Supporting Information

Upcycling Waste Polyoxymethylene to Value-added Chemicals Using Reusable Polymeric Acid Catalysts at ppm Levels

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1. General

All chemicals and solvents were used as received without further purification unless otherwise mentioned. ^{1}H-NMR (500 MHz) and ^{13}C-NMR (125 MHz) spectra were measured with a JEOL JNM ECA-500 spectrometer at 25 °C. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) spectra were measured with a JEOL JNM-ECZ-400 spectrometer at 25 °C. Chemical shifts (δ) are expressed relative to the resonances of the residual non-deuterated solvent for ^{1}H[$CDCl_3$]: ^{1}H (δ) = 7.26 ppm, acetone-d_6: ^{1}H (δ) = 2.05 ppm] and ^{13}C [$CDCl_3$: ^{13}C (δ) = 78.0 ppm, acetone-d_6: ^{13}C = 29.8 and 206.3 ppm]. Absolute values of the coupling constants are given in Hertz (Hz), regardless of their sign. Multiplicities are abbreviated as singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), quintet (quint), multiplet (m), and broad (br) and broad singlet (brs). The solid-state ^{13}C-NMR (cpmas, single pulse, single pulse_dec) spectra were measured with a JEOL JNM ECA-500 spectrometer at 25 °C. The polyoxymethylene (POM) was purchased from Atlantic Research Chemicals and used without further purification.

The GC mass spectrometric measurements (GC-MS) were performed on Agilent 7890B / Agilent 5977B MSD equipped with a capillary column (HP-1ms, 0.25 mm i.d. x 30 m). Reactions using microwave (MW) were carried out with CEM Discover SP. Small-scale reactions (400 mg-scale) were performed in a 10 mL reaction tube, whereas 5 g-scale reactions were performed in a 35 mL reaction tube. The 40g-scale reaction was carried out using EYELA microwave MWO-1000S with MWP-2000 reactor. The FT-IR analysis was performed using an FT/IR-6200 spectrometer with an ATR PRO 450-S accessory (JASCO). The SEM was measured using a TM3030 plus miniscope (SEM, HITACHI) with Quantax 70 (EDS system, Bruker). The Matrix-Assisted Laser Desorption/Ionization-Time of Flight (MALDI-TOF) mass spectroscopy (MS) was measured by using alpha-cyano-4-hydroxycinnamic acid (CHCA) as a matrix in a Bruker rapifleX spectrometer. The ball-milling was performed using Retsch's Mixer Mill MM 400.

2. Market size of POM and its application in different industries

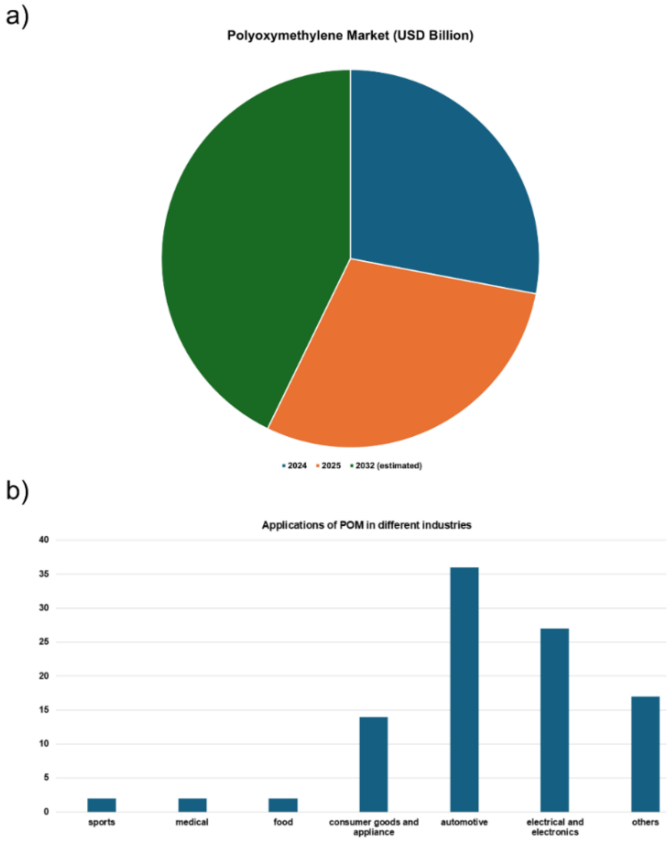


Fig. S1. a) Market size of POM. b) Application of POM in different industries

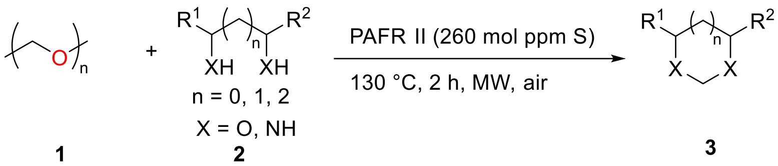
3. Physical and chemical properties of Polymer (1)

Table S1. Properties of POM polymer (1)

entry	properties	data
1	molecular formula	$(CH_2O)_n$
2	appearance	white solid
3	odor	pungent
4	pH	4.0-5.5
5	melting point	170-172 °C
6	flash point	71 °C
7	upper/lower flammability	73 & 7%
8	relative density	0.88g/cm^3 (25 °C)
9	auto-ignition temperature	300 °C

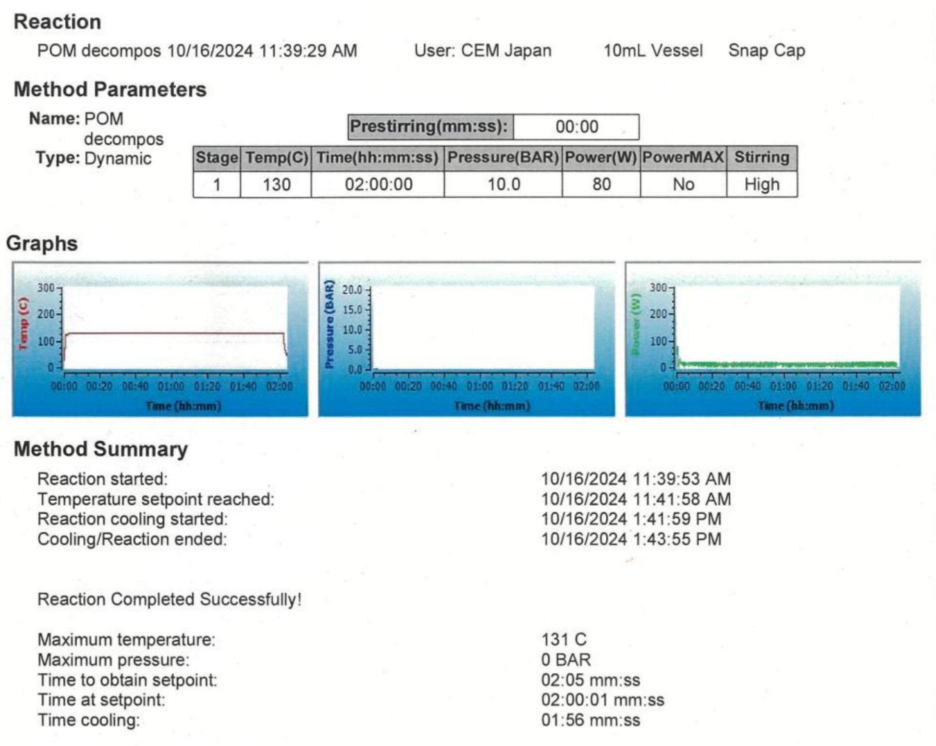
4. Catalysis

4.1. General procedure for POM depolymerization using diols or diamines



1 **2** **3**

A mixture containing POM materials **1** (400 mg, 13.3 mmol (based on monomer), 1 mol equiv), PAFR II (260 mol ppm, 1.1 mg), and diol/diamine **2** (15.96 mmol, 1.2 mol equiv) was introduced into a 10 mL microwave reaction tube. The tube was sealed and subjected to microwave irradiation at 130 °C (max 80 W) using a microwave reactor, with temperature monitored by an infrared sensor and pressure maintained below 10 bar. The reaction was performed for 2 h in the case of pure POM and 6 h for actual plastics (pretreatment: cut into small pieces). The reaction mixture was diluted using $CDCl_3$ (1 mL). To this reaction mixture, 1,3,5-trimethoxybenezene was added as an internal standard. ^{1}H-NMR studies were conducted to determine the yield of **3**.



Reaction

POM decompos 10/16/2024 11:39:29 AM User: CEM Japan 10mL Vessel Snap Cap

Method Parameters

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Type: Dynamic

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Graphs

Method Summary

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Reaction cooling started:	10/16/2024 1:41:59 PM
Cooling/Reaction ended:	10/16/2024 1:43:55 PM

Reaction Completed Successfully!

Maximum temperature:	131 C
Maximum pressure:	0 BAR
Time to obtain setpoint:	02:05 mm:ss
Time at setpoint:	02:00:01 mm:ss
Time cooling:	01:56 mm:ss

Fig. S2: Microwave reaction profile for POM upcycling using 1,3-propanediol.

4.2. Reaction time course measurement

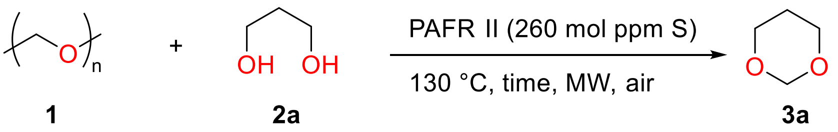


Fig. S3. Reaction time course for POM depolymerization

4.3. Catalyst loading and reaction time course measurement for plastic

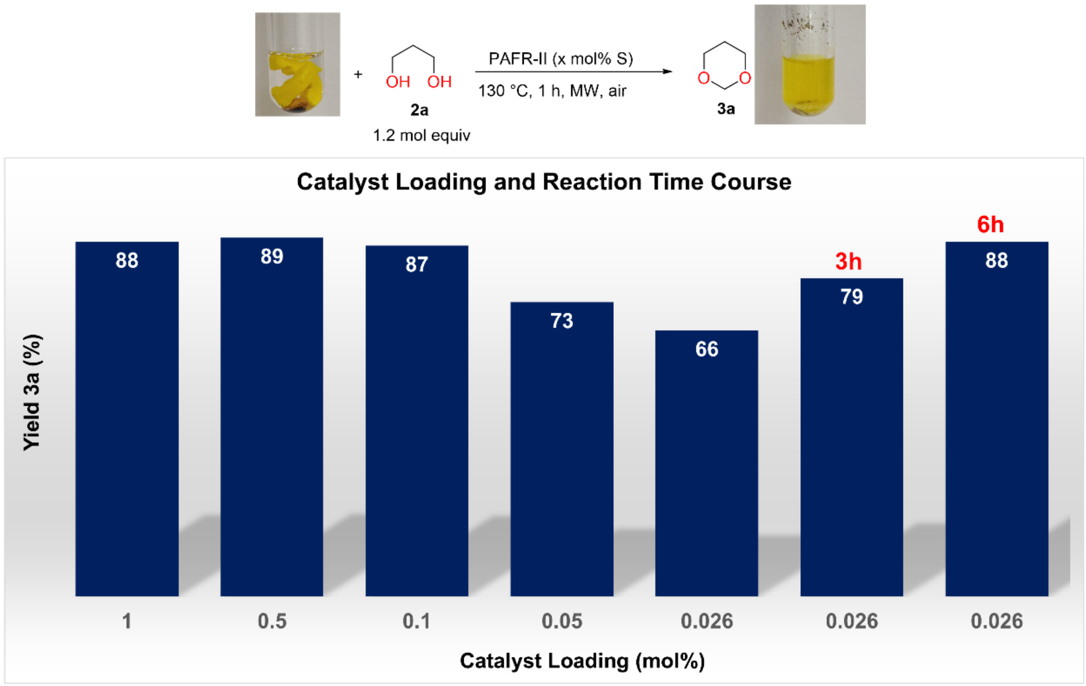
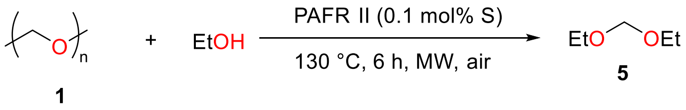


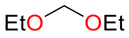
Fig. S4. Catalyst loading and reaction time course for the Keck clip upcycling. The yield of **3a** was determined using ^{1}H-NMR (1,3,5-trimethoxybenzene as the internal standard).

4.4. Procedure for POM depolymerization using ethanol

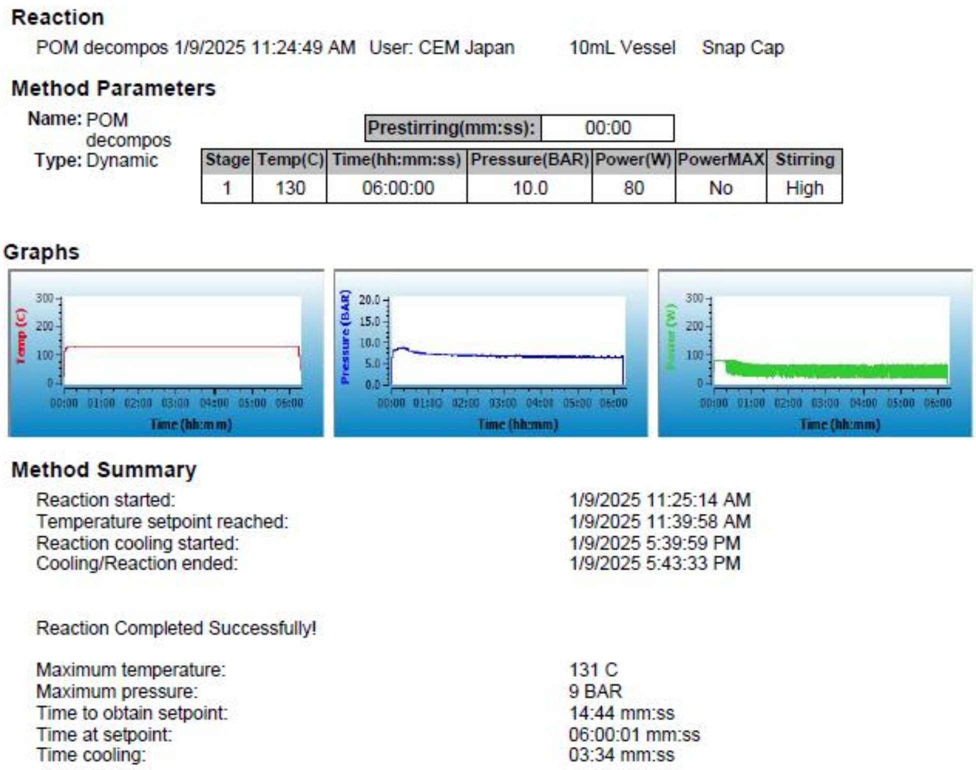


A mixture containing POM materials **1** (100 mg, 3.33 mmol (based on monomer), 1 mol equiv), PAFR II (0.1 mol%, 1.1 mg), and ethanol (33.3 mmol, 10 mol equiv) was introduced into a 10 mL microwave reaction tube. The tube was sealed and subjected to microwave irradiation at 130 °C (max 80 W) using a microwave reactor, with temperature monitored by an infrared sensor and pressure maintained below 10 bar. The reaction was performed for 6 h. The reaction mixture was diluted using $CDCl_3$ (1 mL). To this reaction mixture, 1,3,5-trimethoxybenezene was added as an internal standard. ^{1}H-NMR studies were conducted to determine the yield of **5**.

Diethoxymethane (5, ref 1)



Colorless liquid (15% isolated yield, 52 mg; NMR yield 87%). Purified by fractional distillation. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.64 (s, 2H), 3.59-3.54 (m, 4H), 1.18 (t, *J* = 7.1 Hz, 6H). ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) δ 94.9, 63.1, 15.2.



Reaction

POM decompos 1/9/2025 11:24:49 AM User: CEM Japan 10mL Vessel Snap Cap

Method Parameters

Name: POM decompos
Type: Dynamic

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Stage	Temp(C)	Time(hh:mm:ss)	Pressure(BAR)	Power(W)	PowerMAX	Stirring
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Graphs

Method Summary

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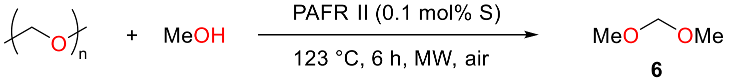
Temperature setpoint reached:	1/9/2025 11:39:58 AM
Reaction cooling started:	1/9/2025 5:39:59 PM
Cooling/Reaction ended:	1/9/2025 5:43:33 PM

Reaction Completed Successfully!

Maximum temperature:	131 C
Maximum pressure:	9 BAR
Time to obtain setpoint:	14:44 mm:ss
Time at setpoint:	06:00:01 mm:ss
Time cooling:	03:34 mm:ss

Fig. S5: Microwave reaction profile for POM upcycling using ethanol.

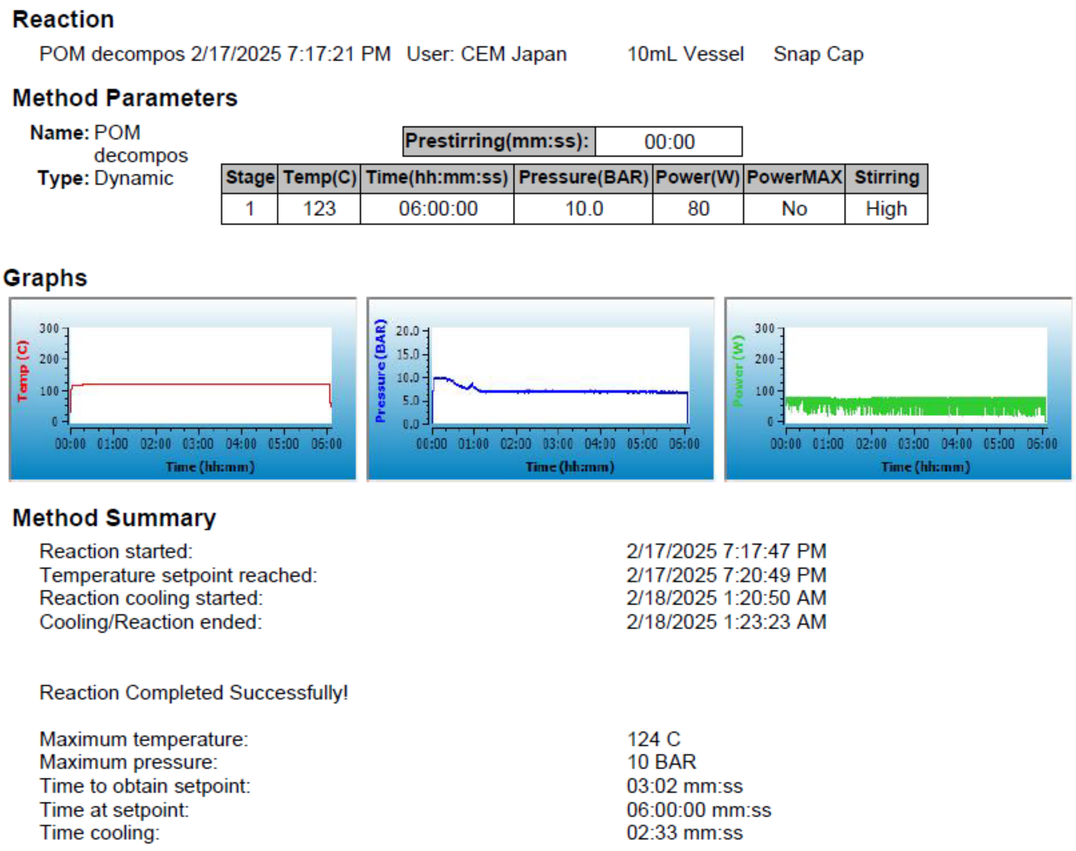
4.5. Procedure for POM depolymerization using methanol



1

6

A mixture containing POM materials **1** (100 mg, 3.33 mmol (based on monomer), 1 mol equiv), PAFR II (0.1 mol%, 1.1 mg), and methanol (33.3 mmol, 10 mol equiv) was introduced into a 10 mL microwave reaction tube. The tube was sealed and subjected to microwave irradiation at 123 °C (max 80 W) using a microwave reactor, with temperature monitored by an infrared sensor and pressure maintained below 10 bar. The reaction was performed for 6 h. The reaction mixture was diluted using $CDCl_3$ (1 mL). To this reaction mixture, 1,3,5-trimethoxybenezene was added as an internal standard. ^{1}H-NMR studies were conducted to determine the yield of **6**.



