Electronic Supplementary Material (ESI) for ChemComm.


# Supporting information for
# Oxo-Rhenium Catalyzed Deoxygenation and Reductive Coupling of Alcohols

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**Reaction of Alcohols with $PPh_3/(PPh_3)_2ReO_2I$**

0.10 mmol (18.4 mg) of benzhydrol, 0.10 mmol (26.2 mg) oftriphenylphosphine, and 11.5 mol% (10 mg) of $(Ph_3P)_2IReO_2$ were added to a thick-walled Ace glass reactor tube containing a magnetic stir bar. 1 mL of benzene was added to the tube. The tube containing the reaction mixture was sealed with a Teflon, front-seal plunger valve and degassed, three times at room temperature with mild vacuum (ca. 60 mmHg) and backfilled with $N_2$. The reactor tube was then placed in an oil bath at 150°C and heated for 24 hours.

Analysis :

To determine 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 $^1H$ NMR spectrum was obtained on a Varian Mercury VX-300 MHz and processed using SpinWorks[1].

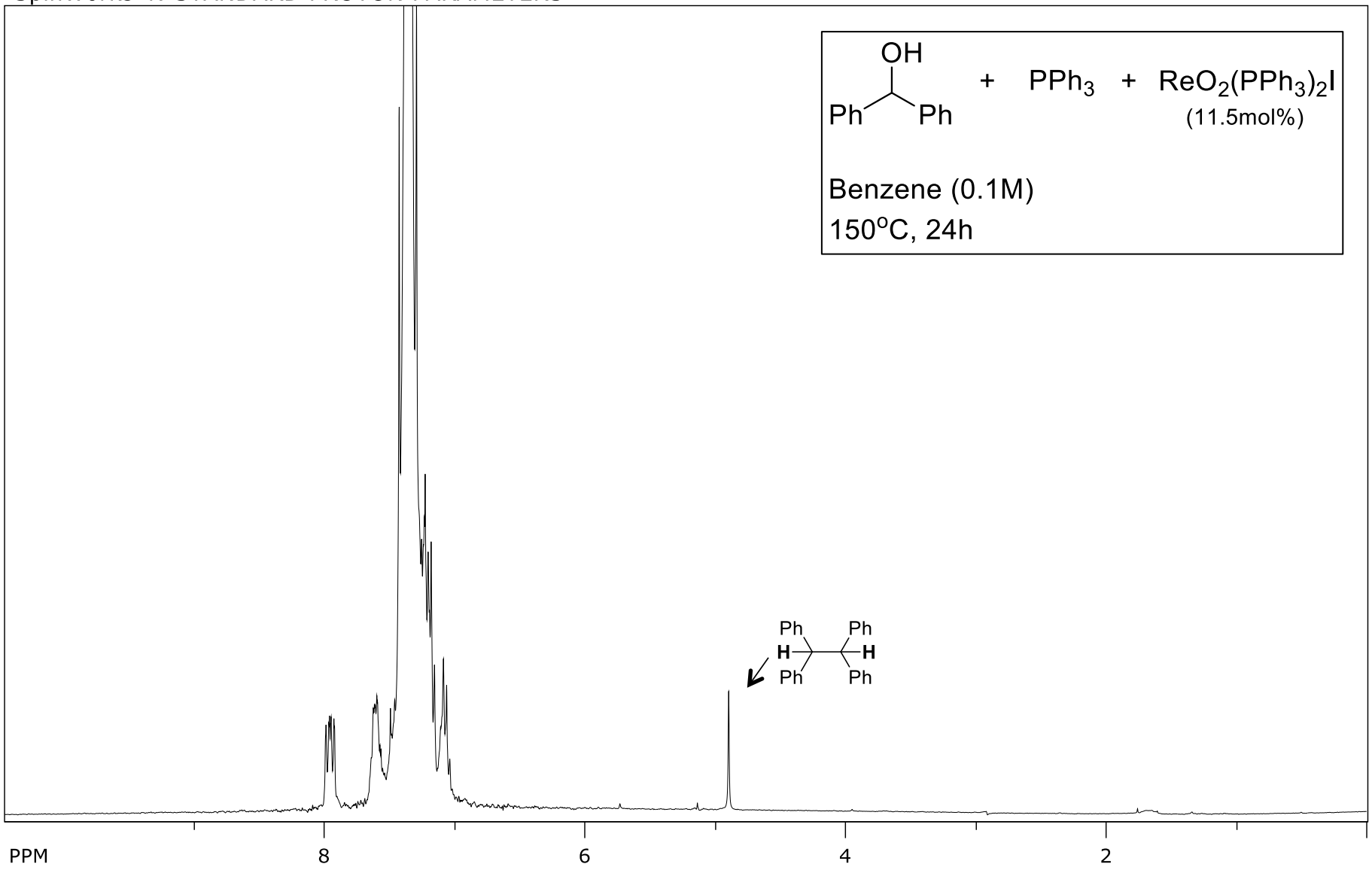
To determine an isolated yield, the reaction was repeated at a 1.0 mmol scale. The reaction mixture was concentrated by rotary evaporation before being added to a silica column. The reaction product was eluted down with dichloromethane, the solvent rotary evaporated and the residue weighed.

**Reaction of Alcohols with $PPh_3/(PPh_3)_2ReO_2I$**

In a typical reaction benzhydrol (1.0 mmol) and $Bu_4N$[(salicyl-2-thiophenyl-hydrazide)$VO_2$] (0.10 mmol) were combined with 5 mL benzene in a glass-lined stainless steel reactor with a magnetic spin bar, then flushed twice and pressurized with CO up to a total pressure of 280 psi (20 atm), and heated at 180 $^oC$ for 24h. The reaction mixture was cooled to room temperature, vented (fume hood), and an aliquot removed for $^1H$ NMR analysis as described above with 5 mL DMSO added as an integration reference.

1) Marat, K. SpinWorks 4.0.1.0 ed. University of Manitoba: Winnipeg, Canada, 2013.

SpinWorks 4: STANDARD PROTON PARAMETERS

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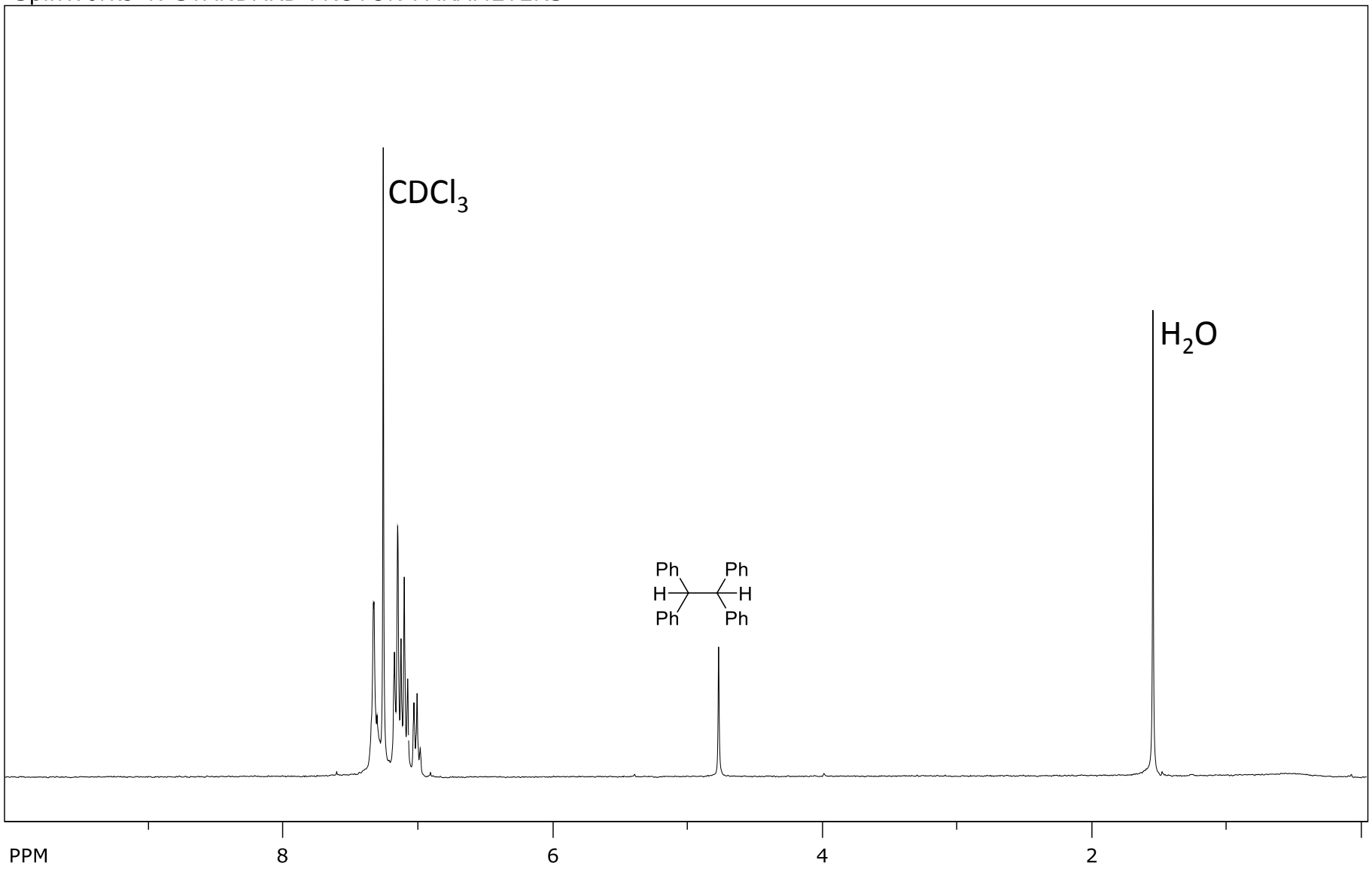
number of scans: 64

freq. of 0 ppm: 300.121714 MHz
processed size: 16384 complex points
LB: 1.500 GF: 0.0000

**Melting point found : 199-200°C**

SpinWorks 4: STANDARD PROTON PARAMETERS

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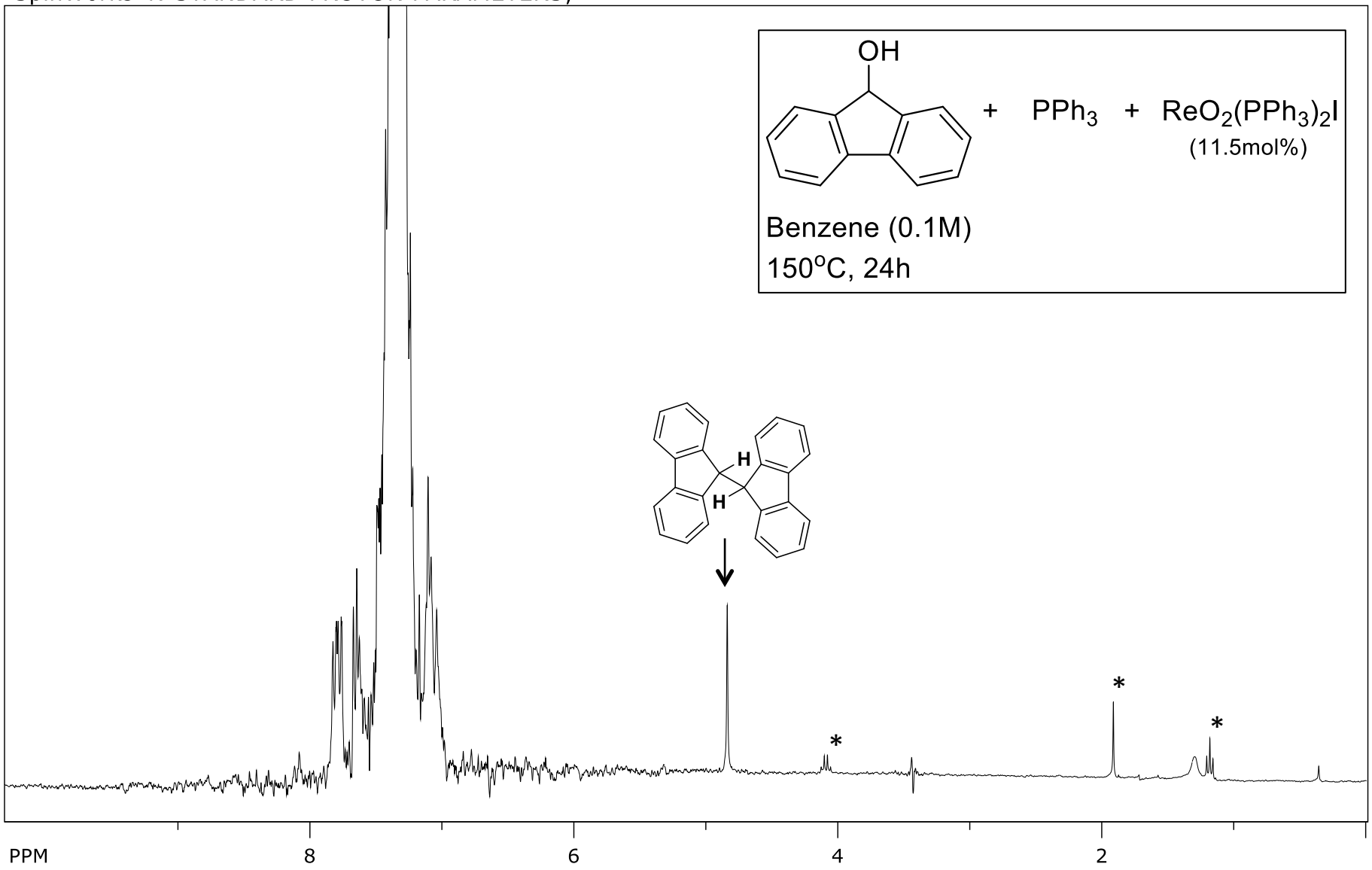
width: 4803.07 Hz = 16.0037 ppm = 0.293156 Hz/pt
number of scans: 32

freq. of 0 ppm: 300.121762 MHz
processed size: 16384 complex points
LB: 1.500 GF: 0.0000

SpinWorks 4: STANDARD PROTON PARAMETERS;

