

Electronic Supplementary Information

Unexpected and divergent mechanosynthesis of furanoid-bridged fullerene dimers C₁₂₀O and C₁₂₀O₂

Gang Shao,^{a,†} Yuan-Yuan Liu,^{a,†} Chuang Niu,^b Zheng-Chun Yin,^b Shi-Qi Ye,^a Yang-Rong Yao,^d Muqing Chen,^e Jun-Shen Chen,^a Xu-Ling Xia,^a Shangfeng Yang,^{*,d} and Guan-Wu Wang^{*,a,b,c}

^aHefei National Research Center for Physical Sciences at the Microscale and Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China

^bKey Laboratory of Functional Molecular Solids, Ministry of Education, Anhui Laboratory of Molecule-Based Materials, and School of Chemistry and Materials Science, Anhui Normal University, Wuhu, Anhui 241002, P. R. China

^cState Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou, Gansu 730000, P. R. China

^dHefei National Research Center for Physical Sciences at the Microscale, CAS Key Laboratory of Materials for Energy Conversion, and Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, Anhui, 230026, P. R. China

^eSchool of Environment and Civil Engineering, Dongguan University of Technology, Dongguan, Guangdong, 523808, P. R. China

[†]Authors with equal contribution.

Table of Contents

1. General Information.....	S2
2. Synthesis and Spectral Data of C ₁₂₀ O and C ₁₂₀ O ₂	S2
3. X-Ray Data of C ₁₂₀ O and C ₁₂₀ O ₂	S5
4. TGA Analyses of C ₁₂₀ O and C ₁₂₀ O ₂	S9
5. ¹⁸ O Labelling Experiments.....	S10
6. Detection of Ferrous Iron.....	S12
7. X-Ray Photoelectron Spectroscopy of the Reaction Mixture.....	S12
8. Device Fabrication and Photovoltaic Parameters.....	S13
9. ¹³ C NMR Spectra of C ₁₂₀ O and C ₁₂₀ O ₂	S15

1. General Information

Commercially available reagents were used without further purification. ^{13}C NMR spectra were recorded on a 500 MHz NMR spectrometer (126 MHz for ^{13}C NMR). ^{13}C NMR chemical shifts were determined relative to that of TMS. High-resolution mass spectra (HRMS) were measured with MALDI-TOF in negative mode. Ball-milling reactions were performed in a custom-made GT 300 mixer mill (milling frequency up to 35 Hz, Fig. S1a) or a custom-made GT 600 mixer mill (milling frequency up to 60 Hz, Fig. S1b) using a stainless steel jar (5 mL) along with 4 stainless steel balls (5 mm in diameter, 0.5 g) and milled vigorously at 25–45 Hz at room temperature. The custom-made GT 300 mixer mill and GT 600 mixer mill are products from Beijing Grinder Instrument Co., Ltd.

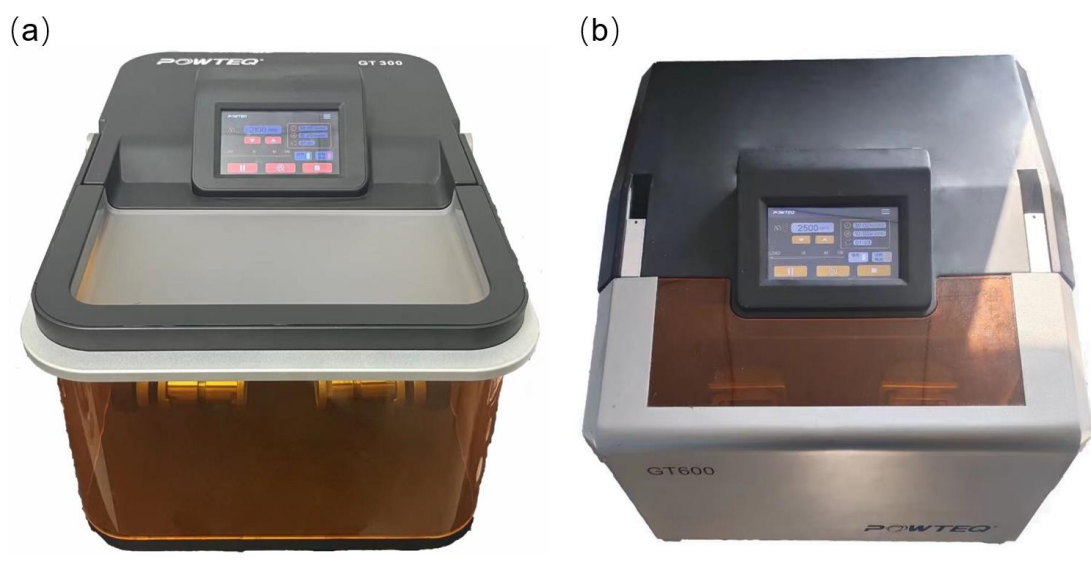
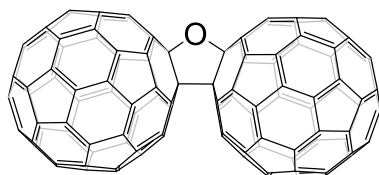


Fig. S1 Photos of (a) custom-made GT 300 mixer mill and (b) custom-made GT 600 mixer mill.

2. Synthesis and Spectral Data of C_{120}O and C_{120}O_2



Synthesis and Spectral Data of C_{120}O :

A mixture of C_{60} (36.0 mg, 0.05 mmol), FeCl_3 (56.1 mg, 0.35 mmol) and H_2O (15.0 μL , 0.75 mmol) together with 4 stainless steel balls (5 mm in diameter) was introduced into a stainless steel jar (5 mL) and milled vigorously (30.0 Hz) in a GT 300 mixer mill at room temperature for 90 min. Afterwards, the reaction mixture was extracted with 1,2-dichlorobenzene (1,2- $\text{C}_6\text{H}_4\text{Cl}_2$) and separated by column chromatography on silica

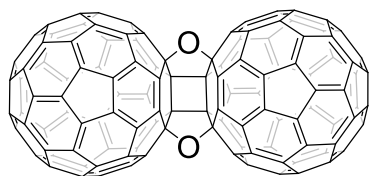
gel with CS₂ as the eluent to remove the insoluble materials and then purification by recycling high-performance liquid chromatography (HPLC) using a Cosmosil Buckyprep-D column (10 × 250 mm, 25 °C, toluene as the eluent, 3.0 mL/min) afforded C₁₂₀O (9.1 mg, 25%) as an amorphous brown solid and unreacted C₆₀ (8.3 mg, 23%).

