Supporting Information

Oxidation-Reductive Coupling of Alcohols Catalyzed by Oxo-Vanadium Complexes

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Preparation of Ligands and Vanadium Complexes

NBu_4VO_3 was prepared as described by Day et al. (V.W. Day, W.G. Klemperer and A. Yagasaki, *Chem. Lett.* 1990, 1267).

Preparation of Salicylimine ligand

Salicaldehyde (1.77 g, 14.5 mmol) was dissolved in methanol (200 mL). 2-Aminophenol (1.58 g, 14.5 mmol) is then added. The solution was heated at reflux for 2 h. After cooling to rt for 1-2 days a dark orange-red crystalline solid formed and was collected by filtration and air dried. NMR: (300 MHz, DMSO-d_6) δ 13.84 (s, 1H), 9.79 (s, 1H), 8.99 (s, 1H), 7.64 (dd, 1H, J = 8.0, 1.7 Hz), 7.46-7.36 (m, 2H), 7.16 (ddd, 1H, J = 8.0, 7.4, 1.6 Hz), 7.03-6.95 (m, 3H), 6.91 (ddd, 1H, J = 8.6, 7.6, 1.4 Hz).

Preparation of S_2-dipic ligand

Pyridine 2,6-dithiocarboxylic acid was prepared using a published procedure. P. B. Chatterjee and D. C. Crans, *Inorg. Chem.* **2012**, 51, 9144-9146.

*Preparation of **2***

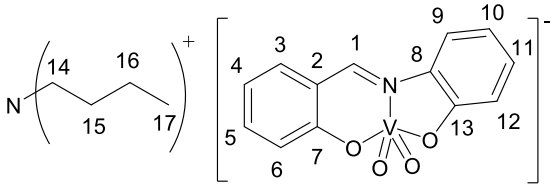
Pyridine 2,6-dithiocarboxylic acid (0.053 g, 0.267 mmol) is dissolved in acetone (50 mL) followed by the addition of Bu_4NVO_3 (0.091 g, 0.266 mmol). The solution turned brown immediately and darkened while stirring overnight. The solvent is removed in vacuo, leaving Bu_4N (S_2-dipic)VO_2 (0.151 g) as a light brown, polycrystalline solid, which was spectroscopically pure and used without further purification in the reactivity study.

IR (KBr pellet, cm^{-1}): 3087 (m, ν_{C-H}), 2962, 2983 (s, ν_{C-H}), 1675 (s, $\nu_{O=C}$), 1491(m, $\nu_{C=C}$), 1342 (w, $\nu_{C=C}$), 949 (m, $\nu_{V=O}$), 751 (m, ν_{V-O}).

^{1}H NMR ($CDCl_3$, ppm, 400 MHz): 8.35 (broad, *para*), 8.20 (broad, *meta*), 3.41 (broad, $NC\underline{\mathbf{H}}_2CH_2CH_2CH_3$), 1.73 (broad, $NCH_2C\underline{\mathbf{H}}_2CH_2CH_3$), 1.46 (broad, $NCH_2CH_2C\underline{\mathbf{H}}_2CH_3$), 0.98 (broad, $NCH_2CH_2CH_2C\underline{\mathbf{H}}_3$).

^{13}C{^{1}H} NMR ($CDCl_3$, ppm, 400 MHz): 167.44 (s, O=C-O), 149.74 (s, *ortho* to N), 144.86 (s, *para* to N), 125.48 (s, *meta* to N), 58.74 (s, $N\underline{\mathbf{C}}H_2CH_2CH_2CH_3$), 23.96 (s, $NCH_2\underline{\mathbf{C}}H_2CH_2CH_3$), 19.70 (s, $NCH_2CH_2\underline{\mathbf{C}}H_2CH_3$), 13.66 (s, $NCH_2CH_2CH_2\underline{\mathbf{C}}H_3$).

*Preparation of **3***



Method 1: NBu_4VO_3 (0.186 g, 0.545 mmol) is dissolved in methanol (50 mL). Then the ligand **1** (0.113 g, 0.545 mmol) was added. The color changed immediately to a dark brown color and the solution was stirred overnight. The solvent was removed under vacuum, leaving dark brown complex **3** (0.295 g) as an amorphous solid, which was spectroscopically pure and used as is in the reactivity study.

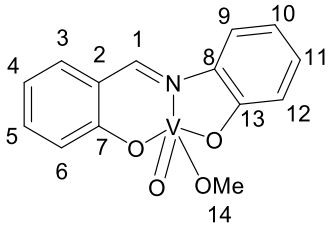
Method 2: NBu_4VO_3 (0.305 g, 0.892 mmol) is dissolved in dry THF (50 mL). Then compound **1** (0.190 g, 0.892 mmol) was added. The color changed immediately to a dark brown color, and the solution was stirred overnight. The solvent was removed under vacuum, leaving catalyst **3** (0.460 g), which was spectroscopically pure.

IR (KBr pellet, cm^{-1}): 3094 (m, ν_{C-H}), 2971 (s, ν_{C-H}), 2876 (s, ν_{C-H}), 1609 (s, $\nu_{N=C}$), 1532 (m, $\nu_{C=C}$), 1472 (m, $\nu_{C=C}$), 1291(m, ν_{N-C}), 981 (s, $\nu_{V=O}$), 752 (m, $\nu_{V=O}$).

^{1}H NMR ($CDCl_3$, ppm, 400 MHz): 9.01 (H1), 7.53 (H9), 7.45 (H6), 7.33 (H4), 7.08 (H11), 7.00 (H12), 6.81 (H5/H3), 6.69 (H10), 3.45 (H14), 1.64 (H15), 1.35 (H16), 0.93 (H17).

^{13}C{^{1}H} NMR ($CDCl_3$, ppm, 400 MHz): 167.11 (s, C7), 164.38 (s, C13), 154.22 (s, C1), 136.88 (s, C2), 133.47 (s, C4), 133.07 (s, C6), 128.56 (s, C11), 121.58 (s, C8), 120.69 (s, C5), 119.84 (s, C12), 117.14 (s, C10), 116.28 (s, C3), 113.86 (s, C9), 58.20 (s, C14), 23.86 (s, C15), 19.61 (s, C16), 13.68 (s, C17).

Preparation of **4**



*From **3** recrystallized in MeOH*: Compound **3** (0.150 g, 0.279 mmol) is dissolved in 25 mL MeOH. The flask was sealed to slow the evaporation. Over the next 2 weeks, crystals began to form on the side of the flask. The solution is then removed, leaving compound **4**, a brown, crystalline solid. The structure of **3**, as a methanol adduct was verified by X-ray diffraction. The NMR and IR data for **3** were in agreement with those reported (Kraehmer, V.; Rehder, D. *Dalton Transactions* **2012**, *41*, 5225-5234).

From $OV(O^iPr)_3$ + LH_2 in MeOH: $OV(O^iPr)_3$ (0.590 g, 2.42 mmol) is dissolved in MeOH (100 mL). To this solution, the imine ligand LH_2 (0.515 g, 2.42 mmol) is added. After stirring overnight, the solvent is removed under vacuum, leaving **4** (0.801 g, 2.37 mmol, 98 %), a dark brown polycrystalline solid, which was spectroscopically pure and used as is in the reactivity study.

IR (KBr pellet, cm^{-1}): 3096 (w, ν_{C-H}), 2942 (w, ν_{C-H}), 1605 (s, $\nu_{N=C}$), 1537 (m, $\nu_{C=C}$), 1451 (m, $\nu_{C=C}$), 1295 (m, ν_{N-C}), 982 (s, $\nu_{V=O}$).

^{1}H NMR ($CDCl_3$, ppm, 400 MHz): 9.17 (s, H1), 7.70 (d, H6, $^3J(^1H\text{-}^1H)$ = 7.8 Hz), 7.63 (t, H4, $^3J(^1H\text{-}^1H)$ = 7.9 Hz), 7.61 (d, H9, $^3J(^1H\text{-}^1H)$ = 7.9 Hz), 7.30 (t, H11, $^3J(^1H\text{-}^1H)$ = 8.1 Hz), 7.20 (d, H3, $^3J(^1H\text{-}^1H)$ = 8.4 Hz), 7.12 (t, H5, $^3J(^1H\text{-}^1H)$ = 7.5 Hz), 7.03 (d, H12, $^3J(^1H\text{-}^1H)$ = 8.2 Hz), 6.97 (t, H10, $^3J(^1H\text{-}^1H)$ = 7.7 Hz), 5.33 (s, H14).

^{13}C{^{1}H} NMR ($CDCl_3$, ppm, 400 MHz): 165.64 (s, C7), 164.66 (s, C13), 154.02 (s, C1), 136.38 (s, C2), 135.40 (s, C4), 132.97 (s, C6), 130.18 (s, C11), 121.26 (s, C5), 121.15 (s, C8), 120.18 (s, C10), 118.37 (s, C3), 116.37 (s, C12), 114.66 (s, C9), 72.82 (s, C14).

Representative Procedure for Oxidation/Reductive Coupling of Alcohols

Into a 10 mL glass pressure tube (Ace Glass) was added the catalyst (0.100 mmol), benzhydrol (0.184 g, 1.00 mmol), 5 mL of benzene and a magnetic spin bar. The tube was purged with nitrogen, manually sealed and then heated with stirring at 150 ^{o}C for 24 h. To determine the percent conversion and a yield by NMR, 300 μL of the reaction mixture were dispensed into an NMR tube, along with 5 μL of DMF and ca. 500 μL of $CDCl_3$. A ^{1}H NMR spectrum was obtained and processed using MestreNova. The integration of the signals relative to the DMF signals is used to ascertain the amounts for percent conversion and yield.

Procedure for Reductive Coupling Kinetics Experiment

In a pressure tube, the catalyst (0.100 mmol) is added to benzhydrol (0.184 g, 1.00 mmol). Benzene (5 mL) is added and the tube is purged with N_2. The tube is then sealed and heated to 150 ^{o}C for 2, 4, 8, 17, or 24 h.

D-Benzhydrol synthesis

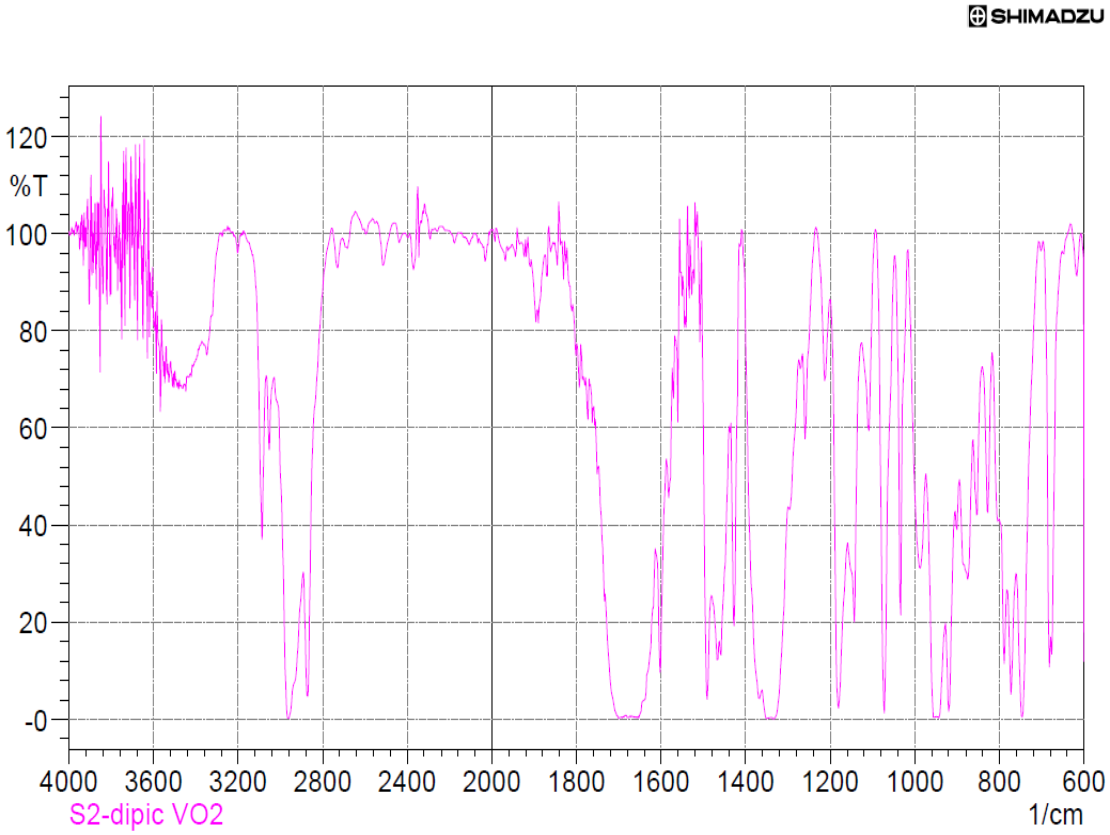
In a dry Schlenk flask, $NaBD_4$ (0.0776 g, 1.85 mmol) is suspended in Et_2O (25 mL) and cooled to 0 ^{o}C. Benzophenone (0.309 g, 1.70 mmol) is added to the flask followed by the dropwise addition of MeOH (20 mL). The solution is stirred overnight and 5 mL of H_2O is added. The solvent is removed in vacuo, the crude product is then dissolved in Et_2O, and the solution dried over Na_2SO_4. After filtration to remove the drying agent, the solvent is removed in vacuo, leaving d-benzhydrol (0.111 g, 0.601 mmol, 35.4%). The EI-Mass spectrum was used to confirm that the product was 98.3% d_1-benzhydrol.

Kinetic Isotope Effect

D_1-benzhydrol (0.111 g, 0.60 mmol) and H_2-benzhydrol (0.107 g, 0.60 mmol) are mixed. In a pressure tube, the catalyst **3** (0.0536 g, 0.100 mmol) is added to the benzhydrol mixture. Benzene (5 mL) is added and the tube is purged with nitrogen, then sealed and heated to 150 ^{o}C for 24 h. MS analysis on page S32.

