# Electronic Supplementary Information

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## Experimental Procedures

### Instrumentation

**NMR spectroscopy:** The $^{1}$H NMR, $^{13}$C NMR, and $^{29}$Si NMR were recorded on high-field Bruker spectrometers (600 and 500 MHz) equipped with a broadband inverse gradient probe head and a high-field JEOL spectrometer (500 MHz), equipped with a 5 mm wide wideband probe. The spectra were referenced to the residual solvent signal (chloroform-*d* – 7.24 ppm, dichloromethane-$d_2$ – 5.32 ppm, toluene-$d_8$ – 7.00 ppm). Two-dimensional NMR spectra were recorded with 2048 data points in the $t_2$ domain and up to 1024 points in the $t_1$ domain, with a 1 s recovery delay.

**Mass spectrometry:** The MALDI mass spectra were recorded on JEOL JMS-S3000 SpiralTOF™-plus Ultra-High Mass Resolution MALDI-TOF MS. ESI mass spectra were recorded on Bruker qTOF compact and Bruker Q-TOF-MS/MS maXis impact spectrometers.

**X-ray diffraction data:** Single-crystal X-ray diffraction data for **10a–A** and **10b–A** were collected at 100 K on XtaLAB Synergy R, DW system (HyPix-Arc 150) κ-geometry diffractometer using Cu Kα radiation. Data reduction and analysis were carried out with the CrysAlis Pro programs (CrysAlis PRO. CrysAlisPro: Rigaku Oxford Diffraction 1.171.41.80a). The structures were solved by direct methods and refined with the full-matrix least-squares technique using the SHELXS[1] and SHELXL-2018/3[2] programs. Hydrogen atoms were placed at calculated positions. Before the last refinement cycle, all H atoms were fixed and allowed to ride on their parent atoms. Anisotropic displacement parameters were refined for all non-hydrogen atoms in **10a-A** and for all non-hydrogen atoms with occupancy factor > 0.5 in **10b-A**. SIMU and ISOR restraints were applied in **10a-A** for disordered components. The geometry of the disordered phenyl rings in **10a-A** was fitted to a regular hexagon applying AFIX constraints, and the geometry of the disordered THF molecules in **10a-A** was restrained by SADI command. In **10b-A** geometry of the disordered ethyl acetate molecules were restrained by SADI and FLAT commands, and the geometry of the triazole ring of the minor component of the disordered spherosilicate stoppers was restrained by DFIX, SADI, and FLAT commands.

Crystal data for compound **10a-A** $C_{73}H_{63}N_3O_{13}Si_8$, $C_{32}H_{34}N_2O_2$, $3(C_4H_8O)$, $M$ = 2109.90, triclinic, $P$-1, $a$ = 13.215(2) Å, $b$ = 13.961(2) Å, $c$ = 32.976(3) Å, $\alpha$ = 80.96(2)º, $\beta$ = 81.34(3)º, $\gamma$ = 65.17(3)º, $V$ = 5428.6(18) Å$^3$, $Z$ = 2, $D_c$ = 1.291 Mg m$^{-3}$, $T$ = 100(2) K, $R$ = 0.0905, $wR$ = 0.2322 (8270 reflections with $I > 2\sigma(I)$) for 1633 variables, CCDC 2249743;

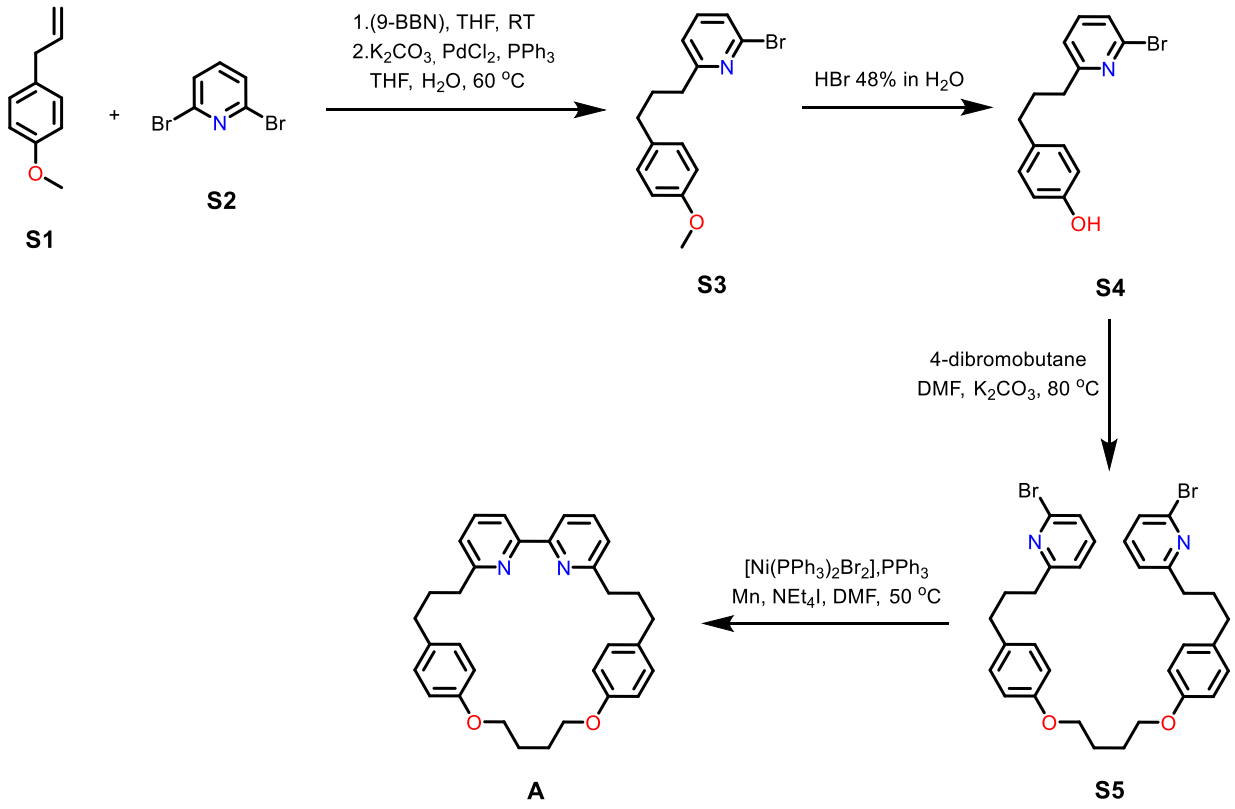
Crystal data for compound **10b-A**: $C_{59}H_{91}N_3O_{13}Si_8$, $C_{32}H_{34}N_2O_2$, $C_4H_8O_2$, $M$ = 1841.78, triclinic, $P$-1, $a$ = 14.151(2) Å, $b$ = 15.072(2) Å, $c$ = 46.449(3) Å, $\alpha$ = 89.53(2)º, $\beta$ = 84.35(2)º, $\gamma$ = 87.50(2)º, $V$ = 9849(2) Å$^3$, $Z$ = 4, $D_c$ = 1.242 Mg m$^{-3}$, $T$ = 100(2) K, $R$ = 0.0550, $wR$ = 0.1522 (32093 reflections with $I > 2\sigma(I)$) for 2865 variables, CCDC 2249744;

**Thermogravimetry:** The thermogravimetric analysis was carried out with METTLER TOLEDO TGA/DSC 3+. The heating rate was 5 K/min, and the inert gas (nitrogen) flow was set to 50 mL/min.

## Synthesis

### The synthesis of macrocycle A.

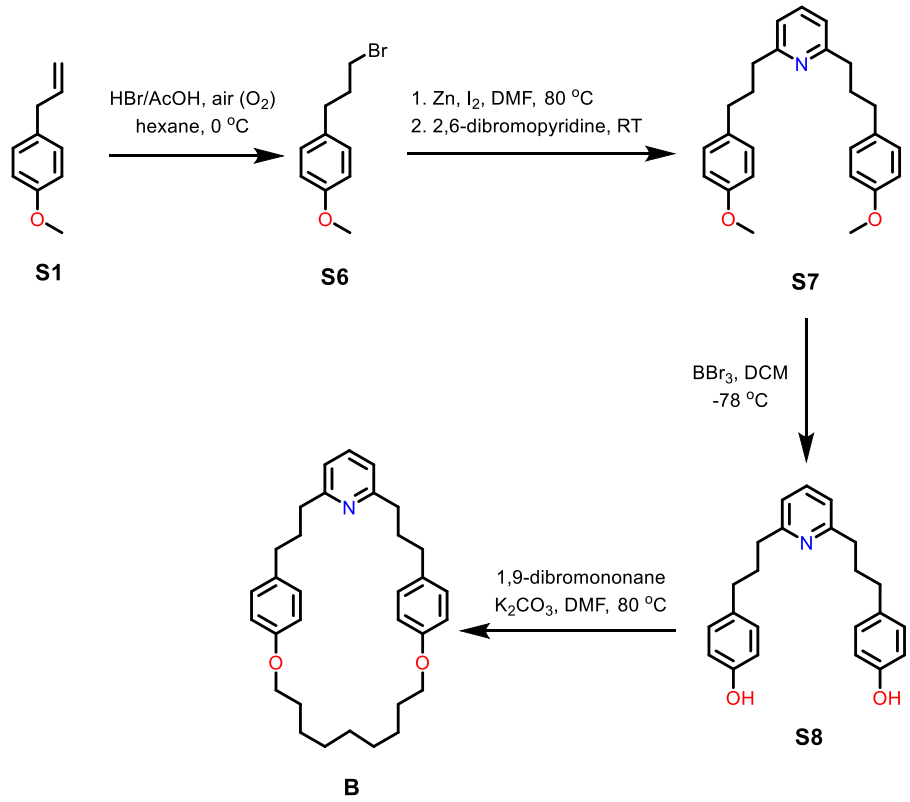
Compounds **S3**,[3] **S4**,[4] **S5**,[4] and **A**[4] were synthesized as described in the literature.




**Scheme S 1.** The synthesis of macrocycle **A.**

**The synthesis of macrocycle B.**

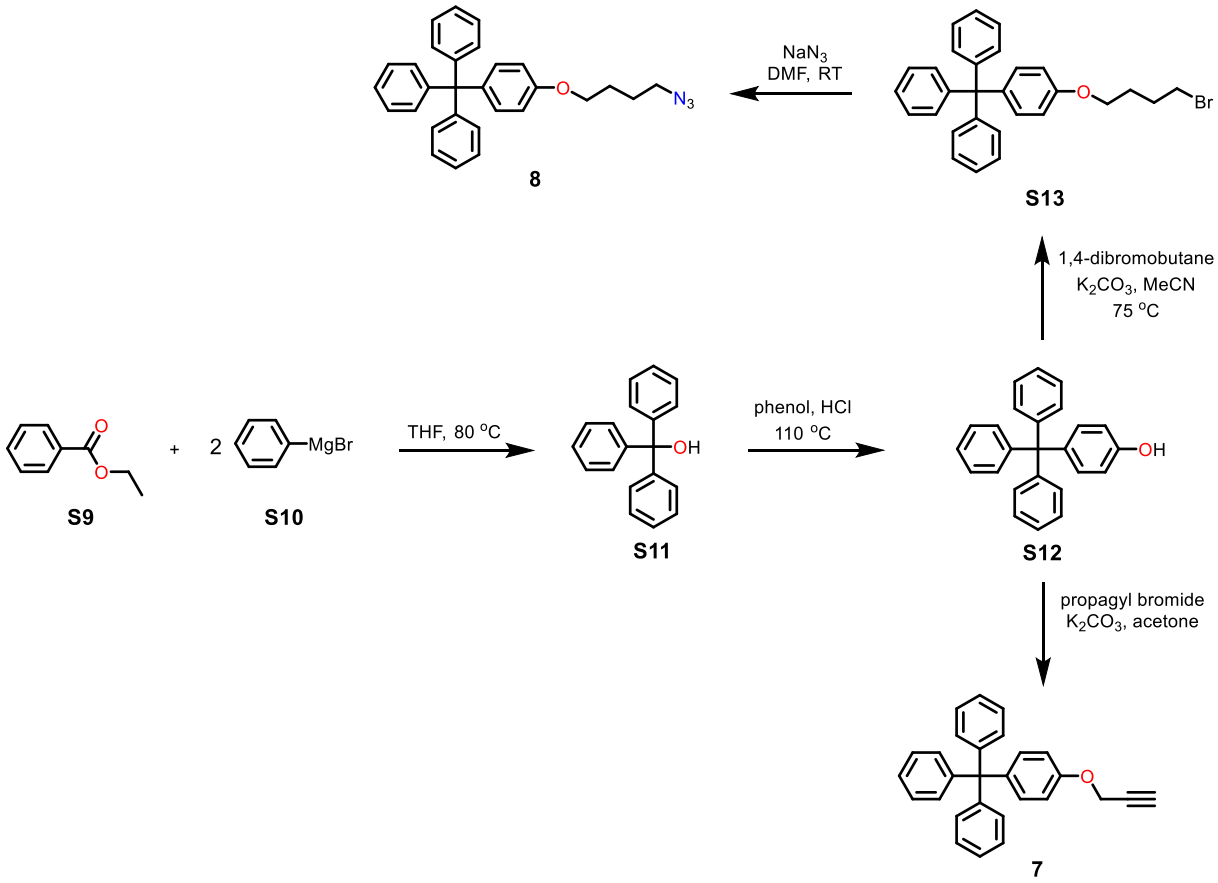
Compounds **S6**,[5] **S7**,[6] and **S8**[6] were synthesized as described in the literature.




**Scheme S 2.** The synthesis of macrocycle **B.**

**The synthesis of trityl stoppers.**

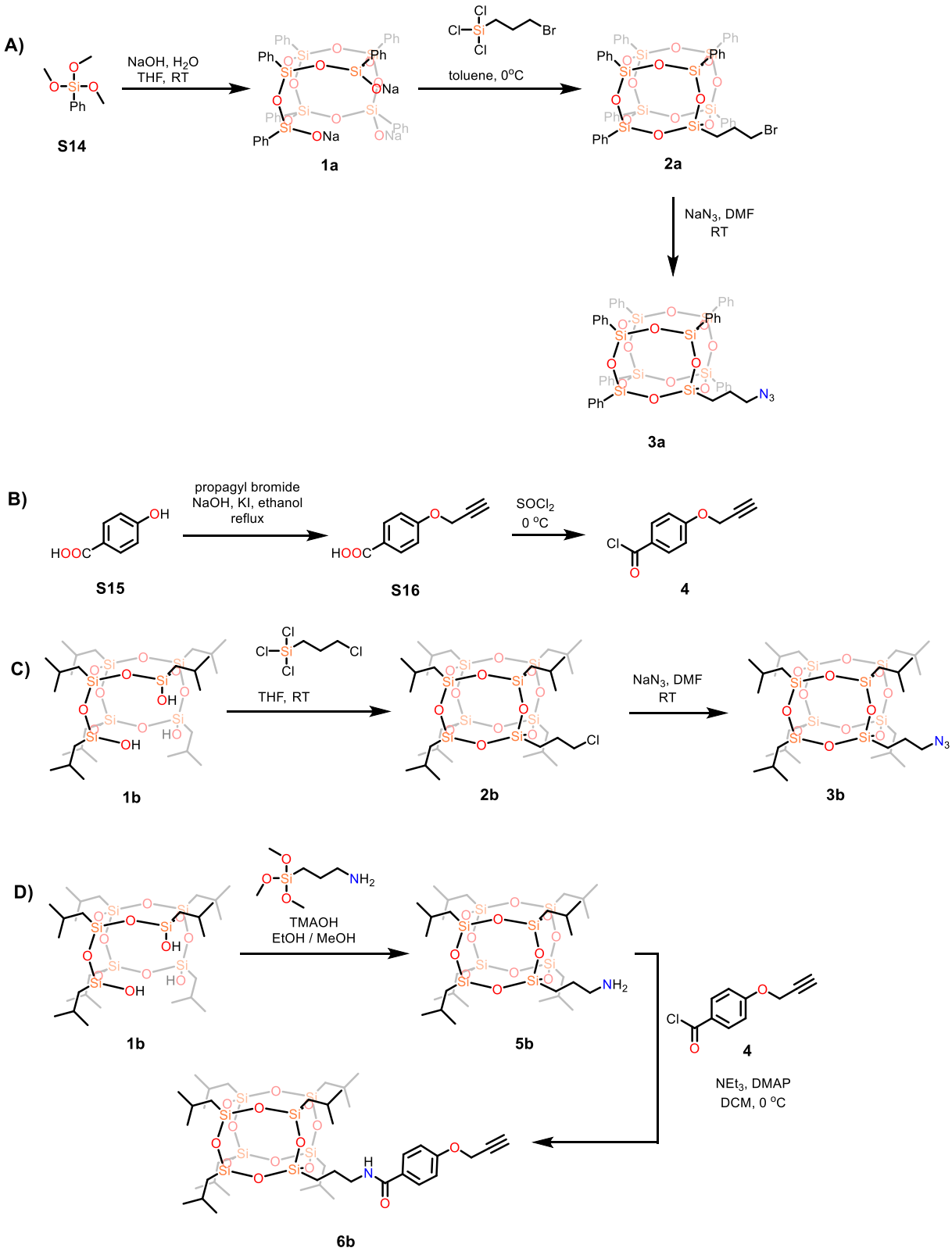
Compounds **S13**,[7] and **7**[8] were synthesized as described in the literature.




**Scheme S 3.** The synthesis of **7** and **8.**

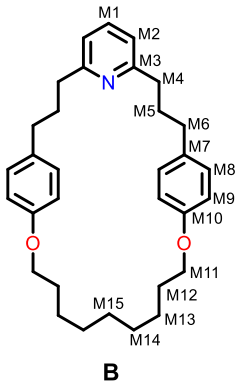
**The synthesis of POSS stoppers.**

Compounds **1a**,[9] **2a**,[9] **3a**,[9] **2b**[10], **3b**[10], and **5b**[11] were synthesized as described in the literature.




**Scheme S 4.** The synthesis of A) **3a**, B) **4**, C) **3b**, and D) **6b**.

**Macrocycle B**



**B**

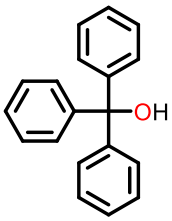
In a 100 mL round-bottom flask containing the solution of 4,4'-(pyridine-2,6-diylbis(propane-3,1-diyl))diphenol **S8** (50 mg, 0.144 mmol) in DMF (50 mL), 1,9-dibromononane (29 µl, 0.143 mmol) and $K_2CO_3$ (500 mg, 3.62 mmol) were added. The reaction mixture was stirred at 80 °C for 48 hours. The solvent was removed under reduced pressure. The residue was partitioned between DCM (50 mL) and $H_2O$ (50 mL). The water phase was extracted with DCM (2 x 50 mL). The collected organic extract was washed with water and brine and dried over anhydrous $Na_2SO_4$. The drying agent was removed *via* gravity filtration, and the filtrate was evaporated to dryness. Flash chromatography (DCM) further purified the resultant crude oil to provide **B** as a colorless oil (22.2 mg, 33%).

**$^1$H NMR** (500 MHz, chloroform-*d*, 300 K) δ (ppm): 7.46 (t, 1H, $^3J$ = 7.6 Hz, $H_{M1}$), 7.03 (d, 4H, $^3J$ = 8.5 Hz, $H_{M8}$), 6.94 (d, 2H, $^3J$ = 7.6 Hz, $H_{M2}$), 6.74 (d, 4H, $^3J$ = 8.6 Hz, $H_{M9}$), 3.92 (t, 4H, $^3J$ = 6.3 Hz, $H_{M11}$), 2.79 (t, 4H, $^3J$ = 7.5 Hz, $H_{M4}$), 2.55 (t, 4H, $^3J$ = 8.2 Hz, $H_{M6}$), 2.06-1.97 (m, 4H, $H_{M5}$), 1.74 (qu, 4H, $^3J$ = 6.6 Hz, $H_{M12}$), 1.50-1.40 (m, 4H, $H_{M13}$), 1.37-1.31 (m, 6H, $H_{M14}$, $H_{M15}$).

**$^{13}$C NMR** (125 MHz, chloroform-*d*, 300 K) δ (ppm): 161.4, 157.2, 136.4, 134.4, 129.3, 120.0, 114.4, 67.5, 37.7, 34.6, 32.2, 28.59, 28.57, 27.9, 25.4.

**HRMS** (ESI+, TOF) *m/z*: 472.3249 $[M+H]^+$, calcd. for $C_{32}H_{42}NO_2^+$ 472.3210

**Triphenylmethanol S11** was obtained under modified literature conditions.[12]



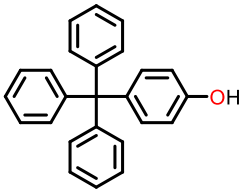
**S11**

In a 25 mL two-neck round-bottom flask, THF (10 mL) and ethyl benzoate **S9** (1.0 g, 6.6 mmol) were introduced. The solution was heated to 80 °C under a nitrogen atmosphere. Subsequently, the solution of phenylmagnesium bromide **S10** in diethyl ether (3 M, 2.41 g, 13.3 mmol) was introduced. The reaction mixture was stirred at 80 °C for 4 hours. After this time, the mixture was cooled to room temperature and quenched by adding 10% hydrochloric acid. The solution was neutralized by adding the saturated aqueous $NaHCO_3$ solution. The crude product was extracted with DCM (3 x 50 mL). The collected organic extracts were combined, washed with water and

brine, and dried over anhydrous $Na_2SO_4$. The drying agent was removed by gravity filtration, and the filtrate was evaporated to dryness. The resultant yellowish solid was recrystallized from DCM/methanol (1/9) to provide **S11** as a white solid (1.32 g, 76%).

**$^1$H NMR** (500 MHz, chloroform-*d*, 300 K) δ (ppm): 7.32-7.24 (m, 15H), 2.76 (s, 2H).

**4-Tritylphenol S12** was obtained under modified literature conditions.[7]

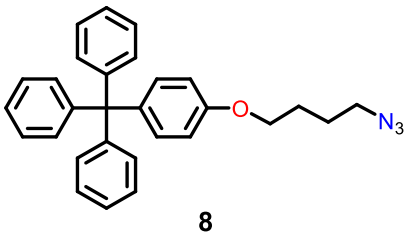



**S12**

In a 50 mL round-bottom flask, triphenylmethanol **S11** (0.5 g, 1.92 mmol), phenol (5.46 g, 58.02 mmol), and hydrochloric acid (1 mL, 37%) were introduced. The solution was heated to 110 °C and stirred for 20 hours under a nitrogen atmosphere. After cooling the mixture to room temperature, DCM (50 mL) and an aqueous solution of NaOH (1M, 50 mL) were introduced. The water phase was extracted with DCM (50 mL x 3). The collected organic extracts were washed with water and brine and dried over anhydrous $Na_2SO_4$. The drying agent was removed *via* gravity filtration, and the filtrate was evaporated to dryness. The resultant yellowish solid was recrystallized from DCM/methanol (1/9) to provide **S12** as a white solid (0.55 g, 85%).
**$^1$H NMR** (500 MHz, chloroform-*d*, 300 K) δ (ppm): 7.24-7.14 (m, 15H), 7.06-7.02 (m, 2H), 6.71-6.67 (m, 2H), 4.57 (s, 1H).

**((4-(4-Azidobutoxy)phenyl)methanetriyl)tribenzene 8** was obtained under modified literature conditions.[13]

***Azides are notoriously unstable and can pose a safety risk.***



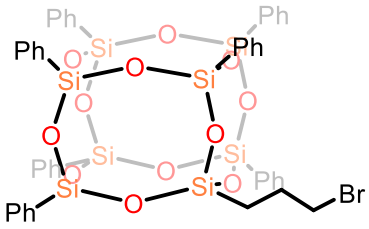

**8**

In a 50 mL round-bottom flask, 4-tritylphenol **S12** (371.4 mg, 0.79 mmol), sodium azide (102.7 mg, 1.58 mmol), and DMF (17 mL) were introduced. The flask was sealed with a rubber septum, and the solution was stirred at room temperature for 22 hours. The solvent was removed under reduced pressure. The residue was partitioned between DCM (50 mL) and $H_2O$ (50 mL). The water phase was extracted with DCM (2 x 50 mL). The collected organic extracts were washed with water and brine and dried over anhydrous $Na_2SO_4$. The drying agent was removed *via* gravity filtration, and the filtrate was

evaporated to dryness. The resultant white solid was recrystallized from DCM/methanol to provide **8** as a white solid (248.7 mg, 73%).

**$^1$H NMR** (500 MHz, chloroform-*d*, 300 K) δ (ppm): 7.31-7.18 (m, 15H), 7.13 (d, 2H, $^3J$ = 9.0 Hz) 6.79 (d, 2H, $^3J$ = 9.0 Hz), 4.00 (t, 2H, $^3J$ = 6.1 Hz), 3.39 (t, 2H, $^3J$ = 6.6 Hz), 1.93-1.86 (m, 2H), 1.86-1.78 (m, 2H).

**3-Bromopropylheptaphenyl POSS 2a** was obtained under modified literature conditions.[10]



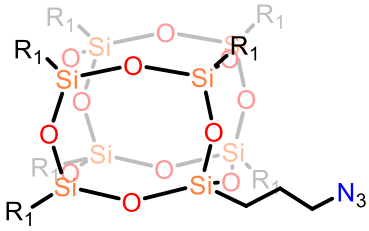
**2a**

To an open cage **1a** (5.015 g, 5.02 mmol) under nitrogen flow, dry toluene (120 mL) was added, resulting in a white suspension. The mixture was cooled to 0 °C, and the solution of 3-bromopropyl(trichlorosilane) (966 µl, 1.55 g, 6.6 mmol) in dry toluene (15 mL) was added dropwise. The mixture was stirred for 24 hours. After this time, the precipitated sodium chloride was removed *via* filtration, and the filtrate was evaporated to dryness. The crude product was purified by reprecipitation from acetone (100 mL). After vacuum drying, the resultant **2a** was obtained as a white precipitate (3.21 g, 59%).

*Analytical data are in agreement with the published one.*

**3-Azidopropylheptaphenyl POSS 3a** was obtained under modified literature conditions.[10]

***Azides are notoriously unstable and can pose a safety risk.***

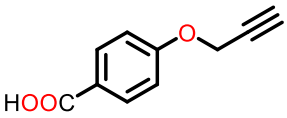


**3a**, $R_1$ = Ph

3-Bromopropylheptaphenyl POSS **2a** (442.7 mg, 0.411 mmol) and sodium azide (26.7 mg, 0.411 mmol) were dissolved in dry DMF (30 mL). The mixture was stirred for 24 hours. After this time, the solution was concentrated on a rotary evaporator. The crude product **3a** was precipitated from cold methanol (50 mL) and dried in a vacuum resulting in a white solid (253.1 mg, 59%).

*Analytical data are in agreement with the published one.*

**4-Propargyloxybenzoic acid S16** was obtained under modified literature conditions.[14]

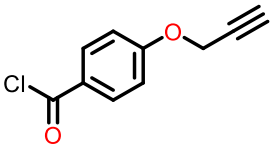



**S16**

4-Hydroxybenzoic acid **S15** (2.0 g, 14.48 mmol) was placed in a three-necked flask and dissolved in ethanol (80 mL). The solution was heated to reflux, and a solution of sodium hydroxide (1.16 g, 29.0 mmol) and potassium iodide (0.24 g, 1.45 mmol) in distilled water (5 mL) was added dropwise. Next, propargyl bromide (2.4 mL, 26.93 mmol) was added slowly, and the solution was stirred under reflux for 72 hours. After this time, the solution was cooled to room temperature, and the 0.1 M hydrochloric acid was added until pH ca. 2 was reached. The mixture was stirred for 24 hours at room temperature until a precipitate formed. The precipitate was filtered off, washed with distilled water (20 mL x 3) and toluene (20 mL x 3), and dried under vacuum to obtain **S16** as a beige solid (1.49 g, 63 %).

*Analytical data are in agreement with the published one.*

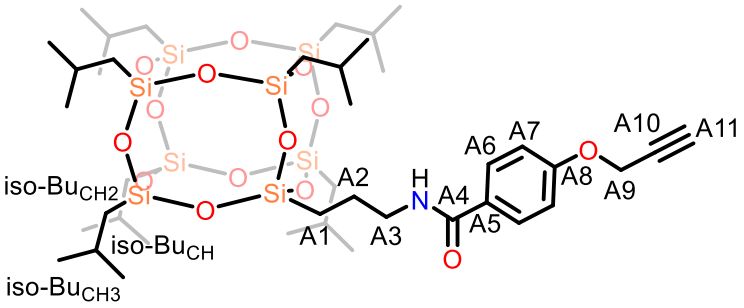
**4-Propargyloxybenzoic acid chloride 4** was obtained under modified literature conditions.[14]




**4**

4-Propargyloxybenzoic acid **S16** (154.2 mg, 0.875 mmol) was dissolved in dry DCM (20 mL) and DMF (5 mL) under a nitrogen atmosphere, and the mixture was cooled to 0 °C. Thionyl chloride $SOCl_2$ (95 µl, 155.3 mg, 1.31 mmol) was added slowly to the stirring solution. The solution was stirred for 4 hours. After this time, solvents were removed using a rotary evaporator. The product was used at once in the next step without further purification.

**Alkyne 6b**




**6b**

The open cage **1b** (504.9 mg, 0.577 mmol) was dissolved in anhydrous DCM (80 mL) under a nitrogen atmosphere. After that, 4-dimethylaminopyridine DMAP (17.6 mg, 0.144 mmol) and triethylamine TEA (161 µl, 116.8 mg, 1.154 mmol) were added. The solution was cooled to 0 °C, and 4-propargyloxybenzoic acid chloride **4** (170.5 mg, 0.875 mmol) was introduced dropwise. The reaction mixture was allowed to warm up to room temperature and left to stir for 48 hours. The mixture was washed with aqueous, saturated sodium bicarbonate, distilled water, 0.05 M hydrochloric acid, and brine. The organic layer was dried over anhydrous $MgSO_4$. The drying agent was removed *via* filtration, and the filtrate was concentrated using a rotary evaporator. The product **6b** was obtained as a white solid after precipitation from acetonitrile (3 x 50 mL) and dried under vacuum (441 mg, 74%).

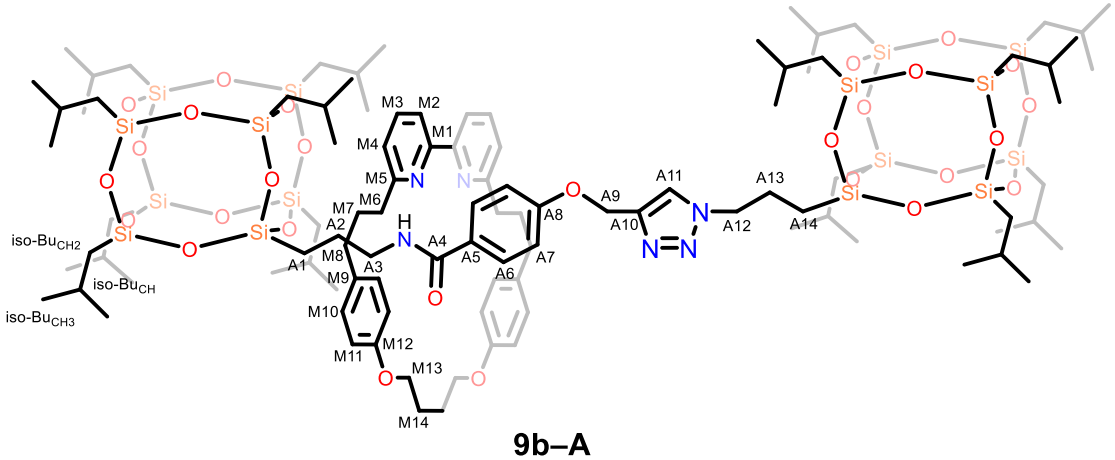
**$^1$H NMR** (500 MHz, chloroform-*d*, 300 K) δ (ppm): 7.71 (d, 2H, $^3J$ = 8.8 Hz, $H_{A6}$), 6.98 (d, $^3J$ = 8.8 Hz, $H_{A7}$), 6.00 (t, 1H, $^3J$ = 5.5, $H_{NH}$), 4.72 (d, 2H, $^4J$ = 2.4 Hz, $H_{A9}$), 3.45-3.39 (m, 2H, $H_{A3}$), 2.51 (t, 1H, $^3J$ = 2.4 Hz, $H_{A11}$) 1.90-1.78 (m, 7H, $H_{iso\text{-}BuCH}$), 1.72-1.64 (m, 2H, $H_{A2}$), 0.95-0.91 (m, 42H, $H_{iso\text{-}BuCH3}$), 0.68-0.63 (m, 2H, $H_{A1}$), 0.60-0.57 (m, 14H, $H_{iso\text{-}BuCH2}$).

**$^{13}$C NMR** (125 MHz, chloroform-*d*, 300 K) δ (ppm): 166.8, 159.9, 128.5, 128.1, 114.7, 77.9, 75.9, 55.8, 42.2, 25.68, 25.66, 23.9, 23.8, 23.1, 22.48, 22.45, 9.5.

**$^{29}$Si NMR** (100 MHz, chloroform-*d*, 300 K) δ (ppm): −67.6, −67.8, −67.9.

**HRMS** (MALDI TOF) $[M+H]^+$ *m/z*: 1054.3390, calcd. for $C_{41}H_{77}NO_{14}Si_8Na^+$ 1054.3406.

**Rotaxane 9b–A**




**9b–A**

In a 5 mL vial with a screw cap, macrocycle **A** (15 mg, 31.3 µmol), alkyne **6b** (38.8 mg, 37.6 µmol), 3-azidopropylhepta-*iso*-butyl POSS **3b** (33.8 mg, 37.5 µmol), $[Cu(CH_3CN)_4]PF_6$ (3 mg, 8 µmol), and DIPEA (5.4 µl, 31 µmol) were dissolved in THF (0.5 mL). After mixing the reagents, the solution immediately turned orange. The vial was sealed, and the cap was secured with a parafilm. The mixture was stirred for 20 hours at room temperature. After this time, the mixture was transferred into a separatory funnel, and DCM (20 mL) was introduced. Subsequently, aqueous ammonia solution (20 mL) and EDTA (200 mg, 0.7 mmol) were added to the solution in a separatory funnel, and upon the one-minute-long shaking, the solution turned colorless. The aqueous phase was extracted with DCM (30 mL). The collected organic extracts were washed with water and brine. The aqueous phase was once more extracted with DCM (30 mL). The collected organic layers were combined and dried over anhydrous $Na_2SO_4$. The filtrate was collected *via* gravity filtration, and the solvent was removed under reduced pressure. The yellowish oil was purified *via* column chromatography (DCM/hexane (1/1) with 0-12% MeCN gradient). The crude product was recrystallized from a DCM/methanol (1/9) to provide **9b–A** as a white solid (46.41 mg, 61.4%).

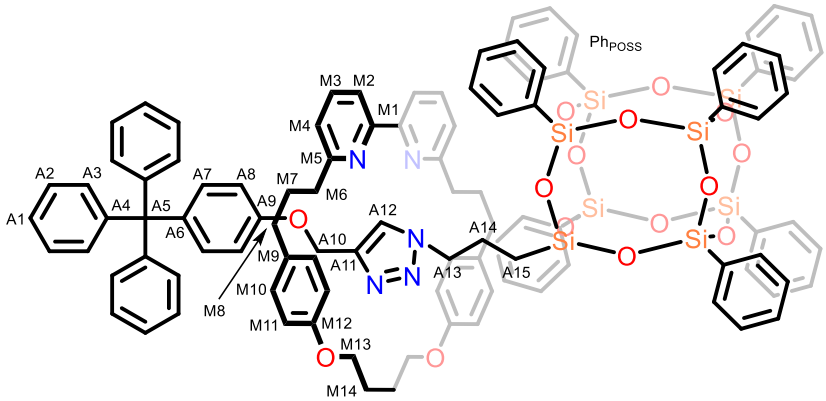
**$^1$H NMR** (600 MHz, chloroform-*d*, 300 K) δ (ppm): 8.26 (t, 1H, $^3J$ = 5.0 Hz, $H_{NH}$), 7.62 (t, 2H, $^3J$ = 7.8 Hz, $H_{M3}$) 7.60 (s, 1H, $H_{A11}$), 7.58 (d, 2H, $^3J$ = 8.8 Hz, $H_{A6}$), 7.41 (d, 2H, $^3J$ = 7.7 Hz, $H_{M2}$), 7.07 (d, 2H, $^3J$ = 7.9 Hz, $H_{M4}$), 6.78 (d, 4H, $^3J$ = 8.6 Hz, $H_{M10}$), 6.73 (d, 4H, $^3J$ = 8.6 Hz, $H_{M11}$), 6.46 (d, 2H, $^3J$ = 8.8 Hz, $H_{A7}$), 4.93 (s, 2H, $H_{A9}$), 4.34-4.22 (m, 6H, $H_{M13}$, $H_{A12}$), 2.63-2.55 (m, 2H, $H_{M8}$), 2.55-2.47 (m, 2H, $H_{M8}$), 2.43-2.85 (m, 6H, $H_{M6}$, $H_{A3}$), 2.14-1.99 (m, 4H, $H_{M14}$), 1.99-1.90 (m, 2H, $H_{A13}$), 1.88-1.68 (m, 18H, $H_{iso\text{-}BuCH}$, $H_{M7}$), 0.96-0.90 (m, 68H, $H_{iso\text{-}BuCH3}$, $H_{A2}$), 0.86 (d, 18H, $^3J$ = 6.6 Hz,

$H_{iso\text{-}BuCH3}$), 0.61-0.55 (m, 24H, $H_{iso\text{-}BuCH2}$, $H_{A14}$), 0.47 (d, 6H, $^{3}J$ = 7.1 Hz, $H_{iso\text{-}BuCH2}$), 0.24-0.18 (m, 2H, $H_{A1}$).

**$^{13}$C NMR** (125 MHz, chloroform-*d*, 300 K) δ (ppm): 165.9, 163.1, 159.4, 157.4, 156.8, 143.9, 136.8, 132.4, 129.5, 129.1, 128.7, 122.5, 121.6, 119.8, 115.1, 112.8, 66.5, 61.9, 52.5, 42.7, 36.3, 25.73, 25.70, 25.68, 25.64, 24.9, 24.1, 23.89, 23.86, 23.84, 22.56, 22.48, 22.43, 21.6, 9.9, 9.3.

**$^{29}$Si NMR** (100 MHz, chloroform-*d*, 300 K) δ (ppm): −66.5, −66.79, −66.85, −66.9.
**HRMS** (MALDI TOF) $[M+H]^+$ *m/z*: 2411.9034, calcd. for $C_{104}H_{181}N_6O_{28}Si_{16}^+$ 2411.9248.

**Rotaxane 10a–A**




**10a–A**

In a 5 mL vial with a screw cap, macrocycle **A** (12.6 mg, 26.4 μmol), ((4-(prop-2-yn-1-yloxy)phenyl)methanetriyl)tribenzene **7** (11.8 mg, 31.5 μmol), 3-azidopropylheptaphenyl POSS **3a** (32.8 mg, 31.5 μmol), $[Cu(CH_3CN)_4]PF_6$ (2.7 mg, 7.2 μmol), DIPEA (4.5 μl, 25.8 μmol) were dissolved in DCM (1 mL). After mixing the reagents, the solution immediately turned orange. The vial was sealed, and the cap was secured with a parafilm. The mixture was stirred for 40 hours at 40 °C. After this time, the mixture was transferred into a separatory funnel, and DCM (20 mL) was introduced. Subsequently, aqueous ammonia solution (20 mL) and EDTA (200 mg, 0.7 mmol) were added to the solution in a separatory funnel, and upon the one-minute-long shaking, the solution turned colorless. The aqueous phase was extracted with DCM (30 mL). The collected organic extracts were washed with water and brine. The aqueous phase was once more extracted with DCM (30 mL). The collected organic layers were combined and dried over anhydrous $Na_2SO_4$. The filtrate was collected *via*

gravity filtration, and the solvent was removed under reduced pressure. The yellowish oil was purified *via* column chromatography (DCM/hexane (1/1) with 0-12% MeCN gradient). The crude product was recrystallized from a DCM/methanol (1/9) to provide **10a–A** as a white solid (29.14 mg, 59%).

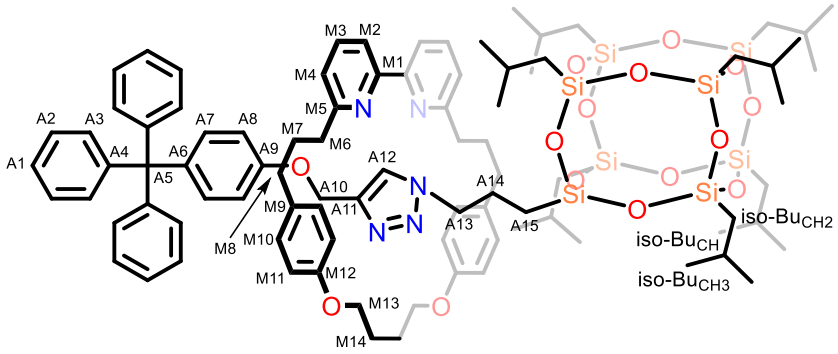
**$^{1}$H NMR** (500 MHz, chloroform-*d*, 300 K) δ (ppm): 8.27 (s, 1H, $H_{A12}$), 7.75-7.70 (m, 10H, $H_{PhPOSS}$), 7.70-7.66 (m, 2H, $H_{PhPOSS}$), 7.46-7.27 (m, 25H, $H_{M3}$, $H_{PhPOSS}$), 7.23-7.10 (m, 17H, $H_{M2}$, $H_{A1}$, $H_{A2}$, $H_{A3}$), 6.84 (d, 2H, $^{3}J$ = 7.7 Hz, $H_{M4}$) 6.82 (d, 2H, $^{3}J$ = 8.8 Hz, $H_{A7}$), 6.51-6.44 (m, 8H, $H_{M10}$, $H_{M11}$), 6.35 (d, 2H, $^{3}J$ = 8.8 Hz, $H_{A8}$), 4.18 (s, 2H, $H_{A10}$), 4.08-4.00 (m, 2H, $H_{M13}$), 4.00-3.91 (m, 2H, $H_{M13}$), 3.42 (t, 2H, $^{3}J$ = 7.6 Hz, $H_{A13}$), 2.39-2.12 (m, 8H, $H_{M6}$, $H_{M8}$), 1.85-1.69 (m, 4H, $H_{M14}$), 1.48-1.39 (m, 6H, $H_{M7}$, $H_{A14}$), 0.51-0.42 (m, 2H, $H_{A15}$).

**$^{13}$C NMR** (150 MHz, chloroform-*d*, 300 K) δ (ppm): 162.6, 157.7, 157.1, 156.3, 147.2, 142.5, 138.1, 134.3, 134.2, 134.1, 133.1, 131.5, 131.1, 130.8, 130.3, 130.2, 129.0, 127.90, 127.88, 127.84, 127.4, 127.3, 125.7, 124.9, 121.3, 119.9, 115.0, 113.5, 66.7, 64.2, 61.2, 51.6, 37.0, 34.7, 32.0, 24.8, 22.1, 9.5.

**$^{29}$Si NMR** (100 MHz, chloroform-*d*, 300 K) δ (ppm): −65.6, −77.76, −77.83, −78.2.

**HRMS** (MALDI TOF) $[M+H]^{+}$ *m/z*: 1893.5220, calcd. for $C_{105}H_{98}N_5O_{15}Si_8^{+}$ 1893.5231.

**Rotaxane 10b–A**




**10b–A**

In a 5 mL vial with a screw cap, macrocycle **A** (15 mg, 31.3 µmol), ((4-(prop-2-yn-1-yloxy)phenyl)methanetriyl)tribenzene **7** (14.1 mg, 37.5 µmol), 3-azidopropylhepta-*iso*-butyl POSS **3b** (33.8 mg, 37.5 µmol), $[Cu(CH_3CN)_4]PF_6$ (3 mg, 8 µmol), DIPEA (5.4 µl, 31 µmol) were dissolved in THF (0.5 mL). After mixing the reagents, the solution

immediately turned orange. The vial was sealed, and the cap was secured with a parafilm. The mixture was stirred for 20 hours at room temperature. After this time, the mixture was transferred into a separatory funnel, and DCM (20 mL) was introduced. Subsequently, aqueous ammonia solution (20 mL) and EDTA (200 mg, 0.7 mmol) were added to the solution in a separatory funnel, and upon the one-minute-long shaking, the solution turned colorless. The aqueous phase was extracted with DCM (30 mL). The collected organic extracts were washed with water and brine. The aqueous phase was once more extracted with DCM (30 mL). The collected organic layers were combined and dried over anhydrous $Na_2SO_4$. The filtrate was collected *via* gravity filtration, and the solvent was removed under reduced pressure. The yellowish oil was purified *via* column chromatography (DCM/hexane (1/1) with 0-12% MeCN gradient). The crude product was recrystallized from a DCM/methanol (1/9) to provide **10b–A** as a white solid (50.06 mg, 91%).

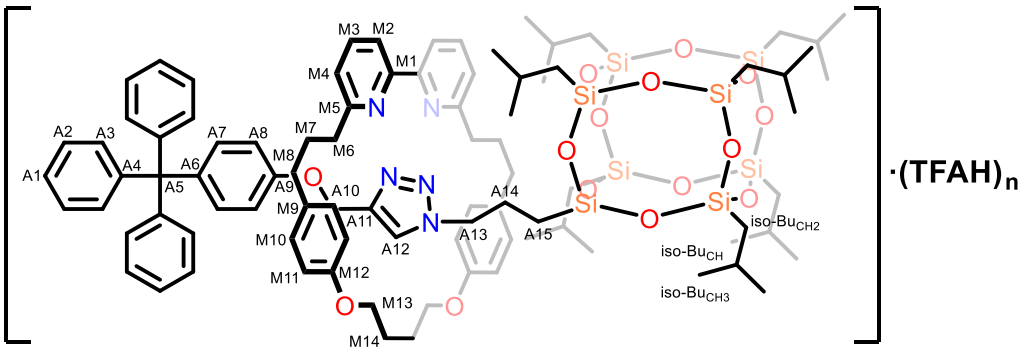
**$^1$H NMR** (500 MHz, chloroform-*d*, 300 K) δ (ppm): 8.30 (s, 1H, $H_{A12}$), 7.55 (t, 2H, $^3J$ = 7.7 Hz, $H_{M3}$), 7.35 (d, 2H, $^3J$ = 7.7 Hz, $H_{M2}$), 7.24-7.14 (m, 15H, $H_{A1}$, $H_{A2}$, $H_{A3}$), 7.03 (d, 2H, $^3J$ = 7.7 Hz, $H_{M4}$), 6.82 (d, 2H, $^3J$ = 8.8 Hz, $H_{A7}$), 6.62 (d, 4H, $^3J$ = 8.6 Hz, $H_{M10}$), 6.55 (d, 4H, $^3J$ = 8.6 Hz, $H_{M11}$), 6.35 (d, 2H, $^3J$ = 8.9 Hz, $H_{A8}$), 4.22-4.13 (m, 2H, $H_{M13}$), 4.19 (s, 2H, $H_{A10}$), 4.13-4.05 (m, 2H, $H_{M13}$), 3.53 (t, 2H, $^3J$ = 7.9 Hz, $H_{A13}$), 2.55-2.39 (m, 8H, $H_{M6}$, $H_{M8}$), 2.04-1.89 (m, 4H, $H_{M14}$) 1.89-1.76 (m, 7H, $H_{iso\text{-}BuCH}$), 1.68-1.56 (m, 4H, $H_{M7}$), 1.49-1.40 (m, 2H, $H_{A14}$), 0.97-0.89 (m, 42H, $H_{iso\text{-}BuCH3}$), 0.58 (d, 14H, $^3J$ = 7.1 Hz, $H_{iso\text{-}BuCH2}$), 0.36-0.30 (m, 2H, $H_{A15}$).

**$^{13}$C NMR** (125 MHz, chloroform-*d*, 300 K) δ (ppm): 162.6, 157.8, 157.2, 156.4, 147.3, 142.8, 138.1, 136.6, 133.1, 131.5, 129.0, 127.3, 125.8, 124.8, 121.4, 119.9, 115.1, 113.5, 66.8, 64.3, 61.3, 51.8, 37.3, 35.0, 32.2, 25.74, 25.68, 24.9, 23.92, 23.88, 23.85, 22.84, 22.54, 22.48, 9.7.

**$^{29}$Si NMR** (100 MHz, chloroform-*d*, 300 K) δ (ppm): −66.6, −66.77, −66.8.

**HRMS** (ESI TOF) $[M+H]^+$ *m/z*: 1753.7383, calcd. for $C_{91}H_{126}N_5O_{15}Si_8^+$ 1753.7433.

**Rotaxane 10b–A·(TFAH)$_n$**

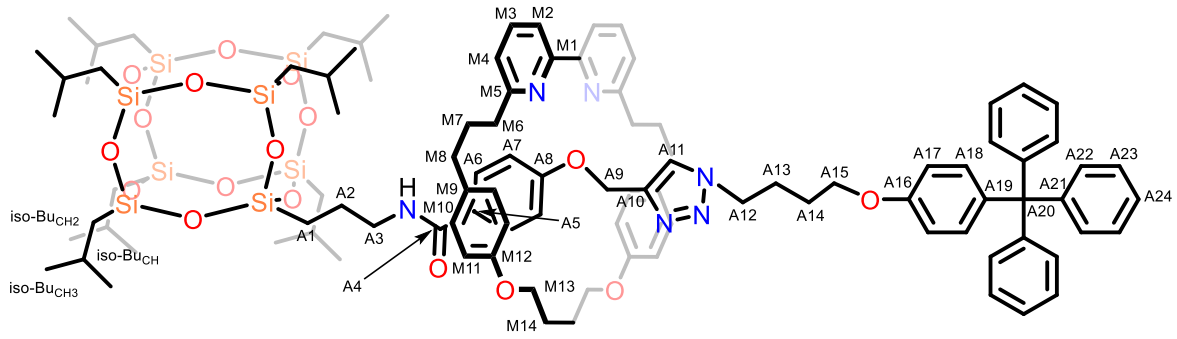



**10b–A·(TFAH)$_n$**

The cationic species was obtained by acidification of the solution containing **10b–A** with ca. two equiv. of trifluoroacetic acid in chloroform-*d*.

**$^1$H NMR** (500 MHz, chloroform-*d*, 300 K) δ (ppm): 8.16 (t, 2H, $^3J$ = 8.0 Hz, $H_{M3}$), 8.03 (d, 2H, $^3J$ = 7.9 Hz, $H_{M2}$), 7.51 (d, 2H, $^3J$ = 7.9 Hz, $H_{M4}$), 7.27-7.15 (m, 15H, $H_{A1}$, $H_{A2}$, $H_{A3}$), 7.08 (d, 2H, $^3J$ = 9.0 Hz, $H_{A7}$), 6.78 (d, 4H, $^3J$ = 8.5 Hz, $H_{M10}$), 6.59 (d, 4H, $^3J$ = 8.6 Hz, $H_{M11}$), 6.44 (d, 2H, $^3J$ = 9.0 Hz, $H_{A8}$), 6.42 (s, 1H, $H_{A12}$), 4.11 (s, 2H, $H_{A10}$), 4.06 (t, 2H, $^3J$ = 7.5 Hz, $H_{A13}$), 4.01-3.89 (m, 4H, $H_{M13}$), 2.68-2.49 (m, 6H, $H_{M6}$, $H_{M8}$), 2.40-2.30 (m, 2H, $H_{M6}$), 2.12-2.01 (m, 2H, $H_{M14}$), 2.01-1.91 (m, 2H, $H_{M14}$), 1.91-1.74 (m, 13H, $H_{M7}$, $H_{A14}$, $H_{iso\text{-}BuCH}$), 0.97-0.86 (m, 42H, $H_{iso\text{-}BuCH3}$), 0.62-0.52 (m, 16H, $H_{iso\text{-}BuCH2}$, $H_{A15}$).

**Rotaxane 11b–A**




**11b–A**

In a 5 mL vial with a screw cap, macrocycle **A** (15 mg, 31.3 µmol), alkyne **6b** (38.8 mg, 37.6 µmol), ((4-(4-azidobutoxy)phenyl)methanetriyl)tribenzene **8** (16.6 mg, 37.6 µmol), $[Cu(CH_3CN)_4]PF_6$ (3 mg, 8 µmol), DIPEA (5.4 µl, 31 µmol) were dissolved in THF (0.5

mL). After mixing the reagents, the solution immediately turned orange. The vial was sealed, and the cap was secured with a parafilm. The mixture was stirred for 20 hours at room temperature. After this time, the mixture was transferred into a separatory funnel, and DCM (20 mL) was introduced. Subsequently, aqueous ammonia solution (20 mL) and EDTA (200 mg, 0.7 mmol) were added to the solution in a separatory funnel, and upon the one-minute-long shaking, the solution turned colorless. The aqueous phase was extracted with DCM (30 mL). The collected organic extracts were washed with water and brine. The aqueous phase was once more extracted with DCM (30 mL). The collected organic layers were combined and dried over anhydrous $Na_2SO_4$. The filtrate was collected *via* gravity filtration, and the solvent was removed under reduced pressure. The yellowish oil was purified *via* column chromatography (DCM /hexane (1/1) with 0-12% MeCN gradient). The crude product was recrystallized from a DCM/methanol (1/9) to provide **11–b** as a white solid (30.82 mg, 51%).

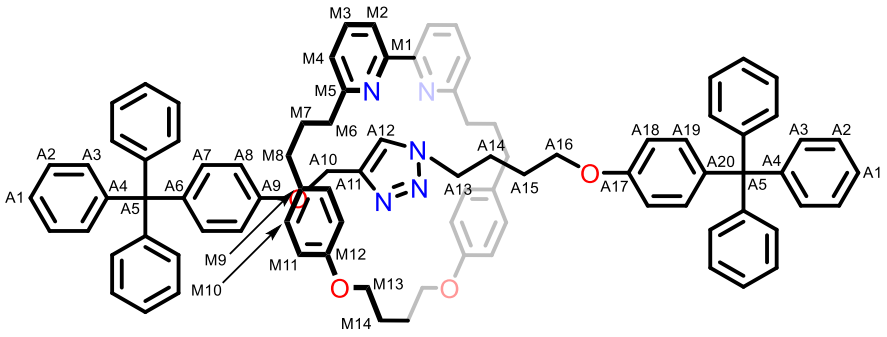
**$^1$H NMR** (500 MHz, chloroform-*d*, 300 K) δ (ppm): 8.03 (s, 1H, $H_{A11}$), 7.59 (d, 2H, $^3J$ = 8.4 Hz, $H_{A6}$), 7.57 (t, 2H, $^3J$ = 7.8 Hz, $H_{M3}$), 7.35 (d, 2H, $^3J$ = 7.7 Hz, $H_{M2}$), 7.26-7.14 (m, 15H, $H_{A22}$, $H_{A23}$, $H_{A24}$), 7.05 (d, 2H, $^3J$ = 7.7 Hz, $H_{M4}$), 7.03 (d, 2H, $^3J$ = 8.8 Hz, $H_{A18}$), 6.94-6.88 (m, 1H, $H_{NH}$), 6.74 (d, 4H, $^3J$ = 8.5 Hz, $H_{M10}$), 6.70 (d, 2H, $^3J$ = 8.8 Hz, $H_{A7}$), 6.66 (d, 4H, $^3J$ = 8.5 Hz, $H_{M11}$), 6.59 (d, 2H, $^3J$ = 8.9 Hz, $H_{A17}$), 4.95 (s, 2H, $H_{A9}$), 4.30-4.20 (m, 2H, $H_{M13}$), 4.17-4.08 (m, 2H, $H_{M13}$), 3.75 (t, 2H, $^3J$ = 7.1 Hz, $H_{A12}$), 3.62 (t, 2H, $^3J$ = 5.8 Hz, $H_{A15}$), 3.01-2.94 (m, 2H, $H_{A3}$), 2.54-2.46 (m, 4H,$H_{M8}$), 2.46-2.32 (m, 4H, $H_{M6}$), 2.12-1.92 (m, 4H, $H_{M14}$), 1.92-1.76 (m, 7H, $H_{iso\text{-}BuCH}$), 1.76-1.64 (m, 4H, $H_{M7}$), 1.42-1.31 (m, 6H, $H_{A2}$, $H_{A13}$, $H_{A14}$), 0.93 (d, 24H, $^3J$ = 6.6 Hz, $H_{iso\text{-}BuCH3}$), 0.90 (d, 18H, $^3J$ = 6.6 Hz, $H_{iso\text{-}BuCH3}$), 0.57 (d, 8H, $^3J$ = 7.1 Hz, $H_{iso\text{-}BuCH2}$), 0.54 (d, 6H, $^3J$ = 7.1 Hz, $H_{iso\text{-}BuCH2}$), 0.51-0.43 (m, 2H, $H_{A1}$).

**$^{13}$C NMR** (125 MHz, chloroform-*d*, 300 K) δ (ppm): 166.4, 162.8, 160.2, 157.4, 157.2, 156.7, 147.1, 142.6, 138.8, 136.8, 132.8, 132.1, 131.1, 129.2, 128.9, 127.9, 127.4, 125.8, 124.0, 121.5, 120.1, 114.9, 113.7, 113.1, 66.7, 66.33, 64.3, 61.9, 49.4, 42.4, 36.7, 34.9, 31.6, 26.1, 26.0, 25.7, 25.6, 24.8, 23.9, 23.8, 22.51, 22.49, 22.44, 9.7.

**$^{29}$Si NMR** (100 MHz, chloroform-*d*, 300 K) δ (ppm): −67.69, −67.73, −67.88, −67.91.

**HRMS** (ESI TOF) $[M+H]^+$ *m/z*: 1944.8353, calcd. for $C_{102}H_{139}N_6O_{17}Si_8^+$ 1944.8379.

**Rotaxane 12–A**




**12–A**

In a 5 mL vial with a screw cap, macrocycle **A** (15 mg, 31.3 μmol), ((4-(prop-2-yn-1-yloxy)phenyl)methanetriyl)tribenzene **7** (14.1 mg, 37.5 μmol), ((4-(4-azidobutoxy)phenyl)methanetriyl)tribenzene **8** (16.6 mg, 37.6 μmol), $[Cu(CH_3CN)_4]PF_6$ (3 mg, 8 μmol), DIPEA (5.4 μl, 31 μmol), and THF (0.5 mL) were dissolved in THF (0.5 mL). After mixing the reagents, the solution immediately turned orange. The vial was sealed, and the cap was secured with a parafilm. The mixture was stirred for 20 hours at room temperature. After this time, the mixture was transferred into a separatory funnel, and DCM (20 mL) was introduced. Subsequently, aqueous ammonia solution (20 mL) and EDTA (200 mg, 0.7 mmol) were added to the solution in a separatory funnel, and upon the one-minute-long shaking, the solution turned colorless. The aqueous phase was extracted with DCM (30 mL). The collected organic extracts were washed with water and brine. The aqueous phase was once more extracted with DCM (30 mL). The collected organic layers were combined and dried over anhydrous $Na_2SO_4$. The filtrate was collected *via* gravity filtration, and the solvent was removed under reduced pressure. The yellowish oil was purified *via* column chromatography (DCM/hexane (1/1) with 0-12% MeCN gradient). The crude product was recrystallized from a DCM/methanol (1/9) to provide **12–A** as a colorless oil (38.5 mg, 96%).

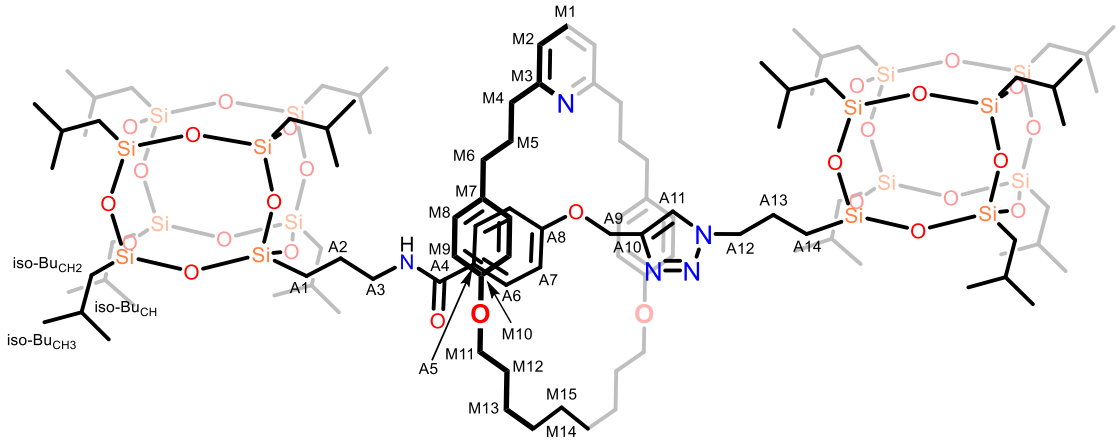
**$^1$H NMR** (500 MHz, chloroform-*d*, 300 K) δ (ppm): 8.19 (s, 1H, $H_{A12}$), 7.49 (t, 2H, $^3J$ = 7.7 Hz, $H_{M3}$), 7.26 (d, 2H, $^3J$ = 7.7 Hz, $H_{M2}$), 7.25-7.10 (m, 30H, $H_{A1}$, $H_{A2}$, $H_{A3}$), 7.04-6.95 (m, 6H, $H_{A7}$, $H_{M4}$, $H_{A19}$), 6.76 (d, 2H, $^3J$ = 8.8 Hz, $H_{A8}$), 6.69 (d, 4H, $^3J$ = 8.5 Hz, $H_{M10}$), 6.59 (d, 4H, $^3J$ = 8.6 Hz, $H_{M11}$), 6.49 (d, 2H, $^3J$ = 8.8 Hz, $H_{A18}$), 4.91 (s, 2H, $H_{A10}$), 4.27-4.19 (m, 2H, $H_{M13}$), 4.01-3.94 (m, 2H, $H_{M13}$), 3.37 (t, 2H, $^3J$ = 6.8 Hz, $H_{A16}$), 3.30

(m, 2H, $H_{A13}$), 2.60-2.31 (m, 8H, $H_{M6}$, $H_{M8}$), 2.1-2.01 (m, 2H, $H_{M14}$), 1.93-1.83 (m, 2H, $H_{M14}$), 1.83-1.61 (m, 4H, $H_{M7}$), 1.09-1.01 (m, 2H, $H_{A15}$), 0.82-0.73 (m, 2H, $H_{A14}$).

**$^{13}$C NMR** (125 MHz, chloroform-*d*, 300 K) δ (ppm): 162.5, 157.6, 157.4, 156.8, 156.5, 147.1, 147.0, 142.3, 139.1, 138.4, 136.7, 133.1, 132.1, 131.9, 131.11, 131.08, 129.3, 127.39, 127.37, 125.81, 125.80, 124.7, 121.4, 120.3, 114.8, 113.4, 113.1, 66.8, 66.3, 64.30, 64.28, 61.7, 48.9, 36.9, 34.7, 33.7, 31.9, 31.7, 25.9, 25.4, 24.7.

**HRMS** (MALDI TOF) $[M+H]^+$ *m/z*: 1287.6593, calcd. for $C_{89}H_{84}N_5O_4^+$ 1287.6550.

**Rotaxane 9b–B**




**9b–B**

In a 5 mL vial with a screw cap, macrocycle **B** (15 mg, 31.8 μmol), alkyne **6b** (38.3 mg, 37.6 μmol), 3-azidopropylhepta-*iso*-butyl POSS **3b** (33.8 mg, 37.5 μmol), $[Cu(CH_3CN)_4]PF_6$ (3 mg, 8 μmol), DIPEA (5.4 μl, 31 μmol) were dissolved in DCM (0.5 mL). After mixing the reagents, the solution immediately turned orange. The vial was sealed, and the cap was secured with a parafilm. The mixture was stirred for 72 hours at room temperature. After this time, the mixture was transferred into a separatory funnel, and DCM (20 mL) was introduced. Subsequently, aqueous ammonia solution (20 mL) and EDTA (200 mg, 0.7 mmol) were added to the solution in a separatory funnel, and upon the one-minute-long shaking, the solution turned colorless. The aqueous phase was extracted with DCM (30 mL). The collected organic extracts were washed with water and brine. The aqueous phase was once more extracted with DCM (30 mL). The collected organic layers were combined and dried over anhydrous $Na_2SO_4$. The filtrate was collected *via* gravity filtration, and the solvent was removed

under reduced pressure. The yellowish oil was purified *via* column chromatography (DCM/hexane (1/1) with 0-12% MeCN gradient). The crude product was recrystallized from a DCM/methanol (1/9) to provide **9b–B** as a white solid (4.9 mg, 6.4%).

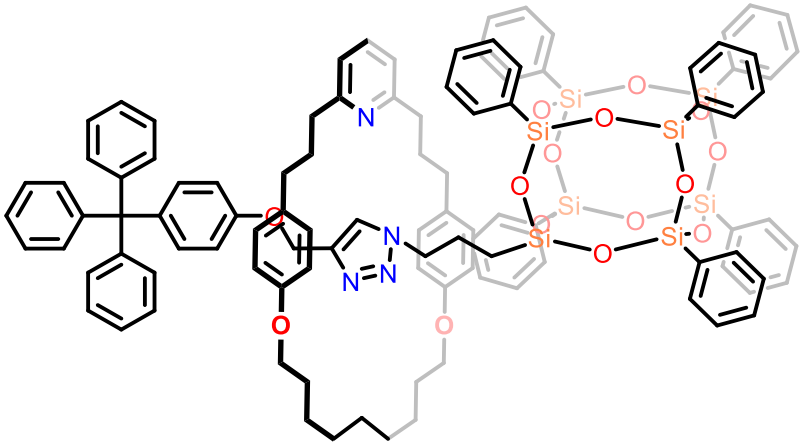
**$^{1}$H NMR** (500 MHz, chloroform-*d*, 300 K) δ (ppm): 7.51 (t, 1H, $^{3}J$ = 7.7 Hz, $H_{M1}$), 7.48 (s, 1H, $H_{A11}$), 7.39 (d, 2H, $^{3}J$ = 8.8 Hz, $H_{A6}$), 7.01 (t, 1H, $^{3}J$ = 5.6 Hz, $H_{NH}$), 6.96 (d, 2H, $^{3}J$ = 7.7 Hz, $H_{M2}$), 6.71 (d, 4H, $^{3}J$ = 8.5 Hz, $H_{M8}$), 6.53 (d, 2H, $^{3}J$ = 8.8 Hz, $H_{A7}$), 6.46 (d, 4H, $^{3}J$ = 8.6 Hz, $H_{M9}$), 4.81 (s, 2H, $H_{A9}$), 4.16 (t, 2H, $^{3}J$ = 7.4 Hz, $H_{A12}$), 3.81 (t, 4H, $^{3}J$ = 6.2 Hz, $H_{M11}$), 3.15-3.08 (m, 2H, $H_{A3}$), 2.62-2.46 (m, 8H, $H_{M4}$, $H_{M6}$), 1.97-1.63 (m, 24H, $H_{A13}$, $H_{\textit{iso}\text{-BuCH}}$, $H_{M5}$, $H_{M12}$), 1.63-1.13 (m, 12H, $H_{M13}$, $H_{M14}$, $H_{M15}$, $H_{A2}$), 0.96-0.89 (m, 84H, $H_{\textit{iso}\text{-BuCH3}}$), 0.61-0.50 (m, 32H, $H_{\textit{iso}\text{-BuCH2}}$, $H_{A14}$, $H_{A1}$).

**$^{13}$C NMR** (125 MHz, chloroform-*d*, 300 K) δ (ppm): 166.3, 161.6, 160.1, 157.2, 143.5, 136.8, 132.6, 129.0, 128.7, 127.3, 122.7, 119.8, 114.2, 113.5, 66.9, 61.8, 52.5, 42.4, 37.1, 34.9, 31.2, 28.9, 28.5, 25.68, 25.66, 23.88, 23.84, 23.83, 22.9, 22.6, 22.46, 22.41, 9.9, 9.4.

**$^{29}$Si NMR** (100 MHz, chloroform-*d*, 300 K) δ (ppm): −67.00, −67.09, −67.15, −67.32, −67.35, −68.1.

**HRMS** (ESI+, TOF) $[M+H]^{+}$ *m/z*: 2404.9749, calcd. for $C_{104}H_{188}N_5O_{28}Si_{16}^{+}$ 2404.9771.

**Rotaxane 10a–B**

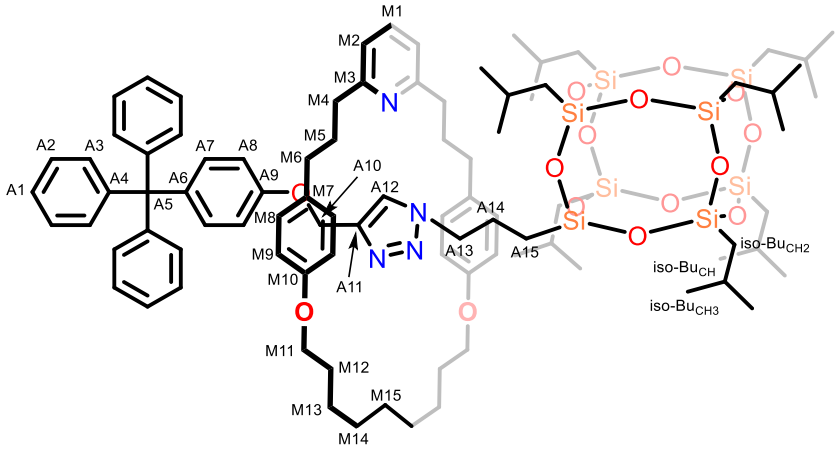


**10a–B**

In a 5 mL vial with a screw cap, macrocycle **B** (15 mg, 31.8 μmol), ((4-(prop-2-yn-1-yloxy)phenyl)methanetriyl)tribenzene **7** (23.8 mg, 63.6 μmol), 3-azidopropyl-heptaphenyl POSS **3a** (66.14 mg, 63.6 μmol), $[Cu(CH_3CN)_4]PF_6$ (3 mg, 8 μmol), DIPEA (5.4 μl, 25.8 μmol) were dissolved in DCM (2,5 mL). After mixing the reagents, the solution immediately turned orange. The vial was sealed, and the cap was secured with a parafilm. The mixture was stirred for 48 hours at 40 °C. After this time, the mixture was transferred into a separatory funnel, and DCM (20 mL) was introduced. Subsequently, aqueous ammonia solution (20 mL) and EDTA (200 mg, 0.7 mmol) were added to the solution in a separatory funnel, and upon the one-minute-long shaking, the solution turned colorless. The aqueous phase was extracted with DCM (30 mL). The collected organic extracts were washed with water and brine. The aqueous phase was once more extracted with DCM (30 mL). The collected organic layers were combined and dried over anhydrous $Na_2SO_4$. The filtrate was collected *via* gravity filtration, and the solvent was removed under reduced pressure. The obtained yellowish oil was analyzed by MALDI mass spectrometry. Only traces of **10a–B** was observed.