¹³C NMR (126 MHz, 1,2-C₆D₄Cl₂, 4.9 mmol dm⁻³ Cr(acac)₃ as relaxation reagent) δ 152.47 (4C), 149.74 (4C), 146.90 (2C), 146.47 (2C), 145.22 (4C), 145.14 (4C), 145.03 (4C), 144.86 (4C), 144.68 (4C), 144.43 (4C), 143.91 (4C), 143.86 (4C), 143.82 (4C), 143.80 (4C), 143.33 (4C), 143.32 (4C), 143.08 (4C), 141.70 (4C), 141.38 (4C), 141.35 (4C), 141.15 (4C), 140.99 (4C), 140.90 (4C), 140.88 (4C), 140.81 (4C), 140.45 (4C), 138.89 (4C), 138.79 (4C), 136.42 (4C), 135.01 (4C), 97.78 (2C, sp³-C of C₆₀), 77.71 (2C, sp³-C of C₆₀);

FT-IR ν/cm⁻¹ (KBr) 1459, 1423, 1260, 1190, 1109, 1047, 1008, 961, 952, 872, 839, 792, 776, 764, 747, 719, 709, 669, 633, 617, 599, 586, 569, 552, 537, 527;

UV-vis (1,2-C₆H₄Cl₂) λ_{max}/nm (log ε) 293 (4.95), 328 (5.04), 434 (3.90), 542 (3.45), 695 (2.81);

MALDI-TOF MS m/z calcd for C₁₂₀O [M]⁻ 1456.9988, found 1456.9984.



Synthesis and Spectral Data of C₁₂₀O₂:

A mixture of C₆₀ (35.8 mg, 0.05 mmol), FeCl₃ (85.3 mg, 0.50 mmol) and H₂O (15.0 μL, 0.75 mmol) together with 4 stainless steel balls (5 mm in diameter) was introduced into a stainless steel jar (5 mL) and milled vigorously (41.7 Hz) in a GT 600 mixer mill at room temperature for 90 min. Afterwards, the reaction mixture was extracted with 1,2-C₆H₄Cl₂ and separated by column chromatography on silica gel with CS₂ as the eluent to remove the insoluble materials and then purification by HPLC using a Cosmosil Buckyprep-D column (10 × 250 mm, 25 °C, toluene as the eluent, 3.0 mL/min) afforded C₁₂₀O₂ (16.5 mg, 45%) as an amorphous brown solid and unreacted C₆₀ (9.7 mg, 27%).

¹³C NMR (126 MHz, 1,2-C₆D₄Cl₂) δ 147.82 (4C), 147.74 (2C), 147.56 (4C), 147.00 (4C), 146.56 (4C), 145.55 (4C), 145.05 (4C), 145.03 (4C), 144.98 (4C), 144.14 (4C), 144.12 (4C), 143.92 (4C), 143.83 (4C), 143.35 (4C), 143.23 (8C), 142.93 (4C), 142.72 (4C), 142.69 (4C), 142.60 (4C), 142.47 (4C), 141.82 (2C), 141.47 (2C), 140.84 (4C), 140.52 (4C), 140.48 (4C), 139.25 (4C), 138.39 (4C), 137.27 (2C), 136.28 (4C), 91.09 (4C, sp³-C of C₆₀);

¹³C NMR (126 MHz, 1,2-C₆D₄Cl₂, 4.9 mmol dm⁻³ Cr(acac)₃ as relaxation reagent) δ 147.83 (6C), 147.58 (4C), 147.02 (4C), 146.58 (4C), 145.55 (4C), 145.05 (12C), 144.15 (8C), 143.93 (4C), 143.85 (4C), 143.34 (4C), 143.25 (8C), 142.94 (4C), 142.71 (12C),

142.49 (4C), 141.90 (2C), 141.49 (2C), 140.85 (4C), 140.52 (8C), 139.27 (4C), 138.40 (4C), 137.28 (2C), 136.29 (4C), 91.09 (4C, sp³-C of C₆₀), 71.13 (4C, sp³-C of C₆₀);
FT-IR ν/cm^{-1} (KBr) 1463, 1424, 1189, 1108, 1047, 1007, 961, 951, 838, 815, 792, 776, 764, 749, 729, 719, 710, 631, 618, 599, 586, 569, 563, 551, 537, 526;
UV-vis (1,2-C₆H₄Cl₂) $\lambda_{\text{max}}/\text{nm}$ (log ϵ) 319 (5.12), 425 (4.12), 632 (2.90), 695 (2.54);
MALDI-TOF MS m/z calcd for C₁₂₀O₂ [M]⁻ 1472.9937, found 1472.9930.

3. X-Ray Data of C₁₂₀O and C₁₂₀O₂

Crystal growth of C₁₂₀O was accomplished by slow evaporation from a mixture containing purified C₁₂₀O dissolved in carbon disulfide and decapyrrylcorannulene (DPC) dissolved in toluene at about 4 °C. Single-crystal X-ray diffraction data were collected on a diffractometer (SuperNova, Rigaku) equipped with a CCD area detector using graphite-monochromated CuK α radiation ($\lambda = 1.54184 \text{ \AA}$) in the scan range of $7.06^\circ < 2\theta < 146.152^\circ$. The structure was solved with direct methods using SHELXT and refined with full-matrix least-squares refinement using the SHELXL program within OLEX2. Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre as deposition number CCDC 2289163.

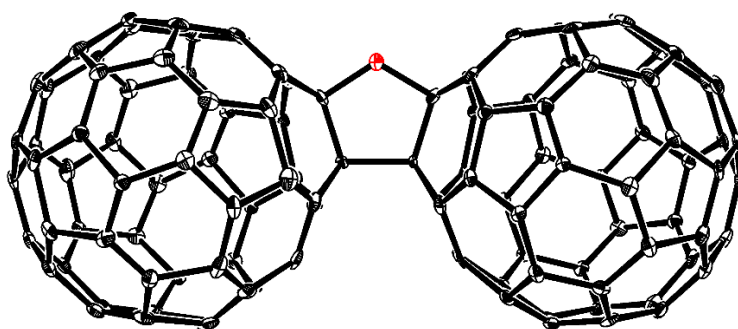


Fig. S2 ORTEP diagram of C₁₂₀O with 10% thermal ellipsoids. The solvent molecules are omitted for clarity.

Table S1 Crystal Data and Structure Refinement for C₁₂₀O.