Configurational stability of 1-phenylethanol under RC conditions

Complex **3** (0.103 g, 0.191 mmol) is placed in a pressure reactor tube. *S*-1-phenylethanol (0.252 g, 2.07 mmol) is added along with benzene (5 mL). The tube is sealed and heated for 2 h. The unreacted alcohol substrate is separated using column chromatography over SiO_2 with a 1:1 mixture of ethyl acetate:hexane as the eluent. The solvents were removed in vacuo, leaving the 1-phenylethanol (0.226 g, 1.85 mmol, 89.6% recovered). Measured optical rotations, ([ROH] = 1.2 g/100 mL, $CHCl_3$): pure *S*-1-phenylethanol: - 0.27^{o}; recovered alcohol after reaction: - 0.076^{o}. % ee = 28, 64 % *S*, 36 % *R*.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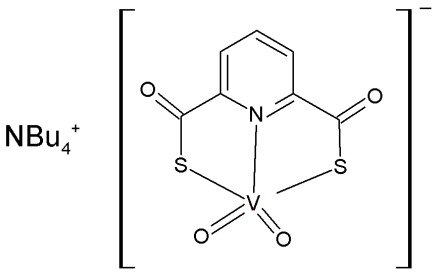
1/cm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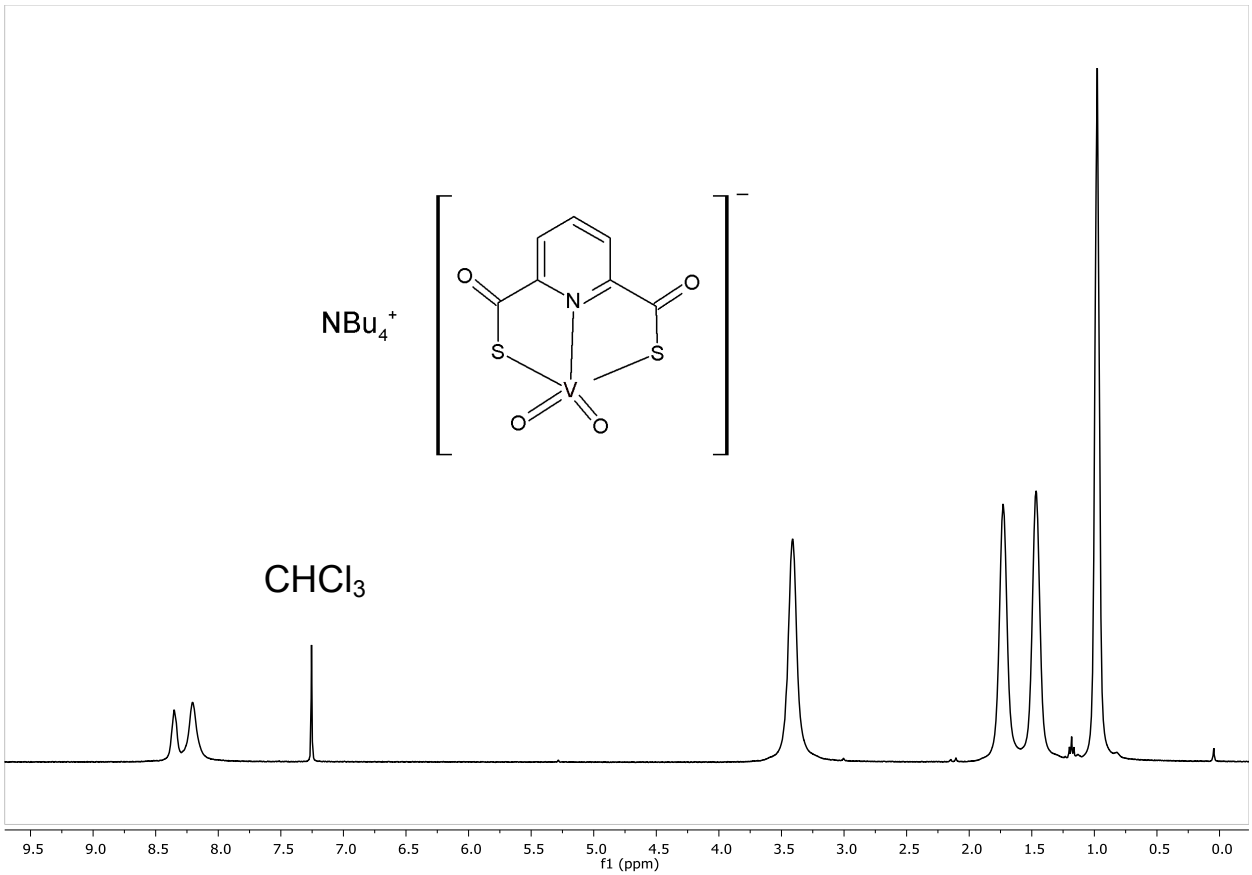
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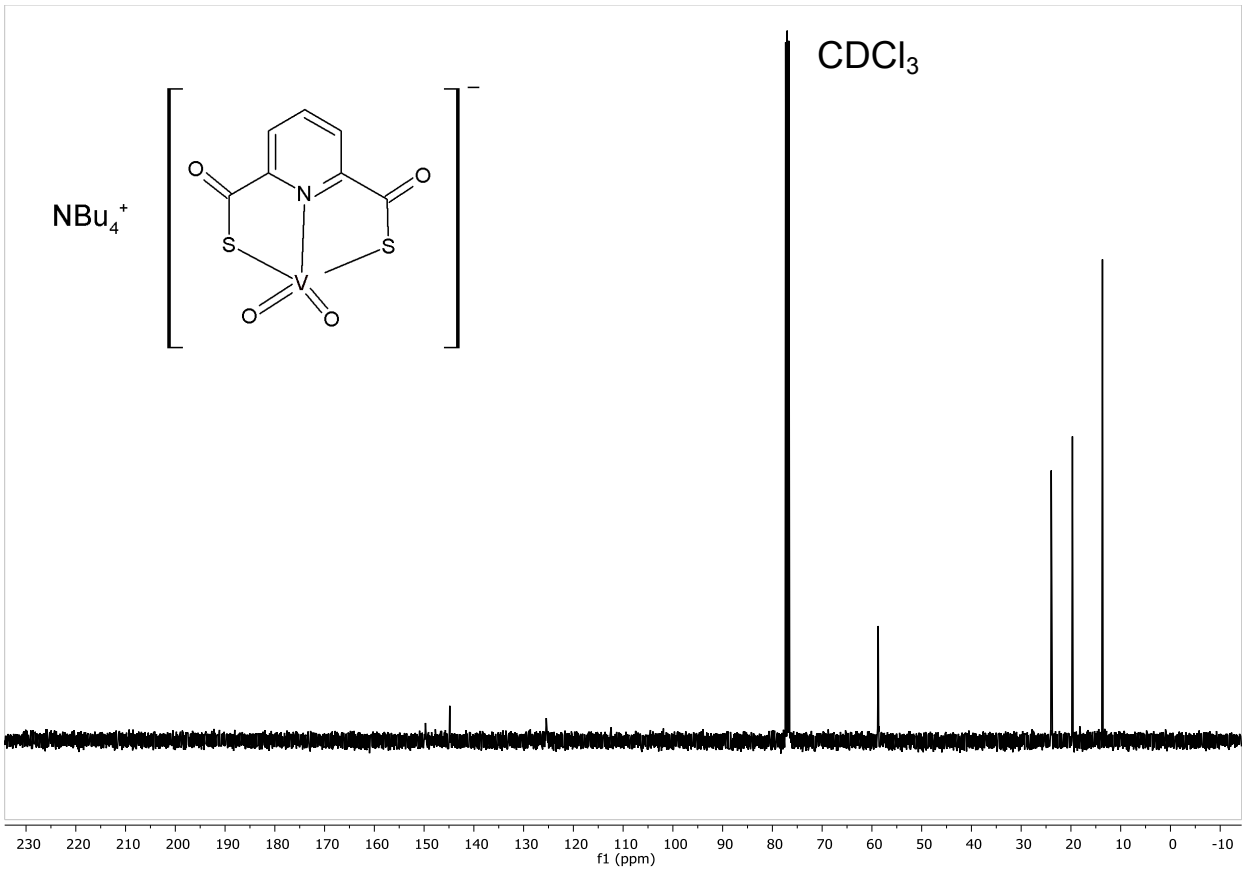
0.0
f1 (ppm)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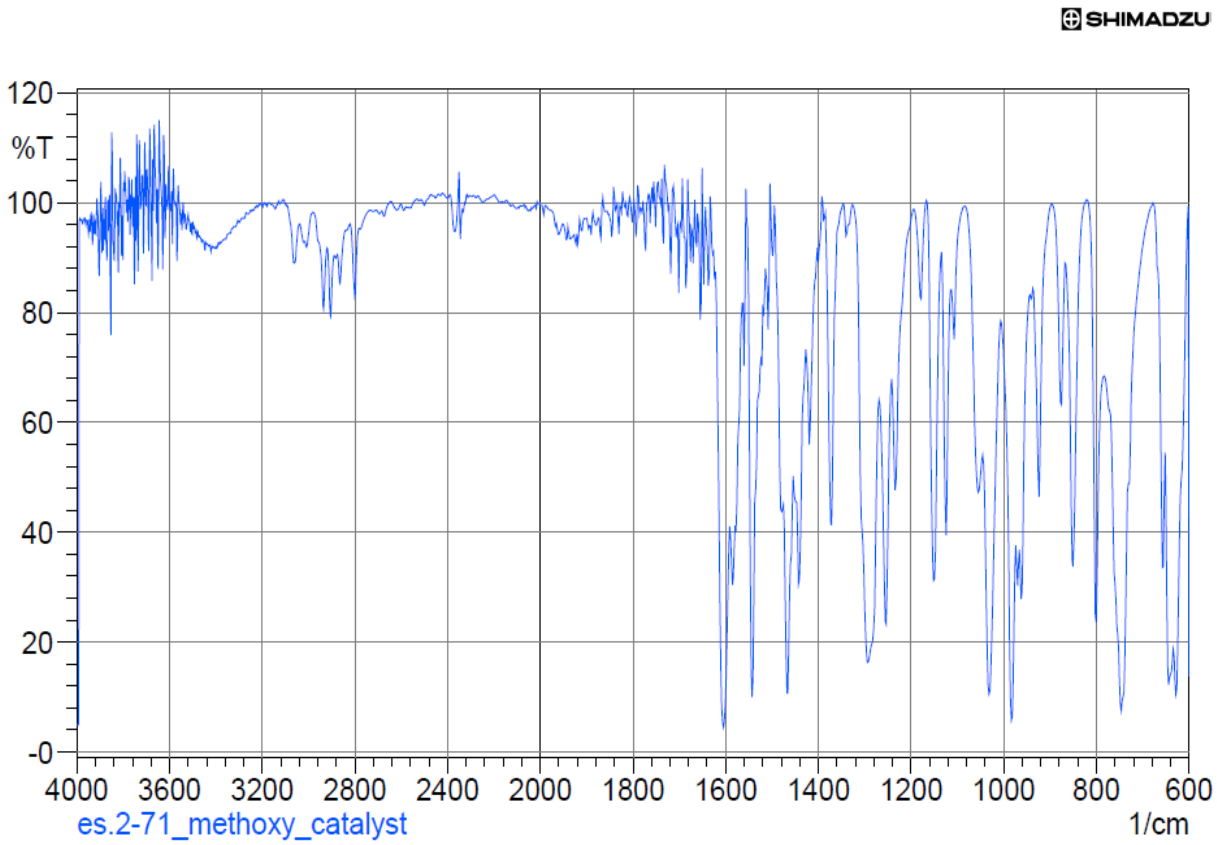
f1 (ppm)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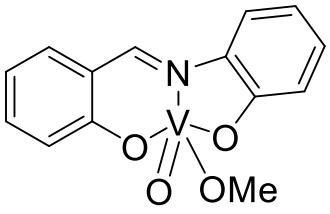
