*Electronic Supplementary Information for*

# Pyrrolizidine and cyclobutane bridged double-caged fullerene derivatives

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## 2. NMR spectra of the synthesized compounds

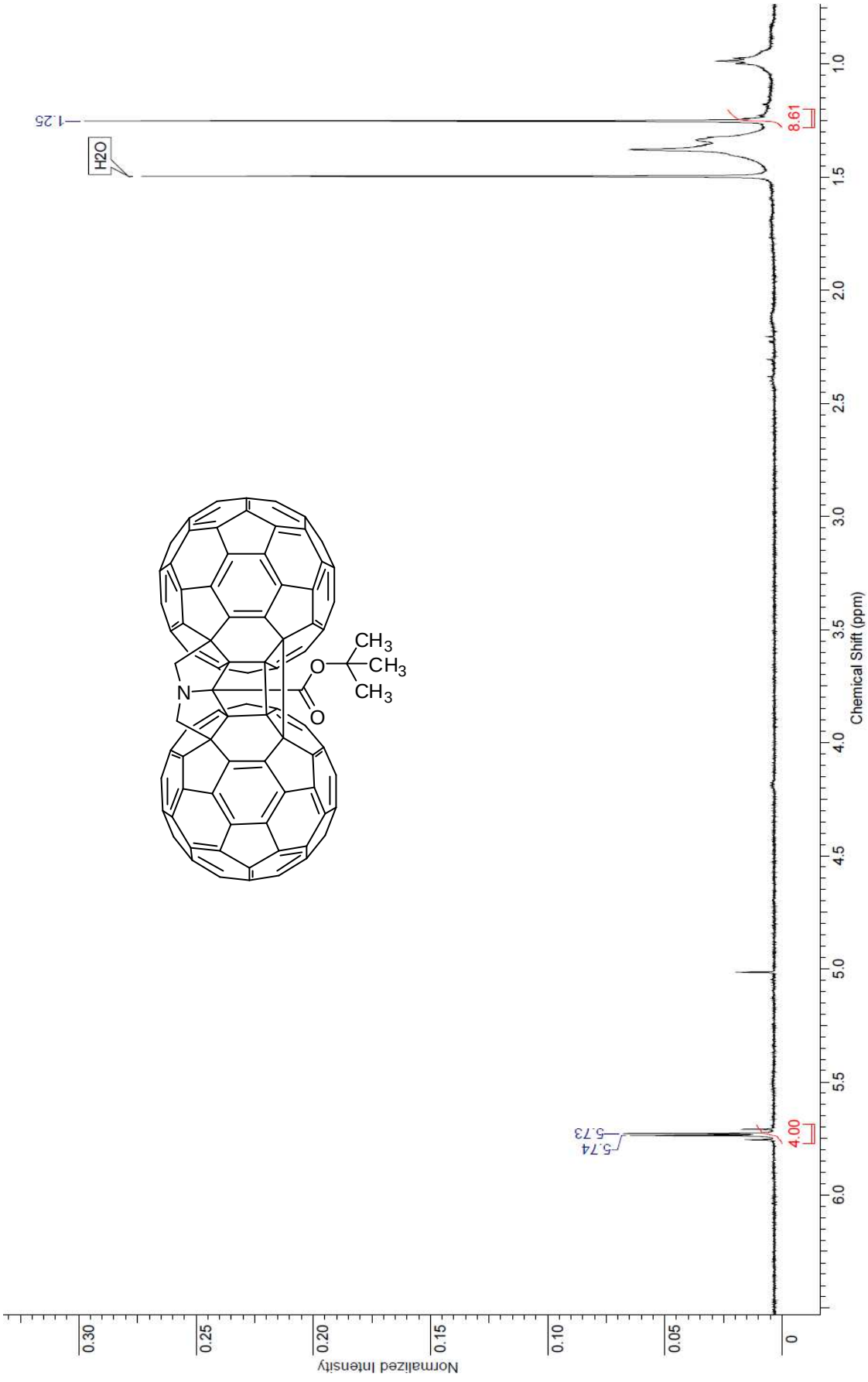



**Figure S 1.** $^{1}$H NMR spectrum of compound **2a**.

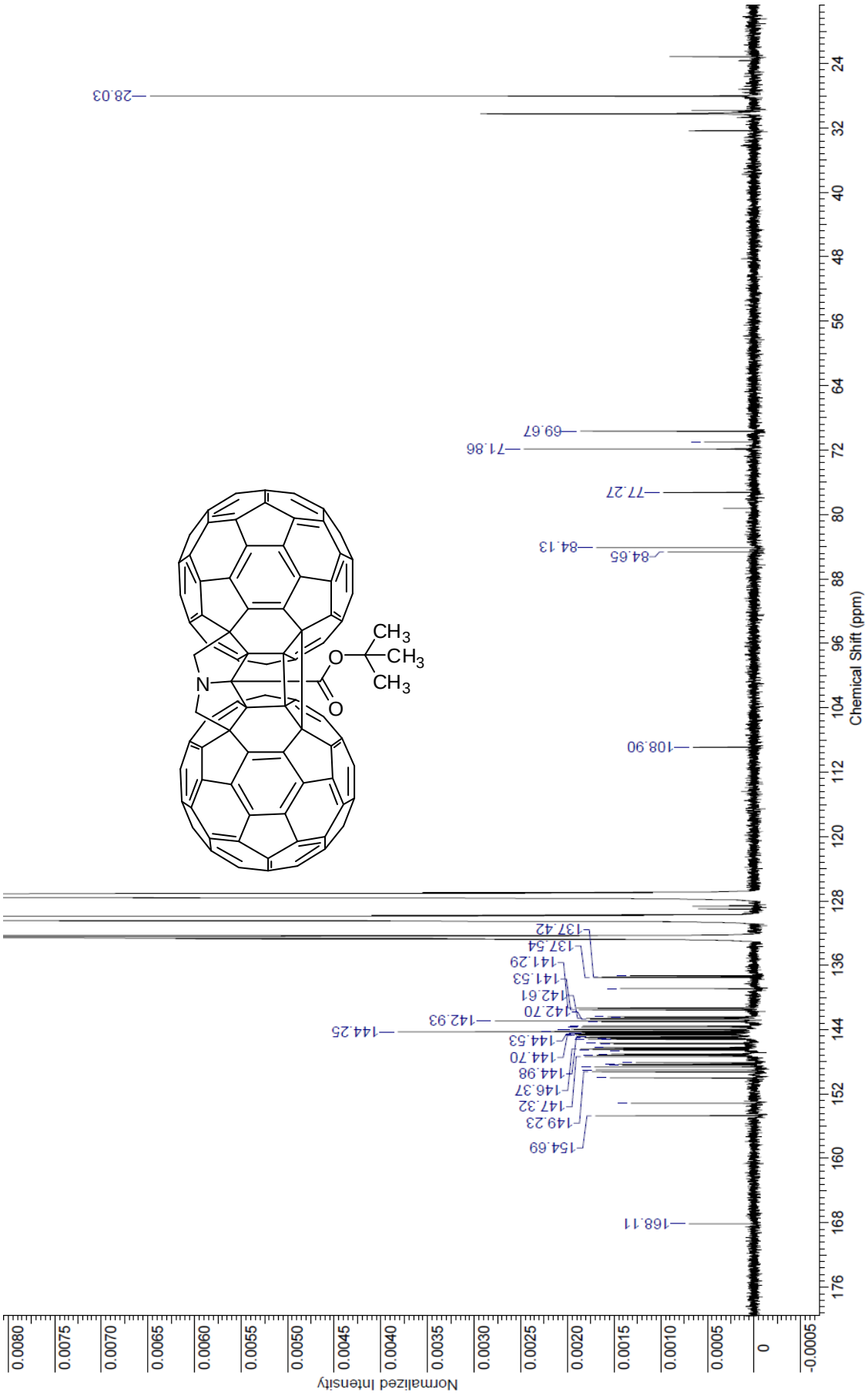



**Figure S 2.** $^{13}$C NMR spectrum of compound **2a**.

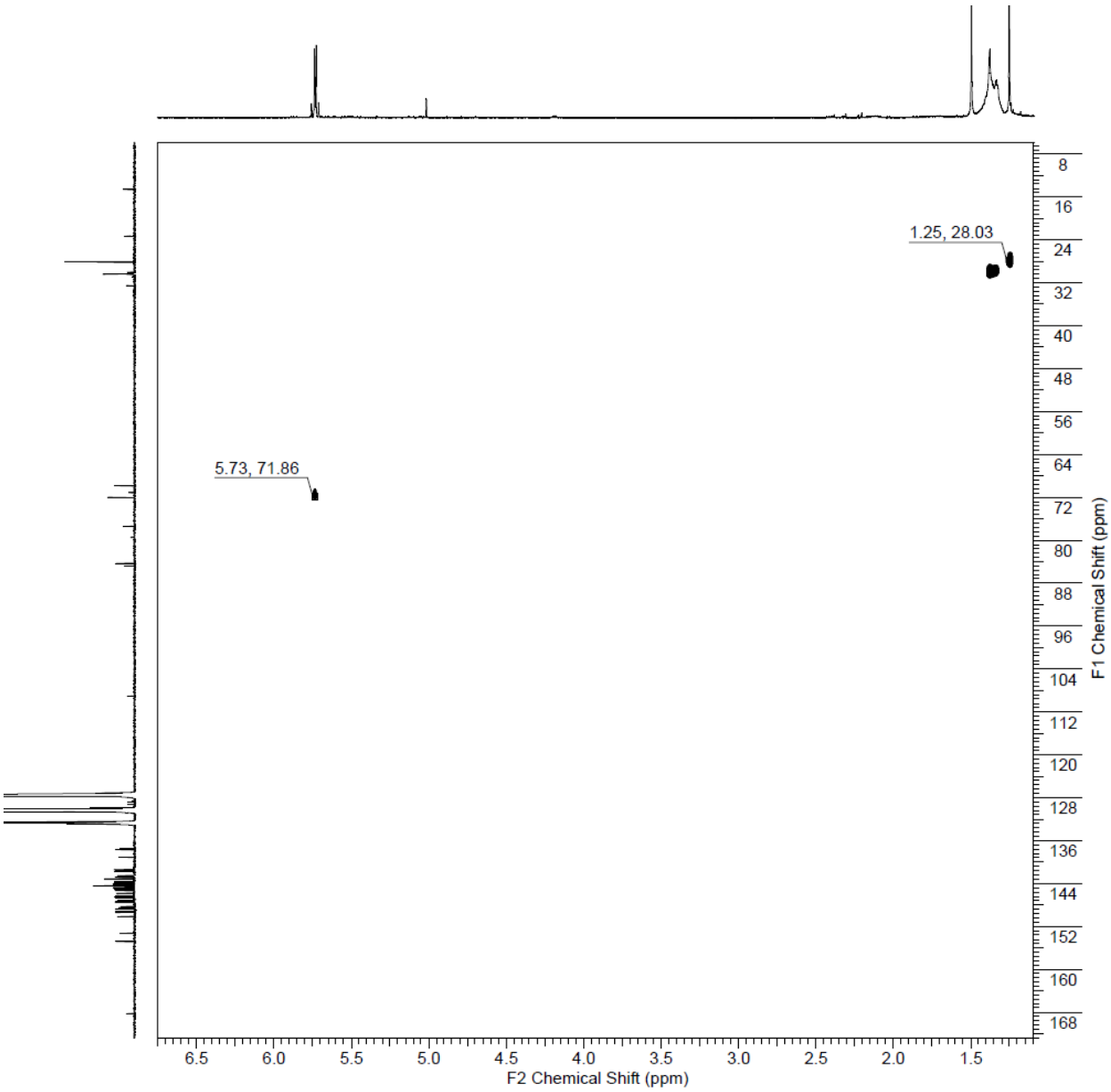



**Figure S 3.** $^{1}H–^{13}C$ HSQC spectrum of compound **2a**.

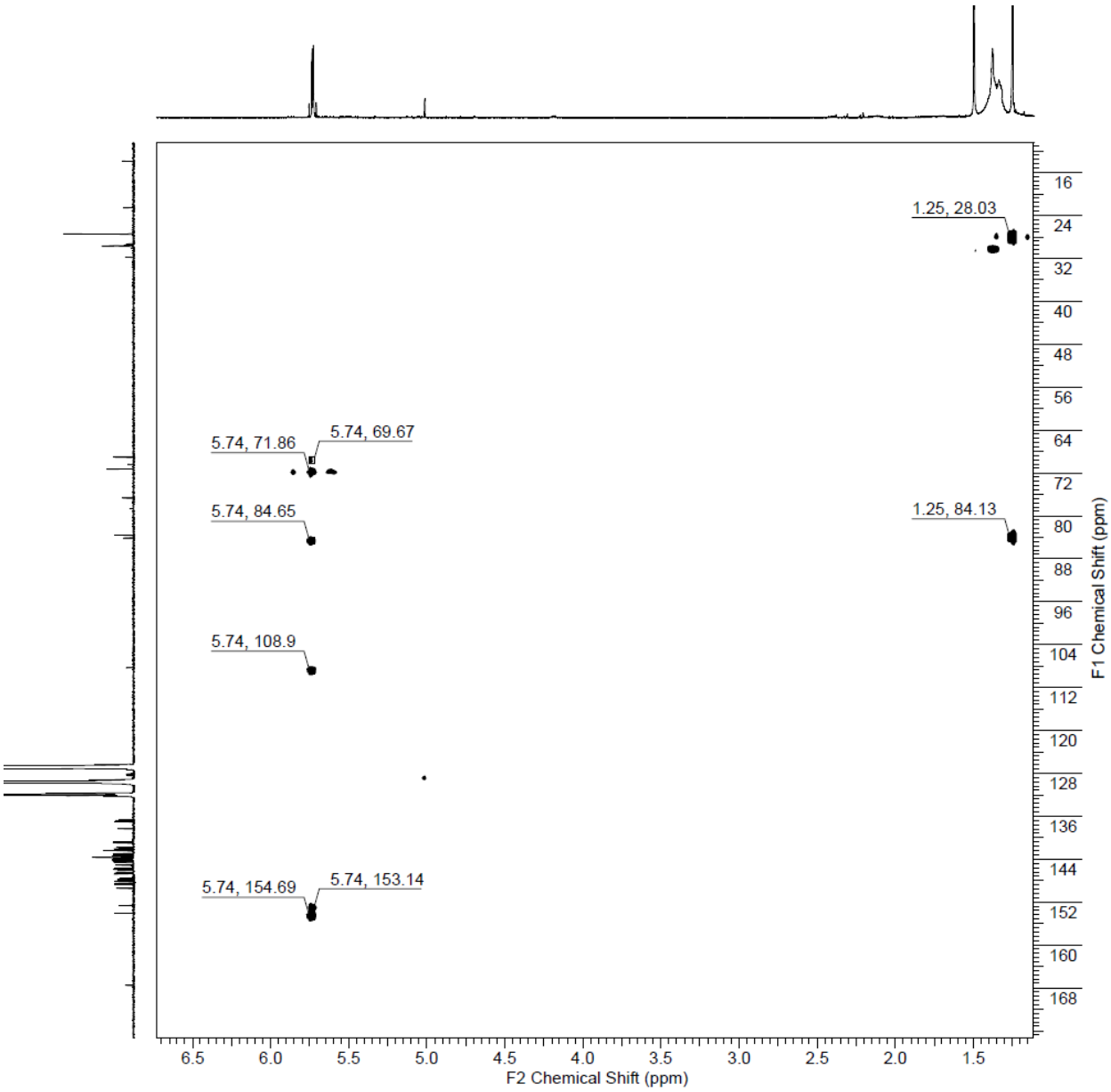