**HRMS** (MALDI TOF) $[M+H]^+$ *m/z*: 1886.5806, calcd. for $C_{105}H_{105}N_4O_{15}Si_8^+$ 1886.5749.

**Rotaxane 10b–B**




**10b–B**

In a 5 mL vial with a screw cap, macrocycle **B** (15 mg, 31.8 µmol), ), ((4-(prop-2-yn-1-yloxy)phenyl)methanetriyl)tribenzene **7** (14.1 mg, 37.5 µmol), 3-azidopropylhepta-*iso*-butyl POSS **3b** (33.8 mg, 37.5 µmol), $[Cu(CH_3CN)_4]PF_6$ (3 mg, 8 µmol), DIPEA (5.4 µl, 31 µmol) were dissolved in DCM (0.5 mL). After mixing the reagents, the solution immediately turned orange. The vial was sealed, and the cap was secured with a parafilm. The mixture was stirred for 48 hours at room temperature. After this time, the mixture was transferred into a separatory funnel, and DCM (20 mL) was introduced. Subsequently, aqueous ammonia solution (20 mL) and EDTA (200 mg, 0.7 mmol) were added to the solution in a separatory funnel, and upon the one-minute-long shaking, the solution turned colorless. The aqueous phase was extracted with DCM (30 mL). The collected organic extracts were washed with water and brine. The aqueous phase was once more extracted with DCM (30 mL). The collected organic layers were combined and dried over anhydrous $Na_2SO_4$. The filtrate was collected *via* gravity filtration, and the solvent was removed under reduced pressure. The obtained yellowish oil was purified *via* flash chromatography (*n*-hexane with 10-60% ethyl acetate gradient) to provide **10b-B** as a pale pink oil (14.2 mg, 25.6%).

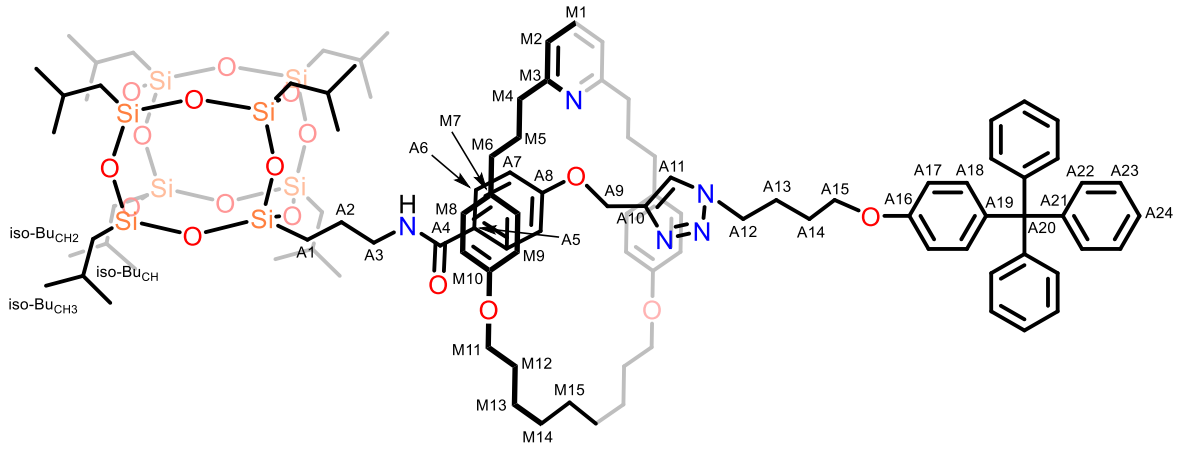
**$^1$H NMR** (500 MHz, chloroform-*d*, 300 K) δ (ppm): 7.38 (t, 1H, $^3J$ = 7.7 Hz, $H_{M1}$), 7.34 (s, 1H, $H_{A12}$), 7.24-7.14 (m, 15H, $H_{A1}$, $H_{A2}$, $H_{A3}$), 6.90 (d, 2H, $^3J$ = 8.8 Hz, $H_{A7}$) 6.86 (d, 2H, $^3J$ = 7.7 Hz, $H_{M2}$), 6.66 (d, 4H, $^3J$ = 8.4 Hz, $H_{M8}$), 6.42 (d, 2H, $^3J$ = 9.3 Hz, $H_{A8}$) 6.41 (d, 4H, $^3J$ = 8.6 Hz, $H_{M9}$), 4.31 (s, 2H, $H_{A10}$), 3.87 (t, 2H, $^3J$ = 7.6 Hz, $H_{A13}$), 3.75 (t, 4H, $^3J$ = 6.2 Hz, $H_{M11}$), 2.64-2.41 (m, 8H, $H_{M4}$, $H_{M6}$), 1.91-1.72 (m, 13H, $H_{iso\text{-}BuCH}$, $H_{M5}$, $H_{A14}$), 1.72-1.56 (m, 4H, $H_{M12}$), 1.44-1.16 (m, 10H, $H_{M13}$, $H_{M14}$, $H_{M15}$), 0.96-0.90 (m, 42H, $H_{iso\text{-}BuCH3}$), 0.63-0.57 (m, 14H, $H_{iso\text{-}BuCH2}$), 0.54-0.49 (m, 2H, $H_{A15}$).

**$^{13}$C NMR** (125 MHz, chloroform-*d*, 300 K) δ (ppm): 161.5, 157.1, 156.3, 147.2, 143.5, 138.4, 136.4, 133.1, 131.7, 131.1, 129.0, 127.42, 127.37, 125.7 123.1, 119.5, 114.2, 113.4, 67.0, 64.3, 61.2, 52.2, 37.7, 35.0, 32.1, 29.7, 29.6, 28.8, 28.5, 25.7, 25.6, 23.9, 23.85, 23.82, 23.53, 23.48, 22.4, 9.6.

**$^{29}$Si NMR** (100 MHz, chloroform-*d*, 300 K) δ (ppm): −67.0, −67.3, −68.0.

**HRMS** (MALDI TOF) $[M+H]^+$ *m/z*: 1746.7934, calcd. for $C_{91}H_{133}N_4O_{15}Si_8^+$ 1746.7939.

**Rotaxane 11b–B**




**11b–B**

In a 5 mL vial with a screw cap, macrocycle **B** (15 mg, 31.8 μmol), alkyne **6b** (65.6 mg, 63.5 μmol), ((4-(4-azidobutoxy)phenyl)methanetriyl)tribenzene **8** (27.5 mg, 63.5 μmol), $[Cu(CH_3CN)_4]PF_6$ (3 mg, 8 μmol), DIPEA (5.4 μl, 31 μmol) were dissolved in DCM (0.5 mL). After mixing the reagents, the solution immediately turned orange. The vial was sealed, and the cap was secured with a parafilm. The mixture was stirred for 48 hours at room temperature. After this time, the mixture was transferred into a separatory funnel, and DCM (20 mL) was introduced. Subsequently, aqueous ammonia solution (20 mL) and EDTA (200 mg, 0.7 mmol) were added to the solution in a separatory funnel, and upon the one-minute-long shaking, the solution turned colorless. The aqueous phase was extracted with DCM (30 mL). The collected organic extracts were washed with water and brine. The aqueous phase was once more extracted with DCM (30 mL). The collected organic layers were combined and dried over anhydrous $Na_2SO_4$. The filtrate was collected *via* gravity filtration, and the solvent was removed under reduced pressure. The yellowish oil was purified *via* column chromatography

(DCM/hexane (1/1) with 0-12% MeCN gradient). The crude product was recrystallized from a DCM/methanol (1/9) to provide **11b–B** as a white solid (14 mg, 22.7%).

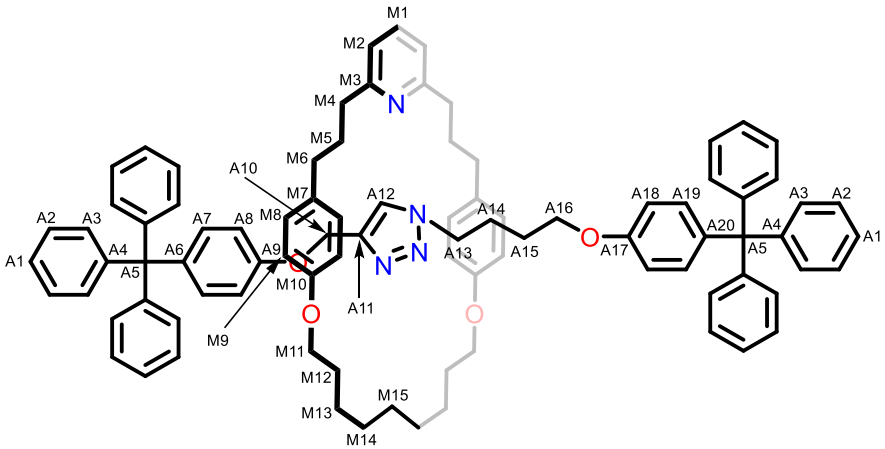
**$^{1}$H NMR** (600 MHz, chloroform-*d*, 300 K) δ (ppm): 7.61 (d, 2H, $^{3}J$ = 8.8 Hz, $H_{A6}$), 7.52 (s, 1H, $H_{A11}$), 7.41 (t, 1H, $^{3}J$ = 7.7 Hz, $H_{M1}$), 7.25-7.14 (m, 15H, $H_{A22}$, $H_{A23}$, $H_{A24}$), 7.03 (d, 2H, $^{3}J$ = 8.9 Hz, $H_{A18}$), 6.89 (d, 2H, $^{3}J$ = 7.7 Hz, $H_{M2}$), 6.85 (d, 2H , $^{3}J$ = 8.8 Hz, $H_{A7}$), 6.73 (d, 4H, $^{3}J$ = 8.5 Hz, $H_{M8}$), 6.58 (d, 2H, $^{3}J$ = 8.9 Hz, $H_{A17}$), 6.47 (d, 4H, $^{3}J$ = 8.5 Hz, $H_{M9}$), 6.24 (t, 1H, $^{3}J$ = 5.7 Hz, $H_{NH}$), 5.04 (s, 2H, $H_{A9}$), 3.85-3.75 (m, 4H, $H_{M11}$), 3.69 (t, 2H, $^{3}J$ = 7.6 Hz, $H_{A12}$), 3.48 (t, 2H, $^{3}J$ = 6.1 Hz, $H_{A15}$), 3.37-3.31 (m, 2H, $H_{A3}$), 2.57-2.49 (m, 8H, $H_{M4}$, $H_{M6}$), 1.88-1.59 (m, 17H, $H_{\textit{iso}\text{-BuCH}}$, $H_{M5}$, $H_{M12}$, $H_{A2}$), 1.48-1.19 (m, 14H, $H_{M13}$, $H_{M14}$, $H_{M15}$, $H_{A13}$, $H_{A14}$), 0.95-0.91 (m, 42H, $H_{\textit{iso}\text{-BuCH3}}$), 0.65-0.61 (m, 2H, $H_{A1}$), 0.61-0,55 (m, 14H, $H_{\textit{iso}\text{-BuCH2}}$).

**$^{13}$C NMR** (150 MHz, chloroform-*d*, 300 K) δ (ppm): 166.7, 161.5, 160.6, 157.2, 156.7, 147.1, 142.9, 138.8, 136.6, 133.2, 132.0, 129.2, 128.6, 127.4, 125.8, 119.7, 114.2, 114.1, 113.2, 66.7, 66.5, 64.3, 62.0, 49.5, 37.5, 32.3, 28.6, 26.2, 26.1, 25.8, 25.69, 25.66, 23.9, 23.8, 23.1, 22.49, 22.46, 9.6.

**$^{29}$Si NMR** (100 MHz, chloroform-*d*, 300 K) δ (ppm): −67.1, −67.5, −67.4.

**HRMS** (MALDI TOF) $[M+H]^{+}$ *m/z*: 1937.8860, calcd. for $C_{102}H_{146}N_5O_{17}Si_8^{+}$ 1937.8886.

**Rotaxane 12–B**




**12–B**

In a 5 mL vial with a screw cap, macrocycle **B** (15 mg, 31.8 μmol), ((4-(prop-2-yn-1-yloxy)phenyl)methanetriyl)tribenzene **7** (14.1 mg, 37.5 μmol), ((4-(4-azidobutoxy)phenyl)methanetriyl)tribenzene **8** (16.6 mg, 37.6 μmol), $[Cu(CH_3CN)_4]PF_6$ (3 mg, 8 μmol), and DIPEA (5.4 μl, 31 μmol) were dissolved in DCM (0.5 mL). After mixing the reagents, the solution immediately turned orange. The vial was sealed, and the cap was secured with a parafilm. The mixture was stirred for 48 hours at room temperature. After this time, the mixture was transferred into a separatory funnel, and DCM (20 mL) was introduced. Subsequently, aqueous ammonia solution (20 mL) and EDTA (200 mg, 0.7 mmol) were added to the solution in a separatory funnel, and upon the one-minute-long shaking, the solution turned colorless. The aqueous phase was extracted with DCM (30 mL). The collected organic extracts were washed with water and brine. The aqueous phase was once more extracted with DCM (30 mL). The collected organic layers were combined and dried over anhydrous $Na_2SO_4$. The filtrate was collected *via* gravity filtration, and the solvent was removed under reduced pressure. The obtained yellowish oil was purified *via* column chromatography (DCM/hexane (1/1) with 0-12% MeCN gradient) to provide **12–B** as a colorless oil (7.8 mg, 19.2%).

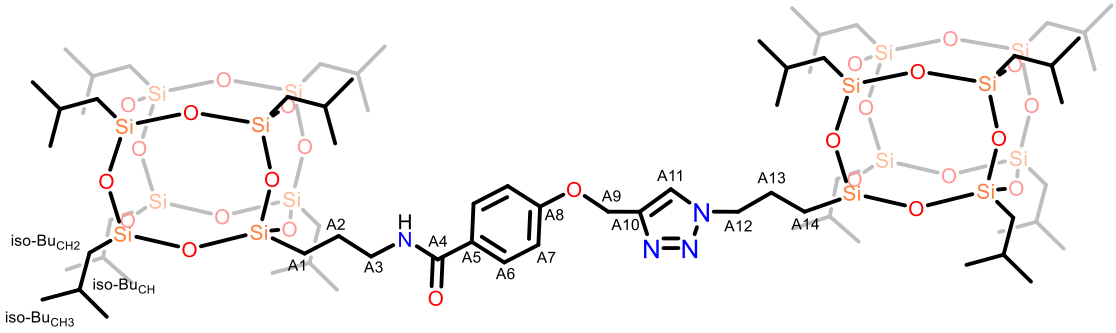
**$^1$H NMR** (600 MHz, chloroform-*d*, 300 K) δ (ppm): 7.49 (s, 1H, $H_{A12}$), 7.35 (t, 1H, $^3J$ = 7.7 Hz, $H_{M1}$), 7.26-7.13 (m, 30H, $H_{A1}$, $H_{A2}$, $H_{A3}$), 7.07 (d, 2H, $^3J$ = 8.9 Hz, $H_{A7}$), 7.02 (d, 2H, $^3J$ = 8.9 Hz, $H_{A19}$), 6.84 (d, 2H, $^3J$ = 7.8 Hz, $H_{M2}$), 6.80 (d, 2H, $^3J$ = 9.0 Hz, $H_{A8}$), 6.72 (d, 4H, $^3J$ = 8.6 Hz, $H_{M8}$), 6.54 (d, 2H, $^3J$ = 9.0 Hz, $H_{A18}$), 6.46 (d, 4H, $^3J$ = 8.6 Hz, $H_{M9}$), 5.00 (s, 2H, $H_{A10}$), 3.82-3.72 (m, 4H, $H_{M11}$), 3.53-3.49 (m, 2H, $H_{A13}$), 3.38 (t, 2H,

$^{3}J$ = 6.0 Hz, $H_{A16}$), 2.57-2.46 (m, 8H, $H_{M4}$, $H_{M6}$), 1.84-1.71 (m, 4H, $H_{M5}$), 1.71-1.59 (m, 4H, $H_{M12}$), 1.45-1.34 (m, 4H, $H_{M13}$), 1.34-1.09 (m, 10H, $H_{M14}$, $H_{M15}$, $H_{A14}$, $H_{A15}$).

**$^{13}$C NMR** (150 MHz, chloroform-*d*, 300 K) δ (ppm): 161.4, 157.2, 156.7, 156.4, 147.1, 143.4, 139.3, 138.7, 136.6, 133.4, 132.2, 132.0, 131.1, 129.3, 127.41, 127.39, 125.8, 123.1, 119.6, 114.15, 113.4, 113.2, 66.7, 66.5, 64.3, 61.8, 49.4, 37.7, 35.0, 32.4, 29.9, 28.8, 28.6, 26.03, 25.98, 25.8.

**HRMS** (MALDI TOF) $[M+H]^+$ *m/z*: 1280.6991, calcd. for $C_{89}H_{91}N_4O_4^+$ 1280.7068.

**Axle 9b**




**9b**

In a 5 mL vial with a screw cap, alkyne **6b** (20 mg, 19.4 μmol), ), 3-azidopropylhepta-*iso*-butyl POSS **3b** (17.5 mg, 19.4 μmol), $[Cu(CH_3CN)_4]PF_6$ (2 mg, 5.3 μmol), DIPEA (0.1 mL, 0.57 mmol) were dissolved in THF (0.3 mL). After mixing the reagents, the solution immediately turned orange. The vial was sealed, and the cap was secured with a parafilm. The mixture was stirred for 20 hours at room temperature. After this time, the mixture was transferred into a separatory funnel, and DCM (20 mL) was introduced. Subsequently, aqueous ammonia solution (20 mL) and EDTA (200 mg, 0.7 mmol) were added to the solution in a separatory funnel, and upon the one-minute-long shaking, the solution turned colorless. The aqueous phase was extracted with DCM (30 mL). The collected organic extracts were washed with water and brine. The aqueous phase was once more extracted with DCM (30 mL). The collected organic layers were combined and dried over anhydrous $Na_2SO_4$. The filtrate was collected *via* gravity filtration, and the solvent was removed under reduced pressure. The yellowish oil was purified *via* column chromatography (DCM/hexane (1/1) with 0-6% MeCN

gradient). The crude product was recrystallized from a DCM/methanol (1/9) to provide **9b** as a white solid (18.3 mg, 48.9%).

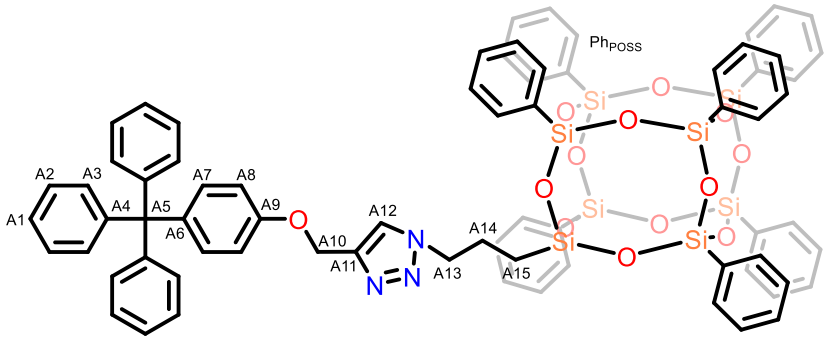
**$^{1}$H NMR** (500 MHz, chloroform-*d*, 300 K) δ (ppm): 7.70 (d, 2H, $^{3}J$ = 8.8 Hz, $H_{A6}$), 7.56 (s, 1H, $H_{A11}$), 7.00 (d, 2H, $^{3}J$ = 8.8 Hz, $H_{A7}$), 6.02-5.97 (m, 1H, $H_{NH}$), 5.22 (s, 2H, $H_{A9}$), 4.33 (t, 2H, $^{3}J$ = 7.2 Hz, $H_{A12}$), 3.44-3.38 (m, 2H, $H_{A3}$), 2.06-1.94 (m, 2H, $H_{A13}$), 1.88-1.75 (m, 14H, $H_{iso\text{-}BuCH}$), 1.75-1.63 (m, 2H, $H_{A2}$), 0.99-0.88 (m, 84H, $H_{iso\text{-}BuCH3}$), 0.69-0.50 (m, 32H, $H_{iso\text{-}BuCH2}$, $H_{A1}$, $H_{A14}$).

**$^{13}$C NMR** (125 MHz, chloroform-*d*, 300 K) δ (ppm): 166.8, 160.7, 143.5, 128.6, 127.8, 122.4, 114.5, 62.2, 52.6, 42.2, 25.66, 25.65, 24.1, 23.87, 23.83, 23.82, 23.1, 22.47, 22.45, 22.41, 9.5, 9.2.

**$^{29}$Si NMR** (100 MHz, chloroform-*d*, 300 K) δ (ppm): −66.5, −66.6, −66.79, −66.82.

**HRMS** (MALDI TOF) $[M+Na]^{+}$ *m/z*: 1955.6442, calcd. for $C_{72}H_{146}N_4O_{26}Si_{16}Na^{+}$ 1955.6438.

**Axle 10a**




**10a**

In a 5 mL vial with a screw cap, ((4-(prop-2-yn-1-yloxy)phenyl)methanetriyl)tribenzene **7** (7.3 mg, 19.4 μmol), azidopropylheptaphenyl POSS **3a** (20.2 mg, 19.4 μmol), $[Cu(CH_3CN)_4]PF_6$ (2 mg, 5.3 μmol), DIPEA (20 μl, 0.11 mmol) were dissolved in THF (3 mL). After mixing the reagents, the solution immediately turned orange. The vial was sealed, and the cap was secured with a parafilm. The mixture was stirred for 48 hours at room temperature. After this time, the mixture was transferred into a separatory funnel, and DCM (20 mL) was introduced. Subsequently, aqueous ammonia solution (20 mL) and EDTA (200 mg, 0.7 mmol) were added to the solution in a separatory funnel, and upon the one-minute-long shaking, the solution turned colorless. The

aqueous phase was extracted with DCM (30 mL). The collected organic extracts were washed with water and brine. The aqueous phase was once more extracted with DCM (30 mL). The collected organic layers were combined and dried over anhydrous $Na_2SO_4$. The filtrate was collected *via* gravity filtration, and the solvent was removed under reduced pressure. The yellowish oil was purified *via* flash chromatography (*n*-hexane with 10-40% ethyl acetate gradient) to provide **10a** as a white oil which solidifies after time (9.11 mg, 33.1%).

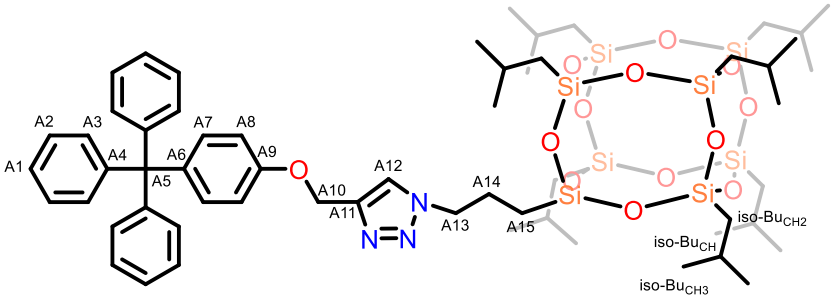
**$^1$H NMR** (500 MHz, chloroform-*d*, 300 K) δ (ppm): 7.76-7.68 (m, $H_{PhPOSS}$), 7.46-7.38 (m, $H_{PhPOSS}$), 7.38-7.30 (m, $H_{PhPOSS}$), 7.24-7.13 (m, 16H, $H_{A12}$, $H_{A1}$ $H_{A2}$, $H_{A3}$), 7.10 (d, 2H, $^3J$ = 8.8 Hz, $H_{A7}$), 6.83 (d, 2H, $^3J$ = 8.9 Hz, $H_{A8}$), 5.06 (s, 2H, $H_{A10}$), 4.27 (t, 2H, $^3J$ = 7.2 Hz, $H_{A13}$), 2.12-2.05 (m, 2H, $H_{A14}$), 0.85-0.80 (m, 2H, $H_{A15}$).

**$^{13}$C NMR** (125 MHz, chloroform-*d*, 300 K) δ (ppm): 156.4, 147.0, 144.0, 139.5, 134.18, 134.16, 134.09, 132.3, 131.1, 131.0, 130.8, 130.1, 130.0, 128.0, 127.89, 127.87, 127.4, 125.9, 122.5, 113.5, 64.3, 62.0, 52.0, 23.9, 8.7.

**$^{29}$Si NMR** (100 MHz, chloroform-*d*, 300 K) δ (ppm): −65.6, −77.76, −77.83, −78.1.

**HRMS** (MALDI TOF) $[M+Na]^+$ *m/z*: 1437.2490, calcd. for $C_{73}H_{63}N_3O_{13}Si_8Na^+$ 1437.2428.

**Axle 10b**




**10b**

In a 5 mL vial with a screw cap, ((4-(prop-2-yn-1-yloxy)phenyl)methanetriyl)tribenzene **7** (7.3 mg, 19.4 μmol), azidopropylhepta-*iso*-butyl POSS **3b** (17.5 mg, 19.4 μmol), $[Cu(CH_3CN)_4]PF_6$ (2 mg, 5.3 μmol), DIPEA (0.1 mL, 0.57 mmol) were dissolved in THF (0.3 mL). After mixing the reagents, the solution immediately turned orange. The vial was sealed, and the cap was secured with a parafilm. The mixture was stirred for 48

hours at room temperature. After this time, the mixture was transferred into a separatory funnel, and DCM (20 mL) was introduced. Subsequently, aqueous ammonia solution (20 mL) and EDTA (200 mg, 0.7 mmol) were added to the solution in a separatory funnel, and upon the one-minute-long shaking, the solution turned colorless. The aqueous phase was extracted with DCM (30 mL). The collected organic extracts were washed with water and brine. The aqueous phase was once more extracted with DCM (30 mL). The collected organic layers were combined and dried over anhydrous $Na_2SO_4$. The filtrate was collected *via* gravity filtration, and the solvent was removed under reduced pressure. The yellowish oil was purified *via* column chromatography (DCM/hexane (1/1) with 0-6% MeCN gradient). The crude product was recrystallized from a DCM/methanol (1/9) to provide **10b** as a white solid (14.4 mg, 58.2%).

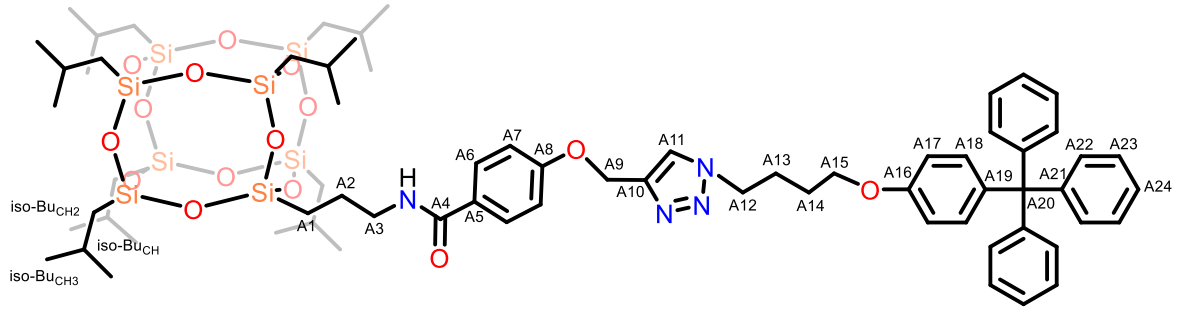
**$^1$H NMR** (500 MHz, chloroform-*d*, 300 K) δ (ppm): 7.55 (s, 1H, $H_{A12}$), 7.24-7.13 (m, 15H, $H_{A1}$, $H_{A2}$, $H_{A3}$), 7.10 (d, 2H, $^3J$ = 8.9 Hz, $H_{A7}$), 6.86 (d, 2H, $^3J$ = 8.9 Hz, $H_{A8}$), 5.16 (s, 2H, $H_{A10}$), 4.33 (t, 2H, $^3J$ = 7.3 Hz, $H_{A13}$), 2.04-1.96 (d, 2H, $H_{A14}$), 1.88-1.76 (m, 7H, $H_{\textit{iso}\text{-BuCH}}$), 0.96-0.90 (m, 42H, $H_{\textit{iso}\text{-BuCH3}}$), 0.66-0.52 (m, 16H, $H_{A15}$, $H_{\textit{iso}\text{-BuCH2}}$).

**$^{13}$C NMR** (125 MHz, chloroform-*d*, 300 K) δ (ppm): 156.4, 147.0, 144.2, 139.6, 132.3, 131.1, 127.4, 125.9, 122.3, 113.5, 64.3, 62.1, 52.5, 25.68, 25.66, 24.1, 23.88, 23.84, 23.83, 22.5, 22.4, 9.3.

**$^{29}$Si NMR** (100 MHz, chloroform-*d*, 300 K) δ (ppm): −67.5, −67.8, −68.6.

**HRMS** (MALDI TOF) $[M+Na]^+$ *m/z*: 1297.4644, calcd. for $C_{59}H_{91}N_3O_{13}Si_8Na^+$ 1297.4617.

**Axle 11b**



**11b**

In a 5 mL vial with a screw cap, alkyne **6b** (20 mg, 19.4 μmol), ((4-(4-azidobutoxy)phenyl)methanetriyl)tribenzene **7** (8.4 mg, 19.4 μmol), $[Cu(CH_3CN)_4]PF_6$ (2 mg, 5.3 μmol), DIPEA (0.1 mL, 0.57 mmol) were dissolved in THF (0.3 mL. The vial was sealed, and the cap was secured with a parafilm. The mixture was stirred for 48 hours at room temperature. After this time, the mixture was transferred into a separatory funnel, and DCM (20 mL) was introduced. Subsequently, aqueous ammonia solution (20 mL) and EDTA (200 mg, 0.7 mmol) were added to the solution in a separatory funnel, and upon the one-minute-long shaking, the solution turned colorless. The aqueous phase was extracted with DCM (30 mL). The collected organic extracts were washed with water and brine. The aqueous phase was once more extracted with DCM (30 mL). The collected organic layers were combined and dried over anhydrous $Na_2SO_4$. The filtrate was collected *via* gravity filtration, and the solvent was removed under reduced pressure. The yellowish oil was purified *via* flash chromatography (*n*-hexane with 10-40% ethyl acetate gradient) to provide **11b** as a white oil that solidifies after the time (5.8 mg, 28.4%).

**$^1$H NMR** (500 MHz, chloroform-*d*, 300 K) δ (ppm): 7.67 (d, 2H, $^3J$ = 8.3 Hz, $H_{A6}$), 7.60 (s, 1H, $H_{A11}$), 7.24-7.14 (m, 15H, $H_{A22}$, $H_{A23}$, $H_{A24}$), 7.09 (d, 2H, $^3J$ = 8.5 Hz, $H_{A18}$), 7.00 (d, 2H, $^3J$ = 8.5 Hz, $H_{A7}$), 6.75 (d, 2H, $^3J$ = 8.5 Hz, $H_{A17}$), 6.07-6.00 (m, 1H, $H_{NH}$), 5.30 (s, 2H, $H_{A9}$), 4.55 (t, 2H, $^3J$ = 6.8 Hz, $H_{A12}$), 4.08 (t, 2H, $^3J$ = 5.7 Hz, $H_{A15}$), 3.60-3.54 (m, 2H, $H_{A3}$), 2.38-2.28 (m, 2H, $H_{A13}$), 2.12-1.97 (m, 9H, $H_{iso\text{-}BuCH}$, $H_{A14}$), 1.97-1.86 (m, 2H, $H_{A2}$), 1.24-1.14 (m, 42H, $H_{iso\text{-}BuCH3}$), 0.95-0.90 (m, 2H, $H_{A1}$), 0.90-0.81 (m, 14H, $H_{iso\text{-}BuCH2}$).

**$^{13}$C NMR** (125 MHz, chloroform-*d*, 300 K) δ (ppm): 166.8, 160.6, 156.6, 147.0, 143.7, 139.3, 132.3, 131.1, 128.6, 127.8, 127.4, 125.9, 122.6, 114.6, 113.1, 66.7, 64.3, 62.1, 50.1, 42.2, 27.3, 26.2, 25.67, 25.65, 23.9, 23.8, 23.1, 22.48, 22.45, 9.5.

