Supporting Information for

Dendrimer-like core cross-linked micelle stabilized ultra-small gold nanocluster as robust catalyst for aerobic oxidation of α-hydroxy ketones in water

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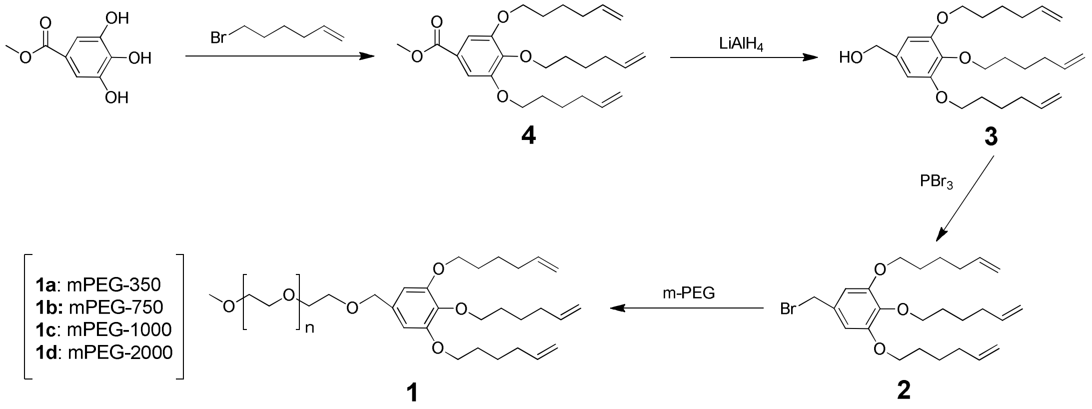
Synthesis

Scheme 1S. Synthesis of compound **1**



Compound 4.[1] Potassium carbonate (6.9 g, 50 mmol) was added to a solution of methyl 3,4,5-trihydroxy benzoate (3.0 g, 16.3 mmol) in DMF (15 mL) at room temperature. After the mixture was stirred at 60 ^{o}C for 2 h, 6-bromo-1-hexene (8.0 mL, 58 mmol) was added slowly. The resulting reaction mixture was further stirred overnight at 80 ^{o}C under N_2, cooled to room temperature, and poured over 1.0 L of icy water. The mixture was then extracted with CH_2Cl_2 (3 × 100 mL). The combined organic phase was washed with brine (50 mL), dried over anhydrous $MgSO_4$, and concentrated *in vacuo* to give the desired product as a colorless liquid (5.29 g). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.25 (s, 2H), 5.85-5.77 (m, 3H), 5.05-4.93 (m, 6H), 4.03-4.00 (t, J = 13.2 , 6H), 3.88 (s, 3H), 2.15-2.08 (m, 6H), 1.85-1.73 (m, 6H), 1.63-1.55 (m, 6H).

Compound 3.[2] To a stirred suspension of $LiAlH_4$ (0.8 g, 21 mmol) in THF (5.0 mL) at 0 ºC was added a solution of compound **4** (2.5 g, 5.8 mmol) in THF (15 mL). The reaction was stirred at room temperature and was monitored by TLC to determine the consumption of the benzoate. The reaction mixture was quenched at 0 ºC with 1N HCl and was then extracted with ethyl acetate. The combined organic layers were dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The resulting residue was used without any further purification to give a colorless liquid for the next step (2.0 g, 86%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.54 (s, 2H), 5.85-5.78 (m, 3H), 5.05-4.93 (m, 6H), 4.57 (s, 2H), 3.98-3.92 (m, 6H), 2.13-2.09 (m, 6H), 1.83-1.71 (m, 6H), 1.61-1.55 (m, 6H).

Compound 2.[3] A solution of PBr_3 (200.0 μL, 2 mmol) in anhydrous CH_2Cl_2 (10.0 mL) was added slowly to a stirred solution of compound **3** (402 mg, 1 mmol) in CH_2Cl_2 (5 mL) at 0 °C. The reaction mixture was stirred for 3 h at room temperature and slowly poured into a large amount of water (50 mL). The product was extracted with $CHCl_3$ (3 × 15 mL). The combined organic phase was washed with brine (20 mL), dried over anhydrous $MgSO_4$, and concentrated *in vacuo* to give a yellow liqud (404.0 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.57 (s, 2H), 5.83-5.79 (m, 3H), 5.05-4.93 (m, 6H), 4.44 (d, *J*= 2.8, 2H), 3.99-3.93 (m, 6H), 2.15-2.10 (m, 6H), 1.83-1.71 (m, 6H), 1.61-1.56 (m, 6H).

Compound 1a.[4] Methyl PEG-350 (337.0 mg, 0.9 mmol) was added to a suspension of sodium hydride (108 mg, 4.5 mmol) in THF (10 mL). The reaction was stirred for 2 h at room temperature. Compound **2** (209 mg, 0.45 mmol) was added slowly and the reaction mixture stirred at room temperature for 15 h. Saturated aqueous ammonium chloride (5.0 mL) was added and the mixture extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were washed with brine (10.0 mL) and dried with anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue purified by column chromatography (CH_2Cl_2: MeOH= 35 : 1) to afford the pure product as a yellow liquid (132.0 mg, 40%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.52 (s, 2H), 5.82-5.80 (m, 3H), 5.04-4.94 (m, 6H), 4.45(s, 2H), 3.97-3.90 (m, 6H), 3.67-3.53 (m, 39H), 3.38 (s, 3H), 2.11-2.09 (m, 6H), 1.82-1.76 (m, 6H), 1.60-1.55 (m, 6H). ^{13}C NMR (400 MHz, $CDCl_3$, δ): 153.05, 138.91, 138.58, 138.50, 137.47, 133.38, 130.97, 124.95, 114.7, 114.6, 114.5, 114.3, 106.2, 73.4, 73.0, 71.9, 70.64, 70.55, 70.50, 69.29, 68.80, 59.03, 33.59, 33.41, 30.15, 29.74, 29.07, 28.84, 25.37, 17.94. High resolution ESI-MS: $[M + Na]^+$ calcd for $C_{60}H_{108}NaO_{21}^+$ 791.4921, found 791.4908. Pairs of peaks correspond to different length oligomers (each pair containing a $[M + Na]^+$).

