

Supporting Information

Reaction mechanism with indano[60]fullerene bromide for evaporable fullerene derivatives

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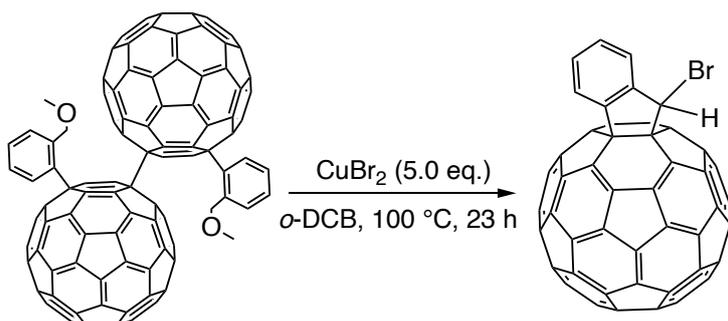
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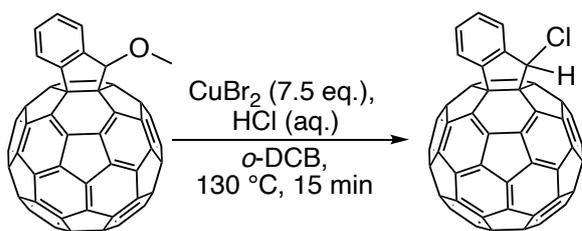
General Method

Nuclear Magnetic Resonance (NMR) was taken by JNM-ECS 400, JNM-ECA 600 and JNM-ECZ400 (JEOL Co., Ltd.) at room temperature unless otherwise noted and reported in parts per million (ppm). ^1H -NMR spectra were referenced to CDCl_3 (7.260 ppm). The data were presented as following order: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, hept = heptet, m = multiplet and/or multiplet resonances), coupling constant in hertz (Hz), and signal area integration in natural numbers, assignment (*italic*). HRMS spectra were recorded by ultrafleXtreme (MALDI-TOF-MS) (Bruker Co., Ltd.). The reaction monitoring was conducted by an analytical high-performance liquid chromatography (HPLC), using COSMOSIL Buckyprep-D column as solid state, toluene/isopropanol (Volume ratio = 7:3) as eluent with a flow rate of 1.0 mL/min.

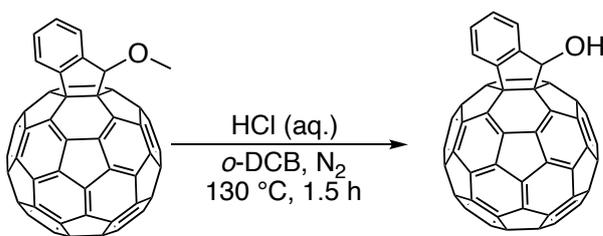
Synthesis of intermediates



Synthesis of indano[60]fullerene bromide. As a premise, Aryl[60]fullerenyl Dimer was synthesized according to our previously reported synthetic methods.¹ Dimer (100.0 mg, 0.06 mmol) was dissolved in *o*-DCB. Then, CuBr_2 (53.5 mg, 0.28 mmol) was added as oxidant. The solution was stirred thoroughly at 110 °C for 23 h. After the reaction, the solvent was evaporated using an evaporator and the residue was separated by chromatography on a silica gel column with CS_2 as eluent to afford the target material 23 mg (43.2%). ^1H NMR (600 MHz, Chloroform-*d*), d 8.12 (dd, $J = 6.3, 2.8$ Hz, 1H), 8.07–8.04 (m, 1H), 7.73–7.67 (m, 2H), 7.39 (s, 1H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 155.92, 155.23, 153.42, 153.87, 147.68, 146.65, 146.63, 146.54, 146.52, 146.45, 146.38, 146.34, 146.32, 146.30, 146.13, 146.09, 145.88, 145.85, 145.73, 145.68, 145.64, 145.61, 144.87, 144.73, 144.62, 144.50, 136.20, 136.16, 135.40 (1C), 131.08, 130.27, 126.14, 128.73, 77.60 (sp^3 -C), 74.68 (sp^3 -C), 60.87(sp^3 -C). HRMS (MALDI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{67}\text{H}_5\text{Br}$ 887.9569; Found 887.9588.

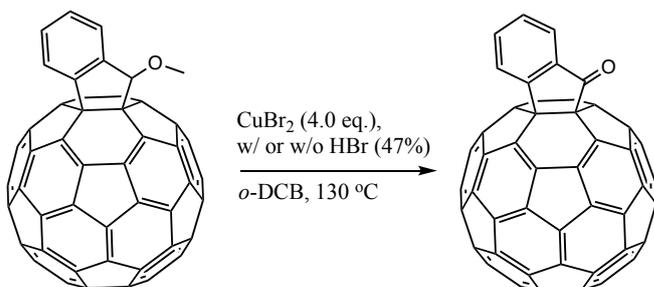


Synthesis of indano[60]fullerene chloride. Methoxy indano[60]fullerene (5.0 mg, 0.006 mmol) was dissolved in *o*-DCB. Then, CuBr₂ (9.9 mg, 0.044 mmol) was added as oxidant along with Hydrogen chloride solution (47% HCl in water). The solution was stirred thoroughly at 130 °C for 15 min. After the reaction, the reaction solution was passed through a short silica gel column to remove salts. Then, the solvent was evaporated using an evaporator and HRMS measurements were conducted on the remaining powder to detect the target material (2.3 mg, 46%). HRMS (MALDI-TOF) *m/z*: [M]⁺ Calcd for C₆₇H₅Cl 844.0074; Found 844.0087.