Reaction

POM decompos 2/17/2025 7:17:21 PM User: CEM Japan 10mL Vessel Snap Cap

Method Parameters

Name: POM decompos
Type: Dynamic

Prestirring(mm:ss):	00:00

Stage	Temp(C)	Time(hh:mm:ss)	Pressure(BAR)	Power(W)	PowerMAX	Stirring
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Graphs

Method Summary

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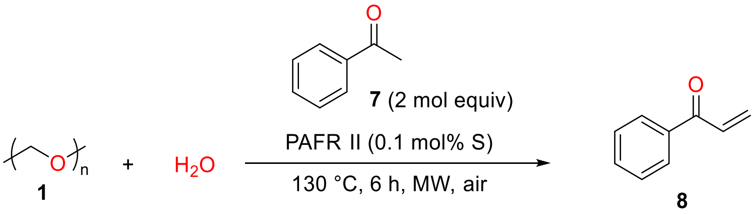
Temperature setpoint reached:	2/17/2025 7:20:49 PM
Reaction cooling started:	2/18/2025 1:20:50 AM
Cooling/Reaction ended:	2/18/2025 1:23:23 AM

Reaction Completed Successfully!

Maximum temperature:	124 C
Maximum pressure:	10 BAR
Time to obtain setpoint:	03:02 mm:ss
Time at setpoint:	06:00:00 mm:ss
Time cooling:	02:33 mm:ss

Fig. S6: Microwave reaction profile for POM upcycling using methanol.

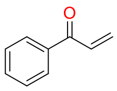
4.6. Procedure for POM depolymerization using water



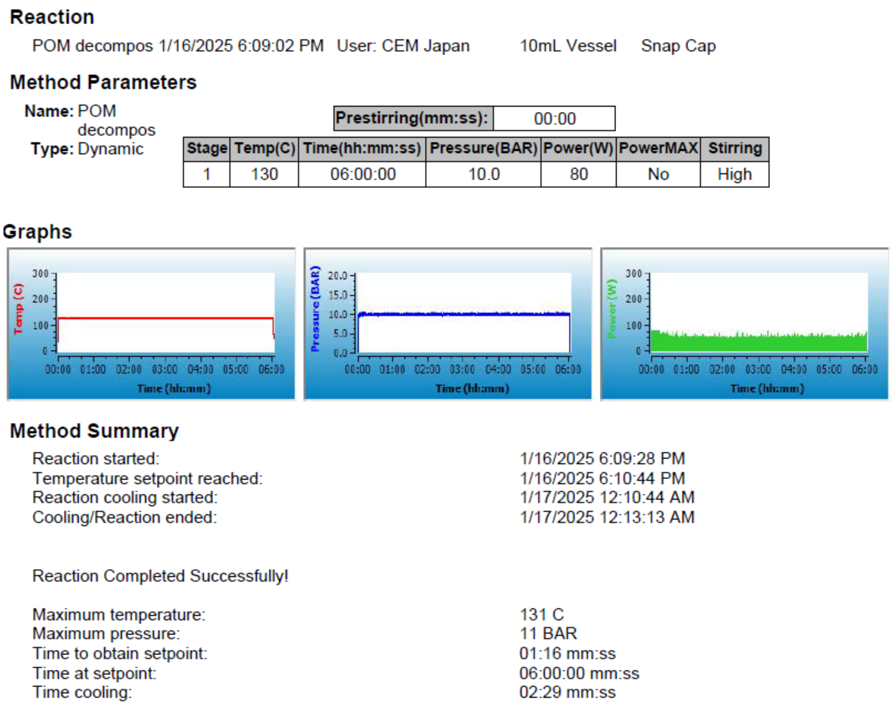
A mixture containing POM materials **1** (100 mg, 3.33 mmol (based on monomer), 1 mol equiv), PAFR II (0.1 mol%, 1.1 mg), water (33.3 mmol, 10 mol equiv), **7** (6.66 mmol, 2 mol equiv) was introduced into a 10 mL microwave reaction tube. The tube was sealed and subjected to microwave irradiation at 130 °C (max 80 W) using a microwave reactor, with temperature monitored by an infrared sensor and pressure maintained below 10 bar. The reaction was performed for 6 h. The reaction mixture was diluted using $CHCl_3$ (2 mL). The catalyst was filtered off from the solution and washed with $CHCl_3$ (10 mL). The eluent was collected. The reaction mixture was dried over $MgSO_4$. The volatiles were evaporated under a vacuum. The crude mass was purified by column chromatography to obtain **8**.

Note: **7** was introduced to trap the formaldehyde generated during the water-mediated depolymerization of **1**. Under these reaction conditions, no depolymerization of **1** proceeded without water.

1-phenylprop-2-en-1-one (8, ref 2)



Gummy liquid (46% isolated yield, 202 mg). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.59-7.55 (m, 1H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.15 (dd, *J* = 17.0, 10.6 Hz, 1H), 6.43 (dd, *J* = 17.0, 1.6 Hz, 1H), 5.93 (dd, *J* = 10.6, 1.6 Hz, 1H). $^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$) δ 191.2, 137.4, 133.1, 132.5, 130.3, 128.8, 128.7.



Reaction

POM decompos 1/16/2025 6:09:02 PM User: CEM Japan 10mL Vessel Snap Cap

Method Parameters

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Type: Dynamic

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Stage	Temp(C)	Time(hh:mm:ss)	Pressure(BAR)	Power(W)	PowerMAX	Stirring
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Graphs

Method Summary

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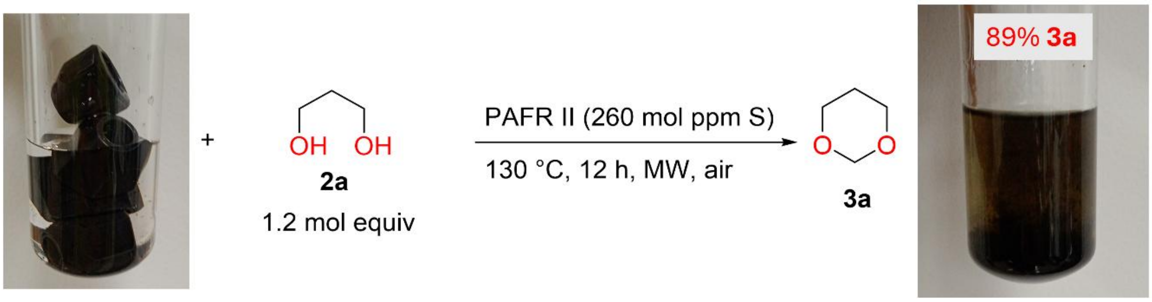
Temperature setpoint reached:	1/16/2025 6:10:44 PM
Reaction cooling started:	1/17/2025 12:10:44 AM
Cooling/Reaction ended:	1/17/2025 12:13:13 AM

Reaction Completed Successfully!

Maximum temperature:	131 C
Maximum pressure:	11 BAR
Time to obtain setpoint:	01:16 mm:ss
Time at setpoint:	06:00:00 mm:ss
Time cooling:	02:29 mm:ss

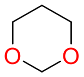
Fig. S7: Microwave reaction profile for POM upcycling using water.

4.7. Procedure for 5g-scale POM depolymerization

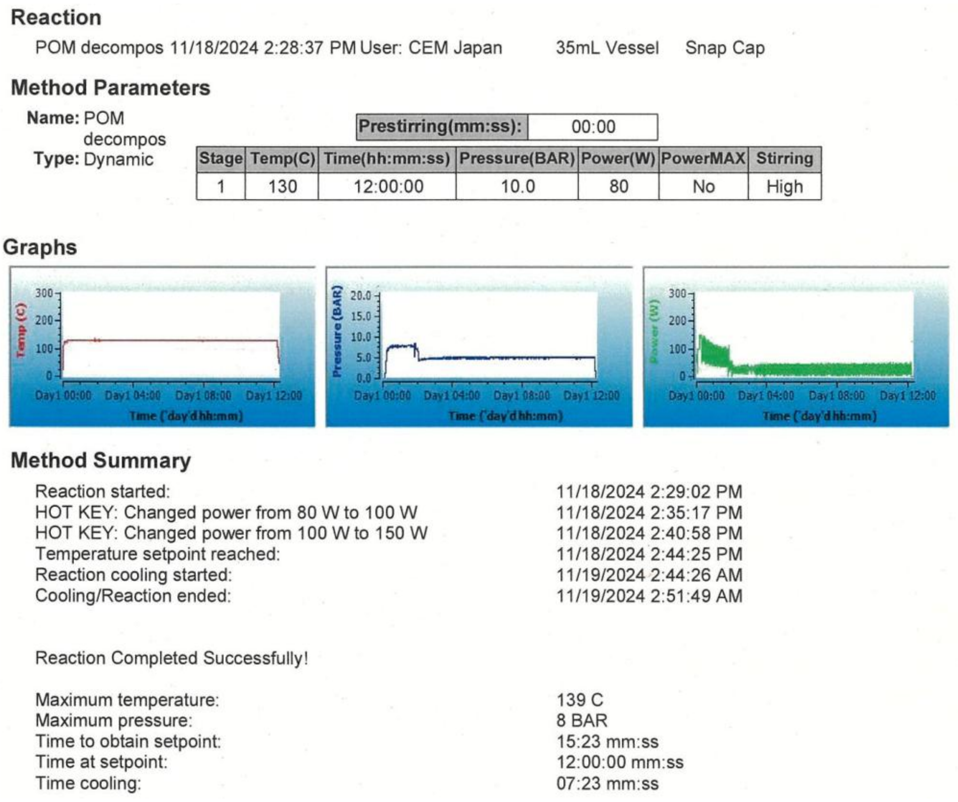


A mixture containing black POM joint (5g, 166.66 mmol, 1 mol equiv), PAFR II (260 mol ppm, 12.5 mg), and 1,3-propanediol **2a** (199.99 mmol, 1.2 mol equiv) was introduced into a 35 mL microwave reaction tube. The tube was sealed and subjected to microwave irradiation at 130 °C (max 80 W) using a microwave reactor, with temperature monitored by an infrared sensor and pressure maintained below 10 bar. The reaction was performed for 12 hours. The reaction mixture was diluted using $CDCl_3$ (3 mL). To this reaction mixture, 1,3,5-trimethoxybenzene was added as an internal standard. ^{1}H-NMR studies were conducted to determine the yield of **3a**.

1,3-dioxane (3a, ref 3)



Colorless liquid (59% isolated yield, 8.77 g; NMR yield 89%). Purified by fractional distillation. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.83 (s, 2H), 3.89 (t, *J* = 5.5 Hz, 4H), 1.78-1.73 (m, 2H). $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$) δ 94.3, 67.0, 26.5.



Reaction

POM decompos 11/18/2024 2:28:37 PM User: CEM Japan 35mL Vessel Snap Cap

Method Parameters

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Type: Dynamic

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Stage	Temp(C)	Time(hh:mm:ss)	Pressure(BAR)	Power(W)	PowerMAX	Stirring
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Graphs

Method Summary

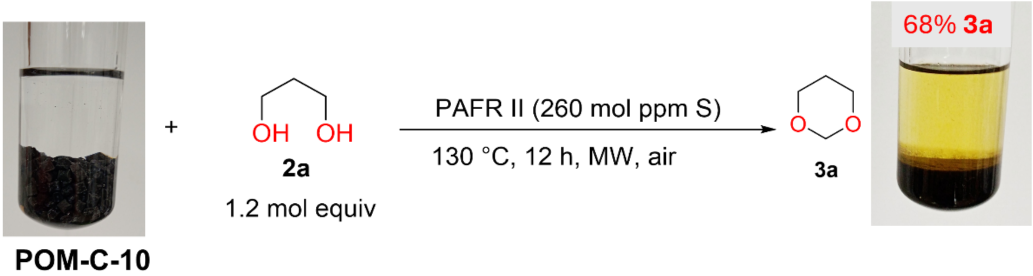
Reaction started:	11/18/2024 2:29:02 PM
HOT KEY: Changed power from 80 W to 100 W	11/18/2024 2:35:17 PM
HOT KEY: Changed power from 100 W to 150 W	11/18/2024 2:40:58 PM
Temperature setpoint reached:	11/18/2024 2:44:25 PM
Reaction cooling started:	11/19/2024 2:44:26 AM
Cooling/Reaction ended:	11/19/2024 2:51:49 AM

Reaction Completed Successfully!

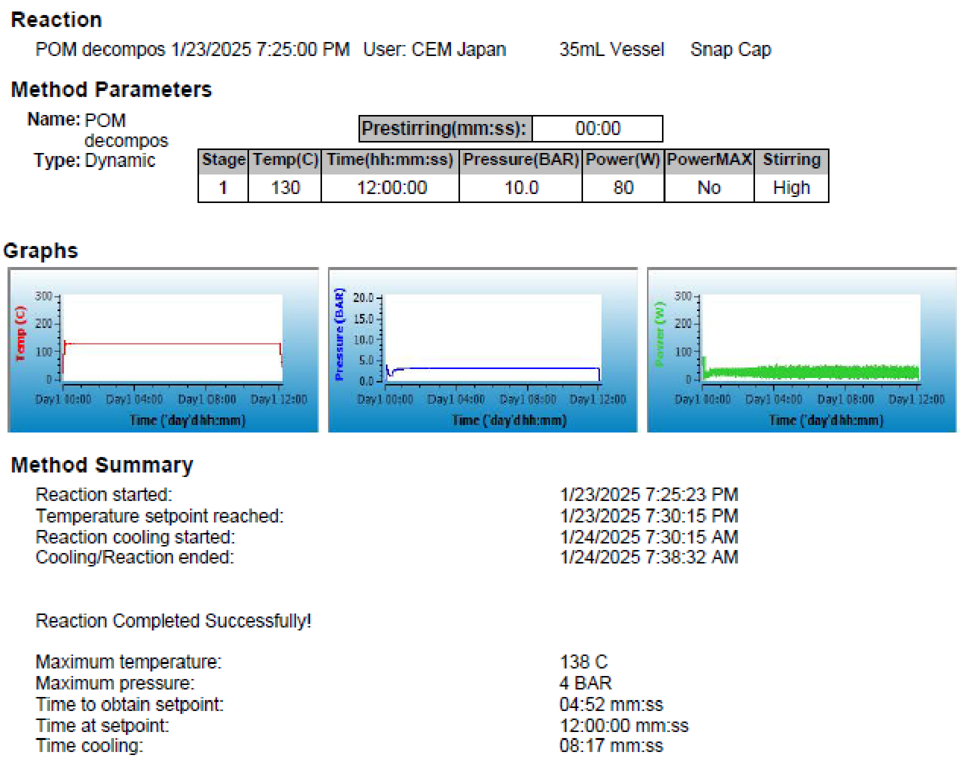
Maximum temperature:	139 C
Maximum pressure:	8 BAR
Time to obtain setpoint:	15:23 mm:ss
Time at setpoint:	12:00:00 mm:ss
Time cooling:	07:23 mm:ss

Fig. S8: Microwave reaction profile for POM upcycling at 5g-scale.

4.8. Procedure for 5g-scale CFRP-POM depolymerization



A mixture containing 10% carbon fiber reinforced polyoxymethylene (CFRP) (5g, 150 mmol; contains 500 mg carbon fiber), PAFR II (260 mol ppm, 11.25 mg), and 1,3-propanediol **2a** (180 mmol, 1.2 mol equiv) was introduced into a 35 mL microwave reaction tube. The tube was sealed and subjected to microwave irradiation at 130 °C (max 80 W) using a microwave reactor, with temperature monitored by an infrared sensor and pressure maintained below 10 bar. The reaction was performed for 12 hours. The reaction mixture was diluted using $CDCl_3$ (3 mL). To this reaction mixture, 1,3,5-trimethoxybenezene was added as an internal standard. ^{1}H-NMR studies were conducted to determine the yield of **3a** (68% yield). The solid residue was collected via filtration. The residue was washed with methanol (30 mL) and diethyl ether (15 mL). The collected solid (residual carbon fiber and catalyst) was dried under a vacuum for 4 h.



Reaction

POM decompos 1/23/2025 7:25:00 PM User: CEM Japan 35mL Vessel Snap Cap

Method Parameters

Name: POM decompos
Type: Dynamic

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Stage	Temp(C)	Time(hh:mm:ss)	Pressure(BAR)	Power(W)	PowerMAX	Stirring
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Graphs

Method Summary

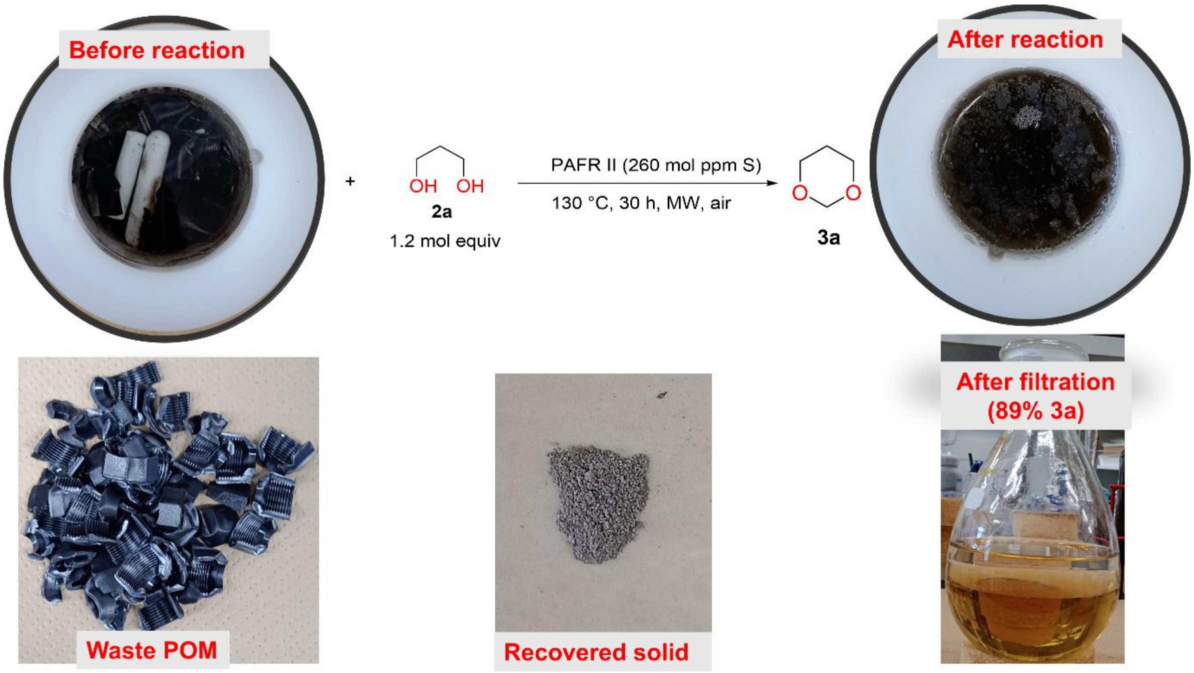
Reaction started:	1/23/2025 7:25:23 PM
Temperature setpoint reached:	1/23/2025 7:30:15 PM
Reaction cooling started:	1/24/2025 7:30:15 AM
Cooling/Reaction ended:	1/24/2025 7:38:32 AM

Reaction Completed Successfully!

Maximum temperature:	138 C
Maximum pressure:	4 BAR
Time to obtain setpoint:	04:52 mm:ss
Time at setpoint:	12:00:00 mm:ss
Time cooling:	08:17 mm:ss

Fig. S9: Microwave reaction profile for CFRP depolymerization in 5g-scale.

