Supporting Information

Ternary deep eutectic solvents for esterification of 2-methylpropenoic acid with alcohols

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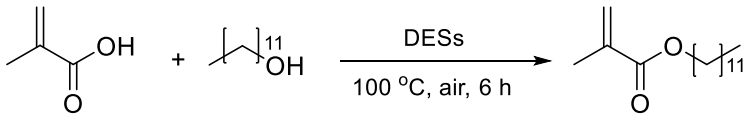
1. General information

All reactions were carried out using oven-dried schlenk tube (25 mL) and magnetic stirring (the speed is 1000 rpm) under air unless otherwise stated. All commercially available compounds were purchased from Energy, Aladdin, J&K or Macklin. TLC was carried out on SiO_2 (silica gel 60 F254, Merck), and initial spot localization achieved using UV light (254 nm) followed by visualization through smoked spots with molybdate phosphate at elevated temperatures for precise localization. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance II-400 spectrometer (400 MHz for ^1H, 101 MHz for ^{13}C). $CDCl_3$ and CH_2Br_2 were used as a solvent and an internal standard, respectively. The chemical shifts were reported in ppm downfield (δ) from CH_2Br_2, the coupling constants J are given in Hz. The peak patterns were indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. IR spectra were recorded on a NEXUS FT-IR spectrometer. Raman spectra were recorded on a DXR Raman Microscope spectrometer.

2. Optimization of the reaction conditions

Table S1 **Effect of DESs**[a]



1a **2a** **3a**

Entry	DESs name	Equivalence ratio	Yield (%)[e]
1	T-DESs-**1**	ChCl/PTSA/HQ (1:1:0.02)	95
2	T-DESs-**2**	TBAC/PTSA/HQ (1:1:0.02)	61
3	T-DESs-**3**	TBAB/PTSA/HQ (1:1:0.02)	51
4	T-DESs-**4**	TBAI/PTSA/HQ (1:1:0.02)	54
5	T-DESs-**5**	TBAHS/PTSA/HQ (1:1:0.02)	26
6	T-DESs-**6**	ChCl/oxalic acid/HQ (1:1:0.02)	47
7	T-DESs-**7**	ChCl/malonic acid/HQ (1:1:0.02)	33
8	T-DESs-**8**	ChCl/maleic acid/HQ (1:1:0.02)	37
9	T-DESs-**9**	ChCl/MCA/HQ (1:1:0.02)	81
10	T-DESs-**10**	ChCl/PTSA/*p*-Benzoquinone (1:1:0.02)	86
11	T-DESs-**11**	ChCl/PTSA/MEHQ (1:1:0.02)	91

12	T-DESs-**12**	ChCl/PTSA/BHT (1:1:0.02)	81
13	DESs-**13**	ChCl/PTSA/HQ (1:1:0)	85
14	T-DESs-**14**	ChCl/PTSA/HQ (1:1:0.005)	95
15	T-DESs-**15**	ChCl/PTSA/HQ (1:1:0.01)	95
16	T-DESs-**16**	ChCl/PTSA/HQ (1:1:0.05)	95
17	T-DESs-**17**	ChCl/malonic acid/HQ (2:1:0.02)	14
18	T-DESs-**18**	TEAB/PTSA/HQ (1:1:0.02)	32
19	T-DESs-**19**	ChCl/MCA/HQ (1:1:0.02)	81
20	T-DESs-**20**	ChCl/$ZnCl_2$/HQ (1:2:0.02)	49
21	T-DESs-**21**	ChCl/$ZnBr_2$/HQ (1:2:0.02)	36
22	T-DESs-**22**	ChCl/maleic acid/HQ (2:1:0.02)	32
23	T-DESs-**23**	ChCl/PTSA/CuCl (1:1:0.02)	93
24	T-DESs-**24**	ChCl/PTSA/$FeCl_3\cdot 6H_2O$ (1:1:0.02)	90
25[b]	DESs-**25**	ChCl/HQ (1:0.02)	14
26[c]	DESs-**26**	PTSA/HQ (1:0.02)	95
27	T-DESs-**27**	ChCl/$SnCl_2\cdot 2H_2O$/HQ (1:2:0.02)	5
28[d]	N-DESs-**28**	HQ (0.02)	19
29	T-DESs-**29**	ChCl/PTSA/HQ (1:2:0.02)	94
30	T-DESs-**30**	ChCl/PTSA/HQ (2:1:0.02)	87
31	T-DESs-**31**	ChCl/PTSA/HQ (2:1:0.025)	94
32	T-DESs-**32**	ChCl/PTSA/HQ (1:1:0.0175)	95
33	T-DESs-**33**	ChCl/PTSA/HQ (1:1:0.015)	97
34	T-DESs-**34**	ChCl/PTSA/HQ (1:1:0.0125)	93
35	T-DESs-**35**	ChCl/TFA/HQ (1:2:0.02)	ND
36	T-DESs-**36**	ChCl/PTSA/HQ (1:1:0.0075)	92
14	T-DESs-**37**	ChCl/$CuCl_2$/HQ (1:2:0.02)	61
38	T-DESs-**38**	ChCl/PTSA/HQ (1:1:0.0025)	95
39	T-DESs-**39**	ChCl/PTSA/HQ (1:1:0.001)	93
40	T-DESs-4**0**	ChCl/PTSA/HQ (1:1:0.0005)	88
41	T-DESs-**41**	ChCl/oxalic acid/HQ (2:1:0.02)	31

[a] Reaction conditions: **1a** (0.01 mol), **2a** (0.01 mol,1.0 equiv.), and DESs (0.01 mol) stir at 100 °C in air for 6 h. [b] ChCl/HQ (0.01 mol), not form DESs. [c] PTSA/HQ (0.01 mol), not form DESs. [d] HQ (0.01 mol). [e] Yield determined by ^{1}H NMR using CH_2Br_2 as internal standard.

Table S2 **Effect of other reaction conditions**[a]

Entry	Temp. (℃)	Time (h)	DESs dosage (eq.)	Yield (%)[b]
1	80	6	1	84
2	90	6	1	85
3	100	6	1	95
4	110	6	1	93
5	120	6	1	89
6	100	3	1	87
7	100	4	1	90
8	100	5	1	91
9	100	7	1	85
10	100	6	0.05	88
11	100	6	0.1	95
12	100	6	0.5	97

[a] The reaction was carried out using **1a** (10 mmol) and **2a** (10 mmol) in air.

[b] Isolated yields.

Table S3 **Effect of ratio (acid : alcohol) on reaction**[a]

Entry	Acid : Alcohol	Yield/%[b]
1	1	95
2	1.2	96
3	1.4	97
4	1.6	97

[a] Reaction conditions: Methacrylate (0.01 mol), Dodecanol (X equiv.) and DESs (0.01 mol) stir at 100 °C for 6 h, in air.

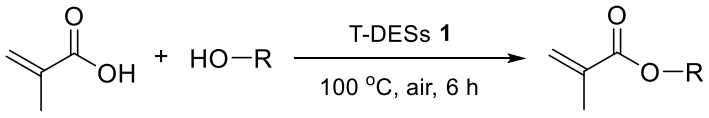
[b] Isolated yield.

3. Experimental procedures

3.1 Representative procedure for the synthesis of T-DESs 1.

A dry schlenk tube (25 mL) with a magnetic rotor was charged with PTSA (10 mmol), ChCl (10 mmol) and HQ (0.2 mmol). The mixture was stirred at 70 ℃ for 20 mins at 800 rpm in air, and T-DESs **1** was formed as a clear and transparent solution.

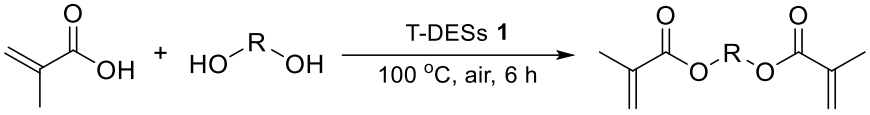
3.2 General procedure for the synthesis of methacrylate.



1a **2** **3**

A dry schlenk tube (25 mL) with a magnetic rotor was charged with **1a (**10 mmol) , **2** (10 mmol) and T-DESs-**1** (1 equiv.). The mixture was stirred at 100 ℃ for 6 h in air. After the reaction completed, the reaction mixture was extracted with petroleum ether (3×5 mL). The combined organic layer was dried over Na_2SO_4, then purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate =5:1) to afford the desired products **3**.

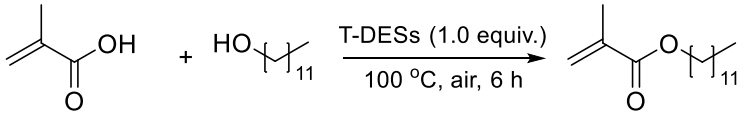
3.3 General procedure for the synthesis of dimethyl methacrylate.



1a **4** **5**

A dry schlenk tube (25 mL) with a magnetic rotor was charged with **1** (20 mmol), **4a-4h** (10 mmol) and T-DESs-**1** (1 equiv.). The mixture was stirred at 100 ℃ for 6 h in air. After the reaction completed, the reaction mixture was extracted with petroleum ether (3×5 mL). The combined organic layer was dried over Na_2SO_4, then the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate =3:1)] to afford **5a-5h**.

3.4 Esterification yield at different catalyst recycling runs.



1a **2a** **3a**

The esterification reaction of 1a with dodecanol (2a) was selected as the model reaction for T-DESs recycling testing. Thus, **2a** (10 mmol) was added to a solution of **1a** (10 mmol) in T-DESs (10 mmol), and the mixture was stirred at 100 ℃ for 6 h in air. After cooling to room temperature, T-DESs and the organic phase were layered significantly. Product **3** was obtained by collecting the organic layer, and T-DESs was regenerated to start a new catalytic cycle. As shown in **Fig. S1**, T-DESs **2** was recycled 6 times without any decrease in activity. As shown in **Fig. S2**, T-DESs **10** was recycled 6 times with slightly decrease in activity. As shown in **Fig. S3**, T-DESs **1** was recycled 14 times with slightly decrease in activity.

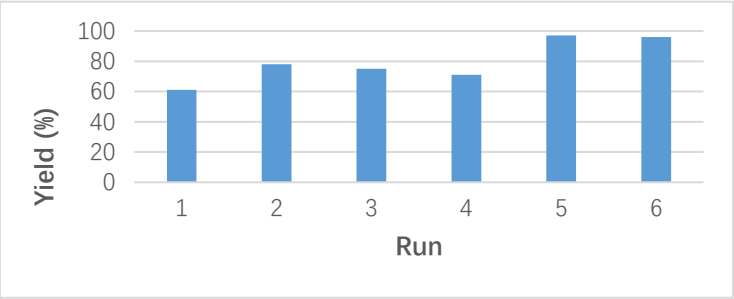


Fig. S1 Esterification yield at different catalyst recycling runs (at T-DESs **2**, 100 °C reaction temperature, 6 hours reaction time.

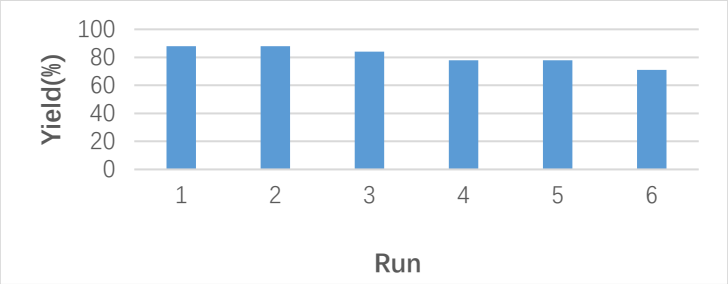


Fig. S2 Esterification yield at different catalyst recycling runs (at T-DESs **10**, 100 °C reaction temperature, 6 hours reaction time.

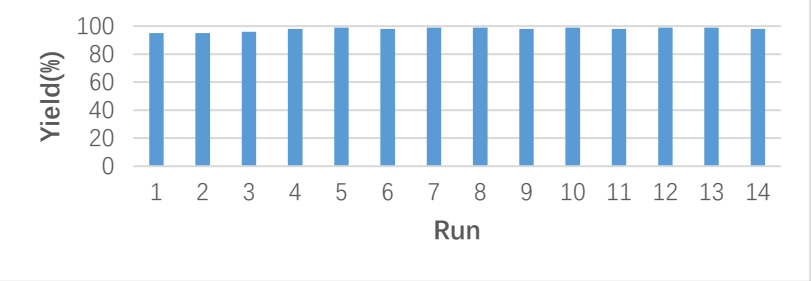


Fig. S3 Esterification yield at different catalyst recycling runs (at T-DESs **1**, 100 °C reaction temperature, 6 hours reaction time.

3.5 Key metric calculations.

According to the quantitative metrics typical of First and Second Pass evaluations in the CHEM21 Metrics Toolkit[1,2], the use of T-DESs **1** as a catalyst for esterification reaction showed superior atom economy (AE), reaction mass efficiency (RME), optimum efficiency (OE), and total process mass intensity (PMI) than traditional catalysts, demonstrating good potential industrial application value.

AE=(molecular weight of product)/(total molecular weightof reactants)×100

RME=(mass of isolated product)/(total mass of reactants)×100

OE=(RME)/(AE)×100

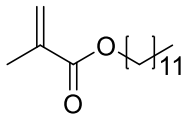
PMI=(total mass in a process or process step)/(mass of product)

Table S4 **The calculations in use of CHEM21 Metrics Toolkit[a]**

Entry	Catalyst	AE	PME	OE	PMI
1	H_2SO_4	93	81	87	1.56
2	acidic resin	94	88	94	1.26
3	heteropoly acid	91	41	45	2.50
4	lonic liquid	94	44	47	2.44
5	metal organic framework material	89	42	47	2.32
6	T-DESs **1**	93	91	98	1.07

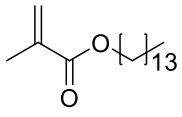
[a]The result is retained as an integer, PMI retains two decimal places.

4. Characterization of products



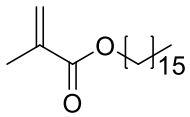
3a

Lauryl methacrylate ester (3a)[3]: Colorless liquid; **^{1}H NMR** (400 MHz, Chloroform-d) δ 6.05 (s, 1H), 5.48 (s, 1H), 4.09 (t, J = 6.7 Hz, 2H), 1.89 (s, 3H), 1.68-1.61 (m, 2H), 1.35-1.24 (m, 18H), 0.83 (t, J = 6.7 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 167.4, 136.6, 125.0, 64.8, 32.0, 29.7, 29.6, 29.6, 29.4, 29.3, 28.7, 26.0, 22.7, 18.3, 14.1.



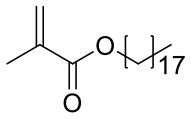
3b

Tetradecyl methacrylate ester (3b): Colorless liquid; **^{1}H NMR** (400 MHz, Chloroform-d): δ 6.09 (s, 1H), 5.54 (s, 1H), 4.13 (t, J = 6.7 Hz, 2H), 1.94 (s, 3H), 1.72-1.62 (m, 2H), 1.38-1.25 (m, 22H), 0.87 (t, J = 6.7 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 167.6, 136.6, 125.1, 64.9, 31.9, 29.69, 29.68, 29.66, 29.65, 29.6, 29.5, 29.4, 29.3, 28.6, 26.0, 22.7, 18.3, 14.1; FT-IR (KBr, cm^{-1}): 2925, 1721, 1638, 1467, 1321, 1296, 1165, 722; HRMS (ESI): $[M+Na]^+$ calcd for $C_{18}H_{34}O_2Na^+$: 305.2457; found: 305.2451.



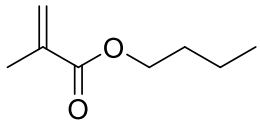
3c

Hexadecyl methacrylate ester (3c): Colorless liquid; **^{1}H NMR** (400 MHz, Chloroform-d): δ 6.09 (s, 1H), 5.53 (s, 1H), 4.12 (t, J = 6.7 Hz, 2H), 1.93 (s, 3H), 1.71 -1.62 (m, 2H), 1.38 – 1.25 (m, 26H), 0.87 (t, J = 6.7 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 167.6, 136.6, 125.1, 64.9, 31.9, 29.69, 29.68, 29.66, 29.65, 29.6, 29.5, 29.4, 29.3, 28.6, 26.0, 22.7, 18.3, 14.1; FT-IR (KBr, cm^{-1}): 2925, 1722, 1638, 1466, 1321, 1296, 1165, 722; HRMS (ESI): $[M+Na]^+$ calcd for $C_{20}H_{38}O_2Na^+$: 333.2770; found: 333.2764.