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number of scans: 32

freq. of 0 ppm: 300.121943 MHz
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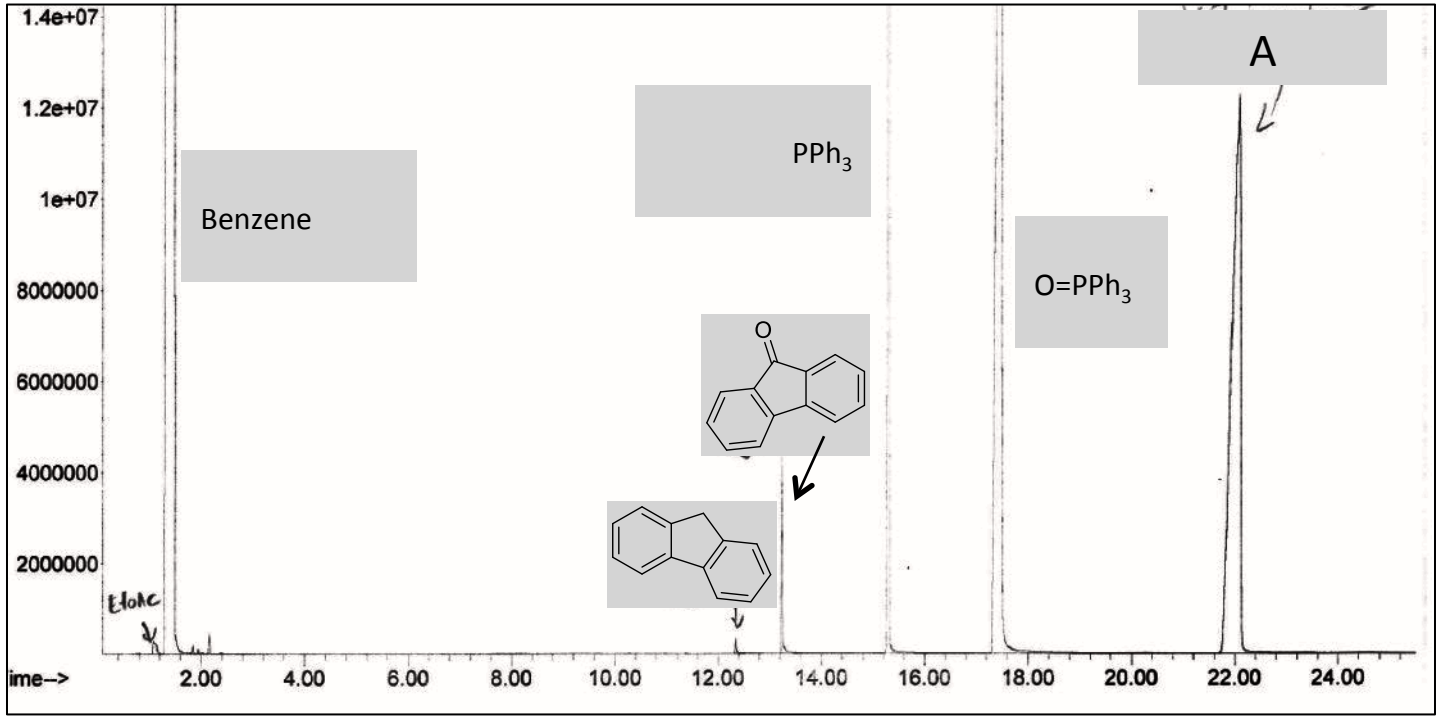
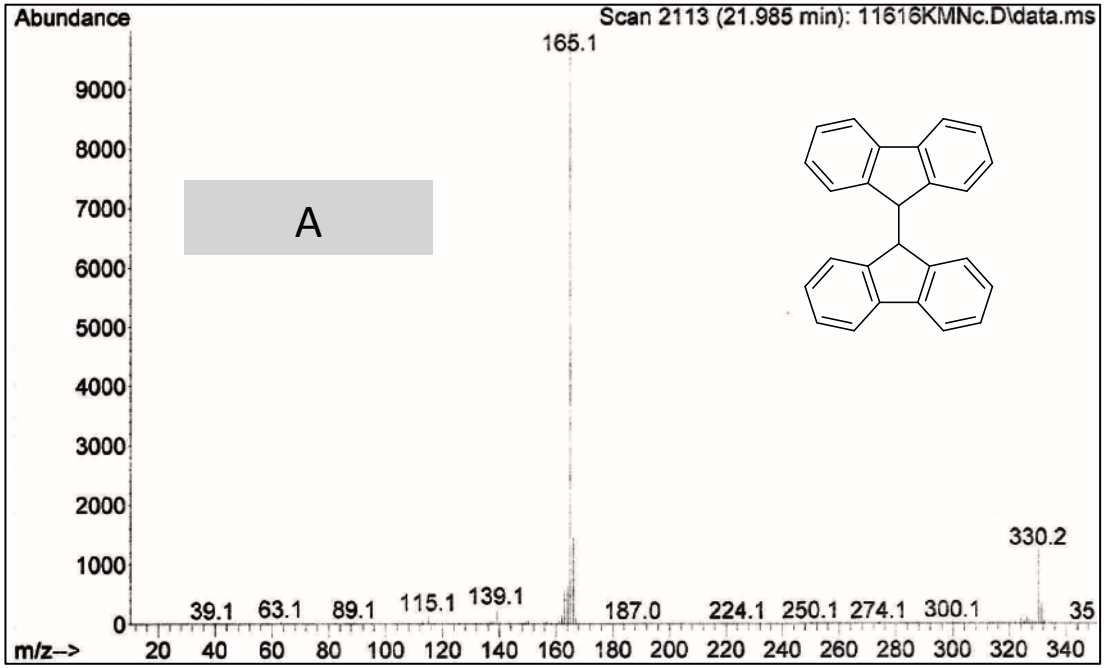
LB: 1.500 GF: 0.0000



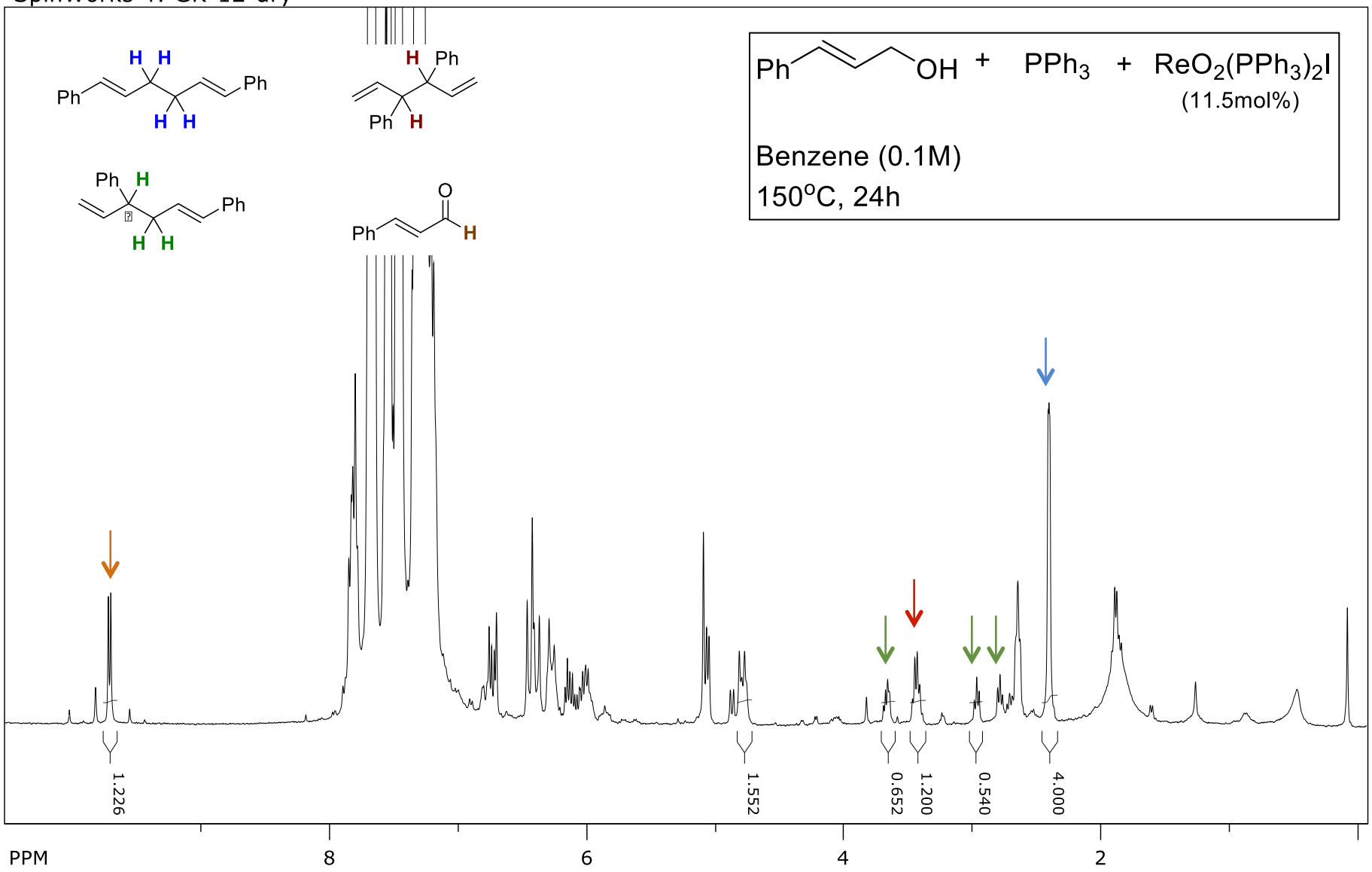
*residual ethyl acetate


1.4e+07
1.2e+07
1e+07
8000000
6000000
4000000
2000000
EtOAc
ime-->
2.00
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00
22.00
24.00
Benzene
PPh3
O=PPh3
A
O


Abundance
Scan 2113 (21.985 min): 11616KMNc.D\data.ms
165.1
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
A
330.2
39.1
63.1
89.1
115.1
139.1
187.0
224.1
250.1
274.1
300.1
m/z-->
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340

# NMR recorded after the reaction solvent was removed under vacuum

SpinWorks 4: GK-12-dry

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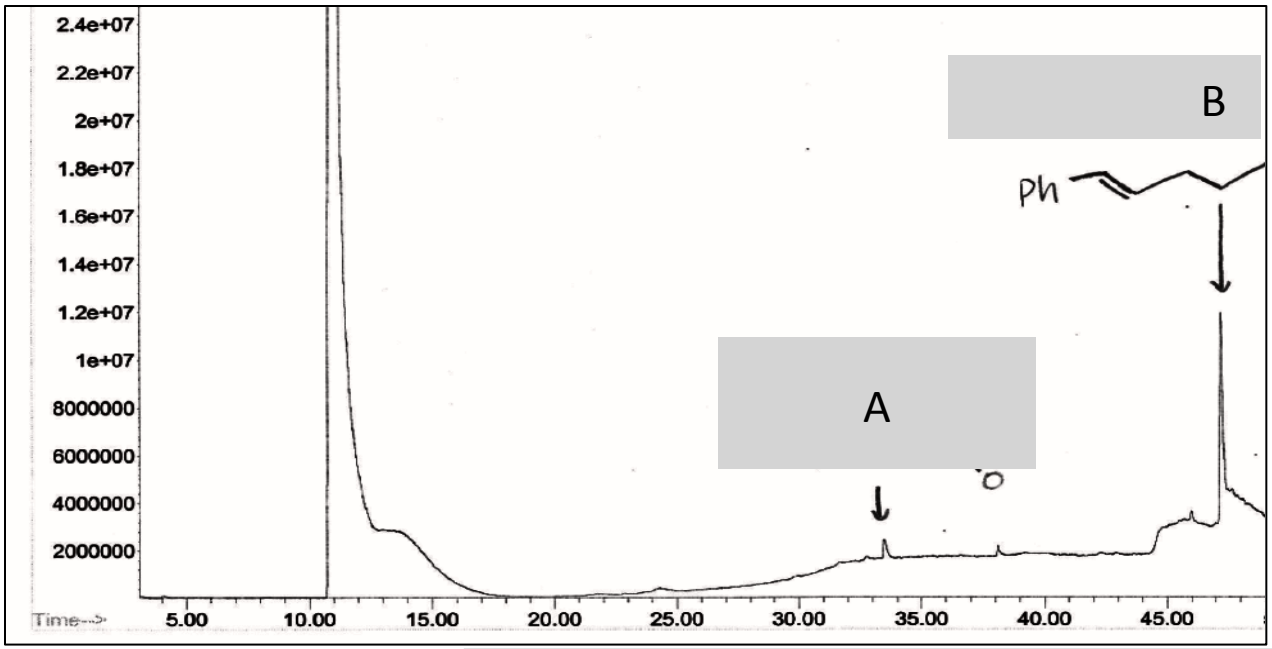
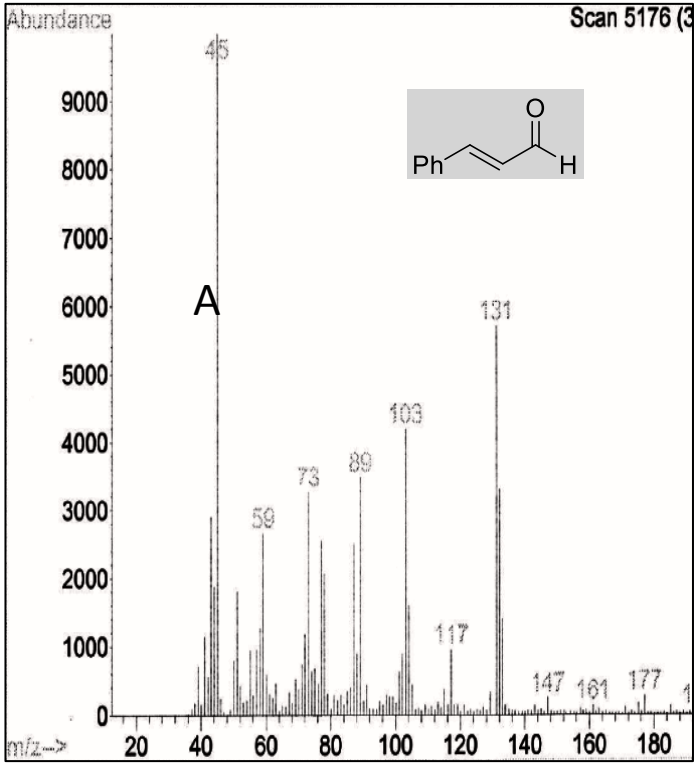
width: 6410.26 Hz = 16.0309 ppm = 0.195626 Hz/pt
number of scans: 8

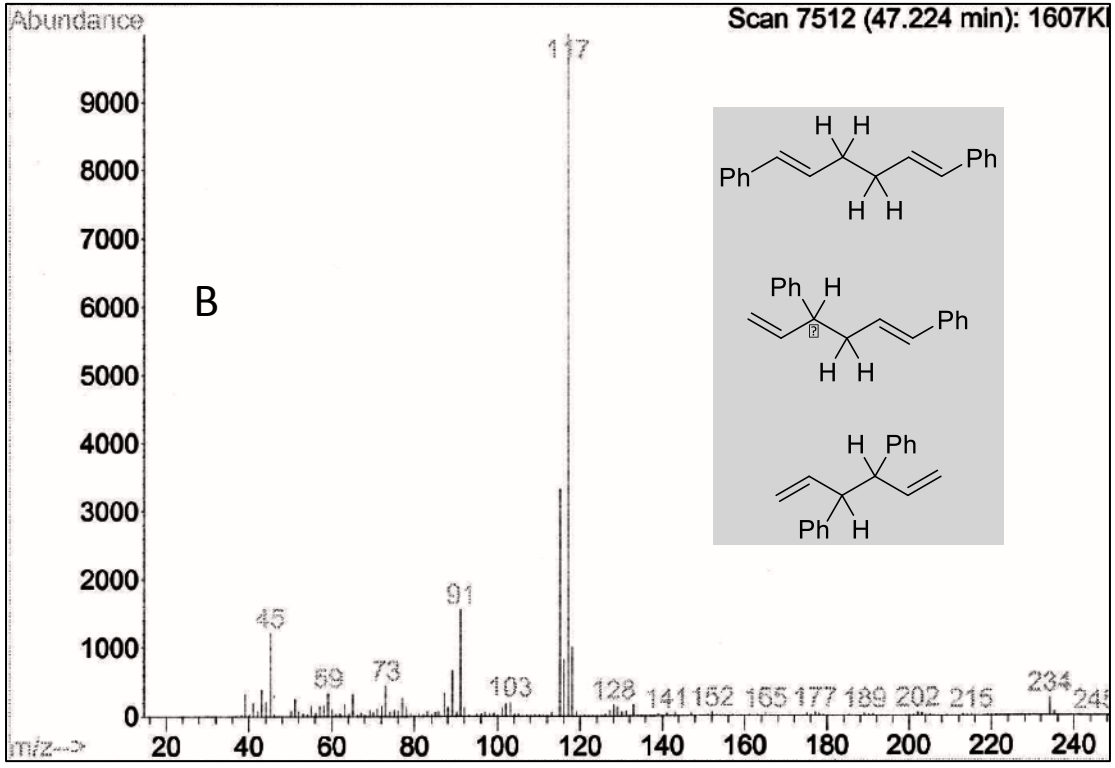
freq. of 0 ppm: 399.865946 MHz
processed size: 32768 complex points
LB: 1.500 GF: 0.0000

The assignment of product structures from the cinnamyl alcohol reaction is based on comparison of the H-NMR spectrum of the product mixture with the reported spectra for the isomeric dienes (ref below) and with computer simulated NMR spectra.

