

## Supporting information

### **Selective formation of dihydrofuran-fused [60] fullerene derivatives by TEMPO mediated [3+2] cycloaddition of medium chain $\beta$ -keto esters to $C_{60}$**

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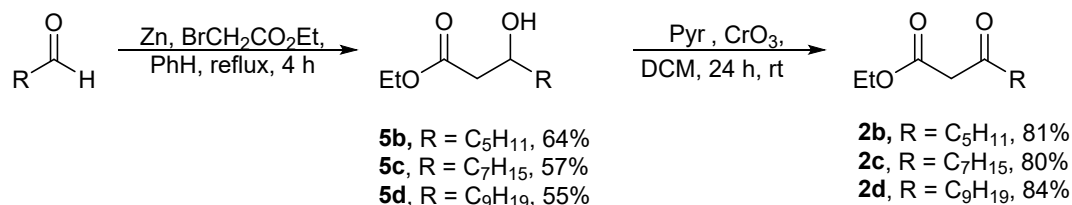
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## General experimental information

Keto ester **2a** was purchased from Sigma Aldrich. All reagents and solvents were purchased from commercial sources, and used without further purifications. All solvents were dried prior to use according to standard literature protocols. Flash chromatography was performed on SiO<sub>2</sub> (0.018–0.032 mm). Thin-layer chromatography (TLC) was carried out on precoated silica gel 60 F<sub>254</sub> plates. IR spectra (ATR) were recorded on a Perkin-Elmer-FT-IR 1725X spectrophotometer;  $\nu$  values are given in cm<sup>-1</sup>. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Ultrashield Avance III (<sup>1</sup>H at 500 MHz, <sup>13</sup>C at 125 MHz) and Bruker Ascend 400 (400 MHz) (<sup>1</sup>H at 400 MHz, <sup>13</sup>C at 100 MHz) spectrometers using CS<sub>2</sub>/CDCl<sub>3</sub> or CDCl<sub>3</sub> as a solvent and TMS as an internal standard. Chemical shifts ( $\delta$ ) are expressed in parts-per million (ppm) and coupling constants (*J*) in Hz. The following abbreviations were used for signal multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sex = sextet, m = multiplet, etc.). Homonuclear 2D (DQF-COSY and NOESY) and heteronuclear 2D <sup>1</sup>H-<sup>13</sup>C spectra (HSQC, HMBC) were recorded with the usual settings. UV spectra were recorded with a COLO NOVEL4S UV-Vis spectrophotometer. The high-resolution MS spectra were taken with Agilent 6210 LC ESI-MS TOF spectrometer. Cyclic Voltammetry and Linear sweep voltammetry measurements were recorded with METROHM Autolab PGSTAT128N, using Glassy carbon electrode as a working electrode, Ag/AgCl as a reference electrode and Platinum sheet electrode as a counter electrode. Tetrabutylammonium hexafluorophosphate (0.01 M) (98%, Sigma-Aldrich) was used as a supporting electrolyte.

## Experimental procedures

### Preparation of $\beta$ -keto esters (2b-d)



**Scheme SI 1.** Synthesis of ethyl 3-hydroxyalcanoate (**5b-d**) and ethyl 3-oxoalcanoate (**2b-d**)

#### Preparation of $\beta$ -hydroxy esters **5b-d** by Reformatsky reaction<sup>[1]</sup>

Into a refluxing suspension of activated zinc dust (1.37 g, 21mmol) and anhydrous benzene (7 mL), a mixture of aldehyde (20 mmol) and ethyl bromoacetate (3.51 g, 21 mmol) in benzene (40 mL) was added during 1 hour (oil bath at 80°C). The mixture was stirred for an additional 1 hour at 80°C, and then the mixture was cooled to 0°C. Then, a solution of 1 M HCl (1 mL) was added, and the reaction mixture was extracted with diethyl ether (3 × 25 mL). The combined organic solutions were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under reduced pressure. The crude product was purified under reduced pressure on a silica gel column, with mixture of petroleum ether and ethyl acetate from 95/5 to 9/1 as eluent, to give the desired  $\beta$ -hydroxy ester.

**Ethyl 3-hydroxyoctanoate (5b)**: 2.41 g (64%); colourless oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  4.17 (q,  $J$  = 7.1 Hz, 2H), 4.03 – 3.97 (m, 1H), 2.97 (bs, 1H), 2.50 (dd,  $J_1$  = 16.4 Hz,  $J_2$  = 3.1 Hz, 1H), 2.40 (dd,  $J_1$  = 16.4 Hz,  $J_2$  = 9.1 Hz, 1H), 1.56 – 1.25 (m, 11H), 0.89 (t,  $J$  = 6.9 Hz, 3H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  172.8, 67.7, 60.3, 41.0, 36.1, 31.3, 24.8, 22.2, 13.8, 13.6 ppm. The obtained spectra were in accordance with the reported in literature.<sup>[2],[3]</sup>

**Ethyl 3-hydroxydecanoate (5c)**: 2.47 g (57%); colourless oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  4.17 (q,  $J$  = 7.2 Hz, 2H), 4.02 – 3.97 (m, 1H), 2.50 (dd,  $J_1$  = 16.4 Hz,  $J_2$  = 3.1 Hz, 1H), 2.40 (dd,  $J_1$  = 16.4 Hz,  $J_2$  = 9.1 Hz, 1H), 1.56 – 1.23 (m, 15H), 0.88 (t,  $J$  = 7.0 Hz, 3H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  172.8, 67.7, 60.3, 41.0, 36.1, 31.4, 29.1, 28.8, 25.1, 22.3, 13.8, 13.7 ppm. The obtained spectra were in accordance with the reported in literature.<sup>[2],[3]</sup>

**Ethyl 3-hydroxydodecanoate (5d)**: 2.69 g (55%); colourless oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  4.17 (q,  $J$  = 7.1 Hz, 2H), 4.03 – 3.96 (m, 1H), 2.95 (bs, 1H), 2.50 (dd,  $J_1$  = 16.4 Hz,  $J_2$  = 3.1 Hz, 1H), 2.40 (dd,  $J_1$  = 16.4 Hz,  $J_2$  = 9.1 Hz, 1H), 1.55 – 1.22 (m, 19H), 0.88 (t,  $J$  = 6.9 Hz, 3H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  173.1, 68.0, 60.6, 41.3, 36.5, 31.9, 29.5, 29.3, 25.4, 22.6, 14.2, 14.1 ppm. The obtained spectra were in accordance with reported in literature.<sup>[2],[3]</sup>

#### Preparation of $\beta$ -keto esters **2b-d** by Collins oxidation of $\beta$ -hydroxy esters<sup>[4]</sup>

Collins reagent was prepared by adding a pyridine (12 mmol) to the suspension of chromium (VI) oxide (6 mmol) in dichlorometane (DCM) (15 mL). The mixture was stirred for 30 min at room temperature, under argon atmosphere, and then the solution of  $\beta$ -hydroxy ester **5b-d** (1 mmol) in DCM (1.5 mL) was added. After

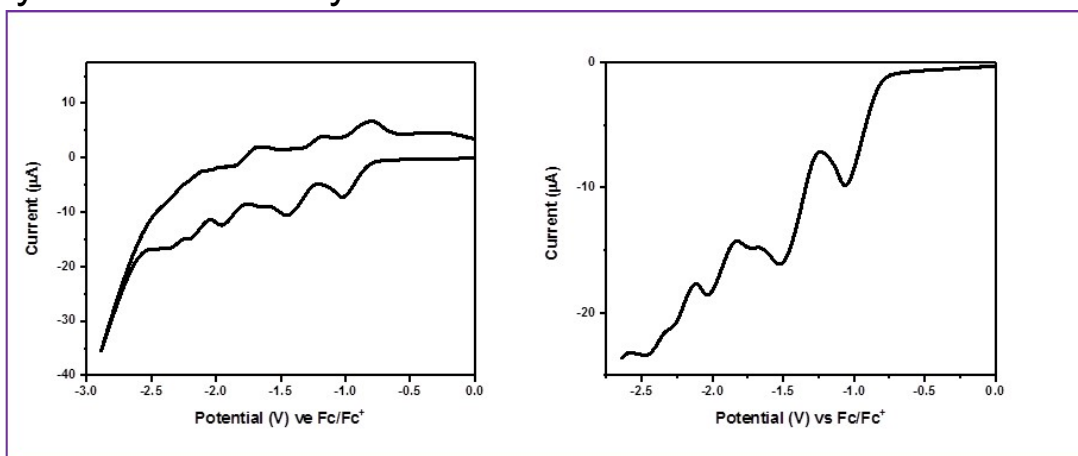
that the reaction mixture was left to stir for 24 h at room temperature. Reaction mixture was then diluted with ether (10 mL), filtrated through a silica gel pad and the residue of chromium reagent was washed with ether (3 x 10 mL). Solvents were removed under reduced pressure, and the residue was chromatographed on a silica gel column with mixture of petroleum ether/ethyl acetate (8:2 v/v) to give a desired  $\beta$ -keto esters **2b-d**.

**Ethyl 3-oxooctanoate (2b):** 150.8 mg (81%); colourless oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  12.09 (enol) (bs, 1H), 4.96 (enol) (s, 1H), 4.19 (q,  $J = 7.1$  Hz, 2H), 3.42 (keto) (s, 2H), 2.52 (keto) (t,  $J = 7.4$  Hz, 2H), 2.18 (enol) (t,  $J = 7.6$  Hz, 2H), 1.62 – 1.56 (m, 2H), 1.33 – 1.26 (m, 4H), 1.27 (t,  $J = 7.1$  Hz, 3H), 0.88 (t,  $J = 6.9$  Hz, 3H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  203.1 (keto) and 181.4 (enol), 171.2 (enol) and 167.4 (keto), 89.1 (enol), 61.4 (keto) and 60.0 (enol), 49.5 (keto), 43.1 (keto) and 35.2 (enol), 31.3 (keto) and 27.6 (enol), 26.0 (enol) and 23.3 (keto), 22.7 (enol) and 22.5 (keto), 14.4 (enol) and 14.2 (keto), 14.0 ppm. The obtained spectra were in accordance with the reported in literature.<sup>[5]</sup>

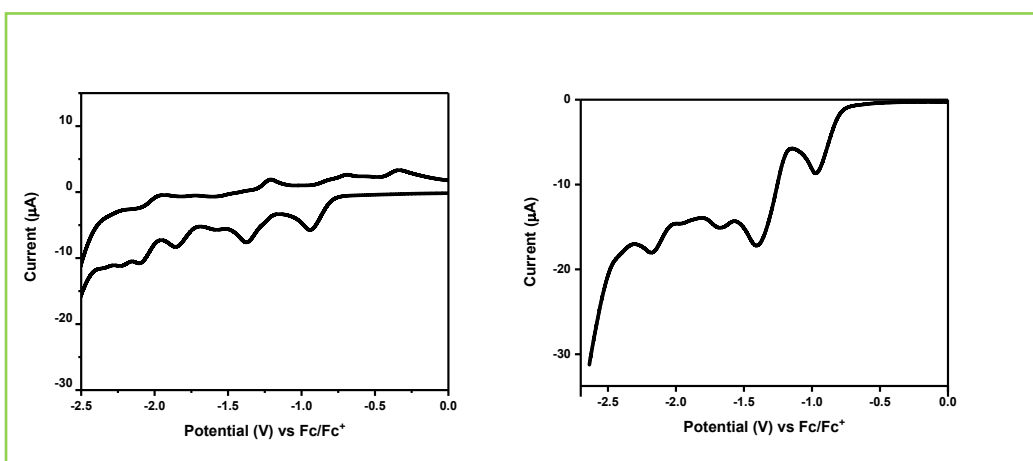
**Ethyl 3-oxodecanoate (2c):** 154.3 mg (80%); colourless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  12.10 (enol) (bs, 1H), 4.97 (enol) (s, 1H), 4.19 (q,  $J = 7.2$  Hz, 2H), 3.43 (keto) (s, 2H), 2.53 (keto) (t,  $J = 7.4$  Hz, 2H), 2.18 (enol) (t,  $J = 7.6$  Hz, 2H), 1.64 – 1.54 (m, 2H), 1.36 – 1.19 (m, 11H), 0.87 (t,  $J = 6.8$  Hz, 3H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  203.2 (keto) and 183.5 (enol), 167.4, 61.5, 49.5, 43.2, 31.8, 29.2, 29.1, 26.4 (enol) and 23.6 (keto), 22.7, 14.3, 14.2 ppm. The obtained spectra were in accordance with the reported in literature.<sup>[6],[7]</sup>

**Ethyl 3-oxododecanoate (2d):** 163.4 mg (84%); colourless oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.96 (enol) (bs, 1H), 4.19 (q,  $J = 7.1$  Hz, 2H), 3.42 (s, 2H), 2.52 (keto) (t,  $J = 7.4$  Hz, 2H), 2.18 (enol) (t,  $J = 7.6$  Hz, 2H), 1.63 – 1.53 (m, 2H), 1.33 – 1.20 (m, 15H), 0.87 (t,  $J = 6.7$  Hz, 3H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  203.1 (keto) and 179.2 (enol), 170.6 (enol) and 167.4 (keto), 89.10 (enol), 61.5 (keto) and 60.03 (enol), 49.5 (keto), 43.2 (keto) and 35.2 (enol), 32.0, 29.5 (2C), 29.4, 29.2, 26.4 (enol) and 23.6 (keto), 22.8, 14.4, 14.2 ppm. The obtained spectra were in accordance with the reported in literature.<sup>[6],[7]</sup>

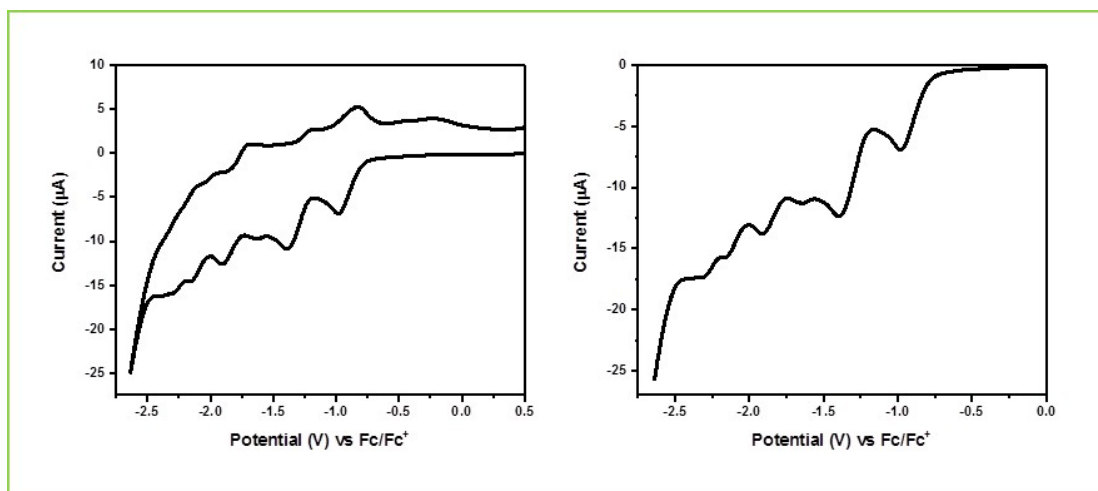
## Cyclic Voltammetry measurements



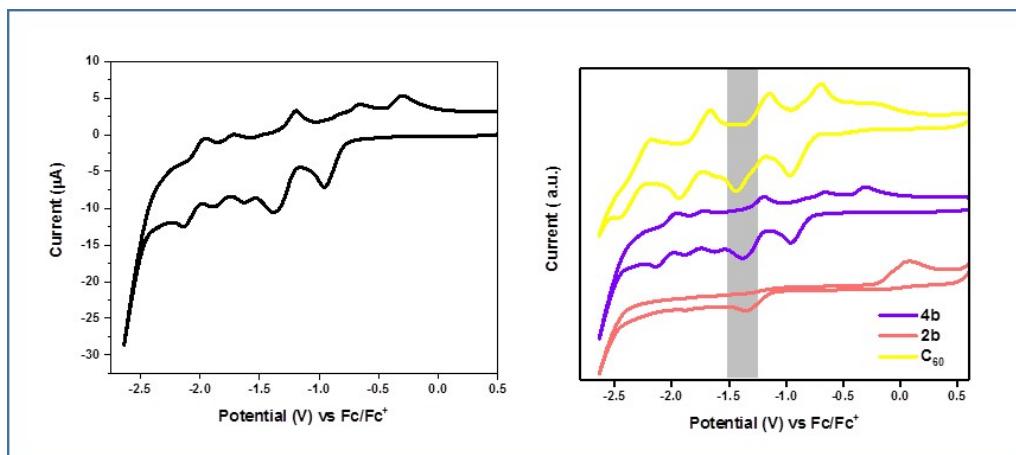
**Figure SI 1.** (left) CV, (right) Linear sweep voltammetry (LSV) of **4d** (1 mg/mL) recorded in ODCB/DMF 10/1, at 50 mVs<sup>-1</sup>, at room temperature, under Argon. Potentials are shown versus Fc/Fc<sup>+</sup>.



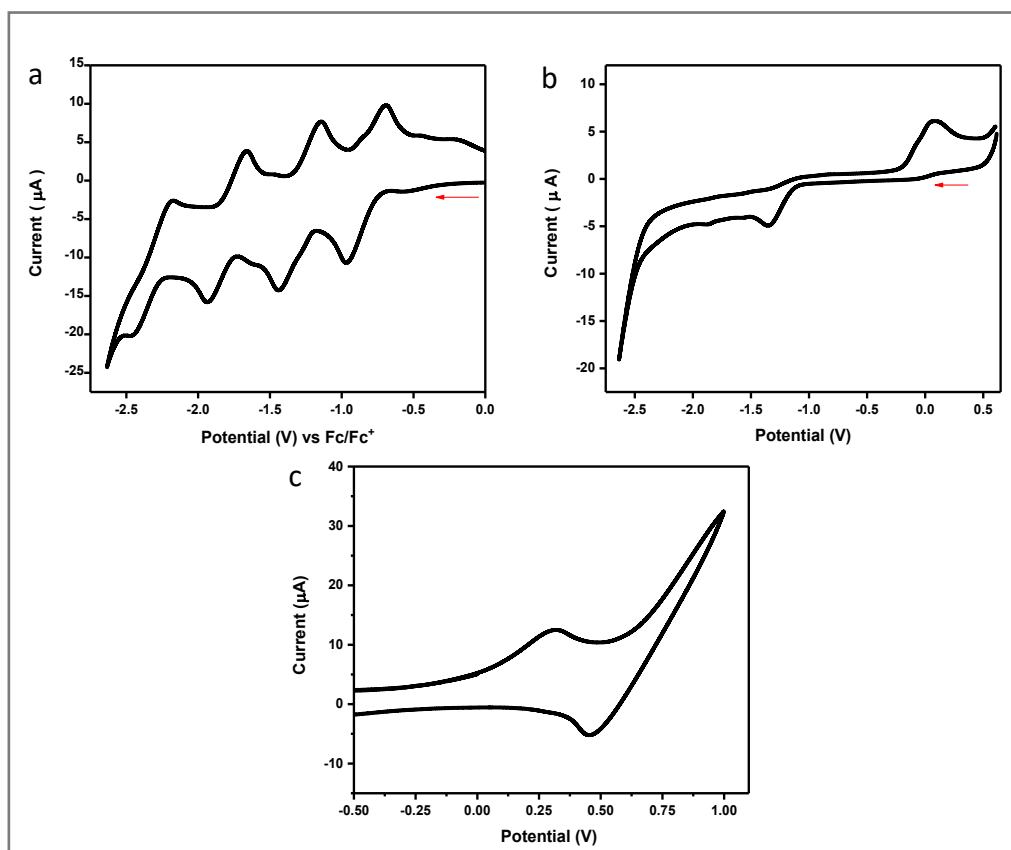
**Figure SI 2.** (left) CV, (right) Linear sweep voltammetry (LSV) of **3d** (1 mg/mL) recorded in ODCB/DMF 10/1, at 50 mVs<sup>-1</sup>, at room temperature, under Argon. Potentials are shown versus Fc/Fc<sup>+</sup>.



**Figure SI 3.** (left) CV, (right) Linear sweep voltammetry (LSV) of **3b** (1 mg/mL) recorded in ODCB/DMF 10/1, at 50 mVs<sup>-1</sup>, at room temperature, under Argon. Potentials are shown versus Fc/Fc<sup>+</sup>.



**Figure SI 4.** (left) CV **4b** (1 mg/mL) recorded in ODCB/DMF 10/1, at 50 mVs<sup>-1</sup>, at room temperature, under Argon. Potentials are shown versus Fc/Fc<sup>+</sup>. (right) Stacked CV graphs of starting compounds **C**<sub>60</sub>, **2b** and the product **4b**.



**Figure SI 5.** Cyclic Voltammograms of a) **C**<sub>60</sub>, b) **2b**, c) ferrocene. Compounds were measured in a concentration of 1 mg/mL in ODCB/DMF 10/1, at 50 mVs<sup>-1</sup>, at room temperature, under Argon. Potentials are shown versus Fc/Fc<sup>+</sup> except for the c).

## Determination of solubility for 3b and 4b in chloroform

The solubility was determined by UV-vis spectroscopy in a following way: standard series of four or six different concentrations and saturated solution were prepared. For all samples the UV-vis spectra were recovered and elaborated data were presented as a graph  $A$  vs  $\mu$  (mg/mL). Standard solutions should have absorbance in the interval 0.3-1.0 while saturated solution must be appropriately diluted to have the absorbance in the mentioned region.

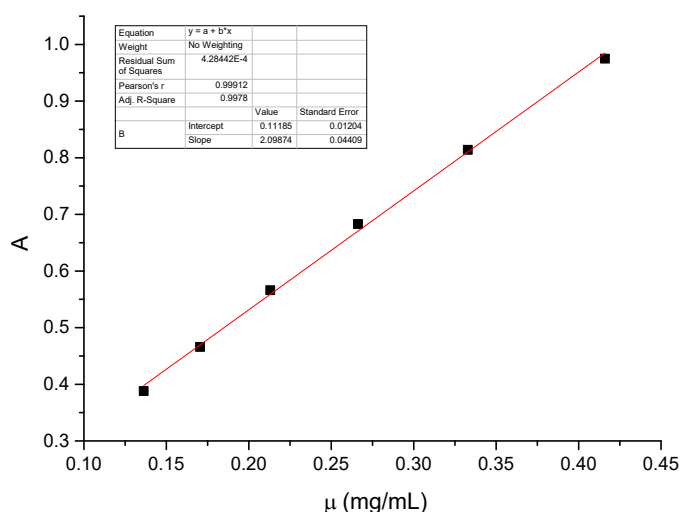
### Compound 3b:

**Preparation of initial solution  $\mu_0$ :** 2.6 mg of **3b** was measured and transferred to a volumetric flask and dissolved by the addition of chloroform to 5 mL. The absorbance of initial solution  $\mu_0$  was out of mentioned region (0.3-1.0).

**Preparation of standard series:** The solution  $\mu_1$  was prepared by diluting 4 mL of  $\mu_0$  to 5 mL in volumetric flask (5 mL) and every second solution was prepared on the same way by diluting of previous one solution.

| Standard solution | $\mu$ (mg/mL) | $A^{429\text{nm}}$ |
|-------------------|---------------|--------------------|
| 1                 | 0.4160        | 0.975              |
| 2                 | 0.3328        | 0.814              |
| 3                 | 0.2662        | 0.683              |
| 4                 | 0.2130        | 0.566              |
| 5                 | 0.1704        | 0.466              |
| 6                 | 0.1363        | 0.388              |

Graph of dependence of absorbance on mass concentration (mg/mL):



**Preparation of saturated solution:** saturated solution was centrifuged and supernatant was taken out and diluted. 200  $\mu\text{L}$  supernatant was measured and diluted to 2 mL in volumetric flask (2 mL) and 1.5 mL of that solution was transferred to a volumetric flask (5 mL) and diluted by addition of chloroform to 5 mL to get



saturated solution that has the absorbance in the mentioned region. The solution thus obtained had absorbance 0.625 and his mass concentration was 0.2445 mg/mL.

*The solubility of compound 3b in chloroform was 8.15 mg/mL.*

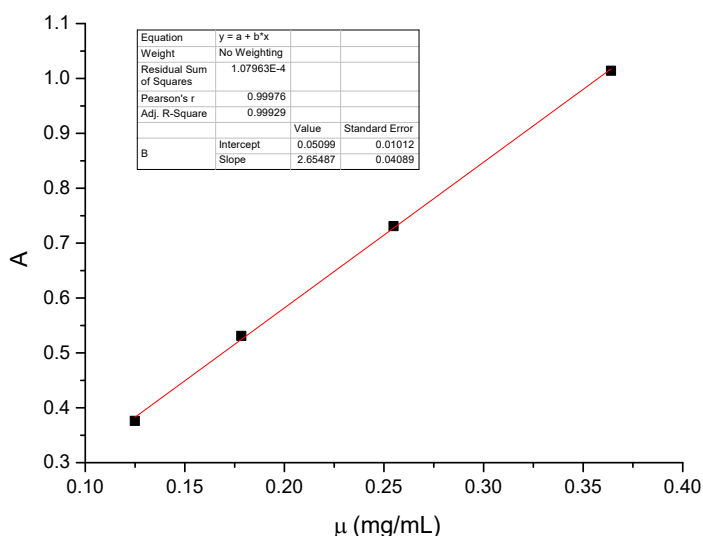
### Compound 4b:

**Preparation of initial solution  $\mu_0$ :** 2.6 mg of **4b** was measured and transferred to a volumetric flask and dissolved by the addition of chloroform to 5 mL. The absorbance of initial solution  $\mu_0$  was out of mentioned region (0.3-1.0).

**Preparation of standard series:** The solution  $\mu_1$  was prepared by diluting 3.5 mL of  $\mu_0$  to 5 mL in volumetric flask (5 mL) and every second solution was prepared on the same way by diluting of previous one solution.

| Standard solution | $\mu$ (mg/mL) | $A^{426nm}$ |
|-------------------|---------------|-------------|
| <b>1</b>          | 0.3640        | 1.014       |
| <b>2</b>          | 0.2548        | 0.731       |
| <b>3</b>          | 0.1784        | 0.531       |
| <b>4</b>          | 0.1249        | 0.376       |

Graph of dependence of absorbance on mass concentration (mg/mL):



**Preparation of saturated solution:** saturated solution was centrifuged and supernatant was taken out and diluted. 200  $\mu$ L supernatant was measured and diluted to 2 mL in volumetric flask (2 mL) and 500  $\mu$ L of that solution was transferred to a volumetric flask and diluted to 5 mL. Then, 4 mL of resulting solution was transferred to a volumetric flask (5 mL) and diluted by addition of chloroform to 5 mL to get saturated solution that has the absorbance in the mentioned region. The solution thus obtained had absorbance 0.725 and mass concentration was 0.2539 mg/mL.

