Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Material

Sequential Nucleophilic Substitution of Pseudorotaxanes Forms Rotaxanes with Various Linking Functionalities and Recycling of the Surrogate Stopper

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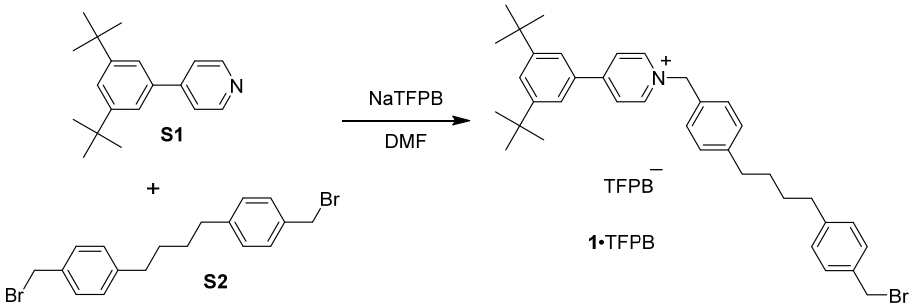
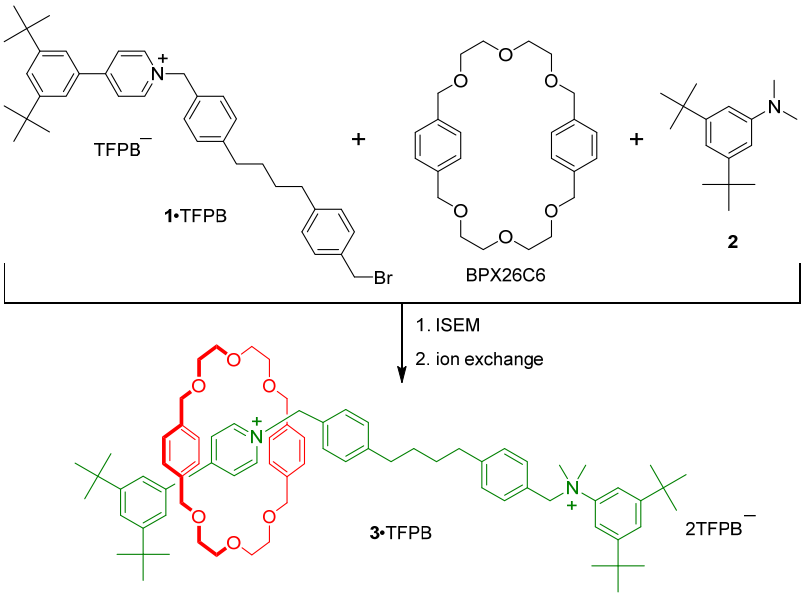
General Methods. All stirrer bars, syringes, needles, and glassware were either heat gun– or oven–dried before use. Unless otherwise indicated, all chemicals were obtained from commercial sources. Reactions were performed under an inert atmosphere of Ar or N_2. Reactions conducted at elevated temperatures were performed using an oil bath as the heating apparatus. Thin-layer chromatography (TLC) was conducted using Merck Art. 5715 silica gel with a thickness of 0.25 mm. Column chromatography was performed employing Kieselgel 60 from Merck (70–230 mesh) or Chromatorex DIOL or NH series from Fuji Silysia (MB100-40/75). Melting points were determined using a Fargo MP-2D melting point apparatus. For NMR spectroscopy, a deuterated solvent was used to stabilize the magnetic field (lock) and for shimming, with the residual protons of the solvent serving as the internal standard. High-resolution mass spectrometry (HRMS) was conducted using either a Bruker microTOF-QII (Q-TOF) or Sciex QSTAR XL (Q-TOF) instrument.

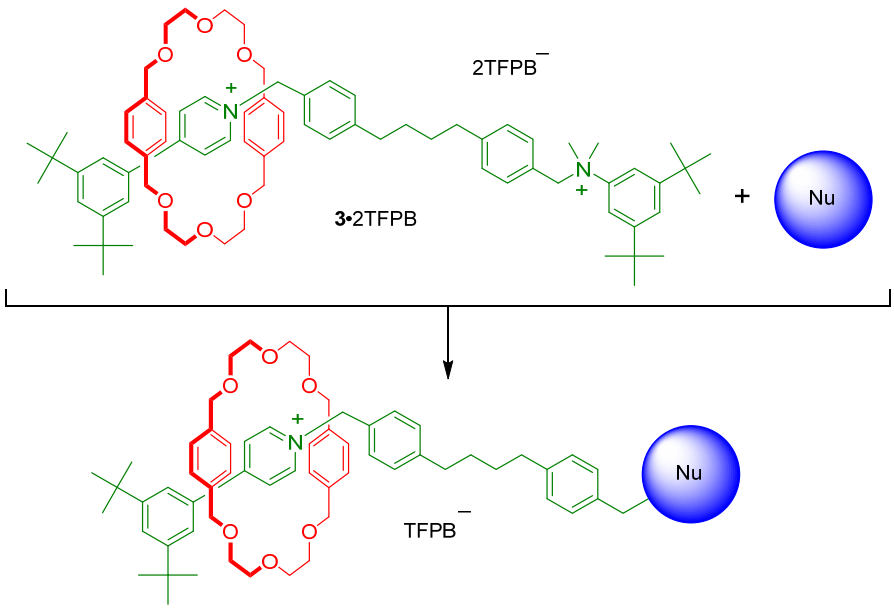


Pyridinium salt 1·TFPB: A solution of the pyridine derivative **S1**[1] (100 mg, 370 µmol), the dibromide **S2**[2] (296 mg, 750 µmol), and NaTFPB (331 mg, 370 µmol) in DMF (3.7 mL) was stirred at room temperature for 16 h. The solution was partitioned between EtOAc (3 × 20 mL) and H_2O (20 mL). The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was purified chromatographically (SiO_2; CH_2Cl_2/hexane, 5:1) to afford the salt **1**·TFPB as a pale-yellow oil (390 mg, 73%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 8.43 (d, *J* = 6.8 Hz, 2H), 8.14 (d, *J* = 6.8 Hz, 2H), 7.75 (t, *J* = 2.0 Hz, 1H), 7.68 (s, 8H), 7.53 (d, *J* = 2.0 Hz, 2H), 7.51 (s, 4H), 7.33–7.20 (m, 6H), 7.11 (d, *J* = 8.0 Hz, 2H), 5.53 (s, 2H), 4.46 (s, 2H), 2.66 (t, *J* = 6.8 Hz, 2H), 2.60 (t, *J* = 6.8 Hz, 2H), 1.66–1.60 (m, 4H), 1.34 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.7 (q, J_{CB} = 50 Hz), 160.2, 153.5, 146.3, 142.9, 142.2, 135.2, 134.8, 132.2, 130.3, 130.2, 129.0, 129.0 (q, *J* =31.3 Hz), 128.8, 128.3, 127.2, 125.6, 124.5 (q, J_{CF} =271 Hz), 122.1, 117.5, 64.5, 64.5, 35.3, 35.1, 33.8, 31.0, 30.7, 30.5; HR-MS (ESI): calcd for $[\mathbf{1}]^+$ $C_{37}H_{45}BrN^+$, *m*/*z* 582.2730; found 582.2707.



Surrogate rotaxane 3·2TFPB (through the ISEM): A solution of the pyridinium salt **1**·TFPB (1.45 g, 1.00 mmol) and BPX26C6[3] (418 mg, 1.00 mmol) in CH_2Cl_2 (10 mL) was concentrated. A solution of the aniline derivative **2**[4] (350 mg, 1.50 mmol, dissolved in a few drops of CH_2Cl_2) was added to the residue and then the solution was concentrated. After sitting at room temperature for 16 h, EtOAc (100 mL) and NaTFPB (886 mg, 1.00 mmol) were added sequentially to the greasy residue. The mixture was partitioned between EtOAc (3 × 100 mL) and H_2O (100 mL). The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was purified chromatographically (Diol-silica gel; CH_2Cl_2/hexane, 3:1) to afford the rotaxane **3**·2TFPB as a white solid (1.70 g, 61%). M.p. 74–75 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.95 (d, *J* = 6.8 Hz, 2H), 7.71 (s, 17H), 7.65–7.60 (m, 3H), 7.54 (s, 10H), 7.36–7.26 (m, 4H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 1.2 Hz, 2H), 6.69 (d, *J* = 8.0 Hz, 2H), 6.52 (s, 8H), 4.62 (s, 2H), 4.56 (s, 2H),) 4.14 (d, *J* = 10.0 Hz, 4H), 4.03 (d, *J* = 10.0 Hz, 4H), 3.74–3.60 (m, 16H), 3.43 (s, 6H), 2.66 (t, *J* = 7.4 Hz, 2H), 2.56 (t, *J* = 7.4 Hz, 2H), 1.68–1.54 (m, 4H), 1.45 (s, 18H), 1.25 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.7 (q, J_{CB} = 50 Hz), 154.9, 154.2, 152.4, 147.1, 145.0, 143.4, 142.6, 136.6, 134.8, 132.8, 131.7, 130.1, 129.3–128.4 (m), 129.3, 128.3, 126.5, 125.7, 124.8, 124.5 (q, J_{CF} = 271 Hz), 122.4, 121.9, 117.4, 113.8, 75.8, 73.4, 71.1, 70.2, 62.9, 52.6, 35.4, 35.3, 35.3, 35.1, 31.2, 31.1, 30.7, 30.6 (two signals were missing, possibly because of signal overlap); HR-MS (ESI): calcd for $[\mathbf{3}]^{2+}$ $C_{77}H_{104}N_2O_6^{2+}$, *m*/*z* 576.3942; found 576.3966.

Surrogate rotaxane 3·2TFPB (in solution): The aniline **2** (12.1 mg, 51.9 μmol) was added to a solution of the pyridinium salt **1**·TFPB (50.0 mg, 34.5 μmol) and BPX26C6 (14.4 mg, 34.5 μmol) in CH_2Cl_2 (0.35 mL) and then the mixture was stirred at room temperature for 16 h. After addition of EtOAc (20 mL) and NaTFPB (30.6 mg, 34.5 μmol), the mixture was partitioned between EtOAc (3 × 20 mL) and H_2O (20 mL). The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was purified chromatographically (Diol-silica gel; CH_2Cl_2/hexane, 3:1) to afford the rotaxane **3**·2TFPB as a white solid (31.4 mg, 32%).



Rotaxane 4·TFPB (from 3·2TFPB in solution): A solution of 3,5-di-*tert*-butylbenzylamine[5] (6.86 mg, 31.3 μmol) and the rotaxane **3**·2TFPB (30.0 mg, 10.4 μmol) in MeCN (100 μL) was stirred at 60 °C for 72 h. After evaporating the solvent under reduced pressure, the residue was purified chromatographically (NH-silica gel; CH_2Cl_2/hexane, 1:4) to afford the rotaxane **4**·TFPB (15.7 mg, 75%) and the surrogate stopper **2** (1.82 mg, 75%) as a pale-yellow oil and a colorless sticky oil, respectively. ^{1}H NMR (400 MHz, CD_3CN) δ = 8.09 (d, *J* = 6.4 Hz, 2H), 7.77–7.65 (m, 15H), 7.57 (s, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.36 (s, 1H), 7.18 (s, 2H), 7.15 (d, *J* = 7.6 Hz, 2H), 6.99 (d, *J* = 7.6 Hz, 2H), 6.52 (s, 8H), 4.93 (s, 2H), 4.16 (d, *J* = 10.0 Hz, 4H), 4.06 (d, *J* = 10.0 Hz, 4H), 3.80–3.62 (m, 20H), 2.74 (t, *J* = 6.8 Hz, 2H), 2.55 (t, *J* = 6.8 Hz, 2H), 1.66–1.59 (m, 4H), 1.50 (s, 18H) , 1.32 (s, 18H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ = 162.2 (q, J_{CB} = 50 Hz), 154.6, 152.8, 151.3, 151.0, 145.8, 144.0, 141.6, 141.4, 137.2, 135.3, 133.5, 130.7, 129.9, 129.3–128.4 (m), 129.2, 128.8, 128.7, 126.9, 125.4, 125.1 (q, J_{CF} = 271 Hz), 123.2, 122.9, 122.5, 121.4, 117.9, 73.8, 71.6, 70.8, 63.4, 57.9, 35.9, 35.8, 35.7, 35.5, 35.1, 31.6, 31.5, 31.4; HR-MS (ESI): calcd for $[\mathbf{4}]^+$ $C_{76}H_{101}N_2O_6^+$, *m*/*z* 1137.7654; found 1137.7687.

Rotaxane 4·TFPB (from 3·2TFPB through the ISEM): A solution of 3,5-di-*tert*-butylbenzylamine (6.90 mg, 31.5 μmol) and the rotaxane **3**·2TFPB (30.0 mg, 10.4 μmol) in MeCN (1 mL) was concentrated. After sitting at 60 °C for 72 h, EtOAc (20 mL) was added to the greasy residue. The mixture was partitioned between EtOAc (3 × 20 mL) and H_2O (20 mL). The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was purified chromatographically (NH-silica gel; CH_2Cl_2/hexane, 1:4) to afford the rotaxane **4**·TFPB as a pale-yellow oil (12.7 mg, 61%).

Rotaxane 4·TFPB (directly from 1·TFPB in solution): 3,5-Di-*tert*-butylbenzylamine (6.90 mg, 31.5 μmol) was added to a solution of the pyridinium salt **1**·TFPB (30.0 mg, 20.7 μmol) and BPX26C6 (8.60 mg, 20.7 μmol) in CH_2Cl_2 (0.21

mL) and then the mixture was stirred at room temperature for 16 h. EtOAc (20 mL) was added and then the mixture was partitioned between EtOAc (3 × 20 mL) and H_2O (20 mL). The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was purified chromatographically (NH-silica gel; CH_2Cl_2/hexane, 1:4) to afford the rotaxane **4**·TFPB as a pale-yellow oil (12.0 mg, 28%).

Rotaxane 4·TFPB (directly from 1·TFPB through the ISEM): A solution of the pyridinium salt **1**·TFPB (30.0 mg, 20.7 μmol) and BPX26C6 (8.60 mg, 20.7 mmol) in CH_2Cl_2 (1 mL) was concentrated. A solution of 3,5-di-*tert*-butylbenzylamine (6.90 mg, 31.5 μmol, dissolved in a few drops of CH_2Cl_2) was added to the residue and then the mixture was concentrated. After sitting at room temperature for 16 h, EtOAc (20 mL) was added to the greasy residue. The mixture was partitioned between EtOAc (3 × 20 mL) and H_2O (20 mL). The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was purified chromatographically (NH-silica gel; CH_2Cl_2/hexane, 1:4) to afford the rotaxane **4**·TFPB as a pale-yellow oil (15.1 mg, 38%).

Rotaxane 5·TFPB (from 3·2TFPB in solution): A solution of 3,5-bis(1,1-dimethylethyl)benzoic acid (17.1 mg, 73.0 μmol) and TBAOH (1M in MeOH, 73.0 μL) in MeOH (0.73 mL) was stirred for 3 min. After evaporating the solvent under reduced pressure, the rotaxane **3**·2TFPB (70.0 mg, 24.3 μmol) and MeCN (0.24 mL) were added to the residue and then the mixture was stirred at 60 °C for 8 h. After cooling to room temperature, the solvent was evaporated and the residue purified chromatographically (Diol-silica gel, CH_2Cl_2/hexane, 1:4) to afford the rotaxane **5**·TFPB (38.2 mg, 78%) and the surrogate stopper **2** (5.30 mg, 91%) as a pale-yellow oil and a colorless sticky oil, respectively. ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.93 (d, J = 6.8 Hz, 2H), 7.87 (d, J = 1.6 Hz, 2H), 7.70 (s, 9H), 7.63 (s, 1H), 7.60 (d, J = 6.8 Hz, 2H), 7.56–7.49 (m, 6H), 7.34−7.24 (m, 6H), 7.04 (d, J = 7.6 Hz, 2H), 6.52 (s, 8H), 5.26 (s, 2H), 4.61 (s, 2H), 4.14 (d, J = 9.6 Hz, 4H), 4.02 (d, J = 9.6 Hz, 4H), 3.70–3.60 (m, 16H), 2.69 (t, J = 7.2 Hz, 2H), 2.56 (t, J = 7.2 Hz, 2H), 1.68–1.55 (m, 4H), 1.45 (s, 18H), 1.31 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.1, 161.6 (q, J_{CB} = 50 Hz), 154.2, 152.4, 151.0, 145.2, 143.4, 142.0, 136.5, 134.7, 133.8, 132.8, 130.0, 129.4, 129.3, 129.3–128.4 (m), 129.0, 128.3, 128.2, 128.0, 127.2, 126.4, 124.7, 124.4 (q, J_{CF} = 272.5 Hz), 123.7, 121.8, 117.3, 73.4, 71.1, 70.2, 66.2, 62.9, 35.4, 35.3, 35.1, 34.8, 31.3, 31.2, 31.0, 30.7; HR-MS (ESI): calcd for $[\mathbf{5}]^{2+}$ $C_{76}H_{98}NO_8^+$, m/z 1152.7287; found 1152.7247.

Rotaxane 5·TFPB (directly from 1·TFPB through the ISEM): A solution of the pyridinium salt **1**·TFPB (30.0 mg, 20.7 μmol) and BPX26C6 (8.60 mg, 20.7 μmol) in CH_2Cl_2 (1 mL) was concentrated. A solution of TBA·3,5-di-*tert*-butylbenzoate (12.6 mg, 34.5 μmol, dissolved in a few drops of CH_2Cl_2) was added to the residue and then the solvent was evaporated. After sitting at room temperature for 16 h, EtOAc (20 mL) was added to the greasy residue. The mixture was partitioned between EtOAc (3 × 20 mL) and H_2O (20 mL). The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was purified chromatographically (Diol-silica gel, CH_2Cl_2/hexane, 1:4) to afford the rotaxane **5**·TFPB as a pale-yellow oil (9.10 mg, 22%).

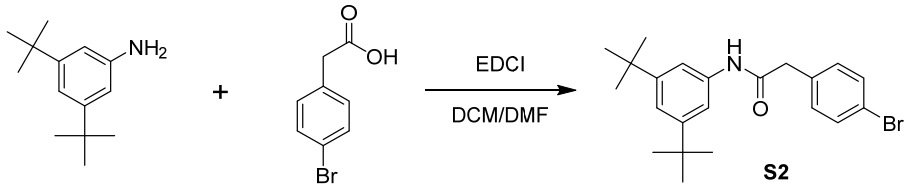
Rotaxane 5·TFPB (directly from 1·TFPB in solution): A solution of the pyridinium salt **1**·TFPB (30.0 mg, 20.7 μmol) and BPX26C6 (8.60 mg, 20.7 μmol) in CH_2Cl_2 (0.21 mL) was concentrated. TBA·3,5-di-*tert*-butylbenzoate (12.6 mg, 34.5 μmol) was added and then the mixture was stirred at room temperature for 16 h. EtOAc (20 mL) was added. The mixture was partitioned between EtOAc (3 × 20 mL) and H_2O (20 mL). The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was purified chromatographically (Diol-silica gel, CH_2Cl_2/hexane, 1:4) to afford the rotaxane **5**·TFPB as a pale-yellow oil (5.30 mg, 13%).

Rotaxane 6·TFPB: A solution of 3,5-bis(1,1-dimethylethyl)benzenemethanethiol[6] (38.3 mg, 162 μmol), the rotaxane **3**·2TFPB (150 mg, 52.0 μmol), and TBAOH (1 M in MeOH, 162 μL) in degassed MeCN (0.52 mL) was stirred at 60 °C for 3 h. After evaporating the solvent under reduced pressure, the residue was purified chromatographically (Diol-silica gel, CH_2Cl_2/hexane, 1:4) to afford the rotaxane **6**·TFPB (72.2 mg, 70%) and the surrogate stopper **2** (9.80 mg, 80%) as a pale-yellow oil and a colorless sticky oil, respectively. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 (d, *J* = 6.4 Hz, 2H), 7.71 (s, 9H), 7.61 (d, *J* = 6.4 Hz, 2H), 7.57–7.49 (m, 6H), 7.35–7.26 (m, 5H), 7.13–6.95 (m, 6H), 6.52 (s, 8H), 4.61 (s, 2H), 4.14 (d, *J* = 9.6 Hz, 4H), 4.03 (d, *J* = 9.6 Hz, 4H), 3.70–3.60 (m, 16H), 3.56 (s, 2H), 3.54 (s, 2H), 2.70 (t, *J* = 7.2 Hz, 2H), 2.55 (t, *J* = 7.2 Hz, 2H), 1.67–1.55 (m, 4H), 1.45 (s, 18H), 1.28 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.6 (q, J_{CB} = 50 Hz), 154.2, 152.4, 150.7, 145.3, 143.4, 140.8, 136.9, 136.5, 135.6, 134.7, 132.8, 130.1, 129.3, 129.0, 128.9–128.4 (m), 128.8, 128.2, 127.5, 127.4, 126.4, 124.8, 124.5 (q, J_{CF} = 271 Hz), 123.1, 120.9, 117.4, 73.4, 71.1, 70.2, 62.9, 36.3, 35.4, 35.4, 35.2, 35.1, 34.7, 31.3, 31.3, 31.0, 30.8; HR-MS (ESI): calcd for [**6**]$^+$ $C_{76}H_{100}NO_6S^+$, *m*/*z* 1154.7266; found 1154.7244.

Rotaxane 7·TFPB: A solution of 3,5-di-*tert*-butylphenol (2.1 mg, 10 μmol) and TBAOH (1 M in MeOH, 10 μL) in MeOH (0.01 mL) was stirred for 3 min. After evaporating the solvent under reduced pressure, MeCN (0.07 mL) and the rotaxane **3**·2TFPB (20 mg, 6.9 μmol) were added to the residue and then the mixture was stirred at 60 °C for 6 h. The solvent was evaporated under reduced pressure and the residue purified chromatographically (Diol-silica gel, CH_2Cl_2/hexane, 1:4) to afford the rotaxane **7**·TFPB (8.90 mg, 64%) and the surrogate stopper **2** (1.30 mg, 80%) as a pale-yellow oil and a colorless sticky oil, respectively. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.93 (d, *J* = 6.4 Hz, 2H), 7.70 (s, 9H), 7.60 (d, *J* = 6.4 Hz, 2H), 7.55–7.48 (m, 6H), 7.34–7.22 (m, 6H), 7.06 (s, 1H), 7.02 (d, *J* = 7.2 Hz, 2H), 6.76 (s, 2H), 6.52 (s, 8H), 4.93 (s, 2H), 4.61 (s, 2H), 4.14 (d, *J* = 9.6 Hz, 4H), 4.03 (d, *J* = 9.6 Hz, 4H), 3.70–3.60 (m, 16H), 2.70 (t, *J* = 6.8 Hz, 2H), 2.57 (t, *J* = 6.8 Hz, 2H), 1.70–1.58 (m, 4H), 1.44 (s, 18H), 1.26 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.7 (q, J_{CB} = 50 Hz), 158.5, 154.2, 152.5, 152.2, 145.3, 143.5, 142.0, 136.6, 134.8, 134.7, 132.9, 130.1, 129.4, 129.1, 129.1–128.4 (m), 129.0, 128.5, 128.4, 127.9, 126.5, 124.9, 124.6 (q, J_{CF} = 271 Hz), 121.9, 117.4, 115.2, 109.0, 73.5, 71.2, 70.3, 69.9, 63.0, 35.5, 35.4, 35.2, 35.0, 31.4, 31.1, 30.8; HR-MS (ESI): calcd for [**7**]$^+$ $C_{75}H_{98}NO_7^+$, *m*/*z* 1124.7338; found 1124.7363.

Rotaxane 8·TFPB: A mixture of dibenzyl malonate[7] (44.4 mg, 160 μmol) and K_2CO_3 (28.1 mg, 200 μmol) in DMSO (0.52 mL) was stirred at room temperature for 3 min. After adding the rotaxane **3**·2TFPB (150 mg, 52.0 μmol), the mixture was stirred at 60 °C for 24 h. The mixture was partitioned between EtOAc (3 × 100 mL) and H_2O (100 mL). The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was purified chromatographically (Diol-silica gel; CH_2Cl_2/hexane,1:4) to afford the [2]rotaxane **8**·TFPB (47.5 mg, 44%) and its derived [3]rotaxane **S1**·TFPB (15.2 mg, 16%) as light-yellow oils and the surrogate stopper **2** (10.91 mg, 90%) as a sticky oil. ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.93 (d, *J* = 6.0 Hz, 2H), 7.69 (s, 9H), 7.59 (d, *J* = 6.0 Hz, 2H), 7.56–7.46 (m, 6H), 7.34–7.21 (m, 10H), 7.21–7.12 (m, 4H), 6.96 (d, *J* = 7.8 Hz, 2H), 6.91 (d, *J* = 7.8 Hz, 2H), 6.51 (s, 8H), 5.08–4.97 (m, 4H), 4.59 (s, 2H), 4.14 (d, *J* = 9.6 Hz, 4H), 4.02 (d, *J* = 9.6 Hz, 4H), 3.71–3.60 (m, 17H), 3.12 (d, *J* = 8.0 Hz, 2H), 2.68 (t, *J* = 6.8 Hz, 2H), 2.51 (t, *J* = 6.8 Hz, 2H), 1.63–1.51 (m, 4H), 1.44 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.5, 161.6 (q, J_{CB} = 50 Hz), 154.2, 152.4, 145.3, 143.4, 140.5, 136.5, 135.1, 134.8, 134.7, 132.8, 130.0 129.3, 129.3−128.4(m), 128.6, 128.4, 128.3, 128.2, 128.0, 126.4, 124.8, 124.5 (q, J_{CF} = 271 Hz), 121.8, 117.3, 73.4, 71.1, 70.2, 67.1, 62.9, 53.8, 35.4, 35.2, 35.1, 34.2, 31.3, 31.0, 30.7 (two signals were missing, possibly because of signal overlap); HR-MS (ESI): calcd for $[\mathbf{8}]^+$ $C_{78}H_{92}NO_{10}^+$, *m*/*z* 1202.6716; found 1202.6711.

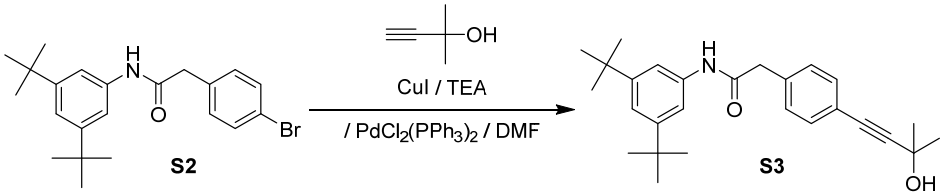
Data for [3]rotaxane **S1**·TFPB: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.02 (d, *J* = 6.8 Hz, 4H), 7.82–7.77 (m, 18H), 7.69 (d, *J* = 6.8 Hz, 4H), 7.62 (s, 8H), 7.60 (d, *J* = 1.6 Hz, 4H), 7.42–7.37 (m, 14H), 7.22–7.16 (m, 4H), 7.06–7.00 (m, 8H), 6.60 (s, 16H), 5.01 (s, 4H), 4.69 (s, 4H), 4.22 (d, *J* = 9.6 Hz, 8H), 4.11 (d, *J* = 9.6 Hz, 8H), 3.84–3.66 (m, 36H), 3.20 (s, 4H), 2.77 (t, *J* = 7.2 Hz, 4H), 2.61 (t, *J* = 7.2 Hz, 4H), 1.76–1.66 (m, 8H), 1.53 (s, 36H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 170.4, 161.6 (q, J_{CB} = 50 Hz), 154.1, 152.2, 145.2, 143.4, 141.1, 136.7, 135.1, 134.7, 133.3, 132.9, 130.1, 130.0, 129.3–128.4 (m), 129.3, 128.3, 128.2, 128.2, 128.0, 126.4, 124.9, 124.5 (q, J_{CF} = 271 Hz), 122.0, 117.4, 73.3, 71.1, 70.2, 66.9, 62.9, 60.5, 38.6, 35.4, 35.2, 35.0, 31.2, 31.1, 30.9 (two signals were missing, possibly because of signal overlap); HR-MS (ESI): calcd for $[M]^{2+}$ $C_{139}H_{168}N_2O_{16}^{2+}$, *m*/*z* 1060.6191; found 1060.6189.



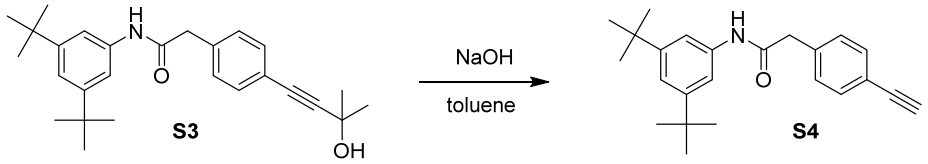
S2

Amide S2: EDCI (933 mg, 4.87 mmol) was added to a solution of 4-bromophenylacetic acid (1.05 g, 4.87 mmol) in CH_2Cl_2 (40 mL) and DMF (40 mL) at 0 °C. After stirring at 0 °C for 15 min, 3,5-di-*tert*-butylaniline (500 mg, 2.47 mmol) was added and then the mixture was stirred at room temperature for 6 h. The mixture was partitioned between EtOAc (100 mL) and 1 M HCl (100 mL). The organic phase was washed with $NaHCO_3$ (2 × 100 mL), dried ($MgSO_4$), and concentrated. The residue was purified chromatographically (SiO_2; EtOAc/hexane, 1:9) to afford the amide **S2** as a white solid (868 mg, 87%). M.p. = 229–230 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.50 (d, *J* = 8.4 Hz, 2H), 7.27 (s, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.16 (s,

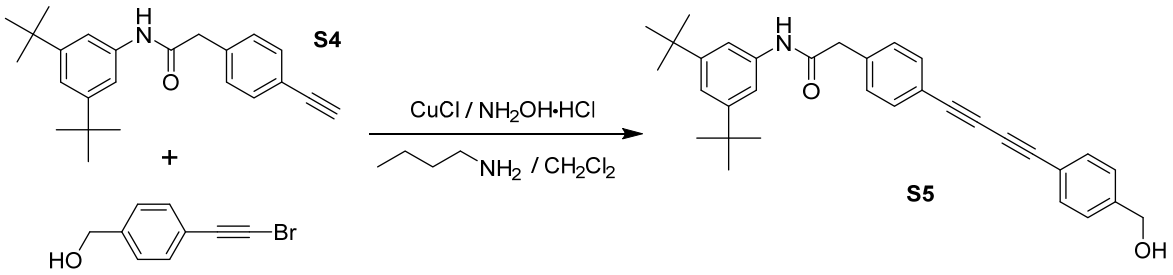
1H), 7.01 (br, 1H), 3.66 (s, 2H), 1.28 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.1, 151.6, 136.8, 133.4, 132.0, 131.1, 121.4, 118.7, 114.4, 44.0, 34.8, 31.3; HR-MS (ESI): calcd for [**S2** + H]$^+$ $C_{22}H_{29}BrNO^+$, *m*/*z* 402.1427; found 402.1429.



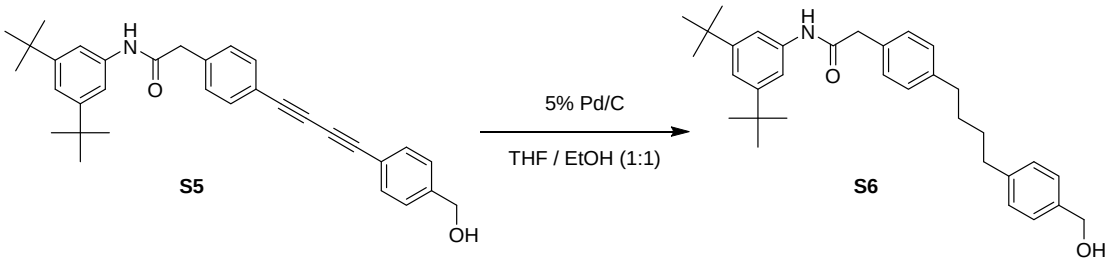
Alcohol S3: Degassed TEA (1.26 g, 124 mmol) was added to a mixture of the amide **S2** (5.00 g, 12.4 mmol), CuI (118 mg, 620 μmol), and $PdCl_2(PPh_3)_2$ (436 mg, 620 μmol) in degassed DMF (62 mL). After stirring at room temperature for 5 min, 2-methyl-3-butyn-2-ol (3.10 g, 37.2 mmol) was added and then the mixture was heated at 70 °C for 16 h. After cooling to room temperature, the mixture was partitioned between EtOAc (100 mL) and H_2O (3 × 100 mL). The organic phase was dried ($MgSO_4$) and concentrated. The residue was purified chromatographically (SiO_2; EtOAc/hexane, 1:3) to afford the amide **S3** as a white solid (4.50 g, 89%). M.p. = 209–210 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.32 (s, 2H), 7.21 (s, 1H), 7.14 (br, 1H), 3.72 (s, 2H), 2.11 (s, 1H), 1.63 (s, 6H), 1.33 (s, 18H); ^{13}C NMR (100MHz, $CDCl_3$) δ = 168.8, 151.5, 137.1, 134.8, 132.1, 129.3, 121.8, 118.6, 114.5, 94.2, 81.6, 65.5, 44.4, 34.8, 31.4, 31.3; HR-MS (ESI): calcd for [**S3** + H]$^+$ $C_{27}H_{36}NO_2^+$, *m*/*z* 406.2741; found 406.2743.



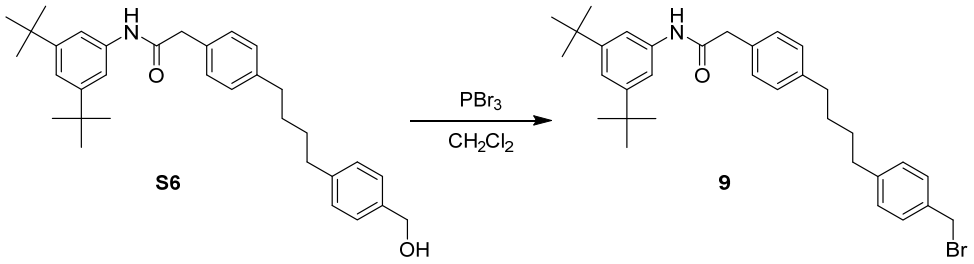
Alkyne S4: A mixture of the amide **S3** (294 mg, 0.725 mmol) and NaOH (58.0 mg, 1.45 mmol) in toluene (24 mL) was heated at 110 °C for 2 h. After cooling to room temperature, the mixture was partitioned between EtOAc (50 mL) and H_2O (3 × 50mL). The organic phase was dried ($MgSO_4$) and concentrated. The solid residue was washed with hexane to afford the alkyne **S4** as pale-yellow solid (141 mg, 56%). M.p. = 208.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.50 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.26 (s, 2H), 7.15 (s, 1H), 6.98 (br, 1H), 3.70 (s, 2H), 3.08 (s, 1H), 1.27 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.3, 151.6, 136.9, 135.3, 132.6, 129.4, 121.2, 118.7, 114.4, 83.1, 77.6, 44.5, 34.8, 31.3; HR-MS (ESI): calcd for [**S4** + H]$^+$ $C_{24}H_{30}NO^+$, *m*/*z* 348.2322; found 348.2328.



Alcohol S5: CuCl (12.5 mg, 127 μmol) and $NH_2OH{\cdot}HCl$ (26.4 mg, 38.0 μmol) were mixed in *n*-$BuNH_2$ (1.9 mL) and deionized water (4.5 mL). After adding a solution of the alkyne **S4** (441 mg 1.27 mmol) in CH_2Cl_2 (5.6 mL), the mixture was stirred at 0 °C for 5 min. A solution of 4-(2-bromoethynyl)benzenemethanol[8] (295 mg, 1.39 mmol) in CH_2Cl_2 (2.8 mL) was added to the mixture via syringe pump over a period of 1 h. The mixture was stirred at room temperature for 2 h before adding saturated $NH_4Cl_{(aq)}$ (50 mL) and partitioning between CH_2Cl_2 (50 mL) and H_2O (3 × 50 mL). The organic phase was dried ($MgSO_4$) and concentrated. The residue was purified chromatographically (SiO_2; EtOAc/hexane, 1:3) to afford the alcohol **S5** as a white solid (405 mg, 67%). M.p. = 210–211 °C; ^{1}H NMR (400 MHz, CD_3SOCD_3) δ = 10.09 (s, 1H), 7.61–7.55 (m, 4H), 7.49 (s, 2H), 7.44–7.35 (m, 4H), 7.10 (s, 1H), 5.33 (t, *J* = 5.6 Hz, 1H), 4.55 (d, *J* = 5.6 Hz, 2H), 3.69 (s, 2H), 1.26 (s, 18H); ^{13}C NMR (100 MHz, CD_3SOCD_3) δ = 168.6, 151.0, 145.2, 139.0, 138.6, 132.7, 132.6, 130.1, 127.0, 119.0, 118.9, 117.4, 113.8, 82.4, 82.0, 73.9, 73.5, 62.8, 43.6, 34.9, 31.6; HR-MS (ESI): calcd for [**S5** + H]$^+$ $C_{33}H_{36}NO_2^+$, *m*/*z* 478.2741; found 478.2729.



Alcohol S6: Pd/C (5%, 90 mg) was added to a solution of the alcohol **S4** (405 mg, 848 μmol) in THF/EtOH (1:1, 42 mL). The mixture was purged with H_2 for 15 min and then stirred under a H_2 atmosphere at room temperature for 45 min. The mixture was filtered through Celite and the filtrate concentrated under reduced pressure. The residue was purified chromatographically (SiO_2; EtOAc/hexane, 1:7) to afford the alcohol **S6** as a white solid (386 mg, 94%). M.p. = 162–163 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.25–7.18 (m, 6H), 7.17–7.10(m, 5H) 7.06 (s, 1H), 4.57 (s, 2H), 3.60 (s, 2H), 2.64–2.56 (m, 4H), 1.64–1.59 (m, 4H), 1.24 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 169.8, 151.5, 141.7, 141.5, 138.4, 137.4, 132.1, 129.4, 129.0, 128.5, 127.1, 118.5, 114.7, 64.9, 44.2, 35.4, 35.4, 31.4, 31.1, 30.9, 30.4; HR-MS (ESI): calcd for [**S6** + Na]$^+$ $C_{33}H_{43}NNaO_2^+$, *m*/*z* 508.3186; found 508.3167.



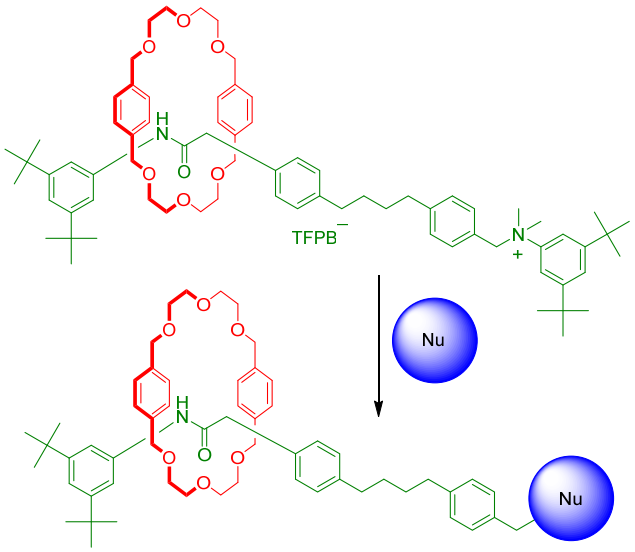
Amide 9: PBr_3 (520 mg, 1.92 mmol) was added to a solution of the alcohol **S6** (888 mg, 1.83 mmol) in CH_2Cl_2 (18.3 mL) at 0 °C and then the mixture was stirred at room temperature for 16 h. After partitioning between CH_2Cl_2 (2 × 100 mL) and H_2O (100 mL), the combined organic phases were dried ($MgSO_4$) and concentrated. The residue was purified chromatographically (SiO_2; EtOAc/hexane, 1:19) to afford the amide **9** as a white solid (926 mg, 92%). M.p. = 163–164 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.28–7.17 (m, 6H), 7.17–7.08 (m, 5H), 7.06 (s, 1H), 4.46 (s, 2H), 3.60 (s, 2H), 2.68–2.53 (m, 4H), 1.68–1.58 (m, 4H), 1.24 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 169.6, 151.5, 142.9, 141.5, 137.4, 135.1, 132.1, 129.4, 129.0, 129.0, 128.8, 118.5, 114.6, 44.31, 35.5, 35.4, 34.9, 33.8, 31.4, 31.0, 30.8; HR-MS (ESI): calcd for $[\mathbf{9} + H]^+$ $C_{33}H_{43}BrNO^+$, *m*/*z* 548.2523; found 548.2516.