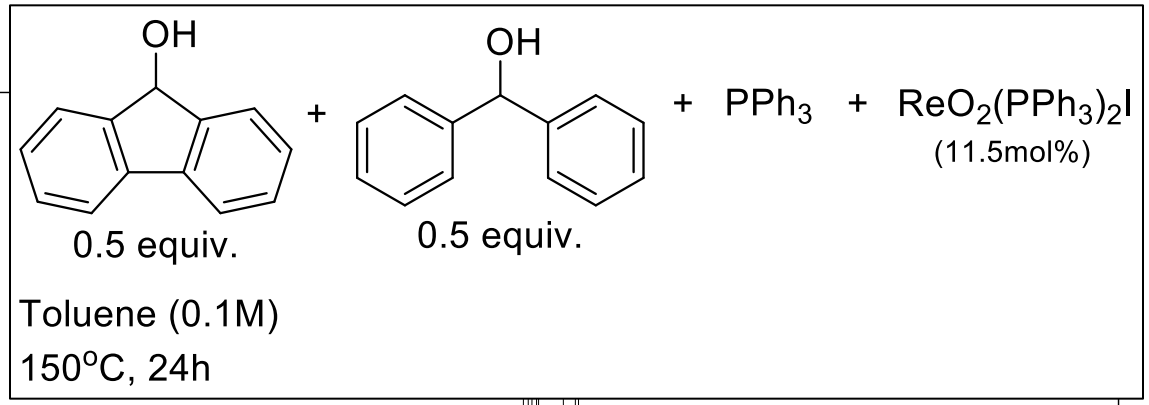
K. Muraoka, M. Nojima, S. Kusabayashi, S. Nagase, J. CHEM. SOC. PERKIN TRANS. II, 761, 1986.


B
Ph
A
O
Time-->
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
45.00


Abundance
Scan 5176 (3
A
O
Ph
H
m/z-->
20
40
60
80
100
120
140
160
180


Abundance
Scan 7512 (47.224 min): 1607KI
B
Ph
Ph
H H
H H
Ph H
Ph
H H
H Ph
Ph H
m/z-->
20
40
60
80
100
120
140
160
180
200
220
240

SpinWorks 4: KN315







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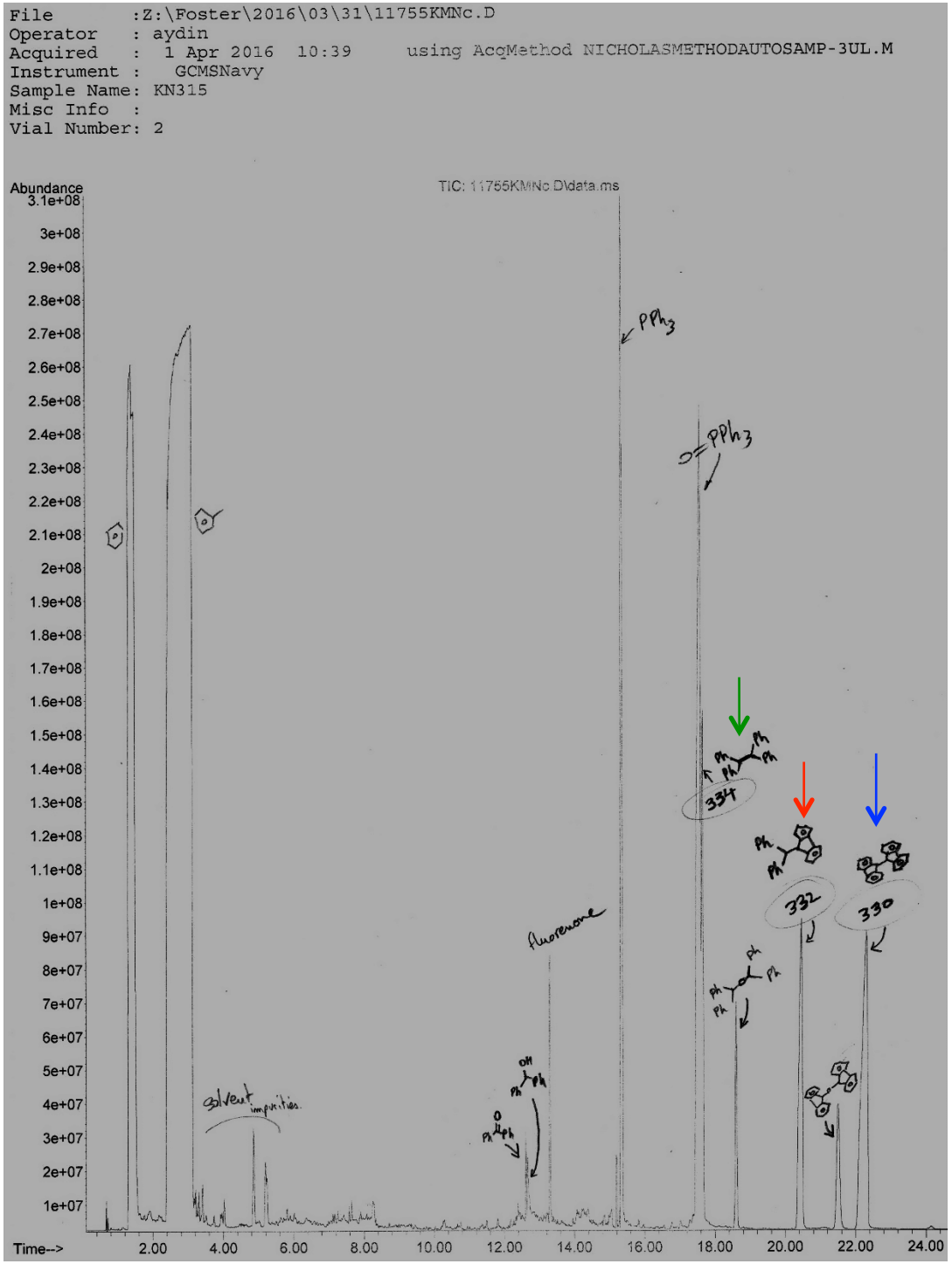
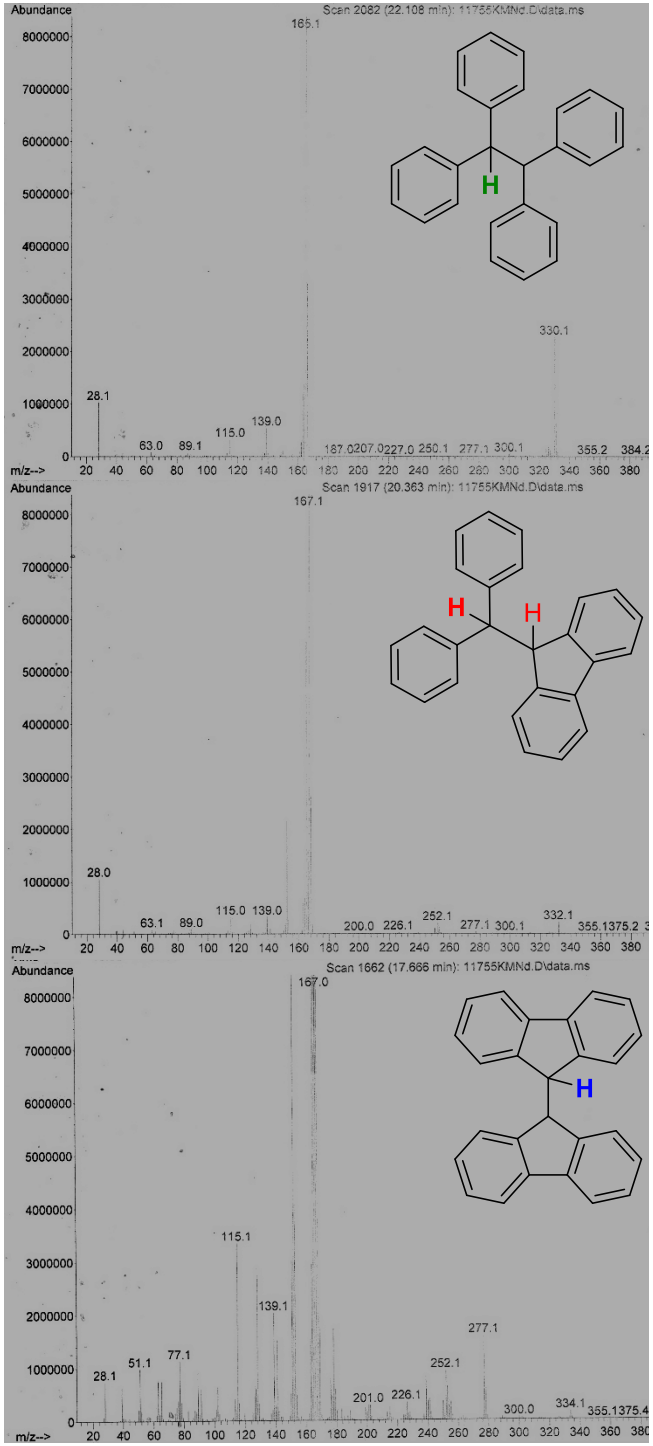
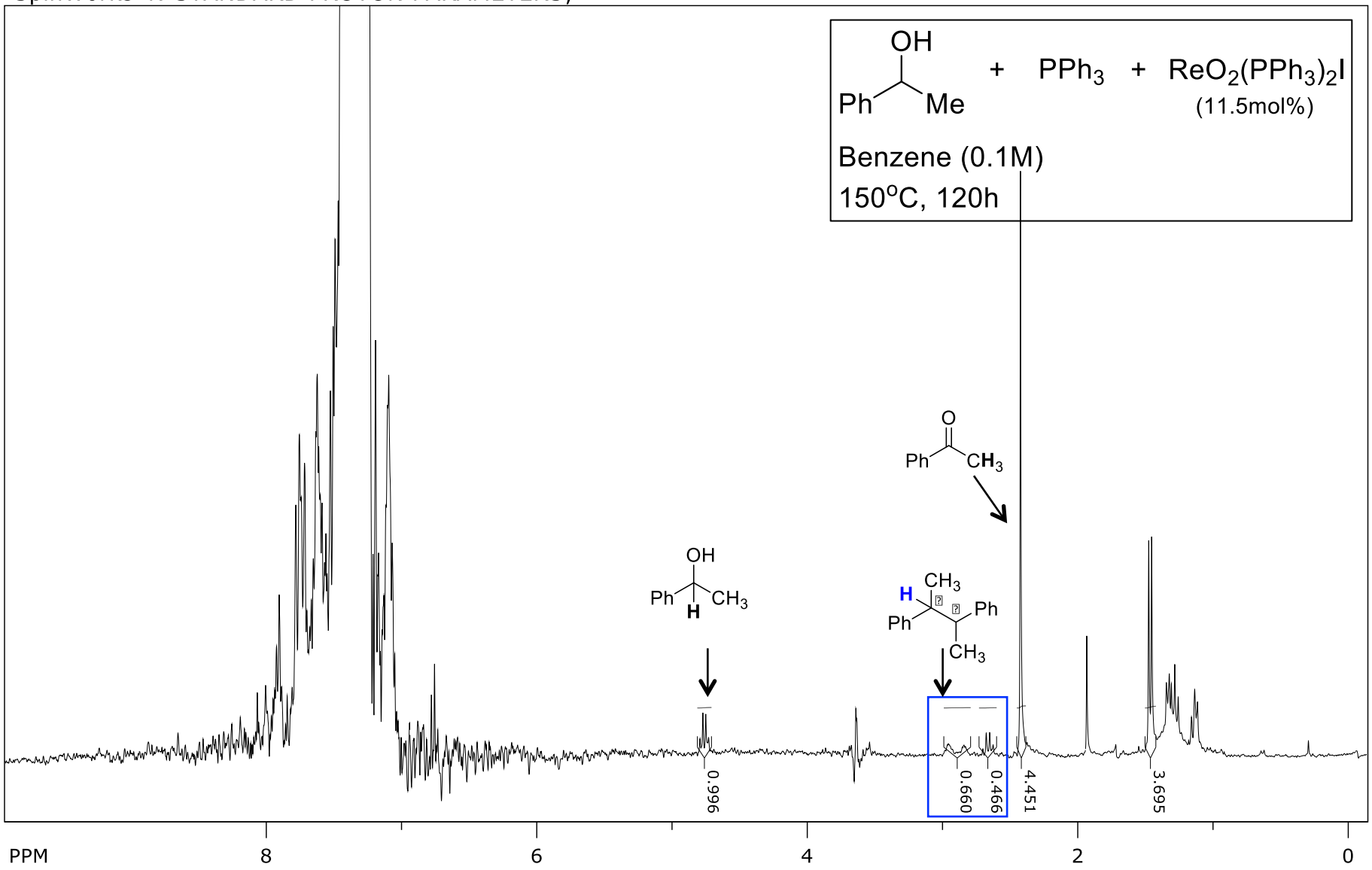
number of scans: 32

freq. of 0 ppm: 399.865946 MHz
processed size: 32768 complex points
LB: 1.500 GF: 0.0000