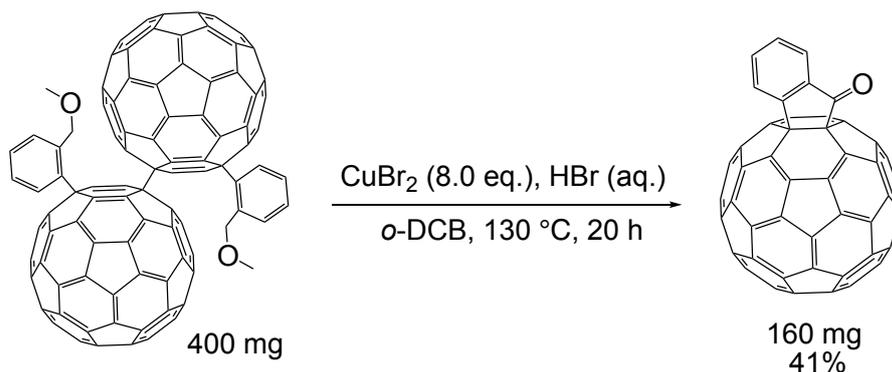
The separation of hydroxy indano[60]fullerene. Methoxy indano[60]fullerene (50.0 mg, 0.06 mmol) and 0.5 ml hydrogen bromide solution (47% HBr in water) were dissolved in 10.0 mL *o*-DCB in the small flask. The reaction system was vacuumed and refilled with N₂ for three time to remove all the oxygen in the solvent. Then the solution was stirred thoroughly at 130 °C for 1.5 hours (Fig.S2). The Hydroxy indano[60]fullerene was separated by chromatography on a silica gel column with CS₂/EA (10:1) as eluent (17.3 mg, 32%). ¹H NMR (594 MHz, CHLOROFORM-D) δ 8.19-8.16 (m, 1H), 8.08 – 8.04 (m, 1H), 7.77 – 7.69 (m, 2H), 7.01 (d, *J* = 9.5 Hz, 1H), 3.04 (d, *J* = 9.8 Hz, 1H). HRMS (MALDI-TOF) *m/z*: [M]⁺ Calcd for C₆₇H₆O 826.0419; Found 826.0415.

Conditions of time-course experiment

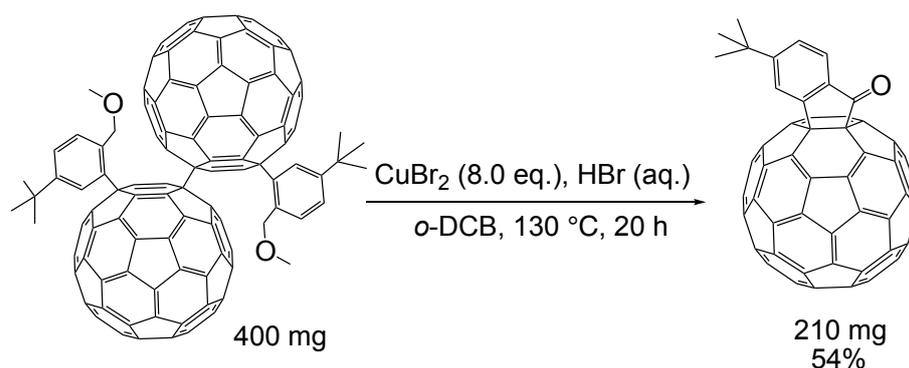


Time-course experiments of indano[60]fullerene ketone. Methoxy indano[60]fullerene (10.0 mg, 12 μmol) was dissolved in *o*-DCB. Then, CuBr_2 (48 μmol) was added as oxidant along with 0.1 mL Hydrogen bromide solution (47% HBr in water). CuBr_2 was used alone for the control group. The mixture was stirred thoroughly at 130°C, and HPLC measurements were performed every couple of hours to monitor the progress of the reaction.

Conditions of one-pot synthesis



One-pot synthesis of indano[60]fullerene ketone. Dimer (400.0 mg, 0.24 mmol) was dissolved in *o*-DCB. Then, CuBr_2 (425.0 mg, 1.90 mmol) was added as oxidant. After vigorously stirring at 130 °C for 1 h, 500 μL Hydrogen bromide solution (47% HBr in water) was added. The solution was stirred thoroughly at 130 °C for 19 h. Finally, the reaction mixture was condensed through evaporating the solvent under vacuum and followed by a silica gel column chromatography (CS_2) to afford the target material (160.0 mg, 41%).



One-pot synthesis of *t*-Bu-indano[60]fullerene ketone. Dimer (400.0 mg, 0.22 mmol) was dissolved in 10 ml *o*-DCB.² Then, CuBr_2 (400.0 mg, 1.79 mmol) was added as oxidant. After vigorously stirring at 130 °C for 1 h, 500 μL Hydrogen bromide solution (47% HBr in water) was added. The solution was stirred thoroughly at 130 °C for 19 h. Finally, the reaction mixture was condensed through evaporating the solvent under vacuum and followed by a

silica gel column chromatography (CS₂) to afford the target material (210.0 mg, 54%).

