Supplementary information for

Preparation of Modified Chitosan Microspheres Supported Copper Catalysts for The Borylation of α,β-Unsaturated Compounds

Wei Wang[1], Zufeng Xiao[1], Chaofan Huang[1], Kewang Zheng[1], Yin Luo[1], Yumin Dong[1], Zitong Shen[1], Wei Li[1,*], Caiqin Qin[1,2 **]

[1] School of Chemistry and Materials Science, Hubei Engineering University, Xiaogan 432000, China

[2] Key Laboratory of Biological Resources and Environmental Biotechnology, Hubei Province

Wei Wang[1] and Zufeng Xiao[1] are contributed equally.

*Correspondence to: Wei Li (E-mail: weili@hbeu.edu.cn)

** Correspondence to: Caiqin Qin (E-mail: *qincq*@hbeu.edu.cn)

General Procedure for CSM@Cu^0Catalyzed Borylation of α,β-Unsaturated Acceptors in Aqueous Media

In a sample vial, acetone (0.5 mL) and H_2O (0.5 mL) were successively added to a mixture of CSM@Cu^0 (3.8 mg, 1 mol %) and $B_2(pin)_2$ (60.9 mg, 0.24 mmol) under air. The reaction mixture was stirred for 0.5 h at room temperature, followed by successive addition of substrate (**4**) (0.2 mmol). After stirring for 8h at room temperature, the reaction mixture was filtered and the filtrate was extracted with EtOAc (20 mL) three times. The combined organic phase was concentrated under reduced pressure and the residue was dissolved in THF (1 mL) and H_2O (0.5 mL). Excess amount of $NaBO_3$•$4H_2O$ (244 mg) was then added and the mixture was stirred at room temperature for 4 h. The aqueous layer was extracted with EtOAc (20 mL) three times, and the combined organic layers were dried over anhydrous Na_2SO_4. After concentrated under reduced pressure, the crude mixture was purified by preparative TLC to afford the desired product **6**.

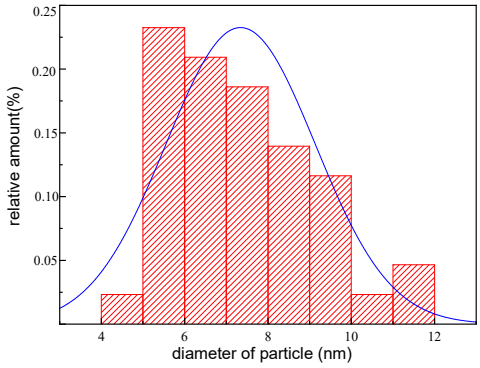


Figure S1. Diameter distribution of copper nanoparticles (CSM@Cu^0)

Table 1S. The content of N, C, H, O of chitosan microspheres (CS) and of modified chitosan microspheres (CSM)

Compound	H(w%)	C(w%)	N(w%)	O(w%)	C:N:O(Atomic%:Atomic%:Atomic%)
CS	6.81	44.91	8.63	39.65	6.04:0.994:4
CSM	5.93	54.23	9.72	30.12	9.6: 1.473:4

Table 2S. The adsorption of the CS and CSM

Entry	Conc. before adsorption (C_0, mg/L)	Adsorption Time (min)	Conc. after adsorption (Ci, mg/L)	Adsorption conc. (mg/L)	Adsorption (%)	Absorption capacity (qi, mg/g)
1[a]	100.63	180	2.62	98.01	97.40	98.01
2[b]	100.32	180	42.71	57.61	57.43	57.43

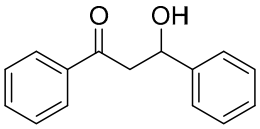
a. CSM, pH =5; b. CS, pH =5

Table. 3S Swelling capability of CSM at different pH value

Entry	pH	Initial quality (m_0, g)	Quality after swelling for 3h (m_i, g)	Quality after drying (m_f, g)	Swelling capability (SC= $\frac{mi-mf}{mf} \times 100\%$)
1	2	0.1036	0.2766	0.0812	240.6
2	3	0.1070	0.2480	0.0939	164.1
3	4	0.1047	0.1528	0.0965	58.3
4	5	0.0999	0.1465	0.0977	49.9

All products are literature-known; obtained analytical data is in full agreement with reported data.