Surrogate rotaxane 10·TFPB (through the ISEM, 2 equiv. of BPX26C6 and NaTFPB): A solution of the amide **9** (17.8 mg, 32.4 μmol), BPX26C6 (27.0 mg, 64.8 μmol), and NaTFPB (57.4 mg, 64.8 μmol) in CH_2Cl_2 (1 mL) was concentrated. The aniline derivative **2** (11.4 mg, 48.8 μmol, dissolved in a few drops of CH_2Cl_2) was added to the residue and then the solvent was evaporated. After sitting at room temperature for 16 h, EtOAc (20 mL) was added to the greasy residue. The mixture was partitioned between EtOAc (3 × 20 mL) and H_2O (20 mL). The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was purified chromatographically (Diol-silica gel; CH_2Cl_2/hexane, 1:2) to afford the rotaxane **10**·TFPB as a white solid. (27.7 mg, 43%). M.p. = 102–103 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.70 (s, 9H), 7.53 (s, 4H), 7.34 (d, *J* = 1.6 Hz, 2H), 7.27–7.12 (m, 10H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.70–6.55 (br, 8H), 4.20–4.10 (m, 8H), 3.95–3.80 (m, 4H), 3.67–3.44 (m, 14H), 3.03 (s, 2H), 2.79–2.62 (m, 4H), 2.01 (s, 6H), 1.76–1.65 (m, 4H), 1.55 (s, 18H), 1.26 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 169.2, 161.6 (q, J_{CB} = 50 Hz), 152.3, 151.6, 146.8, 144.8, 141.5, 137.1, 136.8, 134.7, 133.5, 131.9, 130.1, 129.4, 129.3–128.4 (m), 129.0, 128.5, 125.5, 124.4 (q, J_{CF} = 271 Hz), 123.8, 118.6, 117.4, 117.0 114.4, 73.8, 72.0, 70.5, 68.0, 50.1, 44.3, 35.8, 35.5, 35.2, 34.8, 31.6, 31.2, 31.0, 30.6; HR-MS (ESI): calcd for $[\mathbf{10}]^+$ $C_{73}H_{101}N_2O_7^+$, *m*/*z* 1117.7603; found 1117.7604.

Surrogate rotaxane 10·TFPB (through the ISEM, 1 equiv. of BPX26C6 and NaTFPB): A solution of the amide **9** (243 mg, 442 μmol), BPX26C6 (184 mg, 442 μmol), and NaTFPB (392 mg, 442 μmol) in CH_2Cl_2 (5 mL) was concentrated. The aniline derivative **2** (155 mg, 663 μmol, dissolved in a few drops of CH_2Cl_2) was added to the residue and then the solvent was evaporated. After sitting at room temperature for 16 h, EtOAc (50 mL) was added to the greasy residue. The mixture was partitioned between EtOAc (3 × 50 mL) and H_2O (50 mL). The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was purified

chromatographically (Diol-silica gel; CH_2Cl_2/hexane, 1:2) to afford the rotaxane **10**·TFPB as a white solid (216 mg, 25%).

Surrogate rotaxane 10·TFPB (in solution): The bulky aniline **2** (12.6 mg, 54.0 μmol) was added to a solution of the amide **9** (20.0 mg, 36.4 μmol), BPX26C6 (15.2 mg, 36.4 μmol), and NaTFPB (32.3 mg, 36.4 μmol) in CH_2Cl_2 (0.36 mL). After stirring at room temperature for 16 h, EtOAc (20 mL) was added. The mixture was partitioned between EtOAc (3 × 20 mL) and H_2O (20 mL). The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was purified chromatographically (Diol-silica gel; CH_2Cl_2/hexane, 1:2) to afford the rotaxane **10**·TFPB as a white solid (10.0 mg, 14%).



Rotaxane 11 (from 10·TFPB in solution): A solution of 3,5-di-*tert*-butylbenzylamine (33.2 mg, 150 μmol) and the rotaxane **10**·TFPB (100 mg, 50.0 μmol) in MeCN (0.5 mL) was stirred at 60 °C for 72 h. After evaporating the solvent under reduced pressure, the residue was purified chromatographically (NH-silica gel; EA/hexane, 1:7) to afford the rotaxane **11** (54.6 mg, 98%) and the surrogate stopper **2** (10.2 mg, 90%) as a light-yellow oil and a colorless sticky oil, respectively. ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.94 (s, 1H), 7.46 (d, *J* = 2.0 Hz, 2H), 7.28 (t, *J* = 2.0 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 2.0 Hz, 2H), 7.10–7.07 (m, 3H), 6.90 (s, 8H), 6.85 (d, *J* = 8.0 Hz, 2H), 6.48 (d, *J* = 8.0 Hz, 2H), 4.26–4.18 (m, 8H), 3.70 (s, 4H), 3.53–3.41 (m, 16H), 2.80 (s, 2H), 2.52 (t, *J* = 7.2 Hz, 2H), 2.44 (t, *J* = 7.2 Hz, 2H), 1.55–1.40 (m, 4H), 1.36 (s, 18H), 1.29 (s, 18H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ = 167.3, 150.6, 150.6, 141.5, 140.0, 139.6, 137.8, 137.2, 132.8, 129.9, 128.3, 128.1, 127.5, 127.4, 122.3, 120.8, 115.9, 113.5, 73.0, 72.5, 70.4, 69.5, 69.0, 42.1, 35.3, 35.2, 34.8, 34.6, 31.3, 31.2, 31.2, 29.6 (one signal was missing, possibly because of signal overlap); HR-MS (ESI): calcd for [**11** + H]$^+$ $C_{72}H_{99}N_2O_7^+$, *m*/*z* 1103.7447; found 1103.7468.

Rotaxane 11 (directly from 9 through the ISEM): A solution of the amide **9** (15.0 mg, 27.3 μmol), BPX26C6 (11.4 mg, 27.3 μmol), and NaTFPB (24.2 mg, 27.3 μmol)

in CH_2Cl_2 (1 mL) was concentrated. 3,5-Di-*tert*-butylbenzylamine (8.99 mg, 41.0 μmol, dissolved in a few drops of CH_2Cl_2) was added to the residue and then the organic solvent was evaporated. After sitting at room temperature for 16 h, EtOAc (20 mL) was added to the greasy residue. The mixture was partitioned between EtOAc (3 × 20 mL) and H_2O (20 mL). The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was purified chromatographically (NH-silica gel; EA/hexane, 1:7) to afford the rotaxane **11** as a light-yellow oil (4.40 mg, 15%).

Rotaxane 11 (directly from 9 in solution): 3,5-Di-*tert*-butylbenzylamine (8.99 mg, 41.0 μmol) was added to a solution of the amide **9** (15.0 mg, 27.3 μmol), BPX26C6 (11.4 mg, 27.3 μmol), and NaTFPB (24.2 mg, 27.3 μmol) in CH_2Cl_2 (0.27 mL) and then the mixture was stirred at room temperature for 16 h. EtOAc (20 mL) was added. The mixture was partitioned between EtOAc (3 × 20 mL) and H_2O (20 mL). The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was purified chromatographically (NH-silica gel; EA/hexane, 1:7) to afford the rotaxane **11** as a light-yellow oil (1.60 mg, 5%).

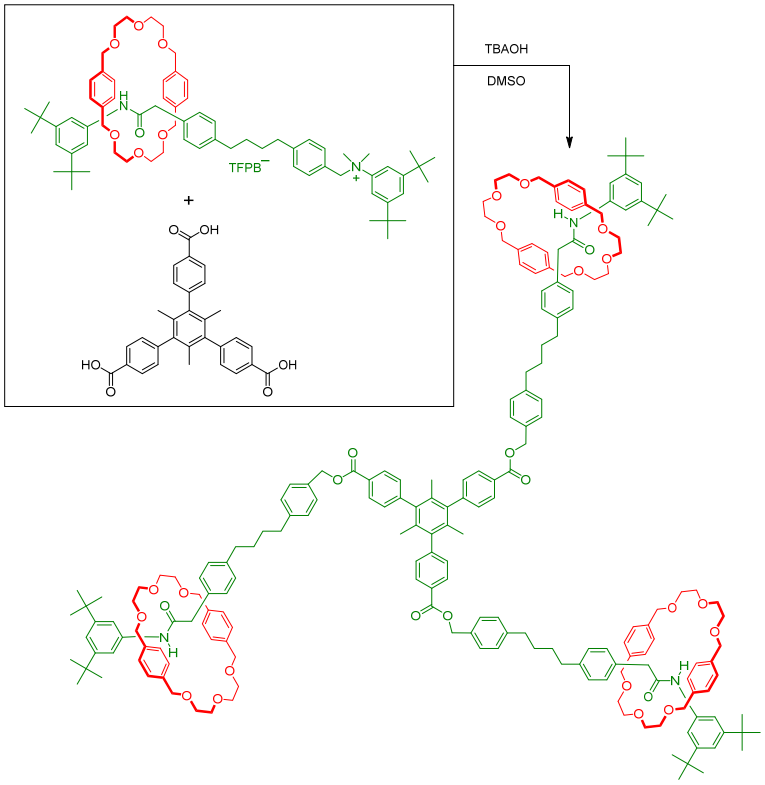
Rotaxane 12: A solution of 3,5-bis(1,1-dimethylethyl)benzoic acid (28.4 mg, 121 μmol) and TBAOH (1 M in MeOH, 121 μL) in MeOH (1.21 mL) was stirred for 3 min. After evaporating the solvent under reduced pressure, the rotaxane **10**·TFPB (80.0 mg, 40.0 μmol) and MeCN (0.4 mL) were added and then the mixture was stirred at 60 °C for 8 h. After cooling to room temperature, the solvent was evaporated and the residue purified chromatographically (SiO_2, EA/hexane, 1:7) to afford the rotaxane **12** (42.9 mg, 97%) and the surrogate stopper **2** (8.80 mg, 94%) as a pale-yellow oil and a colorless sticky oil, respectively. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.97–7.87 (m, 3H), 7.62 (t, *J* = 2.0 Hz, 1H), 7.47 (d, *J* = 1.6 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.09 (s, 1H), 6.93 (s, 8H), 6.89 (d, *J* = 7.6 Hz, 2H), 6.53 (d, *J* = 7.6 Hz, 2H), 5.34 (s, 2H), 4.33–4.19 (m, 8H), 3.62–3.41 (m, 16H), 2.87 (s, 2H), 2.53 (t, *J* = 7.2 Hz, 2H), 2.44 (t, *J* = 7.2 Hz, 2H), 1.54–1.44 (m, 4H), 1.39 (s, 18H), 1.33 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.2, 167.2, 151.0, 150.6, 142.9, 140.0, 139.7, 137.0, 133.5, 132.8, 130.0, 129.6, 128.6, 128.4, 128.0, 127.6, 127.1, 123.9, 115.8, 113.4, 73.2, 70.5, 68.9, 66.4, 42.1, 35.5, 35.3, 35.0, 34.9, 31.7, 31.3, 31.3, 31.0; HR-MS (ESI): calcd for [**12** + H]$^+$ $C_{72}H_{96}NO_9^+$, *m*/*z* 1118.7080; found 1118.7029.

Rotaxane 13: A solution of 3,5-bis(1,1-dimethylethyl)benzenemethanethiol (7.16 mg, 30.0 μmol), the rotaxane **10**·TFPB (20.0 mg, 10.0 μmol), and TBAOH (1 M in MeOH, 30 μL) in degassed MeCN (0.1 mL) was stirred at 60 °C for 3 h. After evaporating the organic solvent under reduced pressure, the residue was purified chromatographically (SiO_2, EA/hexane, 1:8) to afford the rotaxane **13** (10.4 mg, 93%) and the surrogate stopper **2** (1.94 mg, 83%) as a pale-yellow oil and a colorless sticky oil, respectively. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.96 (s, 1H), 7.48 (s, 2H), 7.30 (s, 1H), 7.22–7.09 (m, 7H), 6.94 (s, 8H), 6.89 (d, *J* = 7.6 Hz, 2H), 6.52 (d, *J* = 7.6 Hz, 2H), 4.33–4.23 (m, 8H), 3.64–3.42 (m, 20H), 2.85 (s, 2H), 2.54 (t, *J* = 6.8 Hz, 2H), 2.46 (t, *J* = 6.8 Hz, 2H), 1.60–1.45 (m, 4H), 1.40 (s, 18H), 1.33 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.0, 150.7, 150.6, 141.4, 140.0, 139.7, 137.1, 137.0, 135.4, 132.8, 130.0, 128.8, 128.5, 128.3, 127.5, 123.2, 120.8, 115.6, 113.3, 73.2, 70.5, 68.9, 42.0, 36.2, 35.4, 35.4,

35.3, 34.9, 34.7, 31.7, 31.4, 31.3, 31.0; HR-MS (ESI): calcd for [**13** + H]$^+$ $C_{72}H_{98}NO_7S^+$, *m*/*z* 1120.7059; found 1120.7103.

Rotaxane 14: A solution of 3,5-di-*tert*-butylphenol (12.5 mg, 60.0 μmol) and TBAOH (1 M in MeOH, 60.0 μL) in MeOH (0.6 mL) was stirred for 3 min. After evaporating the solvent under reduced pressure, MeCN (0.4 mL) and the rotaxane **10**·TFPB (80.0 mg, 40.0 μmol) were added to the residue and then the mixture was stirred at 60 °C for 6 h. The solvent was evaporated under reduced pressure and the residue was purified chromatographically (SiO_2, EA/hexane, 1:6) to afford the rotaxane **14** (40.5 mg, 93%) and the surrogate stopper **2** (7.20 mg, 78%) as a pale-yellow oil and a colorless sticky oil, respectively. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92 (s, 1H), 7.47 (d, *J* = 1.6 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.10 (s, 1H), 7.02 (s, 1H), 6.93 (s, 8H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 1.6 Hz, 2H), 6.56 (d, *J* = 8.0 Hz, 2H), 4.96 (s, 2H), 4.32–4.22 (m, 8H), 3.60–3.44 (m, 16H), 2.89 (s, 2H), 2.56 (t, *J* = 7.2 Hz, 2H), 2.46 (t, *J* = 7.2 Hz, 2H), 1.58–1.48 (m, 4H), 1.39 (s, 18H), 1.31 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.1, 158.5, 152.0, 150.6, 142.5, 140.0, 139.6, 137.0, 134.5, 132.7, 130.0, 128.5, 128.3, 127.9, 127.6, 115.8, 114.9, 113.4, 109.1, 73.2, 70.5, 69.8, 68.9, 42.1, 35.4, 35.3, 34.9, 31.6, 31.4, 31.2, 31.0 (one signal was missing, possibly because of signal overlap); HR-MS (ESI): calcd for [**14** + H]$^+$ $C_{71}H_{96}NO_8^+$, *m*/*z* 1090.7130; found 1090.7078.

Rotaxane 15: A mixture of dibenzyl malonate (17.2 mg, 0.06 mmol) and K_2CO_3 (10.8 mg, 7.81 μmol) in DMSO (0.4 mL) was stirred at room temperature for 3 min. After adding the rotaxane **10**·TFPB (80 mg, 0.04 mmol), the mixture was stirred at 60 °C for 24 h. The mixture was partitioned between EtOAc (3 × 100 mL) and H_2O (100 mL). The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was purified chromatographically (Diol-silica gel; CH_2Cl_2/hexane, 1:4) to afford the [2]rotaxane **15** (22.6 mg, 48%) and surrogate stopper **2** (8.90 mg, 95%) as a pale-yellow oil and a colorless sticky oil, respectively. ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.95 (s, 1H), 7.46 (d, *J* = 2.0 Hz, 2H), 7.34–7.24 (m, 6H), 7.22–7.16 (m, 4H), 7.09 (t, *J* = 2.0 Hz, 1H), 7.03 (s, 4H), 6.90 (s, 8H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.47 (d, *J* = 8.8 Hz, 2H), 5.13–5.00 (m, 4H), 4.30–4.15 (m, 8H), 3.72 (t, *J* = 7.6 Hz, 1H), 3.57–3.39 (m, 16H), 3.16 (d, *J* = 7.6 Hz, 2H), 2.78 (s, 2H), 2.48 (t, *J* = 7.2 Hz, 2H), 2.42 (t, *J* = 7.2 Hz, 2H), 1.49–1.44 (m, 4H), 1.37 (s, 18H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ = 168.4, 167.1, 150.5, 141.4, 139.9, 139.8, 137.2, 135.4, 134.7, 132.8, 129.9, 128.5, 128.3, 128.2, 128.1, 128.0, 127.3, 115.7, 113.4, 73.0, 70.4, 68.9, 66.9, 42.0, 35.2, 34.8, 34.2, 31.5, 31.3, 31.3, 31.0, 30.4; (one signal was missing, possibly because of signal overlap) HR-MS (ESI): calcd for [**15** + H]$^+$ $C_{74}H_{90}NO_{11}^+$, *m*/*z* 1168.6508; found 1168.6485.



Rotaxane 17: A solution of 4,4′,4′′-(2,4,6-trimethylbenzene-1,3,5-triyl)tribenzoic acid (**16**)[9] (3.4 mg, 7.1 µmol) and TBAOH (1 M in MeOH, 21.4 µL) in MeOH (0.1 mL) was concentrated to afford a solid, which was washed with EtOAc (3 × 10 mL), dried under vacuum, and dissolved in DMSO (2.5 mL). The rotaxane **10**·TFPB (50 mg, 25 µmol) was added and the mixture stirred at 60 °C for 36 h. The mixture was partitioned between CH_2Cl_2 (3 × 20 mL) and H_2O (20 mL). The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was purified chromatographically (SiO_2, EA/hexane, 1:1) to afford the rotaxane **17** as a colorless oil (15.8 mg, 71%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 8.15 (d, *J* = 8.0 Hz, 6H), 7.96 (s, 3H), 7.51 (s, 6H), 7.38 (d, *J* = 8.0 Hz, 6H), 7.32 (d, *J* = 8.0 Hz, 6H), 7.23 (d, *J* = 8.0 Hz, 6H), 7.16 (s, 3H), 7.04–6.87 (m, 30H), 6.59 (d, *J* = 7.6 Hz, 6H), 5.31 (s, 6H), 4.34–4.24 (m, 24H), 3.62–3.47 (m, 48H), 2.91 (s, 6H), 2.59 (t, *J* = 6.8 Hz, 6H), 2.50 (t, *J* = 6.8 Hz, 6H), 1.69 (s, 9H), 1.58–1.50 (m, 12H), 1.43 (s, 54H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ = 167.2, 166.0, 150.6, 146.7, 142.9, 140.0, 139.6, 139.0, 137.1, 133.3, 132.7, 132.4, 129.8, 129.4, 128.7, 128.4, 128.2, 128.1, 127.5, 115.9, 113.5, 72.9, 70.4, 68.9, 66.5, 42.1, 35.3, 35.2, 34.8, 31.3, 31.2, 31.0, 18.9. (one signal was missing, possibly because of signal overlap) HR-MS (ESI): calcd for [**17** + 2H]$^{2+}$ $C_{201}H_{245}N_3O_{27}^{2+}$, *m*/*z* 1566.3940; found 1566.3865.

Reference

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Figure S1 ^{1}H NMR Spectrum (400 MHz / CD_2Cl_2 / 298 K) of **1**·TFPB

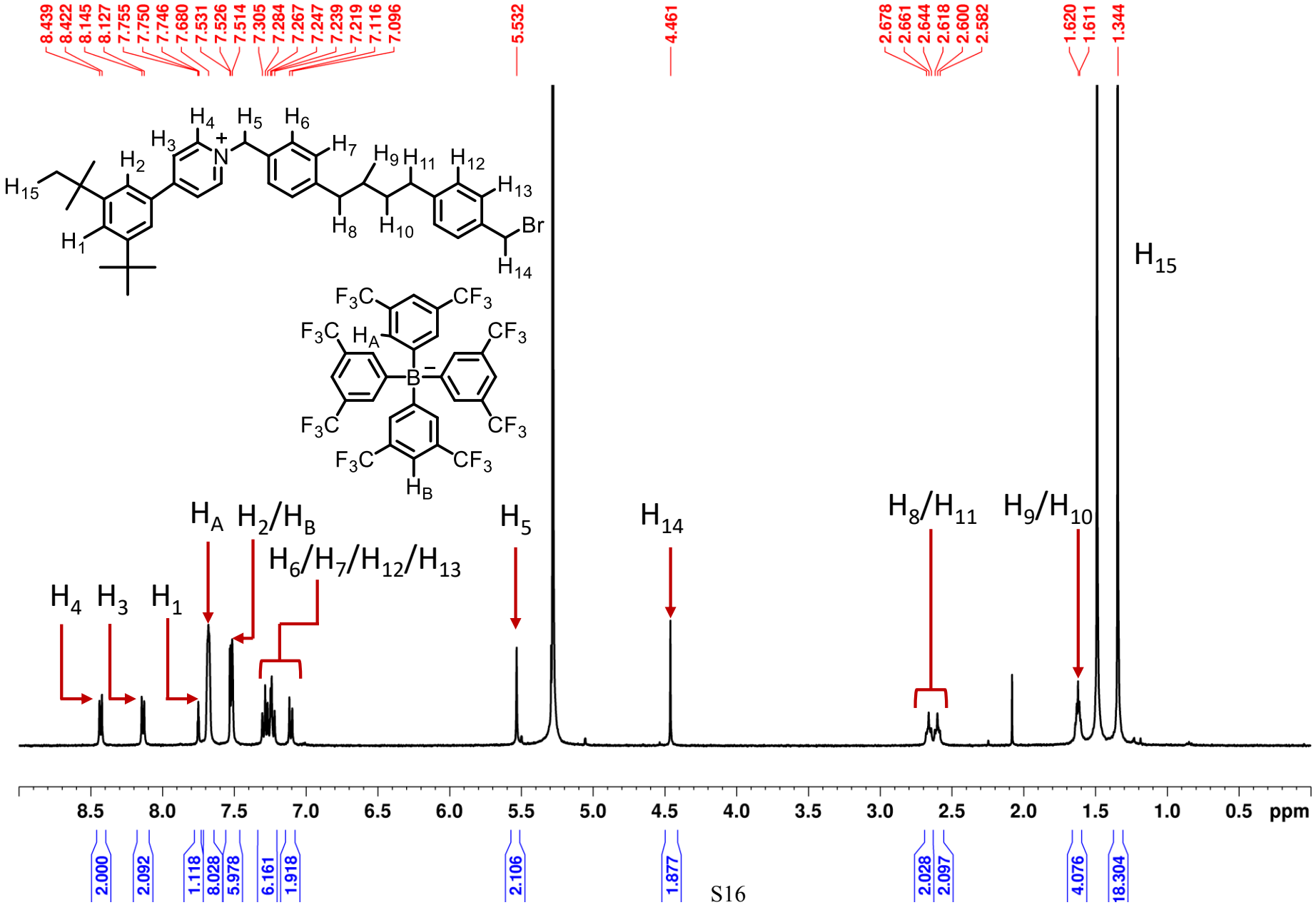


Figure S2 ^{13}C NMR Spectrum (100 MHz / $CDCl_3$ / 298 K) of **1**·TFPB

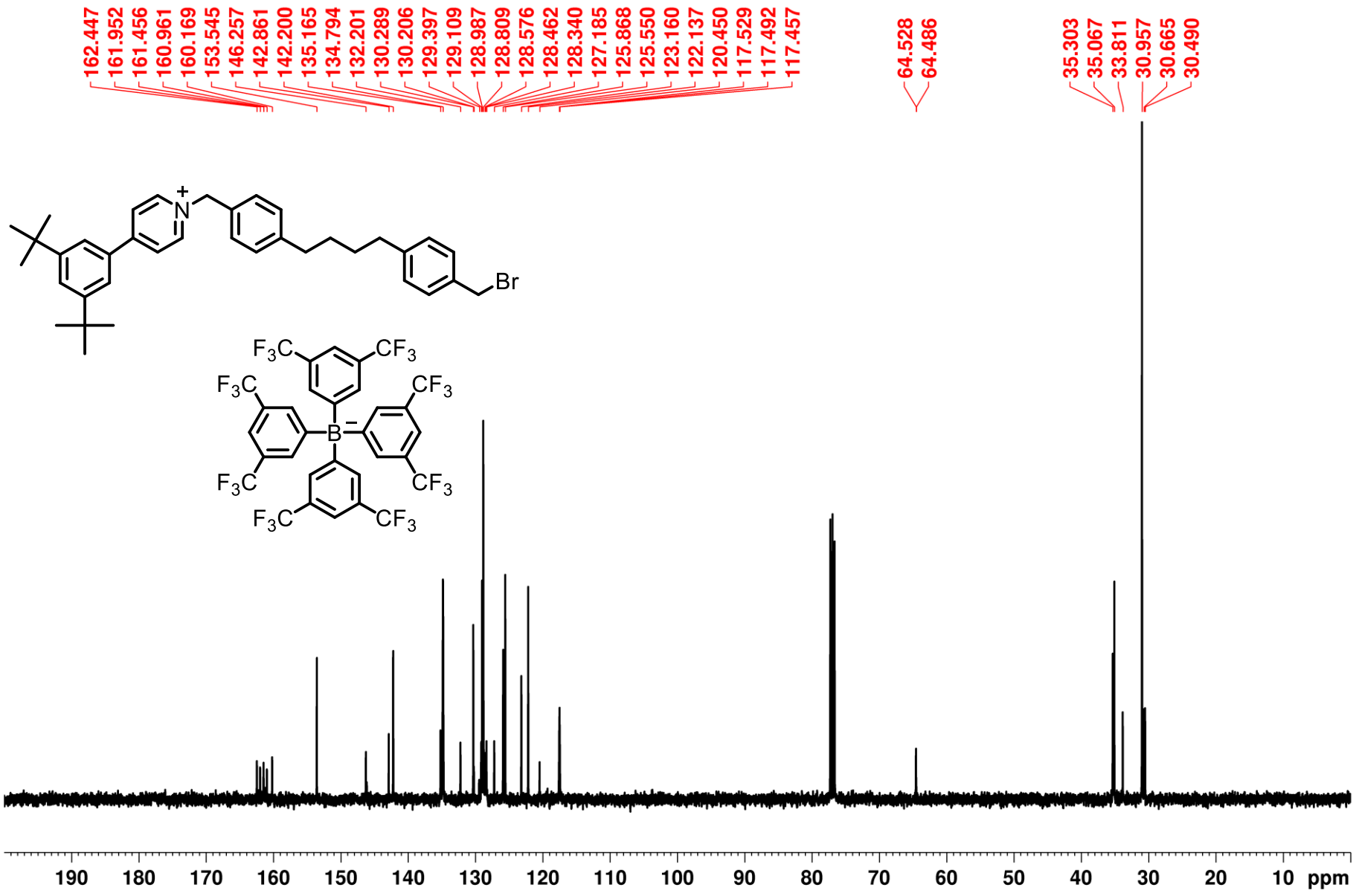


Figure S3 ESI Mass Spectra of Compound **1**·TFPB

Mass Spectrum SmartFormula Report

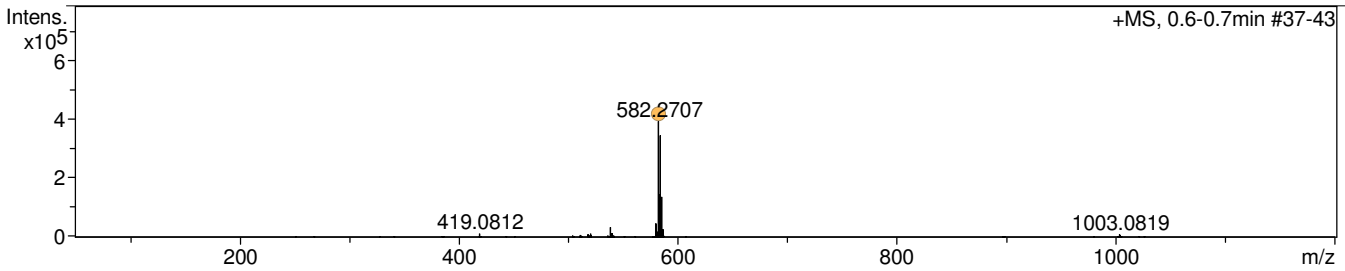
Analysis Info

Analysis Name	D:\Data\Fish\1_Data\2024Q1\240130\240130_pyridine-C4-Br_pw_35_01_34686.d	Acquisition Date	1/30/2024 10:47:21 AM
Method	tune_wide_pos_LCMS_with lock mass_220107-3.m	Operator	BDAL@DE
Sample Name	240130_pyridine-C4-Br_pw	Instrument / Ser#	micrOTOF-Q 228888.10183
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.9 l/min
Scan End	3000 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Waste

+MS, 0.6-0.7min #37-43



Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	mSigma	Score	rdb	e⁻ Conf	N-Rule
582.2707	1	C37H45BrN	582.2730	-2.3	-4.0	55.9	100.00	15.5	even	ok

+MS, 0.6-0.7min #37-43

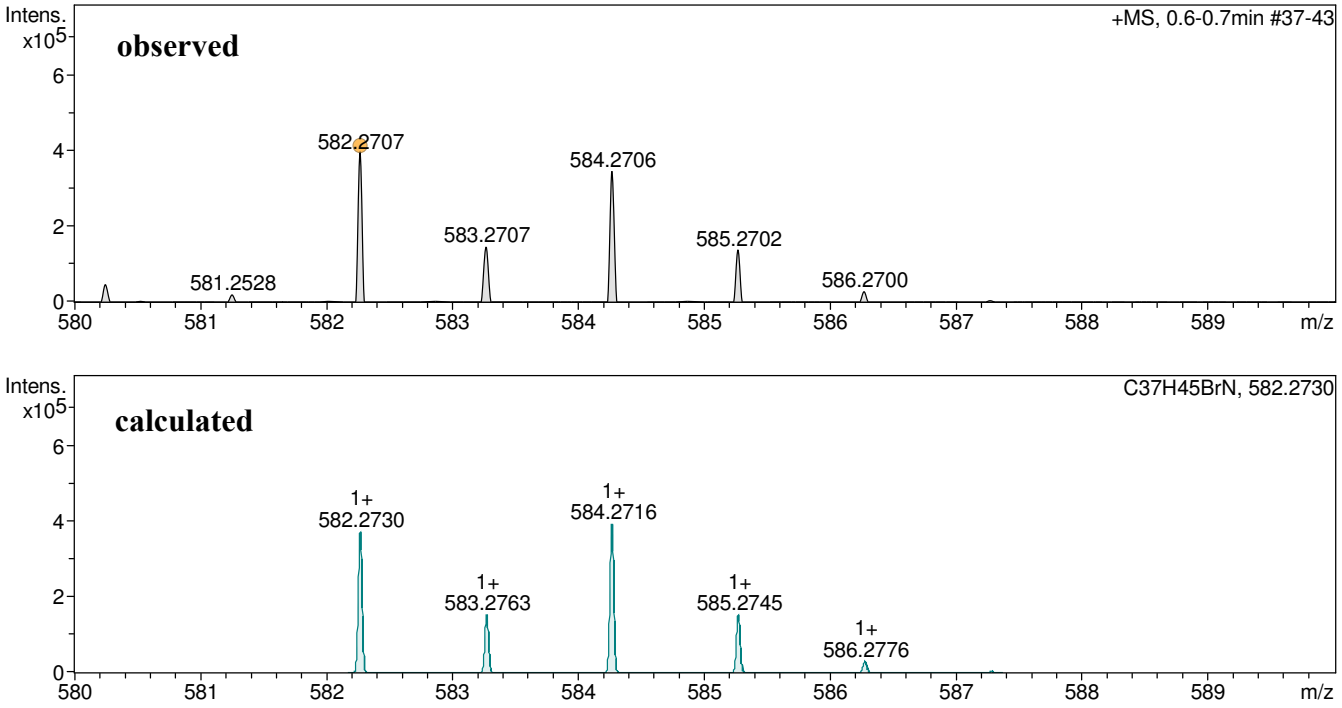


Figure S4 ^{1}H NMR Spectrum (400 MHz / CD_2Cl_2 / 298 K) of **3**·2TFPB

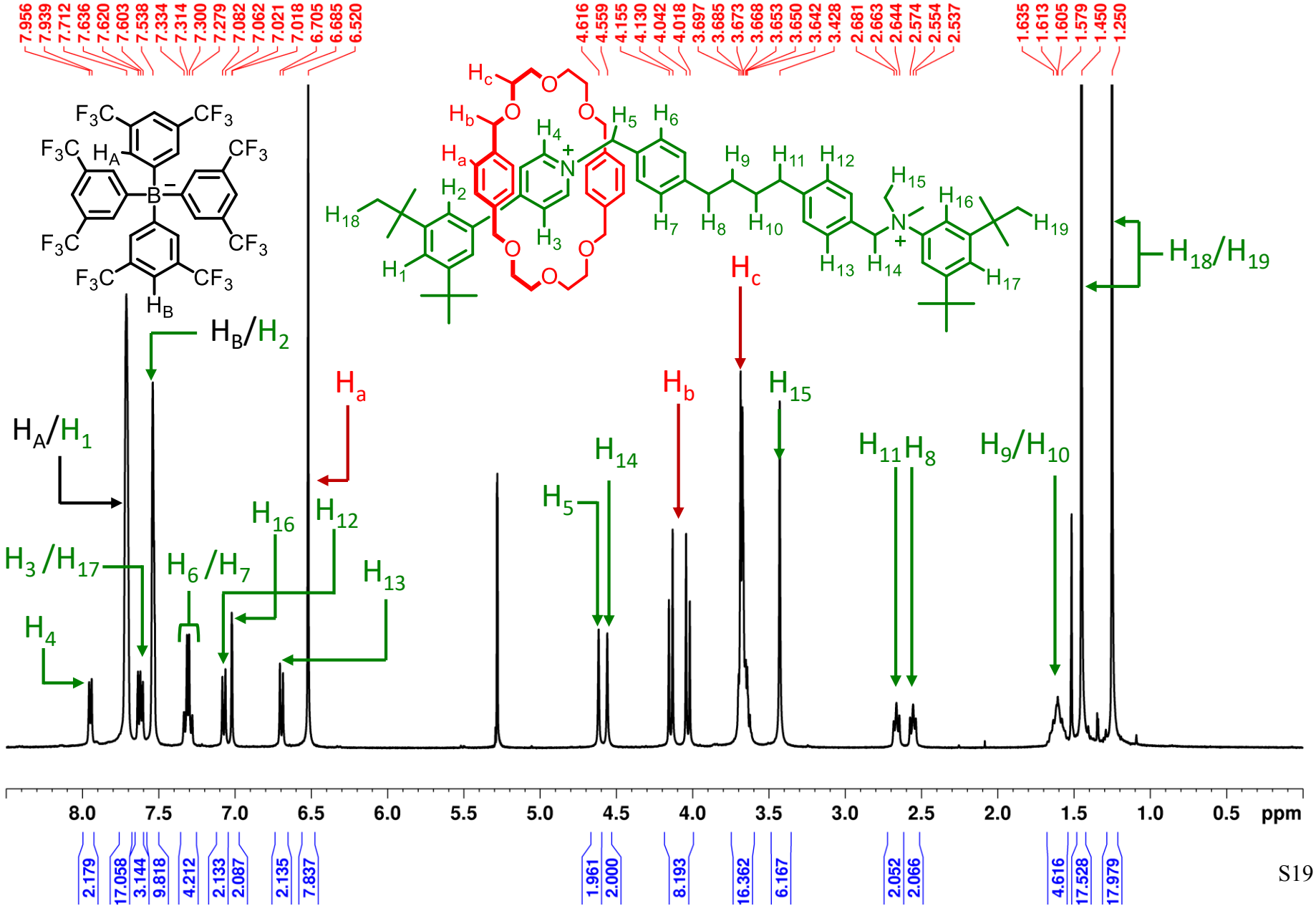


Figure S5 ^{13}C NMR Spectrum (100 MHz / $CDCl_3$ / 298 K) of **3**·2TFPB

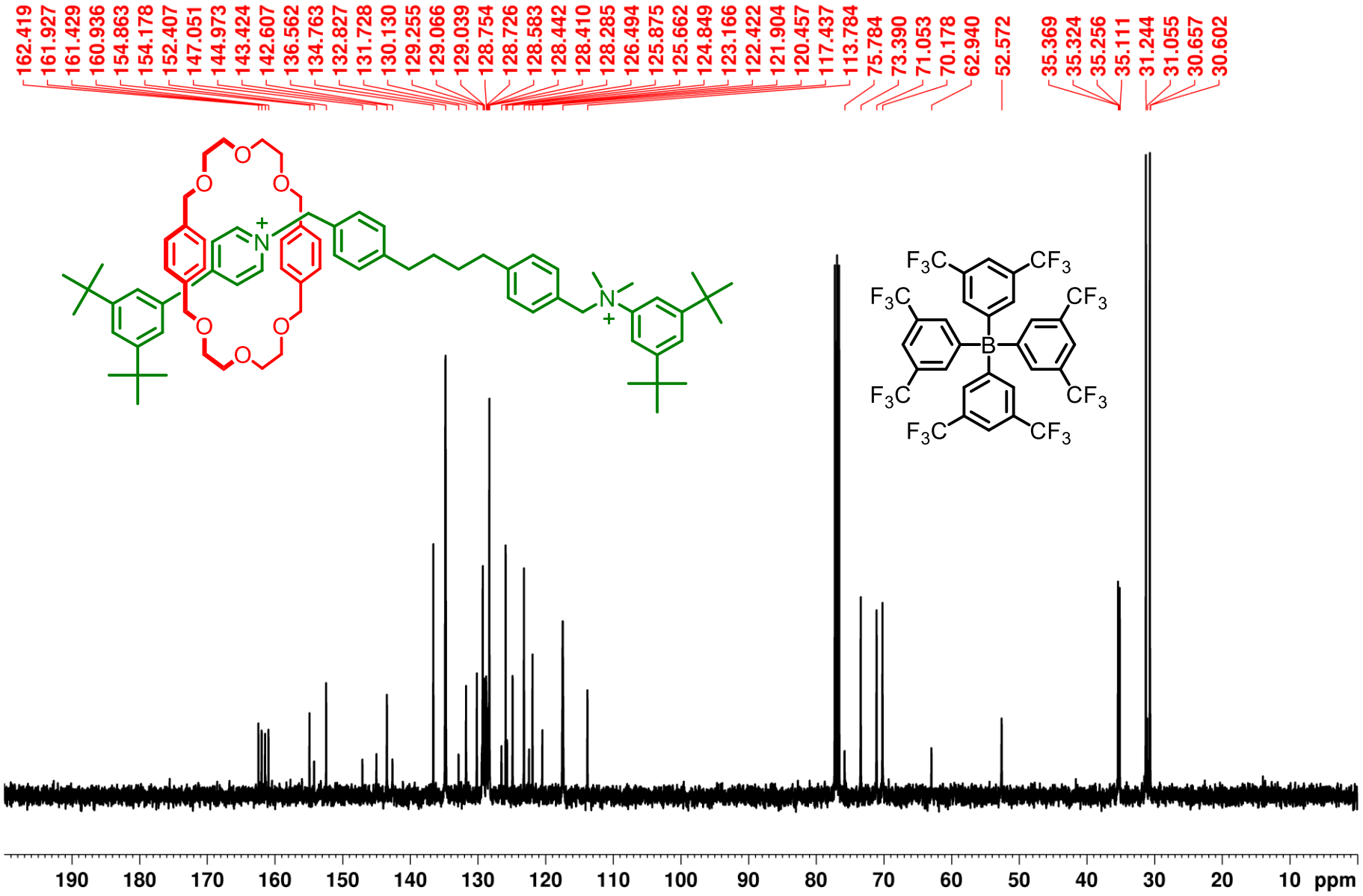


Figure S6 ESI Mass Spectra of Compound **3**·2TFPB

Mass Spectrum SmartFormula Report

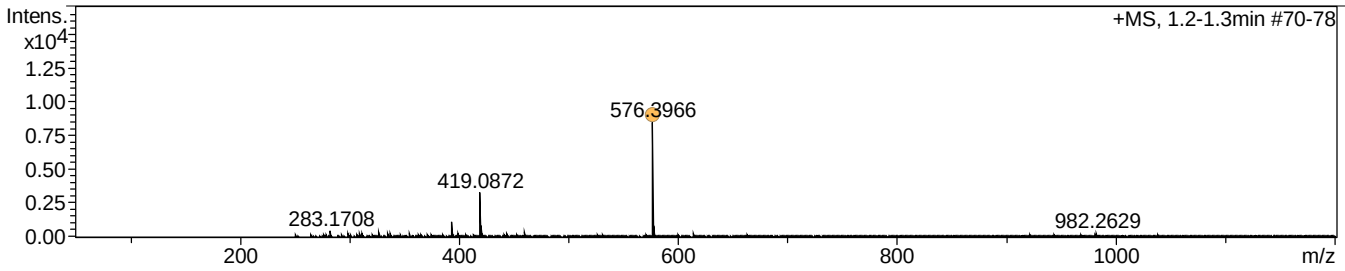
Analysis Info

Analysis Name	D:\Data\fish\data\2023q2(datas)\230529\230529_pyridine-rot-C4_pw_1-72_01_53567.d	Acquisition Date	5/29/2023 9:54:04 AM
Method	tune_wide_pos_LCMS_with lock mass_220107-3.m	Operator	Bruker microTOF-Q II
Sample Name	230529_pyridine-rot-C4_pw	Instrument / Ser#	micrOTOF-Q 228888.10183
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.9 l/min
Scan End	3000 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Waste