4.9. Procedure for 40g-scale POM depolymerization



A mixture containing waste POM (40g, 1333 mmol), PAFR II (260 mol ppm, 100 mg), and 1,3-propanediol **2a** (1600 mmol, 1.2 mol equiv) was introduced into a microwave reaction tube. The tube was sealed and subjected to microwave irradiation at 130 °C (max 80 W) using a microwave reactor, with temperature monitored by an internal thermometer. The reaction was performed for 30 hours. The reaction mixture was diluted using $CDCl_3$ (10 mL). To this reaction mixture, 1,3,5-trimethoxybenezene was added as an internal standard. ^{1}H-NMR studies were conducted to determine the yield of **3a** (89% yield). The solid residue was collected via filtration. The residue was washed with methanol (60 mL) and diethyl ether (30 mL).

4.10. Representative example for NMR yield calculation

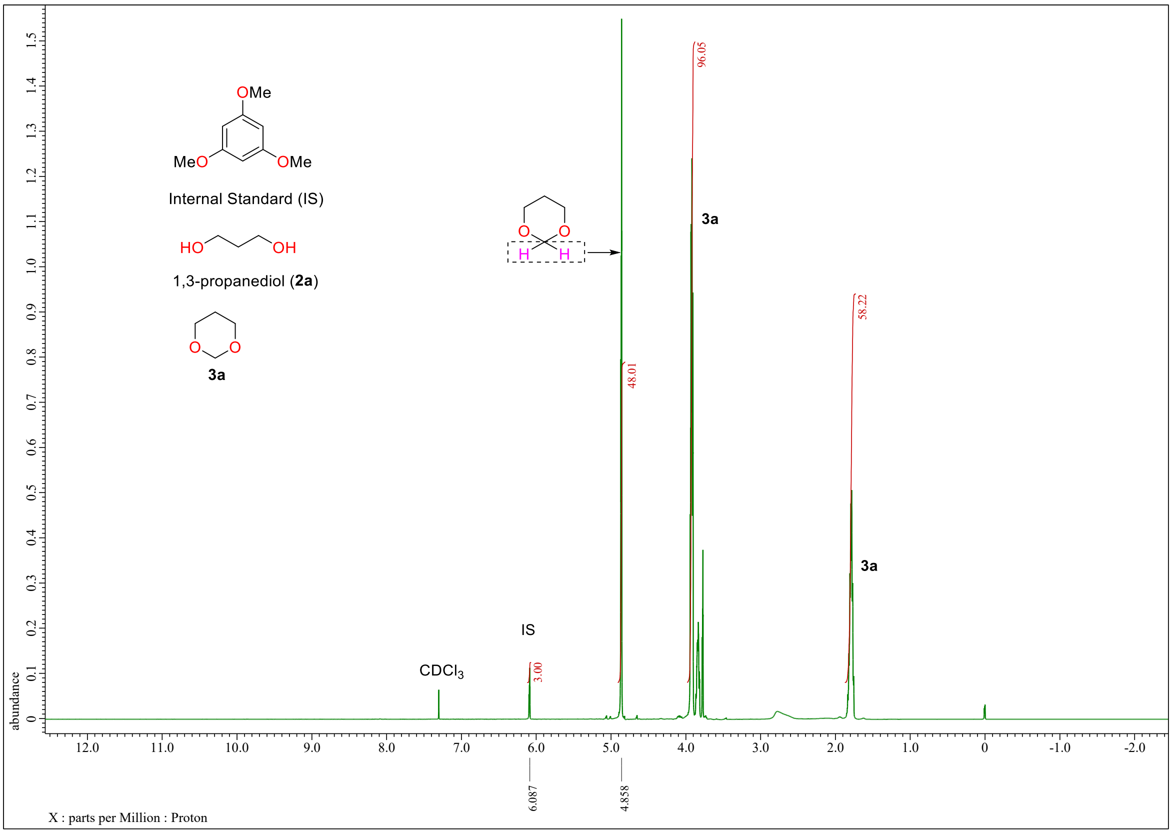


Fig. S10. ^{1}H-NMR spectrum of crude reaction mixture using an internal standard (400 MHz, $CDCl_3$).

The NMR yield was calculated based on the following equation:

% Yield of product = $[(I_P/P_P)(I_{IS}/P_{IS})]$ x $(M_{IS}/Theo\_M_P)$ x 100

I_P means integral of products; P_P means protons of products; I_{IS} means integrals of internal standard; P_{IS} is protons of internal standard; M_{IS} is moles internal standard; $Theo\_M_P$ means theoretical moles of products.

Internal standard (IS) δ 6.1 ppm, 3H; Molecular weight: 168.2 g/mol

Product **3a** δ 4.8 ppm, 2H; Observed integral value is 48

The ratio between **3a** and the Internal standard: (48/2) / (3/3) = 24

The sample contains 92.5 mg of internal standard, which means 92.5/168.19 = 0.55 mmol

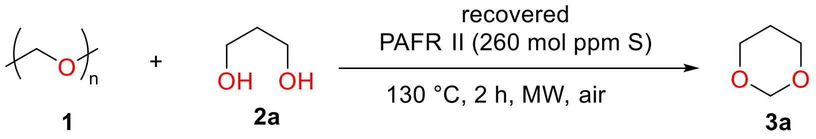
Therefore, the amount of product **3a** in the sample is (24 x 0.55) mmol = 13.2 mmol

The reaction was performed on a 13.3 mmol scale, which means the theoretical yield of **3a** is 13.3 mmol.

Thus, the NMR yield of **3a** in the crude reaction mixture is (13.2/13.3) x 100 = 99.2% ≈ 99%

5. Catalyst reusability

5.1. Catalyst reusability from pure POM material

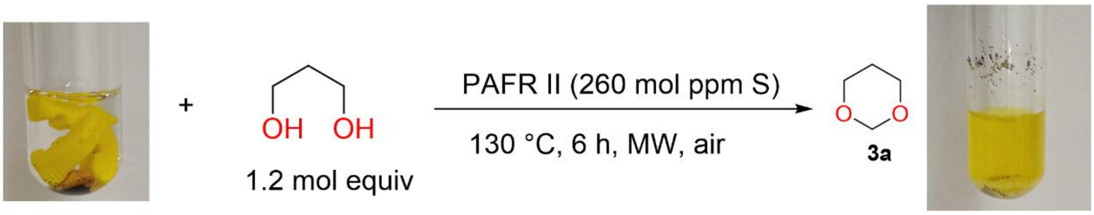


A mixture containing POM materials **1** (13.3 mmol, 1 mol equiv), PAFR II (260 mol ppm, 1.1 mg), and 1,3-propanediol **2a** (15.96 mmol, 1.2 mol equiv) was introduced into a 10 mL microwave reaction tube. The tube was sealed and subjected to microwave irradiation at 130 °C (max 80 W) using a microwave reactor, with temperature monitored by an infrared sensor and pressure maintained below 10 bar. The reaction was performed for 2 h. The reaction mixture was diluted using $CDCl_3$ (1 mL). To this reaction mixture, 1,3,5-trimethoxybenezene was added as an internal standard. ^{1}H-NMR studies were conducted to determine the yield of **3a**. The solid was filtered and washed with water (20 mL), methanol (20 mL), and diethyl ether (10 mL). The solid residue was collected and dried under a vacuum overnight (16 h). The dried catalyst was used for the following reaction in the same reaction vial.

Table S2. Catalyst reusability from POM

entry	number of uses	yield of **3a**
1	1st	99
2	2nd	98
3	3rd	99
4	4th	97
5	5th	98
6	6th	97

5.2. Catalyst reusability from waste plastics (Keck clip)



A mixture containing Keck clip (400 mg, 1 mol equiv), PAFR II (260 mol ppm, 1.1 mg), and 1,3-propanediol **2a** (15.96 mmol, 1.2 mol equiv) was introduced into a 10 mL microwave reaction tube. The tube was sealed and subjected to microwave irradiation at 130 °C (max 80 W) using a microwave reactor, with temperature monitored by an infrared sensor and pressure maintained below 10 bar. The reaction was performed for 6 h. The reaction mixture was diluted using $CDCl_3$ (1 mL). To this reaction mixture, 1,3,5-trimethoxybenezene was added as an internal standard. ^{1}H-NMR studies were conducted to determine the yield of **3a**. The solid was filtered and washed with water (20 mL), methanol (20 mL), and diethyl ether (10 mL). The solid residue was collected and dried under a vacuum overnight (16 h). The dried catalyst was used for the following reaction in the same reaction vial.

Note: The recovered catalyst contains a small amount of insoluble white powder (additives from Keck clip).

Table S3. Catalyst reusability from real plastic (Keck clip)

entry	number of uses	yield of **3a** (%)
1	1st	88
2	2nd	89
3	3rd	88

5.3. SEM images of fresh and recovered catalyst

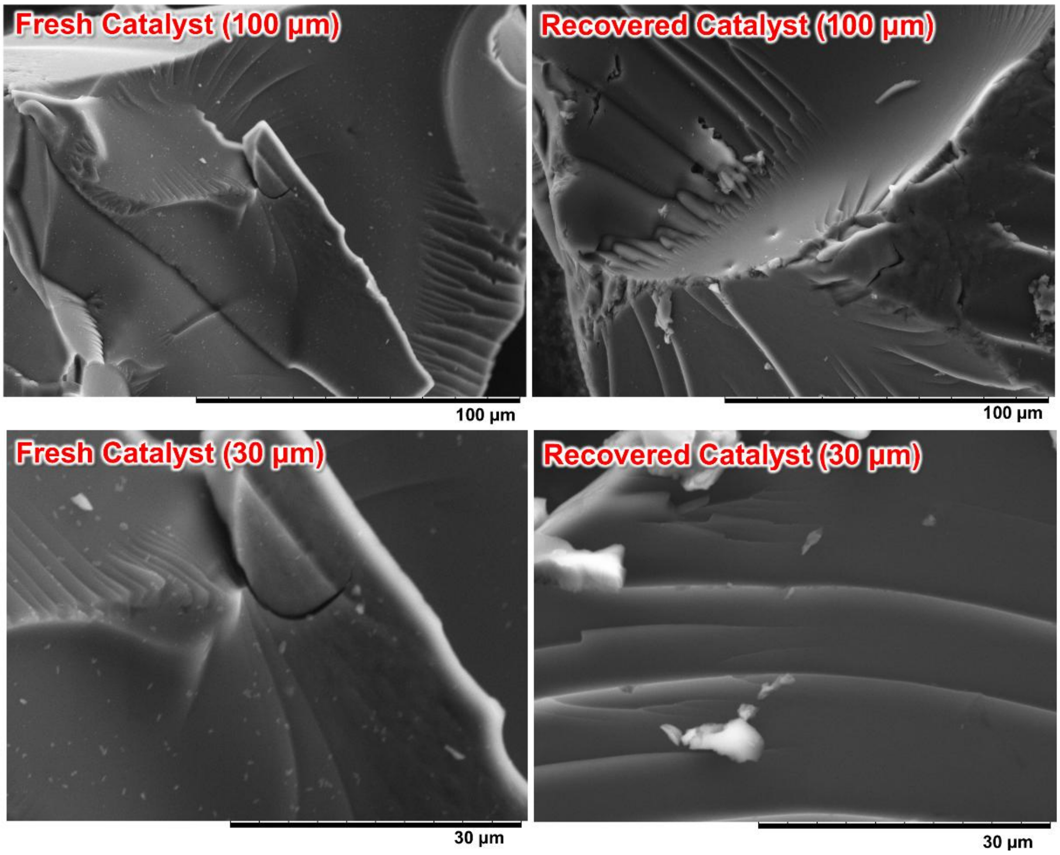


Fig. S11. SEM Images of Fresh and Recovered Catalysts

5.4. FT-IR spectrum of fresh and recovered catalysts

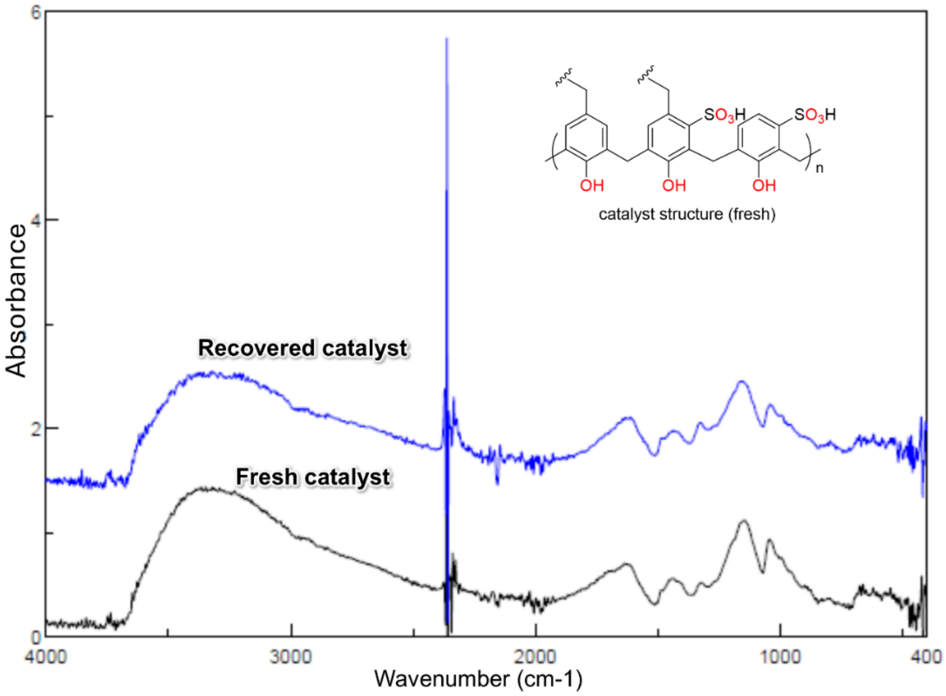
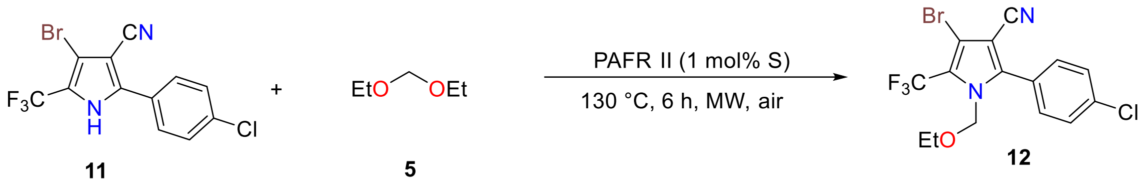


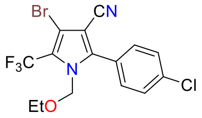
Fig. S12. IR spectrum of Fresh and Recovered catalysts

6. Synthesis of chlorfenapyr



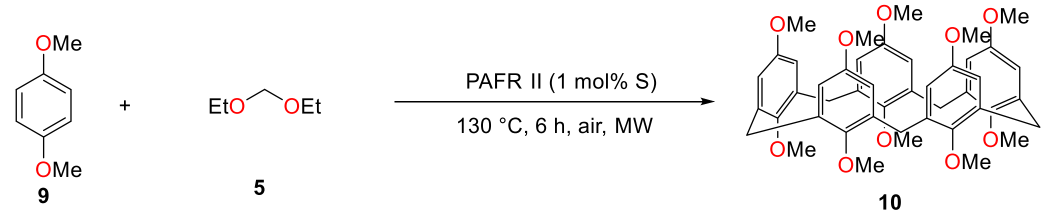
A mixture containing **11** (25 mg, 1 mol equiv), PAFR II (1 mol%, 0.26 mg), and ethylal **5** (374 mg, 3.6 mmol) was introduced into a 10 mL microwave reaction tube. The tube was sealed and subjected to microwave irradiation at 130 °C (max 80 W) using a microwave reactor, with temperature monitored by an infrared sensor and pressure maintained below 10 bar. The reaction was performed for 6 h. The reaction mixture was diluted using $CHCl_3$ (1 mL). The acid catalyst was removed from the reaction mixture via filtration (washed with chloroform). The filtrate was collected and dried under a vacuum. The crude reaction mixture was purified by column chromatography using hexane/ethyl acetate as eluent to get **12**.

Chlorfenapyr (12, ref 4)



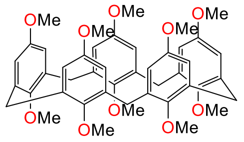
White solid (55% yield, 16 mg). m. p. 98 °C-100 °C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 5.20 (s, 2H), 3.40 (q, *J* = 7.0 Hz, 2H), 1.17 (t, *J* = 7.0 Hz, 3H). $^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$) δ 144.3 (q, *J* = 1.8 Hz), 137.3, 131.3, 129.7, 125.3, 121.2 (q, *J* = 42 Hz), 120.5 (q, *J* = 266 Hz), 113.5, 103.6 (q, *J* = 3.6 Hz), 99.2, 75.5, 64.6, 14.7. ^{19}F-NMR (470 MHz, $CDCl_3$) δ -56.4

7. Synthesis of DMpillar[5]arene



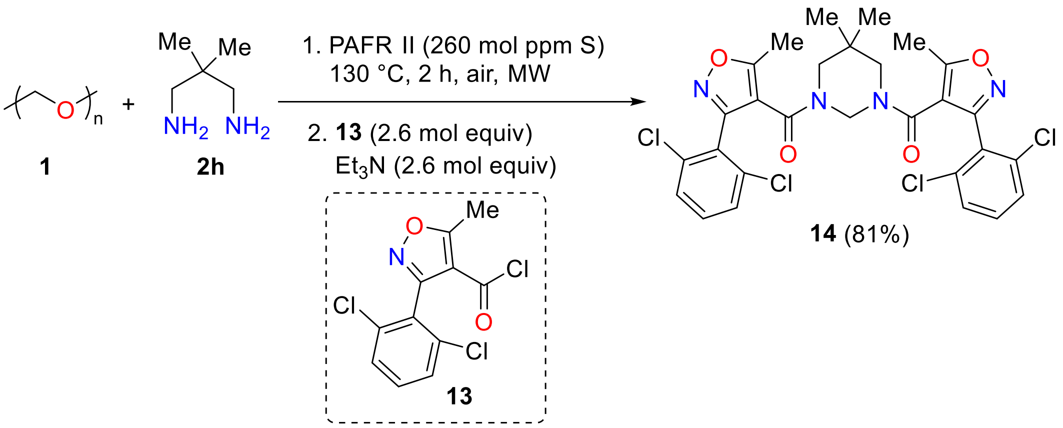
A mixture containing **9** (50 mg, 1 mol equiv), PAFR II (1 mol%, 0.5 mg), and ethylal **5** (1563 mg, 15 mmol) was introduced into a 10 mL microwave reaction tube. The tube was sealed and subjected to microwave irradiation at 130 °C (max 80 W) using a microwave reactor, with temperature monitored by an infrared sensor and pressure maintained below 10 bar. The reaction was performed for 6 h. After the reaction, the reaction mixture was poured into a beaker containing methanol (10 mL). A white precipitate appeared, and the precipitate was collected via filtration and washed with methanol (5 mL). The collected solid was recrystallized from acetonitrile to get pure **10**.

DMpillar[5]arene (10, ref 5)



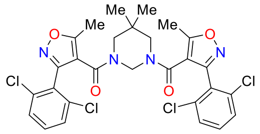
White solid (63% yield, 34 mg). m. p. 248 °C-250 °C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.64 (s, 10H), 3.87 (s, 10H), 3.67 (s, 30H). $^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$) δ 151.5, 127.7, 113.7, 56.2, 29.8. Maldi-TOF Mass: m/z calculated for $C_{45}H_{50}O_{10}$: 750.340; observed: 750.373.

8. One-pot synthesis of herbicides



A mixture containing polymer **1** (100 mg, 3.33 mmol (based on monomer), 1 mol equiv), PAFR II (260 mol ppm, 0.28 mg), and diamine **2h** (4 mmol, 1.2 mol equiv) was introduced into a 10 mL microwave reaction tube. The tube was sealed and subjected to microwave irradiation at 130 °C (max 80 W) using a microwave reactor, with temperature monitored by an infrared sensor and pressure maintained below 10 bar. The reaction was performed for 2 h. After that, the reaction mixture was cooled down to 0 °C. To the crude reaction mixture, Et_3N was added (2.6 mol equiv), followed by portionwise addition of **13** (2.6 mol equiv). The reaction mixture was stirred at 0 °C for 5 minutes, followed by an additional 5 minutes at 24 °C. The reaction mixture was diluted with water (3 mL) and dichloromethane (3 mL). The mixture was then extracted with 30 mL of dichloromethane, using an additional 20 mL of water. The organic layer was collected, and the volatiles were evaporated. The crude solid was recrystallized from $CHCl_3$/Methanol to obtain compound **14**.

