Electronic Supplementary Information

Ether-functionalization of monoethanolamine (MEA) for reversible CO_2 capture under solvent-free condition with high-capacity and low-viscosity

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Table of Contents

1. CO_2 capacity as function of time

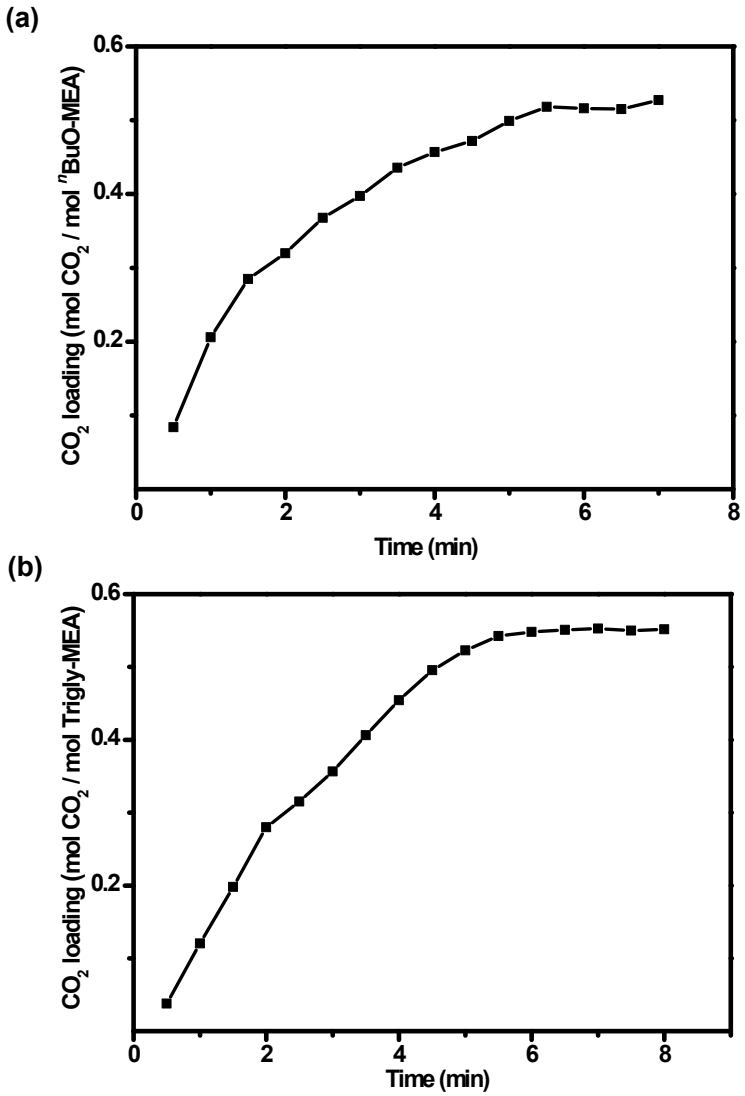


Fig. S1 CO_2 capacity as function of time. (a) ^{n}BuO-MEA; (b) Trigly-MEA. Absorption condition: absorbent (1 mL), 40 ^{o}C, CO_2 (1 bar).

2. Reusability test with ^{n}BuO-MEA.

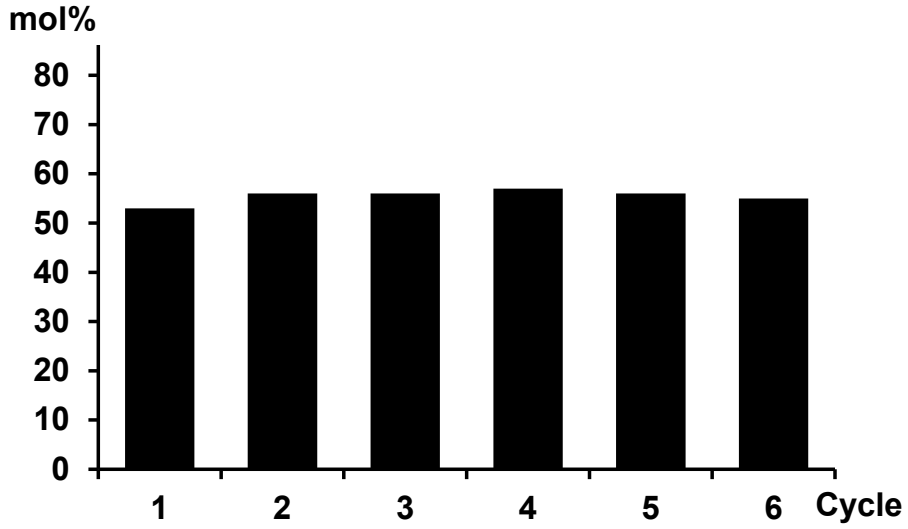


Fig. S2 Reusability of ^{n}BuO-MEA. CO_2 capture (25 ^{o}C, bubbling) and release (75 ^{o}C, open beaker) were performed under ambient pressure.

3. Illustration of DSC measurements

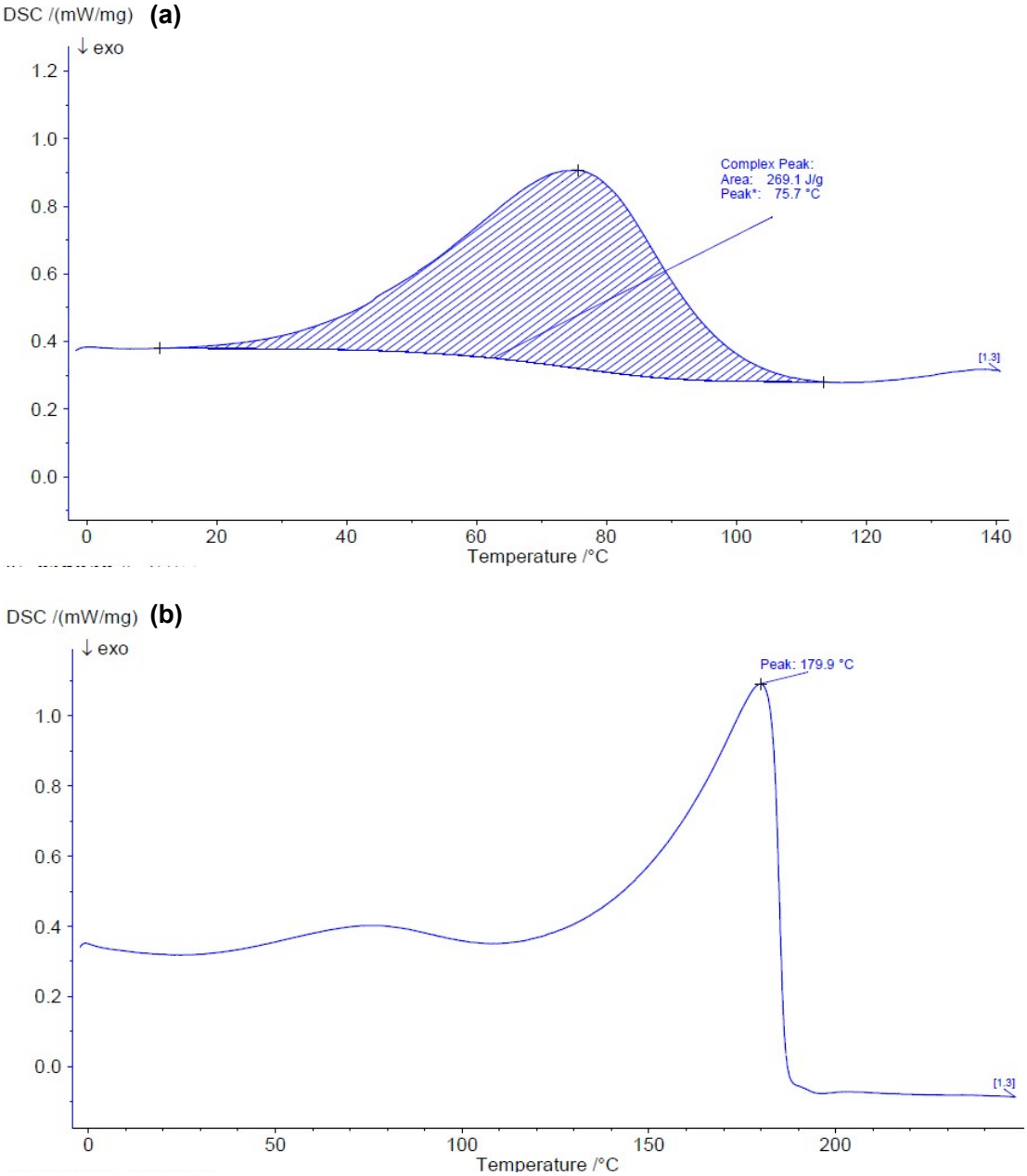


Fig. S3 Example of DSC measurements. (a) Desorption of CO_2-loaded MeO-MEA; (b) evaporation of pristine MeO-MEA.

4. Water content measurements

Table S1 Water content for ether-functionalized MEAs

Entry	Absorbent	Water content (wt%)
1	MeO-MEA	0.78
2	EtO-MEA	0.29
3	^{n}PrO-MEA	0.23
4	^{n}BuO-MEA	0.15
5	^{n}AmylO-MEA	0.17
6	^{n}HexO-MEA	0.18
7	^{i}PrO-MEA	0.37
8	^{t}BuO-MEA	0.34
9	Digly-MEA	0.28
10	Trigly-MEA	0.43
11	^{n}Bu-Digly-MEA	0.14

5. CO_2 capture with moisture

Table S2 CO_2 capture by ether-functionalized MEAs with 20 wt% water at 40 °C[a]

Entry	Absorbent	Capacity (mol%)
1	MeO-MEA	51
2	^{n}BuO-MEA	53
3	^{n}HexO-MEA	53
4	Digly-MEA	52
5	Trigly-MEA	53

[a] Absorption reactions were carried out under ambient pressure.

6. Stability tests

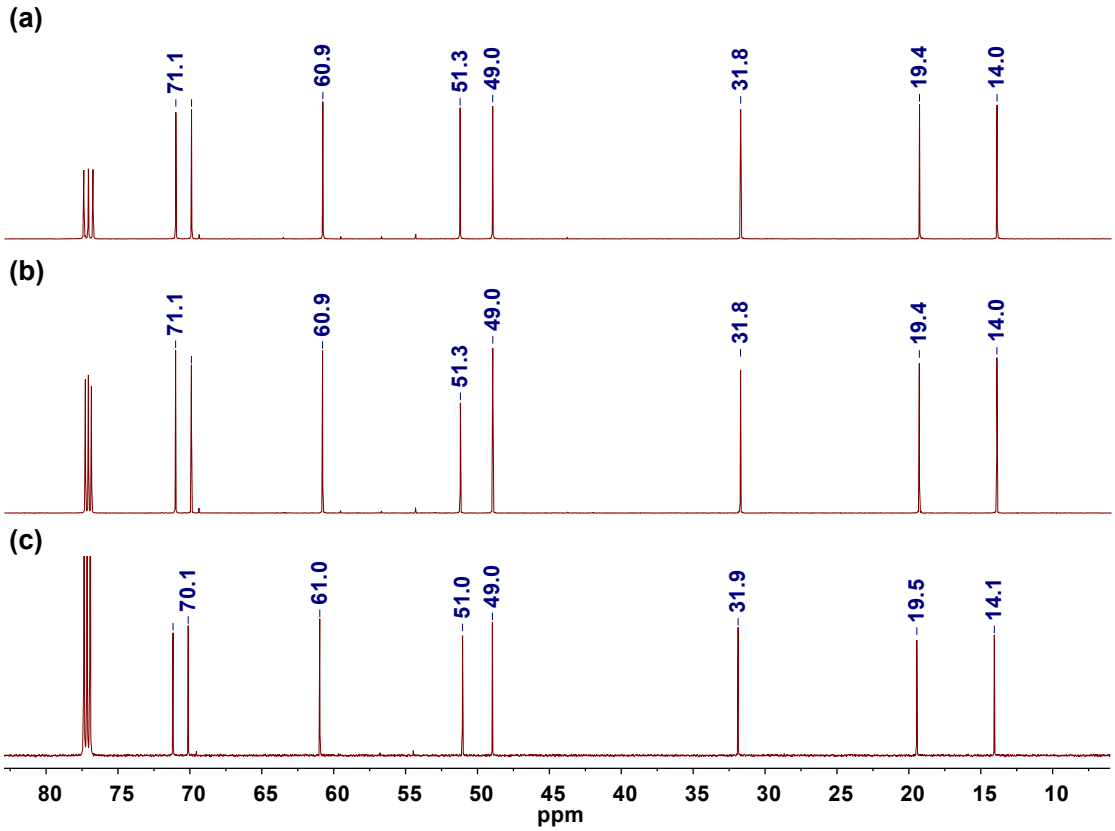


Fig. S4 Stability test for ^{n}BuO-MEA. (a) ^{13}C NMR of pristine ^{n}BuO-MEA; (b) ^{13}C NMR of ^{n}BuO-MEA after heating at 90 ^{o}C under air for 60 h; (c) ^{13}C NMR of ^{n}BuO-MEA after five consecutive absorption (25 ^{o}C, CO_2 bubbling)/desorption (75 ^{o}C, open beaker) cycles.