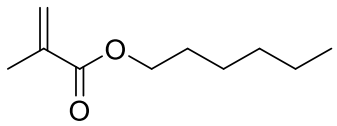
3d

Octadecyl methacrylate (3d): White solid; mp 18-20 ℃; **^{1}H NMR** (400 MHz, Chloroform-d): δ 6.09 (s, 1H), 5.54 (s, 1H), 4.13 (t, J = 6.7 Hz, 2H), 1.94 (s, 3H), 1.71 -1.62 (m, 2H), 1.36-1.25 (m, 30H), 0.87 (t, J = 6.7 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 167.6, 136.6, 125.11, 64.9, 32.0, 29.8, 29.68, 29.66, 29.6, 29.5, 29.4, 29.3, 28.6, 26.0, 22.7, 18.3, 14.1; FT-IR (KBr, cm^{-1}): 2926, 1718, 1637, 1458, 1319, 1295, 1161, 722; HRMS (ESI): $[M+Na]^+$ calcd for $C_{22}H_{42}O_2Na^+$: 361.3083; found: 361.3077.



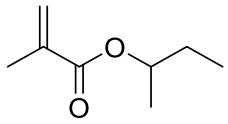
3e

N-butyl methacrylate (3e)[4]: Colorless liquid; **^{1}H NMR** (400 MHz, Chloroform-d): δ 6.08 (s, 1H), 5.52 (s, 1H), 4.13 (t, J = 6.6 Hz, 2H), 1.92 (s, 3H), 1.60-1.67 (m, 2H), 1.45-1.34 (m, 2H), 0.93 (t, J = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 167.5, 136.6, 125.0, 64.5, 30.7, 19.2, 18.2, 13.7.



3f

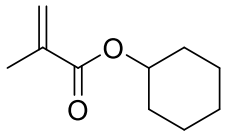
N-hexyl methacrylate (3f)[5]: Colorless liquid; **^{1}H NMR** (400 MHz, Chloroform-d): δ 6.01 (s, 1H), 5.47-5.42 (m, 1H), 4.05 (t, J = 6.7 Hz, 2H), 1.85 (s, 3H), 1.59 (q, J = 7.0 Hz, 2H), 1.33-1.21 (m, 6H), 0.81 (t, J = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 166.3, 135.6, 123.9, 63.7, 30.5, 27.7, 24.7, 21.6, 17.3, 12.9.



3g

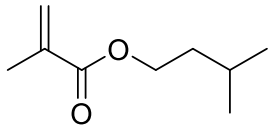
Sec-butyl methacrylate (3g): Colorless liquid; **^{1}H NMR** (400 MHz, Chloroform-d): δ 6.08 (s, 1H), 5.52 (s, 1H), 4.94-4.86 (m, 1H), 1.94 (s, 3H), 1.69-1.54 (m, 2H), 1.24 (d, J = 6.3 Hz, 3H), 0.92 (t, J = 7.5 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 167.1,

136.9, 124.8, 72.4, 28.8, 19.4, 18.3, 9.6; FT-IR (KBr, cm^{-1}): 2932, 1698, 1636, 1456, 1398, 1299, 1204; HRMS (ESI): $[M+Na]^+$ calcd for $C_{13}H_{34}O_2Na^+$: 165.0892; found: 165.0886.



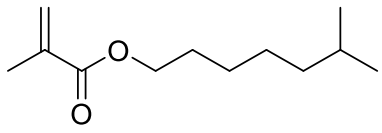
3h

Cyclohexyl methacrylate (3h)[5]: Colorless liquid; **^{1}H NMR** (400 MHz, Chloroform-d): δ 6.09 (s, 1H), 5.53 (s, 1H), 4.87-4.81 (m, 1H), 1.94 (s, 3H), 1.89-1.82 (m, 2H), 1.76-1.70 (m, 2H), 1.56-1.26 (m, 6H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 166.8, 137.0, 124.8, 72.6, 31.5, 25.5, 23.6, 18.3.



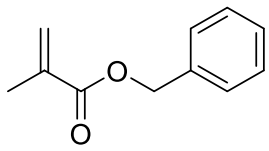
3i

Isoamyl methacrylate (3i): Colorless liquid; **^{1}H NMR** (400 MHz, Chloroform-d): δ 6.09 – 6.04 (m, 1H), 5.54 – 5.48 (m, 1H), 4.14 (t, J = 6.9 Hz, 2H), 1.91 (s, 3H), 1.68 (m, 1H), 1.54 (q, J = 7.0 Hz, 2H), 0.94 – 0.88 (m, 6H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 167.4, 136.5, 125.0, 63.2, 37.3, 25.1, 22.4, 18.2; FT-IR (KBr, cm^{-1}): 2931, 1719, 1637, 1457, 1404, 1297, 1161; HRMS (ESI): $[M+Na]^+$ calcd for $C_{13}H_{34}O_2Na^+$: 179.1048; found: 179.1045.



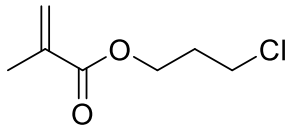
3j

6-Methyl-1-heptanol methacrylate (3j): Colorless liquid; **^{1}H NMR** (400 MHz, Chloroform-d): δ 6.01 (s, 1H), 5.44 (s, 1H), 4.02-3.93 (t, J = 5.7 Hz, 2H), 1.85 (s, 3H), 1.57 – 1.51 (m, 1H), 1.34-1.18 (m, 8H), 0.82 (d, J = 7.4 Hz, 6H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 167.2, 136.5, 124.8, 66.8, 38.8, 30.5, 28.9, 23.9, 22.9, 18.1, 13.8, 10.9; FT-IR (KBr, cm^{-1}): 2930, 1720, 1638, 1459, 1403, 1296, 1168; HRMS (ESI): $[M+Na]^+$ calcd for $C_{12}H_{22}O_2Na^+$: 221.1518; found: 221.1512.



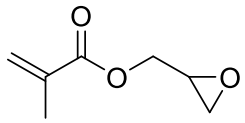
3k

Benzyl methacrylate (3k)[6]: Colorless liquid; **^{1}H NMR** (400 MHz, Chloroform-d): δ 7.39-7.32 (m, 5H), 6.18 (s, 1H), 5.60 (s, 1H), 5.21 (s, 2H), 1.99 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 167.2, 136.3, 136.2, 128.6, 128.1, 128.0, 125.8, 66.4, 18.4.



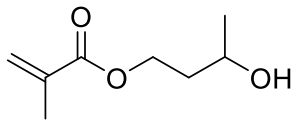
3l

3-chloro-1-propanol methacrylate (3l)[7]: Colorless liquid; **^{1}H NMR** (400 MHz, Chloroform-d): δ 6.14 (s, 1H), 5.60 (s, 1H), 4.32 (t, J = 6.0 Hz, 2H), 3.66 (t, J = 6.4 Hz, 2H), 2.17 (t, J = 6.3 Hz, 2H), 1.97 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 167.2, 136.2, 125.7, 61.4 41.3, 31.7, 18.3.



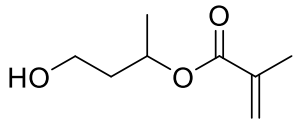
3m

Glycidyl methacrylate (3m)[8]: Colorless liquid; **^{1}H NMR** (400 MHz, Chloroform-d): δ 6.16 (s, 1H), 5.61 (s, 1H), 4.48 (d, J = 12.5 Hz, 1H), 4.00 (d, J = 12.3 Hz, 1H), 3.28 - 3.23 (m, 1H), 2.85 (d, J = 4.6 Hz, 1H), 2.67 (d, J = 2.6 Hz, 1H), 1.96 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 167.0, 135.8, 126.2, 65.1, 49.4, 44.6, 18.3.



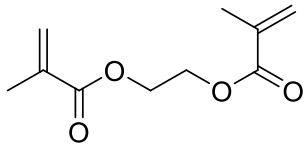
3n

3-hydroxybutyl methacrylate (3n)[9]: Colorless liquid; **^{1}H NMR** (400 MHz, Chloroform-d): δ 6.11 (s, 1H), 5.63-5.53 (m, 1H), 4.47-4.36 (m, 1H), 4.26-4.16 (m, 1H), 3.97 -3.83 (m, 1H), 1.95(s, 3H),1.85-1.74 (m, 2H), 1.25 (d, J = 6.3 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 167.8, 136.2, 125.7, 64.9, 61.9, 38.1, 23.5, 18.3.



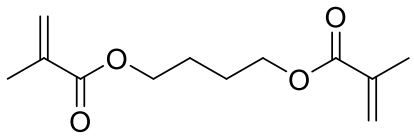
3n'

(methyl)propenoic acid 1-methyl-3-hydroxypropyl ester (3n')[9]: Colorless liquid; **^{1}H NMR** (400 MHz, Chloroform-d): δ 6.11 (s, 1H), 5.63-5.53 (m, 1H), 5.22-5.11 (m, 1H), 3.69-3.63 (m, 1H), 3.61 -3.55 (m, 1H), 1.95(s, 3H),1.85-1.72 (m, 2H), 1.32 (d, J = 6.3 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 167.8, 136.4, 125.7, 68.5, 58.8, 39.2, 23.5, 20.5.



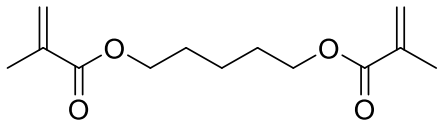
5a

Ethylene glycol dimethyl acrylate (5a)[10]: Colorless liquid; **^{1}H NMR** (400 MHz, Chloroform-d): δ 6.12 (s, 1H), 5.58 (s, 1H), 4.39 (s, 2H), 1.94 (s, 2H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 167.1, 135.9, 126.0, 62.3, 18.2.



5b

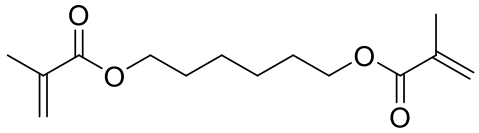
1,4-butanediol dimethyl acrylate (5b)[11]: Colorless liquid; **^{1}H NMR** (400 MHz, Chloroform-d): δ 6.08 (s, 1H), 5.54 (s, 1H), 4.17 (d, J = 5.5 Hz, 2H), 1.92 (s, 3H), 1.82-1.63 (m, 2H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 167.4, 136.3, 125.4, 64.2, 25.4, 18.3.



5c

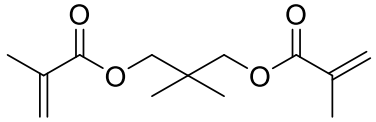
1,5-pentanediol dimethyl acrylate (5c): Colorless liquid; **^{1}H NMR** (400 MHz, Chloroform-d): δ 6.02 (s, 2H), 5.47 (s, 2H), 4.09 (t, J = 6.5 Hz, 4H), 1.82 (s, 6H), 1.69 -1.62 (m, 4H), 1.46-1.38 (m, 2H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 167.4, 136.4, 125.3, 64.4, 28.3, 22.6, 18.4; FT-IR (KBr, cm^{-1}): 2957, 1719, 1637, 1455, 1404, 1297,

1166; HRMS (ESI): $[M+Na]^+$ calcd for $C_{13}H_{34}O_2Na^+$: 263.1259; found: 263.1256.



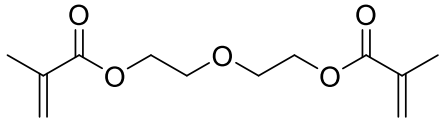
5d

1,6-hexanediol dimethyl acrylate (5d)[12]: Colorless liquid; **^{1}H NMR** (400 MHz, Chloroform-d): δ 6.01 (s, 2H), 5.49-5.43 (m, 2H), 4.06 (t, J = 6.6 Hz, 4H), 1.85 (s, 5H), 1.61 (s, 4H), 1.41-1.29 (m, 4H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 167.3, 136.4, 125.1, 64.5, 28.5, 25.6, 18.2.



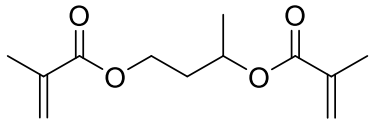
5e

Neopentyl glycol dimethyl acrylate (5e): Colorless liquid; **^{1}H NMR** (400 MHz, Chloroform-d): δ 6.05 (s, 2H), 5.51 (s, 2H), 3.93 (s, 4H), 1.89 (s, 6H), 0.98 (s, 6H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 167.0, 136.1, 125.5, 69.3, 34.9, 21.8, 18.2; FT-IR (KBr, cm^{-1}): 2931, 1716, 1636, 1457, 1398, 1299, 1168; HRMS (ESI): $[M+Na]^+$ calcd for $C_{13}H_{34}O_2Na^+$:263.1259; found: 263.1256.



5f

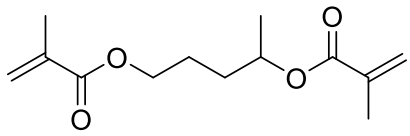
Diethylene glycol dimethacrylate (5f)[13]: Colorless liquid; **^{1}H NMR** (400 MHz, Chloroform-d): δ 6.12 (s, 2H), 5.62-5.56(m, 2H), 4.37-4.28(m, 4H), 3.82-3.74(m, 4H), 1.94(s, 6H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 167.3, 136.1, 125.8, 69.0, 63.7, 18.2.



5g

1,3-butanediol dimethacrylate (5g)[9]: Colorless liquid; **^{1}H NMR** (400 MHz,

Chloroform-d): δ 6.11-6.03 (m, 2H), 5.61-5.48(m, 2H), 5.09-4.99(m, 1H), 4.21-4.07(m, 2H), 2.00-1.89(m, 2H), 1.86(s, 6H), 1.25(d, J = 6.3 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 167.3, 166.8, 136.5, 136.2, 125.6, 125.3, 68.3, 31.1, 34.9, 20.1, 18.27, 18.25.



5h

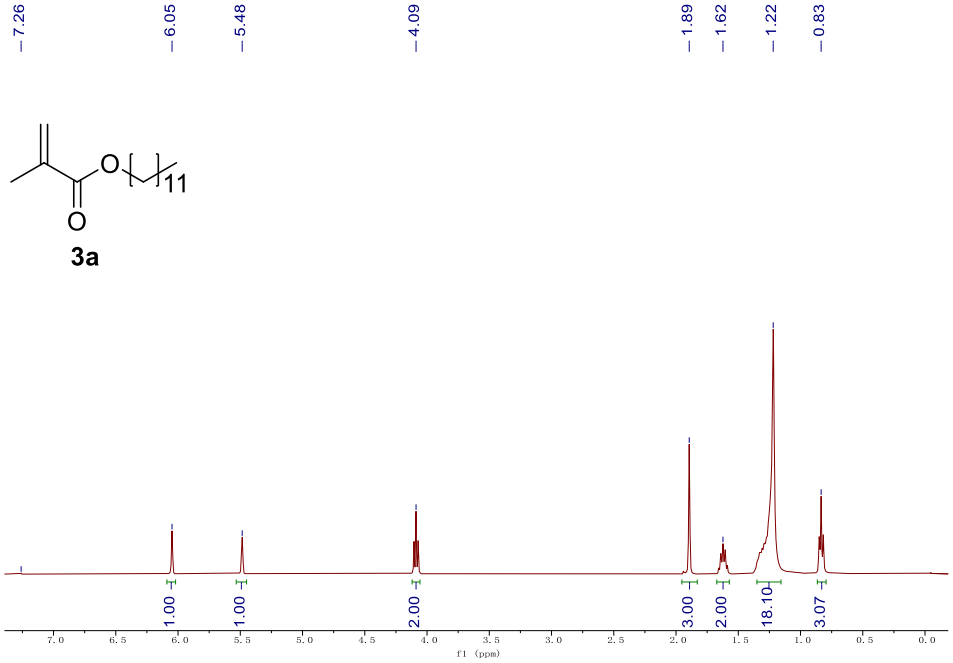
Ethylene propylene dimethacrylate (5h)[14]: Colorless liquid; **^{1}H NMR** (400 MHz, Chloroform-d): δ 6.08-5.96 (m, 2H), 5.53-5.43(m, 2H), 4.99-4.87(m, 1H), 4.13-4.05(m, 2H), 1.87(s, 6H), 1.71-1.58(m, 4H), 1.21(d, J = 6.3 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 167.4, 167.0, 136.7, 136.4, 125.3, 125.1, 70.7, 64.4, 32.4, 24.7, 19.9, 18.3.

