Supporting Information

Optimised Scalable Synthesis of $H_2O@C_{60}$ and a New Synthesis of $H_2@C_{60}$

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General. All reactions were executed under an argon atmosphere. All glassware was dried overnight in an oven heated at 160 °C and cooled down to room temperature in a desiccator over silica gel before assembly, or assembled under argon flow while still hot. Sublimation tubes were degreased with aqua regia, and then rinsed with distilled water, acetone and finally oven dried. When needed, solutions were degassed via three freeze-thaw cycles. All additions were performed using regular air-free techniques. Reactions under high pressure (120 atm) were performed using a Parr reactor. The reaction course was monitored by TLC using Merck silica gel 60 F254 plates detecting the spots using an UV lamp or by HPLC performed on a Cosmosyl Bukyprep analytical column with detection at 326nm. Flash column chromatography was run using Merck silica gel Geduran Si60 (40-63 μm) as stationary phase. NMR spectra were recorded on Bruker AV300, DPX400 or 500 spectrometers. Chemical shifts are reported in ppm and referenced to the residual solvent peak. FT-IR spectra were recorded on a Bruker Alpha-T instrument. UV-Vis spectra were recorded on an Ocean Optics USB2000+ UV/Vis spectrometer. Electrospray mass spectra were recorded in the positive ion mode. The expected peaks due to natural abundance ^{13}C were present but not reported. Note that due to the noise reducing threshold used in processing relative intensities of weak peaks are reduced. High resolution mass spectra were recorded using a solariX (Bruker Daltonics, Bremen, Germany) mass spectrometer equipped with Fourier Transform Ion Cyclotron Resonance (FT-ICR), using positive ion atomospheric pressure photoionisation. All computational experiments were done using the Gaussian 09 software package. Structure optimisation was done using DFT at the B3LYP/6-31G(d) level of theory. NMR spectra were calculated using the GIAO approach at the B3LYP/6-311G(2d,p) level of theory, starting from geometries optimised at the B3LYP/6-31G(d) level of theory.

Materials. Compound **1** was synthesised according to the reported procedure.[1] Molecular sieves were activated by heating at 220 °C under vacuum (1 mmHg) for 4 h and then cooled and stored under argon. Toluene, benzene, o-dichlorobenzene and 1-chloronaphthalene were distilled over sodium under argon atmosphere. Triisopropyl phosphite (95%) was purchased from Sigma-Aldrich Company Ltd. and distilled over sodium under reduced pressure before use. All other solvents and reagents were directly employed as received from the supplier without any further purification.

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[1] K. Kurotobi and Y. Murata, *Science* 2011, **333**, 613-616.

Optimised procedure for the H_2O filling of compound 1:

Compound **1** (600 mg, 0.536 mmol) was placed inside a 40 ml tube equipped with a J.Young valve. The tube was put under an argon atmosphere and 1-chloronaphthalene (17 ml) was added followed by distilled water (54 μl). The solution was degassed and the tube was charged with argon gas (1 atm). The tube was completely immersed inside an oil bath preheated to 100 °C for 48 hours. After this time had elapsed the tube was cooled to room temperature and the solution was poured directly over a silica column packed with toluene. The column was eluted with toluene until all the 1-chloronapthalene was removed. The eluent polarity was then gradually increased to 15% AcOEt in toluene to collect **H_2O@1** (78% H_2O incorporation) (546 mg, 90%).

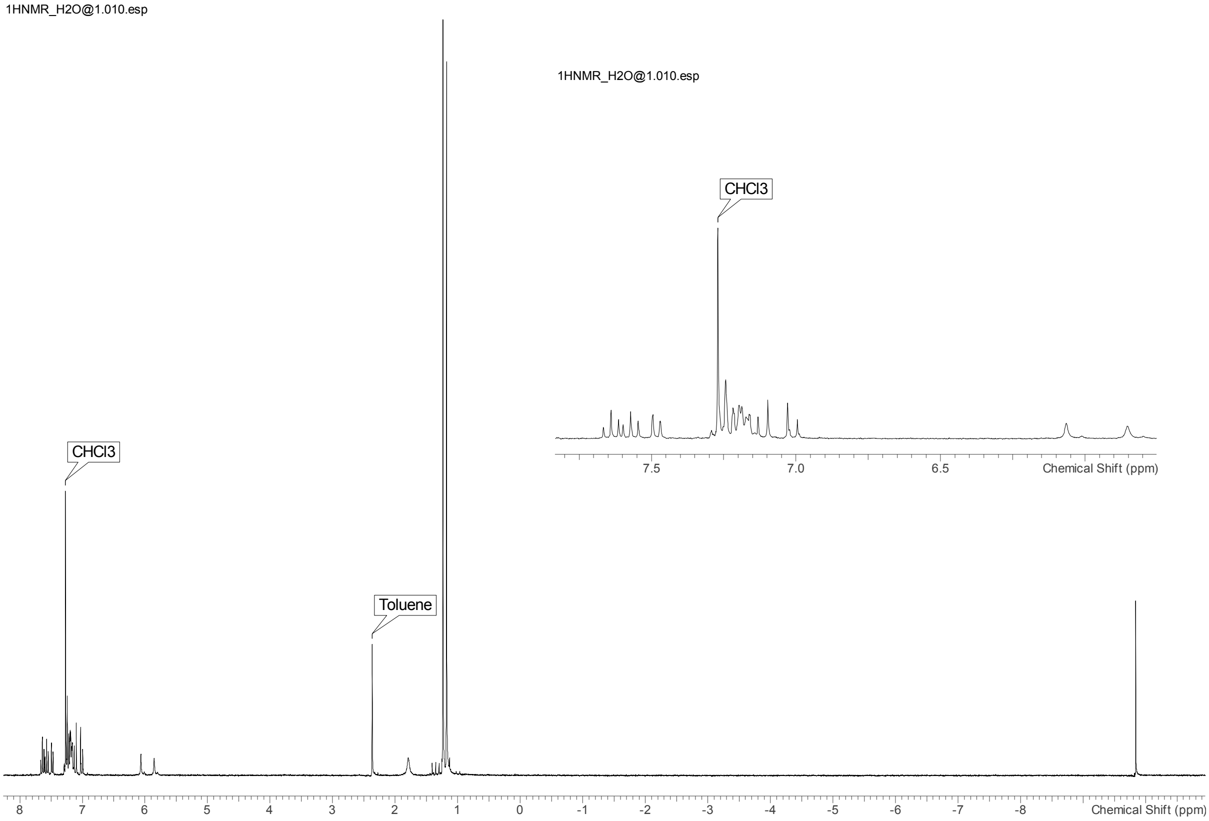
^{1}H NMR: (300 MHz, $CDCl_3$, δ): 7.64 (t, J = 7.8 Hz, 1H, H-4 or H-4' of pyridyl), 7.57 (t, J = 7.8 Hz, 1H, H-4 or H-4' of pyridyl), 7.48 (d, J = 7.8 Hz, 1H, H-3 or H-3' of pyridyl), 7.21 (d, J = 7.8 Hz, 2H, H-5 and H-5' of pyridyl), 7.16 (d, J = 7.8 Hz, 1H, H-3 or H-3' of pyridyl), 7.11 (d, J = 10.0 Hz, 1H, alkene), 7.01 (d, J = 10.0 Hz, 1H, alkene), 6.06 (br s, 1H, OH), 5.85 (br s, 1H, OH), 1.24 (s, 9H, t-butyl group), 1.18 (s, 9H, t-butyl group), -9.84 (s, 1.56H, endohedral H_2O).

^{13}CNMR: (75 MHz, $CDCl_3$, δ): 198.21, 193.6, 168.93, 168.43, 164.11, 162.54, 153.82, 150.24, 149.93, 149.84, 149.69, 149.4, 149.26, 148.92, 148.76, 148.38, 148.18, 148.13, 148, 147.52, 147.48, 147.39, 147.09, 146.59, 146.54, 145.55, 145.46, 145.33, 145.06, 144.79, 144.29, 143.96, 143.69, 143.14, 142.87, 142.62, 142.57, 141.48, 141.36, 140.98, 140.14, 140.1, 140.08, 139.74, 139.17, 138.63, 138.37, 137.31, 137.25, 137.08, 136.94, 136.65, 136.16, 134.96, 134.85, 134.54, 133.76, 133.35, 131.7, 131.62, 130.06, 127.18, 126.86, 119.94, 119.67, 117.49, 116.9, 110.2, 96.37, 59.57, 54.74, 37.81, 37.61, 30.00, 29.85.

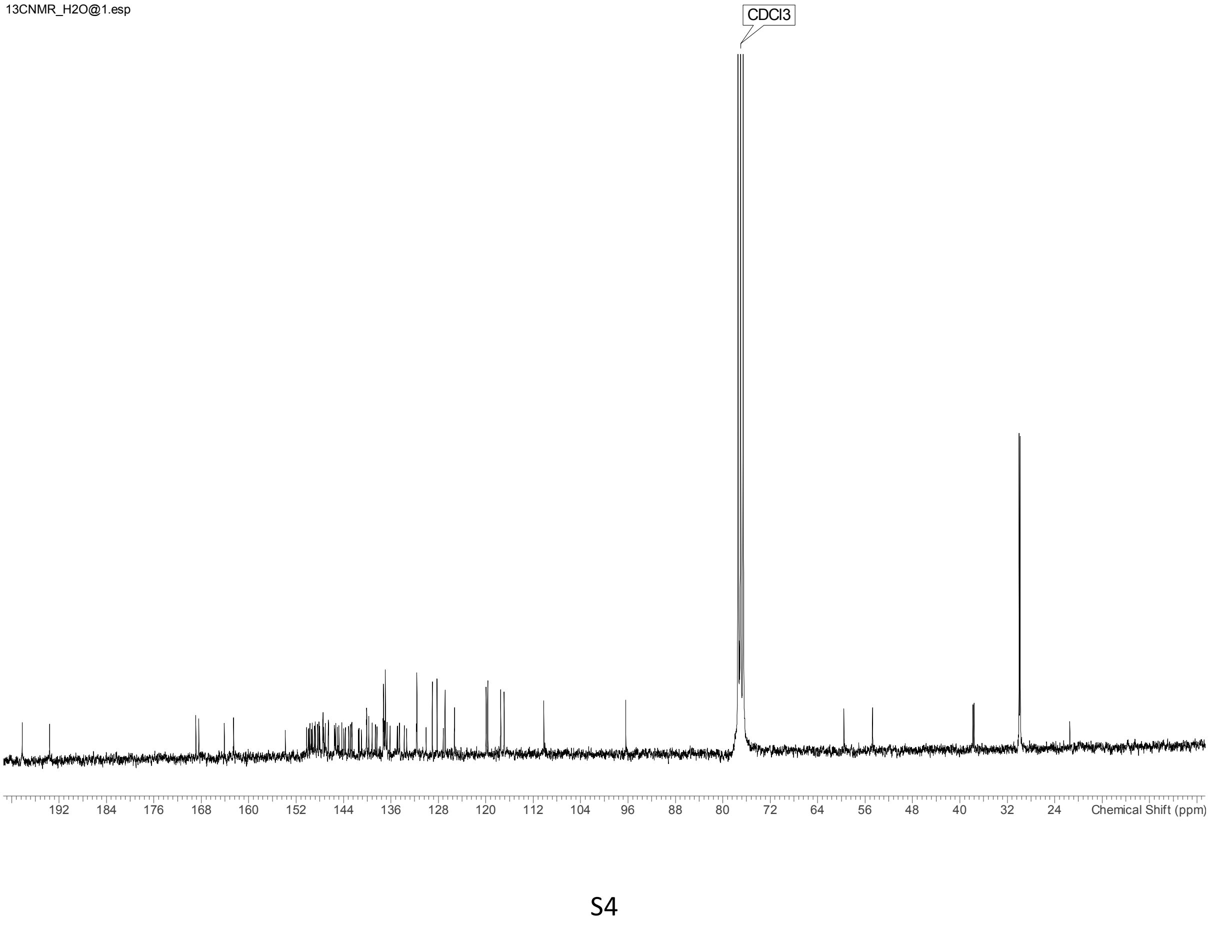
MS-ESI: *m/z* (relative intensity, ion): 1139 (100%, $[M+H]^+$ H_2O@1), 1121 (5%, $[M+H]^+$ 1).

Values agree in accord with reported data.[1]

^{1}HNMR spectrum of compound H_2O@1



^{13}CNMR spectrum of compound H_2O@1



2: Compound **1** (60 mg, 0.053 mmol) was placed inside 50 ml Schlenk flask. The flask was connected to a 5 ml dropping funnel with a pressure regulating arm. The funnel was completely filled with 3Å activated molecular sieves. The top of the dropping funnel was connected to a straight condenser linked to a vacuum/argon inlet. The system was put under argon atmosphere and then toluene was added (20 ml). The apparatus was placed inside an oil bath heated to 120 °C, and the tap of the dropping funnel was closed so that the solvent vapours could start refluxing through the pressure regulating arm and then condense and accumulate inside the dropping funnel. Once the dropping funnel was completely filled up, the tap was opened and the system was refluxed for 2 hours. The reaction mixture was allowed to cool down to room temperature. The solution was transferred to a distillation apparatus under argon atmosphere. The solvent was distilled off under argon to afford compound **2** as a black solid (59 mg, quantitative).

^{1}H NMR: (300 MHz, $CDCl_3$, δ): 7.55 (t, J = 7.5 Hz, 1 H, H-4 or H-4’ of pyridyl), 7.49 (t, J = 7.9 Hz, 1 H, H-4 or H-4’ of pyridyl), 7.31 (d, J = 7.2 Hz, 1 H), 7.12 (d, J = 10.2 Hz, 1 H), 7.15 (d, J = 7.9 Hz, 1 H), 7.13 (d, J = 7.2 Hz, 1 H), 7.09 (d, J = 7.9 Hz, 1 H), 6.90 (d, J = 10.2 Hz, 1 H), 1.09 (s, 9 H), 1.06 (s, 9 H).
^{13}CNMR: (75MHz, $CDCl_3$, δ): 192.11, 187.38, 183.26, 182.32, 168.86, 168.32, 163.66, 162.31, 154.89, 150.01, 149.85, 149.7, 149.39, 149.17, 149.15, 149.12, 148.62, 148.59, 148.17, 147.99, 147.46, 147.4, 147.33, 147.09, 147.02, 146.97, 146.73, 146.14, 145.09, 144.74, 144.68, 144.57, 144.43, 144.19, 143.94, 143.77, 142.9, 142.21, 142.1, 141.12, 140.99, 140, 139.87, 138.98, 138.54, 138.37, 137.96, 137.83, 137.42, 137.12, 137.08, 136.87, 136.81, 136.12, 135.68, 134.9, 134.7, 134.35, 133.47, 133, 132.93, 132.82, 131.57, 130.62, 127.98, 125.9, 120.09, 119.52, 117.59, 117.06, 59.22, 55.04, 37.76, 37.61, 29.93, 29.81.
UV/Vis: CH_2Cl_2 λ_{max} (ε) = 257.48 (71433), 319.83 (30603).
Values agree in accord with reported data.[2]

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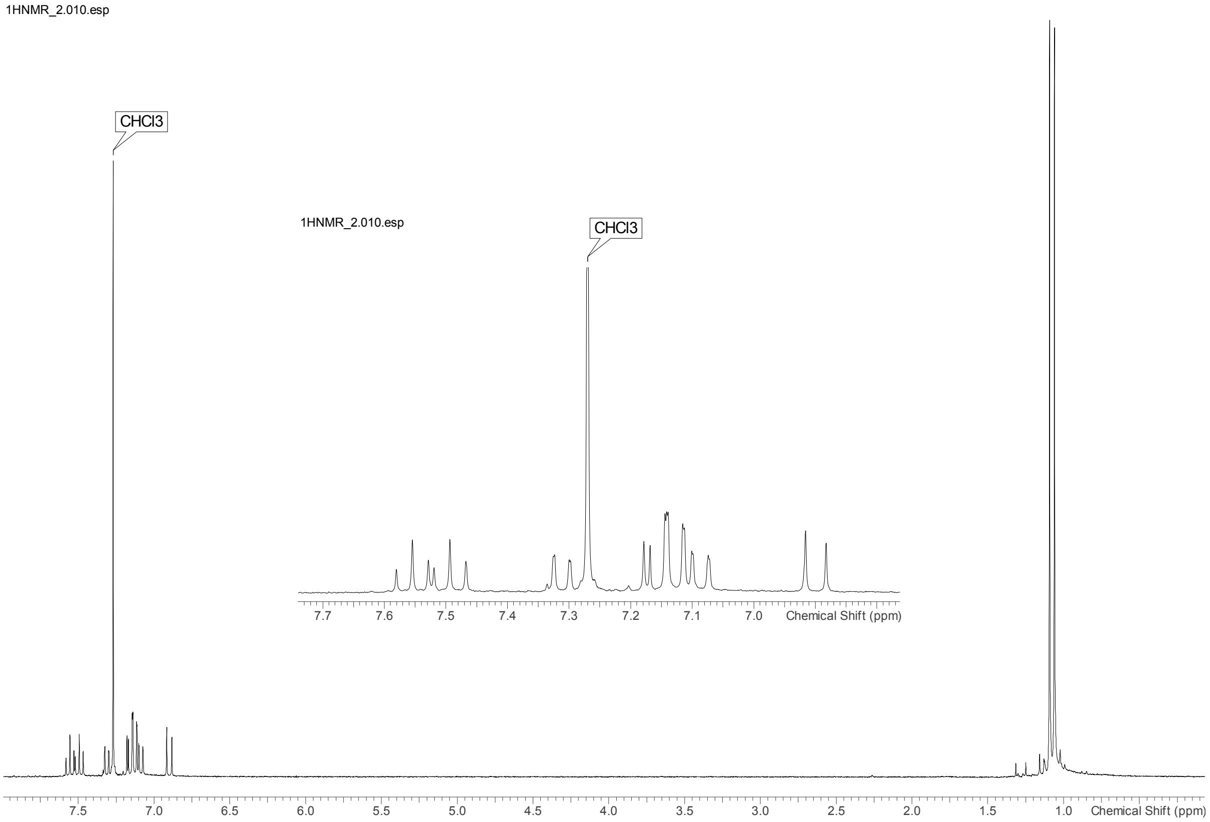
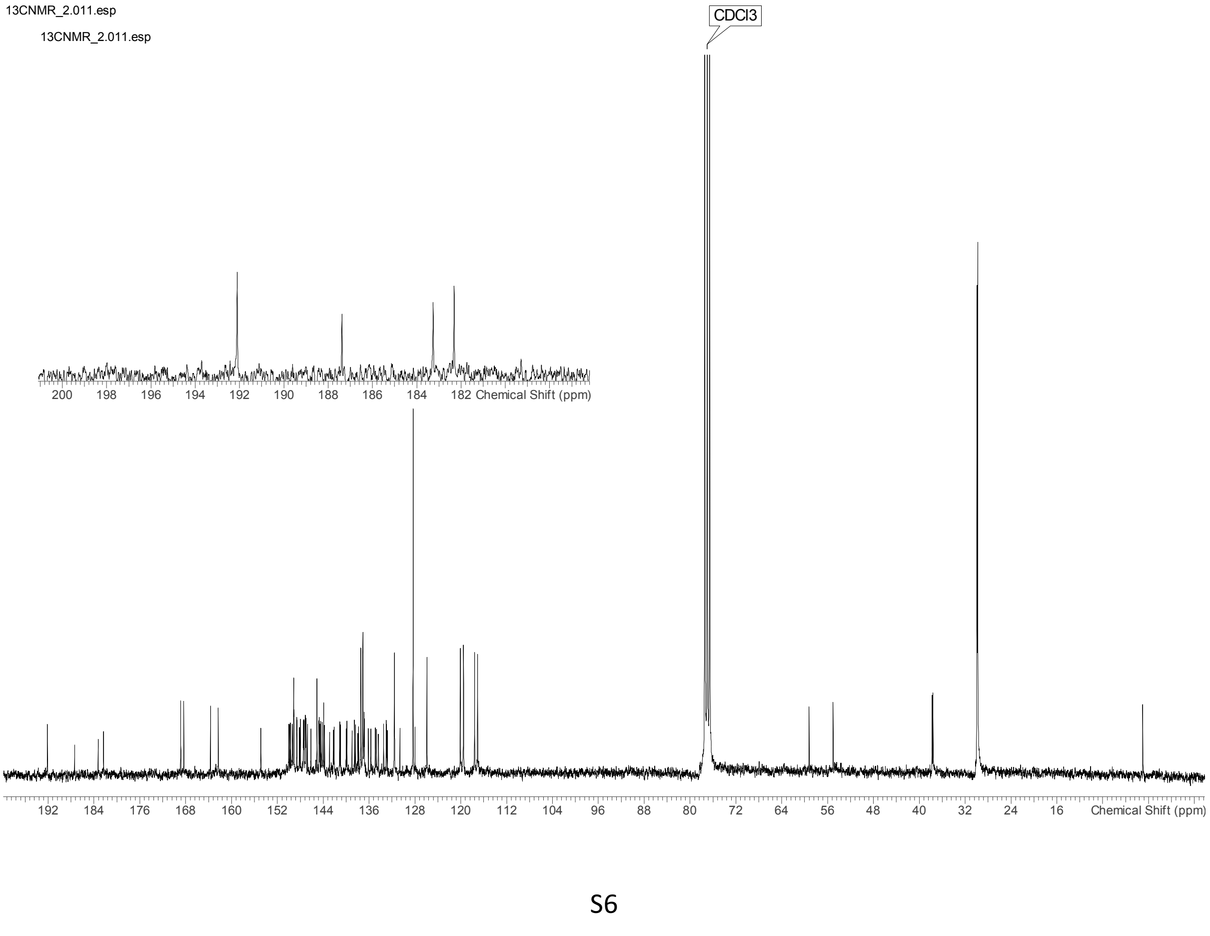
[2] T. Futagoishi, M. Murata, A. Wakamiya, T. Sasamori and Y. Murata, *Org. Lett.***2013**, *15*, 2750–2753