6a. 3-Hydroxy-1,3-diphenylpropan-1-one

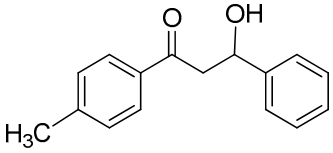


Colorless oil

^{1}H NMR (400 MHz, Chloroform-d) δ 7.96 (d, J = 8.0 Hz, 2H), 7.62 – 7.55 (m, 1H), 7.46 (dd, J = 11.1, 7.6 Hz, 4H), 7.39 (t, J = 7.5 Hz, 2H), 7.34 – 7.28 (m, 1H), 5.36 (t, J = 6.2 Hz, 1H), 3.61 (br, 1H), 3.41 – 3.33 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-d) δ = 199.9, 143.0, 136.5, 133.4, 128.5, 128.4, 128.0, 127.5, 125.6, 69.9, 47.3.

6b. 3-Hydroxy-3-phenyl-1-(*p*-tolyl)propan-1-one

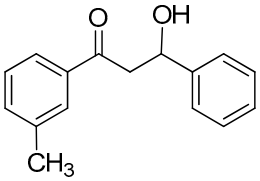


White solid

^{1}H NMR (400 MHz, Chloroform-d) δ 7.86 (d, J = 8.3 Hz, 2H), 7.46 – 7.42 (m, 2H), 7.41 – 7.36 (m, 2H), 7.31 (d, J = 7.3 Hz, 1H), 7.29 – 7.24 (m, 4H), 5.34 (t, J = 7.5 Hz, 1H), 3.66 (br, 1H), 3.38 – 3.31 (m, 2H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 199.8, 144.6, 143.0, 134.1, 129.3, 128.5, 128.2, 127.6, 125.72, 70.1, 47.2, 21.7.

6c. 3-Hydroxy-3-phenyl-1-(*m*-tolyl)propan-1-one



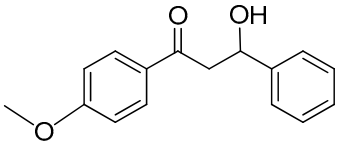
White solid

^{1}H NMR (400 MHz, Chloroform-d) δ 7.78 – 7.73 (m, 2H), 7.47 – 7.43 (m, 2H), 7.42 – 7.28 (m, 5H), 5.34 (td, J = 6.1, 2.0 Hz, 1H), 3.70 (s, 1H), 3.37 (d, J = 6.0 Hz, 2H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 200.3, 142.9, 138.4, 136.5, 134.3, 128.6, 128.5, 128.5, 127.6, 125.7, 125.3, 69.9, 47.3, 21.3.

4. 3-Hydroxy-1-(4-methoxyphenyl)-3-phenylpropan-1-one

6d 3-hydroxy-1-(4-methoxyphenyl)-3-phenylpropan-1-one

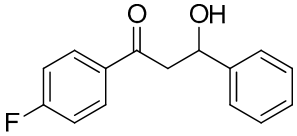


White solid

^{1}H NMR (400 MHz, Chloroform-d) δ 7.96 – 7.90 (m, 2H), 7.47 – 7.42 (m, 2H), 7.41 – 7.34 (m, 2H), 7.31 (d, J = 7.2 Hz, 1H), 6.93 (d, J = 8.9 Hz, 2H), 5.37 – 5.29 (m, 1H), 3.87 (s, 3H), 3.78 –3.73 (br, 1H), 3.37 – 3.24 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-d) δ 199.8, 164.0， 144.6, 143.0, 134.1, 129.3, 128.50 128.24 127.6, 125.7, 70.1, 47.2.

6e. 1-(4-fluorophenyl)-3-hydroxy-3-phenylpropan-1-one

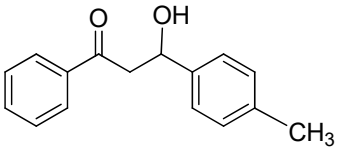


Colorless oil

^{1}H NMR (400 MHz, Chloroform-d) δ 8.02 – 7.93 (m, 2H), 7.47 – 7.41 (m, 2H), 7.41 – 7.35 (m, 2H), 7.34–7.27 (m, 1H), 7.18 – 7.08 (m, 2H), 5.40 – 5.25 (m, 1H), 3.48 (d, J = 2.9 Hz, 1H), 3.42 –3.26 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-d) δ 198.4, 167.2, 164.7, 142.8, 133.0, 133.0, 130.8, 130.8, 128.5, 127.7, 125.7, 115.9, 115.7, 70.0, 47.3.

