.1324 (Δ = 4.6 ppm); *m/z* calcd. for $[C_{23}H_{29}IN_2O_2Na]^+$: 515.1166 ($[M+Na]^+$); found: 515.1141 (Δ = 4.8 ppm); *m/z* calcd. for $[C_{23}H_{29}IN_2O_2K]^+$: 531.0905 ($[M+K]^+$); found: 531.0878 (Δ = 5.0 ppm).

_N_-Methyl-_N_-(2-(_N_-methylhexanamido)ethyl)benzamide (7)



_N_-Methyl-_N_-(2-(methylamino)ethyl)hexanamide (400 mg, 2.2 mmol) and benzoic acid (350 mg, 2.9 mmol) were dissolved in 12 mL DMF under argon atmosphere and cooled to 0 °C. HOBt (11-18% H_2O; 274 mg, 1.4 mmol) and EDC (0.5 mL, 2.9 mmol) were added. After stirring for 6 d the solvent was removed under reduced pressure and the residue was taken up in EtOAc. The organic layer was washed with sodium bicarbonate solution (3x20 mL) and brine (3x20 mL), dried over $MgSO_4$ and evaporated to dryness. The crude product was purified by column chromatography (SiO_2, EtOAc/MeOH 10:1) and the product was obtained as colorless oil (296 mg, 1.0 mmol, 46%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.85 (m, 3H, CH_3), 1.27 (m, 4H, CH_2), 1.60 (m, 2H, CH_2), 2.26 (m, 2H, CH_2), 3.04 (m, 6H, NCH_3), 3.69 (m, 4H, NCH_2), 7.35 (m, 5H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 14.0, 22.6, 24.8, 31.7, 32.7, 35.7, 38.1, 44.2, 44.7, 127.0, 128.4, 129.6, 136.3, 171.7, 174.0 ppm; HR-MS (ESI, pos. mode, DCM/MeOH): *m/z* calcd. for $[C_{17}H_{27}N_2O_2]^+$: 291.2067 ($[M+H]^+$); found: 291.2084 (Δ = 5.8 ppm).

Trivalent alkyl axle (6)

4'-Iodo-_N_-methyl-_N_-(2-(_N_-methylhexanamido)ethyl)-[1,1'-biphenyl]-3-carboxamide (140.0 mg 280 µmol) and 1,3,5-triethynylbenzene (12.0 mg, 80 µmol) were dissolved in 3 mL DMF and 2 mL NEt_3. Under argon atmosphere and exclusion of light, PPh_3 (15.6 mg, 52 µmol), $Pd_2^4{}_3$ (23.8 mg, 26 µmol) and CuI (5.2 mg, 26 µmol) were added and the reaction was stirred at 70 °C for 5 d. After removing the solvent, the residue was purified by column chromatography (SiO_2, DCM/MeOH 20:1) and yielded in a brown solid (73.8 mg, 59 µmol, 74%).

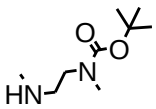
^{1}H NMR (700 MHz, $CDCl_3$) δ = 0.86 (m, 9H, CH_3), 1.28 (m, 12H, CH_2), 1.61 (m, 6H, CH_2), 2.29 (m, 6H, CH_2), 2.73-3.17 (m, 18H, NCH_3), 3.47-3.77 (m, 12H, NCH_2), 7.37-7.70 (m, 27H, ArH); ^{13}C NMR (176 MHz, $CDCl_3$) δ = 13.9, 24.7, 28.5, 31.6, 33.5, 35.6, 38.0, 44.3, 44.8, 88.7, 90.4, 122.1, 124.1, 125.6, 126.2, 127.1, 127.1, 128.0, 128.9, 132.2, 134.1, 137.1, 140.5, 171.4, 173.9 ppm; HR-MS (ESI, pos. mode, DCM/MeOH): *m/z* calcd. for $[C_{81}H_{90}N_6O_6Na]^+$: 1265.6819 ($[M+Na]^+$); found: 1265.6810 (Δ = 0.7 ppm).

Divalent alkyl axle (5)

4'-Iodo-*N*-methyl-*N*-(2-(*N*-methylhexanamido)ethyl)-[1,1'-biphenyl]-3-carboxamide (360.0 mg 1.08 mmol) and 1,4-diethynylbenzene (30 mg, 0.24 mmol) were dissolved in 12 mL DMF and 4 mL NEt_3. Under argon atmosphere and exclusion of light, PPh_3 (64 mg, 0.24 mmol), $Pd_2^4{}_3$ (40 mg, 0.04 mmol) and CuI (21 mg, 0.11 mmol) were added and the reaction was stirred at 70 °C for 2 d. After removing the solvent, the residue was purified by column chromatography (SiO_2, DCM/MeOH 60:1 → 30:1) and yielded in a brown solid (120 mg, 0.14 mmol, 58%).

^{1}H NMR (700 MHz, $CDCl_3$) δ = 0.86 (m, 6H, CH_3), 1.27 (m, 8H, CH_2), 1.61 (m, 4H, CH_2), 2.27 (m, 4H, CH_2), 2.73-3.17 (m, 12H, NCH_3), 3.47-3.76 (m, 8H, NCH_2), 7.37-7.70 (m, 20H, ArH); ^{13}C NMR (176 MHz, $CDCl_3$) δ = 14.1, 24.8, 29.8, 31.8, 33.6, 35.7, 38.2, 44.5, 44.9, 89.5, 90.0, 122.4, 123.8, 125.7, 126.2, 127.2, 128.1, 128.7, 129.0, 131.5, 132.3, 134.8, 137.2, 140.4, 140.6, 171.5, 174.1 ppm; HR-MS (ESI, pos. mode, DCM/MeOH): *m/z* calcd. for $[C_{56}H_{63}N_4O_4]^+$: 855.4844 ($[M+H]^+$); found: 855.4805 (Δ = 4.5 ppm); *m/z* calcd. for $[C_{56}H_{62}N_4O_4Na]^+$: 877.4663 ($[M+Na]^+$); found: 877.4643 (Δ = 2.3 ppm); *m/z* calcd. for $[C_{56}H_{62}N_4O_4K]^+$: 893.4403 ($[M+K]^+$); found: 893.4362 (Δ = 4.6 ppm).

***tert*-Butyl methyl2-(methylamino)ethylcarbamate**

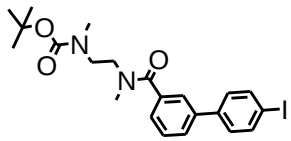


A solution of *N,N'*-dimethyl ethylendiamine (3.0 g, 34 mmol) in 40 mL anhydrous DCM was cooled to 0 °C and di-*tert*-butyl dicarbonate (2.4 g, 11 mmol) was slowly added. After warming up to rt the solvent was removed under reduced pressure and the residue was taken up in EtOAc. The organic layer was washed with brine (3x80 mL), dried over $NaSO_4$ and evaporated to dryness. The product was formed as colorless oil (926 mg, 4.9 mmol, 45%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.38 (s, 9H, $C(CH_3)_3$), 2.37 (s, 3H, NCH_3), 2.65 (t, ^3J = 6.5 Hz, 2H, NCH_2), 2.83 (s, 3H, NCH_3), 3.25 (br, 2H, NCH_2); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 28.5, 36.3, 49.7, 60.4, 79.4, 156.0 ppm.

The results are in good agreement with literature data.[5]

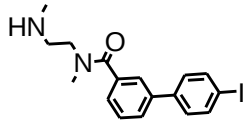
tert-Butyl (2-(4'-iodo-_N_-methyl-[1,1'-biphenyl]-3-ylcarboxamido)ethyl)(methyl) carbamate



tert-Butyl-methyl (2-(methylamino)ethyl)carbamate (361 mg, 1.9 mmol) and 4'-iodobiphenyl-3-carboxylic acid (300 mg, 0.9 mmol) were dissolved in 5 mL DMF under argon atmosphere and cooled to 0 °C. HOBt (11-18% H_2O; 88.9 mg, 0.9 mmol) and EDC (0.24 mL,1.3 mmol) were added. After stirring for 2 d the solvent was removed under reduced pressure and the residue was taken up in EtOAc. The organic layer was washed with sodium bicarbonate solution (3x20 mL) and brine (3x20 mL), dried over $MgSO_4$ and evaporated to dryness. The crude product was purified by column chromatography (SiO_2, EtOAc) and the product was obtained as colorless oil (351 mg, 0.7 mmol, 79%).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.38 (m, 9H, $C(CH_3)_3$), 2.45-3.09 (m, 6H, NCH_3), 3.23-3.69 (m, 4H, NCH_2), 7.26-7.70 (m, 8H, ArH); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 28.4, 33.4, 34.6, 44.9, 45.3, 79.4, 93.6, 125.4, 126.2, 127.1, 127.9, 128.8, 128.9, 137.0, 137.9, 139.7, 140.1, 156.1, 171.1 ppm; HR-MS (ESI, pos. mode, DCM/MeOH): _m/z_ calcd. for $[C_{22}H_{27}IN_2O_3Na]^+$: 517.0959 ($[M+Na]^+$); found: 517.0969 (Δ = 1.9 ppm); _m/z_ calcd. for $[C_{22}H_{27}IN_2O_3K]^+$: 533.0698 ($[M+K]^+$); found: 533.0690 (Δ = 1.5 ppm).

4'-Iodo-_N_-methyl-_N_-(2-(methylamino)ethyl)-[1,1'-biphenyl]-3-carboxamide

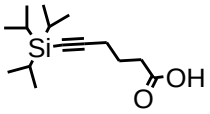


tert-Butyl (2-(4'-iodo-_N_-methyl-[1,1'-biphenyl]-3-ylcarbox-amido)ethyl)(methyl)carbamate (173 mg, 0.35 mmol) was dissolved in 10 mL DCM and a TFA/DCM solution (1.6 mL, 1:1) was added dropwise. After stirring for 40 min the solvent was removed under reduced pressure and the residue was washed with a small amount of 1M NaOH solution. After washing with EtOAc the organic layer was dried over $MgSO_4$ and evaporated. The desired product was obtained as colorless oil (105 mg, 0.27 mmol, 76%).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.28-2.51 (m, 3H, NCH_3), 2.33 (br, 1H, NH), 2.72-2.94 (m, 2H, NCH_2), 3.01-3.11 (m, 3H, NCH_3), 3.39-3.69 (m, 2H, NCH_2), 7.31 (m, 2H, ArH), 7.38 (m, 1H, ArH), 7.44 (m, 1H, ArH), 7.57 (m, 2H, ArH), 7.75 (m, 2H, ArH); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 33.2, 36.2, 36.3, 38.3, 47.2, 49.0, 49.6, 51.0, 93.6, 125.6, 126.1, 126.2, 127.9, 128.1, 129.0, 129.2, 138.0, 139.9, 140.4, 171.8 ppm; HR-MS (ESI, pos. mode, DCM/MeOH): _m/z_ calcd. for $[C_{17}H_{20}IN_2O]^+$: 395.0615 ($[M+H]^+$); found: 395.0625 (Δ = 2.5 ppm); _m/z_ calcd.

for $[C_{17}H_{19}IN_2ONa]^+$: 417.0434 ($[M+Na]^+$); found: 417.0434 (Δ = 0 ppm); *m/z* calcd. for $[C_{17}H_{19}IN_2OK]^+$: 433.0174 ($[M+K]^+$); found: 433.0171 (Δ = 0.7 ppm).

6-(Triisopropylsilyl)-hex-5-ynoic acid

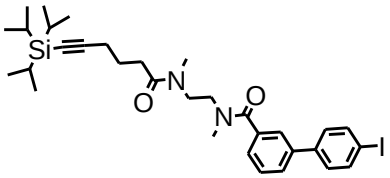


5-Hexynoic acid (1.1 mL, 10 mmol) was dissolved in anhydrous THF (100 mL) under argon atmosphere and cooled to -78 °C. *n*-Butyllithium (2.5 mol in hexane, 8.4 mL, 21 mmol) was added dropwise and the mixture was stirred for 30 min. Triisopropylsilyl chloride (4.9 mL, 22.8 mmol) was added. After stirring for 90 min the reaction was allowed to warm up to rt and was stirred for 4 more hours.

Acetic acid (10%, 40 mL) was added after 20 min and the reaction mixture was washed with brine (200 mL). The organic layer was dried over $NaSO_4$ and the solvent was removed under reduced pressure. The desired product was obtained as yellow oil (2.5 g, 9.3 mmol, 93%).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.05 (m, 18H, CH_3), 1.29 (m, 3H, CH), 1.85 (m, 2H, CH_2), 2.32 (m, 2H, CH_2), 2.53 (m, 2H, CH_2); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 12.4, 18.5, 19.4, 24.5, 34.5, 81.3, 108.0, 173.5 ppm; HR-MS (ESI, pos. mode, DCM/MeOH): *m/z* calcd. for $[C_{15}H_{29}SiO_2^+]$: 269.1931 ($[M+H]^+$); found: 269.1919 (Δ = 17.3 ppm); *m/z* calcd. for $[C_{15}H_{28}SiO_2Na^+]$: 291.1751 ($[M+Na]^+$); found: 291.1751 (Δ = 0 ppm); *m/z* calcd. for $[C_{15}H_{28}SiO_2K^+]$: 307.1490 ($[M+K]^+$); found: 307.1483 (Δ = 2.3 ppm).

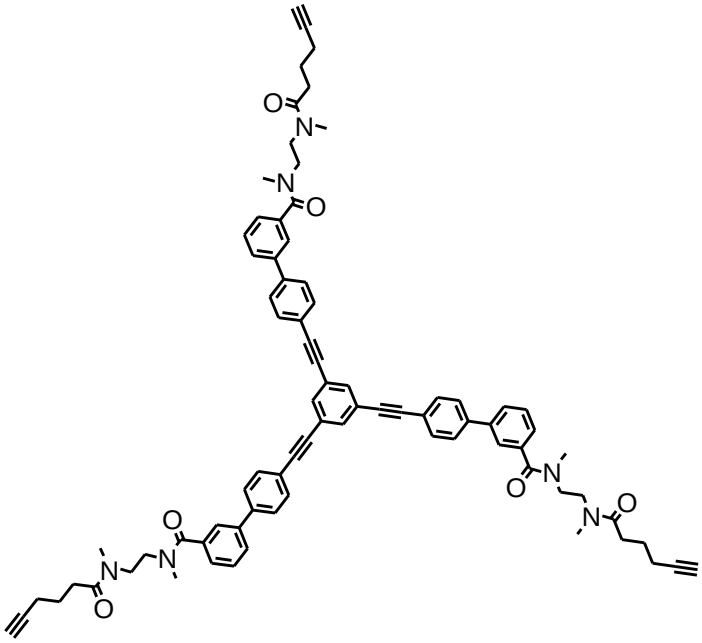
4'-Iodo-*N*-methyl-*N*-(2-(*N*-methyl-6-(trimethylsilyl)hex-5-ynamido)ethyl)-[1,1'-biphenyl]-3-carboxamide

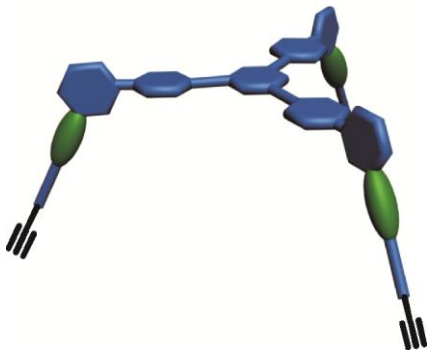


6-(Triisopropylsilyl)-hex-5-ynoic acid (723 mg, 3.9 mmol) and 4'-iodobiphenyl-3-carboxylic acid (646 mg, 2.0 mmol) were dissolved in DMF under argon atmosphere and cooled to 0 °C. HOBt (11-18% H_2O; 178 mg, 1.8 mmol) and EDC (0.5 mL, 2.7 mmol) were added. After stirring for 2 days the solvent was removed under reduced pressure and the residue was taken up in EtOAc. The organic layer was washed with sodium bicarbonate solution (3x20 mL) and brine (3x20 mL), dried over $MgSO_4$ and evaporated to dryness. The crude product was purified by column chromatography (SiO_2, EtOAc) and the product was obtained as colorless oil (891 mg, 1.4 mmol, 70%).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.03 (m, 21H, TIPS), 1.83 (tt, ^{3}J = 6.7 Hz, ^{3}J = 7.6 Hz, 2H, CH_2), 2.31 (t, ^{3}J = 6.7Hz, 2H, CH_2), 2.45 (t, ^{3}J = 7.6 Hz, 2H, CH_2), 2.75-3.16 (m, 6H, NCH_3), 3.45-3.75 (m, 4H, NCH_2), 7.31-7.77 (m, 8H, ArH); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 11.3, 18.7, 19.5, 24.1, 32.14 35.7, 38.2, 44.6, 44.9, 81.1, 100.0, 108.2, 125.5, 126.2, 128.0, 129.0, 137.1, 138.0, 139.9, 140.4, 171.4, 173.3 ppm; HR-MS (ESI, pos. mode, DCM/MeOH): *m/z* calcd. for [$C_{32}H_{46}IN_2O_2Si^+$]: 645.2368 ([M+H]$^+$); found: 645.2347 (Δ = 3.3 ppm); *m/z* calcd. for [$C_{32}H_{45}IN_2O_2SiNa^+$]: 667.2187 ([M+Na]$^+$); found: 667.2185 (Δ = 0.3 ppm); *m/z* calcd. for [$C_{32}H_{45}IN_2O_2SiK^+$]: 683.1927 ([M+K]$^+$); found: 683.1908 (Δ = 2.8 ppm).

Trivalent alkyne axle (9)



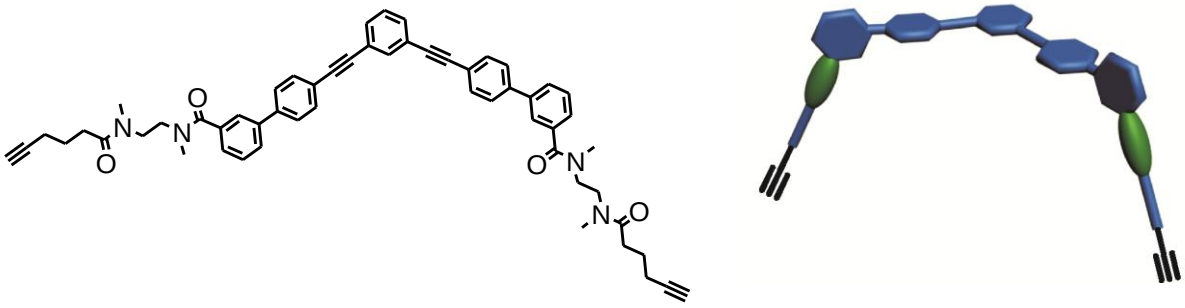


4'-Iodo-*N*-methyl-*N*-(2-(*N*-methyl-6-(triisopropylsilyl)hex-5-ynamido)ethyl)-[1,1'-biphenyl]-3-carboxamide (300 mg, 0.47 mmol) and 1,3,5-triethynylbenzene (21 mg, 0.14 mmol) were dissolved in anhydrous 7 mL DMF and 4.8 mL NEt_3 under argon atmosphere. Pd_2dba_3 (43.9 mg, 0.05 mmol), PPh_3 (37.7 mg, 0.14 mmol) and CuI (9.1 mg, 0.05 mmol) were added under exclusion of light. After stirring for 5 d at 70 °C the mixture was cooled down to rt and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, DCM/MeOH 35:1) and resulted in a red-colored oil, which was dissolved in 8 mL THF and treated dropwise with TBAF (0.66 mL of 1.0 M solution in THF). After stirring for 5 h at rt the reaction mixture was diluted with 20 mL Et_2O and quenched with 20 mL aqueous sodium bicarbonate. The aqueous layer was separated and extracted with Et_2O (3x20 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by column

chromatography (SiO_2, DCM/MeOH 40:1) and the desired product was obtained as brown oil (52 mg, 0.042 mmol, 30%).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.83 (m, 6H, CH_2), 1.93 (t, ^4J = 2.6 Hz, 3H, CH), 2.25 (td, ^3J = 7.2 Hz, ^4J = 2.6 Hz, 6H, CH_2), 2.44 (t, ^3J = 7.2 Hz, 6H, CH_2), 3.10 (m, 18H, NCH_3), 3.74 (m, 12H, NCH_2), 7.36 (m, 3H, ArH), 7.52-7.44 (m, 3H, ArH), 7.67-7.57 (m, 18H, ArH), 7.70 (s, 3H, ArH); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 23.8, 29.8, 32.0, 34.0, 35.7, 38.2, 44.5, 44.9, 69.1, 83.9, 88.8, 90.5, 122.2, 124.2, 125.7, 126.2, 127.2, 128.2, 129.1, 132.0, 132.4, 134.2, 137.1, 140.6, 171.5, 173.1 ppm; HR-MS (ESI, pos. mode, DCM/MeOH): *m/z* calcd. for [$C_{81}H_{78}N_6O_6Na^+$]: 1253.5875 ([M+Na]$^+$); found: 1253.5876 (Δ = 0.1 ppm).

Divalent alkyne axle (8)

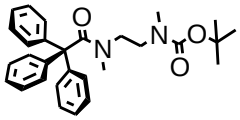


4'-Iodo-*N*-methyl-*N*-(2-(*N*-methyl-6-(triisopropylsilyl)hex-5-ynamido)ethyl)-[1,1'-biphenyl]-3-carboxamide (152 mg, 240 µmol) and 1,3-diethynylbenzene (13.5 mg, 110 µmol) were dissolved in anhydrous 3 mL DMF and 2 mL NEt_3 under argon atmosphere. Pd_2dba_3 (10.1 mg, 11 µmol), PPh_3 (11.6 mg, 44 µmol) and CuI (4.2 mg, 22 mmol) were added under exclusion of light. After stirring for 6 d at 70 °C the mixture was cooled down to rt and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, DCM/MeOH 35:1) and resulted in red-colored oil (103.1 mg, 89 µmol), which was dissolved in 5mL THF and treated dropwise with TBAF (0.54 mL of 1.0 M solution in THF). After stirring for 3 h at rt the reaction mixture was diluted with 2 mL Et_2O and quenched with 2 mL aqueous sodium bicarbonate. The aqueous layer was separated and extracted with Et_2O (3x2 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, DCM/MeOH 40:1) and the desired product was obtained as a brown oil (70 mg, 0.081 mmol, 73%).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.84 (tt, ^3J = 7.0 Hz, 4H, CH_2) 1.94 (t, ^4J = 2.5 Hz, 2H, CH_2), 2.25 (dt, ^4J = 2.5 Hz, ^3J = 7.0 4H, CH_2), 2.45 (t, ^3J = 7.0 Hz, 4H, CH_2), 3.08 (m, 12H, NCH_3), 3.75 (m, 8H, NCH_2), 7.35-7.75 (m, 12H, ArH); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 18.1, 23.8, 32.0, 35.7, 38.2, 44.5, 44.9, 69.2, 83.9, 89.6, 90.0, 122.5, 123.8, 125.7, 126.2, 127.2, 128.2,

128.7, 129.1, 131.5, 132.3, 134.8, 137.1, 140.4, 140.7 171.6, 173.2 ppm; HR-MS (ESI, pos. mode, DCM/MeOH): *m/z* calcd. for $[C_{56}H_{54}N_4O_4Na^+]$: 869.4037 ($[M+Na]^+$); found: 869.4055 (Δ = 2.1 ppm).

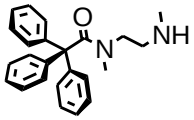
tert-Butyl 2-(_N_-methyl-2,2,2-triphenylacetamido)etylmethylcarbamate



tert-Butylmethyl-2-(methylamino)ethylcarbamate (188 mg, 1.0 mmol) and 2,2,2-triphenylacetyl chloride (322 mg, 1.1 mmol) were dissolved in 30 mL DCM and treated with 0.9 mL NEt_3. After stirring over night, the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, DCM) and the desired product was obtained as slightly yellow oil (403 mg, 0.88 mmol, 88%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.45 (m, 9H, $C(CH_3)_3$), 2.16-2.38 (m, 3H, NCH_3), 2.89 (s, 3H, NCH_3), 3.08-3.56 (m, 4H, NCH_2), 7.18-7.28 (m, 15H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 28.6, 35.1, 36.4, 38.8, 48.6, 50.0, 53.6, 67.5, 79.6, 126.7, 127.9, 130.4, 143.1, 173.0, 173.1 ppm; HR-MS (ESI, pos. mode, DCM/MeOH): *m/z* calcd. for $[C_{29}H_{34}N_2O_3Na^+]$: 481.2462 ($[M+Na]^+$); found: 481.2485 (Δ = 4.7 ppm); *m/z* calcd. for $[C_{29}H_{34}N_2O_3K^+]$: 497.2201 ($[M+K]^+$); found: 497.2229 (Δ = 5.6 ppm).

_N_-Methyl-_N_-(2(methylamino)ethyl)-2,2,2-triphenylacetamide

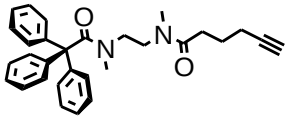


tert-Butyl-2-(*N*-methyl-2,2,2-triphenylacetamido)etylmethylcarbamate (459 mg, 0.84 mmol) was dissolved in 5 mL DCM at rt and treated with TFA (1.8 mL, 8.4 mmol). After stirring for 1 h the solvent was removed under reduced pressure and 10 mL sodium bicarbonate solution were added. The aqueous phase was extracted with DCM (3x10 mL) and the combined organic layers were dried over $NaSO_4$. After removing the solvent, the desired product was obtained as yellow oil (266 mg, 0.74 mmol, 88%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.37 (s, 3H, NCH_3), 2.45 (s, 3H, NCH_3), 2.82 (m, 2H, NCH_2), 3.57 (m, NCH_2), 7.20-7.31 (m, 15H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 36.4, 38.8, 48.7, 50.0 67.5, 126.7, 127.9, 130.4, 143.1, 173.1 ppm; HR-MS (ESI, pos. mode, DCM/MeOH): *m/z* calcd. for $[C_{24}H_{27}N_2O^+]$: 359.2118 ($[M+H]^+$); found: 359.2123 (Δ = 1.3 ppm); *m/z* calcd.

for $[C_{24}H_{26}N_2ONa^+]$: 381.1937 ($[M+Na]^+$); found: 381.1931 (Δ = 1.6 ppm); *m/z* calcd. for $[C_{24}H_{26}N_2OK^+]$: 397.1677 ($[M+K]^+$); found: 397.1671 (Δ = 1.5 ppm).

_N_-(2-(_N_-Methyl-2,2,2-triphenylacetamido)ethyl)-_N_-methylhex-5-ynamide (10)



N-Methyl-*N*-(2(methylamino)ethyl)-2,2,2-triphenylacetamide (245 mg, 0.68 mmol) and hex-5-ynoic acid (100 mg, 0.89 mmol) were dissolved in 5 mL DMF under argon atmosphere and cooled to 0 °C. HOBt (11-18% H_2O; 56 mg, 0.3 mmol) and EDC (0.16 mL, 0.9 mmol) were added. After stirring for 4 d the solvent was removed under reduced pressure and the residue was taken up in 30 mL DCM. The organic layer was washed with 30 mL sodium bicarbonate solution and 30 mL brine and the resulting aqueous phase was extracted with 50 mL Et_2O. The combined organic layers were dried over $MgSO_4$ and evaporated to dryness. The crude product was purified by column chromatography (SiO_2, DCM/MeOH 50:1) and the product was obtained as colorless oil (215 mg, 0.48 mmol, 70%).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.85 (m, 2H, CH_2), 1.96 (t, ^4J = 2.6 Hz, 1H, CH), 2.28 (m, 2H, CH_2), 2.40 (s, 3H, NCH_3), 2.42 (m, 2H, CH_2), 2.95-3.15 (m, 3H, NCH_3), 3.45-3.59 (m, 4H, NCH_2), 7.19-7.28 (m, 15H, ArH); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 18.0, 23.7, 31.9, 35.9, 38.5, 44.1, 47.4, 67.5, 69.1, 83.9, 126.8, 127.9, 130.3, 143.0, 172.6, 173.2 ppm; HR-MS (ESI, pos. mode, DCM/MeOH): *m/z* calcd. for $[C_{30}H_{32}N_2O_2Na^+]$: 475.2356 ($[M+Na]^+$); found: 475.2363 (Δ = 1.5 ppm).

