Efficient Microwave-mediated synthesis of fullerene acceptors for Organic Photovoltaics

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SUPPLEMENTARY MATERIAL

Experimental part

General

General: Chemicals and solvents were purchased from commercial suppliers or purified by standard techniques. For thin-layer chromatography (TLC), silica gel plates (Merck 60 F254) were used and compounds were visualized by irradiation with UV light and/or by treatment with a $KMnO_4$ solution. Flash chromatography was carried out using Macherey–Nagel silica gel (0.04–0.063 mm). MW-assisted syntheses were carried out with a CEM DISCOVER monomode system in closed vessel in manual mode (no remote PC control) with infrared sensor for temperature control and with no pressure control. Petroleum ether refers to the fraction with the boiling range 40–60 °C. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker 250, Bruker 300 MHz or Bruker Avance II 400 MHz spectrometers. HRMS spectra were recorded on MeOH/CH2CL2 or in CH2CL2 with a Waters Q-TOF Premier, with atmospheric pressure chemical ionization (APCI) as ion source.

- ***[70] and [60]PCBM derivatives***

Synthesis of methyl 4-Benzoylbutyrate. This compound was prepared on 5g scale starting from 4-benzoylbutyric acid and MeOH using HCl gas following a procedure previously reported in literature.[1] Methyl 4-Benzoylbutyrate was obtained as a colorless oil (yield: 88%).

Synthesis of methyl 4-Benzoylbutyrate p-Tosylhydrazone (1). Methyl 4-Benzoylbutyrate (4.5 g, 21.8 mmol) and *p*-toluenesulfonyl hydrazide (5.0 g, 1.2 eq) were placed in a round bottom flask and methanol was added (15 mL).The mixture was stirred and refluxed for 6 h and then stirred overnight at room temperature and lastly cooled to -15 °C. The product was collected by filtration, washed with cold methanol and dried under vacuum to obtain 4-Benzoylbutyrate p-Tosylhydrazone as white crystals (yield: 92 %).

General procedure for preparation of 1-phenyl-1-(3-(methoxycarbonyl)propyl)diazomethane. Sodium methoxide (3.73 mg, 0.069 mmol) was added in a glass vial (ca. 10 mL tube) sealed with a teflon septum containing a solution of 4-Benzoylbutyrate p-Tosylhydrazone (17.20 mg, 0.046 mmol) in dry pyridine (2 mL). The mixture was stirred at room temperature for 15 minutes.

Synthesis of PCBM derivatives (2a-c, 3a-c). A solution of C_{60} or C_{70} (50.00 mg) in 3 mL of ODCB (previously sonicated for about 15 minutes) was added to a previously prepared mixture containing the appropriate quantity of 1-Phenyl-1-(3-(methoxycarbonyl)propyl)diazomethane in dry pyridine. The resulting mixture was kept under MW irradiation at 180 °C (48 W) for appropriate time. After cooling down, pyridine was removed under vacuum and the remaining reaction mixture was directly chromatographated on silica gel without removal of the remaining solvent (Silica gel column conditions for C_{60}-derivatives: Hexane/Toluene 3:1 up to 9:1 Toluene/Hexane for monoadduct recovery and then dichlorometane for bisadducts. Column conditions for C_{70}-derivatives: Hexane/Toluene 3:1 up to 2:1 Toluene/Hexane for monoadduct recovery and then dichlorometane for bisadducts recovery). Both mono and bis-adducts were solubilized and transferred to a centrifuge tube using a minimal amount of chloroform and subsequently precipitated with methanol. (**2a**) ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ: 7.92 (d, *J* = 7.2 Hz, 2H; o-H arom), 7.55 (t, *J* = 7.3 Hz, 2H; m-H arom), 7.51-7.41 (m, 1H; p-H arom), 3.68 (s, 3H; O$\underline{C}H_3$), 2.92 (t, *J* = 7.3Hz, 2H; PhC$\underline{C}H_2$), 2.53 (t, *J* = 7.3 Hz, 2H; $\underline{C}H_2CO_2Me$), 2.20 (q, *J* = 7.3 Hz, 2H; $\underline{C}H_2CH_2CO_2Me$). ^{13}C NMR (100 MHz, $CDCl_3/CS_2$) δ: 172.65 ($\underline{C}$=O), 148.46, 147.51, 145.62, 145.01, 144.86, 144.59, 144.47, 144.28, 143.89, 143.57, 142.82, 142.76, 142.02, 141.94, 140.84, 140.60, 137.87, 137.47, 136.48, 131.85, 128.31, 128.10, 79.60 (C_{60} sp^3), 51.64 (O$\underline{C}H_3$), 51.26 (Ph$\underline{C}CH_2$), 33.69, 33.56 (PhC$\underline{C}H_2$ and $\underline{C}H_2CO_2Me$), 22.33 ($\underline{C}H_2CH_2CO_2Me$). HRMS calculated: 933.0891; found: 933.2404 [M-Na]$^+$. (**2b**) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.24-7.31 (m, 10H; H arom), 3.81-3.52 (m, 6H; O$\underline{C}H_3$), 3.23-1.85 (m, 12H; PhC$\underline{C}H_2$, $\underline{C}H_2CO_2Me$ and $\underline{C}H_2CH_2CO_2Me$). HRMS calculated: 1123.1885; found: 1123.3757 [M-Na]$^+$. (**2c**) ^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.23-7.29 (m, 15H; H arom), 3.89-3.35 (m, 9H; O$\underline{C}H_3$), 3.23-1.85 (m, 18H; PhC$\underline{C}H_2$, $\underline{C}H_2CO_2Me$ and $\underline{C}H_2CH_2CO_2Me$). HRMS calculated: 1314.2878; found: 1314.6711 [M-Na]$^+$. (**3a**) ^{1}H NMR (250 MHz, $CDCl_3/CS_2$) δ: 7.93-7.19 (m, 5H; H arom), 3.75, 3.69, 3.52 (s, 3H; O$\underline{C}H_3$ isomers mixture), 2.53-2.37 (m, 4H; PhC$\underline{C}H_2$ and $\underline{C}H_2CO_2Me$), 2-19-1.75 (m, 2H; $\underline{C}H_2CH_2CO_2Me$). HRMS calculated: 1053.0891; found: 1053.0590 [M-Na]$^+$. (**3b**) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96-7.00 (m,10H; H arom), 4.10-3.22 (m, 6H; O$\underline{C}H_3$), 2.71-1.93 (m, 12H; PhC$\underline{C}H_2$, $\underline{C}H_2CO_2Me$ and $\underline{C}H_2CH_2CO_2Me$). HRMS calculated: 1245.1963; found: 1245.1877 [M-Na]$^+$. (**3c**) HRMS calculated: 1433.2878; found: 1433.6976 [M-Na]$^+$.