**$^{29}$Si NMR** (100 MHz, chloroform-*d*, 300 K) δ (ppm): −67.1, −67.28, −67.34.

**HRMS** (MALDI TOF) $[M+Na]^+$ *m/z*: 1488.5595, calcd. for $C_{70}H_{104}N_4O_{15}Si_8Na^+$ 1488.5565.

# NMR spectra

## NMR spectra of macrocycle B

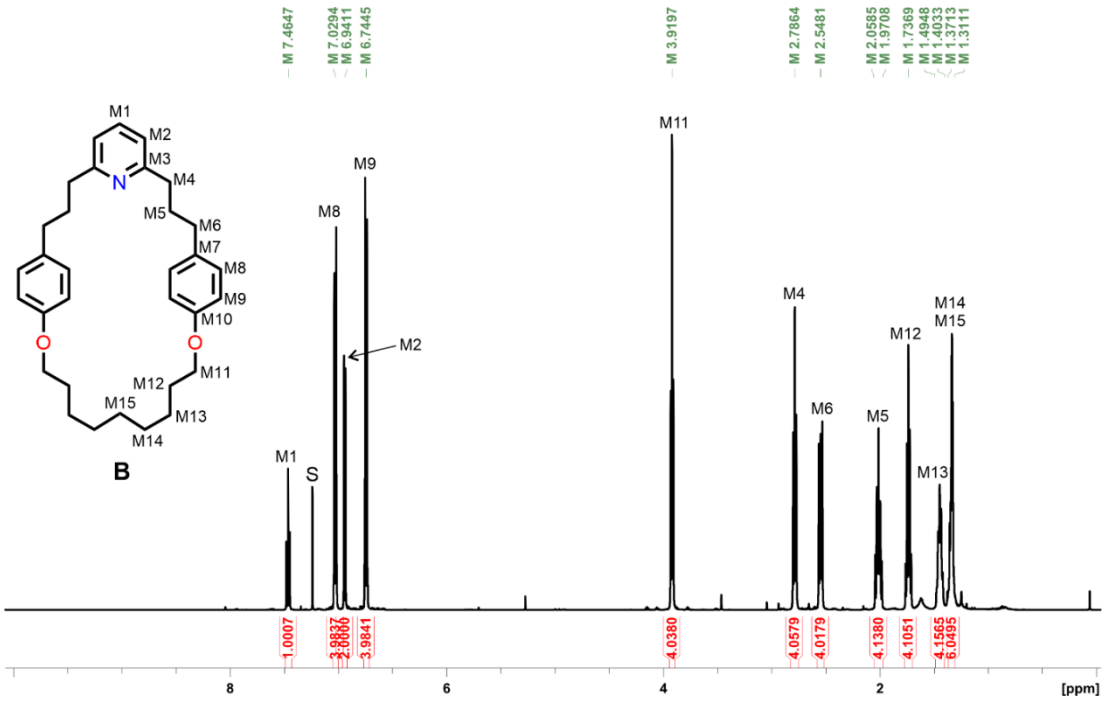



**Figure S 1.** The $^{1}$H NMR spectrum of **B** (chloroform-*d*, 300 K, 500 MHz).

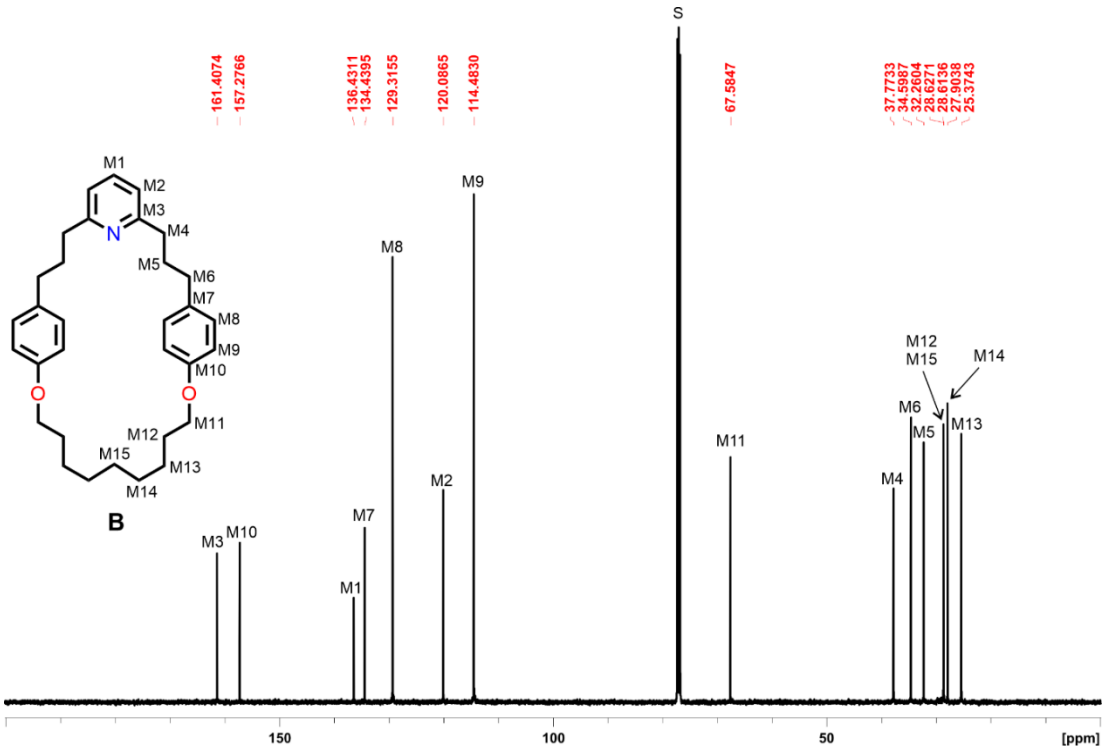



**Figure S 2.** The $^{13}$C NMR spectrum of **B** (chloroform-*d*, 300 K, 125 MHz).

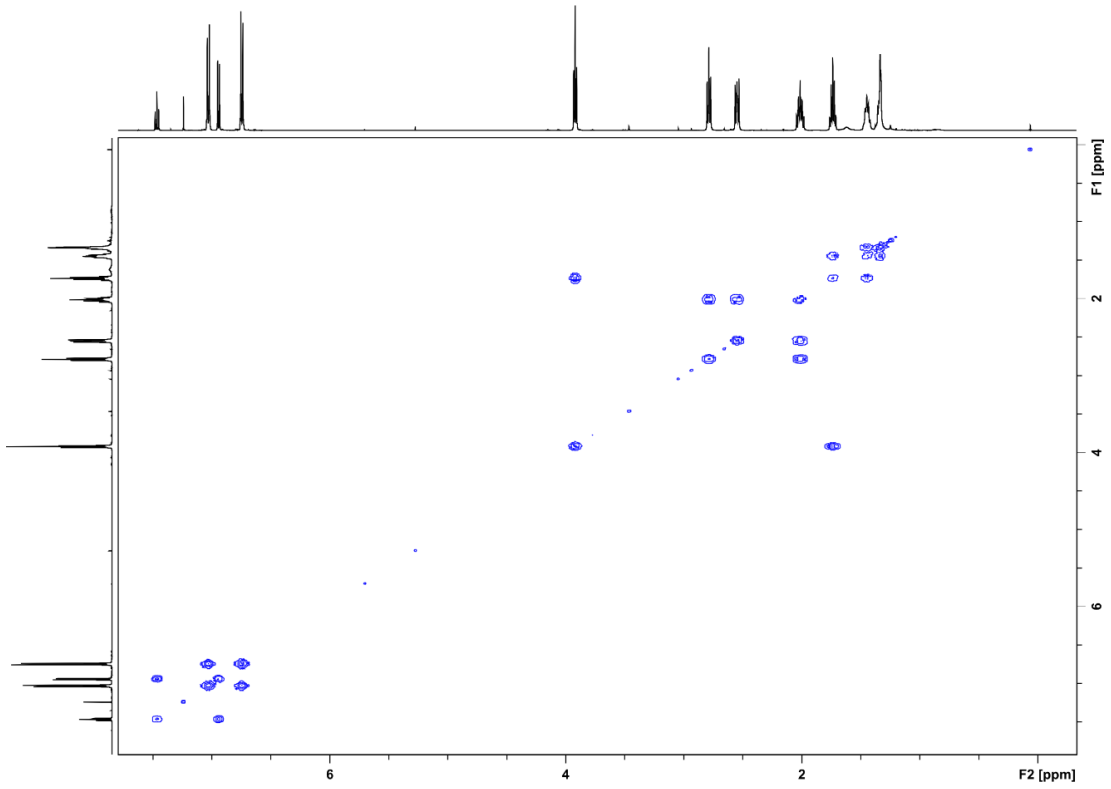



**Figure S 3**. The $^{1}$H-$^{1}$H COSY spectrum of **B** (chloroform-*d*, 300 K, 500 MHz).

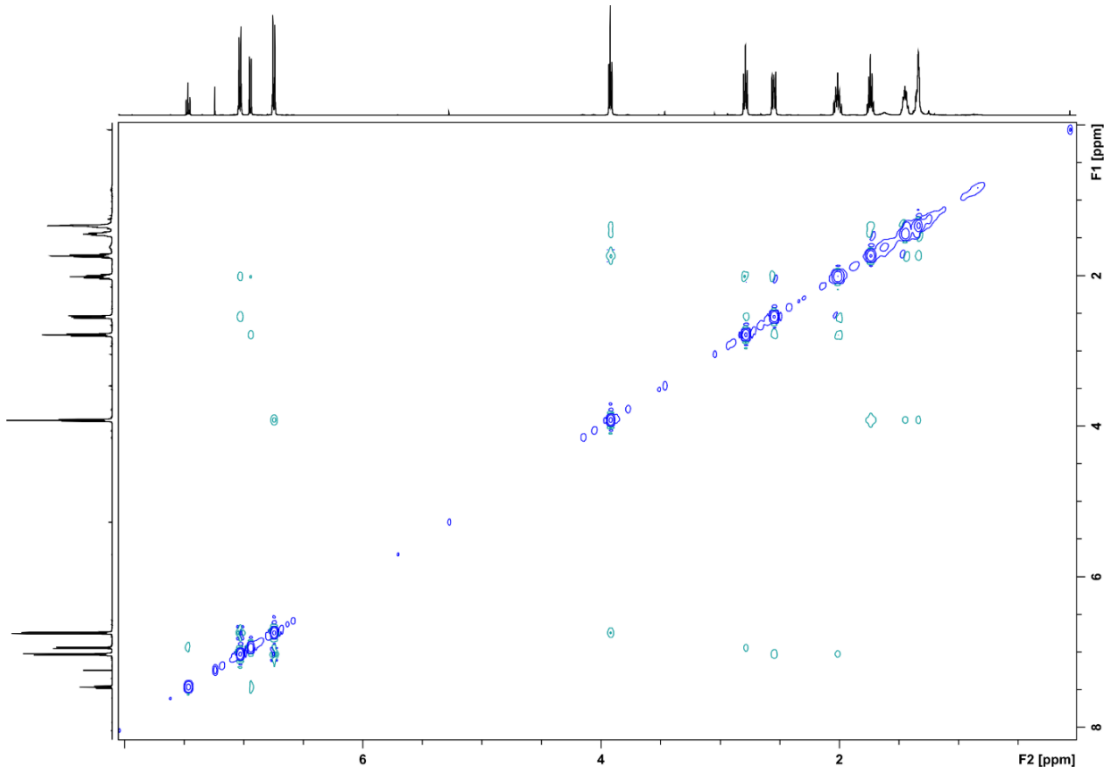



**Figure S 4.** The $^{1}$H-$^{1}$H NOESY spectrum of **B** (chloroform-*d*, 300 K, 500 MHz).

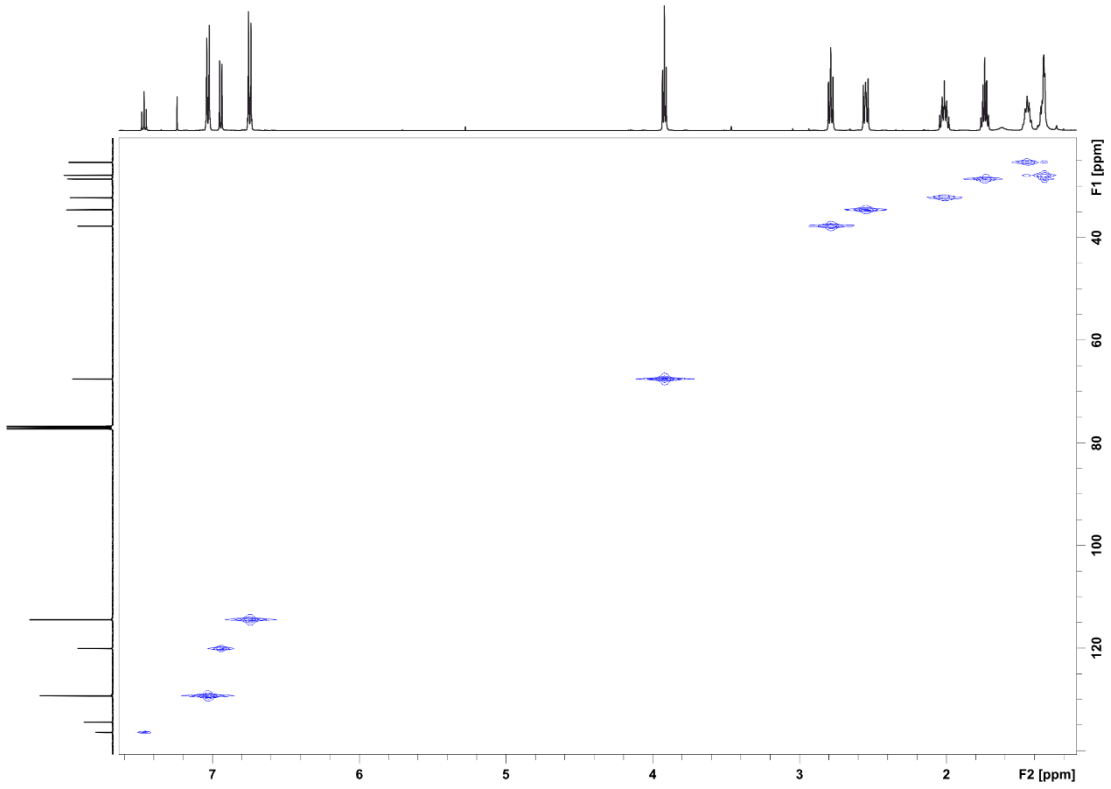



**Figure S 5.** The $^{1}H$-$^{13}C$ HMQC spectrum of **B** (chloroform-*d*, 300 K, 500 MHz).

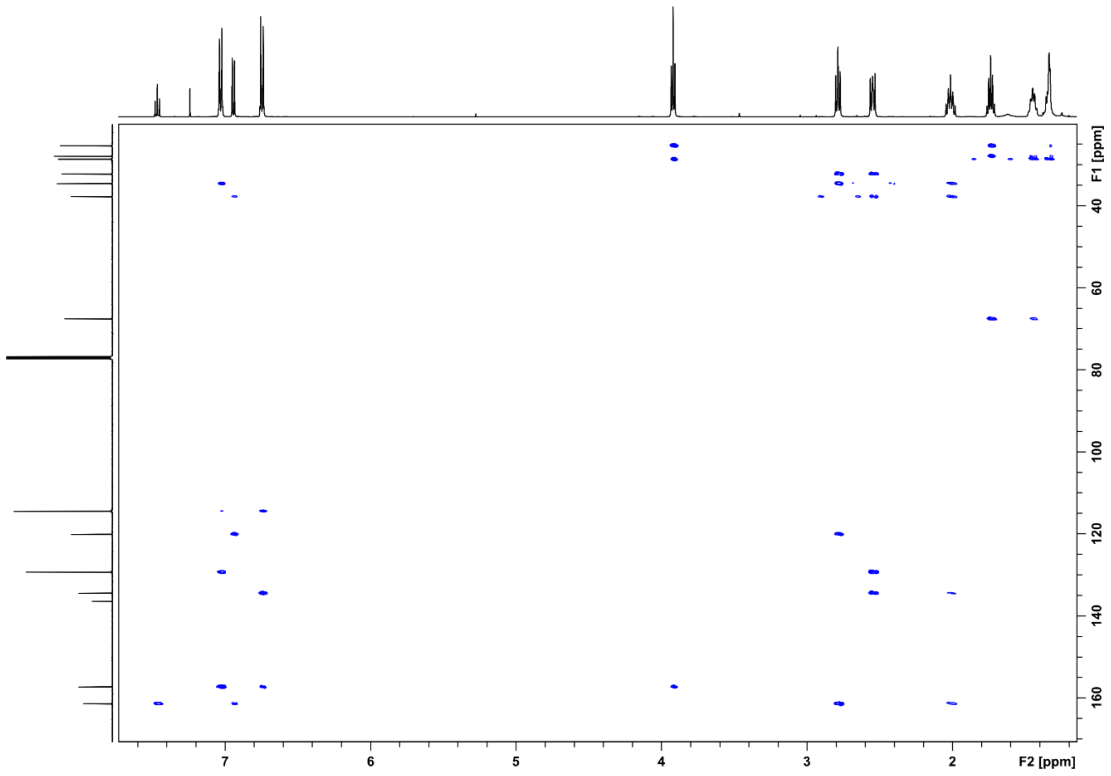



**Figure S 6.** The $^{1}H$-$^{13}C$ HMBC spectrum of **B** (chloroform-*d*, 300 K, 500 MHz).

**NMR spectrum of S11**

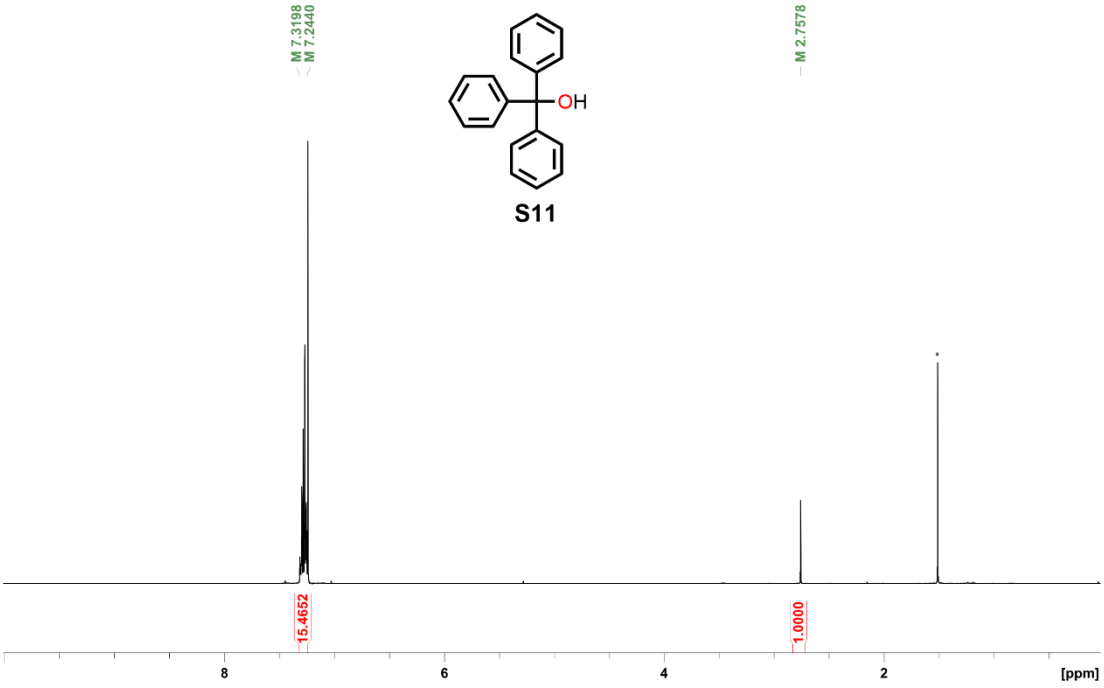



**Figure S 7.** The $^{1}$H NMR spectrum of **S11** (chloroform-*d*, 300 K, 500 MHz).

**NMR spectrum of S12**

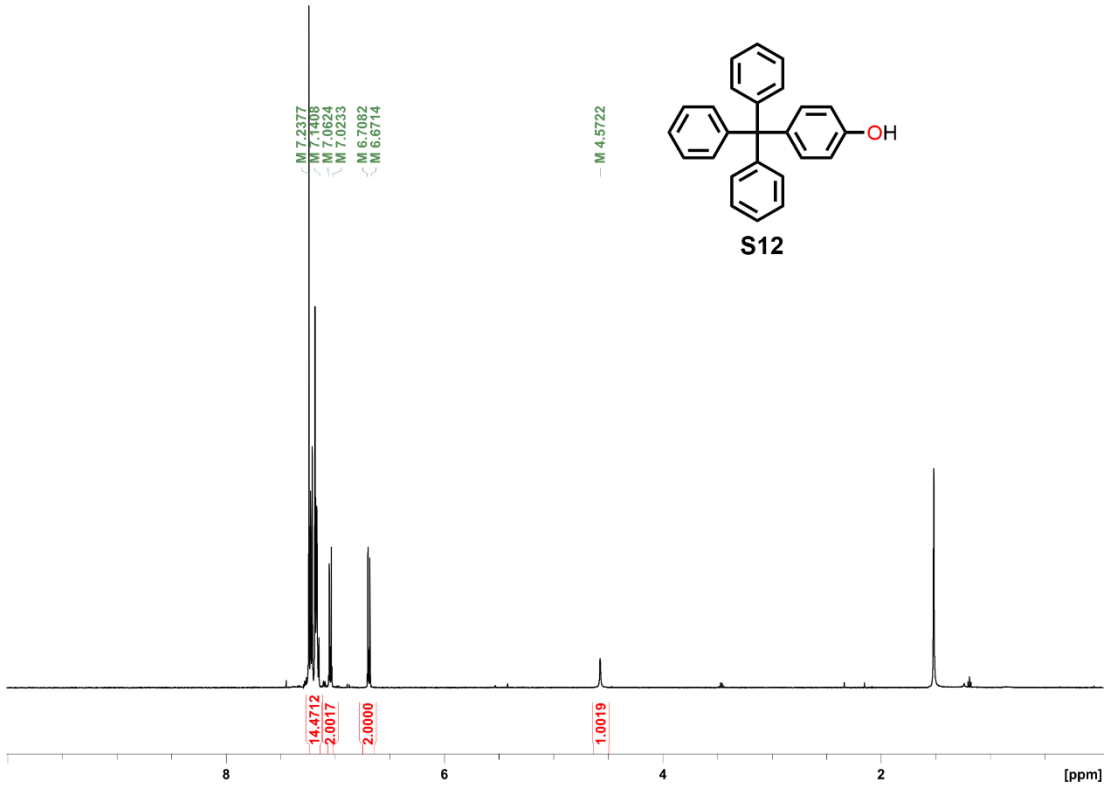



**Figure S 8.** The $^{1}$H NMR spectrum of **S12** (chloroform-*d*, 300 K, 500 MHz).

## NMR spectrum of 8

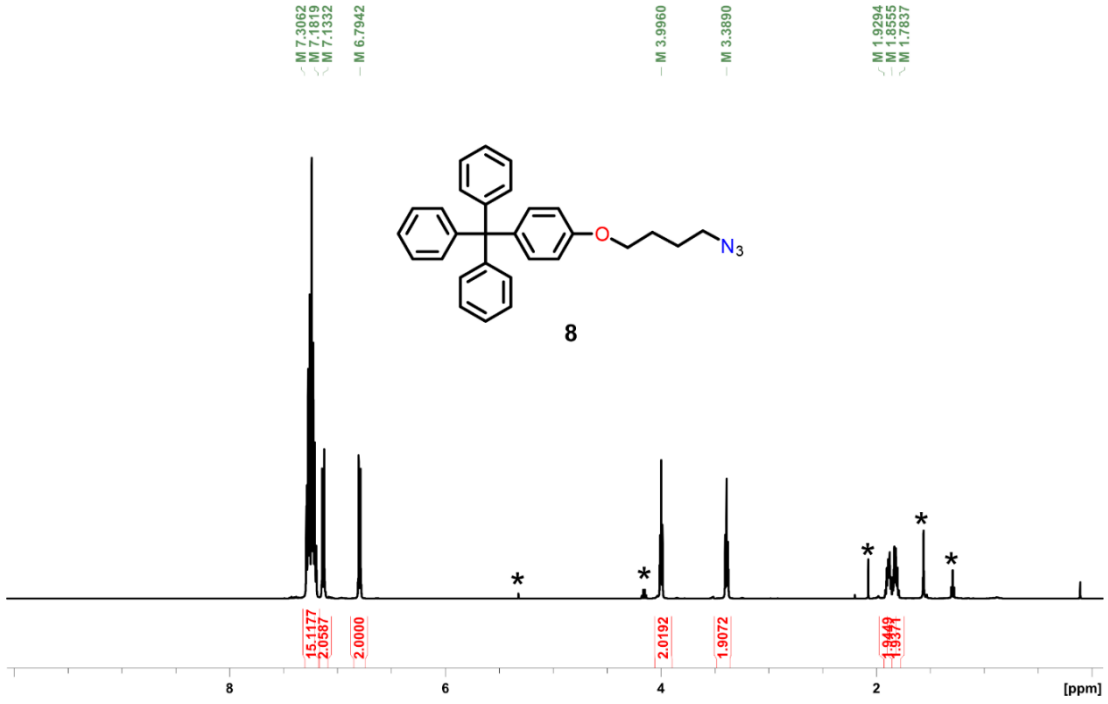



**Figure S 9.** The $^{1}$H NMR spectrum of **8** (chloroform-*d*, 300 K, 500 MHz).

## NMR spectra of 6b

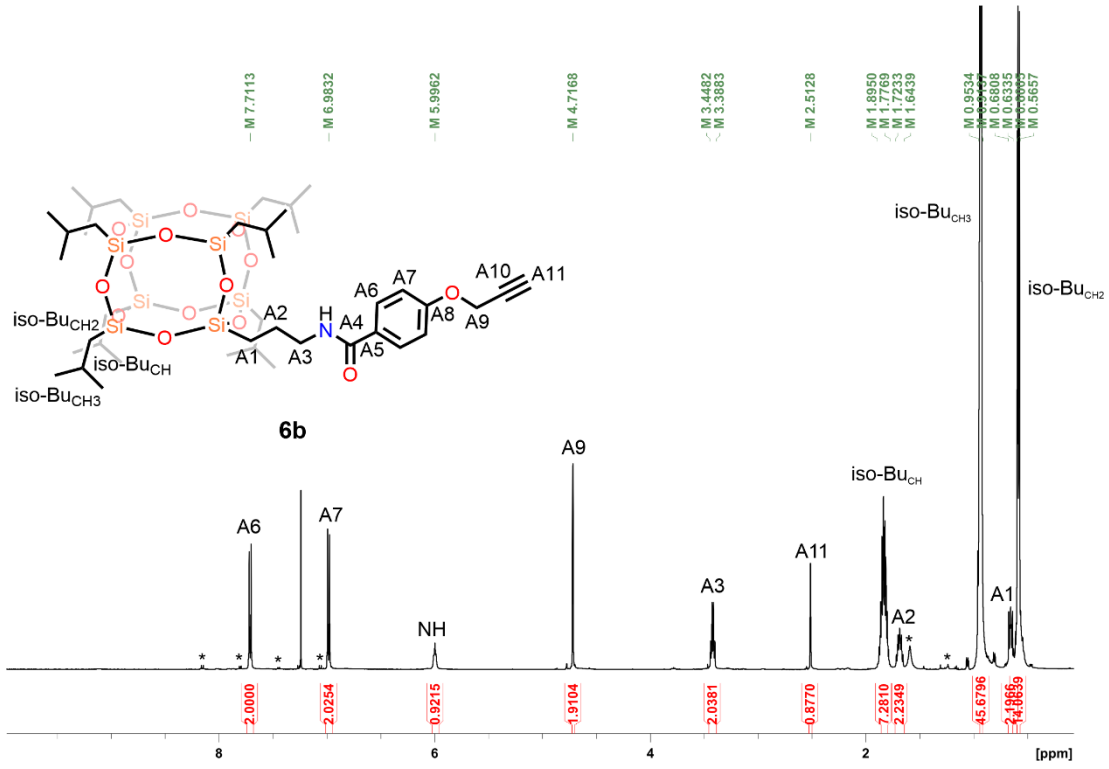



**Figure S 10.** The $^{1}$H NMR spectrum of **6b** (chloroform-*d*, 300 K, 500 MHz).

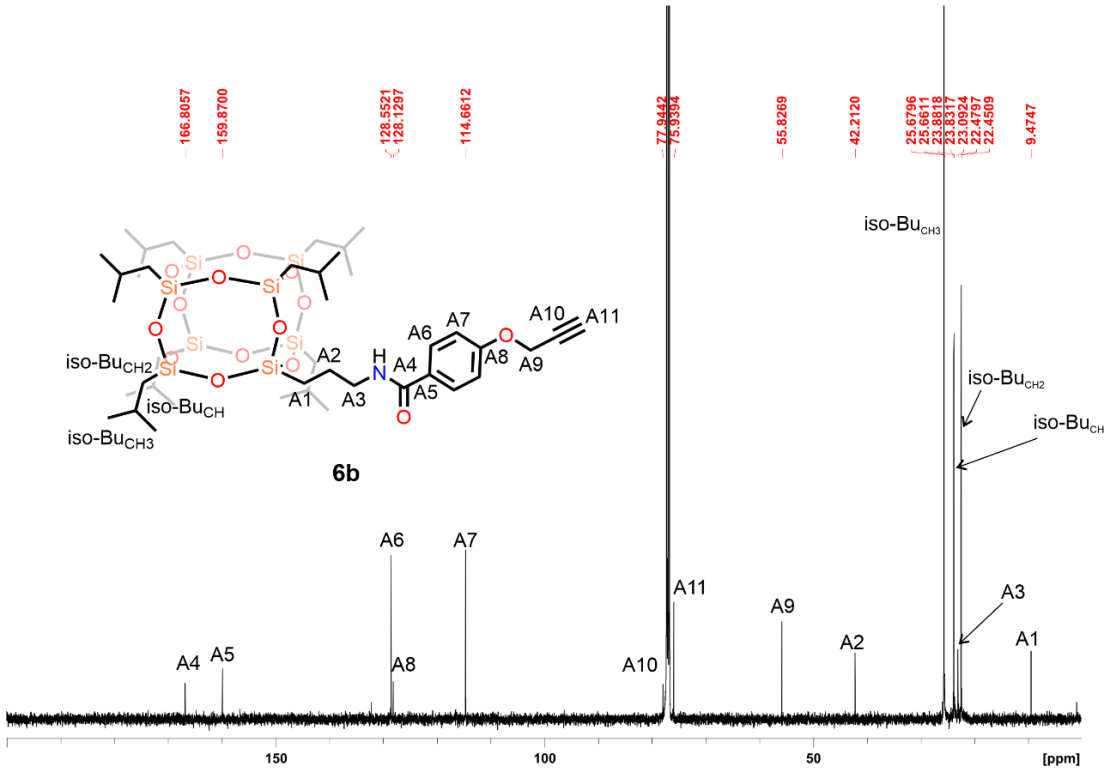



**Figure S 11.** The $^{13}$C NMR spectrum of **6b** (chloroform-*d*, 300 K, 125 MHz).

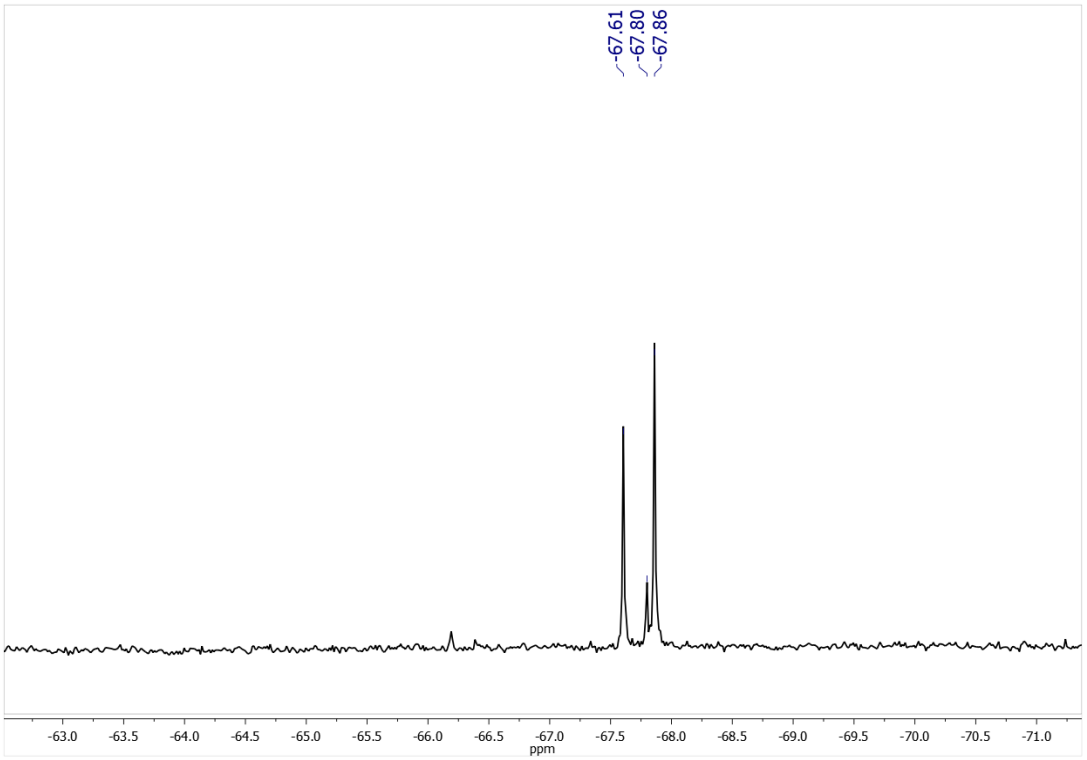



**Figure S 12.** The $^{29}$Si NMR spectrum of **6b** (chloroform-*d*, 300 K, 100 MHz).

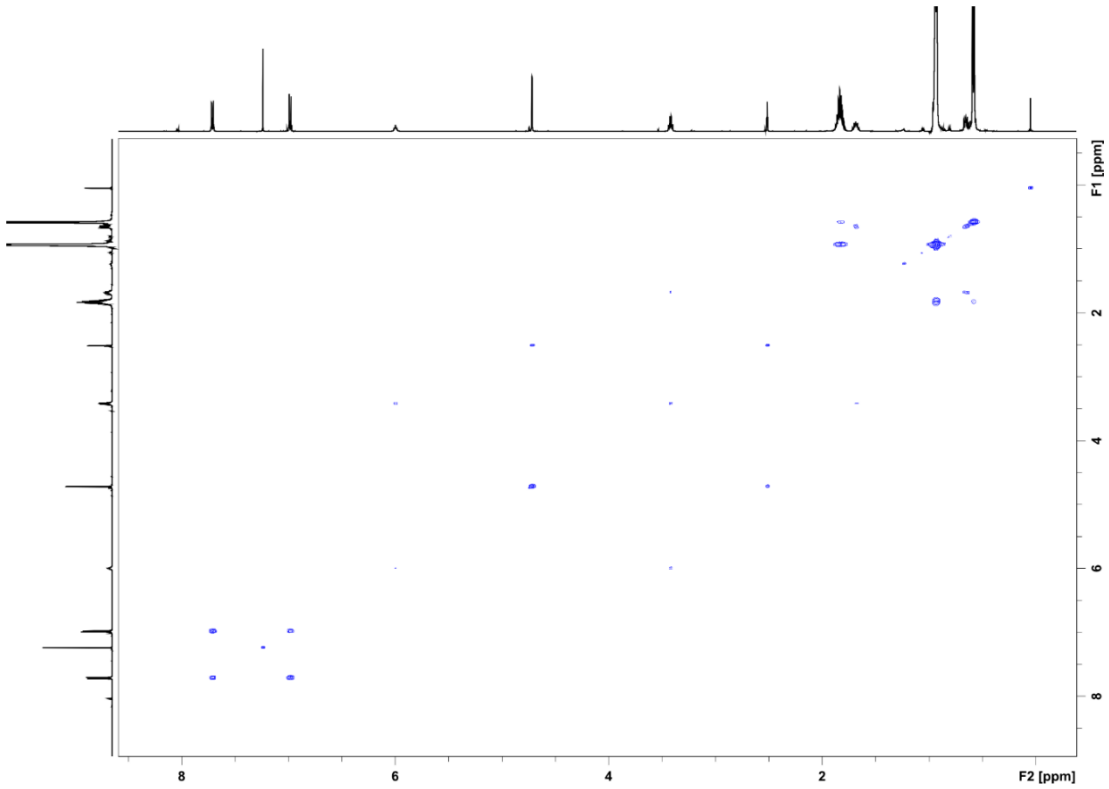



**Figure S 13.** The $^{1}$H-$^{1}$H COSY spectrum of **6b** (chloroform-*d*, 300 K, 500 MHz).

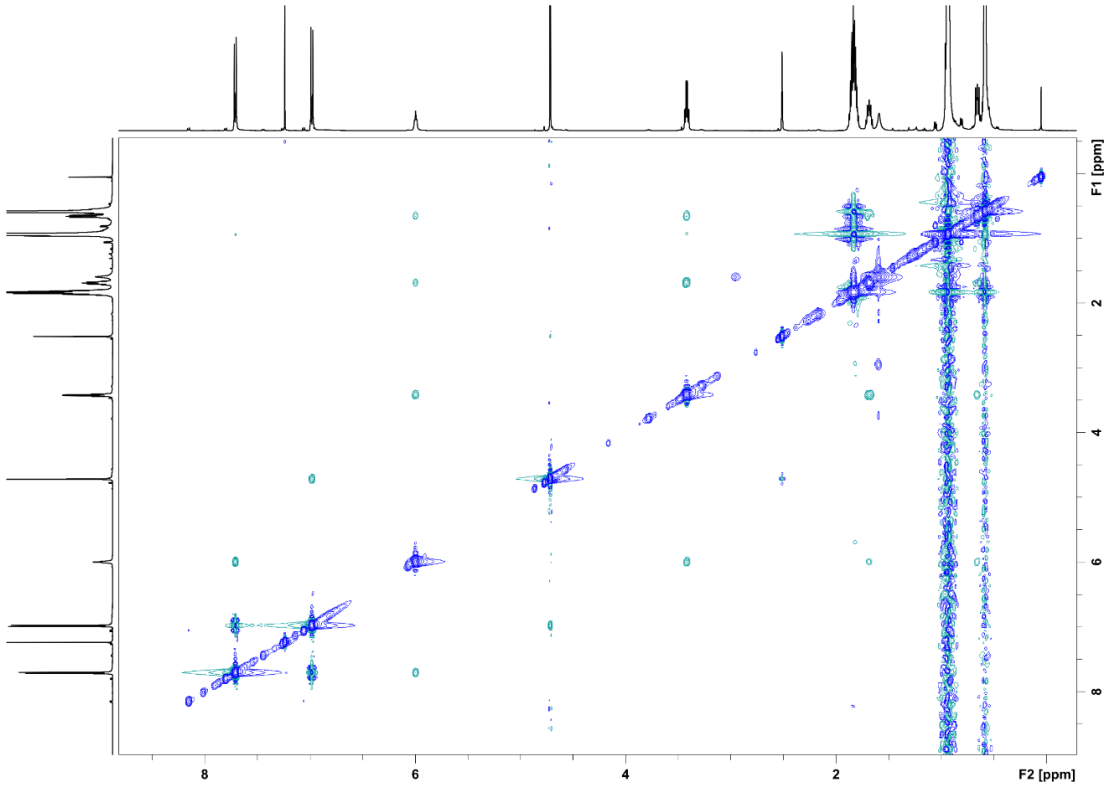



**Figure S 14.** The $^{1}$H-$^{1}$H NOESY spectrum of **6b** (chloroform-*d*, 300 K, 500 MHz).

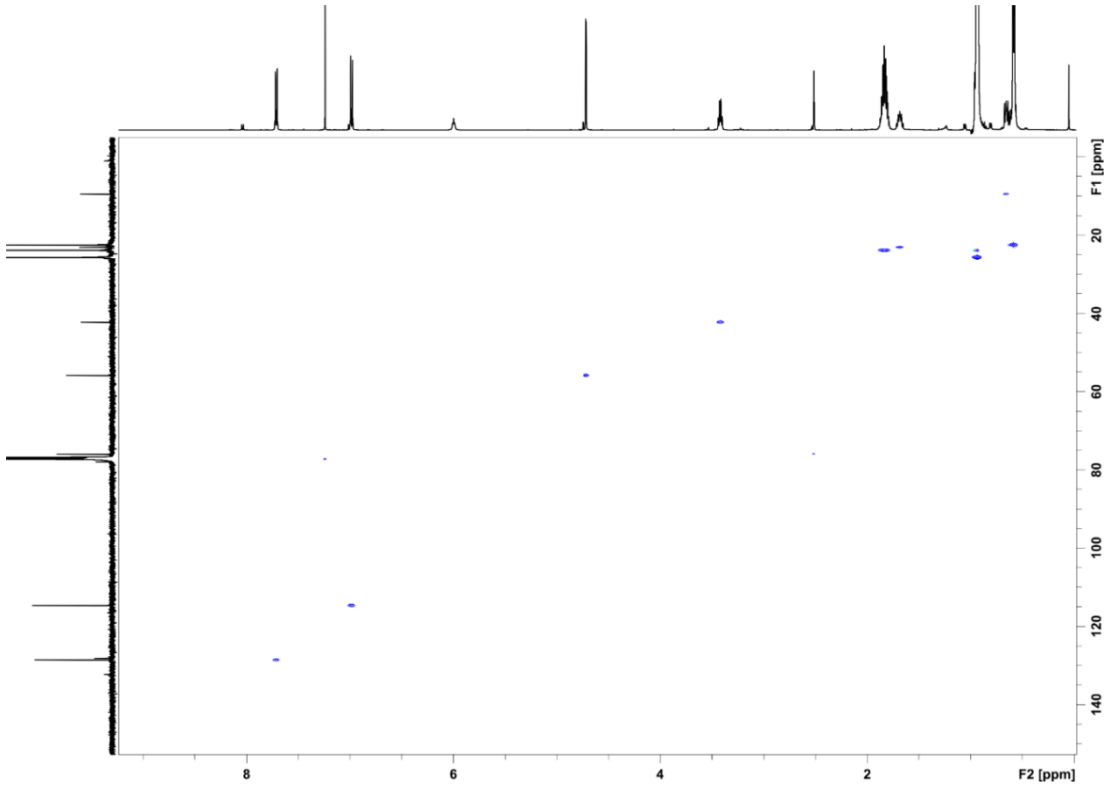



**Figure S 15.** The $^{1}$H-$^{13}$C HSQC spectrum of **6b** (chloroform-*d*, 300 K, 500 MHz).

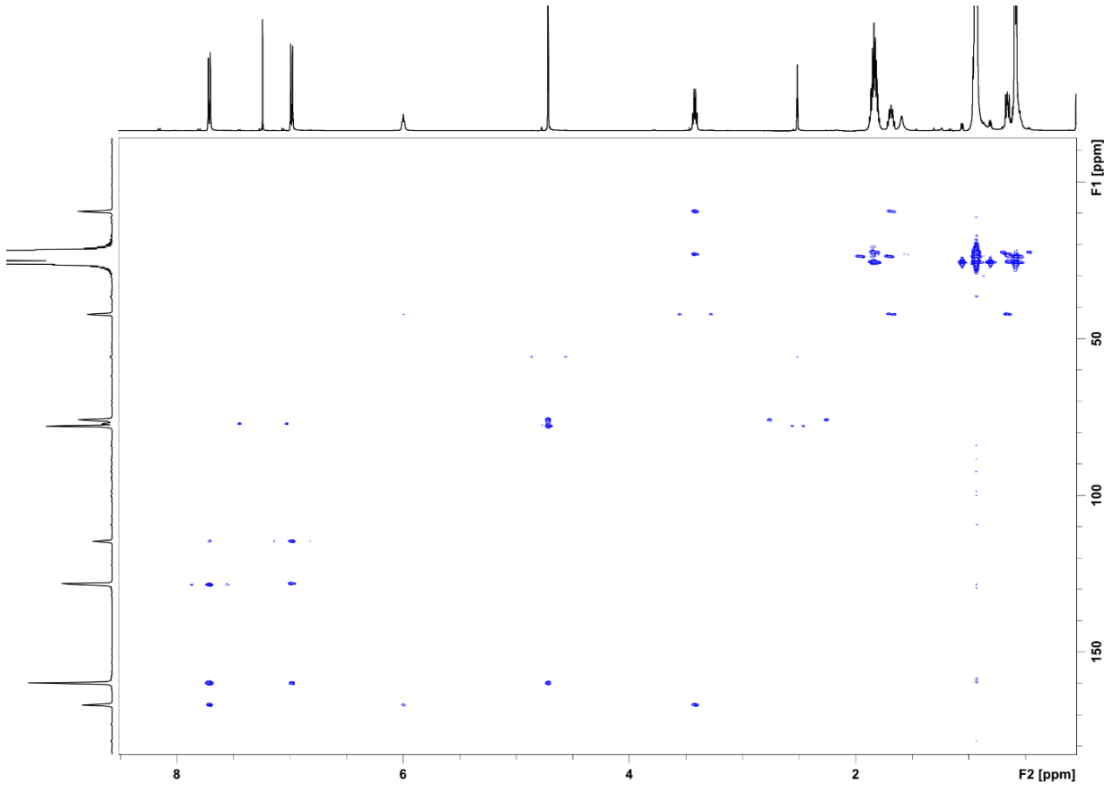



**Figure S 16.** The $^{1}H$-$^{13}C$ HMBC spectrum of **6b** (chloroform-*d*, 300 K, 500 MHz).

## NMR spectra of 9b–A

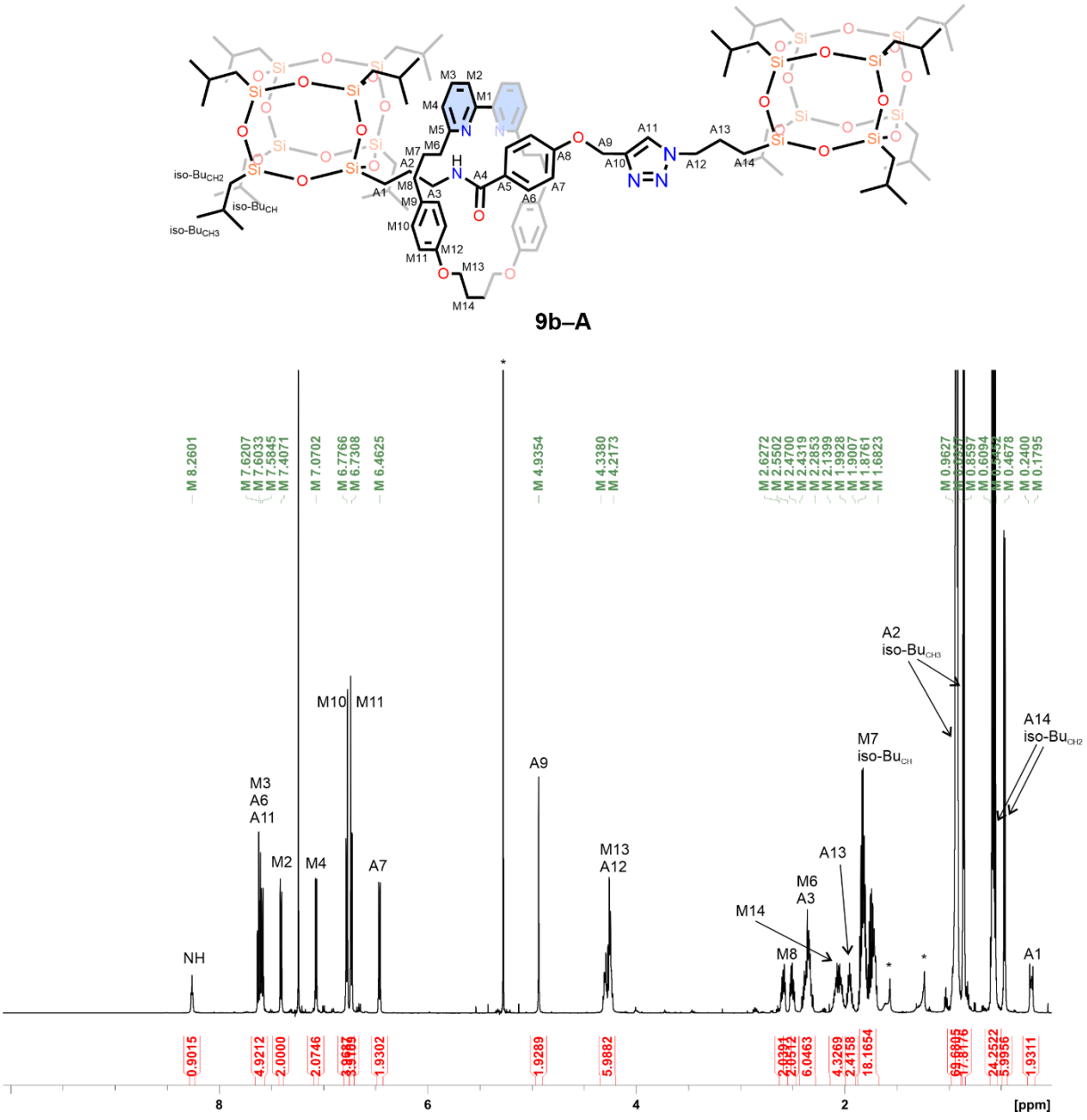



**Figure S 17.** The $^{1}$H NMR spectrum of **9b–A** (chloroform-*d*, 300 K, 600 MHz).

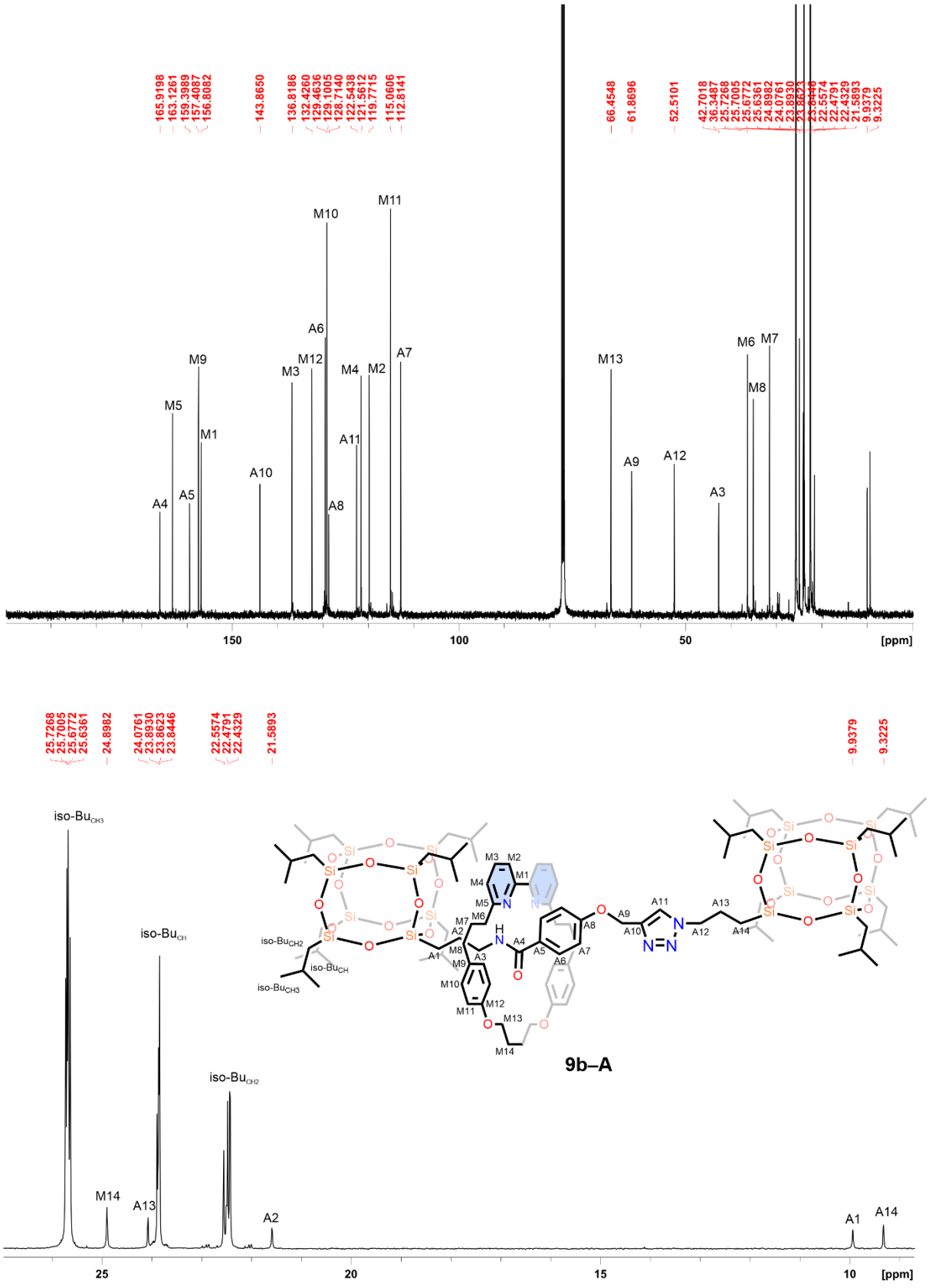



**Figure S 18.** The $^{13}$C NMR spectrum of **9b–A** (chloroform-*d*, 300 K, 125 MHz).

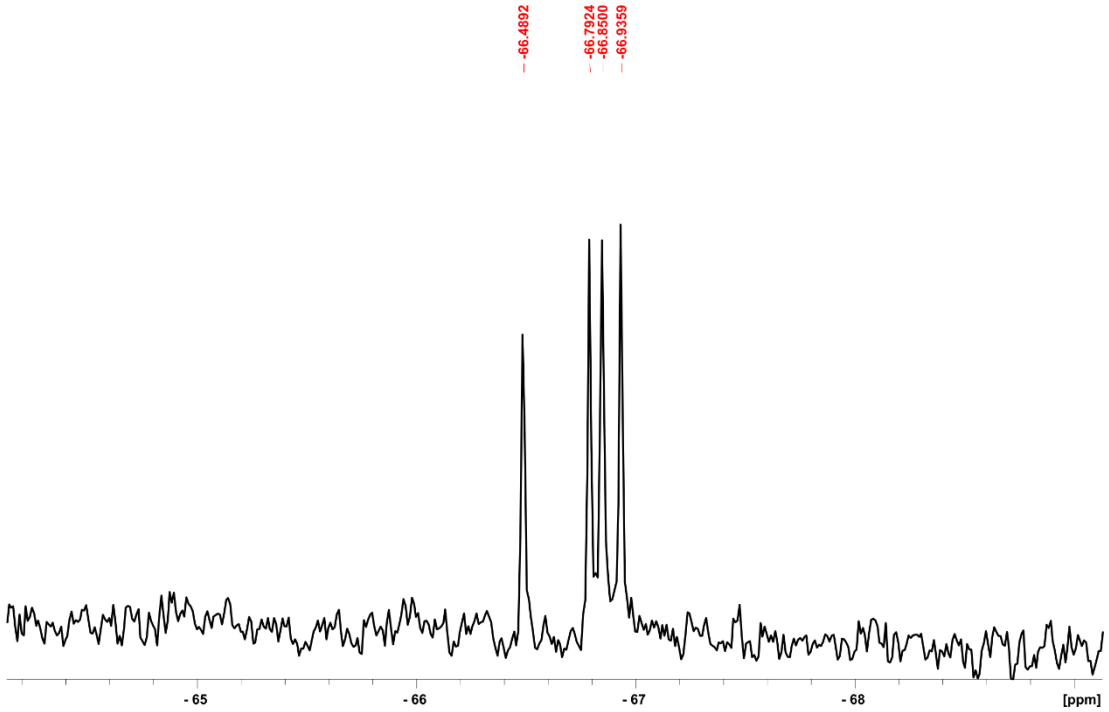



**Figure S 19.** The $^{29}$Si NMR spectrum of **9b–A** (chloroform-*d*, 300 K, 100 MHz).

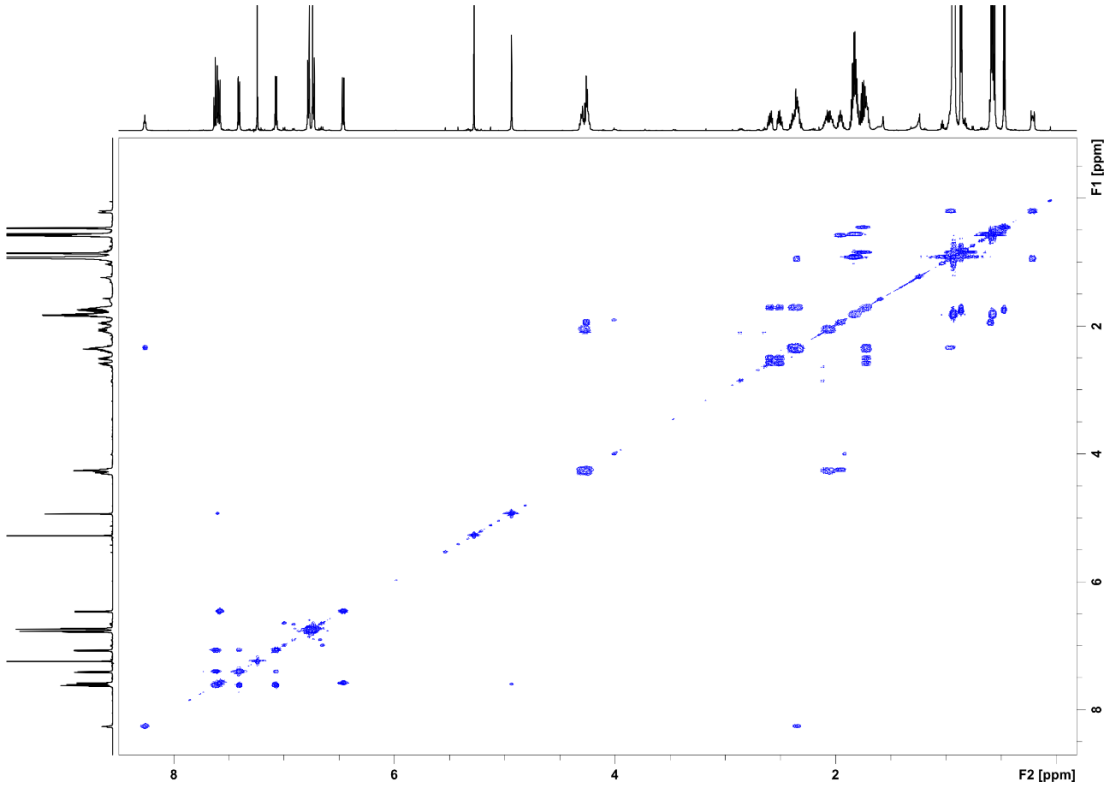



**Figure S 20.** The $^{1}$H-$^{1}$H COSY spectrum of **9b–A** (chloroform-*d*, 300 K, 600 MHz).

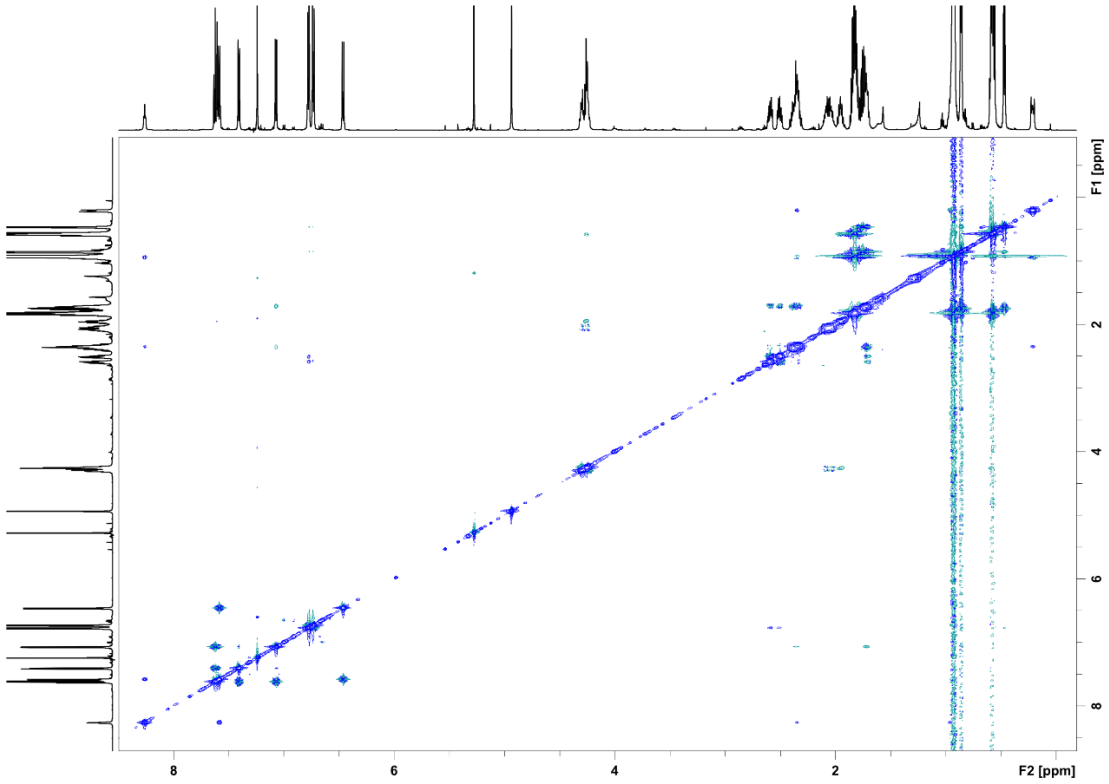



**Figure S 21.** The $^{1}$H-$^{1}$H NOESY spectrum of **9b–A** (chloroform-*d*, 300 K, 600 MHz).

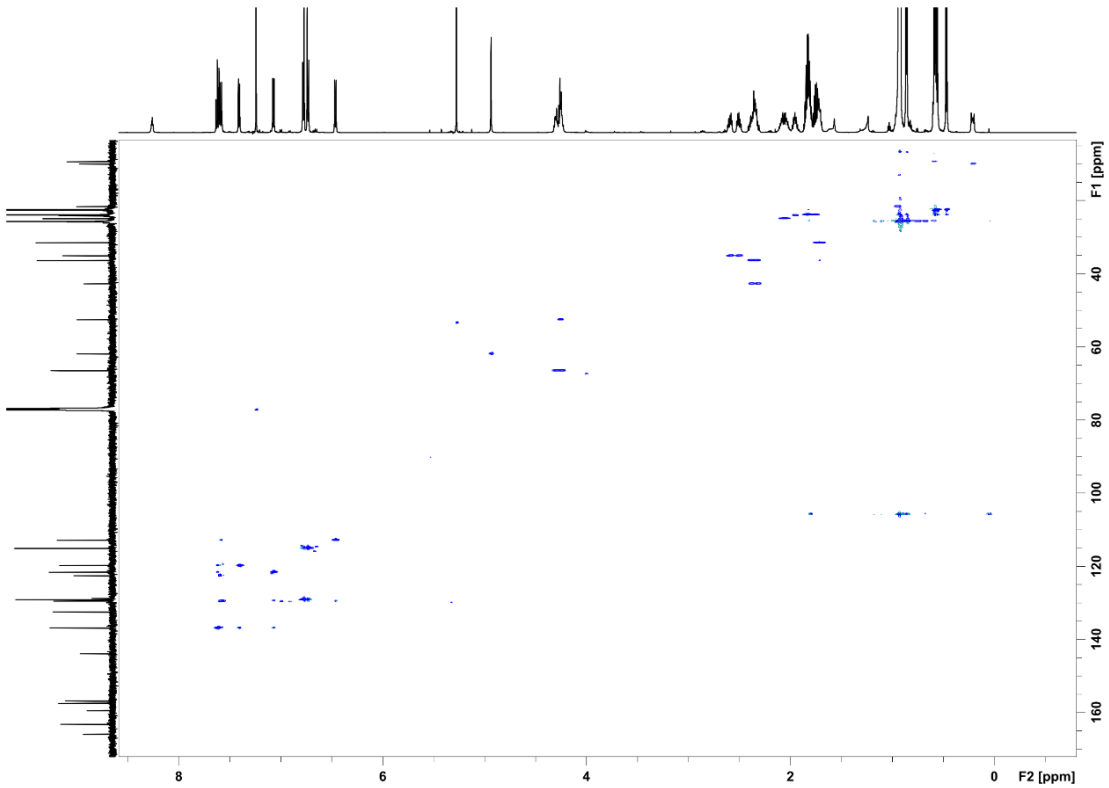



**Figure S 22.** The $^{1}$H-$^{13}$C HSQC spectrum of **9b–A** (chloroform-*d*, 300 K, 600 MHz).

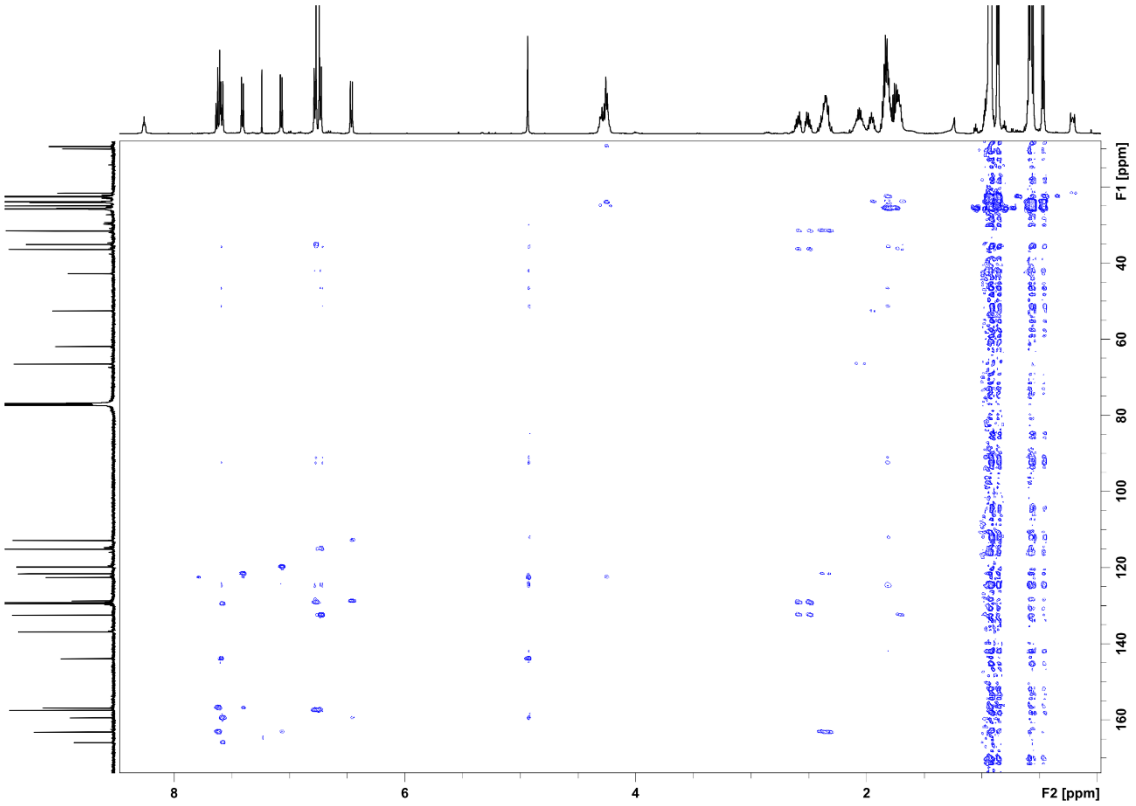



**Figure S 23.** The $^{1}H$-$^{13}C$ HMBC spectrum of **9b–A** (chloroform-*d*, 300 K, 600 MHz).

## NMR spectra of 10a–A

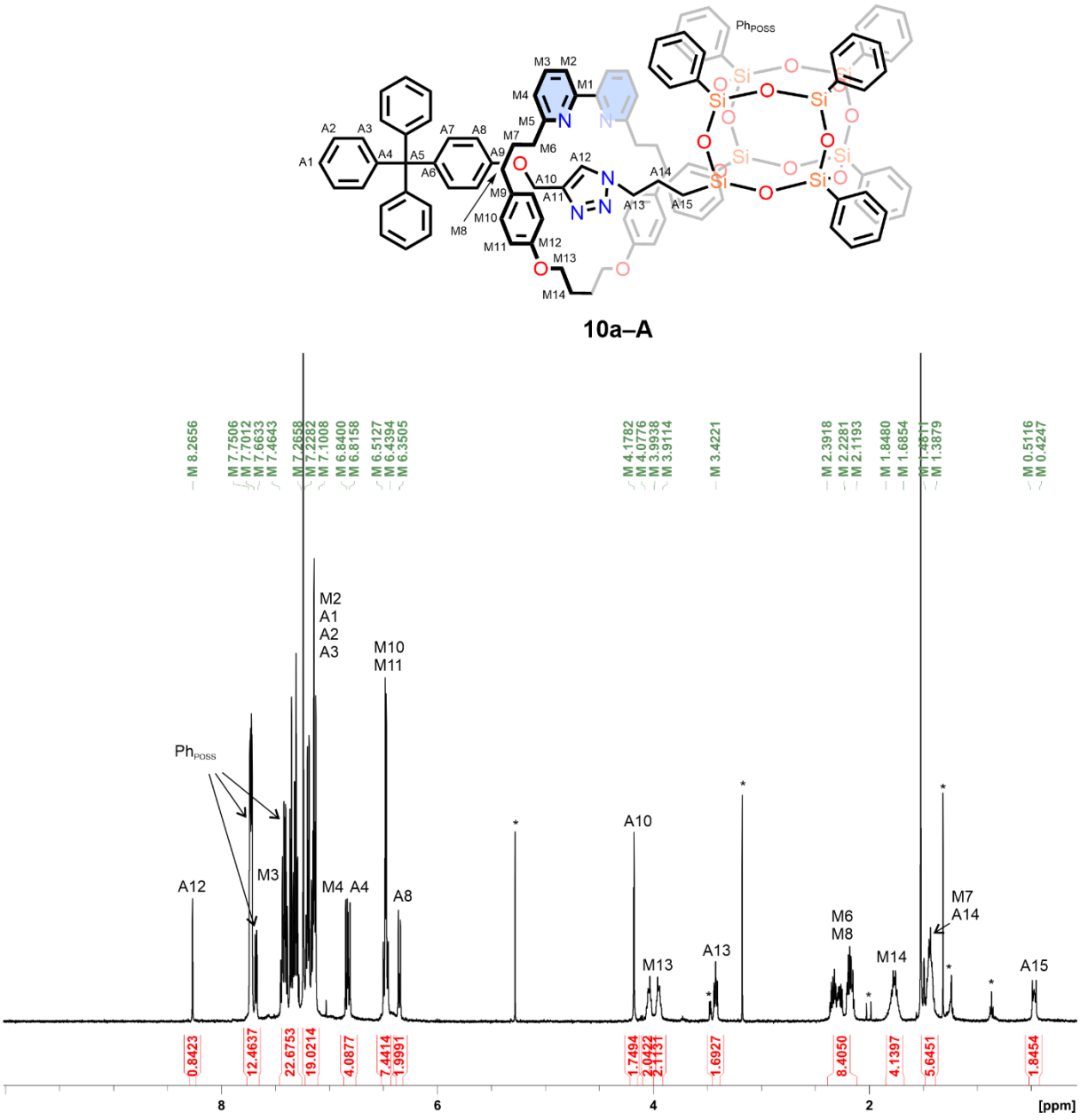



**Figure S 24.** The $^{1}$H NMR spectrum of **10a–A** (chloroform-*d*, 300 K, 500 MHz).

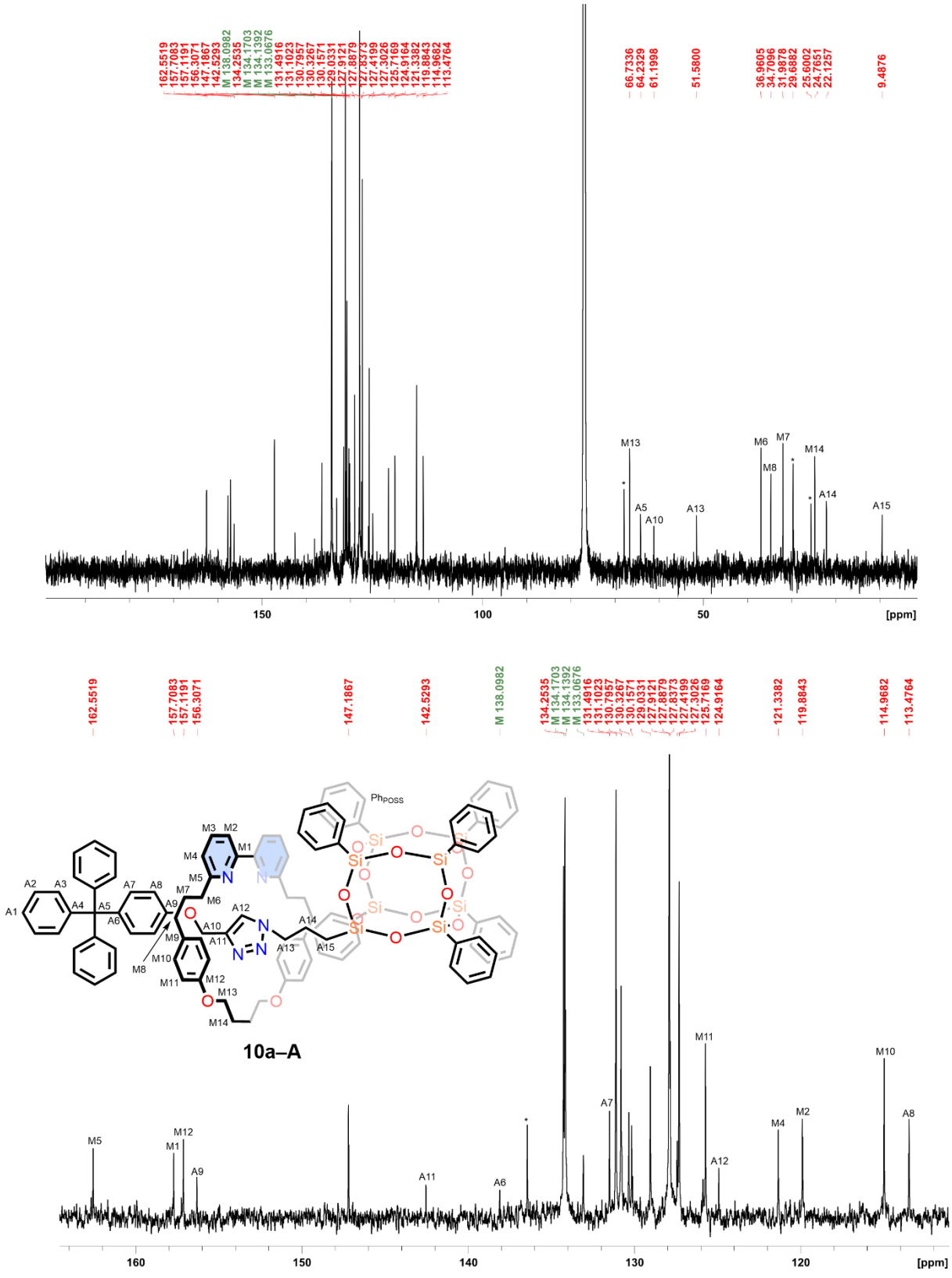



**Figure S 25.** The $^{13}C$ NMR spectrum of **10a–A** (chloroform-*d*, 300 K, 150 MHz).

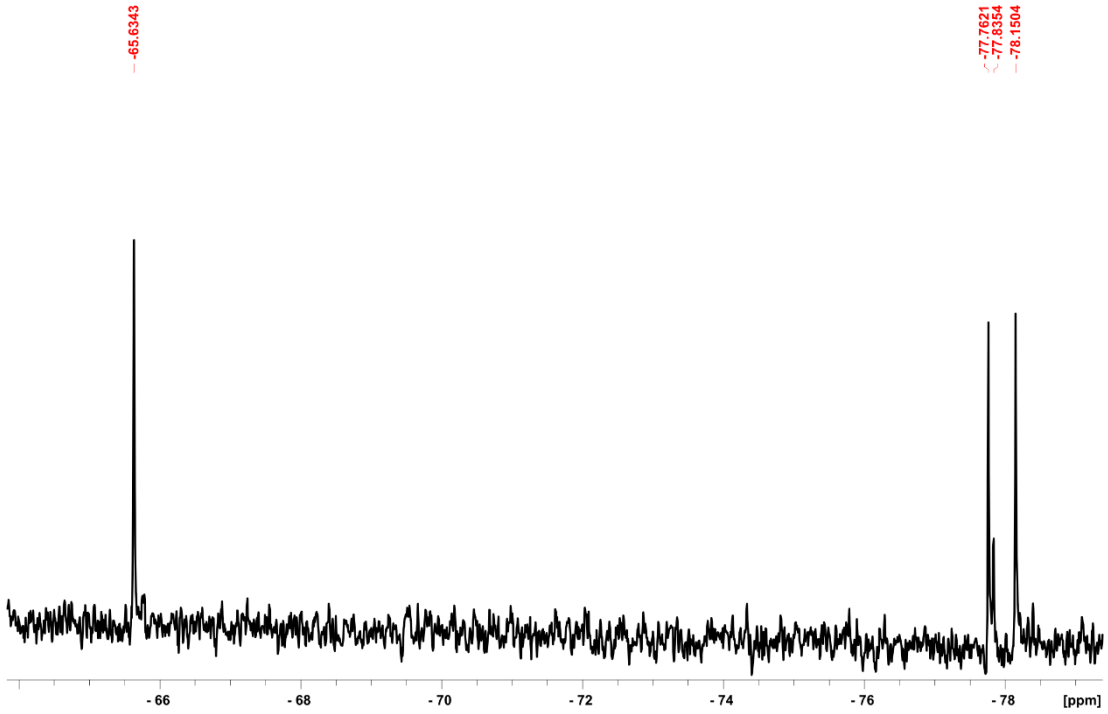



**Figure S 26.** The $^{29}$Si NMR spectrum of **10a–A** (chloroform-*d*, 300 K, 100 MHz).

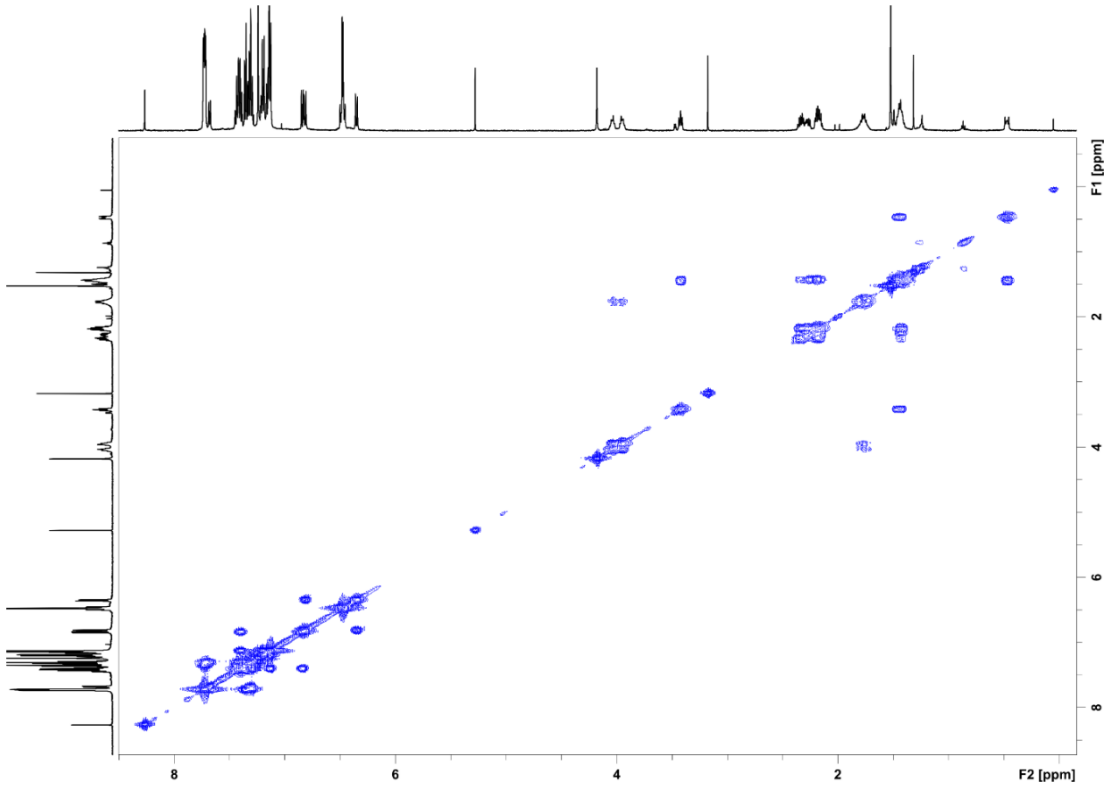