File :Z:\Foster\2016\03\31\11755KMNc.D
Operator : aydin
Acquired : 1 Apr 2016 10:39 using AcqMethod NICHOLASMETHODAUTOSAMP-3UL.M
Instrument : GCMSNavy
Sample Name: KN315
Misc Info :
Vial Number: 2
TIC: 11755KMNc.D\data.ms
Abundance
Time-->
PPh3
O=PPh3
334
332
330
fluorenone
solvent impurities


Scan 2082 (22.108 min): 11755KMNd.D\data.ms
Scan 1917 (20.363 min): 11755KMNd.D\data.ms
Scan 1662 (17.666 min): 11755KMNd.D\data.ms
Abundance
m/z-->

SpinWorks 4: STANDARD PROTON PARAMETERS;

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number of scans: 32

freq. of 0 ppm: 300.121912 MHz
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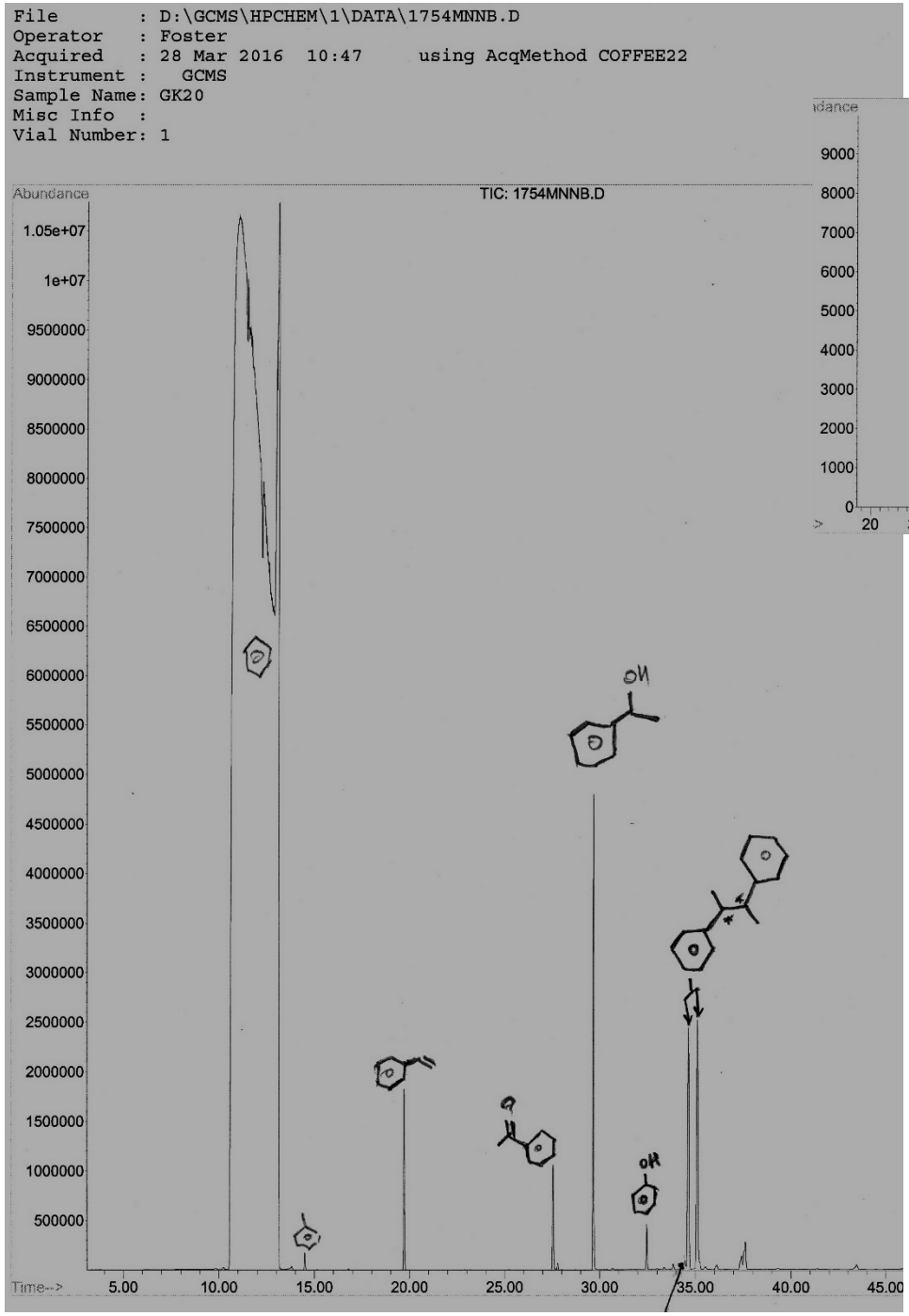
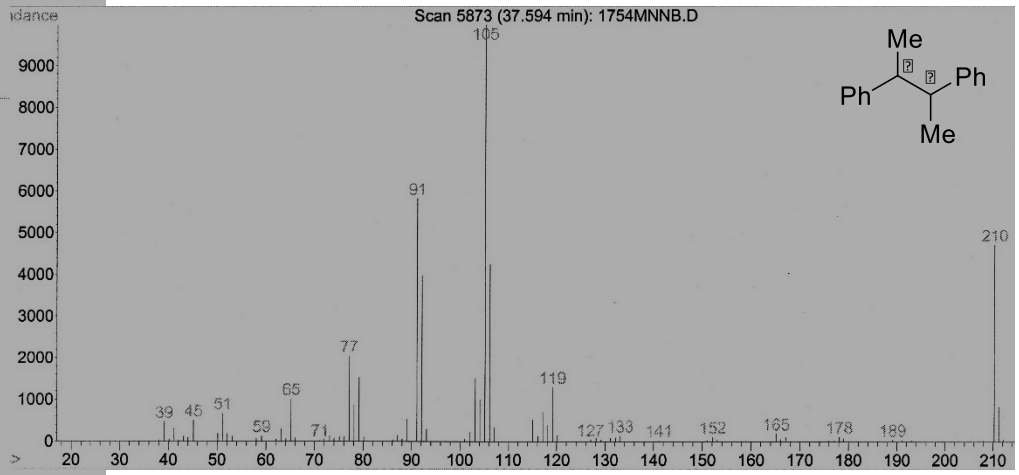
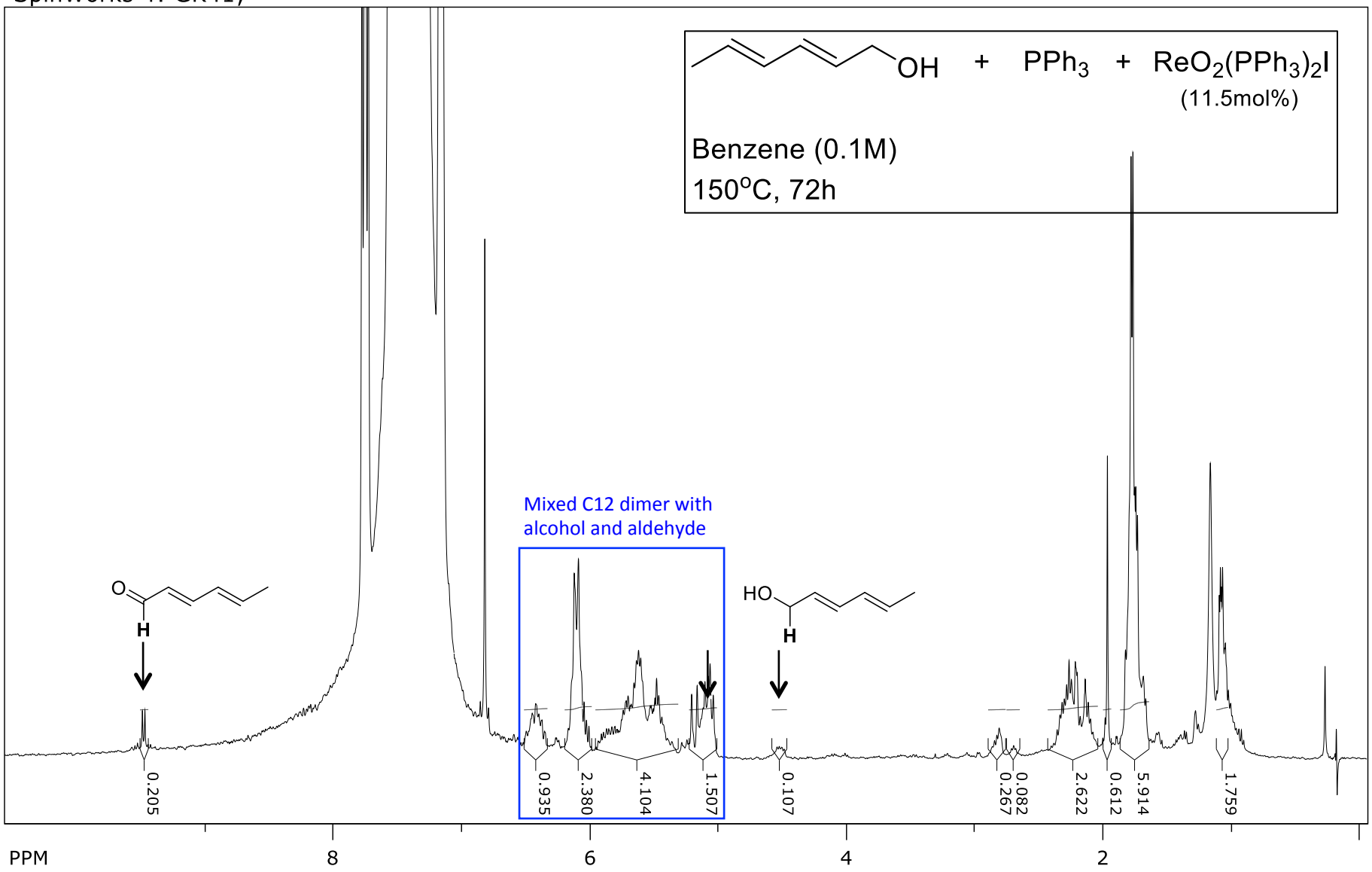
LB: 1.500 GF: 0.0000




**Same mass sprectrum for 35.097min and 37.594min GC peaks**

SpinWorks 4: GK41;

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number of scans: 32

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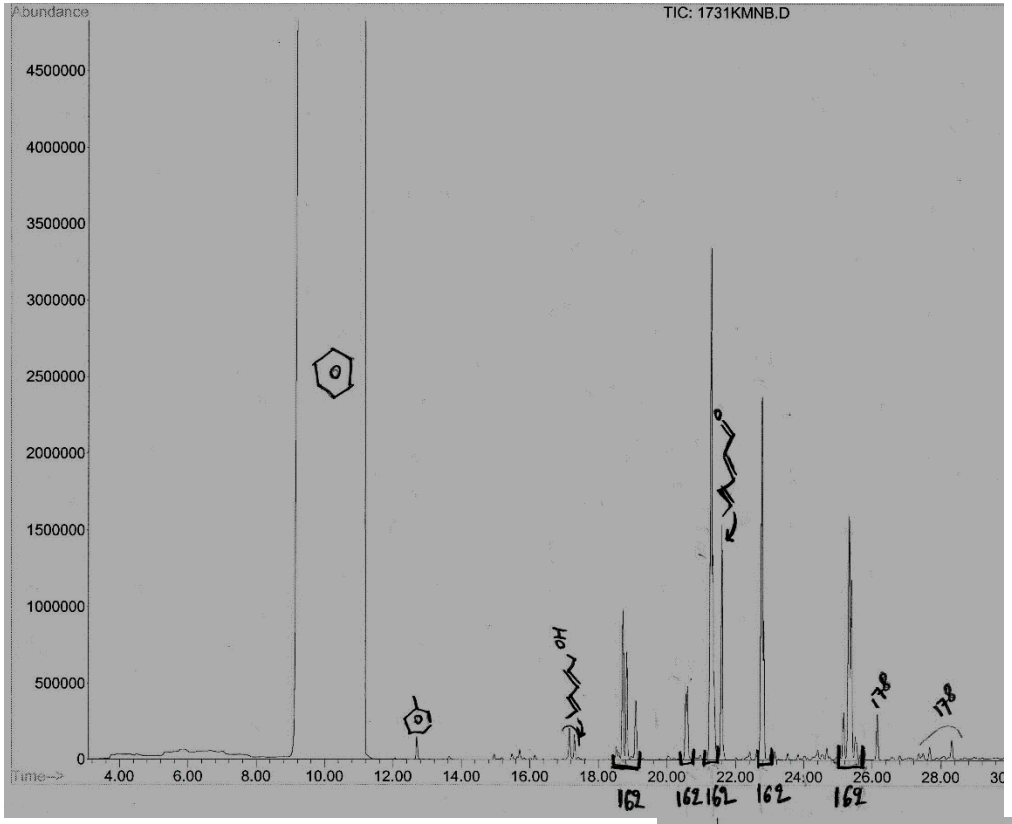
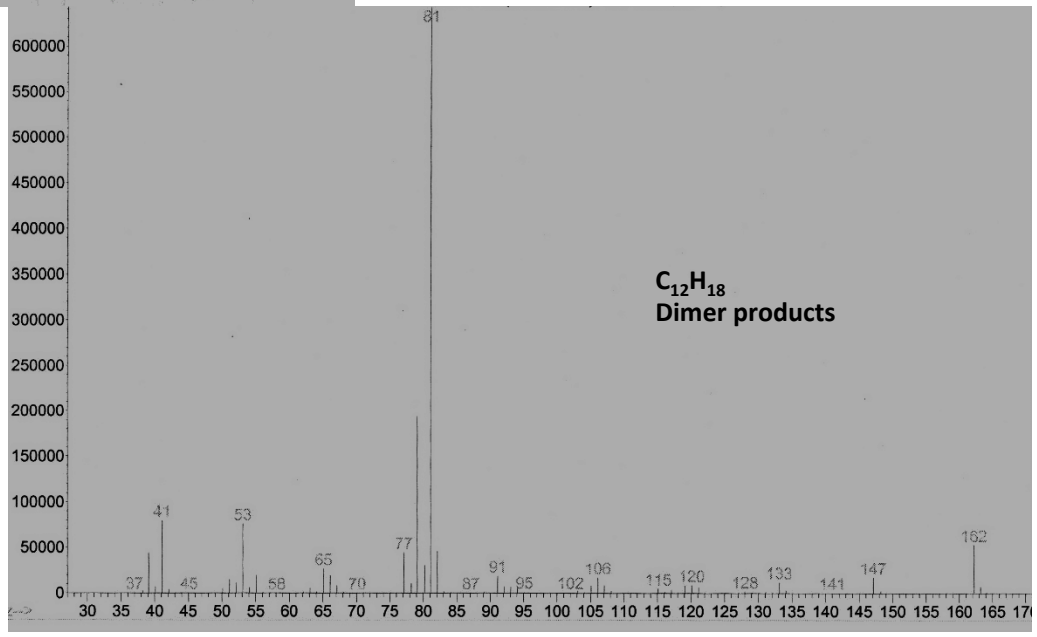
LB: 1.500 GF: 0.0000