Identification code	2289163
Empirical formula	C ₇₂₀ H ₃₂₀ N ₈₀ O ₂
Formula weight	10122.54
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	14.2723(4)
b/Å	29.9136(10)
c/Å	32.5999(10)
α/°	105.970(3)
β/°	94.818(2)
γ/°	100.160(3)
Volume/Å ³	13041.3(7)
Z	1
ρ _{calc} g/cm ³	1.289
μ/mm ⁻¹	0.609
F(000)	5216.0
Crystal size/mm ³	0.20 × 0.20 × 0.05
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	7.06 to 146.152
Index ranges	-10 ≤ h ≤ 17, -36 ≤ k ≤ 37, -40 ≤ l ≤ 35
Reflections collected	92846
Independent reflections	50450 [R _{int} = 0.0845, R _{sigma} = 0.1350]
Data/restraints/parameters	50450/7598/5320
Goodness-of-fit on F ²	0.984
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0778, wR ₂ = 0.1744
Final R indexes [all data]	R ₁ = 0.1376, wR ₂ = 0.2167
Largest diff. peak/hole / e Å ⁻³	0.60/-0.30

Crystal growth of $C_{120}O_2$ was accomplished by slow evaporation from a mixture containing purified $C_{120}O_2$ dissolved in carbon disulfide and DPC dissolved in toluene at about 4 °C. Single-crystal X-ray diffraction data were collected on a diffractometer (SuperNova, Rigaku) equipped with a CCD area detector using graphite-monochromated $CuK\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$) in the scan range of $7.044^\circ < 2\theta < 146.468^\circ$. The structure was solved with direct methods using SHELXT and refined with full-matrix least-squares refinement using the SHELXL program within OLEX2. Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre as deposition number CCDC 2289161.

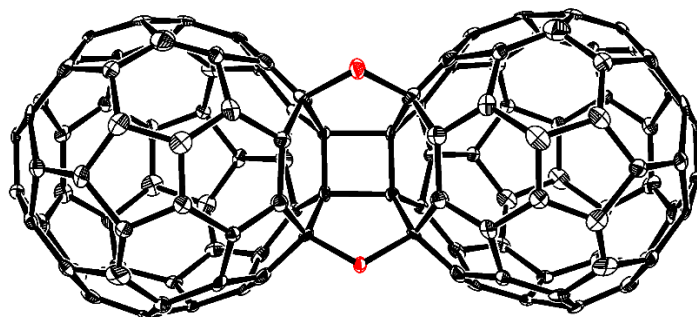


Fig. S3 ORTEP diagram of $C_{120}O_2$ with 10% thermal ellipsoids. The solvent molecules are omitted for clarity.

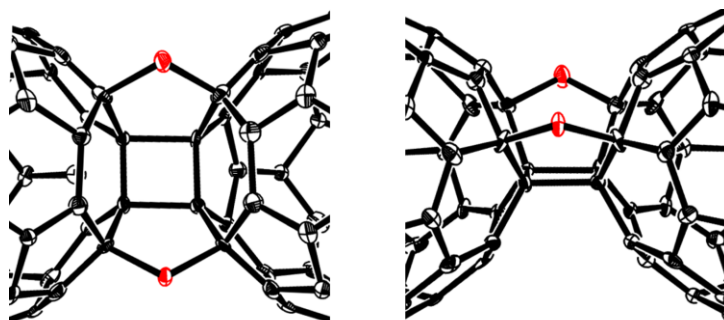


Fig. S4 The top and side views around the two oxygen atoms in $C_{120}O_2$.

Table S2 Crystal Data and Structure Refinement for C₁₂₀O₂.

Identification code	2289161
Empirical formula	C ₇₂₀ H ₃₂₀ N ₈₀ O ₄
Formula weight	10154.54
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	14.3095(3)
b/Å	29.8265(6)
c/Å	32.5209(5)
α/°	105.679(2)
β/°	94.669(2)
γ/°	100.240(2)
Volume/Å ³	13027.4(5)
Z	1
ρ _{calc} g/cm ³	1.294
μ/mm ⁻¹	0.614
F(000)	5232.0
Crystal size/mm ³	0.20 × 0.20 × 0.05
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	7.044 to 146.468
Index ranges	-17 ≤ h ≤ 17, -36 ≤ k ≤ 36, -28 ≤ l ≤ 39
Reflections collected	97104
Independent reflections	50601 [R _{int} = 0.0382, R _{sigma} = 0.0464]
Data/restraints/parameters	50601/11866/5257
Goodness-of-fit on F ²	0.844
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0839, wR ₂ = 0.2327
Final R indexes [all data]	R ₁ = 0.1050, wR ₂ = 0.2603
Largest diff. peak/hole / e Å ⁻³	1.26/-0.67

4. TGA Analyses of C₁₂₀O and C₁₂₀O₂

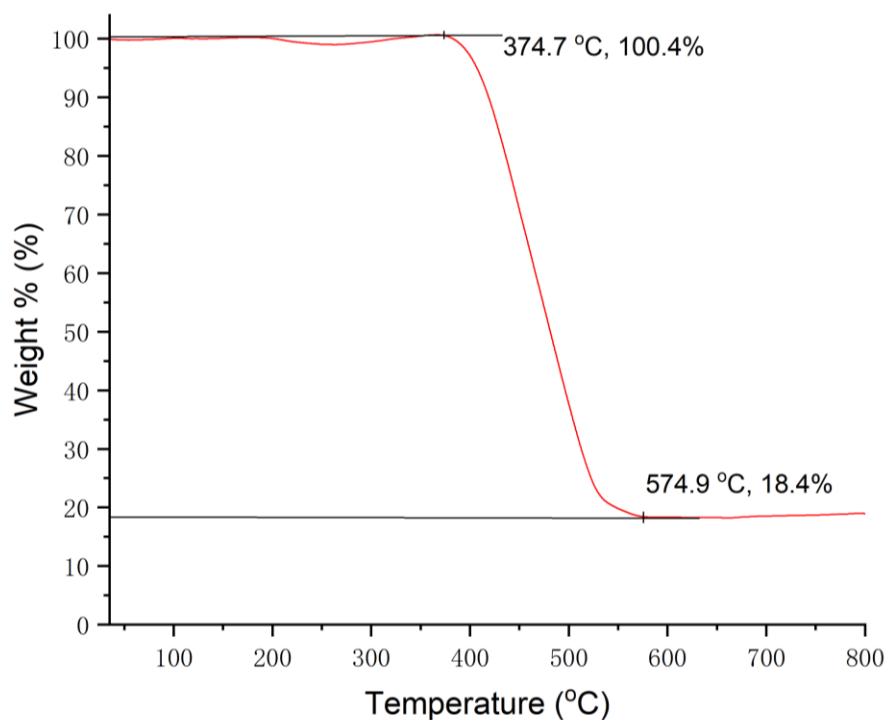


Fig. S5 TGA of C₁₂₀O under a N₂ gas flow with temperature ramp rate of 10 °C/min until 800 °C.