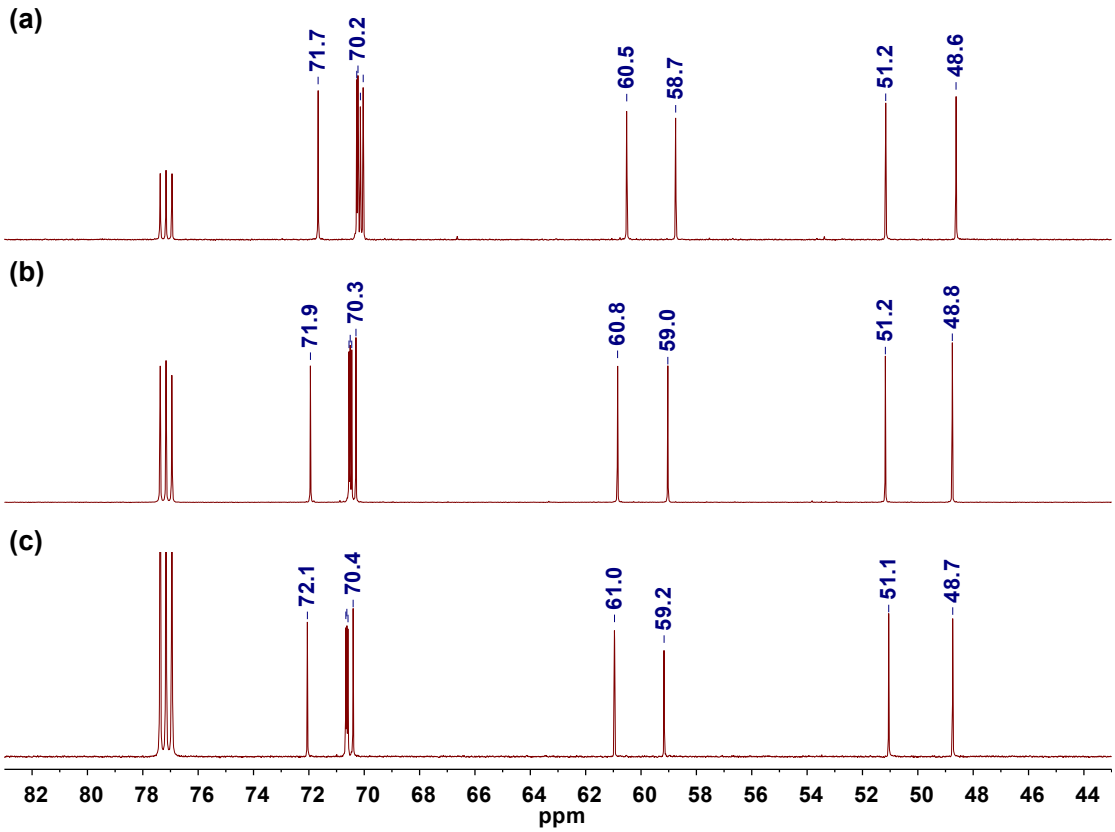


Fig. S5 Stability test for Trigly-MEA. (a) ^{13}C NMR of pristine Trigly-MEA; (b) ^{13}C NMR of Trigly-MEA after heating at 90 ^{o}C under air for 60 h; (c) ^{13}C NMR of Trigly-MEA after five consecutive absorption (25 ^{o}C, CO_2 bubbling)/desorption (75 ^{o}C, open beaker) cycles.

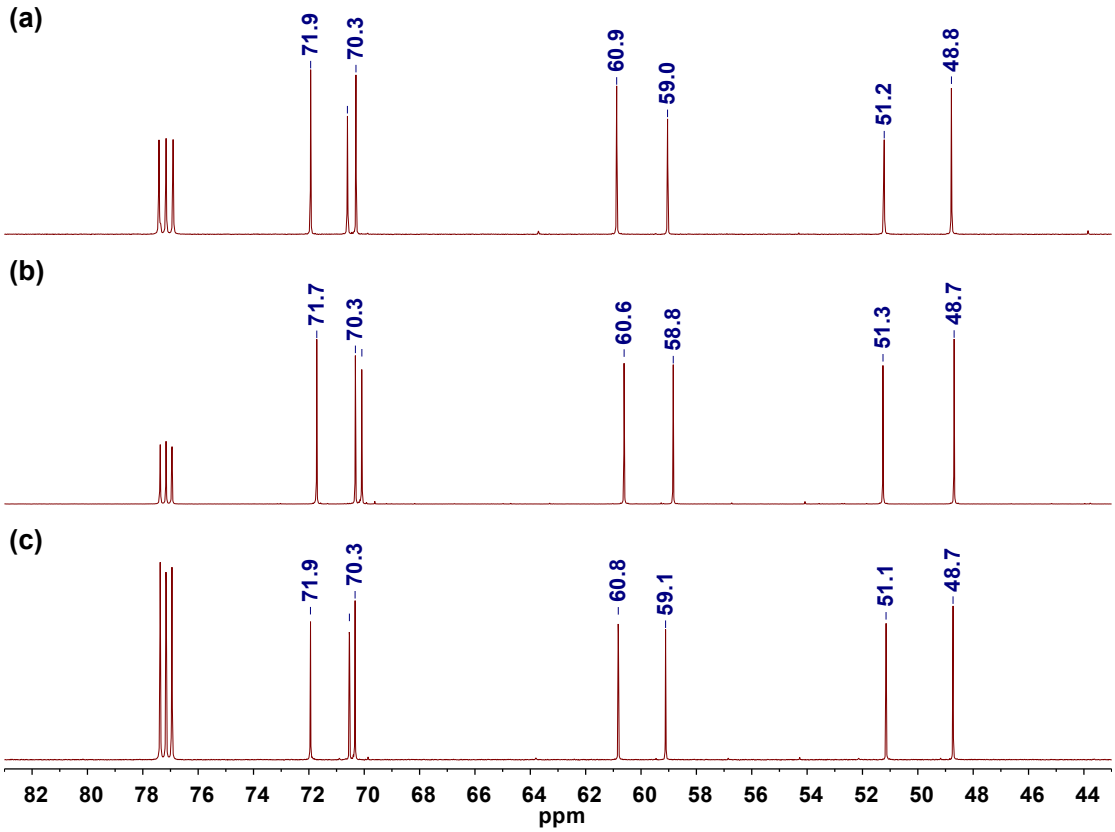


Fig. S6 Stability test for Digly-MEA. (a) ^{13}C NMR of pristine Digly-MEA; (b) ^{13}C NMR of Digly-MEA after heating at 90 ^{o}C under air for 60 h; (c) ^{13}C NMR of Digly-MEA after five consecutive absorption (25 ^{o}C, CO_2 bubbling)/desorption (75 ^{o}C, open beaker) cycles.

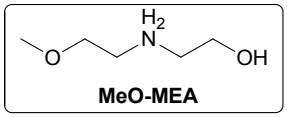
7. CO_2 capture under high pressure

Table S3 CO_2 capture under high pressure at 35 °C

Entry	Absorbent	Pressure (bar)	Capacity (wt%)
1	^{n}BuO-MEA	20	23
		30	28
2	Trigly-MEA	20	21
		30	27
3	aMDEA[a]	20	19
		30	21
4	Selexol[b]	20	12
		30	19

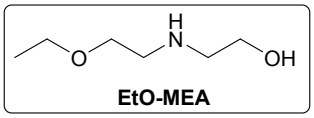
[a] aMDEA (2 mL) was comprised of MDEA (45 wt%) and piperazine (5 wt%); [b] Selexol (2 mL) was simplified as poly(ethylene glycol) dimethyl ether (Mn ~250).

8. Characterization data for ether-functionalized MEAs



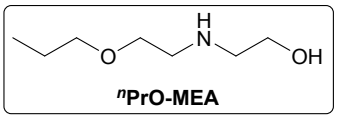
MeO-MEA

2-((2-methoxyethyl)amino)ethan-1-ol (**MeO-MEA**): b.p. 67-70 °C at 0.39 Torr. **^{1}H NMR** (400 MHz, $CDCl_3$): δ=3.63-3.58 (m, 2H), 3.48-3.43 (m, 2H), 3.32 (s, 3H), 2.77-2.70 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ=72.0, 60.9, 58.8, 51.3, 48.9. HRMS (ESI, m/z): calcd for $C_5H_{14}NO_2$ $[M+H]^+$: 120.1702, found: 120.1017.



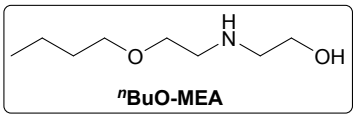
EtO-MEA

2-((2-ethoxyethyl)amino)ethan-1-ol (**EtO-MEA**): b.p. 68-78 °C at 0.39 Torr. **^{1}H NMR** (400 MHz, $CDCl_3$): δ=3.63-3.57 (m, 2H), 3.51-3.41 (m, 4H), 2.78-2.70 (m, 4H), 1.15 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ=69.8, 66.5, 60.9, 51.3, 49.1, 15.2. HRMS (ESI, m/z): calcd for $C_6H_{16}NO_2$ $[M+H]^+$: 134.1910, found: 134.1181.



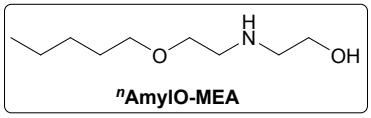
***n*PrO-MEA**

2-((2-propoxyethyl)amino)ethan-1-ol (***n*PrO-MEA**): b.p. 82-86 °C at 0.39 Torr. **^{1}H NMR** (400 MHz, $CDCl_3$): δ=3.62-3.56 (m, 2H), 3.48 (t, *J* = 5.1 Hz, 2H), 3.34 (t, *J* = 6.7 Hz, 2H), 2.77-2.68 (m, 4H), 1.60-1.47 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ=72.9, 69.9, 60.9, 51.3, 49.1, 22.9, 10.6. HRMS (ESI, m/z): calcd for $C_7H_{18}NO_2$ $[M+H]^+$: 148.2180, found: 148.1338.



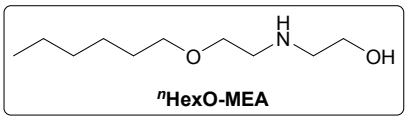
***n*BuO-MEA**

2-((2-butoxyethyl)amino)ethan-1-ol (***n*BuO-MEA**): b.p. 87-90 °C at 0.39 Torr. **^{1}H NMR** (400 MHz, $CDCl_3$): δ=3.63-3.57 (m, 2H), 3.51-3.46 (m, 2H), 3.39 (t, *J* = 6.7 Hz, 2H), 2.77-2.70 (m, 4H), 1.56-1.46 (m, 2H), 1.37-1.25 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ=71.1, 70.0, 60.9, 51.3, 49.0, 31.8, 19.4, 14.0. HRMS (ESI, m/z): calcd for $C_8H_{20}NO_2$ $[M+H]^+$: 162.2450, found: 162.1497.



***n*AmylO-MEA**

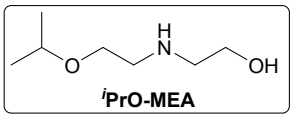
2-((2-(pentyloxy)ethyl)amino)ethan-1-ol (***n*AmylO-MEA**): b.p. 95-102 °C at 0.39 Torr. **^{1}H NMR** (400 MHz, $CDCl_3$): δ=3.61 (m, 2H), 3.50 (t, *J* = 5.2 Hz, 2H), 3.40 (t, *J* = 6.8 Hz, 2H), 2.79-2.72 (m, 4H), 1.55 (p, *J* = 6.9 Hz, 2H), 1.35-1.22 (m, 4H), 0.87 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ=71.4, 70.1, 60.9, 51.3, 49.0, 29.4, 28.4, 22.6, 14.1. HRMS (ESI, m/z): calcd for $C_9H_{22}NO_2$ $[M+H]^+$: 176.2720, found: 176.1653.



***n*HexO-MEA**

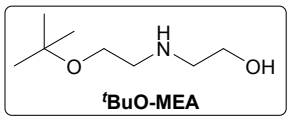
2-((2-(hexyloxy)ethyl)amino)ethan-1-ol (***n*HexO-MEA**): b.p. 96-102 °C at 0.39 Torr.**^{1}H NMR**

(400 MHz, $CDCl_3$): δ=3.63-3.58 (m, 2H), 3.49 (t, *J* = 5.1 Hz, 2H), 3.40 (t, *J* = 6.8 Hz, 2H), 2.79-2.71 (m, 4H), 1.58-1.48 (m, 2H), 1.36-1.18 (m, 6H), 0.85 (t, *J* = 6.5 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ=71.5, 70.0, 60.9, 51.3, 49.0, 31.8, 29.7, 25.9, 22.7, 14.1. HRMS (ESI, m/z): calcd for $C_{10}H_{24}NO_2$ $[M+H]^+$: 190.2990, found: 190.1806.



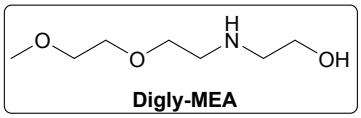
^{i}PrO-MEA

2-((2-isopropoxyethyl)amino)ethan-1-ol (**^{i}PrO-MEA**): b.p. 66-68 °C at 0.39 Torr. **^{1}H NMR** (400 MHz, $CDCl_3$): δ=3.64-3.60 (m, 2H), 3.60-3.53 (m, 1H), 3.52-3.49 (m, 2H), 2.76 (t, *J* = 5.2 Hz, 4H), 1.14 (d, *J* = 6.1 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ=71.8, 67.3, 60.9, 51.3, 49.3, 22.1. HRMS (ESI, m/z): calcd for $C_7H_{18}NO_2$ $[M+H]^+$: 148.2180, found: 148.1337.



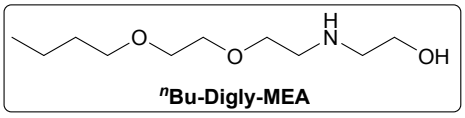
^{t}BuO-MEA

2-((2-(tert-butoxy)ethyl)amino)ethan-1-ol (**^{t}BuO-MEA**): b.p. 75-78 °C at 0.39 Torr. **^{1}H NMR** (400 MHz, $CDCl_3$): δ=3.66-3.61 (m, 2H), 3.47 (t, *J* = 5.2 Hz, 2H), 2.80-2.73 (m, 4H), 1.22-1.17 (m, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ=73.0, 60.9, 51.1, 49.6, 27.7. HRMS (ESI, m/z): calcd for $C_8H_{20}NO_2$ $[M+H]^+$: 162.2450, found: 162.1500.



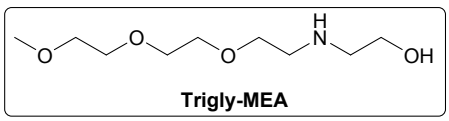
Digly-MEA

2-((2-(2-methoxyethoxy)ethyl)amino)ethan-1-ol (**Digly-MEA**): b.p. 95-97 °C at 0.39 Torr. **^{1}H NMR** (400 MHz, $CDCl_3$): δ=3.62-3.53 (m, 6H), 3.52-3.48 (m, 2H), 3.34 (s, 3H), 2.80-2.76 (m, 2H), 2.75-2.71 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ=71.9, 70.6, 70.3, 60.9, 59.0, 51.2, 48.8. HRMS (ESI, m/z): calcd for $C_7H_{18}NO_3$ $[M+H]^+$: 164.2170, found: 164.1288.