**Figure S 4.** $^{1}H–^{13}C$ HMBC spectrum of compound **2a**.

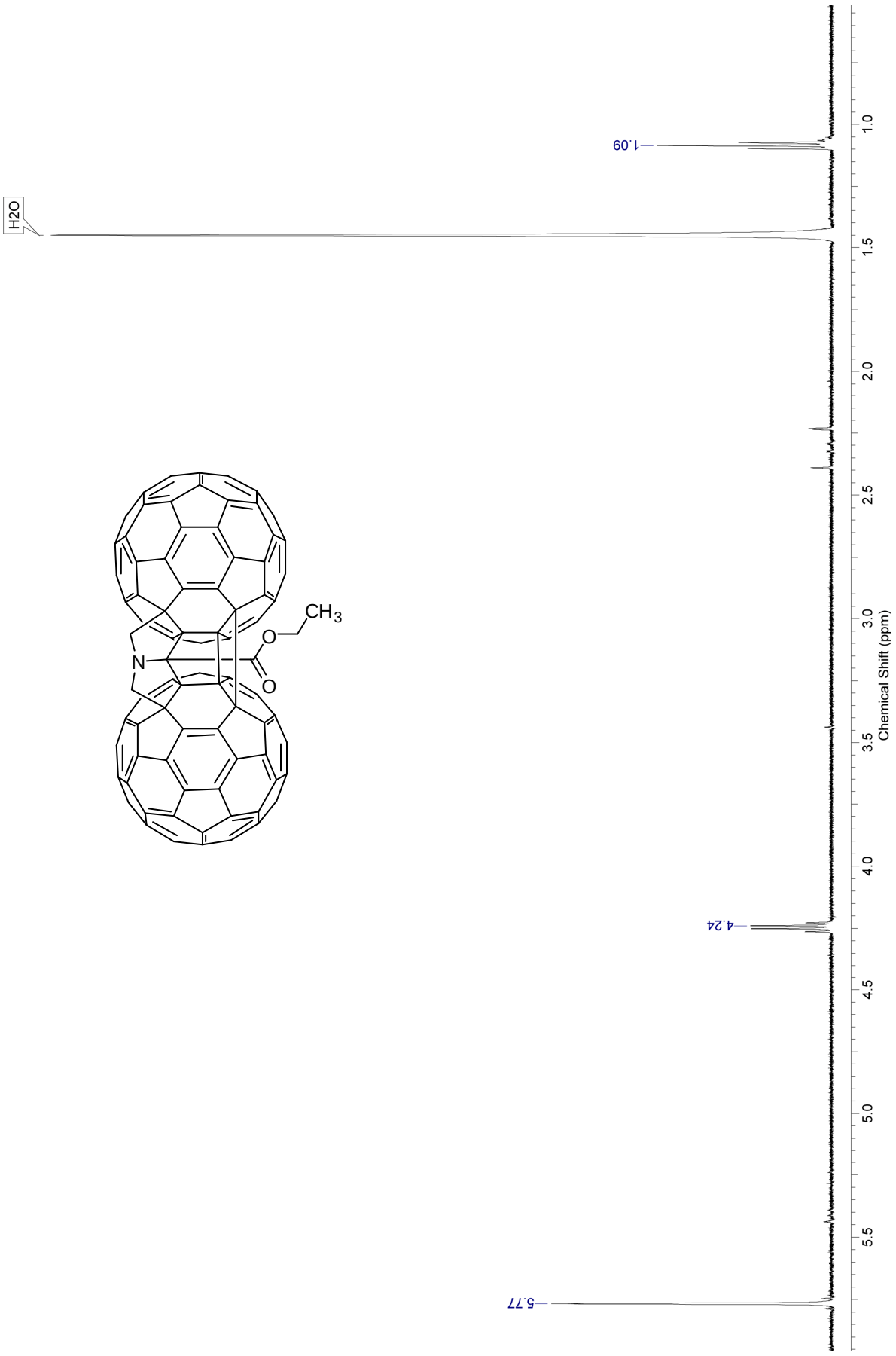



**Figure S 5.** $^{1}$H NMR spectrum of compound **2b**.

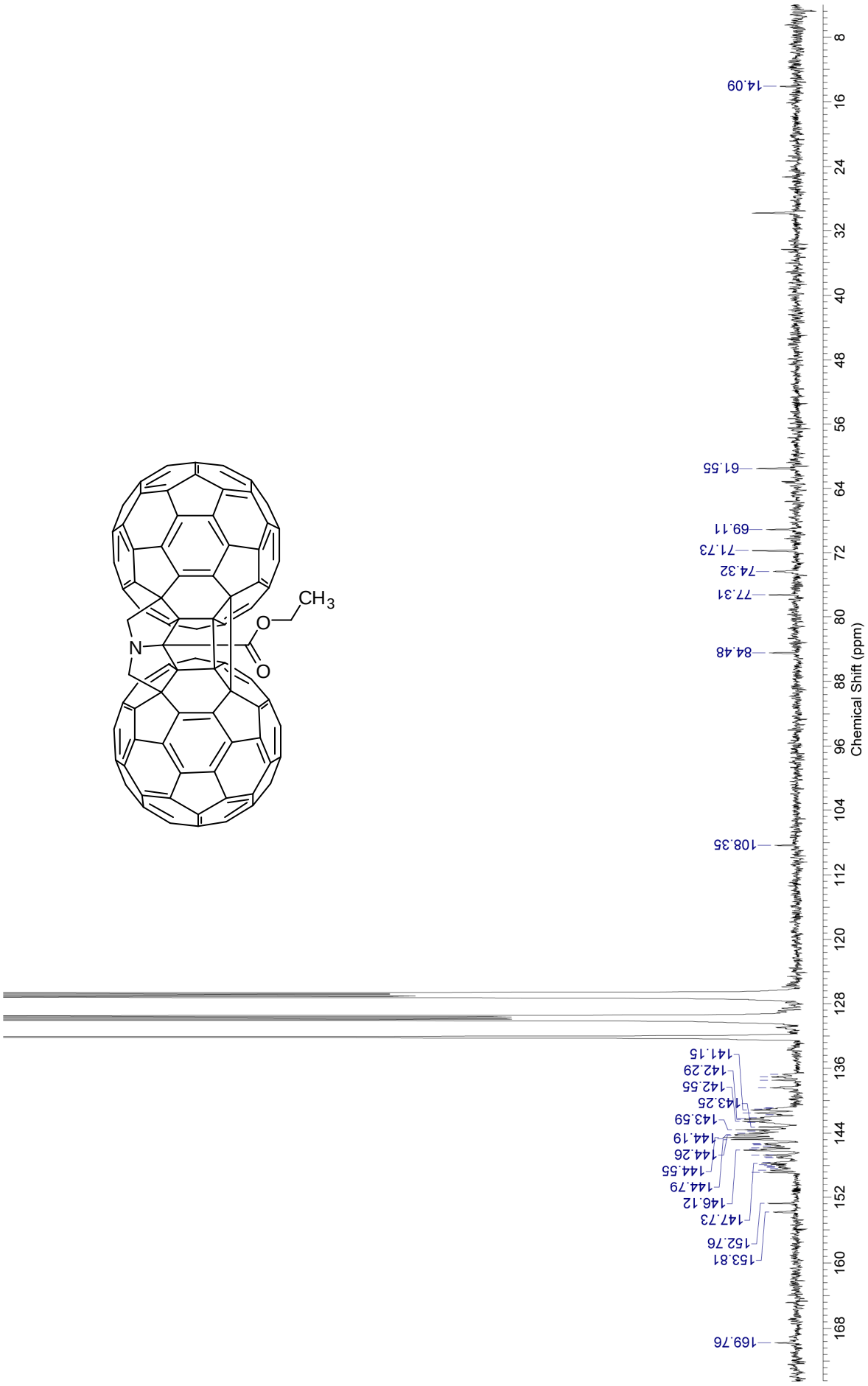



**Figure S 6.** $^{13}$C NMR spectrum of compound **2b**.

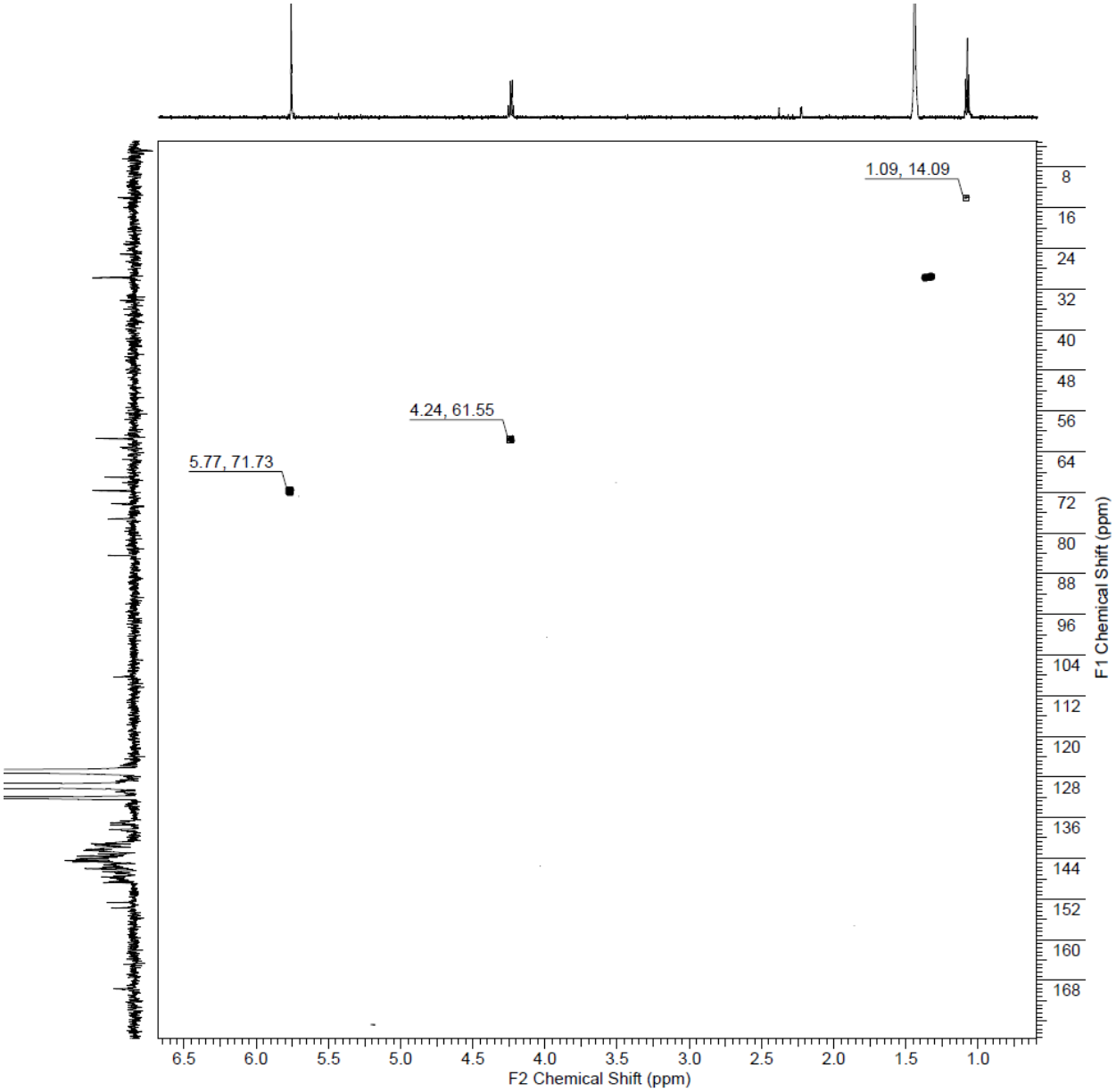



**Figure S 7.** $^{1}H–^{13}C$ HSQC spectrum of compound **2b**.

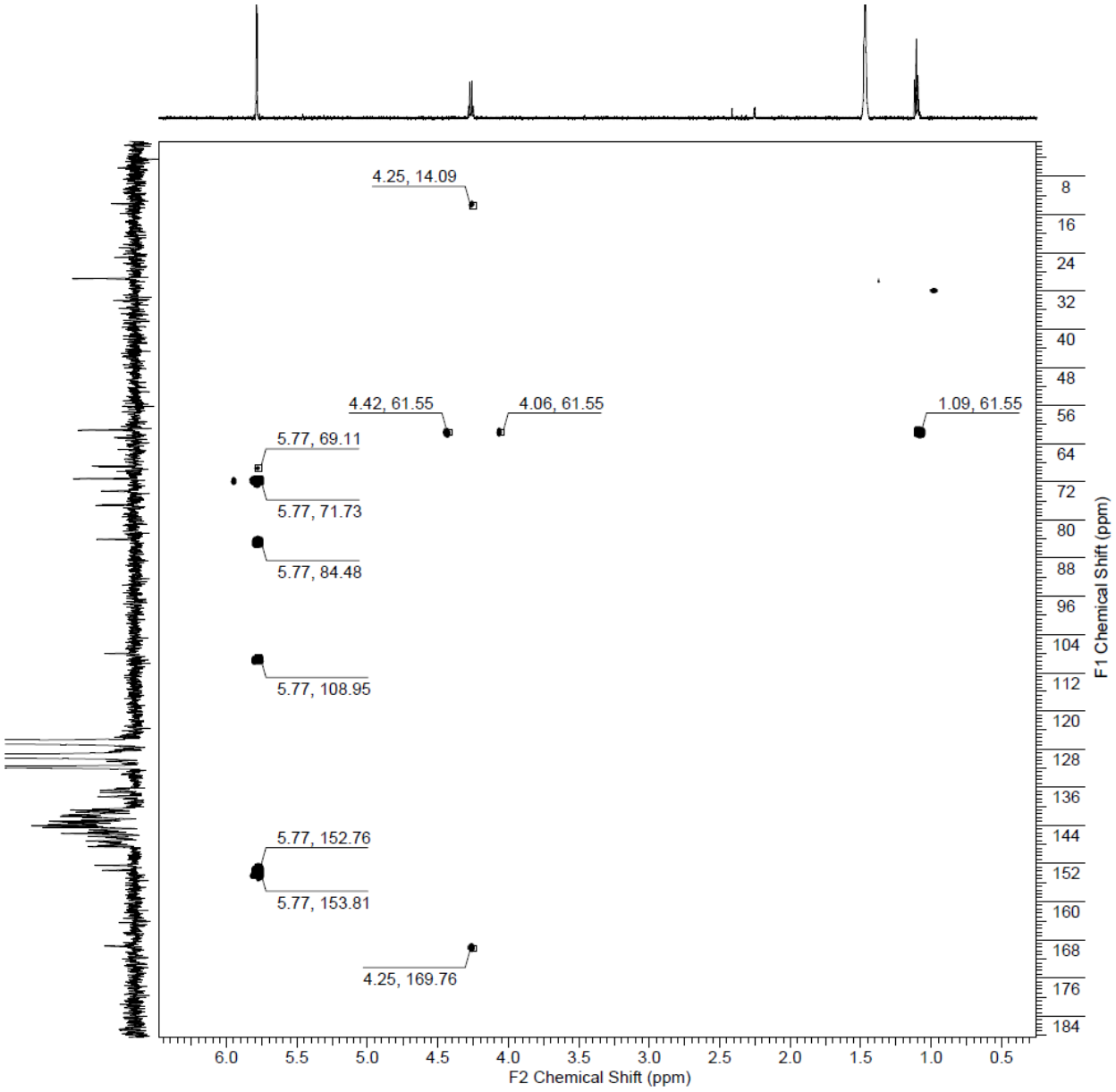



**Figure S 8.** $^{1}H–^{13}C$ HMBC spectrum of compound **2b**.

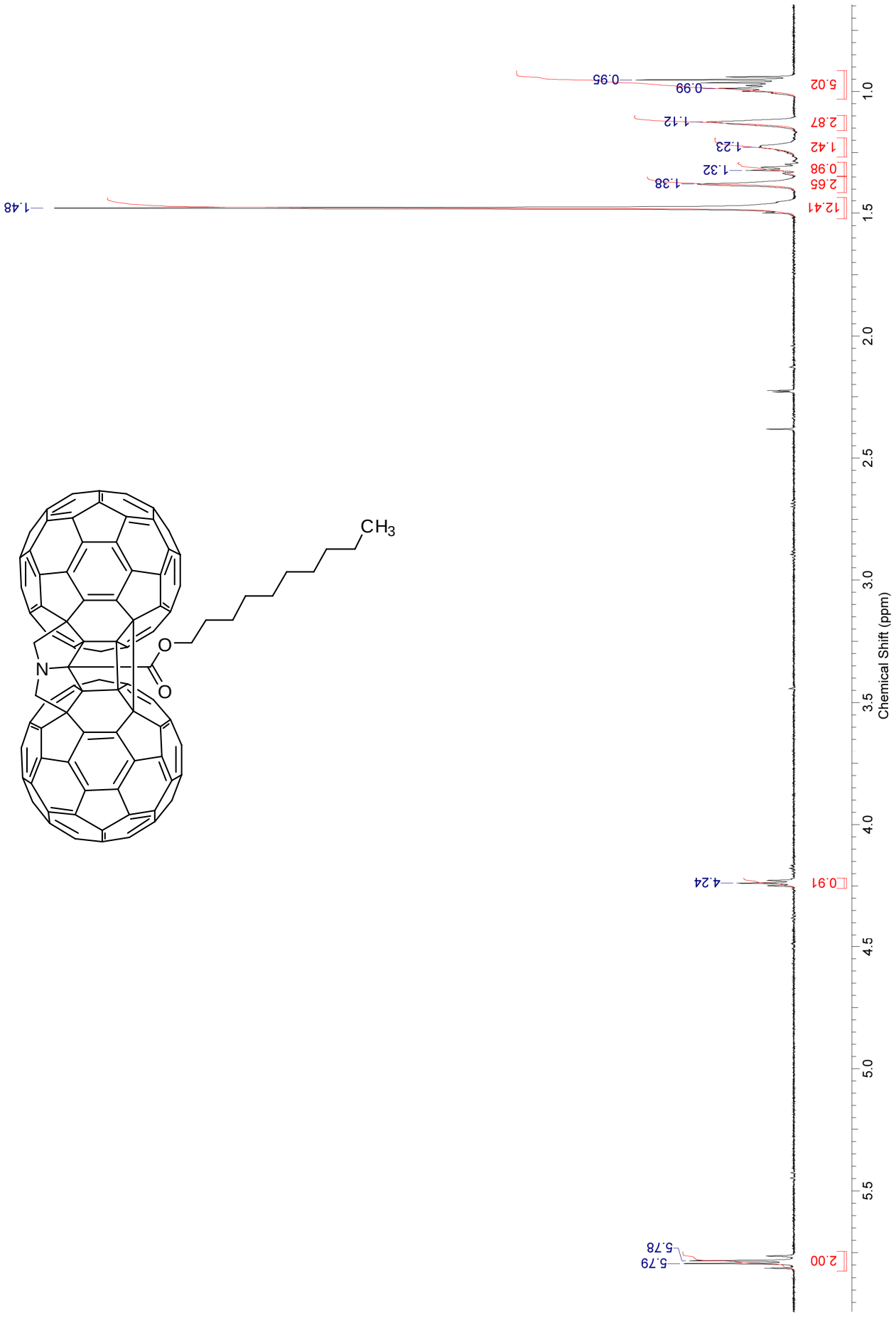