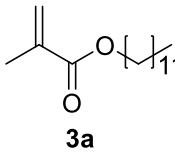
5. References

1. S. Abou-Shehada, P. Mampuys, B. U. W. Maes, J. H. Clarka and L. Summerton, *Green Chem.*, 2017, **19**, 249-258.
2. C. R. McElroy, A. Constantinou, L. C. Jones, L. Summerton and J. H. Clark, *Green Chem*., 2015, **17**, 3111-3121.
3. H. Fouilloux, W. Qiang, C. Robert, V. Placet, and C. M. Thomas, *Angew. Chem. Int. Ed.*, 2021, **60**, 19374-19382.
4. S. A. Dergunov, *ChemComm.*, 2021, **57**, 10612-10615.
5. M. Hatano, F, Yoshiro, T. Shimmura, M. Katsuhiko, S. Kamiya, M. Toshikatsu, and I. Kazuaki, *Org. Lett.*, 2011, **13** (3), 426-429.
6. W. Shen, Q. Wu, X. Gong, G. Ao and F. Liu, *Green Chem.*, 2019, **21**, 2983-2987.
7. Z. Fang, A. Ito, H. Luo, A. L. Dennis, C. J. Javier, L. Alibabaei and M. J. Thomas, *Dalton Trans.*, 2015, **44**, 8640-8648.
8. B. Guerdener, V. Ayzac, S. Norsic, P. Besognet, V. Bounor-Legaré, V. Monteil, V. Dufaud, J. Raynaud and Y. Chalamet, *Green Chem.*, 2023, **25**, 6355-6364.
9. Current Patent Assignee: NAGOYA UNIVERSITY - JP2019/26618, 2019, A
10. Y. He, C. Wang, P. Zou, R. Lin, E. Hu and H. Xin, *Angew. Chem. Int. Ed.*, 2023, **62**, e202308309.
11. S.A. Dergunov and E. Pinkhassik, *Angew. Chem.*, 2020, **132**, 18563-18569.
12. U. Guenther, K. Albertand M. Grossa, *J. Magn. Reson.*, 1992, **98**, 593-598.
13. S. A. Chesnokov, M. Y. Zakharina, A. S. Shaplov, E. I. Lozinskaya, I. A. Malyshkina, G. A. Abakumov, F. Vidal and Y. S. Vygodskii, *J. Polym Sci.*, 2010, **48**, 2388-2409.
14. P. Voigt, N. Kiriy, K. Jähnichen and B. Voit, *ACS Sustainable Chem. Eng.*, 2024, **12**, 1984-1996.

6. NMR Spectra

^{1}H NMR, 400 MHz, $CDCl_3$



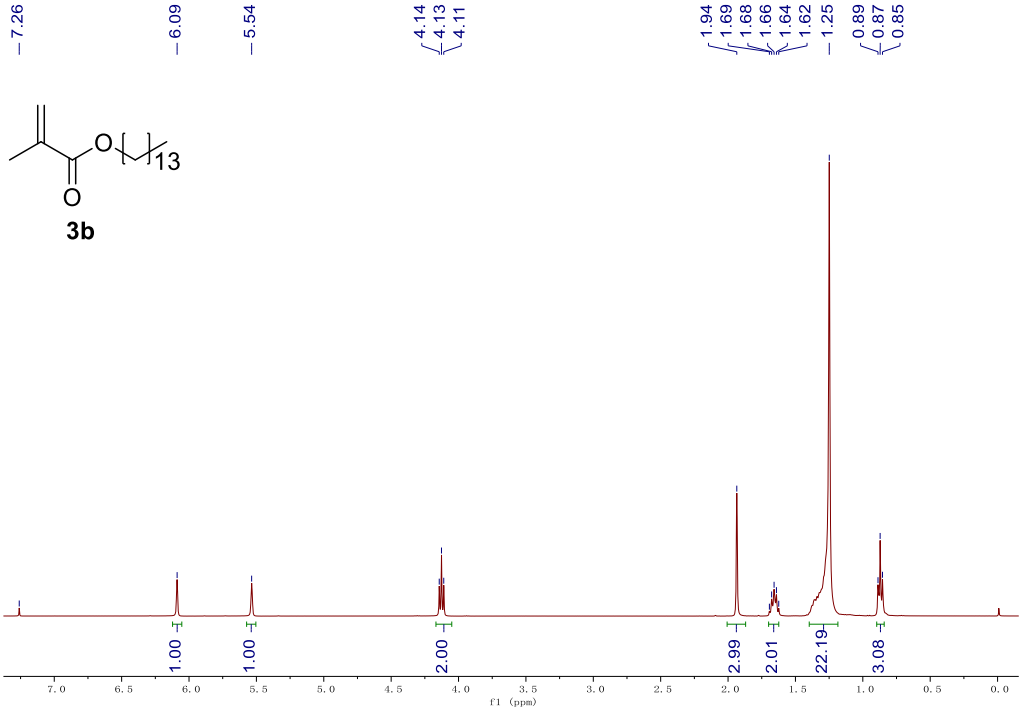


3a

^{13}C NMR, 101 MHz, $CDCl_3$

3a

^{1}H NMR, 400 MHz, $CDCl_3$



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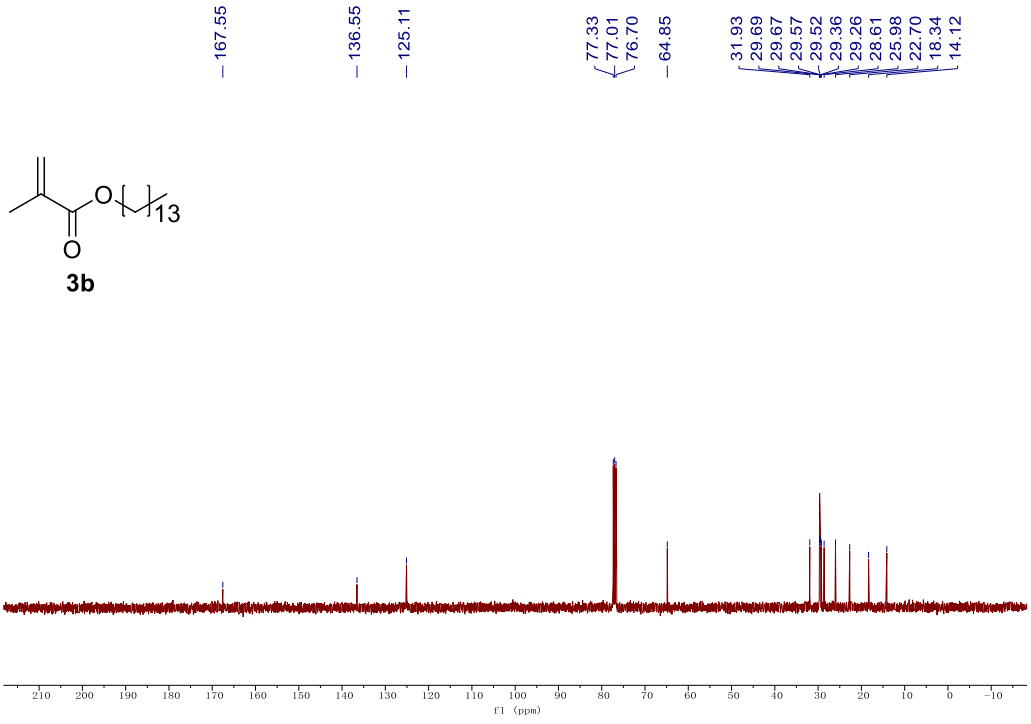

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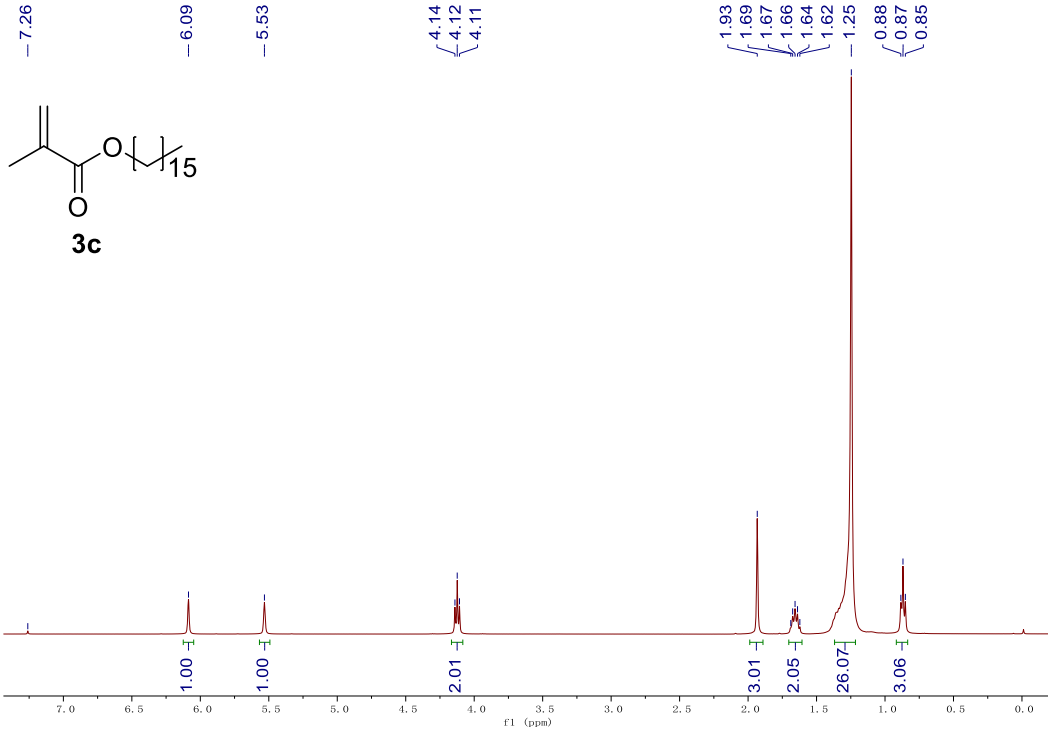

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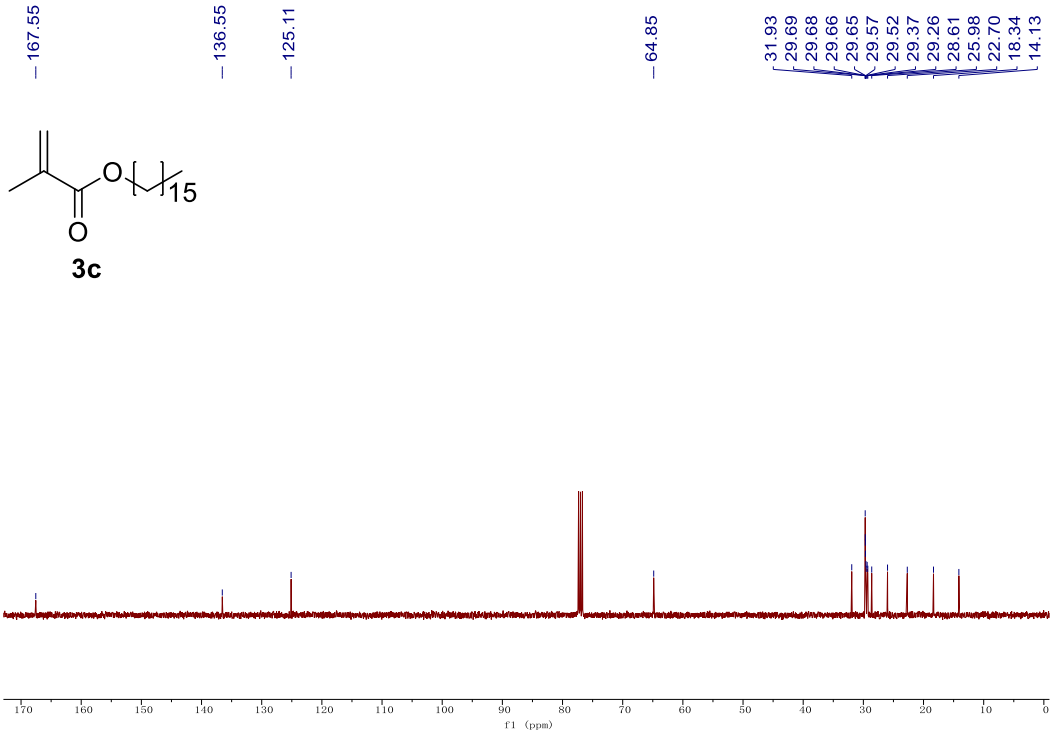

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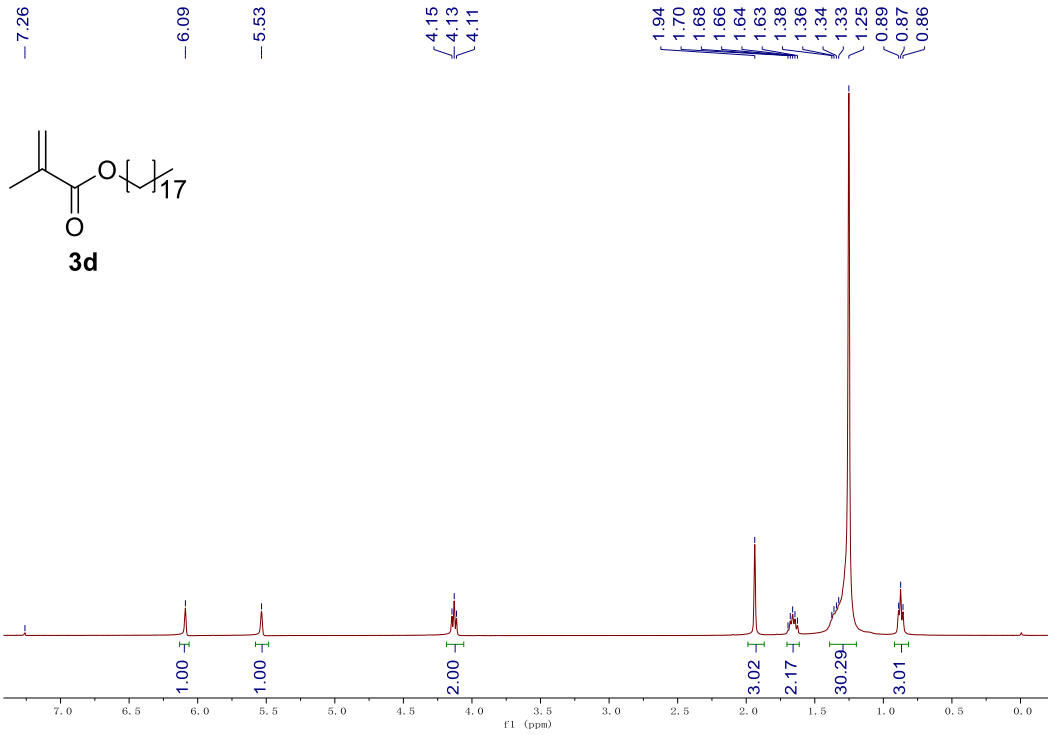

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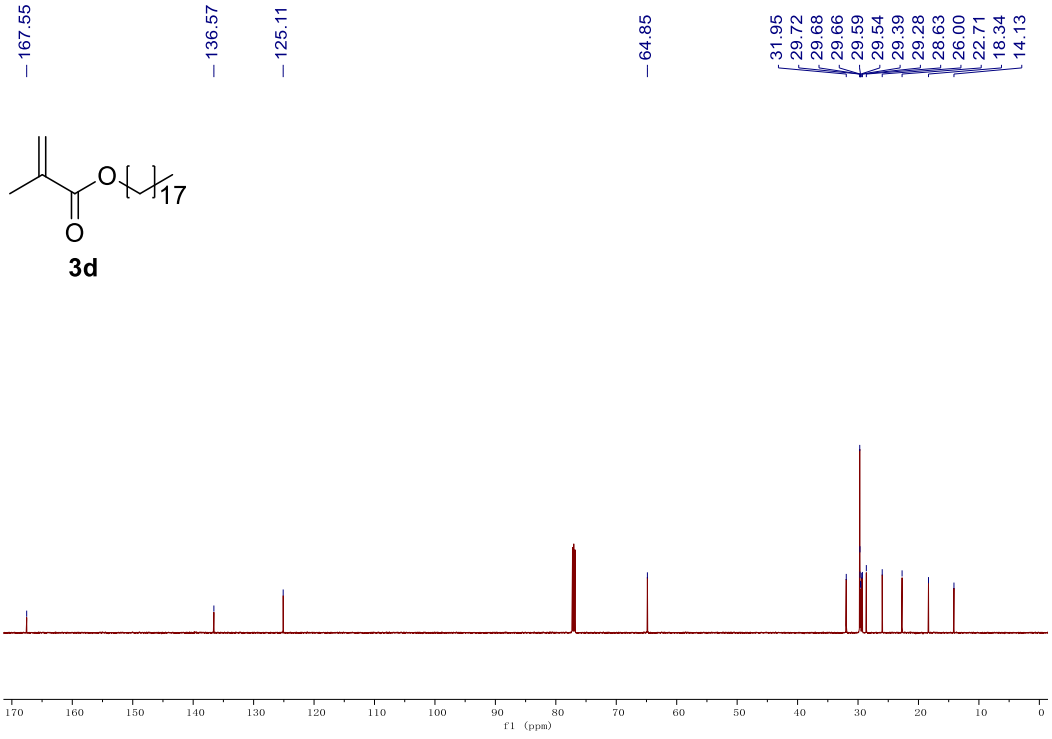

