Palladium catalyzed isomerization of alkene: a pronounced influence of an *o*-phenol hydroxyl group

Jinmin Fan, Changfeng Wan, Qiang Wang, Linfeng Gao, Xiaoqi Zheng and Zhiyong Wang*

Hefei National Laboratory for Physical Science at Microscale, Joint- Lab of Green Synthetic Chemistry and Department of Chemistry
University of Science and Technology of China
Hefei, 230026 (P. R. China)
Fax: (+86) 551-360-3185
E-mail: zwang3@ustc.edu.cn

Contents:

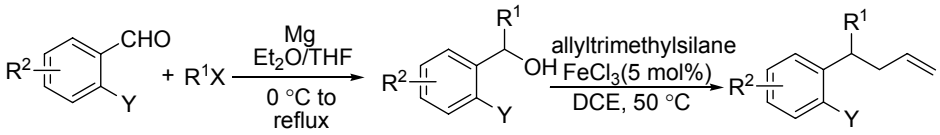
General Remarks: ^{1}H NMR and ^{13}C NMR were recorded on a Bruker AC-300 FT (^{1}H: 300 MHz, ^{13}C: 75 MHz) using TMS as internal reference. The chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz respectively. Infrared samples were recorded on a Perkin-Elmer 2000 FTIR spectrometer. Toluene was distilled from sodium/benzophenone. DCE was distilled from CaH_2 and stored over 4 Å molsieves in screw-cap flask. DMSO and DMF was predried over 4 Å molsieves and stored in screw-cap flask. 4 Å molsieves was predried in oven at 250 ˚C for 48 h. All commercially available reagents were used as received.

1. General procedure for the isomerization of alkene:

$PdCl_2$ (8.8 mg, 0.05 mmol) and $FeCl_3$ (8.1 mg, 0.05 mmol) were added to a solution of **1a** (112.0 mg, 0.5 mmol) in 1,2-dichloroethane (1.5 mL). The resulting mixture was warmed to 50 ˚C for 5 h, then the mixture was extracted with CH_2Cl_2 twice. The combined organic extracts were dried over Na_2SO_4 and filtered. Solvents were evaporated under reduced pressure. The residue was purified by column chromatography on silica gel using PE-EtOAc (20:1, v/v) as eluent to give **2a** as a yellow oil (103.0 mg, 92%).

2. Synthesis of substrates 1a-1r

2.1 Synthesis of substrates 1a-1m (Scheme SI-1).



R^1=Ph, X=Br, R^2=H, Y=OH	**1a**
R^1=Ph, X=Br, R^2=H, Y=H	**1b**
R^1=Ph, X=Br, R^2=H, Y=OMe	**1c**
R^1=Ph, X=Br, R^2=3-OH, Y=H	**1d**
R^1=Ph, X=Br, R^2=4-OH, Y=H	**1e**
R^1=Ph, X=Br, R^2=5-OMe, Y=OH	**1f**
R^1=Ph, X=Br, R^2=5-Cl, Y=OH	**1g**
R^1=Ph-*p*-Me, X=Br, R^2=H, Y=OH	**1h**
R^1=Ph-*p*-Me, X=Br, R^2=5-Br, Y=OH	**1i**
R^1=Me, X=I, R^2=H, Y=OH	**1j**
R^1=Me, X=I, R^2=OMe, Y=OH	**1k**
R^1=Me, X=I, R^2=5-Br, Y=OH	**1l**
R^1=Me, X=I, R^2=3,5-di-*tert*-butyl, Y=OH	**1m**

Scheme SI-1. synthesis of **1a-1m**.

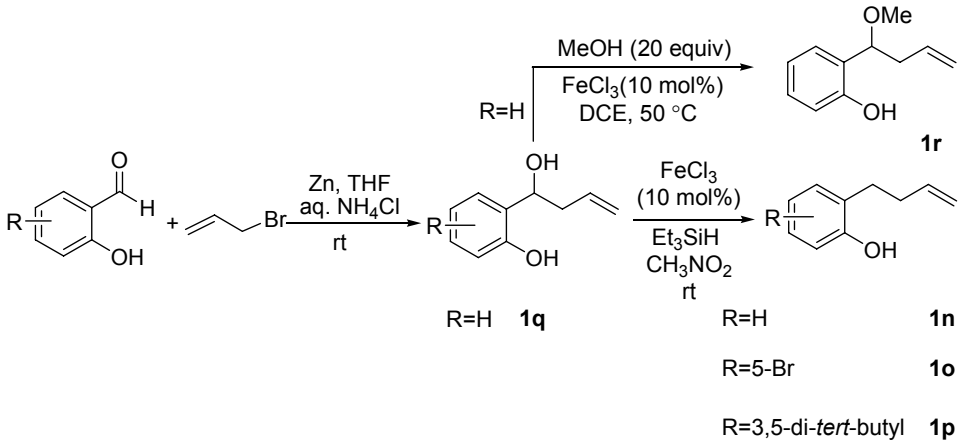
General procedure for the Grignard additions:

To a solution of magnesium (80.0 mmol) and a granule of I_2 in anhydrous Et_2O (30 ml) was added dropwise a solution of bromobenzene (80.0 mmol) in anhydrous Et_2O (20 ml), controlling the speed to maintain ether boiling. After adding, the system was refluxed for 30 min. Then cooled to 0 ˚C, a solution of salicylaldehyde (20.0 mmol) in THF (20 ml) was added dropwise to the mixture in 15 min, and then the system was refluxed for a subsequent 30 min. After fefluxing, saturated NH_4Cl was added dropwise to the system at 0 ˚C, then the resulting solution was extracted with Et_2O (50 ml× 3).The combined organic extracts were dried with anhydrous sodium sulphate and concentrated in vacuo. The residue was chromatographed on silica gel eluting with petroleum ether/EtOAc (6 : 1) to give **2-(hydroxy(phenyl)methyl)phenol** as a white solid (3.64 g, 91%).

General procedure for the allylation with allylsilane[1]

To a solution of **2-(hydroxy(phenyl)methyl)phenol** and allyltrimethylsilane (1.5 equiv) in DCE was added $FeCl_3$ (10 mol%) quickly. The resulting mixture was warmed to 50 ˚C. After 45 min, the mixture was extracted with CH_2Cl_2 twice. The combined organic extracts were dried over Na_2SO_4 and filtered. Solvents were evaporated under reduced pressure. The residue was purified by column chromatography on silica gel using PE-EtOAc (10 : 1, v/v) as eluent to give **1a** as a yellow oil with 84% yield.

2.2 Synthesis of substrates 1n-1r (Scheme SI-2)



Scheme SI-2. synthesis of **1n-1r**

General procedure for allylation of salicylaldehyde in aqueous medium[2]

To a mixture of salicylaldehyde (1 mmol) in 2 mL of THF and 4 mL of saturated NH_4Cl solution was added zinc powder (0.130 g, 2mmol) and allyl bromide (0.242g, 2 mmol) at room temperature. After the mixture was stirred for 4 h and it was extracted with ethyl acetate for three times. The combined organic extracts were dried using anhydrous Na_2SO_4 and evaporated under reduced pressure; The residue was then purified by column chromatography over silica gel to afford **2-(1-hydroxybut-3-enyl)phenol 1q** as a yellow oil.

General procedure for the reduction of allylation product to 2-(but-3-enyl)phenol 1n-1p

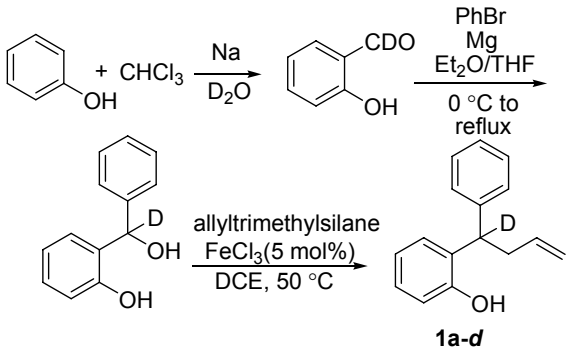
To a solution of **2-(1-hydroxybut-3-enyl)phenol 1q** and triethylsilane (2.2 equiv) in CH_3NO_2 was added $FeCl_3$ (10 mol%) quickly. The resulting mixture was stirred for 5 h at room temperature

under N_2 atmosphere. Then the solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel using PE-EtOAc (20: 1 to 10: 1, v/v) as eluent to give **1n** as a yellow oil with 28% yield. (for **1o**, 20% yield was obtained, surprisingly, for **1p**, the yield was 62%).

Procedure for synthesis of 1r

To a solution of **1q** and MeOH (20 equiv) in DCE was added $FeCl_3$ (10 mol%) quickly. The resulting mixture was warmed to 50 ˚C. After 5 h, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel using PE-EtOAc (10: 1, v/v) as eluent to give **1r** as a yellow oil with 74% yield.

2.3 Synthesis of deuterium substrate 1a-*d* (Scheme SI-3)[3]



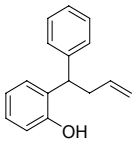
---

1. M. Yasuda, T. Saito, M. Ueba, A. Baba, *Angew. Chem*. **2004**, *116*,1438-1440; *Angew. Chem. Int. Ed*. **2004**, *43*, 1414-1416.
2. Einhorn,C.; Luche, J.-L. *J. Organoment. Chem.* **1987**, *322*, 177-183.
3. For the procedure of Reimer-Tiemann reaction, see: D. S. Kemp, J. Org. Chem.1971, 36, 202.

3. Characterization data of all substances

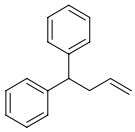
3.1. Characterization data for substrates 1a-1r

2-(1-phenylbut-3-enyl)phenol (1a)



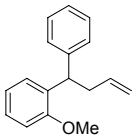
The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.35-7.17 (m, 6 H), 7.11-7.06 (m, 1 H), 6.96-6.91 (m, 1 H), 6.71-6.68 (m, 1 H), 5.86-5.72 (m, 1 H), 5.09-4.96 (m, 2 H), 4.91 (s, 1 H), 4.36 (t, J = 7.8 Hz, 1 H), 2.87-2.79 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 153.5, 143.9, 137.0, 130.8, 128.7, 128.4, 128.0, 127.6, 126.6, 121.0, 116.5, 116.1, 44.4, 39.2; IR (KBr, cm^{-1}): ν = 3535, 3064, 3028, 2925, 1639, 1593, 1494, 1453, 1328, 1197, 1116, 1087, 994, 913, 842, 752, 700; GC-MS (EI) calc. $C_{16}H_{16}O$ (M^+): 224. Found: 224.

but-3-ene-1,1-diyldibenzene (1b)



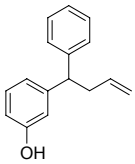
The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.27-7.20 (m, 8 H), 7.16-7.12 (m, 2 H), 5.75-5.66 (m, 1 H), 5.04-4.91 (m, 2 H), 3.99 (t, J = 7.8 Hz, 1 H), 2.83-2.77 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 144.6, 137.0, 128.5, 128.1, 126.3, 116.4, 51.4, 40.1; IR (KBr, cm^{-1}): ν = 3026, 2916, 1639, 1599, 1493, 1450, 1377, 1155, 1075, 1031, 970, 913, 844, 740, 699, 579; GC-MS (EI) calc. $C_{16}H_{16}$ (M^+): 208. Found: 208.

1-methoxy-2-(1-phenylbut-3-enyl)benzene (1c)



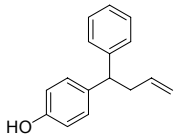
The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.23-7.18 (m, 5 H), 7.13-7.09 (m, 2 H), 6.91-6.88 (m, 1 H), 6.78 (d, J = 8.4 Hz, 1 H), 5.81-5.65 (m, 1 H), 5.03-4.88 (m, 2 H), 4.49 (t, J = 7.8 Hz, 1 H), 3.70 (s, 3 H), 2.79-2.74 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 157.3, 144.7, 137.5, 133.3, 128.5, 128.4, 128.1, 127.4, 126.1, 120.7, 116.1, 111.0, 55.7, 43.6, 39.4; IR (KBr, cm^{-1}): ν = 3062, 3027, 2934, 1639, 1599, 1491, 1439, 1346, 1289, 1242, 1123, 1052, 1030, 994, 911, 842, 752, 699, 648, 591; GC-MS (EI) calc. $C_{17}H_{18}O$ (M^+): 238. Found: 238.

3-(1-phenylbut-3-enyl)phenol (1d)



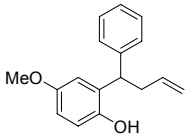
The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.18-7.09 (m, 6 H), 6.81 (d, J = 7.5 Hz, 1 H), 6.68-6.59 (m, 2 H), 5.74-5.63 (m, 1 H), 5.10 (br, 1 H), 5.04-4.91 (m, 2 H), 3.93 (t, J = 7.8 Hz, 1 H), 2.79-2.74 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 155.1, 146.1, 143.8, 136.3, 129.1, 128.0, 127.5, 125.8, 120.0, 115.9, 114.5, 112.8, 50.6, 39.4; IR (KBr, cm^{-1}): v = 3393, 3063, 3026, 2976, 1639, 1597, 1491, 1451, 1363, 1257, 1153, 1076, 997, 914, 875, 783, 700, 580; GC-MS (EI) calc. $C_{16}H_{16}O$ (M^+): 224. Found: 224.

4-(1-phenylbut-3-enyl)phenol (1e)



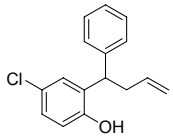
The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.25-7.12 (m, 5 H), 7.07 (d, J = 8.4 Hz, 2 H), 6.71 (d, J = 8.4 Hz, 2 H), 5.75-5.65 (m, 1 H), 5.33 (br, 1 H), 5.04-4.92 (m, 2 H), 3.93 (t, J = 7.8 Hz, 1 H), 2.78-2.73 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 153.9, 145.1, 137.1, 137.0, 129.2, 128.6, 128.0, 126.3, 116.4, 115.5, 50.5, 40.3; IR (KBr, cm^{-1}): v = 3386, 3026, 2929, 1612, 1510, 1498, 1449, 1360, 1237, 1159, 1065, 912, 845, 698, 576; GC-MS (EI) calc. $C_{16}H_{16}O$ (M^+): 224. Found: 224.

4-methoxy-2-(1-phenylbut-3-enyl)phenol (1f)



The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.41-7.30 (m, 5 H), 6.97 (s, 1 H), 6.76-6.70 (m, 2 H), 5.95-5.80 (m, 1 H), 5.20-5.08 (m, 2 H), 4.90 (s, 1 H), 4.45 (t, J = 7.8 Hz, 1 H), 3.87 (s, 3 H), 2.96-2.88 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 153.8, 147.2, 143.0, 136.8, 132.1, 128.6, 128.2, 126.5, 116.7, 116.5, 114.7, 111.7, 55.8, 44.4, 39.0; IR (KBr, cm^{-1}): v = 3412, 3027, 2936, 2834, 1639, 1600, 1505, 1431, 1333, 1286, 1201, 1095, 1042, 995, 912, 805, 700, 591; GC-MS (EI) calc. $C_{17}H_{18}O_2$ (M^+): 254. Found: 254.

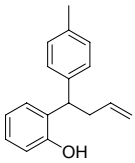
4-chloro-2-(1-phenylbut-3-enyl)phenol (1g)



The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.46-7.35 (m, 6 H), 7.19-7.16 (m, 1 H), 6.78 (d, J = 8.7 Hz, 1 H), 5.95-5.80 (m, 1 H), 5.22-5.11 (m, 3 H), 4.43 (t, J = 7.8 Hz, 1 H), 2.95-2.89 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 152.0, 142.9, 136.3, 132.6, 128.7, 128.2, 128.1, 127.2, 126.7, 125.7, 117.2, 116.8, 44.2, 38.8; IR (KBr, cm^{-1}): v = 3533,

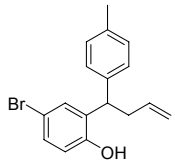
3078, 2926, 1640, 1600, 1492, 1450, 1414, 1321, 1266, 1198, 1162, 1111, 994, 916, 811, 700, 652; GC-MS (EI) calc. $C_{16}H_{15}ClO$ (M^+): 258. Found: 258.

2-(1-p-tolylbut-3-enyl)phenol (1h)



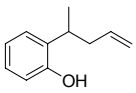
The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.30-7.22 (m, 1 H), 7.17-7.08 (m, 5 H), 6.95-6.86 (m, 1 H), 6.71 (d, J = 7.8 Hz, 1 H), 5.35-5.18 (m, 1 H), 5.08-4.95 (m, 2 H), 4.83 (s, 1 H), 4.28 (t, J = 7.8 Hz, 1 H), 2.86-2.74 (m, 2 H), 2.30 (s, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 153.5, 140.7, 137.0, 136.1, 130.9, 129.4, 128.4, 128.1, 127.5, 121.0, 116.5, 116.2, 43.9, 39.2, 21.2; IR (KBr, cm^{-1}): ν = 3530, 3021, 2922, 1640, 1598, 1510, 1453, 1329, 1257, 1204, 1118, 1087, 1043, 994, 913, 818, 752, 718, 621; GC-MS (EI) calc. $C_{17}H_{18}O$ (M^+): 238. Found: 238.

4-bromo-2-(1-p-tolylbut-3-enyl)phenol (1i)



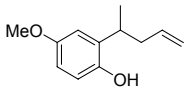
The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.33 (m, 1 H), 7.17-7.07 (m, 5 H), 6.58 (d, J = 8.4 Hz, 1 H), 5.79-5.62 (m, 1 H), 5.12 (s, 1 H), 5.06-4.95 (m, 2 H), 4.22 (t, J = 7.8 Hz, 1 H), 2.83-2.72 (m, 2 H), 2.29 (s, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 152.6, 139.7, 136.4, 133.2, 131.0, 130.1, 129.4, 127.9, 117.7, 116.7, 113.0, 43.9, 38.8, 21.0; IR (KBr, cm^{-1}): ν = 3422, 2922, 1639, 1511, 1489, 1411, 1320, 1266, 1163, 1101, 1042, 993, 914, 811, 733, 629; HRMS calc. $C_{17}H_{17}BrO$ (M^+): 316.0463. Found: 316.0454.

2-(pent-4-en-2-yl)phenol (1j)



The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.16 (d, J = 7.5 Hz, 1 H), 7.08-7.02 (m, 1 H), 6.92-6.87 (m, 1 H), 6.71 (d, J = 8.1 Hz, 1 H), 5.83-5.69 (m, 1 H), 5.06-4.90 (m, 2 H), 4.85 (s, 1 H), 3.18-3.11 (m, 1 H), 2.44-2.37 (m, 1 H), 2.33-2.26 (m, 1 H), 1.24 (d, J = 6.9 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 153.0, 137.5, 133.0, 127.4, 126.9, 121.1, 116.2, 115.6, 41.4, 32.5, 20.2; IR (KBr, cm^{-1}): ν = 3449, 3074, 2964, 1639, 1590, 1502, 1452, 1330, 1175, 994, 913, 828, 752; GC-MS (EI) calc. $C_{11}H_{14}O$ (M^+): 162. Found: 162.

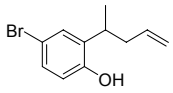
4-methoxy-2-(pent-4-en-2-yl)phenol (1k)



The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 6.76 (d, J = 3.0 Hz, 1

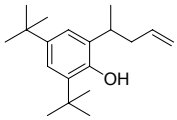
H), 6.69 (d, J = 2.7 Hz, 1 H), 6.63-6.60 (m, 1 H), 5.78-5.73 (m, 1 H), 5.14 (s, 1 H), 5.07-4.96 (m, 2 H), 3.77 (s, 3 H), 3.20-3.13 (m, 1 H), 2.49-2.35 (m, 1 H), 2.33-2.28 (m, 1 H), 1.24 (d, J = 6.9 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 153.0, 146.3, 136.5, 133.6, 115.3, 112.7, 110.4, 55.0, 40.4, 31.8, 19.3; IR (KBr, cm^{-1}): v = 3411, 2962, 1640, 1610, 1505, 1431, 1344, 1289, 1269, 1201, 1041, 914, 872, 804, 711; GC-MS (EI) calc. $C_{12}H_{16}O2$ (M^+): 192. Found: 192.

4-bromo-2-(pent-4-en-2-yl)phenol (1l)



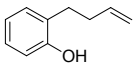
The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.25 (s, 1 H), 7.16 (d, J = 8.1 Hz, 1 H), 6.63 (d, J = 8.1 Hz, 1 H), 5.82-5.65 (m, 1 H), 5.06-4.98 (m, 3 H), 3.18-3.06 (m, 1 H), 2.40-2.25 (m, 2 H), 1.24 (d, J = 6.3 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 152.2, 136.9, 135.5, 130.3, 129.6, 117.3, 116.5, 113.2, 41.1, 32.6, 20.0; IR (KBr, cm^{-1}): v = 3449, 2956, 1639, 1491, 1413, 1321, 1268, 1168, 1103, 993, 915, 808, 630; GC-MS (EI) calc. $C_{11}H_{13}BrO$ (M^+): 240. Found: 240.

2,4-di-tert-butyl-6-(pent-4-en-2-yl)phenol (1m)



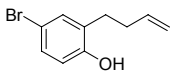
The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.19 (d, J = 2.1 Hz, 1 H), 7.07 (d, J = 2.1 Hz, 1 H), 5.88-5.74 (m, 1 H), 5.12-5.02 (m, 2 H), 4.79 (s, 1 H), 3.04-2.97 (m, 1 H), 2.43-2.31 (m, 2 H), 1.45 (s, 9 H), 1.32 (s. 9 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 149.1, 142.3, 137.2, 134.6, 131.7, 121.5, 121.0, 116.5, 41.8, 34.9, 34.3, 32.8, 31.7, 30.1, 20.4; IR (KBr, cm^{-1}): v = 3407, 2960, 1640, 1476, 1417, 1361, 1294, 1188, 1117, 1043, 914, 877, 818, 764, 646; HRMS calc. $C_{19}H_{30}O$ (M^+): 274.2297. Found: 274.2292.

2-(but-3-enyl)phenol (1n)



The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.16-7.08 (m, 2 H), 6.92-6.87 (m, 1 H), 6.77 (d, J = 7.8 Hz, 1 H), 5.97-5.88 (m, 1 H), 5.13-5.00 (m, 2 H), 4.88 (s, 1 H), 2.74-2.71 (m, 2 H), 2.44-2.37 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 152.8, 137.5, 129.5, 127.1, 126.5, 120.1, 114.6, 114.3, 33.1, 28.4; IR (KBr, cm^{-1}): v = 3443, 2926, 1639, 1591, 1503, 1455, 1330, 1234, 1170, 1116, 1042, 996, 912, 848, 752; GC-MS (EI) calc. $C_{10}H_{12}O$ (M^+): 148. Found: 148.

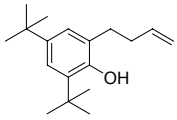
4-bromo-2-(but-3-enyl)phenol (1o)



The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.25-7.23 (m, 1 H), 7.19-7.15 (m, 1 H), 6.64 (d, J = 8.4 Hz, 1 H), 5.92-5.74 (m, 1 H), 5.09-4.99 (m, 2 H), 4.81 (s, 1 H), 2.69-2.64 (m, 2 H), 2.38-2.34 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 152.3, 137.8, 133.0,

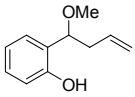
130.0, 129.7, 117.1, 115.6, 112.6, 33.6, 29.6; IR (KBr, cm^{-1}): ν = 3423, 2927, 1633, 1491, 1411, 1266, 1165, 1115, 914, 807, 627; HRMS calc. $C_{10}H_{11}BrO$ (M^+): 225.9993. Found: 225.9988.

2-(but-3-enyl)-4,6-di-tert-butylphenol (1p)



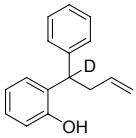
The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.18 (d, J = 2.4 Hz, 1 H), 7.01 (d, J = 2.4 Hz, 1 H), 5.95-5.84 (m, 1 H), 5.14-5.01 (m, 2 H), 4.72 (s, 1 H), 2.68-2.63 (m, 2 H), 2.42-2.36 (m, 2 H), 1.43 (s. 9 H), 1.29 (s, 9 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 150.1, 142.5, 138.3, 135.4, 126.8, 124.7, 122.2, 115.7, 34.5, 34.2, 31.9, 30.5, 30.2, 29.9; IR (KBr, cm^{-1}): ν = 2957, 2868, 1640, 1479, 1416, 1296, 1194, 1149, 997, 913, 877, 761; HRMS calc. $C_{18}H_{28}O$ (M^+): 260.2140. Found: 260.2146.

2-(1-methoxybut-3-enyl)phenol (1r)



The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.85 (s, 1 H), 7.21-7.16 (m, 1 H), 6.95-6.92 (m, 1 H), 6.88-6.80 (m, 2 H), 5.81-5.72 (m, 1 H), 5.11-5.05 (m, 2 H), 4.34-4.30 (m, 1 H), 3.40 (s, 3 H), 2.70-2.63 (m, 1 H), 2.53-2.46 (m, 1 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 155.5, 134.2, 129.2, 128.6, 119.8, 117.7, 117.0, 85.6, 57.4, 40.5; IR (KBr, cm^{-1}): ν = 3373, 2936, 1641, 1586, 1490, 1457, 1351, 1239, 1080, 997, 917, 837, 755; GC-MS (EI) calc. $C_{11}H_{14}O_2$ (M^+): 178. Found: 178.

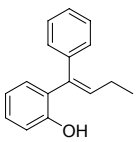
Deuterium 2-(1-phenylbut-3-enyl)phenol (1a-*d*)



The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.35-7.17 (m, 6 H), 7.11-7.06 (m, 1 H), 6.96-6.91 (m, 1 H), 6.71-6.68 (m, 1 H), 5.86-5.72 (m, 1 H), 5.09-4.96 (m, 2 H), 4.91 (s, 1 H), 2.87-2.79 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 153.5, 143.9, 137.0, 130.8, 128.7, 128.4, 128.0, 127.6, 126.6, 121.0, 116.5, 116.1, 44.4, 39.2; IR (KBr, cm^{-1}): ν = 3535, 3064, 3028, 2925, 1639, 1593, 1494, 1453, 1328, 1197, 1116, 1087, 994, 913, 842, 752, 700; HRMS calc. $C_{16}H_{15}DO$ (M^+): 225.1264. Found: 225.1269.

3.1. Characterization data for products

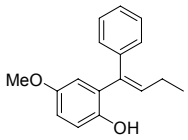
(E)-2-(1-phenylbut-1-enyl)phenol (2a)



The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.26-7.21 (m, 6 H),

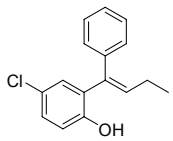
7.04-6.90 (m, 3 H), 6.37 (t, J = 7.5 Hz, 1 H), 5.06 (s, 1 H), 2.05 (dq, J_1 = 7.5 Hz, J_2 = 7.5 Hz, 2 H), 1.02 (t, J = 7.5 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 153.1, 140.5, 135.2, 135.1, 130.8, 129.3, 128.7, 127.7, 126.6, 125.8, 120.7, 115.5, 23.5, 14.2; IR (KBr, cm^{-1}): ν = 3524, 2966, 2872, 1580, 1486, 1449, 1334, 1284, 1193, 1148, 1033, 910, 828, 755, 698; HRMS calc. $C_{16}H_{16}O$ (M^+): 224.1201. Found: 224.1204.

(E)-4-methoxy-2-(1-phenylbut-1-enyl)phenol (2f)



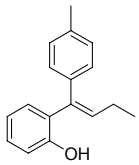
The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.35-7.12 (m, 5 H), 6.91-6.80 (m, 2 H), 6.56 (s, 1 H), 6.36 (t, J = 7.5 Hz, 1 H), 4.73 (s, 1 H), 3.72 (s, 3 H), 2.06 (dq, J_1 = 7.5 Hz, J_2 = 7.5 Hz, 2 H), 1.03 (t, J = 7.5 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 153.7, 147.2, 135.8, 134.9, 129.2, 128.6, 127.6, 126.5, 116.5, 116.0, 115.7, 115.4, 55.8, 23.4, 14.0; IR (KBr, cm^{-1}): ν = 3528, 2964, 2872, 1596, 1491, 1446, 1360, 1274, 1212, 1145, 1039, 952, 852, 772, 697; HRMS (EI) calc. $C_{17}H_{18}O_2$ (M^+): 254.1307. Found: 254.1302.

(E)-4-chloro-2-(1-phenylbut-1-enyl)phenol (2g)



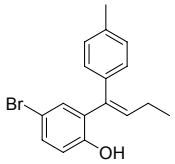
The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.30-7.21 (m, 6 H), 7.04-6.92 (m, 2 H), 6.40 (t, J = 7.5 Hz, 1 H), 5.07 (s, 1 H), 2.07 (dq, J_1 = 7.5 Hz, J_2 = 7.5 Hz, 2 H), 1.06 (t, J = 7.5 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 152.2, 135.7, 133.4, 130.1, 129.1, 128.7, 127.8, 126.5, 116.7, 23.4, 13.9; IR (KBr, cm^{-1}): ν = 3522, 2966, 2872, 1597, 1480, 1408, 1326, 1266, 1194, 1079, 943, 881, 764, 666; HRMS calc. $C_{16}H_{15}ClO$ (M^+): 258.0811. Found: 258.0816.

(E)-2-(1-p-tolylbut-1-enyl)phenol (2h)



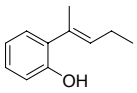
The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.24-6.92 (m, 8 H), 6.34 (t, J = 7.5 Hz, 1 H), 5.04 (s, 1 H), 2.31 (s, 3 H), 2.04 (dq, J_1 = 7.5 Hz, J_2 = 7.5 Hz, 2 H), 1.01 (t, J = 7.5 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 153.5, 138.2, 135.3, 134.0, 130.6, 130.4, 129.3, 129.1, 128.8, 126.4, 120.5, 120.3, 115.3, 23.3, 21.1, 14.0; IR (KBr, cm^{-1}): ν = 3515, 2965, 2872, 1606, 1484, 1457, 1334, 1284, 1196, 1035, 932, 817, 754, 685; HRMS calc. $C_{17}H_{18}O$ (M^+): 238.1358. Found: 238.1353.

(E)-4-bromo-2-(1-p-tolylbut-1-enyl)phenol (2i)



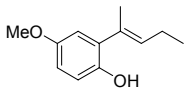
The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.37-7.33 (m, 1 H), 7.16-7.08 (m, 5 H), 6.87 (d, J = 5.7 Hz, 1 H), 6.34 (t, J = 7.5 Hz 1 H), 5.01 (s, 1 H), 2.33 (s, 3 H), 2.04 (dq, J_1 = 7.5 Hz, J_2 = 7.5 Hz, 2 H), 1.03 (t, J = 7.5 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 152.9, 138.1, 137.9, 134.9, 133.0, 132.0, 129.6, 129.5, 129.2, 126.5, 117.3, 112.3, 23.4, 21.2, 14.1; IR (KBr, cm^{-1}): ν = 3516, 2965, 2871, 1569, 1476, 1412, 1325, 1264, 1195, 1074, 941, 817, 720, 611; HRMS calc. $C_{17}H_{17}BrO$ (M^+): 316.0463. Found: 316.0469.

(E)-2-(pent-2-en-2-yl)phenol (2j)



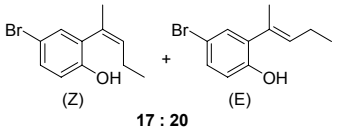
The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.18-7.07 (m, 2 H), 6.93-6.88 (m, 2 H), 5.64-5.52 (m, 2 H), 2.24 (dq, J_1 = 7.5 Hz, J_2 = 7.5 Hz, 2 H), 1.99 (s, 3 H), 1.07 (t, J = 7.5 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 152.0, 133.5, 131.6, 131.1, 128.4, 128.2, 120.3, 115.4, 21.9, 17.9, 14.2; IR (KBr, cm^{-1}): ν = 3512, 2965, 2873, 1578, 1487, 1448, 1340, 1282, 1222, 1182, 1037, 909, 828, 753; GC-MS (EI) calc. $C_{11}H_{14}O$ (M^+): 162. Found: 162.