Compound 1b.[4] **1b** was prepared as above. The solvent was removed under reduced pressure and the residue purified by column chromatography (CH_2Cl_2: MeOH= 35 : 1) to afford the pure product as a yellow liquid (400 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.52 (s, 2H), 5.81-5.77 (m, 3H), 5.03-4.93 (m, 6H), 4.44 (s, 2H), 3.97-3.91 (m, 6H), 3.66-3.53 (m, 59H), 3.36 (s, 3H), 2.11-2.08 (m, 6H), 1.81-1.77 (m, 6H), 1.60-1.54 (m, 6H). ^{13}C NMR (400 MHz, $CDCl_3$, δ): 153.05, 138.89, 138.56, 137.50, 133.39, 114.65, 114.36, 106.23, 73.46, 73.05, 71.92, 70.64, 70.55, 70.50, 69.30, 68.81, 59.01, 33.57, 33.40, 30.14, 29.73, 29.06, 28.83, 25.35, 17.91. High resolution ESI-MS: $[M + Na]^+$ calcd for $C_{60}H_{108}NaO_{21}^+$ 1187.7281, found 1187.7128. Pairs of peaks correspond to different length oligomers (each pair containing a $[M + Na]^+$).

Compound 1c.[4] **1c** was prepared as above. The solvent was removed under reduced pressure and the residue purified by column chromatography (CH_2Cl_2: MeOH= 35 : 1) to afford the pure product as a yellow liquid (600.0 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.52 (s, 2H), 5.82-5.81 (m, 3H), 5.04-4.93 (m, 6H), 4.44 (s, 2H), 3.98-3.91 (m, 6H), 3.65-3.37 (m, 65H), 3.37 (s, 3H), 2.14-2.07 (m, 6H), 1.86-1.72 (m, 6H), 1.63-1.55 (m, 6H). ^{13}C NMR (400 MHz, $CDCl_3$, δ): 153.03, 138.89, 138.56, 137.44, 133.37, 114.66, 114.37, 106.18, 73.46, 73.05, 72.62, 71.90, 70.62, 70.23, 69.28, 68.78, 61.64, 59.01, 33.57, 33.39, 30.12, 29.72, 29.05, 28.82, 25.34, 17.93. High resolution ESI-MS: $[M + Na]^+$ calcd for $C_{70}H_{128}NaO_{26}^+$ 1407.8592, found 1407.8497. Pairs of peaks correspond to different length oligomers (each pair containing a $[M + Na]^+$).

Compound 1d.[4] **1d** was prepared as above. The solvent was removed under reduced pressure and the residue purified by column chromatography (CH_2Cl_2: MeOH= 30 : 1) to afford the product as a yellow solid (710.0 mg, 36%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.52 (s, 2H), 5.84-5.76 (m, 3H), 5.03-4.92 (m, 6H), 4.44 (s, 2H), 3.97-3.92 (m, 6H), 3.65-3.53 (m, 124H), 3.37 (s, 3H), 2.13-2.07 (m, 6H), 1.81-1.71 (m, 6H), 1.62- 1.52 (m, 6H). ^{13}C NMR (400 MHz, $CDCl_3$, δ): 153.07, 138.94, 138.60, 137.44, 133.40, 114.71, 114.42, 106.17, 73.51, 73.08, 71.95, 70.67, 69.31, 68.79, 59.08, 33.63, 33.45, 30.17, 29.76, 29.72, 28.85, 25.38, 22.72, 14.18. High resolution ESI-MS: $[M + Na]^+$ calcd for $C_{108}H_{204}NaO_{45}^+$ 2245.3606, found 2245.2442. Pairs of peaks correspond to different length oligomers (each pair containing a $[M + Na]^+$).

References

1. S. Zhang and Y. Zhao, *ACS Nano*, 2011, **5**, 2637-2646.
2. M. Sutter; L. Pehlivan and R. Lafon, *Green Chem.,*2013, **15**, 3020-3026.
3. K. Tanabe, T. Yasuda, M. Yoshio and T. Kato, *Org. Lett.,* 2007, **9**, 4271-4274.
4. Y. Li; K. M. Mullen; T. D. W. Claridge; P. J. Costa; V. Felix and P. D. Beer, *Chem. Commun*.**,** 2009**,** 7134-7136.

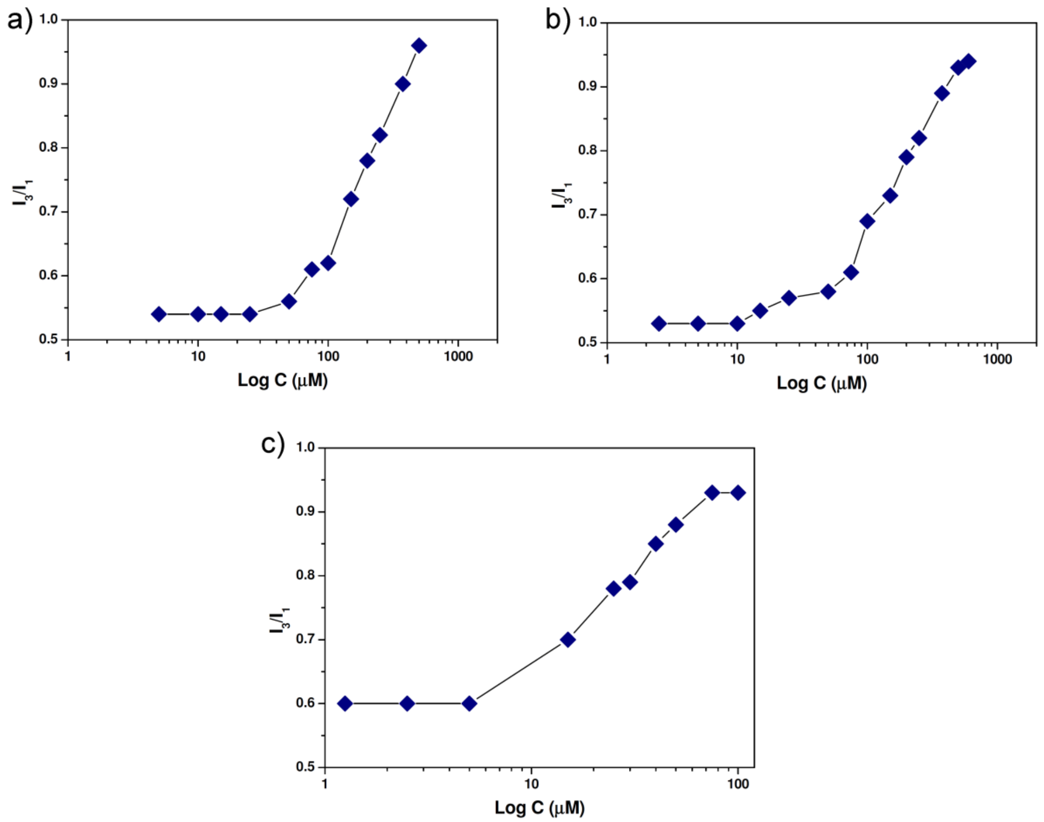


Fig. 1S Pyrene I_3/I_1 ratio as a function of concentrations of (a) **1b**, (b) **1c**, and (c) **1d.** [pyrene] = 1.0 × 10^{-7} mol/L.

