

A Novel Palladium-catalyzed Hydroalkoxylation of Alkenes with a Migration of Double Bond

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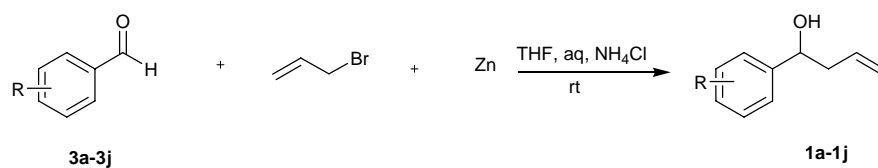
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Synthesis of substances

Additional experiments

Characterization data for the products

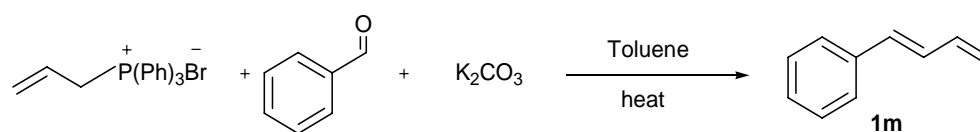
Synthesis of substances 1a-1j (Scheme SI-1).¹



Scheme SI-1. Synthesis of 1a-1k.

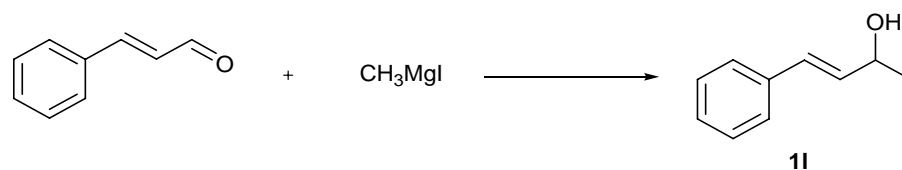
All of the starting materials 3a-3k are commercially available.

Synthesis of substances 1k (Scheme SI-2).²



Scheme SI-2 Synthesis of 1k

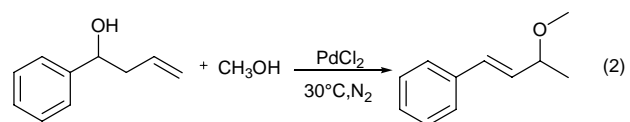
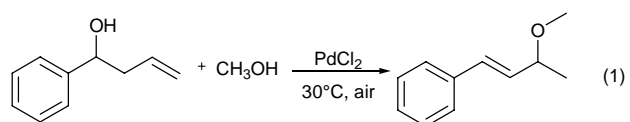
Synthesis of substances 1k (Scheme SI-3).



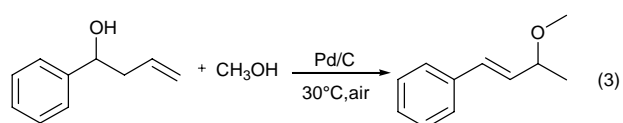
Scheme SI-3 Synthesis of 1l

1 C. Einhorn, J.-L. Luche, *J. Organomet. Chem.* 1987, **322**, 177.

2 T. B. Attra,; Y. L. Bigot,; R. E. Gharbi,; M. Delmas,; A. Gaset, *Synth. Commun*; 1992, **22**, 1421.

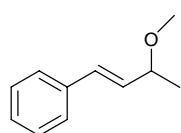


After performing the two experiments, we found the desired products are obtained with same yields under nitrogen or air. Besides, we also observed that the Pd black was formed due to the reduction of alcohols. But, the process of hydroalkoxylation performs much faster than the reduction.



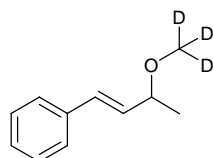
The experimental result that the reaction did not happen when Pd/C was used as the catalyst also provides prove to the Pd(II) catalysis.

Characterization data for the products



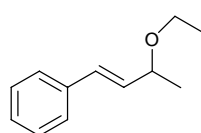
(E)-(3-methoxybut-1-enyl)benzene (2a)

^1H NMR (CDCl_3 , 300MHz, ppm): δ = 7.41-7.22 (m, 5H), 6.54 (d, J = 15.9 Hz, 1H), 6.09 (dd, J = 15.9 Hz, 7.5 Hz, 1H), 3.92-3.87 (m, 1H), 3.32 (s, 3H), 1.33 (d, J = 6.3 Hz, 3H). ^{13}C NMR (CDCl_3 , 75MHz, ppm): δ = 136.8, 131.6, 131.5, 128.7, 127.8, 126.6, 78.3, 56.2, 21.6. IR (liquid film, cm^{-1}): ν = 3027, 2975, 2927, 2820, 1686, 1494, 1450, 1369, 1199, 1139, 1111, 1084, 1042, 968, 748, 693. HRMS calc. $\text{C}_{11}\text{H}_{14}\text{O}$: 162.1045. Found: 162.1040.



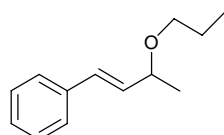
d_3 -(E)-(3-methoxybut-1-enyl)benzene (d_3 -2a)

^1H NMR (CDCl_3 , 300MHz, ppm): δ = 7.41-7.21 (m, 5H), 6.53 (d, J = 15.9 Hz, 1H), 6.09 (dd, J = 15.9 Hz, 7.5 Hz, 1H), 4.05-3.96 (m, 1H), 1.33 (d, J = 6.3 Hz, 3H). ^{13}C NMR (CDCl_3 , 75MHz, ppm): δ = 136.8, 131.6, 131.4, 128.7, 127.7, 126.6, 78.1, 21.6. IR (liquid film, cm^{-1}): ν = 3027, 2965, 2928, 2854, 2234, 2192, 2057, 1598, 1494, 1448, 1368, 1150, 1121, 1092, 1021, 968, 747, 693. HRMS calc. $\text{C}_{11}\text{H}_{11}\text{D}_3\text{O}$: 165.1233. Found: 165.1231.



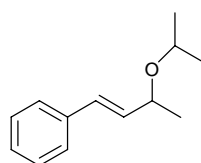
(E)-(3-ethoxybut-1-enyl)benzene (2b)

^1H NMR (CDCl_3 , 300MHz, ppm): δ = 7.38-7.21 (m, 5H), 6.51 (d, J = 15.9 Hz, 1H), 6.12 (dd, J = 15.9 Hz, 7.5 Hz, 1H), 4.05-3.96 (m, 1H), 3.62-3.52 (m, 1H), 3.47-3.37 (m, 1H), 1.33 (d, J = 6.3 Hz, 3H), 1.21 (t, J = 7.2 Hz, 3H). ^{13}C NMR (CDCl_3 , 75MHz, ppm): δ = 136.9, 132.3, 130.9, 128.7, 127.7, 126.6, 76.4, 63.7, 21.9, 15.6. IR (liquid film, cm^{-1}): ν = 3027, 2975, 2929, 2869, 1598, 1493, 1447, 1369, 1317, 1092, 967, 748, 693. HRMS calc. $\text{C}_{12}\text{H}_{16}\text{O}$: 176.1201 Found: 176.1223.



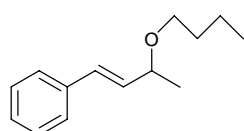
(E)-(3-propoxybut-1-enyl)benzene (2c)

^1H NMR (CDCl_3 , 300MHz, ppm): δ = 7.41-7.23 (m, 5H), 6.51 (d, J = 15.9 Hz, 1H), 6.12 (dd, J = 15.9 Hz, 7.2 Hz, 1H), 4.01-3.97 (m, 1H), 3.48-3.42 (m, 1H), 3.35-3.30 (m, 1H), 1.64-1.56 (m, 2H), 1.32 (d, J = 6.0 Hz, 3H), 0.92 (t, J = 7.5 Hz, 3H). ^{13}C NMR (CDCl_3 , 75MHz, ppm): δ = 137.0, 132.4, 130.8, 128.7, 127.7, 126.6, 76.5, 23.3, 21.8, 10.8. IR (liquid film, cm^{-1}): ν = 3060, 2969, 2931, 2874, 1598, 1494, 1451, 1369, 1318, 1090, 967, 748, 693. HRMS calc. $\text{C}_{13}\text{H}_{18}\text{O}$: 190.1358. Found: 190.1339



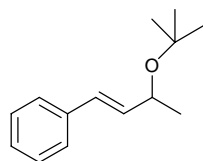
(E)-(3-isopropoxybut-1-enyl)benzene (2d)

^1H NMR (CDCl_3 , 300MHz, ppm): δ = 7.40-7.20 (m, 5H), 6.50 (d, J = 16.2 Hz, 1H), 6.07 (dd, J = 15.9 Hz, 7.2 Hz, 1H), 4.16-4.10 (m, 1H), 3.75-3.67 (m, 1H), 1.31 (d, J = 6.3 Hz, 3H), 1.17 (d, J = 6.3 Hz, 3H), 1.15 (d, J = 6.3 Hz, 3H). ^{13}C NMR (CDCl_3 , 75MHz, ppm): δ = 137.0, 133.0, 130.3, 128.7, 127.6, 126.6, 73.6, 68.6, 23.5, 22.3, 21.9. IR (liquid film, cm^{-1}): ν = 3056, 2921, 1644, 1459, 1374, 1258, 1102, 800. HRMS calc. $\text{C}_{13}\text{H}_{18}\text{O}$: 190.1358. Found: 190.1366.



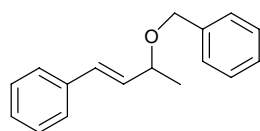
(E)-(3-butoxybut-1-enyl)benzene (2e)

^1H NMR (CDCl_3 , 300MHz, ppm): δ = 7.40-7.23 (m, 5H), 6.51 (d, J = 15.9 Hz, 1H), 6.07 (dd, J = 15.9 Hz, 7.5 Hz, 1H), 4.00-3.96 (m, 1H), 3.54-3.46 (m, 1H), 3.39-3.31 (m, 1H), 1.59-1.52 (m, 2H), 1.41-1.31 (m, 5H), 0.91 (t, J = 7.2 Hz, 3H). ^{13}C NMR (CDCl_3 , 75MHz, ppm): δ = 137.0, 132.5, 130.8, 128.7, 127.7, 126.6, 68.6, 32.2, 21.8, 19.6, 14.1. IR (liquid film, cm^{-1}): ν = 3026, 2957, 2871, 1459, 1369, 1243, 1090, 973, 747, 692. HRMS calc. $\text{C}_{14}\text{H}_{20}\text{O}$: 204.1514. Found: 204.1512.



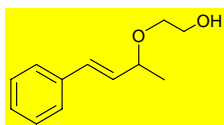
(E)-(3-tert-butoxybut-1-enyl)benzene (2f)

^1H NMR (CDCl_3 , 300MHz, ppm): δ = 7.37-7.20 (m, 5H), 6.48 (d, J = 15.9 Hz, 1H), 6.23 (dd, J = 15.9 Hz, 6.0 Hz, 1H), 4.31-4.27 (m, 1H), 1.27 (d, J = 6.3 Hz, 3H), 1.24 (s, 9H). ^{13}C NMR (CDCl_3 , 75MHz, ppm): δ = 137.5, 135.2, 128.6, 128.1, 127.3, 126.4, 74.1, 68.4, 28.7, 23.9. IR (liquid film, cm^{-1}): ν = 3027, 2975, 2929, 2868, 1688, 1598, 1494, 1449, 1369, 1316, 1153, 1092, 967, 748, 693. HRMS calc. $\text{C}_{14}\text{H}_{20}\text{O}$: 204.1514. Found: 204.1516.



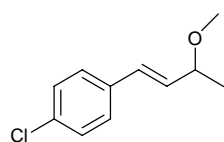
(E)-(3-(benzyloxy)but-1-enyl)benzene (2g)

^1H NMR (CDCl_3 , 300MHz, ppm): δ = 7.41-7.22 (m, 10H), 6.54 (d, J = 15.9 Hz, 1H), 6.17 (dd, J = 15.9 Hz, 7.5 Hz, 1H), 6.54 (d, J = 15.9 Hz, 1H), 4.62 (d, J = 12.0 Hz, 1H), 4.44 (d, J = 12.0 Hz, 1H), 4.15-4.06 (m, 1H), 1.38 (d, J = 6.6 Hz, 3H). ^{13}C NMR (CDCl_3 , 75MHz, ppm): δ = 138.9, 136.8, 131.9, 131.5, 128.7, 128.5, 127.8, 127.6, 126.6, 76.0, 70.2, 21.9. IR (liquid film, cm^{-1}): ν = 3029, 2972, 2925, 2855, 1599, 1494, 1452, 1369, 1145, 1072, 968, 746, 694. HRMS calc. $\text{C}_{17}\text{H}_{18}\text{O}$: 238.1358 Found: 238.1349.



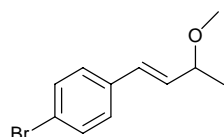
(E)-2-(4-phenylbut-3-en-2-yloxy)ethanol (2h)

^1H NMR (CDCl_3 , 300MHz, ppm): δ = 7.40-7.22 (m, 5H), 6.54 (d, J = 15.9 Hz, 1H), 6.11 (dd, J = 15.9 Hz, 7.5 Hz, 1H), 4.10-4.01 (m, 1H), 3.74 (t, J = 7.5 Hz, 2H), 3.67-3.61 (m, 1H), 3.52-3.45 (m, 1H), 2.05 (br, 1H), 1.36 (d, J = 6.3 Hz, 3H). ^{13}C NMR (CDCl_3 , 75MHz, ppm): δ = 136.6, 131.5, 128.7, 127.8, 126.6, 77.2, 69.5, 62.1, 21.7. IR (liquid film, cm^{-1}): ν = 3433, 3027, 2974, 2929, 2866, 1494, 1450, 1371, 1147, 1106, 1061, 968, 750, 694. HRMS calc. $\text{C}_{13}\text{H}_{18}\text{O}_2$: 206.1307 Found: 206.1303



(E)-1-chloro-4-(3-methoxybut-1-enyl)benzene (2j)

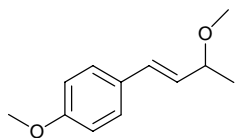
^1H NMR (CDCl_3 , 400MHz, ppm): δ = 7.33-7.26 (m, 4H), 6.49 (d, J = 15.9 Hz, 1H), 6.07 (dd, J = 15.9 Hz, 7.5 Hz, 1H), 3.90-3.87 (m, 1H), 3.32 (s, 3H), 1.32 (d, J = 6.3 Hz, 3H). ^{13}C NMR (CDCl_3 , 100MHz, ppm): δ = 135.3, 133.3, 132.3, 130.1, 128.8, 127.7, 78.0, 56.2, 21.4. IR (liquid film, cm^{-1}): ν = 3029, 2977, 2928, 1593, 1491, 1370, 1352, 1199, 1110, 1090, 969, 854, 809. HRMS calc. $\text{C}_{11}\text{H}_{13}\text{ClO}$: 196.0655. Found: 196.0646.



(E)-1-bromo-4-(3-methoxybut-1-enyl)benzene (2k)

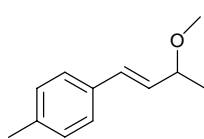
^1H NMR (CDCl_3 , 300MHz, ppm): δ = 7.45-7.43 (m, 2H), 7.25 (d, J = 8.4 Hz, 2H), 6.47 (d, J = 15.9 Hz, 1H), 6.09 (dd, J = 15.9 Hz, 7.5 Hz, 1H),

3.91-3.86 (m, 1H), 3.32 (s, 3H), 1.32 (d, $J = 6.3$ Hz, 3H). ^{13}C NMR (CDCl_3 , 75MHz, ppm): $\delta = 135.7, 132.5, 131.8, 130.1, 128.1, 121.5, 78.0, 56.3, 21.4$. IR (liquid film, cm^{-1}): $\nu = 2926, 1728, 1487, 1462, 1423, 1371, 1259, 1109, 1075, 1038, 1011, 970, 804$ HRMS calc. $\text{C}_{11}\text{H}_{13}\text{BrO}$: 240.0150 Found: 240.0139.



