

Supporting information

Hydroxyalkylation of [60]Fullerene: Free Radical Addition of Alcohols to C₆₀

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Table of Contents

1. General Considerations.....	S2
2. General Procedure for the TBADT-Catalyzed Photochemical Reactions of Alcohols 1–7 with C ₆₀	S3
3. Synthetic Procedure and Spectral Data of Functionalized Fullerenes 1a–7a	S4
4. ¹ H NMR, ¹³ C NMR, and UV-vis Spectra of Functionalized Fullerenes 1a–7a	S11
5. Synthetic Procedure and Spectral Data of <i>n</i> -butanol- <i>d</i> ₁ (3-d ₁)	S23
6. Experimental Procedure and ¹ H NMR Spectrum of the Reaction of C ₆₀ with 3-d ₁	S23

1. General Considerations

Unless otherwise noted, all materials including dry solvents were obtained from commercial suppliers and used without further purification. Tetrabutylammonium decatungstate (TBADT) was prepared according to procedure reported in the literature.¹

¹H NMR and ¹³C NMR spectra were recorded on Bruker AMX-500 MHz (125 MHz for ¹³C) and DPX-300 MHz (75 MHz for ¹³C) spectrometers, in CDCl₃, CDCl₃/CS₂, *o*-DCB-*d*₄/CS₂ or acetone-*d*₆/CS₂ solutions. Chemical shifts are reported in ppm downfield from Me₄Si, by using the residual solvent peak as internal standard. UV-vis spectra were performed on a Shimadzu MultiSpec-1501 UV/Visible spectrometer. HPLC analysis was conducted on a Marathon III instrument equipped with a 5C18-MS (4.6 × 250 mm, Nacalai Tesque) reversed phase column with detection at 310 nm. A mixture of toluene/acetonitrile (1:1 v/v) was used as eluent at 1 mL/min flow rate. Semi-preparative HPLC was performed with a Marathon III instrument equipped with a Cosmosil 5PBB column (10 × 250 mm, Nacalai Tesque) with detection at 310 nm. A mixture of toluene/acetonitrile (4:1 v/v) was used as eluent (unless otherwise noted) at 5 mL/min flow rate. Flash column chromatography was carried out on SiO₂ (silica gel 60, SDS, 230-400 mesh ASTM). Evaporation of the solvents was accomplished with a rotary evaporator or by high vacuum distillation. Negative-ion MALDI spectra were recorded for all the new compounds using DCTB as the matrix. Photochemical reactions were carried out by using a 300-W xenon lamp as the light source.

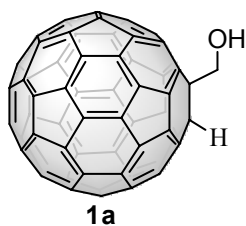
¹ D. C. Duncan, T. L. Netzel, C. L. Hill, *Inorg. Chem.* **1995**, *34*, 4640.

2. General Procedure for the TBADT-Catalyzed Photochemical Reactions of Alcohols 1–7 with C₆₀

Unless otherwise noted in the individual procedures below, a solution of C₆₀ (20 mg, 0.028 mmol) in a mixture of chlorobenzene/acetonitrile 85:15 (70 mL) was added in a 150-mL glass flask containing a magnetic stirring bar. This solution was degassed by performing three freeze-pump-thaw cycles under argon, and then TBADT (46 mg, 0.014 mmol) and the organic substrate 1–7 (5.6 mmol) were added. The resulting solution was septum-capped and purged for 20 min with argon. This solution was subsequently irradiated at 5–10 °C using an ice water bath, while a constant, slow argon stream was maintained over the solution (the progress of all reactions was monitored by HPLC). Then, the solvent was distilled from the reaction mixture under reduced pressure, and the remaining crude product was centrifuged three times with acetonitrile HPLC grade. The isolated product was further purified by flash column chromatography (unless otherwise noted, the eluent used was a mixture of hexane/toluene 4:1 v/v) and/or semi-preparative HPLC (eluent: toluene/acetonitrile 4:1 v/v, 5 mL/min flow rate, detection at 310 nm) to afford the corresponding fullerene adducts 1a–7a, along with a small amount of a complex mixture of several unidentified byproducts. Blank experiments in the absence of TBADT and/or light showed no reaction.

3. Synthetic Procedure and Spectral Data of Functionalized Fullerenes 1a–7a

➤ Functionalized Fullerene **1a**

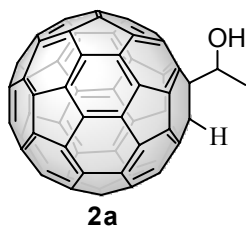


Compound **1a** has been prepared following the general procedure described in Section 2, by using 20 mg (0.028 mmol) of C₆₀, 46 mg (0.014 mmol) of TBADT and 200 equiv (5.6 mmol) of methanol (**1**), in a mixture of chlorobenzene/acetonitrile 85:15 (70 mL). The progress of the reaction was monitored by analytical HPLC (5C18-MS, 4.6 × 250 mm, elution with 1:1 toluene/acetonitrile at 1 mL/min flow rate, detection at 310 nm, retention time of **1a**: 7.3 min). The reaction mixture was irradiated at 5–10 °C for 30 min, after which time the reaction solvent and the excess of methanol were evaporated under reduced pressure. Acetonitrile was then added and the resulting suspension was centrifuged at 4100 rpm for 10 min (3 times). The resulting crude precipitate was further purified by flash column chromatography on silica using a gradient elution (3:2 hexane/toluene to 20% hexane in toluene) to afford compound **1a** in 30% yield. Data are consistent with a previous report on this compound.²

¹H NMR (500 MHz, CDCl₃/CS₂): δ 6.77 (s, 1H), 5.43 (d, *J* = 6 Hz, 2H), 2.75 (t, *J* = 6 Hz, 1H, OH); UV-vis (CHCl₃): λ_{max} (nm) = 256, 324, 430; MS (MALDI, negative, DCTB): *m/z* calcd for C₆₁H₄O [M[−]]: 752.026, found: 752.028.

² C. Siedschlag, H. Luftmann, C. Wolff, J. Mattay, *Tetrahedron* **1997**, 53, 3587.

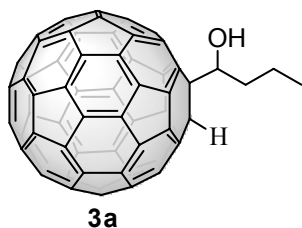
➤ Functionalized Fullerene **2a**



Compound **2a** has been prepared following the general procedure described in Section 2, by using 20 mg (0.028 mmol) of C₆₀, 46 mg (0.014 mmol) of TBADT and 200 equiv (5.6 mmol) of ethanol (EtOH) **2**, in a mixture of chlorobenzene/acetonitrile 85:15 (70 mL). The progress of the reaction was monitored by analytical HPLC (5C18-MS, 4.6 × 250 mm, elution with 1:1 toluene/acetonitrile at 1 mL/min flow rate, detection at 310 nm, retention time of **2a**: 7.5 min). The reaction mixture was irradiated at 5–10 °C for 25 min, after which time the reaction solvent and the excess of ethanol were evaporated under reduced pressure. Acetonitrile was then added and the resulting suspension was centrifuged at 4100 rpm for 10 min (3 times). The resulting crude precipitate was further purified by flash column chromatography on silica using a gradient elution (4:1 hexane/toluene to 10% hexane in toluene) to afford compound **2a** in 30% yield. Data are consistent with a previous report on this compound.²

¹H NMR (500 MHz, CDCl₃/CS₂): δ 6.83 (s, 1H), 5.57 (m, 1H), 2.81 (d, *J* = 5 Hz, 1H, OH), 2.38 (d, *J* = 6 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃/CS₂): δ 154.09, 153.65, 153.30, 152.35, 147.34, 147.21, 147.13, 147.03, 146.98, 146.60, 146.38, 146.34, 146.27, 146.26, 146.14, 146.13, 146.09, 145.67, 145.53, 145.52, 145.37, 145.34, 145.30, 145.28, 145.27, 144.66, 144.61, 144.36, 143.14, 143.13, 142.55, 142.50, 142.34, 142.32, 142.30, 142.02, 142.00, 141.94, 141.92, 141.62, 141.59, 141.57, 141.56, 141.54, 141.52, 140.34, 140.33, 140.12, 139.91, 136.94, 136.86, 136.21, 135.99, 76.53, 71.86, 55.61, 20.25; UV-vis (CHCl₃): λ_{max} (nm) = 257, 327, 431; MS (MALDI, negative, DCTB): *m/z* calcd for C₆₂H₆O [M[−]]: 766.042, found: 766.047.

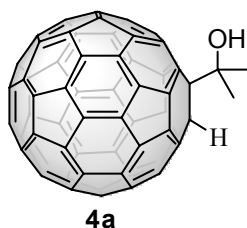
➤ Functionalized Fullerene **3a**



Compound **3a** has been prepared following the general procedure described in Section 2, by using 20 mg (0.028 mmol) of C₆₀, 46 mg (0.014 mmol) of TBADT and 200 equiv (5.6 mmol) of *n*-butanol **3**, in a mixture of chlorobenzene/acetonitrile 85:15 (70 mL). The progress of the reaction was monitored by analytical HPLC (5C18-MS, 4.6 × 250 mm, elution with 1:1 toluene/acetonitrile at 1 mL/min flow rate, detection at 310 nm, retention time of **3a**: 7.3 min). The reaction mixture was irradiated at 5–10 °C for 20 min, after which time the reaction solvent and the excess of *n*-butanol were evaporated under reduced pressure. Acetonitrile was then added and the resulting suspension was centrifuged at 4100 rpm for 10 min (3 times). The resulting crude precipitate was further purified by flash column chromatography on silica (4:1 hexane/toluene) to afford compound **3a** in 30% yield.