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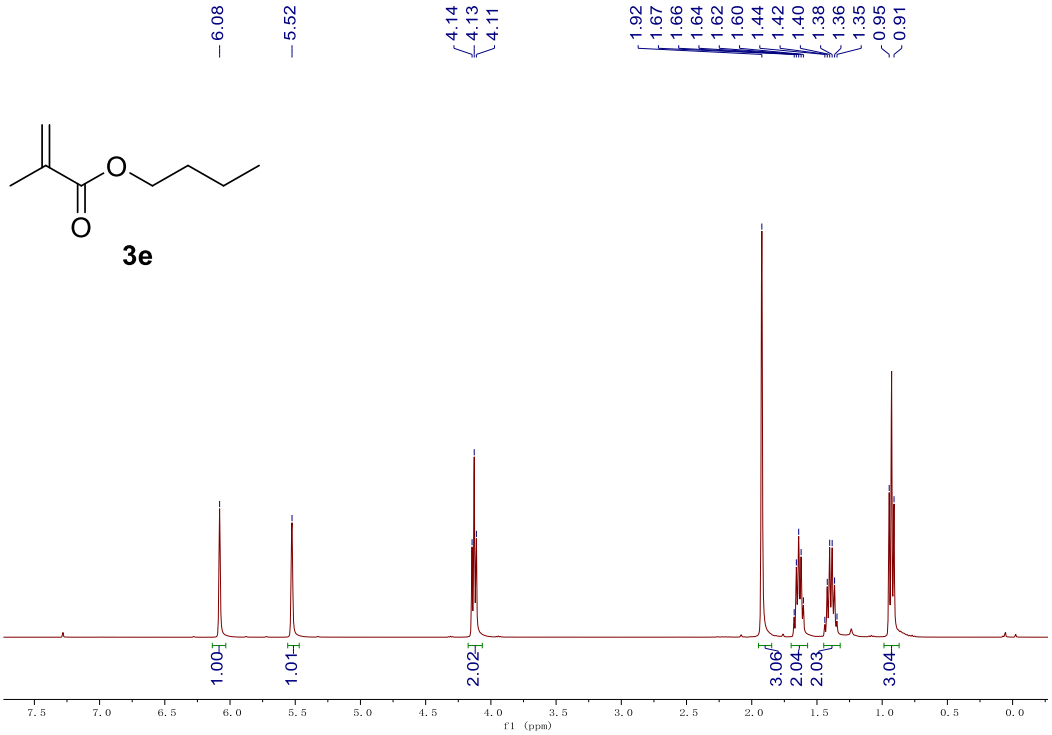

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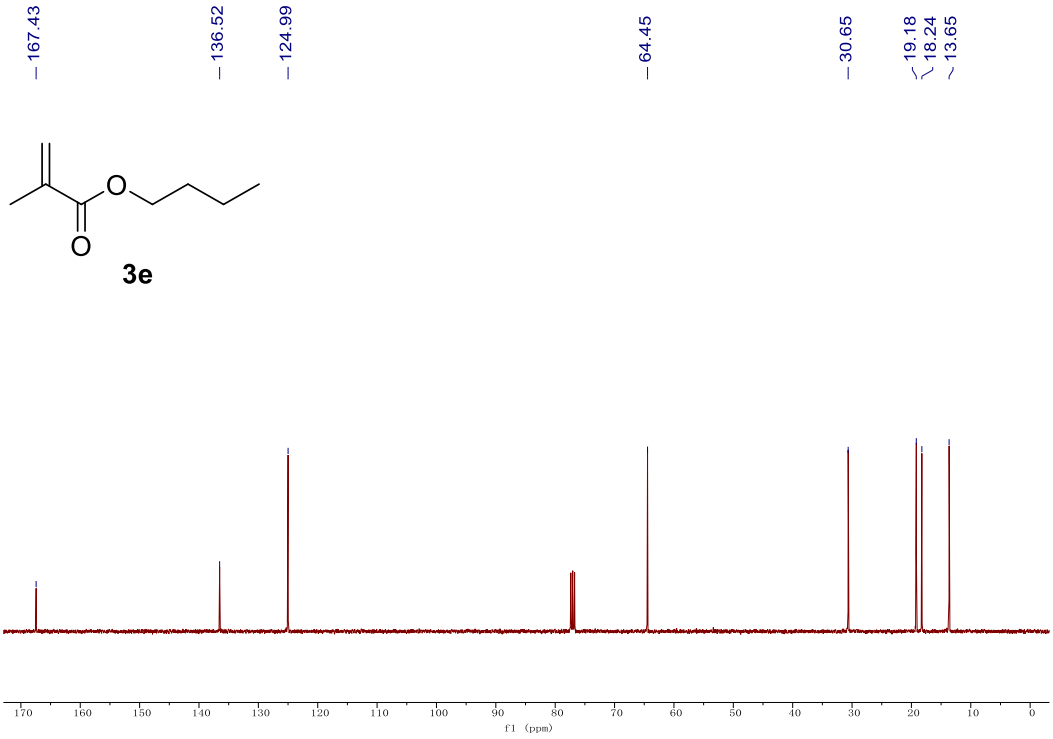

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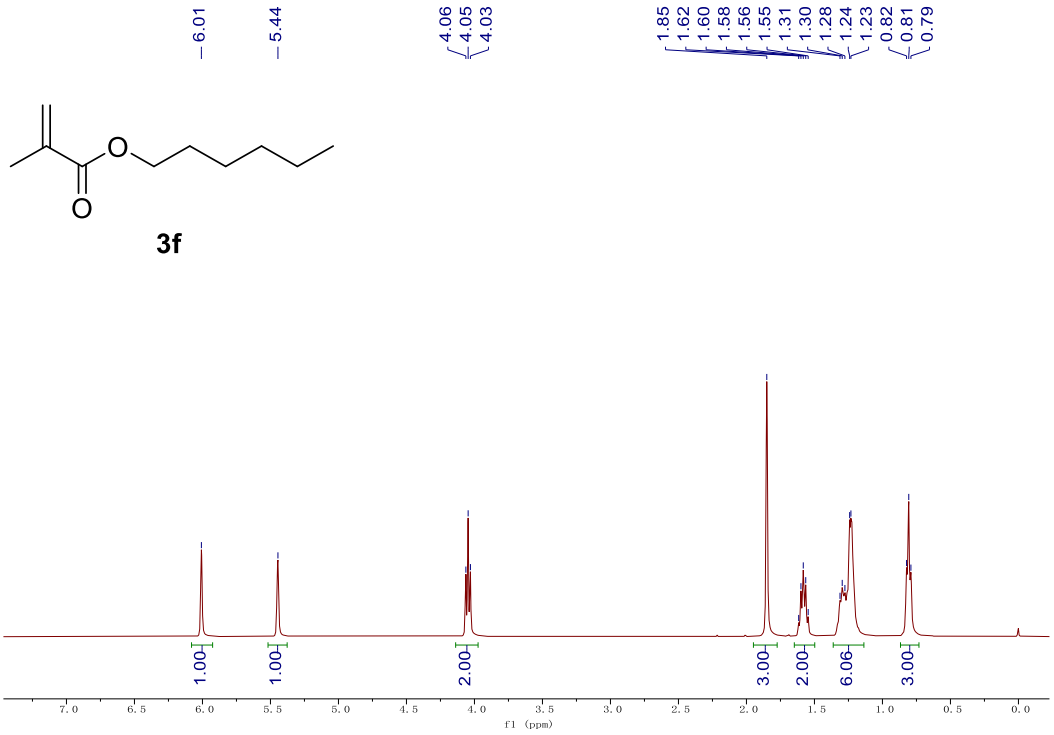

3f

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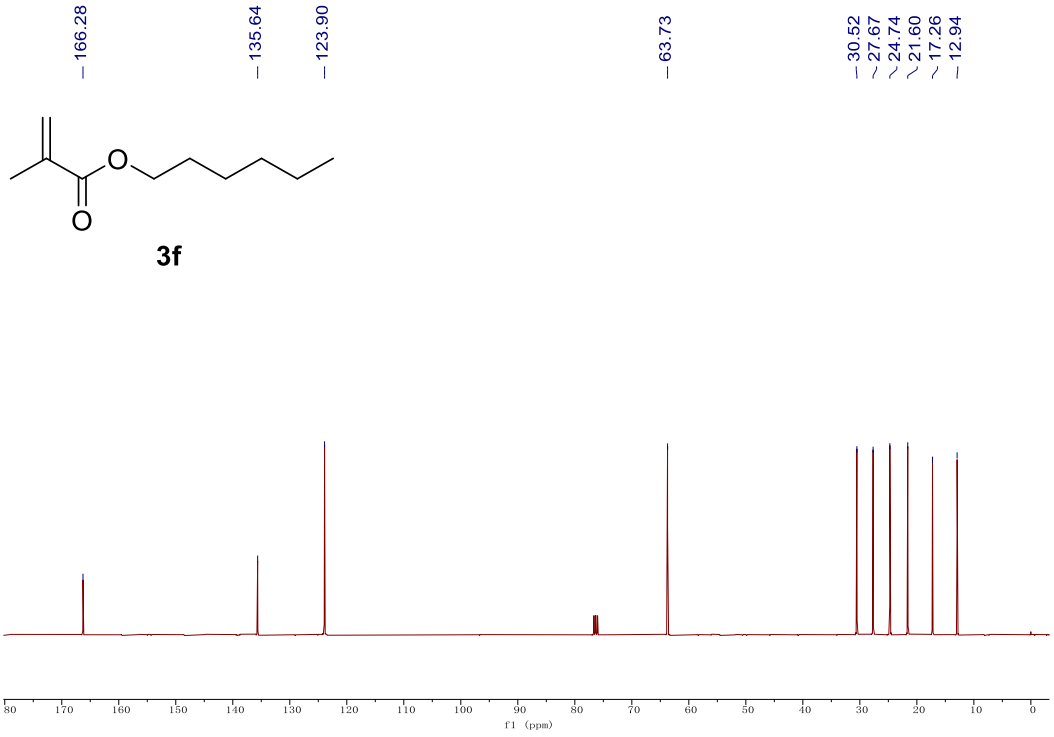

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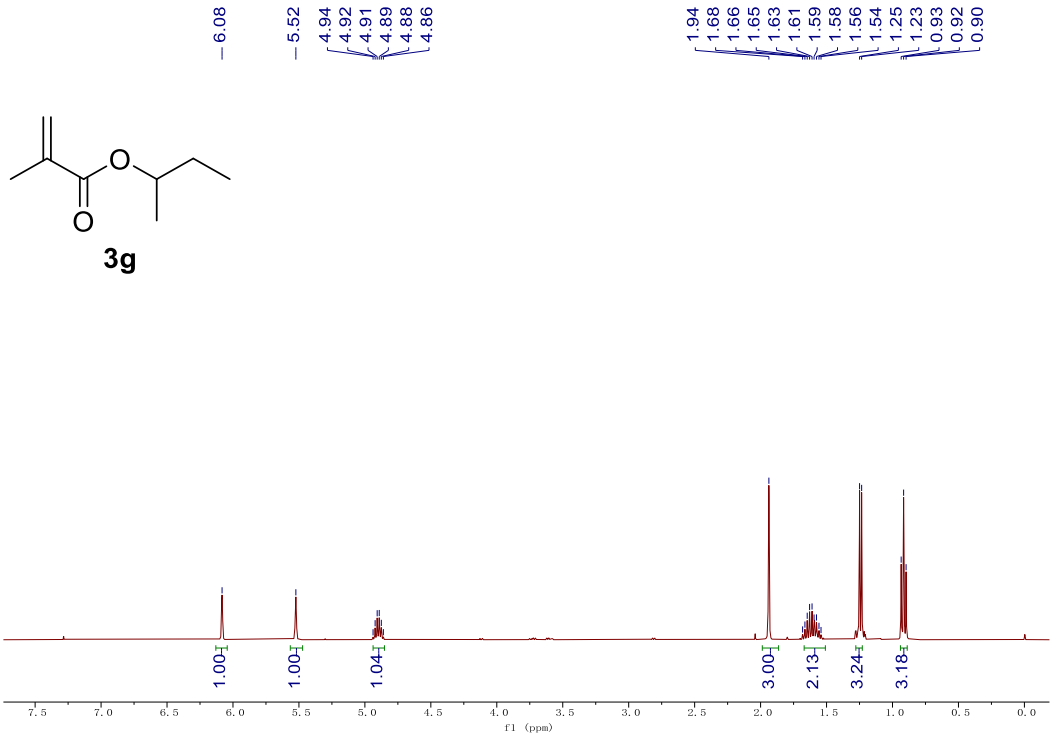

3g

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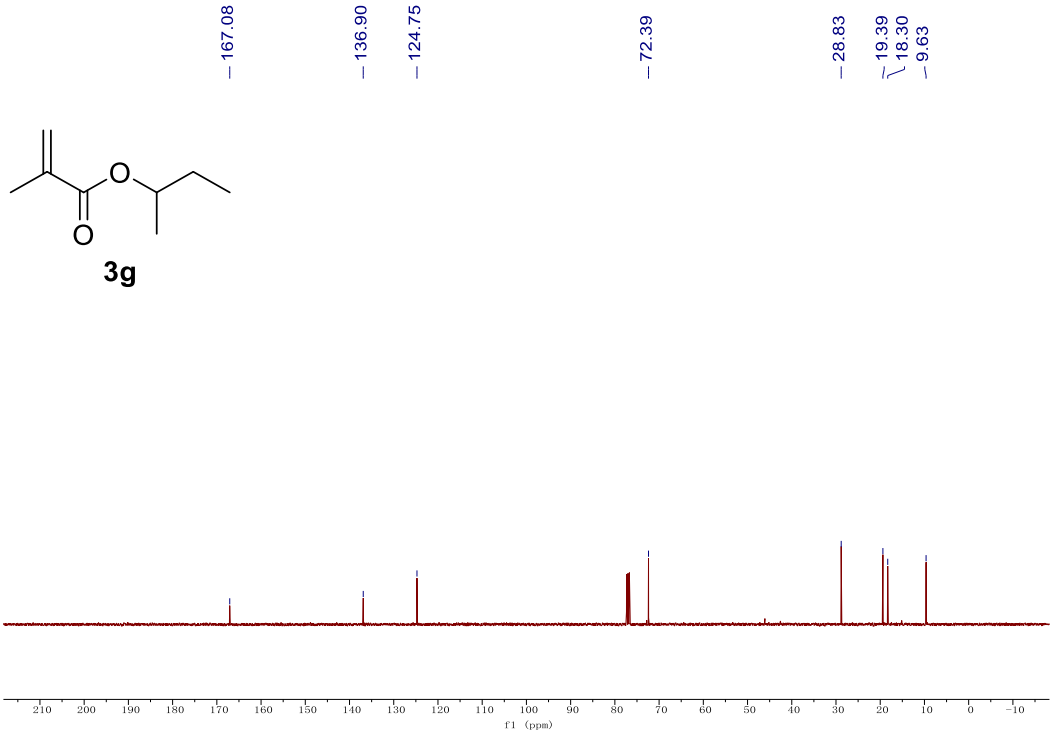