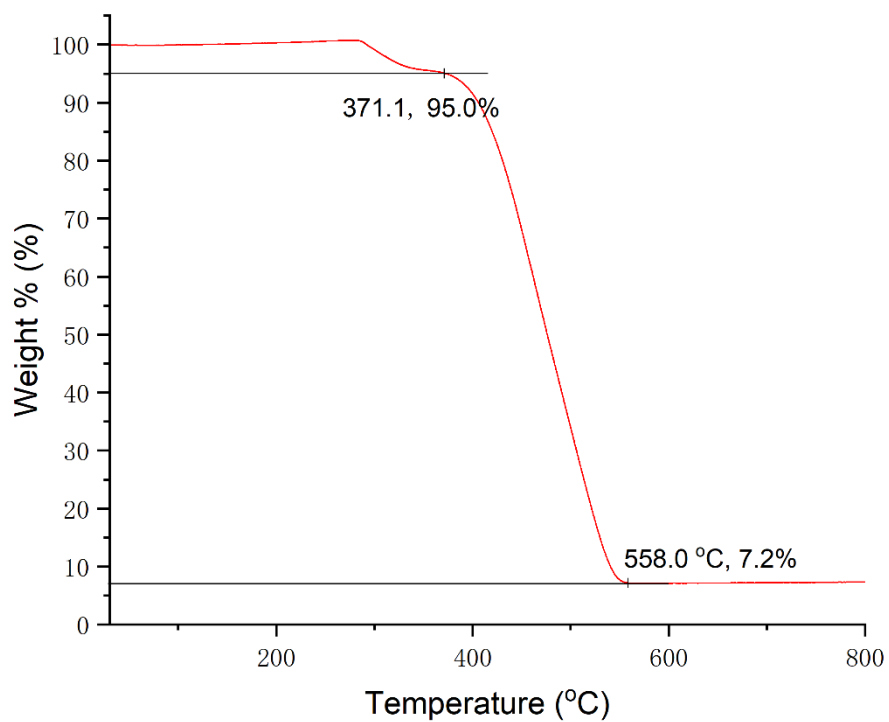


Fig. S6 TGA of C₁₂₀O₂ under a N₂ gas flow with temperature ramp rate of 10 °C/min until 800 °C.

5. ^{18}O Labelling Experiments

A mixture of C_{60} (36.3 mg, 0.05 mmol), FeCl_3 (83.9 mg, 0.50 mmol) and 10 atom % ^{18}O of H_2O (15.0 μL , 0.75 mmol) together with 4 stainless steel balls (5 mm in diameter) was introduced into a stainless steel jar (5 mL) and milled vigorously (41.7 Hz) in a GT 600 mixer mill at room temperature for 90 min. Afterwards, the reaction mixture was extracted with 1,2- $\text{C}_6\text{H}_4\text{Cl}_2$ and separated by column chromatography on silica gel with CS_2 as the eluent. Then the reaction mixture was analyzed by HRMS, and $\text{C}_{120}^{16}\text{O}_2$ without ^{18}O and $\text{C}_{120}^{16}\text{O}^{18}\text{O}$ with ^{18}O were detected.

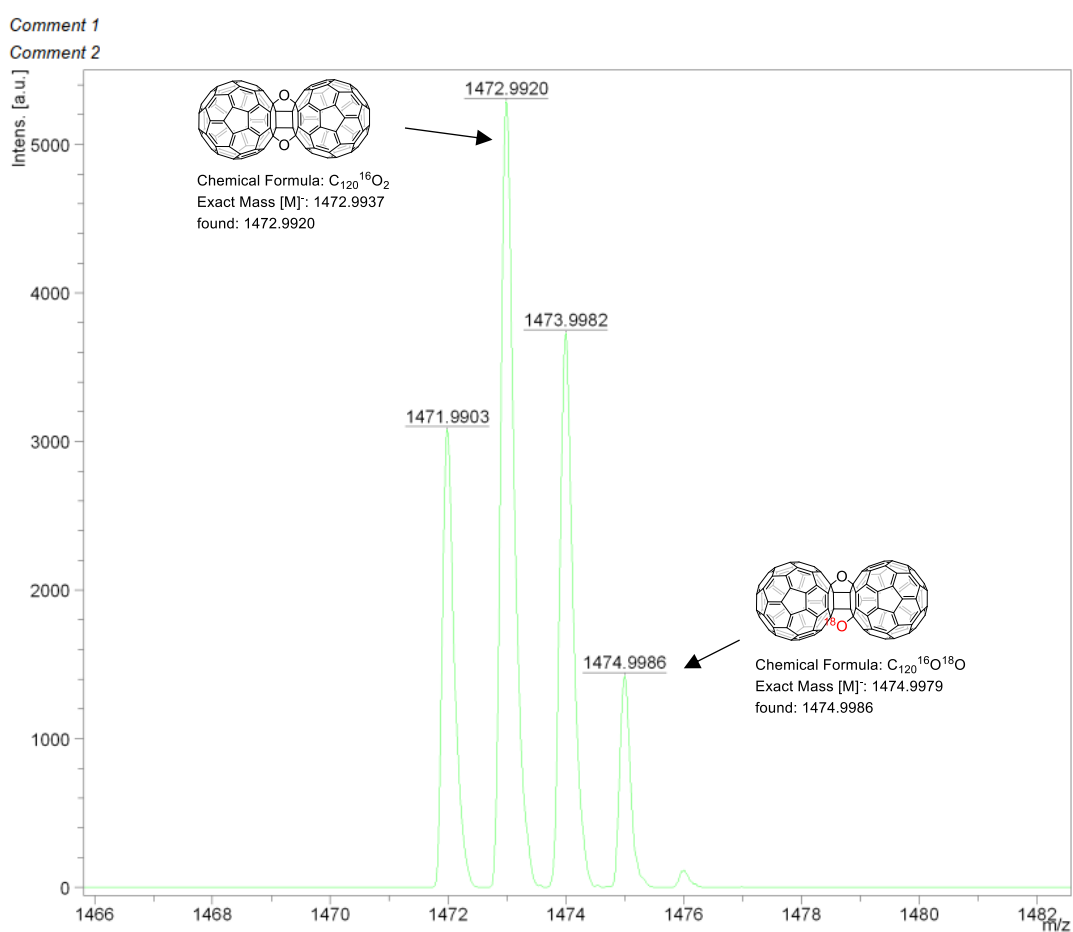


Fig. S7 Mass spectrum of the reaction mixture obtained by using 10 atom % ^{18}O of H_2O .