Trivalent host molecule (3)

TLM **1a** (100 mg, 100 µmol) and 1,3,5-triethynylbenzene (3 mg, 33 µmol) were dissolved in 4 mL anhydrous DMF and 1 mL NEt_3 under argon atmosphere. PPh_3 (3.5 mg, 13 µmol) and $PdCl_2(PPh_3)_2$ (3 mg, 4 µmol) and CuI (1.3 mg, 7 µmol) were added under exclusion of light. After stirring for 6 d at rt the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, DCM/EE 6:1) and resulted in a white solid (50 mg, 18 µmol, 55%).

^{1}H NMR (700 MHz, $CDCl_3$) δ = 1.51 (br, 12H, CH_2), 1.64 (br, 24H, CH_2), 2.18 (s, 36H, CH_3), 2.20 (s, 36H, CH_3), 2.26 (br, 12H, CH_2), 2.32 (br, 12H, CH_2), 6.98 (s, 24H, ArH), 7.13 (br, 6H, NH), 7.72 (s, 3H, ArH), 8.04 (s, 3H, isophth. H), 8.15 (t, ^3J = 7.5 Hz, 3H, isophth. H), 8.32 (s, 6H, isophth. H), 8.50 (d, ^3J = 7.5 Hz, 6H, isophth. H), 8.86 (br, 6H, NH); ^{13}C NMR (176 MHz, $CDCl_3$) δ = 19.1, 19.3, 23.0, 29.8, 36.ß, 45.2, 89.1, 90.1, 123.8, 125.7, 126.7, 130.5, 131.1,

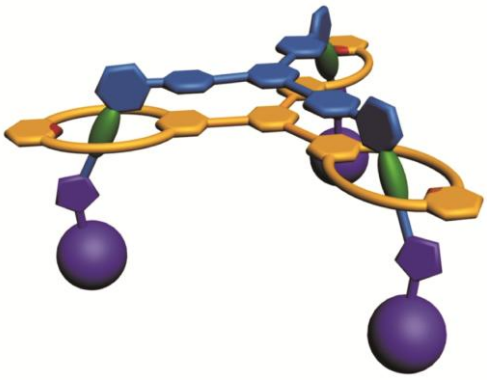
134.5, 134.8, 135.8, 148.7, 161.3 ppm; HR-MS (ESI, pos. mode, $CHCl_3$/MeOH): *m/z* calcd. for $[C_{189}H_{190}N_{15}O_{12}Na]^{2+}$: 1442.2303 ($[M+H+Na]^{2+}$); found: 1442.2285 (Δ = 1.2 ppm); *m/z* calcd. for $[C_{189}H_{190}N_{15}O_{12}K]^{2+}$: 1450.2172 ($[M+H+K]^{2+}$); found: 1450.2120 (Δ = 3.6 ppm); *m/z* calcd. for $[C_{189}H_{189}N_{15}O_{12}Na_2]^{2+}$: 1453.2212 ($[M+2Na]^{2+}$); found: 1453.2205 (Δ = 0.5 ppm); *m/z* calcd. for $[C_{189}H_{189}N_{15}O_{12}NaK]^{2+}$: 1461.2082 ($[M+Na+K]^{2+}$); found: 1461.2087 (Δ = 0.3 ppm).

Divalent host molecule (2)

TLM **1a** (200 mg, 200 µmol) and 1,3-diethynylbenzene (11.1 mg, 88 µmol) were dissolved in 5 mL anhydrous DMF and 1.5 mL NEt_3 under argon atmosphere. PPh_3 (7.3 mg, 28 µmol) and $PdCl_2(PPh_3)_2$ (7.0 mg , 8 µmol) and CuI (4.3 mg, 23 µmol) were added under exclusion of light. After stirring for 4 d at rt the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, DCM/EE 12:1 → 6:1) and resulted in a white solid (175 mg, 90 µmol, 49%).

^{1}H NMR (700 MHz, $CDCl_3$) δ = 1.51 (br, 8H, CH_2), 1.64 (br, 16H, CH_2), 2.20 (s, 48H, CH_3), 2.25 (br, 8H, CH_2), 2.32 (br, 8H, CH_2), 6.97 (s, 8H, ArH), 6.99 (s, 8H, ArH), 7.14 (br, 4H, NH), 7.38 (m, 1H, ArH), 7.55 (m, 2H, ArH), 7.73 (m, 1H, ArH), 8.04 (s, 2H, isophth.H), 8.15 (t, ^3J = 7.7 Hz, 2H, isophth. H), 8.33 (s, 4H, isophth. H), 8.51 (d, ^3J = 7.7 Hz, 4H, isophth. H), 8.87 (br, 4H, NH); ^{13}C NMR (176 MHz, $CDCl_3$) δ = 14.3, 23.0, 26.5, 36.0, 45.3, 88.3, 91.3, 123.1, 125.7, 126.7, 170.1, 128.9, 130.4, 130.9, 132.3, 134.4, 134.7, 135.7, 135.8, 139.8, 148.9, 161.3, 171.3 ppm; HR-MS (ESI, pos. mode, $CHCl_3$/MeOH): *m/z* calcd. for $[C_{128}H_{128}N_{10}O_8H]^+$: 1933.9989 ($[M+H]^+$); found: 1934.0173 (Δ = 9.5 ppm); *m/z* calcd. for $[C_{128}H_{128}N_{10}O_8Na]^+$: 1955.9809 ($[M+Na]^+$); found: 1955.9921 (Δ = 5.7 ppm).

Trivalent rotaxane (13)

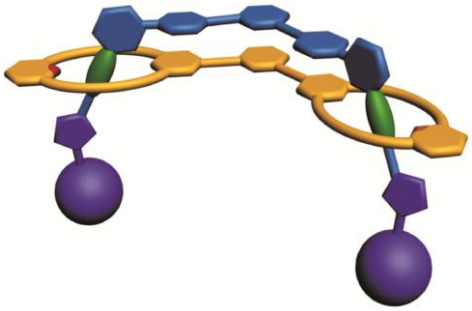


Trivalent host molecule **3** (32.5 mg, 11.4 µmol), trivalent alkyne axle **9** (14 mg, 11.4 µmol), azide stopper **11** (45.3 mg, 125.3 µmol), bromotris(triphenylphosphine)copper (4.3 mg, 4.6 µmol) and 10 µL NEt_3 were dissolved in 3 mL DCM. After stirring for 14 d at 45 °C in a sealed

tube the solvent was removed under reduced pressure. The residue was purified by chromatography (SiO_2, DCM/MeOH 80:1 → 40:1) and the product was obtained as yellow oil (43.7 mg, 8.4 µmol, 74%).

^{1}H NMR (700 MHz, $CDCl_3$) δ = 0.88 (m, 6H, CH_2), 1.42 (m, 6H, CH_2), 1.51 (br, 12H, CH_2), 1.63 (br, 24H, CH_2), 1.83 (m, 6H, CH_2), 1.88 (m, 18H, NCH_3), 2.20 (br, 72H, CH_3), 2.24 (br, 12H, NCH_2), 2.26 (br, 12H, CH_2), 2.33 (br, 12H, CH_2), 6.90 (m, 12H, ArH), 6.97 (s, 12H, ArH), 6.99 (s, 12H, ArH), 7.22 (m, 45H, ArH), 7.41 (s, 3H, ArH), 7.42-7.69 (m, 27H, ArH), 7.73 (s, 3H, triazole H), 8.06 (s, 3H, ArH), 8.16 (t, ^{3}J = 7.7 Hz, 3H, isophth. H), 8.35 (s, 6H, isophth. H), 8.51 (d, ^{3}J = 7.7 Hz, 6H, isophth. H), 8.83 (s, 3H, isophth. H), 8.87 (br, 6H, NH), 10.35 (br, 6H, NH) ppm; HR-MS (ESI, pos. mode, $CHCl_3$/MeOH): *m/z* calcd. for $[C_{345}H_{324}N_{30}O_{18}Na_3]^{3+}$: 1747.8346 ($[M+3Na]^{3+}$); found: 1747.8302 (Δ = 2.5 ppm); *m/z* calcd. for $[C_{345}H_{324}N_{30}O_{18}Na_2K]^{3+}$: 1753.4936 ($[M+2Na+K]^{3+}$); found: 1753.4917 (Δ = 1.1 ppm); *m/z* calcd. for $[C_{345}H_{324}N_{30}O_{18}NaK_2]^{3+}$: 1758.8182 ($[M+Na+2K]^{3+}$); found: 1758.8110 (Δ = 4.1 ppm).

Divalent rotaxane (12)

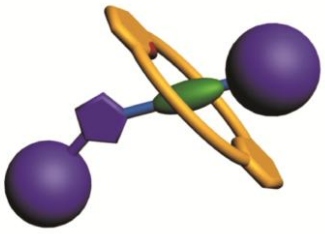


Divalent wheel **2** (13.7 mg, 7.1 µmol), divalent alkyne axle **8** (6 mg, 7.1 µmol), azide stopper **11** (18.9 mg, 52.3 µmol), bromotris(triphenylphosphine)copper (2.6 mg, 2.8 µmol) and 6 µL NEt_3 were dissolved in 2 mL DCM. After stirring for 14 d at 45 °C in a sealed tube the solvent was removed under reduced pressure. The residue was purified through dialysis (Spectrumlabs dialysis tubes with an MWCO of 2000 Dalton and a diameter of 45 mm, MeOH/DCM 1:3) over night and the product was obtained as yellow oil (23.5 mg, 6.7 µmol, 94%).

^{1}H NMR (700 MHz, $CDCl_3$) δ = 0.88 (m, 4H, CH_2), 1.43 (m, 4H, CH_2), 1.51 (br, 8H, CH_2), 1.61 (br, 16H, CH_2), 1.89 (m, 4H, CH_2), 1.93 (m, 12H, NCH_3), 2.03 (br, 8H, NCH_2), 2.17 (br, 24H, CH_3), 2.20 (br, 24H, CH_3), 2.22 (br, 8H, CH_2), 2.34 (br, 8H, CH_2), 6.92 (m, 8H, ArH), 6.98 (s, 8H, ArH), 7.00 (s, 8H, ArH), 7.22 (m, 30H, ArH), 7.40-7.68 (m, 24H, ArH), 7.71 (s, 2H, triazole H), 8.15 (m, 2H, isophth. H), 8.34 (s, 4H, isophth. H), 8.43 (m, 4H, isophth. H), 8.70 (s, 2H, isophth. H), 8.74 (br, 4H, NH), 10.38 (br, 4H, NH) ppm; HR-MS (ESI, pos. mode, $CHCl_3$/MeOH): *m/z* calcd. for $[C_{234}H_{222}N_{20}O_{12}]^{2+}$: 1752.8715 ($[M+2H]^{2+}$); found: 1752.8658 (Δ

= 3.3 ppm); *m/z* calcd. for $[C_{234}H_{221}N_{20}O_{12}Na]^{2+}$: 1763.8624 ($[M+H+Na]^{2+}$); found: 1763.8552 (Δ = 4.1 ppm); *m/z* calcd. for $[C_{234}H_{221}N_{20}O_{12}K]^{2+}$: 1771.8493 ($[M+H+K]^{2+}$); found: 1771.8453 (Δ = 2.3 ppm).

Monovalent rotaxane (14)



TLM **1a** (29 mg, 28.1 µmol), monovalent alkyne axle **10** (12.7 mg, 28.1 µmol), azide stopper **11** (40.6 mg, 112 µmol), bromotris(triphenylphosphine)copper (5.2 mg, 5.6 µmol) and NEt_3 (20 µL) were dissolved in 5 mL DCM. After stirring for 14 d at 45 °C in a sealed tube the solvent was removed under reduced pressure. The residue was purified by chromatography (SiO_2, DCM/MeOH 100:1 → 50:1) and the product was obtained as yellow oil (17.6 mg, 9.5 µmol, 34%).

^{1}H NMR (700 MHz, $CDCl_3$) δ = 0.89 (m, 2H, CH_2), 1.25 (m, 2H, CH_2), 1.51 (br, 4H, CH_2), 1.63 (br, 8H, CH_2), 1.93 (m, 2H, CH_2), 1.97 (m, 6H, NCH_3), 2.07 (m, 4H, NCH_2), 2.16 (s, 12H, CH_3), 2.19 (s, 12H, CH_3), 2.27 (br, 8H, CH_2), 6.74 (m, 2H, ArH), 6.86 (m, 2H, ArH), 6.96 (s, 4H, ArH), 6.98 (s, 4H, ArH), 7.21 (m, 30H, ArH), 7.47 (s, 2H, triazole H), 8.15 (t, ^{3}J = 8.0 Hz, 1H, isophth. H), 8.27 (s, 1H, isophth. H), 8.47 (d, ^{3}J = 8.0 Hz, 2H, isophth. H), 8.51 (s, 2H, isophth. H), 8.93 (br, 2H, NH), 10.06 (br, 2H, NH) ppm; HR-MS (ESI, pos. mode, CH_2Cl_2/MeOH): *m/z* calcd. for $[C_{114}H_{114}IN_{10}O_6^+]$: 1845.7962 ($[M+H]^+$); found: 1845.7913 (Δ = 2.7 ppm); *m/z* calcd. for $[C_{114}H_{113}IN_{10}O_6Na^+]$: 1867.7781 ($[M+Na]^+$); found: 1867.7694 (Δ = 4.7 ppm); *m/z* calcd. for $[C_{114}H_{113}IN_{10}O_6K^+]$: 1883.7521 ($[M+Na]^+$); found: 1883.7455 (Δ = 3.5 ppm).

2. Crystallographic Data

Colorless single crystals of **7•1a** were obtained by vapor diffusion of di-isopropyl ether into a dichloromethane solution of **7•1a.** Data were collected at 123 K on an Agilent SuperNova Dual diffractometer with Atlas detector using mirror-monochromatized Cu-*K*α (λ = 1.54180 Å) radiation. CrysAlisPro program (Agilent Technologies, version 1.171.36.21, **2012**) was used for the data collection and processing. The intensities were corrected for absorption using the multi-scan absorption correction method. The structure was solved by direct methods with SHELXS-97[6] and refined by full-matrix least-squares methods using the SHELXL-97[6] program within the Olex2[7] set of programs. All C-H hydrogen positions were calculated using a riding atom model with SHELX-97[6] default parameters. The non-H atoms were refined anisotropically, with the exception of heavily disordered atoms of axle **7** which was refined isotropically. Crystal data for **7•1a** (CCDC-938974): colorless blocks, 0.30 × 0.25 × 0.20 mm , *FW* = 1322.43, $C_{76}H_{88}I_1N_7O_8$, monoclinic, space group $P2_1$, *a* = 17.0807(5) Å, *b* = 9.5870(3) Å, *c* = 20.1987(6) Å, *β* = 93.695(3)°, *V* = 3300.71(17) Å^3, *Z* = 2, D_c = 1.331 g/cm^3, F000 = 1388, μ= 4.279 mm^{-1}, *x* = 0.300(13), T = 123.0(1) K, $2\theta_{max}$ = 67.50^o, 11572 reflections, 10790 with $I_o > 2\sigma(I_o)$, R_{Int} = 0.0496, 776 parameters, 127 restraints, GoF = 1.117, R = 0.1014 [$I_o > 2\sigma(I_o)$], wR= 0.2347 (all reflections), -0.1051 < Δρ < 0.745 e/Å^3.

3. NMR experiments

To study the binding behavior of the mono- and multivalent complexes NMR experiments have been performed. Since there is a fast exchange on the NMR timescale in case of the monovalent pseudorotaxane we could evaluate the binding constant by NMR titration analysis.[8,9] Solution of TLM **1a** (c = 5 mM, 0.6 mL) were placed in an NMR tube and treated with various amounts of axle **7** (c = 50 mM). After each injection, a ^{1}H NMR spectrum was recorded. The true guest concentrations in the solution under study were determined by integration of the signals for the wheel versus the integration of the signals for guest protons. The binding constants were determined based on 1:1 binding model by fitting the experimental data with equation 1.

$$\delta_{obs} = \delta_0 + \frac{\Delta\delta_{max}}{2[M]_0}\left[\frac{1}{K_a} + [M]_0 + [G]_0 - \sqrt{\left(\frac{1}{K_a} + [M]_0 + [G]_0\right)^2 - 4[M]_0[G]_0}\right] \qquad \text{(eq. 1)}$$

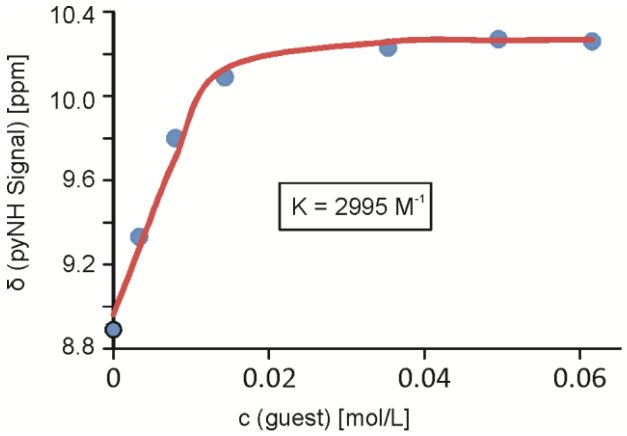


Figure S1 Evaluation of the NMR titration of the monovalent pseudorotaxane **7•1b**.

The divalent as well as the trivalent pseudorotaxanes show as slow exchange on the NMR timescale and two sets of signals could be observed. In case of the divalent complexes, a strong peak broadening occurs which makes a quantitative analysis of the binding situation difficult.

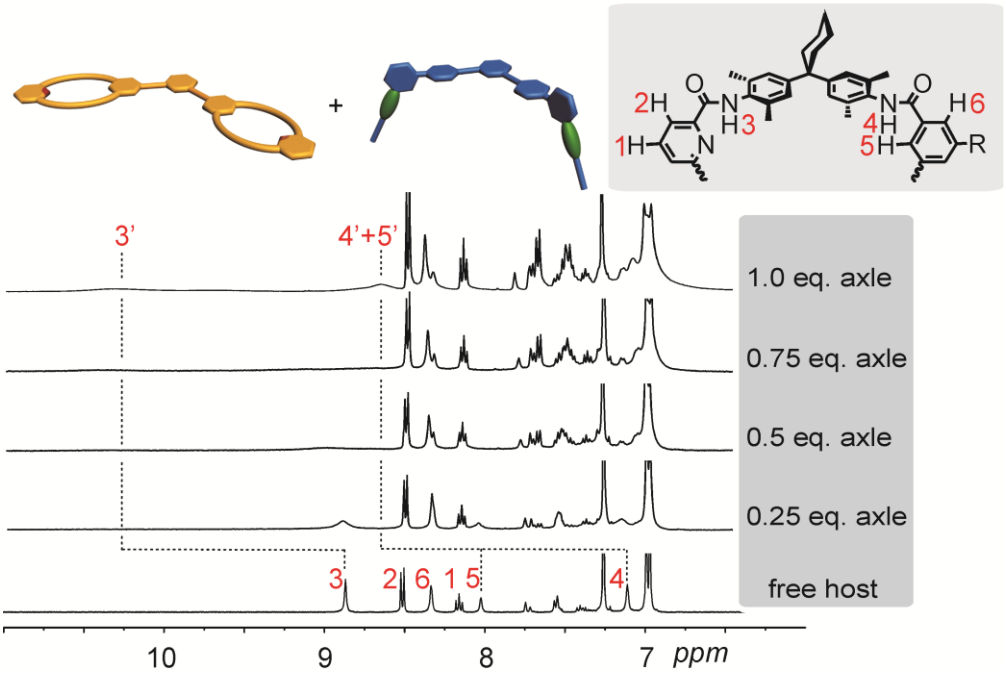


Figure S2 NMR titration of divalent pseudorotaxane **5•2** in $CDCl_3$ measured with the 400 MHz instrument at rt.

4. ITC Measurements

ITC experiments were performed at 298 K in dry $CHCl_3$ on a TAM III (Waters GmbH, TA Instruments, Eschborn, Germany). In a typical titration experiment, a solution of **1b**, **2** or **3** (800 µL, 1-2 mM) was placed in the sample cell. A solution of **5**, **6** or **7** (250 µL, 10-20 mM) was placed in an injection syringe and was added stepwise. The titration schedule consisted of 25 consecutive injections with a 15 min interval in between. Heats of dilution were measured by blank titrations. The obtained data were analyzed with the instruments internal software package and was fitted with a 1:1, 2:1 and 3:1 binding model.

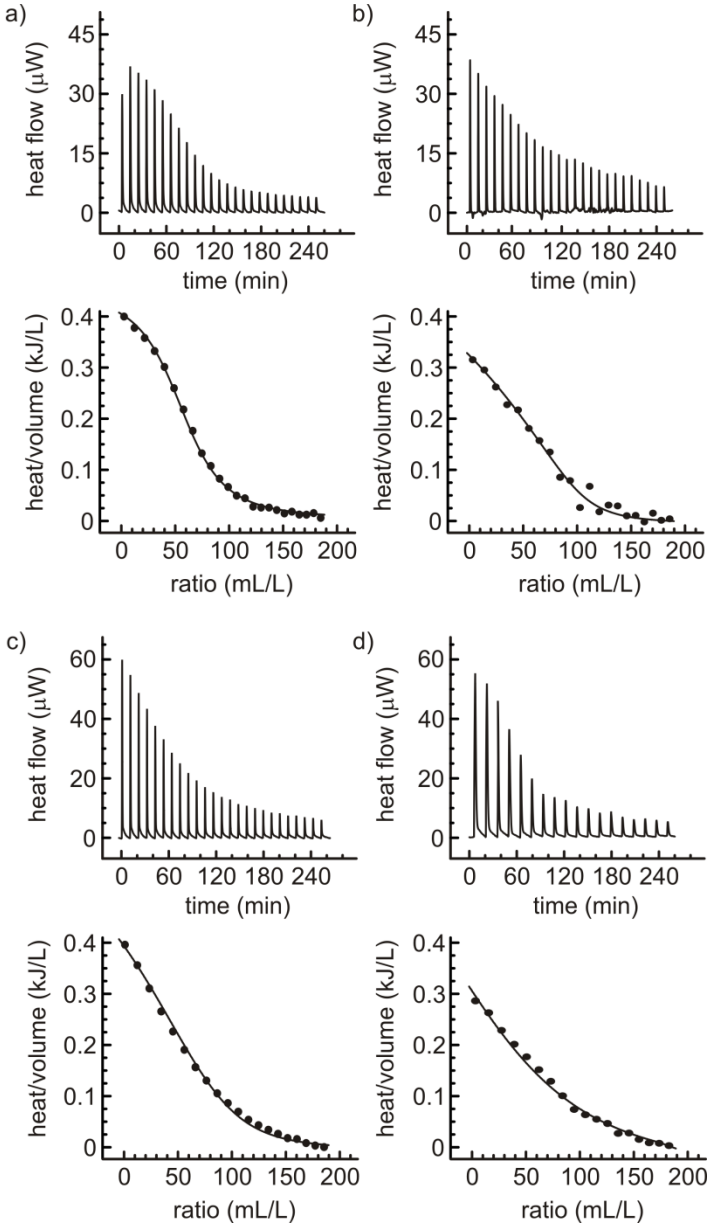


Figure S3 ITC plots of the titration of a) divalent macrocycle **2** (cell) and divalent axle **5** (syringe), b) monovalent macrocycle **1b** (cell) and divalent axle **5** (syringe), c) divalent macrocycle **2** (cell) and monovalent axle **7** (syringe) and d) monovalent macrocycle **1b** (cell) and monovalent axle **7** (syringe) in $CHCl_3$.

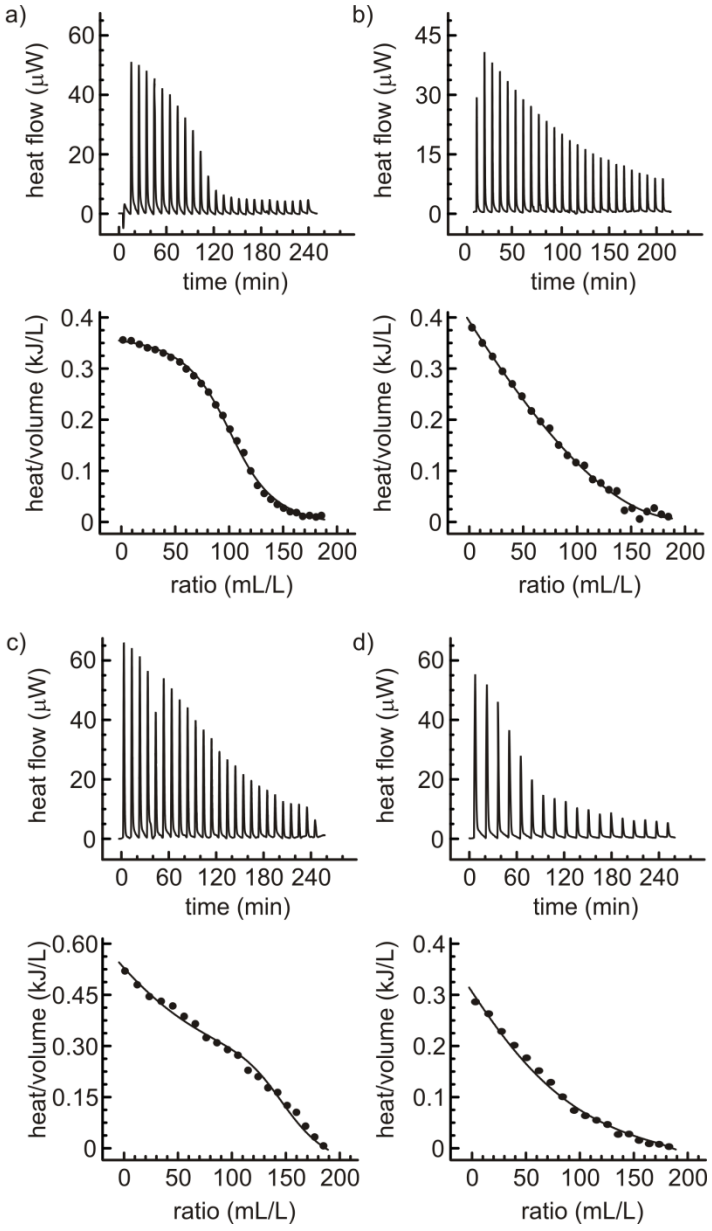


Figure S4 ITC plots of the titration of a) trivalent macrocycle **3** (cell) and trivalent axle **6** (syringe), b) monovalent macrocycle **1b** (cell) and trivalent axle **6** (syringe), c) trivalent macrocycle **3** (cell) and monovalent axle **7** (syringe) and d) monovalent macrocycle **1b** (cell) and monovalent axle **7** (syringe) in $CHCl_3$.

5. UV/Vis and Fluorescence Measurements

The UV/Vis measurements were performed on a *Varian* Cary 50 Bio Photospectrometer (Xenon lamp) at room temperature. Solutions of the compounds **3**, **6**, and **6•3** in dichloromethane ($2 \cdot 10^{-5}$ M) were measured in sealed *Suprasil* quartz cuvettes with a path length of 1 cm.

