

Supporting Information

for

Hexacoordinate Ru-based olefin metathesis catalysts with pH-responsive N-heterocyclic carbene (NHC) and N-donor ligands for ROMP reactions in non-aqueous, aqueous and emulsion conditions

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¹H, ¹³C and ³¹P NMR spectra of the synthesized Ru-complexes 9, 11 and 12 as well as kinetic experimental data

NMR-Spectroscopy (20 °C unless stated otherwise)

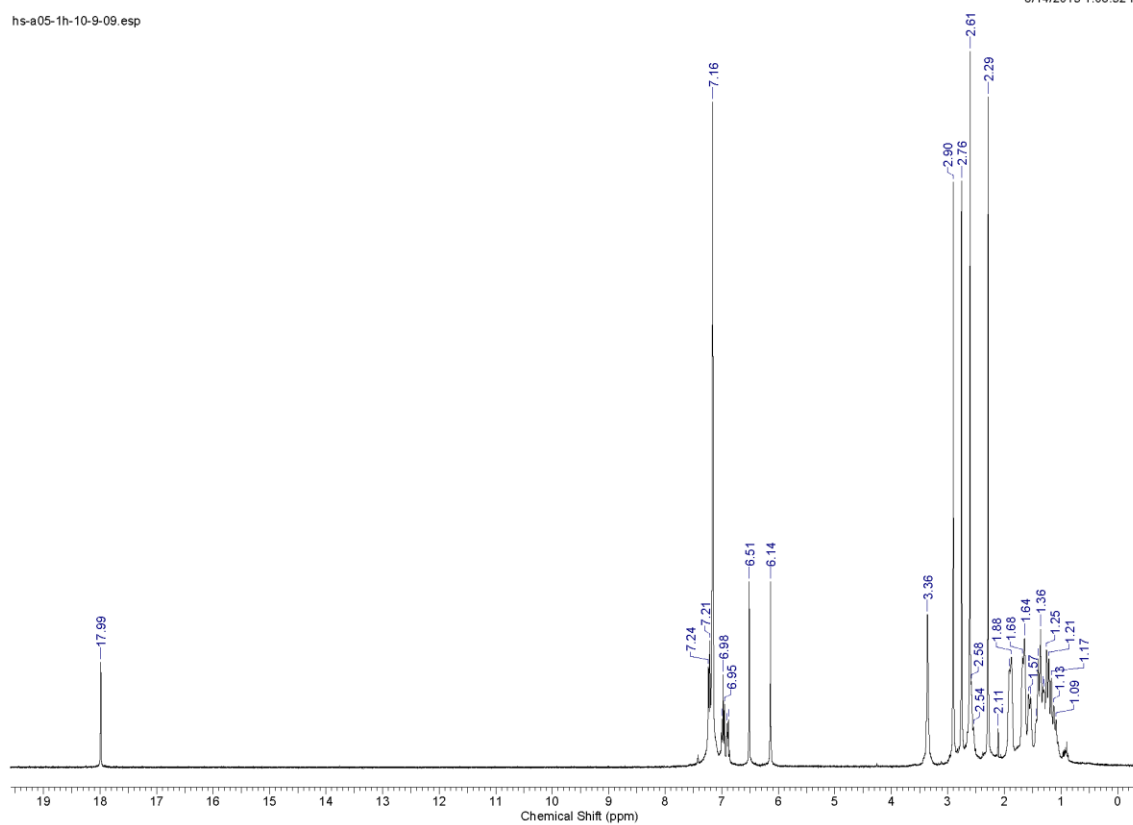
Complex 9

¹H NMR

This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

6/14/2015 1:06:52 PM

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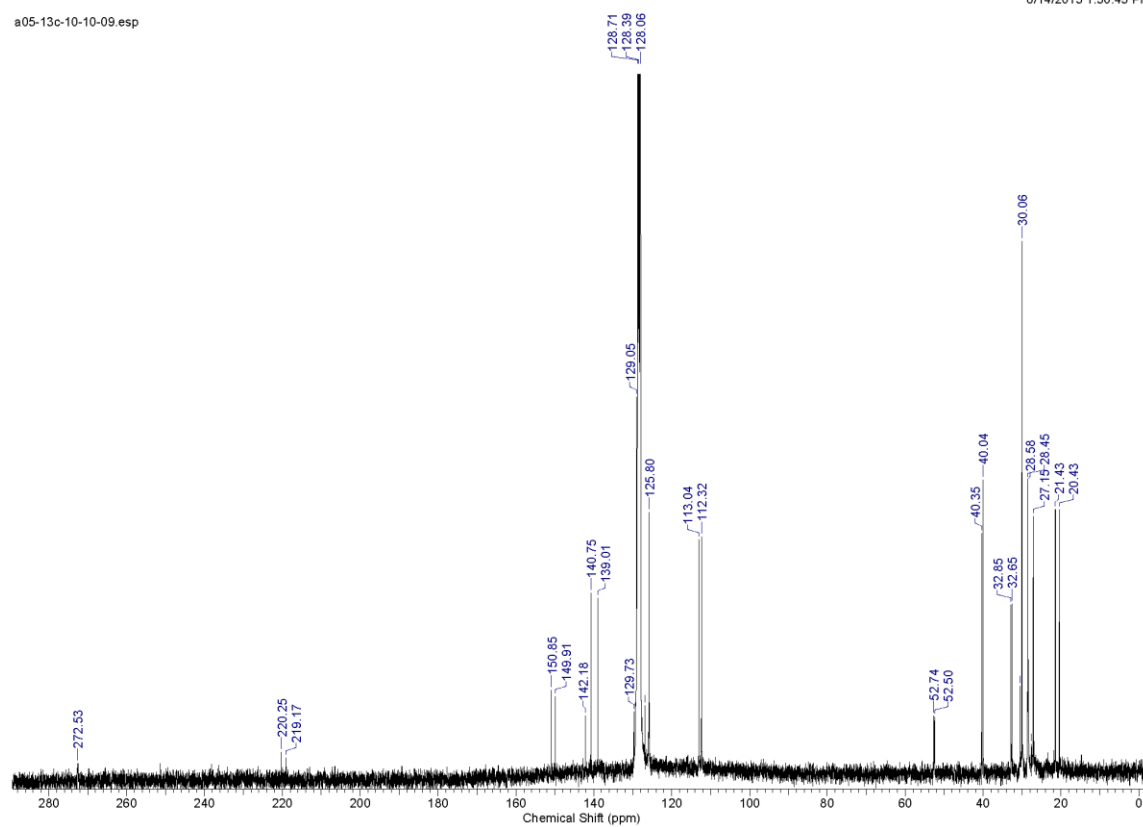