A mixture of C₆₀ (36.5 mg, 0.05 mmol), FeCl₃ (85.7 mg, 0.50 mmol) and 95 atom % ¹⁸O of H₂O (17.0 μL, 0.75 mmol) together with 4 stainless steel balls (5 mm in diameter) was introduced into a stainless steel jar (5 mL) and milled vigorously (41.7 Hz) in a GT 600 mixer mill at room temperature for 90 min. Afterwards, the reaction mixture was extracted with 1,2-C₆H₄Cl₂ and separated by column chromatography on silica gel with CS₂ as the eluent. Then the reaction mixture was analyzed by HRMS, and C₁₂₀¹⁸O₂ and C₁₂₀¹⁶O¹⁸O with ¹⁸O were detected.

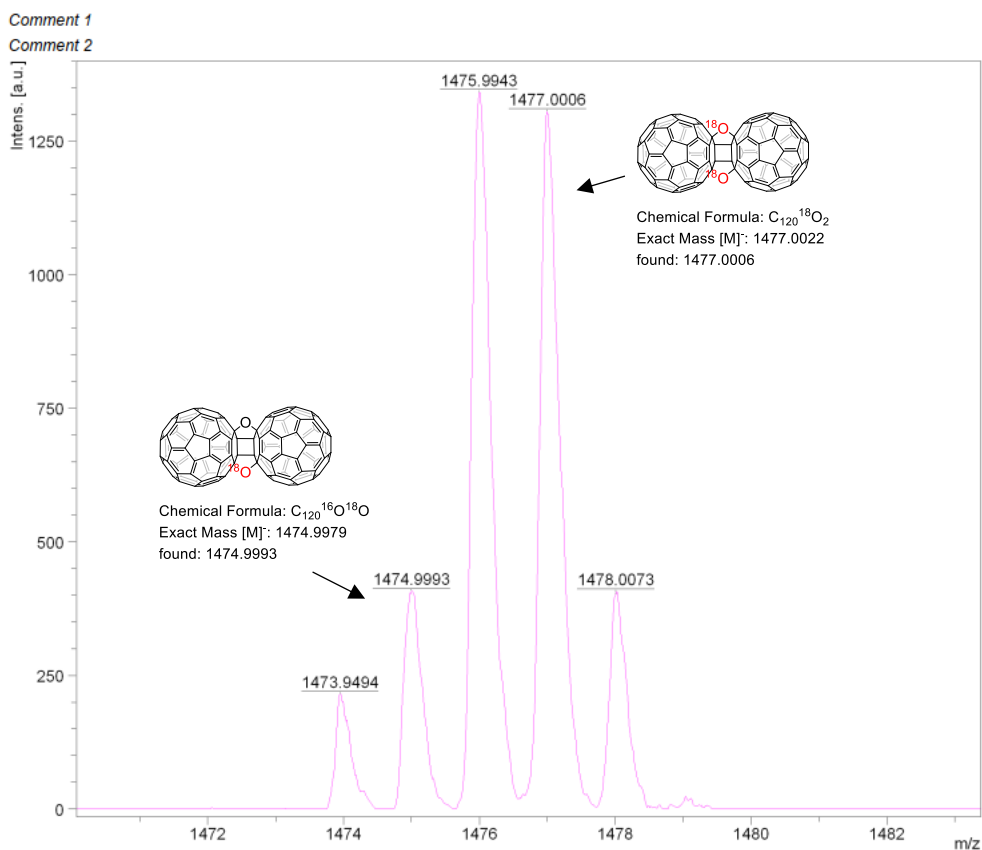


Fig. S8 Mass spectrum of the reaction mixture obtained by using 95 atom % ¹⁸O of H₂O.

6. Detection of Ferrous Iron

A mixture of C_{60} (35.8 mg, 0.05 mmol), $FeCl_3$ (85.0 mg, 0.50 mmol) and H_2O (15.0 μ L, 0.75 mmol) together with 4 stainless steel balls (5 mm in diameter) was introduced into a stainless steel jar (5 mL) and milled vigorously (41.7 Hz) in a GT 600 mixer mill at room temperature for 90 min. Afterwards, the reaction mixture was extracted with 5 mL of water and filtered to obtain a light green aqueous solution (Fig. S9c). Then, the aqueous solution of potassium ferricyanide (1%, w/v) was mixed with the aqueous solution of the reaction mixture, resulting in a Turnbull's blue precipitate (Fig. S9d). In comparison, the aqueous solution of the reactants was a yellow aqueous solution (Fig. S9a), and after mixing the aqueous solution of the reactants with the aqueous solution of potassium ferricyanide, no Turnbull's blue precipitate was formed (Fig. S9b).

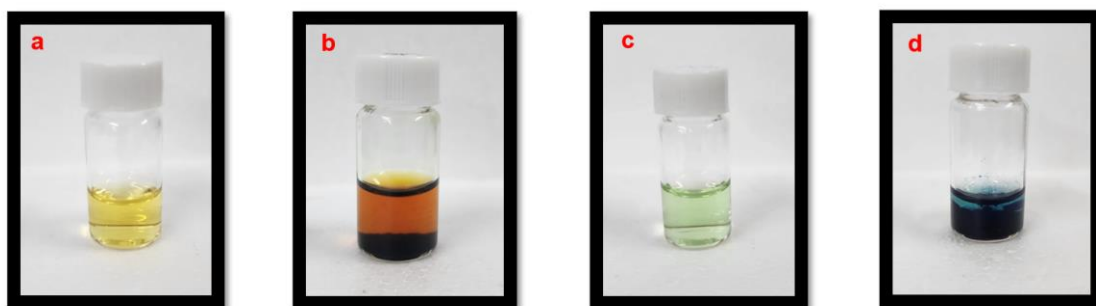


Fig. S9 (a) The color of the aqueous solution of reactants. (b) The color of the aqueous solution resulting from the mixture of reactants and potassium ferricyanide. (c) The color of the aqueous solution of the reaction mixture. (d) The color of the aqueous solution resulting from the reaction mixture and potassium ferricyanide.