+MS, 1.2-1.3min #70-78



Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	mSigma	Score	rdb	e⁻ Conf	N-Rule
576.3966	1	C77H104N2O6	576.3942	-2.4	-4.2	29.6	100.00	27.0	even	ok

+MS, 1.2-1.3min #70-78

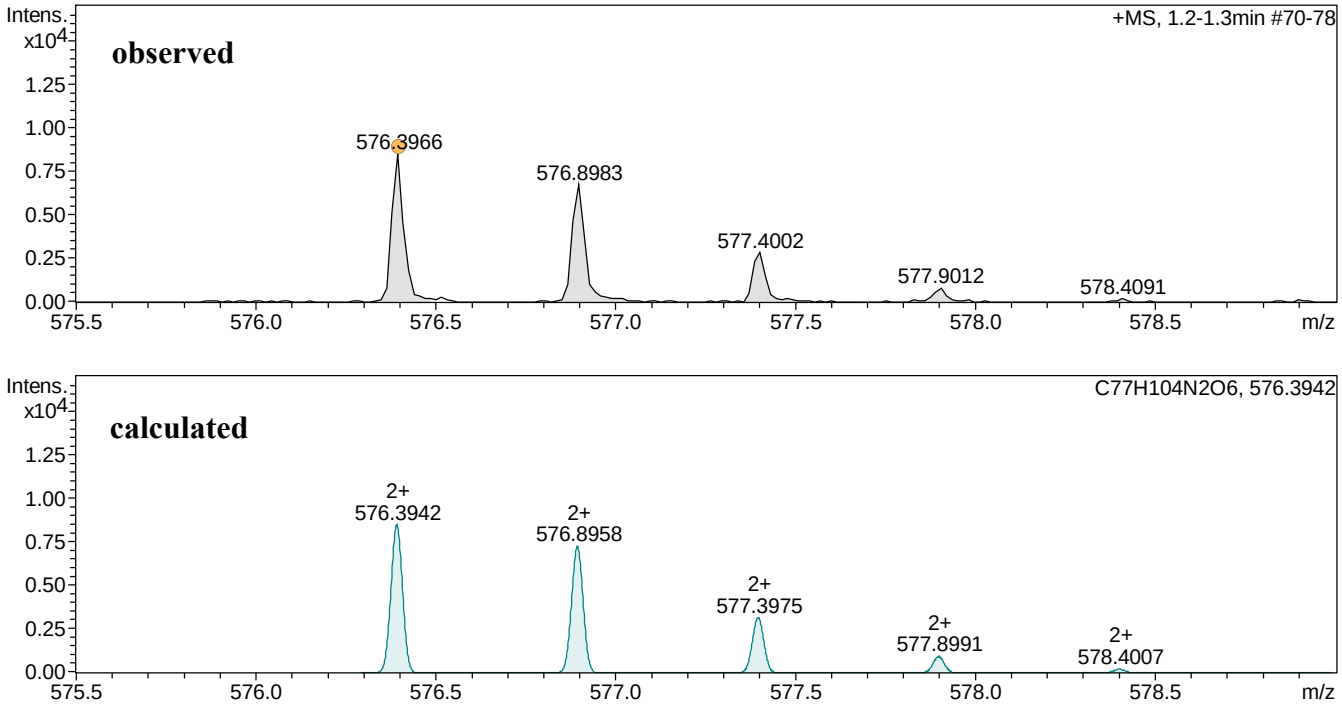


Figure S7 ^{1}H NMR Spectrum (400 MHz / CD_3CN / 298 K) of **4**·TFPB

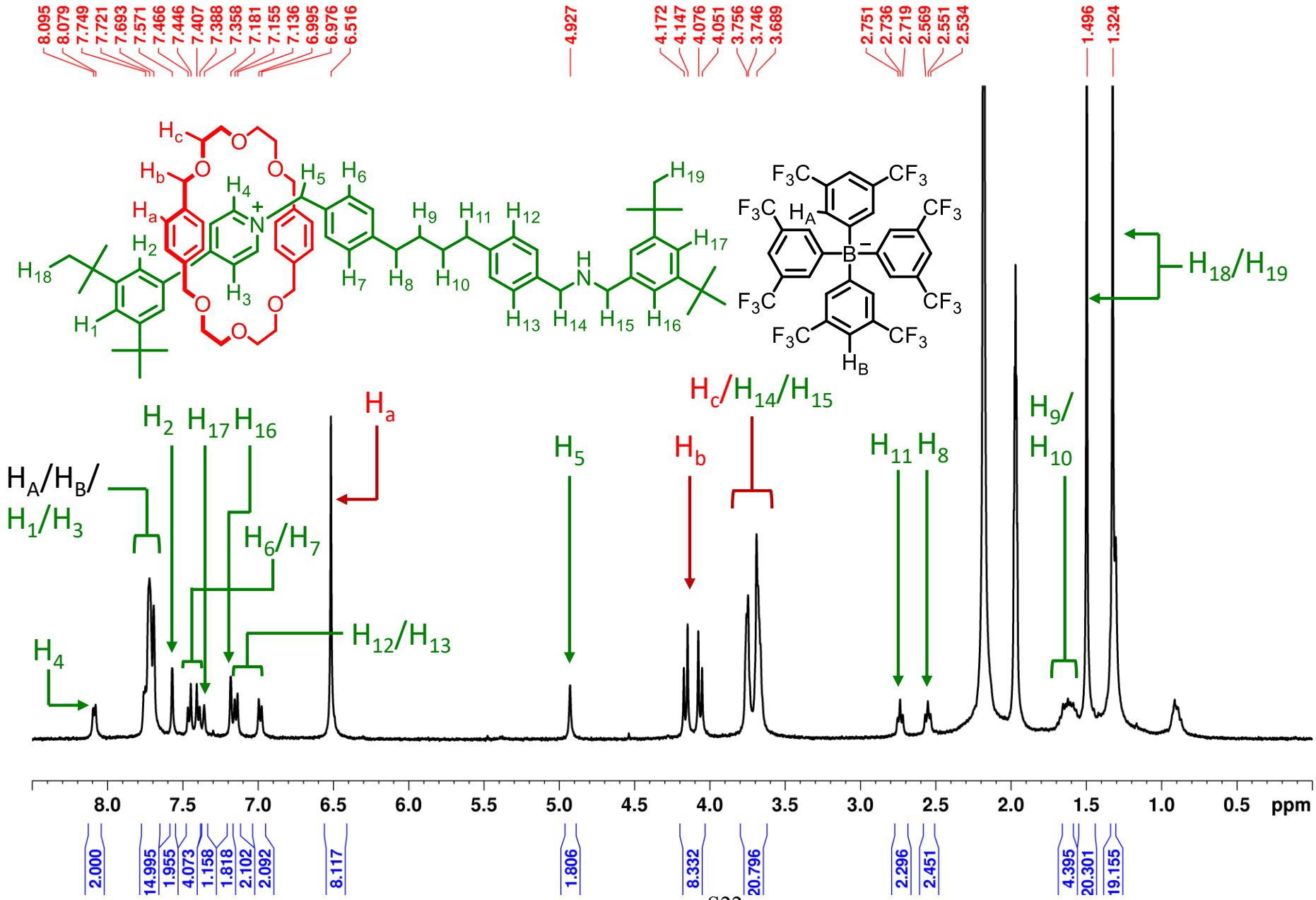


Figure S8 ^{13}C NMR Spectrum (100 MHz / CD_2Cl_2 / 298 K) of Rotaxane **4**·TFPB

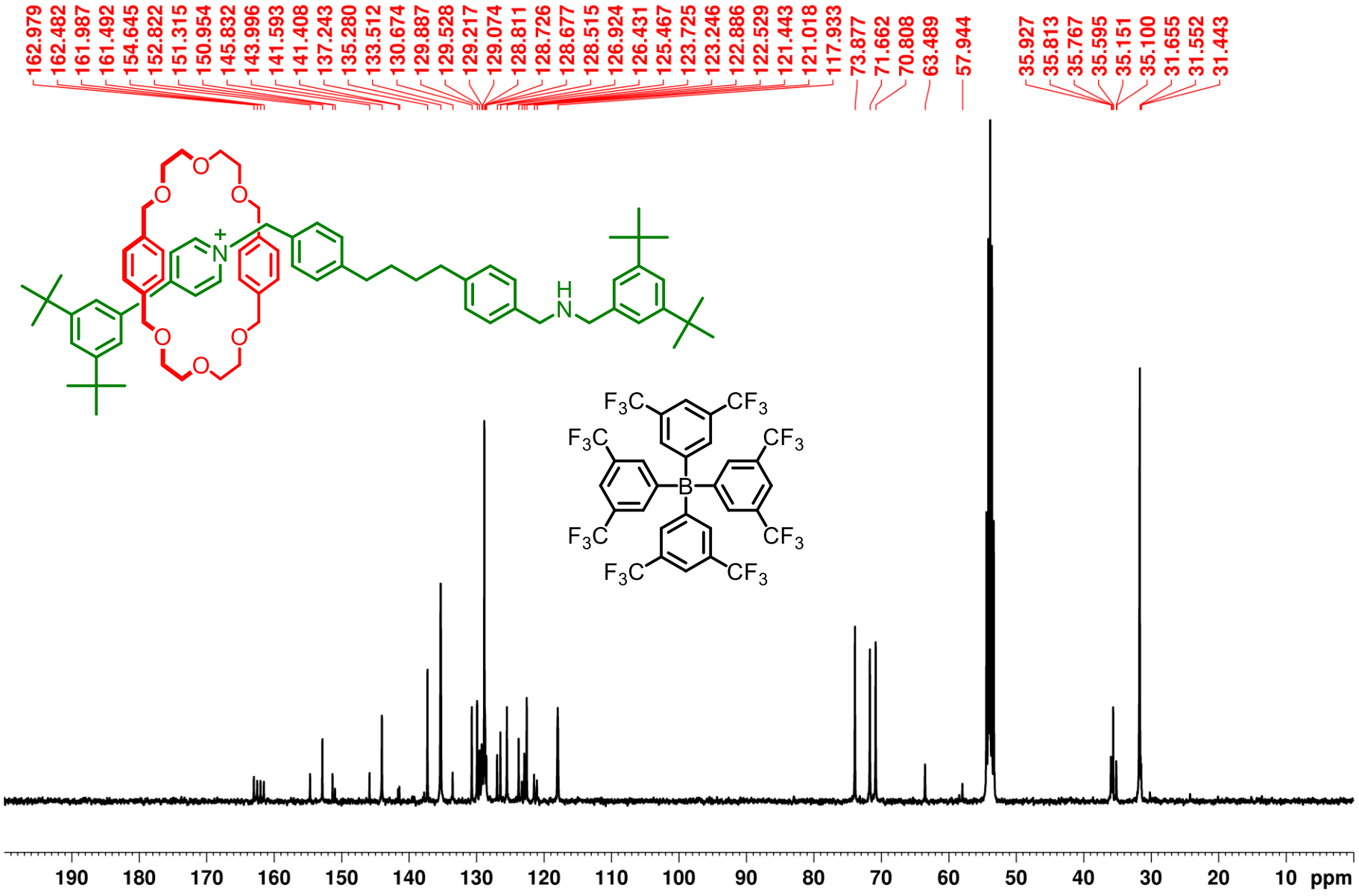


Figure S9 ESI Mass Spectra of Compound **4**·TFPB

Mass Spectrum SmartFormula Report

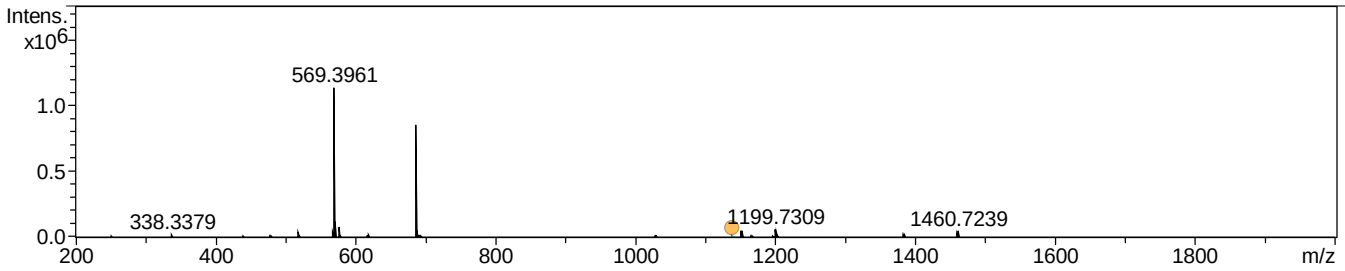
Analysis Info

Analysis Name	D:\Data\Fish\Data\2023Q3(datas)\230721\230721_amide-C4-rot-amineH_pw_1-61_01_54413.d	Acquisition Date	7/21/2023 12:03:10 PM
Method	tune_wide_pos_LCMS_with lock mass_220107-3.m	Operator	Bruker microTOF-Q II
Sample Name	230721_amide-C4-rot-amineH_pw	Instrument / Ser#	micrOTOF-Q 228888.10183
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.9 l/min
Scan End	3000 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Waste

+MS, 0.2-0.2min #10-12



Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	mSigma	Score	rdb	e⁻ Conf	N-Rule
1137.7687	1	C76H101N2O6	1137.7654	-3.3	-2.9	20.5	100.00	27.5	even	ok

+MS, 0.2-0.2min #10-12

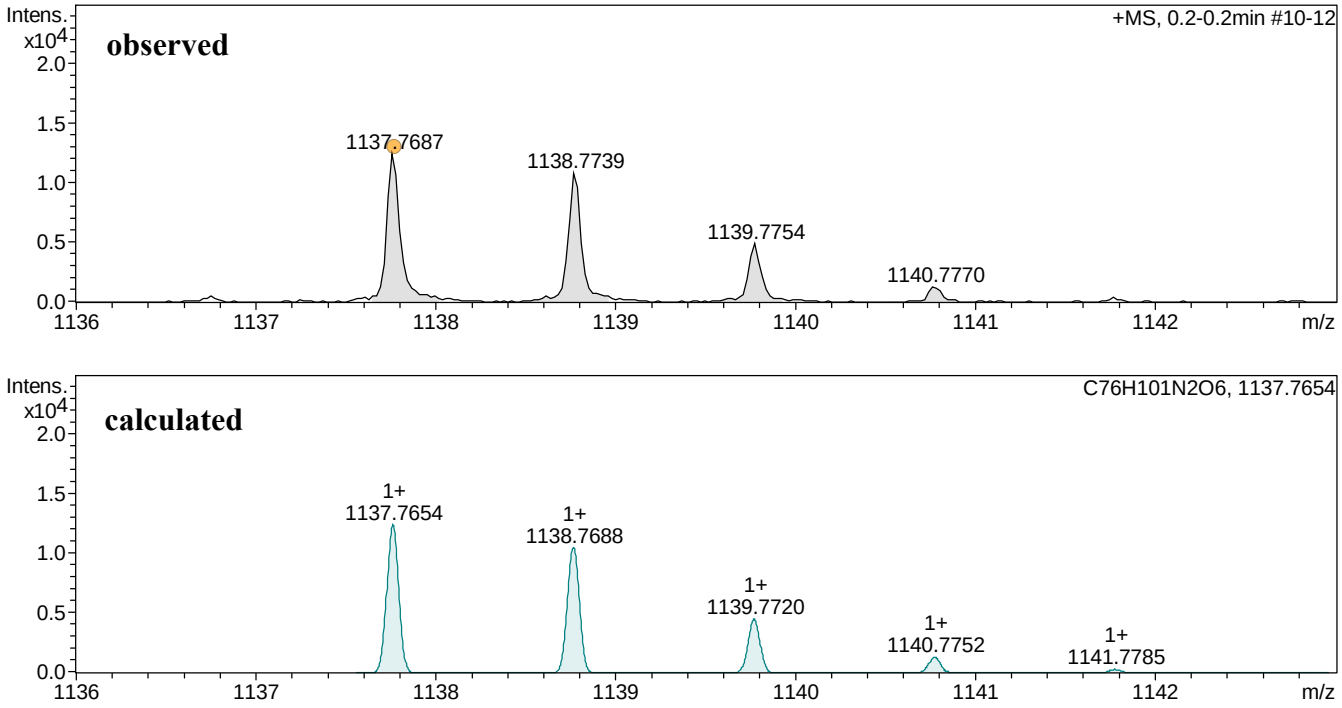


Figure S10 ^{1}H NMR Spectrum (400 MHz / CD_2Cl_2 / 298 K) of **5**·TFPB

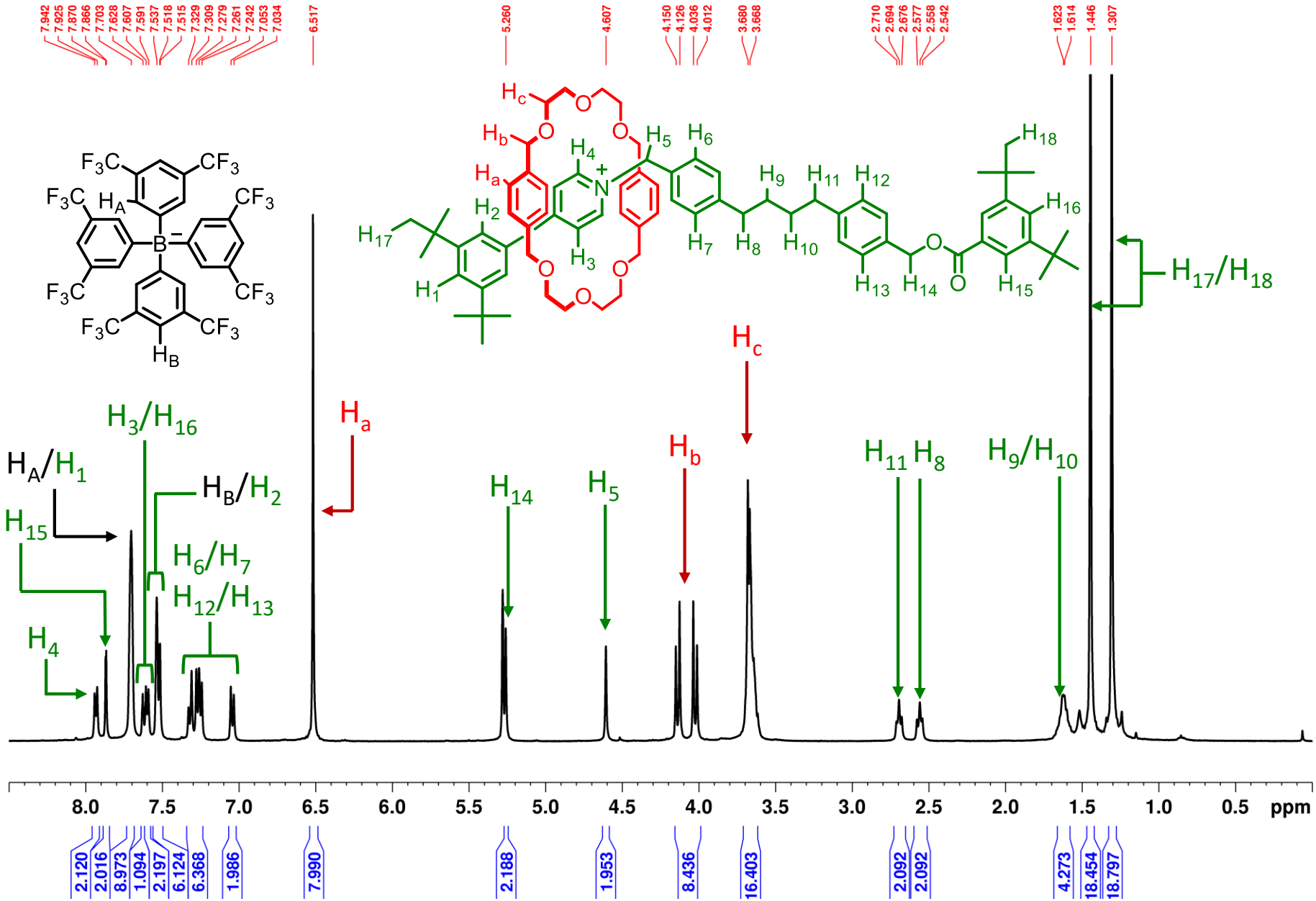


Figure S11 ^{13}C NMR Spectrum (100 MHz / $CDCl_3$ / 298 K) of **5**·TFPB

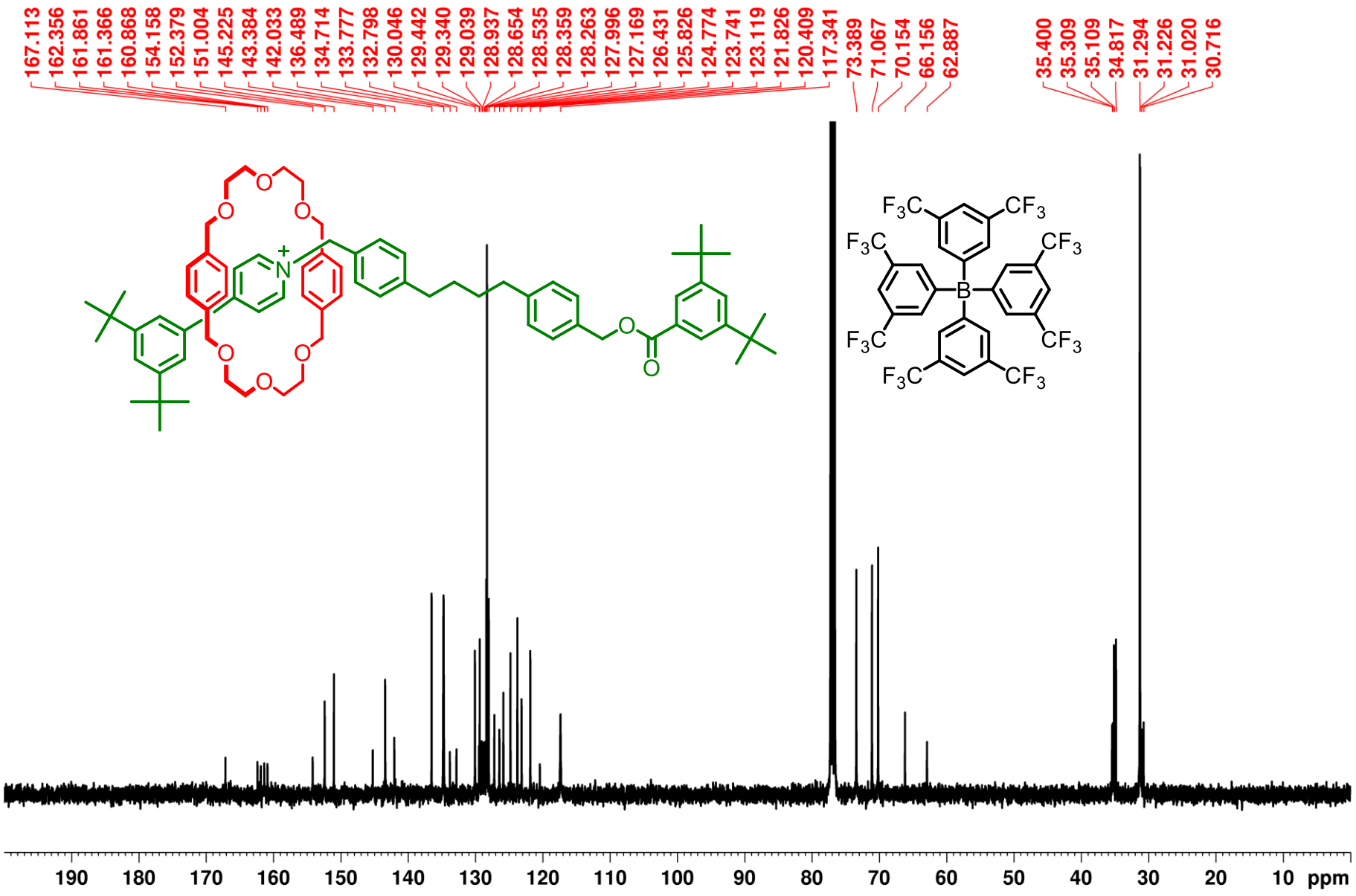


Figure S12 ESI Mass Spectra of Compound **5**•TFPB

Mass Spectrum SmartFormula Report

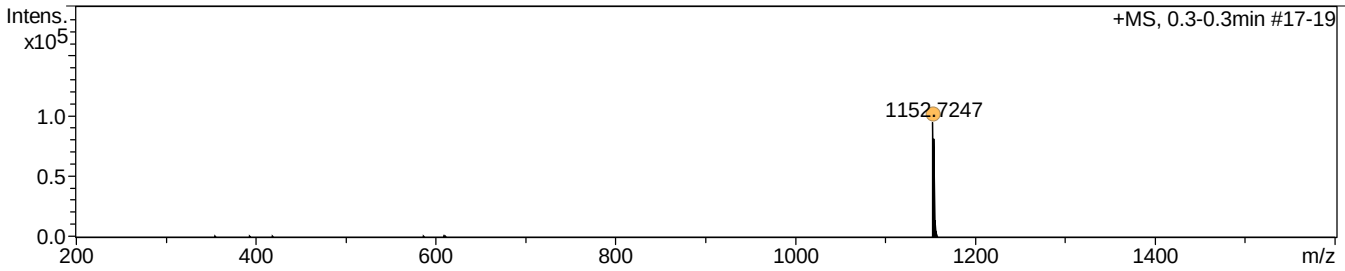
Analysis Info

Analysis Name	D:\Data\fish\data\2023q2(datas)\230529\230529_pyridine-rot-C4-acid_pw_1-75_01_53573.d	Acquisition Date	5/29/2023 10:28:21 AM
Method	tune_wide_pos_LCMS_with lock mass_220107-3.m	Operator	Bruker microTOF-Q II
Sample Name	230529_pyridine-rot-C4-acid_pw	Instrument / Ser#	micrOTOF-Q 228888.10183
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.9 l/min
Scan End	3000 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Waste

+MS, 0.3-0.3min #17-19



Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	mSigma	Score	rdb	e¯ Conf	N-Rule
1152.7247	1	C76H98NO8	1152.7287	-4.0	-3.5	56.5	100.00	28.5	even	ok

+MS, 0.3-0.3min #17-19

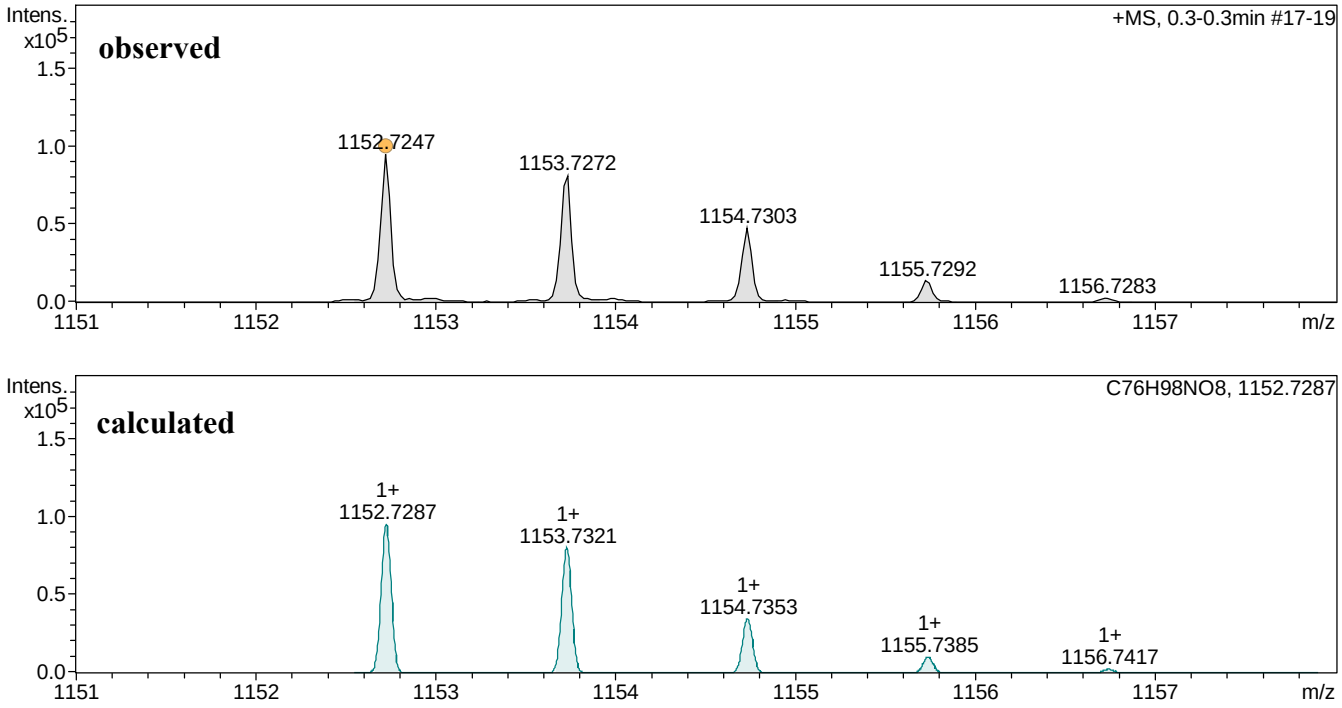


Figure S13 ^{1}H NMR Spectrum (400 MHz / CD_2Cl_2 / 298 K) of **6**·TFPB

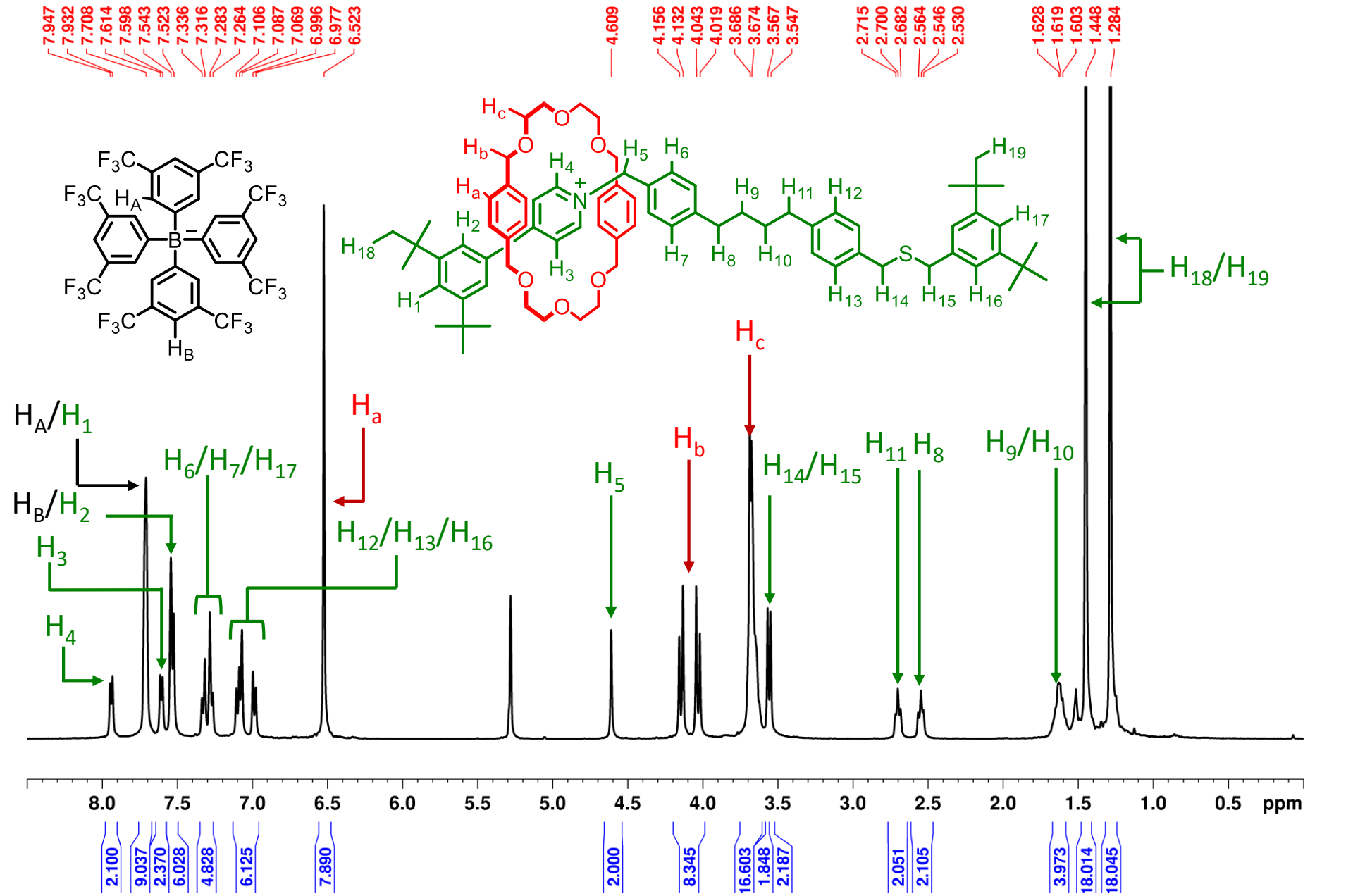


Figure S14 ^{13}C NMR Spectrum (100 MHz / $CDCl_3$ / 298 K) of **6**·TFPB

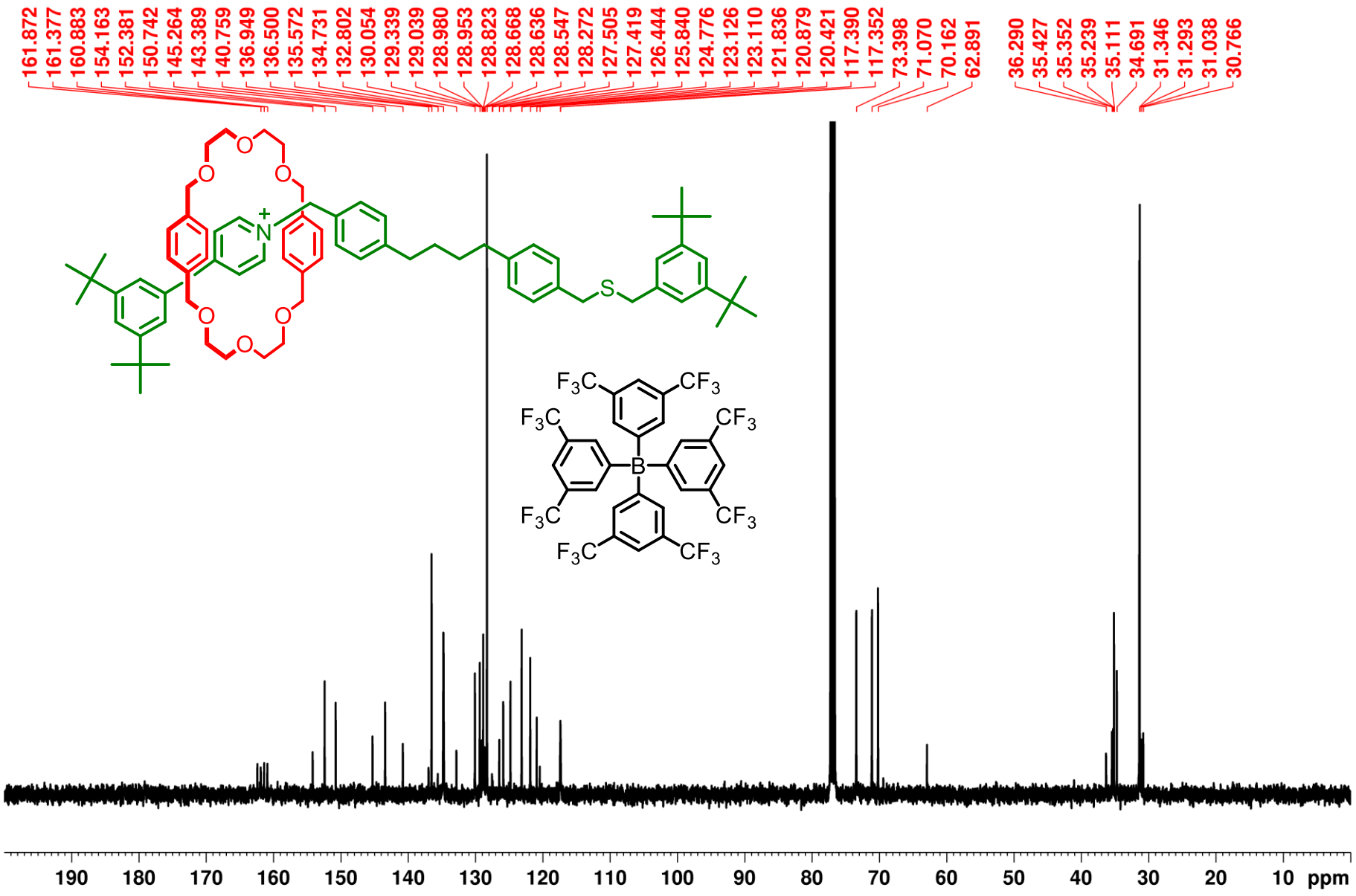


Figure S15 ESI Mass Spectra of Compound **6**•TFPB

Mass Spectrum SmartFormula Report

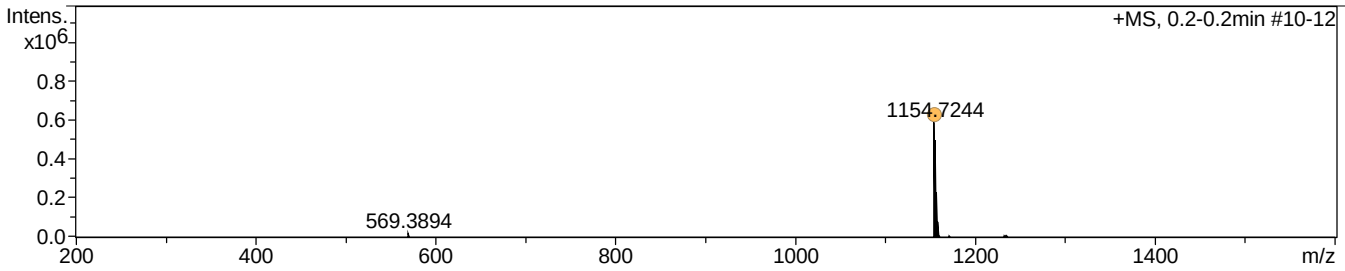
Analysis Info

Analysis Name	D:\Data\fish\data\2023q2(datas)\230529\230529_pyridine-rot-C4-thio_pw_1-74_01_53571.d	Acquisition Date	5/29/2023 10:16:56 AM
Method	tune_wide_pos_LCMS_with lock mass_220107-3.m	Operator	Bruker microTOF-Q II
Sample Name	230529_pyridine-rot-C4-thio_pw	Instrument / Ser#	micrOTOF-Q 228888.10183
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.9 l/min
Scan End	3000 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Waste

+MS, 0.2-0.2min #10-12



Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	mSigma	Score	rdb	e⁻ Conf	N-Rule
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+MS, 0.2-0.2min #10-12

