Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information For

A simple, solvent free method for transforming bio-derived aldehydes into cyclic acetals for renewable diesel fuels

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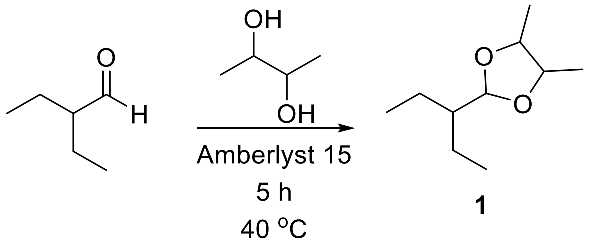
Materials and methods

All chemicals and reagent grade solvents were obtained from commercial vendors and were used as received. ^{1}H and ^{13}C NMR spectra were obtained at room temperature on a Bruker AV400 MHz spectrometer, with chemical shifts (δ) referenced to the residual solvent signal (^{1}H and ^{13}C). GC/MS analysis was carried out using a Hewlett-Packard 6890 GC system equipped with a Hewlett-Packard 5973 mass selective detector. FT-IR measurements were collected on a Perkin Elmer Spectrum Two FT-IR, where a drop of compound was pressed between two KBr plates, FT-IR shifts are: very strong (vs), strong (s), medium (m), and weak (w). Combustion calorimeter measurements were performed using an IKA C1 compact combustion calorimeter, the NHOC was calculated by taking into consideration the hydrogen content and subtracting from the gross heat of combustion. DSC measurements were performed using a Netzsch DCS 204 F1 Phoenix. Viscosity and density measurements were performed using an Anton Paar SVM 3001. Elemental analysis was performed by Atlantic Microlabs. YSI measurements were performed by Prof. Charles McEnally at Yale University.



Scheme S1. Synthesis of 2-(1-Ethylpropyl)-4,5-dimethyl-1,3-dioxolane (**1**).

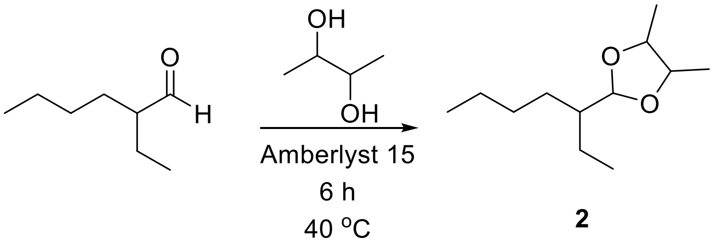
Synthesis of *2-(1-Ethylpropyl)-4,5-dimethyl-1,3-dioxolane* (**1**). 2-Ethylbutyraldehyde (3.135 g, 31.30 mmol), 2,3-Butanediol (4.685 g, 46.77 mmol), and Amberlyst 15 (0.198 g) were combined in a 20 mL scintillation vial. The apparatus was heated to 40 °C with stirring (500 rpm). After 4 h the reaction was allowed to sit for 15 min, where two distinct layers formed, the top layer contained the reaction product while the bottom (aqueous) layer contained remaining 2,3-Butanediol and water. The organic phase was decanted and an aliqout diluted with methanol for GCMS to reveal > 99 % conversion to the desired product. An aliquot of the resulting liquid was analyzed by NMR to yield **1** as a mixture of three diastereomers (5.084 g, 96.6% isolated yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.06 (d, *J* = 3.5 Hz, 0.2H), 4.96 (d, *J* = 3.2 Hz, 0.2H), 4.78 (d, *J* = 3.3 Hz, 0.6H), 4.17 (q, *J* = 5.3 Hz, 0.4H), 4.07 (q, *J* = 5.4 Hz, 1.2H), 3.54 (app. oct., *J* = 6.6 Hz, 0.4H), 1.58 – 1.28 (m, 5H), 1.25 (d, *J* = 5.7 Hz, 0.7H), 1.19 (d, *J* = 5.7 Hz, 0.7H), 1.10 (d, *J* = 5.2 Hz, 4.6H), 0.89 (app. t, *J* = 7.2 Hz, 6H). *Note*: Fractional hydrogen integrations represent diastereomeric ratios.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 105.11, 104.96, 104.20, 79.53, 78.12, 74.29, 74.07, 45.43, 44.98, 44.42, 24.86, 21.07, 21.00, 20.97, 20.94, 17.34, 16.78, 15.36, 14.28, 11.51, 11.44, and 11.38.

FTIR (cm^{-1}): 2966 (vs), 2937 (s), 2877 (s), 1458 (m), 1419 (w), 1380 (m), 1339 (w), 1182 (w), 1105 (vs), 1038 (m), 983 (w), and 924 (w).

Anal. Calcd for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.61; H, 11.80.



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Scheme S2. Synthesis of 2-(1-Ethylpentyl)-4,5-dimethyl-1,3-dioxolane (**2**).

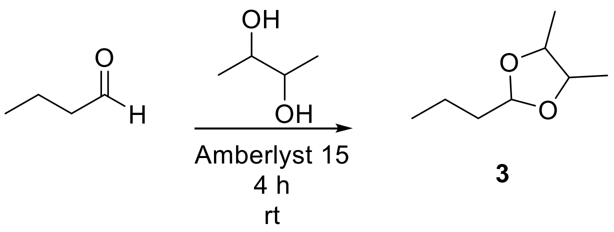
Synthesis of *2-(1-Ethylpentyl)-4,5-dimethyl-1,3-dioxolane* (**2**). 2-Ethylhexanal (4.346 g, 33.89 mmol), 2,3-Butanediol (6.030 g, 60.20 mmol), and Amberlyst 15 (0.201 g) were combined in a 20 mL scintillation vial. The apparatus was heated to 40 ℃ with stirring (500 rpm). After 6 h the reaction was allowed to sit for 15 min, where two distinct layers formed, the top layer contained the reaction product while the bottom (aqueous) layer contained remaining 2,3-Butanediol and water. The organic phase was decanted and an aliqout diluted with methanol for GCMS to reveal > 99 % conversion to the desired product.An aliquot of the resulting liquid was analyzed by NMR to yield **2** as a mixture of three diastereomers (6.520 g, 96.1% isolated yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.08 (d, *J* = 3.8 Hz, 0.2H), 4.99 (d, *J* = 2.9 Hz, 0.2H), 4.80 (d, *J* = 3.1 Hz, 0.6H), 4.20 (q, *J* = 5.1 Hz, 0.3H), 4.09 (h, *J* = 6.4 Hz, 1.2H), 3.56 (app. oct., *J* = 6.5 Hz, 0.5H), 1.59 –1.24 (m, 9.5H), 1.21 (d, *J* = 5.7 Hz, H), 1.13 (d, *J* = 5.2 Hz, 4.5H), 0.91 (m, *J* = 9.2, 6.5 Hz, 6H). *Note*: Fractional hydrogen integrations represent diastereomeric ratios.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 105.26, 105.11, 104.34, 79.53, 78.15, 74.32, 74.08, 74.32, 74.08, 74.06, 43.94, 43.44, 42.87, 29.47, 29.39, 28.17, 28.14, 28.07, 23.16, 23.11, 21.57, 21.52, 21.47, 17.35, 16.77, 15.34, 14.27, 14.03, 11.56, 11.49, and 11.41.

FTIR (cm^{-1}): 2960 (vs), 2931 (vs), 2873 (vs), 1457 (m), 1378 (m), 1340 (w), 1309 (w), 1179 (w), 1108 (vs), 1039 (m), 1000 (w), and 972 (w).

Anal. Calcd for $C_{12}H_{24}O_2$: C, 71.95; H, 12.08. Found: C, 71.01; H, 12.35.



Scheme S3. Synthesis of 4,5-Dimethyl-2-propyl-1,3-dioxolane (**3**).

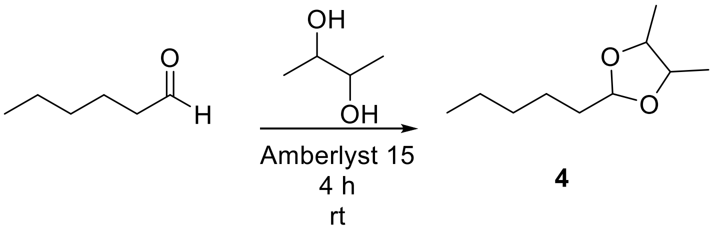
Synthesis of *4,5-Dimethyl-2-propyl-1,3-dioxolane* (**3**). Butyraldehyde (4.028 g, 55.86 mmol), 2,3-Butanediol (8.028 g, 89.08 mmol), and Amberlyst 15 (0.401 g) were combined in a 20 mL scintillation vial. The apparatus was stirred (500 rpm) at room temperature. After 4 h the reaction was allowed to sit for 15 min, where two distinct layers formed, the top layer contained the reaction product while the bottom (aqueous) layer contained remaining 2,3-Butanediol and water. The organic phase was decanted and an aliqout diluted with methanol for GCMS to reveal > 99 % conversion to the desired product. An aliquot of the resulting liquid was analyzed by NMR to yield **3** as a mixture of three diastereomers (7.494 g, 93.0% isolated yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.13 (t, J = 4.9 Hz, 0.1H), 4.99 (t, J = 4.7 Hz, 0.3H), 4.82 (t, J = 4.7 Hz, 0.6H), 4.17 (p, J = 5.3 Hz, 0.2H), 4.06 (h, J = 6.3 Hz, 1.1H), 3.73 (d, J = 5.4 Hz, 0.1H), 3.55 (q, J = 6.0 Hz, 0.6H), 1.66 – 1.32 (m, 4H), 1.24 (d, J = 5.0 Hz, 2H), 1.17 (d, J = 5.1 Hz, 2H), 1.09 (d, J = 5.4 Hz, 4H), 0.90 (t, J = 7.4 Hz, 3H). *Note:* Fractional hydrogen integrations represent diastereomeric ratios.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 103.12, 103.01, 102.32, 79.66, 78.00, 74.29, 74.10, 70.74, 37.33, 36.76, 36.73, 17.31, 17.23, 17.20, 16.91, 15.41, 14.22, and 14.00.

FTIR (cm^{-1}): 2962 (vs), 2935 (vs), 2874 (vs), 1459 (m), 1378 (s), 1322 (w), 1234 (w), 1147 (s), 1120 (vs), 1032 (w), 983 (w), 957 (m), 911 (m), and 837 (w).

Anal. Calcd for $C_8H_{16}O_2$: C, 66.63; H, 11.18. Found: C, 66.17; H, 11.41.