7. X-Ray Photoelectron Spectroscopy of the Reaction Mixture

To further gain insight into the reaction mechanism, the crude reaction mixture was subjected to X-ray photoelectron spectroscopy (XPS) analysis. The peaks at the Fe $2p_{3/2}$ level located at 711.4 eV, 709.9 eV and 715.0 eV belonged to the Fe^{3+} , Fe^{2+} and Fe $2p_{3/2}$ level satellite peaks, respectively. While the peaks at the Fe $2p_{1/2}$ level located at 725.0 eV, 723.69 eV and 729.3 eV were attributed to the Fe^{3+} , Fe^{2+} and Fe $2p_{1/2}$ level satellite peaks, respectively. The confirmed presence of Fe^{2+} after the completion of the reaction strongly indicated that $FeCl_3$ played an oxidizing role in the reaction and was reduced to divalent iron ions.

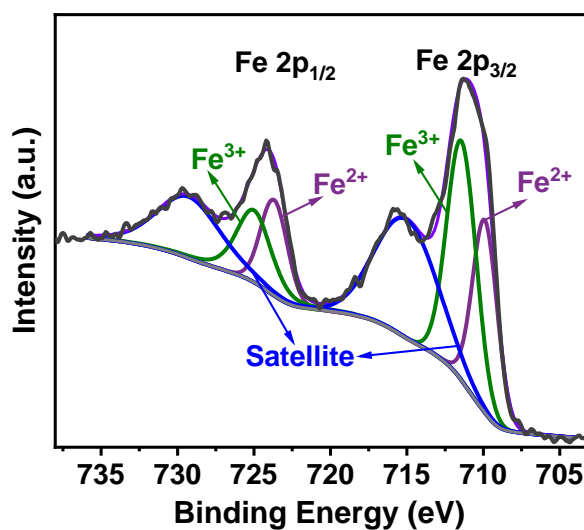


Fig. S10 XPS spectra of the reaction mixture.

8. Device Fabrication and Photovoltaic Parameters

Indium-doped tin oxide (ITO) glass substrates were cleaned by sequential treatment with detergent, deionized water, acetone and isopropanol in an ultrasonic bath for 20 min, respectively. The cleaned ITO glass was treated with UV-ozone for 15 min. A 30-nm thick layer of poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) was fabricated by spin-coating an aqueous dispersion onto ITO glass (4000 rpm for 30 s). PEDOT:PSS substrates were annealed at 150 °C for 15 min. 5-(5-(4,8-Bis(4-chloro-5-(2-ethylhexyl)thiophen-2-yl)-6-methylbenzo[1,2-b:4,5-b']dithiophen-2-yl)-4-(2-butyloctyl)thiophen-2-yl)-8-(4-(2-butyloctyl)-5-methylthiophen-2-yl)dithieno[3',2':3,4;2'',3'':5,6]benzo[1,2-c][1,2,5]thiadiazole (D18-Cl) as donor and 2,2'-((2Z,2'Z)-((12,13-bis(3-ethylheptyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4e]thieno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]thieno[3,2-b]indole-2,10-diyl)bis(methaneylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1*H*-indene-2,1-diylidene))dimalononitrile (N3) as acceptor were mixed in chloroform in a weight ratio of 1:1.4, with a total concentration of 12.5 mg/mL as a reference solution. Subsequently, the fullerene C₆₀ or C₁₂₀O₂ was added as the third component at a ratio of 1:1.4:0.12 for the D18-Cl:N3:fullerene derivative. Then, the above active blend in chloroform was spin-coated onto a PEDOT:PSS layer. *N,N'*-Bis[3-(dimethylamino)propyl]perylene-3,4,9,10-tetracarboxylic diimide (PDIN, 2 mg/mL) in MeOH:AcOH (1000:3) solution was spin-coated onto the active layer (5000 rpm for 30 s) as the electron transfer layer. Ag (~80 nm) was evaporated onto

PDIN (pressure ca. 10^{-4} Pa). The effective area for the devices was 4 mm². *J-V* curves were measured by using an intensity-tunable xenon lamp-based SAN-EI-XES-50S2 solar simulator (Japan, AM 1.5G, 100 mW/cm²).

Table S3. Photovoltaic Parameters of Solar Cells.

Active layer	V_{OC} (V)	J_{SC} (mA/cm ²)	FF (%)	PCE (%) ^[a]
D18-Cl:N3 (1:1.4)	0.87	26.41	75.03	17.27 (17.05 ± 0.19)
D18-Cl:N3:C ₁₂₀ O ₂ (1:1.4:0.12)	0.86	28.05	74.08	17.94 (17.89 ± 0.05)
D18-Cl:N3:C ₆₀ (1:1.4:0.12)	0.85	26.68	69.24	15.77 (15.22 ± 0.28)

^[a]The average values in parentheses were calculated from 5 devices.