**Figure S 27.** The $^{1}$H-$^{1}$H COSY spectrum of **10a–A** (chloroform-*d*, 300 K, 600 MHz).

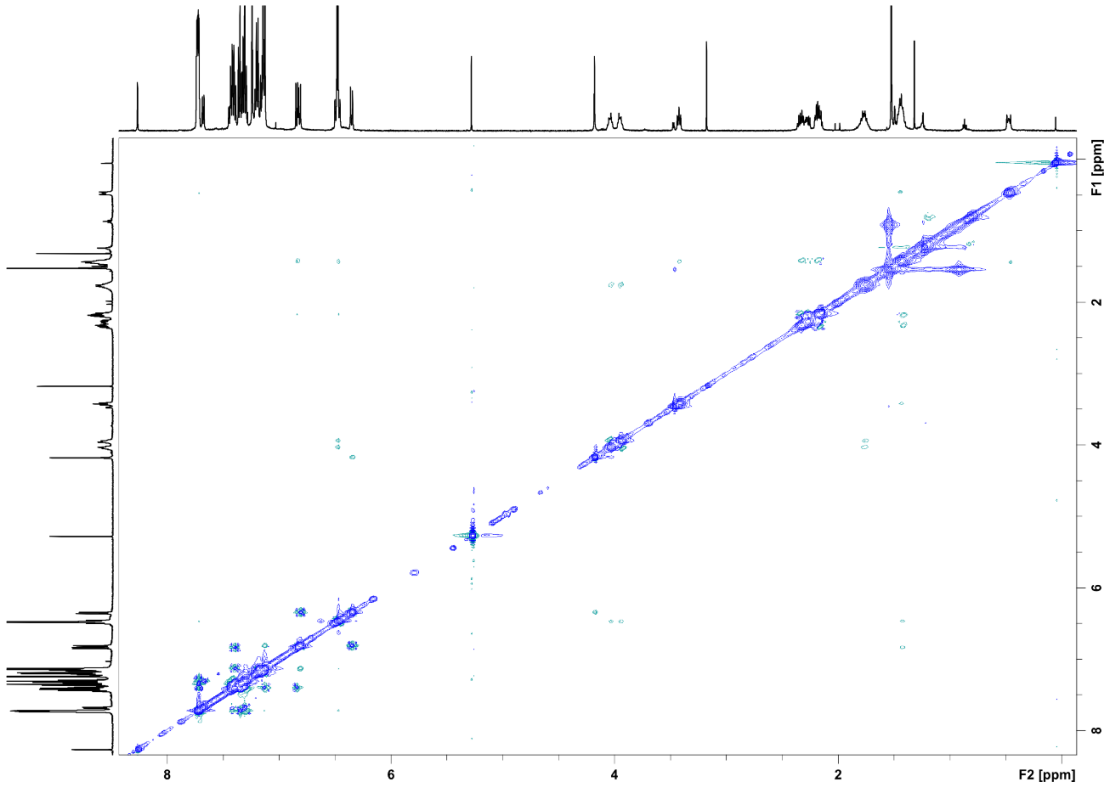



**Figure S 28.** The $^{1}$H-$^{1}$H NOESY spectrum of **10a–A** (chloroform-*d*, 300 K, 500 MHz).

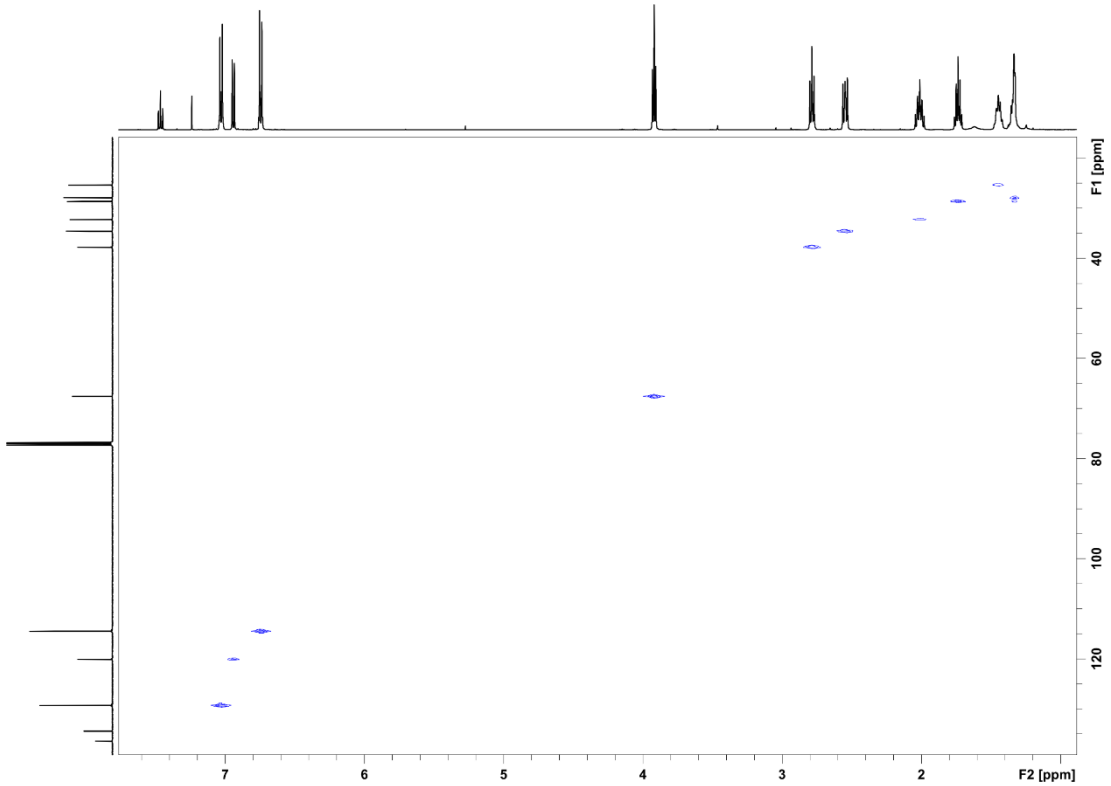



**Figure S 29.** The $^{1}$H-$^{13}$C HSQC spectrum of **10a–A** (chloroform-*d*, 300 K, 500 MHz).

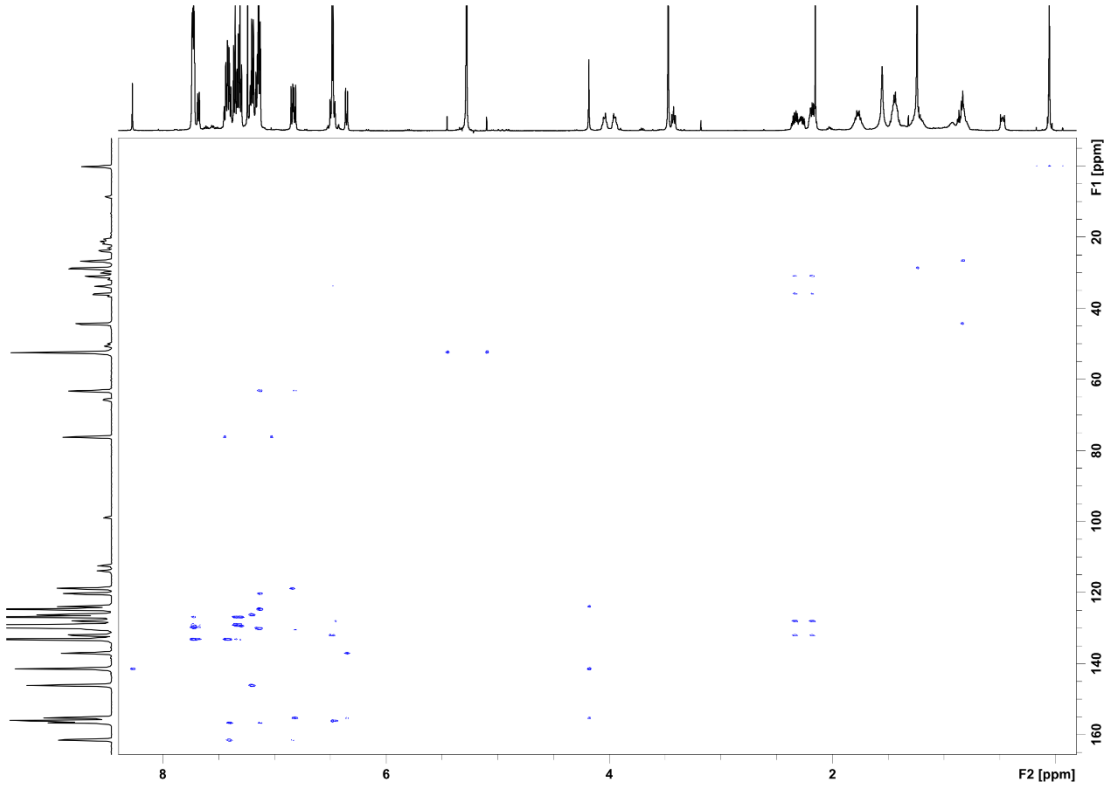



**Figure S 30.** The $^{1}$H-$^{13}$C HMBC spectrum of **10a–A** (chloroform-*d*, 300 K, 500 MHz).

## NMR spectra of 10b–A

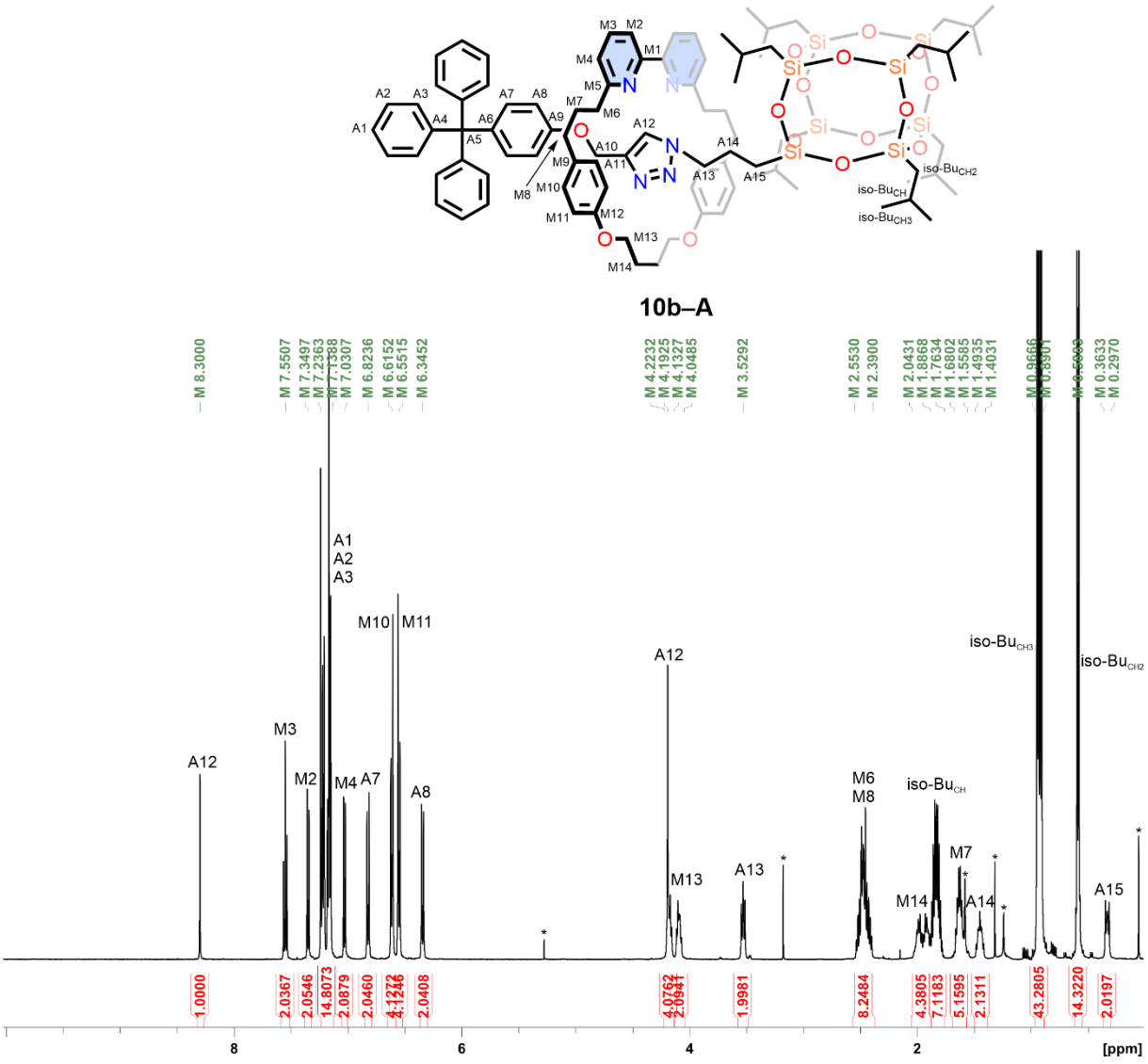



**Figure S 31.** The $^{1}$H NMR spectrum of **10b–A** (chloroform-*d*, 300 K, 500 MHz).

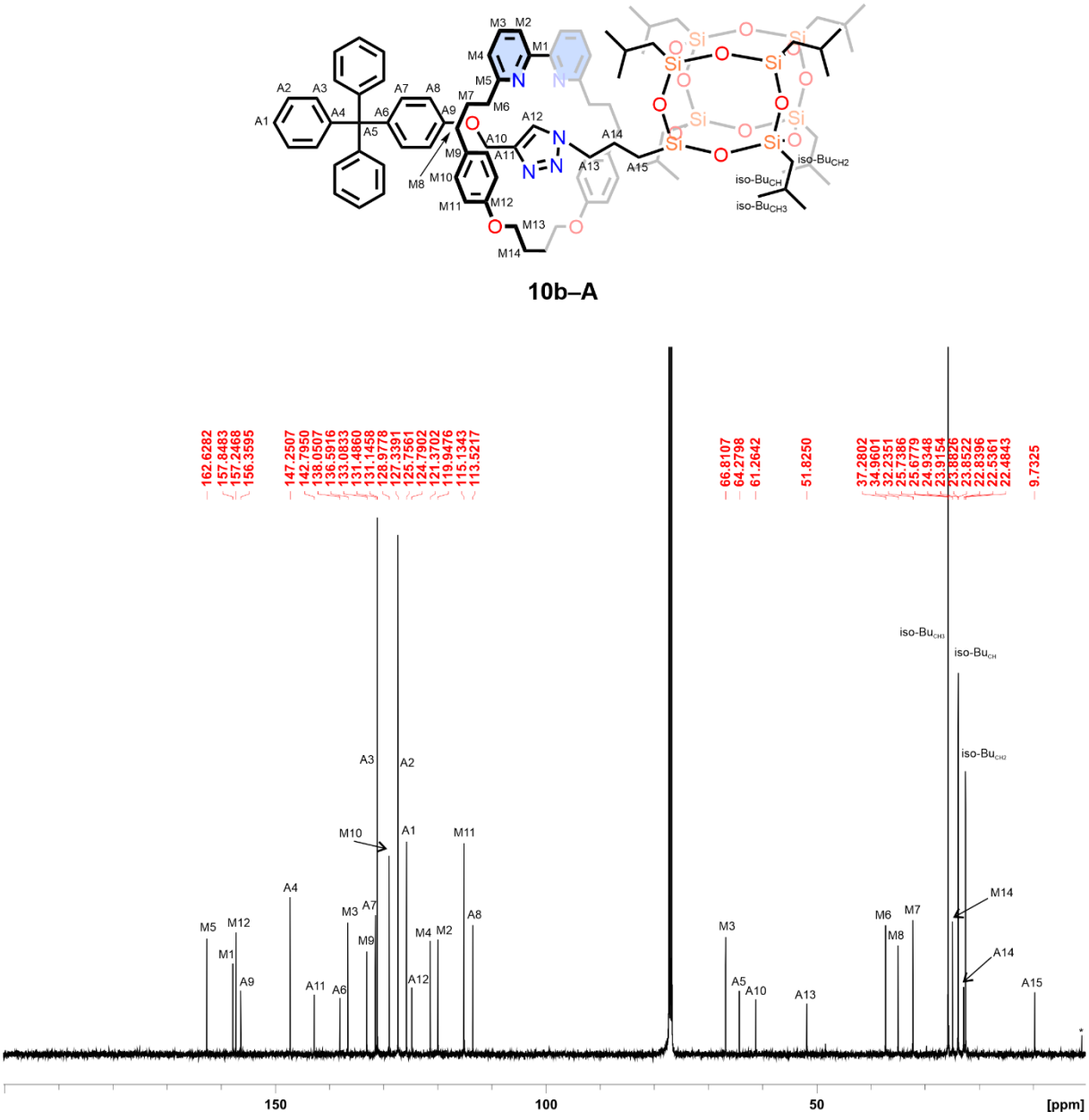



**Figure S 32.** The $^{13}$C NMR spectrum of **10b–A** (chloroform-*d*, 300 K, 125 MHz).

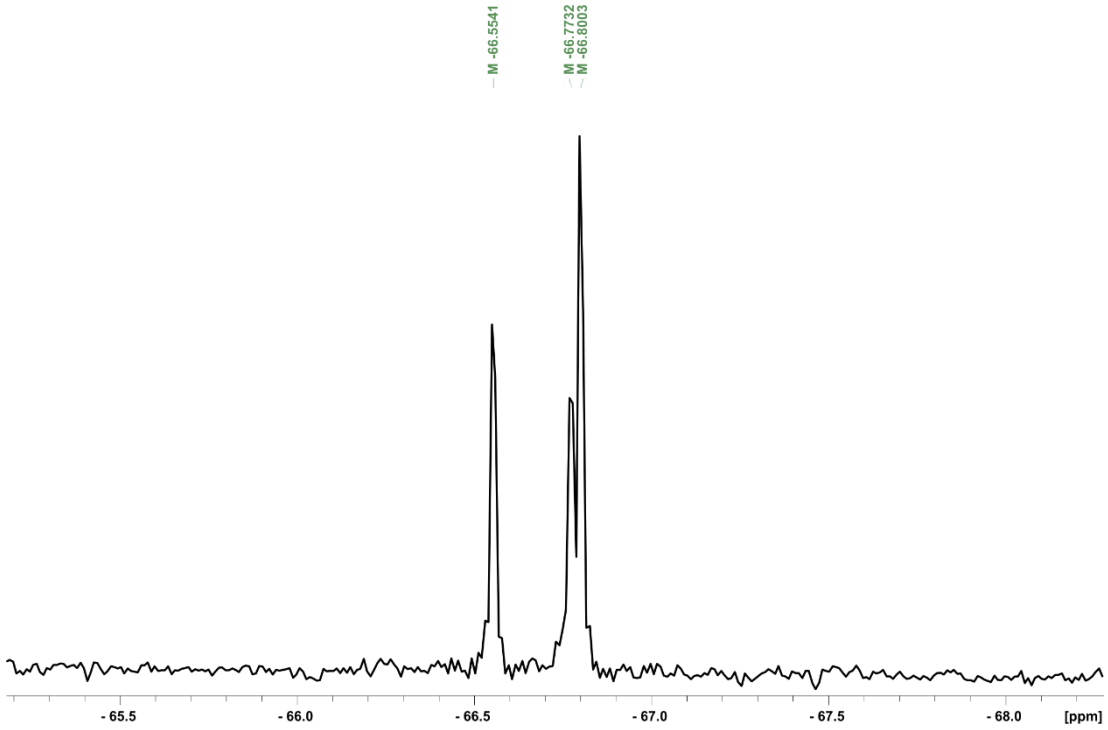



**Figure S 33.** The $^{29}$Si NMR spectrum of **10b–A** (chloroform-*d*, 300 K, 100 MHz).

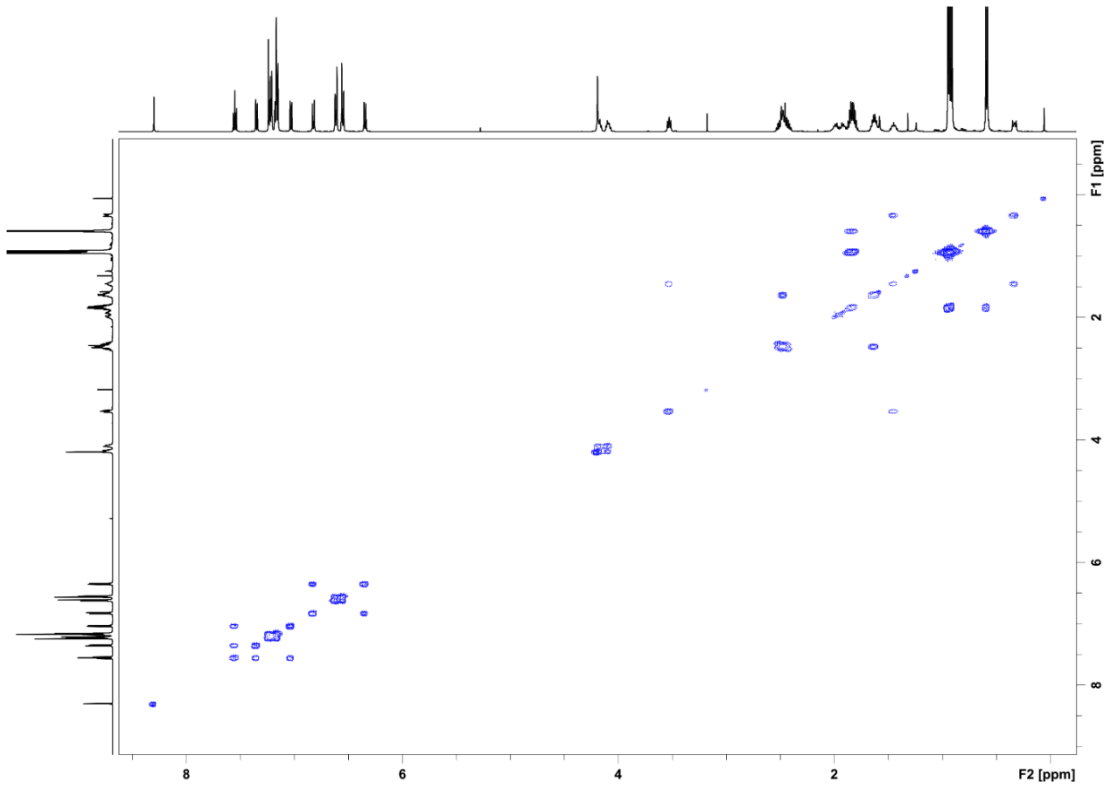



**Figure S 34.** The $^{1}$H-$^{1}$H COSY spectrum of **10b–A** (chloroform-*d*, 300 K, 500 MHz).

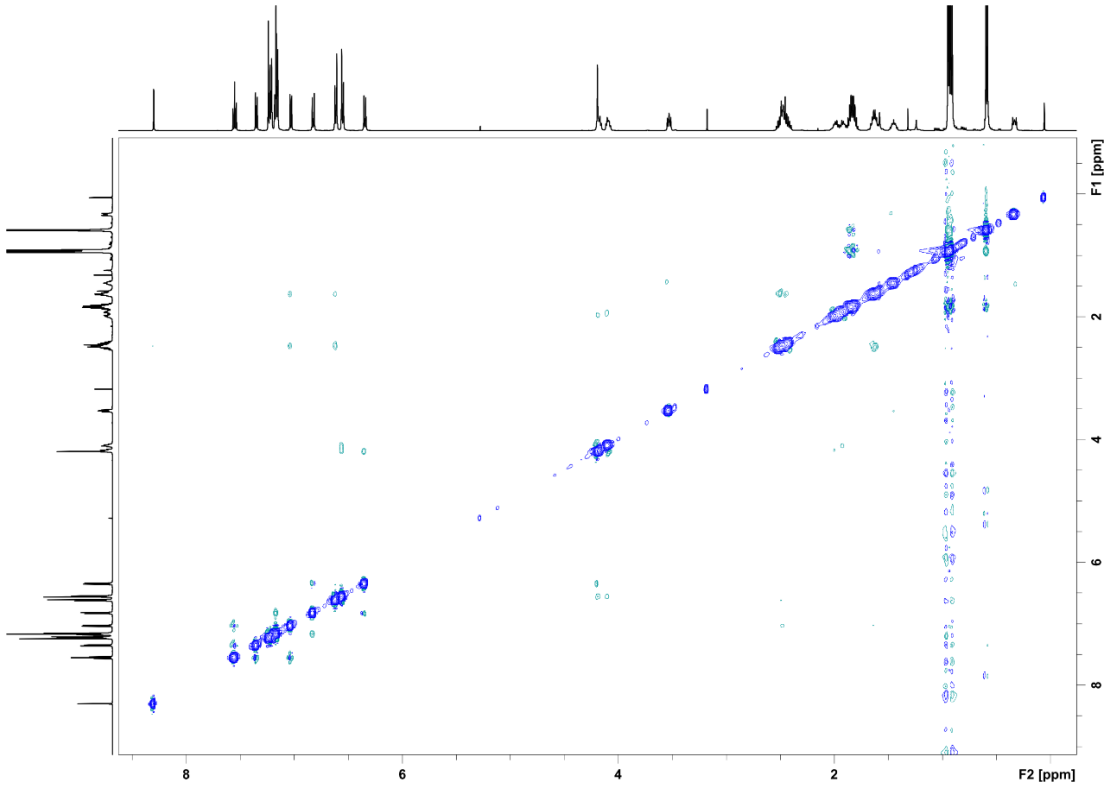



**Figure S 35.** The $^{1}$H-$^{1}$H NOESY spectrum of **10b–A** (chloroform-*d*, 300 K, 500 MHz).

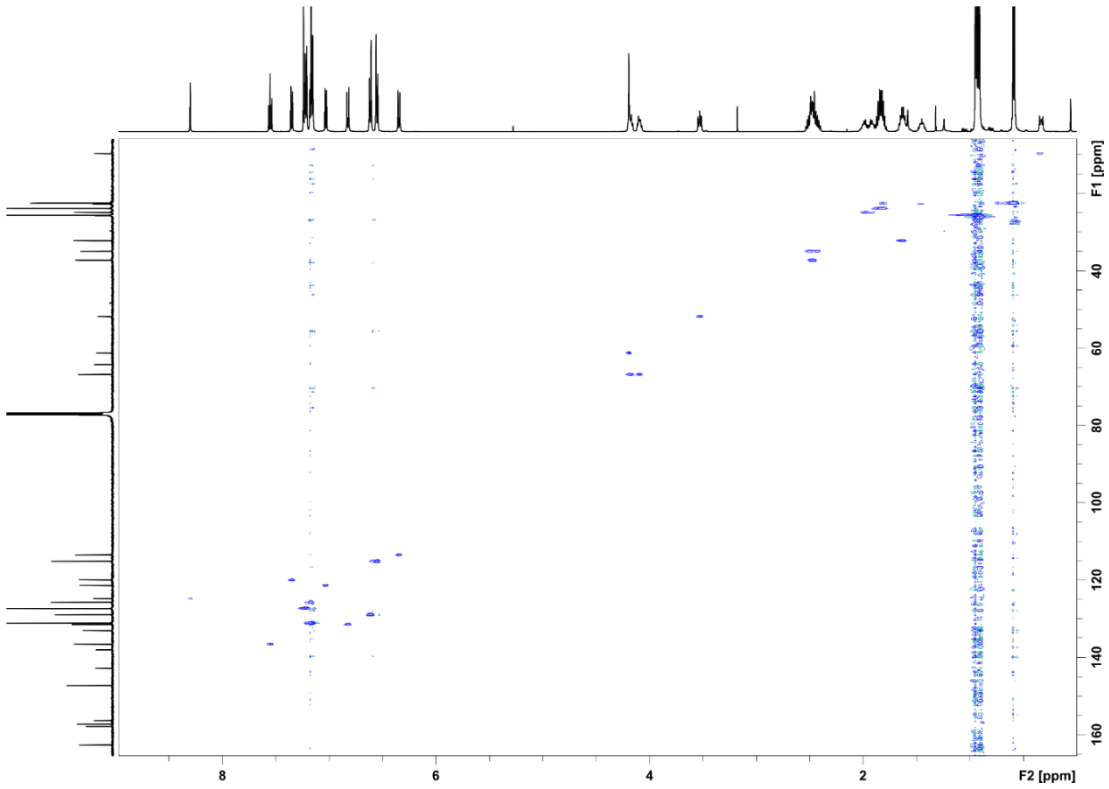



**Figure S 36.** The $^{1}$H-$^{13}$C HSQC spectrum of **10b–A** (chloroform-*d*, 300 K, 500 MHz).

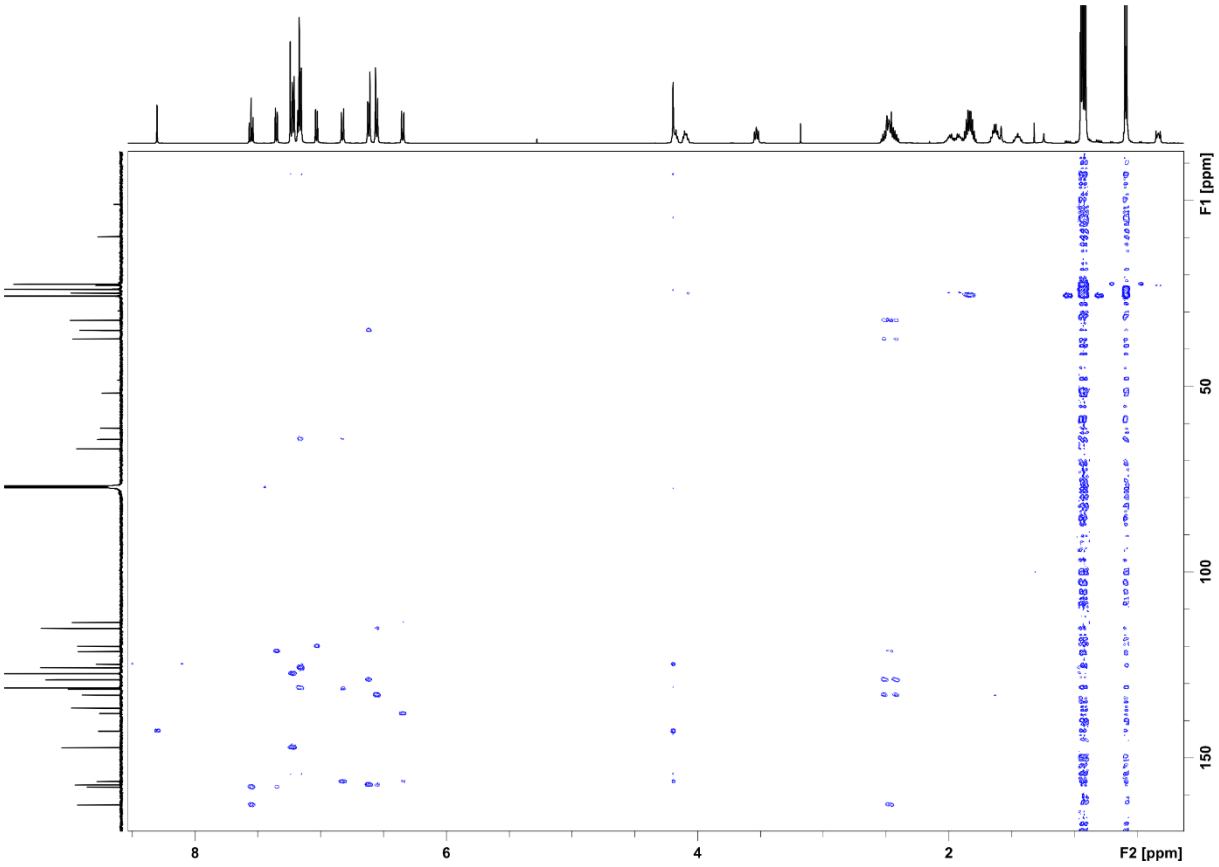



**Figure S 37.** The $^{1}H$-$^{13}C$ HMBC spectrum of **10b–A** (chloroform-*d*, 300 K, 500 MHz).

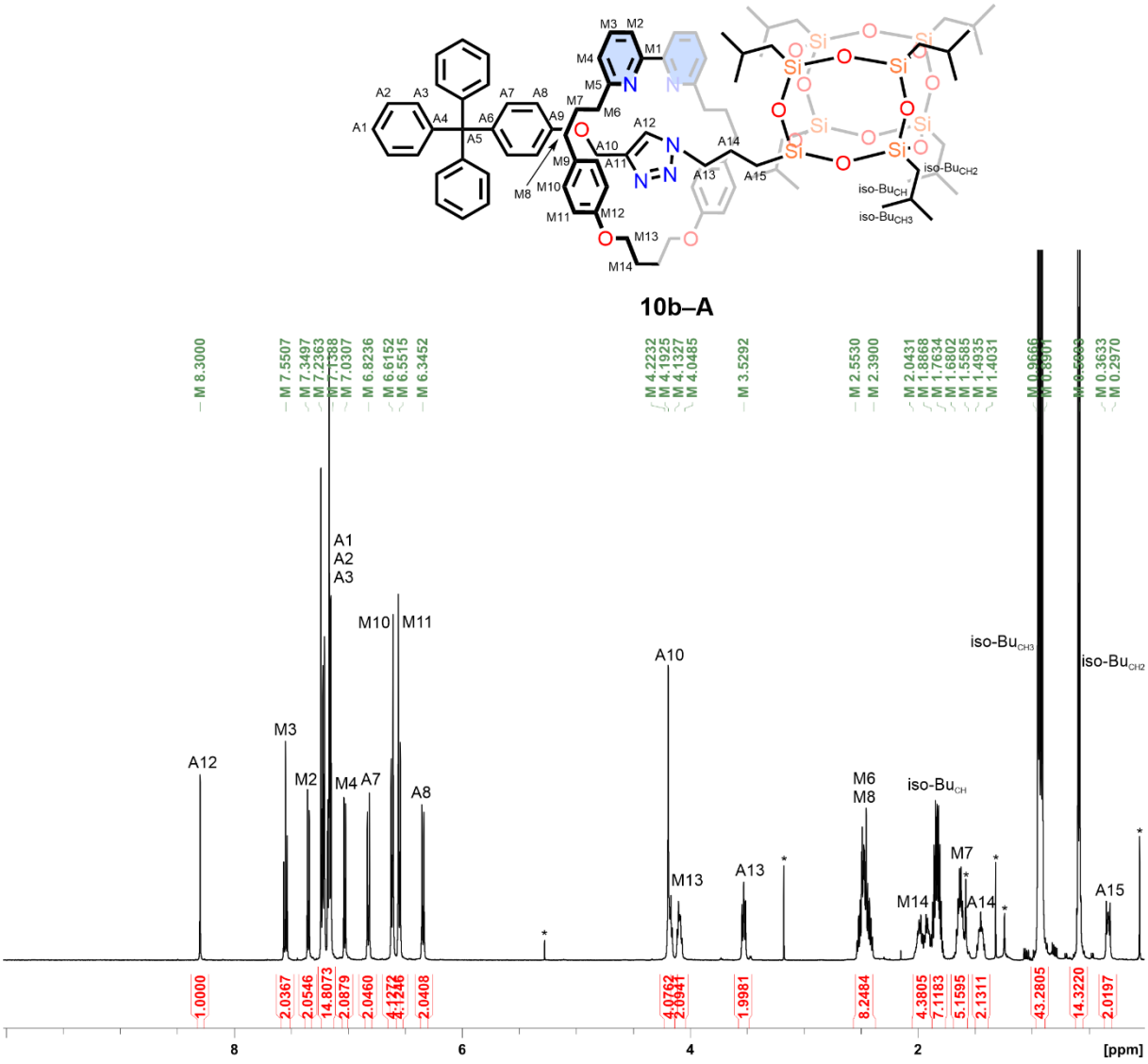



**Figure S 38.** The $^{1}$H NMR spectrum of **10b–A** (dichloromethane-$d_2$, 300 K, 600 MHz).

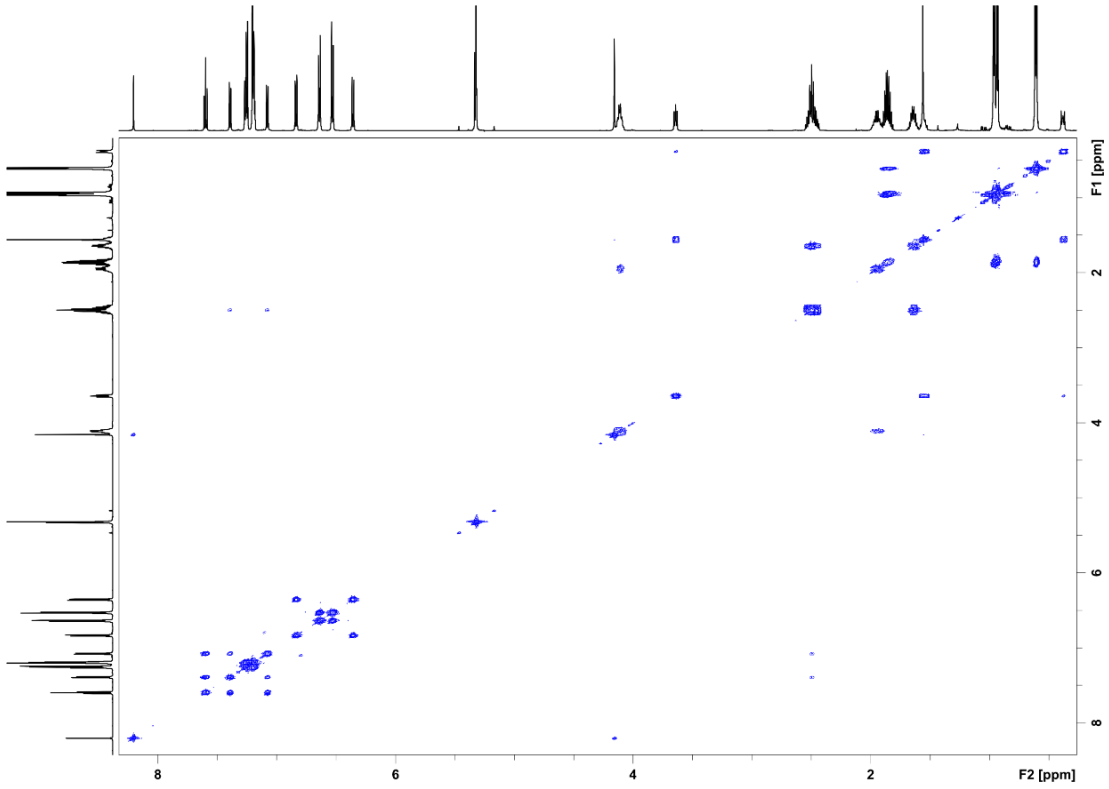



**Figure S 39.** The $^{1}$H-$^{1}$H COSY spectrum of **10b–A** (dichloromethane-$d_2$, 300 K, 600 MHz).

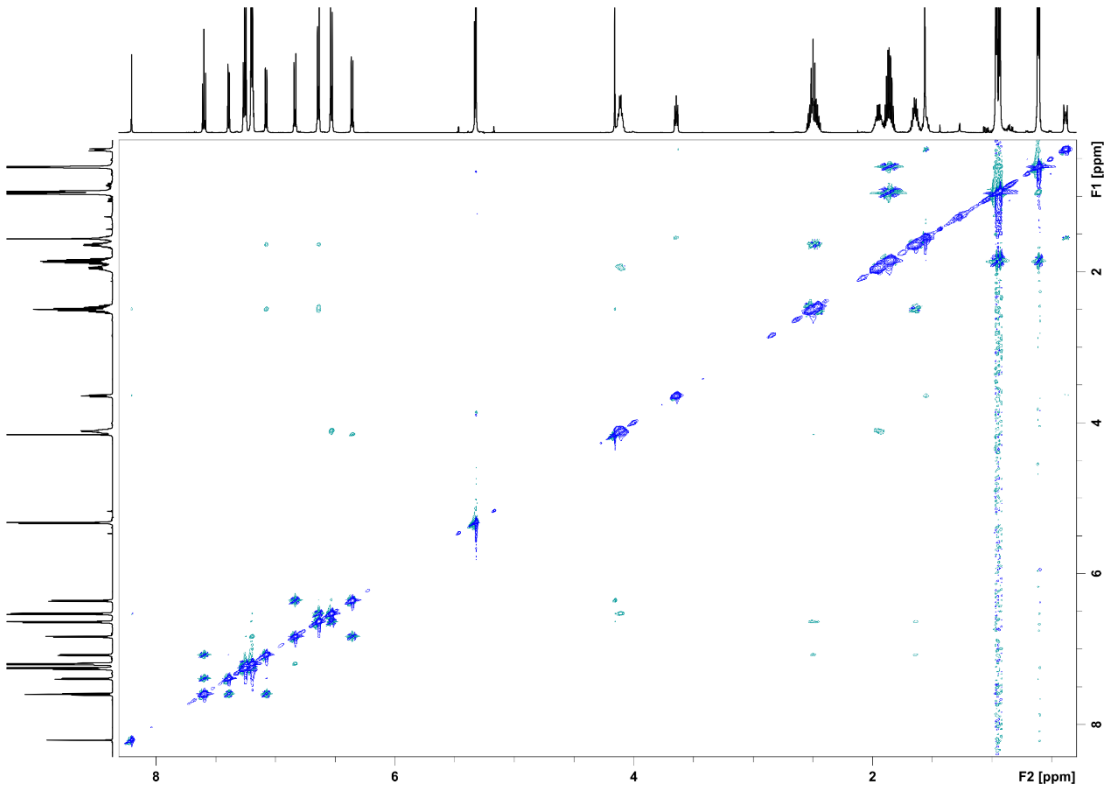



**Figure S 40.** The $^{1}$H-$^{1}$H NOESY spectrum of **10b–A** (dichloromethane-$d_2$, 300 K, 600 MHz).

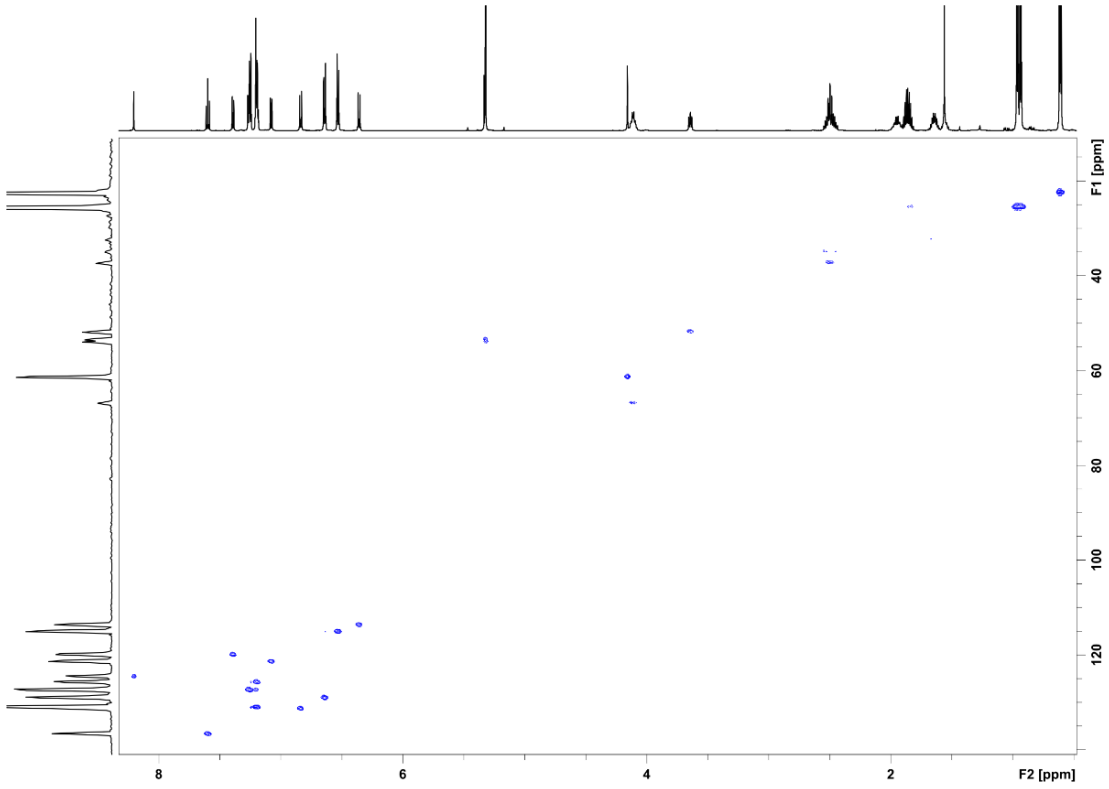



**Figure S 41.** The $^{1}$H-$^{13}$C HMQC spectrum of **10b–A** (dichloromethane-$d_2$, 300 K, 600 MHz).

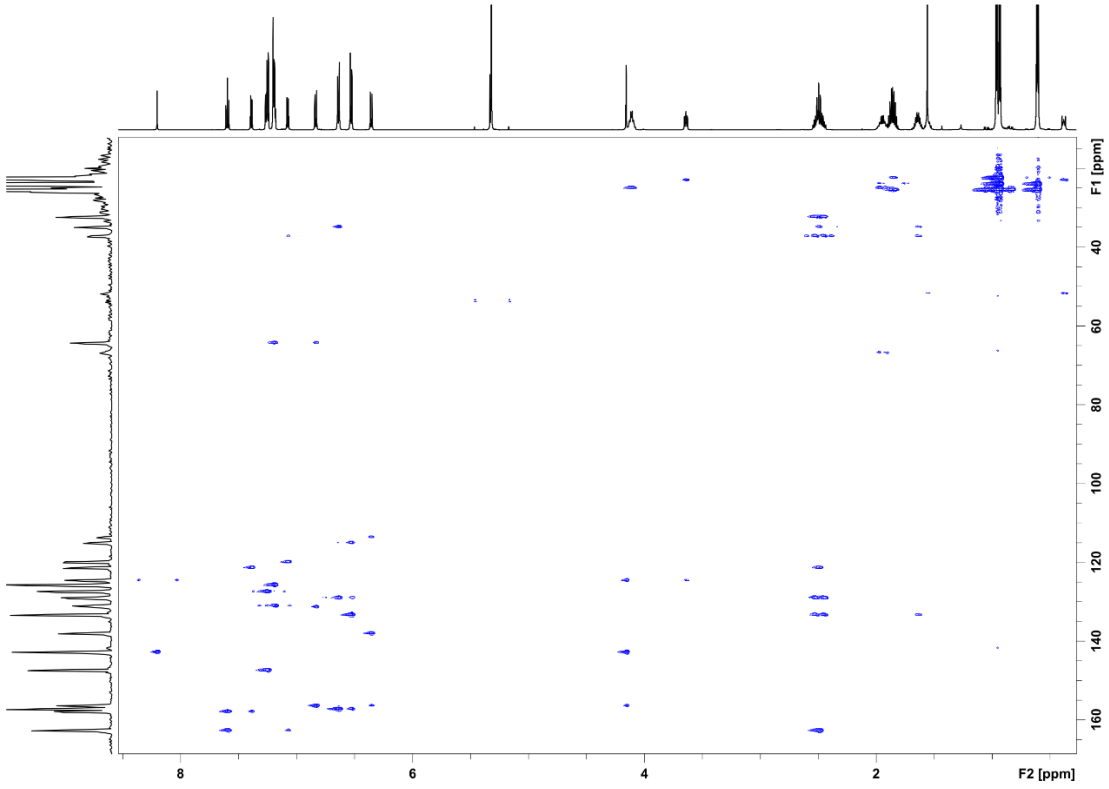



**Figure 42** The $^{1}$H-$^{13}$C HMBC spectrum of **10b–A** (dichloromethane-$d_2$, 300 K, 500 MHz).

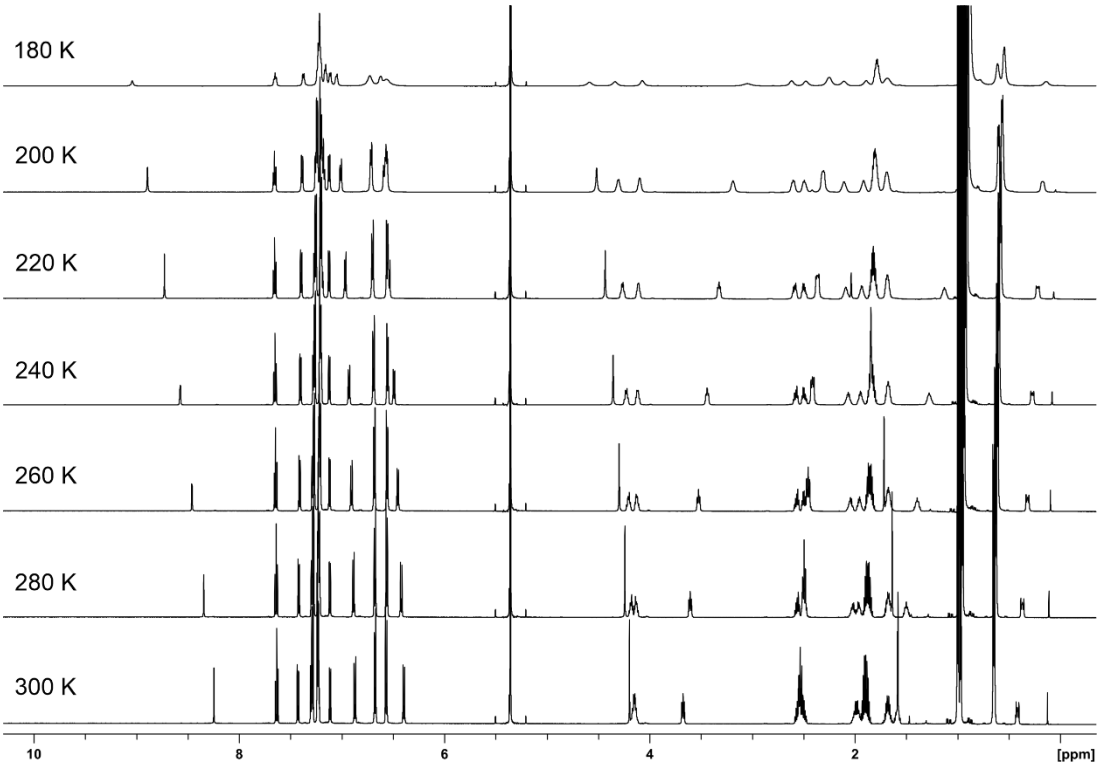



**Figure S 43.** The $^{1}$H NMR spectra of **10b–A** (dichloromethane-$d_2$, 600 MHz) recorded at the 180 – 300 K temperature range.

## NMR spectra of rotaxane 10b–A·(TFAH)$_n$

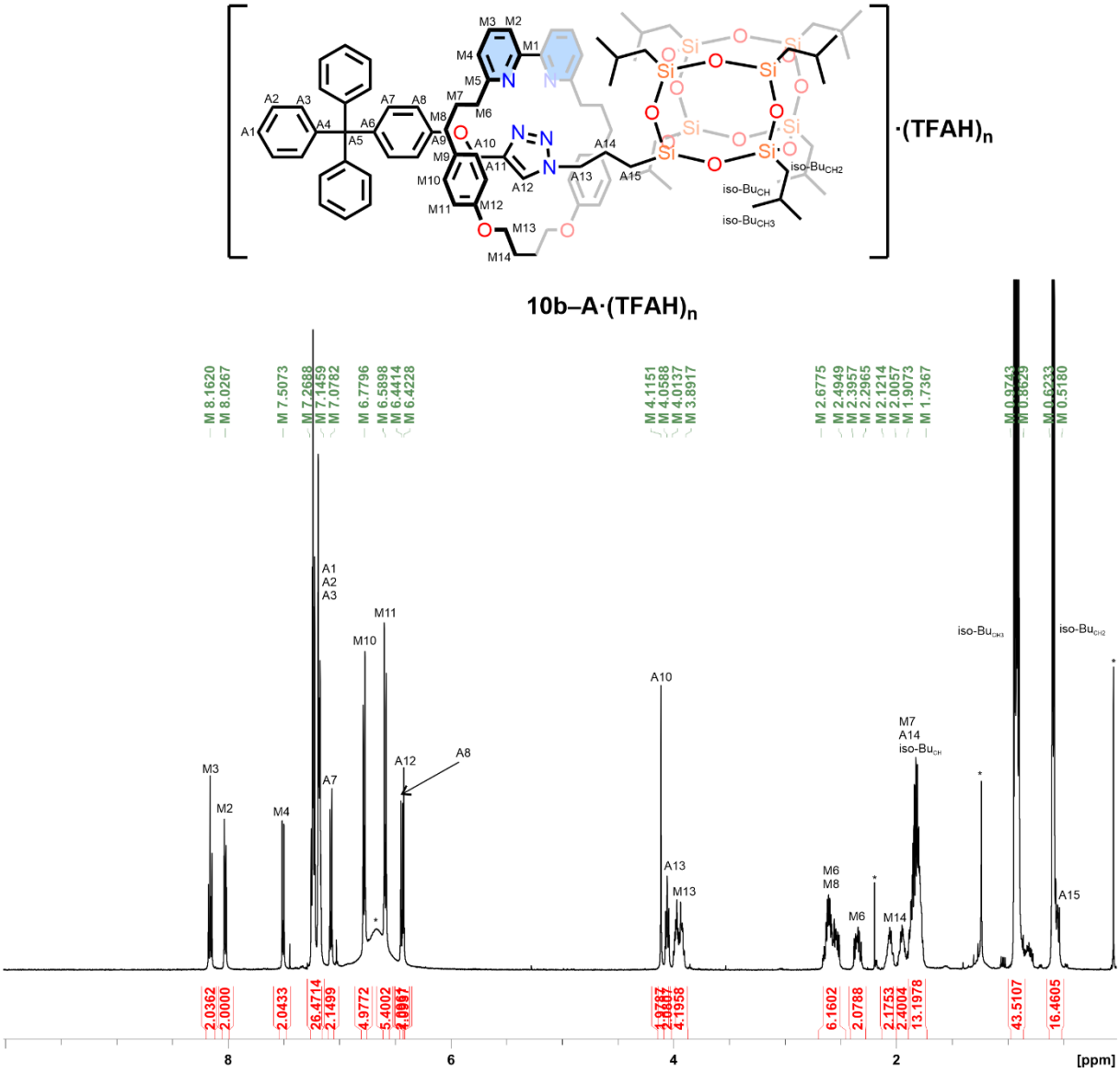



**Figure S44.** The $^1$H NMR spectrum of **10b–A·(TFAH)$_n$** (chloroform-*d*, 300 K, 500 MHz).

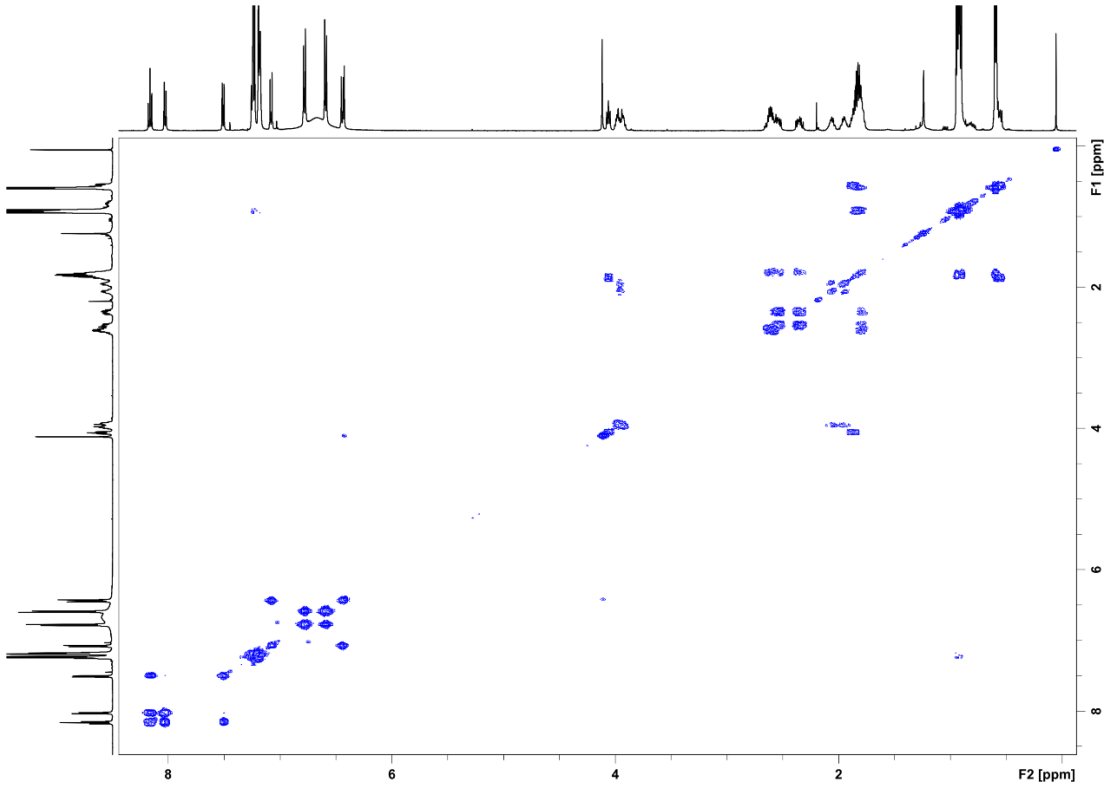



**Figure S 45.** The $^{1}$H-$^{1}$H COSY spectrum of **10b–A·(TFAH)$_n$** (chloroform-*d*, 300 K, 500 MHz).

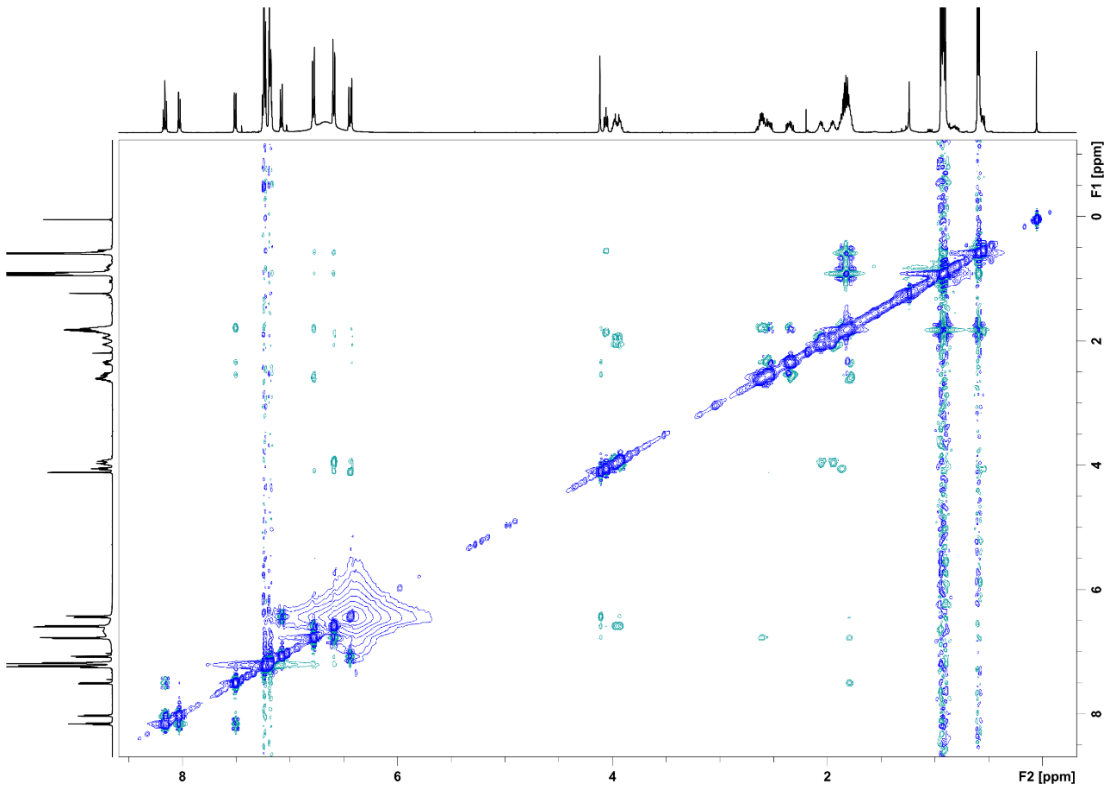



**Figure S 46.** The $^{1}$H-$^{1}$H NOESY spectrum of **10b–A·(TFAH)$_n$** (chloroform-*d*, 300 K, 500 MHz).

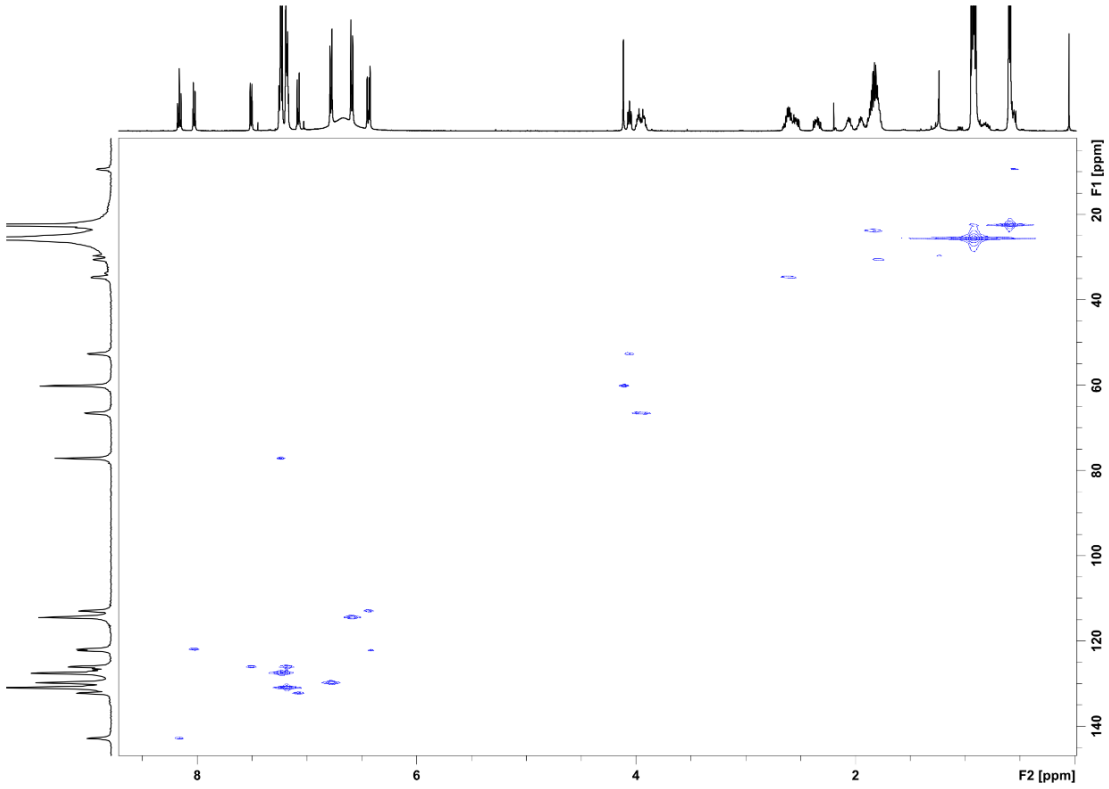



**Figure S 47.** The $^{1}$H-$^{13}$C HMQC spectrum of **10b–A·(TFAH)$_n$** (chloroform-*d*, 300 K, 500 MHz).

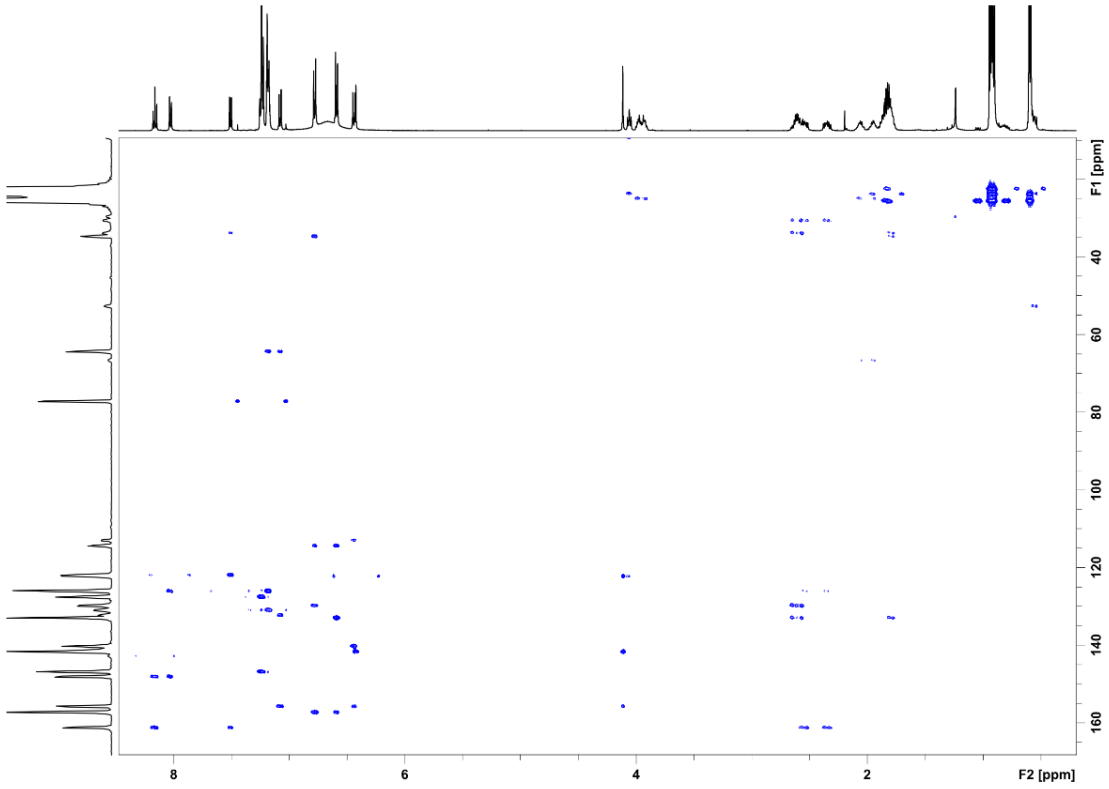



**Figure S 48** The $^{1}$H-$^{13}$C HMBC spectrum of **10b–A·(TFAH)$_n$** (chloroform-*d*, 300 K, 500 MHz).

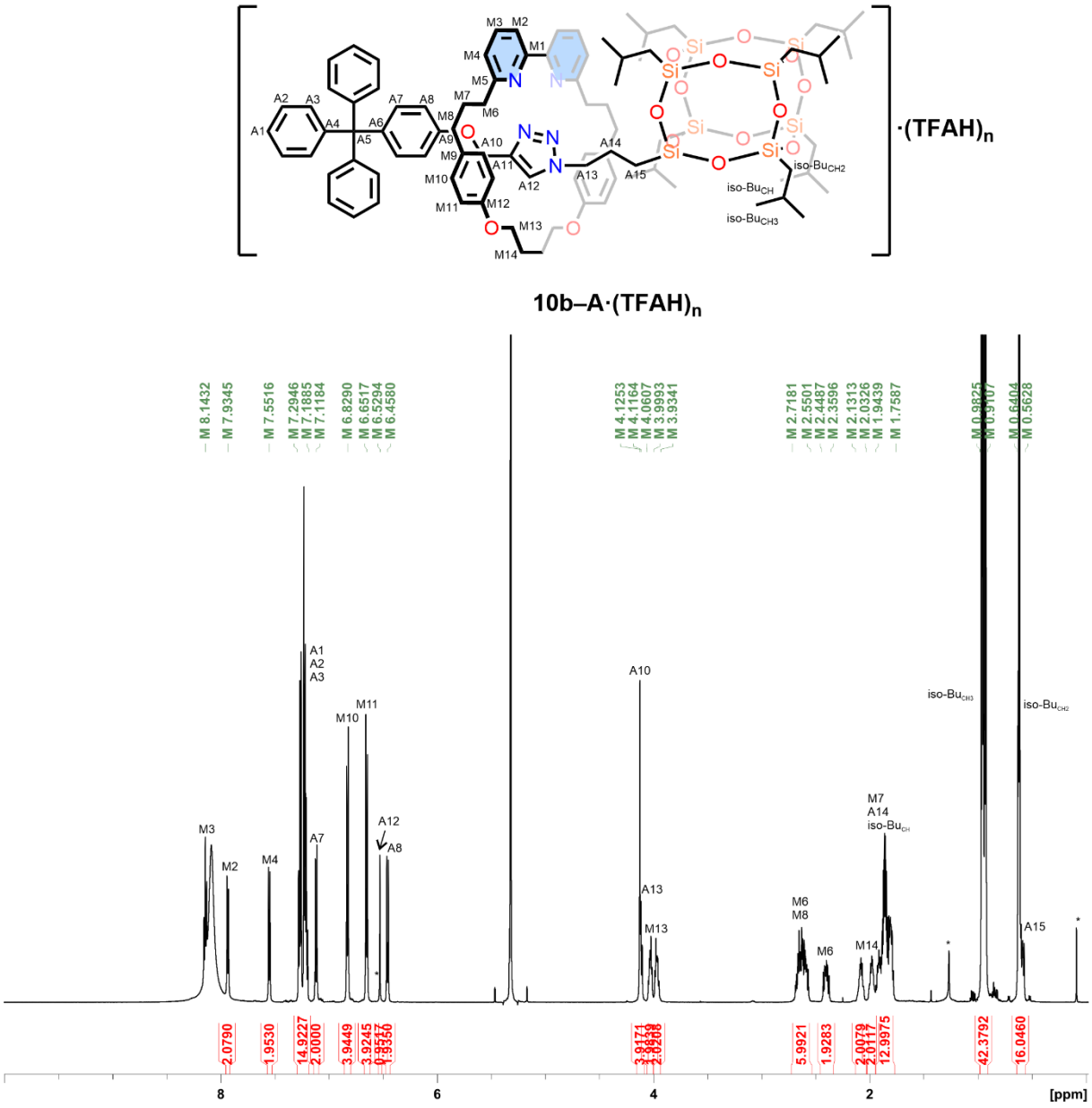



**Figure S 49.** The $^{1}$H NMR spectrum of **10b–A·(TFAH)$_n$** (dichloromethane-$d_2$, 300 K, 600 MHz).

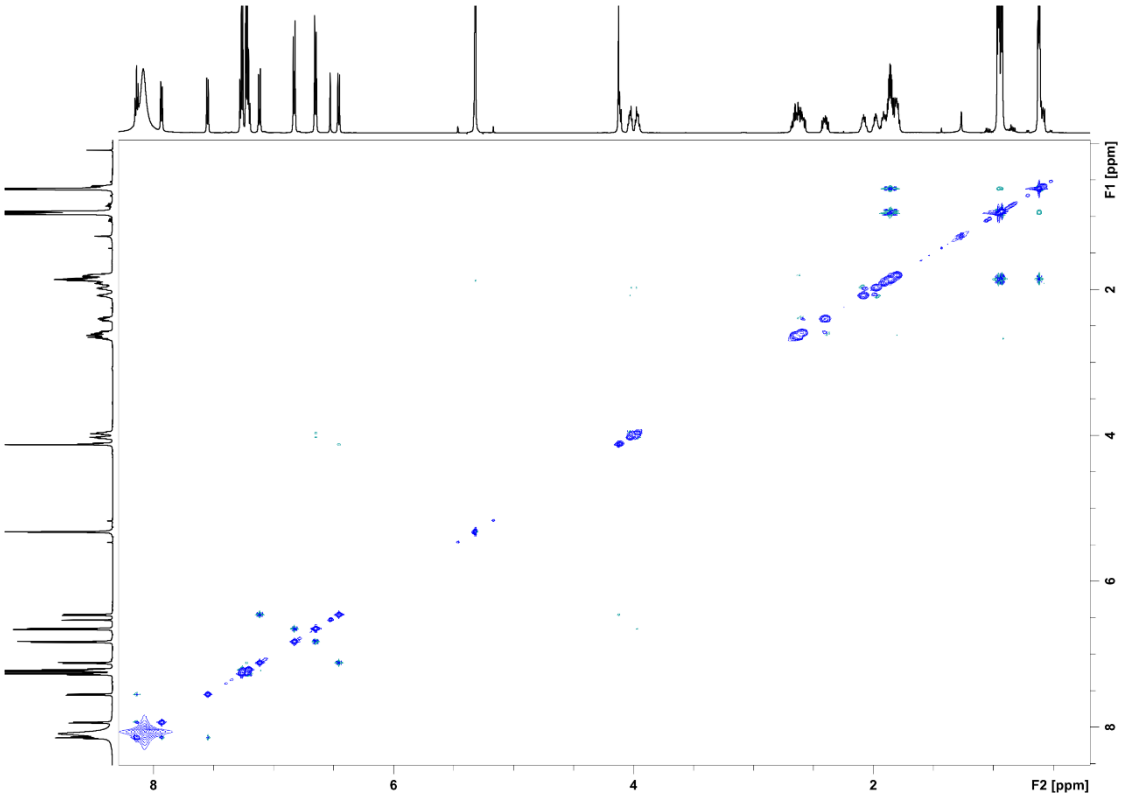



**Figure S 50.** The $^{1}$H-$^{1}$H COSY spectrum of **10b–A·(TFAH)$_n$** (dichloromethane-$d_2$, 300 K, 600 MHz).

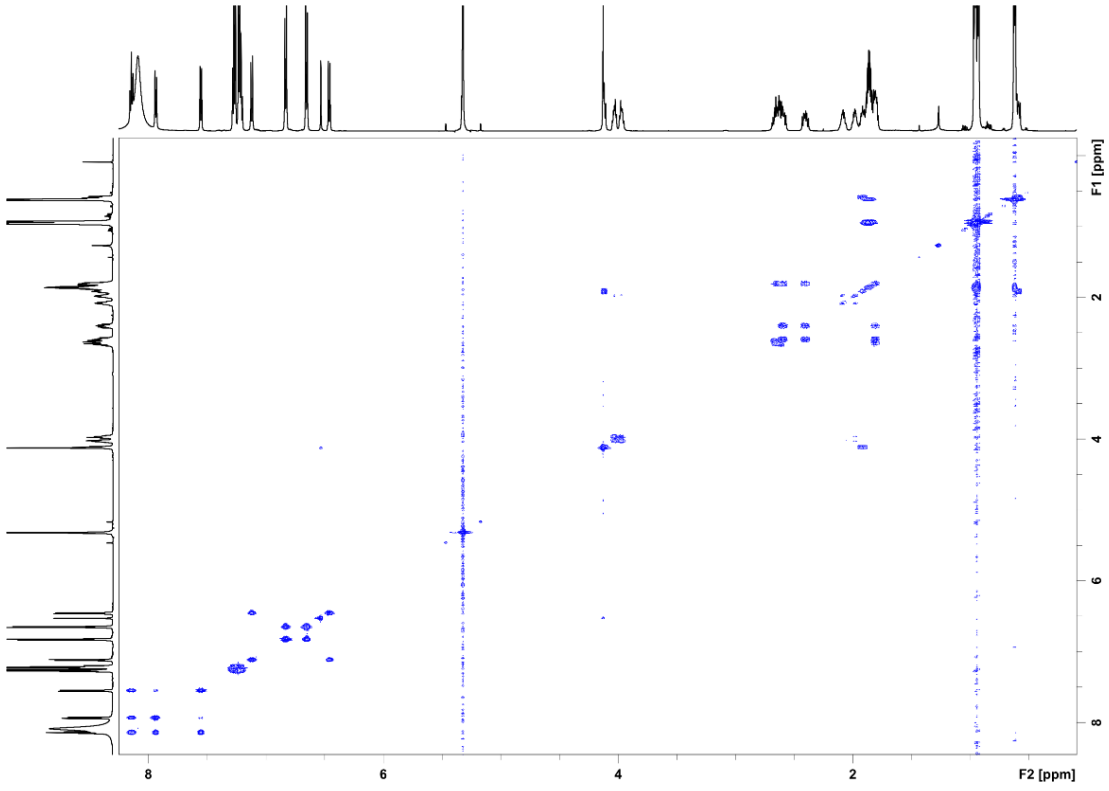



**Figure S 51.** The $^{1}$H-$^{1}$H NOESY spectrum of **10b–A·(TFAH)$_n$** (dichloromethane-$d_2$, 300 K, 600 MHz).

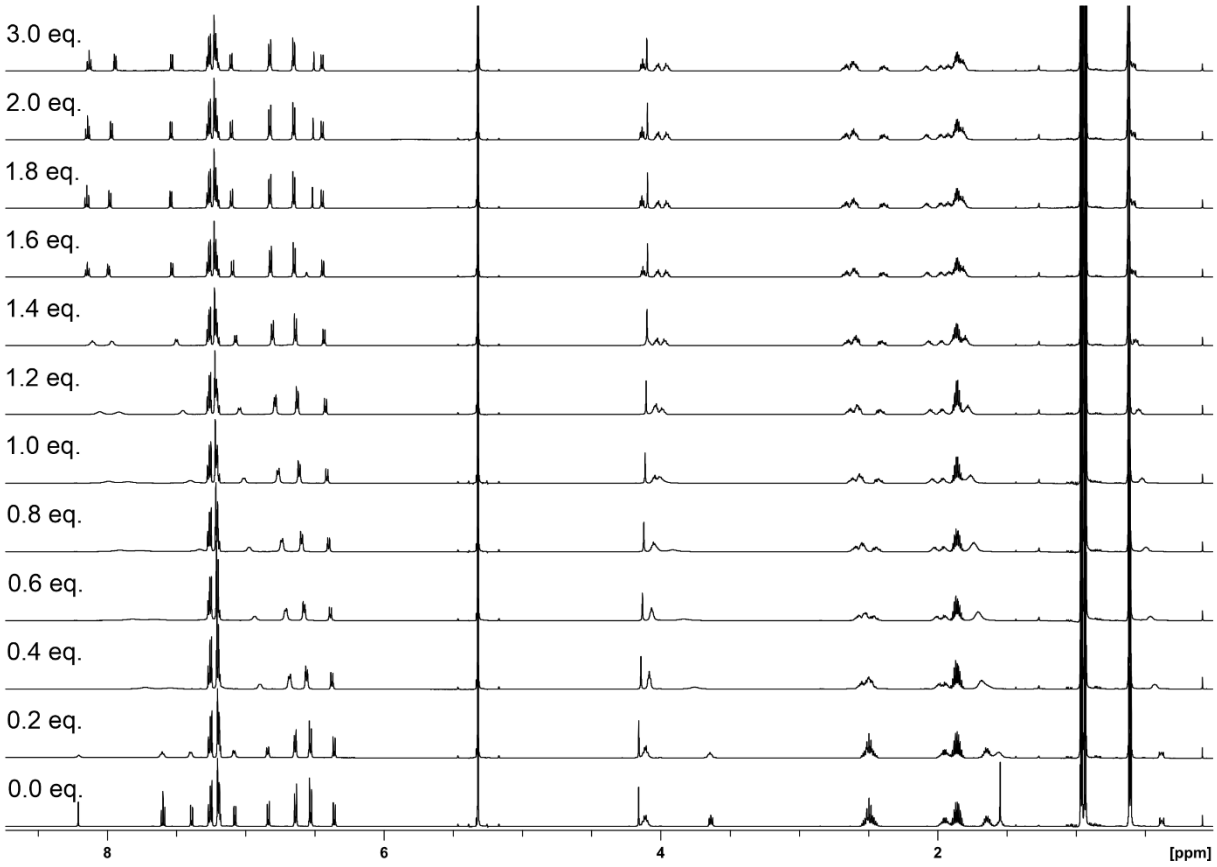



**Figure S 52.** The $^{1}$H NMR spectra recorded during titration of **10b–A** with trifluoroacetic acid (dichloromethane-$d_2$, 300 K, 600 MHz).

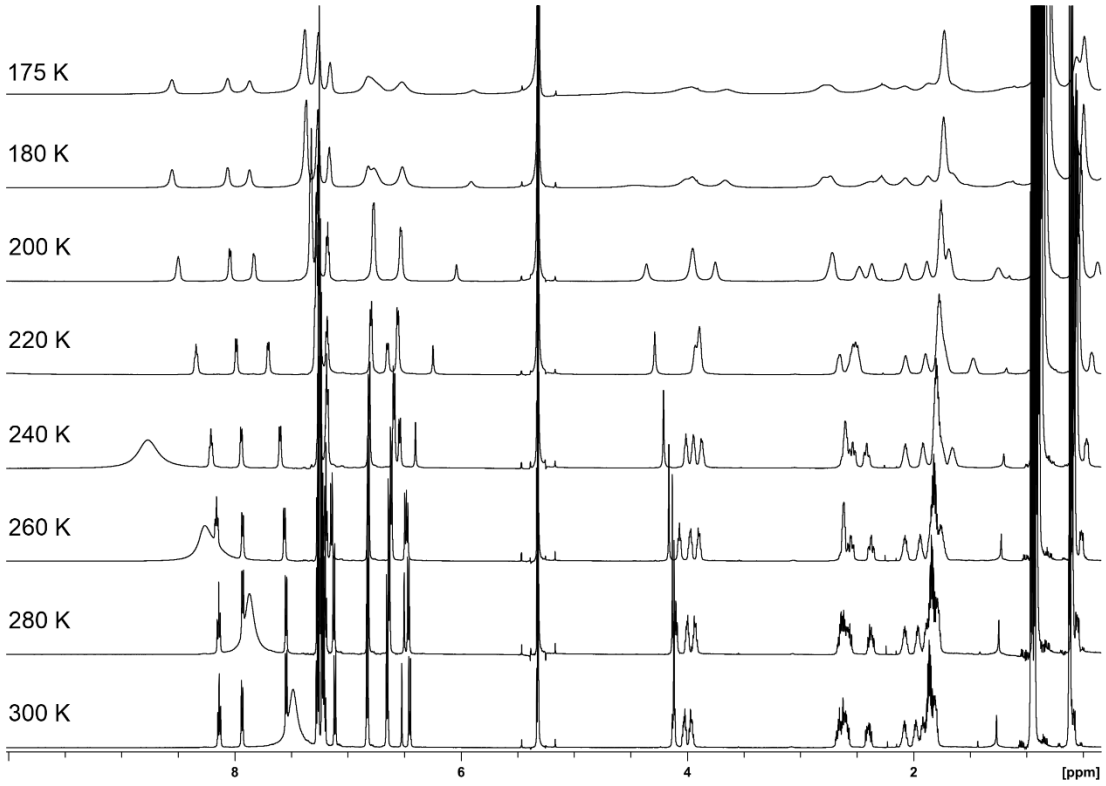



**Figure S 53**. The $^{1}$H NMR spectra of **10b–A·(TFAH)$_n$** recorded at the 300–175 K range (dichloromethane-$d_2$, 600 MHz).