**Figure S 9.** $^{1}$H NMR spectrum of compound **2c**.

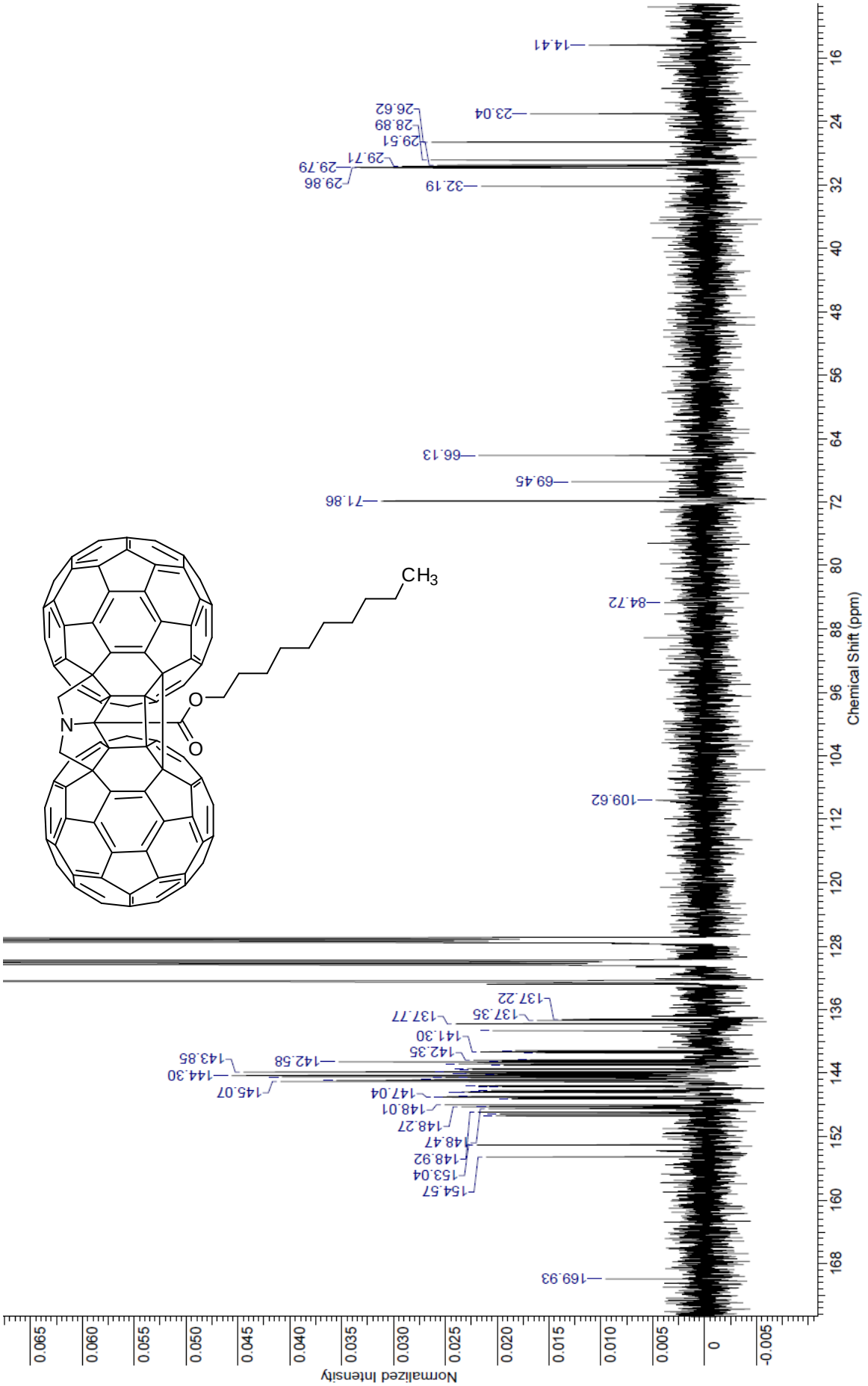



**Figure S 10.** $^{13}$C NMR spectrum of compound **2c**.

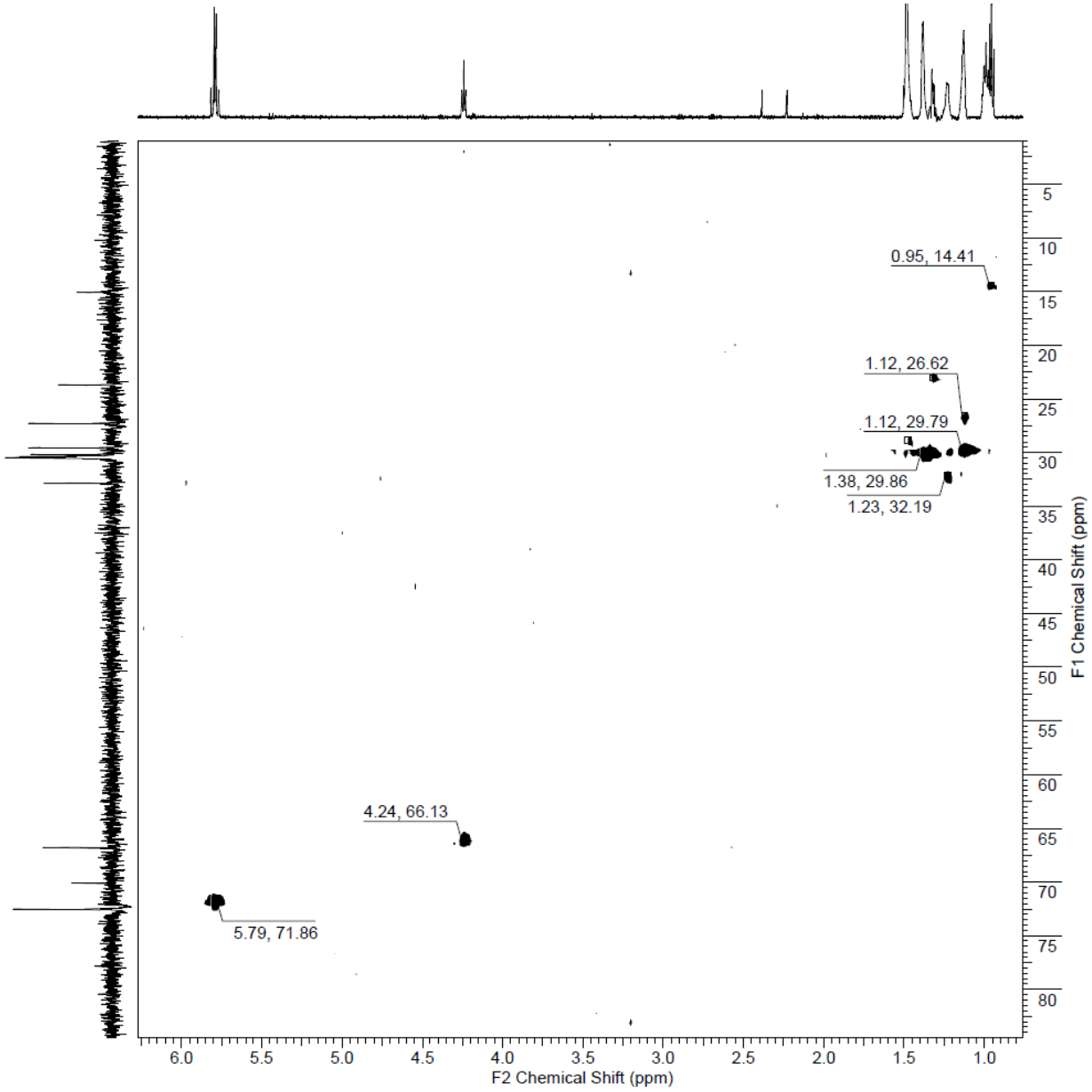



**Figure S 11.** $^{1}H–^{13}C$ HSQC spectrum of compound **2c**.

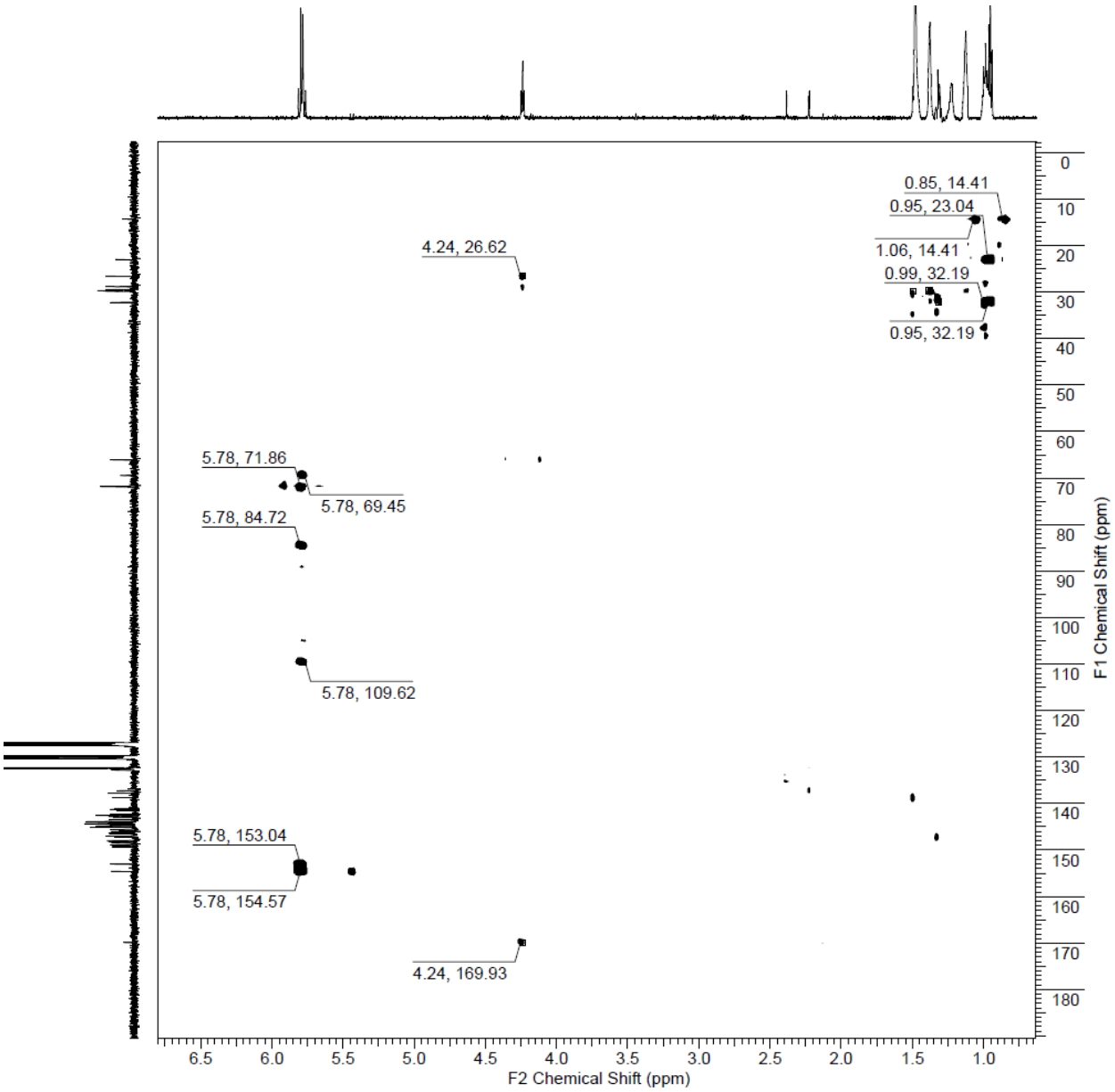



**Figure S 12.** $^{1}H–^{13}C$ HMBC spectrum of compound **2c**.

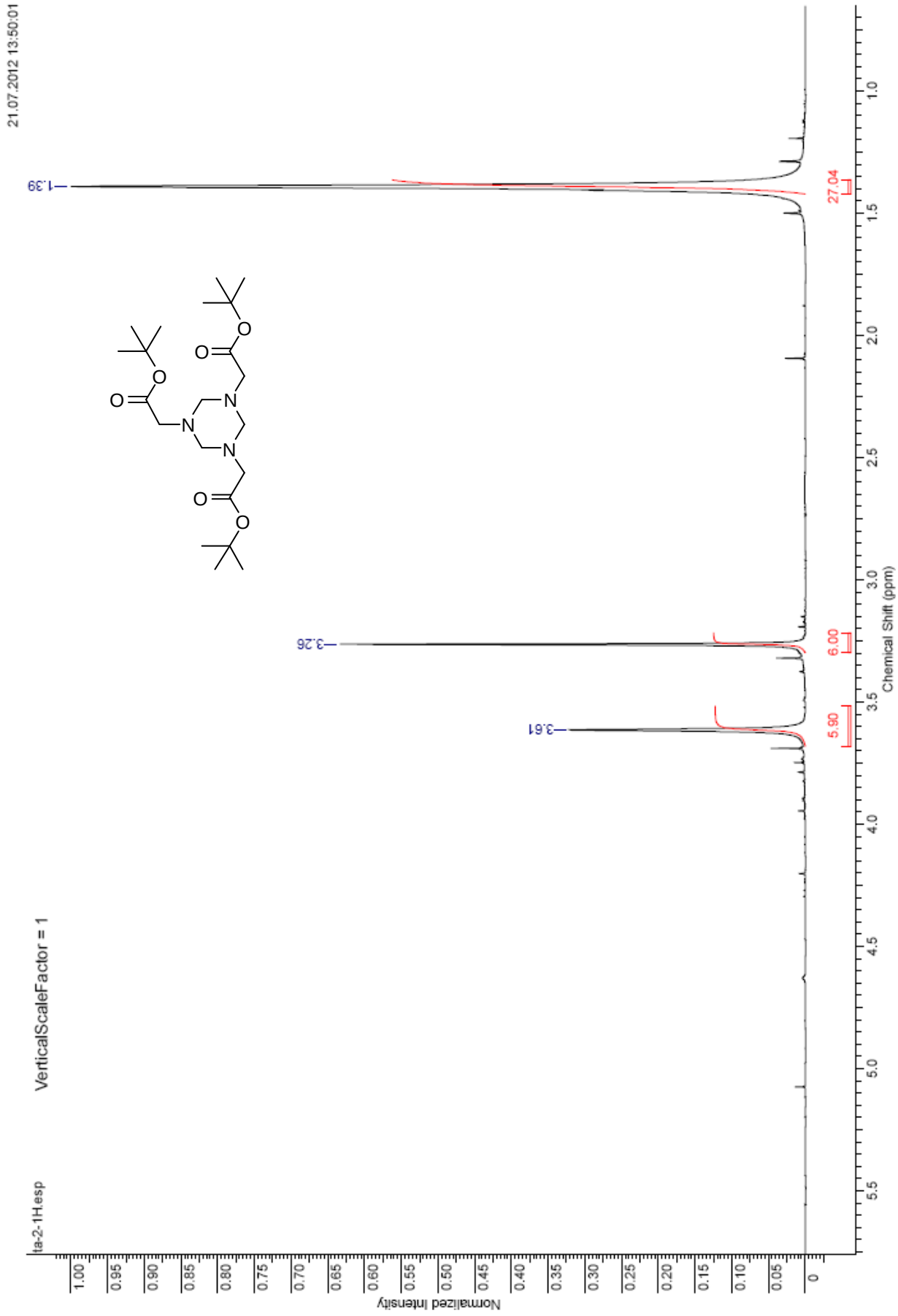



**Figure S 13.** $^{1}$H NMR spectrum of compound **3a**.

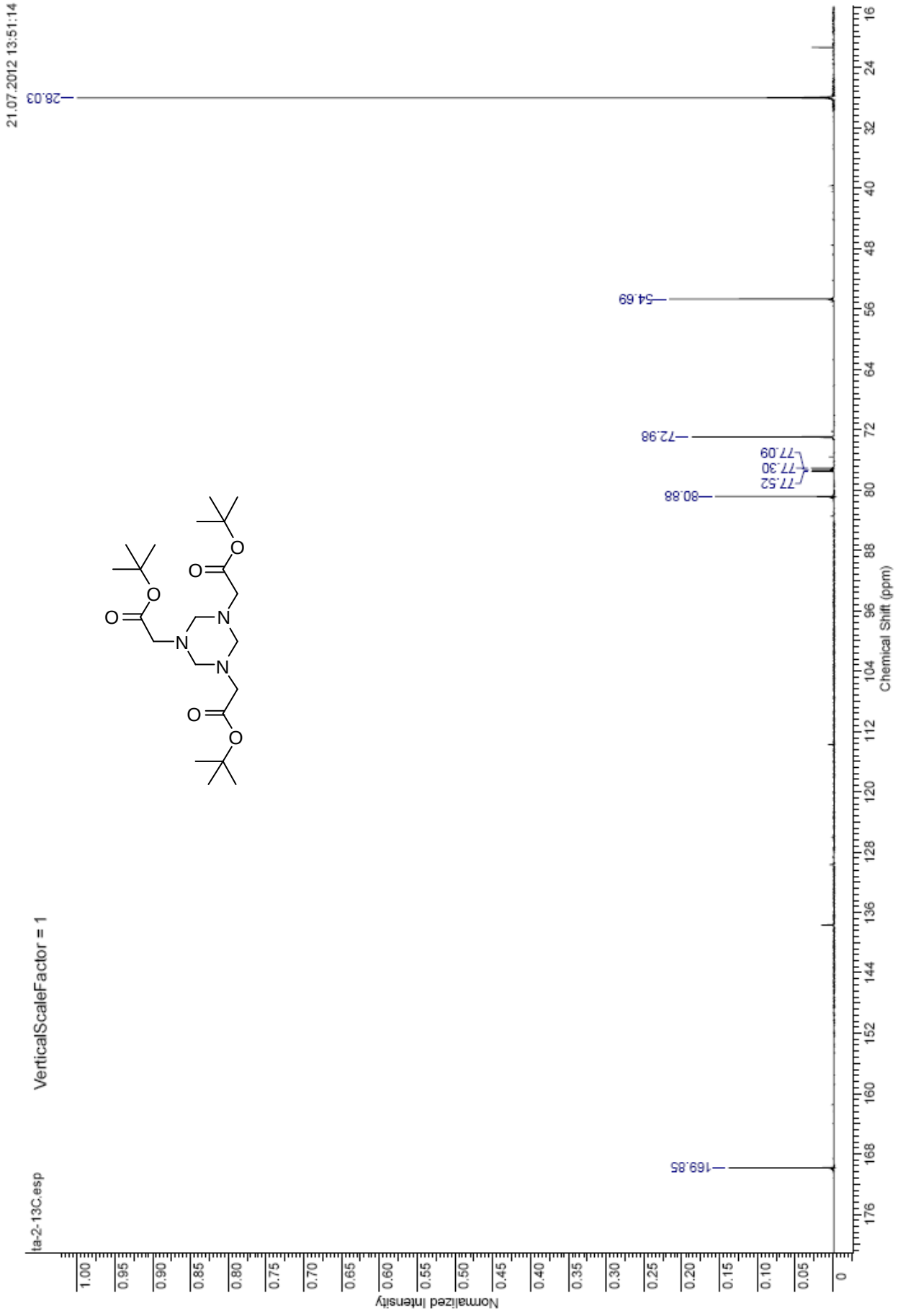



**Figure S 14.** $^{13}$C NMR spectrum of compound **3a**.

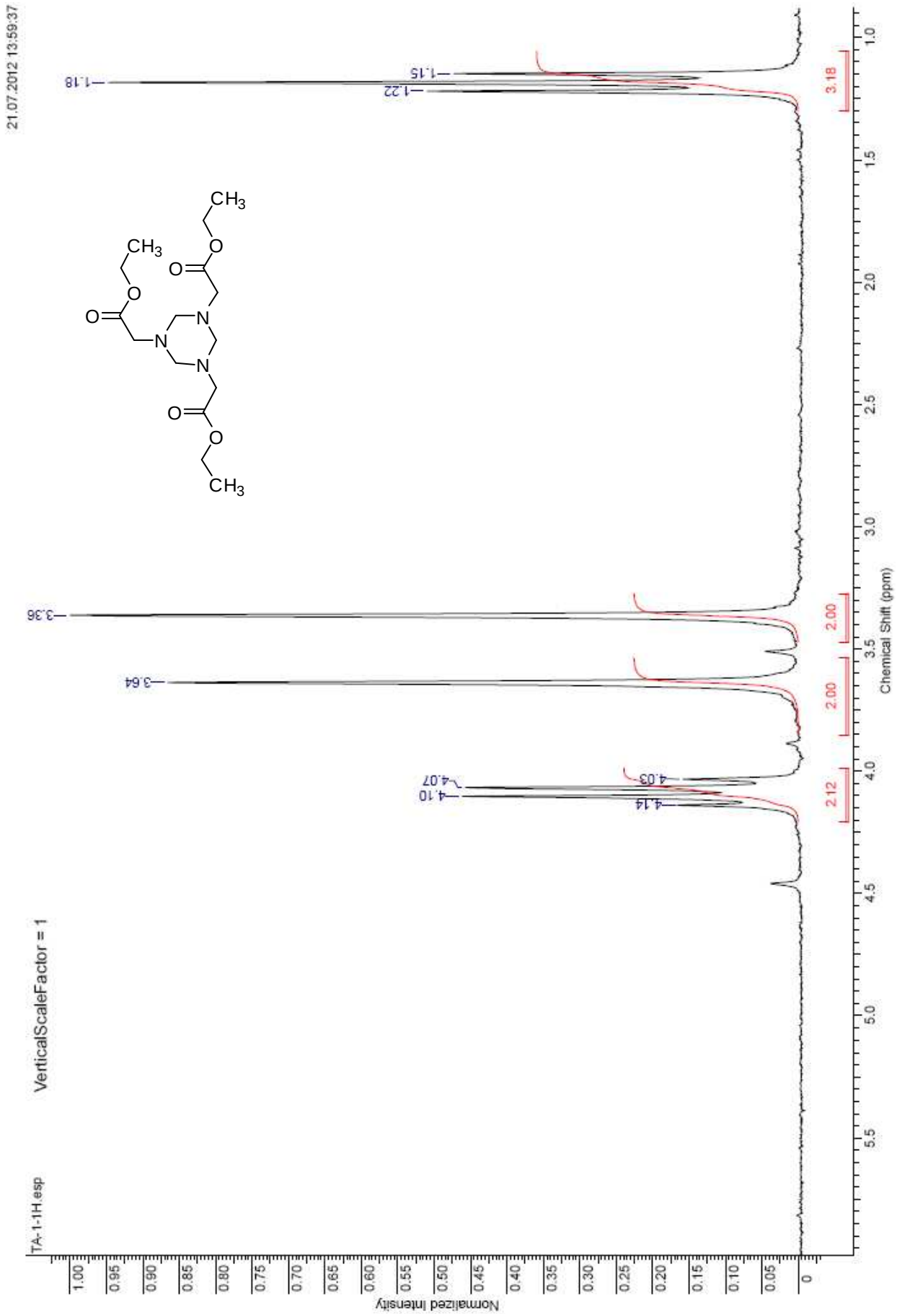