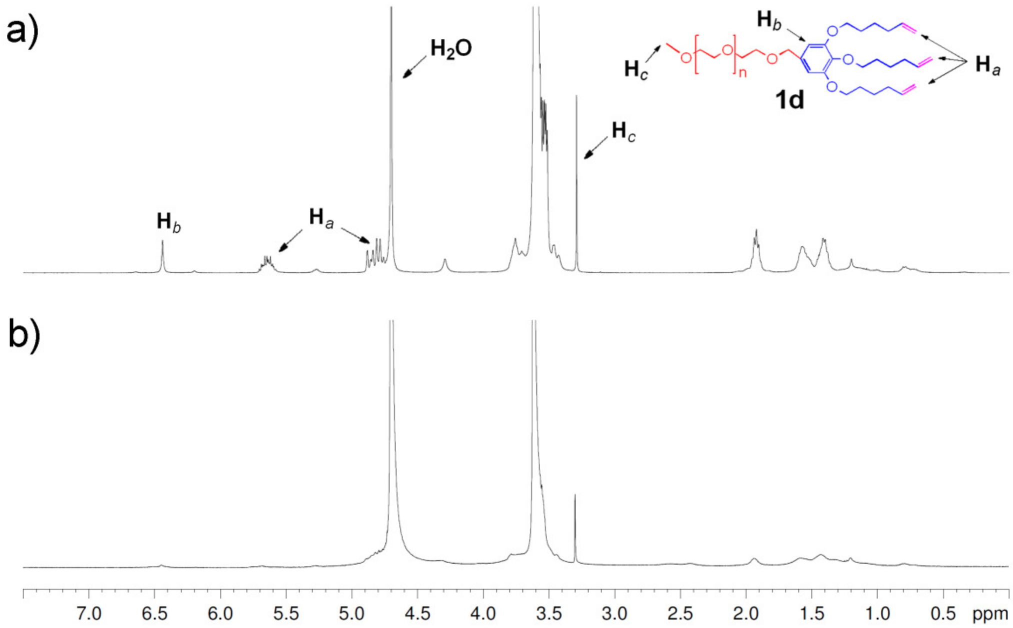


Fig. 2S ^1H NMR spectra of a 0.5 mM aqueous solution of **1d** (a) in D_2O, and (b) after cross-linking with DTT and dialysis.

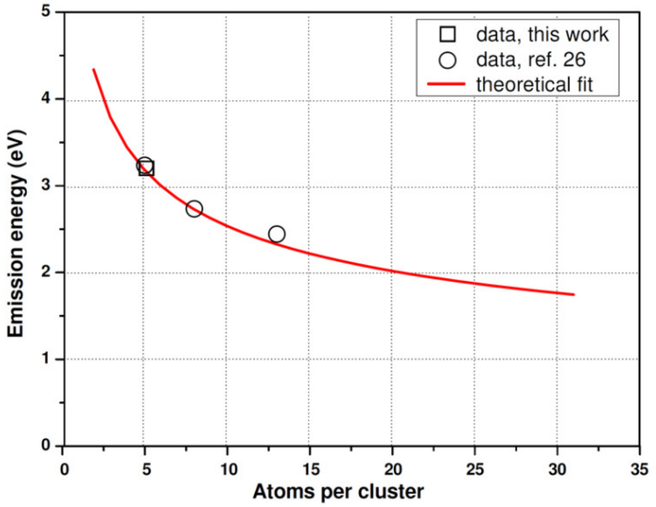


Fig. 3S Plot of the emission energy, *E* versus number of gold atoms per cluster, *N*. The reported data points (○) by Zheng *et al.* were fitted by the theoretical curve (solid line): $E = E_{\text{Fermi}}/N_{1/3}$, E_{Fermi} = 5.5 eV – the Fermi energy of bulk gold. The data point (□) was obtained experimentally and confirmed theoretically.

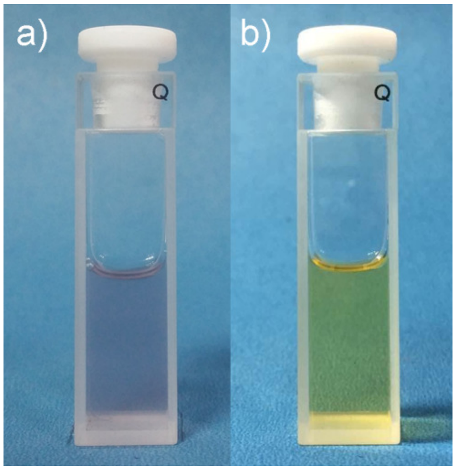


Fig. 4S Comparison of pictures of catalyst Au@DCCMs before reaction (a), and after recycle 48 times (b).

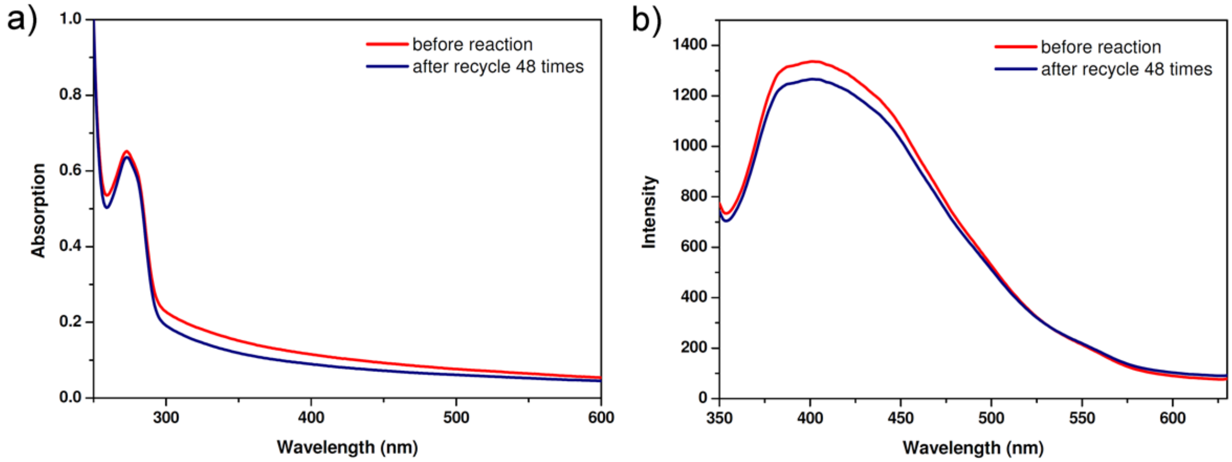
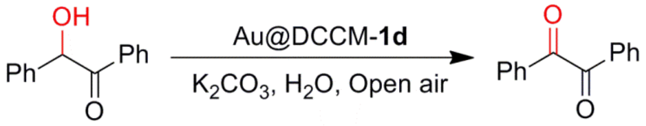


Fig. 5S Comparison of UV-Vis (a) and emission (b) spectra of Au@DCCMs before reaction and after recycle 48 times. λ_{ex} = 330 nm, [$AuCl_4^-$]/[**1d**] = 0.5.