All multivalent axles and macrocycles show a relatively strong fluorescence during irradiation of light with a wavelength of λ = 365 nm. The fluorescence spectra were obtained on a *PerkinElmer* LS 50 B-luminescence spectrometer (Xenon lamp) at room temperature. All measurements were performed with an excitation wavelength of λ_{ex} = 290 nm. Solutions of **3**, **6** and **6•3** in dichloromethane ($2 \cdot 10^{-5}$ M) were measured in sealed *Suprasil* fluorescence cuvettes with a path length of 1 cm. For the titration, a solution of trivalent macrocycle **3** in DCM ($2 \cdot 10^{-5}$ M) was titrated stepwise by a solution of trivalent axle **6** in DCM ($2 \cdot 10^{-5}$ M). The intensities at a wavelength of λ = 500 nm were plotted against the equivalents of guest solution. The spectra and curves were illustrated with *IgorPro* (Wavemetrics Inc., Lake Oswego, Oregon/USA).

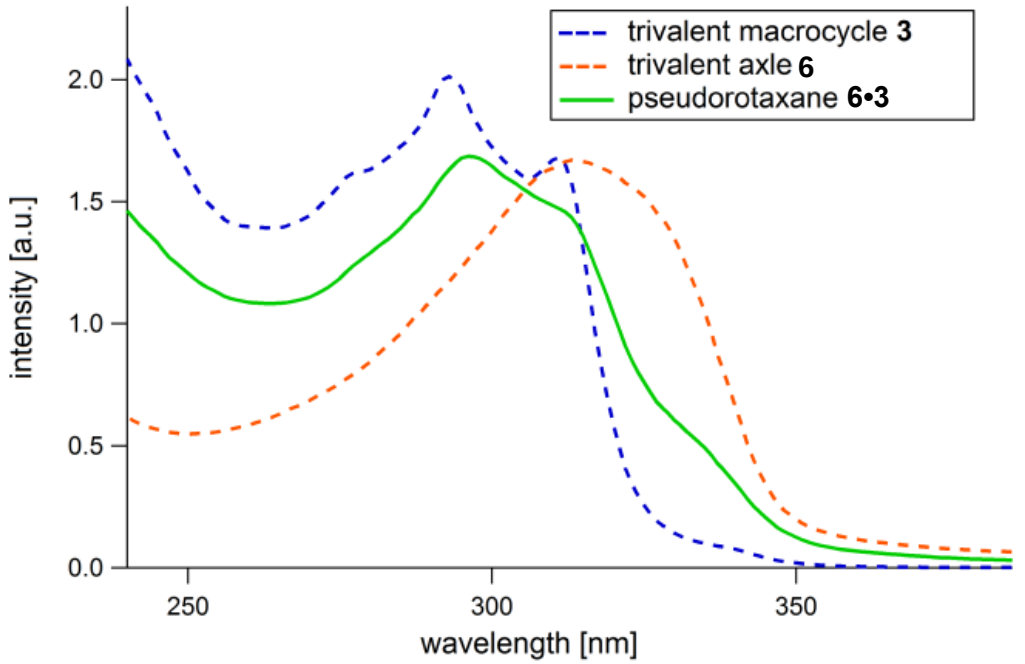


Figure S5 UV/Vis spectra of a) trivalent macrocycle **3** (blue), trivalent axle **6** (orange) and the resulting complex **6•3** (green).

Table 1. Spectroscopic data of UV/Vis and fluorescence measurements

	Absorption		Fluorescence
	λ_{max} [nm]	ε [$M^{-1} \cdot cm^{-1}$]	λ_{max} [nm]
Trivalent axle 6	314	83400	361
Trivalent macrocycle 3	293	100650	356
Pseudorotaxane 6•3	296	84310	393

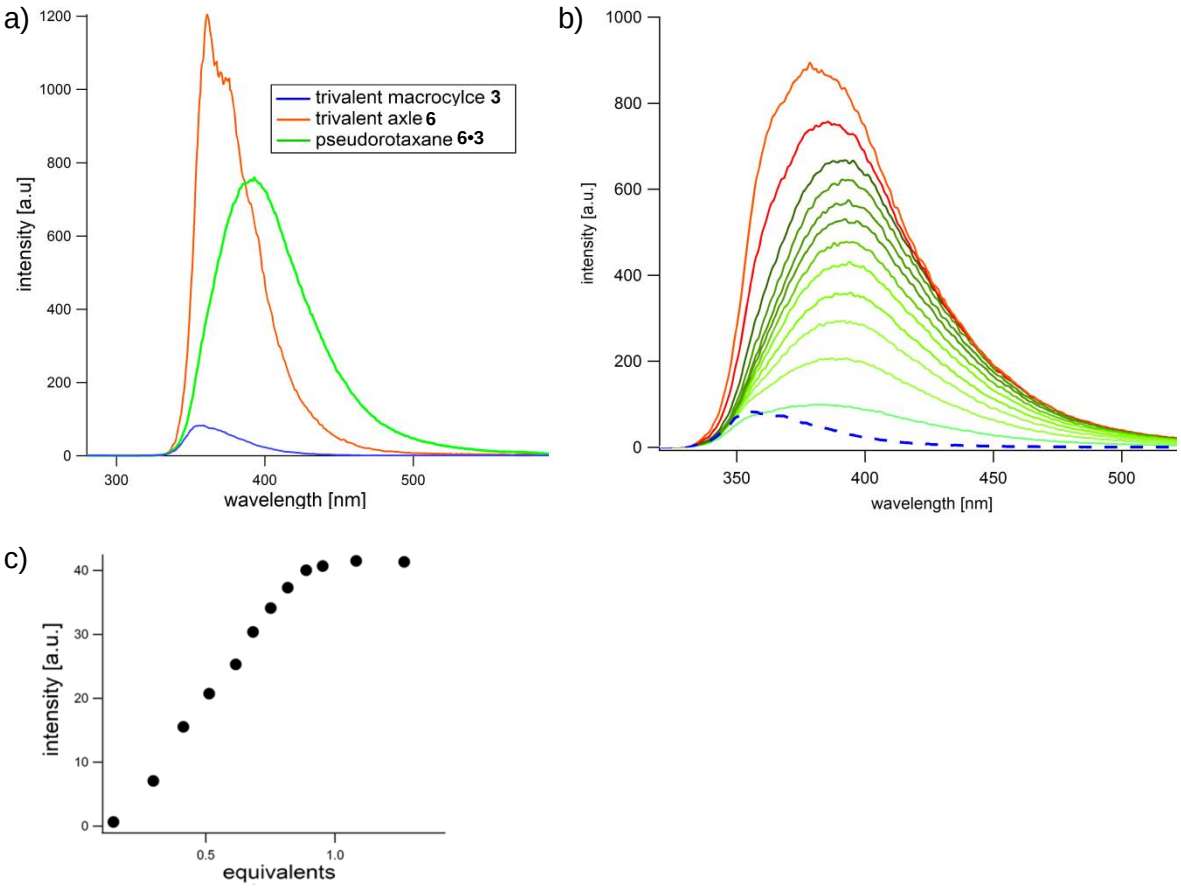


Figure S6 a) Fluorescence spectrum of trivalent macrocycle **3** (blue), trivalent axle **6** (orange) and the resulting pseudorotaxane **6•3** (green), b) stacked fluorescence spectra of trivalent macrocycle **3** after addition of 0.14, 0.30, 0.41, 0.51, 0.61, 0.75, 0.81, 0.95, 1.08, and 1.26 equivalents of trivalent axle **6**, c) titration curve of the intensities at a wavelength of λ = 500 nm against the equivalents of the guest which confirms the 1:1 binding model since no change can be observed by adding more than one equivalent.

6. Statistical factors

Determination of statistical factors

Monovalent axle with monovalent host (case D):

The binding situation of diamide axles in tetralactam macrocycles (TLM) is well studied and confirmed by crystal structures.[3,11-14] In case of the complex formation between monovalent axle and monovalent TLM, two different microspecies are distinguishable due to the fact that both, the axle and the TLM, are non-symmetric as it is shown in Figure S7.

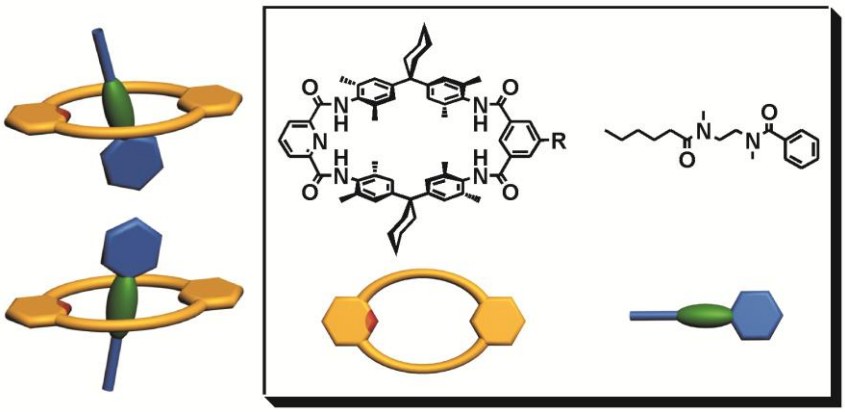


Figure S7 Schematic representation of the two different microspecies of the monovalent pseudorotaxane.

Following the Direct Count Method, the statistical factor for such an equilibrium is simply given by the ratio of the number of chemically plausible different microspecies of the products to the starting materials.

$$K^D = (2\,K_{mono})^3 = 8\,K_{mono}^3 \qquad \text{(eq. 2)}$$

Monovalent axle with trivalent host (case C):

Analyzing the binding of the monovalent axle with the trivalent host leads to the following results: In case of the first axle's threading there are the same two possible orientation as shown above. Additionally this axle can not only thread into one macrocyclic cavity but there is a choice between three. This results in 2*3 = 6 different microspecies.

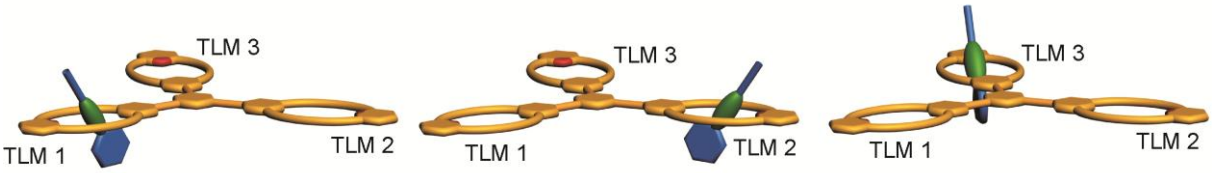


Figure S8 Three different possibilities of the same oriented axle to bind to the trivalent host.

Within the second axle's threading, two more possible binding orientations for the second axle come along which results in 2*2 = 4 possible orientations. Additionally, there are again three possibilities which of the host cavities are filled (TLM1+2, TLM2+3, or TLM3+1). In summary, 4*3 = 12 different microspecies can be distinguished.

If three monovalent axles bind to the trivalent host there are 2 different orientations for each axle possible and since there is just one option to fill all macrocycles, no further factor has to be included which means that in sum 2*2*2 = 8 different microspecies are possible.

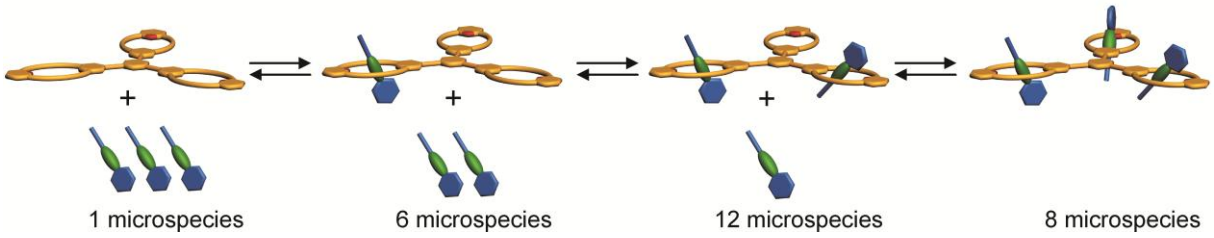


Figure S9 Statistical factors for the stepwise threading of three monovalent axle molecules into the trivalent guest.

$$K^C = K_1^C\ K_2^C\ K_3^C = 6\ K_{mono} 2\ K_{mono} \frac{2}{3} K_{mono} = 8K_{mono}^3 \qquad \text{(eq. 3)}$$

Trivalent axle with monovalent host (case B):

For the binding situation between the trivalent axle and monovalent host we get the same statistical factors as in case C which results in the following equation.

$$K^B = K_1^B\ K_2^B\ K_3^B = 6\ K_{mono} 2\ K_{mono} \frac{2}{3} K_{mono} = 8K_{mono}^3 \qquad \text{(eq. 3)}$$

Trivalent axle with trivalent host (case A):

For the first threading step there are again two different orientations possible how the first arm of the axle binds into the cavity of a macrocycle. This time we do not only have three different host binding stations but also three different axle binding stations that can be involved in the complexation which results in 2*3*3 = 18 different microspecies.

If a second axle arm is threading in, this arm can only come from the same side (top or bottom) as the first one. The resulting two possible orientations are shown in Figure 4. Again there are three possible combination of axle binding stations involved in the complex formation and also three which host cavities are involved. Therefore the same number of microspezies 2*3*3 = 18 can be distinguished.

The threading of the last arm of the axle leads to a decrease of the number of 3*2 = 6 microspecies.

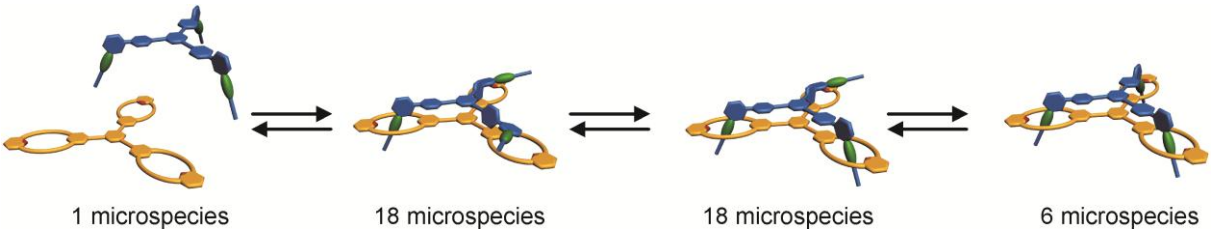


Figure S10 Statistical factors for the stepwise threading of the trivalent guest with the trivalent host.

$$K^A = 18K_{mono}K_{mono}\frac{1}{3}K_{mono}EM_1EM_2 = 6K_{mono}^3EM_1EM_2 \qquad \text{(eq. 5)}$$

The two effective molarities EM_1 and EM_2 correspond to the two cyclization steps that occur upon the second and third threading.

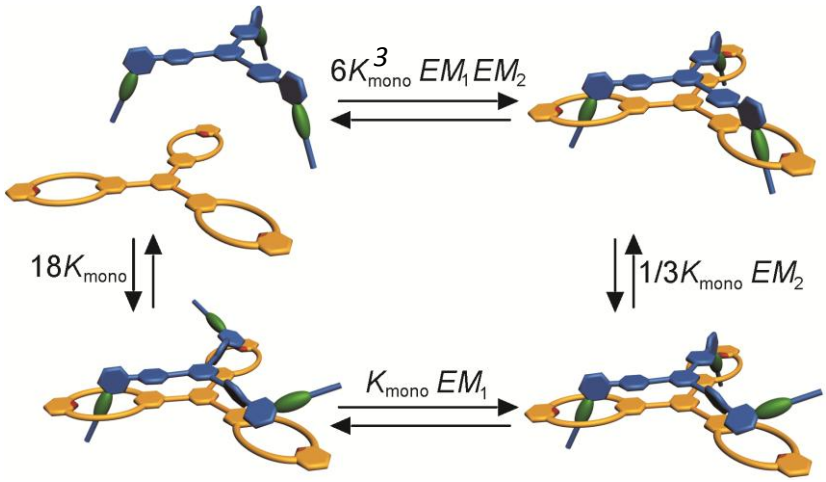


Figure S11 Schematic description of the stepwise threading for the trivalent pseudorotaxane

Overall, we obtain:

$$K_{trivalent} = \frac{K^AK^D}{K^BK^C} = \frac{6\ {K_{mono}}^3\ EM_1\ EM_2\ 8\ {K_{mono}}^3}{8\ {K_{mono}}^3\ 8\ {K_{mono}}^3} = \frac{3}{4}EM_1EM_2 \qquad \text{(eq. 6)}$$

From the double mutant cycle analysis of the trivalent and monovalent pseudorotaxanes alone, it is not possible to determine both effective molarities separately. One would obtain only the product of both. In order to arrive at an estimate for the two effective molarities, it is therefore necessary to determine EM_1 by a double mutant analysis of the divalent analogue as discussed in the next chapter. This analysis is based on the assumption that the presence of the third, non-threaded binding site in the trivalent system does not change the effective molarity of the second binding step.

7. Double mutant cycle for the divalent system

The same way as explained for the trivalent system the statistical factors for the divalent components were determined which yields in the double mutant cycle shown in Figure S12 and equation 7.

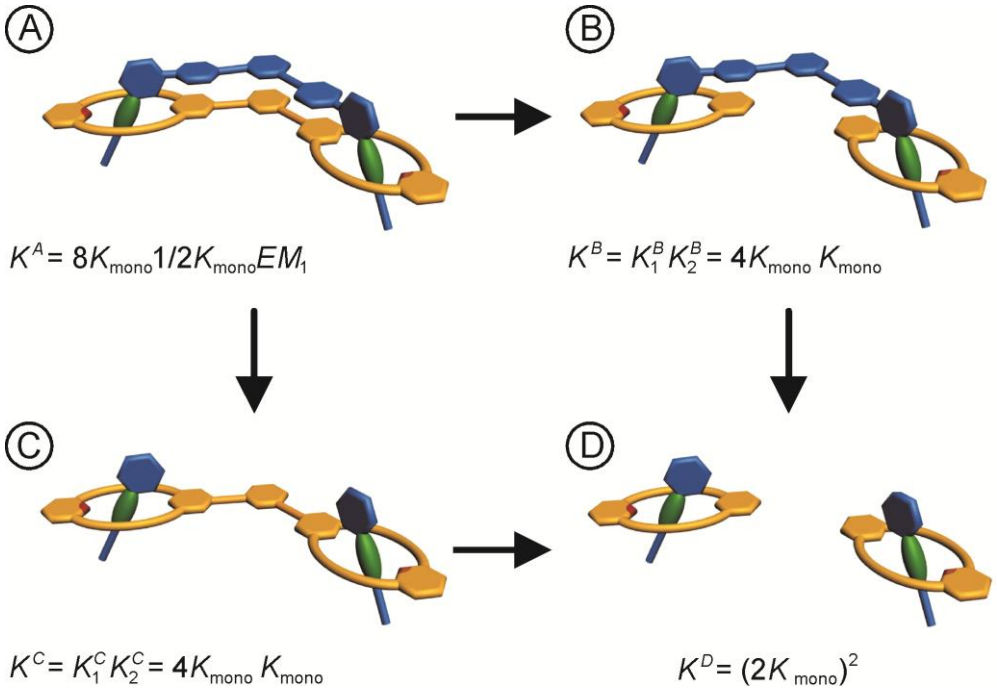


Figure S12 Doubel mutant cycle for the divalent angled pseudorotaxane.

$$K_{divalent} = \frac{4\,K_{mono}{}^2\,EM_1\,4\,K_{mono}{}^2}{4\,K_{mono}{}^2\,4\,K_{mono}{}^2} = EM_1 \qquad \text{(eq. 7)}$$

8. ESI-MS/MS results

All ESI-MS/MS experiments were performed utilizing an ESI-IMS-MS/MS instrument: Synapt G2-S HDMS (Waters Co., Manchester, UK). UPLC-grade solvents (Biosolve) were used throughout the experiments.

Instrumental Parameters: Flow rate: 10 µL/min; Capillary voltage (kV): 3,3; Sampling Cone voltage: 40 V; Source Offset: 80 V; Source temperature: 80 °C; Desolvation temperature: 250 °C; Cone Gas flow rate: 0 L/h; Desolvation Gas flow rate: 500 L/h; Nebulizer pressure: 6,0 bar. The instrument was equipped with an rf generator suitable for m/z values of up to 8 kDa. The instrument was optimized for optimal transmission of each ion isolated (transfer rf voltages, travelling waveform frequencies and wave heights). “Target enhanced mass” for the respective quasi-molecular ion was used throughout the experiments. For better isolation, the LM resolution was increased from 4.7 (standard value) to 10. To prevent loss of fragment ion intensities, the Collision Energy (CE) was applied directly in front of the TOF analyzer (transfer collision cell), not in front of the TWIMS cell (trap collision cell). The CE used is given in the label of the respective mass spectrum. All samples were dissolved in dichloromethane with 10% methanol and 0.1 to 1% formic acid. For calculating the mass and labeling the peaks always the most abundant mass was used.

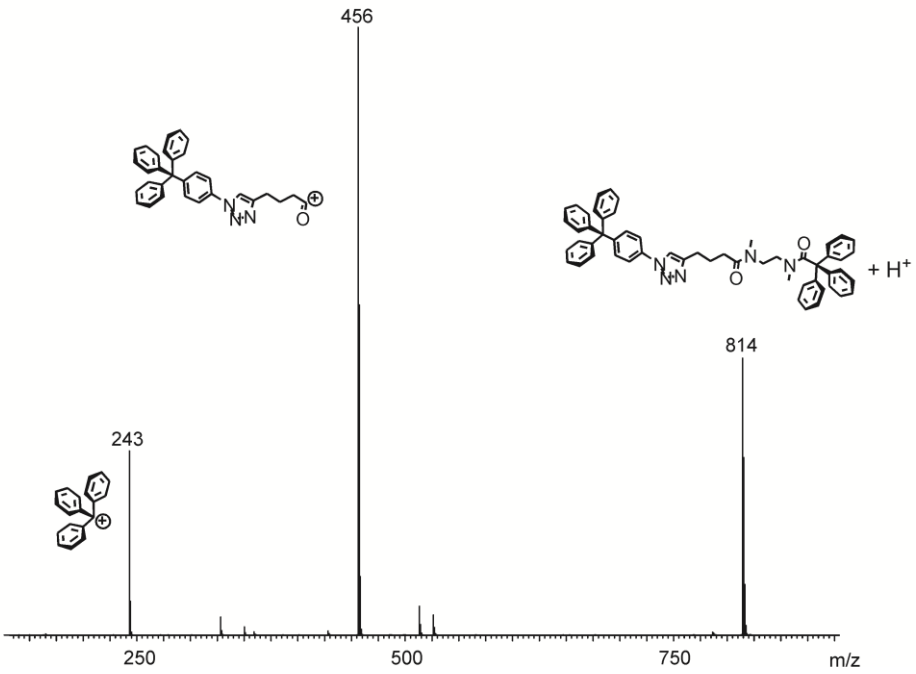


Figure S13 Isolation and fragmentation of the protonated free monovalent stoppered axle (*m/z* calcd. for $[C_{55}H_{52}N_5O_2]^+$: 814.4115 ($[M+H]^+$); found: 814.4112 (Δ = 0.4 ppm)). The two main fragments are shown in the spectrum (*m/z* calcd. for $[C_{31}H_{26}N_3O]^+$: 456.2070; found: 456.2072 (Δ = 0.4 ppm); *m/z* calcd. for $[C_{19}H_{15}]^+$: 243.1168; found: 243.1171 (Δ = 1.2 ppm)). The collision energy was CE = 20 eV.

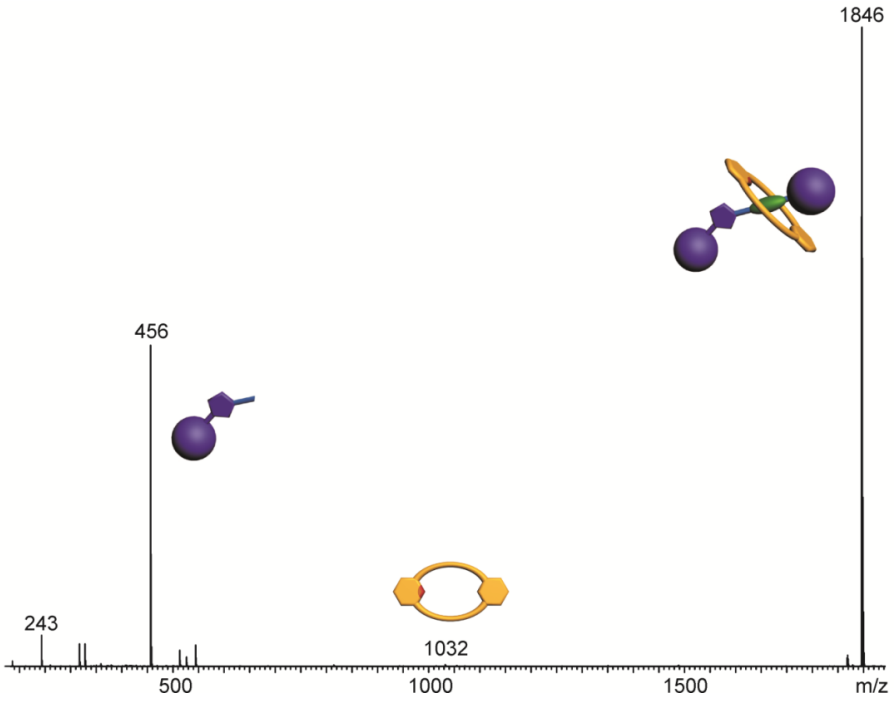


Figure S14 Isolation and fragmentation of the protonated monovalent rotaxane (*m/z* calcd. for $[C_{114}H_{114}IN_{10}O_6]^+$: 1846.7994 ($[M+H]^+$); found: 1846.7933 (Δ = 3.3 ppm)). The collision energy was CE = 40eV

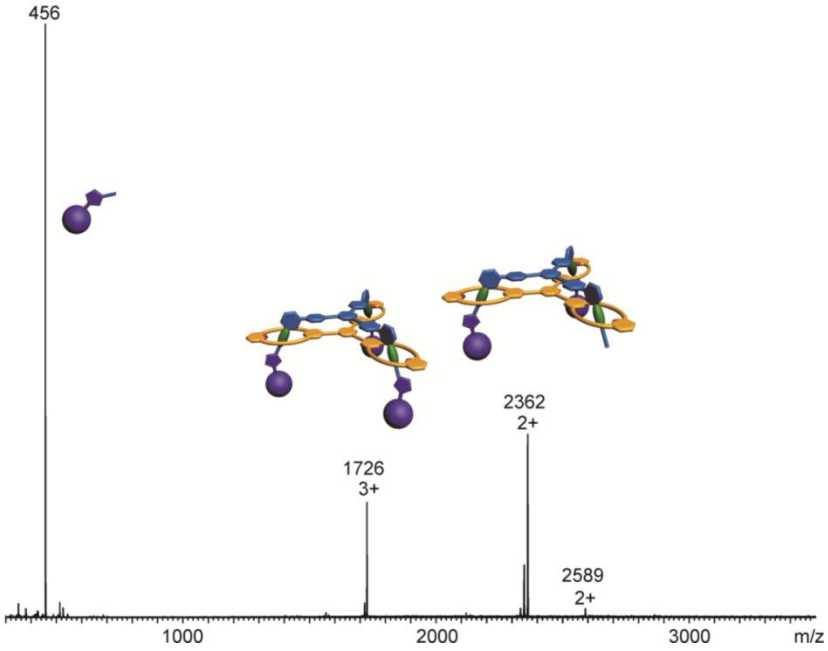


Figure S15 Isolation and fragmentation of the triple protonated trivalent rotaxane (*m/z* calcd. for $[C_{345}H_{327}N_{30}O_{18}]^{3+}$: 1726.8558 ($[M+3H]^{3+}$); found: 1726.8478 (Δ = 4.6 ppm)). Apart from the typical axle fragment at *m/z* = 456 also the two times stoppered doubly charged rotaxane fragment was found (*m/z* calcd. for $[C_{314}H_{303}N_{27}O_{17}]^{2+}$: 2362.1802; found: 2362.1731 (Δ = 3.0 ppm)). The small losses with masses around *m/z* = 28 can be explained by the loss of small fragments like N_2 (from the triazole) or C_2H_4. The signal at *m/z* = 2589 is the triply stoppered rotaxane precursor after losing one charge. The collision energy was CE = 40 eV.

