

Electronic Supplementary Information

Regioselective Acylation and Carboxylation of [60]Fulleroidindoline via Electrochemical Synthesis

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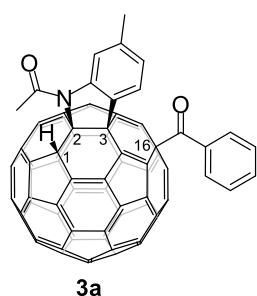
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General Methods

All electrochemical reactions were performed under argon atmosphere using a SHANGHAI CHENHUA CHI630D workstation. Tetra-*n*-butylammonium perchlorate (TBAP) was recrystallized from absolute ethanol and dried in a vacuum at 313 K prior to use. All the chemicals were obtained commercially. Among these chemicals, liquid chemicals such as acetyl chloride, benzoyl chloride, and ethyl chloroformate were distilled at each boiling point prior to use, due mainly to their high sensitivity towards humidity, others were used without further purification. Controlled potential electrolysis (CPE) was carried out on a potentiostat/galvanostat using an “H” type cell consisting of two platinum gauze electrodes (serving as working and counter electrodes, respectively) and a saturated calomel reference electrode (SCE). The SCE was separated from the bulk of the solution by a fritted-glass bridge of low porosity, which contained the solvent/supporting electrolyte mixture.

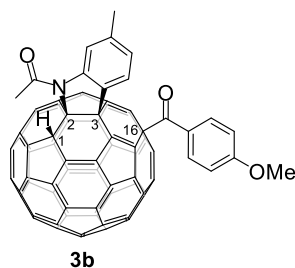
Synthesis of the dianion 1^{2-} : 26.0 mg (0.030 mmol) of [60]fulleroidindoline **1** was dissolved in 25.0 mL of anhydrous *o*-dichlorobenzene (ODCB) solution containing 0.1 M TBAP. Then the solution was electroreduced at -1.1 V vs SCE under an argon atmosphere at room temperature. When the theoretical number of coulombs required for a full conversion of **1** to 1^{2-} was reached, the electrolysis was terminated after about 5.0 h, and a dark-green solution of 1^{2-} was obtained.

Experimental procedures and spectral data for products **3a–3g**.

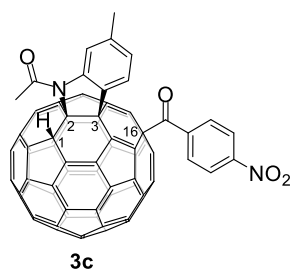


Synthesis of compound **3a:** After the electrolysis of the **1** (26.0 mg, 0.030 mmol), the dianion 1^{2-} reacted with benzoyl chloride (17.5 μ L, 0.150 mmol) and NaH (57–63% oil dispersion, 12.0 mg, 0.300 mmol). After being stirred at 0 $^{\circ}$ C for 5 h, the resulting mixture was directly filtered through a silica gel (200–300 mesh) plug with CS_2/CH_2Cl_2 (1:1 v/v) to remove the supporting electrolyte and insoluble materials, and then evaporated in vacuo to remove the solvent. Next, the residue was further separated on a silica gel column (400–500 mesh) with CS_2/CH_2Cl_2 (4:1 v/v) as the eluent to afford product **3a** (17.5 mg, 60%) as an amorphous brown solid along with unreacted **1** (0.6 mg, 2%). If the dianion 1^{2-} reacted with benzoyl chloride in the absence of NaH under the same conditions, then the 1,2,3,4-adduct **4** (5.9 mg, 23%) and product **3a** (11.2 mg, 38%) were obtained along with unreacted **1** (1.1 mg, 4%). 1H NMR (400 MHz, $CS_2/CDCl_3$) δ 8.39 (d, J = 8.0 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.7 Hz, 2H), 7.41 (d, J = 7.8 Hz, 1H), 7.29 (s, 1H), 7.04 (d, J = 7.8 Hz, 1H), 5.95 (s, 1H), 2.76 (s, 3H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CS_2/CDCl_3$, all 1C unless indicated) δ 196.06 (C=O), 167.78 (C=O), 152.39, 152.08, 151.38, 150.04, 149.83, 149.22, 148.81, 148.52, 148.26, 147.93,

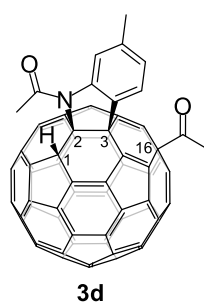
147.86, 147.73, 147.36, 147.18, 147.14 (2C), 146.91, 146.86, 146.41, 146.40, 145.99 (2C), 145.95, 145.92, 145.53, 145.37, 145.33, 144.82 (2C), 144.80, 144.72, 144.54, 144.42, 144.31, 144.14, 143.84, 143.65, 143.42, 143.31, 143.05, 142.13, 141.93, 141.79, 141.72 (2C), 141.69, 141.55, 141.35, 141.24, 141.10, 140.63, 140.14, 139.93 (aryl C), 138.84, 137.70, 137.54 (aryl C), 137.47, 137.38, 135.44 (aryl C), 133.14 (aryl C), 129.16 (2C, aryl C), 128.72 (2C, aryl C), 128.61 (aryl C), 125.80 (aryl C), 125.42 (aryl C), 115.11 (aryl C), 83.58 (sp³-C of C₆₀), 69.89 (sp³-C of C₆₀), 62.42 (sp³-C of C₆₀), 56.81 (sp³-C of C₆₀), 26.84, 22.25; UV-vis (CHCl₃) λ_{max} nm (log ε) 251.0 (5.1), 318.5 (4.6), 403.5 (4.0), 440.0 (3.9), 525.5 (3.2), 703.5 (2.5); FT-IR ν/cm⁻¹ (KBr) 2922, 2860, 1668, 1599, 1499, 1439, 1366, 1304, 1236, 1180, 1086, 1020, 964, 858, 802, 748, 691, 604, 528; MALDI-TOF MS *m/z* calcd for C₇₆H₁₆NO₂ [M+H]⁺ 974.1176, found 974.1165.



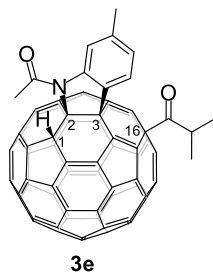
Synthesis of compound 3b: After the electrolysis of the **1** (26.0 mg, 0.030 mmol), the dianion **1**²⁻ reacted with *p*-anisoyl chloride (20.5 μL, 0.150 mmol) and NaH (57–63% oil dispersion, 12.0 mg, 0.300 mmol). After being stirred at 0 °C for 5 h, the resulting mixture was directly filtered through a silica gel (200–300 mesh) plug with CS₂/CH₂Cl₂ (1:1 v/v) to remove the supporting electrolyte and insoluble materials, and then evaporated in vacuo to remove the solvent. Next, the residue was further separated on a silica gel (400–500 mesh) column with CS₂/CH₂Cl₂ (4:1 v/v) as the eluent to afford product **3b** (17.9 mg, 59%) as an amorphous brown solid along with unreacted **1** (1.1 mg, 4%). ¹H NMR (400 MHz, TCE-*d*₂) δ 8.55 (d, *J* = 8.9 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.29 (s, 1H), 7.04 (d, *J* = 7.8 Hz, 1H), 7.00 (d, *J* = 8.9 Hz, 2H), 5.92 (s, 1H), 3.83 (s, 3H), 2.74 (s, 3H), 2.45 (s, 3H); ¹³C NMR (100 MHz, TCE-*d*₂, all 1C unless indicated) δ 194.79 (C=O), 169.08 (C=O), 164.29 (aryl C), 152.98, 152.71, 152.50, 150.47, 150.05, 149.56, 149.05, 148.77, 148.49, 148.21, 148.06, 147.90, 147.62, 147.56, 147.49, 147.47, 147.17 (2C), 146.64, 146.60, 146.26, 146.20, 146.19, 146.17, 145.72, 145.61, 145.53, 145.09, 145.03, 144.98, 144.92, 144.75, 144.64, 144.56, 144.25, 144.08, 143.67, 143.56, 143.46, 143.11, 142.46, 142.11, 141.99, 141.88, 141.79, 141.75, 141.72, 141.57, 141.40, 141.36, 141.12, 140.62 (aryl C), 140.31, 139.30, 137.95, 137.53, 137.51, 135.81 (aryl C), 132.45 (2C, aryl C), 129.82 (aryl C), 128.86 (aryl C), 125.91 (aryl C), 125.68 (aryl C), 115.65 (aryl C), 114.60 (2C, aryl C), 83.78 (sp³-C of C₆₀), 69.99 (sp³-C of C₆₀), 62.59 (sp³-C of C₆₀), 57.00 (sp³-C of C₆₀), 56.07, 27.60, 22.55; UV-vis (CHCl₃) λ_{max} nm (log ε) 253.5 (5.1), 325.0 (4.8), 403.5 (4.2), 443.5 (4.0), 522.0 (3.5), 706.0 (3.1); FT-IR ν/cm⁻¹ (KBr) 2960, 2920, 1660, 1590, 1500, 1440, 1370, 1340, 1300, 1260, 1170, 1110, 1030, 964, 860, 802, 748, 702, 663, 609, 561, 528; MALDI-TOF MS *m/z* calcd for C₇₇H₁₇NO₃Na [M+Na]⁺ 1026.1101, found 1026.1114.



Synthesis of compound 3c: After the electrolysis of the **1** (26.0 mg, 0.030 mmol), the dianion **1**²⁻ reacted with *p*-nitrobenzoyl chloride (27.8 mg, 0.150 mmol) and NaH (57–63% oil dispersion, 120.0 mg, 3.000 mmol). After being stirred at 0 °C for 2 h, the resulting mixture was directly filtered through a silica gel (200–300 mesh) plug with CS₂/CH₂Cl₂ (1:1 v/v) to remove the supporting electrolyte and insoluble materials, and then evaporated in vacuo to remove the solvent. However, further purification on a silica gel (400–500 mesh) column would cause product **3c** to completely decompose. Accordingly, the residue was purified by semi-preparative HPLC on a Buckyprep column (10 × 250 mm, eluent: toluene, 5 mL/min flow rate, detection at 325 nm) to afford product **3c** (14.8 mg, 48%) as an amorphous brown solid along with unreacted **1** (1.0 mg, 4%). If the dianion **1**²⁻ reacted with *p*-nitrobenzoyl chloride in the presence of 10 equiv of NaH under the same conditions, then the 1,2,3,4-adduct **4** (14.1 mg, 54%) was exclusively obtained along with unreacted **1** (1.1 mg, 4%). ¹H NMR (400 MHz, TCE-*d*₂) δ 8.42 (d, *J* = 8.9 Hz, 2H), 8.31 (d, *J* = 8.9 Hz, 2H), 7.38 (d, *J* = 7.7 Hz, 1H), 7.33 (s, 1H), 7.12 (d, *J* = 7.7 Hz, 2H), 5.96 (s, 1H), 2.75 (s, 3H), 2.49 (s, 3H); ¹³C NMR (100 MHz, TCE-*d*₂, all 1C unless indicated) δ 197.27 (C=O), 169.08 (C=O), 152.49, 150.88, 150.70, 150.34, 150.22 (aryl C), 150.17, 149.48, 149.12, 148.88, 148.53, 148.22, 148.10, 147.71, 147.53, 147.46, 147.42, 147.41, 147.05, 146.84, 146.77, 146.69, 146.32, 146.29, 146.20, 146.17, 145.70, 145.58, 145.52, 145.14, 145.12, 145.06, 145.00, 144.84, 144.67, 144.59, 144.55, 144.48, 144.17, 143.68, 143.48, 143.24, 142.83, 142.22, 142.15, 142.14, 142.02, 141.89, 141.85, 141.82, 141.74, 141.63, 141.42, 141.04, 140.94, 140.42, 137.89, 137.71, 137.67, 137.48, 136.40 (aryl C), 130.06 (2C, aryl C), 128.76 (aryl C), 125.97 (aryl C), 125.37 (aryl C), 124.35 (2C, aryl C), 115.84 (aryl C), 83.89 (sp³-C of C₆₀), 69.75 (sp³-C of C₆₀), 62.70 (sp³-C of C₆₀), 57.04 (sp³-C of C₆₀), 27.59, 22.58; UV-vis (CHCl₃) λ_{max} nm (log ε) 254.5 (5.0), 321.0 (4.6), 402.5 (4.0), 439.0 (3.9), 521.0 (3.4), 705.5 (3.0); FT-IR ν/cm⁻¹ (KBr) 2922, 2852, 1668, 1599, 1525, 1498, 1435, 1369, 1342, 1302, 1248, 1223, 1178, 1130, 1093, 1032, 1011, 964, 847, 820, 746, 702, 604, 561, 528; MALDI-TOF MS *m/z* calcd for C₇₆H₁₃N₂O₄ [M-H]⁺ 1017.0870, found 1017.0882.

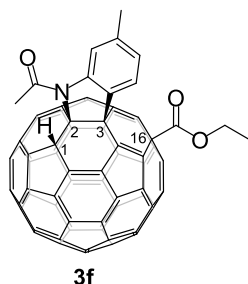


Synthesis of compound 3d: After the electrolysis of the **1** (26.0 mg, 0.030 mmol), the dianion **1**²⁻ reacted with acetyl chloride (10.5 μ L, 0.150 mmol) and NaH (57–63% oil dispersion, 120.0 mg, 3.000 mmol). After being stirred at 0 °C for 5 h, the resulting mixture was directly filtered through a silica gel (200–300 mesh) plug with CS₂/CH₂Cl₂ (1:1 v/v) to remove the supporting electrolyte and insoluble materials, and then evaporated in vacuo to remove the solvent. Next, the residue was further separated on a silica gel (400–500 mesh) column with CS₂/CH₂Cl₂ (4:1 v/v) as the eluent to afford product **3d** (10.9 mg, 40%) as an amorphous brown solid along with unreacted **1** (2.1 mg, 8%). ¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, *J* = 7.8 Hz, 1H), 7.38 (s, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 6.01 (s, 1H), 2.98 (s, 3H), 2.82 (s, 3H), 2.57 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, all 1C unless indicated) δ 202.61 (C=O), 168.82 (C=O), 152.89, 152.32, 150.31, 150.28, 150.17, 149.55, 149.09, 148.78, 148.54, 148.22, 148.02, 147.62, 147.50, 147.45 (2C), 147.31, 147.08, 147.00, 146.86, 146.64, 146.31 (2C), 146.27, 146.24, 145.74, 145.57, 145.44, 145.19, 145.05, 145.03, 144.97, 144.96, 144.81, 144.66, 144.55, 144.37, 144.09, 143.70, 143.69, 143.17, 142.39, 142.28, 142.21, 142.12, 141.99, 141.84, 141.75 (2C), 141.57, 141.47, 140.98, 140.44 (aryl C), 140.38, 138.74, 138.12, 137.53, 137.42, 135.28 (aryl C), 129.21 (aryl C), 125.96 (aryl C), 125.93 (aryl C), 115.39 (aryl C), 83.84 (sp³-C of C₆₀), 71.44 (sp³-C of C₆₀), 62.80 (sp³-C of C₆₀), 57.04 (sp³-C of C₆₀), 27.49, 27.35, 22.40; UV-vis (CHCl₃) λ_{max} nm (log ϵ) 251.0 (5.0), 318.5 (4.6), 401.5 (4.0), 446.0 (3.8), 524.0 (3.2), 702.5 (2.3); FT-IR ν/cm^{-1} (KBr) 2920, 2855, 1717, 1665, 1603, 1501, 1435, 1362, 1302, 1256, 1169, 1086, 1036, 802, 606, 527; MALDI-TOF MS *m/z* calcd for C₇₁H₁₄NO₂ [M+H]⁺ 912.1019, found 912.1002.