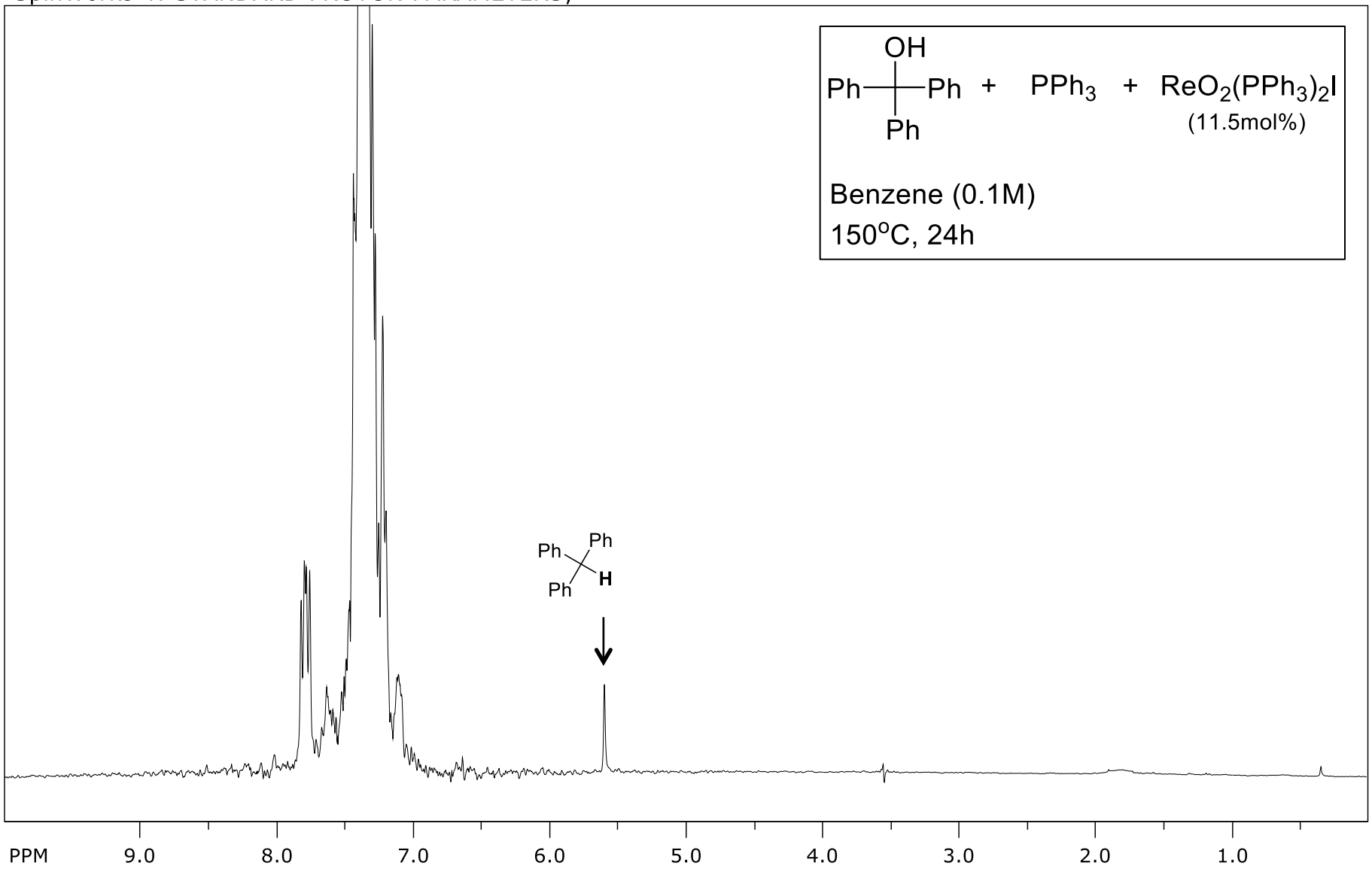



**Same mass spectrum for all the 162 marked GC pics**




**$C_{12}H_{18}$**
**Dimer products**

SpinWorks 4: STANDARD PROTON PARAMETERS;

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number of scans: 32

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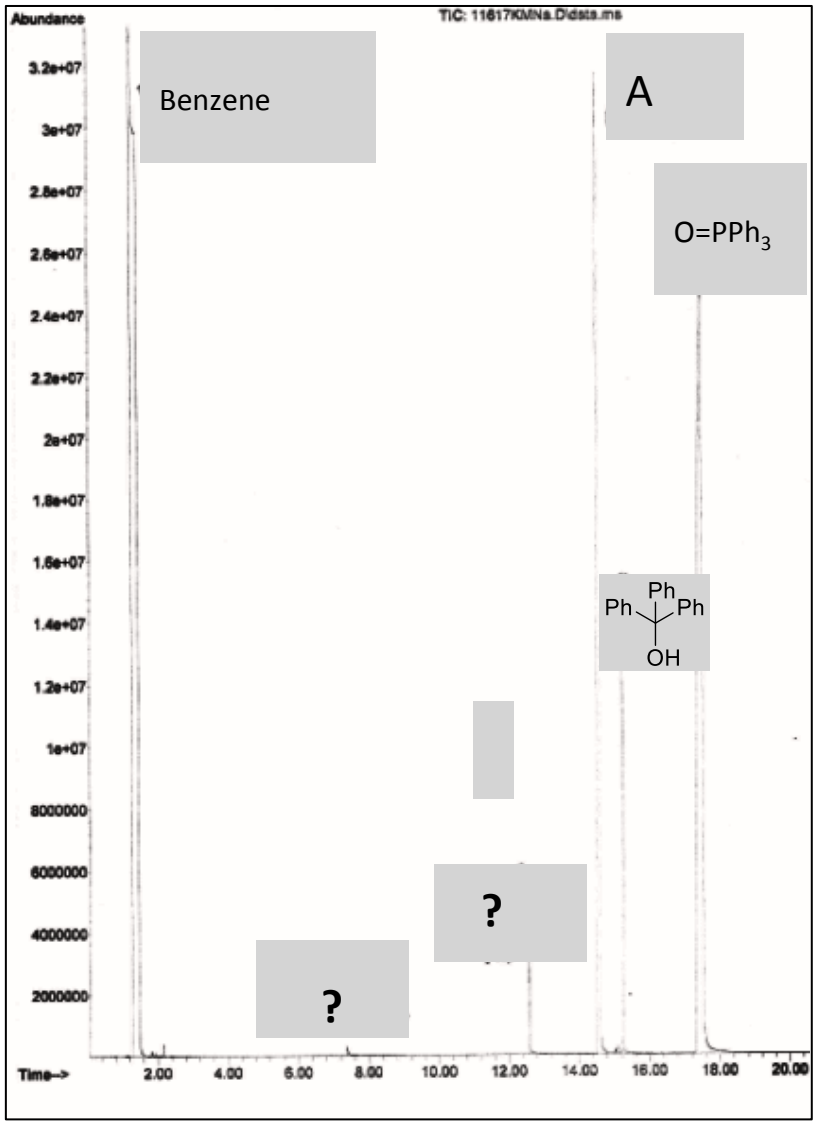
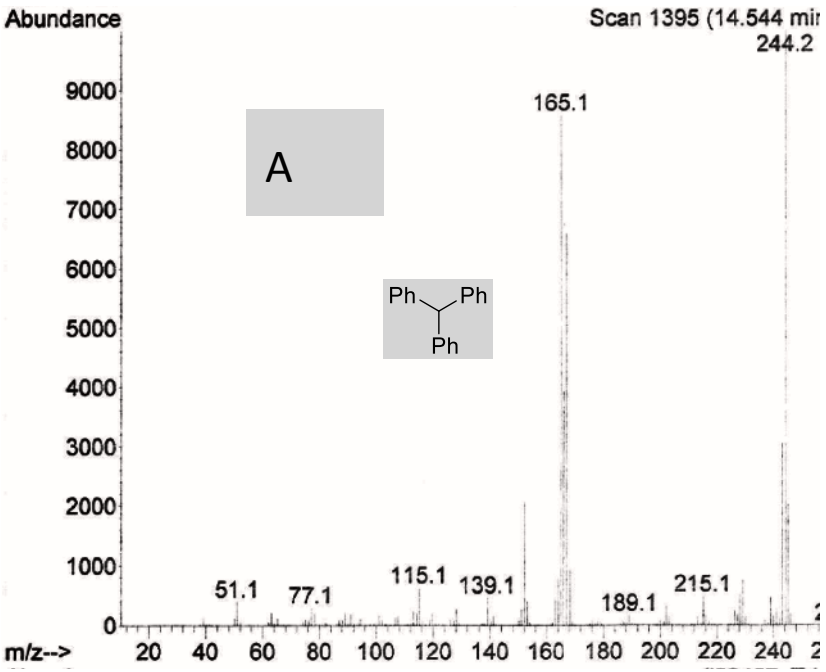
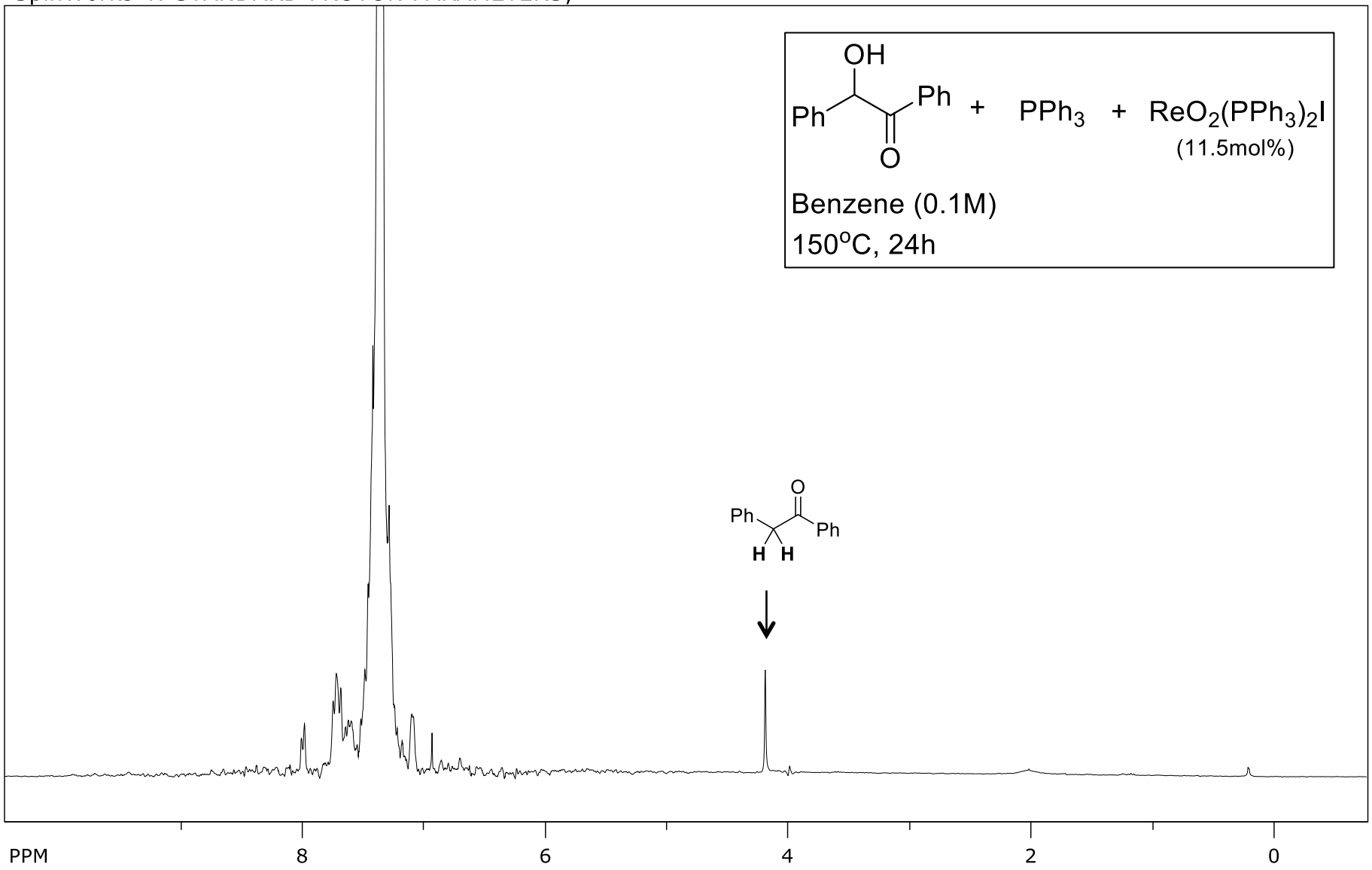
processed size: 16384 complex points
LB: 1.500 GF: 0.0000


Abundance
TIC: 11617KMNa.D\data.ms
Benzene
A
O=PPh3
Ph
Ph
Ph
OH
?
?
Time-->


Abundance
Scan 1395 (14.544 mi
244.2
165.1
A
Ph
Ph
Ph
51.1
77.1
115.1
139.1
189.1
215.1
m/z-->

SpinWorks 4: STANDARD PROTON PARAMETERS;