**Figure S 15.** $^{1}$H NMR spectrum of compound **3b**.

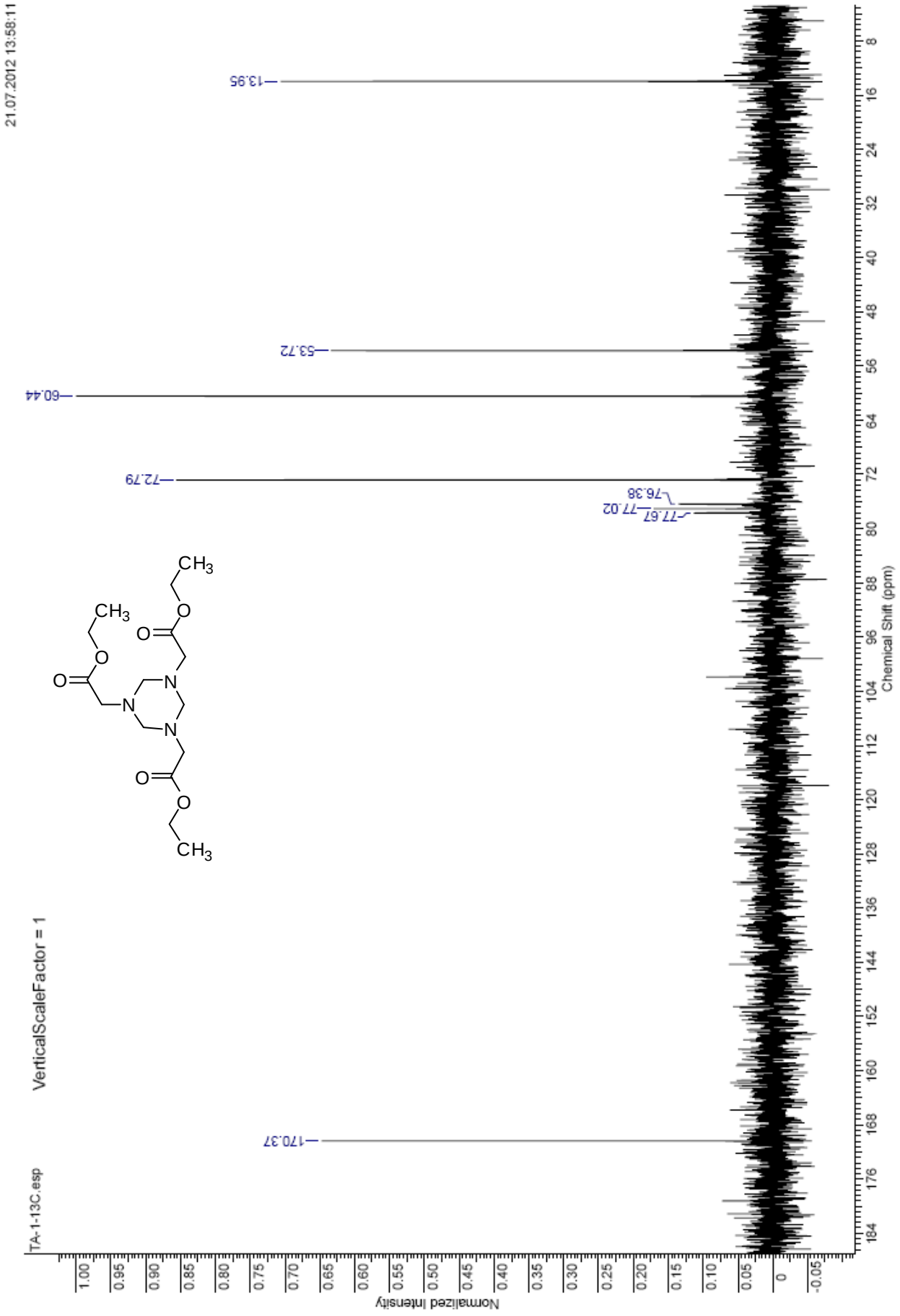



**Figure S 16.** $^{13}$C NMR spectrum of compound **3b**.

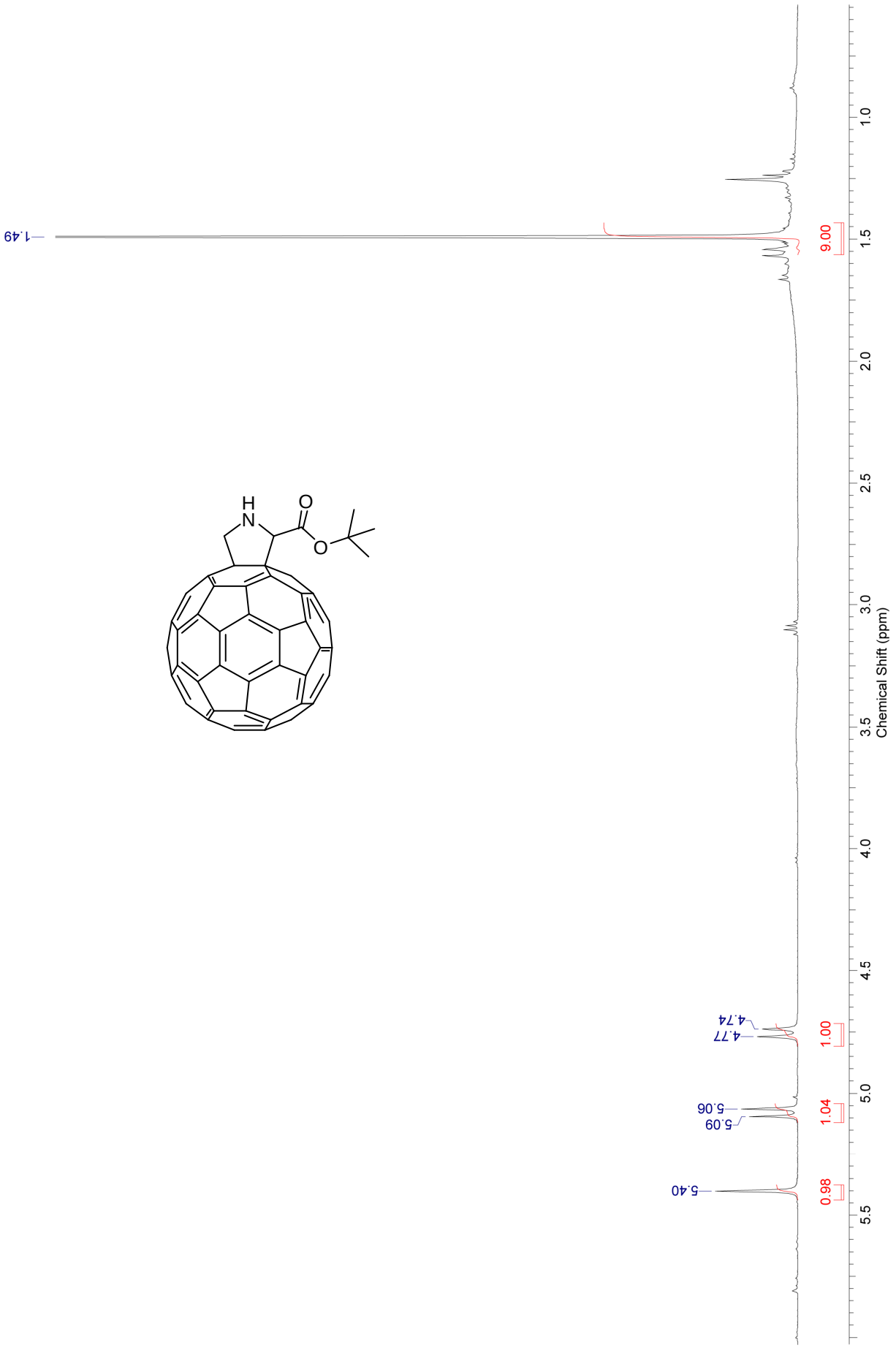



**Figure S 17.** $^{1}$H NMR spectrum of compound **1a**.

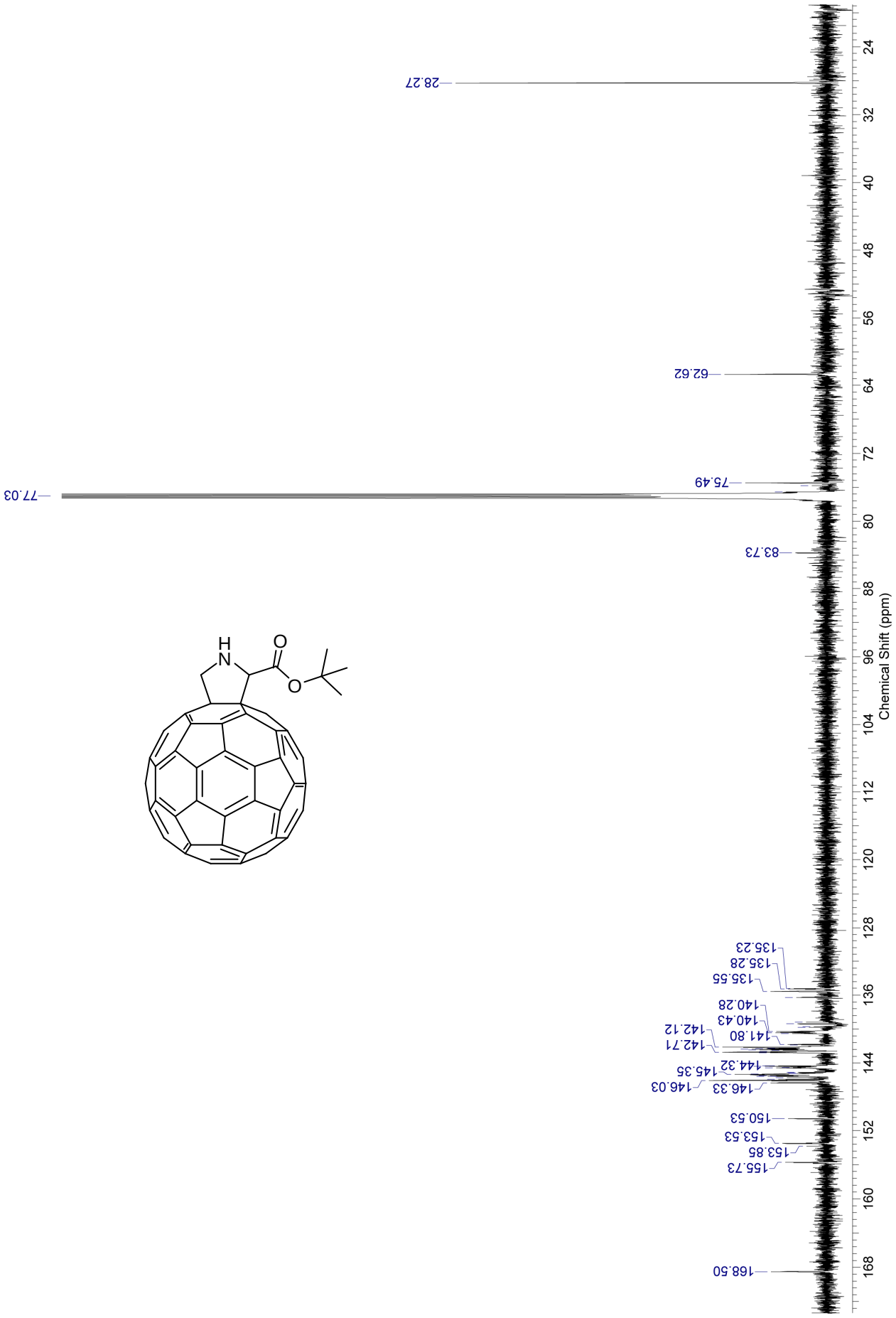



**Figure S 18.** $^{13}$C NMR spectrum of compound **1a**.

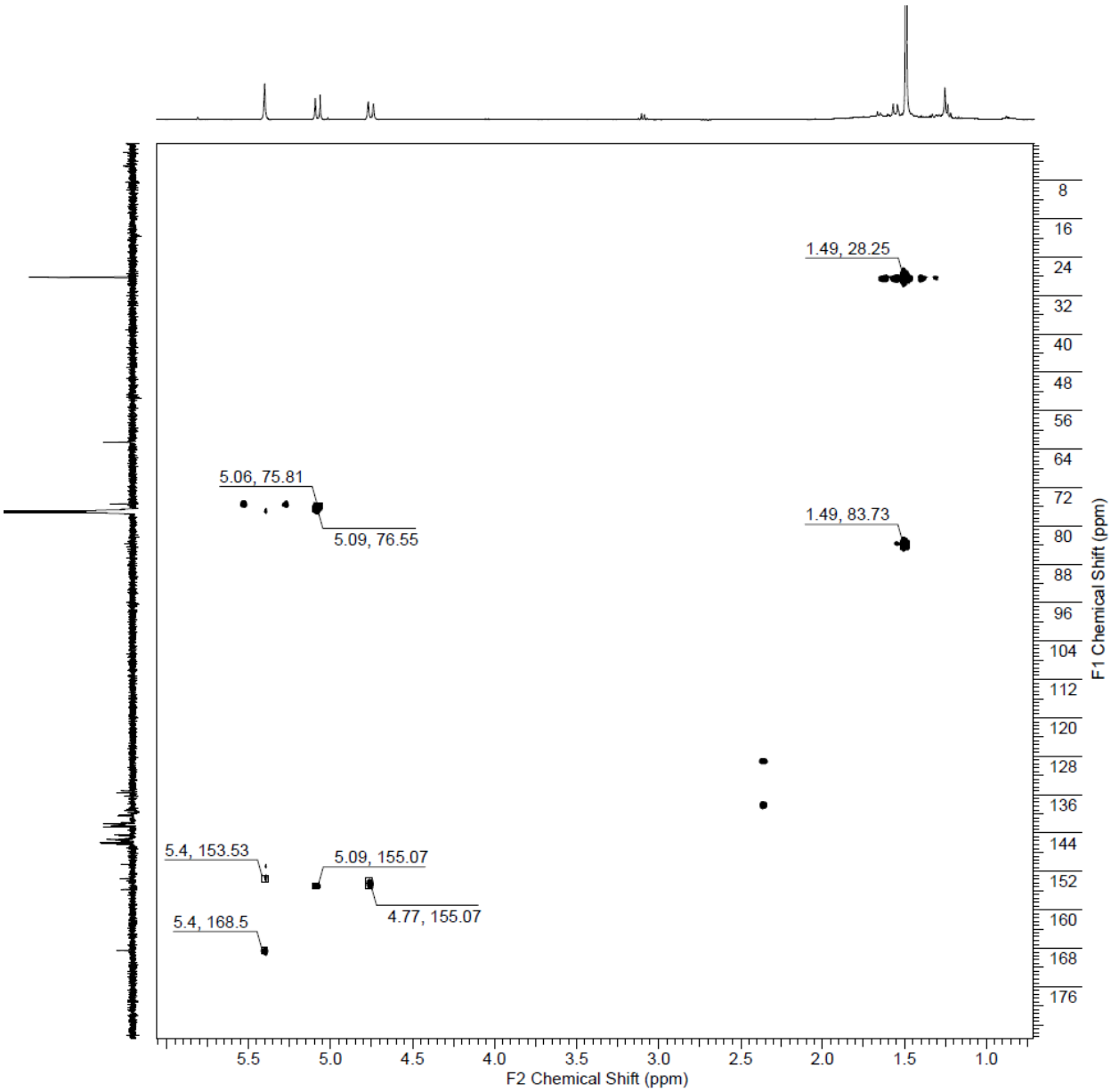



**Figure S 19.** $^{1}H–^{13}C$ HMBC spectrum of compound **1a**.

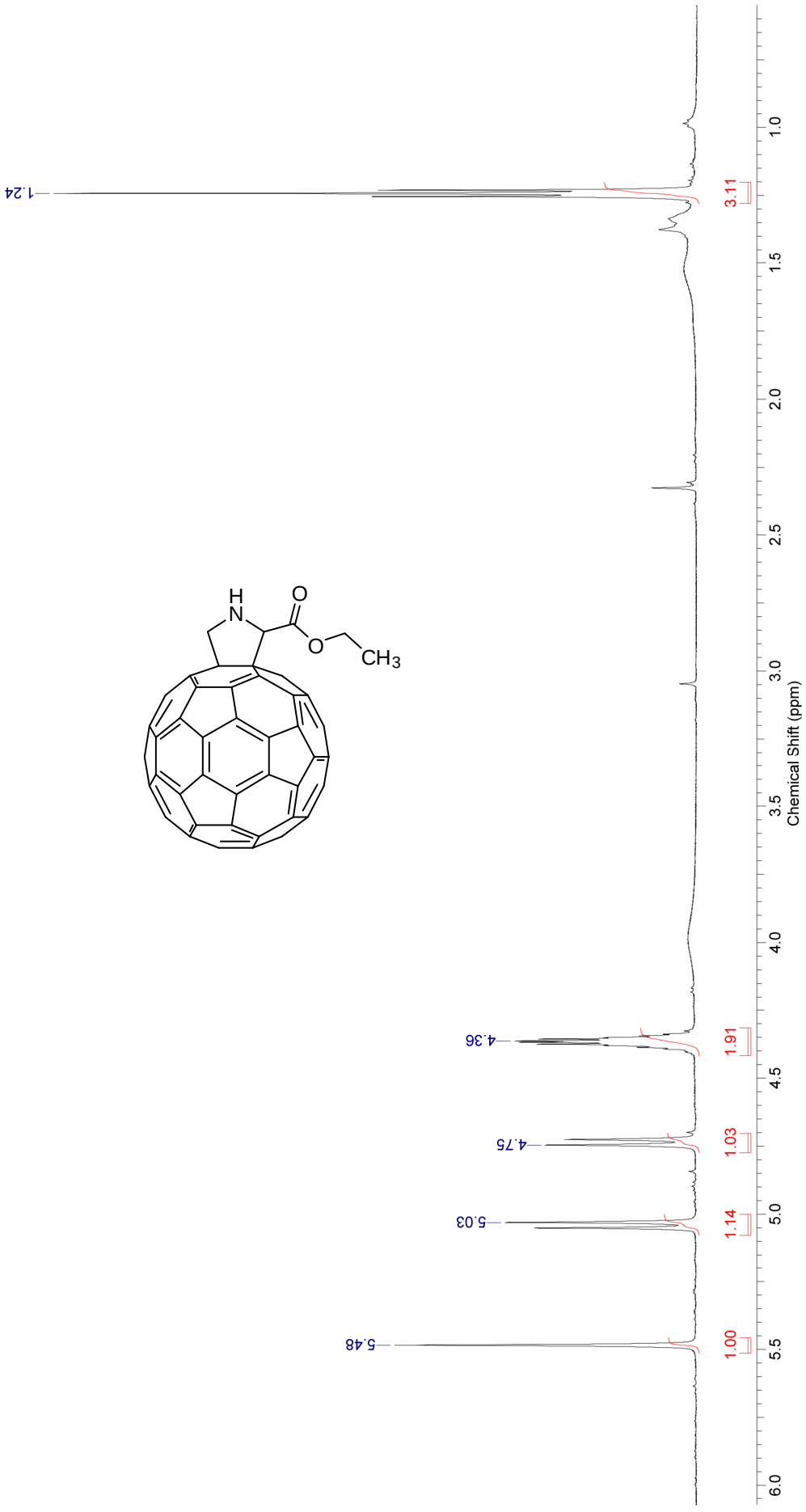