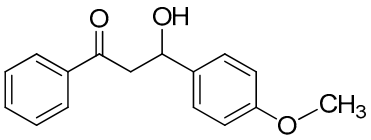
6f. 3-Hydroxy-1-phenyl-3-(*p*-tolyl)propan-1-one



Colorless oil

^{1}H NMR (400 MHz, Chloroform-d) δ 7.99 – 7.92 (m, 2H), 7.61 – 7.55 (m, 1H), 7.51 – 7.42 (m, 2H), 7.36 – 7.30 (m, 2H), 7.19 (d, J = 7.8 Hz, 2H), 5.32 (s, 1H), 3.54 (d, J = 2.7 Hz, 1H), 3.45 – 3.30 (m, 2H), 2.36 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-d) δ 200.0, 140.0, 137.2, 136.5, 133.5, 129.1, 128.6, 128.0, 125.6, 69.8, 47.34, 21.06.

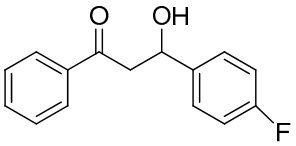
6g. 3-Hydroxy-3-(4-methoxyphenyl)-1-phenylpropan-1-one



White solid

^{1}H NMR (400 MHz, Chloroform-d) δ 7.99 – 7.93 (m, 2H), 7.61 – 7.55 (m, 1H), 7.47 (dd, J = 8.4, 7.0 Hz, 2H), 7.41 – 7.34 (m, 2H), 6.95 – 6.88 (m, 2H), 5.30 (s, 1H), 3.81 (s, 3H), 3.52 (d, J = 2.8 Hz, 1H), 3.43 – 3.29 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-d) δ 200.0, 158.9, 136.5, 135.1, 133.4, 128.5, 128.0, 126.9, 113.8, 69.6, 55.1, 47.2.

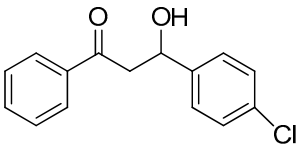
6h. 3-(4-fluorophenyl)-3-hydroxy-1-phenylpropan-1-one



Colorless oil

^{1}H NMR (400 MHz, Chloroform-d) δ 8.00 – 7.92 (m, 2H), 7.64 – 7.56 (m, 1H), 7.47 (t, J = 7.7 Hz, 2H), 7.44 – 7.38 (m, 2H), 7.12 – 7.01 (m, 2H), 5.52 – 5.08 (m, 1H), 3.62 (d, J = 2.9 Hz, 1H), 3.49 – 3.07 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-d) δ 200.00, 163.4, 160.9, 138.7, 138.7, 136.5, 133.7, 128.7, 128.1, 127.4, 127.3, 115.4, 115.2, 69.4, 47.3.

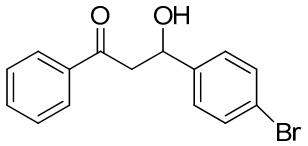
6i. 3-(4-chlorophenyl)-3-hydroxy-1-phenylpropan-1-one



Colorless oil

^{1}H NMR (400 MHz, Chloroform-d) δ 7.98 – 7.91 (m, 2H), 7.64 – 7.56 (m, 1H), 7.50 – 7.43 (m, 2H), 7.40 – 7.31 (m, 4H), 5.33 (dt, J = 7.6, 3.7 Hz, 1H), 3.64 (q, J = 3.0 Hz, 1H), 3.40 – 3.25 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-d) δ 199.8, 141.4, 136.3, 133.7, 133.2, 128.6, 128.6, 128.0, 127.1, 127.1, 77.3, 76.7, 69.3, 47.2.

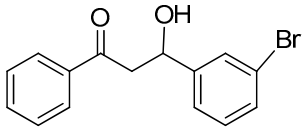
6j. 3-(4-bromophenyl)-3-hydroxy-1-phenylpropan-1-one



Colorless oil

^{1}H NMR (400 MHz, Chloroform-d) δ 7.97 – 7.92 (m, 2H), 7.64 – 7.57 (m, 1H), 7.54 – 7.44 (m, 4H), 7.34 (s, 2H), 5.30 (s, 2H), 3.63 (d, J = 3.0 Hz, 1H), 3.41 – 3.24 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-d) δ 199.9, 141.9, 136.4, 133.8, 131.6, 128.7, 128.1, 127.5, 121.4, 69.4, 47.2.