9. NMR Spectra of C₁₂₀O and C₁₂₀O₂

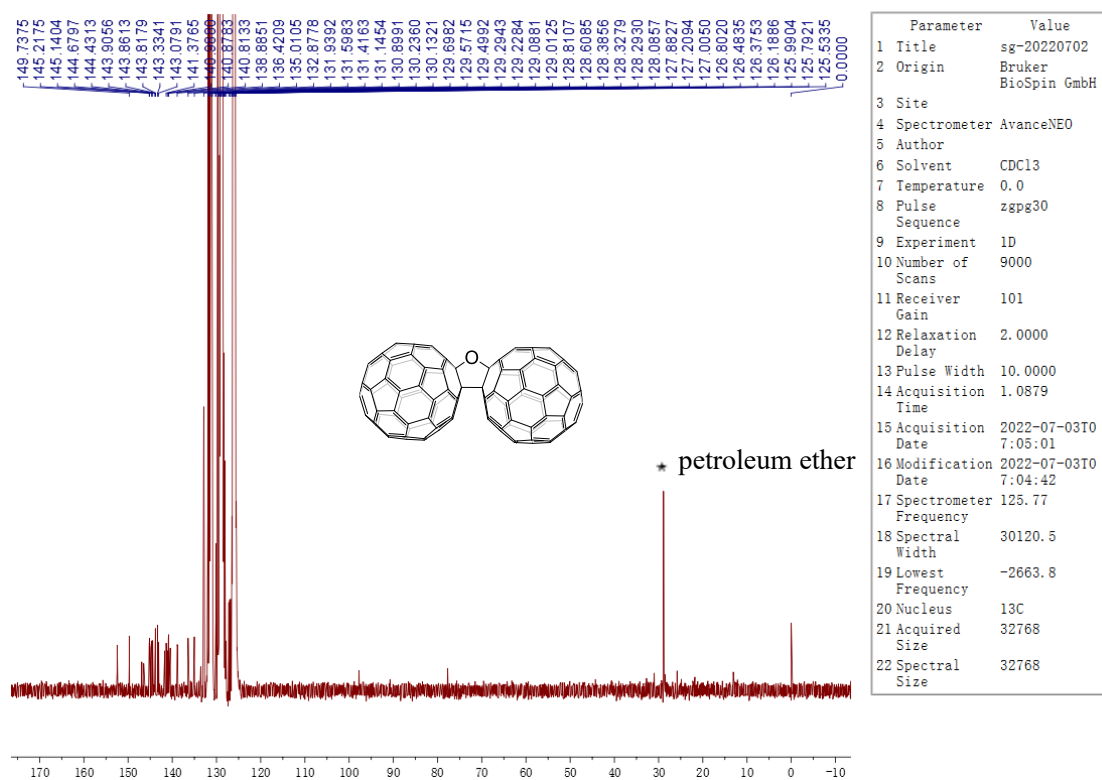


Fig. S11 ¹³C NMR (126 MHz, 1,2-C₆D₄Cl₂, 4.9 mmol dm⁻³ Cr(acac)₃ as relaxation reagent) of C₁₂₀O.

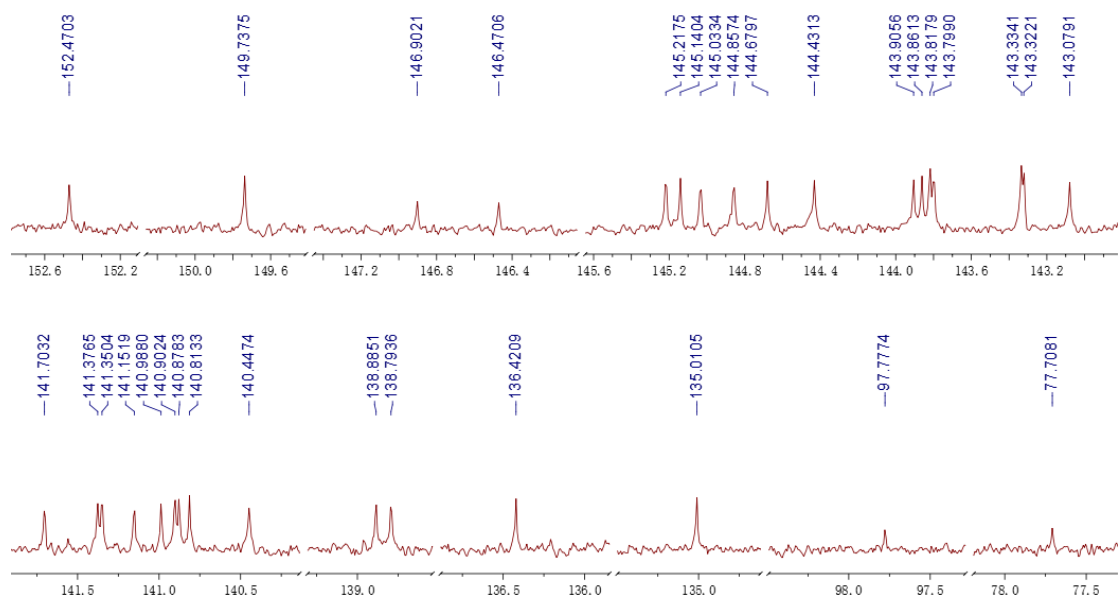


Fig. S12 Expanded ¹³C NMR (126 MHz, 1,2-C₆D₄Cl₂, 4.9 mmol dm⁻³ Cr(acac)₃ as relaxation reagent) of C₁₂₀O.

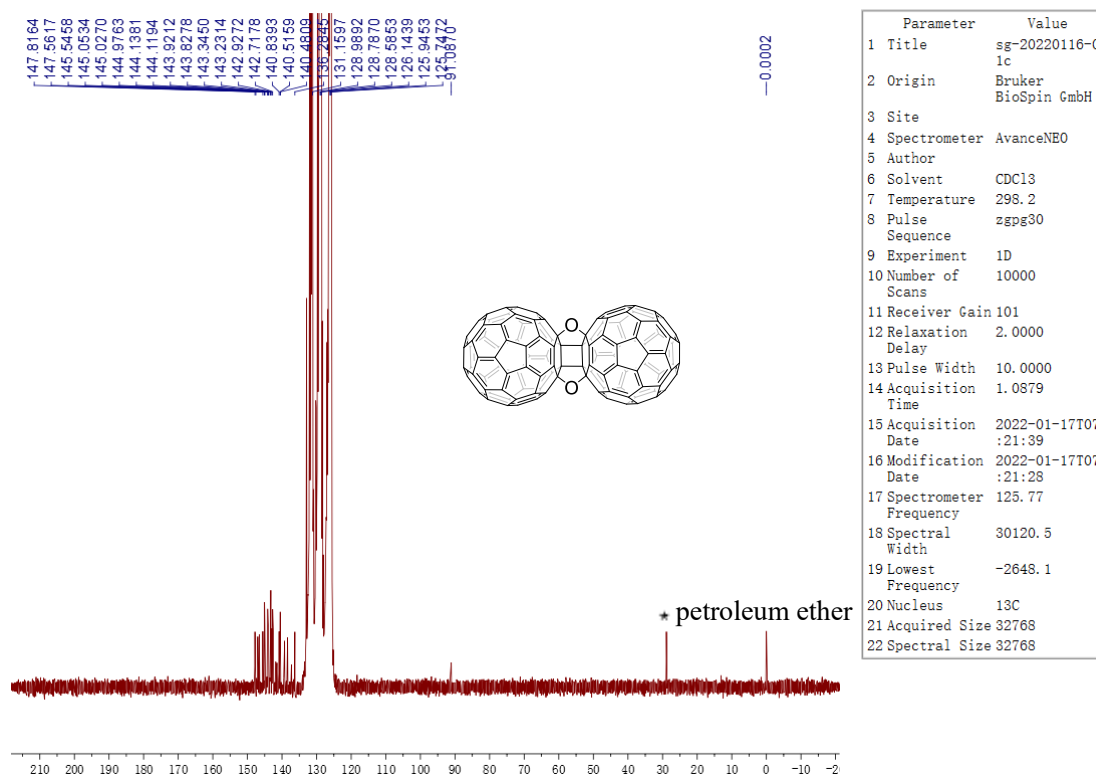


Fig. S13 ^{13}C NMR (126 MHz, 1,2- $C_6D_4Cl_2$) of $C_{12}O_2$.