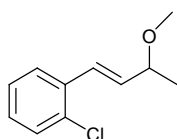
(E)-1-methoxy-4-(3-methoxybut-1-enyl)benzene (2l)

^1H NMR (CDCl_3 , 300MHz, ppm): $\delta = 7.35\text{-}7.31$ (m, 2H), 6.87-6.85 (m, 2H), 6.47 (d, $J = 15.9$ Hz, 1H), 5.95 (dd, $J = 16.2$ Hz, 7.8 Hz, 1H), 3.89-3.81 (m, 1H), 3.79 (s, 3H), 3.31 (s, 3H), 1.32 (d, $J = 6.3$ Hz, 3H). ^{13}C NMR (CDCl_3 , 75MHz, ppm): $\delta = 159.4, 131.0, 129.6, 129.4, 127.8, 114.1, 78.4, 56.1, 55.4, 21.7$. IR (liquid film, cm^{-1}): $\nu = 2960, 2928, 1608, 1512, 1462, 1300, 1248, 1176, 1108, 1082, 1036, 969, 819$. HRMS calc. $\text{C}_{12}\text{H}_{16}\text{O}_2$: 192.1150 Found: 192.1159.



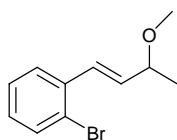
(E)-1-(3-methoxybut-1-enyl)-4-methylbenzene (2m)

^1H NMR (CDCl_3 , 300MHz, ppm): $\delta = 7.29$ (d, $J = 7.8$ Hz, 2H), 7.13 (d, $J = 7.8$ Hz, 2H), 6.50 (d, $J = 15.9$ Hz, 1H), 6.02 (dd, $J = 15.9$ Hz, 7.5 Hz, 1H), 3.90-3.85 (m, 1H), 3.31 (s, 3H), 2.34 (s, 3H), 1.32 (d, $J = 6.3$ Hz, 3H). ^{13}C NMR (CDCl_3 , 75MHz, ppm): $\delta = 137.6, 134.0, 131.4, 130.6, 129.4, 126.5, 78.3, 56.1, 21.6, 21.3$. IR (liquid film, cm^{-1}): $\nu = 3023, 2975, 2926, 2855, 2819, 1513, 1459, 1370, 1198, 1139, 1110, 1082, 969, 800$. HRMS calc. $\text{C}_{12}\text{H}_{16}\text{O}$: 176.1201 Found: 176.1199.



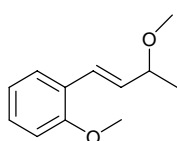
(E)-1-chloro-2-(3-methoxybut-1-enyl)benzene (2n)

^1H NMR (CDCl_3 , 400MHz, ppm): $\delta = 7.55\text{-}7.53$ (m, 1H), 7.36-7.34 (m, 1H), 7.23-7.17 (m, 2H), 6.92 (d, $J = 15.9$ Hz, 1H), 6.08 (dd, $J = 15.9$ Hz, 7.6 Hz, 1H), 3.96-3.92 (m, 1H), 3.34 (s, 3H), 1.34 (d, $J = 6.4$ Hz, 3H). ^{13}C NMR (CDCl_3 , 100MHz, ppm): $\delta = 135.0, 134.4, 133.2, 129.8, 128.7, 127.7, 127.0, 126.9, 78.1, 56.2, 21.5$. IR (liquid film, cm^{-1}): $\nu = 3063, 2977, 2929, 2821, 1591, 1470, 1441, 1369, 1354, 1200, 1143, 1110, 1083, 1037, 969, 751, 693$. HRMS calc. $\text{C}_{11}\text{H}_{13}\text{ClO}$: 196.0655. Found: 196.0653.



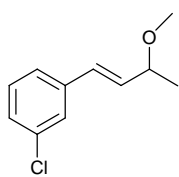
(E)-1-bromo-2-(3-methoxybut-1-enyl)benzene (2o)

^1H NMR (CDCl_3 , 300MHz, ppm): $\delta = 7.56\text{-}7.52$ (m, 2H), 7.30-7.24 (m, 1H), 7.13-7.08 (m, 1H), 6.87 (d, $J = 15.9$ Hz, 1H), 6.02 (dd, $J = 15.9$ Hz, 7.5 Hz, 1H), 3.97-3.92 (m, 1H), 3.35 (s, 3H), 1.34 (d, $J = 6.3$ Hz, 3H). ^{13}C NMR (CDCl_3 , 75MHz, ppm): $\delta = 136.8, 134.6, 133.1, 130.0, 129.0, 127.6, 127.3, 123.8, 78.0, 56.3, 21.5$. IR (liquid film, cm^{-1}): $\nu = 3060, 2975, 2928, 2820, 1588, 1466, 1438, 1369, 1353, 1200, 1142, 1109, 1042, 1024, 967, 751, 667$. HRMS calc. $\text{C}_{11}\text{H}_{13}\text{BrO}$: 240.0150. Found: 240.0153.



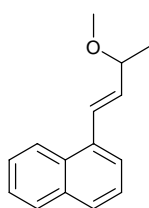
(E)-1-methoxy-2-(3-methoxybut-1-enyl)benzene (2p)

^1H NMR (CDCl_3 , 300MHz, ppm): $\delta = 7.48\text{-}7.45$ (m, 1H), 7.22 (d, $J = 7.5$ Hz, 1H), 6.95-6.83 (m, 3H), 6.10 (dd, $J = 15.9$ Hz, 7.8 Hz, 1H), 3.90-3.83 (m, 4H), 3.32 (s, 3H), 1.33 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (CDCl_3 , 75MHz, ppm): $\delta = 156.9, 132.1, 128.8, 127.0, 126.4, 125.8, 120.8, 111.1, 78.7, 56.1, 55.6, 21.7$. IR (liquid film, cm^{-1}): $\nu = 2974, 2931, 1597, 1490, 1463, 1291, 1244, 1107, 1082, 1029, 975, 751$. HRMS calc. $\text{C}_{12}\text{H}_{16}\text{O}_2$: 192.1150. Found: 192.1143



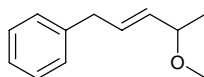
(E)-1-chloro-3-(3-methoxybut-1-enyl)benzene (2q)

$^1\text{H NMR}$ (CDCl_3 , 400MHz, ppm): δ = 7.38-7.37 (m, 1H), 7.26-7.22 (m, 3H), 6.48 (d, J = 15.9 Hz, 1H), 6.11 (dd, J = 15.9 Hz, 7.4 Hz, 1H), 3.91-3.87 (m, 1H), 3.32 (s, 3H), 1.32 (d, J = 6.4 Hz, 3H). $^{13}\text{C NMR}$ (CDCl_3 , 100MHz, ppm): δ = 138.7, 134.6, 133.2, 129.90, 129.86, 127.6, 126.4, 124.7, 77.9, 56.2, 21.4. IR (liquid film, cm^{-1}): ν = 3062, 2978, 2923, 2821 1594, 1566, 1475, 1370, 1352, 1111, 968, 779, 685. HRMS calc. $\text{C}_{11}\text{H}_{13}\text{ClO}$: 196.0655. Found: 196.0659.



(E)-1-(3-methoxybut-1-enyl)naphthalene (2r)

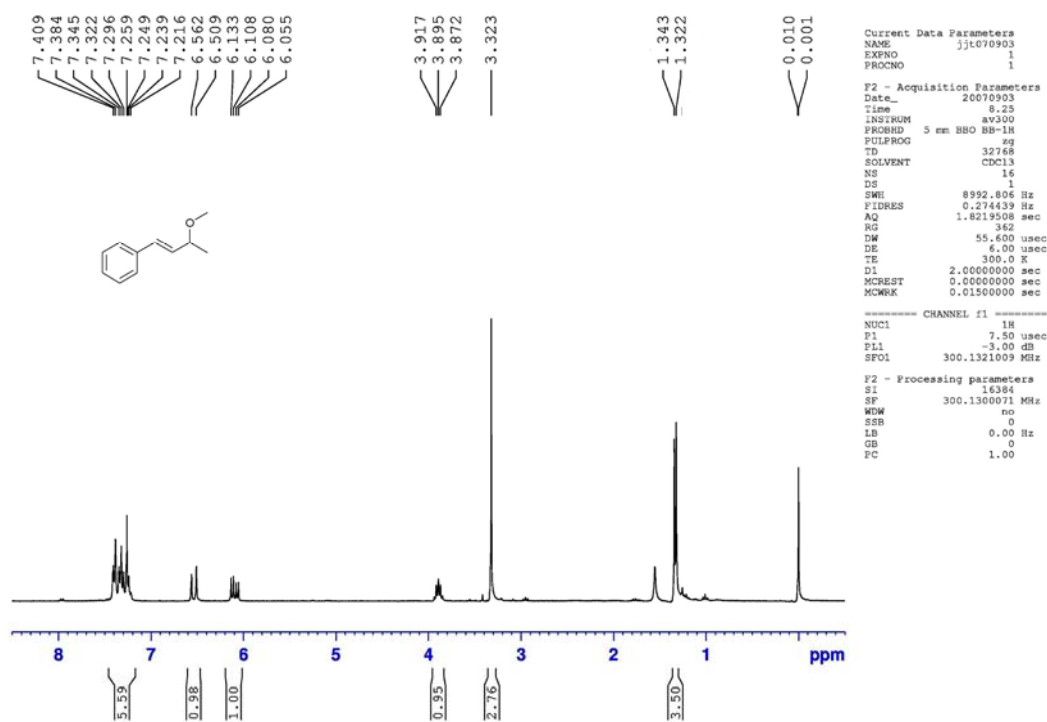
$^1\text{H NMR}$ (CDCl_3 , 400MHz, ppm): δ = 8.13-8.11 (m, 1H), 7.86-7.84 (m, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.61 (d, J = 6.8Hz, 1H), 7.52-7.43 (m, 3H), 7.29 (d, J = 15.7 Hz, 1H), 6.13 (dd, J = 15.7 Hz, 7.6 Hz, 1H), 4.04-4.01 (m, 1H), 3.41 (s, 3H), 1.41 (d, J = 6.0 Hz, 3H). $^{13}\text{C NMR}$ (CDCl_3 , 100MHz, ppm): δ = 134.9 134.6, 133.8, 131.3, 128.71, 128.65, 128.1, 126.2, 125.9, 125.8, 124.1, 123.8, 78.4, 56.3, 21.7. IR (liquid film, cm^{-1}): ν = 3058, 2976, 2928, 2819, 1590, 1447, 1395, 1369, 1198, 1141, 1111, 1087, 969, 794, 775. HRMS calc. $\text{C}_{15}\text{H}_{16}\text{O}$: 212.1201. Found: 212.1209.



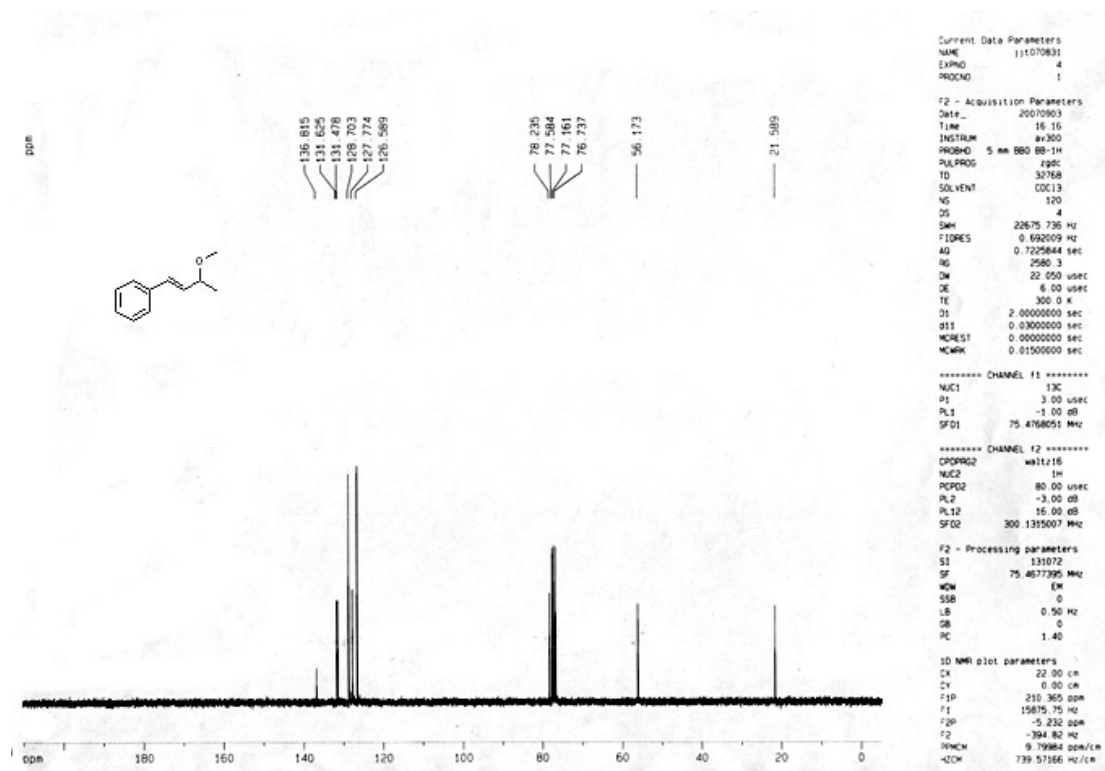
(E)-1-(4-methoxybut-2-enyl)benzene (2s)

$^1\text{H NMR}$ (CDCl_3 , 300MHz, ppm): δ = 7.32-7.17 (m, 5H), 5.80-5.72 (m, 1H), 5.42 (dd, J = 15.3 Hz, 7.5 Hz, 1H), 3.73-3.67 (m, 1H), 3.39 (d, J = 6.6 Hz, 2H), 3.26 (s, 3H), 1.41 (d, J = 6.0 Hz, 3H). $^{13}\text{C NMR}$ (CDCl_3 , 75MHz, ppm): δ = 140.4, 133.4, 131.6, 128.7, 128.6, 128.4, 78.0, 56.0, 38.8, 21.5. IR (liquid film, cm^{-1}): ν = 3028, 2977, 2929, 2819, 1494, 1452, 1370, 1200, 1114, 1090, 1044, 972, 844, 745, 699. HRMS calc. $\text{C}_{12}\text{H}_{16}\text{O}$: 176.1201. Found: 176.1200.