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O
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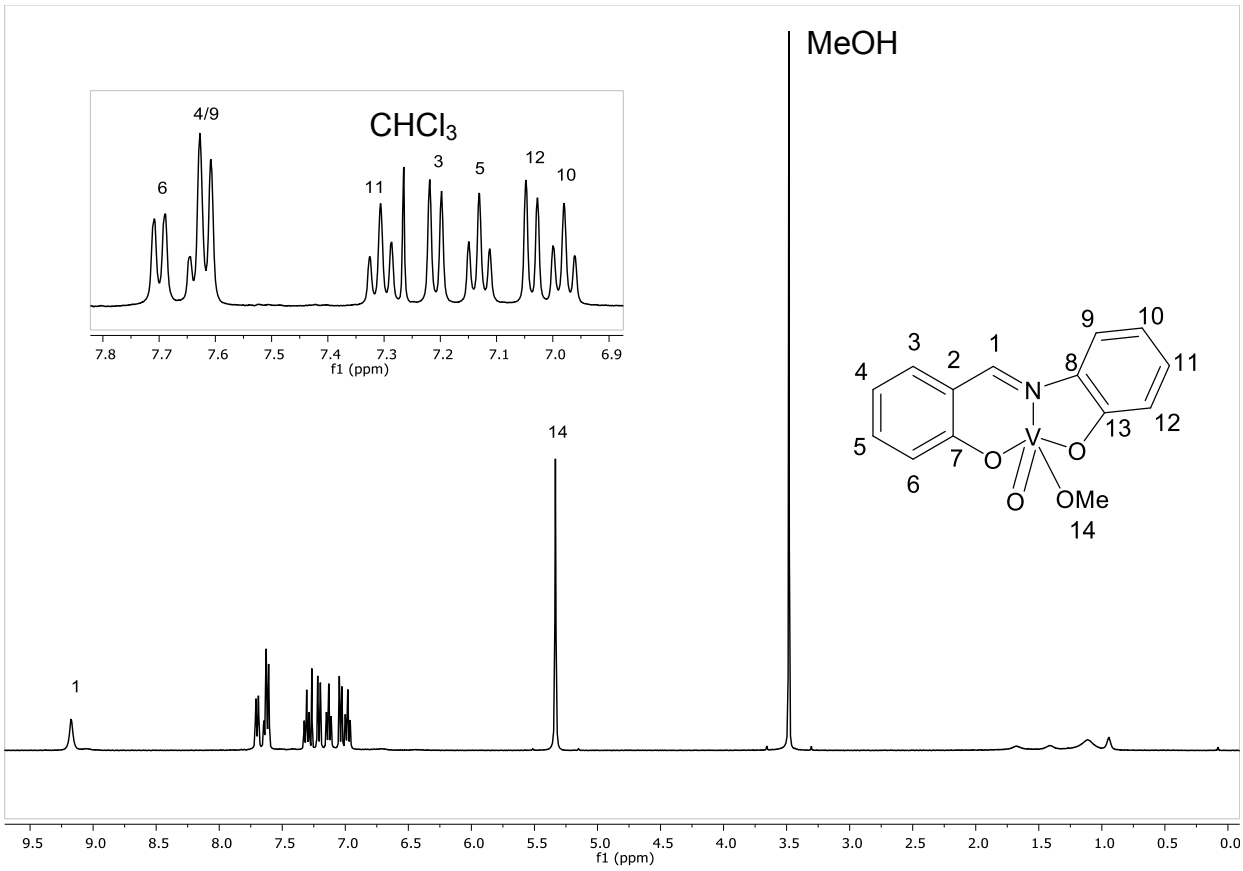
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f1 (ppm)
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f1 (ppm)
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V
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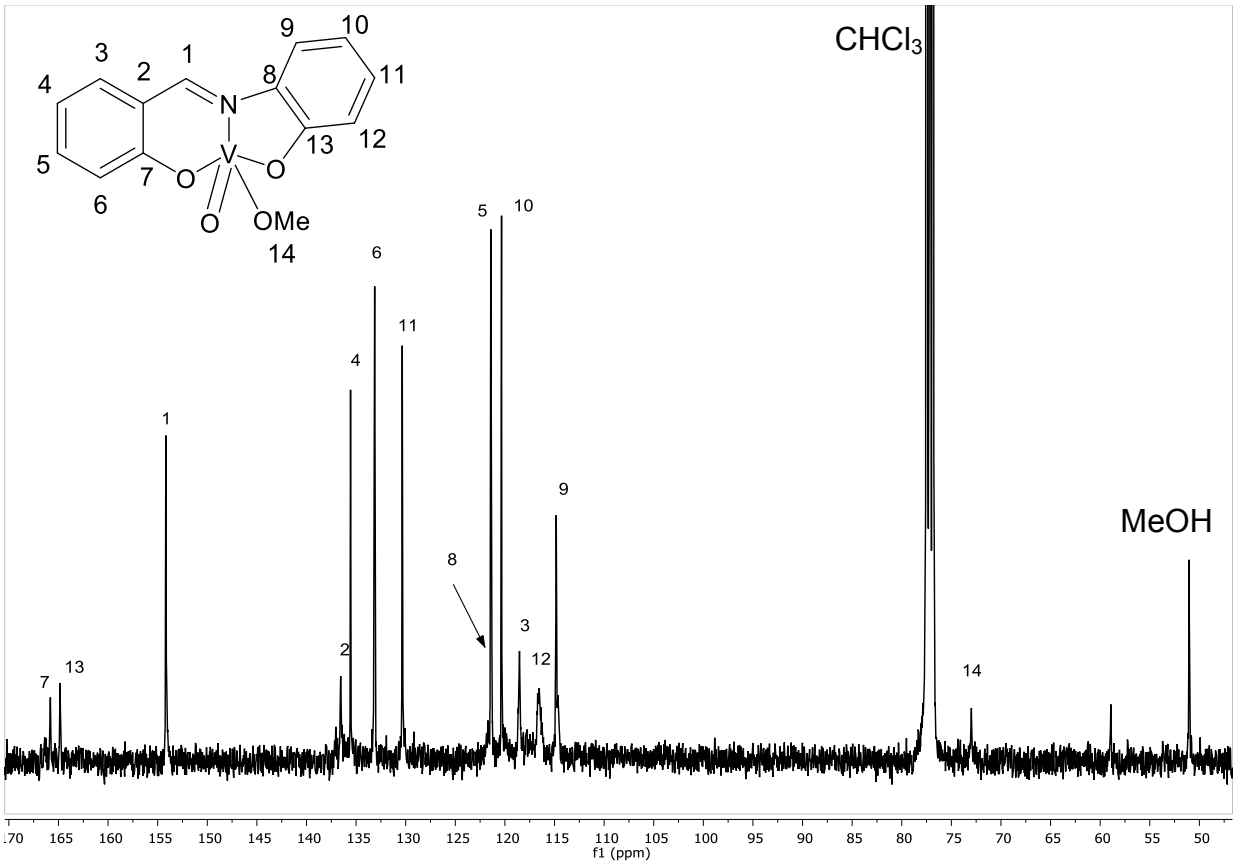
O
O
OMe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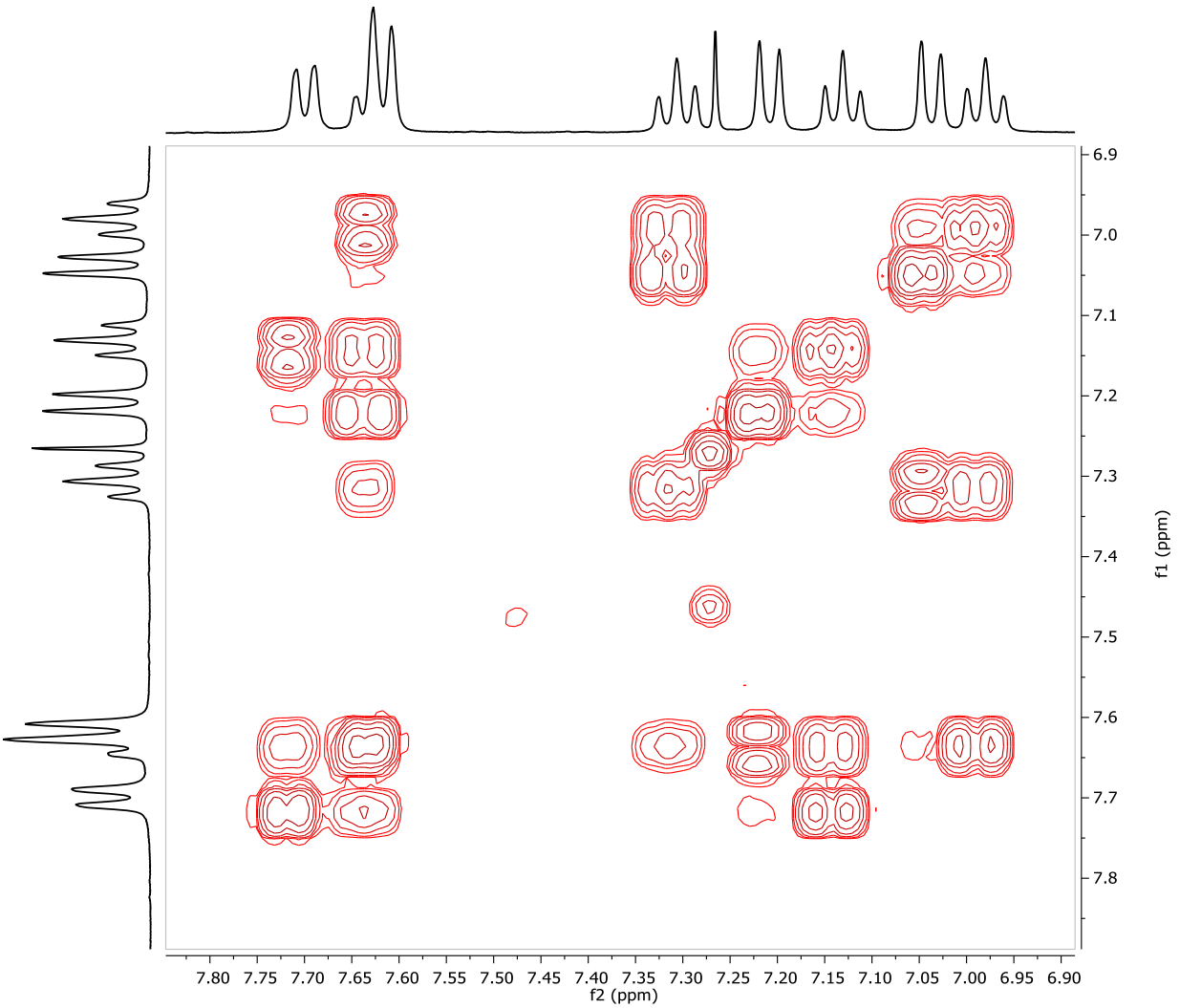
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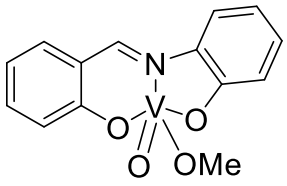
f2 (ppm)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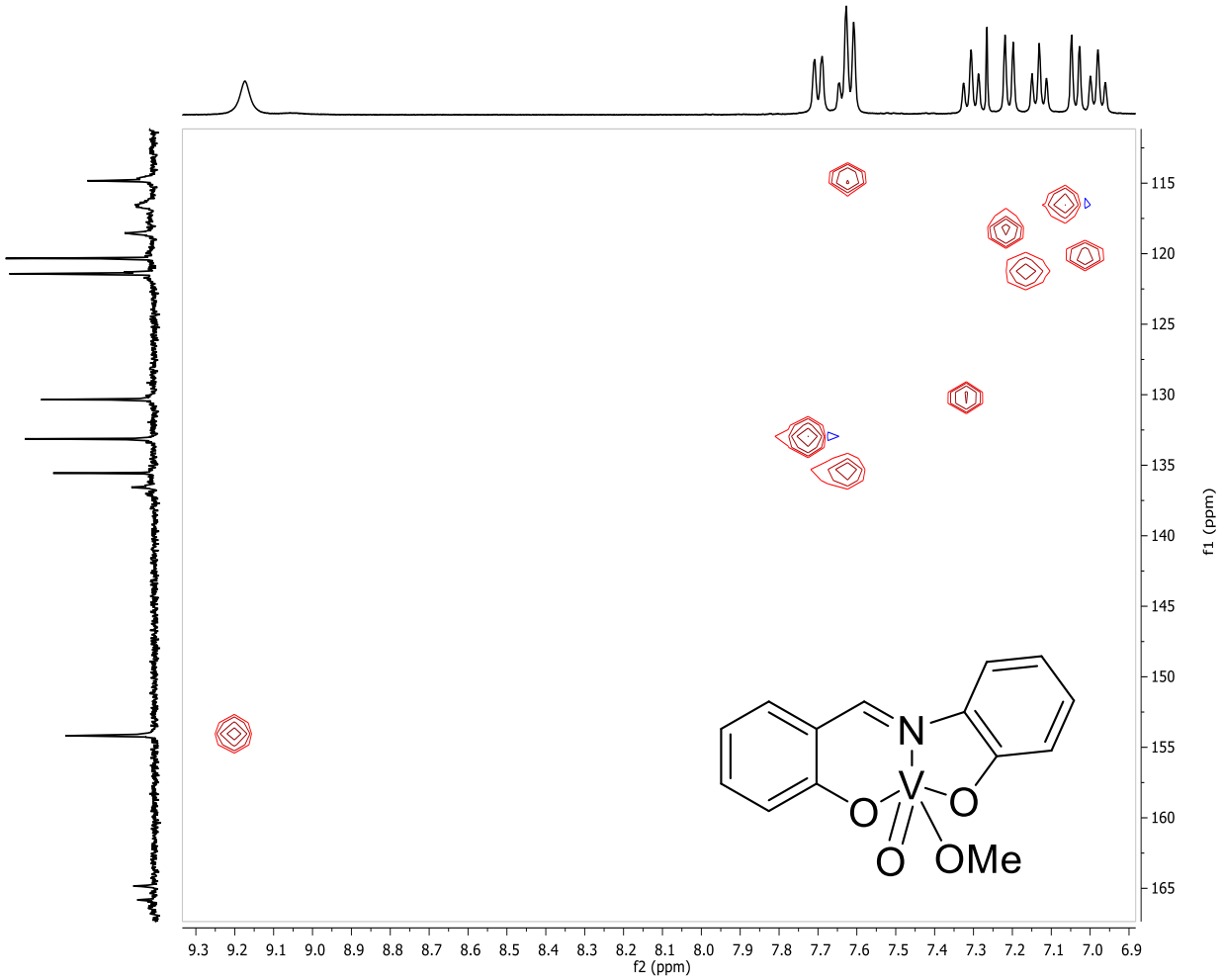
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V
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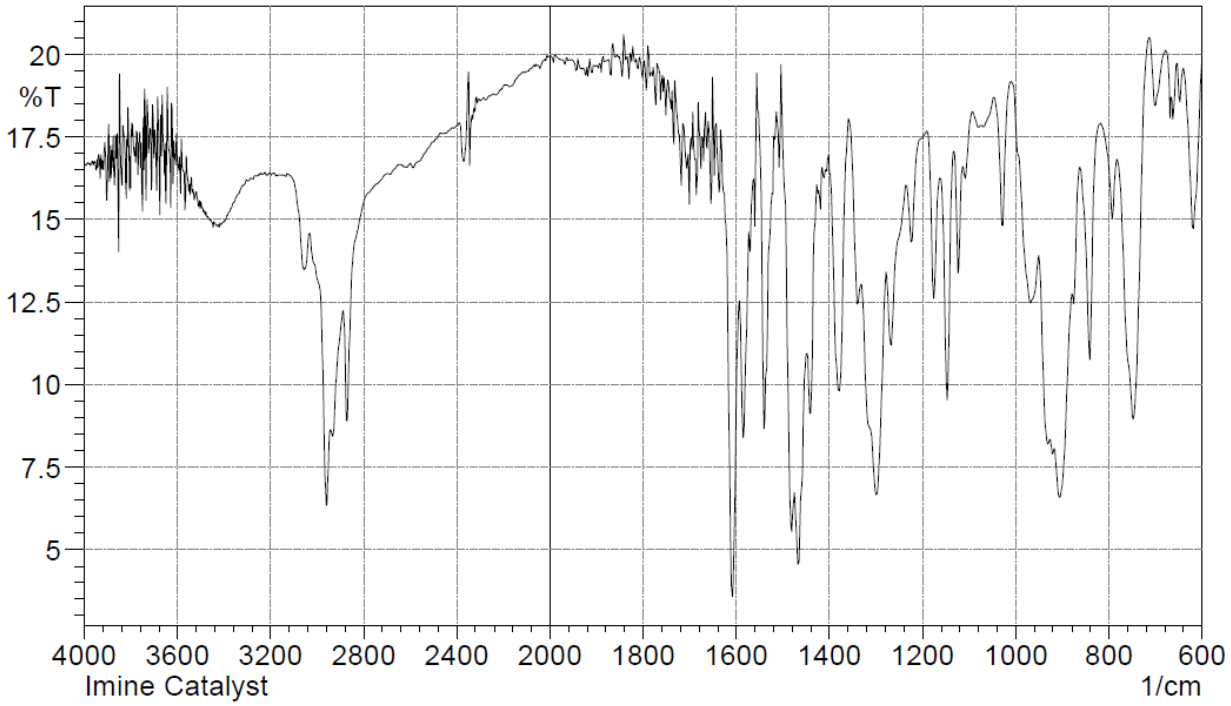
O
O
OMe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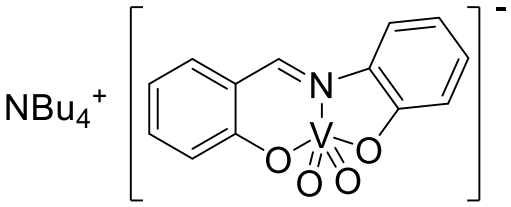
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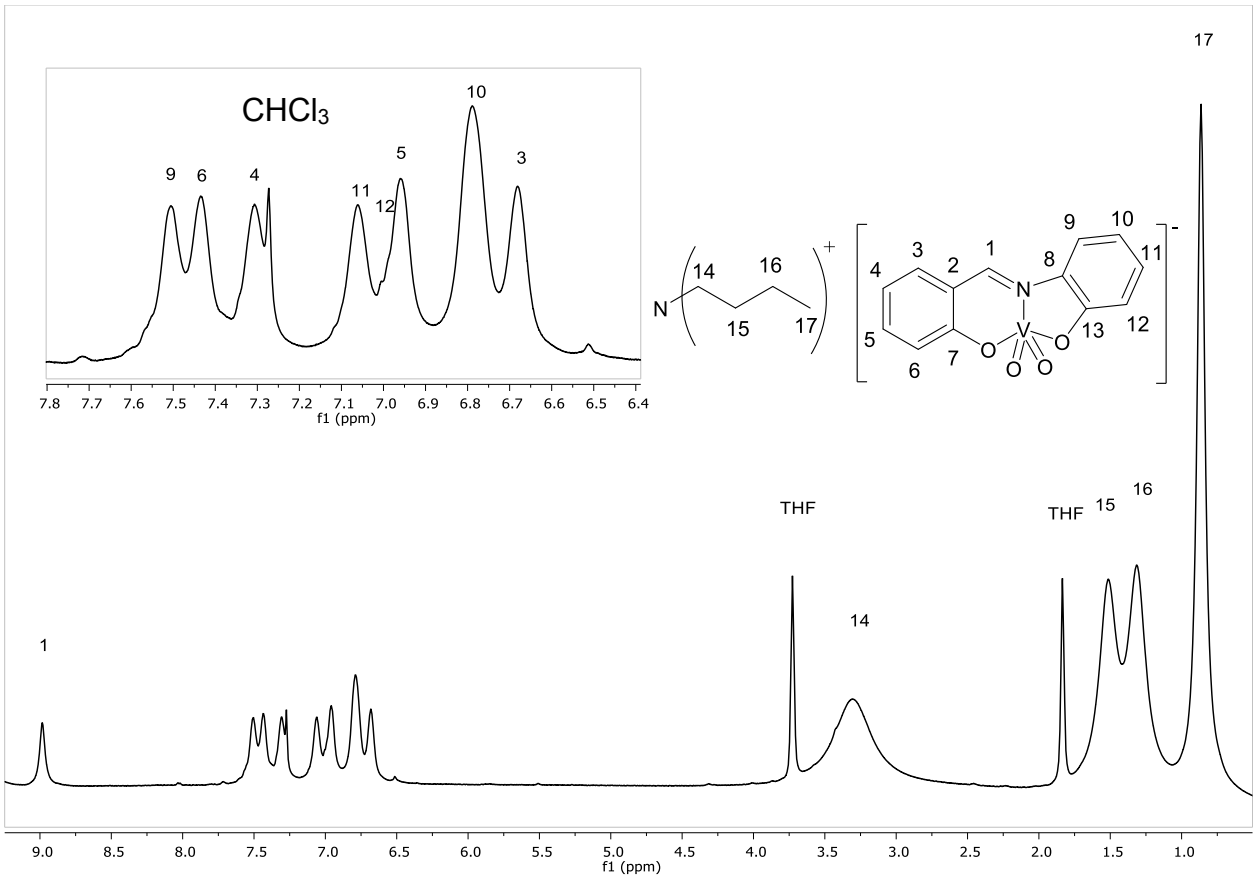
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12