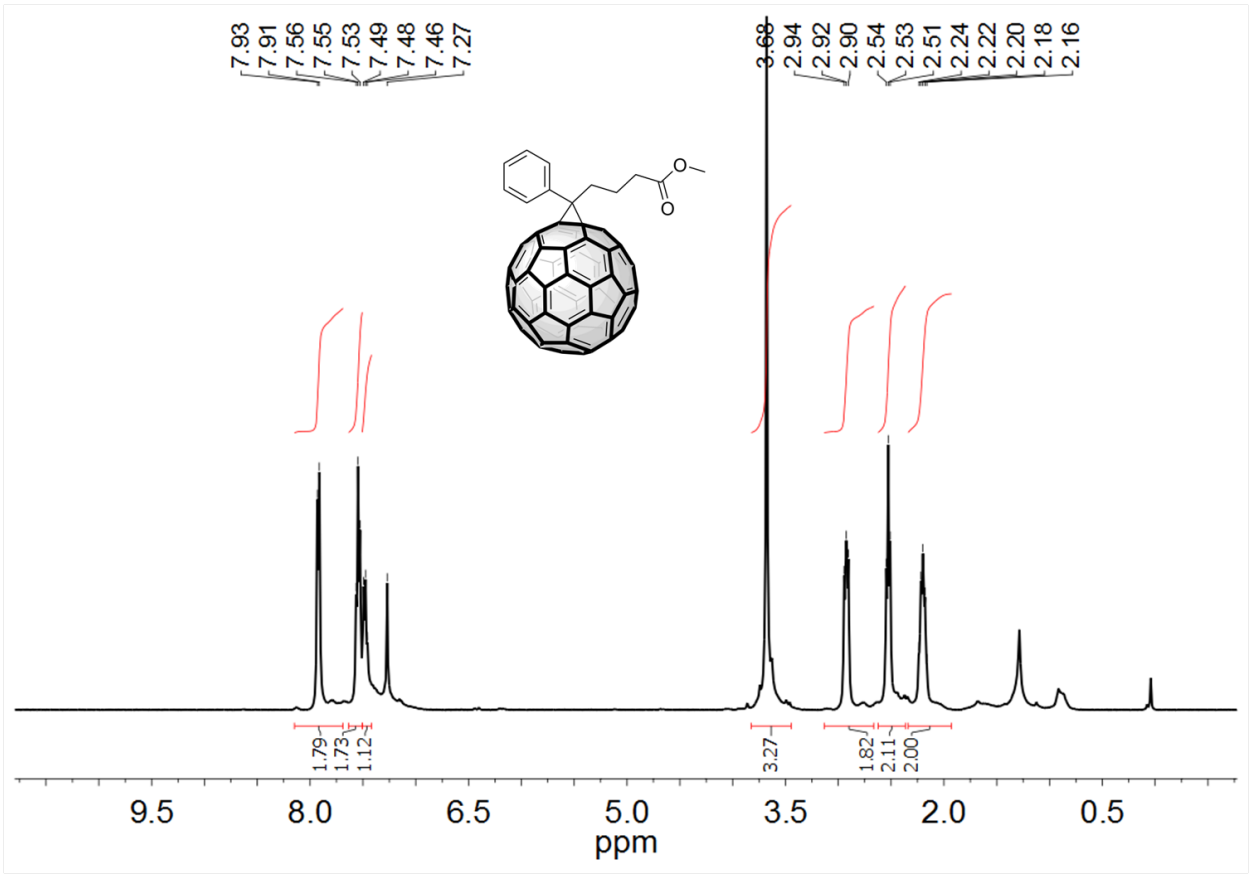


Figure S1. ^{1}H NMR Spectrum of **2a**

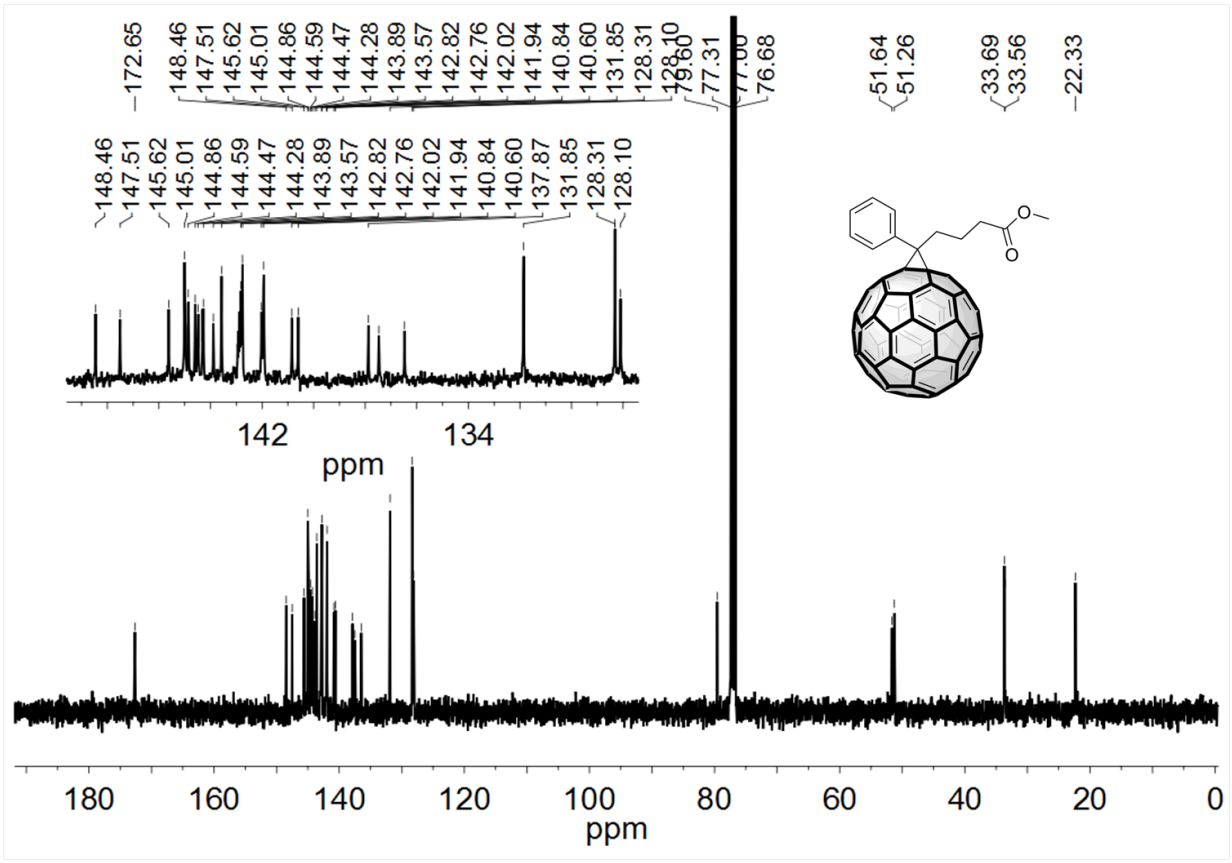


Figure S2. ^{13}C NMR Spectrum of **2a**

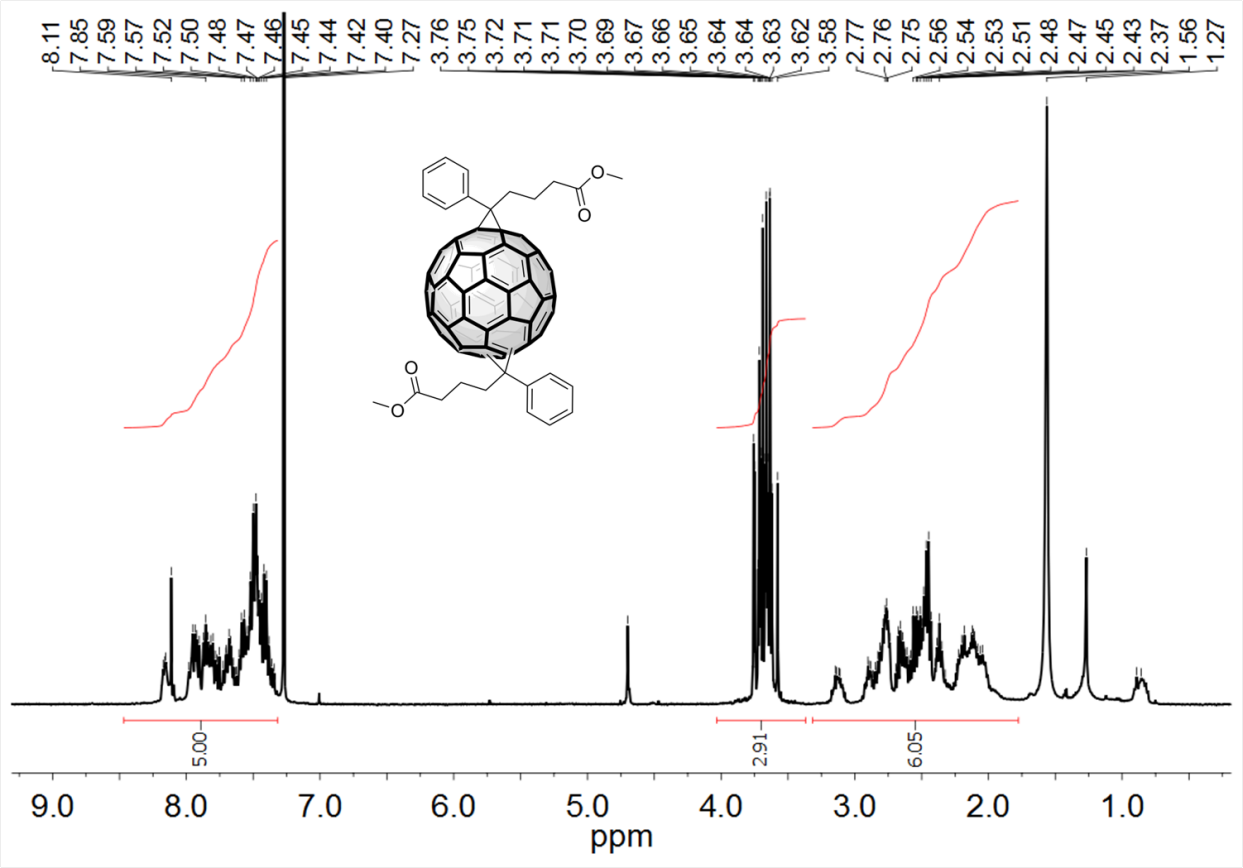


Figure S3. ^{1}H NMR Spectrum of **2b**

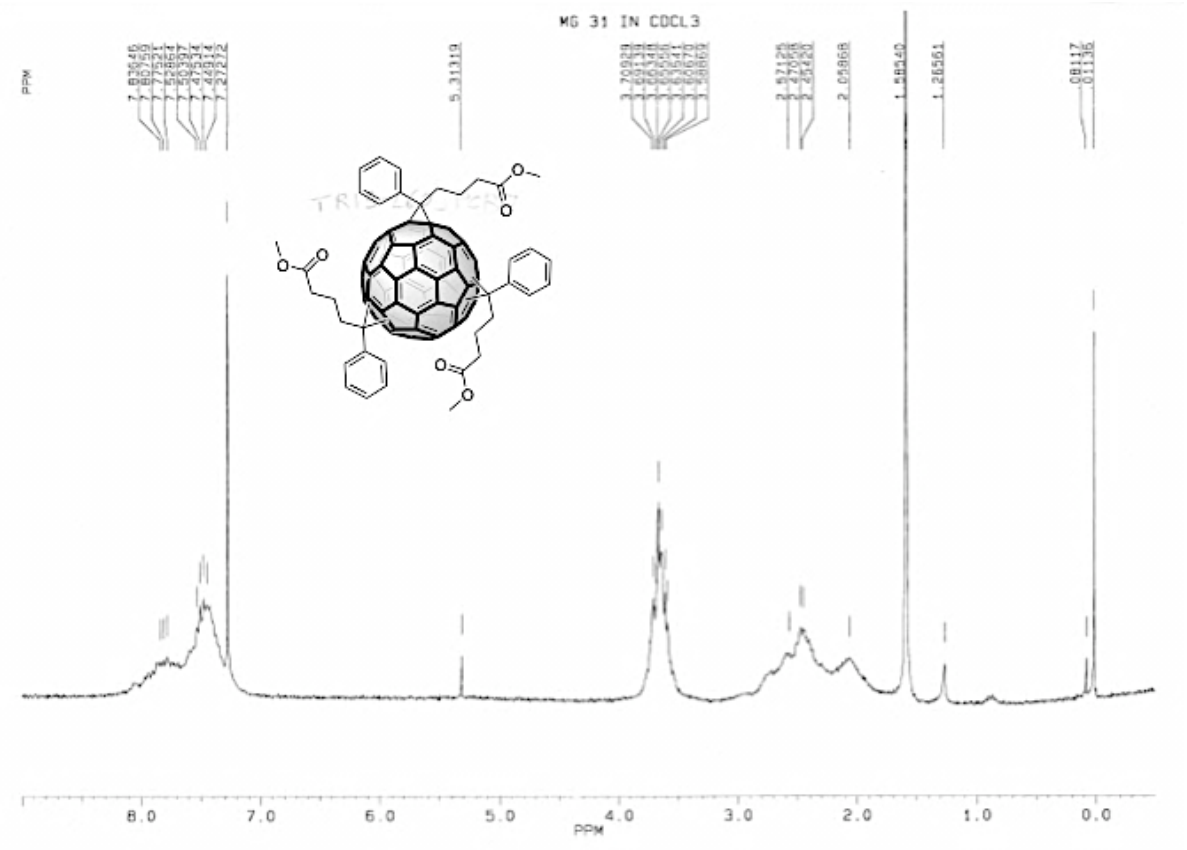


Figure S4. ^{1}H NMR Spectrum of **2c**

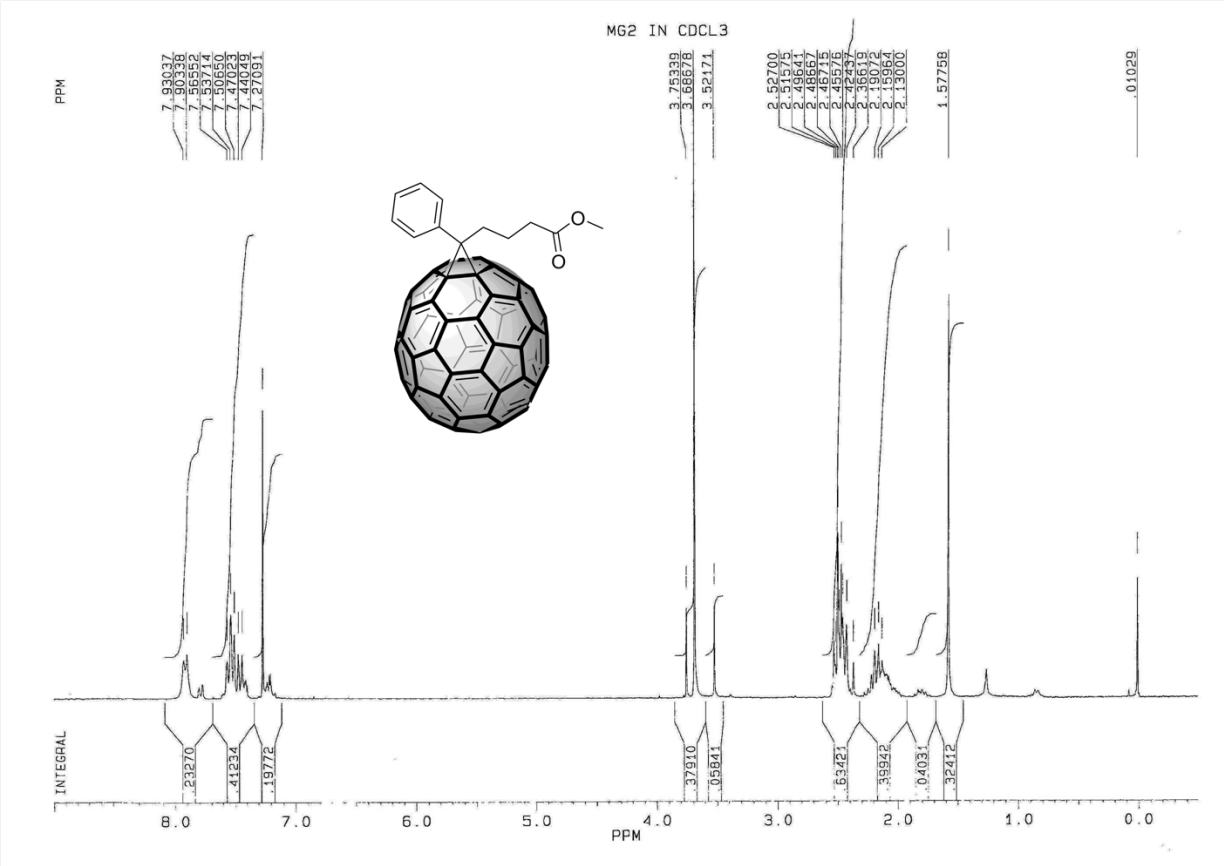


Figure S5. ^{1}H NMR Spectrum of **3a**

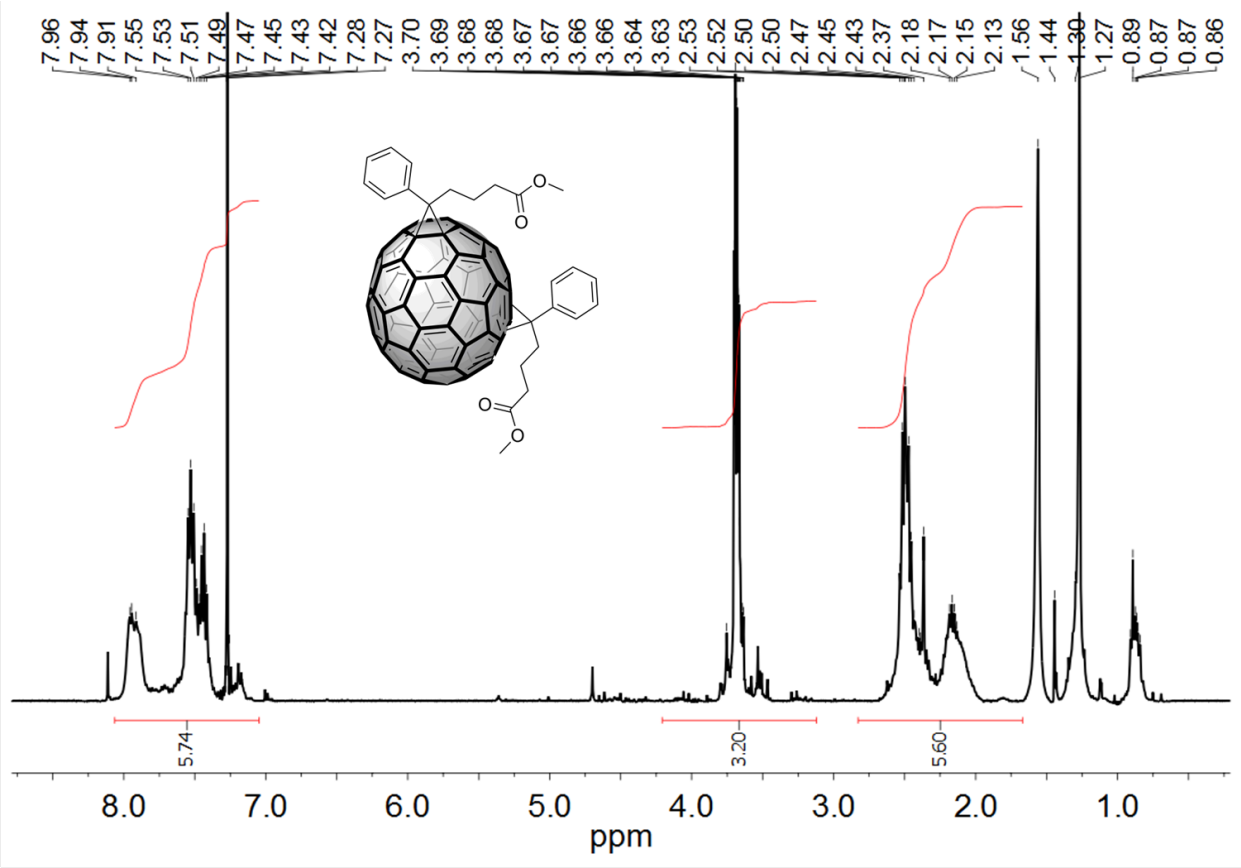


Figure S6. ^{1}H NMR Spectrum of **3b.**

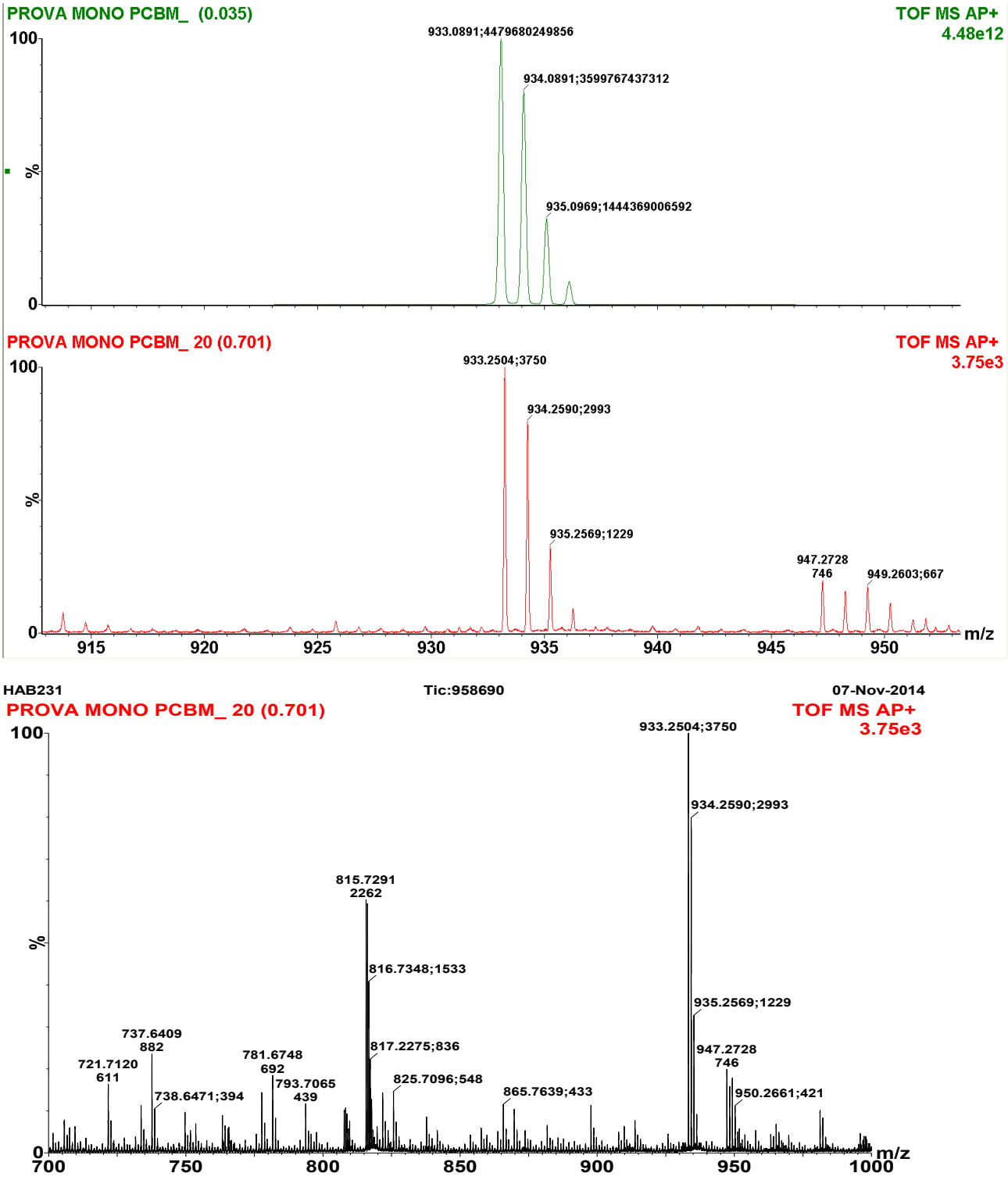


Figure S7. From the top: simulated, experimental and full HRMS spectrum of **2a.**

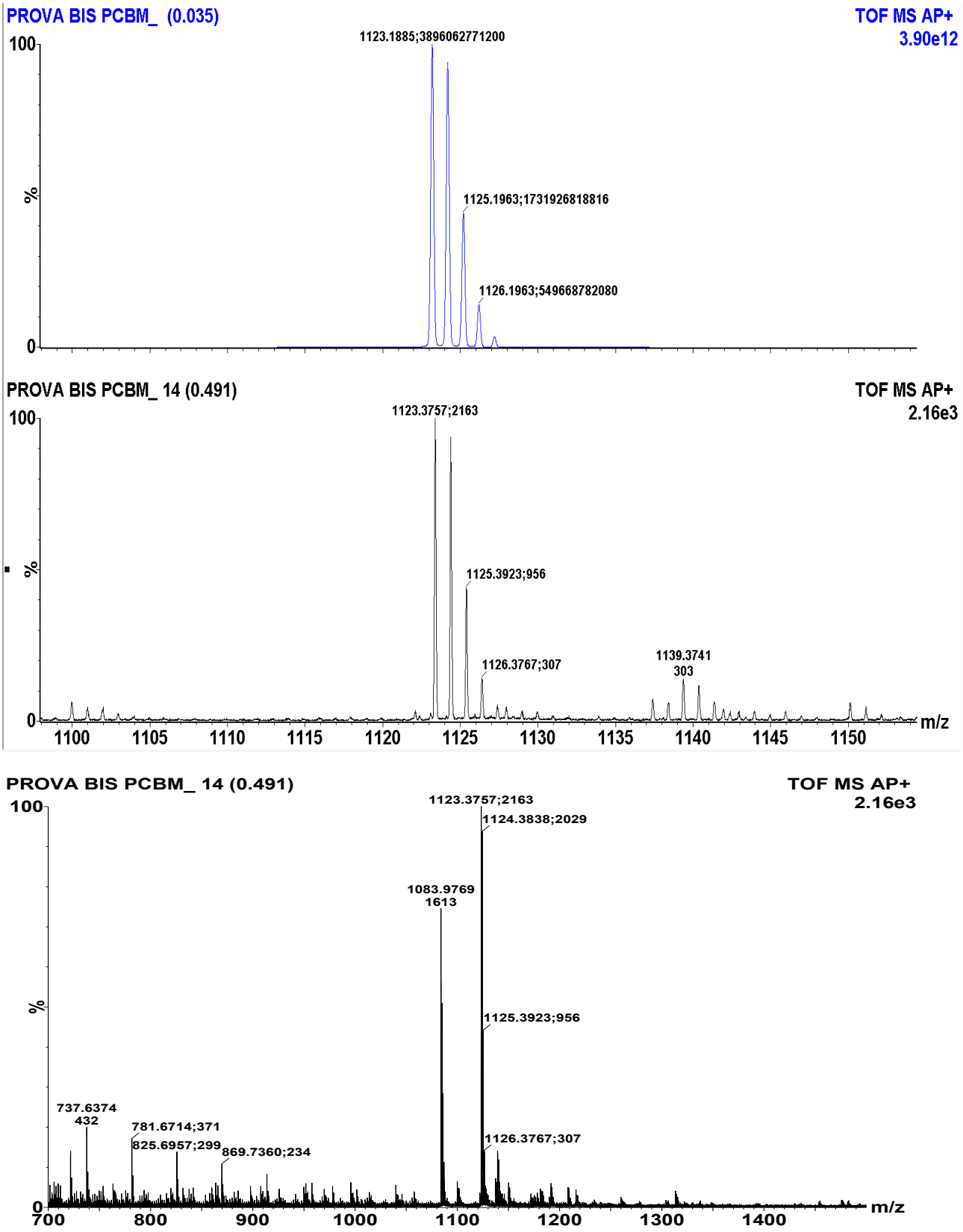


Figure S8. From the top: simulated, experimental and full HRMS spectrum of **2b.**