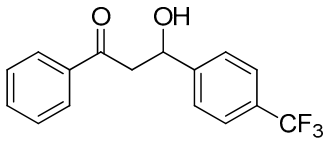
6k. 3-(3-bromophenyl)-3-hydroxy-1-phenylpropan-1-one



Colorless oil

^{1}H NMR (400 MHz, Chloroform-d) δ 8.02 – 7.96 (m, 2H), 7.67 – 7.61 (m, 2H), 7.55 – 7.44 (m, 3H), 7.39 (dt, J = 7.9, 1.4 Hz, 1H), 7.31 – 7.27 (m, 1H), 5.36 (d, J = 4.6 Hz, 1H), 3.79 (d, J = 3.1 Hz, 1H), 3.56 – 3.15 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-d) δ 199.8, 145.2, 136.2, 133.7, 130.6, 130.1, 128.8, 128.7, 128.1, 124.3, 122.6, 69.2, 47.1.

6l 3-Hydroxy-1-phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one

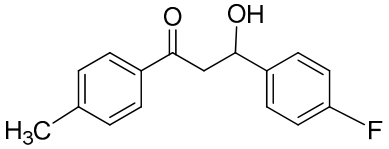


Colorless oil

^{1}H NMR (400 MHz, Chloroform-d) δ 7.99 – 7.92 (m, 2H), 7.64 (d, J = 8.2 Hz, 2H), 7.58 (dd, J = 11.8, 7.8 Hz, 3H), 7.48 (t, J = 7.8 Hz, 2H), 7.37 (d, J = 5.8 Hz, 1H), 5.45 – 5.37 (m, 1H), 3.72 (d, J = 3.1 Hz, 1H), 3.46 – 3.29 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 199.8, 146.9, 136.3, 133.8, 128.8, 128.1, 126.0, 125.5, 125.5, 69.4, 47.2.

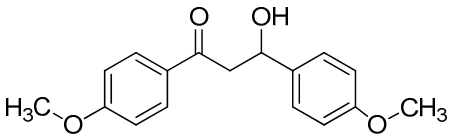
6m. 3-(4-fluorophenyl)-3-hydroxy-1-(p-tolyl)propan-1-one



Colorless oil

^{1}H NMR (400 MHz, Chloroform-d) δ 7.89 – 7.81 (m, 2H), 7.45 – 7.36 (m, 2H), 7.30 – 7.23 (m, 3H), 7.11 – 7.01 (m, 2H), 5.37 – 5.27 (m, 1H), 3.71 (d, J = 2.8 Hz, 1H), 3.41 – 3.22 (m, 2H), 2.42 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-d) δ 199.6, 163.3, 160.8, 144.6, 138.8, 138.7, 133.9, 129.3, 128.2, 127.4, 127.3, 115.3, 115.1, 77.3, 76.9, 76.6, 69.4, 47.1, 21.6.

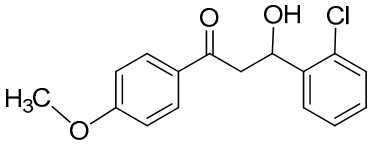
6n. 3-Hydroxy-1,3-bis(4-methoxyphenyl)propan-1-one



White solid

^{1}H NMR (400 MHz, Chloroform-d) δ 7.97 – 7.88 (m, 2H), 7.42 – 7.32 (m, 2H), 6.91 (t, J = 8.4 Hz, 4H), 5.26 (td, J = 6.2, 2.5 Hz, 1H), 3.83 (d, J = 23.1 Hz, 6H), 3.72 (t, J = 2.4 Hz, 1H), 3.29 (d, J = 6.1 Hz, 2H).
^{13}C NMR (101 MHz, Chloroform-d) δ 198.8, 163.9, 159.1, 135.3, 130.5, 129.7, 127.0, 113.9, 113.8, 69.8, 55.5, 55.3, 46.9.

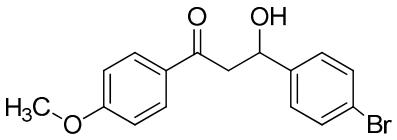
6o. 3-(2-chlorophenyl)-3-hydroxy-1-(4-methoxyphenyl)propan-1-one



White solid

^{1}H NMR (400 MHz, Chloroform-d) δ 7.97 – 7.90 (m, 2H), 7.72 (dd, J = 7.6, 1.7 Hz, 1H), 7.37 – 7.30 (m, 2H), 7.23 (td, J = 7.6, 1.7 Hz, 1H), 6.95 – 6.89 (m, 2H), 5.66 (d, J = 9.7 Hz, 1H), 4.06 (dt, J = 3.1, 1.5 Hz, 1H), 3.86 (d, J = 0.9 Hz, 3H), 3.58 – 3.44 (m, 1H), 3.07 (dd, J = 17.5, 9.6 Hz, 1H).
^{13}C NMR (101 MHz, Chloroform-d) δ 198.8, 163.9, 140.4, 131.0, 130.5, 129.4, 129.2, 128.4, 127.2, 127.2, 113.8, 66.9, 55.7, 44.7.