¹³C NMR

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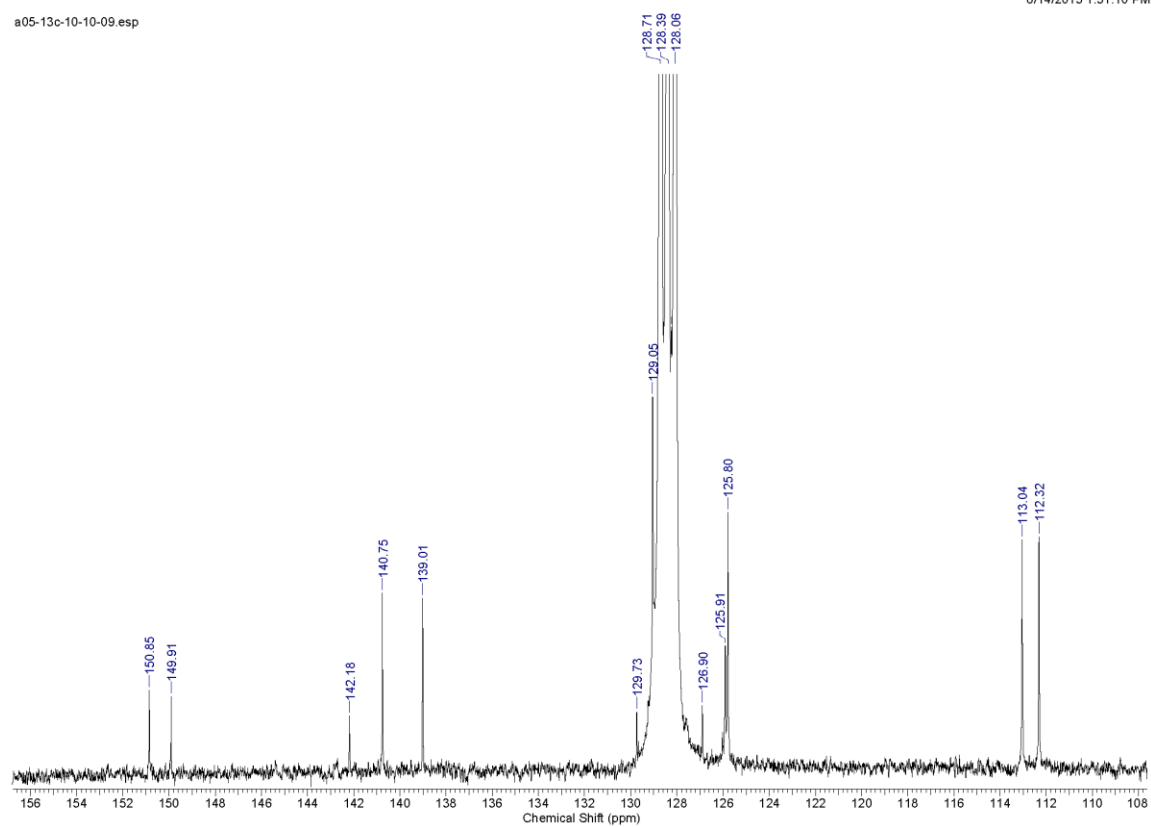


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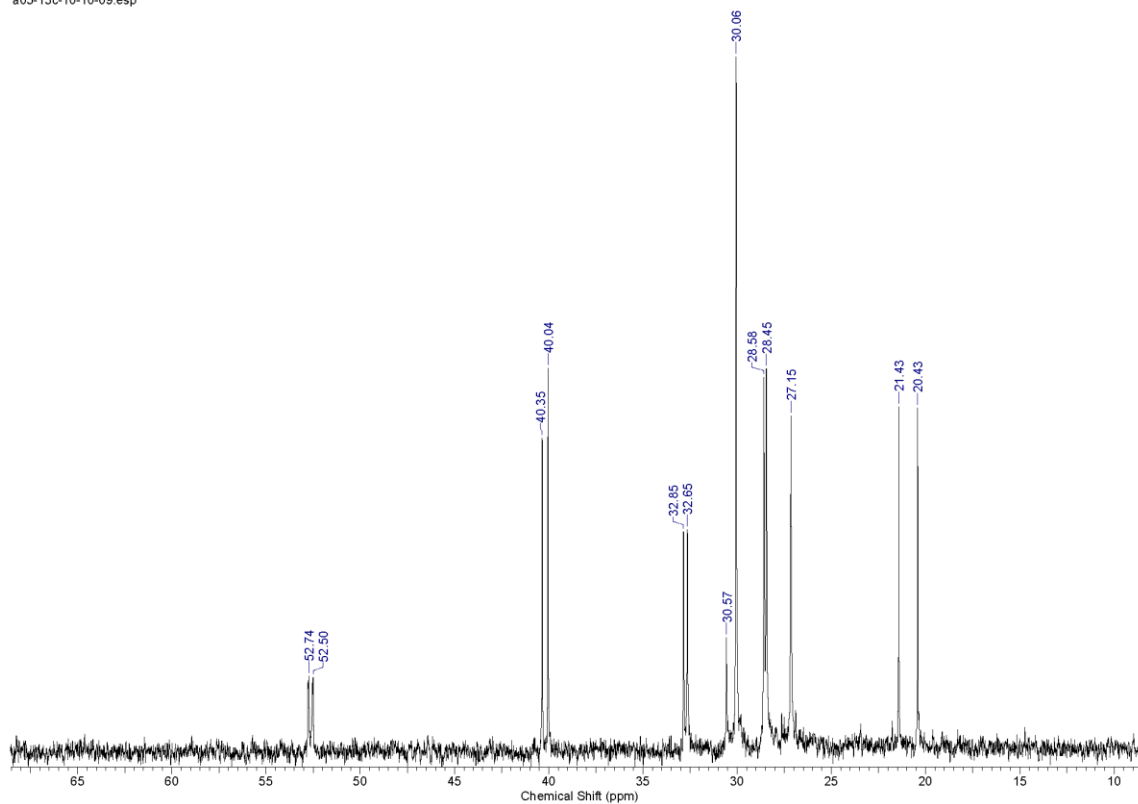
This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