4

Scheme S4. Synthesis of 4,5-Dimethyl-2-pentyl-1,3-dioxolane (**4**).

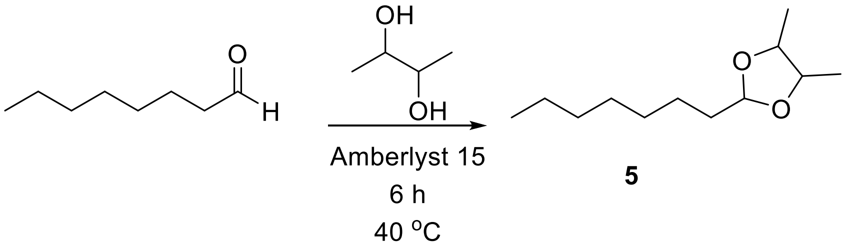
Synthesis of *4,5-Dimethyl-2-pentyl-1,3-dioxolane* (**4**). Hexanal (4.029 g, 40.22 mmol), 2,3-Butanediol (7.772 g, 86.24 mmol), and Amberlyst 15 (0.413 g) were combined in a 20 mL scintillation vial. The apparatus was stirred (500 rpm). After 4 h the reaction was allowed to sit for 15 min, where two distinct layers formed, the top layer contained the reaction product while the bottom (aqueous) layer contained remaining 2,3-Butanediol and water. The organic phase was decanted and an aliqout diluted with methanol for GCMS to reveal > 99 % conversion to the desired product. An aliquot of the resulting liquid was analyzed by NMR to yield **4** as a mixture of three diastereomers (6.571 g, 94.8% isolated yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.13 (t, *J* = 5.0 Hz, 0.1H), 4.98 (t, *J* = 4.8 Hz, 0.3H), 4.81 (t, *J* = 4.8 Hz, 0.6H), 4.16 (p, *J* = 5.4 Hz, 0.2H), 4.06 (h, *J* = 6.3 Hz, 1.1H), 3.73 (q, *J* = 5.6 Hz, 0.1H), 3.55 (dd, *J* = 7.7, 4.6 Hz, 0.6H), 1.59 (qd, *J* = 7.4, 5.0 Hz, 2H), 1.44 – 1.21 (m, 7H), 1.18 (d, *J* = 5.1 Hz, 1H), 1.10 (d, *J* = 5.3 Hz, 4H), 0.92 – 0.78 (m, 3H). *Note*: Fractional hydrogen integrations represent diastereomeric ratios.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 103.32, 103.23, 102.52, 79.67, 78.01, 74.30, 74.12, 70.75, 35.22, 34.67, 31.77, 23.71, 23.58, 22.54, 17.24, 16.98, 16.92, 15.42, 14.22, and 13.92.

FTIR (cm^{-1}): 2957 (vs), 2931 (vs), 2863 vs), 1460 (m), 1418 (w), 1378 (s), 1145 (s), 1118 (vs), 1082 (s), 1041 (m), 993 (w), 929 (m), and 889 (w).

Anal. Calcd for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70; O. Found: C, 69.09; H, 11.77.



Scheme S5. Synthesis of 4,5-Dimethyl-2-heptyl-1,3-dioxolane (**5**).

Synthesis of *4,5-Dimethyl-2-heptyl-1,3-dioxolane* (**5**). Octanal (4.003 g, 31.22 mmol), 2,3-Butanediol (7.142 g, 79.25 mmol), and Amberlyst 15 (0.385 g) were combined in a 20 mL scintillation vial. The apparatus was heated to 40 ℃ with stirring (500 rpm). After 6 h the reaction was allowed to cool for 15 min. Upon cooling, two distinct layers formed, the top layer contained the reaction product while the bottom (aqueous) layer contained remaining 2,3-Butanediol and water. The organic phase was decanted and an aliqout diluted with methanol for GCMS to reveal > 99 % conversion to the desired product. An aliquot of the resulting liquid was analyzed by NMR to yield **5** as a mixture of three diastereomers (6.072 g, 97.1 % isolated yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.09 (t, J = 4.9 Hz, 0.1H), 4.95 (t, J = 4.7 Hz, 0.4H), 4.77 (t, J = 4.8 Hz, 0.5H), 4.13 (h, J = 5.6 Hz, 0.2H), 4.02 (h, J = 6.2 Hz, 1H), 3.68 (d, J = 5.9 Hz, 0.1H), 3.51 (dd, J = 7.7, 4.5 Hz, 0.7H), 1.55 (qd, J = 7.4, 4.9 Hz, 1.8H), 1.47 (dd, J = 9.1, 5.1 Hz, 0.2H), 1.38 – 1.12 (m, 12H), 1.06 (d, J = 5.3 Hz, 4H), 0.80 (t, J = 6.5 Hz, 3H). *Note*: Fractional hydrogen integrations represent diastereomeric ratios.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 103.27, 103.18, 102.47, 79.62, 77.96, 74.25, 74.06, 70.68, 35.22, 34.637, 34.65, 31.70, 29.50, 29.46, 29.14, 23.98, 23.85, 22.55, 17.18, 16.94, 16.85, 15.36, 14.16, and 13.94.

FTIR (cm^{-1}): 2957 (vs), 2931 (vs), 2866 (vs), 1463 (m), 1413 (w), 1379 (s), 1346 (w), 1320 (w), 1146 (vs), 1082 (s), 1041 (m), 998 (m), 929 (m), and 893 (w).

Anal. Calcd for $C_{12}H_{24}O_2$: C, 71.95; H, 12.08. Found: C, 71.77; H, 12.30.

Large scale reaction

A representative example of the scalability of these reactions is as follows. 2-Ethylhexanal (20.066 g, 156.5 mmol), 2,3-Butanediol (29.248 g, 324.5 mmol), and Amberlyst 15 (1.624 g) were combined in a 100 mL round bottom flask. The apparatus was heated to 40 ℃ with stirring (500 rpm). After 15 h the reaction was allowed to cool for 15 min. Upon cooling, two distinct layers formed, the top layer contained the reaction product while the bottom (aqueous) layer contained remaining 2,3-Butanediol and water. The organic phase was decanted and an aliqout diluted with methanol for GCMS to reveal > 98 % conversion to the desired product. The remaining reaction mixture was washed with cyclohexane (3 x 3 mL) and the resultant organic phase again decanted. The organic phases were combined and dried over $MgSO_4$. The solvent was removed *in vacuo*. and an aliquot of the resulting liquid was analyzed by NMR to yield **2** as a mixture of three diastereomers (30.490 g, 97.3% isolated yield).

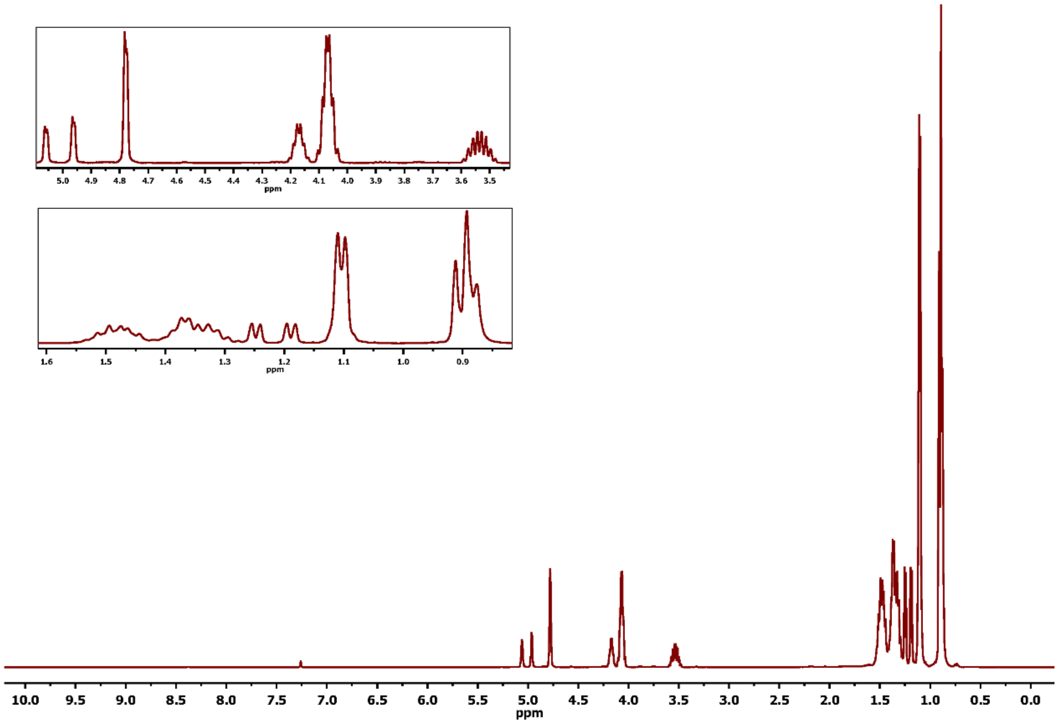


Figure S1. 400 MHz ^{1}H NMR spectrum of (**1**).

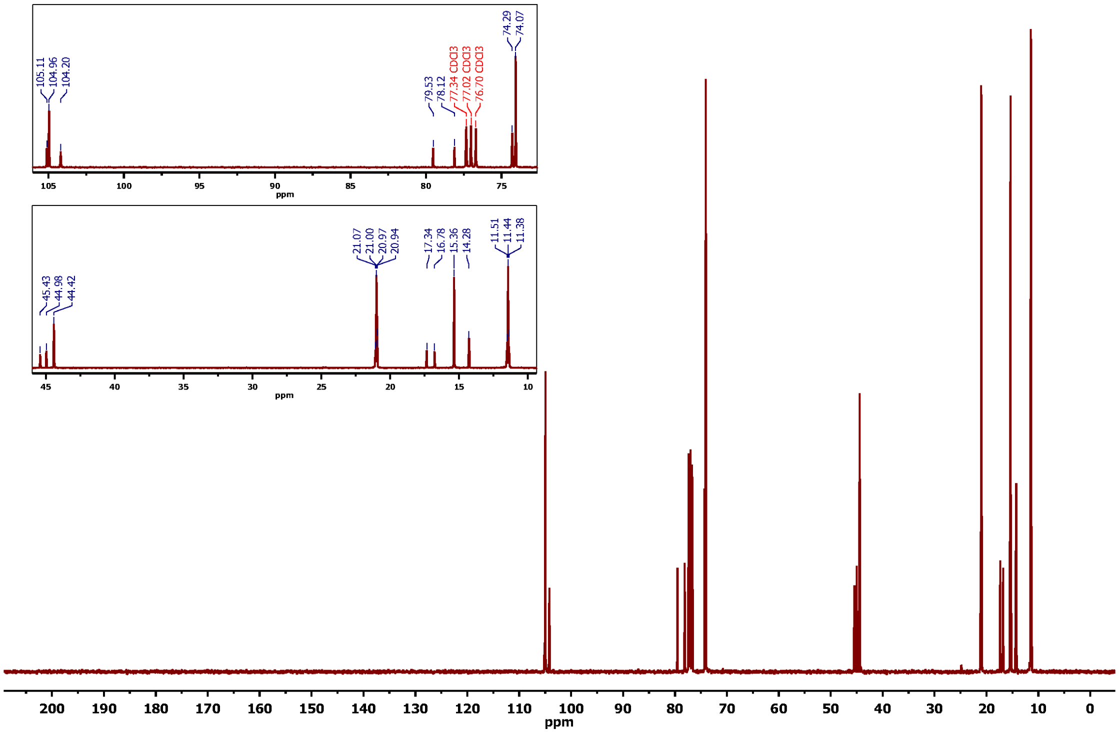


Figure S2. 101 MHz ^{13}C NMR spectrum of (**1**).

