Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Synthesis of Open-cage Fullerene-based Unidirectional H-Bonding Network and its Coordination to Titanium

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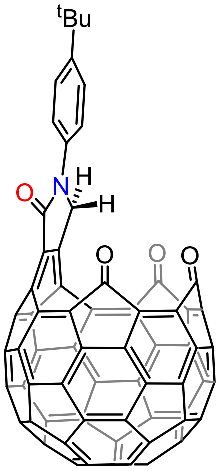
All reagents were used as received. All solvents were used as received. The reactions were carried out under atmosphere condition. The NMR spectra were obtained at 25 °C with 400 and 500MHz spectrometers (^{1}H and ^{13}C NMR spectra for the same compound were obtained with different spectrometers and different solvents in some cases). Chemical shifts are given in ppm relative to TMS or $CDCl_3$ (for ^{13}C NMR). ESI-FT-ICR-HRMS spectra were recorded in positive mode. UV/vis spectra are measured with Perkin Elmer Lambda 35 UV/vis spectrometer. Chromatographic purifications were carried out with silica gel of mesh 200-300. Known compounds were characterized by comparison of their ^{1}H NMR data with literature data as cited.
Note: common impurities such as residue solvent toluene and grease from silica gel are sometimes impossible to be removed from the fullerene derivatives by routine flash column chromatography. Further purification by a diffusion-precipitation procedure was usually required to obtain pure samples. The diffusion-precipitation solvents are CS_2/EtOH or CS_2/CH_3CN or $CHCl_3$/EtOH.

Preparation of Compound 2:



Method 1

Compound **1** (768.6 mg, 0.69 mmol) was desolved in 51 mL *o*dichlorobenzene (*o*DCB), and then 76 mL hydrochloric acid (37%) and 380 mL acetic acid were added into the reaction vessel. The resulting solution was stirred at 60 °C for 15 minutes. The solution was concentrated in vacuo. The residue was dissolved in *o*DCB again, and then chromatographed on a silica gel column eluting with petroleum ether to remove *o*DCB. Eluting with toluene/ ethyl acetate (20 : 1) removed other products, then eluting with toluene/ ethyl acetate (10 : 1) gave a black band as compound **2** (55.9 mg, 0.061 mmol, 8.8 %).

Method 2

Compound **1** (640.0 mg, 0.58 mmol) was desolved in 300 mL *o*DCB, and then 170 mL hydrochloric acid (37%), 1.2 L acetic acid and 3.2 g hydroquinone (0.029 mol) were added into the reaction vessel. The resulting solution was divided into two equal parts and stirred at room temperature for 30 minutes and then heated up to 60 °C for 15 minutes until compound **1** converted completely. The solution was washed by 300 mL water for three times. The organic layer was separated, dried by anhydrous Na_2SO_4, and then chromatographed on a silica gel column eluting with petroleum ether to remove *o*DCB. Eluting with toluene/ ethyl acetate (20 : 1) removed some imputiry, then eluting with toluene/ ethyl acetate (10 : 1) gave a black band as compound **2** (277.2 mg, 0.30 mmol, 51.7 %).

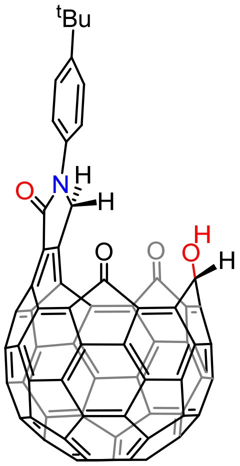
Characterization data for 2:

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.6 Hz, 2H), 7.65 (d, *J* = 8.6 Hz, 2H), 6.71 (dd, *J* = 18.9, 9.0 Hz, 1H), 5.15 (dd, *J* = 18.9, 4.8 Hz, 1H), 1.46 (s, 9H), -9.60 (s, 0.5H). (H_2O@Compound **2**)

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.63, 185.74, 184.28, 165.00, 151.30, 150.41, 150.08, 149.91, 149.77, 149.51, 149.20, 148.85, 148.80, 148.31, 147.26, 147.04, 146.71, 146.70, 146.44, 146.33, 146.29, 146.15, 146.11, 146.06, 145.89, 145.86, 143.96, 143.77, 143.62, 143.57, 143.54, 143.00, 142.84, 142.76, 142.72, 142.61, 142.49, 141.87, 141.63, 141.18, 139.52, 138.39, 137.82, 137.30, 136.86, 136.83, 136.72, 136.70, 135.77, 135.72, 134.99, 134.75, 131.94, 128.15, 127.46, 126.51, 126.48, 126.19, 125.26, 120.83, 53.09 (CH_2), 34.76 (C), 31.64 (($(CH_3)_3$)).

ESI-FT-ICR-HRMS-Positive $C_{69}H_{16}NO_4$ (M + H^+) calculated 922.1045, found 922.1074.

Preparation of Compound 3:



Compound **2** (35.0 mg, 0.038 mmol) was dissolved in 15 mL $CHCl_3$, and then excess of KBH_4 (41.0 mg, 0.76 mmol, dispersed in 5 mL EtOH) were added into the reaction vessel. The reaction was quenched 5 minutes later by adding 5 mL acetic acid. The solution was washed by 15 mL water for three times. The organic layer was separated, dried by anhydrous Na_2SO_4 and concentrated in vacuo. The residue was dissolved in CS_2, and then chromatographed on a silica gel column eluting with CS_2/ethyl acetate (50 : 1) to give a black band as compound **3** (9.5 mg, 0.010 mmol, 27.1 %, brsm. 49.4%). 15.8 mg of unreacted compound **2** was recovered.

Characterization data for 3:

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.5 Hz, 2H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.55

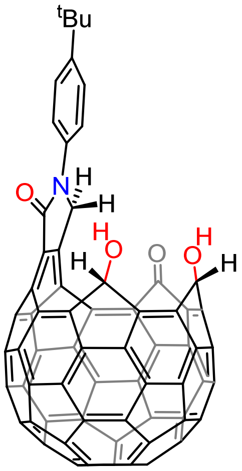
(s, 1H), 6.41 (d, *J* = 18.7 Hz, 1H), 5.21 (d, *J* = 18.7 Hz, 1H), 4.72 (s, 1H), 1.45 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.91, 193.19, 165.59, 151.85, 151.36, 151.19, 150.48, 150.20, 149.99, 149.73, 149.47, 149.21, 149.14, 149.03, 148.46, 148.10, 148.00, 146.85, 146.80, 146.78, 146.50, 146.38, 146.33, 146.21, 145.93, 145.76, 144.89, 144.84, 144.70, 144.55, 144.48, 144.27, 143.81, 143.22, 143.12, 143.06, 143.03, 142.90, 142.51, 141.30, 140.85, 140.60, 140.42, 140.08, 140.03, 139.72, 138.22, 137.25, 136.81, 136.10, 135.90, 135.88, 135.39, 132.07, 127.93, 127.90, 126.50, 119.71, 119.69, 79.92 (CH), 52.64 (CH_2), 34.74 (C), 31.62 ($(CH_3)_3$).

ESI-FT-ICR-HRMS-Positive $C_{69}H_{18}NO_4$ (M + H^+) calculated 924.1258, found 924.1230.

ESI-FT-ICR-HRMS-Positive $C_{69}H_{17}NNaO_4$ (M + Na^+) calculated 946.1030, found 946.1050.

Preparation of Compound 4:



Compound **2** (48.7 mg, 0.053 mmol) was dissolved in 50 mL $CHCl_3$, and then $NaBH_4$ (4.0 mg, 0.10 mmol, dispersed in 3 mL EtOH) were added into the reaction vessel. The reaction was terminated upon confirmation of complete conversion of compound **2** as indicated by TLC (about 10 minutes). The solution was quenched by 5 mL acetic acid and then washed by 50 mL water for three times. The organic layer was separated, dried by anhydrous Na_2SO_4 and concentrated in vacuo. The residue was dissolved in CS_2, and then chromatographed on a silica gel column eluting with CS_2/ethyl acetate (50 : 1) to give a red band as compound **4** (16.6 mg, 0.018 mmol, 33.9 %).

Characterization data for 4:

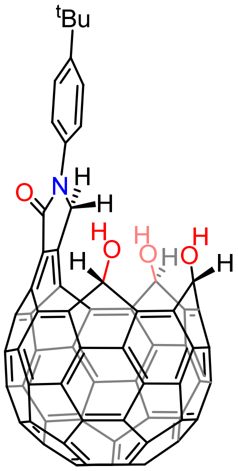
^{1}H NMR (400 MHz, d4-*o*DCB) δ 8.22 (d, *J* = 8.5 Hz, 2H), 7.80 (s, 1H), 7.65 (d, *J* = 8.5 Hz, 2H), 6.94 (d, *J* = 18.9 Hz, 1H), 5.17 (d, *J* = 19.0 Hz, 1H), 1.57 (s, 9H). (One of CH signal was overlapped with solvent peak.)

^{1}H NMR (400 MHz, d4-*o*DCB) δ 8.24 (d, *J* = 8.6 Hz, 2H), 7.97 (s, 1H), 7.91 (s, 1H), 7.66 (d, *J* = 8.6 Hz, 2H), 7.57 (s, 1H), 7.16 (s, 1H), 6.92 (d, *J* = 18.9 Hz, 1H), 5.20 (d, *J* = 18.9 Hz, 1H), 1.58 (s, 9H), -9.13 (s, 1.50 H). (H_2O@Compound **4**)

^{13}C NMR (126 MHz, d4-*o*DCB) δ 193.20, 169.20, 151.59, 150.99, 149.70, 149.66, 149.23, 149.04, 149.01, 148.55, 148.52, 148.43, 148.31, 147.89, 147.64, 147.41, 147.29, 146.76, 146.47, 146.36, 145.85, 145.42, 145.31, 144.89, 144.72, 144.22, 143.74, 143.43, 142.92, 142.73, 142.44, 142.21, 141.80, 141.78, 141.53, 141.47, 141.45, 141.29, 141.26, 140.99, 140.79, 140.27, 139.79, 138.88, 138.81, 138.60, 138.12, 136.47, 135.49, 135.48, 135.40, 135.00, 134.77, 125.73, 120.12, 80.00 (CH), 78.72 (CH), 53.03 (CH_2), 33.97 (C), 30.85 ($(CH_3)_3$). (Some signals of carbon on fullerene skeleton could not be assigned because of disturbance of solvent peaks.)
ESI-FT-ICR-HRMS-Positive $C_{69}H_{20}NO_4$ ($M + H^+$) calculated 926.1422, found 926.1387.
ESI-FT-ICR-HRMS-Positive $C_{69}H_{19}NNaO_4$ ($M + Na^+$) calculated 948.1168, found 948.1201.
ESI-FT-ICR-HRMS-Positive $C_{69}H_{21}NNaO_5$ ($M + Na^+ + H_2O$) calculated 966.1301, found 966.1312.

Crystals of compound **4** suitable for single crystal X-ray diffraction were obtained from slow evaporation in d4-*o*DCB. Crystal Data for $C_{6.21}H_{2.28}C_{l0.48}N_{0.07}O_{0.28}S$ (M =99.33 g/mol): triclinic, space group P-1 (no. 2), a = 9.9983(2) Å, b = 16.3521(4) Å, c = 19.4651(5) Å, α = 102.1630(10)°, β = 90.8690(10)°, γ = 105.0910(10)°, V = 2995.41(12) $Å^3$, Z = 29, T = 100(2) K, μ(synchrotron) = 0.320 mm^{-1}, D_{calc} = 1.597 g/cm^3, 38088 reflections measured (2.428° $\leqslant 2\theta \leqslant$ 46.33°), 9868 unique (R_{int} = 0.0241, R_{sigma} = 0.0214) which were used in all calculations. The final R_1 was 0.0545 ($I > 2\sigma(I)$) and wR_2 was 0.1595 (all data).
CCDC 1882632 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Preparation of Compound 5:



Compound **4** (29.7 mg, 0.032 mmol) was desolved in 15 mL $CHCl_3$, and then Et_3SiH (52 μL, 0.33 mmol) and $B(C_6F_5)_3$ (8.1 mg, 0.016 mmol) were added into the reaction vessel. The resulting solution was stirred at room temperature for 6 hours. Then the solution was quenched by 15 mL water. The organic layer was separated, dried by anhydrous Na_2SO_4 and concentrated in vacuo. The residue was dissolved in CH_2Cl_2, and then chromatographed on a silica gel column eluting with CH_2Cl_2 to give a red band as compound **5** (17.1 mg, 0.018 mmol, 57.6 %).

Characterization data for 5:

^1H NMR (500 MHz, $CDCl_3$) δ 9.64 (s, 1H), 9.02 (d, J = 3.5 Hz, 1H), 8.43 (s, 1H), 7.87 (d, J = 8.6 Hz, 2H), 7.76 (s, 1H), 7.59 (overlapped, J = 8.5 Hz, 3H), 7.55 (s, 1H), 7.03 (d, J = 18.7 Hz, 1H), 4.85 (d, J = 18.7 Hz, 1H), 1.44 (s, 9H).

^1H NMR (400 MHz, d4-*o*DCB) δ 9.84 (s, 1H), 9.18 (d, J = 5.0 Hz, 1H), 8.94 (s, 1H), 8.13 (d, J = 8.5 Hz, 2H), 7.76 (s, 1H), 7.69 (overlapped, J = 8.5 Hz, 3H), 7.55 (s, 1H), 7.11 (overlapped, 1H), 4.84 (d, J = 18.7 Hz, 1H), 1.56 (s, 9H), -9.30 (s, 1.7 H). (H_2O@Compound **5**)

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.74, 150.81, 150.75, 150.56, 150.45, 150.35, 150.32, 149.95, 149.50, 149.42, 149.26, 149.07, 149.06, 148.18, 147.94, 147.45, 147.38, 146.98, 146.92, 146.78, 146.19, 146.05, 146.00, 145.84, 145.28, 145.05, 144.67, 144.01, 144.00, 143.89, 143.87, 143.49, 142.65, 142.49, 142.28, 141.93, 141.45, 141.35, 140.86, 140.85, 140.76, 140.70, 140.64, 140.44, 140.32, 139.85, 139.73, 139.67, 139.53, 136.45, 136.17, 135.53, 133.24, 131.48, 131.09, 127.12, 126.94, 126.50, 121.28, 81.26 (CH), 80.97 (CH), 80.85 (CH), 56.10 (CH_2), 34.69 (C), 31.47 ($(CH_3)_3$).

ESI-FT-ICR-HRMS-Positive $C_{69}H_{22}NO_4$ (M + H^+) calculated 928.1523, found 928.1543.

ESI-FT-ICR-HRMS-Positive $C_{69}H_{21}LiNO_4$ (M + Li^+) calculated 934.1631, found 934.1625.

ESI-FT-ICR-HRMS-Positive $C_{69}H_{23}NLiO_5$ (M + Li^+ + H_2O) calculated 952.1759, found 952.1731.

Crystals of compound **5•EtOH** suitable for single crystal X-ray diffraction were obtained from slow diffusion in a two phases system of CS_2 and EtOH. Crystal Data for $C_{143}H_{54}N_2O_{10}S_2$ (M = 2024.00 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 10.4701(3) Å, b = 25.0970(11) Å, c = 16.2566(6) Å, β = 91.218(3)°, V = 4270.8(3) Å^3, Z = 2, T = 179.98(11) K, μ(MoKα) = 0.145 mm^{-1}, D_{calc} = 1.574 g/cm^3, 31081 reflections measured (4.216° ≤ 2θ ≤ 54.97°), 9749 unique (R_{int} = 0.0313, R_{sigma} = 0.0400) which were used in all calculations. The final R_1 was 0.0613 ($I > 2\sigma(I)$) and wR_2 was 0.1617 (all data).

CCDC 1882633 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Crystals of compound **H_2O@5•EtOH** suitable for single crystal X-ray diffraction were obtained from slow diffusion in a two phases system of CS_2 and EtOH. Crystal Data for $C_{143}H_{57.4}N_2O_{11.7}S_2$ (M =2054.63 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 10.4595(4) Å, b = 25.0584(10) Å, c = 16.2556(7) Å, β = 91.316(4)°, V =

4259.4(3) Å^3, $Z = 2$, $T = 179.99(10)$ K, μ(Mo Kα) = 0.149 mm^{-1}, $D_{calc} = 1.602$ g/cm^3, 31983 reflections measured (4.104° ⩽ 2θ ⩽ 54.968°), 9738 unique ($R_{int} = 0.0554$, $R_{sigma} = 0.0597$) which were used in all calculations. The final R_1 was 0.0681 ($I > 2\sigma(I)$) and wR_2 was 0.1679 (all data).

CCDC 1882635 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

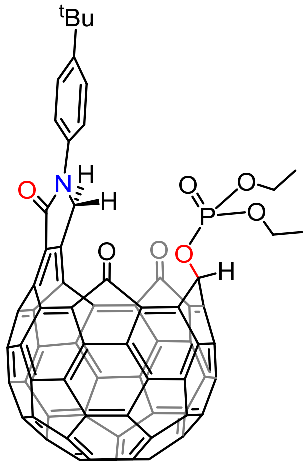
Crystals of compound **H_2O@5•Nopol** suitable for single crystal X-ray diffraction were obtained from slow diffusion in a two phases system of CS_2 and Nopol. Crystal Data for $C_{81}H_{42.7}NO_{5.85}S_2$ (M = 1187.58 g/mol): triclinic, space group P-1 (no. 2), $a = 10.43660(10)$ Å, $b = 16.3952(3)$ Å, $c = 16.8240(3)$ Å, $\alpha = 110.8690(10)°$, $\beta = 99.0190(10)°$, $\gamma = 100.6190(10)°$, $V = 2565.14(7)$ Å^3, $Z = 2$, $T = 180.00(10)$ K, μ (Mo Kα) = 0.174 mm^{-1}, $D_{calc} = 1.538$ g/cm^3, 27699 reflections measured (4.092° ⩽ 2θ ⩽ 50.056°), 9056 unique ($R_{int} = 0.0222$, $R_{sigma} = 0.0267$) which were used in all calculations. The final R_1 was 0.0773 ($I > 2\sigma(I)$) and wR_2 was 0.1970 (all data).

CCDC 1882636 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Crystals of compound **H_2O@5** suitable for single crystal X-ray diffraction were obtained from slow diffusion in a two phases system of CS_2 and CH_3CN. Crystal Data for $C_{70}H_{22.75}NO_{4.875}S_2$ (M = 1019.76 g/mol): monoclinic, space group Cc (no. 9), $a = 14.4203(2)$ Å, $b = 27.3088(4)$ Å, $c = 10.35690(10)$ Å, $\beta = 94.1820(10)°$, $V = 4067.70(9)$ Å^3, $Z = 4$, $T = 180.00(10)$ K, μ(Mo Kα) = 0.203 mm^{-1}, $D_{calc} = 1.665$ g/cm^3, 26233 reflections measured (4.916° ⩽ 2θ ⩽ 54.962°), 8361 unique ($R_{int} = 0.0175$, $R_{sigma} = 0.0192$) which were used in all calculations. The final R_1 was 0.0433 ($I > 2\sigma(I)$) and wR_2 was 0.1202 (all data).