## NMR spectra of rotaxane 11b–A

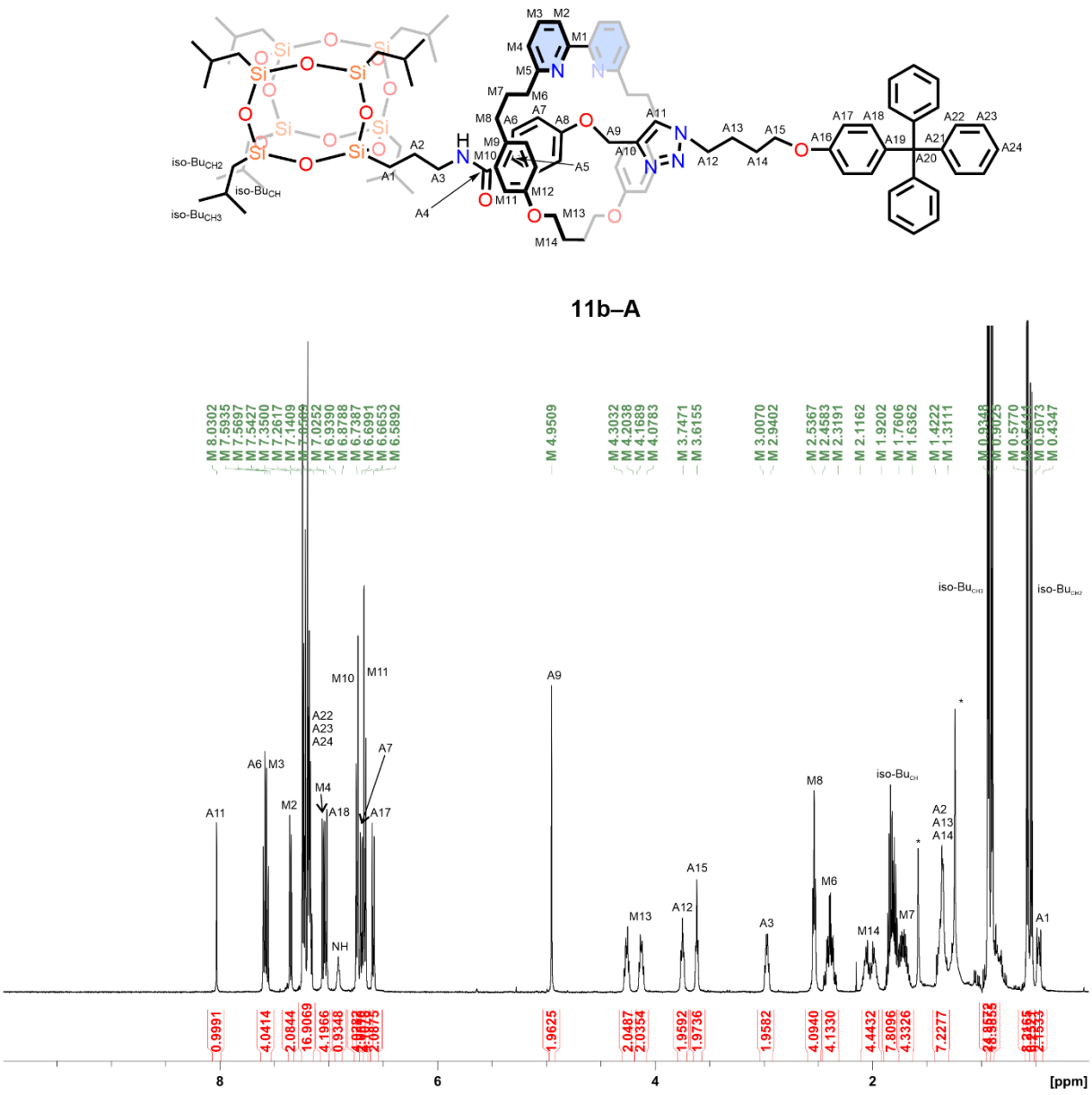



**Figure S 54.** The $^{1}$H NMR spectrum of **11b–A** (chloroform-*d*, 300 K, 500 MHz).

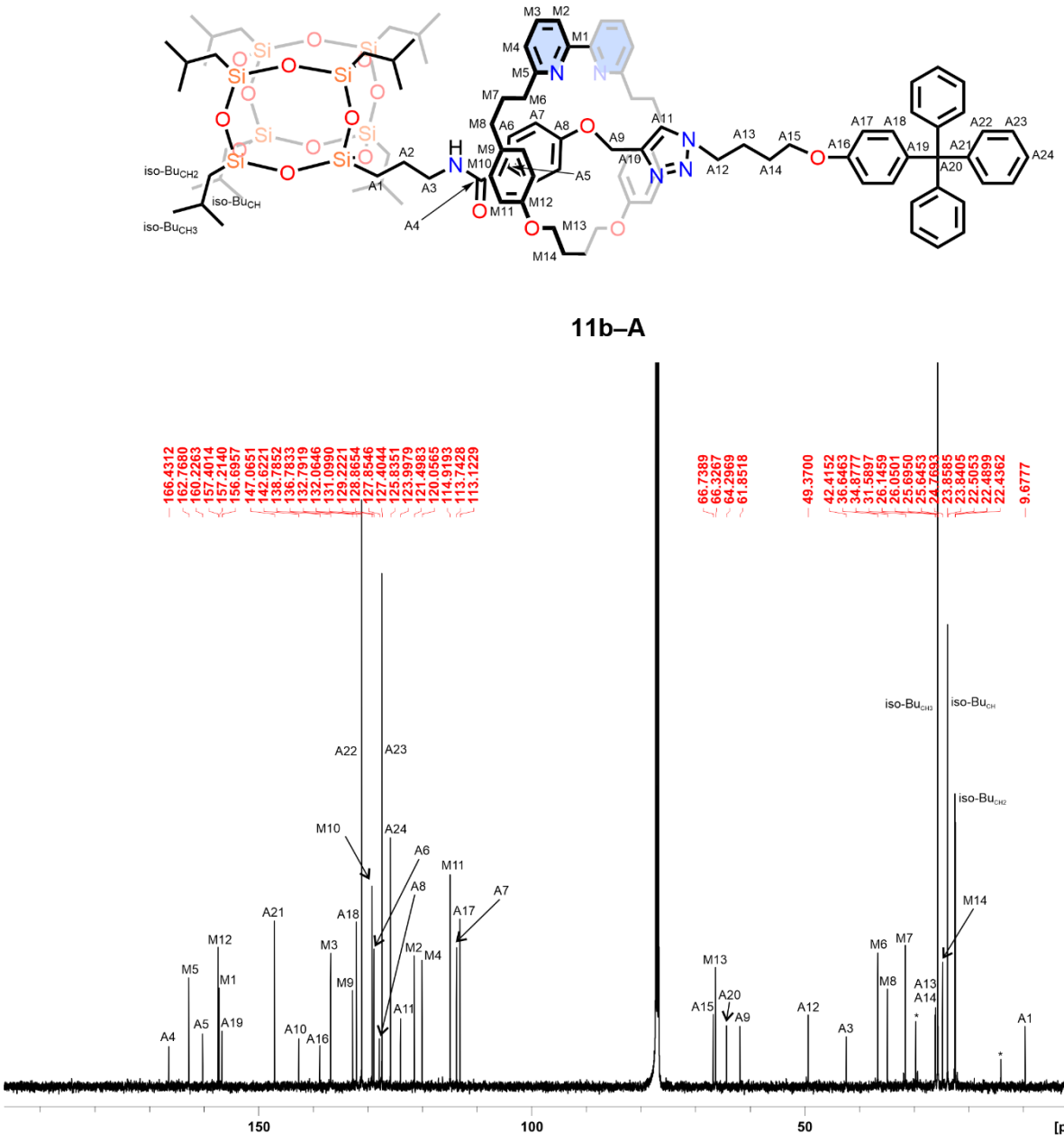



**Figure S 55.** The $^{13}$C NMR spectrum of **11b–A** (chloroform-*d*, 300 K, 125 MHz).

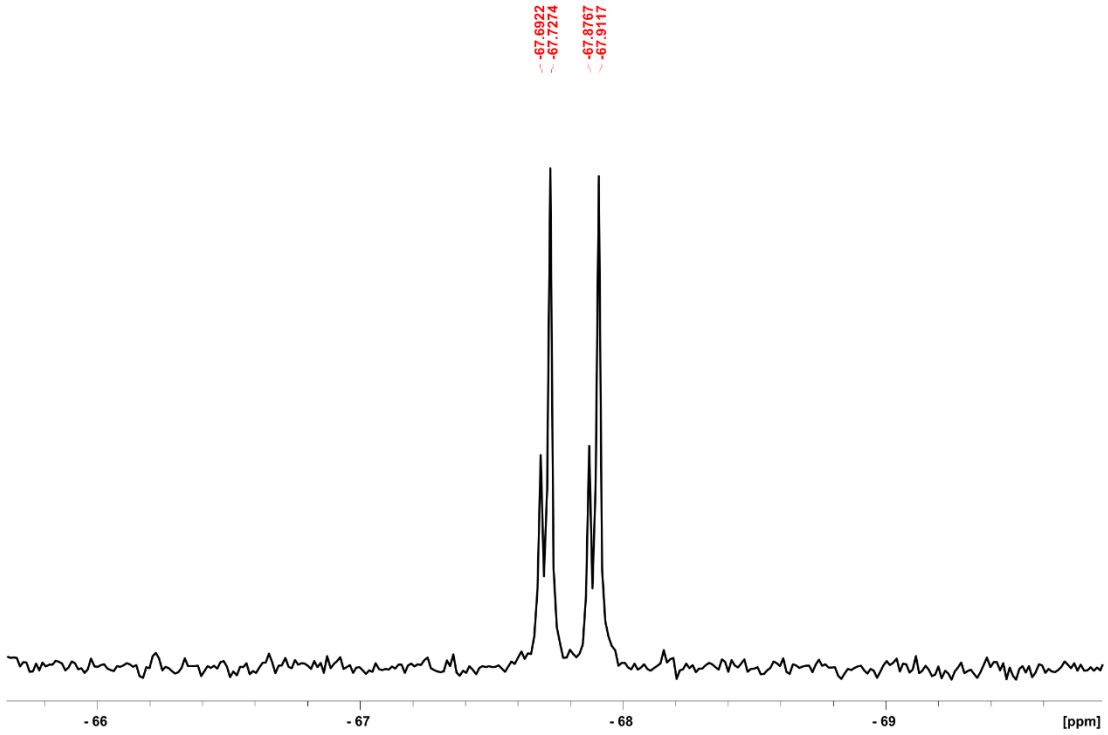



**Figure S 56.** The $^{29}$Si NMR spectrum of **11b–A** (chloroform-*d*, 300 K, 100 MHz).

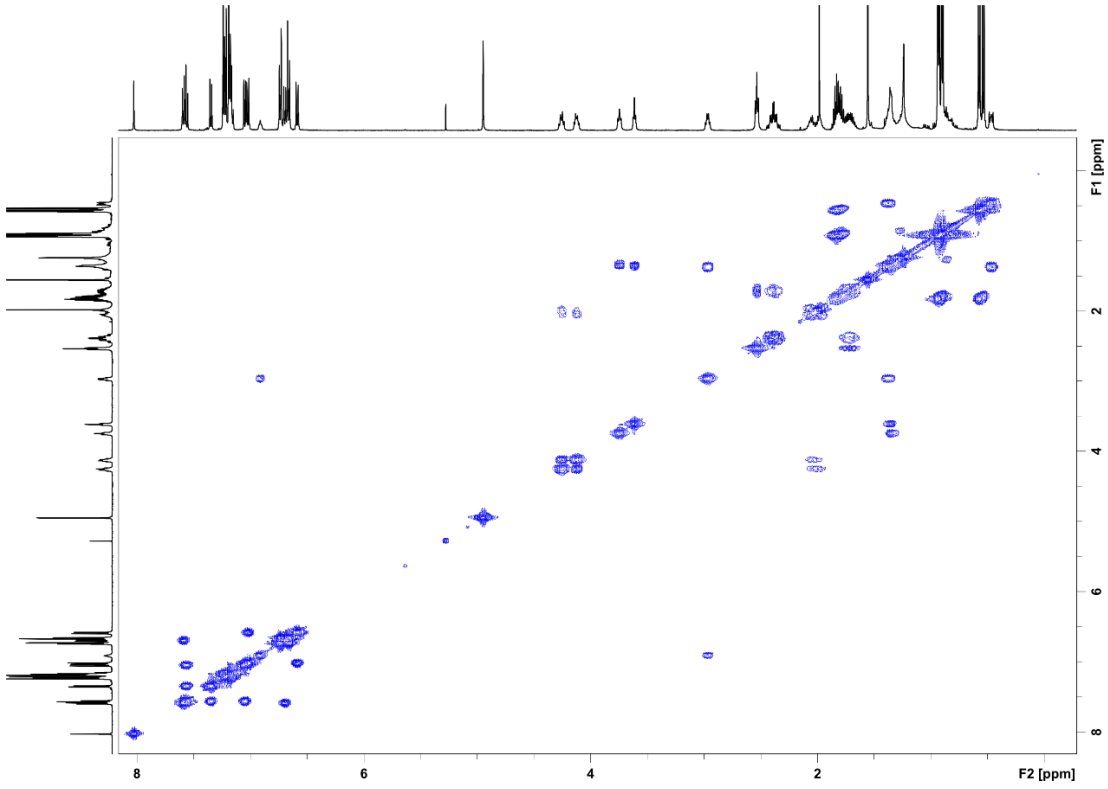



**Figure S 57.** The $^{1}$H-$^{1}$H COSY spectrum of **11b–A** (chloroform-*d*, 300 K, 500 MHz).

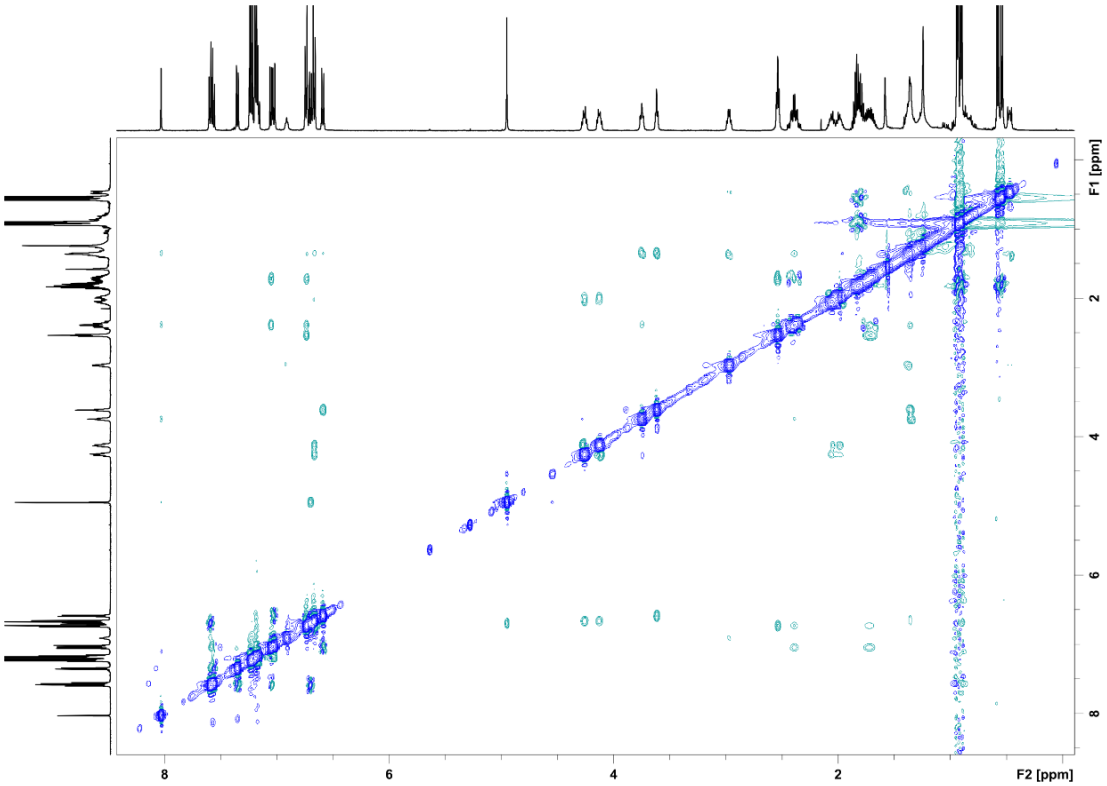



**Figure S 58.** The $^{1}$H-$^{1}$H NOESY spectrum of **11b–A** (chloroform-*d*, 300 K, 500 MHz).

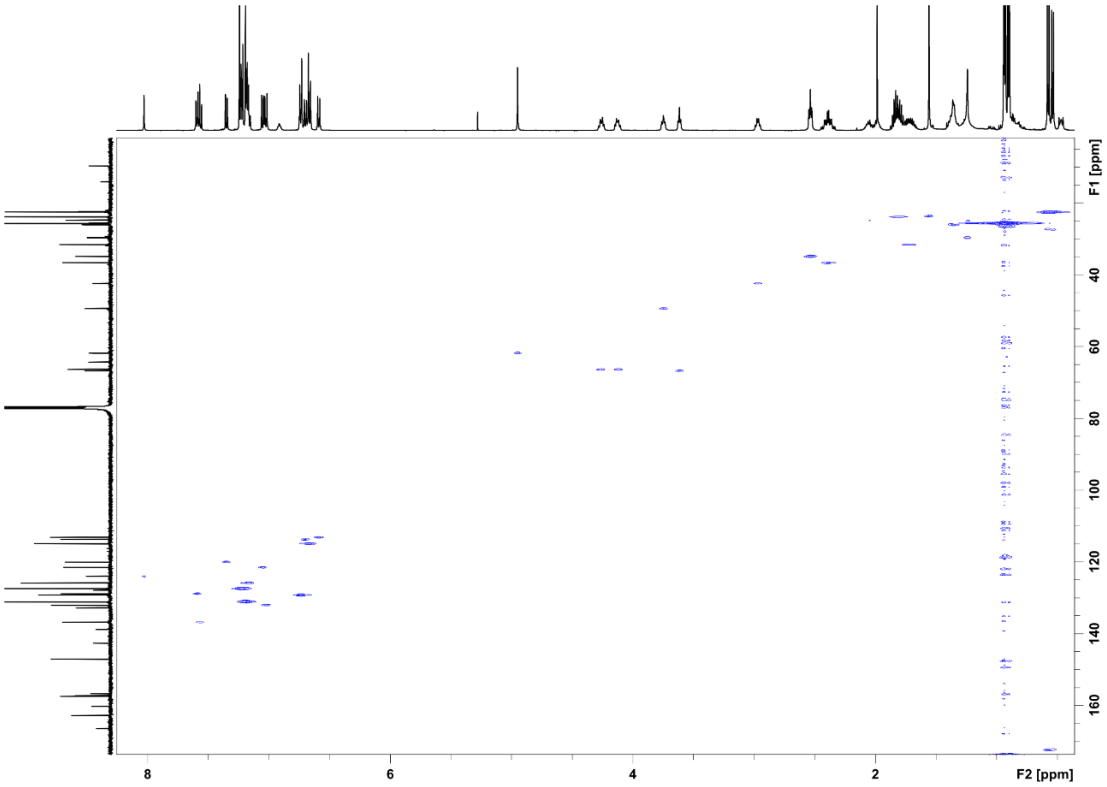



**Figure S 59.** The $^{1}$H-$^{13}$C HSQC spectrum of **11b–A** (chloroform-*d*, 300 K, 500 MHz).

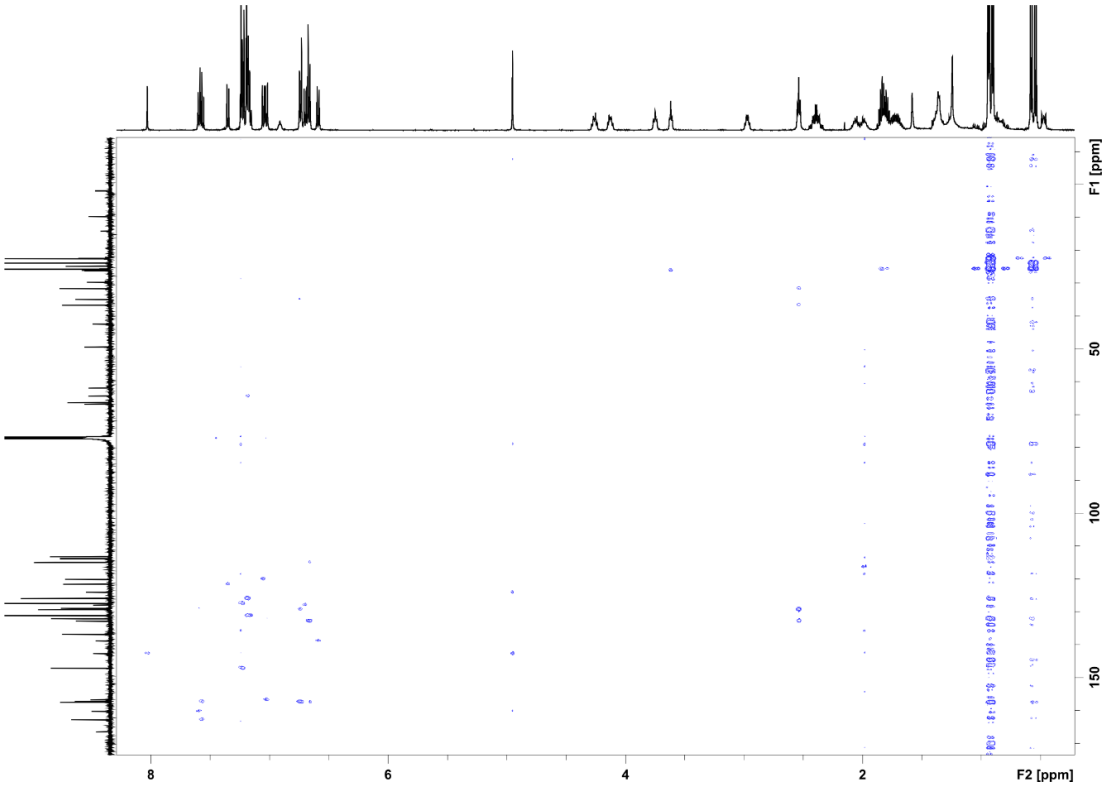



**Figure S 60.** The $^{1}H$-$^{13}C$ HMBC spectrum of **11b–A** (chloroform-*d*, 300 K, 500 MHz).

## NMR spectra of 12–A

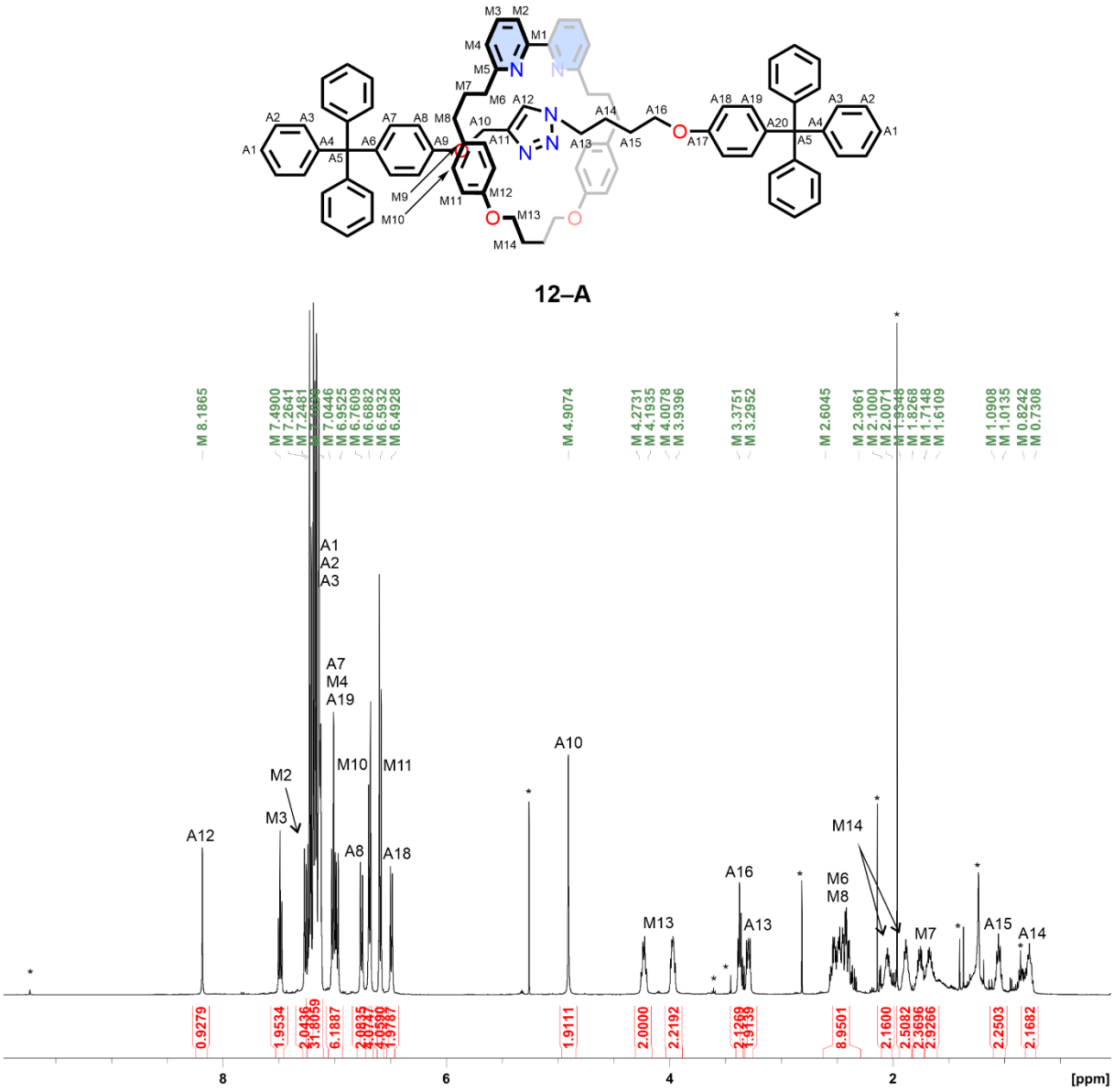



**Figure S 61.** The $^{1}$H NMR spectrum of **12–A** (chloroform-*d*, 300 K, 500 MHz).

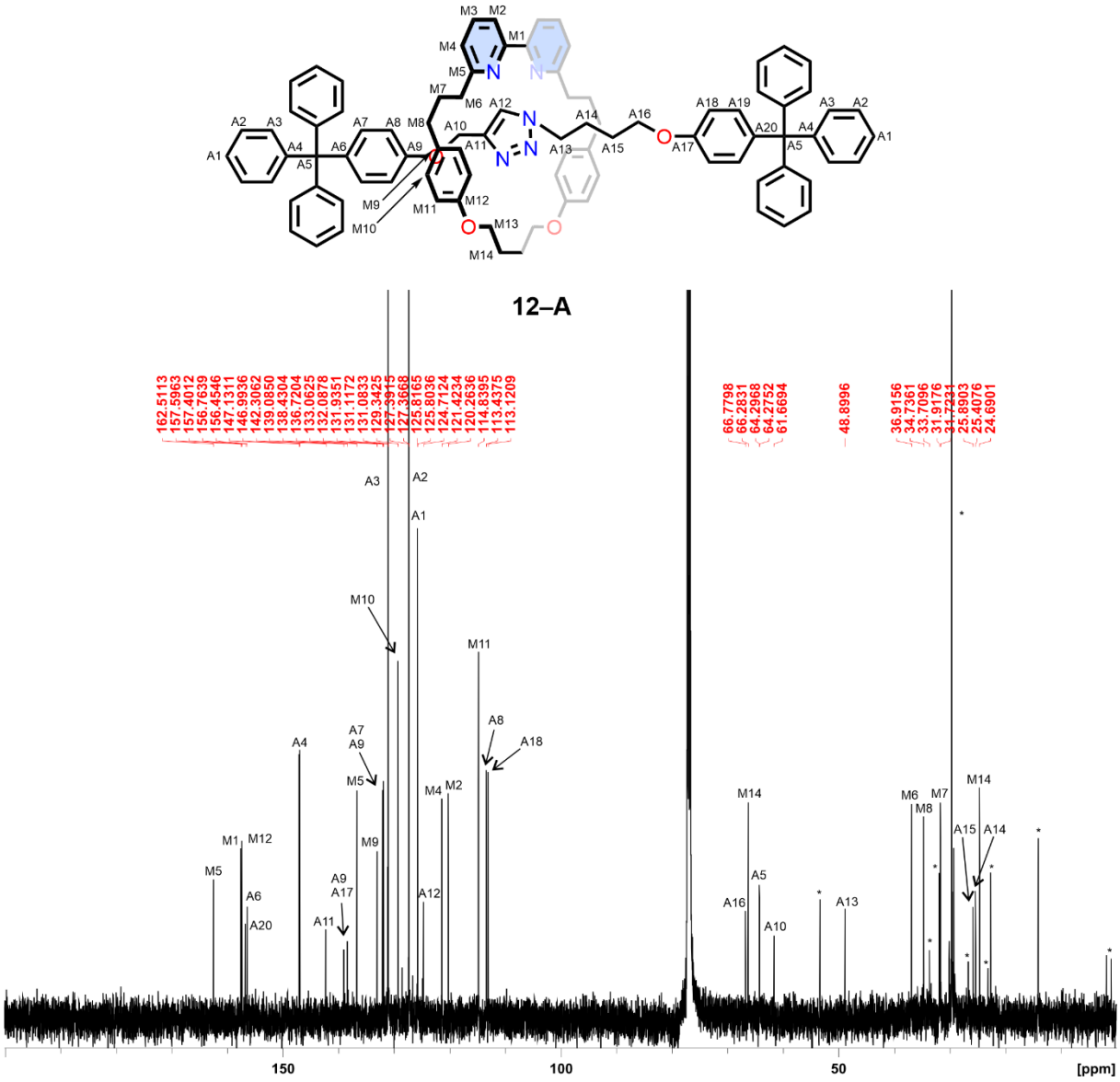



**Figure S 62.** The $^{13}$C NMR spectrum of **12–A** (chloroform-*d*, 300 K, 125 MHz).

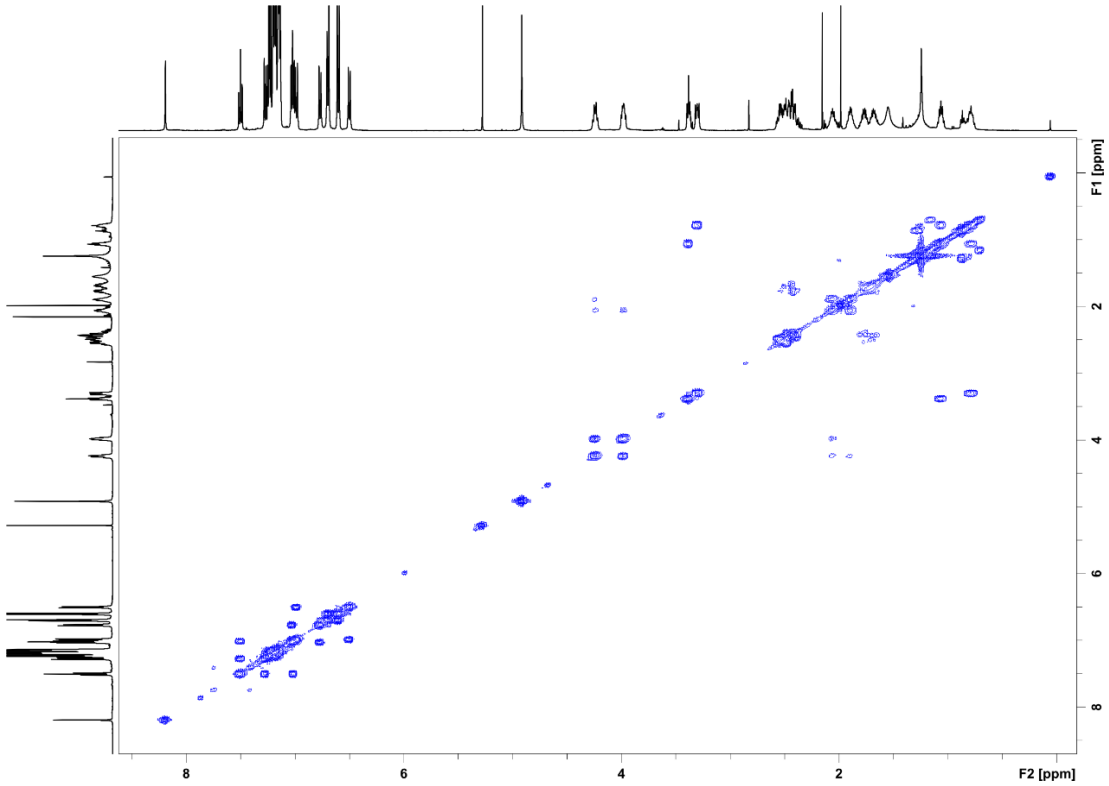



**Figure S 63.** The $^{1}$H-$^{1}$H COSY spectrum of **12–A** (chloroform-*d*, 300 K, 500 MHz).

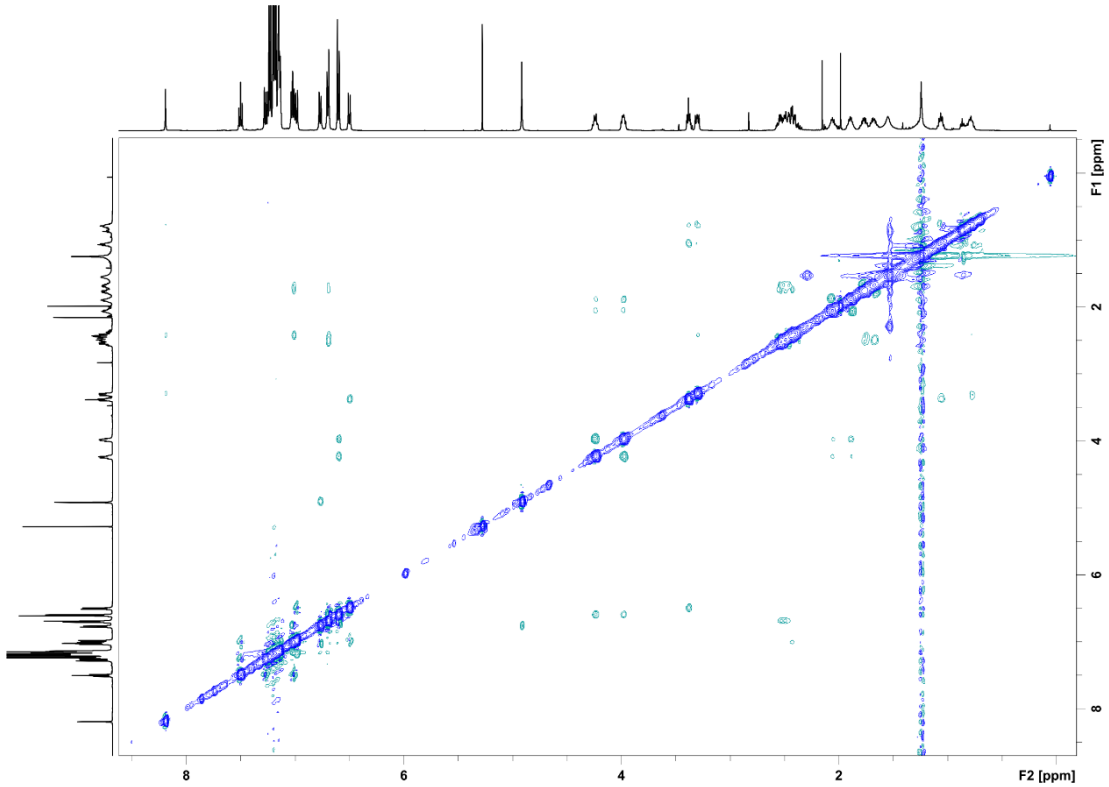



**Figure S 64.** The $^{1}$H-$^{1}$H NOESY spectrum of **12–A** (chloroform-*d*, 300 K, 500 MHz).

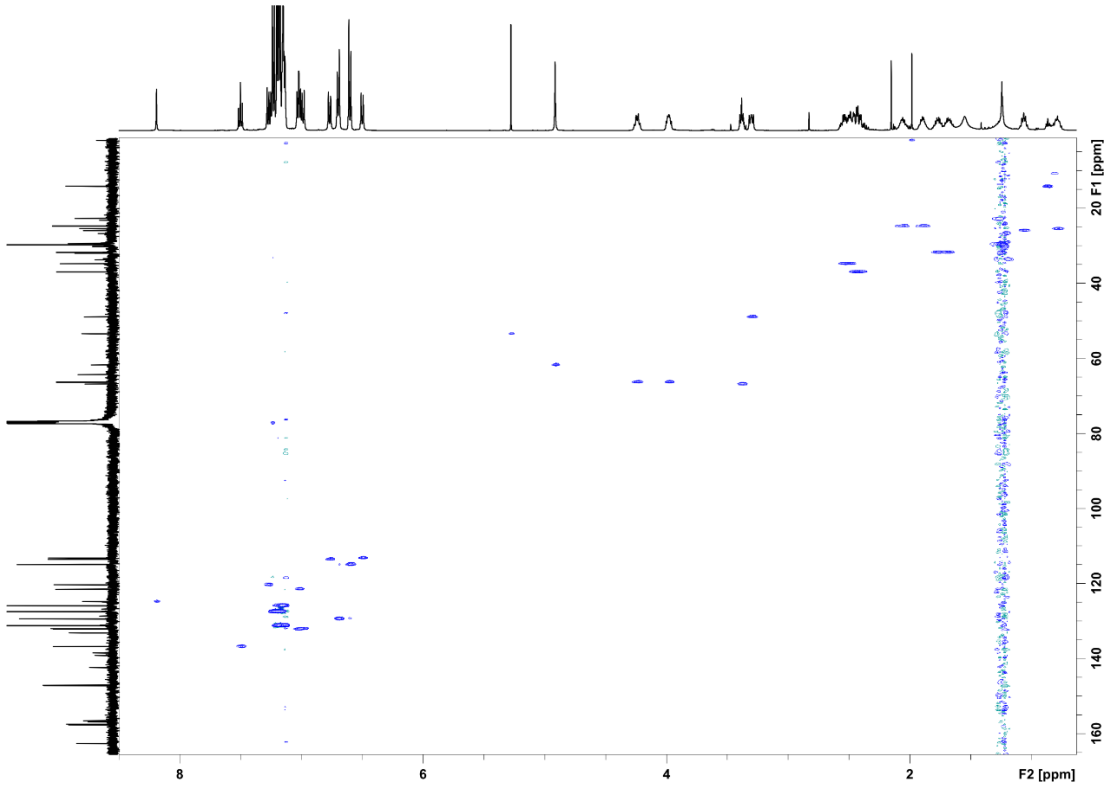



**Figure S 65.** The $^{1}$H-$^{13}$C HSQC spectrum of **12–A** (chloroform-*d*, 300 K, 500 MHz).

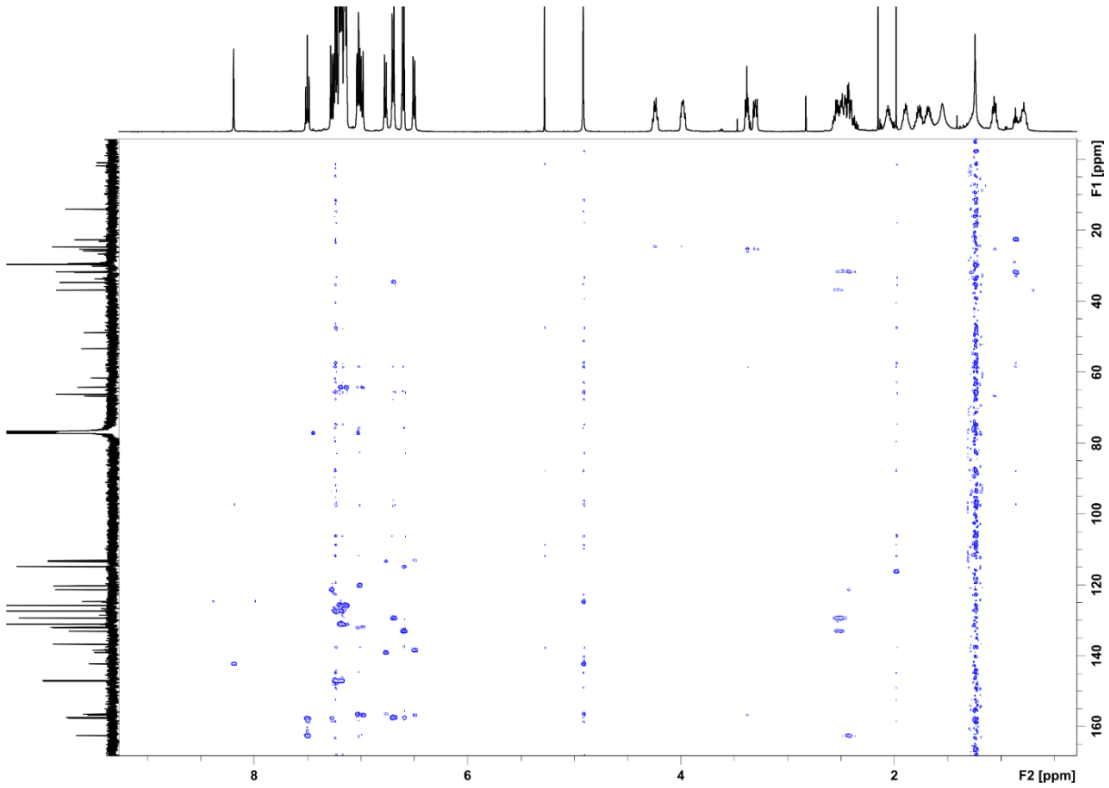



**Figure S 66.** The $^{1}$H-$^{13}$C HMBC spectrum of **12–A** (chloroform-*d*, 300 K, 500 MHz).

## NMR spectra of 9b–B

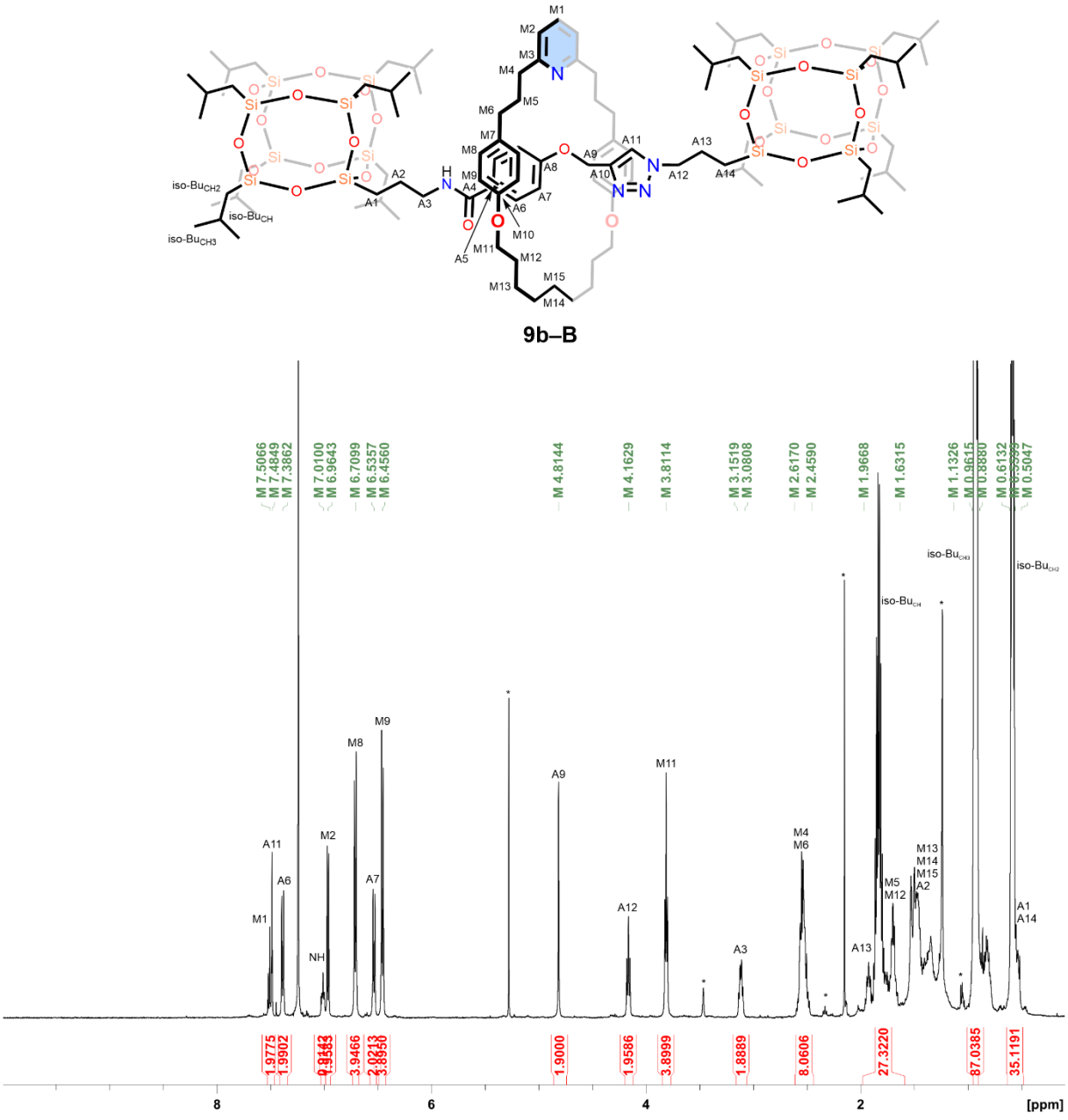



**Figure S 67.** The $^{1}$H NMR spectrum of **9b–B** (chloroform-*d*, 300 K, 500 MHz).

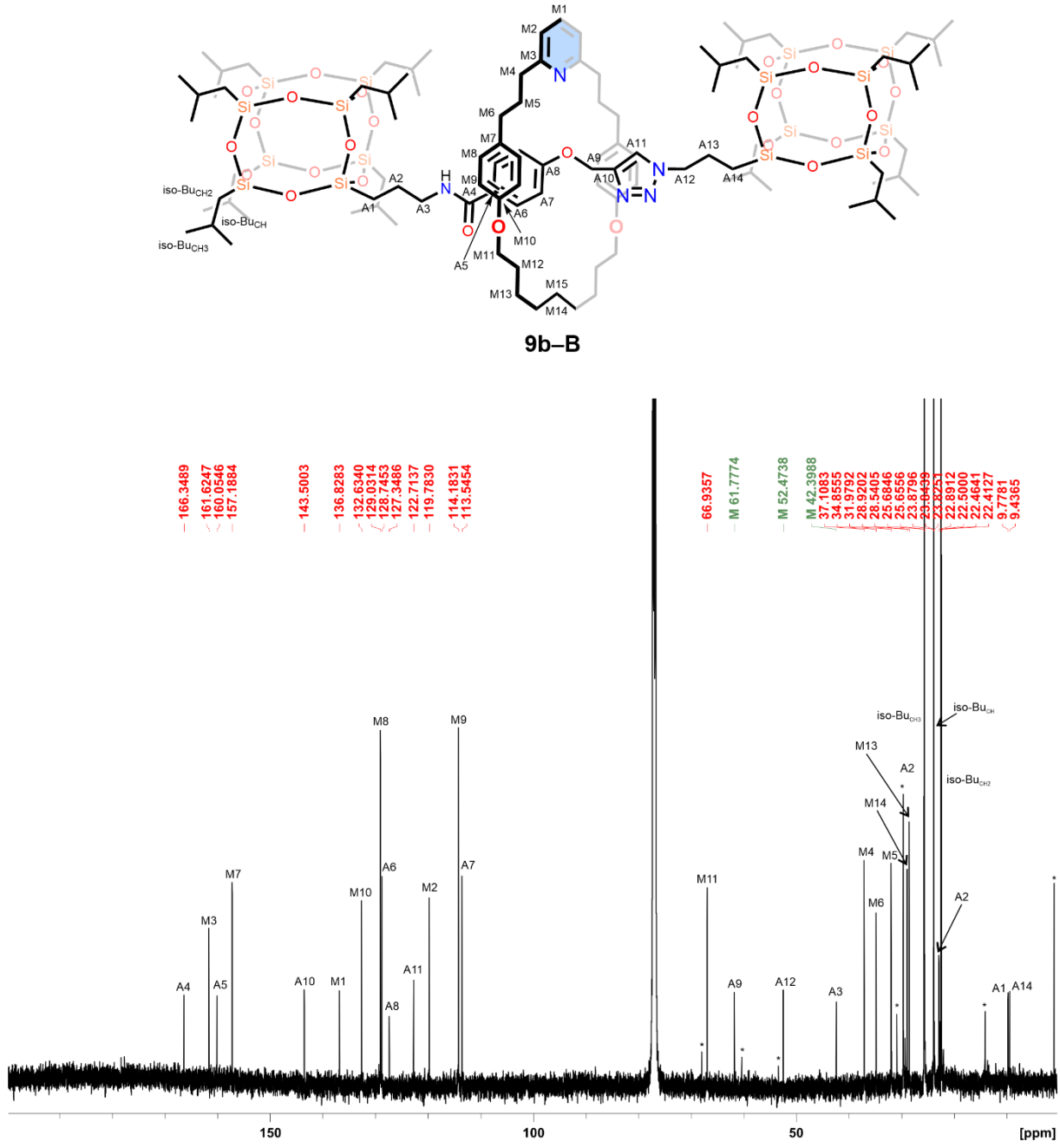



**Figure S 68.** The $^{13}$C NMR spectrum of **9b–B** (chloroform-*d*, 300 K, 125 MHz).

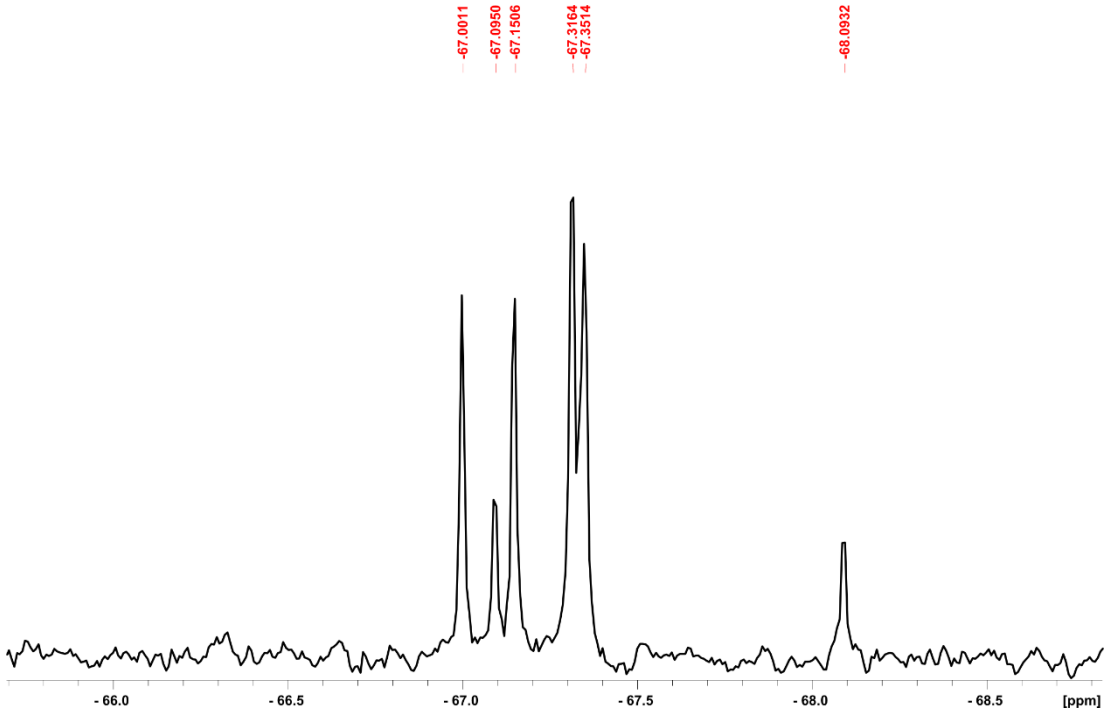



**Figure S 69.** The $^{29}$Si NMR spectrum of **10b–B** (chloroform-*d*, 300 K, 100 MHz).

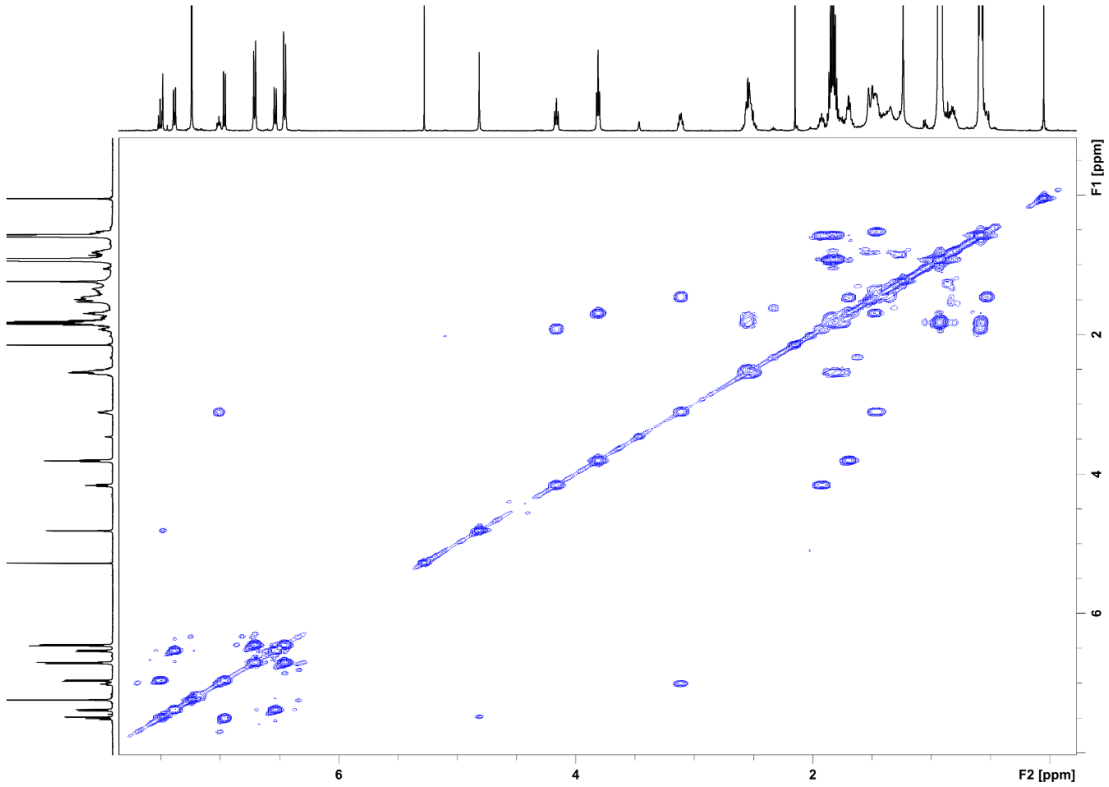



**Figure S 70.** The $^{1}$H-$^{1}$H COSY spectrum of **9b–B** (chloroform-*d*, 300 K, 500 MHz).

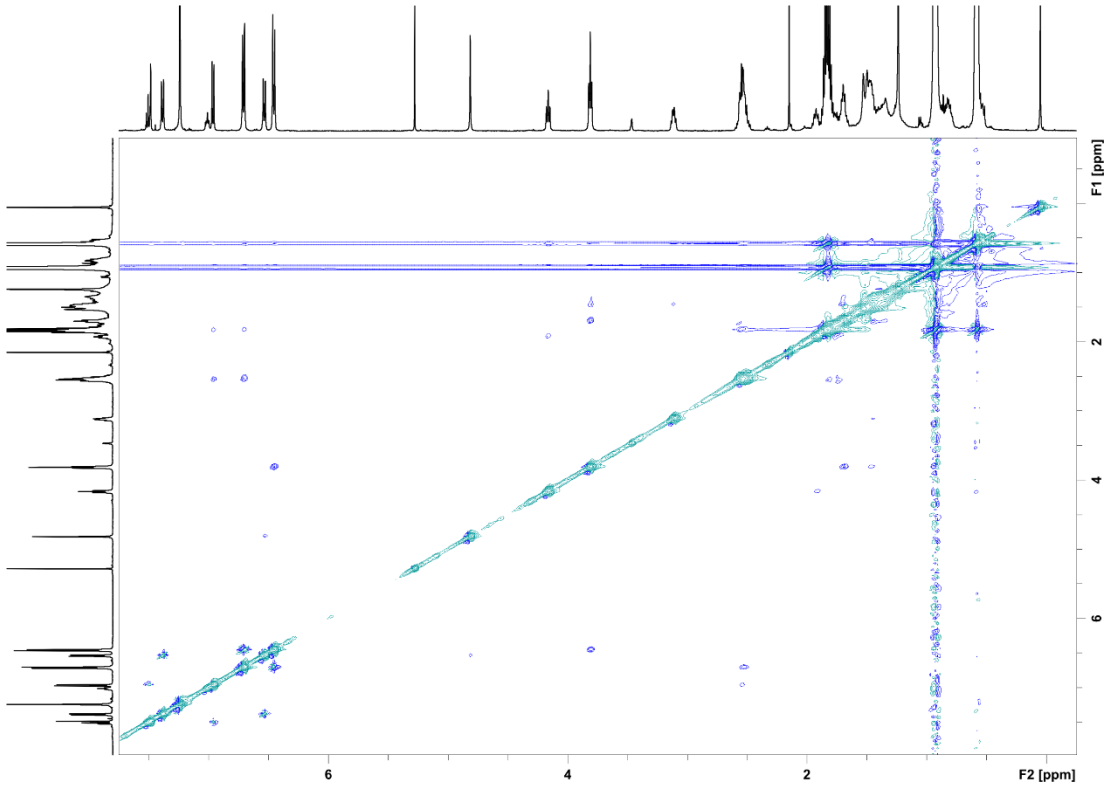



**Figure S 71.** The $^{1}$H-$^{1}$H NOESY spectrum of **9b–B** (chloroform-*d*, 300 K, 500 MHz).

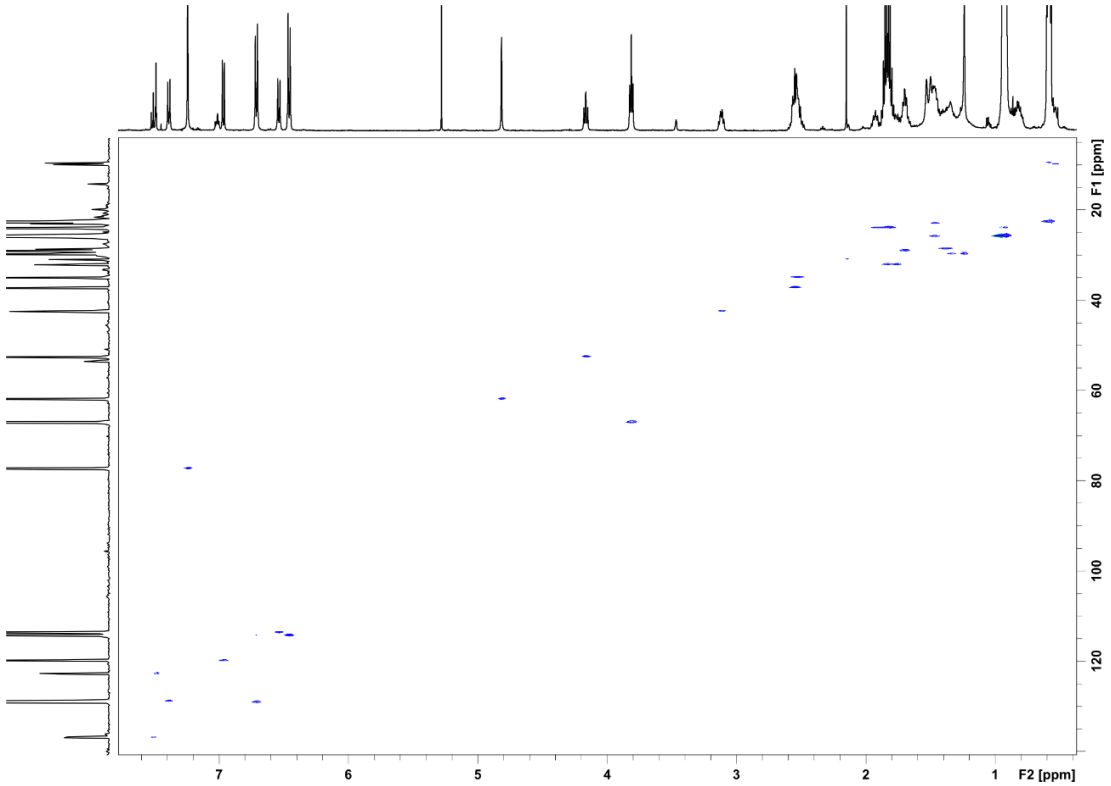



**Figure S 72.** The $^{1}$H-$^{13}$C HSQC spectrum of **9b–B** (chloroform-*d*, 300 K, 500 MHz).

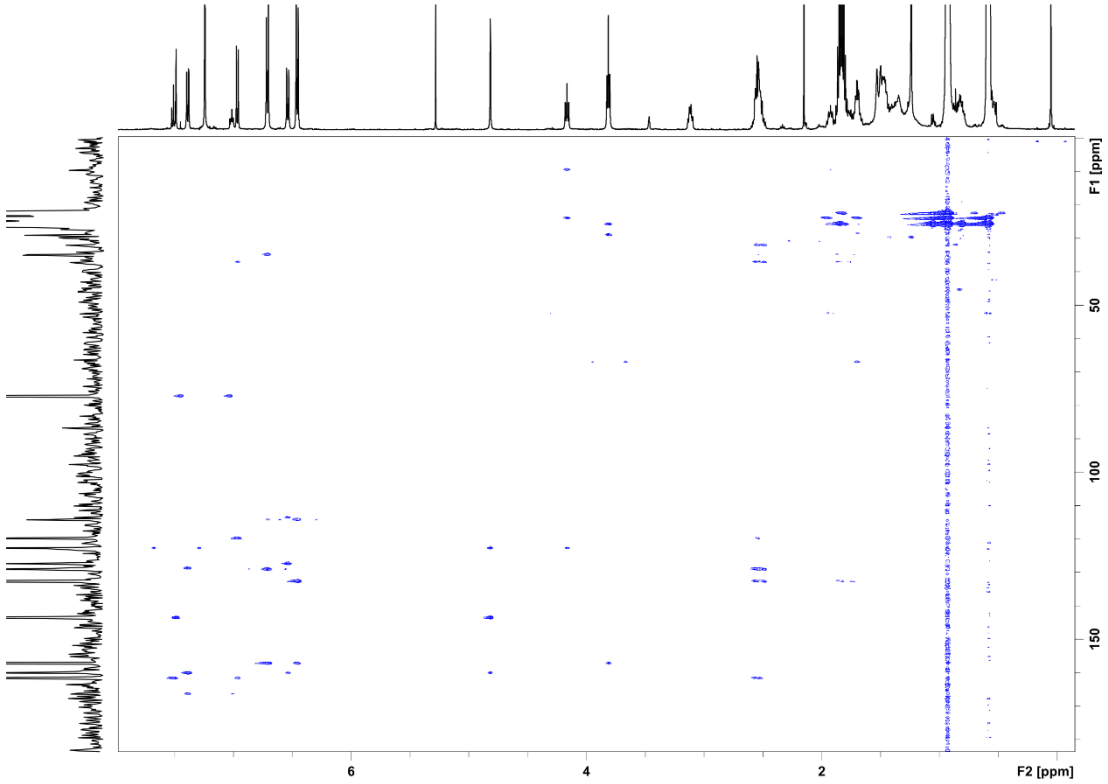



**Figure S 73.** The $^{1}$H-$^{13}$C HMBC spectrum of **9b–B** (chloroform-*d*, 300 K, 500 MHz).

## NMR spectra of 10b–B

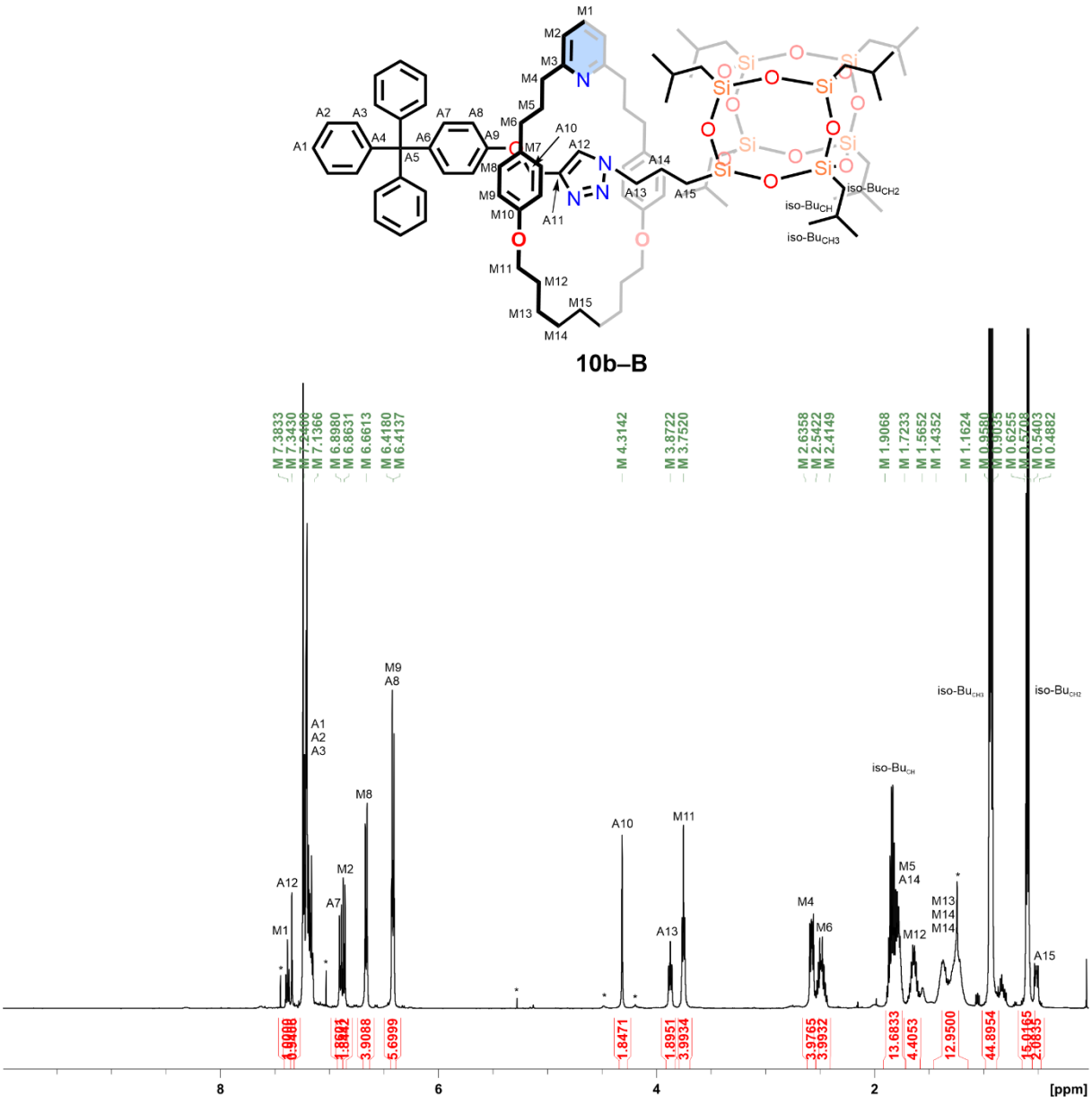



**Figure S 74.** The $^{1}$H NMR spectrum of **10b–B** (chloroform-*d*, 300 K, 500 MHz).

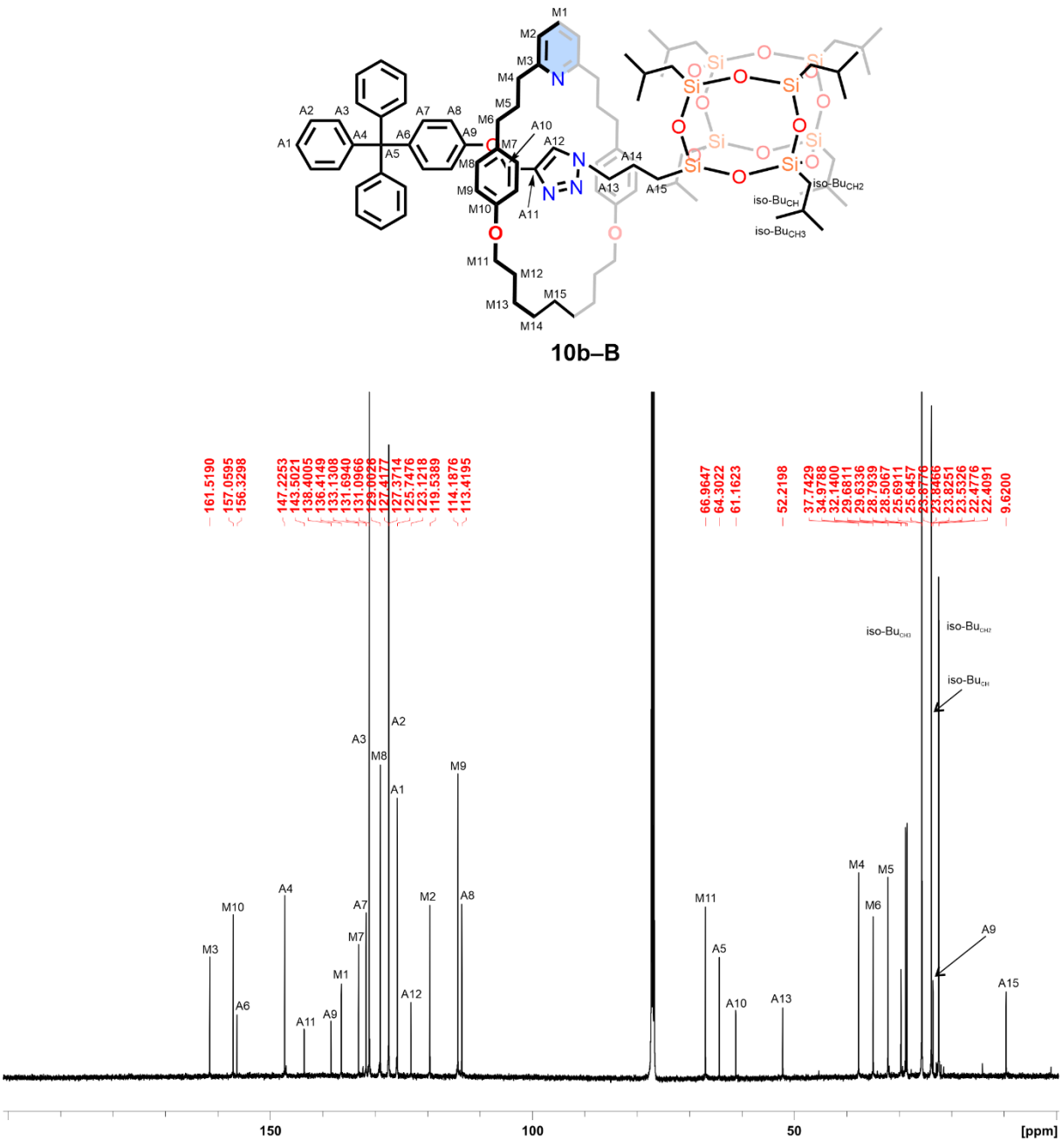



**Figure S 75.** The $^{13}$C NMR spectrum of **10b–B** (chloroform-*d*, 300 K, 125 MHz).

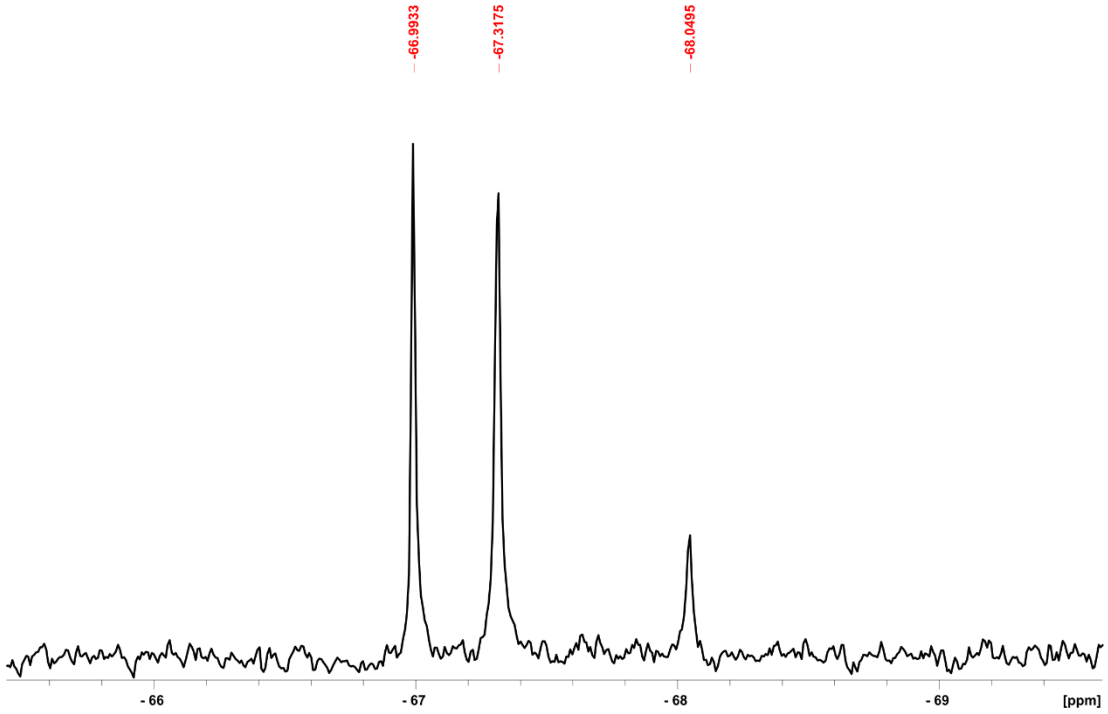



**Figure S 76.** The $^{29}$Si NMR spectrum of **10b–B** (chloroform-*d*, 300 K, 100 MHz).

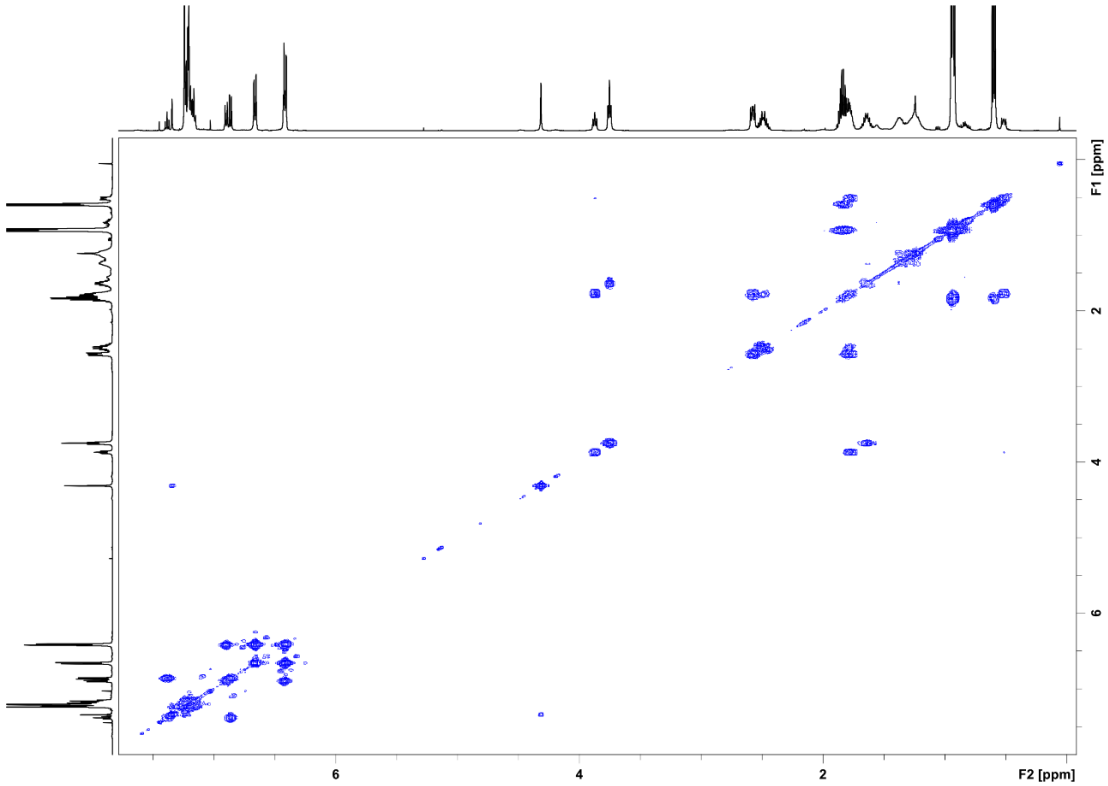



**Figure S 77.** The $^{1}$H-$^{1}$H COSY spectrum of **10b–B** (chloroform-*d*, 300 K, 500 MHz).

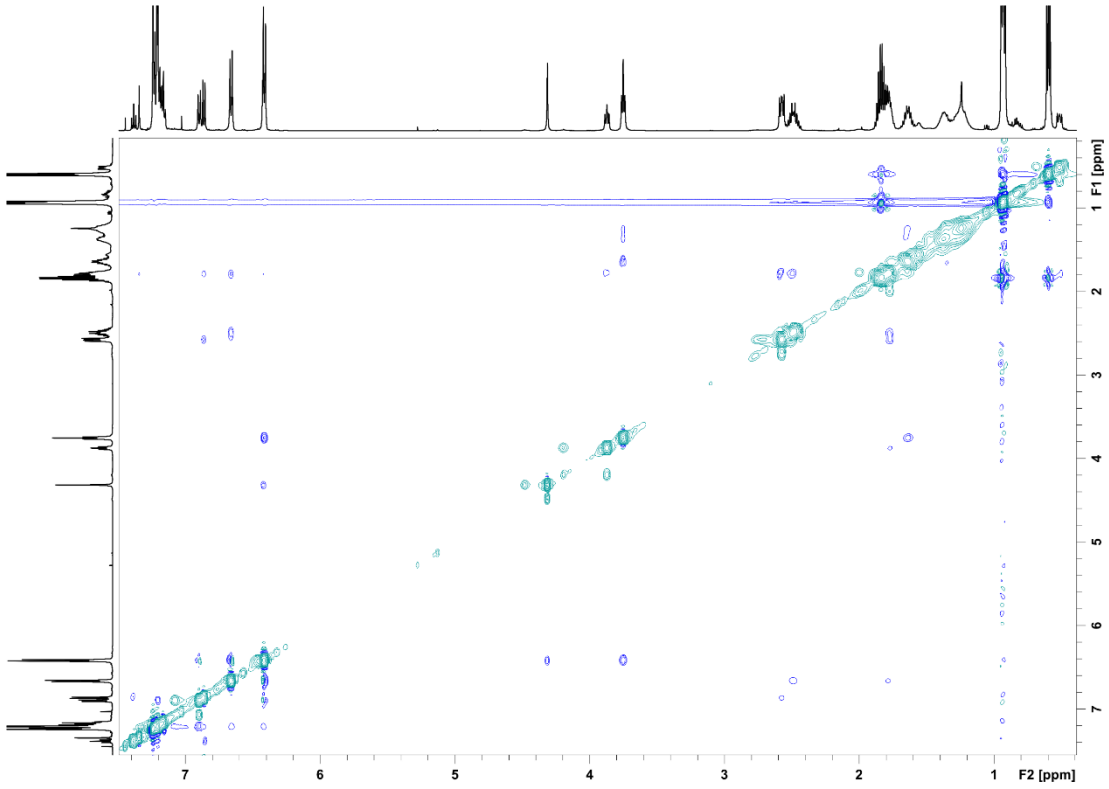



**Figure S 78.** The $^{1}$H-$^{1}$H NOESY spectrum of **10b–B** (chloroform-*d*, 300 K, 500 MHz).

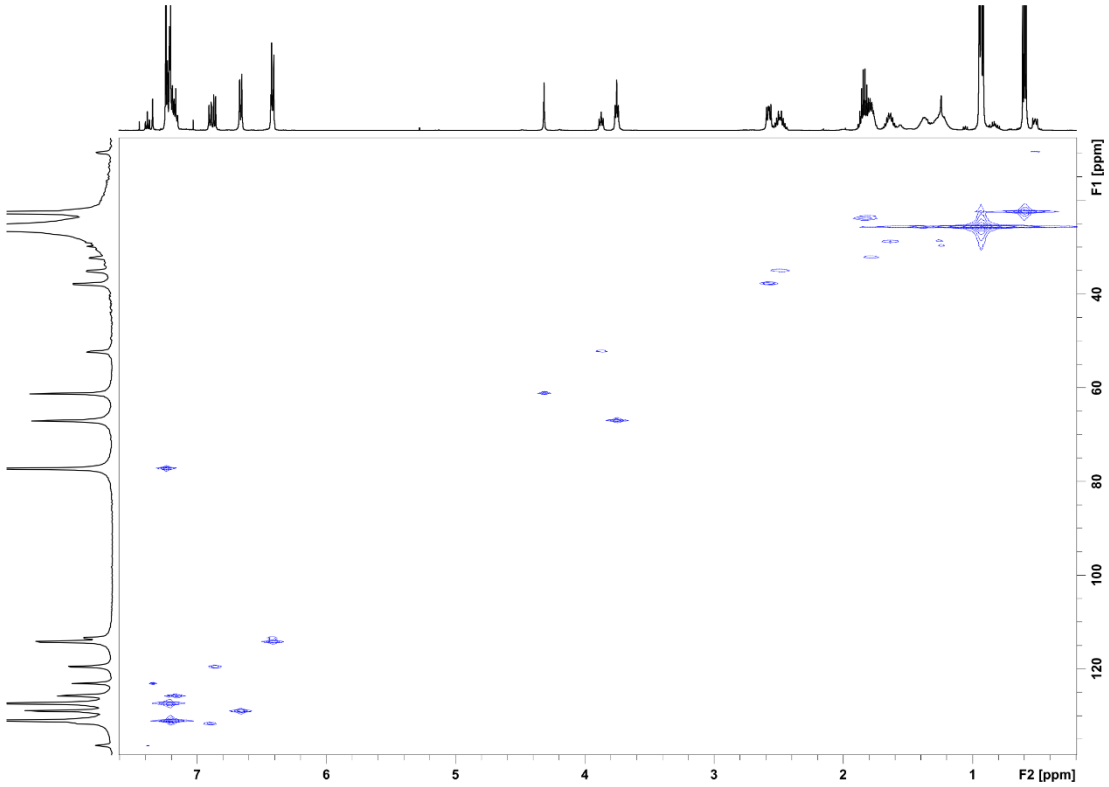