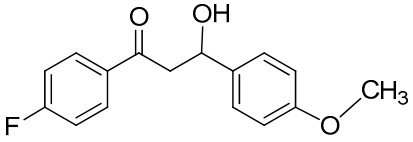
6p. 3-(4-bromophenyl)-3-hydroxy-1-(4-methoxyphenyl)propan-1-one



White solid

^{1}H NMR (400 MHz, Chloroform-d) δ 7.92 (d, J = 9.0 Hz, 2H), 7.50 (d, J = 8.5 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 6.94 (d, J = 9.0 Hz, 2H), 5.32 – 5.25 (m, 1H), 3.88 (s, 3H), 3.80 (d, J = 2.9 Hz, 1H), 3.37 – 3.18 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-d) δ 198.4, 163.9, 142.1, 131.5, 130.5, 129.4, 127.4, 121.2, 113.8, 69.5, 55.4, 46.6.

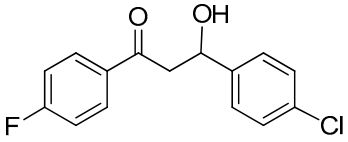
6q 1-(4-fluorophenyl)-3-hydroxy-3-(4-methoxyphenyl)propan-1-one



White solid

^{1}H NMR (400 MHz, Chloroform-d) δ 8.01 – 7.93 (m, 2H), 7.39 – 7.32 (m, 2H), 7.17 – 7.08 (m, 2H), 6.94 – 6.86 (m, 2H), 5.28 (d, J = 8.8 Hz, 1H), 3.81 (s, 3H), 3.51 – 3.44 (m, 1H), 3.40 – 3.22 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-d) δ 198.5, 167.3, 164.7, 159.1, 135.0, 133.1, 133.0, 130.9, 130.8, 127.0, 115.9, 115.7, 113.9, 69.6, 55.3, 47.3, 29.7.

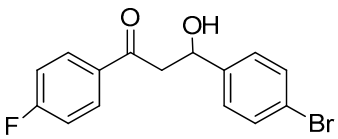
6r. 3-(4-chlorophenyl)-1-(4-fluorophenyl)-3-hydroxypropan-1-one



Colorless oil

^{1}H NMR (400 MHz, Chloroform-d) δ 8.02 – 7.92 (m, 2H), 7.35 (dd, J = 3.2, 1.6 Hz, 4H), 7.14 (t, J = 8.4 Hz, 2H), 5.31 (t, J = 6.1 Hz, 1H), 3.60 (d, J = 6.4 Hz, 1H), 3.36 – 3.23 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-d) δ 198.2, 167.3, 164.8, 141.2, 133.3, 132.8, 132.8, 130.8, 130.7, 128.7, 127.1, 116.0, 115.8, 69.3, 47.1.

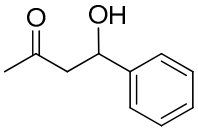
6s. 3-(4-bromophenyl)-1-(4-fluorophenyl)-3-hydroxypropan-1-one



Colorless oil

^{1}H NMR (400 MHz, Chloroform-d) δ 7.98 (ddd, J = 8.8, 5.3, 1.4 Hz, 2H), 7.51 (dd, J = 8.3, 1.4 Hz, 2H), 7.32 (dd, J = 8.3, 1.3 Hz, 2H), 7.14 (td, J = 8.6, 1.4 Hz, 2H), 5.31 (d, J = 3.2 Hz, 1H), 3.55 (dd, J = 3.0, 1.2 Hz, 1H), 3.31 (dd, J = 5.8, 1.1 Hz, 2H).
^{13}C NMR (101 MHz, Chloroform-d) δ 197.9, 167.2, 164.7, 141.9, 132.8, 132.8, 131.5, 130.8, 130.7, 127.4, 121.3, 115.9, 115.7, 69.2, 47.1.

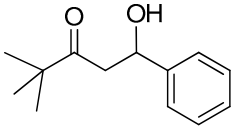
6t. 4-Hydroxy-4-phenylbutan-2-one



Colorless oil

^{1}H NMR (400 MHz, Chloroform-d) δ 7.29 – 7.24 (m, 4H), 7.22 – 7.17 (m, 1H), 5.06 (dd, J = 9.1, 3.4 Hz, 1H), 3.26 (s, 1H), 2.88 – 2.65 (m, 2H), 2.10 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-d) δ 208.9, 142.7, 128.4, 127.6, 125.5, 69.8, 51.9, 30.7.