(E)-4-methoxy-2-(pent-2-en-2-yl)phenol (2k)



The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 6.86-6.82 (m, 1 H), 6.75-6.71 (m, 1 H), 6.58 (d, J = 7.5 Hz, 1 H), 5.69 (t, J = 7.5 Hz, 1 H), 4.83 (s, 1 H), 3.76 (s, 3 H), 1.97 (s, 3 H), 1.85 (dq, J_1 = 7.5 Hz, J_2 = 7.5 Hz, 2 H), 0.92 (t, J = 7.5 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 145.7, 133.4, 130.8, 115.5, 113.9, 113.8, 113.2, 112.4, 55.9, 25.1, 22.7, 14.2; IR (KBr, cm^{-1}): ν = 3450, 2962, 2873, 1589, 1493, 1423, 1364, 1275, 1218, 1165, 1040, 856, 810, 762; GC-MS (EI) calc. $C_{12}H_{16}O2$ (M^+): 192. Found: 192.

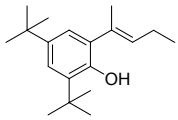
(E)-4-bromo-2-(pent-2-en-2-yl)phenol compound with (Z)-4-bromo-2-(pent-2-en-2-yl)phenol (17:20) (2l)



The title mixture was a yellow oil (with a trace of byproducts from NMR). ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.27-7.14 (m, 2 H), 6.82-6.77 (m, 1 H), 5.22 (m, 0.38 H), 5.63 (s, 0.5 H), 5.55 (m, 0.51 H), 5.26 (s, 0.5 H), 2.28-2.18 (m, 1.11 H), 1.96 (s, 3 H), 1.88-1.80 (m, 0.95 H), 1.06 (t, J = 7.5 Hz, 1.64 H), 0.93 (t, J = 7.5 Hz, 1.19 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 151.5, 134.1, 134.0, 131.0, 130.8, 130.6, 117.0, 116.6, 24.7, 22.4, 21.6, 20.9, 14.0, 13.8; IR (KBr, cm^{-1}): ν = 3511, 2965, 2874, 1594, 1481, 1403, 1376, 1265, 1210, 1175, 1044, 909, 816, 759, 734;

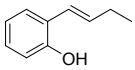
GC-MS(EI): two peaks and both are 240.

(E)-2,4-di-tert-butyl-6-(pent-2-en-2-yl)phenol (2m)



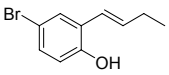
The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.19 (d, J = 2.7 Hz, 1 H), 6.93 (d, J = 2.7 Hz, 1 H), 5.80 (s, 1 H), 5.05 (t, J = 7.5 Hz, 1 H), 2.23 (dq, J_1 = 7.5 Hz, J_2 = 7.5 Hz, 2 H), 2.00 (s, 3 H), 1.07 (t, J = 7.5 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 148.1, 141.5, 135.0, 133.8, 133.5, 132.4, 122.6, 115.4, 35.3, 34.4, 31.8, 29.8, 21.9, 18.5, 14.2; IR (KBr, cm^{-1}): ν = 3506, 2961, 2872, 1600, 1489, 1442, 1362, 1264, 1201, 1168, 1119, 1032, 909, 878, 817, 767, 648; HRMS calc. $C_{19}H_{30}O$ (M^+): 274.2297. Found: 274.2295.

(E)-2-(but-1-enyl)phenol (2n)



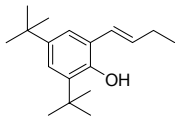
The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.30 (d, J = 7.5 Hz, 1 H), 7.10-7.05 (m, 1 H), 6.89-6.84 (m, 1 H), 6.77 (d, J = 8.1 Hz, 1 H), 6.55 (d, J = 15.9 Hz, 1 H), 6.28-6.19 (m, 1 H), 5.10 (s, 1 H), 2.27-2.22 (m, 2 H), 1.09 (t, J = 7.5 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ =153.0, 135.3, 128.1, 127.9, 127.5, 123.2, 121.0, 115.8, 26.6, 13.8; IR (KBr, cm^{-1}): ν = 3424, 2964, 2872, 1605, 1486, 1455, 1331, 1242, 1132, 1087, 971, 908, 879, 798, 750; GC-MS (EI) calc. $C_{10}H_{12}O$ (M^+): 148. Found: 148.

(E)-4-bromo-2-(but-1-enyl)phenol (2o)



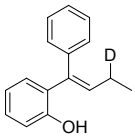
The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 8.13 (s,1 H), 7.27-7.24 (m, 1 H), 7.04-7.03 (m, 1 H), 6.74 (d, J = 8.4 Hz, 1 H), 5.82-5.64 (m, 1 H), 5.09 (s, 1 H), 3.58-3.51 (m, 2 H), 1.24 (t, J = 6.9 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 155.1, 133.7, 131.8, 130.8, 130.3, 118.9, 118.0, 111.7, 40.5, 13.9; IR (KBr, cm^{-1}): ν = 3339, 2976, 2876, 1578, 1481, 1370, 1246, 1167, 1075, 993, 912, 819, 734; HRMS calc. $C_{10}H_{11}BrO$ (M^+): 225.9993. Found: 225.9988.

(E)-2-(but-1-enyl)-4,6-di-tert-butylphenol (2p)



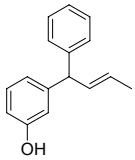
The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.25 (d, J = 2.4 Hz, 1 H), 7.11 (d, J = 2.4 Hz, 1 H), 6.50 (d, J = 15.9 Hz, 1 H), 6.22-6.11 (m, 1 H), 5.25 (s, 1 H), 2.36-2.25 (m, 2 H), 1.46 (s, 9 H), 1.34 (s, 9 H), 1.16 (t, J = 7.5 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 150.0, 142.1, 137.3, 129.5, 124.0, 123.2, 122.8, 121.9, 31.7, 30.2, 30.0, 29.8, 26.6, 13.8; IR (KBr, cm^{-1}): ν = 3355, 2960, 1599, 1468, 1368, 1217, 1061, 980, 910, 824, 737; HRMS calc. $C_{18}H_{28}O$ (M^+): 260.2140. Found: 260.2146.

Deuterium (E)-2-(1-phenylbut-1-enyl)phenol (2a-*d*)



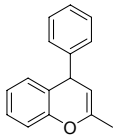
The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.28-7.23 (m, 6 H), 7.02-6.94 (m, 3 H), 6.37 (t, J = 7.5 Hz, 1 H), 5.02 (s, 1 H), 2.05 (dq, J_1 = 7.5 Hz, J_2 = 7.5 Hz, 1 H), 1.03 (t, J = 7.5 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 153.1, 140.5, 135.2, 135.1, 130.8, 129.3, 128.7, 127.7, 126.6, 125.8, 120.7, 115.5, 23.5, 14.2; IR (KBr, cm^{-1}): v = 3524, 2966, 2872, 1580, 1486, 1449, 1334, 1284, 1193, 1148, 1033, 910, 838, 755, 698; HRMS calc. $C_{16}H_{15}DO$ (M^+): 225.1264. Found: 225.1258.

(E)-3-(1-phenylbut-2-enyl)phenol (3d)



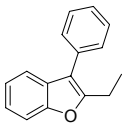
The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.30-7.10 (m, 6 H), 6.75 (d, J = 7.5 Hz, 7.5 Hz, 1 H), 6.65 (d, J = 6.3 Hz, 2 H), 5.92-5.84 (m, 1 H), 5.45-5.40 (m, 1 H), 5.19 (s, 1 H), 4.60 (d, J = 7.5 Hz, 1 H), 1.71 (d, J = 3.9 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 155.6, 146.2, 140.1, 132.9, 129.6, 128.6, 128.4, 127.1, 126.3, 121.0, 115.6, 113.2, 54.0, 18.0; IR (KBr, cm^{-1}): v = 3398, 3025, 1596, 1491, 1450, 1364, 1262, 1150, 1030, 970, 873, 779, 699; HRMS calc. $C_{16}H_{16}O$ (M^+): 224.1201. Found: 224.1208.

2-methyl-4-phenyl-4H-chromene (4a)



The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.31-7.14 (m, 5 H), 7.11-7.7.08 (m, 1 H), 6.94-6.89 (m, 2 H), 4.77 (d, J = 3.6 Hz, 1 H), 4.62 (d, J = 3.6 Hz, 1 H), 1.95 (s, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 147.3, 147.0, 129.9, 128.6, 128.3, 127.6, 126.5, 125.5, 123.2, 116.7, 116.4, 100.6, 41.0, 19.4; IR (KBr, cm^{-1}): v = 3426, 3027, 2921, 1699, 1584, 1486, 1453, 1382, 1320, 1229, 1168, 1105, 1075, 938, 836, 754, 700; HRMS calc. $C_{16}H_{14}O$ (M^+): 222.1045. Found: 222.1047.

2-ethyl-3-phenylbenzofuran (5a)



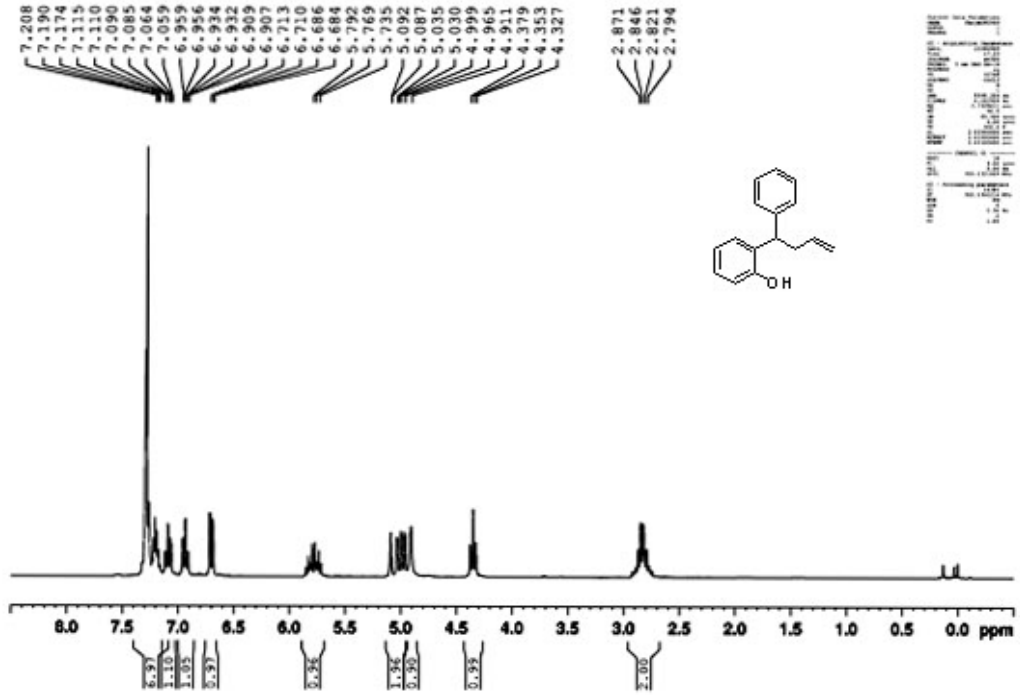
The title compound was a yellow oil. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.91 (d, J = 2.5 Hz, 1 H), 7.79 (d, J = 2.5 Hz, 1 H), 7.50-7.47 (m, 3 H), 7.43-7.35 (m, 4 H), 2.90 (q, J = 7.5 Hz, 2 H), 1.37 (t, J = 7.5 Hz, 3 H); ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): δ = 158.0, 153.8, 139.7, 131.9, 128.9, 128.5, 127.8, 123.7, 122.7, 119.6, 116.7, 111.0, 20.4, 13.0; IR (KBr, cm^{-1}): v = 3423, 3061, 2975, 1618, 1590, 1497, 1424, 1378, 1310, 1244, 1191, 1155, 1076, 984, 908, 848, 733, 700; HRMS

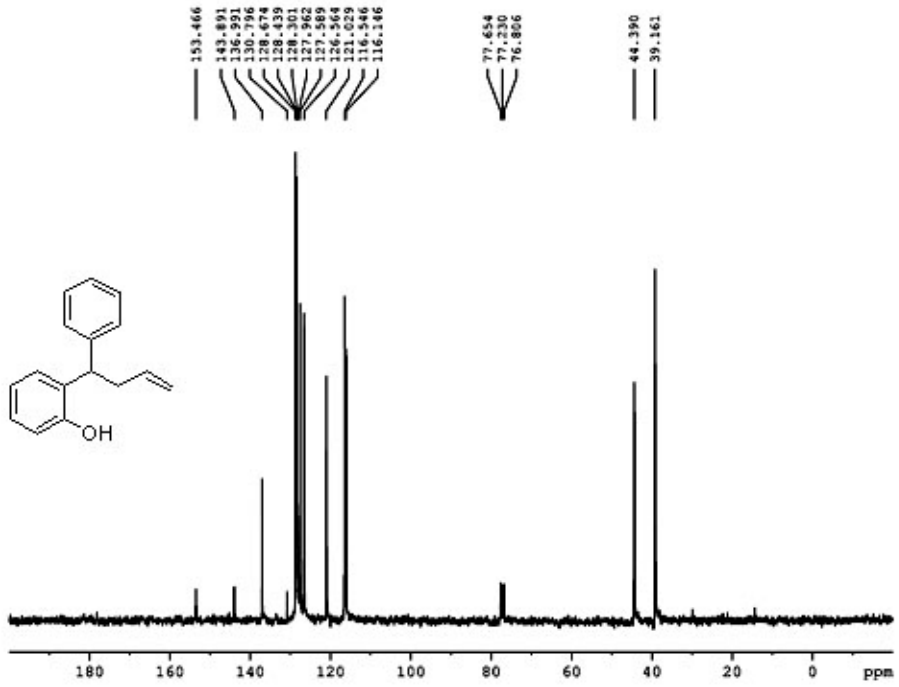
calc. $C_{16}H_{14}O$ (M^+): 222.1045. Found: 222.1055.

4. NMR Spectras of all compounds

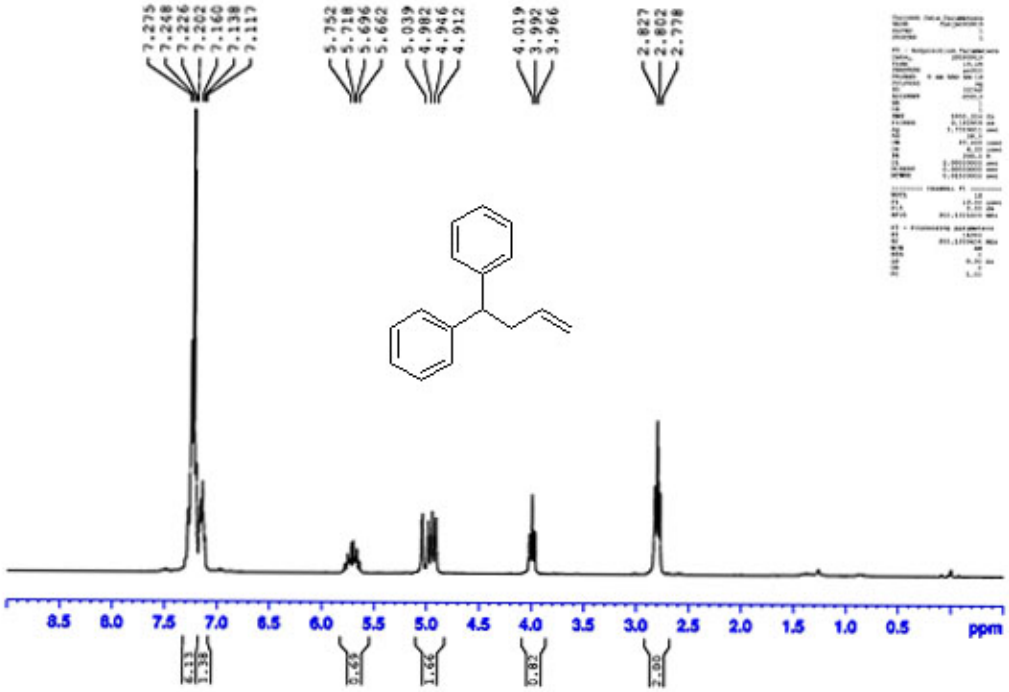
4.1 NMR Spectras of the substrates 1a-1r

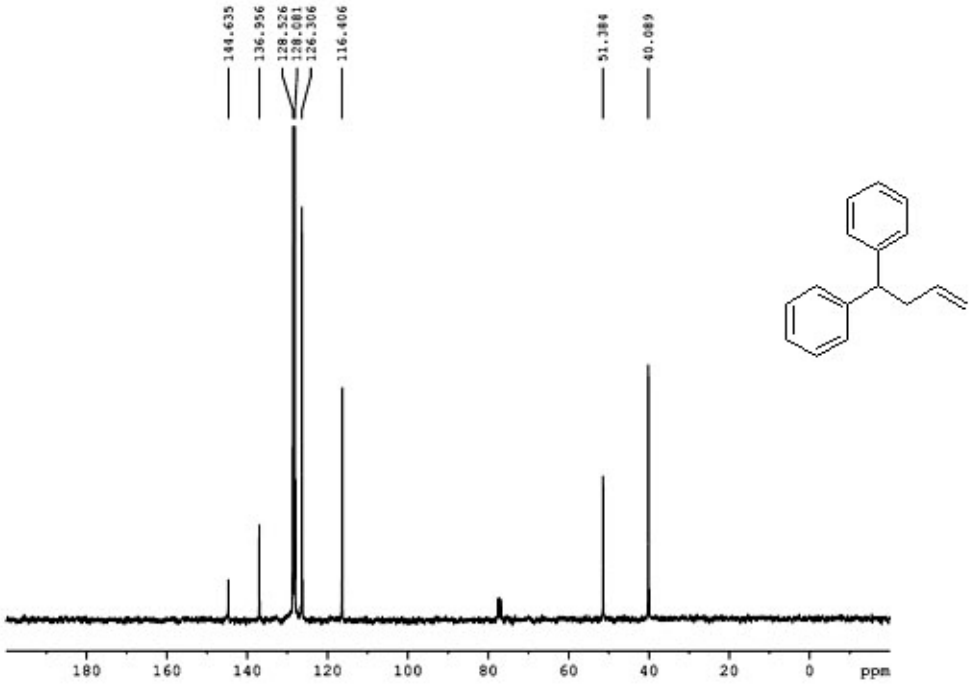
1a



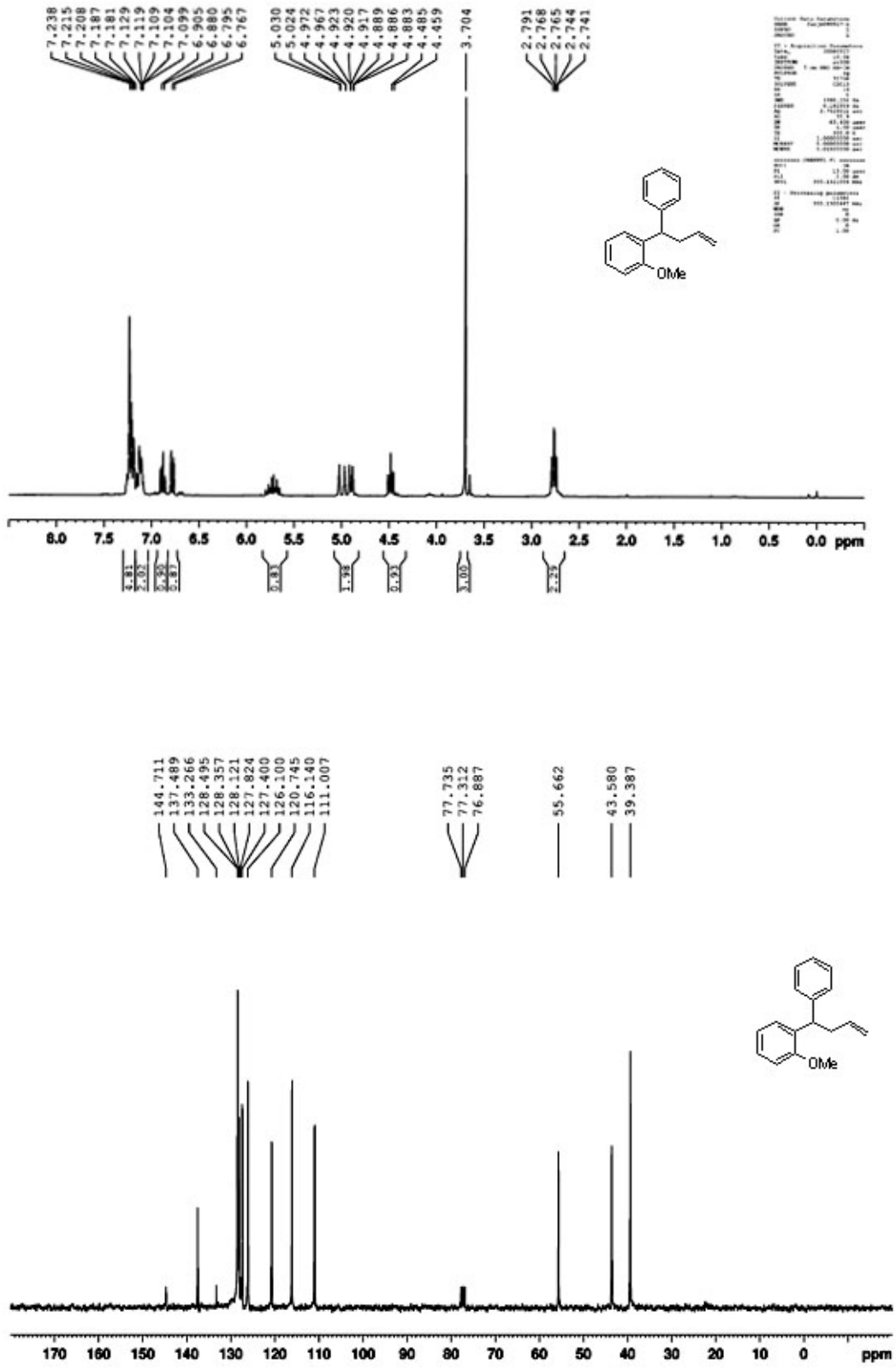


1b

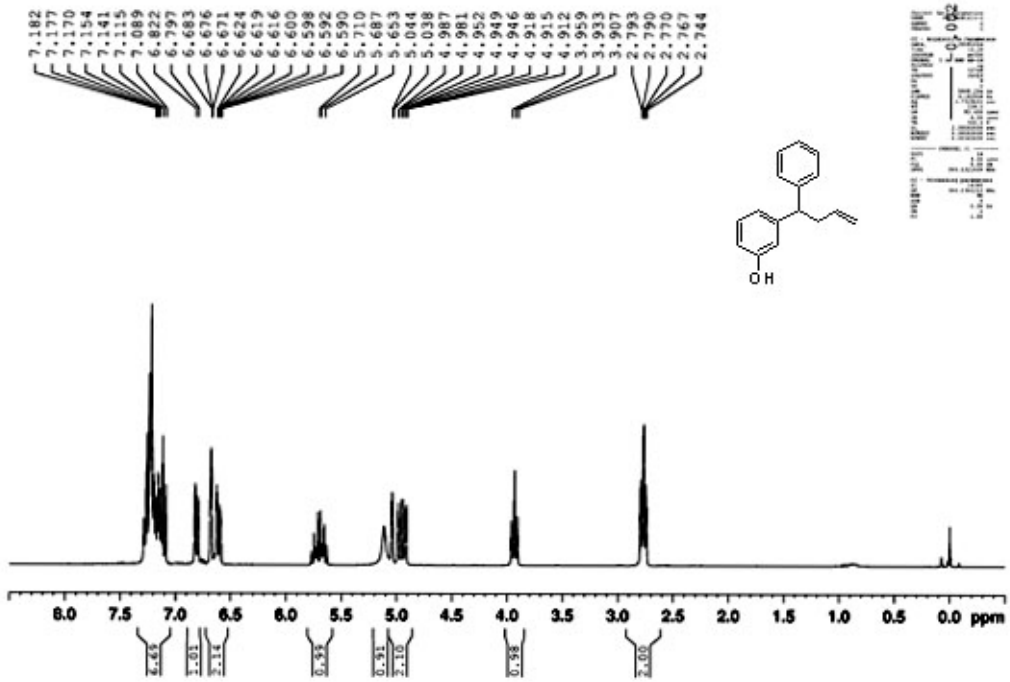

7.275
7.248
7.226
7.202
7.160
7.138
7.117
5.752
5.718
5.696
5.662
5.039
4.982
4.946
4.912
4.019
3.992
3.966
2.827
2.802
2.778
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
6.11
1.38
0.69
1.66
0.82
2.00

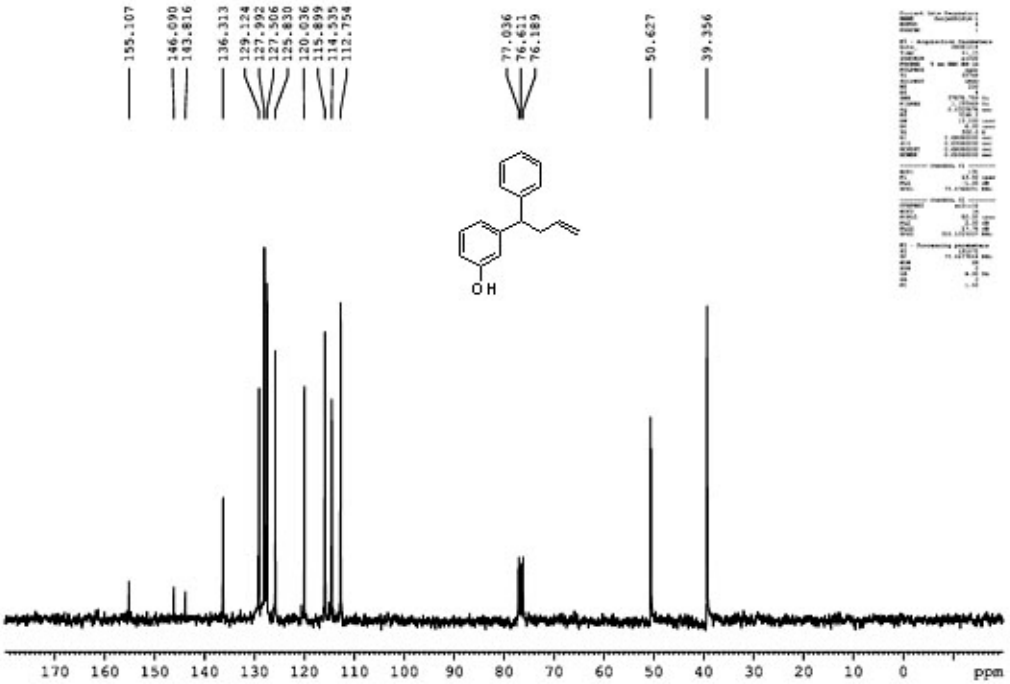

144.635
136.956
128.526
128.081
126.306
116.406
51.384
40.089
180
160
140
120
100
80
60
40
20
0
ppm

1c

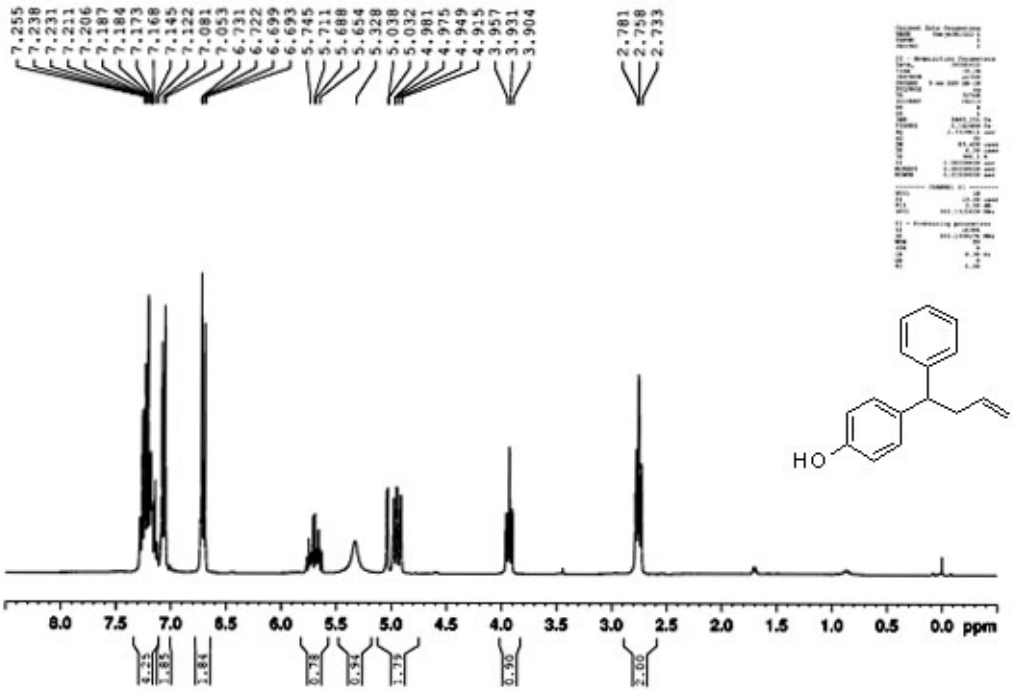

7.238
7.215
7.208
7.187
7.181
7.129
7.119
7.109
7.104
7.099
6.905
6.880
6.795
6.767
5.030
5.024
4.972
4.967
4.923
4.920
4.917
4.889
4.886
4.883
4.485
4.459
3.704
2.791
2.768
2.765
2.744
2.741
OMe
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
144.711
137.489
133.266
128.495
128.357
128.121
127.824
127.400
126.100
120.745
116.140
111.007
77.735
77.312
76.887
55.662
43.580
39.387
OMe
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

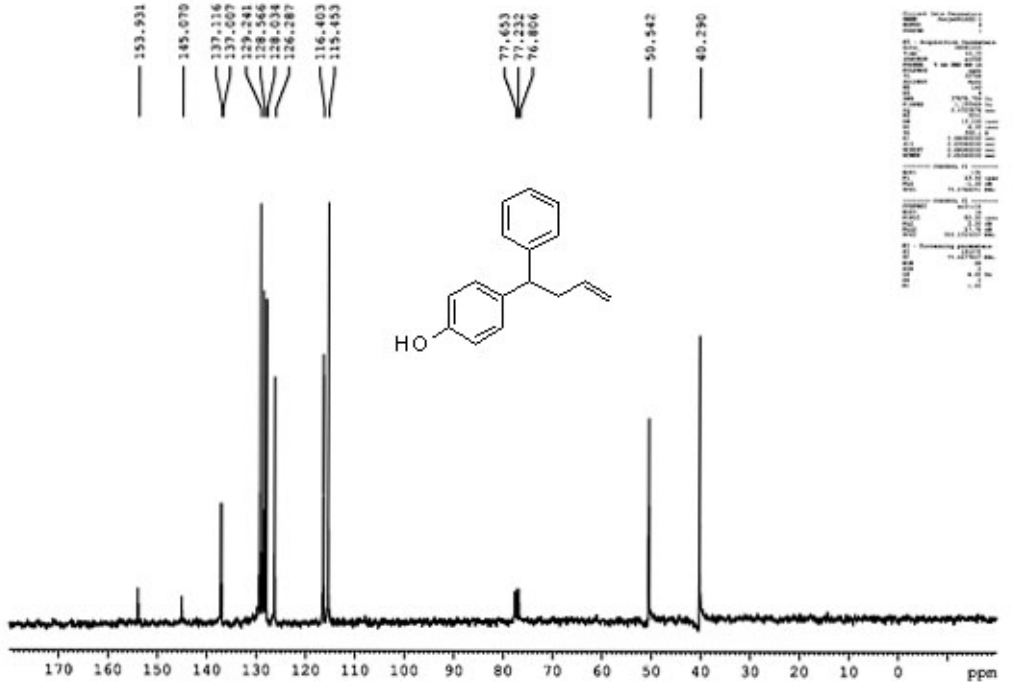
1d


7.182
7.177
7.170
7.154
7.141
7.115
7.089
6.822
6.797
6.683
6.676
6.671
6.624
6.619
6.616
6.600
6.598
6.592
6.590
5.710
5.687
5.653
5.044
5.038
4.987
4.981
4.952
4.949
4.946
4.918
4.915
4.912
3.959
3.933
3.907
2.793
2.790
2.770
2.767
2.744
OH
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 ppm
6.69
1.01
2.14
0.93
0.91
2.10
0.98
2.00