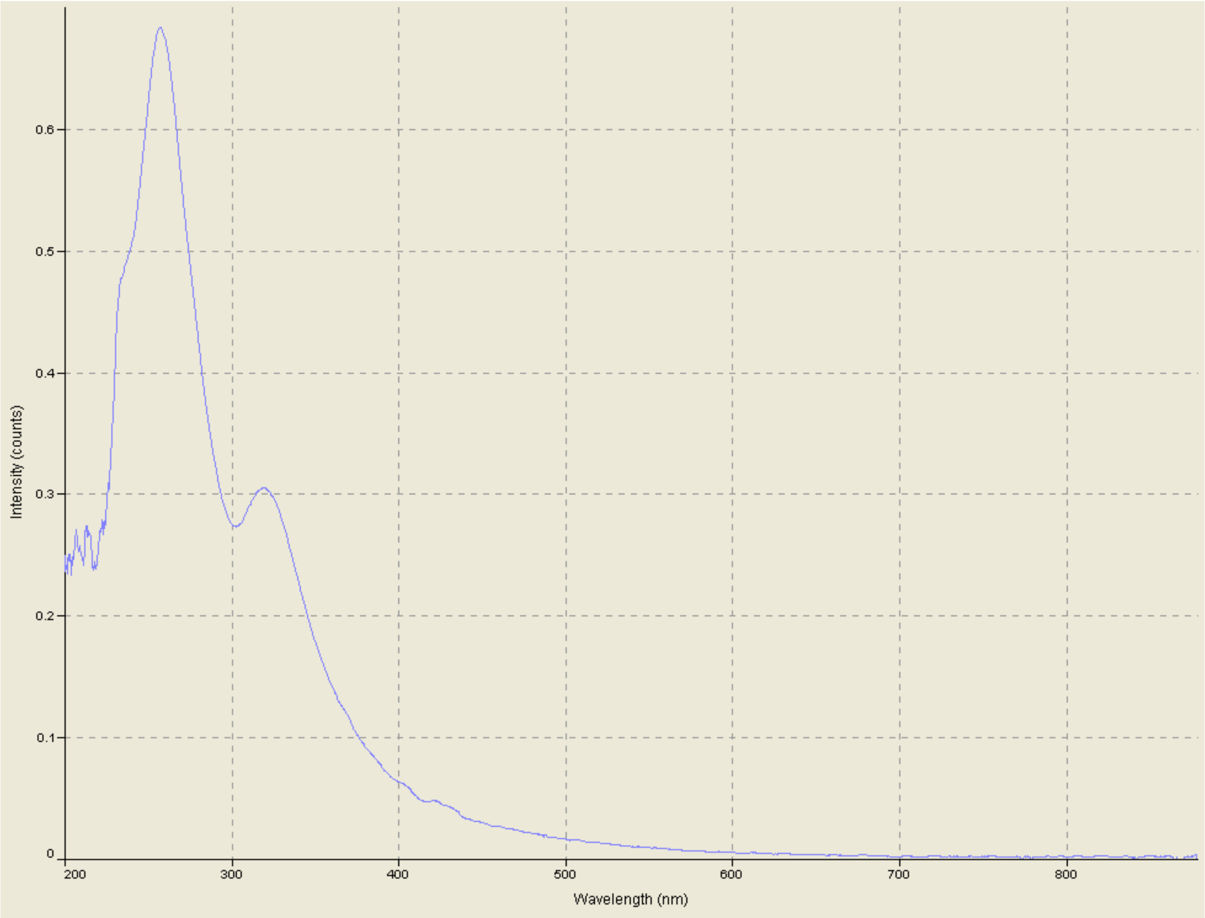
^{1}HNMR spectrum of compound 2



^{13}CNMR spectrum of compound 2



UV spectrum of compound 2

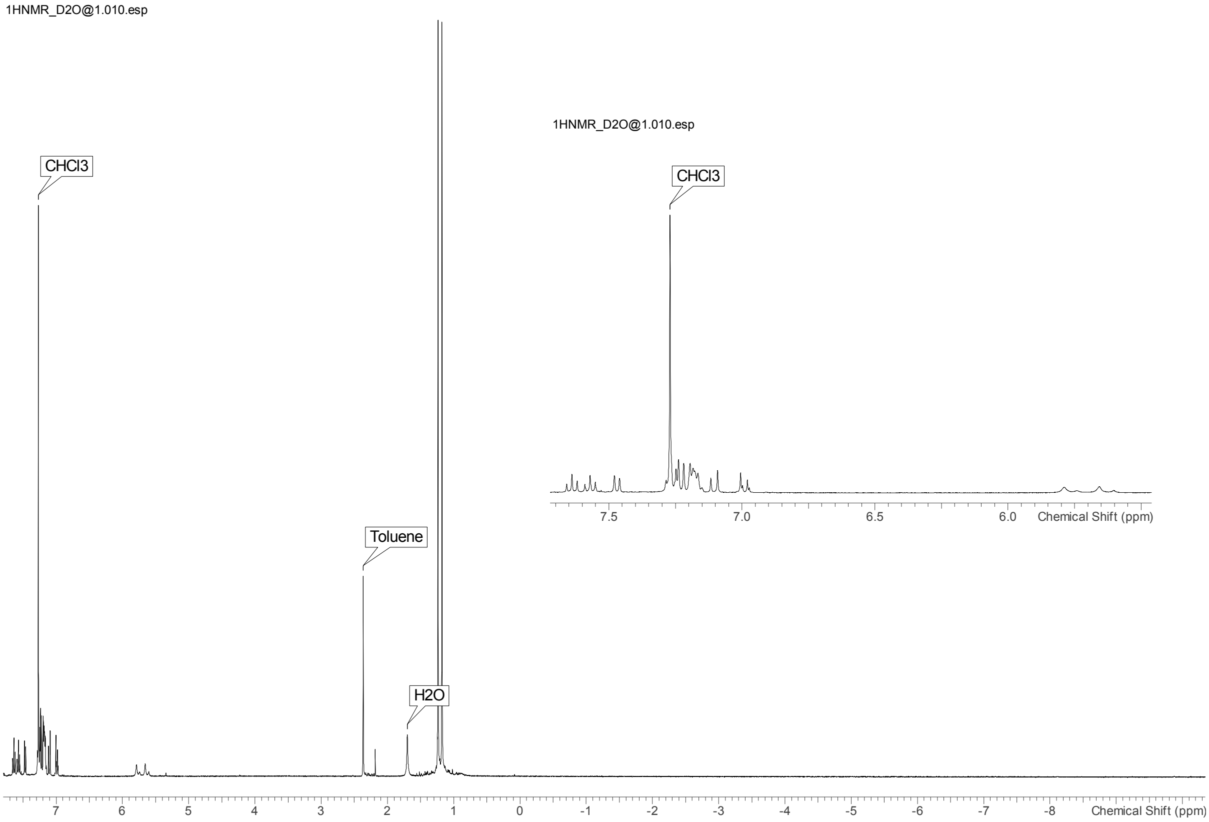


Optimised procedure for the D_2O filling of compound 2 under low pressure conditions:

Compound **2** (143 mg, 0.130 mmol), freshly prepared as described above, was dissolved in distilled 1-chloronapthalene (5ml). The solution was transferred to a 40ml Schlenk tube fitted with a J.Young tap under argon atmosphere. D_2O (99.990%D, 100 µl) was added and the tube was sealed and completely immersed inside an oil bath preheated to 100 °C. After 48 hours the tube was cooled to room temperature and the solution was poured directly over a silica column packed with toluene. The column was eluted with toluene until all the 1-chloronapthalene was removed. The eluent polarity was then gradually increased to 15% AcOEt in toluene to collect the **D_2O@1** (133 mg, 90%).

^{1}H NMR: (400 MHz, $CDCl_3$, δ): 7.64 (t, J = 7.8 Hz, 1H, H-4 or H-4’ of pyridyl), 7.57 (t, J = 7.8 Hz, 1H, H-4 or H-4’ of pyridyl), 7.47 (d, J = 7.8 Hz, 1H, H-3 or H-3’ of pyridyl), 7.21 (d, J = 7.8 Hz, 2H, H-5 and H-5’ of pyridyl), 7.16 (d, J = 7.8 Hz, 1H, H-3 or H-3’ of pyridyl), 7.10 (d, J = 10.1 Hz, 1H, alkene), 6.99 (d, J = 10.1 Hz, 1H, alkene), 5.79 (br s, 1H, OH), 5.66 (br s, 1H, OH), 1.24 (s, 9H, t-butyl group), 1.18 (s, 9H, t-butyl group).

^{1}HNMR spectrum of compound D_2O@1



Reaction of H_2O@1 with triisopropyl phosphite: Compound **H_2O@1** (323 mg, 0.288 mmol) was placed inside an oven dried Schlenk tube fitted with a J. Young tap. The tube was filled with argon gas and distilled toluene (32 ml) was added. The mixture was degassed and the tube charged with argon gas. Triisopropyl phosphite was added under argon then the tube was sealed and heated to 120 °C for 17 hours. The reaction mixture was allowed to cool down to room temperature and concentrated under vacuum. The mixture was purified by flash column chromatography (eluent: toluene) to collect two bands at R_f 0.95 and 0.3 (toluene). The solvent was evaporated to afford respectively **H_2O@3** (106 mg, 34%) and **H_2O@4** (100 mg, 31%) as black solids.

H_2O@3: ^{1}H NMR: (400 MHz, $CDCl_3$, δ): 7.79 (t, J = 7.8 Hz, 2H, H-4 of pyridyl), 7.72 (d, J = 7.8 Hz, 2H, H-2 or H-3 of pyridyl), 7.33 (d, J = 7.8 Hz, 2H, H-2 or H-3 of pyridyl), 6.48 (s, 2H, alkene), 1.37 (s, 18H, t-butyl groups), -6.08 (s, 1.56H, endohedral H_2O).

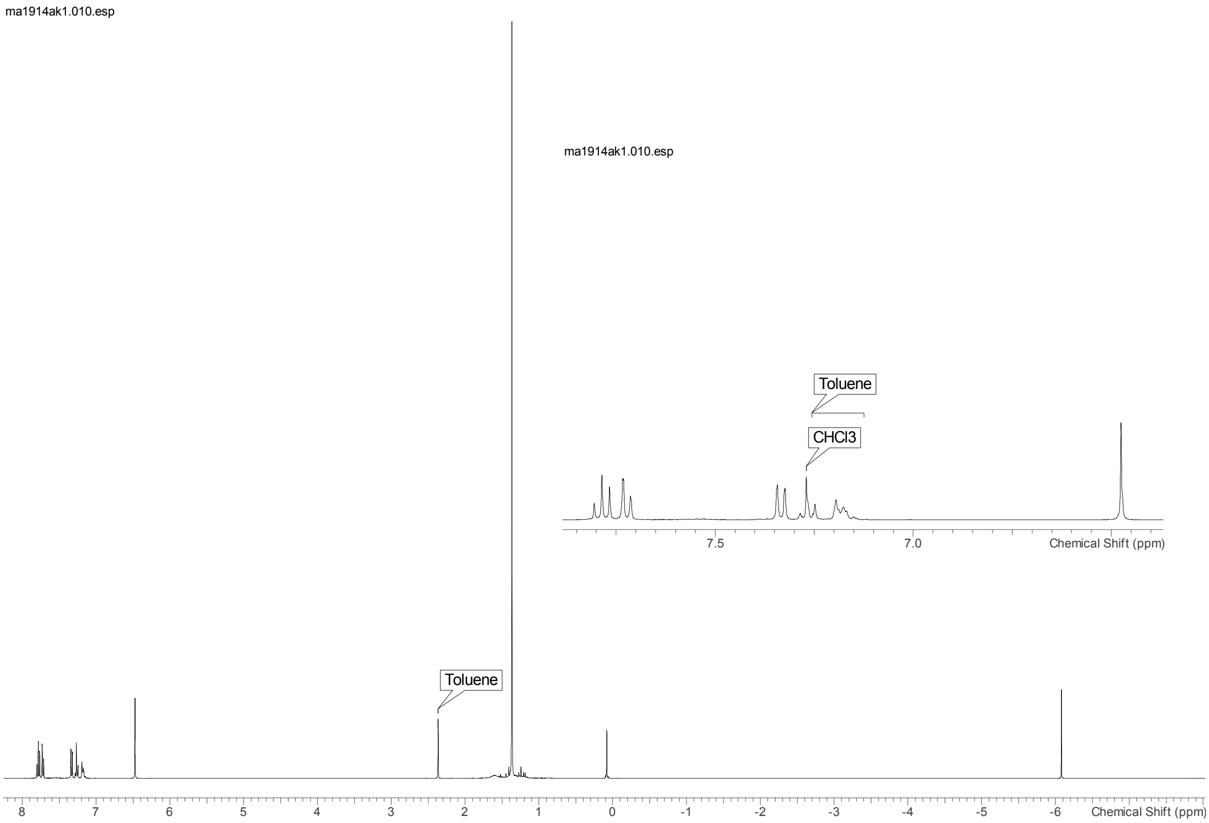
H_2O@3: **^{13}C NMR:** (75 MHz, $CDCl_3$, δ): 168.87, 164.78, 152.47, 149.74, 145.71, 145.64, 145.58, 144.76, 144.56, 144.49, 144.35, 144.33, 144.04, 143.99, 143.97, 143.74, 143.57, 142.12, 141.32, 140.69, 140.65, 140.5, 140.14, 138.33, 137.3, 137.16, 137.08, 136.96, 136.76, 135.28, 135.07, 130.73, 127.47, 120.77, 117.16, 57.48, 37.74, 30.01.

Upon contact with air in solution **H_2O@3** started to transform into **H_2O@5** which was visible as an impurity in the ^{13}C NMR and MS spectra.

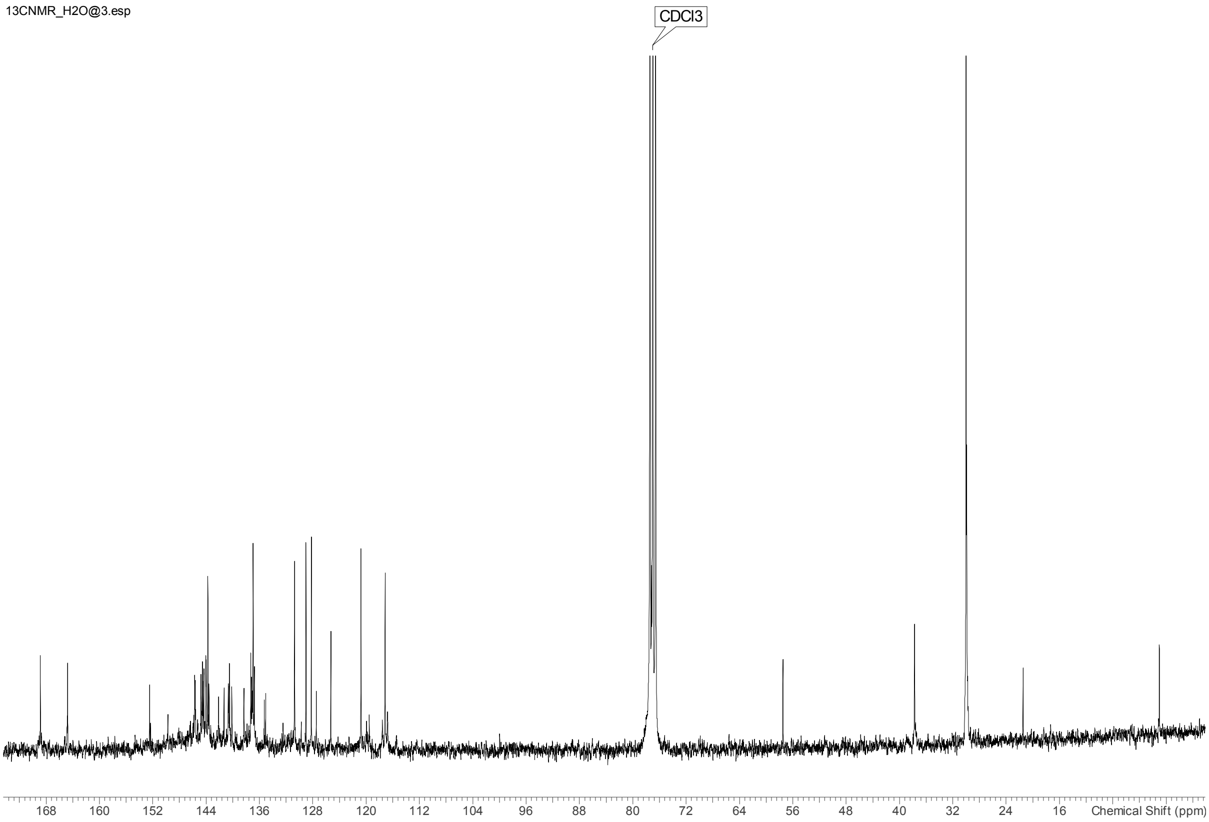
MS-ESI: *m/z* (relative intensity, ion): 1089 (23%, $[M+H]^+$ **H_2O@5**), 1057 (39%, $[M+H]^+$ **H_2O@3**), 536 (100%, $[M+2H]^{2+}$ **5**), 529 (38%, $[M+2H]^{2+}$ **H_2O@3**).

Values agree in accord with reported data.[1]

^{1}HNMR spectrum of compound H_2O@3



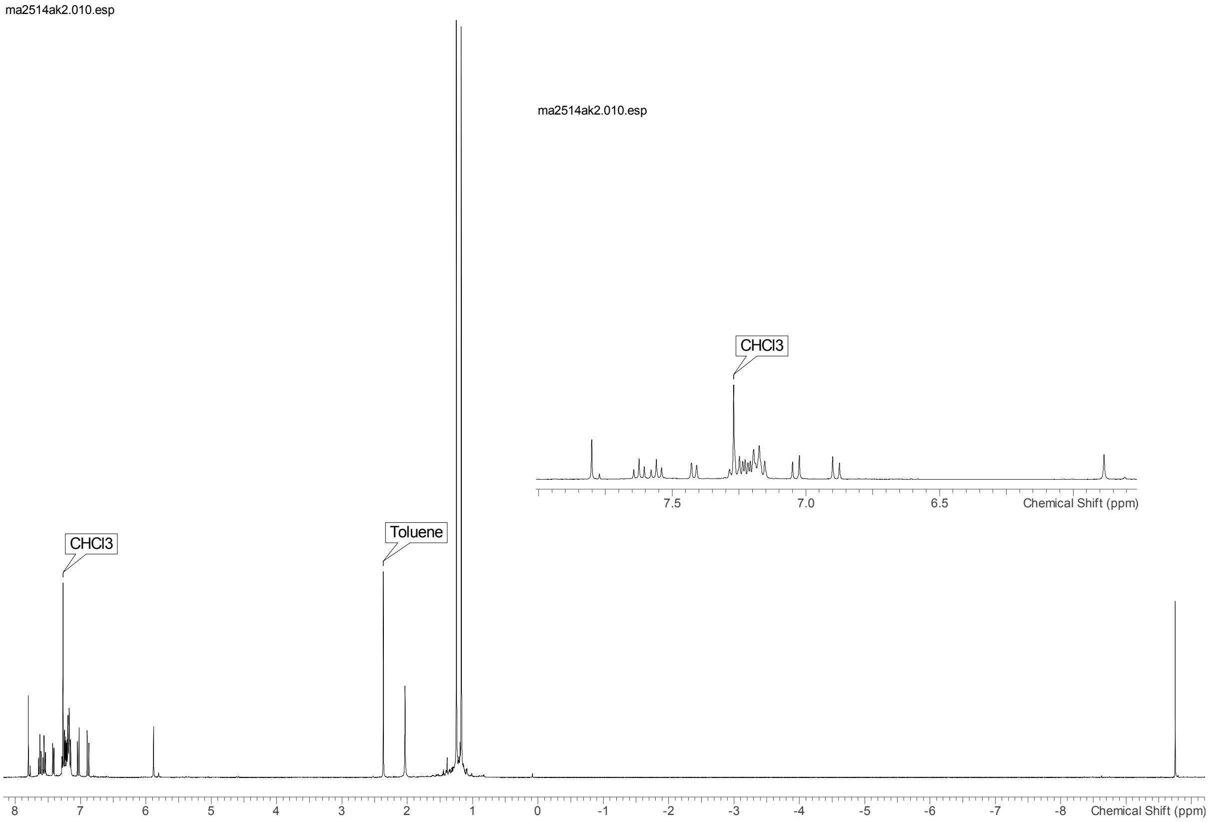
^{13}CNMR spectrum of compound H_2O@3



H_2O@4: **^{1}H NMR:** (400 MHz, $CDCl_3$, δ): 7.80 (s, 1 H), 7.62 (t, J = 7.9 Hz, 1 H), 7.56 (t, J = 7.9 Hz, 1 H), 7.42 (d, J = 7.9 Hz, 1 H), 7.23 (d, J = 7.9 Hz, 1 H), 7.22 (d, J = 7.9 Hz, 1 H), 7.16 (d, J = 7.9 Hz, 1 H), 7.04 (d, J = 10.2 Hz, 1 H), 6.89 (d, J = 10.2 Hz, 1 H), 5.88 (s, 1H), 1.25 (s, 9 H), 1.17 (s, 9 H), -9.75 (s, 1.32 H).