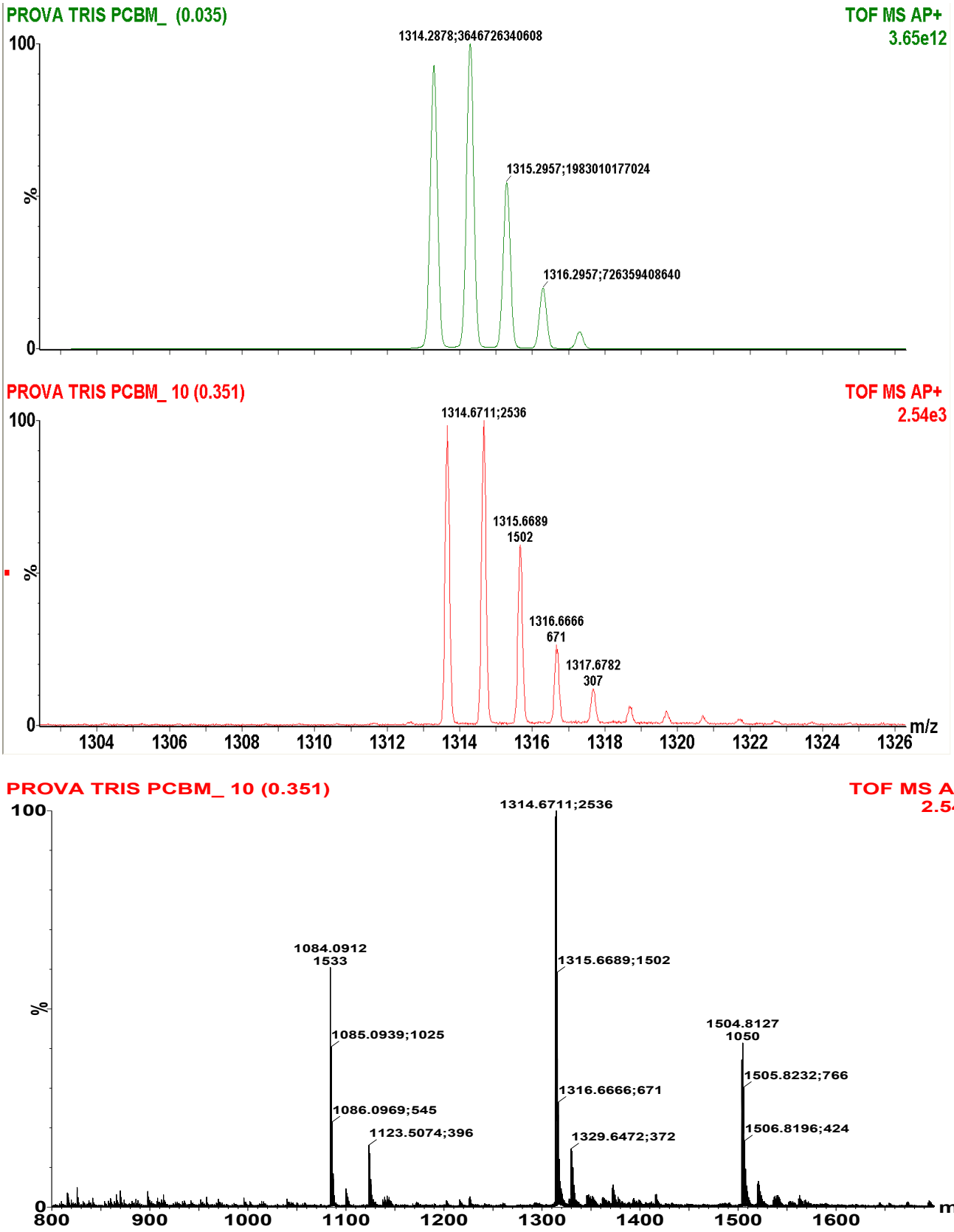


Figure S9. From the top: simulated, experimental and full HRMS spectrum of **2c.**

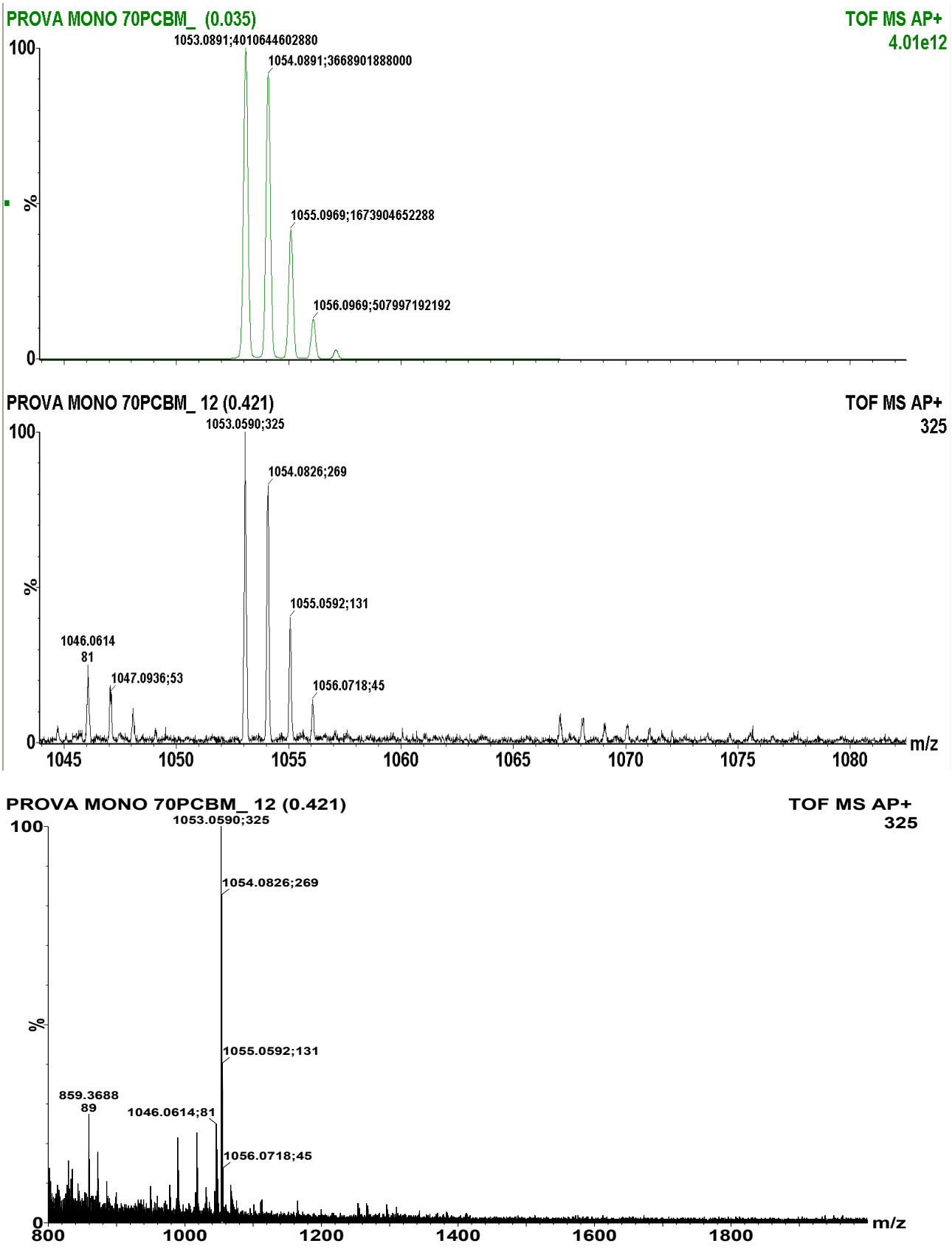


Figure S10. From the top: simulated, experimental and full HRMS spectrum of **3a.**

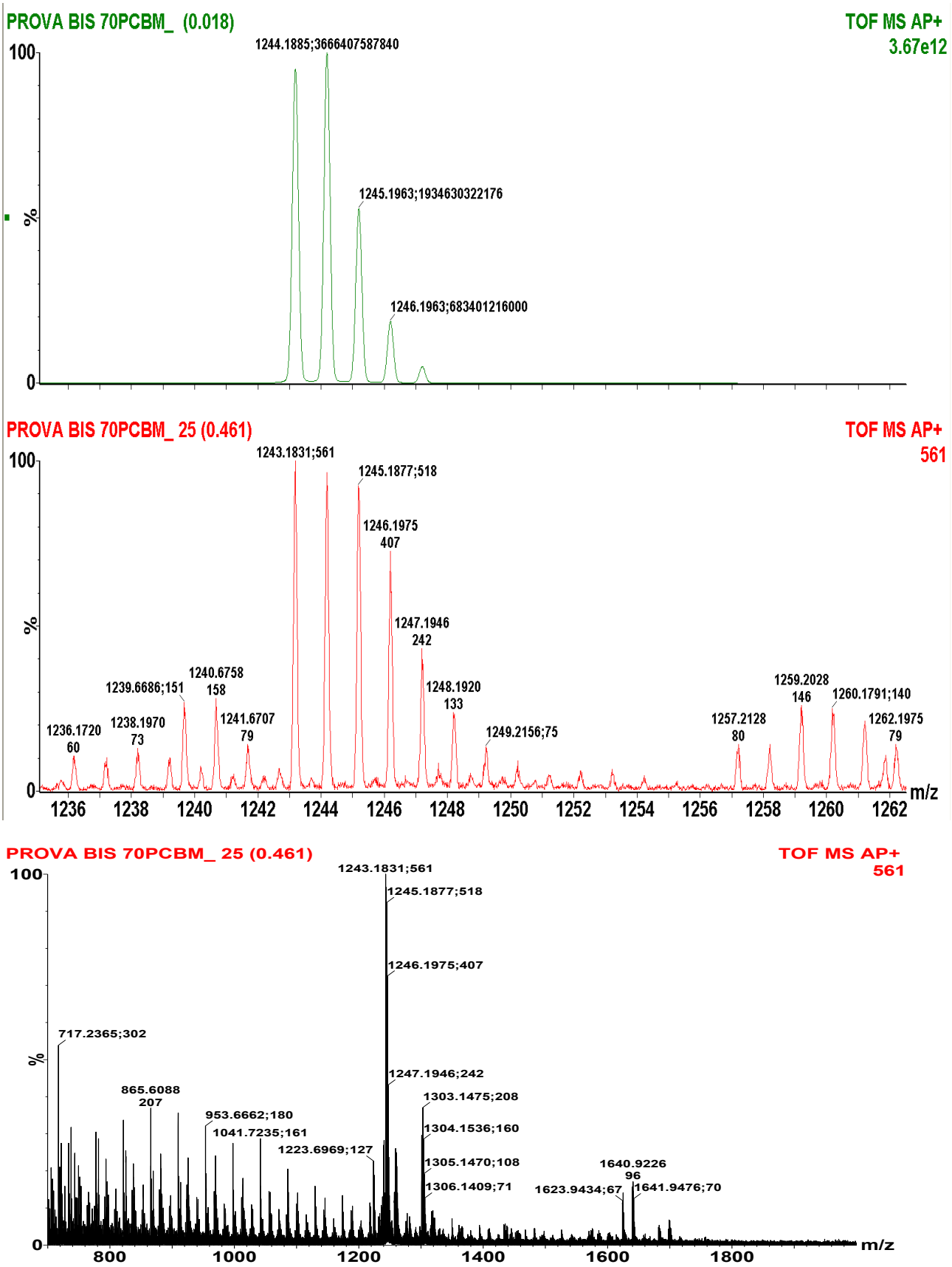
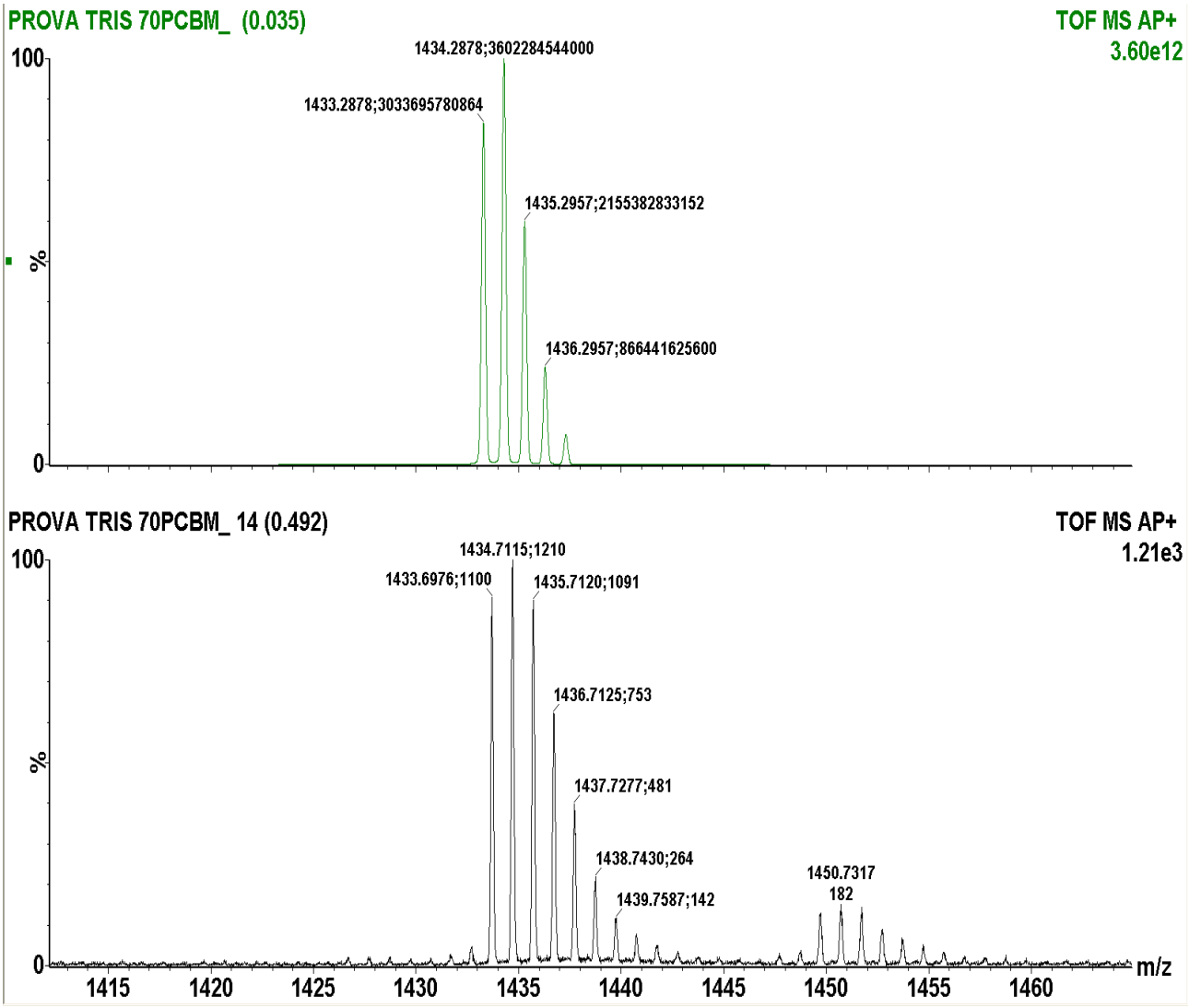


Figure S11. From the top: simulated, experimental and full HRMS spectrum of **3b.**



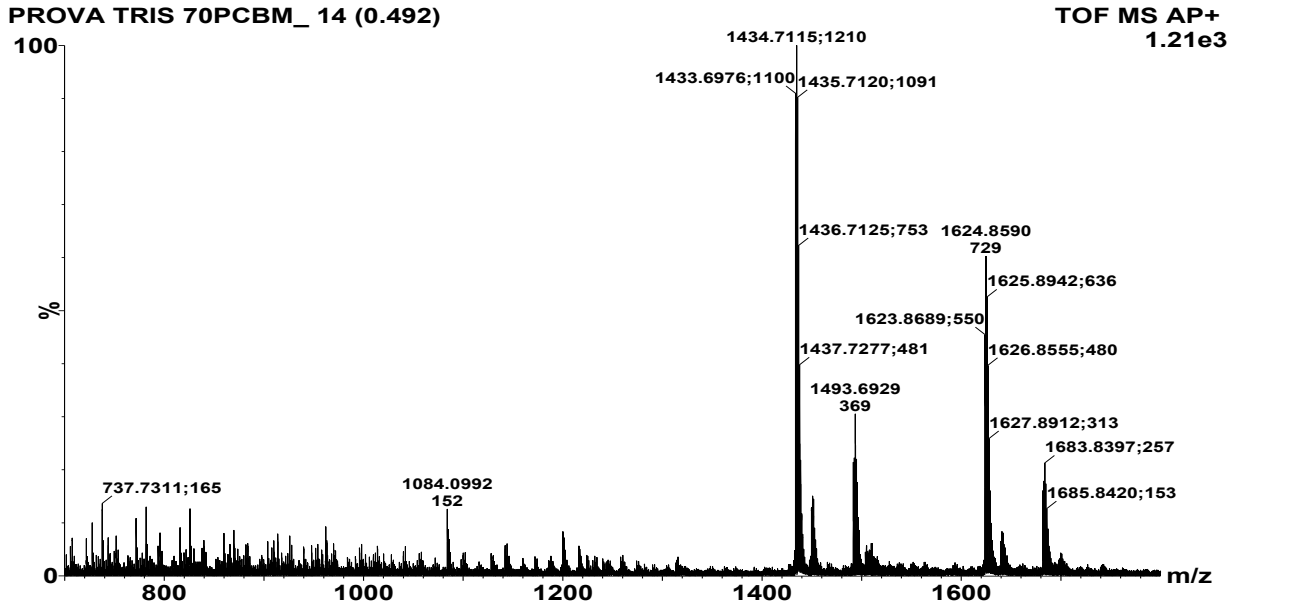


Figure S12. From the top: simulated, experimental and full HRMS spectrum of **3c.**

- ***[70] and [60]DPM6 derivatives***

Synthesis of 4,4'-dihexyloxybenzophenone-p-Tosylhydrazone (4). The synthesis of this compound was carried out following procedures previously reported in literature.[2-4] This compound was prepared starting from commercially available 4,4'-dihydroxybenzophenone in two synthetic steps and on 5g scale.

