Separation, recovery and reuse of *N*-heterocyclic carbene catalysts in transesterification reactions

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Supporting information

General information：

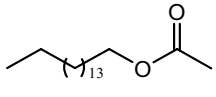
All catalyzed reactions were carried out under an inert atmosphere of argon by Schlenk techniques. Benzene was distilled from sodium and benzophenone under argon and stored over molecular sieves. Potassium *tert*-butoxide was stored under argon in a glovebox. All esters and alcohols purchased from Sigma-Aldrich were degassed prior to use. ^{1}H NMR and ^{13}C NMR spectra were acquired by Varian Mercury (400 and 100 MHz, respectively). Thin layer chromatography was performed by using SiliCycle Silica Gel 60 F_{254} TLC plates. Flash column chromatography was performed over SiliCycle silica gel 40-63 μm. N-Heterocyclic carbenes were synthesized according to literature procedures.[1]

General procedure: The NHC-catalyzed transesterification/acylation reaction:

Under an atmosphere of argon, an oven-dried reaction vessel was charged with potassium *tert*-butoxide (11.2 mg, 0.1 mmol), IMes·HCl (51.1 mg, 0.15 mmol) and benzne (5 mL). The mixture was stirred at room temperature for 1 h. Then alcohol (1 mmol) and ester (5 mmol) were added sequentially. The resulting mixture was stirred at 80 °C for 10 h. After cooling to room temperature, hydrogen chloride in diethyl ether (1 mL, 0.1 mmol, 0.1M) was added into the solution dropwise. Diethyl ether (3 mL) was added to facilitate the precipitation when necessary. IMes·HCl was filtered out, washed by ethyl ether (1 mL × 3) and dried in vacuo to get a quantitative regeneration. The filtrate was concentrated in vacuo and the residue was purified by column chromatography (SiO_2, hexane/ethyl acetate 19:1) to yield the desired product.

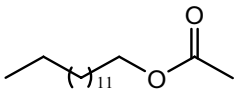
The identity of product was confirmed by comparison with literature spectroscopic data:
3a[2], **3c**[3], **3d**[4], **3e**[5], **3f**[6], **3g**[7], **3i**[2], **3j**[2], **3k**[8], **3l**[8], **3m**[9], **3n**[10], **3o**[4], **3p**[11], **3q**[12], **3r**[13]

Hexadecyl acetate (**3a**):



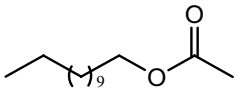
Colourless liquid. ^{1}H NMR (400MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.8 Hz, 3 H), 1.25–1.34 (m, 26 H), 1.48–1.62 (m, 2 H), 2.04 (s, 3 H), 4.04 (t, *J* =6.8 Hz, 2 H); ^{13}C NMR (100MHz, $CDCl_3$) δ 14.4, 21.3, 22.9, 26.2, 28.8, 29.5, 29.6, 29.8, 29.8, 29.9, 29.9, 32.2, 64.9, 171.5.

Tetradecyl acetate (**3b**):



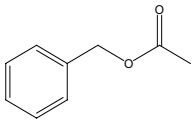
Light yellow oil. ^{1}H NMR (400MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.8 Hz, 3 H), 1.25–1.34 (m, 22 H), 1.57–1.64 (m, 2 H), 2.04 (s, 3 H), 4.04 (t, *J* =6.6 Hz, 2 H); ^{13}C NMR (100MHz, $CDCl_3$) δ 14.0, 20.9, 22.7, 25.9, 28.6, 29.2, 29.3, 29.5, 29.5, 29.6, 29.6, 29.7, 31.9, 64.6, 171.1; MS (EI) *m/z* (%) 256, 197, 196, 168, 154, 140, 125, 111, 97, 83 (100), 69, 55, 43; HRMS calcd. for $C_{16}H_{32}O_2$ $[M]^+$: 256.2402, found 256.2399.

Dodecyl acetate (**3c**):



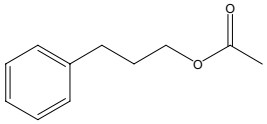
Colourless liquid. ^{1}H NMR (400MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.8 Hz, 3 H), 1.25–1.34 (m, 18 H), 1.48–1.62 (m, 2 H), 2.03 (s, 3 H), 4.04 (t, *J* =6.8 Hz, 2 H); ^{13}C NMR (100MHz, $CDCl_3$) δ 14.1, 21.0, 22.7, 25.9, 28.6, 29.3, 29.4, 29.5, 29.6, 29.6, 31.9, 64.7, 171.3.