MS-ESI: *m/z* (relative intensity, ion): 1123 (100%, $[M+H]^+$, **H_2O@4**), 1105 (23%, $[M+H]^+$, empty **4**)

^{1}HNMR spectrum of compound $H_2O@4$



Preparation of 4 from 1: Compound **1** (30 mg, 0.027 mmol) was placed inside a 5 ml Schlenk tube fitted with a Rotaflo valve under argon atmosphere. Distilled toluene (3 ml) was added. Once the substrate had dissolved trisopropyl phosphite (0.450 ml) was added. The mixture was reacted at room temperature for 24 hours and then purified by flash column chromatography (eluent: toluene). The fractions containing the spot located at R_f 0.3 (toluene) were collected and evaporated to afford compound **4** as a black solid (22 mg, 76%).

^{1}H NMR: (300 MHz, $CDCl_3$, δ): 7.76 (s, 1 H), 7.62 (t, J = 7.9 Hz, 1 H), 7.55 (t, J = 7.9 Hz, 1 H), 7.42 (d, J = 7.9 Hz, 1 H), 7.23 (d, J = 7.9 Hz, 1 H), 7.22 (d, J = 7.9 Hz, 1 H), 7.16 (d, J = 7.9 Hz, 1 H), 7.03 (d, J = 10.2 Hz, 1 H), 6.88 (d, J = 10.2 Hz, 1 H), 5.20 (s broad, 1H), 1.25 (s, 9 H), 1.17 (s, 9 H).

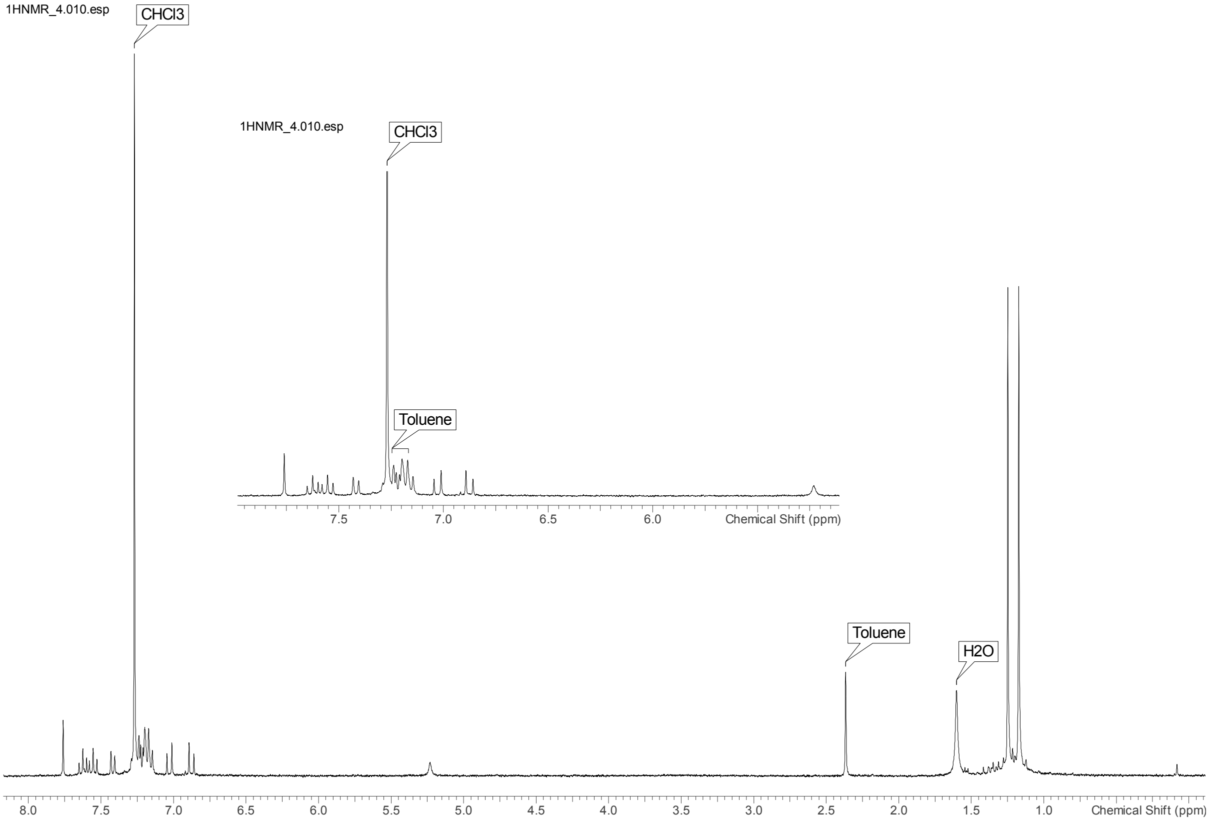
^{13}C NMR: (75 MHz, $CDCl_3$, δ): 198.63, 194.6, 168.77, 168.32, 164.25, 162.91, 152.98, 150.15, 149.84, 149.66, 149.26, 149.24, 148.89, 148.74, 148.58, 148.38, 148.35, 147.8, 147.65, 147.44, 147.19, 147.05, 146.94, 146.9, 146.57, 146.16, 145.96, 145.93, 145.55, 145.16, 144.37, 143.96, 143.86, 143.79, 143.38, 142.29, 141.8, 141.28, 141.15, 140.98, 140.68, 139.92, 138.7, 138.65, 138.45, 137.12, 136.95, 136.86, 136.7, 136.56, 135.7, 135.47, 134.65, 133.87, 133.5, 132.38, 131.56, 131.24, 130.26, 129.01, 128.2, 127.27, 126.77, 125.27, 119.87, 119.79, 117.38, 116.8, 94.91, 80.87, 59.26, 54.73, 37.77, 37.56, 29.97, 29.83.

IR: (ν, cm^{-1}) 2958, 1765, 1695, 1573, 1516, 1445.

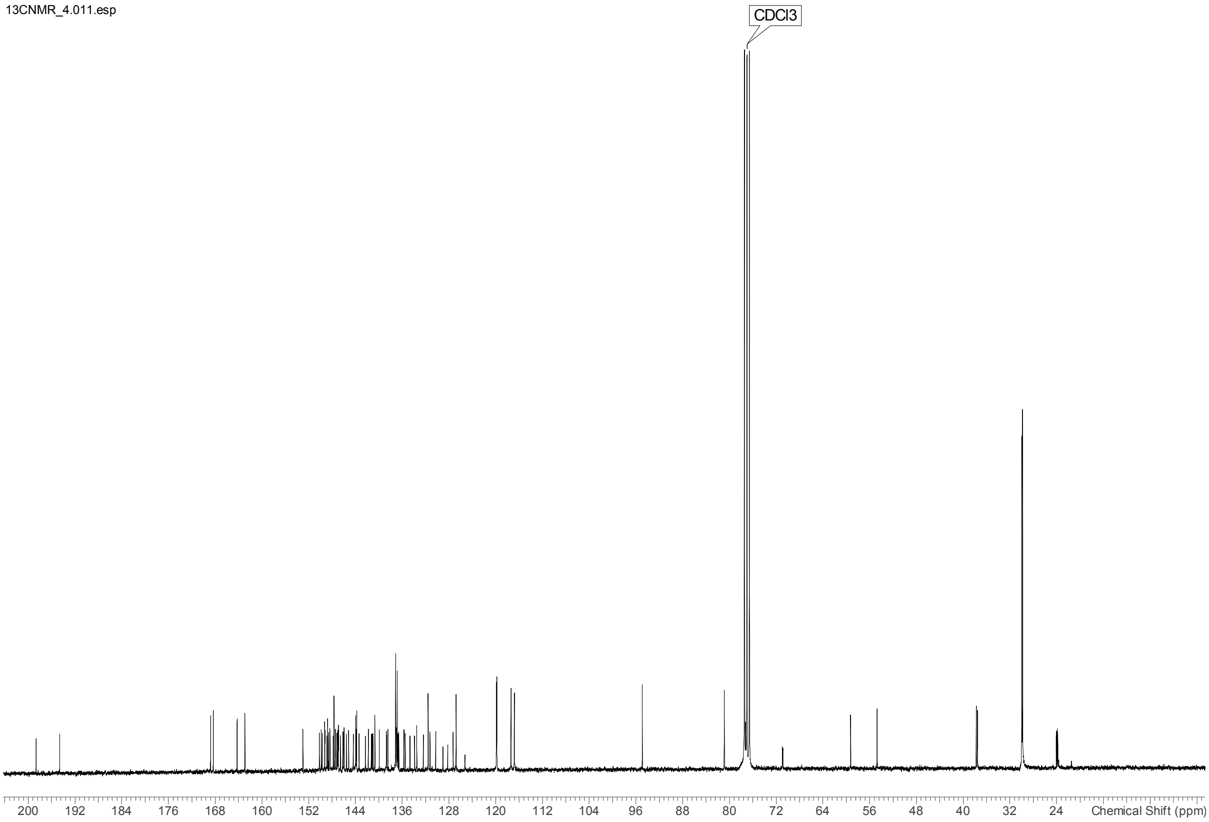
UV/Vis: CH_2Cl_2 λ_{max} (ε) = 257.11 (71971), 325.36 (30794).

MS-ESI: *m/z* (relative intensity, ion):1105 (17%, $[M+H]^+$ **4**), 167 (100%).

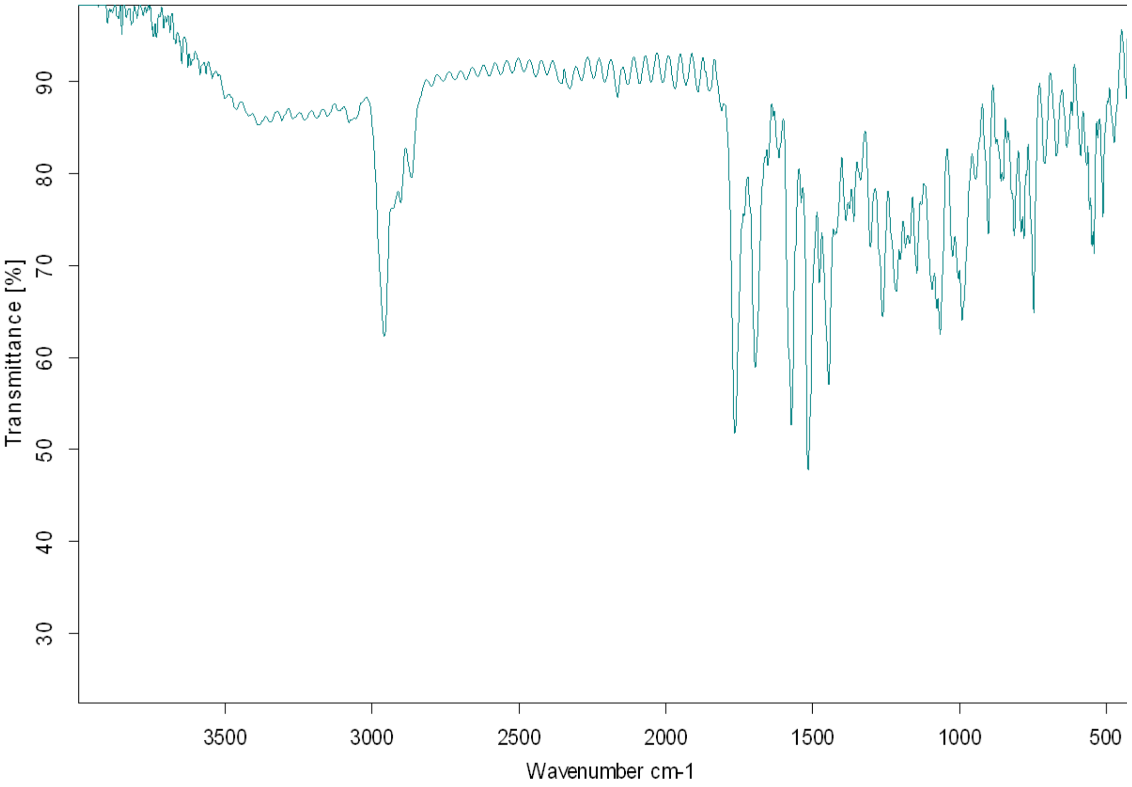
^{1}HNMR spectrum of compound 4



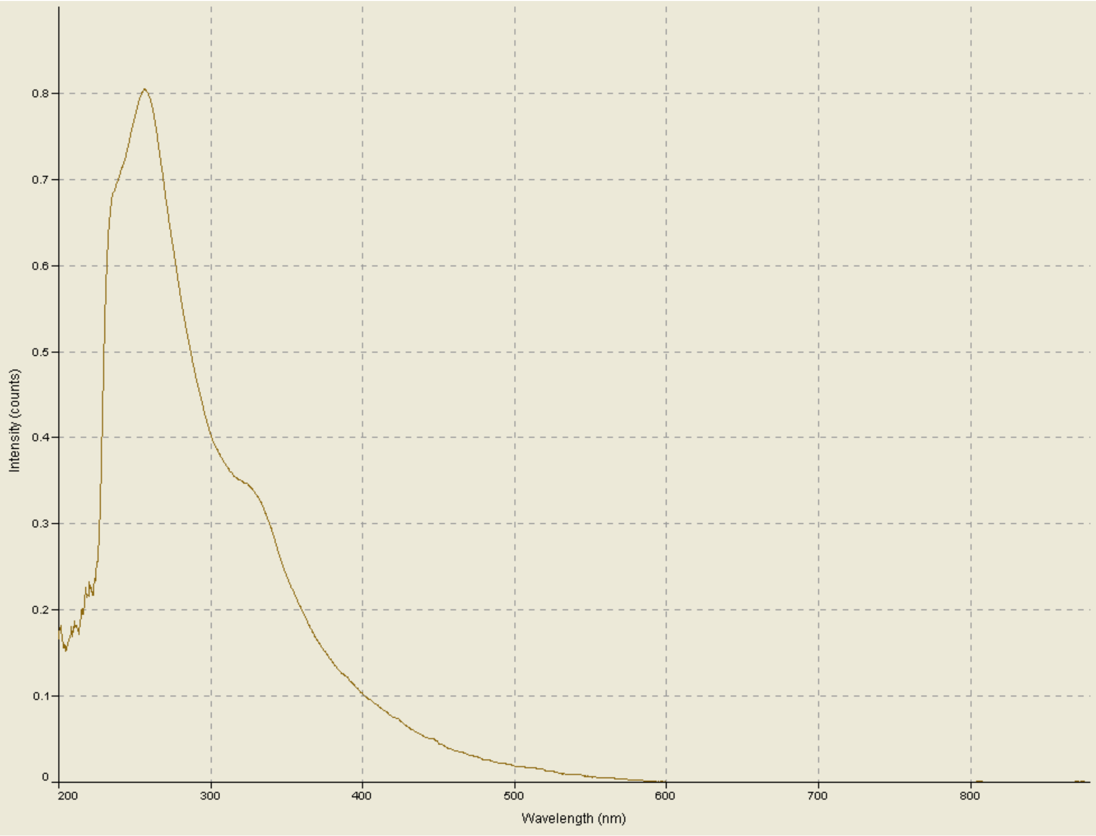
^{13}CNMR spectrum of compound 4



IR spectrum of compound 4

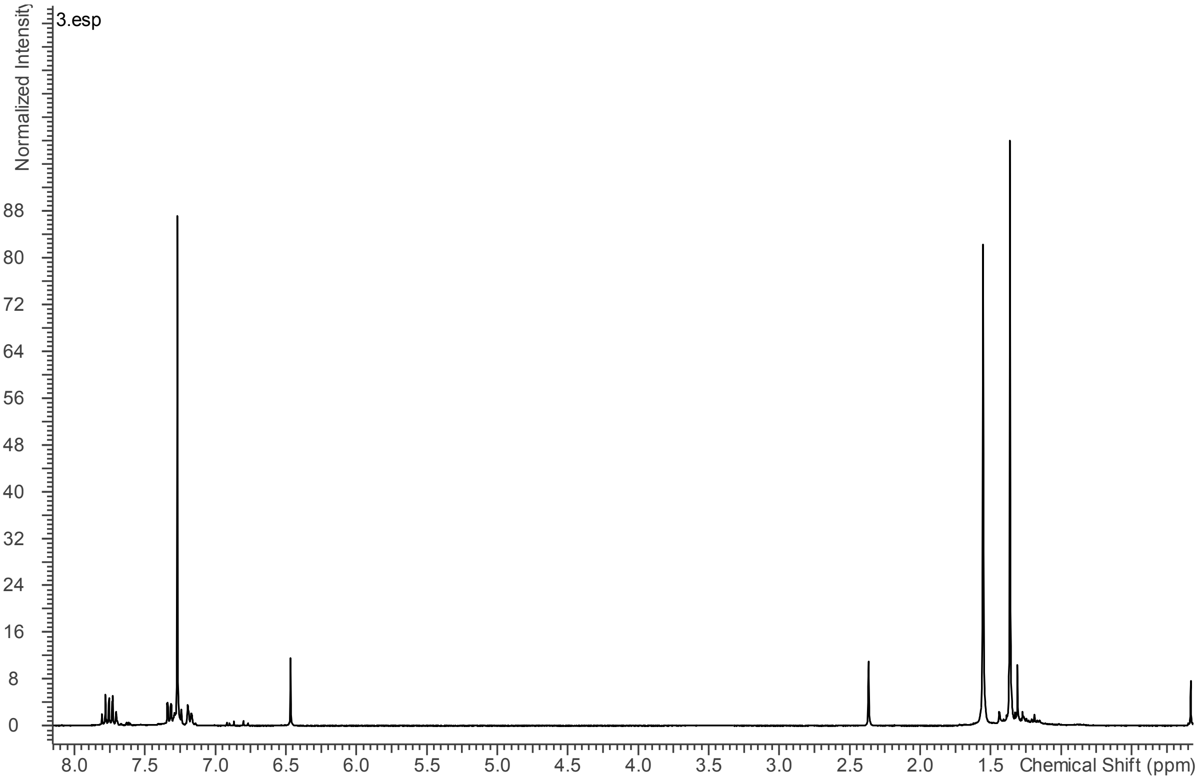


UV spectrum of compound 4



Reactivity of 2 towards triisopropyl phosphite at room temperature: A solution of compound **2** (10 mg, 0.09 mmol) in distilled toluene (1 ml) was placed inside a 5 ml Schlenk tube fitted with a J.Young tap. Triisopropyl phosphite (0.15 ml) was added under argon and the reaction was left at room temperature for 24 hours. The reaction mixture was purified by flash column chromatography (toluene) to collect a fraction at R_f 0.95. The solvent was evaporated to dryness to afford compound **3** as a black solid (3 mg, 33%).

^{1}HNMR spectrum of compound 3



^{1}H NMR: (300 MHz, $CDCl_3$, δ): 7.79 (t, J = 7.6 Hz, 2H), 7.72 (d, J = 7.6 Hz, 2H), 7.33 (d, J = 7.6 Hz, 2H), 6.47 (s, 2H), 1.37 (s, 18H).

MS-ESI: *m/z* (relative intensity, ion): 1039 (15%, $[M+H]^+$ empty **3**), 173 (100).

H_2O@5: Compound **H_2O@1** (73 mg, 0.064 mmol) and triphenylphosphine (269 mg, 1.03 mmol) were placed inside a round bottom flask equipped with a straight condenser. The system was put under argon atmosphere. Distilled toluene (6 ml) was added. Once a homogeneous solution was afforded the tube was placed inside an oil bath preheated to 120 °C for 15 hours. The reaction mixture was then concentrated and purified by flash column chromatography (eluent 1:1 toluene/hexane to remove excess phosphine then toluene to collect the product). The fractions containing the spot at R_f 0.48 (toluene) were collected and evaporated to afford **H_2O@5** as a black solid (64 mg, 84%).

^{1}H NMR: (300 MHz, $CDCl_3$, δ): 7.69 (t, J = 7.8 Hz, 1H, H-4 of pyridyl), 7.66 (t, J = 7.8 Hz, 1H, H-4 of pyridyl) 7.52 (d, 1H, J = 7.8 Hz, H-2 or H-3 of pyridyl) 7.40 (d, 1H, J = 7.8 Hz, H-2 or H-3 of pyridyl), 7.25-7.21 (m, 2H, H-2 or H-3 of pyridyl), 7.21-7.17 (m, 2H, H of alkene) 1.27 (s, 9H, t-butyl), 1.19 (s, 9H, t-butyl), -8.78 (s, 1.56H, endohedral H_2O).

^{13}**CNMR:** (125 MHz, odcb-d4, δ): 199.09, 191.38, 168.83, 168.53, 165.34, 162.34, 154.52, 150, 148.66, 147.78, 147.69, 147.57, 147.3, 146.43, 146.25, 146.16, 146.12, 145.98, 145.66, 145.58, 145.54, 145.49, 145.37, 145.3, 144.93, 144.54, 144.51, 144.43, 144.1, 143.78, 143.72, 142.57, 142.52, 141.99, 141.84, 141.73, 141.52, 140.69, 140.35, 140.2, 140.17, 140.08, 139.99, 139.47, 139.38, 139.29, 138.52, 138.35, 138.24, 137.33, 137.27, 137.15, 136.39, 135.85, 135.64, 134.8, 133.63, 132.66, 132.54, 132.48, 132.1, 131.03, 130.22, 129.01, 128.19, 127.37, 125.31, 120.09, 119.7, 117.47, 116.76, 61.07, 54.81, 37.61, 37.52,29.97 29.86.