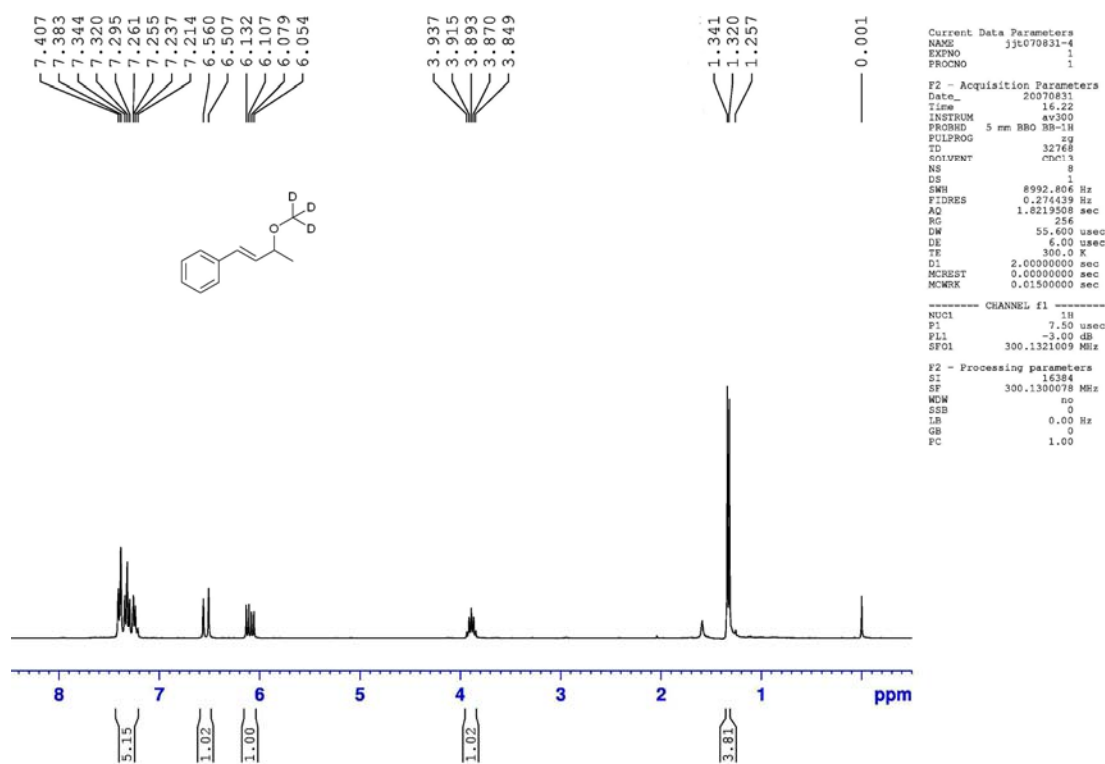
2a ($^1\text{H NMR}$)



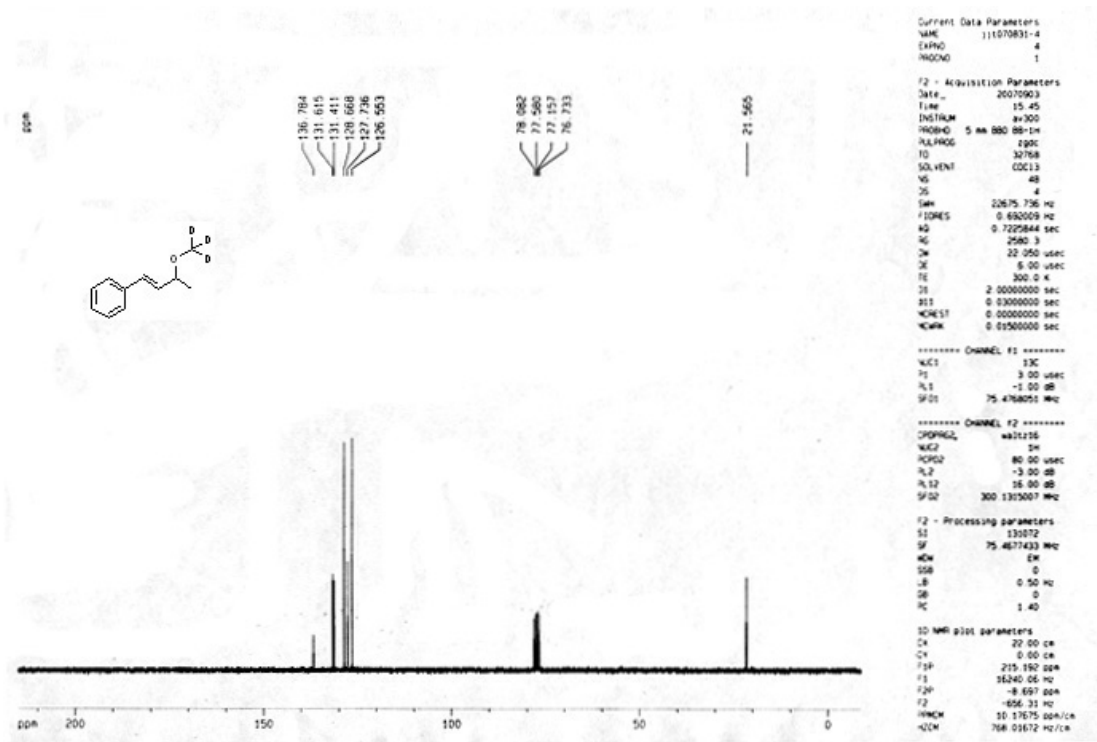
2a (^{13}C NMR)



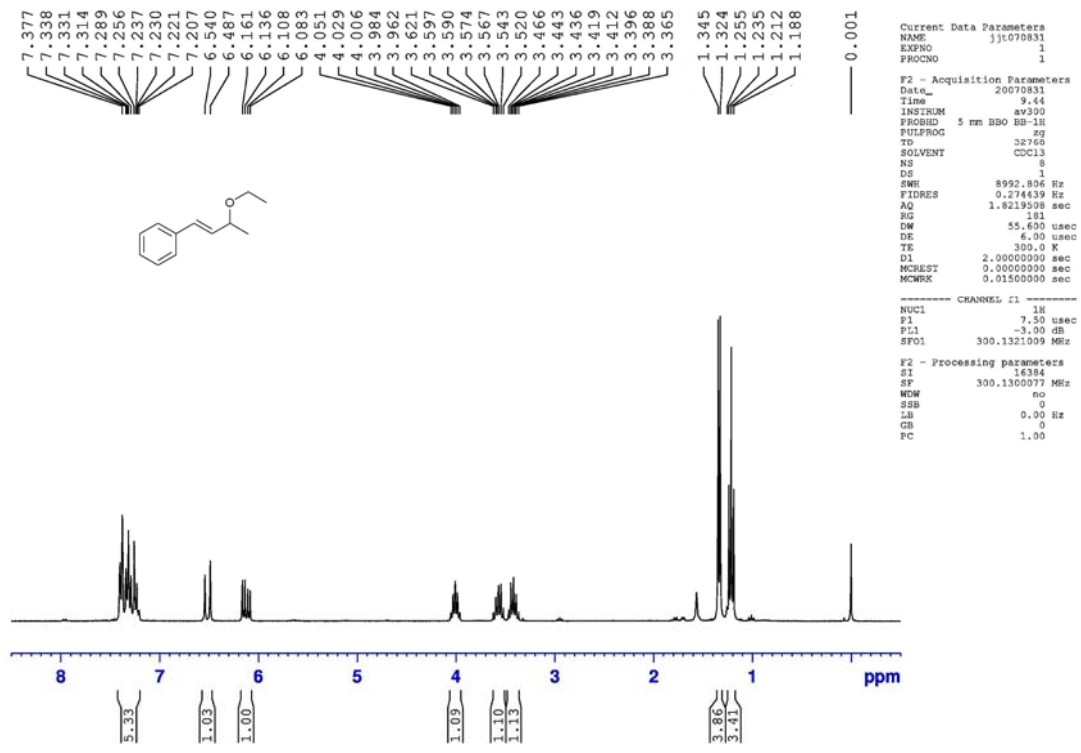
d_3 -2a (^1H NMR)



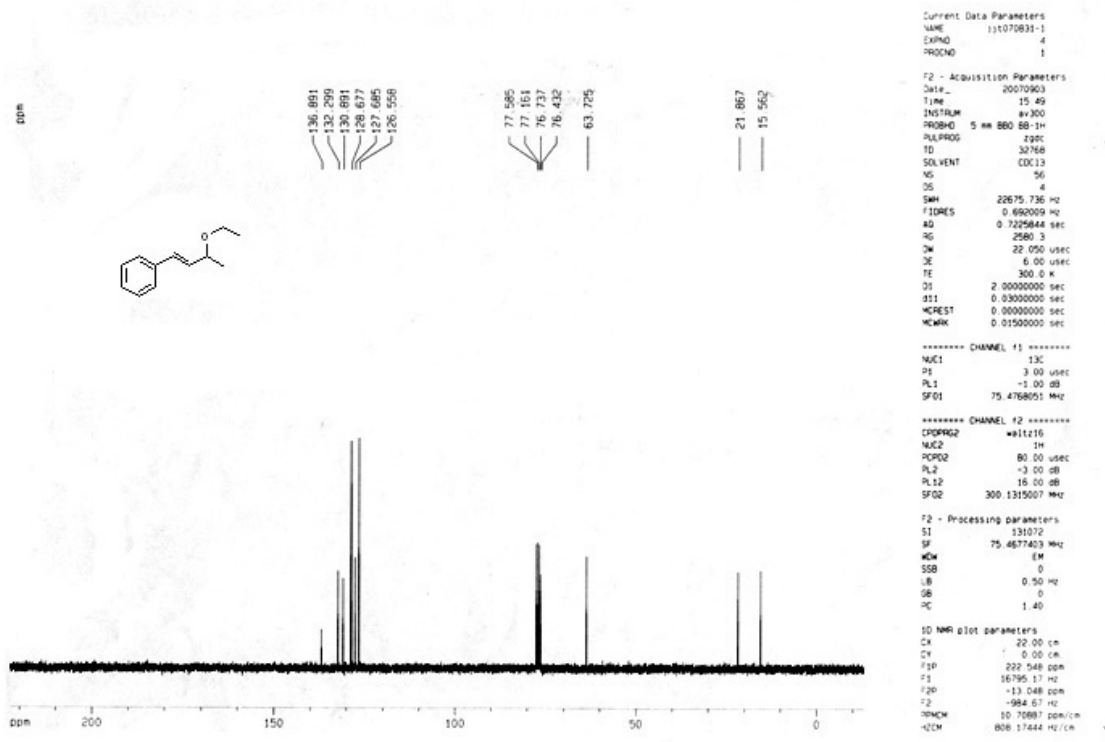
*d*₃-2a (¹³C NMR)



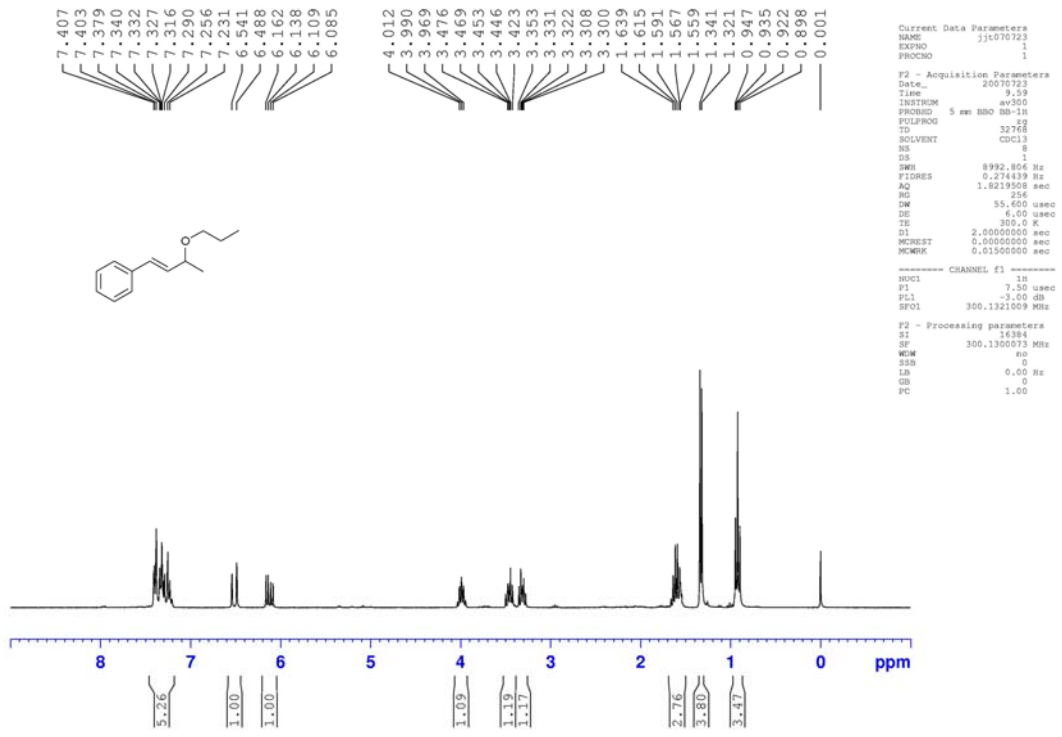
2b (¹H NMR)



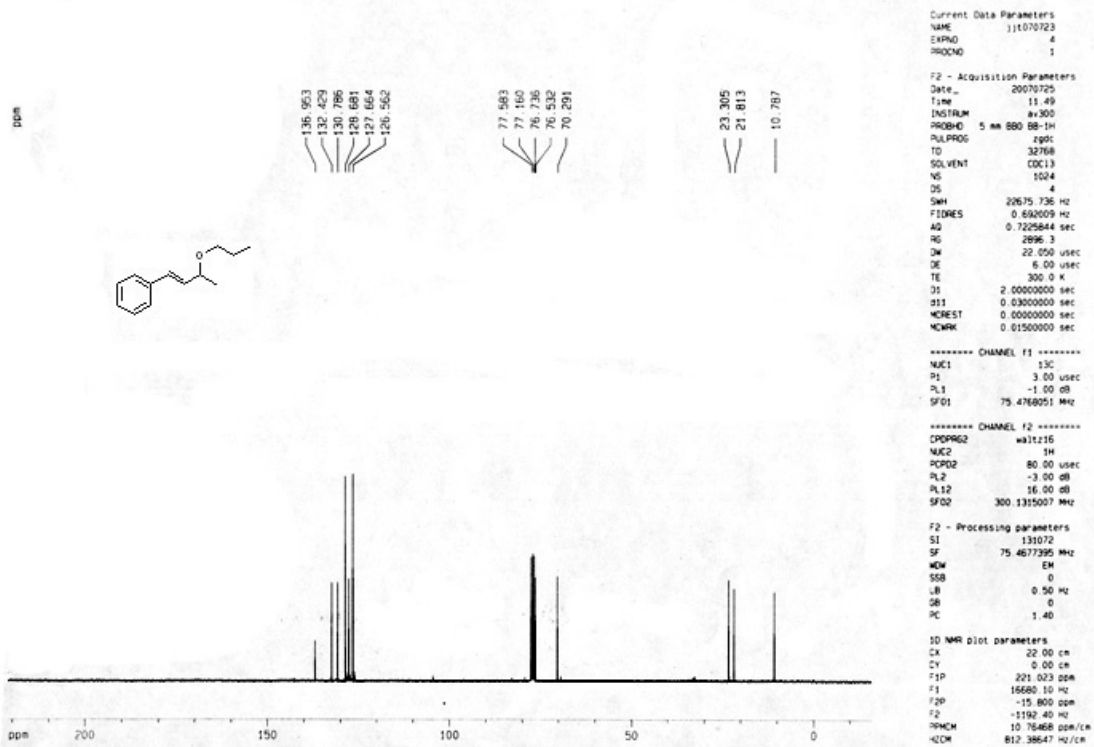
2b (¹³C NMR)



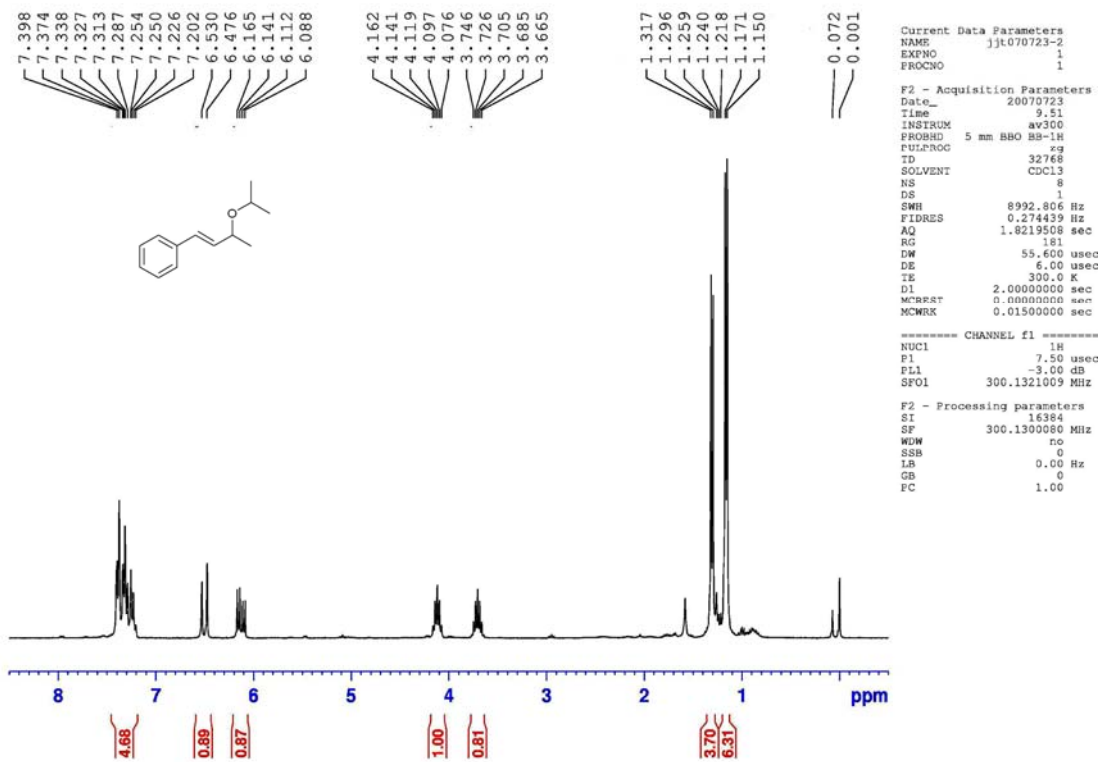
2c (¹H NMR)