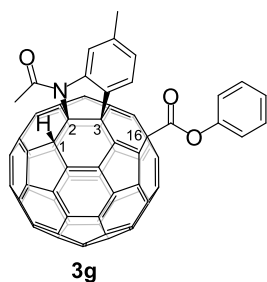


Synthesis of compound 3e: After the electrolysis of the **1** (26.0 mg, 0.030 mmol), the dianion **1**²⁻ reacted with isobutyl chloride (15.5 μ L, 0.150 mmol) and NaH (57–63% oil dispersion, 12.0 mg, 0.300 mmol). After being stirred at 0 °C for 5 h, the resulting mixture was directly filtered through a silica gel (200–300 mesh) plug with CS₂/CH₂Cl₂ (1:1 v/v) to remove the supporting electrolyte and insoluble materials, and then evaporated in vacuo to remove the solvent. Next, the residue was further separated on a silica gel (400–500 mesh) column with CS₂/CH₂Cl₂ (4:1 v/v) as the eluent to afford product **3e** (11.1 mg, 39%) as an amorphous brown solid along with unreacted **1** (1.5 mg, 5%). ¹H NMR (400 MHz, TCE-*d*₂) δ 7.44 (d, *J* = 7.8 Hz, 1H), 7.31 (s, 1H), 7.17 (d, *J* = 7.8 Hz, 1H), 5.93 (s, 1H), 3.98 (hept, *J* = 6.6 Hz, 1H), 2.75 (s, 3H), 2.49 (s, 3H), 1.36 (d, *J* = 6.7 Hz, 3H), 1.30 (d, *J* = 6.7 Hz, 3H); ¹³C NMR (100 MHz, TCE-*d*₂, all 1C unless indicated) δ 209.84 (C=O), 169.09 (C=O), 153.12, 151.95, 150.40, 150.27, 150.15, 149.68, 149.03, 148.72, 148.52, 148.22, 147.98, 147.80, 147.57, 147.54, 147.49, 147.33, 147.14, 147.09, 146.79, 146.60, 146.29 (2C), 146.23 (2C), 145.66, 145.56, 145.43, 145.04 (2C),

144.93 (2C), 144.91, 144.77, 144.67, 144.53, 144.32, 144.07, 143.74, 143.65, 143.19, 142.47, 142.24, 142.20, 142.12, 141.85, 141.77, 141.69, 141.62, 141.52, 141.49, 141.11, 140.70 (aryl C), 140.35, 139.19, 138.36, 137.75, 137.46, 134.84 (aryl C), 129.20 (aryl C), 125.98 (aryl C), 125.82 (aryl C), 115.68 (aryl C), 83.70 (sp³-C of C₆₀), 71.31 (sp³-C of C₆₀), 62.68 (sp³-C of C₆₀), 57.04 (sp³-C of C₆₀), 37.54, 27.64, 22.59, 20.86, 20.77; UV-vis (CHCl₃) λ_{max} nm (log ε) 252.0 (5.0), 318.5 (4.6), 401.5 (4.0), 437.0 (3.9), 526.5 (3.4), 704.5 (3.1); FT-IR ν/cm⁻¹ (KBr) 2962, 2922, 2854, 1714, 1668, 1599, 1498, 1439, 1371, 1342, 1302, 1259, 1174, 1093, 1036, 964, 858, 802, 698, 604, 561, 530; MALDI-TOF MS *m/z* calcd for C₇₃H₁₈NO₂ [M+H]⁺ 940.1338, found 940.1332.



Synthesis of compound 3f: After the electrolysis of the **1** (26.0 mg, 0.030 mmol), the dianion **1**²⁻ reacted with ethyl chloroformate (14.5 μL, 0.150 mmol) and NaH (57–63% oil dispersion, 12.0 mg, 0.300 mmol). After being stirred at 25 °C for 24 h, the resulting mixture was directly filtered through a silica gel (200–300 mesh) plug with CS₂/CH₂Cl₂ (1:1 v/v) to remove the supporting electrolyte and insoluble materials, and then evaporated in vacuo to remove the solvent. Next, the residue was further separated on a silica gel (400–500 mesh) column with CS₂/CH₂Cl₂ (4:1 v/v) as the eluent to afford product **3f** (8.6 mg, 30%) as an amorphous brown solid along with unreacted **1** (9.5 mg, 37%). ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, *J* = 7.7 Hz, 1H), 7.38 (s, 1H), 7.23 (d, *J* = 7.7 Hz, 1H), 6.00 (s, 1H), 4.59 (q, *J* = 7.1 Hz, 2H), 2.82 (s, 3H), 2.57 (s, 3H), 1.49 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃, all 1C unless indicated) δ 169.32 (C=O), 168.78 (C=O), 152.82, 152.34, 150.18, 150.07, 149.91, 149.29, 149.02, 148.69, 148.47, 148.19, 147.89, 147.44, 147.38, 147.35, 147.32, 147.23 (2C), 146.98, 146.75, 146.62, 146.37, 146.30, 146.17, 146.12, 145.62, 145.47, 145.37, 145.02, 144.99, 144.96, 144.82, 144.77, 144.74, 144.61, 144.49, 144.17, 144.01, 143.59 (2C), 142.99, 142.34, 142.24, 142.07 (2C), 141.87, 141.76, 141.65, 141.60, 141.58, 141.20, 140.94, 140.41 (aryl C), 140.23, 138.14, 138.11, 137.33, 137.00, 135.34 (aryl C), 129.09 (aryl C), 126.13 (aryl C), 125.76 (aryl C), 115.43 (aryl C), 83.83 (sp³-C of C₆₀), 63.64, 62.71 (sp³-C of C₆₀), 61.83 (sp³-C of C₆₀), 57.00 (sp³-C of C₆₀), 27.34, 22.41, 14.52; UV-vis (CHCl₃) λ_{max} nm (log ε) 251.0 (5.0), 318.0 (4.6), 403.0 (4.0), 443.5 (3.8), 524.5 (3.2), 699.5 (2.4); FT-IR ν/cm⁻¹ (KBr) 2951, 2920, 2855, 1734, 1667, 1594, 1499, 1438, 1369, 1341, 1300, 1220, 1093, 1021, 858, 845, 791, 605, 562, 529; MALDI-TOF MS *m/z* calcd for C₇₂H₁₆NO₃ [M+H]⁺ 942.1125, found 942.1114.



Synthesis of compound 3g: After the electrolysis of the **1** (26.0 mg, 0.030 mmol), the dianion **1**²⁻ reacted with phenyl chloroformate (18.5 μ L, 0.150 mmol) and NaH (57–63% oil dispersion, 12.0 mg, 0.300 mmol). After being stirred at 25 °C for 24 h, the resulting mixture was directly filtered through a silica gel (200–300 mesh) plug with CS₂/CH₂Cl₂ (1:1 v/v) to remove the supporting electrolyte and insoluble materials, and then evaporated in vacuo to remove the solvent. Next, the residue was further separated on a silica gel (400–500 mesh) column with CS₂/CH₂Cl₂ (4:1 v/v) as the eluent to afford product **3g** (7.7 mg, 26%) as an amorphous brown solid along with unreacted **1** (11.7 mg, 45%). ¹H NMR (400 MHz, TCE-*d*₂) δ 7.84 (d, *J* = 7.7 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.36–7.26 (m, 4H), 7.18 (d, *J* = 7.8 Hz, 1H), 5.96 (s, 1H), 2.75 (s, 3H), 2.51 (s, 3H); ¹³C NMR (100 MHz, TCE-*d*₂, all 1C unless indicated) δ 169.10 (C=O), 168.41 (C=O), 152.89, 151.51, 150.97, 150.49, 150.17, 149.34, 149.32, 149.09, 148.80, 148.52, 148.26, 147.97, 147.44, 147.42, 147.41, 147.38, 147.29 (2C), 146.98, 146.76, 146.69, 146.38, 146.37, 146.24 (2C), 145.61, 145.54, 145.43, 145.16, 145.12, 145.10, 145.04, 144.98, 144.83, 144.68, 144.57, 144.33, 144.11, 143.65, 143.59, 143.10, 142.32, 142.28, 142.18, 142.01, 141.90, 141.81, 141.76, 141.73, 141.71, 141.33, 141.08, 140.88 (aryl C), 140.31, 138.04, 137.48, 137.42, 137.38, 135.87 (aryl C), 130.20 (2C, aryl C), 128.94 (aryl C), 127.13 (aryl C), 126.07 (aryl C), 125.86 (aryl C), 121.59 (2C, aryl C), 115.76 (aryl C), 83.86 (sp³-C of C₆₀), 62.76 (sp³-C of C₆₀), 61.48 (sp³-C of C₆₀), 57.09 (sp³-C of C₆₀), 27.60, 22.62; UV-vis (CHCl₃) λ_{max} nm (log ϵ) 252.5 (5.0), 319.0 (4.6), 403.5 (4.0), 440.0 (3.8), 524.0 (3.0), 729.5 (2.9); FT-IR ν/cm^{-1} (KBr) 2922, 2852, 1755, 1666, 1597, 1495, 1437, 1371, 1302, 1254, 1188, 1088, 1036, 987, 827, 742, 701, 687, 604, 565, 530; MALDI-TOF MS *m/z* calcd for C₇₆H₁₅NO₃ [M]⁺ 989.1046, found 989.1055.

Synthesis of 2a in the presence of NaH or molecular sieves before electrolysis. NaH (57–63% oil dispersion, 12.0 mg, 0.300 mmol) or 4 Å molecular sieves (1.5 g) was added before the electrolysis process. After the electrolysis of **1** (26.0 mg, 0.030 mmol), the dianion **1**²⁻ reacted with benzoyl chloride (17.5 μ L, 0.150 mmol). After being stirred at 0 °C for 5 h, the resulting mixture was directly filtered through a silica gel (200–300 mesh) plug with CS₂/CH₂Cl₂ (1:1 v/v) to remove the supporting electrolyte and insoluble materials, and then evaporated in vacuo to remove the solvent. Next, the residue was further separated on a silica gel (400–500 mesh) column with CS₂/CH₂Cl₂ (4:1 v/v) as the eluent to afford product **3a** (16.8 mg, 58% in the presence of NaH; 11.7 mg, 40% in the presence of molecular sieves), 1,2,3,4-adduct **4** (0.8 mg, 3% in the presence of NaH; 5.7 mg, 22% in the presence of molecular sieves) along with unreacted **1** (1.1 mg, 4%).

Investigation of possible proton source from the Hofmann elimination of electrolyte.

After the electrolysis of **1** (26.0 mg, 0.030 mmol), the solution of **1**²⁻ was vigorously stirred at 0 °C under an argon atmosphere for 36 h. After that, the resulting mixture was directly filtered through a silica gel (200–300 mesh) plug with CS₂/CH₂Cl₂ (1:1 v/v) to remove the supporting electrolyte and insoluble materials, and then evaporated in vacuo to remove the solvent to recover unreacted **1** (21.3 mg, 82%).

Reaction of 1²⁻ with 2a quenched by D₂O. After the electrolysis of **1** (26.0 mg, 0.030 mmol), the dianion **1**²⁻ reacted with benzoyl chloride (17.5 μL, 0.150 mmol) and NaH (57–63% oil dispersion, 12.0 mg, 0.300 mmol). After being stirred at 0 °C for 5 h, then quenched by D₂O (60.0 μL, 3.0 mmol) for 30 mins. The resulting mixture was directly filtered on a silica gel (200–300 mesh) plug with CS₂/CH₂Cl₂ (1:1 v/v) to remove the supporting electrolyte and insoluble materials, and then evaporated in vacuo to remove the solvent. Next, the residue was further separated on a silica gel (400–500 mesh) column with CS₂/CH₂Cl₂ (4:1 v/v) as the eluent to afford product **3a** (17.0 mg, 58%) as an amorphous brown solid along with unreacted **1** (0.8 mg, 3%).

Reaction of 1²⁻ with 2a quenched by CD₃COOD. After the electrolysis of **1** (26.0 mg, 0.030 mmol), the dianion **1**²⁻ reacted with benzoyl chloride **2a** (17.5 μL, 0.150 mmol) and NaH (57–63% oil dispersion, 12.0 mg, 0.300 mmol). After being stirred at 0 °C for 5 h, then quenched by CD₃COOD (180.0 μL, 3.0 mmol) for 30 min. The resulting mixture was directly filtered through a silica gel (200–300 mesh) plug column with CS₂/CH₂Cl₂ (1:1 v/v) to remove the supporting electrolyte and insoluble materials, and then evaporated in vacuo to remove the solvent. Next, the residue was further separated on a silica gel (400–500 mesh) column with CS₂/CH₂Cl₂ (4:1 v/v) as the eluent to afford product **3a**-H(D) (17.1 mg, 59%) as an amorphous brown solid along with unreacted **1** (1.0 mg, 4%).

Reaction of 1²⁻ with 2c in the presence of TEMPO. After the electrolysis of **1** (26.0 mg, 0.030 mmol), the dianion **1**²⁻ reacted with *p*-nitrobenzoyl chloride **2c** (27.8 mg, 0.150 mmol), NaH (57–63% oil dispersion, 120.0 mg, 3.000 mmol) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (10.3 mg, 0.06 mmol). After being stirred at 0 °C for 2 h, the resulting mixture was directly filtered through a silica gel (200–300 mesh) plug with CS₂/CH₂Cl₂ (1:1 v/v) to remove the supporting electrolyte and insoluble materials, and then evaporated in vacuo to remove the solvent. The residue further was purified by semi-preparative HPLC on a Buckyprep column (10 × 250 mm, eluent: toluene, 5 mL/min flow rate, detection at 325 nm) to afford product **3c** (13.3 mg, 43%) along with unreacted **1** (1.2 mg, 5%).