General procedure for preparation of 4,4'-(diazomethylene)bis(hexyloxybenzene). Sodium methoxide (3.73 mg, 0.069 mmol) was added in a glass vial (ca. 10 mL tube) sealed with a teflon septum containing a solution of 4,4'-Dihexyloxybenzophenone-p-Tosylhydrazone (25.30 mg, 0.046 mmol) in dry pyridine (2 mL). The mixture was stirred at room temperature for 15 minutes.

Synthesis of DPM6 derivatives (5a-b, 6a-b). A solution of C_{60} or C_{70} (50.00 mg) in 3 mL of ODCB (previously sonicated for about 15 minutes) was added to a previously prepared mixture containing the appropriate quantity of 4,4'-(diazomethylene)bis(hexyloxybenzene) in dry pyridine. The resulting mixture was kept under MW irradiation at 180 °C (48 W) for appropriate time. After cooling down, pyridine was removed under vacuum and the remaining reaction mixture was directly chromatographated on silica gel without removal of the remaining solvent (Silica gel column conditions for C_{60}-derivatives: CS_2 to recover unreacted C_{60} and then Hexane/Toluene 4:1 and 3:1 for monoadduct recovery and finally Hexane/toluene 1:1 for bisadducts recovery. Column conditions for C_{70}-derivatives: CS_2 to recover unreacted C_{70} and then Hexane/Toluene 6:1 and 4:1 for monoadduct recovery and finally Hexane/Toluene 2:1 for bisadducts recovery). Both mono and bis-adducts were solubilized and transferred to a centrifuge tube using a minimal amount of chloroform and subsequently precipitated with methanol. (**5a**) ^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.97 (d, *J* = 8.6 Hz, 4H), 6.98 (d, *J* = 8.6 Hz, 4H), 3.98 (t, *J* = 6.5 Hz, 4H; O$\underline{C}H_2$), 1.97-1.68 (m, 4H; OCH$_2\underline{C}H_2$), 1.54-1.19 (m, 12H; -CH_2-), 0.91 (t, *J* = 6.6 Hz, 6H; $CH_2\underline{C}H_3$). ^{13}C NMR (62.5 MHz, $CDCl_3/CS_2$) δ: 158.68 ($\underline{C}_{Ar}$-O), 148.48, 145.34, 145.10, 145.02, 144.63, 144.52, 144.18, 143.78, 142.92, 142.85, 142.23, 142.05, 140.76, 138.17, 131.75, 131.20, 114.60, 79.57 (C_{60} sp^3), 68.00 (O$\underline{C}H_2$), 57.30 (C_{DPM}), 31.67, 29.35, 25.85, 22.73, 14.09. HRMS calculated: 1087.2637; found: 1087.2247 [M-H]$^+$. (**5b**) ^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.20-7.50 (m, 8H), 7.12-6.60 (m, 8H), 4.08-3.78 (m, 8H; O$\underline{C}H_2$), 2.04-1.1 (m, 32H, -CH_2-), 1.1-0.64 (m, 12H; $CH_2\underline{C}H_3$). HRMS calculated: 1453.5195; found: 1453.4471 [M-Na]$^+$. (**6a**) ^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.95, 7.83, 7.46 (d, *J* = 7.9 Hz, 4H), 6.95, 6.65 (d, *J* = 7.9 Hz, 4H), 3.99, 3.80 (m, 4H; isomers mixture), 2.09-1.12 (m, 16H; OCH$_2\underline{C}H_2$ and -CH_2-), 1.12-0.68 (m, 6H; $CH_2\underline{C}H_3$). ^{13}C NMR (100 MHz, $CDCl_3/CS_2$) δ: 158.42, 155.69, 155.41, 151.83, 150.95, 150.61, 150.30, 149.18, 148.99, 148.90, 148.26, 148.05, 147.77, 147.29, 147.19, 146.85, 146.73, 145.82, 145.49, 145.25, 144.26, 143.71, 143.53, 143.11, 142.38, 141.42, 141.35, 139.81, 138.57, 137.16, 136.58, 133.74, 132.56, 131.52, 131.14, 130.99, 130.60, 130.38, 114.53, 114.19, 106.59, 71.72, 69.62, 67.83, 67.65, 65.46, 43.03, 40.73, 31.65, 29.31, 25.83, 22.76, 14.11. HRMS calculated: 1208.2637; found: 1208.2496 [M-H]$^+$. (**6b**) ^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.21-7.33 (m, 8H), 7.21-6.49 (m, 8H), 4.26-3.60 (m, 8H; O$\underline{C}H_2$), 2.03-1.08 (m, 32H, -CH_2-), 1.08-0.73 (m, 12H; $CH_2\underline{C}H_3$). HRMS calculated: 1570.5195; found: 1570.5037 [M-H]$^+$.