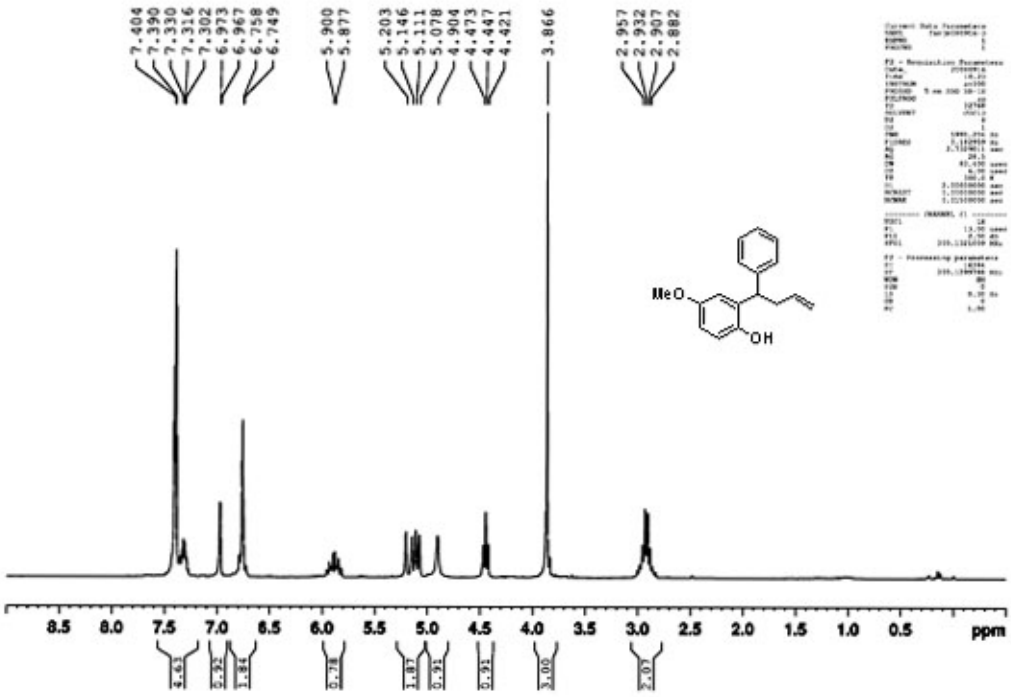

155.107
146.690
143.816
136.313
129.124
127.992
127.506
125.830
120.036
115.899
114.535
112.754
77.036
76.611
76.189
50.627
39.356
OH
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

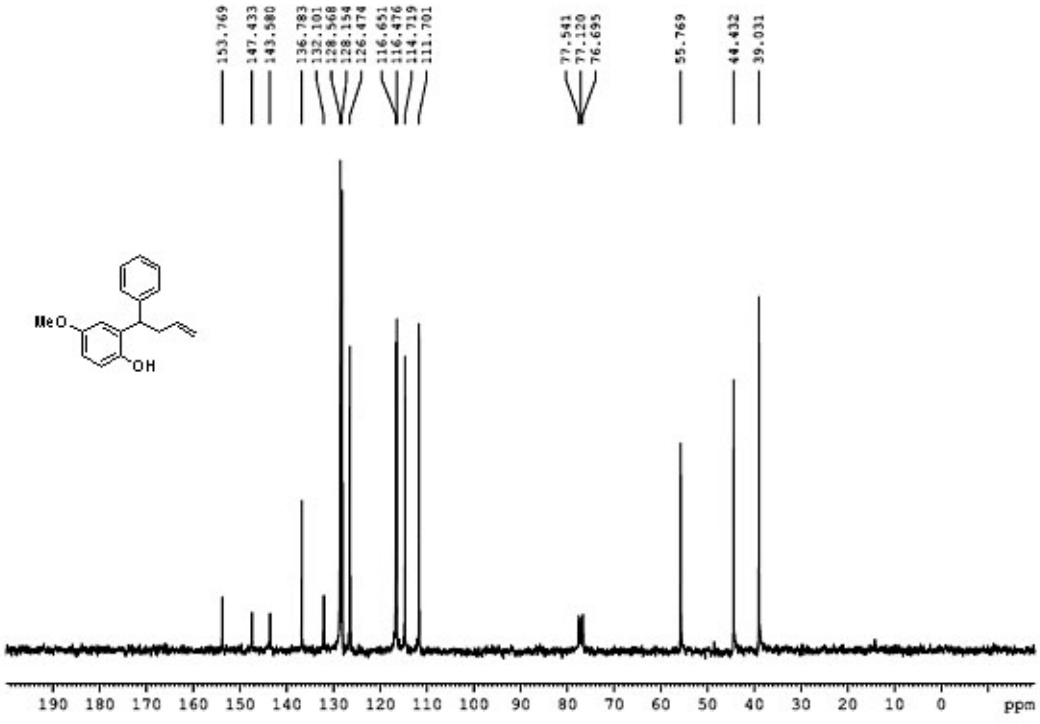
1e


7.255
7.238
7.231
7.211
7.206
7.187
7.184
7.173
7.168
7.145
7.122
7.081
7.053
6.731
6.722
6.699
6.693
5.745
5.711
5.688
5.654
5.328
5.038
5.032
4.981
4.975
4.949
4.915
3.957
3.931
3.904
2.781
2.758
2.733
HO
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 ppm
2.25
1.85
1.84
0.78
0.94
1.19
0.90
2.00

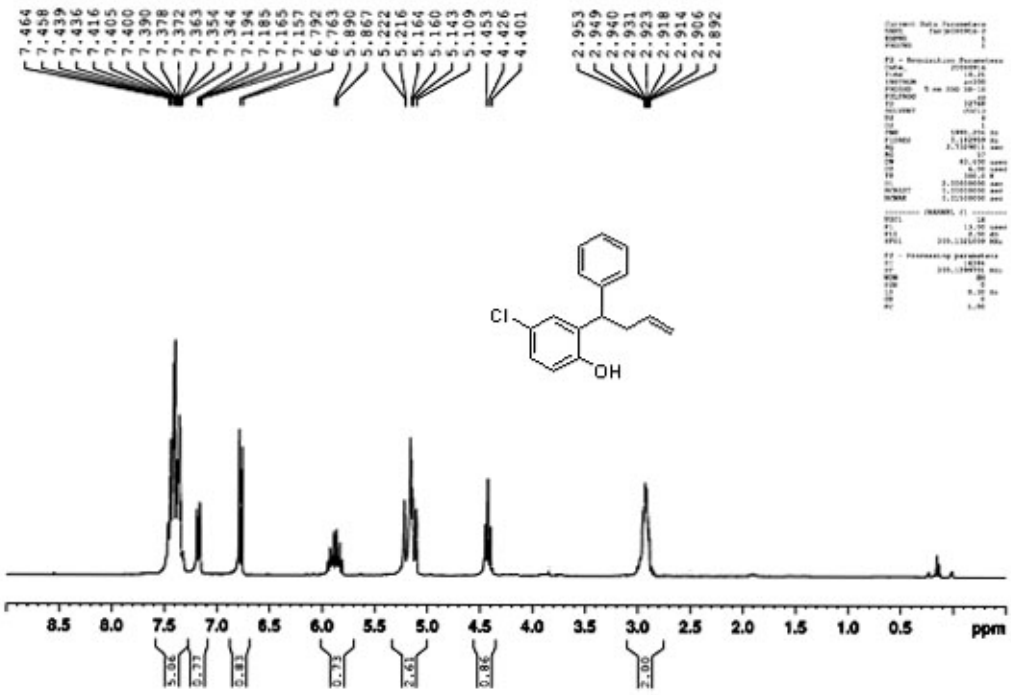

153.931
145.079
137.116
137.007
129.241
128.566
128.034
126.287
116.403
115.453
77.653
77.232
76.806
50.542
40.290
HO
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

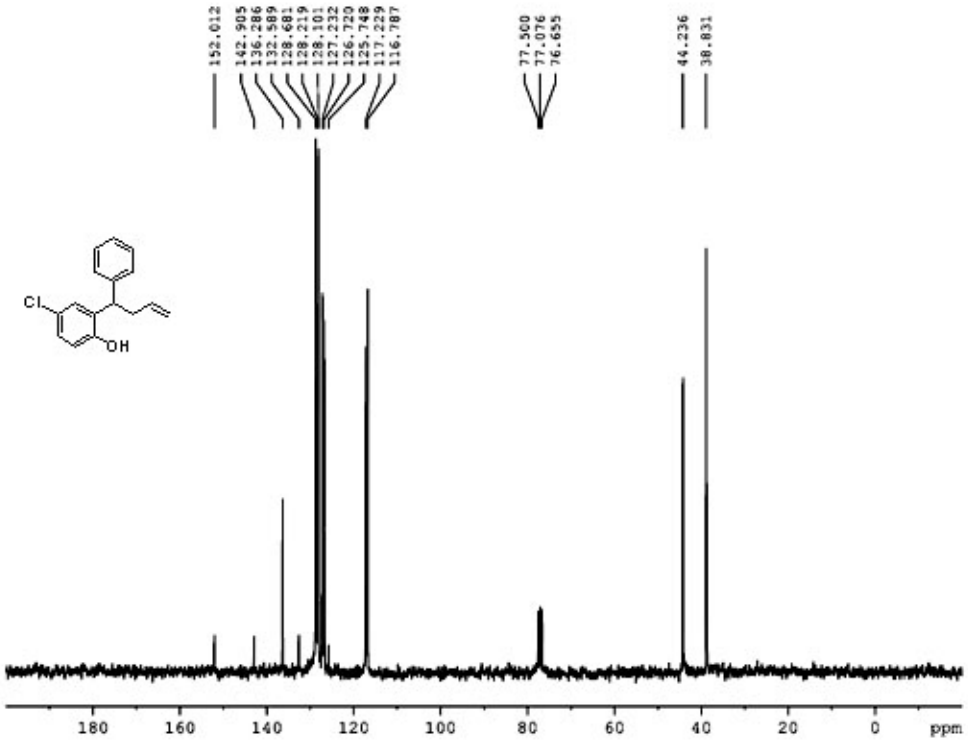
1f


7.404
7.390
7.330
7.316
7.302
6.973
6.967
6.758
6.749
5.900
5.877
5.203
5.146
5.111
5.078
4.904
4.473
4.447
4.421
3.866
2.957
2.932
2.907
2.882
MeO
OH
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 ppm
4.63
2.92
1.84
0.78
1.87
0.91
0.91
3.00
2.03

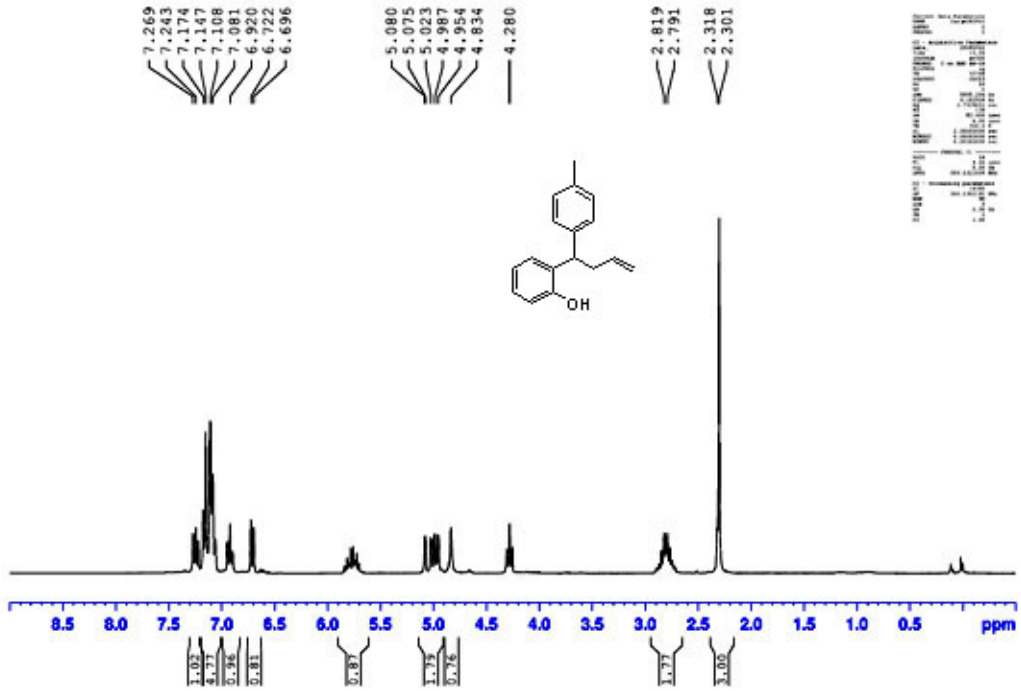

153.769
147.433
143.580
136.783
132.101
128.568
128.154
126.474
116.651
116.476
114.719
111.701
77.541
77.120
76.695
55.769
44.432
39.031
MeO
OH
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

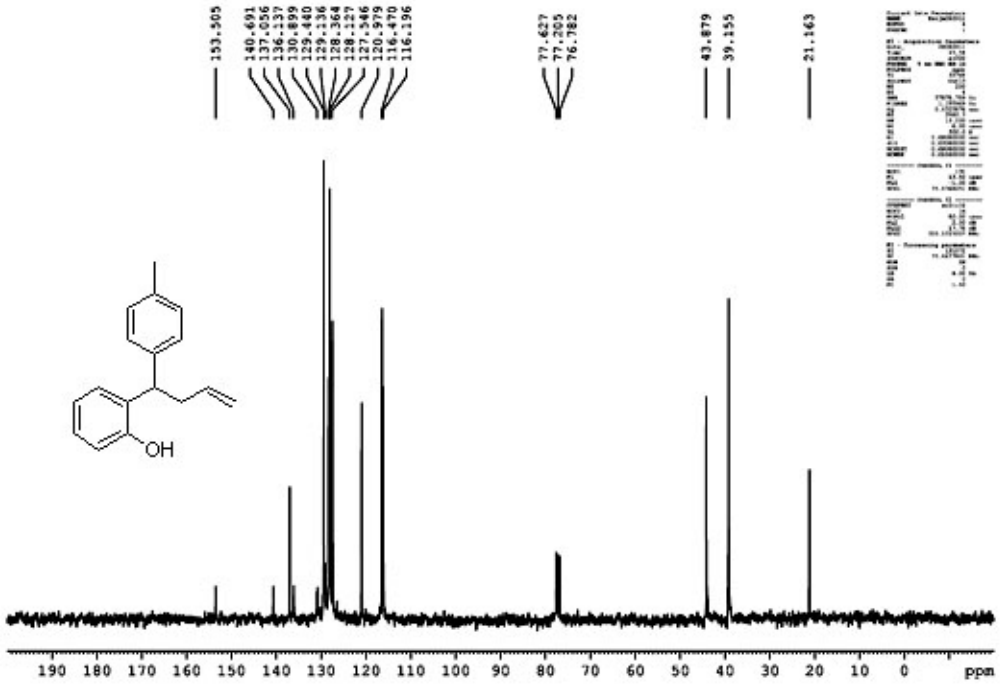
1g


7.464
7.458
7.439
7.436
7.416
7.405
7.400
7.390
7.378
7.372
7.363
7.354
7.344
7.194
7.185
7.165
7.157
6.792
6.763
5.890
5.867
5.222
5.216
5.164
5.160
5.143
5.109
4.453
4.426
4.401
2.953
2.949
2.940
2.931
2.923
2.918
2.914
2.906
2.892
Cl
OH
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
ppm
5.06
2.37
0.83
0.73
2.61
0.86
2.00

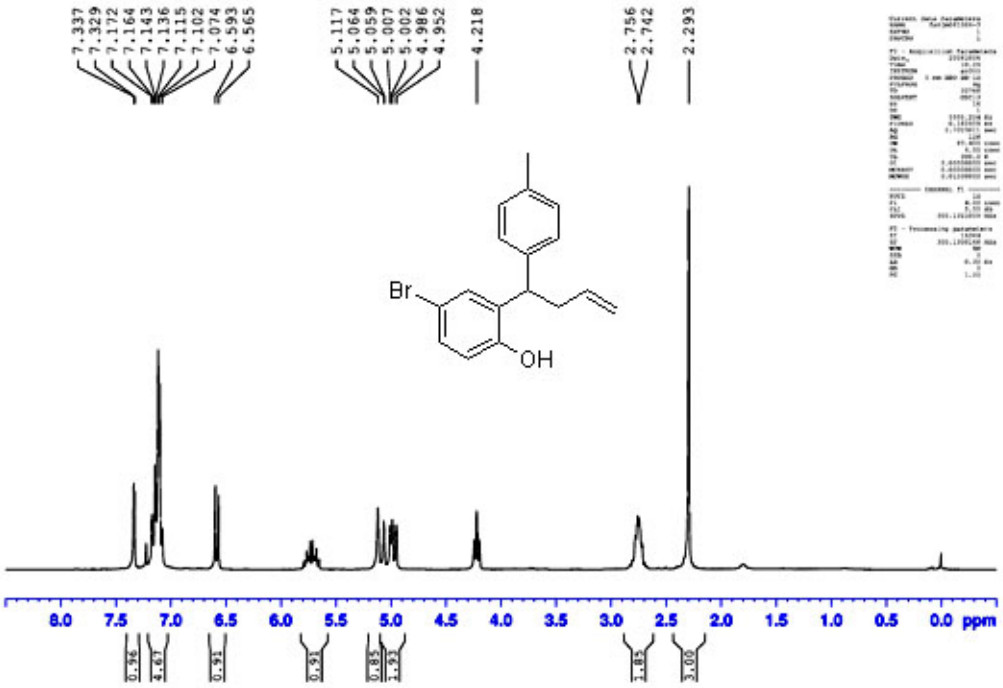

152.012
142.905
136.286
132.589
128.681
128.219
128.101
127.232
126.729
125.748
117.229
116.787
77.500
77.076
76.655
44.236
38.831
Cl
OH
180
160
140
120
100
80
60
40
20
0
ppm

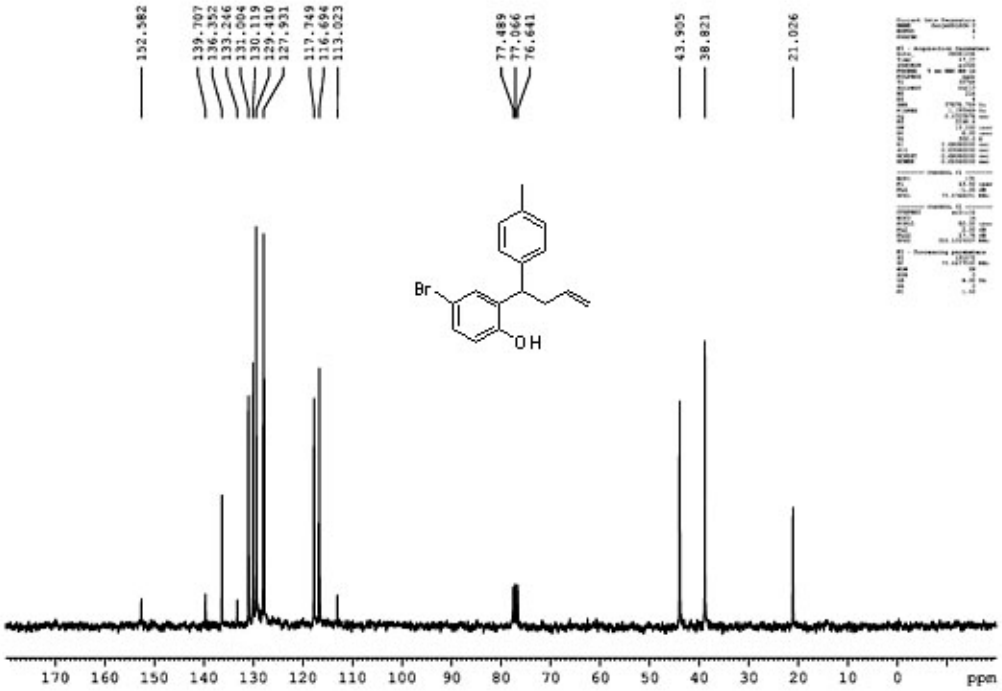
1h


7.269
7.243
7.174
7.147
7.108
7.081
6.920
6.722
6.696
5.080
5.075
5.023
4.987
4.954
4.834
4.280
2.819
2.791
2.318
2.301
OH
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 ppm
1.02
4.77
0.96
0.81
0.87
1.75
0.76
1.77
3.00

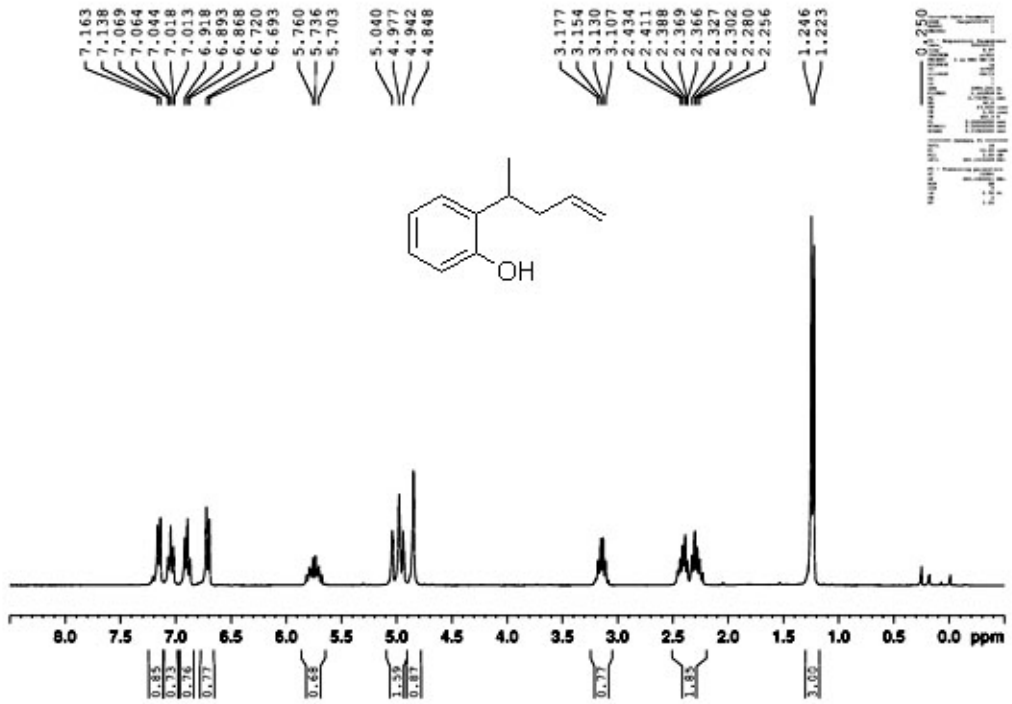

153.505
140.691
137.056
136.137
130.899
129.440
129.136
128.364
128.127
127.346
120.979
116.470
116.196
77.627
77.205
76.782
43.879
39.155
21.163
OH
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

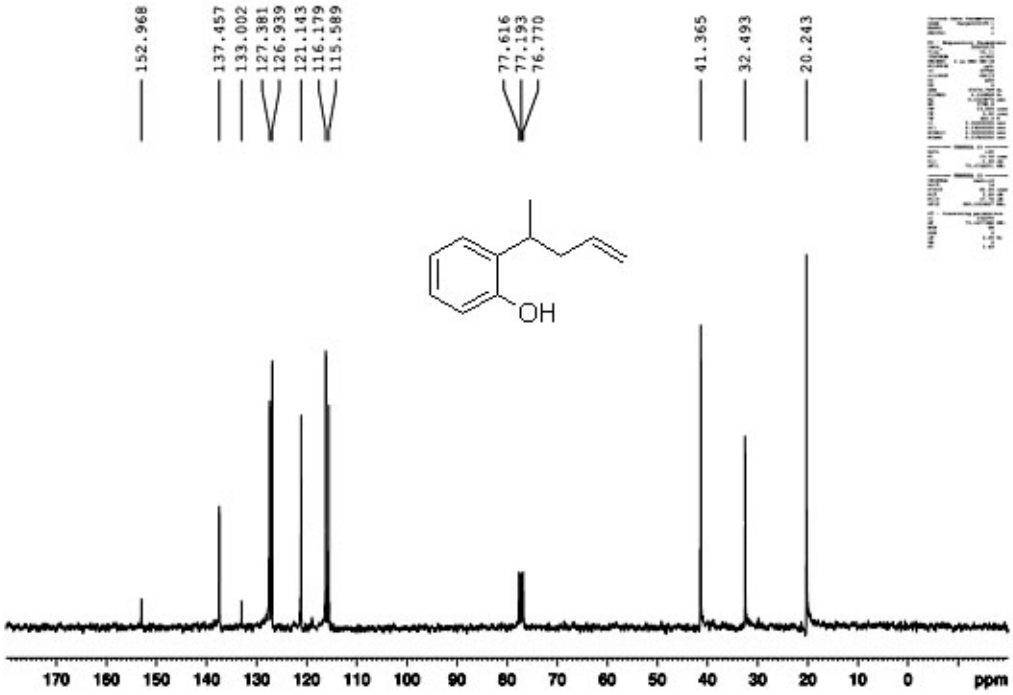
1i


7.337
7.329
7.172
7.164
7.143
7.136
7.115
7.102
7.074
6.593
6.565
5.117
5.064
5.059
5.007
5.002
4.986
4.952
4.218
2.756
2.742
2.293
Br
OH
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 ppm
0.96
4.67
0.91
0.91
0.85
2.00
1.85
3.00

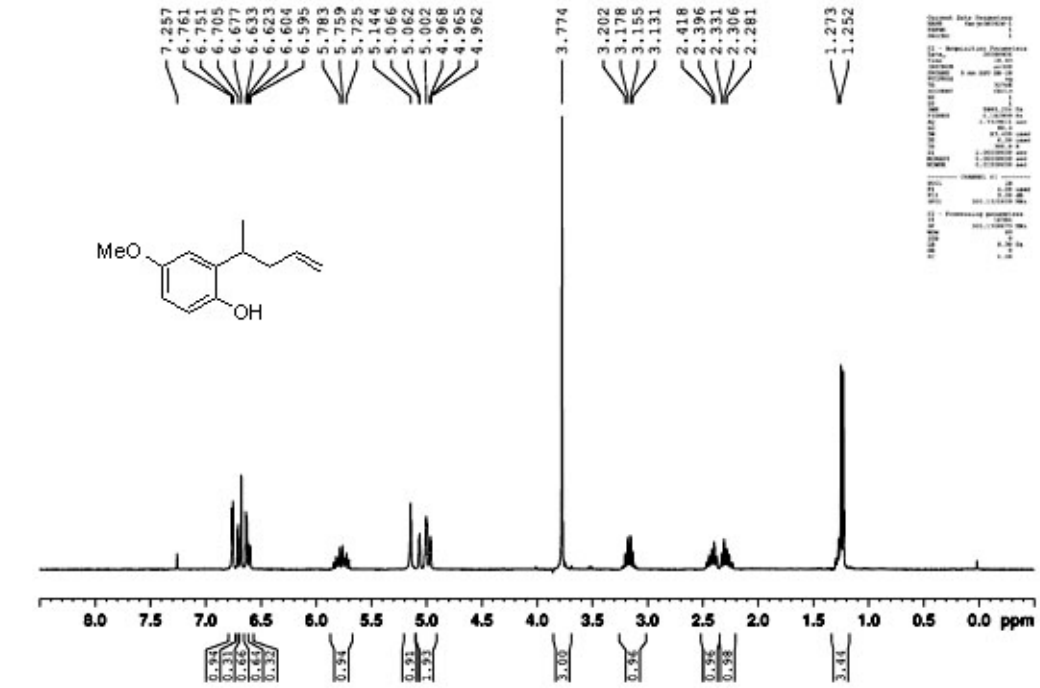

152.582
139.707
136.352
133.246
131.094
130.119
129.410
127.931
117.749
116.696
113.023
77.489
77.066
76.641
43.905
38.821
21.026
Br
OH
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

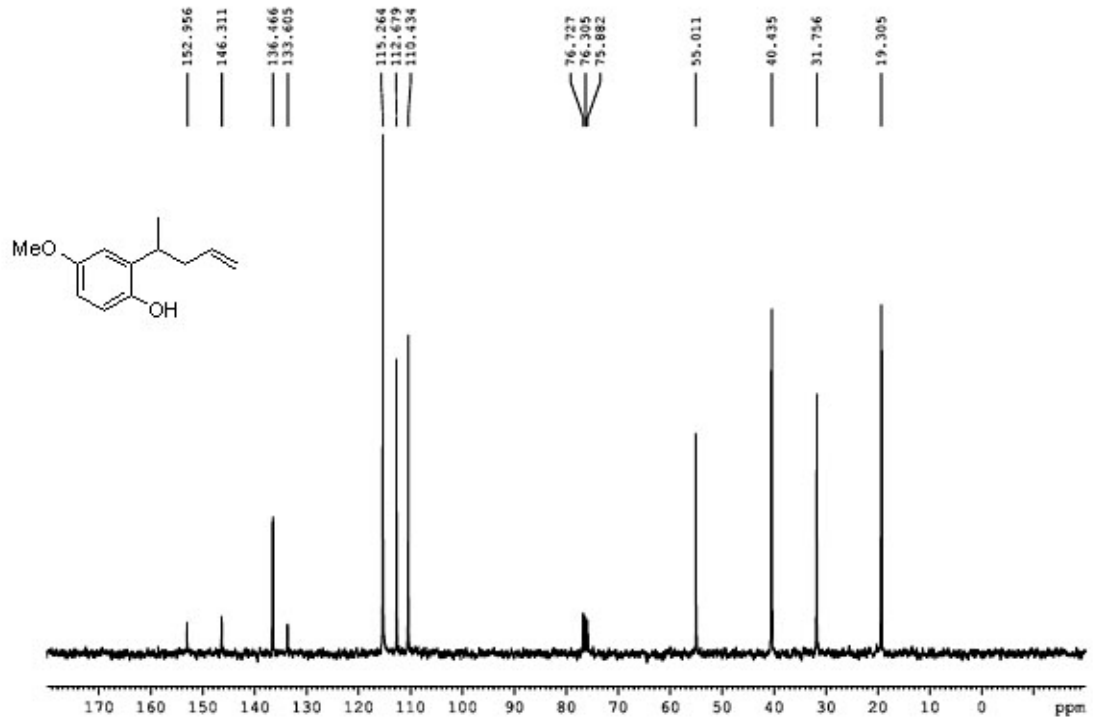
1j


7.163
7.138
7.069
7.064
7.044
7.018
7.013
6.918
6.893
6.868
6.720
6.693
5.760
5.736
5.703
5.040
4.977
4.942
4.848
3.177
3.154
3.130
3.107
2.434
2.411
2.388
2.369
2.366
2.327
2.302
2.280
2.256
1.246
1.223
0.250
OH
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 ppm
0.85
0.73
0.76
0.77
0.68
1.39
0.87
0.77
1.85
3.00

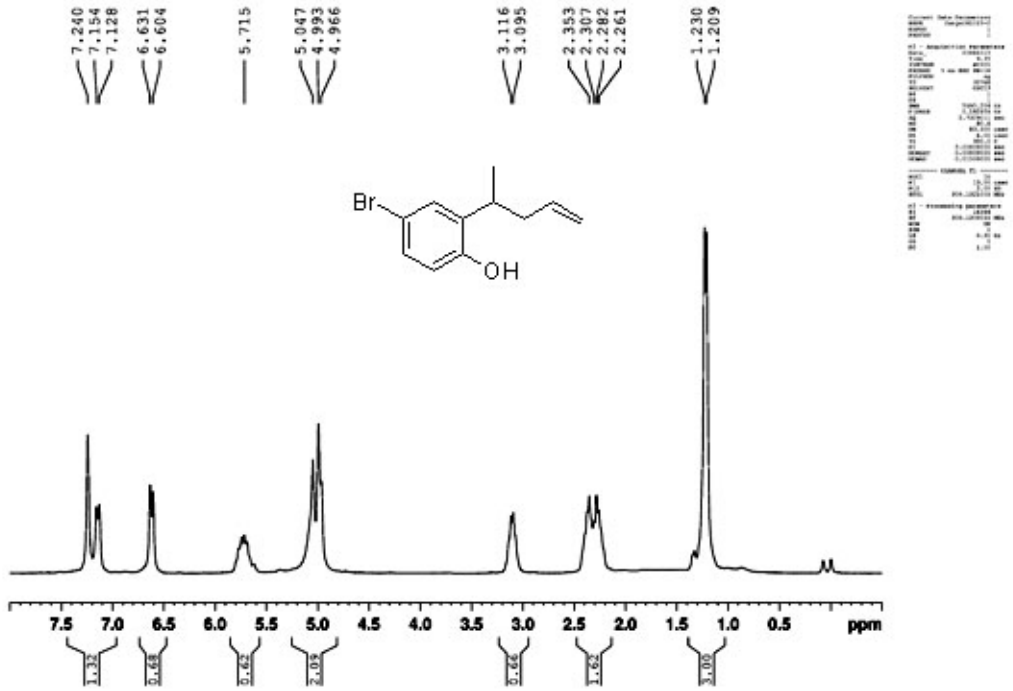

152.968
137.457
133.002
127.381
126.939
121.143
116.179
115.589
77.616
77.193
76.770
41.365
32.493
20.243
OH
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