Benzyl acetate (**3d**):



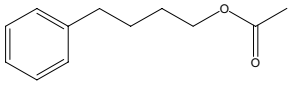
Colourless liquid. ^{1}H NMR (400MHz, $CDCl_3$) δ 2.11 (s, 3H,), 5.12 (s, 2H), 7.33-7.36 (m, 5H); ^{13}C NMR (100MHz, $CDCl_3$) δ 21.3, 66.6, 128.5, 128.5, 128.7, 128.8, 136.2, 171.1.

3-Phenylpropyl acetate (**3e**):



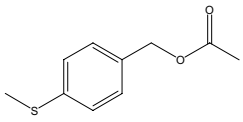
Colourless liquid. ^{1}H NMR (400MHz, $CDCl_3$) δ 1.94-2.05 (m, 2H), 2.06 (s, 3H), 2.68 (t, *J* =7.6 Hz, 2 H), 4.10 (t, *J* =6.8 Hz, 2 H), 7.19-7.23 (m, 3 H), 7.28-7.32 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 21.0, 30.2, 32.2, 63.8, 126.0, 128.4, 128.4, 141.2, 171.2.

4-Phenylbutyl acetate (**3f**):



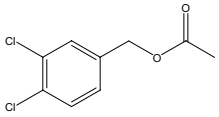
Light yellow oil. ^{1}H NMR (400MHz, $CDCl_3$) δ 1.67-1.73 (m, 4H), 2.06 (s, 3H), 2.67 (t, *J* =9.2 Hz, 2 H), 4.11 (t, *J* =8.4 Hz, 2 H), 7.19-7.24 (m, 3 H), 7.28-7.34 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 21.2, 28.0, 28.5, 35.7, 64.6, 126.1, 128.6, 128.7, 142.3,171.4.

4-(Methylthio)benzyl acetate (**3g**):



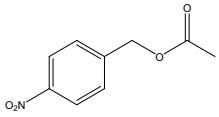
Colourless liquid. ^{1}H NMR (400MHz, $CDCl_3$) δ 2.09 (s, 3H), 2.48 (s, 3H), 5.06 (s, 2 H), 7.23-7.29 (m, 4 H); ^{13}C NMR (100MHz, $CDCl_3$) δ 15.7, 21.0, 65.9, 126.5, 129.0, 132.6, 138.8, 170.9.

3,4-Dichlorobenzyl acetate (**3h**):



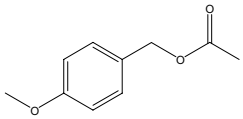
Colourless liquid. ^{1}H NMR (400MHz, $CDCl_3$) δ 2.11 (s, 3H), 5.04 (s, 2 H), 7.17-7.20 (m, 1 H), 7.42-7.45 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 20.9, 64.7, 127.4, 130.1, 130.5, 132.3, 132.7, 136.1, 170.6; MS (EI) *m/z* (%) 218, 176 (100), 161, 159, 141, 123, 111, 89, 75, 43; HRMS calcd. for $C_9H_8O_2Cl_2$ $[M]^+$: 217.9901, found 217.9907.

4-Nitrobenzyl acetate (**3i**):



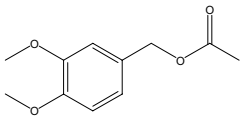
White solid. ^{1}H NMR (400MHz, $CDCl_3$) δ 2.07 (s, 3H), 5.04 (s, 2 H), 7.53 (d, *J* = 8.8 Hz, 2H), 8.22 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 21.1, 65.0, 124.0, 128.6, 143.5, 147.9, 170.8.

4-Methoxybenzyl acetate (**3j**):



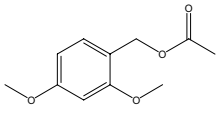
Colourless liquid. ^{1}H NMR (400MHz, $CDCl_3$) δ 2.08 (s, 3H), 3.81 (s, 3H), 5.04 (s, 2H), 6.88 (d, *J* = 8.80 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 21.1, 55.3, 66.1, 113.9, 128.0, 130.1, 159.5, 170.2.

3,4-Dimethoxybenzyl acetate (**3k**):



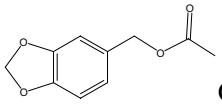
Colourless liquid. ^{1}H NMR (400MHz, $CDCl_3$) δ 2.08 (s, 3H), 3.87 (s, 3H), 3.88 (s, 3H), 5.03 (s, 2H), 6.83-6.93 (m, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 21.3, 56.1, 66.7, 111.2, 112.1, 121.6, 128.6, 149.2, 149.4, 171.2.

2,4-Dimethoxybenzyl acetate (**3l**):



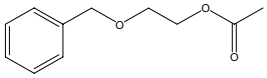
Colourless liquid. ^{1}H NMR (400MHz, $CDCl_3$) δ 2.10 (s, 3H), 3.76 (s, 3H), 3.79 (s, 3H), 5.13 (s, 2H), 6.81 (d, *J* = 1.6 Hz, 2H) 6.91 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 21.3, 56.0, 56.3, 61.8, 111.8, 113.9, 115.9, 125.5, 151.9, 153.7, 171.2.