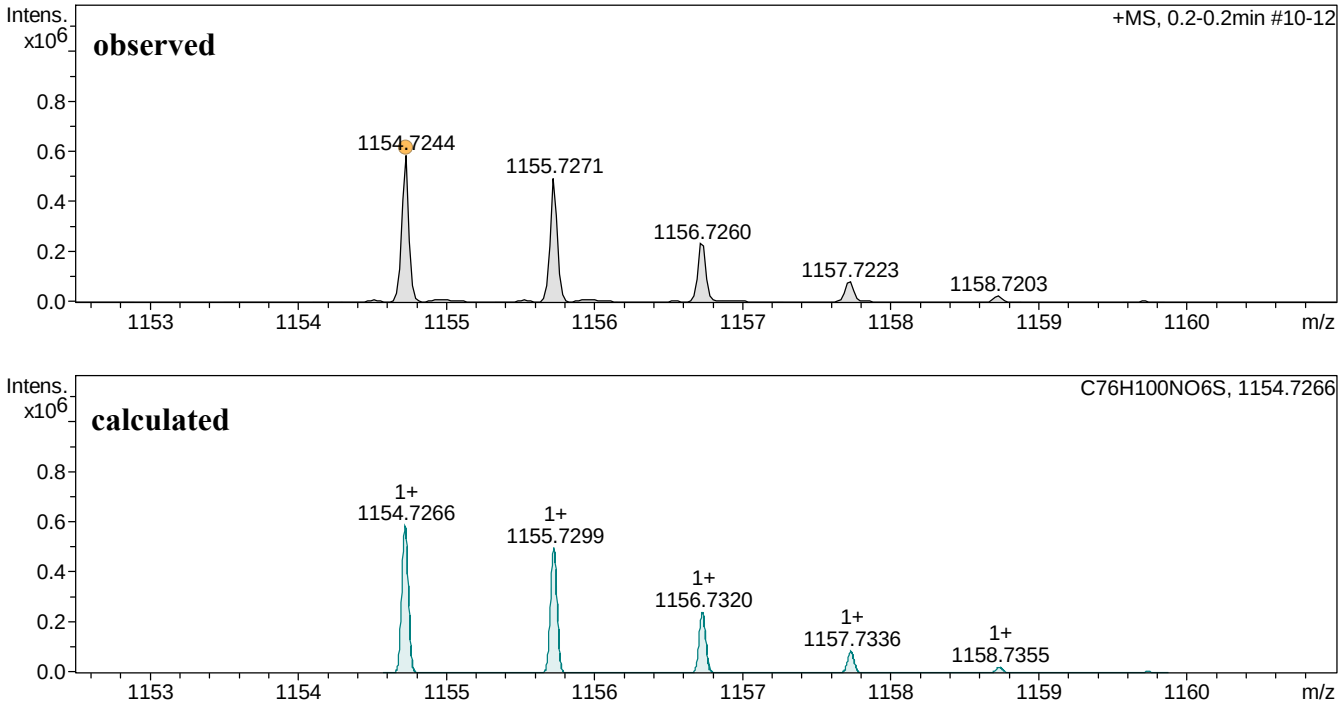


Figure S16 ^{1}H NMR Spectrum (400 MHz / CD_2Cl_2 / 298 K) of **7**·TFPB

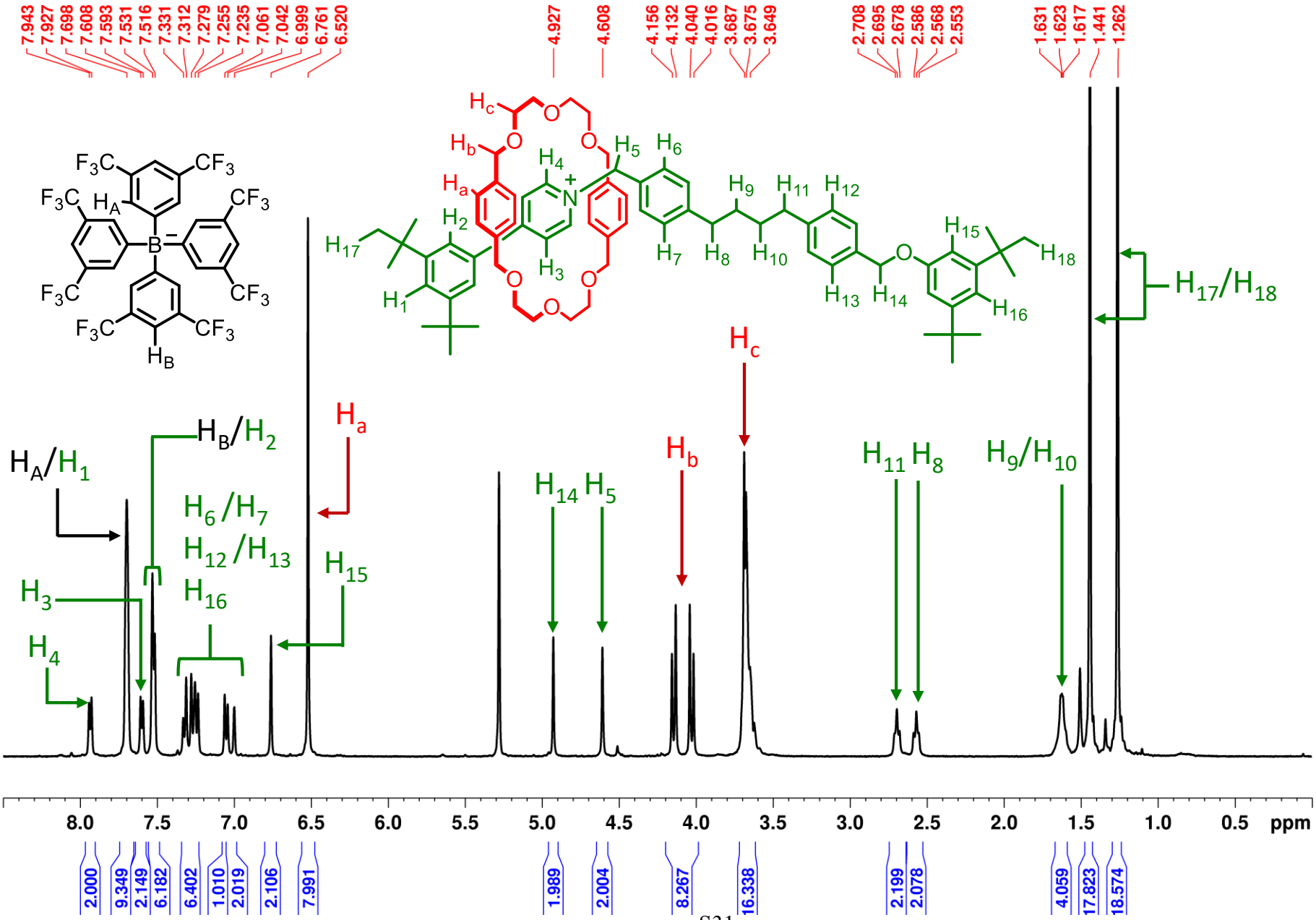


Figure S17 ^{13}C NMR Spectrum (100 MHz / $CDCl_3$ / 298 K) of **7**·TFPB

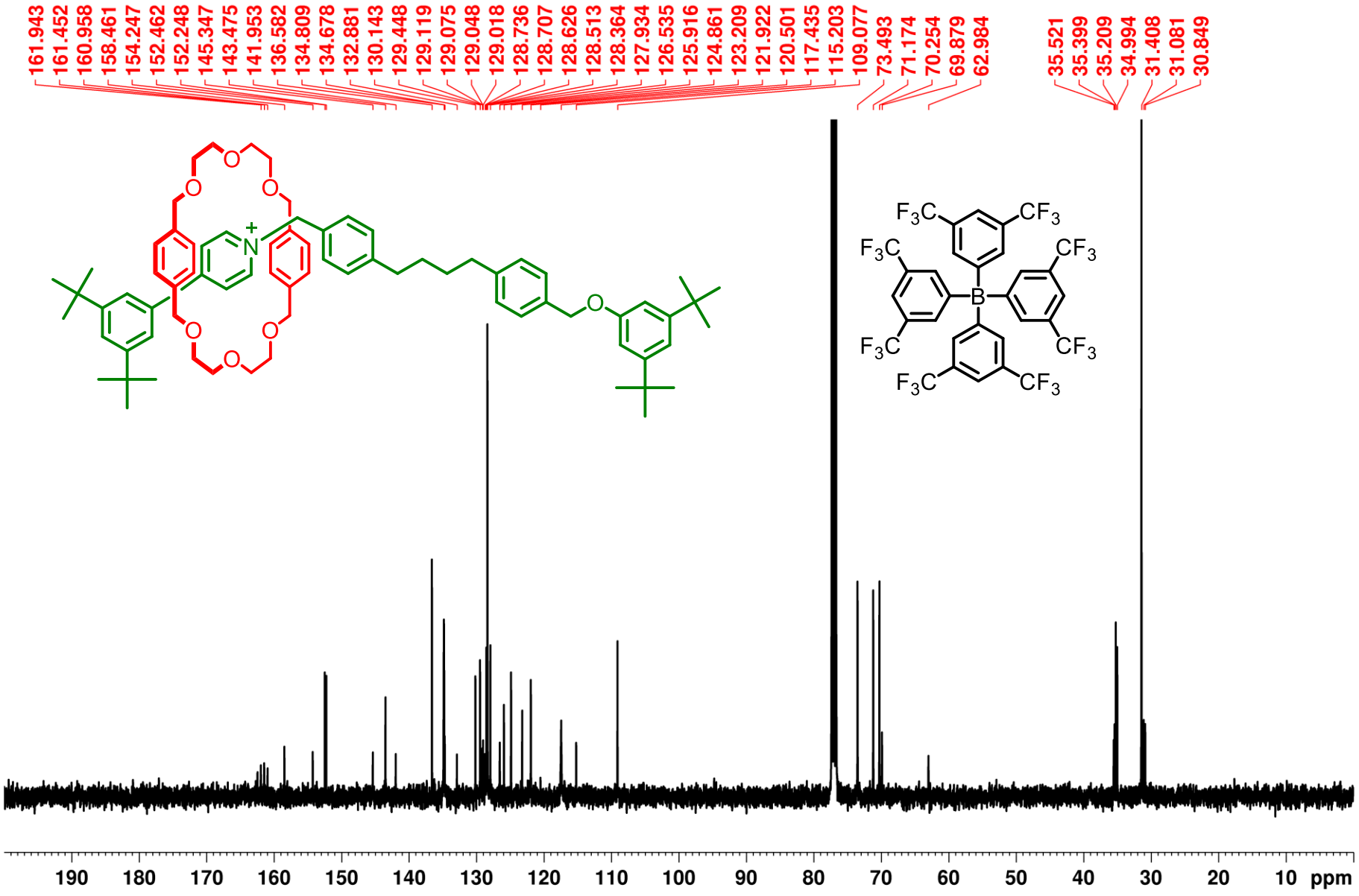


Figure S18 ESI Mass Spectra of Compound **7**•TFPB

Mass Spectrum SmartFormula Report

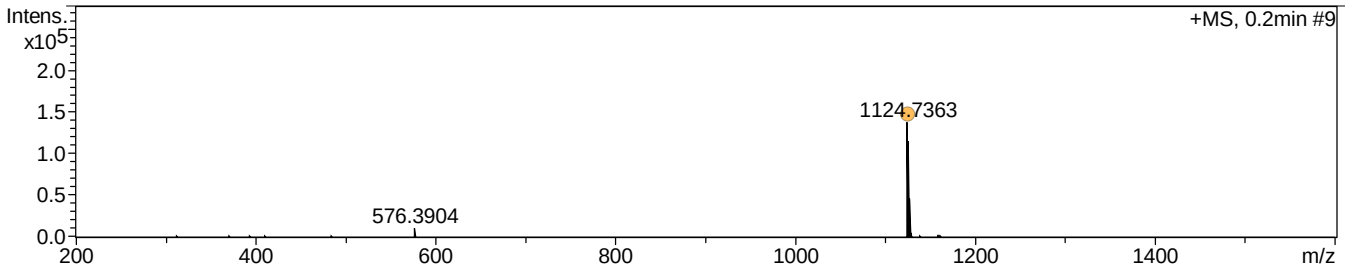
Analysis Info

Analysis Name	D:\Data\fish\data\2023q2(datas)\230529\230529_pyridine-rot-C4-phen_pw_1-73_01_53569.d	Acquisition Date	5/29/2023 10:05:29 AM
Method	tune_wide_pos_LCMS_with lock mass_220107-3.m	Operator	Bruker microTOF-Q II
Sample Name	230529_pyridine-rot-C4-phen_pw	Instrument / Ser#	micrOTOF-Q 228888.10183
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.9 l/min
Scan End	3000 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Waste

+MS, 0.2min #9



Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	mSigma	Score	rdb	e¯ Conf	N-Rule
1124.7363	1	C75H98NO7	1124.7338	-2.5	-2.2	11.2	100.00	27.5	even	ok

+MS, 0.2min #9

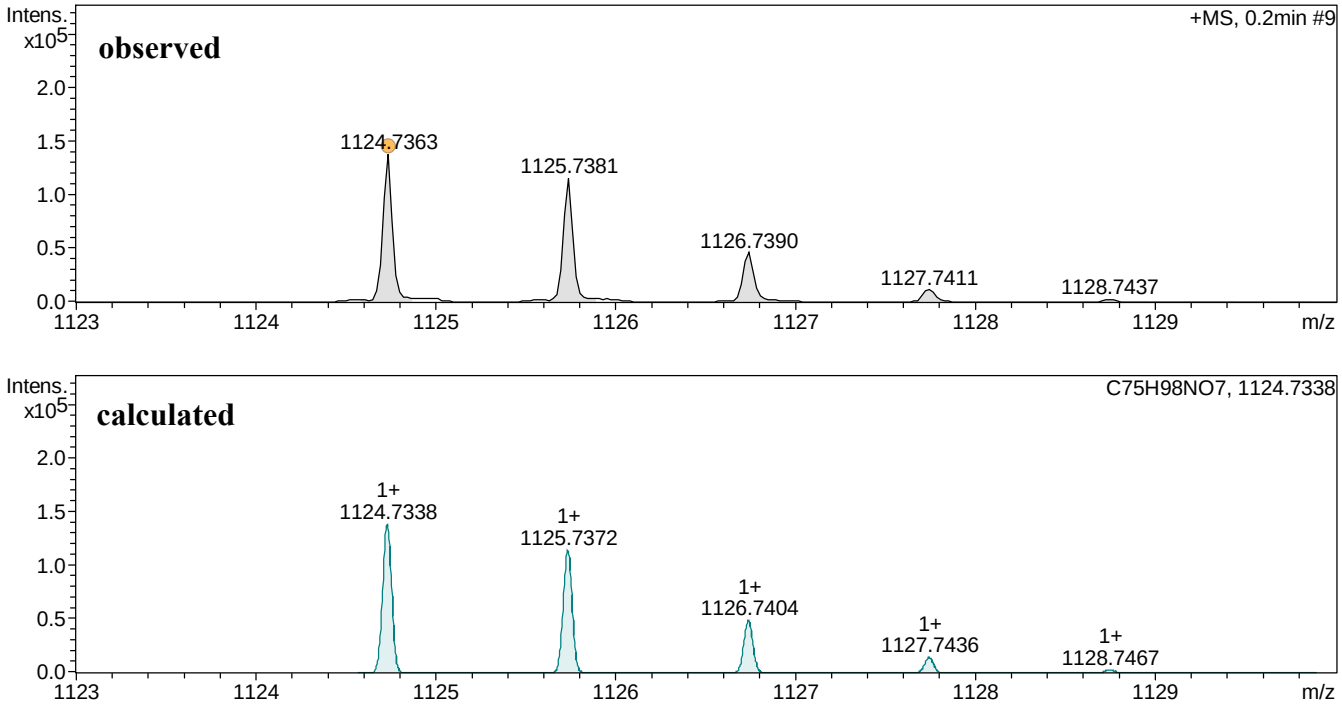


Figure S19 ^{1}H NMR Spectrum (400 MHz / CD_2Cl_2 / 298 K) of **8**·TFPB

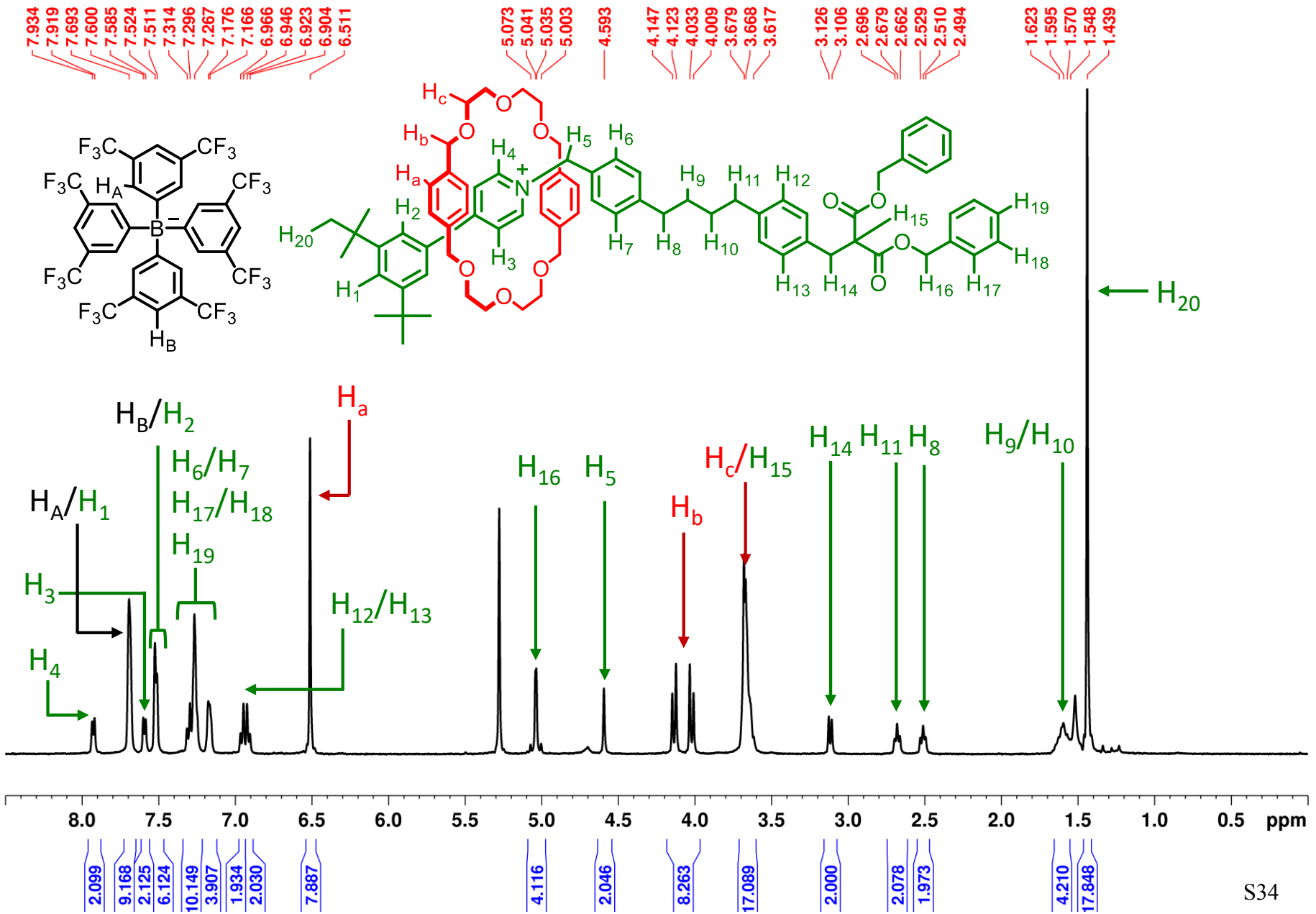


Figure S20 ^{13}C NMR Spectrum (100 MHz / $CDCl_3$ / 298 K) of **8**·TFPB

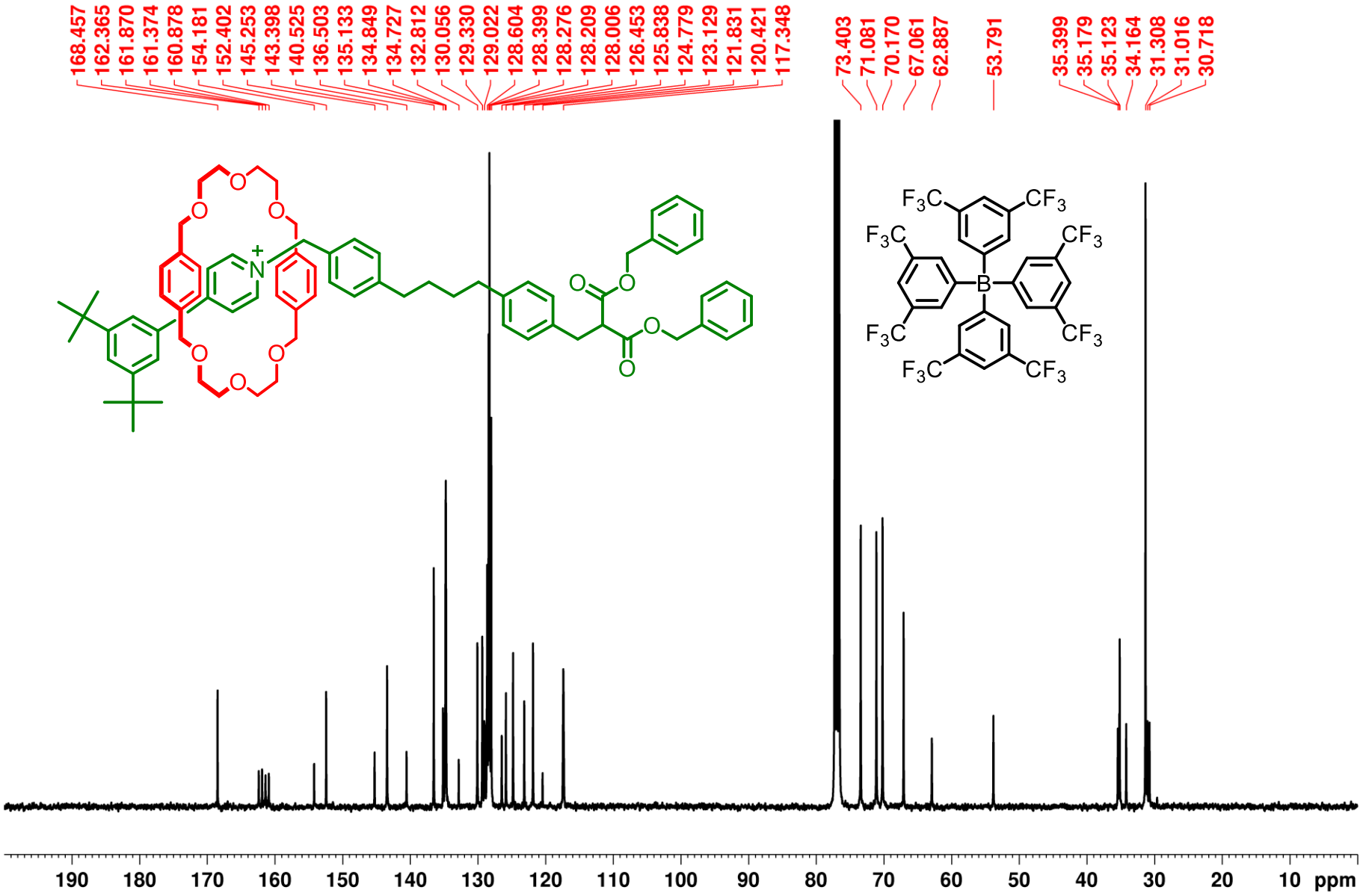


Figure S21 ESI Mass Spectra of Compound **8**•TFPB

Mass Spectrum SmartFormula Report

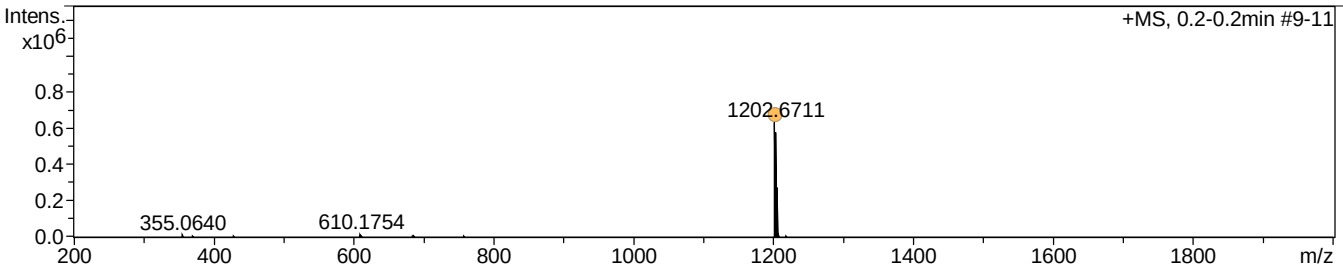
Analysis Info

Analysis Name	D:\Data\fish\data\2023q2(datas)\230605\230605_pyridinum-malonate-2_pw_1-1_01_53700.d	Acquisition Date	6/5/2023 10:50:29 AM
Method	tune_wide_pos_LCMS_with lock mass_220107-3.m	Operator	Bruker microTOF-Q II
Sample Name	230605_pyridinum-malonate-2_pw	Instrument / Ser#	micrOTOF-Q 228888.10183
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.9 l/min
Scan End	3000 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Waste

+MS, 0.2-0.2min #9-11



Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	mSigma	Score	rdb	e⁻ Conf	N-Rule
1202.6711	1	C78H92NO10	1202.6716	0.5	0.4	29.5	100.00	33.5	even	ok

+MS, 0.2-0.2min #9-11

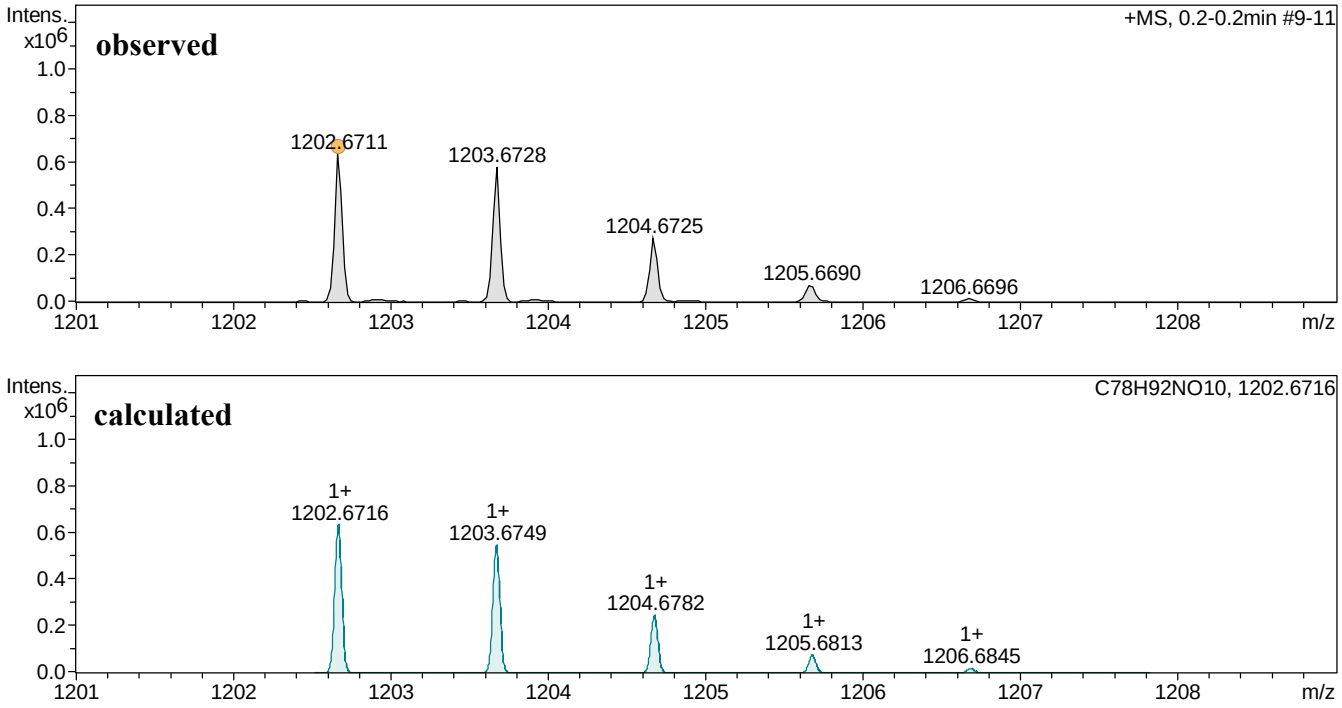


Figure S22 ^{1}H NMR Spectrum (400 MHz / CD_2Cl_2/ 298 K) of **S1**·TFPB

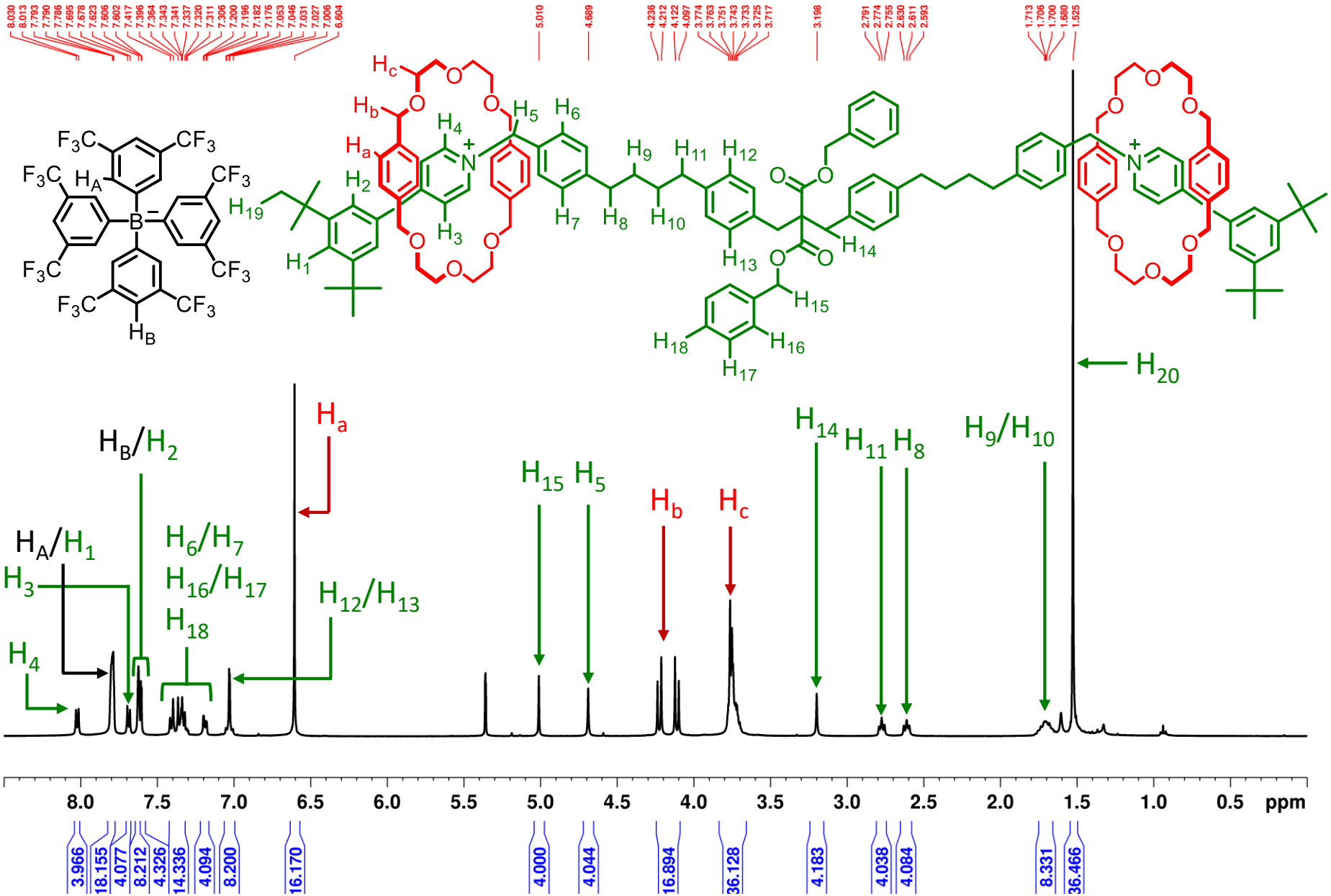


Figure S23 ^{13}C NMR Spectrum (100 MHz / $CDCl_3$ / 298 K) of **S1**·TFPB

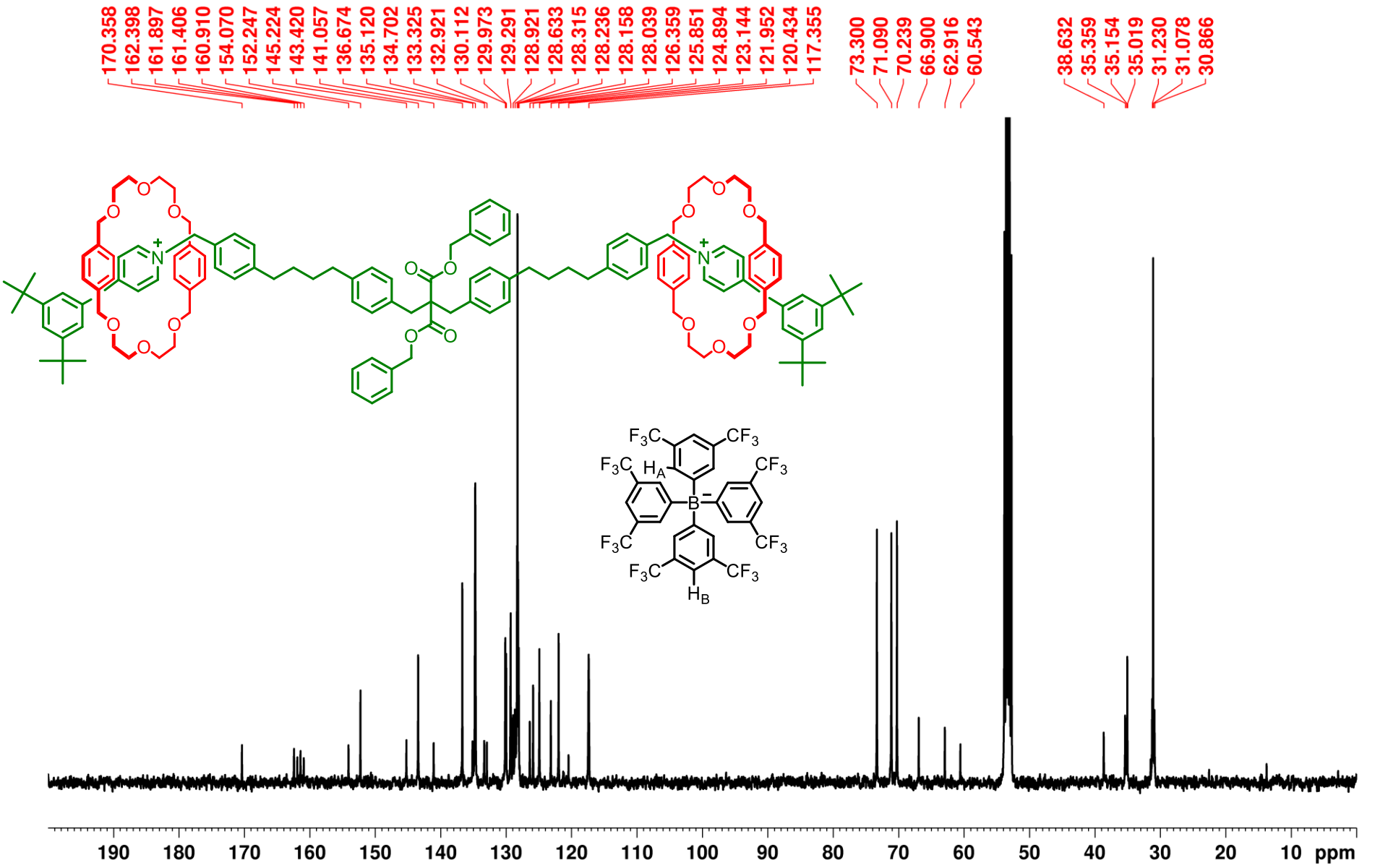


Figure S24 ESI Mass Spectra of Compound **S1**•2TFPB

Mass Spectrum SmartFormula Report

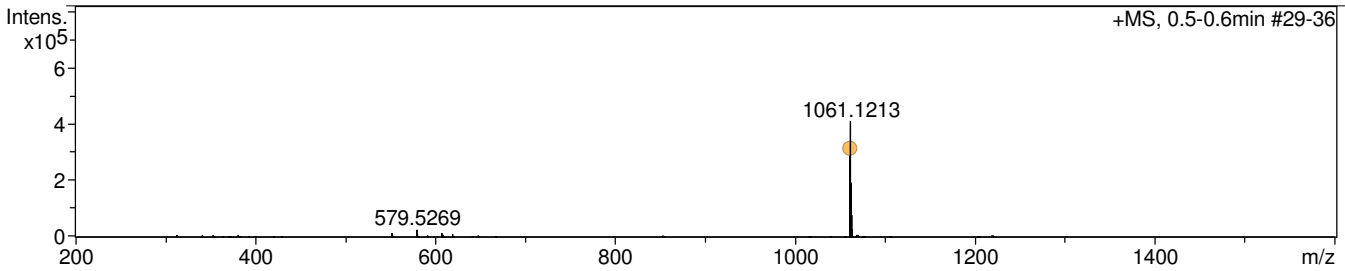
Analysis Info

Analysis Name	D:\Data\Fish\1_Data\2024Q2\240430\240430_pyridine-C4-3-rot-ma_pw_46_01_35771.d	Acquisition Date	4/30/2024 3:39:26 PM
Method	tune_wide_pos_LCMS_with lock mass_220107-3.m	Operator	BDAL@DE
Sample Name	240430_pyridine-C4-3-rot-ma_pw	Instrument / Ser#	micrOTOF-Q 228888.10183
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.9 l/min
Scan End	3000 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Waste

+MS, 0.5-0.6min #29-36



Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	mSigma	Score	rdb	e⁻ Conf	N-Rule
1060.6187	1	C139H168N2O16	1060.6191	-0.5	-0.5	33.6	100.00	57.0	even	ok