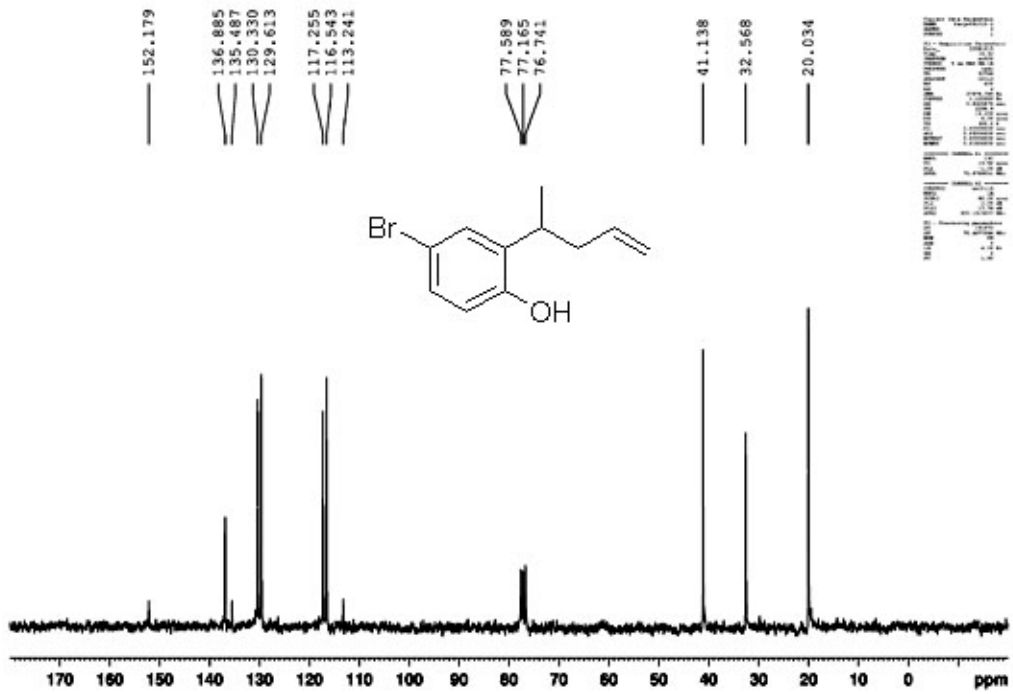
1k


7.257
6.761
6.751
6.705
6.677
6.633
6.623
6.604
6.595
5.783
5.759
5.725
5.144
5.066
5.062
5.002
4.968
4.965
4.962
3.774
3.202
3.178
3.155
3.131
2.418
2.396
2.331
2.306
2.281
1.273
1.252
MeO
OH
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 ppm
0.94
0.33
0.66
0.44
0.32
0.94
0.91
1.93
3.00
0.96
0.96
0.58
3.41

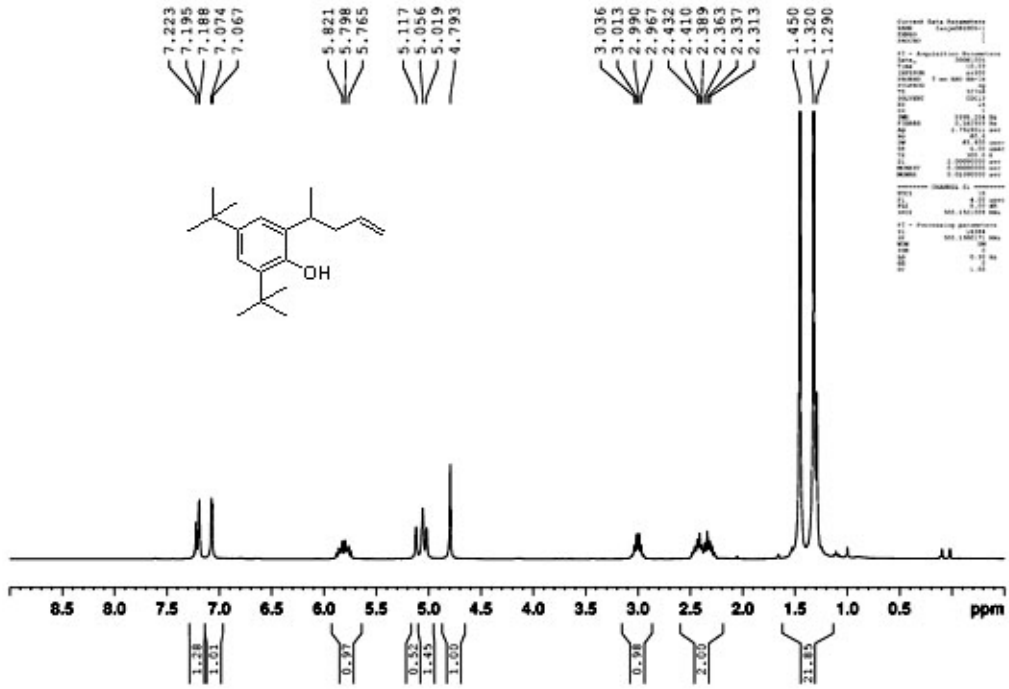

152.956
146.311
136.466
133.605
115.264
112.679
110.434
76.727
76.305
75.882
55.011
40.435
31.756
19.305
MeO
OH
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

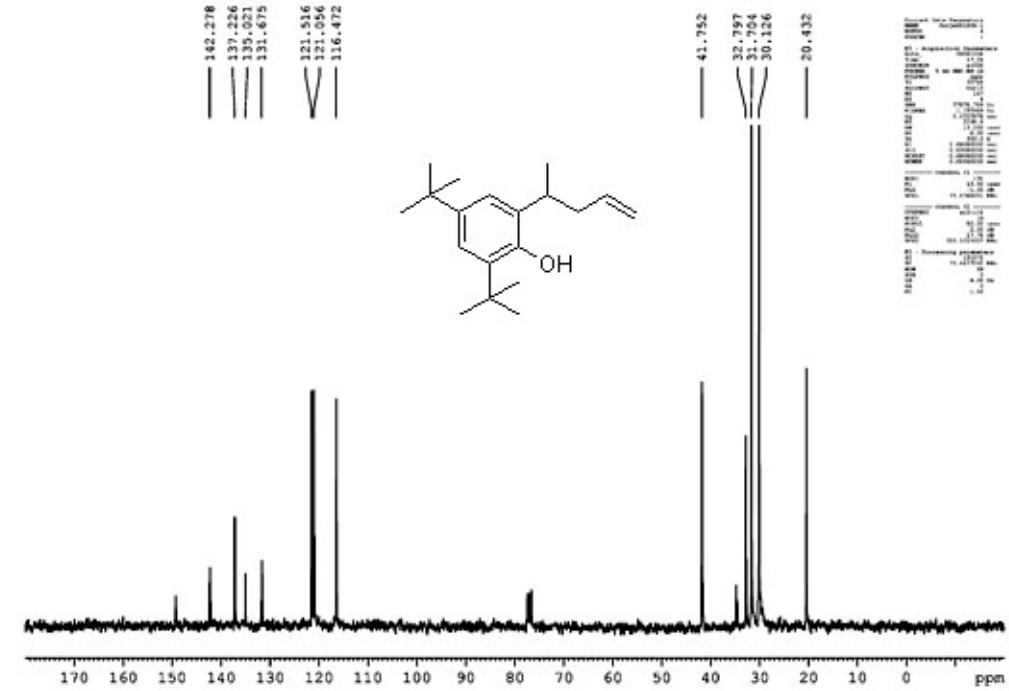
1l


7.240
7.154
7.128
6.631
6.604
5.715
5.047
4.993
4.966
3.116
3.095
2.353
2.307
2.282
2.261
1.230
1.209
Br
OH
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 ppm

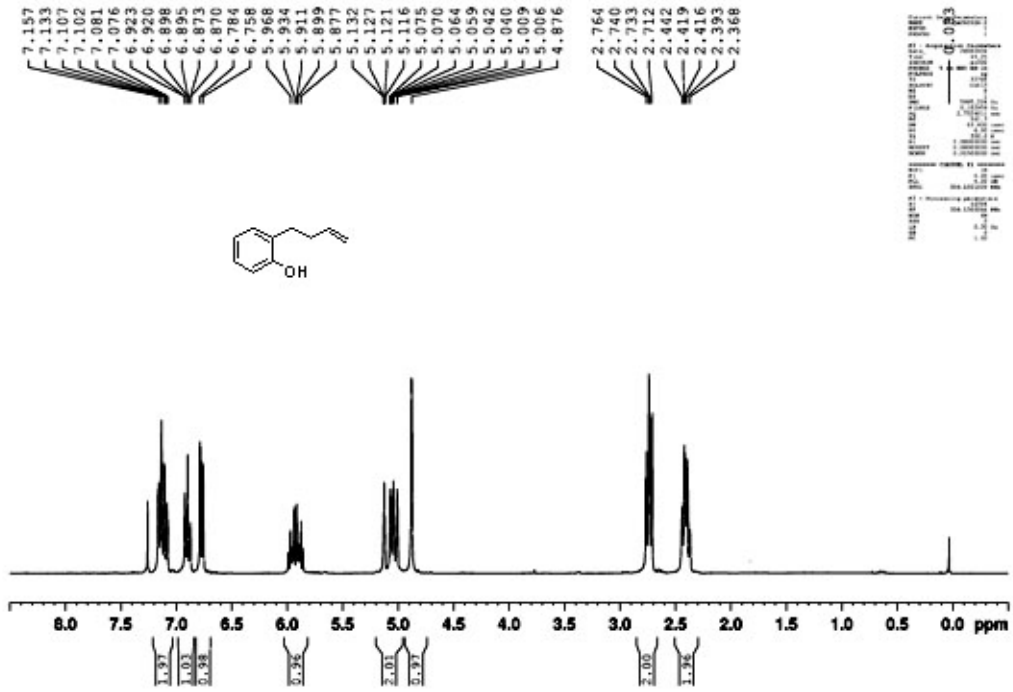

152.179
136.885
135.487
130.330
129.613
117.255
116.543
113.241
77.589
77.165
76.741
41.138
32.568
20.034
Br
OH
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

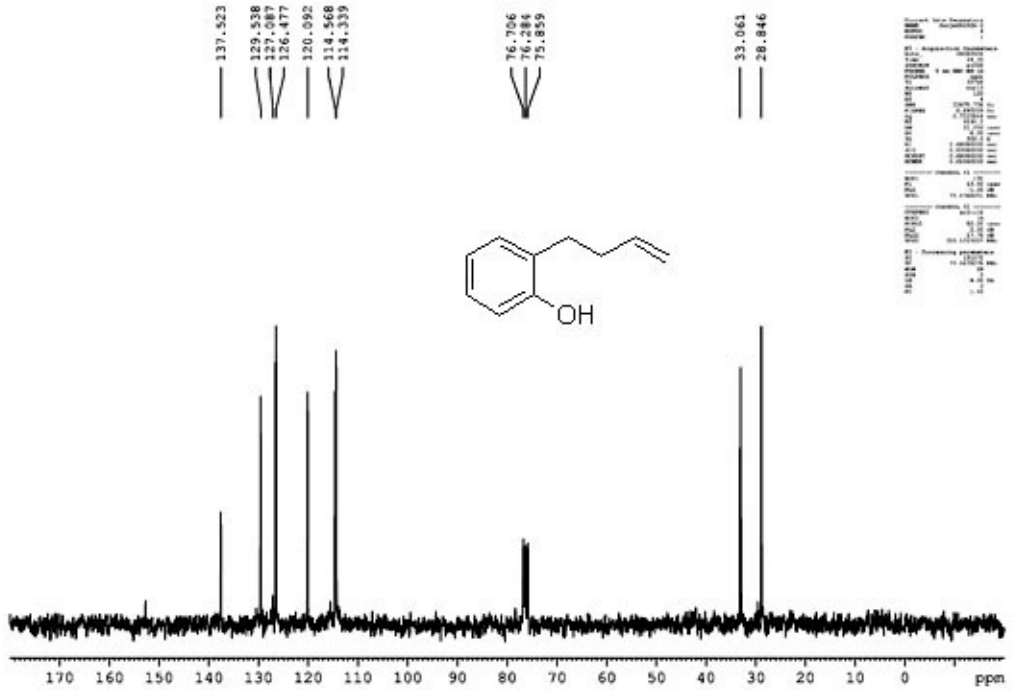
1m


7.223
7.195
7.188
7.074
7.067
5.821
5.798
5.765
5.117
5.056
5.019
4.793
3.036
3.013
2.990
2.967
2.432
2.410
2.389
2.363
2.337
2.313
1.450
1.320
1.290
OH
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 ppm
1.28
1.61
0.97
0.52
1.45
1.00
0.98
2.00
21.85

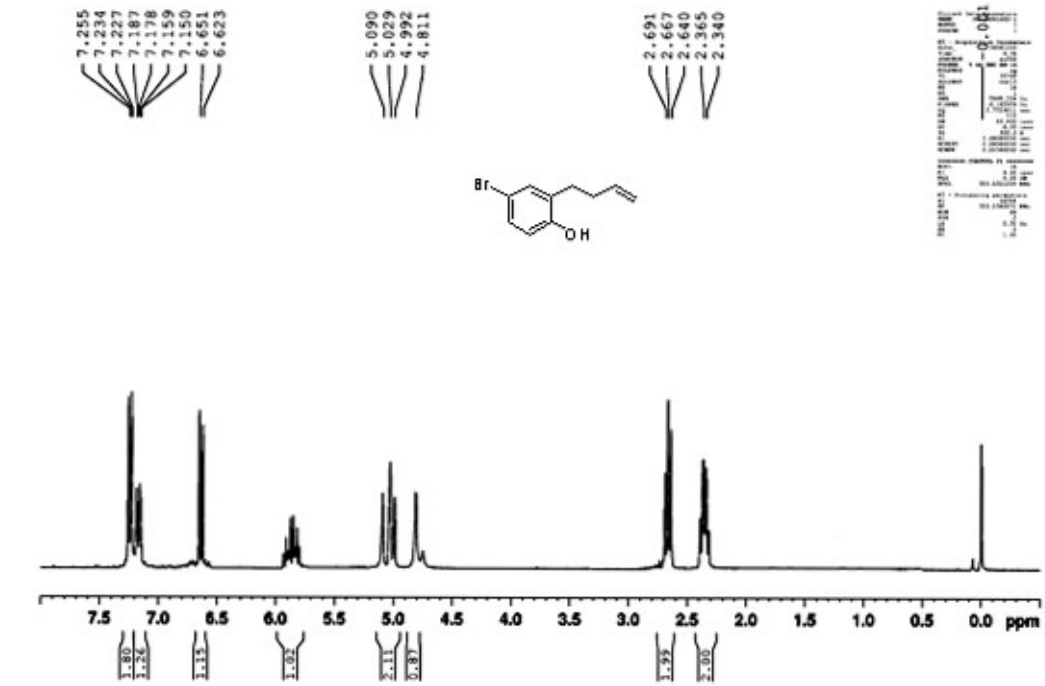

142.278
137.226
135.021
131.675
121.516
121.056
116.472
41.752
32.797
31.704
30.126
20.432
OH
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

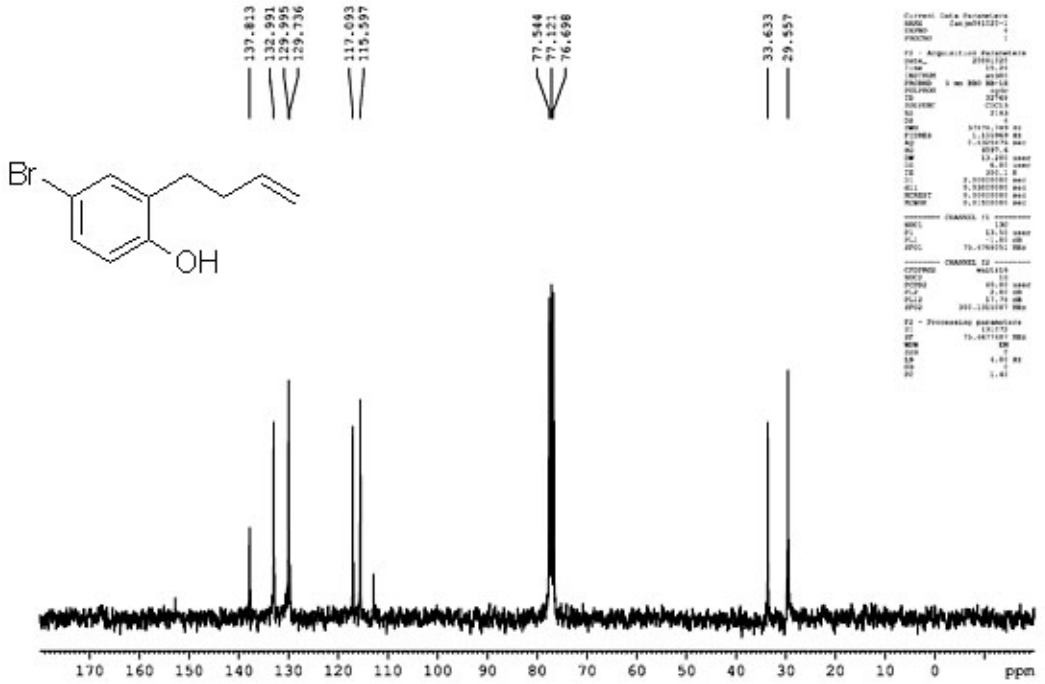
1n


7.157
7.133
7.107
7.102
7.081
7.076
6.923
6.920
6.898
6.895
6.873
6.870
6.784
6.758
5.968
5.934
5.911
5.899
5.877
5.132
5.127
5.121
5.116
5.075
5.070
5.064
5.059
5.042
5.040
5.009
5.006
4.876
2.764
2.740
2.733
2.712
2.442
2.419
2.416
2.393
2.368
OH
6.0
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 ppm
1.97
1.03
0.98
0.96
2.01
0.97
2.00
1.96

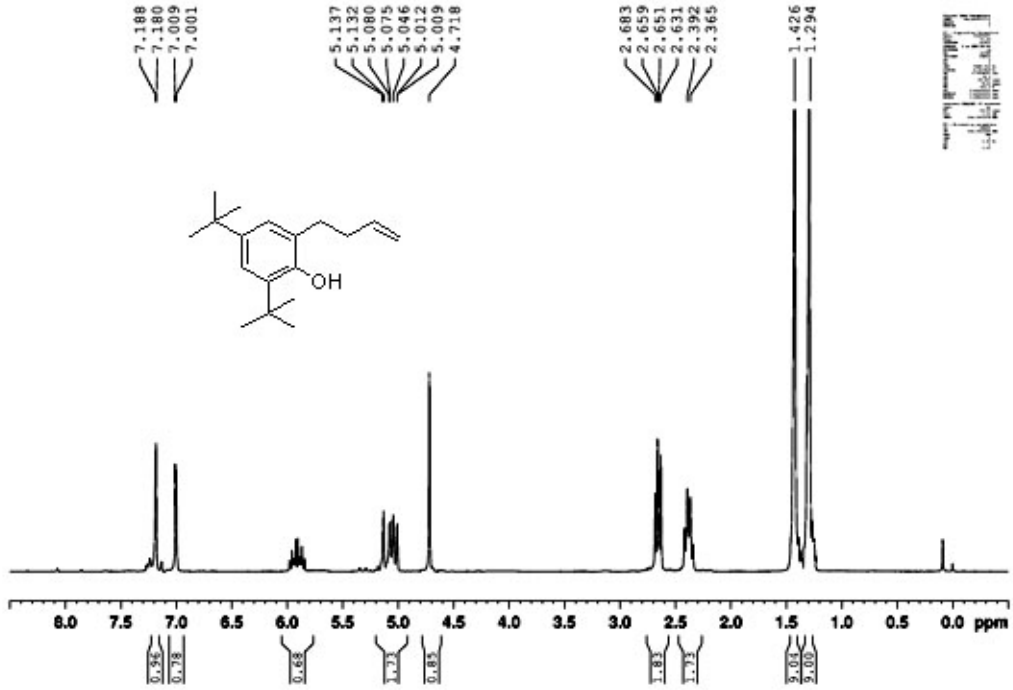

137.523
129.538
127.087
126.477
120.092
114.568
114.339
76.706
76.286
75.859
33.061
28.846
OH
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

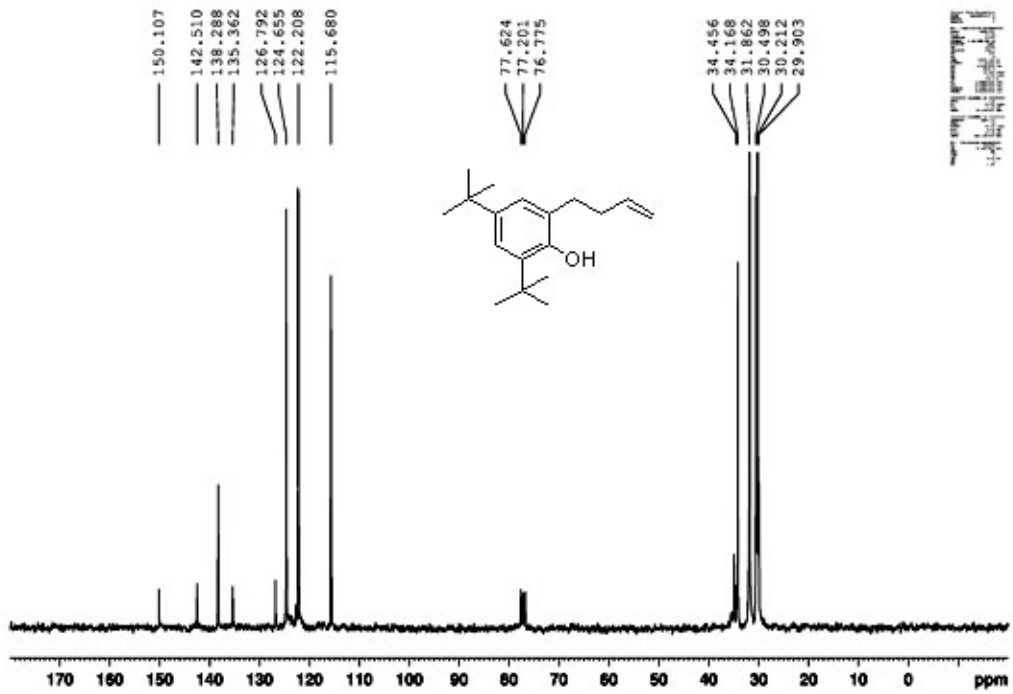
1o


7.255
7.234
7.227
7.187
7.178
7.159
7.150
6.651
6.623
5.090
5.029
4.992
4.811
2.691
2.667
2.640
2.365
2.340
Br
OH
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
ppm

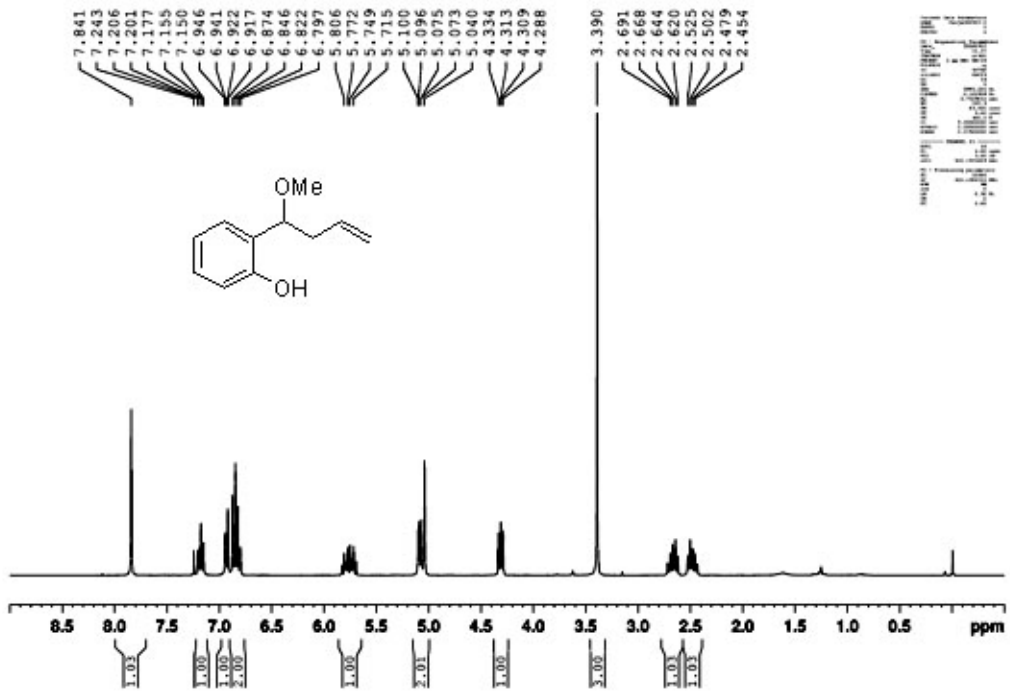

137.813
132.991
129.995
129.736
119.693
115.597
77.544
77.121
76.698
33.633
29.557
Br
OH
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

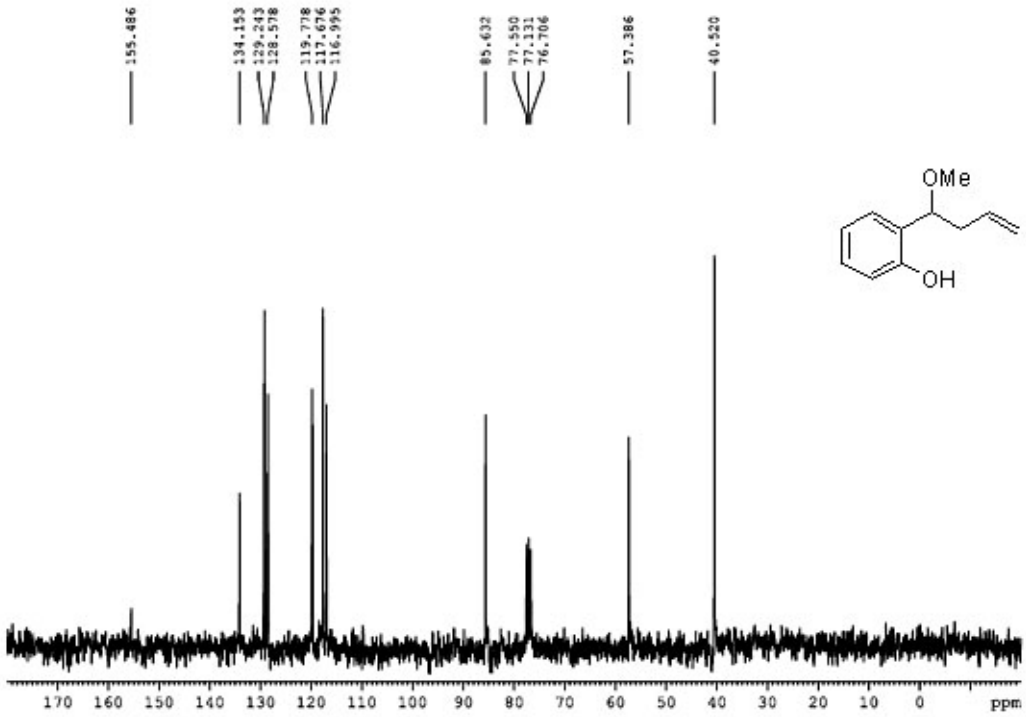
1p


7.188
7.180
7.009
7.001
5.137
5.132
5.080
5.075
5.046
5.012
5.009
4.718
2.683
2.659
2.651
2.631
2.392
2.365
1.426
1.294
OH
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 ppm
0.96
0.78
0.68
1.73
0.85
1.83
1.75
9.04
9.00

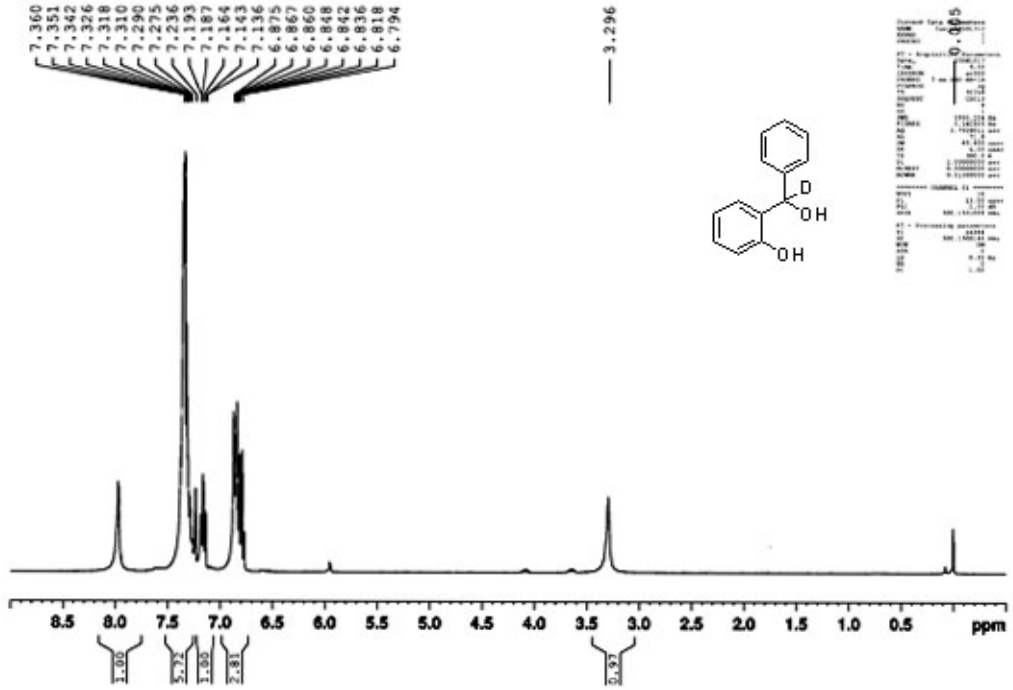

150.107
142.510
138.288
135.362
126.792
124.655
122.208
115.680
77.624
77.201
76.775
34.456
34.168
31.862
30.498
30.212
29.903
OH
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