*The solubility of compound 4b in chloroform was 31.74 mg/mL.*

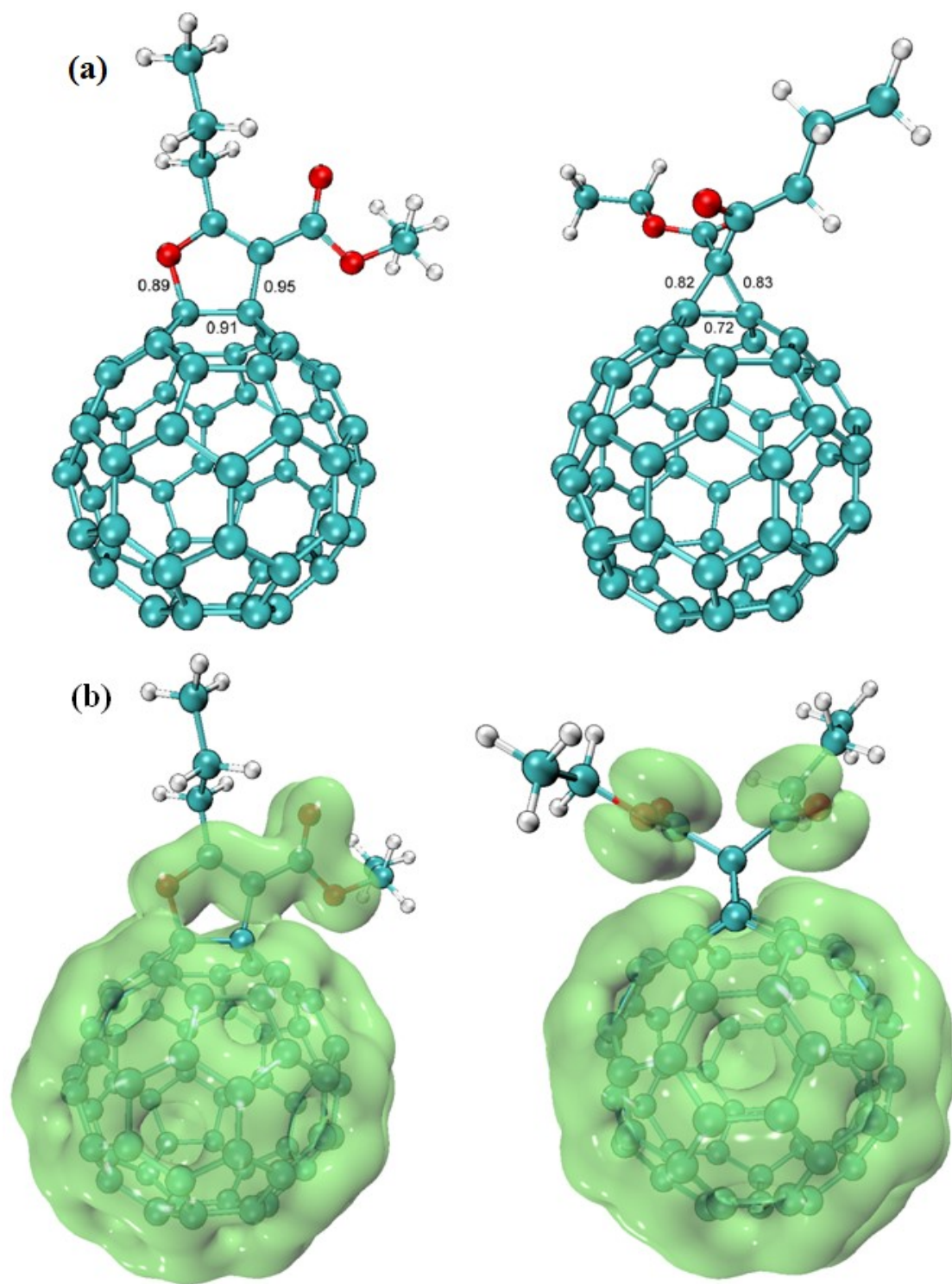
## Electronic structure calculations

Following the verified procedure when dealing with fullerene derivatives computationally<sup>[8-10]</sup> the geometries of all synthesized methanofullerenes (**4a-d**) and furanofullerenes (**3a-d**) were fully optimized with Perdew, Burke, and Ernzerhoff (PBE)<sup>[11]</sup> exchange-correlation functional using 6-311G(d,p) basis set. To save computational time the geometry of alky chains were set to most stable zig-zag conformation and no further conformational search for possible alky chain conformations were done. All DFT calculations were performed in Gaussian 09 quantum-chemistry program<sup>[12]</sup>. The electronic properties of investigated compounds, including Becke orbital composition analysis<sup>[13]</sup> and Mayer bond order analysis<sup>[14]</sup>, were analyzed on calculated PBE/PBE/6-311G(d,p) wavefunctions using MultiWfn (version 3.6) software.<sup>[15]</sup>

**Table S1.** Absolute and relative energies of furano- and methanofullerenes

| Compound  | Absolute energy (a.u.) <sup>a</sup> | Relative energy (kcal/mol) |
|-----------|-------------------------------------|----------------------------|
| <b>3a</b> | -2821.255063                        | 0.00                       |
| <b>4a</b> | -2821.242162                        | 8.10                       |
| <b>3b</b> | -2899.788036                        | 0.00                       |
| <b>4b</b> | -2899.775084                        | 8.13                       |
| <b>3c</b> | -2978.320892                        | 0.00                       |
| <b>4c</b> | -2978.307885                        | 8.16                       |
| <b>3d</b> | -3056.853742                        | 0.00                       |
| <b>4d</b> | -3056.840681                        | 8.20                       |

<sup>a</sup>Electronic energies calculated with PBE/PBE/6-311G(d,p) method



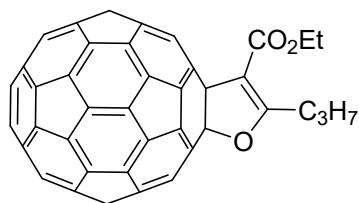
**Figure SI 6.** (a) Mayer bond orders and (b)  $\pi$ -electron densities for compounds 3a and 4a.

## Literature

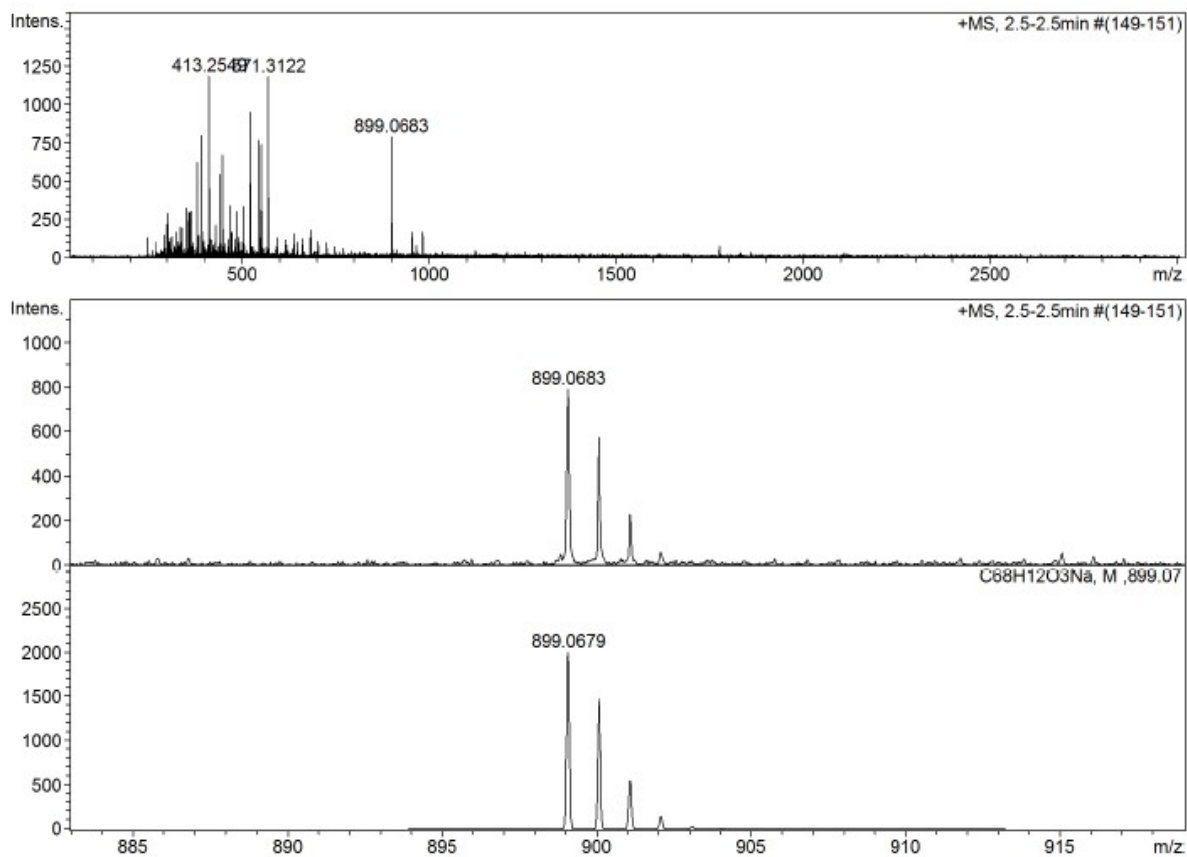
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## Spectral data of furanofullerenes

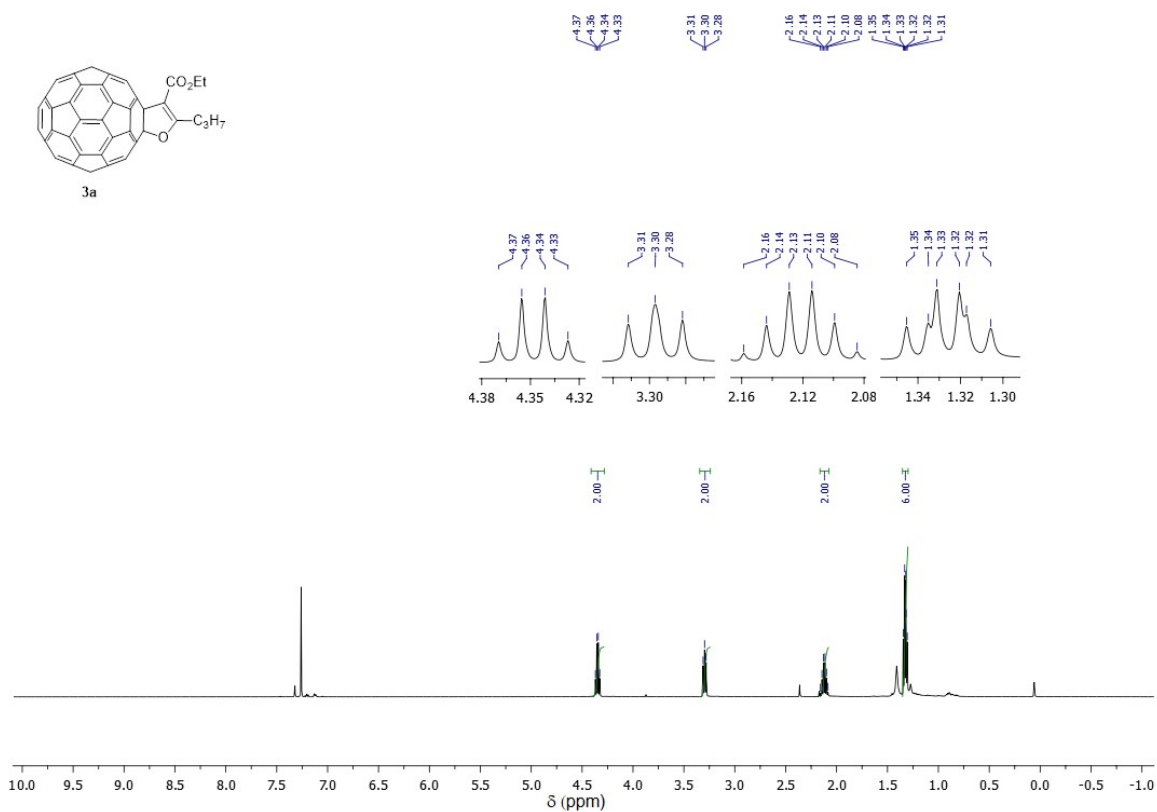
### Spectral data of 3a



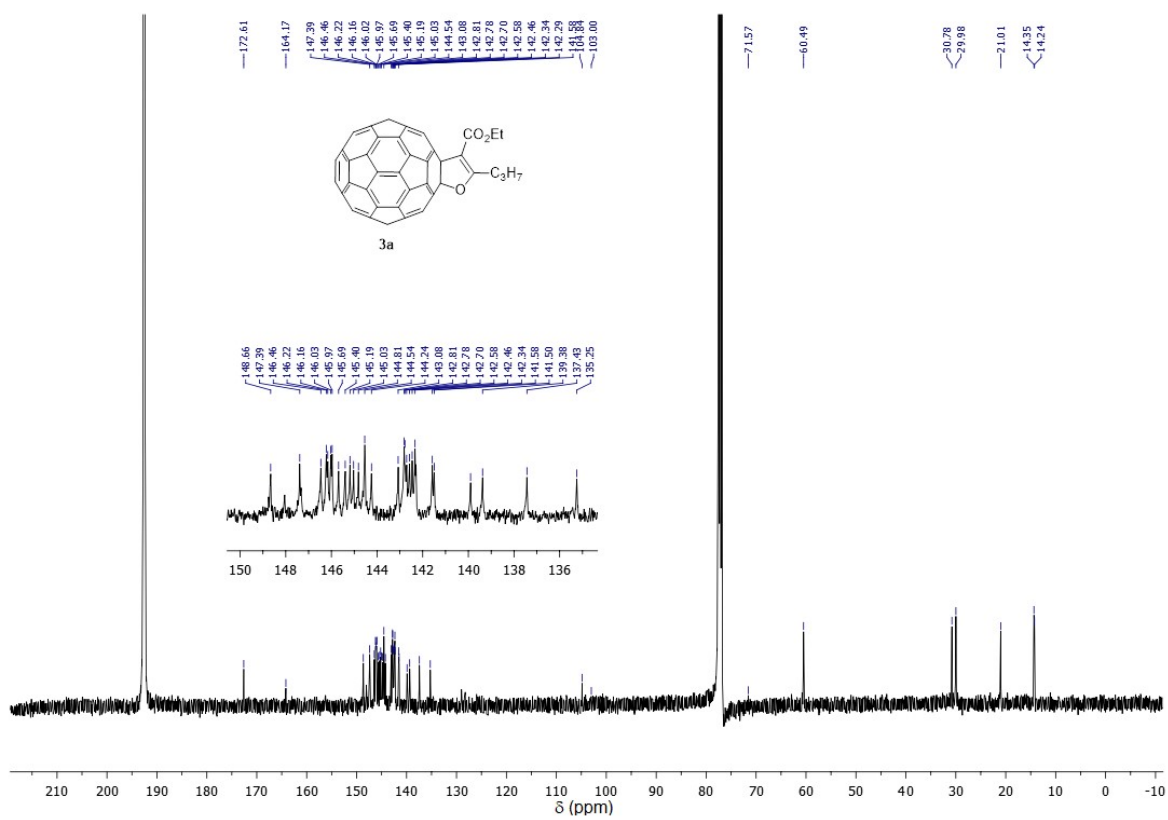
**3a**



**Figure SI 7.** Positive HRMS of compound **3a**.



**Figure SI 8.** <sup>1</sup>H NMR spectrum (500 MHz) of **3a** recorded in CS<sub>2</sub>/CDCl<sub>3</sub>.



**Figure SI 9.** <sup>13</sup>C NMR spectrum (100 MHz) of **3a** recorded in CS<sub>2</sub>/CDCl<sub>3</sub>.

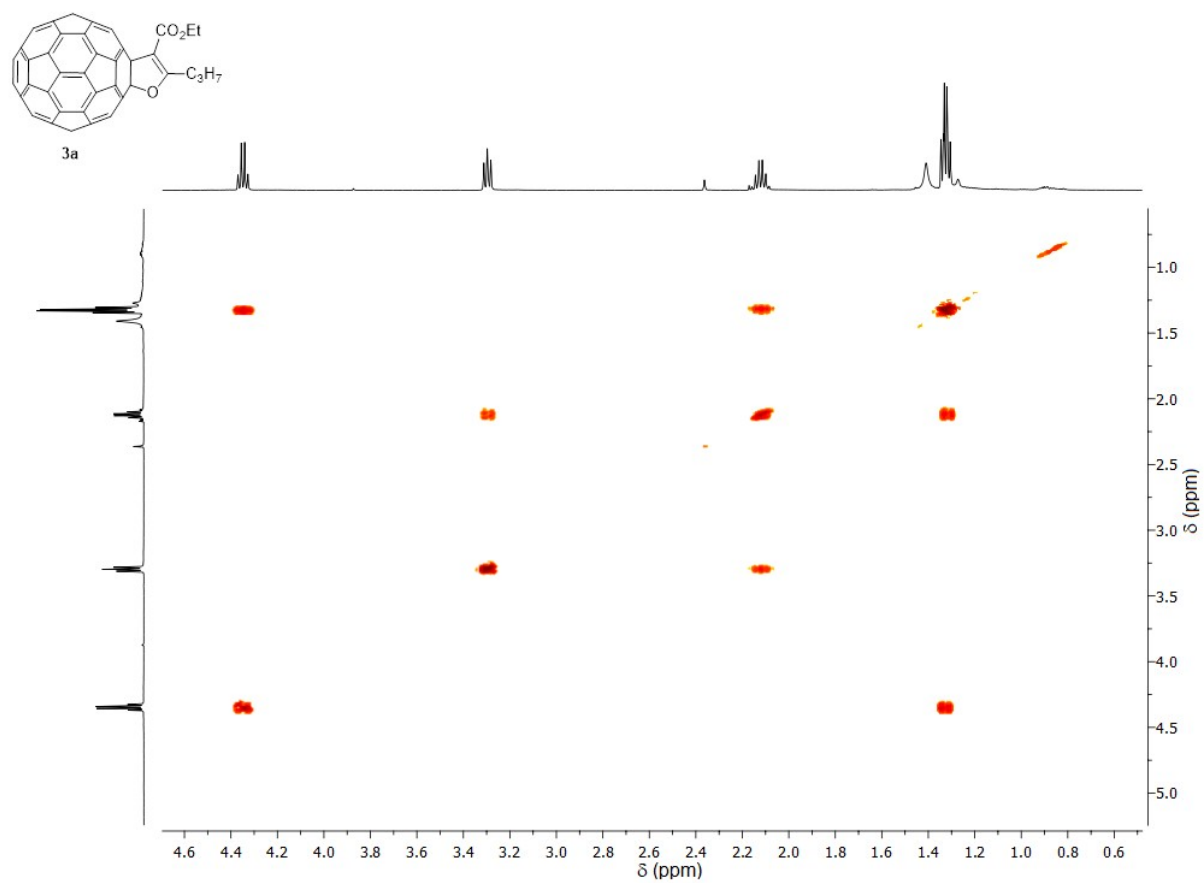


Figure SI 10. COSY NMR spectrum of **3a** in  $\text{CS}_2/\text{CDCl}_3$ .

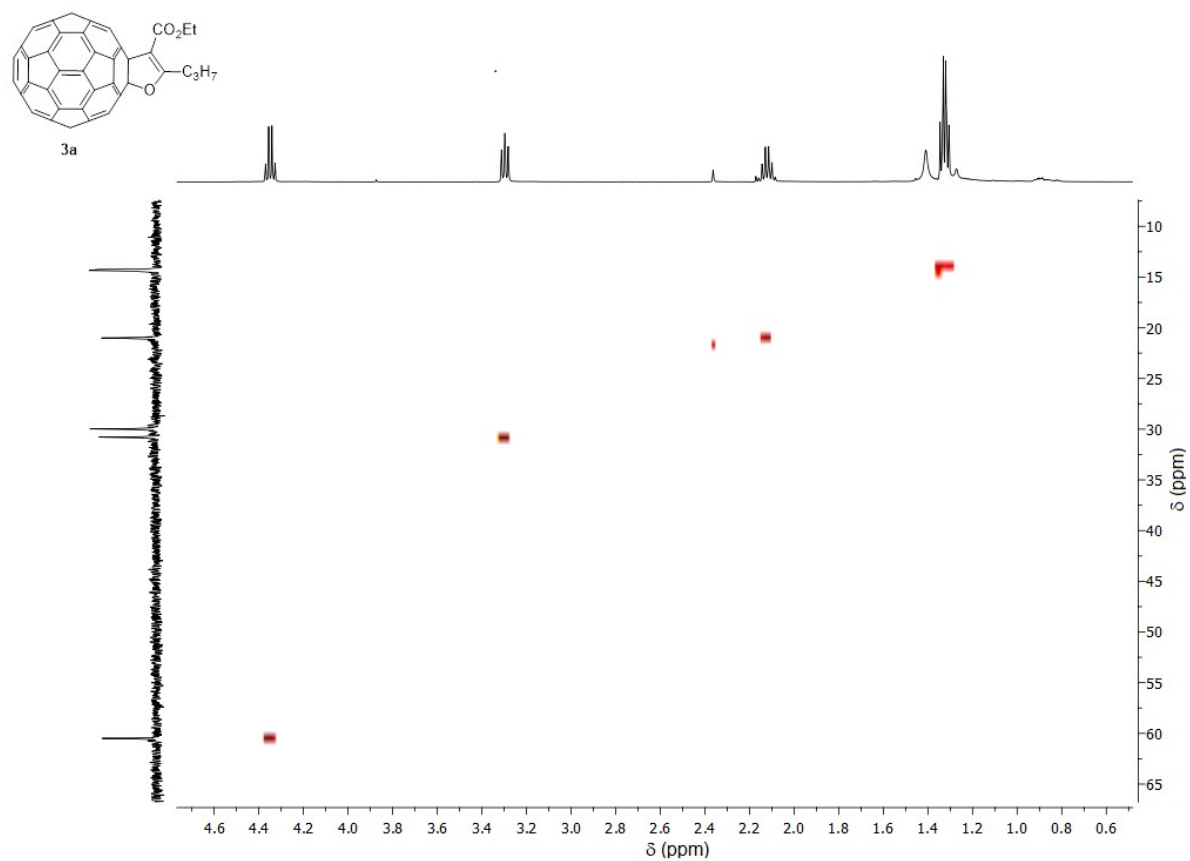


Figure SI 11. HSQC NMR spectrum of **3a** in  $\text{CS}_2/\text{CDCl}_3$ .

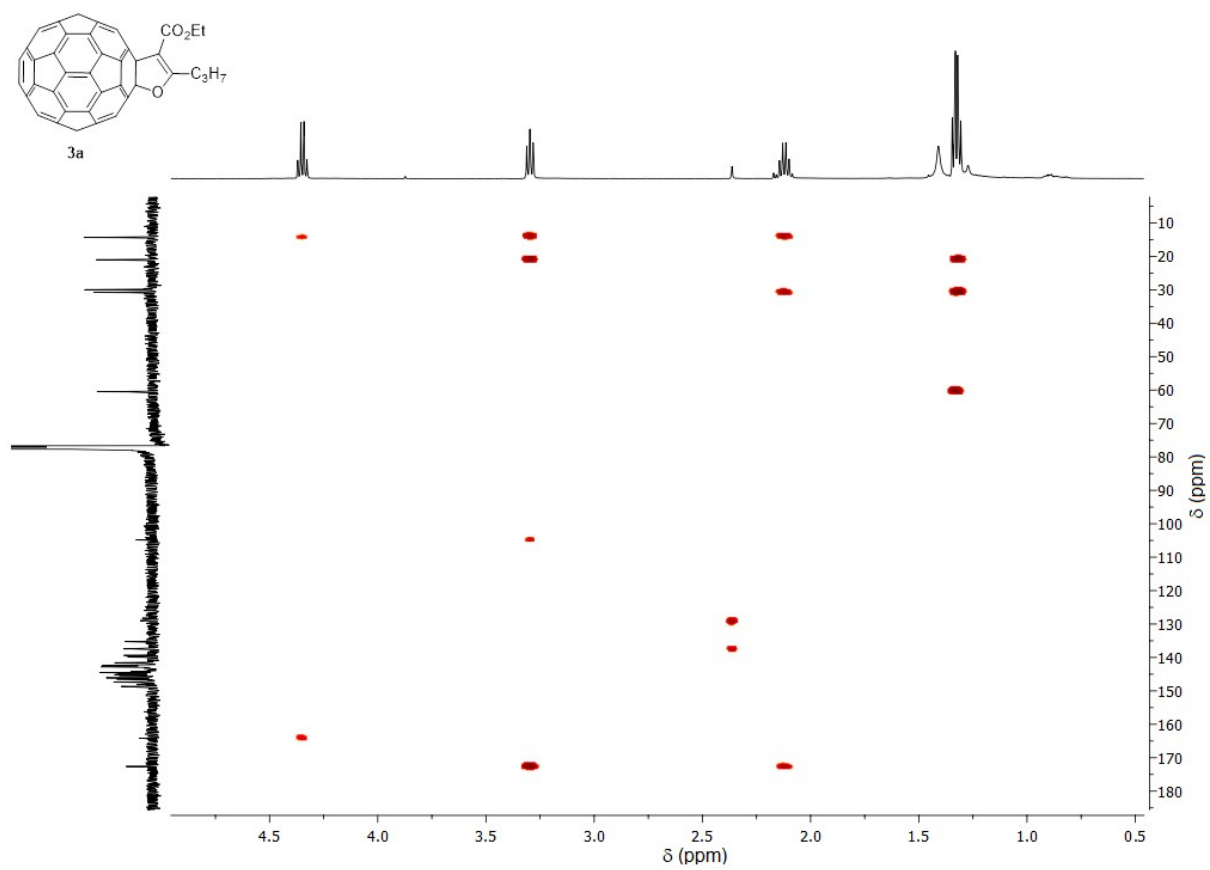
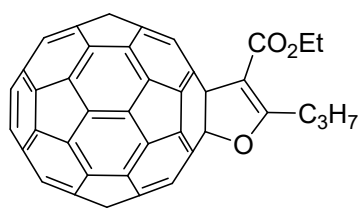
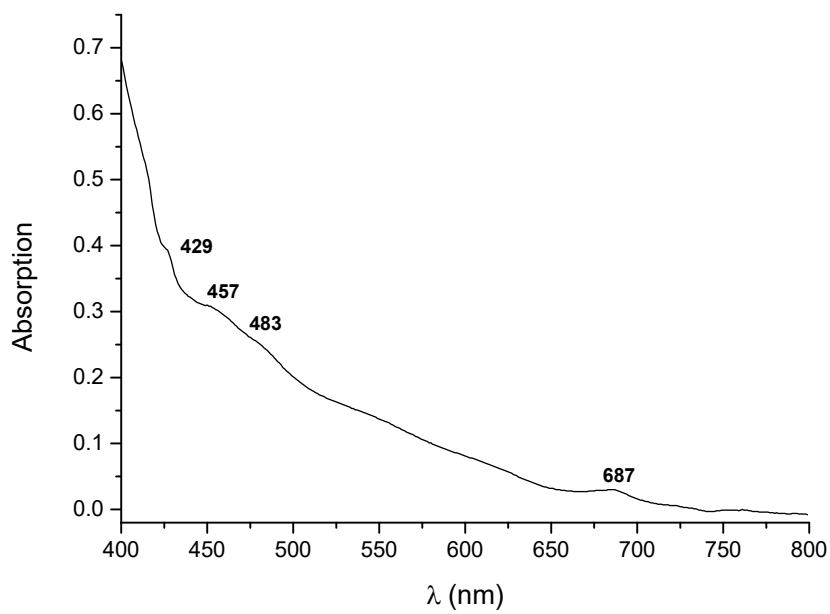


Figure SI 12. HMBC NMR spectrum of **3a** in CS<sub>2</sub>/CDCl<sub>3</sub>.