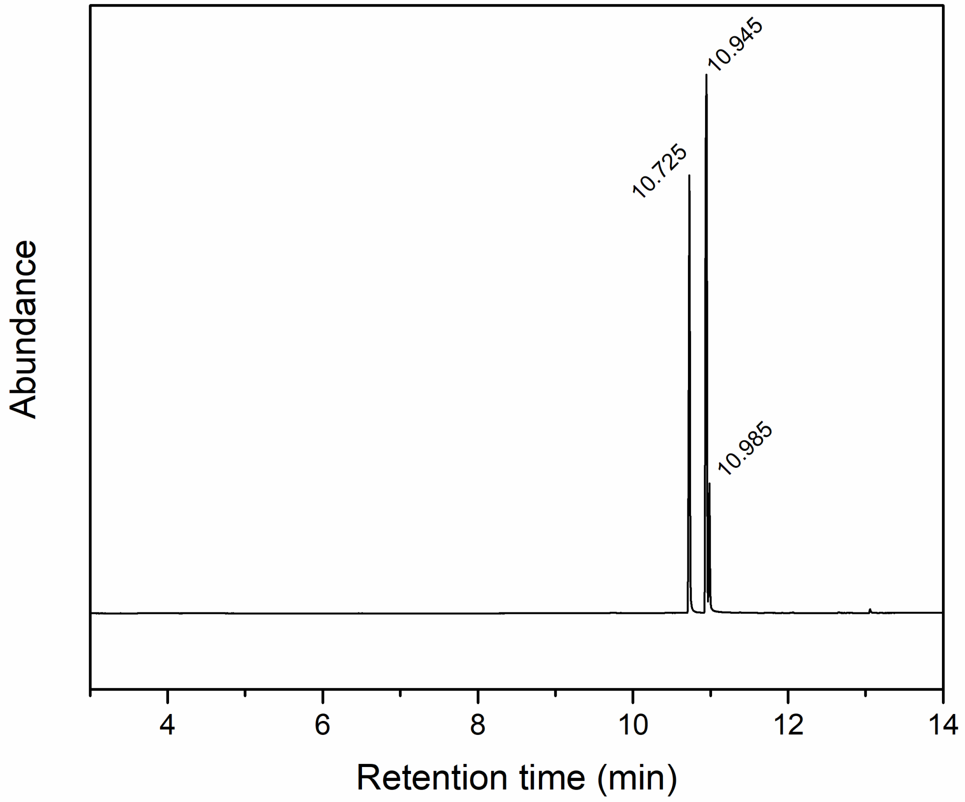


Figure S3. GC trace of (**1**).

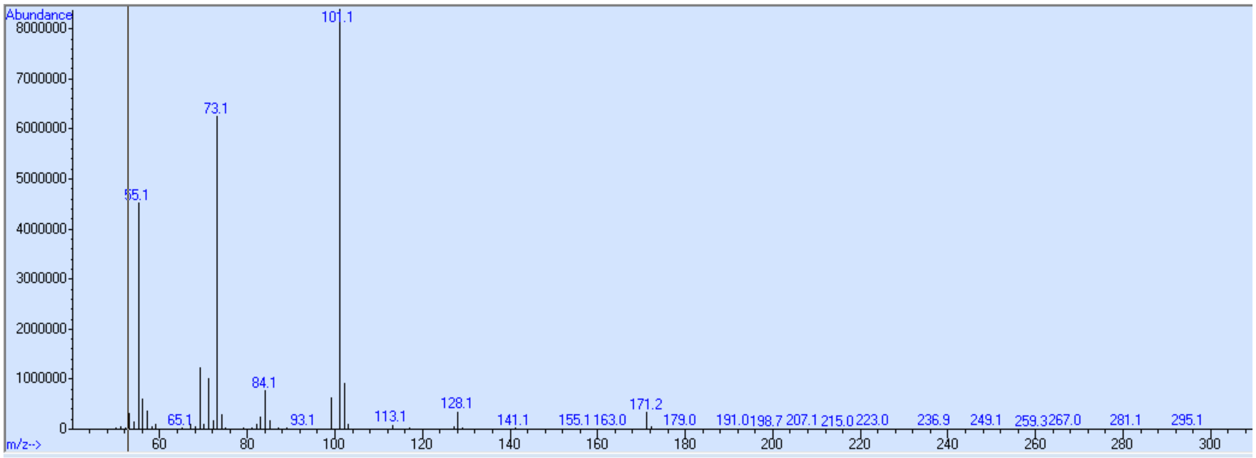


Figure S4. MS of (**1**)

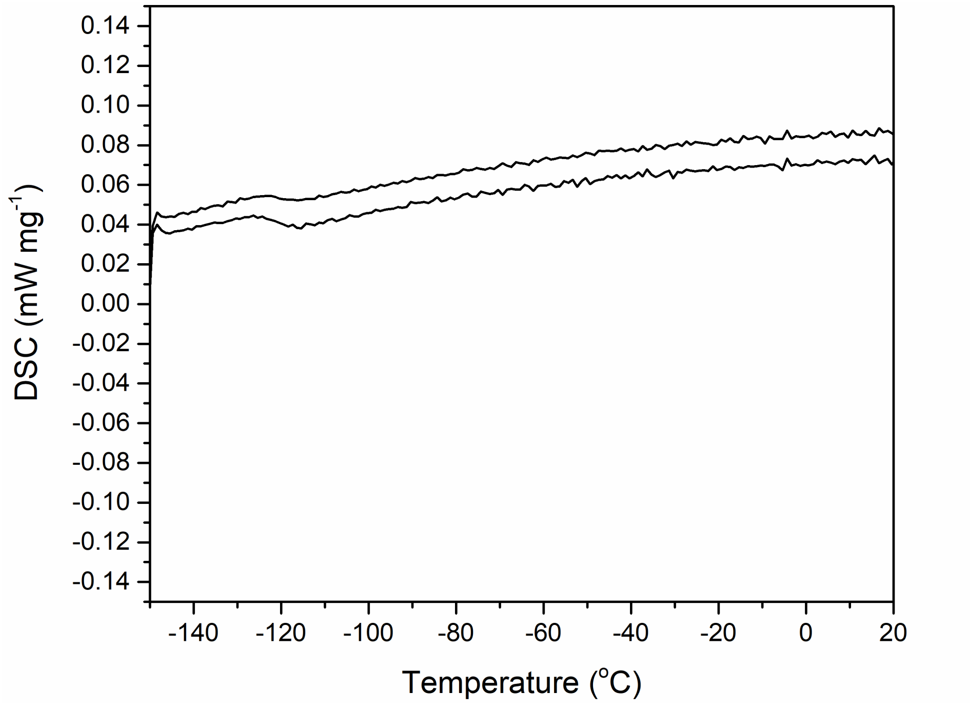


Figure S5. DSC trace of (**1**).

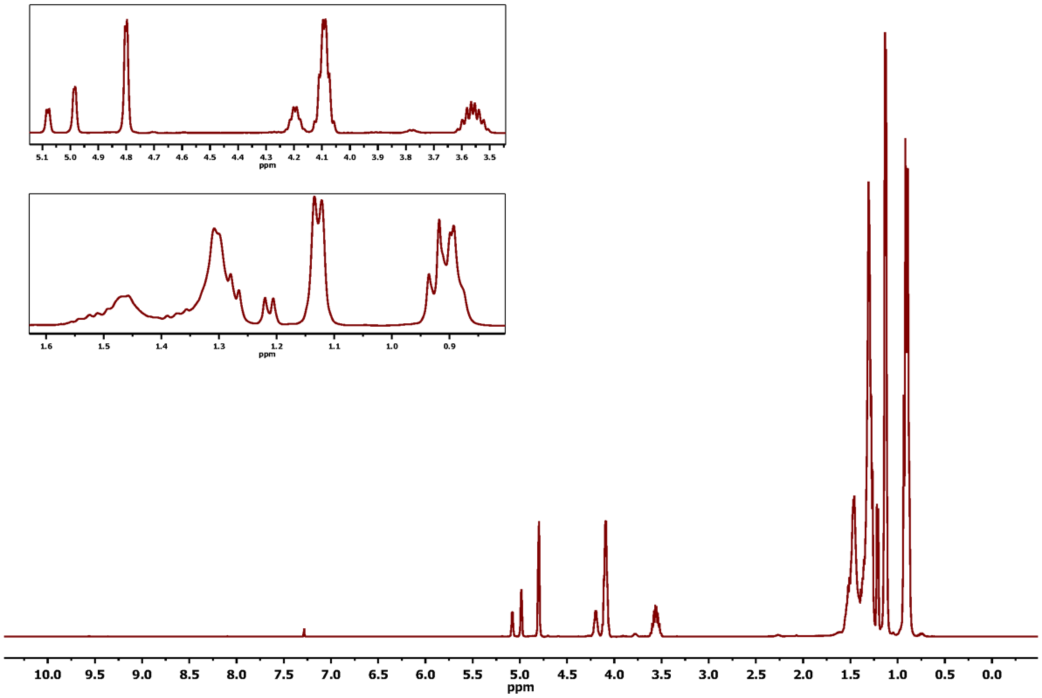


Figure S6. 400 MHz ^{1}H NMR spectrum of (**2**).