3g

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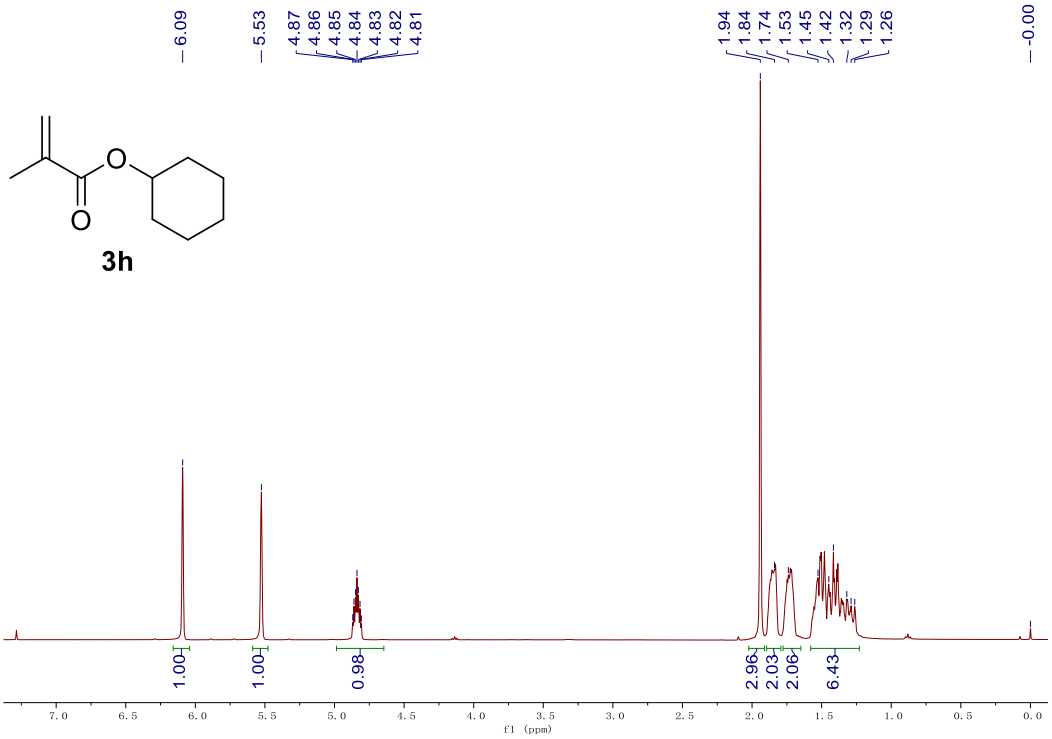

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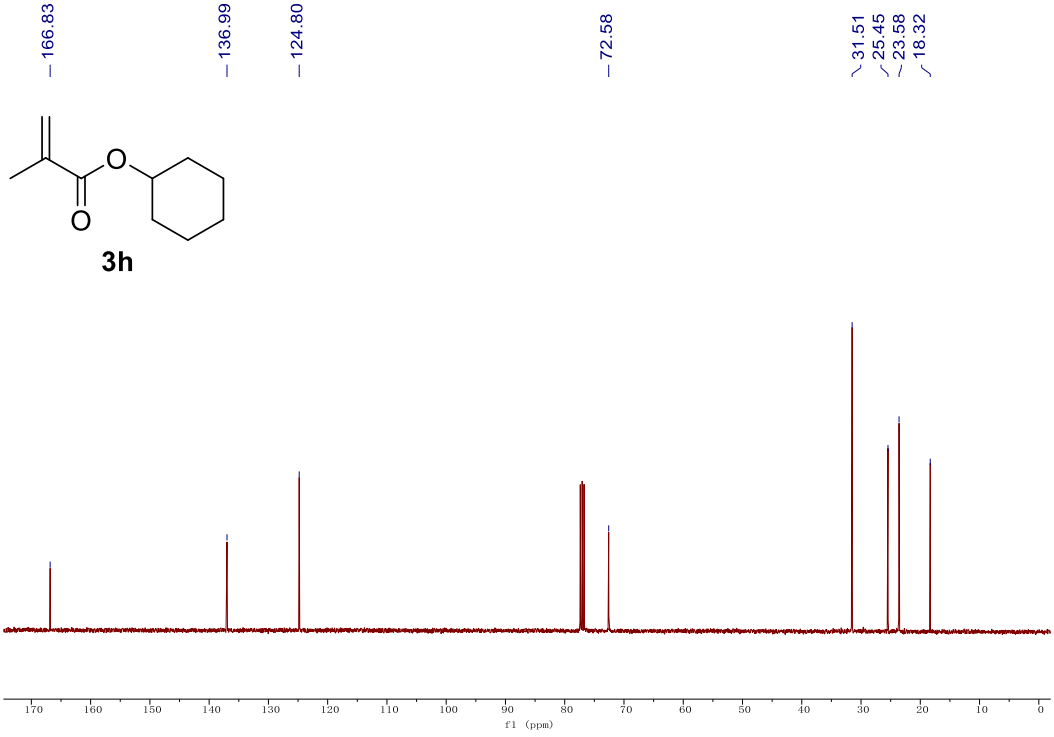

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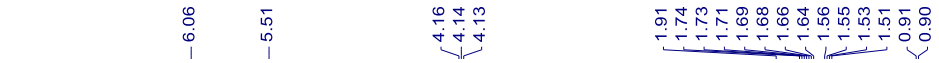

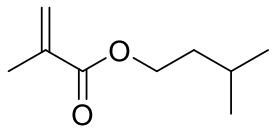

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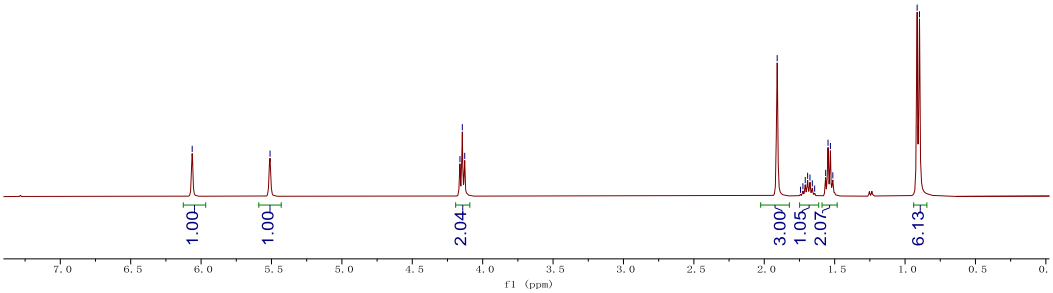

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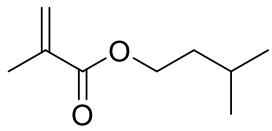

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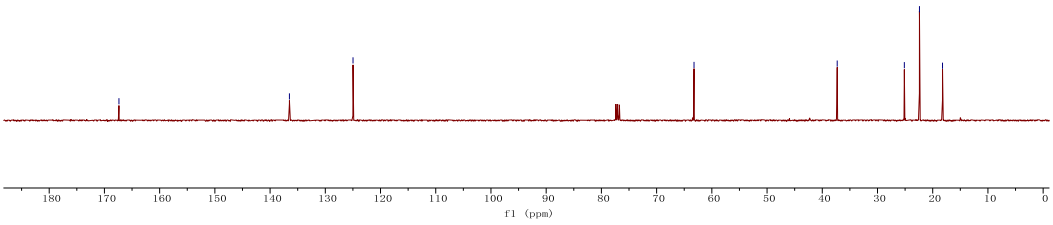

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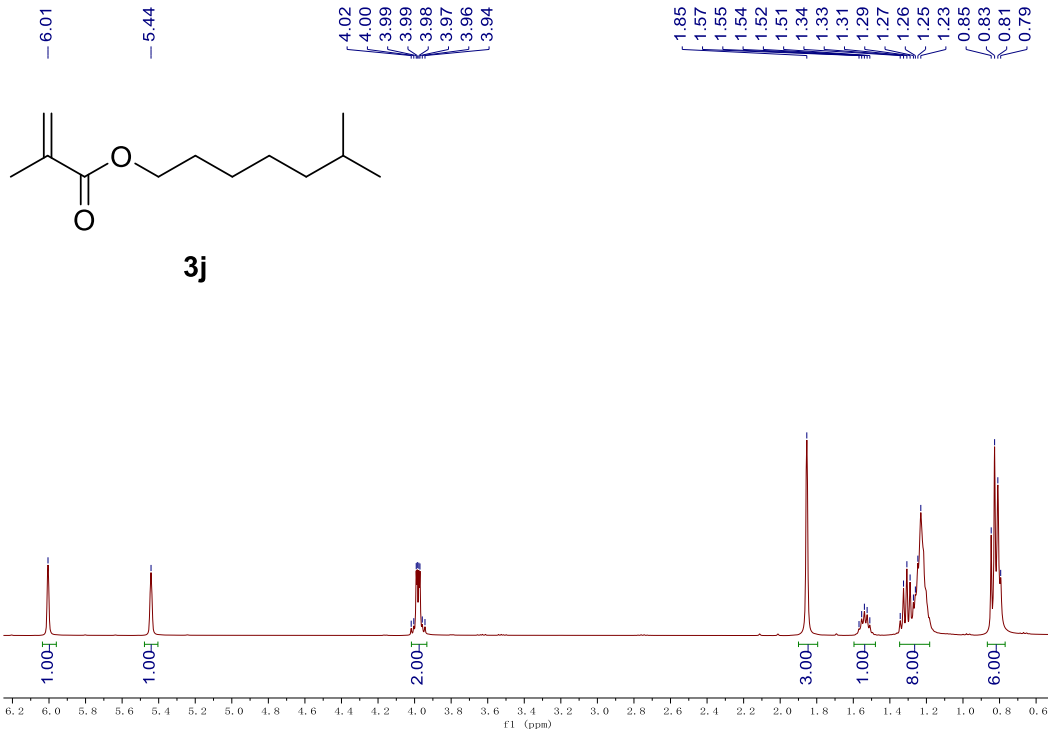

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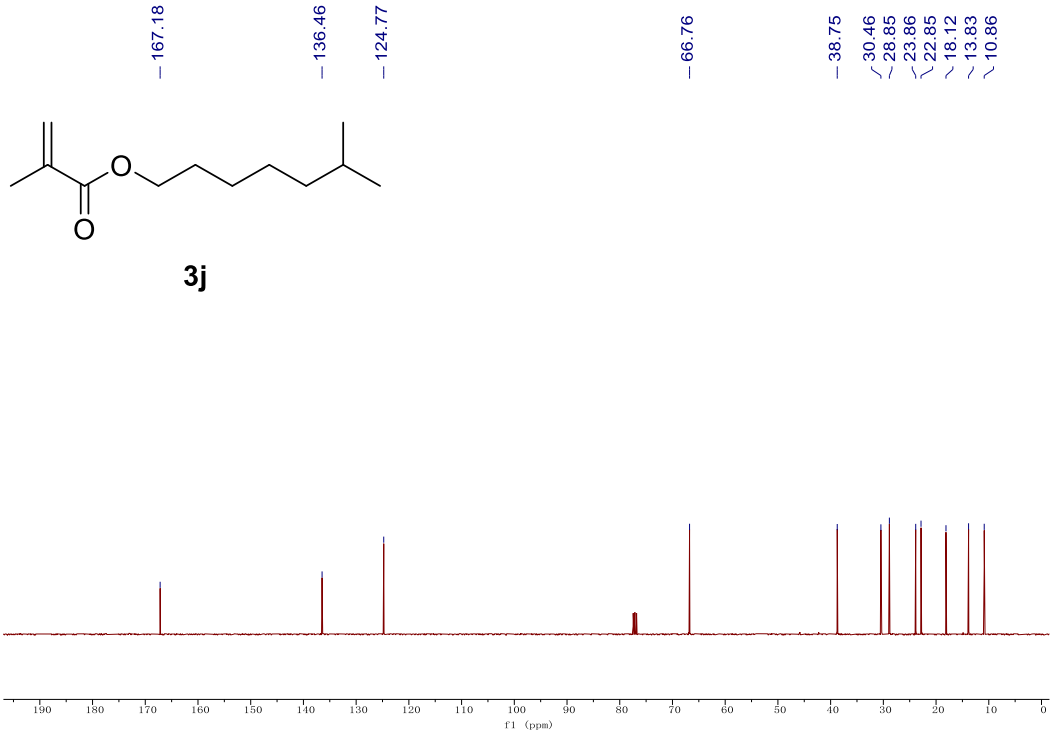
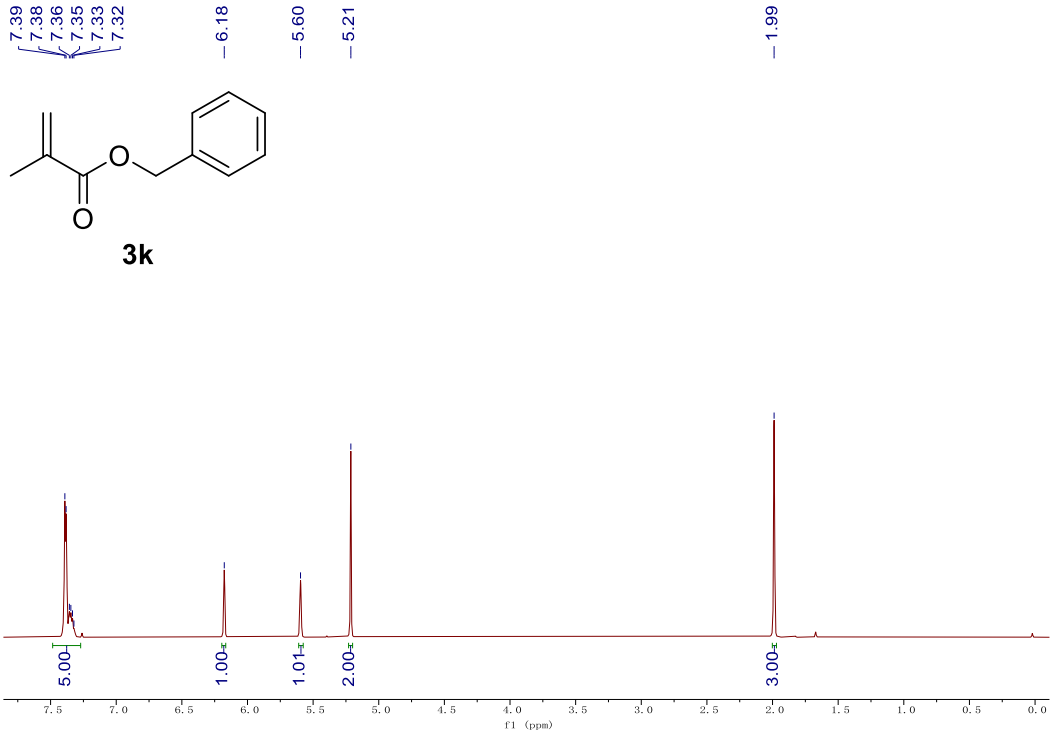
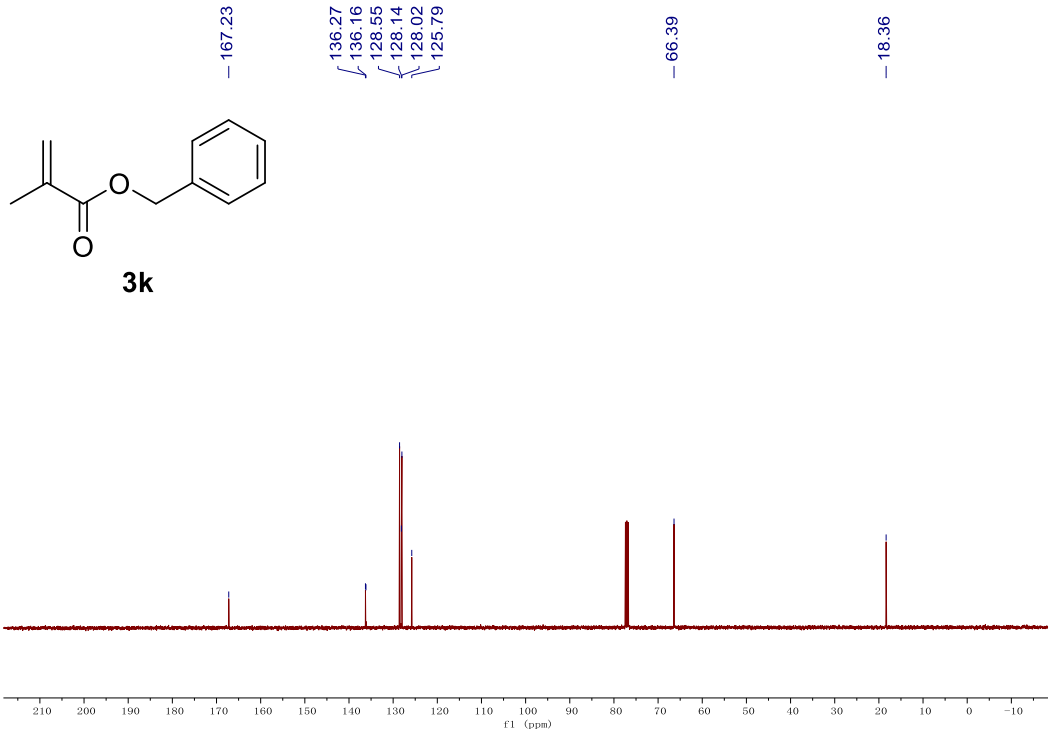