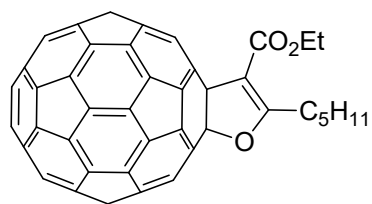
**3a**



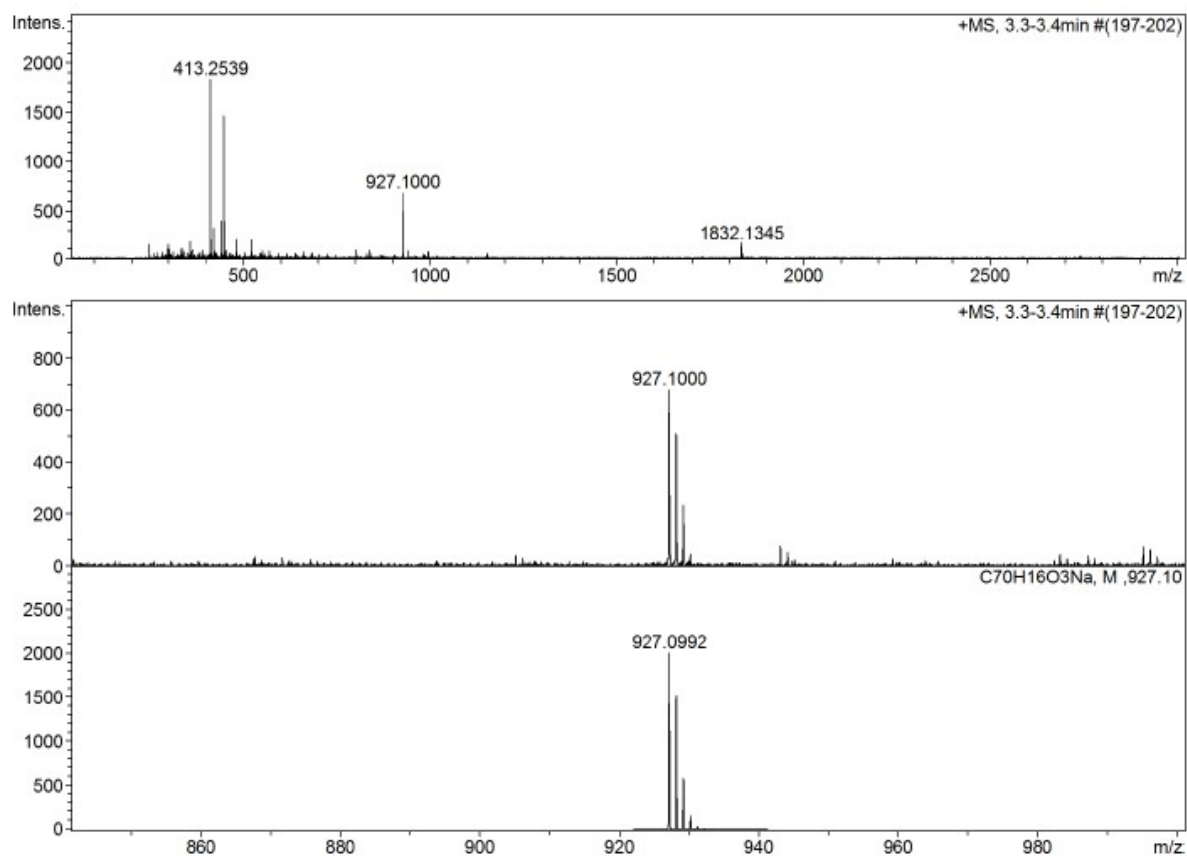
| $\lambda$<br>(nm) | $\epsilon$<br>( $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ) |
|-------------------|--|
| 429               | 3780   |
| 457               | 3000   |
| 483               | 2450   |
| 687               | 300  |

**Figure SI 13.** UV-Vis absorption spectrum of compound **3a** in  $\text{CHCl}_3$ .

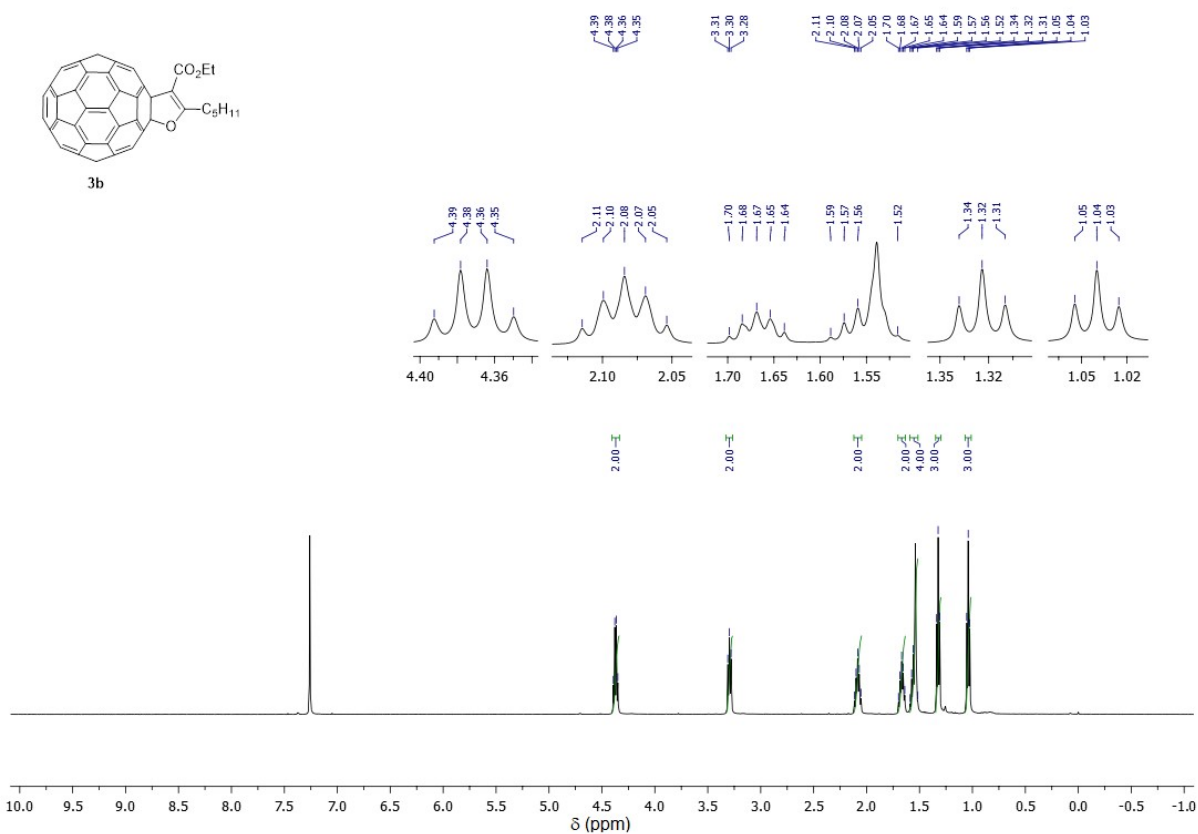
## Spectral data of 3b



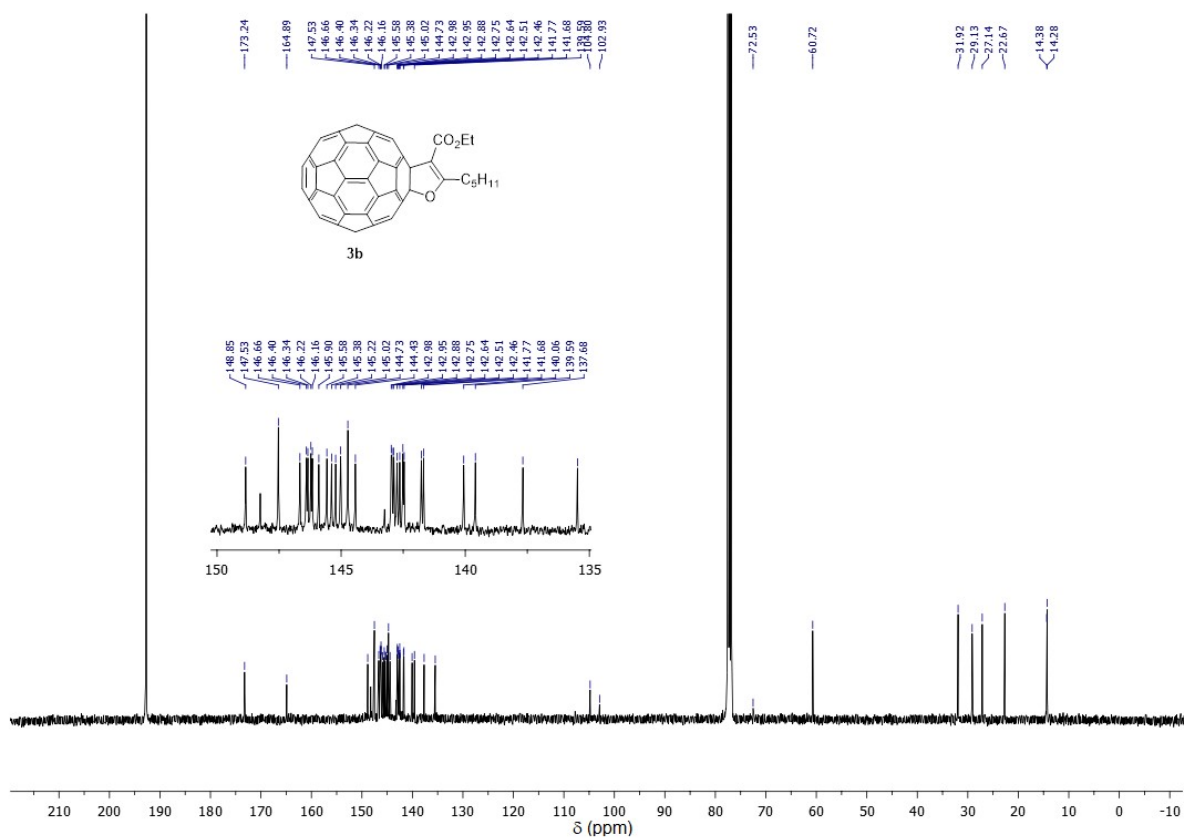
**3b**



**Figure SI 14.** Positive HRMS of compound **3b**.



**Figure SI 15.**  $^1\text{H}$  NMR spectrum (500 MHz) of **3b** recorded in  $\text{CS}_2/\text{CDCl}_3$ .



**Figure SI 16.**  $^{13}\text{C}$  NMR spectrum (100 MHz) of **3b** recorded in  $\text{CS}_2/\text{CDCl}_3$ .

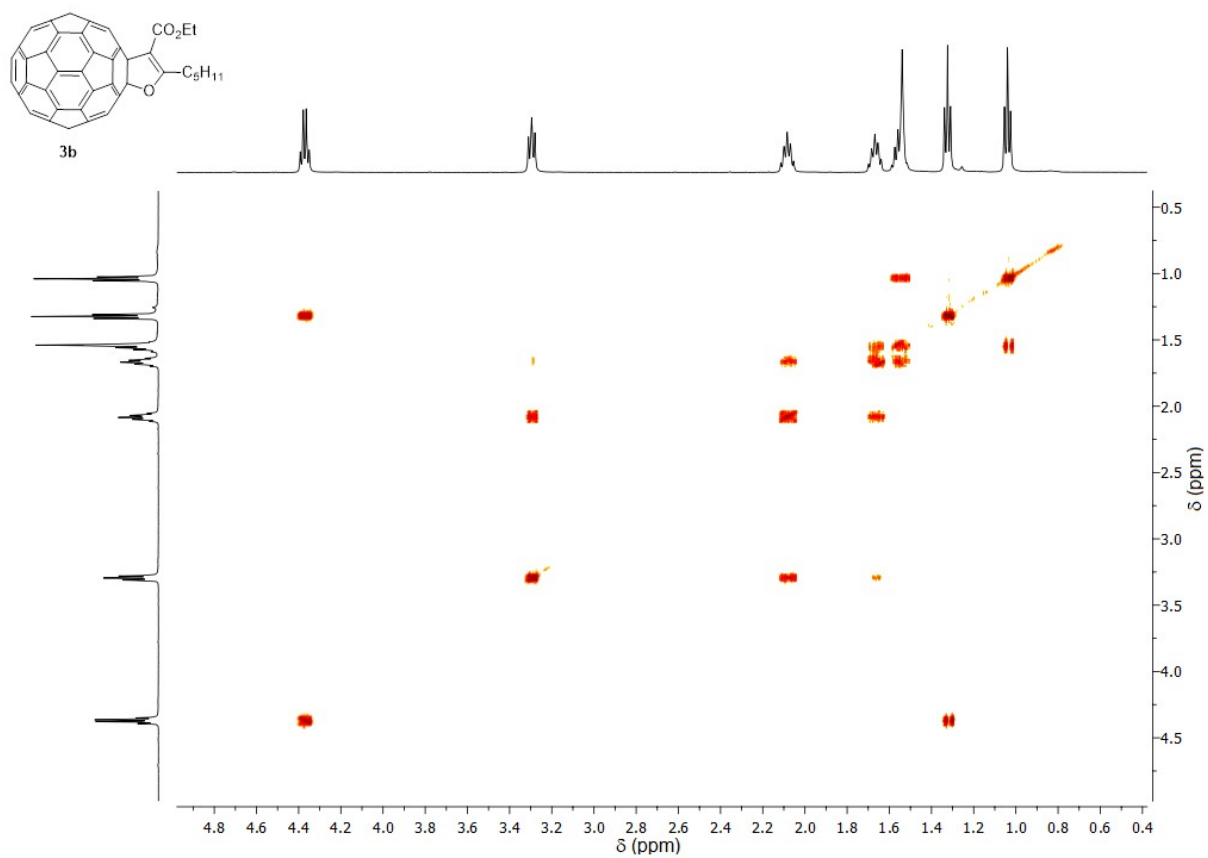


Figure SI 17. COSY NMR spectrum of **3b** in CS<sub>2</sub>/CDCl<sub>3</sub>.

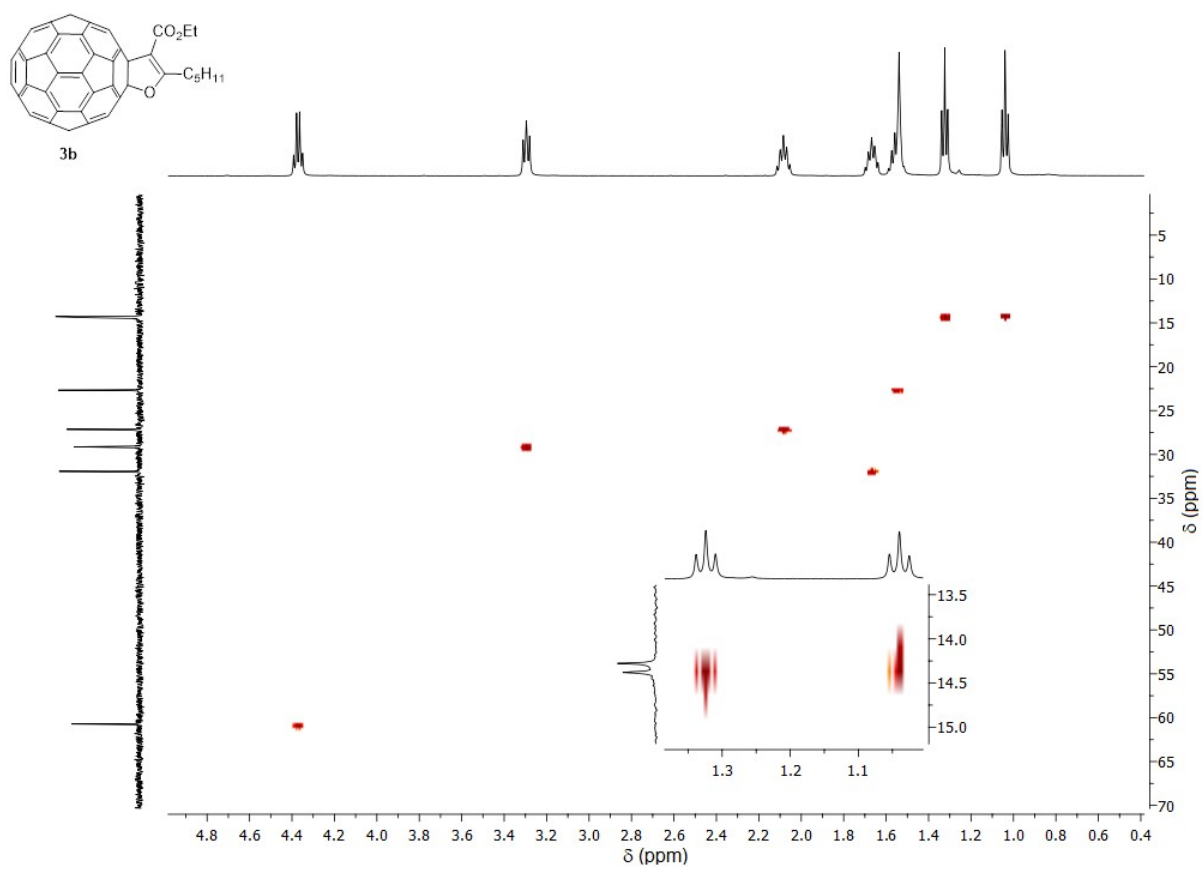
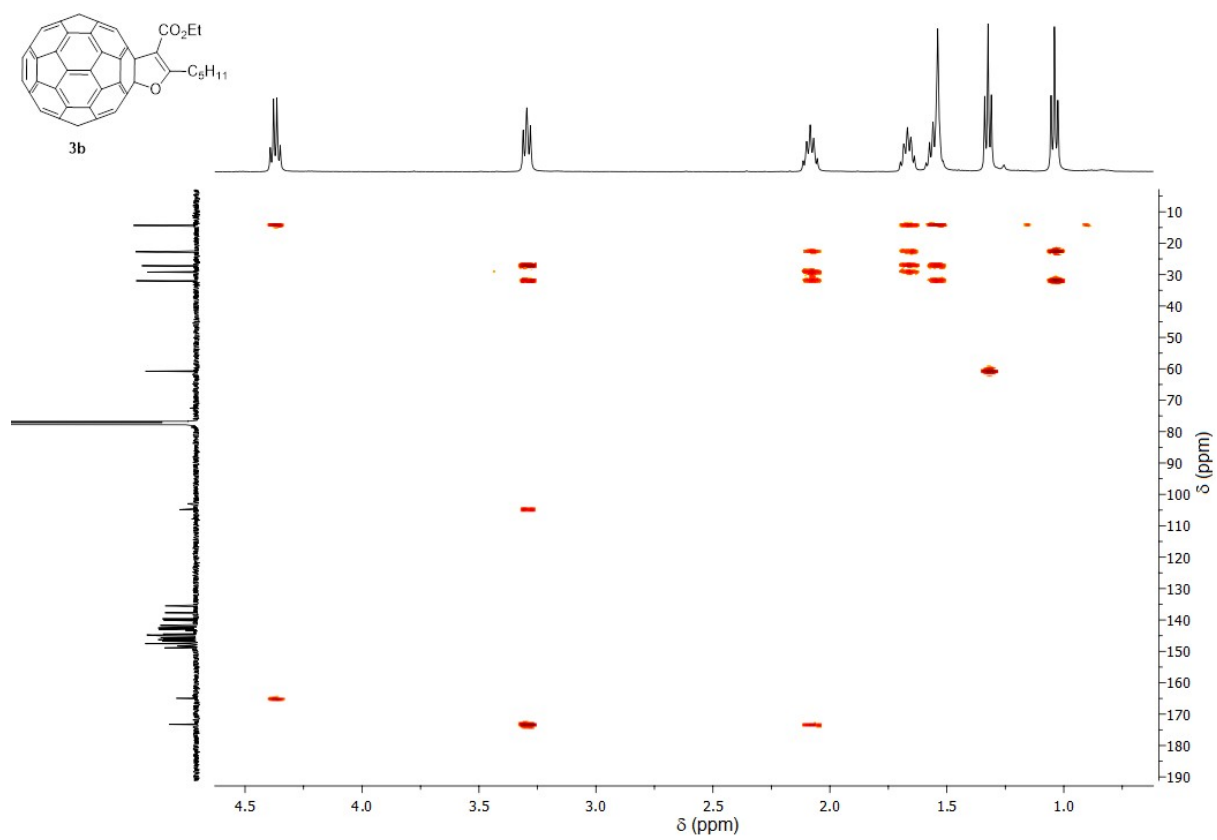
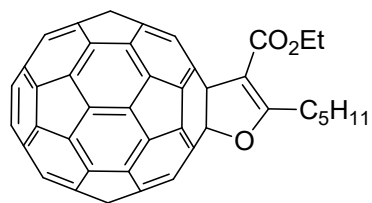
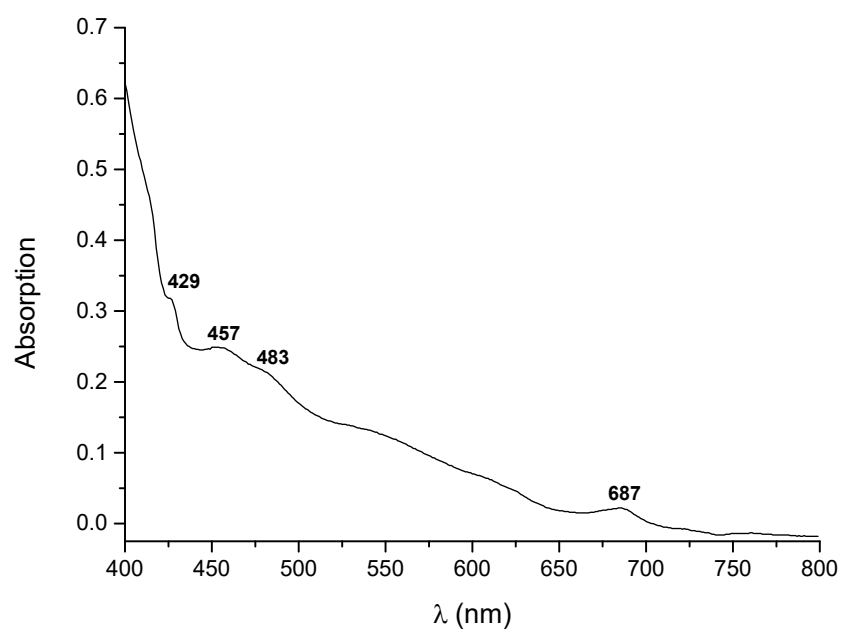


Figure SI 18. HSQC NMR spectrum of **3b** in CS<sub>2</sub>/CDCl<sub>3</sub>.