**Figure S 79.** The $^{1}$H-$^{13}$C HMQC spectrum of **10b–B** (chloroform-*d*, 300 K, 500 MHz).

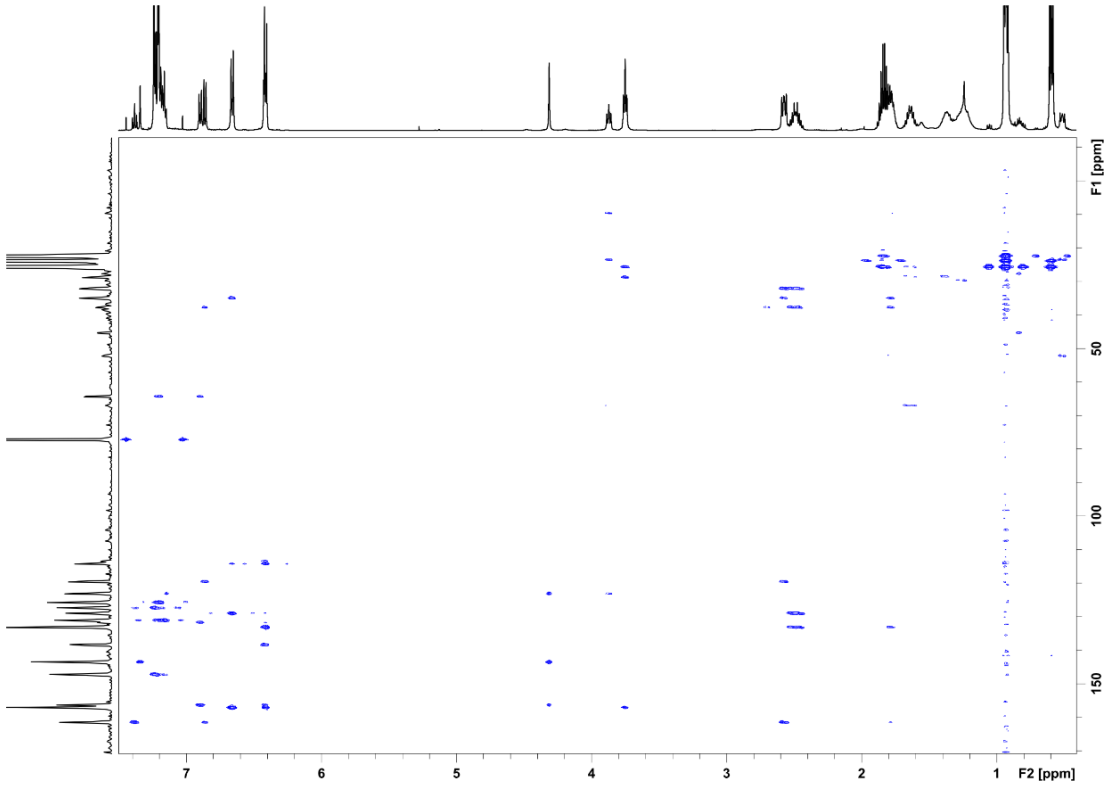



**Figure S 80.** The $^{1}H$-$^{13}C$ HMBC spectrum of **10b–B** (chloroform-*d*, 300 K, 500 MHz).

## NMR spectra of 11b–B

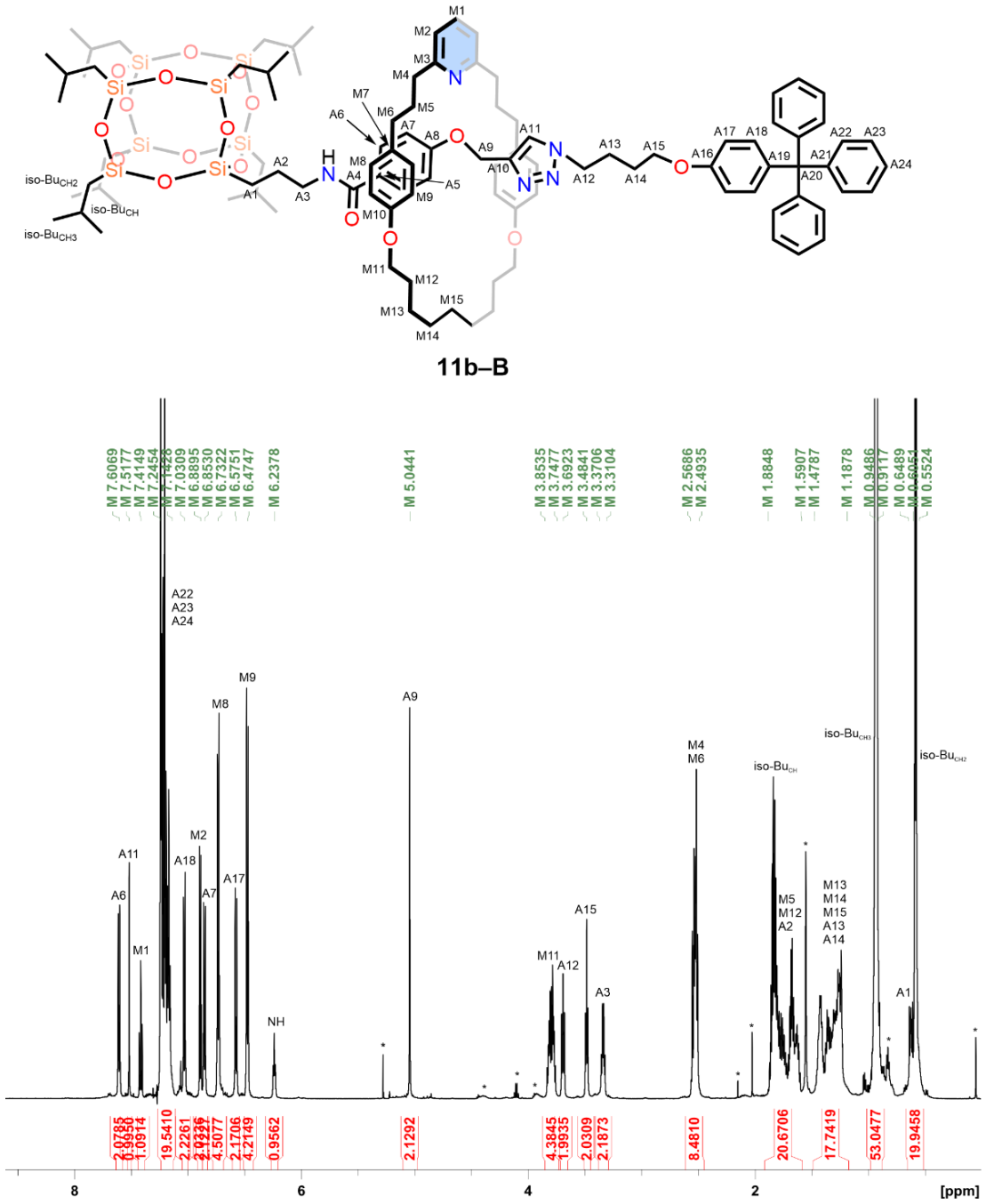



**Figure S 81.** The $^{1}$H NMR spectrum of **11b–B** (chloroform-*d*, 300 K, 600 MHz).

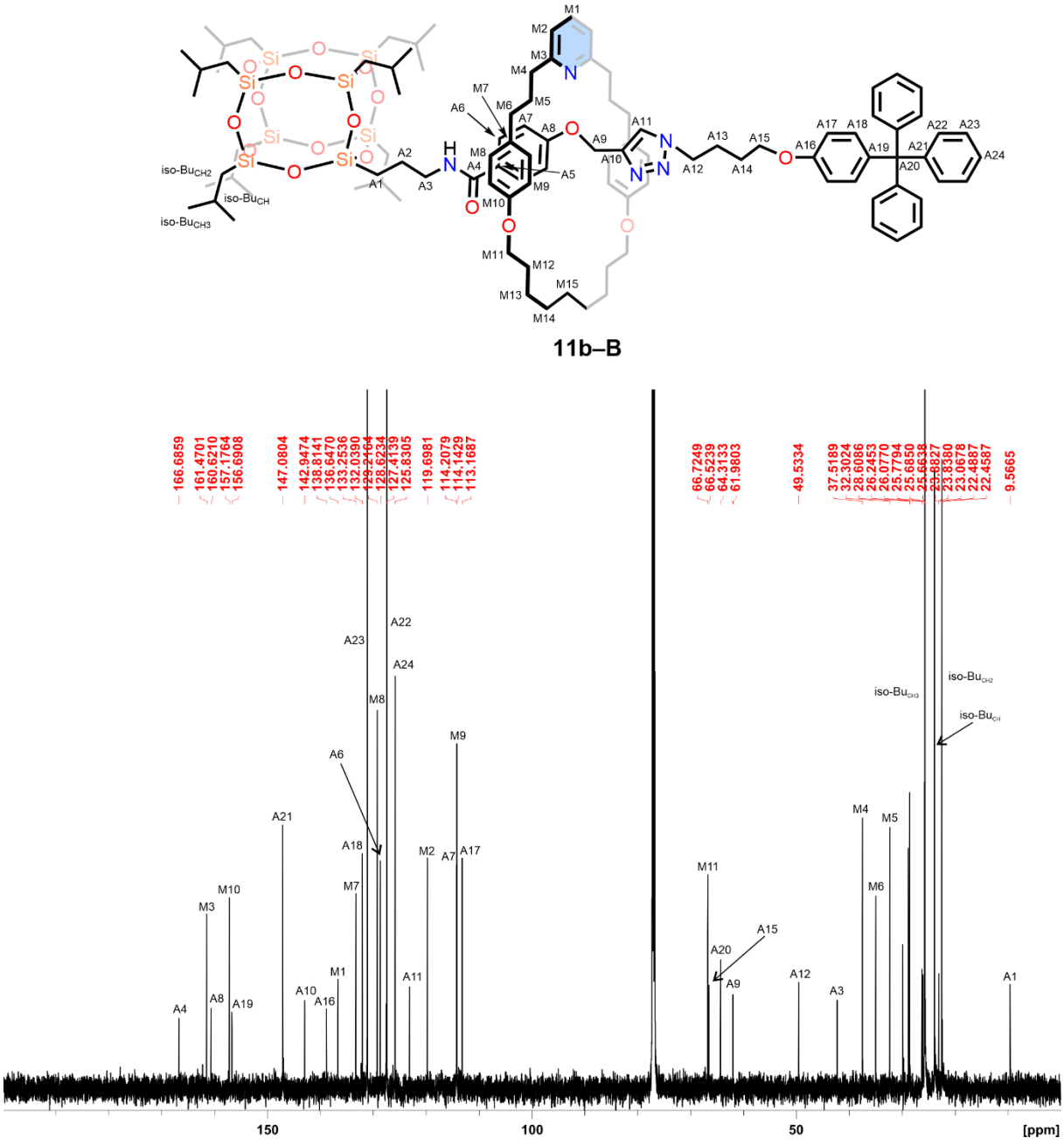



**Figure S 82.** The $^{13}$C NMR spectrum of **11b–B** (chloroform-*d*, 300 K, 150 MHz).

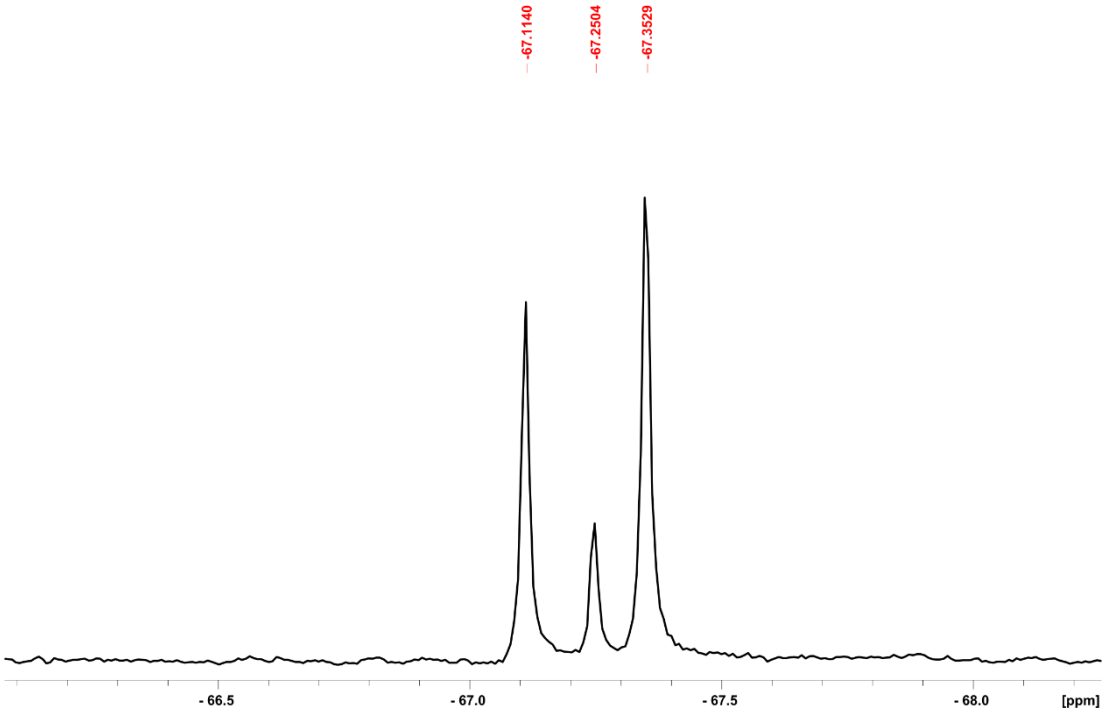



**Figure 83.** The $^{29}$Si NMR spectrum of **11b–B** (chloroform-*d*, 300 K, 100 MHz).

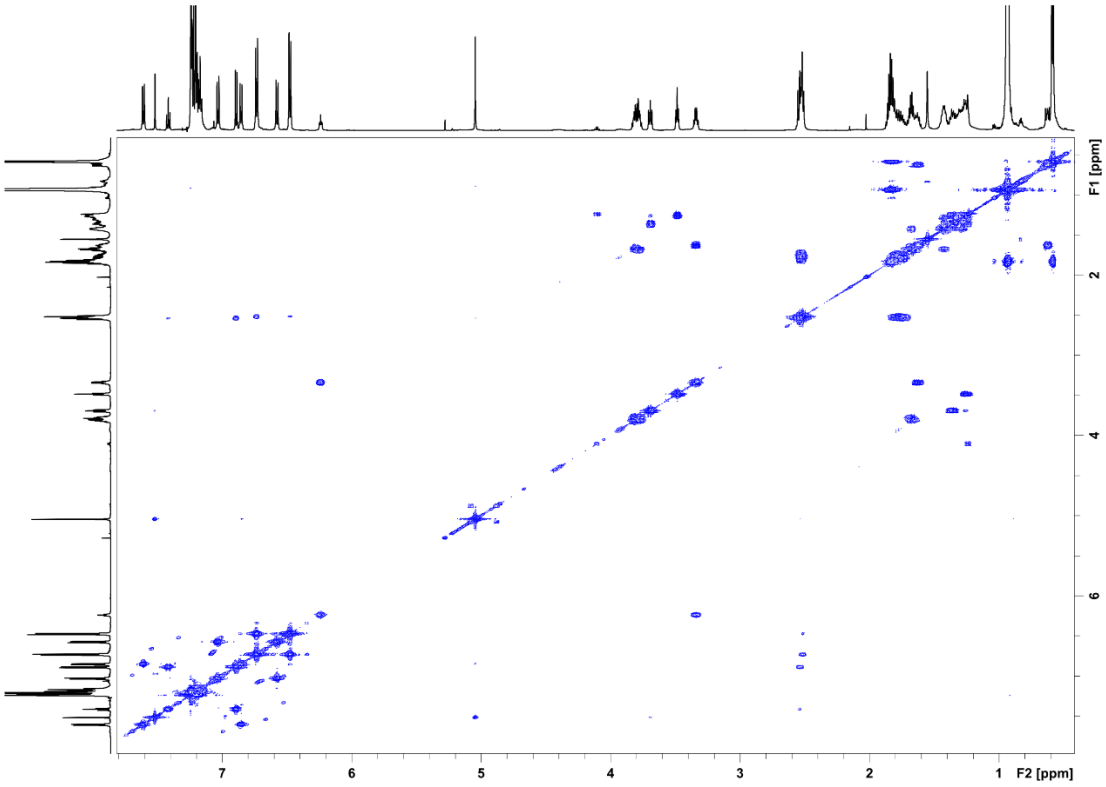



**Figure S 84.** The $^{1}$H-$^{1}$H COSY spectrum of **11b–B** (chloroform-*d*, 300 K, 600 MHz).

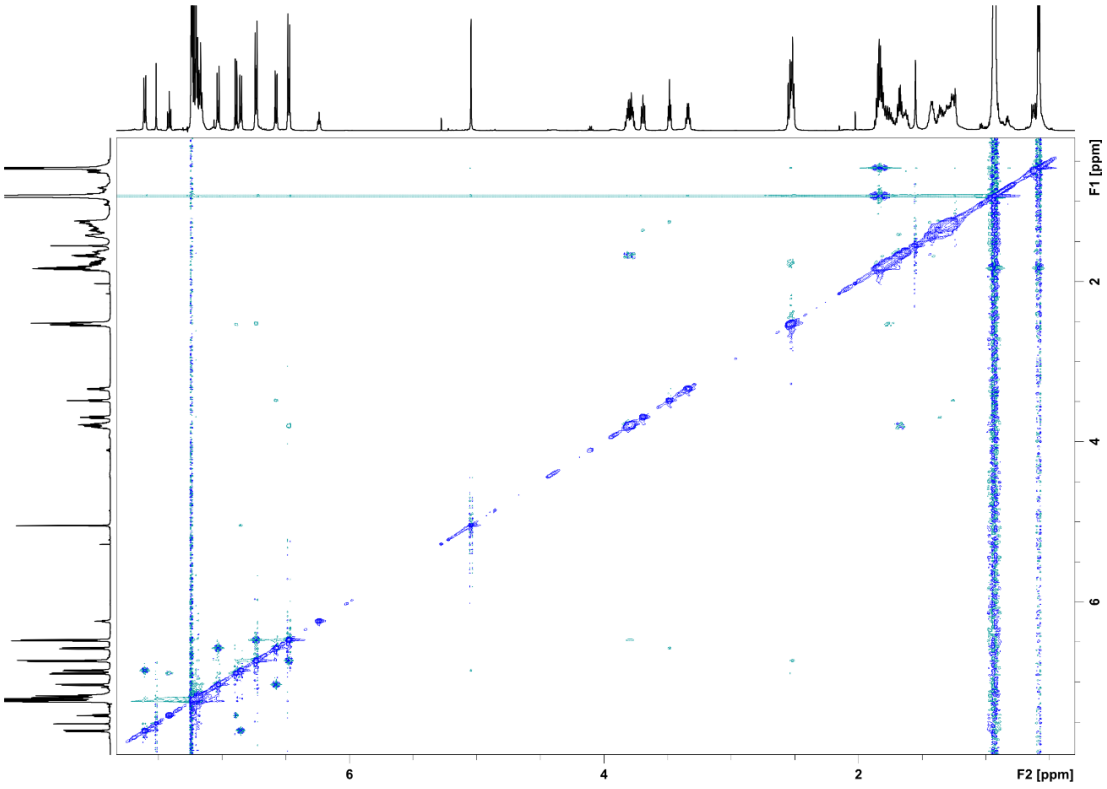



**Figure S 85.** The $^{1}$H-$^{1}$H NOESY spectrum of **11b–B** (chloroform-*d*, 300 K, 600 MHz).

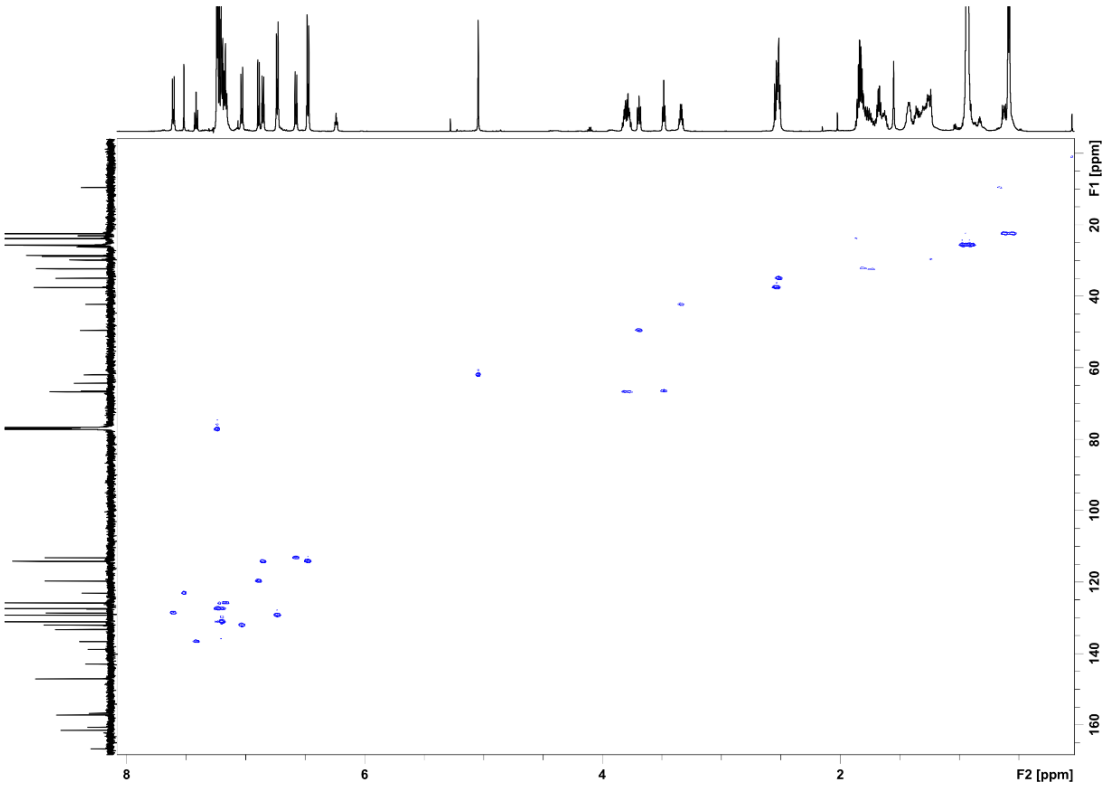



**Figure S 86.** The $^{1}$H-$^{13}$C HMQC spectrum of **11b–B** (chloroform-*d*, 300 K, 600 MHz).

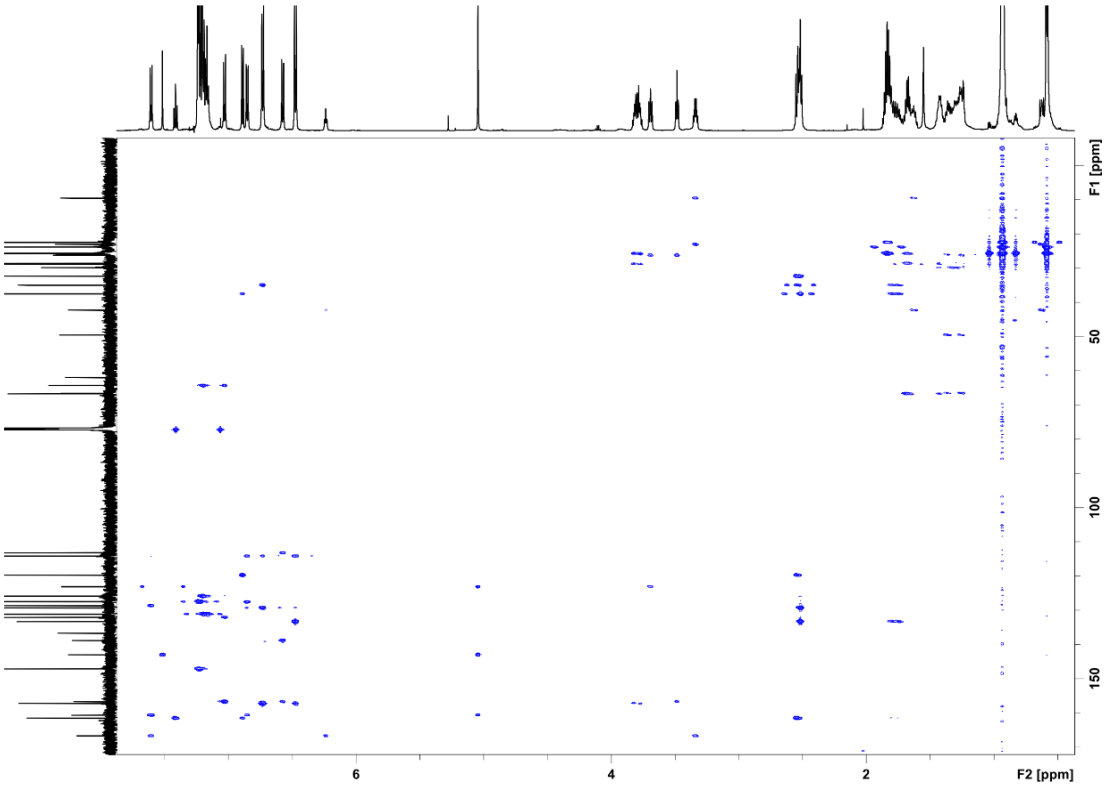



**Figure S 87.** The $^{1}H$-$^{13}C$ HMBC spectrum of **11b–B** (chloroform-*d*, 300 K, 500 MHz).

## NMR spectra of 12–B

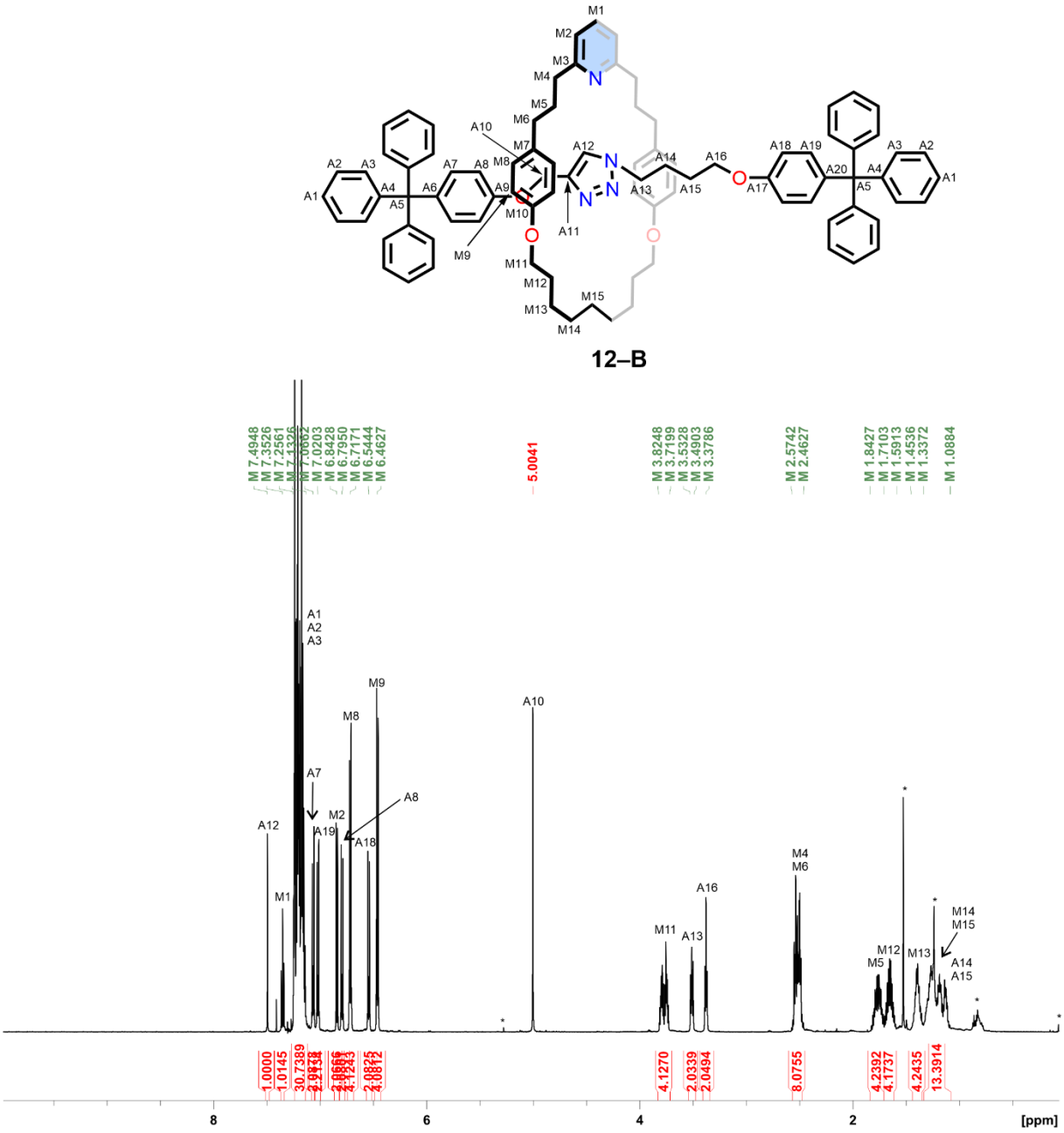



**Figure S 88.** The $^{1}$H NMR spectrum of **12–B** (chloroform-*d*, 300 K, 600 MHz).

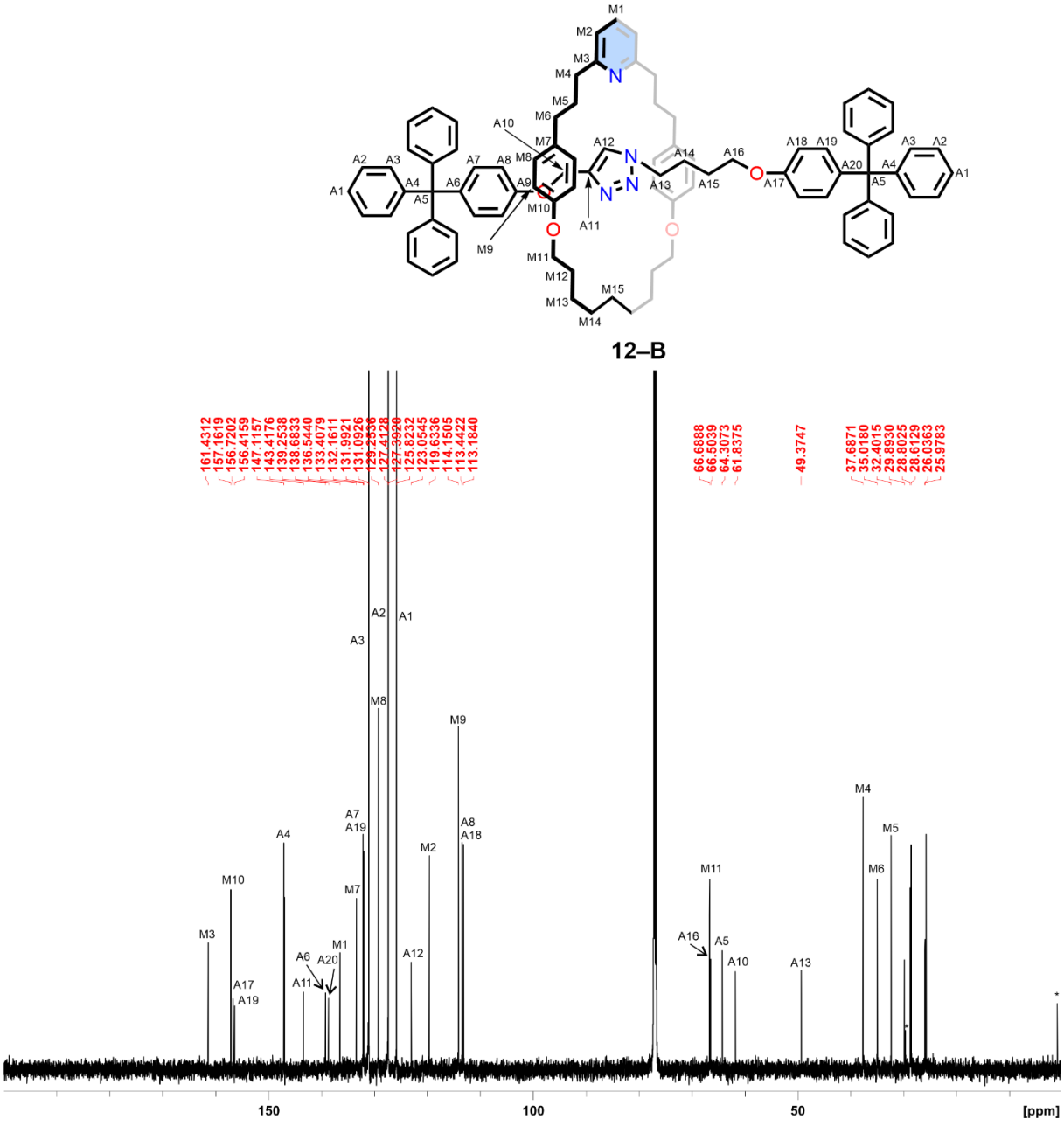



**Figure S 89.** The $^{13}$C NMR spectrum of **12–B** (chloroform-*d*, 300 K, 150 MHz).

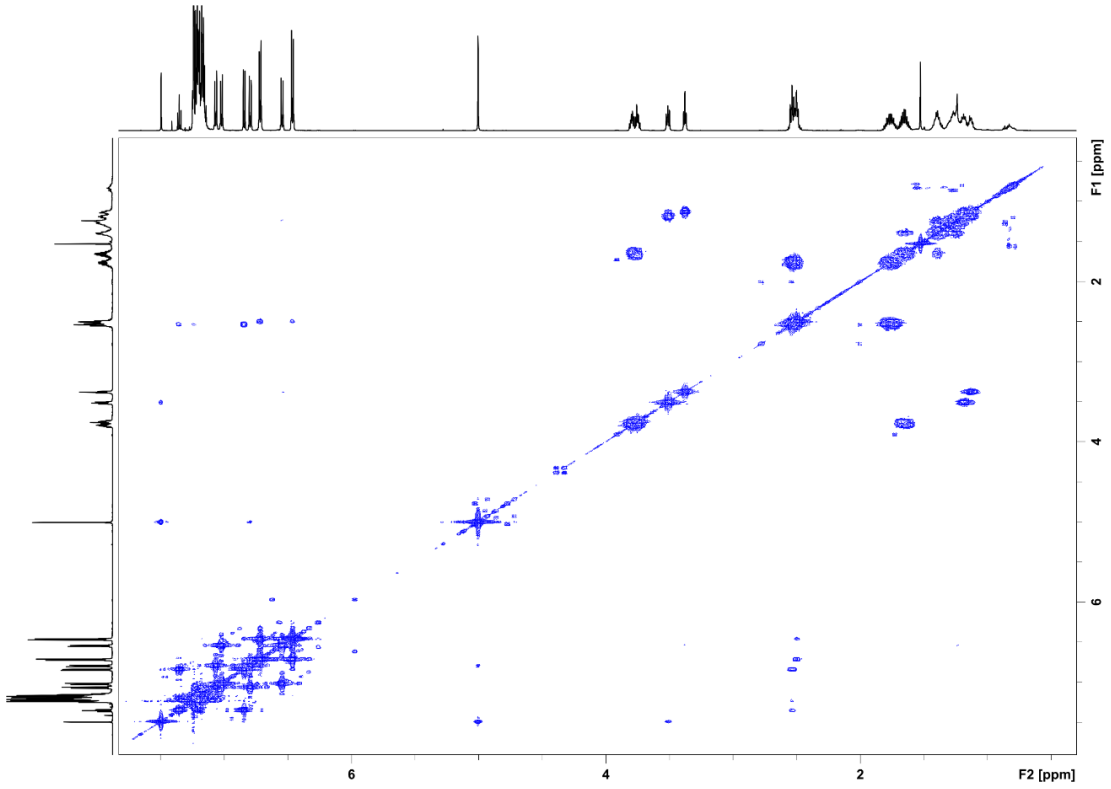



**Figure S 90.** The $^{1}$H-$^{1}$H COSY spectrum of **12–B** (chloroform-*d*, 300 K, 600 MHz).

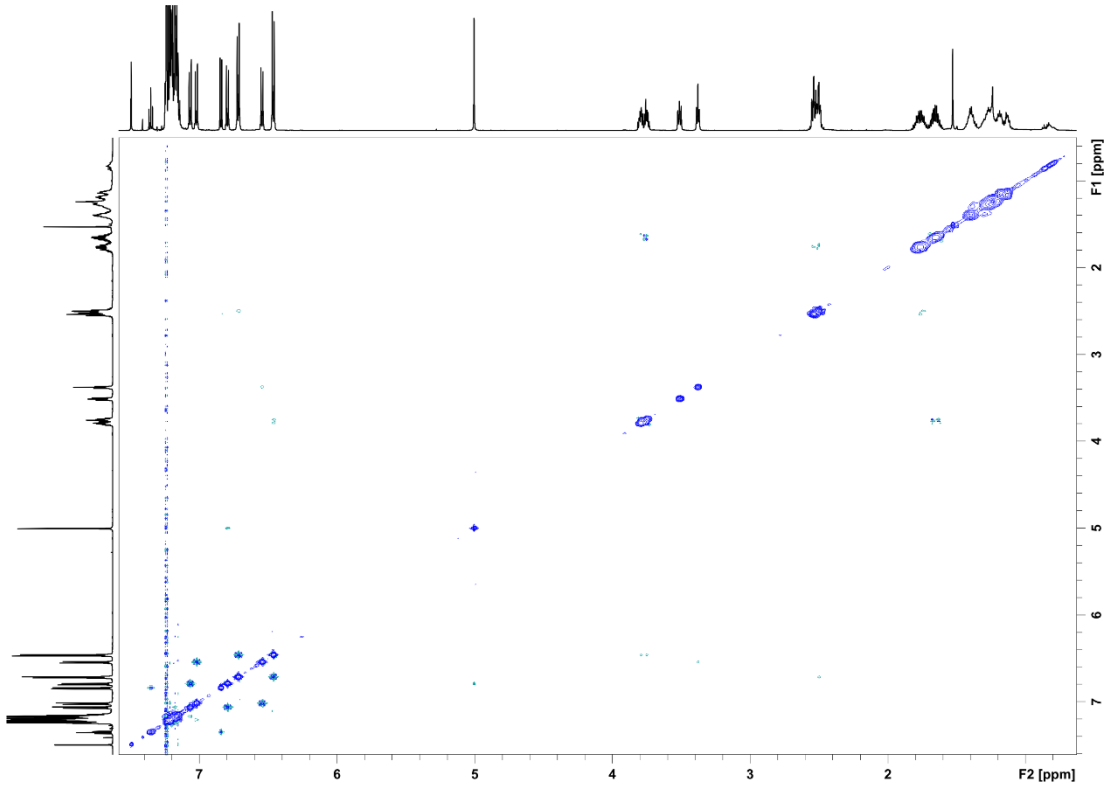



**Figure S 91.** The $^{1}$H-$^{1}$H NOESY spectrum of **12–B** (chloroform-*d*, 300 K, 600 MHz).

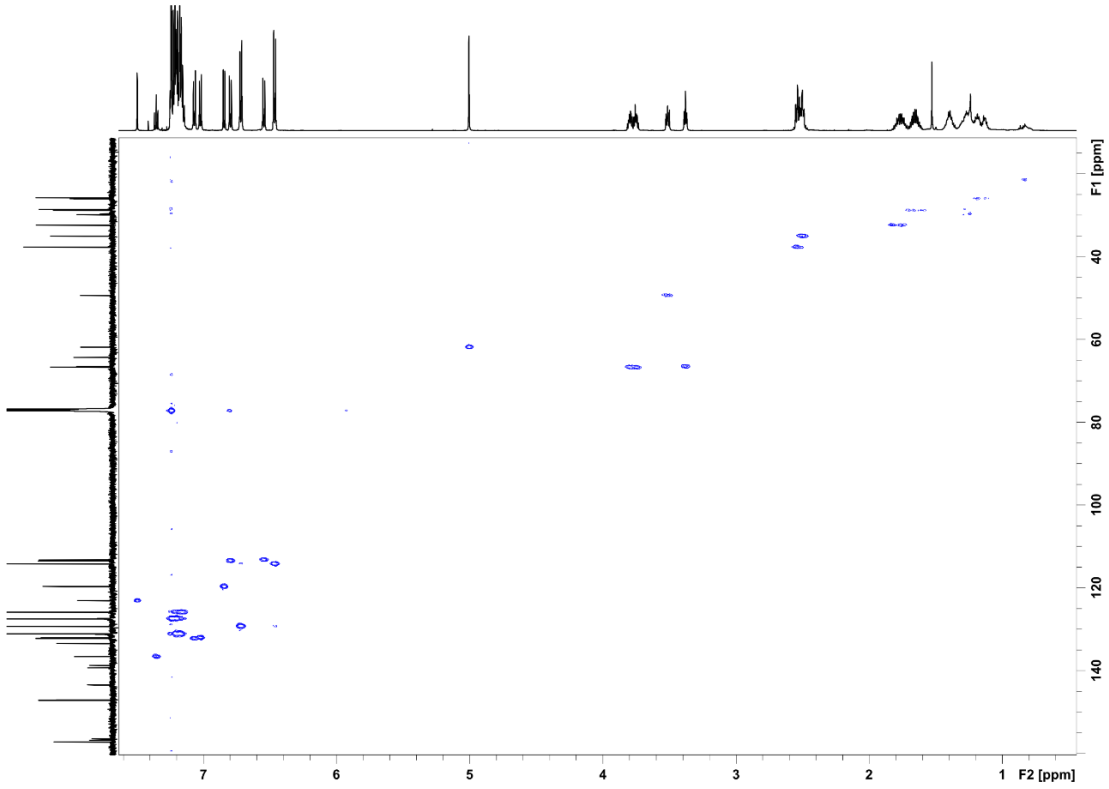



**Figure S 92.** The $^{1}$H-$^{13}$C HMQC spectrum of **12–B** (chloroform-*d*, 300 K, 600 MHz).

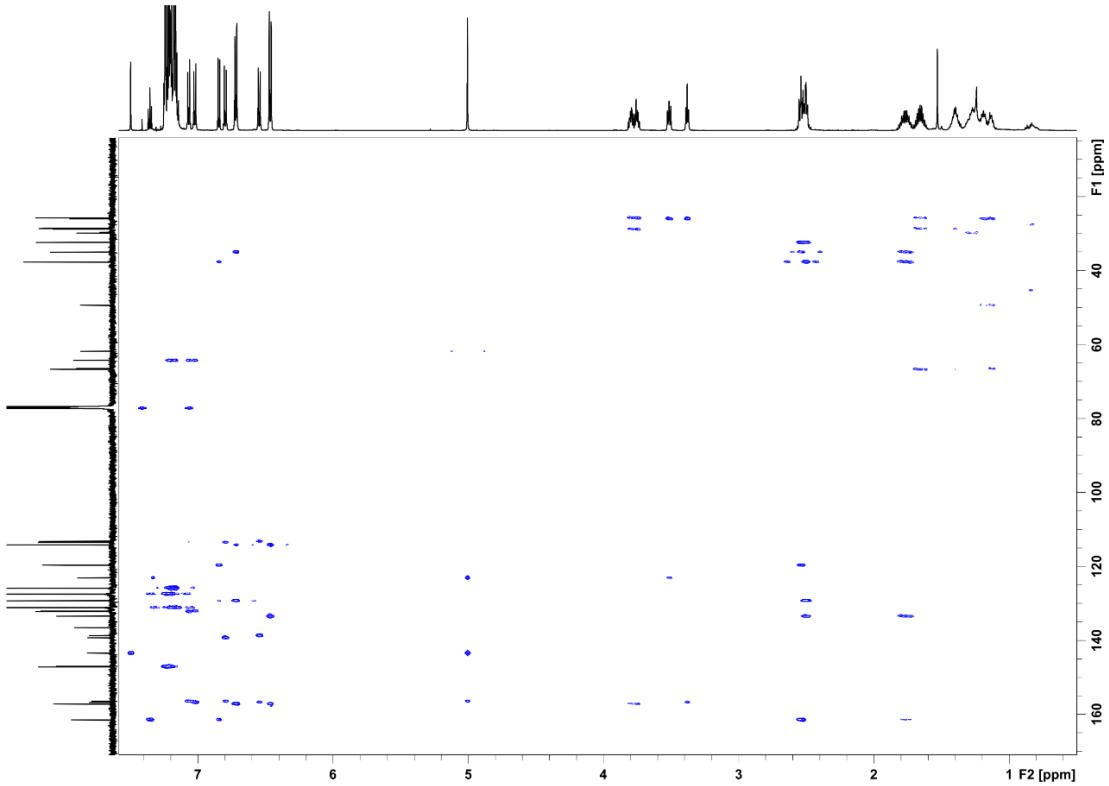



**Figure S 93.** The $^{1}$H-$^{13}$C HMBC spectrum of **12–B** (chloroform-*d*, 300 K, 600 MHz).

## NMR spectra of 9b

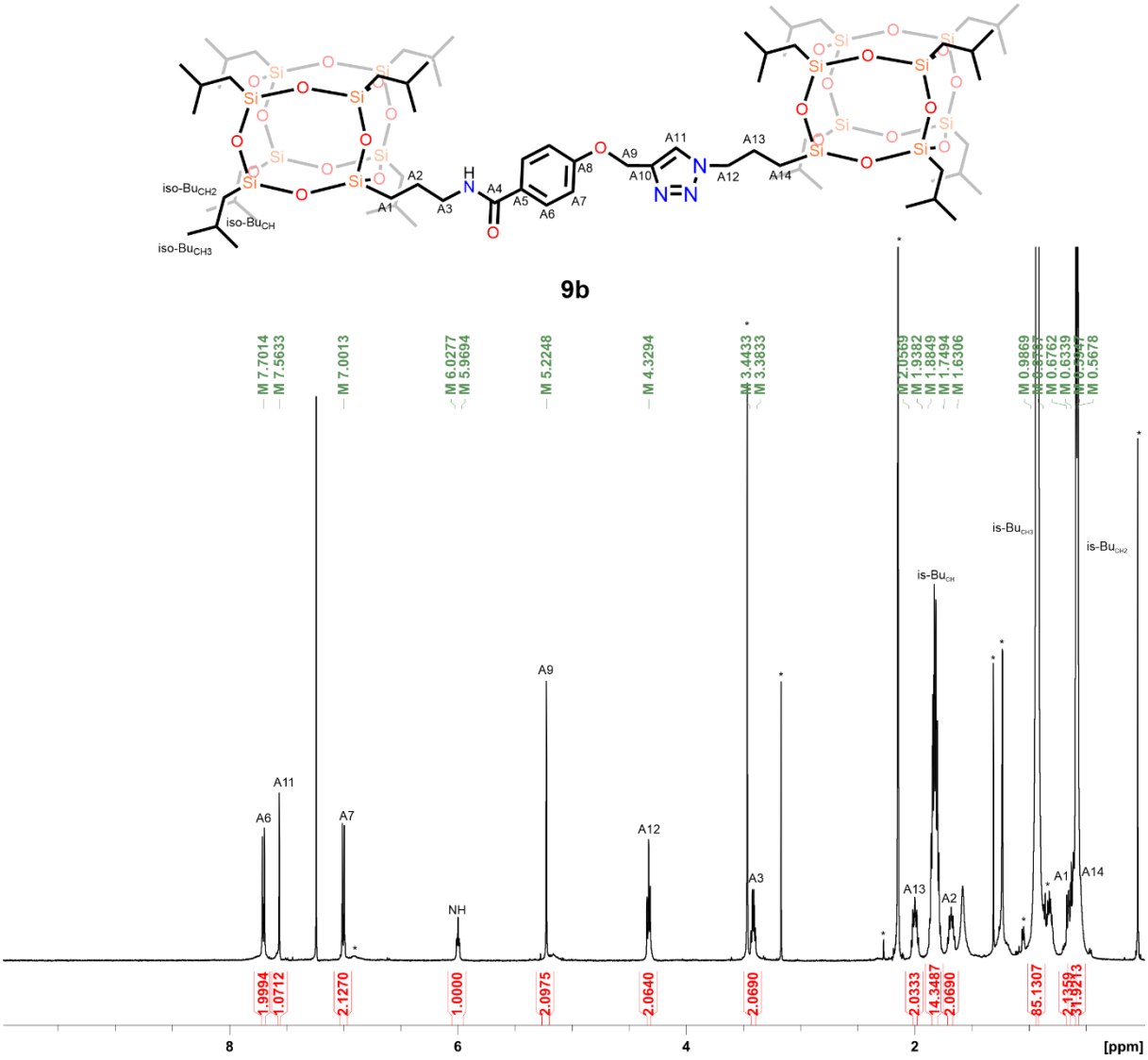



**Figure S 94.** The $^{1}$H NMR spectrum of **9b** (chloroform-*d*, 300 K, 500 MHz).

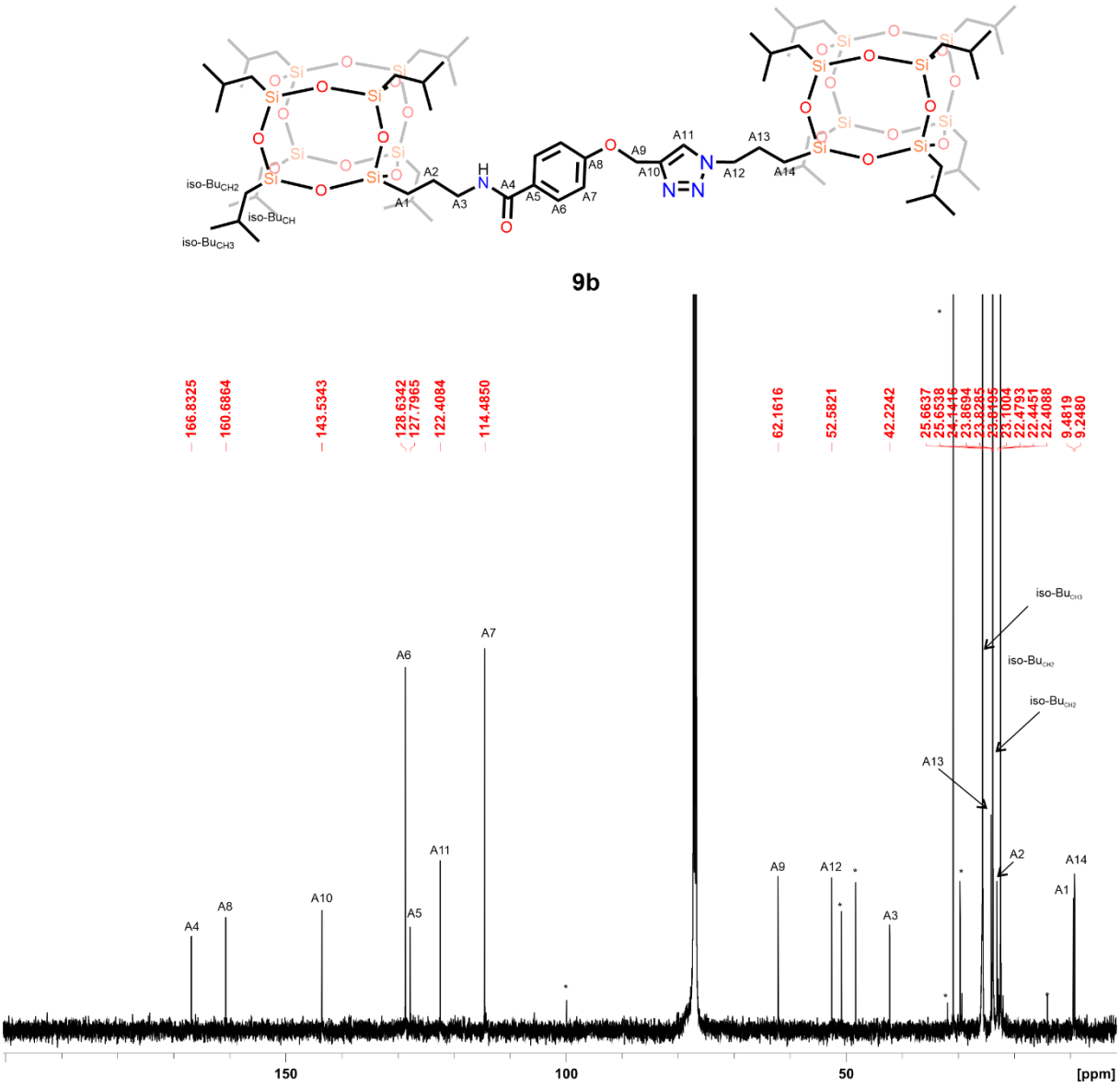



**Figure S 95.** The $^{13}C$ NMR spectrum of **9b** (chloroform-*d*, 300 K, 125 MHz).

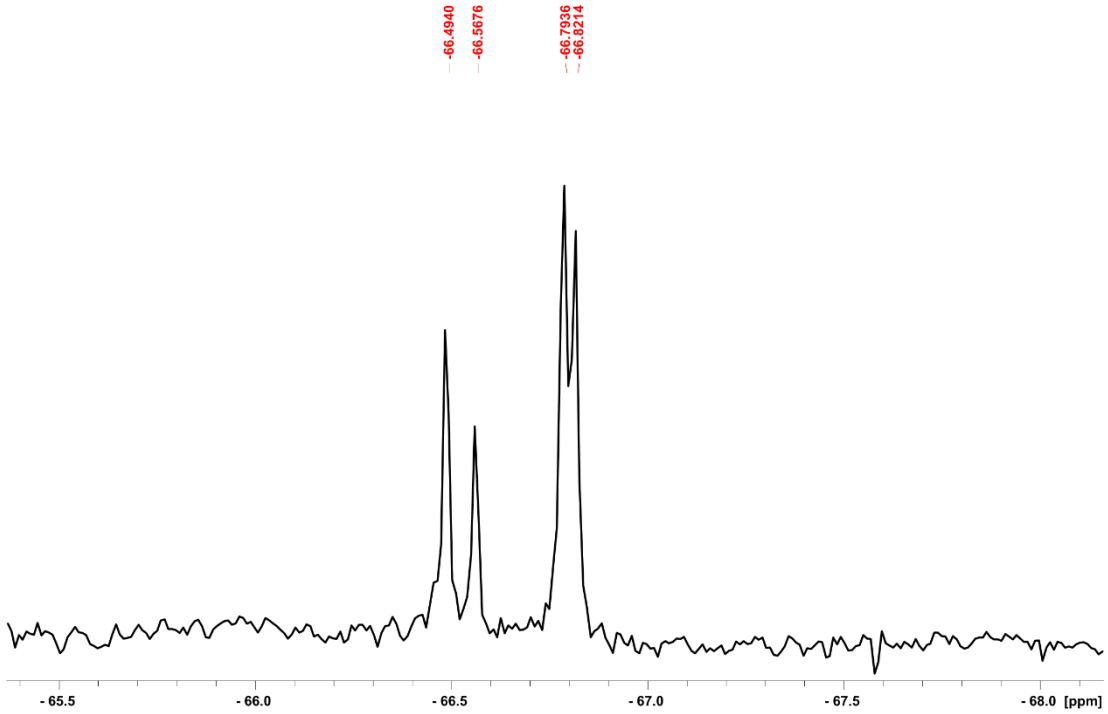



**Figure S 96.** The $^{29}$Si NMR spectrum of **9b** (chloroform-*d*, 300 K, 100 MHz).

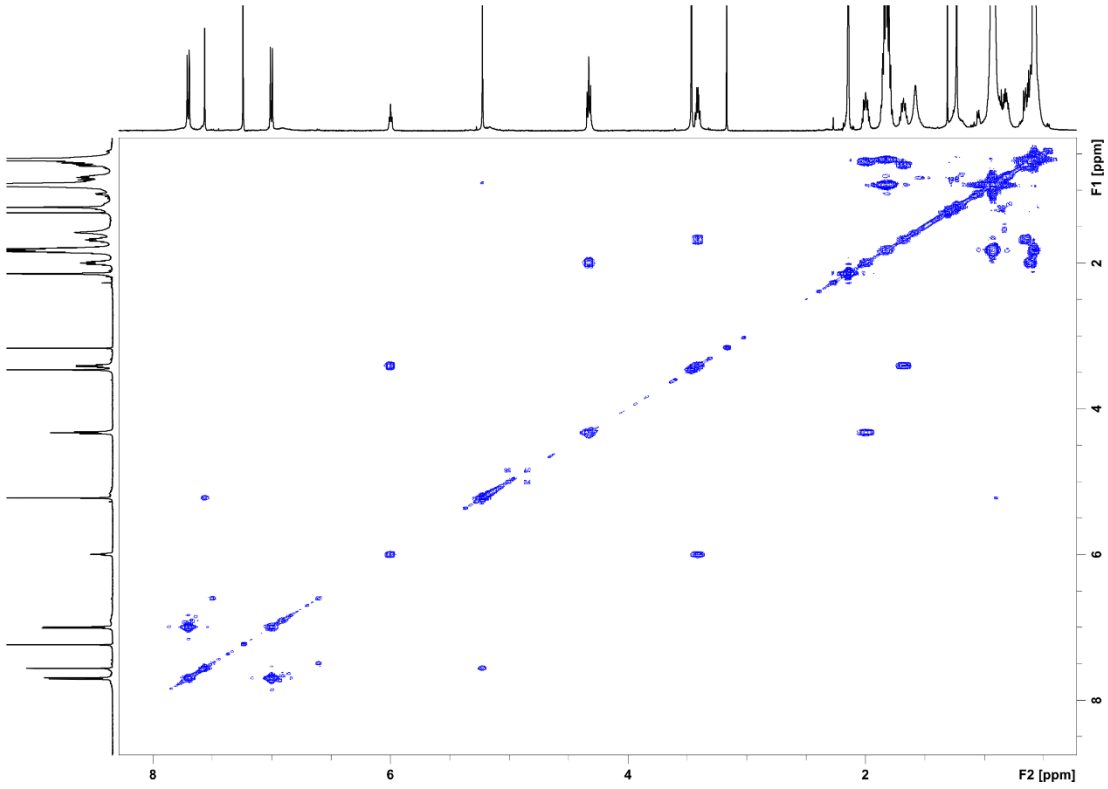



**Figure S 97.** The $^{1}$H-$^{1}$H COSY spectrum of **9b** (chloroform-*d*, 300 K, 500 MHz).

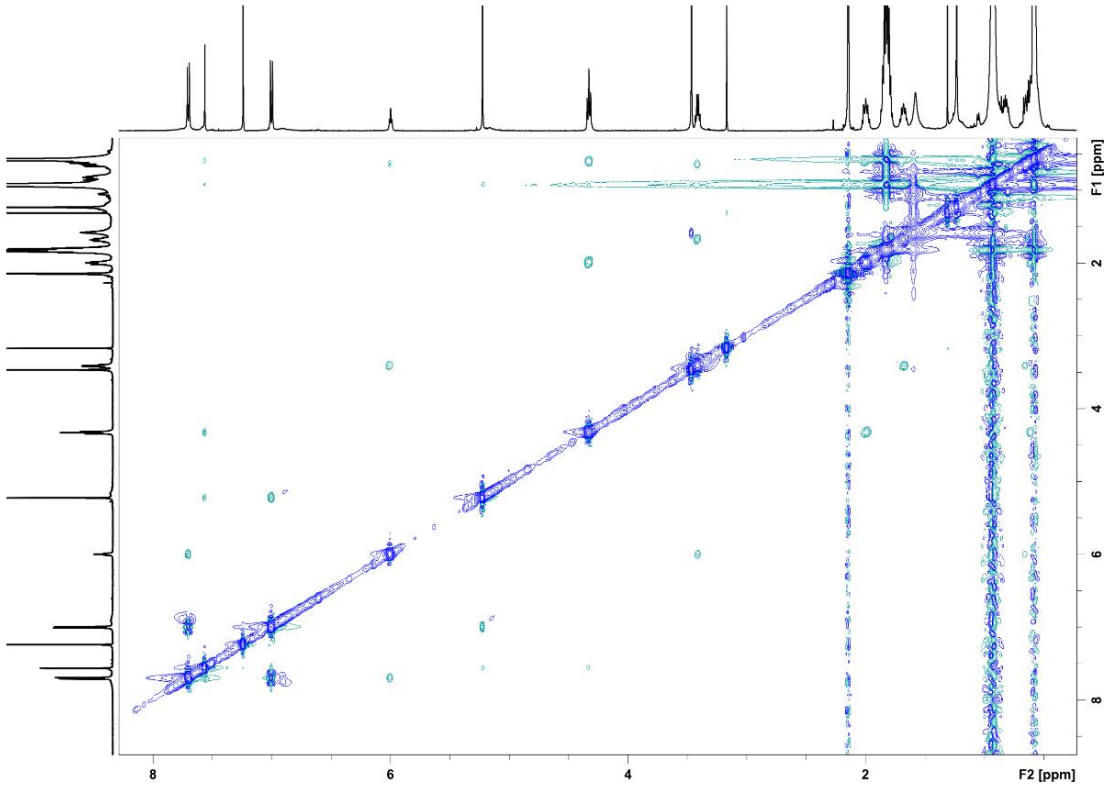



**Figure S 98.** The $^{1}$H-$^{1}$H NOESY spectrum of **9b** (chloroform-*d*, 300 K, 500 MHz).

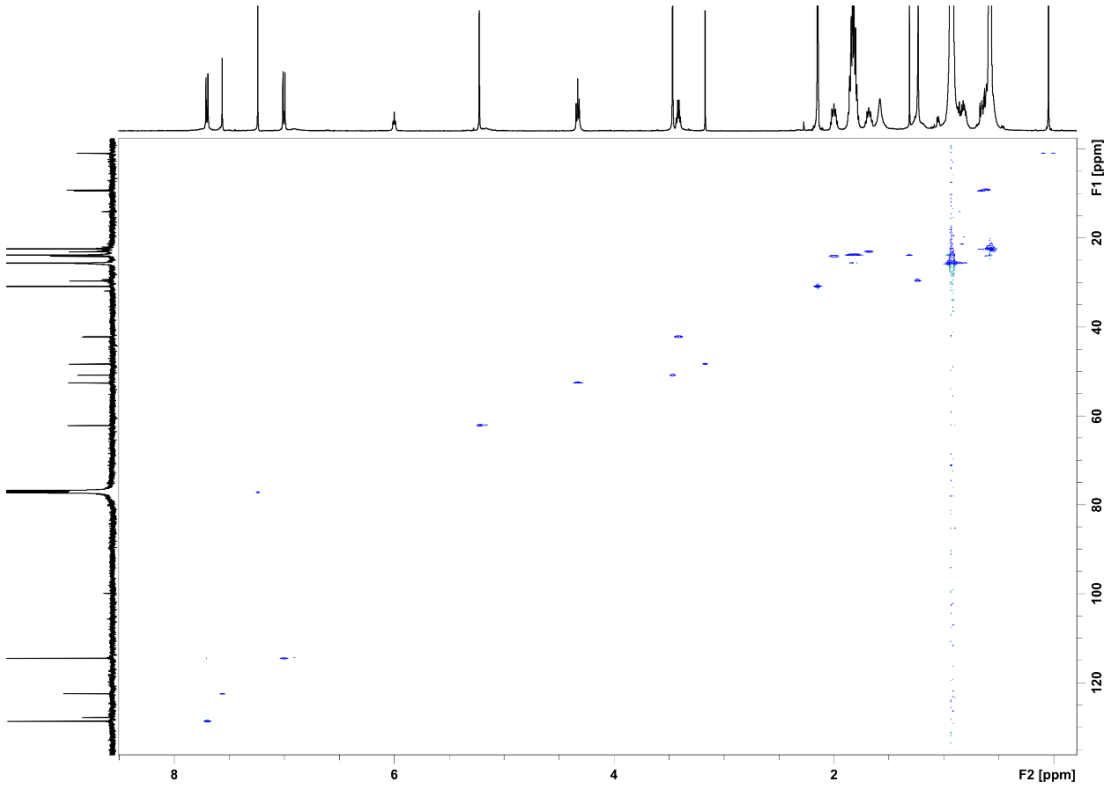



**Figure S 99**. The $^{1}$H-$^{13}$C HSQC spectrum of **9b** (chloroform-*d*, 300 K, 500 MHz).

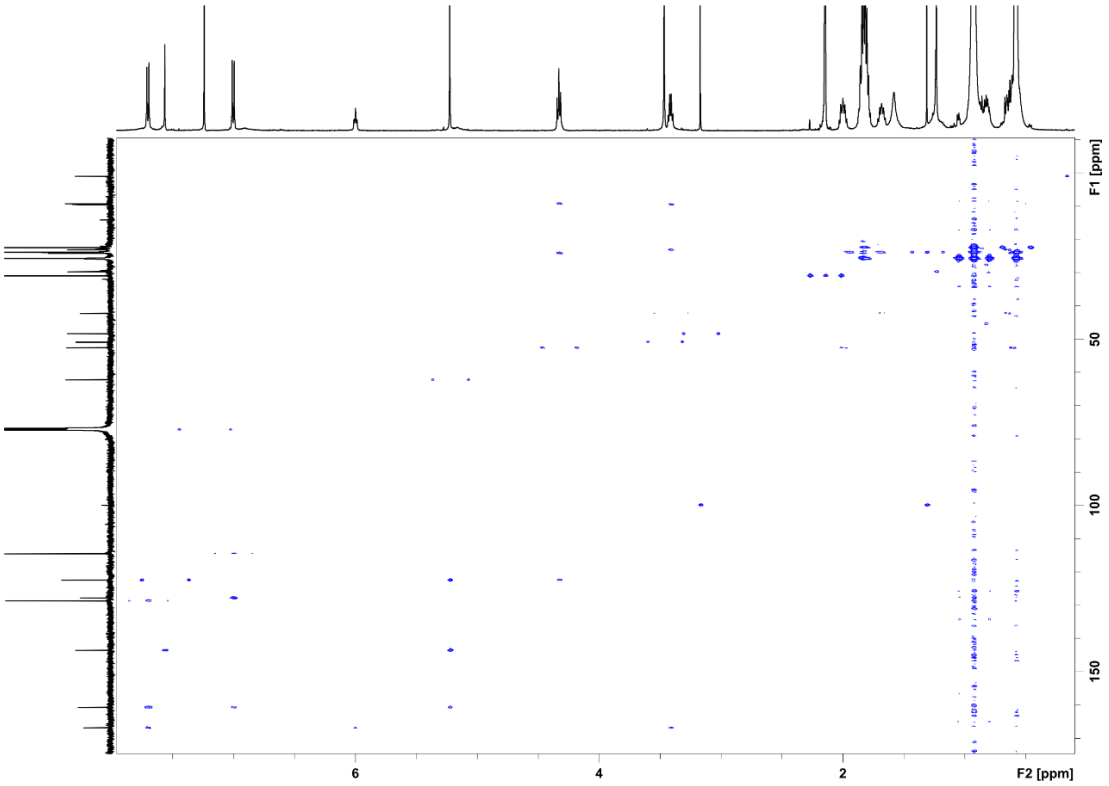



**Figure S 100.** The $^{1}H$-$^{13}C$ HMBC spectrum of **9b** (chloroform-*d*, 300 K, 500 MHz).

## NMR spectra of 10a

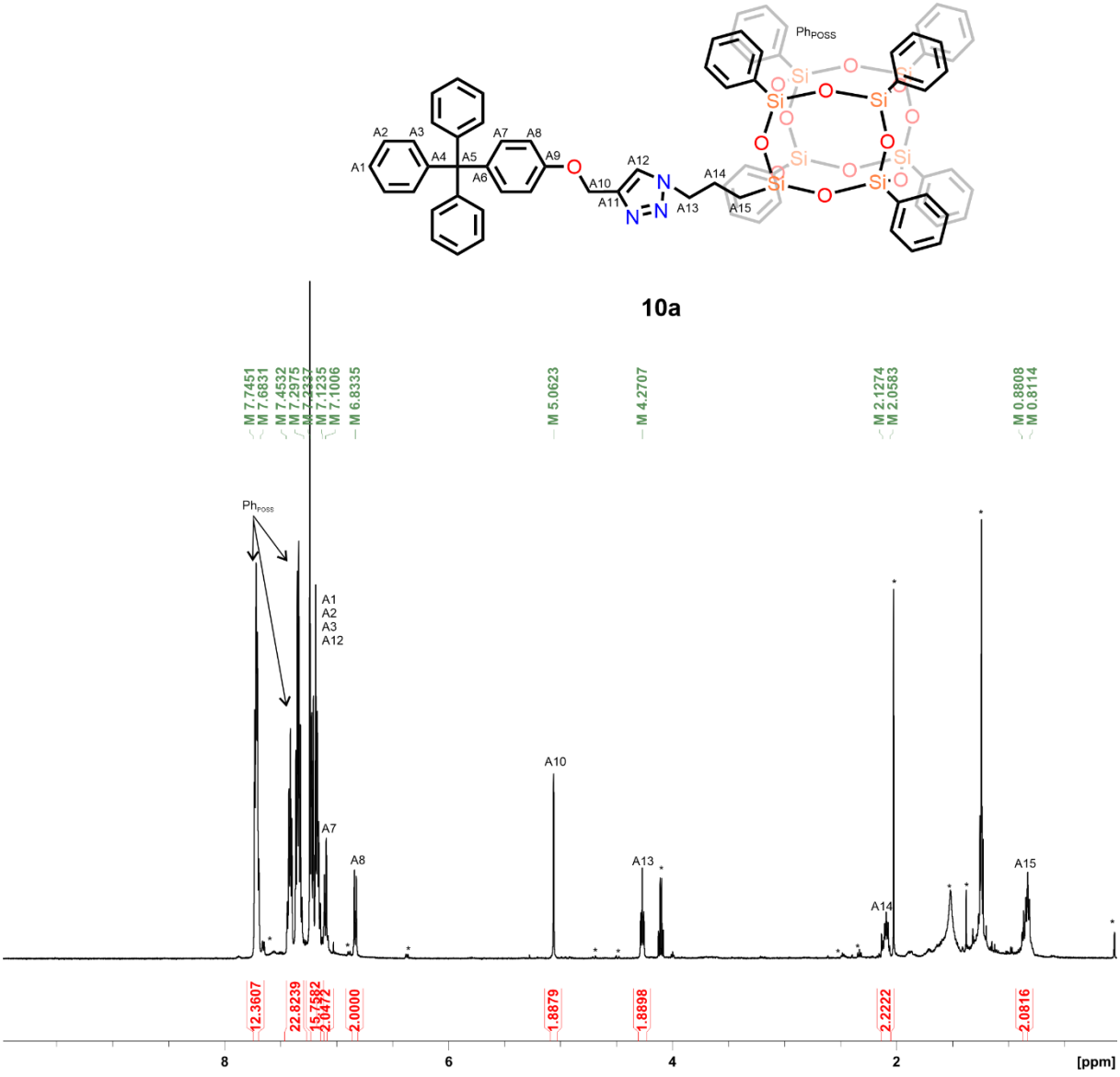



**Figure S 101.** The $^{1}$H NMR spectrum of **10a** (chloroform-*d*, 300 K, 500 MHz).

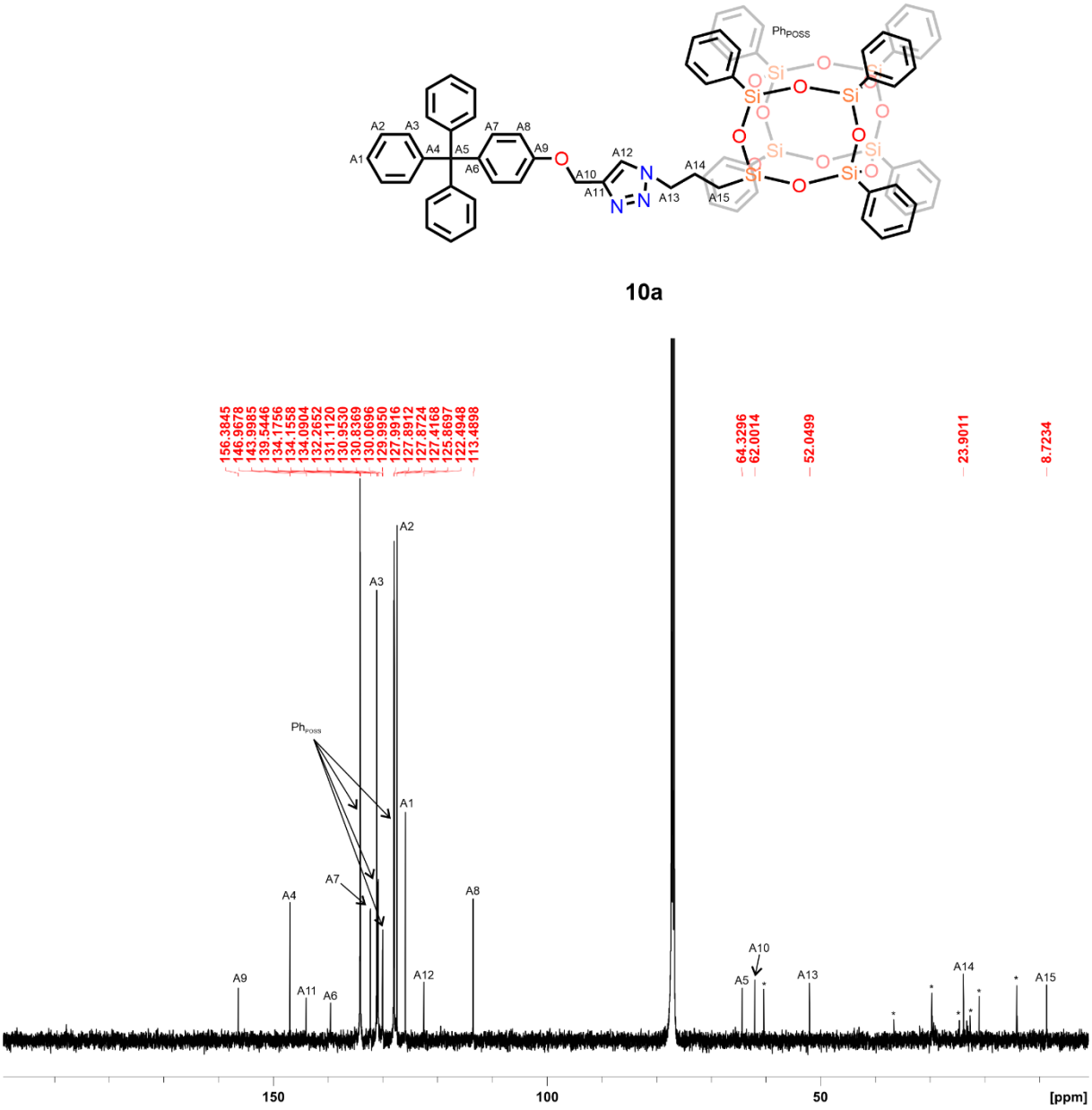



**Figure S 102.** The $^{13}$C NMR spectrum of **10a** (chloroform-*d*, 300 K, 125 MHz).

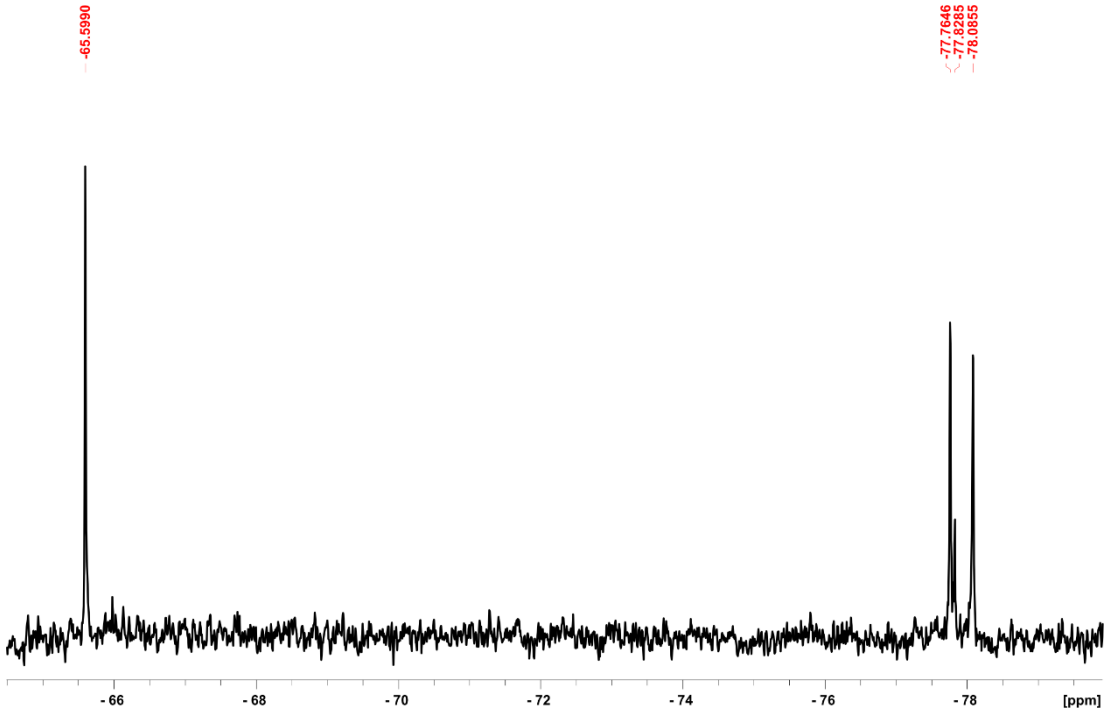



**Figure S 103.** The $^{29}$Si NMR spectrum of **10a** (chloroform-*d*, 300 K, 100 MHz).

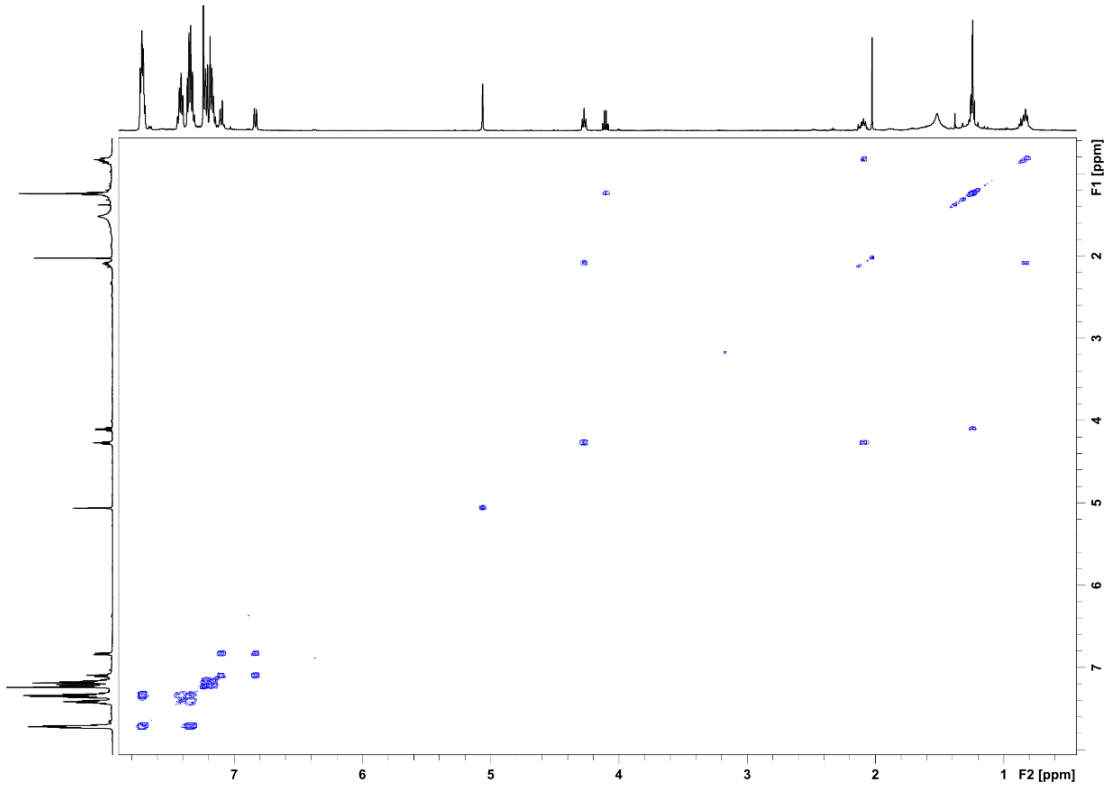