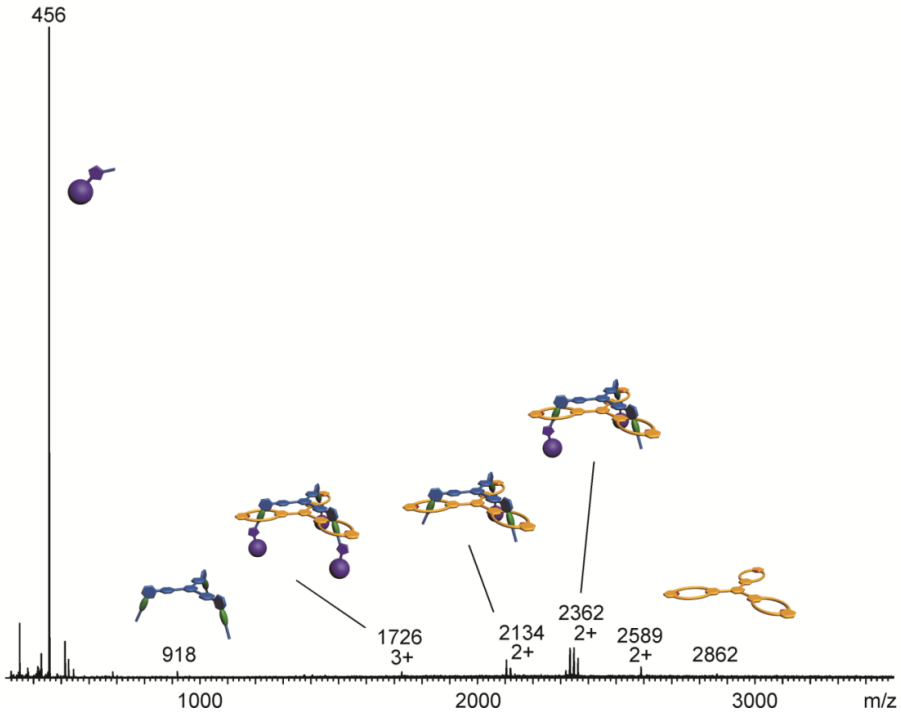


Figure S16 Isolation and fragmentation of the triply protonated trivalent rotaxane. By increasing the collision energy to CE = 50 eV also the singly stoppered rotaxane fragment (*m/z* calcd. for $[C_{283}H_{276}N_{24}O_{16}]^{2+}$: 2134.5803; found: 2134.5659 (Δ = 6.7 ppm)) as well as the free axle after losing all three stoppers and other small fragments are detectable. Only after loss of the third stopper, the host molecule is not attached to some axle (fragment) and can be detected (*m/z* calcd. for $[C_{189}H_{190}N_{15}O_{12}]^{+}$: 2863.4777; found: 2863.4741 (Δ = 1.3 ppm)).

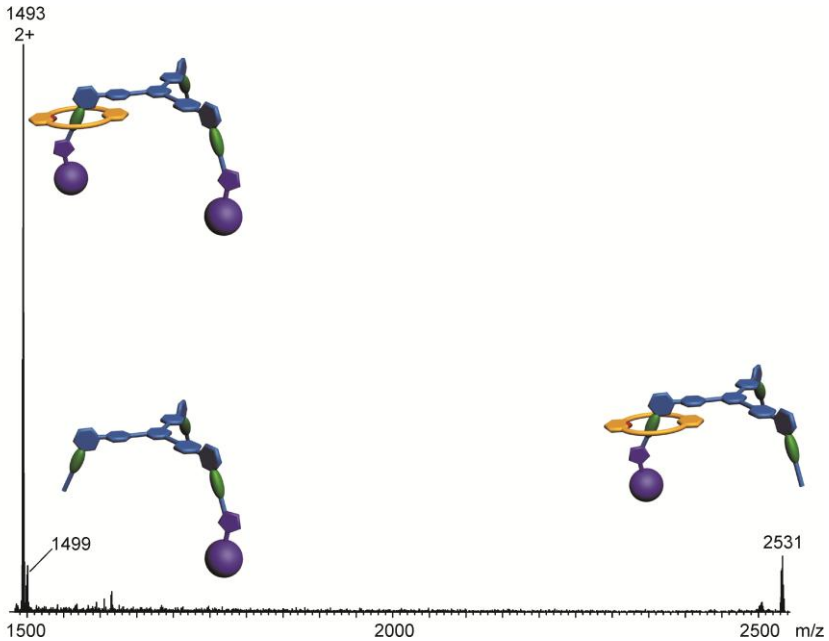


Figure S17 Isolation and fragmentation of the two times stoppered trivalent axle containing one monovalent TLM (*m/z* calcd. for $[C_{190}H_{180}IN_{17}O_{10}]^{2+}$: 1494.1597 ($[M+2H]^{2+}$); found: 1494.1649 (Δ = 3.5 ppm)). As fragments there are the monostoppered axle still containing the TLM (*m/z* calcd. for $[C_{159}H_{154}IN_{14}O_{9}]^{2+}$: 2531.1094; found: 2531.1240 (Δ = 5.8 ppm)) as well as the monostoppered axle without TLM (*m/z* calcd. for $[C_{100}H_{91}N_{9}O_{5}]^{+}$: 1499.7248; found: 1499.7217 (Δ = 2.1 ppm)) are detectable in nearly the same ratio. The collision energy was CE = 30 eV.

9. ^{1}H and ^{13}C NMR spectra

Before showing the original ^{1}H and ^{13}C NMR spectra, let us briefly discuss one point taking divalent axle **8** as an example. If one looks at the ^{1}H NMR spectrum of this compound (Figure S18), one might arrive at the conclusion that the compound is not pure.

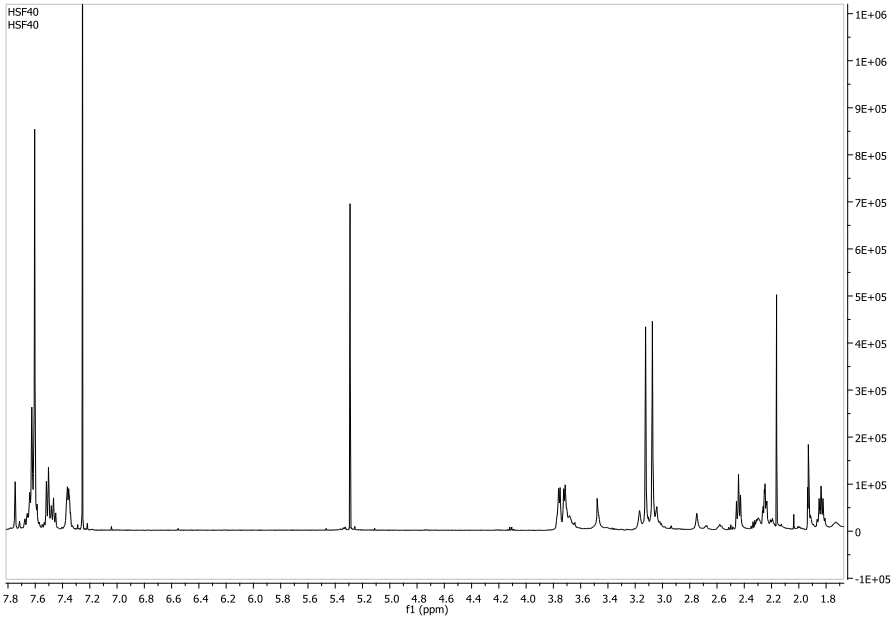


Figure S18 ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of divalent alkyne axle **8**.

However, we need to take into account the fact that the diamide binding station bears two tertiary amides, which do not have an as strong preference for the trans-amide configuration as analogous secondary amides. Consequently, the *trans*-amide is more stable and thus more prominent as compared to the *cis*-amide, but the *cis*-amide is prominent enough to appear clearly in the spectra. Even, if one considers that the two arms of the divalent axle are separated sufficiently so that they do not feel each other, four isomers are possible for each arm: *trans*/*trans*, *trans*/*cis*, *cis*/*trans* and *cis*/*cis*. The energy differences between both isomers thus lead to different sets of signals for each isomer, which appear with different integrations.

In order to provide an example, in which this is quite clearly visible, we analysed the ^{1}H, ^{1}H COSY NMR spectrum of **8**. In particular the hexynoyl side chain shows the presence of different sets of signals quite nicely (Figure S19). This example is simpler to analyse than e.g. the N-methyl or N-methylene groups as the hexynoyl chain only feels the influence of the adjacent amide group.

Three larger signals correspond to H^a – H^c of the *trans*-isomer (blue labels, blue dotted lines). H^b couples to both other protons. H^a in addition exhibits a small coupling constant to the alkyne proton. The assignment is thus unambiguous. In addition three smaller signals are observed for the same protons, which however correspond to the *cis*-isomer (red labels, red

dotted lines). The coupling pattern is the same as for the *trans*-isomer, but the signals are shifted in position. We rule out the presence of small amounts of hexynoic acid, which could also account for such a second set of signals, if the purification of the compound would be incomplete, as the acid has a very different retention time on silica columns and because the signal shifts are different from those assigned to the *cis*-isomer.

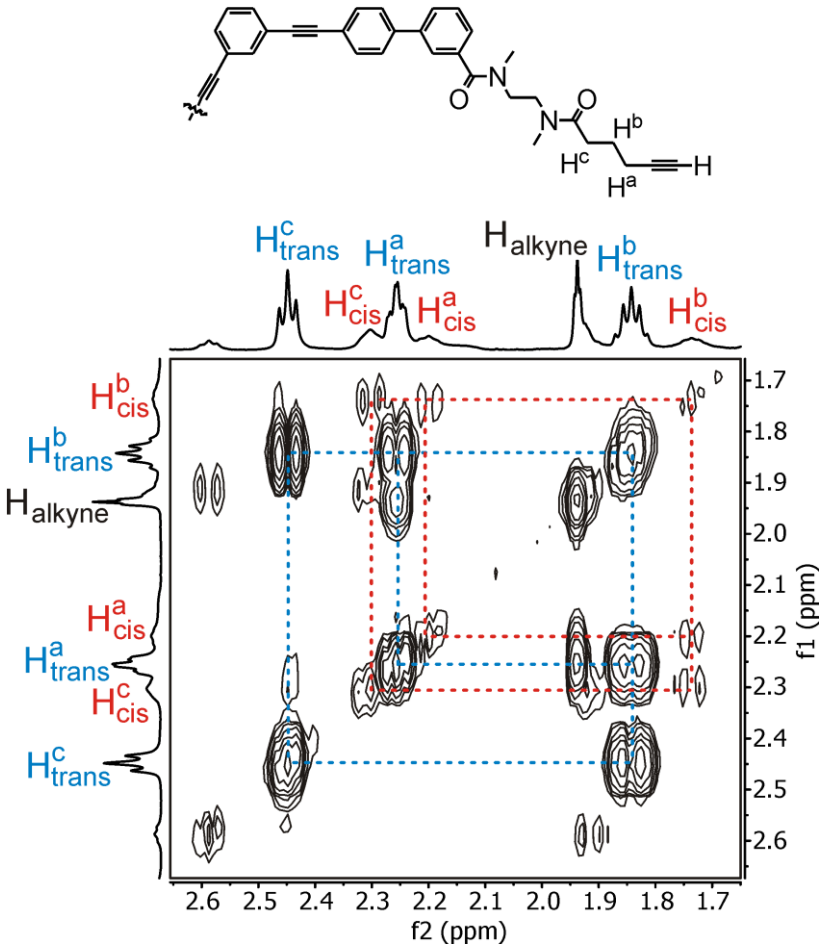


Figure S19 Partial ^{1}H, ^{1}H COSY NMR spectrum (500 MHz, $CDCl_3$) of divalent alkyne axle **8**.

From these considerations, we conclude the complex NMR spectra of all compounds (in particular the di- and trivalent axles) used in this study that contain diamide stations to be caused by the rather complex *cis*/*trans*-isomerism of the amide groups.

Other attempts to obtain evidence for the purity of these compounds failed unfortunately. Elemental analysis, for example, does not give accurate results because of solvent impurities which we were unable to completely remove even upon prolonged heating at high vacuum.

Benzyl-methyl(2-(*N*-methylhexanamido)ethyl)carbamate

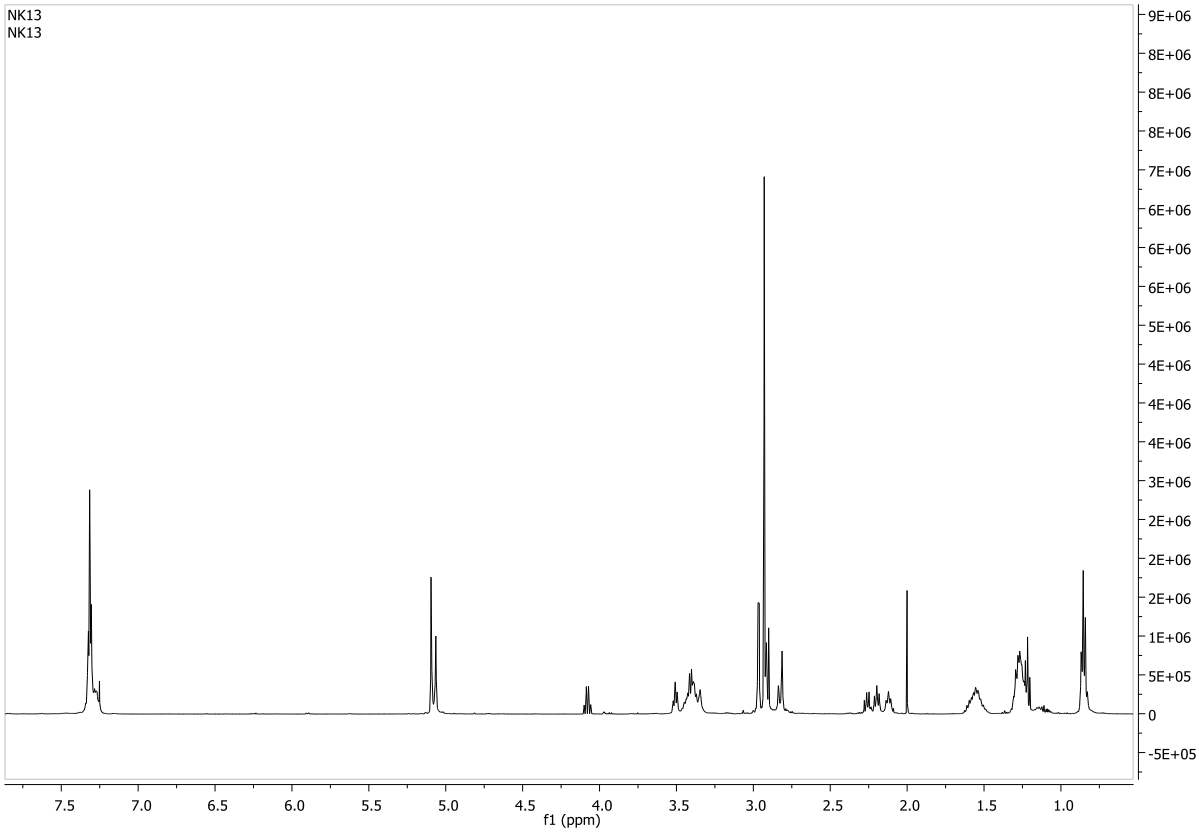


Figure S20 ^{1}H NMR spectrum (500 MHz, $CDCl_3$).

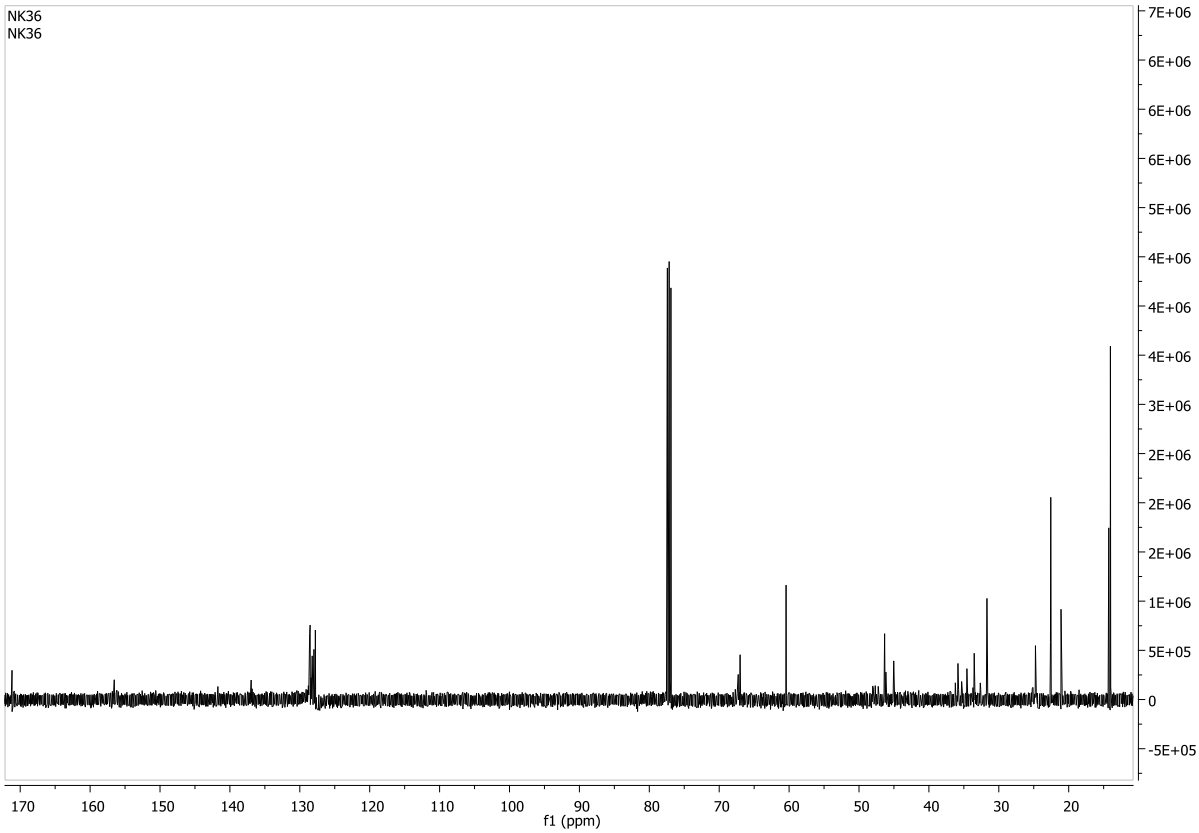


Figure S21 ^{13}C NMR spectrum (126 MHz, $CDCl_3$).

N-Methyl-*N*-(2-(methylamino)ethyl)hexanamide

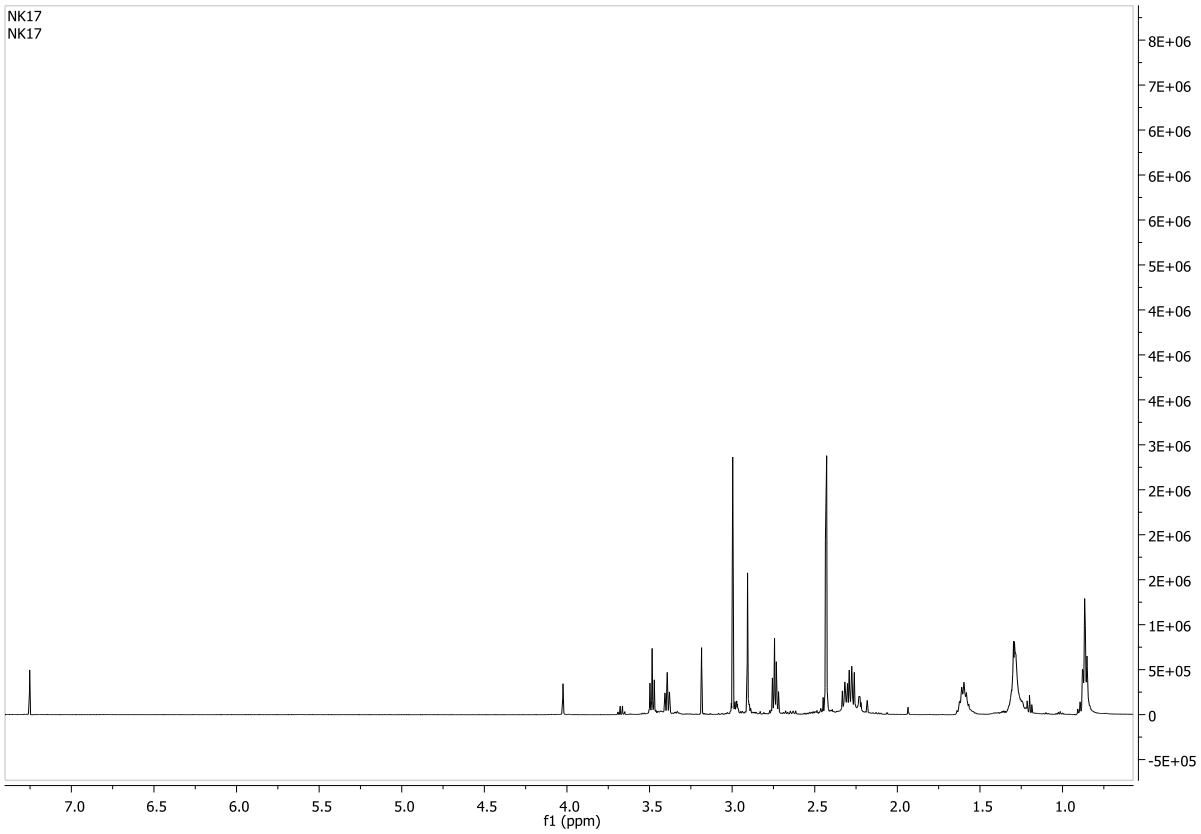


Figure S22 ^{1}H NMR spectrum (500 MHz, $CDCl_3$).

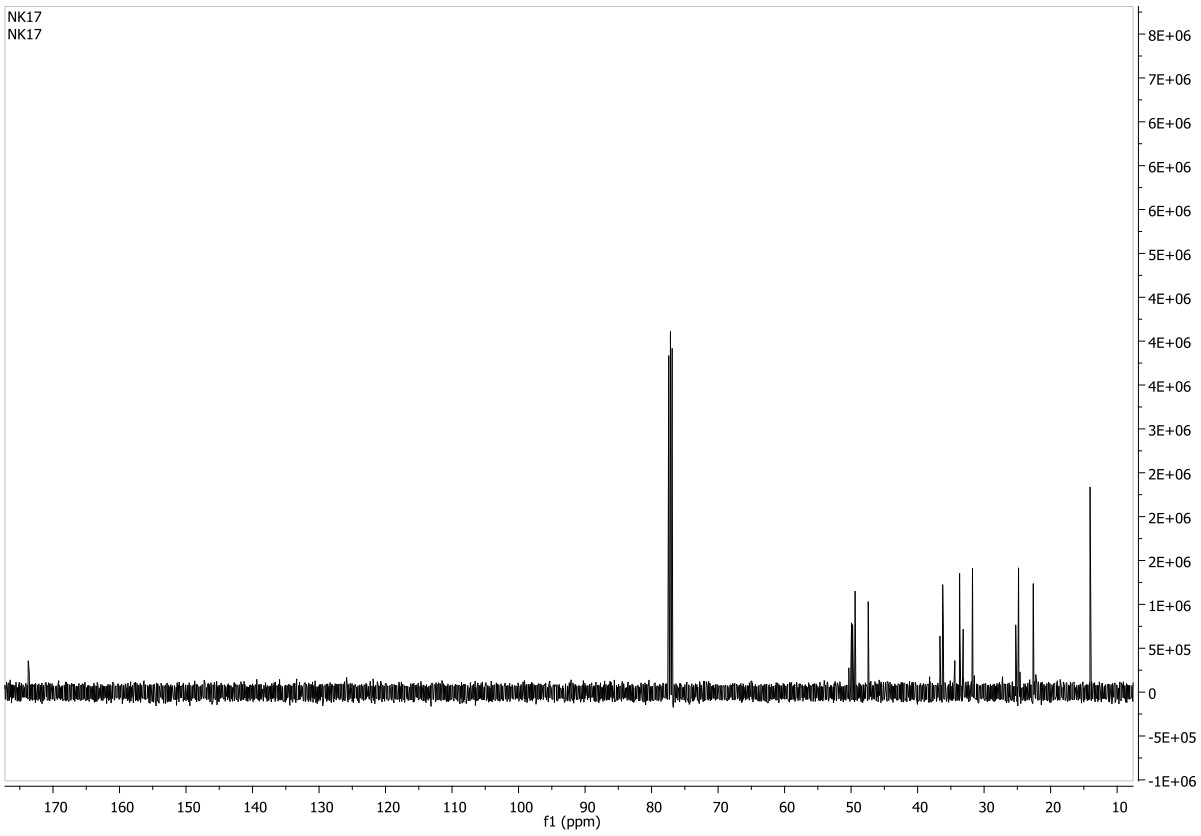


Figure S23 ^{13}C NMR spectrum (101 MHz, $CDCl_3$).

4'-Iodobiphenyl-3-carboxylic acid

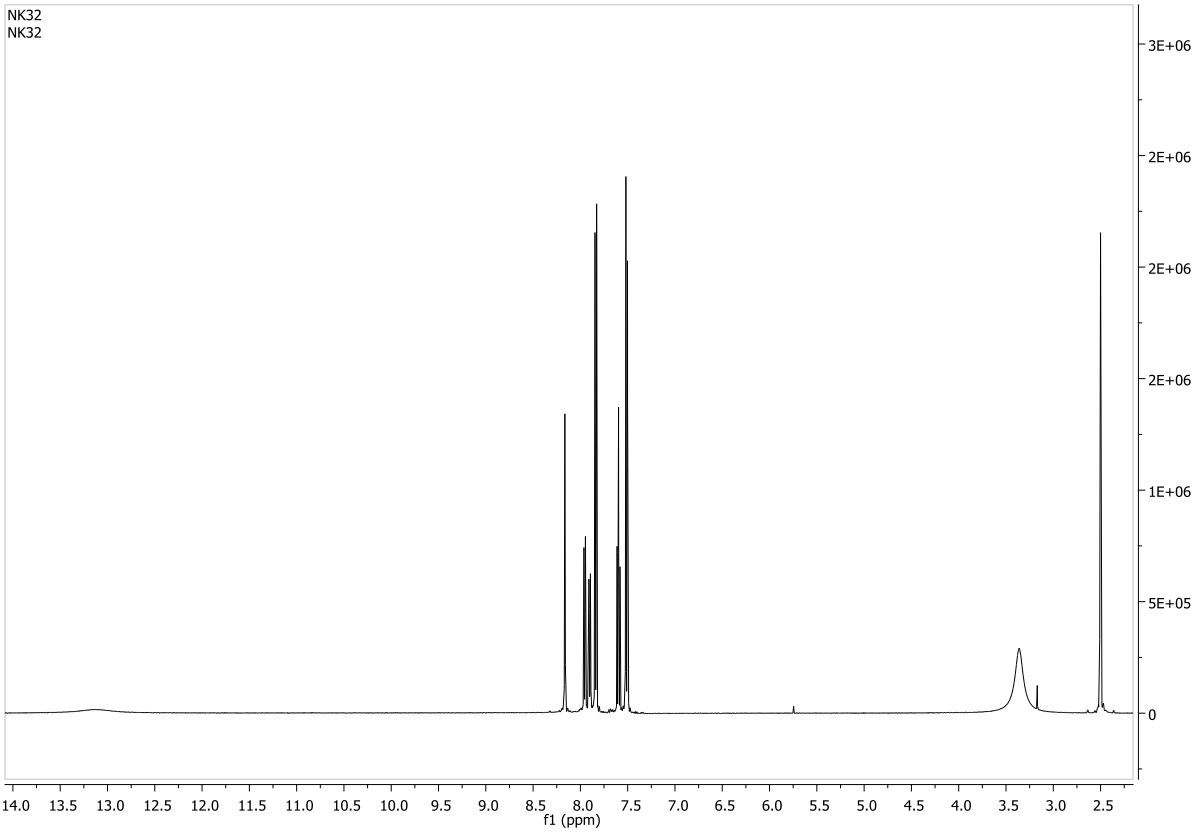


Figure S24 ^{1}H NMR spectrum (500 MHz, DMSO).