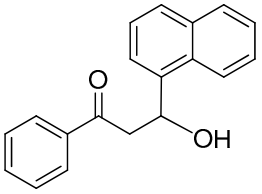
6u. 1-Hydroxy-4,4-dimethyl-1-phenylpentan-3-one



Colorless oil

^{1}H NMR (400 MHz, Chloroform-d) δ 7.29 – 7.21 (m, 4H), 7.20 – 7.14 (m, 1H), 5.03 (d, J = 3.0 Hz, 1H), 3.47 (d, J = 3.0 Hz, 1H), 2.81 – 2.73 (m, 2H), 1.03 (s, 9H).
^{13}C NMR (101 MHz, Chloroform-d) δ 216.7, 143.0, 128.4, 127.4, 125.6, 70.0, 45.4, 44.3, 26.1.

6v. 3-Hydroxy-3-(naphthalen-1-yl)-1-phenylpropan-1-one

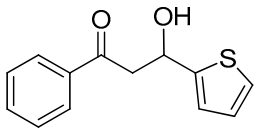


White solid

^{1}H NMR (400 MHz, Chloroform-d) δ 8.09 – 8.03 (m, 1H), 7.99 – 7.93 (m, 2H), 7.92 – 7.87 (m, 1H), 7.84 – 7.78 (m, 2H), 7.63 – 7.41 (m, 6H), 6.16 (dt, J = 9.3, 2.5 Hz, 1H), 3.76 (d, J = 2.8 Hz, 1H), 3.62 – 3.38 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-d) δ 200.3, 138.4, 136.4, 133.7, 133.6, 129.8, 129.0, 128.6, 128.1, 128.0, 126.2, 125.6, 125.5, 123.1, 122.7, 66.7, 46.7.

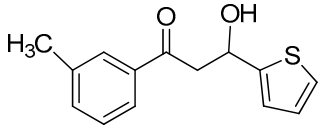
6w. 3-hydroxy-1-phenyl-3-(thiophen-2-yl)propan-1-one



Colorless oil

^{1}H NMR (400 MHz, Chloroform-d) δ 8.00 – 7.91 (m, 2H), 7.62 – 7.53 (m, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.28 – 7.21 (m, 1H), 7.02 (dd, J = 3.5, 1.1 Hz, 1H), 6.97 (dd, J = 4.9, 3.6 Hz, 1H), 5.64 – 5.52 (m, 1H), 3.77 – 3.69 (m, 1H), 3.57 – 3.41 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-d) δ 199.4, 146.6, 136.3, 133.6, 128.6, 128.0, 126.6, 124.6, 123.5, 66.4, 47.1.

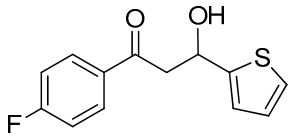
6x 3-Hydroxy-3-(thiophen-2-yl)-1-(m-tolyl)propan-1-one



Colorless oil

^{1}H NMR (400 MHz, Chloroform-d) δ 7.79 – 7.73 (m, 2H), 7.44 – 7.33 (m, 2H), 7.30 – 7.25 (m, 1H), 7.06 – 7.02 (m, 1H), 6.99 (dd, J = 5.0, 3.5 Hz, 1H), 5.60 (s, 1H), 3.81 (s, 1H), 3.57 – 3.43 (m, 2H), 2.42 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-d) δ 199.8, 146.6, 138.5, 136.4, 134.5, 128.6, 128.6, 126.7, 125.3, 124.6, 123.5, 66.4, 47.1, 21.3.

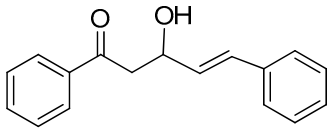
6y. 1-(4-fluorophenyl)-3-hydroxy-3-(thiophen-2-yl)propan-1-one



Colorless oil

^{1}H NMR (400 MHz, Chloroform-d) δ 8.00 (dd, J = 8.7, 5.5 Hz, 2H), 7.30 – 7.25 (m, 1H), 7.15 (t, J = 8.6 Hz, 2H), 7.04 (d, J = 3.4 Hz, 1H), 6.99 (dd, J = 5.1, 3.6 Hz, 1H), 5.60 (d, J = 7.2 Hz, 1H), 3.64 (d, J = 3.1 Hz, 1H), 3.56 – 3.39 (m, 2H), 1.26 (s, 1H).
^{13}C NMR (101 MHz, Chloroform-d) δ 197.8, 167.3, 164.8, 146.5, 132.9, 130.9, 130.8, 126.7, 124.7, 123.5, 116.0, 115.7, 66.5, 47.1, 29.7.