+MS, 0.5-0.6min #29-36

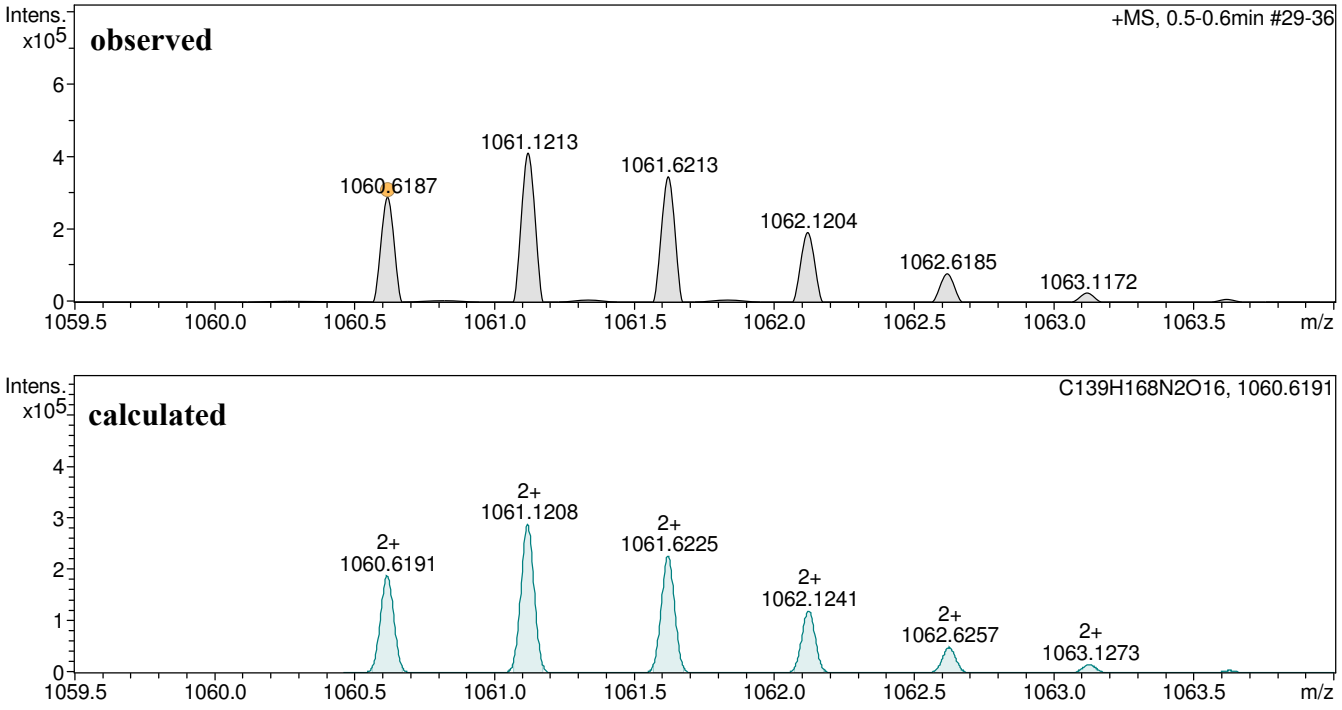


Figure S25 ^{1}H NMR Spectrum (400 MHz / $CDCl_3$ / 298 K) of **S2**

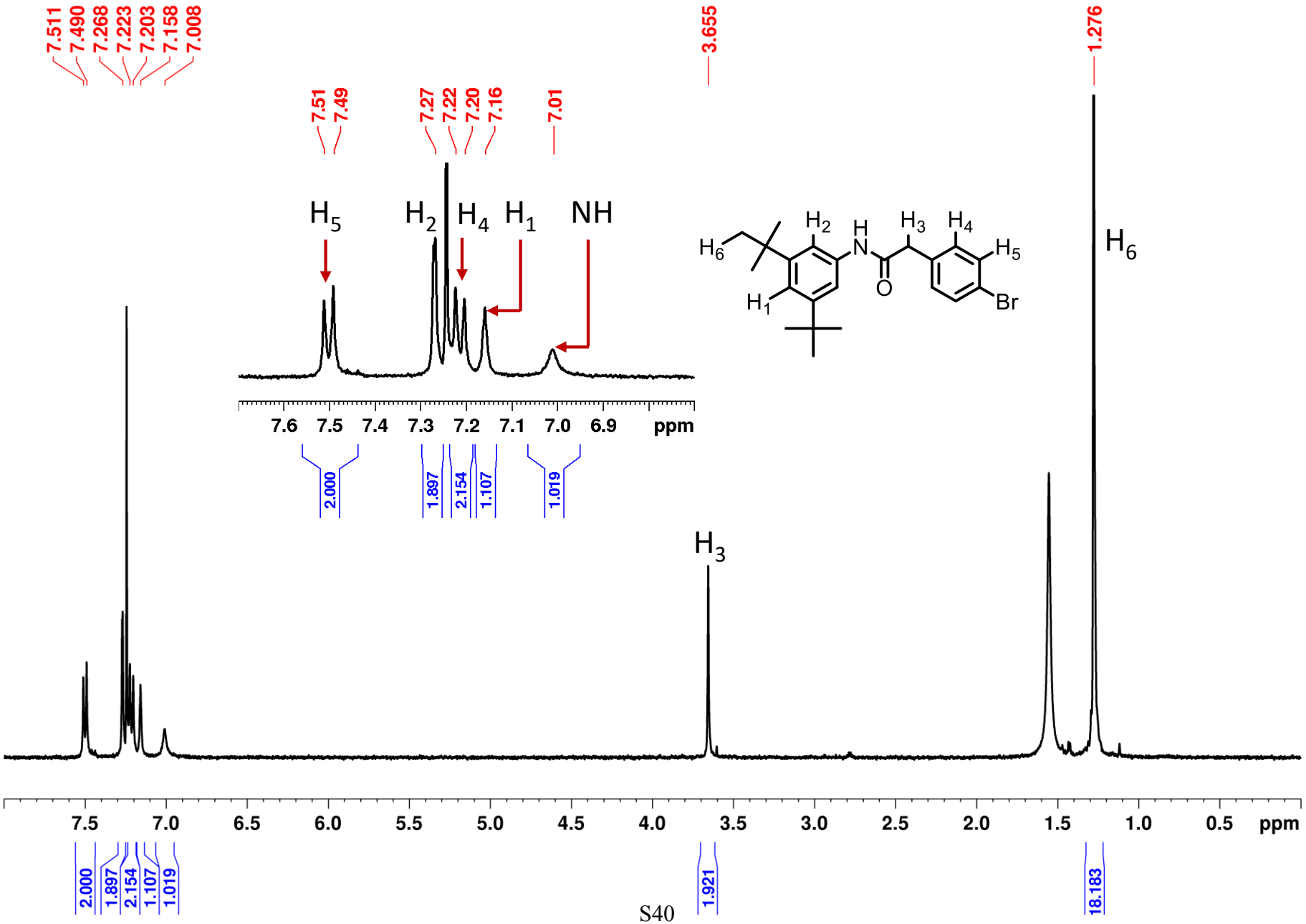


Figure S26 ^{13}C NMR Spectrum (100 MHz / $CDCl_3$ / 298 K) of **S2**

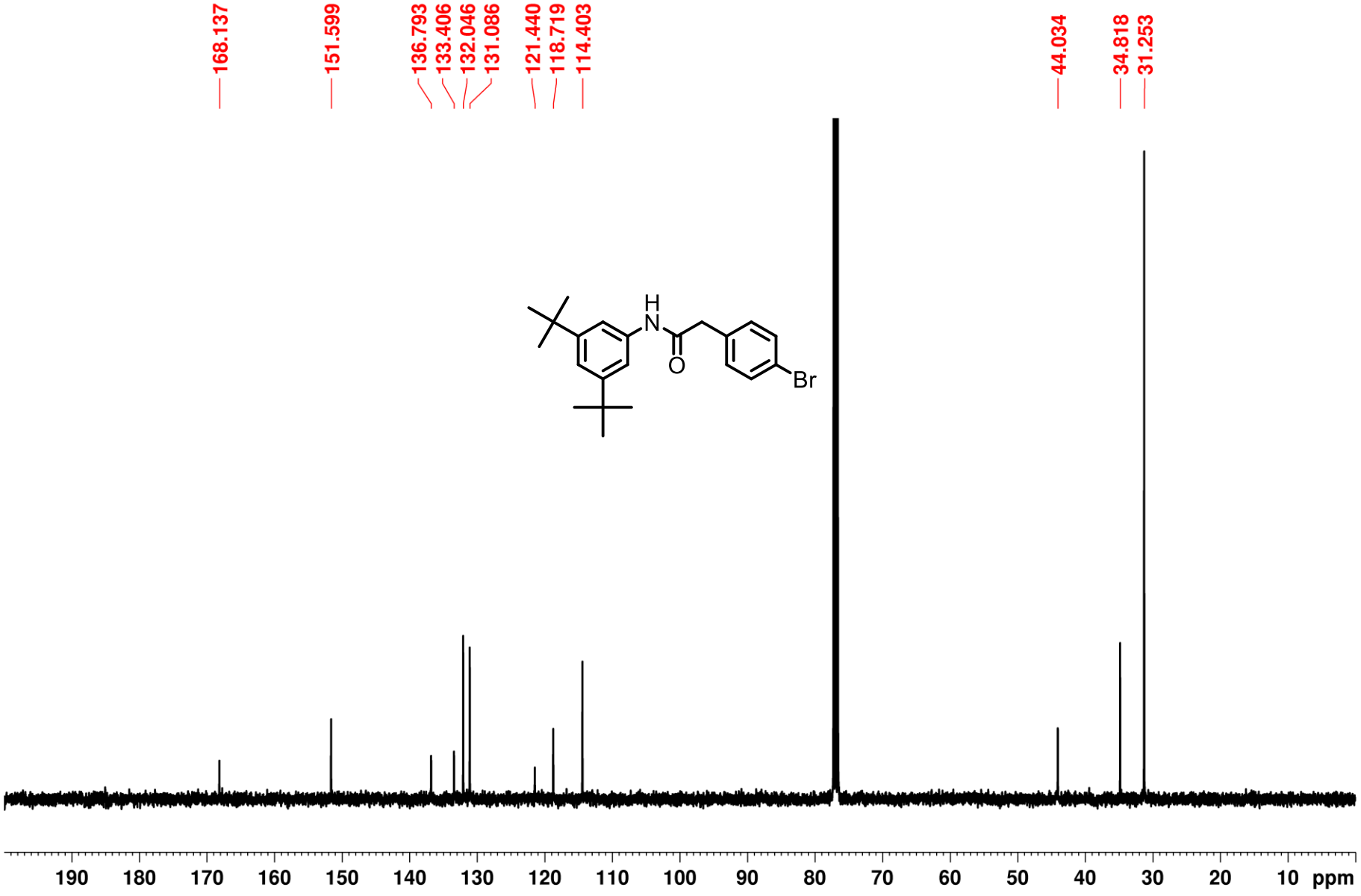


Figure S27 ESI Mass Spectra of Compound **S2**

Mass Spectrum SmartFormula Report

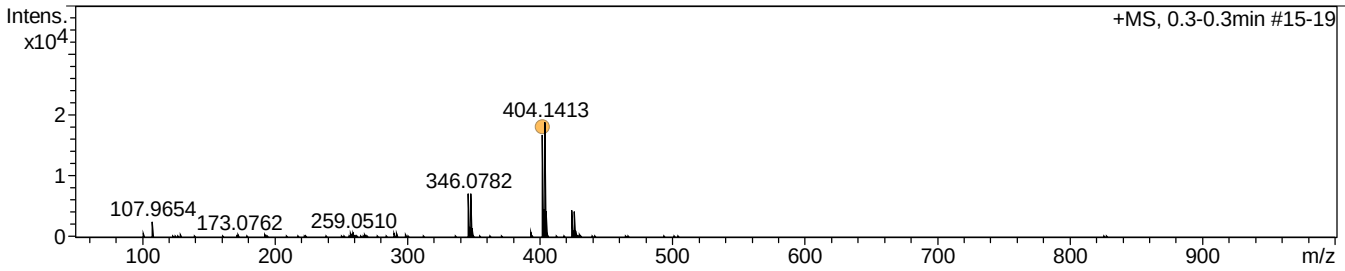
Analysis Info

Analysis Name	D:\Data\fish\data\2023q2(datas)\230612\230612_amide-Br_pl_1-52_01_53840.d	Acquisition Date	6/12/2023 12:40:38 PM
Method	tune_low_pos_LCMS_with lock mass_220107-3.m	Operator	Bruker microTOF-Q II
Sample Name	230612_amide-Br_pl	Instrument / Ser#	micrOTOF-Q 228888.10183
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.9 l/min
Scan End	3000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste

+MS, 0.3-0.3min #15-19



Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	mSigma	Score	rdb	e¯ Conf	N-Rule
402.1429	1	C22H29BrNO	402.1427	0.2	0.4	48.7	100.00	8.5	even	ok

+MS, 0.3-0.3min #15-19

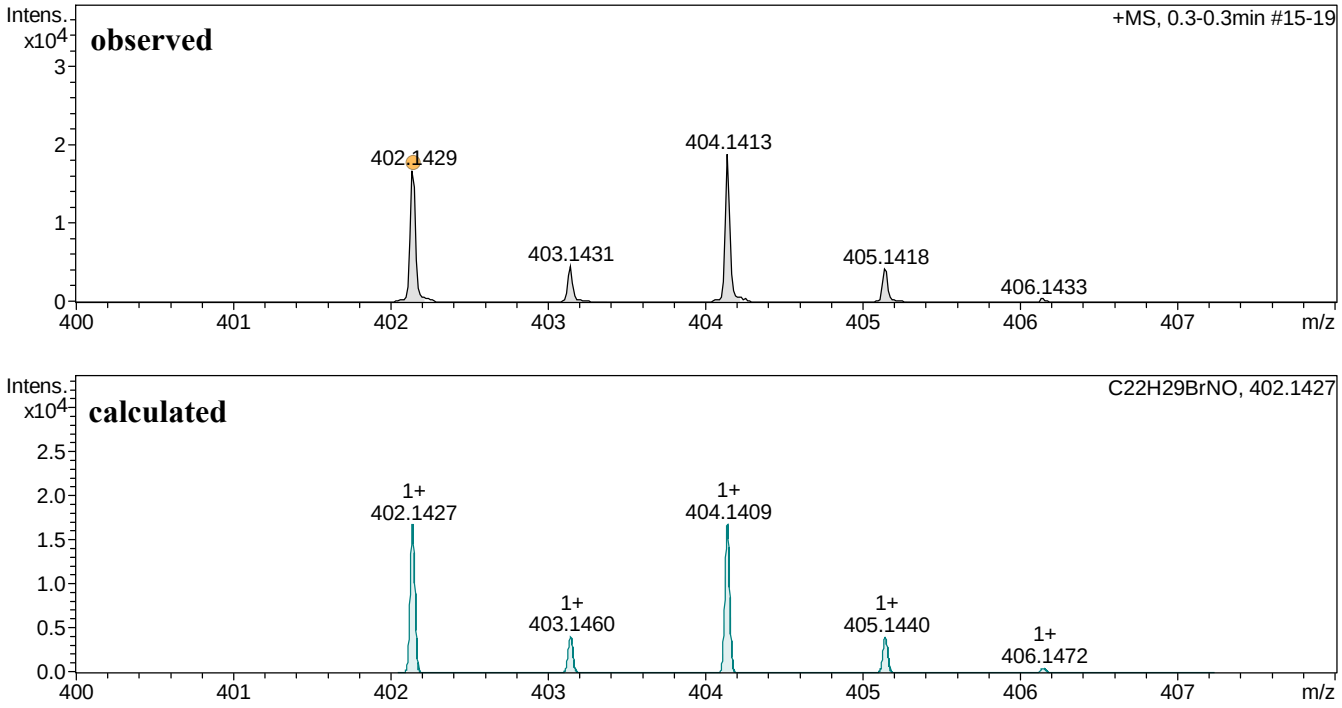


Figure S28 ^{1}H NMR Spectrum (400 MHz / CD_2Cl_2 / 298 K) of **S3**

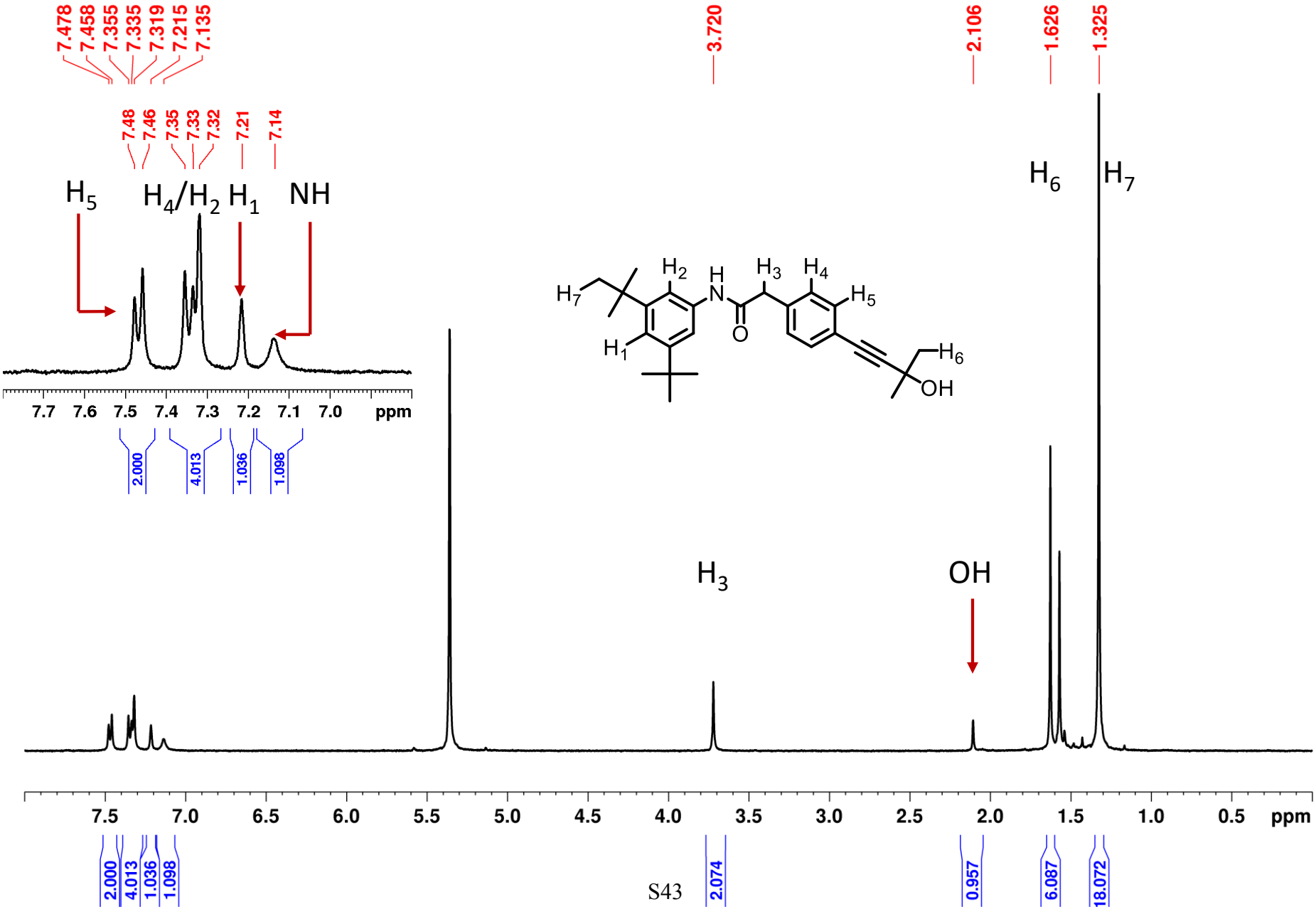


Figure S29 ^{13}C NMR Spectrum (100 MHz / $CDCl_3$ / 298 K) of **S3**

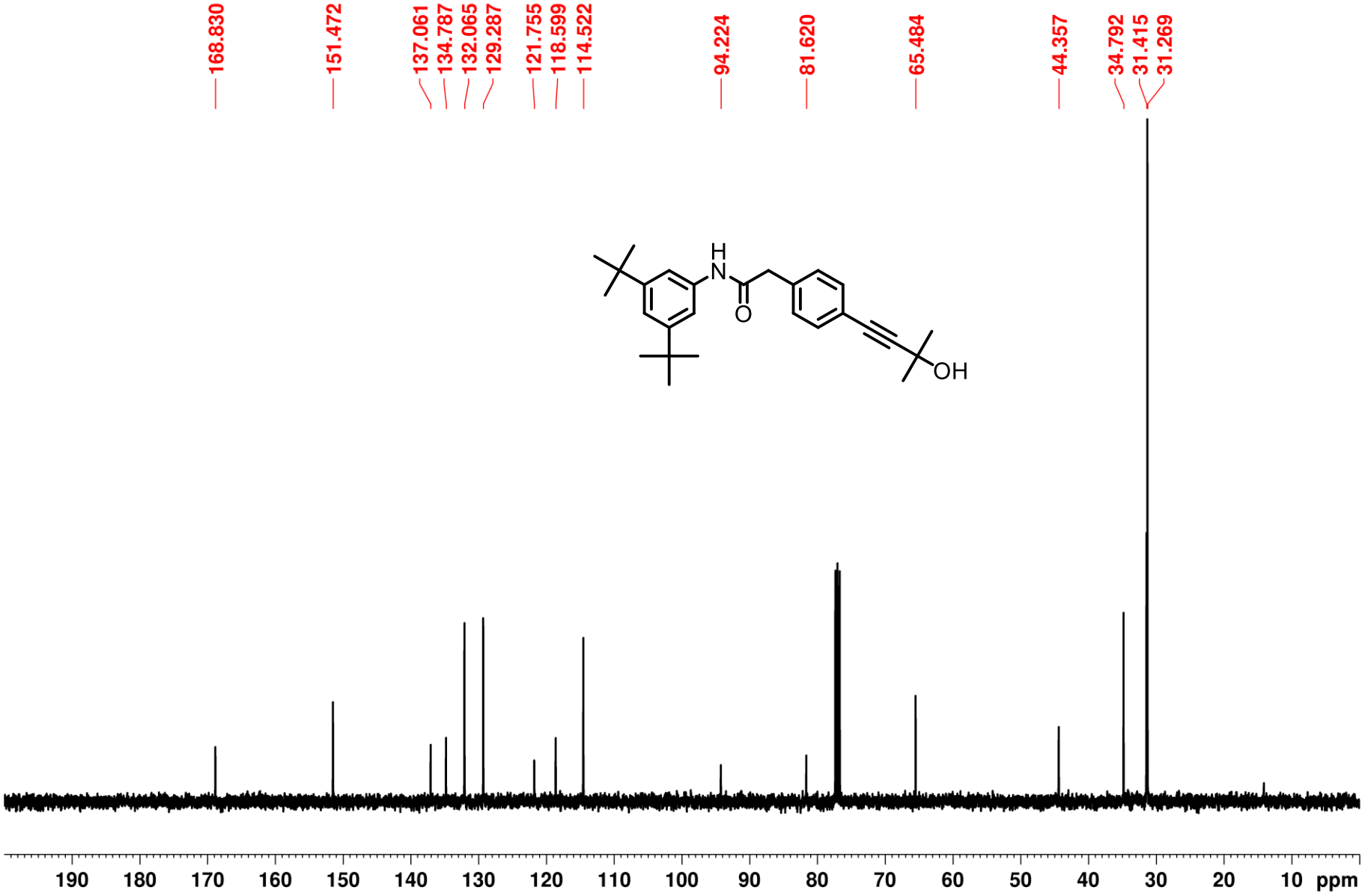


Figure S30 ESI Mass Spectra of Compound **S3**

Mass Spectrum SmartFormula Report

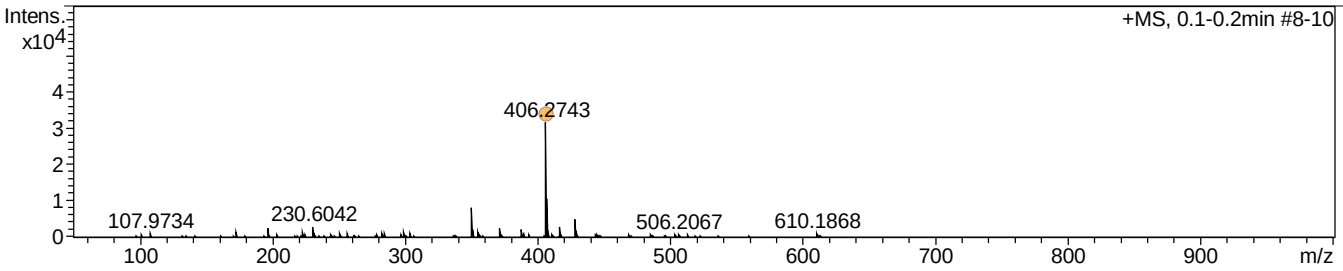
Analysis Info

Analysis Name	D:\Data\Fish\Data\2023Q2(datas)\230612\230612_amide-yne-OH_pl_1-53_01_53841.d	Acquisition Date	6/12/2023 12:46:21 PM
Method	tune_low_pos_LCMS_with lock mass_220107-3.m	Operator	Bruker microTOF-Q II
Sample Name	230612_amide-yne-OH_pl	Instrument / Ser#	micrOTOF-Q 228888.10183
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.9 l/min
Scan End	3000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste

+MS, 0.1-0.2min #8-10



Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	mSigma	Score	rdb	e¯ Conf	N-Rule
406.2743	1	C27H36NO2	406.2741	0.3	0.7	15.0	100.00	10.5	even	ok

+MS, 0.1-0.2min #8-10

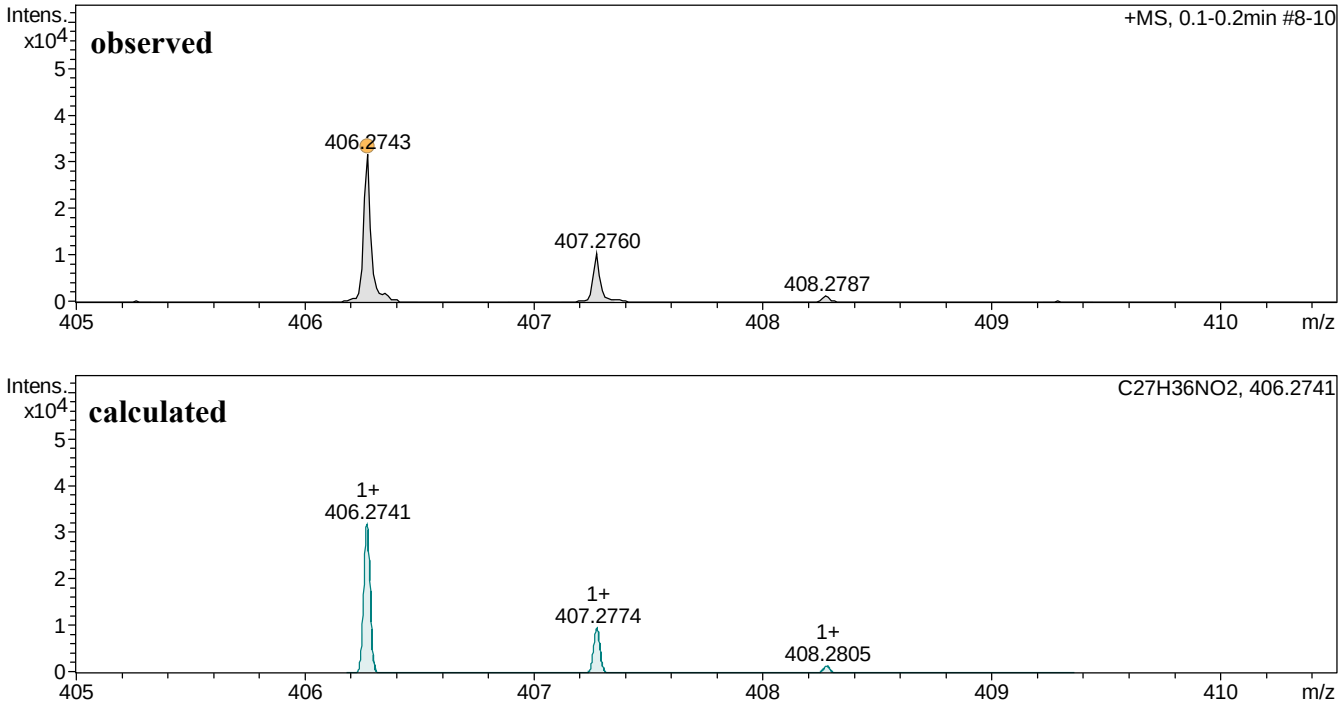


Figure S31 ^{1}H NMR Spectrum (400 MHz / $CDCl_3$ / 298 K) of **S4**

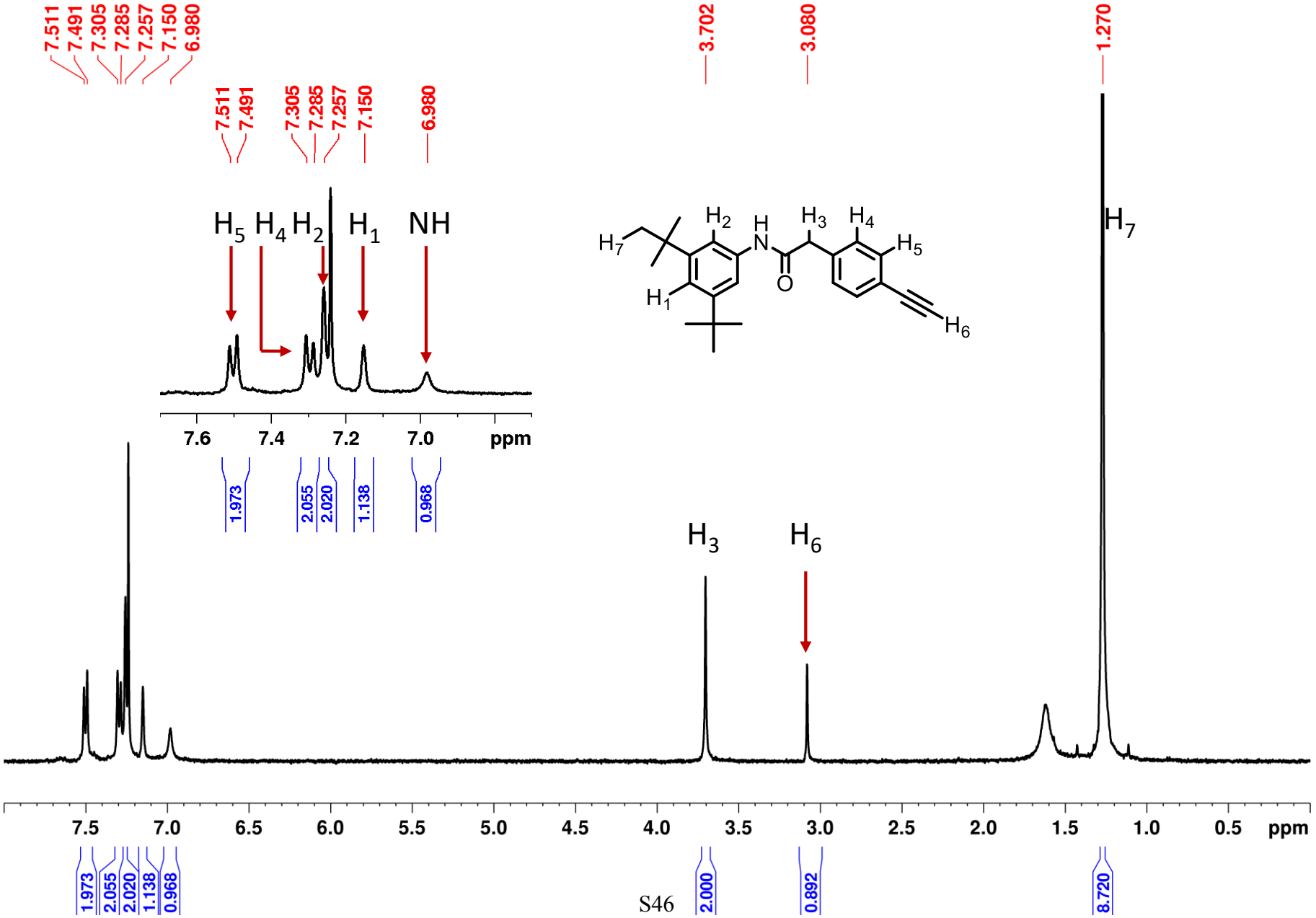


Figure S32 ^{13}C NMR Spectrum (100 MHz / $CDCl_3$ / 298 K) of **S4**

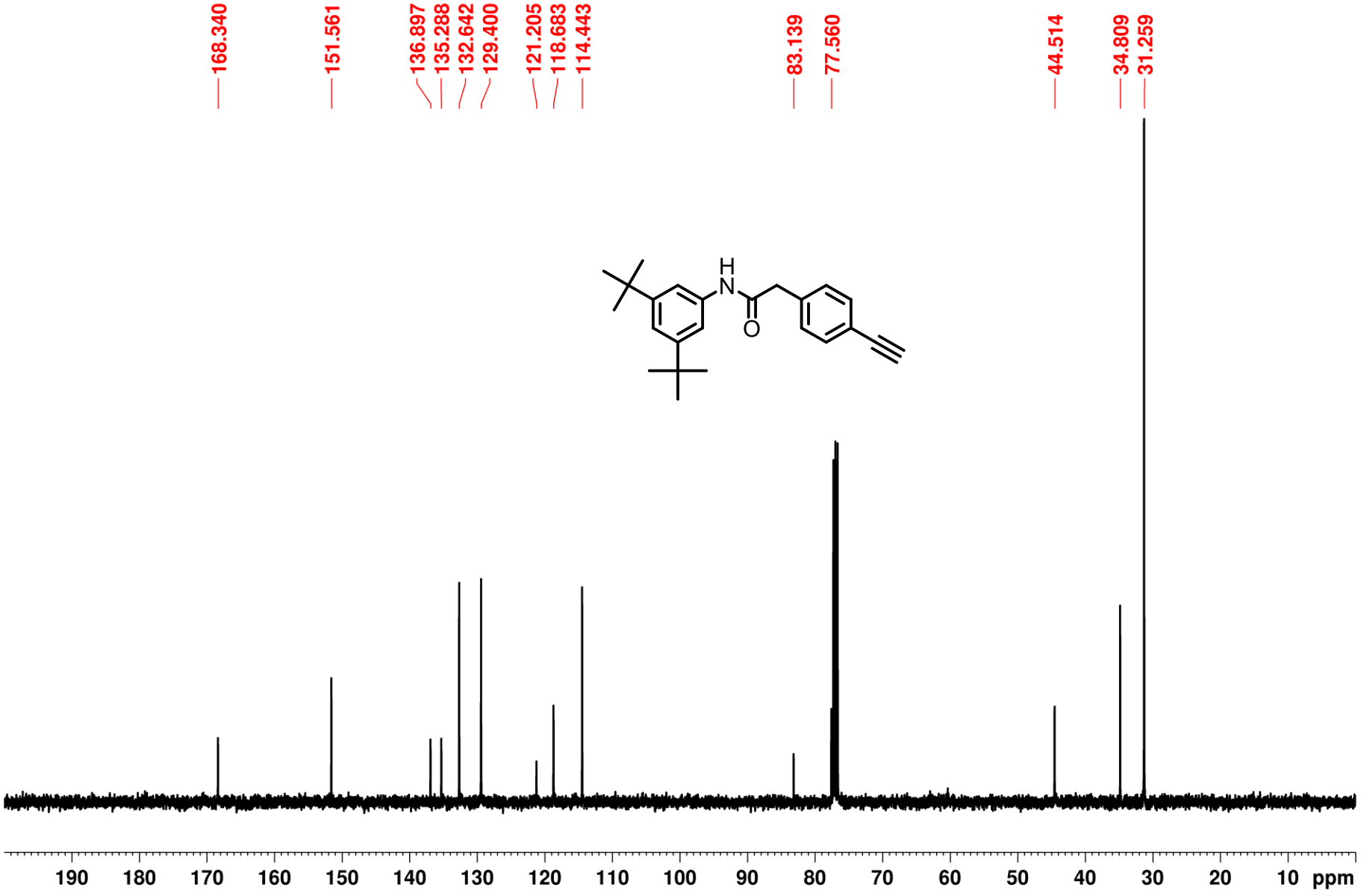


Figure S33 ESI Mass Spectra of Compound **S4**

Mass Spectrum SmartFormula Report

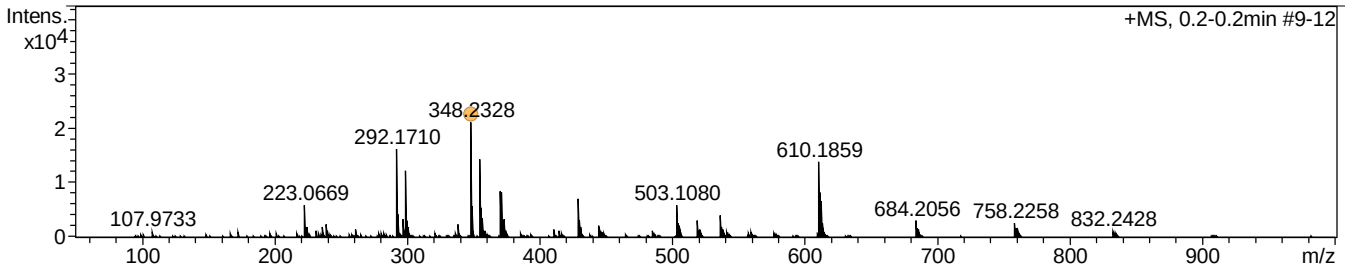
Analysis Info

Analysis Name	D:\Data\Fish\Data\2023Q2(datas)\230612\230612_amide-yne_pl_1-54_01_53842.d	Acquisition Date	6/12/2023 12:52:03 PM
Method	tune_low_pos_LCMS_with lock mass_220107-3.m	Operator	Bruker microTOF-Q II
Sample Name	230612_amide-yne_pl	Instrument / Ser#	micrOTOF-Q 228888.10183
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.9 l/min
Scan End	3000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste

+MS, 0.2-0.2min #9-12



Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	mSigma	Score	rdb	e⁻ Conf	N-Rule
348.2328	1	C24H30NO	348.2322	0.6	1.7	0.8	100.00	10.5	even	ok