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a05-13c-10-10-09.esp

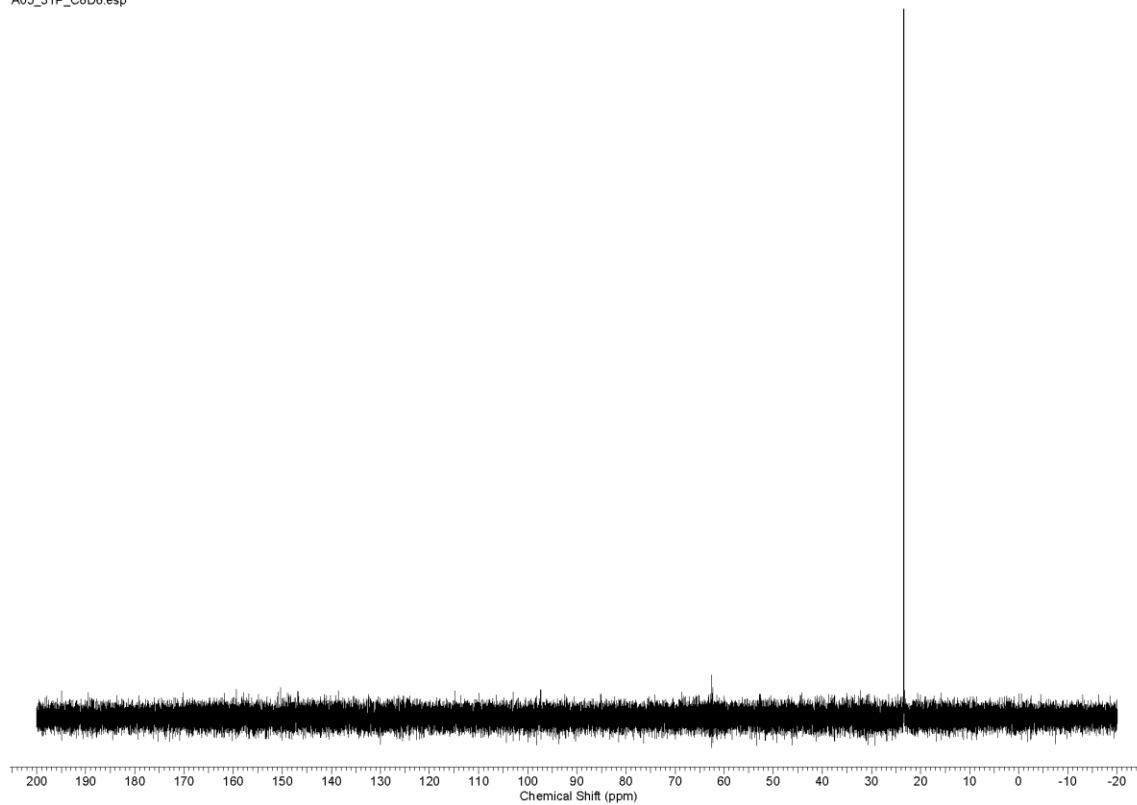


³¹P NMR

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6/14/2015 1:51:07 PM

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Complex 11

¹H NMR

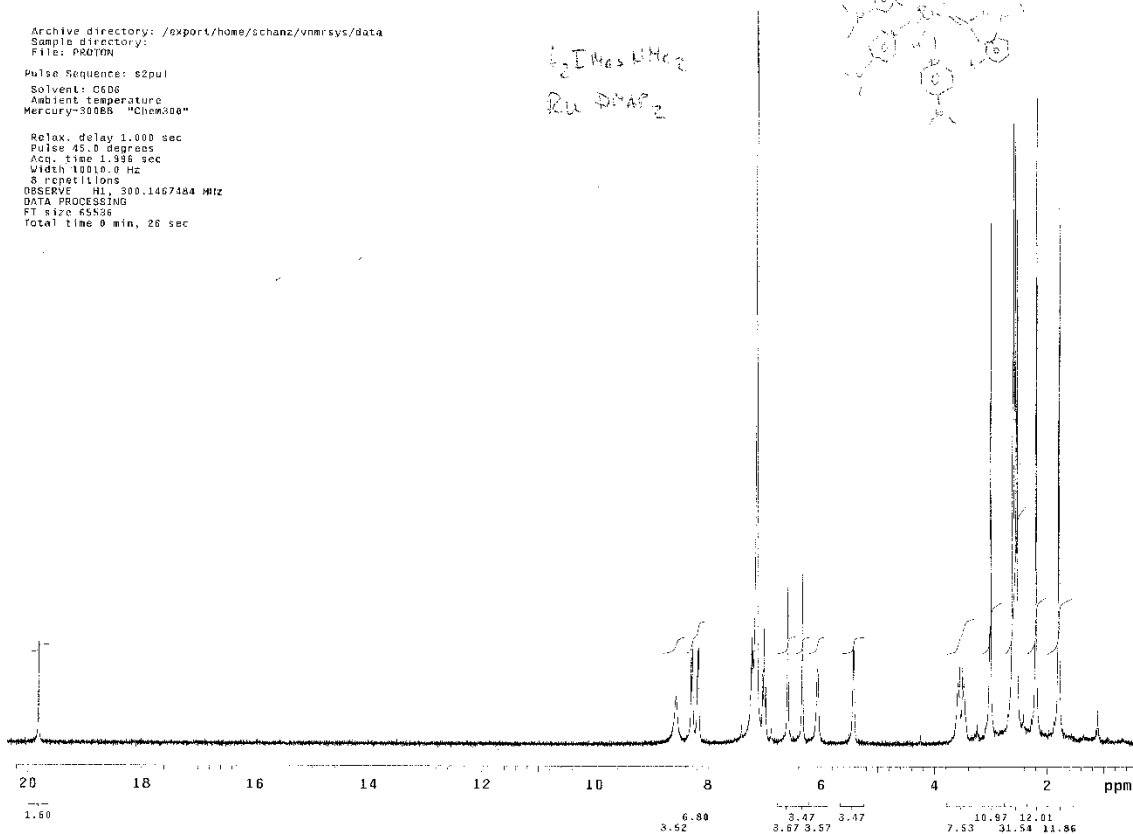
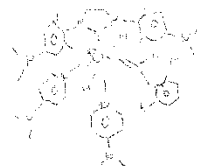
AP0101-0001-001

Archive directory: /export/home/schanz/vnmr/sys/data
Sample directory:
File: PROTON

Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
Mercury-30088 "Chem300"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.999 sec
Width 10010.0 Hz
8 repetitions
OBSERVE F1: 300.1467184 MHz
DATA PROCESSING
FT size 65436
Total time 0 min, 26 sec