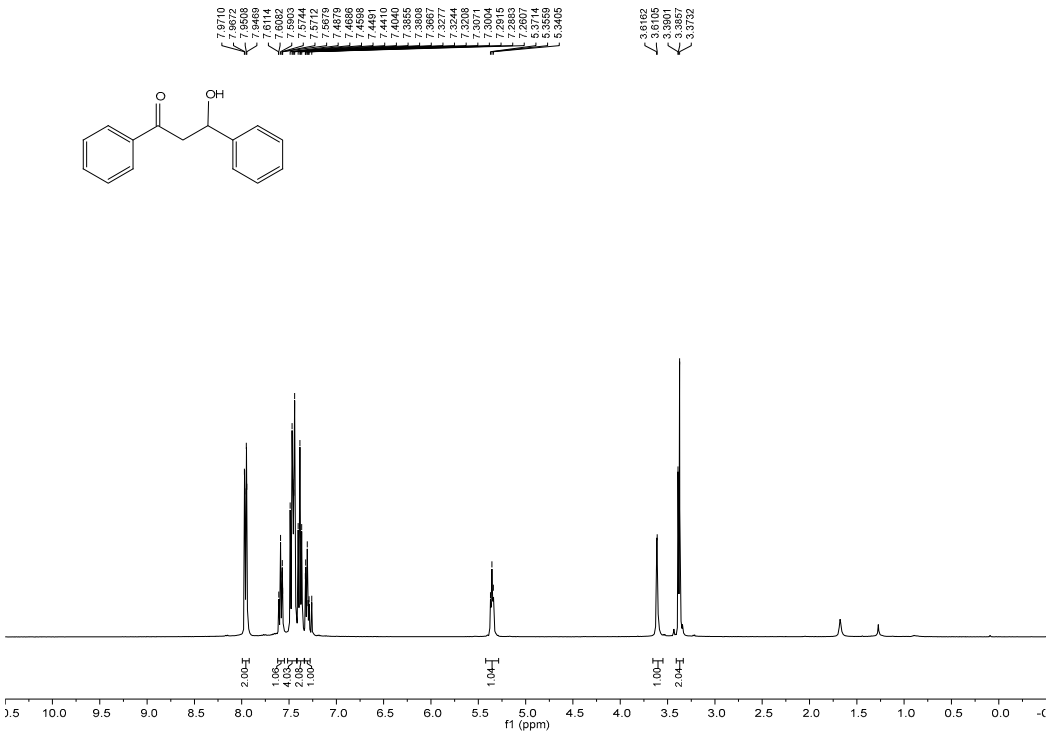
6z 3-Hydroxy-1,5-diphenylpent-4-en-1-one