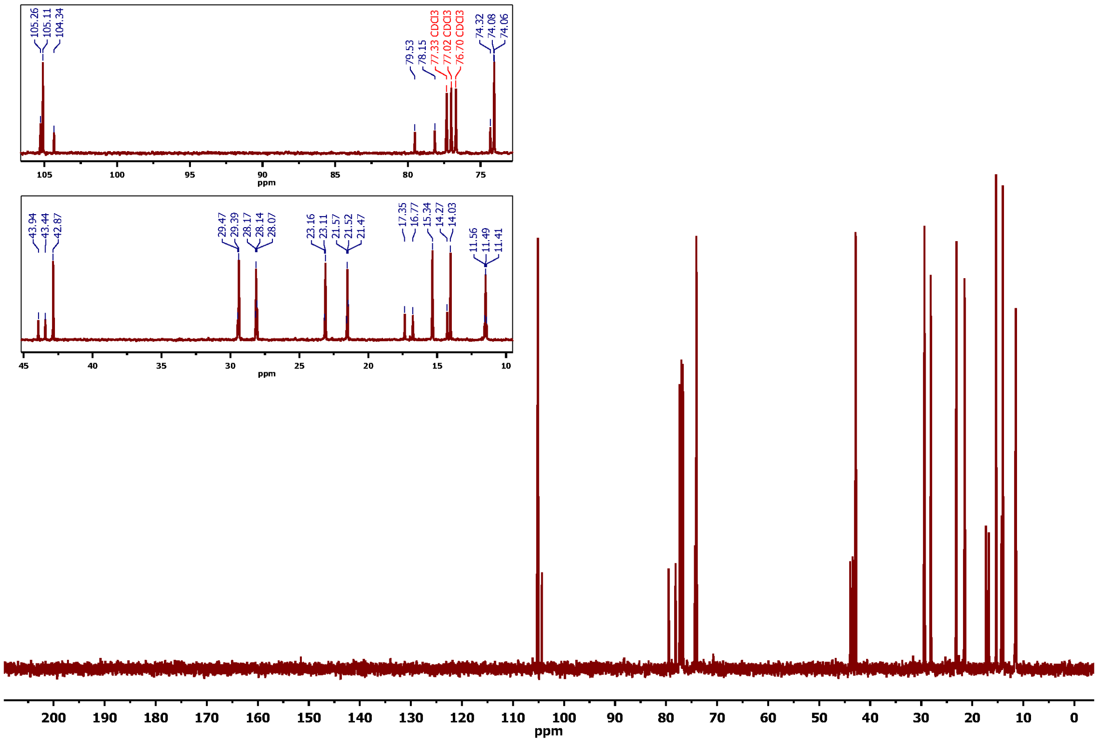


Figure S7. 101 MHz ^{13}C NMR spectrum of (**2**).

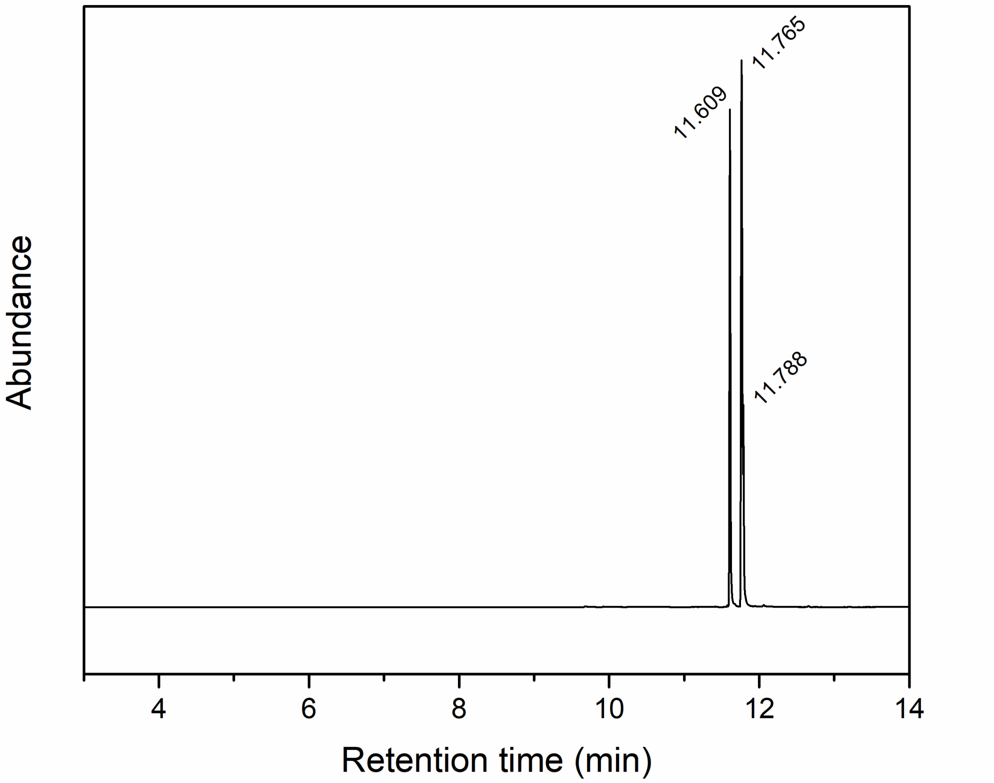


Figure S8. GC trace of (**2**).

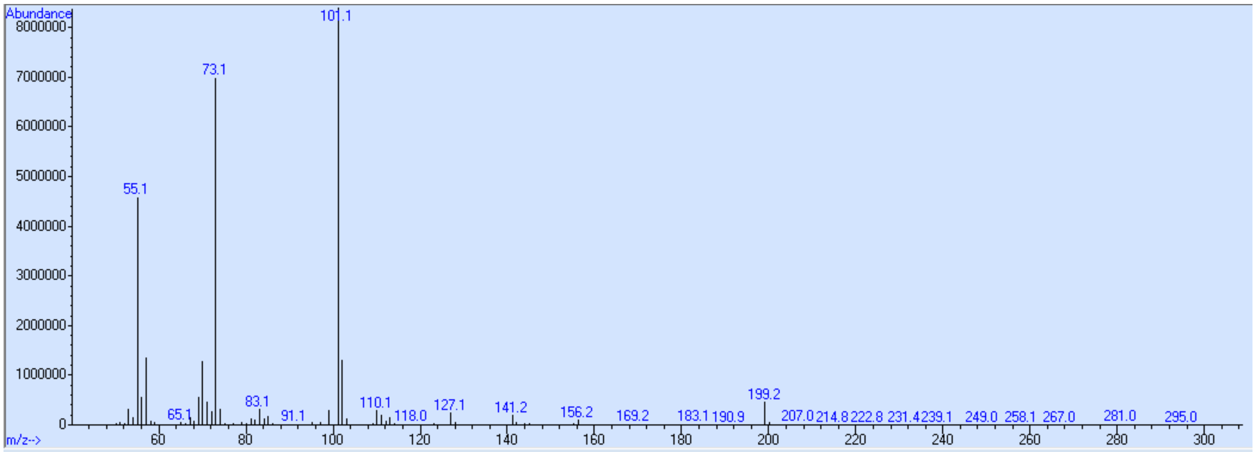


Figure S9. MS of (**2**)

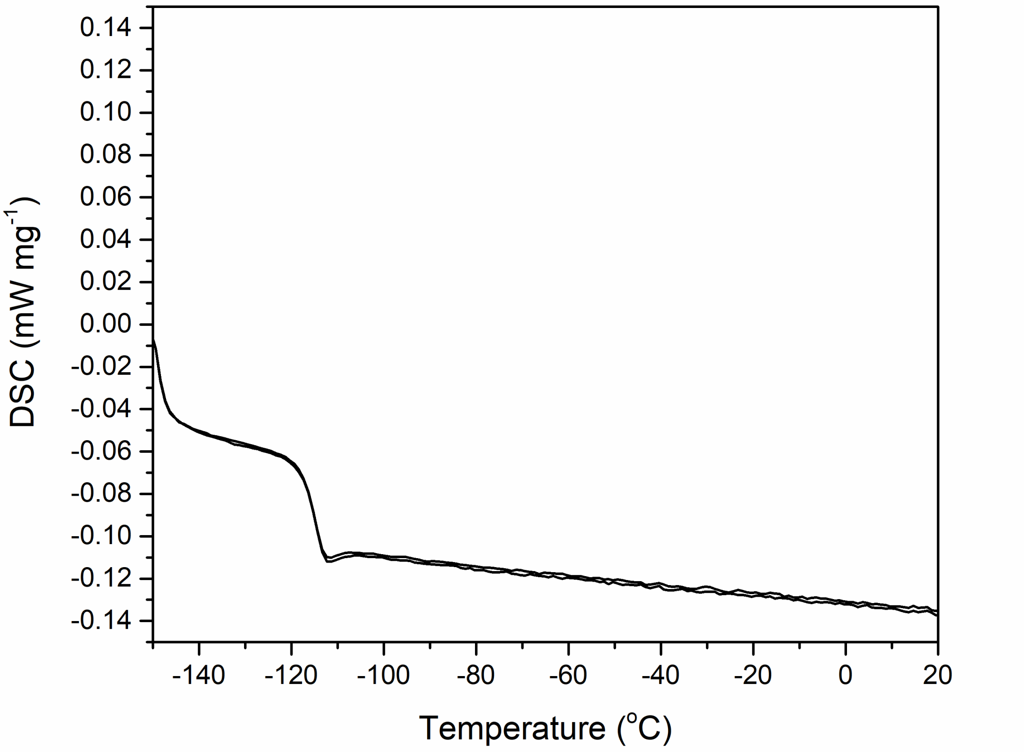


Figure S10. DSC trace of (**2**).