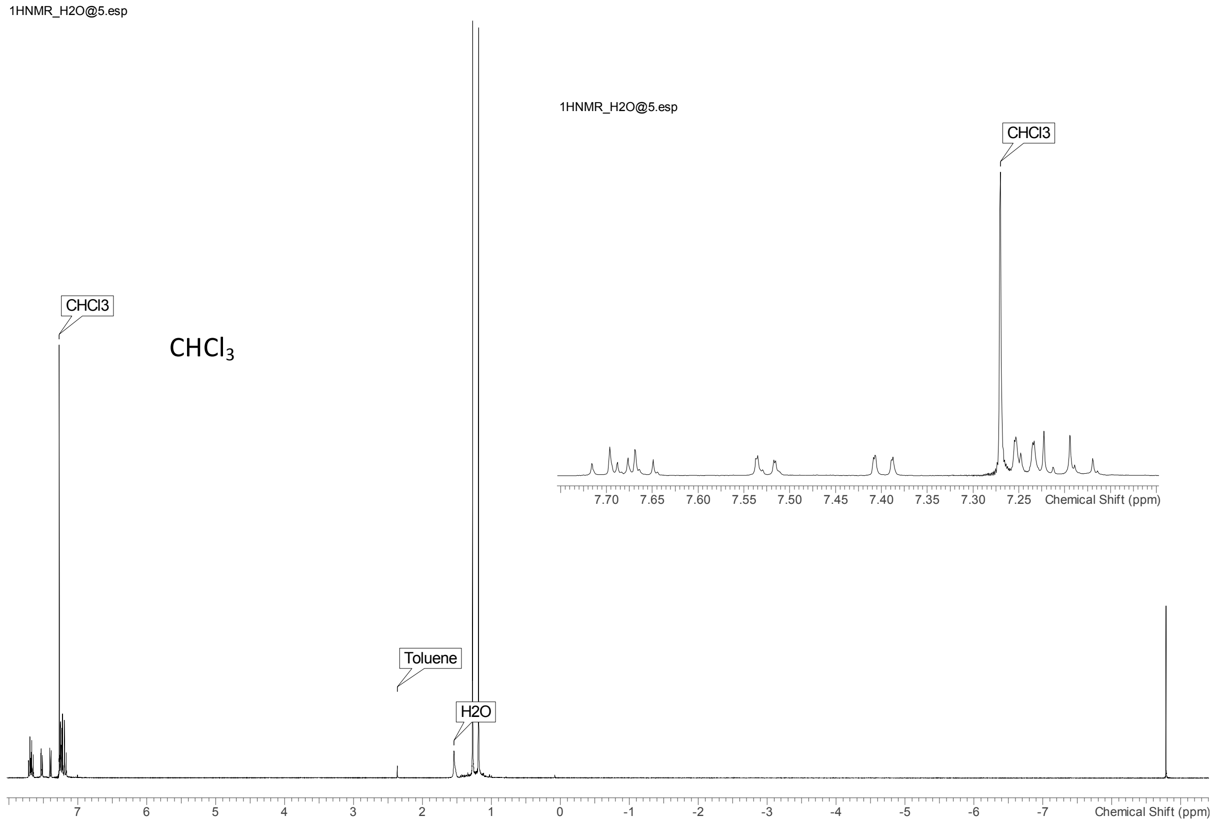
In the ^{13}C NMR spectrum some peaks show a lower intensity peak located up to 0.1 ppm lower shift attributable to empty **5**.

IR: (ν, cm^{-1}) 2956, 1745, 1697, 1571, 1477, 1444.

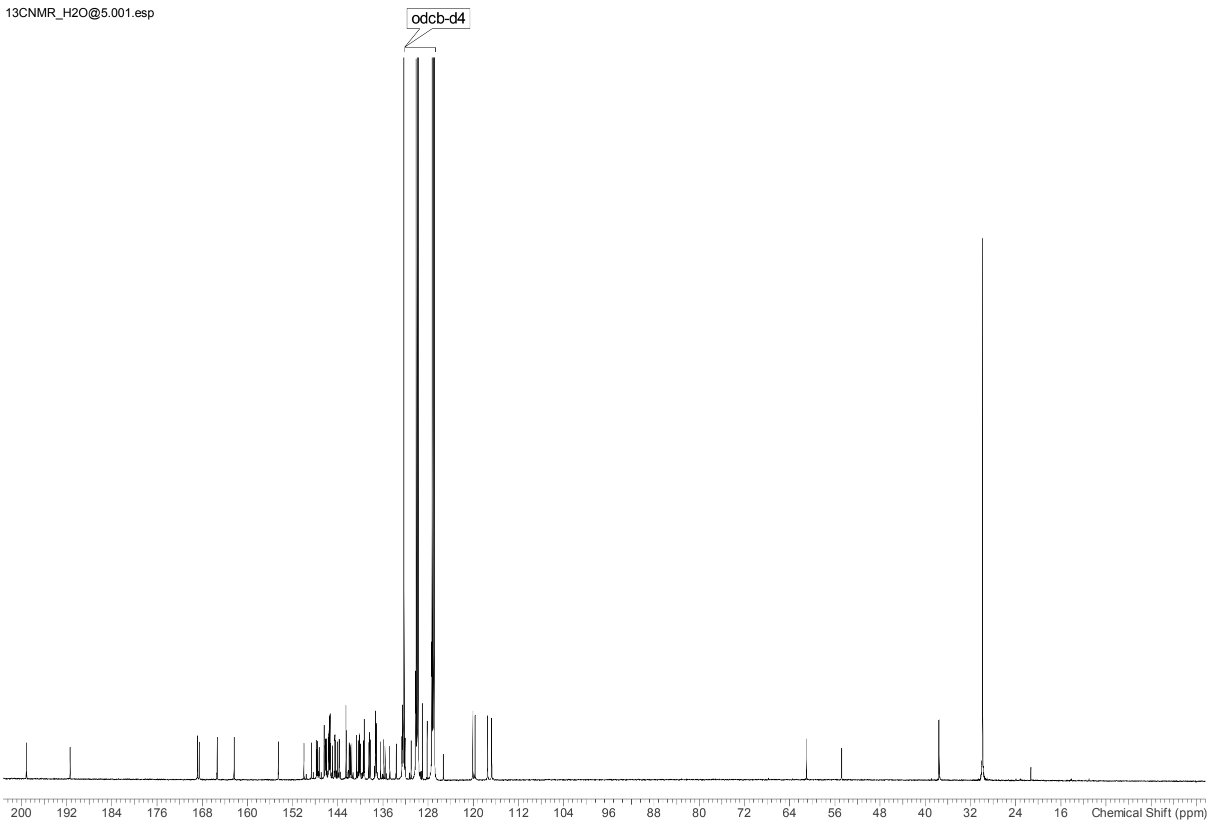
UV/Vis: CH_2Cl_2 λ_{max} (ε) = 257.11(103983), 324.62 (45315).

MS-ESI: *m/z* (relative intensity, ion): 1152 (17% [M+MeCN+Na]$^+$), 1089 (100%, [M+H]$^+$ **H_2O@5**), 1071 (16% [M+H]$^+$ empty **5**).

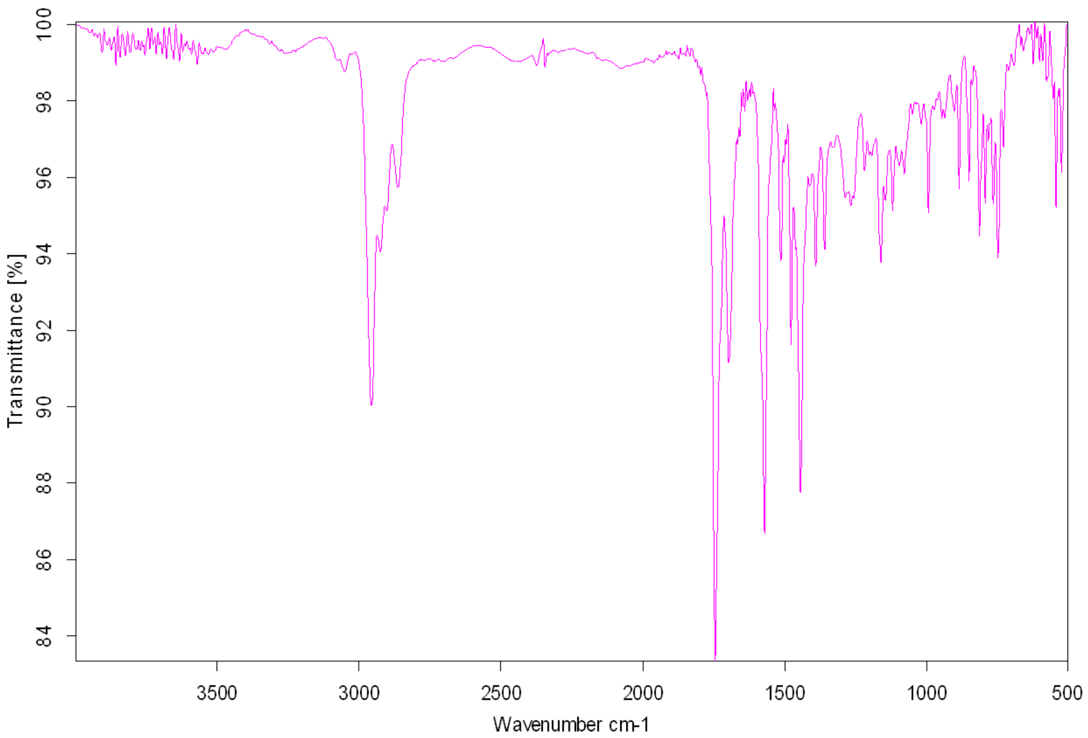
^{1}HNMR spectrum of compound H_2O@5



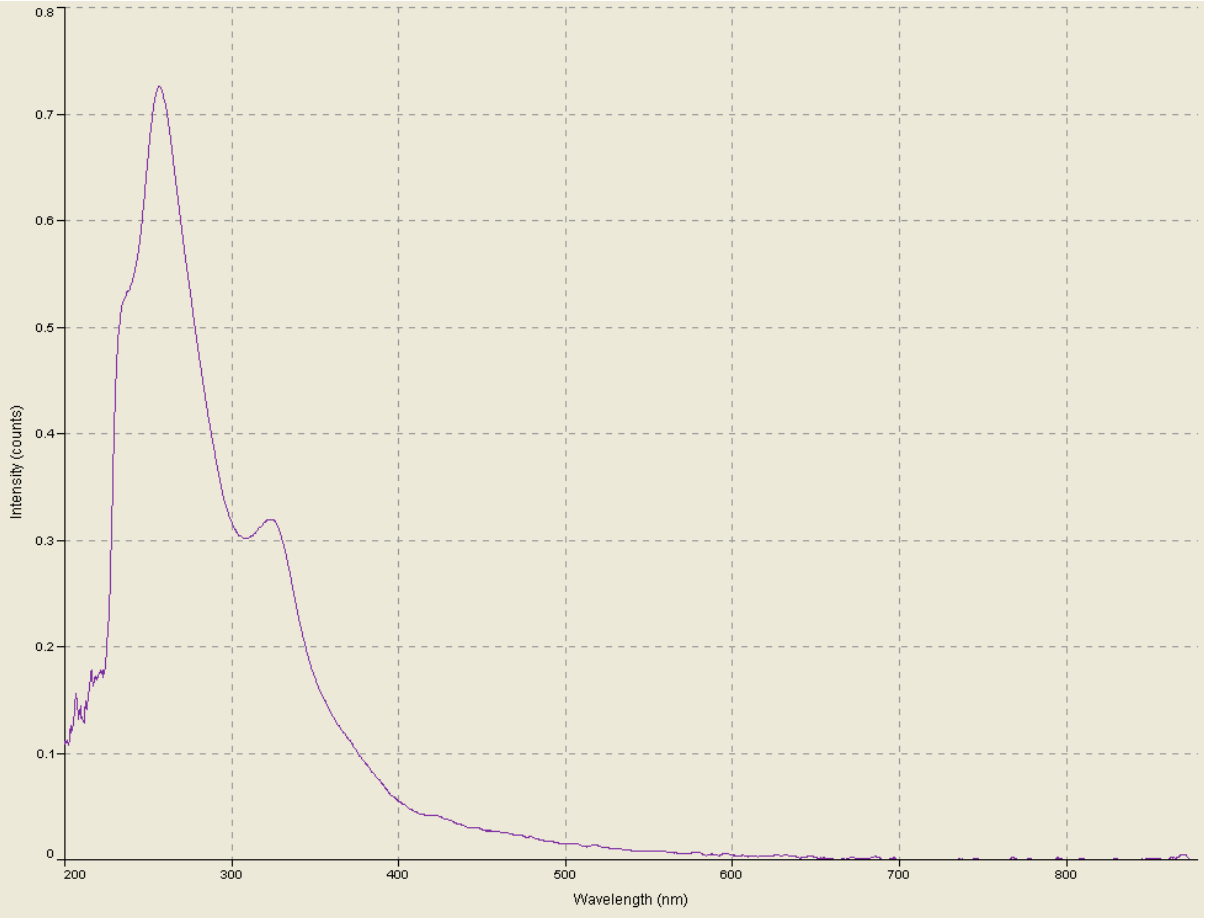
^{13}CNMR spectrum of compound H_2O@5



IR spectrum of compound H_2O@5



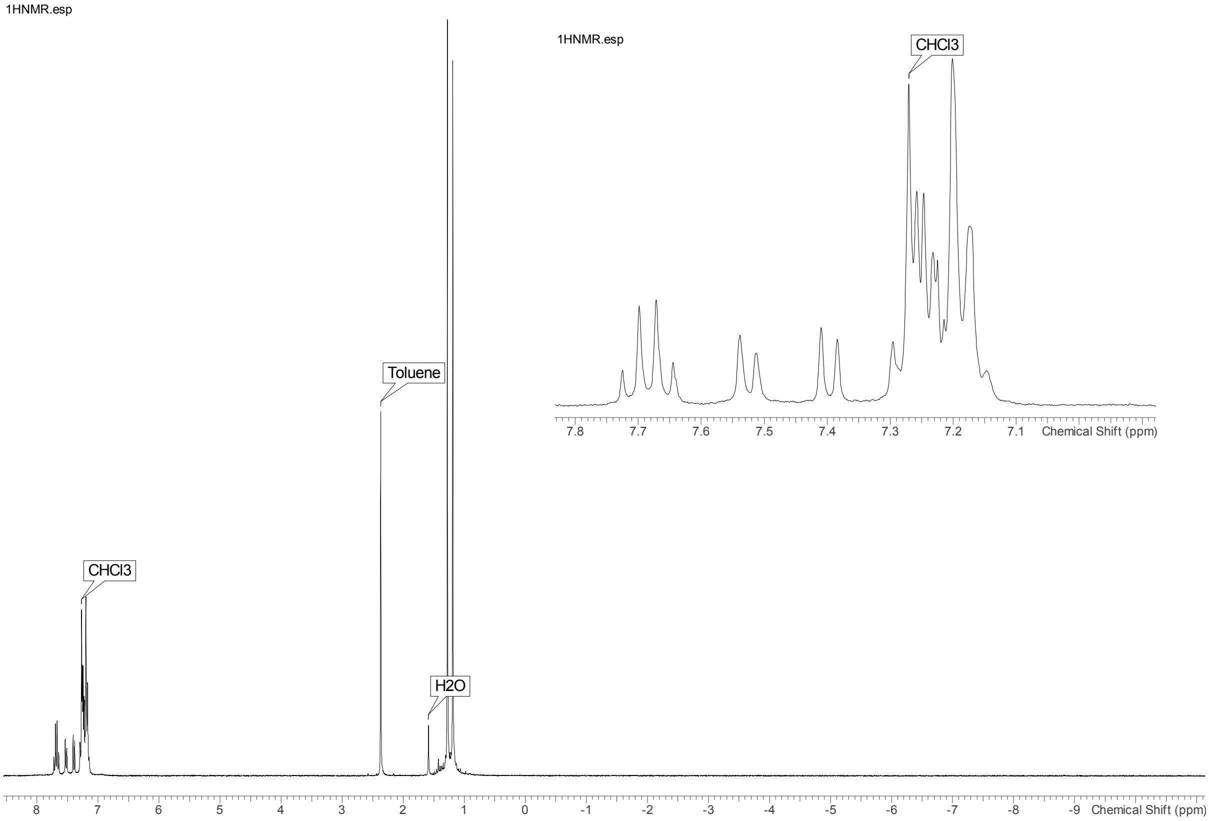
UV spectrum of compound H_2O@5



An analogous experiment run on **D_2O@1** afforded **D_2O@5** as a black solid. All spectra look identical to those of **H_2O@5**, except for the absence of the signal at δ -8.78 ppm in the ^{1}H NMR spectrum.

^{1}H NMR: (300 MHz, $CDCl_3$, δ): 7.69 (t, J = 7.8 Hz, 1H, H-4 of pyridyl), 7.66 (t, J = 7.8 Hz, 1H, H-4 of pyridyl) 7.52 (d, 1H, J = 7.8 Hz, H-2 or H-3 of pyridyl) 7.40 (d, 1H, J = 7.8 Hz, H-2 or H-3 of pyridyl), 7.25-7.21 (m, 2H, H-2 or H-3 of pyridyl), 7.21-7.17 (m, 2H, H of alkene) 1.28 (s, 9H, t-butyl), 1.19 (s, 9H, t-butyl).

^{1}HNMR spectrum of compound $D_2O@5$

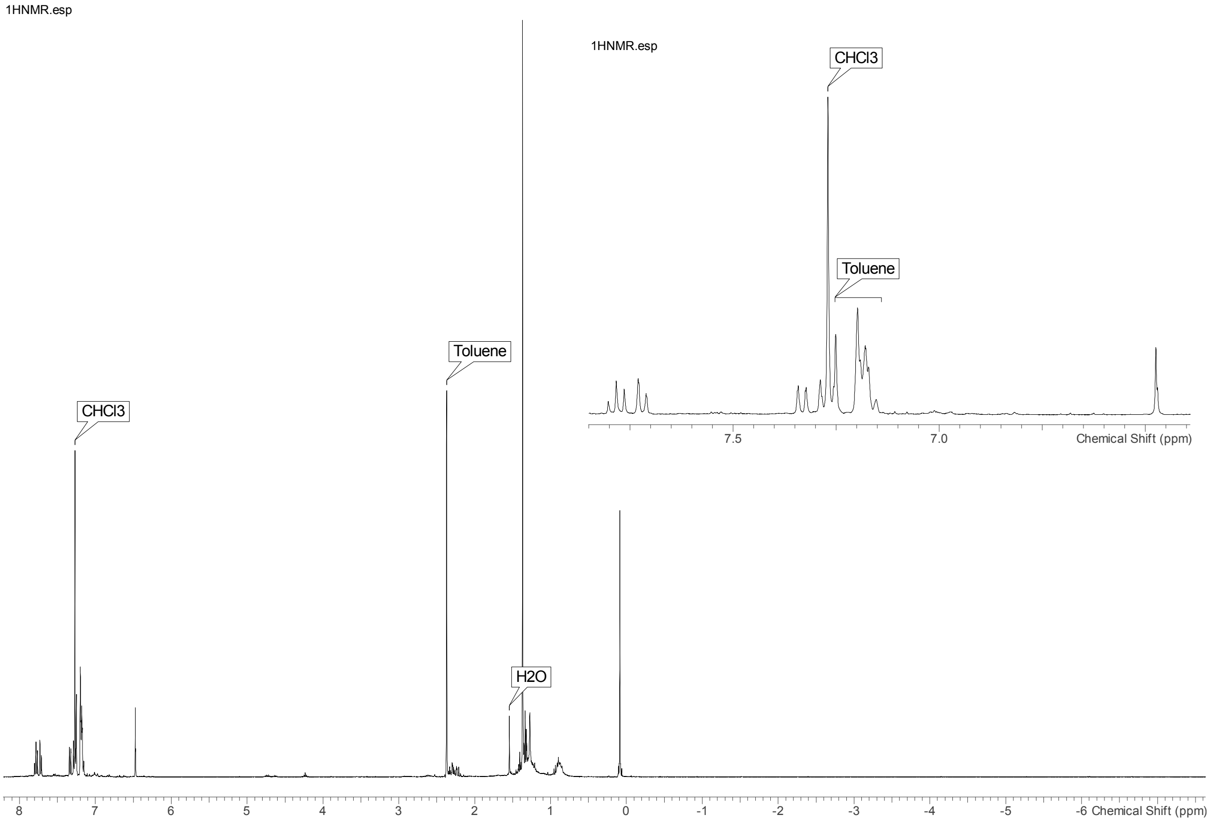


Preparation of $H_2O@3$ from $H_2O@5$ Compound **$H_2O@5$** (420 mg, 0.386 mmol) was placed inside a round bottom flask connected to a straight condenser under argon atmosphere. Distilled toluene was added (42 ml) followed by triisopropyl phosphite (1.5 ml). The reaction mixture was refluxed for 26 hours and then allowed to cool down to room temperature. The mixture was concentrated and purified by flash column chromatography (eluent: toluene). The fractions containing the spot at R_f 0.95 were collected and evaporated to dryness to afford **$H_2O@3$** as a black solid (349 mg, 84%). Data as above.

An analogous experiment run on **$D_2O@5$** afforded **$D_2O@3$** as a black solid. All spectra look identical to those of **$H_2O@3$**, except for the absence of the signal at δ -6.08 ppm in the ^{1}H NMR spectrum.

$D_2O@3$: ^{1}H NMR: (400 MHz, $CDCl_3$, δ): 7.78 (t, J = 7.8 Hz, 2H, H-4 of pyridyl), 7.72 (d, J = 7.8 Hz, 2H, H-2 or H-3 of pyridyl), 7.33 (d, J = 7.8 Hz, 2H, H-2 or H-3 of pyridyl), 6.47 (s, 2H, alkene), 1.37 (s, 18H, t-butyl groups).

^{1}HNMR spectrum of compound D_2O@3



H_2@1: Compound **1** (50 mg) was placed inside a glass tube; Activated 3Å molecular sieves (1.4 g) and o-dichlorobenzene were added (12 ml). The tube was placed inside a Parr steel reactor. The reactor was sealed and then flushed by pressurising to 10 atm of hydrogen gas and then releasing the pressure (3 times). The reactor was then charged with hydrogen (120 atm) and the bottom part was immersed inside an oil bath preheated to 120 °C for 24 hours. After 20 hours the bomb was allowed to cool down to room temperature and the pressure was released. The reaction mixture was poured over a short silica column packed with toluene and eluted first with toluene to remove the o-dichlorobenzene and then with a 15% AcOEt in toluene solution to collect **H_2@1** as a black solid (46 mg, 91%, 60% filling factor by ^{1}H NMR).