(5,5-dimethyldihydropyrimidine-1,3(2H,4H)-diyl)bis((3-(2,6-dichlorophenyl)-5-methylisoxazol-4-yl)methanone) (14, ref 6)



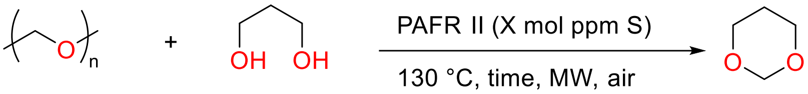
White solid (81% yield, 1.7 g). m. p. 228 °C-230 °C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.39-7.28 (m, 6H), 4.78 (brs, 2H), 3.34-2.70 (br, m, 4H), 2.54 (s, 6H), 0.78 (s, 6H). $^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$) δ 162.2, 156.8, 135.8, 131.6, 128.6, 128.3, 127.3, 112.5, 57.9, 57.1, 32.3, 23.2, 12.4.

9. Preparation of microplastics

The microplastics were prepared by ball milling the black polyacetal joints (850 mg) using a ZrO_2 ball at a speed of 30 Hz. After 35 minutes of ball milling, we directly transferred 400 mg of these microplastics to a microwave reaction tube without any further purifications.

10. Chemical kinetics studies

10.1. Kinetics for catalyst



1 (400 mg, 1 equiv)

2a (1.2 equiv)

3a

Table S4. Calculation of initial rates using different catalyst loadings

X mol	**3a** yield (%)		v = initial rate	ln(v)	lnX
ppm	5 mins	8 mins	d[**3a**]/dt		
260	27	46	6.33	1.84	5.56
300	34	56	7.33	1.99	5.70
325	31	56	8.33	2.12	5.78
350	35	62	9	2.19	5.86

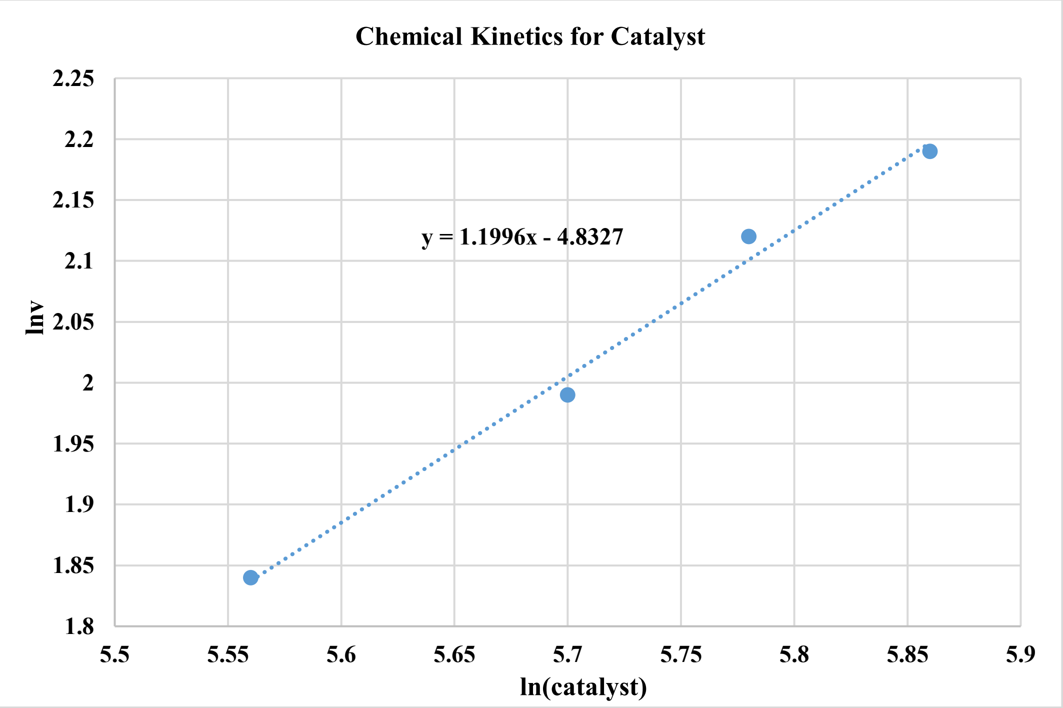


Fig. S13: Graphical plot ln(v) vs lnX

v is the rate of reaction, n is the order of the reaction

Rate = v = kX^n, where k is the rate constant.

$\ln v = n \ln X + C$ where C is a constant

Therefore, the order of the reaction is $n = 1.19 \approx 1$

10.2. Kinetics for 1,3-propanediol (2a)

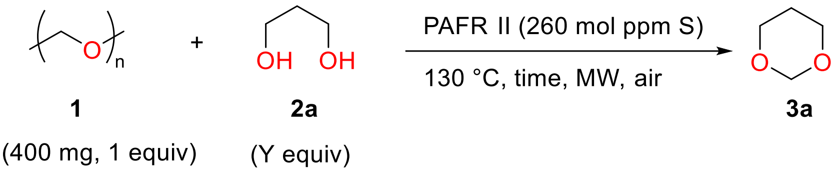


Table S5. Calculation of initial rates using different 1,3-propanediol (**2a**) amounts

Y mol equiv	**3a** yield (%) 5 mins	8 mins	v = initial rate d[**3a**]/dt	ln(v)	lnY
1	19	37	6	1.79	0
1.2	27	46	6.33	1.84	0.18
1.5	36	53	5.66	1.78	0.41
1.75	39	57	6	1.78	0.56

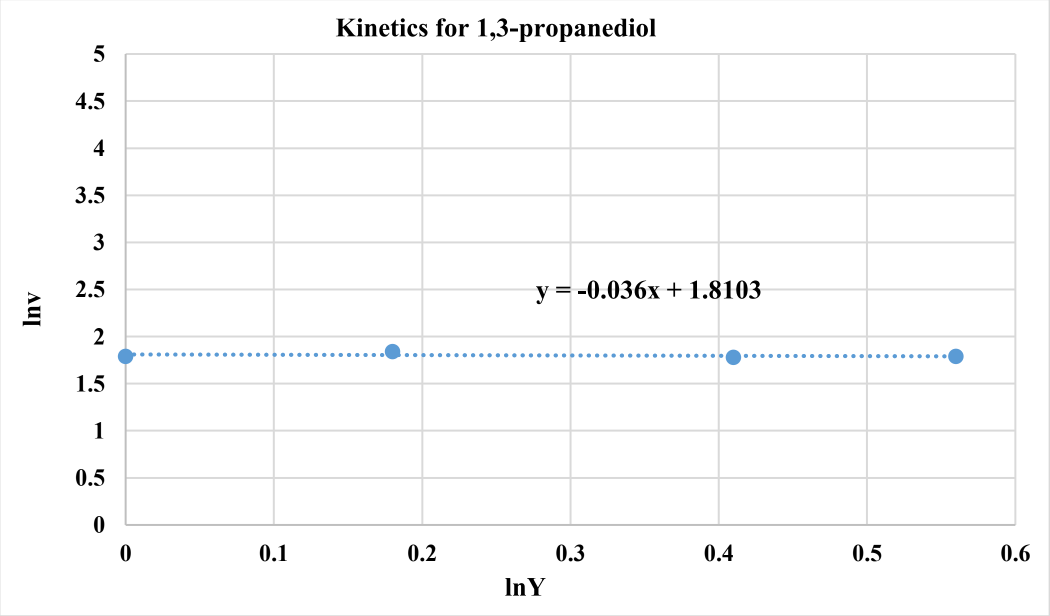


Fig. S14: Graphical plot ln(v) vs lnY

v is the rate of reaction, n is the order of the reaction

Rate = v = kY^n, where k is the rate constant.

lnv = nlnY + C, where C is a constant

Therefore, the order of the reaction is n = 0.036 ≈ 0

10.3. Kinetics for polymer (1)

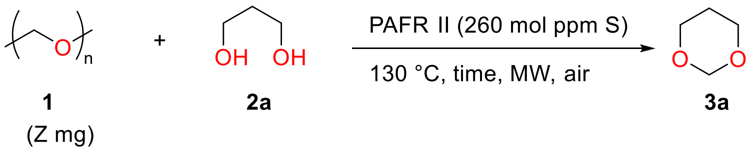


Table S6. Calculation of initial rates using different polymer (**1**) amounts

Z	**3a** yield (%)		v = initial rate	ln(v)	lnZ
mg	5 mins	8 mins	d[**3a**]/dt		
325	26	40	4.66	1.53	5.78
350	18	32	4.66	1.53	5.86
375	28	45	5.66	1.73	5.93
400	27	46	6.33	1.84	5.99
425	25	43	6	1.79	6.05
450	22	40	6	1.79	6.11

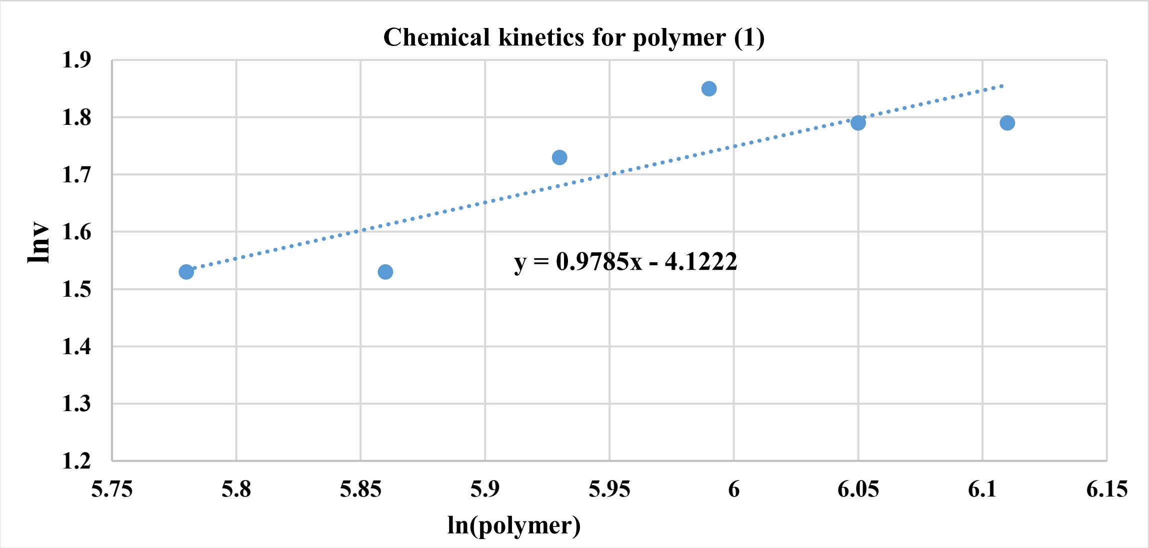


Fig. S15: Graphical plot ln(v) vs lnZ

v is the rate of reaction, n is the order of the reaction

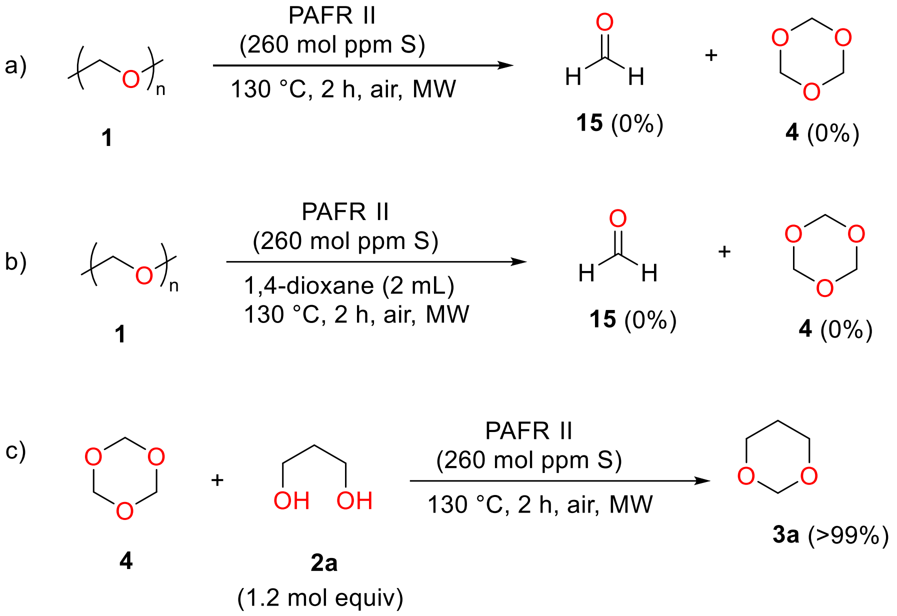
Rate = v = kZ^n, where k is the rate constant.

lnv = nlnZ + C where C is a constant

Therefore, the order of the reaction is n = 0.978 ≈ 1

Discussion: Due to the heterogeneous nature of the catalyst and polymer, it is challenging to obtain fine fittings; however, we are able to estimate the rate of reactions for each component. Based on the kinetics shown above, the reaction follows first-order dependence for PAFR II catalyst and POM polymer, whereas it follows zero-order dependence for 1,3-propanediol. Based on these results, the interaction between two solid materials (catalyst and polymer) is the rate-determining step for this reaction.

11. Mechanistic studies



11.1. IR studies to identify the coordination site

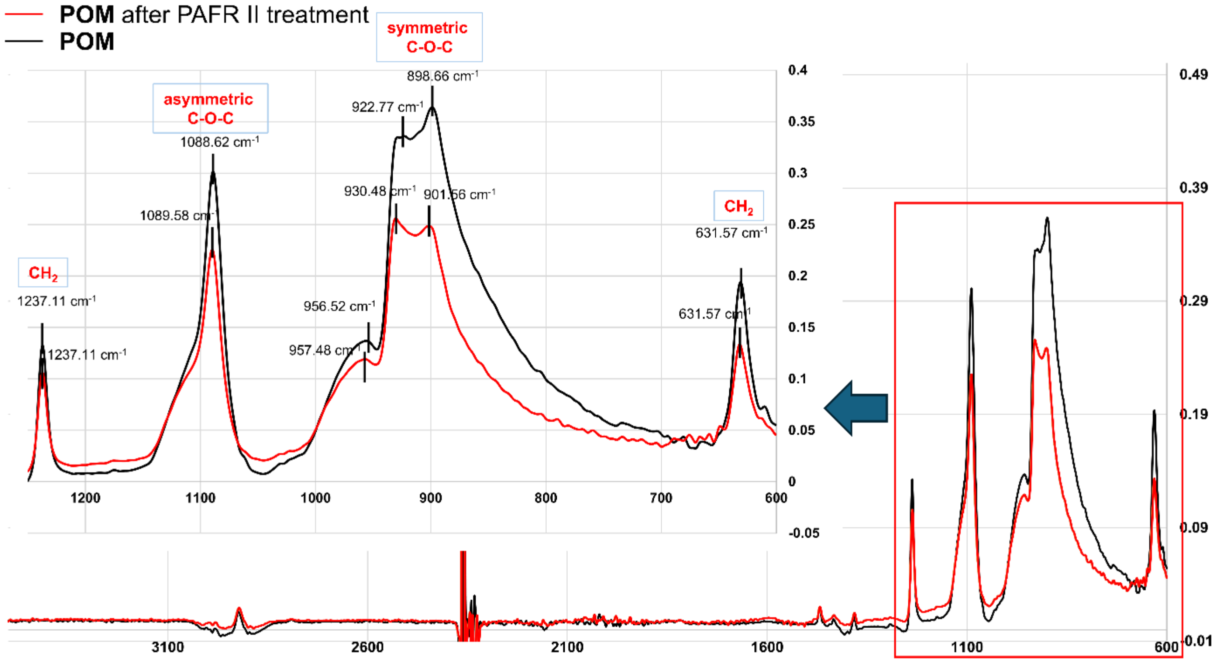


Fig. S16. IR spectra of POM (**1**) and POM after PAFR II treatment under microwave

The sample "POM after PAFR II treatment" was prepared by mixing POM and PAFR II in a 1:1 ratio and irradiating (microwave) it at 80 °C for 10 mins. No change in the stretching frequencies of C–H bonds was observed by IR spectras. For example, the signals at 1237.11 cm^{-1} and 631.57 cm^{-1} remain exactly the same in pure POM and POM after PAFR II treatment. However, signal shifting was observed for C–O bonds. The asymmetric C–O stretching frequency at 1088.62 cm^{-1} in POM shifted to 1089.58 cm^{-1}, and similarly, the symmetric C–O stretching frequency at 922.77 cm^{-1} and 898.66

cm^{-1} shifted to 930.48 cm^{-1} and 901.55 cm^{-1}. These signal shifts indicate that the coordination site in the POM polymer is the oxygen atom that accepts the proton from PAFR II. Additionally, the intensity of the C–O stretching frequencies was significantly reduced after PAFR II treatment, indicating weakening of the C–O bond and possibly protonation of the oxygen atom. Thus, based on these observations, we proposed that the coordination site in the polymer is the oxygen atom.

12. Life cycle assessment (LCA) analysis

Method

A cradle-to-gate life cycle assessment (LCA) was conducted to evaluate and compare the environmental performance of three production routes for 1,3-dioxane:

(i) the conventional synthesis route using solar electricity,

(ii) the microwave-assisted conversion of polyoxymethylene (POM) under grid electricity, and

(iii) the renewable-powered microwave-assisted route, in which the POM production stage was supplied by solar electricity.

The functional unit was defined as 1 kg of 1,3-dioxane produced, and all results were expressed in kg CO_2-eq per kg 1,3-dioxane. The system boundary covered raw material extraction, feedstock preparation, and chemical conversion. The construction of experimental equipment, as well as product use and disposal stages, were excluded. Inventory data for the conventional route was taken from the IDEA v3.1 database.[7] The renewable-power scenario replaced the default Japanese grid mix with "Electricity, solar, Japan" from the same database to represent a low-carbon electricity source. As this study focuses on CO_2 emissions, the Life Cycle Impact Assessment (LCIA) was performed using the IPCC 2013 GWP 100a (Intergovernmental Panel on Climate Change, Global Warming Potential) method.[8]

All modeling and analysis were conducted in SimaPro v9.5.0.2.

Result

The life cycle assessment results for the three production routes are summarized in terms of Global Warming Potential (GWP, 100 years), expressed as kg CO_2-eq per kg of 1,3-dioxane produced. The microwave-assisted POM conversion using grid electricity showed the highest emission intensity, reaching 15.25 kg CO_2-eq / kg product, mainly due to the high electricity consumption of the microwave process. In contrast, when the electricity supply for POM production was replaced with solar power, the total emissions decreased drastically to 1.88 kg CO_2-eq / kg product, corresponding to an almost 88% reduction compared with the grid-powered case. The conventional synthesis route exhibited an intermediate value of 6.08 kg CO_2-eq / kg product, which was lower than the grid-based experimental route but still considerably higher than the renewable-powered scenario. These results indicate that the carbon intensity of electricity plays a dominant role in determining the overall environmental performance of 1,3-dioxane production, whereas process type and reaction efficiency have secondary effects.

Discussion

The LCA results illustrate the potential environmental advantages of the POM-based route for 1,3-dioxane production. Although the current laboratory-scale process still shows relatively high greenhouse gas emissions due to the electricity-intensive nature of the microwave-assisted conversion, its environmental performance can be substantially improved when coupled with low-carbon or renewable energy sources. This finding reveals that the POM-based conversion possesses clear potential for sustainable chemical synthesis under appropriate energy conditions. Compared with the conventional synthesis pathway, the POM-based approach represents a promising alternative for low-carbon chemical production, particularly if future process development can enhance energy efficiency and conversion yield. The contribution analysis indicates that electricity consumption dominates the environmental impact, and the results are highly sensitive to the electricity mix. Hence, optimization should focus on reducing power demand and integrating renewable electricity, which are key to unlocking the full environmental benefits of this pathway. In contrast, the conventional route is primarily influenced by the carbon intensity of its feedstocks rather than electricity use. This difference highlights that process electrification fundamentally reshapes the emission profile—transforming electricity from a minor to a major factor and thus making clean energy availability crucial for sustainability.