$\frac{1}{2}$ I Mas 4MHz
Ru DMAP₂

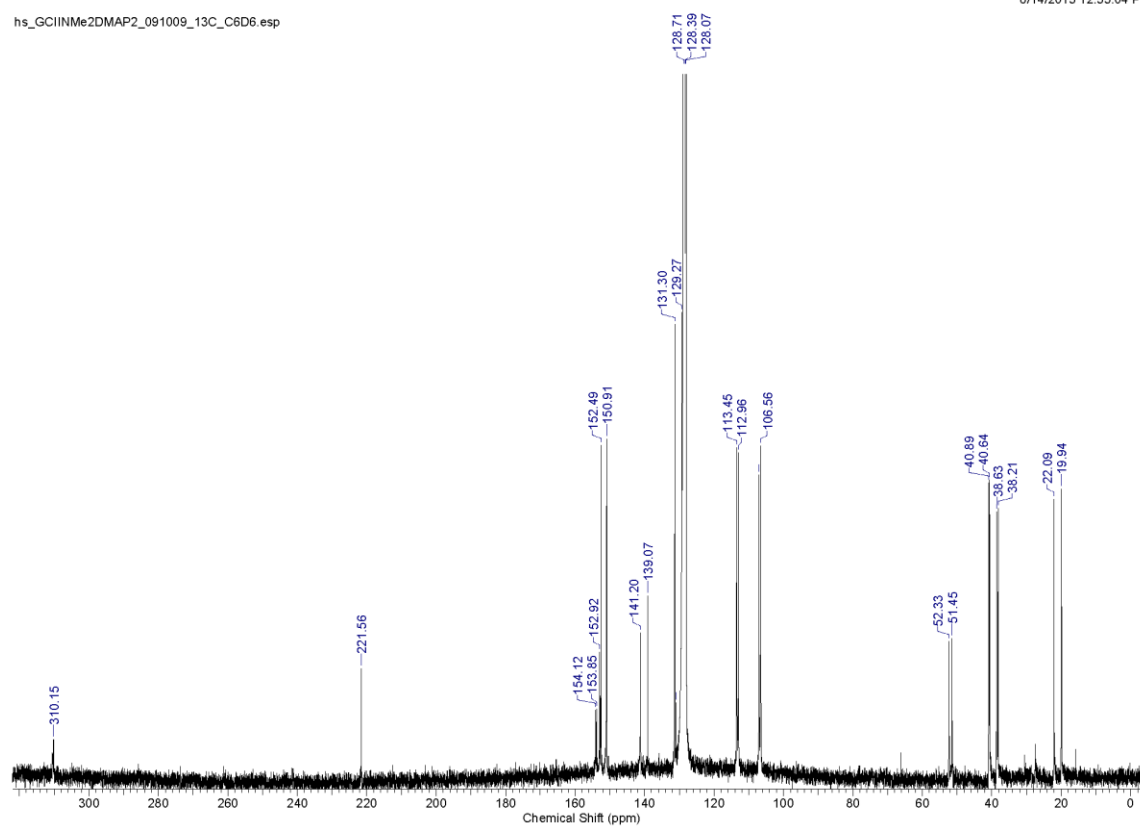


¹³C NMR

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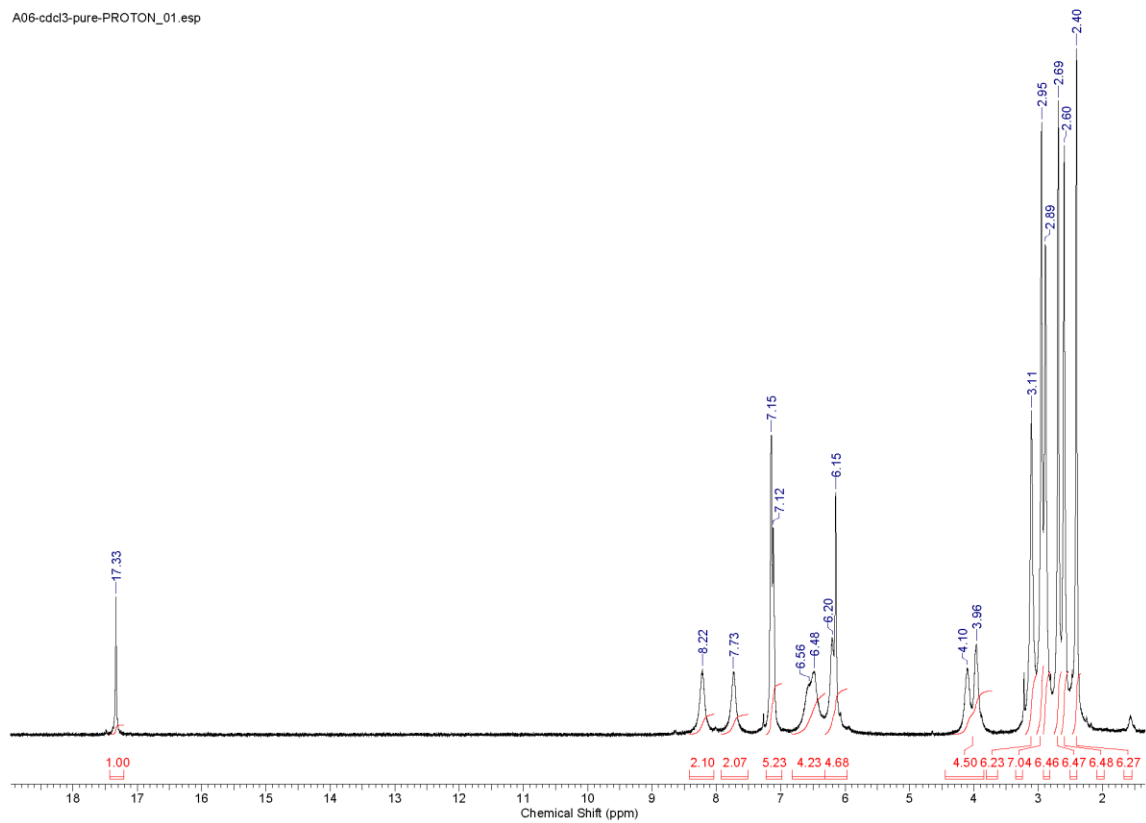
Complex 12