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V
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O
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THF
THF
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16
14
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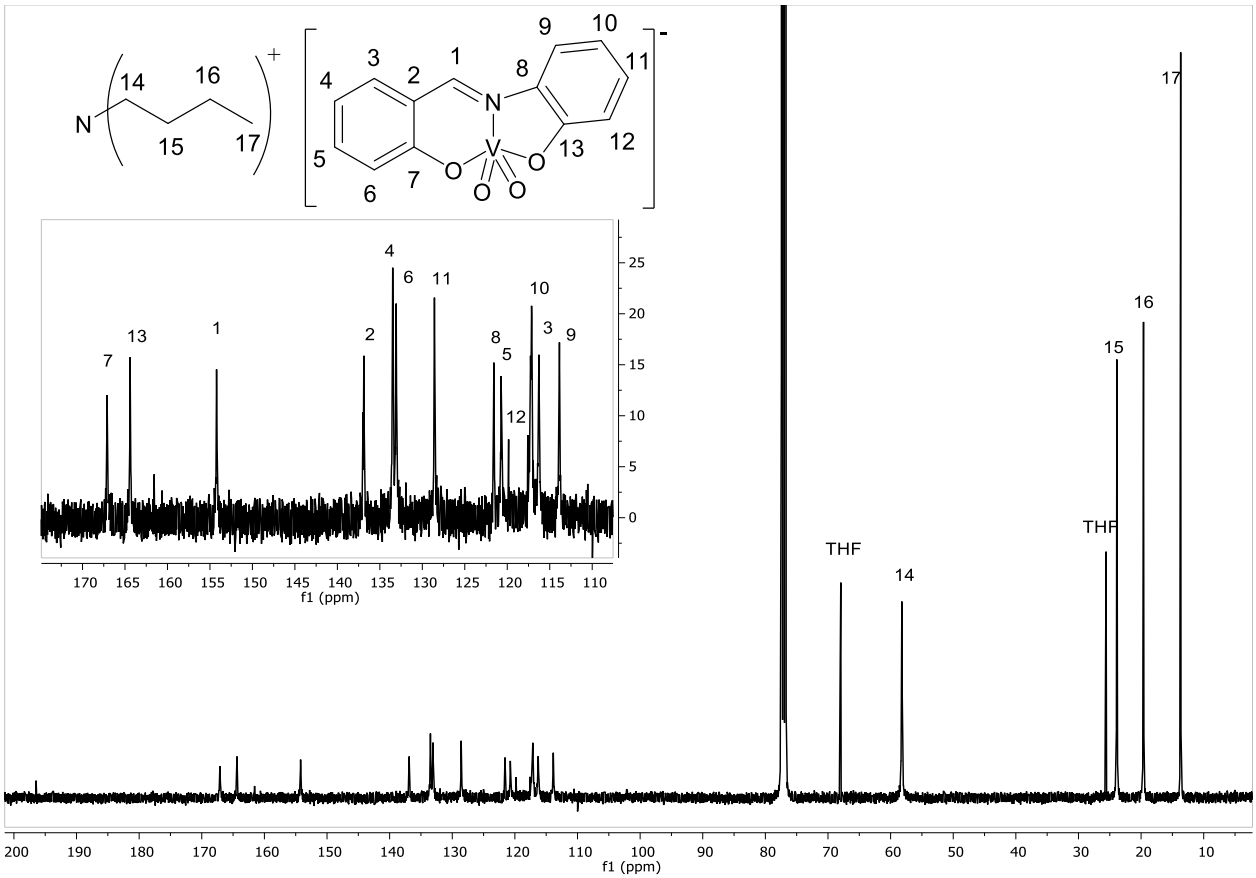
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O
-
4
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11
10
13
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2
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3
9
7
5
12
25
20
15
10
5
0
170 165 160 155 150 145 140 135 130 125 120 115 110
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16
15
THF
THF
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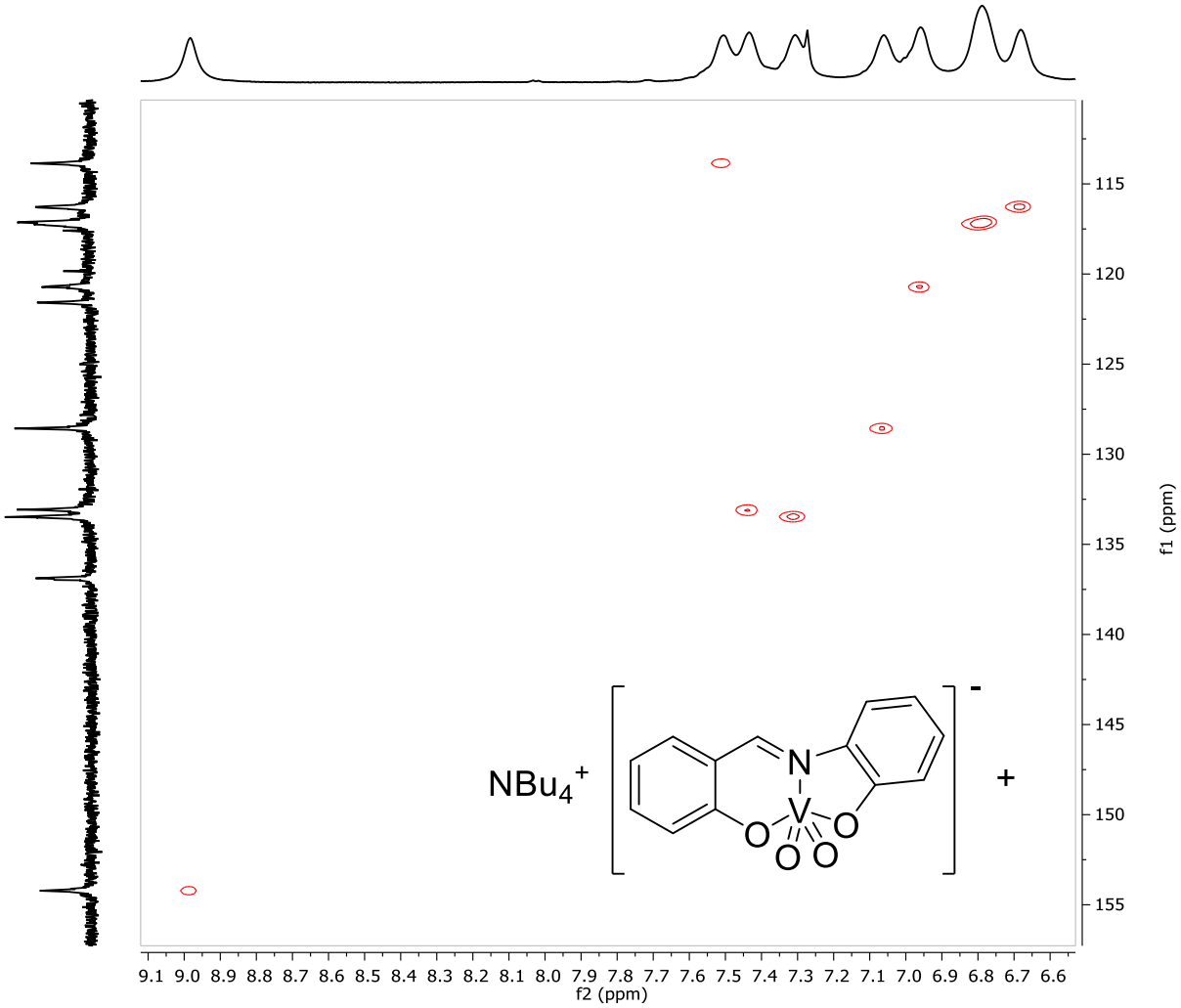
f1 (ppm)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V
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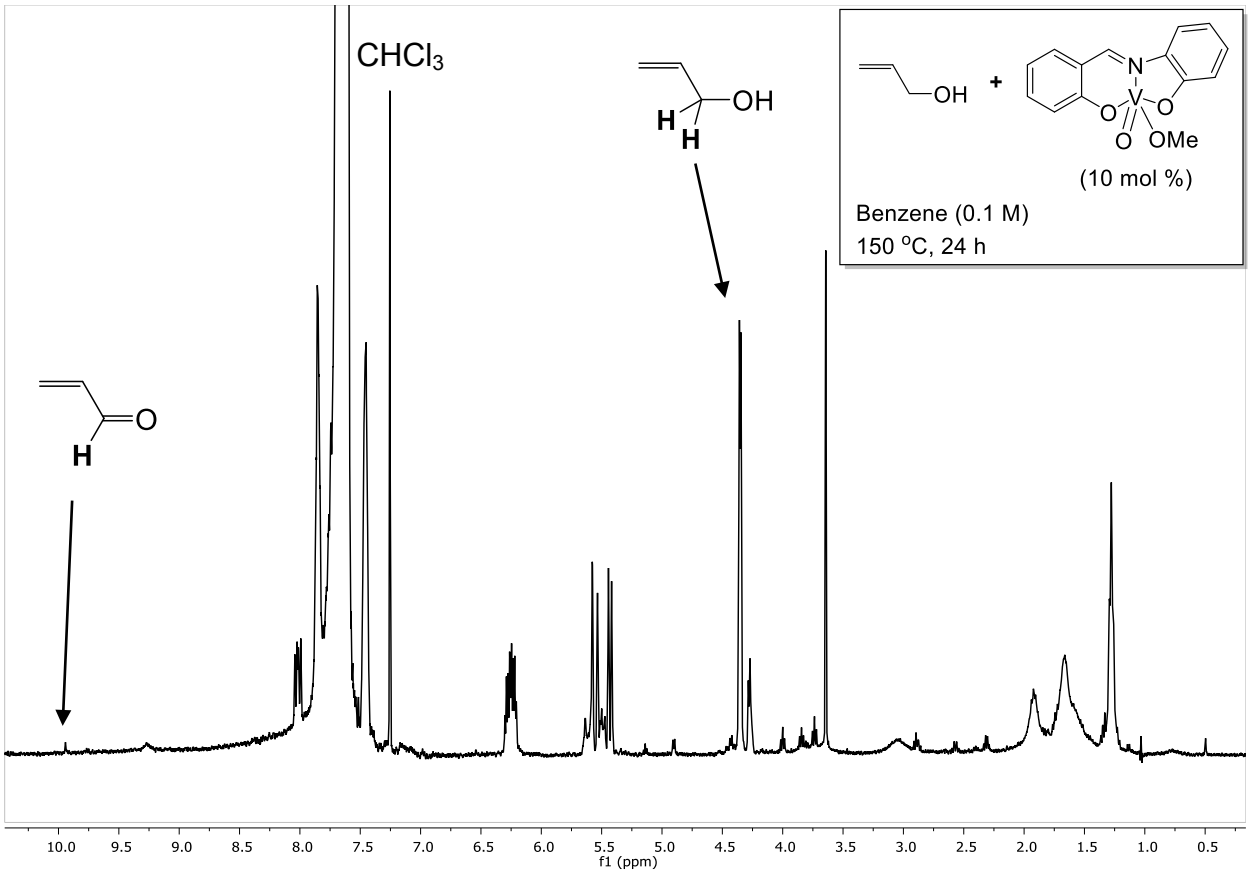
O
O
O
-
+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H
OH
+
N
V
O
O
O
OMe
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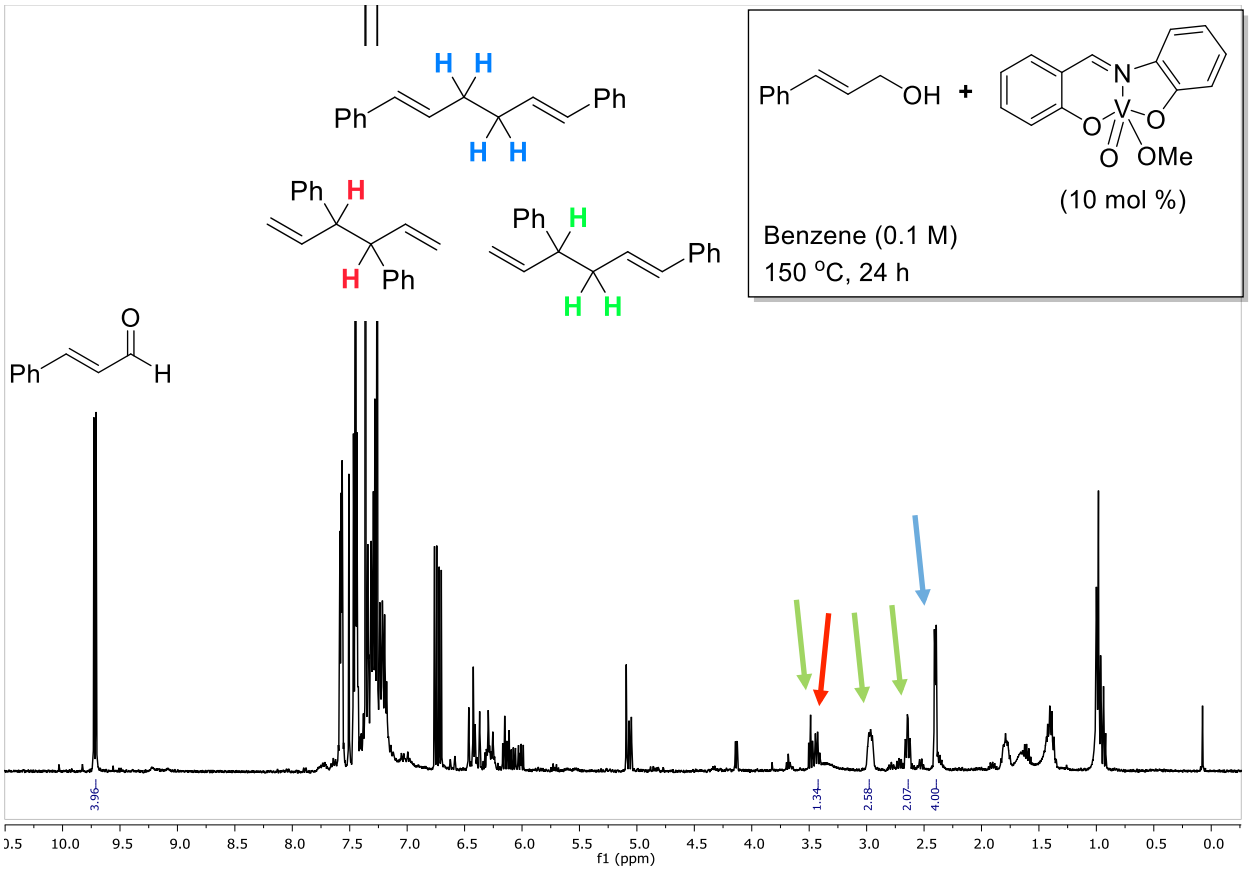
f1 (ppm)