Overall, this preliminary LCA supports the sustainability potential of POM-based conversion for 1,3-dioxane synthesis. While this study focuses only on CO_2 emissions at the process level, future work should expand the assessment scope to include other environmental indicators and scale-up considerations, enabling a more comprehensive understanding of how POM-derived synthesis can contribute to low-carbon chemical manufacturing.

13. References

1. M. J. Cullen, M. G. Davidson, M. D. Jones, J. A. Stewart, Valorization of polyoxymethylene (POM) waste as a C1 synthon for industrially relevant dialkoxymethanes and cyclic aminals. *RSC Sustainability* 2025, **3**, 1114–1121.
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14. Solid-State NMR

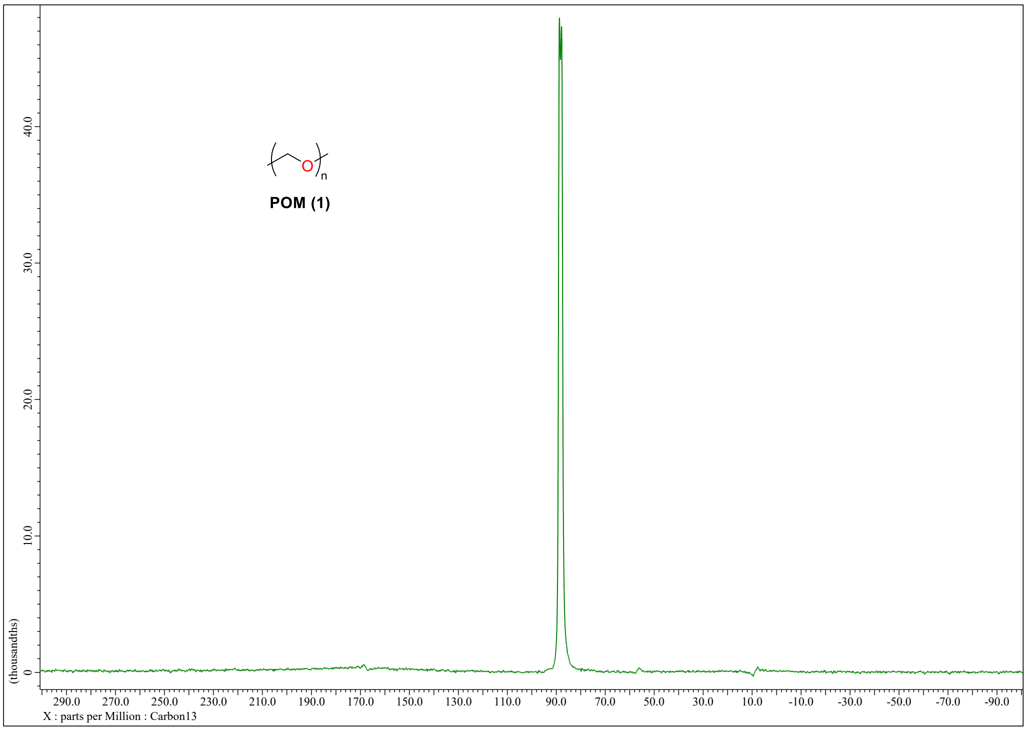


Fig. S17-1. Solid-state ^{13}C-NMR{cpmas} spectrum of POM (4800 scans).

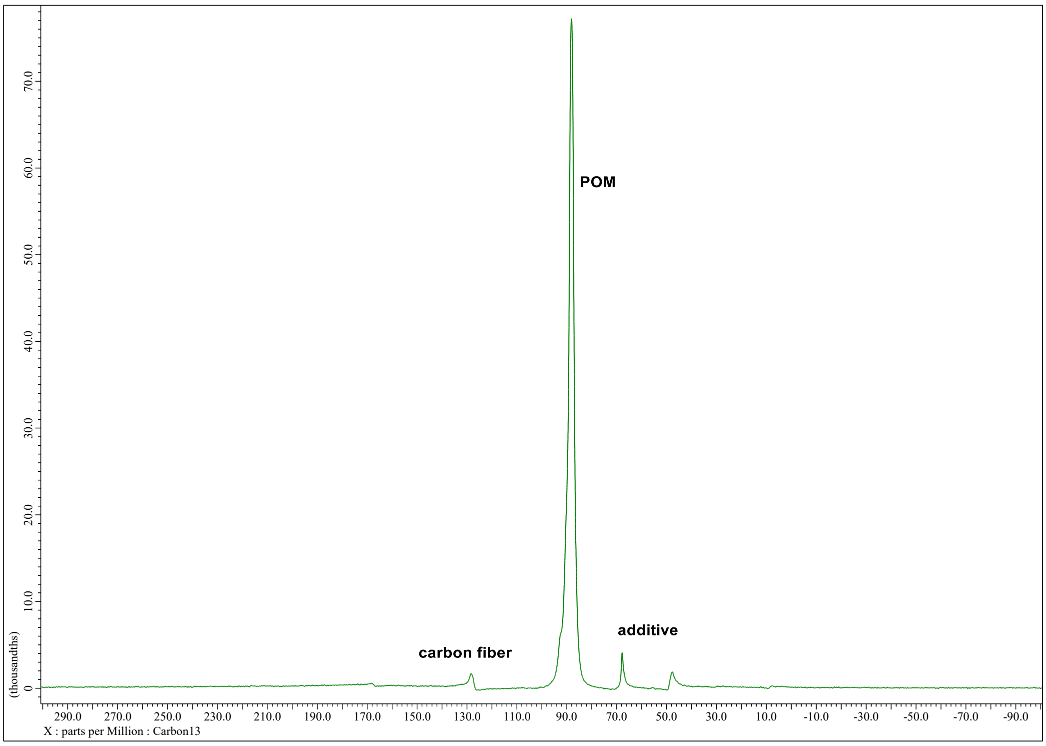


Fig. S17-2. Solid-state ^{13}C-NMR{cpmas} spectrum of POM-C-10 (12000 scans).

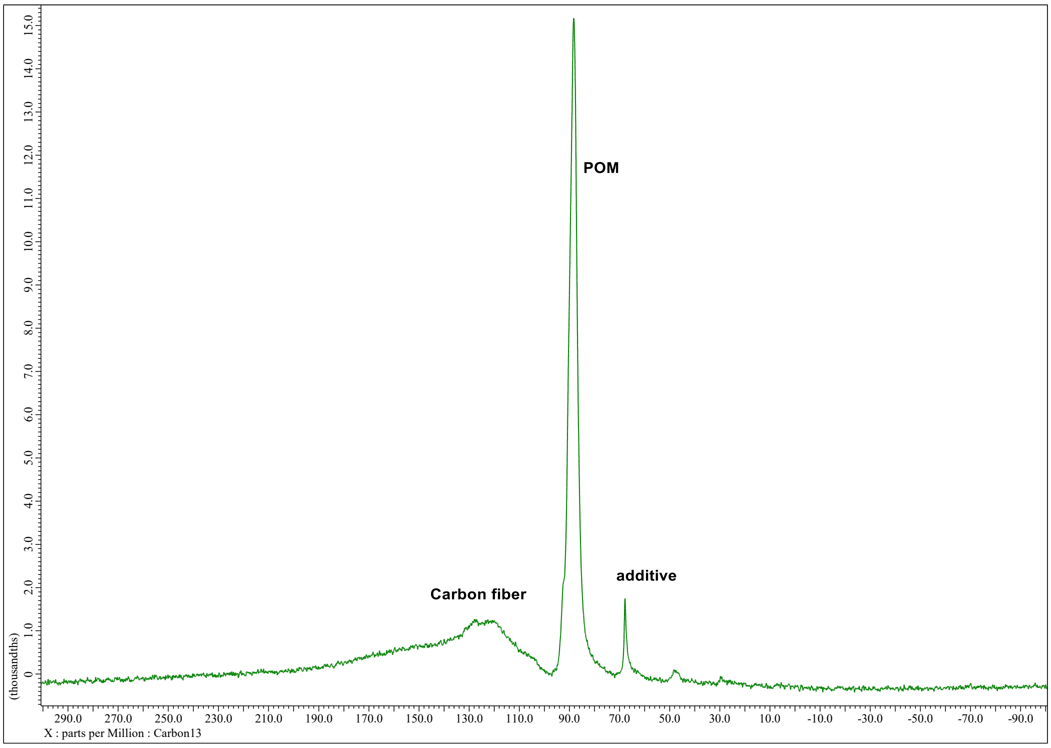


Fig. S17-3. Solid-state ^{13}C-NMR{single pulse_dec} spectrum of POM-C-10 (12000 scans).

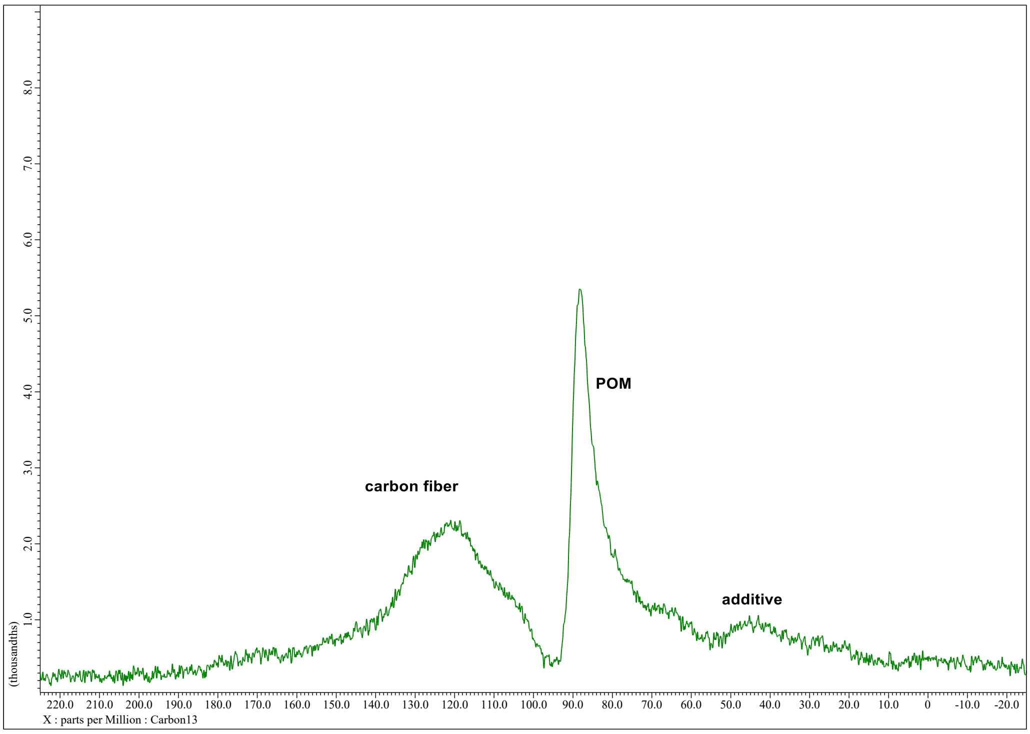


Fig. S17-4. Solid-state ^{13}C-NMR{single pulse} spectrum of POM-C-10 (12000 scans).

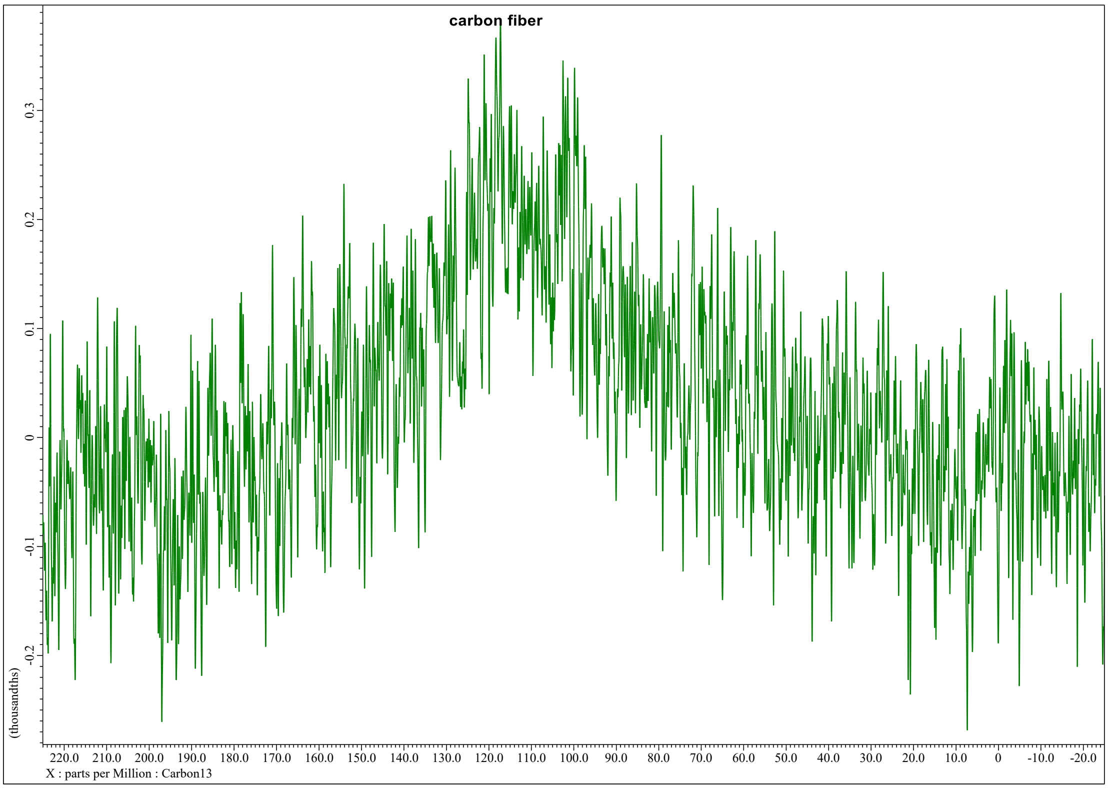


Fig. S17-5. Solid-state ^{13}C-NMR{single pulse} spectrum of recovered carbon fiber **(**12000 scans).

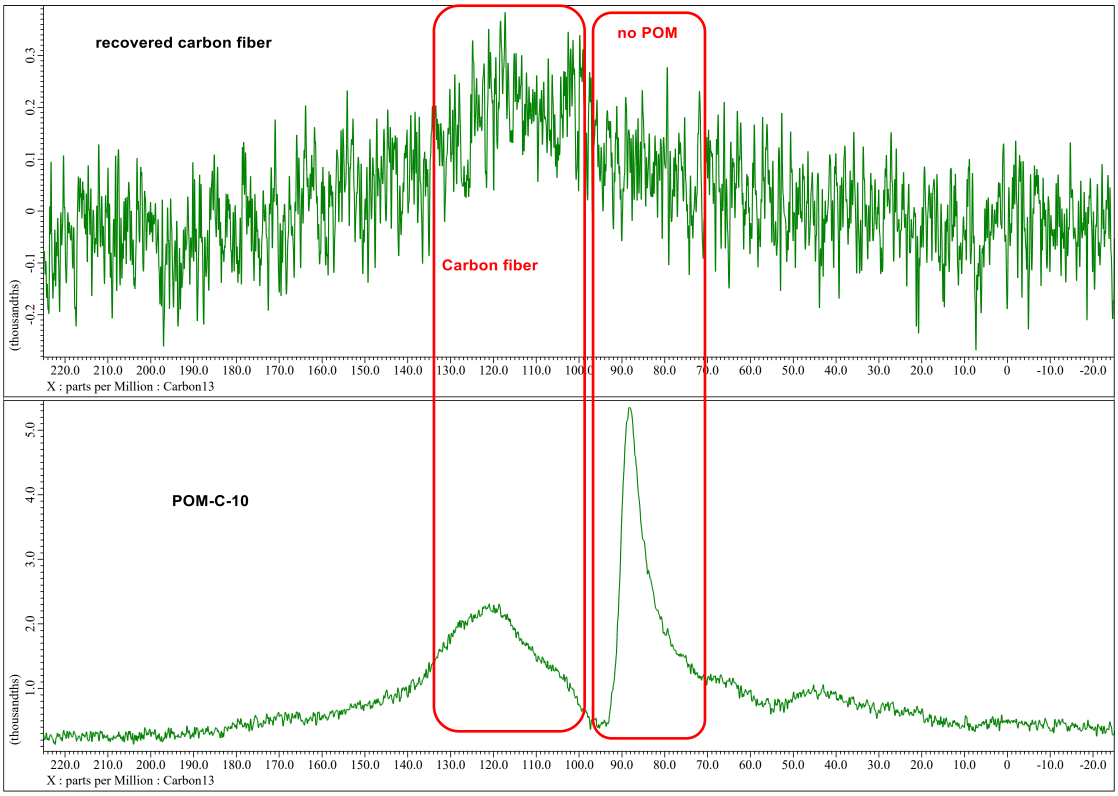


Fig. S17-6. Comparison between the recovered carbon fiber (top) and POM-C-10 (bottom) (^{13}C-NMR{single pulse}).

15. NMR spectras

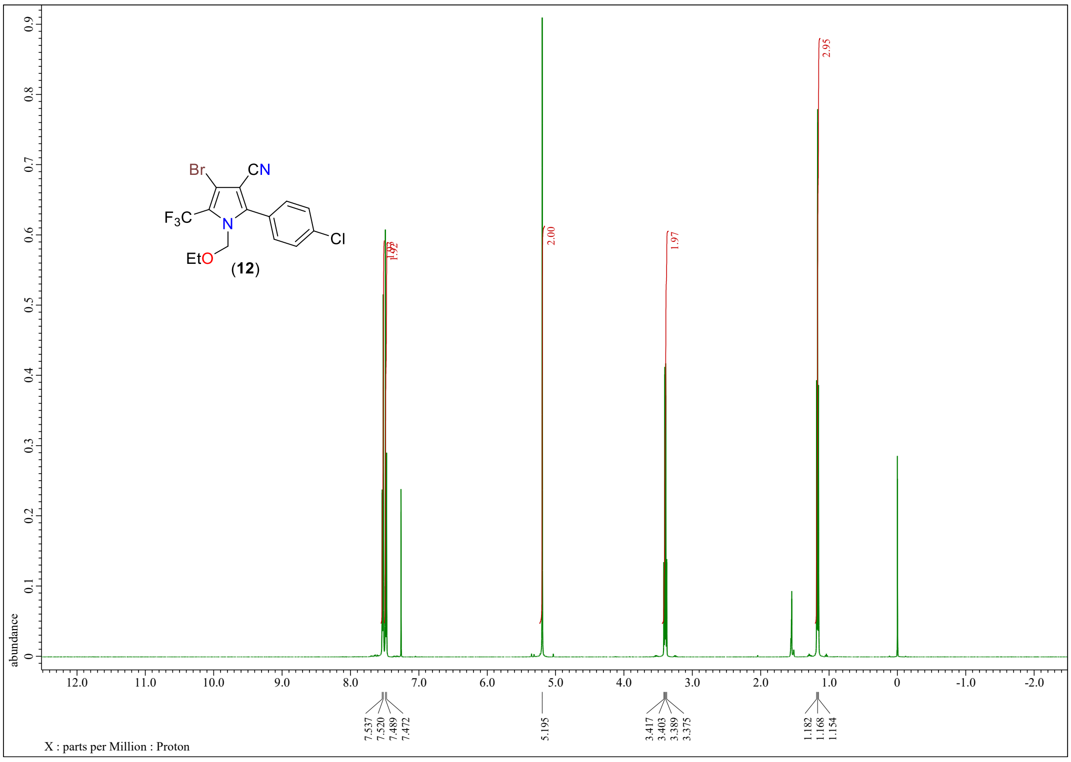


Fig. S18-1. ^{1}H-NMR spectrum of **12** (500 MHz, $CDCl_3$).