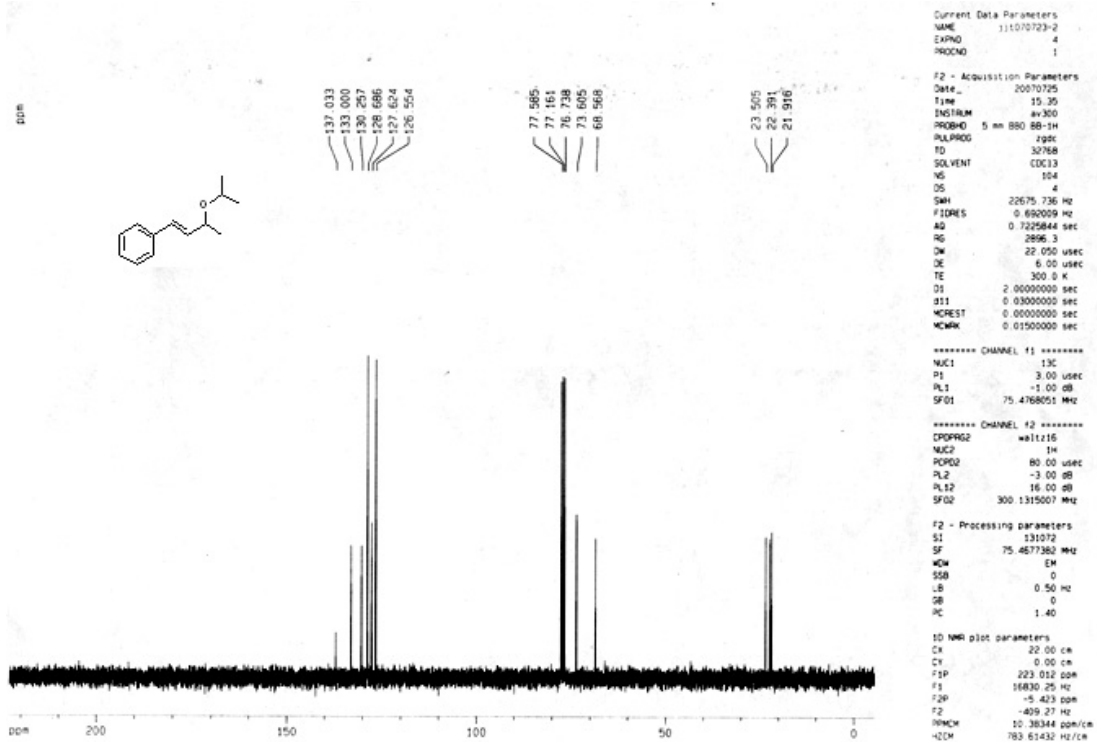
2c (¹³C NMR)



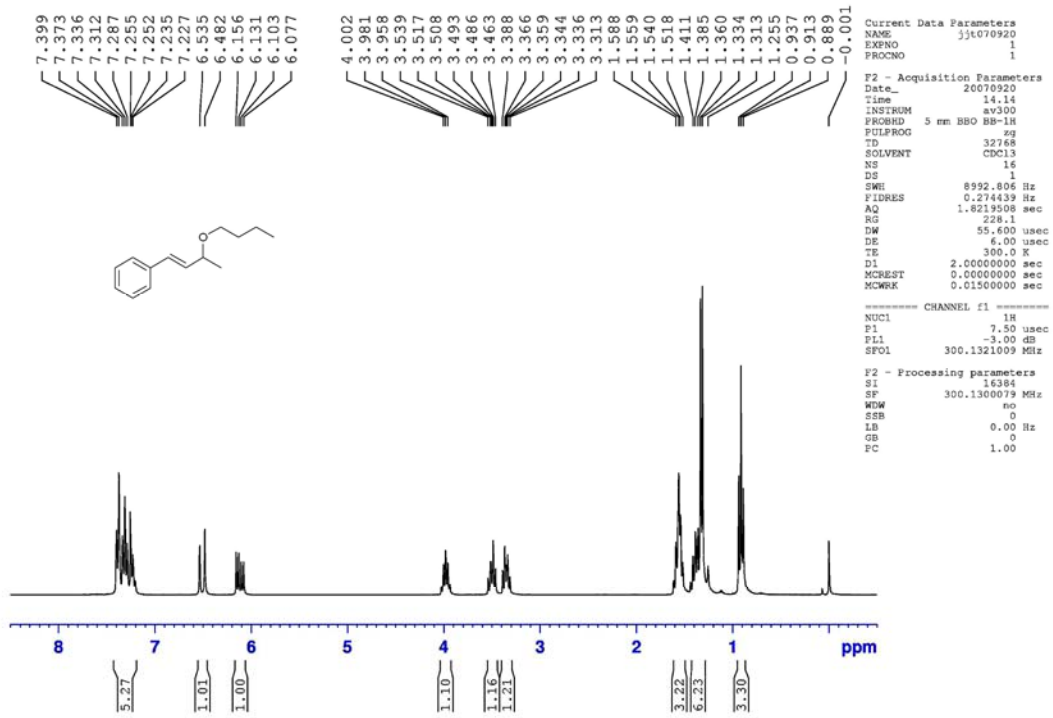
2d (¹H NMR)



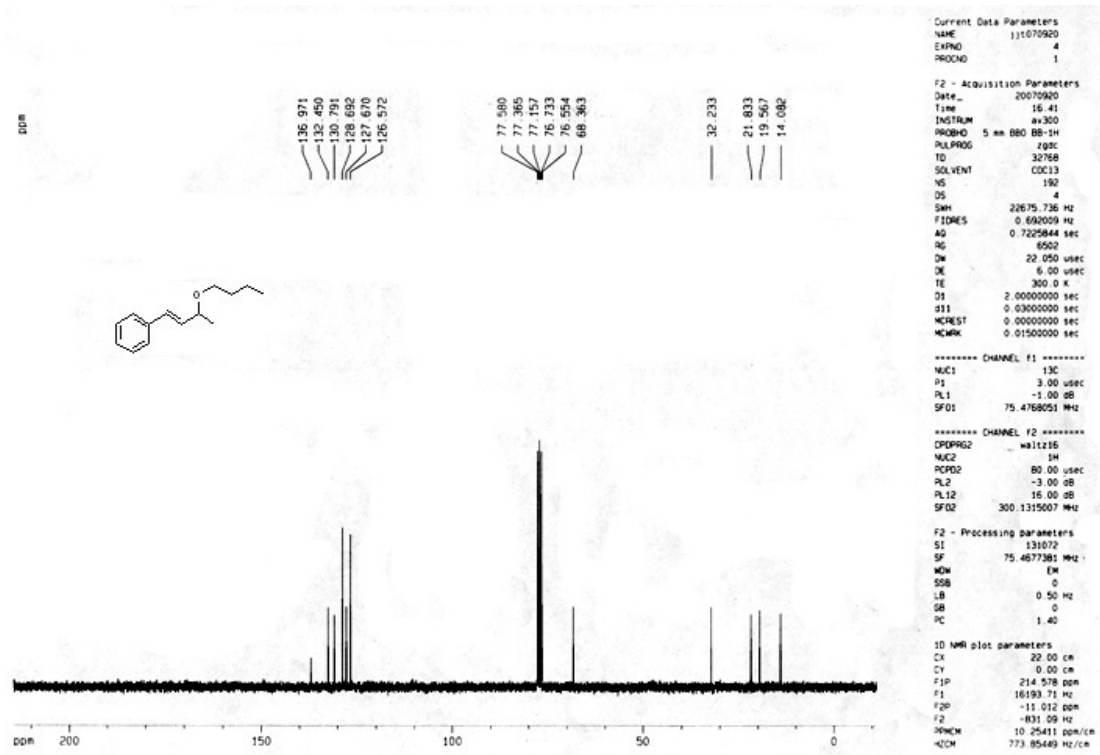
2d (¹³C NMR)



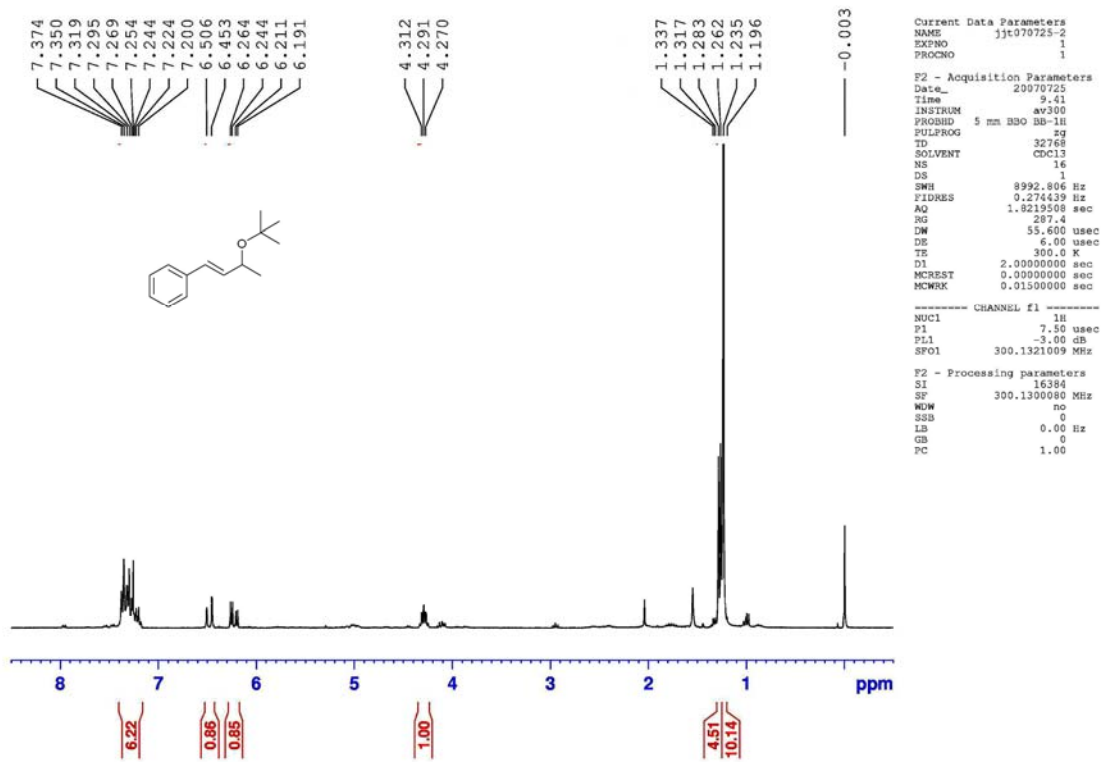
2e (¹H NMR)



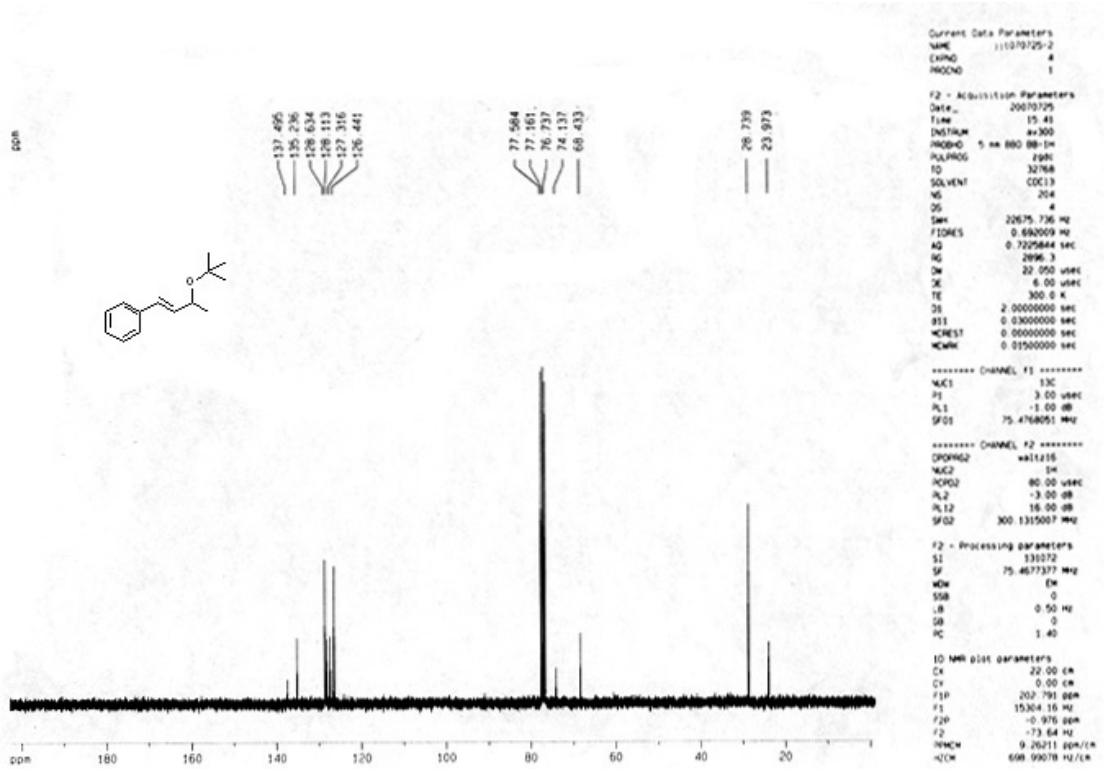
2e (¹³C NMR)



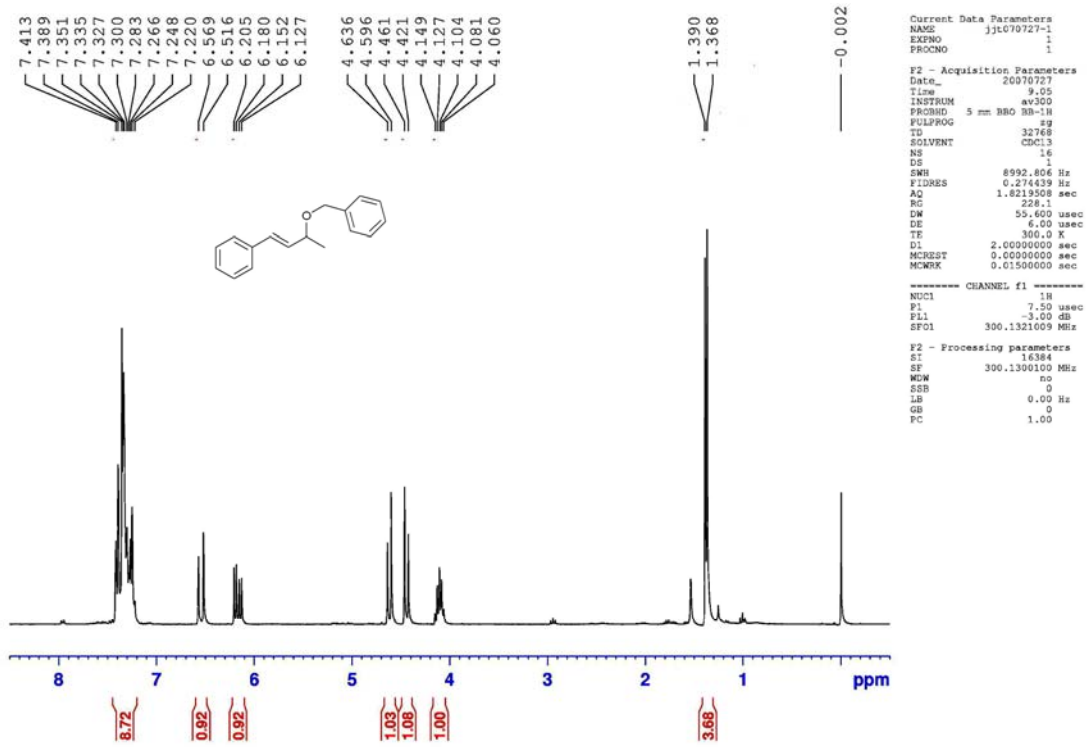
2f (¹H NMR)