¹H NMR

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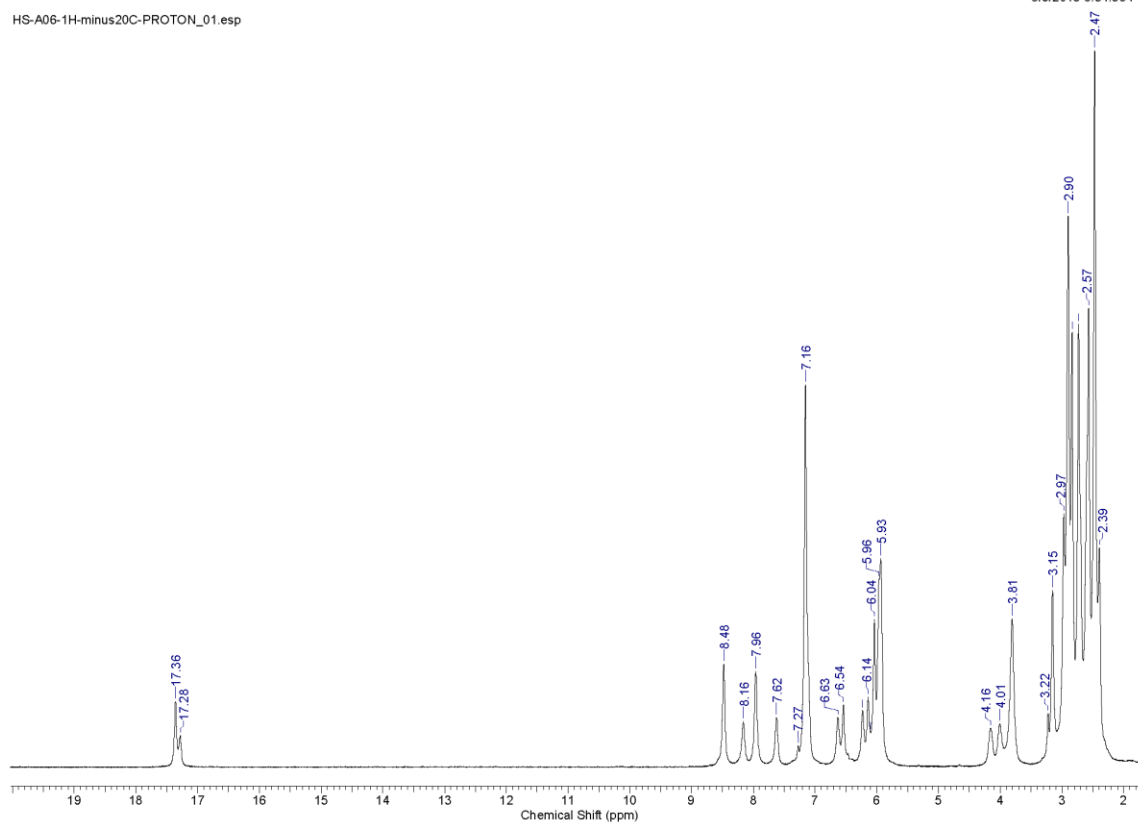


^1H NMR (-20 °C)

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8/9/2015 6:54:56 PM

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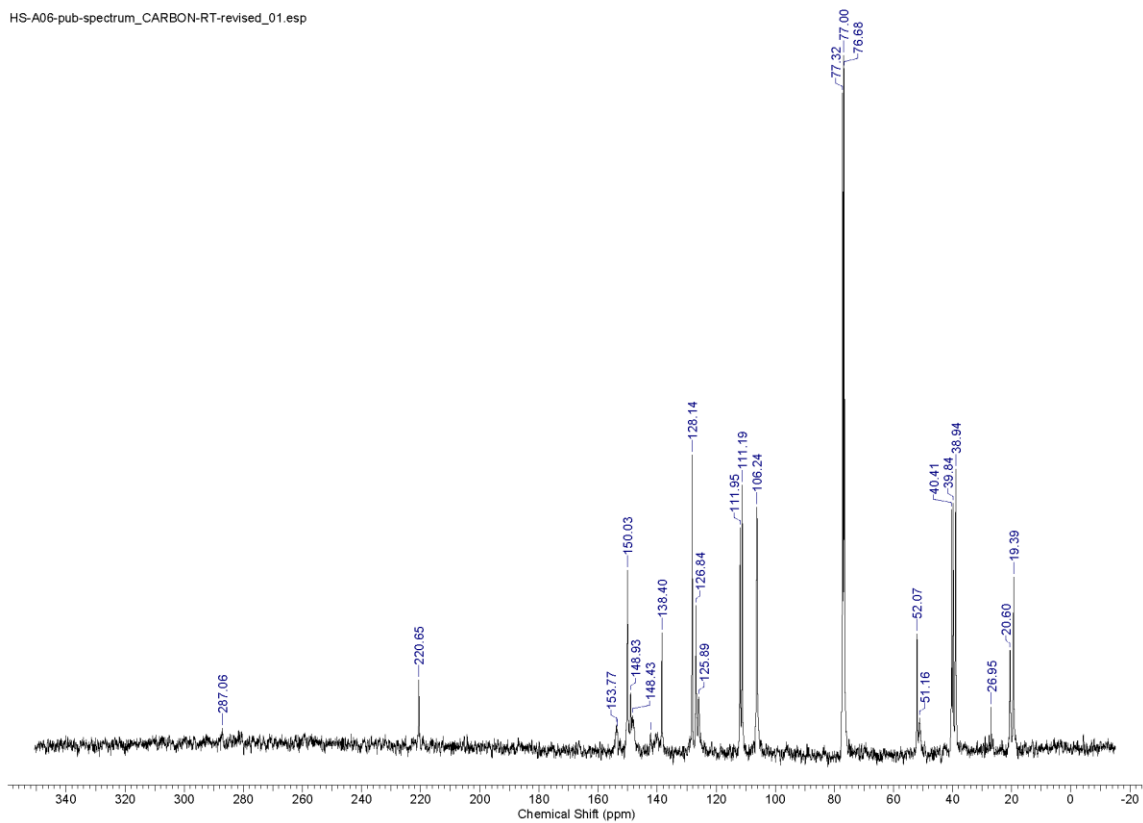


¹³C NMR

This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

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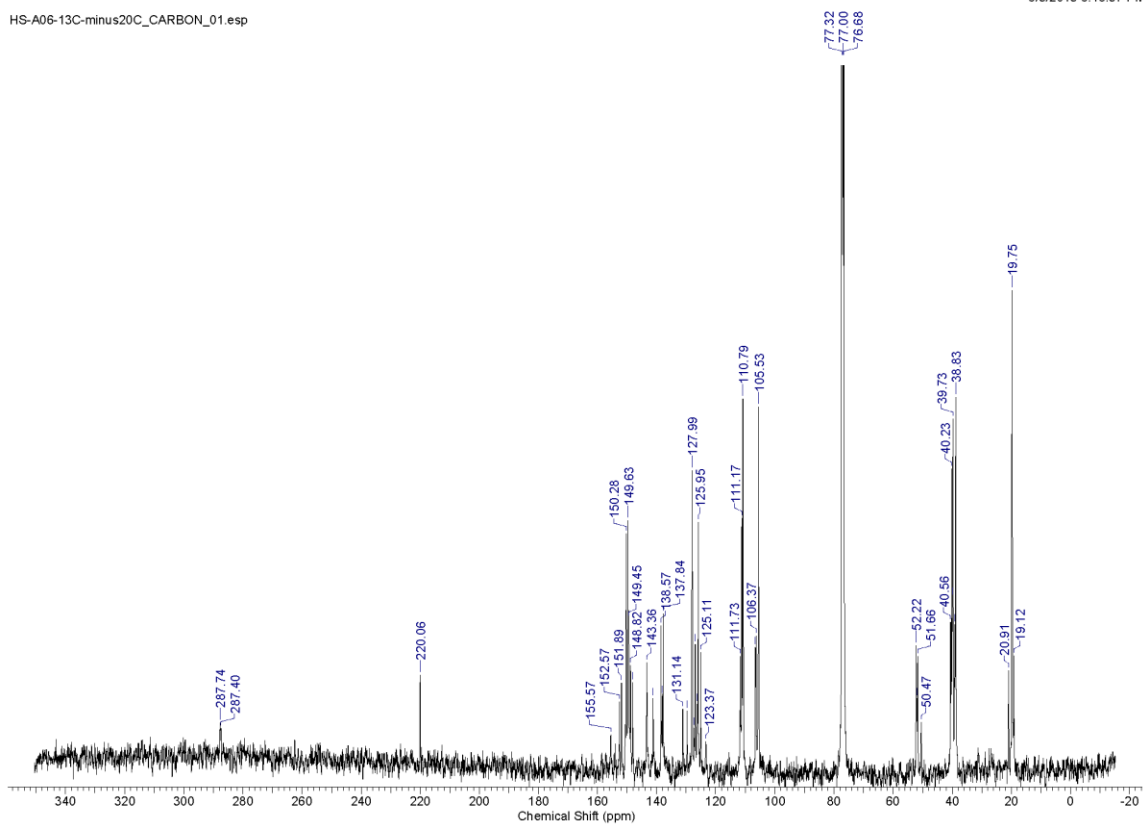