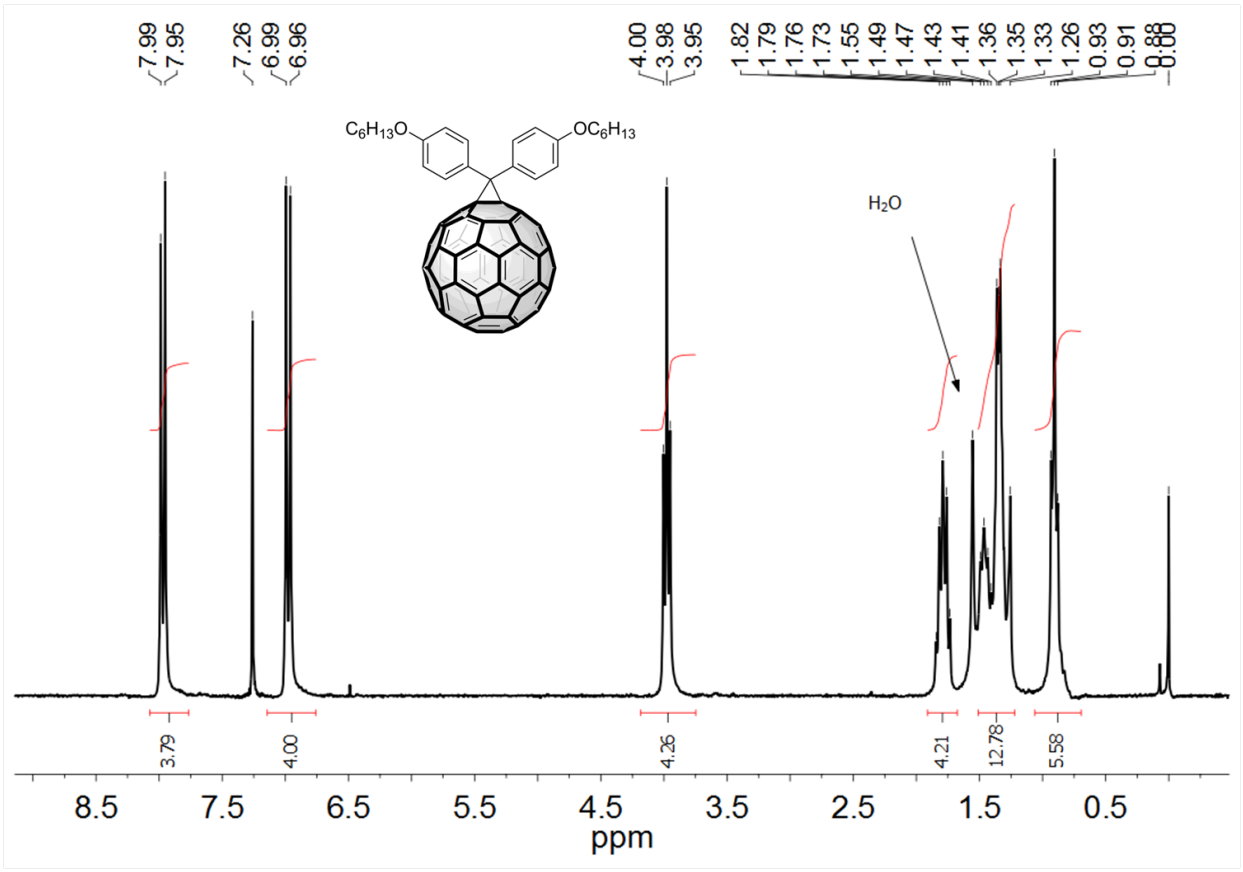


Figure S13. [1]H NMR Spectrum of **5a**

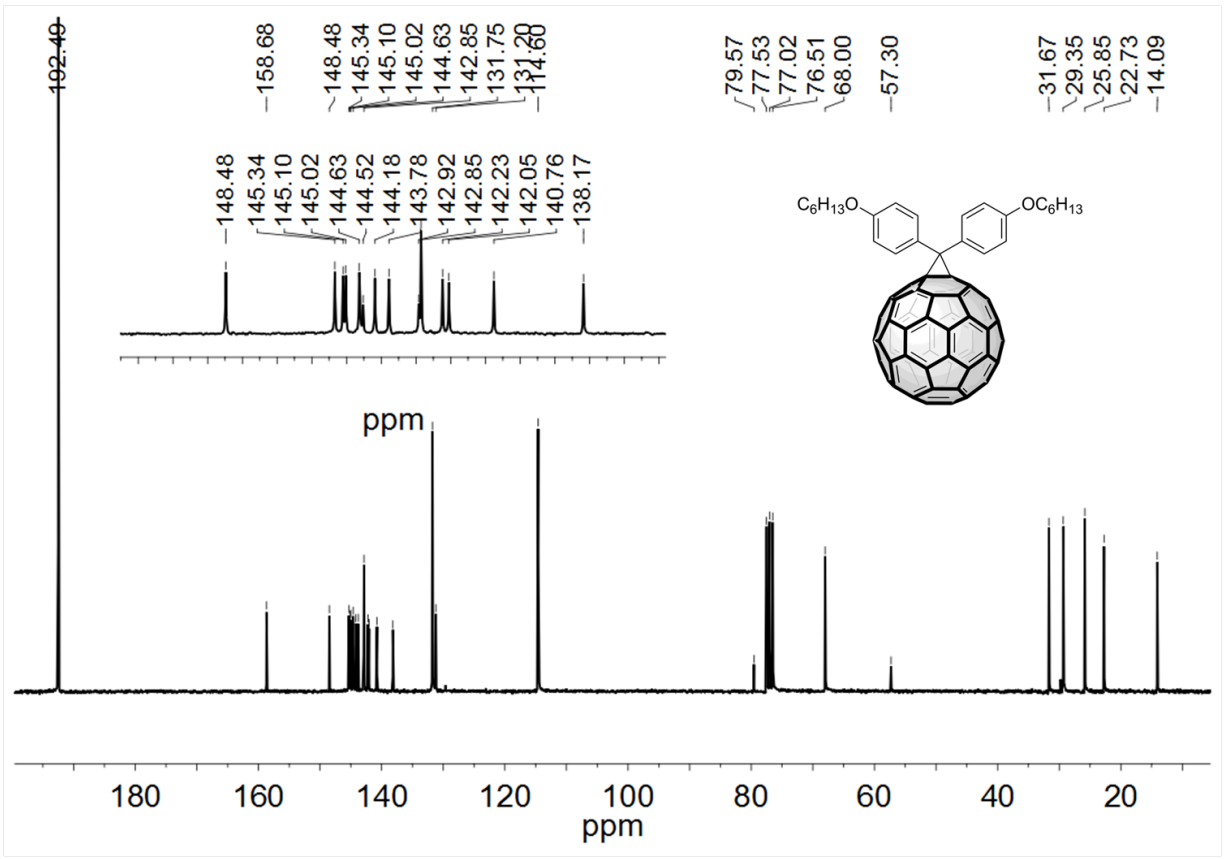


Figure S14. [13]C NMR Spectrum of **5a**

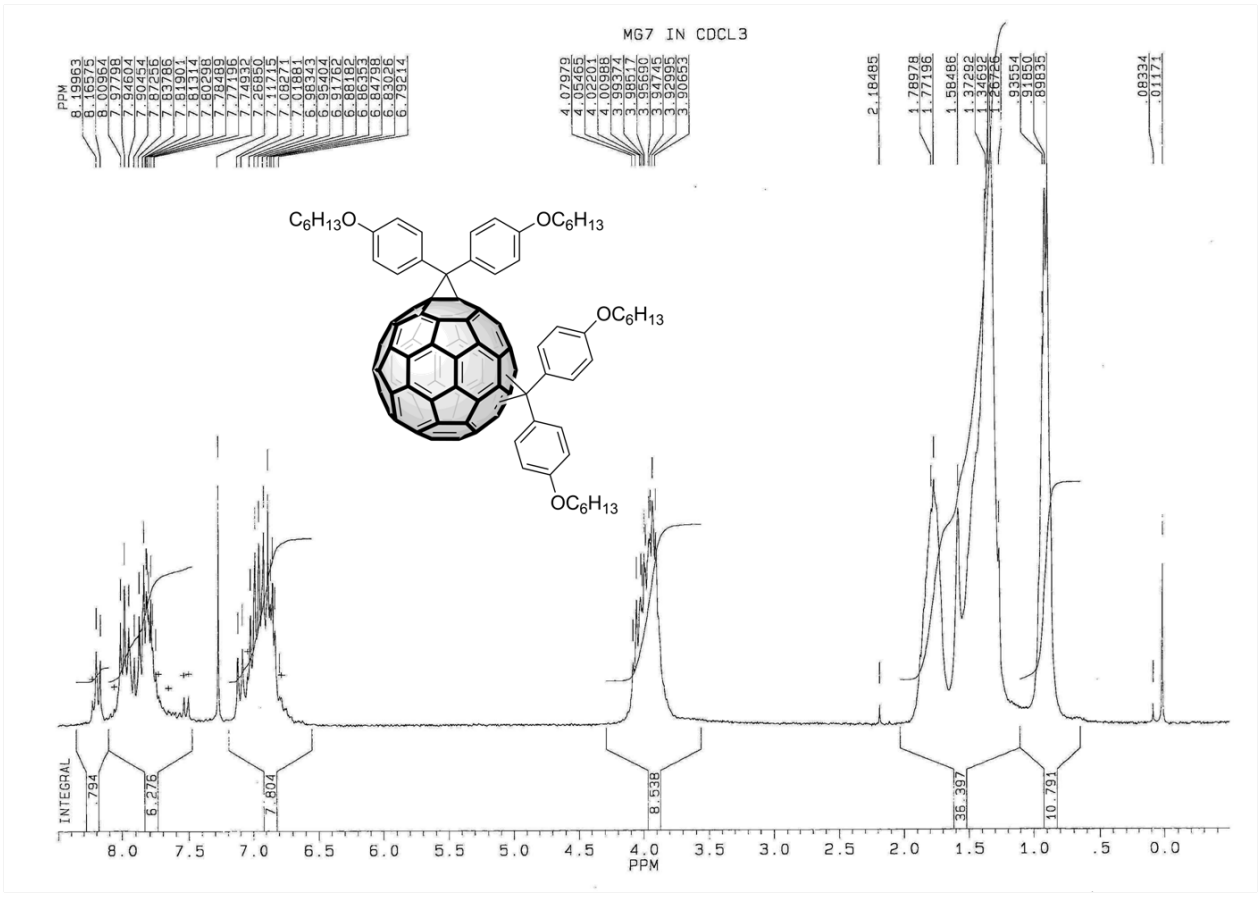


Figure S15. ^{1}H NMR Spectrum of **5b**

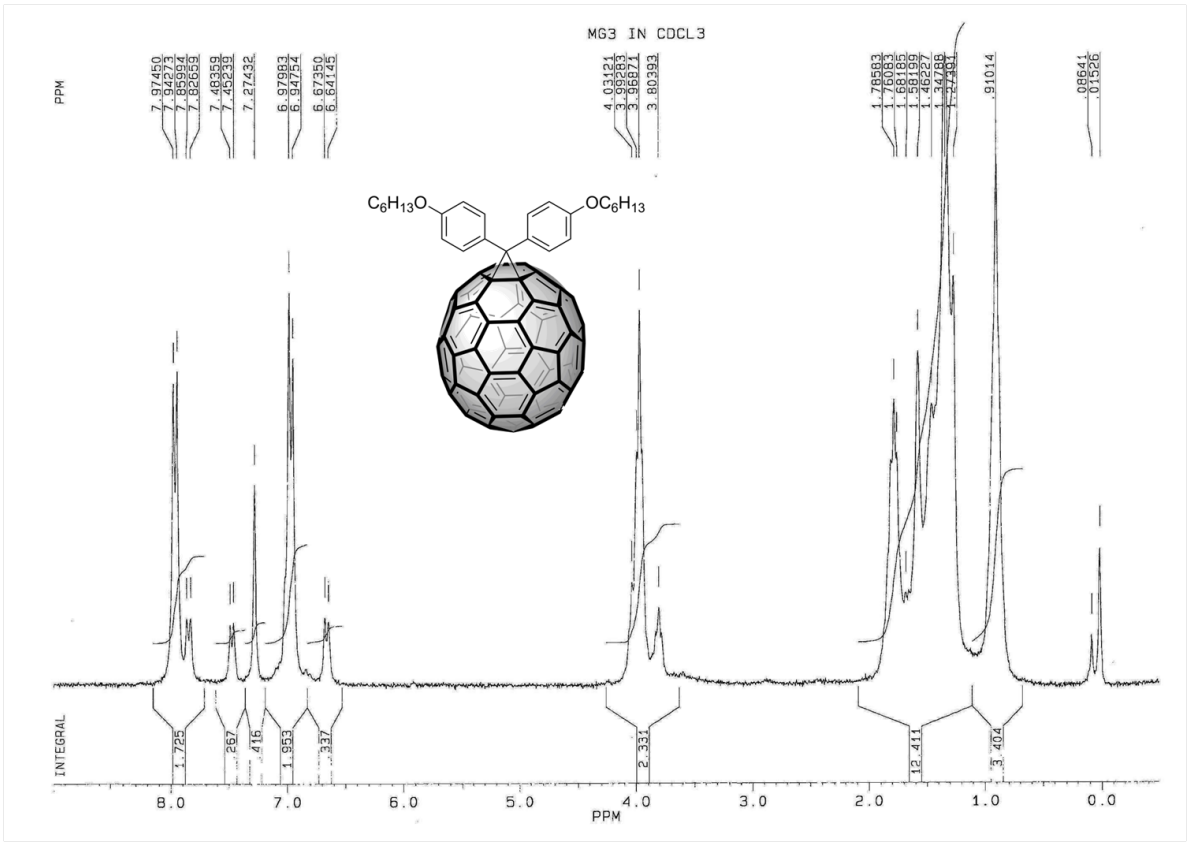


Figure S16. ^{1}H NMR Spectrum of **6a**

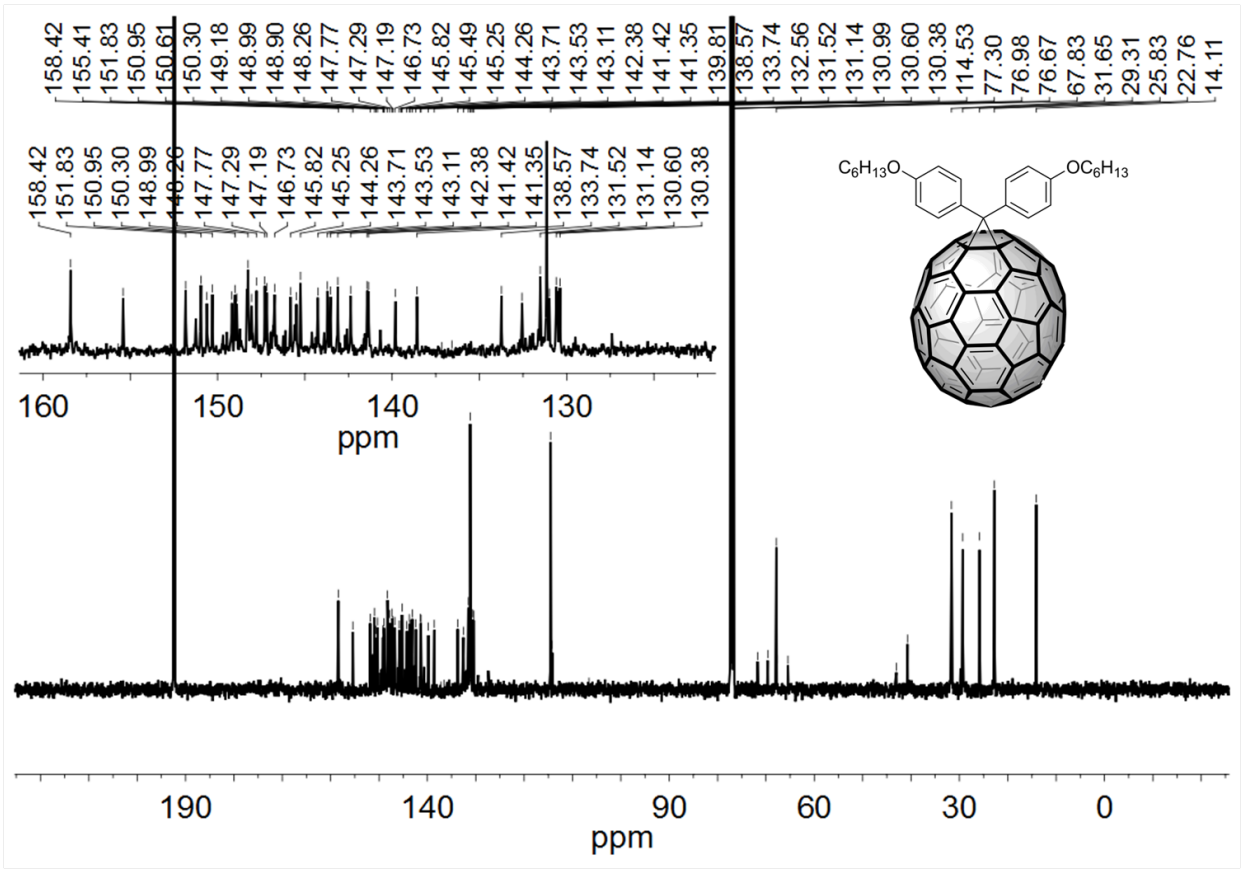


Figure S17. ^{13}C NMR Spectrum of **6a**

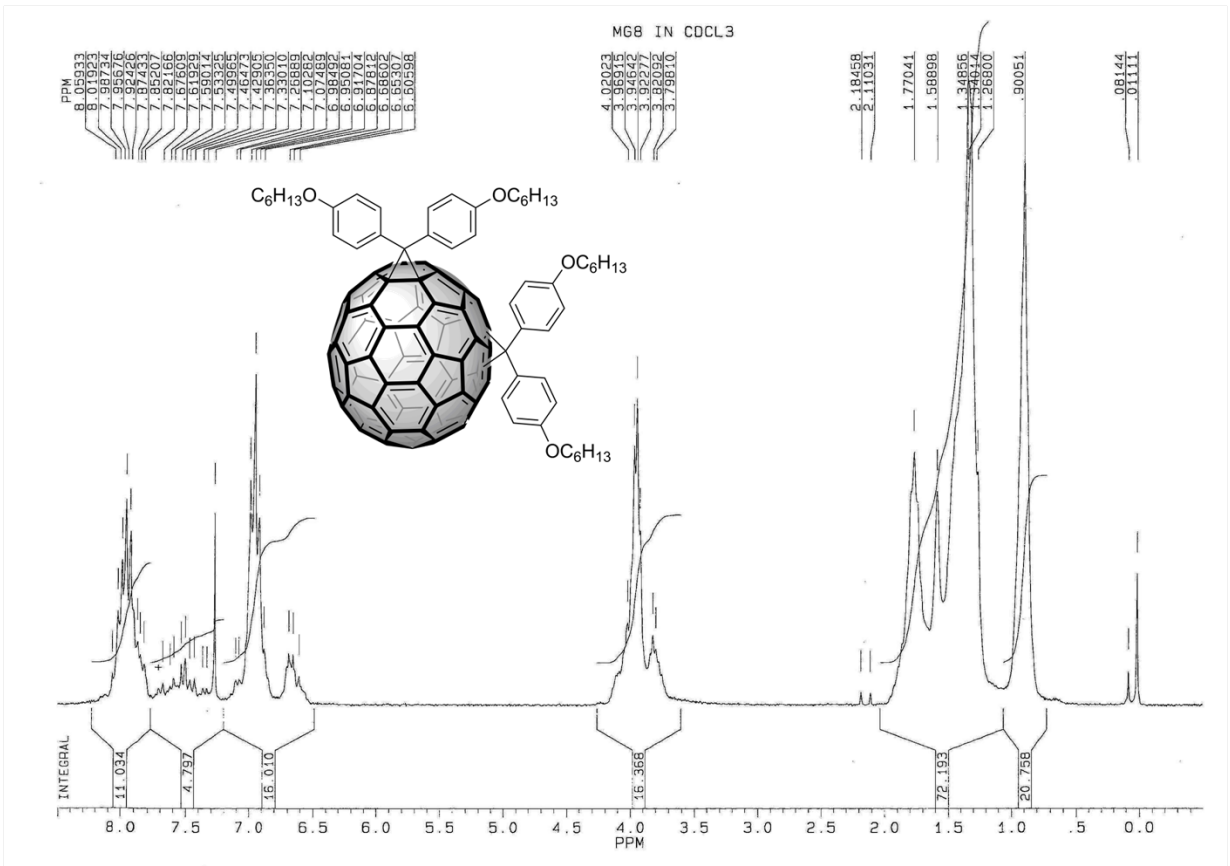


Figure S18. ^{1}H NMR Spectrum of **6b**

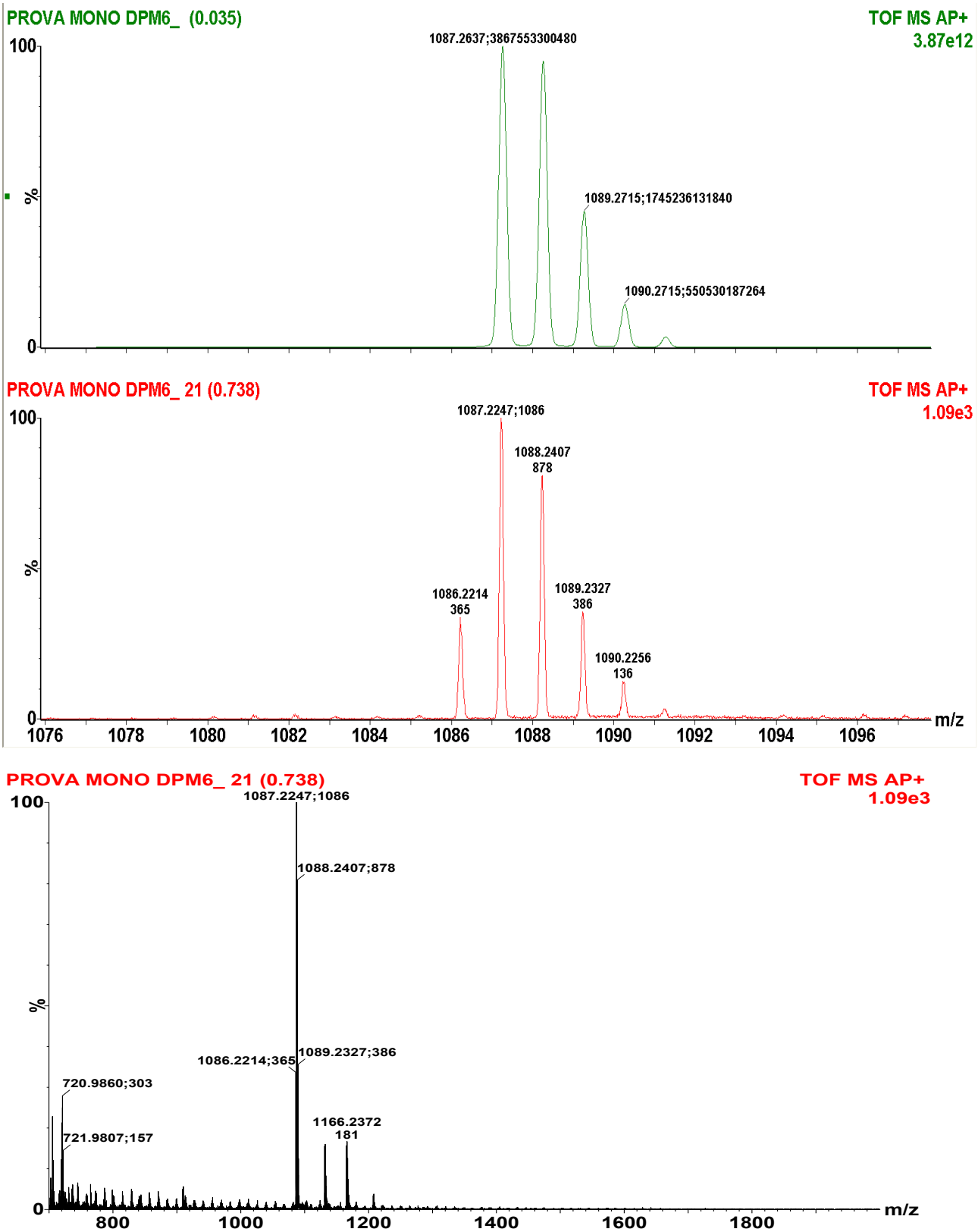


Figure S19. From the top: simulated, experimental and full HRMS spectrum of **5a.**

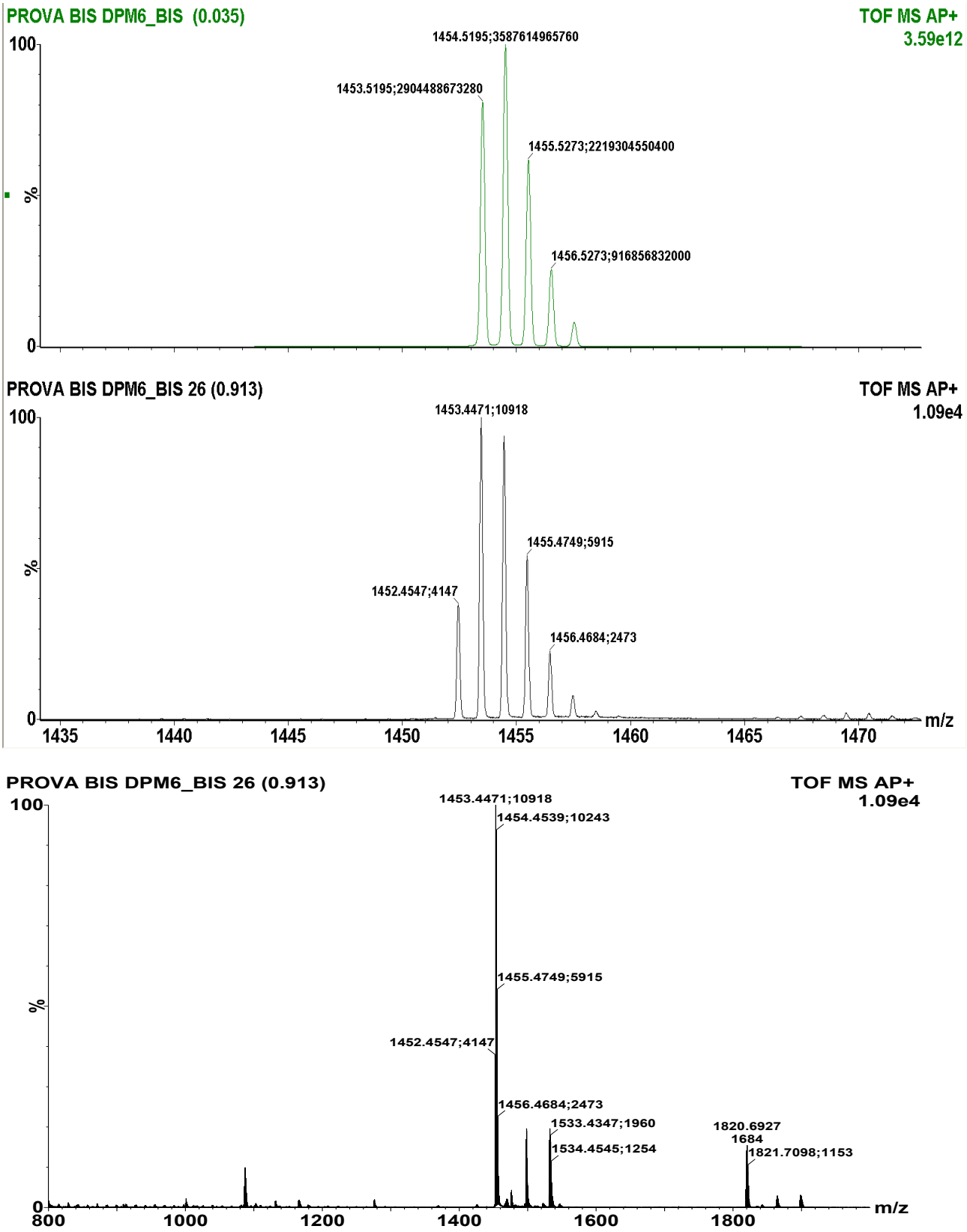


Figure S20. From the top: simulated, experimental and full HRMS spectrum of **5b.**