3j

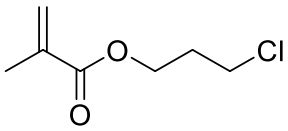
^{1}H NMR, 400 MHz, $CDCl_3$



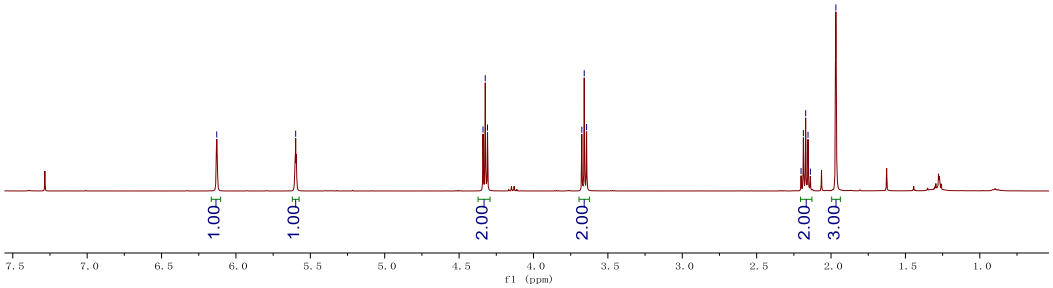
^{13}C NMR, 101 MHz, $CDCl_3$



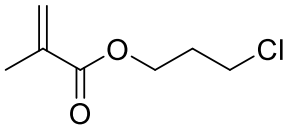
^{1}H NMR, 400 MHz, $CDCl_3$



3l



^{13}C NMR, 101 MHz, $CDCl_3$



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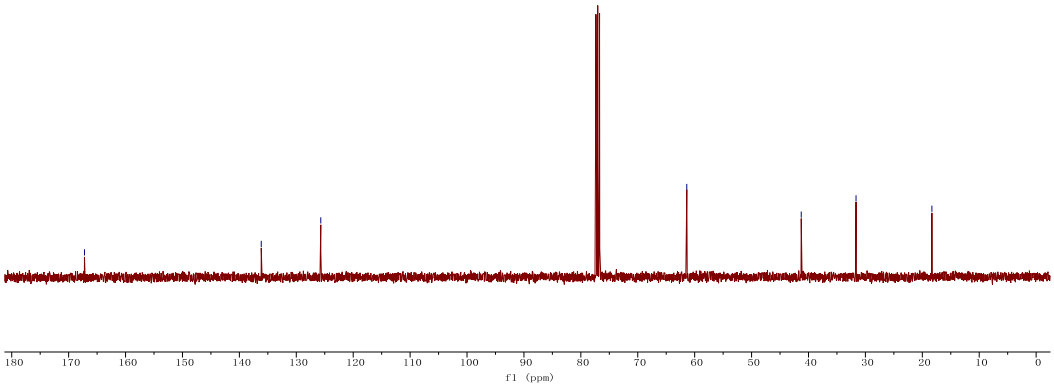
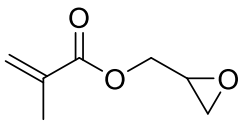
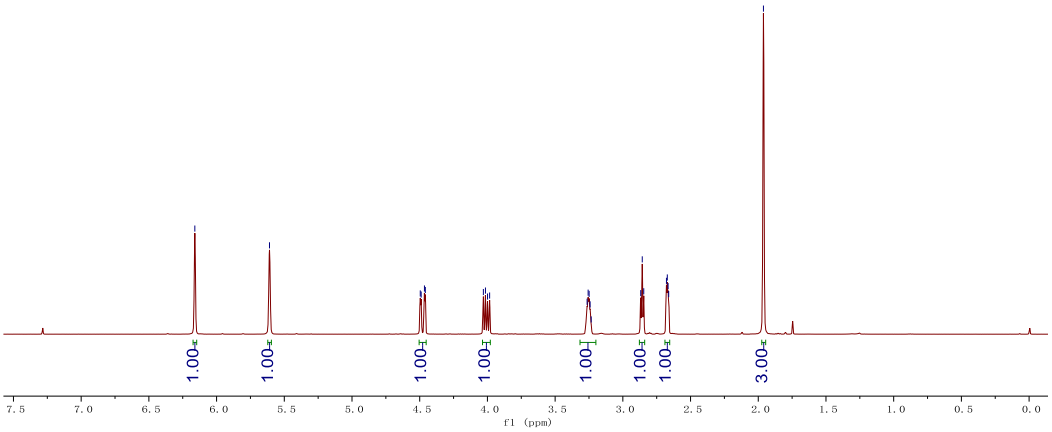


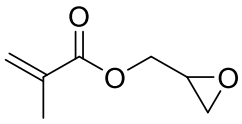
^{1}H NMR, 400 MHz, $CDCl_3$



3m



^{13}C NMR, 101 MHz, $CDCl_3$



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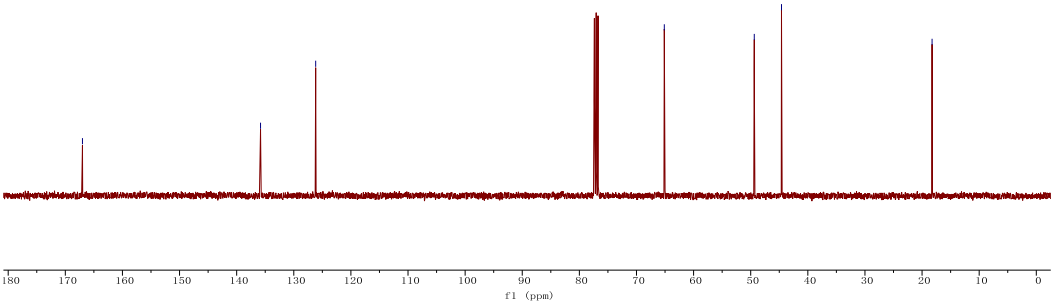
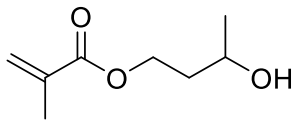
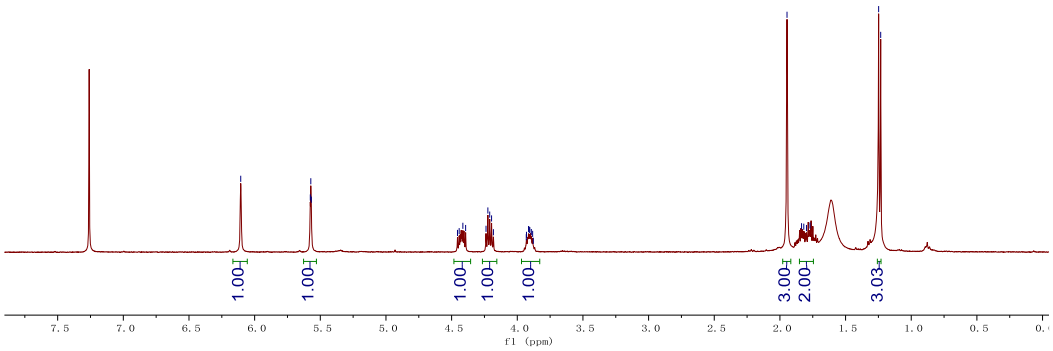


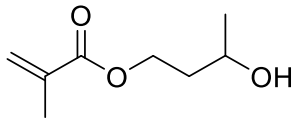
^{1}H NMR, 400 MHz, $CDCl_3$



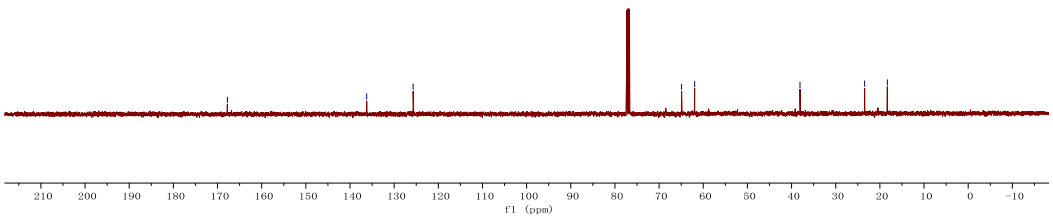
3n



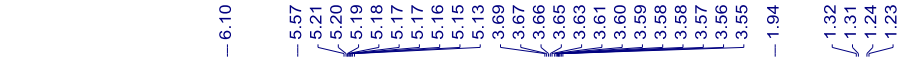
^{13}C NMR, 101 MHz, $CDCl_3$

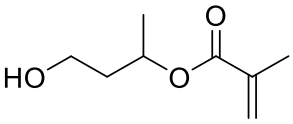


3n

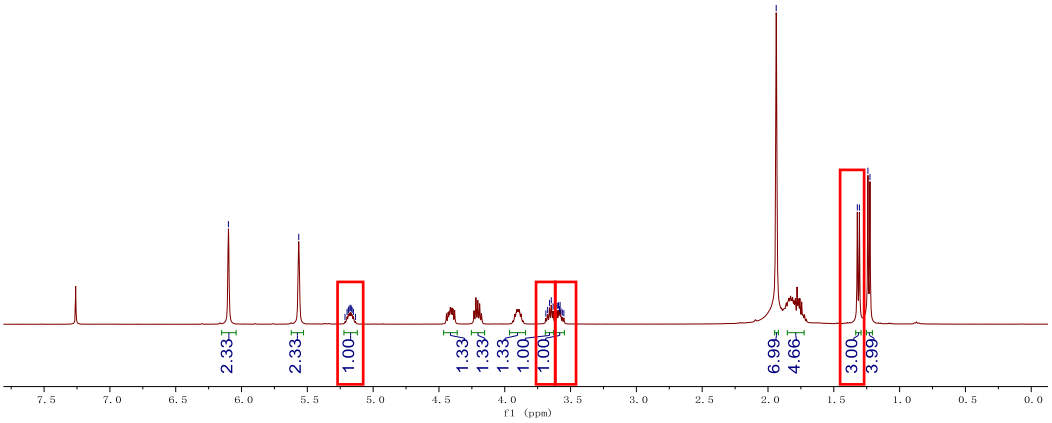


^{1}H NMR, 400 MHz, $CDCl_3$

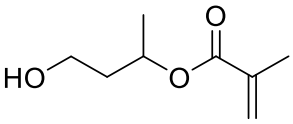




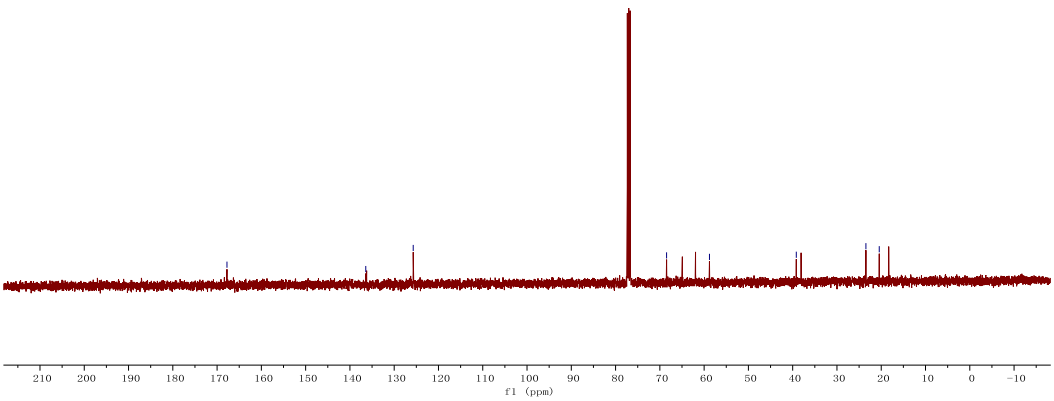
3n'(mixed with 3n)



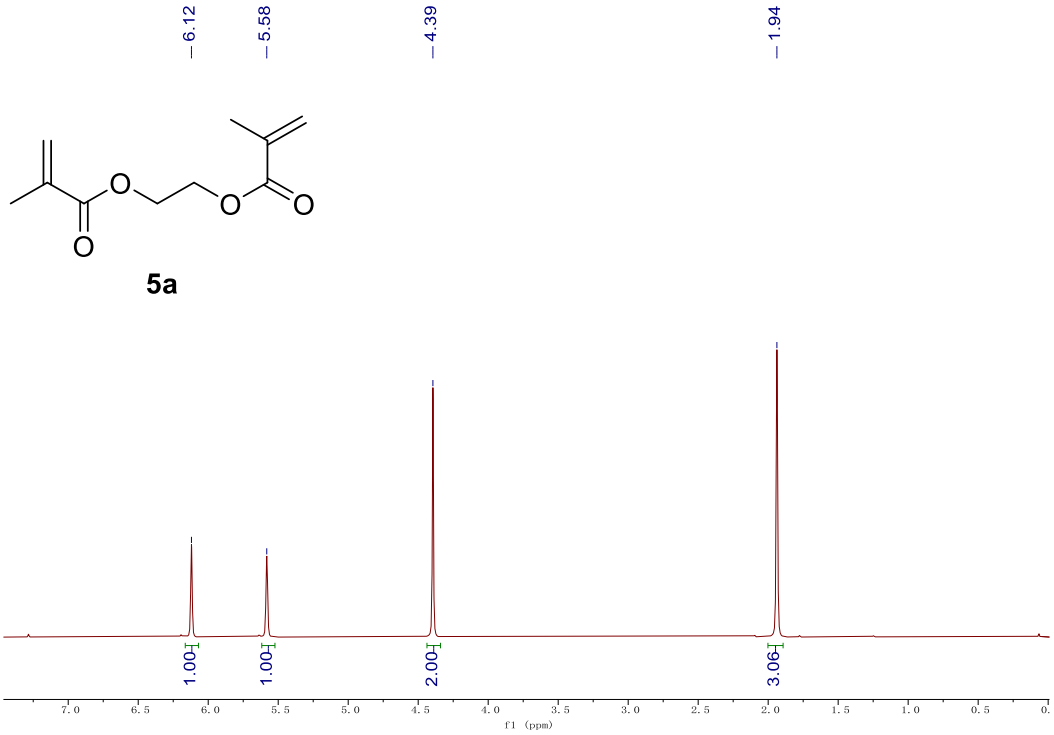
^{13}C NMR, 101 MHz, $CDCl_3$



3n'(mixed with 3n)