**Figure S 104.** The $^{1}$H-$^{1}$H COSY spectrum of **10a** (chloroform-*d*, 300 K, 500 MHz).

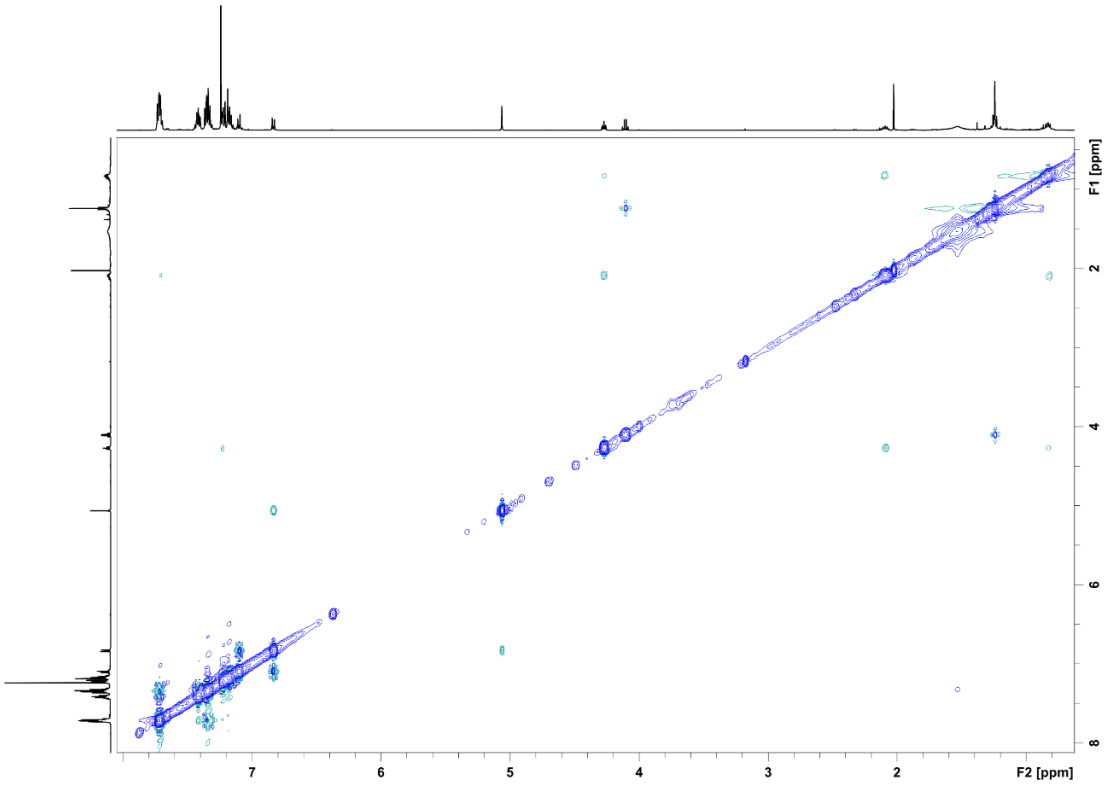



**Figure S 105.** The $^{1}$H-$^{1}$H NOESY spectrum of **10a** (chloroform-*d*, 300 K, 500 MHz).

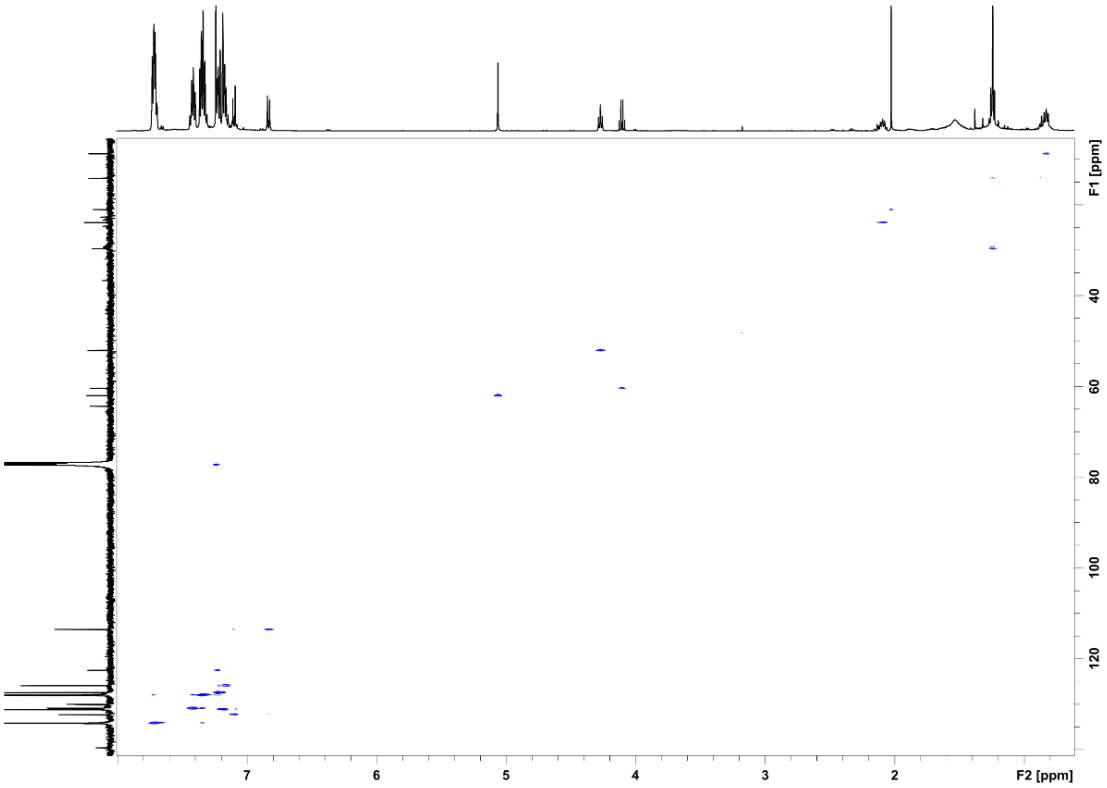



**Figure S 106.** The $^{1}$H-$^{13}$C HSQC spectrum of **10a** (chloroform-*d*, 300 K, 500 MHz).

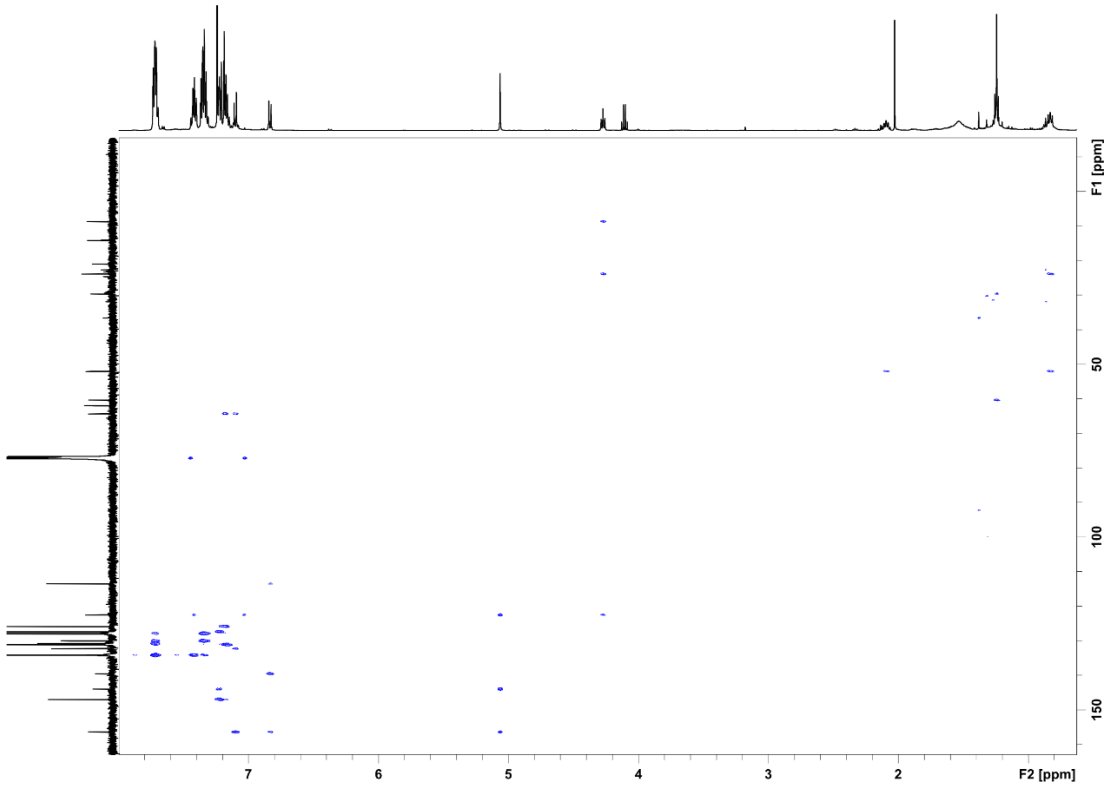



**Figure S 107.** The $^{1}H$-$^{13}C$ HMBC spectrum of **10a** (chloroform-*d*, 300 K, 500 MHz).

## NMR spectra of 10b

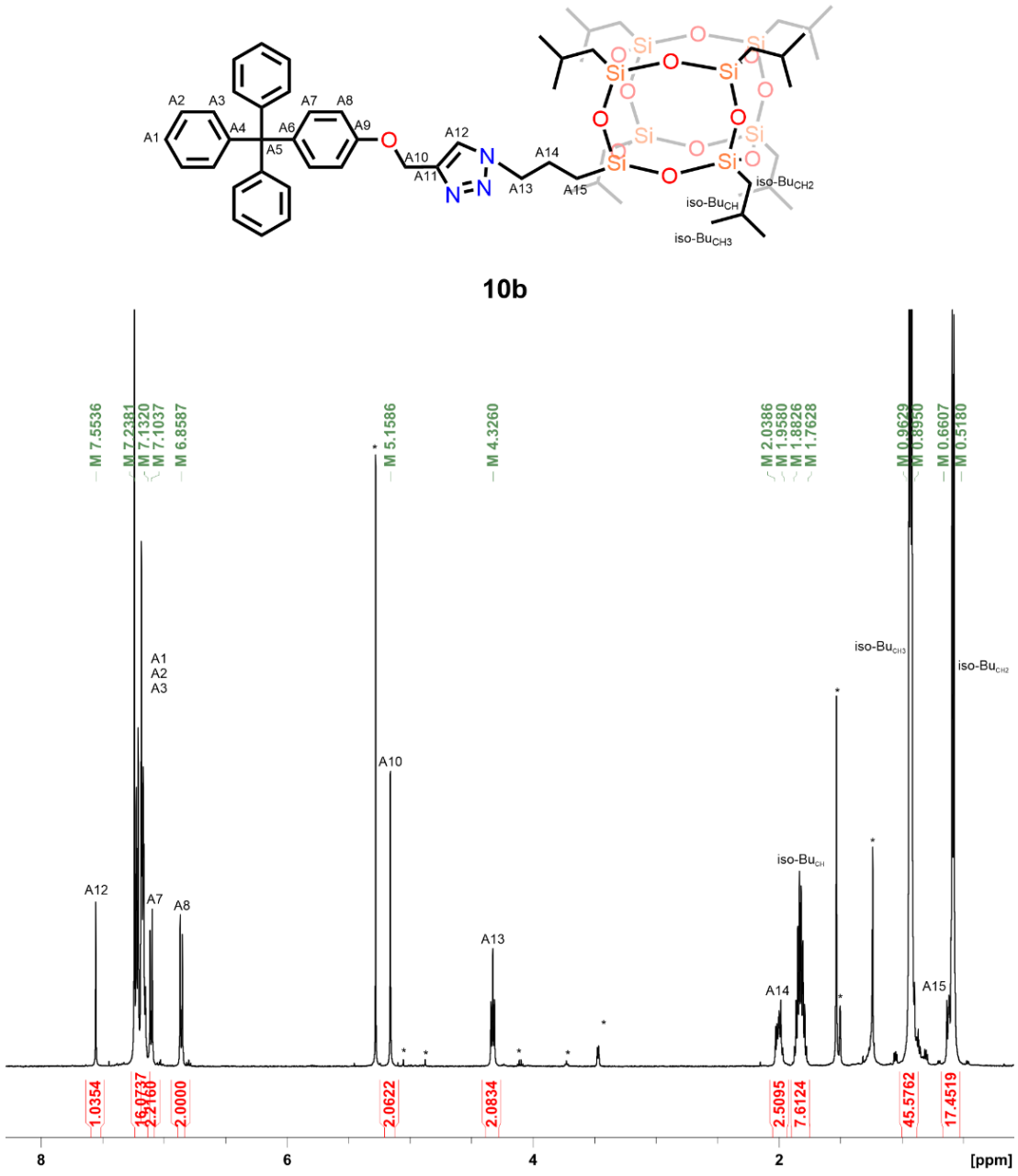



**Figure S 108.** The $^{1}$H NMR spectrum of **10b** (chloroform-*d*, 300 K, 500 MHz).

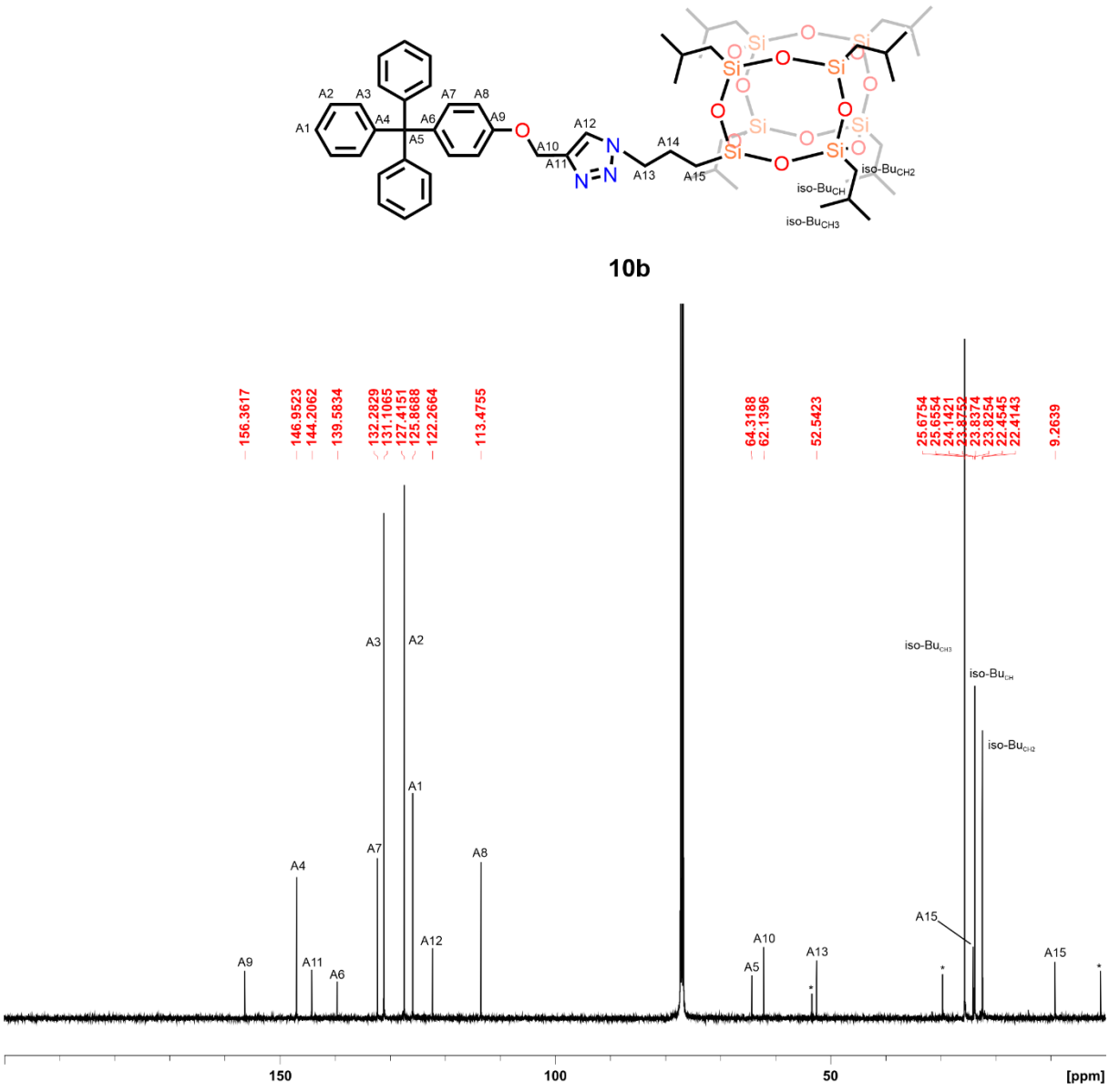



**Figure S 109.** The $^{13}$C NMR spectrum of **10b** (chloroform-*d*, 300 K, 125 MHz).

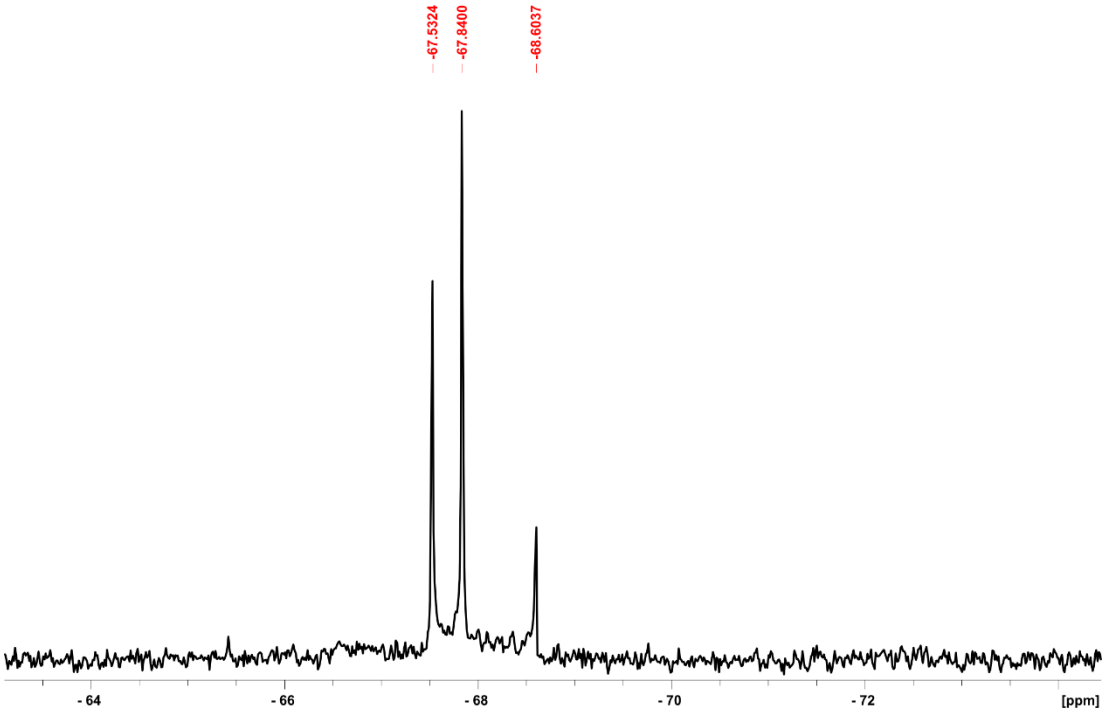



**Figure S 110.** The $^{29}$Si NMR spectrum of **10b** (chloroform-*d*, 300 K, 100 MHz).

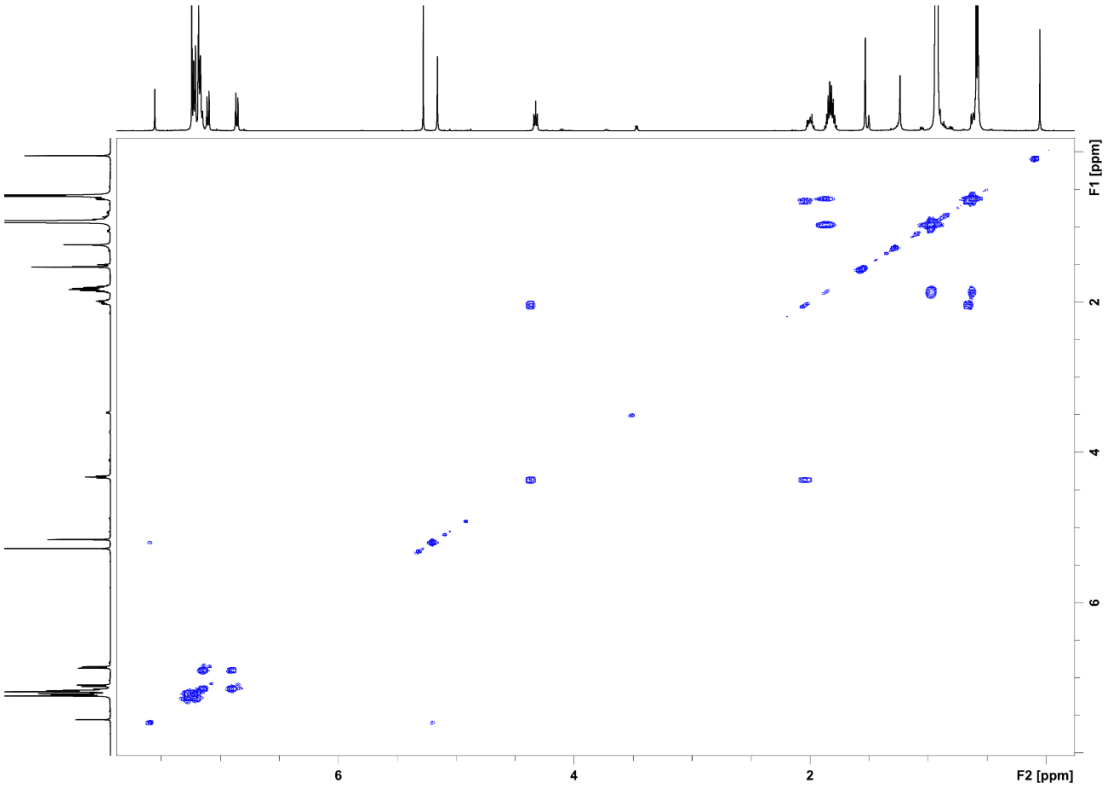



**Figure S 111.** The $^{1}$H-$^{1}$H COSY spectrum of **10b** (chloroform-*d*, 300 K, 500 MHz).

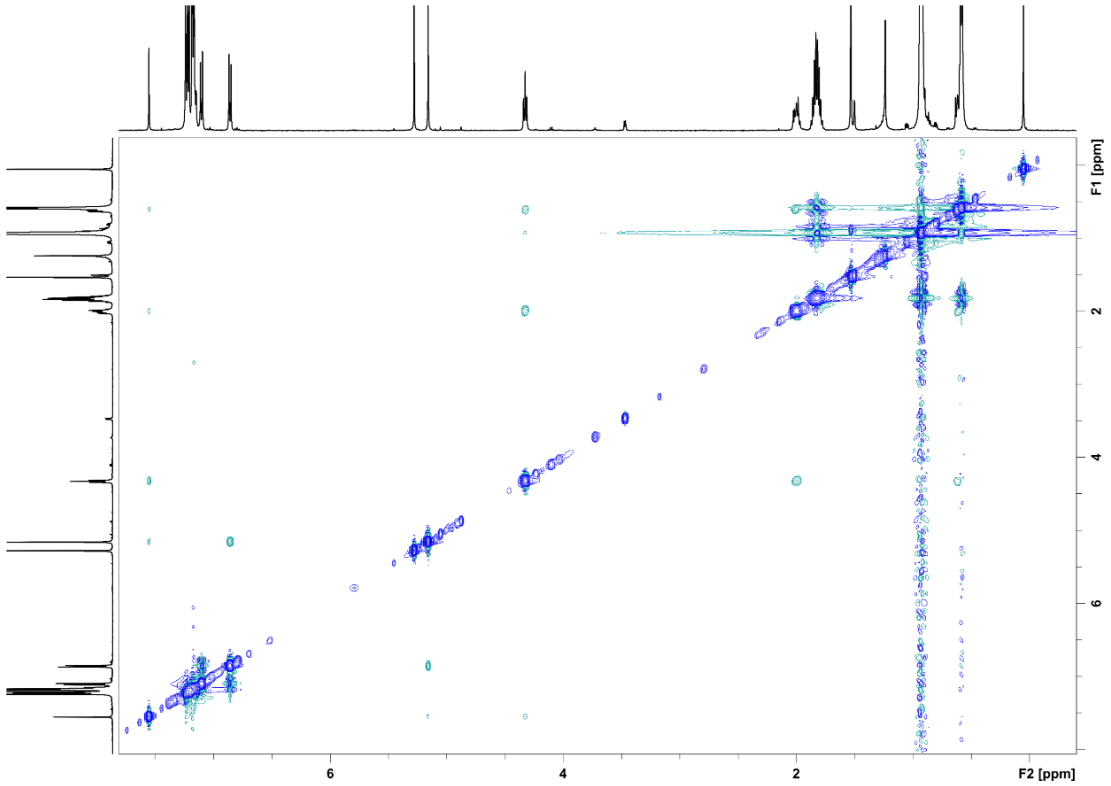



**Figure S 112.** The $^{1}$H-$^{1}$H NOESY spectrum of **10b** (chloroform-*d*, 300 K, 500 MHz).

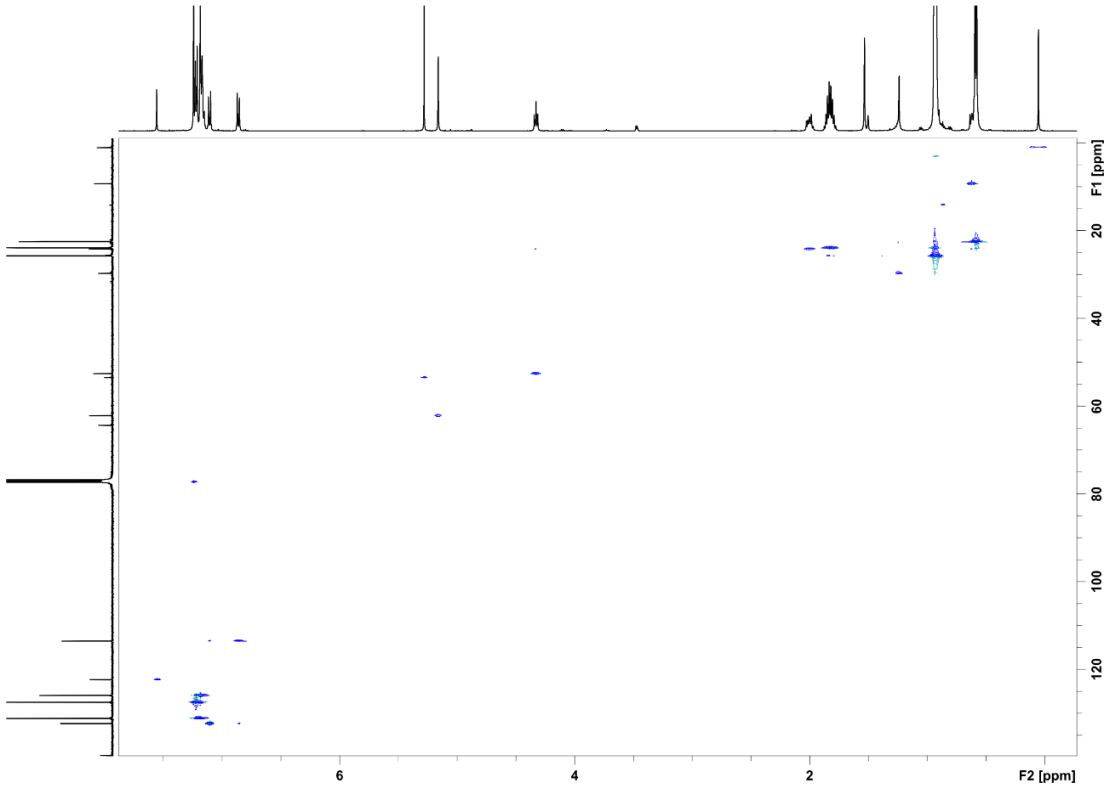



**Figure S 113.** The $^{1}$H-$^{13}$C HSQC spectrum of **10b** (chloroform-*d*, 300 K, 500 MHz).

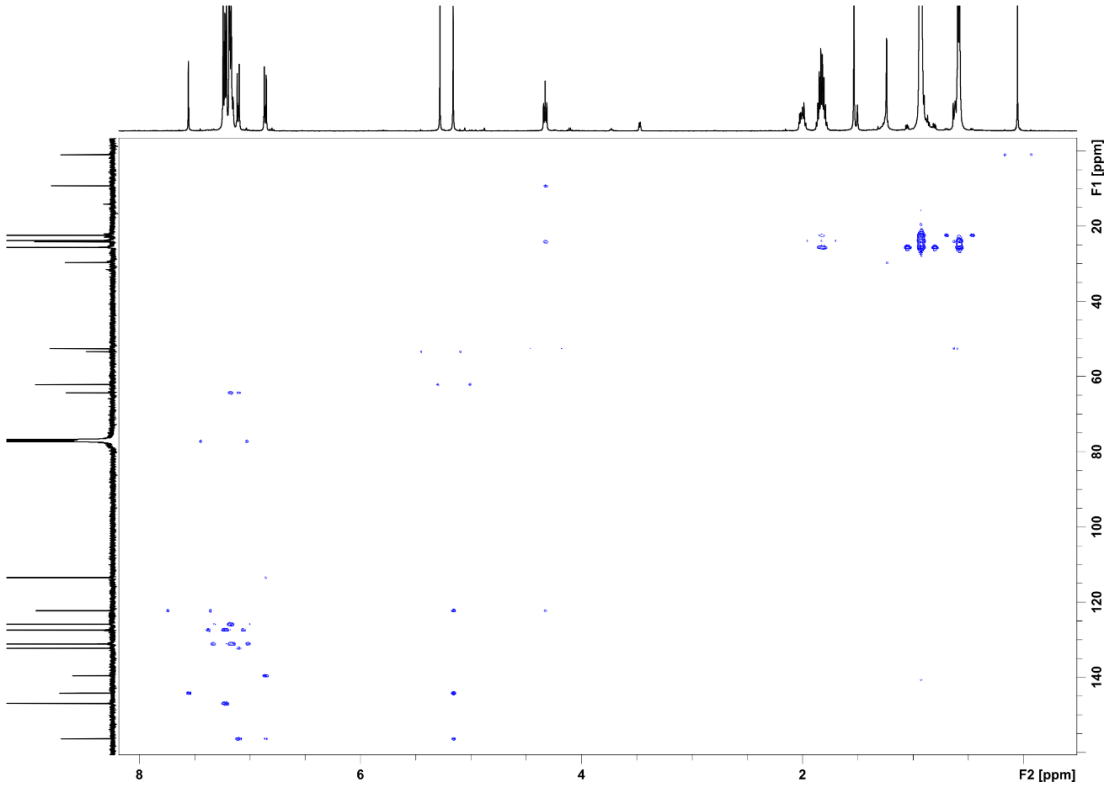



**Figure S 114.** The $^{1}H$-$^{13}C$ HMBC spectrum of **10b** (chloroform-*d*, 300 K, 500 MHz).

## NMR spectra of 11b

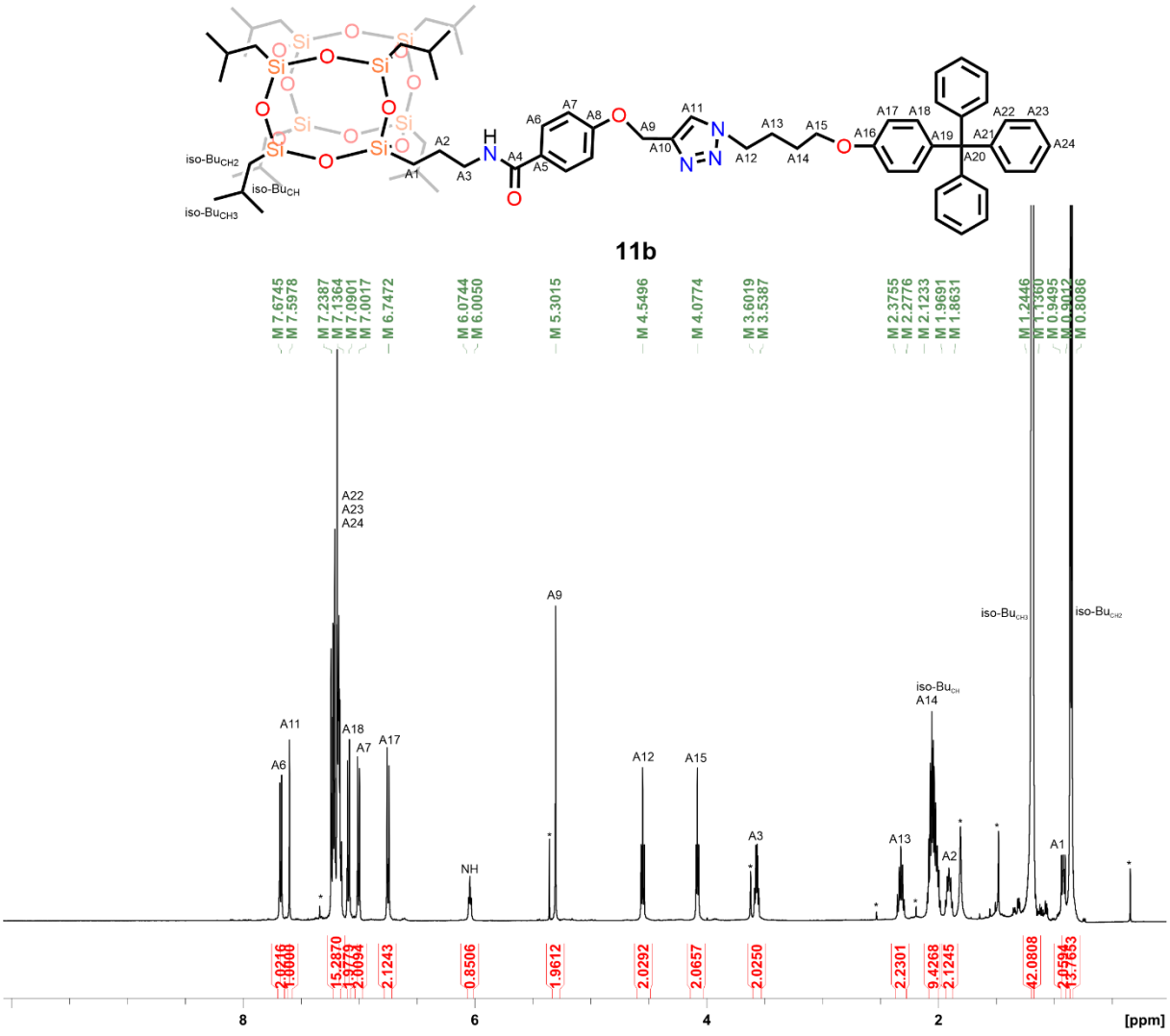



**Figure S 115.** The $^{1}$H NMR spectrum of **11b** (chloroform-*d*, 300 K, 500 MHz).

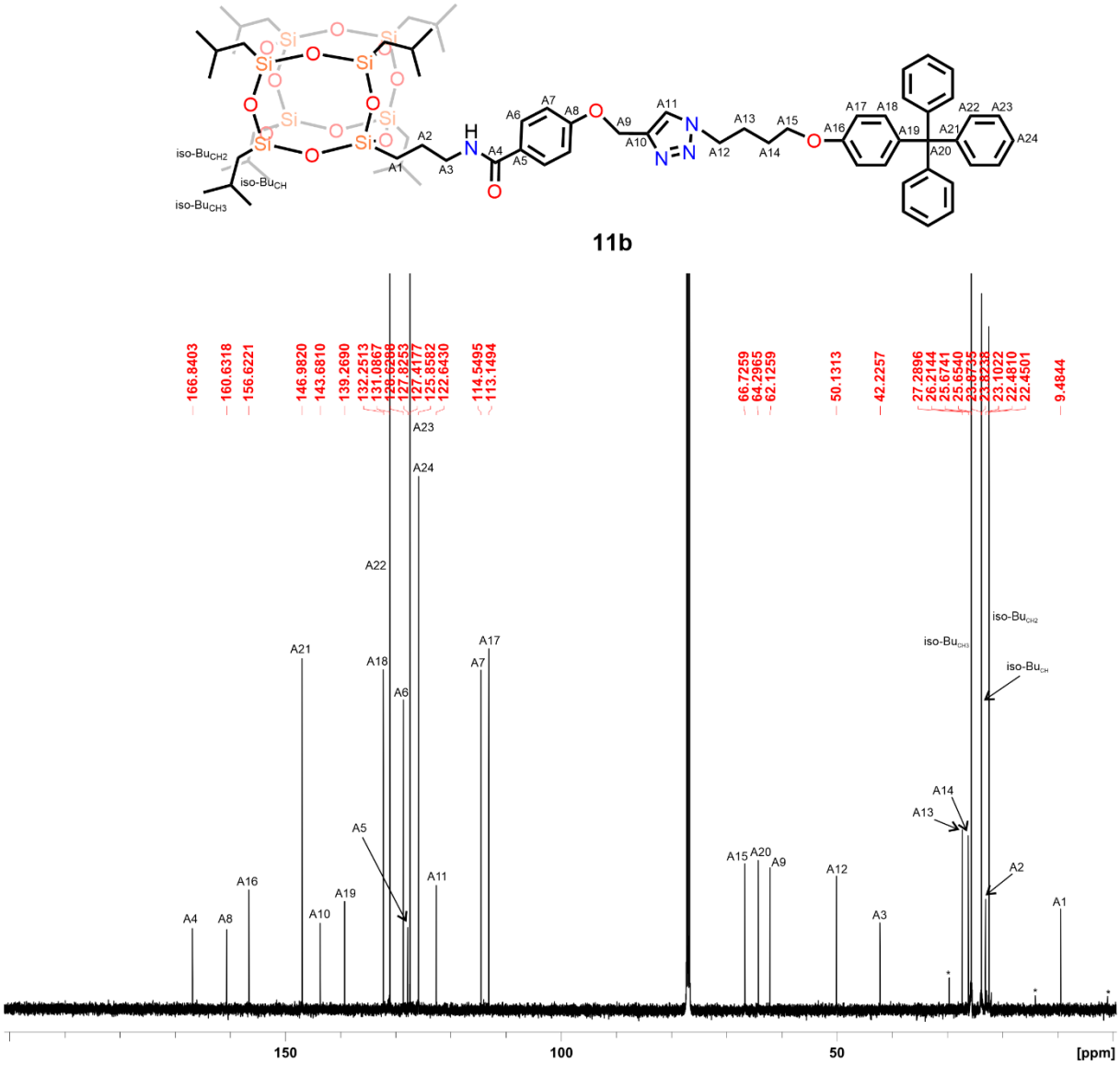



**Figure S 116.** The $^{13}$C NMR spectrum of **11b** (chloroform-*d*, 300 K, 125 MHz).

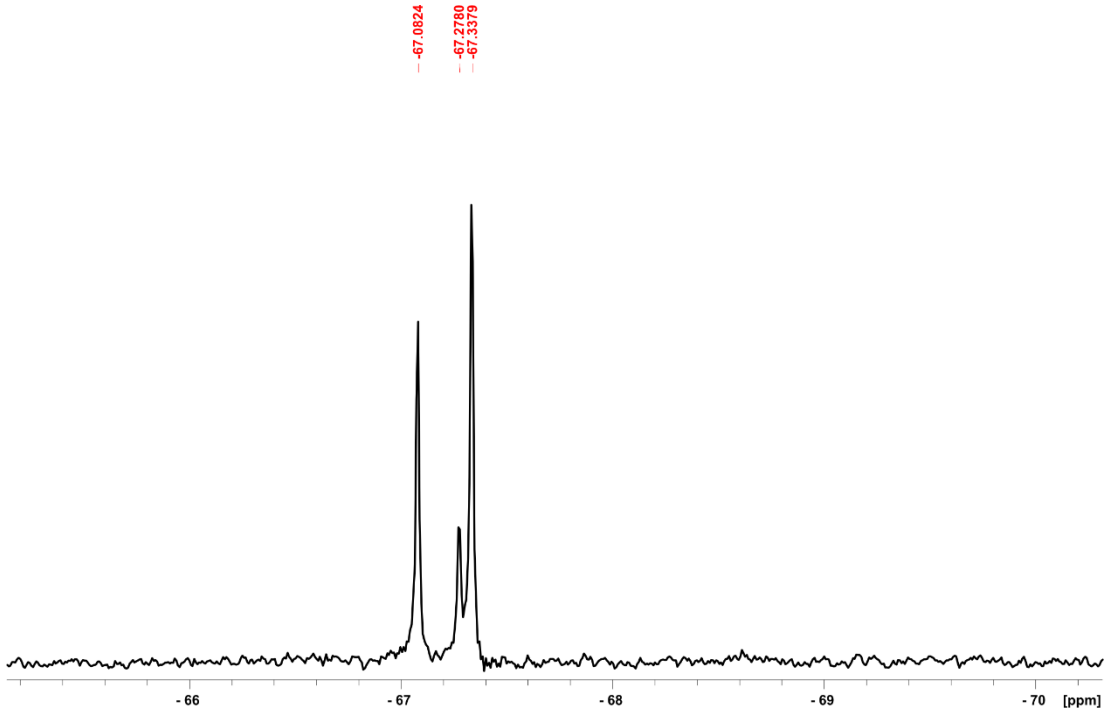



**Figure S 117.** The $^{29}$Si NMR spectrum of **11b** (chloroform-*d*, 300 K, 100 MHz).

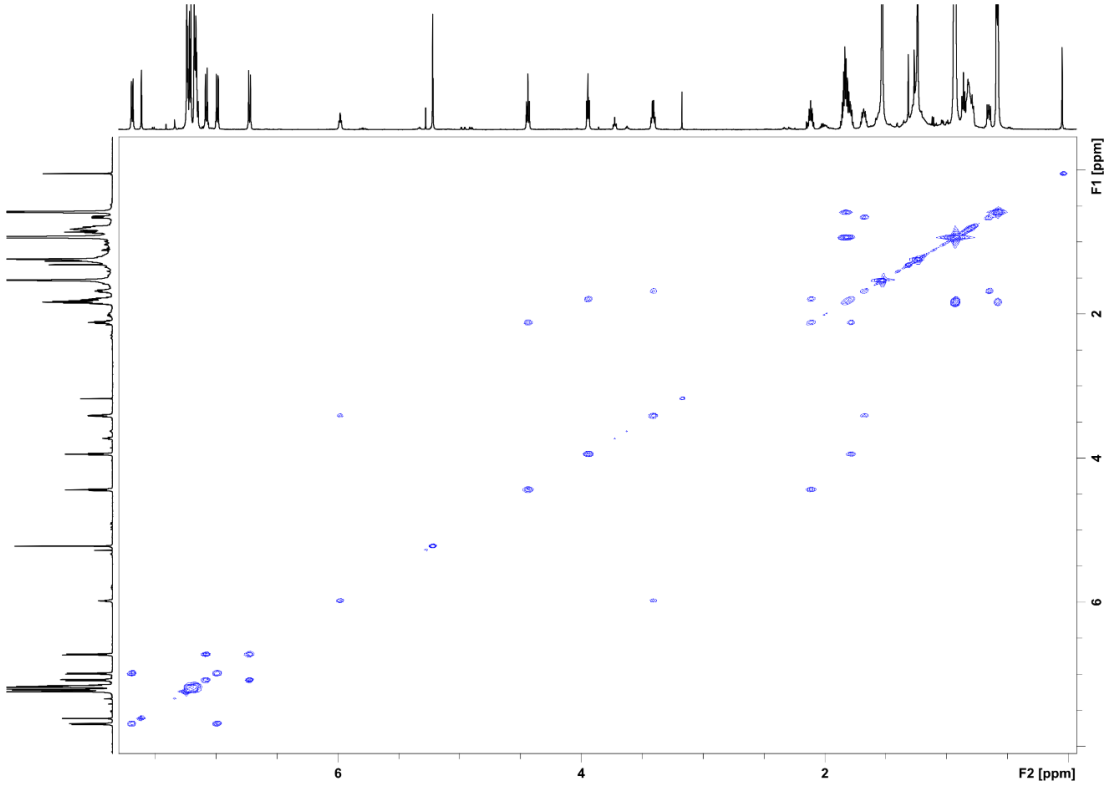



**Figure S 118.** The $^{1}$H-$^{1}$H COSY spectrum of **11b** (chloroform-*d*, 300 K, 600 MHz).

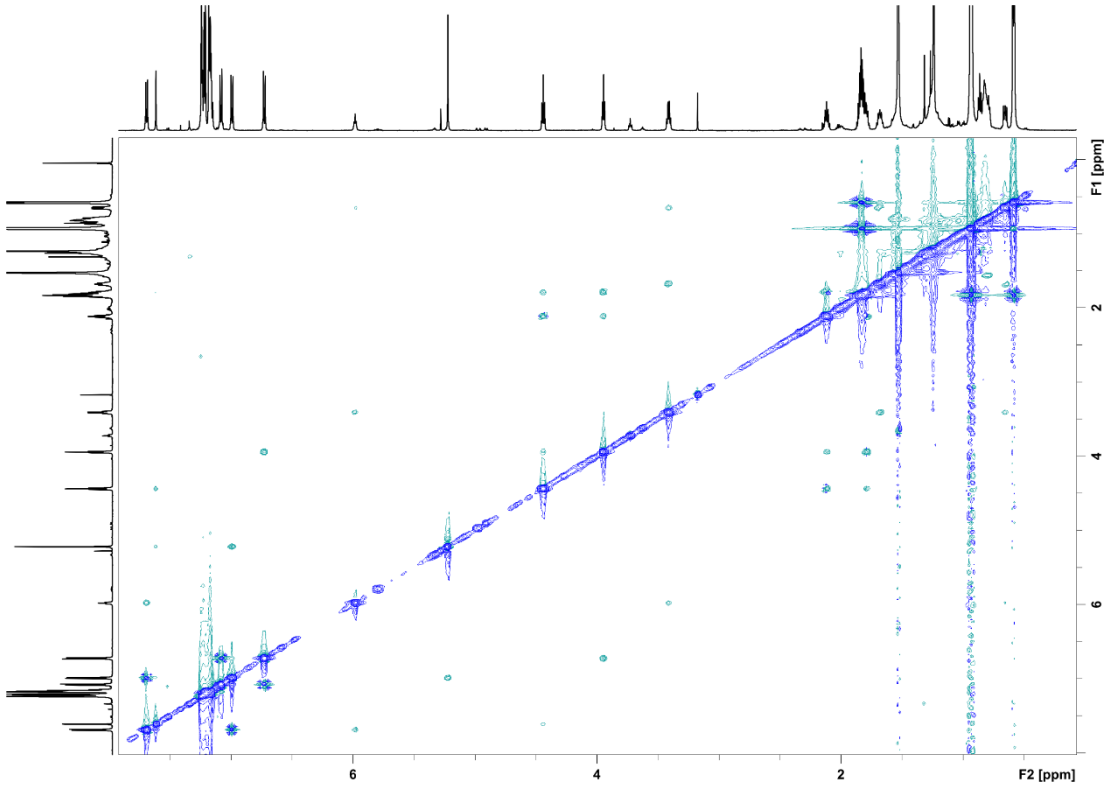



**Figure S 119.** The $^{1}$H-$^{1}$H NOESY spectrum of **11b** (chloroform-*d*, 300 K, 600 MHz).

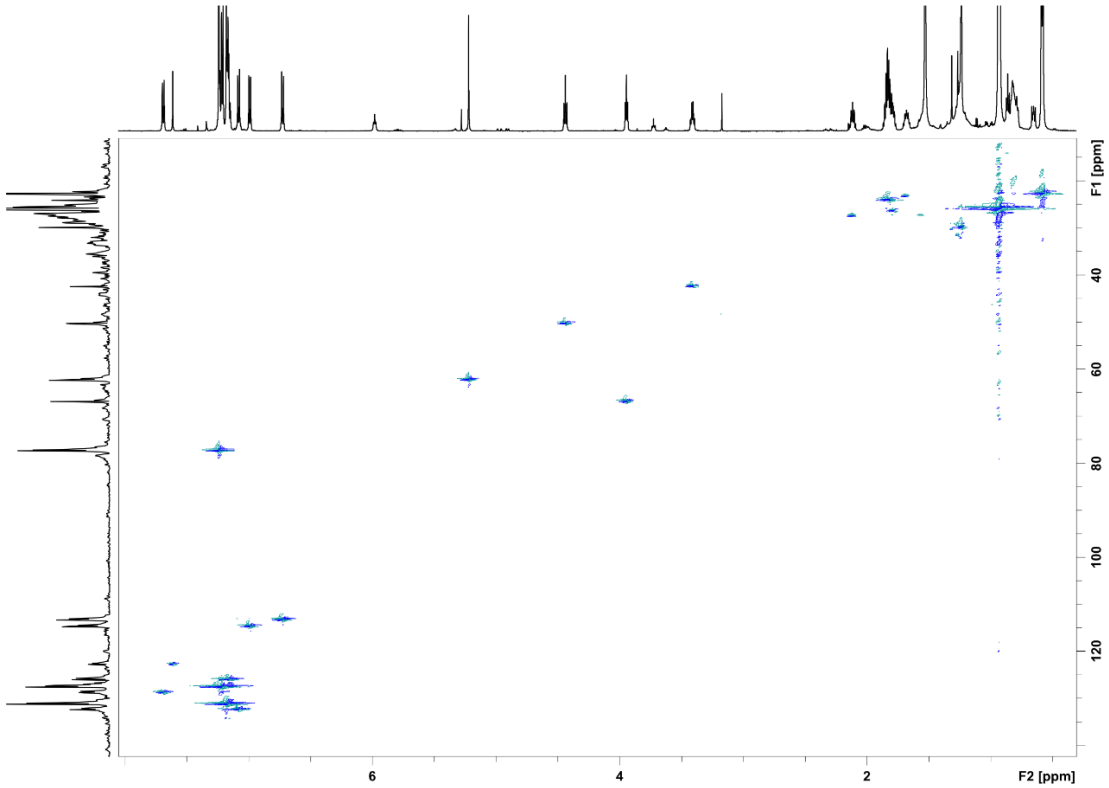



**Figure S 120.** The $^{1}$H-$^{13}$C HSQC spectrum of **11b** (chloroform-*d*, 300 K, 600 MHz).

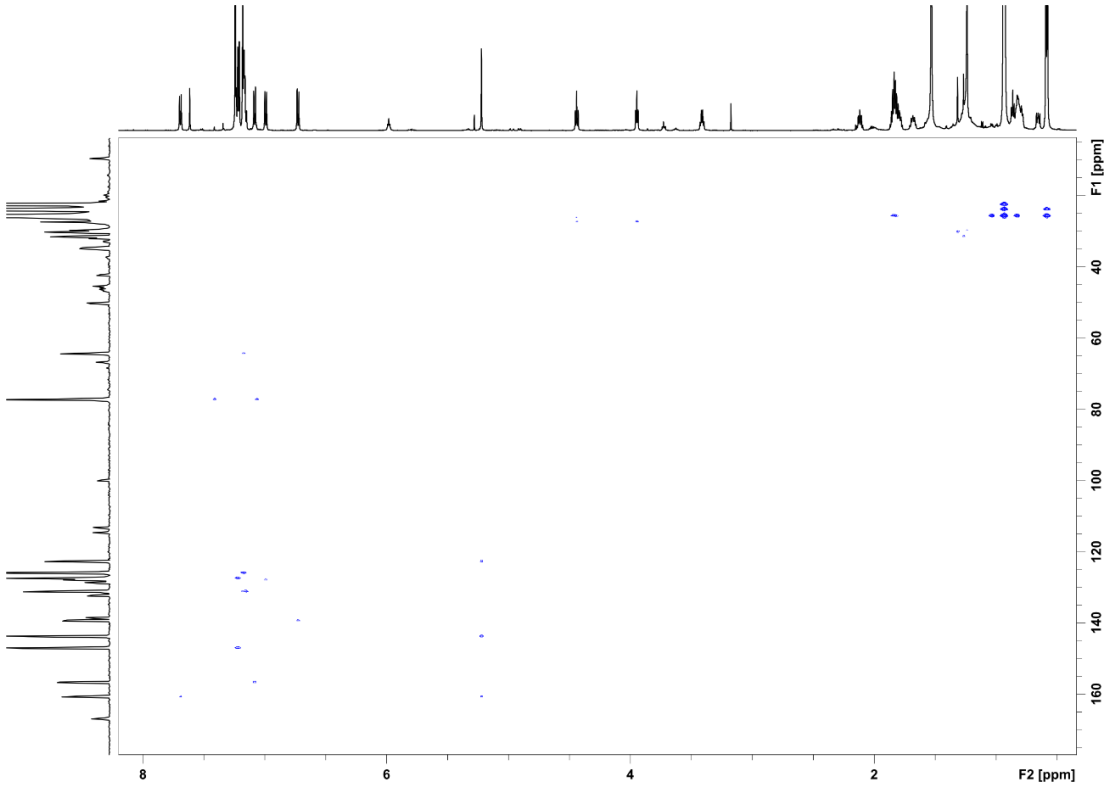



**Figure S 121.** The $^{1}H$-$^{13}C$ HMBC spectrum of **11b** (chloroform-*d*, 300 K, 600 MHz).

**Stability and reactivity of 10b–A**

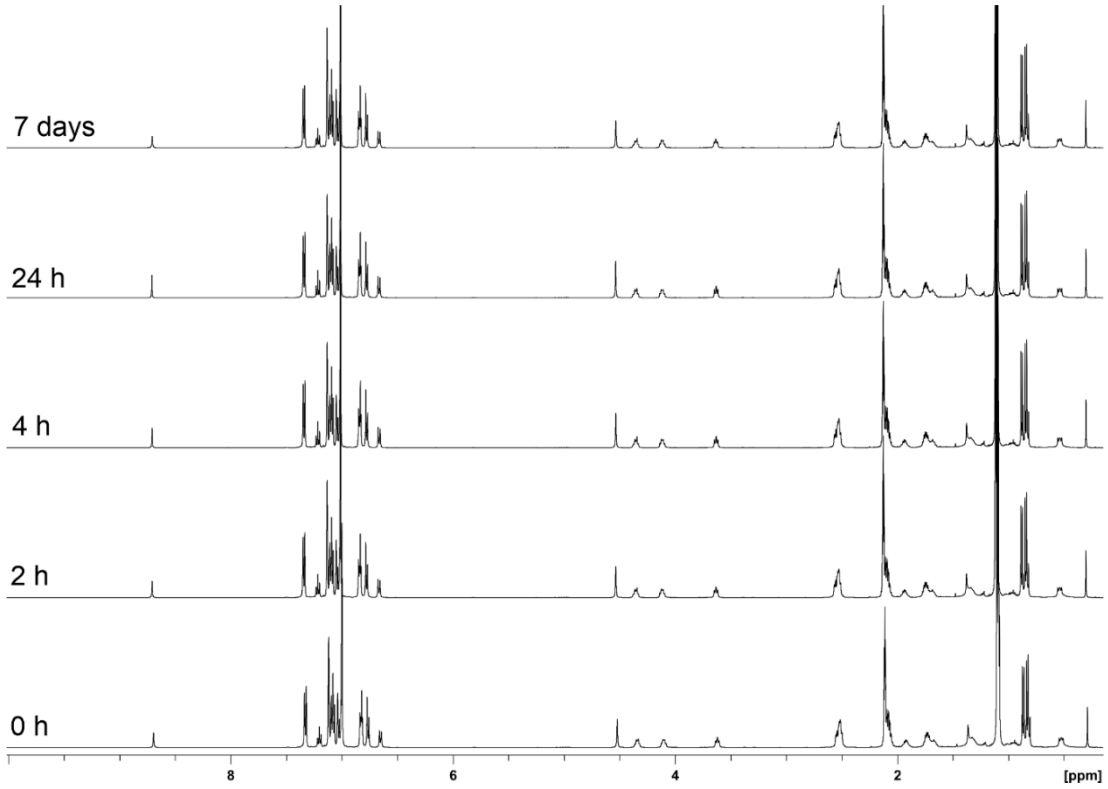



**Figure S 122.** The $^{1}$H NMR spectra recorded over seven days for the solution of **10b–A** in toluene-$d_8$ heating at 100 °C (toluene-$d_8$, 300 K, 500 MHz).

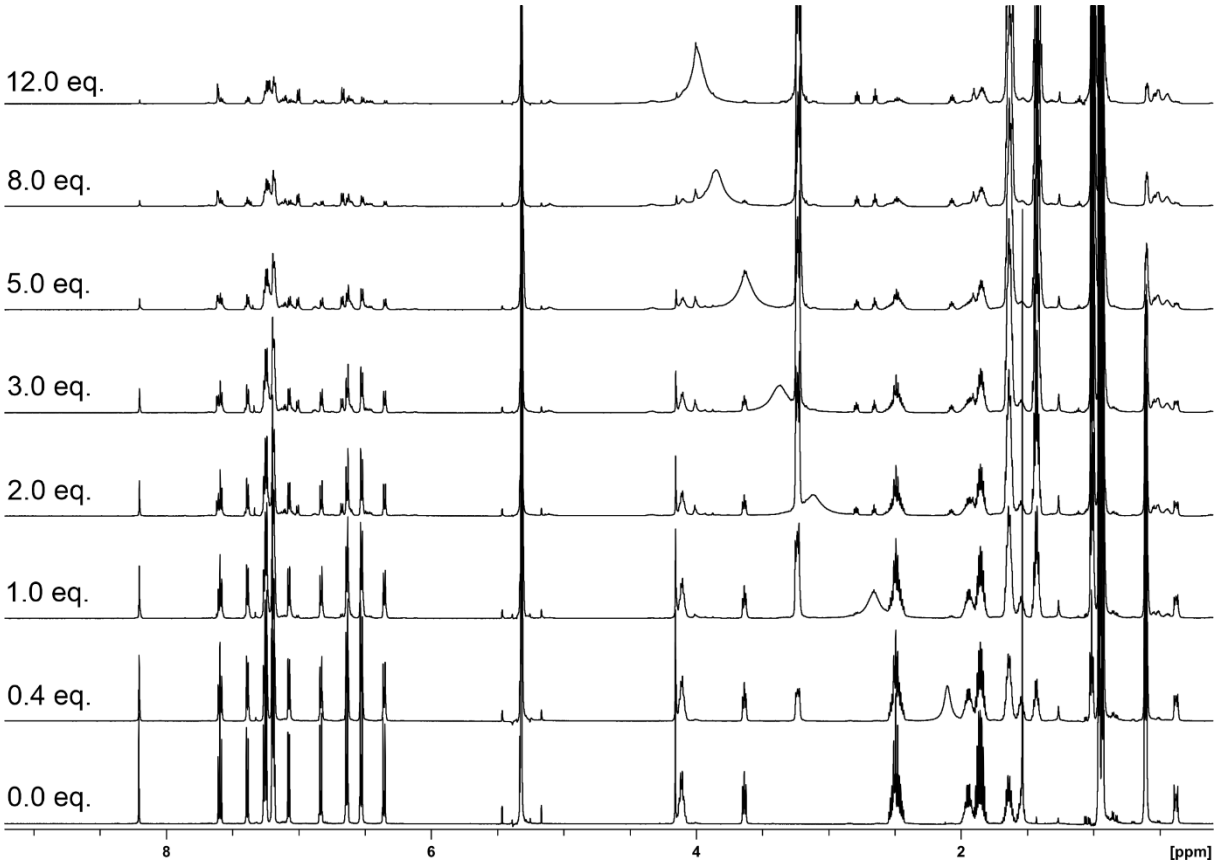



**Figure S 123.** The $^{1}$H NMR spectra recorded during titration of **10b–A** with TBAF (solution in dichloromethane-$d_2$) (dichloromethane-$d_2$, 300 K, 600 MHz).

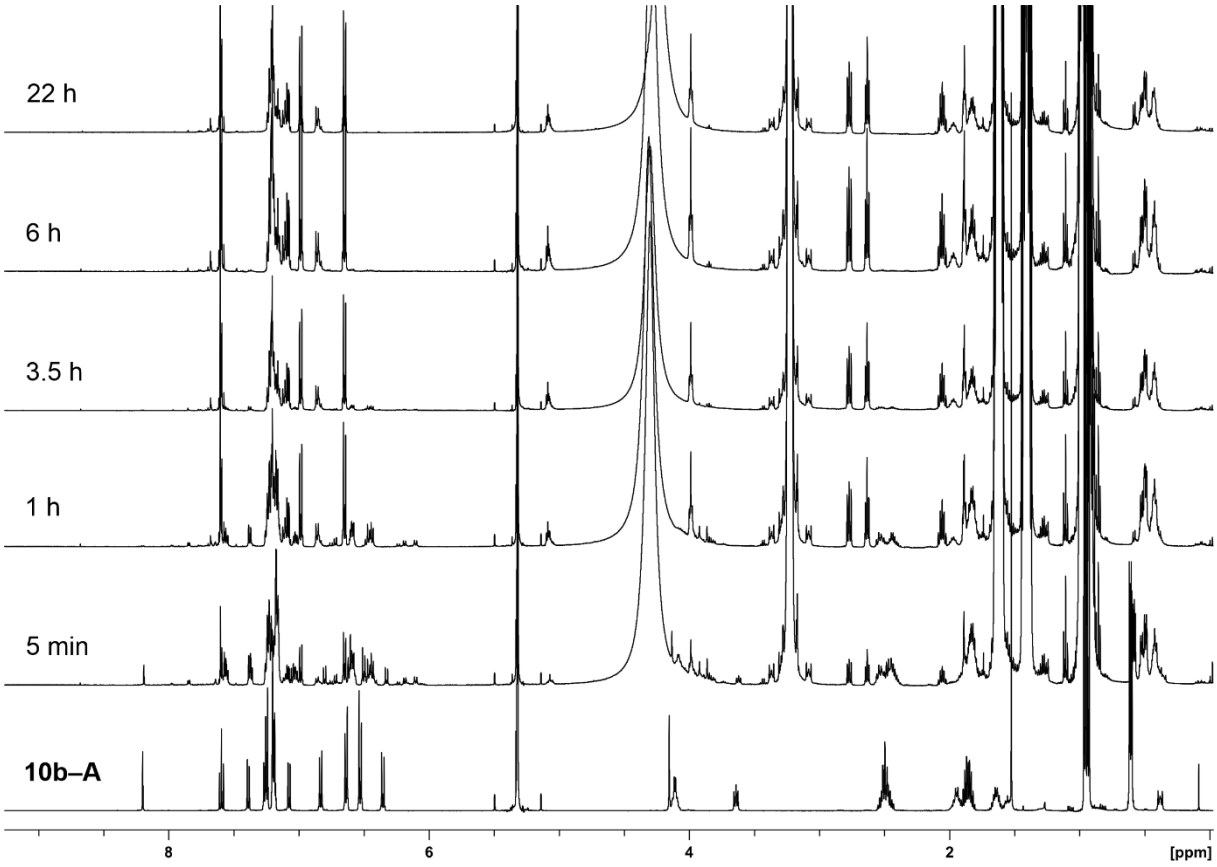



**Figure S 124.** The $^{1}$H NMR spectra recorded over 22 hours for the solution of **10b–A** in the presence of 30 equiv. of TBAF (dichloromethane-$d_2$, 300 K, 500 MHz).

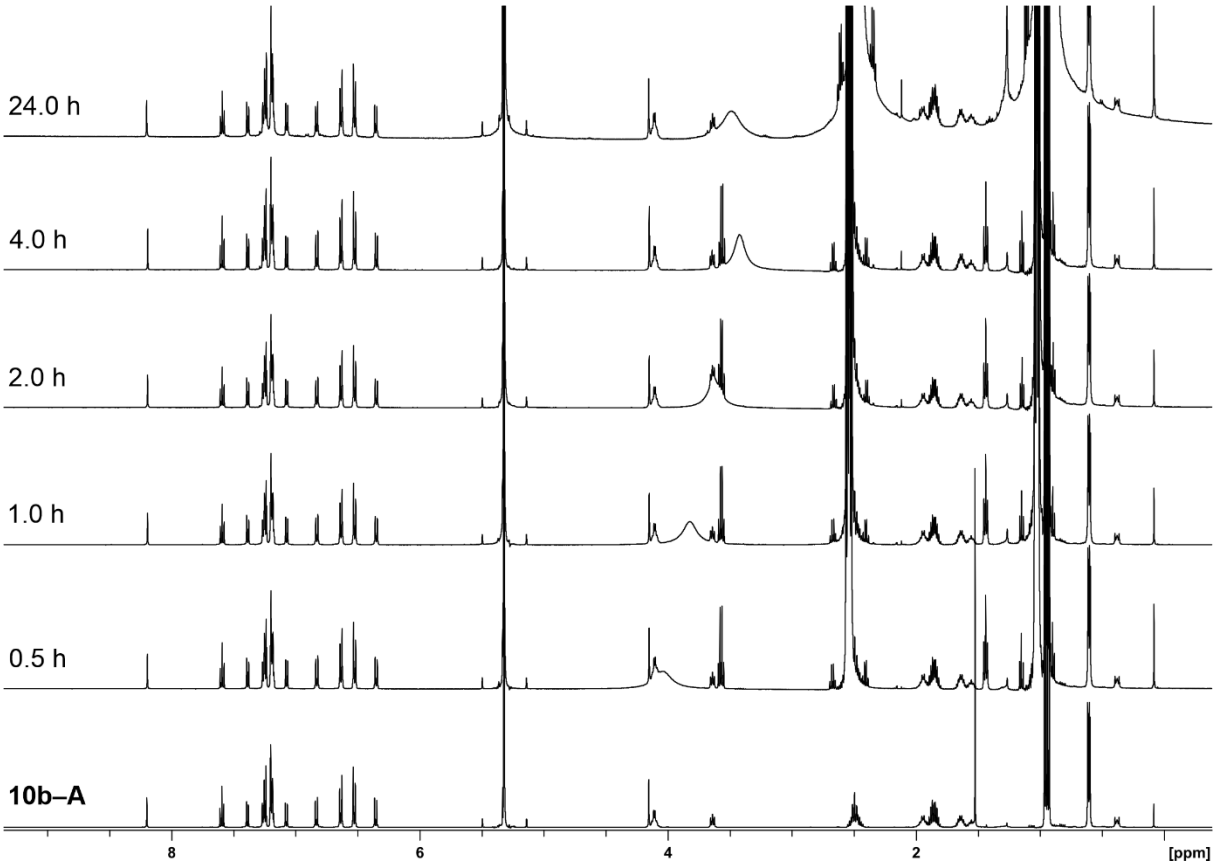



**Figure S 125**. The $^{1}$H NMR spectra recorded for the samples of **10b–A** stirred in the presence of 30 equiv. of hydrochloric acid (dichloromethane-$d_2$, 300 K, 500 MHz). After a given time, the acid was neutralized with TEA, and the sample was prepared in DCM-$d_2$.