Piperonyl acetate (**3m**):



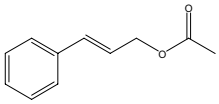
Colourless liquid. ^{1}H NMR (400MHz, $CDCl_3$) δ 2.08 (s, 3H), 4.99 (s, 2H), 5.95(s, 2H), 6.77-6.84 (m, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 21.3, 66.5, 101.4, 108.5, 109.3, 122.5, 129.9, 147.9, 148.0, 171.1; MS (EI) *m/z* (%) 194, 152, 135 (100), 122, 105, 93, 77, 65, 63, 51; HRMS calcd. for $C_{10}H_{10}O_4$ $[M]^+$: 194.0579, found 194.0572.

2-(Benzyloxy)ethyl acetate (**3n**):



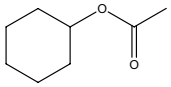
Light yellow oil. ^{1}H NMR (400MHz, $CDCl_3$) δ 2.09 (s, 3H), 3.67 (m, 2H), 4.25 (m, 2H), 4.57 (s, 2H), 7.27-7.36 (m, 5H); ^{13}C NMR (100MHz, $CDCl_3$) δ 21.0, 63.6, 67.8, 73.2, 127.8, 127.8, 128.5, 137.8, 171.1.

Cinnamyl acetate (**3o**):



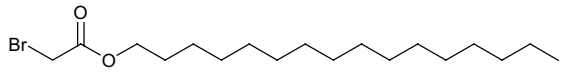
Colourless liquid. ^{1}H NMR (400MHz, $CDCl_3$) δ 2.10 (s, 3H), 4.72 (d, J = 6.3 Hz, 2H), 6.25-6.33 (m, 1H), 6.64 (d, J = 15.6 Hz, 1H), 7.24-7.41 (m, 5H); ^{13}C NMR (100MHz, $CDCl_3$) δ 21.3, 65.3, 123.4, 126.9, 128.3, 128.9, 134.5, 136.4, 171.1.

Cyclohexyl acetate (**3p**):



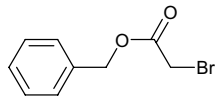
Colourless liquid. ^{1}H NMR (400MHz, $CDCl_3$) δ 1.22–1.46 (m, 5H), 1.52–1.58 (m, 1H), 1.71–1.74 (m, 2H), 1.86–1.88 (m, 2H), 2.06 (s, 3H), 4.71–4.77 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 21.4, 23.8, 25.4, 31.7, 73.0, 171.0.

Hexadecyl Bromoethanoate (**3q**):



Colourless liquid. ^{1}H NMR (400MHz, $CDCl_3$) δ 0.87 (t, J = 6.8 Hz, 3 H), 1.25–1.37 (m, 26 H), 1.63–1.67 (m, 2 H), 3.82 (s, 2 H), 4.16 (t, J =6.8 Hz, 2 H); ^{13}C NMR (100MHz, $CDCl_3$) δ14.1, 22.7, 25.7, 25.9, 28.4, 29.2, 29.4, 29.5, 29.5, 29.6, 29.7, 29.7, 31.9, 66.5, 167.3.

Benzyl 2-Bromoacetate (**3r**):



pale yellow liquid. ^{1}H NMR (400MHz, $CDCl_3$) δ 3.88 (s, 2H,), 5.21 (s, 2H), 7.36-7.39 (m, 5H); ^{13}C NMR (100MHz, $CDCl_3$) δ 25.8, 67.9, 128.4, 128.6, 128.7, 135.0, 167.1.

IMes-HO*t*Bu in C_6D_6: ^{1}H NMR (300MHz, C_6D_6) δ 6.73 (s, 4H, Ar**H**), 6.33 (s, 2H, C_4**H**), 2.07 (s, 18H, C**H**$_3$), 1.03 (s, 9H, C(C**H**$_3$)$_3$)