¹H NMR (500 MHz, CDCl₃/CS₂): δ 6.82 (s, 1H), 5.33 (m, 1H), 2.78–2.85 (m, 2H), 2.65–2.73 (m, 1H), 2.13–2.23 (m, 1H), 1.89–1.99 (m, 1H), 1.32 (t, *J* = 7.5 Hz, 3H); ¹H NMR (500 MHz, *o*-DCB-*d*₄/CS₂): δ 6.60 (s, 1H), 5.13 (m, 1H), 2.73 (m, 1H), 2.64 (m, 1H), 2.53 (m, 1H), 2.03 (m, 1H), 1.78 (m, 1H), 1.16 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (125 MHz, *o*-DCB-*d*₄/CS₂): δ 154.72, 154.23, 153.22, 147.69, 147.49, 147.14, 146.71, 146.68, 146.62, 146.49, 146.44, 146.10, 145.83, 145.81, 145.71, 145.63, 145.02, 144.98, 144.77, 144.75, 143.47, 143.27, 142.87, 142.84, 142.74, 142.69, 142.38, 142.35, 142.31, 142.04, 142.01, 142.00, 141.95, 141.92, 141.88, 140.62, 140.60, 140.43, 140.26, 137.32, 137.26, 136.68, 136.49, 80.77, 72.36, 56.48, 36.56, 20.90, 14.89; UV-vis (CHCl₃): λ_{max} (nm) = 257, 327, 432; MS (MALDI, negative, DCTB): *m/z* calcd for C₆₄H₁₀O [M[−]]: 794.1, found: 794.3.

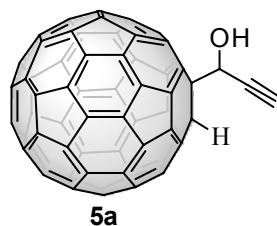
➤ Functionalized Fullerene **4a**



Compound **4a** has been prepared following the general procedure described in Section 2, by using 20 mg (0.028 mmol) of C₆₀, 46 mg (0.014 mmol) of TBADT and 200 equiv (5.6 mmol) of 2-propanol **4**, in a mixture of chlorobenzene/acetonitrile 85:15 (70 mL). The progress of the reaction was monitored by analytical HPLC (5C18-MS, 4.6 × 250 mm, elution with 1:1 toluene/acetonitrile at 1 mL/min flow rate, detection at 310 nm, retention time of **4a**: 7.4 min). The reaction mixture was irradiated at 5–10 °C for 10 min, after which time the reaction solvent and the excess of 2-propanol were evaporated under reduced pressure. Acetonitrile was then added and the resulting suspension was centrifuged at 4100 rpm for 10 min (3 times). The resulting crude precipitate was further purified by flash column chromatography on silica using a gradient elution (4:1 hexane/toluene to 20% hexane in toluene) to afford compound **4a** in 25% yield.

¹H NMR (500 MHz, CDCl₃/CS₂): δ 6.98 (s, 1H), 2.38 (s, 6H); ¹³C NMR (125 MHz, CDCl₃/CS₂): δ 154.55, 152.70, 147.65, 147.35, 147.07, 146.38, 146.28, 146.17, 146.10, 145.73, 145.45, 145.37, 145.28, 145.27, 144.69, 144.34, 143.17, 142.62, 142.60, 142.31, 142.07, 141.69, 141.48, 141.46, 140.44, 139.37, 136.84, 136.10, 75.16, 57.03, 27.89; UV-vis (CHCl₃): λ_{max} (nm) = 257, 326, 432; MS (MALDI, negative, DCTB): *m/z* calcd for C₆₃H₈O [M[−]]: 780.058, found: 780.065.

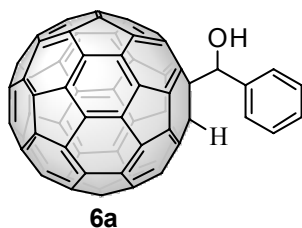
➤ Functionalized Fullerene **5a**



Compound **5a** has been prepared following the general procedure described in Section 2, by using 20 mg (0.028 mmol) of C₆₀, 46 mg (0.014 mmol) of TBADT and 200 equiv (5.6 mmol) of 2-propyn-1-ol **5**, in a mixture of chlorobenzene/acetonitrile 85:15 (70 mL). The progress of the reaction was monitored by analytical HPLC (5C18-MS, 4.6 × 250 mm, elution with 1:1 toluene/acetonitrile at 1 mL/min flow rate, detection at 310 nm, retention time of **5a**: 5.4 min). The reaction mixture was irradiated at 5–10 °C for 40 min, after which time the reaction solvent and the excess of 2-propyn-1-ol were evaporated under reduced pressure. Acetonitrile was then added and the resulting suspension was centrifuged at 4100 rpm for 10 min (3 times). The resulting crude precipitate was further purified by flash column chromatography on silica using a gradient elution (3:2 hexane/toluene to 20% hexane in toluene) to afford compound **5a** in 35% yield.

¹H NMR (500 MHz, CDCl₃/CS₂): δ 6.93 (s, 1H), 6.11 (dd, *J*₁ = 2 Hz, *J*₂ = 5 Hz, 1H), 3.20 (d, *J* = 5 Hz, 1H), 3.09 (d, *J* = 2 Hz, 1H); ¹H NMR (500 MHz, acetone-*d*₆/CS₂): δ 7.07 (s, 1H), 6.43 (d, *J* = 5 Hz, 1H), 6.14 (dd, *J*₁ = 2 Hz, *J*₂ = 5 Hz, 1H), 3.37 (d, *J* = 2.0 Hz, 1H); ¹³C NMR (75 MHz, acetone-*d*₆/CS₂): δ 156.56, 156.26, 156.11, 154.90, 149.26, 149.05, 149.02, 148.92, 148.83, 148.04, 147.97, 147.82, 147.79, 147.77, 147.74, 147.52, 147.29, 147.20, 147.02, 146.97, 146.94, 146.39, 146.36, 146.20, 146.17, 144.79, 144.77, 144.73, 144.19, 144.16, 143.72, 143.70, 143.29, 143.25, 143.19, 141.88, 141.83, 141.41, 139.33, 139.12, 138.32, 138.23, 84.49, 78.55, 72.94, 72.56, 58.39; UV-vis (CHCl₃): λ_{max} (nm) = 257, 325, 430; MS (MALDI, negative, DCTB): *m/z* calcd for C₆₃H₄O [M⁻]: 776.0, found: 776.2.

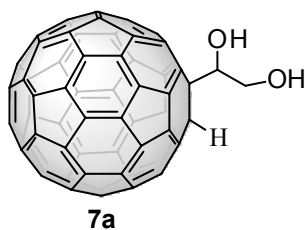
➤ Functionalized Fullerene **6a**



Compound **6a** has been prepared following the general procedure described in Section 2, by using 20 mg (0.028 mmol) of C₆₀, 46 mg (0.014 mmol) of TBADT and 200 equiv (5.6 mmol) of benzyl alcohol **6**, in a mixture of chlorobenzene/acetonitrile 85:15 (70 mL). The progress of the reaction was monitored by analytical HPLC (5C18-MS, 4.6 × 250 mm, elution with 1:1 toluene/acetonitrile at 1 mL/min flow rate, detection at 310 nm, retention time of **6a**: 6.3 min). The reaction mixture was irradiated at 5–10 °C for 25 min, after which time the reaction solvent was evaporated under reduced pressure. Acetonitrile was then added and the resulting suspension was centrifuged at 4100 rpm for 10 min (3 times). The resulting crude precipitate was further purified by flash column chromatography on silica using a gradient elution (1:1 hexane/toluene to 20% hexane in toluene) to afford compound **6a** in 15% yield.

¹H NMR (500 MHz, CDCl₃/CS₂): δ 7.45–7.96 (m, 5H), 6.98 (s, 1H), 6.52 (s, 1H), 3.23 (br s, 1H, -OH); ¹³C NMR (75 MHz, *o*-DCB-*d*₄/CS₂): δ 154.44, 154.13, 152.36, 147.71, 147.23, 147.20, 146.92, 146.42, 146.40, 146.34, 146.28, 146.19, 146.14, 146.06, 145.77, 145.76, 145.59, 145.51, 145.48, 145.41, 145.34, 145.31, 145.29, 145.26, 145.16, 145.12, 144.68, 144.54, 144.43, 143.84, 142.55, 141.63, 139.41, 132.60, 128.51, 128.45, 119.97, 82.86, 77.70, 56.62; UV-vis (CHCl₃): λ_{max} (nm) = 258, 328, 432; MS (MALDI, negative, DCTB): *m/z* calcd for C₆₇H₈O [M⁻]: 828.058, found: 828.067.