CCDC 1882638 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Preparation of Compound 6:



Compound **2** (54.6 mg, 0.059 mmol) was dissolved in 50 mL $CHCl_3$, and then $P(OEt)_3$ (51 μL, 0.30 mmol) were added into the reaction vessel. The reaction was terminated upon confirmation of complete conversion of compound **2** as indicated by TLC (about 20 minutes). The solution was directly chromatographed on a silica gel column eluting with toluene/ethyl acetate (50:1) to remove impurities and toluene/ ethyl acetate (10:1) to give a black band as compound **7** (44.3 mg, 0.042 mmol, 70.6%).

Characterization data for 6:

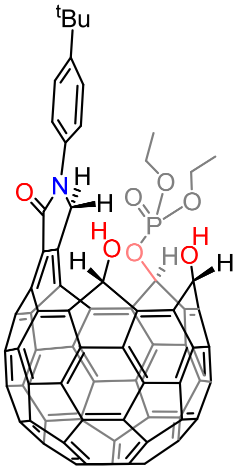
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 12.8 Hz, 1H), 8.11 (d, *J* = 8.7 Hz, 2H), 7.55 (d, *J* = 8.7 Hz, 2H), 6.70 (d, *J* = 18.5 Hz, 1H), 5.10 (d, *J* = 18.5 Hz, 1H), 4.69 – 4.55 (m, 2H), 4.52 – 4.43 (m, 2H), 1.47 – 1.45 (m, 3H), 1.42 (s, 9H), 1.28 – 1.25 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.53, 186.80, 164.97, 151.89, 151.16, 150.58, 150.49, 150.03, 149.98, 149.56, 149.15, 148.95, 148.81, 148.12, 147.43, 147.00, 146.93, 146.75, 146.57, 146.44, 146.18, 146.17, 146.03, 145.96, 145.94, 145.19, 144.70, 144.63, 143.91, 143.79, 143.55, 143.19, 143.10, 142.91, 142.82, 142.80, 142.72, 142.60, 142.39, 142.07, 141.68, 141.03, 140.40, 140.33, 139.98, 139.94, 138.28, 137.55, 137.35, 136.93, 136.53, 136.28, 135.93, 135.81, 132.27, 129.39, 127.96, 126.92, 125.73, 119.93, 82.69 (CH), 65.89 (OCH_2), 65.84 (OCH_2), 65.05 (OCH_2), 65.00 (OCH_2), 52.80 (CH_2), 34.65 (C), 31.62 ($(CH_3)_3$), 16.61 (CH_3), 16.56 (CH_3), 16.42 (CH_3), 16.37 (CH_3).

^{31}P NMR (202 MHz, $CDCl_3$) δ 1.24.

ESI-FT-ICR-HRMS-Positive $C_{73}H_{27}NO_7P$ ($M + H^+$) calculated 1060.1492, found 1060.1520.

Preparation of Compound 7:



Compound **4** (31.9 mg, 0.034 mmol) was dissolved in 30 mL $CHCl_3$, and then $P(OEt)_3$ (1.8 mL, 10.4 mmol) and HOAc (0.5 mL) were added into the reaction vessel. The resulting solution was stirred at room temperature overnight. The reaction was terminated upon confirmation of complete conversion of compound **4** as indicated by TLC (about 10 hours). The solution was concentrated in vacuo and then dissolved in

CS_2, chromatographed on a silica gel column eluting with CS_2/ethyl acetate (50 : 1) to remove impurities. Elution with CS_2/ ethyl acetate (10 : 1) gave a red band as compound **7** (22.5 mg, 0.021 mmol, 61.7 %).

Characterization data for 7:

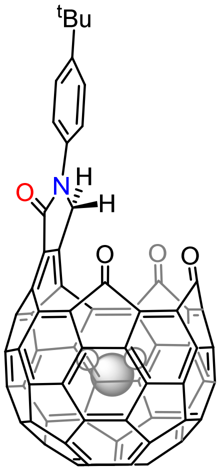
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.5 Hz, 2H), 7.59 (overlapped, *J* = 8.2 Hz, 3H), 6.79 (s, 1H), 6.69 (s, 1H), 5.99 (d, *J* = 19.1 Hz, 1H), 4.86 (d, *J* = 28.2 Hz, 1H), 4.57 – 4.46 (m, 2H), 4.43 – 4.32 (m, 2H), 1.51 (t, *J* = 7.0 Hz, 3H), 1.42 (s, 9H), 1.38 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.84, 154.15, 151.94, 151.58, 151.21, 151.11, 151.10, 150.20, 150.18, 150.03, 149.88, 149.72, 149.63, 149.60, 149.57, 149.00, 148.68, 148.25, 146.92, 146.82, 146.72, 146.36, 146.34, 146.29, 145.90, 145.81, 145.15, 144.19, 143.88, 143.84, 143.82, 143.63, 143.58, 143.43, 143.26, 142.73, 142.67, 142.32, 142.27, 141.79, 141.76, 141.62, 140.13, 139.92, 139.53, 139.51, 138.68, 138.53, 137.66, 136.30, 136.26, 135.57, 135.04, 134.35, 132.47, 132.03, 130.15, 126.55, 121.43, 80.00 (CH), 79.03 (CH), 67.37 (OCH_2), 67.13 (OCH_2), 66.30 (OCH_2), 66.19 (OCH_2), 54.35 (CH_2), 53.07 (CH), 34.83 (C), 31.55 ($(CH_3)_3$), 16.88 (CH_3), 16.83 (CH_3), 16.63 (CH_3), 16.58 (CH_3).

^{31}P NMR (202 MHz, $CDCl_3$) δ 22.31.

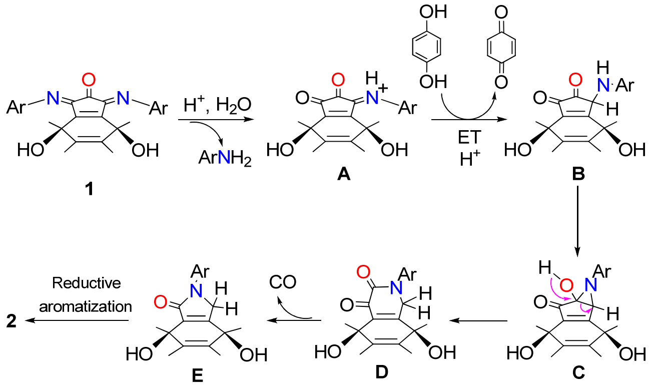
ESI-FT-ICR-HRMS-Positive $C_{73}H_{31}NO_7P$ ($M + H^+$) calculated 1064.1825, found 1064.1833.

Preparation of $H_2O@2$:

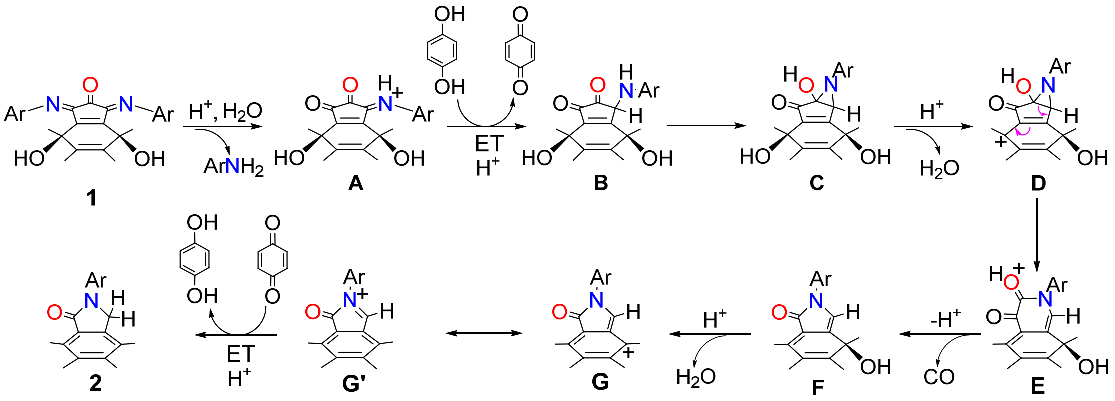


Compound **2** (144.2 mg, 0.16 mmol) was dissolved in 30 mL *o*DCB, then 1 mL water was added into the reaction vessel. The resulting solution was stirred at 80°C for 12 hours. For ^{1}H NMR measurement, the sample was prepared by using *o*DCB-D_4 (0.6 mL) as the solvent for 5 mg sample and one drop of water. ^{1}H NMR showed the encapsulation ratio reached 58%.

Proposed mechanism for the formation of 2 from 1:

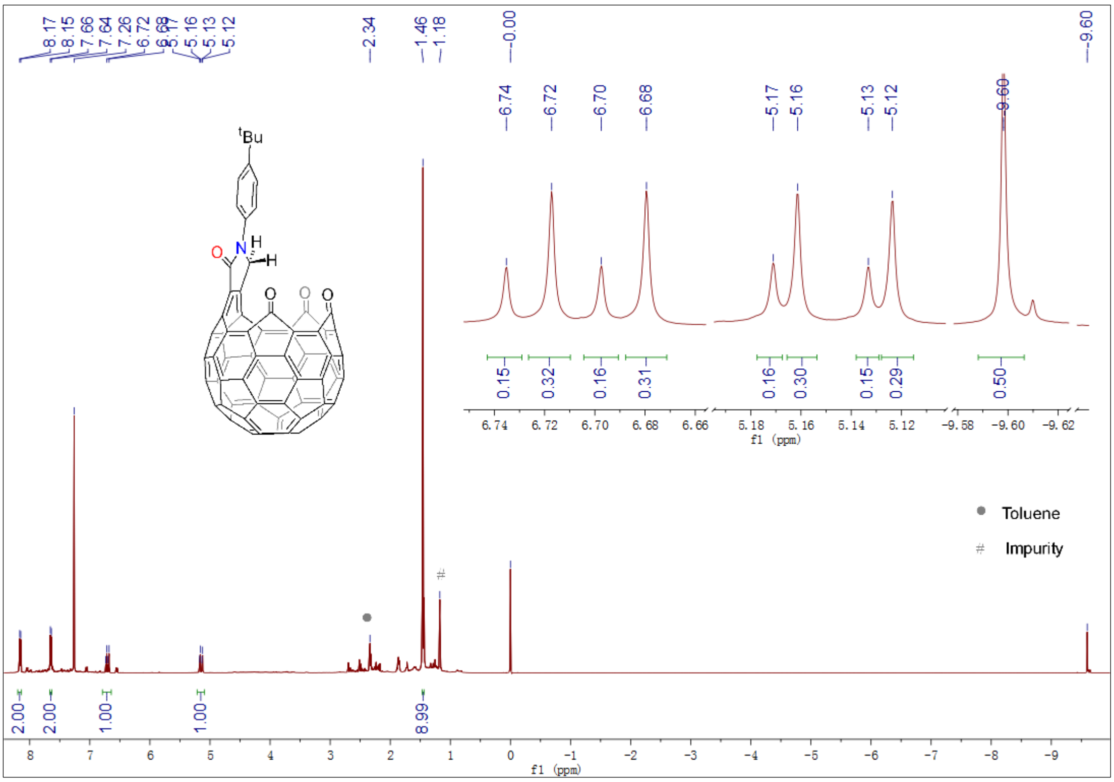


or

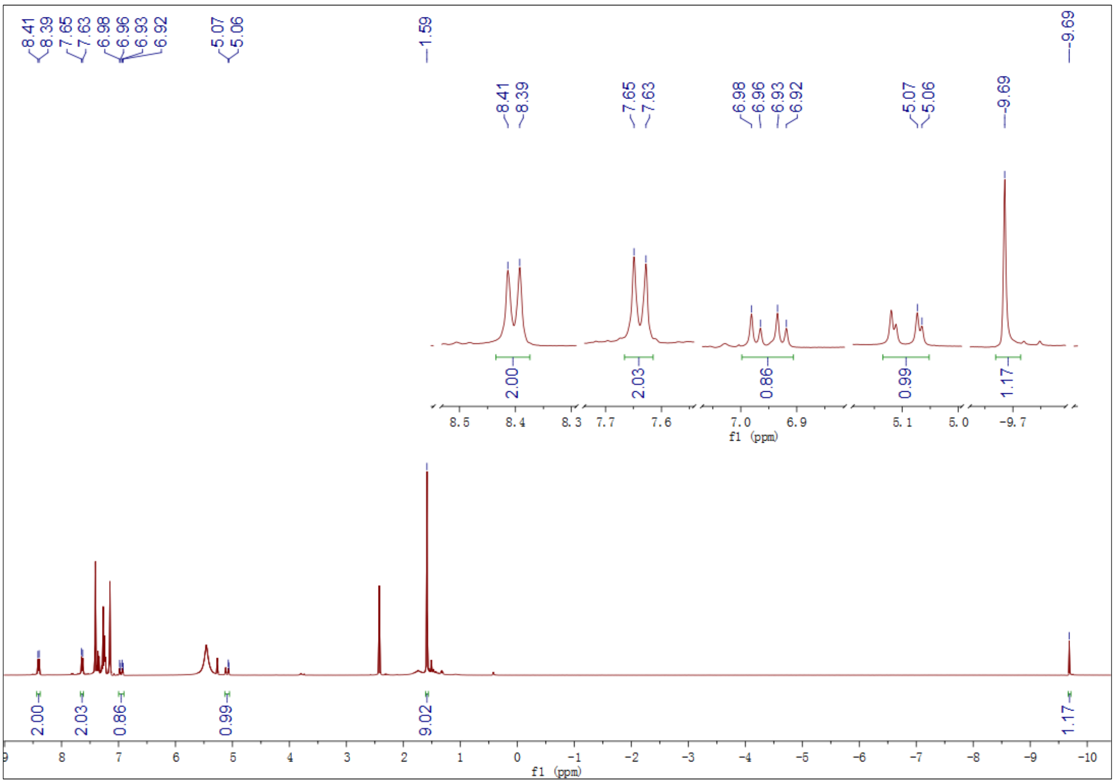


The conversion from **1** to **2** involved loss of two hydroxyl groups and a carbonyl group. The mechanism is quite complicated. The above Scheme shows two possible pathways. In the first pathway, the first step is the hydrolysis of one of the two imino groups to form **A** as originally designed. Due to the electron withdrawing effect of the newly formed carbonyl group, the second imino group was reduced into the anilinyl group in **B**. Addition of hydrophenone accelerated this reduction step. Without the added hydroquinone some unknown reducing reagents such as the small amount of aniline hydrolyzed from the first step may have acted as the reducing reagent. Then the amino nitrogen added to the carbonyl carbon to form an aminal intermediate **C**. Ring-opening rearrangement of **C** gave the methylene group in **D**. Decarbonylation from **D** to **E** involved ring contraction from a 6- to 5-menmbered ring. The final reductive aromatization step is analogous to other classical reactions. The aromatization step could have taken place in one of the earlier intermediates. The second pathway involved fullerene cation intermediates. The fullerene centered-cations are stablized by conjugation with the cage double bonds. Electron transfer from the hydroquinone is essential in the reduction processes. Other pathways are also possible. Detailed mechanism study remains to be carried out.

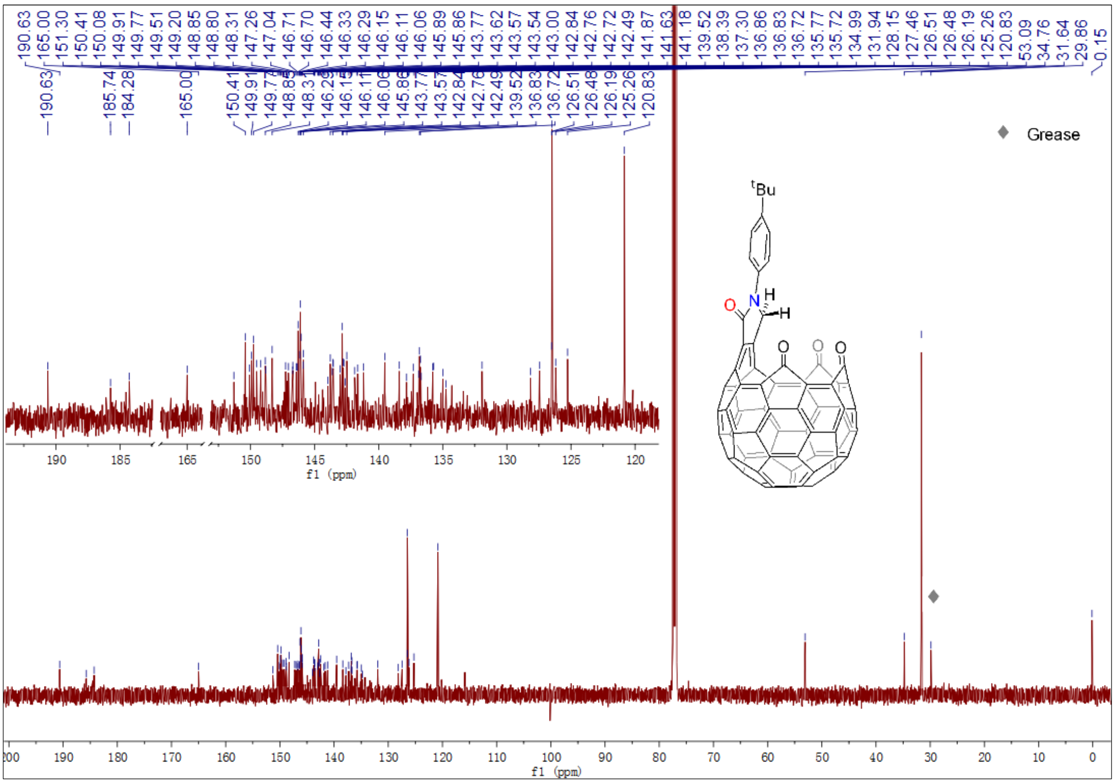
^{1}H NMR of Compound **H_2O@2** (25%) in $CDCl_3$