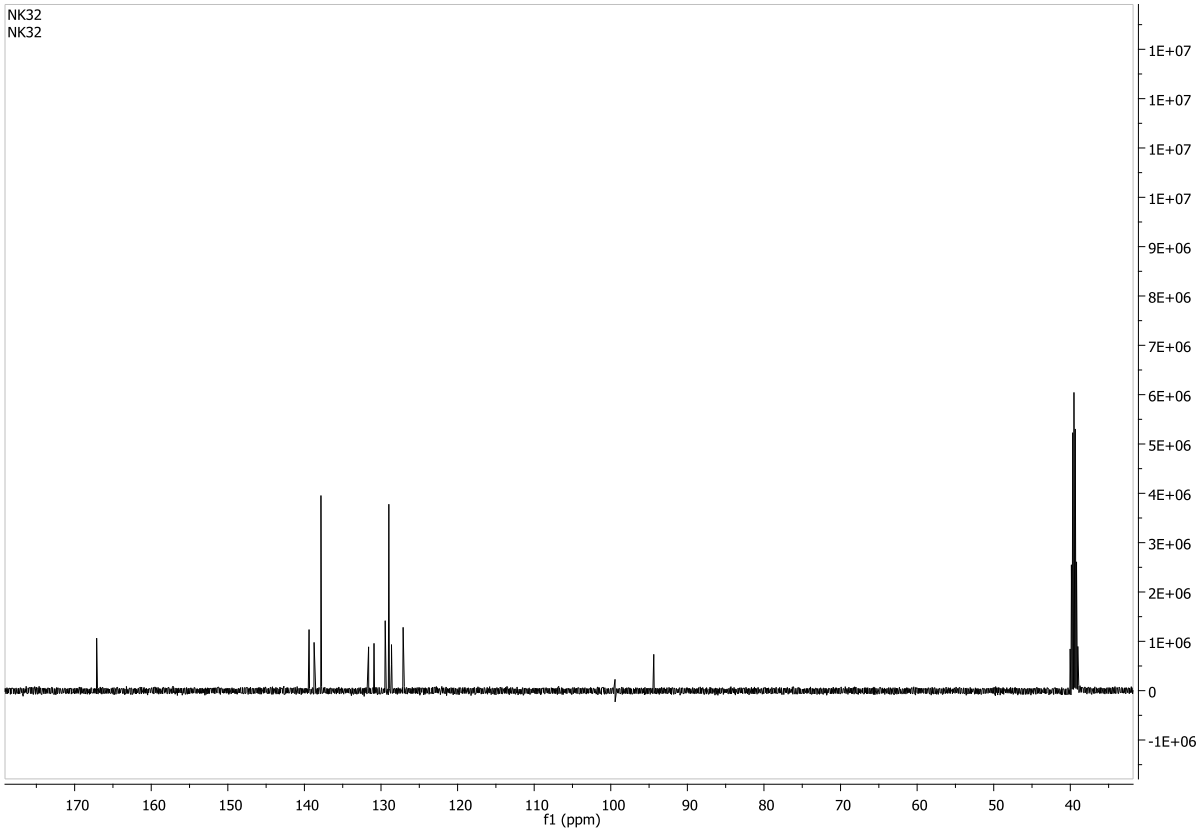


Figure S25 ^{13}C NMR spectrum (126 MHz, DMSO).

4'-Iodo-*N*-methyl-*N*-(2-(*N*-methylhexanamido)ethyl)-[1,1'-biphenyl]-3-carboxamide

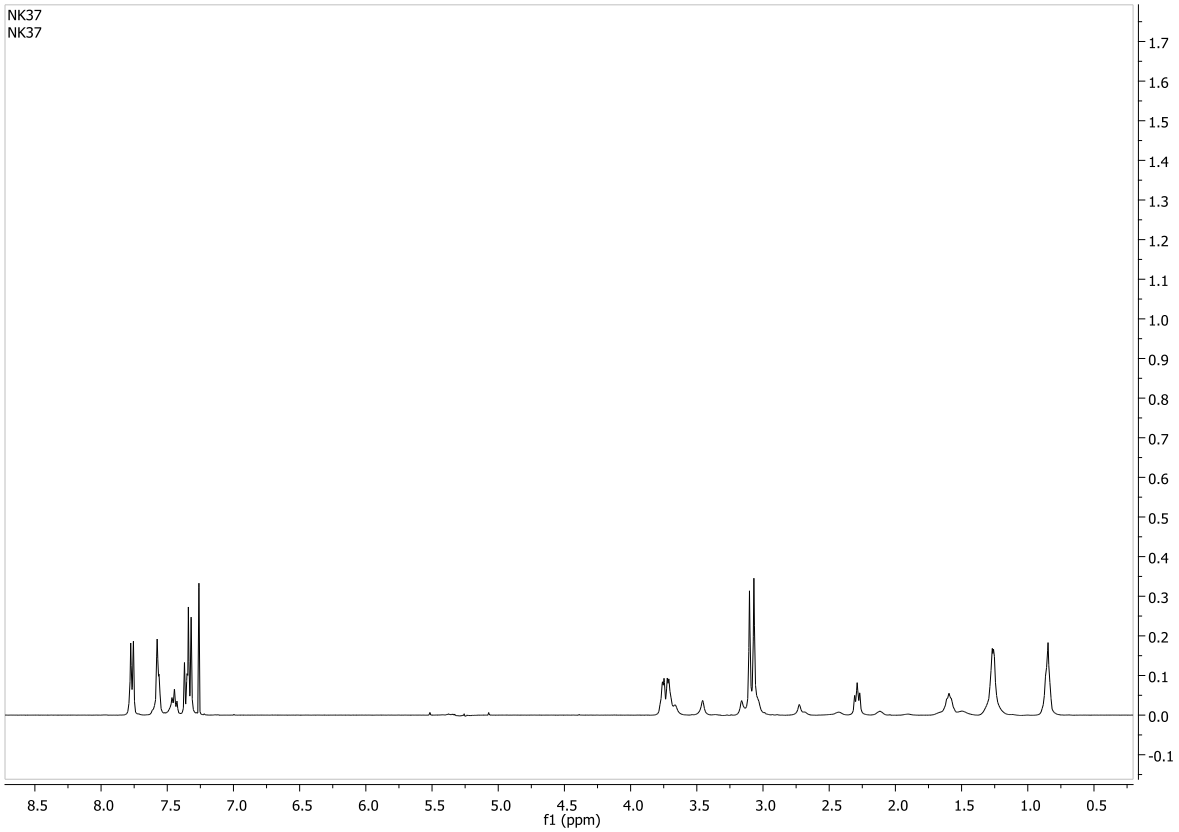


Figure S26 ^{1}H NMR spectrum (400 MHz, $CDCl_3$).

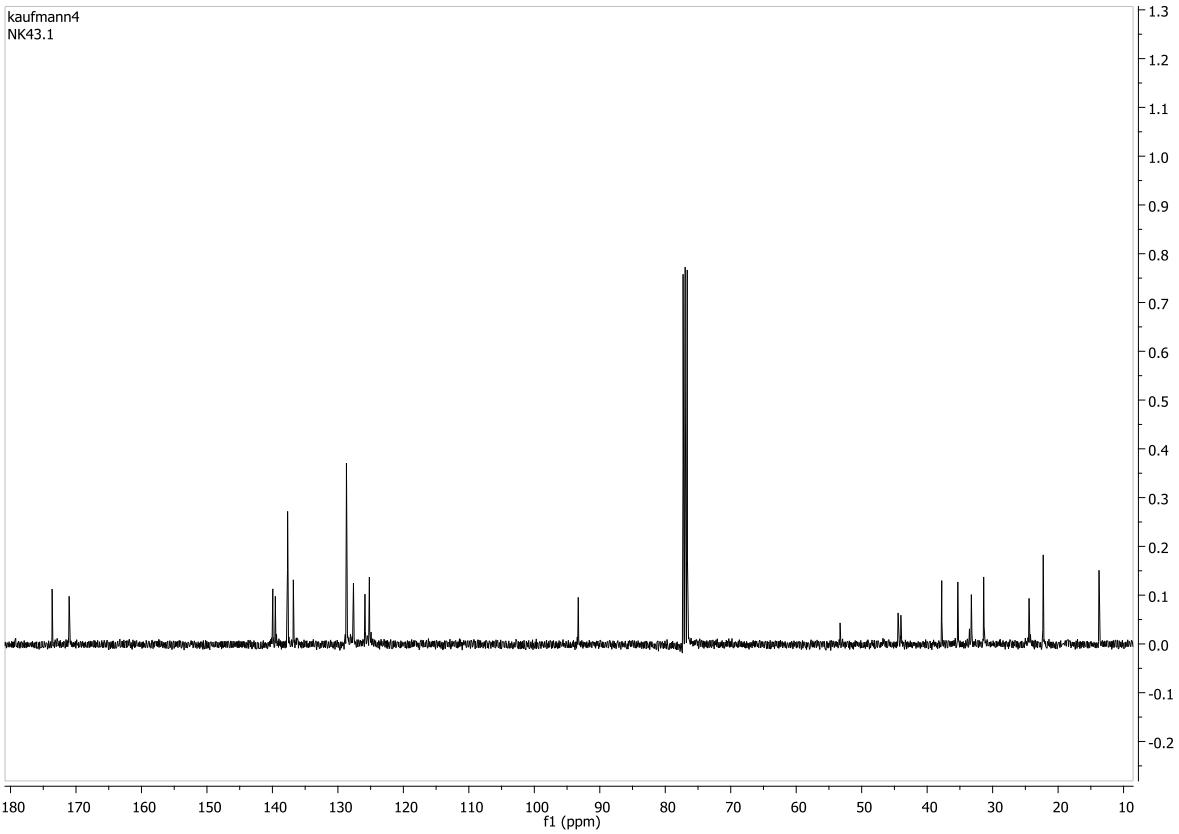


Figure S27 ^{13}C NMR spectrum (101 MHz, $CDCl_3$).

N-Methyl-*N*-(2-(*N*-methylhexanamido)ethyl)benzamide (4)

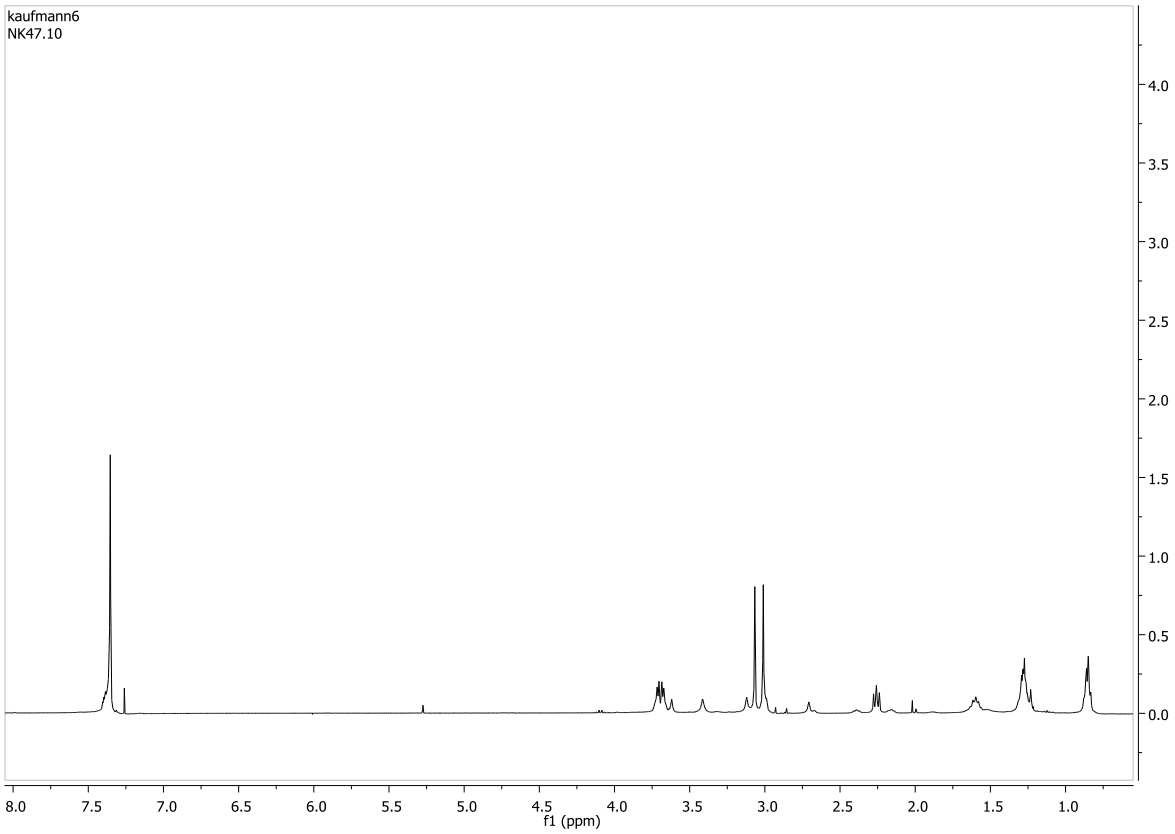


Figure S28 ^{1}H NMR spectrum (400 MHz, $CDCl_3$).

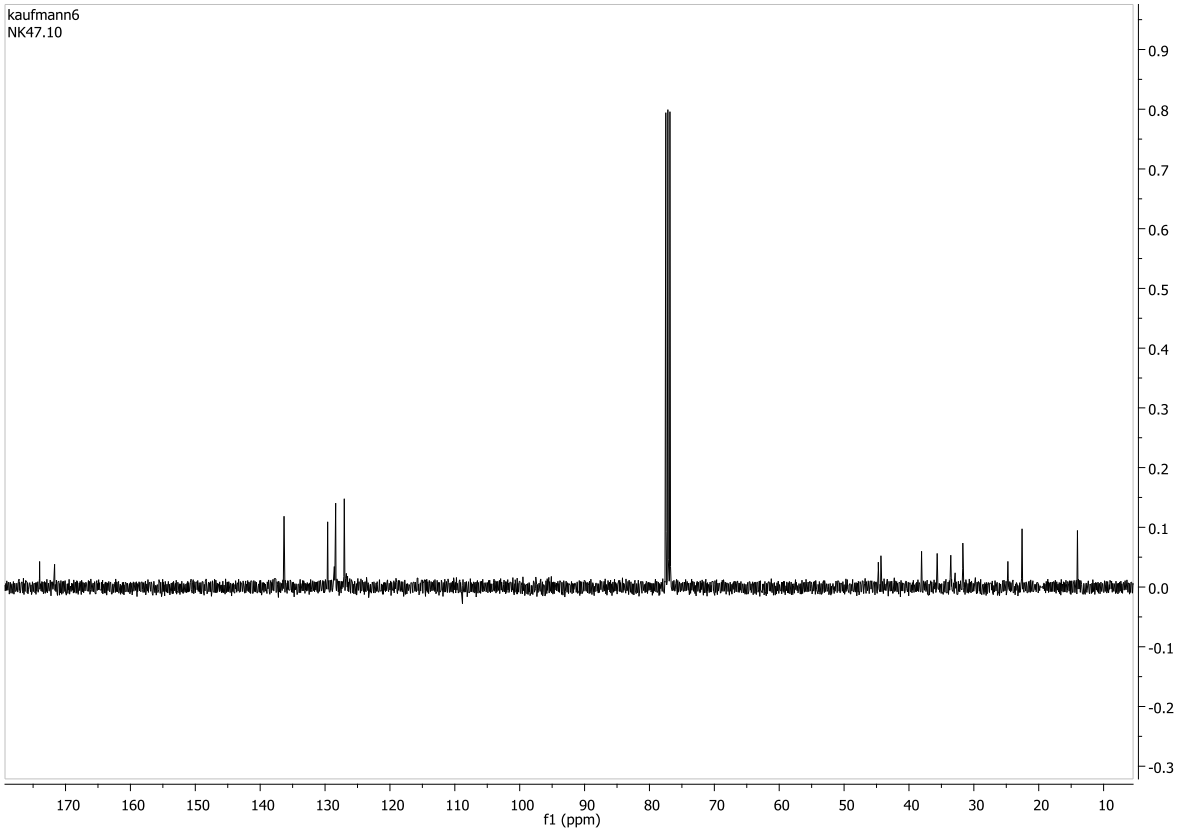


Figure S29 ^{13}C NMR spectrum (101 MHz, $CDCl_3$).

Trivalent alkyl axle (6)

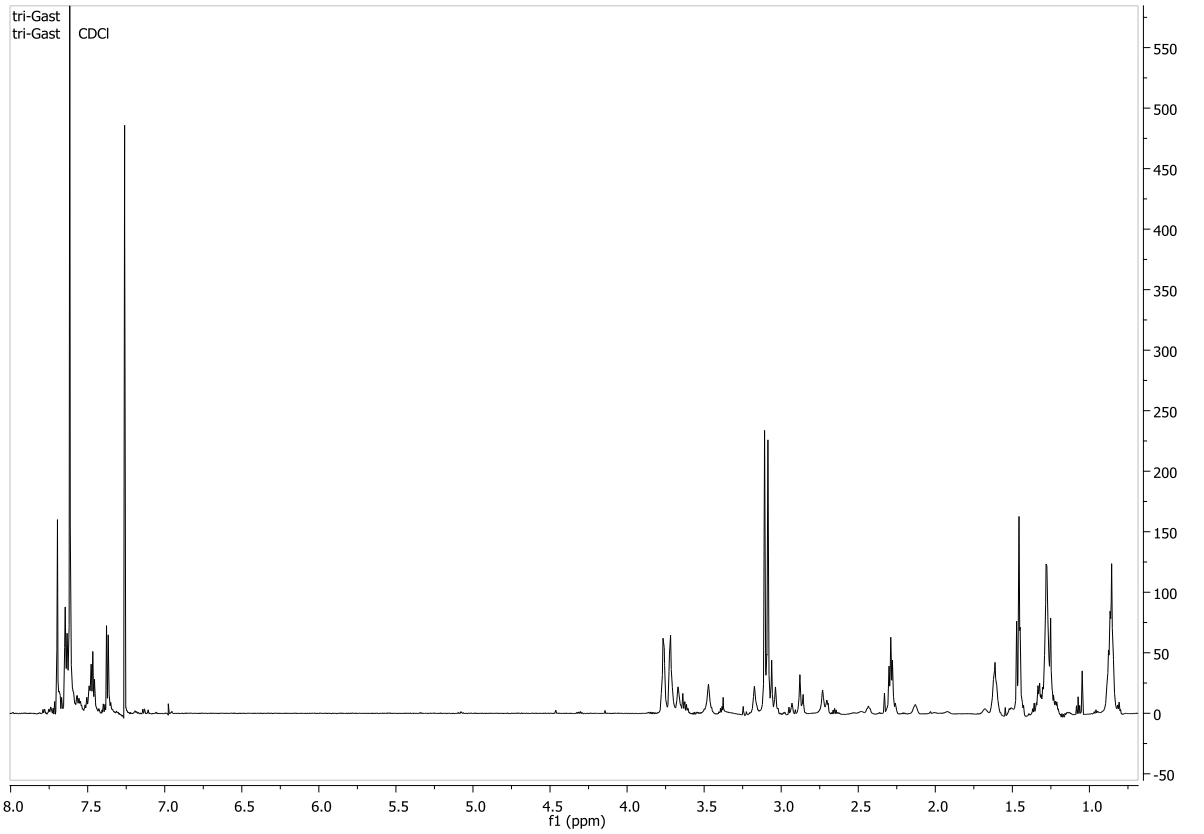


Figure S30 ^{1}H NMR spectrum (700 MHz, $CDCl_3$).

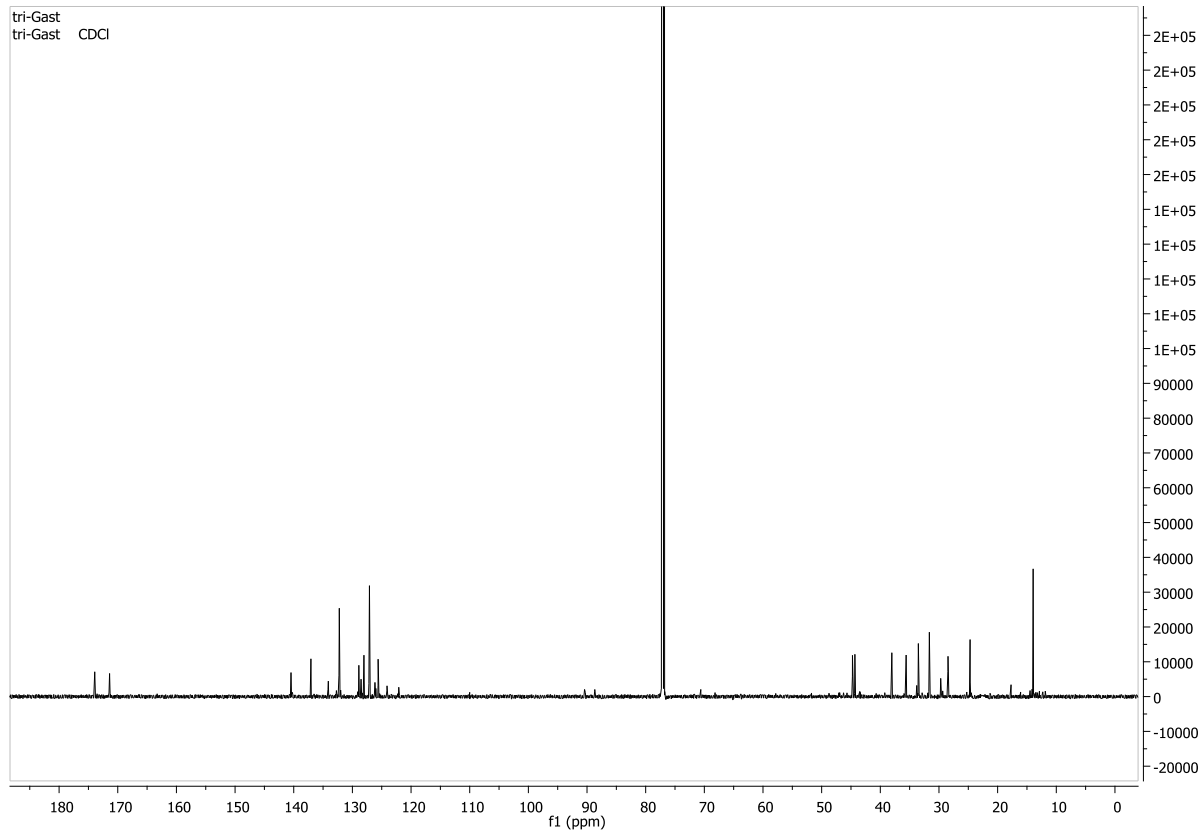


Figure S31 ^{13}C NMR spectrum (176 MHz, $CDCl_3$).

Divalent alkyl axle (5)

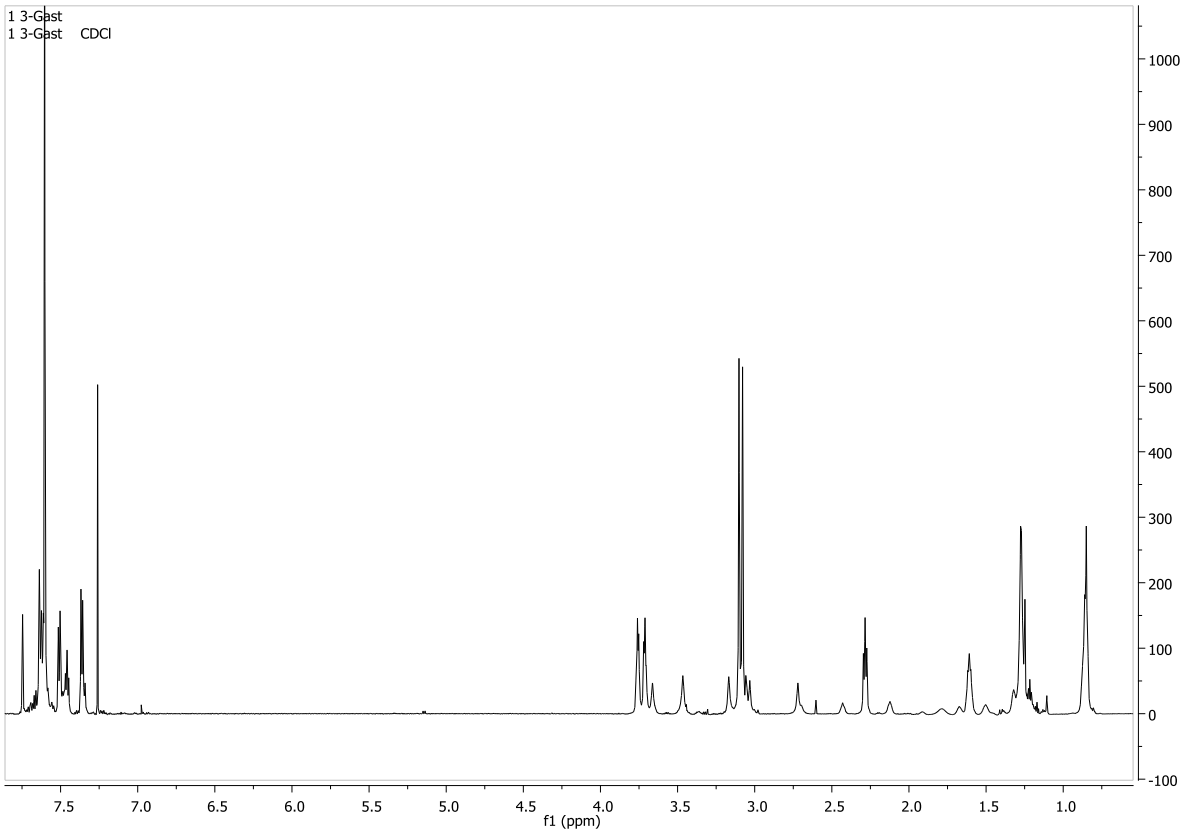


Figure S32 ^{1}H NMR spectrum (700 MHz, $CDCl_3$).