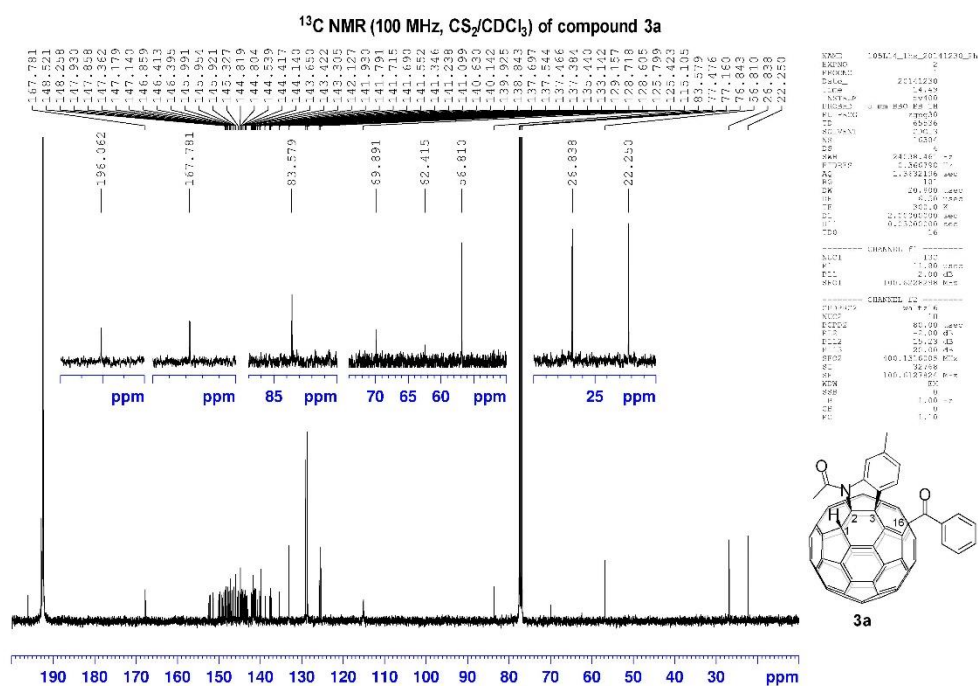
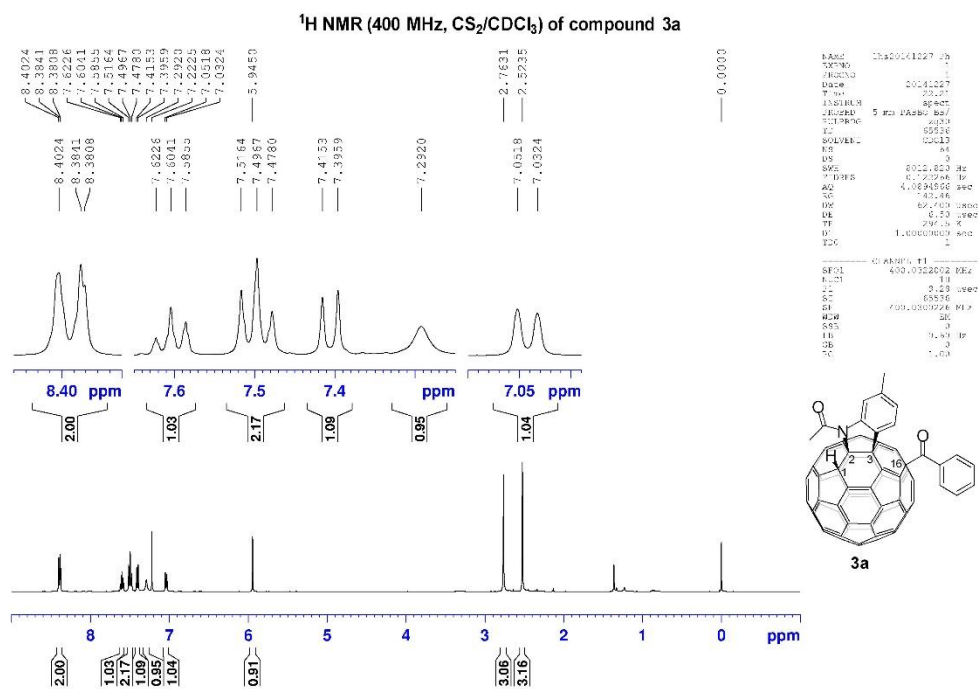
Treatment of 3b under basic conditions. Ketone **3b** (6.0 mg, 6.0 μmol) and NaOH (4.8 mg, 0.12 mmol) were added in a 15-mL reaction vessel containing a magnetic stirring bar. Then, the solid mixture was thoroughly degassed through five freeze-pump-thaw cycles, and subsequently filled with argon or oxygen. Next, the degassed toluene (4.0 mL) and CH₃CN (0.75 mL) were added into the vessel. The resulting mixture was stirred

vigorously at ambient temperature (25 °C) under argon or oxygen atmosphere. After the color of the solution turned to brown (argon: 21 h; oxygen: 5 h), the resulting solution was neutralized with 1N HCl and then evaporated in vacuo. Next, the residue was dissolved in toluene and filtrated to remove the insoluble salts. Finally, [60]fulleroindoline **1** and *p*-methoxybenzoic acid were monitored by HPLC and GC-MS analysis, respectively. Column chromatography of the residue on silica gel (CS₂/CH₂Cl₂ 4:1 v/v) provided **1** (2.1 mg, 41% under argon atmosphere; 3.7 mg, 71% under oxygen atmosphere).

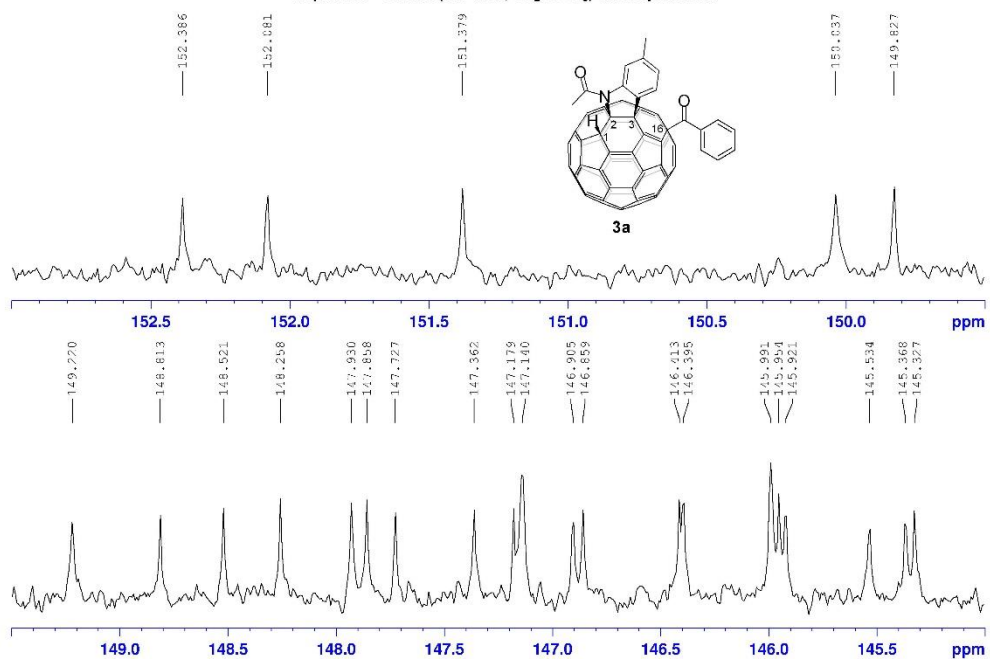
Attempted conversion of 3b to 3a under basic conditions. Ketone **3b** (10.3 mg, 10.0 μmol) and NaOH (8.0 mg, 0.05 mmol) were added in a 15-mL reaction vessel containing a magnetic stirring bar. Then, the solid mixture was thoroughly degassed through five freeze-pump-thaw cycles, and subsequently filled with argon. Next, the degassed anhydrous ODCB (4.0 mL) and CH₃CN (1.0 mL) were added into the vessel. The resulting mixture was stirred vigorously at ambient temperature (25 °C) under argon for 10 min. Later, benzoyl chloride (12.0 μL, 0.1 mmol) was added, the resulting mixture immediately turned into brownish from dark green. After 5 h, the solvent was directly removed under vacuum. Further separation was performed on a silica gel column (CS₂/CH₂Cl₂ 4:1 v/v), providing **1** (5.2 mg, 52%) along with recovered **3b** (2.4 mg, 23%).

Treatment of 3c under acidic conditions. Ketone **3c** (6.0 mg, 6.0 μmol) and trifluoroacetic acid (4.8 μL, 0.06 mmol) were added in a 15-mL reaction vessel containing a magnetic stirring bar. Then the solid mixture was thoroughly degassed by performing five freeze-pump-thaw cycles, and subsequently filled with argon. Next, the degassed toluene (4.0 mL) was added into the vessel. The resulting mixture was stirred vigorously at ambient temperature (25 °C) under argon atmosphere. After the reaction was over, the resulting solution was evaporated under reduce pressure. The residue was purified by flash column chromatography on silica gel (CS₂/CH₂Cl₂ 1:1 v/v), affording 1,2,3,4-adduct **4** (4.5 mg, 88%). ¹H NMR of compound **4** (400 MHz, CS₂/CDCl₃) δ 7.97 (d, *J* = 7.6 Hz, 1H), 7.41 (s, 1H), 7.27 (d, *J* = 7.6 Hz, 1H), 6.35 (d, *J* = 1.7 Hz, 1H), 6.32 (d, *J* = 1.7 Hz, 1H), 2.87 (s, 3H), 2.59 (s, 3H).

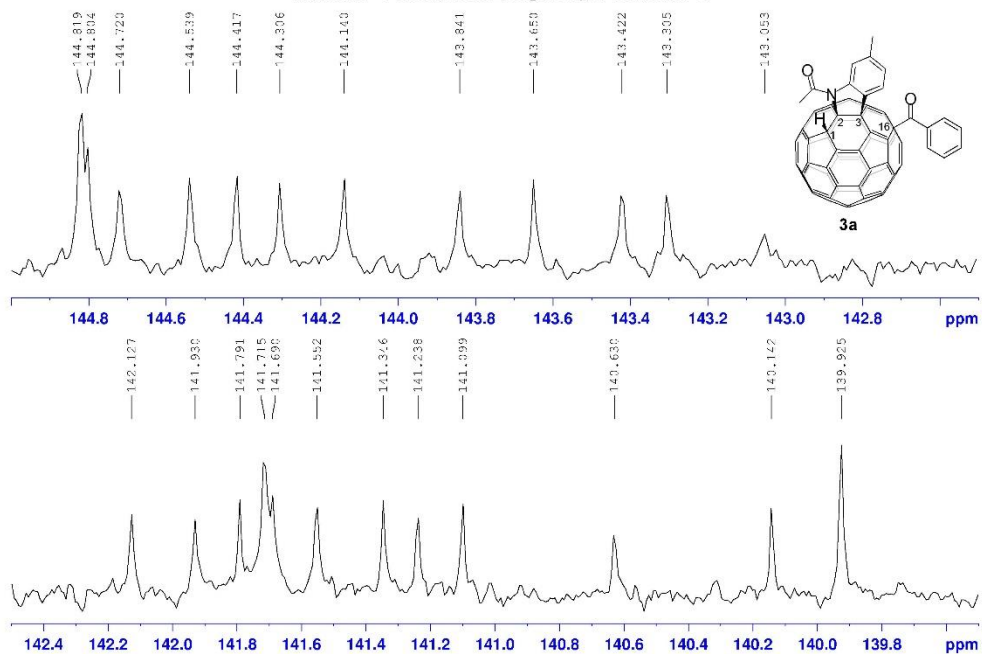
¹H NMR and ¹³C NMR spectra of compounds 3a–3g.



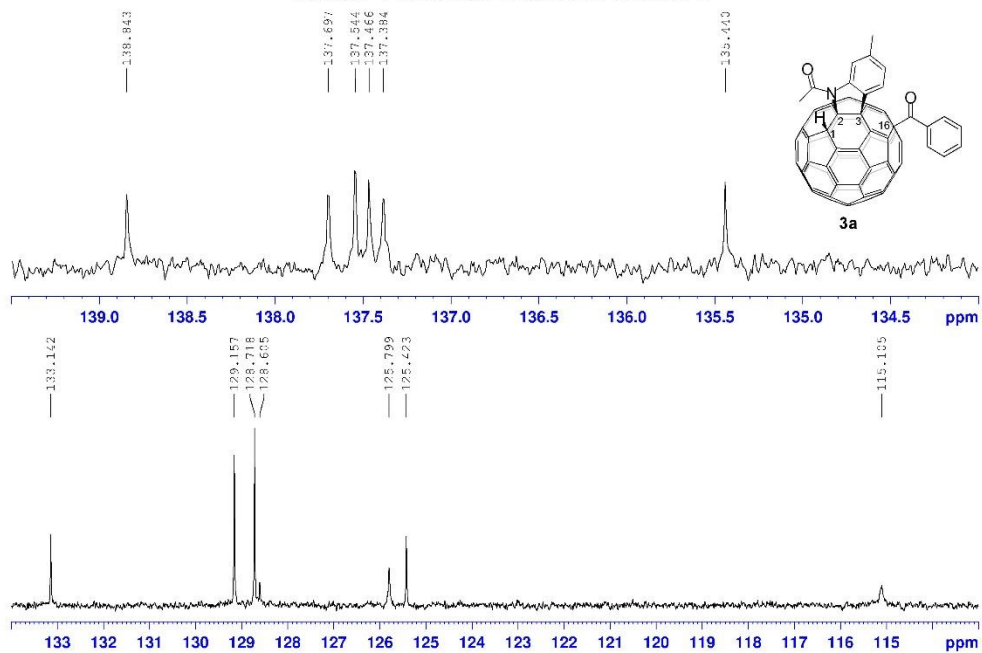
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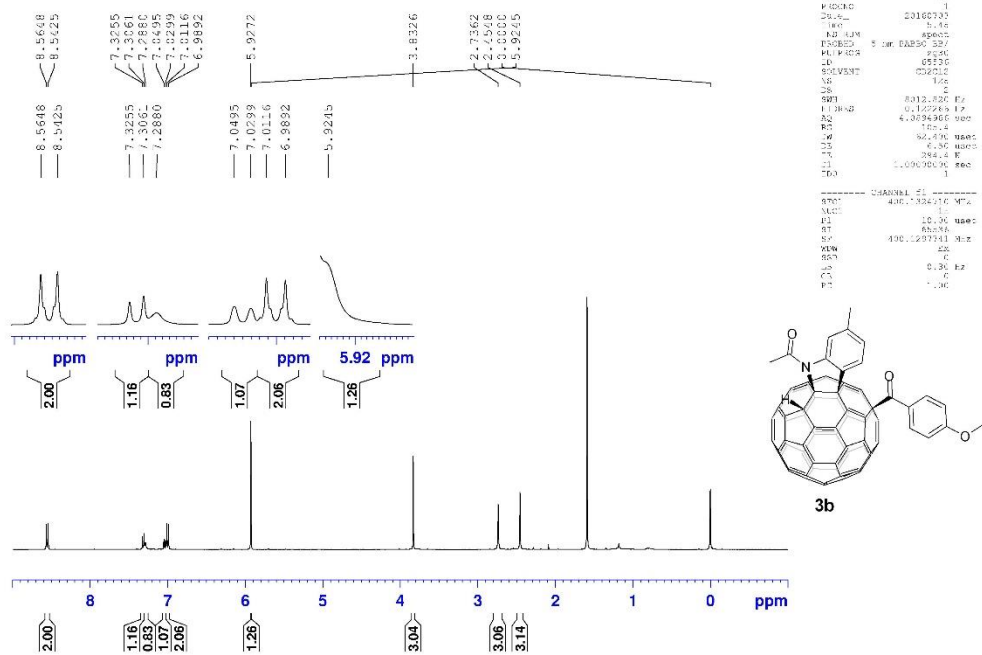
Expanded ^{13}C NMR (100 MHz, $\text{CS}_2/\text{CDCl}_3$) of compound 3a