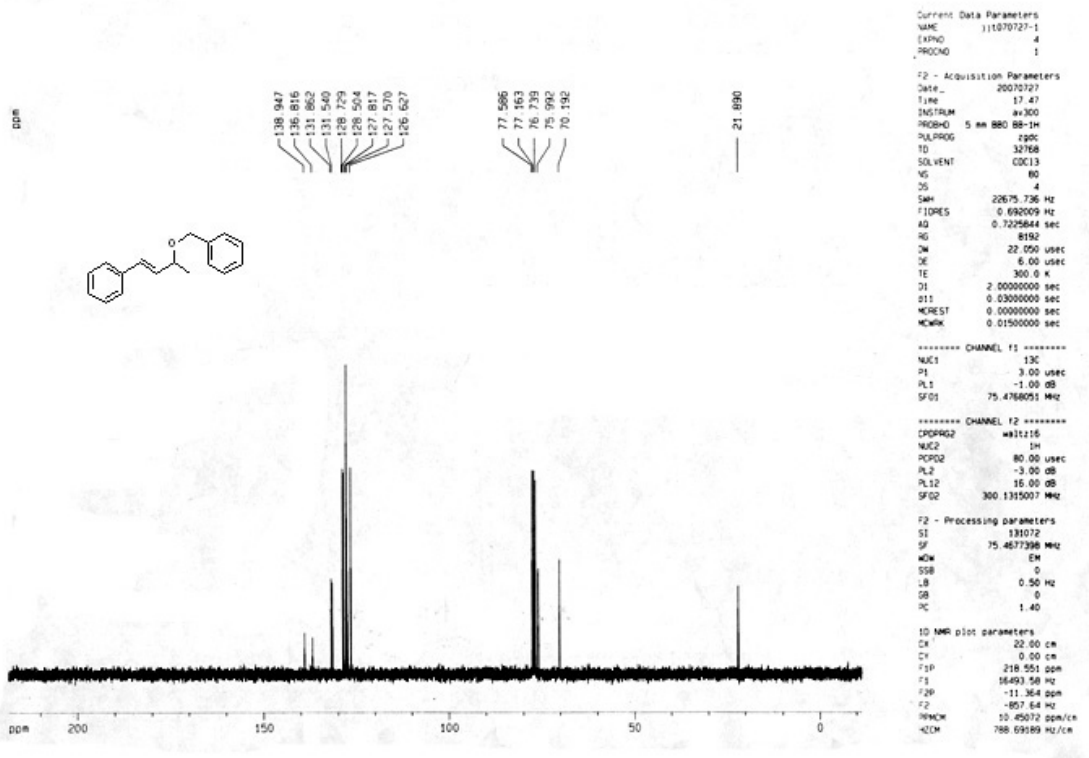
2f (¹³C NMR)



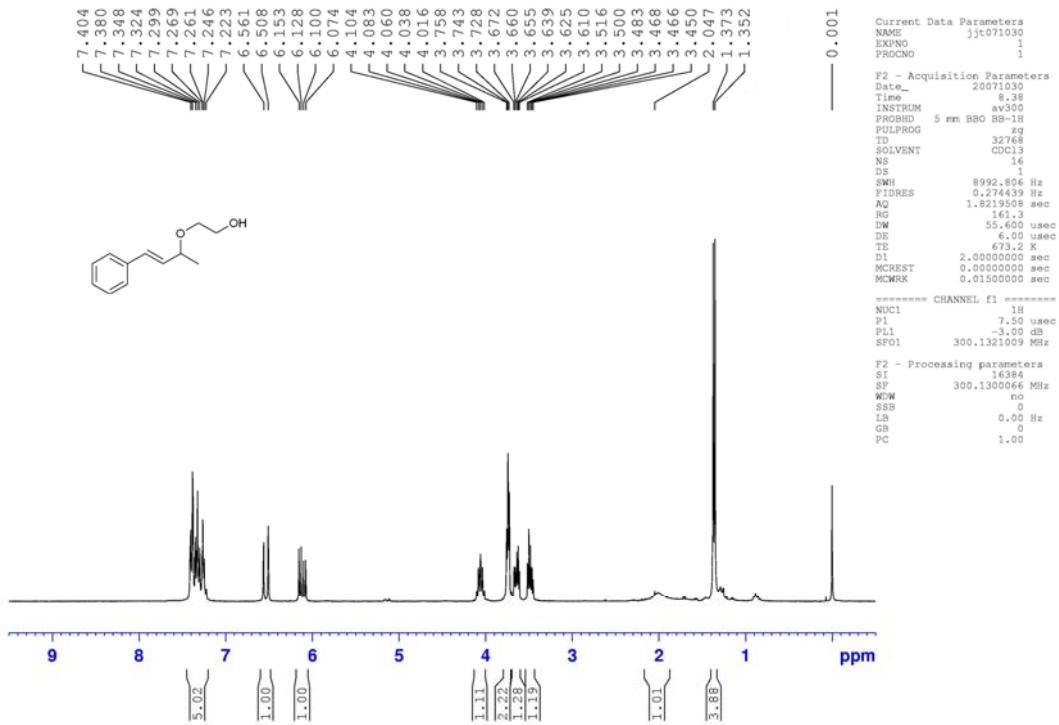
2g (¹H NMR)



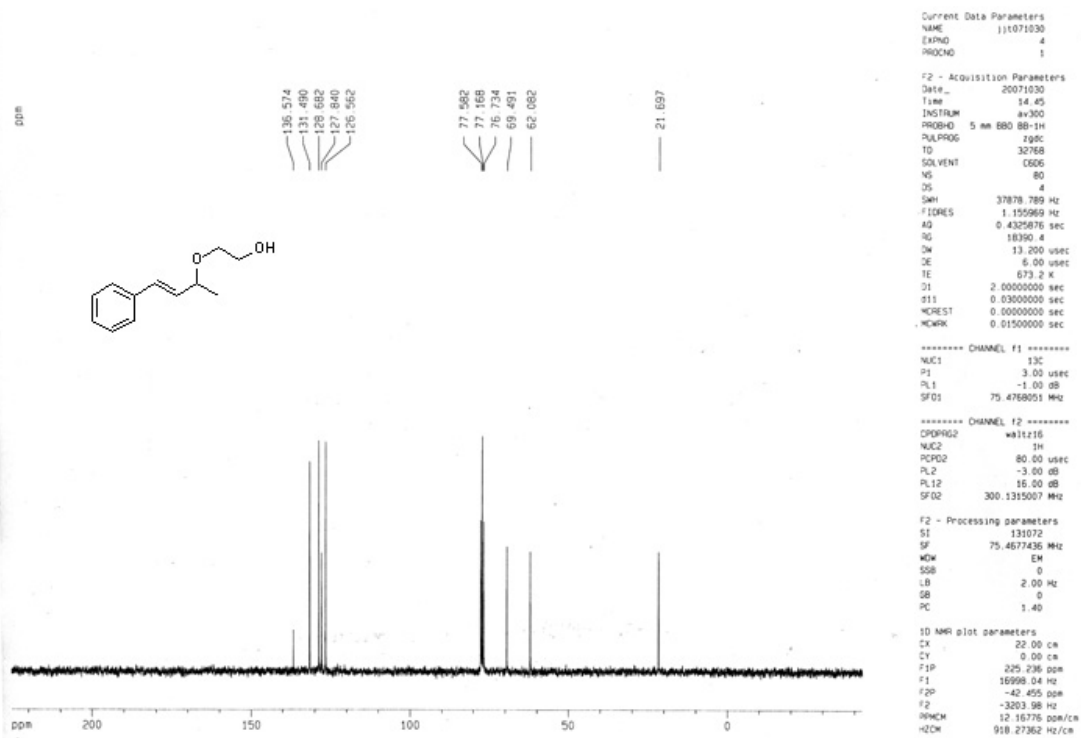
2g (¹³C NMR)



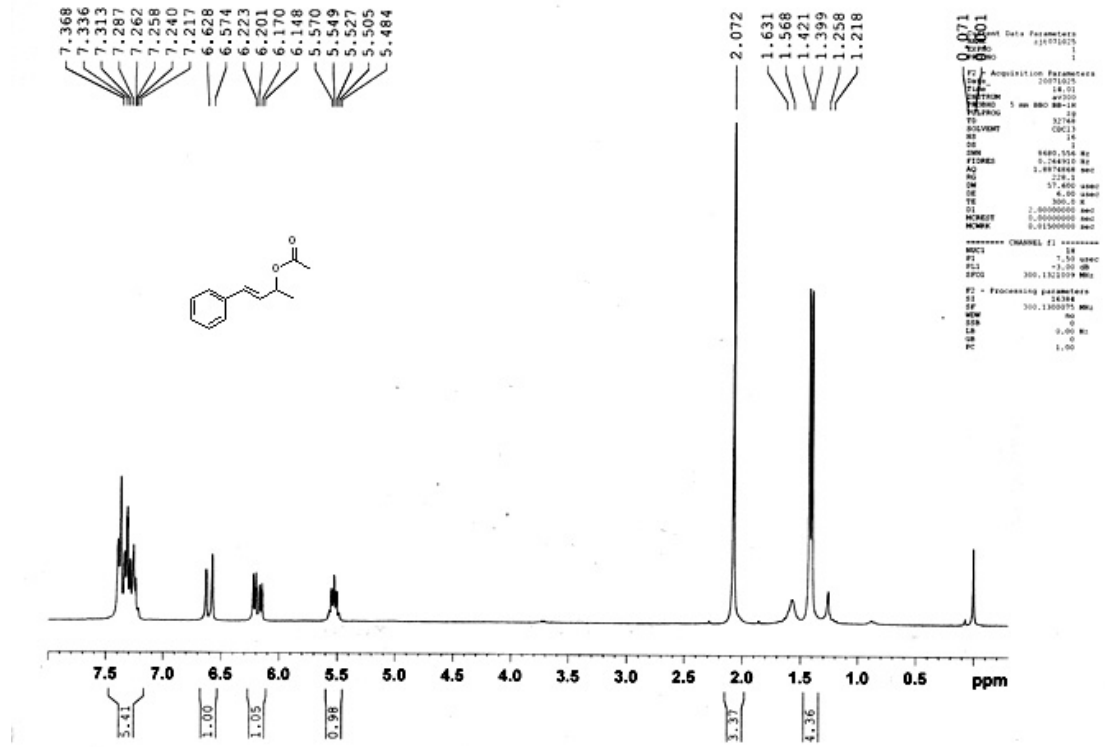
2h (¹H NMR)



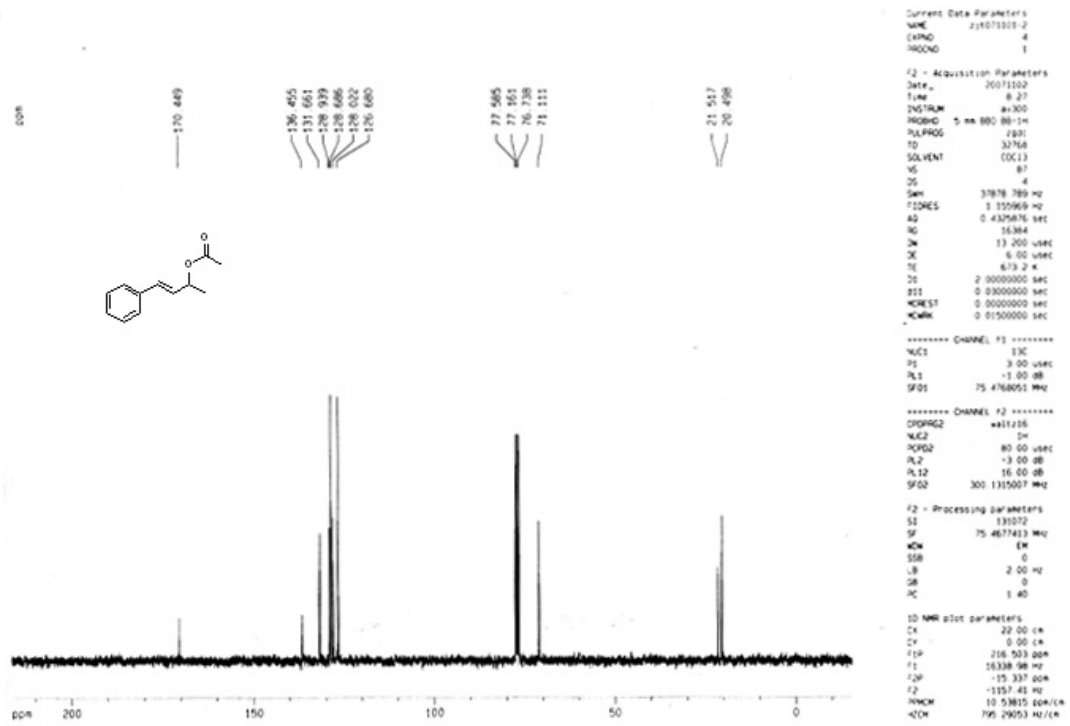
2h (¹³C NMR)



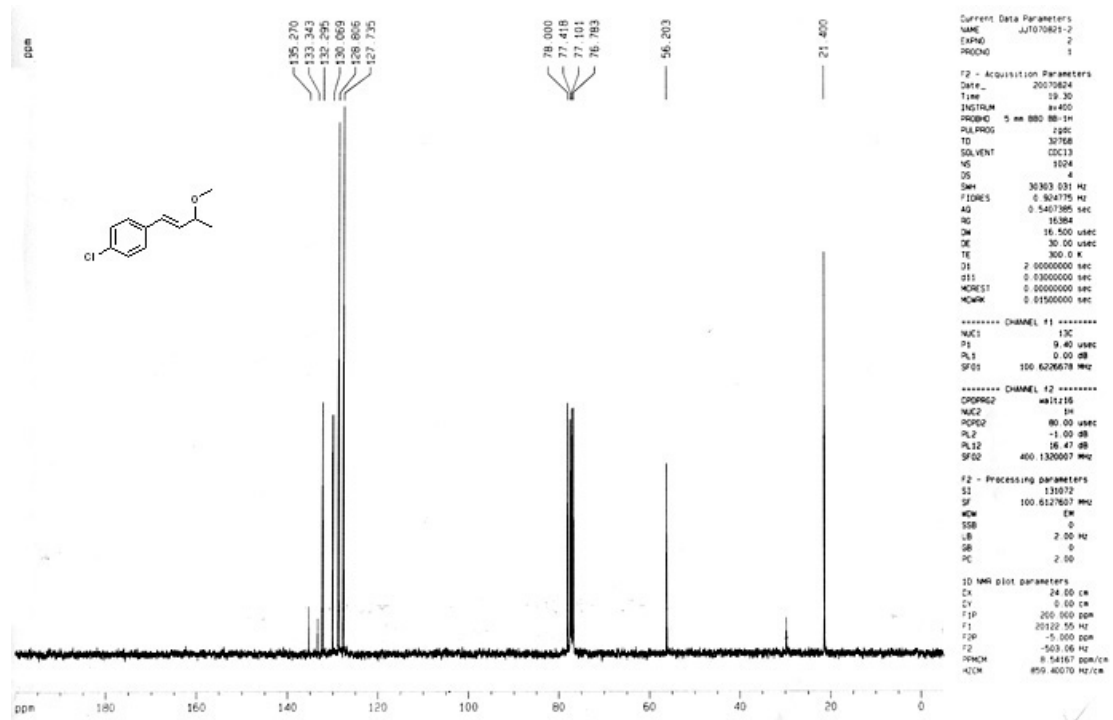
2i (¹H NMR)