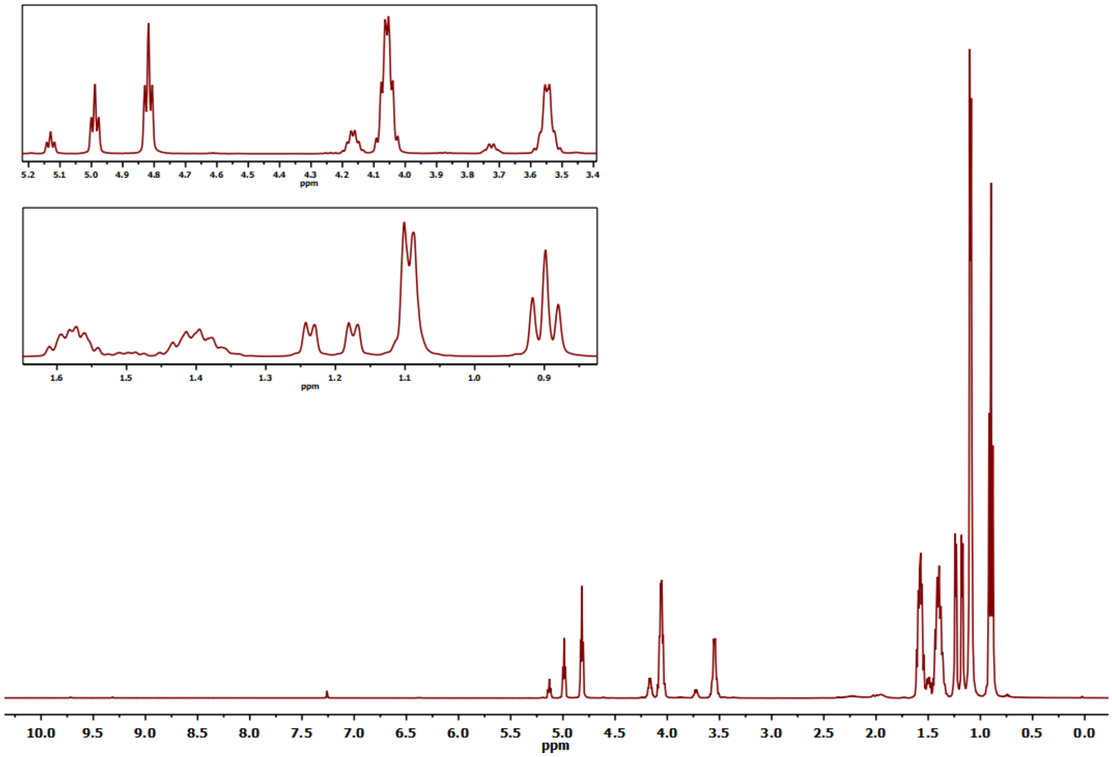


Figure S11. 400 MHz ^{1}H NMR spectrum of (**3**).

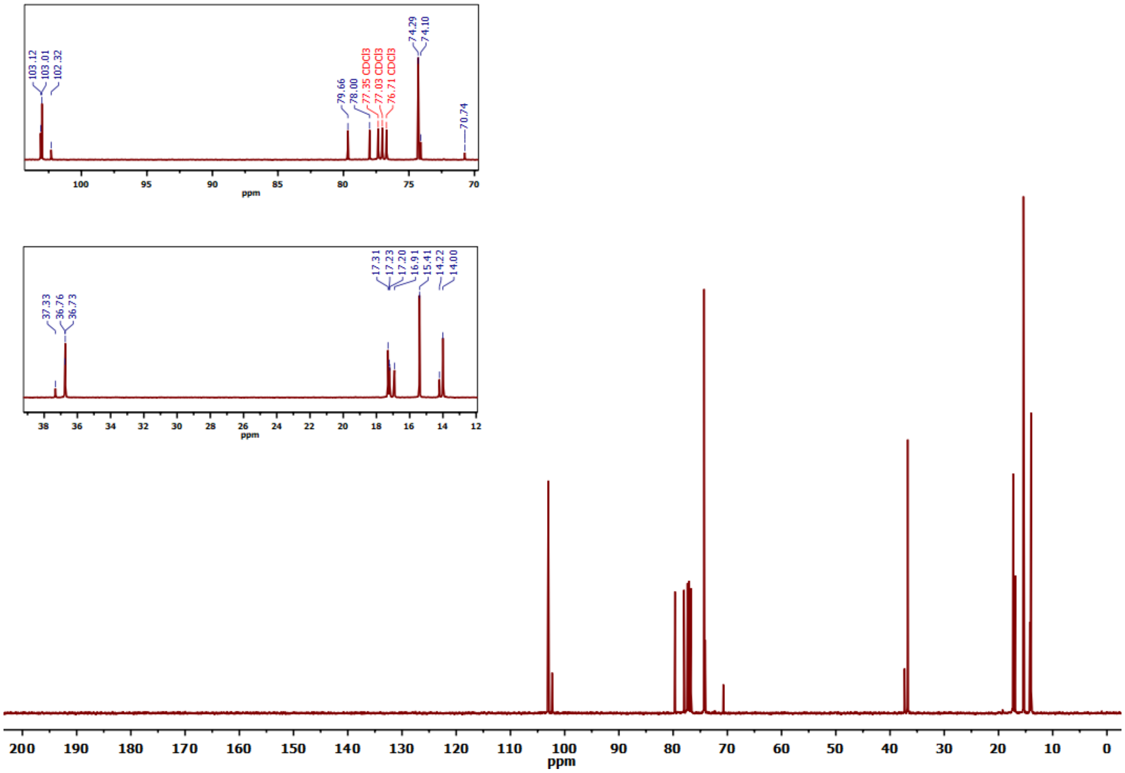


Figure S12. 101 MHz ^{13}C NMR spectrum of (**3**).

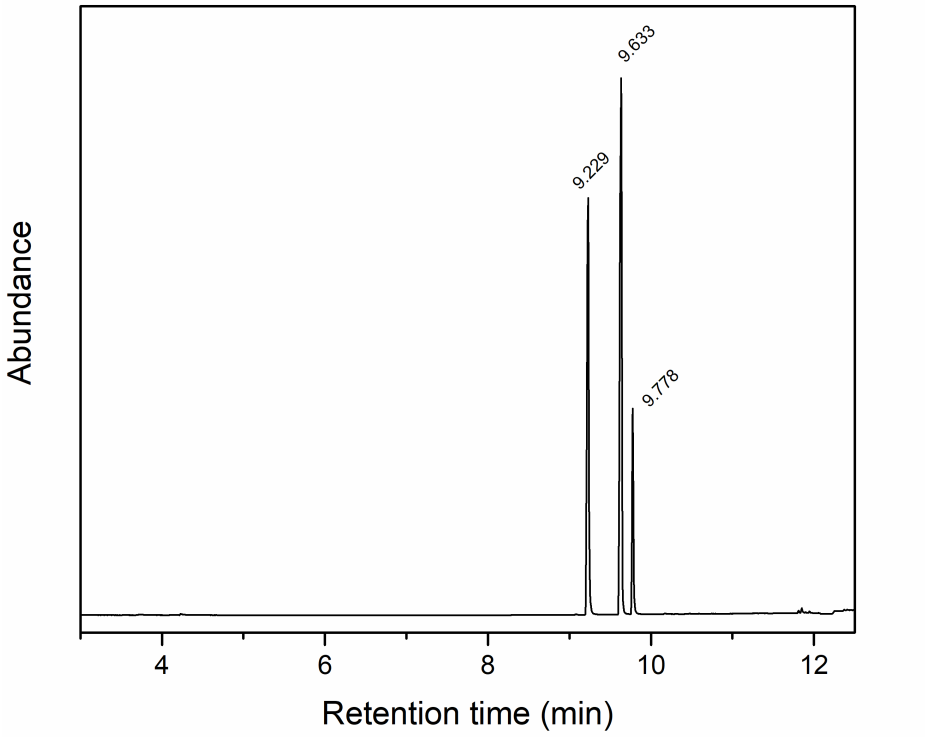


Figure S13. GC trace of (**3**).

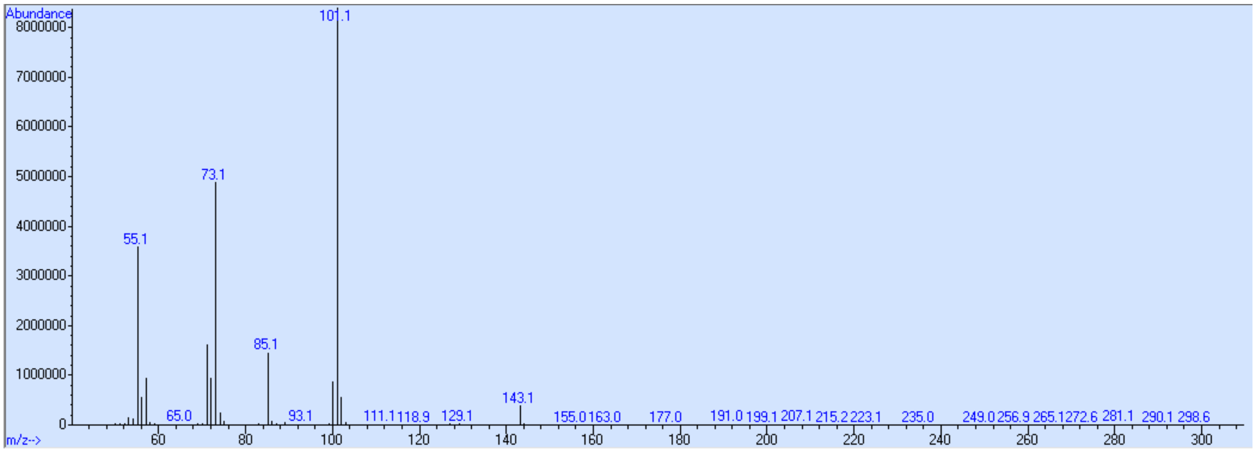


Figure S14. MS of (**3**)

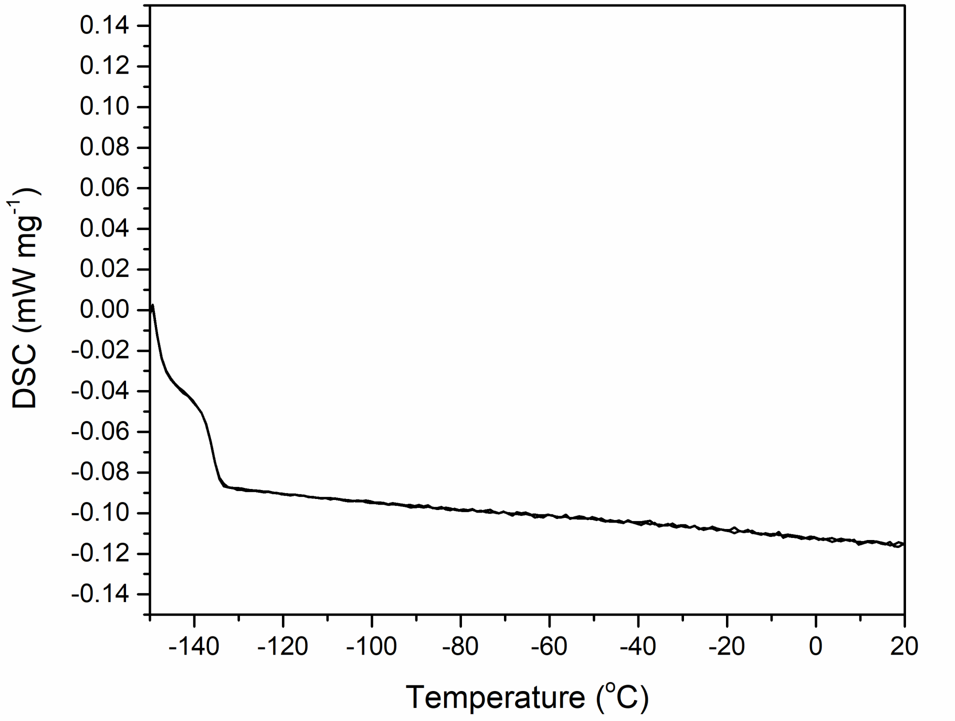


Figure S15. DSC trace of (**3**).