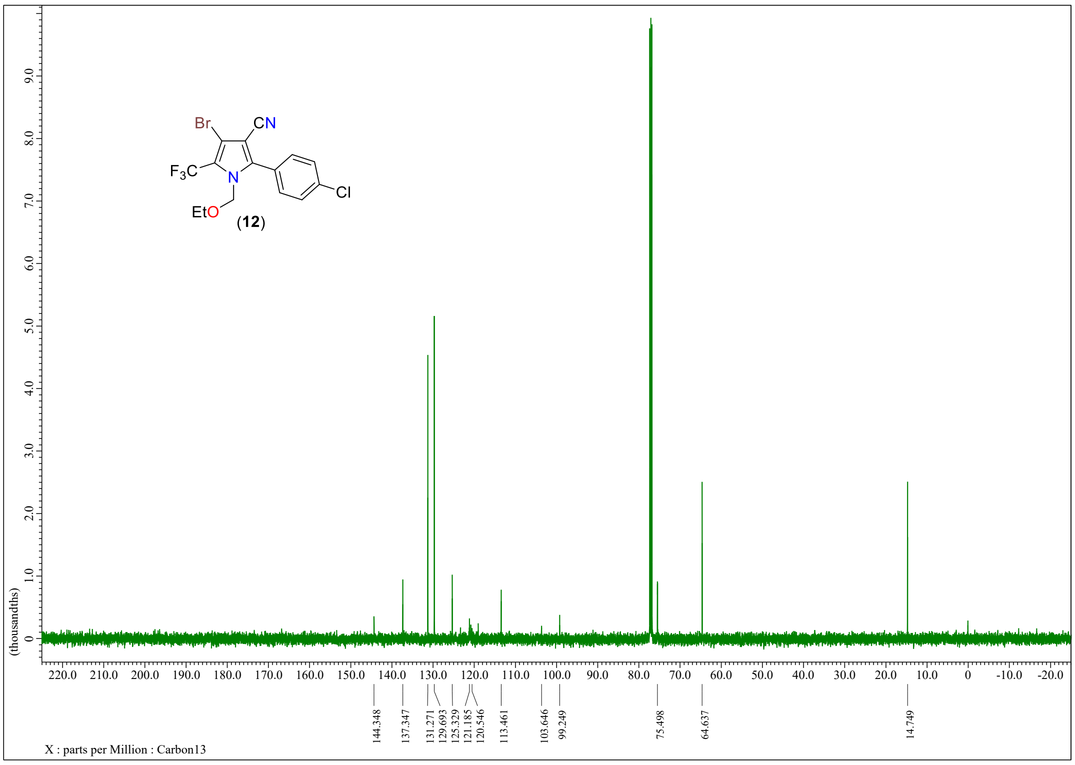


Fig. S18-2. ^{13}C-NMR spectrum of **12** (125 MHz, $CDCl_3$).

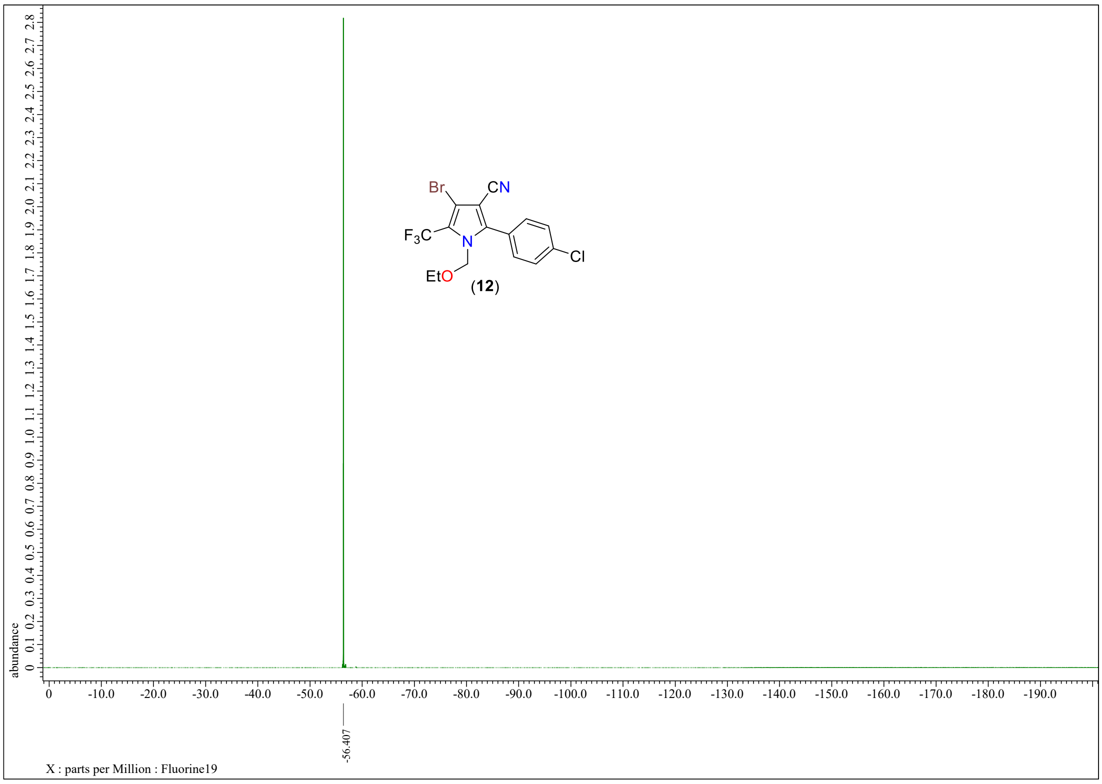


Fig. S18-3. ^{19}F-NMR spectrum of **12** (470 MHz, $CDCl_3$).

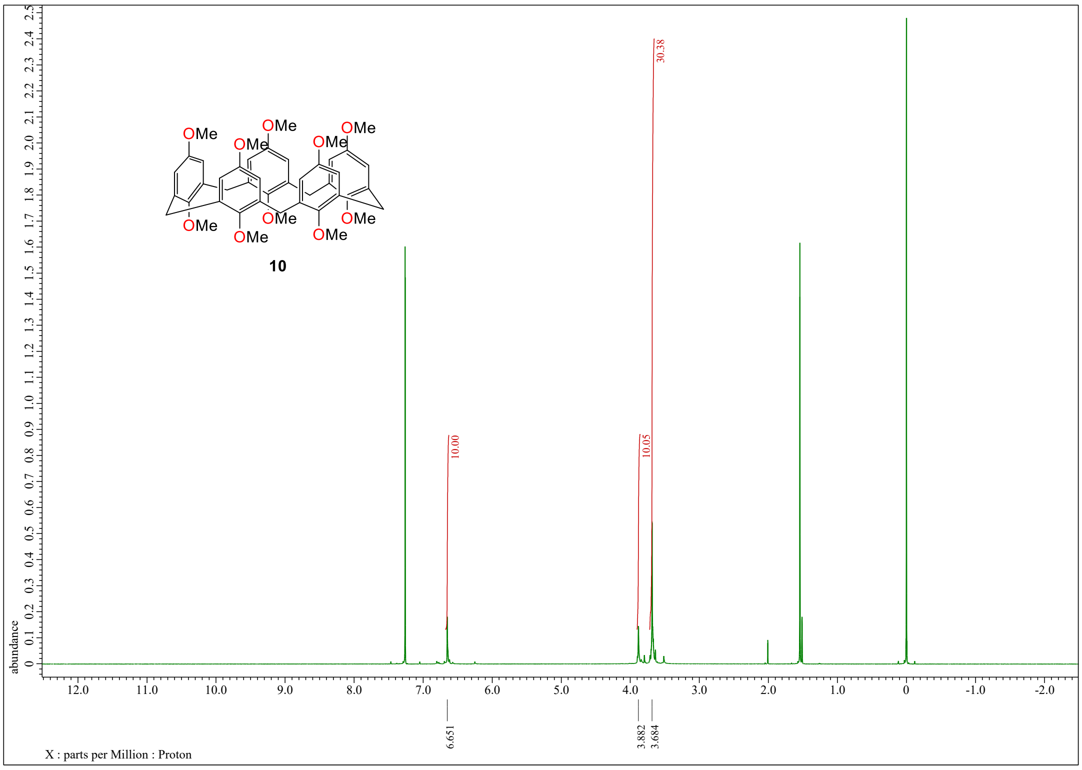


Fig. S19-1. ^{1}H-NMR spectrum of **10** (500 MHz, CDCl$_3$).

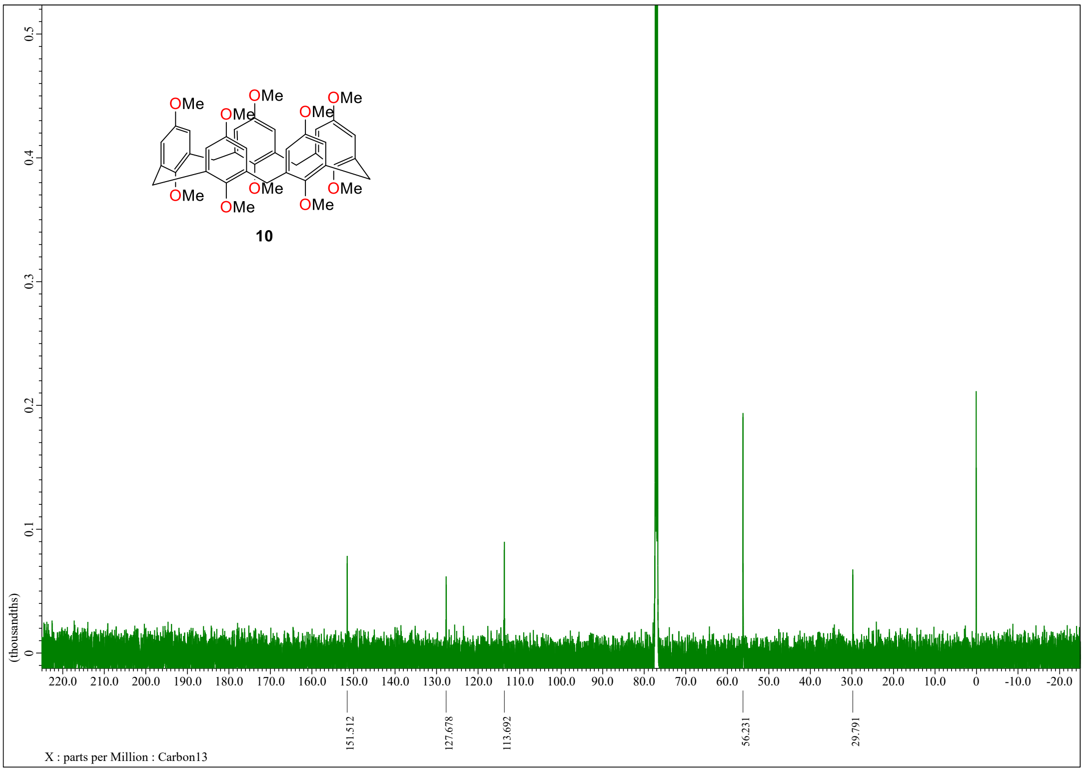


Fig. S19-2. ^{13}C-NMR spectrum of **10** (125 MHz, CDCl$_3$).

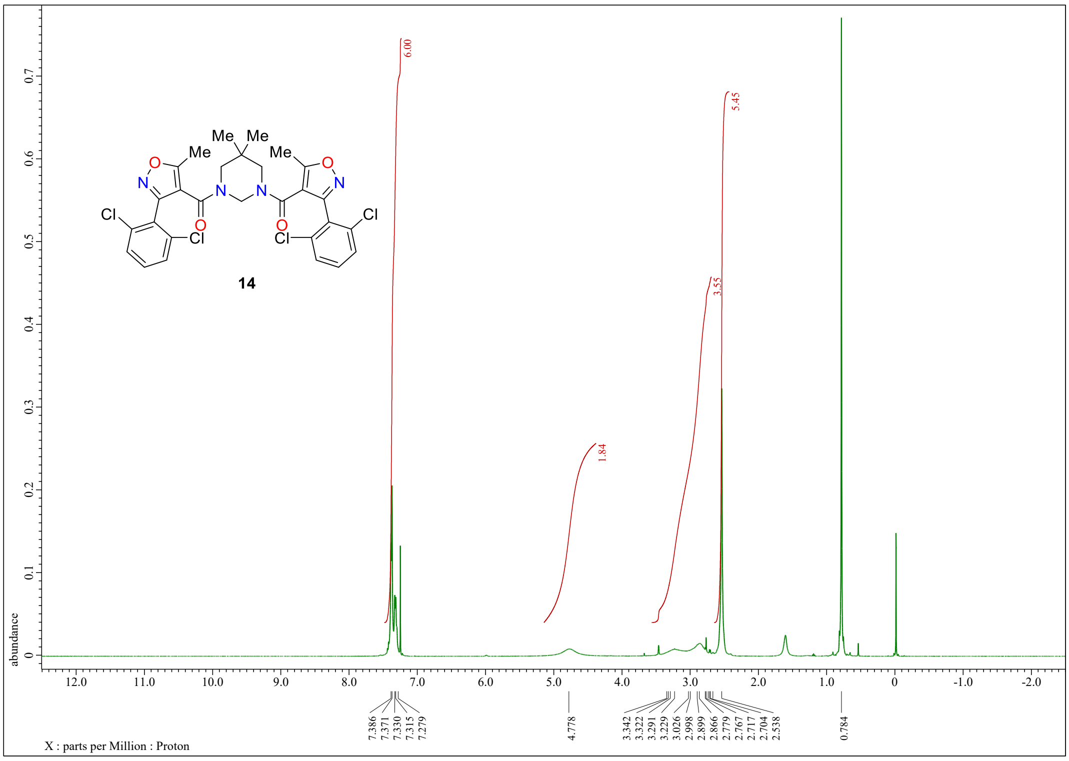


Fig. S20-1. ^{1}H-NMR spectrum of **14** (500 MHz, $CDCl_3$).

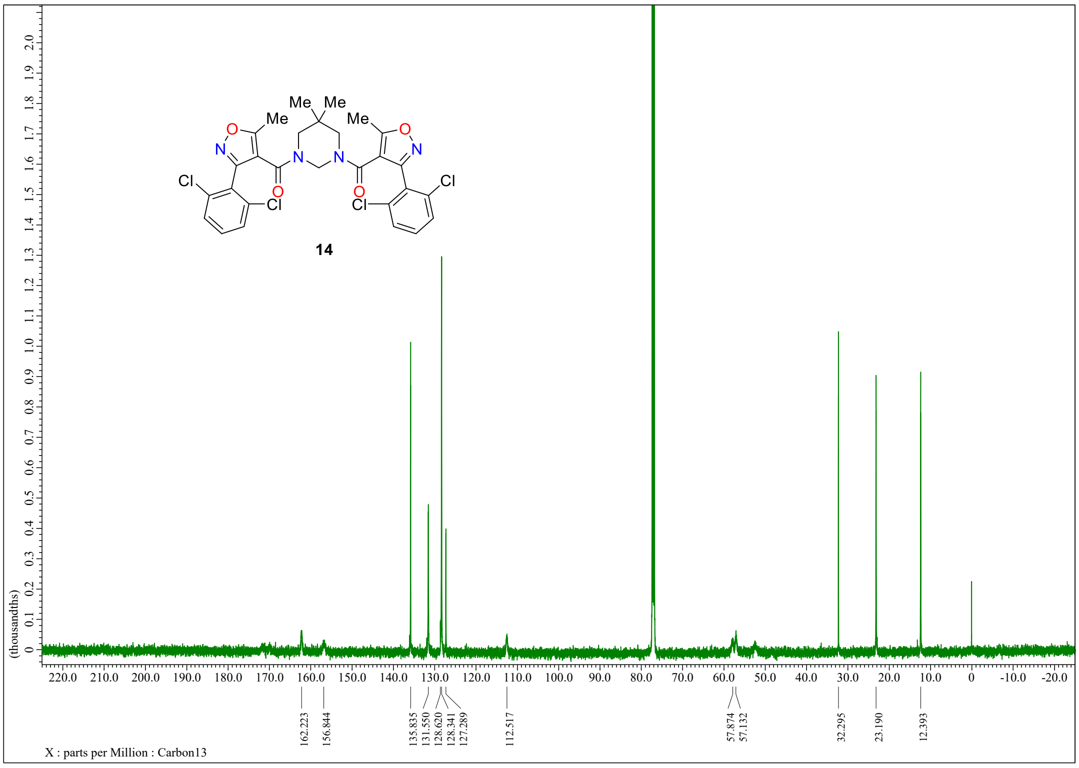


Fig. S20-2. ^{13}C-NMR spectrum of **14** (125 MHz, $CDCl_3$).

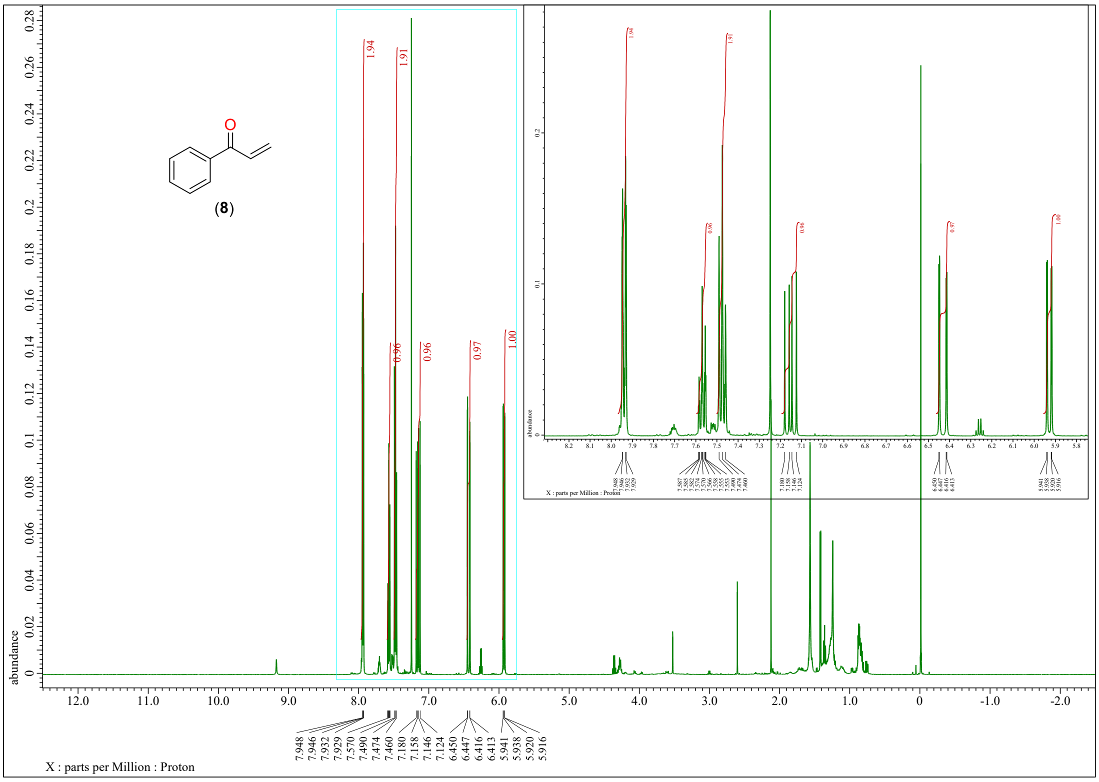


Fig. S21-1. ^{1}H-NMR spectrum of **8** (500 MHz, $CDCl_3$).