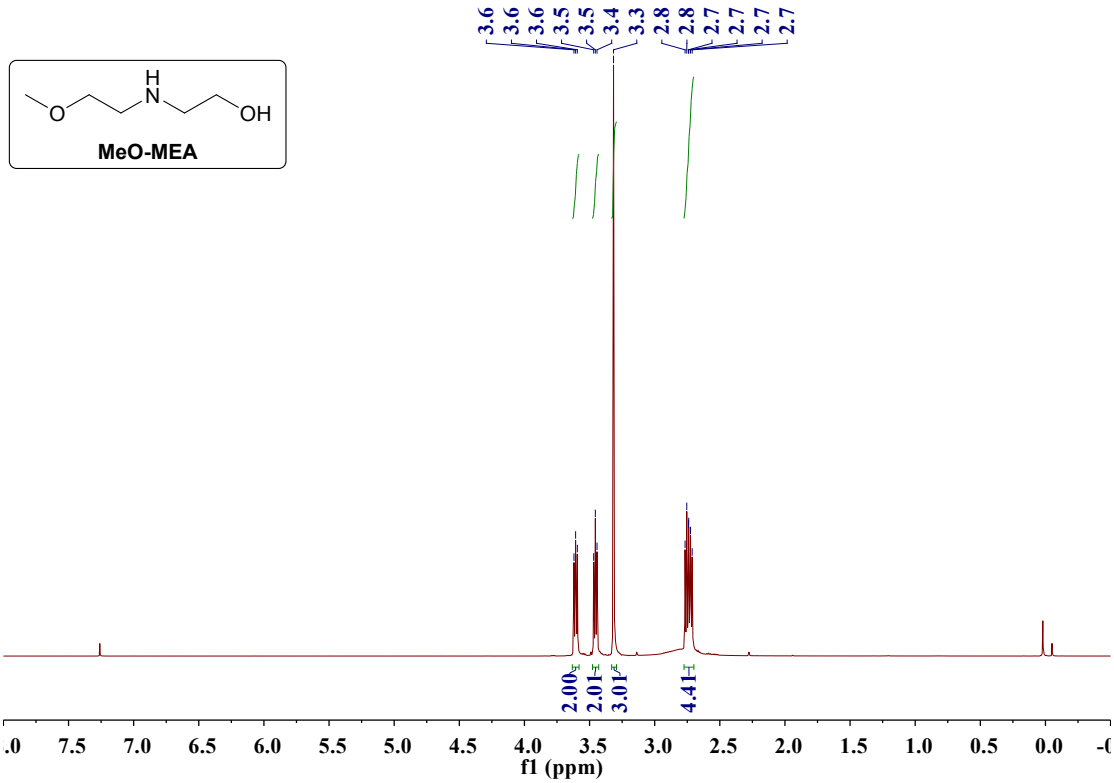
^{n}Bu-Digly-MEA

2-((2-(2-butoxyethoxy)ethyl)amino)ethan-1-ol (**^{n}Bu-Digly-MEA**): b.p. 121-126 °C at 0.39 Torr. **^{1}H NMR** (400 MHz, $CDCl_3$): δ=3.63-3.51 (m, 8H), 3.43 (t, *J* = 6.7 Hz, 2H), 2.80-2.71 (m, 4H), 1.54 (dt, *J* = 14.7, 6.8 Hz, 2H), 1.33 (dq, *J* = 14.6, 7.3 Hz, 2H), 0.89 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ=71.2, 70.5, 70.4, 70.0, 60.8, 51.1, 48.7, 31.7, 19.3, 13.9. HRMS (ESI, m/z): calcd for $C_{10}H_{24}NO_3$ $[M+H]^+$: 206.2980, found: 206.1758.



Trigly-MEA

2,5,8-trioxa-11-azatridecan-13-ol (**Trigly-MEA**): b.p. 140-145 °C at 0.39 Torr. **^{1}H NMR** (400 MHz, $CDCl_3$): δ=3.61-3.51 (m, 10H), 3.51-3.47 (m, 2H), 3.32 (s, 3H), 2.77-2.73 (m, 2H), 2.73-2.69 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ=71.9, 70.5, 70.5, 70.4, 70.3, 60.8, 59.0, 51.2, 48.8. HRMS (ESI, m/z): calcd for $C_9H_{22}NO_4$ $[M+H]^+$: 208.2700, found: 208.1549.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3.6
3.6
3.5
3.5
3.4
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2.00
2.01
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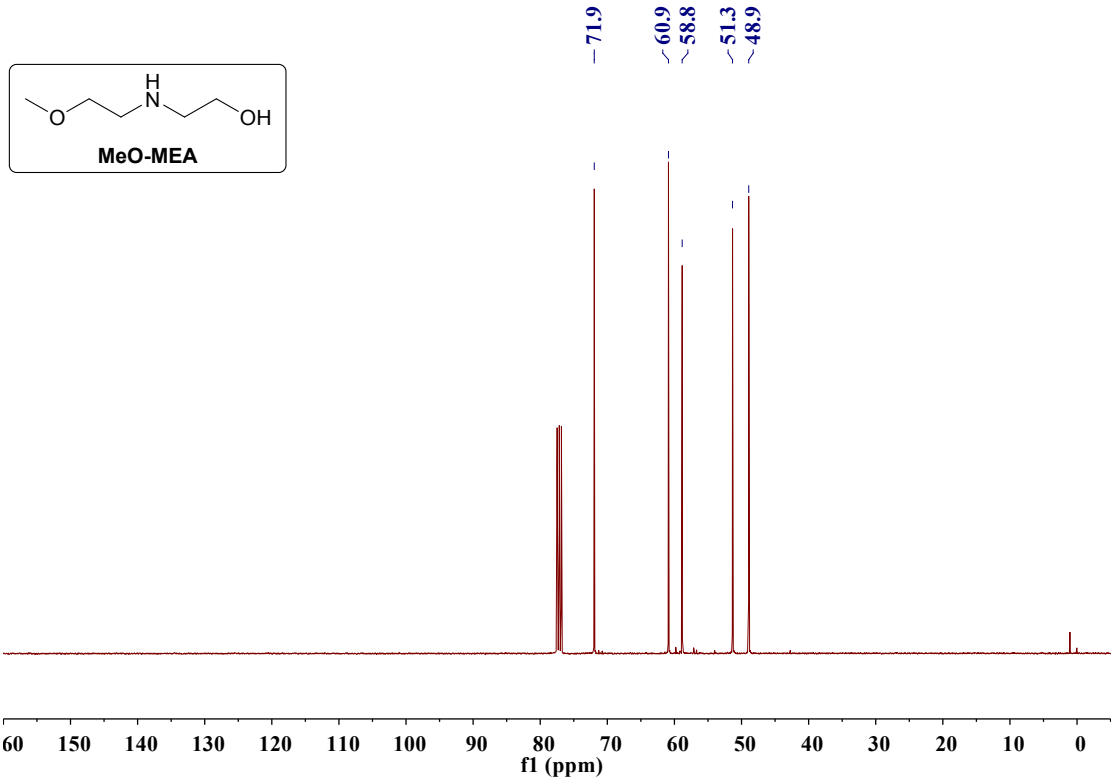
fl (ppm)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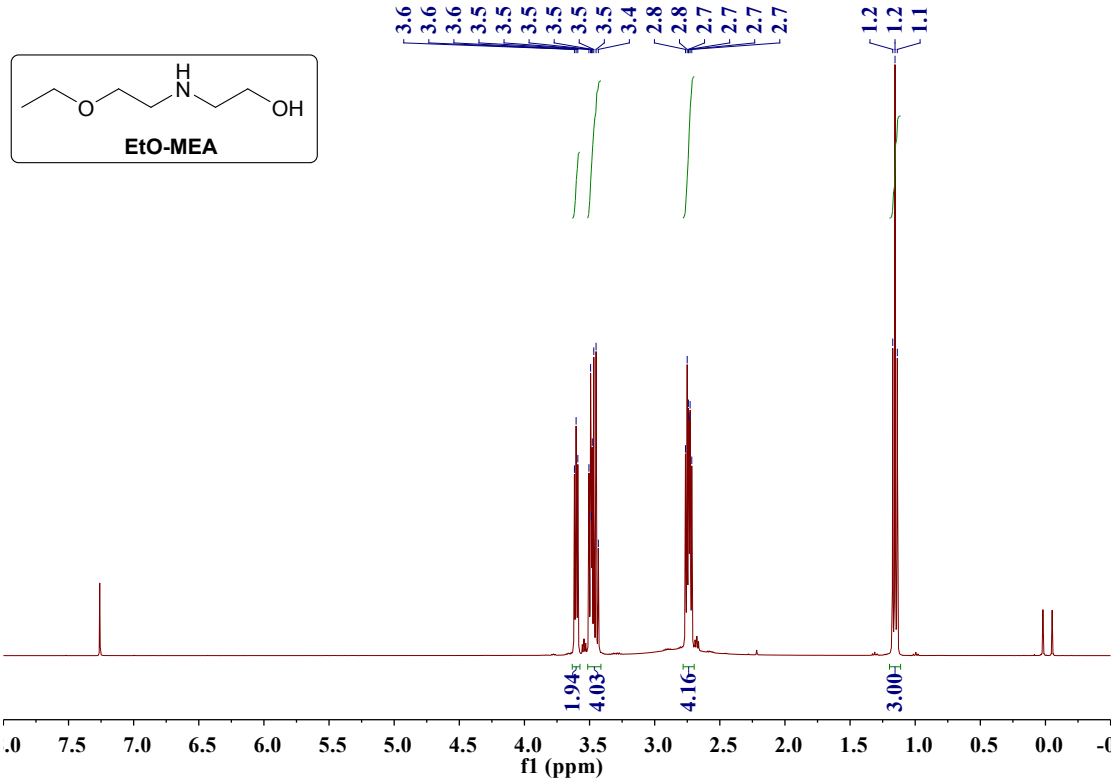
58.8
51.3
48.9
fl (ppm)