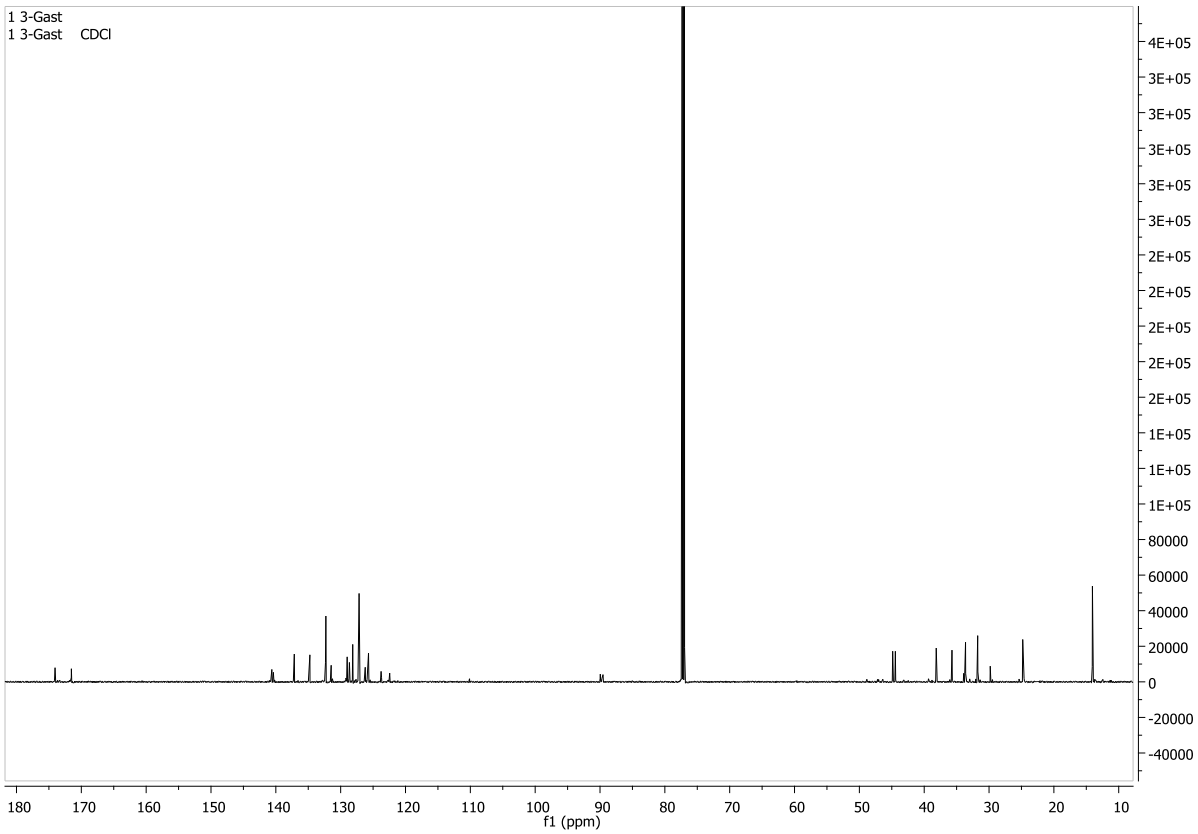


Figure S33 ^{13}C NMR spectrum (176 MHz, $CDCl_3$).

tert-Butyl (2-(4'-iodo-*N*-methyl-[1,1'-biphenyl]-3-ylcarboxamido)ethyl)(methyl) carbamate

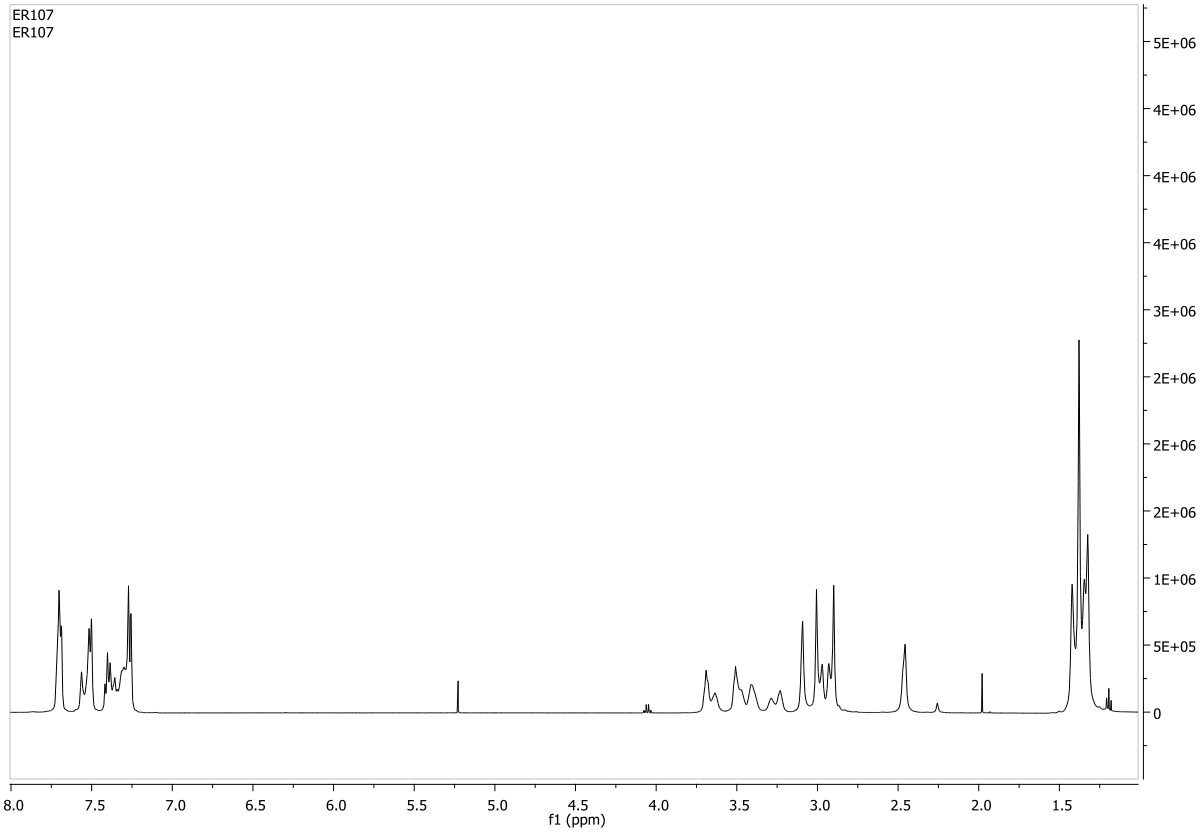


Figure S34 ^{1}H NMR spectrum (500 MHz, $CDCl_3$).

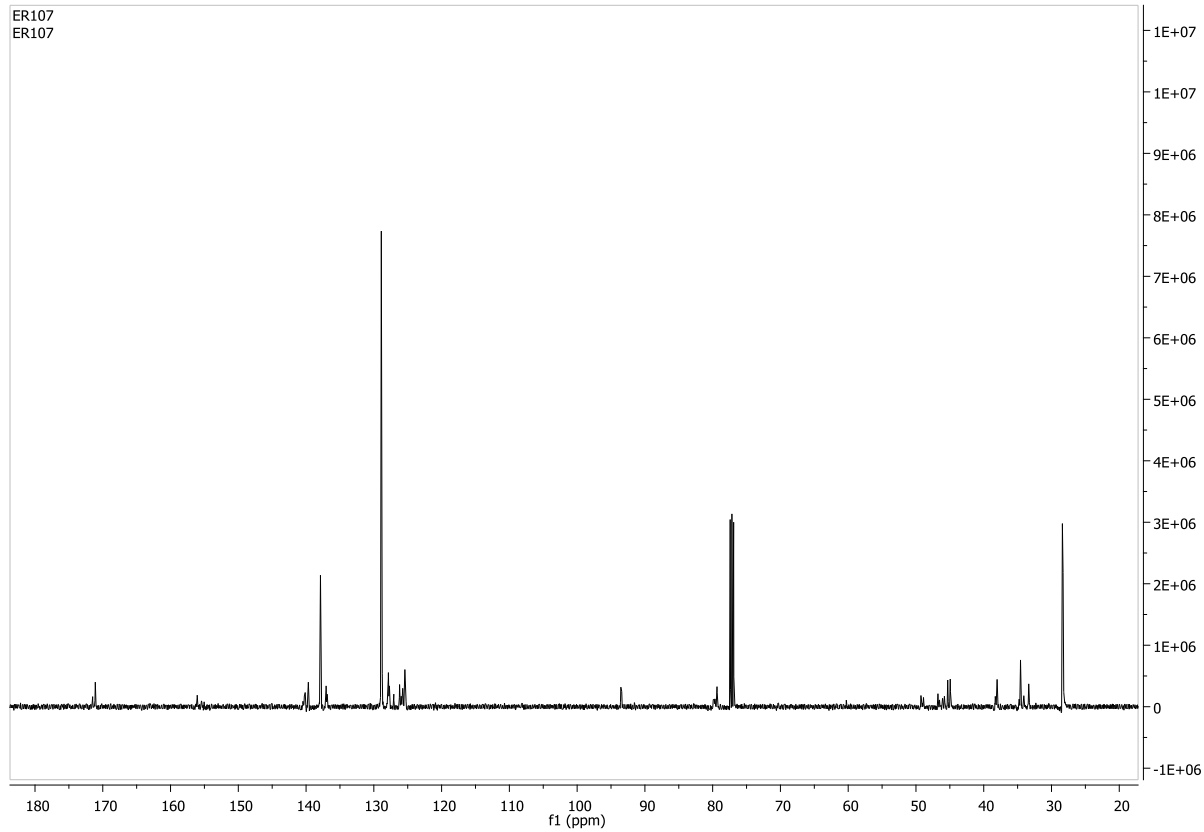


Figure S35 ^{13}C NMR spectrum (126 MHz, $CDCl_3$).

4'-Iodo-*N*-methyl-*N*-(2-(methylamino)ethyl)-[1,1'-biphenyl]-3-carboxamide

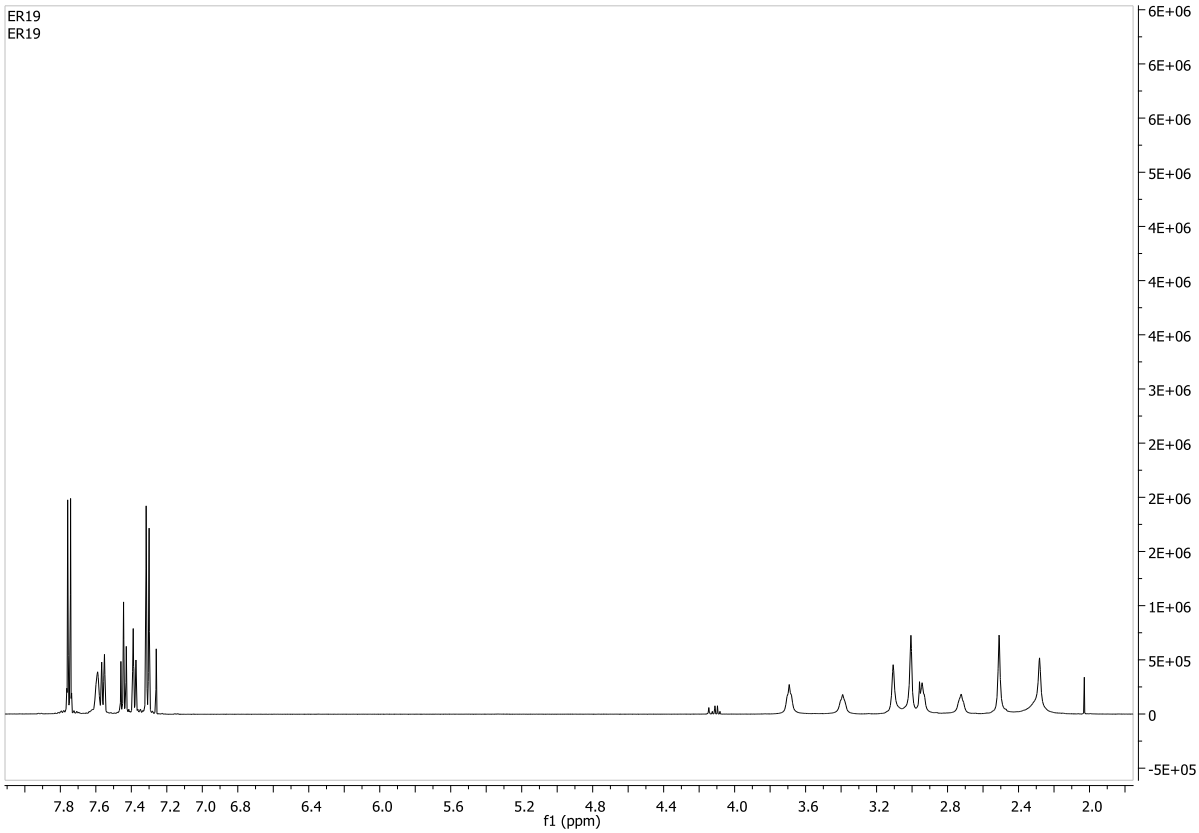


Figure S36 ^{1}H NMR spectrum (500 MHz, $CDCl_3$).

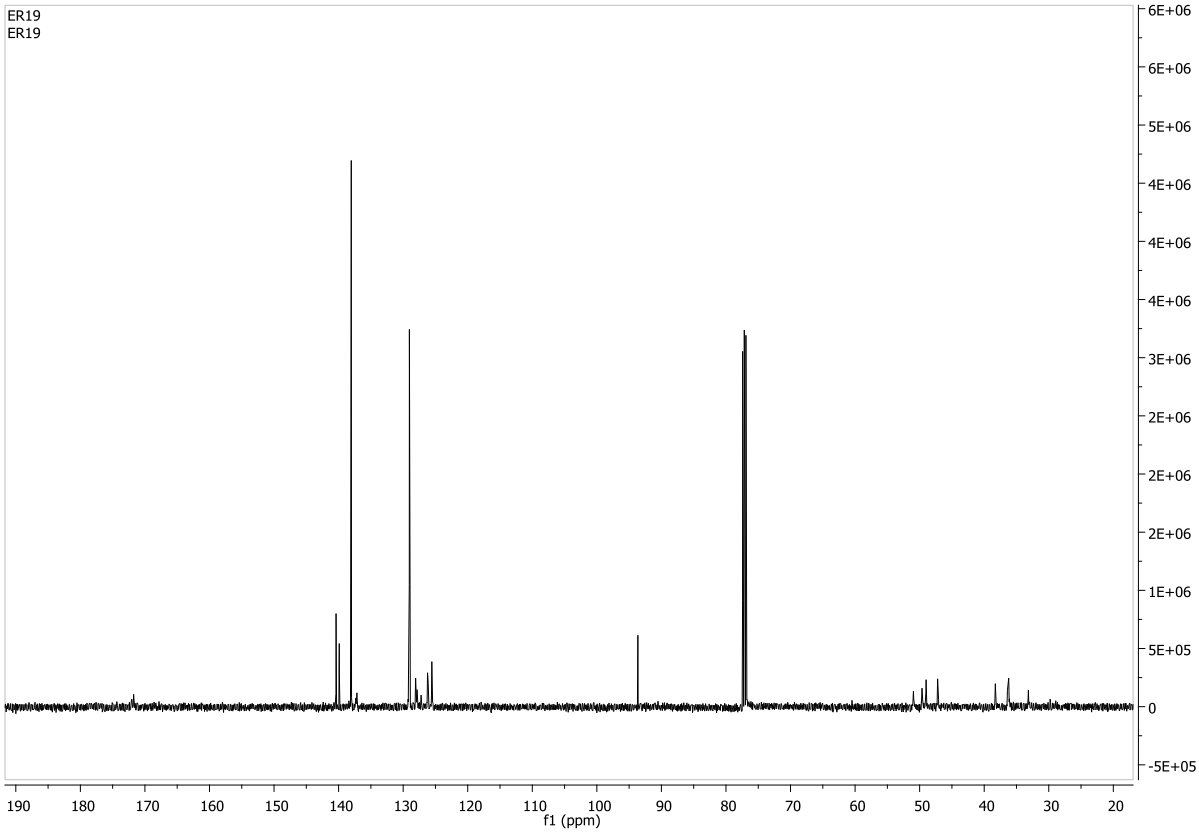


Figure S37 ^{13}C NMR spectrum (126 MHz, $CDCl_3$).

6-(Triisopropylsilyl)-hex-5-ynoic acid

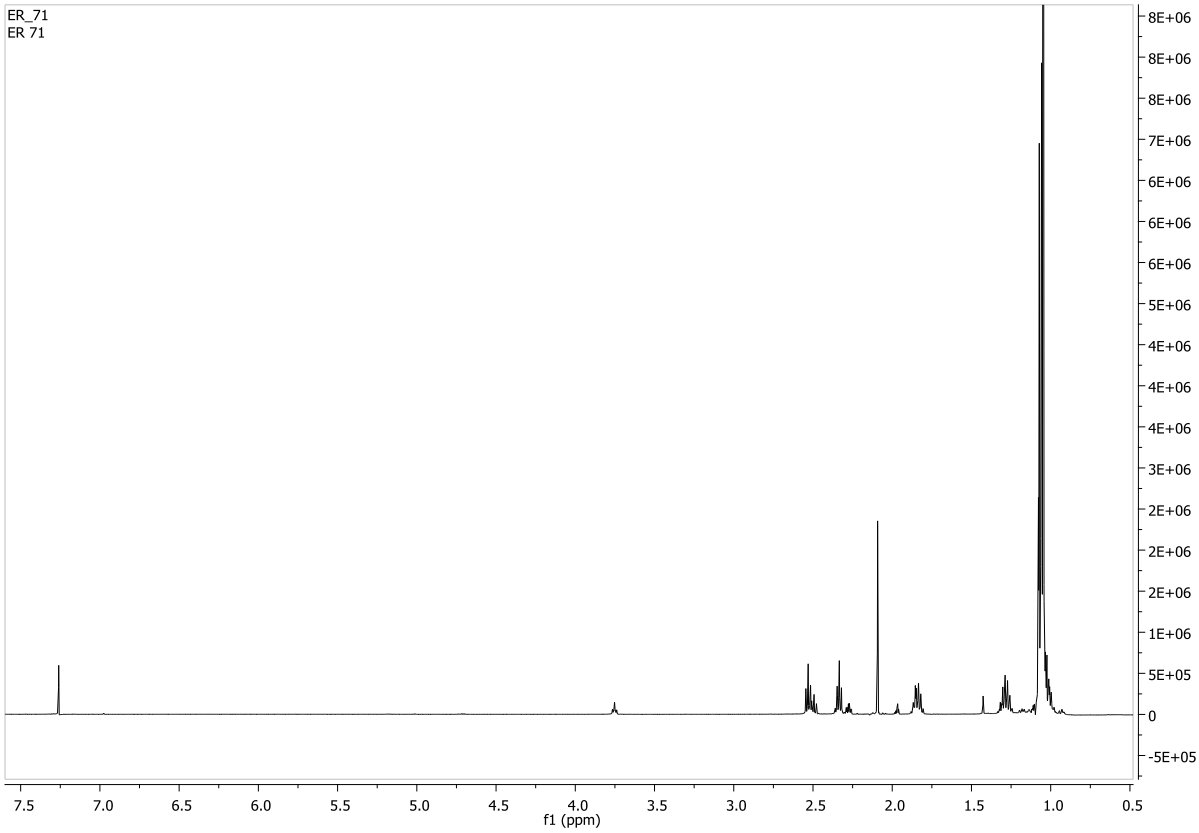


Figure S38 ^{1}H NMR spectrum (500 MHz, $CDCl_3$).

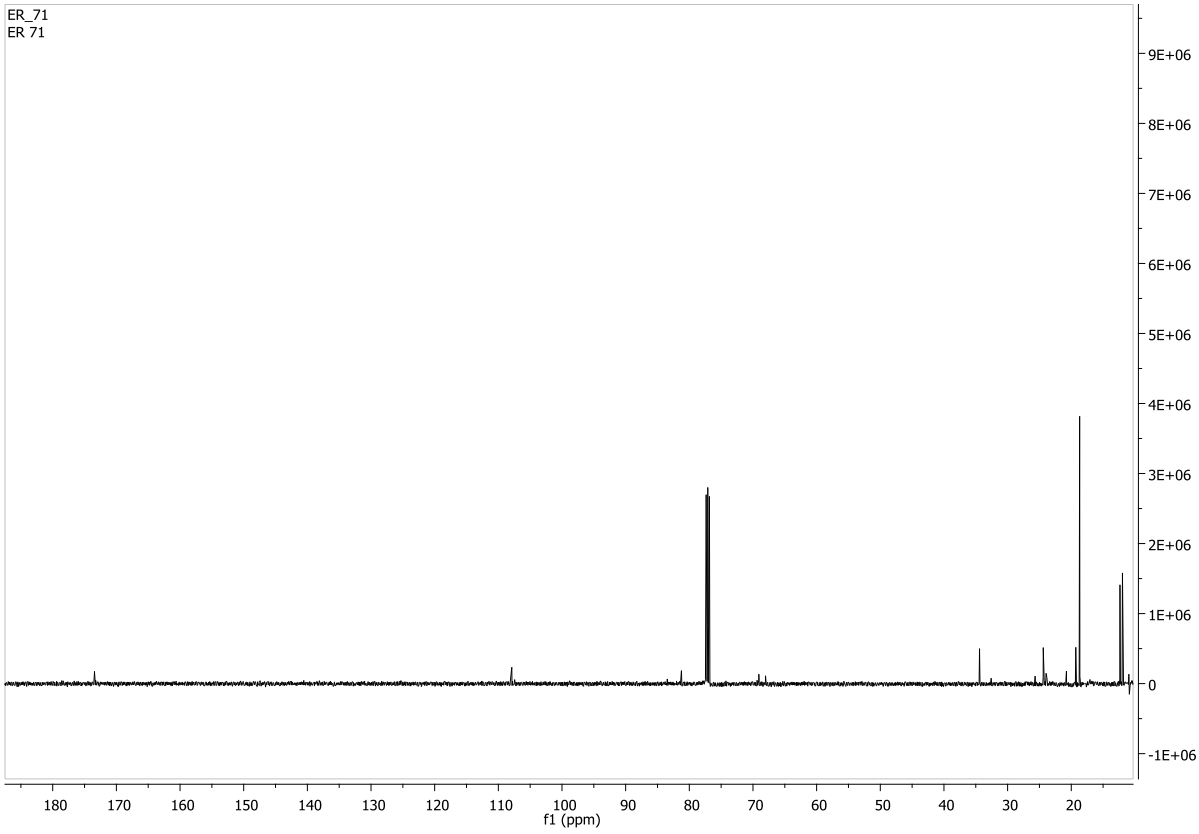


Figure S39 ^{13}C NMR spectrum (126 MHz, $CDCl_3$).

4'-Iodo-*N*-methyl-*N*-(2-(*N*-methyl-6-(trimethylsilyl)hex-5-ynamido)ethyl)-[1,1'-biphenyl]-3-carboxamide

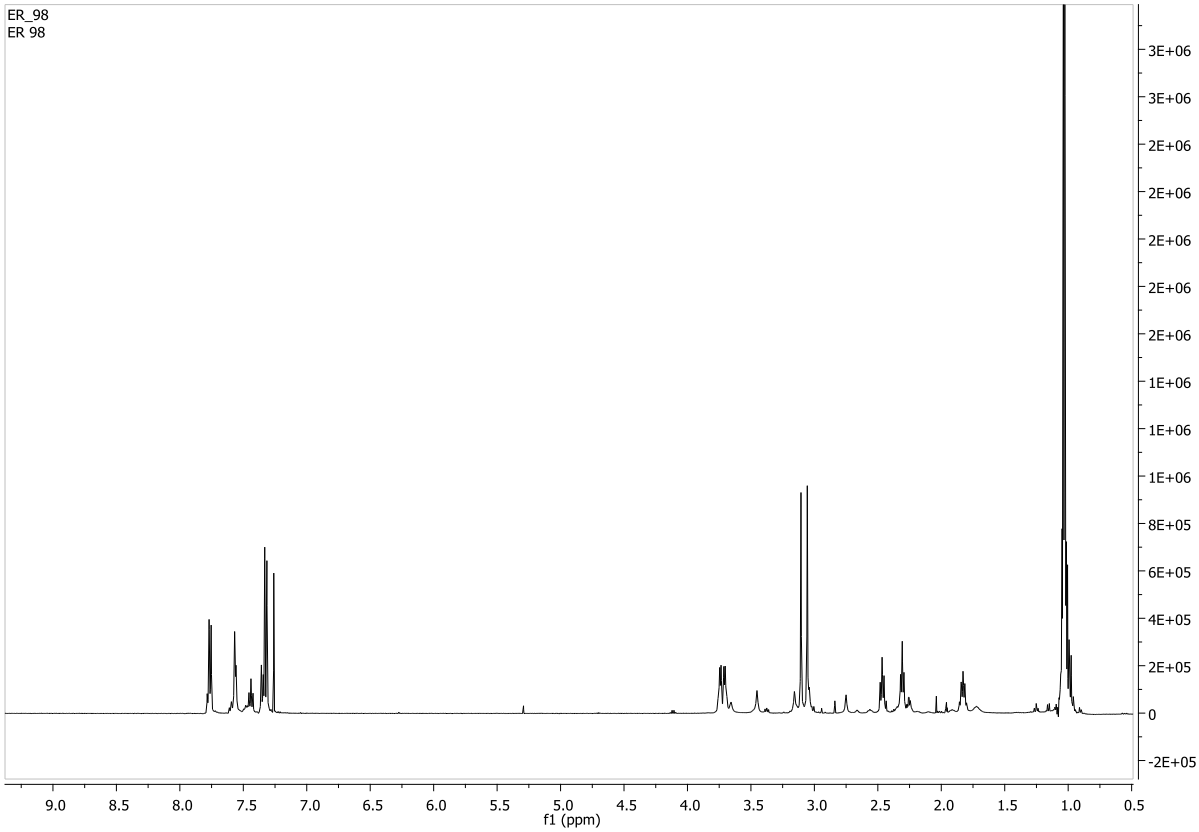


Figure S40 ^{1}H NMR spectrum (500 MHz, $CDCl_3$).

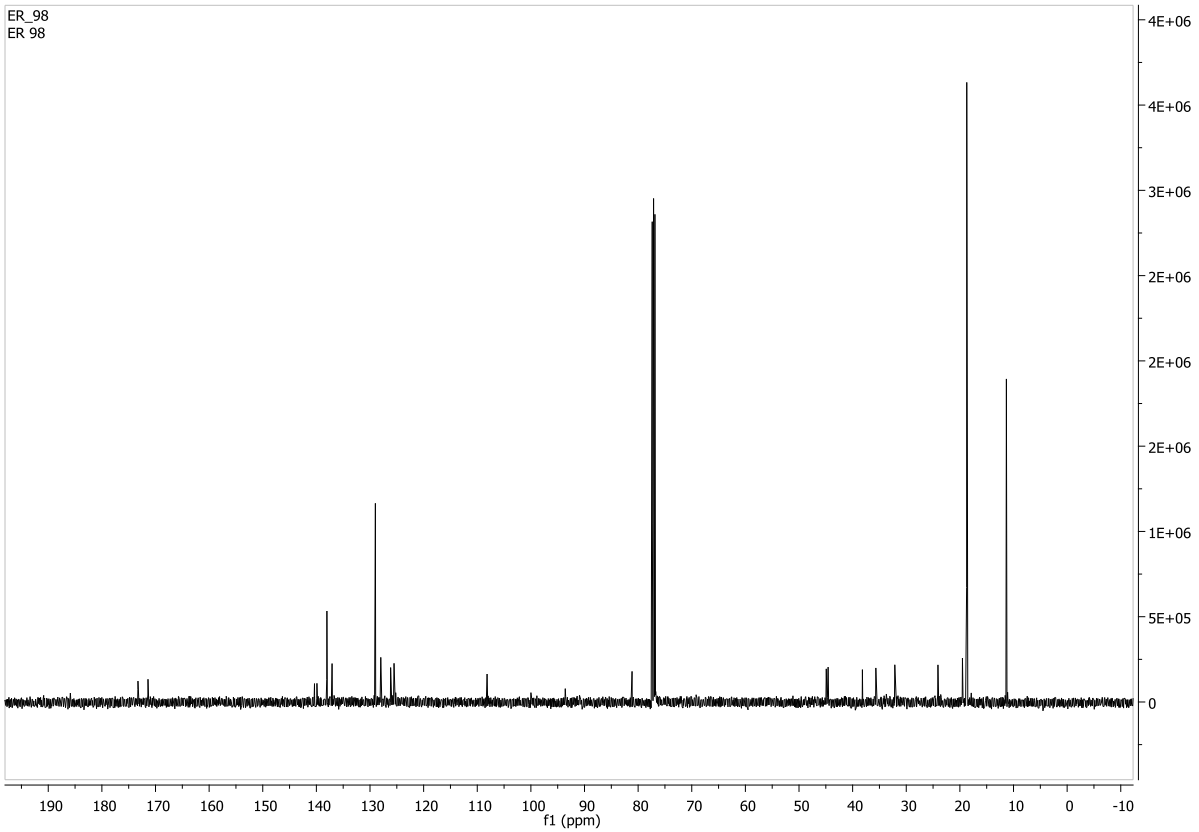


Figure S41 ^{13}C NMR spectrum (126 MHz, $CDCl_3$).