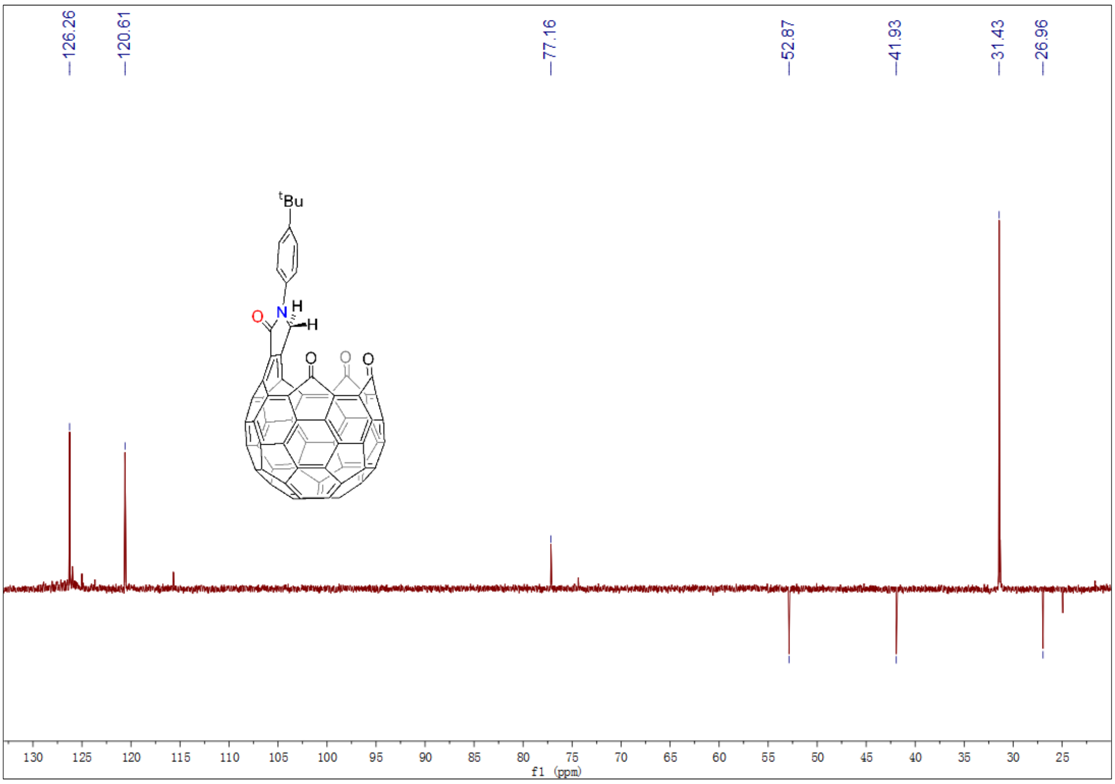
^{1}H NMR of Compound **H_2O@2** (58%) in $CDCl_3$



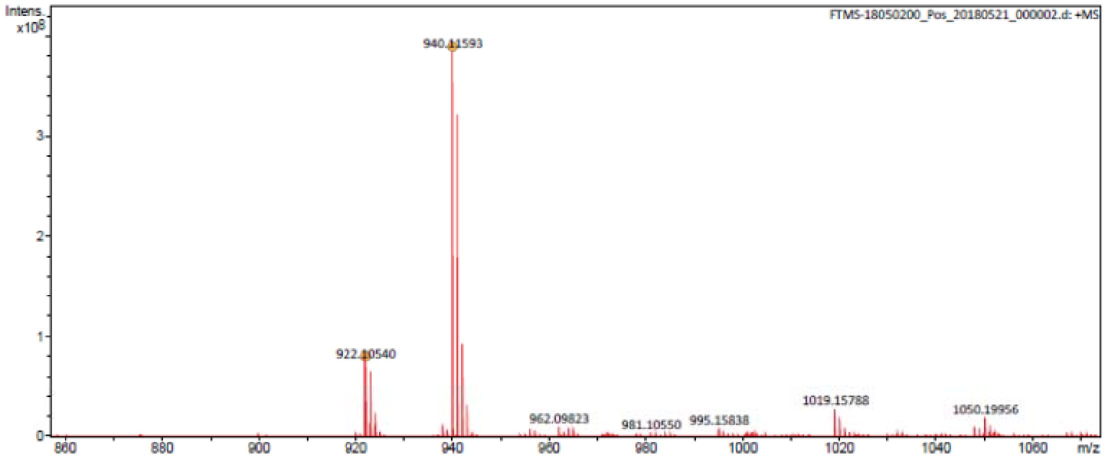
^{13}C NMR of Compound **2** in $CDCl_3$



DEPT of Compound **2** in $CDCl_3$

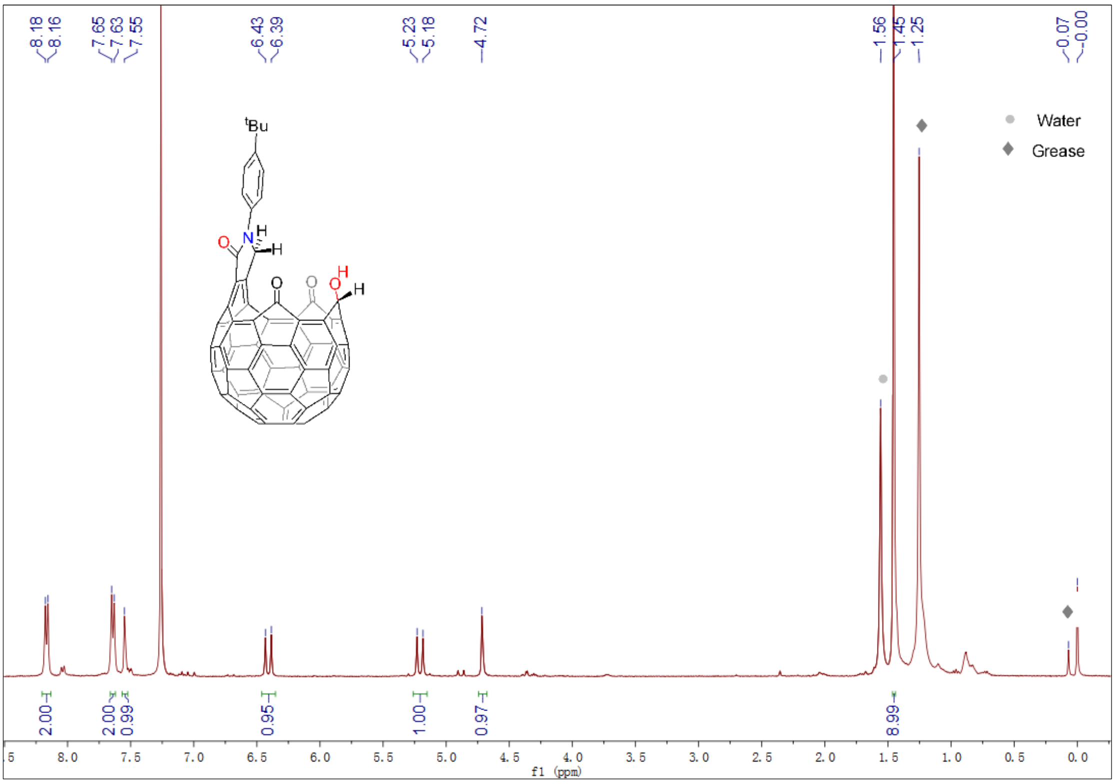


MS of Compound **2&H_2O@2**

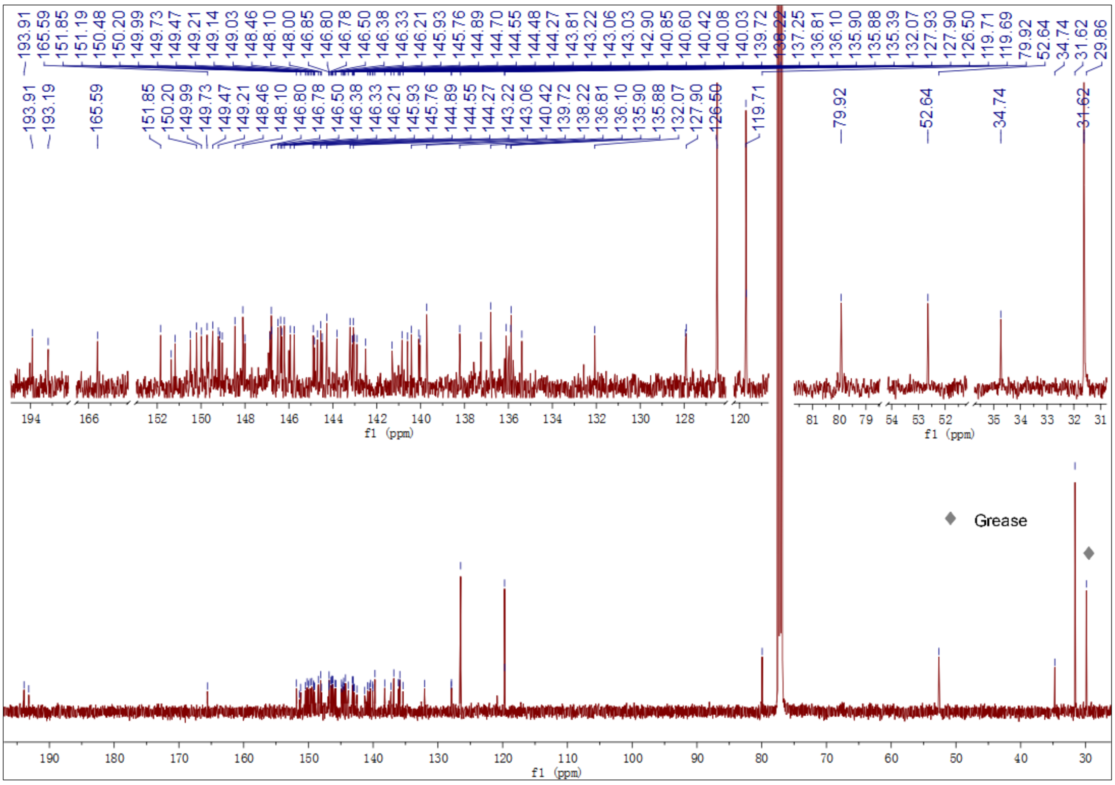


Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
922.105395	1	C69H16NO4	100.00	922.107384	2.2	-2.5	54.5	63.0	even	ok
940.115930	1	C69H18NO5	100.00	940.117949	2.1	-2.7	43.2	62.0	even	ok

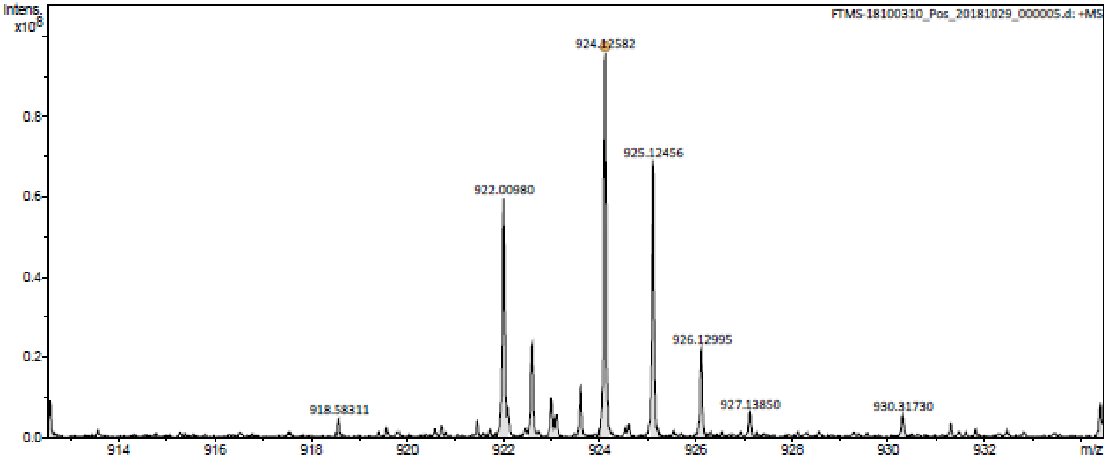
^{1}H NMR of Compound **3** in $CDCl_3$



^{13}C NMR of Compound **3** in $CDCl_3$

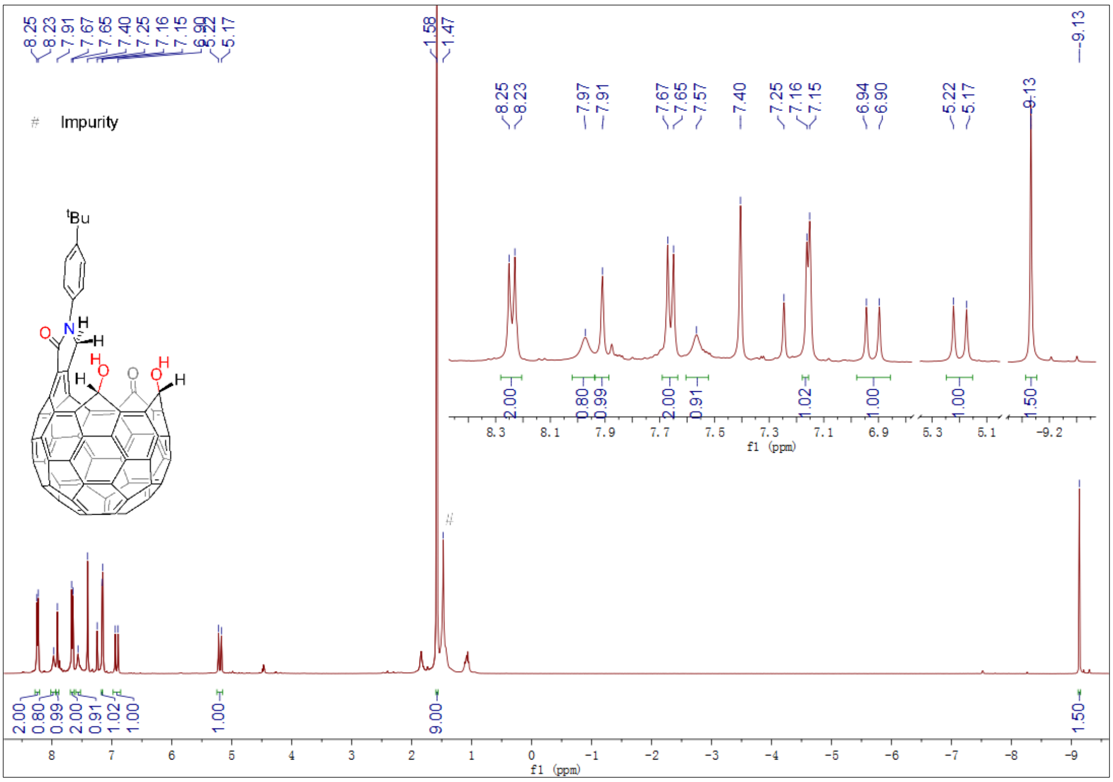


MS of Compound **3**

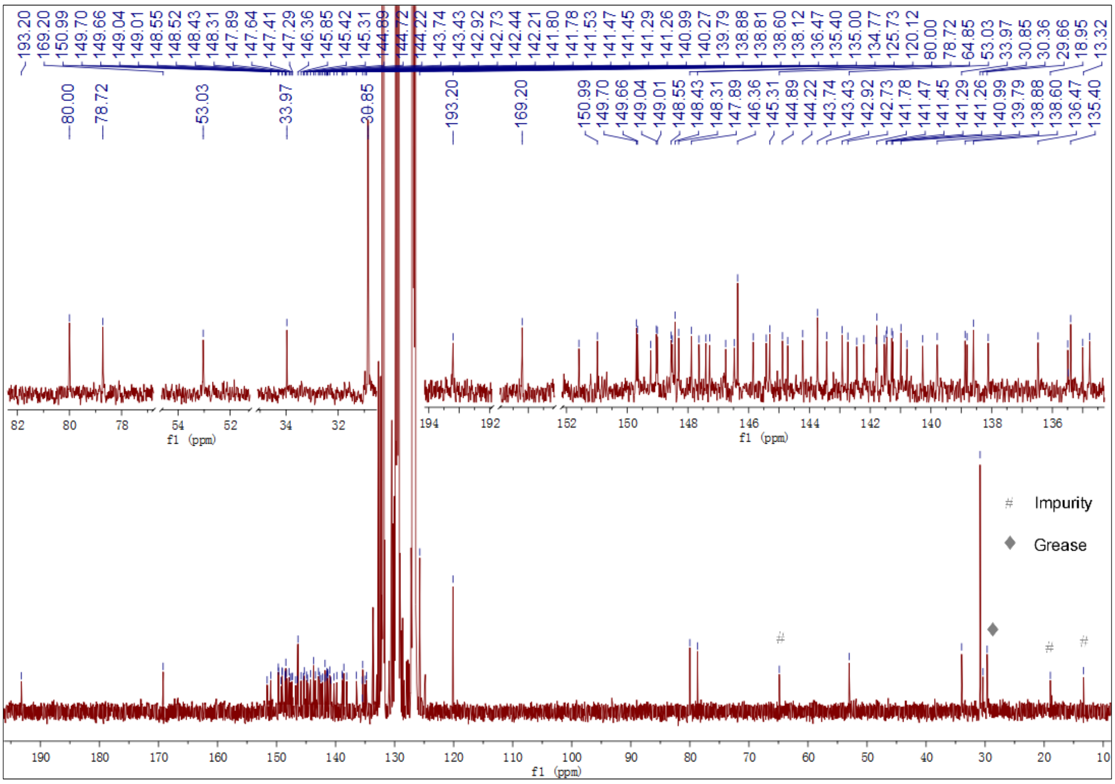


Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e$^-$ Conf	N-Rule
924.12582	1	C69H16NO4	100.00	924.12303	-3.02	-1.67	29.8	62.0	even	ok

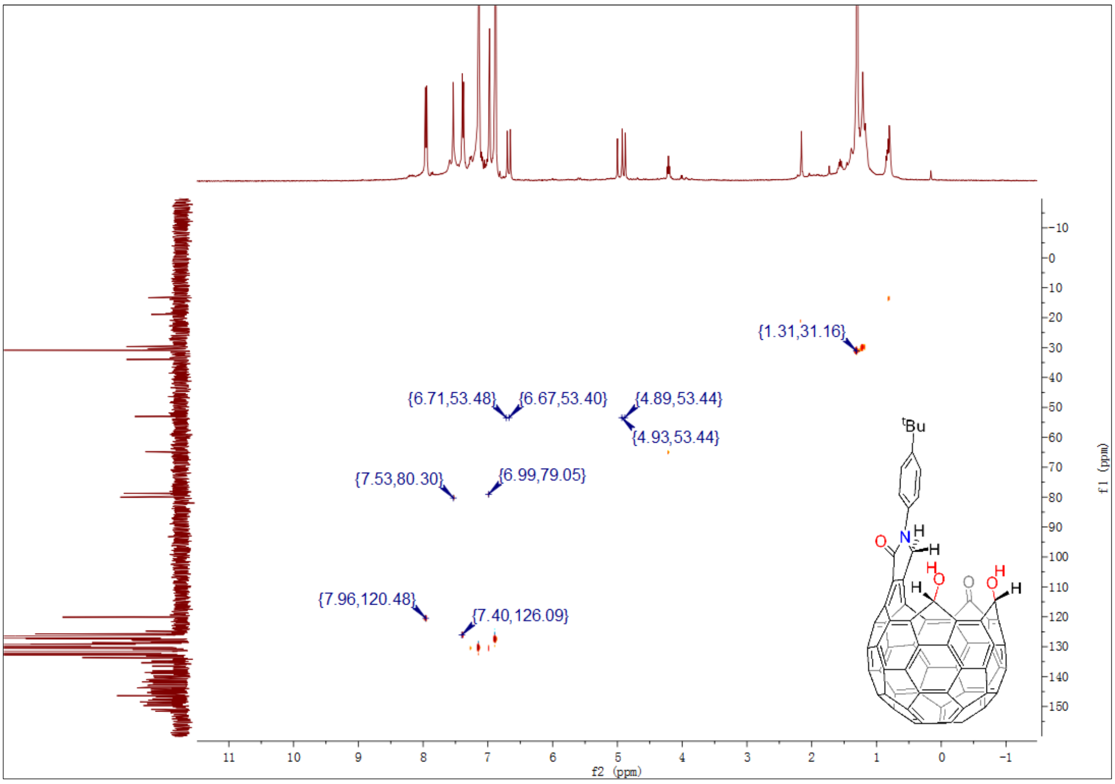
^{1}H NMR of Compound **H$_2$O@4** (75%) in d4-*o*DCB