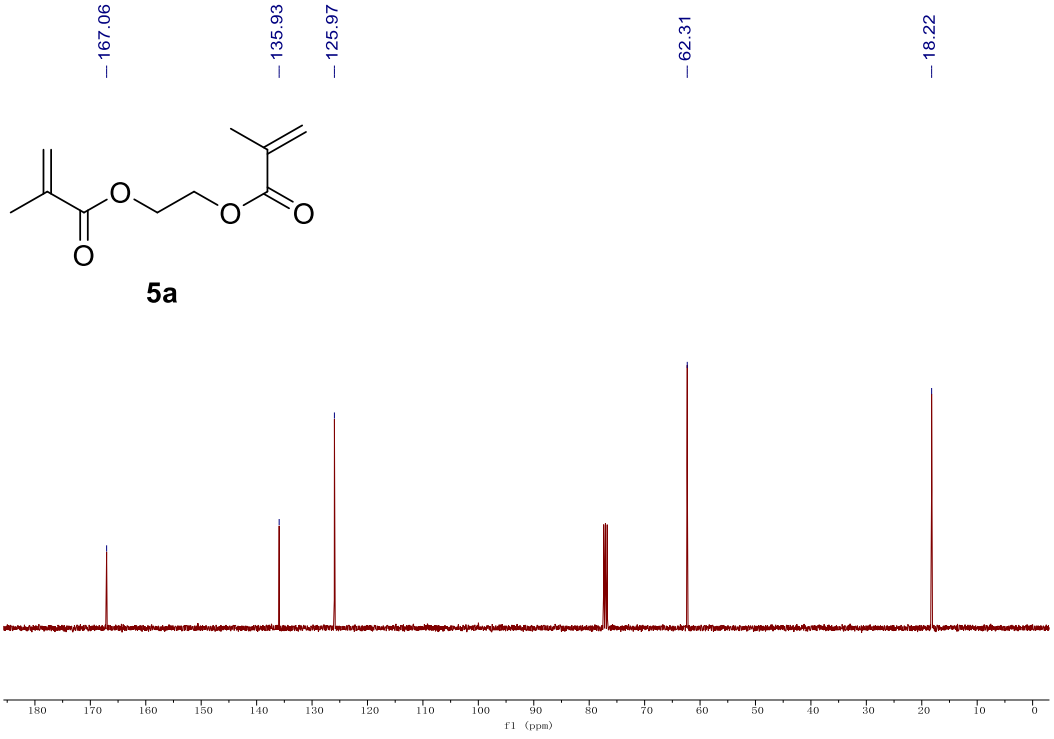


^{1}H NMR, 400 MHz, $CDCl_3$



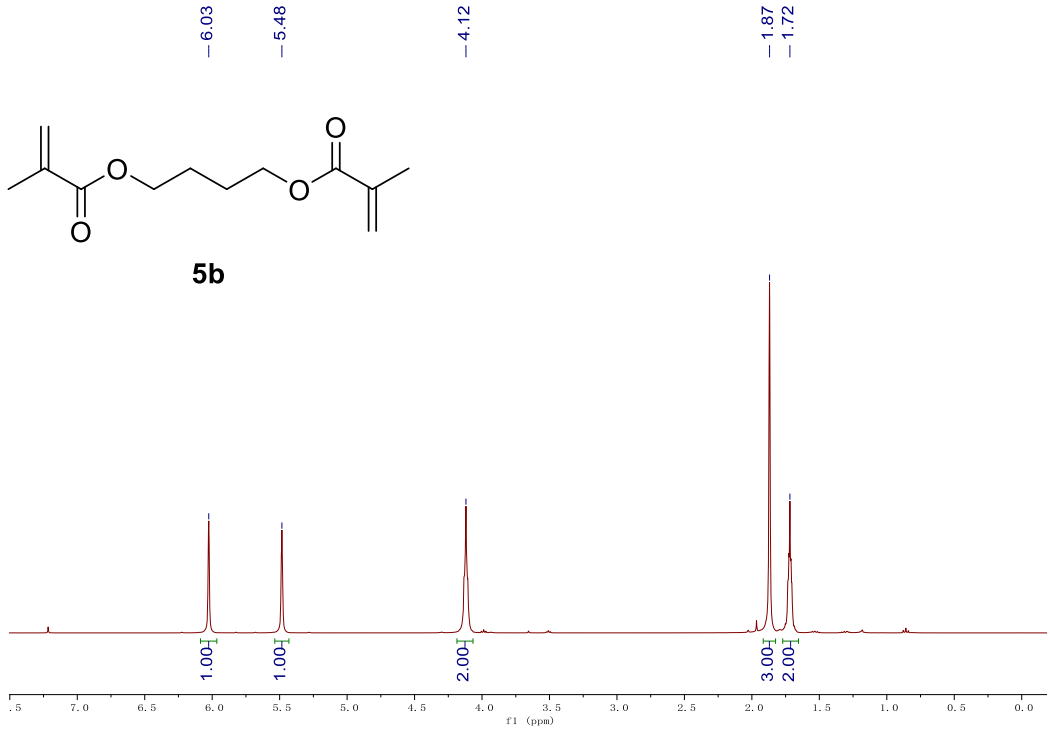
5a

^{13}C NMR, 101 MHz, $CDCl_3$



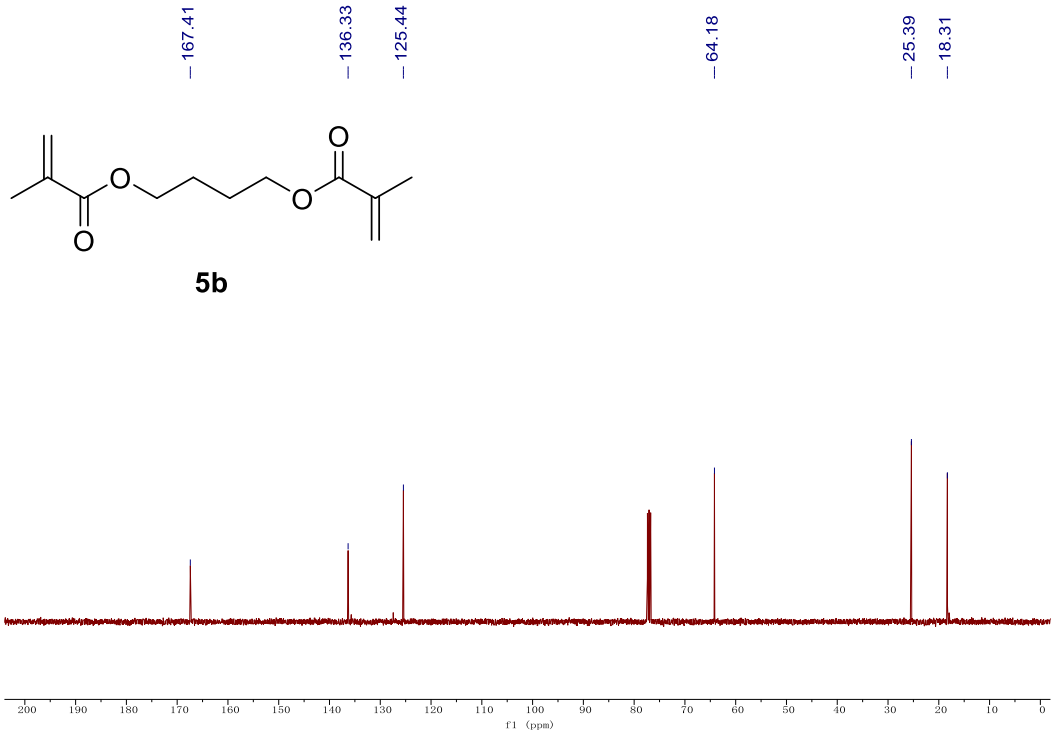
5a

^{1}H NMR, 400 MHz, $CDCl_3$



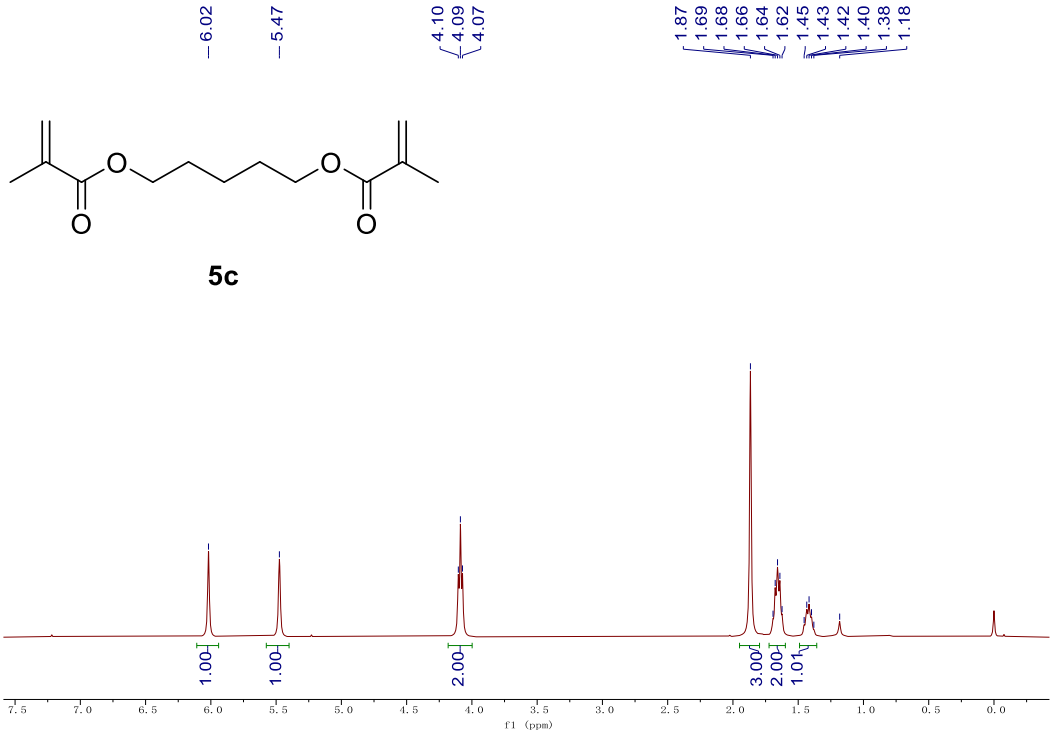
5b

^{13}C NMR, 101 MHz, $CDCl_3$



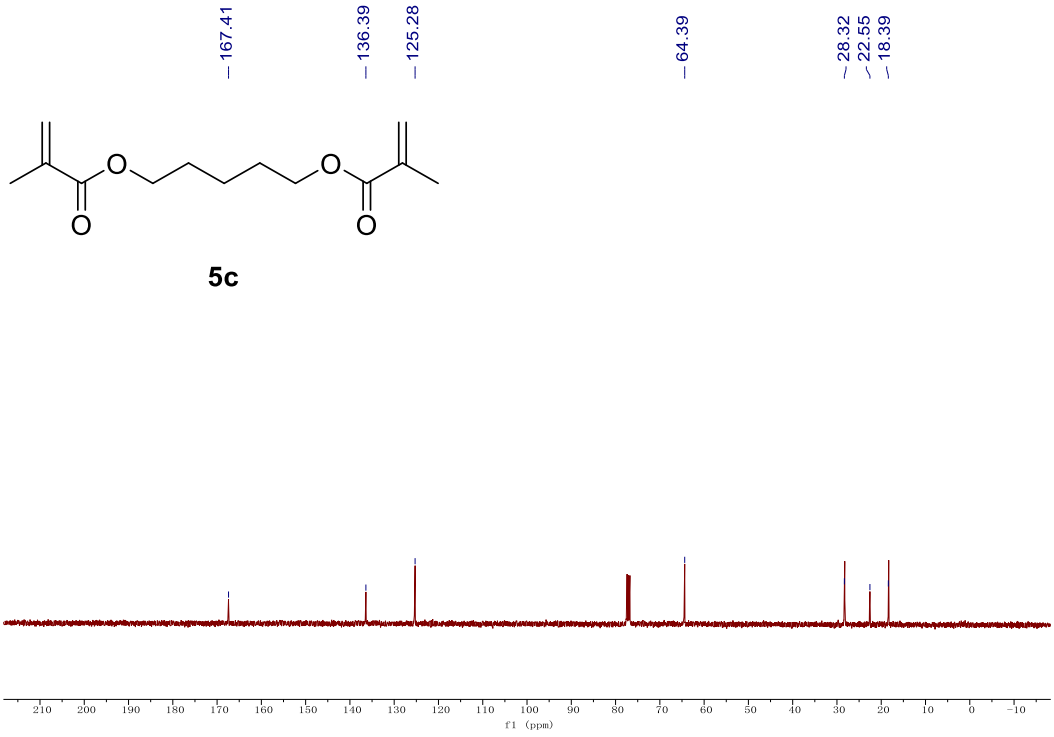
5b

^{1}H NMR, 400 MHz, $CDCl_3$



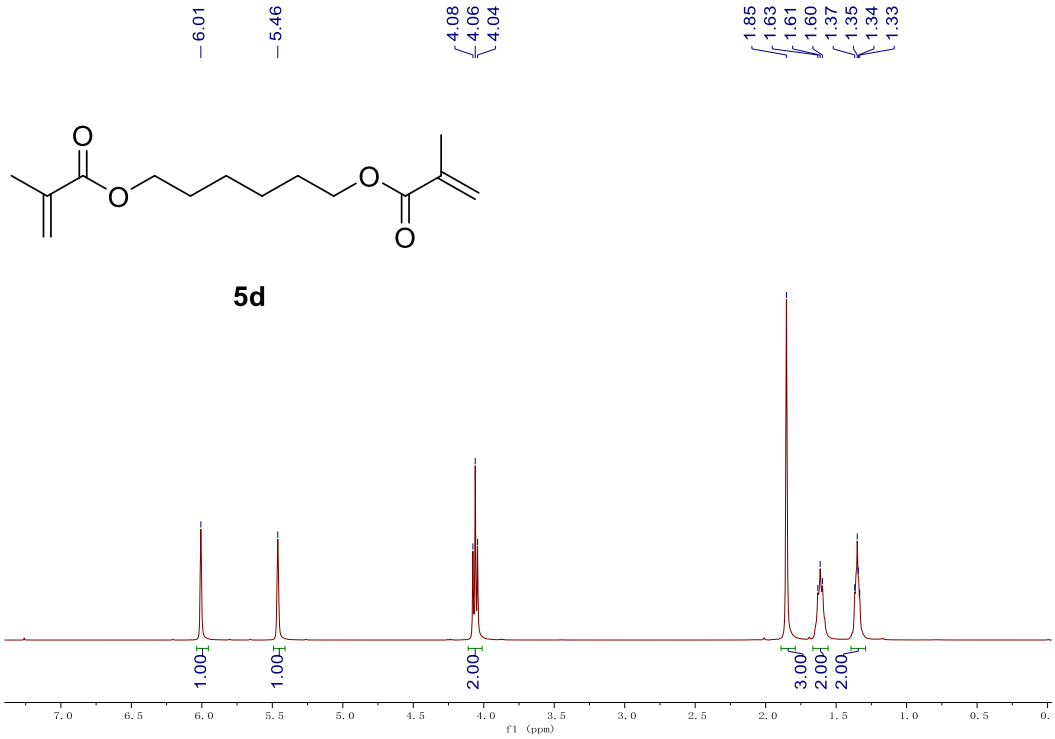
5c

^{13}C NMR, 101 MHz, $CDCl_3$



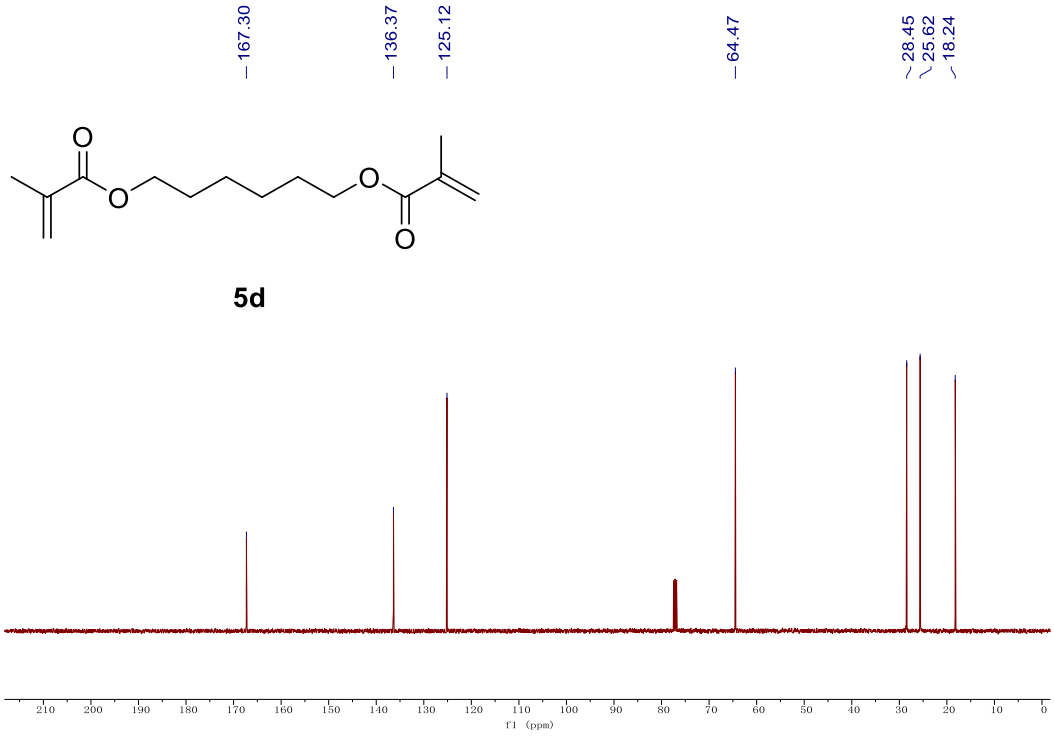
5c

^{1}H NMR, 400 MHz, $CDCl_3$



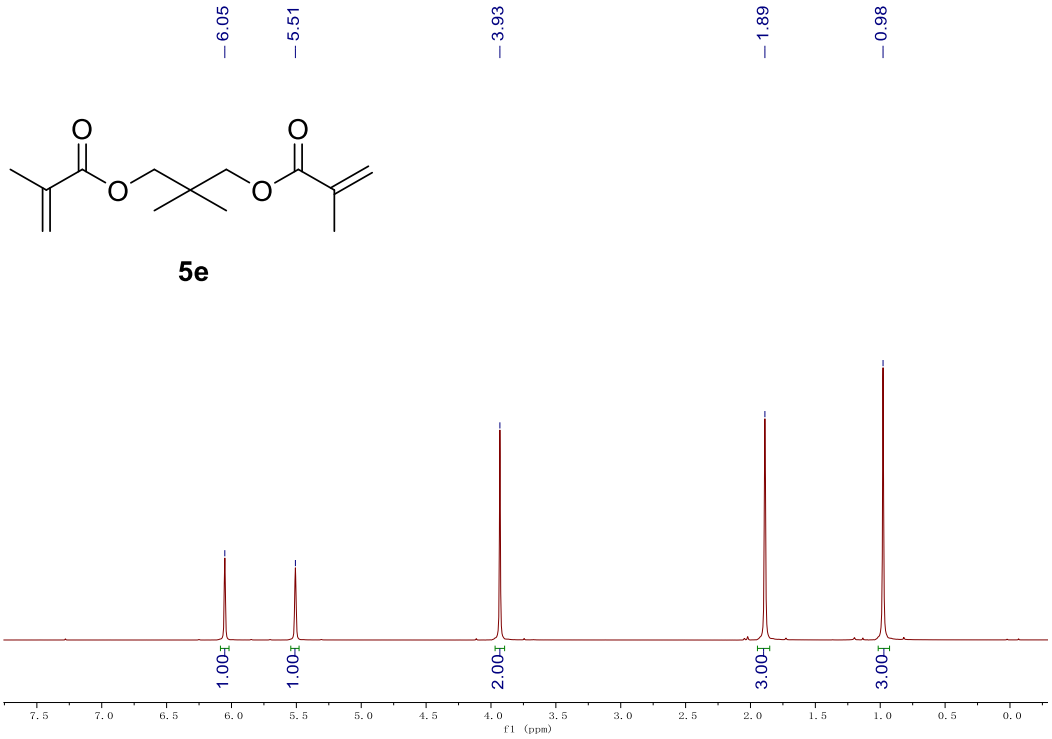