Trivalent alkyne axle (9)

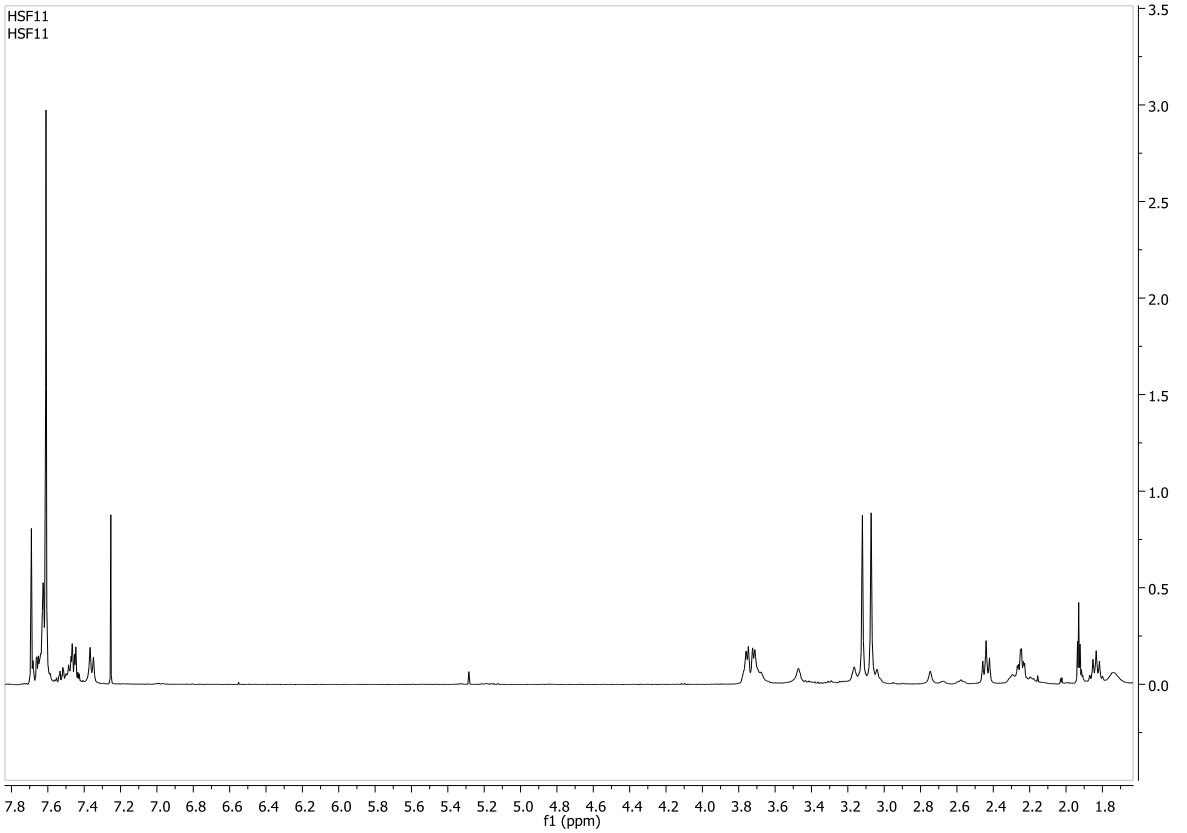


Figure S42 ^{1}H NMR spectrum (500 MHz, $CDCl_3$).

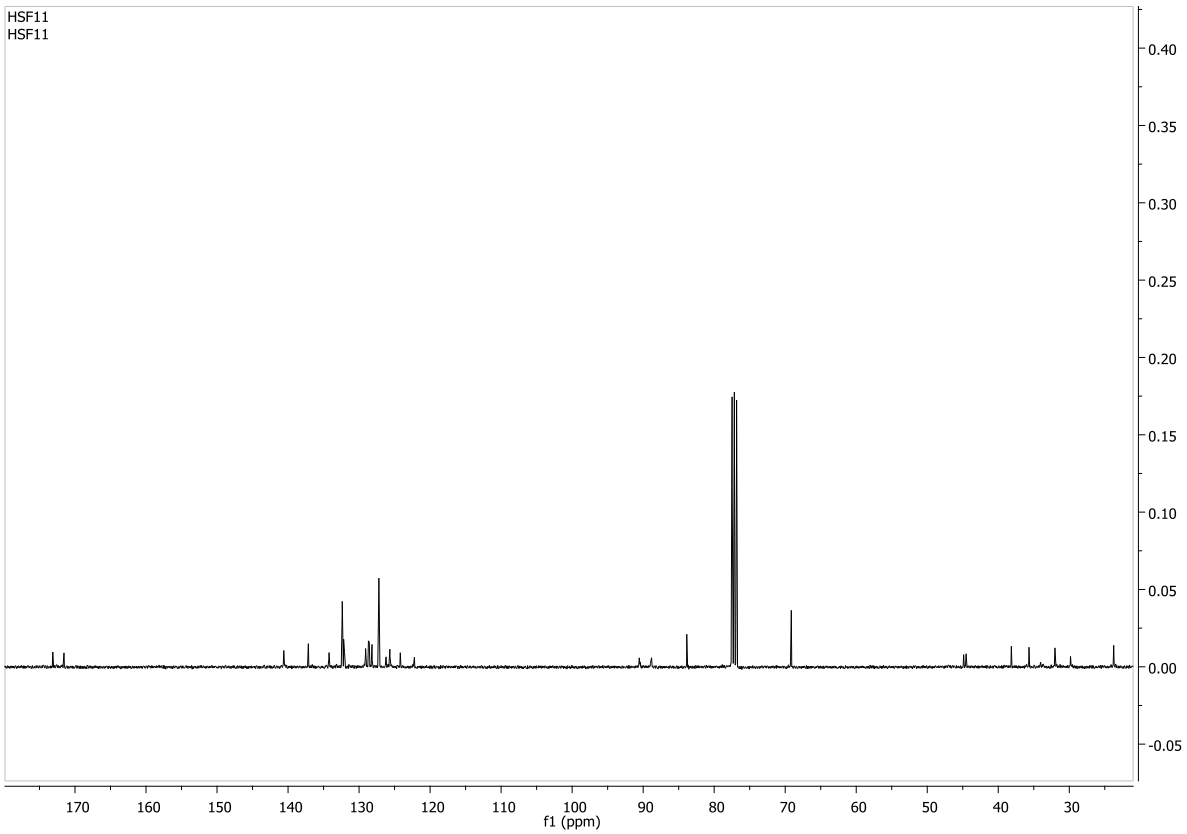


Figure S43 ^{13}C NMR spectrum (126 MHz, $CDCl_3$).

Divalent alkyne axle (8)

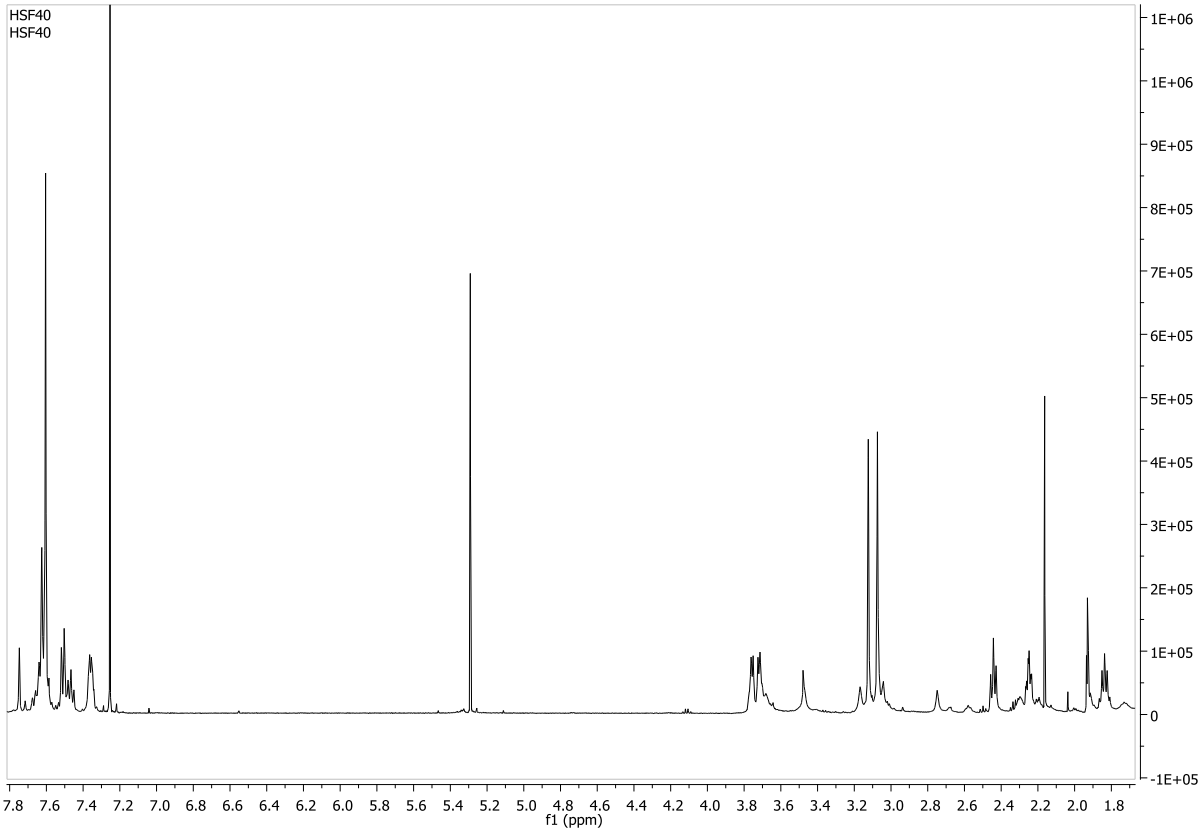


Figure S44 ^{1}H NMR spectrum (500 MHz, $CDCl_3$).

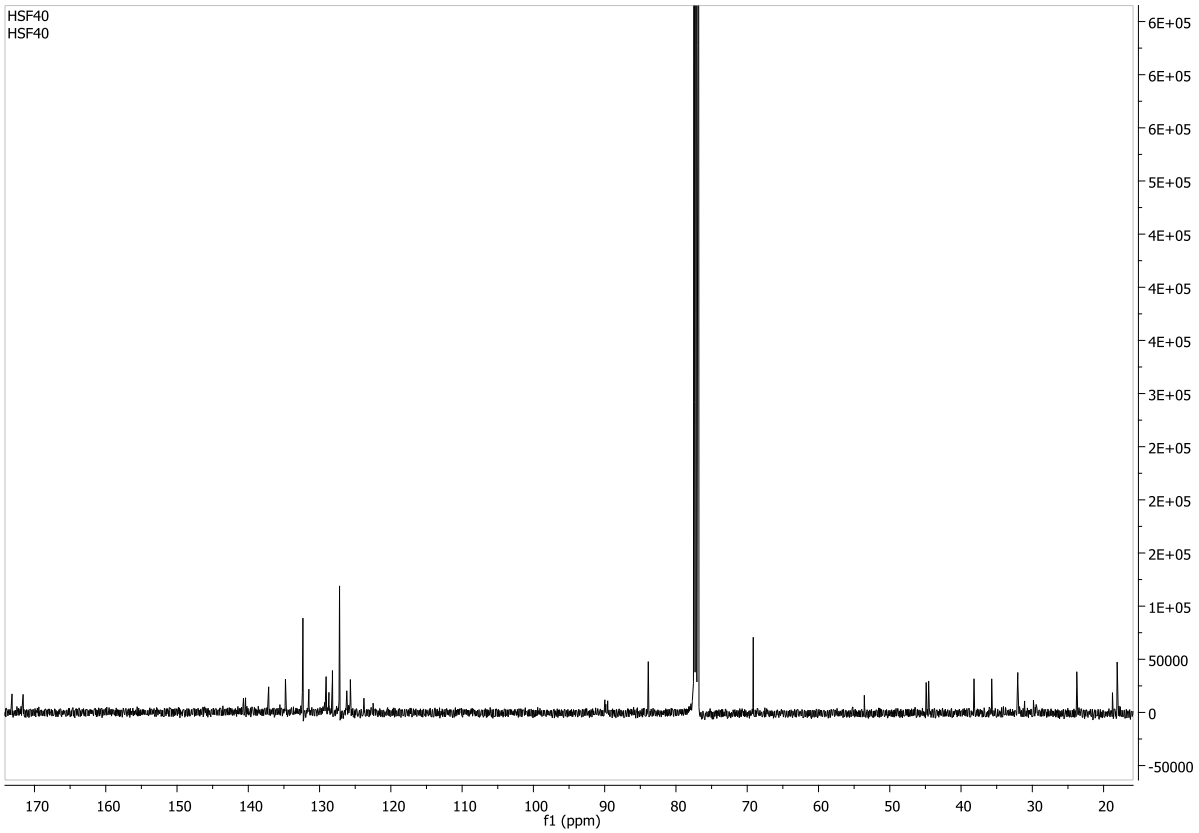


Figure S45 ^{13}C NMR spectrum (126 MHz, $CDCl_3$).

tert-Butyl 2-(*N*-methyl-2,2,2-triphenylacetamido)etylmethylcarbamate

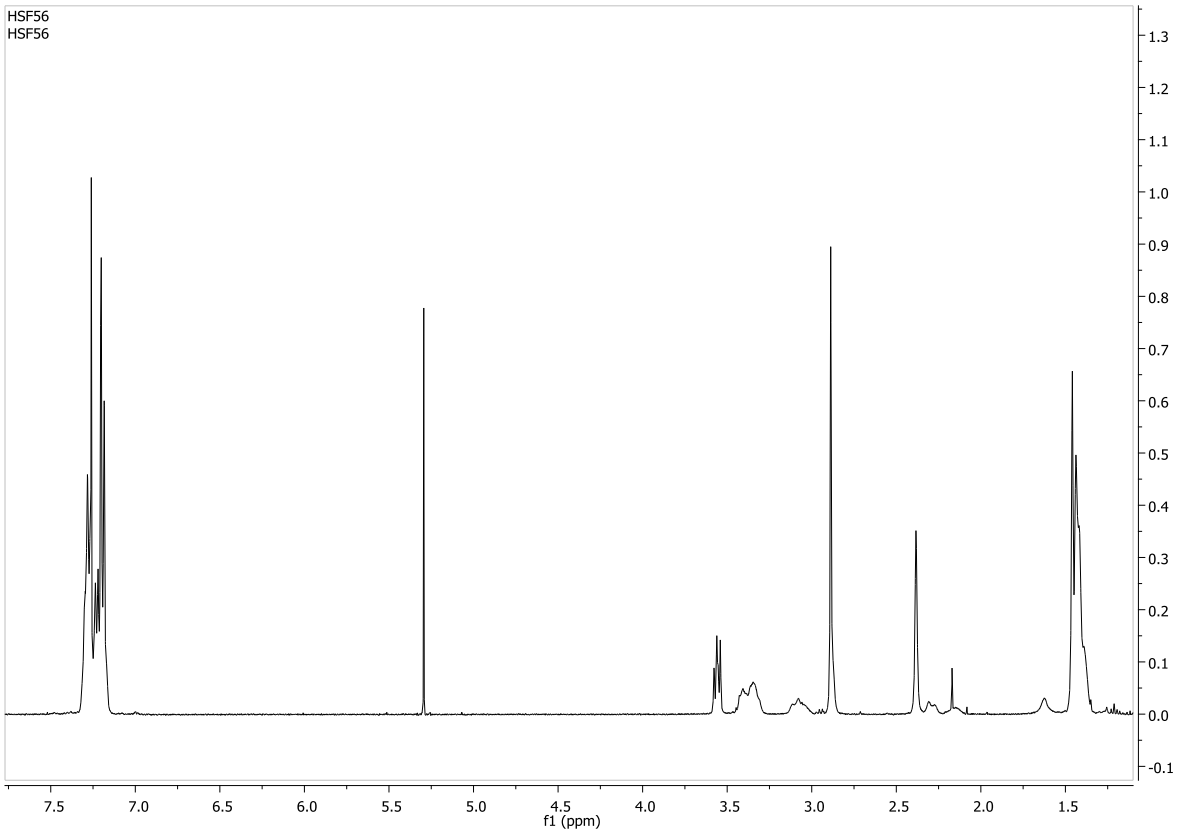


Figure S46 ^{1}H NMR spectrum (400 MHz, $CDCl_3$).

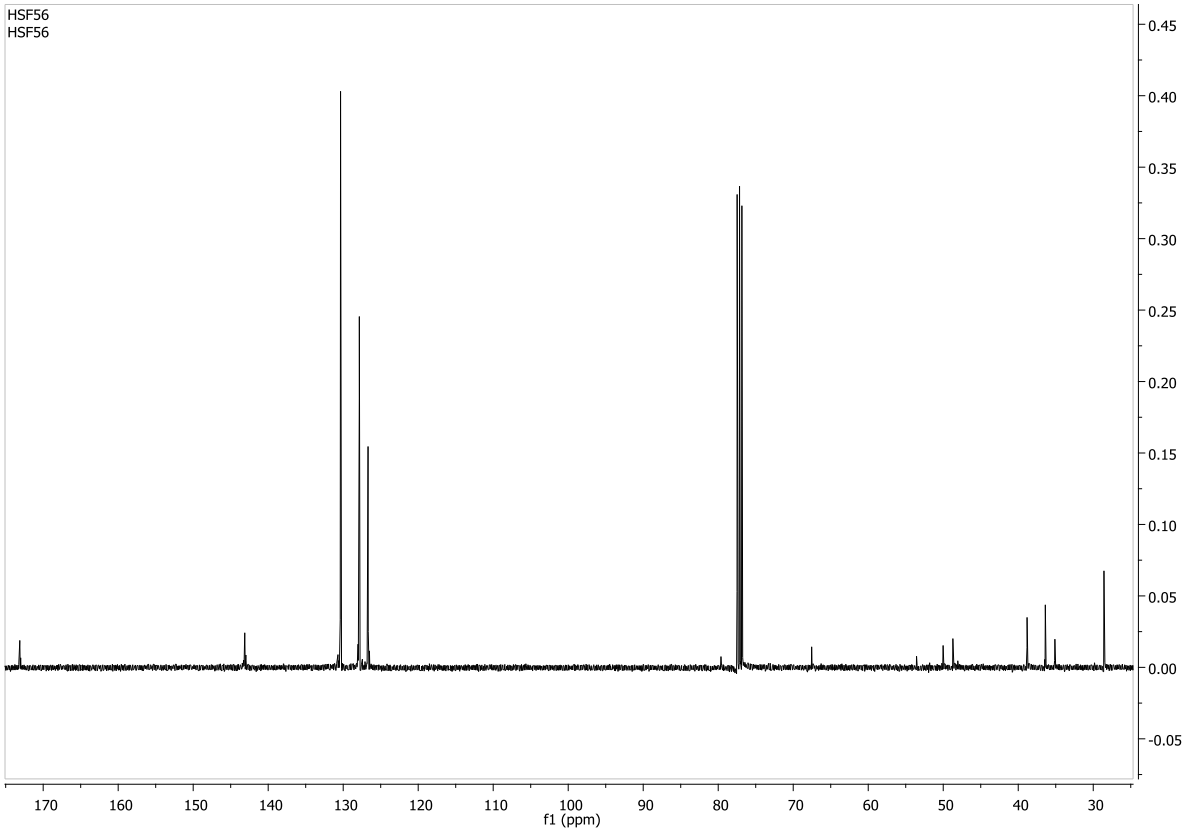


Figure S47 ^{13}C NMR spectrum (101 MHz, $CDCl_3$).

N-Methyl-*N*-(2(methylamino)ethyl)-2,2,2-triphenylacetamide

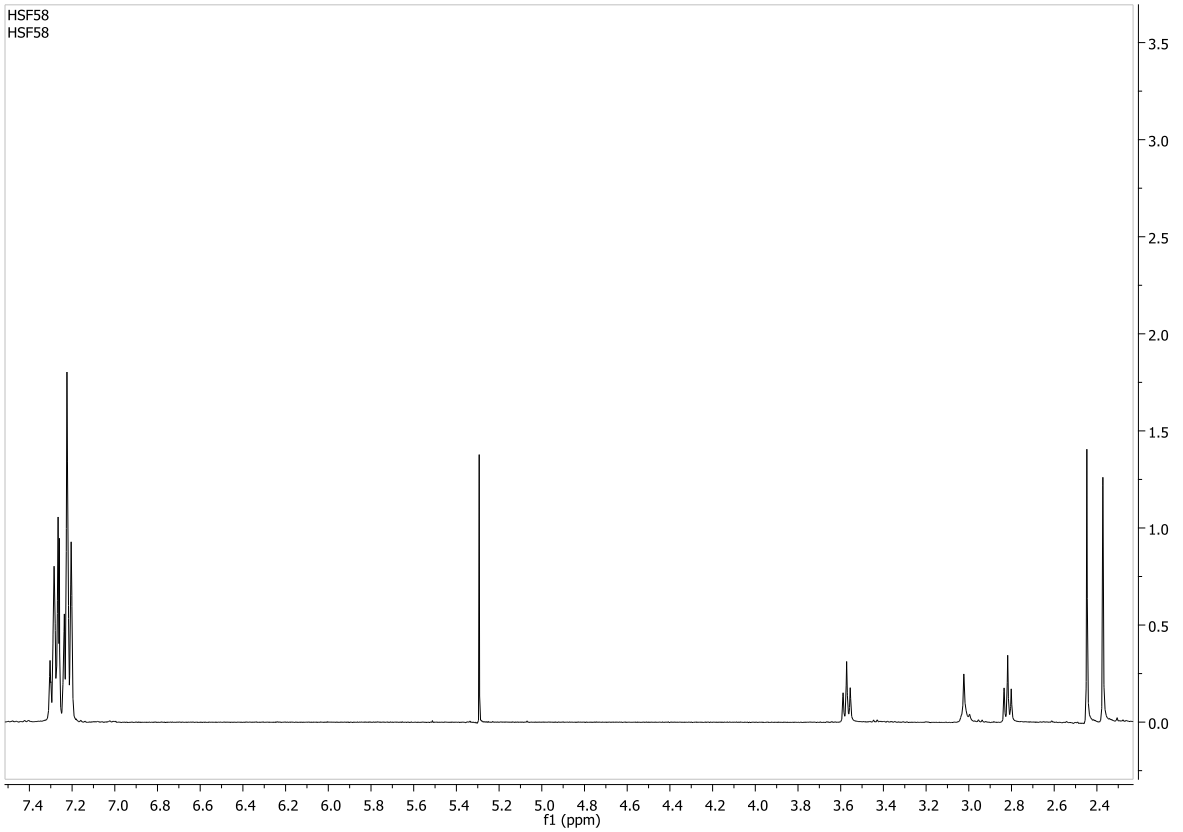


Figure S48 ^{1}H NMR spectrum (400 MHz, $CDCl_3$).

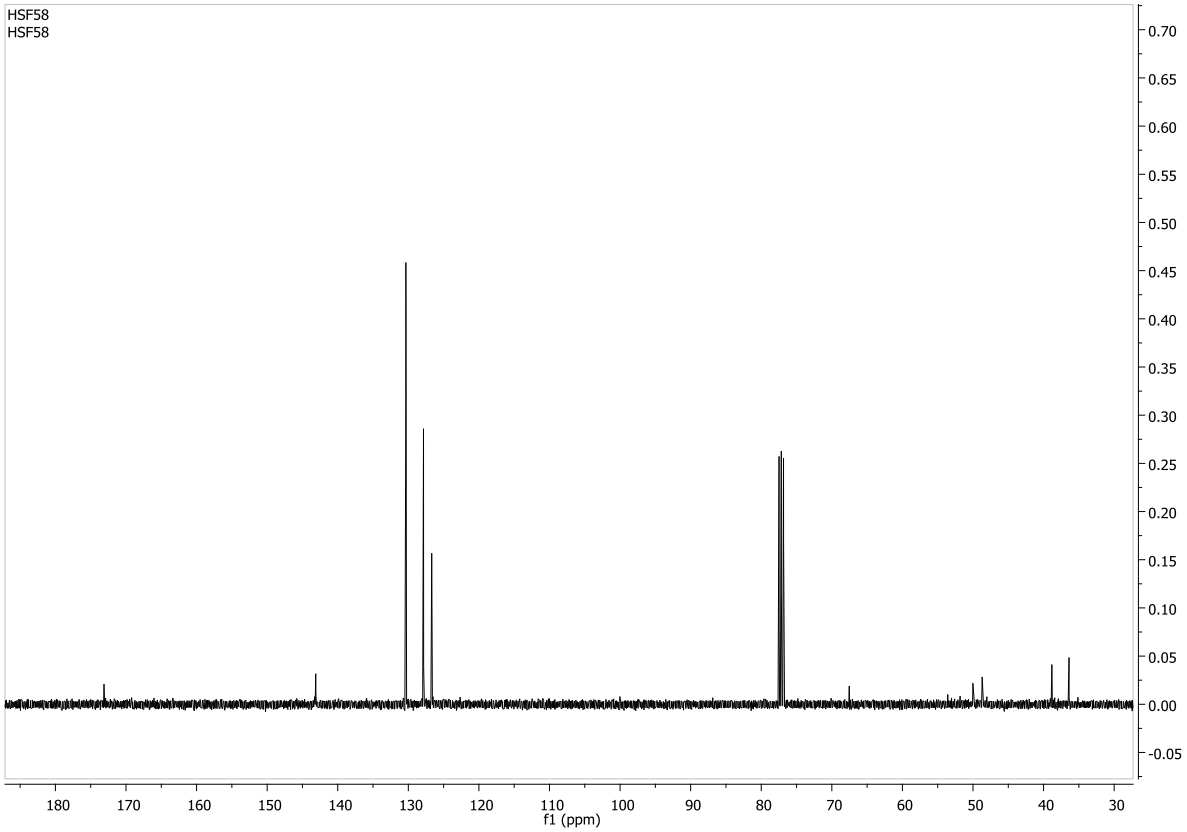


Figure S49 ^{13}C NMR spectrum (101 MHz, $CDCl_3$).