➤ Functionalized Fullerene **7a**



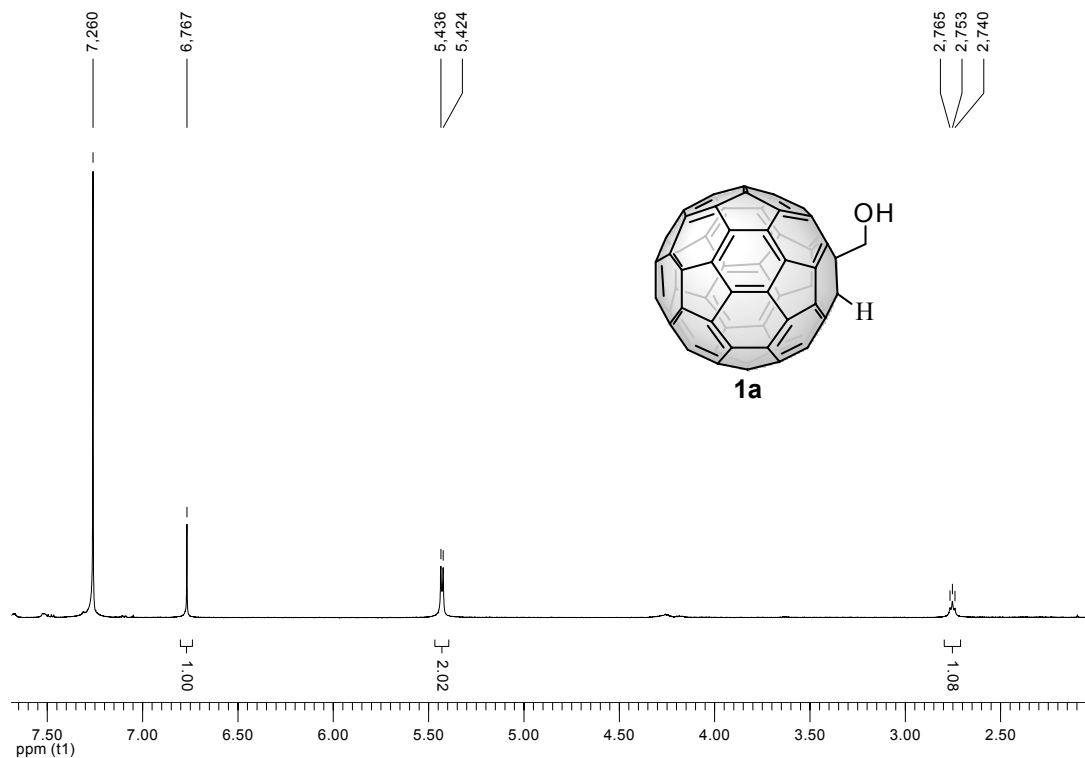
Compound **7a** has been prepared following the general procedure described in Section 2, by using 20 mg (0.028 mmol) of C₆₀, 46 mg (0.014 mmol) of TBADT and 200 equiv (5.6 mmol) of ethylene glycol **7**, in a mixture of chlorobenzene/acetonitrile 85:15 (70 mL). The progress of the reaction was monitored by analytical HPLC (5C18-MS, 4.6 × 250 mm, elution with 1:1 toluene/acetonitrile at 1 mL/min flow rate, detection at 310 nm). The reaction mixture was irradiated at 5–10 °C for 25 min, after which time the reaction solvent was evaporated under reduced pressure. Acetonitrile was then added and the resulting suspension was centrifuged at 4100 rpm for 10 min (3 times). The resulting crude precipitate was further purified by flash column chromatography on silica using a gradient elution (toluene to 20% ethyl acetate in toluene) to afford compound **7a** in 30% yield. Owing to the low solubility of **7a** no ¹³C NMR spectrum was recorded.

¹H NMR (500 MHz, *o*-DCB-*d*₄/CS₂): δ 6.77 (s, 1H), 5.28 (m, 1H), 4.68 (m, 2H), 3.59 (d, *J* = 3 Hz, 1H, -OH), 2.15 (m, 1H, -OH); UV-vis (CHCl₃): λ_{max} (nm) = 257, 327, 431; MS (MALDI, negative, DCTB): *m/z* calcd for C₆₂H₆O₂ [M[−]]: 782.037, found: 782.042.

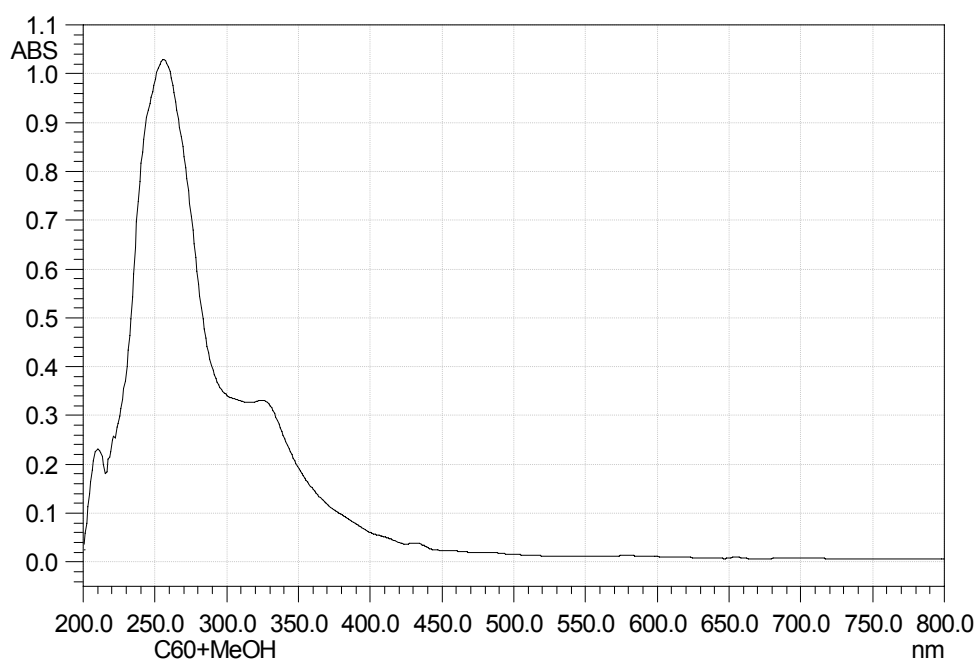
4. ^1H NMR, ^{13}C NMR, and UV-vis Spectra of Functionalized Fullerenes 1a–7a

➤ Compound 1a

a) ^1H NMR (500 MHz, $\text{CDCl}_3/\text{CS}_2$)

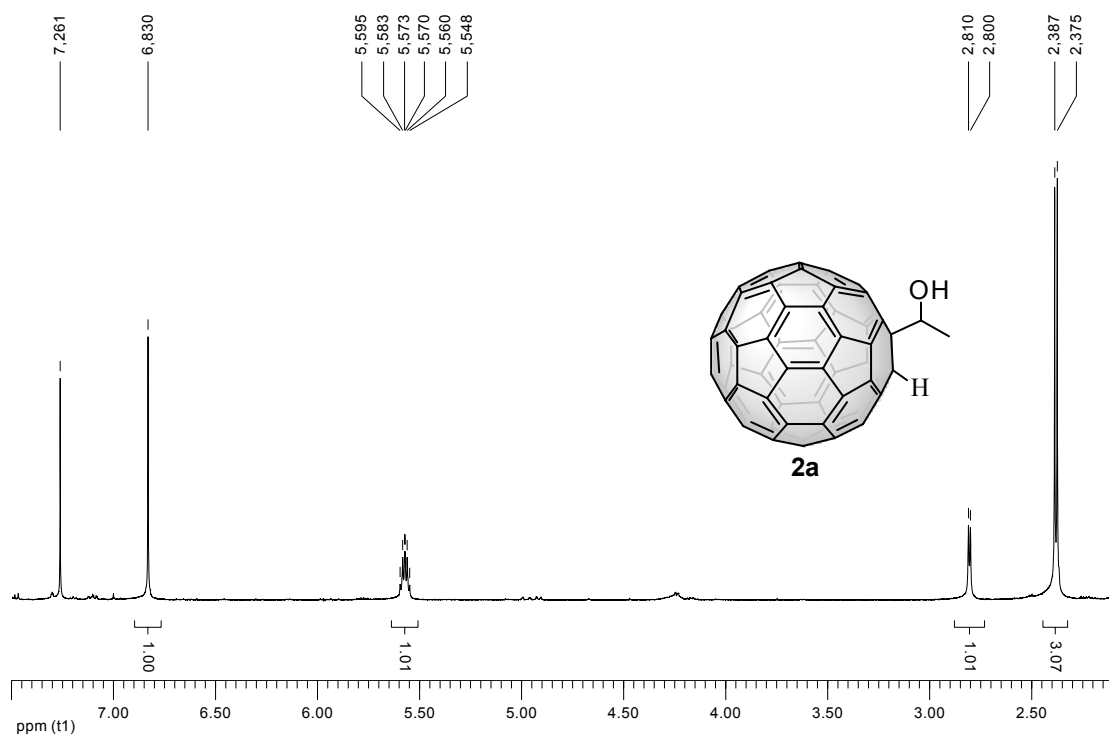


b) UV-vis (CHCl_3)