¹³C NMR (-20 °C)

This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

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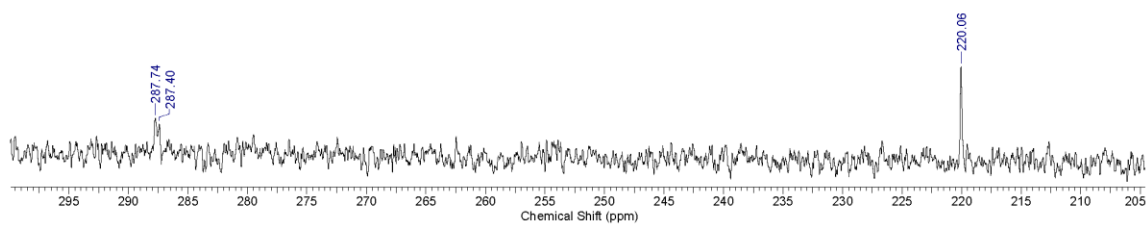


Expanded Spectra

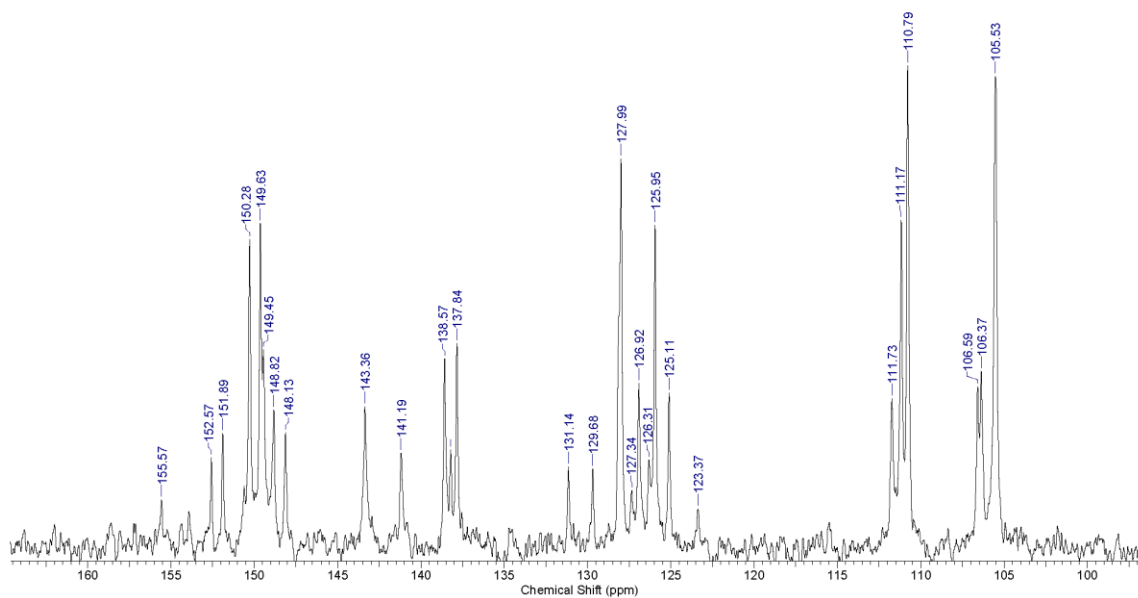
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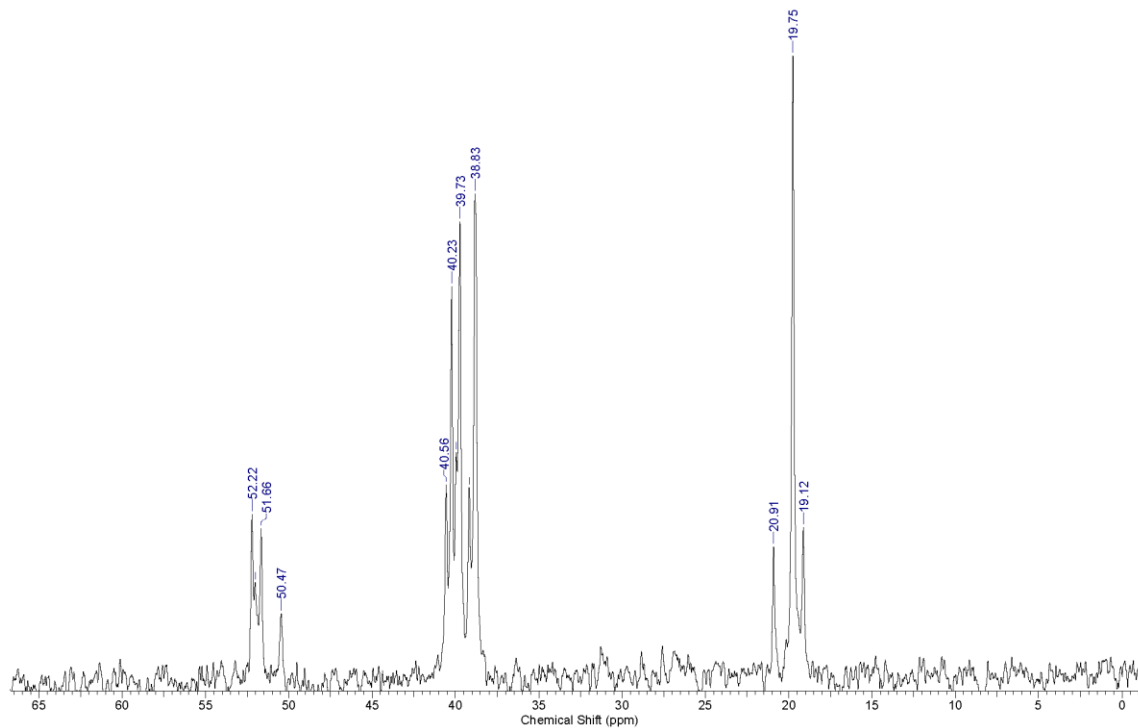
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HS-A06-13C-minus20C_CARBON_01.esp