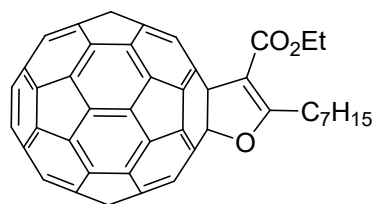
**3b**



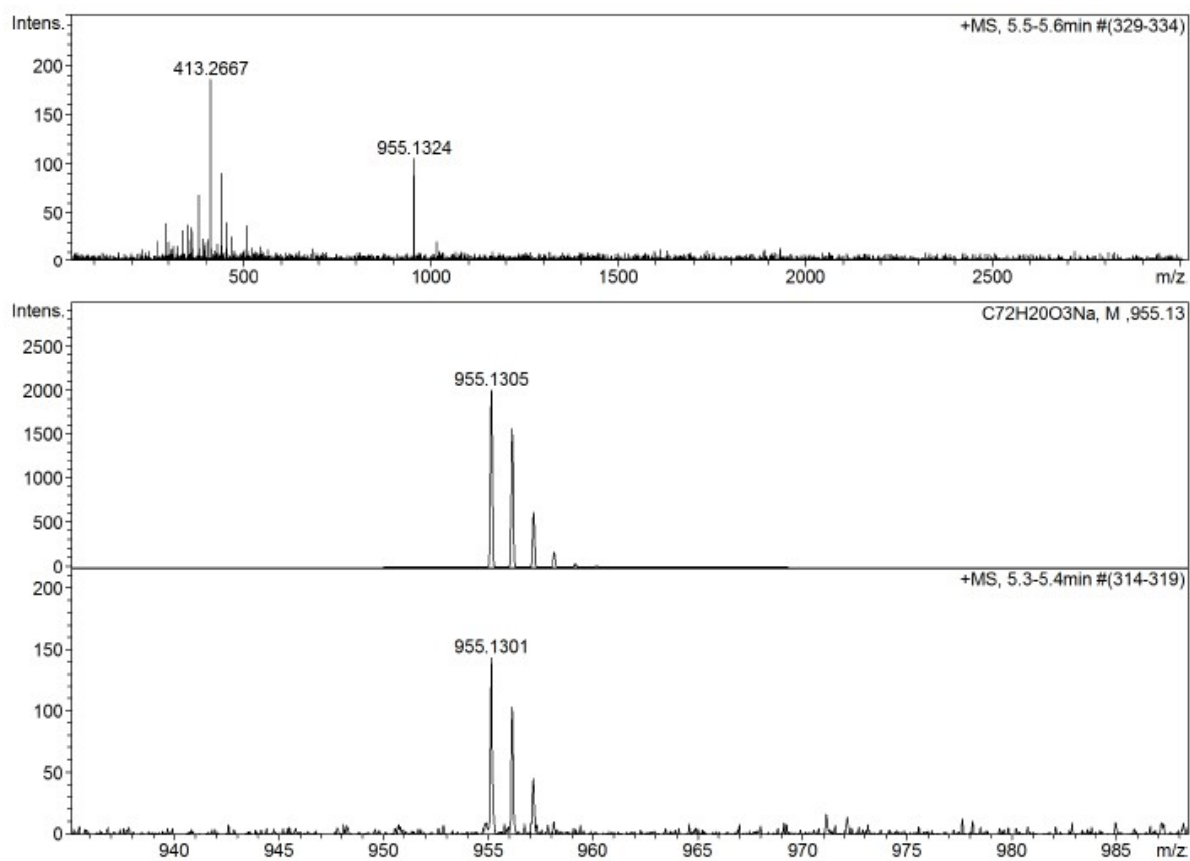
| $\lambda$<br>(nm) | $\epsilon$<br>( $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ) |
|-------------------|--|
| 429               | 3344   |
| 457               | 2756   |
| 483               | 2344   |
| 687               | 233  |

**Figure SI 20.** UV-Vis absorption spectrum of compound **3b** in  $\text{CHCl}_3$ .

## Spectral data of 3c



**3c**



**Figure SI 21.** Positive HRMS of compound 3c.

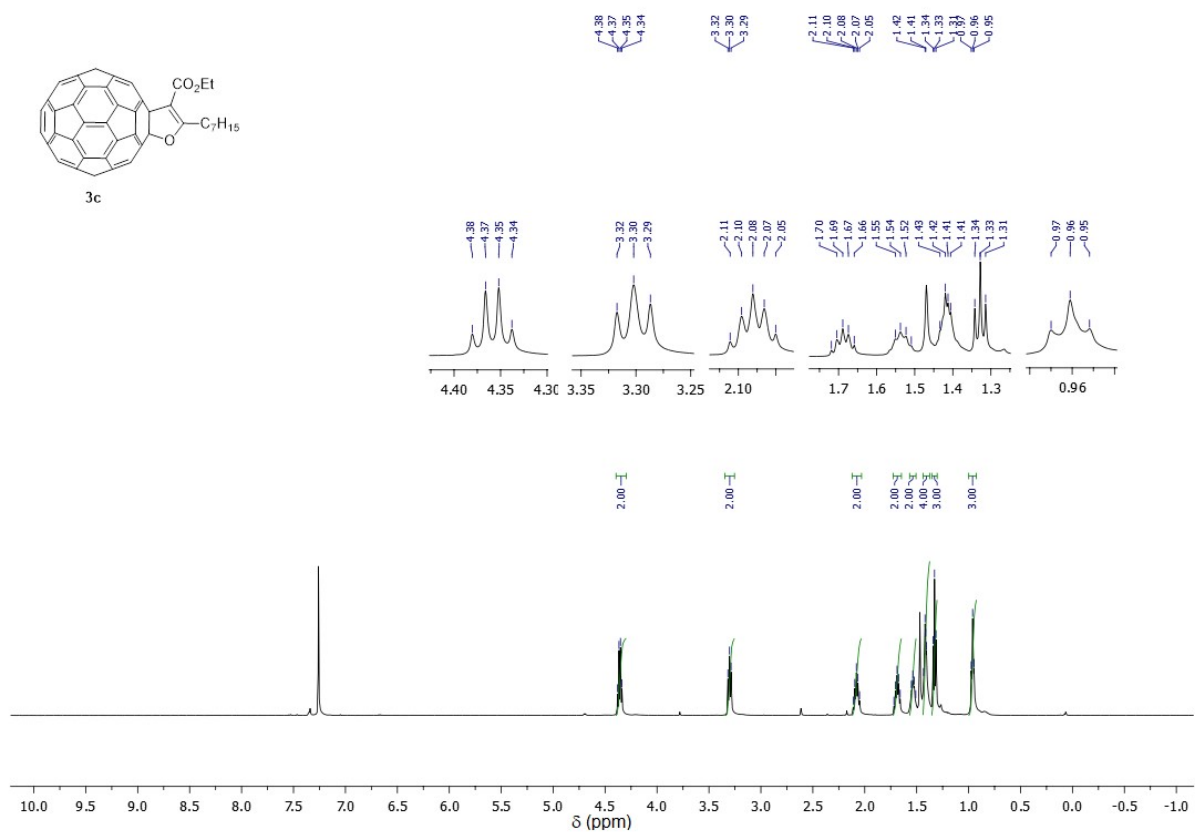


Figure SI 22.  $^1\text{H}$  NMR spectrum (500 MHz) of **3c** recorded in CS<sub>2</sub>/CDCl<sub>3</sub>.

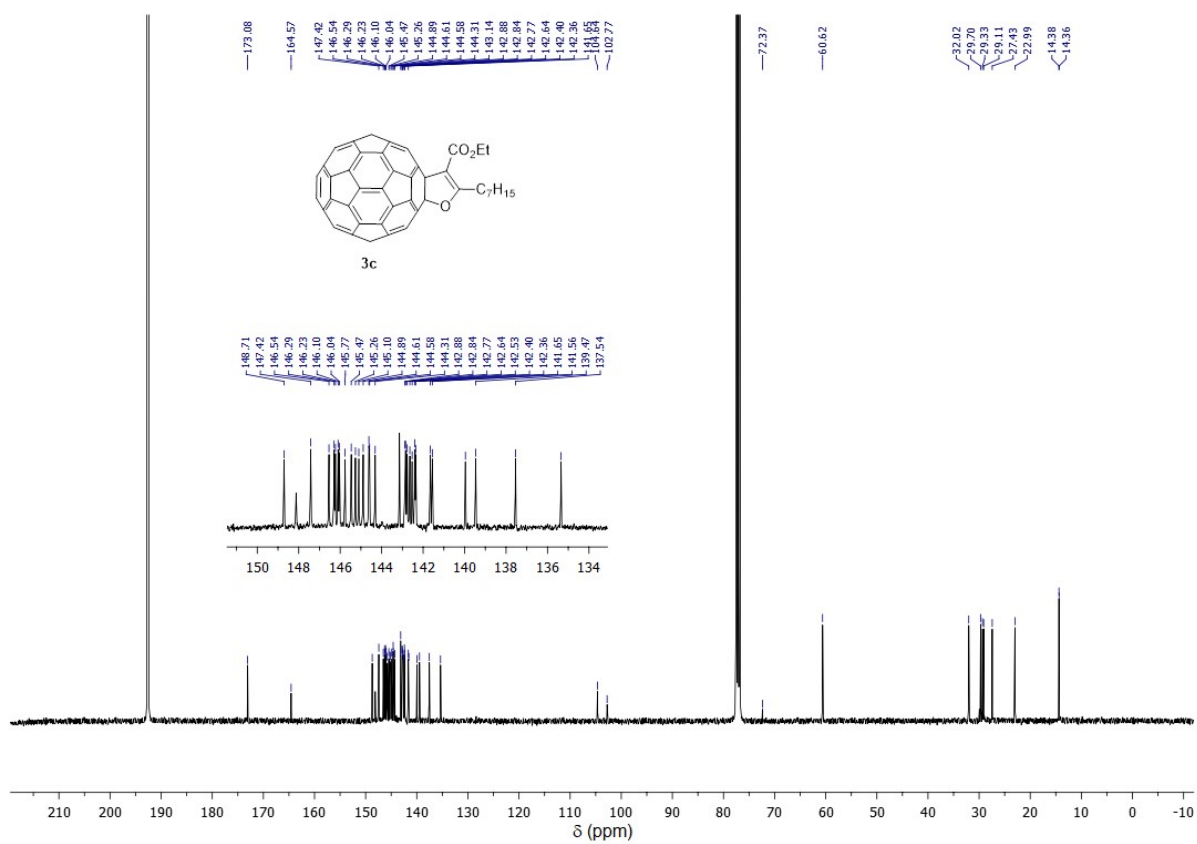


Figure SI 23.  $^{13}\text{C}$  NMR spectrum (100 MHz) of **3c** recorded in CS<sub>2</sub>/CDCl<sub>3</sub>.



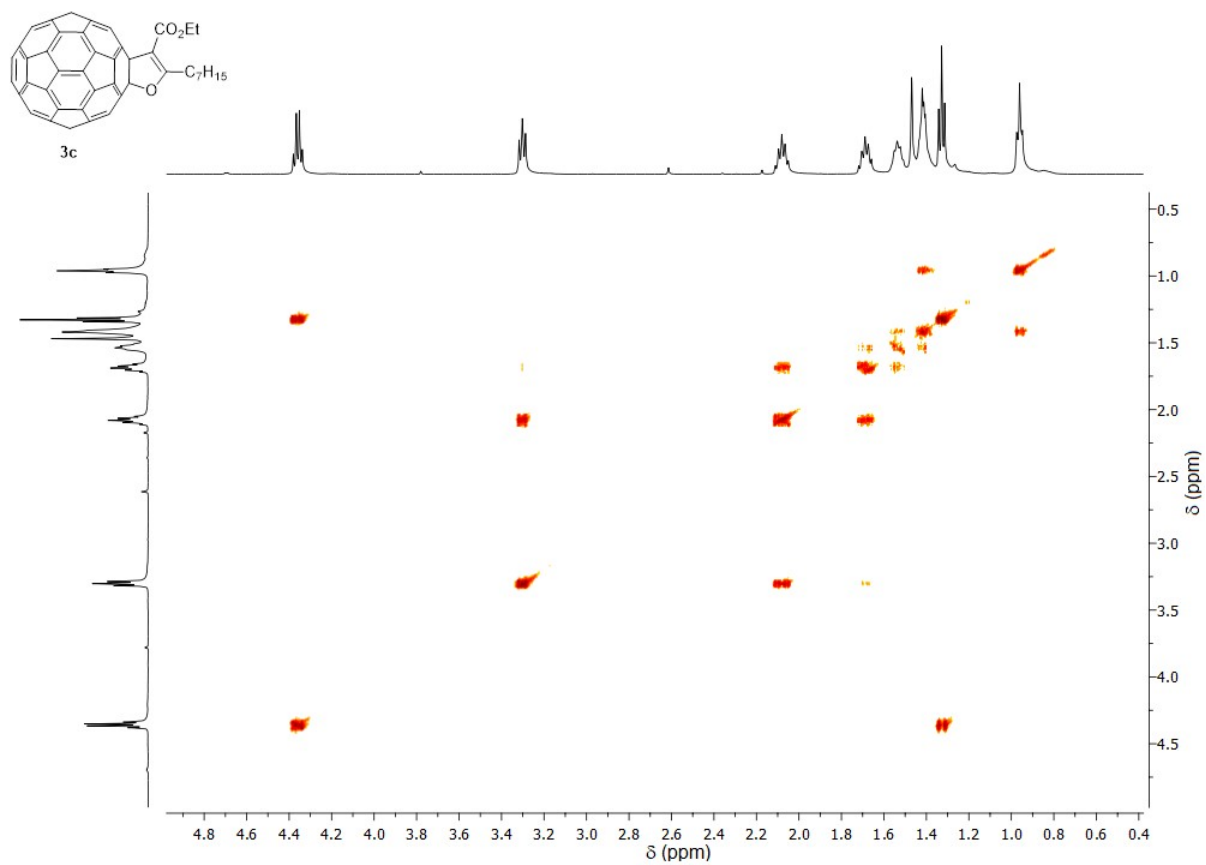


Figure SI 24. COSY NMR spectrum of **3c** in  $\text{CS}_2/\text{CDCl}_3$ .

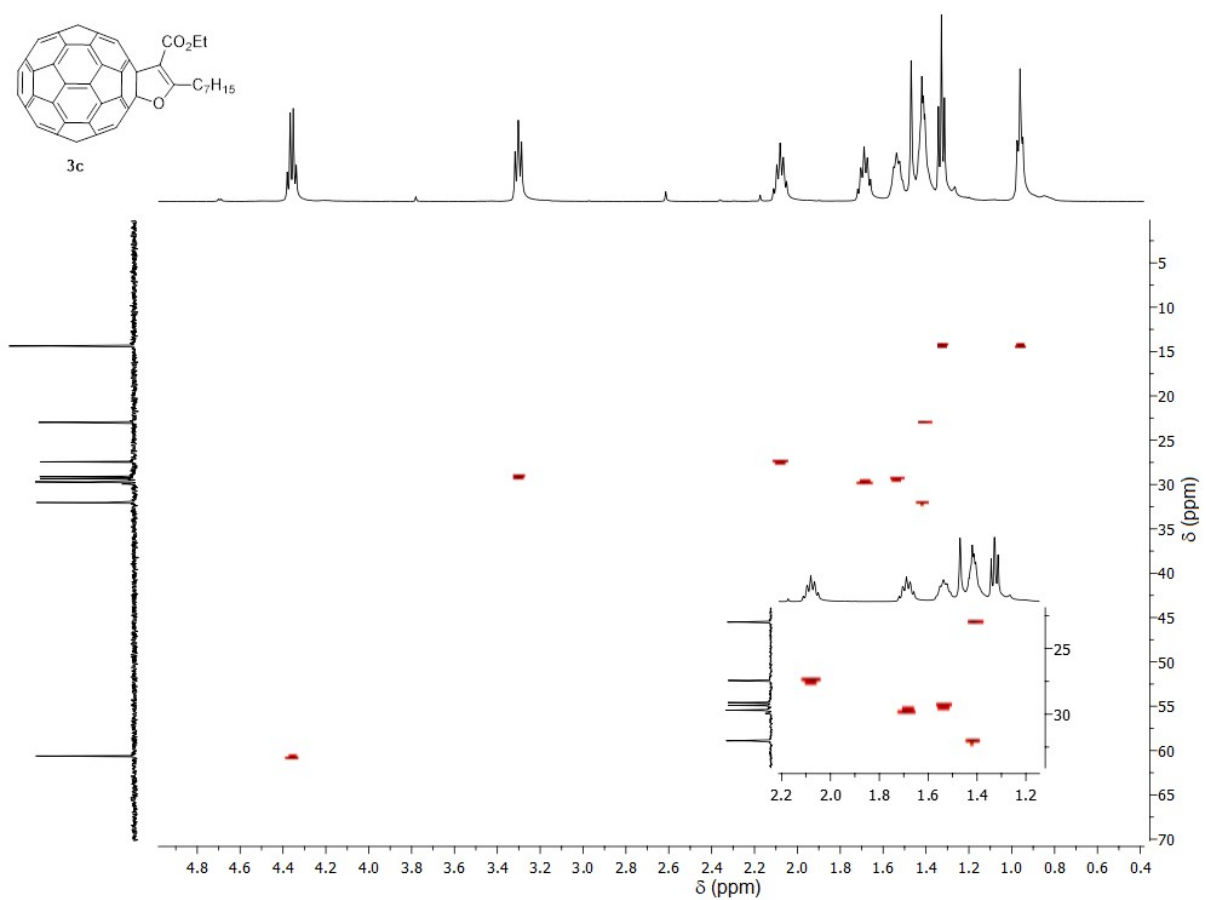


Figure SI 25. HSQC NMR spectrum of **3c** in  $\text{CS}_2/\text{CDCl}_3$ .

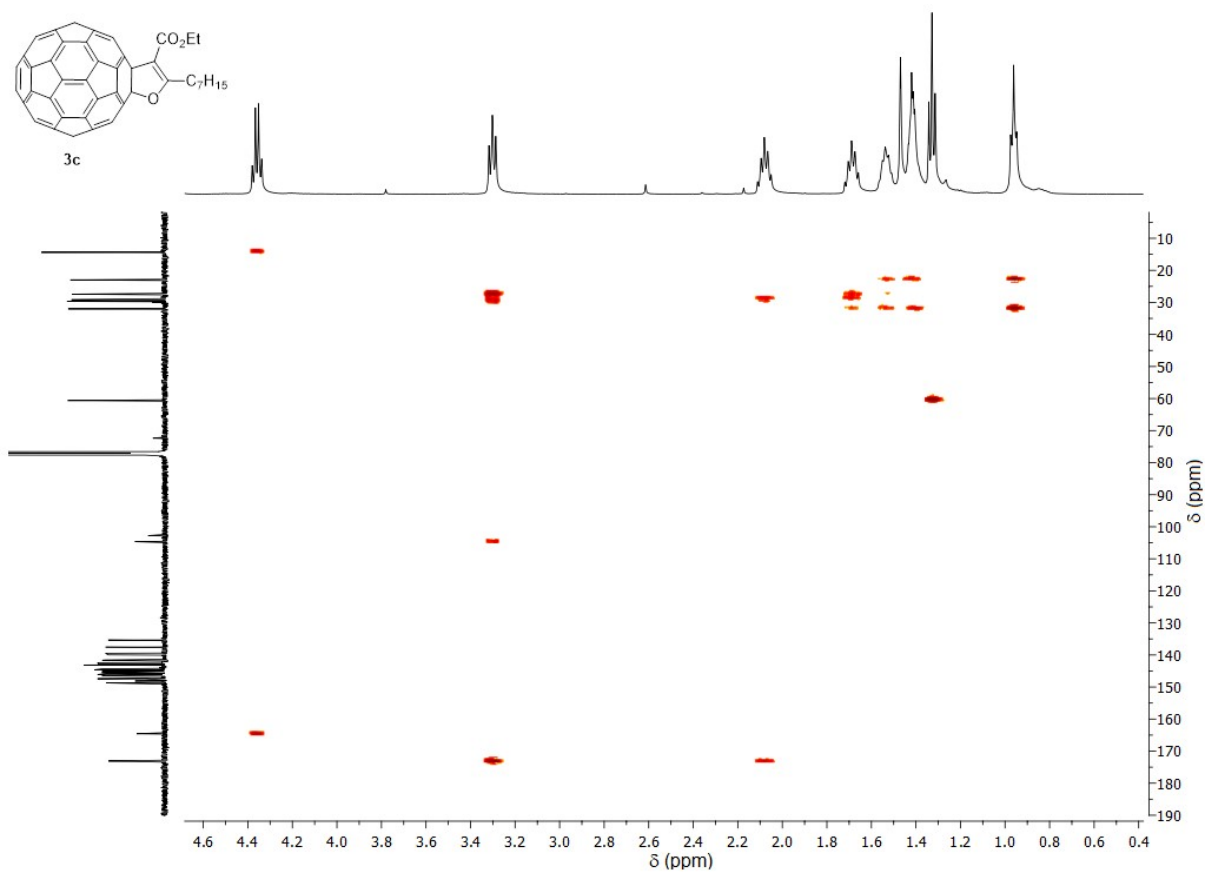
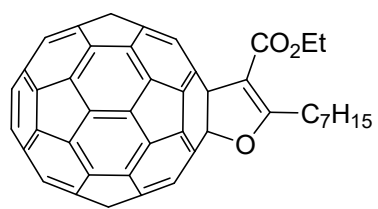
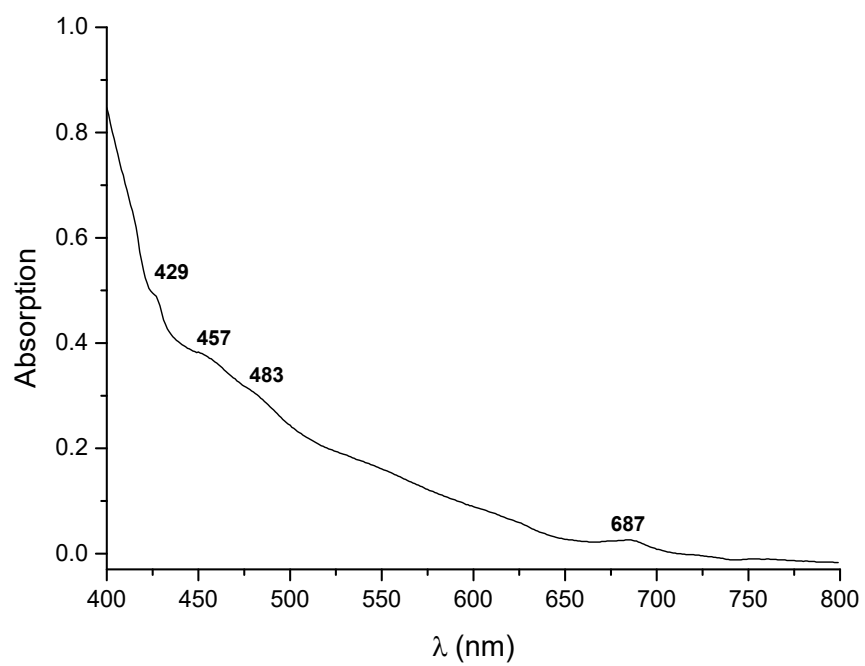


Figure SI 26. HMBC NMR spectrum of **3c** in CS<sub>2</sub>/CDCl<sub>3</sub>.



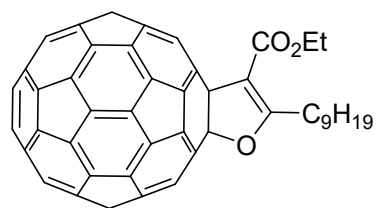
**3c**



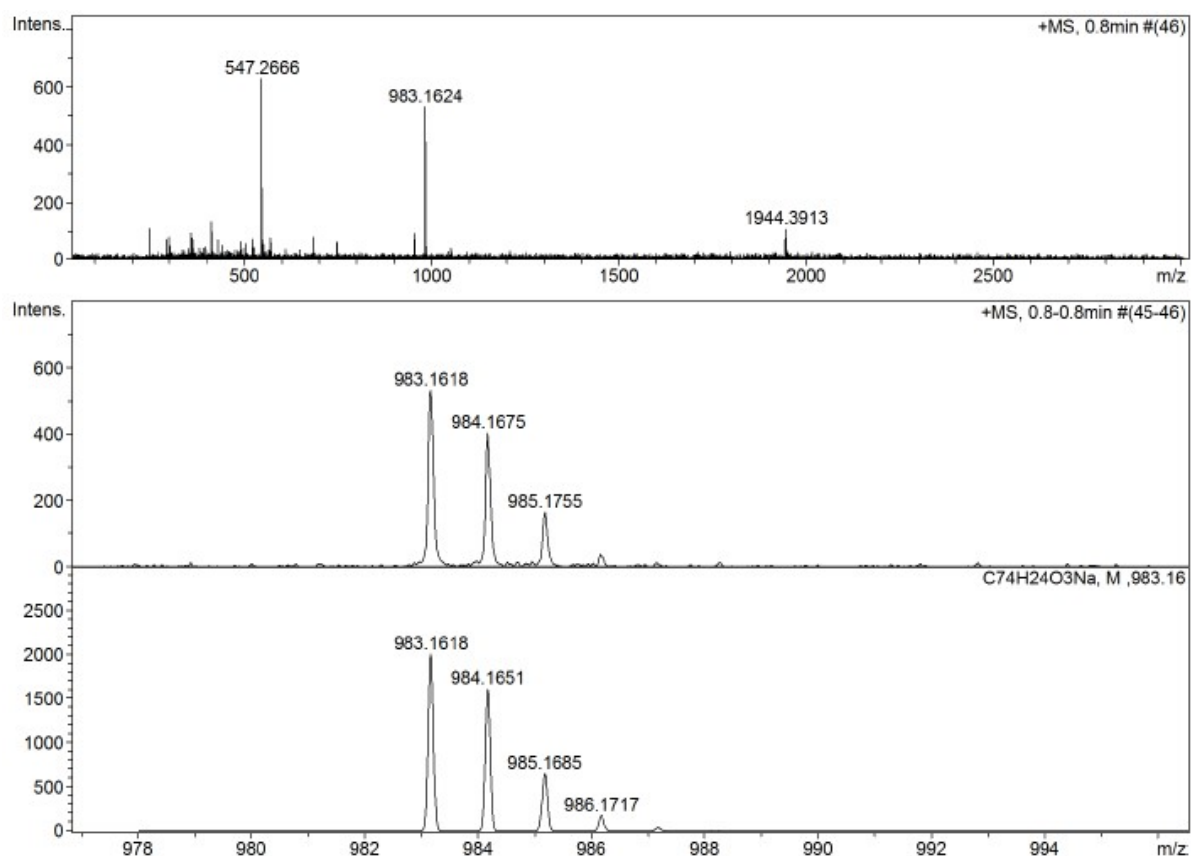
| $\lambda$<br>(nm) | $\epsilon$<br>( $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ) |
|-------------------|--|
| 429               | 3541   |
| 457               | 2782   |
| 483               | 2248   |
| 687               | 188  |