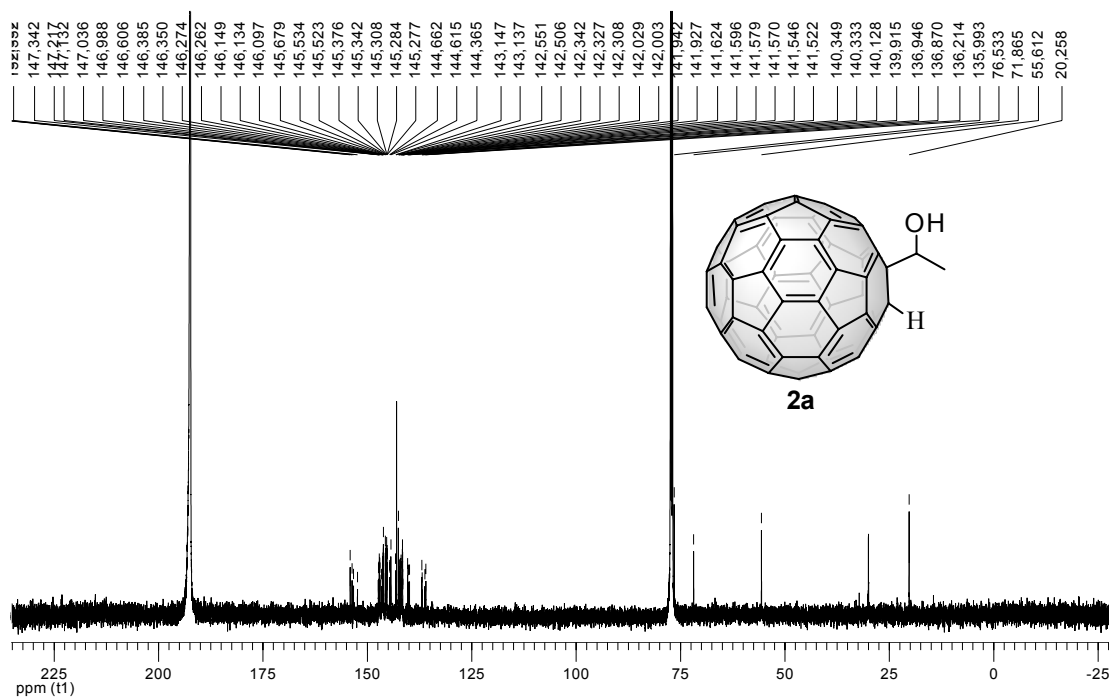


➤ Compound **2a**

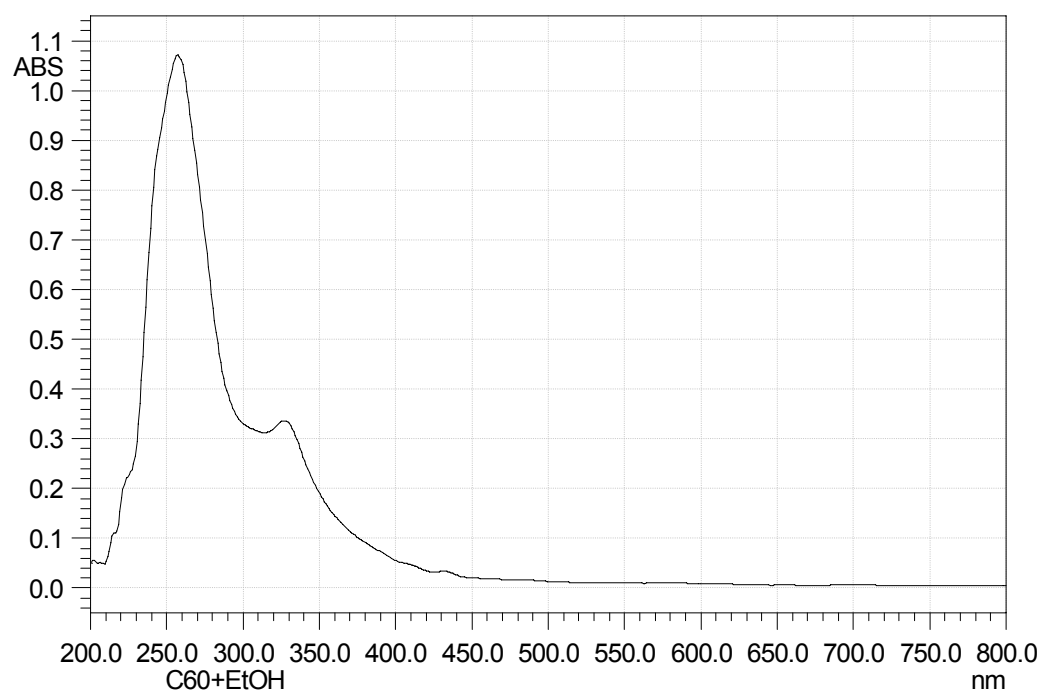
a) ^1H NMR (500 MHz, $\text{CDCl}_3/\text{CS}_2$)



b) ^{13}C NMR (125 MHz, $\text{CDCl}_3/\text{CS}_2$)

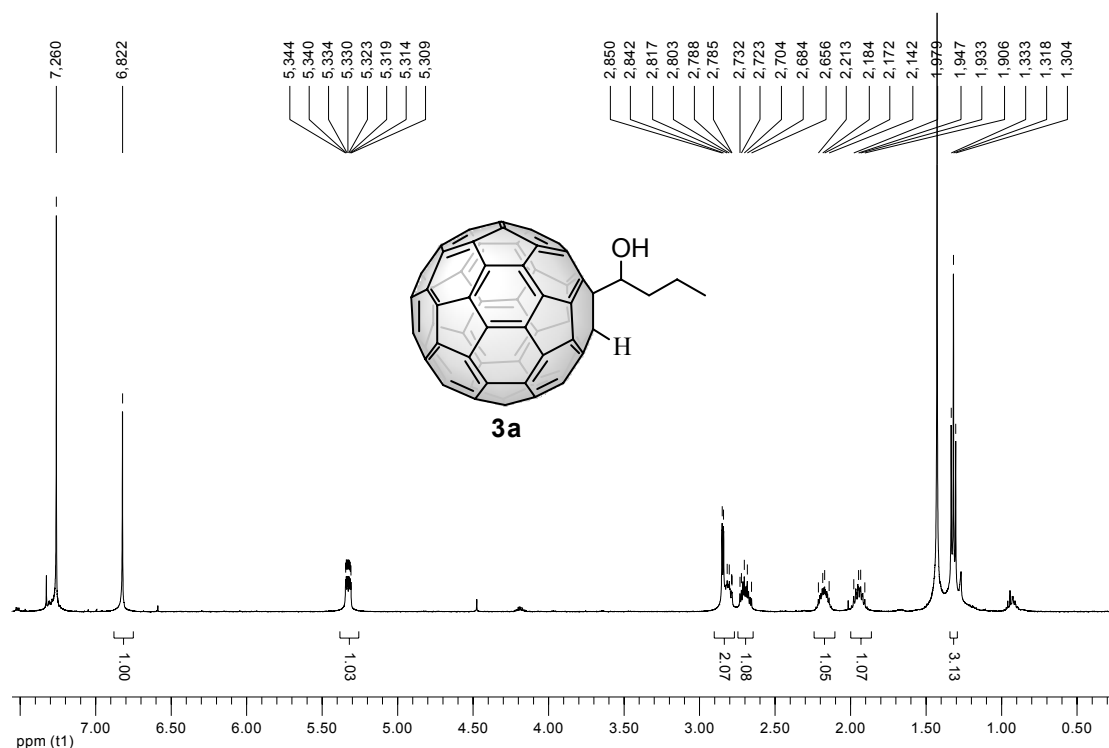


c) UV-vis (CHCl_3)