Expanded ^{13}C NMR (100 MHz, $\text{CS}_2/\text{CDCl}_3$) of compound 3a



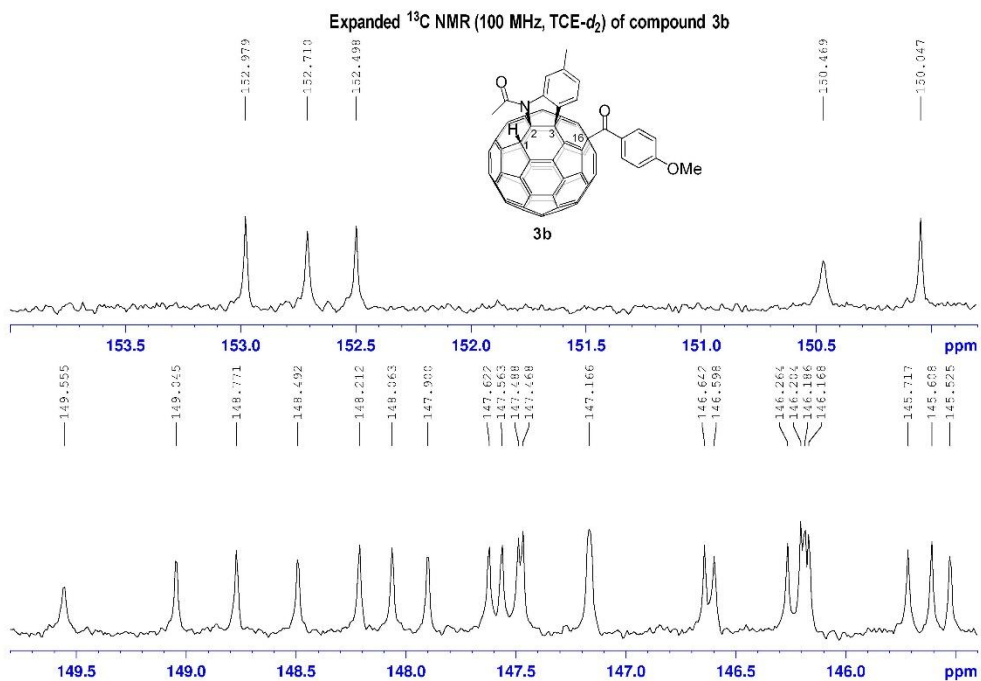
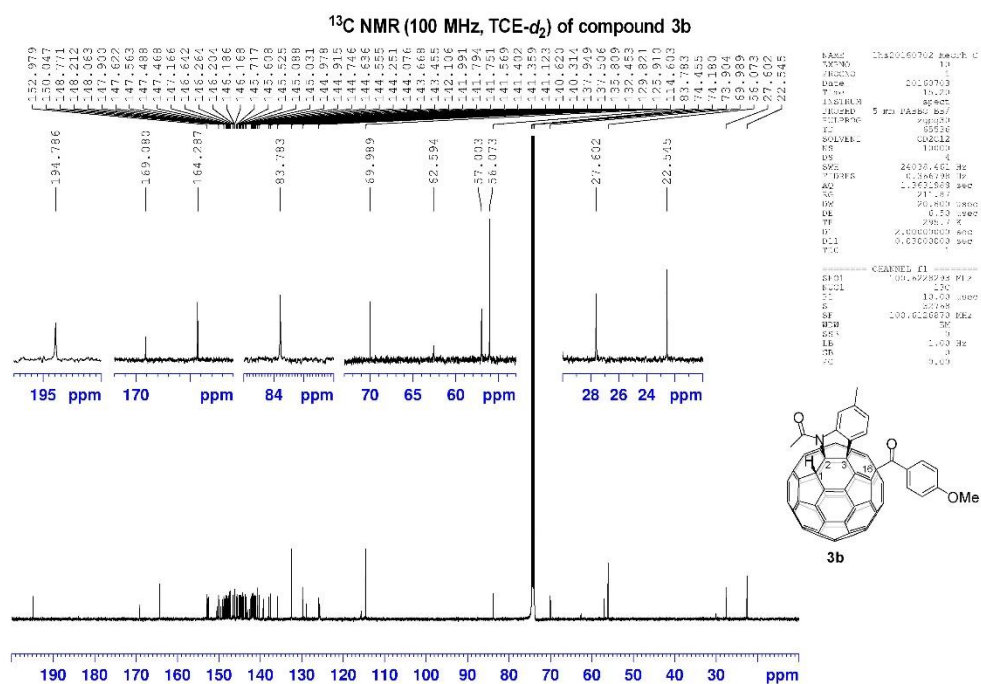
^1H NMR (400 MHz, TCE-d_2) of compound 3b

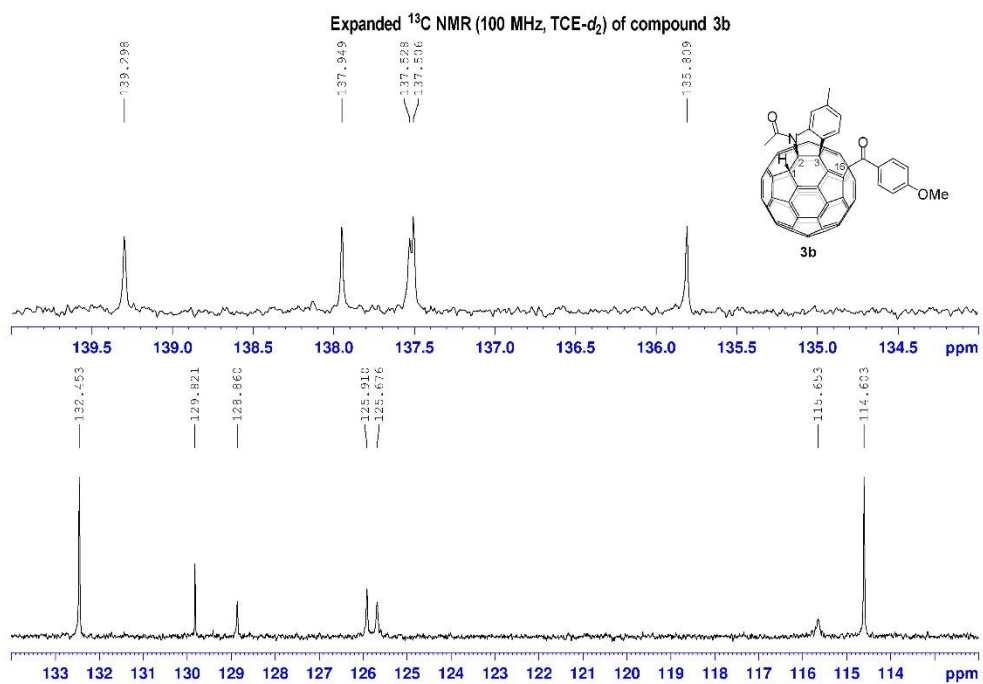
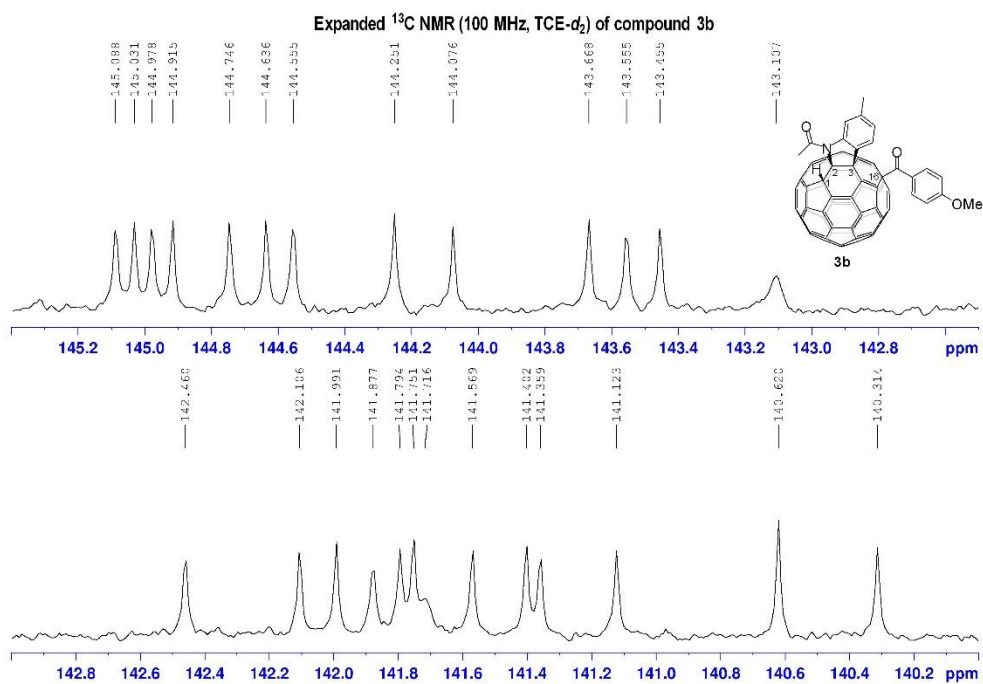


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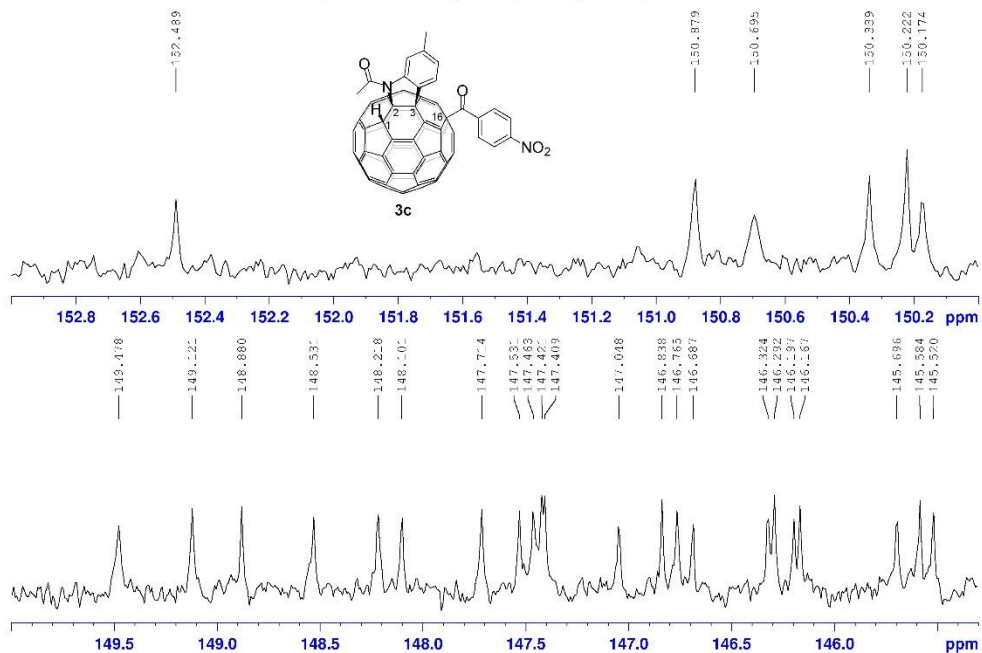
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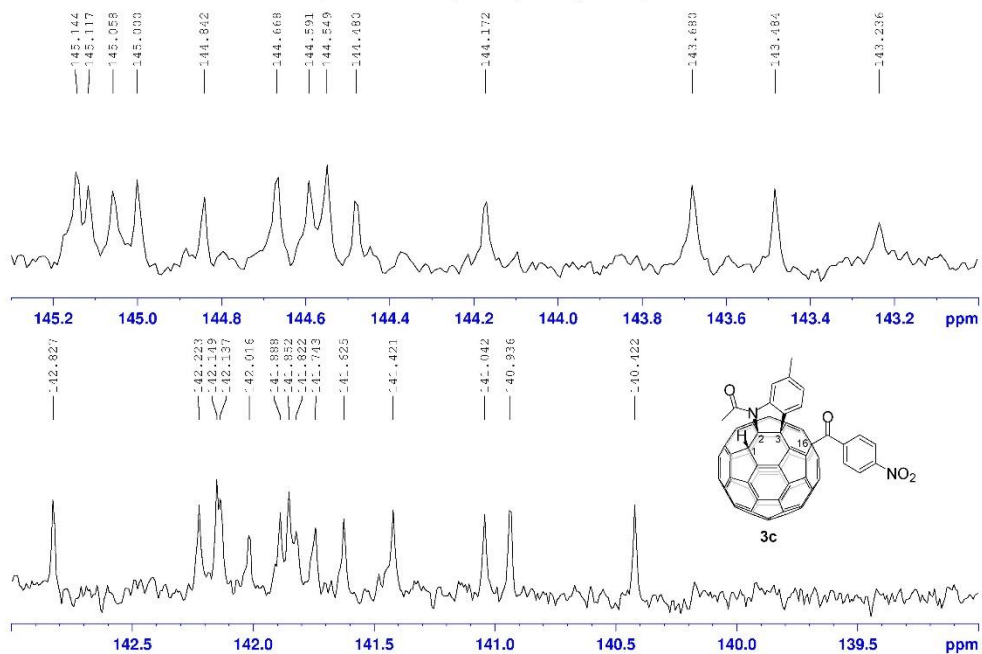




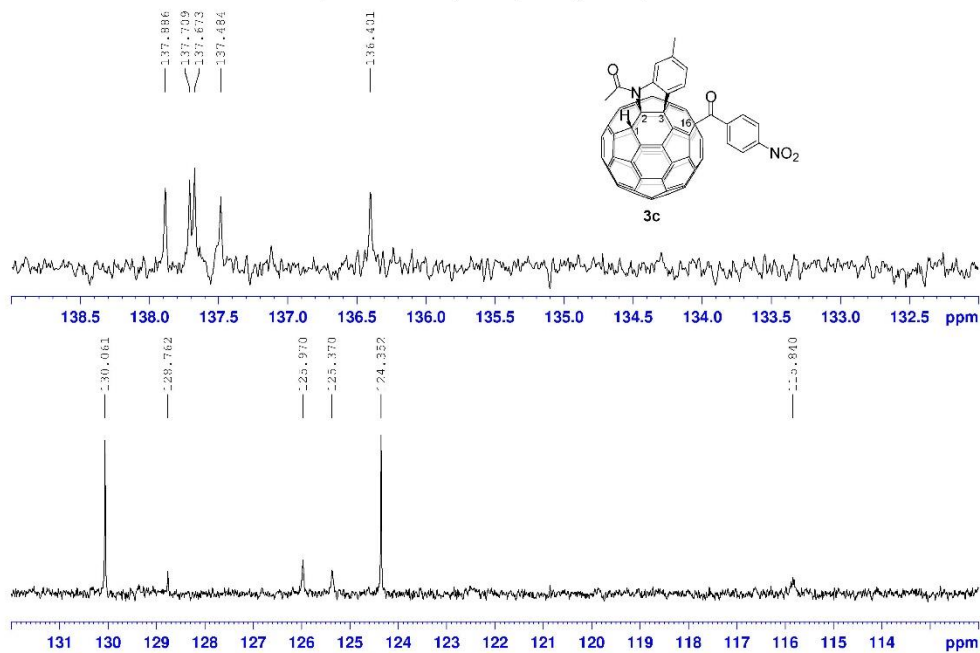
Expanded ^{13}C NMR (100 MHz, TCE-d_2) of compound **3c**