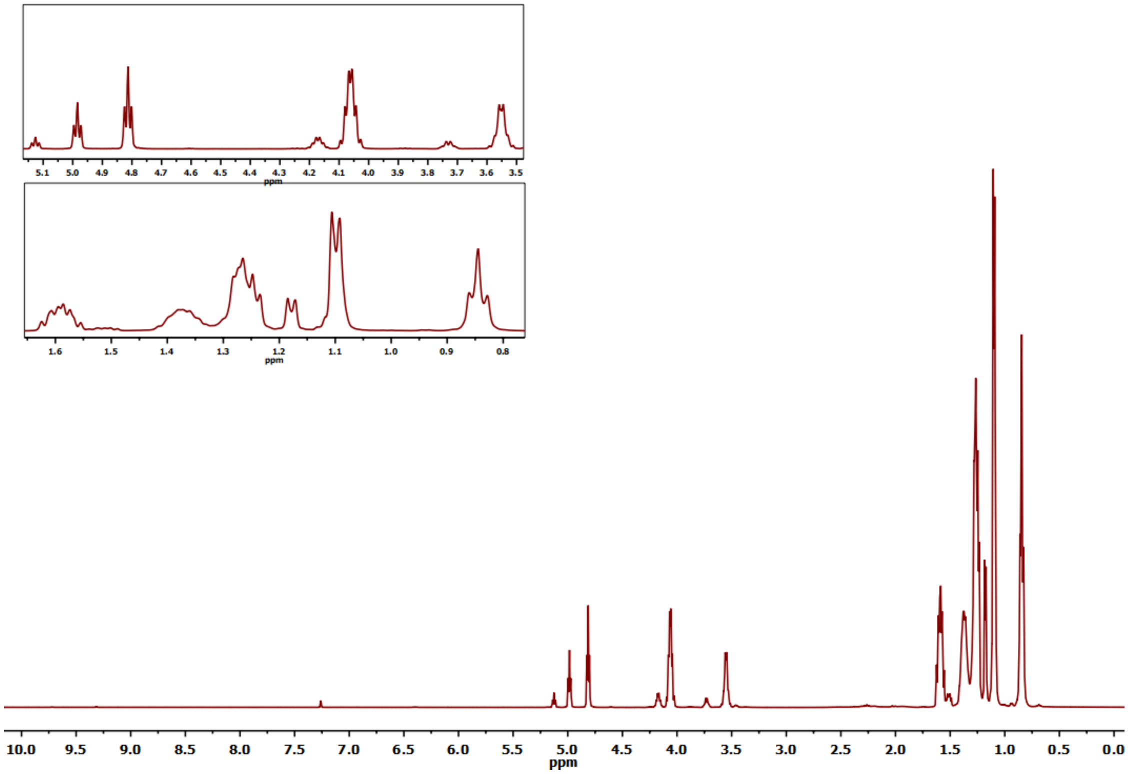


Figure S16. 400 MHz ^{1}H NMR spectrum of (**4**).

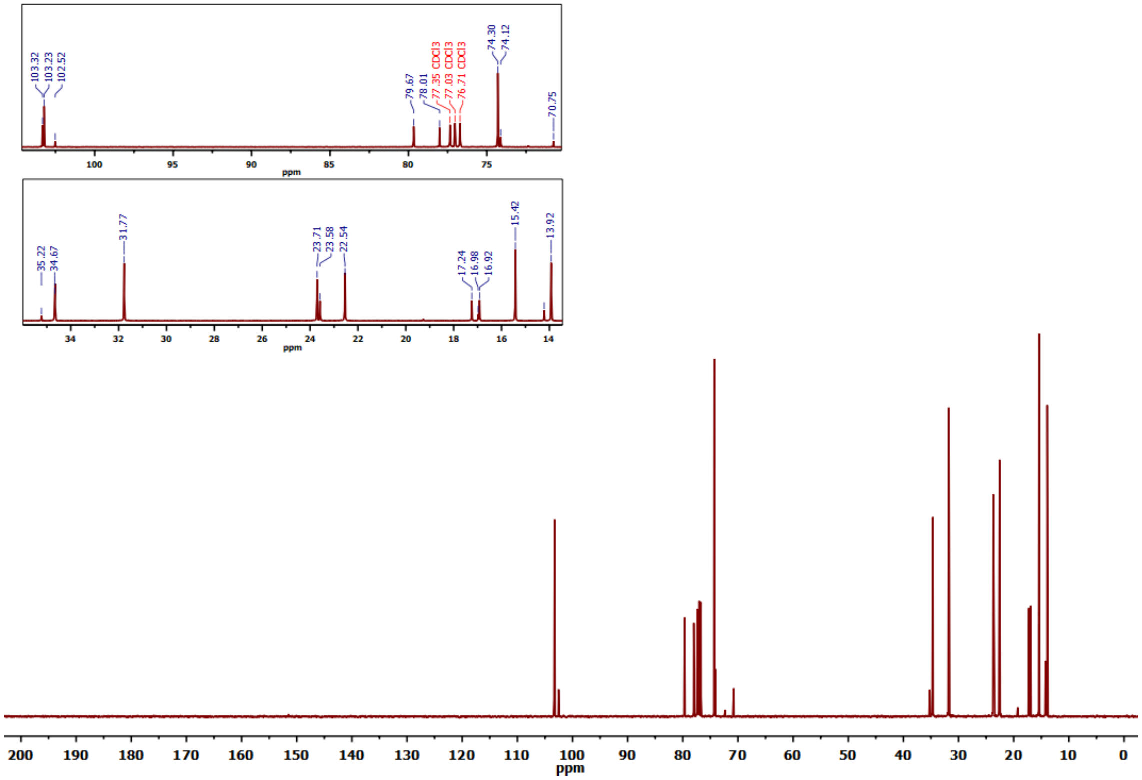


Figure S17. 101 MHz ^{13}C NMR spectrum of (**4**).

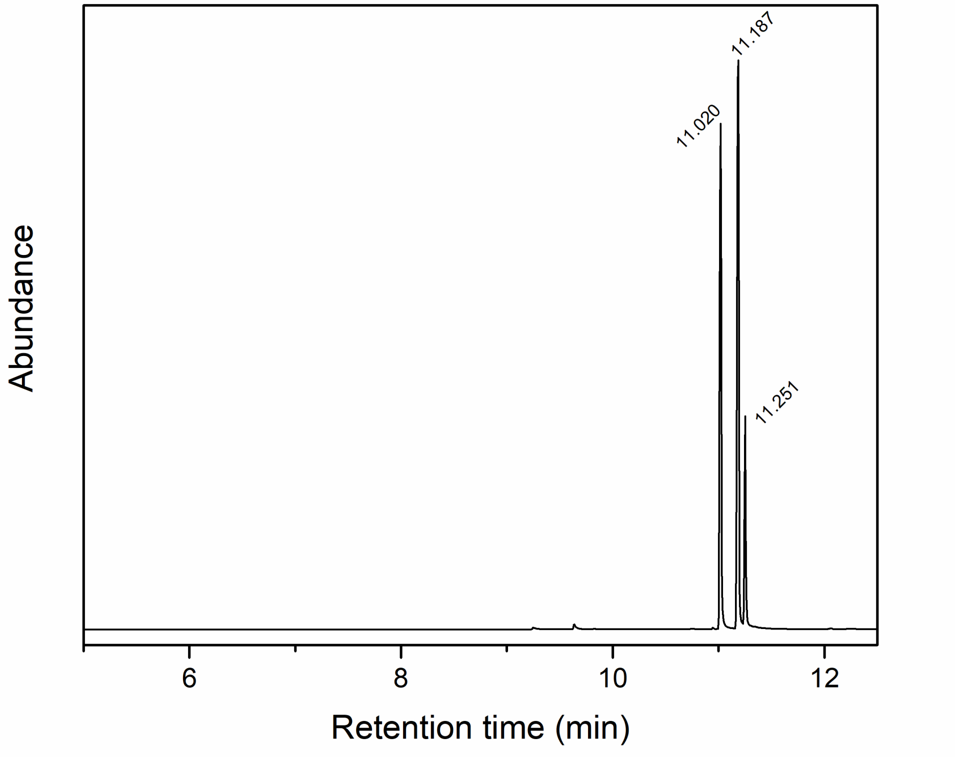


Figure S18. GC trace of (**4**).