EtO-MEA
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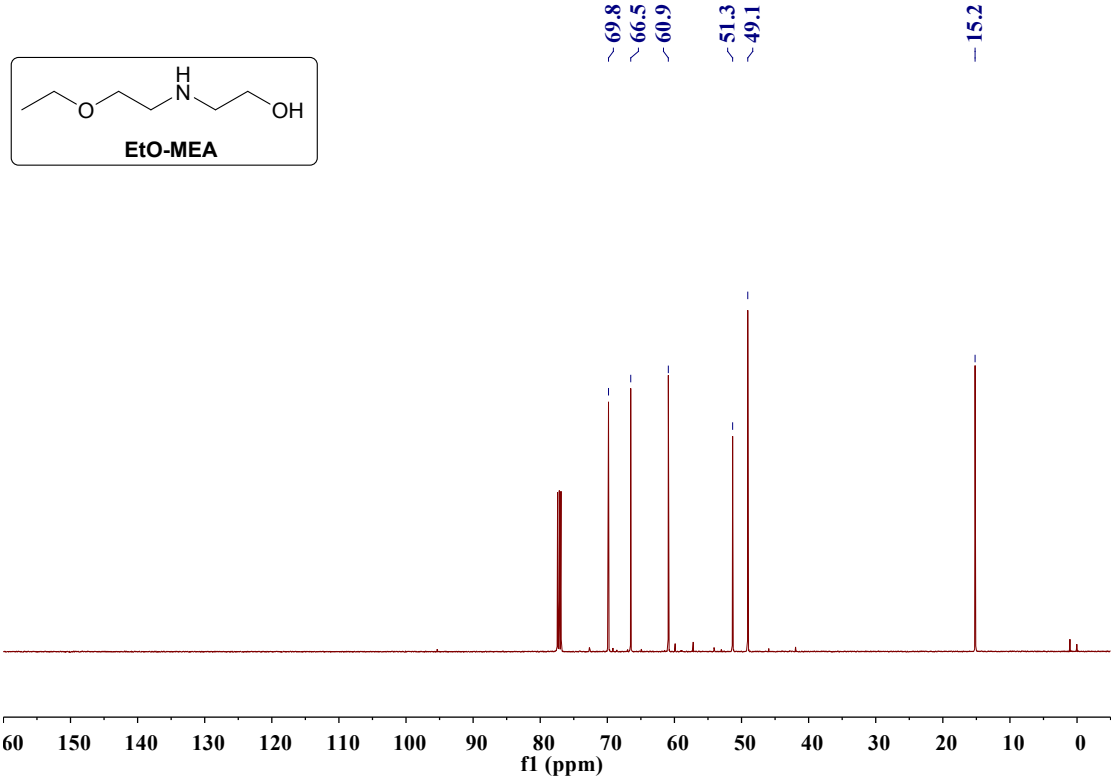
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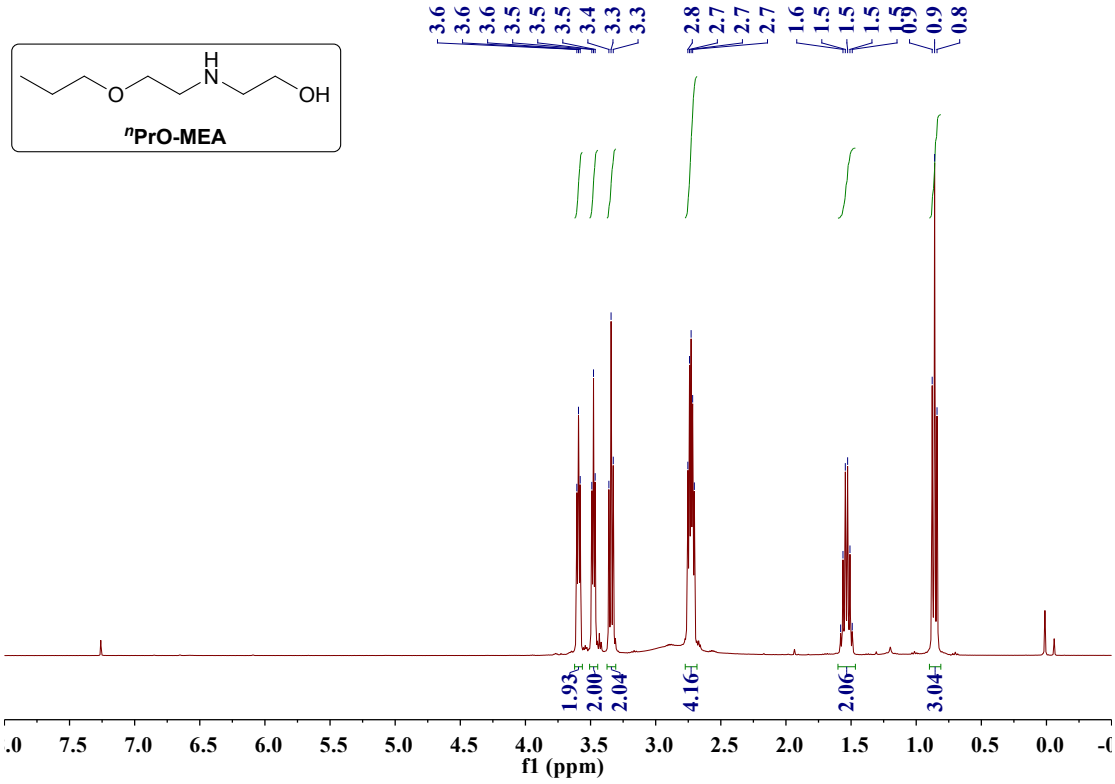
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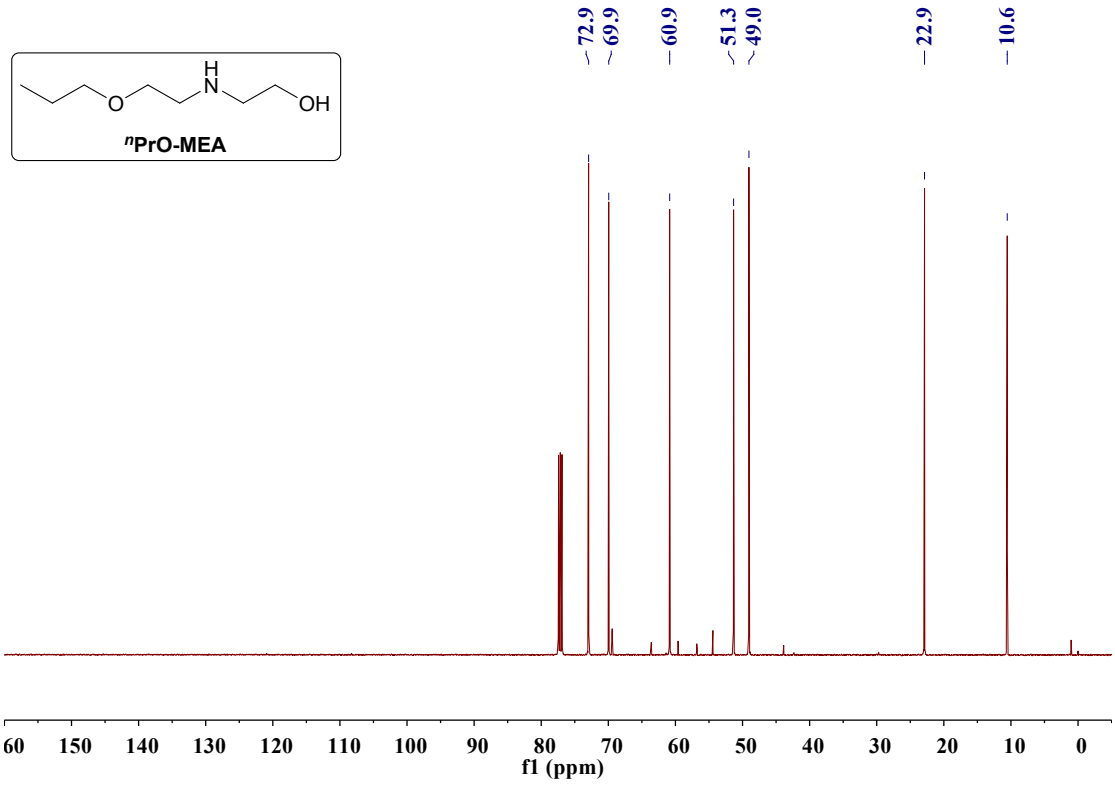
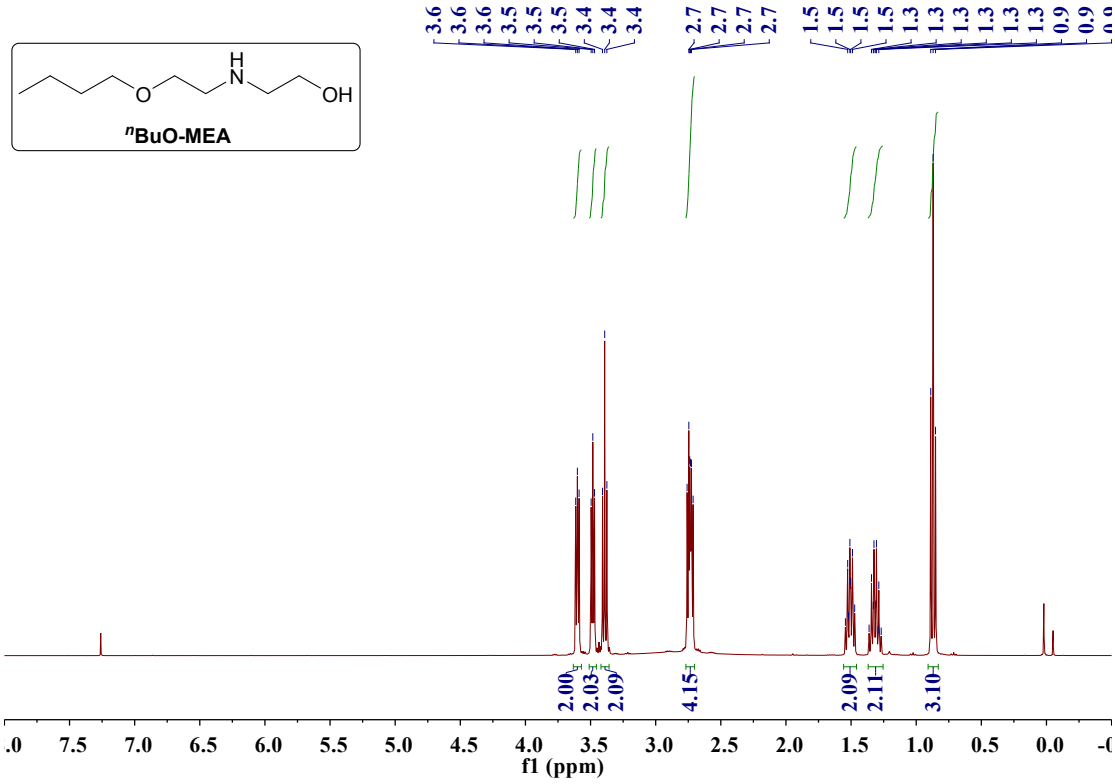