^{1}H-NMR: (400 MHz, $CDCl_3$, δ): 7.64 (t, J = 7.8 Hz, 1H, H-4 or H-4’ of pyridyl), 7.57 (t, J = 7.8 Hz, 1H, H-4 or H-4’ of pyridyl), 7.50 (d, J = 7.8 Hz, 1H, H-3 or H-3’ of pyridyl), 7.21 (d, J = 7.8 Hz, 2H, H-5 and H-5’ of pyridyl), 7.16 (d, J = 7.8 Hz, 1H, H-3 or H-3’ of pyridyl), 7.11 (d, J = 10.0 Hz, 1H, vinylene), 7.01 (d, J = 10.0 Hz, 1H, vinylene), 6.20 (br s, 1H, OH), 5.96 (br s, 1H, OH), 1.24 (s, 9H, t-butyl group), 1.18 (s, 9H, t-butyl group), -7.17 (s, 1.22H, endohedral H_2).

^{13}CNMR: (125 MHz, odcb-d_4, δ): 198.88, 194.28, 168.7, 168.3, 164.54, 162.9, 153.68, 149.86, 149.33, 149.03, 148.86, 148.25, 147.72, 147.43, 147.01, 146.6, 146.42, 146.01, 145.18, 144.98, 144.75, 144.39, 144.3, 144.25, 144.16, 143.46, 143.39, 142.64, 142.51, 142.19, 142.11, 141.93, 141.07, 141.02, 140.61, 140.37, 140.19, 140.06, 139.82, 137.91, 137.18, 137.08, 137.02, 136.24, 136.14, 135.82, 135.62, 134.85, 134.54, 133.89, 133.83, 135.82, 135.62, 134.85, 134.54, 133.89, 133.83, 131.77, 131.62, 131.24, 130.94, 130.6, 129.01, 128.75, 119.88, 110.28, 96.69, 59.75, 54.88, 37.67, 37.46, 29.95, 29.81.

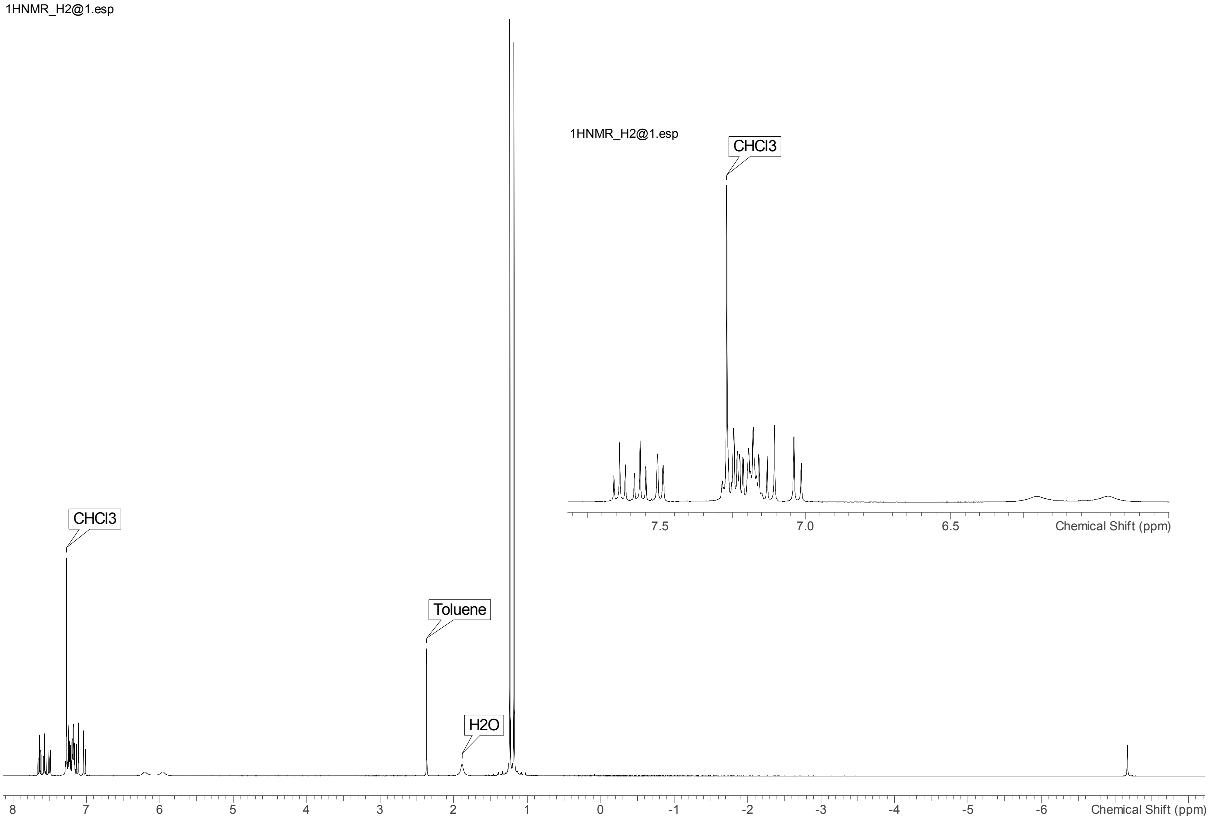
Peaks due to empty **1** were observed up to 0.1 ppm lower shift than those due to **H2@1**.

IR: (ν, cm^{-1}) 2958, 1760, 1693, 1572, 1515, 1444.

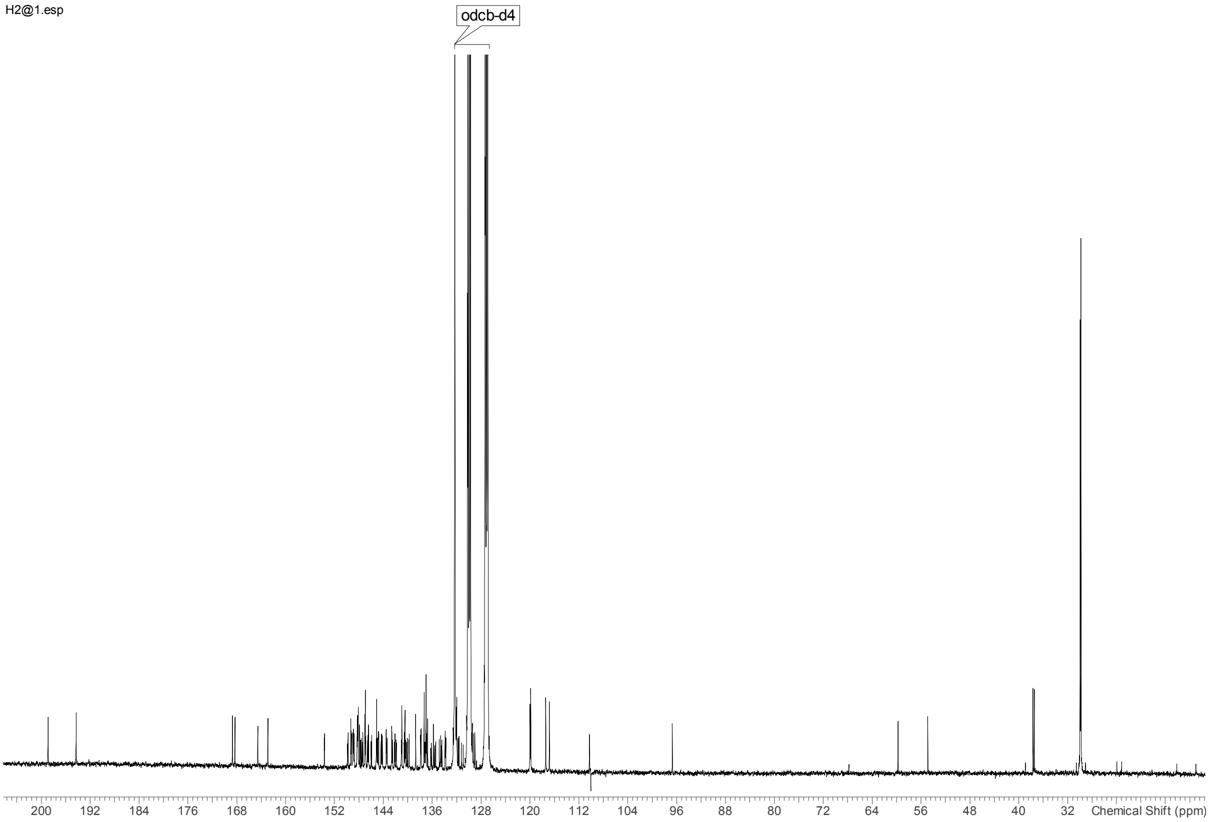
UV/Vis: CH_2Cl_2 λ_{max} (ε) = 256.73 (71870).

MS-ESI: *m/z* (relative intensity, ion): 1123 (90%, $[M+H]^+$ **H_2@1**), 1121 (100%, $[M+H]^+$ empty **1**).

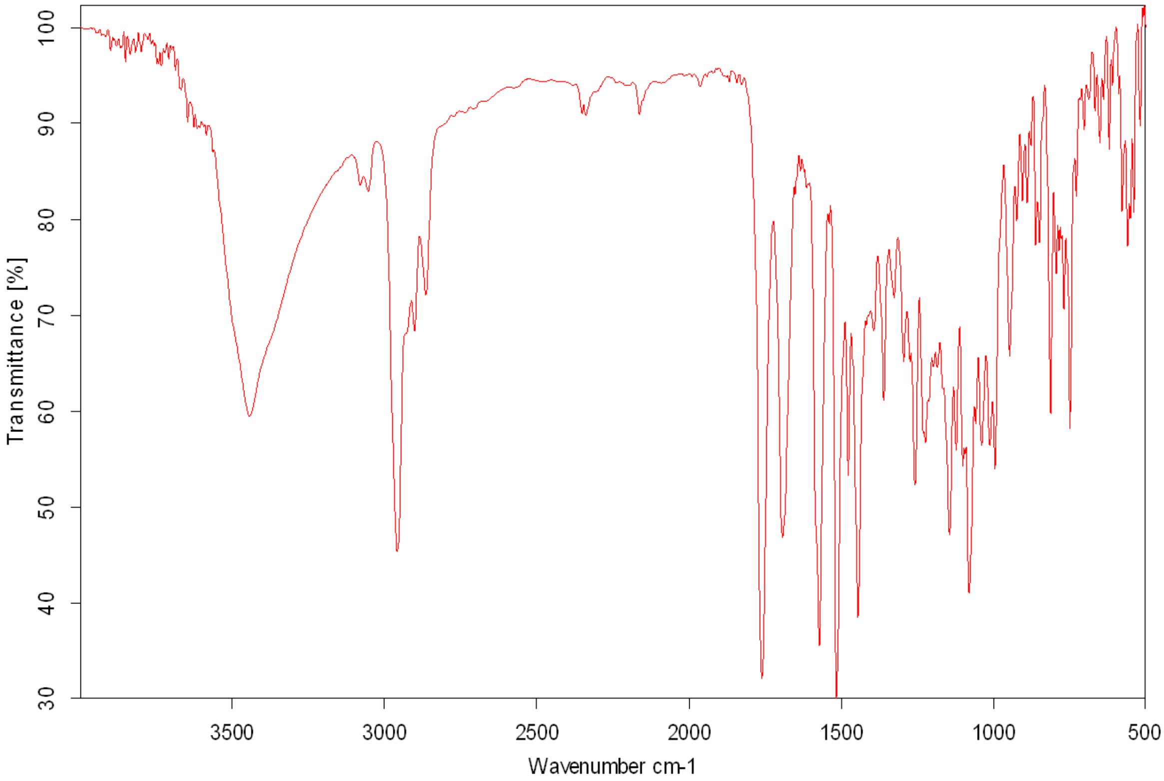
^{1}HNMR spectrum of compound H_2@1



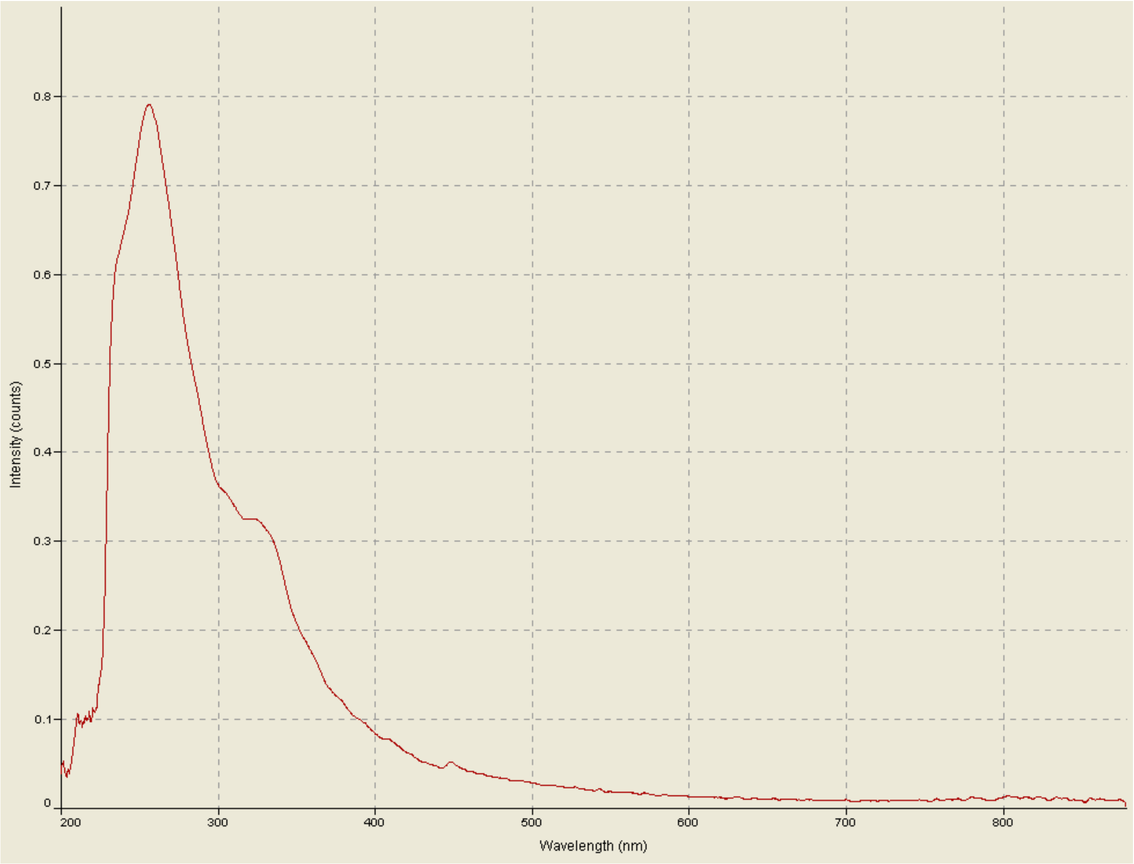
^{13}CNMR spectrum of compound $H_2@1$



IR spectrum of compound $H_2@1$



UV spectrum of compound H_2@1



H_2@5: Compound **1** (200 mg 0.178 mmol) was placed inside a glass tube. Activated 3Å molecular sieves were added (~1 g) followed by o-dichlorobenzene (10 ml). The tube was placed inside a Parr reactor. The reactor was sealed and purged by pressurising it with 10 atm of hydrogen and then releasing the pressure (3 times). The reactor was then charged with hydrogen (120 atm) and the bottom part was immersed inside an oil bath preheated to 120 °C for 24 hours. The reactor was allowed to cool down to room temperature and depressurised then triphenylphosphine (730 mg) was added. The reactor was pressurised again and heated to 120 °C for 17 hours. The reaction mixture was cooled to room temperature and the pressure released. The reaction mixture was then concentrated and purified by flash column chromatography (eluent 1:1 toluene/hexane to remove excess phosphine then toluene to collect the product) to afford **H_2@5** as a black solid (161 mg, 84%, 60% incorporation of H_2 by NMR).

^{1}H-NMR: (300 MHz, $CDCl_3$, δ): 7.69 (t, J = 7.8 Hz, 1H, H-4 of pyridyl), 7.66 (t, J = 7.8 Hz, 1H, H-4 of pyridyl) 7.52 (d, 1H, J = 7.8 Hz, H-2 or H-3 of pyridyl) 7.40 (d, 1H, J = 7.8 Hz, H-2 or H-3 of pyridyl), 7.25-7.21 (m, 2H, H-2 or H-3 of pyridyl), 7.21-7.17 (m, 2H, H alkene) 1.27 (s, 9H, t-butyl), 1.19 (s, 9H, t-butyl), -5.69 (s, 1.22H, endohedral H_2).

^{13}C-NMR: (125 MHz, odcb-d_4, δ): 199.21, 191.46, 168.83, 168.51, 165.45, 162.43, 154.61, 149.69, 148.41, 148.33, 147.54, 147.51, 147.34, 147.04, 146.52, 146.42, 146.33, 146.15, 145.96, 145.72, 145.68, 145.65, 145.57, 145.49, 145.43, 145.39, 145.24, 145.05, 144.78, 144.64, 144.36, 144.28, 143.93, 143.63, 142.55, 142.34, 142.19, 141.93, 141.69, 141.64, 141.37, 140.7, 140.66, 140.31, 140.16, 139.9, 139.73, 139.53, 139.37, 139.31, 138.43, 137.5, 137.32, 137.12, 137.06, 136.23, 136.09, 134.8, 134.77, 133.86, 120.09, 119.71, 117.45, 116.73, 61.04, 54.85, 37.62, 37.53, 29.86, 29.83,.

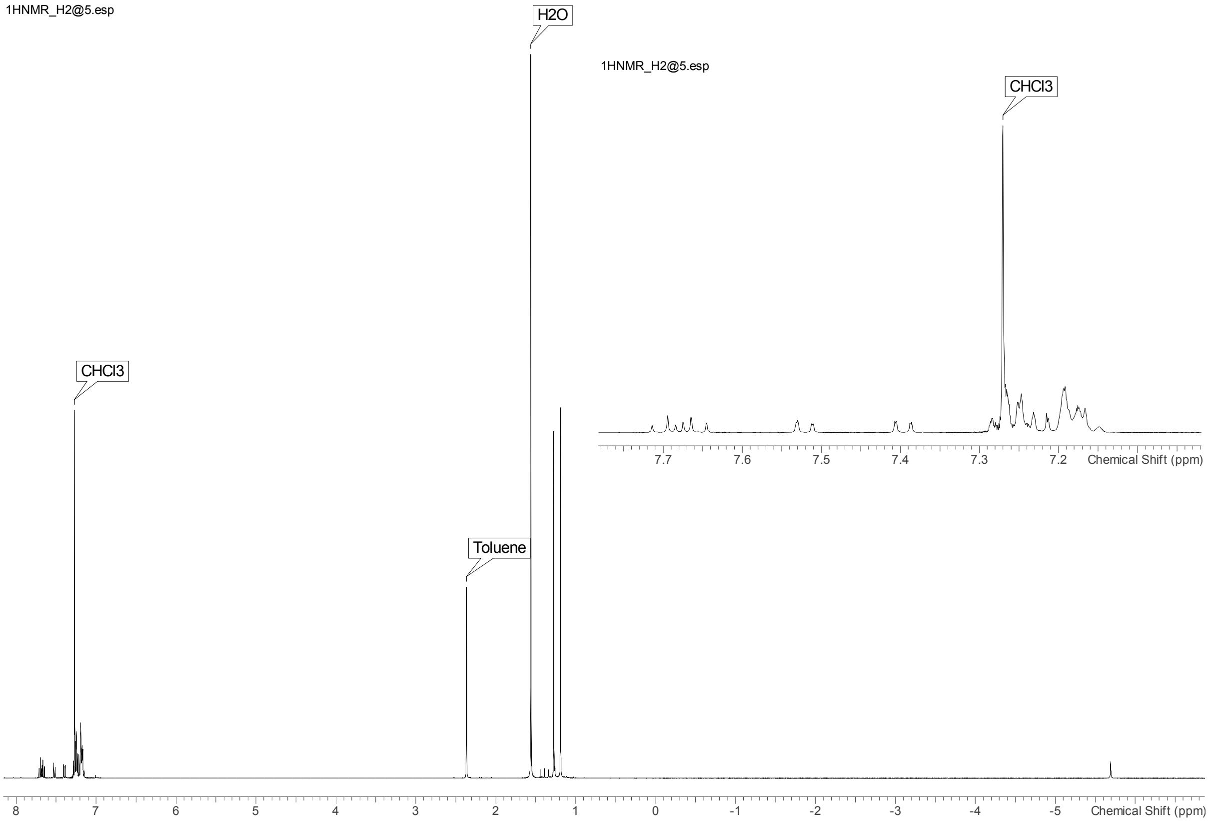
In the ^{13}C NMR spectrum some peaks show a lower intensity peak located ~0.1 ppm apart attributable to empty **5**.

IR: (ν, cm^{-1}) 2958, 1745, 1697, 1571, 1444.