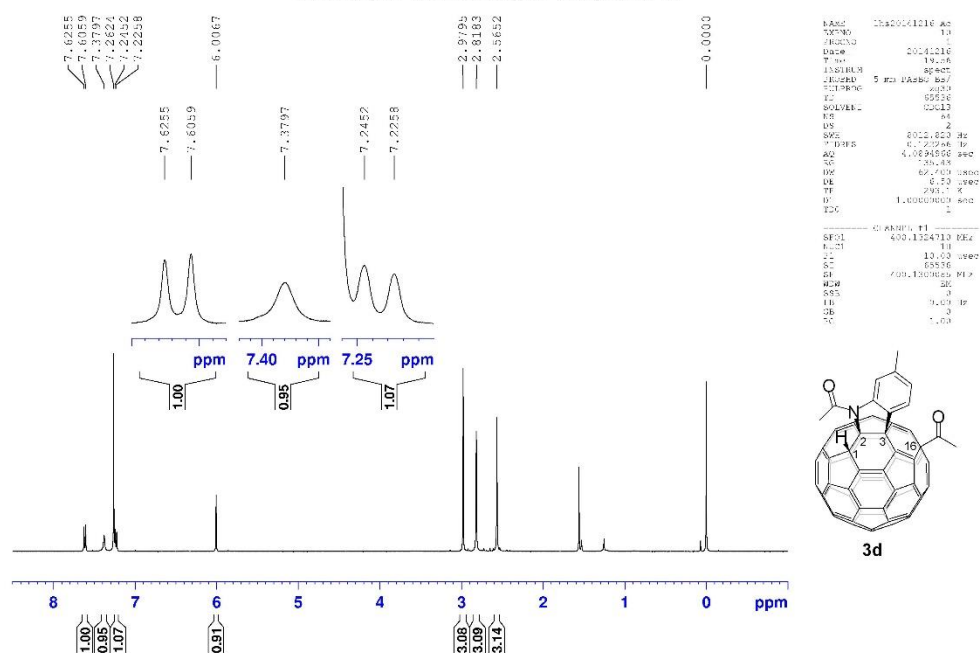
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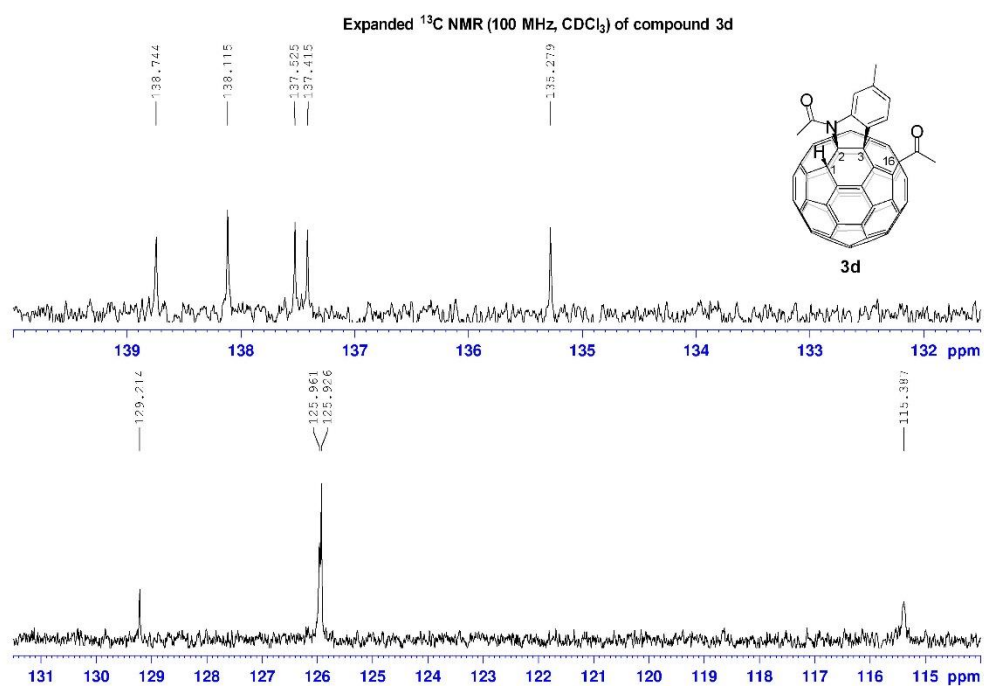
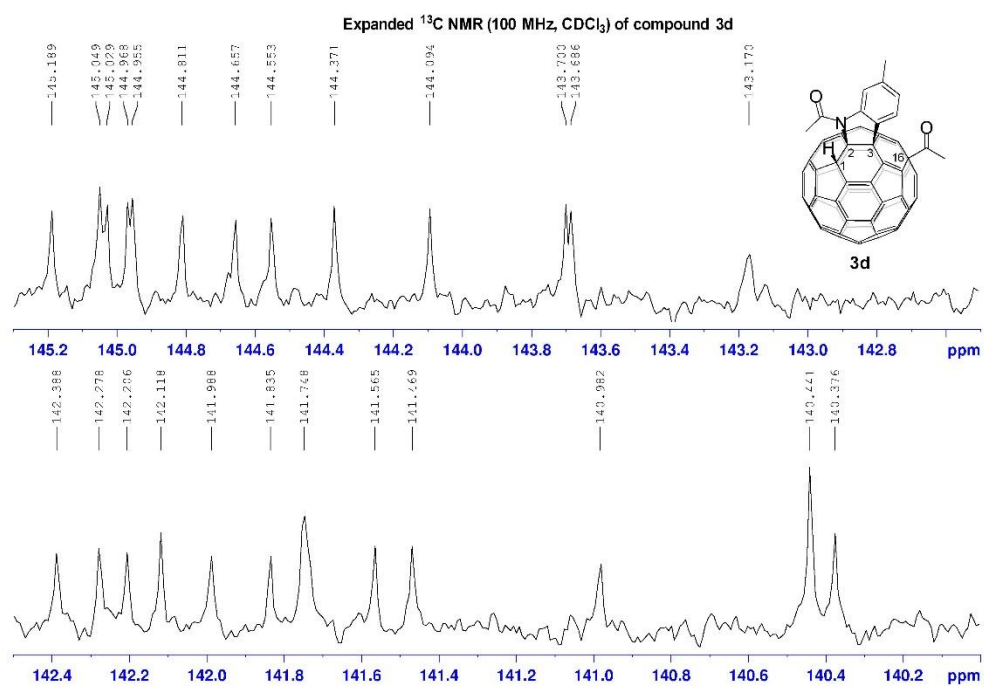


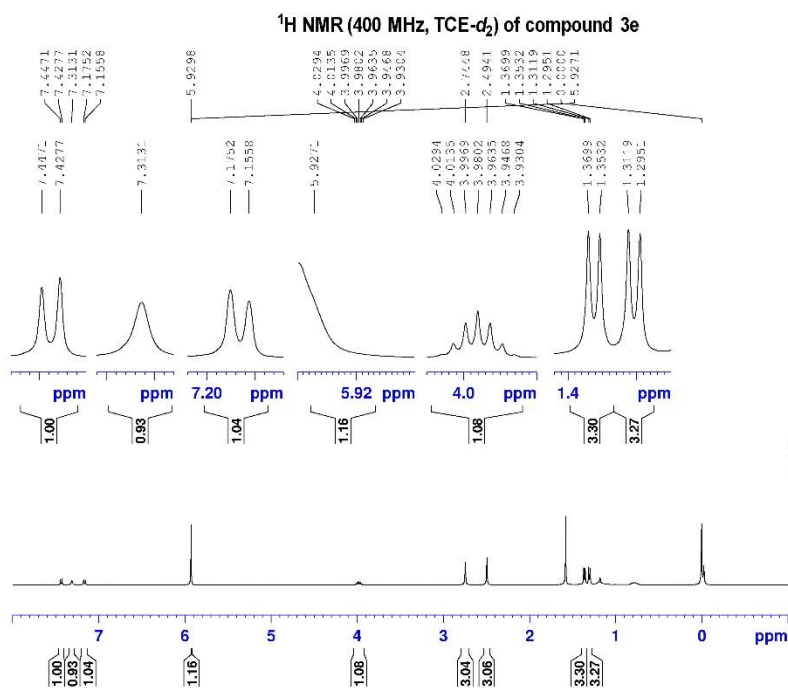
Expanded ^{13}C NMR (100 MHz, TCE-d_2) of compound 3c



^1H NMR (400 MHz, CDCl_3) of compound 3d

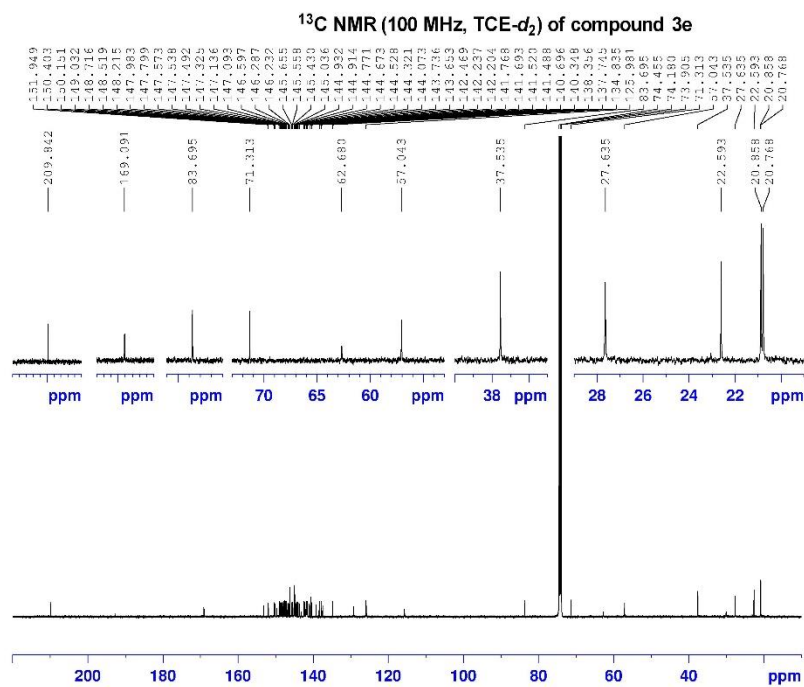
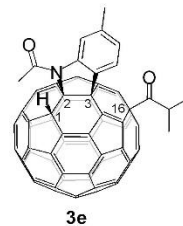






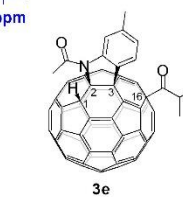
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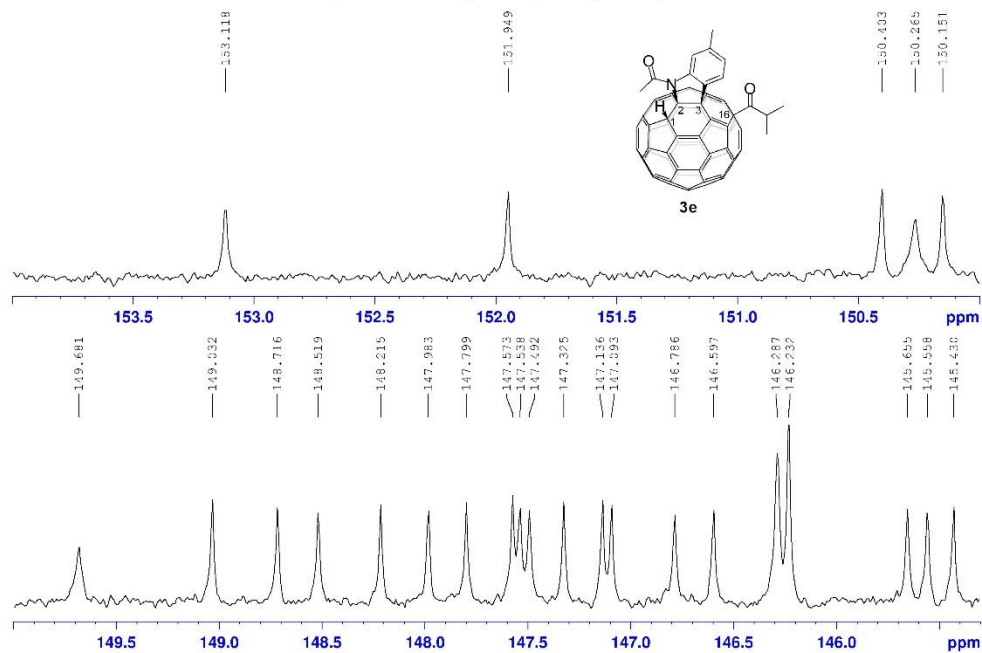


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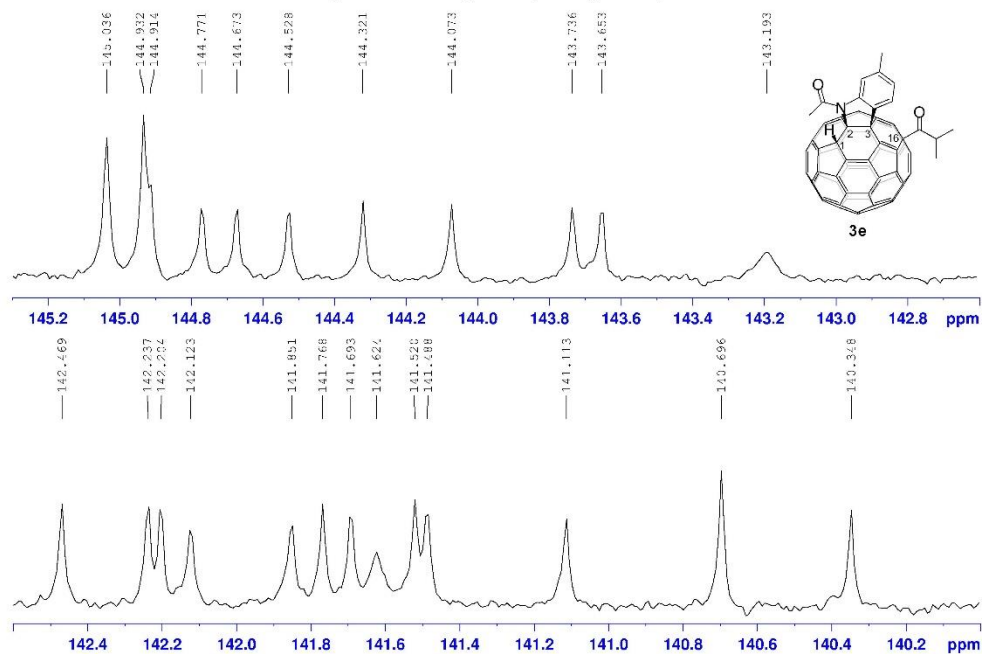
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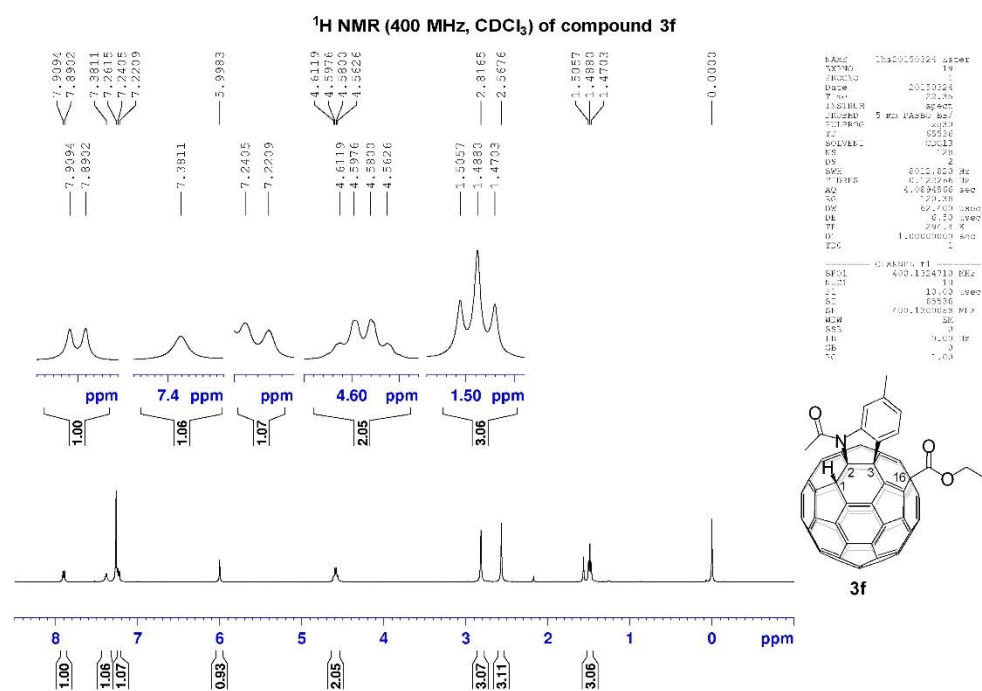
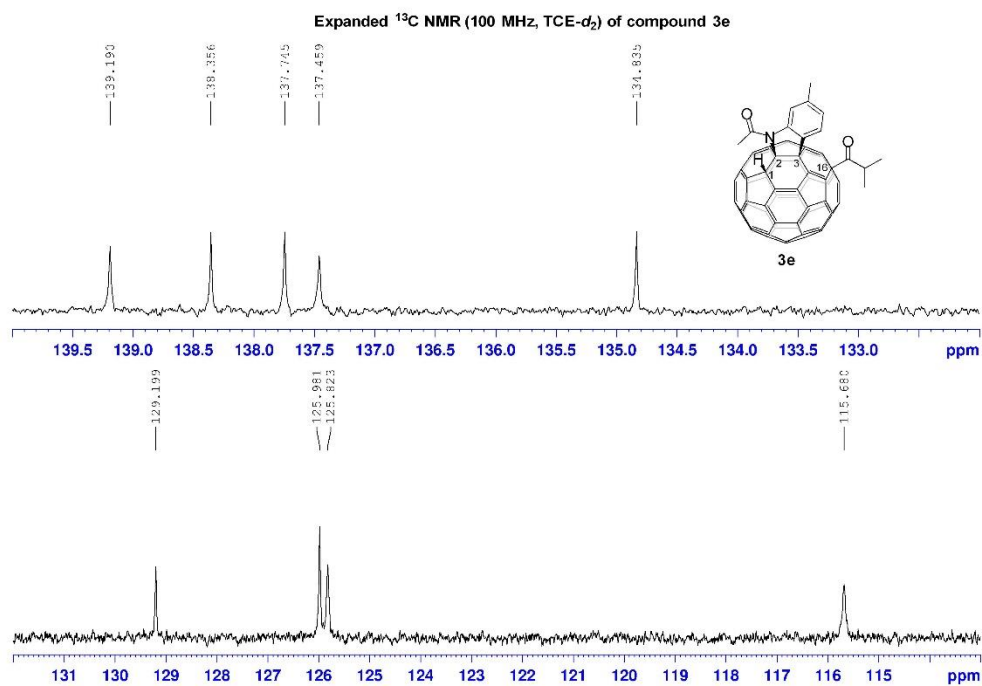