nPrO-MEA
f1 (ppm)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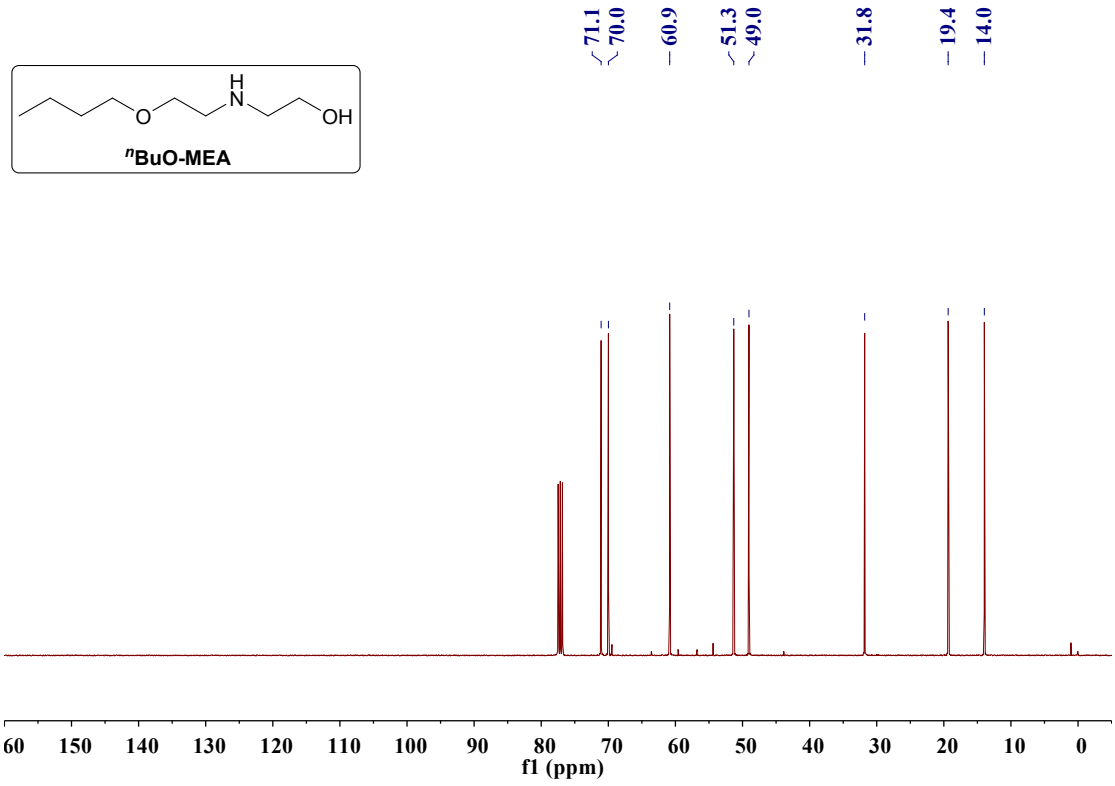
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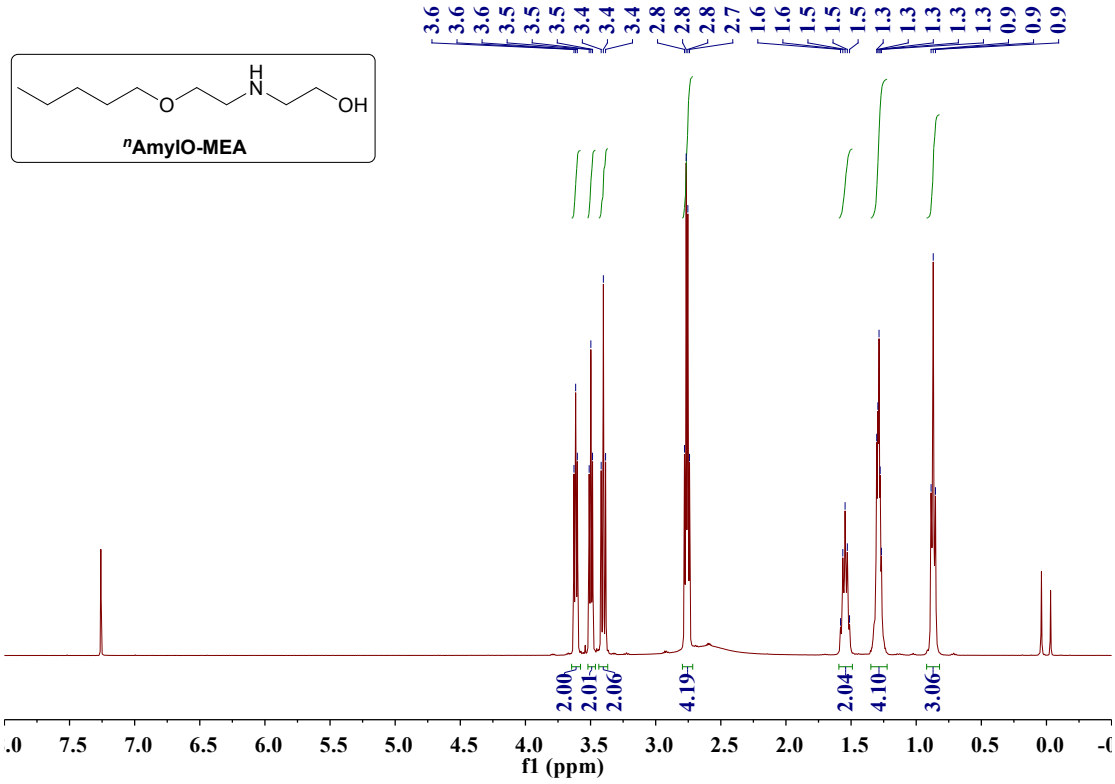
nAmylO-MEA
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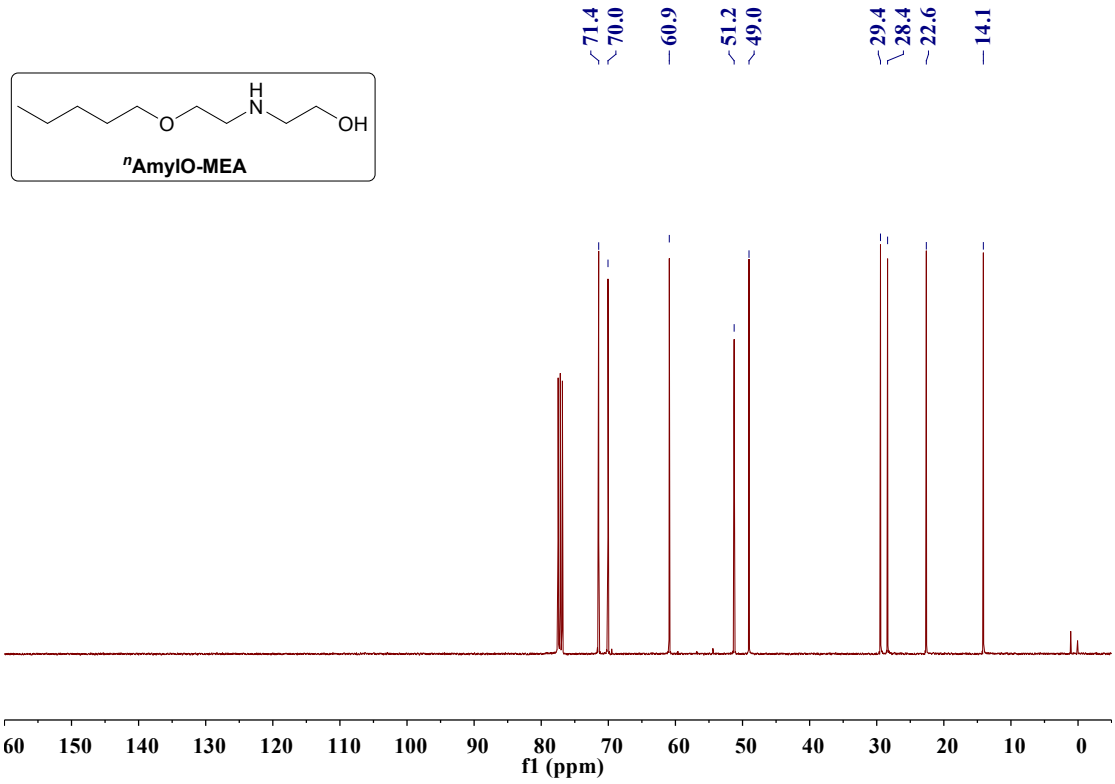
f1 (ppm)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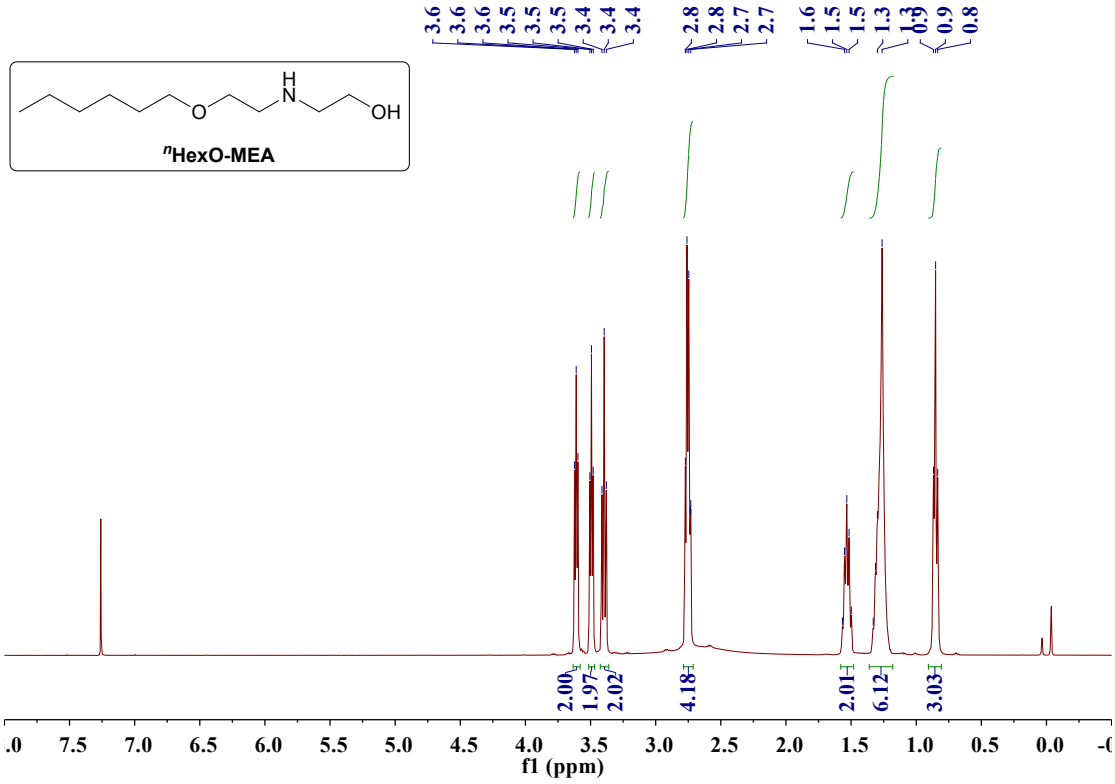
f1 (ppm)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3.6
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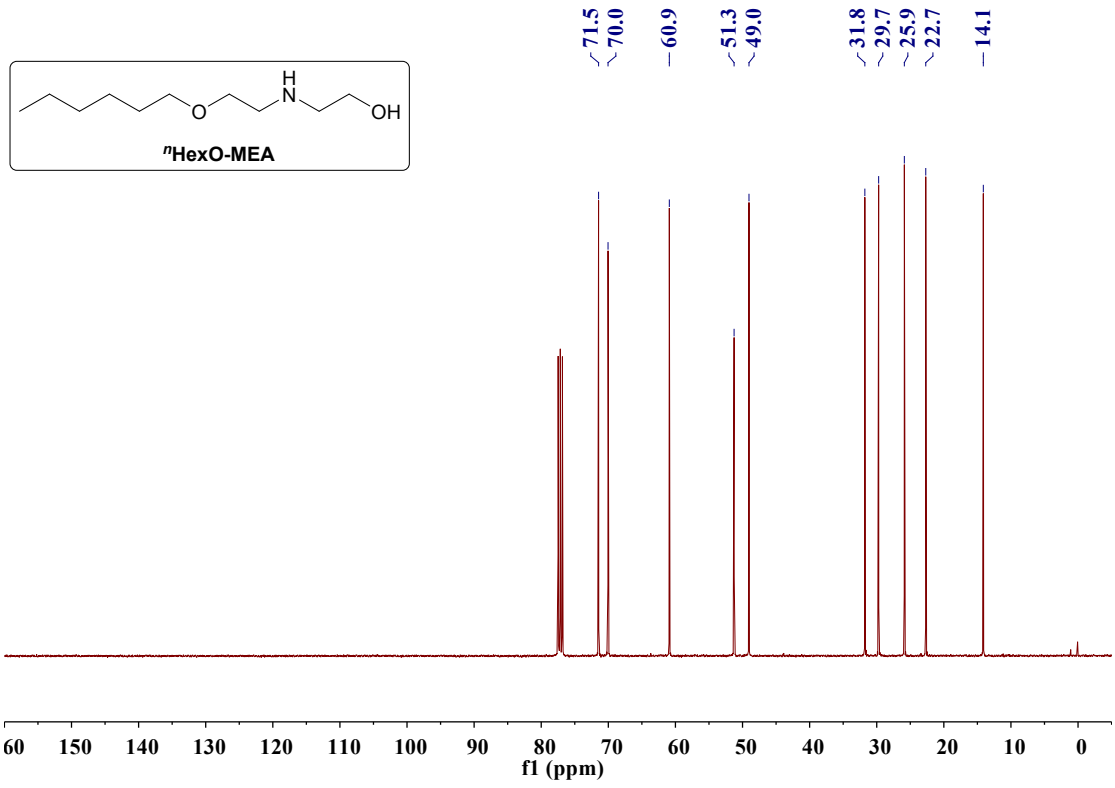
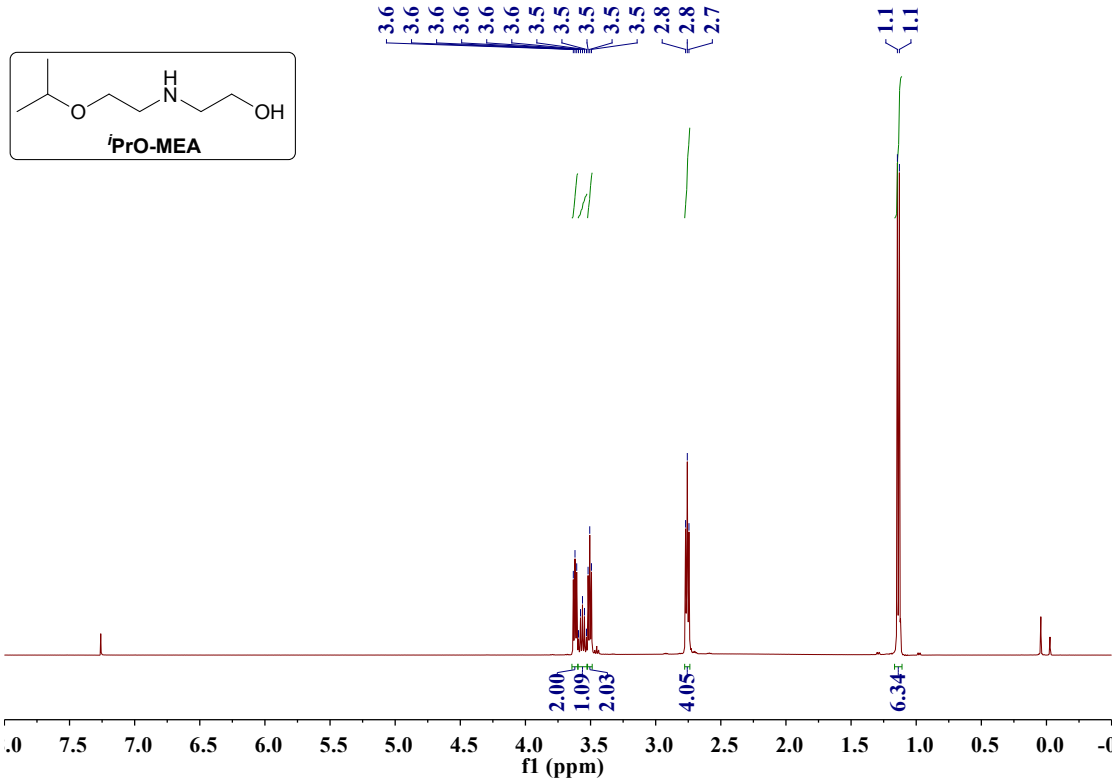
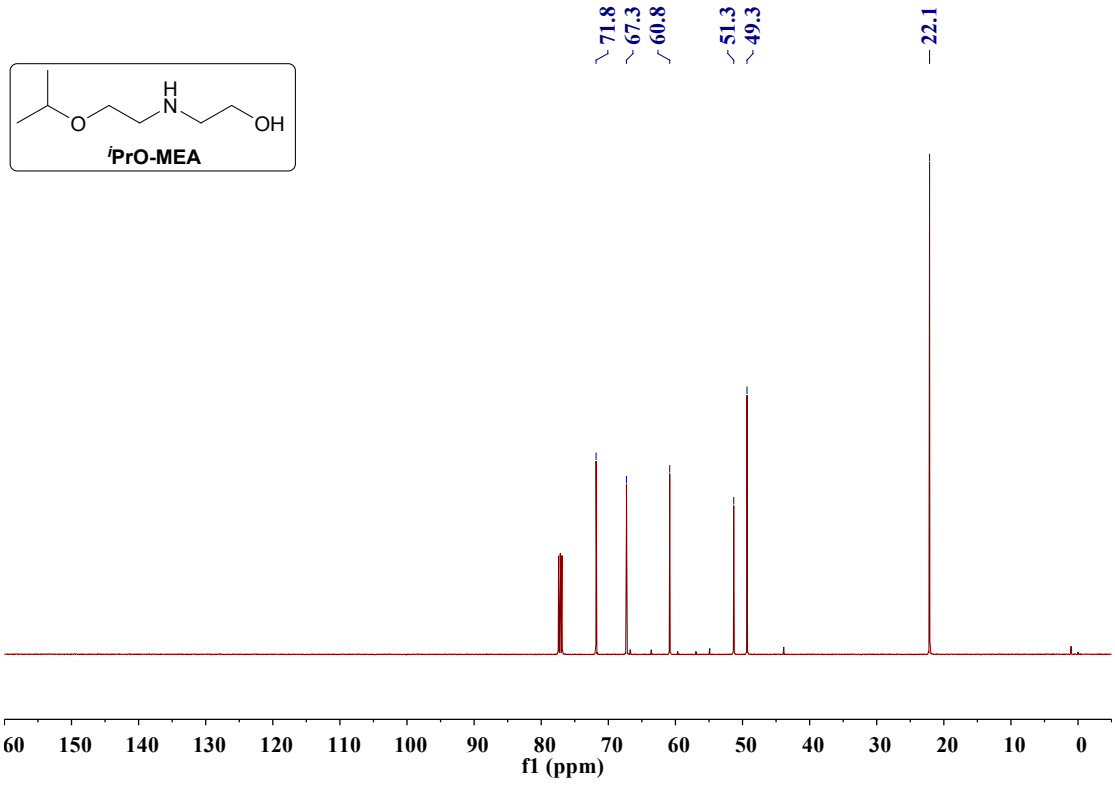
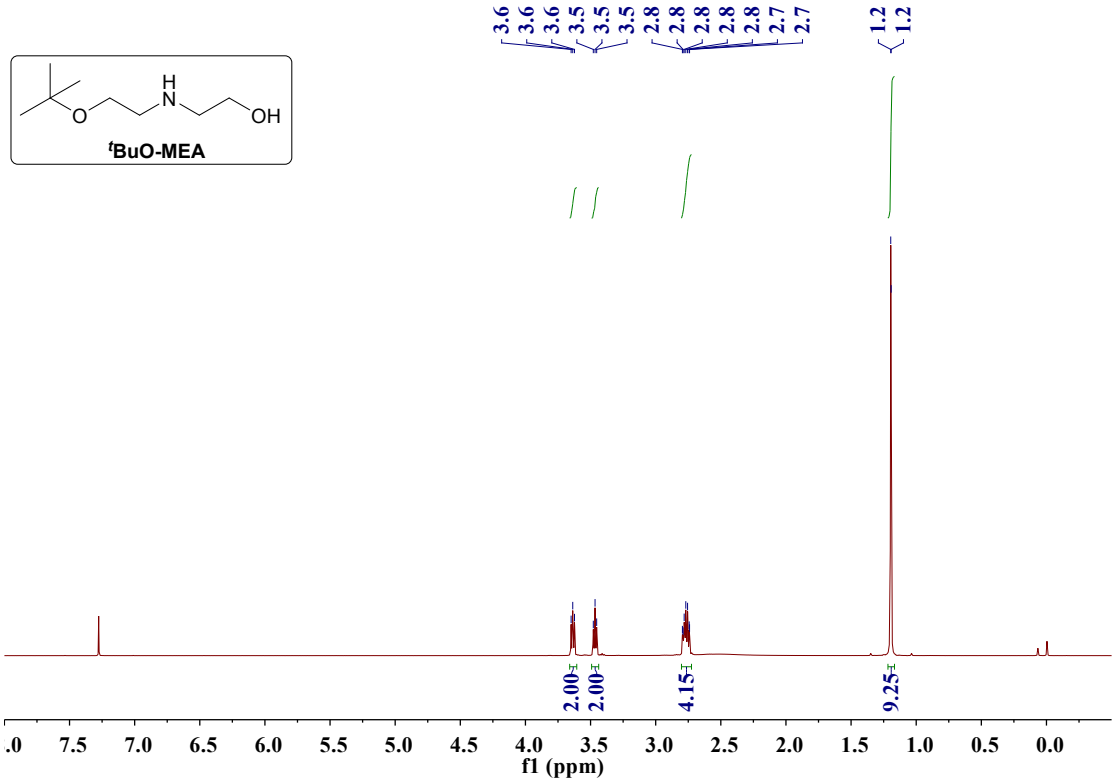
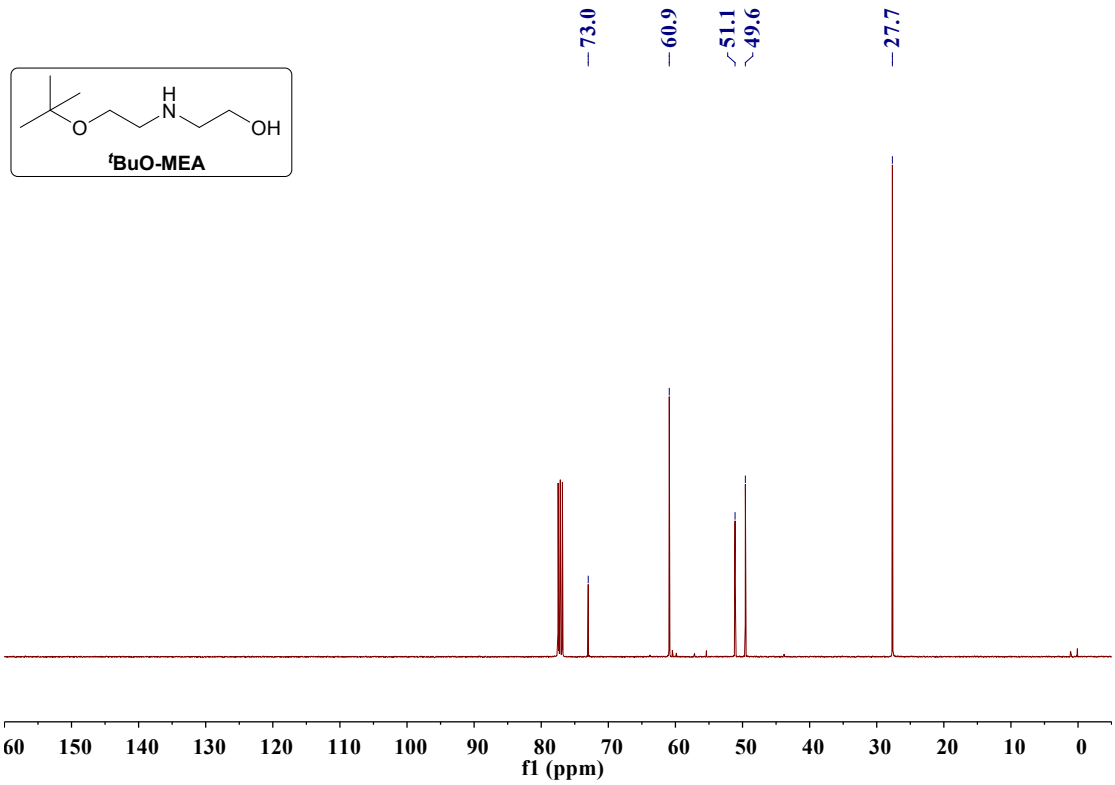
3.4
3.4
2.8
2.8
2.7
2.7
1.6
1.5
1.5
1.3
1.3
0.9
0.8
H
N
O
OH
nHexO-MEA
2.00
1.97
2.02
4.18
2.01
6.12
3.03
f1 (ppm)