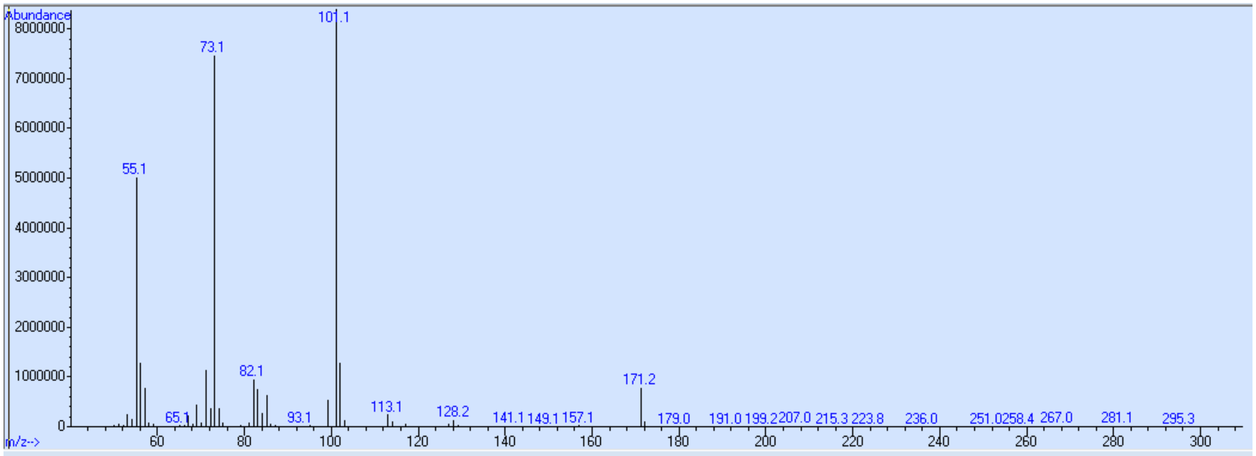


Figure S19. MS of (**4**)

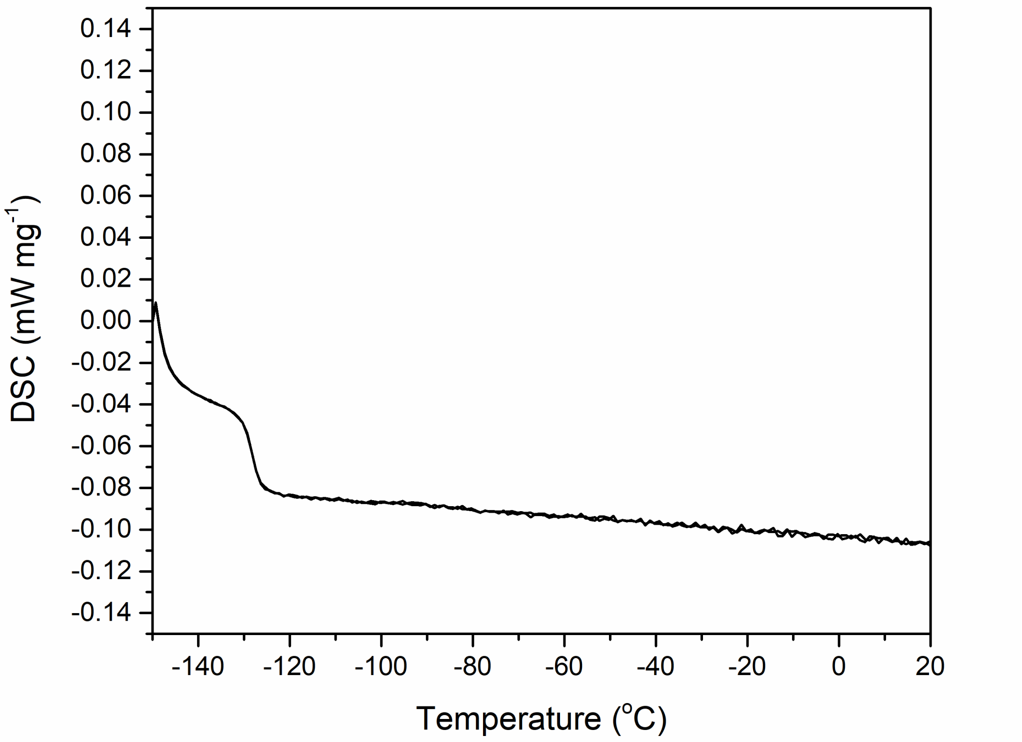


Figure S20. DSC trace of (**4**).

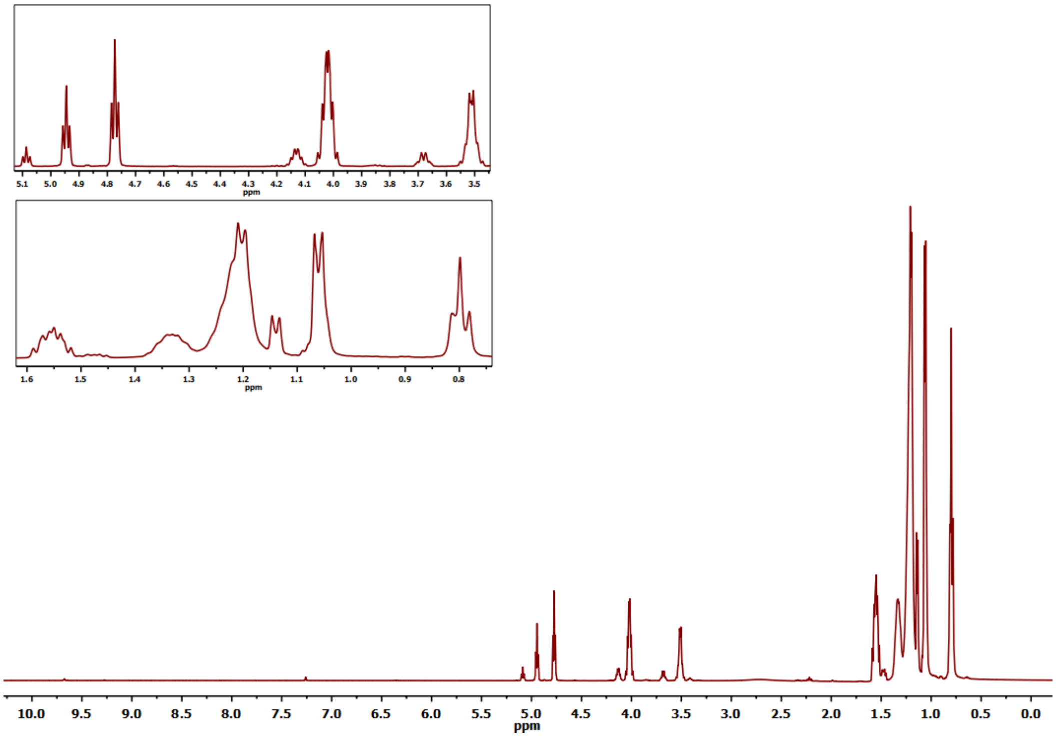


Figure S21. 400 MHz ^{1}H NMR spectrum of (**5**).

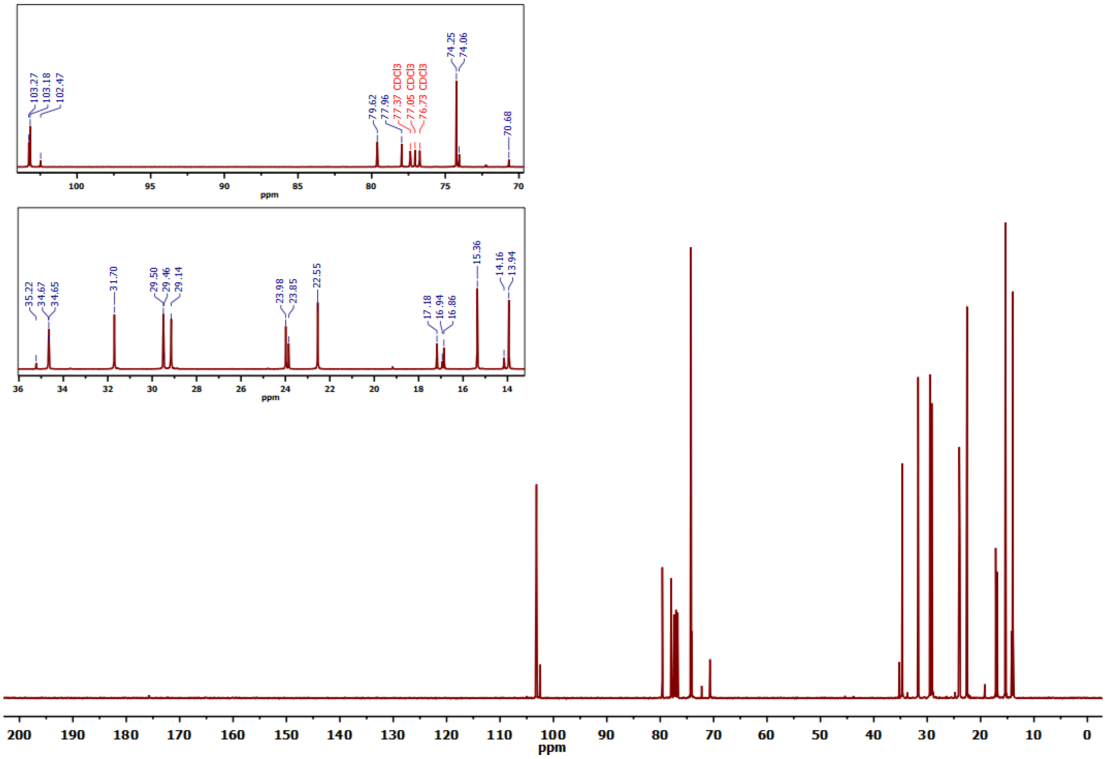


Figure S22. 101 MHz ^{13}C NMR spectrum of (**5**).

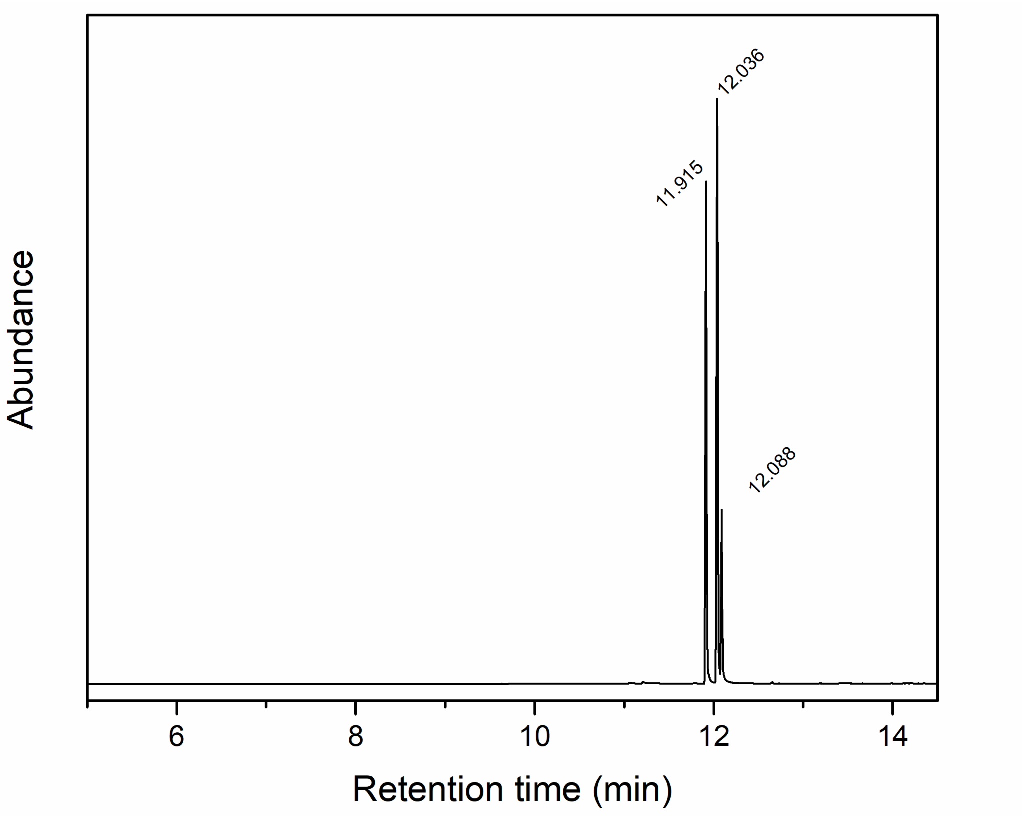


Figure S23. GCMS trace of (**5**).