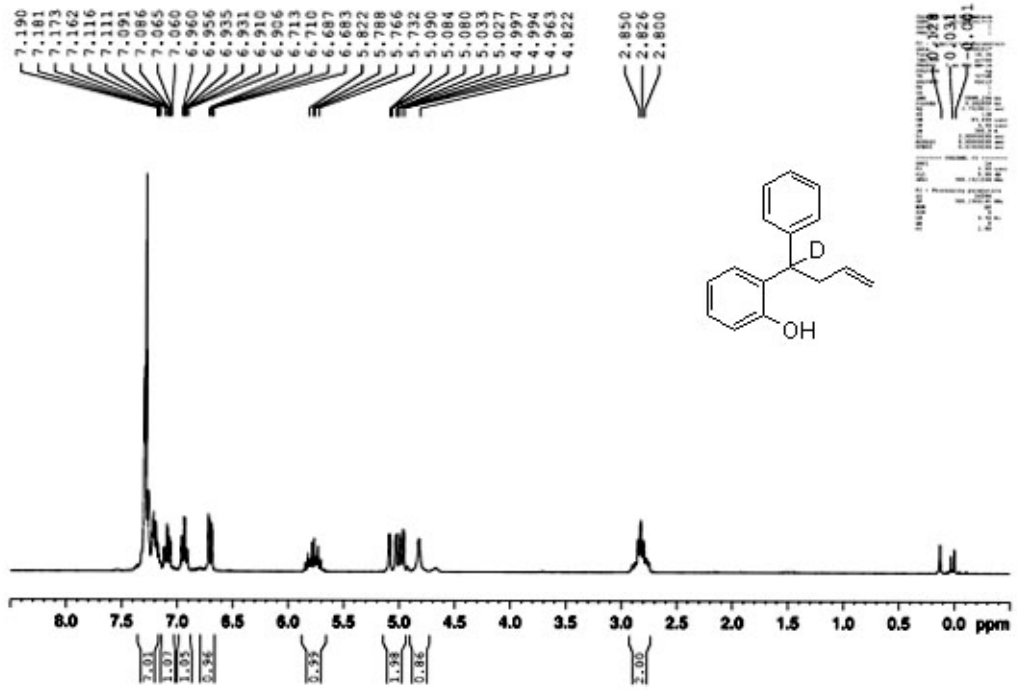
1r


7.841
7.243
7.206
7.201
7.177
7.155
7.150
6.946
6.941
6.922
6.917
6.874
6.846
6.822
6.797
5.806
5.772
5.749
5.715
5.100
5.096
5.075
5.073
5.040
4.334
4.313
4.309
4.288
3.390
2.691
2.668
2.644
2.620
2.525
2.502
2.479
2.454
OMe
OH
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 ppm
1.03
1.00
1.00
2.00
1.00
2.01
1.00
3.00
1.03
1.03


155.486
134.153
129.243
128.578
119.778
117.676
116.995
85.632
77.550
77.131
76.706
57.386
40.520
OMe
OH
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

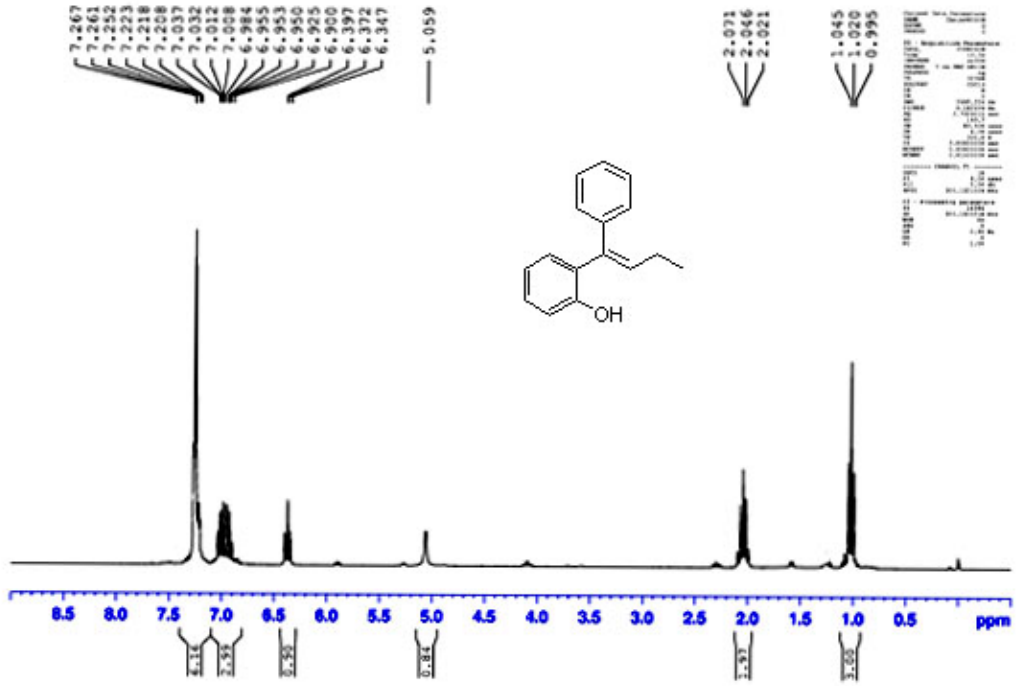
1a-*d*

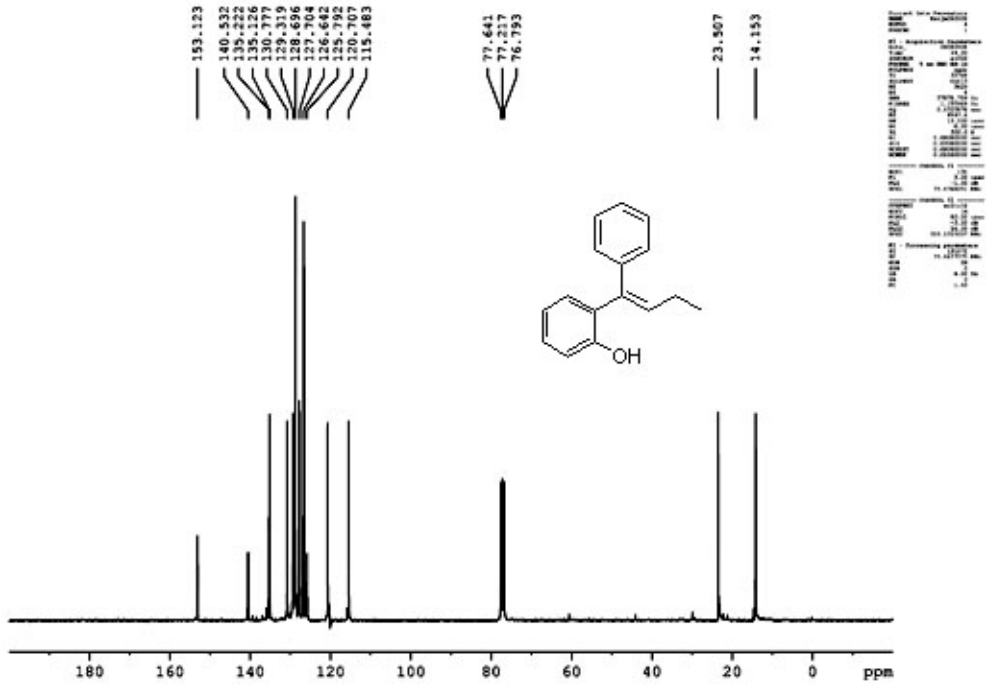

7.360
7.351
7.342
7.326
7.318
7.310
7.290
7.275
7.236
7.193
7.187
7.164
7.143
7.136
6.875
6.867
6.860
6.848
6.842
6.836
6.818
6.794
3.296
D
OH
OH
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
5.72
1.00
2.81
0.97

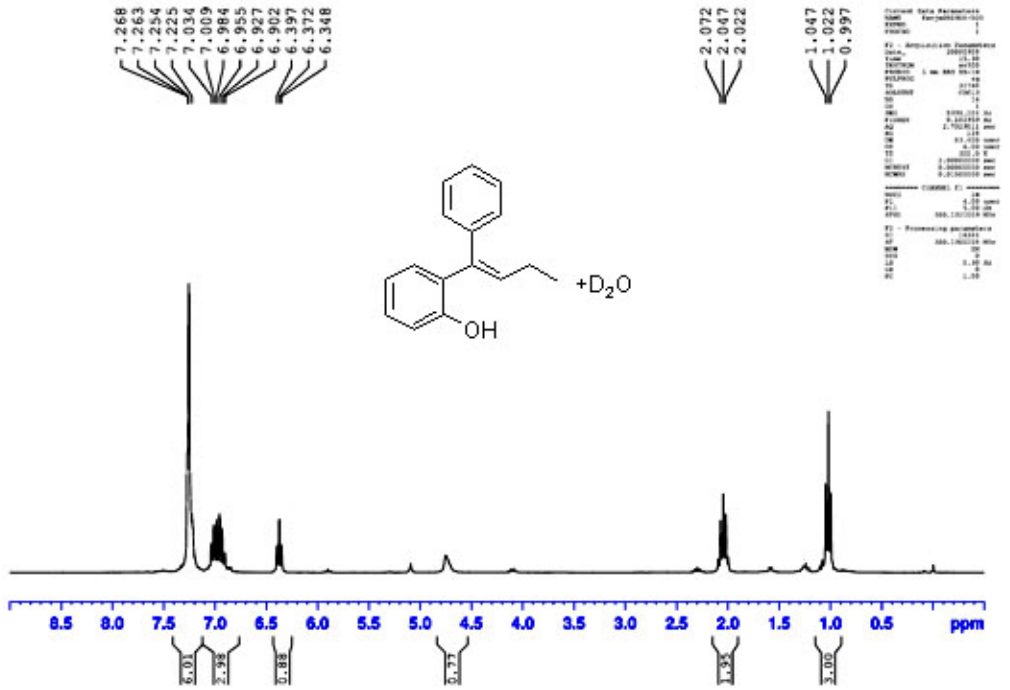

7.190
7.181
7.173
7.162
7.116
7.111
7.091
7.086
7.065
7.060
6.960
6.956
6.935
6.931
6.910
6.906
6.713
6.710
6.687
6.683
5.822
5.788
5.766
5.732
5.090
5.084
5.080
5.033
5.027
4.997
4.994
4.963
4.822
2.850
2.826
2.800
D
OH
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.01
1.07
1.05
0.96
0.93
1.98
0.86
3.00

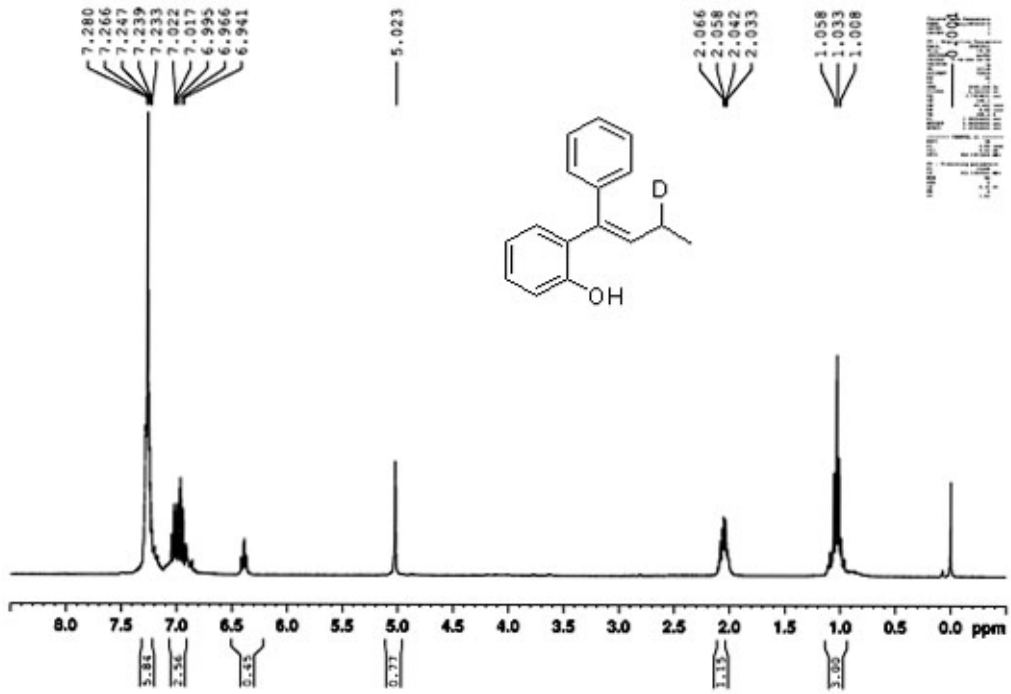
4.1 NMR Spectras of the products

2a, 2a-*d*

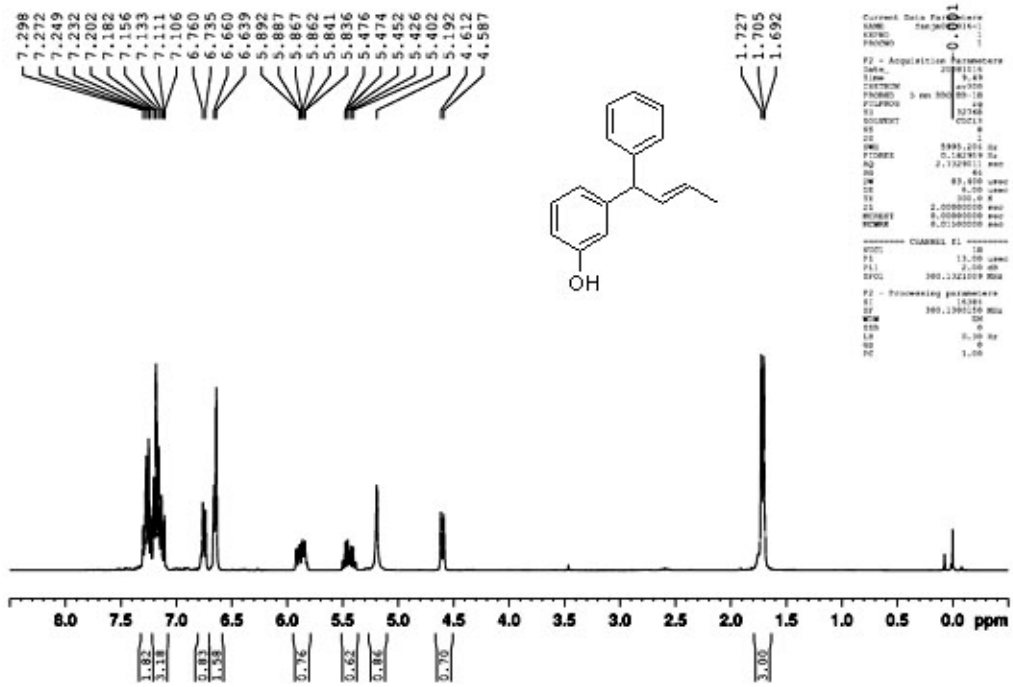


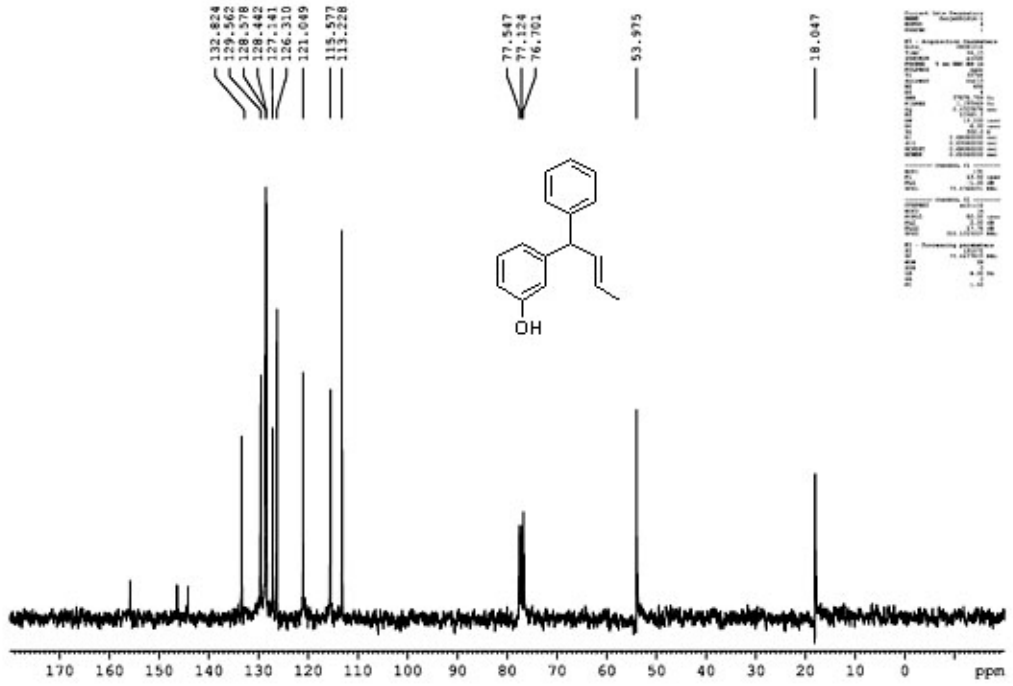



7.268
7.263
7.254
7.225
7.034
7.009
6.984
6.955
6.927
6.902
6.397
6.372
6.348
2.072
2.047
2.022
1.047
1.022
0.997
+D2O
OH
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
6.01
2.98
0.88
0.77
1.85
3.00

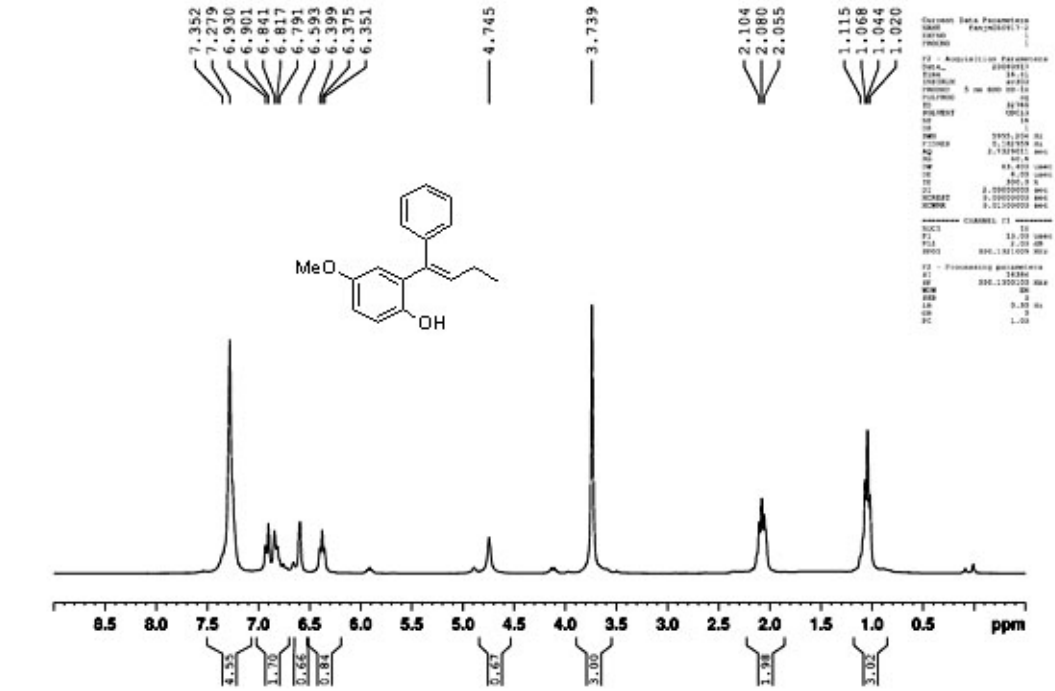

7.280
7.266
7.247
7.239
7.233
7.022
7.017
6.995
6.966
6.941
5.023
2.066
2.058
2.042
2.033
1.058
1.033
1.008
D
OH
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
5.84
2.56
0.45
0.77
1.15
3.00

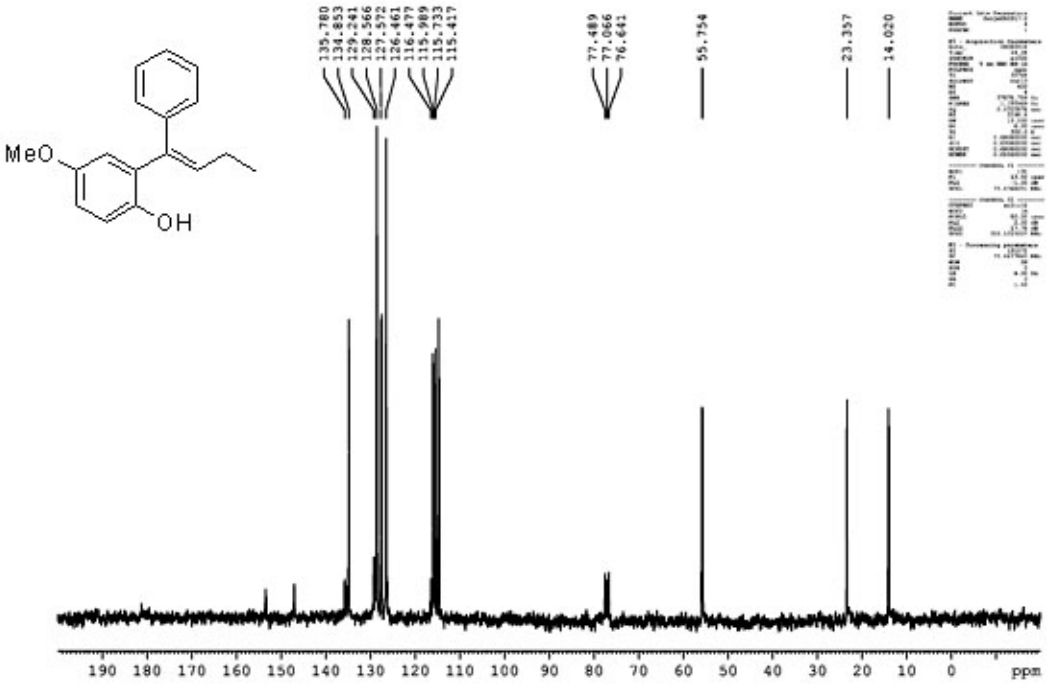
3d


7.298
7.272
7.249
7.232
7.202
7.182
7.156
7.133
7.111
7.106
6.760
6.735
6.660
6.639
5.892
5.887
5.867
5.862
5.841
5.836
5.476
5.474
5.452
5.426
5.402
5.192
4.612
4.587
1.727
1.705
1.692
OH
6.0 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 ppm
1.82
3.18
0.83
1.58
0.76
0.62
0.86
0.76
3.00

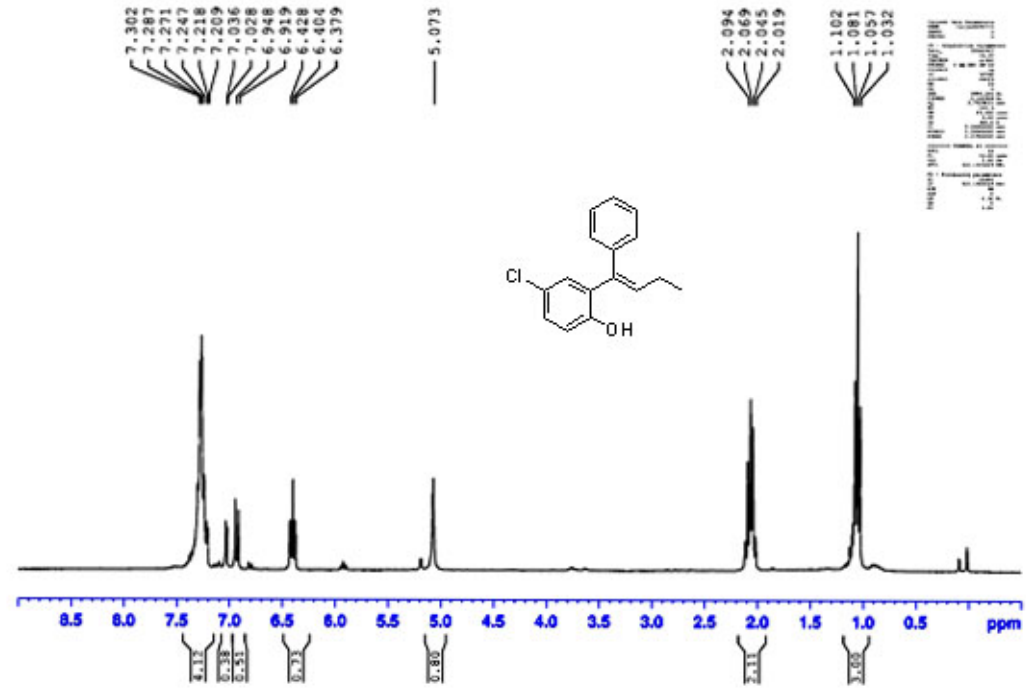

132.824
129.562
128.578
128.442
127.141
126.310
121.049
115.577
113.228
77.547
77.124
76.701
53.975
18.047
OH
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

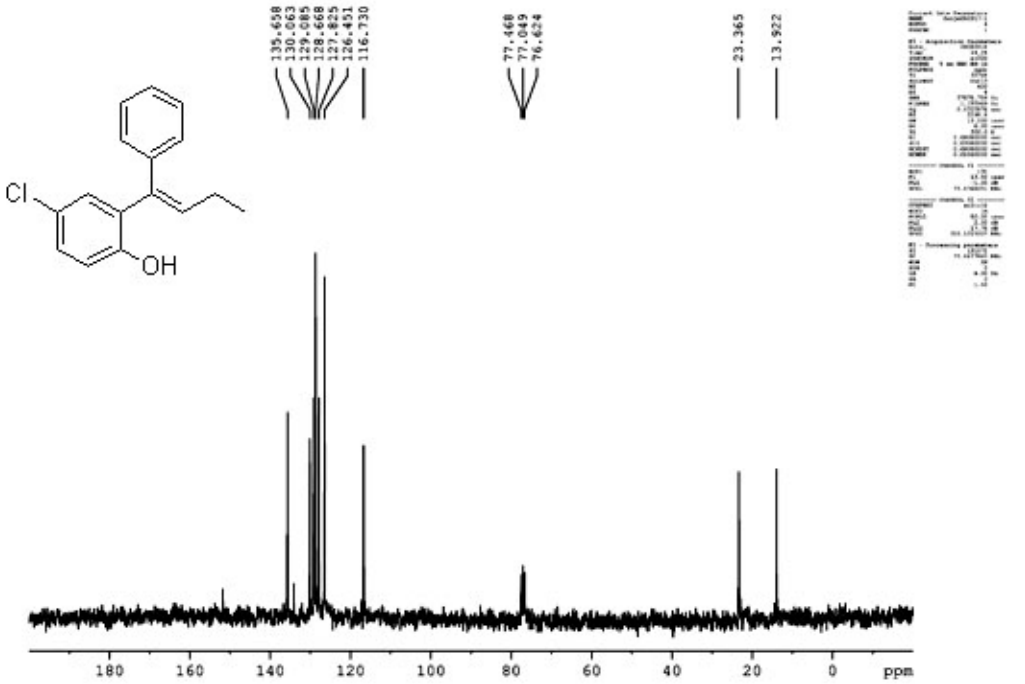
2f


7.352
7.279
6.930
6.901
6.841
6.817
6.791
6.593
6.399
6.375
6.351
4.745
3.739
2.104
2.080
2.055
1.115
1.068
1.044
1.020
MeO
OH
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 ppm
4.35
1.70
0.66
0.84
0.67
3.00
1.98
3.02

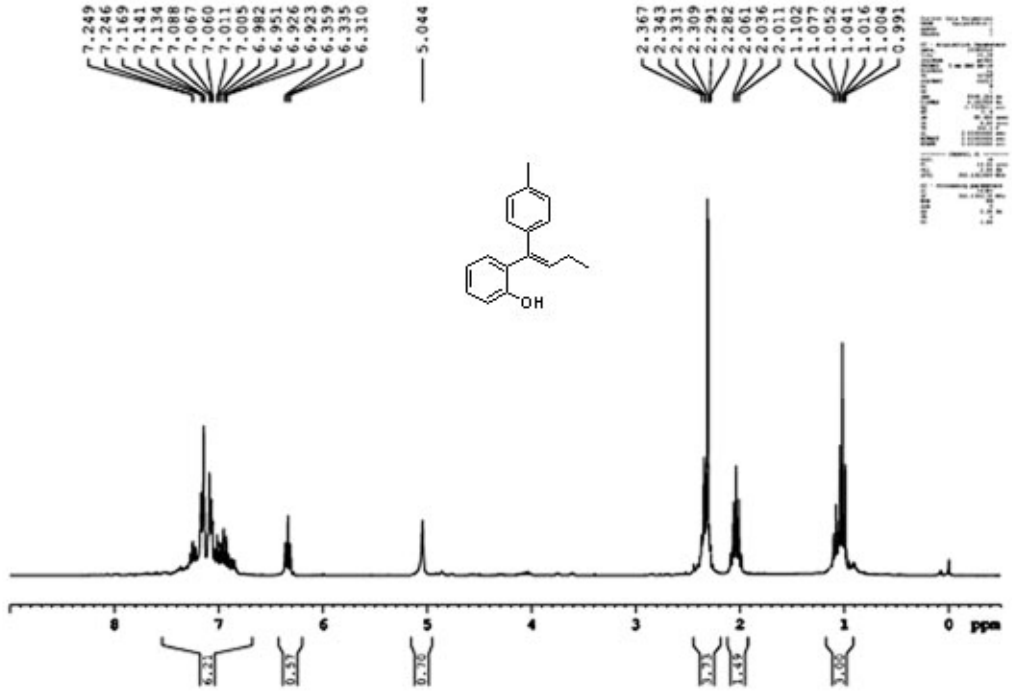

135.780
134.853
129.241
128.566
127.572
126.461
116.497
115.989
115.733
115.417
77.489
77.066
76.641
55.754
23.357
14.020
MeO
OH
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

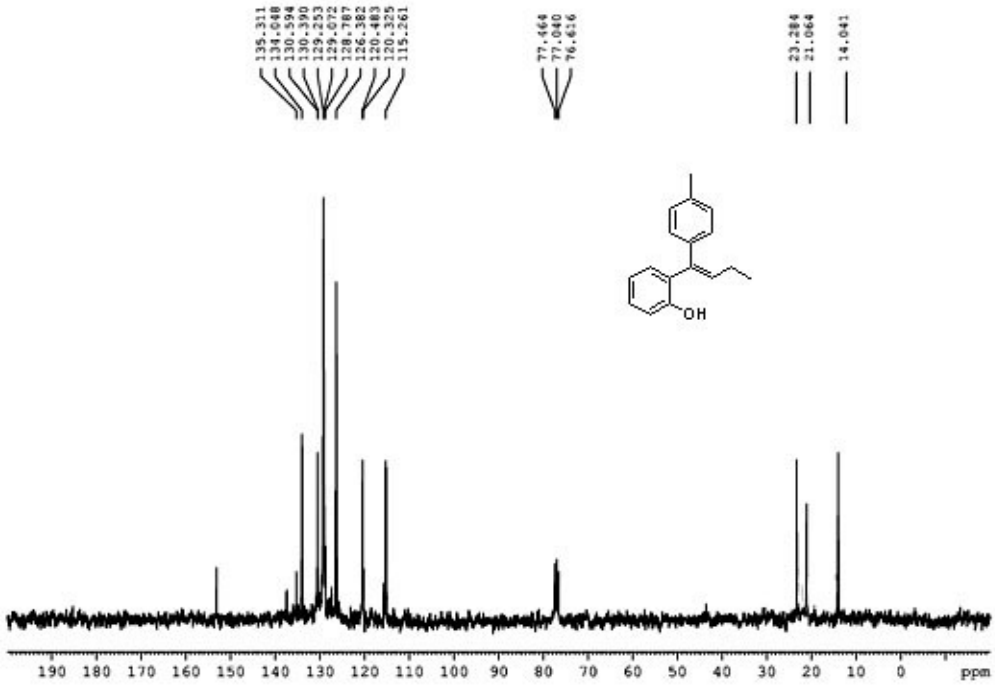
2g


7.302
7.287
7.271
7.247
7.218
7.209
7.036
7.028
6.948
6.919
6.428
6.404
6.379
5.073
2.094
2.069
2.045
2.019
1.102
1.081
1.057
1.032
Cl
OH
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
ppm