HS-A06-13C-minus20C-CARBON_01.esp



Kinetic Data

ROMP of COE

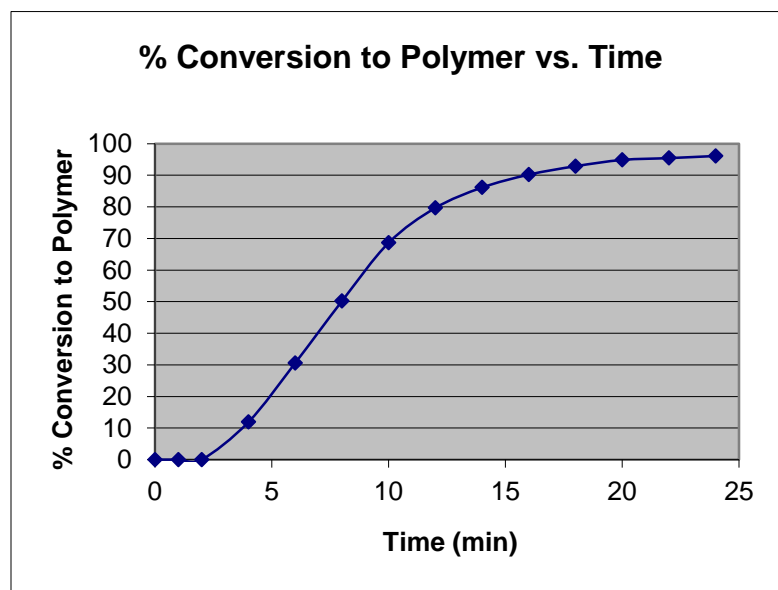
Catalyst 9

Room Temperature

0.8% conversion after 1 hour

At 60 degrees C

t (min.)	% conversion
0	0
1	0
2	0
4	11.89
6	30.56
8	50.13
10	68.6
12	79.64
14	86.1
16	90.18
18	92.85
20	94.84
22	95.42
24	96.09



Catalyst 11

DMAP catalyst (no acid)

t (min)	% Conversion to Polymer
0	0
4	39.25
8	60.89
10	71.33
13	80.99
16	90.17
19	93.43

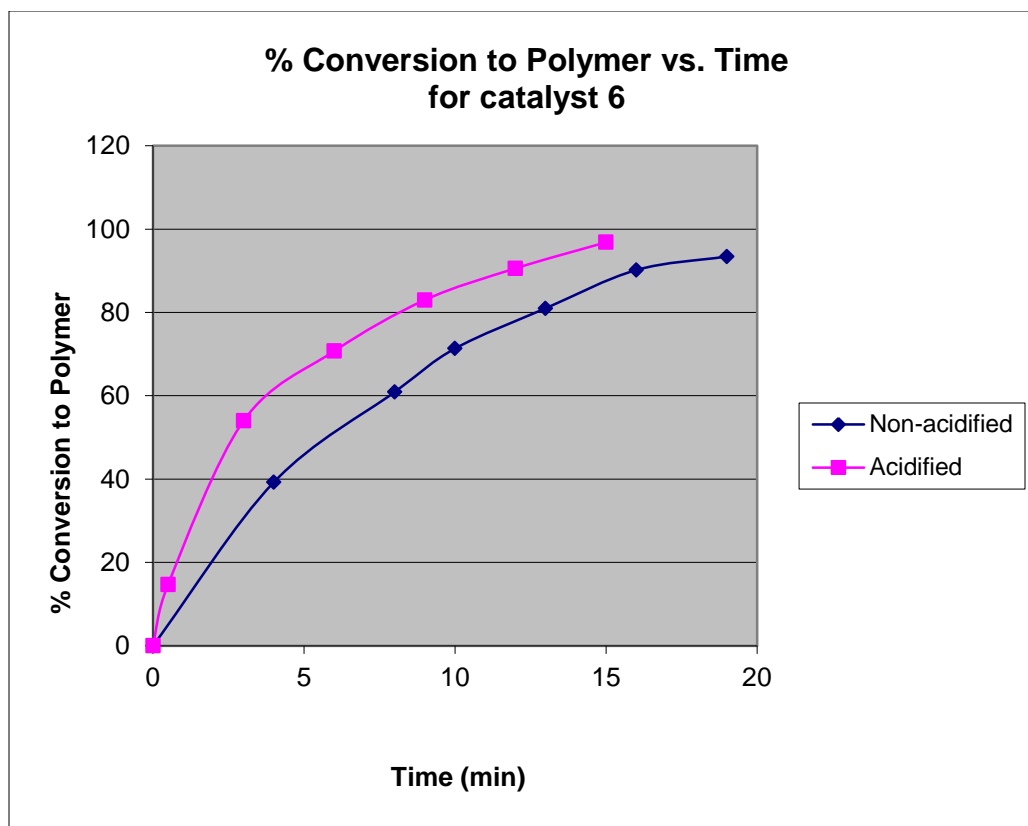
DMAP catalyst (+ 2 equiv H₃PO₄)

T (min)	% Conversion to Polymer
0	0
1	28.62
3	54
6	70.72
9	82.99
12	90.57
15	96.84

DMAP catalyst (+ 2 equiv H₃PO₄)

t (min)	% Conversion to Polymer
0	0
1	11.33
3	21.21
6	27.98
9	32.37
12	35.8
30	40.76

no change after 30 min.



Catalyst 12

Room Temperature

No acid-- 3.91% conversion after 1 hour

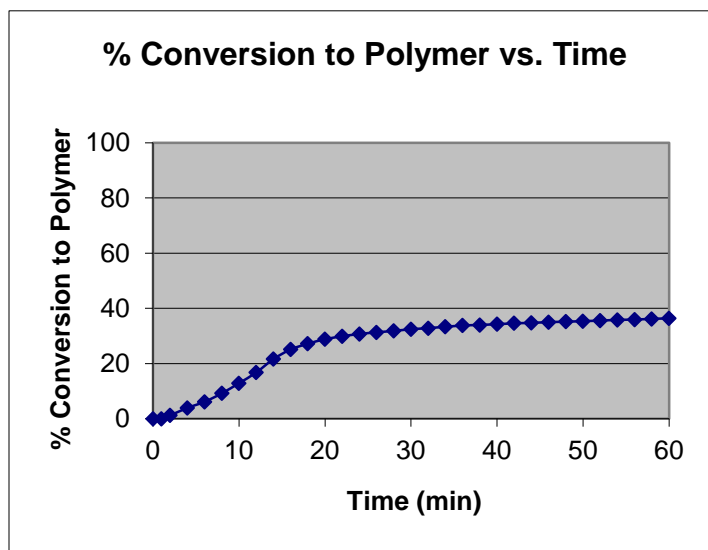
with 2 equiv H₃PO₄ 0.9% conversion after 1 hour