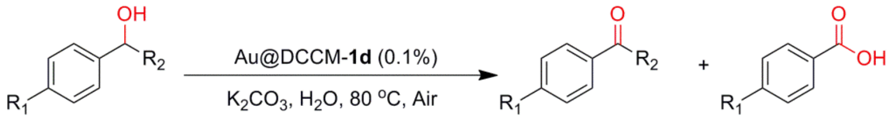
Table 1S. Optimization of the aerobic oxidation of benzoin to benzyl catalysed by Au@DCCM-1d in water.



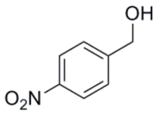
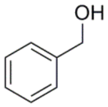
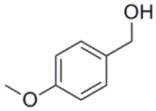
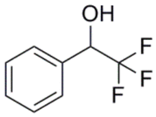
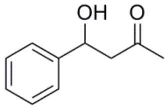
Entry	Au@DCCM-**1d**	T (°C)	Au/benzoin (%)	time (h)	Yield (%)[b]
1	50%Au	30	2	24	7.8
2	50%Au	40	2	14	16
3	50%Au	50	2	14	100
4	2%Au	50	2	6	19.6
5	10%Au	50	2	6	23.8
6	30%Au	50	2	6	22.1
7	40%Au	50	2	6	24.2
8	45%Au	50	2	6	29.9
9	50%Au	50	2	6	33.1
10	55%Au	50	2	6	29.2
11	60%Au	50	2	6	29.9
12	100%Au	50	2	6	25.7
13	50%Au	50	1	40	100
14	50%Au	50	0.5	48	100
15	**50%Au**	**50**	**0.1**	**48**	**100**
16	50%Au	50	0.05	72	49
17	0%Au	50	0	48	2.2

[a] Reaction conditions: α-hydroxyketone (16 mg, 0.077 mmol), Au@DCCM-**1d**, K_2CO_3 (32 mg, 0.23 mmol), H_2O (2 mL), open air. [b] Yields were determined by ^1H NMR analysis.

Table 2S. Au@DCCMs catalysed aerobic oxidation of benzylic alcohols in water.[a]