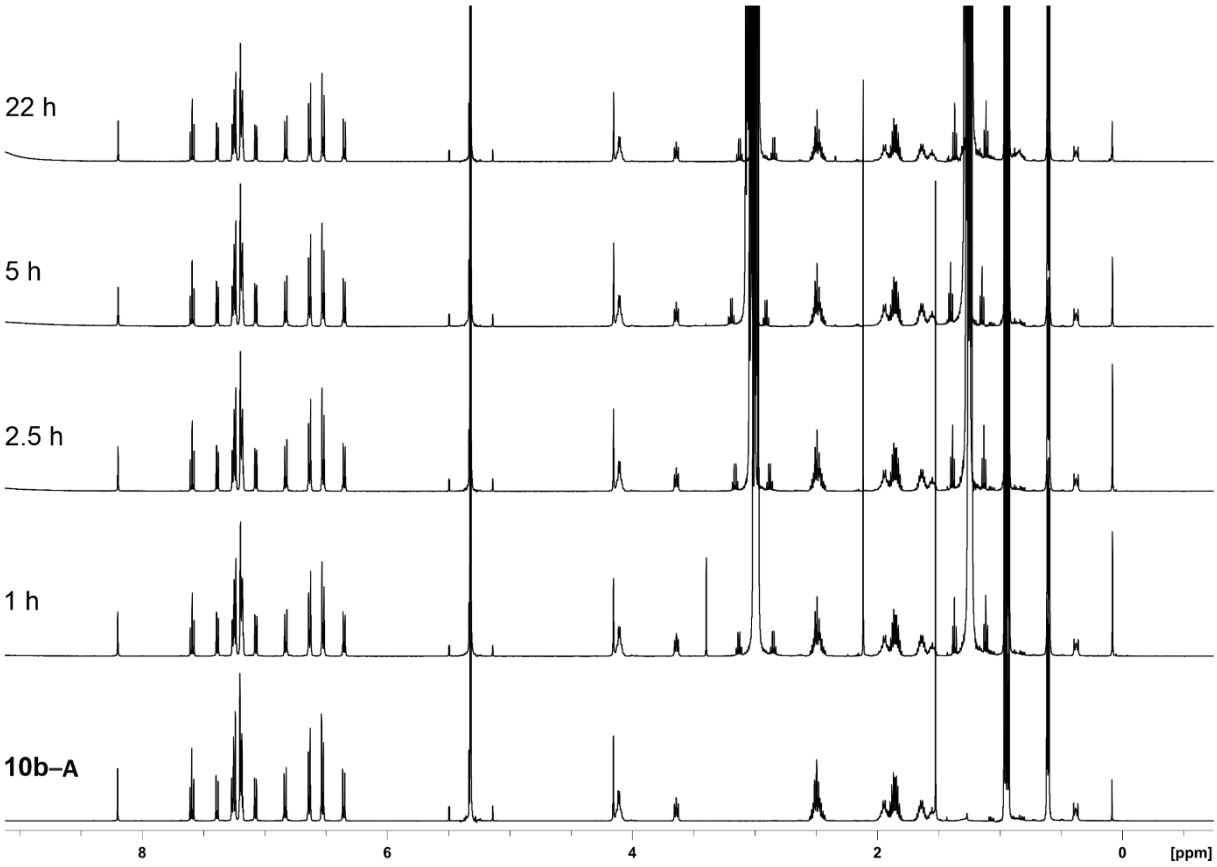



**Figure S 126.** The $^{1}$H NMR spectra recorded for the samples **10b–A** stirred in the presence of 30 equiv. of TFA (dichloromethane-$d_2$, 300 K, 500 MHz). After a given time, the acid was neutralized with TEA, and the sample was prepared in DCM-$d_2$.

## High-resolution mass spectra

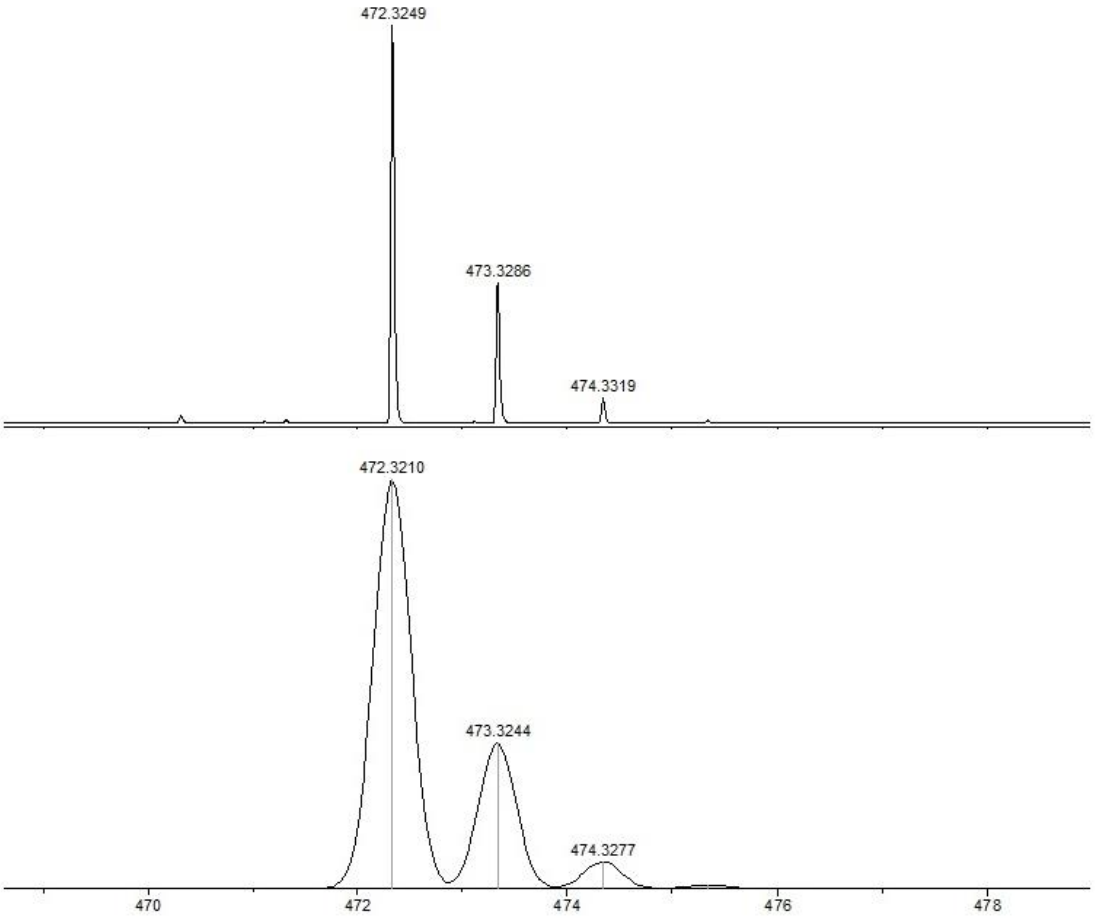



**Figure S 127.** The high-resolution mass spectrum of **B** (ESI TOF). Top: experimental spectrum, bottom: simulated isotopic pattern.

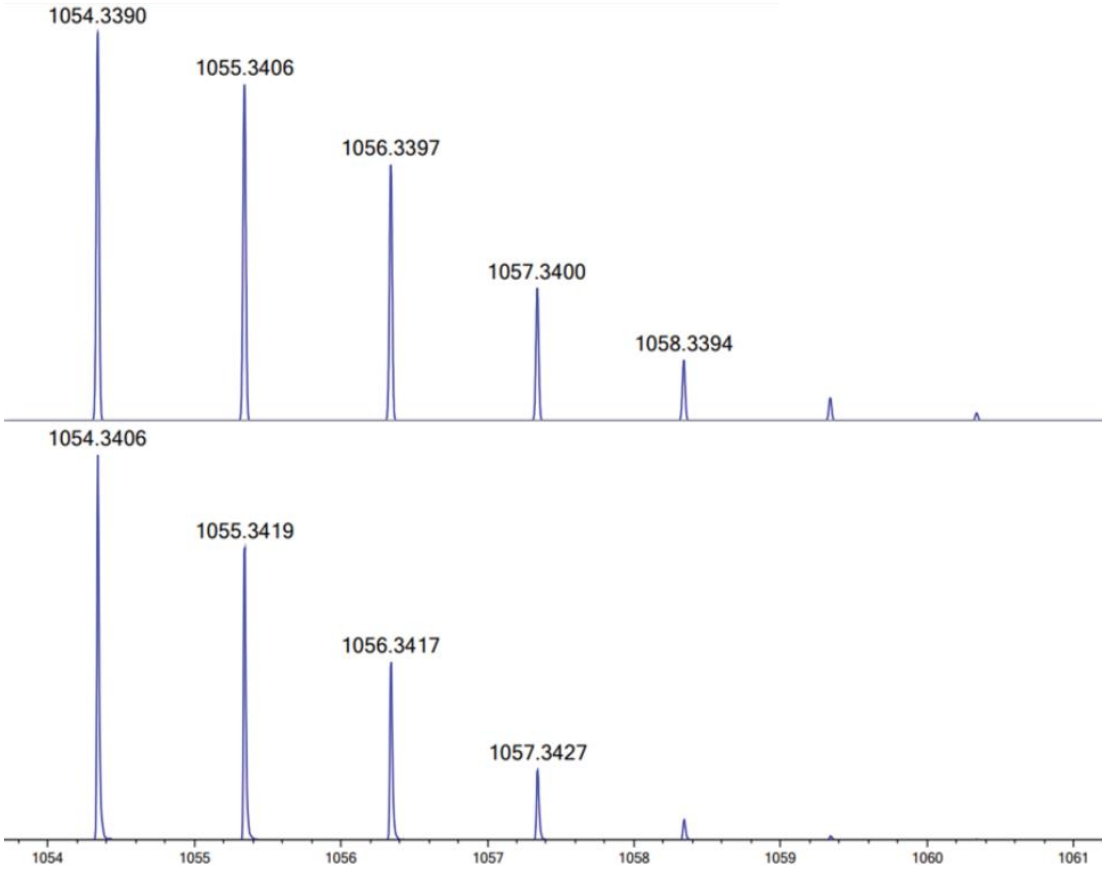



**Figure S 128.** The high-resolution mass spectrum of **6b** (MALDI TOF). Top: experimental spectrum, bottom: simulated isotopic pattern.

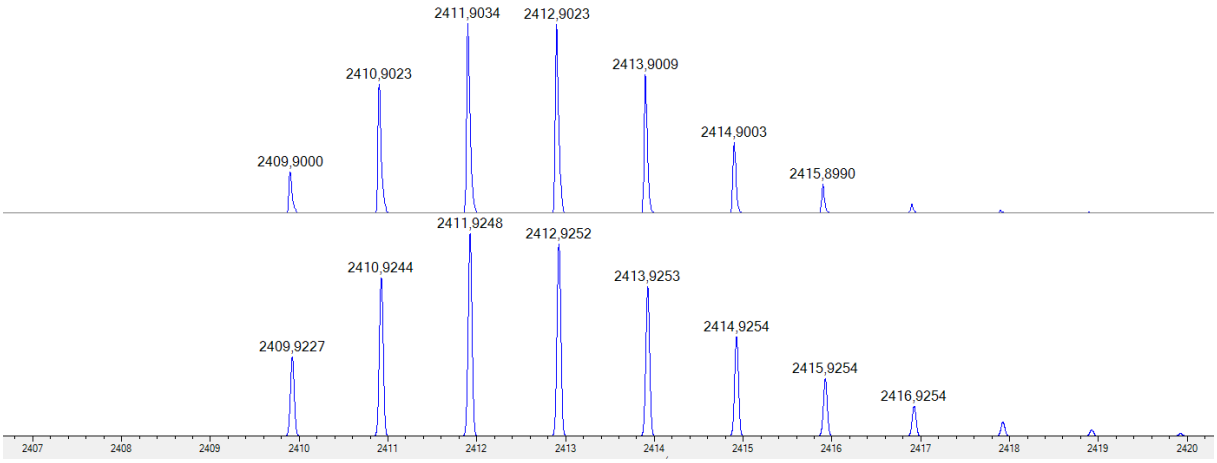



**Figure S 129.** The high-resolution mass spectrum of **9b–A** (MALDI TOF). Top: experimental spectrum, bottom: simulated isotopic pattern.

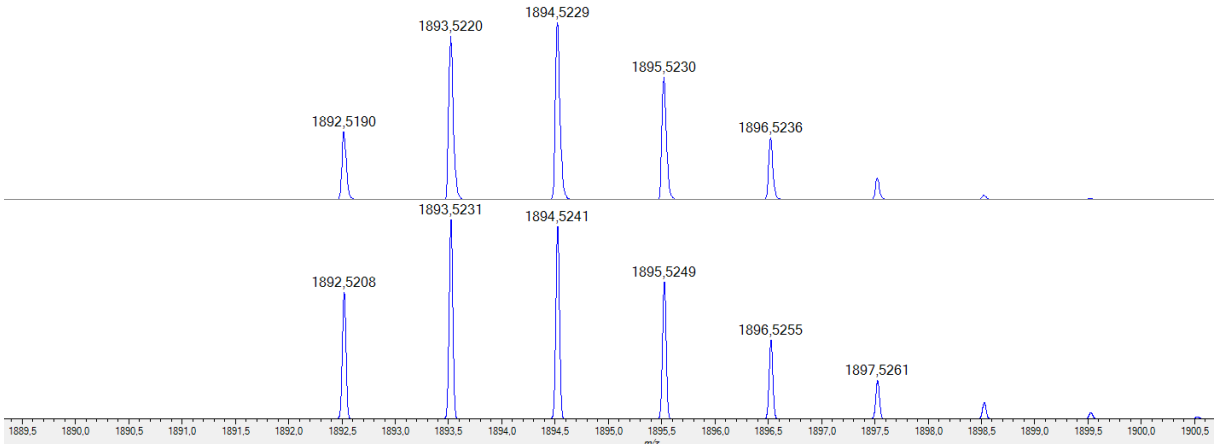



**Figure S 130.** The high-resolution mass spectrum of **10a–A** (MALDI TOF). Top: experimental spectrum, bottom: simulated isotopic pattern.

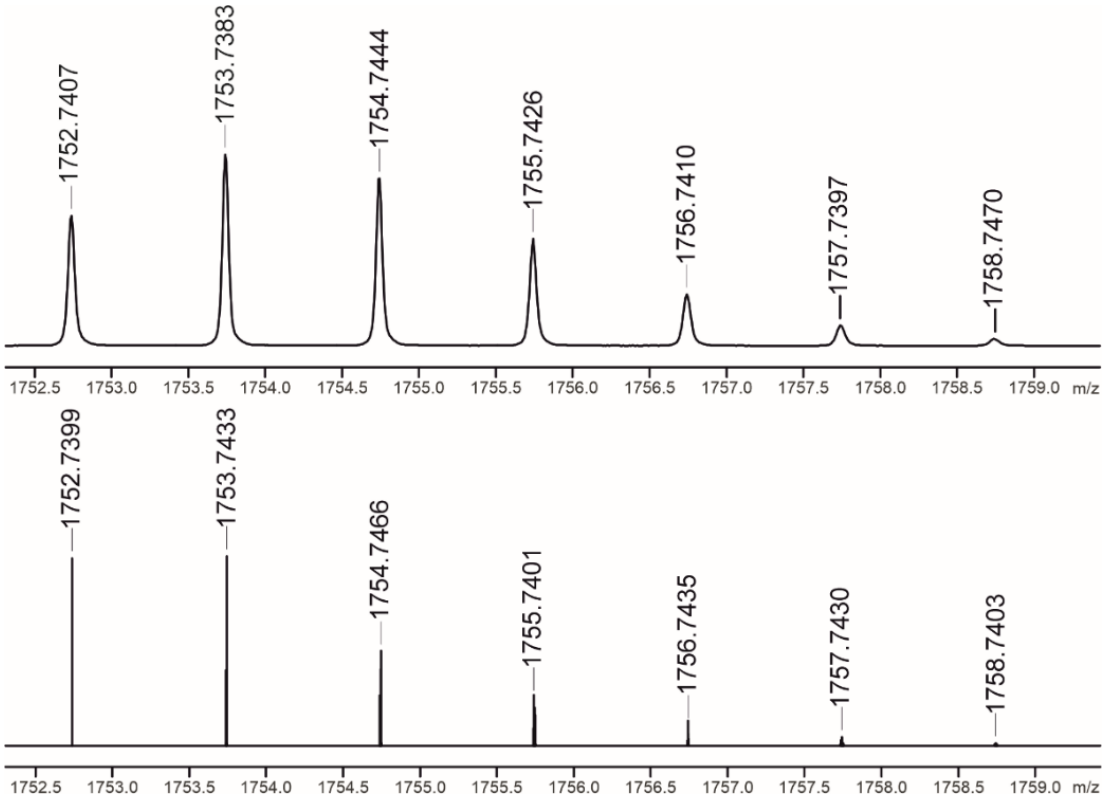



**Figure S 131.** The high-resolution mass spectrum of **10b–A** (ESI TOF). Top: experimental spectrum, bottom: simulated isotopic pattern.

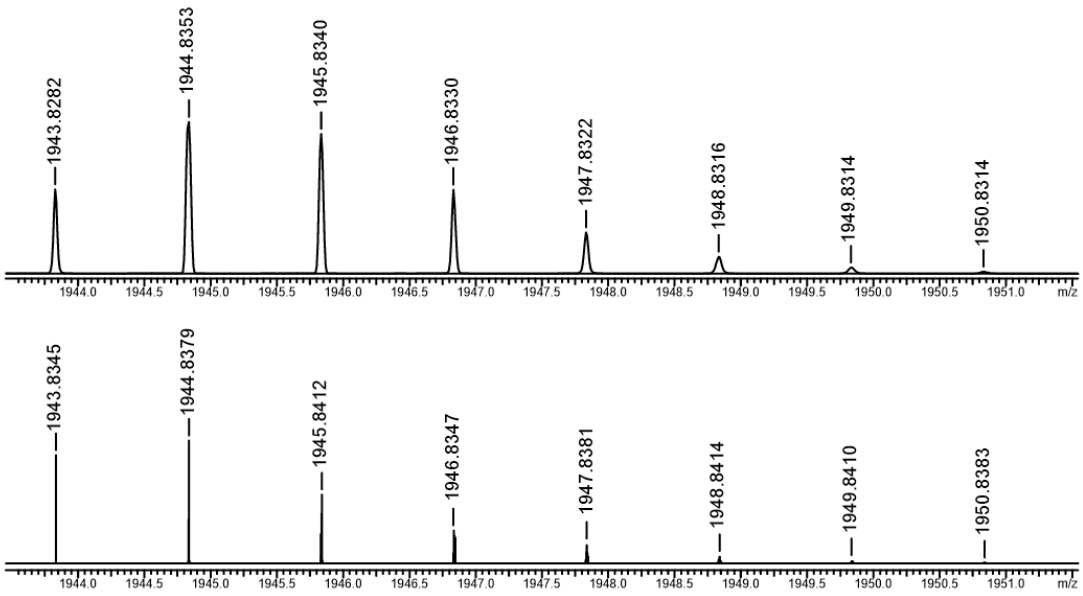



**Figure S 132.** The high-resolution mass spectrum of **11b–A** (ESI TOF). Top: experimental spectrum, bottom: simulated isotopic pattern.

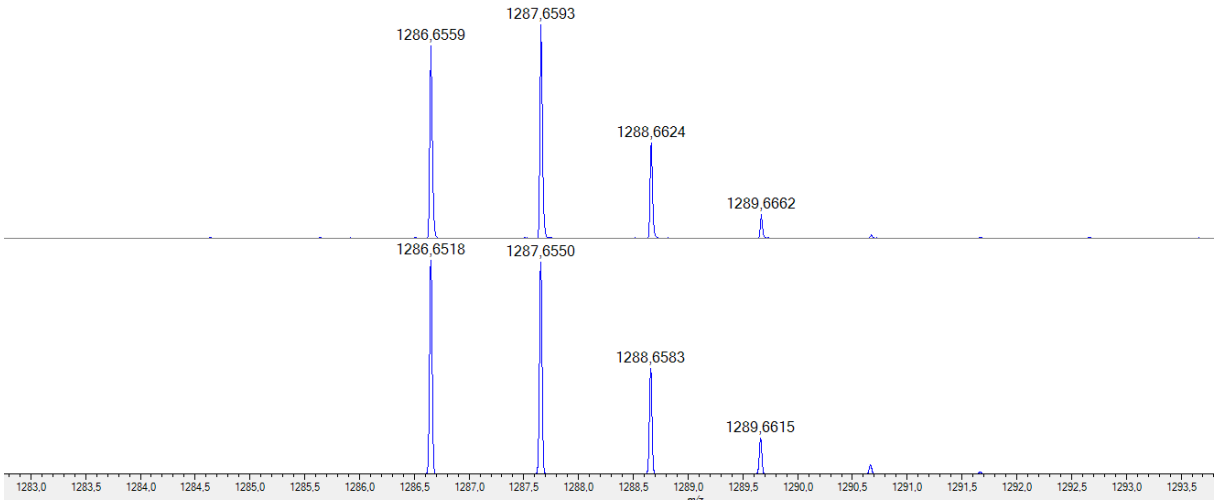



**Figure S 133.** The high-resolution mass spectrum of **12–A** (MALDI TOF). Top: experimental spectrum, bottom: simulated isotopic pattern.

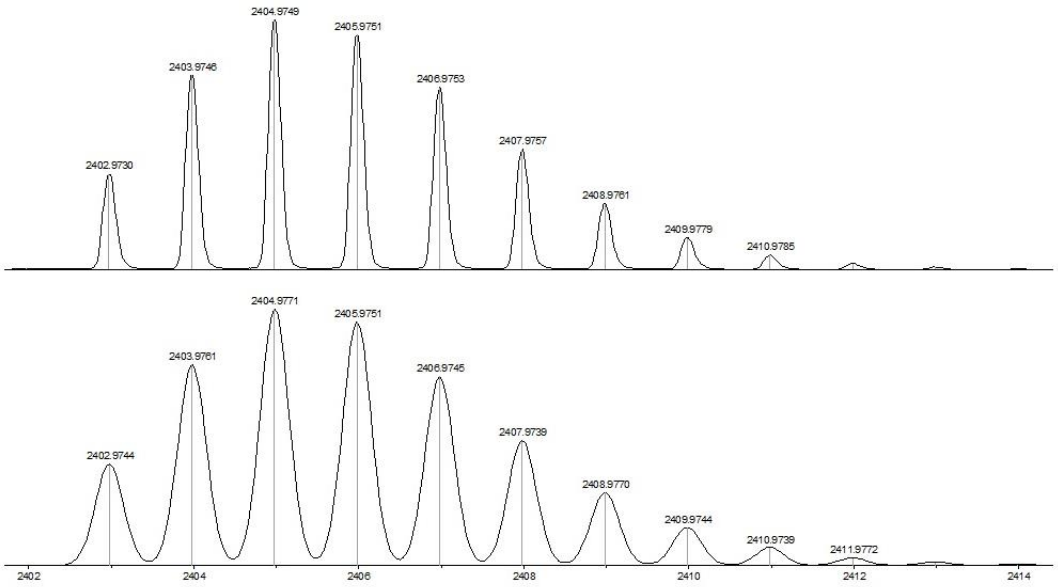



**Figure S 134.** The high-resolution mass spectrum of **9a–B** (ESI+ TOF). Top: experimental spectrum, bottom: simulated isotopic pattern.

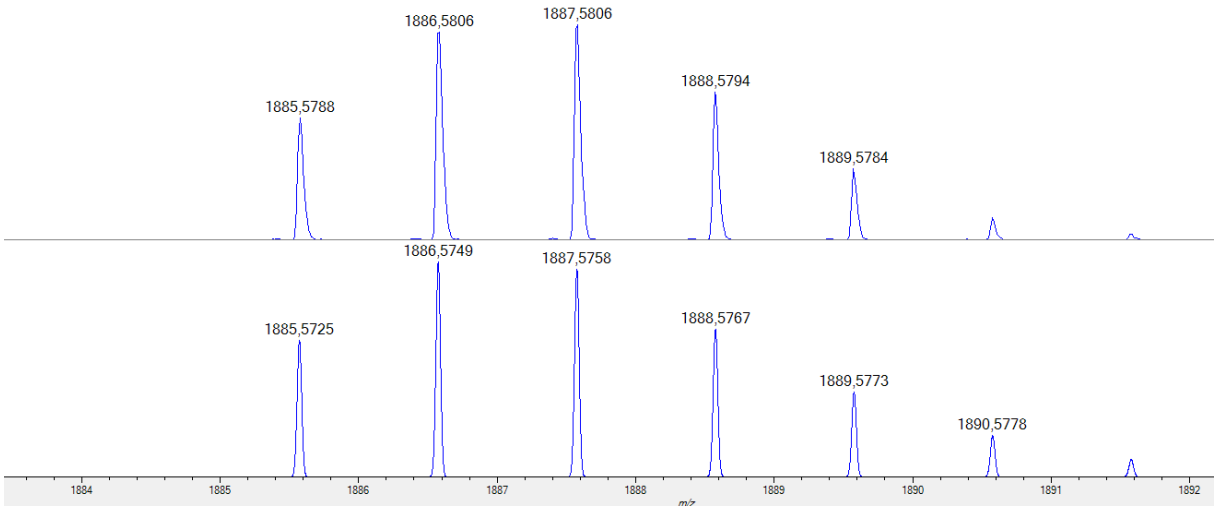



**Figure S 135.** The high-resolution mass spectrum of **10a–B** (MALDI TOF). Top: experimental spectrum, bottom: simulated isotopic pattern.

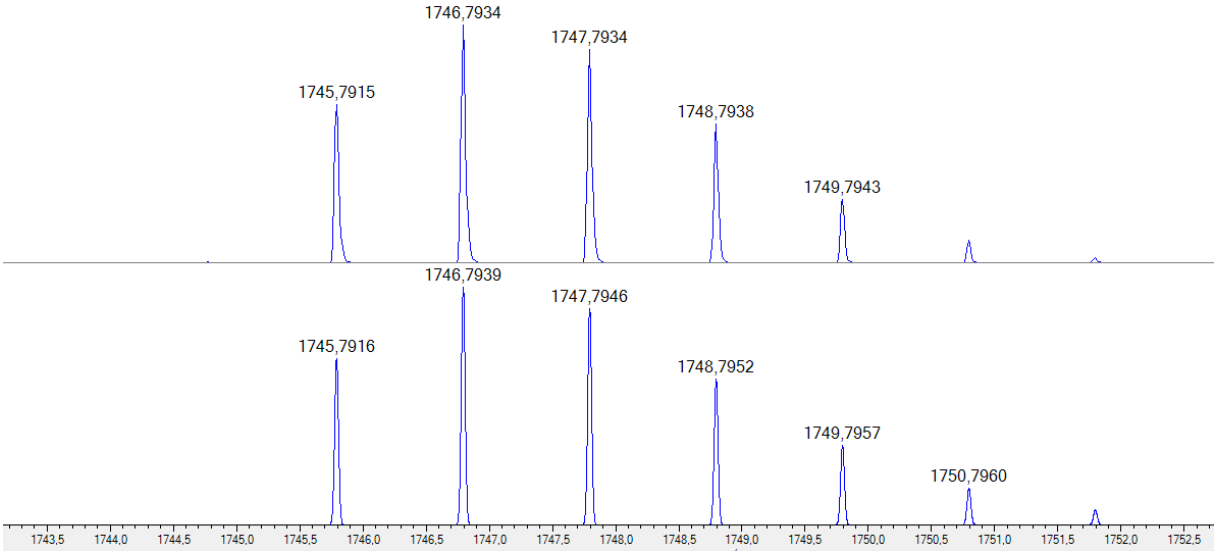



**Figure S 136.** The high-resolution mass spectrum of **10b–B** (MALDI TOF). Top: experimental spectrum, bottom: simulated isotopic pattern.

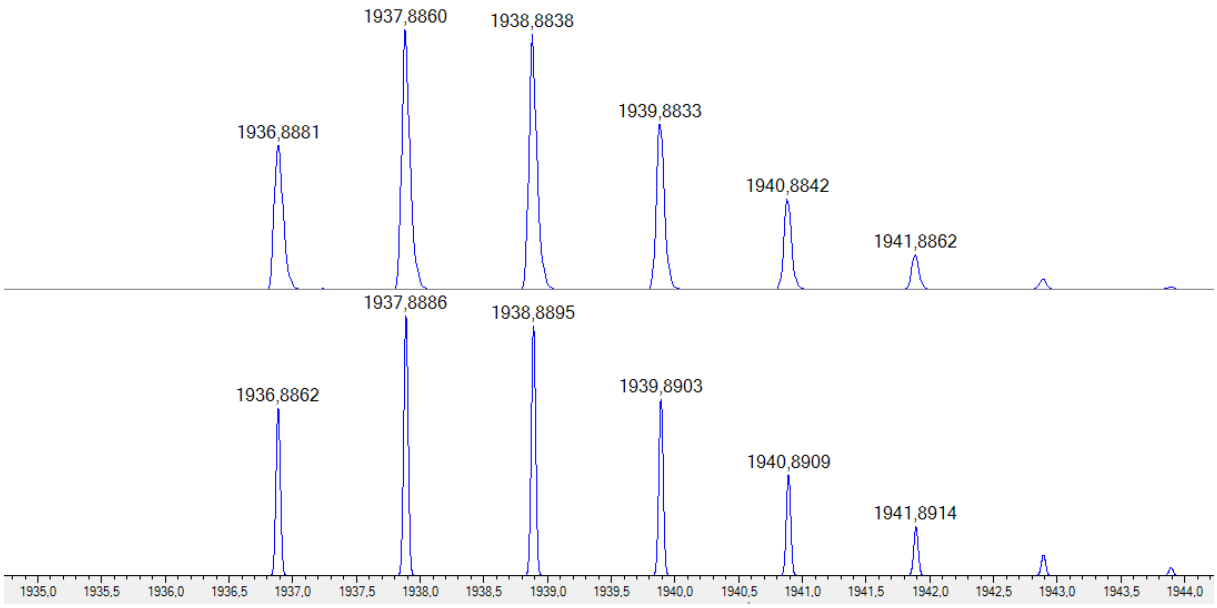



**Figure S 137.** The high-resolution mass spectrum of **11b–B** (MALDI TOF). Top: experimental spectrum, bottom: simulated isotopic pattern.

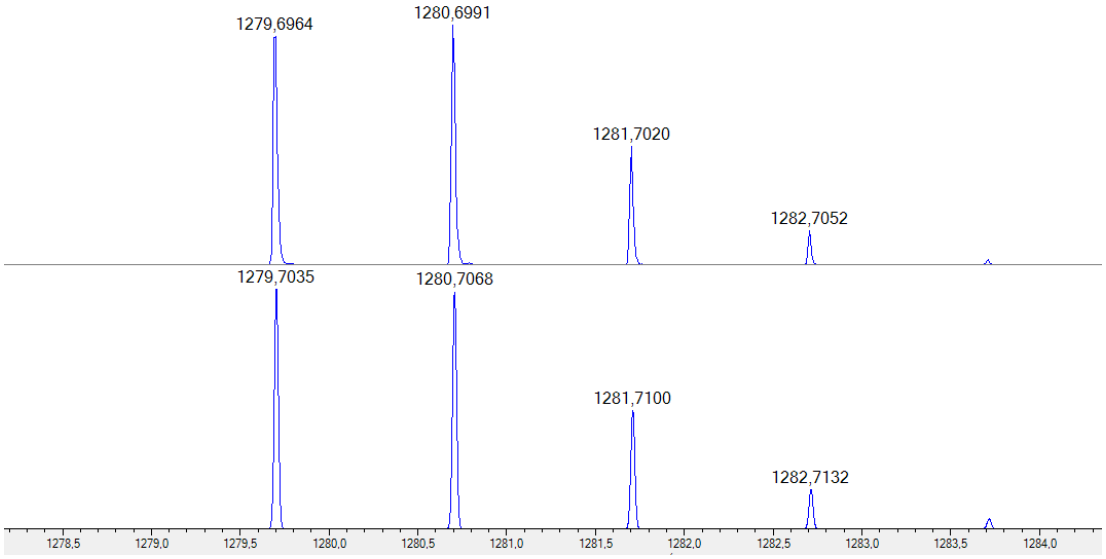



**Figure S 138.** The high-resolution mass spectrum of **12–B** (MALDI TOF). Top: experimental spectrum, bottom: simulated isotopic pattern.

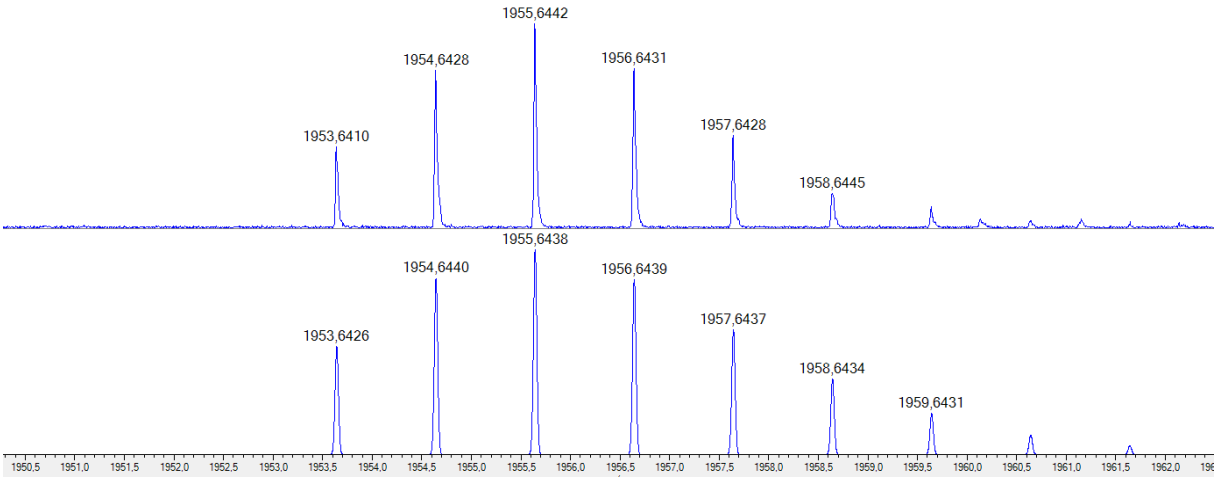



**Figure S 139.** The high-resolution mass spectrum of **9b** (MALDI TOF). Top: experimental spectrum, bottom: simulated isotopic pattern.

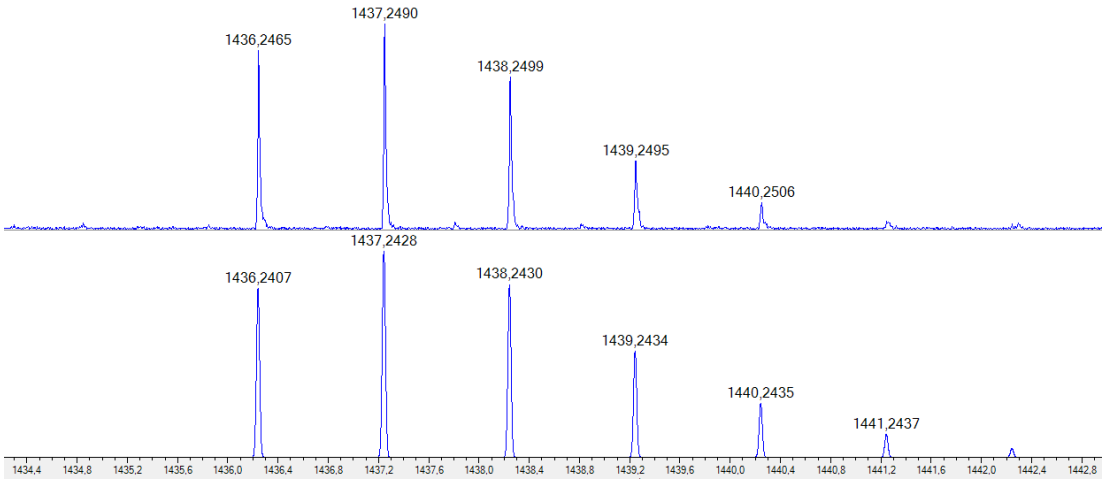



**Figure S 140.** The high-resolution mass spectrum of **10a** (MALDI TOF). Top: experimental spectrum, bottom: simulated isotopic pattern.

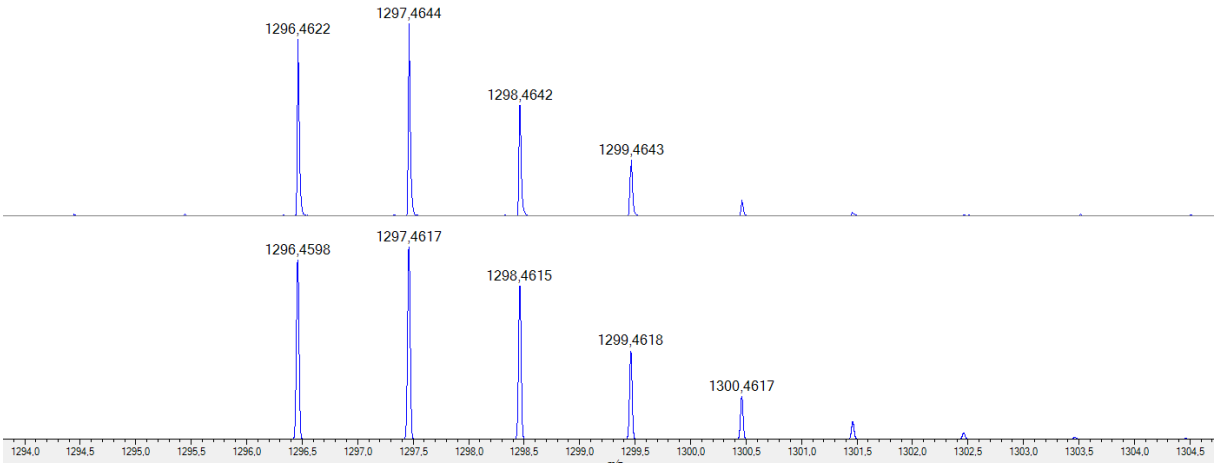



**Figure S 141.** The high-resolution mass spectrum of **10b** (MALDI TOF). Top: experimental spectrum, bottom: simulated isotopic pattern.

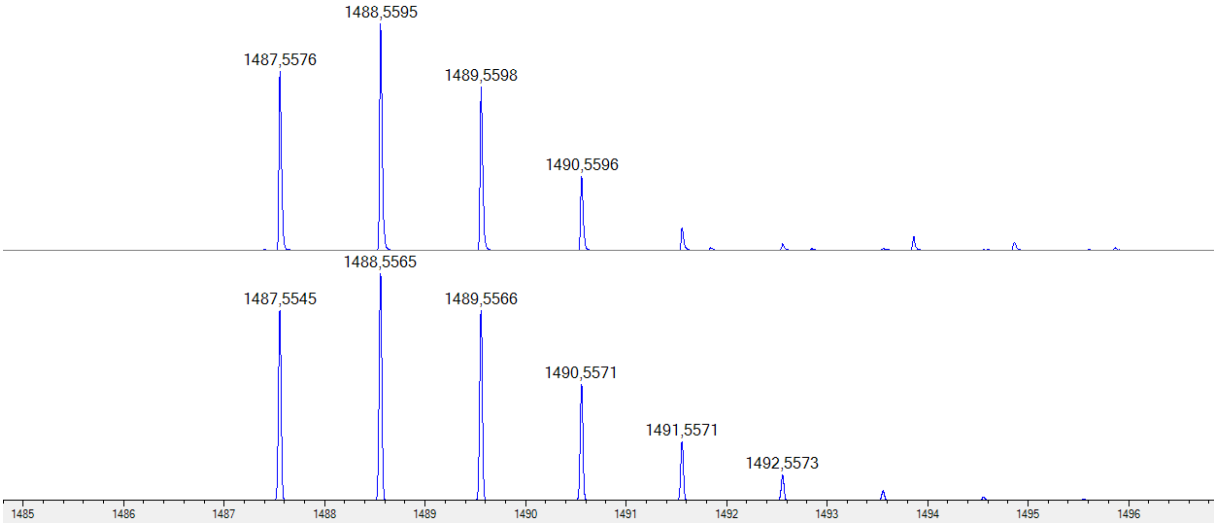



**Figure S 142.** The high-resolution mass spectrum of **11b** (MALDI TOF). Top: experimental spectrum, bottom: simulated isotopic pattern.

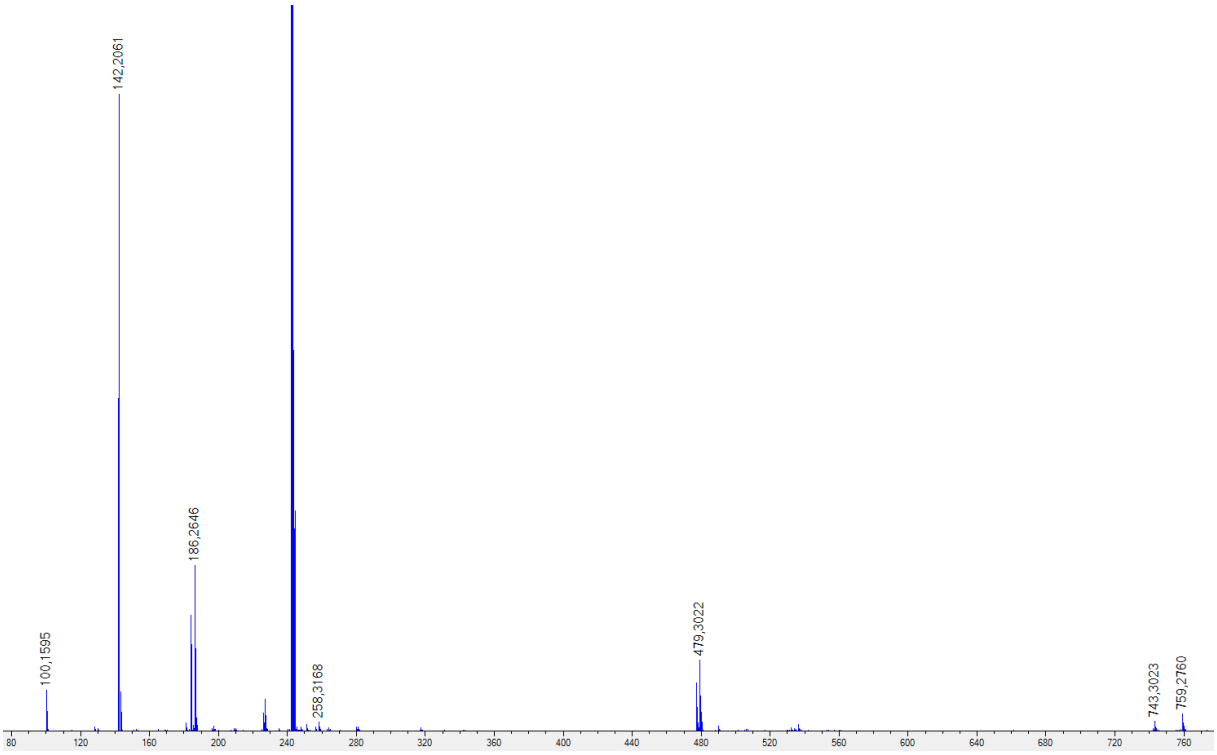



**Figure S 143.** The MALDI TOF mass spectrum of the product mixture obtained from the reaction of **10b–A** with 30 equiv. of TBAF over 22 hours-long stirring in dichloromethane-$d_2$.

## Thermogravimetric data

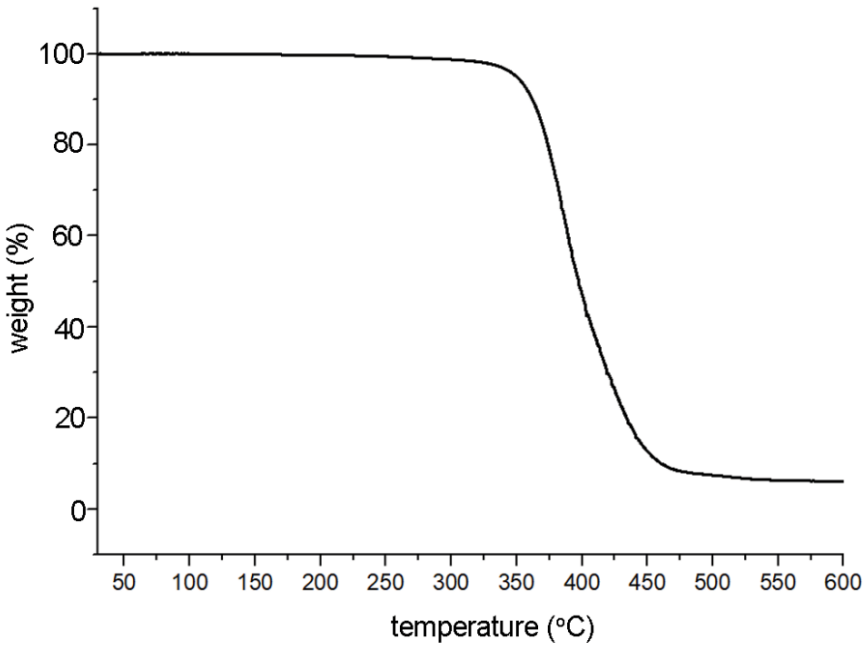



**Figure S 144.** The TGA curve of **9b–A** recorded with the heating rate of 5°C/min. in the nitrogen atmosphere.

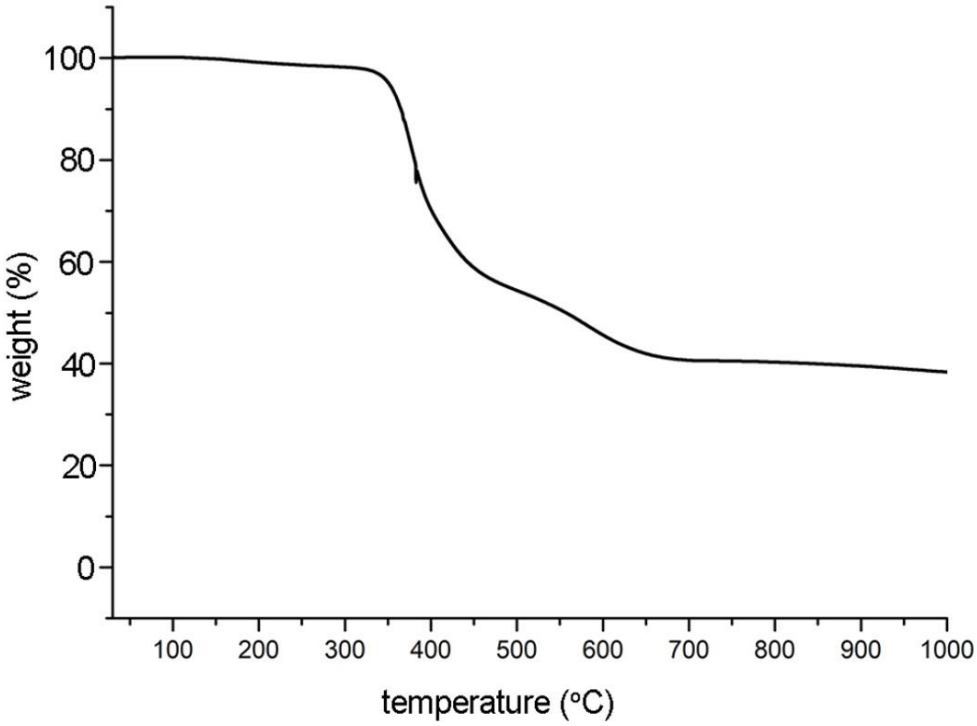



**Figure S 145.** The TGA curve of **10a–A** recorded with the heating rate of 5°C/min. in the nitrogen atmosphere.

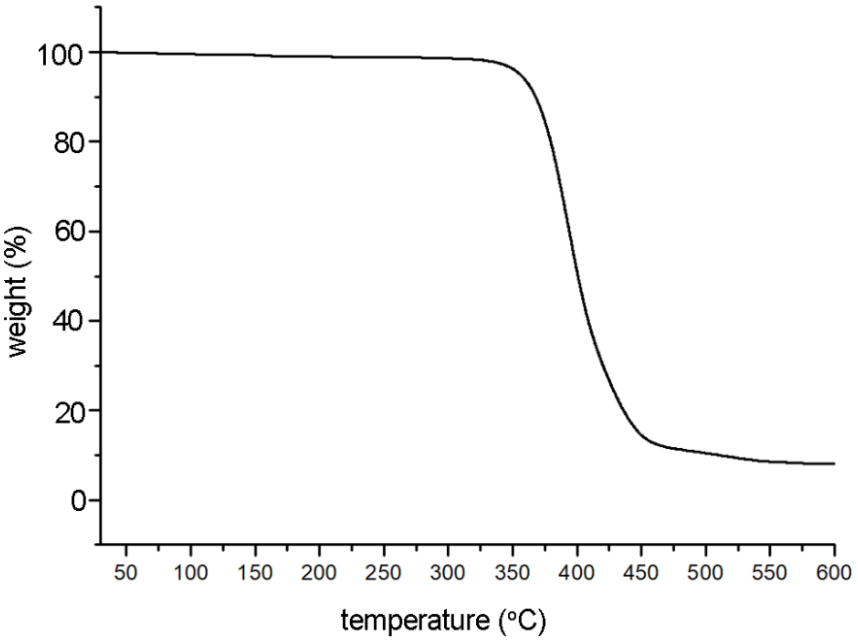



**Figure S 146.** The TGA curve of **10b–A** recorded with the heating rate of 5°C/min. in the nitrogen atmosphere.

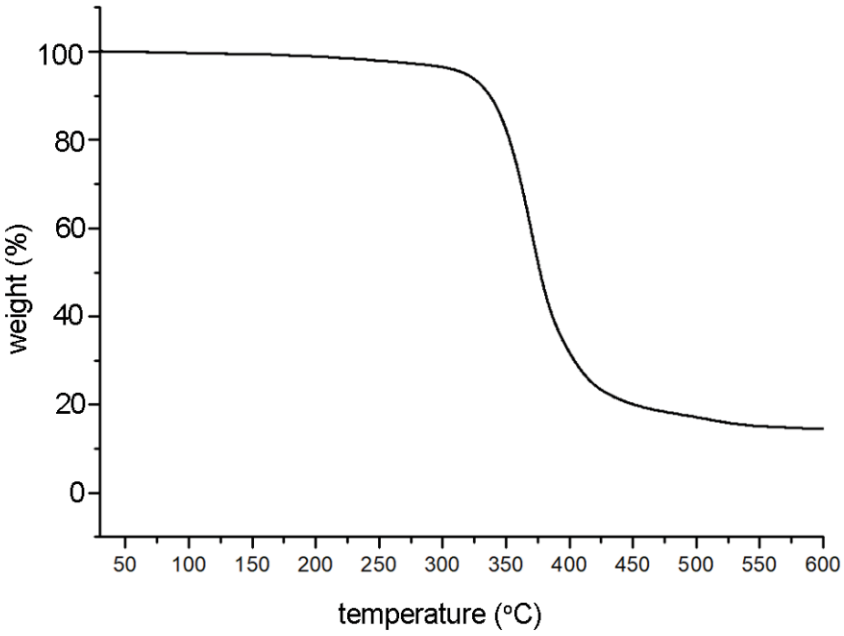



**Figure S 147.** The TGA curve of **11b–A** recorded with the heating rate of 5°C/min. in the nitrogen atmosphere.

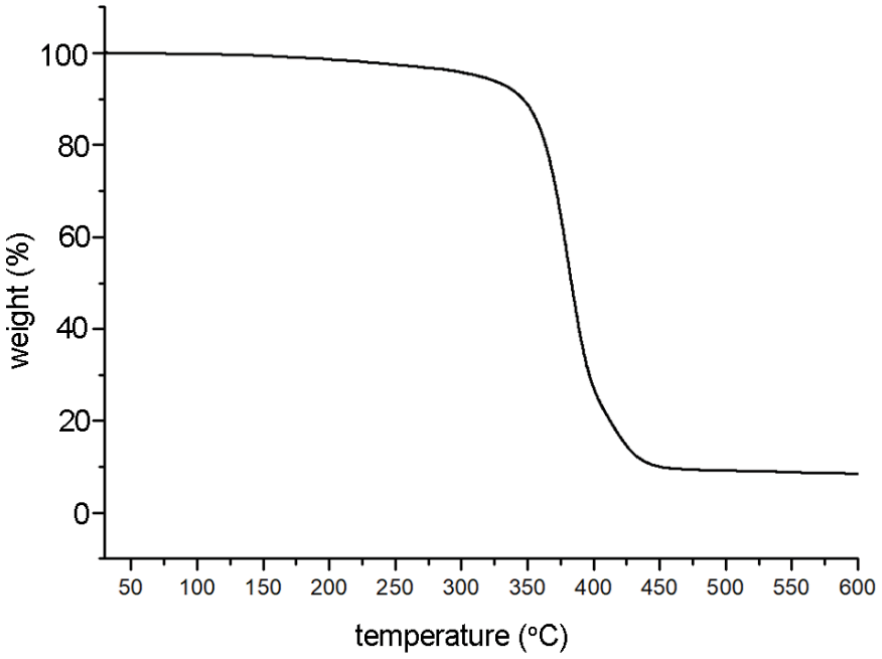



**Figure S 148.** The TGA curve of **12–A** recorded with the heating rate of 5°C/min. in the nitrogen atmosphere.

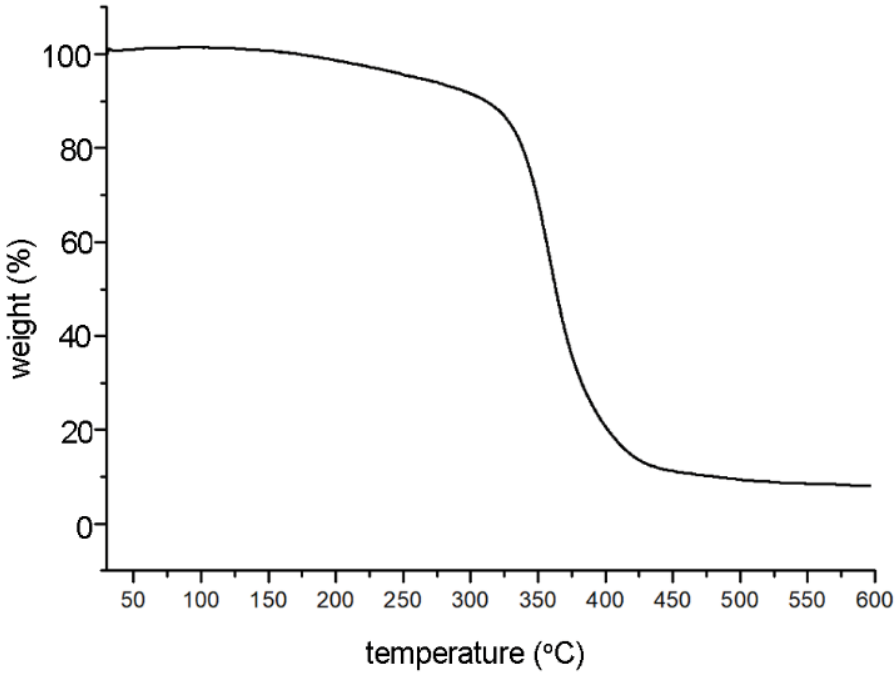



**Figure S 149.** The TGA curve of **9b–B** recorded with the heating rate of 5°C/min. in the nitrogen atmosphere.

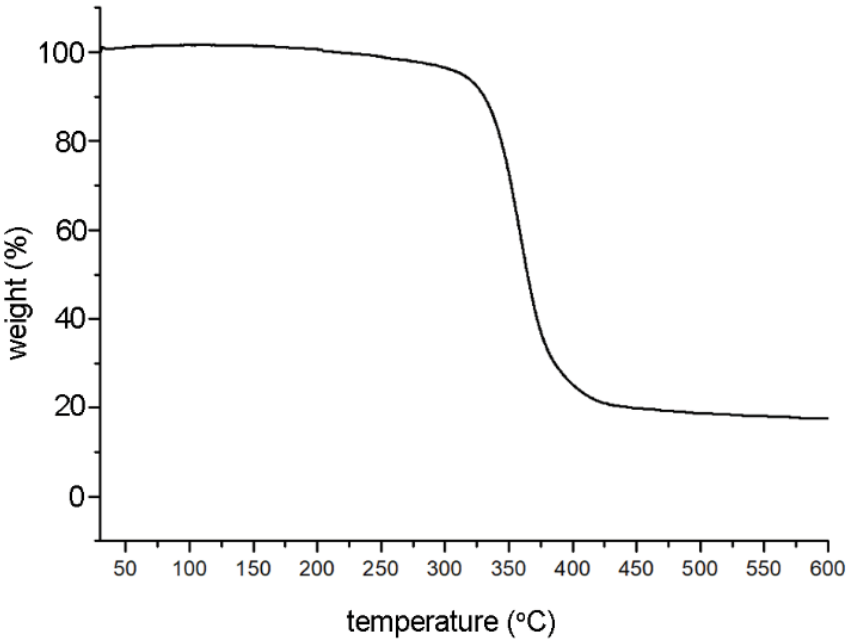



**Figure S 150.** The TGA curve of **10b–B** recorded with the heating rate of 5°C/min. in the nitrogen atmosphere.

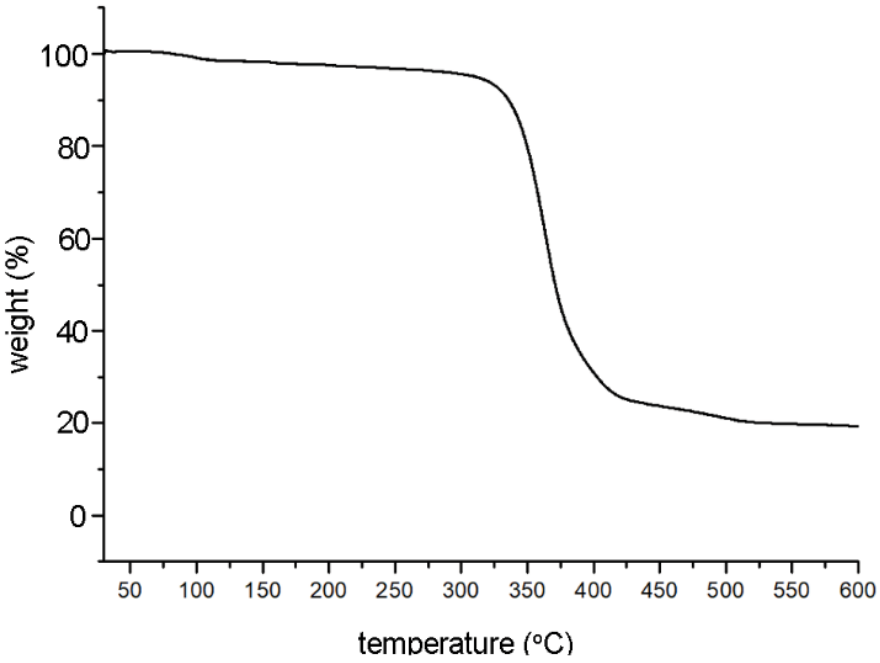



**Figure S 151.** The TGA curve of **11b–B** recorded with the heating rate of 5°C/min. in the nitrogen atmosphere.

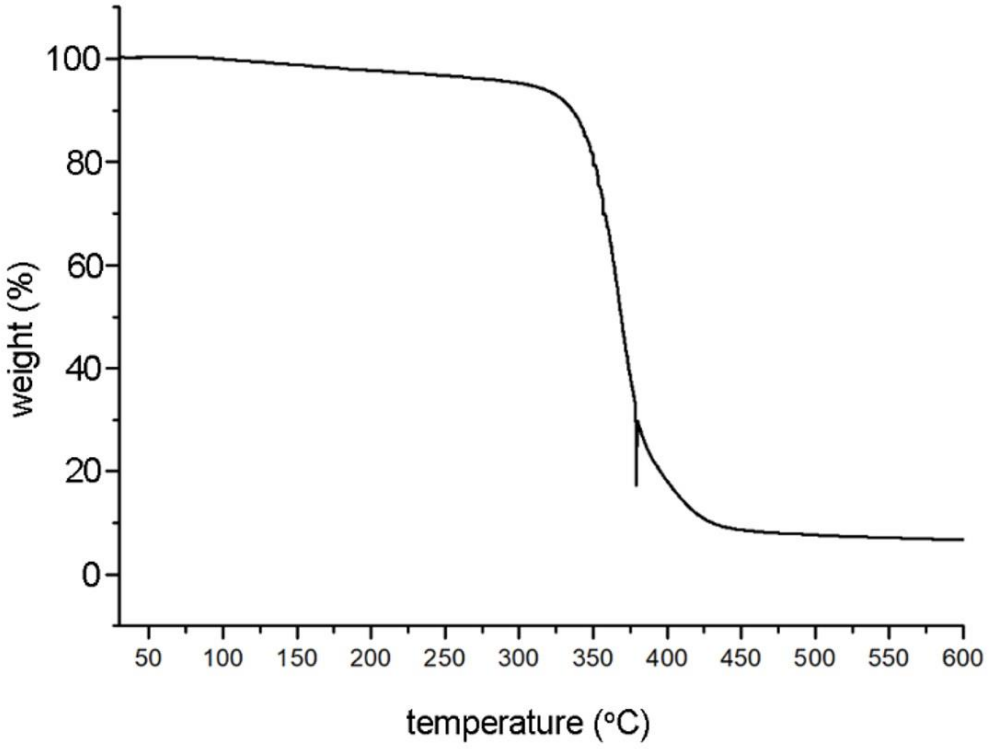



**Figure S 152.** The TGA curve of **12–B** recorded with the heating rate of 5°C/min. in the nitrogen atmosphere.

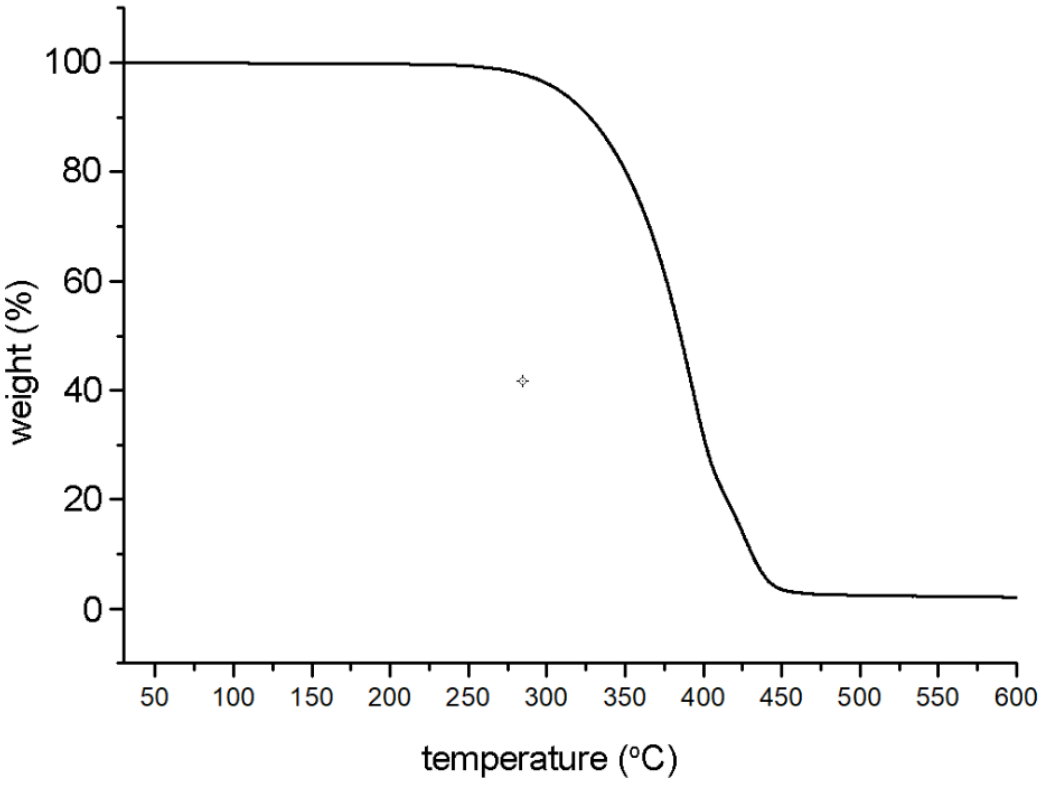



**Figure S 153.** The TGA curve of **A** recorded with the heating rate of 5°C/min. in the nitrogen atmosphere.

## X-ray molecular structures

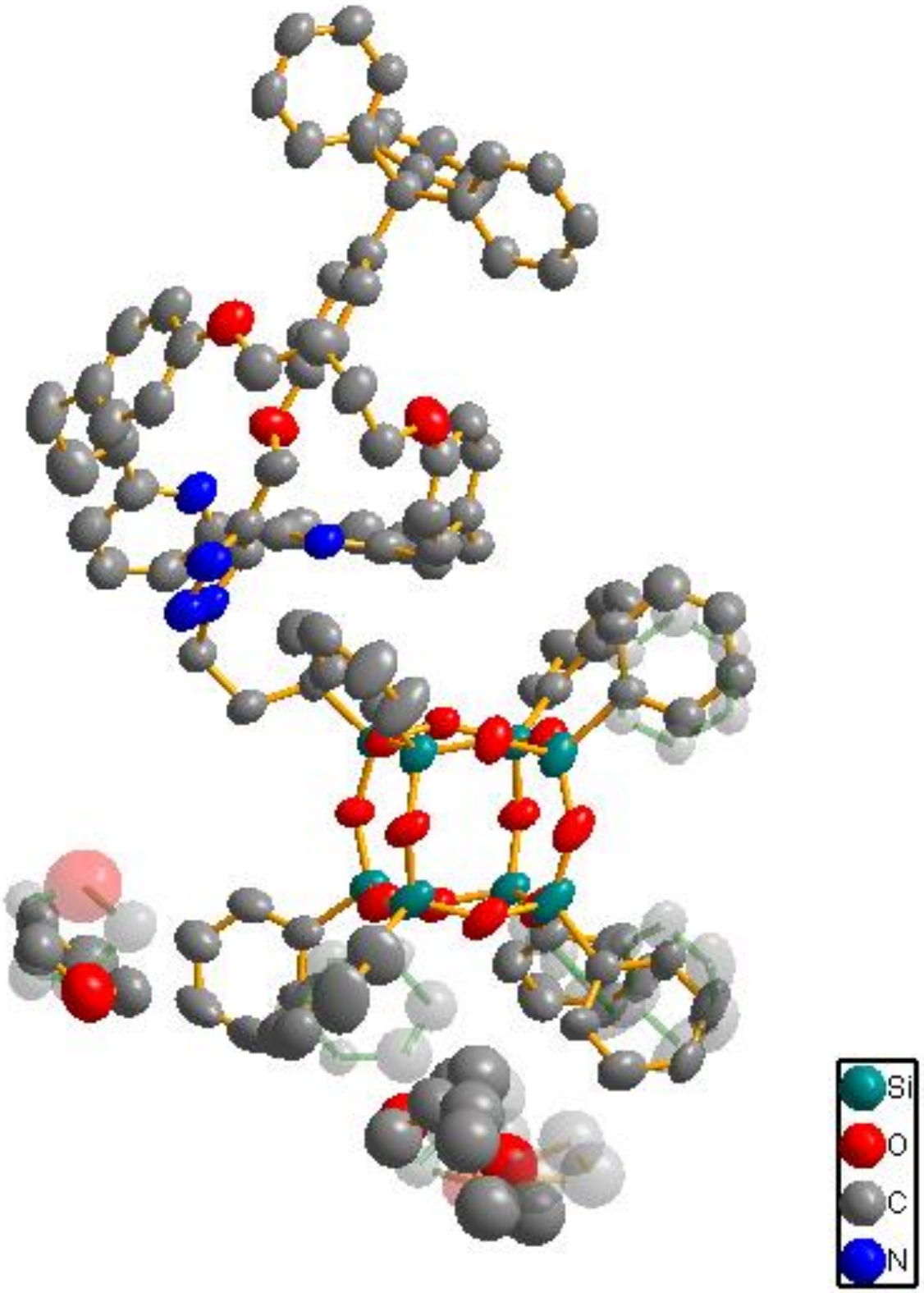



**Figure S 154.** An asymmetric part of **10a-A**. Atomic displacement parameters are shown with 50% probability. The minor component of the disordered molecules are marked by transparency. Hydrogen atoms were omitted for clarity.

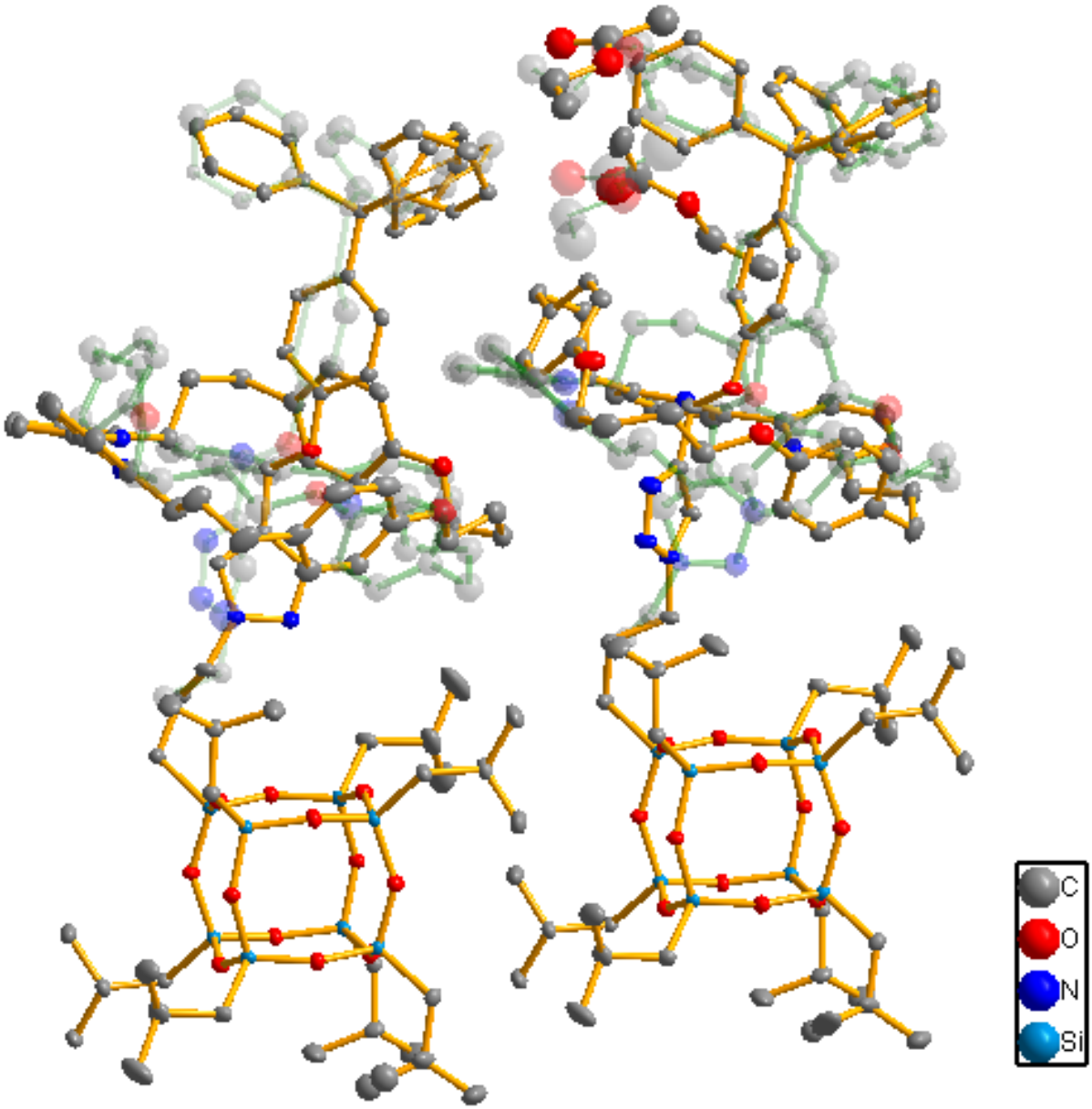



**Figure S 155.** An asymmetric part of **10b-A**. Atomic displacement parameters are shown with 50% probability. The minor component of the disordered molecules are marked by transparency. Hydrogen atoms were omitted for clarity.

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