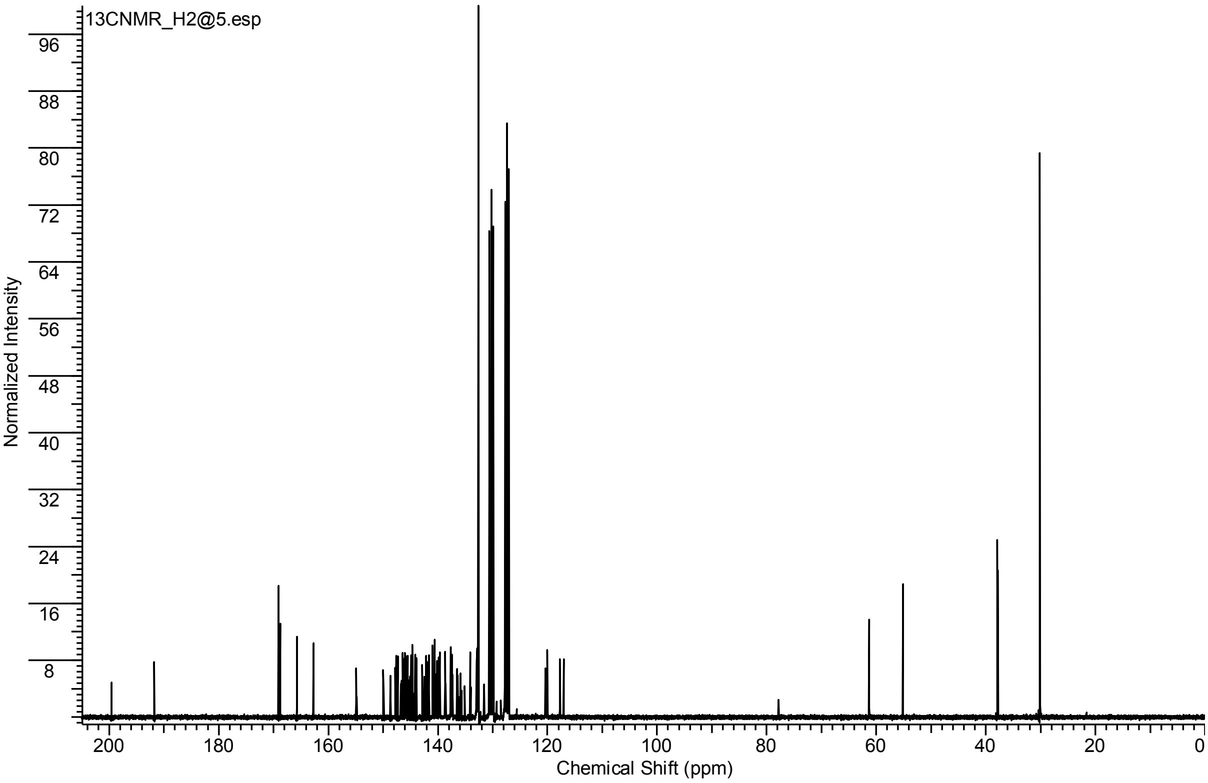
UV/Vis: CH_2Cl_2 λ_{max} (ε) = 257.11 (102326), 323.88 (42892).

MS-ESI: *m/z* (relative intensity, ion): 1073.4 (99%, $[M+H]^+$ **H_2@5**), 1071.7 (50% $[M+H]^+$ empty **5**)

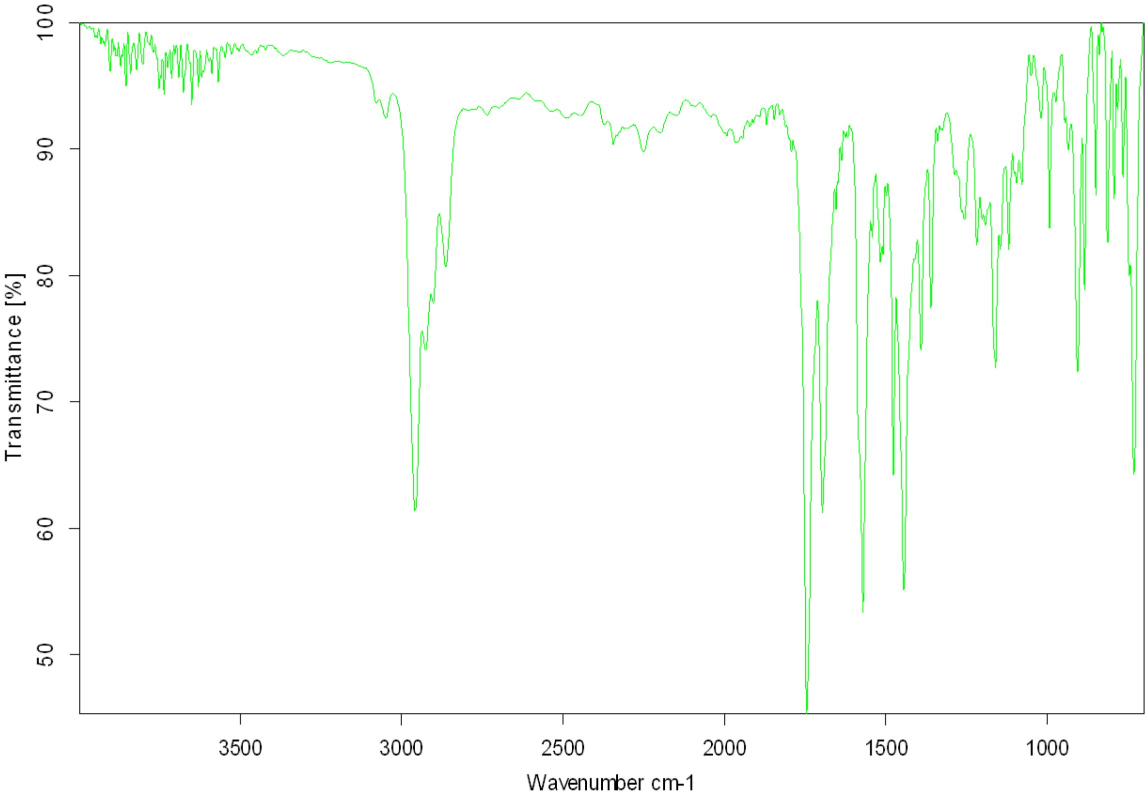
^{1}HNMR spectrum of compound H_2@5



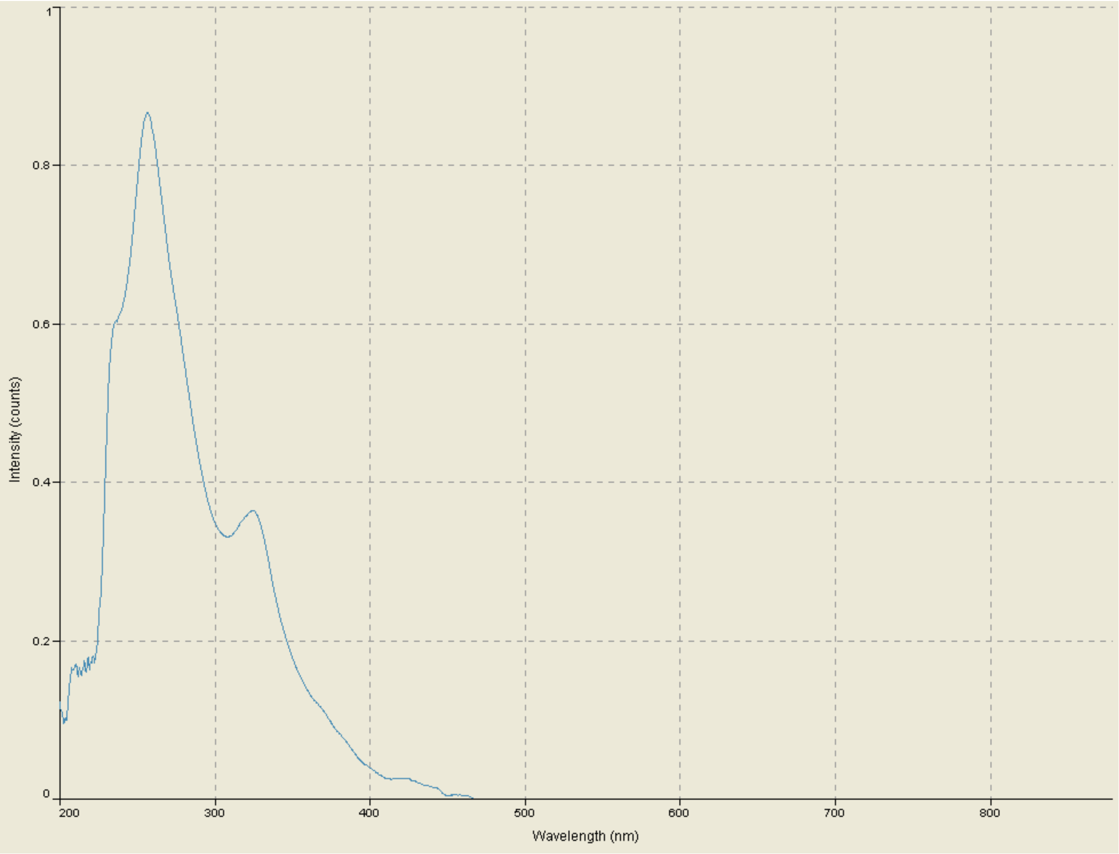
^{13}CNMR spectrum of compound H_2@5



IR spectrum of compound H_2@5



UV spectrum of compound H_2@5



H_2@3: Compound **1** (50 mg, 0.045mmol) was placed inside a glass tube. Activated 3Å molecular sieves were added (~1 g) followed by o-dichlorobenzene (12 ml). The tube was placed inside a Parr reactor. The reactor was sealed and purged by pressurising it with 10 atm of hydrogen and then releasing the pressure (3 times). The reactor was then charged with hydrogen (120 atm) and the bottom part was immersed inside an oil bath preheated to 120 °C for 24 hours. The reactor was let cool down to room temperature and depressurised then triisopropyl phosphite (0.7 ml) was added. The reactor was pressurised with H_2 again and heated to 120 °C for 17 hours. The reaction mixture was cooled to room temperature and the pressure released. The reaction mixture was evaporated to dryness by vacuum distillation to afford a black solid that was purified by flash column chromatography (toluene) to afford **H_2@3** as a black solid (24 mg, 50%).

Preparation of H_2@3 from H_2@5: Compound **H_2@5** (161 mg, 0.15 mmol) was placed inside a round bottom flask connected to a straight condenser under argon atmosphere. Distilled toluene was added (16 ml) followed by triisopropyl phosphite (0.6 ml). The reaction mixture was refluxed for 26 hours and then allowed to cool down to room temperature. The mixture was concentrated and purified by flash column chromatography (eluent: toluene).

The fractions containing the spot at R_f 0.95 were collected and evaporated to dryness to afford **H_2@3** as a black solid (133 mg, 84%).

^{1}H-NMR: (400 MHz, $CDCl_3$, δ): 7.78 (t, 2H, J = 7.7 Hz, H-4 of pyridyl), 7.72 (d, 2H, J = 7.7 Hz, H-3 of pyridyl), 7.33 (d, 2H, J = 7.7 Hz, H-5 of pyridyl), 6.47 (s, 2H, alkene), 1.36 (s, 18H, t-butyl), –2.86 (s, 1.22H, H_2).

^{13}CNMR: (125MHz, odcb-d4, δ): 168.71, 165.01, 152.5, 149.69, 145.58, 145.18, 144.51, 144.43, 144.34, 144.11, 143.99, 143.92, 143.7, 143.67, 143.57, 143.46, 143.4, 143.19, 142.42, 141.41, 140.55, 140.44, 140.38, 140.32, 140.02, 138.11, 137.05, 136.96, 135.29, 134.98, 130.77, 129.01, 128.21, 127.75, 120.85, 117.06, 57.6, 37.58, 29.95,

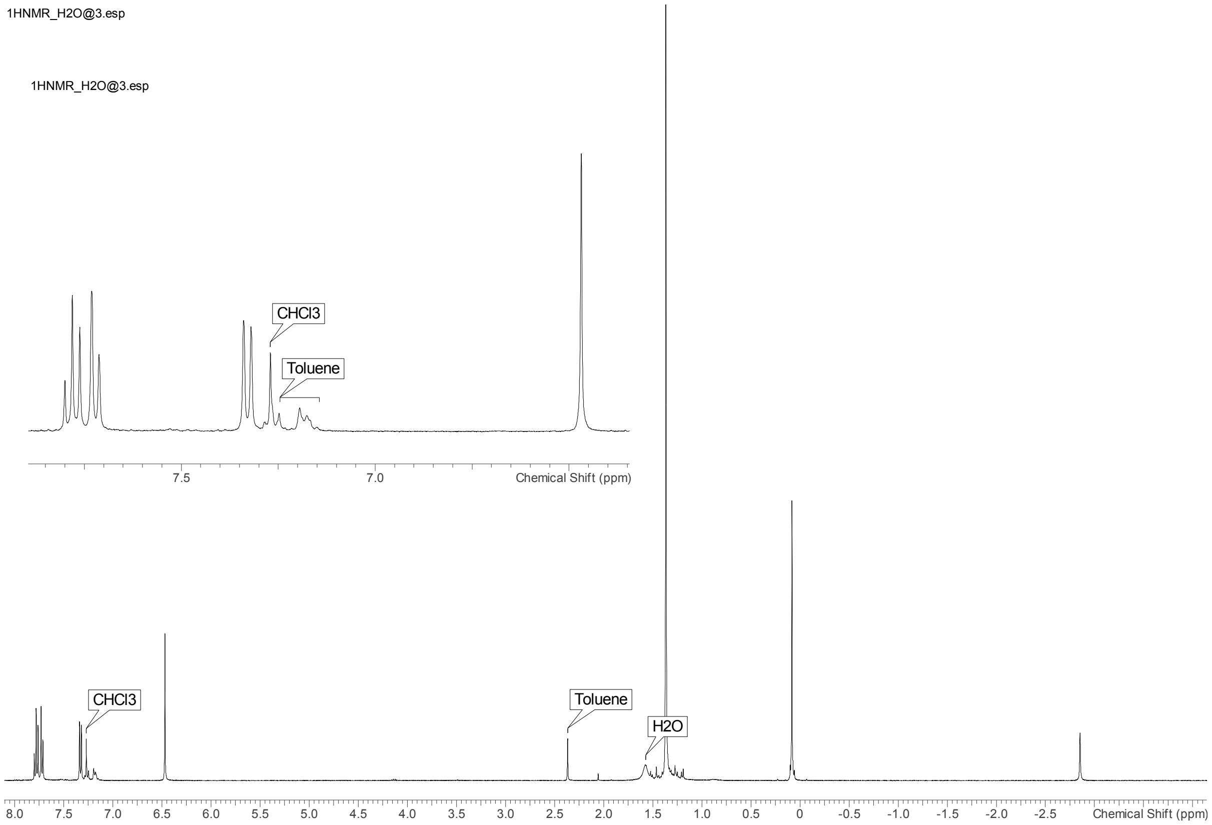
In the ^{13}C NMR spectrum some peaks show a lower intensity peak located ~0.1 ppm apart attributable to empty **3**.

IR: (ν, cm^{-1}) 2957, 1572, 1446.

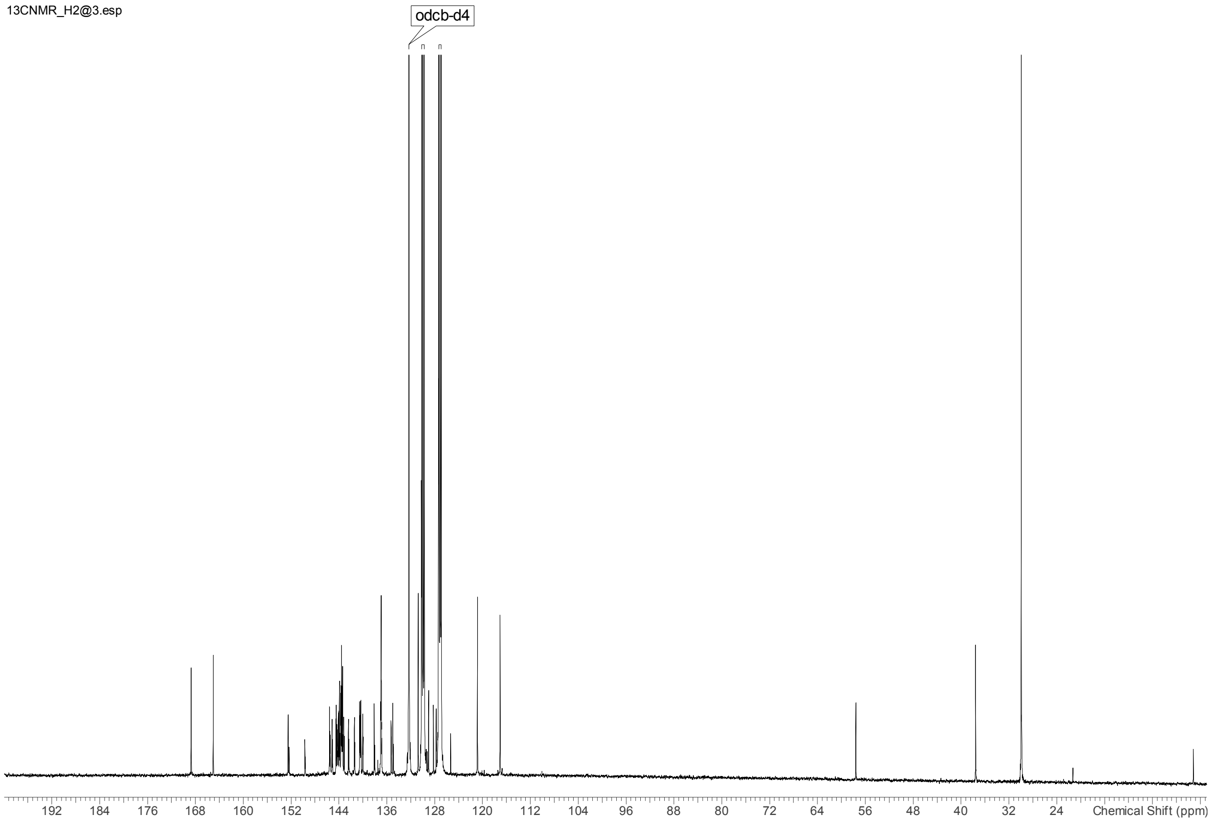
UV/Vis: CH_2Cl_2 λ_{max} (ε) = 262.33 (131417), 328.67 (48549).

MS-ESI: *m/z* (relative intensity, ion): 1041 (23%, $[M+H]^+$ **H_2@3**), 1039 (21%, $[M+H]^+$ empty **3**), 521 (100%, $[M+2H]^{2+}$ **H_2@3**), 520 (18%, $[M+2H]^{2+}$ **3**).