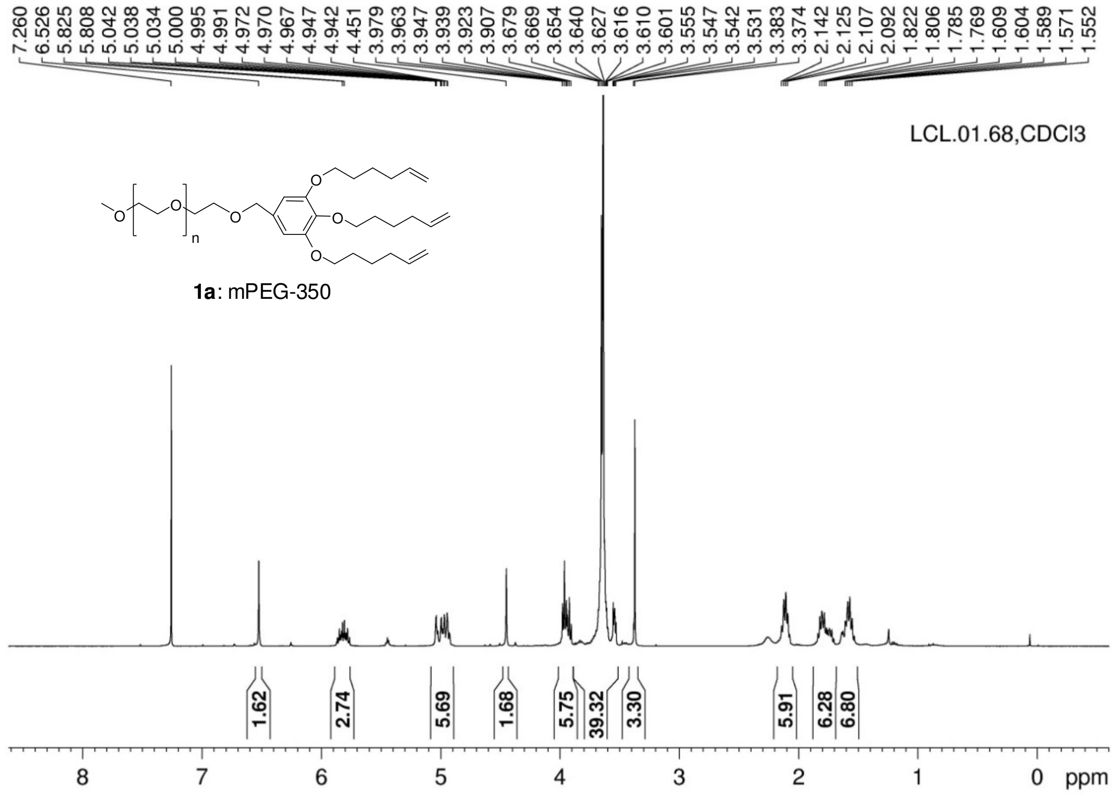


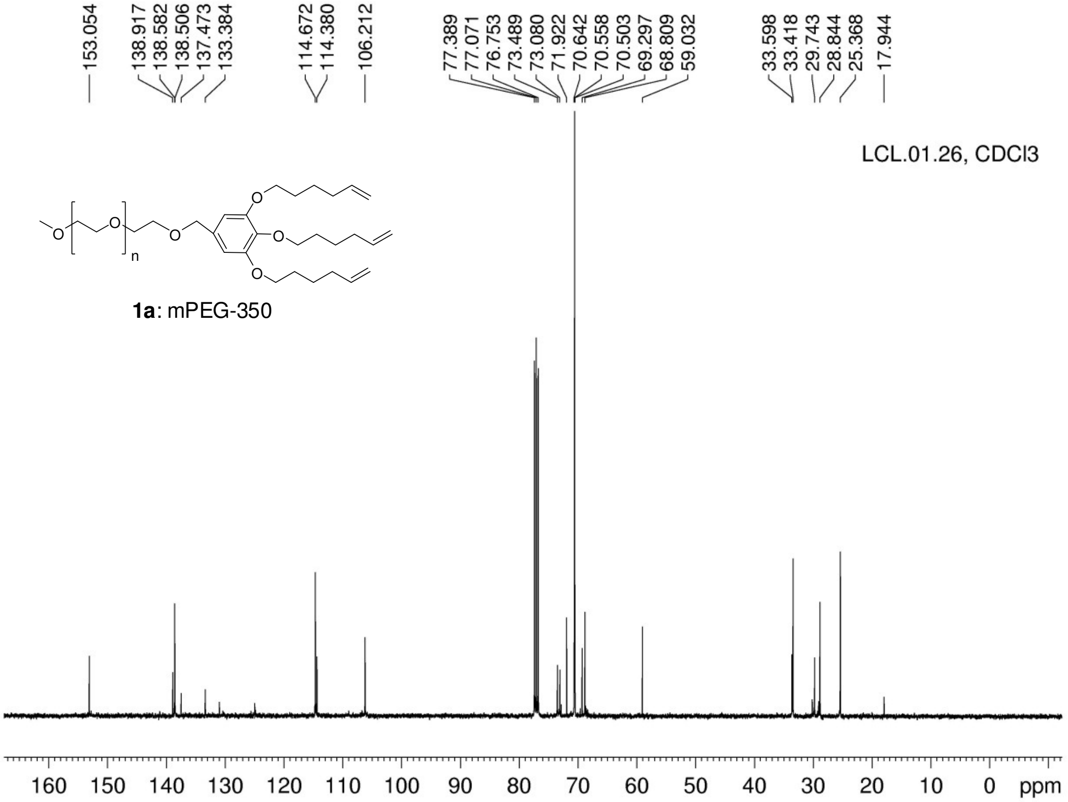
P-1 **P-2**

Entry	benzylic alcohol	t (h)	**P-1** (%)[b]	**P-2** (%)[b]
1		60	13.5	85.3
2		72	2.6	26.8
3		72	—	8.7
4		72	40.1	—
5		40	>98	—

[a] Reaction conditions: benzylic alcohol (0.077 mmol), Au@DCCM-1d (0.077 µmol, for Au), K_2CO_3 (32 mg, 0.23 mmol), H_2O (2 mL), open air, 80 °C. [b] Yields were determined by ^1H NMR analysis.

^{1}H, ^{13}C NMR, and MS Spectra of Key Compounds 1a-1d.