**Figure SI 27.** UV-Vis absorption spectrum of compound **3c** in  $\text{CHCl}_3$ .

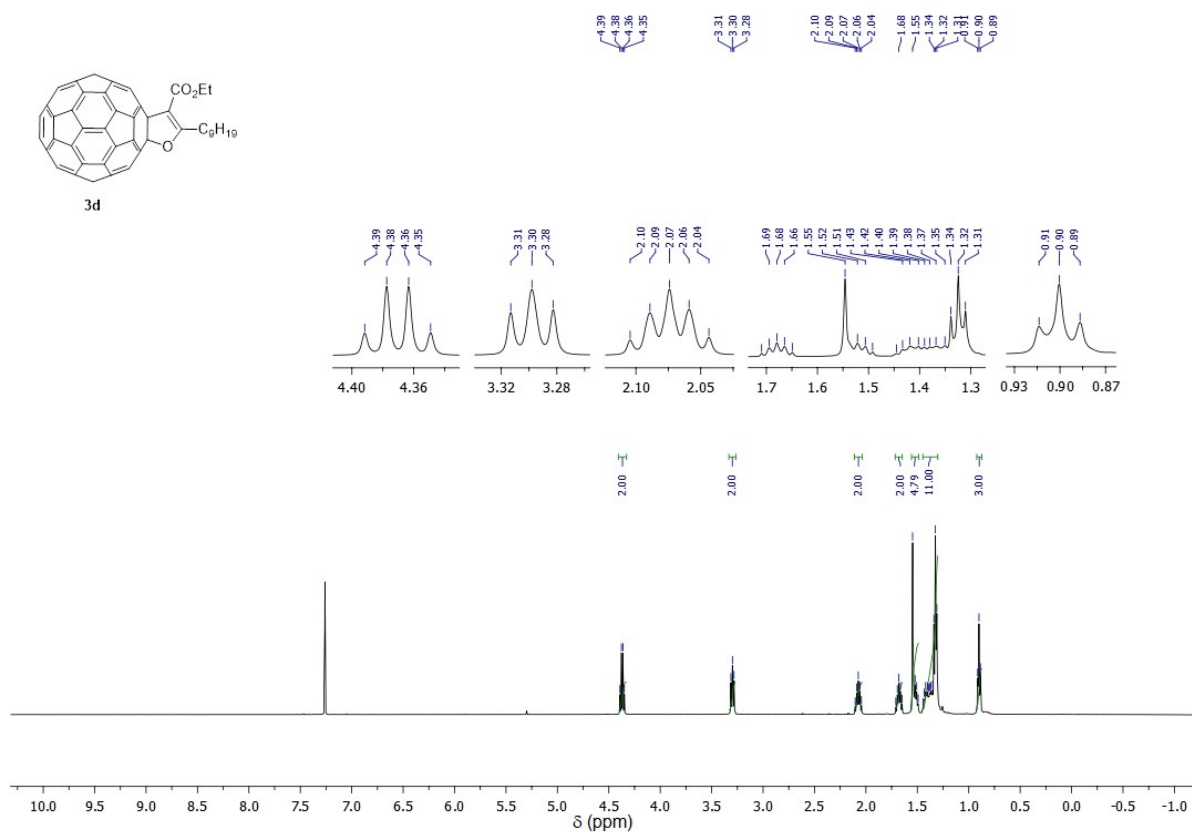
## Spectral data of 3d



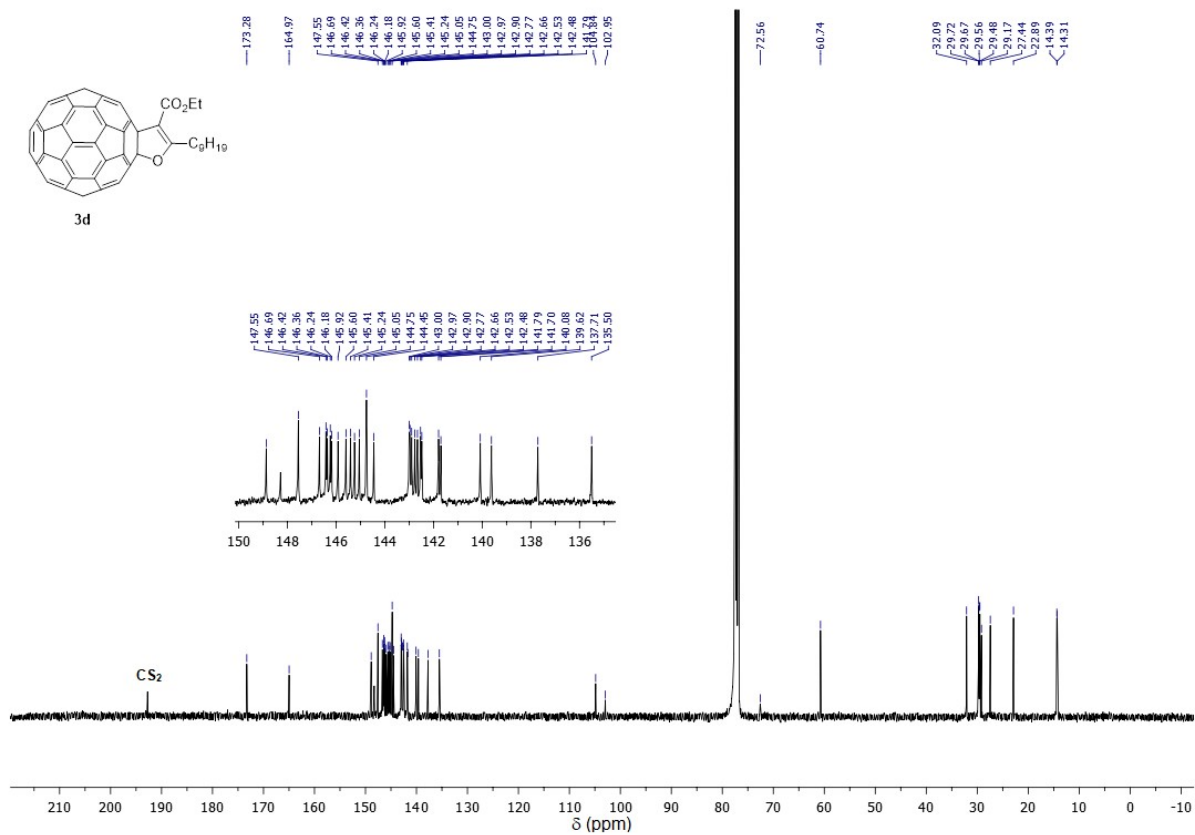
**3d**



**Figure SI 28.** Positive HRMS of compound 3d.



**Figure SI 29.**  $^1\text{H}$  NMR spectrum (500 MHz) of **3d** recorded in  $\text{CS}_2/\text{CDCl}_3$ .



**Figure SI 30.**  $^{13}\text{C}$  NMR spectrum (100 MHz) of **3d** recorded in  $\text{CS}_2/\text{CDCl}_3$ .

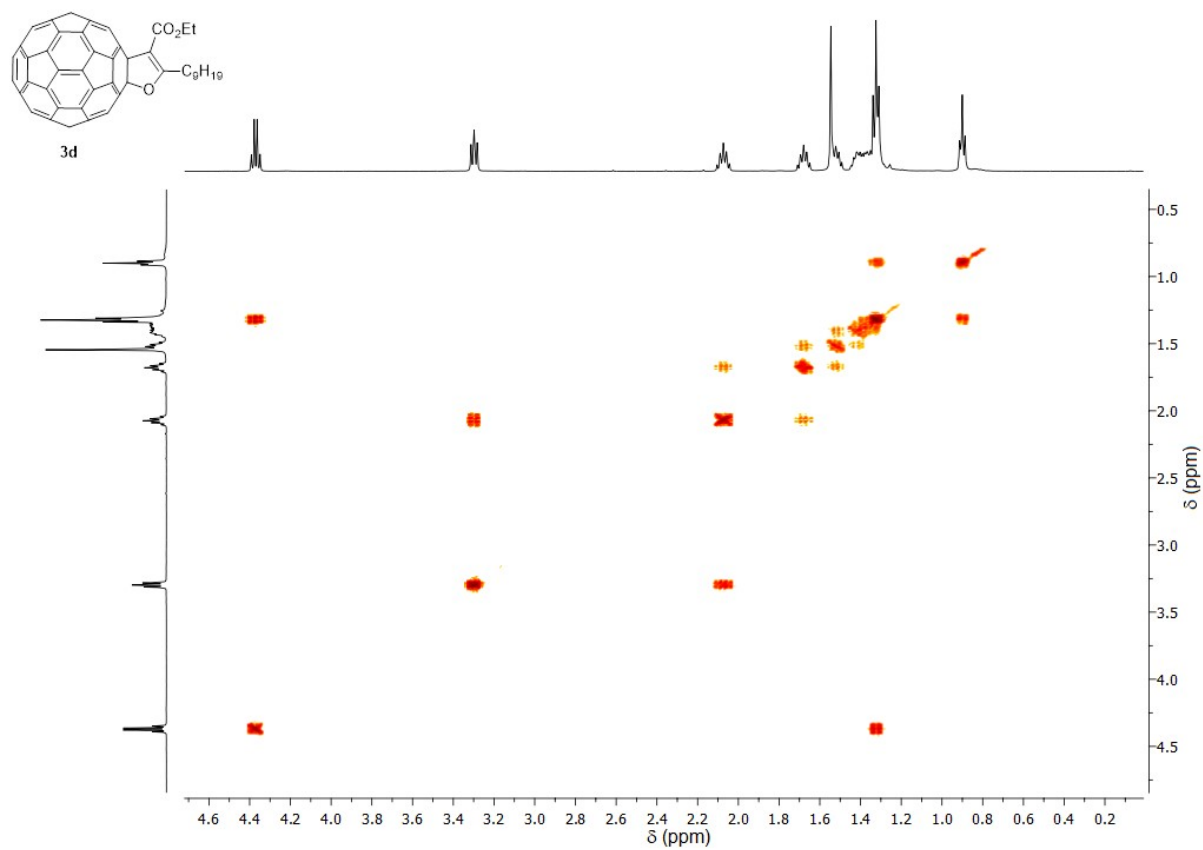


Figure SI 31. COSY NMR spectrum of **3d** in  $\text{CS}_2/\text{CDCl}_3$ .

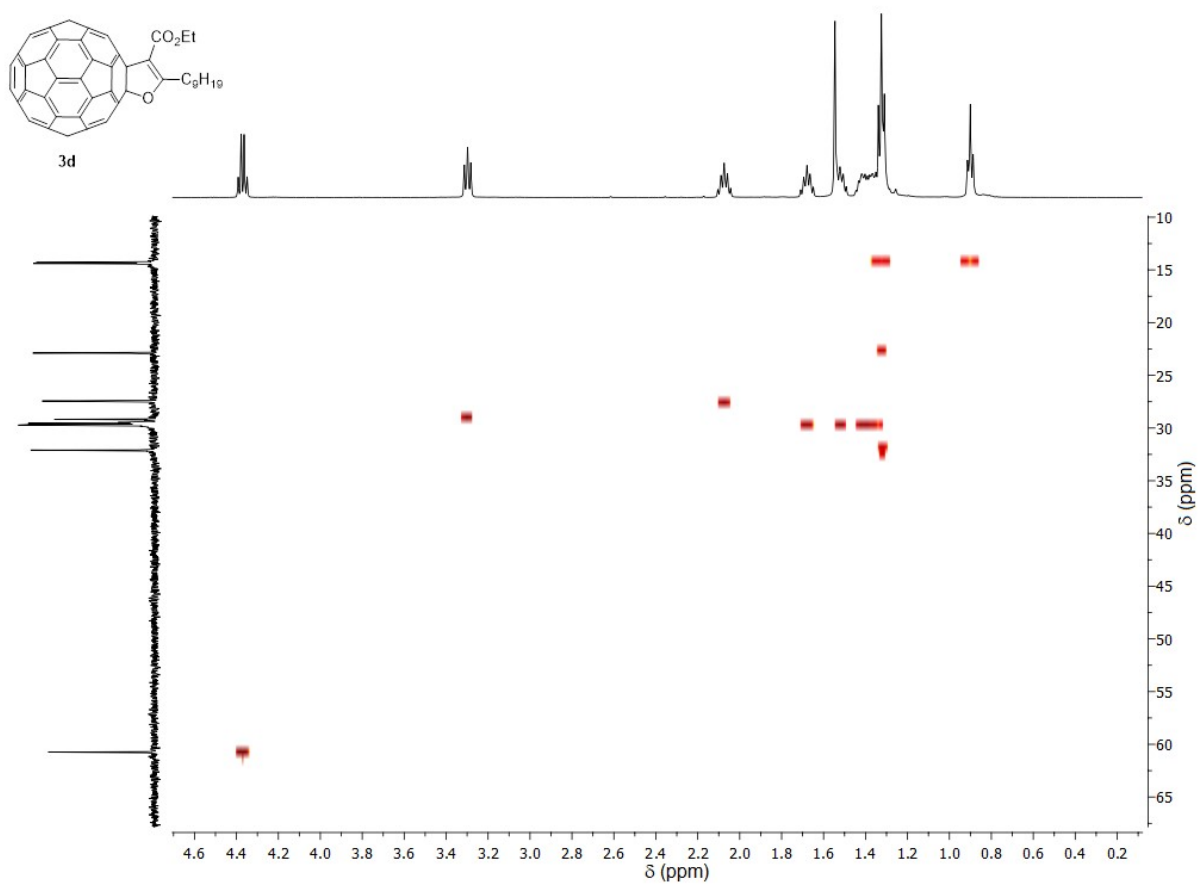
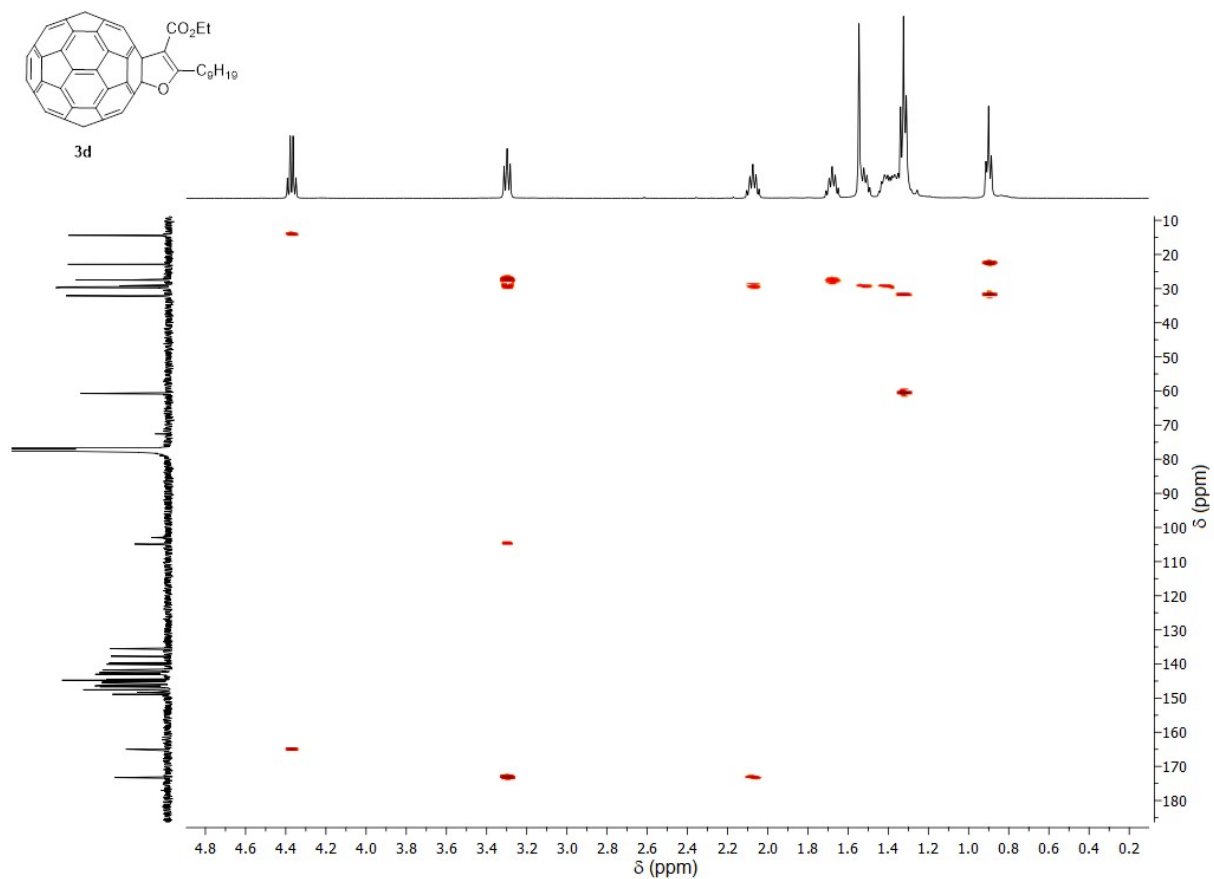
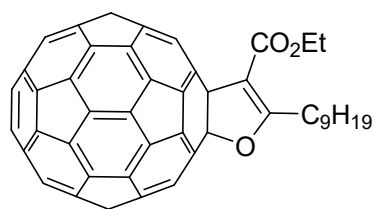
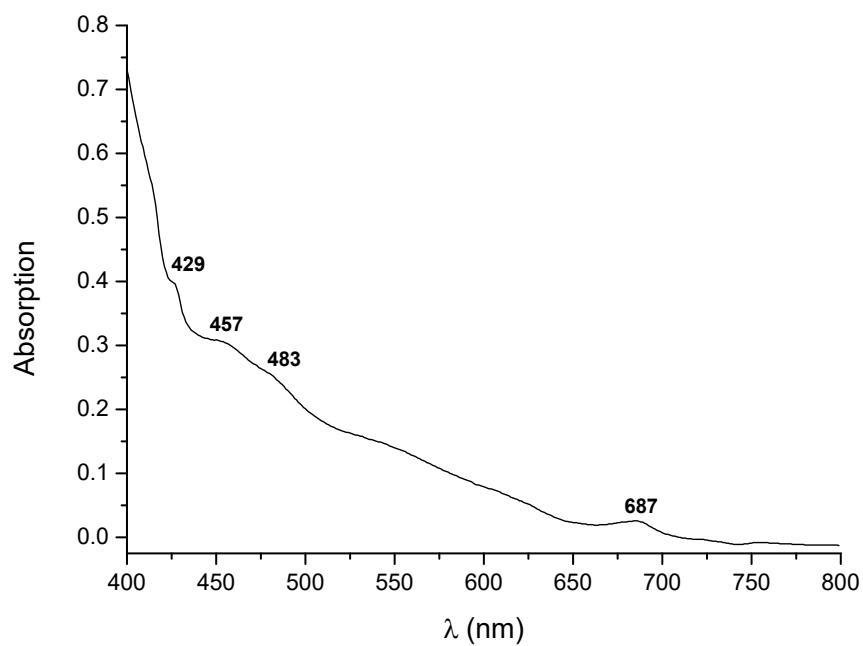


Figure SI 32. HSQC NMR spectrum of **3d** in  $\text{CS}_2/\text{CDCl}_3$ .





**3d**



| $\lambda$<br>(nm) | $\epsilon$<br>( $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) |
|-------------------|--|
| 429               | 3445   |
| 457               | 2745   |
| 483               | 2264   |
| 687               | 227  |

**Figure SI 34.** UV-Vis absorption spectrum of compound **3d** in  $\text{CHCl}_3$ .



# Spectral data of methanofullerenes

## Spectral data of 4a

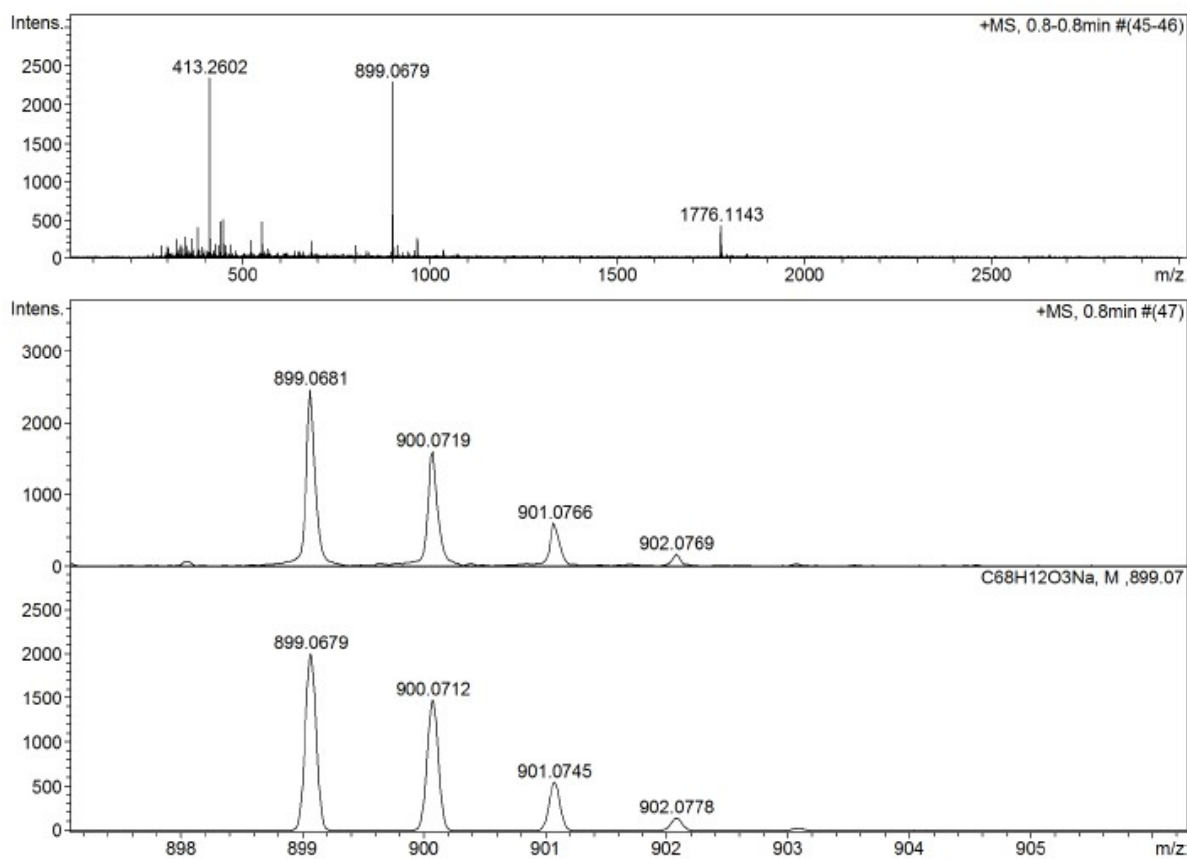
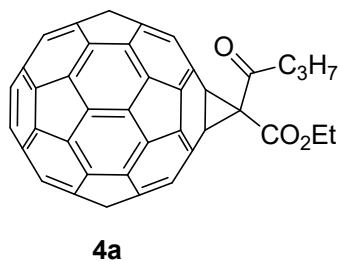
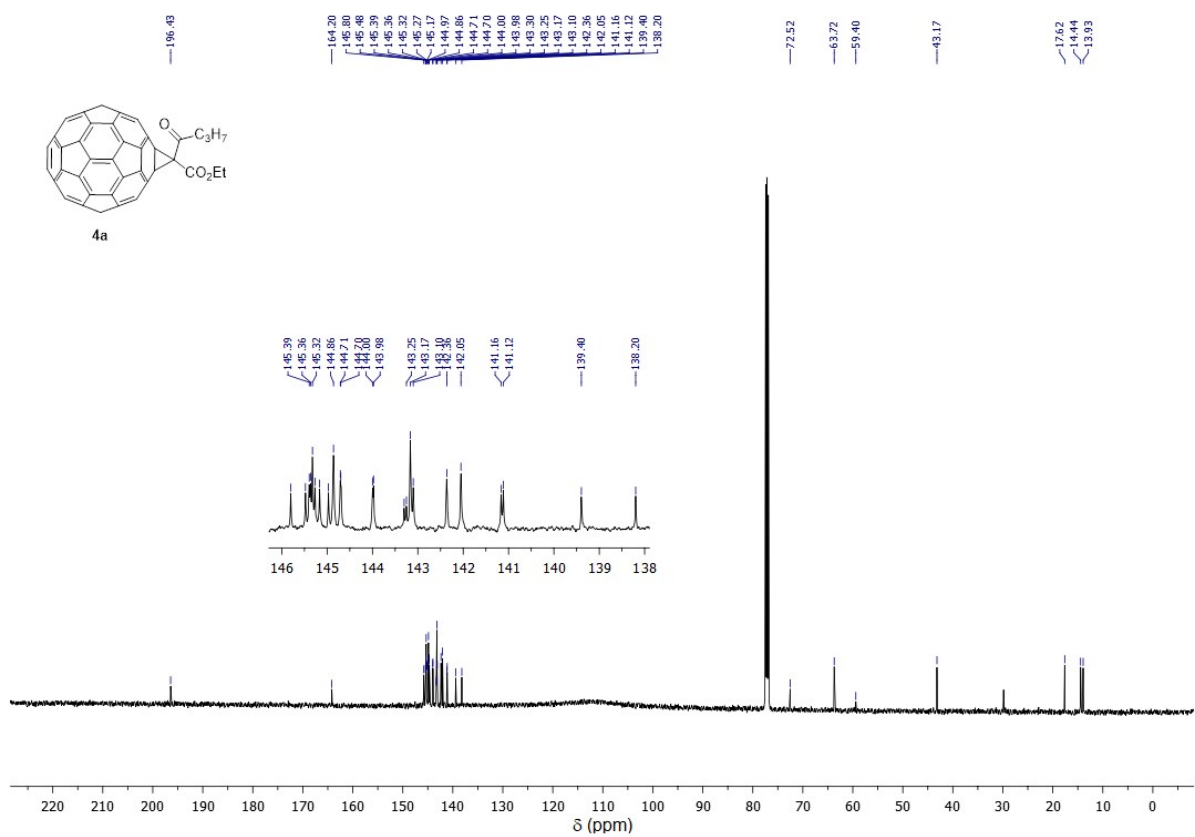
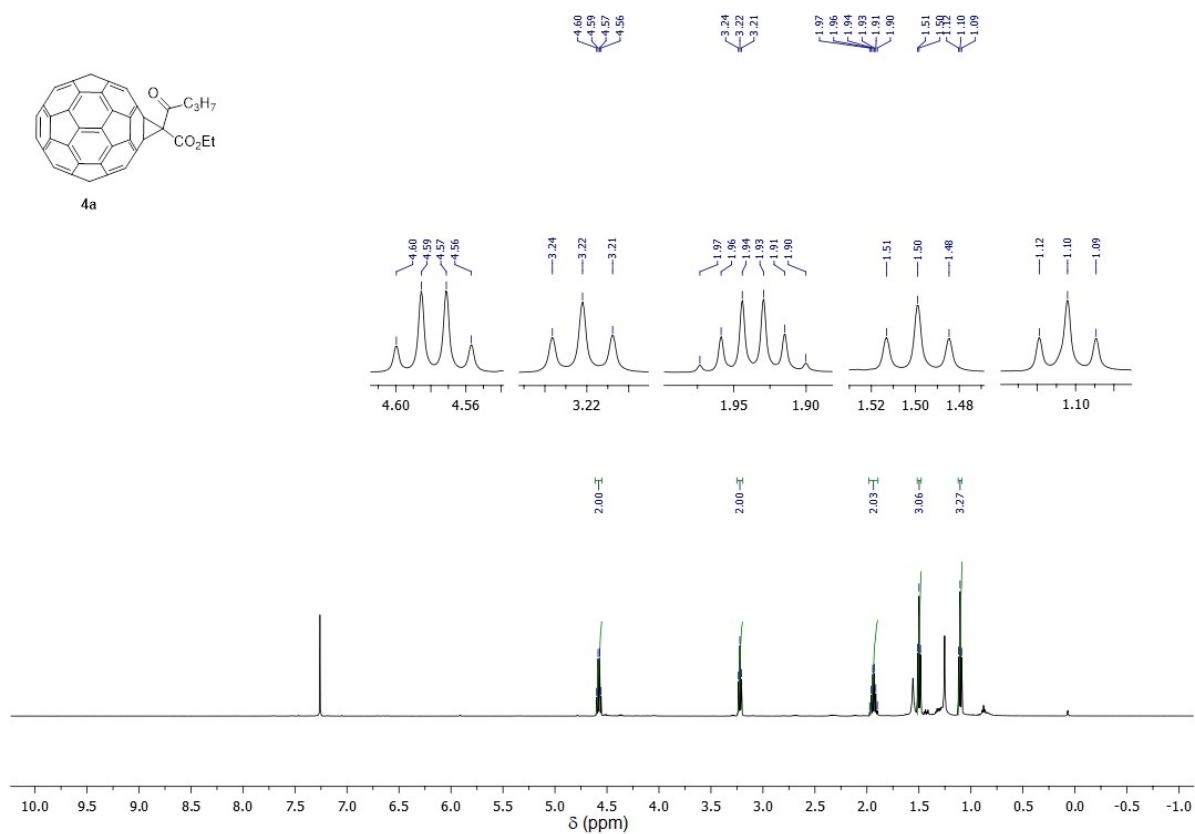
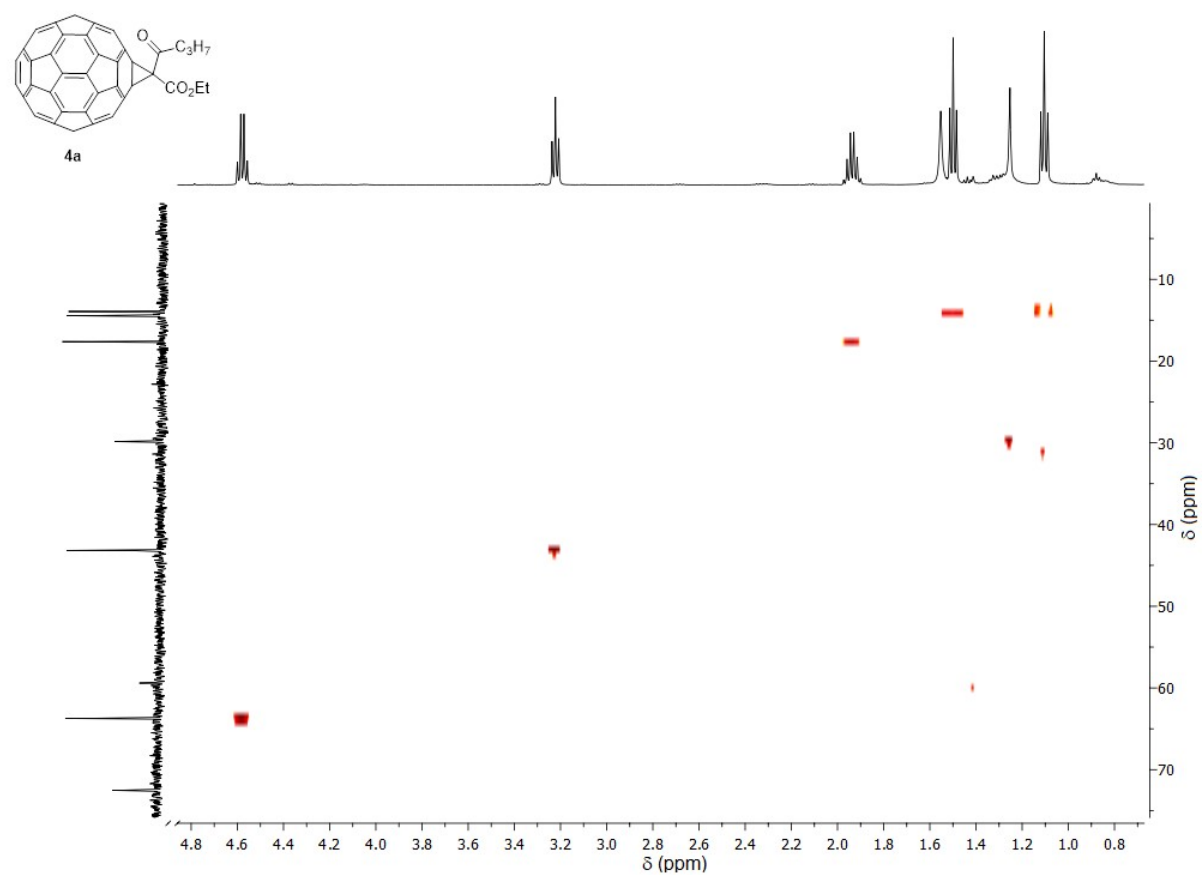
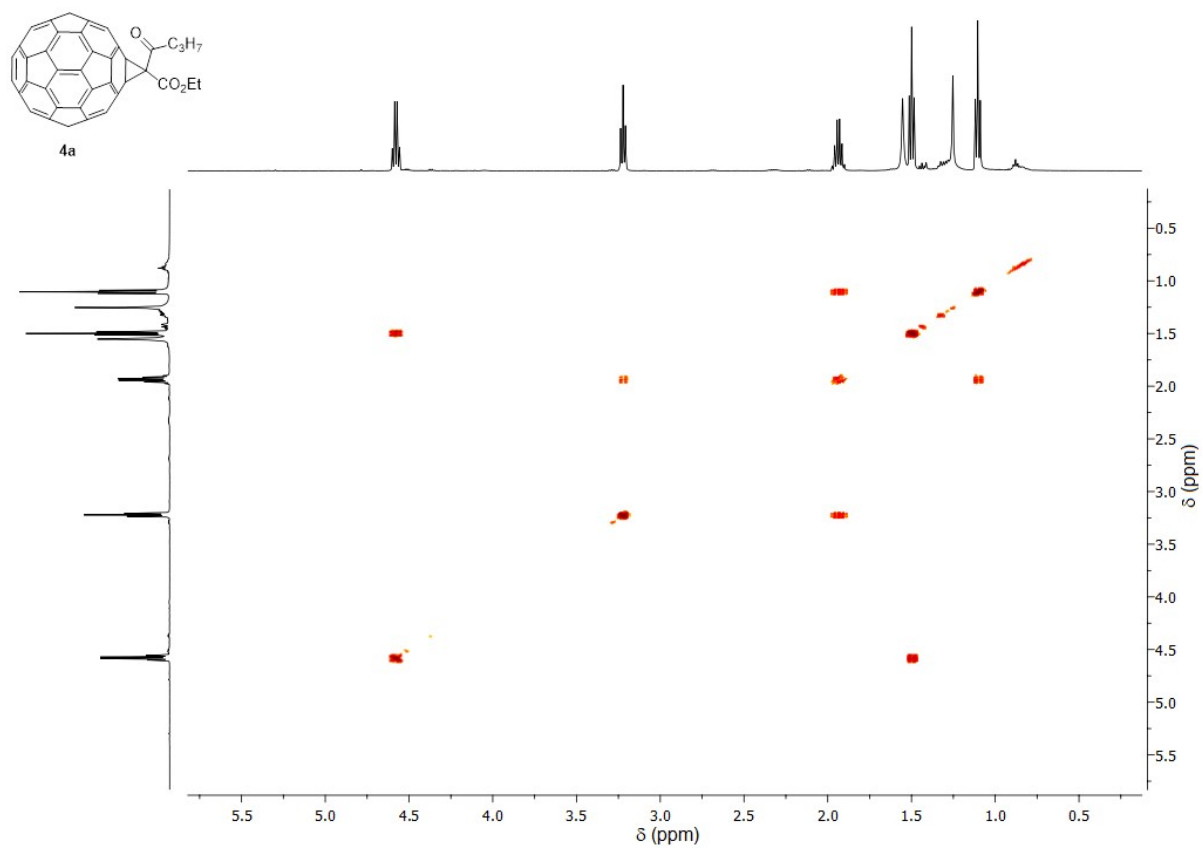