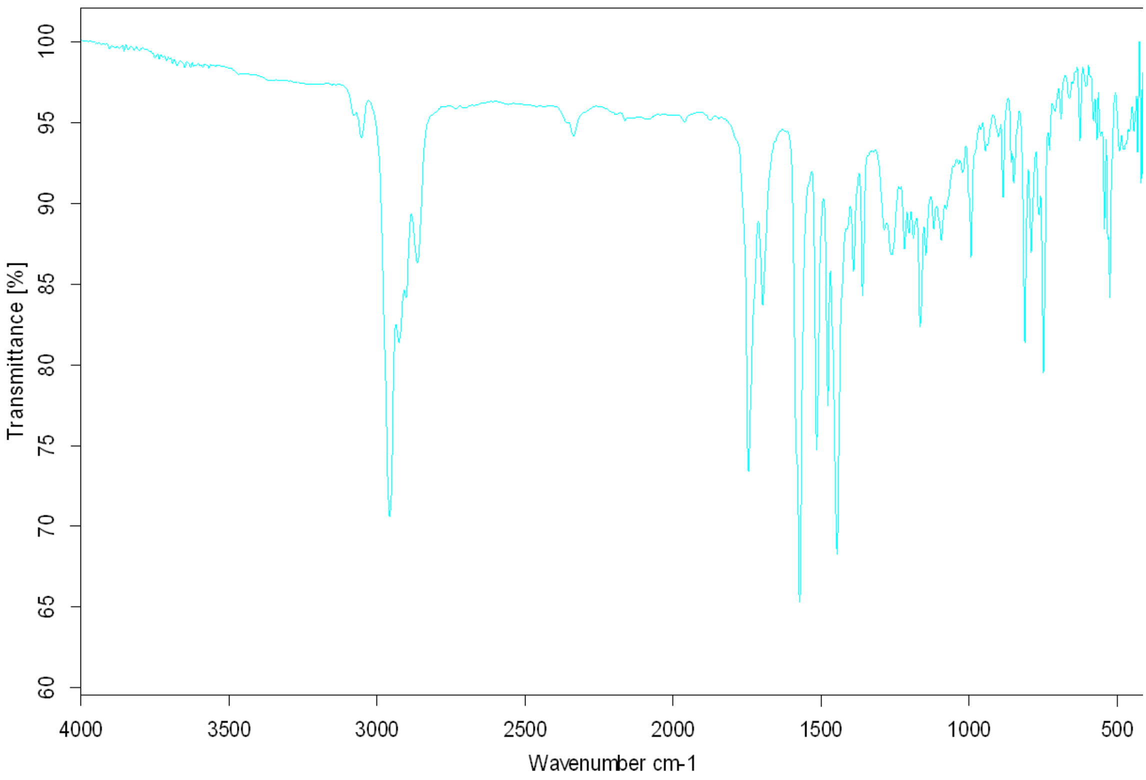
^{1}HNMR spectrum of compound H_2@3



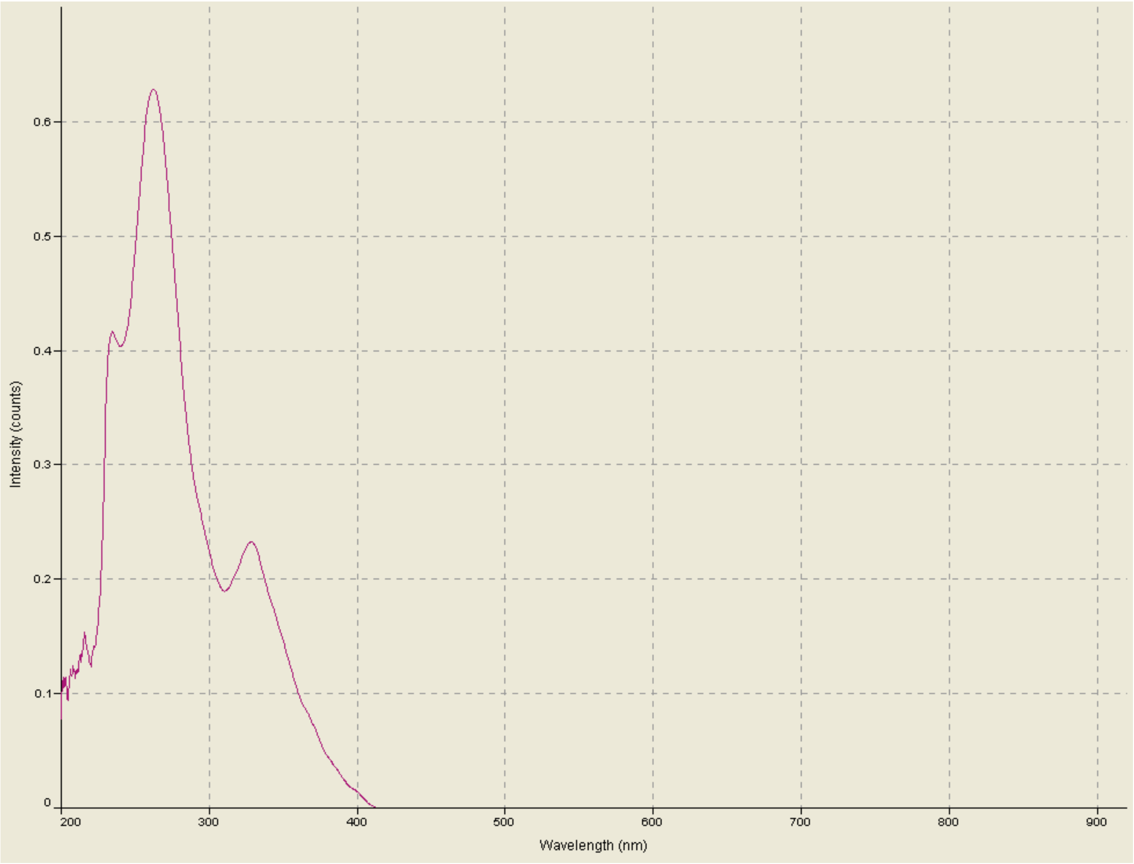
^{13}CNMR spectrum of compound H_2@3



IR spectrum of compound H_2@3



UV spectrum of compound H_2@3

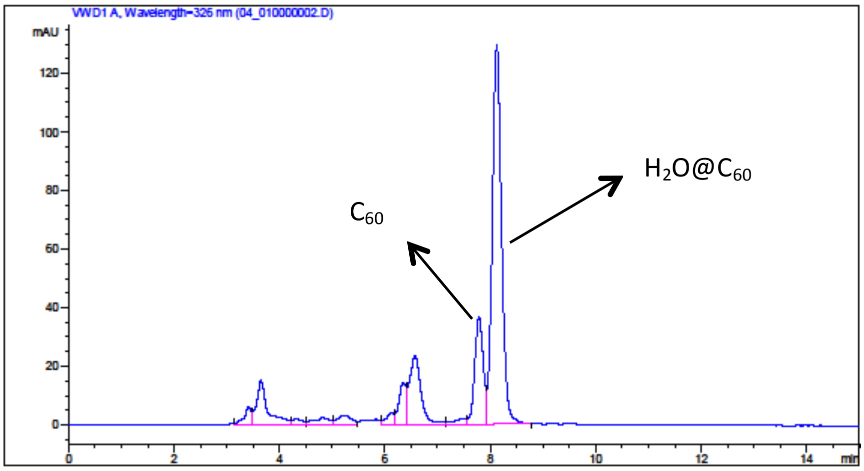


Preparation of C_{60} endofullerenes via reaction with N-Phenyl maleimide:

Compound **$H_2O@3$** (106 mg, 0.1 mmol) and N-phenyl maleimide (71 mg, 0.41 mmol) were placed inside a round bottom flask fitted with a straight condenser under argon atmosphere. 1-chloronaphthalene (5 ml) was added. The solution was degassed and the system was again put under argon gas. The reaction mixture was refluxed for 22 hours (the reaction progress can be monitored by HPLC on a buckyprep column). The reaction mixture was allowed to cool down to room temperature and poured over a silica column packed with toluene. The column was eluted with toluene to collect a purple band. This solution was concentrated under reduced pressure and then evaporated to dryness by vacuum distillation to afford **$H_2O@C_{60}$** as a black solid (67 mg, 90%).

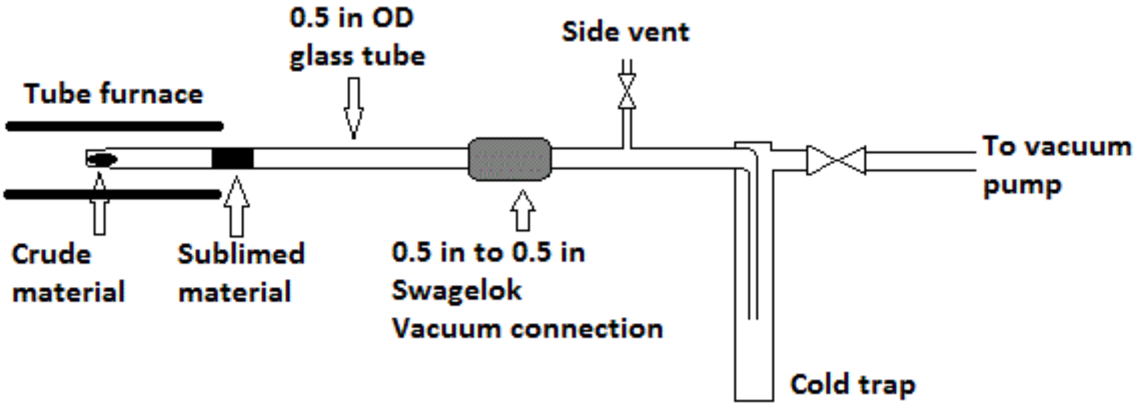
HPLC chromatogram of a 78% filled, flash chromatographed $H_2O@C_{60}$ sample

(buckyprep, toluene, detection at 326nm).



This solid was washed with diethyl ether (3 times), then collected and placed inside a straight glass tube (0.5in OD, 12 in long). The tube was connected to the sublimation apparatus depicted below that was then evacuated to 10^{-5} Torr.

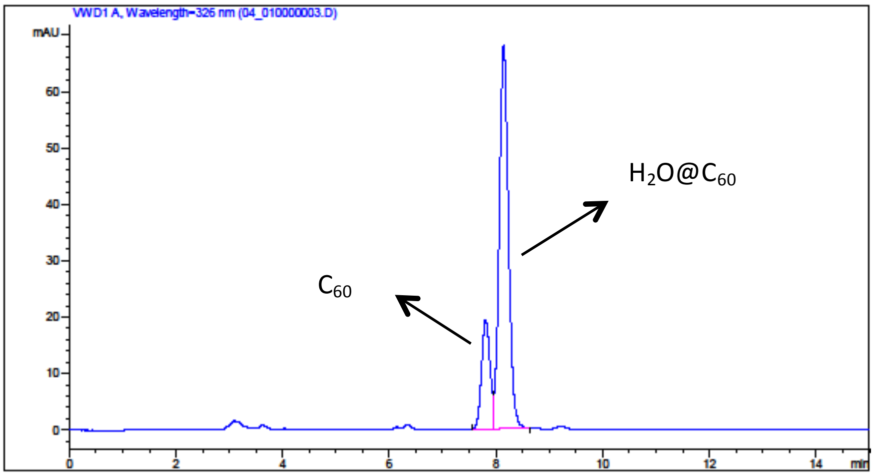
Sublimation apparatus



The furnace was heated from room temperature to 550 °C with a ramp rate of 10 °C/min. The furnace temperature was kept at 550 °C until the deposition on the cold part of the tube stopped. The system was allowed to cool down to room temperature and the apparatus was then isolated from the vacuum pump. The apparatus was then brought back to ambient pressure carefully opening the side vent. The sublimation tube was removed, the section containing the sublimate was cut and the material was collected to afford **$H_2O@C_{60}$** as a black solid (54mg, sublimation yield 81% and overall yield 72%).

HPLC chromatogram of a 78% filled, flash chromatographed $H_2O@C_{60}$ sample

(buckyprep, toluene, detection at 326nm).



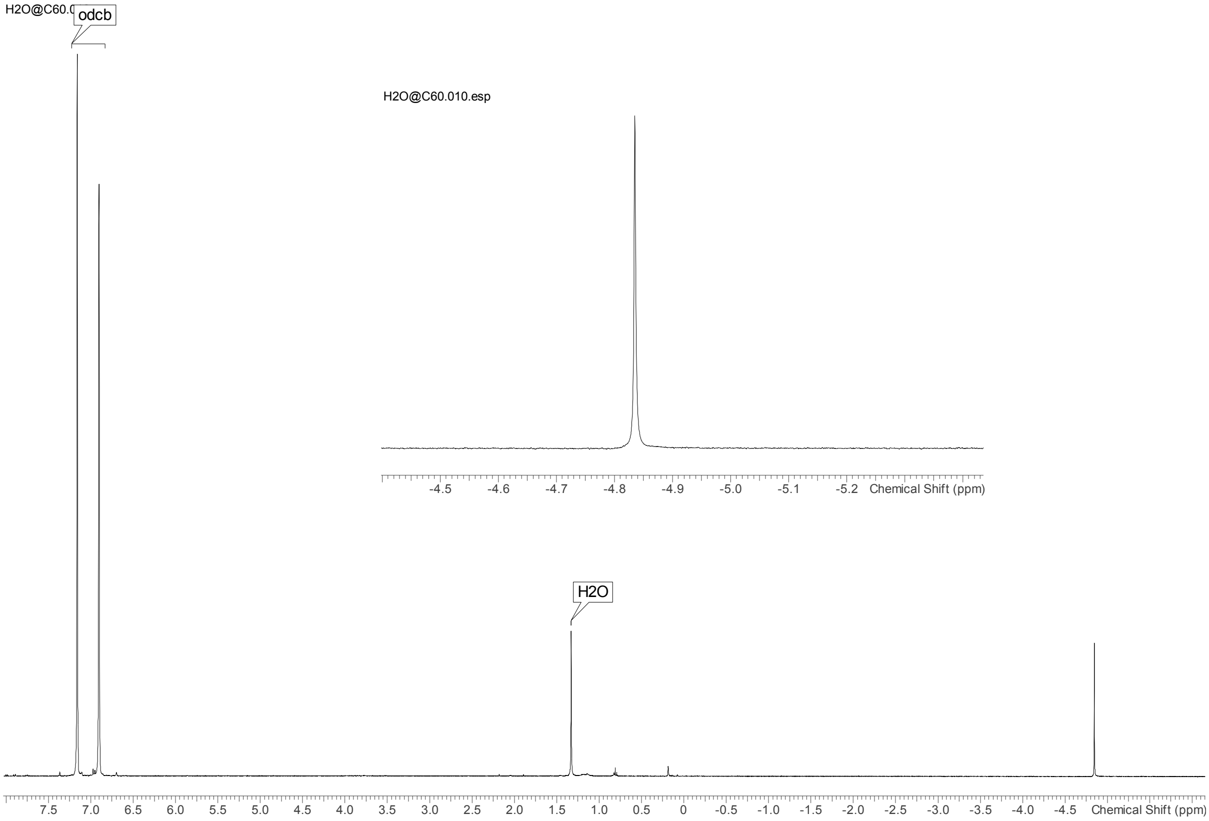
^{1}H NMR: (400 MHz, odcb-d4, δ): 4.85 (endohedral H_2O).

^{13}C NMR: (100 MHz, odcb-d4, δ): 142.83 ($H_2O@$ C_{60}), 142.72 (empty C_{60}).

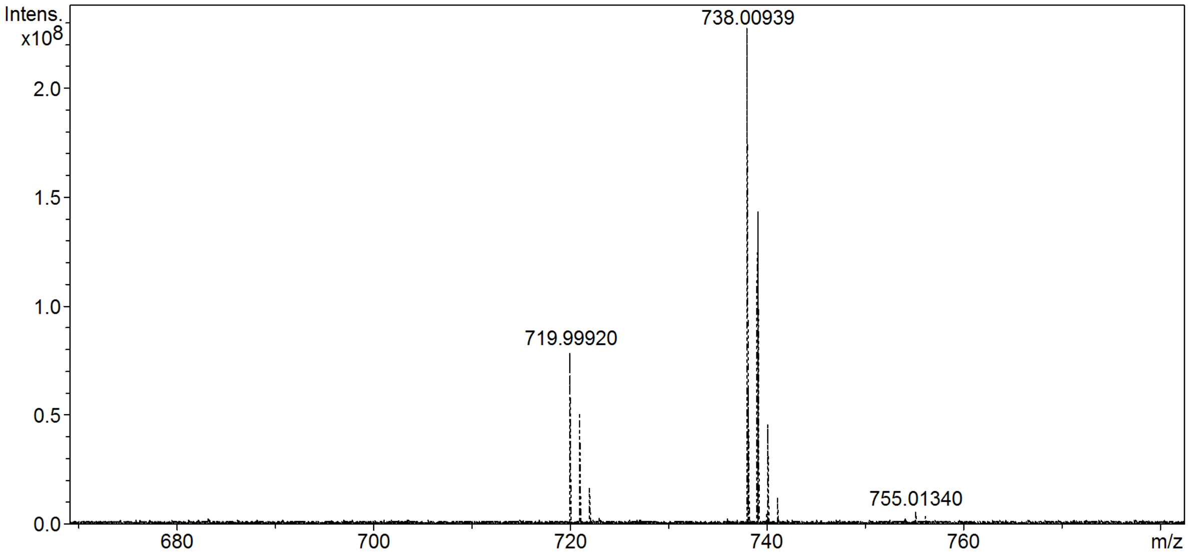
HRMS-APCI (*m/z*): $[M]^+$ calcd for $C_{60}H_2O$, 738.010; found, 738.009.

Values agree in accord with reported data.[1]

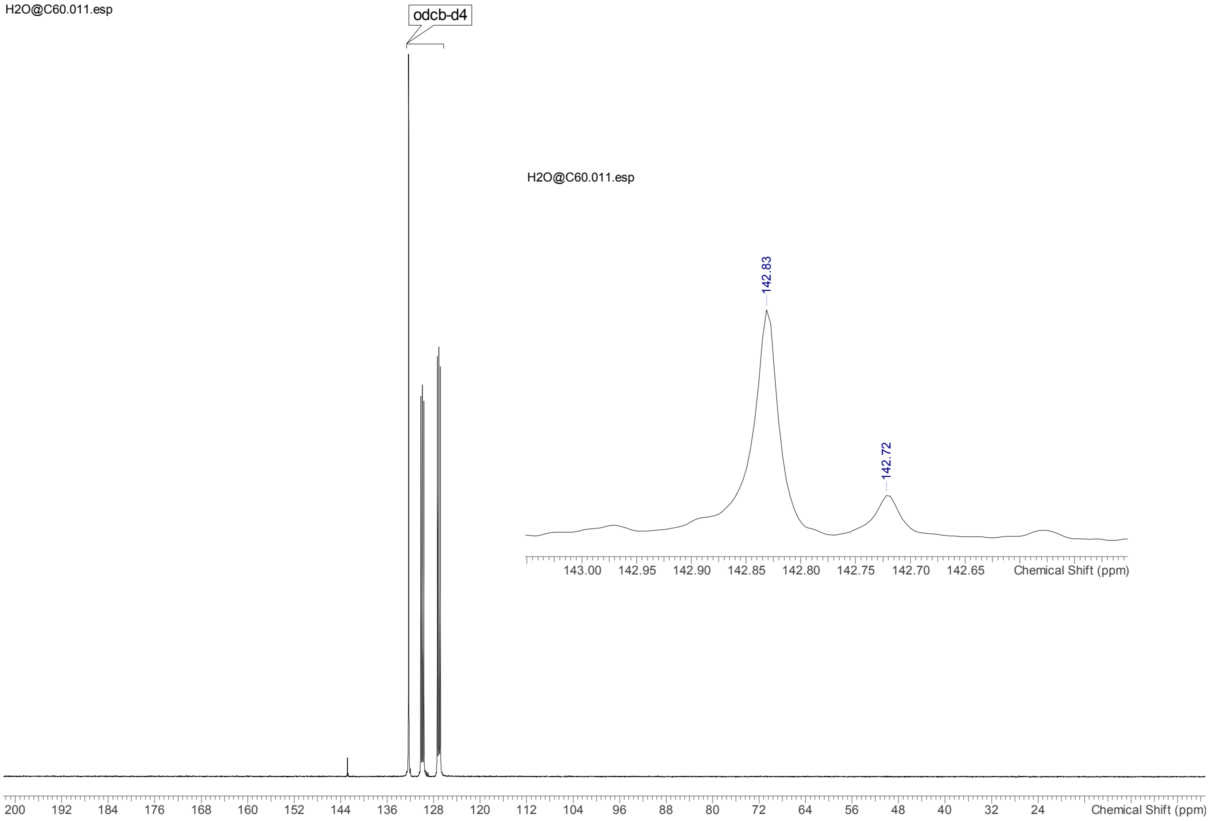
^{1}HNMR spectrum of compound $H_2O@C_{60}$



APCI-MS spectrum of compound $H_2O@C_{60}$



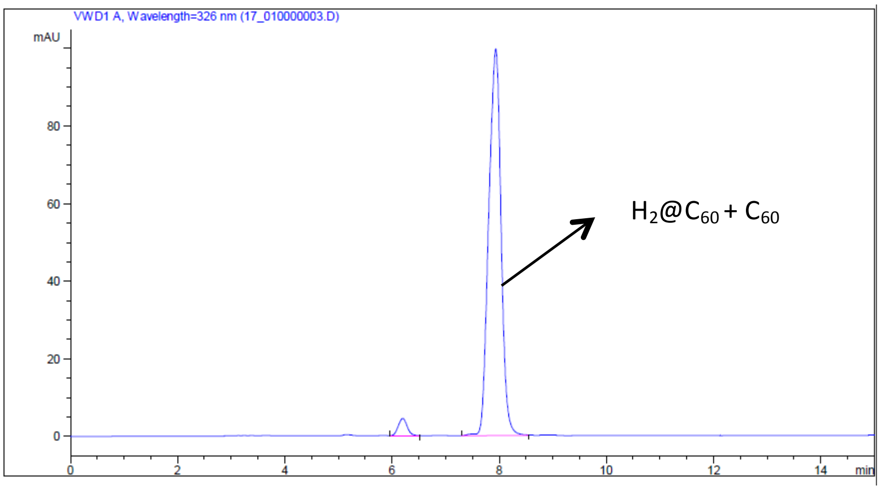
^{13}CNMR spectrum of compound $H_2O@C_{60}$



The same procedure repeated on **H_2@3** (138 mg 0.130 mmol) afforded **$H_2@C_{60}$** (68 mg, 72%) after flash chromatography and sublimation.

HPLC chromatogram of a 60% filled, flash chromatographed $H_2@C_{60}$ sample

(buckyprep, toluene, detection at 326nm).



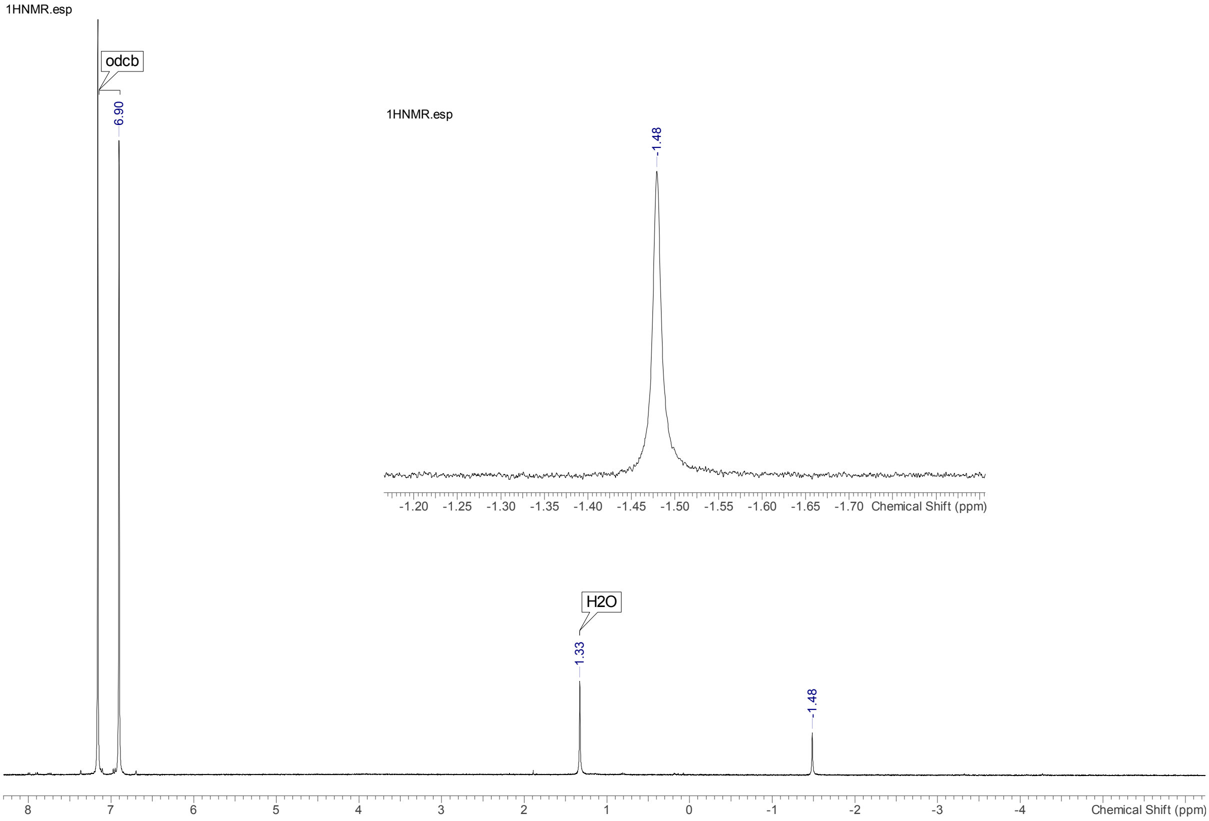
^{1}H NMR: (400 MHz, odcb-d4, δ): -1.48 (endohedral H_2).