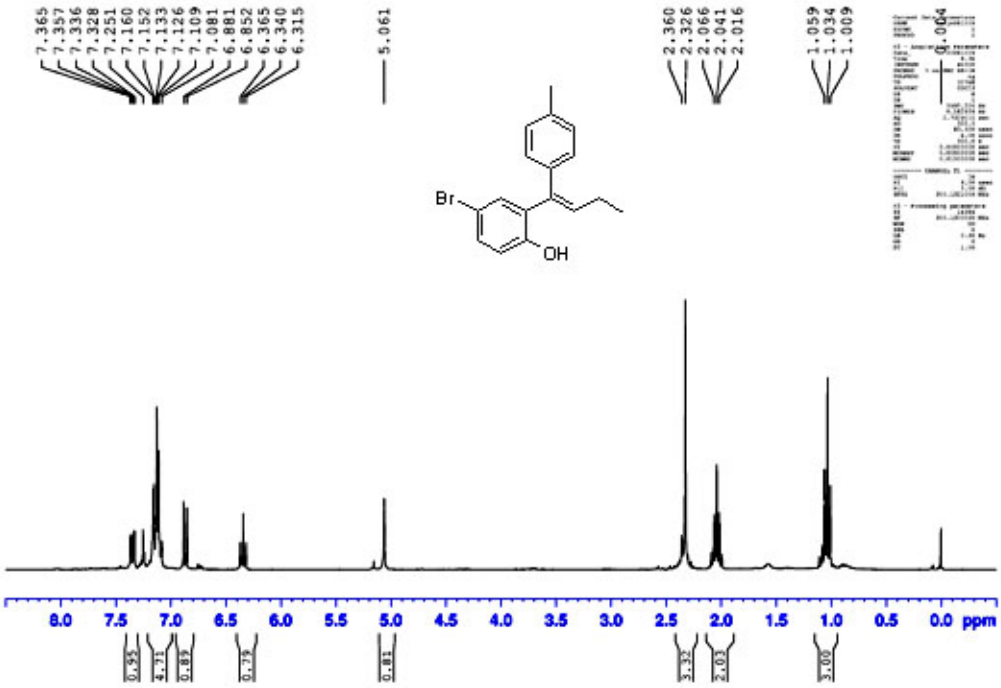

135.658
130.063
129.085
128.668
127.825
126.451
116.730
77.468
77.049
76.624
23.365
13.922
Cl
OH
180
160
140
120
100
80
60
40
20
0
ppm

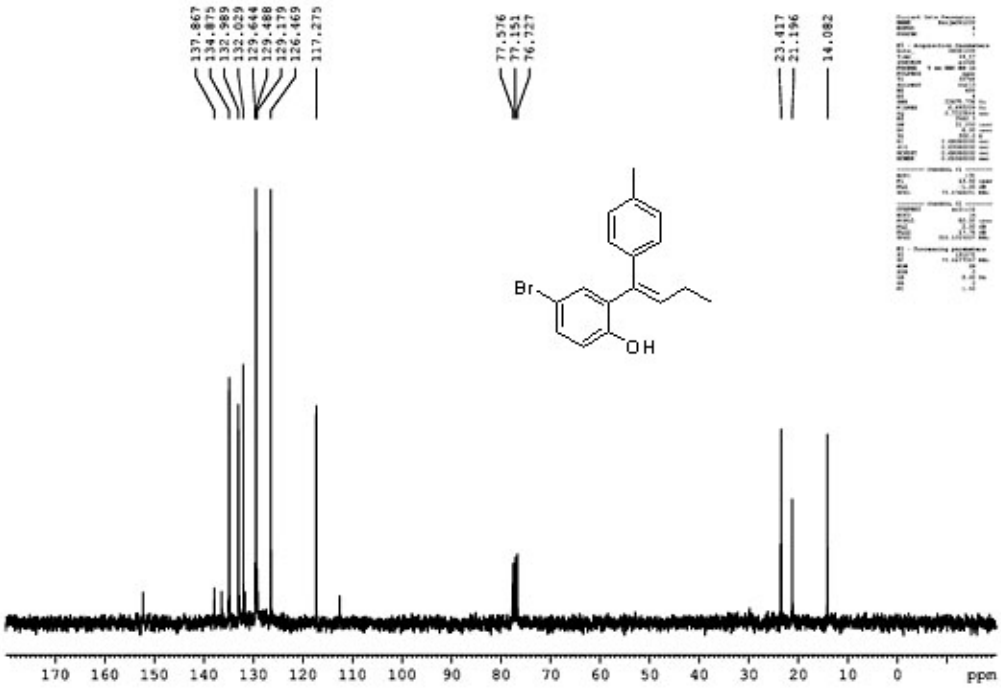
2h


7.249
7.246
7.169
7.141
7.134
7.088
7.067
7.060
7.011
7.005
6.982
6.951
6.926
6.923
6.359
6.335
6.310
5.044
2.367
2.343
2.331
2.309
2.291
2.282
2.061
2.036
2.011
1.102
1.077
1.052
1.041
1.016
1.004
0.991
OH
8
7
6
5
4
3
2
1
0
ppm
6.21
0.97
0.76
2.33
1.45
3.00

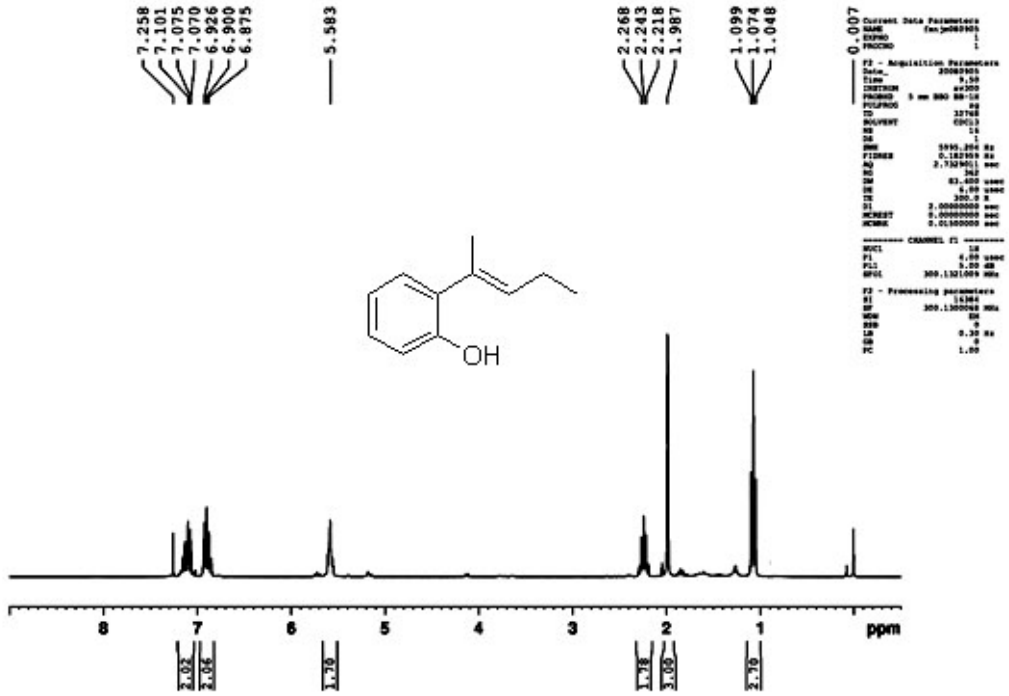

135.311
134.648
130.594
130.390
129.253
129.072
128.787
126.382
120.483
120.325
115.261
77.464
77.040
76.616
23.284
21.064
14.041
OH
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

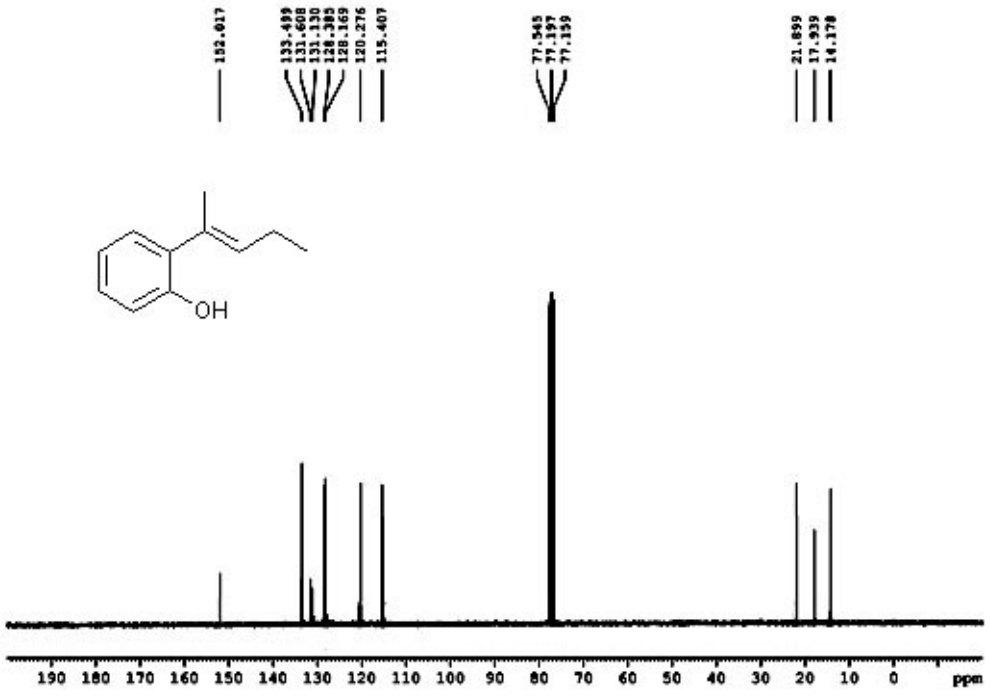
2i


7.365
7.357
7.336
7.328
7.251
7.160
7.152
7.133
7.126
7.109
7.081
6.881
6.852
6.365
6.340
6.315
5.061
2.360
2.326
2.066
2.041
2.016
1.059
1.034
1.009
0.064
Br
OH
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 ppm
0.95
4.71
0.82
0.79
0.81
3.33
2.03
3.00

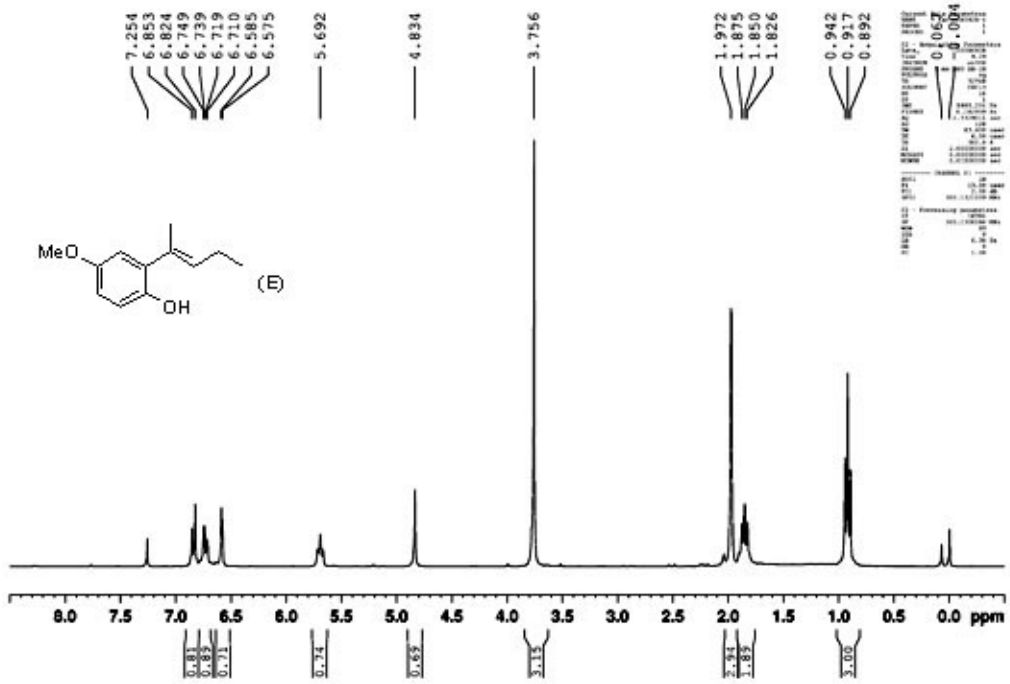

137.867
134.875
133.989
132.029
129.444
129.488
129.179
126.469
117.275
77.576
77.151
76.727
23.417
21.196
14.082
Br
OH
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

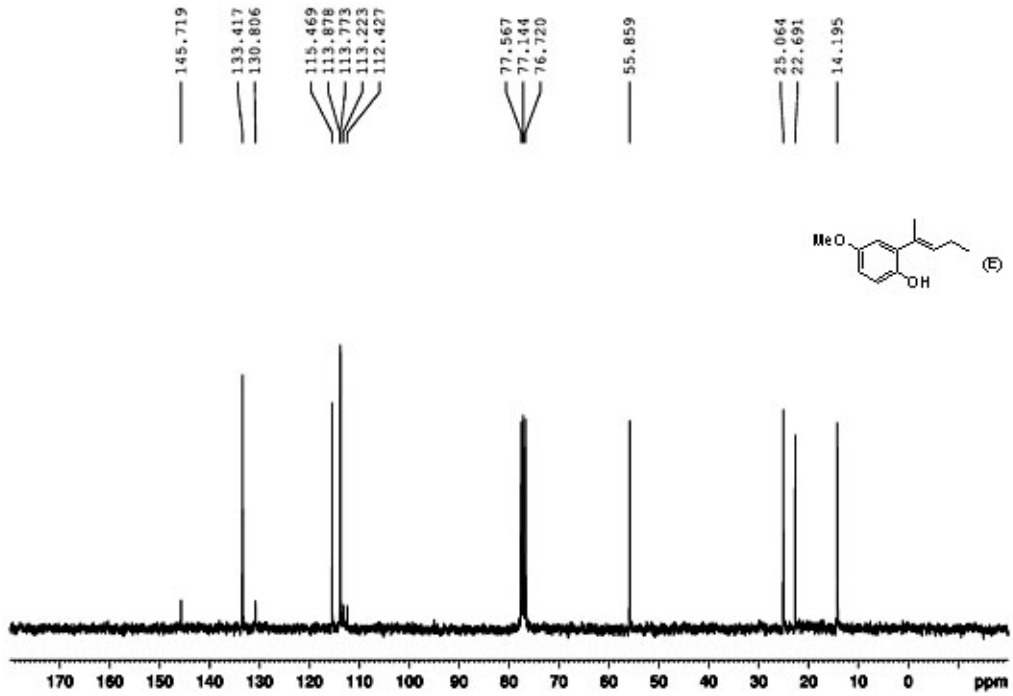
2j


7.258
7.101
7.075
7.070
6.926
6.900
6.875
5.583
2.268
2.243
2.218
1.987
1.099
1.074
1.048
0.007
OH
8
7
6
5
4
3
2
1
ppm
2.02
2.06
1.30
1.78
3.00
2.70

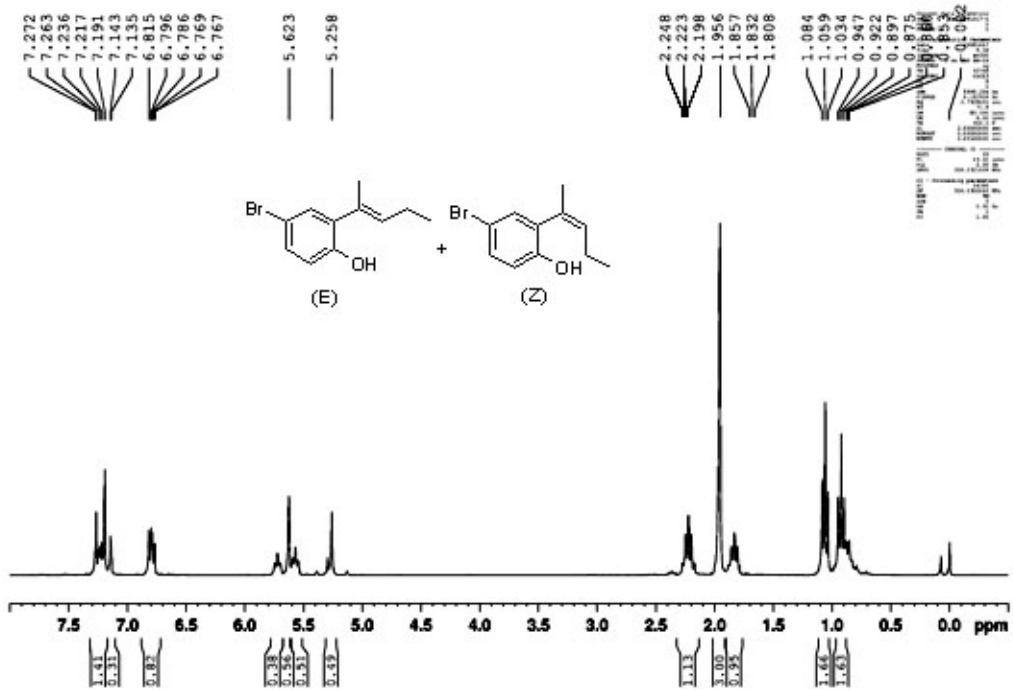

152.017
133.499
131.608
131.130
128.385
128.169
120.276
115.407
77.345
77.197
77.050
21.899
17.939
14.178
OH
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

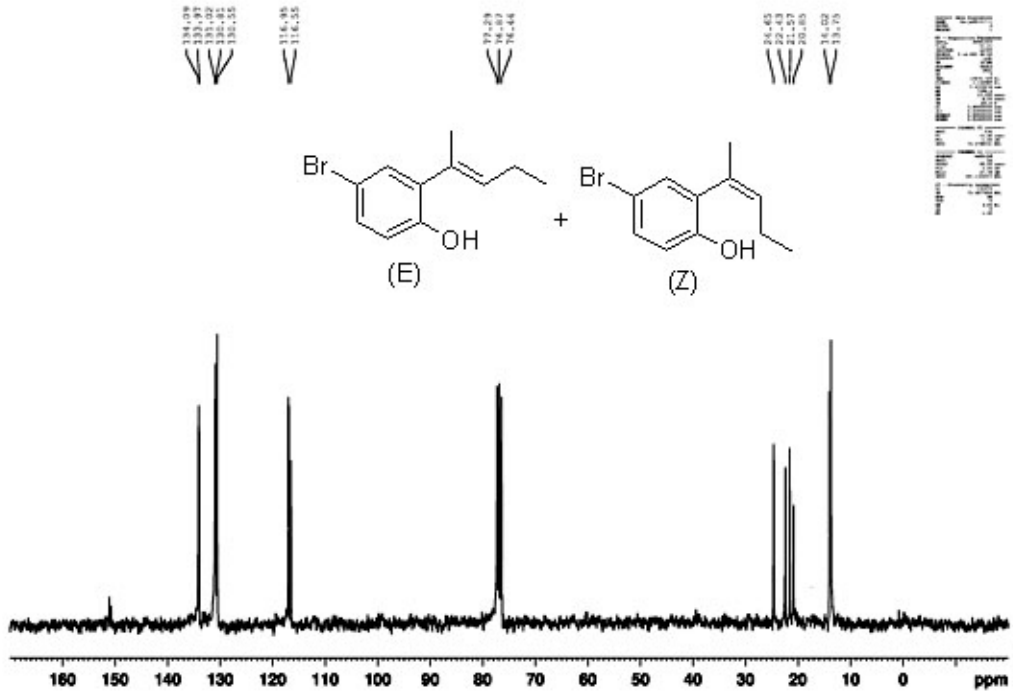
2k


7.254
6.853
6.824
6.749
6.739
6.719
6.710
6.585
6.575
5.692
4.834
3.756
1.972
1.875
1.850
1.826
0.942
0.917
0.892
MeO
OH
(E)
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 ppm

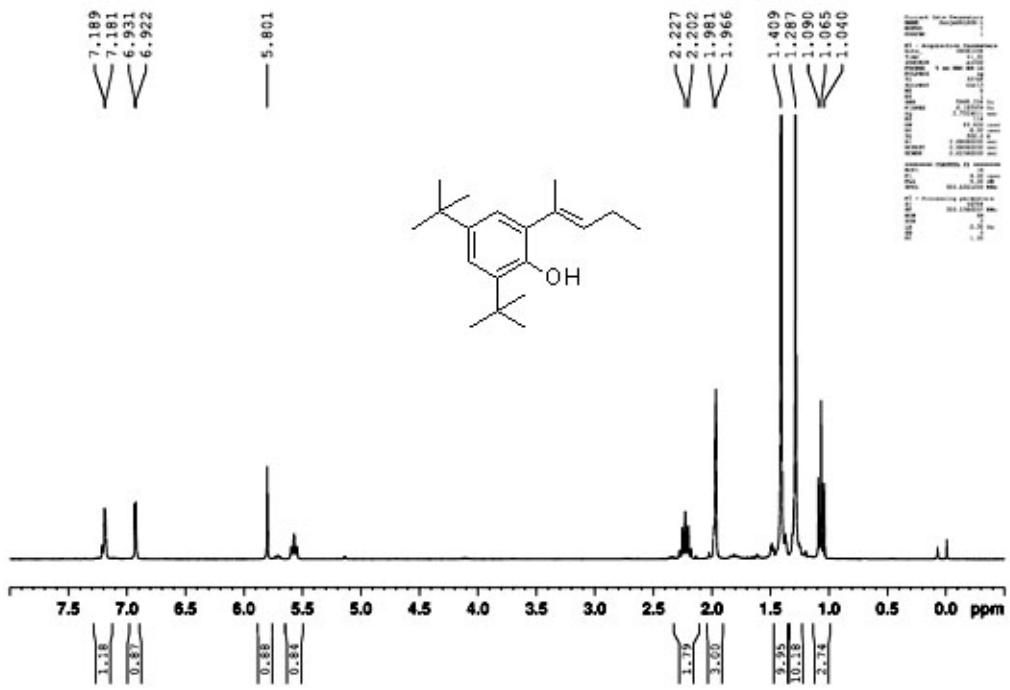

145.719
133.417
130.806
115.469
113.878
113.773
113.223
112.427
77.567
77.144
76.720
55.859
25.064
22.691
14.195
MeO
OH
(E)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

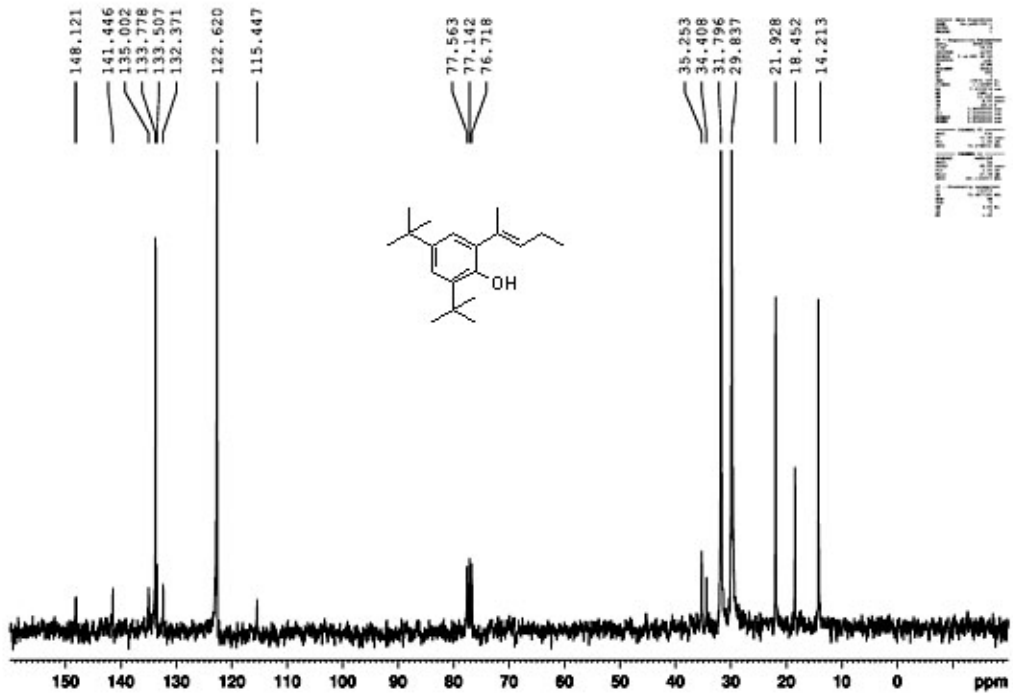
2l



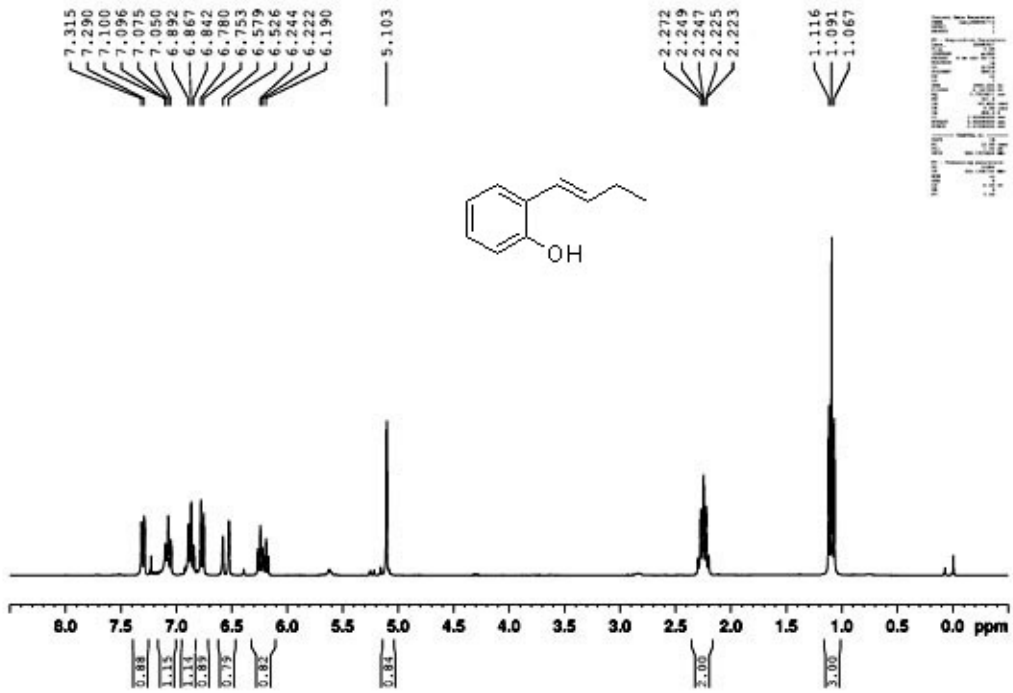


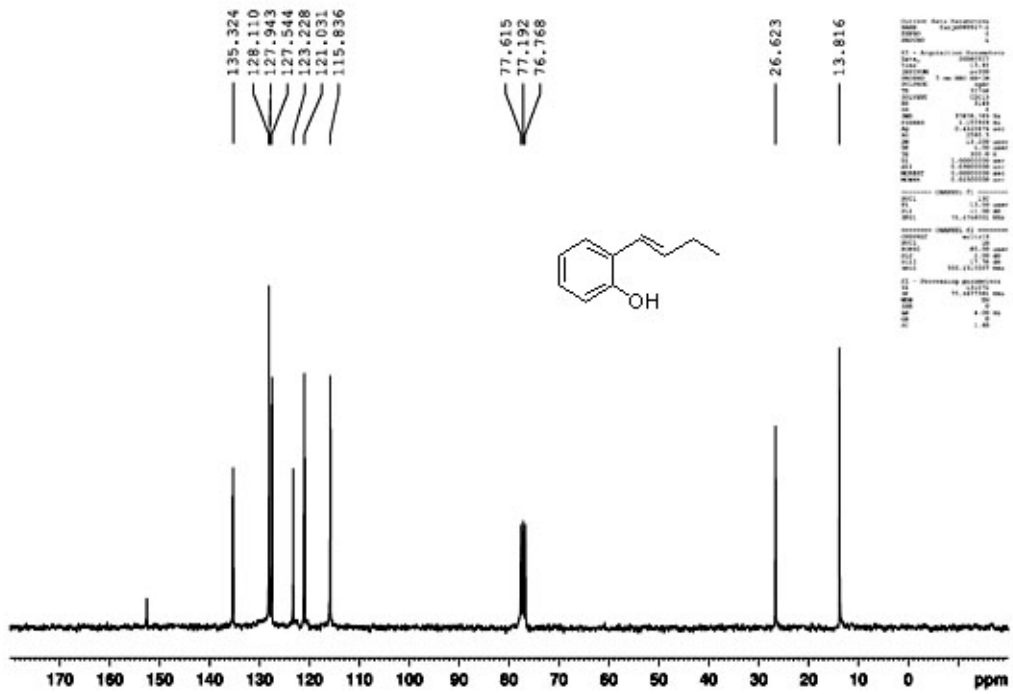
2m


7.189
7.181
6.931
6.922
5.801
2.227
2.202
1.981
1.966
1.409
1.287
1.090
1.065
1.040
OH
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 ppm
1.18
0.87
0.88
0.84
1.79
3.00
9.95
10.18
2.74

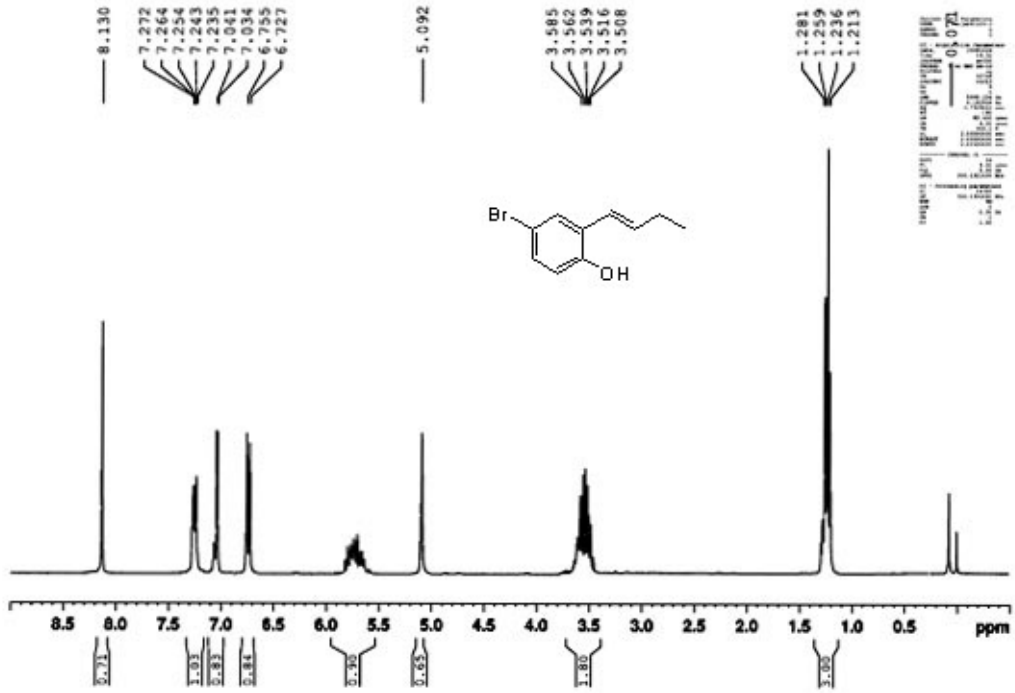

148.121
141.446
135.002
133.778
133.507
132.371
122.620
115.447
77.563
77.142
76.718
35.253
34.408
31.796
29.837
21.928
18.452
14.213
OH
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

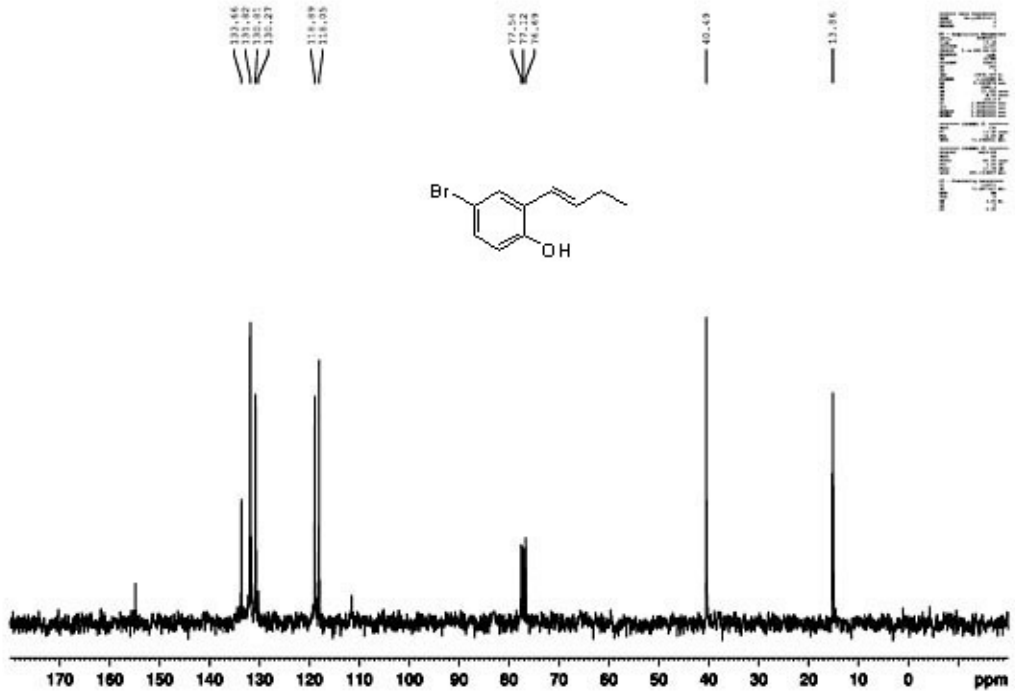
2n


7.315
7.290
7.100
7.096
7.075
7.050
6.892
6.867
6.842
6.780
6.753
6.579
6.526
6.244
6.222
6.190
5.103
2.272
2.249
2.247
2.225
2.223
1.116
1.091
1.067
OH
6.0
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
ppm
0.88
1.15
1.14
0.89
0.79
0.82
0.84
2.00
3.00