Figure SI 35. Positive HRMS of compound 4a.





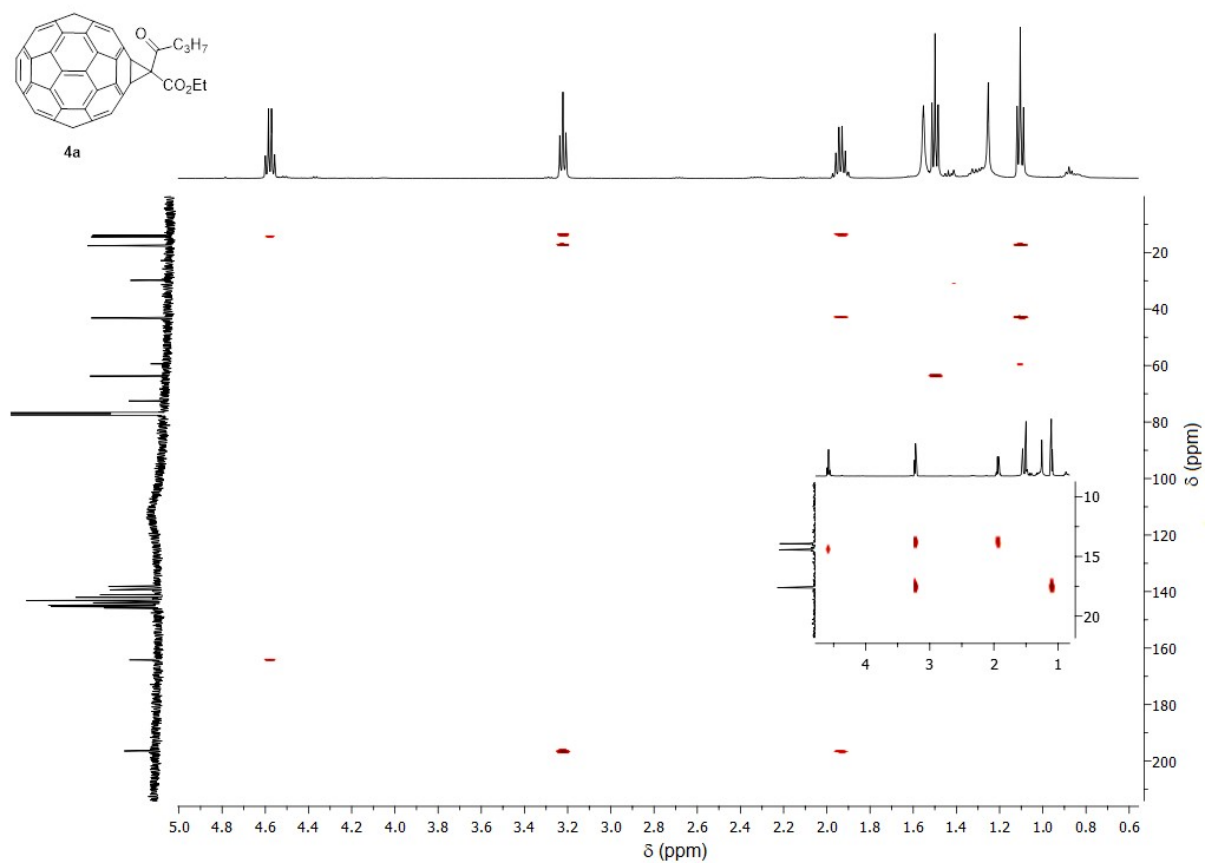
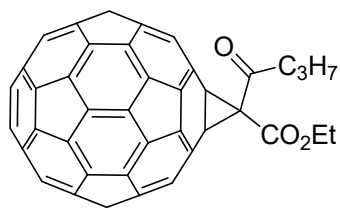
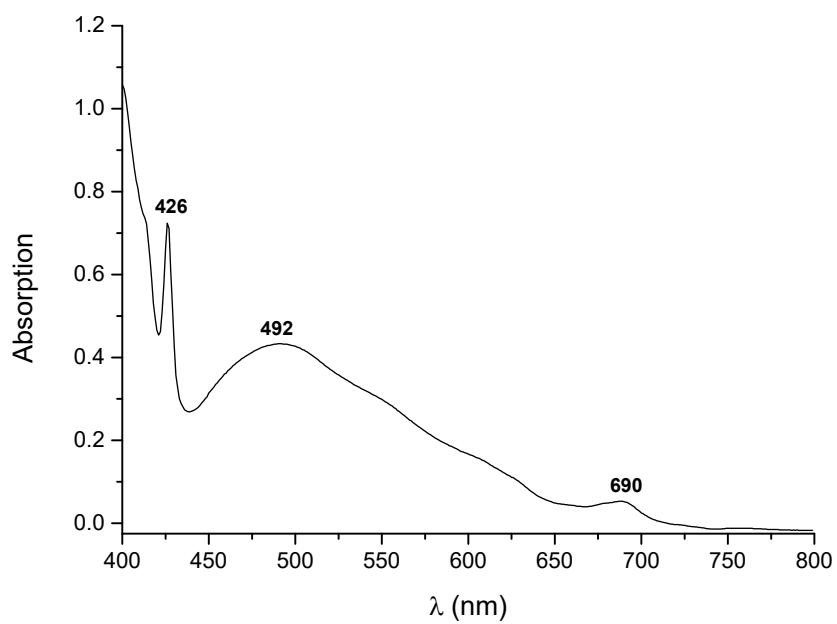


Figure SI 40. HMBC NMR spectrum of **4a** in  $\text{CDCl}_3$ .



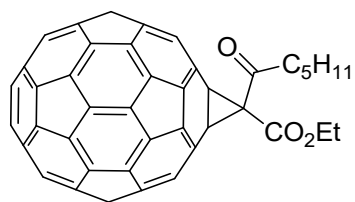
**4a**



| $\lambda$ (nm) | $\epsilon$ ( $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ) |
|----------------|---|
| 426            | 2117  |
| 492            | 1266  |
| 690            | 152   |

**Figure SI 41.** UV-Vis absorption spectrum of compound **4a** in  $\text{CHCl}_3$ .

## Spectral data of 4b



4b

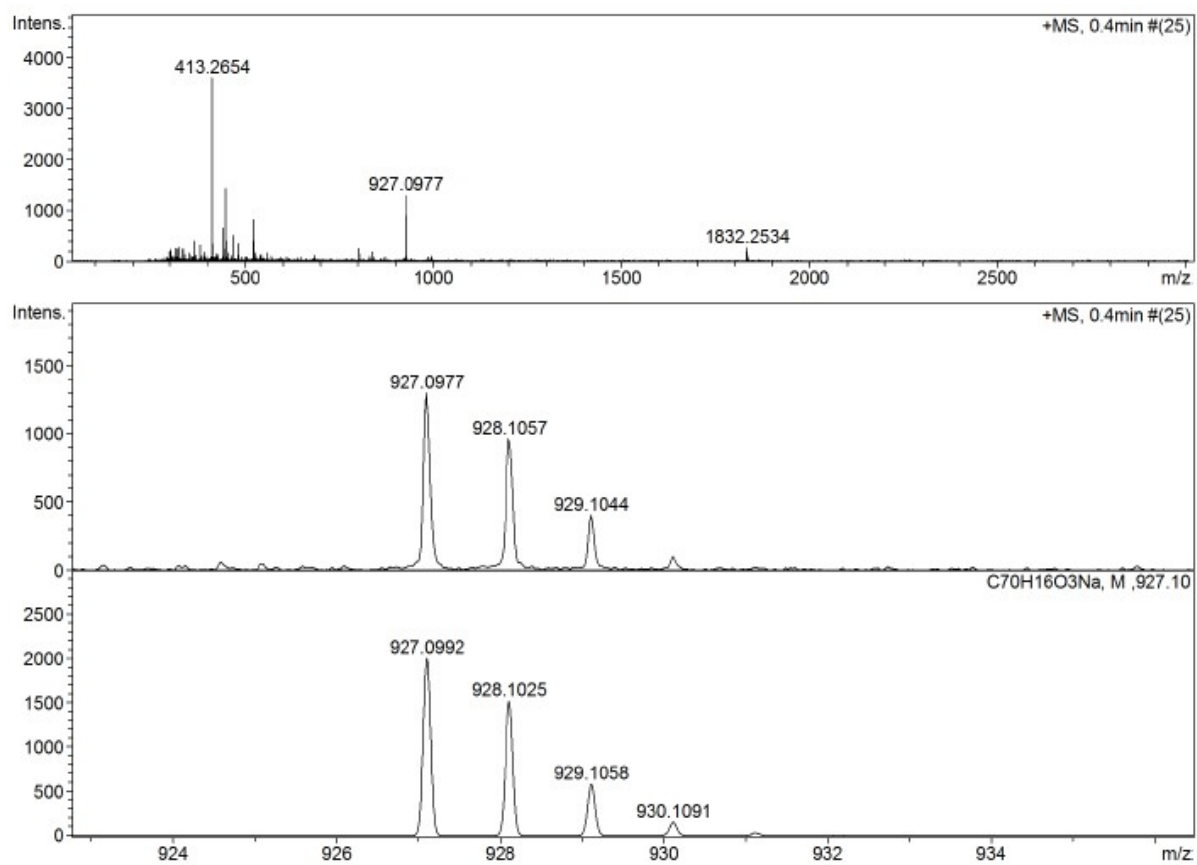
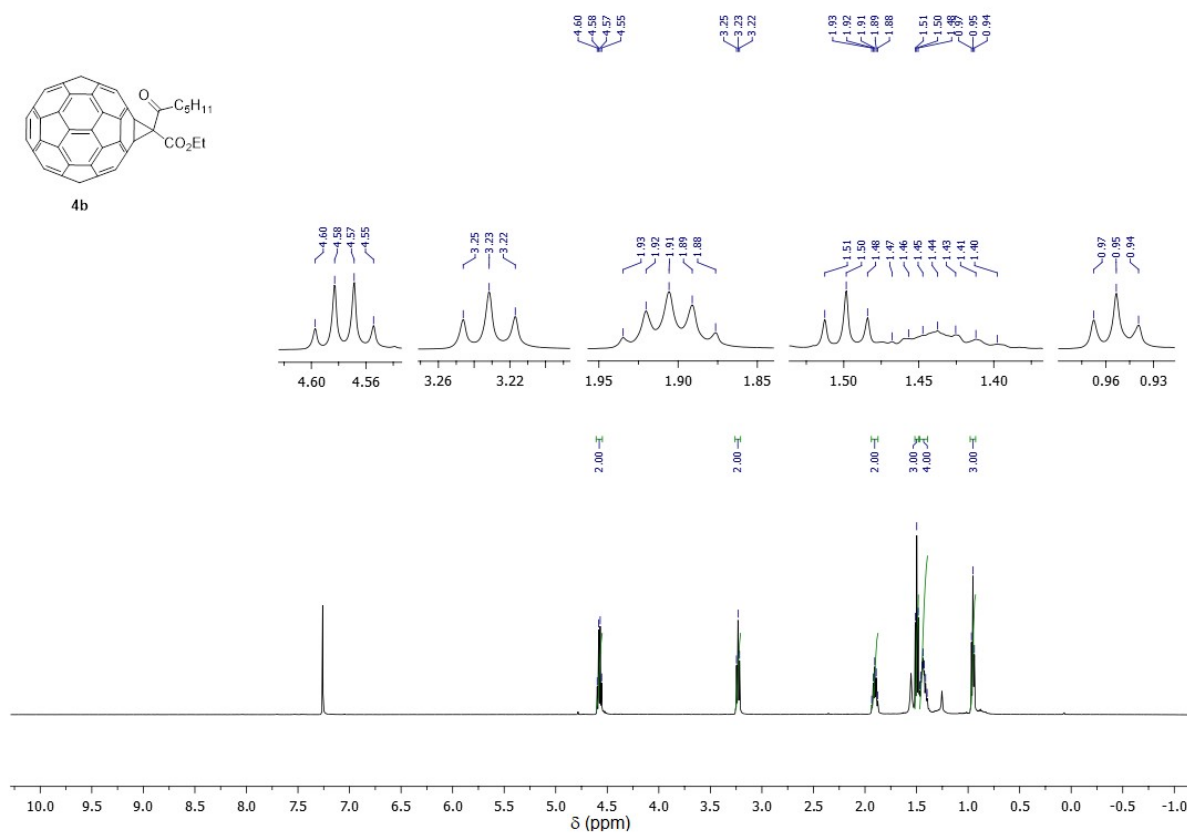
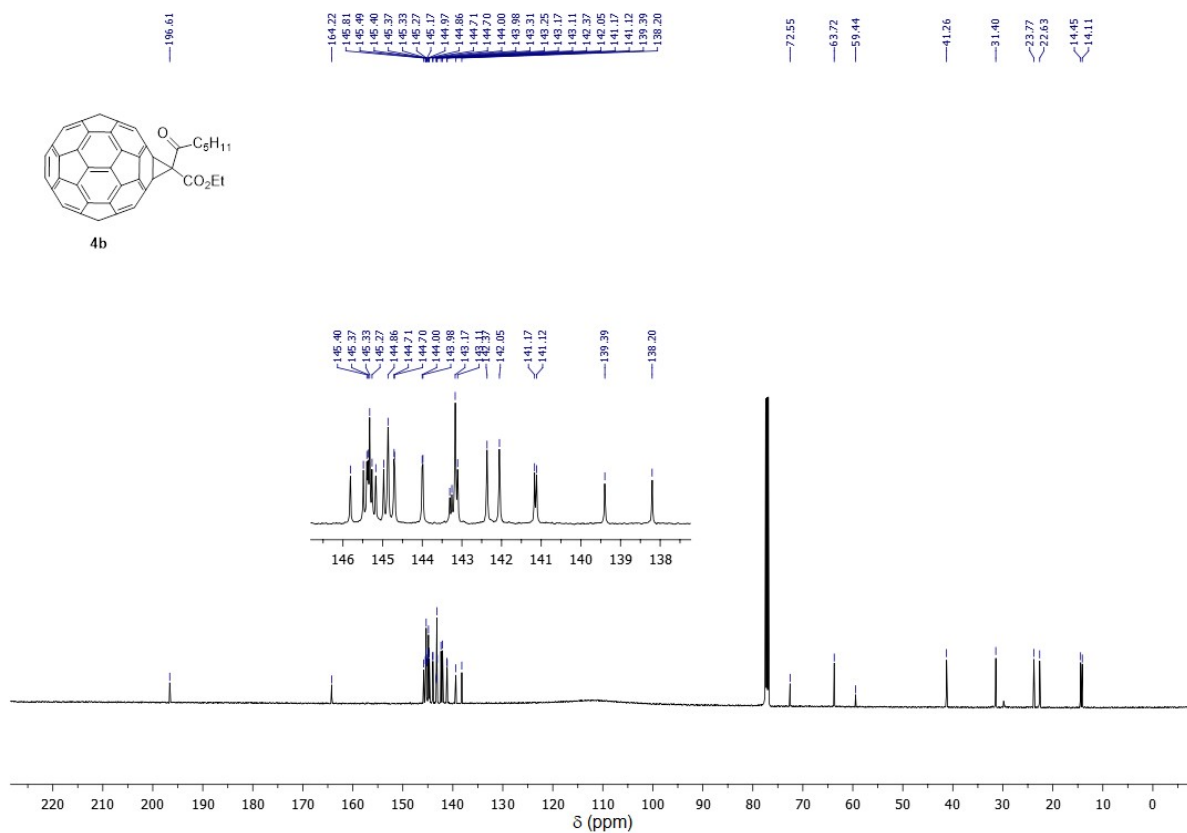


Figure SI 42. Positive HRMS of compound 4b.



**Figure SI 43.**  $^1\text{H}$  NMR spectrum (500 MHz) of **4b** recorded in  $\text{CDCl}_3$ .



**Figure SI 44.**  $^{13}\text{C}$  NMR spectrum (125 MHz) of **4b** recorded in  $\text{CDCl}_3$ .

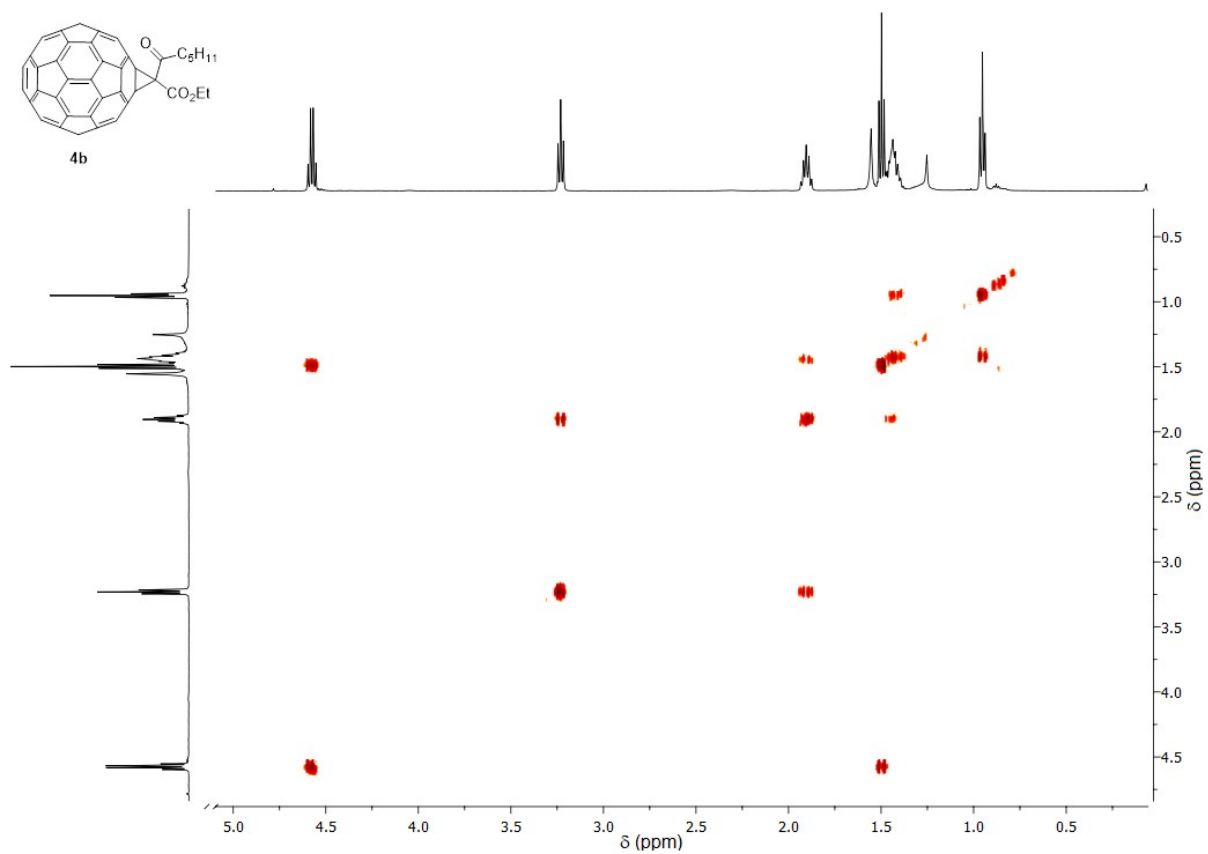


Figure SI 45. COSY NMR spectrum of **4b** in CDCl<sub>3</sub>.