Ph
OH
+
N
V
O
O
O
OMe
(10 mol %)
Benzene (0.1 M)
150 °C, 24 h
H H
Ph
Ph
H H
Ph H
H Ph
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H H
Ph
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Ph
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1.34
2.58
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4.00
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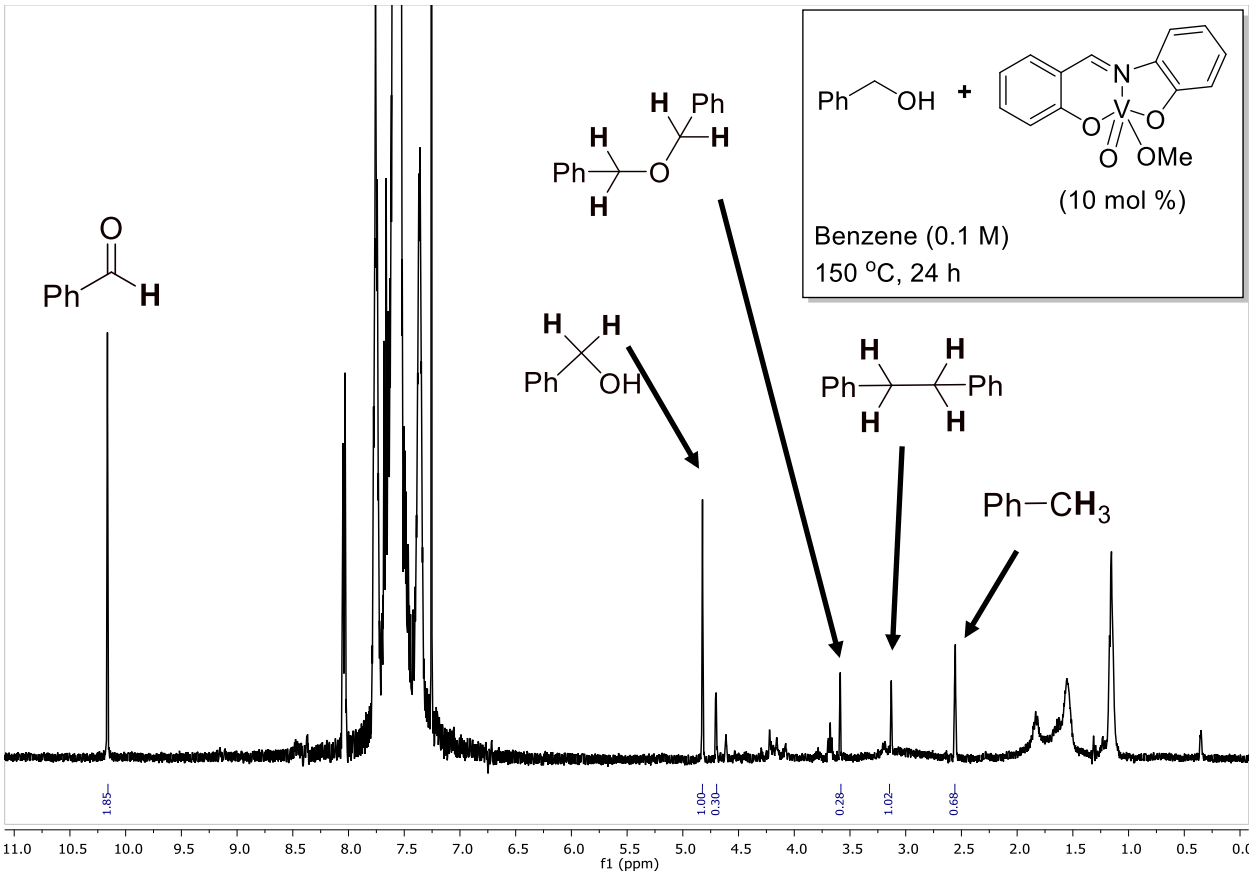
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V
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(10 mol %)
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1.02