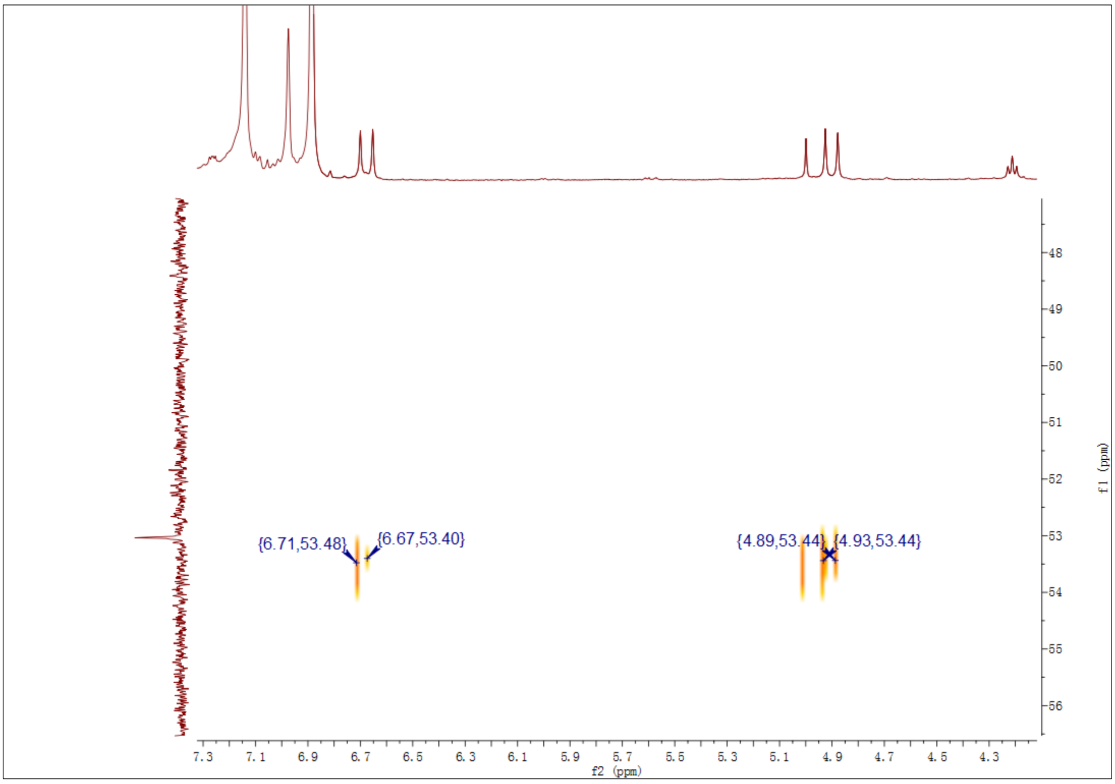


^{13}C NMR of Compound **4** in d4-*o*DCB

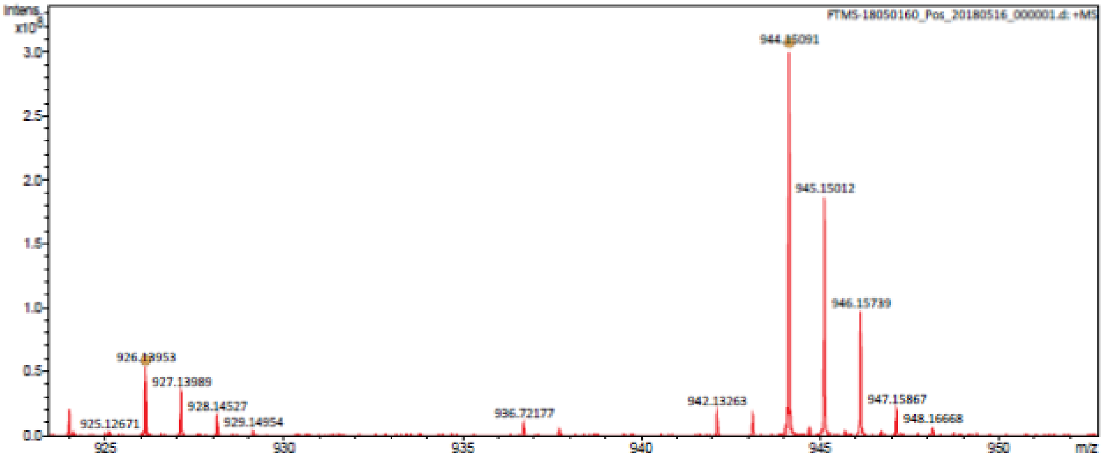


HSQC of Compound **4** in d4-*o*DCB



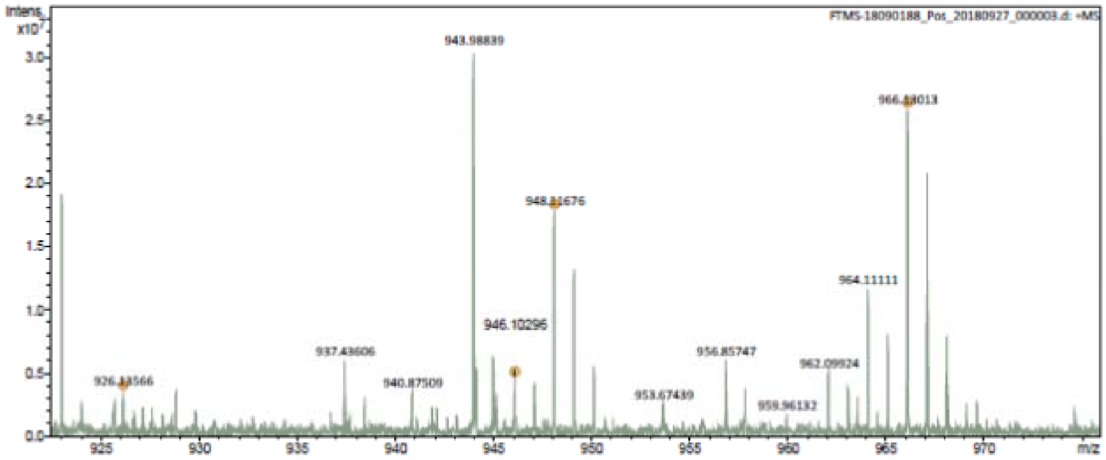


MS of Compound **4&H_2O@4 (H^+)**



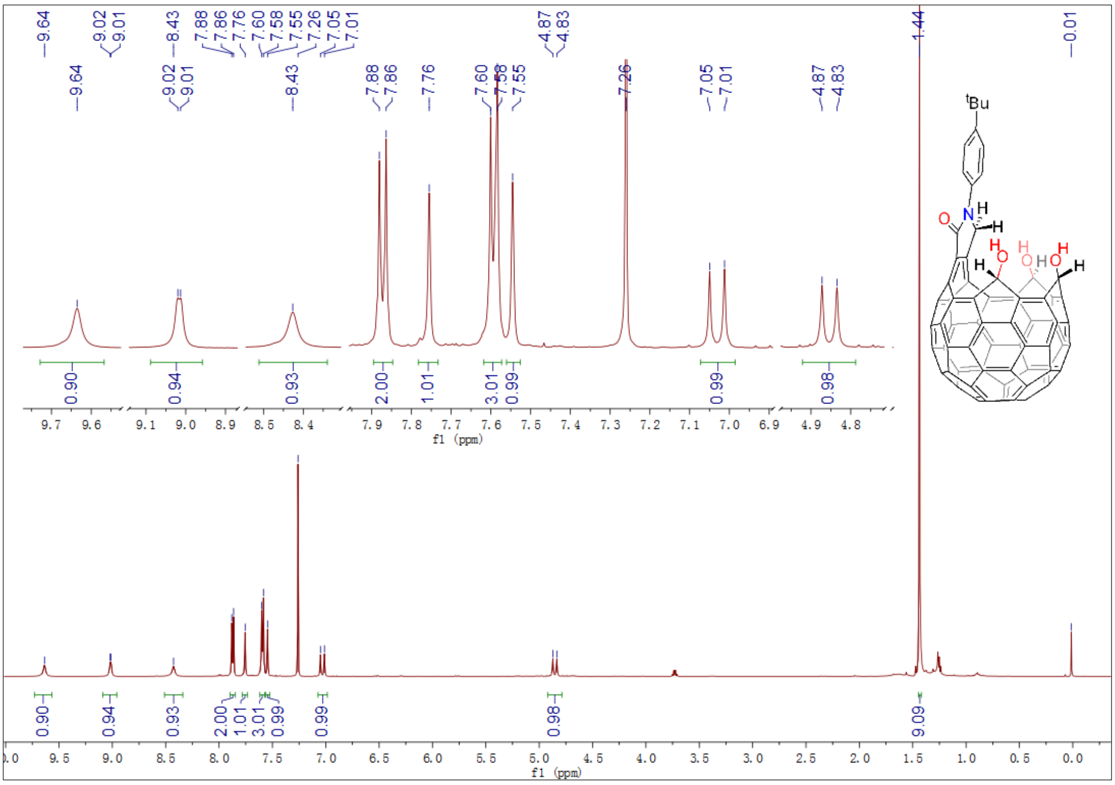
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
926.139526	1	C69H20NO4	100.00	926.138685	-0.9	0.1	47.0	61.0	even	ok
944.150909	1	C69H22NO5	100.00	944.149249	-1.8	-0.7	62.7	60.0	even	ok

MS of Compound **3&4&H_2O@4 (Na^+)**

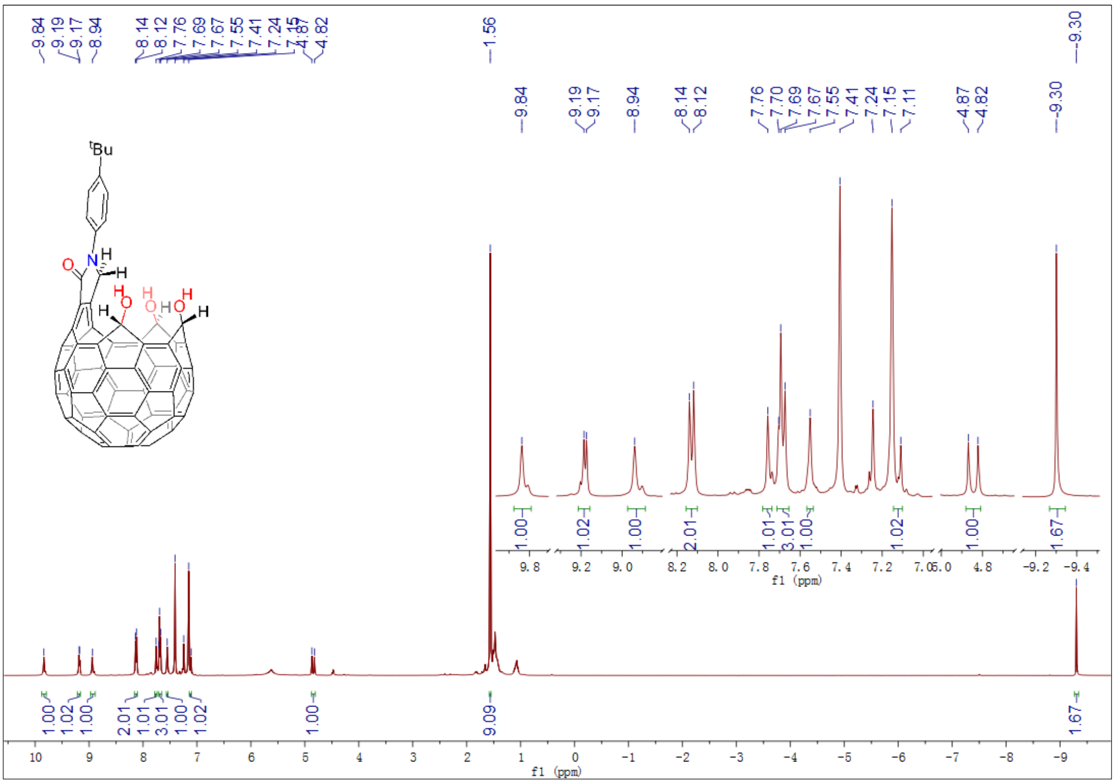


Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
926.13566	1	C69H20NO4	100.00	926.13868	3.27	1.42	102.1	61.0	even	ok
946.10296	1	C69H17NNaO4	100.00	946.10498	2.13	0.71	531.7	62.0	even	ok
948.11676	1	C69H19NNaO4	100.00	948.12063	4.08	2.59	14.0	61.0	even	ok
966.13013	1	C69H21NNaO5	100.00	966.13119	1.10	1.30	26.3	60.0	even	ok

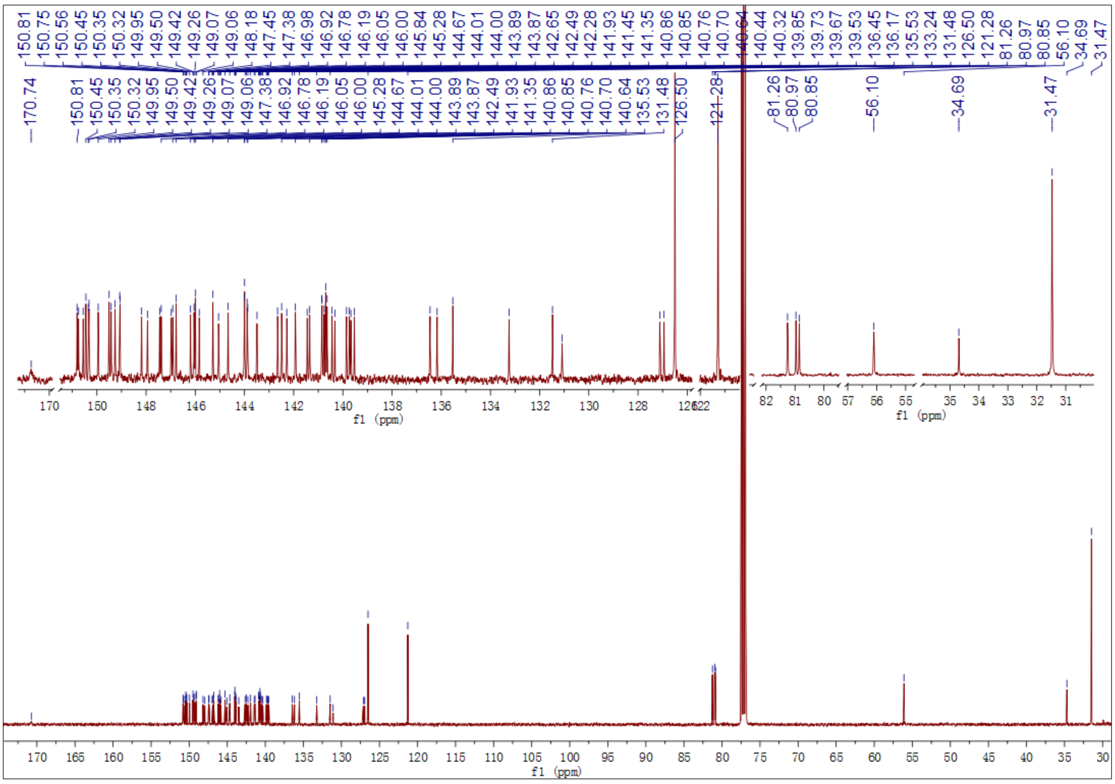
^{1}H NMR of Compound **5** in $CDCl_3$



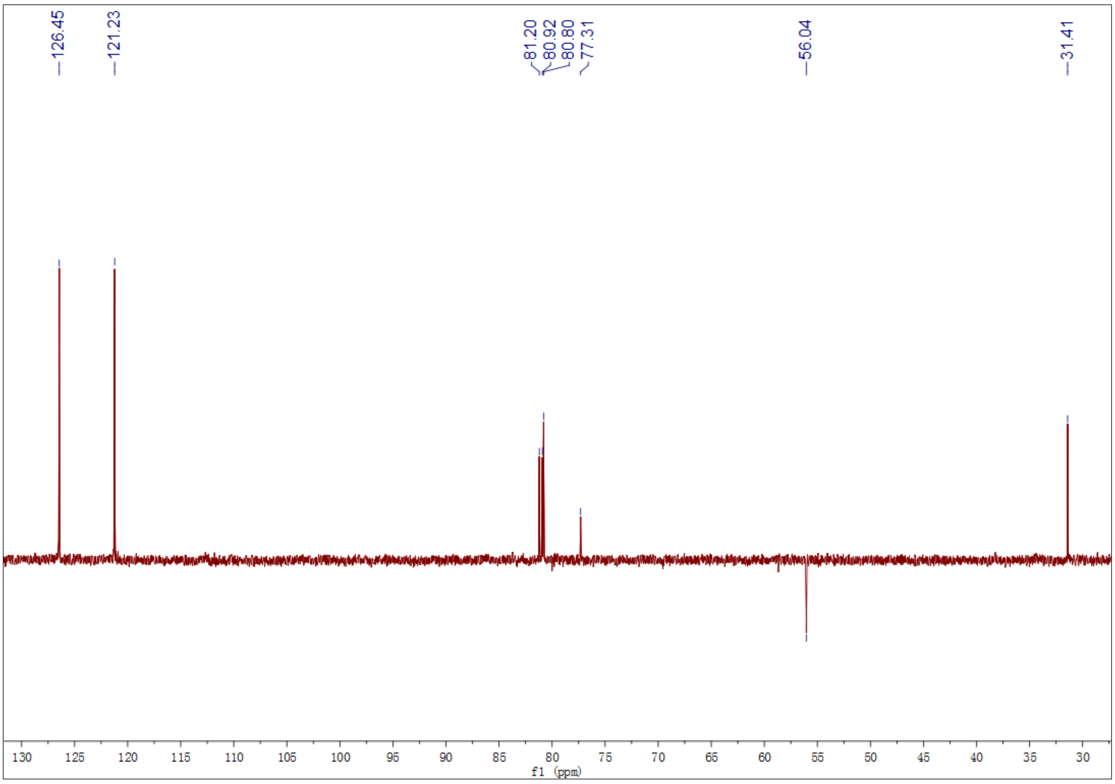
^{1}H NMR of Compound **H_2O@5** (83%) in d4-*o*DCB