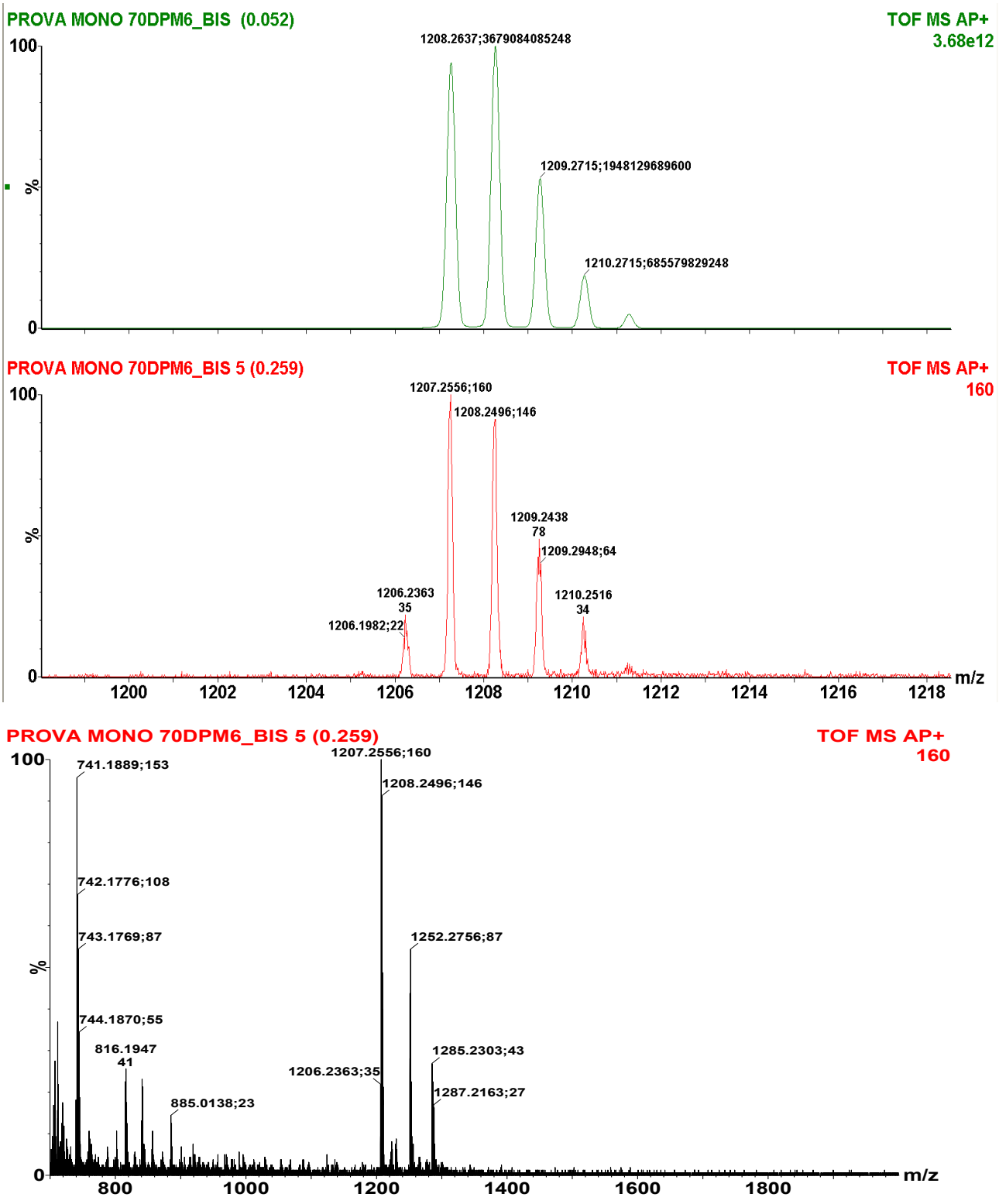


Figure S21. From the top: simulated, experimental and full HRMS spectrum of **6a.**

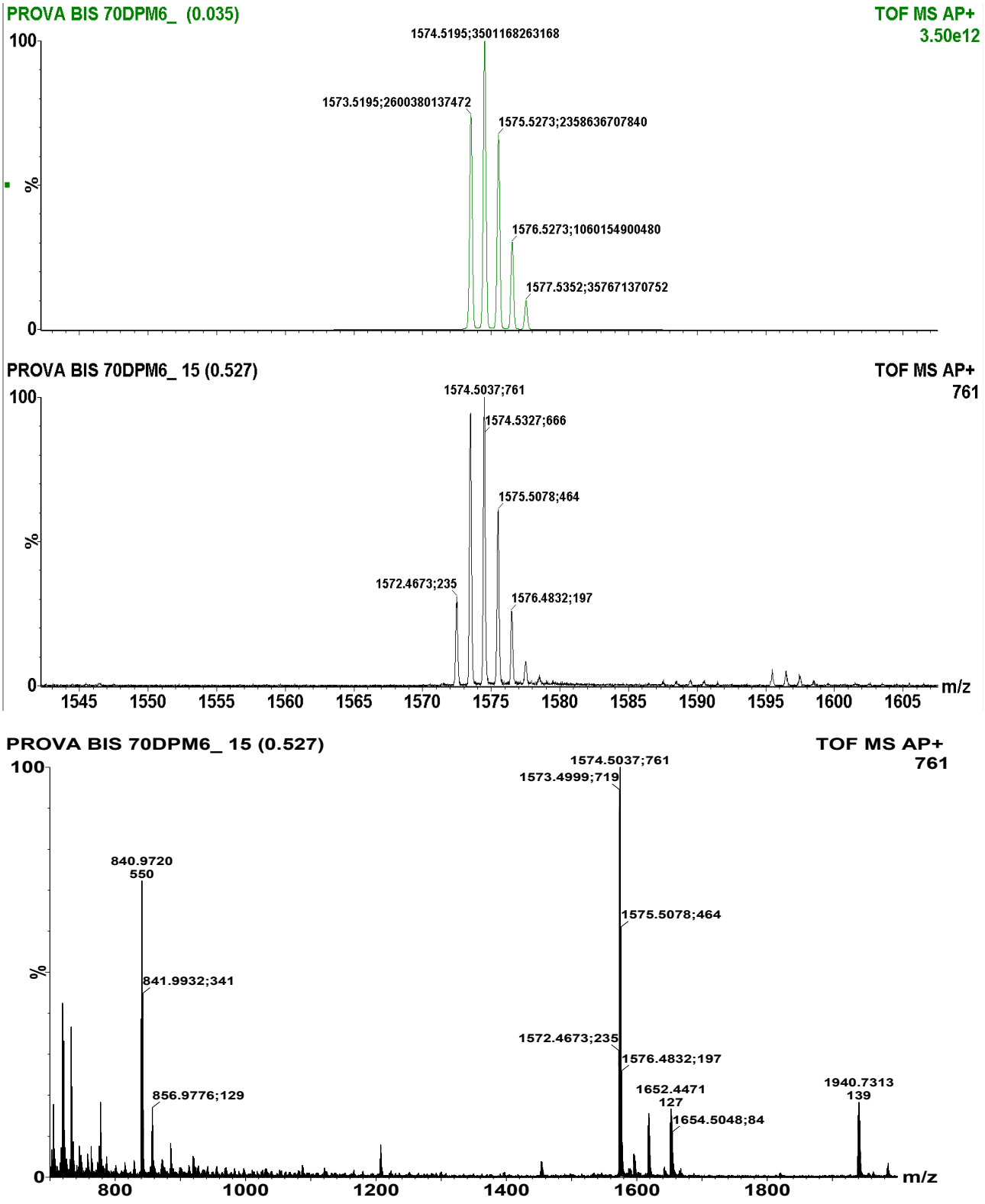


Figure S22. From the top: simulated, experimental and full HRMS spectrum of **6b.**

- ***[70] and [60]BHN derivatives***

Synthesis of sultine (7). The synthesis of this compound was carried out following a procedure previously reported in literature.[5] To a solution in DMF (75 mL) of 1,2-bis(bromomethyl)benzene (1.15 g, 4.230 mmol), Sodium hydroxymethanesulfinate (rongalite, 2.60 g, 16.902 mmol) and tetrabutylammonium bromide (413.00 mg, 1.268 mmol) were added. The mixture was stirred at 0°C under argon atmosphere for 4 h. Then water was added and the mixture was extracted three times with dichloromethane. The organic layer was dried over Na_2SO_4, and the solvent was evaporated at 25°C to give colorless oil (627.35 mg, 88.2%). The crude product was used in the next reaction step without further purification.

Synthesis of BHN derivatives (8a-c, 9a-b). To a solution of C_{60} or C_{70} (50.00 mg) in 4 mL of ODCB (previously sonicated for about 20 minutes), the appropriate amount of sultine was added. The resulting mixture was kept under MW irradiation at appropriate temperature (7-10 W) for appropriate time. After cooling down, the reaction mixture was precipitated with methanol. The recovered residue was solubilized in a minimal amount of chloroform and precipitated again with methanol. Methanol was removed and the residue was solubilized in dichloromethane, adsorbed on silica and chromatographated (Silica gel column conditions for C_{60}-derivatives: Hexane/Toluene from 15:1 to 5:1 for mono- and bisadducts and finally 2:1 for trisadducts. Column conditions for C_{70}-derivatives: Hexane/Toluene from 15:1 to 5:1 for mono- and bisadducts and finally 2:1). Both mono and bis-adducts were solubilized and transferred to a centrifuge tube using a minimal amount of chloroform and subsequently precipitated with methanol. (**8a**) ^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.68 (m, 2H), 7.57 (m, 2H), 4.81 (m, 2H), 4.72 (m, 2H). (**8b**) ^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.00-7.30 (m, 8H), 5.18-3.36 (m, 8H). HRMS calculated: 929.1330; found: 929.0865 $[M-H]^+$. (**9b**) ^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.95-6.96 (m, 8H), 4.74-3.10 (m, 8H). HRMS calculated: 1049.1331; found: 1049.0826 $[M-H]^+$.