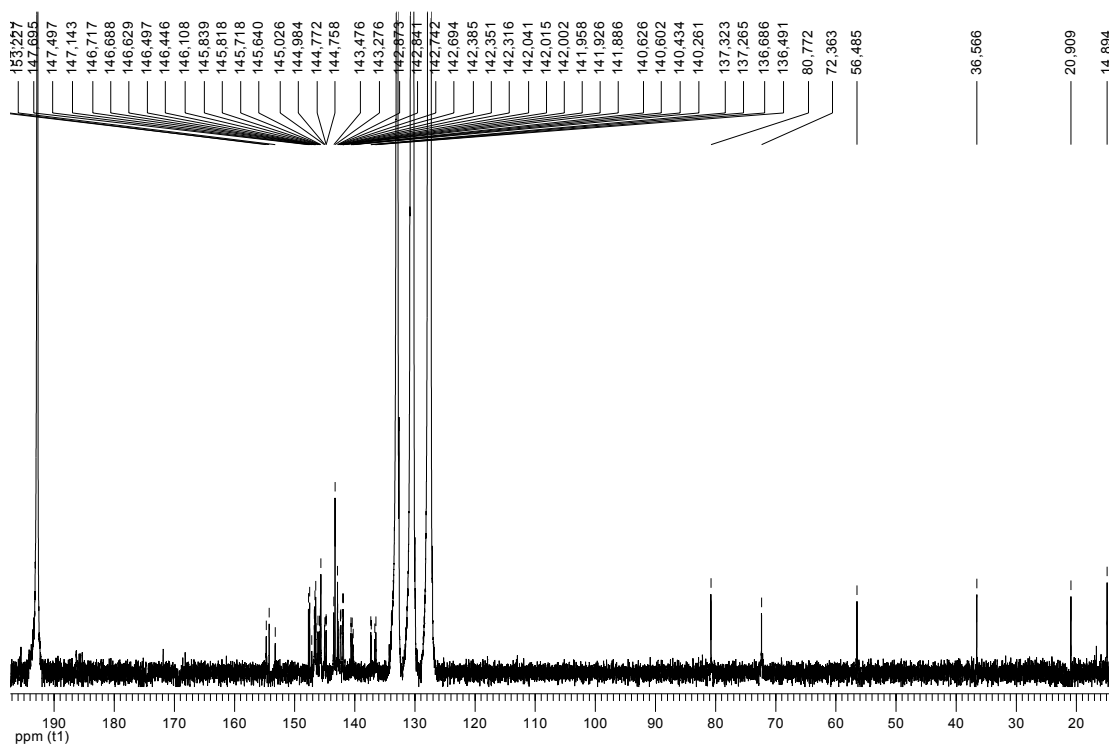


➤ Compound **3a**

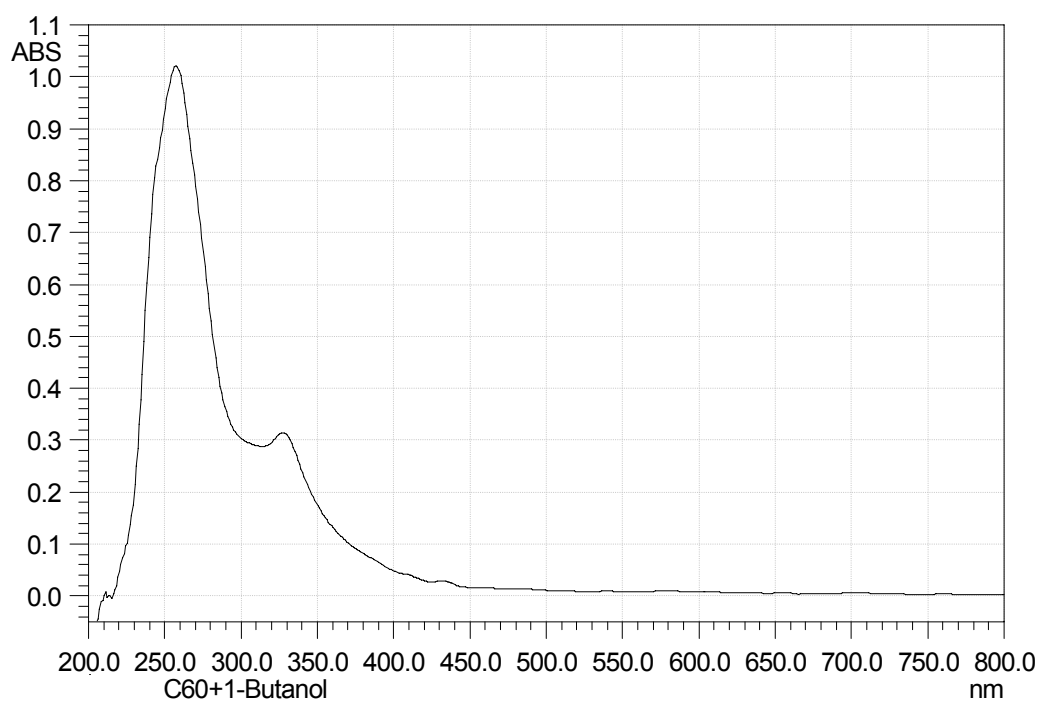
a) ^1H NMR (500 MHz, $\text{CDCl}_3/\text{CS}_2$)



b) ^{13}C NMR (125 MHz, $o\text{-DCB-}d_4/\text{CS}_2$)

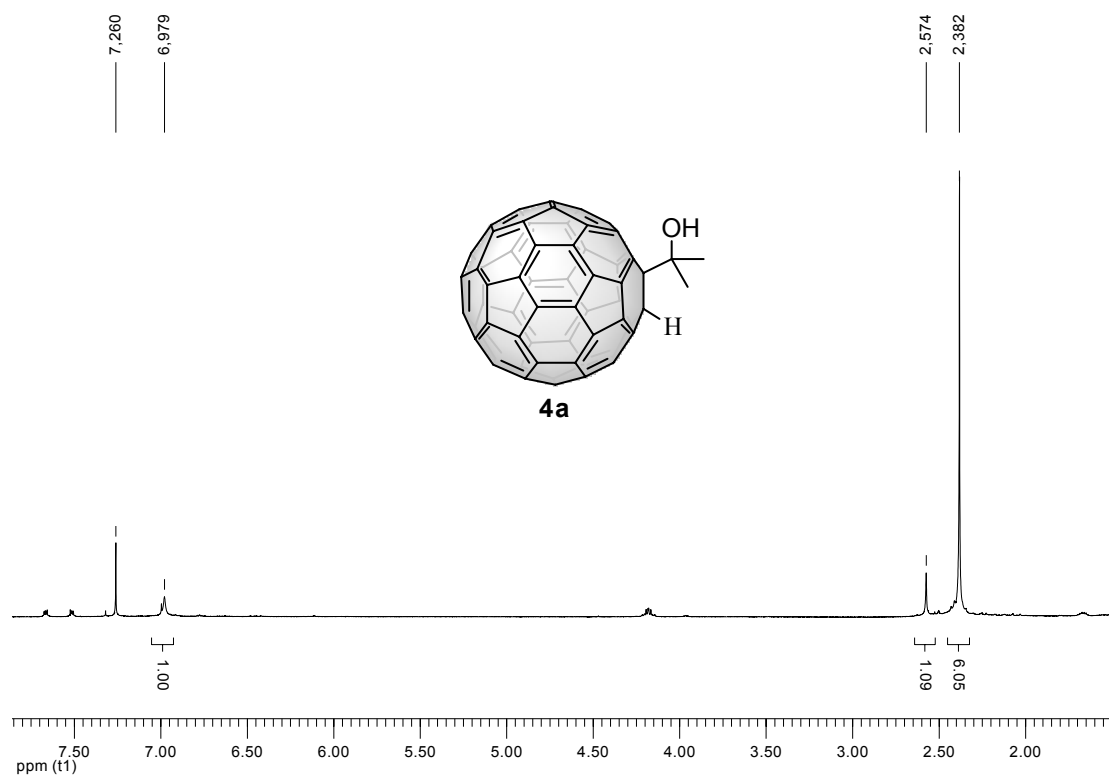


c) UV-vis (CHCl_3)