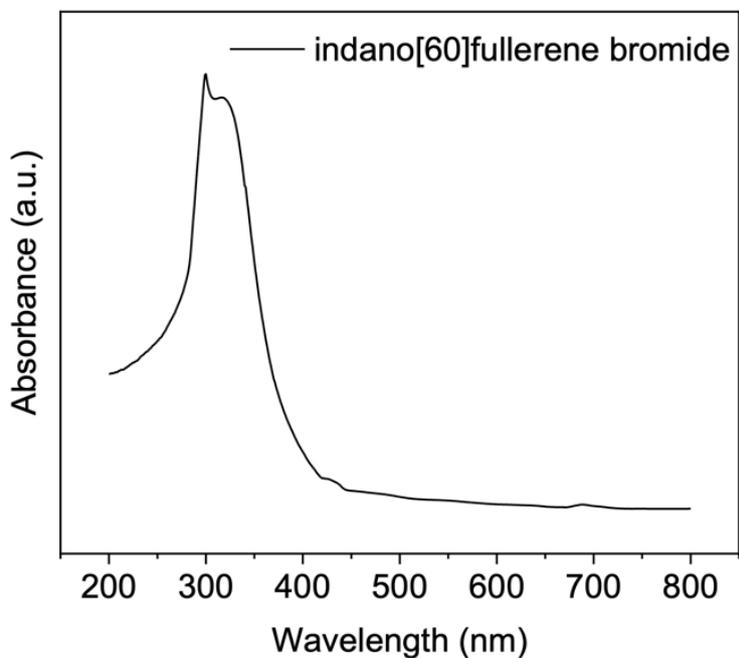


Fig.S1 Uv–Vis absorption spectra of indano[60]fullerene bromide.

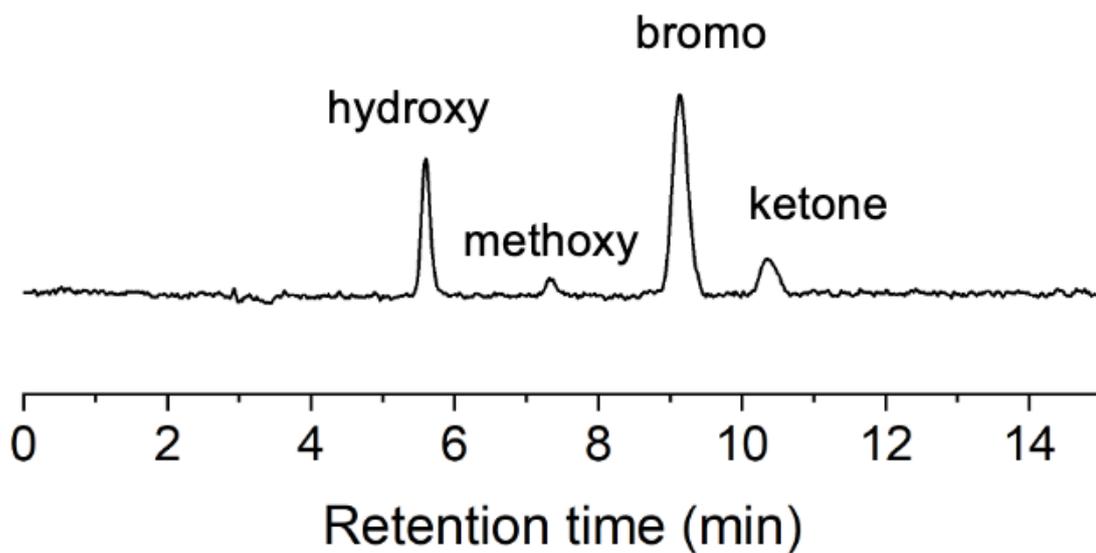


Fig.S2. HPLC retention time of the reaction conducted with 47% HBr under the protection of N₂.

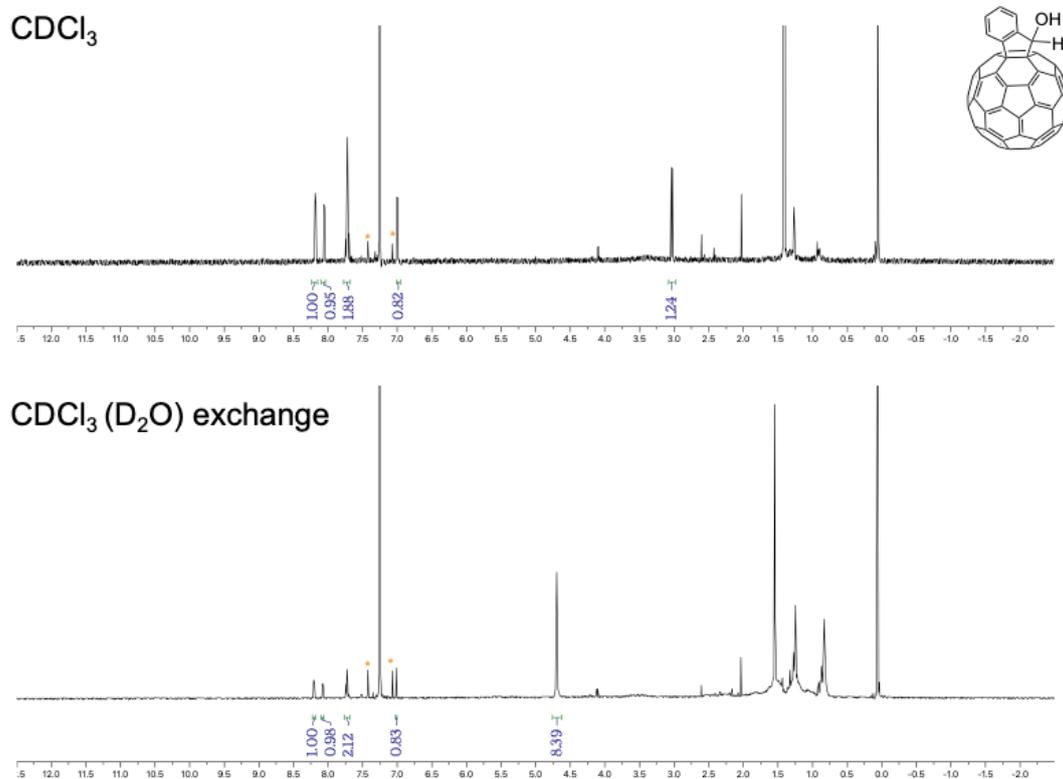
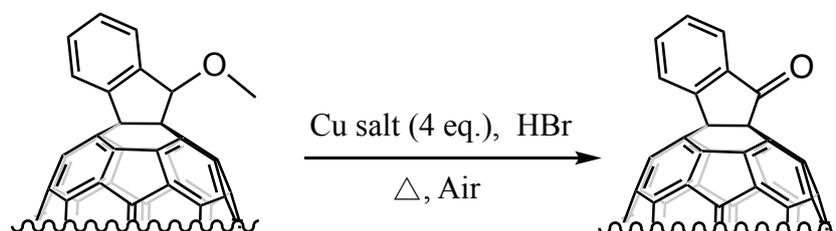