**Figure S 20.** $^{1}$H NMR spectrum of compound **1b**.

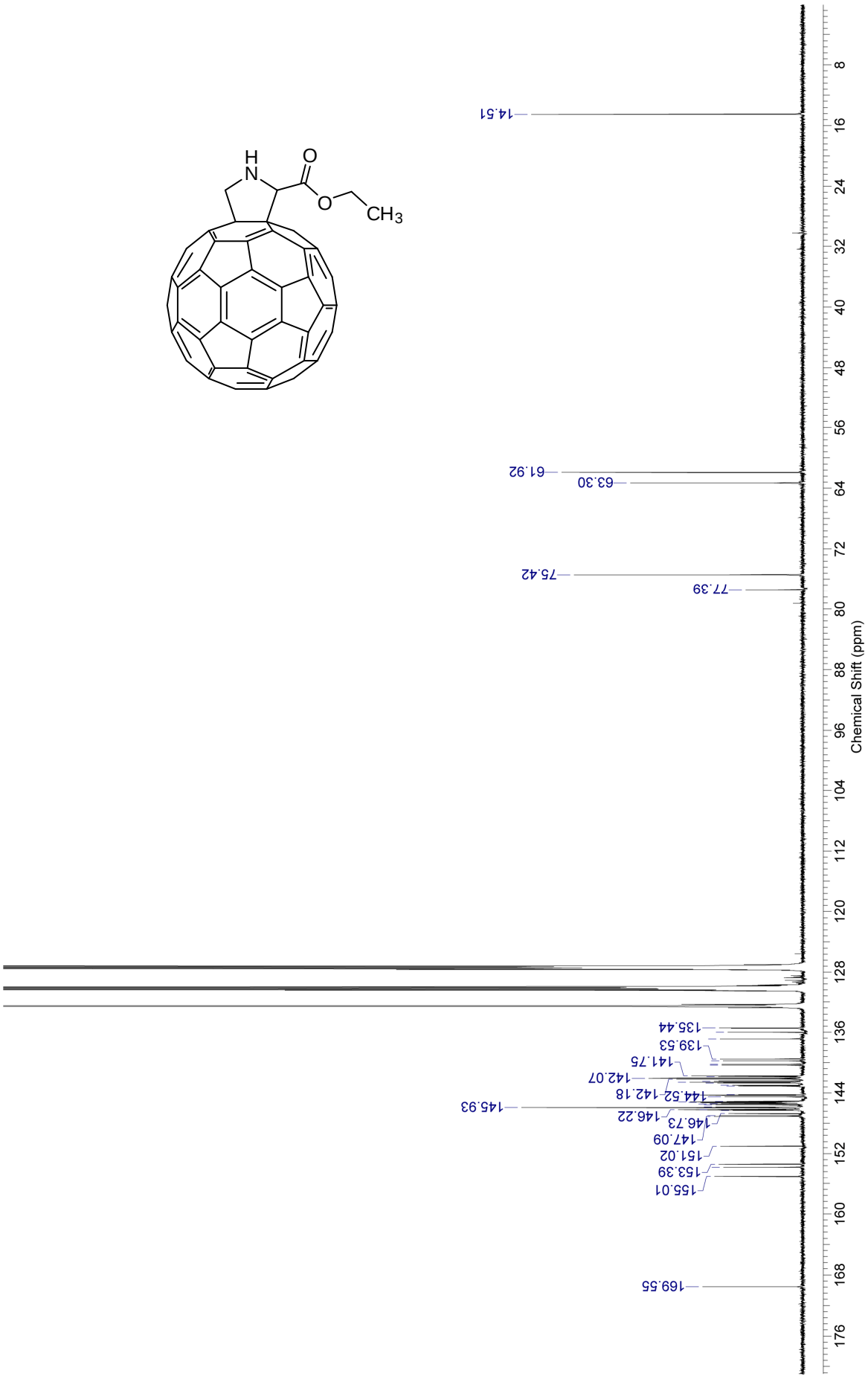



**Figure S 21.** $^{13}$C NMR spectrum of compound **1b**.

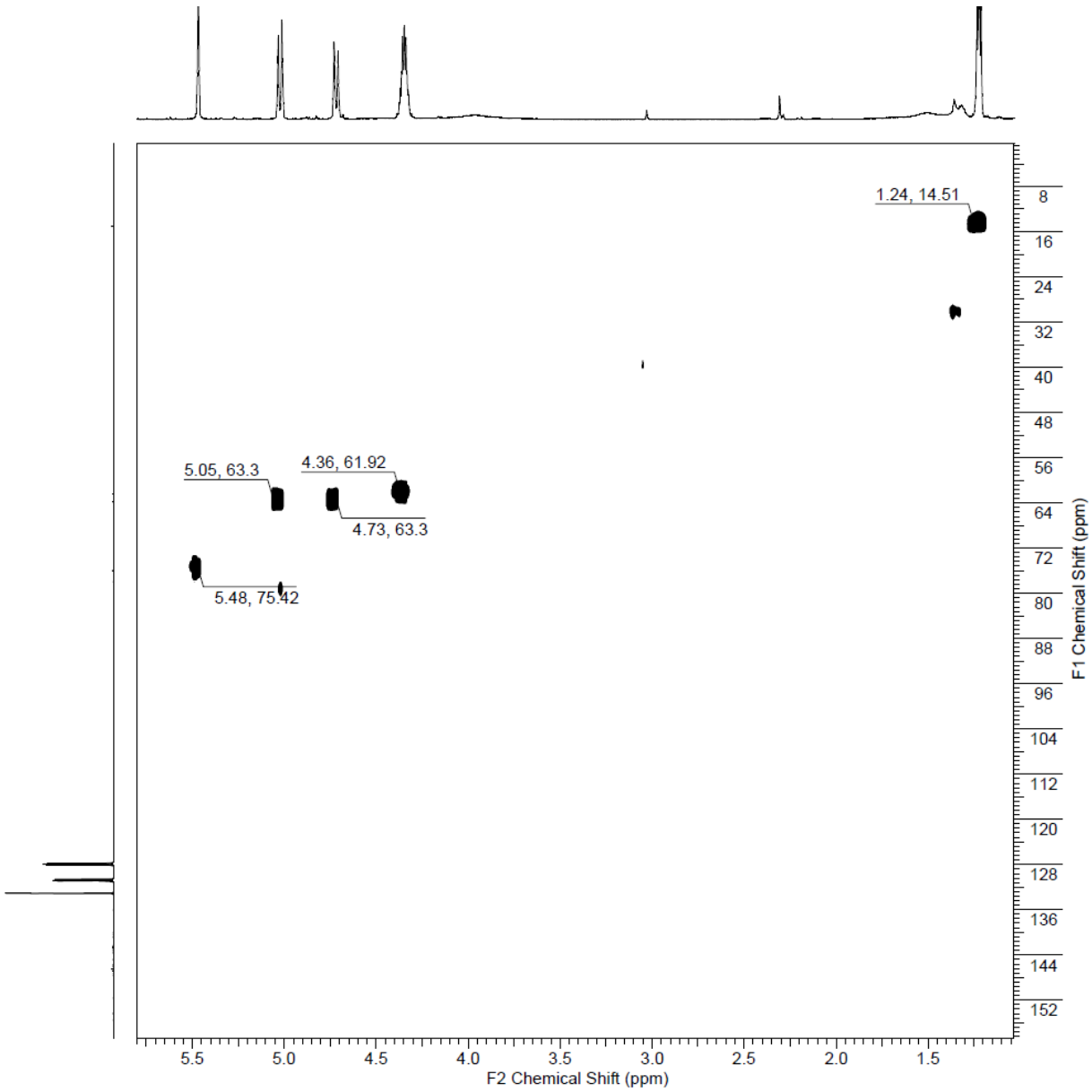



**Figure S 22.** $^{1}H–^{13}C$ HSQC spectrum of compound **1b**.

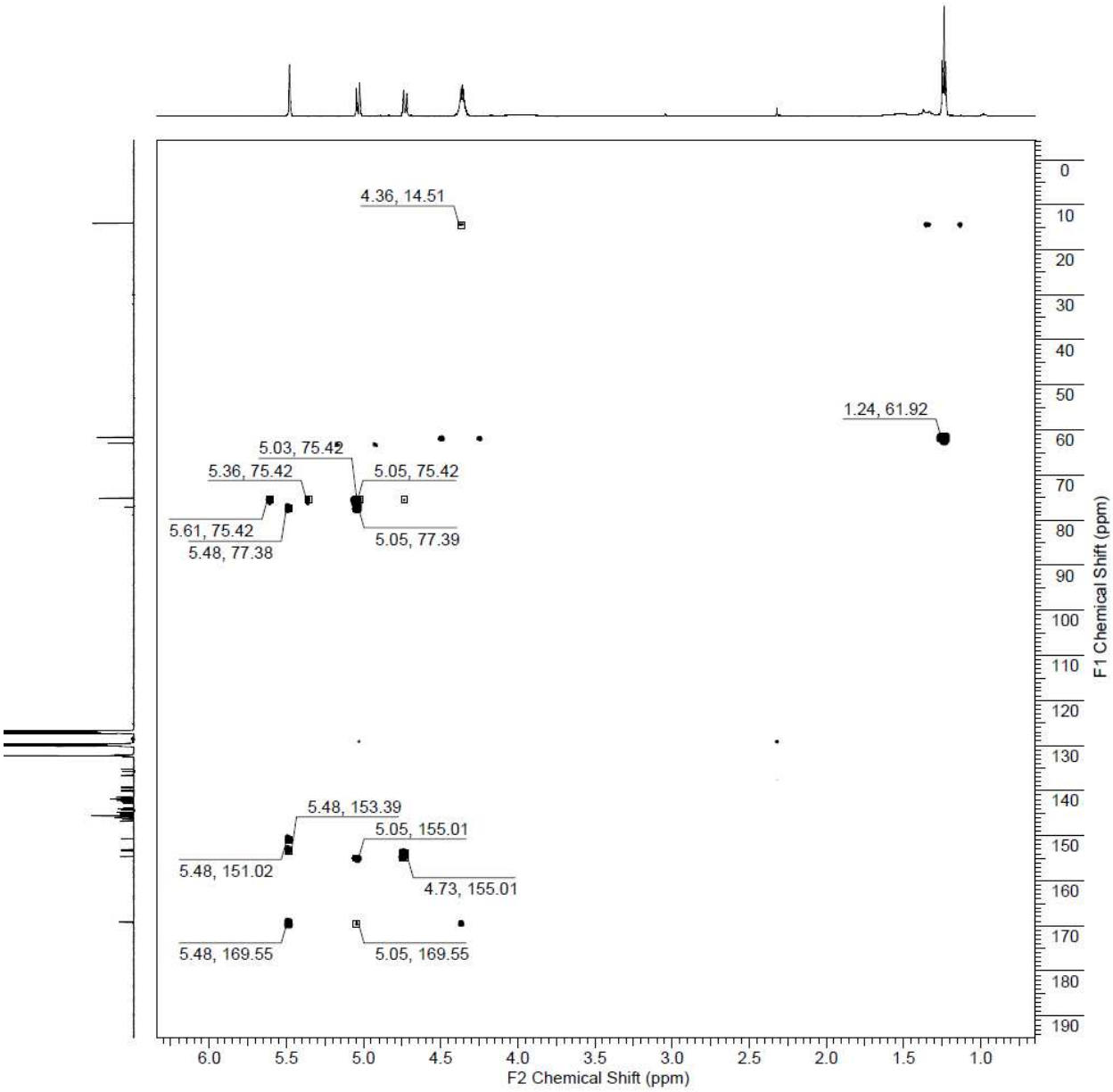



**Figure S 23.** $^{1}H–^{13}C$ HMBC spectrum of compound **1b**.

## 3. Mass spectra of the synthesized compounds

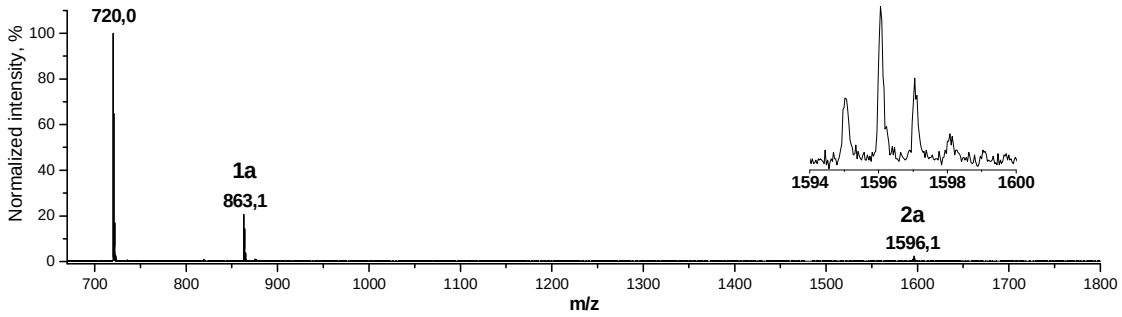



**Figure S 24.** MALDI mass spectrum of the reaction mixture after synthesis of **1a**. Inset: mass range 1594–1600.

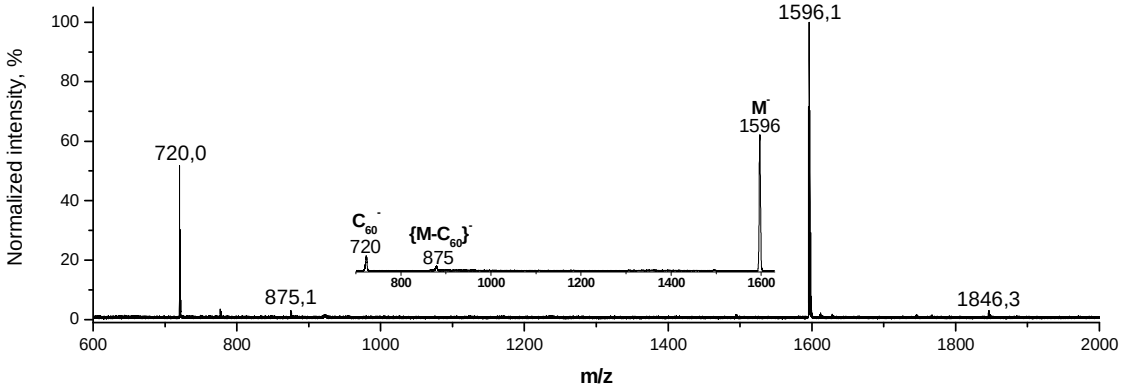