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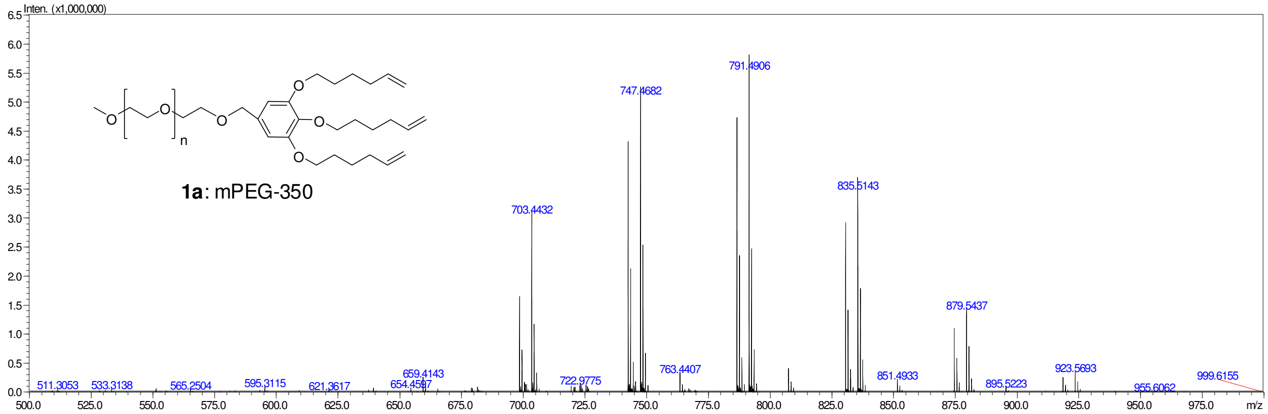
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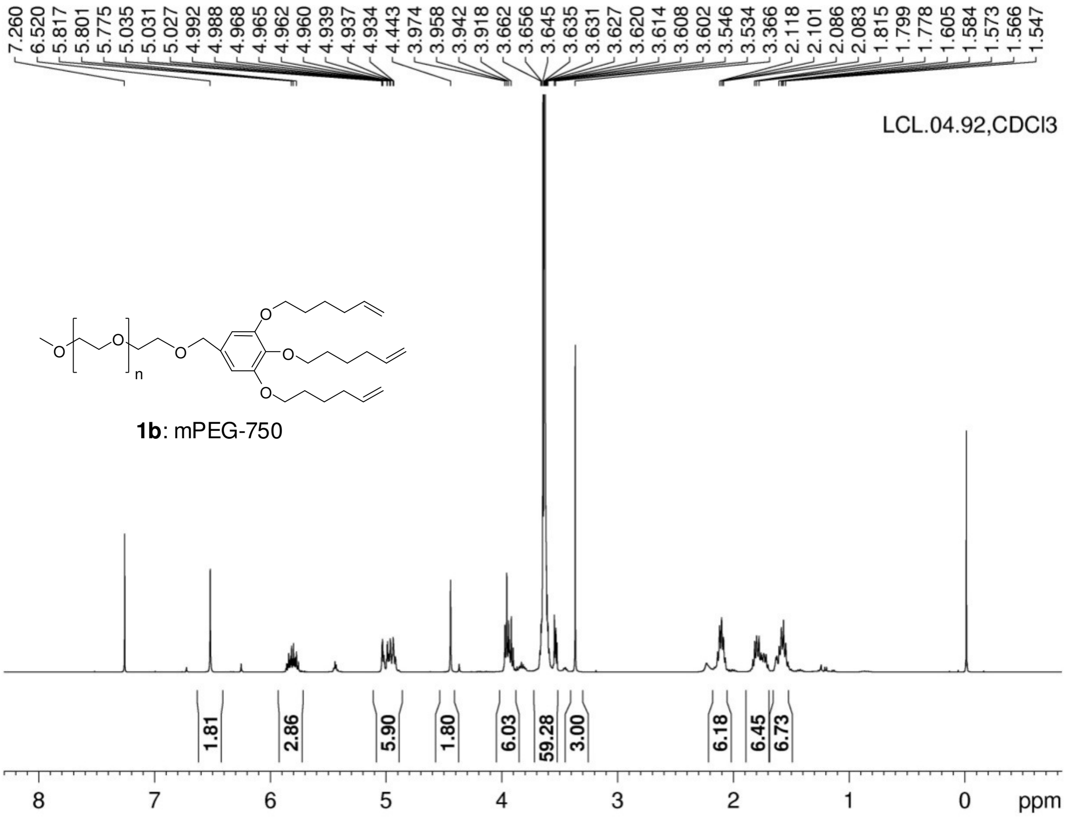
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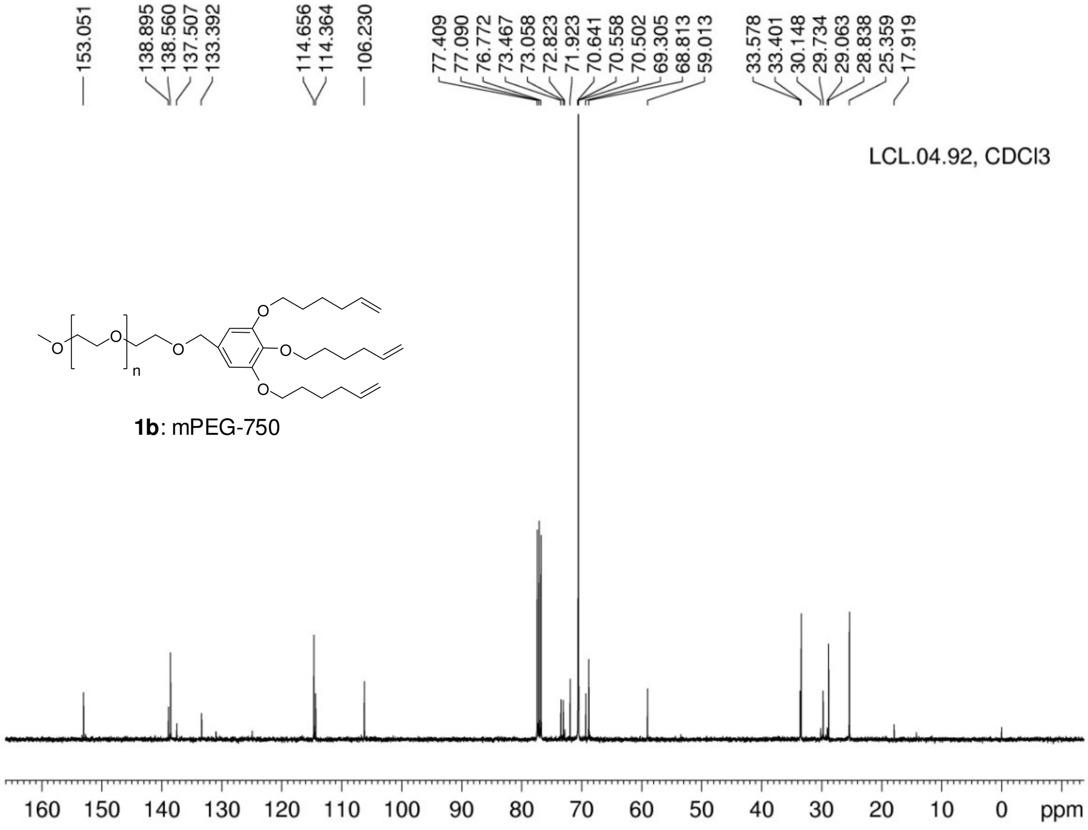
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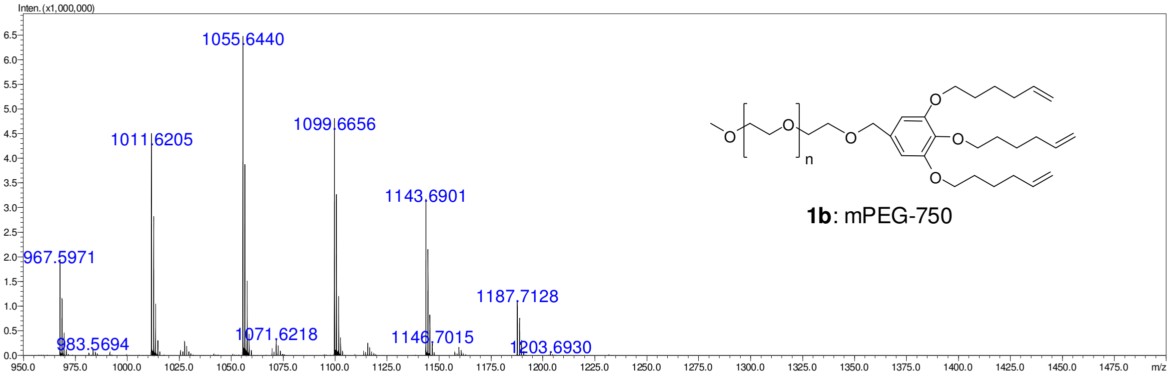