N-(2-(*N*-Methyl-2,2,2-triphenylacetamido)ethyl)-*N*-methylhex-5-ynamide

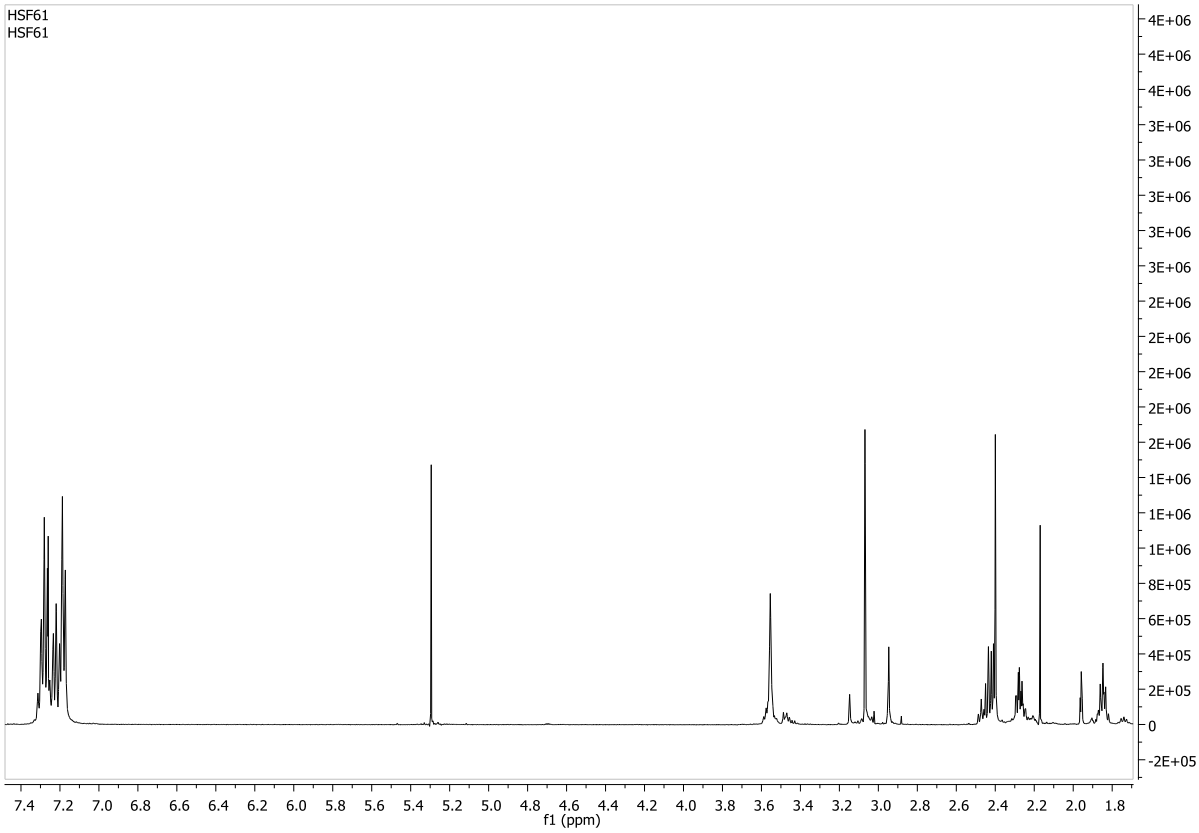


Figure S50 ^{1}H NMR spectrum (500 MHz, $CDCl_3$).

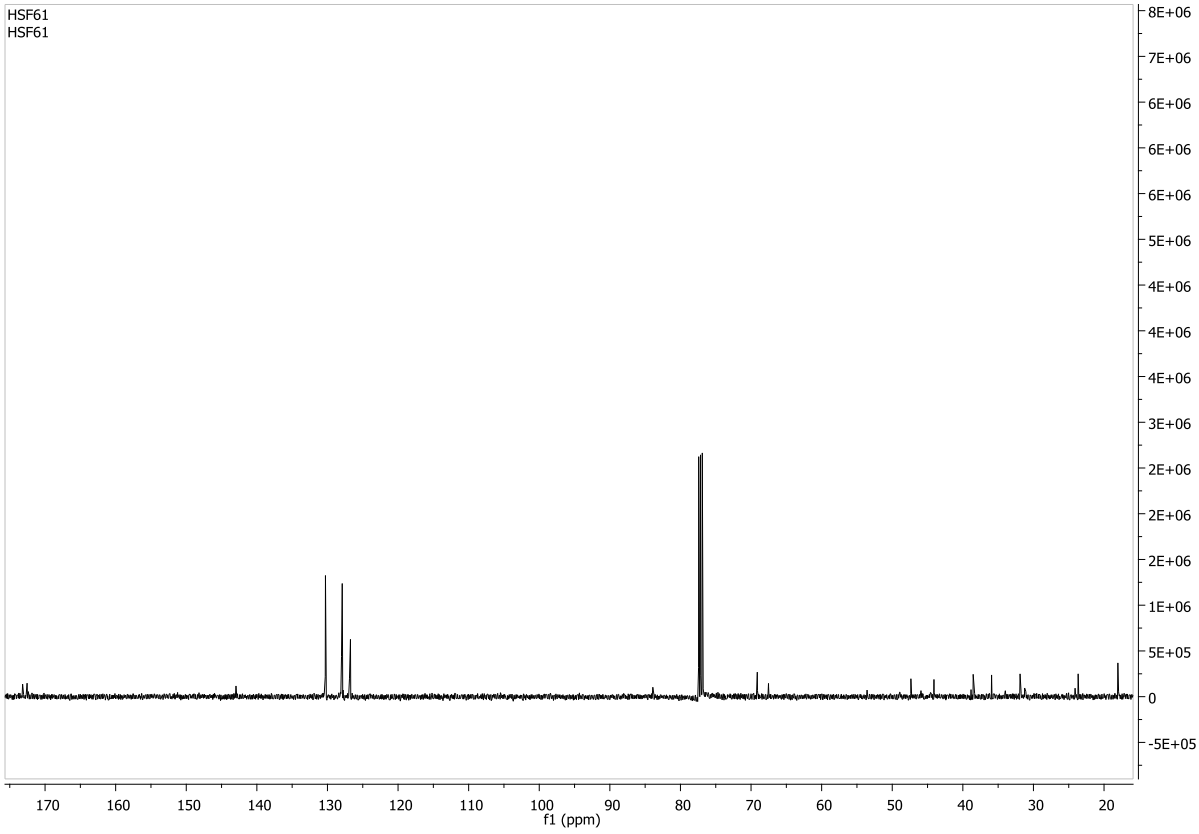


Figure S51 ^{13}C NMR spectrum (126 MHz, $CDCl_3$).

Trivalent host molecule (3)

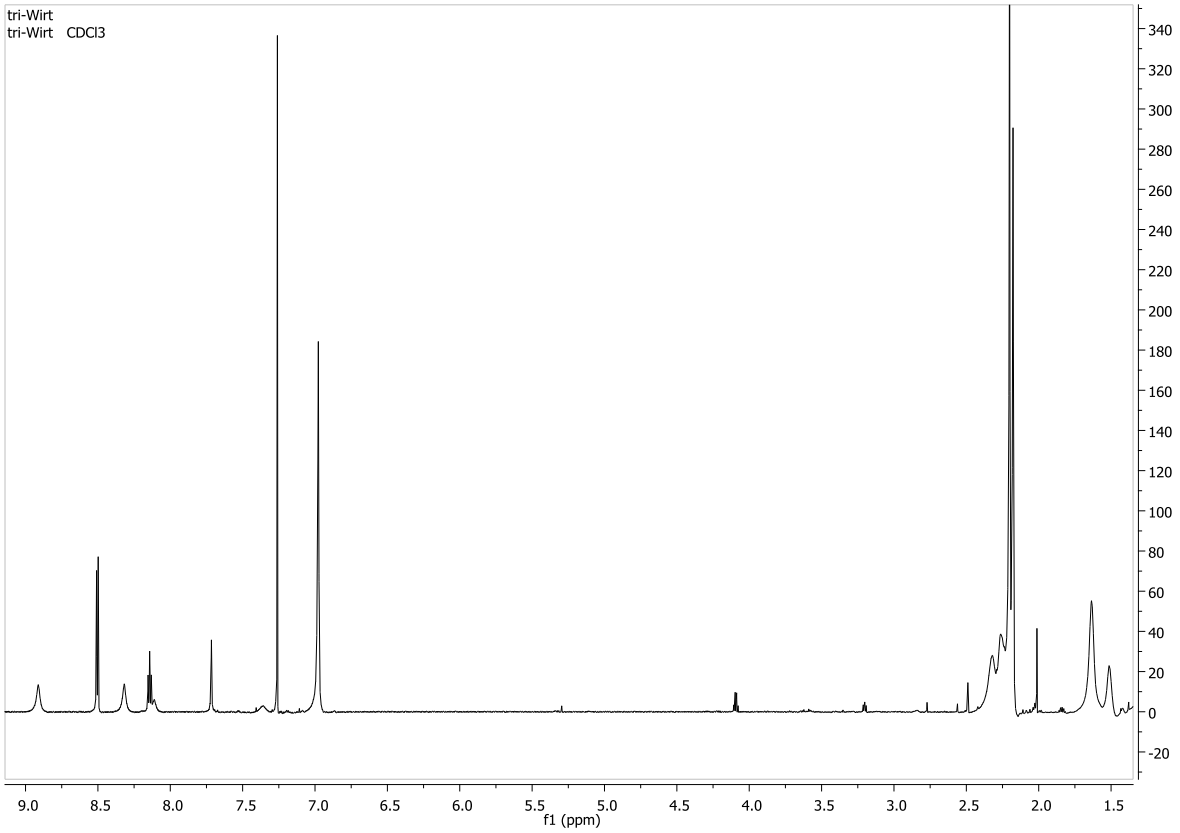


Figure S52 ^{1}H NMR spectrum (700 MHz, $CDCl_3$).

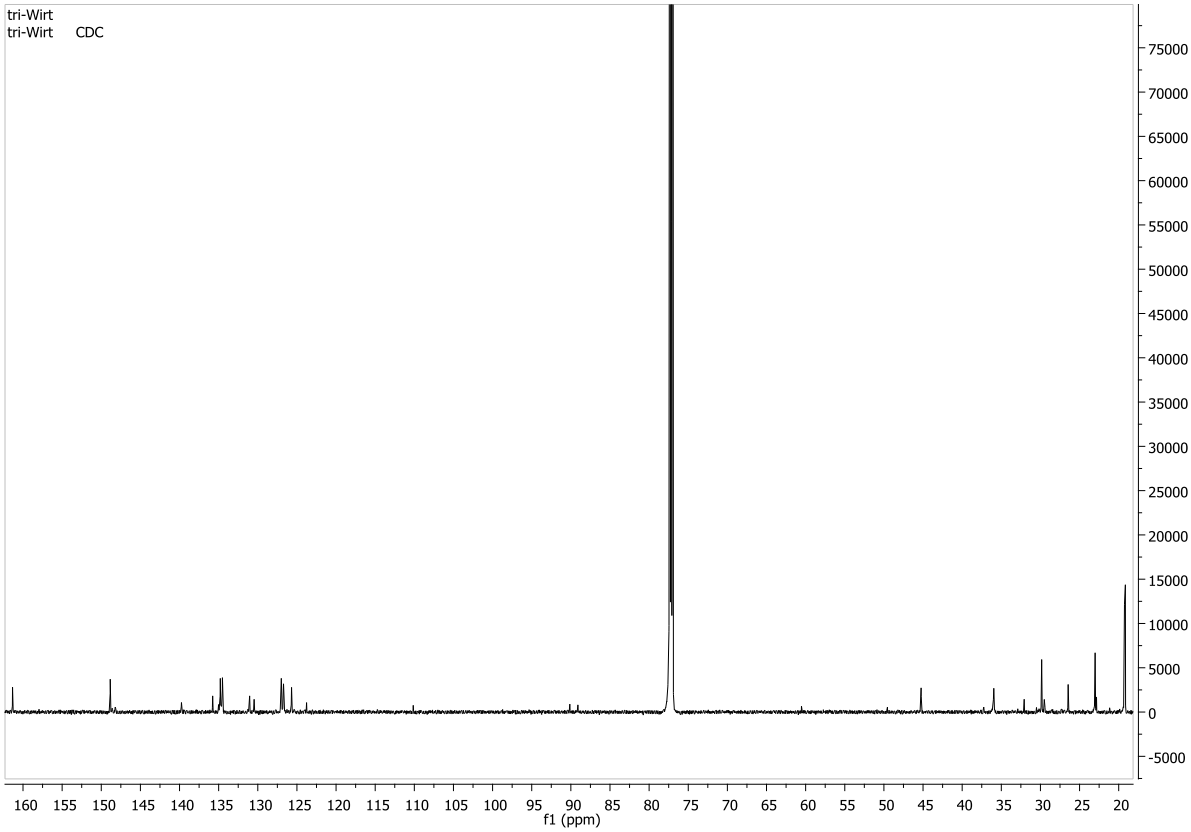


Figure S53 ^{13}C NMR spectrum (176 MHz, $CDCl_3$).

Divalent host molecule (2)

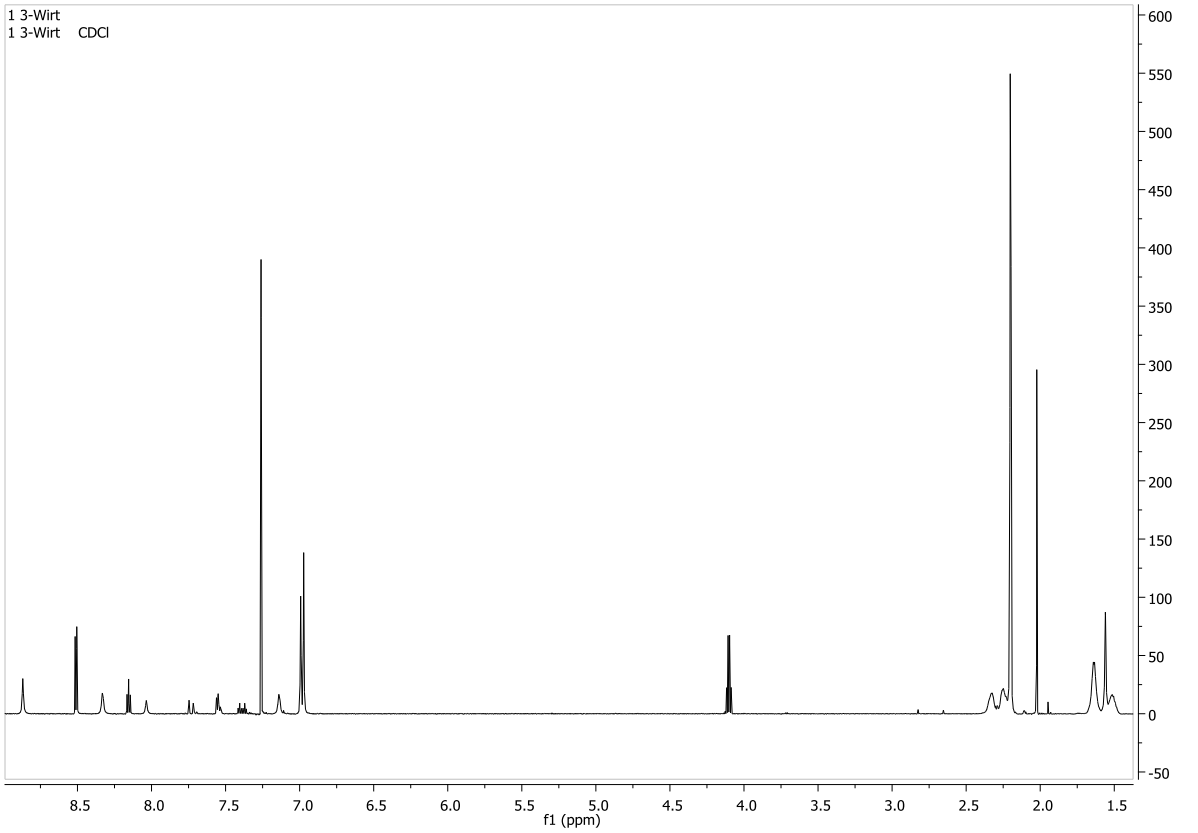


Figure S54 ^{1}H NMR spectrum (700 MHz, $CDCl_3$).

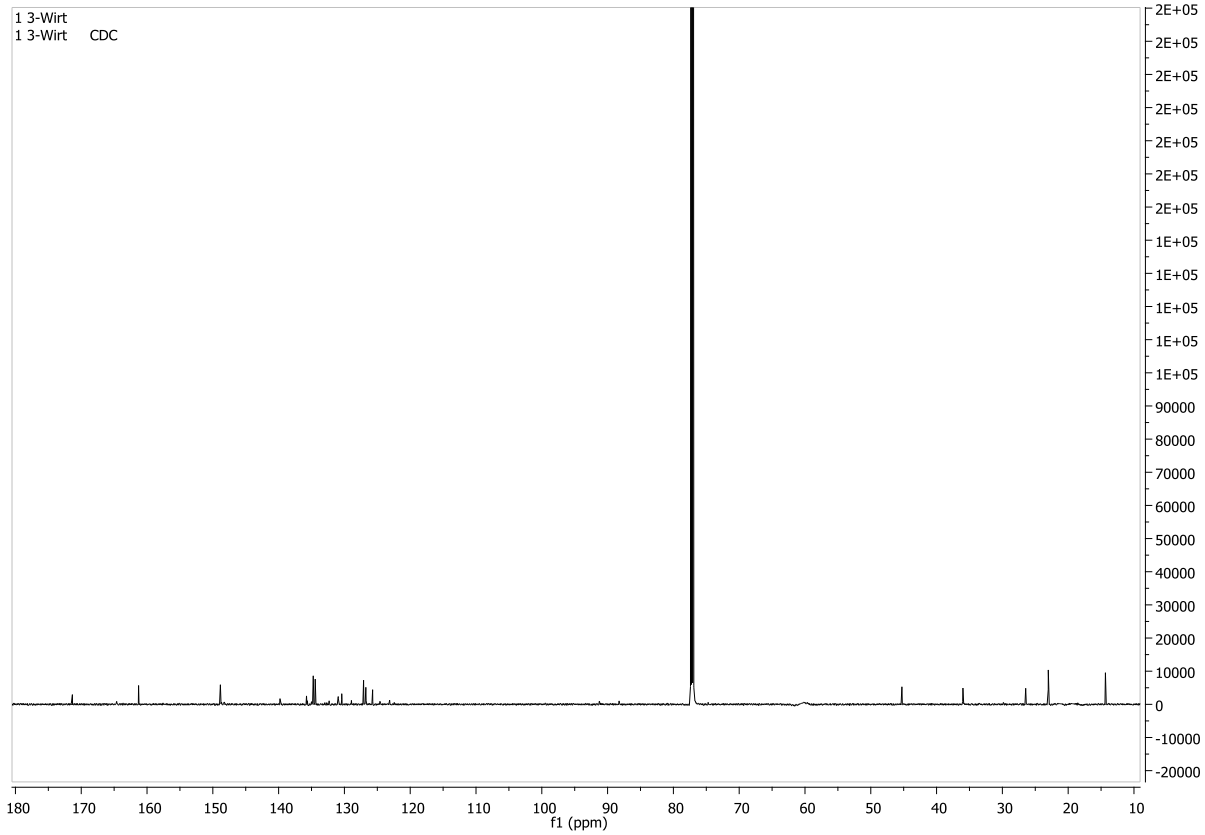


Figure S55 ^{13}C NMR spectrum (176 MHz, $CDCl_3$).

The ^{13}C NMR spectra of the three rotaxanes below are difficult to evaluate because of the overlap of several sets of signals that can be traced back to the existence of *cis*- and *trans*-isomers of the diamide stations coinciding with dynamic processes.

Trivalent rotaxane (13)

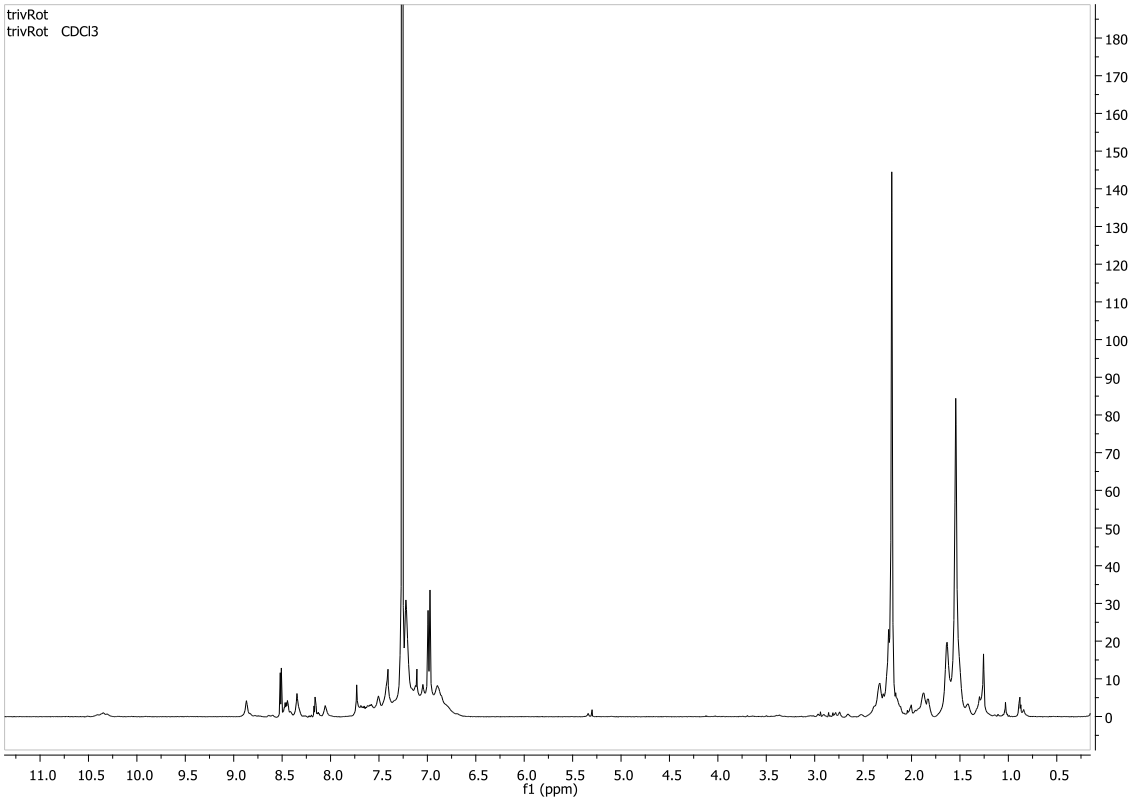


Figure S56 ^{1}H NMR spectrum (700 MHz, $CDCl_3$).

Divalent rotaxane (12)

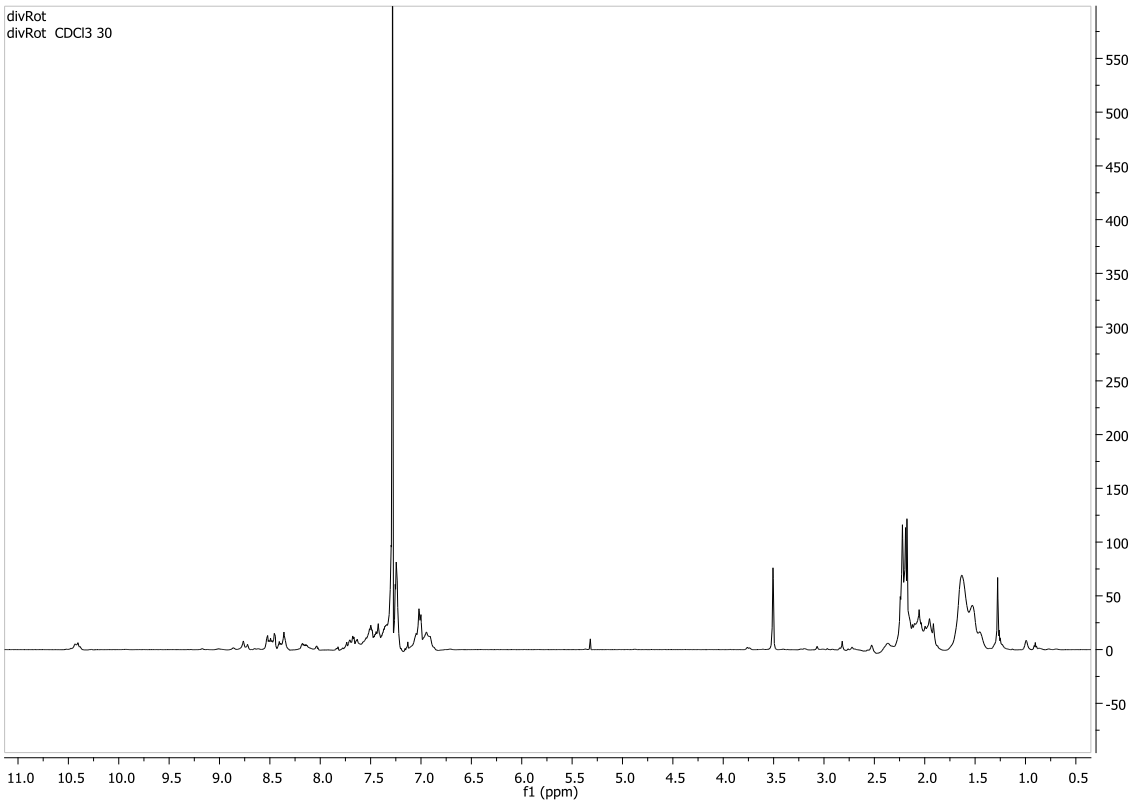


Figure S57 ^{1}H NMR spectrum (700 MHz, $CDCl_3$).

Monovalent rotaxane (14)

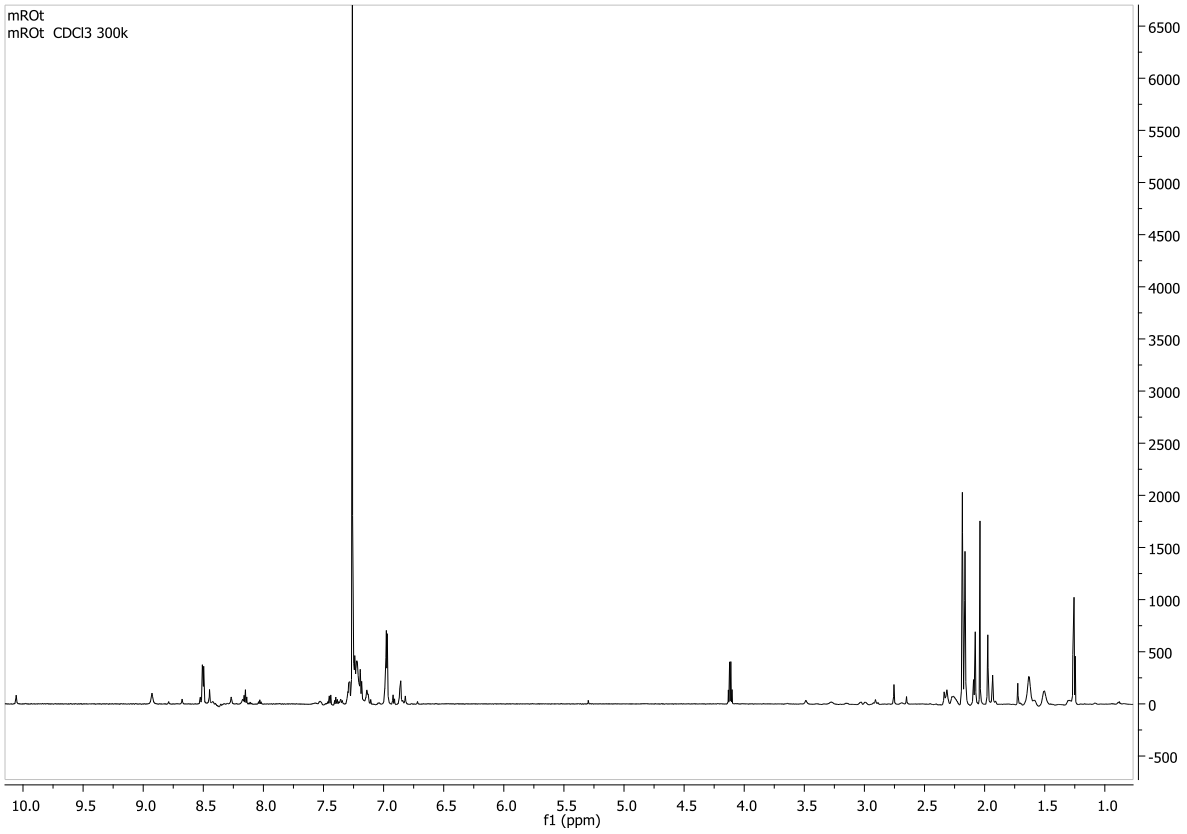


Figure S58 ^{1}H NMR spectrum (700 MHz, $CDCl_3$).

10. References

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