+MS, 0.2-0.2min #9-12

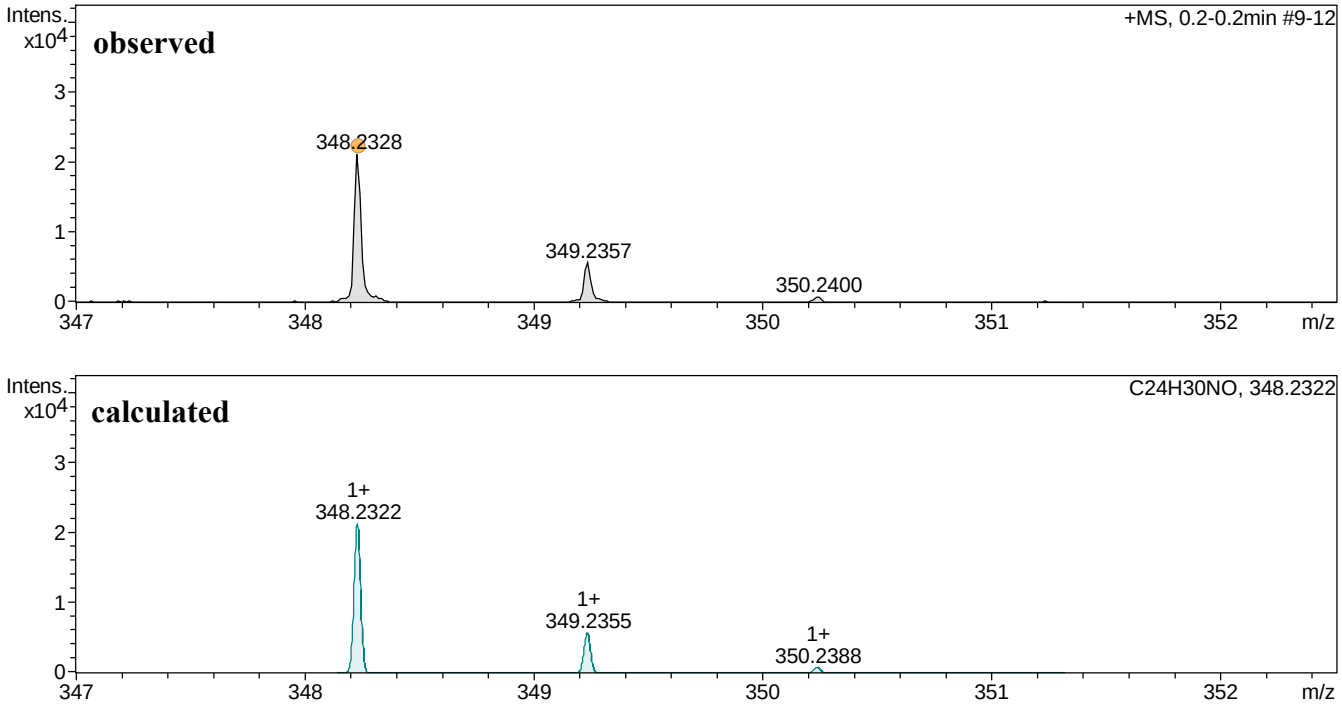


Figure S34 ^{1}H NMR Spectrum (400 MHz / CD_3SOCD_3 / 298 K) of **S5**

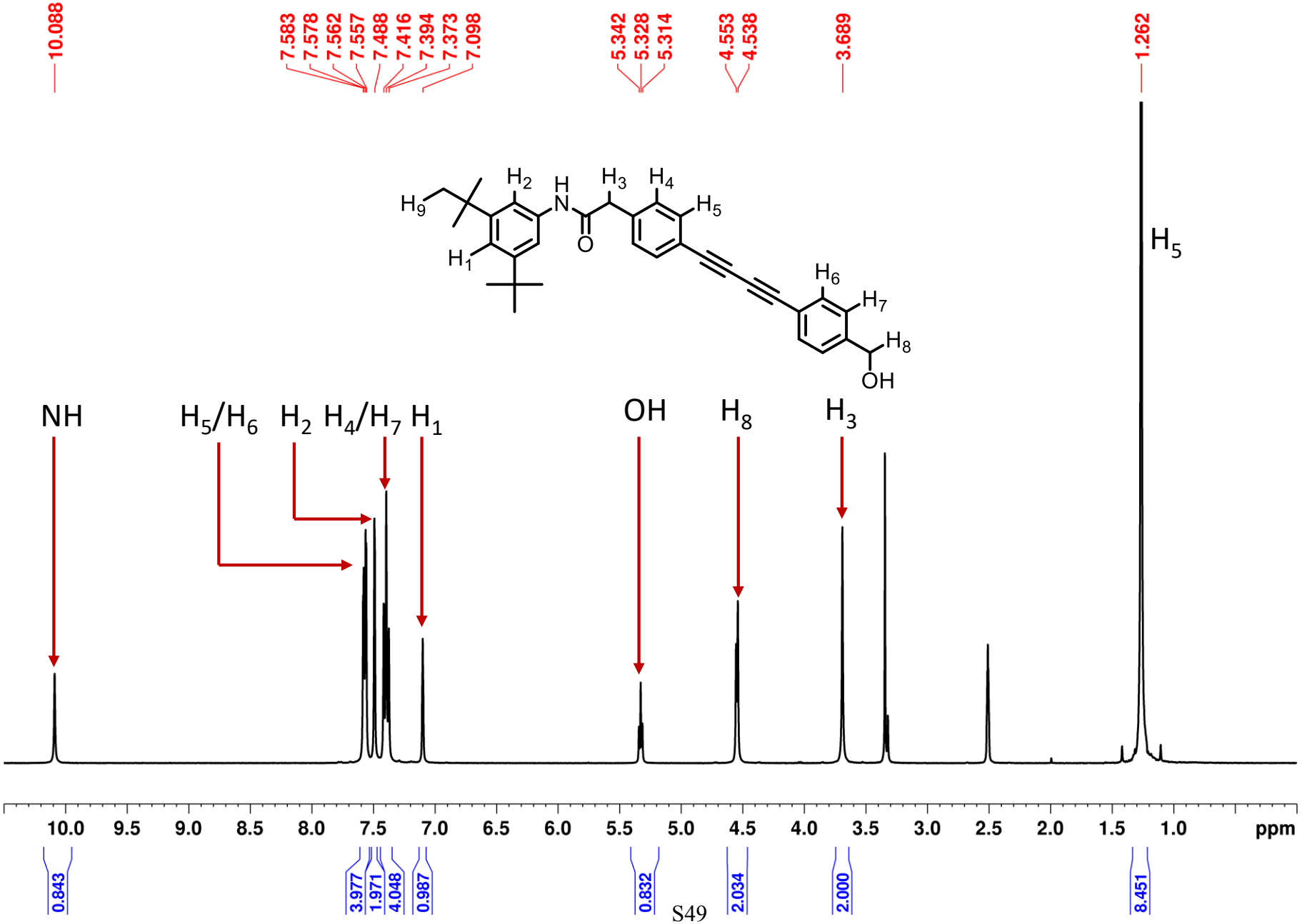


Figure S35 ^{13}C NMR Spectrum (100 MHz / CD_2Cl_2 / 298 K) of **S5**

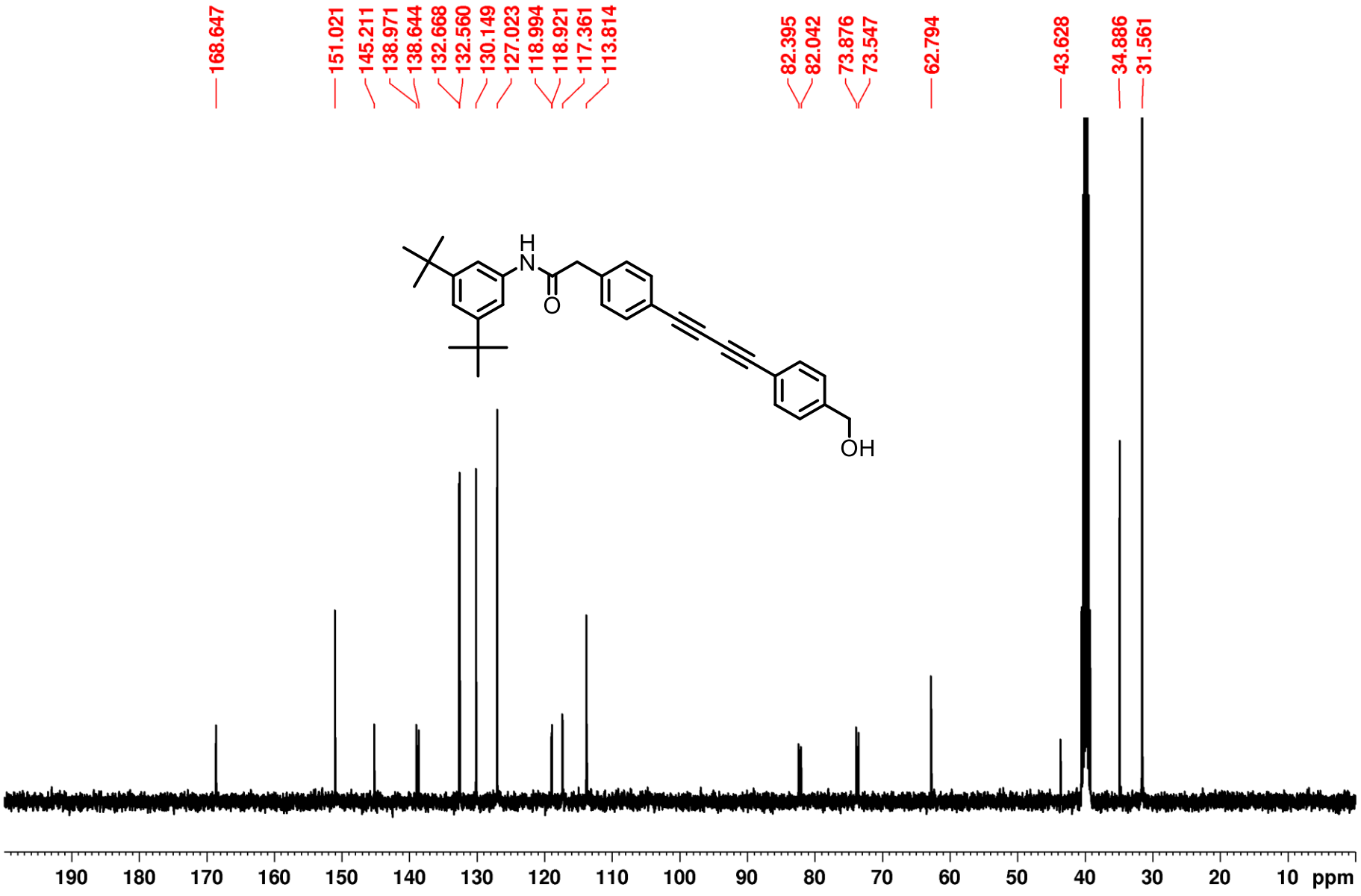


Figure S36 ESI Mass Spectra of Compound **S5**

Mass Spectrum SmartFormula Report

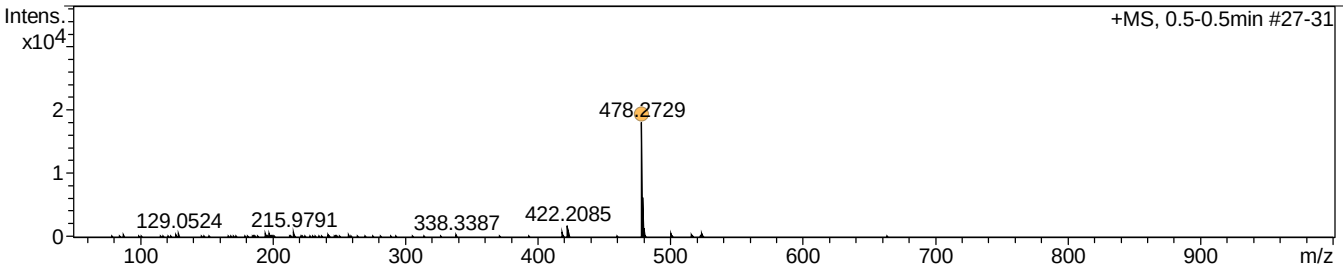
Analysis Info

Analysis Name	D:\Data\fish\data\2023q2(datas)\230626\230626-2_amide-diyne-OH_pl_1-79_01_53986.d	Acquisition Date	6/26/2023 3:03:22 PM
Method	tune_low_pos_LCMS_with lock mass_220107-3.m	Operator	Bruker microTOF-Q II
Sample Name	230626-2_amide-diyne-OH_pl	Instrument / Ser#	micrOTOF-Q 228888.10183
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.9 l/min
Scan End	3000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste

+MS, 0.5-0.5min #27-31



Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	mSigma	Score	rdb	e⁻ Conf	N-Rule
478.2729	1	C33H36NO2	478.2741	1.2	2.5	12.4	100.00	16.5	even	ok

+MS, 0.5-0.5min #27-31

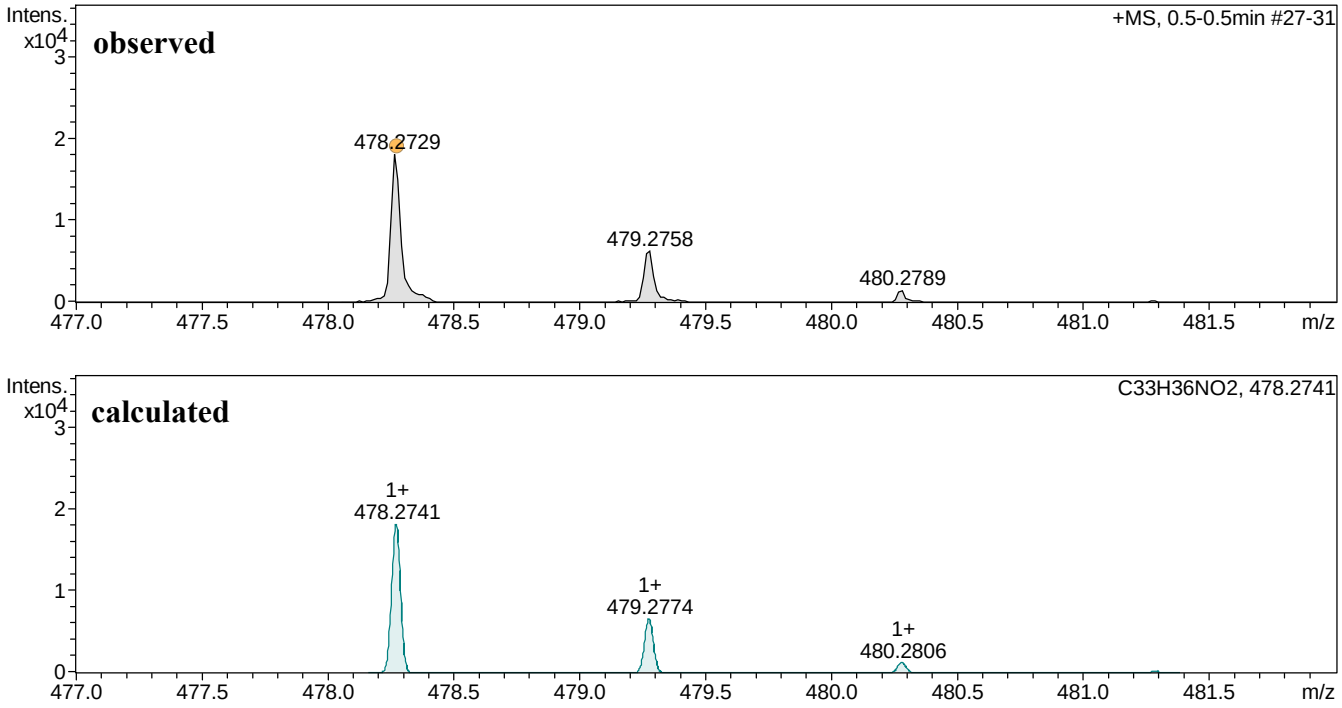


Figure S37 ^{1}H NMR Spectrum (400 MHz / CD_2Cl_2 / 298 K) of **S6**

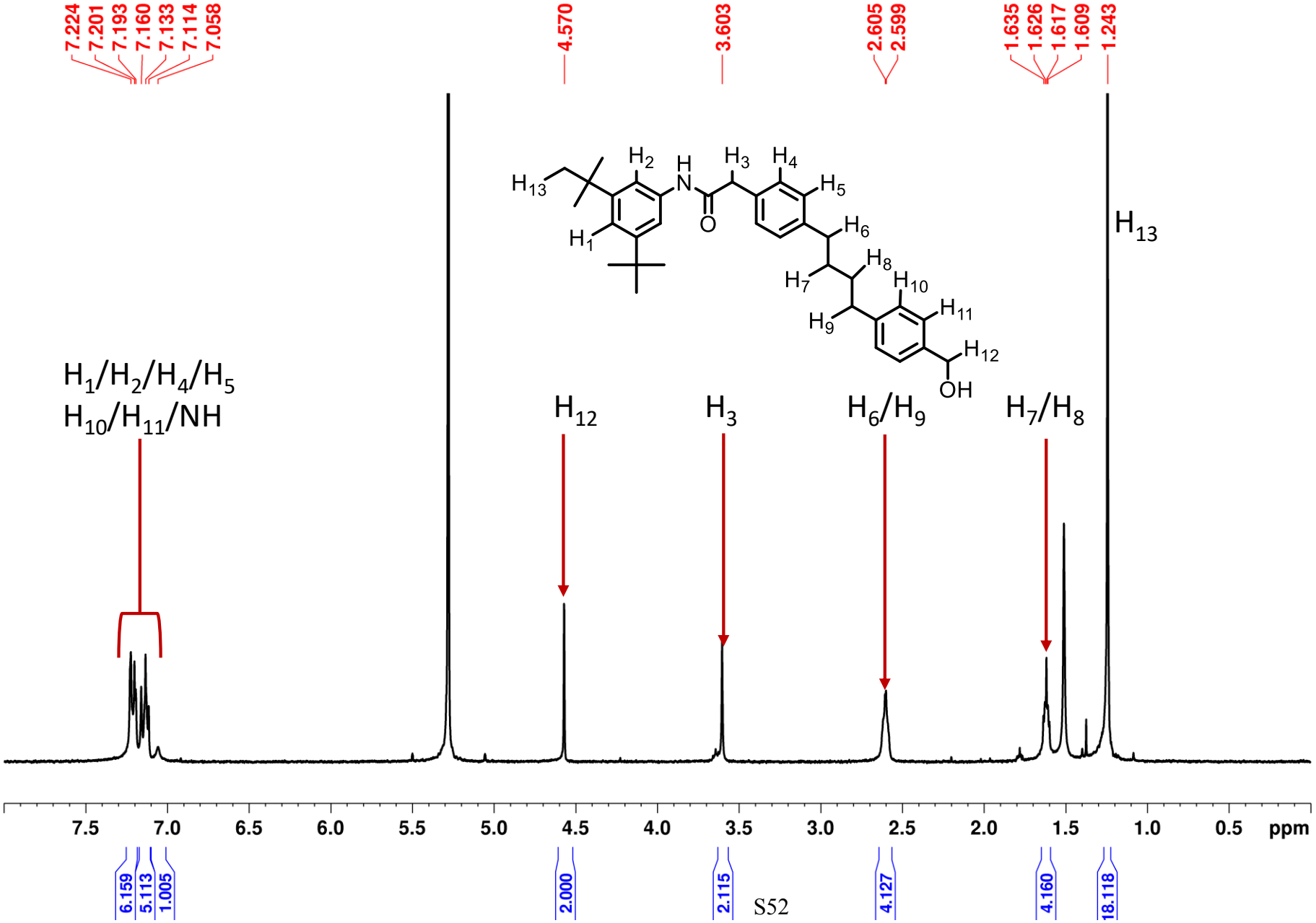


Figure S38 ^{13}C NMR Spectrum (100 MHz / $CDCl_3$ / 298 K) of **S6**

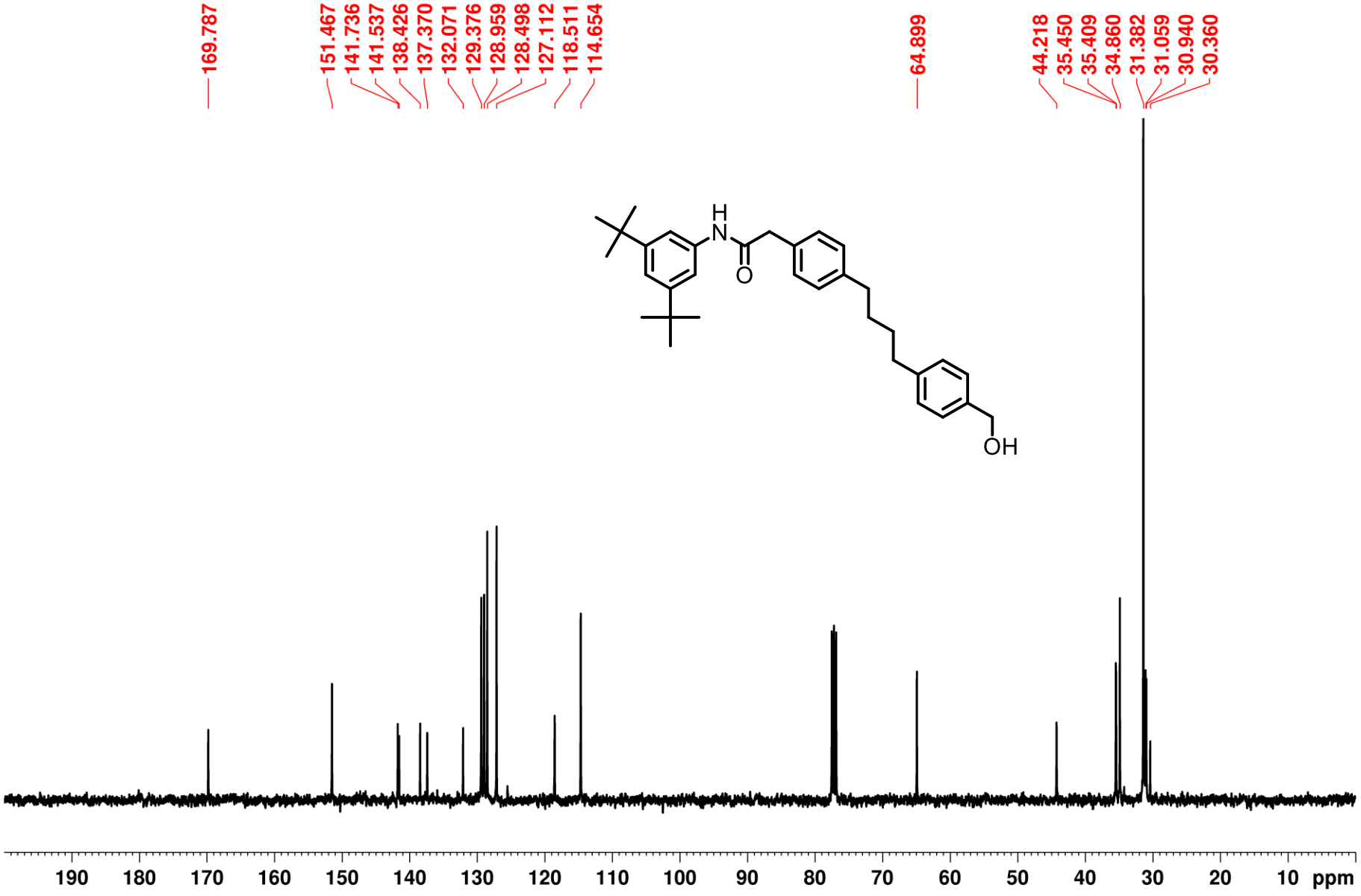


Figure S39 ESI Mass Spectra of Compound **S6**

Mass Spectrum SmartFormula Report

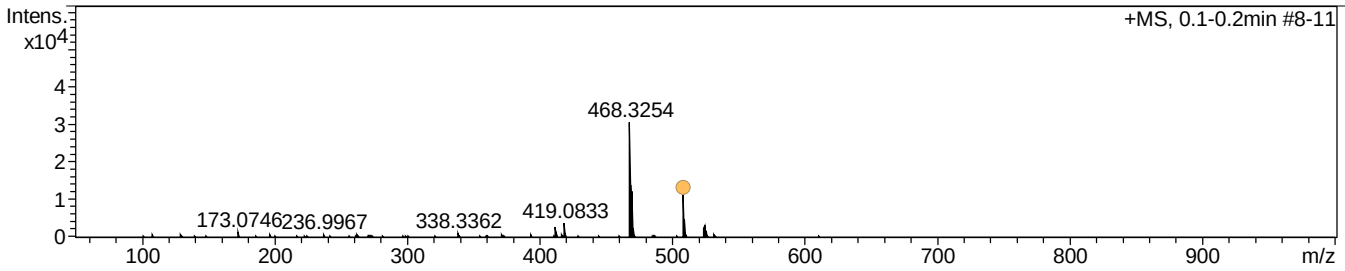
Analysis Info

Analysis Name	D:\Data\fish\data\2023q2(datas)\230626\230626_amide-C4-OH_pl_1-80_01_53976.d	Acquisition Date	6/26/2023 10:48:35 AM
Method	tune_low_pos_LCMS_with lock mass_220107-3.m	Operator	Bruker microTOF-Q II
Sample Name	230626_amide-C4-OH_pl	Instrument / Ser#	micrOTOF-Q 228888.10183
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.9 l/min
Scan End	3000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste

+MS, 0.1-0.2min #8-11



Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	mSigma	Score	rdb	e⁻ Conf	N-Rule
508.3167	1	C33H43NNaO2	508.3186	1.9	3.8	33.1	100.00	12.5	even	ok

+MS, 0.1-0.2min #8-11

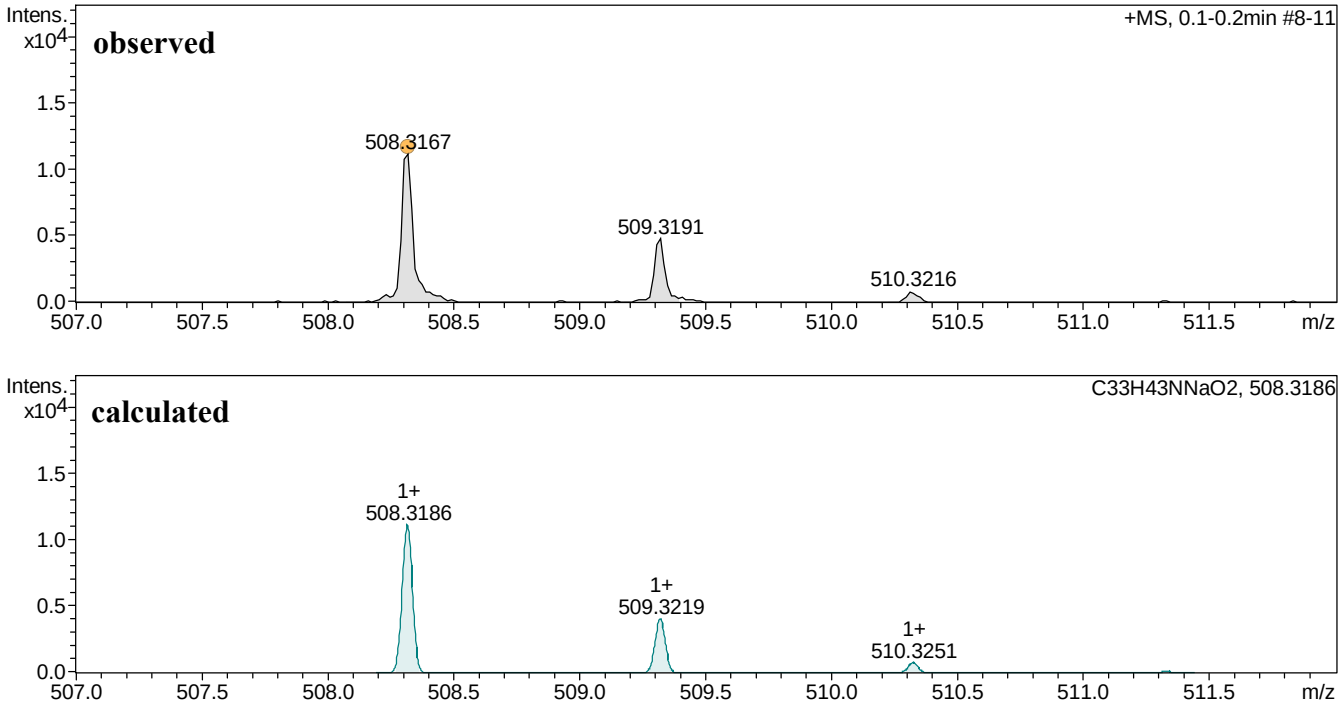


Figure S40 ^{1}H NMR Spectrum (400 MHz / CD_2Cl_2 / 298 K) of **9**

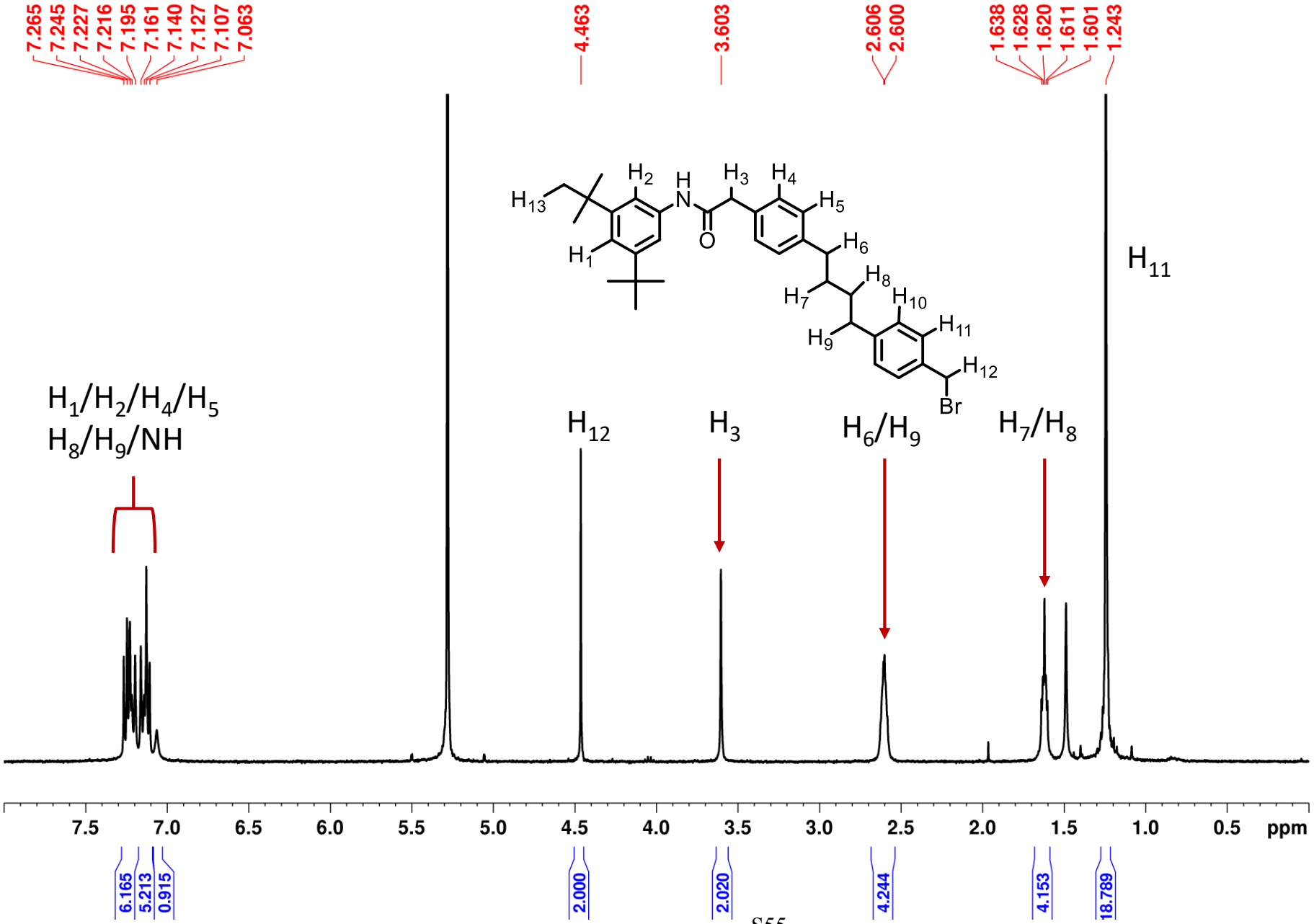


Figure S41 ^{13}C NMR Spectrum (100 MHz / $CDCl_3$ / 298 K) of **9**

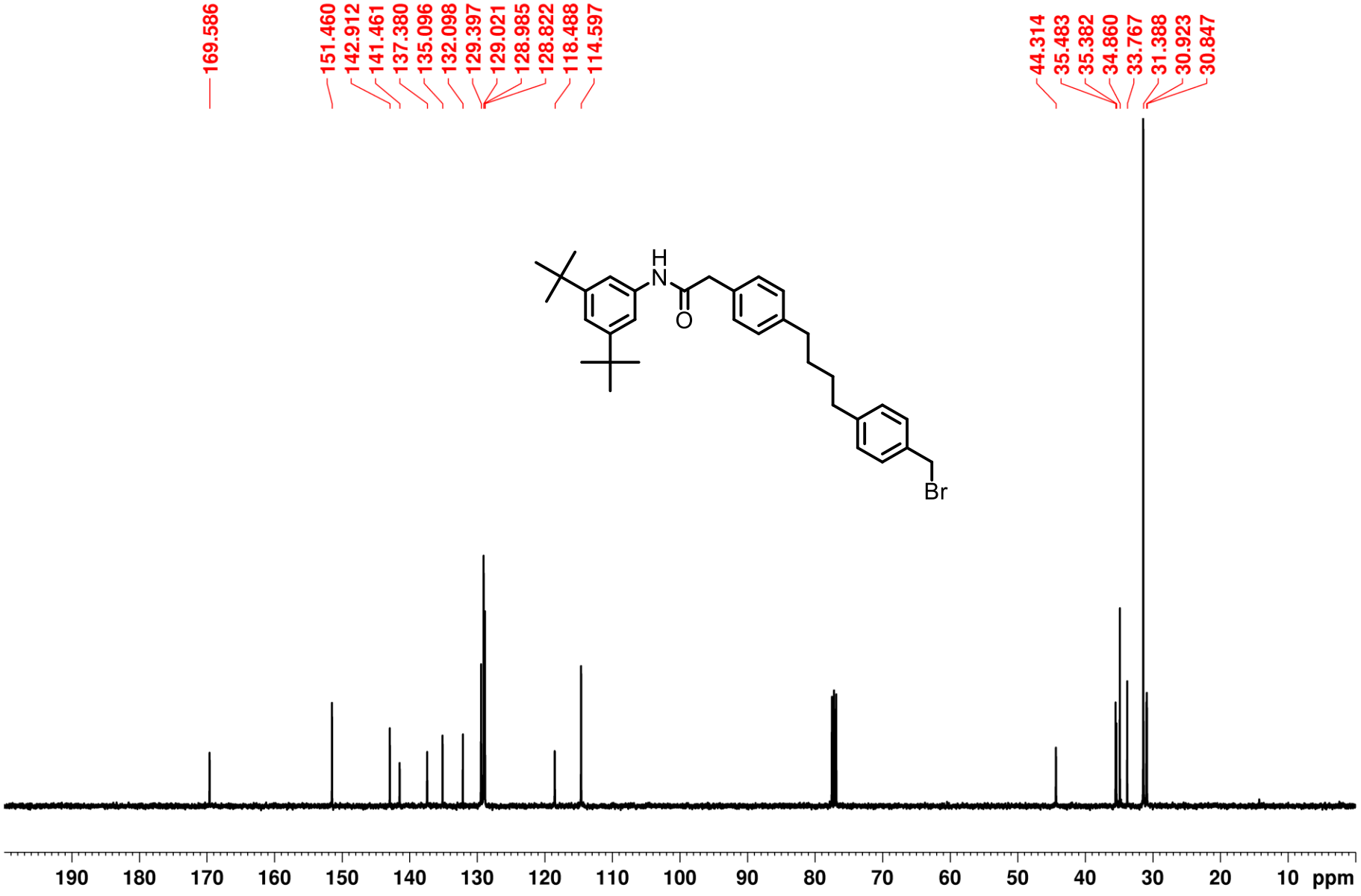


Figure S42 ESI Mass Spectra of Compound **9**

Mass Spectrum SmartFormula Report

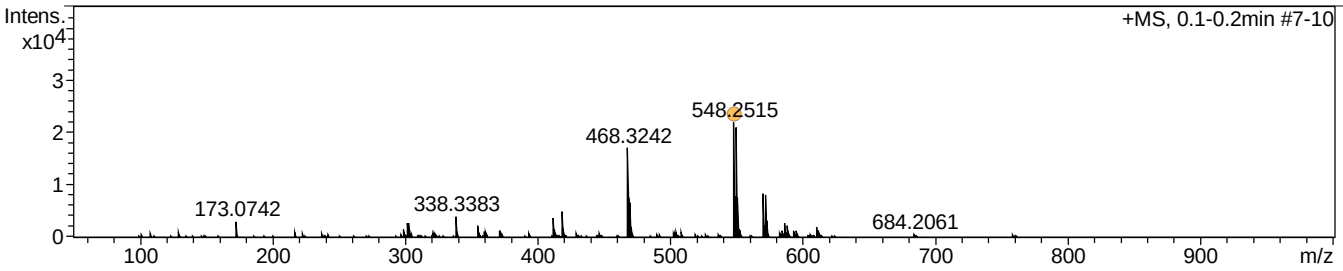
Analysis Info

Analysis Name	D:\Data\fish\data\2023q2(datas)\230626\230626_amide-C4-Br_pl_1-81_01_53977.d	Acquisition Date	6/26/2023 10:54:18 AM
Method	tune_low_pos_LCMS_with lock mass_220107-3.m	Operator	Bruker microTOF-Q II
Sample Name	230626_amide-C4-Br_pl	Instrument / Ser#	micrOTOF-Q 228888.10183
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.9 l/min
Scan End	3000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste

+MS, 0.1-0.2min #7-10



Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	mSigma	Score	rdb	e⁻ Conf	N-Rule
548.2515	1	C33H43BrNO	548.2523	-0.8	-1.4	25.8	100.00	12.5	even	ok

+MS, 0.1-0.2min #7-10

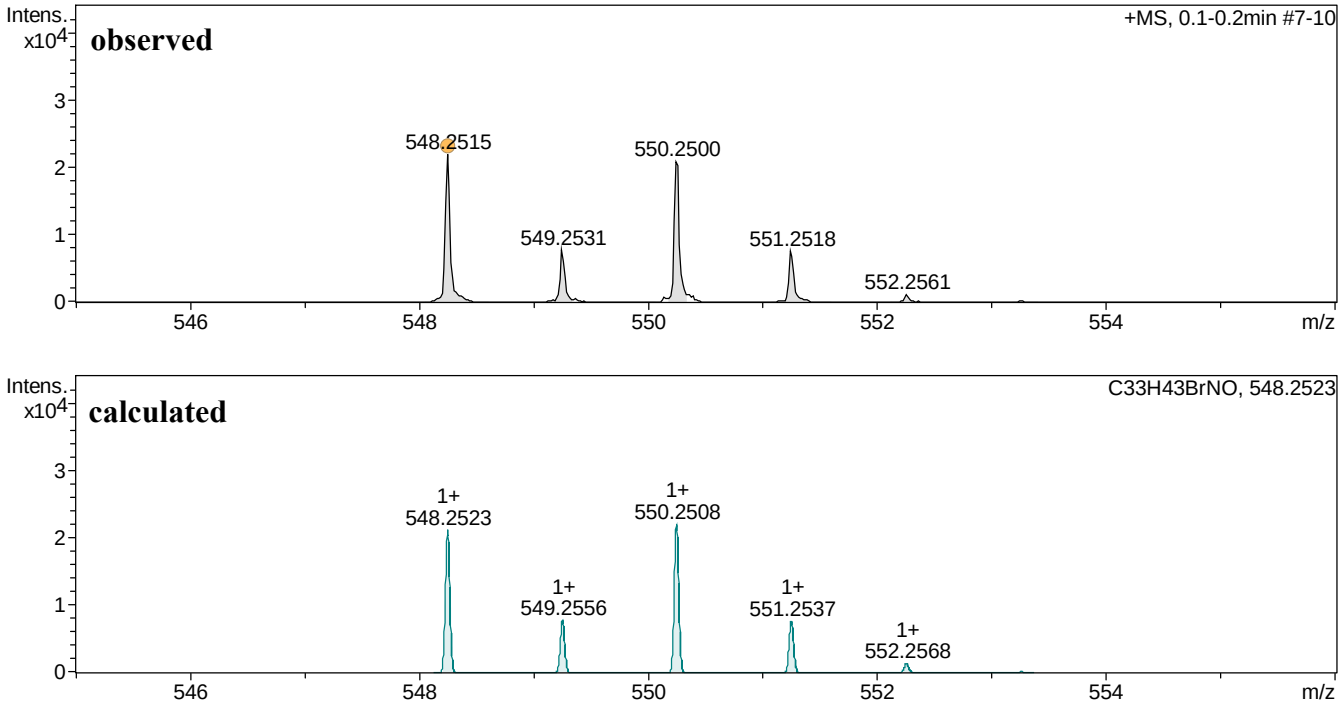


Figure S43 ^{1}H NMR Spectrum (400 MHz / CD_2Cl_2 / 298 K) of **10**·TFPB

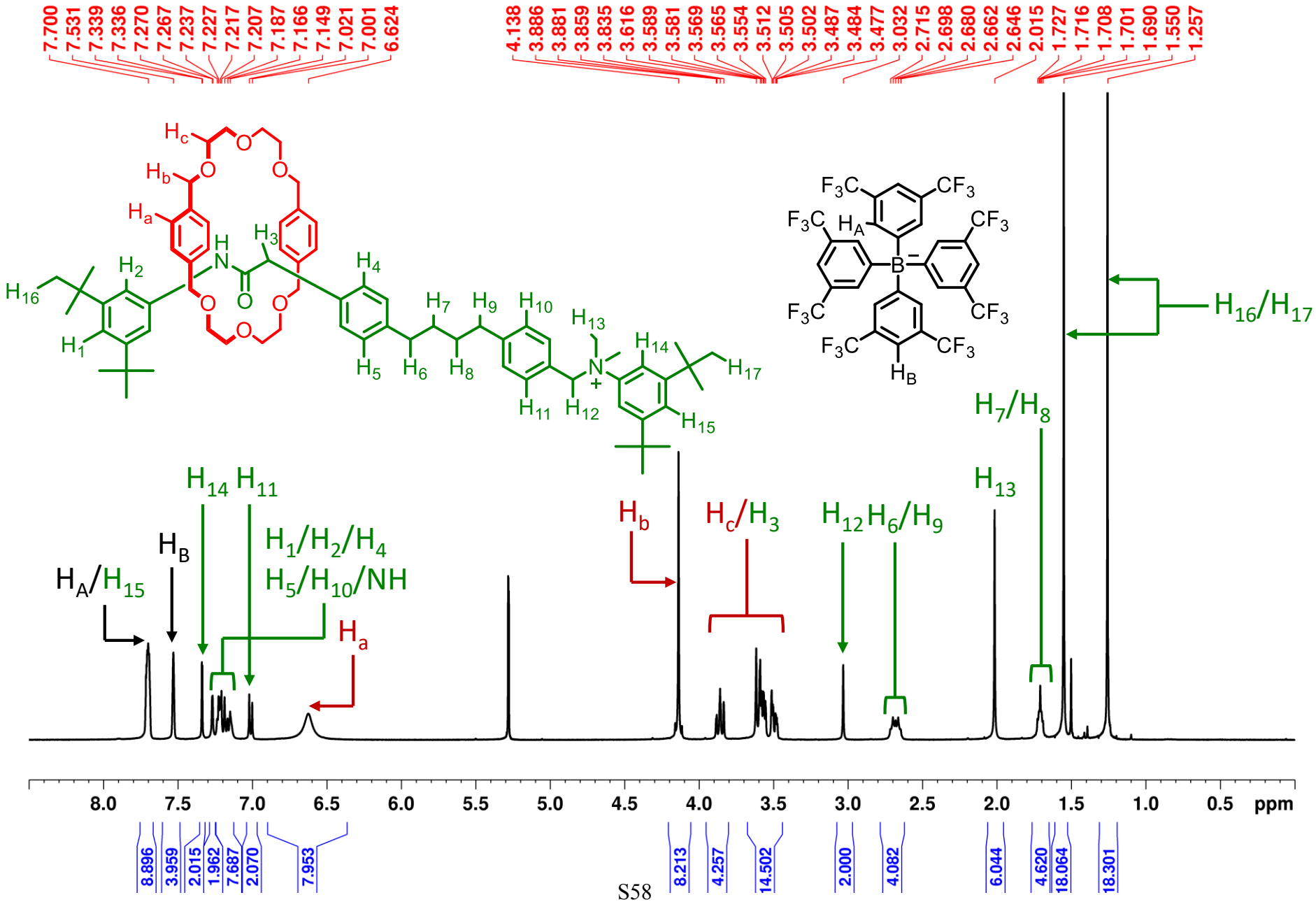


Figure S44 ^{13}C NMR Spectrum (100 MHz / $CDCl_3$ / 298 K) of **10**·TFPB

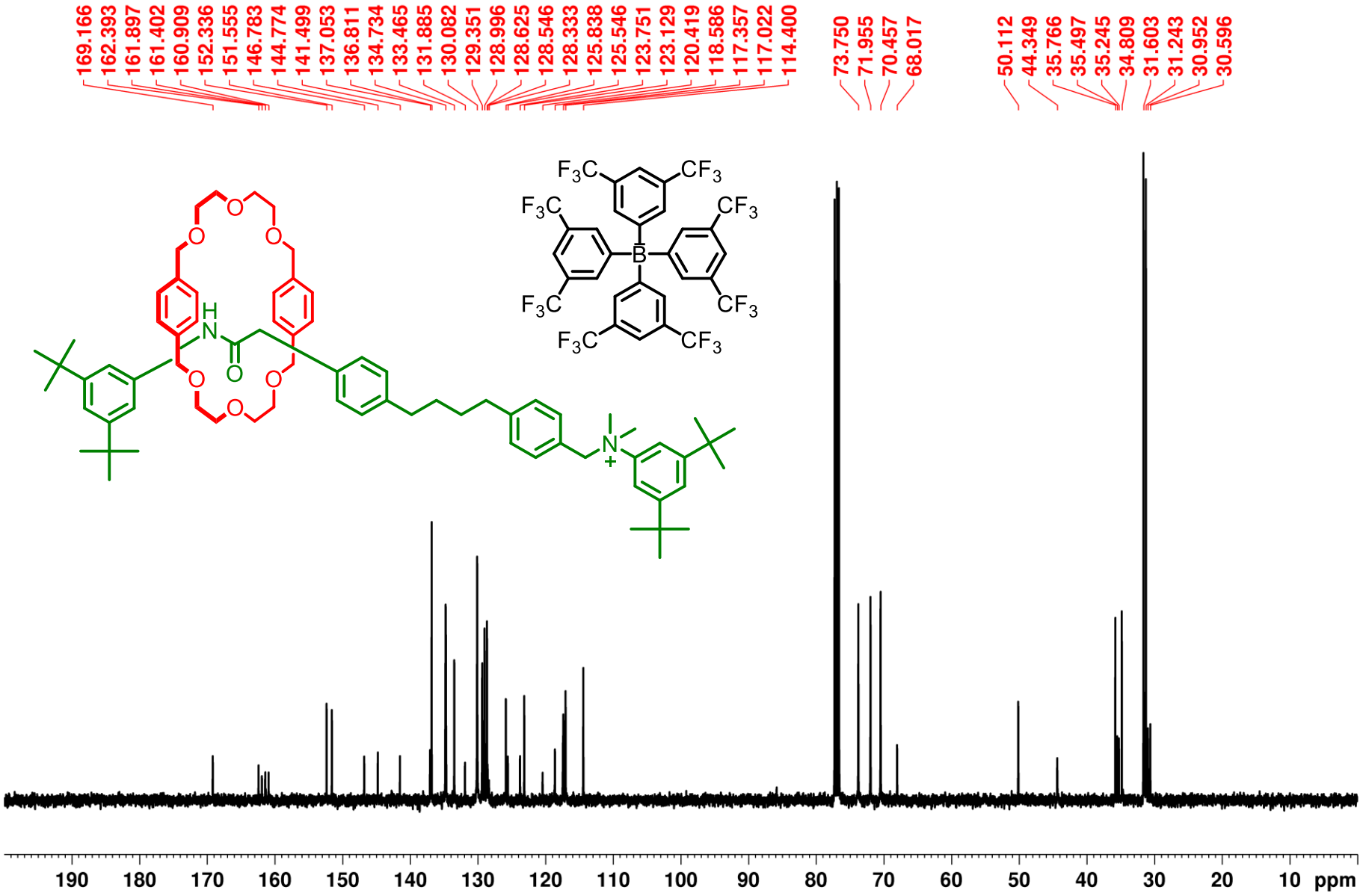


Figure S45 ESI Mass Spectra of Compound **10**·TFPB

Mass Spectrum SmartFormula Report

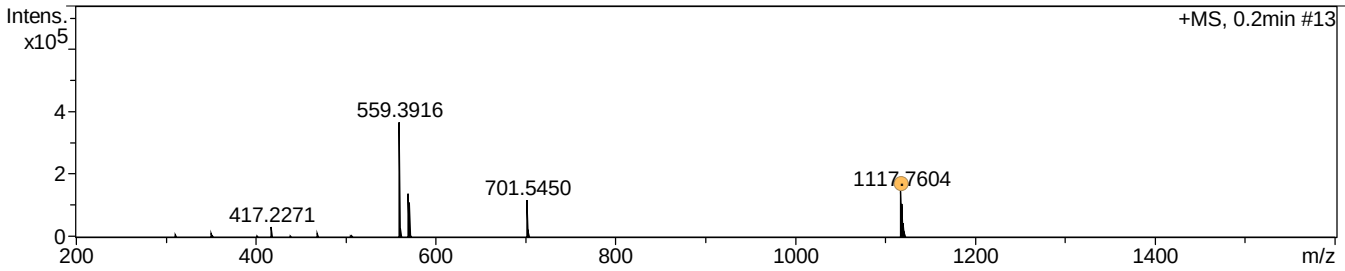
Analysis Info

Analysis Name	D:\Data\fish\data\2023q2(datas)\230516\230516_amide-C4-rotaxane_pw_1-36_01_53378.d	Acquisition Date	5/16/2023 3:19:46 PM
Method	tune_wide_pos_LCMS_with lock mass_220107-3.m	Operator	Bruker microTOF-Q II
Sample Name	230516_amide-C4-rotaxane_pw	Instrument / Ser#	micrOTOF-Q 228888.10183
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.9 l/min
Scan End	3000 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Waste