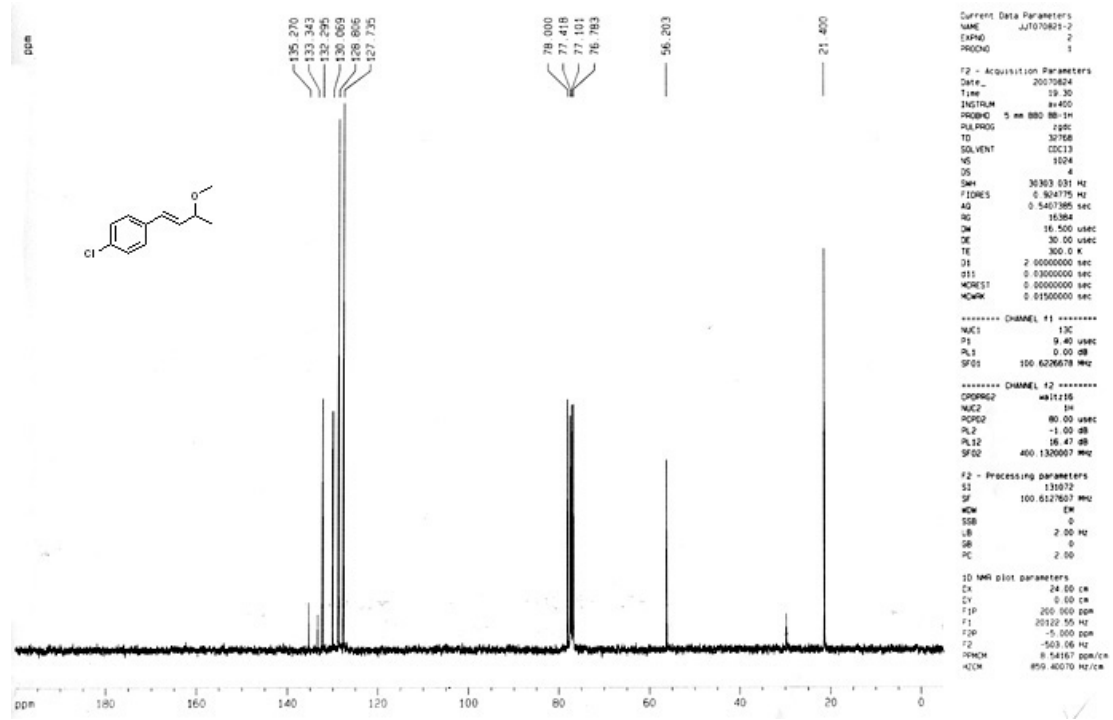
2i (¹³C NMR)



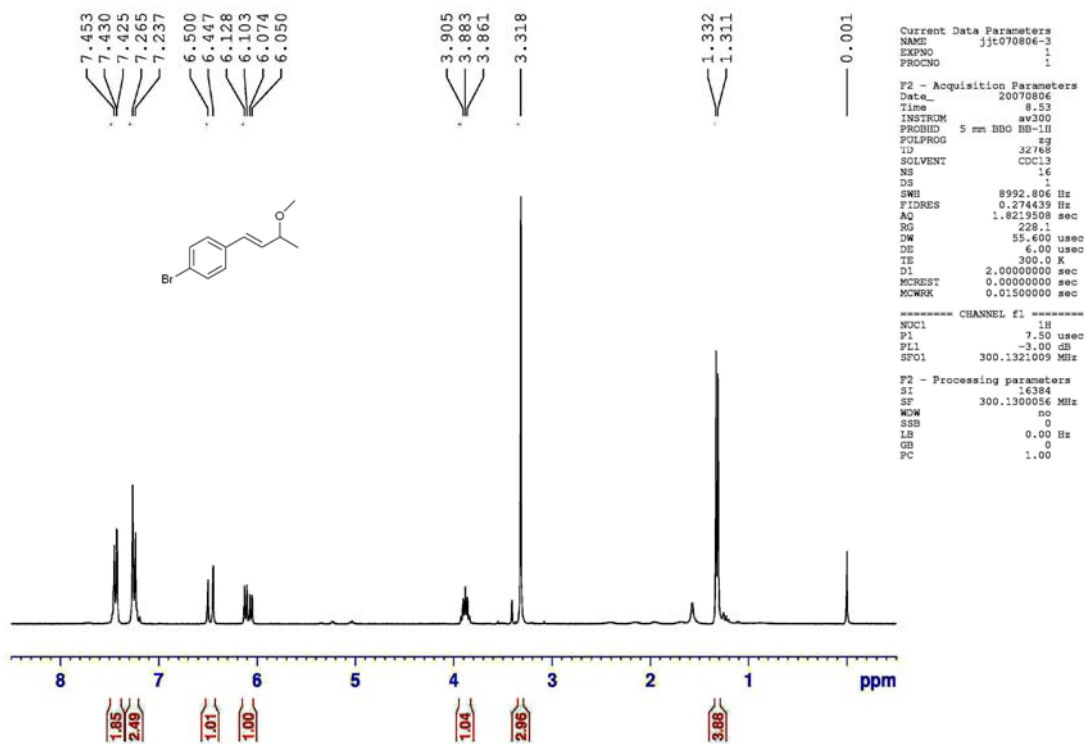
2j (¹H NMR)



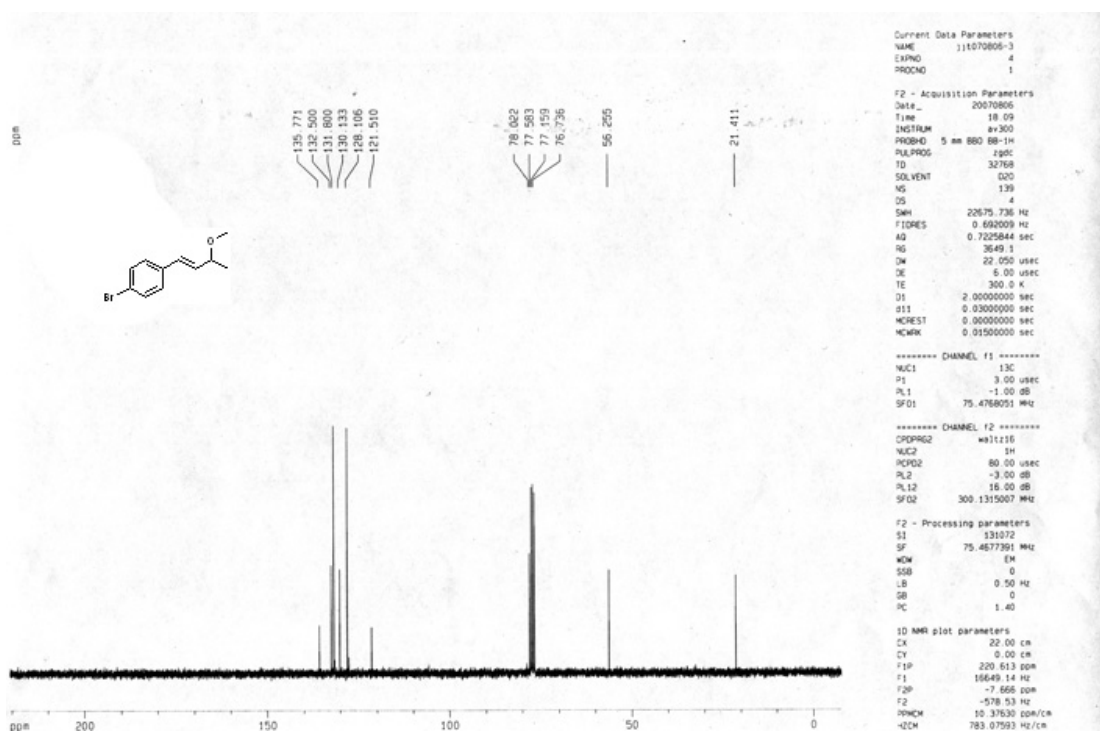
2j (¹³C NMR)



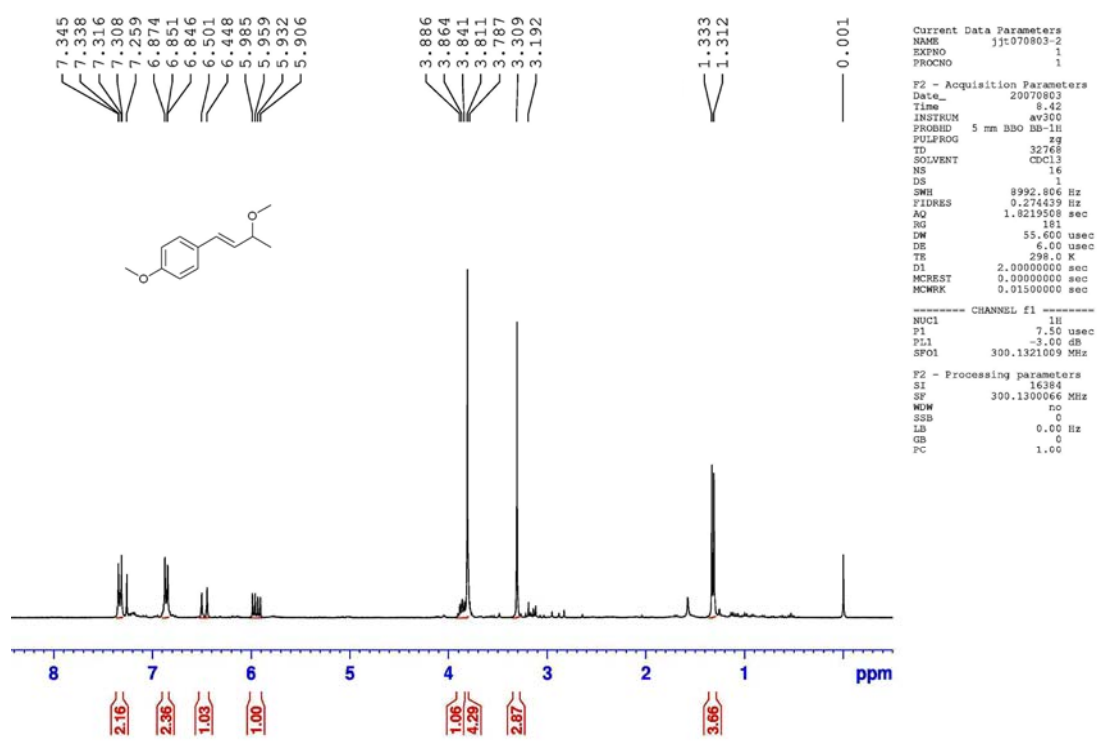
2k (¹H NMR)



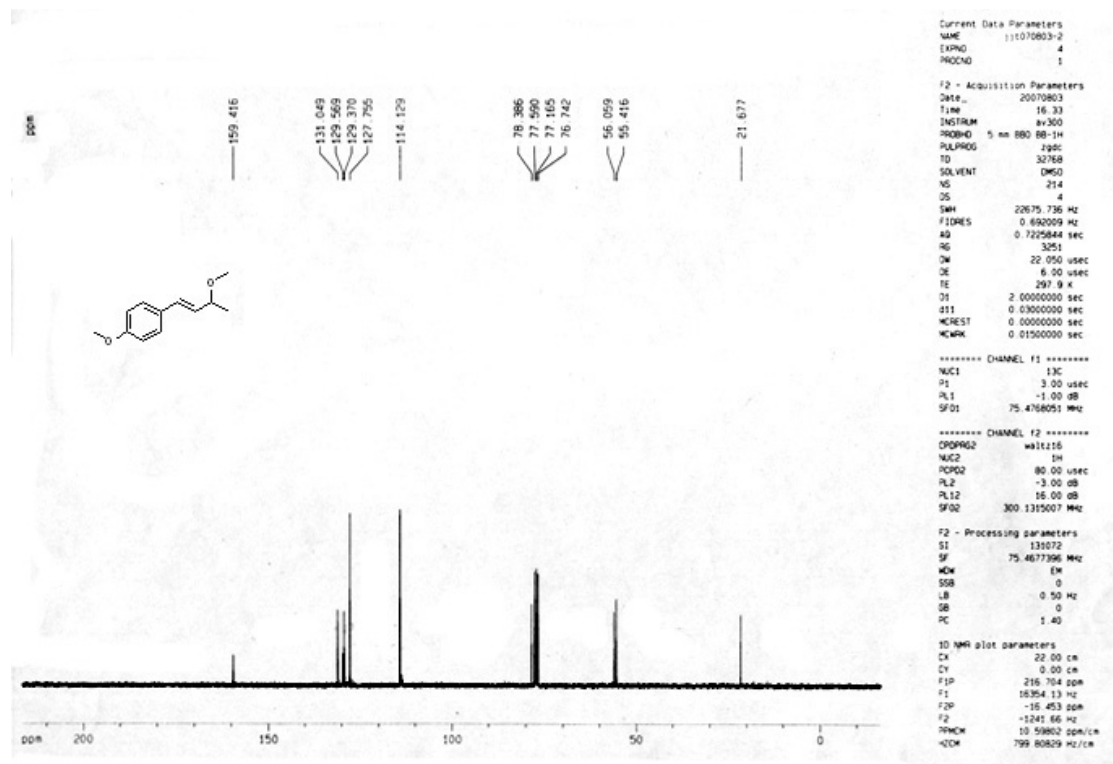
2k (¹³C NMR)



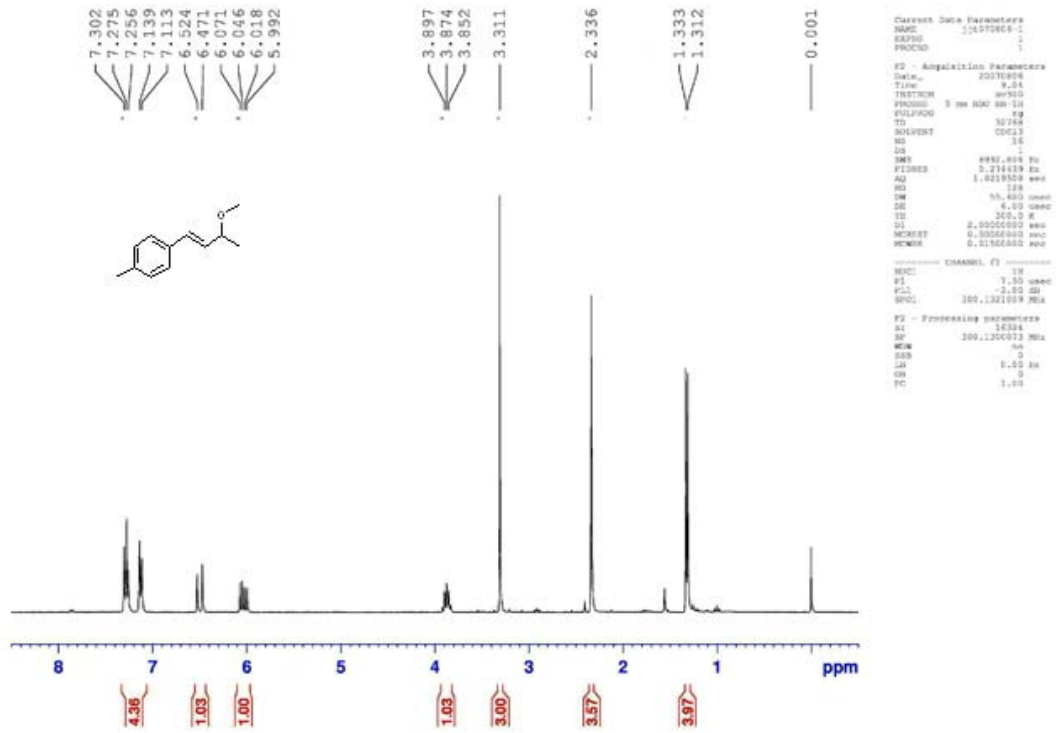
21 (¹H NMR)