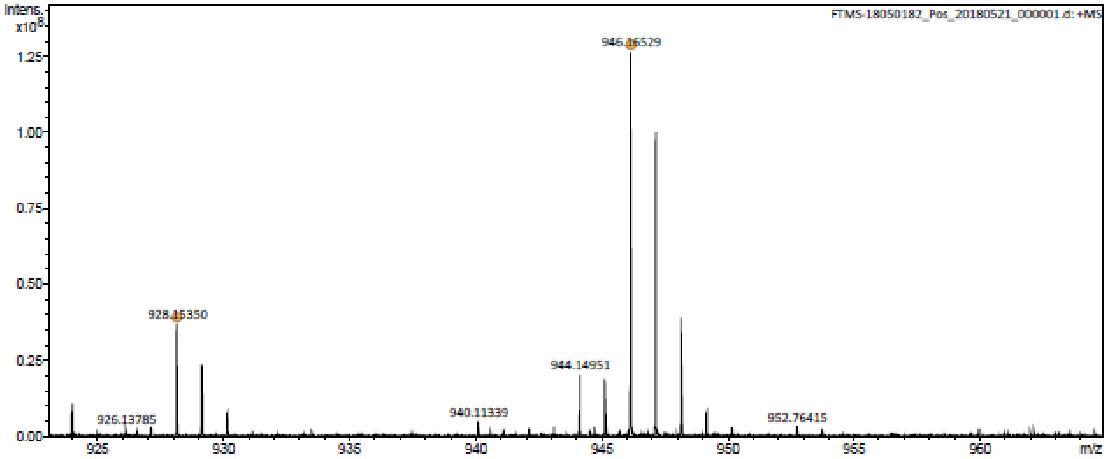
^{13}C NMR of Compound **5** in CDCl$_3$



DEPT of Compound **5** in CDCl$_3$

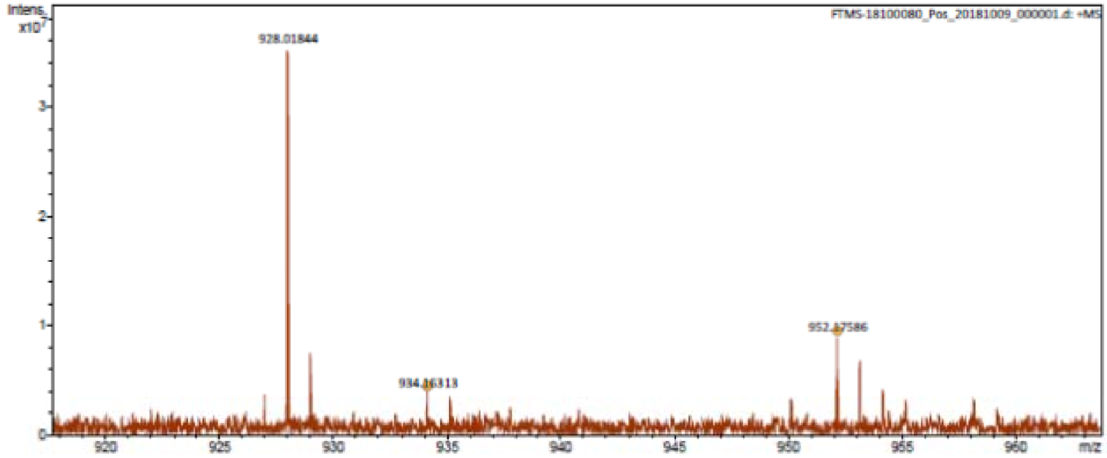


MS of Compound **5&H_2O@5 (H^+)**



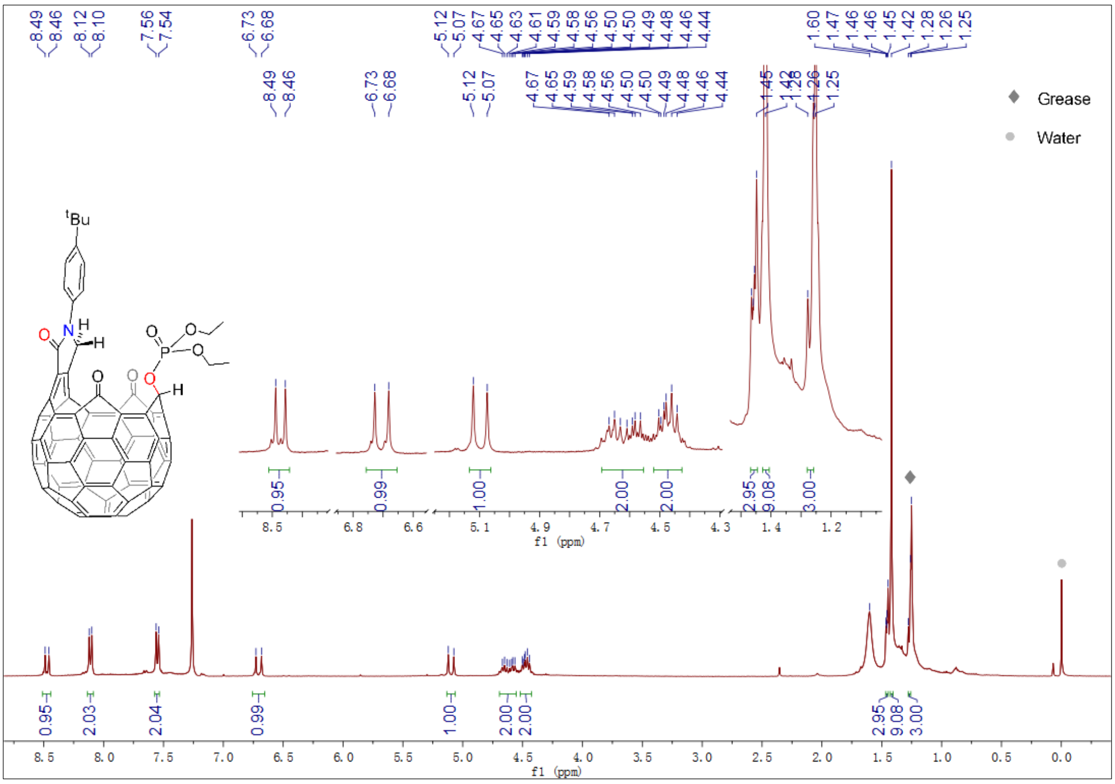
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
928.153496	1	C69H22NO4	100.00	928.154335	0.9	0.0	69.2	60.0	even	ok
946.165285	1	C69H24NO5	100.00	946.164899	-0.4	1.5	18.0	59.0	even	ok

MS of Compound **5&H_2O@5 (Li^+)**

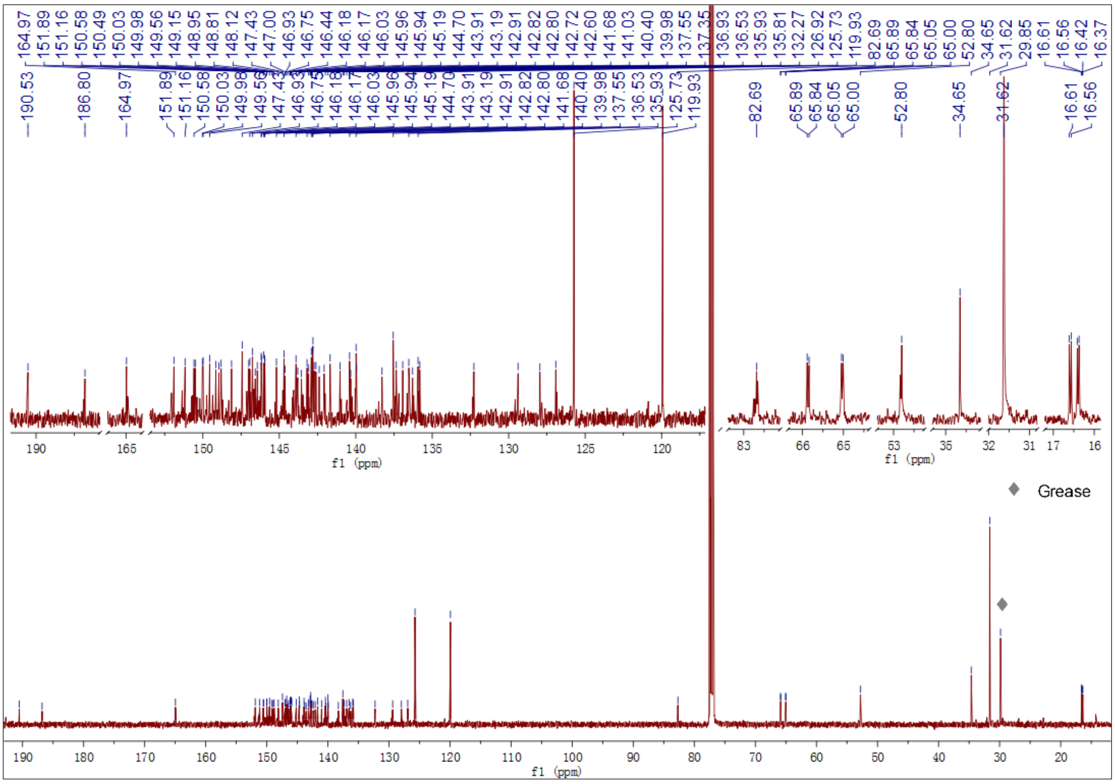


Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
934.16313	1	C69H21LiNO4	100.00	934.16251	-0.51	-0.15	n.a.	60.0	even	ok
952.17586	1	C69H23LiNO5	100.00	952.17308	-2.77	-1.39	89.2	59.0	even	ok

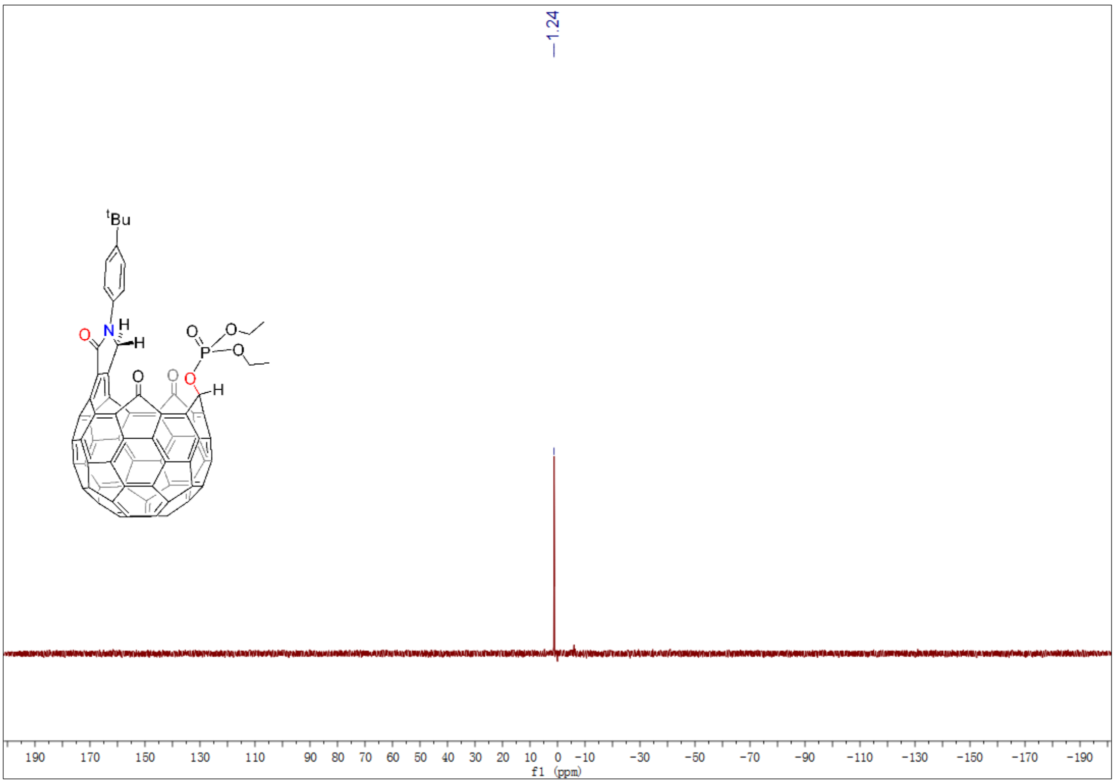
^{1}H NMR of Compound **6** in CDCl$_3$



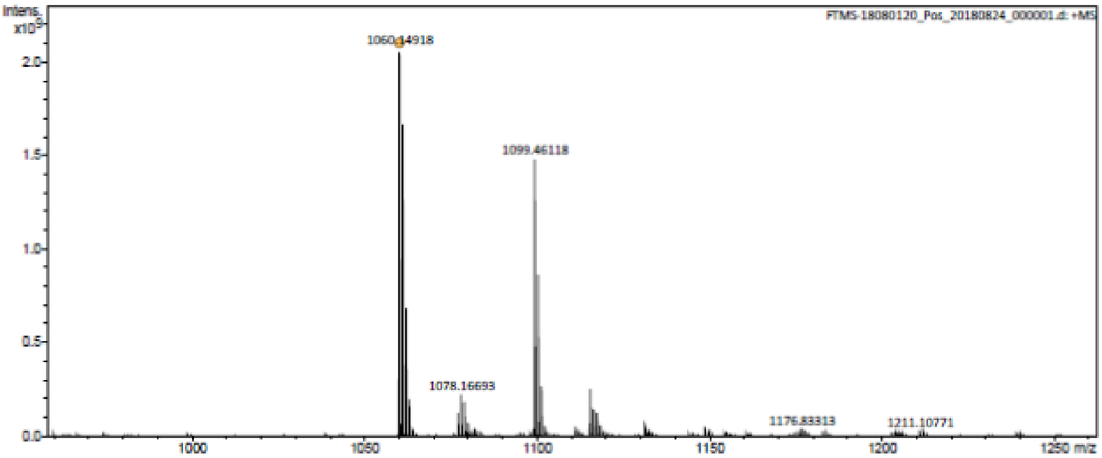
^{13}C NMR of Compound **6** in CDCl$_3$



^{31}P NMR of Compound **6** in $CDCl_3$

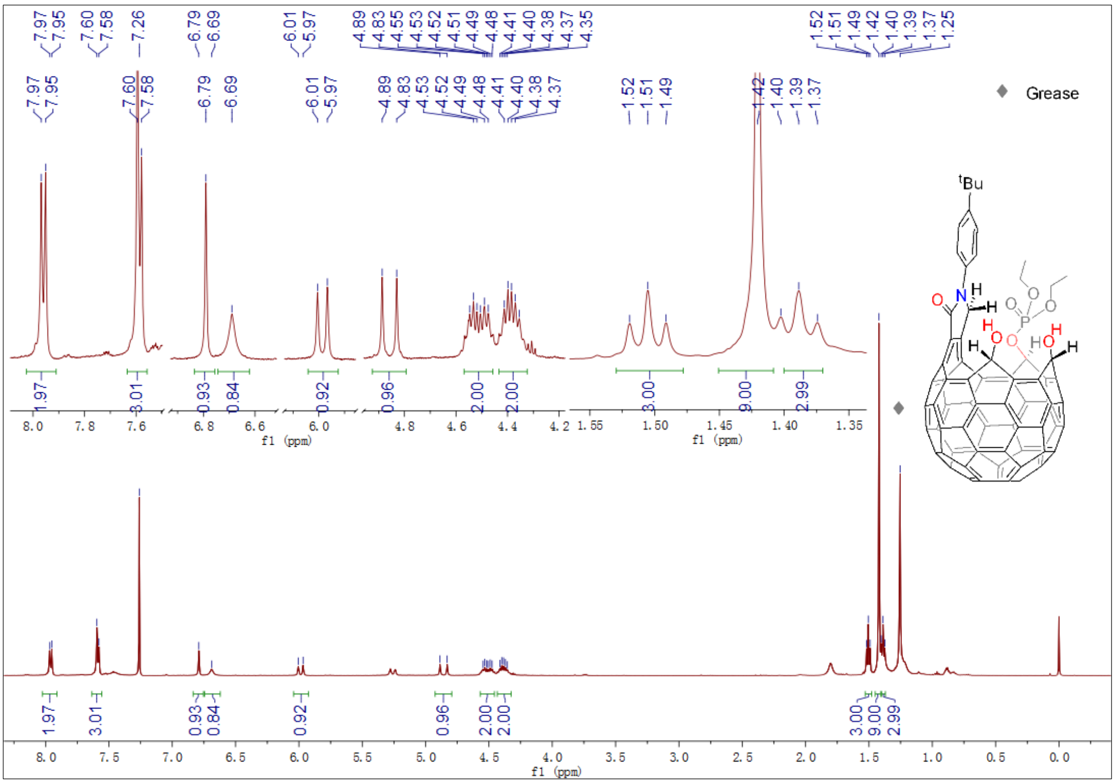


MS of Compound **6**

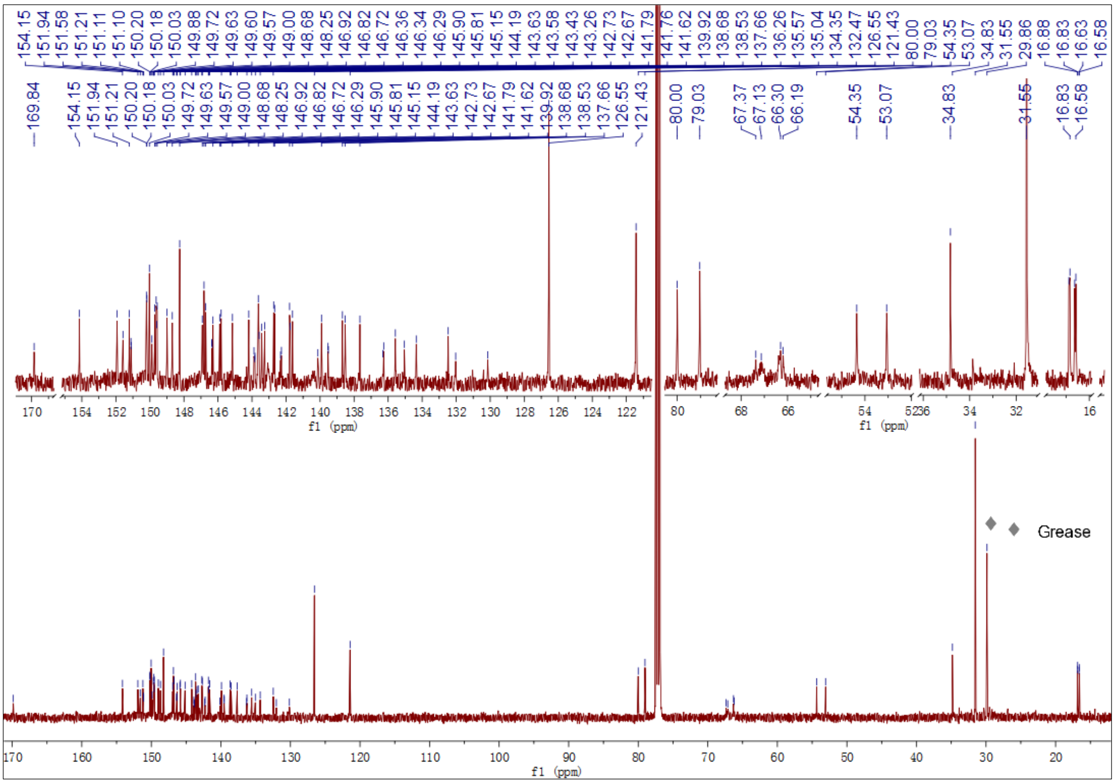


Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1060.149179	1	C73H27NO7P	100.00	1060.151965	2.6	0.8	2.6	62.0	even	ok