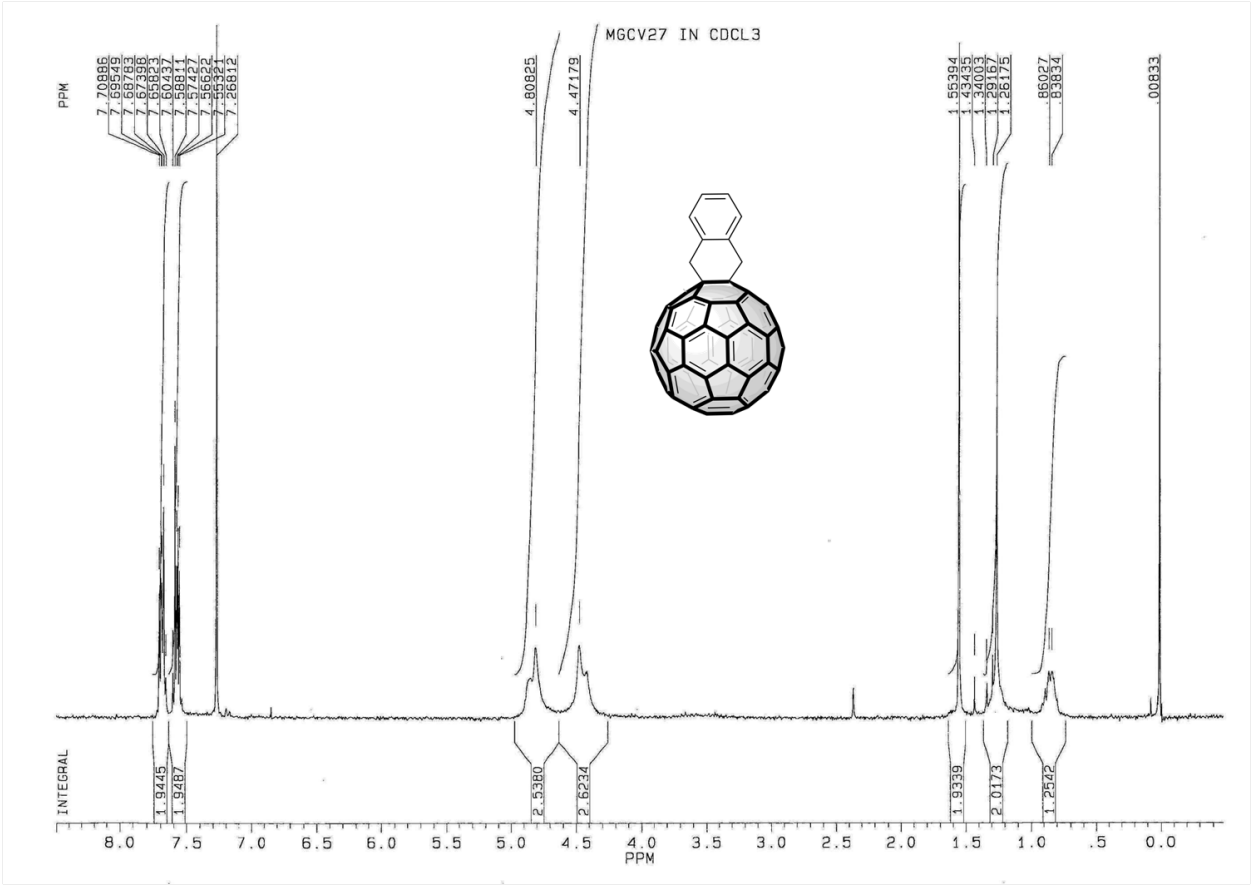


Figure S23. ^{1}H NMR Spectrum of **8a**

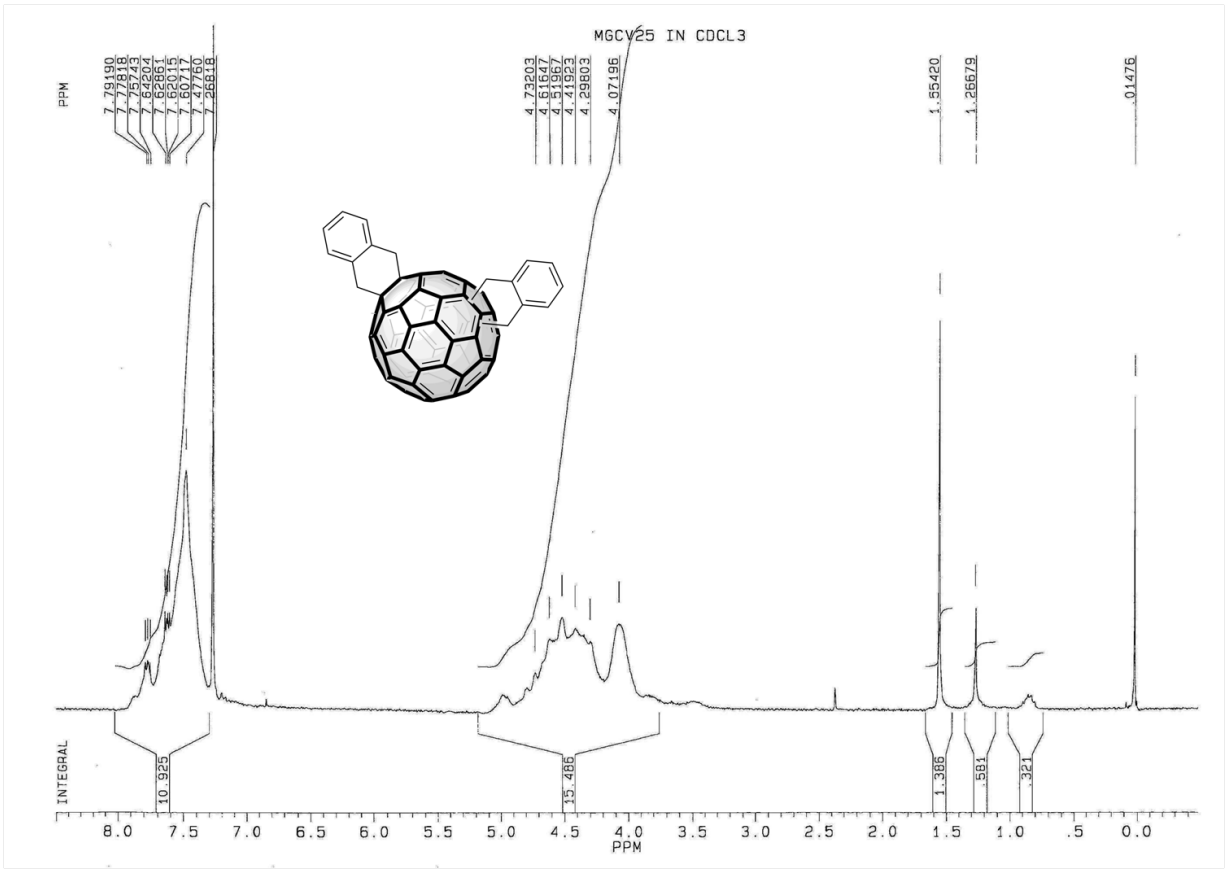


Figure S24. ^{1}H NMR Spectrum of **8b**

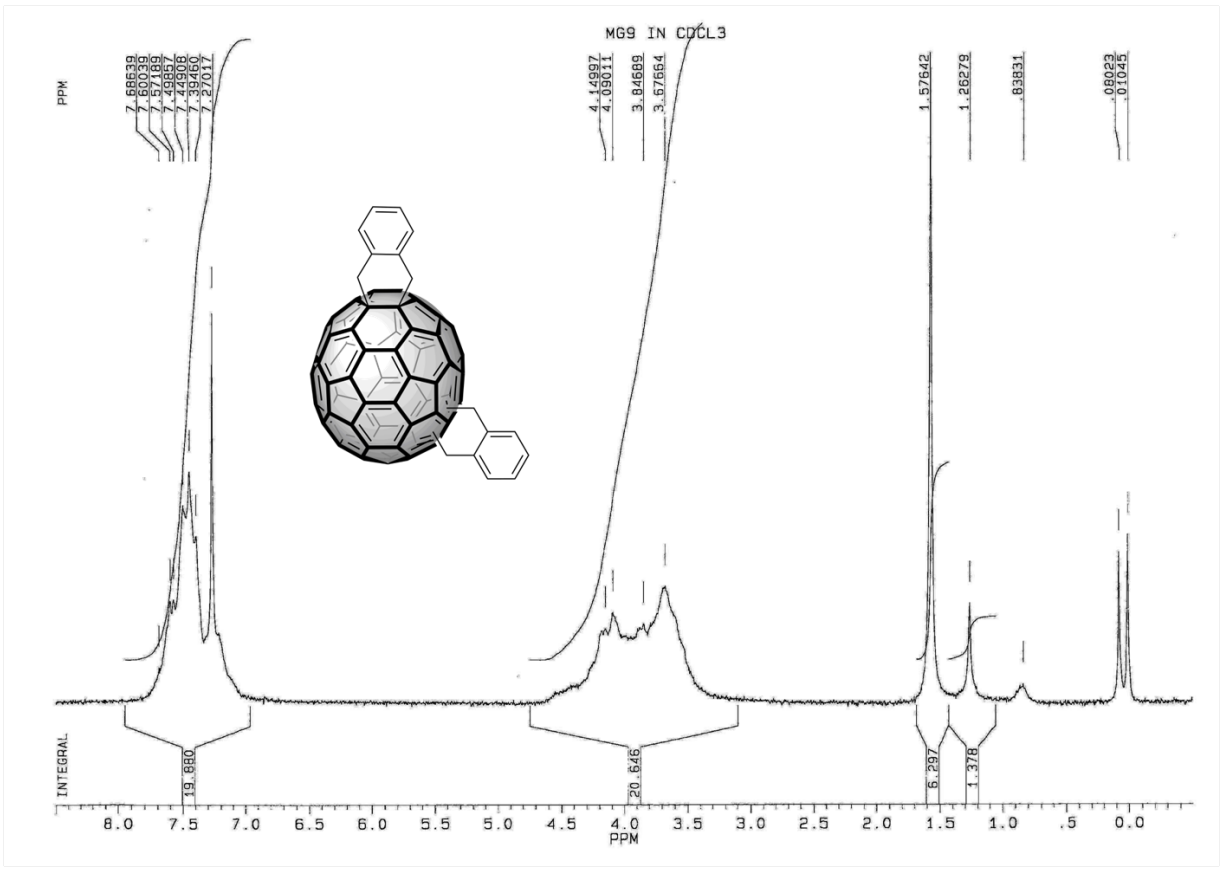


Figure S25. ^{1}H NMR Spectrum of **9b**

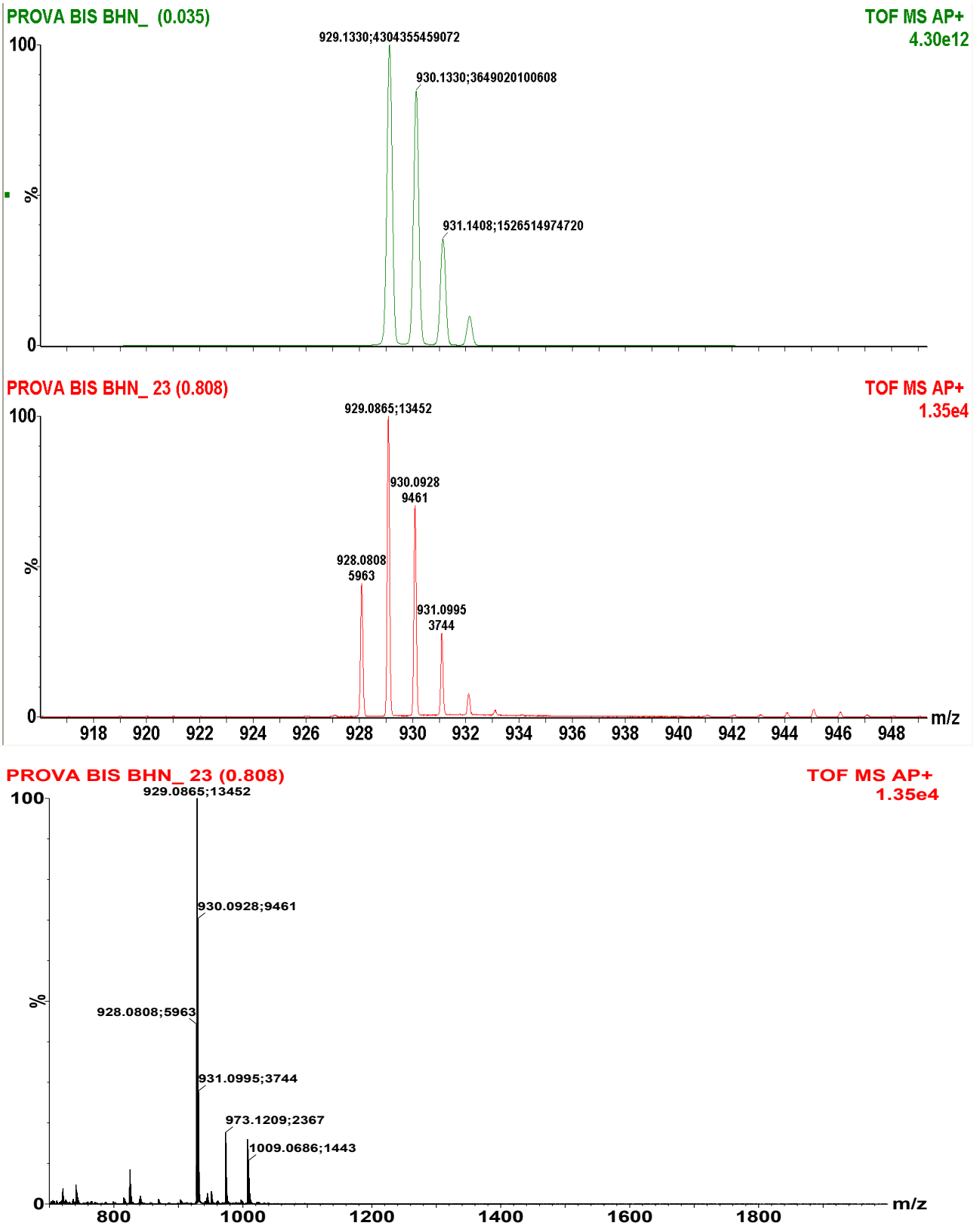


Figure S26. From the top: simulated, experimental and full HRMS spectrum of **8b.**

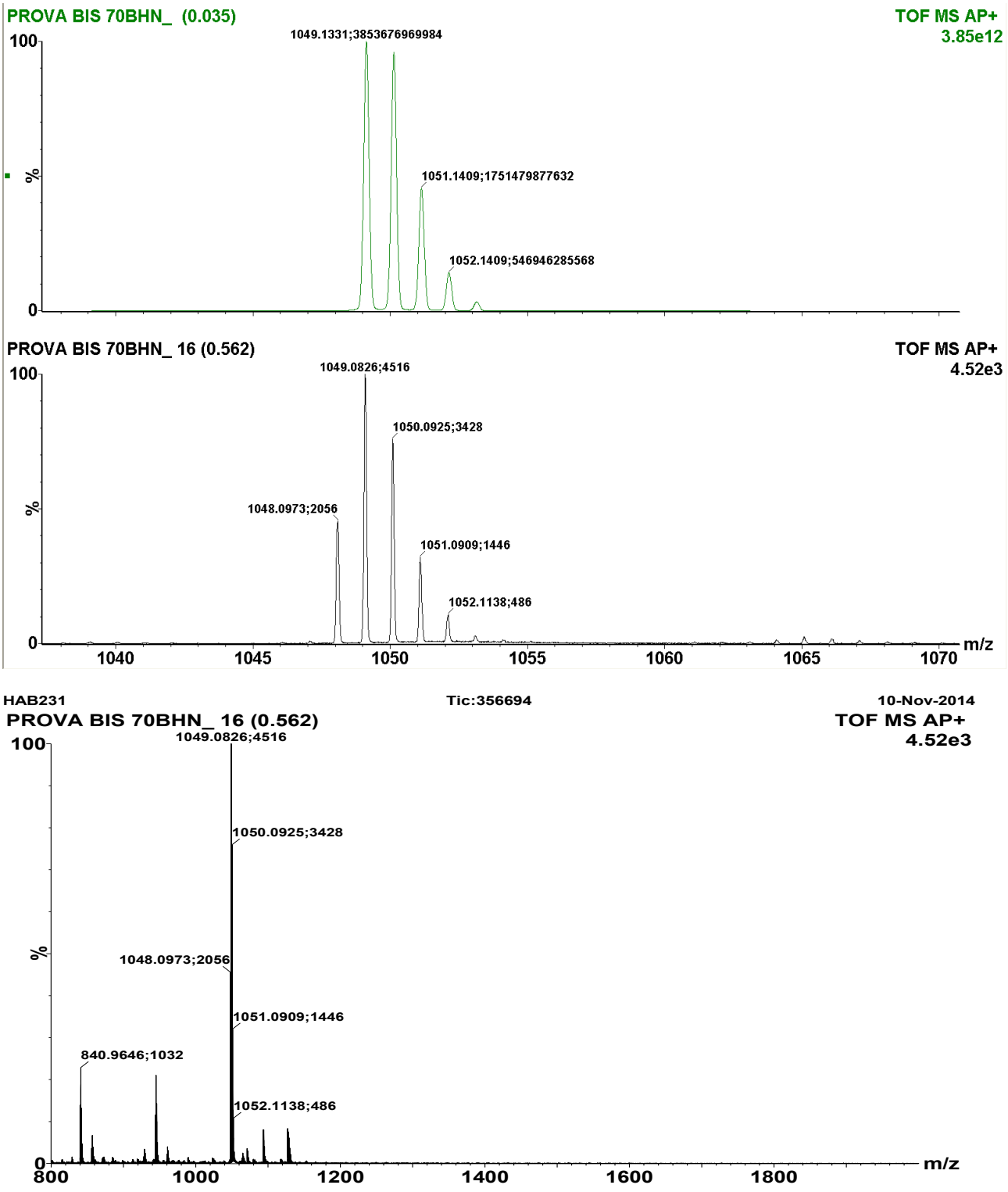


Figure S27. From the top: simulated, experimental and full HRMS spectrum of **9b.**

- ***[70] and [60]ICBA derivatives***

Synthesis of ICBA derivatives (11a-c, 12a-b). To a solution of C_{60} or C_{70} (50.00 mg) in 4 mL of ODCB (previously sonicated for about 20 minutes), the appropriate amount of indene **(10)** was added. The resulting mixture was kept under MW irradiation at 180 °C (25 W) for appropriate time. After cooling down, the reaction mixture was precipitated with methanol. The recovered residue was solubilized in a minimal amount of chloroform and precipitated again with methanol. Methanol was removed and the residue was solubilized in dichloromethane, adsorbed on silica and chromatographated (Silica gel column conditions for C_{60}-derivatives: Hexane/Chloroform 25:1 and then 20:1 for monoadduct, 10:1 for bisadducts mixture and finally 1:1 for trisadducts. Column conditions for C_{70}-derivatives: Hexane/Chloroform 30:1 and then 25:1 for monoadducts, 15:1 and then 9:1 for bisadducts and finally 5:1 for trisadducts). Both mono and bis-adducts were solubilized and transferred to a centrifuge tube using a minimal amount of chloroform and subsequently precipitated with methanol. (**11b**) ^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.01-7.12 (m, 8H), 5.41-2.34 (m, 8H). HRMS calculated: 953.1252; found: 953.0886 $[M-H]^+$. (**11c**) HRMS calculated: 1068.1877; found: 1068.1566 $[M-H]^+$. (**12a**) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.32-7.28 (m, 3H), 7.24-6.88 (m, 1H). 4.94-2.10 (m, 4H; isomers mixture). (**12b**) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.87-6.72 (m, 8H), 5.19-1.97 (m, 8H). HRMS calculated: 1072.1252; found: 1072.0819 $[M-H]^+$.