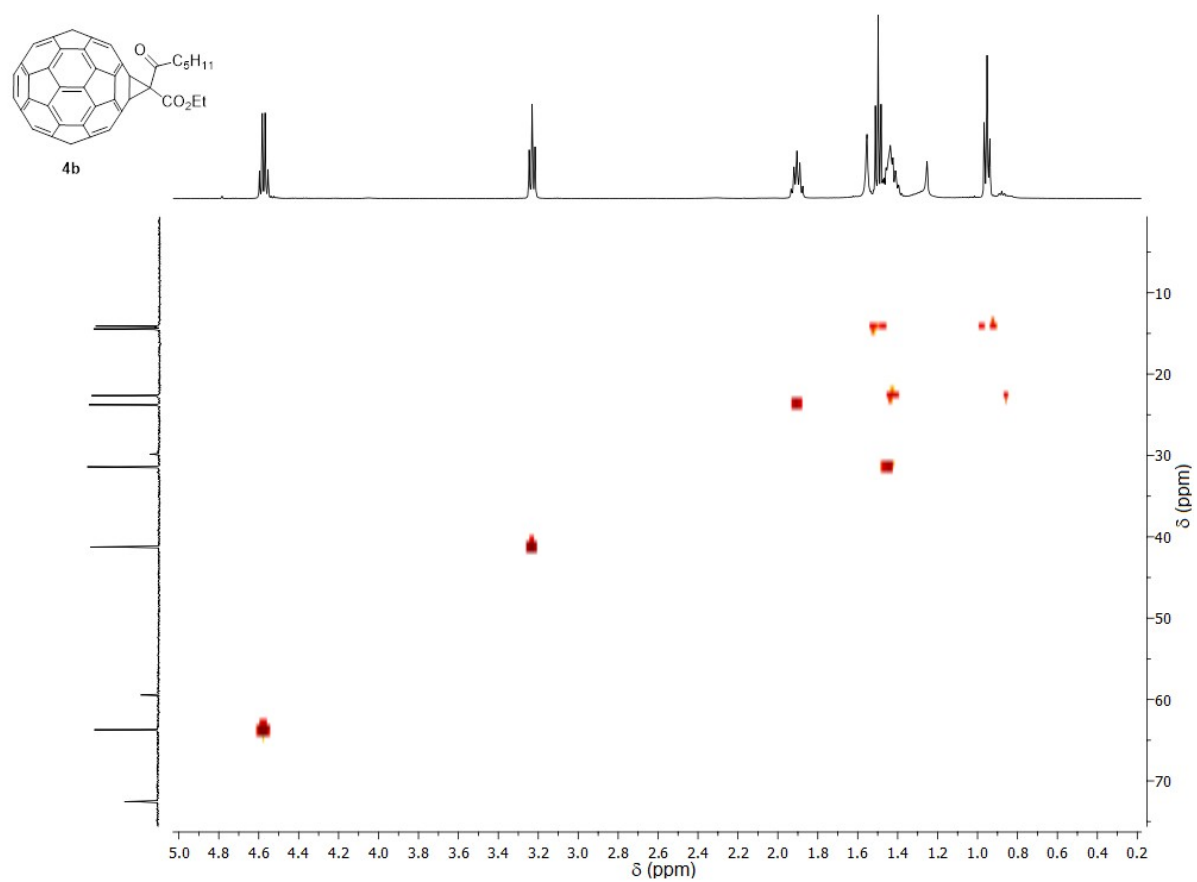


Figure SI 46. HSQC NMR spectrum of **4b** in CDCl<sub>3</sub>.



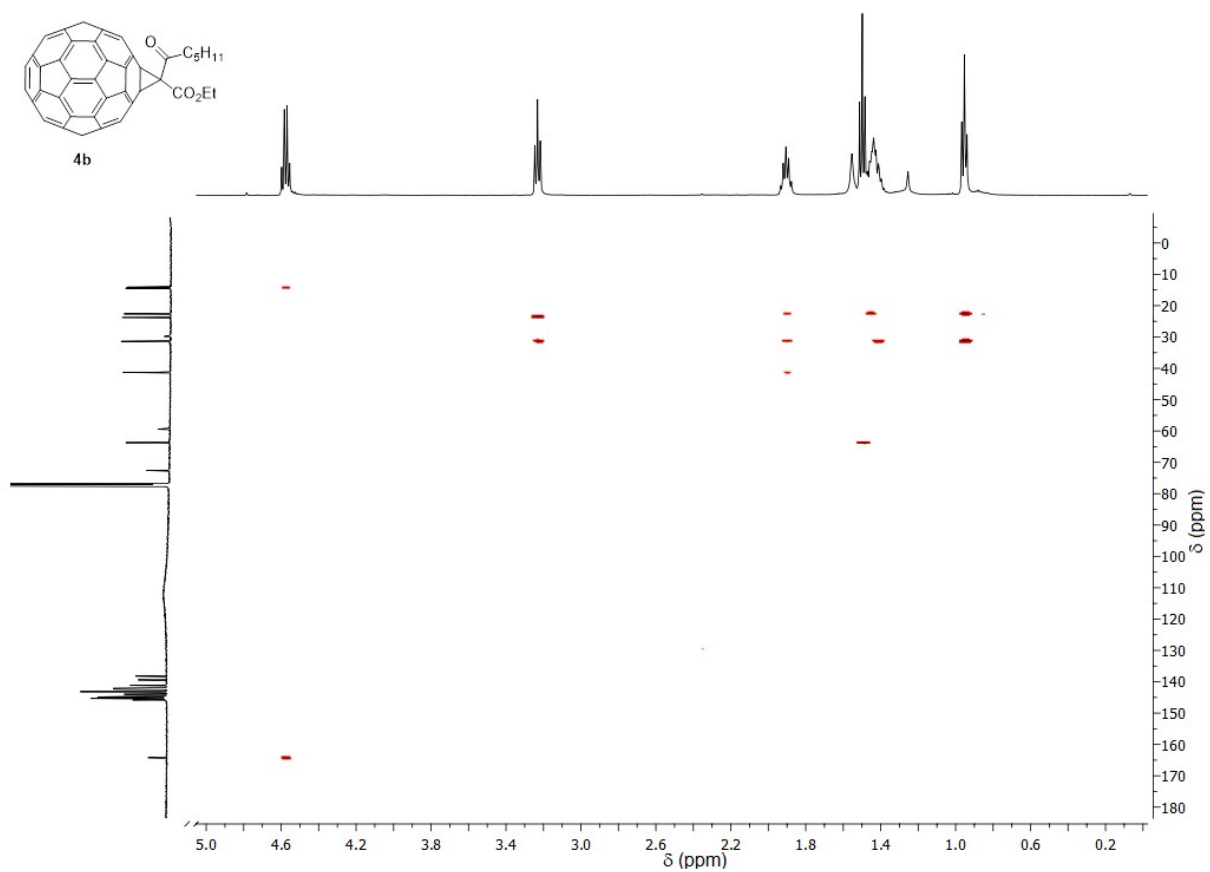
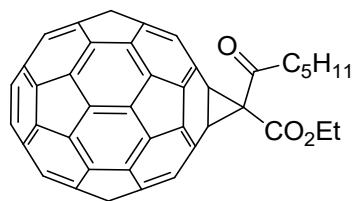
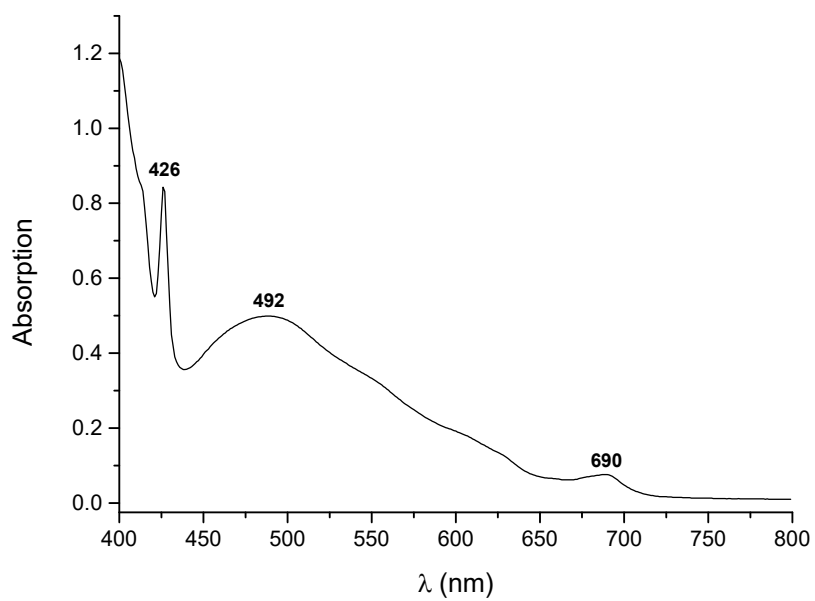


Figure SI 47. HMBC NMR spectrum of **4b** in CDCl<sub>3</sub>.



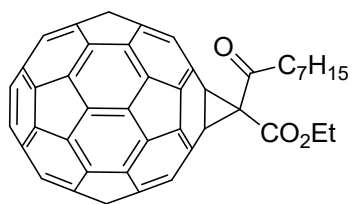
**4b**



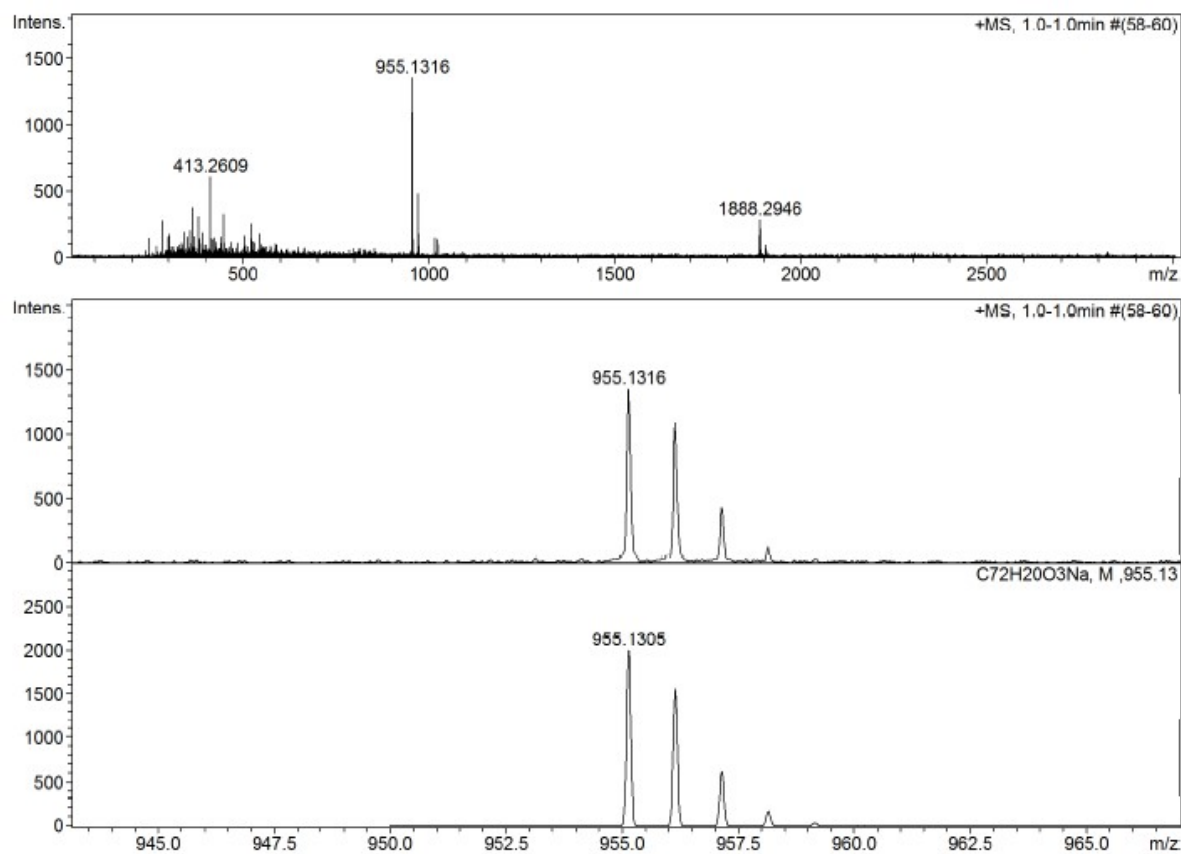
| $\lambda$<br>(nm) | $\epsilon$<br>( $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ) |
|-------------------|--|
| 426               | 2201   |
| 492               | 1300   |
| 690               | 198  |

**Figure SI 48.** UV-Vis absorption spectrum of compound **4b** in  $\text{CHCl}_3$ .

## Spectral data of 4c



**4c**



**Figure SI 49.** Positive HRMS of compound **4c**.

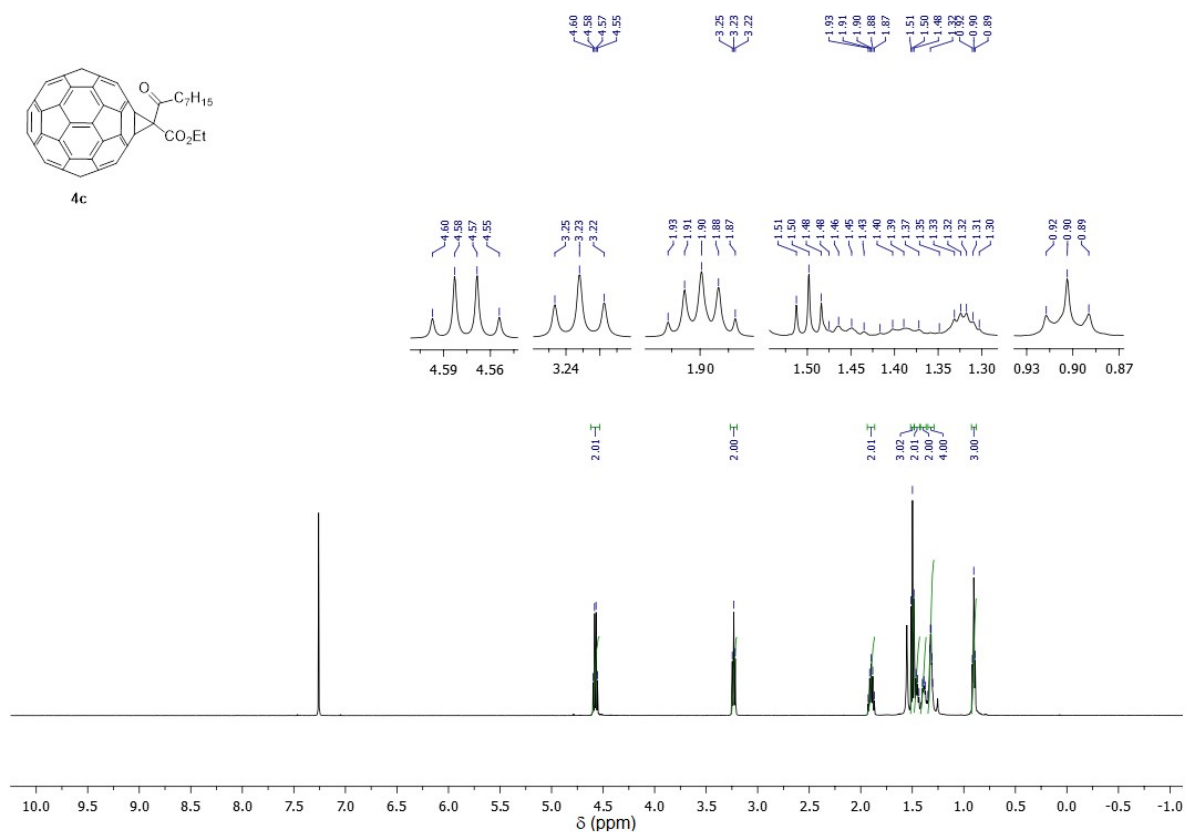


Figure SI 50.  $^1\text{H}$  NMR spectrum (500 MHz) of **4c** recorded in  $\text{CDCl}_3$ .

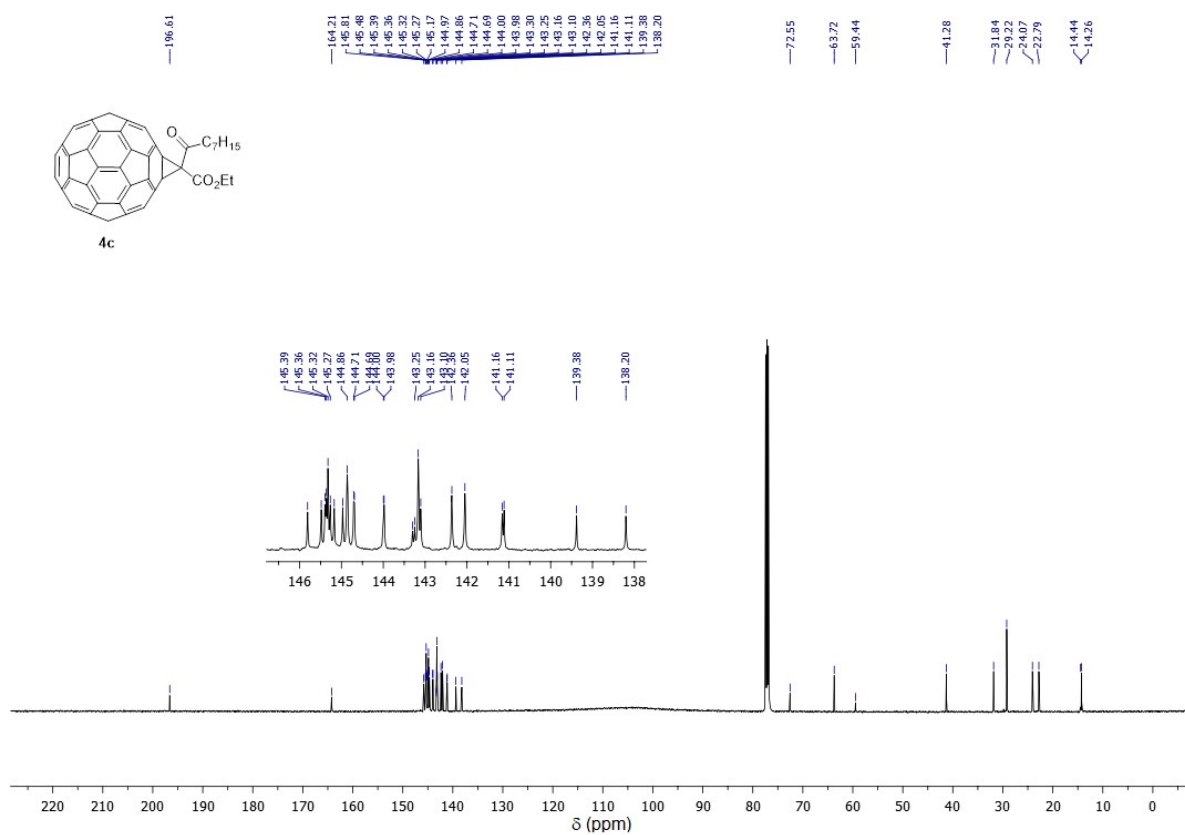
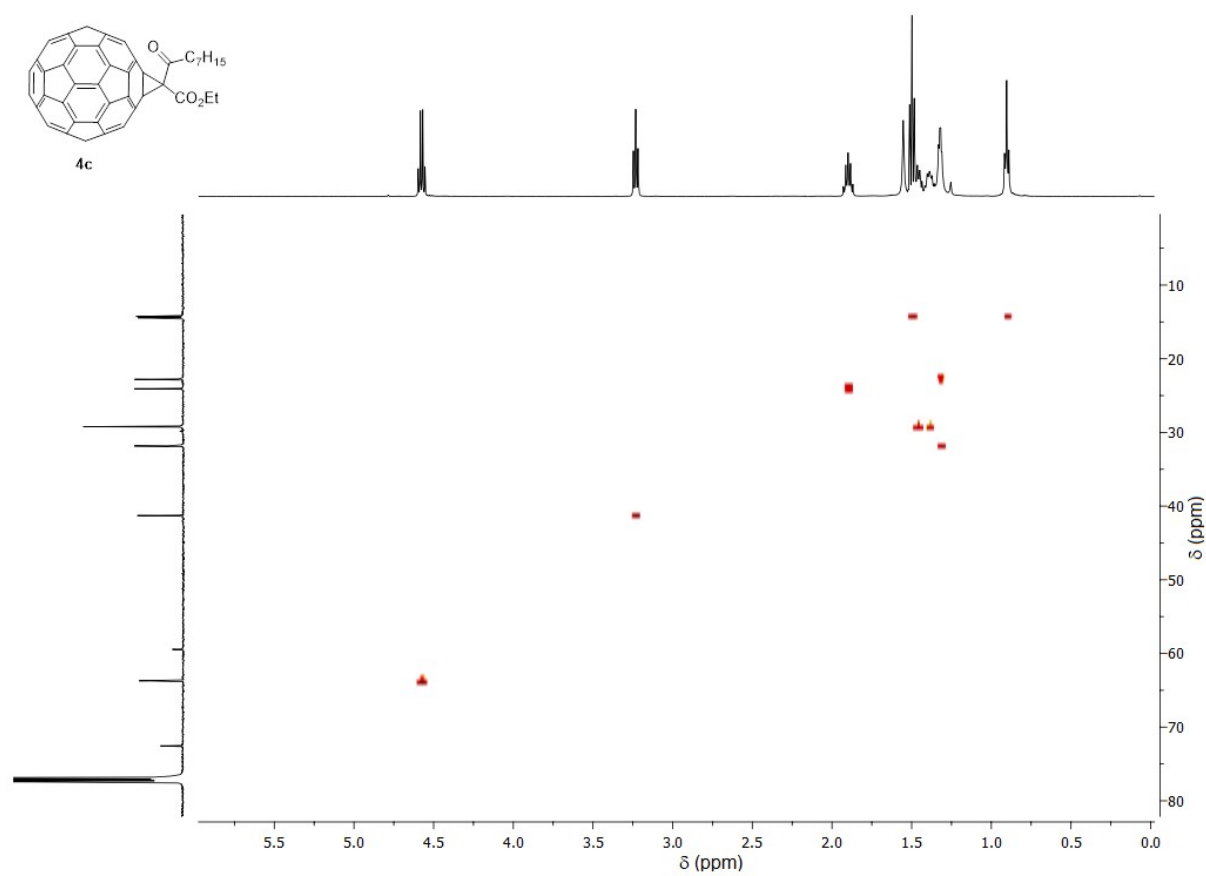
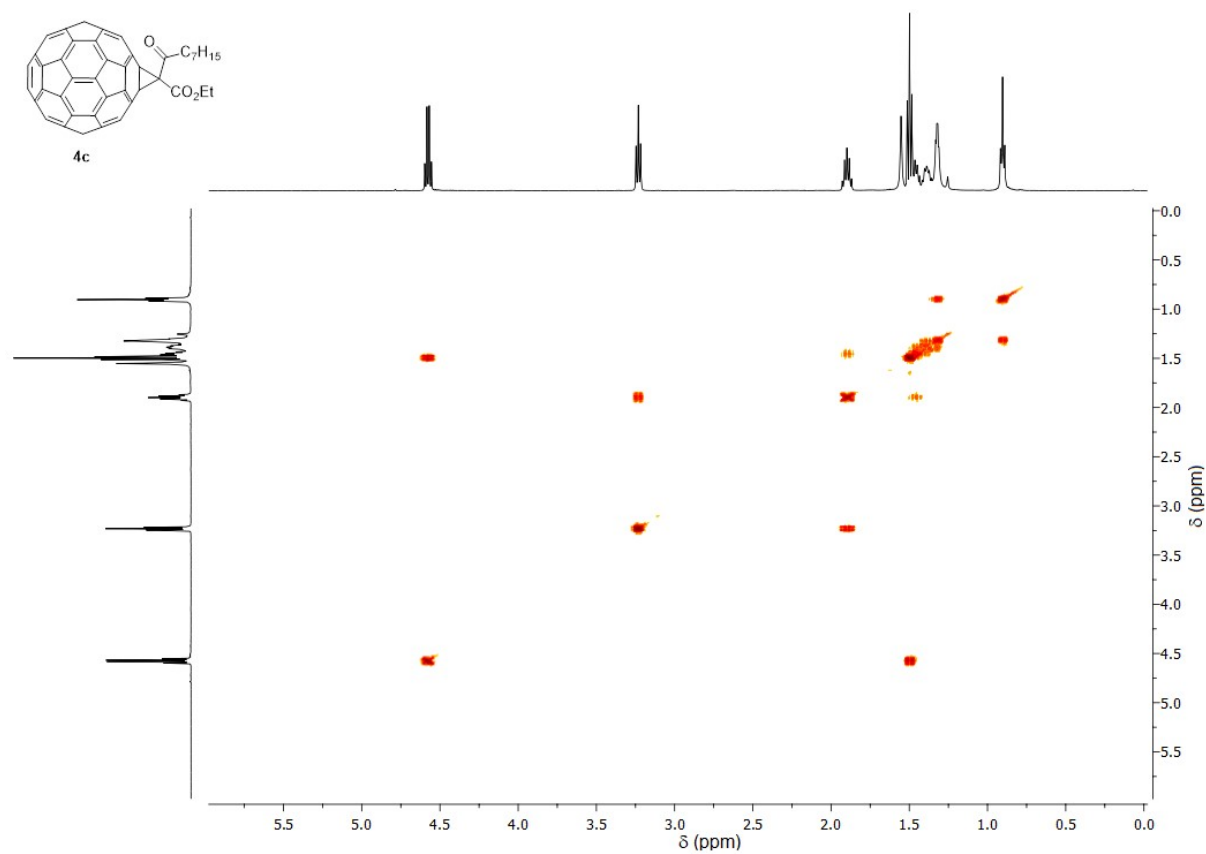
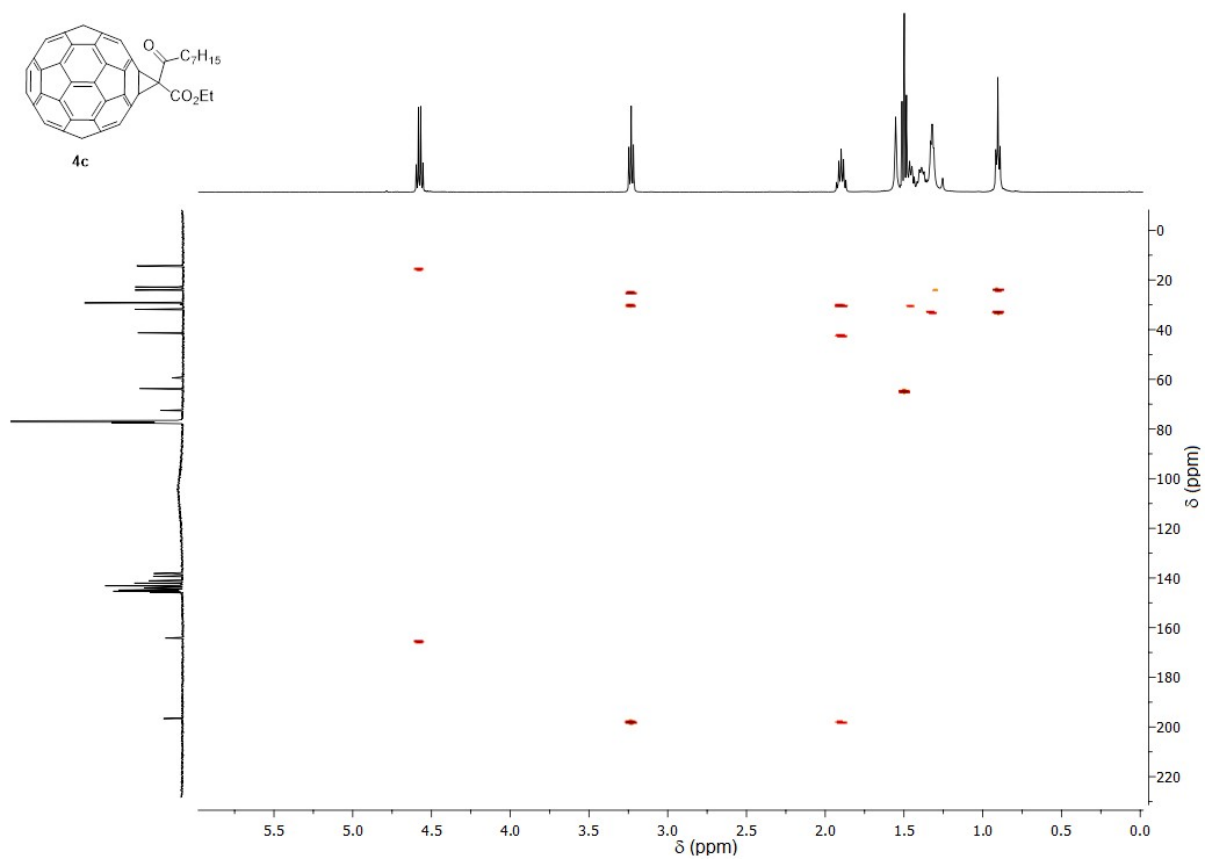
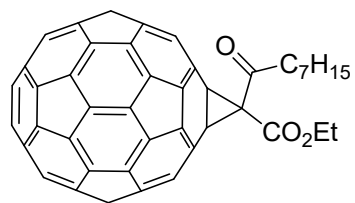


Figure SI 51.  $^{13}\text{C}$  NMR spectrum (125 MHz) of **4c** recorded in  $\text{CDCl}_3$ .