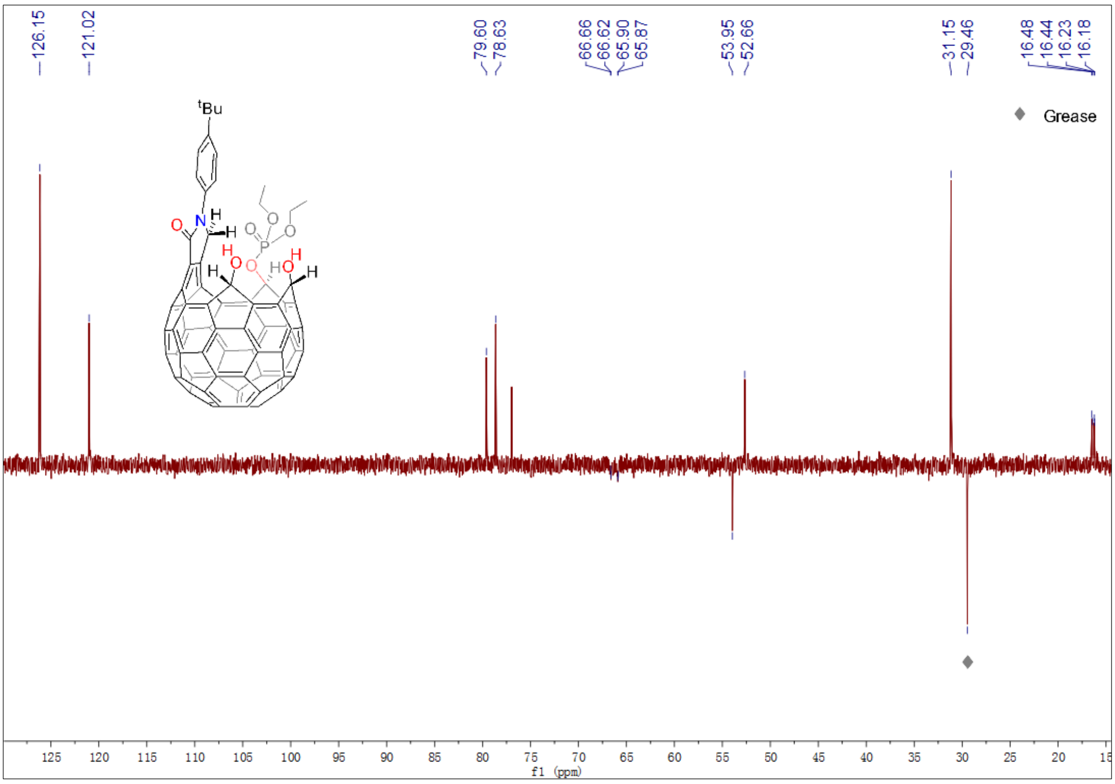
^{1}H NMR of Compound **7** in $CDCl_3$



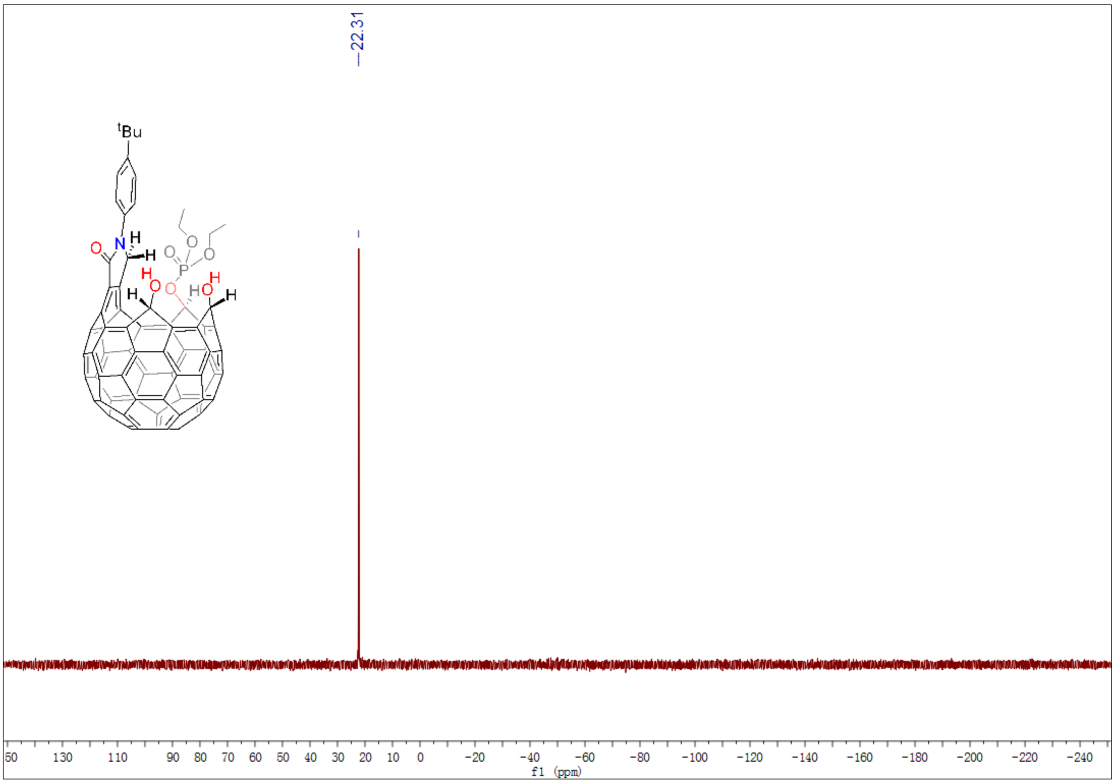
^{13}C NMR of Compound **7** in $CDCl_3$



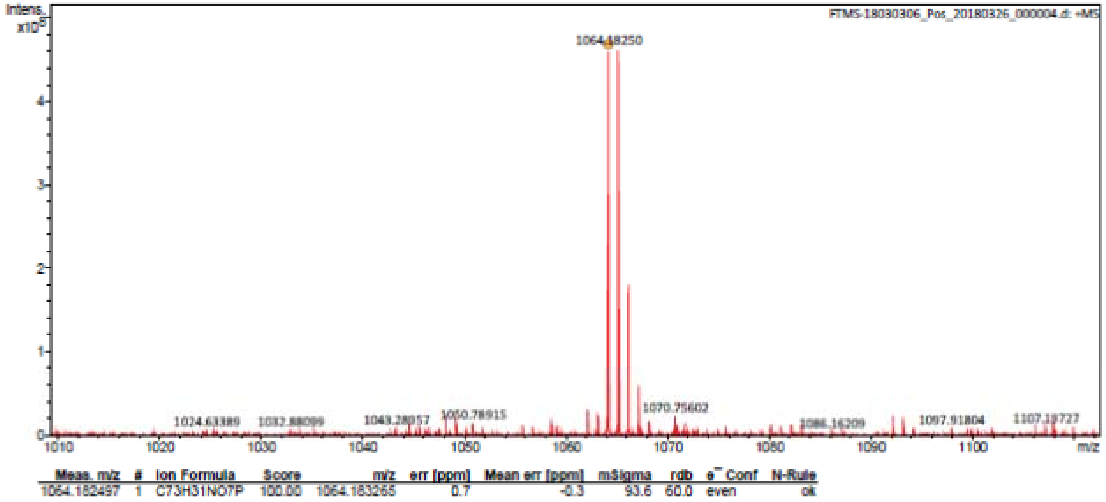
DEPT of Compound **7** in CDCl$_3$



^{31}P NMR of Compound **7** in CDCl$_3$

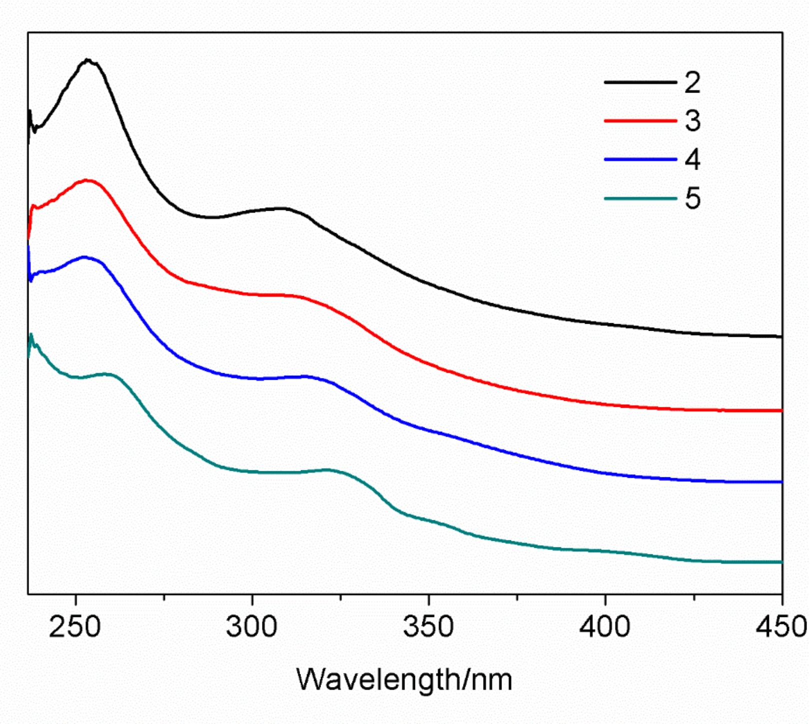


MS of Compound **7**

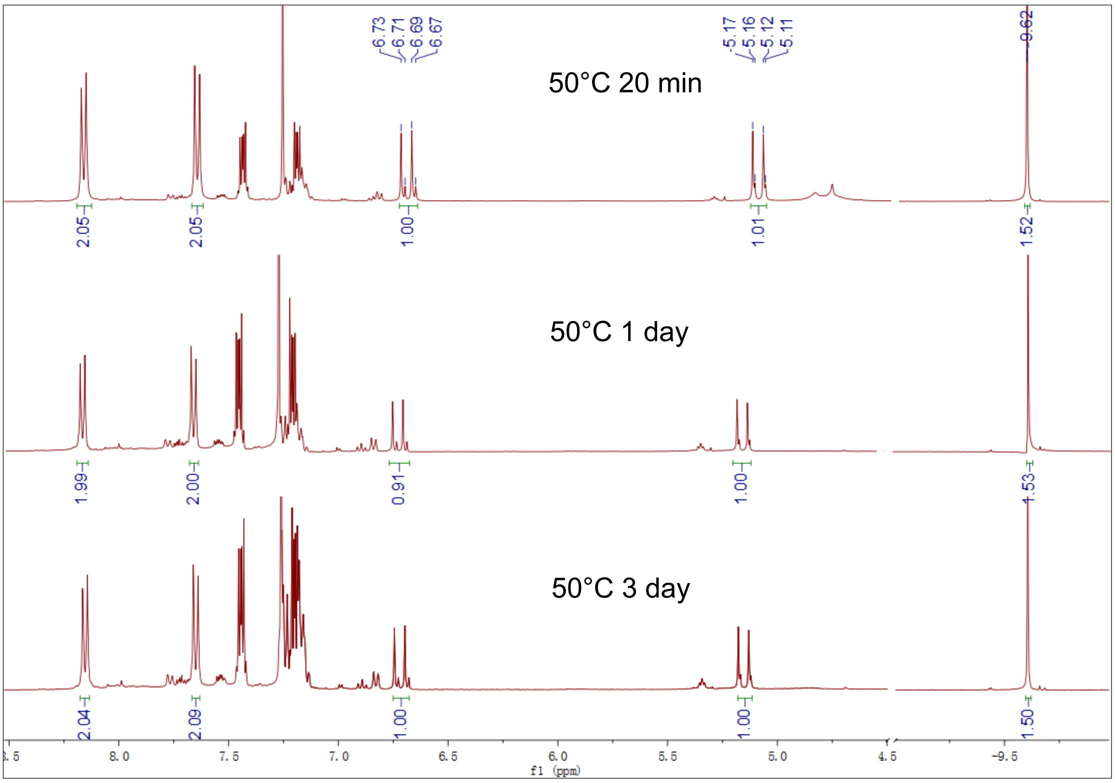


Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1064.182497	1	C73H31NO7P	100.00	1064.183265	0.7	-0.3	93.6	60.0	even	ok

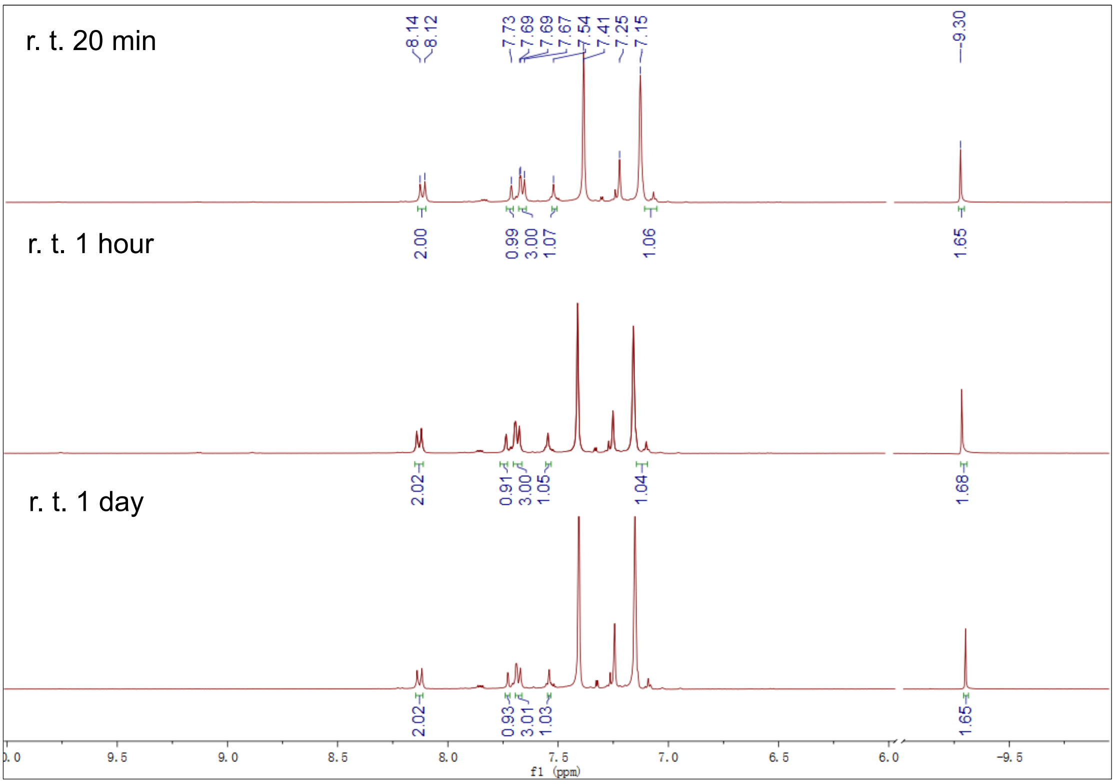
UV-Vis spectra for compound **2, 3, 4, 5**



H/D Exchange of Compound **H_2O@2**



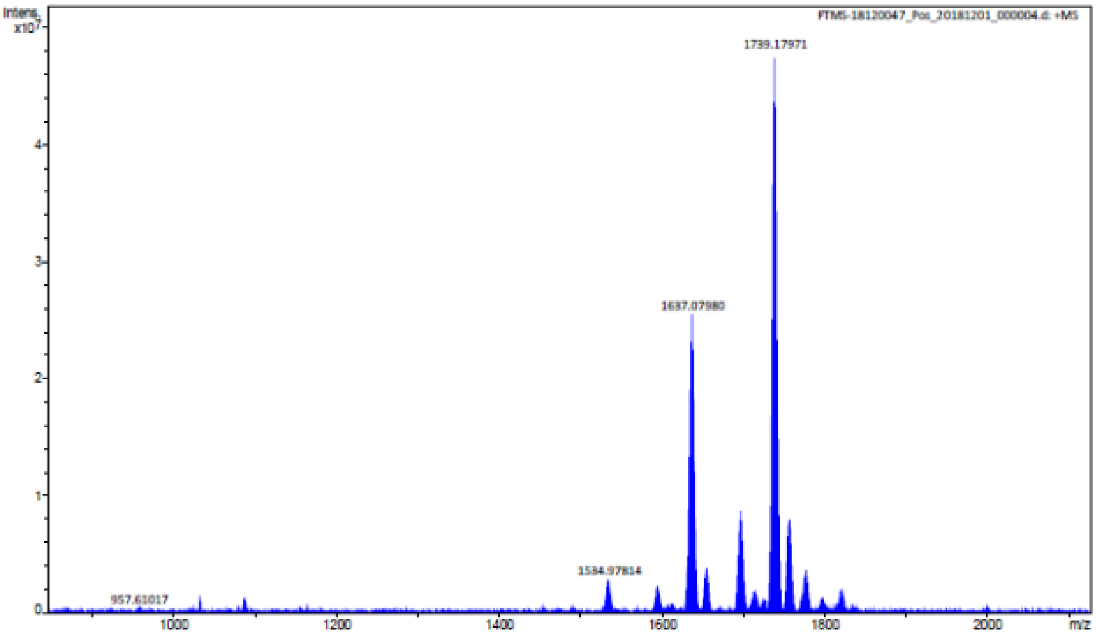
H/D Exchange of Compound **H_2O@5**

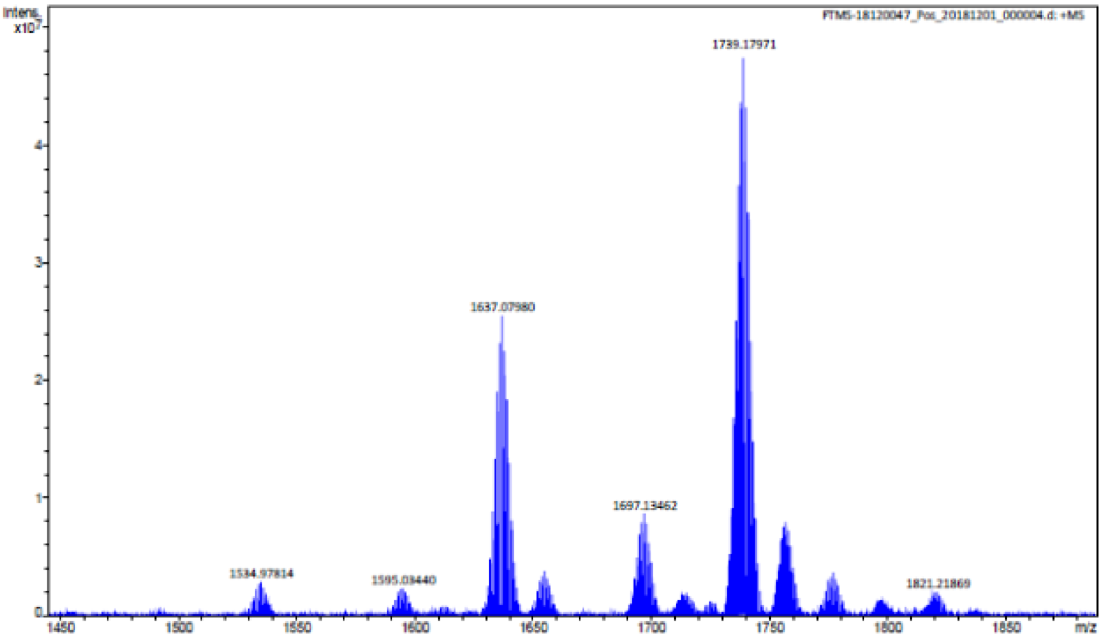


Coordination with Ti(O^{i}Pr)$_4$

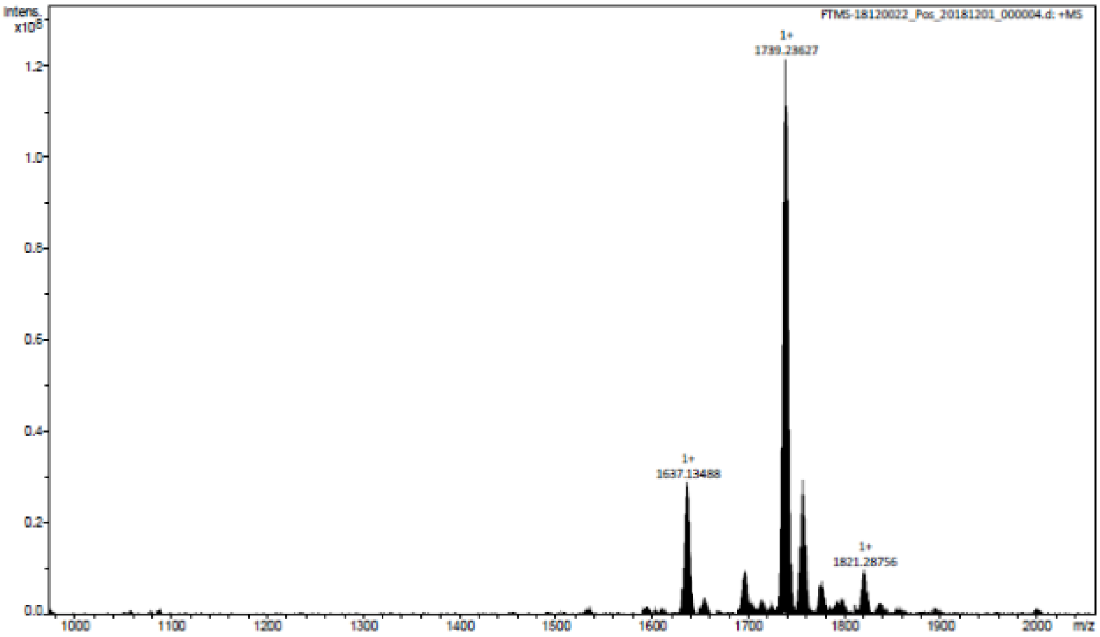
The coordination properties of the open-cage compounds were studied by ESI-MS method. Titanium isopropoxide reacted readily with all the open-cage compounds yielding very polar products as indicated by TLC. So far it was not possible to either isolate a pure product by column chromatography or obtain single crystals from the reactions. The following mass spectra were obtained from a sample containing the open-cage compound and excess Ti(O^{i}Pr)$_4$ in toluene.