Fig.S3 The ¹H NMR of hydroxy indano[60]fullerene before and after D₂O exchange. The spinning sidebands of chloroform are marked with asterisks.

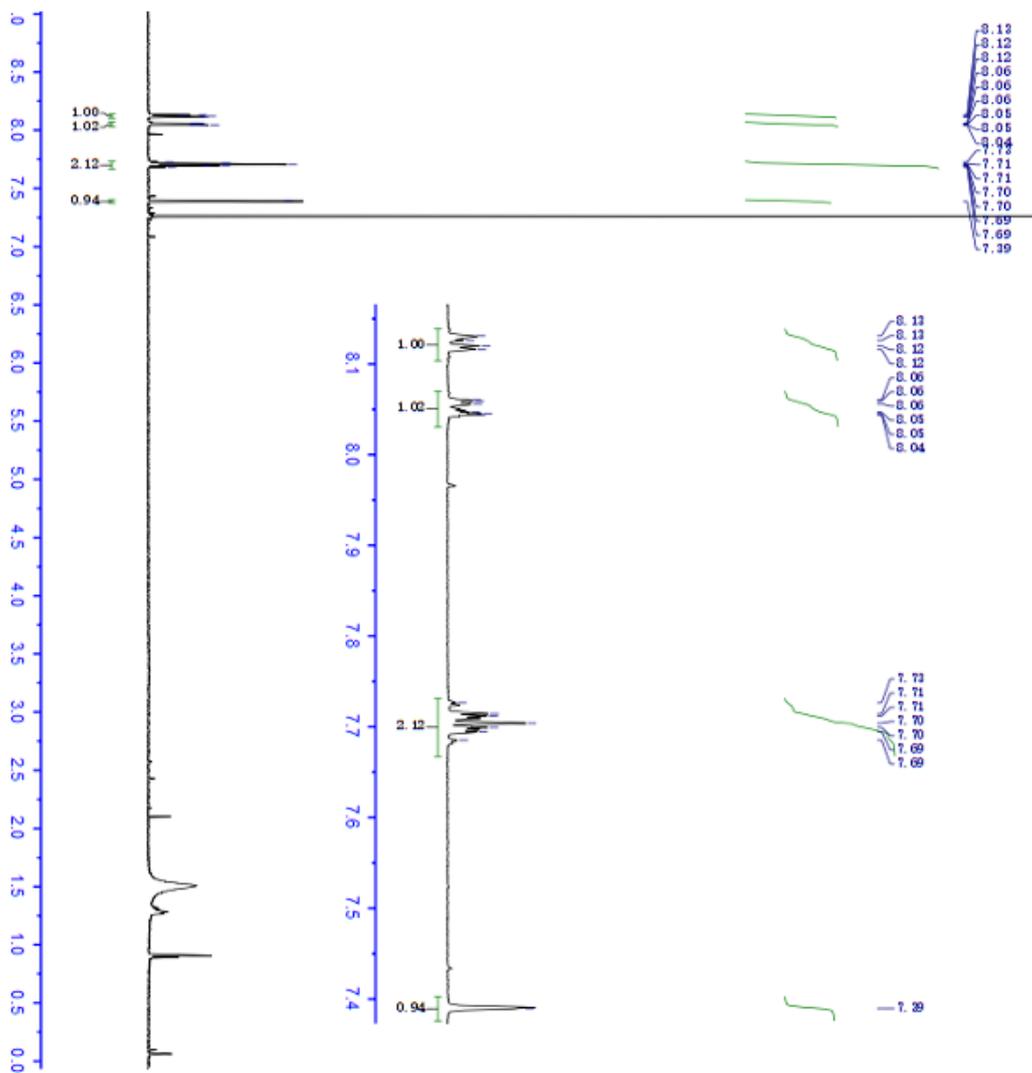
Table S1 Reaction optimization from methoxy indano[60]fullerene to indano[60]fullerene ketone^a



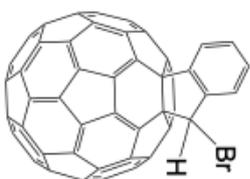
Entry	Cu salt	HBr (eq.)	Temp. (°C)	Time (h)	Yield ^b
1	CuBr ₂	0	130	3	5
2	CuBr ₂	10	130	3	30
3	CuBr ₂	25	130	3	33
4	CuBr ₂	50	130	3	37
5	CuBr ₂	75	130	3	37
6	CuBr ₂	75	130	6	44
7	CuBr ₂	75	130	18	87
8	CuBr ₂	0	130	18	55
9	CuSO ₄	75	130	3	18
10	CuBr ₂	75	110	6	41

^a Unless otherwise noted, all the reactions were performed with 0.015 mmol of methoxy indano[60]fullerene in *o*-DCB (10 mL) under an air atmosphere in a 30 ml vial with cap. ^b HPLC conversion yield.