^{13}C NMR: (400 MHz, odcb-d4, δ): 142.79 ($H_2@C_{60}$), 142.72 (empty C_{60}).

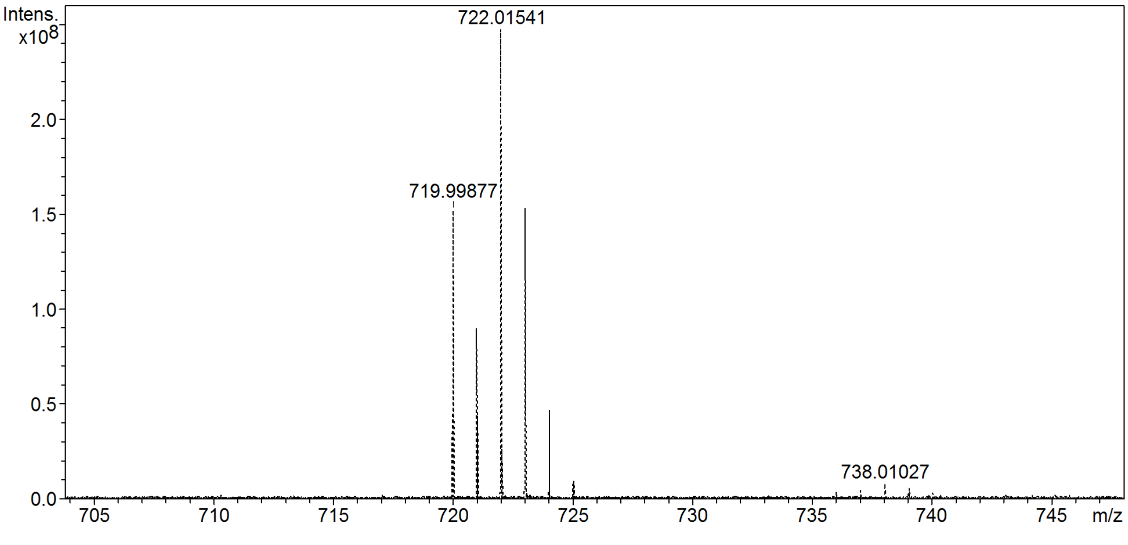
HRMS-APCI (*m/z*): $[M]^+$ calcd for $C_{60}H_2$, 722.015; found, 722.015.

Values agree in accord with reported data.[3]

^{1}HNMR spectrum of compound $H_2@C_{60}$



APCI-MS spectrum of compound $H_2@C_{60}$



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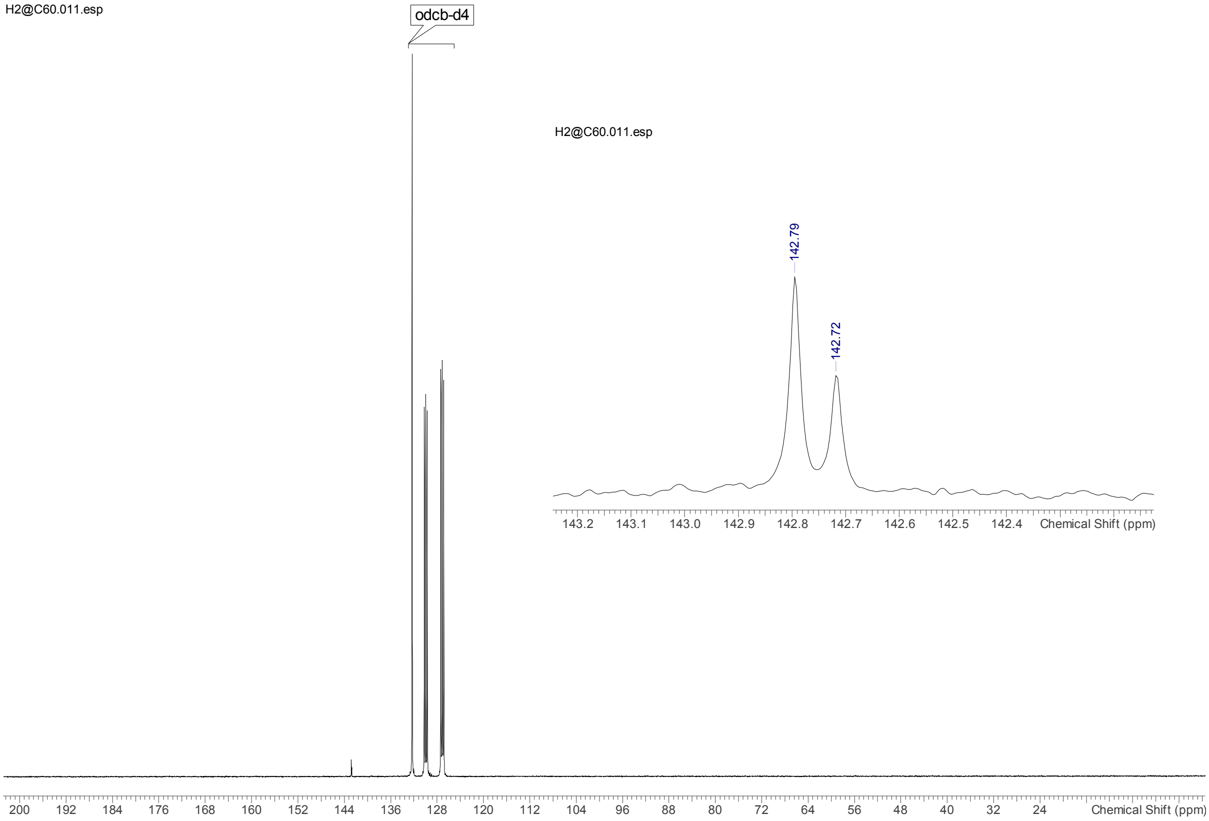
[3] Komatsu, K.; Murata, M.; Murata, Y. *Science* **2005**, *307*, 238-240.

The MS spectrum shows trace amounts of $H_2O@C_{60}$ not detectable by NMR.

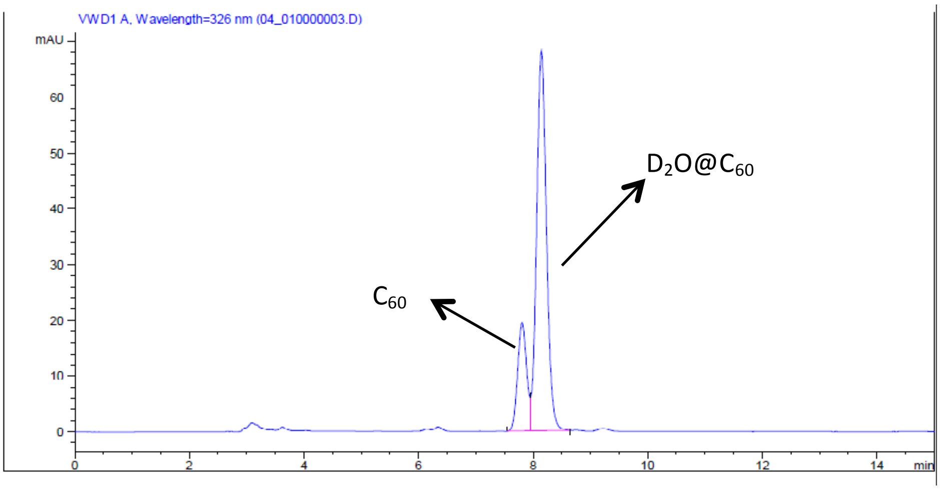
^{13}CNMR spectrum of compound $H_2@C_{60}$



The same procedure repeated on **$D_2O@3$** (155 mg 0.149 mmol) afforded **$D_2O@C_{60}$** (79 mg, 72%) after flash chromatography and sublimation.

HPLC chromatogram of a 78% filled, flash chromatographed $D_2O@C_{60}$ sample

(buckyprep, toluene, detection at 326nm).



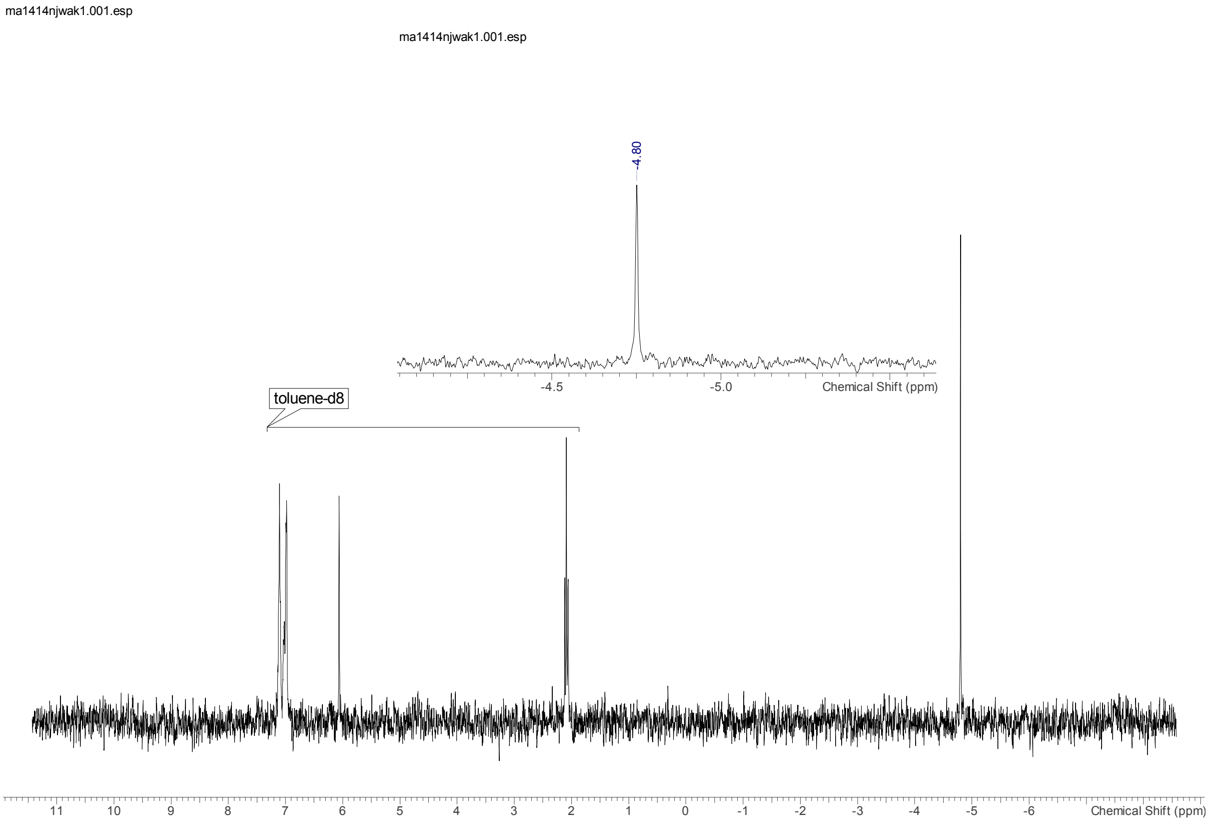
^{2}H NMR: (77 MHz, toluene, δ):- 4.80 (s, D_2O@ C_{60}).

^{13}C NMR: (100 MHz, odcb-d4, δ): 142.83 (D_2O@ C_{60}), 142.72 (empty C_{60}).

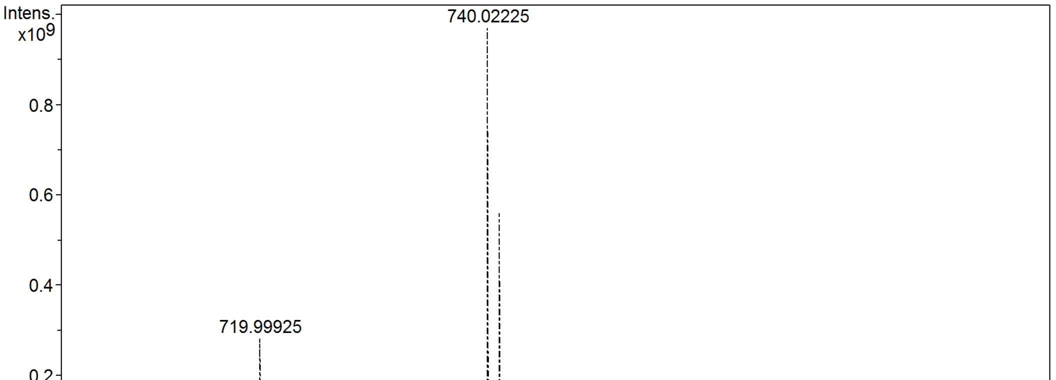
HRMS-APCI (*m/z*): $[M]^+$ calcd for $C_{60}D_2O$, 740.022; found, 740.022.

Values agree in accord with reported data.[1]

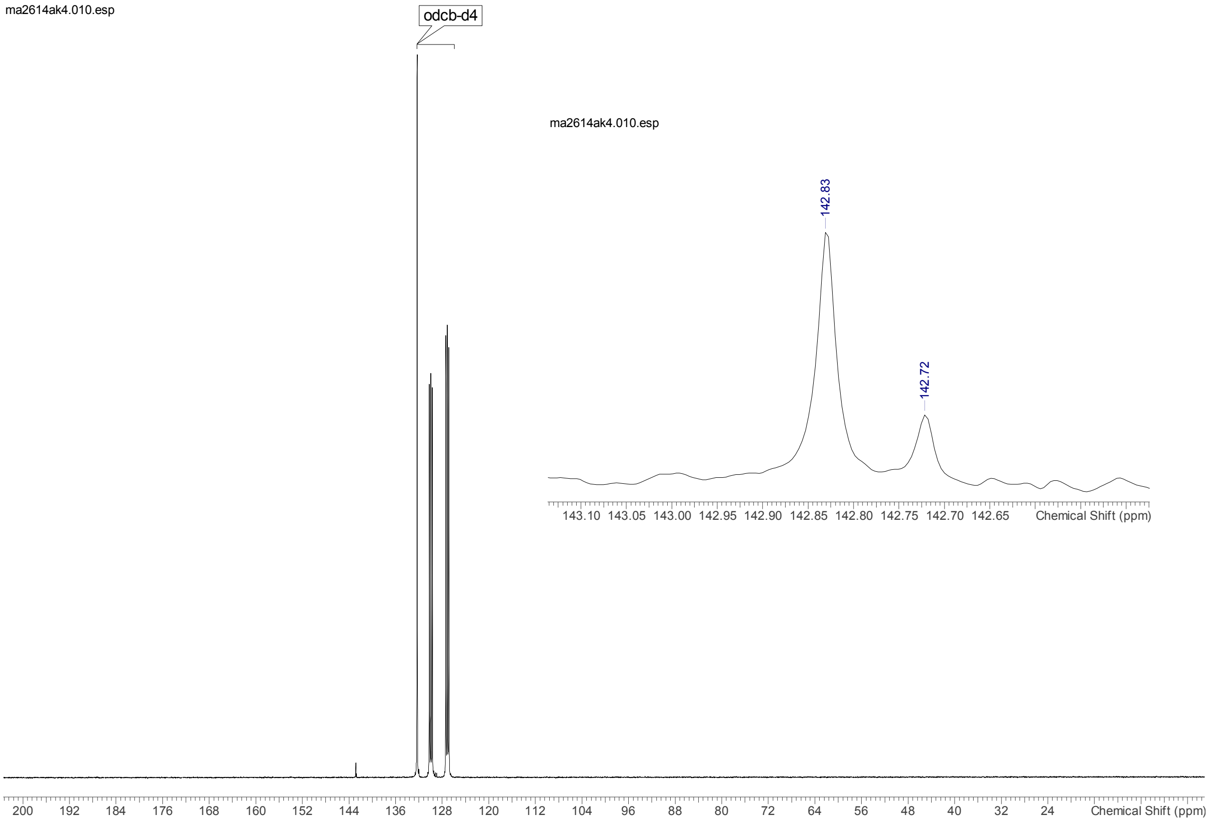
^{2}HNMR spectrum of compound D_2O@C_{60}



APCI-MS spectrum of compound D_2O@C_{60}

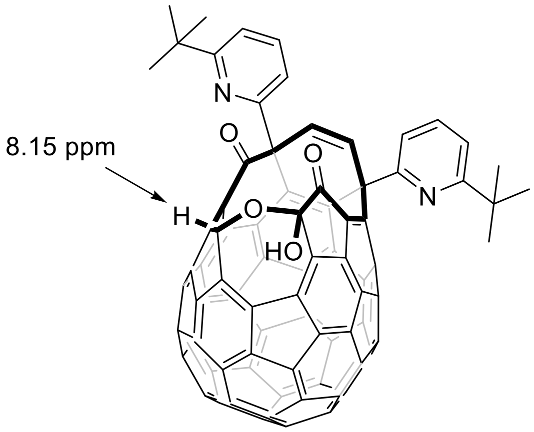


^{13}CNMR spectrum of compound $D_2O@C_{60}$

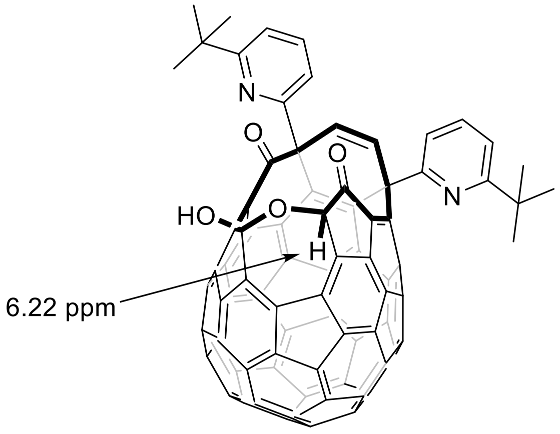


DFT calculations

Predicted chemical shift for the characteristic proton of compound **4** and its regioisomer **4a**. Indicated proton is observed at δ_H 7.76 ppm.



4



4a

B3LYP/6-31G(d) optimised Cartesian coordinates of **4**

```
SCF Done:  E(RB3LYP) =  -3551.78651939     A.U.
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C	-0.96290100	-1.13106000	-1.85123300
C	-1.23020300	-1.58026700	-0.56053600
C	-1.02755000	1.19485000	-1.04957800
C	0.05503900	0.49519300	-3.17532500
C	0.59969300	-0.79114000	-3.57147100
C	-0.02151100	-1.78751400	-2.72918300
C	0.71985600	-2.85974100	-2.24980000
C	-0.41221900	-2.67402100	-0.02494600
C	-1.20618800	-2.11442900	2.30691600
C	0.13961500	1.14556100	3.87233400
C	0.32052000	2.02243800	2.67017400
C	-0.43022500	2.27739600	1.52663700
C	0.25345200	2.81749200	0.35285900
C	-0.14137900	2.35550500	-0.98949800
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C	2.78619200	0.28300400	-3.92078200

C	2.24643500	1.52383500	-3.57005800
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C	2.48015300	3.47910300	-0.59052700
C	1.55130500	3.34381500	0.50438800
C	2.32611900	3.01120800	1.67029500
C	1.75203100	2.22379600	2.65003900
C	-0.14303200	-2.62990800	1.40091300
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C	3.28079400	-1.77530200	2.33057000
C	3.44796300	-2.74329800	1.27585600
C	4.41298600	-2.62230000	0.27671700
C	5.25111700	-1.45966200	0.26927000
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C	4.33587600	1.65199900	1.78304600
C	3.67492800	0.74830900	2.70475400
C	2.46367000	1.12726700	3.25377100
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C	1.83557900	-3.63680700	-0.36784300
C	2.81978800	-3.45617000	-1.41658800
C	4.08617000	-2.96583600	-1.10022100
C	4.72383700	-1.98888400	-1.95967100
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C	3.81172500	3.13413300	-0.11634600
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C	-2.72664800	-0.16653600	2.65382000
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C	-2.70261000	4.16253500	1.45321700
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C	-4.51838600	4.88009200	0.05033100
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H	-3.56271100	6.13620600	1.52122100
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C	-5.69668000	-3.80127200	0.93506400
C	-5.22385200	-3.67467100	2.24151900
C	-4.12883400	-2.85937500	2.49892800
H	-6.54843200	-4.43742200	0.72659500
H	-5.70459300	-4.21608400	3.05224500
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H	-2.79163100	1.82751400	3.27026400
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C	-5.51900100	3.18684700	-1.63254500
C	-5.45281000	-3.20225400	-1.57041700
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C	-4.27333500	-3.81762000	-2.35861000
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B3LYP/6-31G(d) optimised Cartesian coordinates of **4a**

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C	0.64074500	-0.42046700	-3.61782700
C	0.01732600	-1.49360300	-2.87773600
C	0.76175800	-2.60205900	-2.49354100
C	-0.39691500	-2.62916900	-0.27707800

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C	-0.44615400	2.16525000	1.73455700
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C	2.08185900	3.32236800	-1.54944100
C	2.46929400	3.57488500	-0.24582900
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C	2.30094800	2.91404700	1.96371900
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C	-0.13771700	-2.71019700	1.14616000
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C	3.45869300	-2.79099500	1.06651700
C	4.42662100	-2.57161700	0.08861300
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C	3.64674200	0.56599900	2.80141600
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H	-3.36900600	-2.98381200	-2.53691500
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