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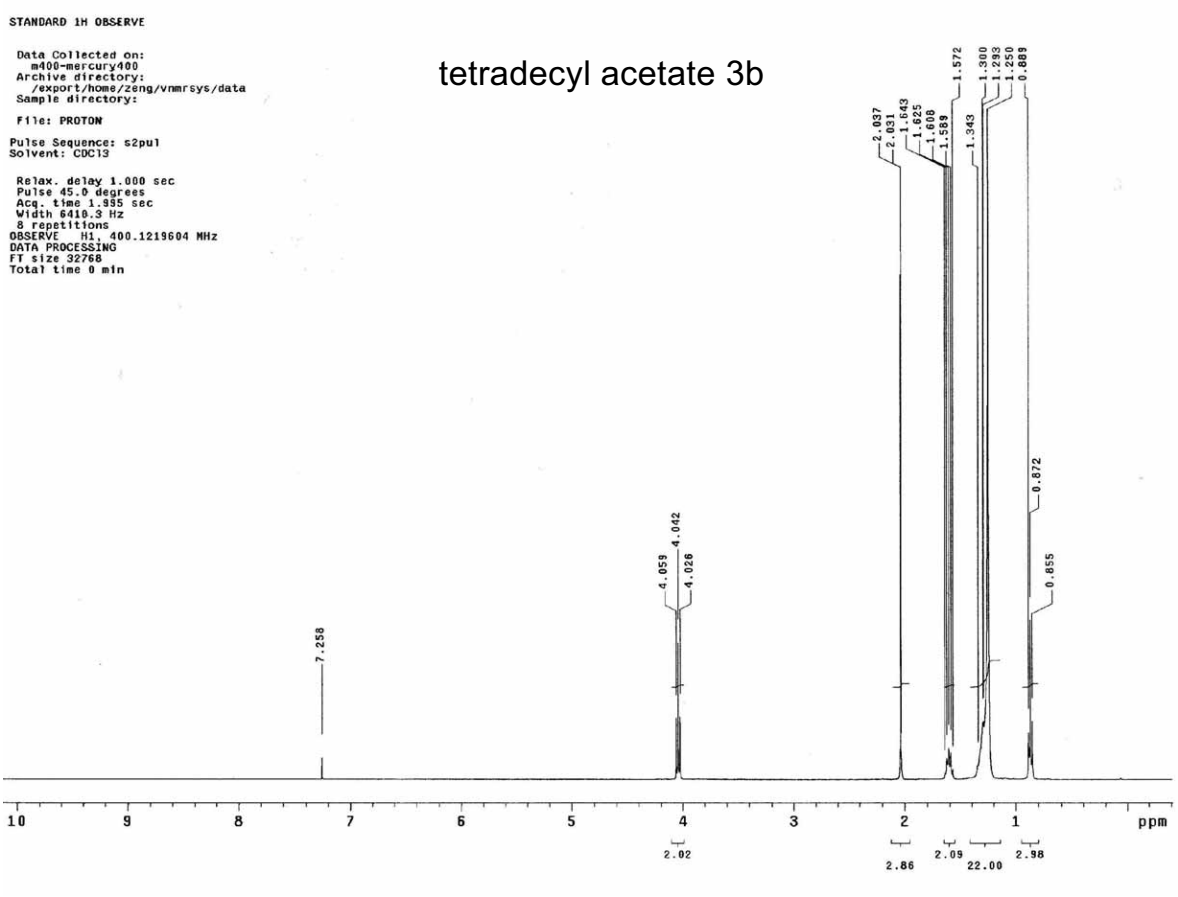
STANDARD 1H OBSERVE
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m400-mercury400
Archive directory:
/export/home/zeng/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
Solvent: CDCl3
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Pulse 45.0 degrees
Acq. time 1.955 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 400.1219604 MHz
DATA PROCESSING
FT size 32768
Total time 0 min
tetradecyl acetate 3b
7.258
4.059
4.042
4.026
2.037
2.031
1.643
1.625
1.608
1.589
1.572
1.343
1.300
1.293
1.250
0.889
0.872
0.855
10
9
8
7
6
5
4
3
2
1
ppm
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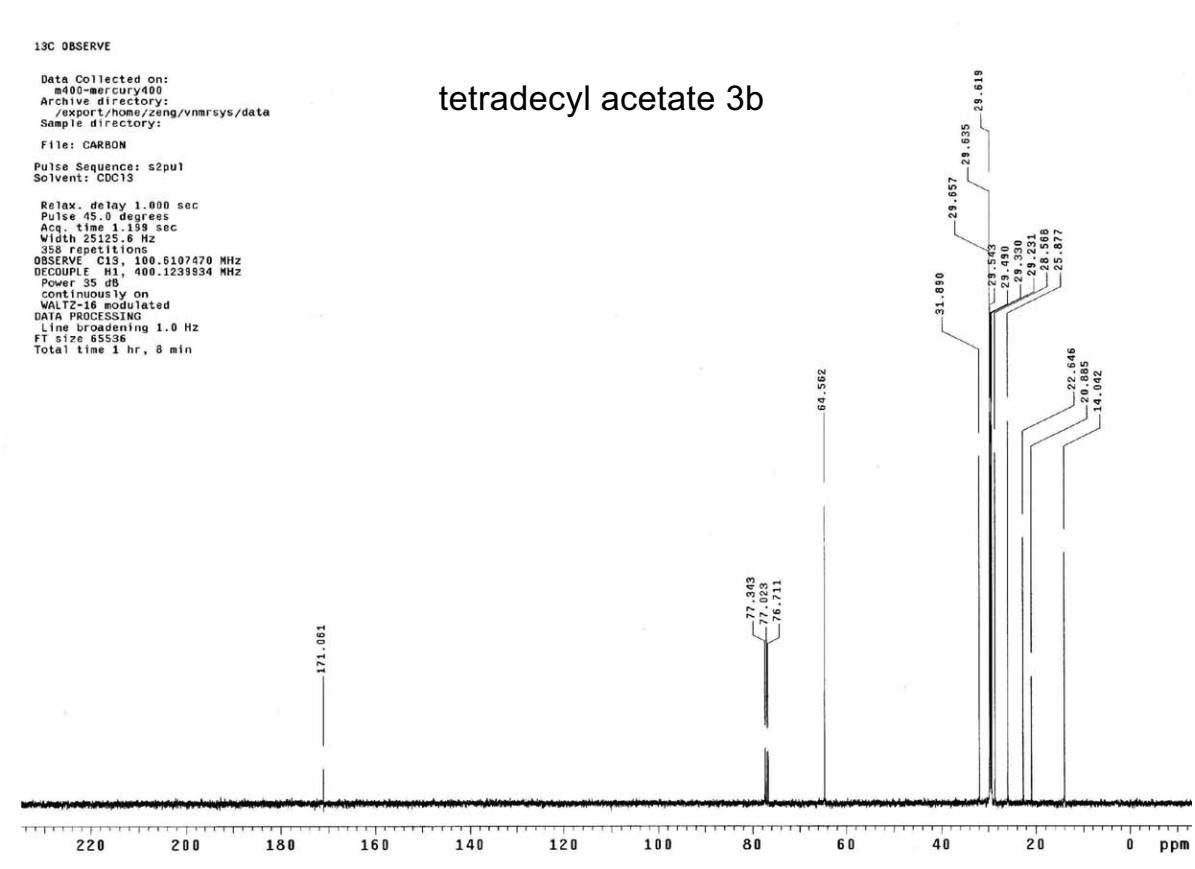
2.09
22.00
2.98