**Figure S 25.** MALDI mass spectrum of compound **2a**. Inset: PSD spectrum of $M^-$, M= **2a**.

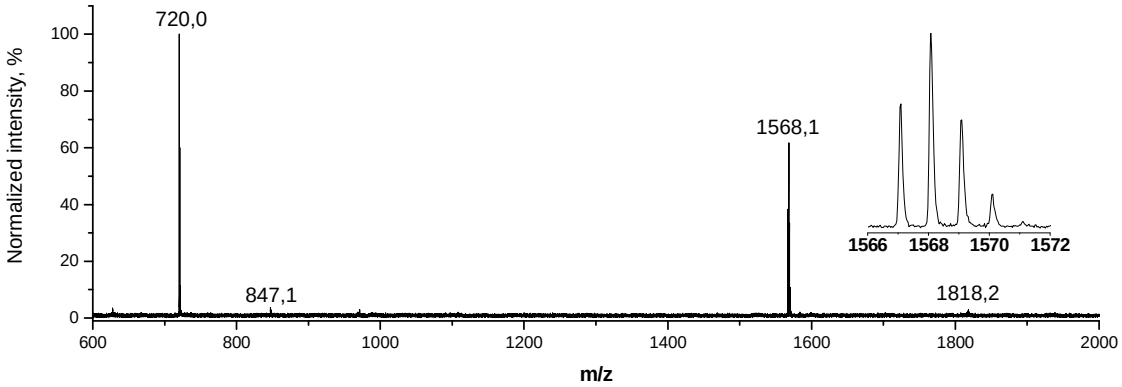



**Figure S 26.** MALDI mass-spectrum of compound **2b**. Inset: mass range 1566–1572.

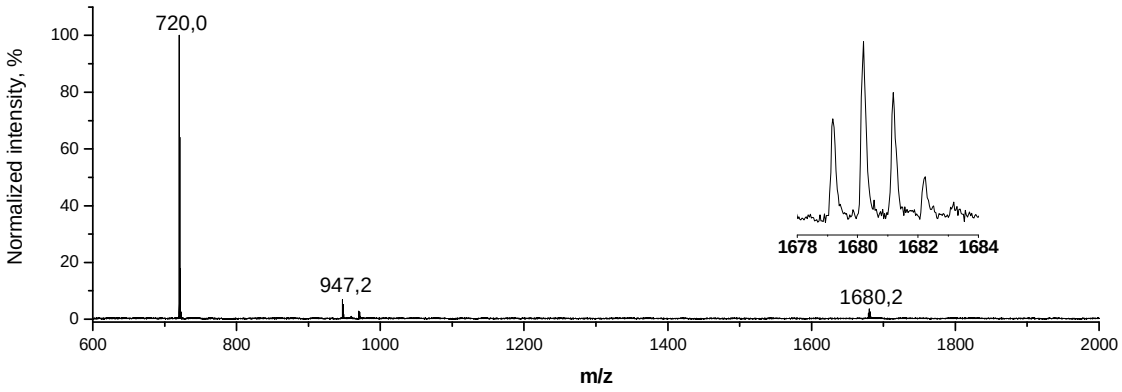



**Figure S 27.** MALDI mass-spectrum of compound **2c**. Inset: mass range 1678–1684.

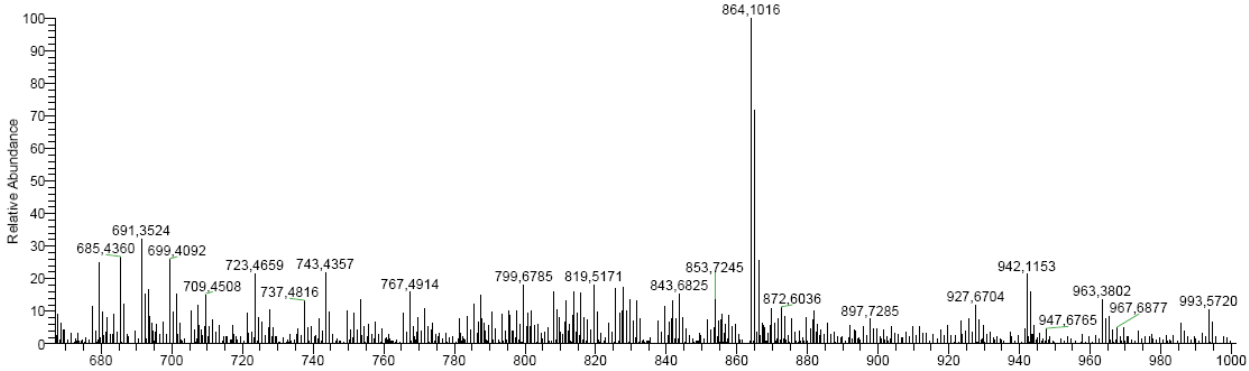



**Figure S 28.** HRMS spectrum (ESI) of compound **1a**.

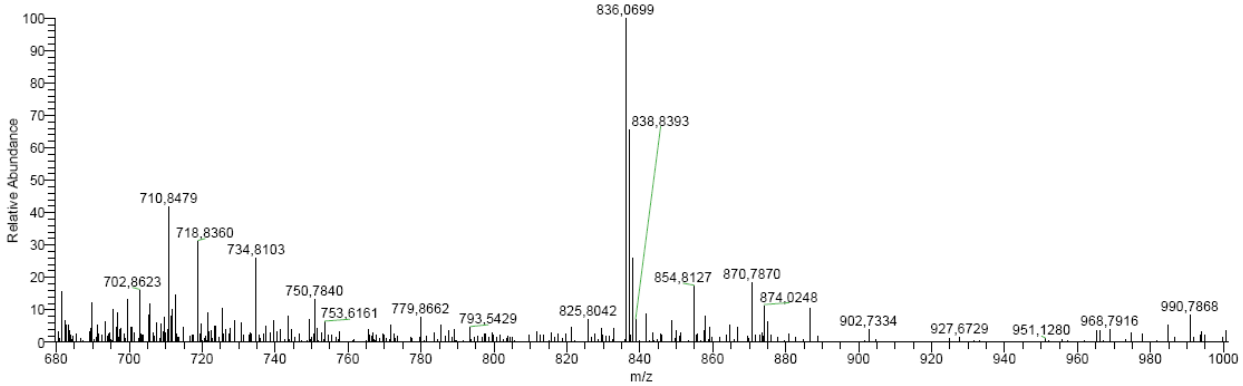