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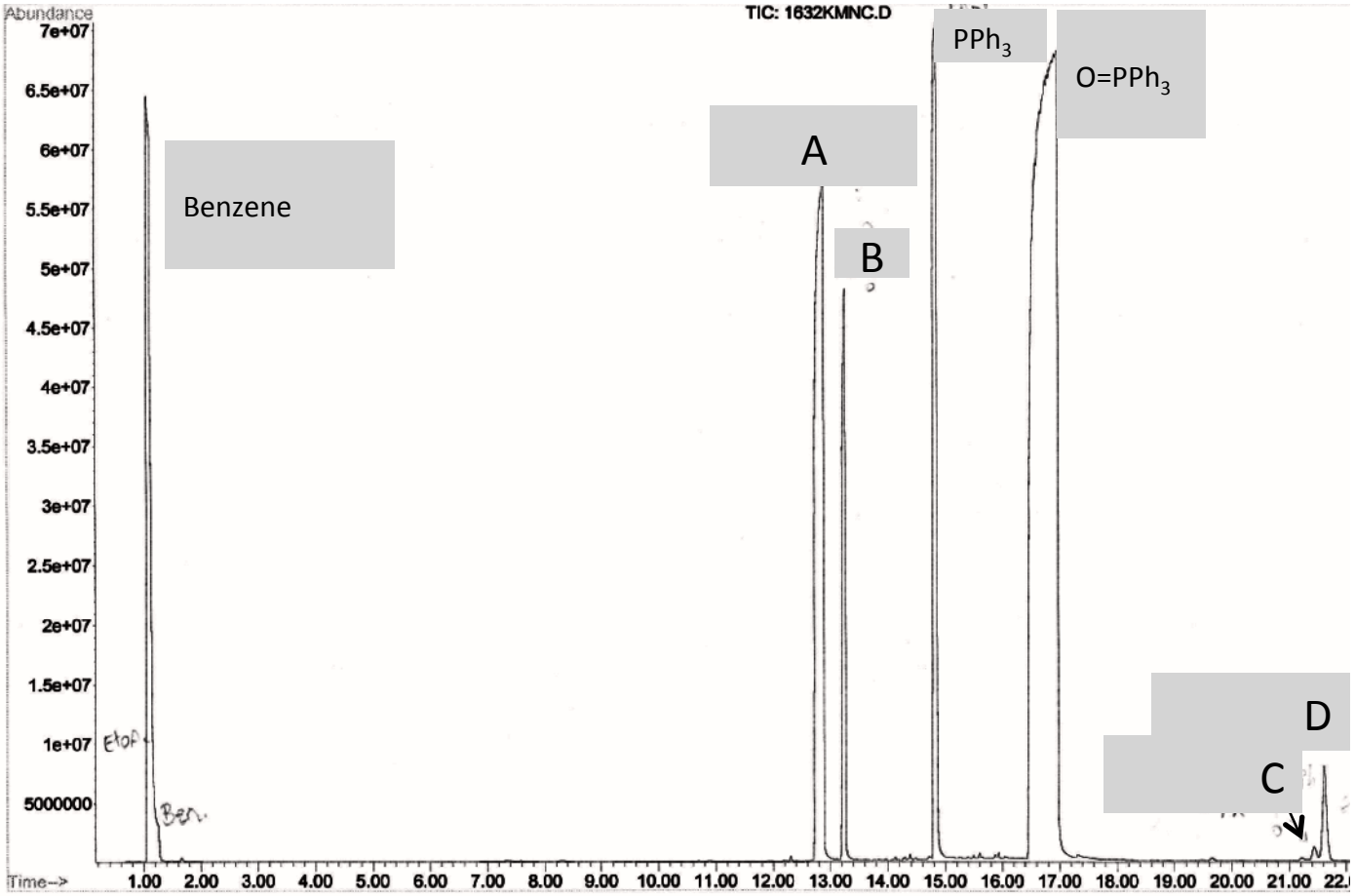
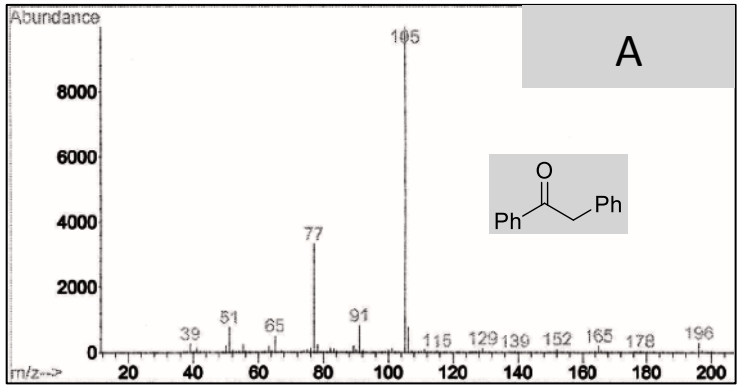
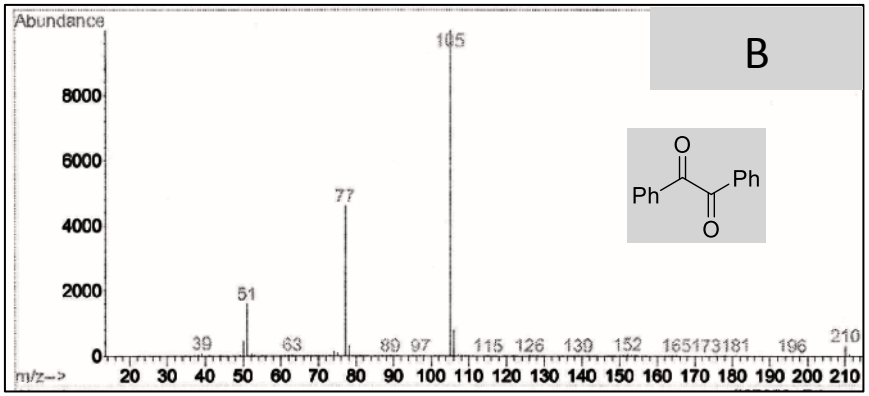
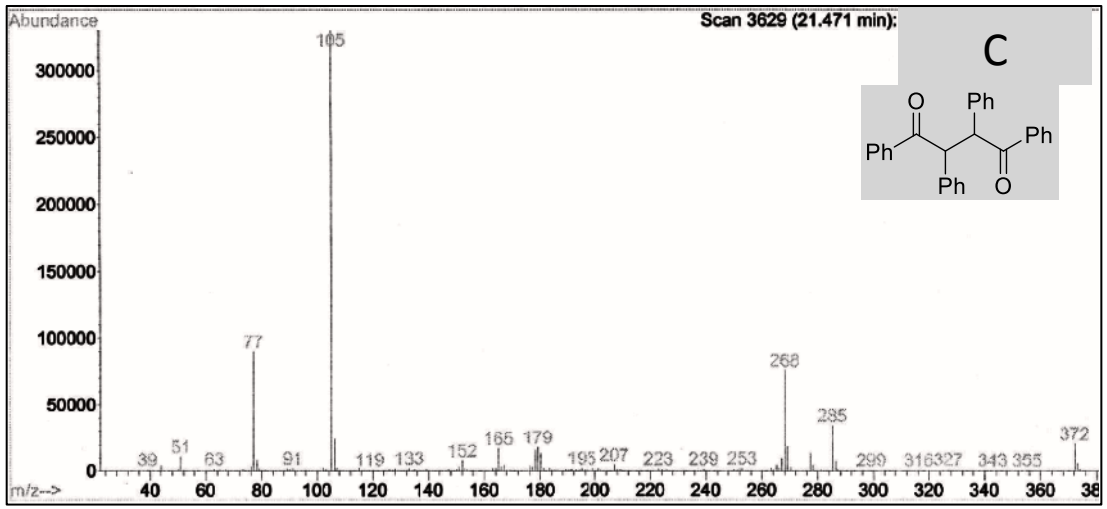

TIC: 1632KMNC.D
Abundance
7e+07
6.5e+07
6e+07
5.5e+07
5e+07
4.5e+07
4e+07
3.5e+07
3e+07
2.5e+07
2e+07
1.5e+07
1e+07
5000000
Time-->
1.00 2.00 3.00 4.00 5.00 6.00 7.00 8.00 9.00 10.00 11.00 12.00 13.00 14.00 15.00 16.00 17.00 18.00 19.00 20.00 21.00
Benzene
A
B
PPh3
O=PPh3
C
D


A
Abundance
m/z-->
105
77
39
51
65
91
115
129
139
152
165
178
196
O
Ph
Ph


B
Abundance
m/z-->
105
77
51
39
63
89
97
115
126
139
152
165
173
181
196
210
O
Ph
Ph
O


C
Scan 3629 (21.471 min):
Abundance
m/z-->
105
77
268
285
372
39
51
63
91
119
133
152
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179
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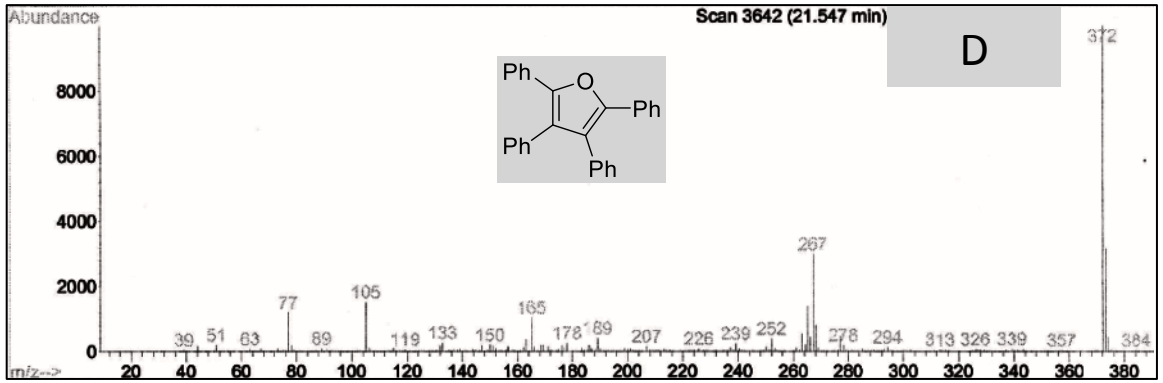
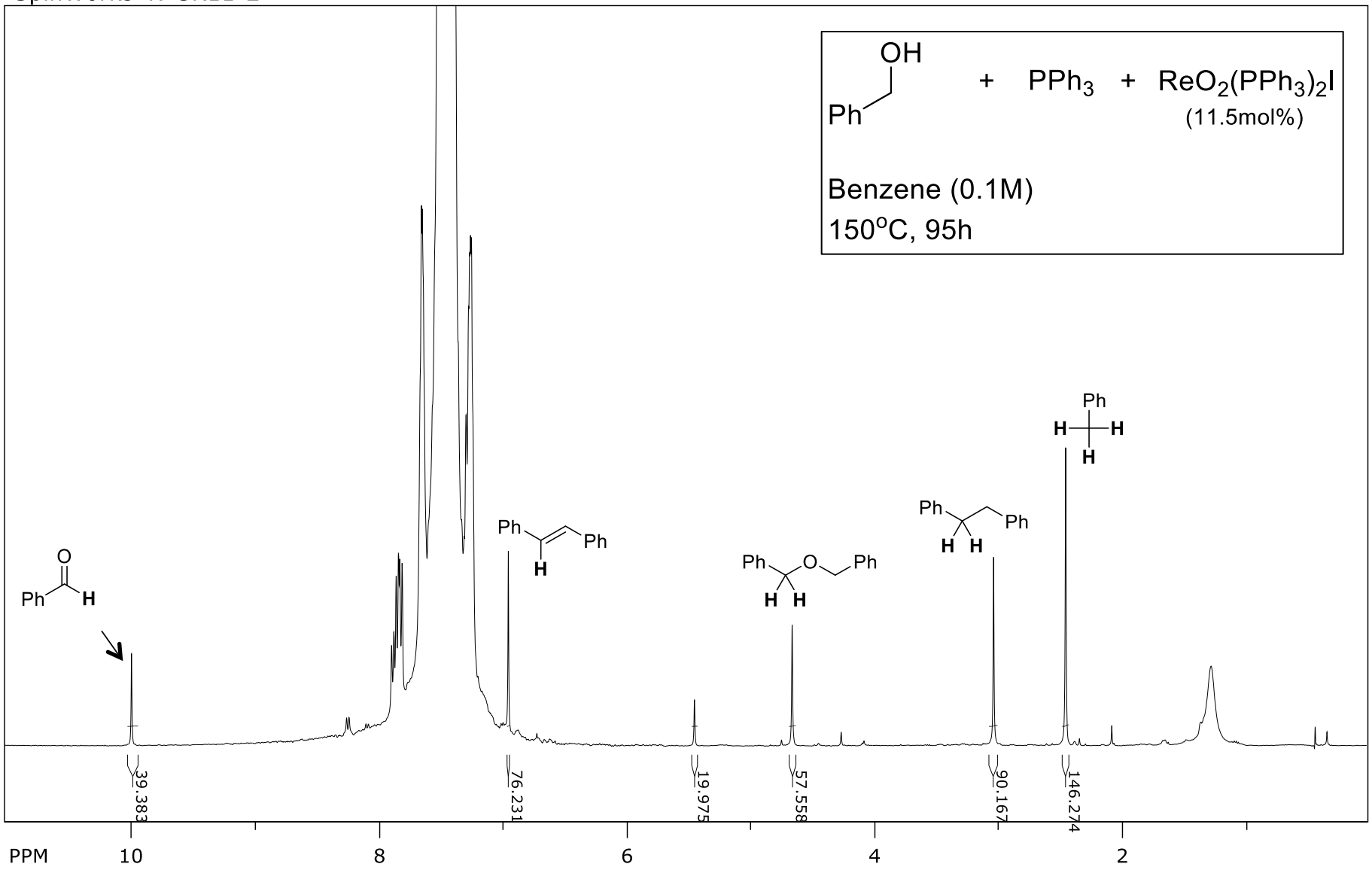
316
327
343
355
O
Ph
Ph
Ph
Ph
O


D
Scan 3642 (21.547 min)
Abundance
m/z-->
372
267
105
77
165
39
51
63
89
119
133
150
178
189
207
226
239
252
278
294
313
326
339
357
384
Ph
O
Ph
Ph
Ph

SpinWorks 4: GK11-2

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number of scans: 32

freq. of 0 ppm: 399.866064 MHz
processed size: 32768 complex points
LB: 1.500 GF: 0.0000