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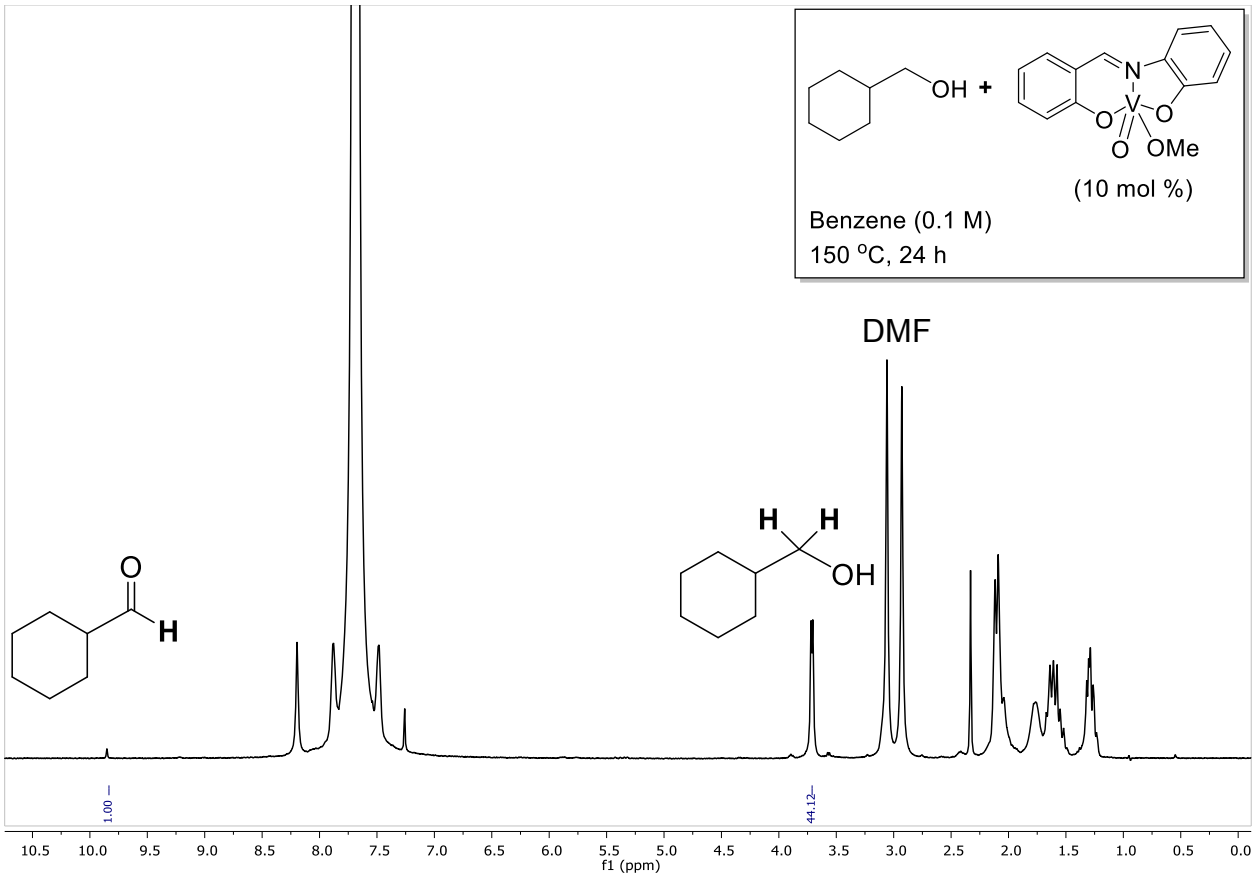
f1 (ppm)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V
O
O
O
OMe
(10 mol %)
Benzene (0.1 M)
150 °C, 24 h
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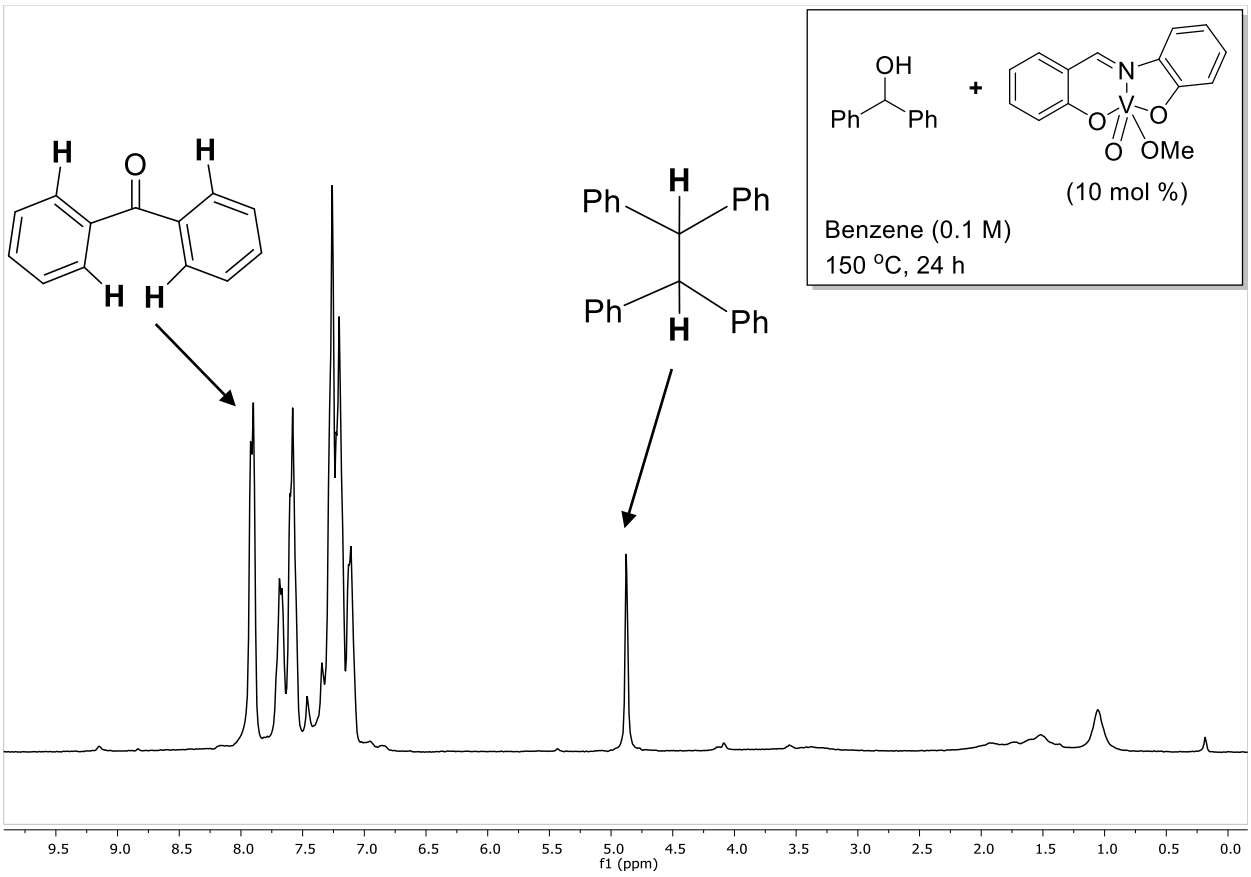
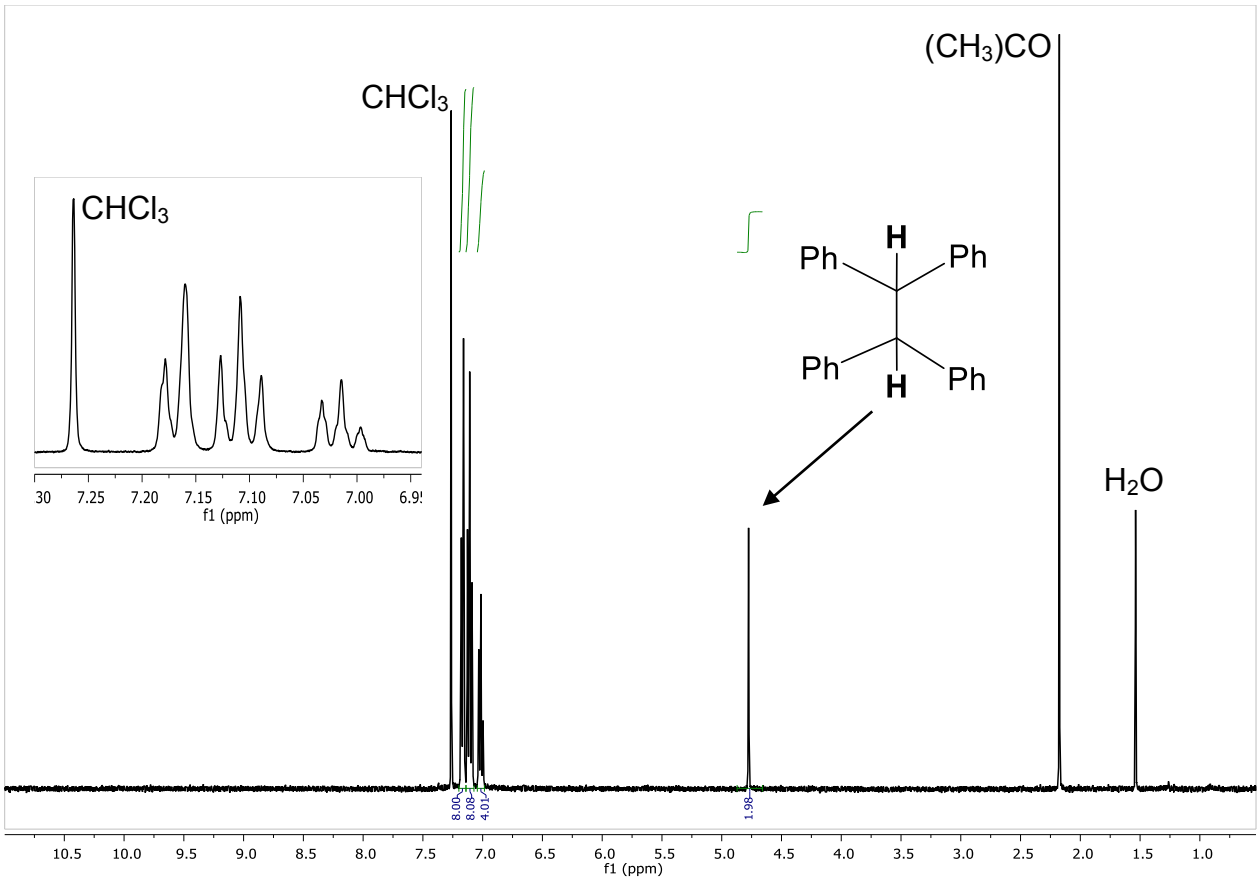
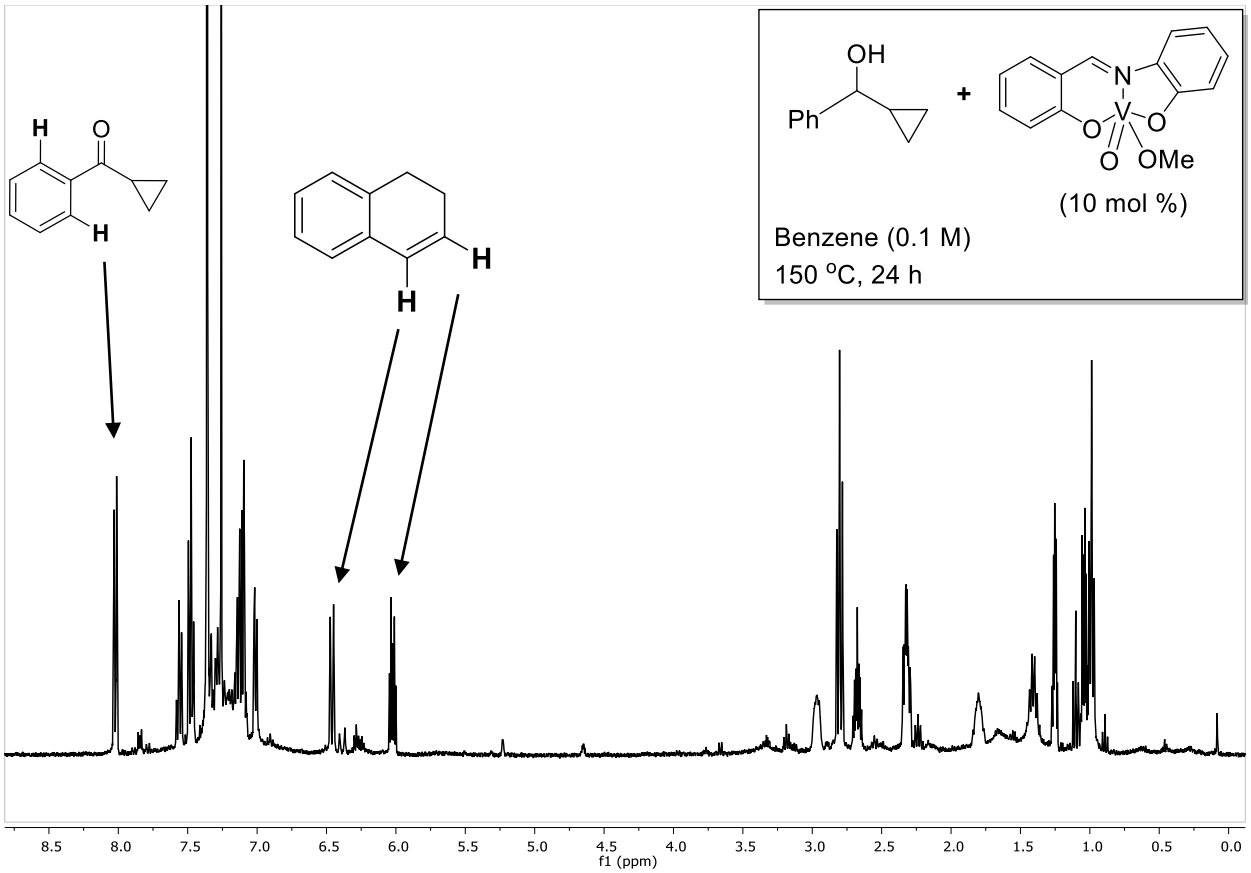
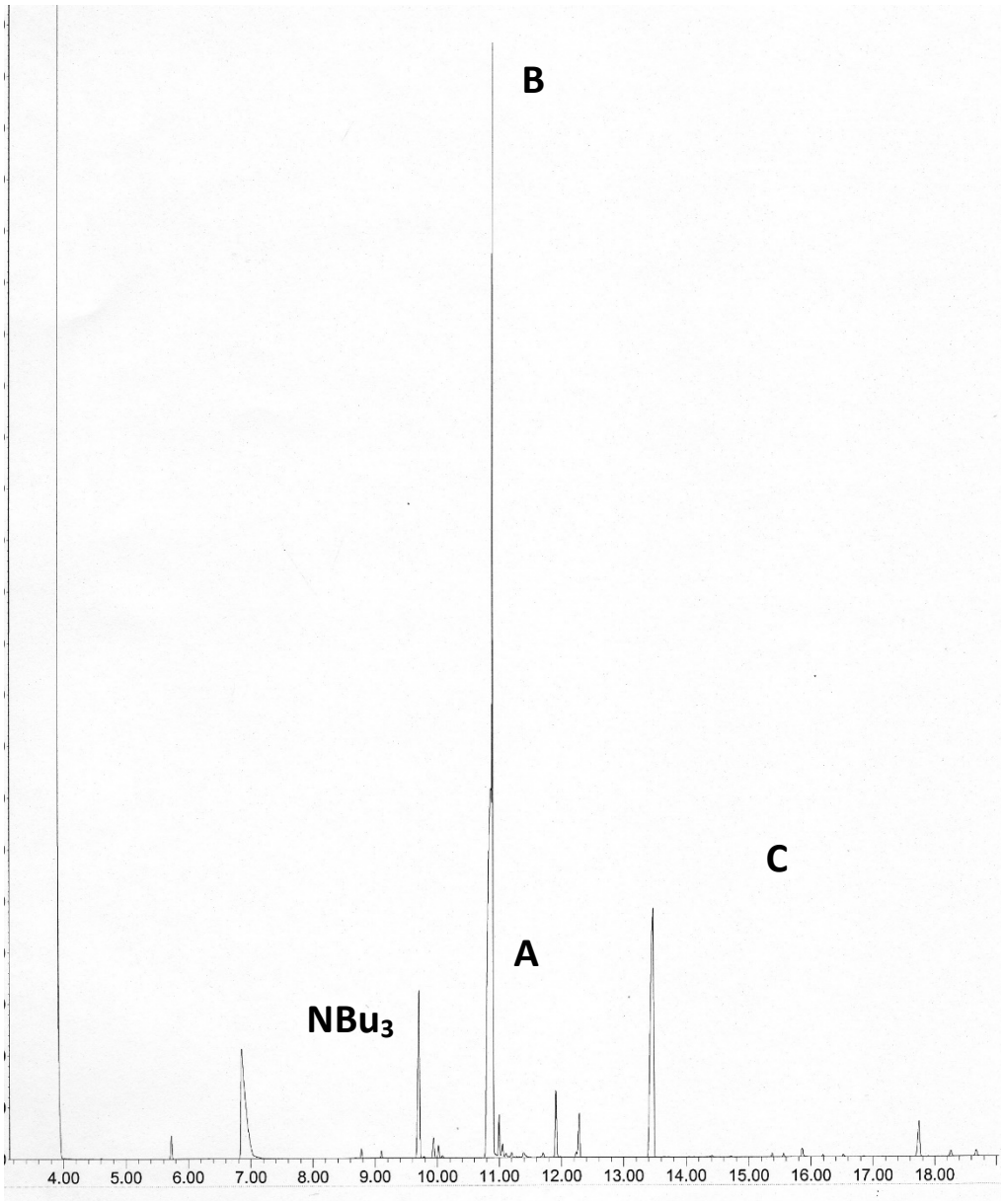
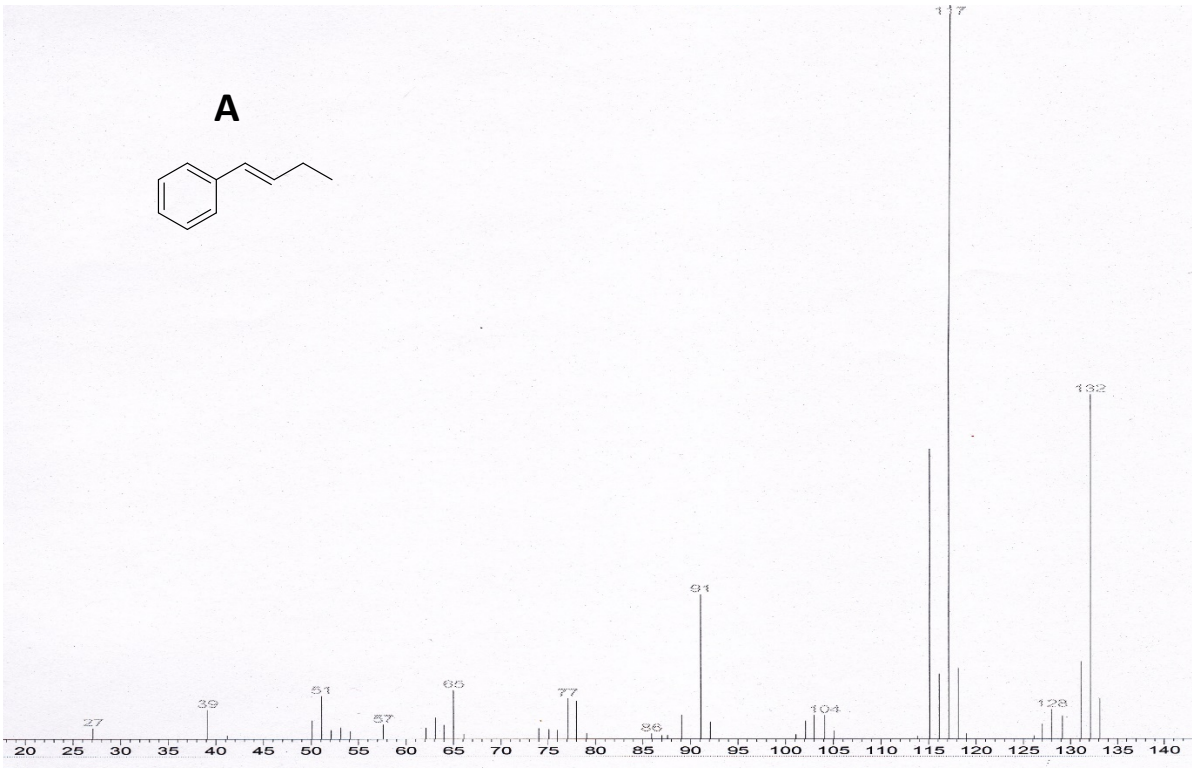
H
H
H
OH
1.00
44.12
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