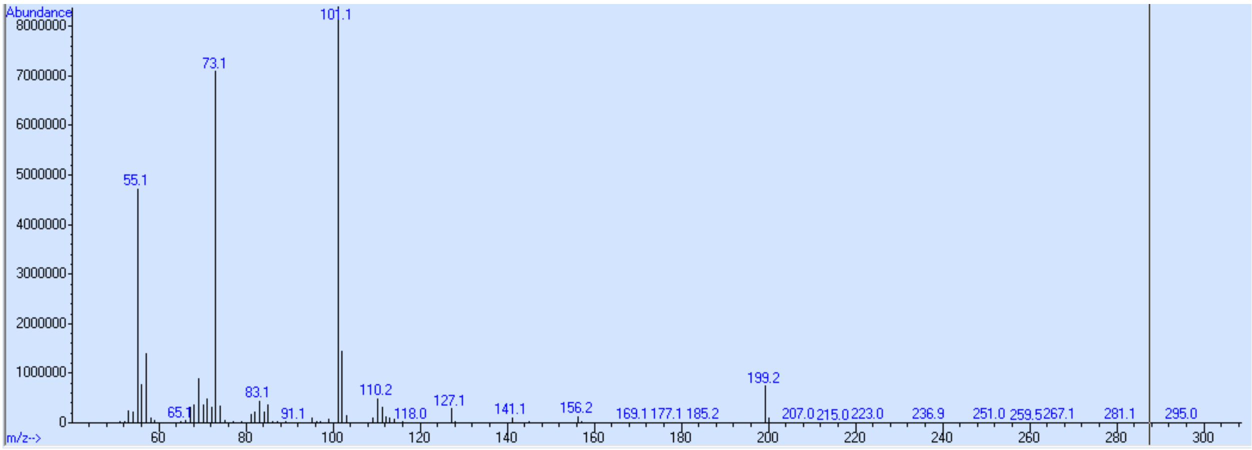


Figure S24. MS of (**5**)

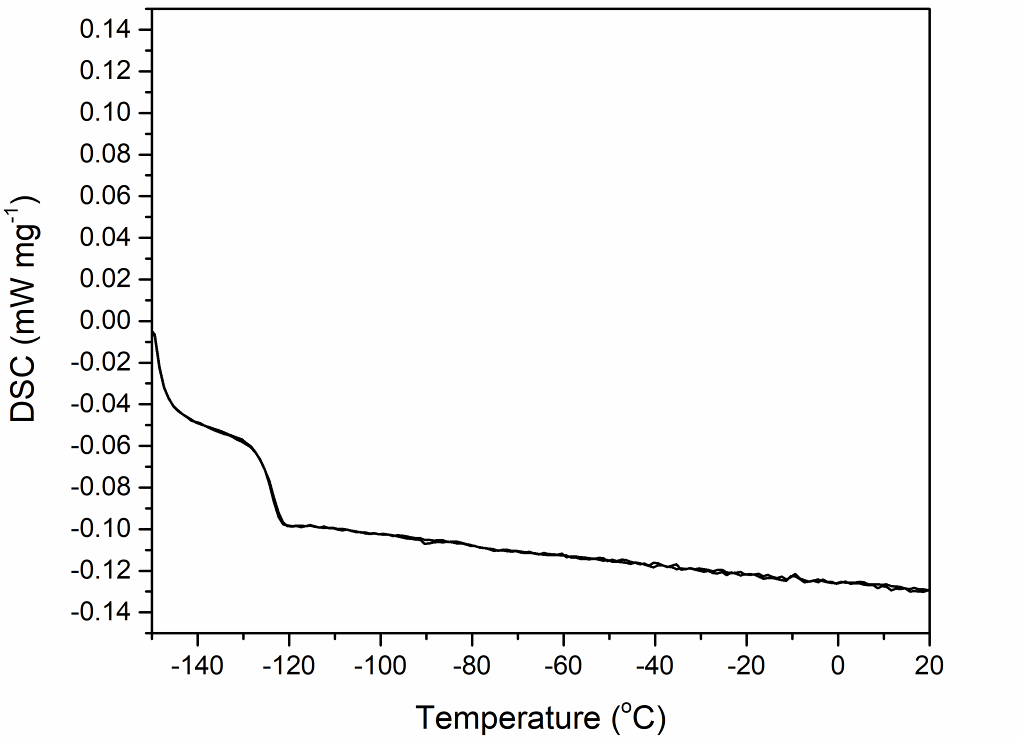


Figure S25. DSC trace of (**5**).

Catalyst recycling

2-Ethylbutyraldehyde (3.215 g, 32.10 mmol), 2,3-Butanediol (4.963 g, 55.07 mmol), and Amberlyst 15 (0.350 g) were combined in a 20 mL scintillation vial. The apparatus was heated to 40 °C with stirring (500 rpm). After 5 h the reaction was complete and allowed to cool for 15 min. Upon cooling, the organic layer was decanted to yield the desired product, **1**, in 100 % selectivity as evidenced by GCMS. This process was repeated for catalyst runs 2 through 10. To ensure efficient mixing between the aldehyde, BDO, and catalyst, the aqueous layer was removed upon completion of runs 3, 5, 7, and 9. Each successive reaction was loaded with 2-Ethylbutyraldehyde and 2,3-Butanediol, detailed below in Table S1.

Table S1. Catalyst recycle results.

Run	2-Ethylbutyraldehyde (mmol)	2,3-Butanediol (mmol)	Isolated yield (%)
1	32.10	55.07	87.2
2	32.05	53.99	88.2
3	31.30	55.84	96.6
4	31.66	56.71	93.3
5	31.96	60.25	93.7
6	32.51	59.55	91.2
7	32.03	55.69	92.7
8	31.99	57.45	94.0
9	31.95	58.08	95.2
10	32.07	56.92	93.0

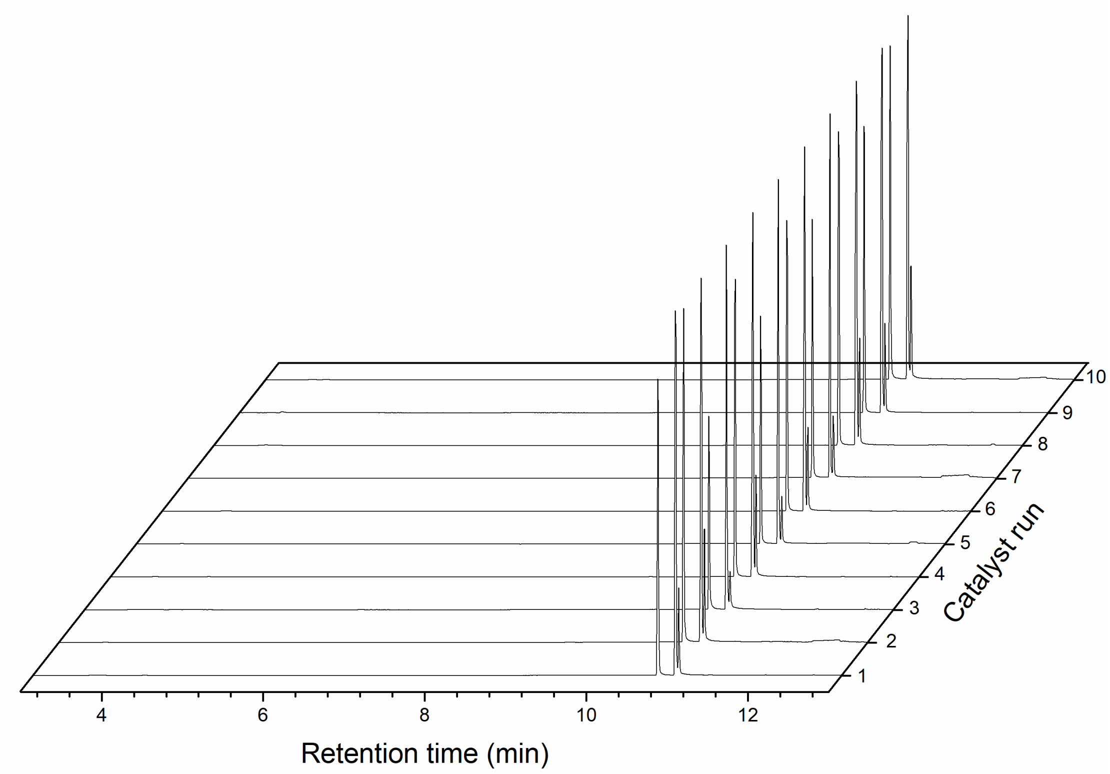


Figure S26. GCMS traces of catalyst recycle runs 1-10.

Calculation of atom economy and carbon yield

The following equation was used to determine the atom economy:

$$atom\ economy = \frac{(mass\ of\ atoms\ in\ desired\ product)}{(mass\ of\ atoms\ in\ reactants)} * 100$$

The following equation was used to determine the carbon yield:

$$\%\ Carbon\ yield = \frac{(mmol\ carbon\ in\ product) * (isolated\ yield)}{(mmol\ carbon\ in\ reactant)} * 100$$

Note that the only side product in this reaction is water, so the carbon efficiency is 100% for every reaction, therefore the carbon yield is the same as the isolated yield of analytically pure product.