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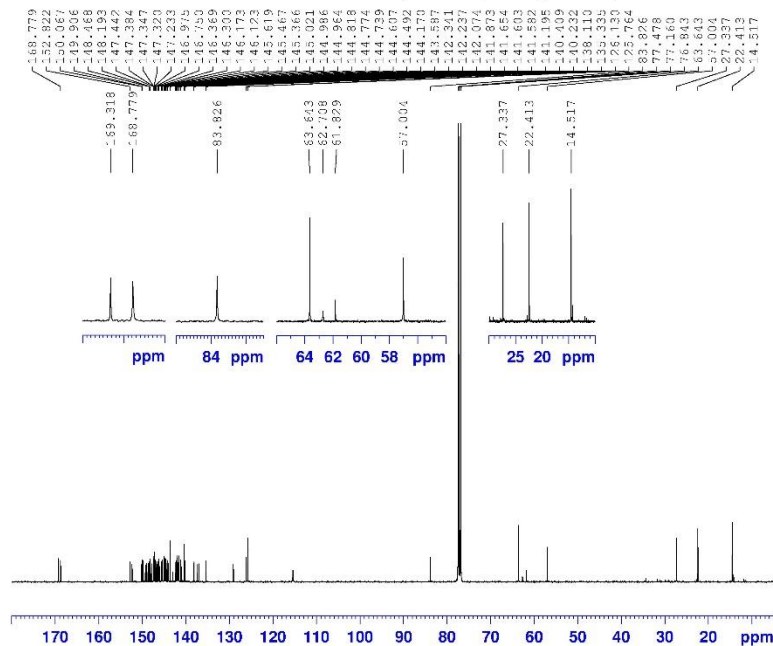


Expanded ^{13}C NMR (100 MHz, TCE-d_2) of compound 3e

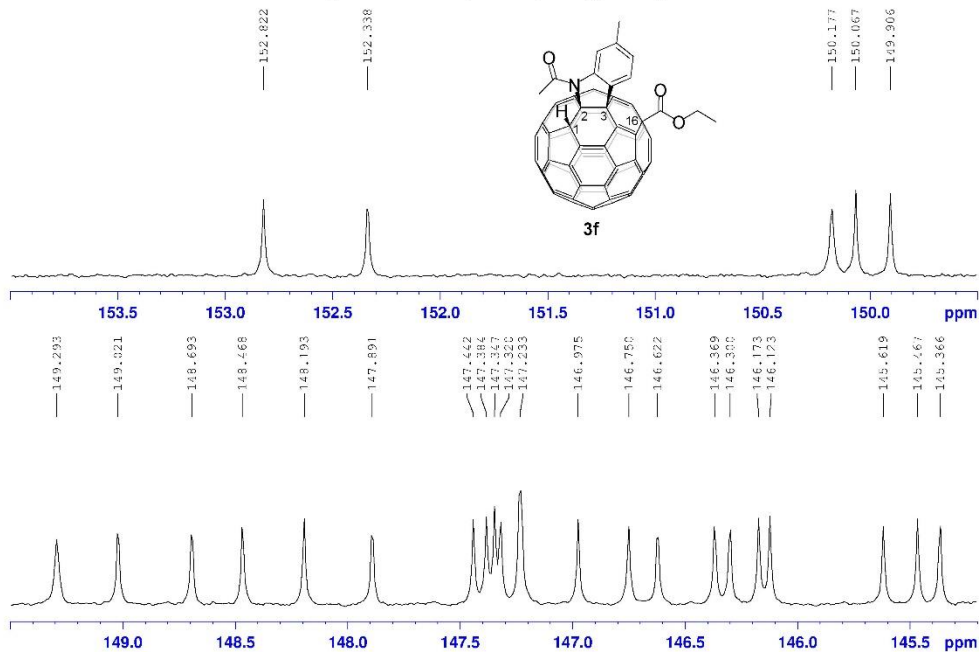


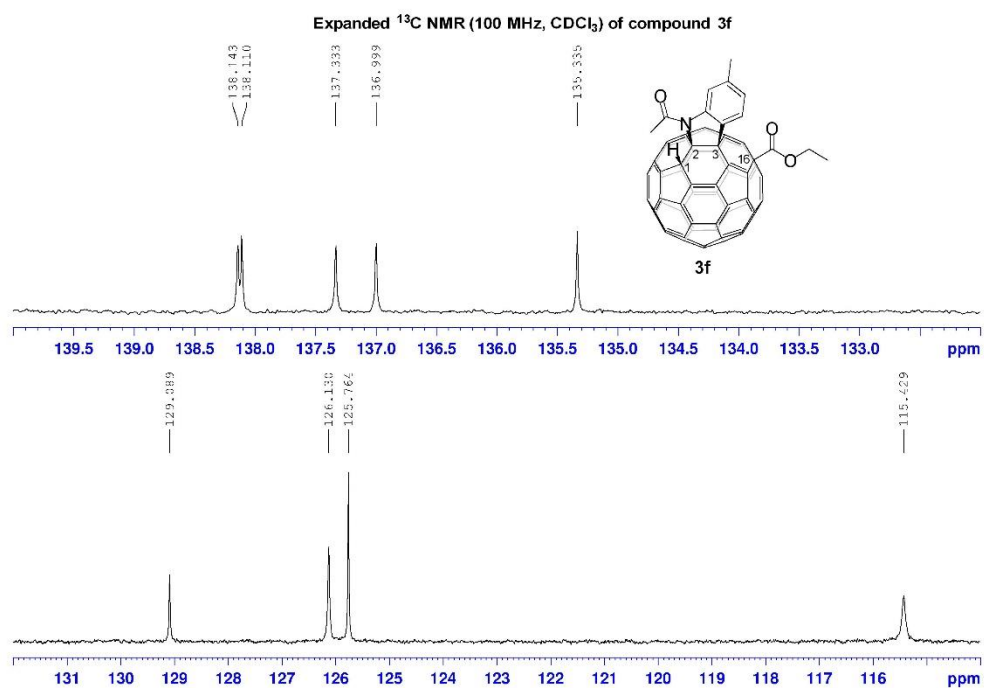
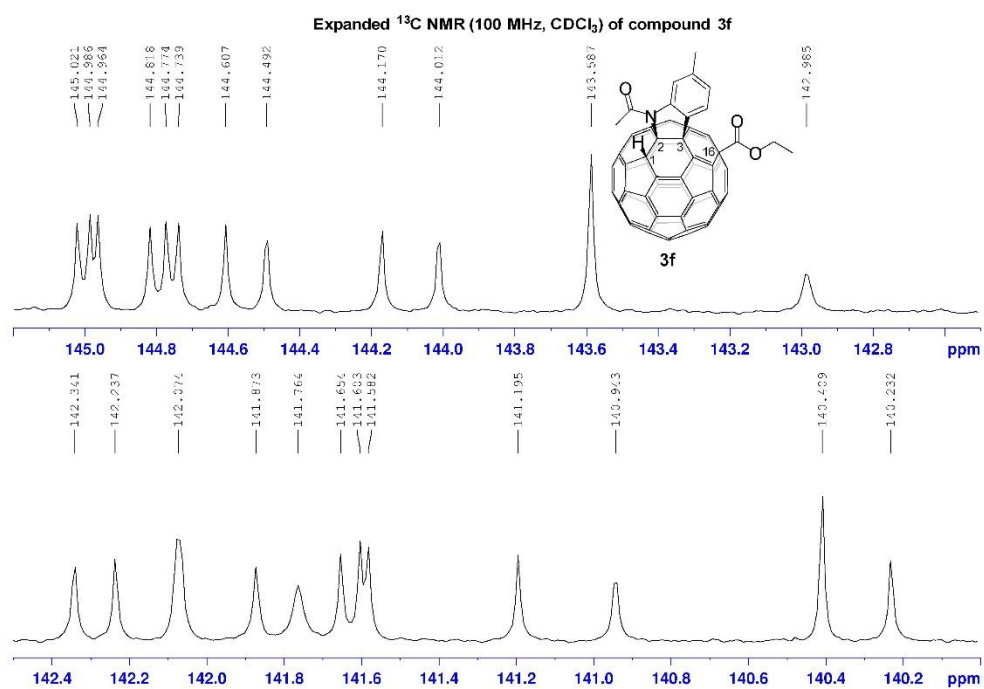


¹³C NMR (100 MHz, CDCl₃) of compound 3f

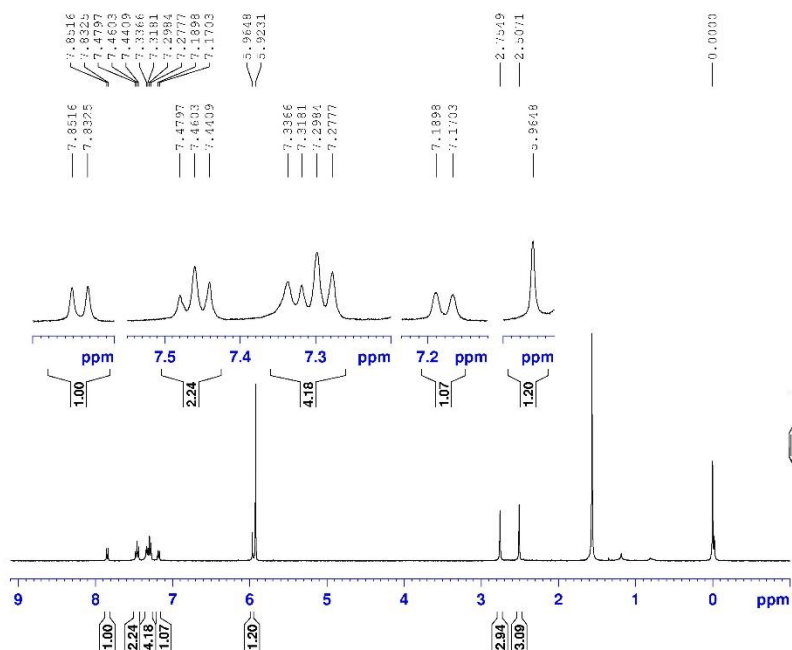


Expanded ¹³C NMR (100 MHz, CDCl₃) of compound 3f

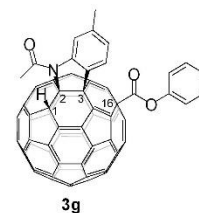




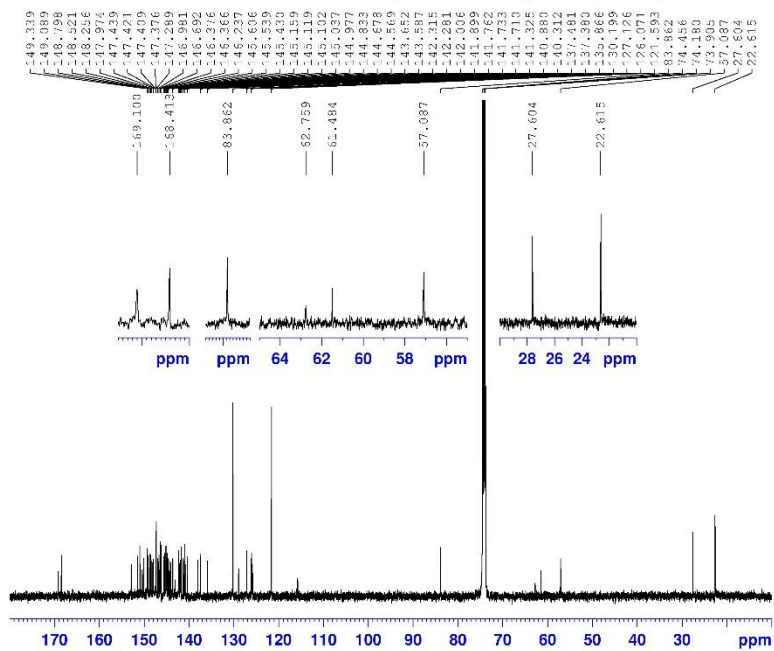
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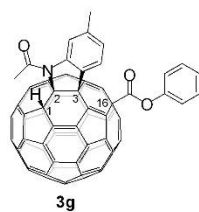
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F31: 400.136
F32: 400.136
F33: 400.136
F34: 400.136
F35: 400.136
F36: 400.136
F37: 400.136
F38: 400.136
F39: 400.136
F40: 400.136
F41: 400.136
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F43: 400.136
F44: 400.136
F45: 400.136
F46: 400.136
F47: 400.136
F48: 400.136
F49: 400.136
F50: 400.136
F51: 400.136
F52: 400.136
F53: 400.136
F54: 400.136
F55: 400.136
F56: 400.136
F57: 400.136
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F65: 400.136
F66: 400.136
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F85: 400.136
F86: 400.136
F87: 400.136
F88: 400.136
F89: 400.136
F90: 400.136
F91: 400.136
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F97: 400.136
F98: 400.136
F99: 400.136
F100: 400.136
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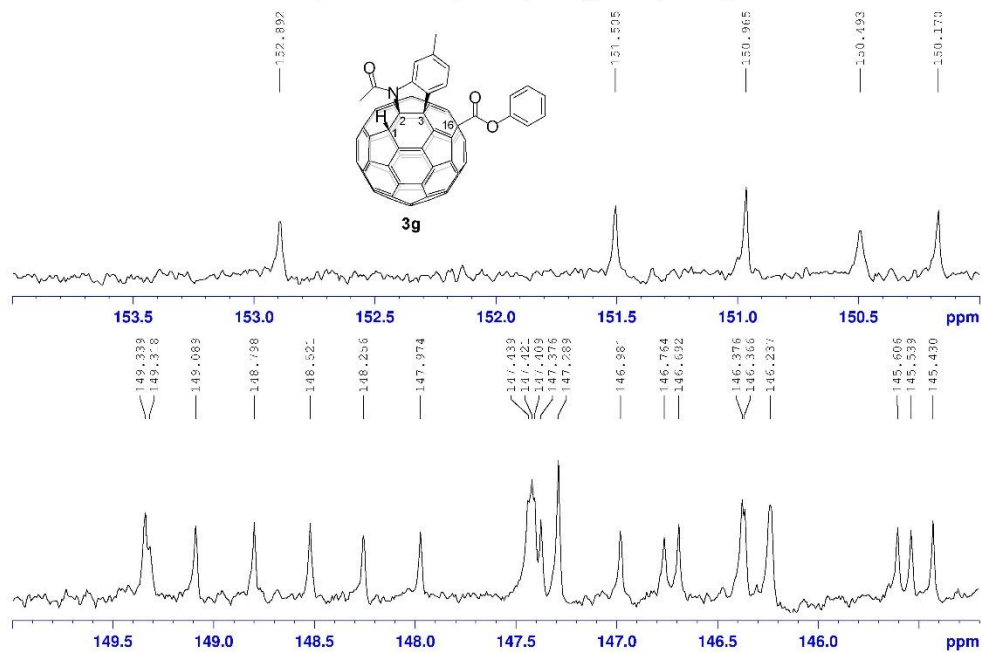
¹³C NMR (100 MHz, TCE-d₂) of compound 3g