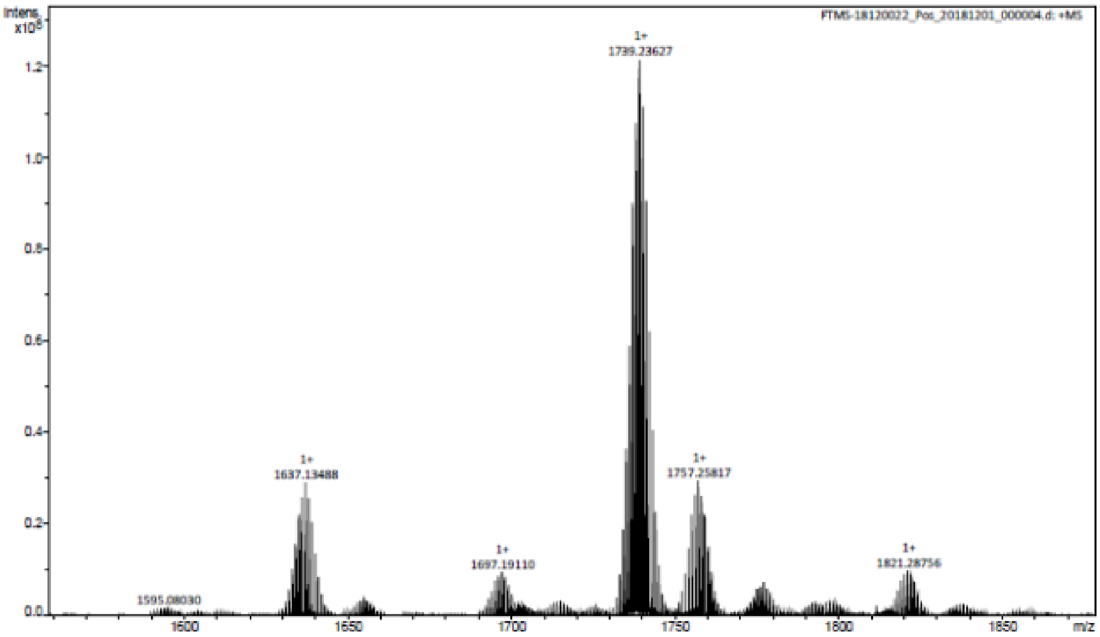
MS of **2&Ti** Complexes



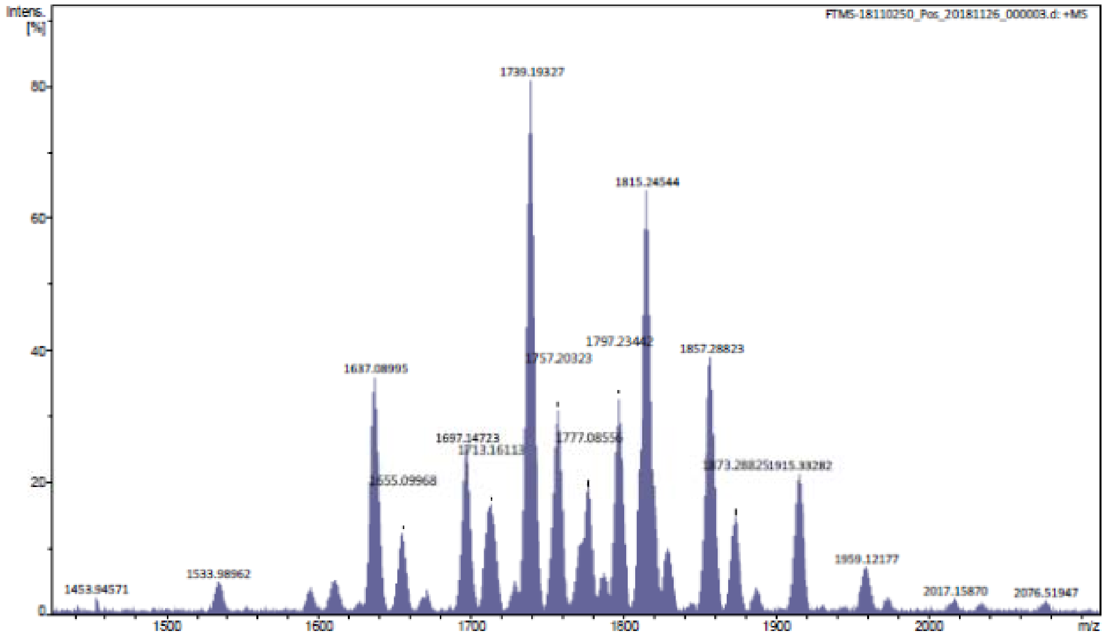


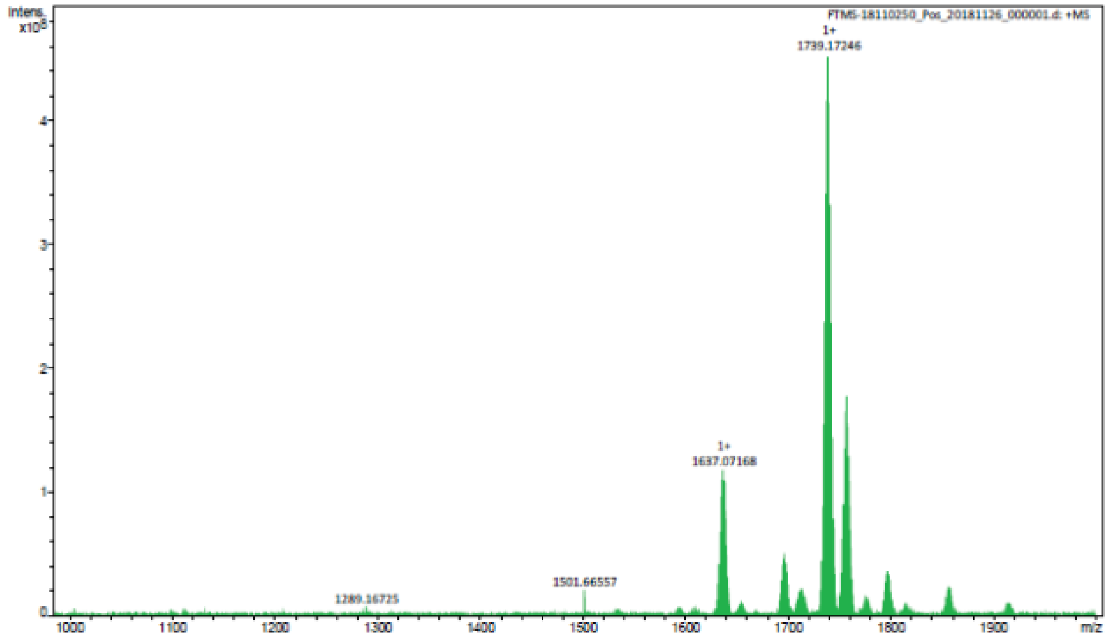
MS of **3&Ti** Complexes

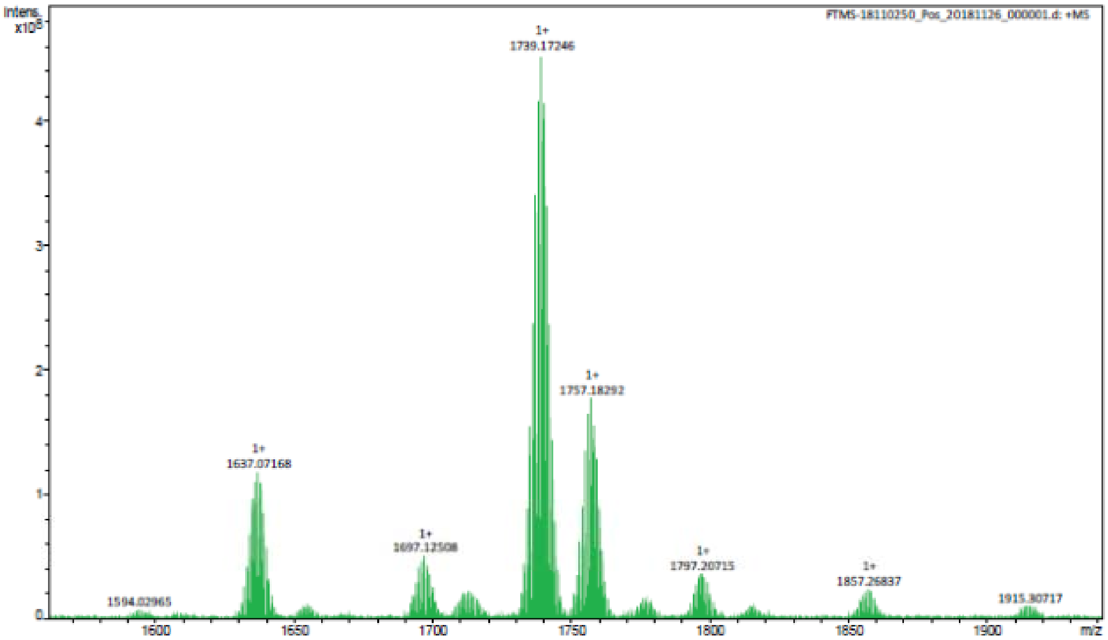




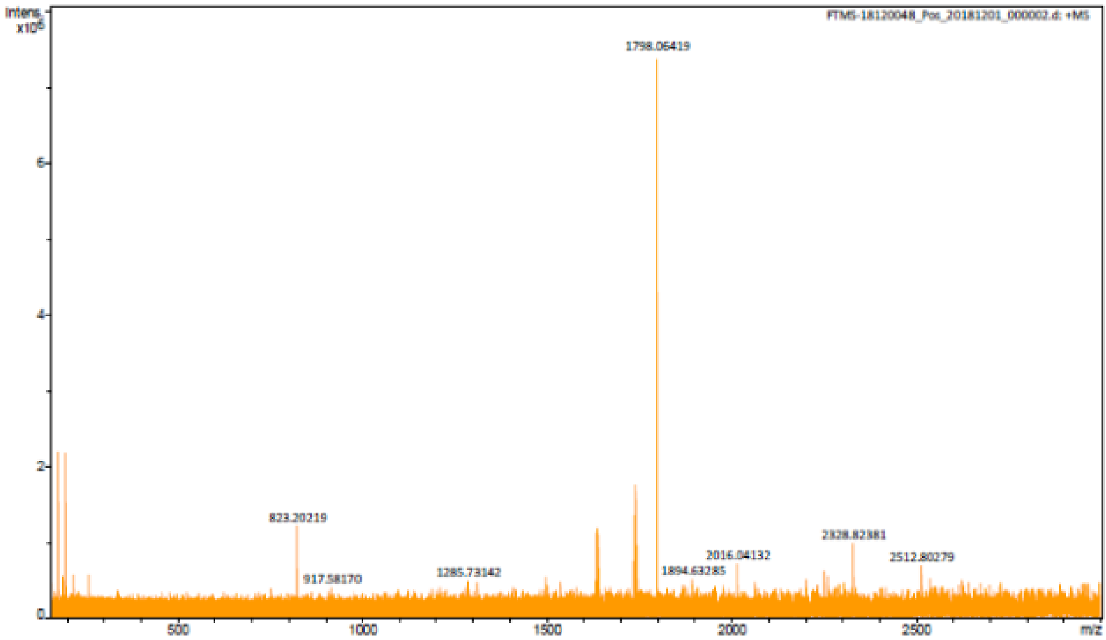
MS of **4&Ti** Complexes using tow different ESI conditions

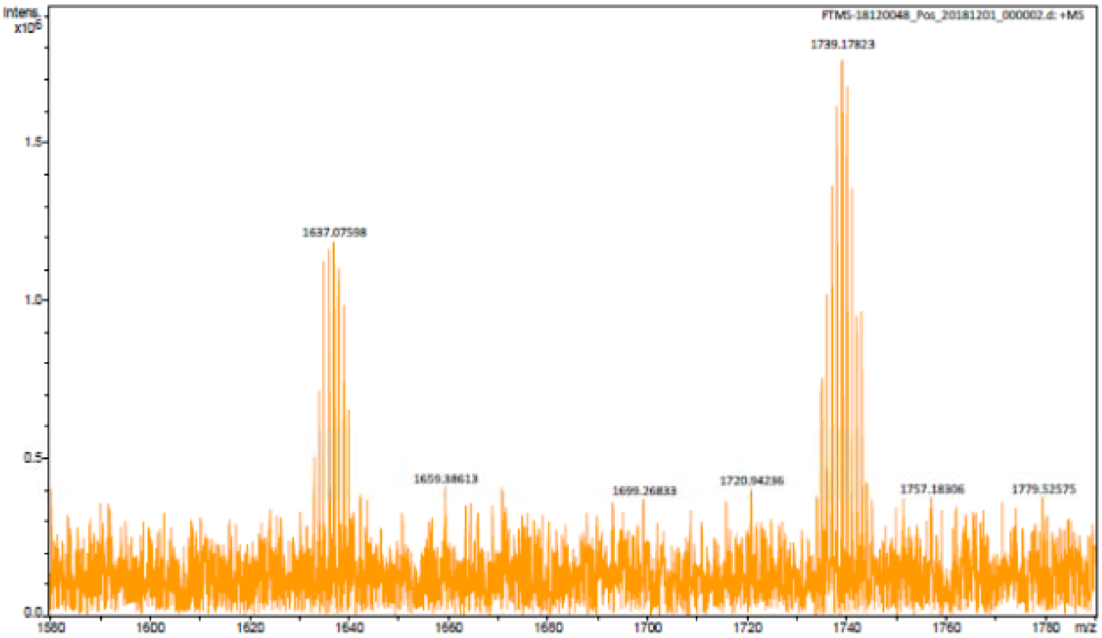






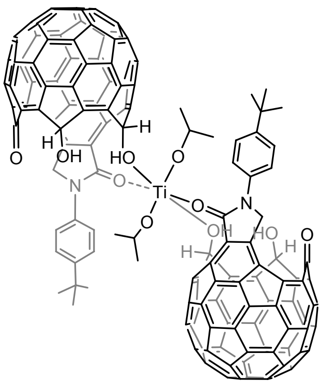
MS of **5&Ti** Complexes

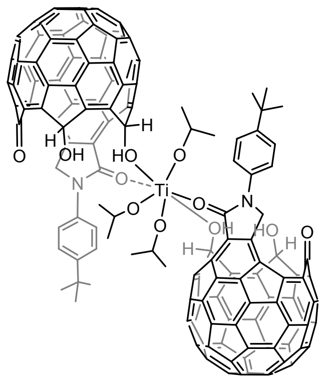


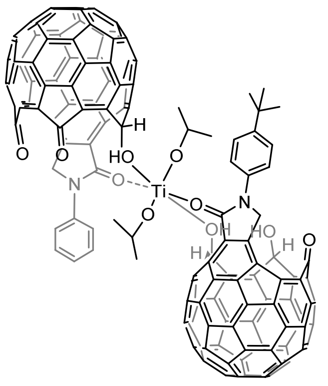

Intens.
x10^6
FTMS-18120048_Pos_20181201_000002.d: +MS
1739.17823
1637.07598
1659.38613
1699.26833
1720.94236
1757.18306
1779.52575
1.5
1.0
0.5
0.0
1580
1600
1620
1640
1660
1680
1700
1720
1740
1760
1780
m/z

Proposed structures of Ti complexes with molecular weights corresponding to the above mass spectra

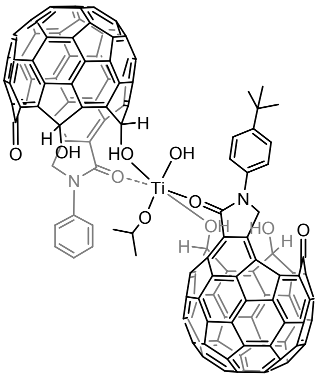
m/z: 2017.3135	**m/z: 2076.3632**	**m/z: 1959.2353**
$C_{144}H_{52}N_2O_{10}Ti(III)^+$	$C_{147}H_{59}N_2O_{11}Ti(IV)^+$	$C_{140}H_{42}N_2O_{10}Ti(III)^+$
M	M+OCH(CH$_3$)$_2$	M-(^{t}Bu+H)-2H