**Figure S 29.** HRMS spectrum (ESI) of compound **1b**.

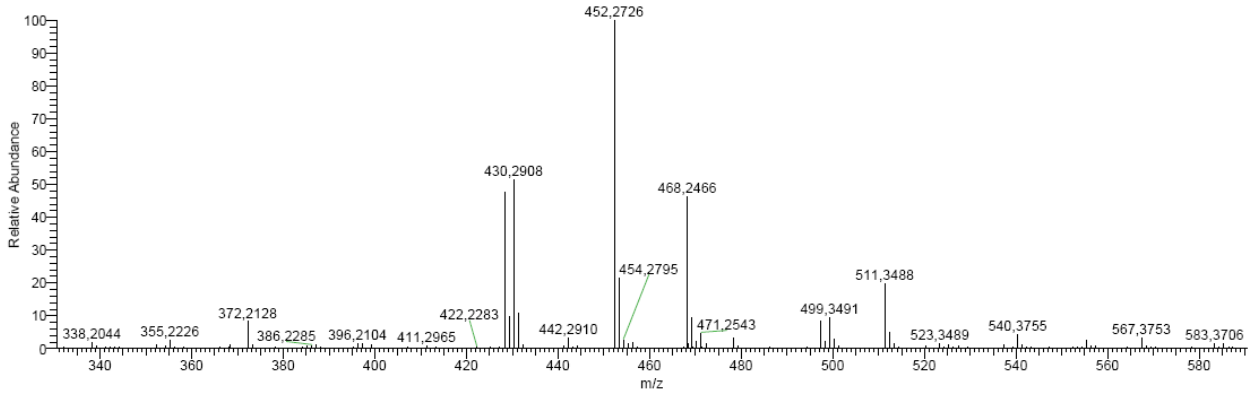



**Figure S 30.** HRMS spectrum (ESI) of compound **3a**.

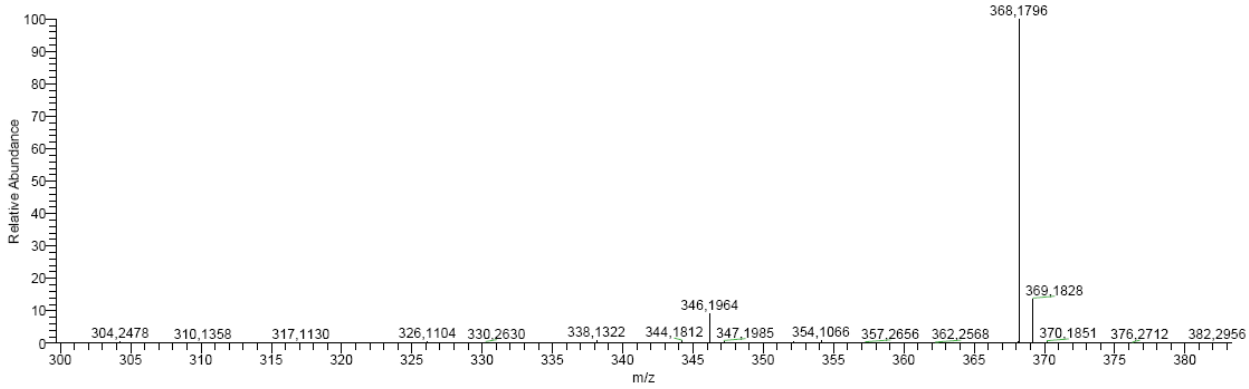



**Figure S 31.** HRMS spectrum (ESI) of compound **3b**.

## 4. UV/Vis spectra of compounds 1a-c and 2a-c

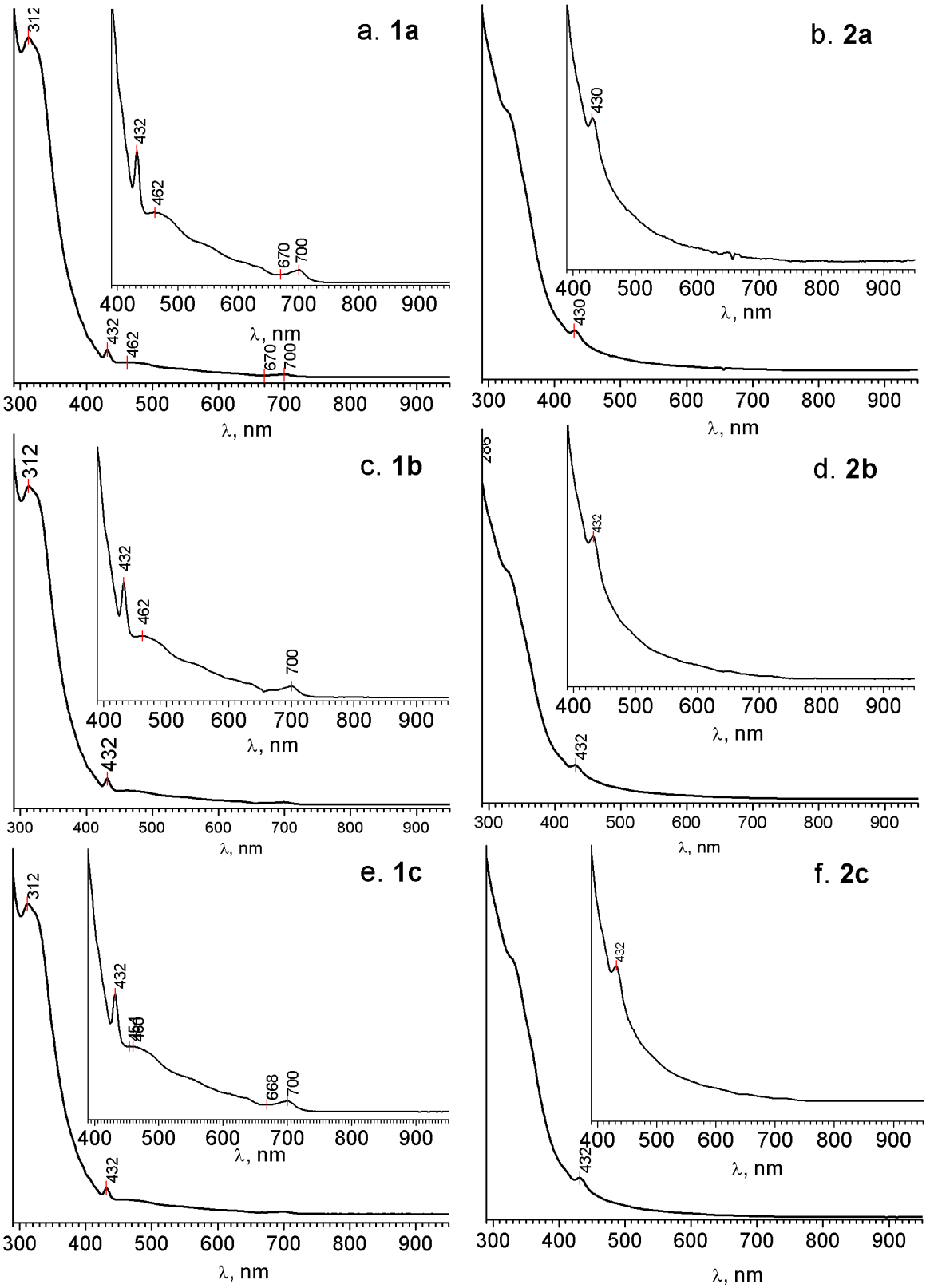



**Figure S 32.** UV/Vis spectra of fulleropyrrolidines **1a**–**1c** and double-caged derivatives **2a**–**2c** (solvent toluene, 290–950 nm range).

## 5. Quantum chemical calculations

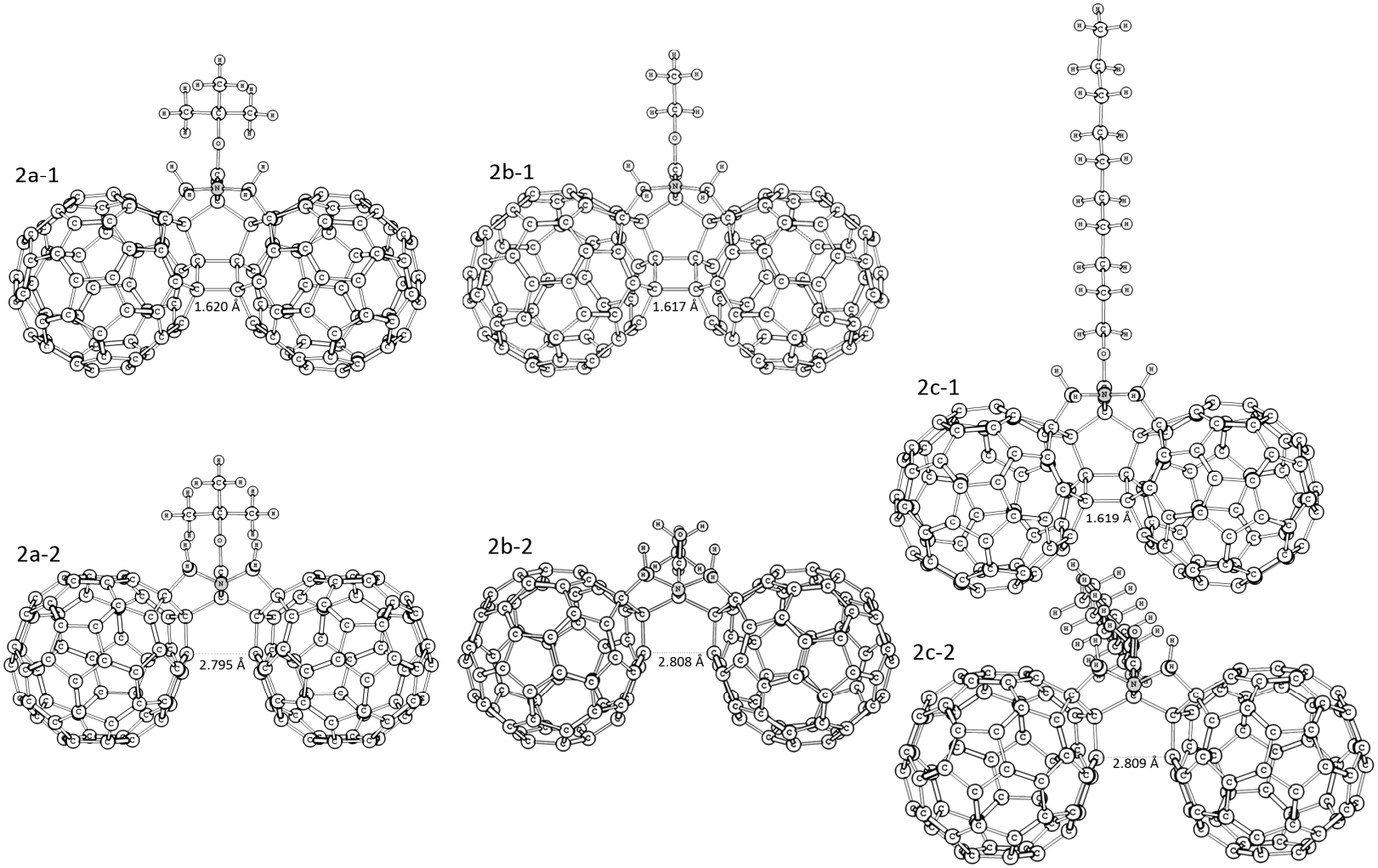
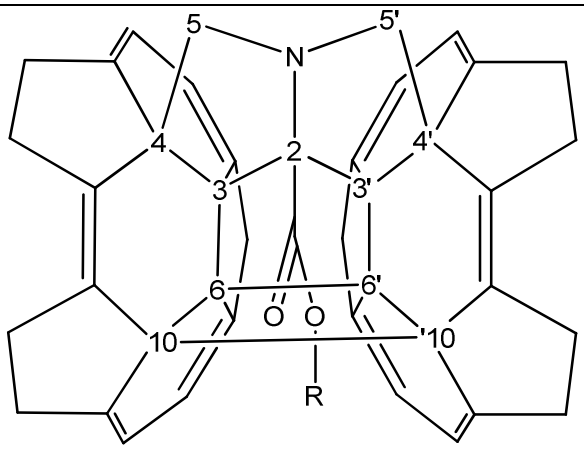