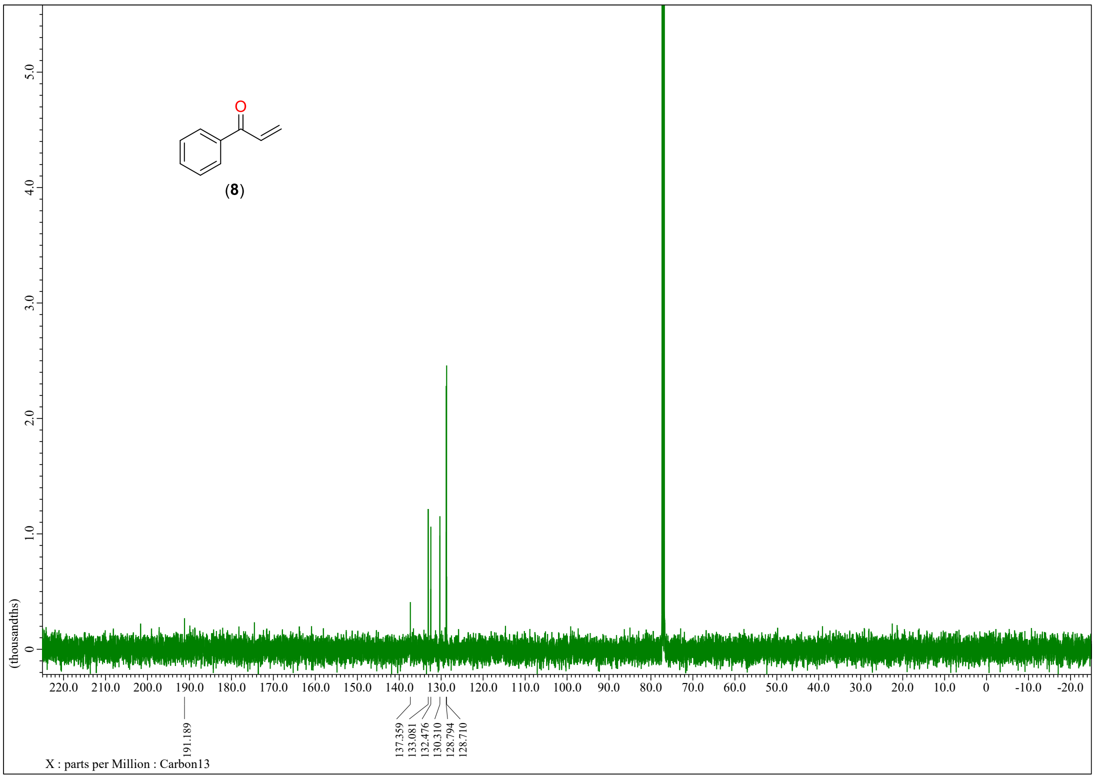


Fig. S21-2. ^{13}C-NMR spectrum of **8** (125 MHz, $CDCl_3$).

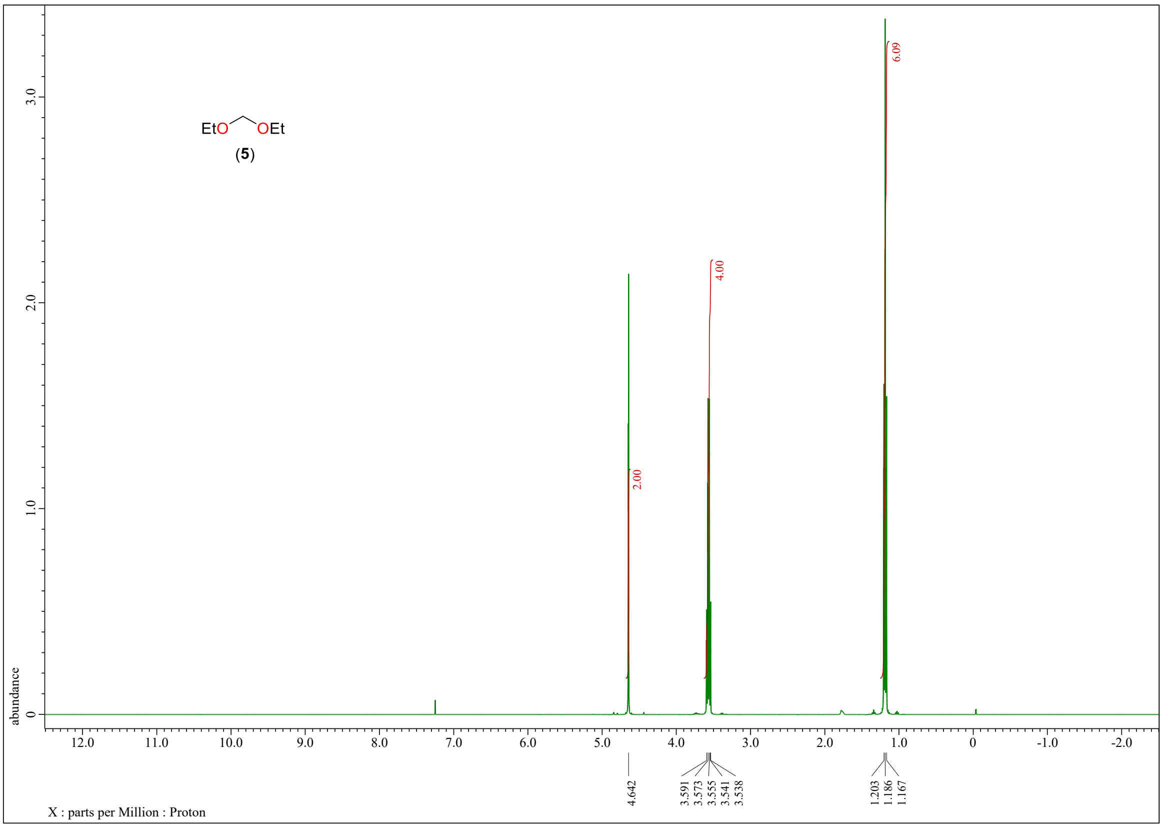


Fig. S22-1. ^{1}H-NMR spectrum of **5** (400 MHz, CDCl$_3$).

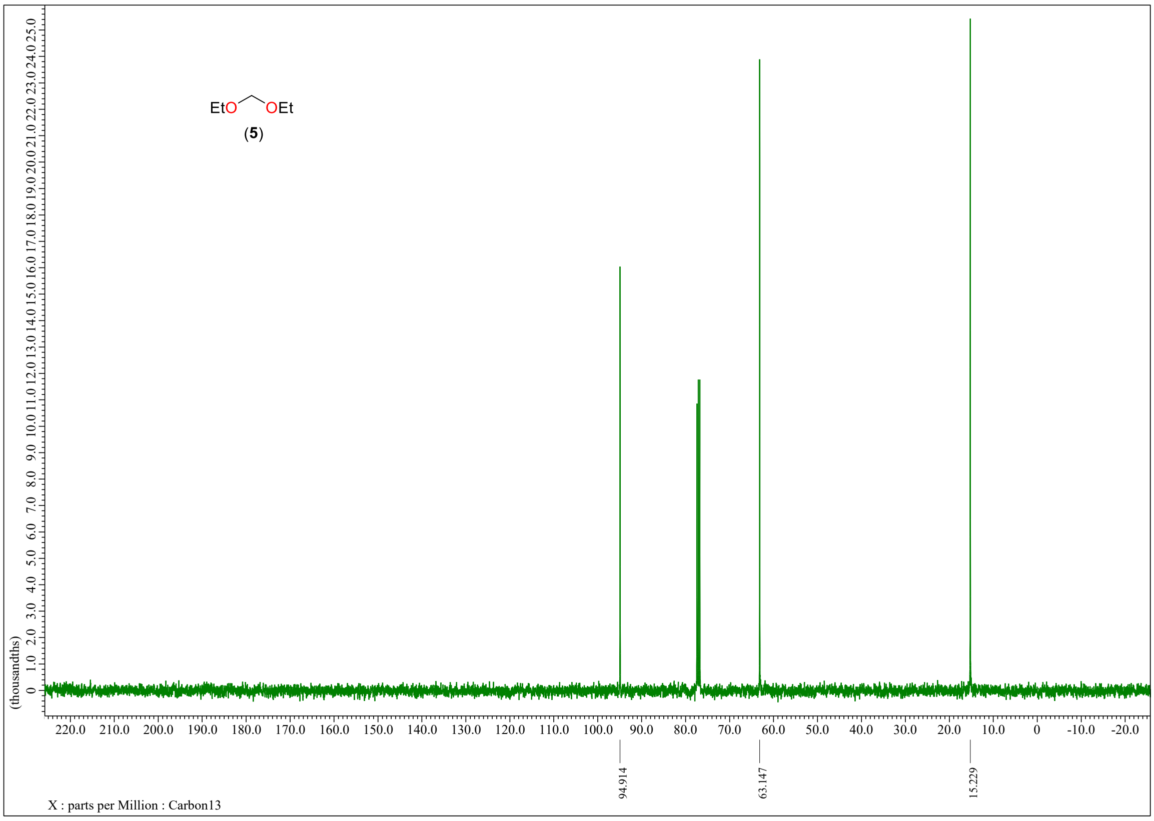


Fig. S22-2. ^{13}C-NMR spectrum of **5** (100 MHz, CDCl$_3$).

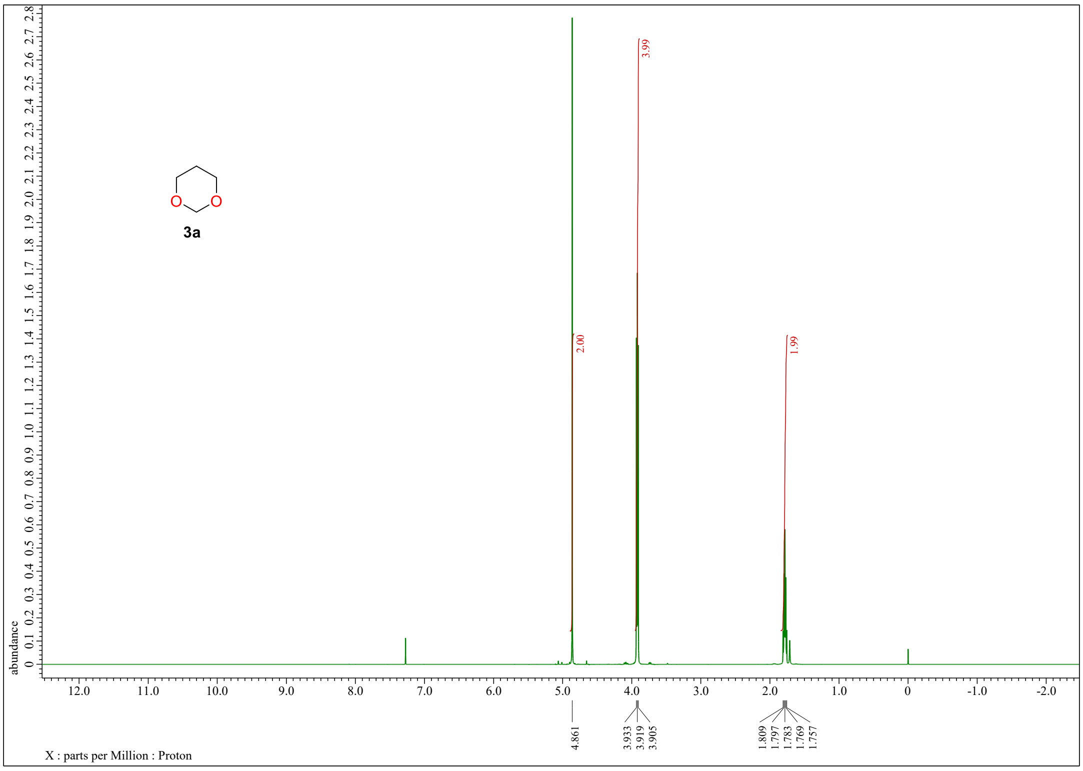


Fig. S23-1. ^{1}H-NMR spectrum of **3a** (500 MHz, $CDCl_3$).

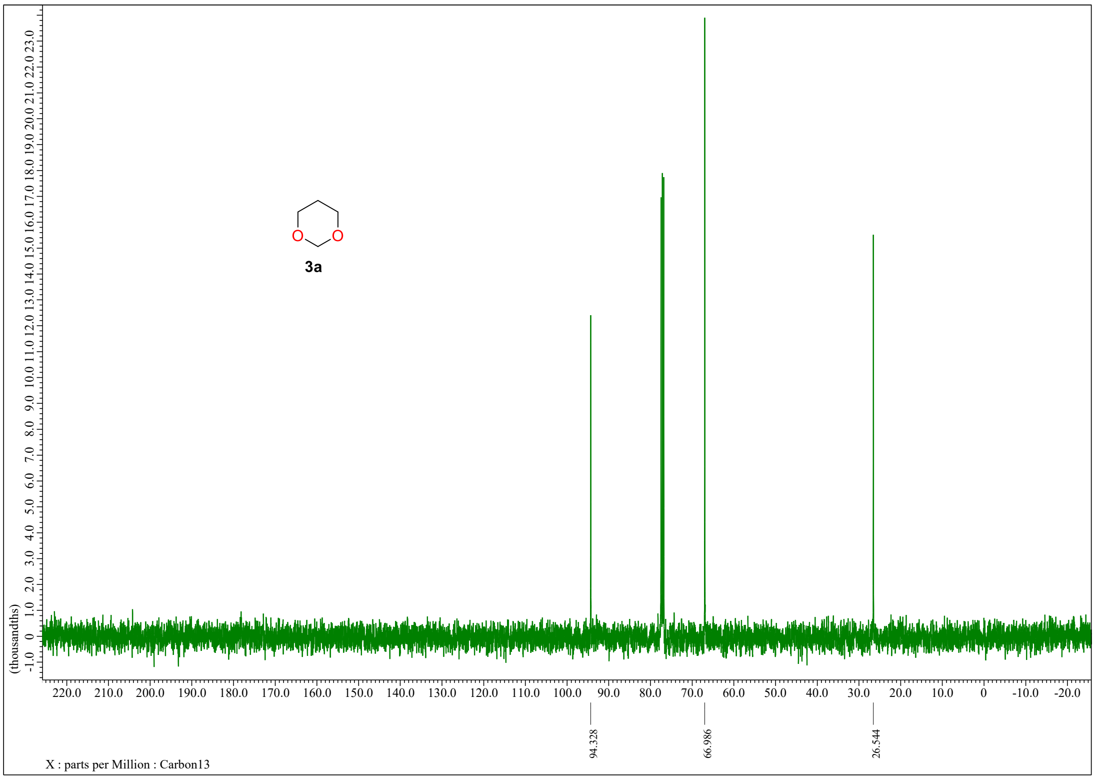


Fig. S23-2. ^{13}C-NMR spectrum of **3a** (125 MHz, $CDCl_3$).

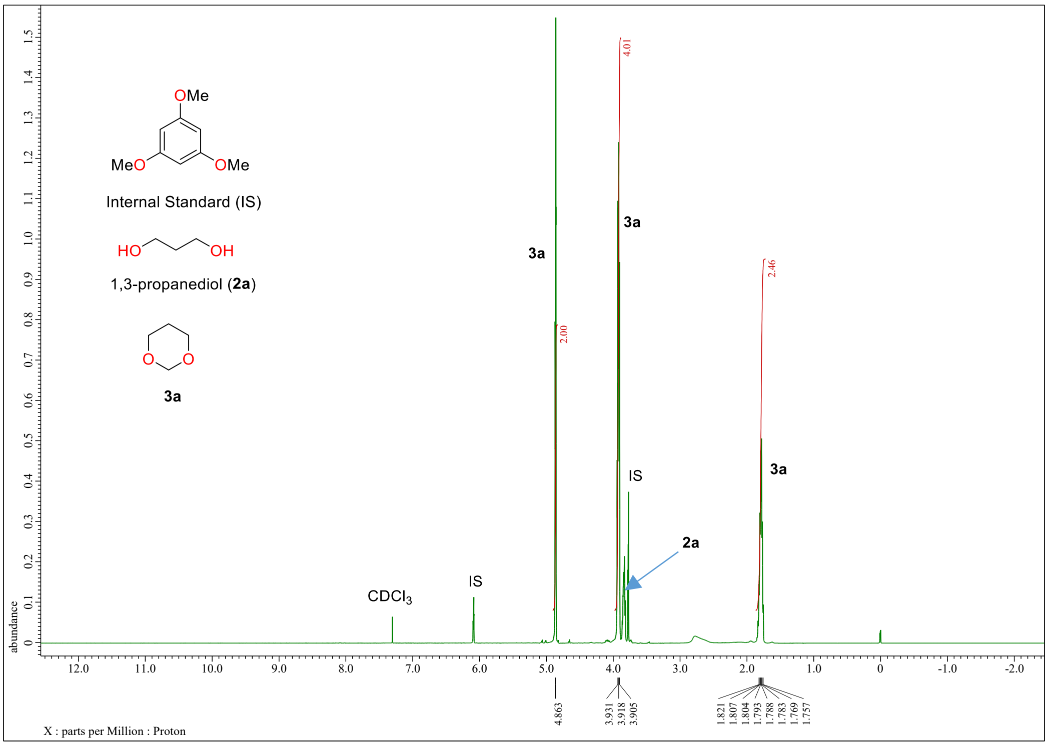


Fig. S24-1. ^{1}H-NMR spectrum of crude reaction mixture using 1,3-propanediol (400 MHz, $CDCl_3$).

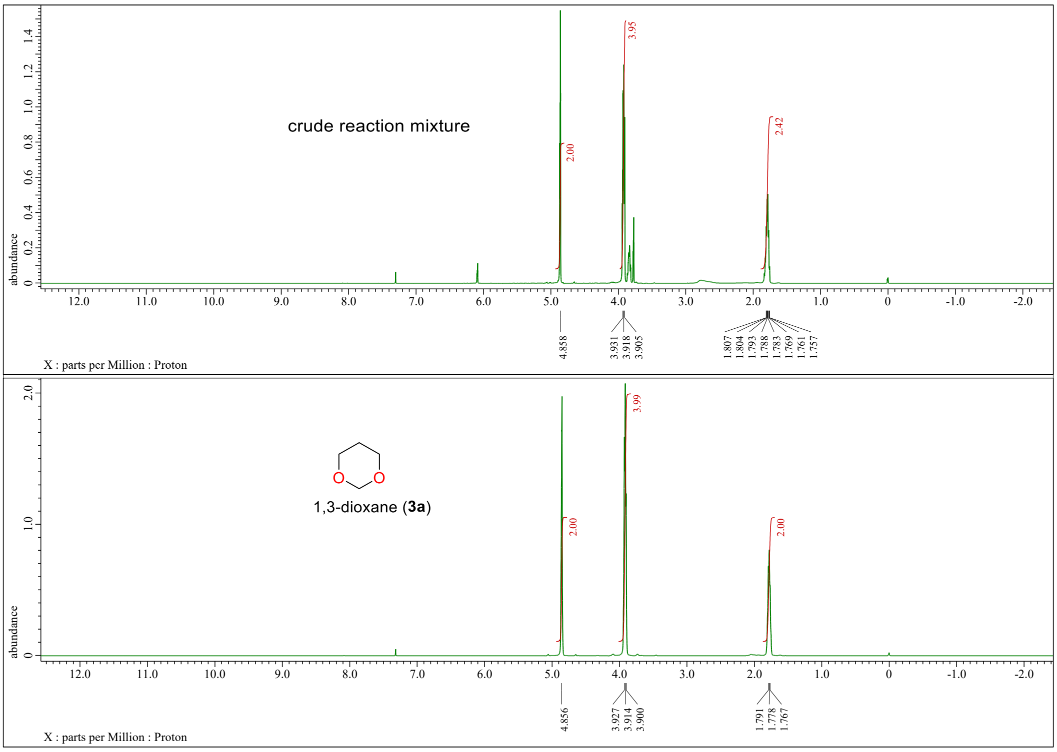


Fig. S24-2. Comparison between the crude reaction mixture (top) and **3a** (bottom) (400 MHz, $CDCl_3$).