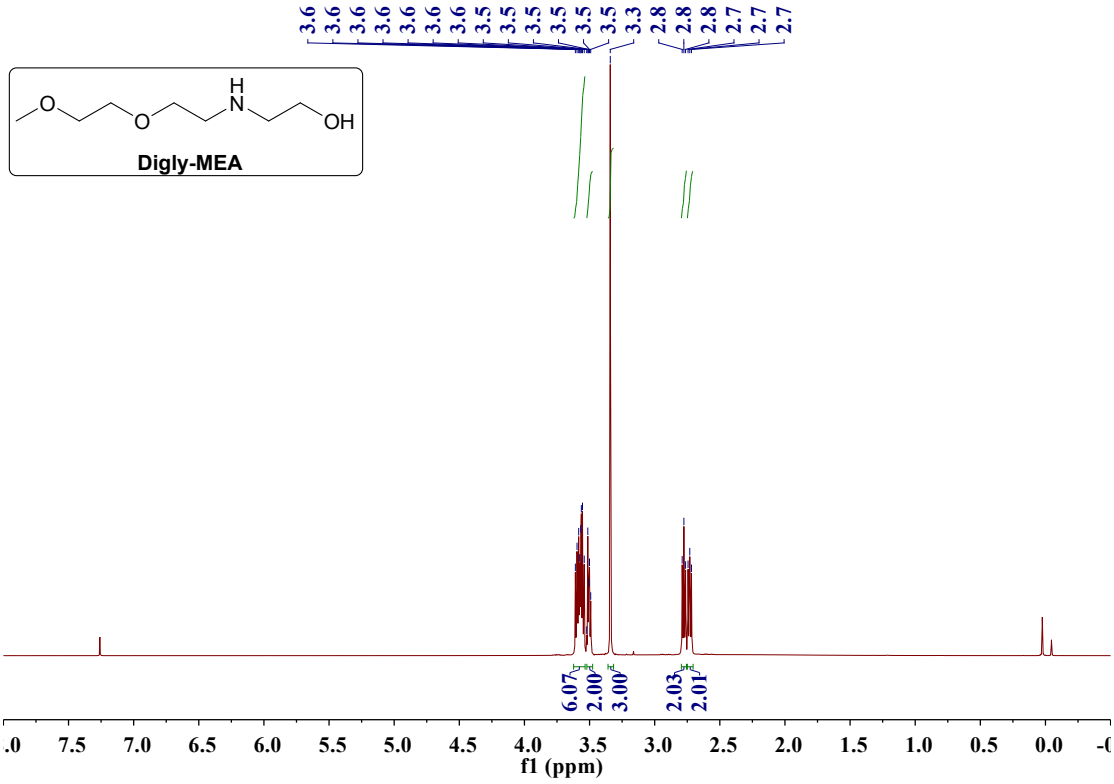

71.5
70.0
60.9
51.3
49.0
31.8
29.7
25.9
22.7
14.1
H
N
O
OH
nHexO-MEA
f1 (ppm)

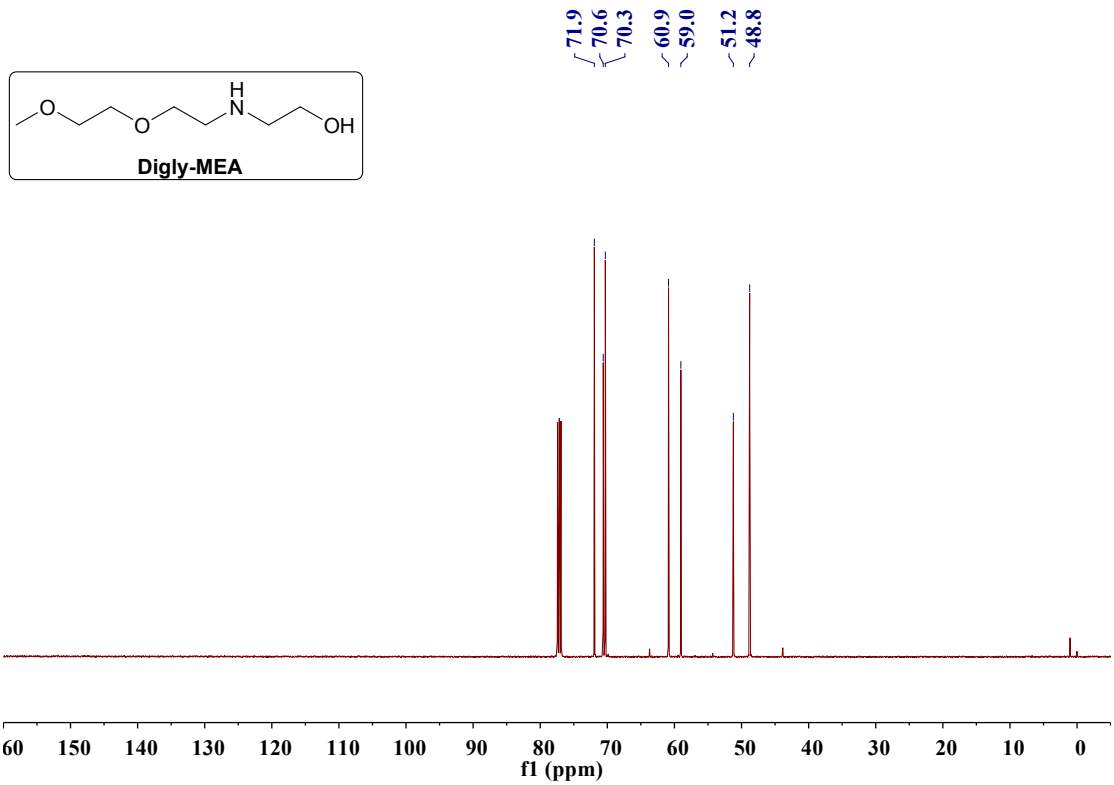

3.6
3.6
3.6
3.6
3.6
3.6
3.5
3.5
3.5
3.5
3.5
2.8
2.8
2.7
1.1
1.1
H
N
O
OH
iPrO-MEA
2.00
1.09
2.03
4.05
6.34
f1 (ppm)

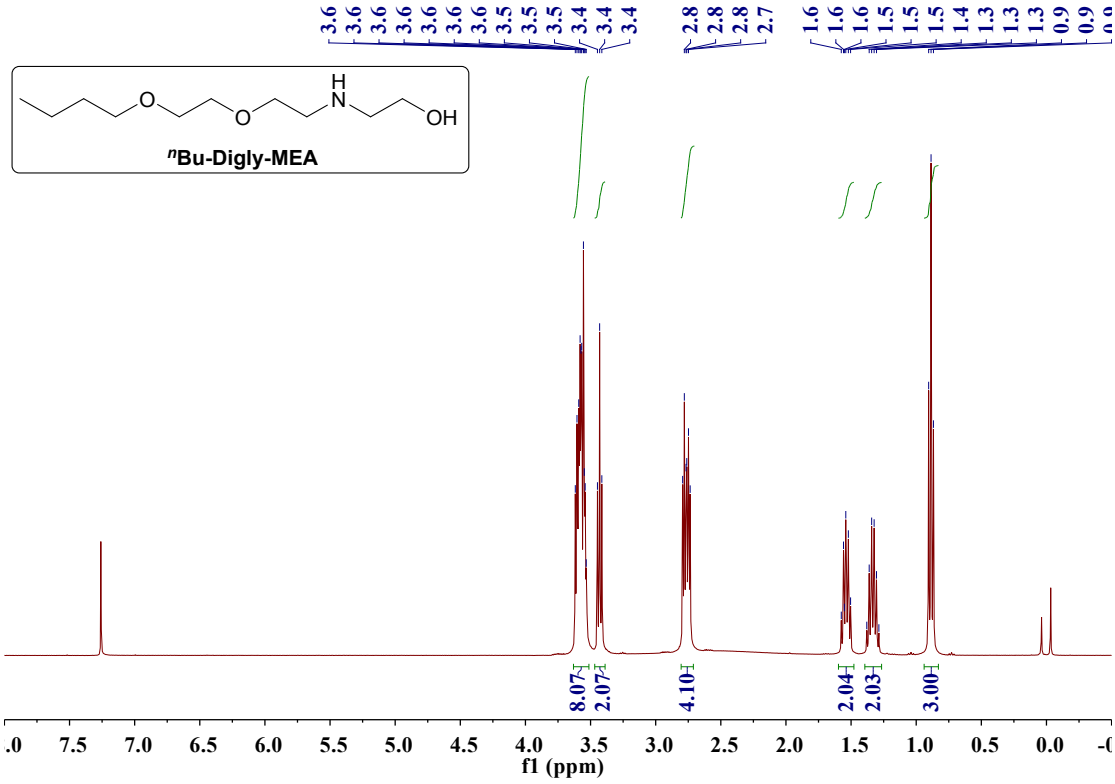

71.8
67.3
60.8
51.3
49.3
22.1
H
N
O
OH
iPrO-MEA
f1 (ppm)

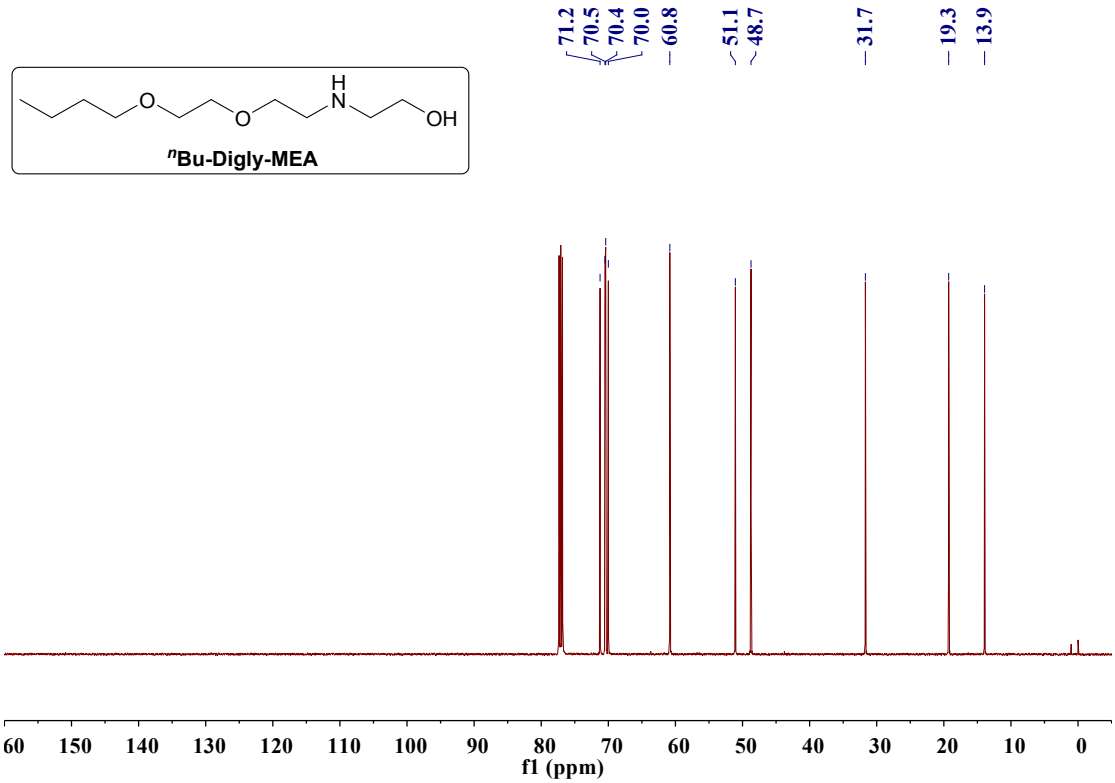

3.6
3.6
3.6
3.5
3.5
3.5
2.8
2.8
2.8
2.8
2.8
2.7
2.7
1.2
1.2
H
N
O
OH
tBuO-MEA
2.00
2.00
4.15
9.25
.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