5d

^{13}C NMR, 101 MHz, $CDCl_3$



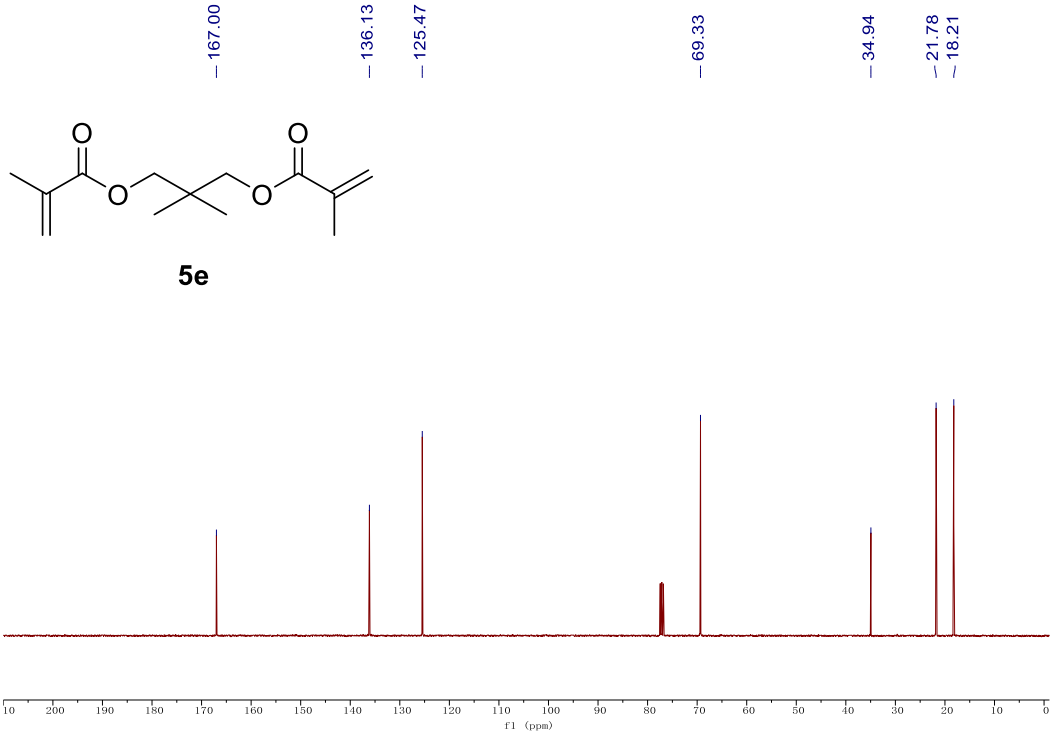
5d

^{1}H NMR, 400 MHz, $CDCl_3$



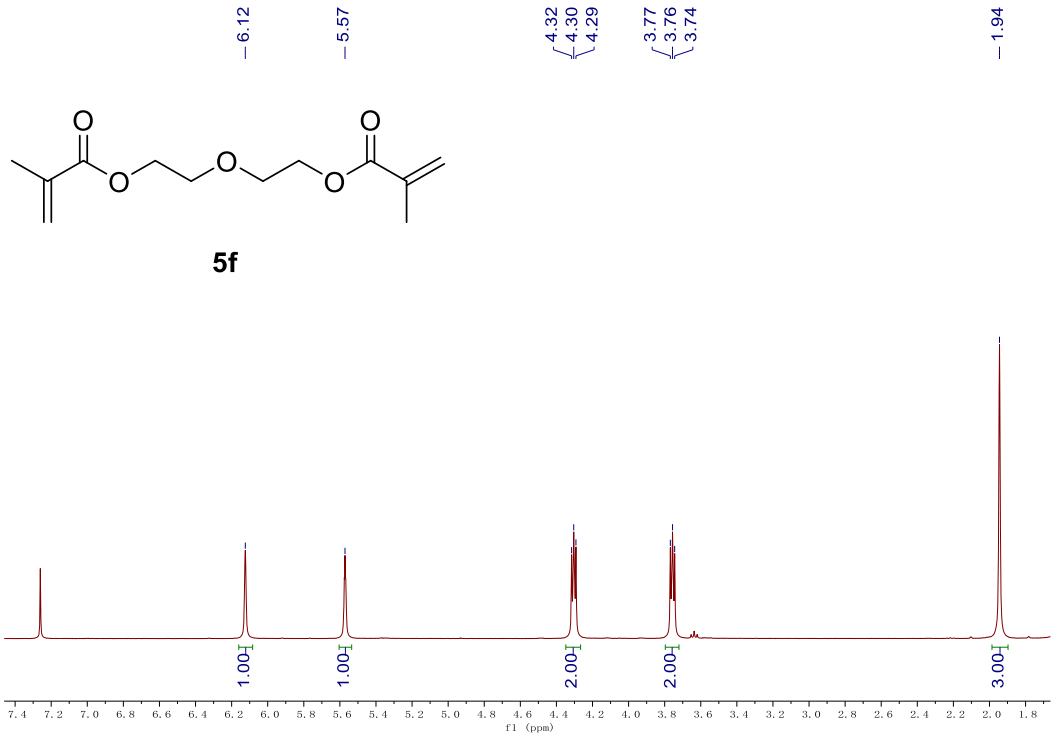
5e

^{13}C NMR, 101 MHz, $CDCl_3$



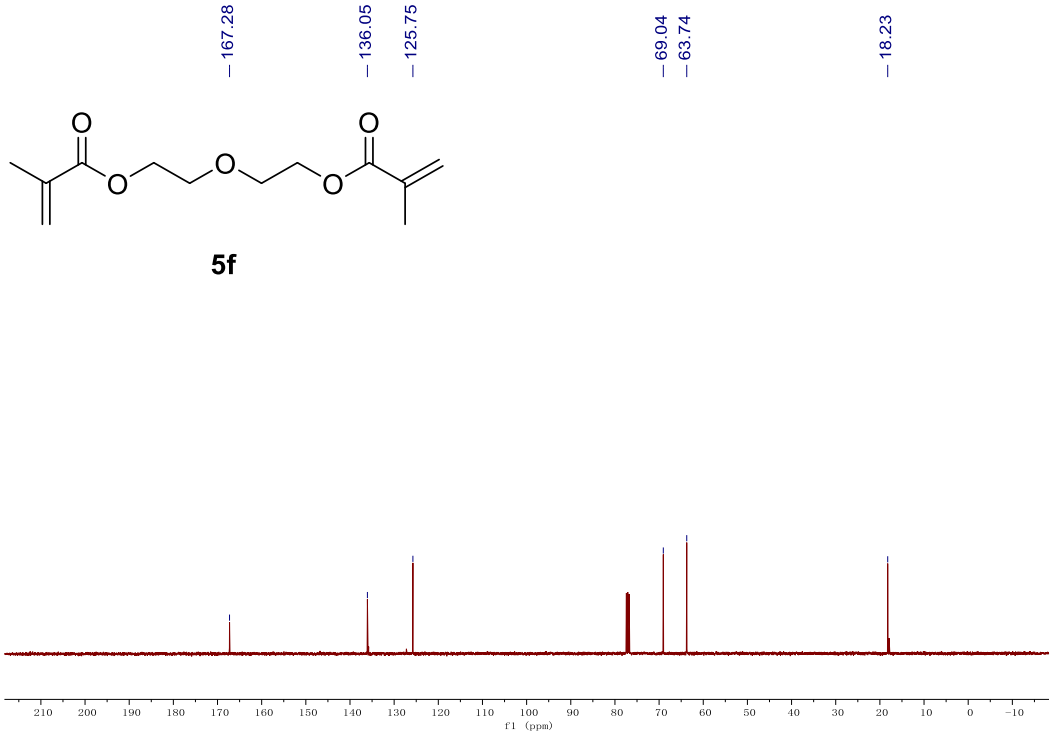
5e

^{1}H NMR, 400 MHz, $CDCl_3$



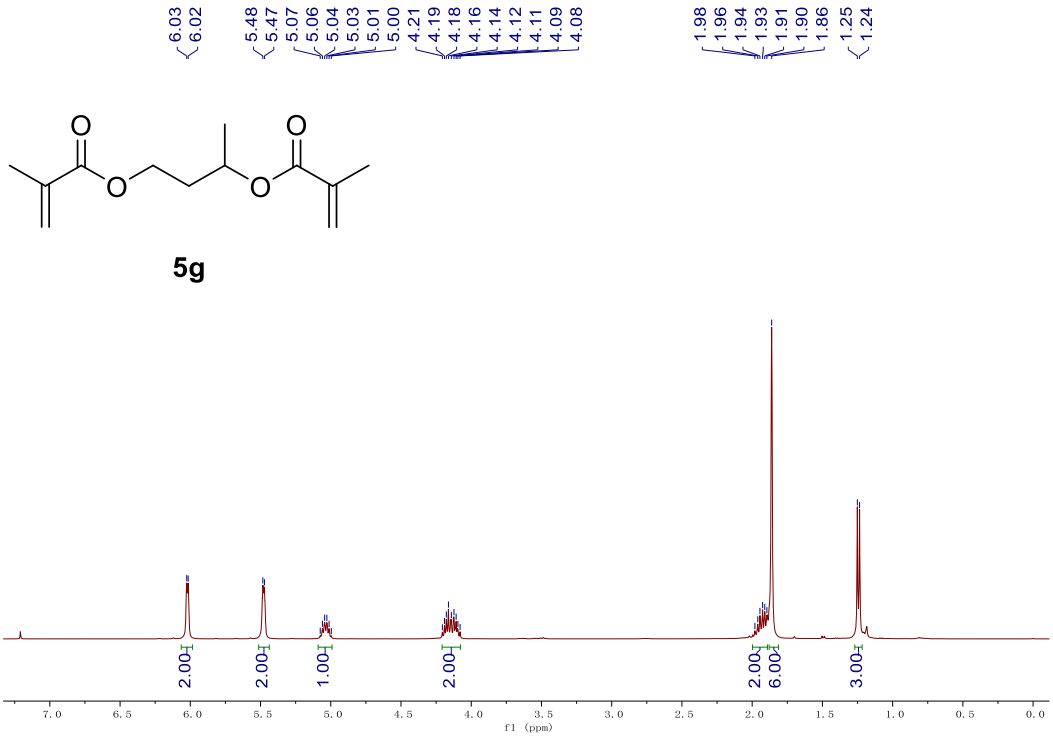
5f

^{13}C NMR, 101 MHz, $CDCl_3$



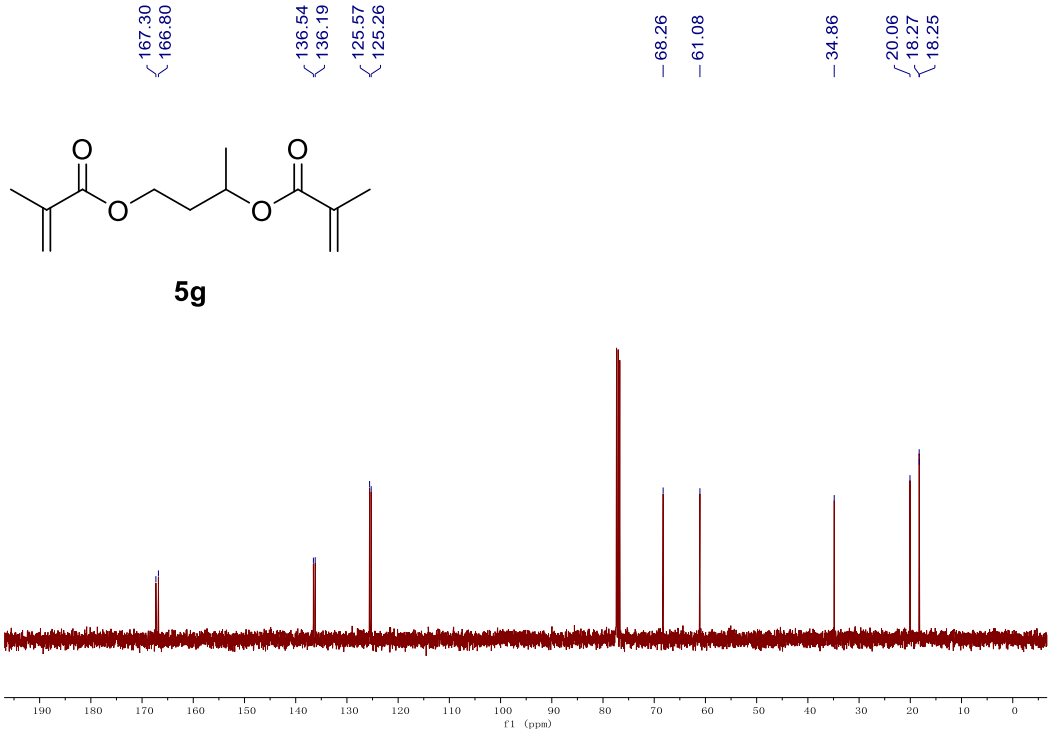
5f

^{1}H NMR, 400 MHz, $CDCl_3$



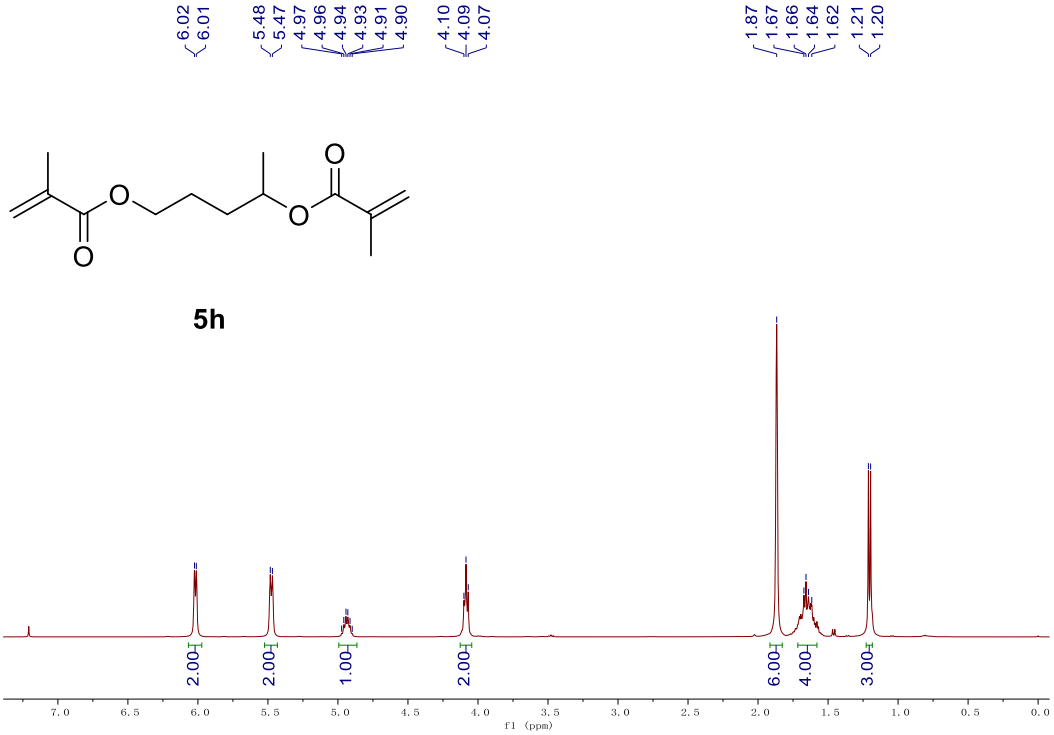
5g

^{13}C NMR, 101 MHz, $CDCl_3$



5g

^{1}H NMR, 400 MHz, $CDCl_3$



^{13}C NMR, 101 MHz, $CDCl_3$