**Figure S 33.** Side views of two configurations of the DFT-optimized double-caged derivatives **2a–c** (the best conformation are shown)

**Table S 1.** Relative DFT energy values (PBE/TZ2P, kJ·mol$^{-1}$) of various configurations of double-caged derivatives **2a**–**2c** (structures are shown on figures 34 at page *S*29)

| **Configuration #** | **2a** | **2b** | **2c** |
|---|---|---|---|
| 1 (*cis*-1) | 0 | 0 | 0 |
| 2 (without cyclobutane bridge) | 33.5 | 28.4 | 28.8 |

**Table S 2.** Experimental and DFT-calculated (PBE/TZ2P) $^{13}$C chemical shifts for **2a**, **2b**, **2c** and their $C_s$-symmetrical configurations #1 and #2 (for structures see figures 34 at page *S*29)

| **Comp.** | **Carbon atom** | **$^{13}$C chemical shift (ppm)** | | | **Scheme of carbon atom numeration** |
|---|---|---|---|---|---|
| | | **Exp.** | **Predicted for configuration** | | |
| | | | **1** | **2** | |
| **2a** | C(2) | 108.95 | 109.0 | 101.5 |  |
| | C(3) | 84.65 | 87.5 | 80.3 | |
| | C(4) | 69.67 | 72.8 | 75.8 | |
| | C(5) | 71.86 | 67.2 | 54.7 | |
| | C(6) | 77.27 | 78.2 | 148.0 | |
| | C(10) | 70.99 | 74.3 | 133.5 | |
| | C(O) | 168.11 | 164.4 | 163.1 | |
| | O–$CMe_3$ | 84.13 | 84.0 | 87.0 | |
| | $CH_3$ | 28.03 | 20.7 | 21.6 | |
| | | | | | |
| **2b** | C(2) | 108.35 | 110.0 | 97.8 | |
| | C(3) | 84.48 | 87.8 | 79.4 | |
| | C(4) | 69.11 | 72.3 | 75.8 | |
| | C(5) | 71.73 | 68.7 | 54.1 | |
| | C(6) | 77.31 | 78.3 | 148.3 | |
| | C(10) | 74.32 | 74.1 | 133.4 | |
| | C(O) | 169.76 | 165.1 | 162.7 | |
| | O–$CH_2$ | 61.55 | 60.3 | 58.6 | |
| | $CH_3$ | 14.09 | 7.1 | 5.3 | |
| | | | | | |
| **2c** | C(2) | 109.53 | 109.4 | 97.9 | |
| | C(3) | 84.64 | 87.6 | 79.3 | |
| | C(4) | 69.08 | 72.6 | 75.8 | |
| | C(5) | 71.86 | 67.6 | 54.1 | |
| | C(6) | – | 78.3 | 148.3 | |
| | C(10) | – | 74.1 | 133.4 | |
| | C(O) | 169.93 | 164.5 | 162.4 | |
| | O–$CH_2$ | 66.13 | 64.8 | 63.6 | |
| | $CH_3$ | 14.41 | 8.5 | 7.4 | |

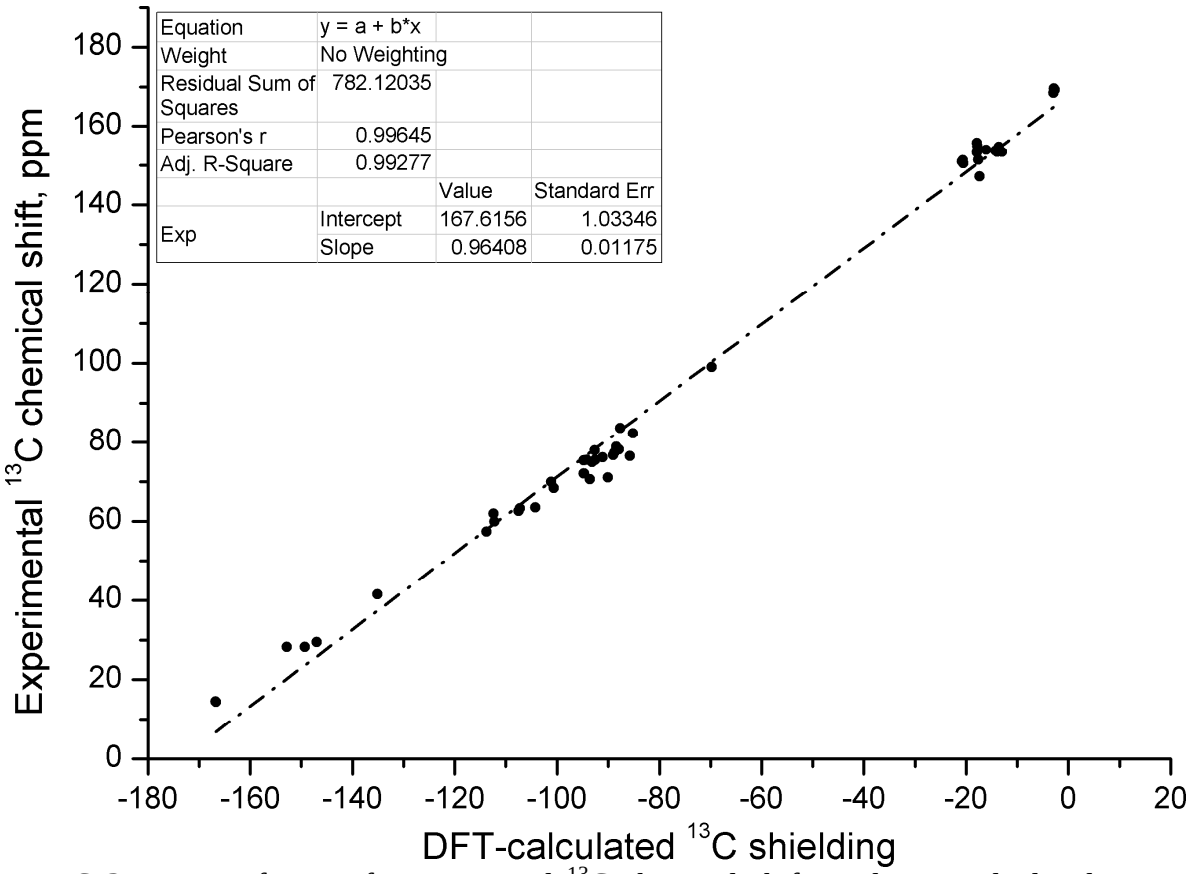
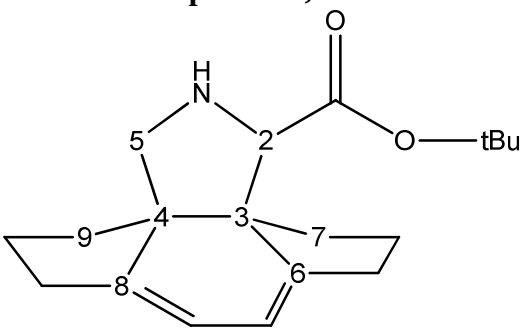
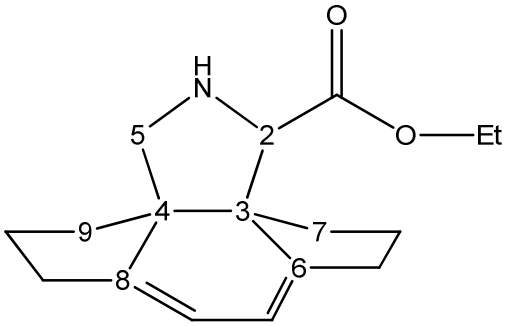
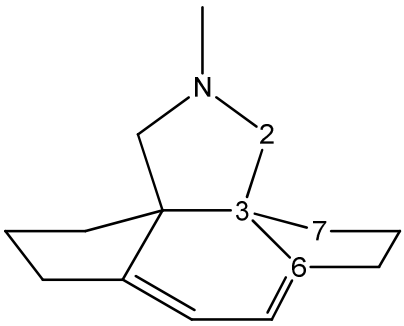
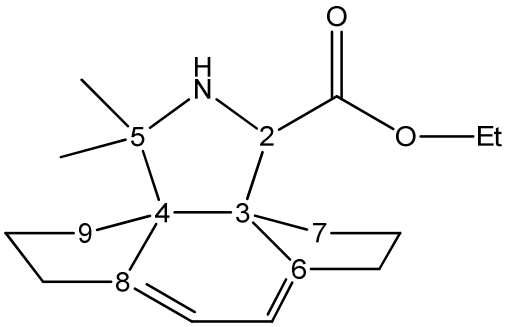
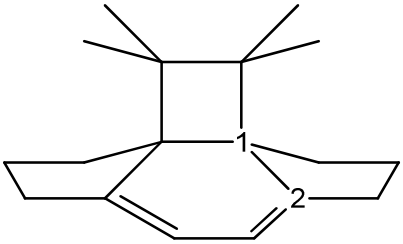
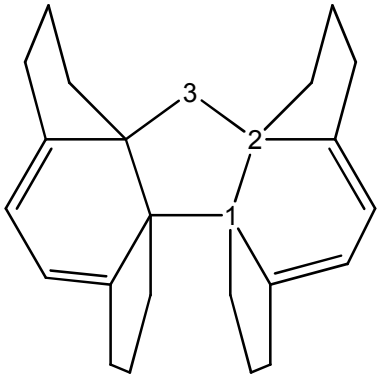
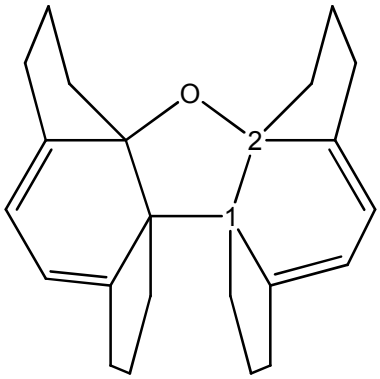
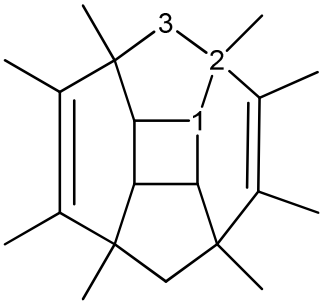



**Figure S 34.** Linear fitting of experimental $^{13}$C chemical shifts and DFT-calculated isotropic shielding values (PBE/TZ2P) for related fullerene derivatives (see Table S4 for details).

**Table S3.** Experimental $^{13}C$ chemical shifts, DFT-calculated isotropic shielding values (PBE/TZ2P) and predicted $^{13}C$ chemical shifts for related fullerene derivatives.

| Compound | Carbon atom | $^{13}C$ chemical shift (ppm) | | |
|---|---|---|---|---|
| | | Exp. | DFT predicted | |
| | | | isotropic shielding | Fitted value |
| **Fpr-O*t*Bu, 1a**  | C(2) | 75.49 | –94.2 | 75.49 |
| | C(3) | 76.55 | –89.0 | 76.7 |
| | C(4) | 75.81 | –92.5 | 75.5 |
| | C(5) | 62.62 | –107.5 | 62.62 |
| | C(O) | 168.5 | –2.9 | 168.5 |
| | C–$Me_3$ | 83.73 | –87.7 | 83.73 |
| | $CH_3$ | 28.27 | –152.9 | 28.27 |
| | C(6) | 150.53 | –20.6 | 150.53 |
| | C(7) | 153.53 | –13.7 | 153.53 |
| | C(8) | 155.73 | –17.9 | 155.73 |
| | C(9) | 153.85 | –13.9 | 153.85 |
| **Fpr-OEt, 1b**  | C(2) | 75.42 | –94.8 | 75.42 |
| | C(3) | 77.39 | –88.7 | 77.39 |
| | C(4) | 78.29 | –92.6 | 78 |
| | C(5) | 63.3 | –107.2 | 63.3 |
| | C(O) | 169.55 | –2.8 | 169.55 |
| | $OCH_2$ | 61.92 | –112.4 | 61.92 |
| | $CH_3$ | 14.51 | –166.7 | 14.51 |
| | C(6) | 151.02 | –20.8 | 151.02 |
| | C(7) | 153.39 | –13.9 | 153.39 |
| | C(8) | 155.01 | –17.8 | 155.01 |
| | C(9) | 153.79 | –14.2 | 153.79 |
| **MeFP [S1]**  | C(2) | 69.97 | –101.1 | 69.97 |
| | C(3) | 71.07 | –90.1 | 71.07 |
| | C(6) | 154.72 | –13.6 | 154.72 |
| | C(7) | 147.2 | –17.4 | 147.2 |
| | $CH_3$ | 41.48 | –135.1 | 41.48 |
| **$Me_2$FPr-OEt [S2]**  | C(2) | 72.1 | –94.7 | 72.1 |
| | C(3) | 78.2 | –87.9 | 78.2 |
| | C(4) | 76.5 | –85.8 | 76.5 |
| | C(5) | 70.6 | –93.6 | 70.6 |
| | C(O) | 169.2 | –2.6 | 169.2 |
| | $OCH_2$ | 61.9 | –112.4 | 61.9 |
| | $CH_3$(Et) | 14.4 | –166.7 | 14.4 |
| | C(6) | 151.3 | –20.6 | 151.3 |
| | C(7) | 153.4 | –13.0 | 153.4 |
| | C(8) | 153.3 | –17.9 | 153.3 |
| | C(9) | 154 | –16.1 | 154 |
| | $CH_3$(1) | 28.2 | –149.3 | 28.2 |

| | | | | |
|---|---|---|---|---|
| | $CH_3$(2) | 29.4 | –147.0 | 29.4 |
| **[6,6]-$C_{120}$ [S3]**   | C(1) | 76.22 | –91.1 | 79.8 |
| | C(2) | 151.42 | –17.7 | 150.6 |
| **$C_{120}CH_2$ [S4]**   | C(1) | 82.4 | –85.1 | 85.5 |
| | C(2) | 68.4 | –100.6 | 70.6 |
| | C(3), $CH_2$ | 59.9 | –112.2 | 59.5 |
| **$C_{120}O$ [S4]**   | C(1) | 78.9 | –88.4 | 82.4 |
| | C(2) | 99 | –69.7 | 100.4 |
| **$C_{120}(CH_2)_2$ [S5]**   | C(1) | 74.93 | –93.2 | 77.8 |
| | C(2) | 63.52 | –104.2 | 67.2 |
| | C(3), $CH_2$ | 57.35 | –113.7 | 58.0 |

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