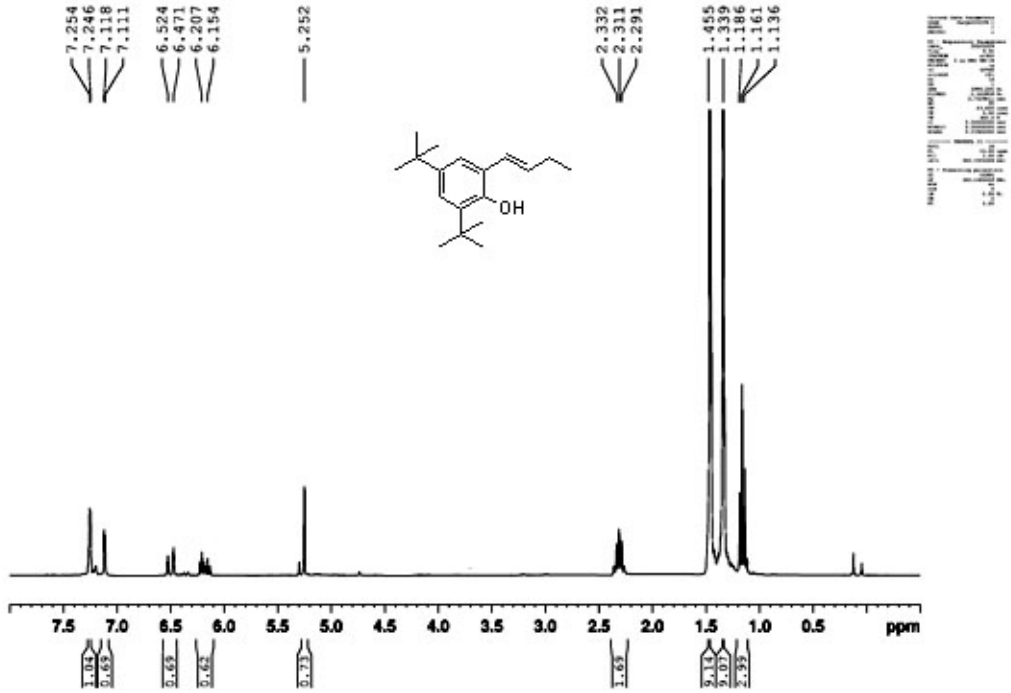

135.324
128.110
127.943
127.544
123.228
121.031
115.836
77.615
77.192
76.768
26.623
13.816
OH
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

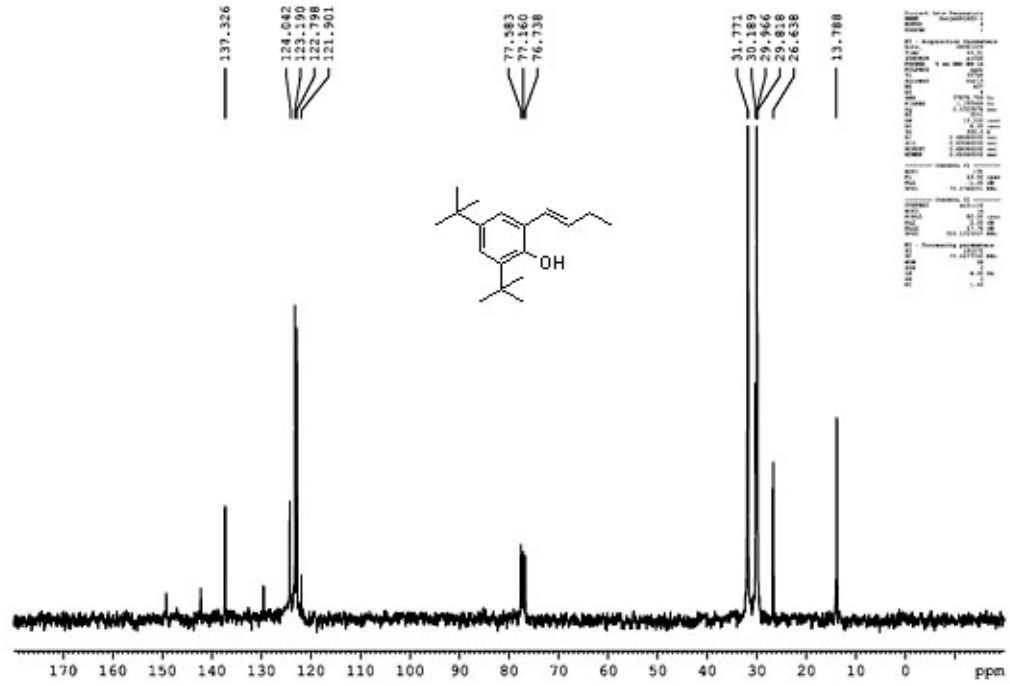
2o


8.130
7.272
7.264
7.254
7.243
7.235
7.041
7.034
6.755
6.727
5.092
3.585
3.562
3.539
3.516
3.508
1.281
1.259
1.236
1.213
Br
OH
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 ppm

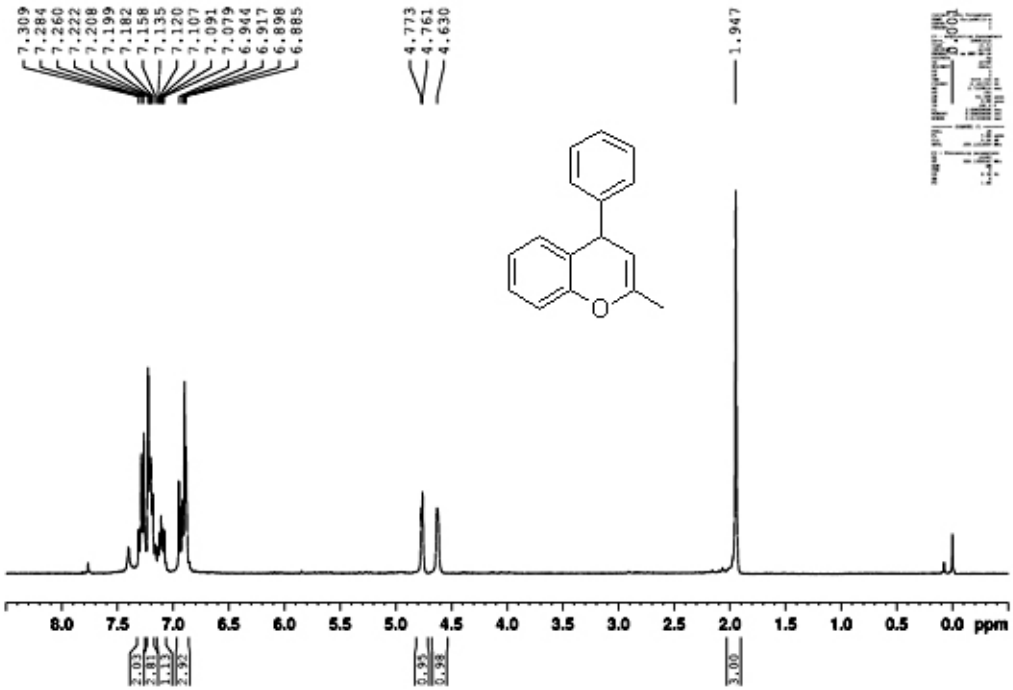

Br
OH
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

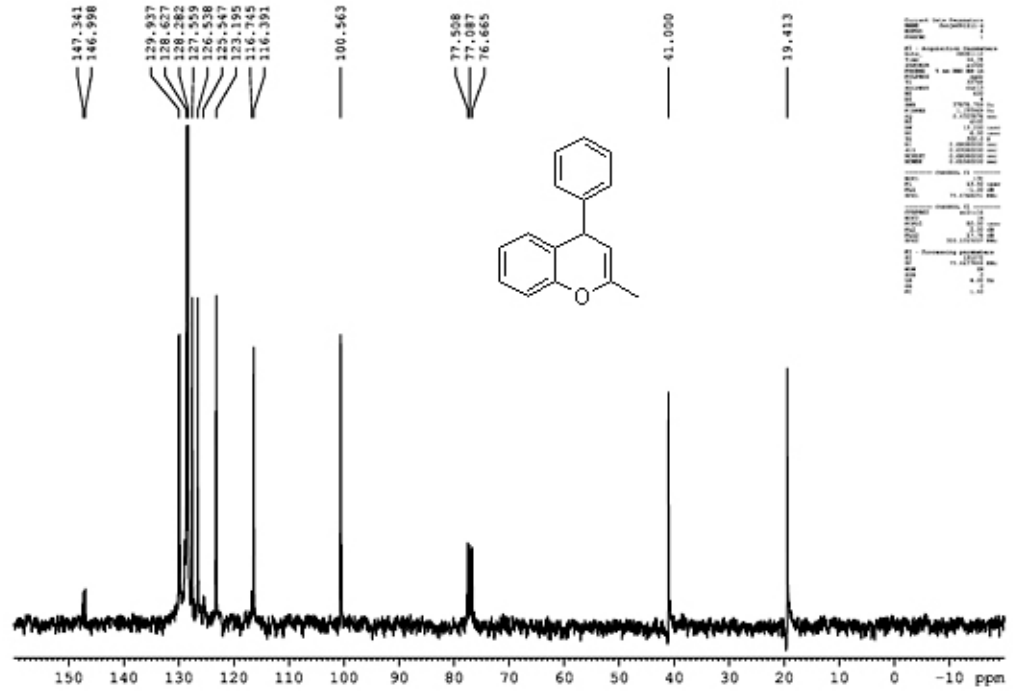
2p


7.254
7.246
7.118
7.111
6.524
6.471
6.207
6.154
5.252
2.332
2.311
2.291
1.455
1.339
1.186
1.161
1.136
OH
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 ppm
1.04
0.69
0.69
0.62
0.73
1.69
9.14
2.07
2.95

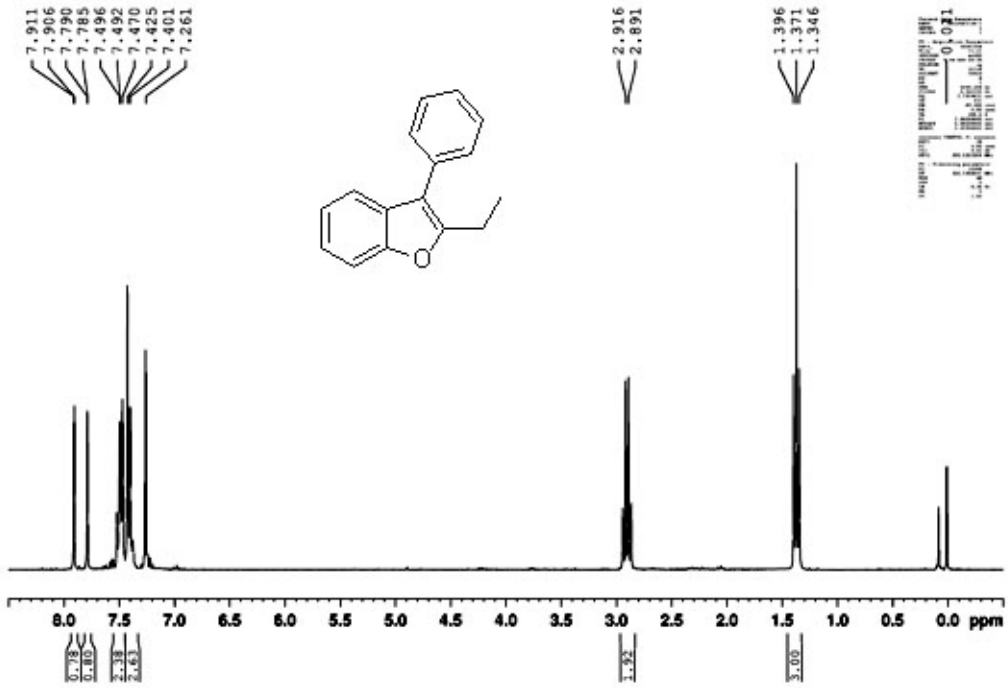

137.326
124.642
123.190
122.798
121.901
77.583
77.160
76.738
31.771
30.189
29.966
29.818
26.638
13.780
OH
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

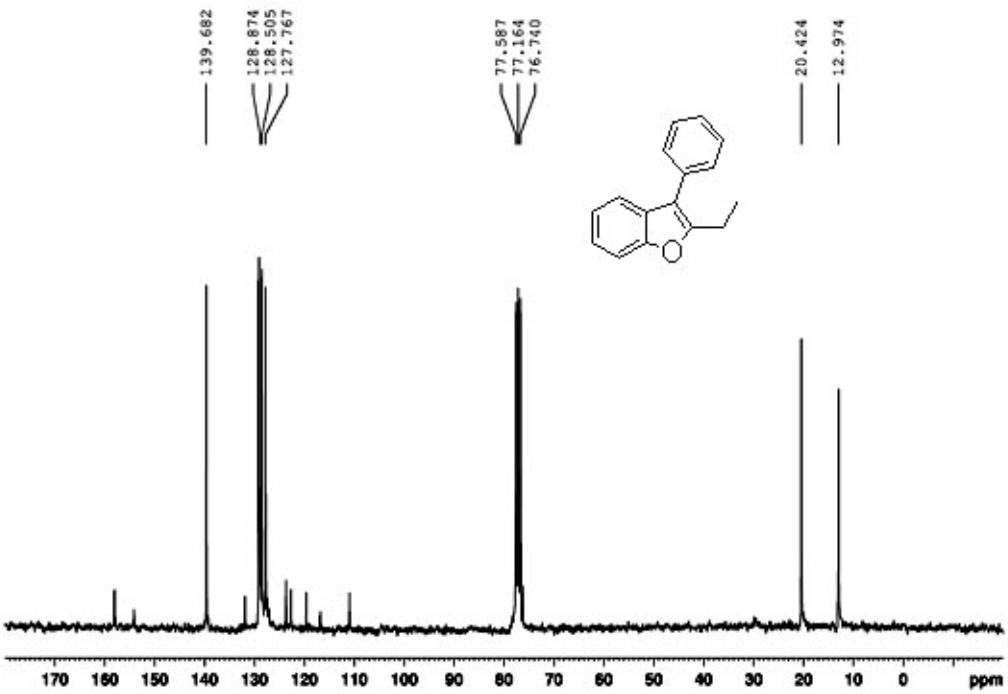
4a


7.309
7.284
7.260
7.222
7.208
7.199
7.182
7.158
7.135
7.120
7.107
7.091
7.079
6.944
6.917
6.898
6.885
4.773
4.761
4.630
1.947
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 ppm
2.03
2.81
1.13
2.92
0.95
0.98
3.00

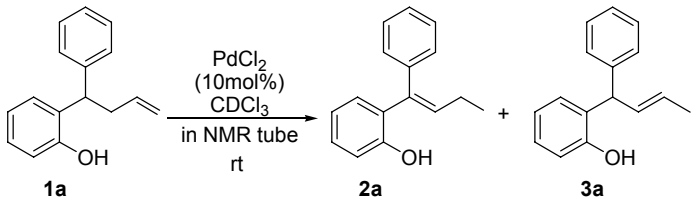

147.341
146.998
129.937
128.627
128.282
127.559
126.538
125.547
123.195
116.745
116.391
100.563
77.508
77.087
76.665
41.000
19.413
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

5a

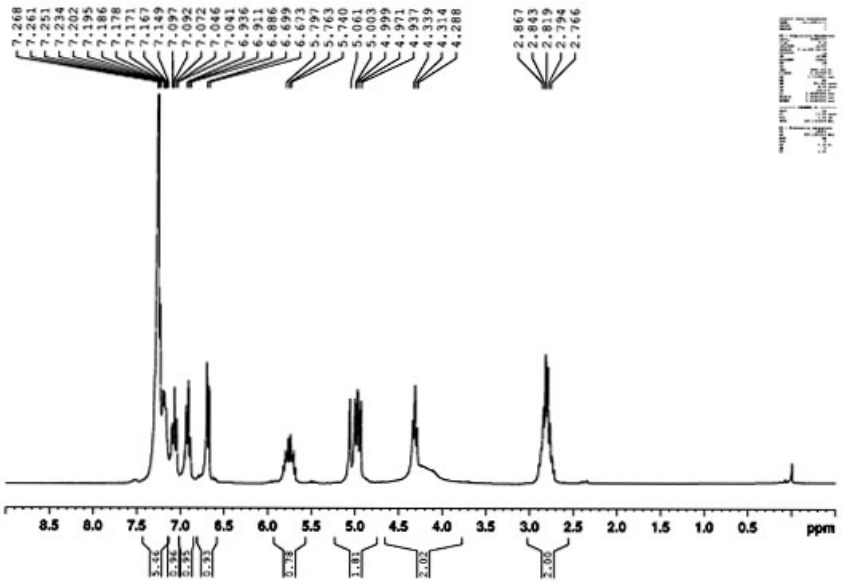

7.911
7.906
7.790
7.785
7.496
7.492
7.470
7.425
7.401
7.261
2.916
2.891
1.396
1.371
1.346
0.078
0.080
2.38
2.63
1.92
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


139.682
128.874
128.505
127.767
77.587
77.164
76.740
20.424
12.974
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

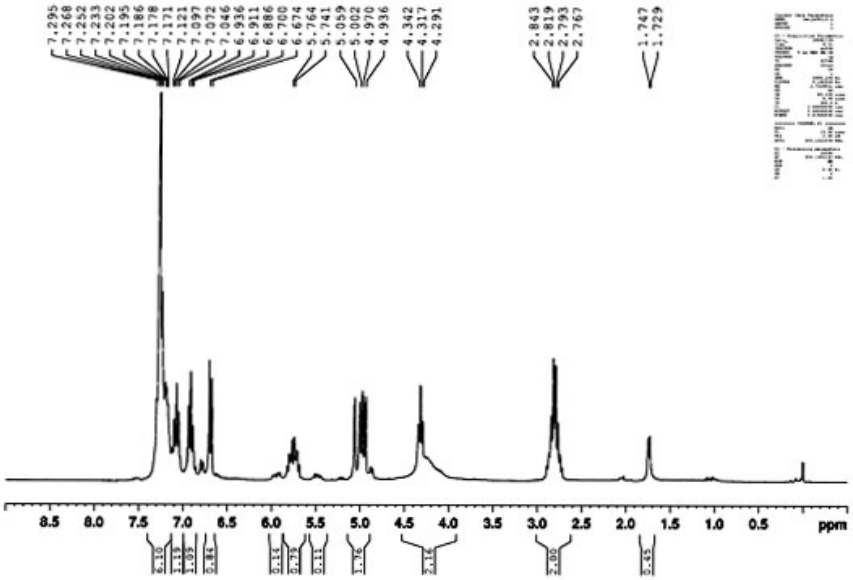
5. Interval NMR experiment



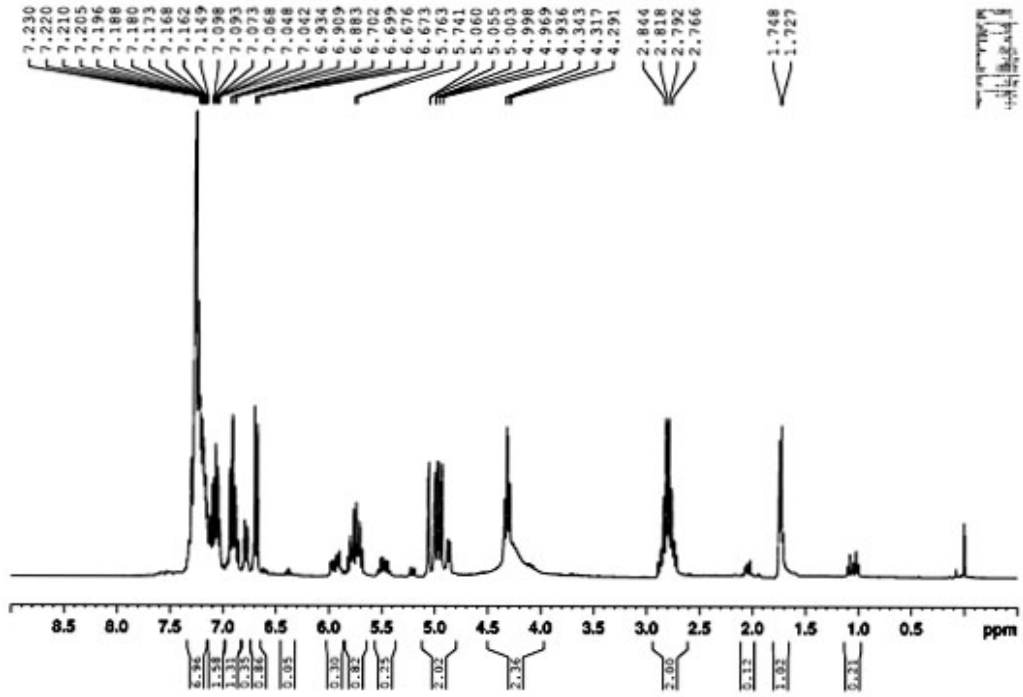
1a **2a** **3a**



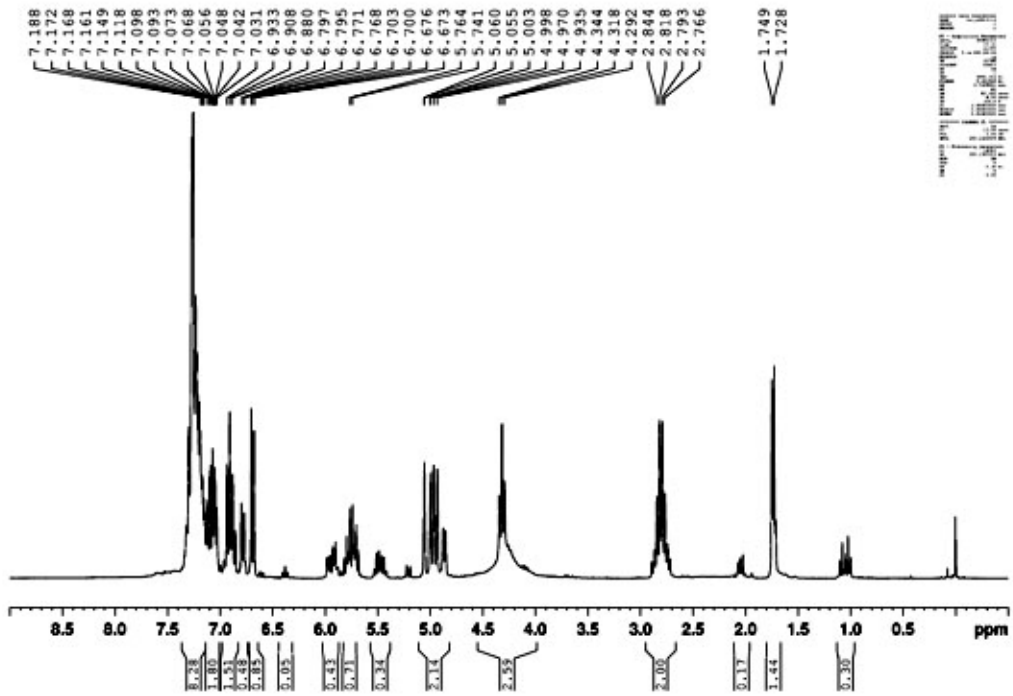
5min



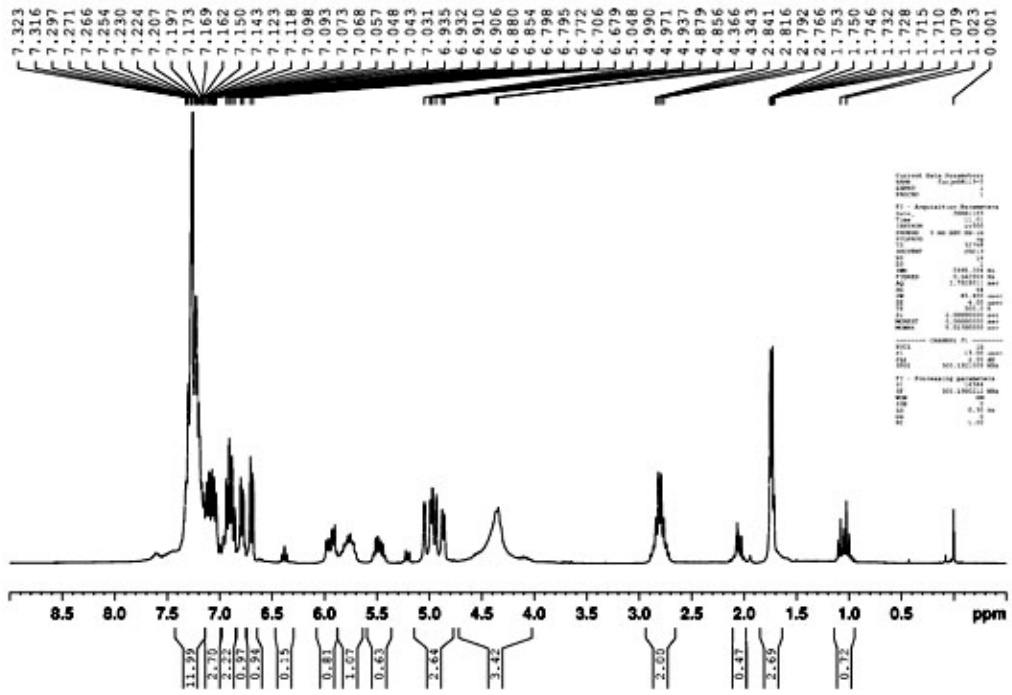
20 min


7.230
7.220
7.210
7.205
7.196
7.188
7.180
7.173
7.168
7.162
7.149
7.098
7.093
7.073
7.068
7.048
7.042
6.934
6.909
6.883
6.702
6.699
6.676
6.673
5.763
5.741
5.060
5.055
5.003
4.998
4.969
4.936
4.343
4.317
4.291
2.844
2.818
2.792
2.766
1.748
1.727
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 ppm
6.96
1.58
1.31
0.95
0.86
0.85
0.70
0.82
0.25
2.02
2.16
2.00
0.13
1.02
0.81

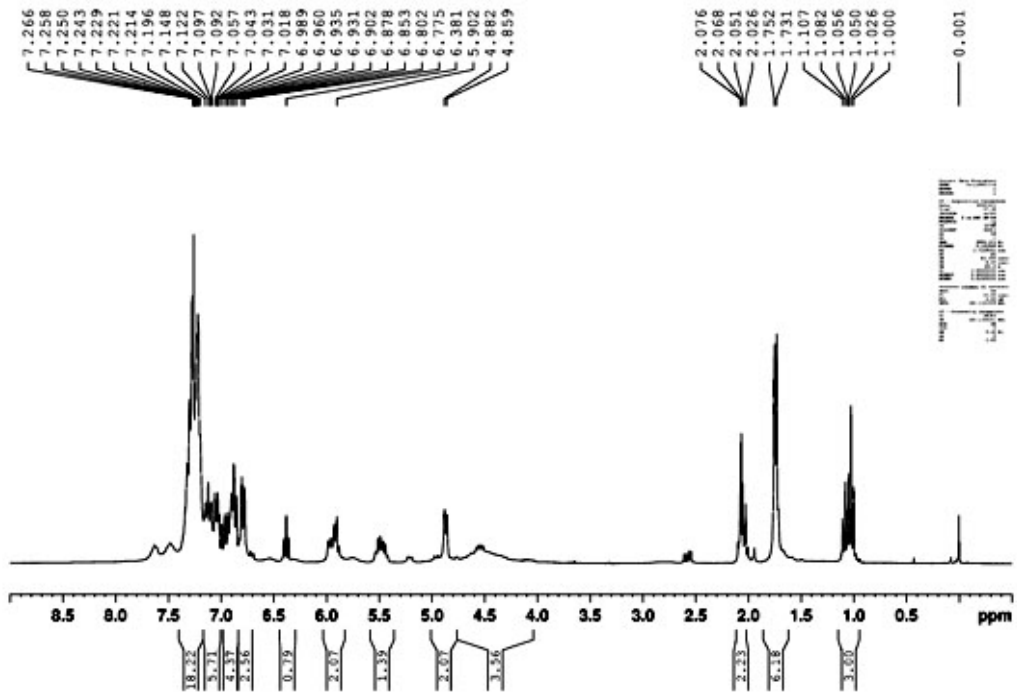
30min


7.188
7.172
7.168
7.161
7.149
7.118
7.098
7.093
7.073
7.068
7.056
7.048
7.042
7.031
6.933
6.908
6.880
6.797
6.795
6.771
6.768
6.703
6.700
6.676
6.673
5.764
5.741
5.060
5.055
5.003
4.998
4.970
4.935
4.344
4.318
4.292
2.844
2.818
2.793
2.766
1.749
1.728
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 ppm
2.28
1.80
1.53
0.48
0.85
0.05
0.42
0.71
0.24
2.14
2.59
2.00
0.17
1.44
0.30

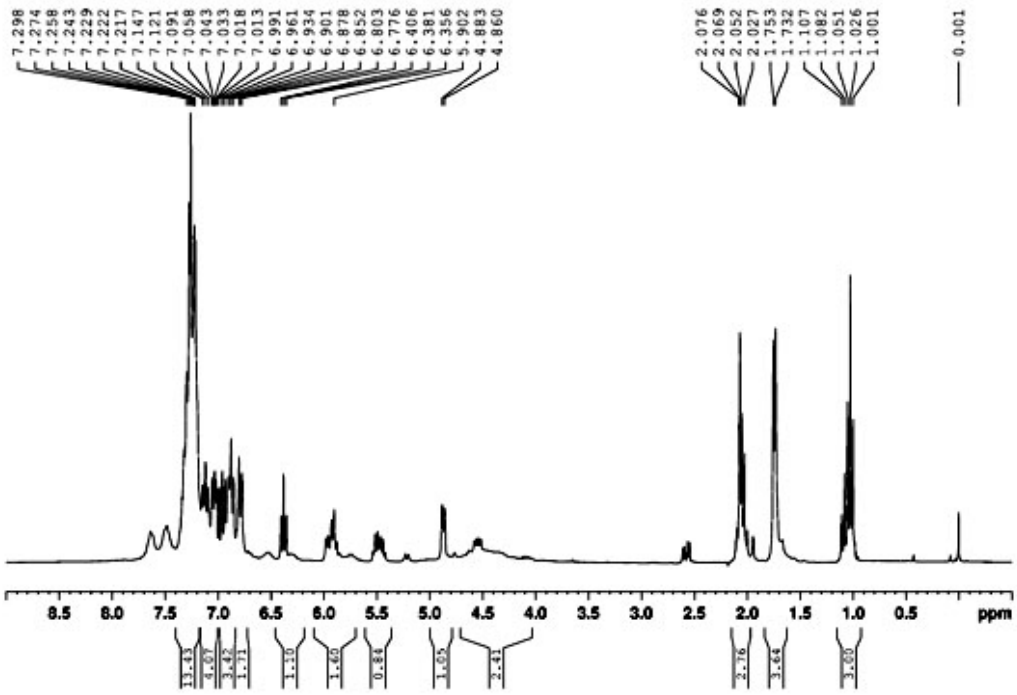
45 min


7.323
7.316
7.297
7.271
7.266
7.254
7.230
7.224
7.207
7.197
7.173
7.169
7.162
7.150
7.143
7.123
7.118
7.098
7.093
7.073
7.068
7.057
7.048
7.043
7.031
6.935
6.932
6.910
6.906
6.880
6.854
6.798
6.795
6.772
6.706
6.679
5.048
4.990
4.971
4.937
4.879
4.856
4.366
4.343
2.841
2.816
2.792
2.766
1.753
1.750
1.746
1.732
1.728
1.715
1.710
1.079
1.023
0.001
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 ppm
11.99
2.70
2.22
0.97
0.94
0.15
0.81
1.07
0.63
2.64
3.42
2.00
0.47
2.69
0.72