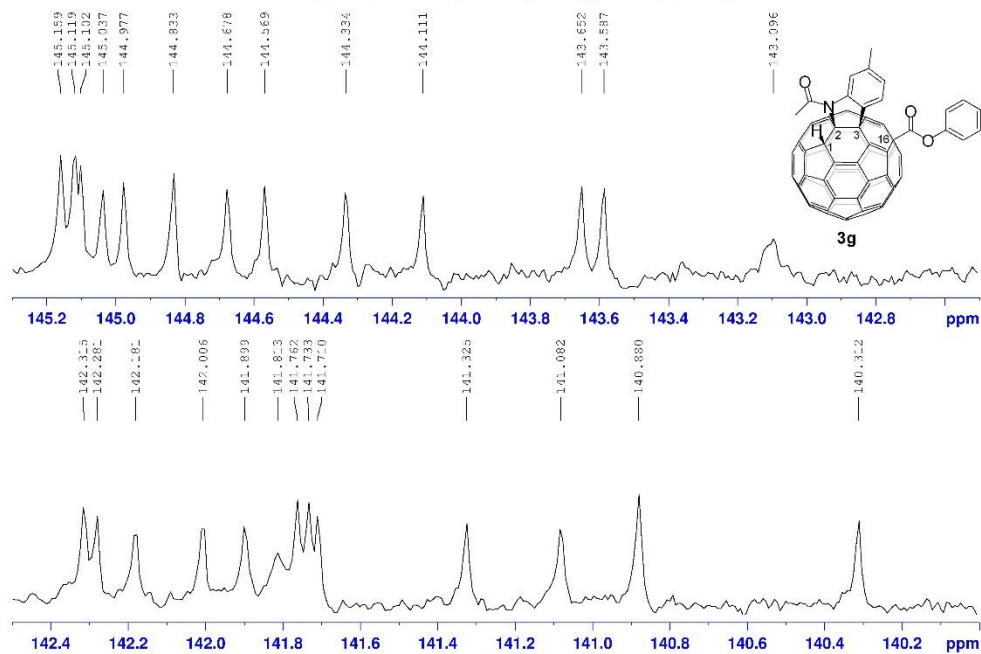
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EXPNO: 2
PROCNO: 1
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Time: 11:29
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F4: 100.626
F5: 100.626
F6: 100.626
F7: 100.626
F8: 100.626
F9: 100.626
F10: 100.626
F11: 100.626
F12: 100.626
F13: 100.626
F14: 100.626
F15: 100.626
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F18: 100.626
F19: 100.626
F20: 100.626
F21: 100.626
F22: 100.626
F23: 100.626
F24: 100.626
F25: 100.626
F26: 100.626
F27: 100.626
F28: 100.626
F29: 100.626
F30: 100.626
F31: 100.626
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F33: 100.626
F34: 100.626
F35: 100.626
F36: 100.626
F37: 100.626
F38: 100.626
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F45: 100.626
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F51: 100.626
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F55: 100.626
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F58: 100.626
F59: 100.626
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F63: 100.626
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F65: 100.626
F66: 100.626
F67: 100.626
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F97: 100.626
F98: 100.626
F99: 100.626
F100: 100.626
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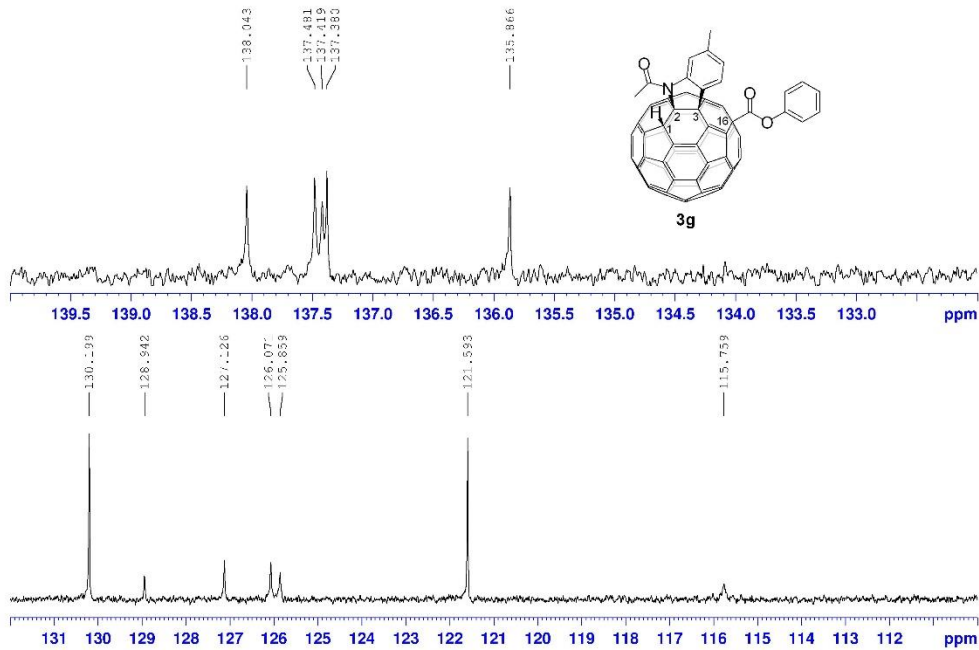
Expanded ^{13}C NMR (100 MHz, TCE-d_2) of compound **3g**



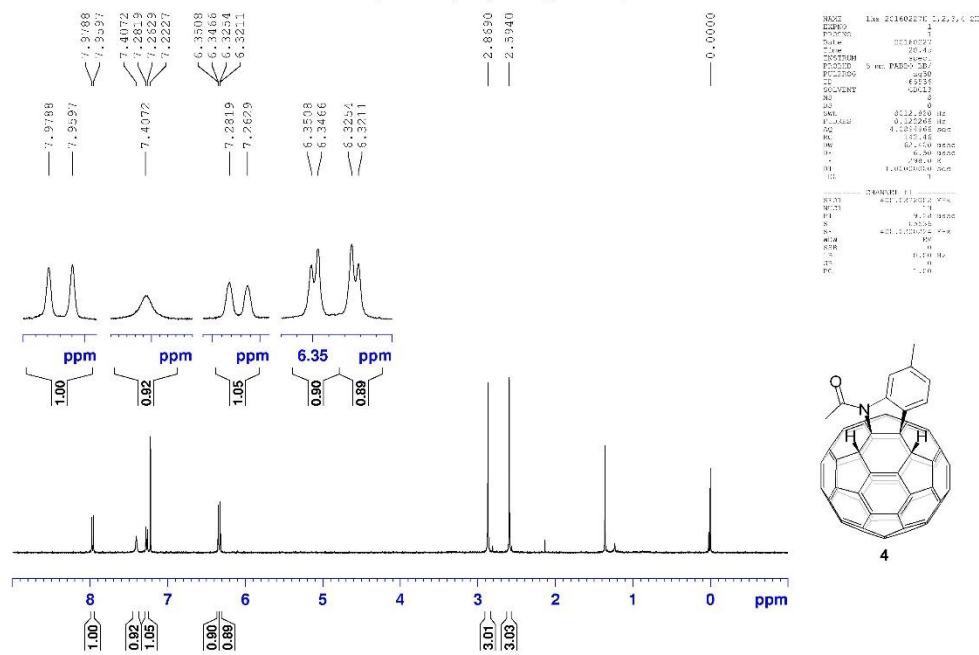
Expanded ^{13}C NMR (100 MHz, TCE-d_2) of compound **3g**



Expanded ^{13}C NMR (100 MHz, TCE-d_2) of compound 3g



^1H NMR (400 MHz, $\text{CS}_2/\text{CDCl}_3$) of compound 4



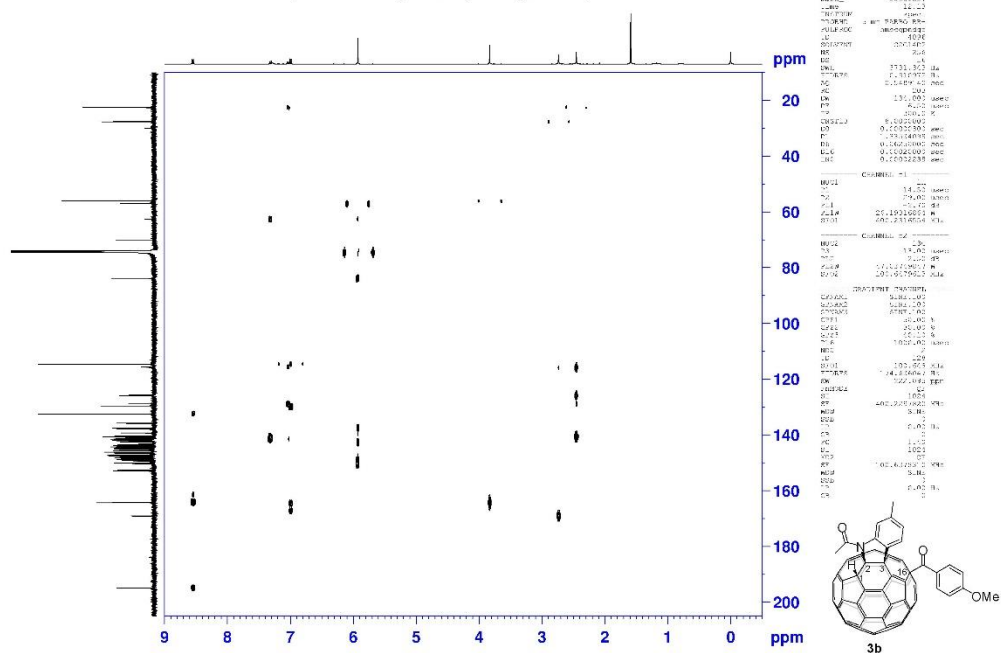
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NAME 4x 20160226 (1,1,1,1-t)
EXPNO 1
PROCNO 1
SOLVENT 20160226
PULSEPRG zgpg30
PROBHD 5 mm BBO-1H
PROCNO 400
F2 400.141000 MHz
SOLVENT CDCl3
NS 1638
DS 4
AQ 0.11180000 sec
RG 327.5000 Hz
FIDRES 0.1222495 Hz
AQRES 4.10110000 sec
NUC1 1H
NUC2 13C
PC 1.00
  
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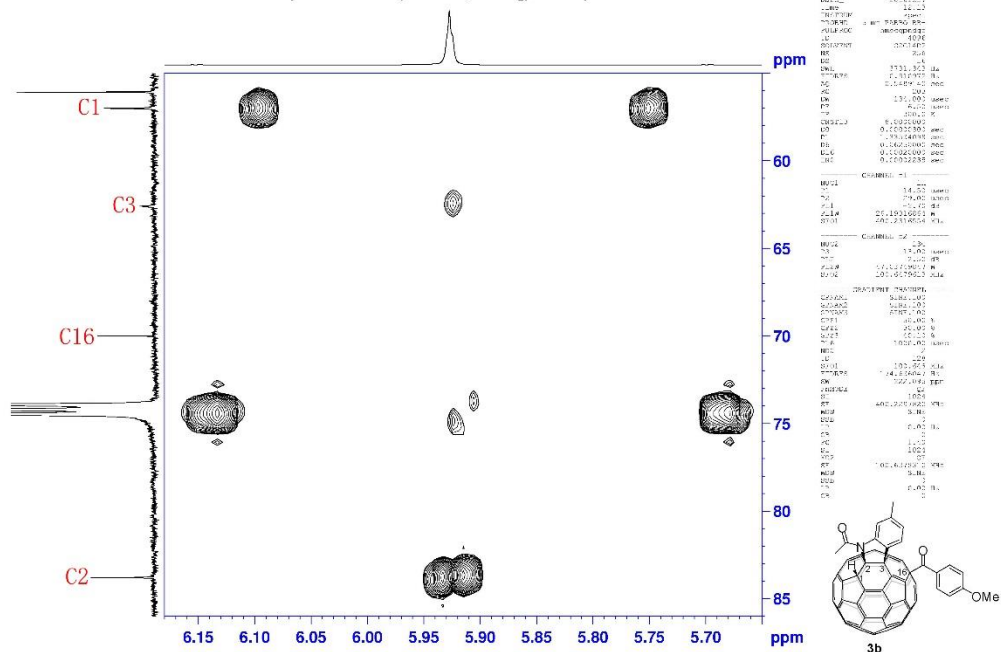
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NAME 4
EXPNO 1
PROCNO 1
SOLVENT 20160226
PULSEPRG zgpg30
PROBHD 5 mm BBO-1H
PROCNO 400
F2 400.141000 MHz
SOLVENT CDCl3
NS 1638
DS 4
AQ 0.11180000 sec
RG 327.5000 Hz
FIDRES 0.1222495 Hz
AQRES 4.10110000 sec
NUC1 1H
NUC2 13C
PC 1.00
  
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Expanded HMBC (400 MHz, TCE-d₂) of compound 3b



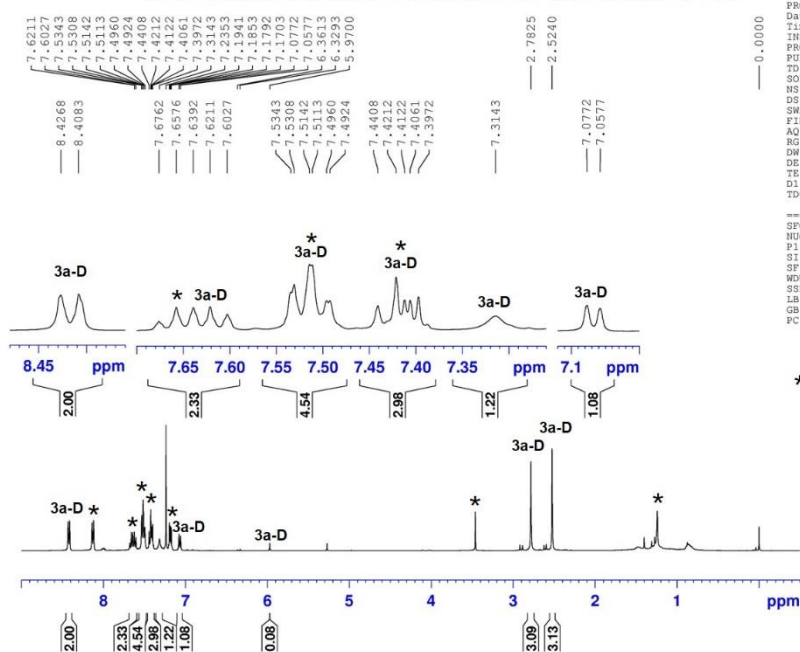
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EXPNO	1
PROCNO	1
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PROBHD	5 mm 1H/13
NUC1	13C
NUC2	1H
PCPDPRG2	zgpg30
PCPDPRG1	zgpg30
PCPDPRG3	zgpg30
PCPDPRG4	zgpg30
PCPDPRG5	zgpg30
PCPDPRG6	zgpg30
PCPDPRG7	zgpg30
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PCPDPRG96	zgpg30
PCPDPRG97	zgpg30
PCPDPRG98	zgpg30
PCPDPRG99	zgpg30
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Expanded HMBC (400 MHz, TCE-d₂) of compound 3b



NAME	176-0338-2016-2-1-04-000
EXPNO	1
PROCNO	1
F2	50.013
F3	121.2
PROBHD	5 mm 1H/13
NUC1	13C
NUC2	1H
PCPDPRG2	zgpg30
PCPDPRG1	zgpg30
PCPDPRG3	zgpg30
PCPDPRG4	zgpg30
PCPDPRG5	zgpg30
PCPDPRG6	zgpg30
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PCPDPRG96	zgpg30
PCPDPRG97	zgpg30
PCPDPRG98	zgpg30
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PCPDPRG100	zgpg30