13C OBSERVE
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m400-mercury400
Archive directory:
/export/home/zeng/vnmrsys/data
Sample directory:
File: CARBON
Pulse Sequence: s2pul
Solvent: CDCl3
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.199 sec
Width 25125.6 Hz
358 repetitions
OBSERVE C13, 100.6107470 MHz
DECOUPLE H1, 400.1239934 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 1 hr, 8 min
tetradecyl acetate 3b
171.061
77.343
77.023
76.711
64.562
31.890
29.618
29.635
29.657
29.543
29.490
29.330
29.231
28.568
25.877
22.646
20.885
14.042
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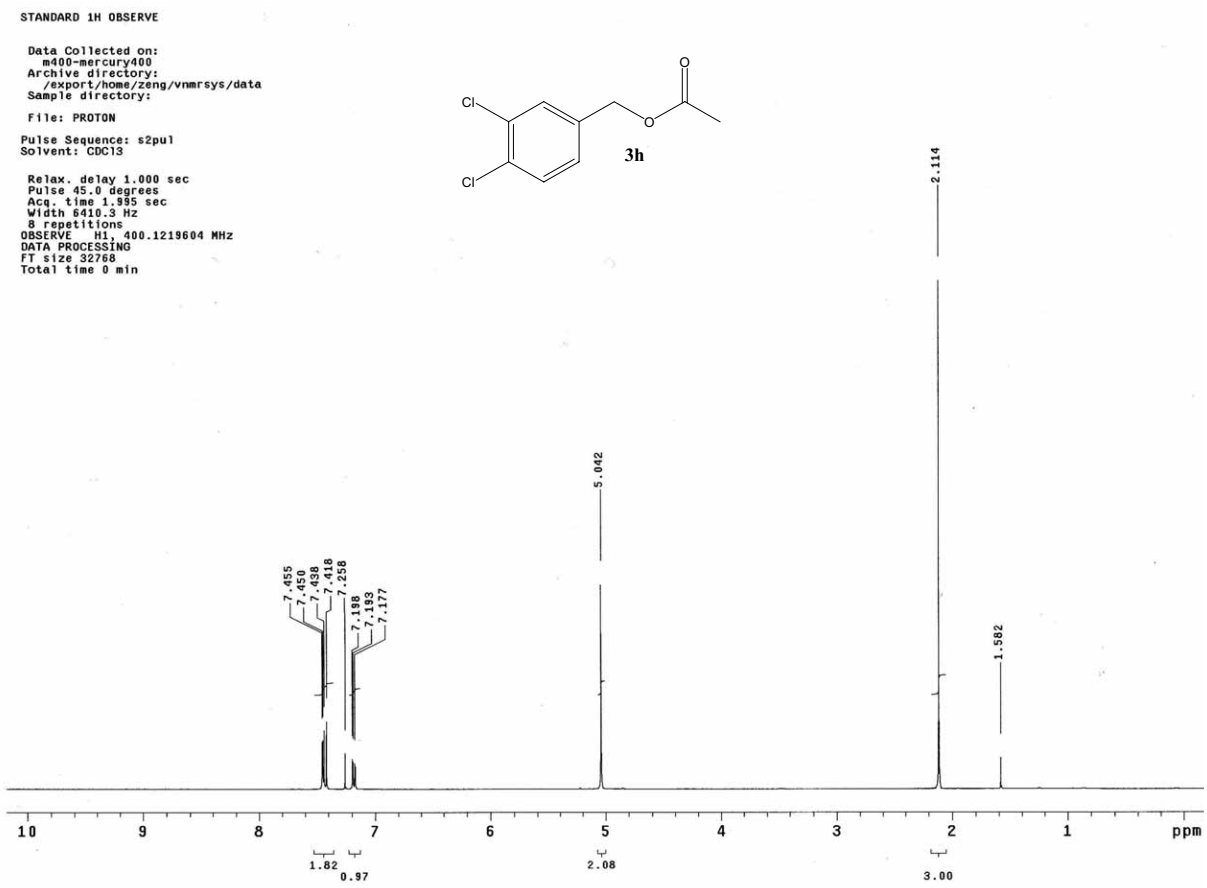
200
180
160
140
120
100
80
60
40
20
0
ppm