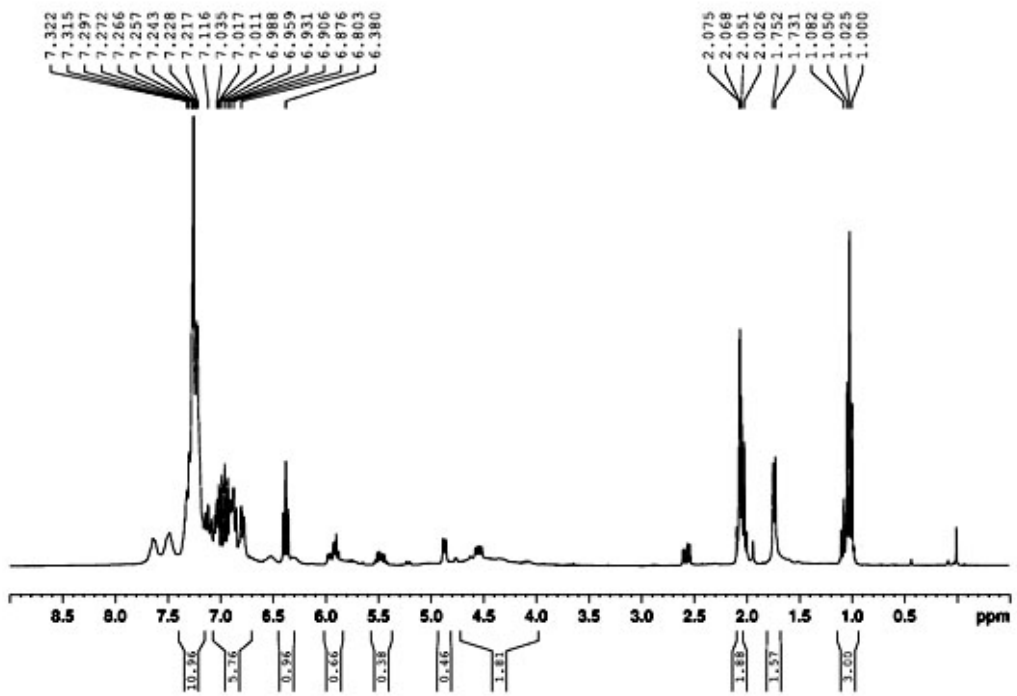
1h


7.266
7.258
7.250
7.243
7.229
7.221
7.214
7.196
7.148
7.122
7.097
7.092
7.057
7.043
7.031
7.018
6.989
6.960
6.935
6.931
6.902
6.878
6.853
6.802
6.775
6.381
5.902
4.882
4.859
2.076
2.068
2.051
2.026
1.752
1.731
1.107
1.082
1.056
1.050
1.026
1.000
0.001
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 ppm
18.22
5.71
4.19
2.56
0.79
2.07
1.39
2.07
3.56
2.23
6.18
3.00

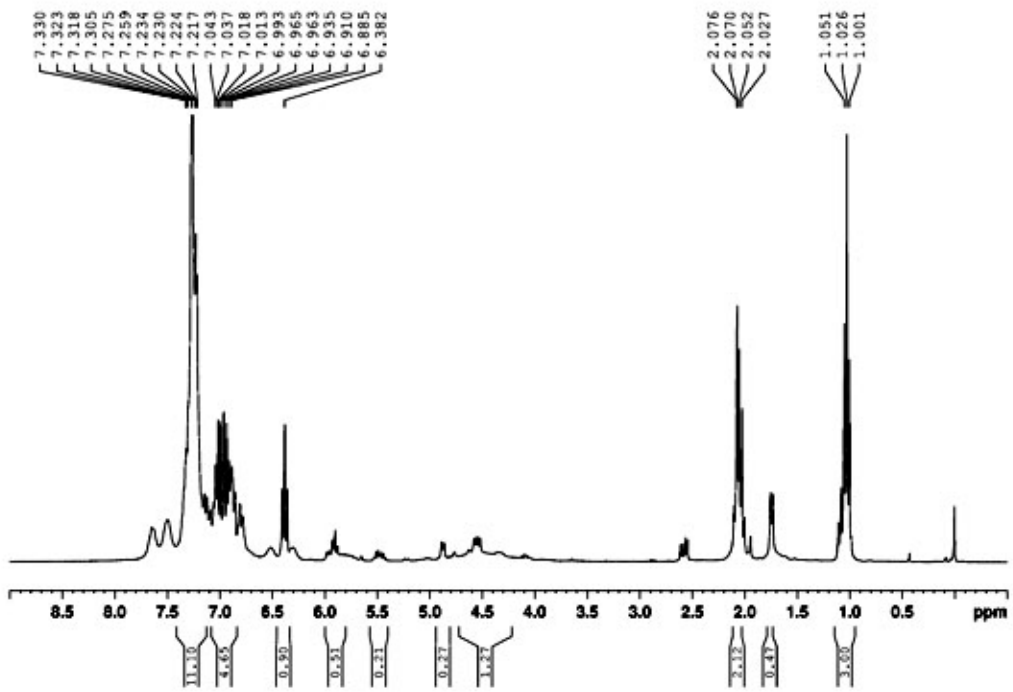
4h


7.298
7.274
7.258
7.243
7.229
7.222
7.217
7.147
7.121
7.091
7.058
7.043
7.033
7.018
7.013
6.991
6.961
6.934
6.901
6.878
6.852
6.803
6.776
6.406
6.381
6.356
5.902
4.883
4.860
2.076
2.069
2.052
2.027
1.753
1.732
1.107
1.082
1.051
1.026
1.001
0.001
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 ppm
13.43
4.07
3.42
1.71
1.10
1.46
0.84
1.05
2.41
2.76
3.64
3.00

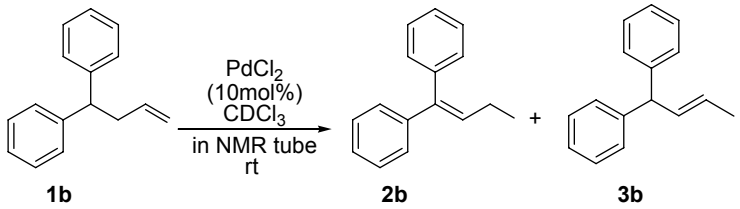
6h

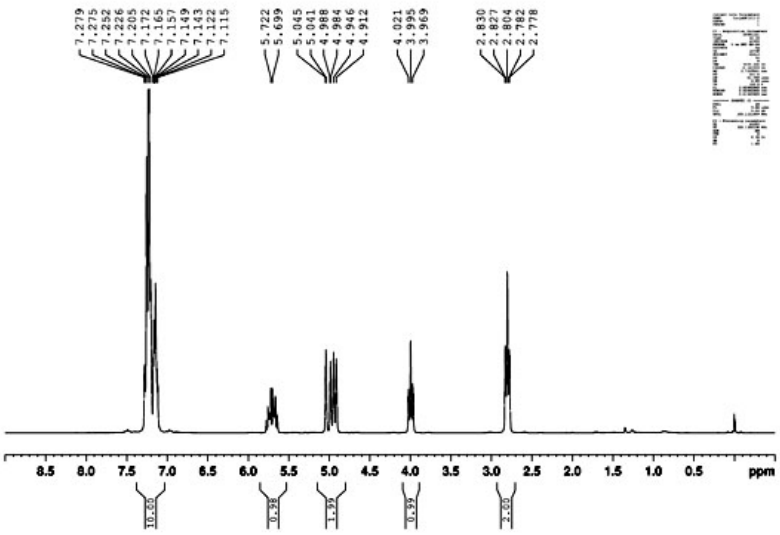

7.322
7.315
7.297
7.272
7.266
7.257
7.243
7.228
7.217
7.116
7.035
7.017
7.011
6.988
6.959
6.931
6.906
6.876
6.803
6.380
2.075
2.068
2.051
2.026
1.752
1.731
1.082
1.050
1.025
1.000
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
10.96
3.76
0.96
0.66
0.38
0.46
1.87
1.88
1.57
3.00

8h

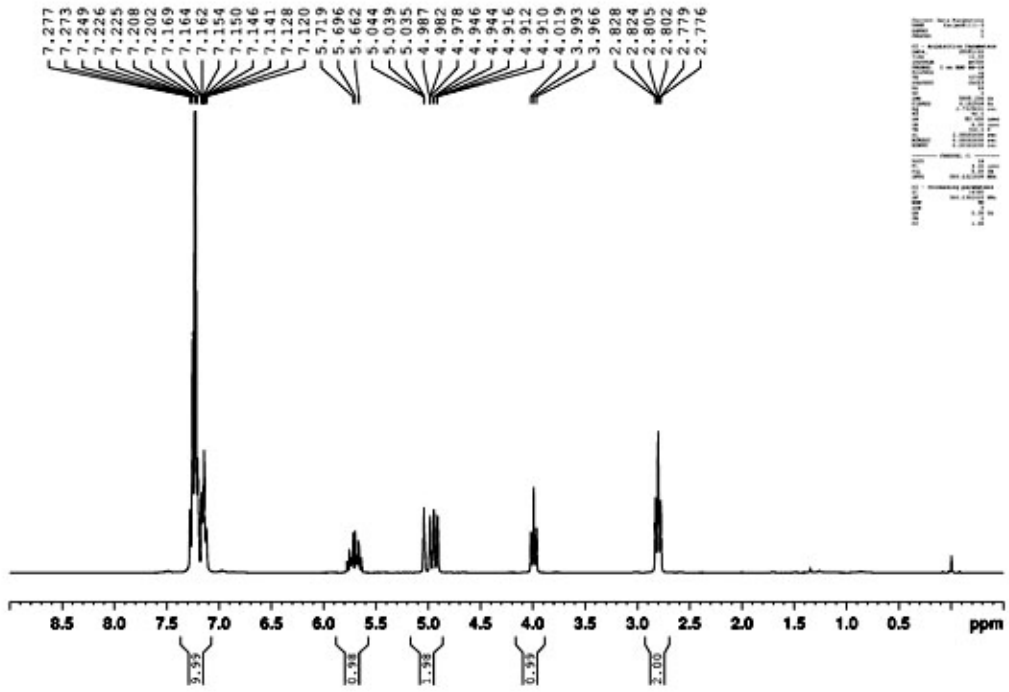

7.330
7.323
7.318
7.305
7.275
7.259
7.234
7.230
7.224
7.217
7.043
7.037
7.018
7.013
6.993
6.965
6.963
6.935
6.910
6.885
6.382
2.076
2.070
2.052
2.027
1.051
1.026
1.001
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
11.10
4.65
0.90
0.51
0.21
0.27
1.27
2.18
0.47
3.00

12h

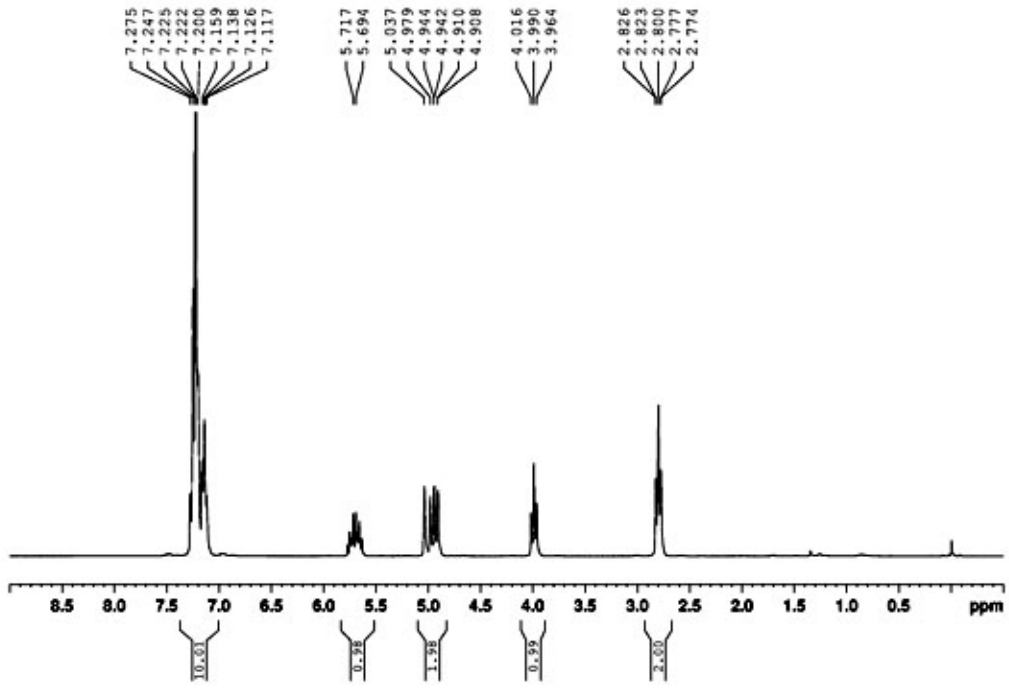

PdCl2
(10mol%)
CDCl3
in NMR tube
rt
+
1b
2b
3b


7.279
7.275
7.252
7.226
7.205
7.172
7.165
7.157
7.149
7.133
7.122
7.115
5.722
5.699
5.045
5.041
4.988
4.984
4.946
4.912
4.021
3.995
3.969
2.830
2.827
2.804
2.782
2.778
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 ppm
10.00
0.98
1.99
0.99
2.00

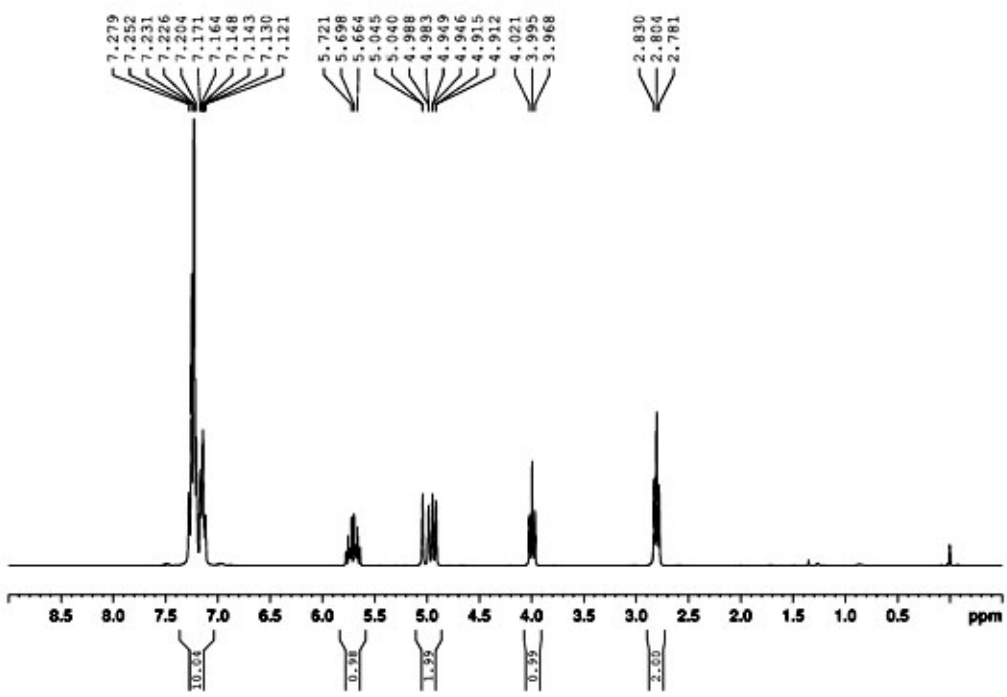
5min


7.277
7.273
7.249
7.226
7.225
7.208
7.202
7.169
7.164
7.162
7.154
7.150
7.146
7.141
7.128
7.120
5.719
5.696
5.662
5.044
5.039
5.035
4.987
4.982
4.978
4.946
4.944
4.916
4.912
4.910
4.019
3.993
3.966
2.828
2.824
2.805
2.802
2.779
2.776
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 ppm
9.99
0.98
1.98
0.99
2.00

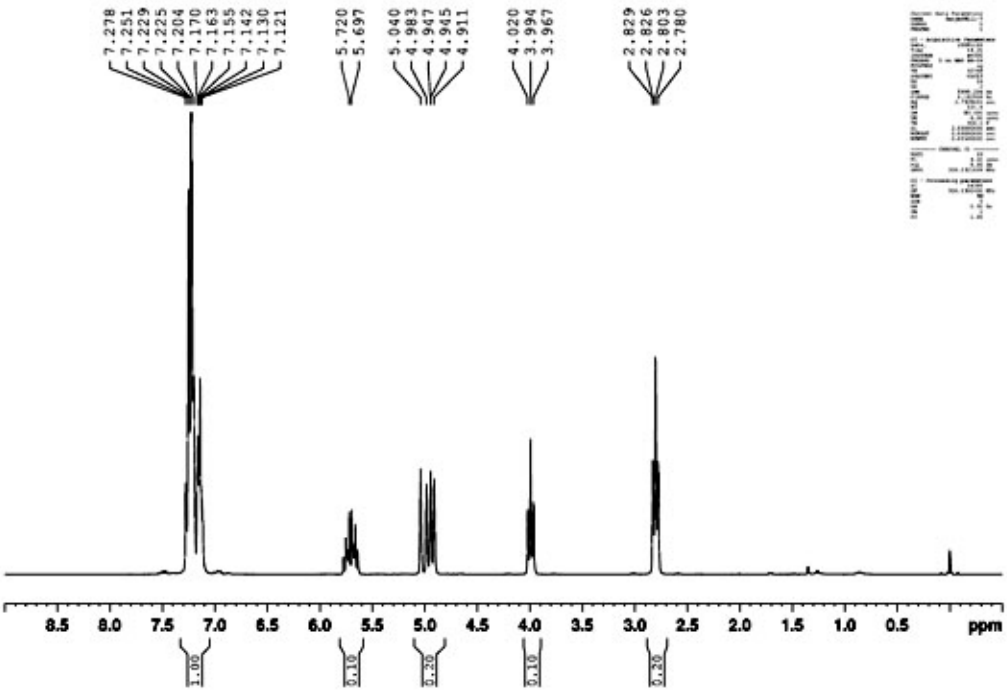
20min


7.275
7.247
7.225
7.222
7.200
7.159
7.138
7.126
7.117
5.717
5.694
5.037
4.979
4.944
4.942
4.910
4.908
4.016
3.990
3.964
2.826
2.823
2.800
2.777
2.774
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 ppm
10.01
0.98
1.98
0.99
2.00

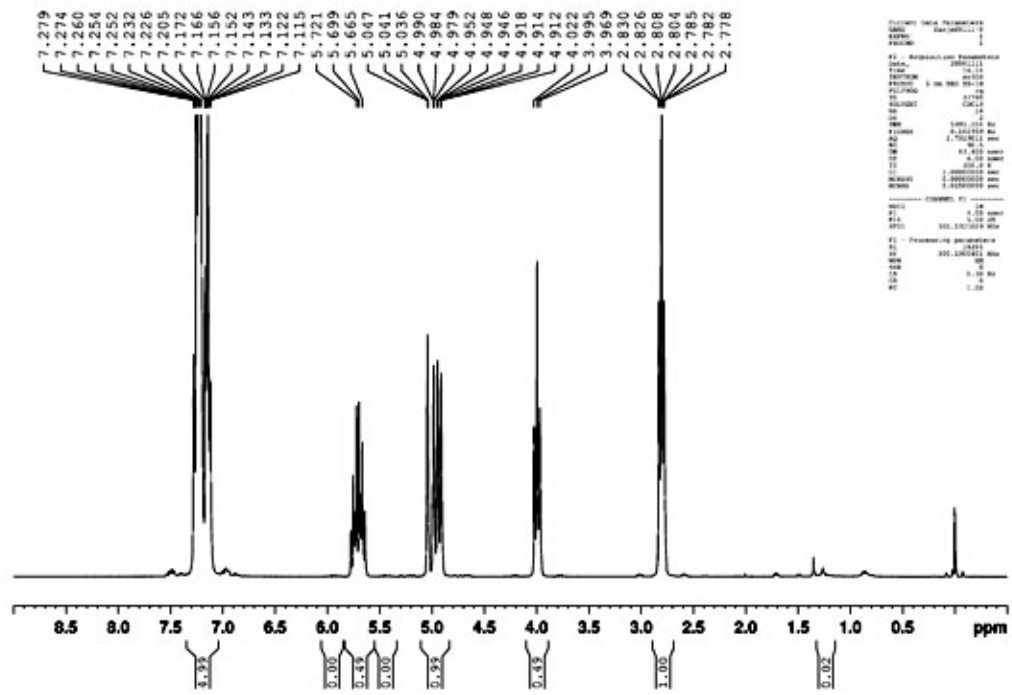
30min


7.279
7.252
7.231
7.226
7.204
7.171
7.164
7.148
7.143
7.130
7.121
5.721
5.698
5.664
5.045
5.040
4.988
4.983
4.949
4.946
4.915
4.912
4.021
3.995
3.968
2.830
2.804
2.781
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 ppm
10.04
0.98
1.99
0.99
2.00

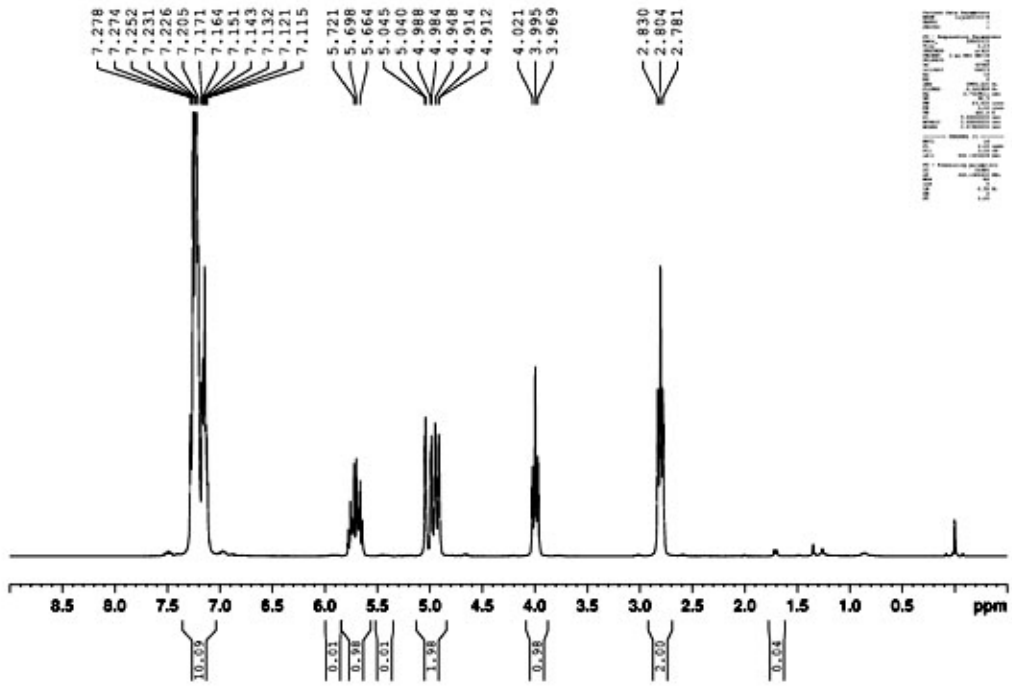
1h


7.278
7.251
7.229
7.225
7.204
7.170
7.163
7.155
7.142
7.130
7.121
5.720
5.697
5.040
4.983
4.947
4.945
4.911
4.020
3.994
3.967
2.829
2.826
2.803
2.780
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 ppm
1.00
0.10
0.20
0.10
0.20

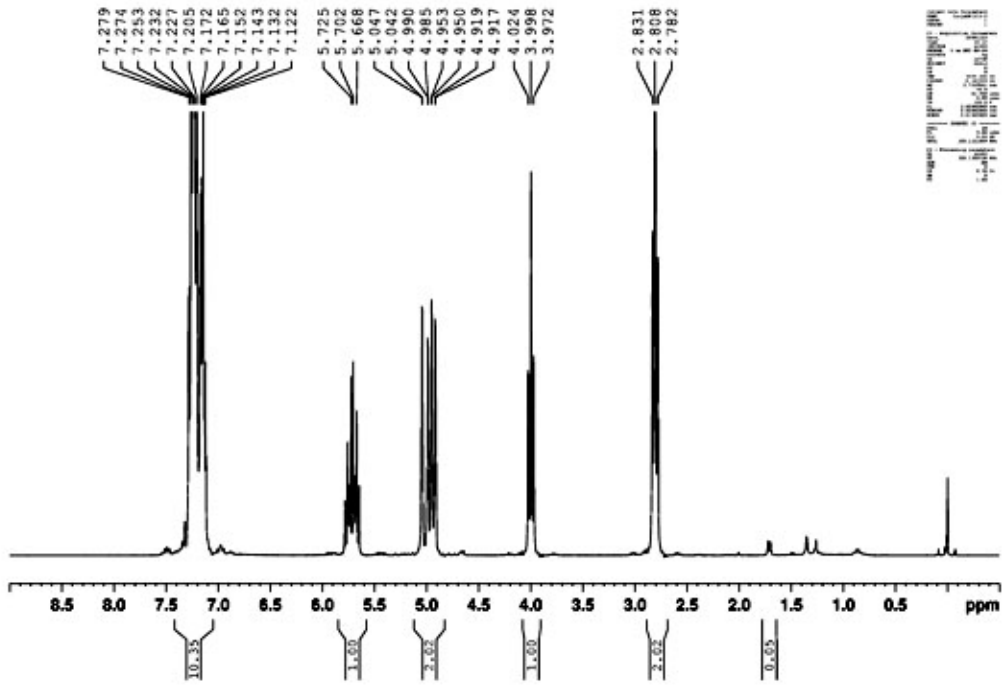
4h


7.279
7.274
7.260
7.254
7.252
7.232
7.226
7.205
7.172
7.166
7.156
7.152
7.143
7.133
7.122
7.115
5.721
5.699
5.665
5.047
5.041
5.036
4.990
4.984
4.979
4.952
4.948
4.946
4.918
4.914
4.912
4.022
3.995
3.969
2.830
2.826
2.808
2.804
2.785
2.782
2.778
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 ppm
1.93
0.00
0.49
0.00
0.99
0.49
1.00
0.02

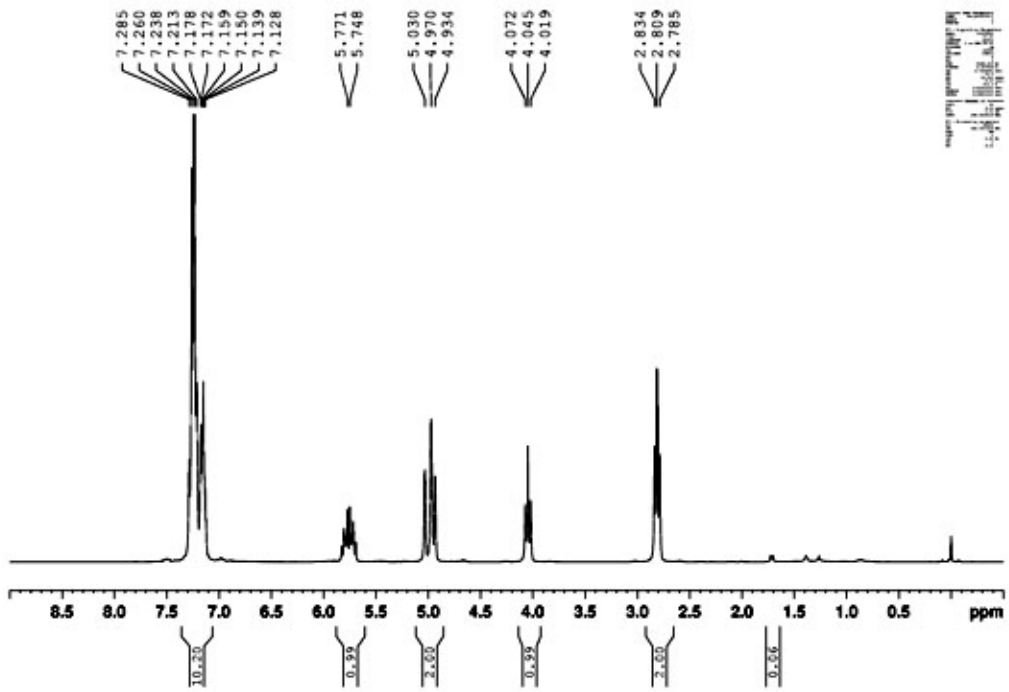
6h


7.278
7.274
7.252
7.231
7.226
7.205
7.171
7.164
7.151
7.143
7.132
7.121
7.115
5.721
5.698
5.664
5.045
5.040
4.988
4.984
4.948
4.914
4.912
4.021
3.995
3.969
2.830
2.804
2.781
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 ppm
10.69
0.01
0.98
0.01
1.98
0.98
2.00
0.64

18h

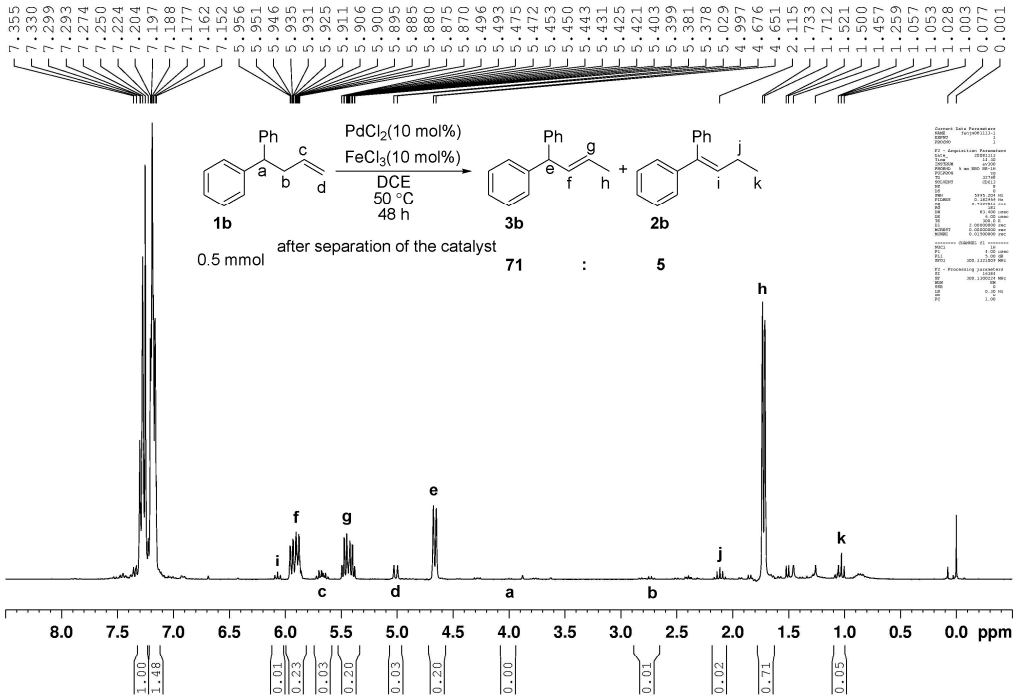

7.279
7.274
7.253
7.232
7.227
7.205
7.172
7.165
7.152
7.143
7.132
7.122
5.725
5.702
5.668
5.047
5.042
4.990
4.985
4.953
4.950
4.919
4.917
4.024
3.998
3.972
2.831
2.808
2.782
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
10.35
1.00
2.02
1.00
2.02
0.65

30h


7.285
7.260
7.238
7.213
7.178
7.172
7.159
7.150
7.139
7.128
5.771
5.748
5.030
4.970
4.934
4.072
4.045
4.019
2.834
2.809
2.785
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 ppm
10.20
0.99
2.00
0.99
2.00
0.56

45h

1b in the optimized conditions



NOESY of 2a