OH
Ph
Ph
+
N
V
O
O
O
OMe
(10 mol %)
Benzene (0.1 M)
150 °C, 24 h
H
O
H
H
H
Ph
H
Ph
Ph
H
Ph
9.5 9.0 8.5 8.0 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)

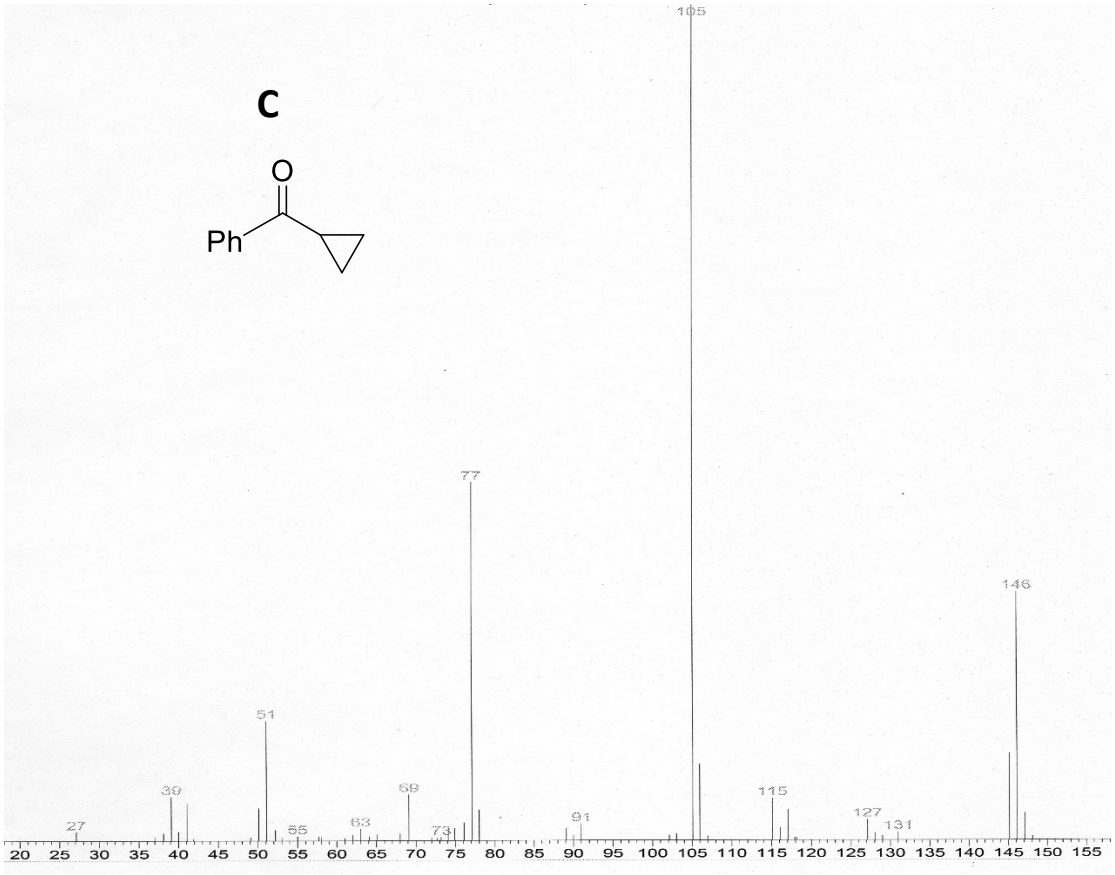

CHCl3
(CH3)CO
H2O
Ph
Ph
Ph
Ph
H
H
f1 (ppm)

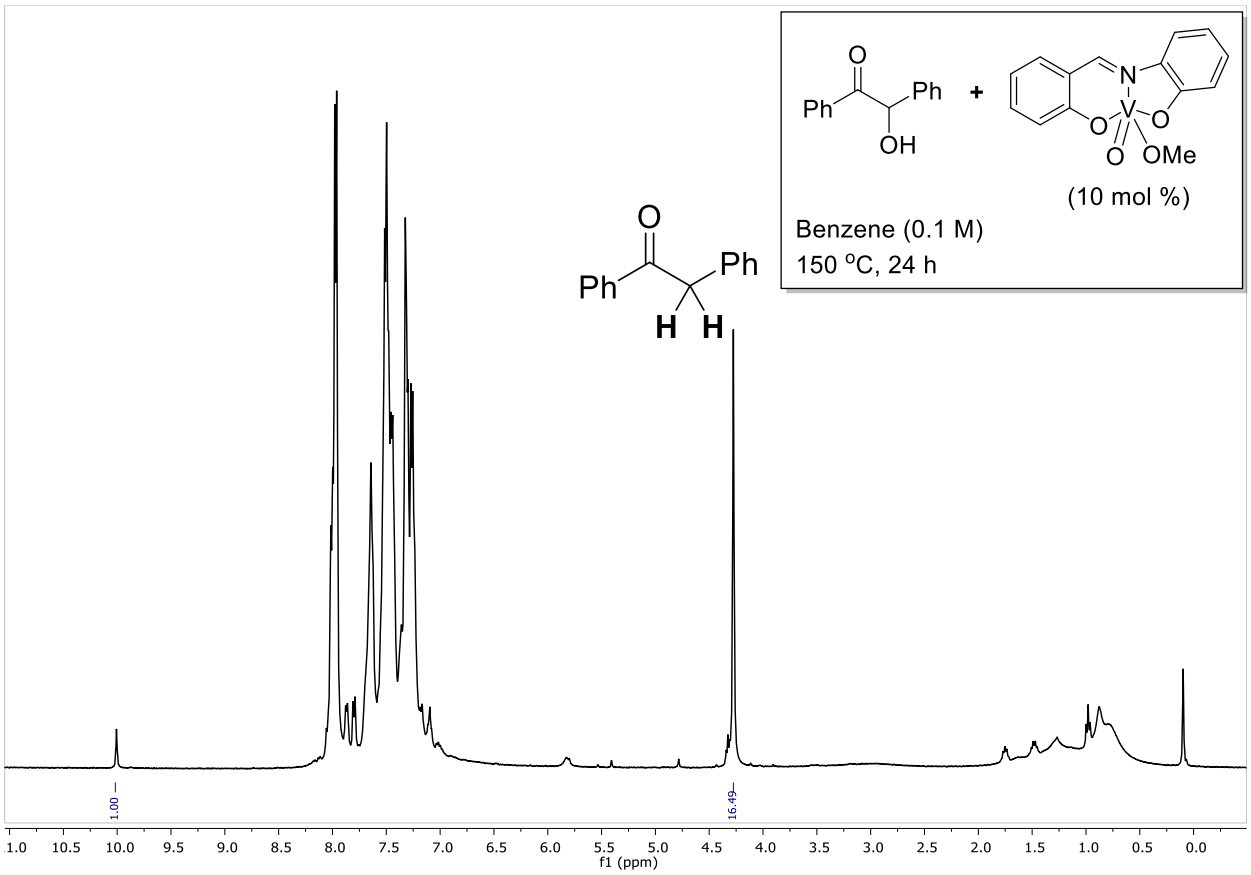

OH
Ph
+
N
V
O
O
O
OMe
(10 mol %)
Benzene (0.1 M)
150 °C, 24 h
H
O
H
H
H
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

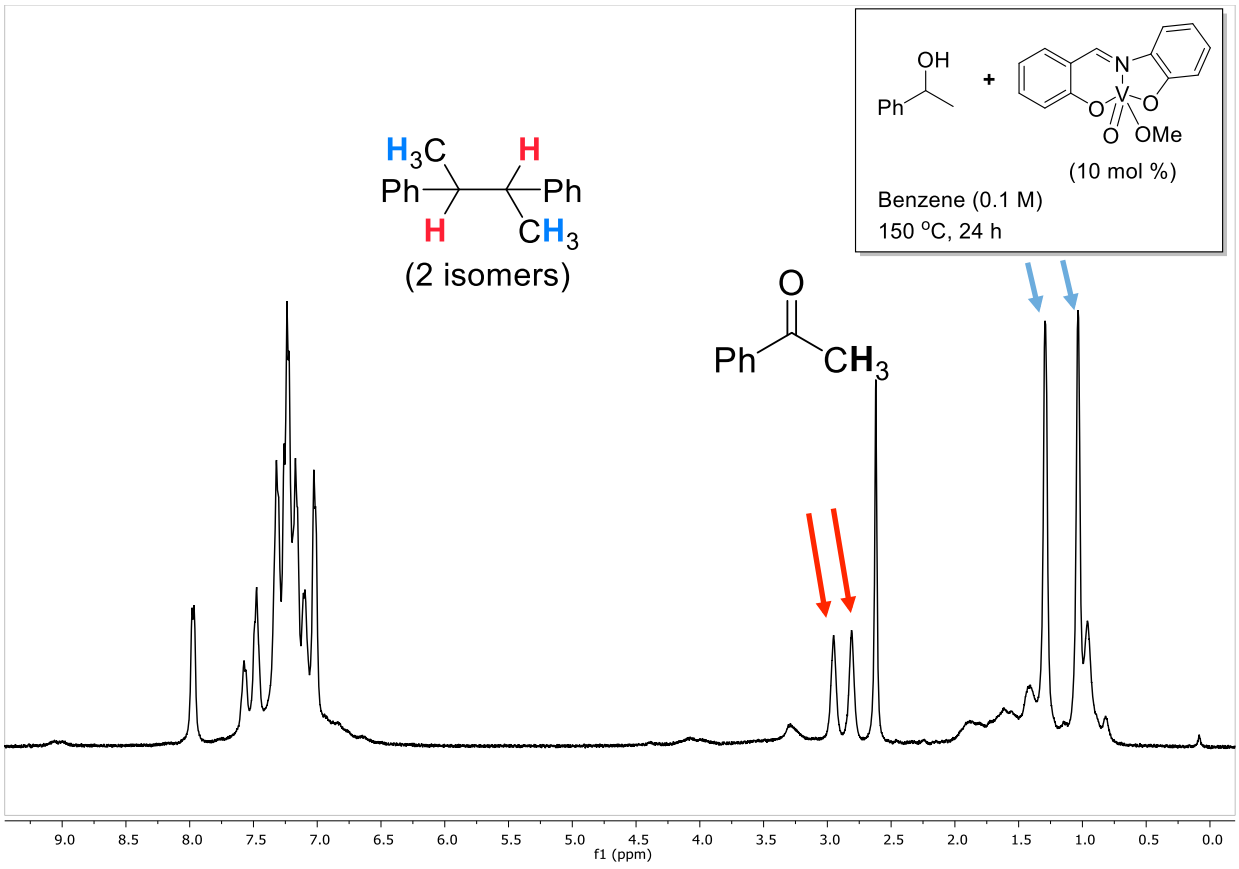

B
C
A
NBu3
4.00
5.00
6.00
7.00
8.00
9.00
10.00
11.00
12.00
13.00
14.00
15.00
16.00
17.00
18.00


A
117
132
91
65
51
39
77
57
27
104
128
86
20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140


B
130
115
127
64
51
77
102
89
86
44
40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135


C
O
Ph
105
77
146
51
39
59
115
27
55
63
73
91
127
131
20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155


O
Ph
Ph
OH
+
N
V
O
O
O
OMe
(10 mol %)
Benzene (0.1 M)
150 °C, 24 h
O
Ph
Ph
H H
1.00
16.49
1.0 10.5 10.0 9.5 9.0 8.5 8.0 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)