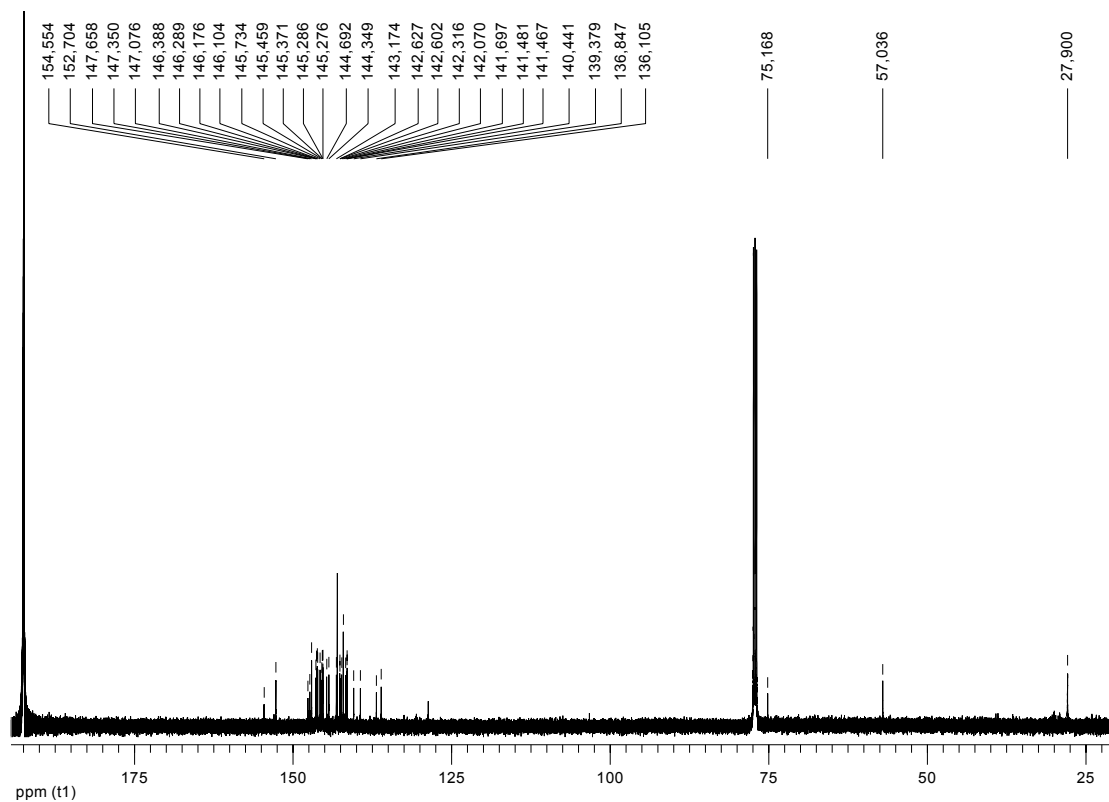


➤ Compound **4a**

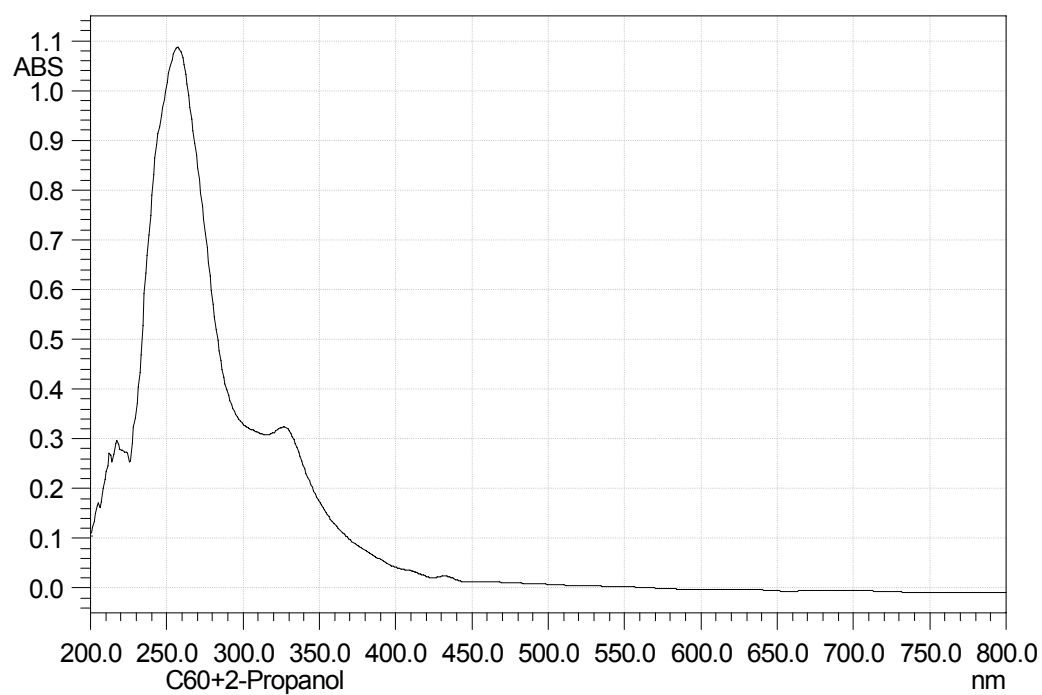
a) ^1H NMR (500 MHz, $\text{CDCl}_3/\text{CS}_2$)



b) ^{13}C NMR (125 MHz, $\text{CDCl}_3/\text{CS}_2$)

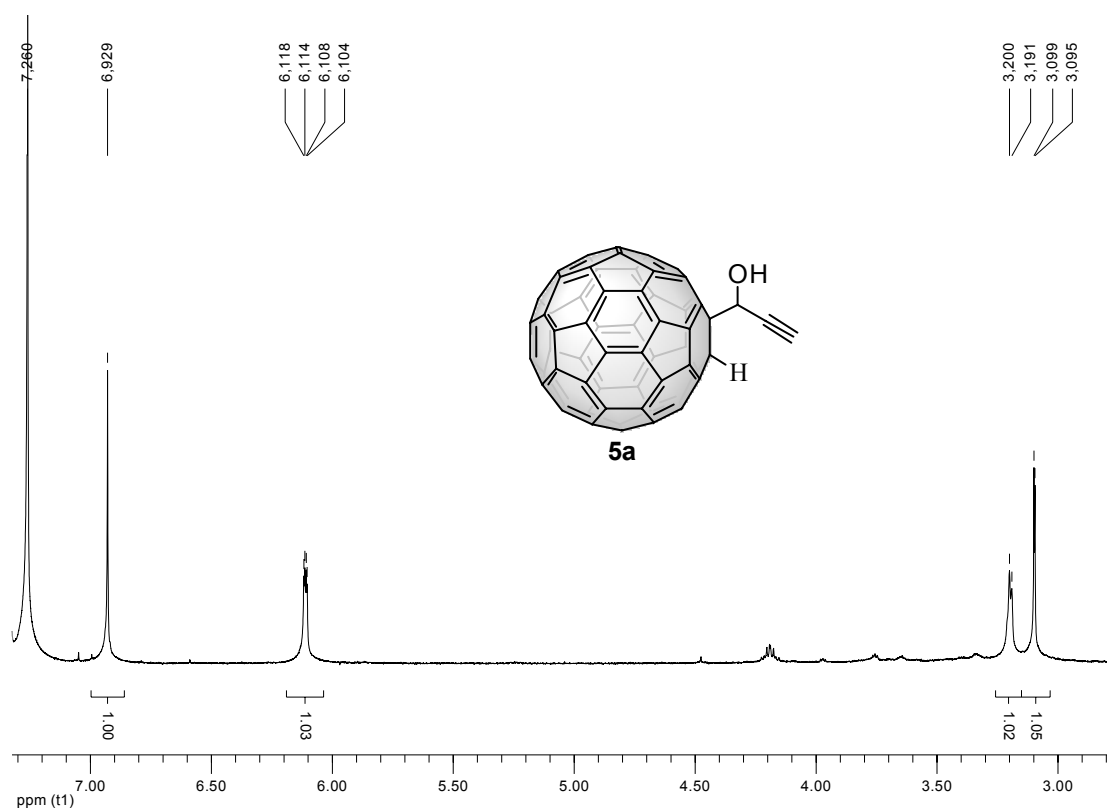


c) UV-vis (CHCl_3)