At 60 degrees

C

t (min.)	% Conversion
0	0
1	0
2	1.21
4	3.89
6	6.12
8	9.18
10	12.86
12	16.73

14	21.58
16	25.07
18	27.15
20	28.78
22	29.84
24	30.69
26	31.28
28	31.81
30	32.4
32	32.81
34	33.29
36	33.75
38	33.97
40	34.22
42	34.56
44	34.71
46	34.98
48	35.14
50	35.33
52	35.54
54	35.79
56	35.91
58	36.17
60	36.34
120	37.78
180	no change



RCM of DEDAM

Catalyst 10

RCM of DEDAM

1.0 mM solution in C6D6

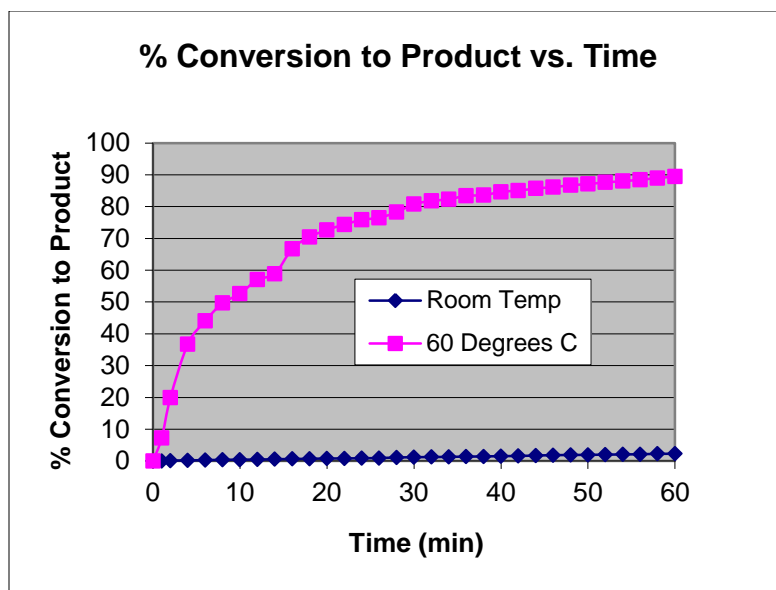
1.0% catalyst loading

Room Temperature

t (min.)	% Conversion
0	0
1	0
2	0.12
4	0.2
6	0.27
8	0.37
10	0.42
12	0.45
14	0.56
16	0.63
18	0.7
20	0.78
22	0.81
24	0.87
26	0.93
28	1.1
30	1.19
32	1.24
34	1.29
36	1.38
38	1.43
40	1.53
42	1.58
44	1.72
46	1.83
48	1.89
50	1.93
52	2
54	2.06
56	2.13
58	2.24
60	2.27

At 60 degrees C

T (min.)	% Conversion
0	0
1	7.23
2	19.9
4	36.72
6	44.05
8	49.64
10	52.6
12	57.04
14	58.87
16	66.73
18	70.46
20	72.67
22	74.35
24	75.86
26	76.48
28	78.23
30	80.79
32	81.76
34	82.33
36	83.39
38	83.59
40	84.62
42	85.05
44	85.67
46	86.15
48	86.68
50	87.12
52	87.59
54	88.01
56	88.43
58	88.98
60	89.43
120	93.98



Catalyst 11

RCM of
DEDAM

1.0 mM solution in
C6D6
1.0% catalyst loading

Room Temperature

No acid-- 7.2% conversion after 0.5 hours

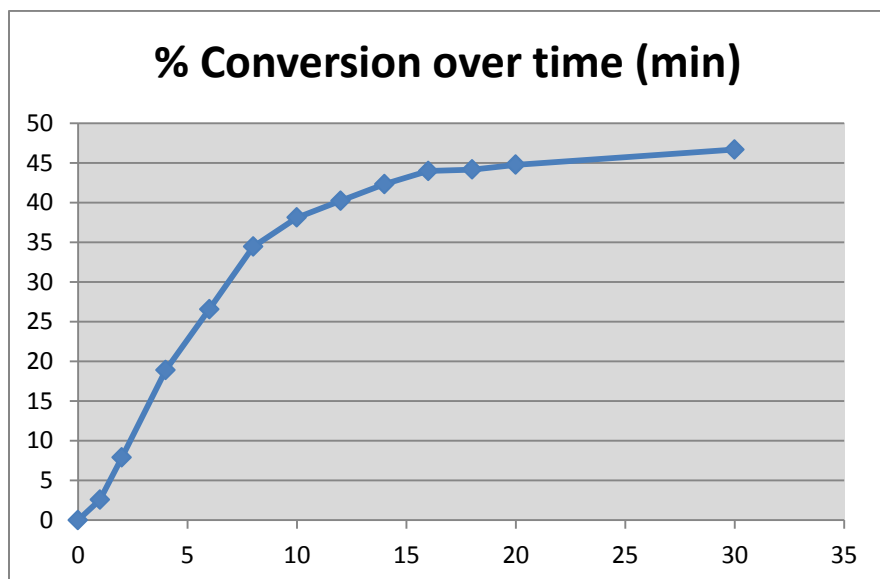
with 2 equiv

H₃PO₄

t (min.)	% Conversion
0	0
1	2.55
2	7.90
4	18.90
6	26.56
8	34.44
10	38.11
12	40.23
14	42.32
16	43.98
18	44.15
20	44.76
30	46.67
60	47.43
120	47.35

with 4 equiv
H₃PO₄

t (min.)	% Conversion
0	0
1	1.85
2	4.66
4	7.21
6	8.31
8	8.93
10	9.15
30	13.76
60	No change



Catalyst 12

RCM of
DEDAM

1.0 mM solution in
C₆D₆
1.0% catalyst loading

Room Temperature

No acid-- 1.22% conversion after 1 hour

At 60 degrees

C

t (min.)	% Conversion
0	0
1	1.27
2	5.43

4	10.19
6	18.53
8	24.68
10	30.25
12	33.19
14	37.42
16	39.64
18	41.68
20	43.4
22	45.16
24	46.69
26	47.53
28	48.62
30	49.67
32	50.53
34	51.52
36	52.39
38	53.11
40	53.98
42	54.66
44	54.91
46	55.15
48	55.83
50	56.11
52	56.46
54	56.79
56	56.98
58	57.02
60	57.23
120	60.21
180	61.09
240	no change