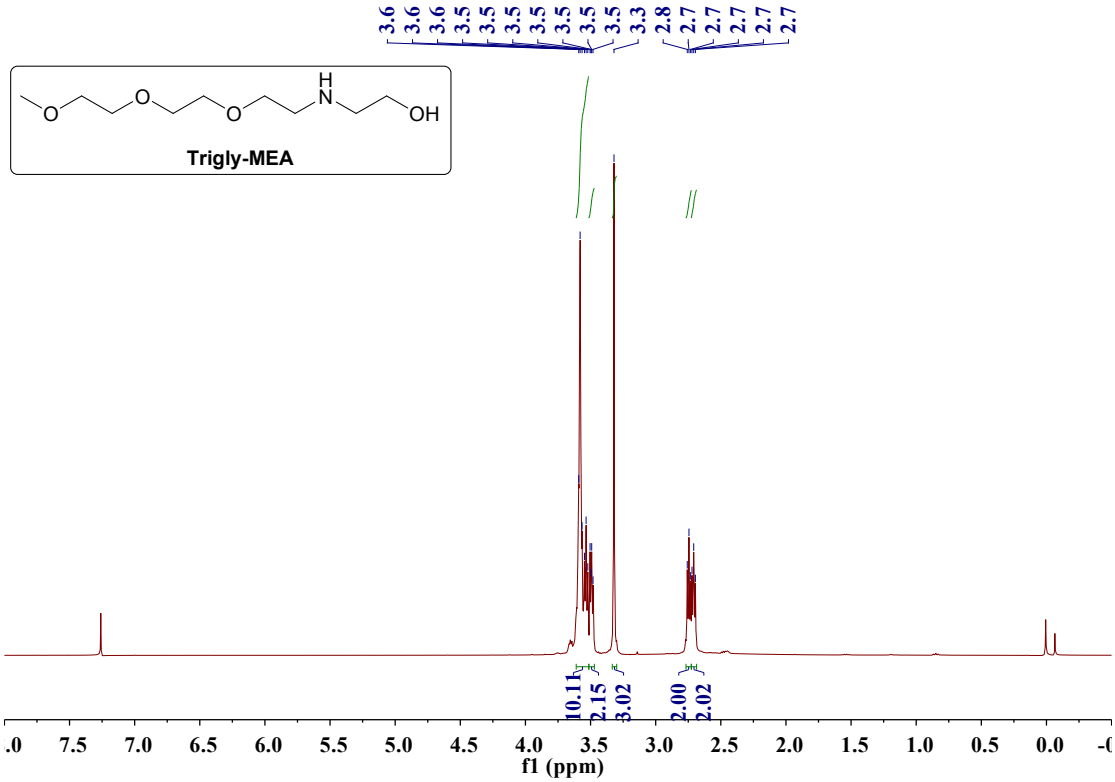

73.0
60.9
51.1
49.6
27.7
H
N
O
OH
tBuO-MEA
60 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

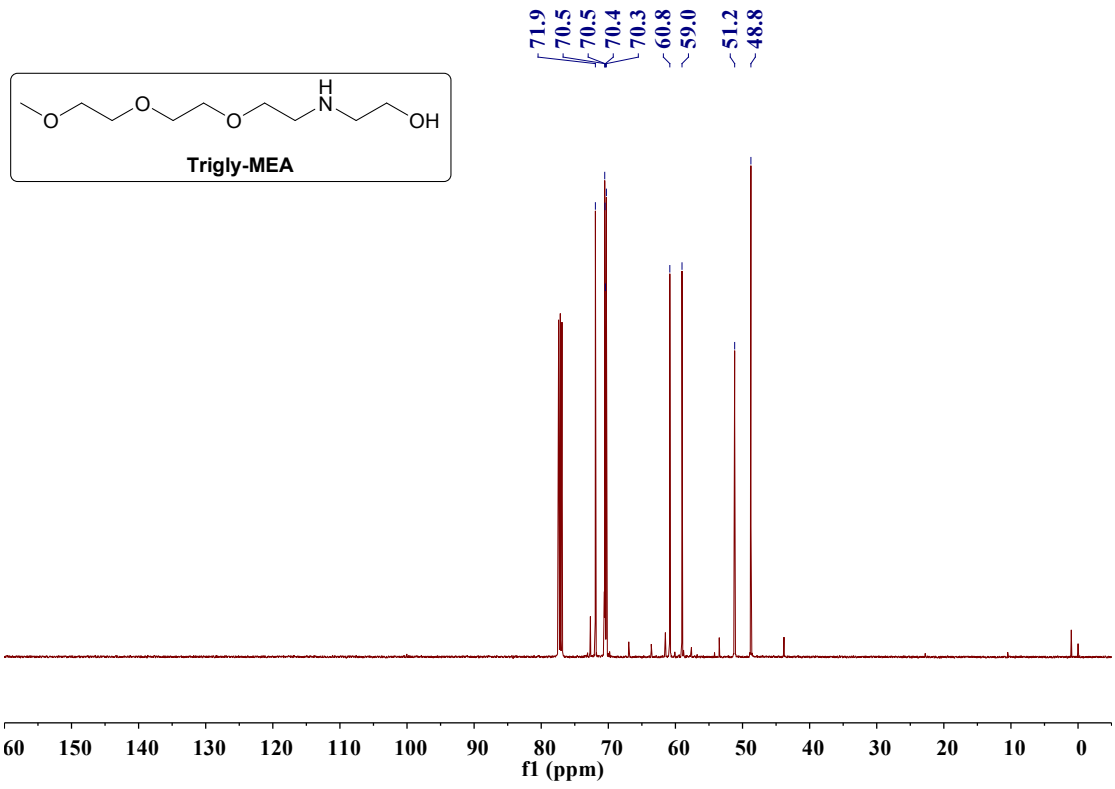

3.6
3.5
3.3
2.8
2.7
H
N
O
OH
Digly-MEA
6.07
2.00
3.00
2.03
2.01
f1 (ppm)

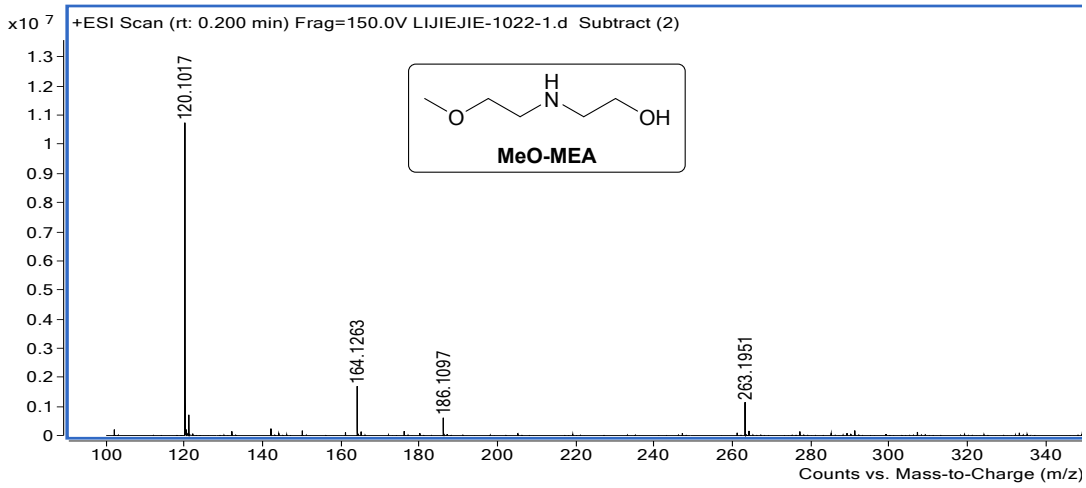

71.9
70.6
70.3
60.9
59.0
51.2
48.8
H
N
O
OH
Digly-MEA
f1 (ppm)

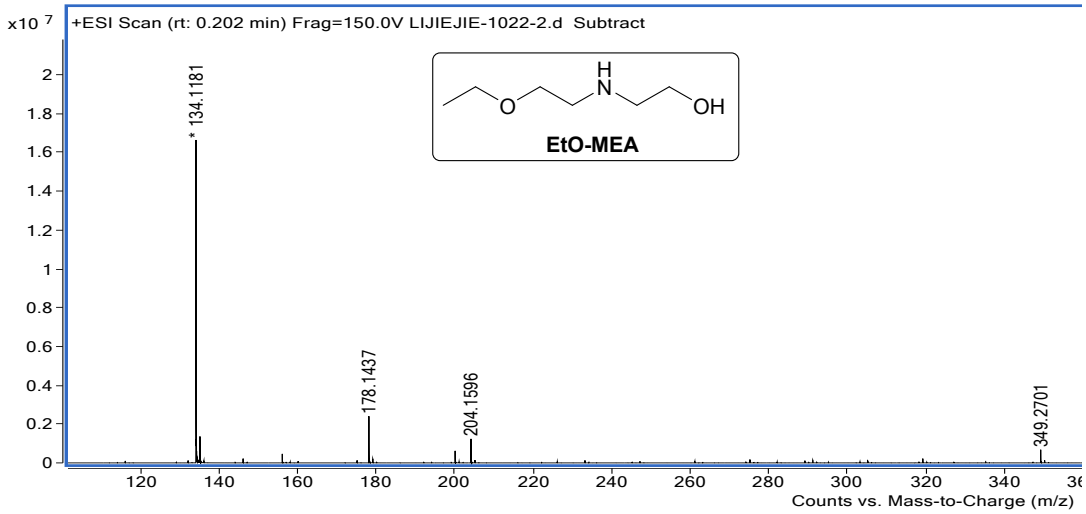

3.6
3.6
3.6
3.6
3.6
3.6
3.6
3.5
3.5
3.5
3.4
3.4
3.4
2.8
2.8
2.8
2.7
1.6
1.6
1.6
1.5
1.5
1.5
1.4
1.3
1.3
1.3
0.9
0.9
H
N
O
O
OH
nBu-Digly-MEA
8.07
2.07
4.10
2.04
2.03
3.00
f1 (ppm)

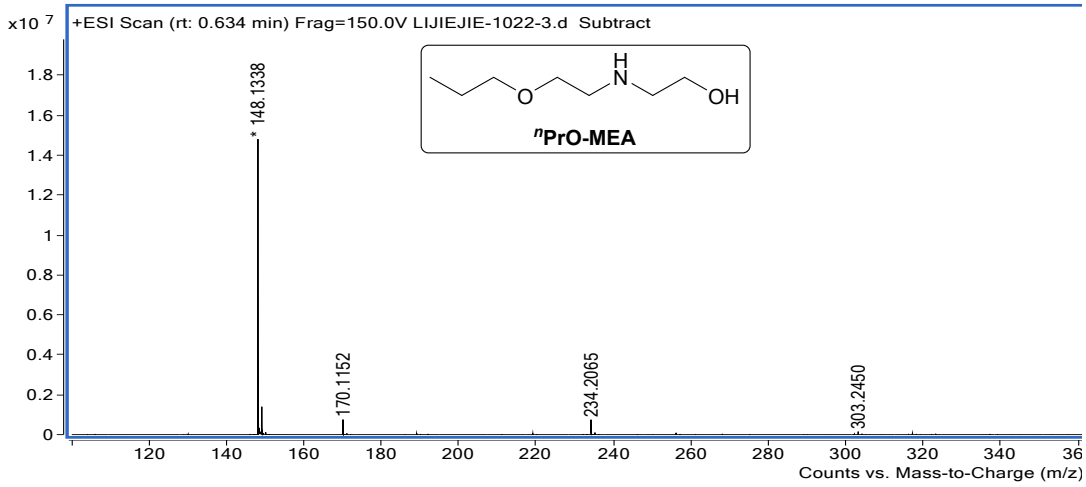

71.2
70.5
70.4
70.0
60.8
51.1
48.7
31.7
19.3
13.9
H
N
O
O
OH
nBu-Digly-MEA
f1 (ppm)

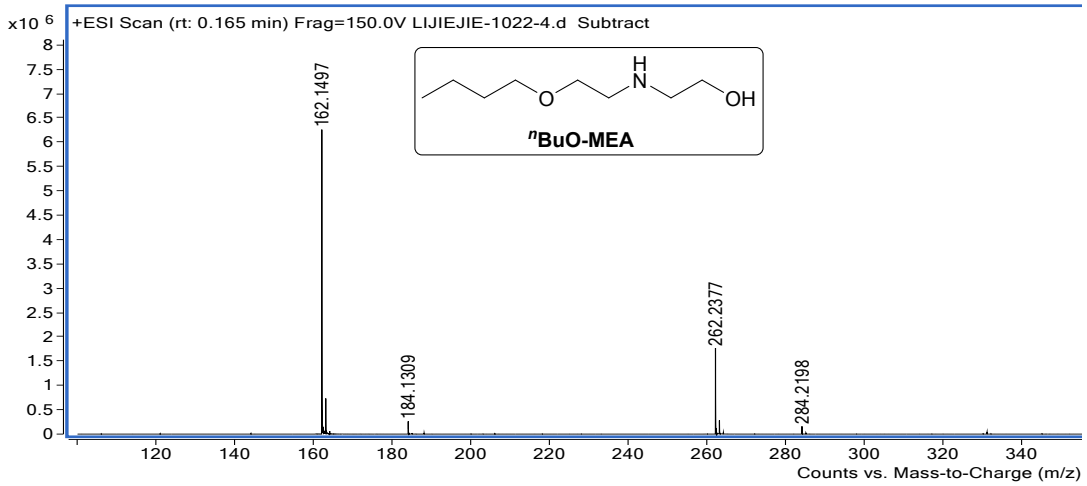

3.6
3.6
3.6
3.5
3.5
3.5
3.5
3.5
3.5
3.3
2.8
2.7
2.7
2.7
2.7
2.7
Trigly-MEA
10.11
2.15
3.02
2.00
2.02
f1 (ppm)