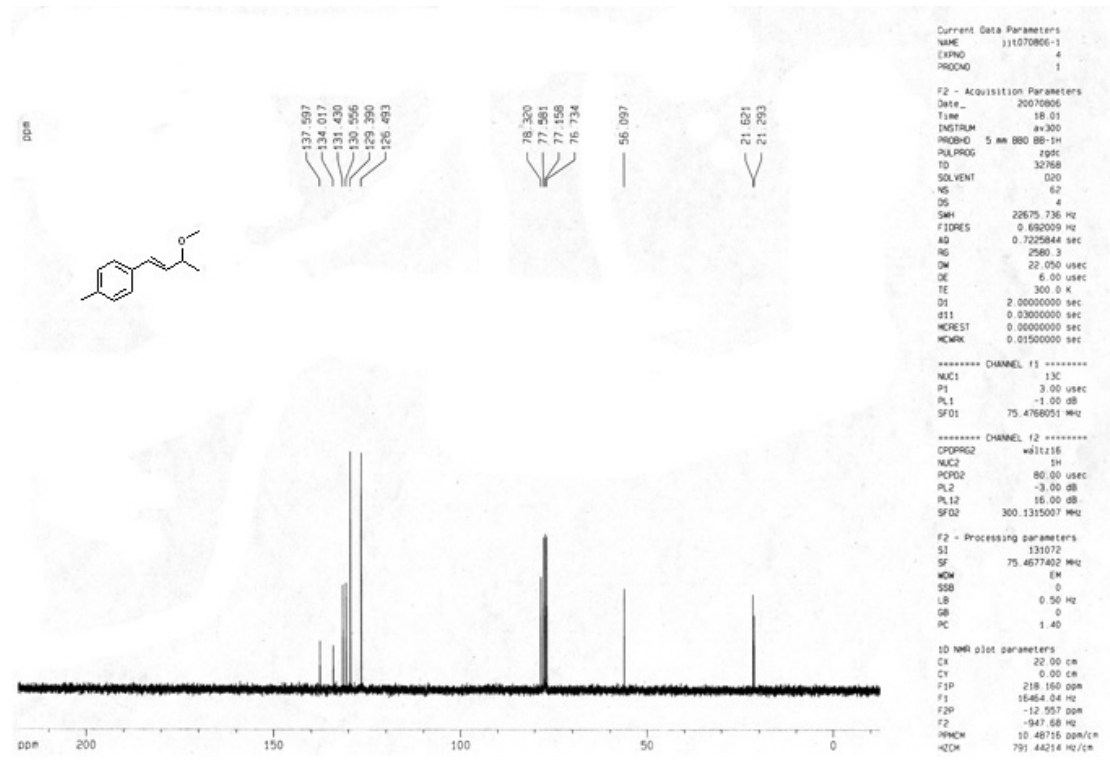
21 (¹³C NMR)



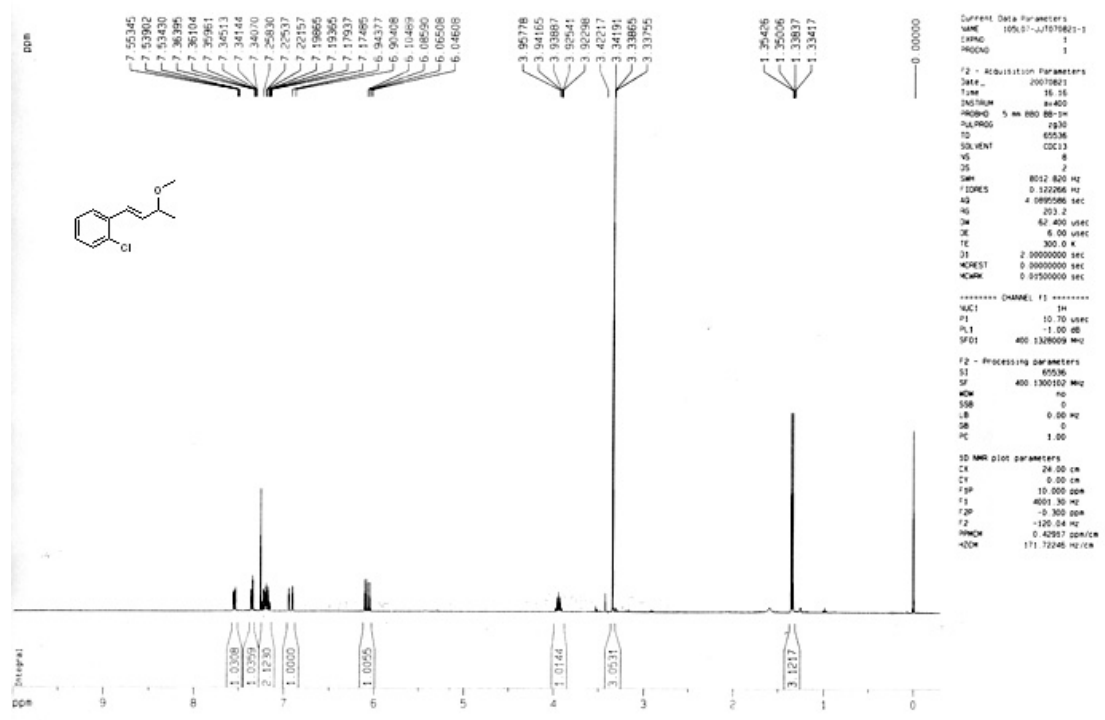
2m (¹H NMR)



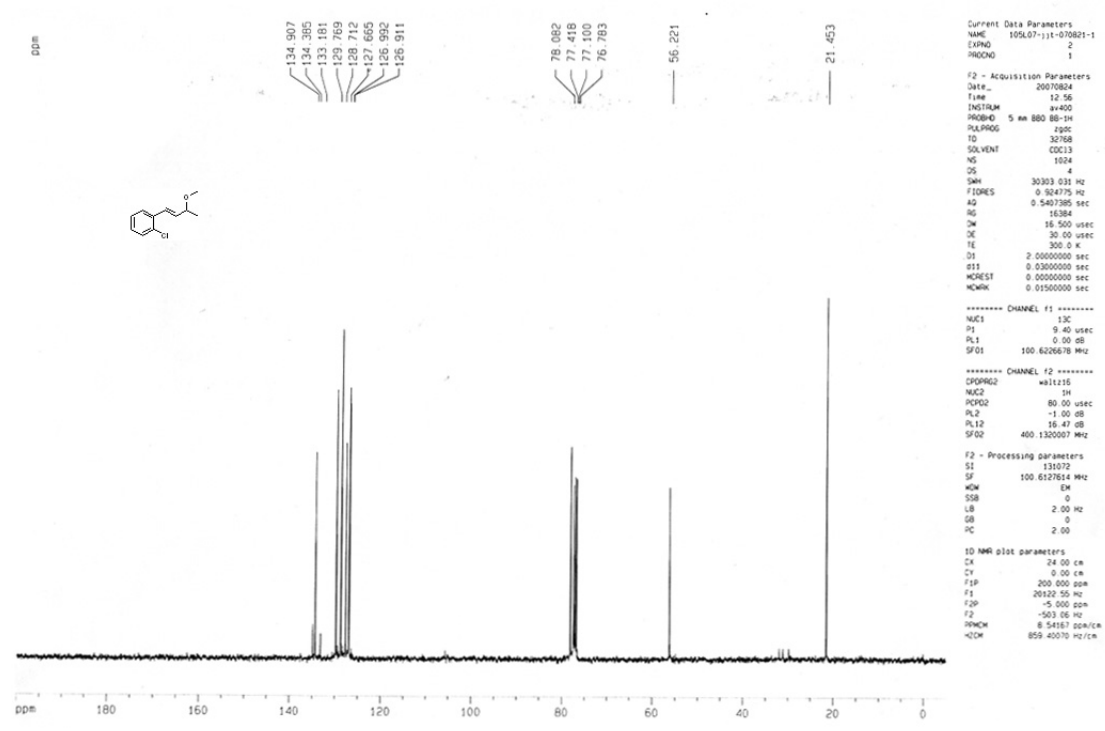
2m (¹³C NMR)



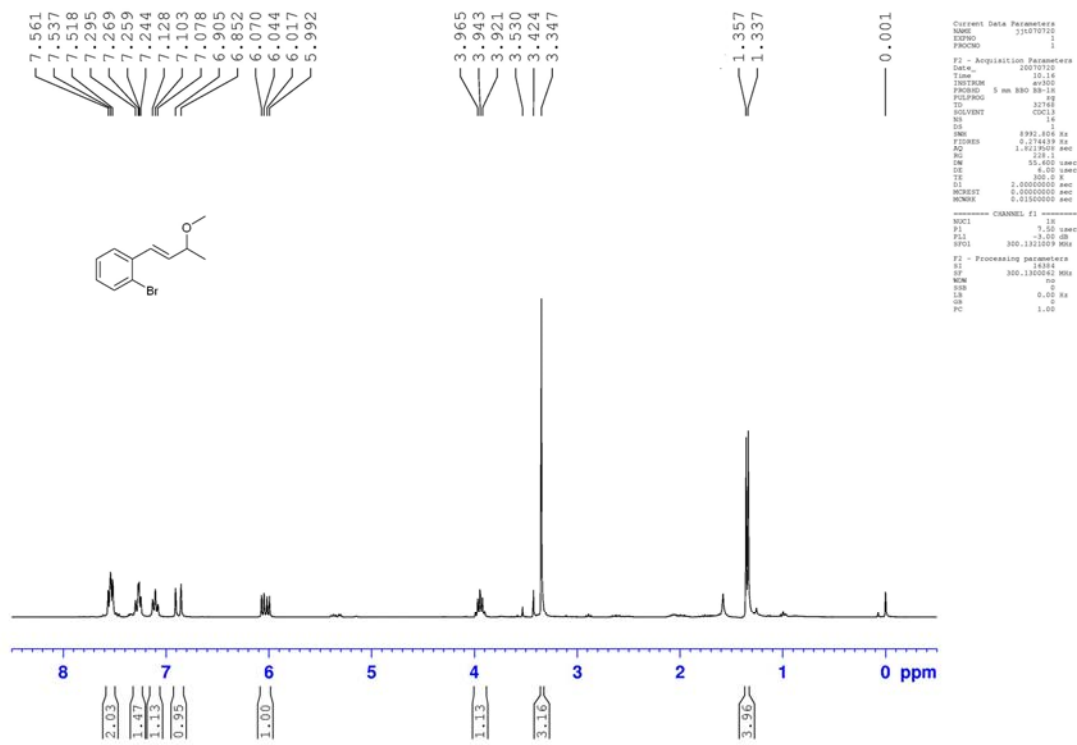
2n (¹H NMR)



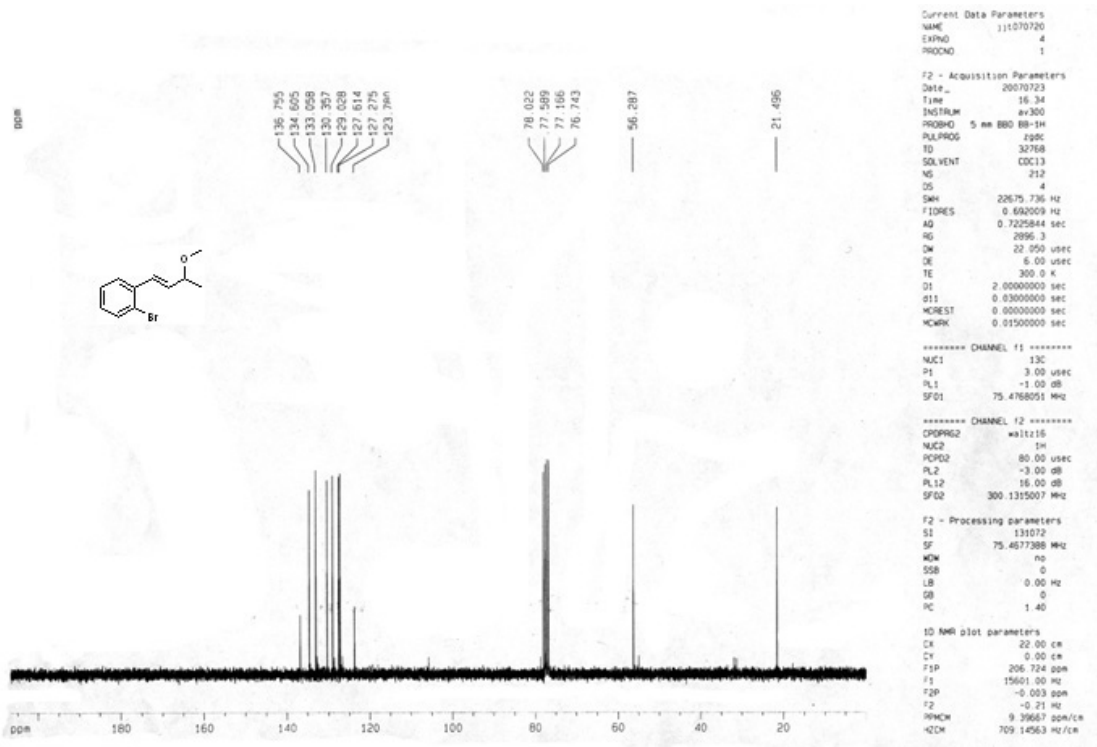
2n (¹³C NMR)



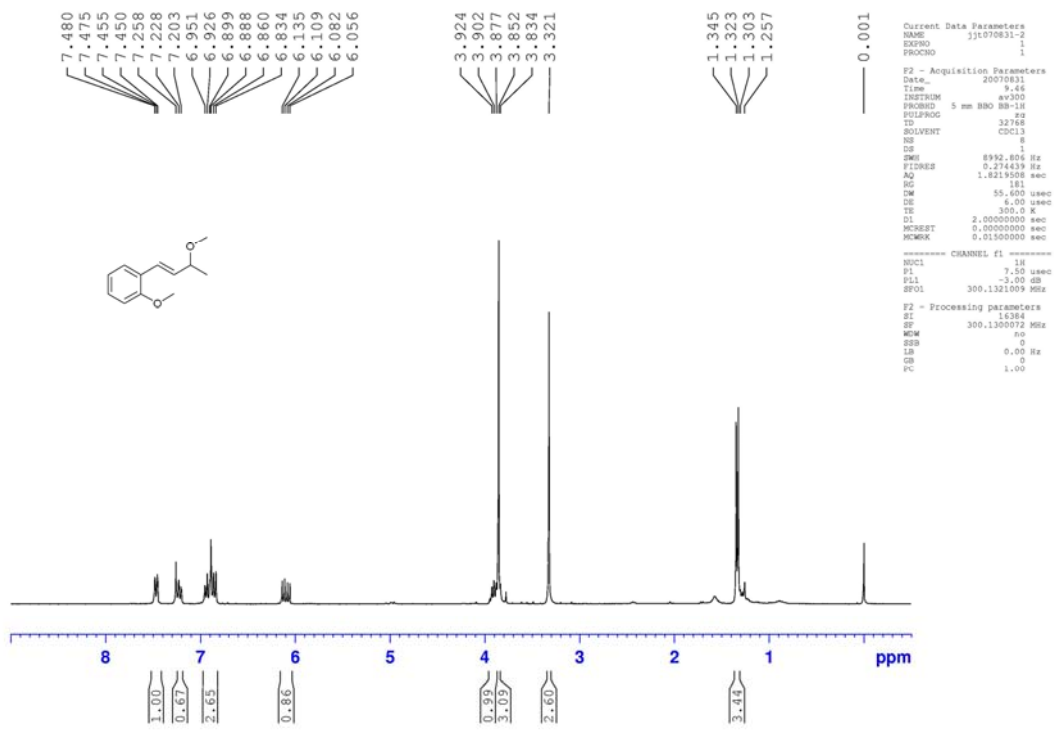
2o (¹H NMR)