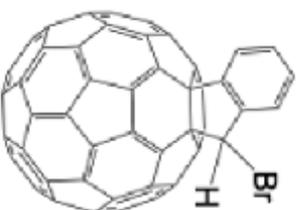
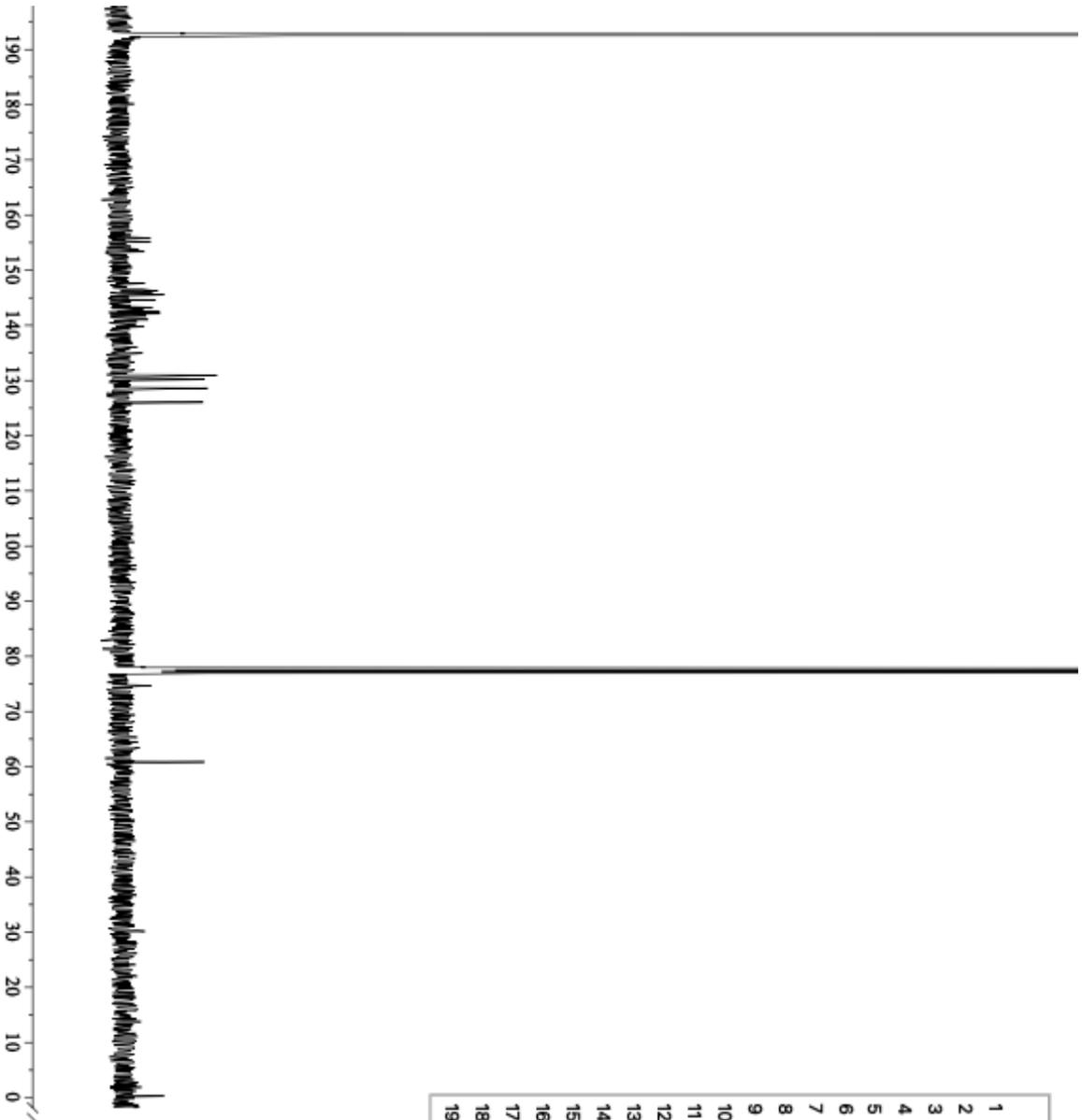
1. NMR spectra