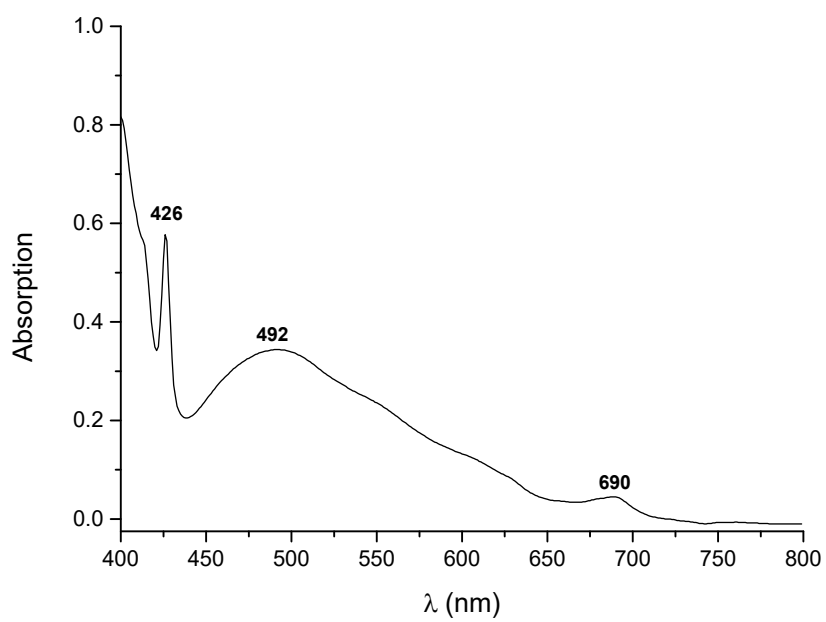




**Figure SI 54.** HMBC NMR spectrum of **4c** in CDCl<sub>3</sub>.



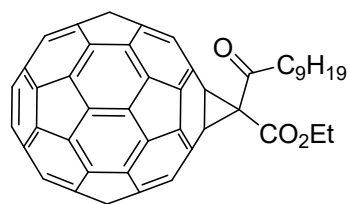
**4c**



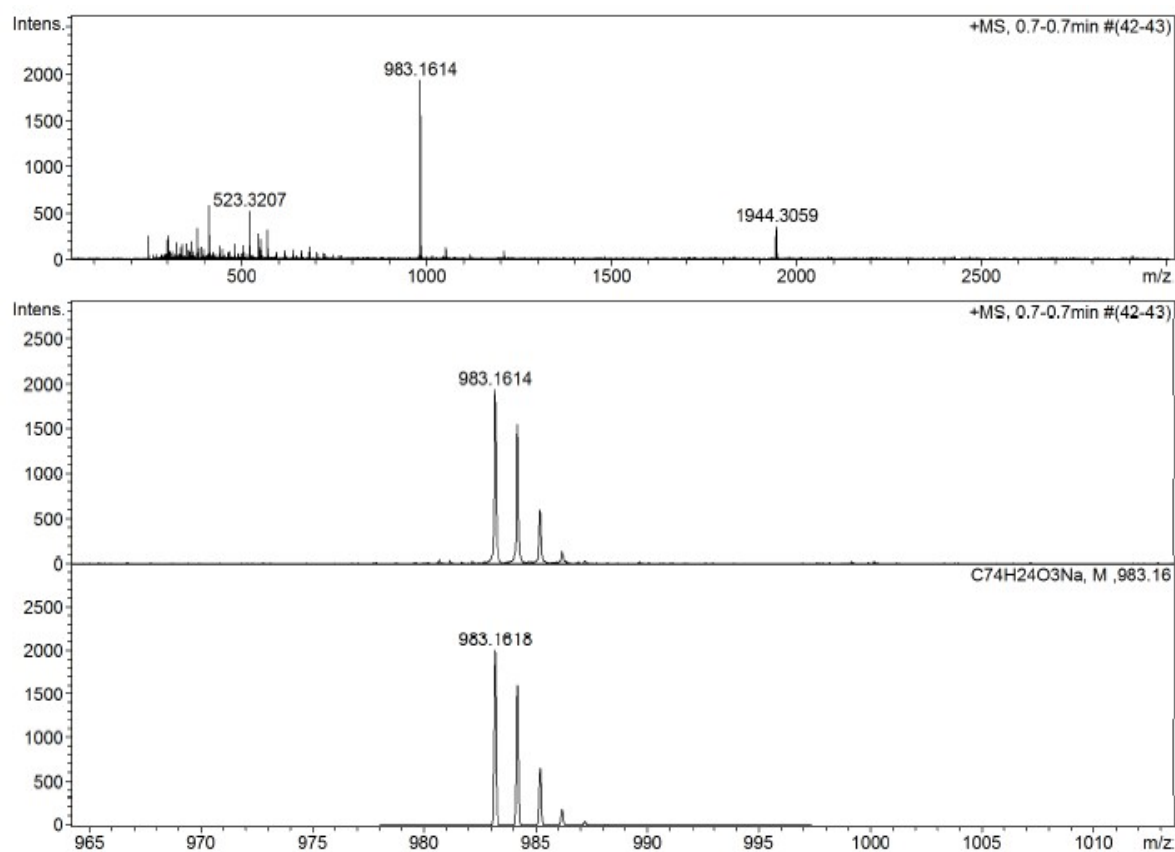
| $\lambda$<br>(nm) | $\epsilon$<br>( $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) |
|-------------------|--|
| 426               | 2186   |
| 492               | 1303   |
| 690               | 170  |

**Figure SI 55.** UV-Vis absorption spectrum of compound **4c** in  $\text{CHCl}_3$ .

## Spectral data of 4d

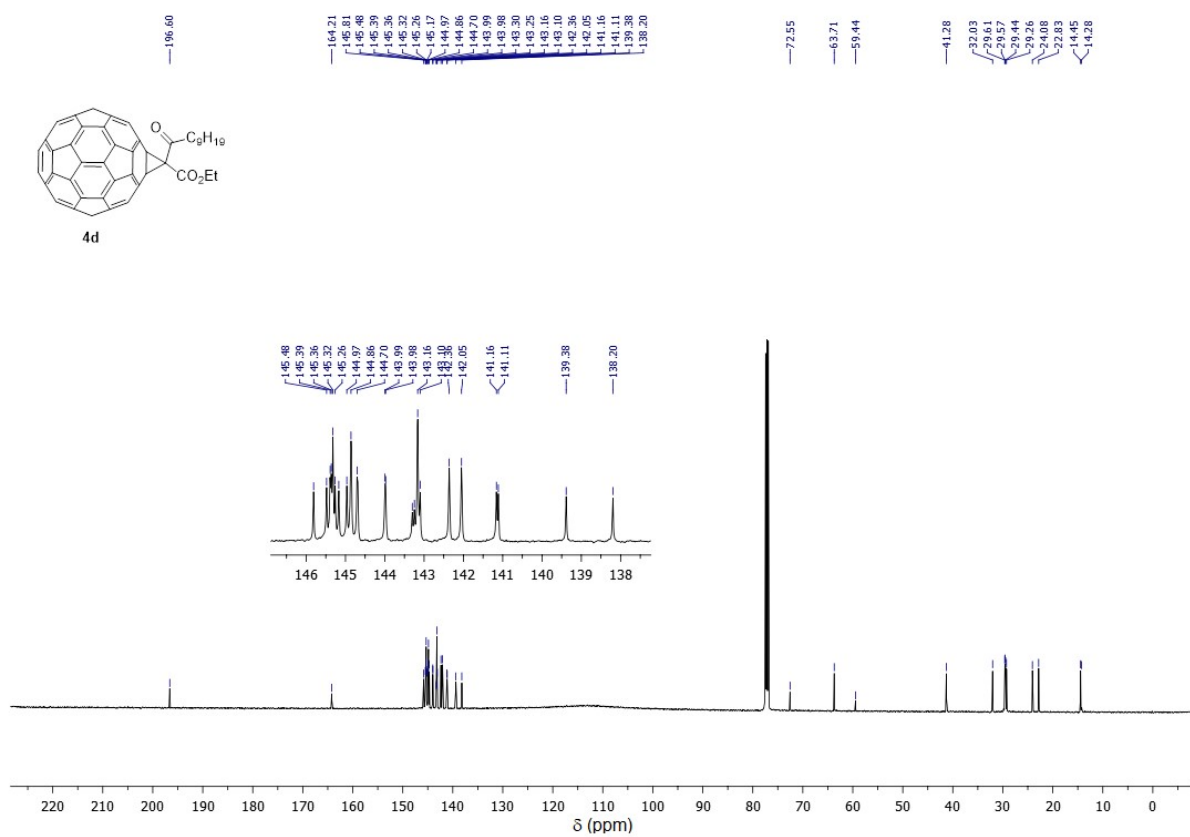
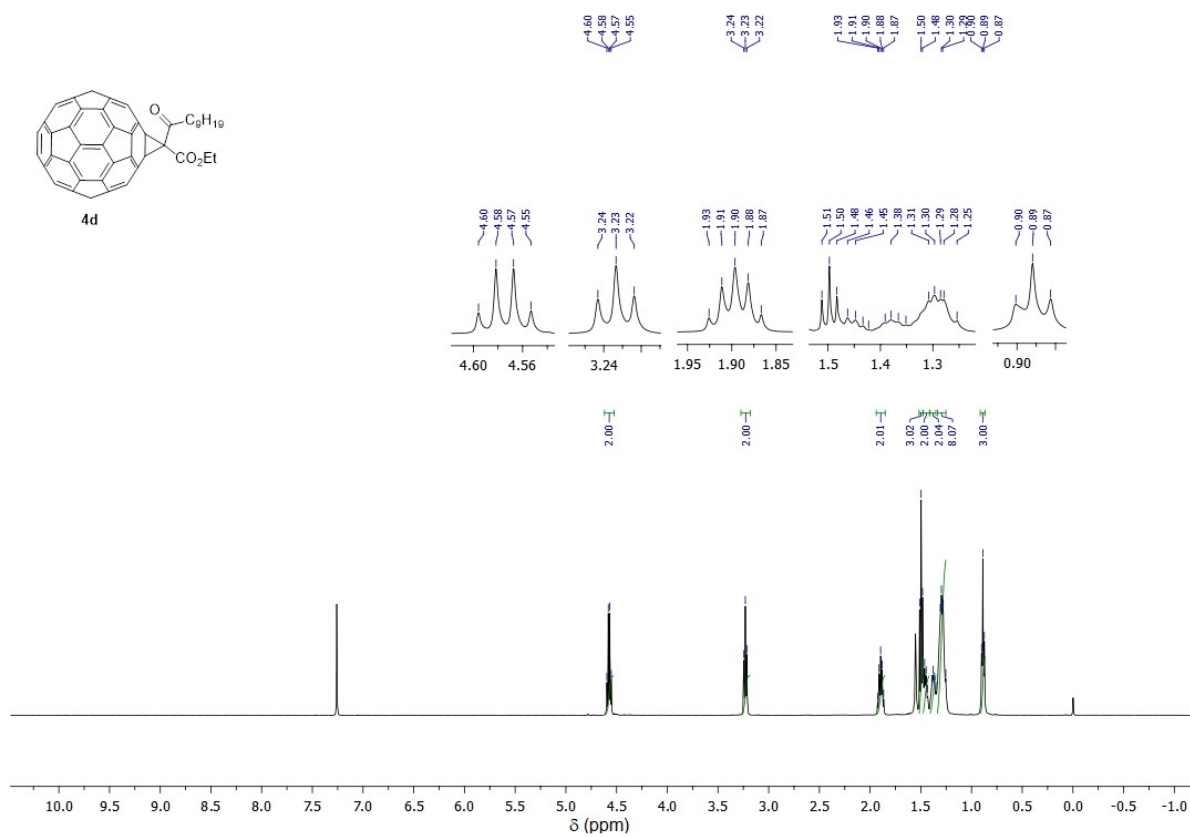


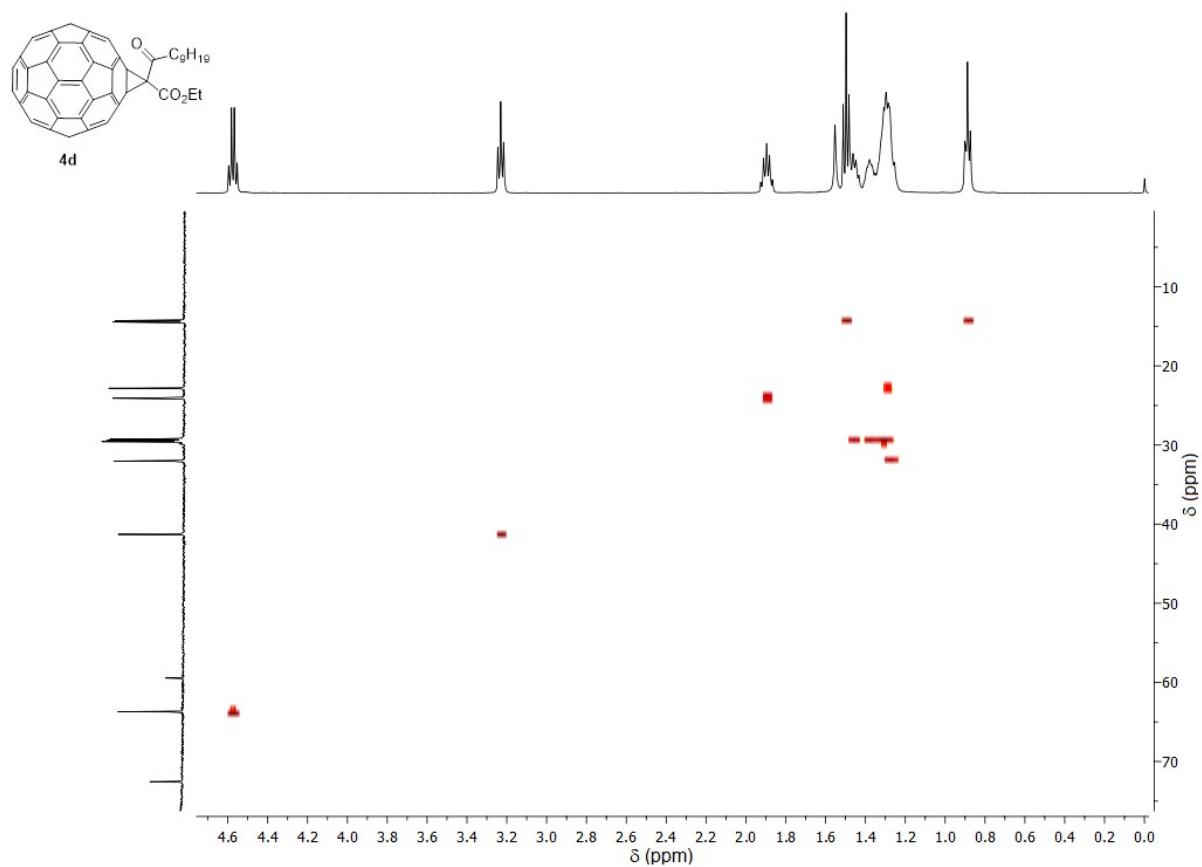
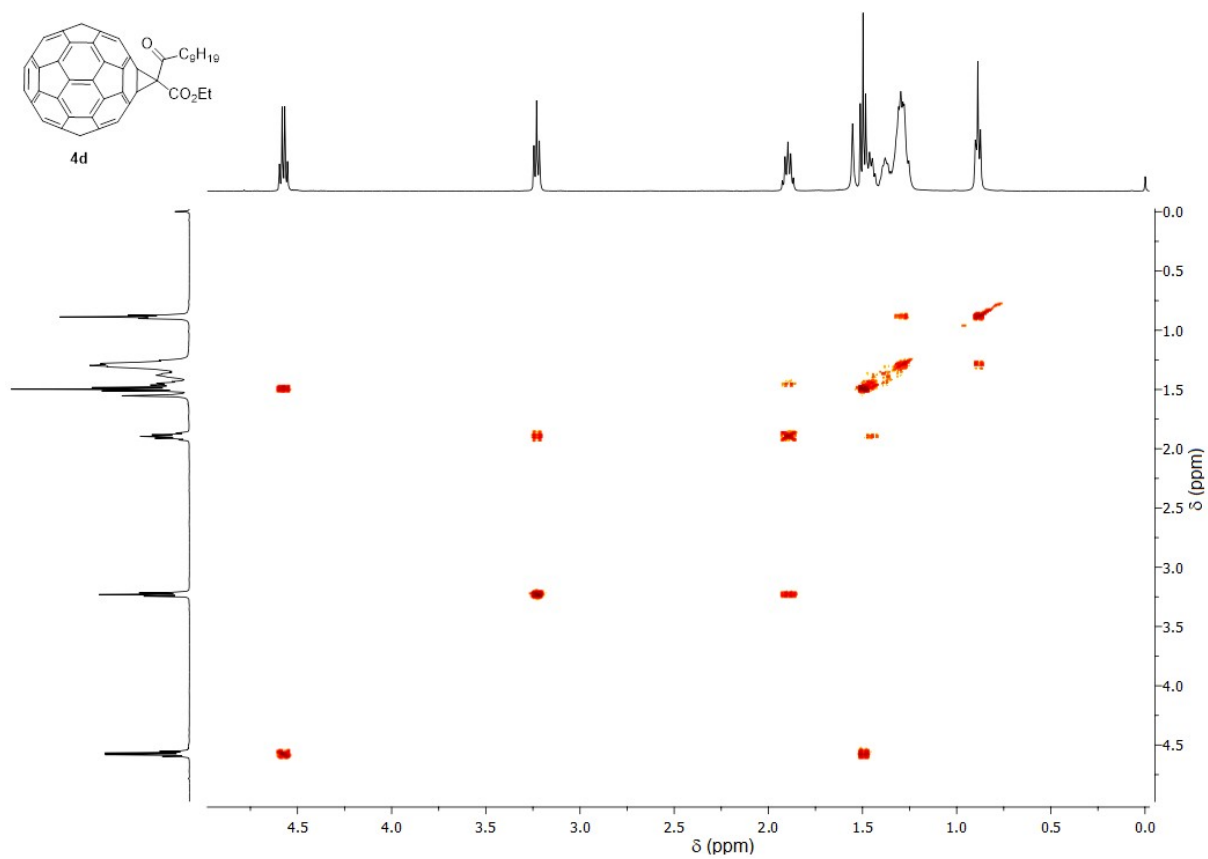
**4d**

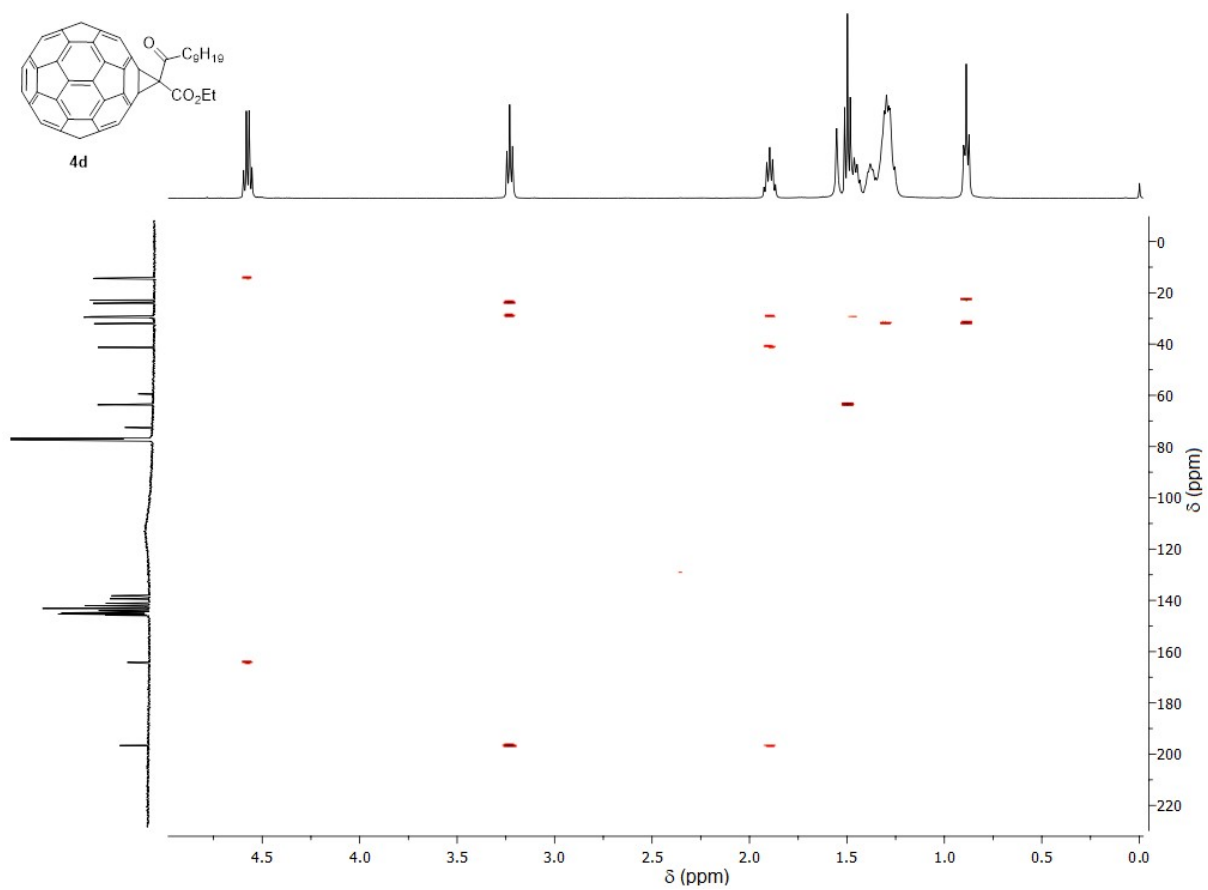


**Figure SI 56.** Positive HRMS of compound 4d.

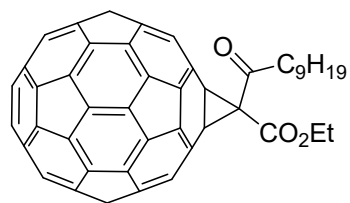




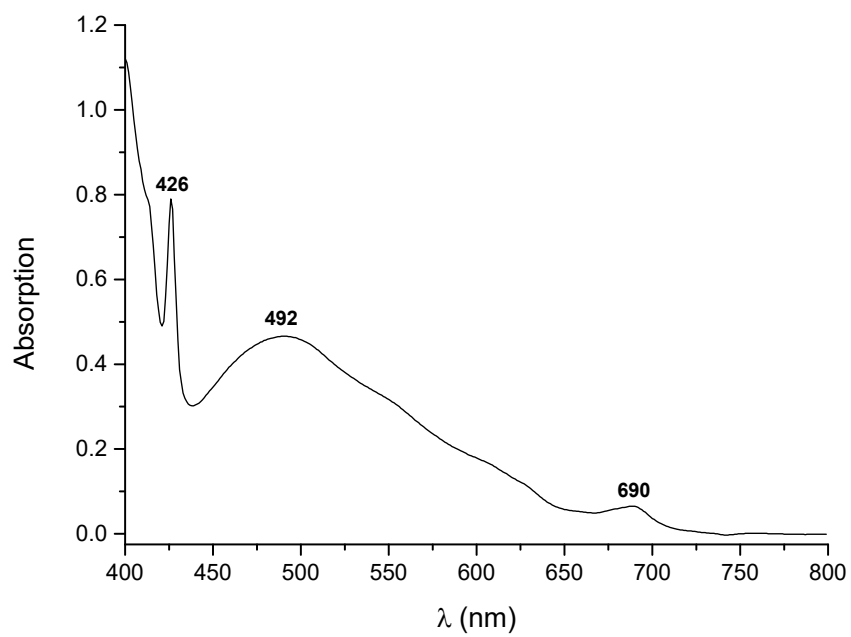




**Figure SI 61.** HMBC NMR spectrum of **4d** in CDCl<sub>3</sub>.



**4d**



| $\lambda$<br>(nm) | $\epsilon$<br>( $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) |
|-------------------|--|
| 426               | 2182   |
| 492               | 1287   |
| 690               | 180  |

**Figure SI 62.** UV-Vis absorption spectrum of compound **4d** in  $\text{CHCl}_3$ .