OH
Ph
+
N
V
O
O
O
OMe
(10 mol %)
Benzene (0.1 M)
150 °C, 24 h
H3C
H
Ph
Ph
H
CH3
(2 isomers)
O
Ph
CH3
9.0
8.5
8.0
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)

```
File        : D:\GCMS\HPCHEM\1\DATA\1902KMNB.D
Operator    : Foster
Acquired    : 10 Jan 2017  13:37     using AcqMethod COFFEE22
Instrument :   GCMS
Sample Name: 1-49
Misc Info   : Scan; 20:1 split; 1uL
Vial Number: 1
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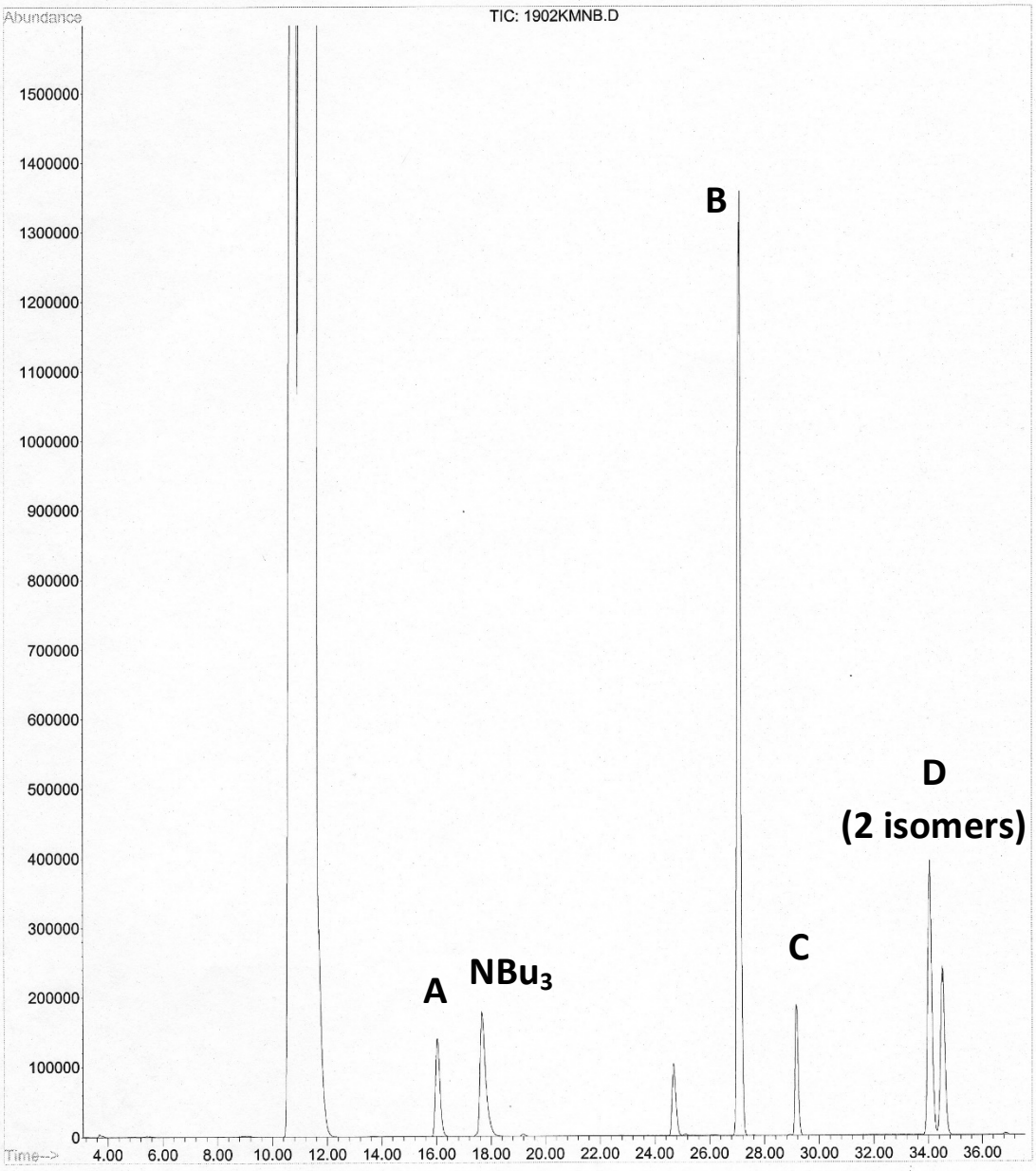
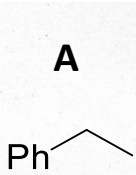
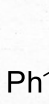


A


Ph

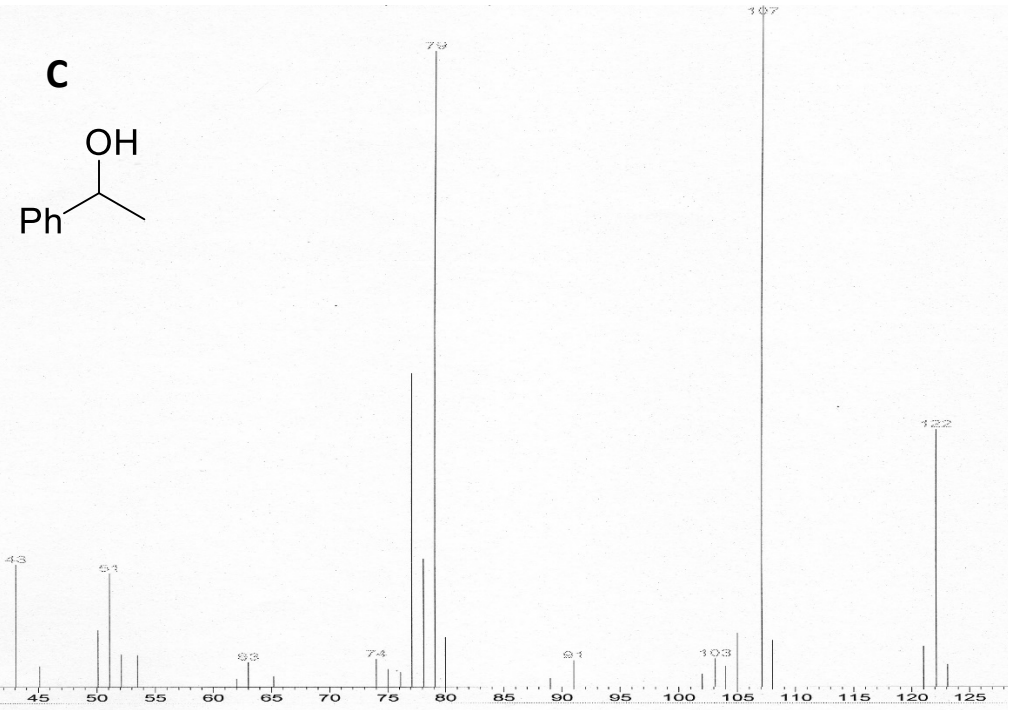
106
77
51
39
65
91
30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115

B

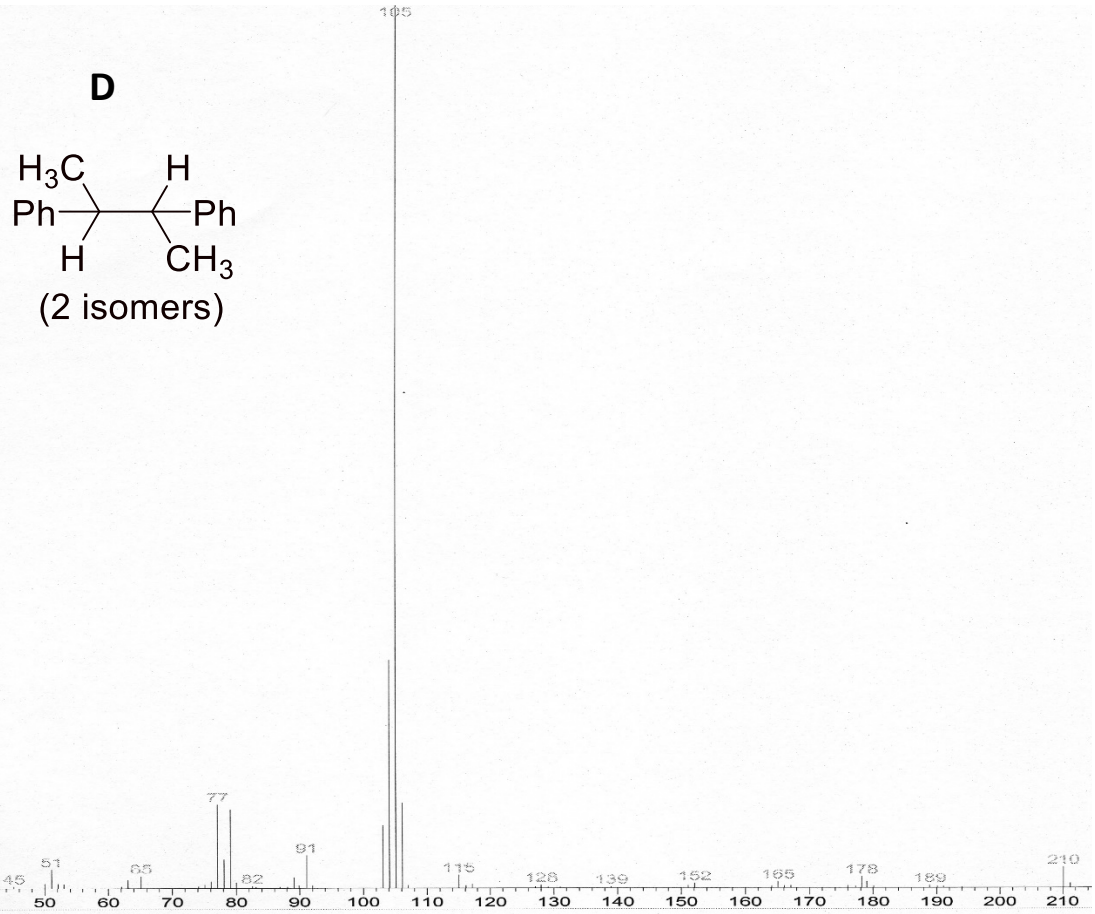

O
Ph
CH3

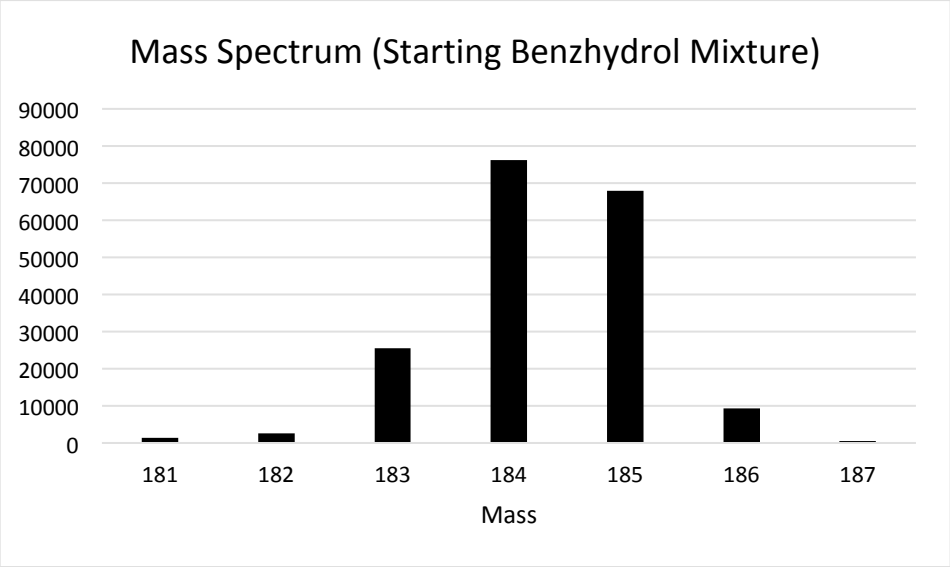
105
77
120
51
39
74
63
91
102
30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125

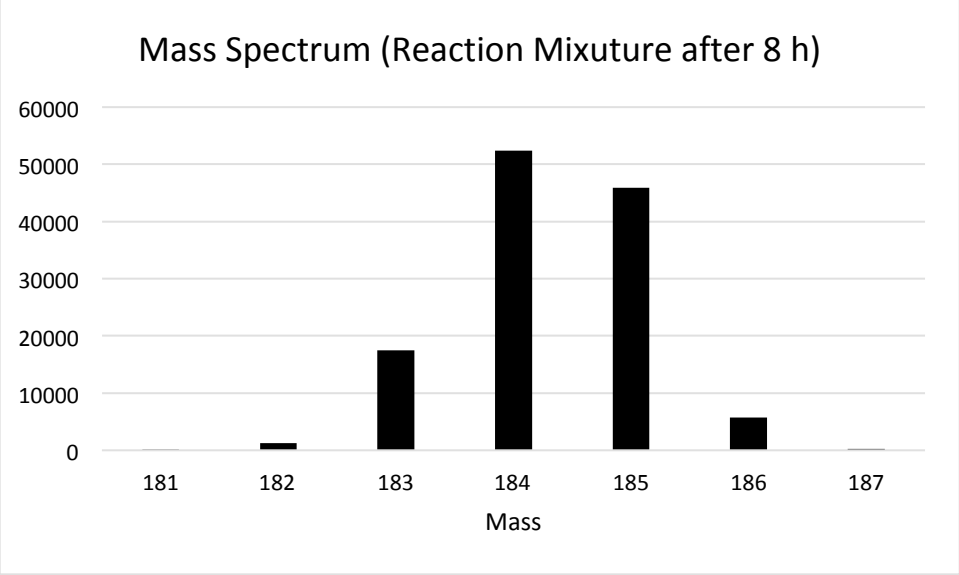
C


OH
Ph
107
79
122
43
51
39
93
74
91
103
35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125

D


H3C
H
Ph
Ph
H
CH3
(2 isomers)
105
77
91
39
45
51
65
82
115
128
139
152
165
178
189
210
40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210


Mass Spectrum (Starting Benzhydrol Mixture)
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
181
182
183
184
185
186
187
Mass


Mass Spectrum (Reaction Mixuture after 8 h)
60000
50000
40000
30000
20000
10000
0
181
182
183
184
185
186
187
Mass

Computational Methods

The B3LYP [a] method resident in Gaussian 09 [b] was used to determine the energy minimized structures and electronic energies of Figure 2 (0 K, vacuum); the 6-31-G(d) basis set was used for H, C, N, O atoms and LANL2DZ for V.

[a] D. Becke, "Density-functional thermochemistry. III. The role of exact exchange," J. Chem. Phys. **98** (1993) 5648-52.

[b] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Aus:n, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Mar:n, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.