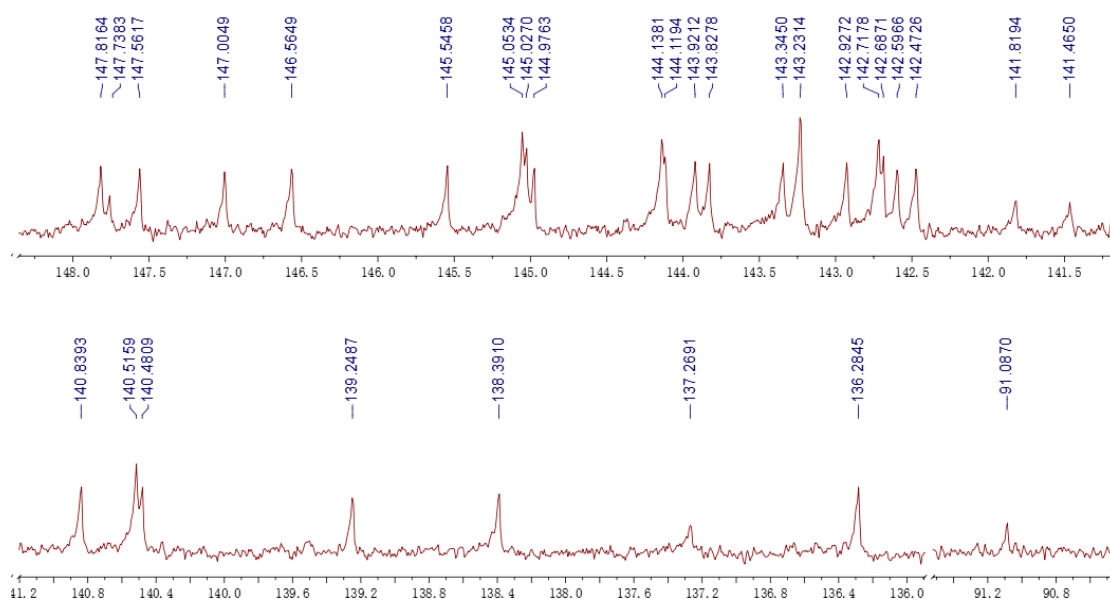


Fig. S14 Expanded ^{13}C NMR (126 MHz, 1,2- $C_6D_4Cl_2$) of $C_{12}O_2$.

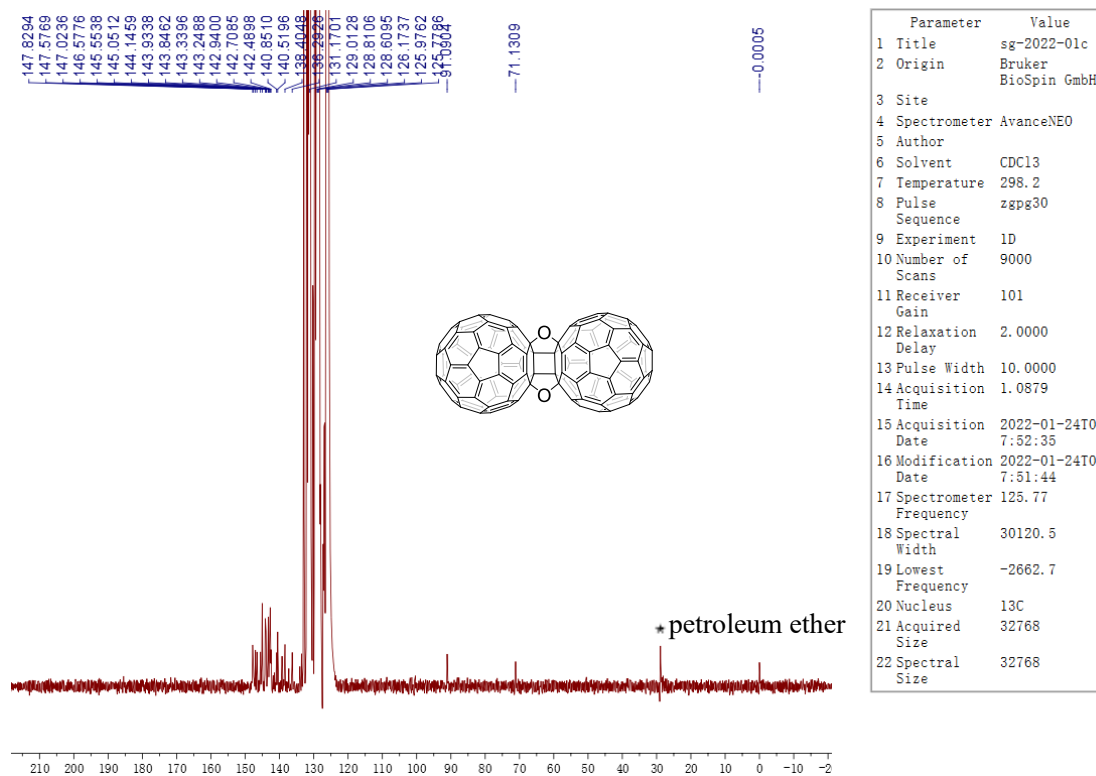


Fig. S15 ¹³C NMR (126 MHz, 1,2-C₆D₄Cl₂, 4.9 mmol dm⁻³ Cr(acac)₃ as relaxation reagent) of C₁₂₀O₂.

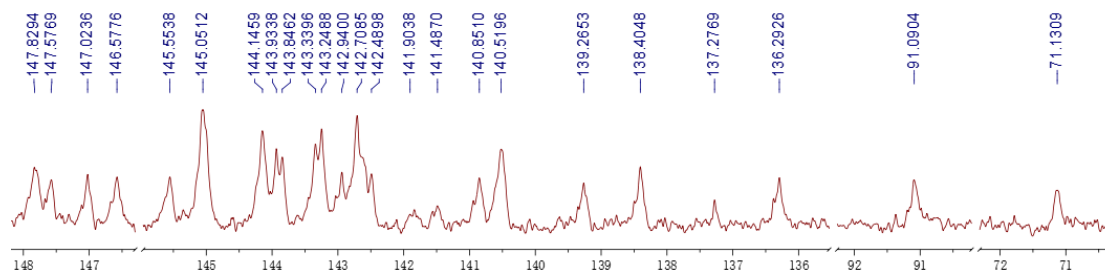


Fig. S16 Expanded ¹³C NMR (126 MHz, 1,2-C₆D₄Cl₂, 4.9 mmol dm⁻³ Cr(acac)₃ as relaxation reagent) of C₁₂₀O₂.