STANDARD 1H OBSERVE
Data Collected on:
m400-mercury400
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Sample directory:
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Pulse Sequence: s2pul
Solvent: CDCl3
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.995 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 400.1219604 MHz
DATA PROCESSING
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Total time 0 min
Cl
Cl
O
O
3h
7.455
7.450
7.438
7.418
7.258
7.188
7.183
7.177
5.042
2.114
1.582
10
9
8
7
6
5
4
3
2
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ppm
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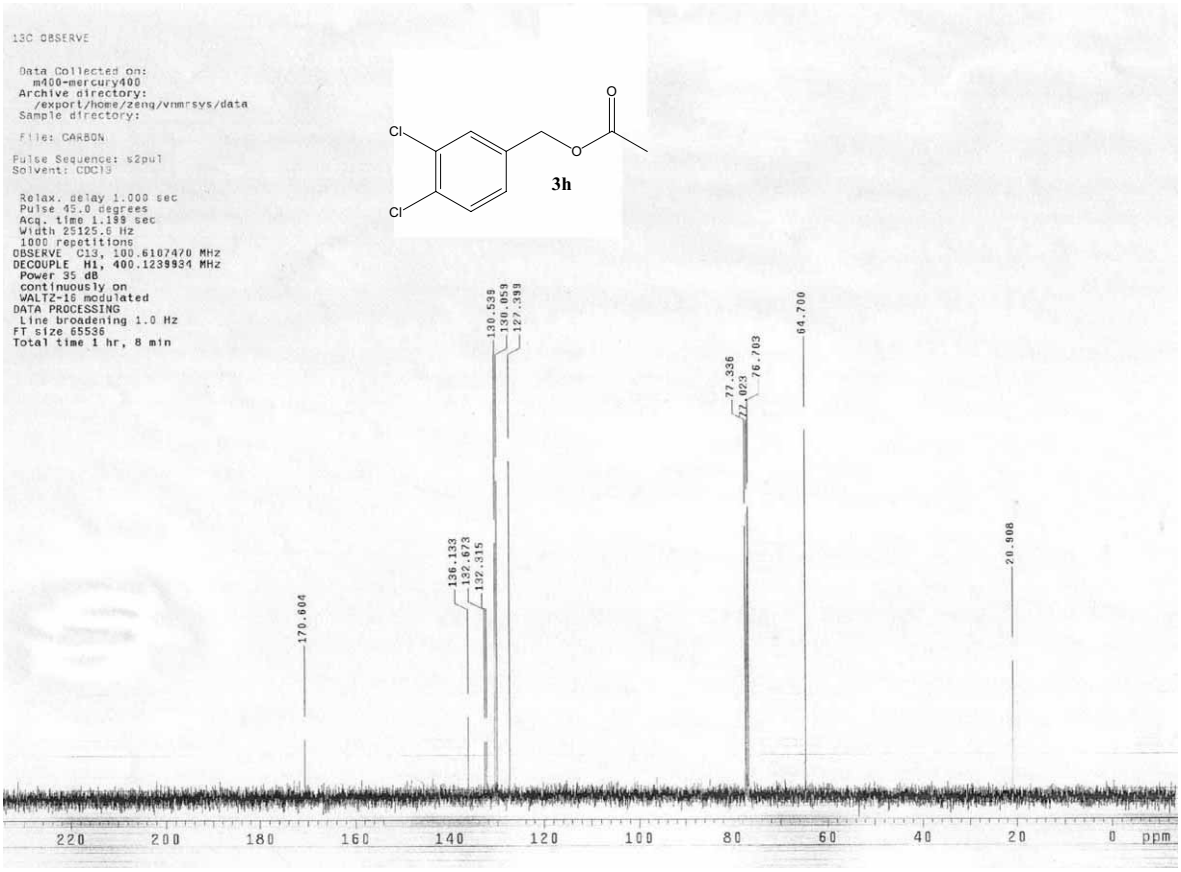
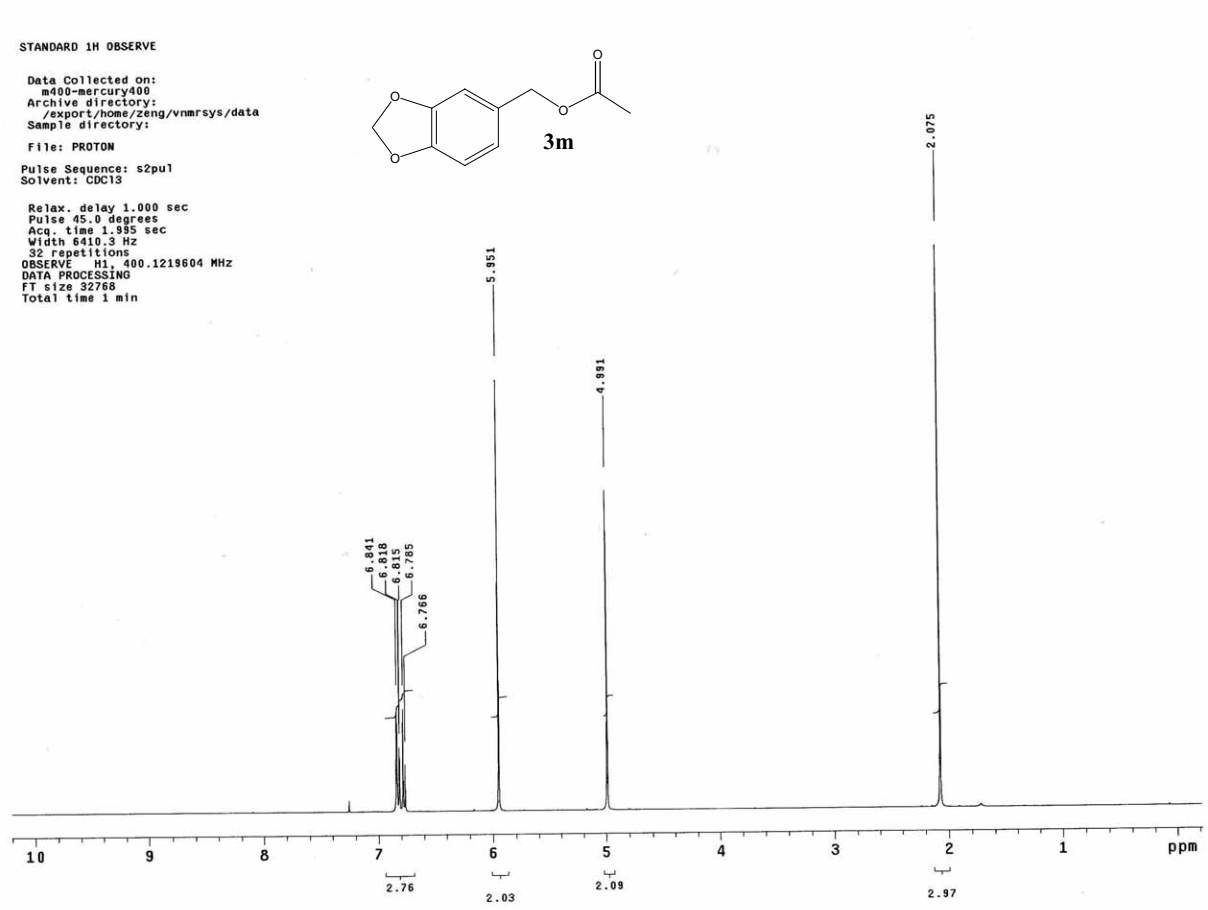
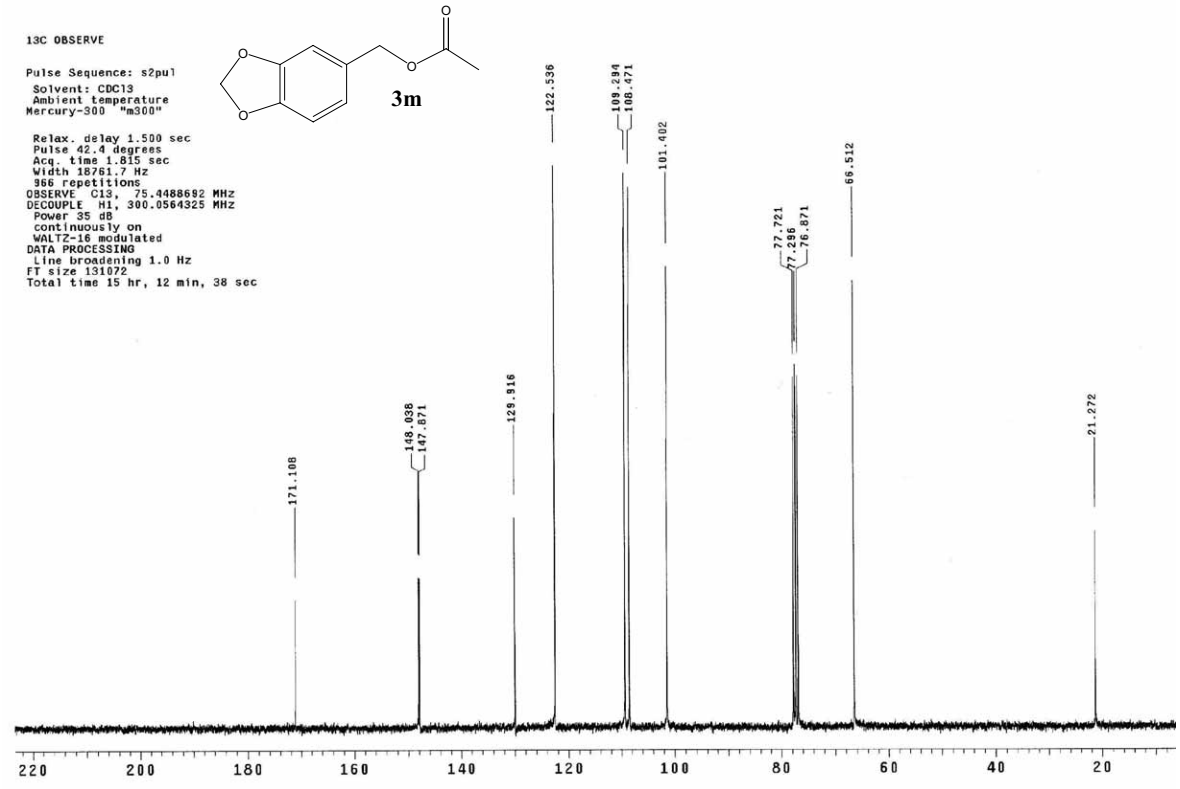
0.97
2.08
3.00