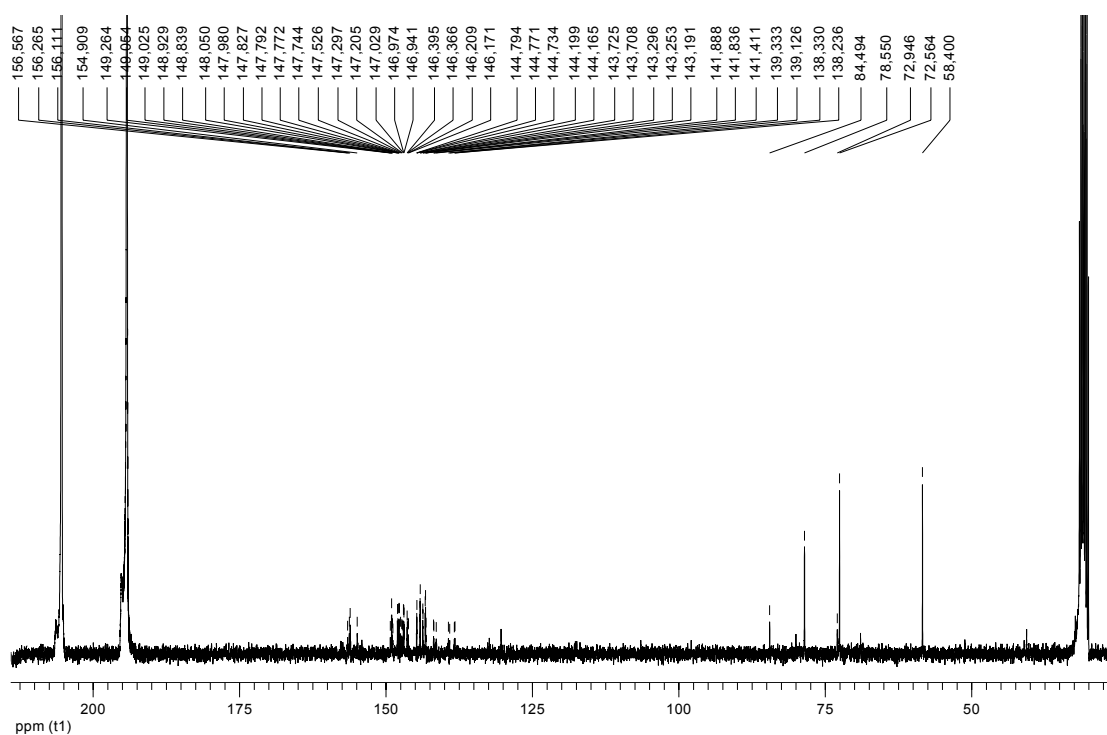


Compound **5a**

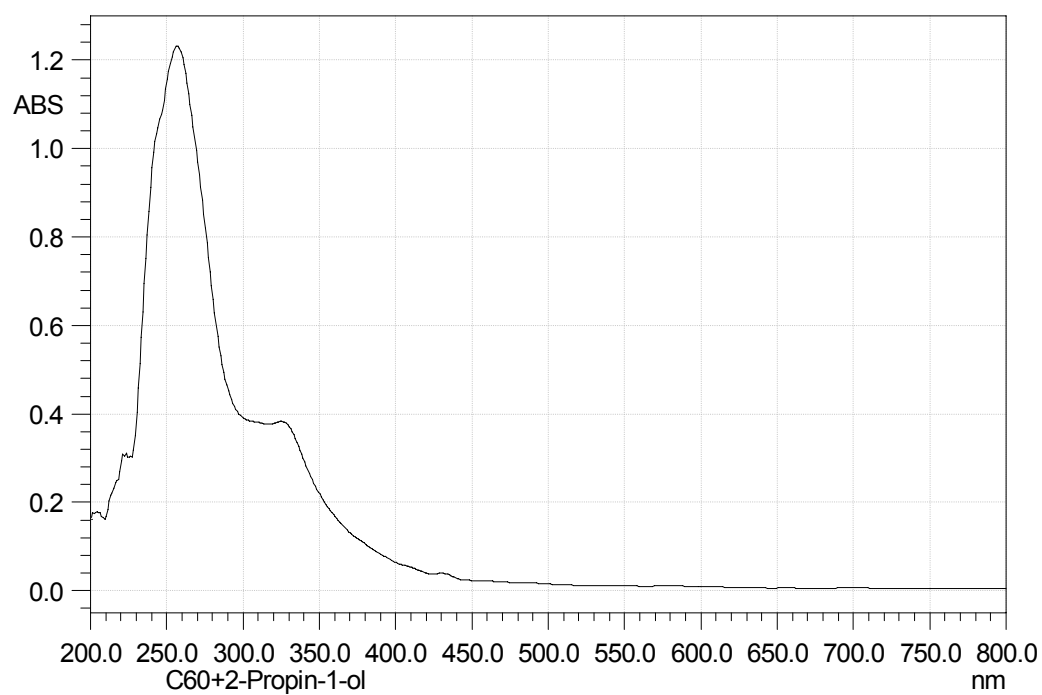
a) ^1H NMR (500 MHz, $\text{CDCl}_3/\text{CS}_2$)



b) ^{13}C NMR (75 MHz, $\text{acetone-}d_6/\text{CS}_2$)

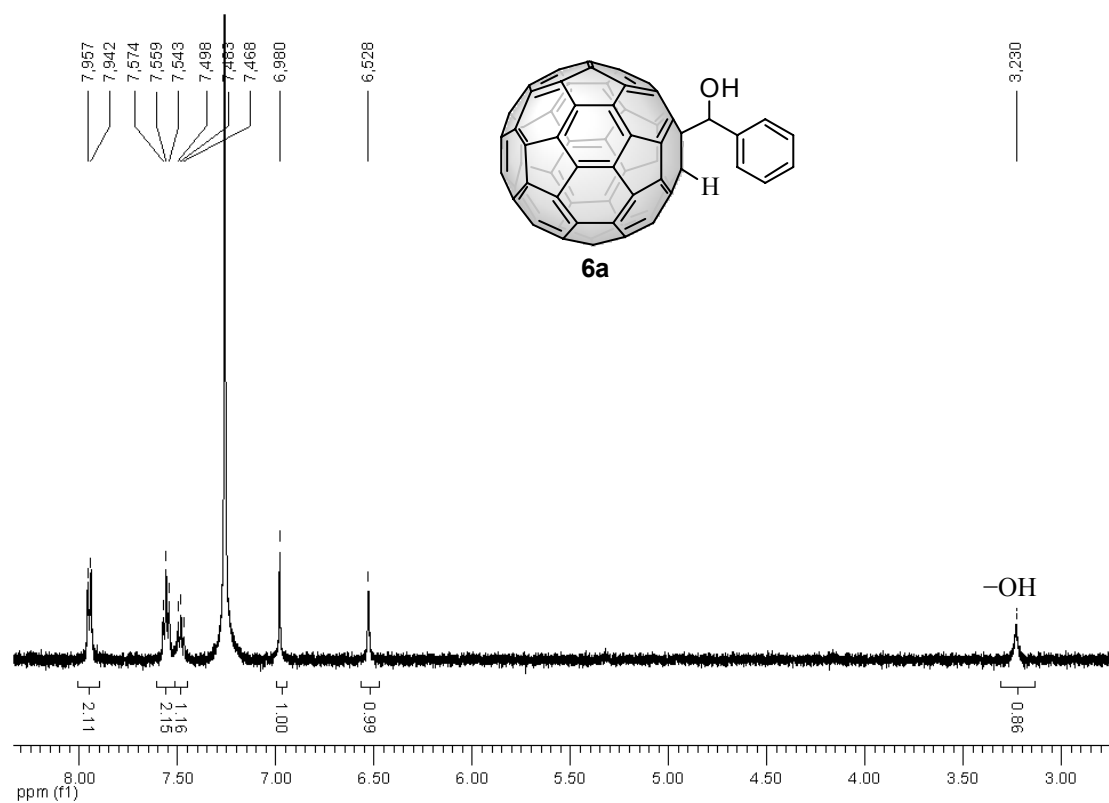


c) UV-vis (CHCl_3)

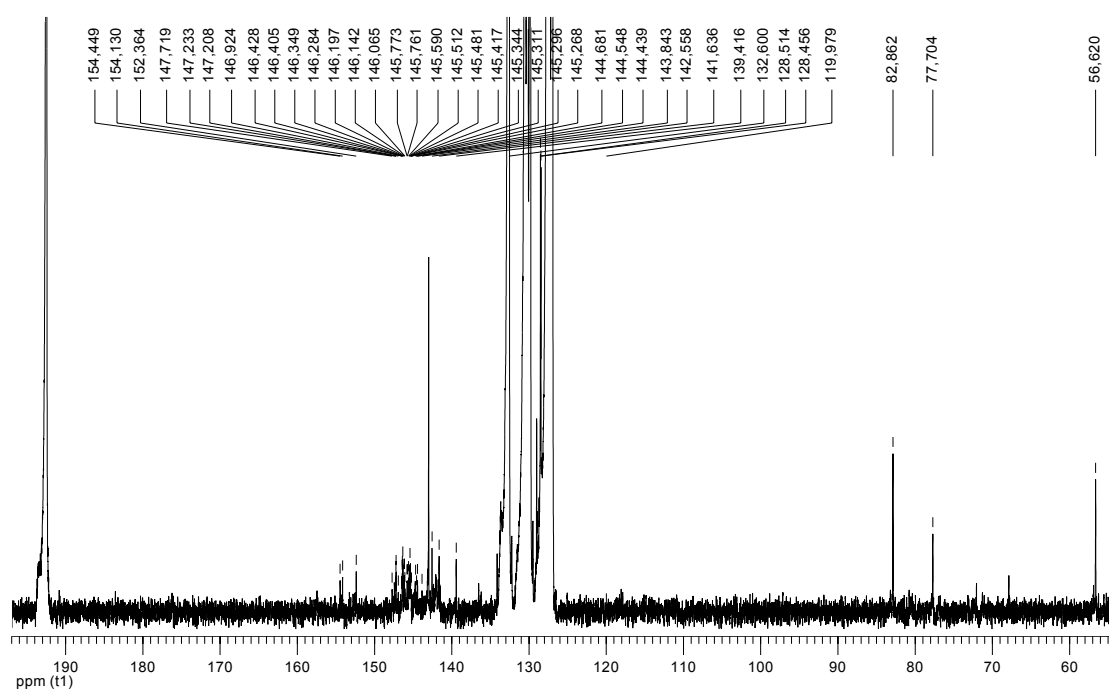


➤ Compound **6a**

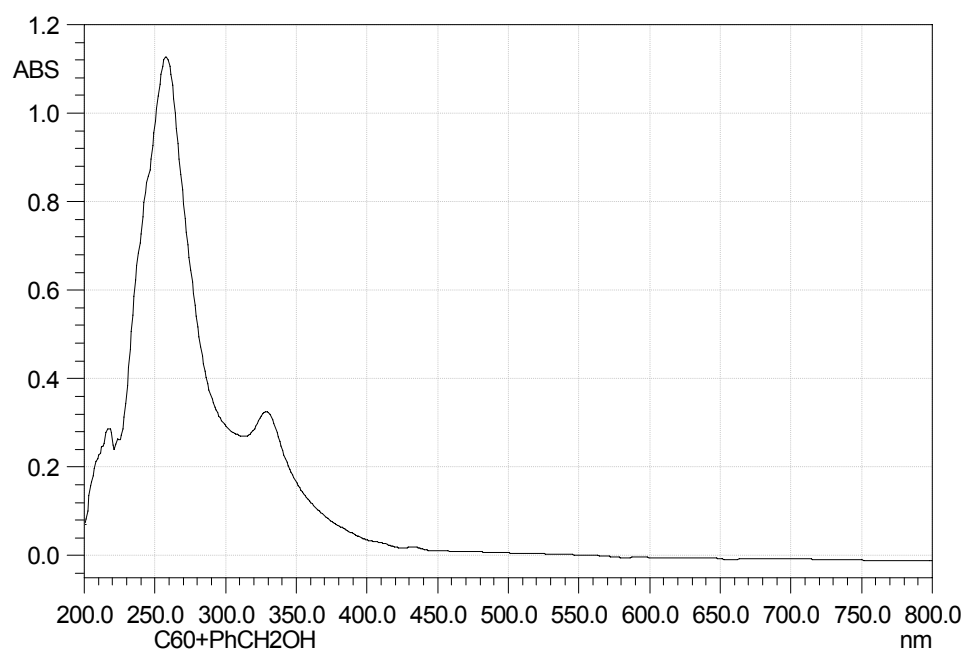
a) ^1H NMR (500 MHz, $\text{CDCl}_3/\text{CS}_2$)



b) ^{13}C NMR (75 MHz, $o\text{-DCB-}d_4/\text{CS}_2$)