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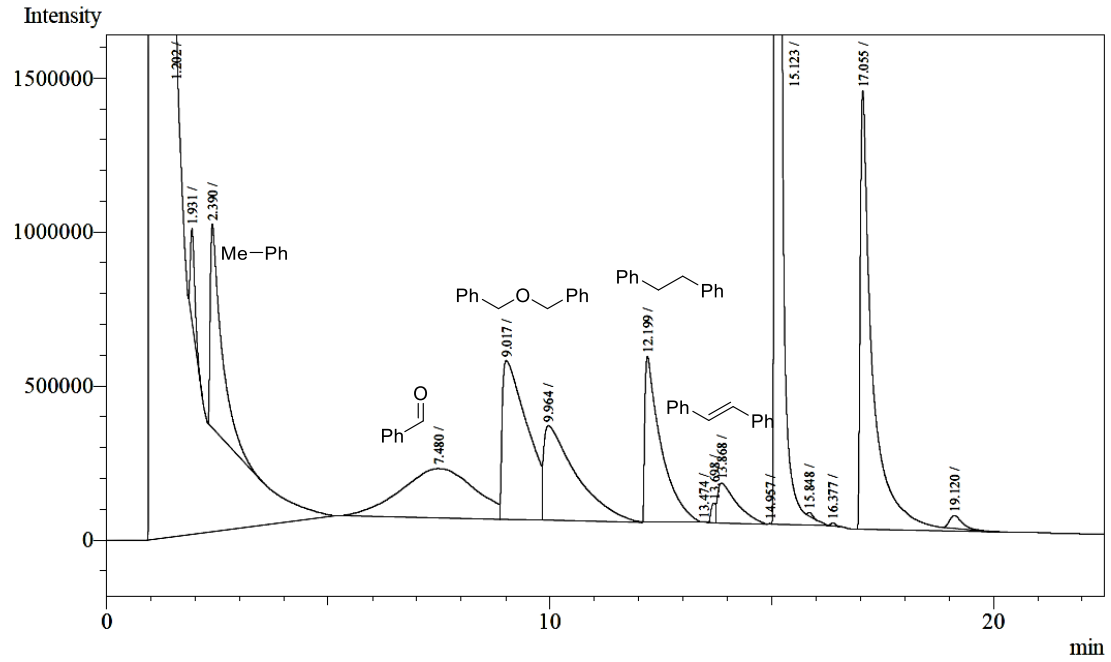
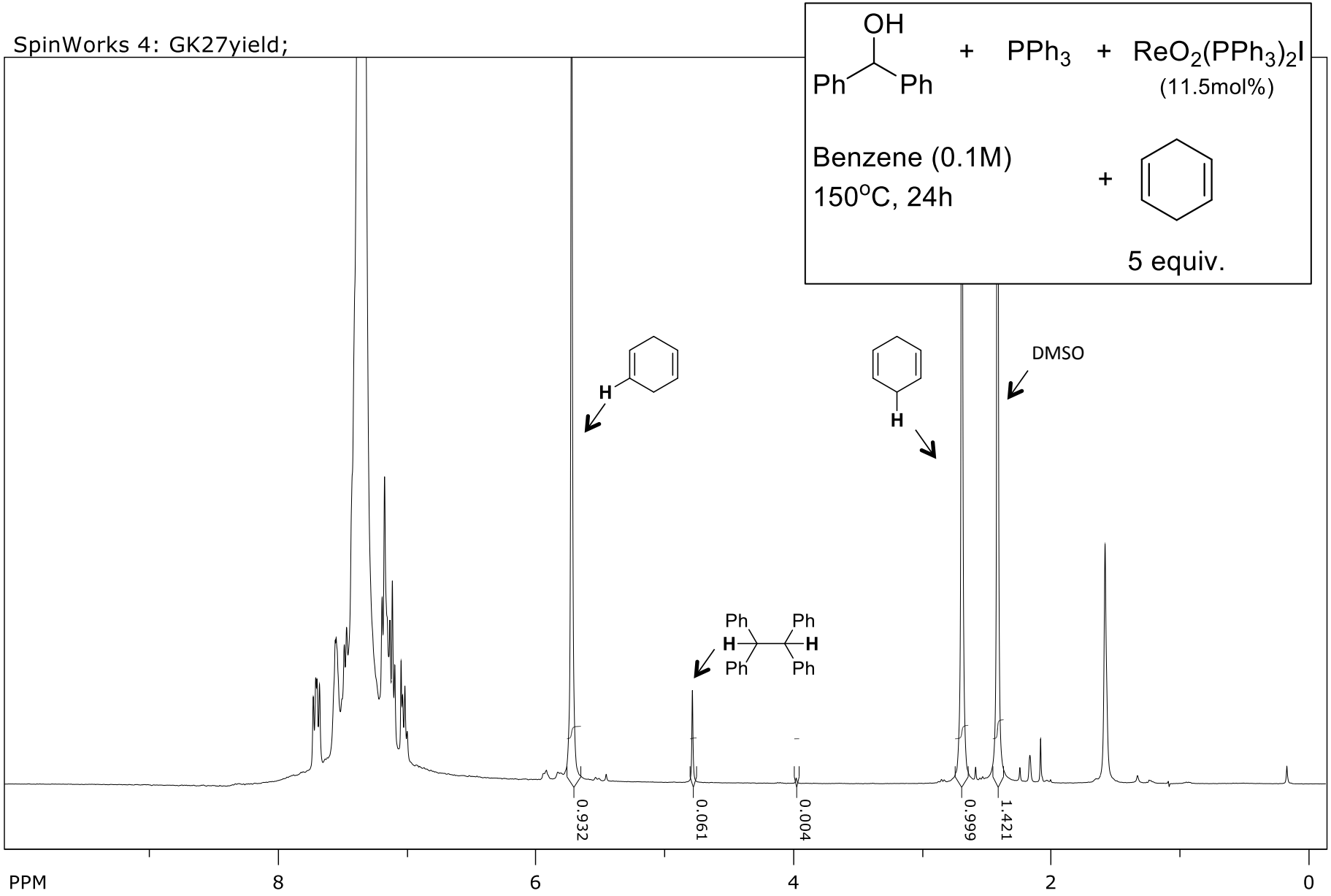



| Peak# | Ret.Time | Area | Height | Conc. | Unit | Mark | ID# | Cmpd Name |
|---|---|---|---|---|---|---|---|---|
| 1 | 1.202 | 21531647921 | 318973622 | 99.027 | | S | | |
| 2 | 1.931 | 2126166 | 306718 | 0.010 | | T | | |
| 3 | 2.390 | 11777596 | 661125 | 0.054 | | T | | |
| 4 | 7.480 | 18292224 | 159180 | 0.084 | | | | |
| 5 | 9.017 | 19844079 | 514613 | 0.091 | | V | | |
| 6 | 9.964 | 15629716 | 306863 | 0.072 | | V | | |
| 7 | 12.199 | 13740611 | 538516 | 0.063 | | S | | |
| 8 | 13.474 | 10374 | 1726 | 0.000 | | T | | |
| 9 | 13.698 | 418127 | 62539 | 0.002 | | | | |
| 10 | 13.868 | 3901623 | 129416 | 0.018 | | V | | |
| 11 | 14.957 | 9544 | 2890 | 0.000 | | | | |
| 12 | 15.123 | 97277991 | 14457729 | 0.447 | | SV | | |
| 13 | 15.848 | 90164 | 11398 | 0.000 | | T | | |
| 14 | 16.377 | 74124 | 10134 | 0.000 | | | | |
| 15 | 17.055 | 27447199 | 1422535 | 0.126 | | S | | |
| 16 | 19.120 | 823592 | 41747 | 0.004 | | T | | |
| Total | | 21743111051 | 337600751 | | | | | |

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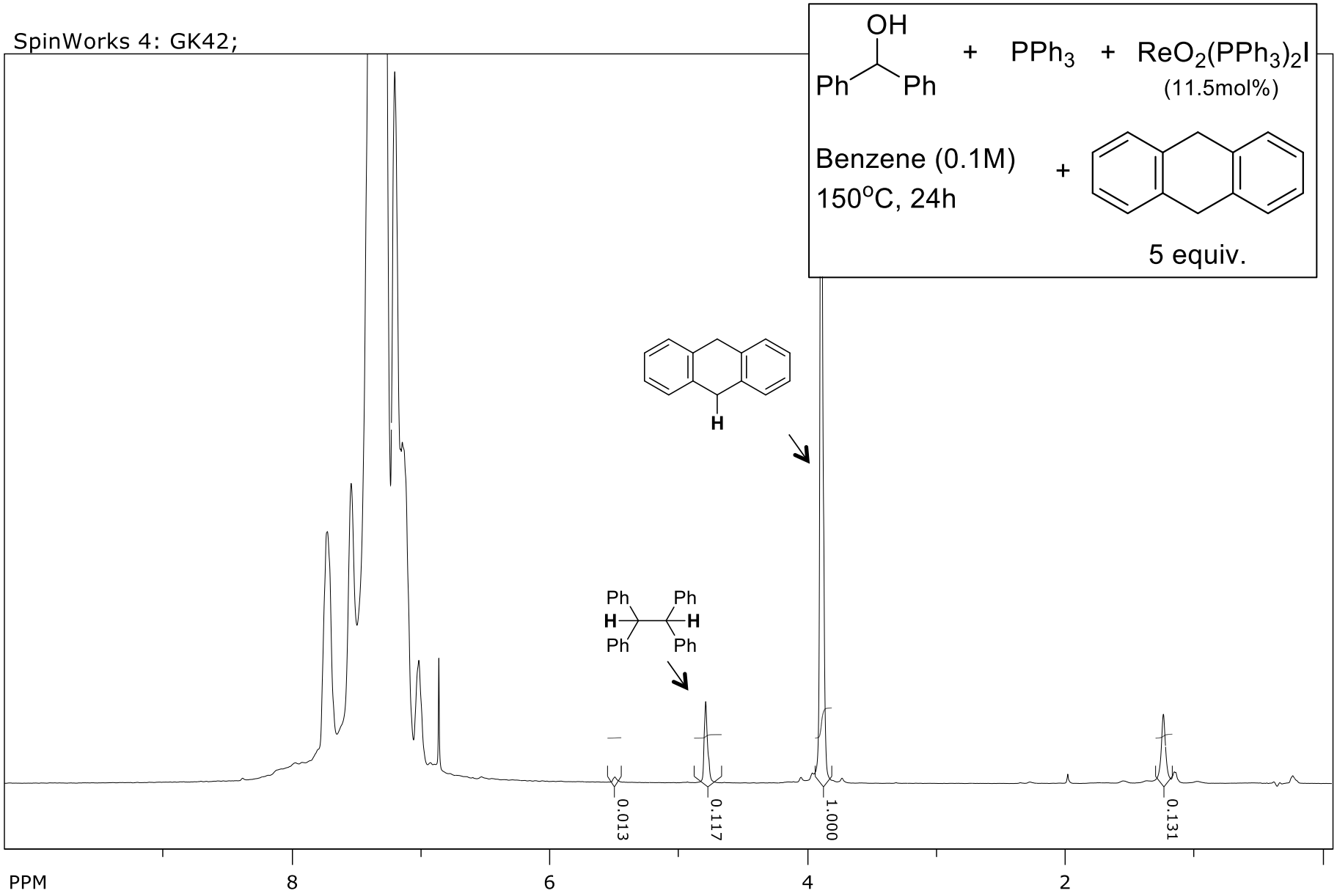
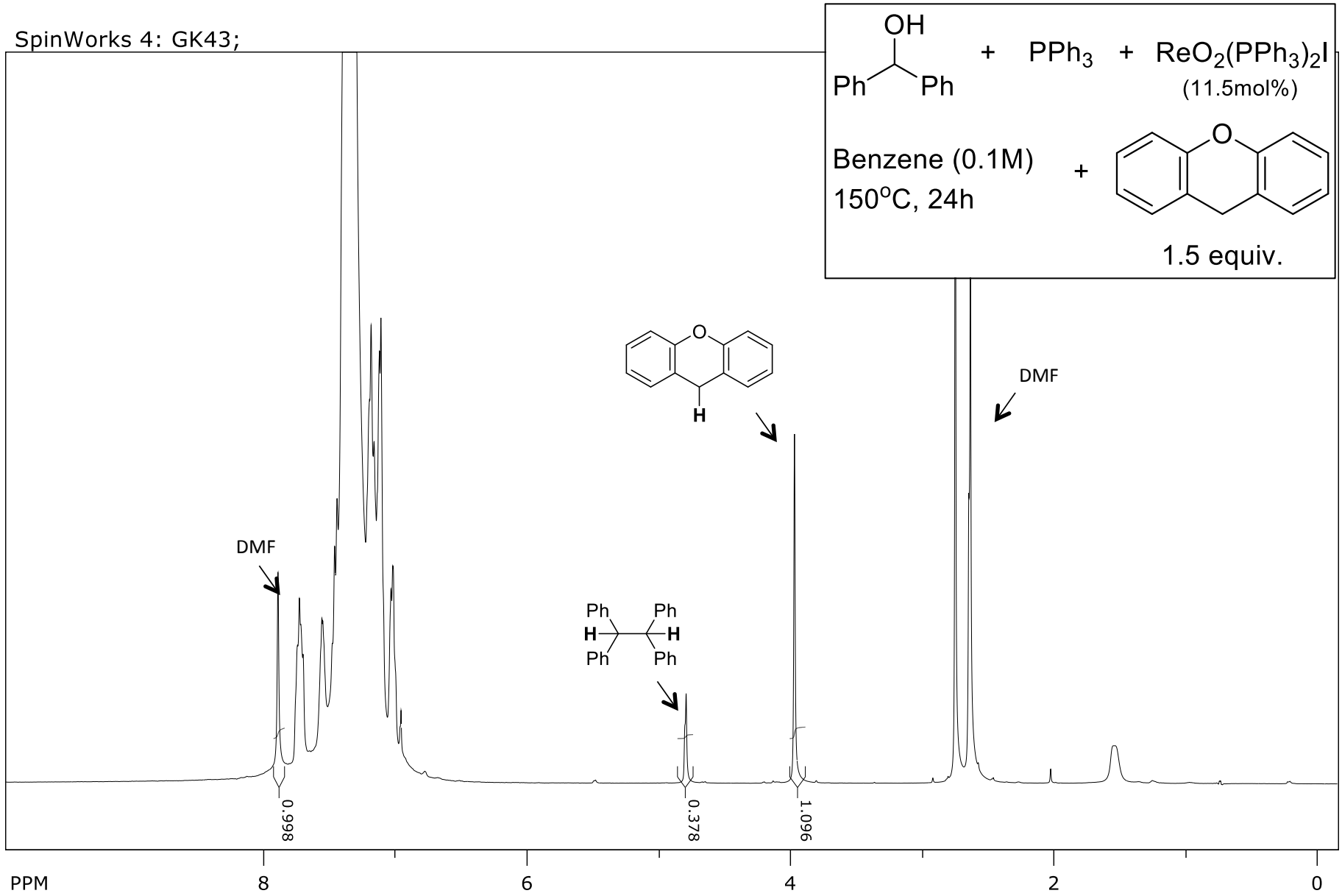
number of scans: 8

freq. of 0 ppm: 399.866030 MHz
processed size: 32768 complex points
LB: 1.500 GF: 0.0000




file: ..._26Feb16_01\GK42_PROTON_01.fid\fid block# 1 expt: "s2pul"
transmitter freq.: 399.868346 MHz
time domain size: 32768 points
width: 6410.26 Hz = 16.0309 ppm = 0.195625 Hz/pt
number of scans: 32

freq. of 0 ppm: 399.866104 MHz
processed size: 32768 complex points
LB: 1.500 GF: 0.0000




file: ..._04Mar16_01\GK43_PROTON_01.fid\fid block# 1 expt: "s2pul"
transmitter freq.: 399.868346 MHz
time domain size: 32768 points
width: 6410.26 Hz = 16.0309 ppm = 0.195625 Hz/pt
number of scans: 32

freq. of 0 ppm: 399.866064 MHz
processed size: 32768 complex points
LB: 1.500 GF: 0.0000

*Computational Methods*

The B3LYP [a] method resident in Gaussian 09 [b] was used to determine the energy minimized structures of Figure 4; the 6-31-G(d) basis set was used for H, C, O atoms and LANL2DZ for Re.

[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.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, 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.