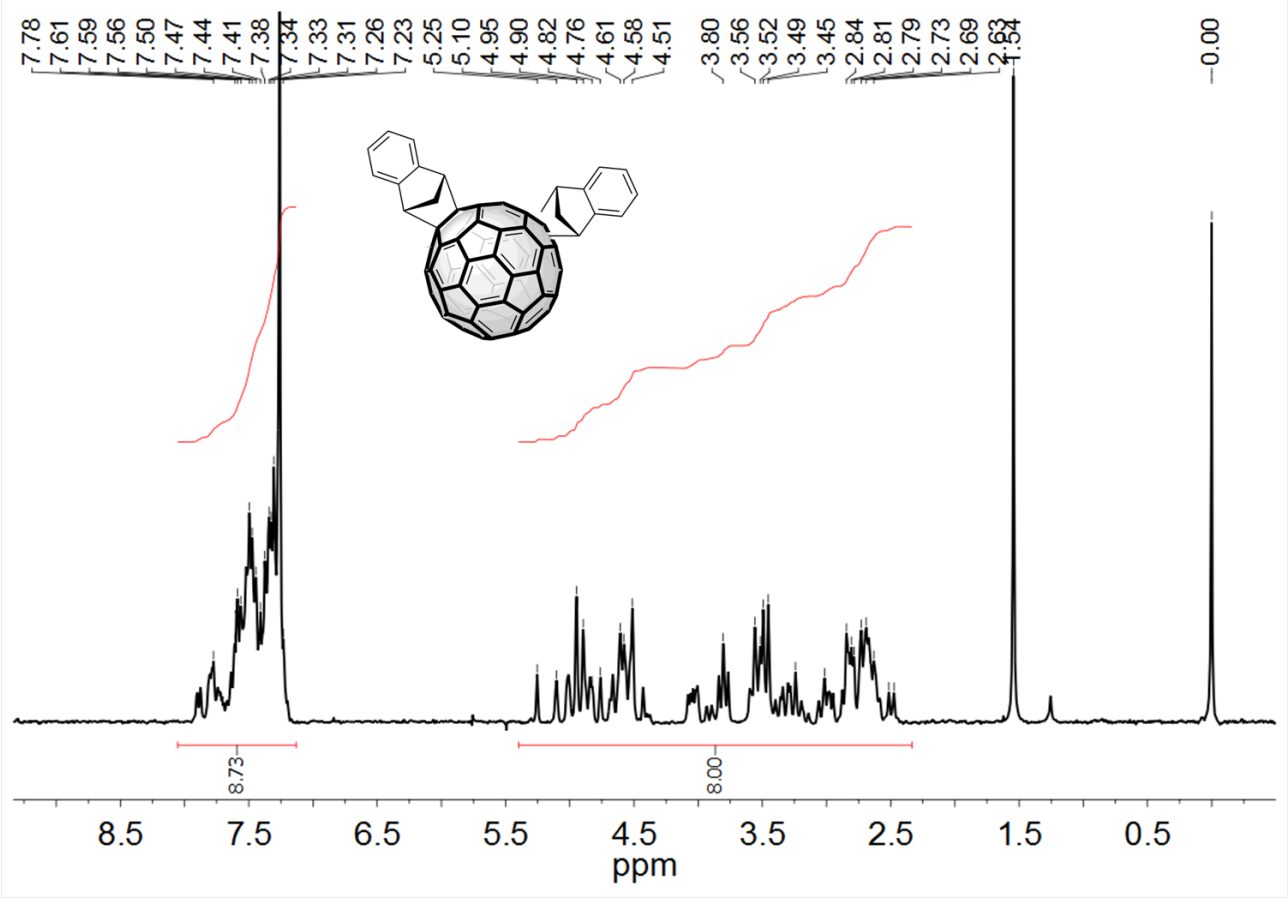


Figure S28. ^{1}H NMR Spectrum of **11b**

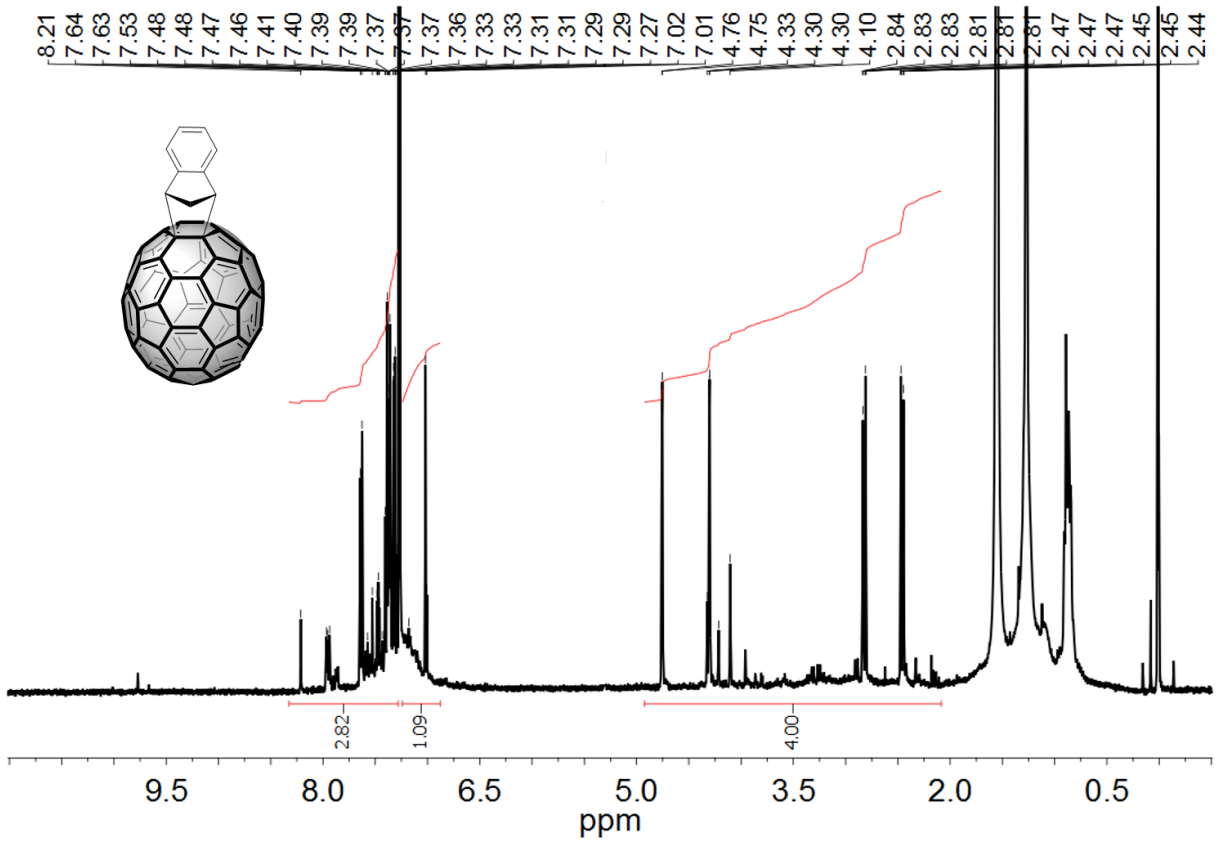


Figure S29. ^{1}H NMR Spectrum of **12a**

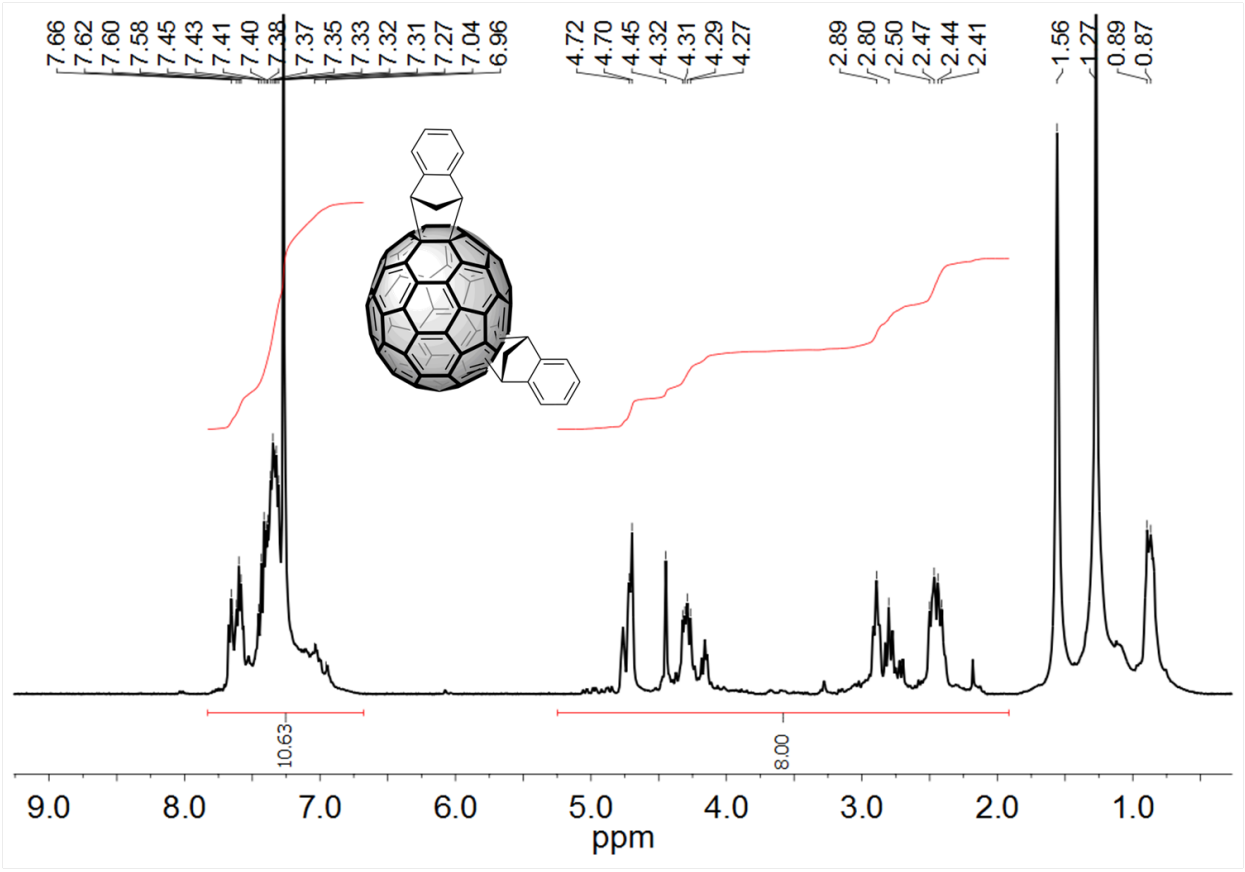


Figure S30. ^{1}H NMR Spectrum of **12b**

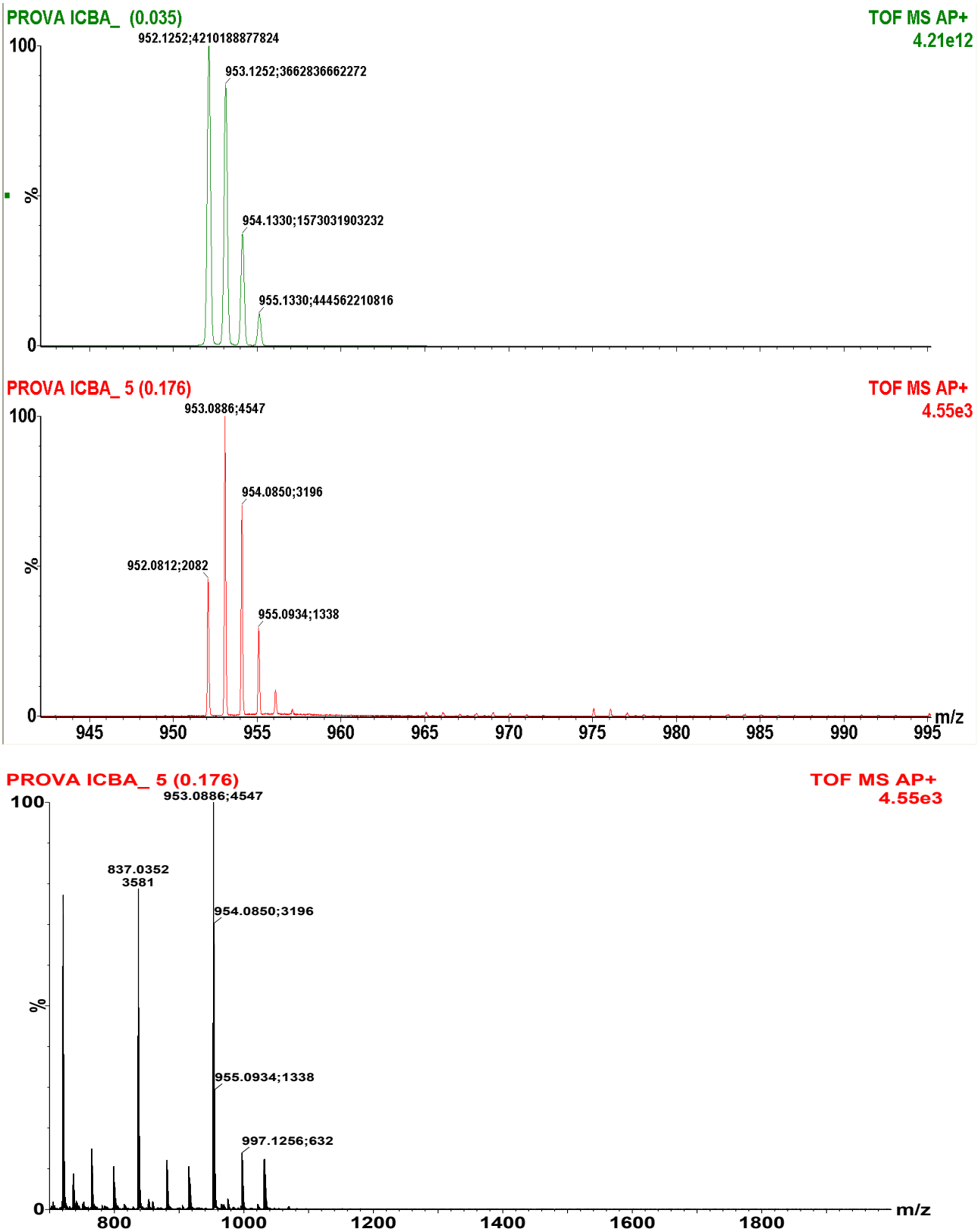


Figure S31. From the top: simulated, experimental and full HRMS spectrum of **11b.**

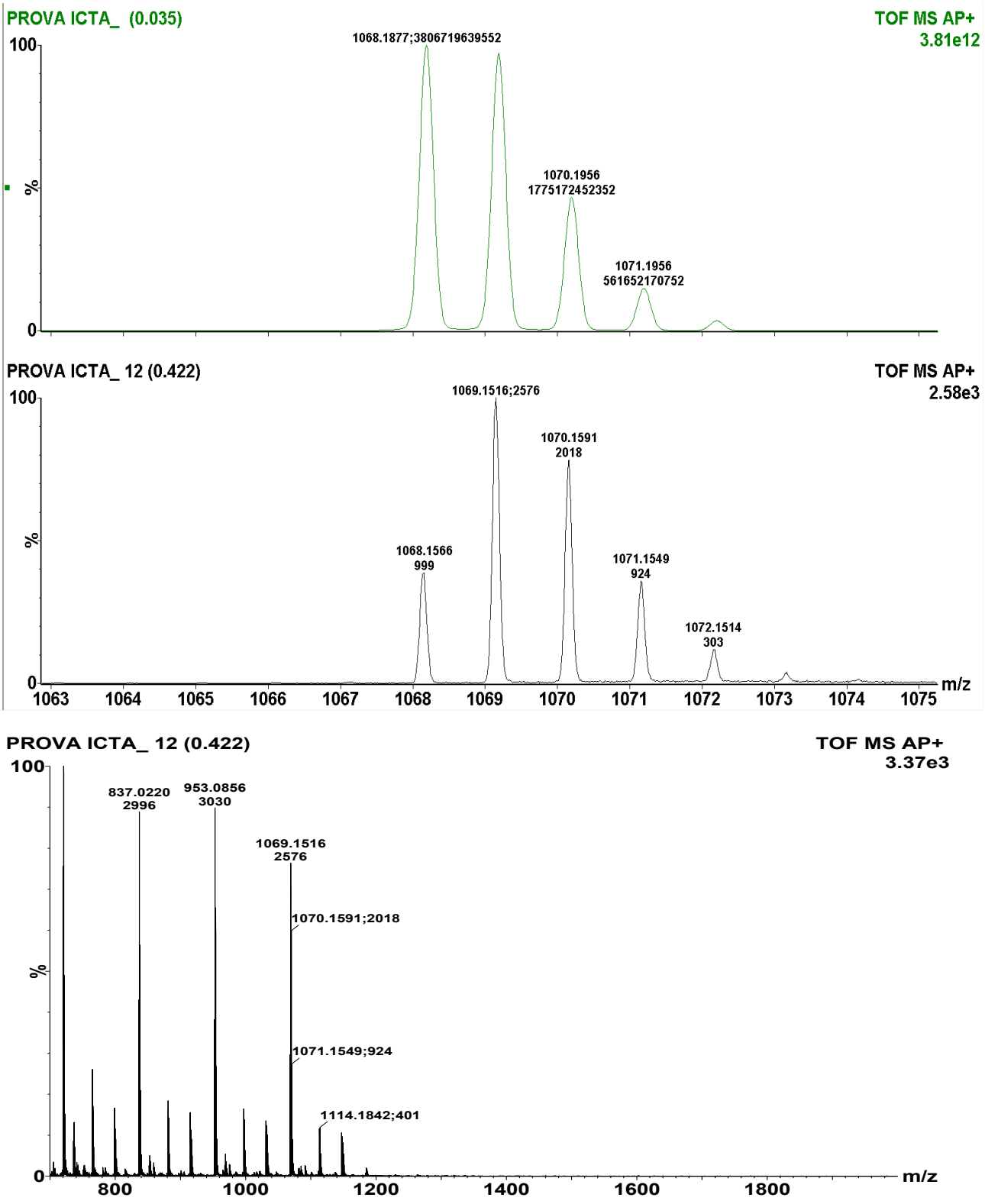


Figure S32. From the top: simulated, experimental and full HRMS spectrum of **11c.**

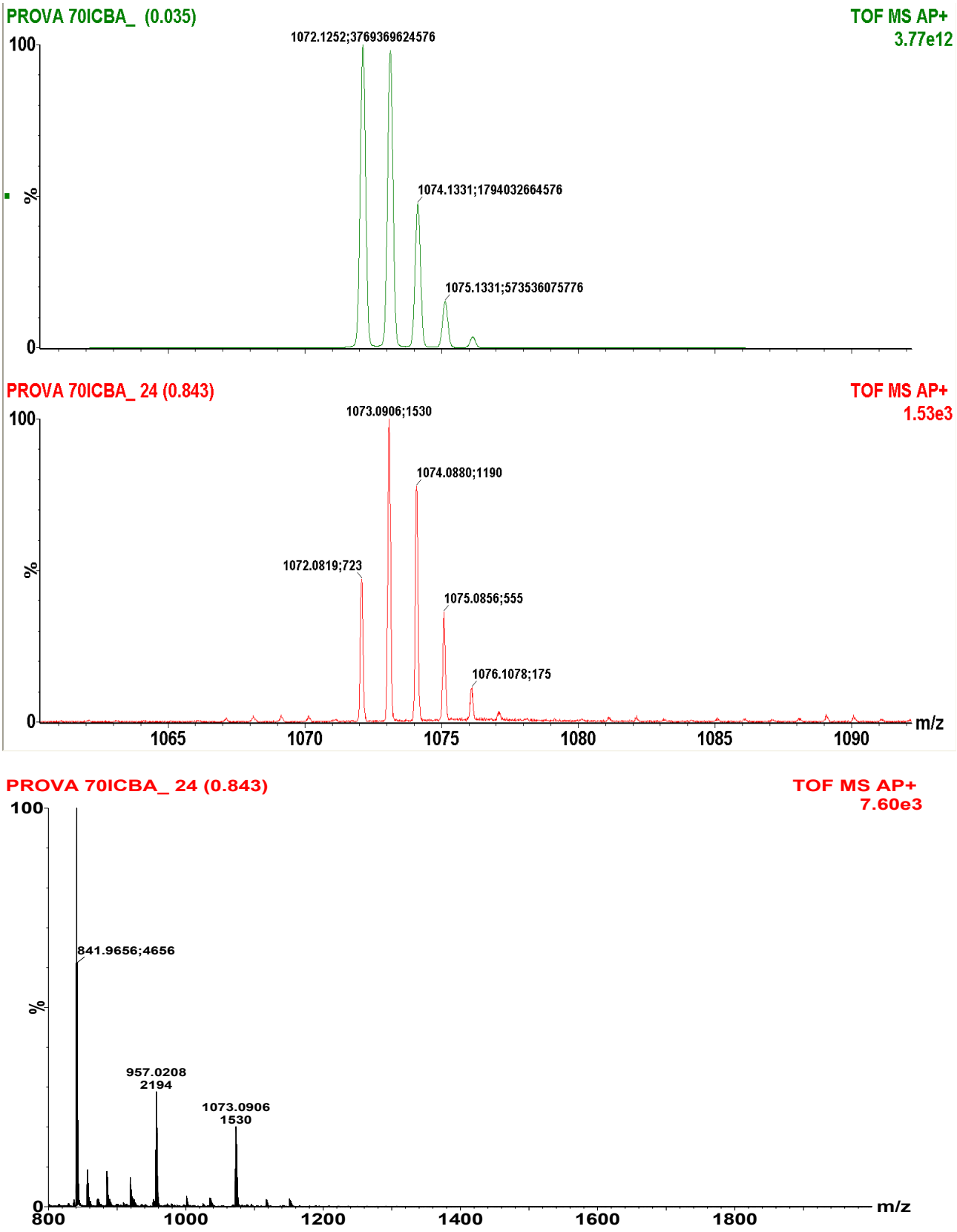


Figure S33. From the top: simulated, experimental and full HRMS spectrum of **12b.**

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