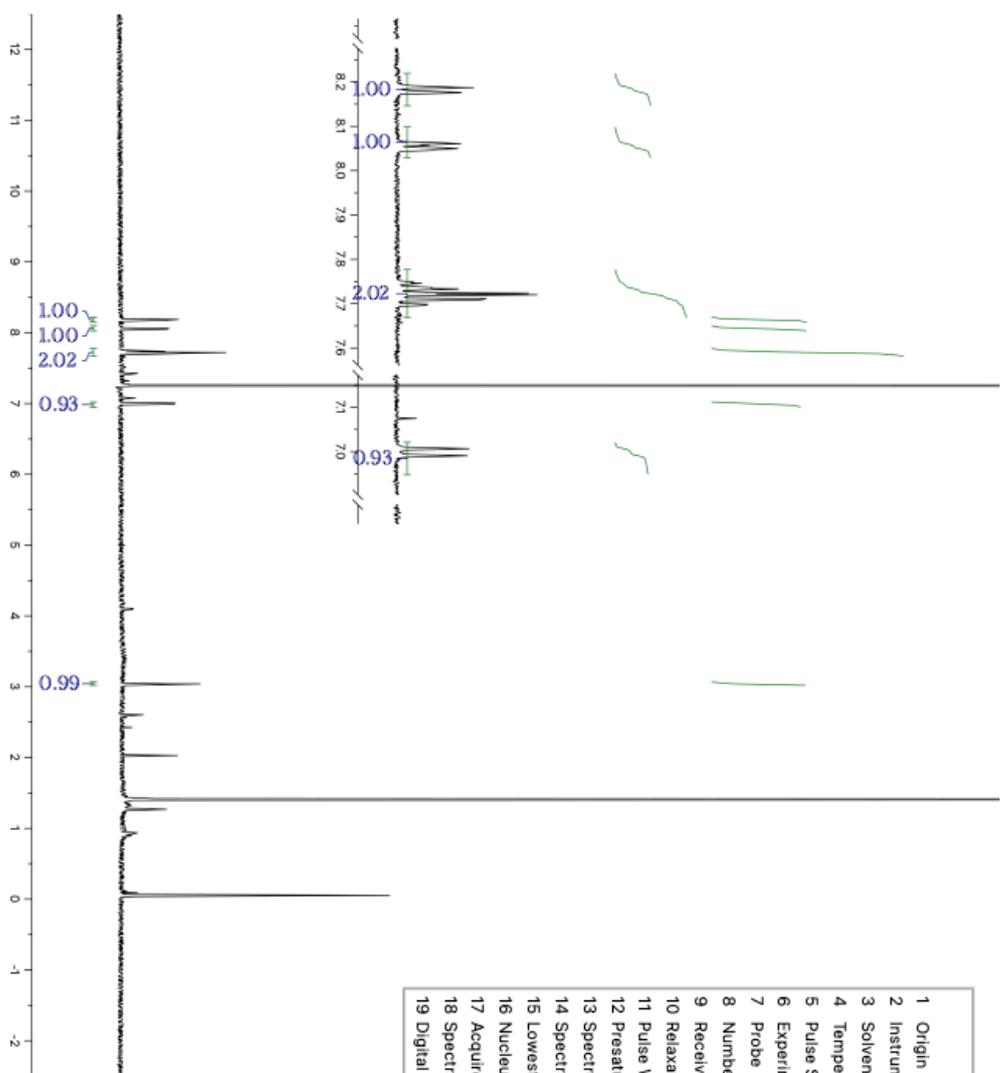


Parameter	Value
1 Orbitin	JEOL
2 Author	deltis
3 Solvent	CHLOROFORM-D
4 Temperature	22.3
5 Pulse Sequence	singlepulse ez2
6 Probe	2156
7 Number of Scans	32
8 Receiver Gain	56.0
9 Relaxation Delay	3.0000
10 Pulse Width	5.6000
11 Presaturation Frequency	
12 Acquisition Time	2.9413
13 Spectrometer Frequency	594.17
14 Spectral Width	8912.7
15 Lower Frequency	-1479.5
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	104888

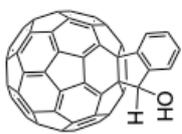


Parameter	値
1 Origin	JEOL
2 Instrument	JNM-ECZ400S/L1
3 Solvent	CHLOROFORM-D
4 Temperature	22.1
5 Pulse Sequence	carbon_auto.jxp
6 Experiment	1D
7 Probe	2803
8 Number of Scans	13312
9 Receiver Gain	50.0
10 Relaxation Delay	2.2891
11 Pulse Width	3.3767
12 Presaturation Frequency	
13 Spectrometer Frequency	100.53
14 Spectral Width	25252.1
15 Lowest Frequency	-2573.5
16 Nucleus	¹³ C
17 Acquired Size	22439
18 Spectral Size	52429
19 Digital Resolution	0.48