**XYZ Coordinates**

**$PhCH_2OH$**

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 0.013089 | -1.062824 | 0.113005 |
| 2 | 6 | 0 | -0.438959 | 0.260943 | 0.081628 |
| 3 | 6 | 0 | 0.497744 | 1.295520 | -0.023954 |
| 4 | 6 | 0 | 1.863269 | 1.016186 | -0.085329 |
| 5 | 6 | 0 | 2.307960 | -0.306835 | -0.052972 |
| 6 | 6 | 0 | 1.378274 | -1.343955 | 0.042488 |
| 7 | 1 | 0 | -0.713387 | -1.865847 | 0.178870 |
| 8 | 1 | 0 | 0.156456 | 2.328378 | -0.062077 |
| 9 | 1 | 0 | 2.578130 | 1.830821 | -0.168478 |
| 10 | 1 | 0 | 3.370773 | -0.527557 | -0.107622 |
| 11 | 1 | 0 | 1.716366 | -2.377006 | 0.061562 |
| 12 | 6 | 0 | -1.911463 | 0.582383 | 0.205690 |
| 13 | 1 | 0 | -2.156626 | 0.761694 | 1.266922 |
| 14 | 1 | 0 | -2.128268 | 1.519017 | -0.333193 |
| 15 | 8 | 0 | -2.684251 | -0.497714 | -0.306502 |
| 16 | 1 | 0 | -3.608928 | -0.336287 | -0.067302 |

**$MeReO_2$**

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 75 | 0 | 0.059576 | -0.000022 | 0.070789 |
| 2 | 6 | 0 | -1.953937 | -0.000881 | -0.182084 |
| 3 | 1 | 0 | -2.212760 | -0.000830 | 0.911873 |
| 4 | 1 | 0 | -2.381700 | 0.899309 | -0.630898 |
| 5 | 1 | 0 | -2.381712 | -0.900863 | -0.631187 |
| 6 | 8 | 0 | 0.888433 | 1.444820 | -0.241615 |
| 7 | 8 | 0 | 0.890518 | -1.443653 | -0.241696 |

**$PhCH_2OH$-$ReO_2Me$**

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 4.443043 | 1.386882 | 0.089428 |
| 2 | 6 | 0 | 3.188616 | 1.012449 | 0.567321 |
| 3 | 6 | 0 | 2.751008 | -0.316205 | 0.444252 |
| 4 | 6 | 0 | 3.588855 | -1.260175 | -0.167020 |
| 5 | 6 | 0 | 4.846138 | -0.885102 | -0.642679 |
| 6 | 6 | 0 | 5.273004 | 0.438092 | -0.515223 |
| 7 | 1 | 0 | 4.775524 | 2.415824 | 0.191614 |
| 8 | 1 | 0 | 2.543449 | 1.749138 | 1.040010 |
| 9 | 1 | 0 | 3.258012 | -2.291952 | -0.261590 |
| 10 | 1 | 0 | 5.490775 | -1.624435 | -1.109131 |
| 11 | 1 | 0 | 6.252195 | 0.730479 | -0.883844 |
| 12 | 6 | 0 | 1.384579 | -0.708677 | 0.917553 |
| 13 | 1 | 0 | 1.286996 | -1.787549 | 1.055261 |
| 14 | 1 | 0 | 1.089491 | -0.195396 | 1.830959 |
| 15 | 8 | 0 | 0.376933 | -0.303283 | -0.100342 |
| 16 | 75 | 0 | -1.715544 | 0.074875 | -0.174608 |
| 17 | 8 | 0 | -2.089245 | 1.745027 | -0.176979 |
| 18 | 8 | 0 | -2.688262 | -1.101609 | -0.945783 |
| 19 | 6 | 0 | -1.616699 | -0.538891 | 1.854187 |
| 20 | 1 | 0 | -2.619857 | -0.691111 | 2.262157 |
| 21 | 1 | 0 | -1.046383 | -1.468702 | 1.980311 |
| 22 | 1 | 0 | -1.124839 | 0.244691 | 2.445898 |
| 23 | 1 | 0 | 0.813756 | -0.187903 | -0.958157 |

**PhCH2O-ReMe(O)(OH)**

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 3.755218 | 1.518825 | -0.011274 |
| 2 | 6 | 0 | 2.565596 | 0.899076 | 0.367813 |
| 3 | 6 | 0 | 2.475585 | -0.500762 | 0.395018 |
| 4 | 6 | 0 | 3.591377 | -1.264919 | 0.037740 |
| 5 | 6 | 0 | 4.786106 | -0.644256 | -0.333627 |
| 6 | 6 | 0 | 4.868850 | 0.748346 | -0.359149 |
| 7 | 1 | 0 | 3.815415 | 2.603514 | -0.032787 |
| 8 | 1 | 0 | 1.698676 | 1.500743 | 0.630835 |
| 9 | 1 | 0 | 3.525794 | -2.350464 | 0.050638 |
| 10 | 1 | 0 | 5.647459 | -1.248021 | -0.606050 |
| 11 | 1 | 0 | 5.796730 | 1.233518 | -0.649880 |
| 12 | 6 | 0 | 1.186857 | -1.168370 | 0.802422 |
| 13 | 1 | 0 | 1.312044 | -2.252892 | 0.882463 |
| 14 | 1 | 0 | 0.834553 | -0.790555 | 1.770832 |
| 15 | 8 | 0 | 0.164543 | -0.941968 | -0.196261 |
| 16 | 75 | 0 | -1.446759 | -0.018244 | -0.197285 |
| 17 | 8 | 0 | -1.118807 | 1.781245 | 0.370840 |
| 18 | 1 | 0 | -1.550346 | 2.001378 | 1.222330 |
| 19 | 8 | 0 | -2.673112 | -0.193813 | -1.340582 |
| 20 | 6 | 0 | -2.494005 | -0.208177 | 1.601867 |
| 21 | 1 | 0 | -2.952090 | 0.734487 | 1.944672 |
| 22 | 1 | 0 | -3.261687 | -0.984746 | 1.552045 |
| 23 | 1 | 0 | -1.754145 | -0.520915 | 2.354473 |

**$MeRe(O)OH(PMe_3)OCH_2Ph$**

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 8 | 0 | -0.687104 | 0.536288 | -1.724947 |
| 2 | 8 | 0 | -1.563389 | -2.035253 | 0.102925 |
| 3 | 8 | 0 | 1.052748 | -0.959113 | -0.793316 |
| 4 | 6 | 0 | 0.066268 | 0.137338 | 1.704306 |
| 5 | 1 | 0 | -0.063978 | -0.693759 | 2.412392 |
| 6 | 1 | 0 | 1.138456 | 0.340917 | 1.618734 |
| 7 | 1 | 0 | -0.413111 | 1.020536 | 2.146709 |
| 8 | 75 | 0 | -0.761279 | -0.560415 | -0.123503 |
| 9 | 1 | 0 | 0.188492 | 0.367031 | -2.130636 |
| 10 | 6 | 0 | 2.179123 | -1.383947 | -0.065235 |
| 11 | 1 | 0 | 2.555470 | -2.297753 | -0.552246 |
| 12 | 1 | 0 | 1.910427 | -1.675701 | 0.961793 |
| 13 | 15 | 0 | -2.759814 | 0.829116 | 0.239536 |
| 14 | 6 | 0 | -2.375157 | 2.622616 | 0.238247 |
| 15 | 1 | 0 | -1.855975 | 2.859481 | -0.694440 |
| 16 | 1 | 0 | -3.288348 | 3.222674 | 0.317532 |
| 17 | 1 | 0 | -1.712786 | 2.862104 | 1.075661 |
| 18 | 6 | 0 | -3.697414 | 0.542470 | 1.793105 |
| 19 | 1 | 0 | -4.572472 | 1.198966 | 1.861384 |
| 20 | 1 | 0 | -4.026044 | -0.500947 | 1.825297 |
| 21 | 1 | 0 | -3.044374 | 0.721780 | 2.652829 |
| 22 | 6 | 0 | -4.000980 | 0.633623 | -1.098161 |
| 23 | 1 | 0 | -4.854206 | 1.309279 | -0.967655 |
| 24 | 1 | 0 | -3.506609 | 0.840056 | -2.051800 |
| 25 | 1 | 0 | -4.355579 | -0.401723 | -1.111039 |
| 26 | 6 | 0 | 3.305083 | -0.360520 | -0.014999 |
| 27 | 6 | 0 | 4.503821 | -0.689046 | 0.634857 |
| 28 | 6 | 0 | 3.183308 | 0.903348 | -0.599337 |
| 29 | 6 | 0 | 5.554265 | 0.224710 | 0.701771 |
| 30 | 1 | 0 | 4.614309 | -1.671058 | 1.092337 |
| 31 | 6 | 0 | 4.235379 | 1.821781 | -0.534134 |
| 32 | 1 | 0 | 2.259031 | 1.163382 | -1.104379 |
| 33 | 6 | 0 | 5.423255 | 1.487380 | 0.115696 |
| 34 | 1 | 0 | 6.475643 | -0.046993 | 1.210967 |
| 35 | 1 | 0 | 4.123858 | 2.800852 | -0.993889 |
| 36 | 1 | 0 | 6.241152 | 2.201396 | 0.166180 |

**MeRe(O)PMe3(OH)O·**

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 8 | 0 | 0.222149 | -1.702798 | 0.993857 |
| 2 | 8 | 0 | 0.911295 | 1.626785 | 0.640462 |
| 3 | 8 | 0 | 2.547960 | -0.703876 | 0.429426 |
| 4 | 6 | 0 | 1.026054 | -0.033624 | -1.876931 |
| 5 | 1 | 0 | 2.024399 | 0.261571 | -2.212820 |
| 6 | 1 | 0 | 0.836886 | -1.065850 | -2.198654 |
| 7 | 1 | 0 | 0.272135 | 0.622112 | -2.322139 |
| 8 | 75 | 0 | 0.940769 | -0.034724 | 0.227382 |
| 9 | 1 | 0 | 0.960172 | -2.308782 | 1.184998 |
| 10 | 15 | 0 | -1.708935 | 0.122572 | 0.140491 |
| 11 | 6 | 0 | -2.558833 | -1.309197 | -0.633954 |
| 12 | 1 | 0 | -2.210363 | -2.220583 | -0.140929 |
| 13 | 1 | 0 | -3.648162 | -1.231130 | -0.542867 |
| 14 | 1 | 0 | -2.292480 | -1.367632 | -1.694363 |
| 15 | 6 | 0 | -2.422049 | 1.591381 | -0.707420 |
| 16 | 1 | 0 | -3.515274 | 1.612776 | -0.629191 |
| 17 | 1 | 0 | -2.008305 | 2.499126 | -0.257685 |
| 18 | 1 | 0 | -2.143069 | 1.579771 | -1.765985 |
| 19 | 6 | 0 | -2.424884 | 0.200593 | 1.831581 |
| 20 | 1 | 0 | -3.520262 | 0.236621 | 1.806852 |
| 21 | 1 | 0 | -2.099402 | -0.682723 | 2.388040 |
| 22 | 1 | 0 | -2.046046 | 1.091149 | 2.342950 |

**$PhCH_2(\cdot)$**

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -1.376711 | 0.633862 | -0.083776 |
| 2 | 6 | 0 | 0.007586 | 0.679921 | -0.130509 |
| 3 | 6 | 0 | 0.707151 | 1.921993 | -0.066401 |
| 4 | 6 | 0 | -0.078099 | 3.108074 | 0.047536 |
| 5 | 6 | 0 | -1.461963 | 3.049721 | 0.093312 |
| 6 | 6 | 0 | -2.124441 | 1.815181 | 0.028309 |
| 7 | 1 | 0 | -1.885728 | -0.325324 | -0.134384 |
| 8 | 1 | 0 | 0.582013 | -0.239161 | -0.217414 |
| 9 | 1 | 0 | 0.430045 | 4.067991 | 0.098352 |
| 10 | 1 | 0 | -2.037221 | 3.967986 | 0.180276 |
| 11 | 1 | 0 | -3.209315 | 1.774221 | 0.064605 |
| 12 | 6 | 0 | 2.111878 | 1.975054 | -0.113568 |
| 13 | 1 | 0 | 2.706668 | 1.071365 | -0.199386 |
| 14 | 1 | 0 | 2.641388 | 2.921037 | -0.064056 |

**MeReO(OH)O (·)**

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 8 | 0 | 0.991461 | 1.564749 | -0.002313 |
| 2 | 8 | 0 | -0.918614 | -0.268226 | 1.483455 |
| 3 | 8 | 0 | -0.920522 | -0.272159 | -1.481687 |
| 4 | 6 | 0 | 1.499849 | -1.285510 | 0.000851 |
| 5 | 1 | 0 | 2.103399 | -1.106186 | -0.895945 |
| 6 | 1 | 0 | 2.103826 | -1.103895 | 0.896876 |
| 7 | 1 | 0 | 1.151437 | -2.322170 | 0.002252 |
| 8 | 75 | 0 | -0.127133 | 0.034701 | -0.000024 |
| 9 | 1 | 0 | 1.958608 | 1.447857 | -0.002097 |

**$MeReO_3$**

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 8 | 0 | 0.543909 | 1.664498 | -0.030893 |
| 2 | 8 | 0 | 0.541155 | -0.859857 | -1.426434 |
| 3 | 8 | 0 | 0.541132 | -0.806324 | 1.457365 |
| 4 | 6 | 0 | -2.008979 | 0.001496 | -0.000040 |
| 5 | 1 | 0 | -2.366553 | -0.498802 | 0.905438 |
| 6 | 1 | 0 | -2.365407 | 1.036194 | -0.019248 |
| 7 | 1 | 0 | -2.366543 | -0.532060 | -0.886330 |
| 8 | 75 | 0 | 0.081904 | -0.000011 | 0.000001 |

**$PhCH_3$**

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -1.201444 | 1.205289 | 0.002199 |
| 2 | 6 | 0 | 0.194129 | 1.202402 | -0.008985 |
| 3 | 6 | 0 | 0.913896 | 0.000222 | -0.011389 |
| 4 | 6 | 0 | 0.194385 | -1.202271 | -0.008982 |
| 5 | 6 | 0 | -1.201060 | -1.205493 | 0.002198 |
| 6 | 6 | 0 | -1.905116 | -0.000141 | 0.008471 |
| 7 | 1 | 0 | -1.739014 | 2.150176 | 0.001555 |
| 8 | 1 | 0 | 0.734218 | 2.146899 | -0.017836 |
| 9 | 1 | 0 | 0.734728 | -2.146640 | -0.017849 |
| 10 | 1 | 0 | -1.738458 | -2.150479 | 0.001552 |
| 11 | 1 | 0 | -2.991869 | -0.000325 | 0.013921 |
| 12 | 6 | 0 | 2.425551 | 0.000097 | 0.009375 |
| 13 | 1 | 0 | 2.809992 | -0.012911 | 1.038355 |
| 14 | 1 | 0 | 2.834300 | -0.879700 | -0.499566 |
| 15 | 1 | 0 | 2.834048 | 0.892352 | -0.477447 |

**Electronic Energies for species in Figure 1 (Hartrees)**

| | |
|---|---|
| $PhCH_2OH$ | -346.76763 |
| $MeReO_2$ (D) | -269.45828 |
| (PhCH2OH)$ReMeO_2$(E) | -616.25844 |
| (PhCH2O)ReMeO(OH) (A) | -616.27151 |
| MeRe(O)OH($PMe_3$)$OCH_2$Ph (A') | -1077.43788 |
| MeRe(O)PMe3(OH)O· (F') | -806.44649 |
| $MeReO_3$ | -344.74852 |
| $PhCH_3$ | -271.56665 |
| $MeReO_2OH$ (F) | -345.33628 |
| $PhCH_2$(·) | -270.91514 |