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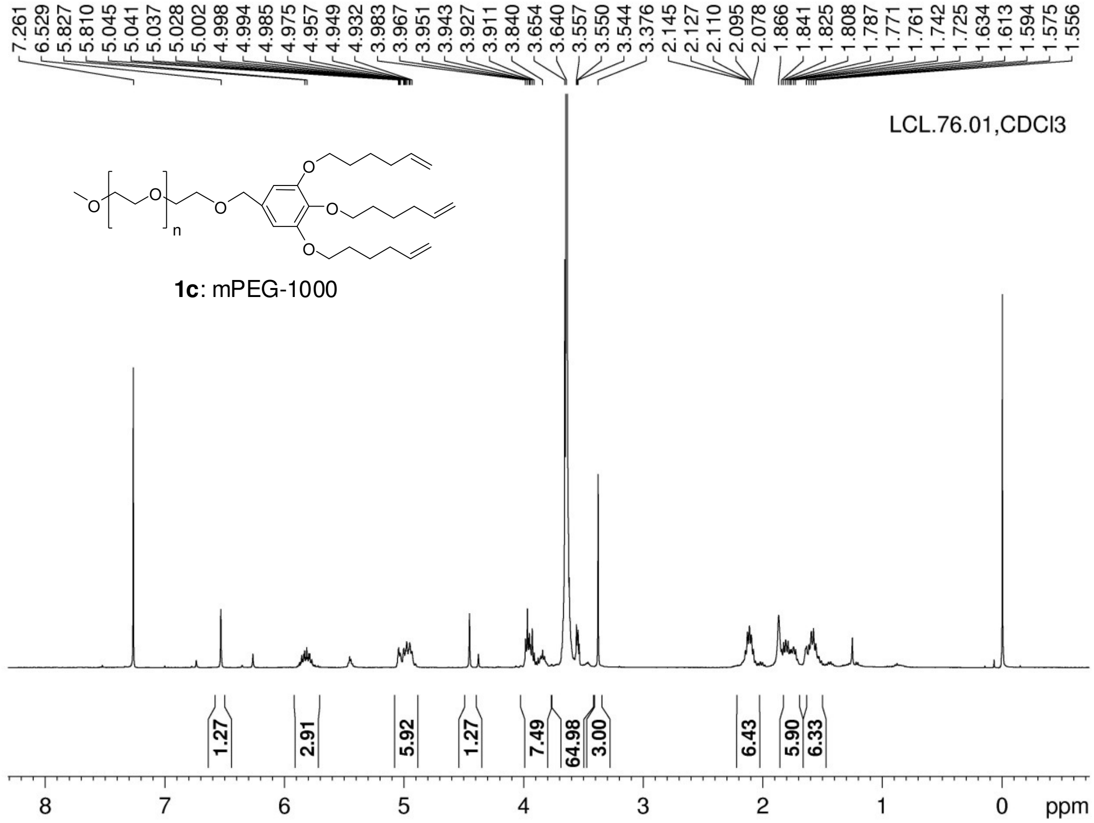