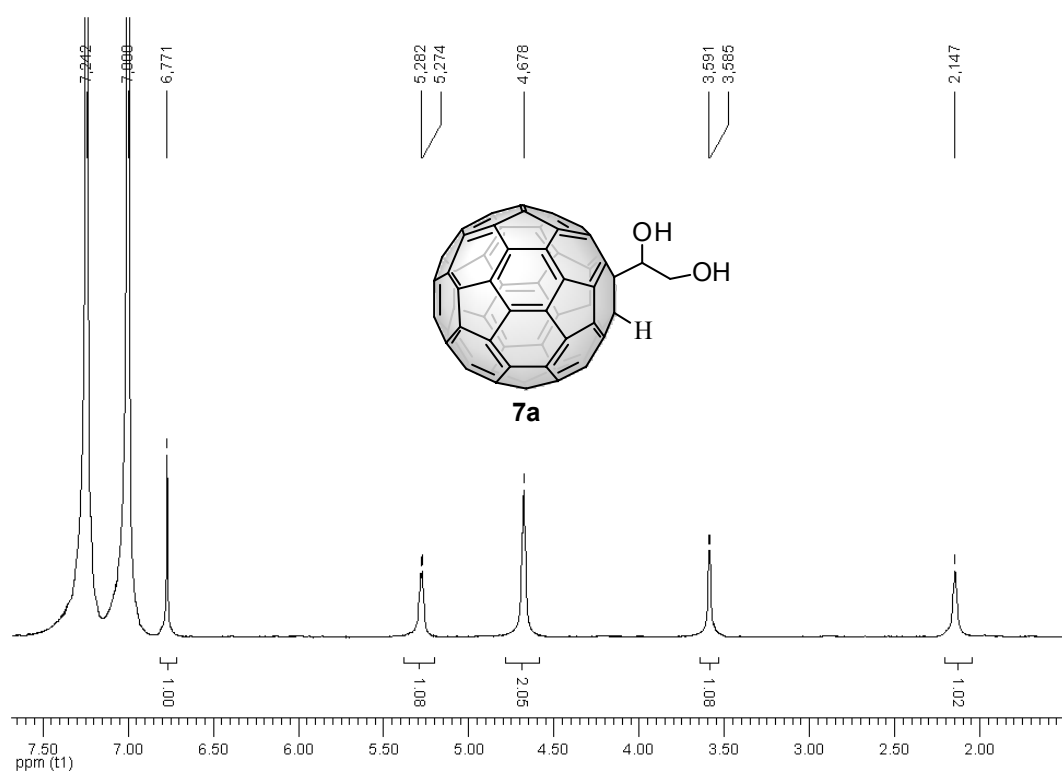


c) UV-vis (CHCl_3)

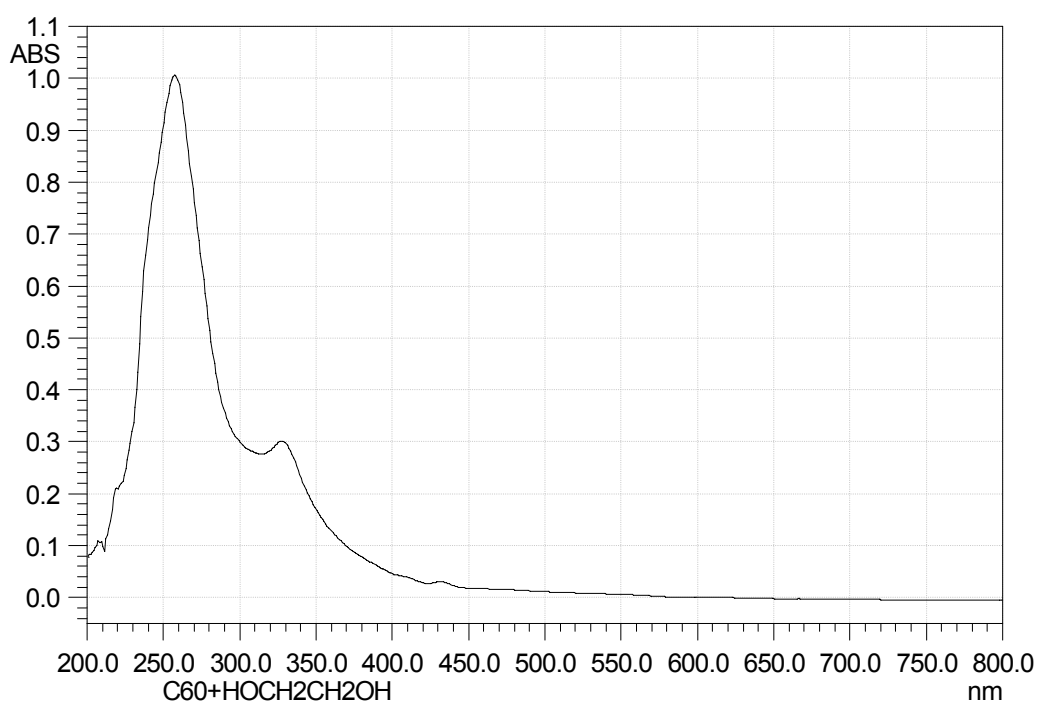


➤ Compound **7a**

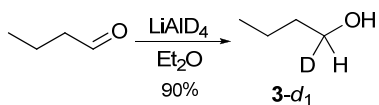
a) ^1H NMR (500 MHz, *o*-DCB- d_4 /CS $_2$)



b) UV-vis (CHCl $_3$)

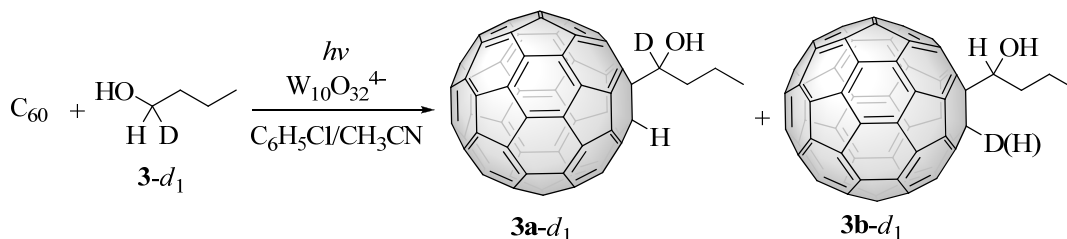


5. Synthetic Procedure and Spectral Data of *n*-butanol-*d*₁ (**3-d**₁)



To a cooled solution (0 °C) of lithium aluminum deuteride LiAlD₄ (175 mg, 4.2 mmol) in anhydrous Et₂O (25 mL) under an Ar atmosphere, was slowly added a solution of the commercially available butyraldehyde (1 g, 14 mmol) in anhydrous Et₂O (25 mL). The reaction was then warmed to room temperature and stirred for 2 h. The mixture was treated with H₂O and 10% NaOH, and extracted twice with Et₂O. The layers were separated, the organic phase dried (MgSO₄) and concentrated *in vacuo* to afford the desired *n*-butanol-*d*₁ (**3-d**₁) in 90% yield. ¹H NMR (500 MHz, CDCl₃): δ 3.56 (m, 1H), 1.49 (m, 2H), 1.34 (m, 2H), 0.89 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 61.77 (triplet, *J*_{C-D} = 21.4 Hz), 34.55, 18.86, 13.76; MS: *m/z* (relative intensity): 74.1 (M-1, 10), 57.0 (M-18, 100), 41.0 (M-34, 85).

6. Experimental Procedure and ¹H NMR Spectrum of the Reaction of C₆₀ with **3-d**₁



The reaction was performed following the general procedure described in Section 2, by using 20 mgr (0.028 mmol) of C₆₀, 46 mg (0.014 mmol) of TBADT, and 200 equiv (5.6 mmol) *n*-butanol-*d*₁ (**3-d**₁) in a mixture of chlorobenzene/acetonitrile 85:15 (70 mL). The progress of the reaction was monitored by analytical HPLC (5C18-MS, 4.6

× 250 mm, elution with 1:1 toluene/acetonitrile at 1 mL/min flow rate, detection at 310 nm, retention time: 7.3 min). The reaction mixture was irradiated at 5–10 °C for 25 min, after which time the reaction solvent and the excess of **3-d**₁ were evaporated under reduced pressure. Acetonitrile was then added and the resulting suspension was centrifuged at 4100 rpm for 10 min (3 times). The resulting crude precipitate was further purified by flash column chromatography on silica (4:1 hexane/toluene) to afford an inseparable mixture of compounds **3a-d**₁ and **3b-d**₁ in 25% yield. Purification could be also achieved with semi-preparative HPLC (elution with 4:1 toluene/acetonitrile at 5 mL/min flow rate, detection at 310 nm, retention time: 13.7 min).