+MS, 0.2min #13



Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	mSigma	Score	rdb	e⁻ Conf	N-Rule
1117.7604	1	C73H101N2O7	1117.7603	0.0	0.0	28.9	100.00	24.5	even	ok

+MS, 0.2min #13

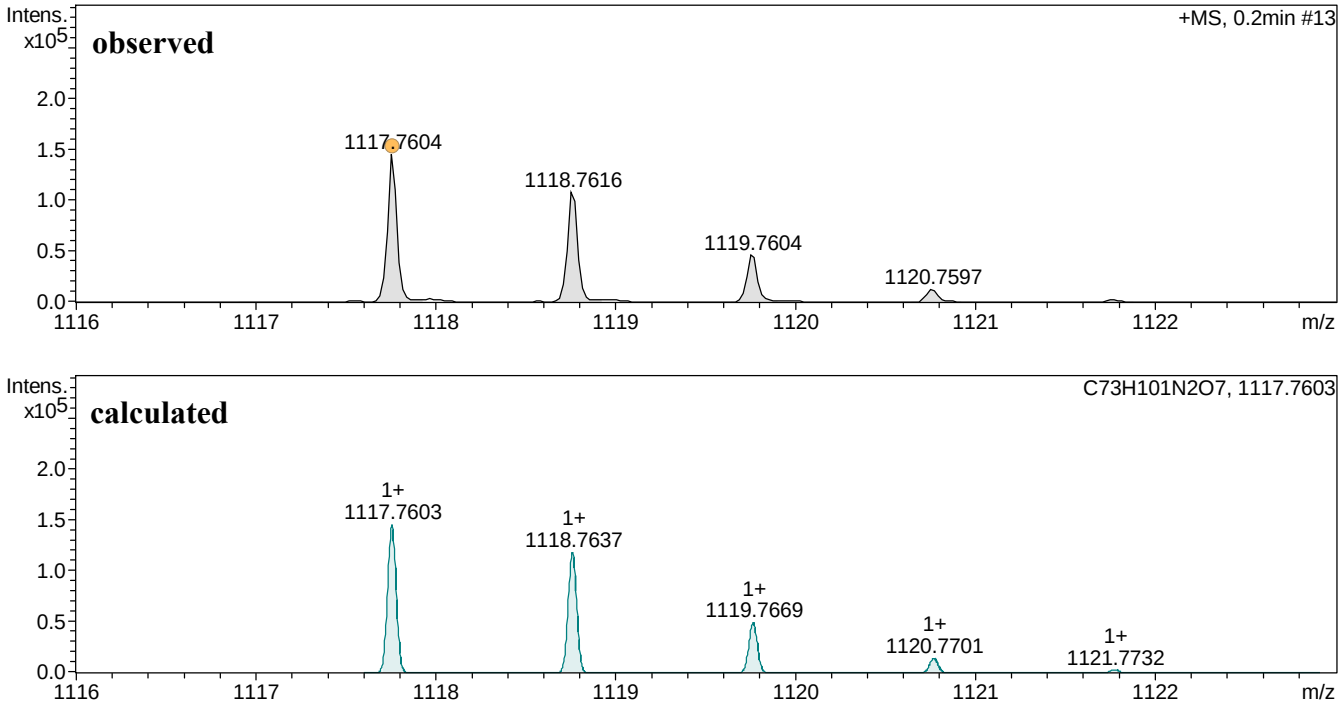


Figure S46 ^{1}H NMR Spectrum (400 MHz / CD_2Cl_2 / 298 K) of **11**

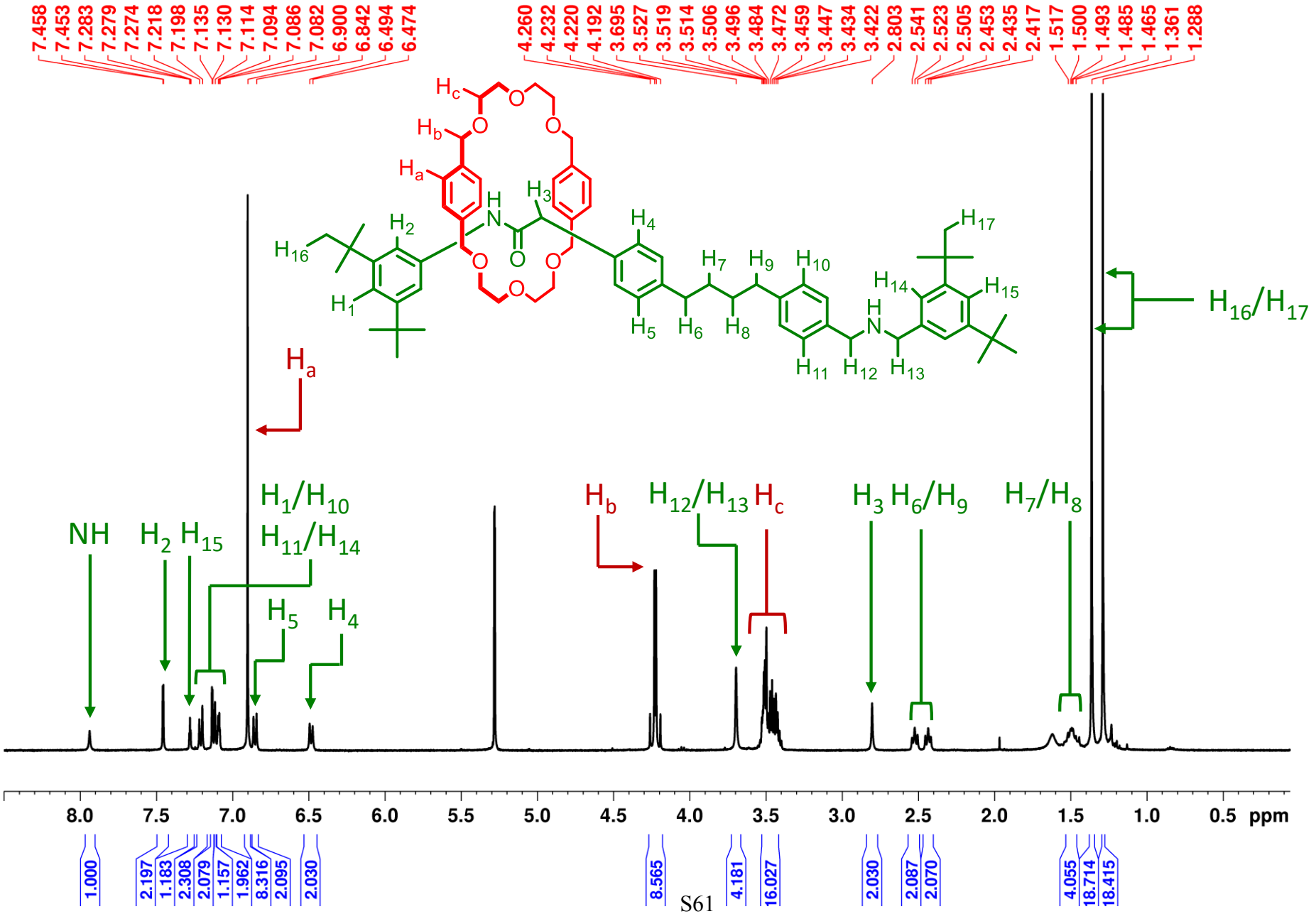


Figure S47 ^{13}C NMR Spectrum (100 MHz / CD_2Cl_2 / 298 K) of **11**

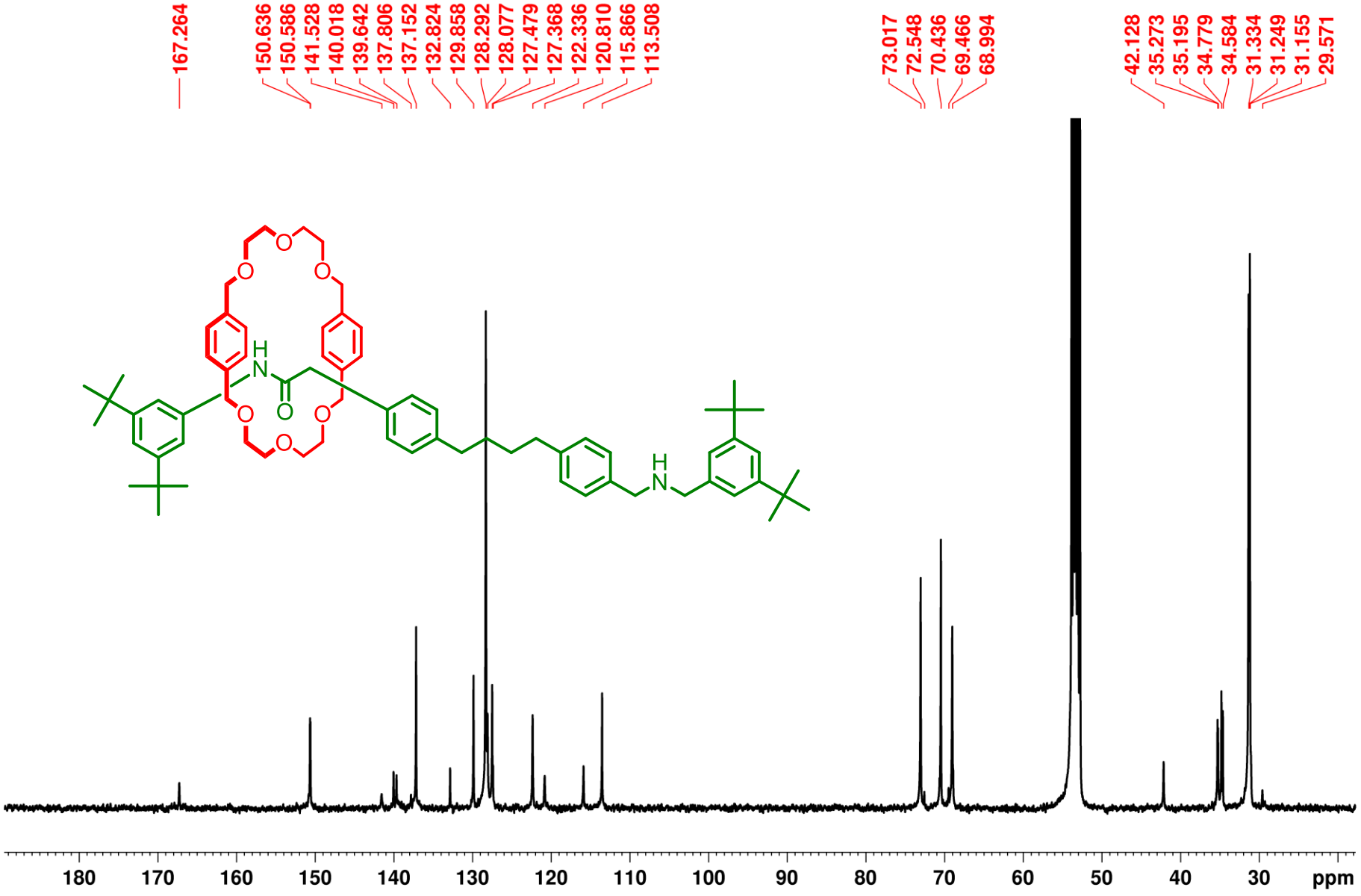


Figure S48 ESI Mass Spectra of Compound **11**

Mass Spectrum SmartFormula Report

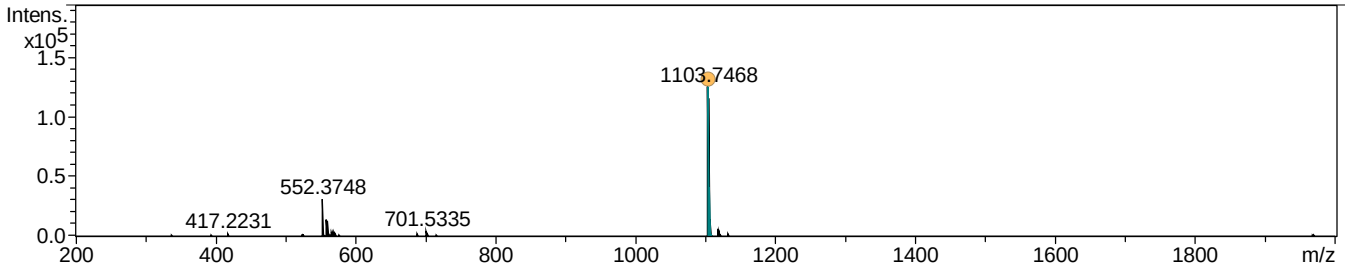
Analysis Info

Analysis Name	D:\Data\Fish\Data\2023Q3(datas)\230721\230721_amide-C4-rot-amine_pw_1-60_01_54412.d	Acquisition Date	7/21/2023 11:57:27 AM
Method	tune_wide_pos_LCMS_with lock mass_220107-3.m	Operator	Bruker microTOF-Q II
Sample Name	230721_amide-C4-rot-amine_pw	Instrument / Ser#	micrOTOF-Q 228888.10183
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.9 l/min
Scan End	3000 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Waste

+MS, 0.1min #5



Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	mSigma	Score	rdb	e¯ Conf	N-Rule
1103.7468	1	C72H99N2O7	1103.7447	-2.1	-1.9	69.8	100.00	24.5	even	ok

+MS, 0.1min #5

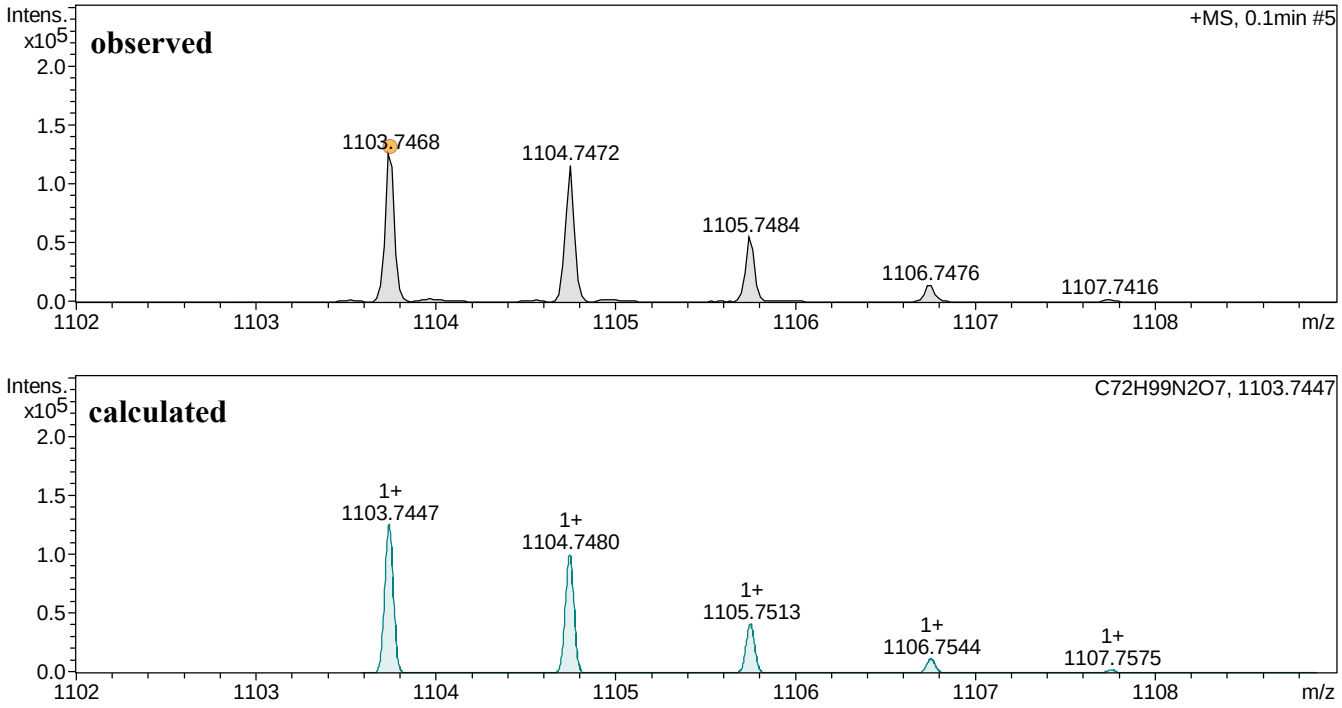


Figure S49 ^{1}H NMR Spectrum (400 MHz / $CDCl_3$ / 298 K) of **12**

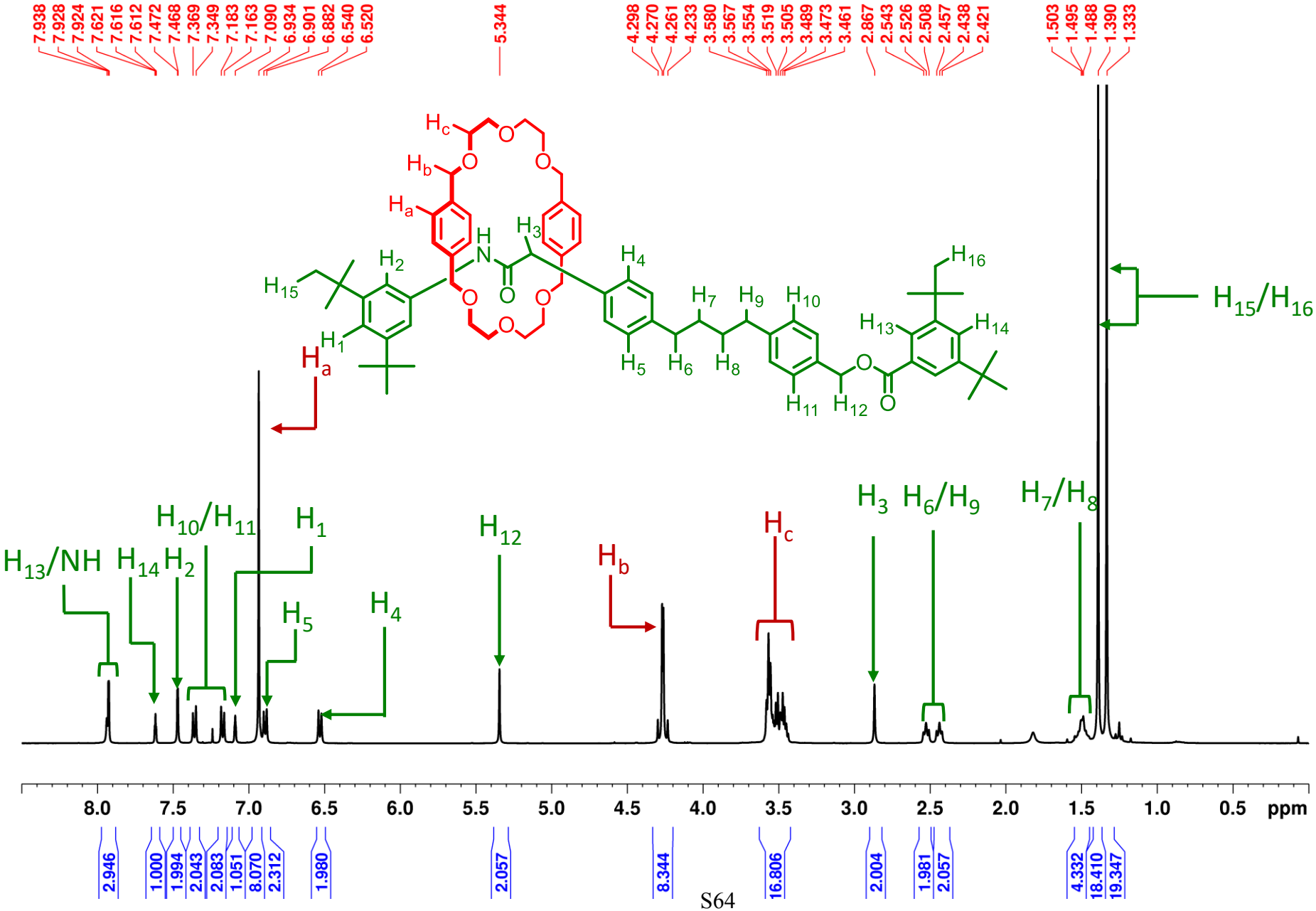


Figure S50 ^{13}C NMR Spectrum (100 MHz / $CDCl_3$ / 298 K) of **12**

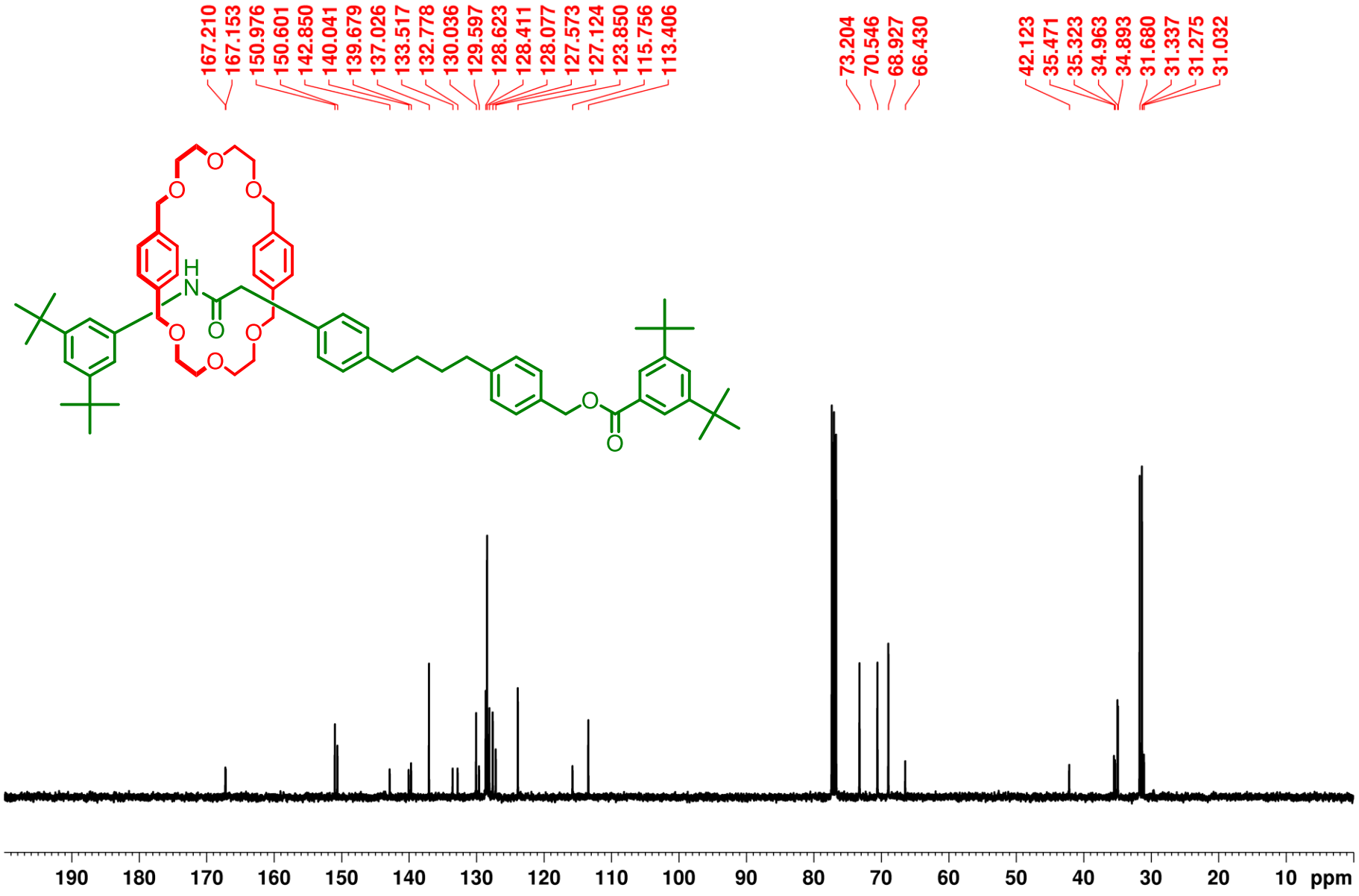


Figure S51 ESI Mass Spectra of Compound **12**

Mass Spectrum SmartFormula Report

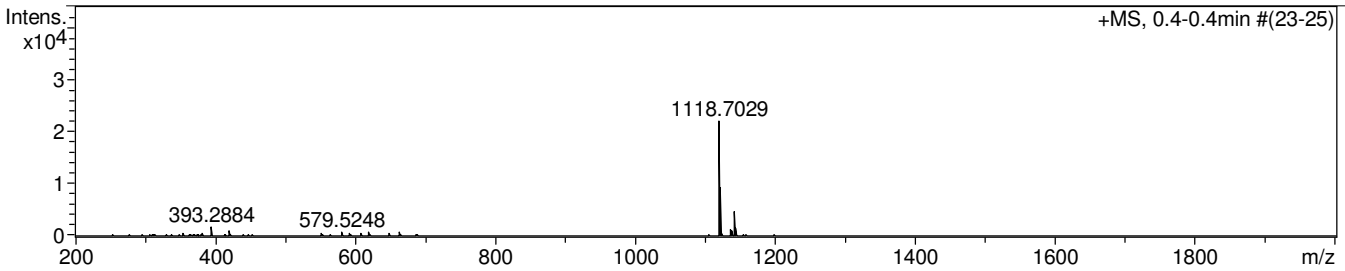
Analysis Info

Analysis Name	D:\Data\MS core facility\microTOF QII\Raw data\230711\230711_amide-C4-rot-acid_pw_1-89_01_54202.d	Acquisition Date	7/11/2023 1:00:20 PM
Method	tune_wide_pos_LCMS_with lock mass_220107-3.m	Operator	Bruker microTOF-Q II
Sample Name	230711_amide-C4-rot-acid_pw	Instrument / Ser#	micrOTOF-Q 10183
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.9 l/min
Scan End	3000 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Waste

+MS, 0.4-0.4min #(23-25)



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1118.7029	1	C 72 H 96 N O 9	100.00	1118.7080	5.0	4.5	49.4	25.5	even	ok

+MS, 0.4-0.4min #(23-25)

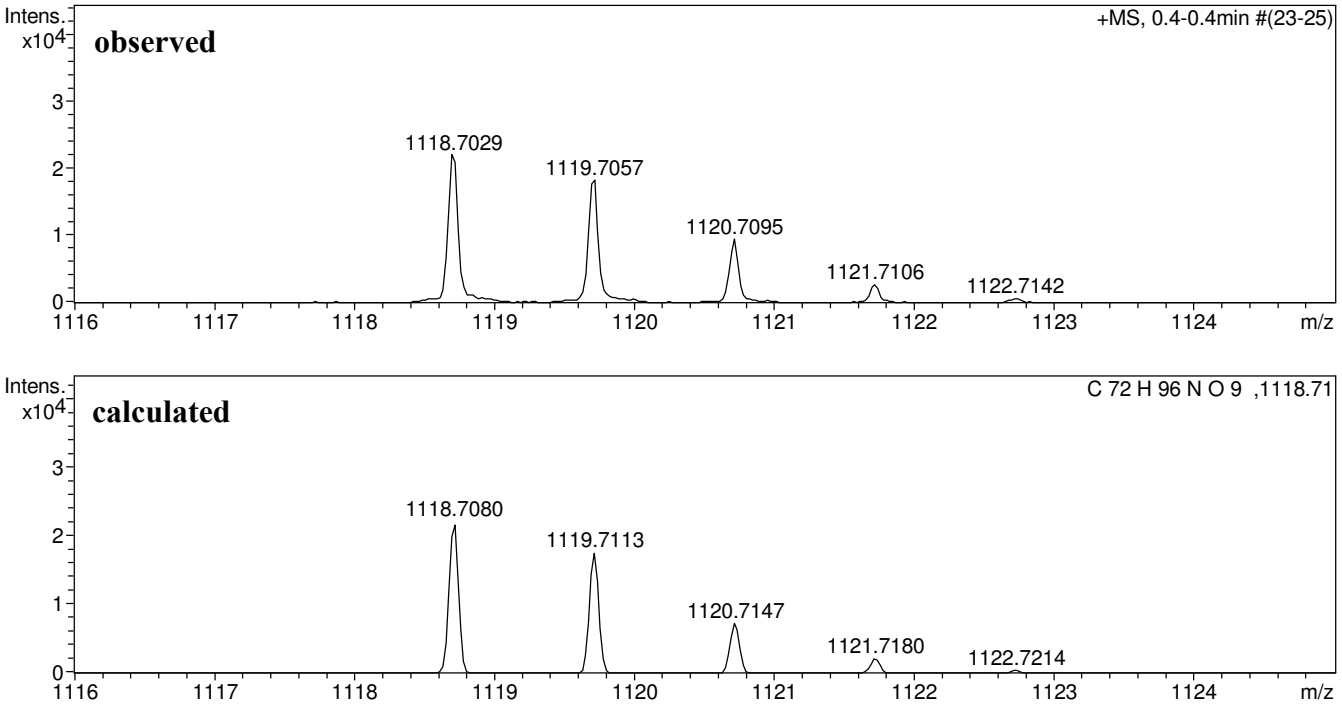


Figure S52 ^{1}H NMR Spectrum (400 MHz / $CDCl_3$ / 298 K) of **13**

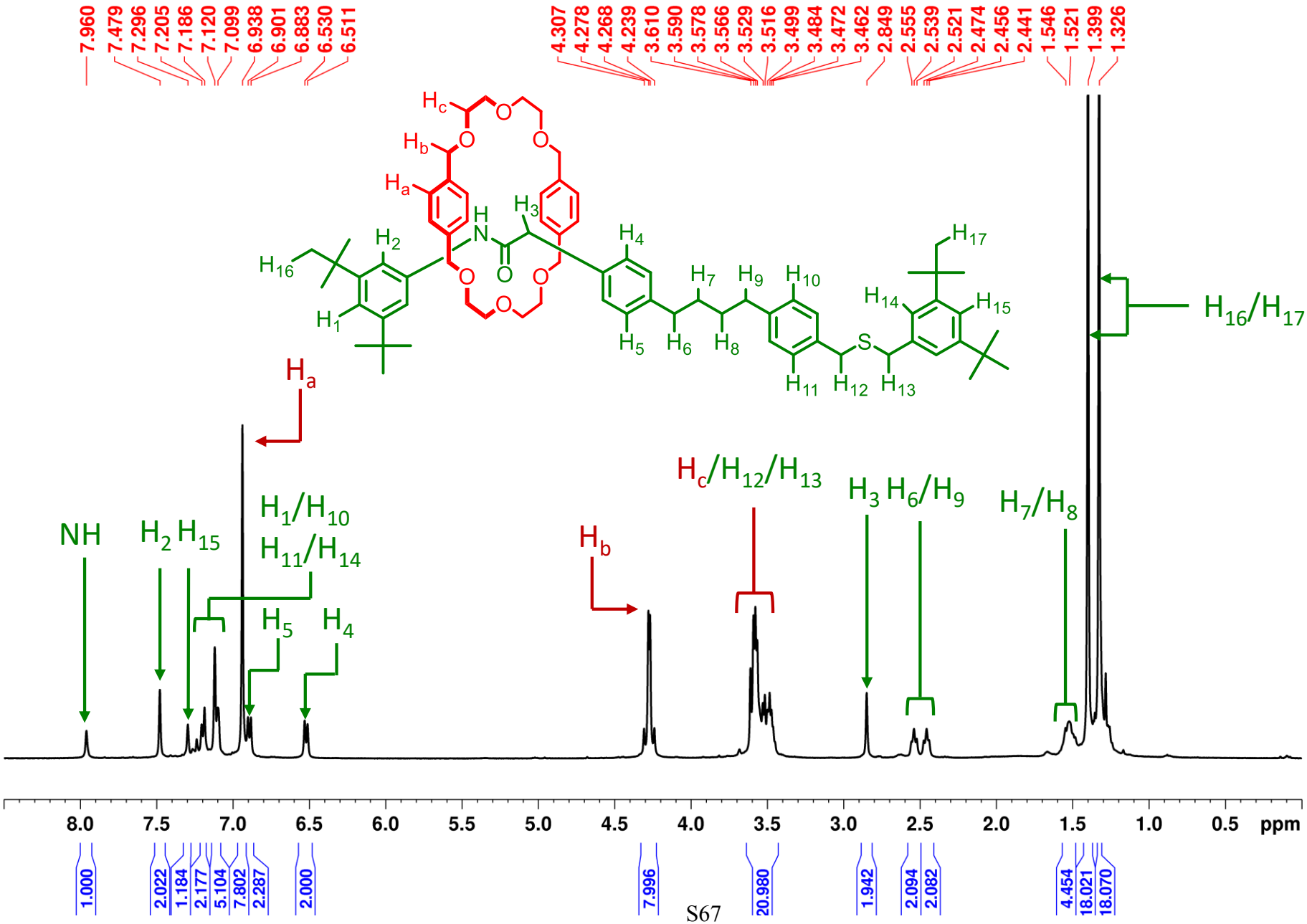


Figure S53 ^{13}C NMR Spectrum (100 MHz / $CDCl_3$ / 298 K) of **13**

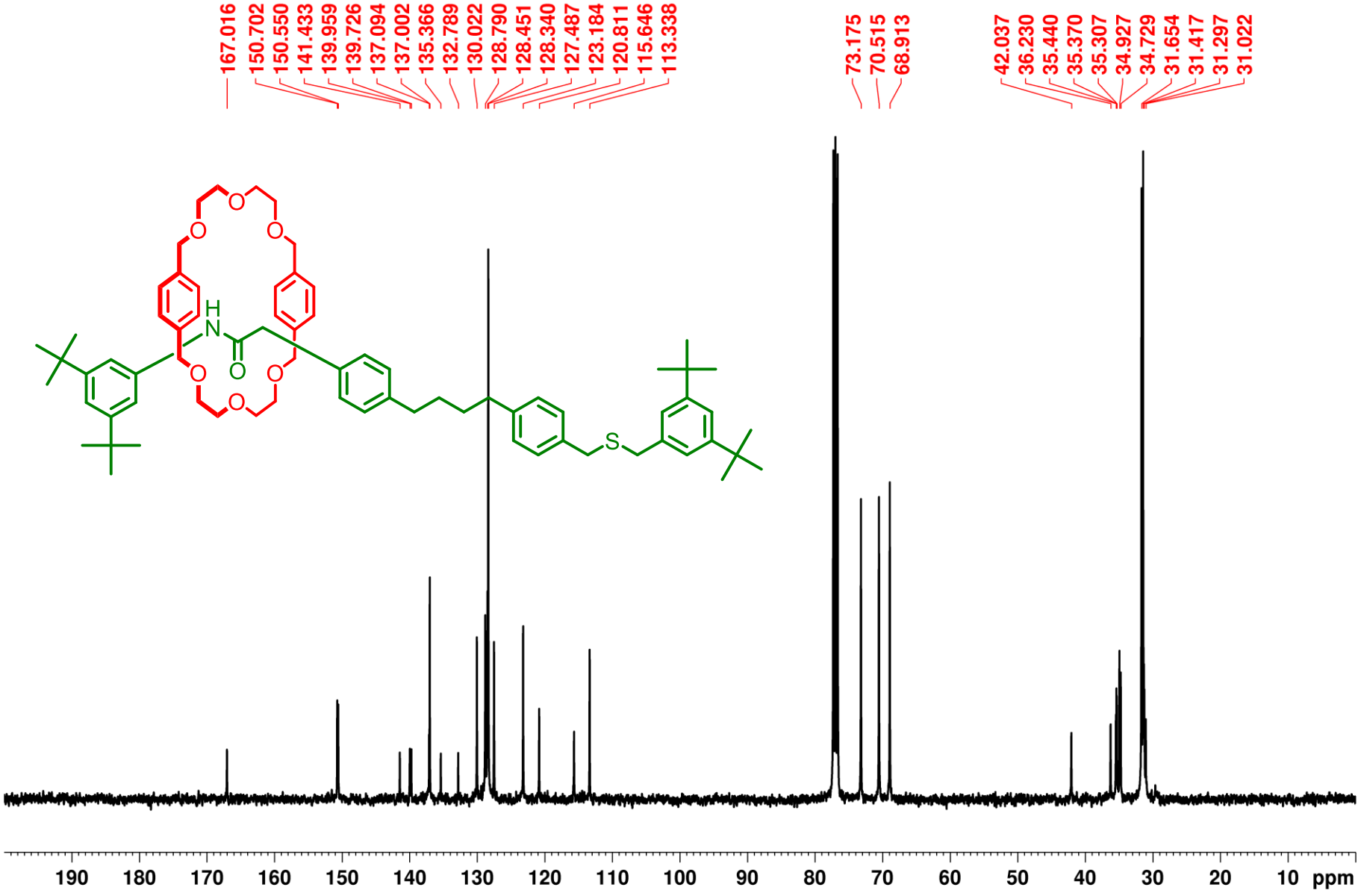


Figure S54 ESI Mass Spectra of Compound **13**

Mass Spectrum SmartFormula Report

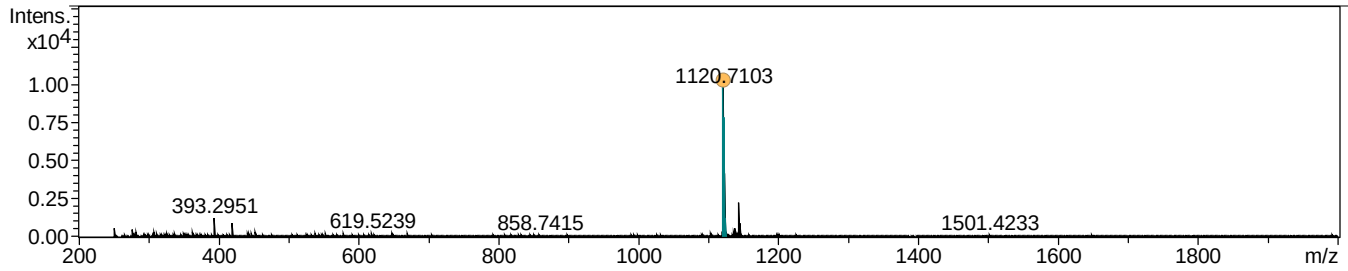
Analysis Info

Analysis Name	D:\Data\Fish\Data\2023Q3(datas)\230721\230721_amide-Ca-rot-thiol_pw_1-58_01_54410.d	Acquisition Date	7/21/2023 11:45:59 AM
Method	tune_wide_pos_LCMS_with lock mass_220107-3.m	Operator	Bruker microTOF-Q II
Sample Name	230721_amide-Ca-rot-thiol_pw	Instrument / Ser#	micrOTOF-Q 228888.10183
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.9 l/min
Scan End	3000 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Waste