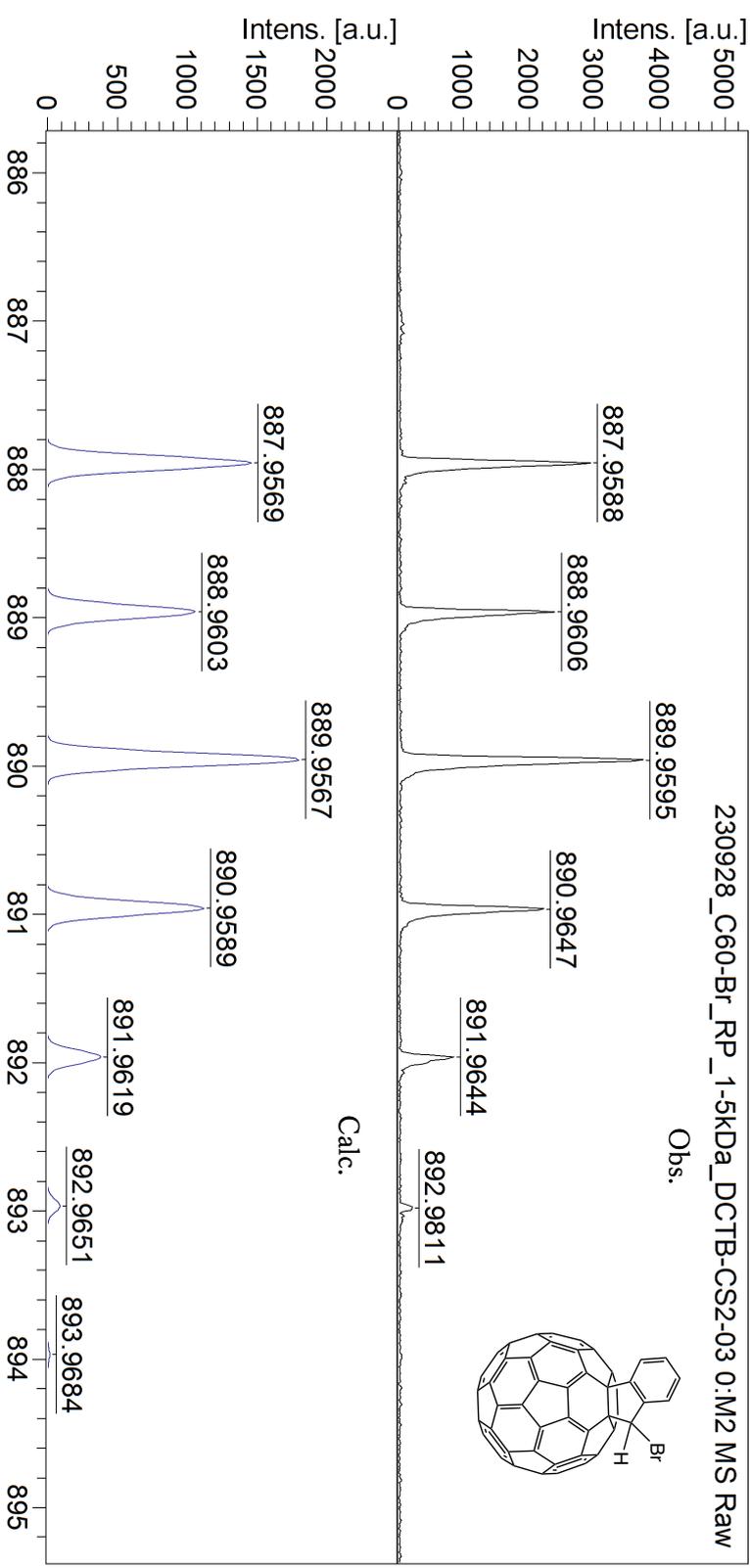


Parameter	値
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2 Instrument	ECA 600
3 Solvent	CHLOROFORM-D
4 Temperature	24.3
5 Pulse Sequence	single_pulse.ex2
6 Experiment	1D
7 Probe	2756
8 Number of Scans	8
9 Receiver Gain	56.0
10 Relaxation Delay	5.0000
11 Pulse Width	6.6000
12 Presaturation Frequency	
13 Spectrometer Frequency	594.17
14 Spectral Width	8912.7
15 Lowest Frequency	-1485.5
16 Nucleus	¹ H
17 Acquired Size	32768
18 Spectral Size	104858
19 Digital Resolution	0.08



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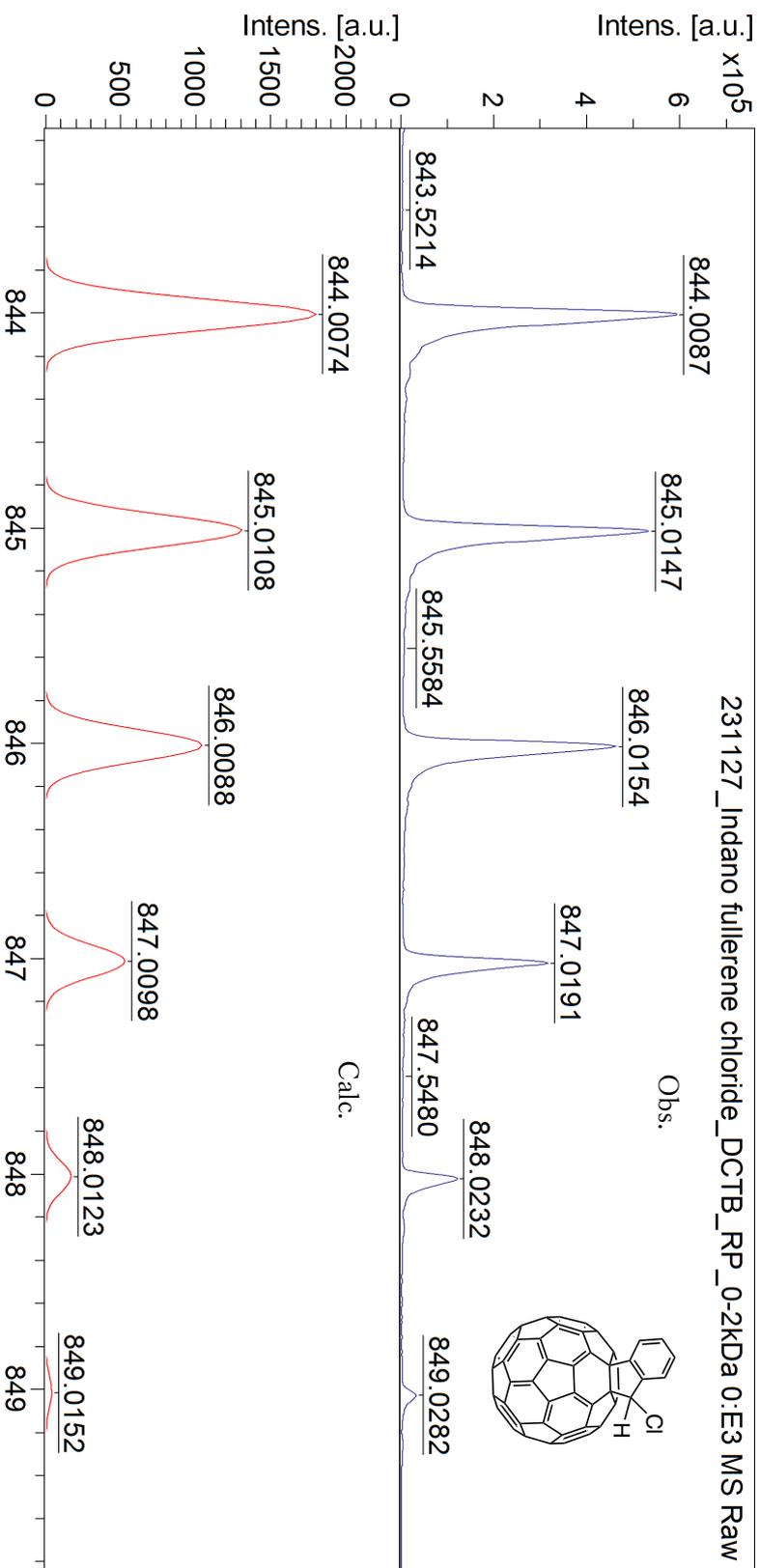