¹H NMR (400 MHz, CS₂/CDCl₃) of resulting mixture quenched by CD₃COOD



```

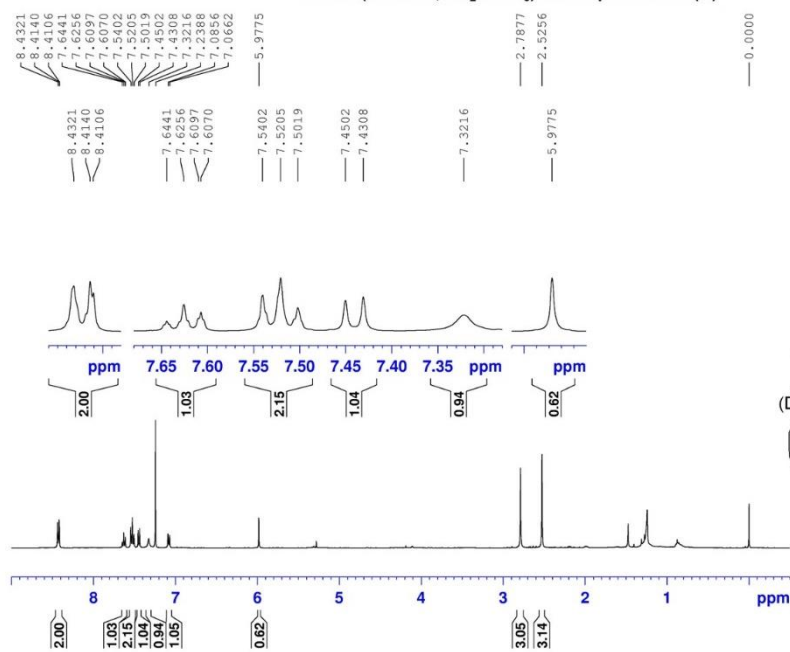
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EXPNO 10
PROCNO 1
Date_ 20170110
Time 14.28
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 128
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 120.38
DM 62.400 usec
DE 6.50 usec
TE 292.0 K
D1 1.0000000 sec
TDO 1
    
```

```

----- CHANNEL f1 -----
SFO1 400.1324710 MHz
NUC1 1H
P1 10.00 usec
SI 65536
SF 400.1300203 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
    
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*: Non-fullerene impurities

¹H NMR (400 MHz, CS₂/CDCl₃) of compound 3a-H(D)



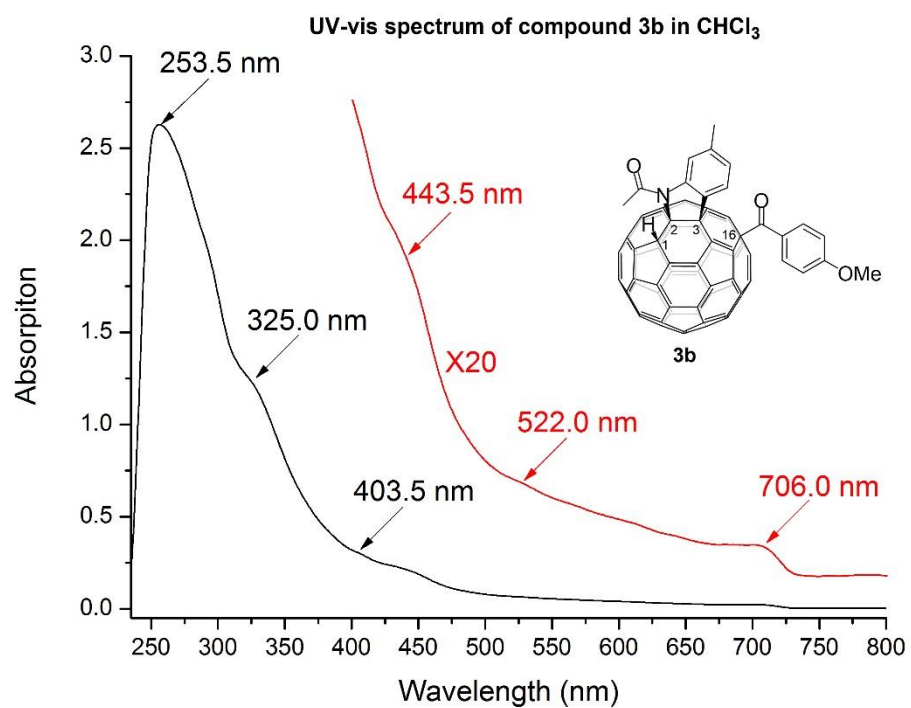
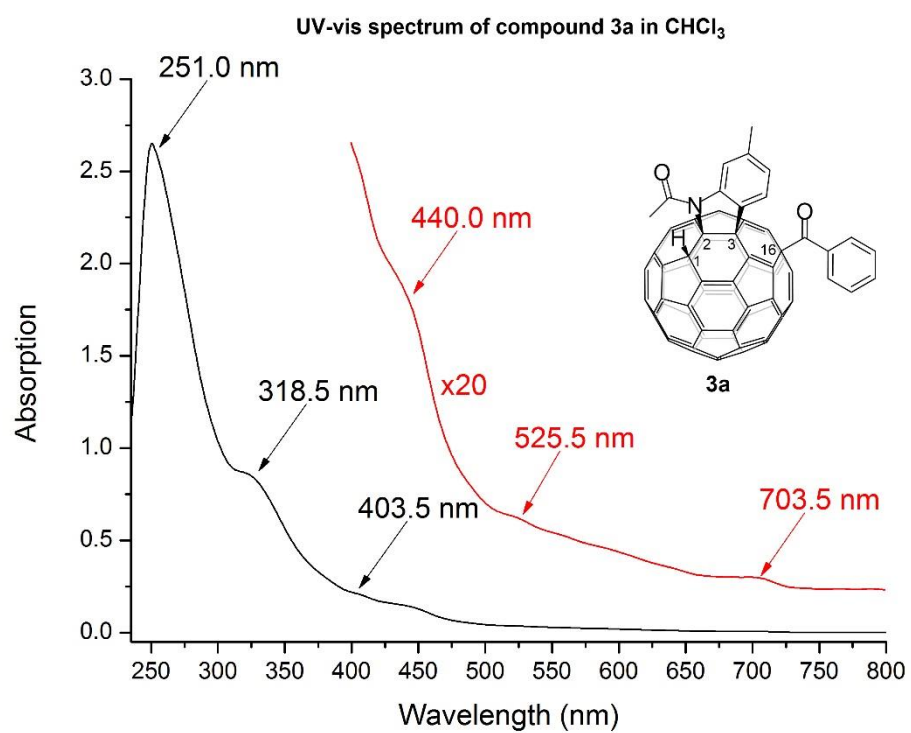
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NAME 1hs-20170110-DAC-3a-D
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PROCNO 1
Date_ 20170110
Time 9.54
INSTRUM spect
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PULPROG zg30
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SOLVENT CDCl3
NS 128
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 120.38
DM 62.400 usec
DE 6.50 usec
TE 292.0 K
D1 1.0000000 sec
TDO 1
    
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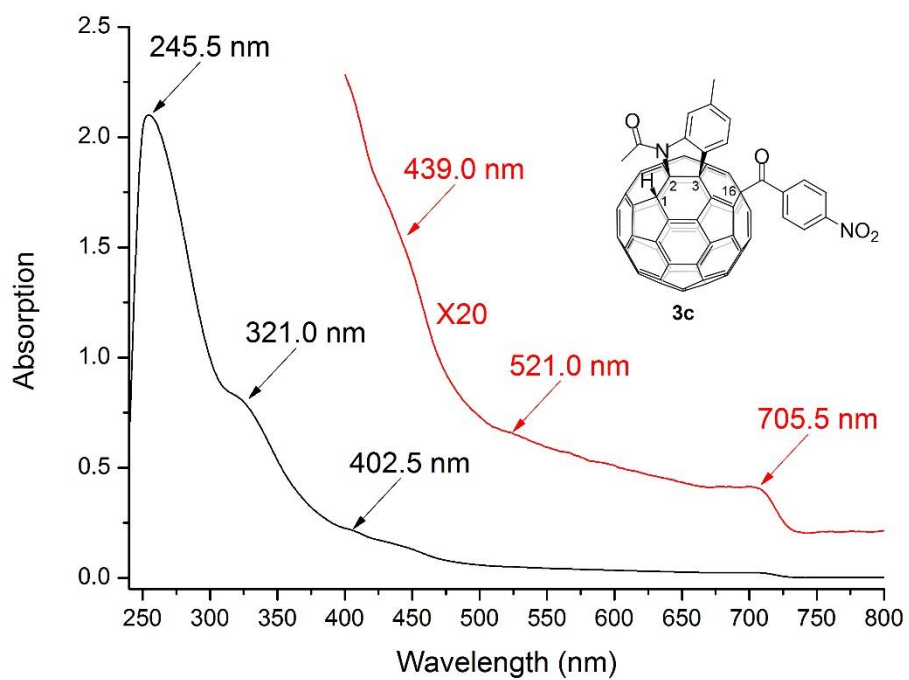
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----- CHANNEL f1 -----
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NUC1 1H
P1 10.00 usec
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WDW EM
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PC 1.00
    
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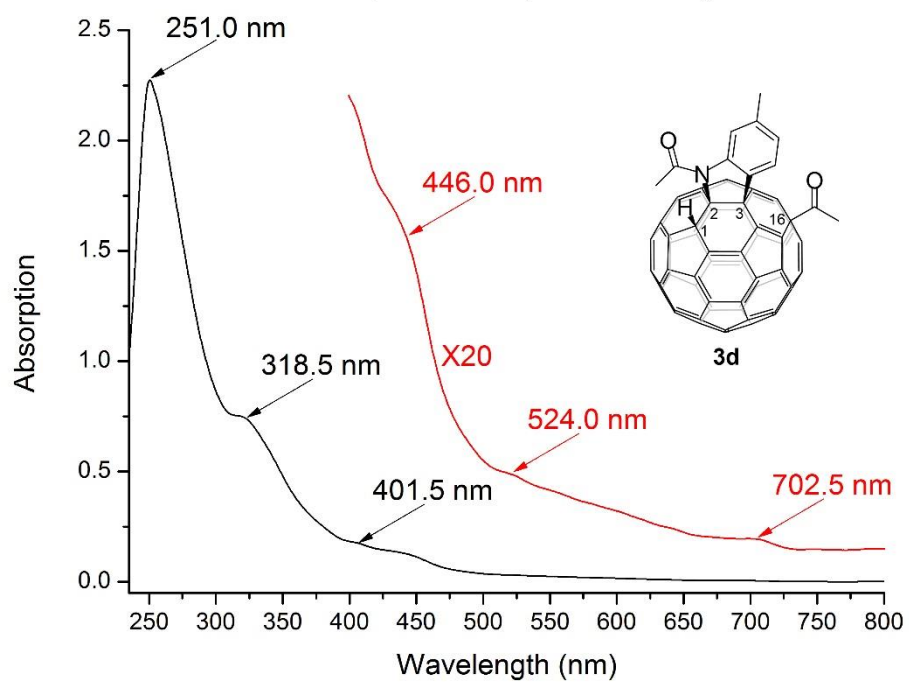
UV-vis spectra of compounds 3a–3g.

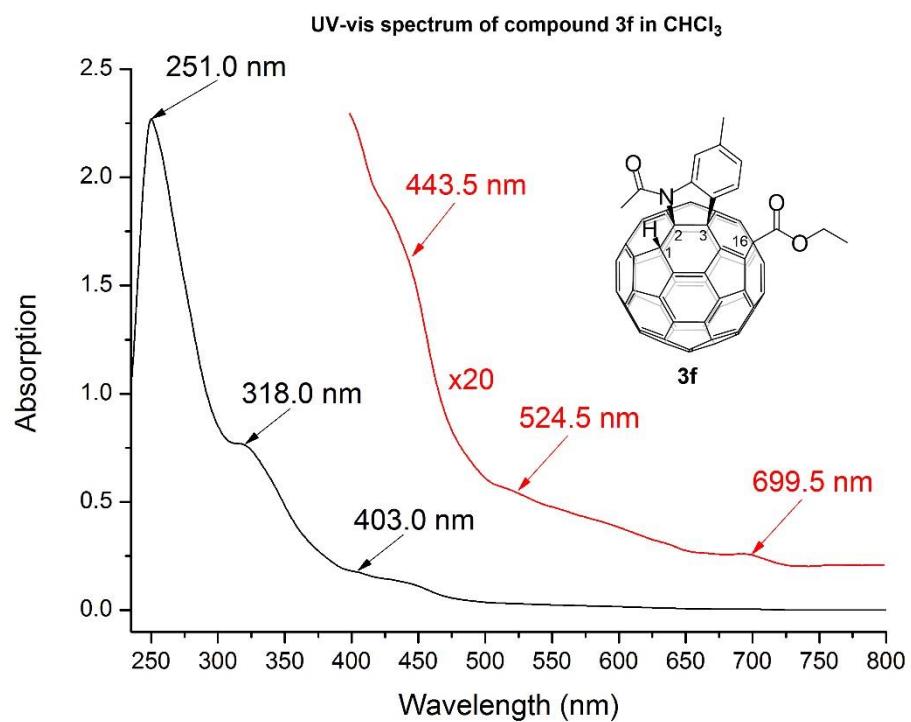
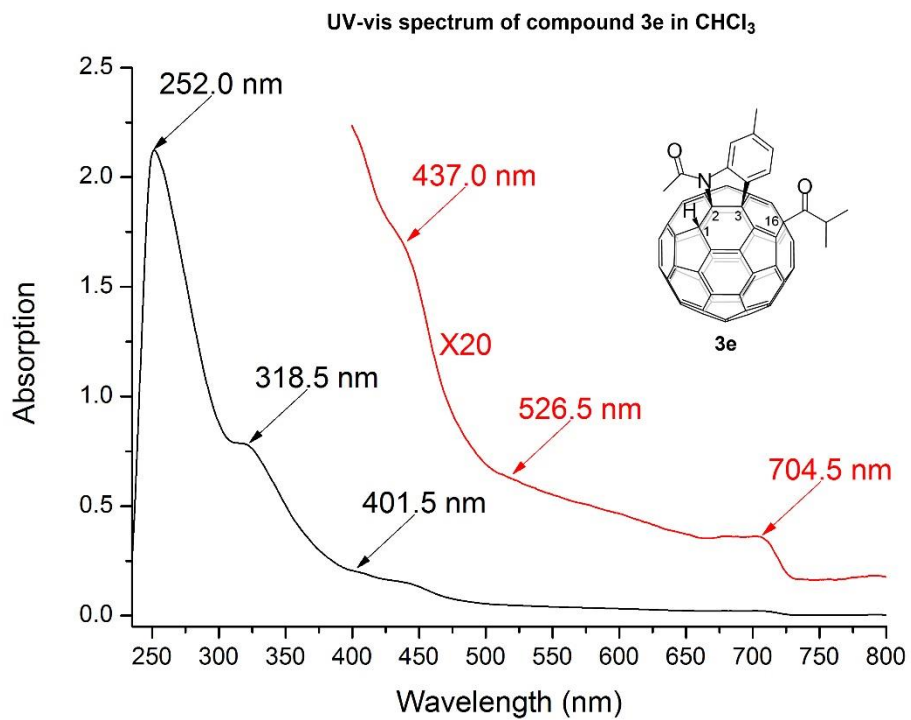


UV-vis spectrum of compound 3c in CHCl₃



UV-vis spectrum of compound 3d in CHCl₃





UV-vis spectrum of compound 3g in CHCl₃