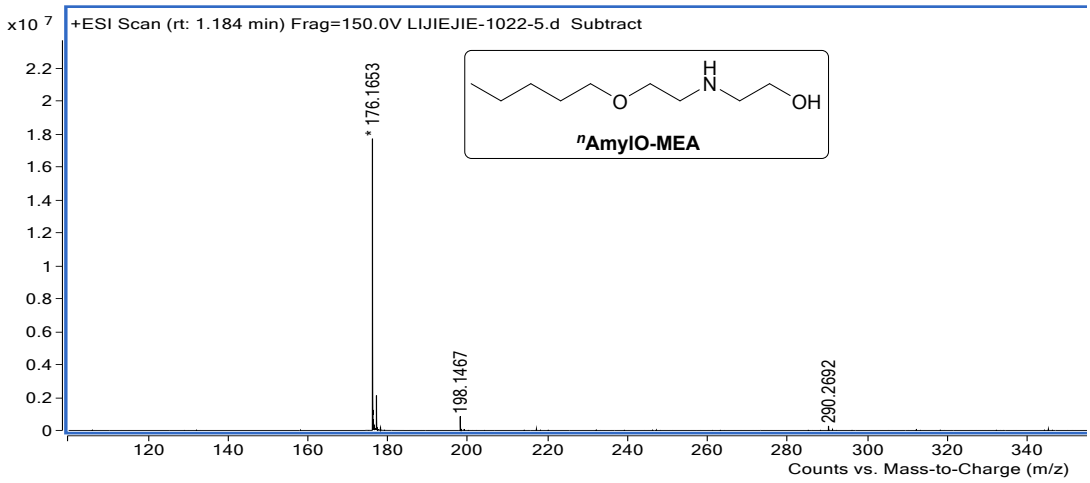

71.9
70.5
70.5
70.4
70.3
60.8
59.0
51.2
48.8
Trigly-MEA
f1 (ppm)

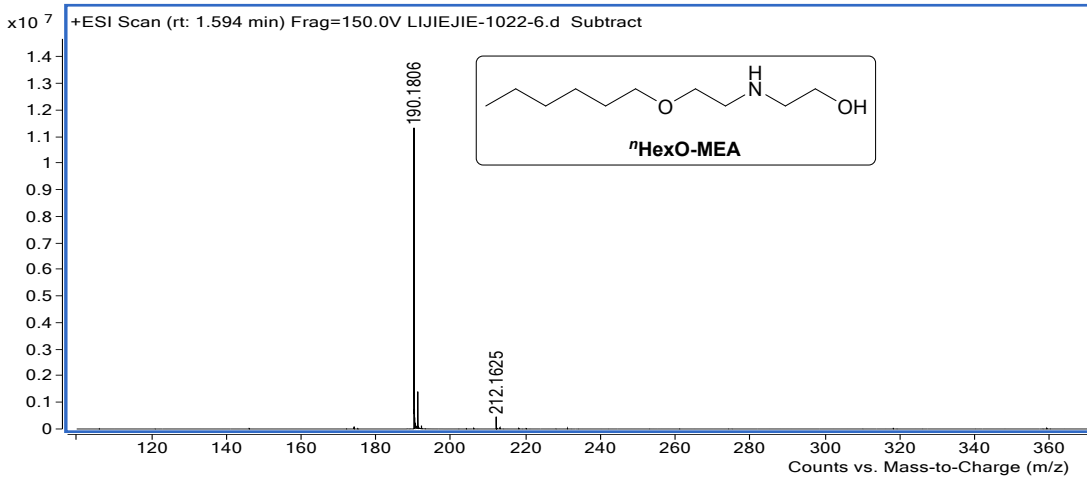

x10 7
+ESI Scan (rt: 0.200 min) Frag=150.0V LIJIEJIE-1022-1.d Subtract (2)
120.1017
164.1263
186.1097
263.1951
MeO-MEA
Counts vs. Mass-to-Charge (m/z)

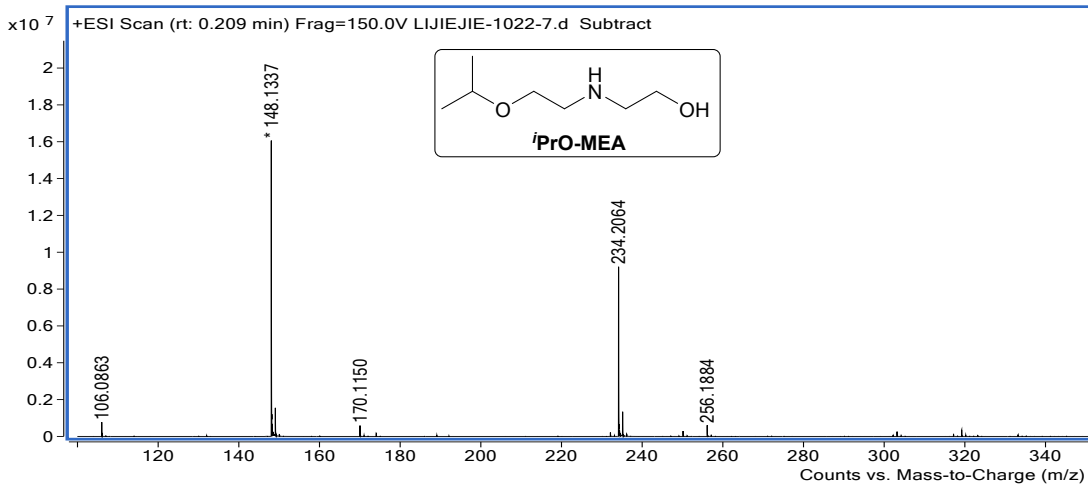

x10 7
+ESI Scan (rt: 0.202 min) Frag=150.0V LIJIEJIE-1022-2.d Subtract
* 134.1181
178.1437
204.1596
349.2701
EtO-MEA
Counts vs. Mass-to-Charge (m/z)

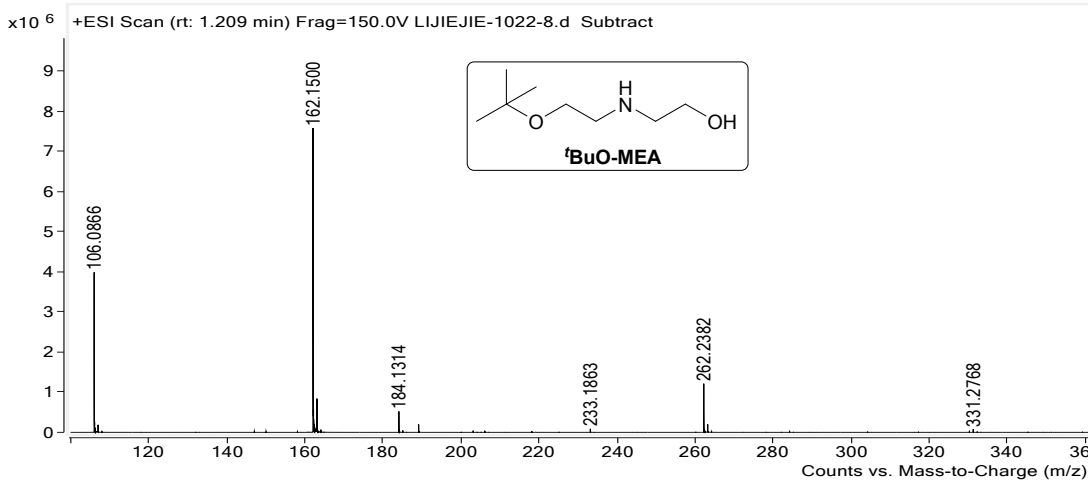

x10 7
+ESI Scan (rt: 0.634 min) Frag=150.0V LIJIEJIE-1022-3.d Subtract
* 148.1338
170.1152
234.2065
303.2450
nPrO-MEA
Counts vs. Mass-to-Charge (m/z)

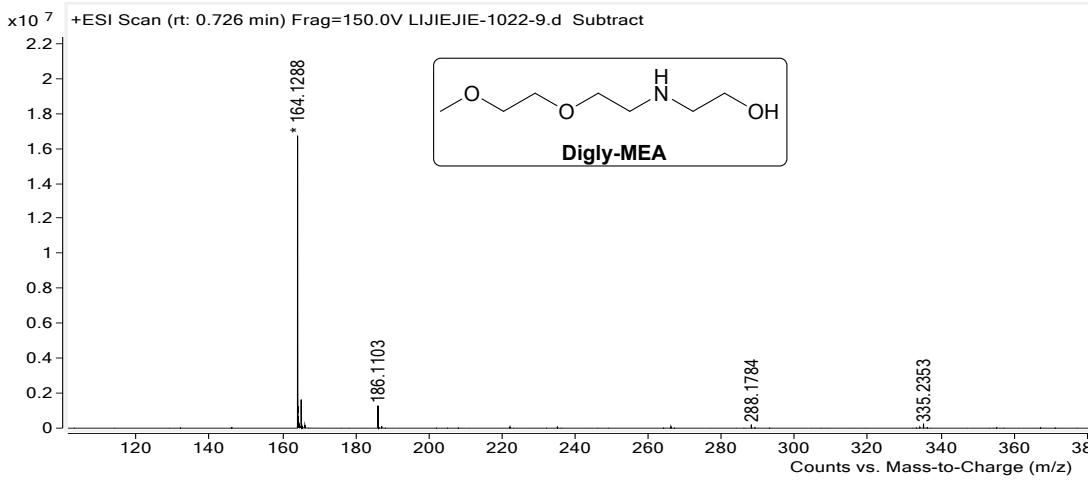

x10 6
+ESI Scan (rt: 0.165 min) Frag=150.0V LIJIEJIE-1022-4.d Subtract
162.1497
184.1309
262.2377
284.2198
nBuO-MEA
Counts vs. Mass-to-Charge (m/z)

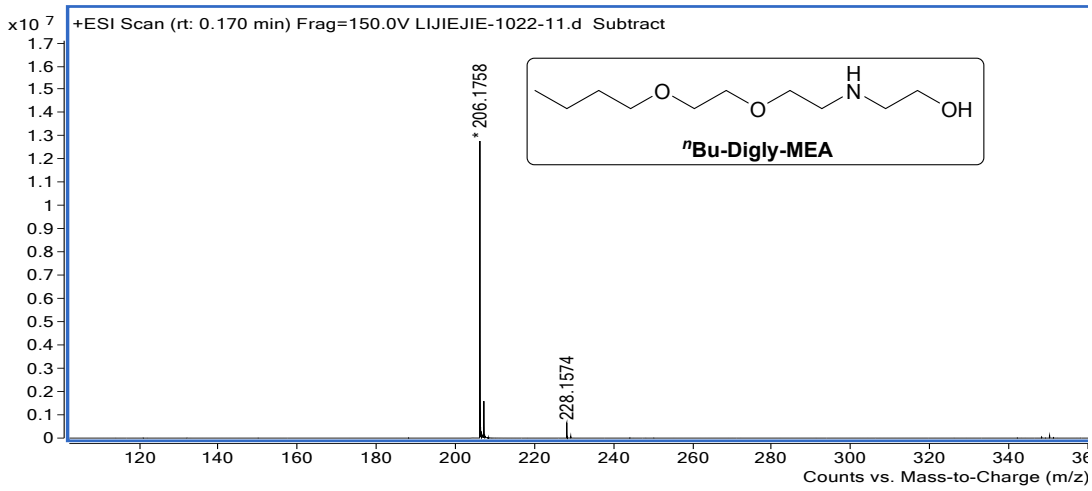

x10 7
+ESI Scan (rt: 1.184 min) Frag=150.0V LIJIEJIE-1022-5.d Subtract
176.1653
198.1467
290.2692
nAmylO-MEA
Counts vs. Mass-to-Charge (m/z)

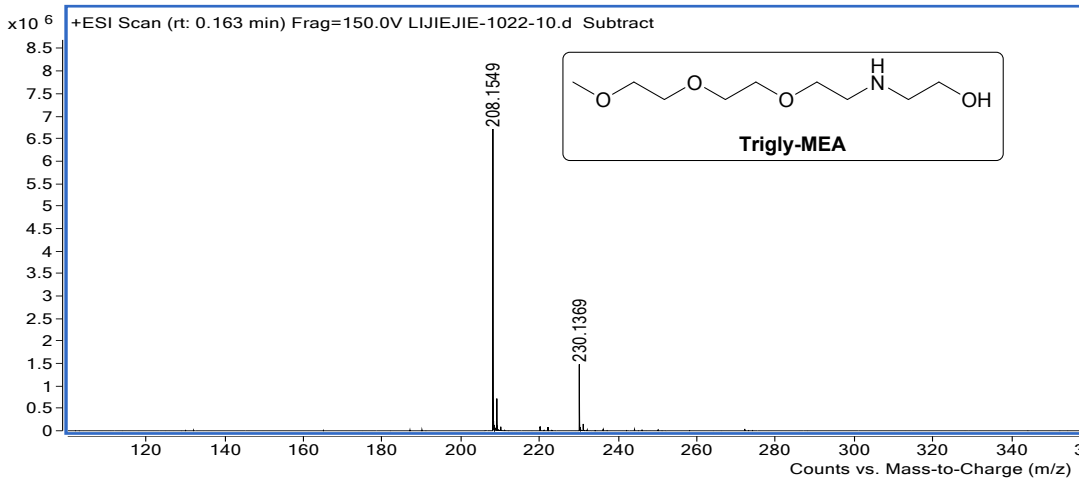

x10 7
+ESI Scan (rt: 1.594 min) Frag=150.0V LIJIEJIE-1022-6.d Subtract
190.1806
212.1625
nHexO-MEA
Counts vs. Mass-to-Charge (m/z)


x10 7
+ESI Scan (rt: 0.209 min) Frag=150.0V LIJIEJIE-1022-7.d Subtract
* 148.1337
234.2064
106.0863
170.1150
256.1884
iPrO-MEA
Counts vs. Mass-to-Charge (m/z)


x10 6
+ESI Scan (rt: 1.209 min) Frag=150.0V LIJIEJIE-1022-8.d Subtract
162.1500
106.0866
184.1314
233.1863
262.2382
331.2768
tBuO-MEA
Counts vs. Mass-to-Charge (m/z)


x10 7
+ESI Scan (rt: 0.726 min) Frag=150.0V LIJIEJIE-1022-9.d Subtract
* 164.1288
186.1103
288.1784
335.2353
Digly-MEA
Counts vs. Mass-to-Charge (m/z)


x10 7
+ESI Scan (rt: 0.170 min) Frag=150.0V LIJIEJIE-1022-11.d Subtract
* 206.1758
228.1574
O
O
H
N
OH
nBu-Digly-MEA
Counts vs. Mass-to-Charge (m/z)


x10 6
+ESI Scan (rt: 0.163 min) Frag=150.0V LIJIEJIE-1022-10.d Subtract
208.1549
230.1369
O
O
O
H
N
OH
Trigly-MEA
Counts vs. Mass-to-Charge (m/z)