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2. HRMS spectra

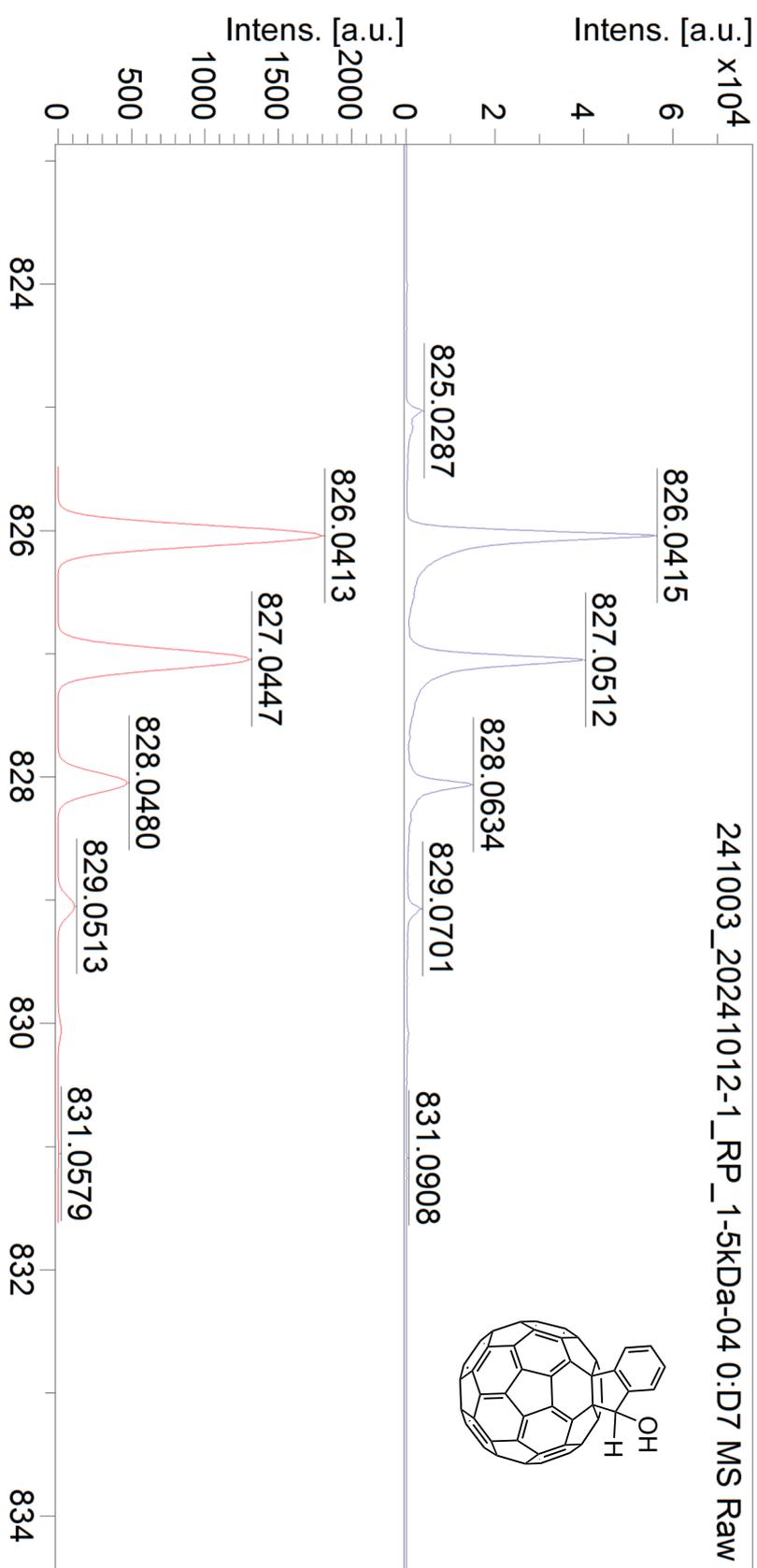
Comment 1
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Comment 1

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Reference

1. H.-S. Lin, I. Jeon, Y. Chen, X.-Y. Yang, T. Nakagawa, S. Maruyama, S. Manzhos, and Y. Matsuo, *Chem. Mater.*, 2019, **31**, 8432–8439.
2. Q.-J. Shui, S. Shan, Y.-C. Zhai, S. Aoyagi, S. Izawa, M. Huda, C.-Y. Yu, L. Zuo, H. Chen, H.-S. Lin, and Y. Matsuo, *J. Am. Chem. Soc.*, 2023, **145**, 27307–27315.