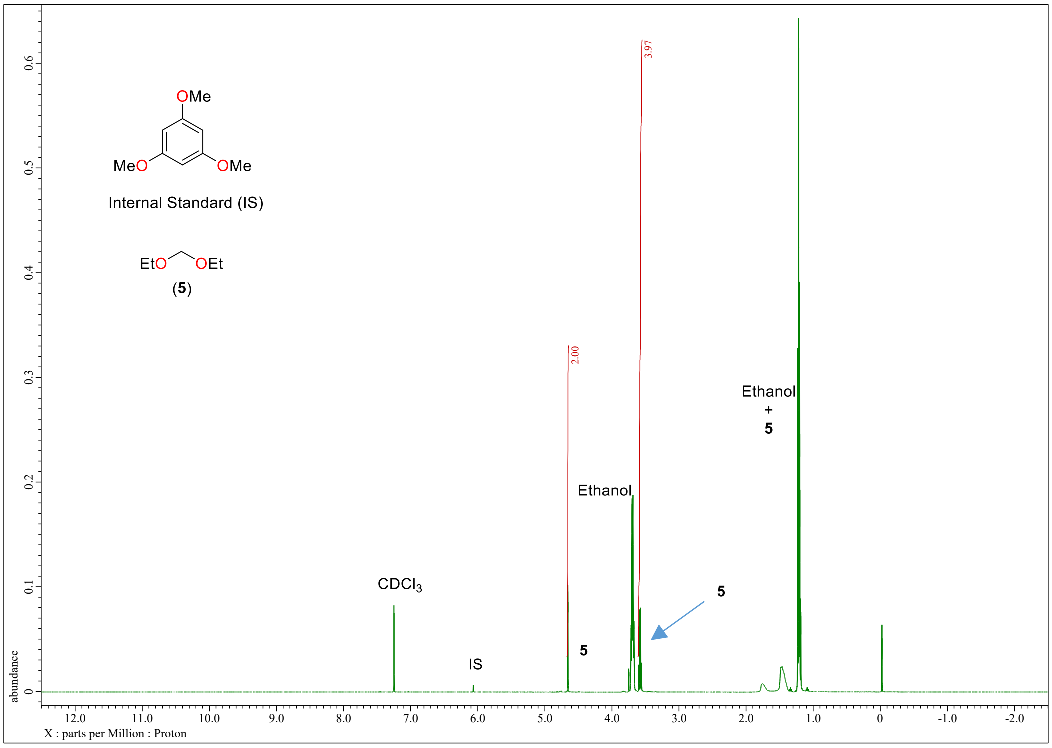


Fig. S25. ^{1}H-NMR spectrum of crude reaction mixture using ethanol (500 MHz, $CDCl_3$).

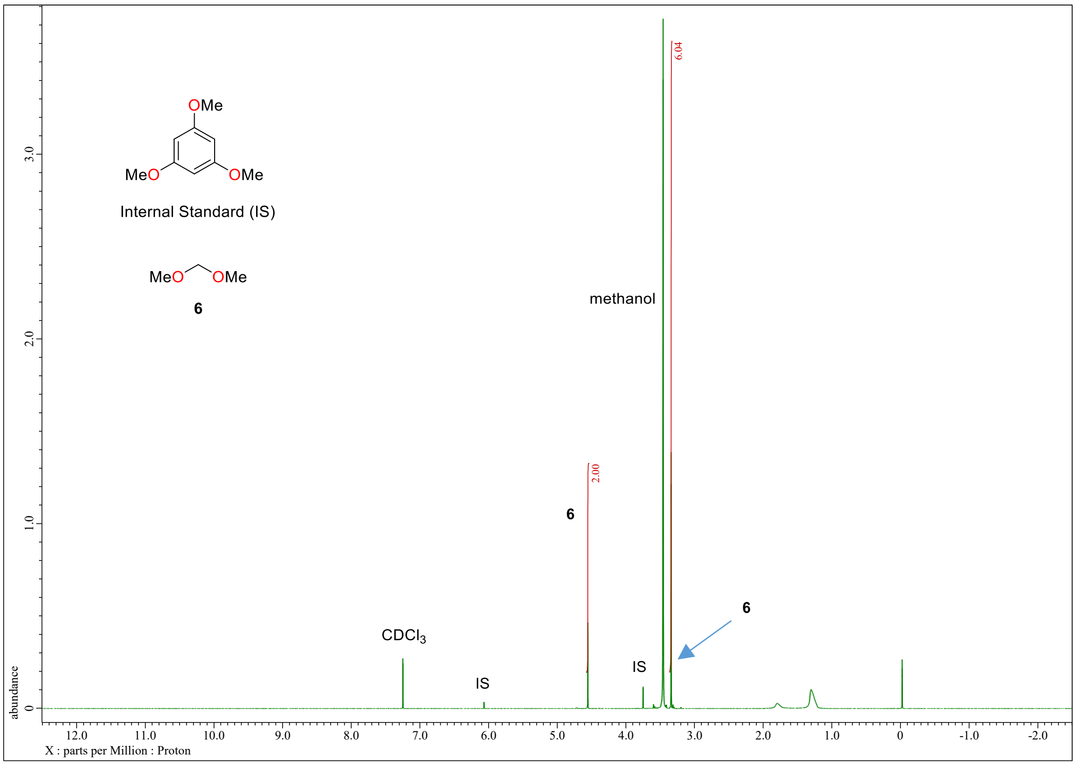


Fig. S26. ^{1}H-NMR spectrum of crude reaction mixture using methanol (500 MHz, $CDCl_3$).

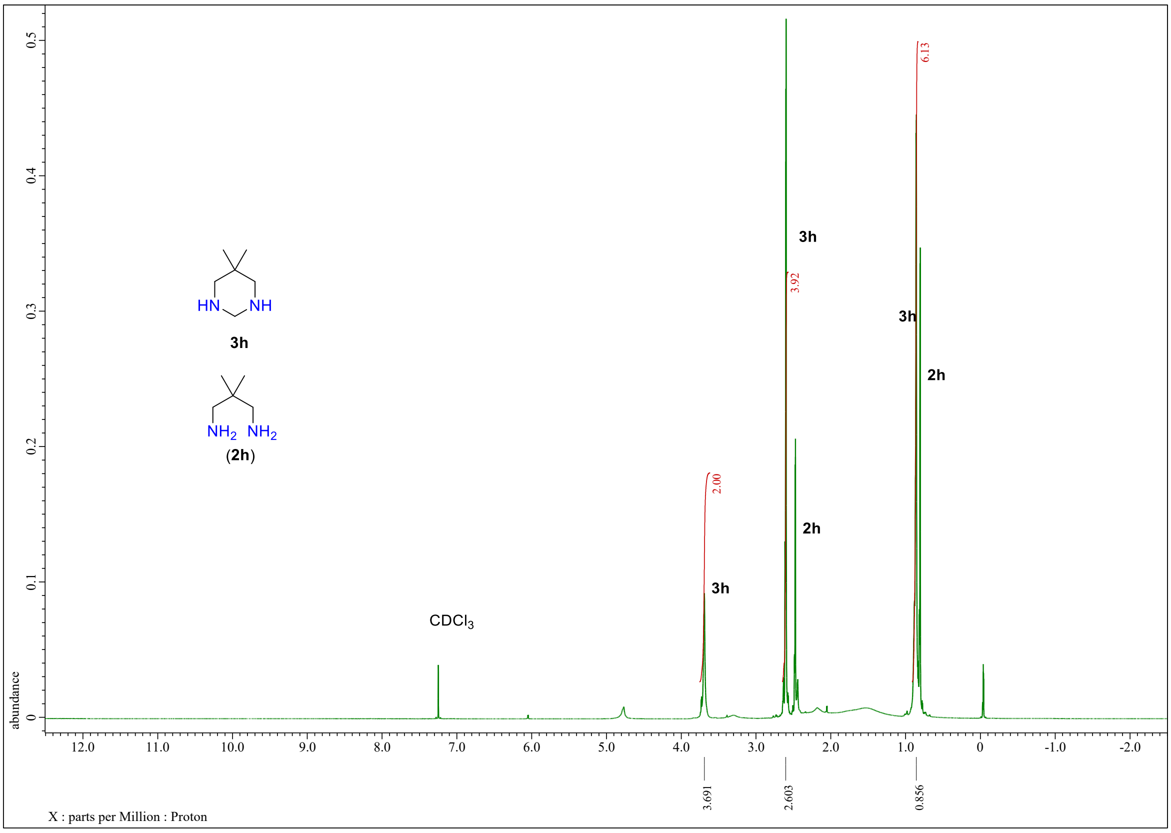
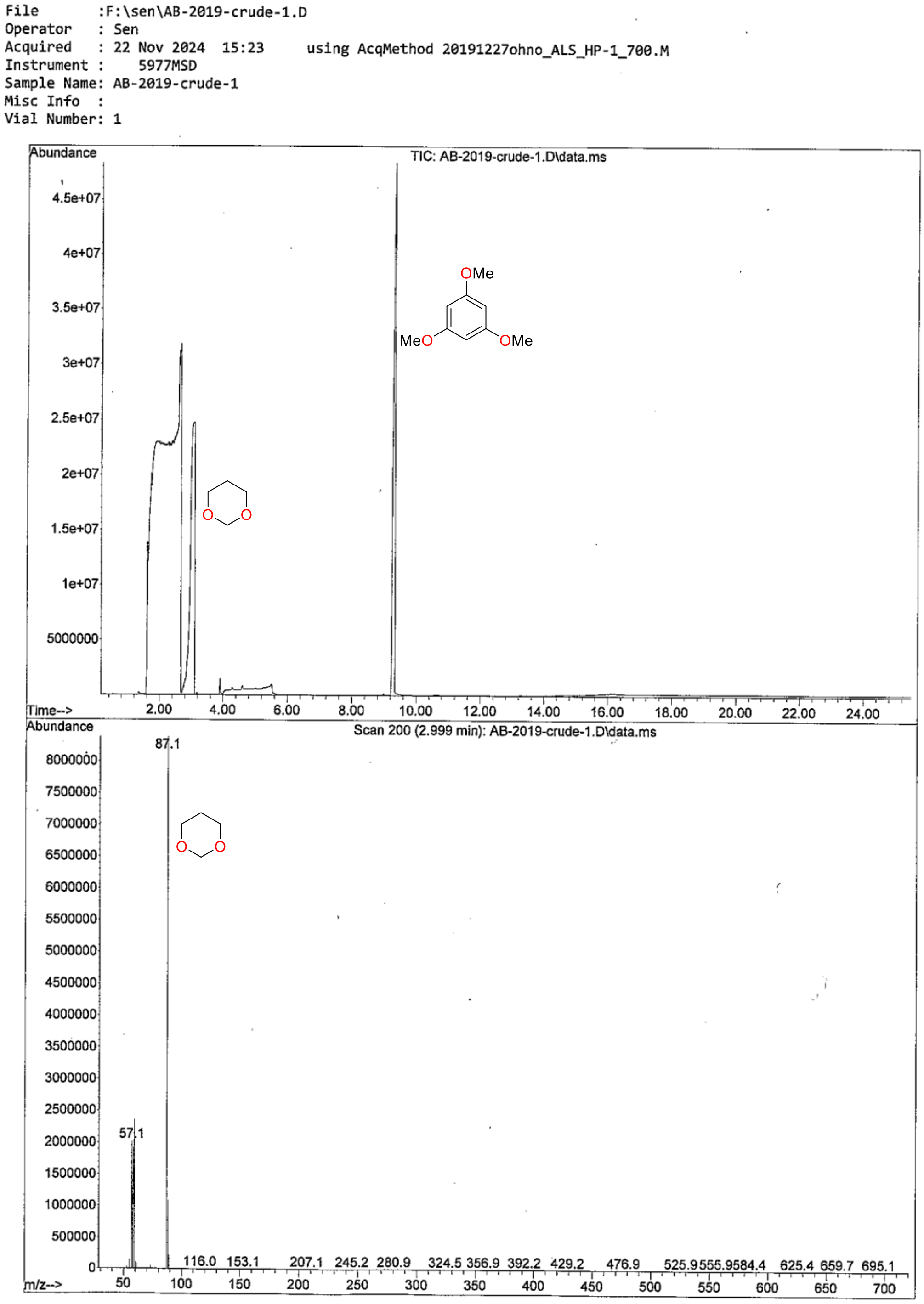


Fig. S27. ^{1}H-NMR spectrum of crude reaction mixture using **2h** (500 MHz, CDCl$_3$).

16. Crude GC and GC-MS



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Operator   : Sen
Acquired   : 22 Nov 2024  15:23     using AcqMethod 20191227ohno_ALS_HP-1_700.M
Instrument :    5977MSD
Sample Name: AB-2019-crude-1
Misc Info  :
Vial Number: 1
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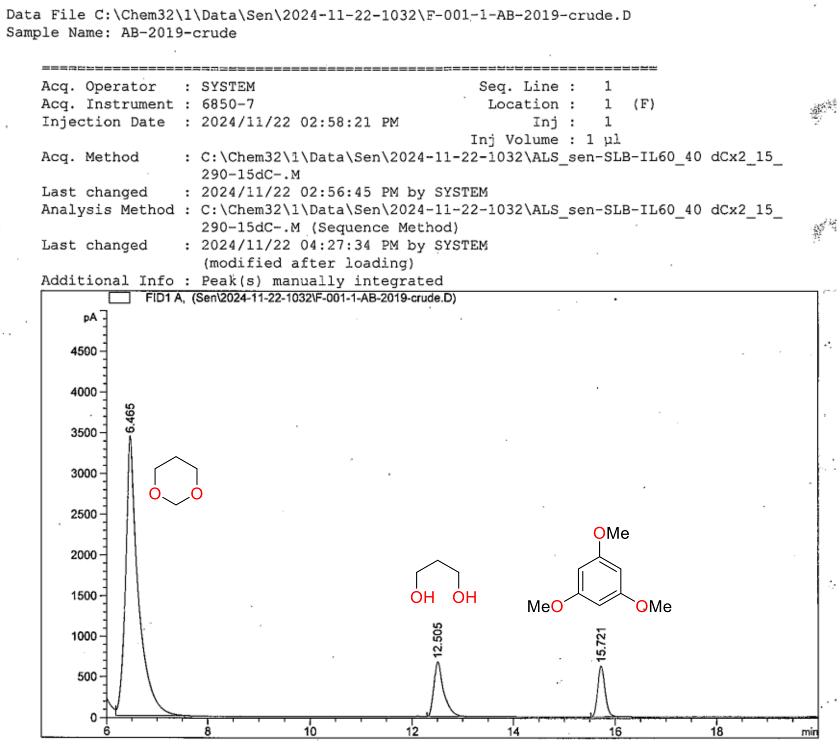
Fig. S28. GC-MS of the crude reaction mixture.



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Data File C:\Chem32\1\Data\Sen\2024-11-22-1032\F-001-1-AB-2019-crude.D
Sample Name: AB-2019-crude

    =====================================================================
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    Acq. Instrument : 6850-7                            Location :   1  (F)
    Injection Date  : 2024/11/22 02:58:21 PM                 Inj :   1
                                                    Inj Volume : 1 µl
    Acq. Method     : C:\Chem32\1\Data\Sen\2024-11-22-1032\ALS_sen-SLB-IL60_40 dCx2_15_
                      290-15dC-.M
    Last changed    : 2024/11/22 02:56:45 PM by SYSTEM
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                      290-15dC-.M (Sequence Method)
    Last changed    : 2024/11/22 04:27:34 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
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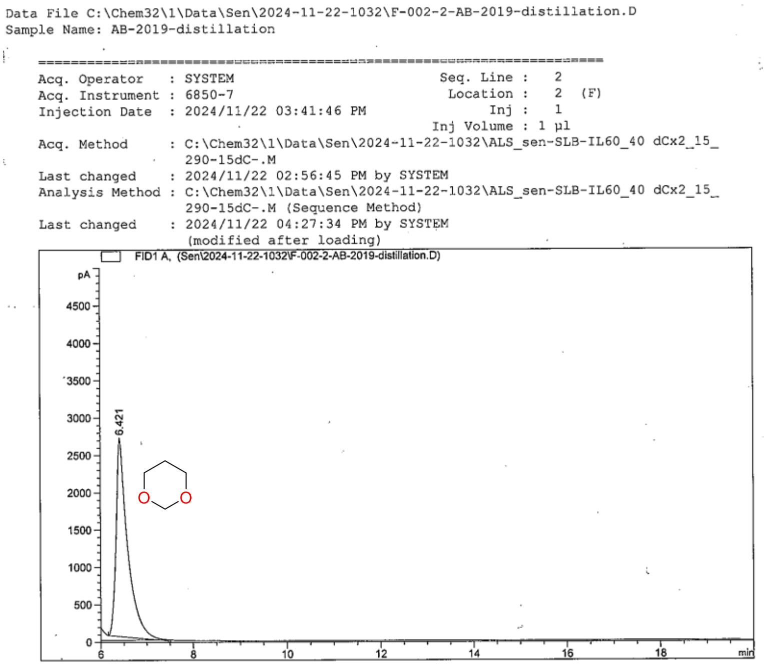
Fig. S29. GC spectrum of the crude reaction mixture.



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Data File C:\Chem32\1\Data\Sen\2024-11-22-1032\F-002-2-AB-2019-distillation.D
Sample Name: AB-2019-distillation

    =====================================================================
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                                                    Inj Volume : 1 µl
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                      290-15dC-.M
    Last changed    : 2024/11/22 02:56:45 PM by SYSTEM
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Fig. S30. GC spectrum of the pure product.

17. MALDI-MS

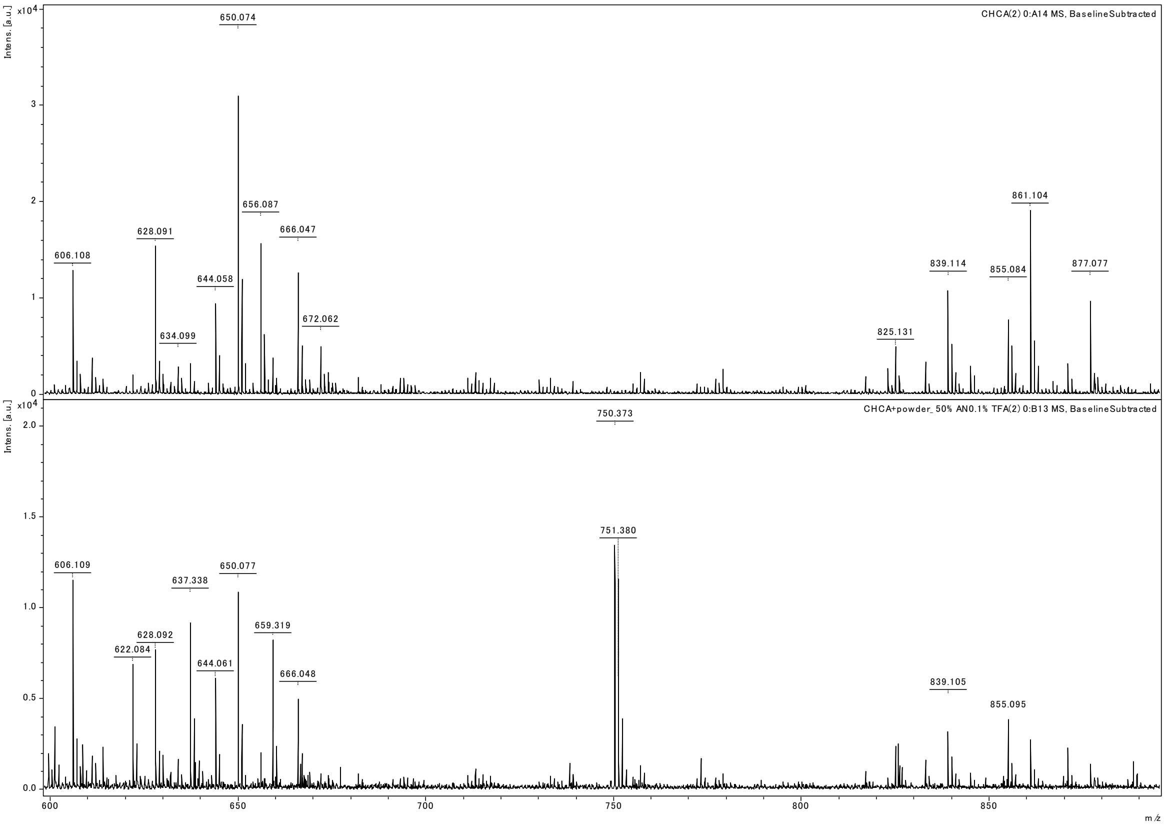

Fig. S31. MALDI-MS for DMpillar[5]arene (**10**).