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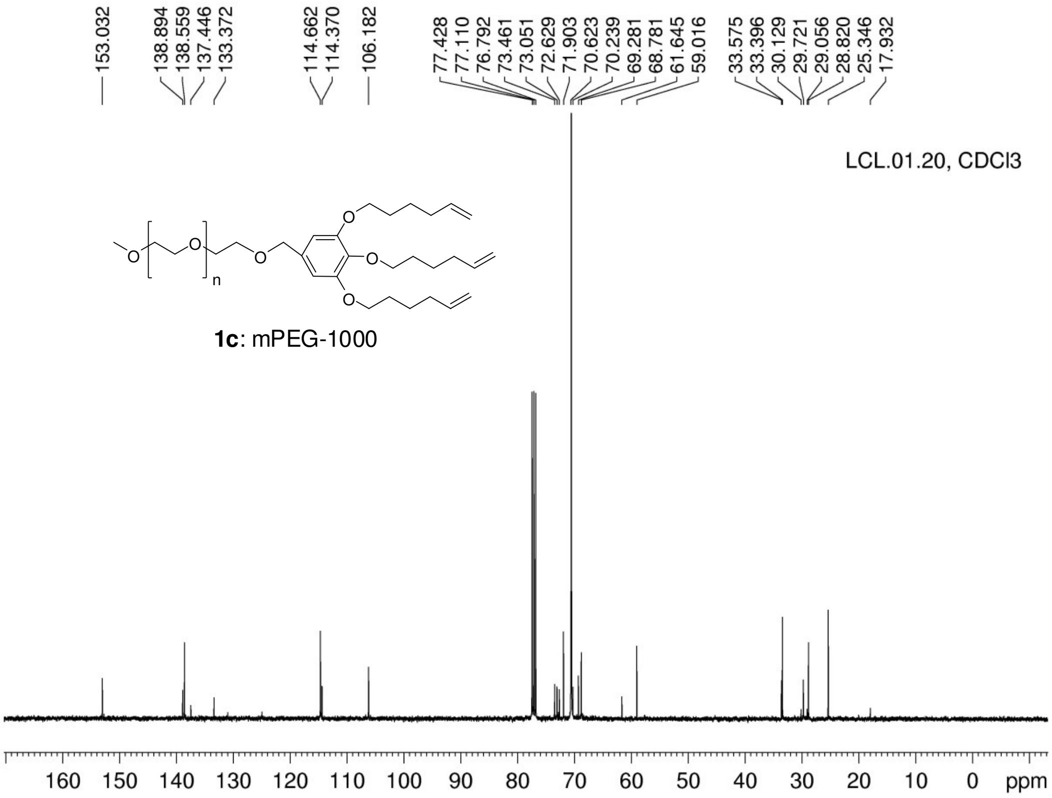
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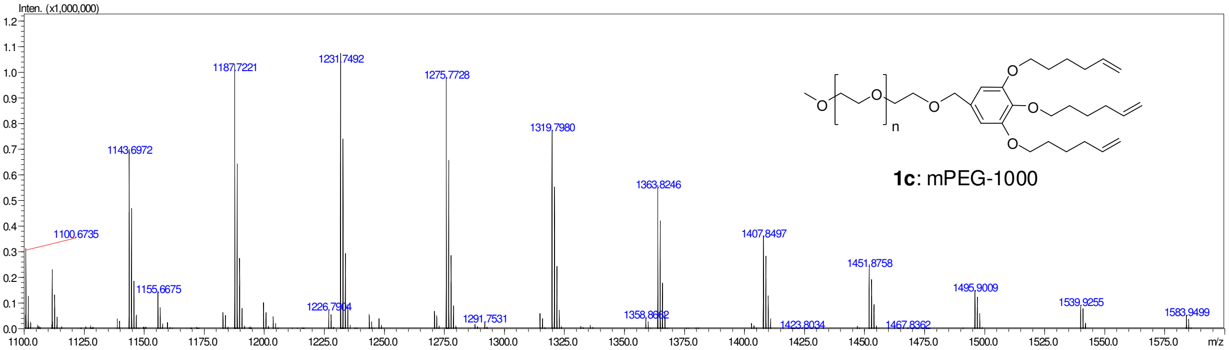
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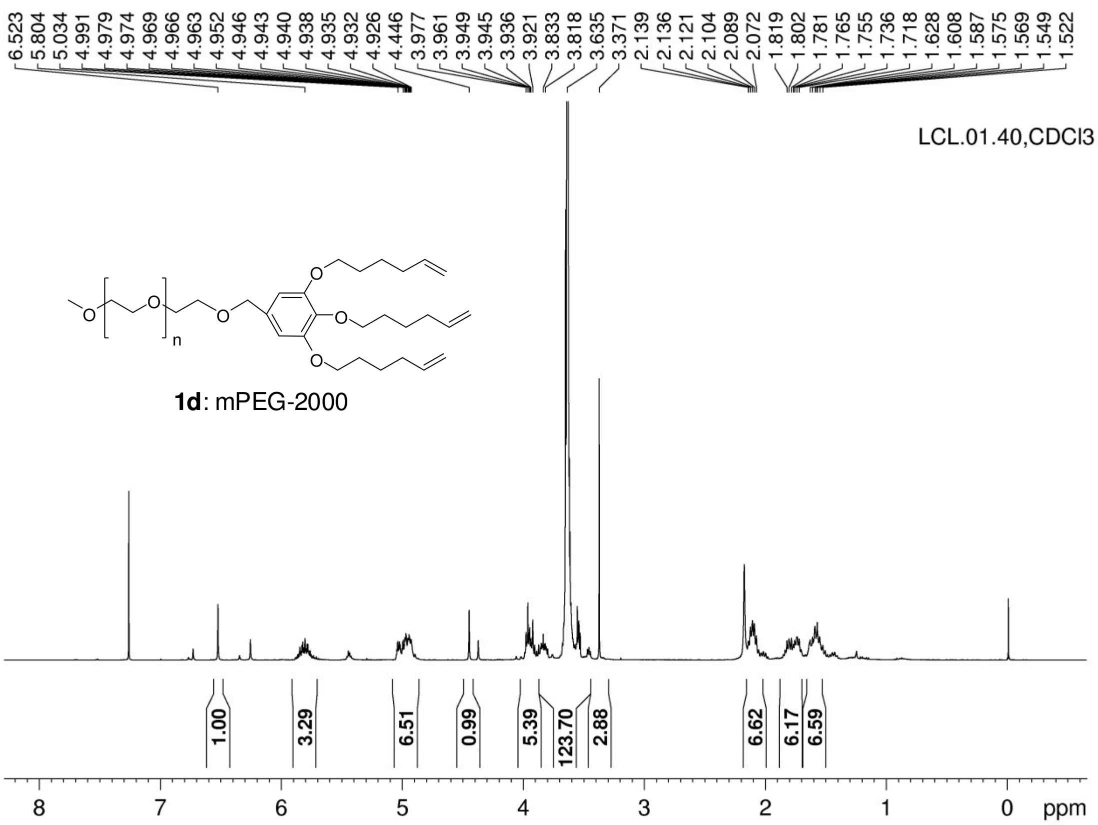
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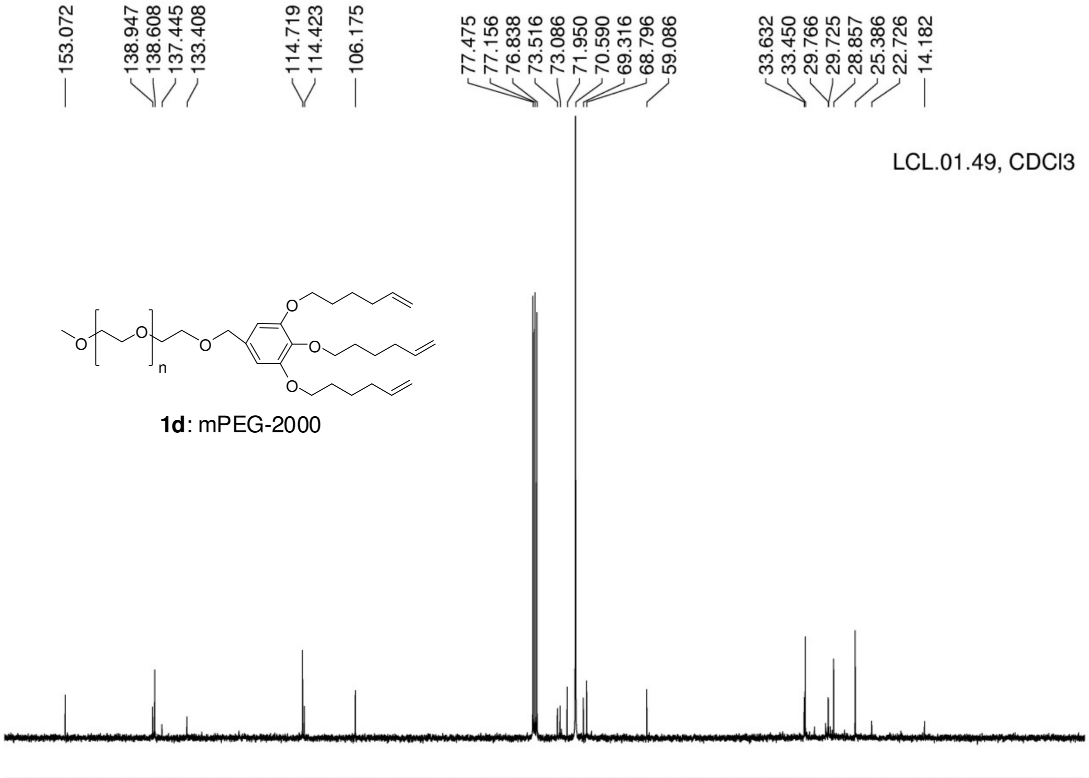
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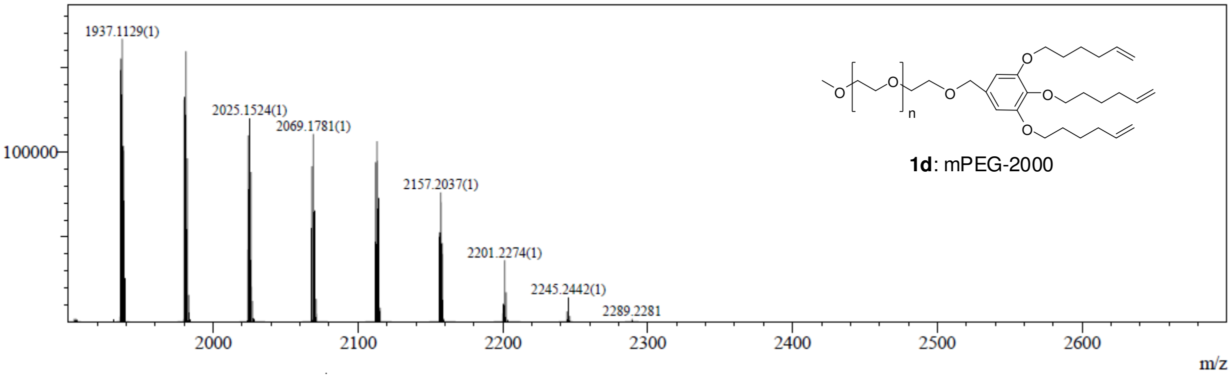
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O
O

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