13C OBSERVE
Data Collected on:
m400-mercury400
Archive directory:
/export/home/zeng/vnmrsys/data
Sample directory:
File: CARBON
Pulse Sequence: s2pul
Solvent: CDCl3
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.199 sec
Width 25125.6 Hz
1000 repetitions
OBSERVE C13, 100.6107470 MHz
DECOUPLE H1, 400.1299934 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 1 hr, 8 min
Cl
Cl
O
O
3h
170.604
136.133
132.673
132.315
130.538
130.053
127.393
77.336
77.023
76.703
64.700
20.908
220
200
180
160
140
120
100
80
60
40
20
0
ppm


STANDARD 1H OBSERVE
Data Collected on:
m400-mercury400
Archive directory:
/export/home/zeng/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
Solvent: CDCl3
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.995 sec
Width 6410.3 Hz
32 repetitions
OBSERVE H1, 400.1219604 MHz
DATA PROCESSING
FT size 32768
Total time 1 min
3m
5.951
4.991
2.075
6.841
6.818
6.815
6.785
6.766
10
9
8
7
6
5
4
3
2
1
ppm
2.76
2.03
2.09
2.97


13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300 "m300"
Relax. delay 1.500 sec
Pulse 42.4 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
966 repetitions
OBSERVE C13, 75.4488692 MHz
DECOUPLE H1, 300.0564325 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 15 hr, 12 min, 38 sec
3m
122.536
109.284
108.471
101.402
77.721
77.296
76.871
66.512
171.108
148.038
147.871
129.916
21.272
220
200
180
160
140
120
100
80
60
40
20