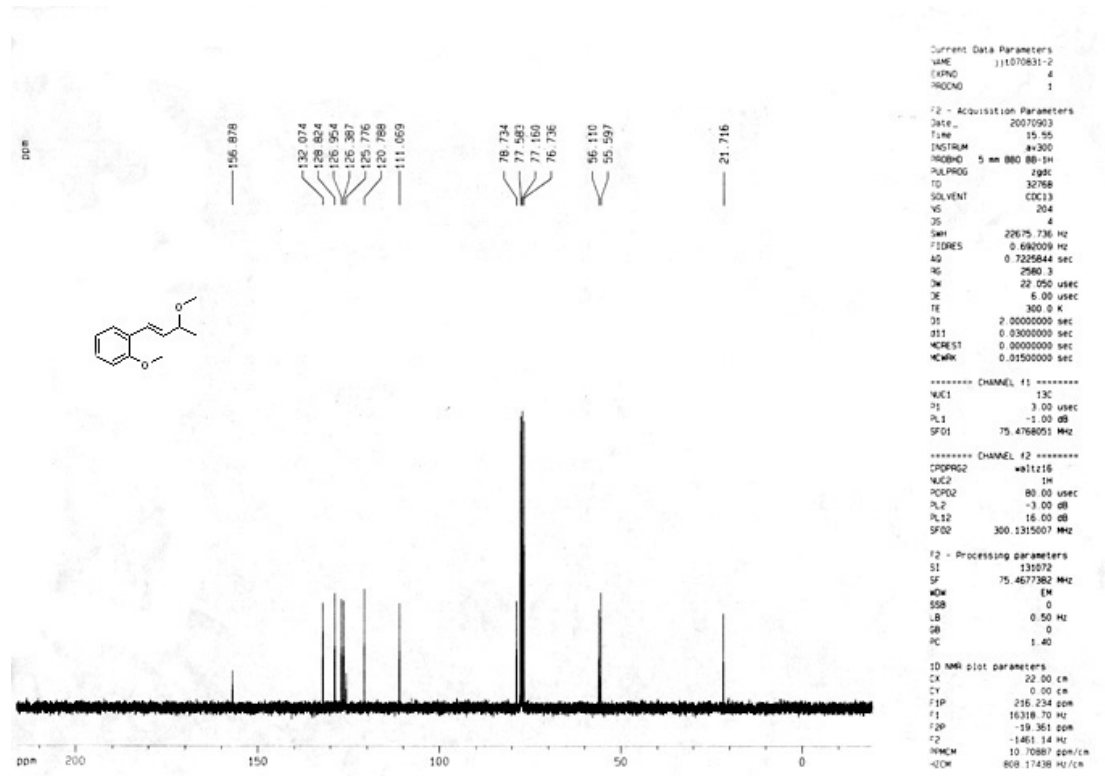
2o (¹³C NMR)



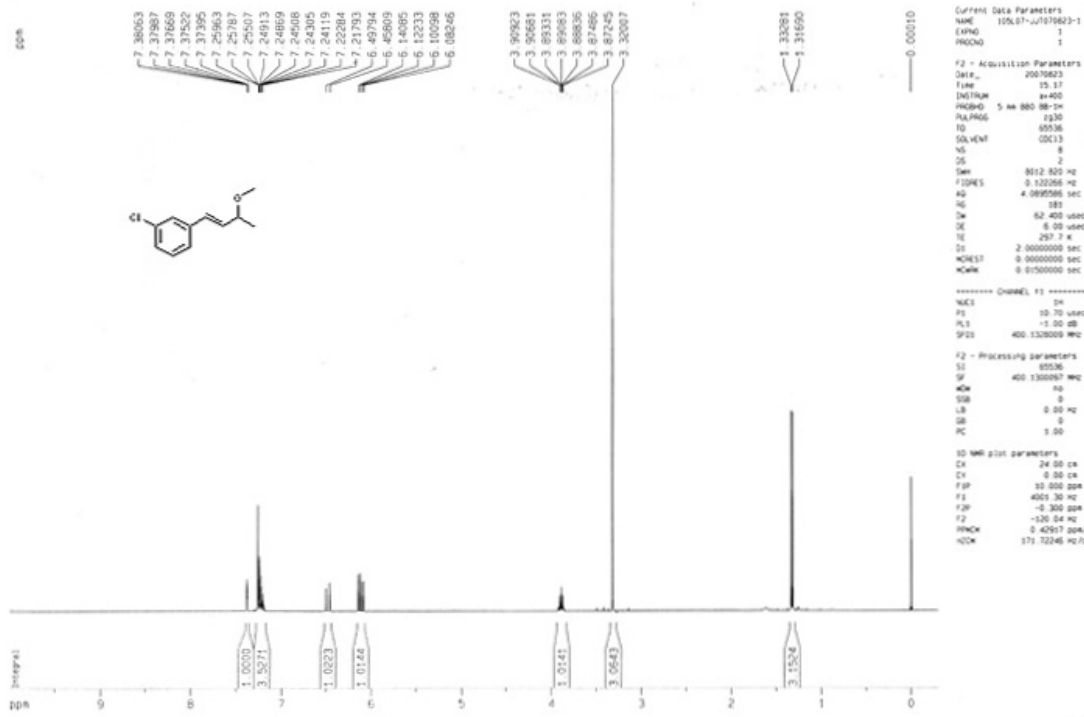
2p (¹H NMR)



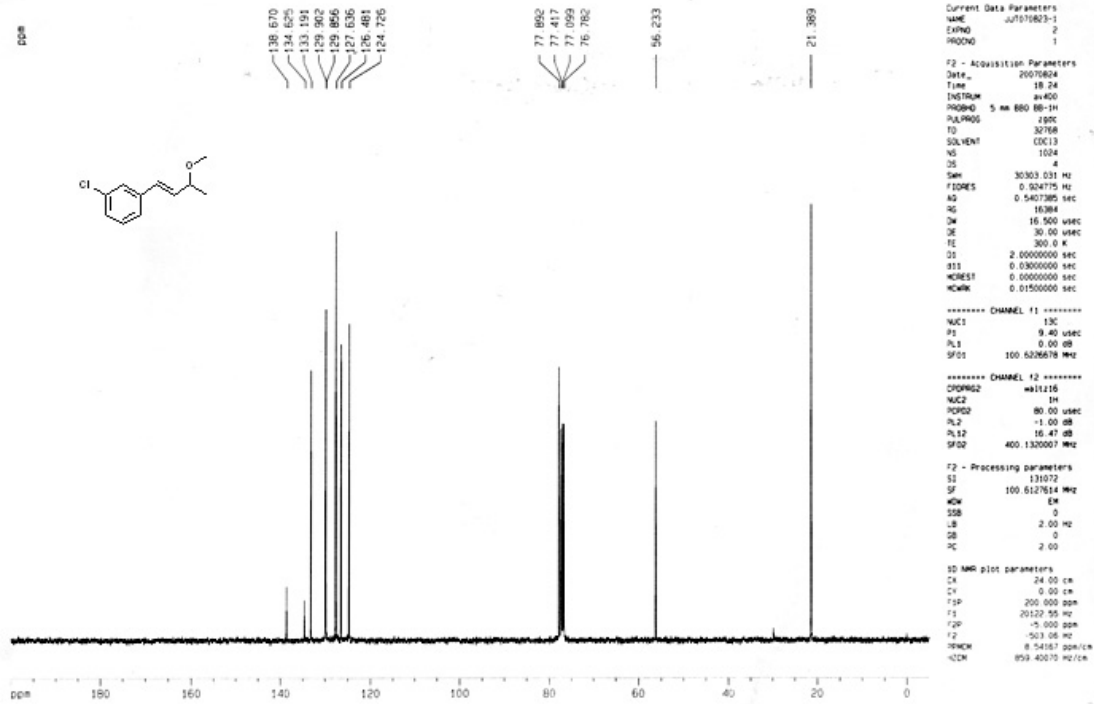
2p (¹³C NMR)



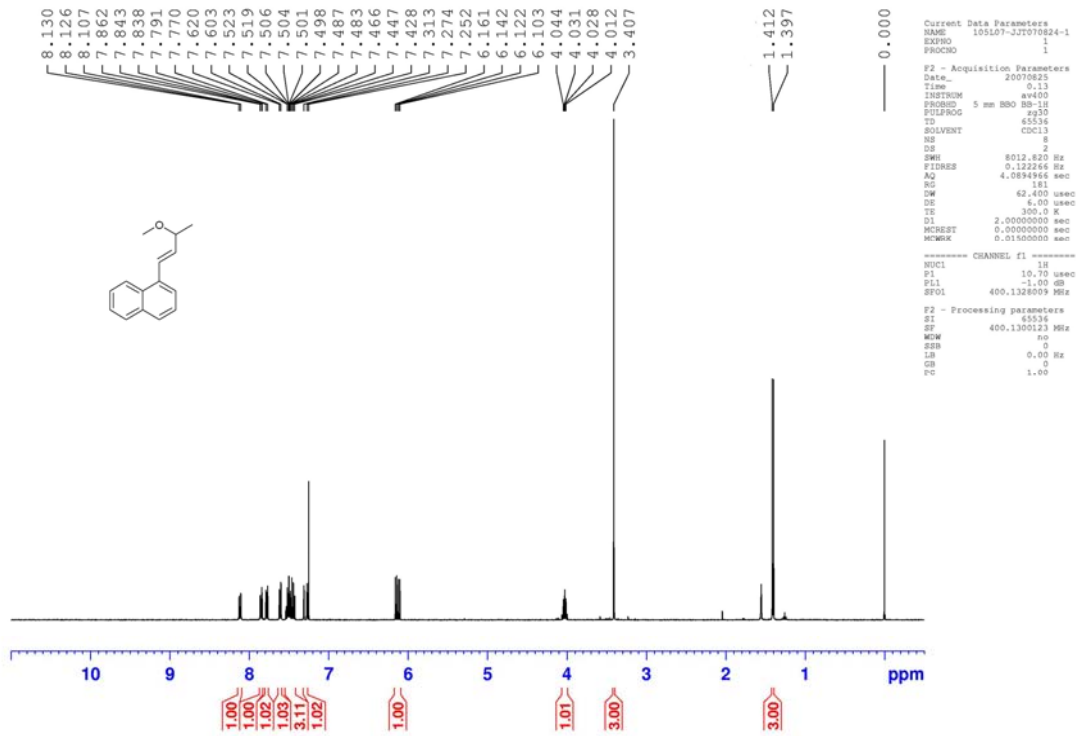
2q (¹H NMR)



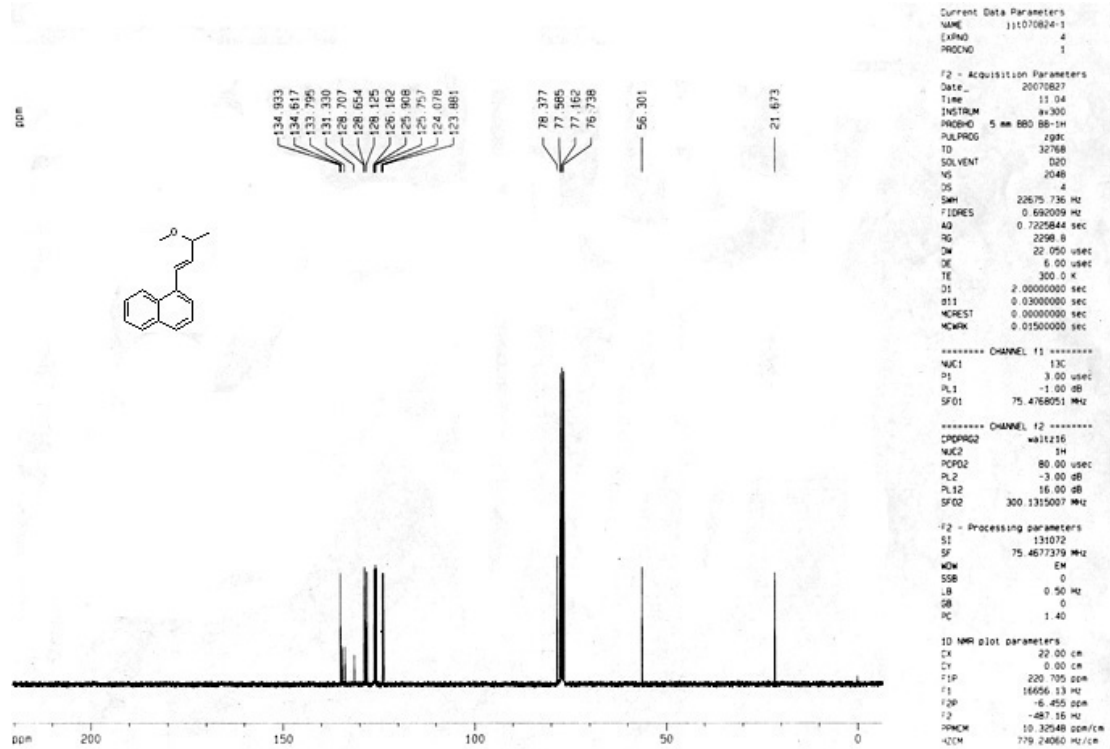
2q (¹³C NMR)



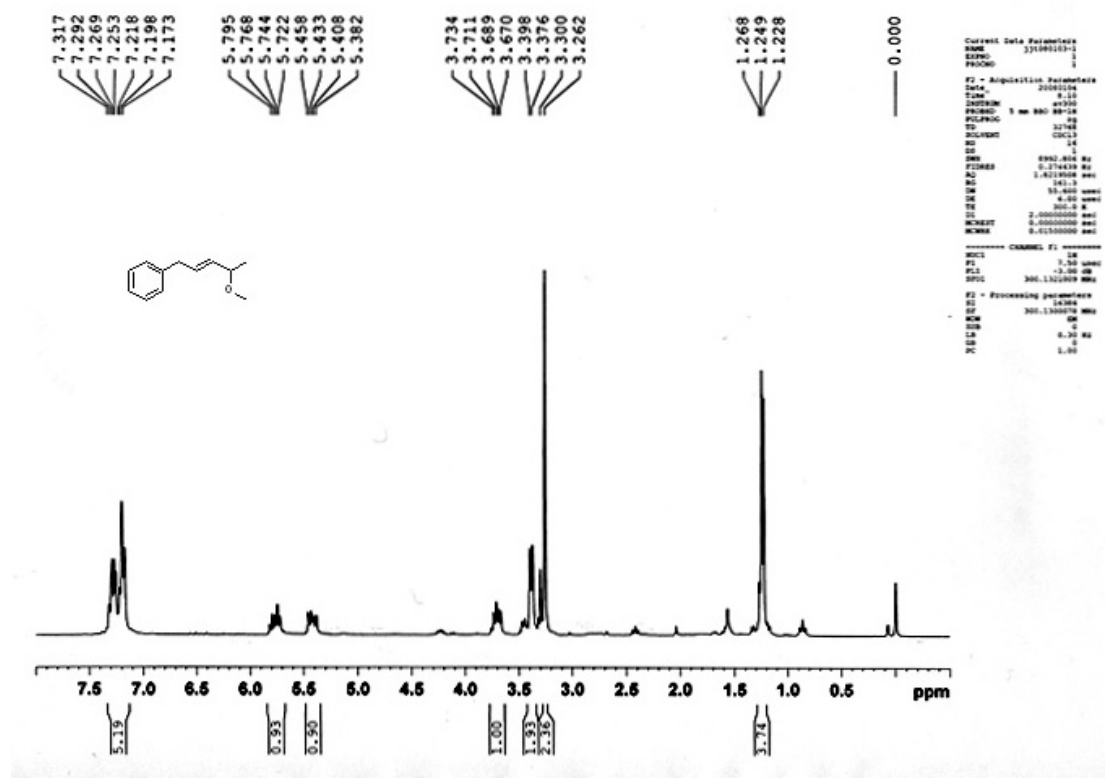
2r (¹H NMR)



2r (¹³C NMR)



2s (¹H NMR)



2s (¹³C NMR)