+MS, 0.6-0.7min #35-41



Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	mSigma	Score	rdb	e¯ Conf	N-Rule
1120.7103	1	C72H98NO7S	1120.7059	4.5	4.0	29.0	100.00	24.5	even	ok

+MS, 0.6-0.7min #35-41

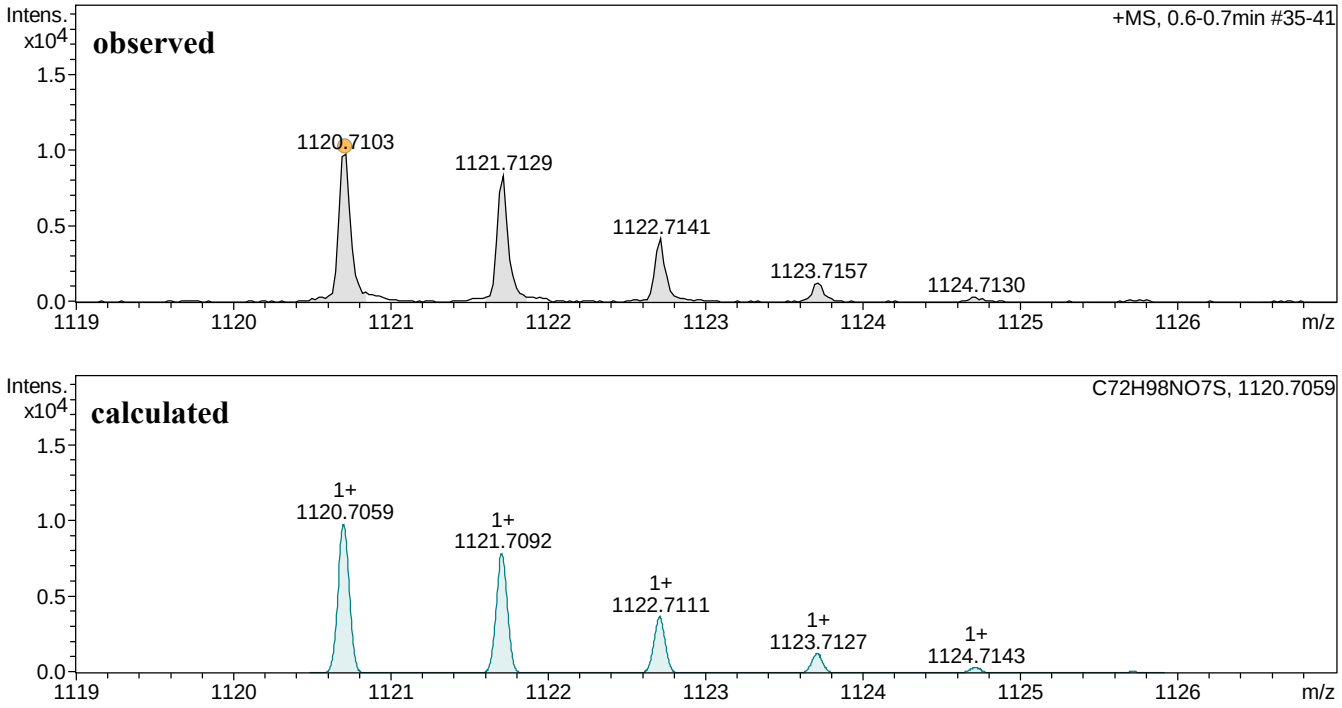


Figure S55 ^{1}H NMR Spectrum (400 MHz / $CDCl_3$ / 298 K) of **14**

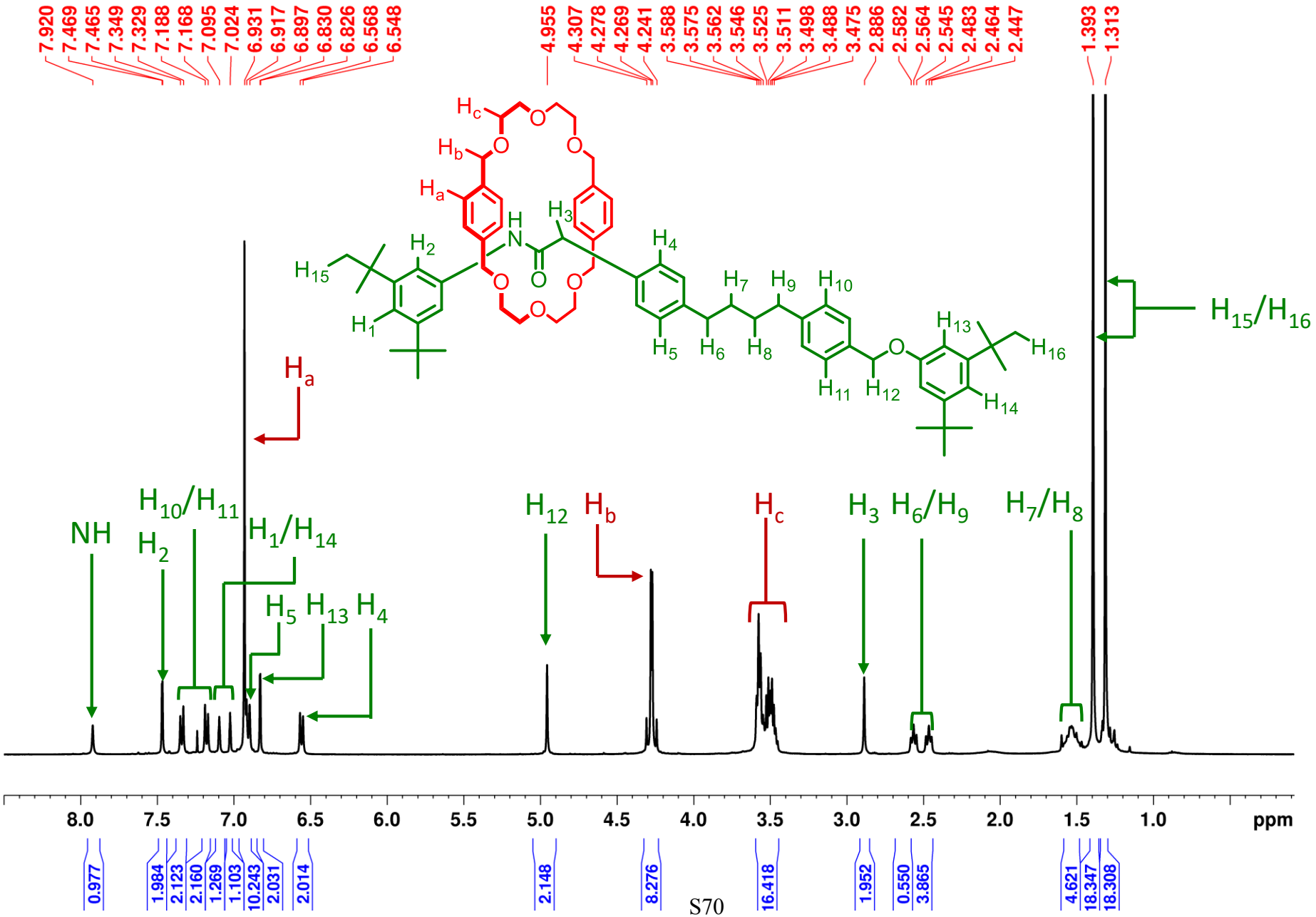


Figure S56 ^{13}C NMR Spectrum (100 MHz / $CDCl_3$ / 298 K) of **14**

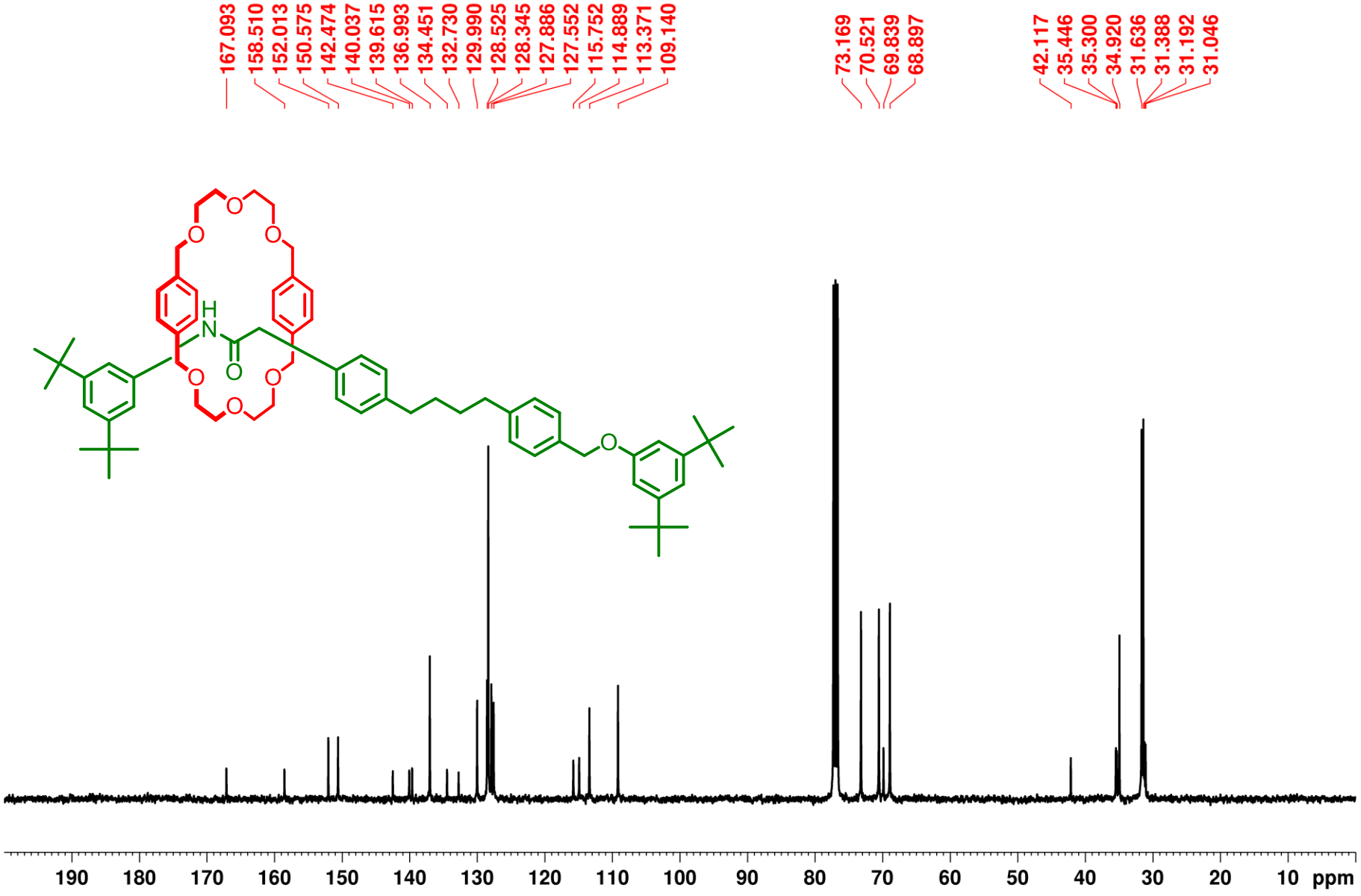


Figure S57 ESI Mass Spectra of Compound **14**

Mass Spectrum SmartFormula Report

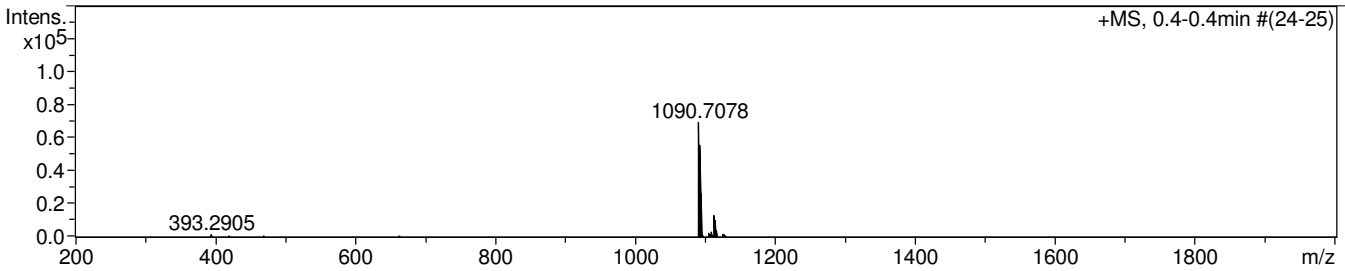
Analysis Info

Acquisition Date	7/11/2023 1:06:03 PM		
Analysis Name	D:\Data\MS core facility\microTOF QII\Raw data\230711\230711_amide-C4-rot-phenol_pw_1-90_01_54203.d		
Method	tune_wide_pos_LCMS_with lock mass_220107-3.m	Operator	Bruker microTOF-Q II
Sample Name	230711_amide-C4-rot-phenol_pw	Instrument / Ser#	micrOTOF-Q 10183
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.9 l/min
Scan End	3000 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Waste

+MS, 0.4-0.4min #(24-25)



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1090.7078	1	C 71 H 96 N O 8	100.00	1090.7130	5.3	4.8	29.9	24.5	even	ok

+MS, 0.4-0.4min #(24-25)

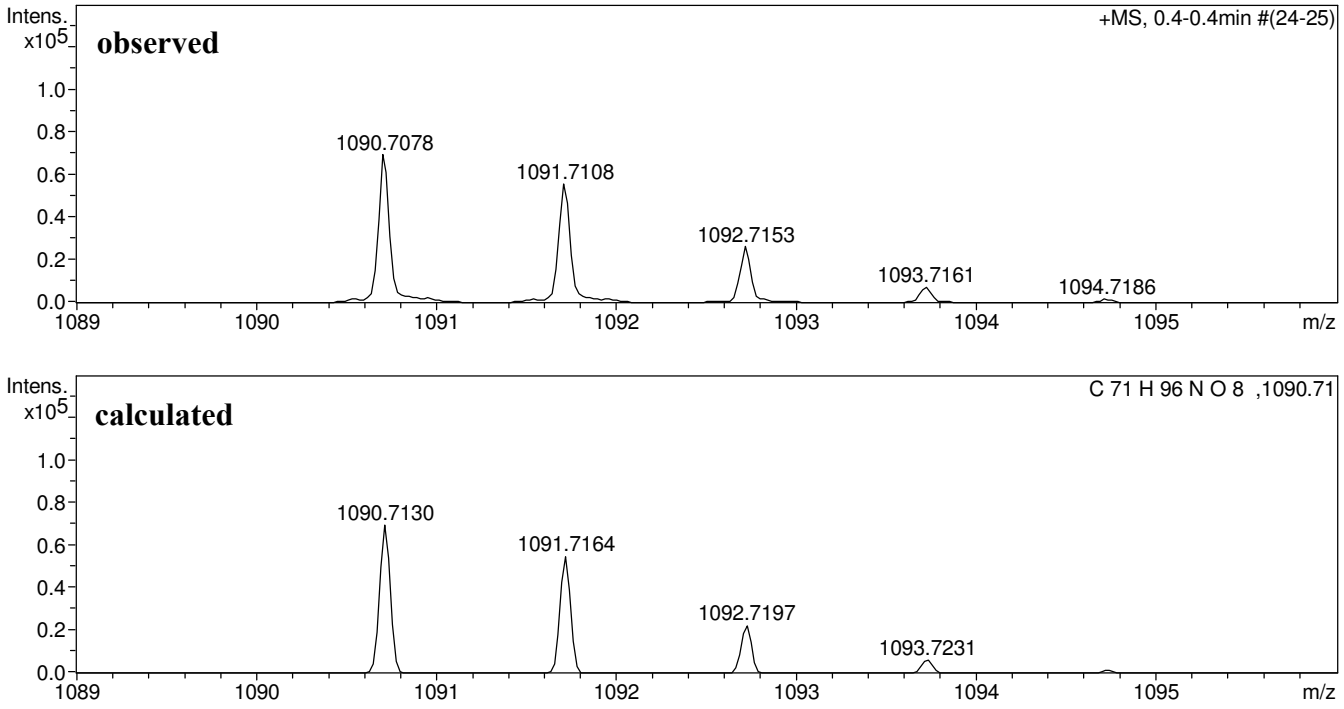


Figure S58 ^{1}H NMR Spectrum (400 MHz / CD_2Cl_2 / 298 K) of **15**

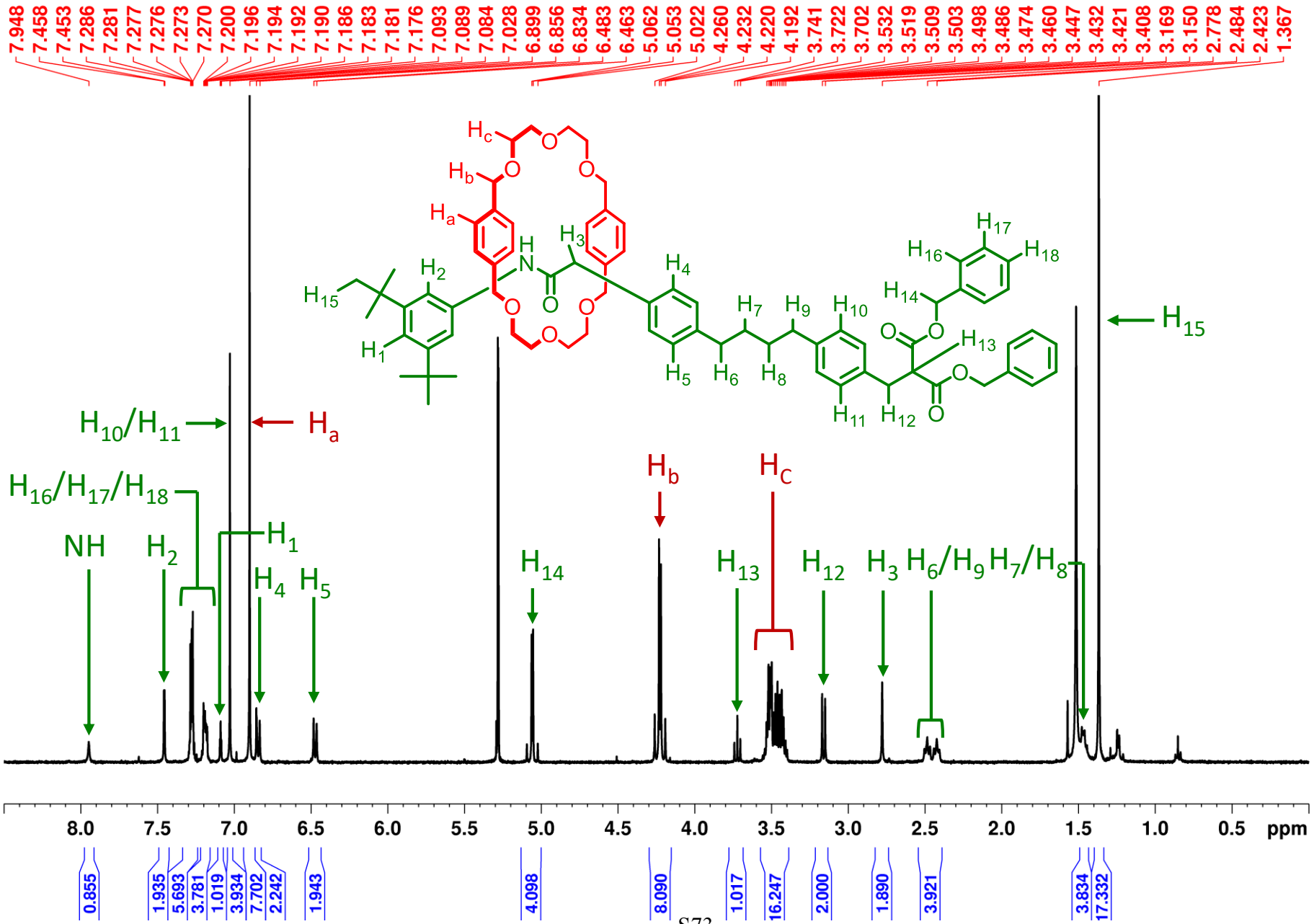


Figure S59 ^{13}C NMR Spectrum (100 MHz / CD_2Cl_2/ 298 K) of Rotaxane **15**

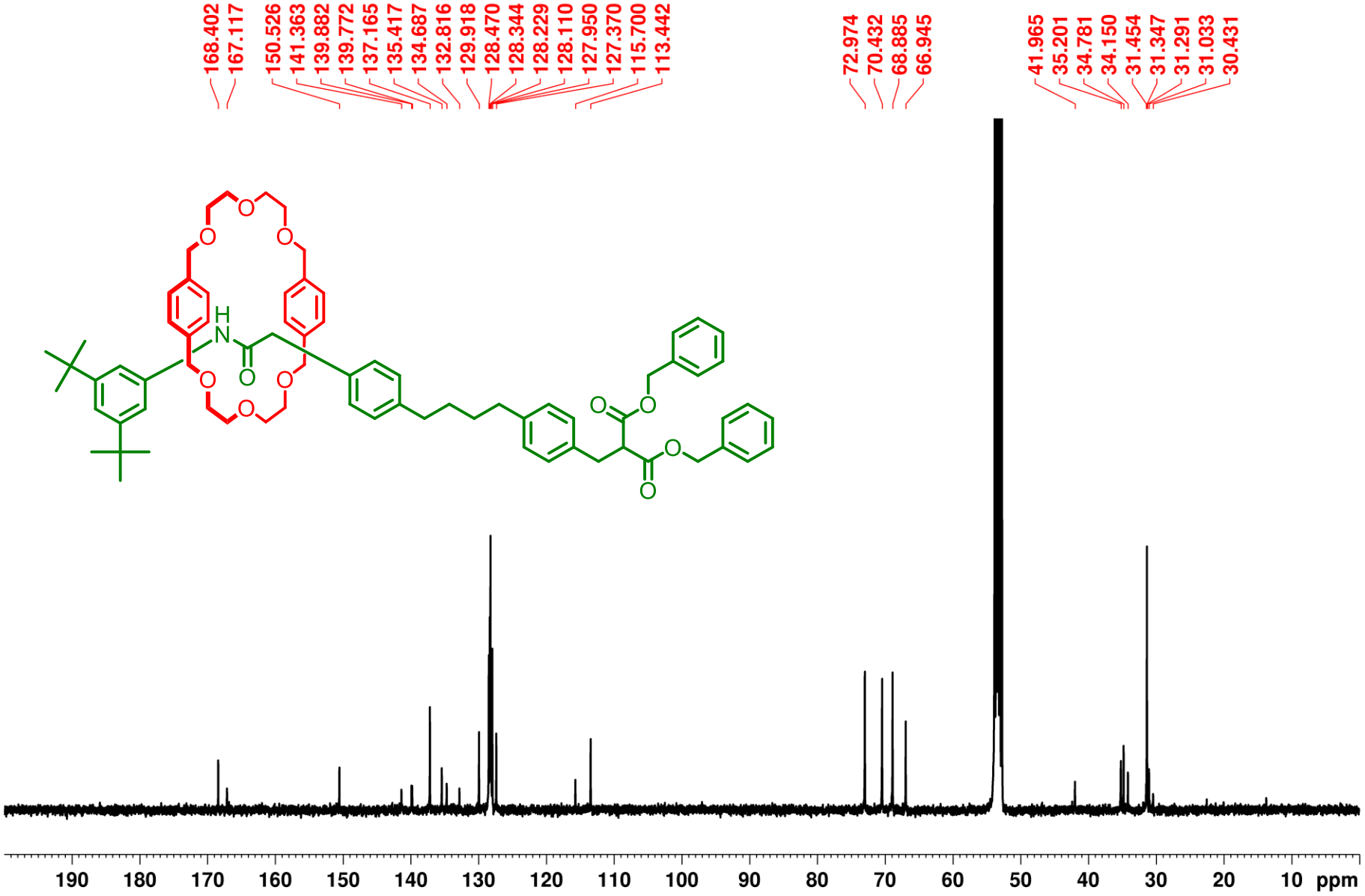


Figure S60 ESI Mass Spectra of Compound **15**

Mass Spectrum SmartFormula Report

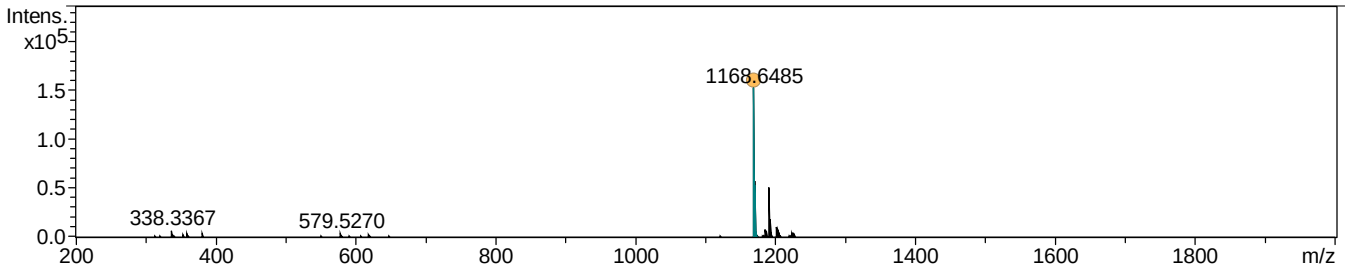
Analysis Info

Analysis Name	D:\Data\Fish\Data\2023Q3(datas)\230721\230721_amide-C4-rot-malon_pw_1-59_01_54411.d	Acquisition Date	7/21/2023 11:51:43 AM
Method	tune_wide_pos_LCMS_with lock mass_220107-3.m	Operator	Bruker microTOF-Q II
Sample Name	230721_amide-C4-rot-malon_pw	Instrument / Ser#	micrOTOF-Q 228888.10183
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.9 l/min
Scan End	3000 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Waste

+MS, 0.2-0.3min #13-18



Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1168.6485	1	C74H90NO11	1168.6508	2.4	2.0	21.8	30.5	even	ok

+MS, 0.2-0.3min #13-18

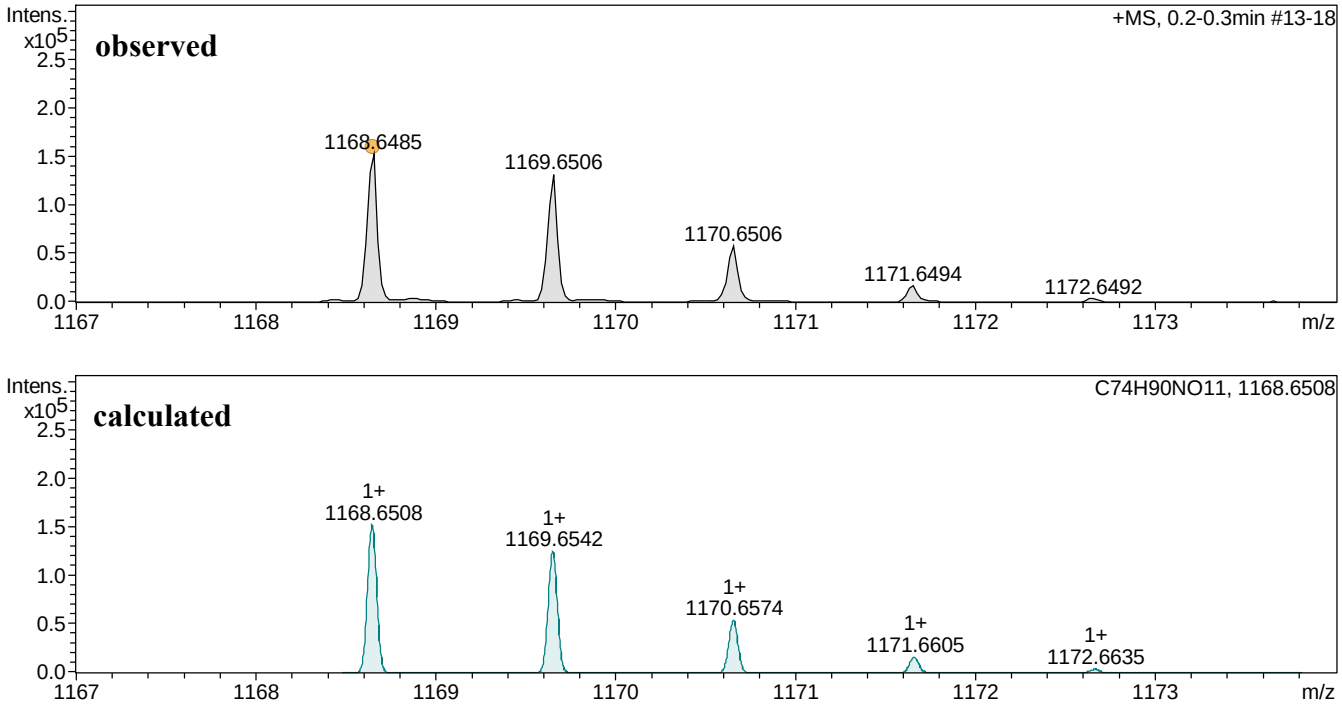


Figure S61 ^{1}H NMR Spectrum (400 MHz / CD_2Cl_2 / 298 K) of Rotaxane **17**

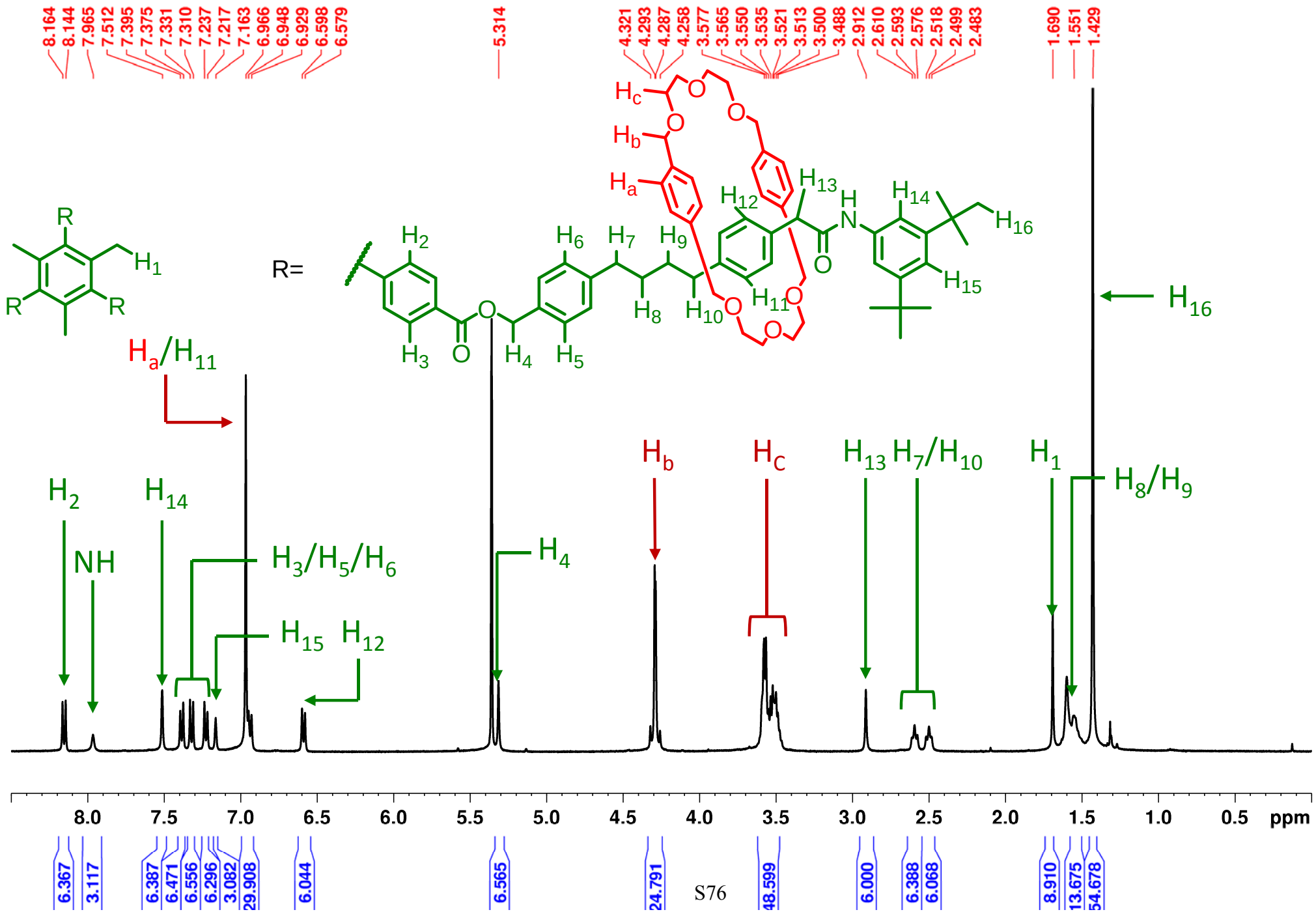


Figure S62 ^{13}C NMR Spectrum (100 MHz / CD_2Cl_2/ 298 K) of Rotaxane **17**

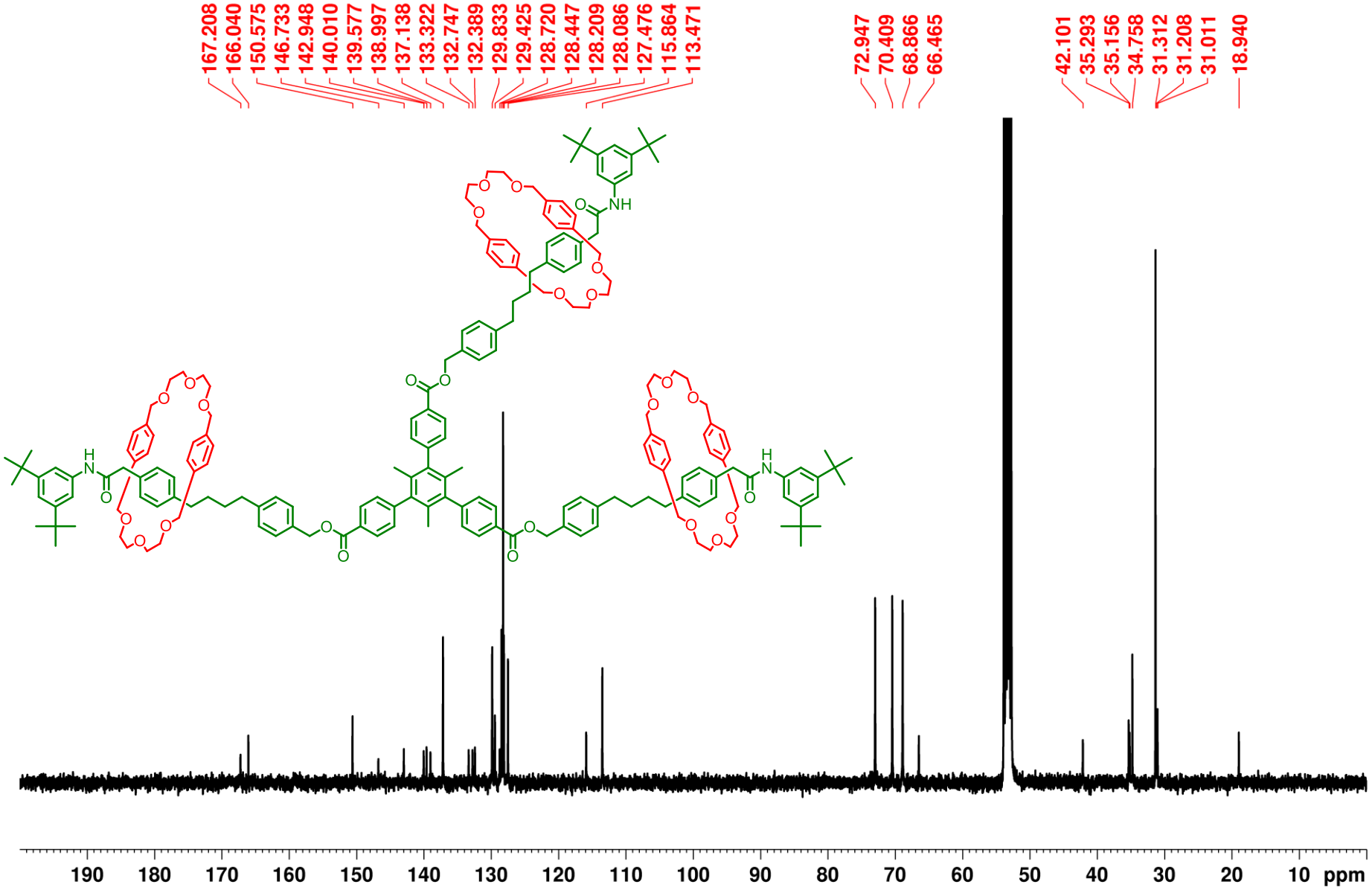


Figure S63 ESI Mass Spectra of Compound **17**

Mass Spectrum SmartFormula Report

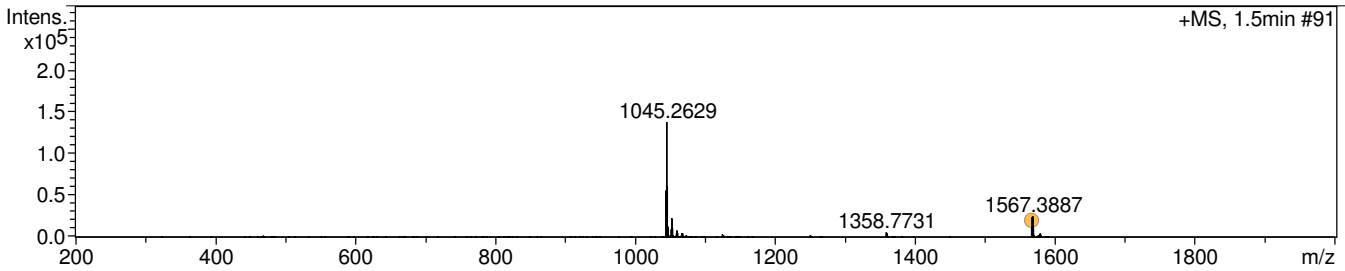
Analysis Info

Analysis Name	D:\Data\Fish\1_Data\2024Q2\240430\240430_4-rotaxane_pw_47_01_35772.d	Acquisition Date	4/30/2024 3:45:32 PM
Method	tune_wide_pos_LCMS_with lock mass_220107-3.m	Operator	BDAL@DE
Sample Name	240430_4-rotaxane_pw	Instrument / Ser#	micrOTOF-Q 228888.10183
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.9 l/min
Scan End	3000 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Waste

+MS, 1.5min #91



Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	mSigma	Score	rdb	e⁻ Conf	N-Rule
1566.3865	1	C201H245N3O27	1566.3940	-7.5	-4.8	31.5	100.00	81.0	even	ok

+MS, 1.5min #91