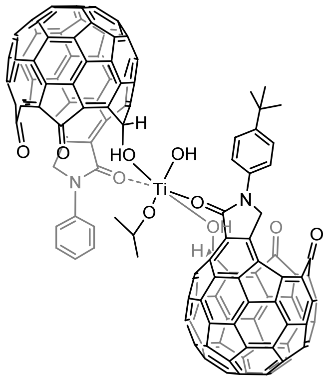


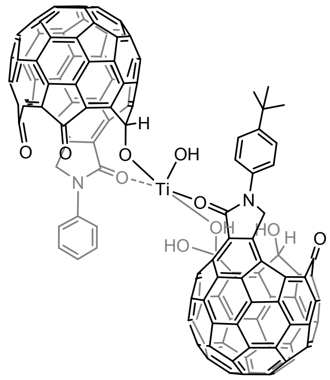




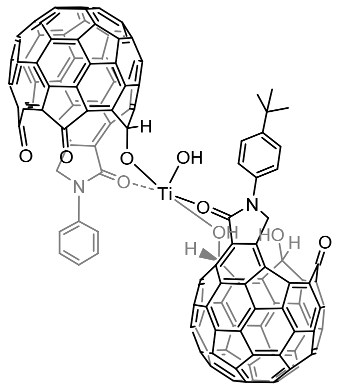
m/z: 1919.6820	**m/z: 1915.1727**	**m/z: 1873.5305**
$C_{137}H_{38}N_2O_{10}Ti(III)^+$	$C_{137}H_{34}N_2O_{10}Ti(III)^+$	$C_{134}H_{28}N_2O_{10}Ti(III)^+$
M-(^{t}Bu+H)-(^{i}Pr+H)	M-(^{t}Bu+H)-4H-(^{i}Pr+H)	M-(^{t}Bu+H)-3H-(O^{i}Pr)-(^{i}Pr+H)+O

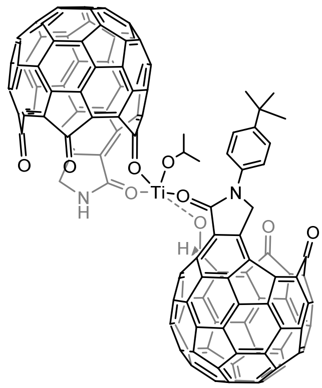


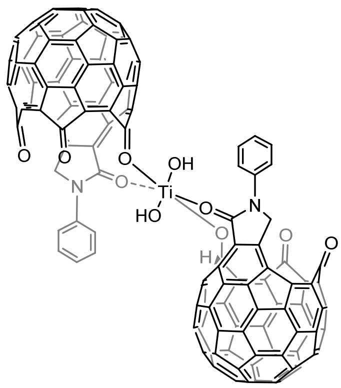


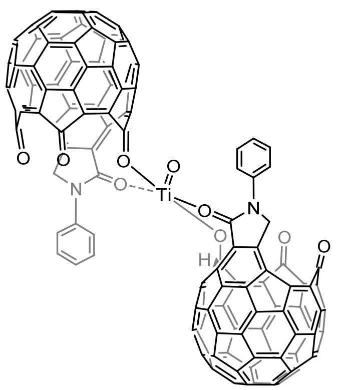
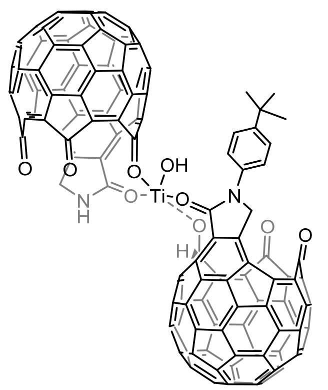
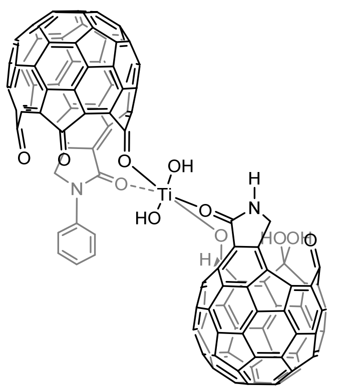
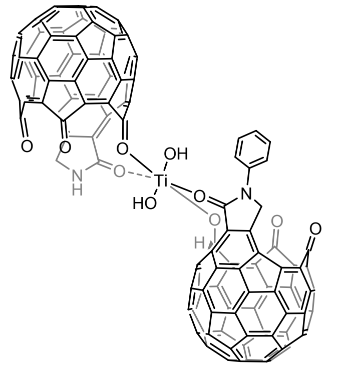
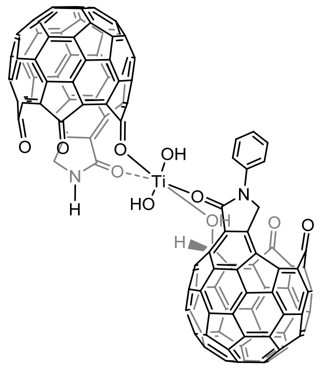
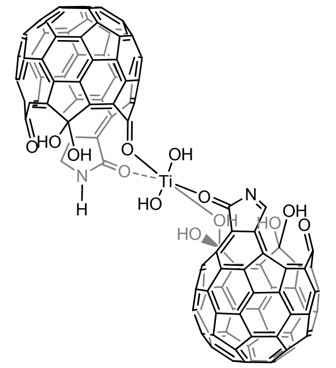
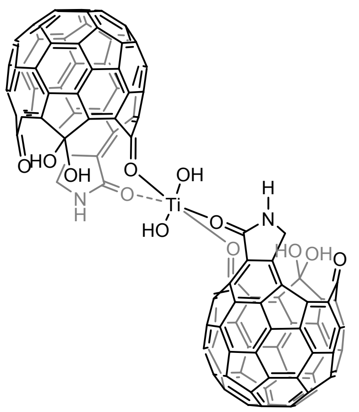
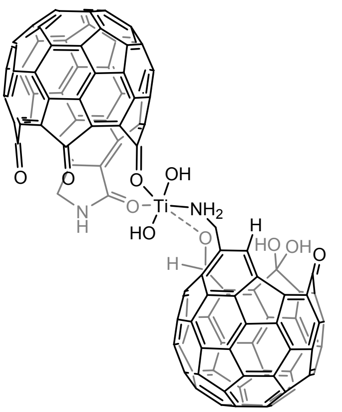
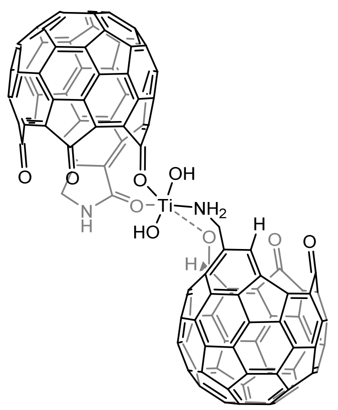


m/z: 1857.1308	**m/z: 1819.1151**	**m/z: 1814.0396**
$C_{134}H_{28}N_2O_9Ti(III)^+$	$C_{131}H_{26}N_2O_9Ti(III)^+$	$C_{130}H_{17}N_2O_{10}Ti(III)$
M-(^{t}Bu+H)-3H-(O^{i}Pr)-(^{i}Pr+H)	M-(C$_6$H$_4$^{t}Bu+H)-7H-(O^{i}Pr)	M-2(^{t}Bu+H)-7H-2(^{i}Pr+H)



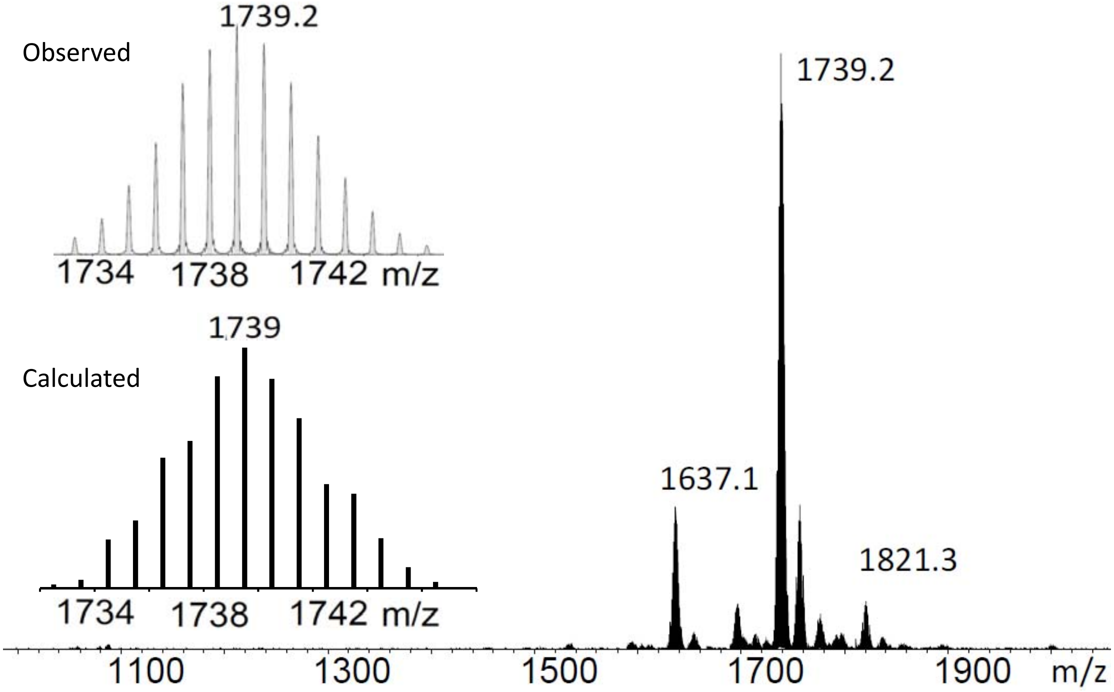




m/z: 1796.0291	**m/z: 1777.0682**	**m/z: 1756.0189**
$C_{130}H_{15}N_2O_9Ti(III)$ $M-2(^tBu+H)-7H-2(O^iPr)+O$	$C_{128}H_{20}N_2O_9Ti(III)^+$ $M-(C_6H_4{}^tBu+H)-7H-(^iPr+H)-(O^iPr)$	$C_{124}H_{15}N_2O_{11}Ti(III)$ $M-2(^tBu+H)-C_6H_4-7H-2(^iPr+H)+H_2O$
		
m/z: 1738.0083	**m/z: 1739.0162**	**m/z: 1712.9852**
$C_{124}H_{13}N_2O_{10}Ti(III)$ $M-(C_6H_4{}^tBu+H)-(^tBu+H)-7H-2(^iPr+H)$	$C_{124}H_{14}N_2O_{10}Ti(III)^+$ $M-(C_6H_4{}^tBu+H)-(^tBu+H)-6H-2(^iPr+H)$	$C_{118}H_{12}N_2O_{13}Ti(III)^+$ $M-2(C_6H_4{}^tBu+H)-8H-2(^iPr+H)+2H_2O+O$
		
m/z: 1696.9903	**m/z: 1654.0083**	**m/z: 1635.9978**
$C_{118}H_{12}N_2O_{12}Ti(III)^+$ $M-2(C_6H_4{}^tBu+H)-8H-2(^iPr+H)+2H_2O$	$C_{117}H_{12}N_2O_{10}Ti(III)$ $M-2(C_6H_4{}^tBu+H)-(CO+2H)-7H-2(^iPr+H)+H_2O$	$C_{117}H_{11}N_2O_9Ti(III)$ $M-2(C_6H_4{}^tBu+H)-(CO+2H)-7H-2(^iPr+H)$
		

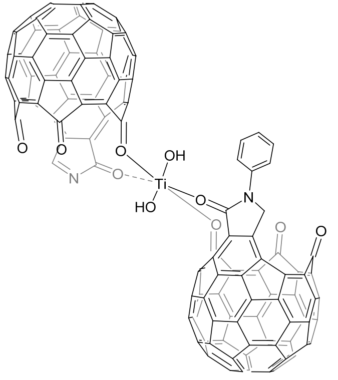
The isotope pattern of the signals indicates that a mixture of a few different structures with similar molecular weights was overlapped. This can be explained by the stepwise oxidation of the hydroxyl groups resulting loss of two hydrogen atoms. Theoretical calculation of a mixture containing the following five closely related species with different number of hydroxyl groups in 1:2:4:2:1 ratio showed very close pattern to that observed for the signal at 1739.2 m/z as shown in the following figure (calculation details on pages SI35-38).

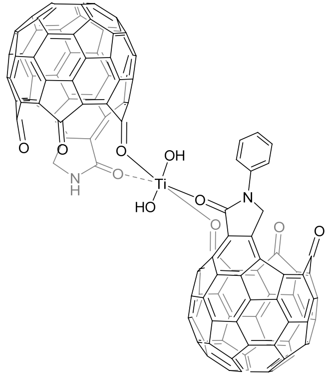
Calculation of m/z 1739

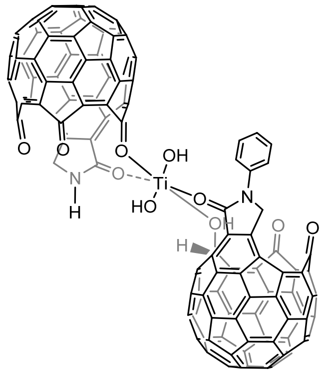


m/z: 1739 was calculated by the MS of compounds A-E in the ratio 0.5:1:2:1:0.5 respectively.

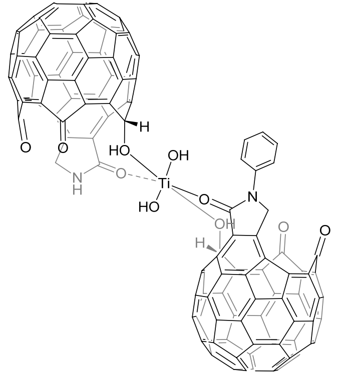
A = m/z: 1734.9848	**B = m/z: 1737.0005**	**C = m/z: 1739.0162**
$C_{124}H_{10}N_2O_{10}Ti(III)^+$ $M-(C_6H_4{}^tBu+H)-({}^tBu+H)-10H-2({}^iPr+H)$	$C_{124}H_{12}N_2O_{10}Ti(III)^+$ $M-(C_6H_4{}^tBu+H)-({}^tBu+H)-8H-2({}^iPr+H)$	$C_{124}H_{14}N_2O_{10}Ti(III)^+$ $M-(C_6H_4{}^tBu+H)-({}^tBu+H)-6H-2({}^iPr+H)$

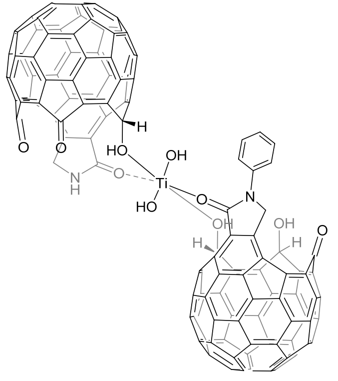






D = m/z: 1741.0318	**E = m/z: 1743.0474**
$C_{124}H_{16}N_2O_{10}Ti(III)^+$ $M-(C_6H_4{}^tBu+H)-({}^tBu+H)-4H-2({}^iPr+H)$	$C_{124}H_{18}N_2O_{10}Ti(III)^+$ $M-(C_6H_4{}^tBu+H)-({}^tBu+H)-2H-2({}^iPr+H)$





m/z 1735		
ms	Percentage of Mass distribution calculated for $C_{124}H_{10}N_2O_{10}Ti(III)$	Calcd x 0.5
1747	0.000	0.000
1746	0.000	0.000
1745	0.000	0.000
1744	0.000	0.000
1743	0.000	0.000
1742	0.000	0.000
1741	0.000	0.000

1740	0.000	0.000
1739	0.024	0.012
1738	0.158	0.079
1737	0.432	0.216
1736	0.820	0.410
1735	1.138	0.569
1734	0.922	0.461
1733	0.188	0.094
1732	0.084	0.042

m/z 1737

ms	Percentage of Mass distribution calculated for $C_{124}H_{12}N_2O_{10}$Ti(III)	Calcd x 1
1747	0.000	0.000
1746	0.000	0.000
1745	0.000	0.000
1744	0.000	0.000
1743	0.000	0.000
1742	0.000	0.000
1741	0.034	0.034
1740	0.143	0.143
1739	0.431	0.431
1738	0.819	0.819
1737	1.147	1.147
1736	0.922	0.922
1735	0.187	0.187
1734	0.083	0.083
1733	0.000	0.000
1732	0.000	0.000

m/z 1739

ms	Percentage of Mass distribution calculated for $C_{124}H_{14}N_2O_{10}$Ti(III)	Calcd x 2
1747	0.000	0.000
1746	0.000	0.000
1745	0.000	0.000
1744	0.000	0.000
1743	0.027	0.054
1742	0.114	0.227
1741	0.324	0.647
1740	0.615	1.229
1739	0.854	1.707
1738	0.692	1.383
1737	0.141	0.281
1736	0.023	0.125

1735	0.000	0.000
1734	0.000	0.000
1733	0.000	0.000
1732	0.000	0.000
m/z 1741		
ms	Percentage of Mass distribution calculated for $C_{124}H_{16}N_2O_{10}$Ti(III)	Calcd x 1
1747	0.000	0.000
1746	0.000	0.000
1745	0.020	0.020
1744	0.148	0.148
1743	0.431	0.431
1742	0.473	0.473
1741	1.122	1.122
1740	0.921	0.921
1739	0.533	0.533
1738	0.083	0.083
1737	0.000	0.000
1736	0.000	0.000
1735	0.000	0.000
1734	0.000	0.000
1733	0.000	0.000
1732	0.000	0.000
m/z 1743		
ms	Percentage of Mass distribution calculated for $C_{124}H_{18}N_2O_{10}$Ti(III)	Calcd x 0.5
1747	0.020	0.010
1746	0.144	0.072
1745	0.452	0.216
1744	0.820	0.410
1743	1.138	0.569
1742	0.922	0.461
1741	0.188	0.094
1740	0.084	0.042
1739	0.000	0.000
1738	0.000	0.000
1737	0.000	0.000
1736	0.000	0.000
1735	0.000	0.000
1734	0.000	0.000
1733	0.000	0.000
1732	0.000	0.000

m/z	1735x0.5	1737x1	1739x2	1741x1	1743x0.5	Sum
1747	0.000	0.000	0.000	0.000	0.010	0.010
1746	0.000	0.000	0.000	0.000	0.072	0.072
1745	0.000	0.000	0.000	0.020	0.216	0.236
1744	0.000	0.000	0.000	0.148	0.410	0.558
1743	0.000	0.000	0.054	0.431	0.569	1.054
1742	0.000	0.000	0.227	0.473	0.461	1.161
1741	0.000	0.034	0.647	1.122	0.094	1.896
1740	0.000	0.143	1.229	0.921	0.042	2.334
1739	0.012	0.431	1.707	0.533	0.000	2.683
1738	0.079	0.819	1.383	0.083	0.000	2.364
1737	0.216	1.147	0.281	0.000	0.000	1.644
1736	0.410	0.922	0.125	0.000	0.000	1.456
1735	0.569	0.187	0.000	0.000	0.000	0.756
1734	0.461	0.083	0.000	0.000	0.000	0.544
1733	0.094	0.000	0.000	0.000	0.000	0.094
1732	0.042	0.000	0.000	0.000	0.000	0.042