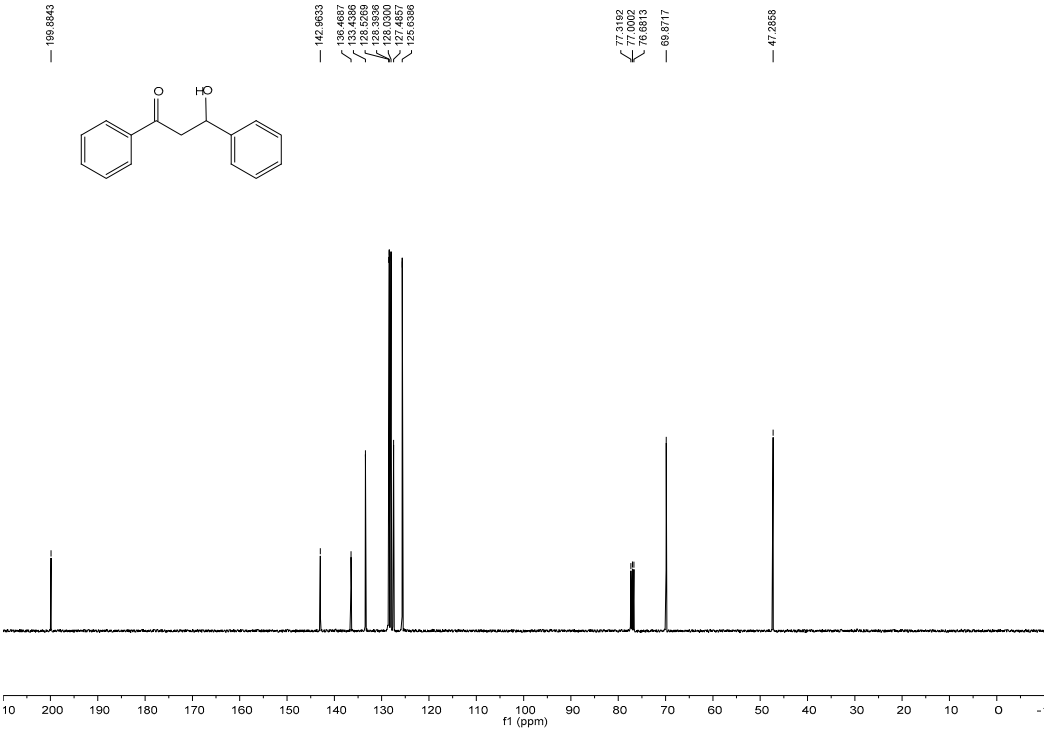


Colorless oil

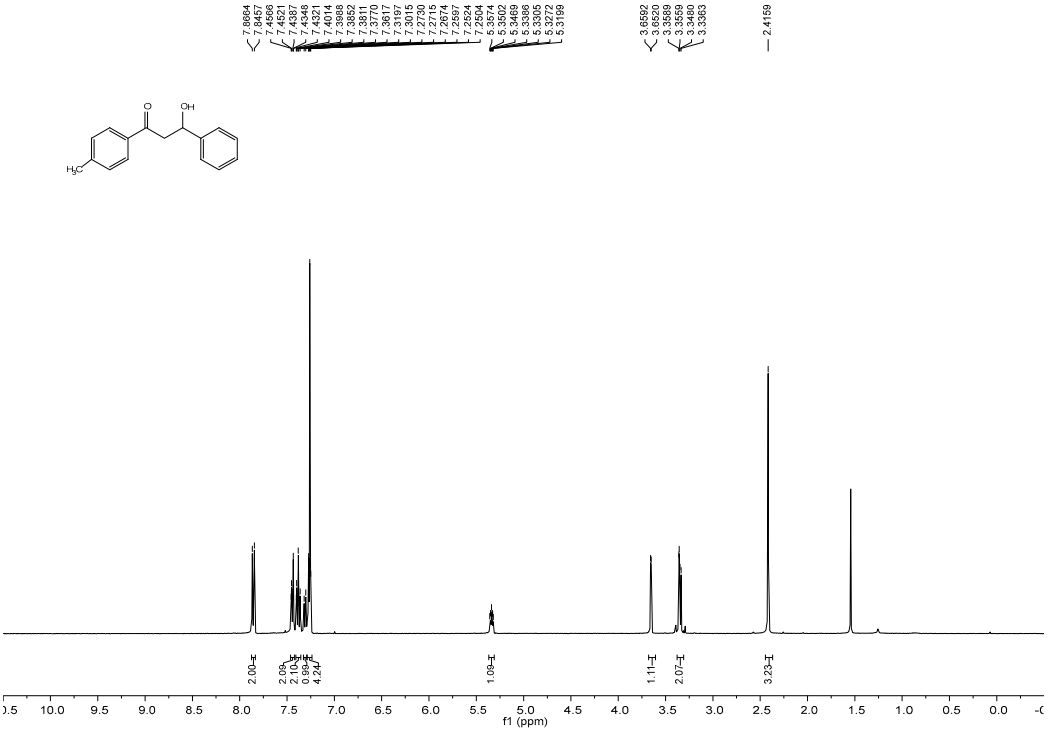
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 – 7.95 (m, 2H), 7.59 (d, J = 7.4 Hz, 1H), 7.49 (dd, J = 8.4, 7.1 Hz, 2H), 7.42 – 7.36 (m, 2H), 7.36 – 7.29 (m, 2H), 7.28 – 7.20 (m, 2H), 6.72 (dd, J = 16.0, 1.3 Hz, 1H), 6.32 (dd, J = 15.9, 6.1 Hz, 1H), 4.96 (d, J = 6.3 Hz, 1H), 3.43 – 3.38 (m, 1H), 3.32 – 3.27 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-d) δ 200.0, 136.5, 136.5, 133.6, 130.4, 130.2, 128.7, 128.6, 128.1, 127.7, 126.4, 68.6, 45.1, 29.6.

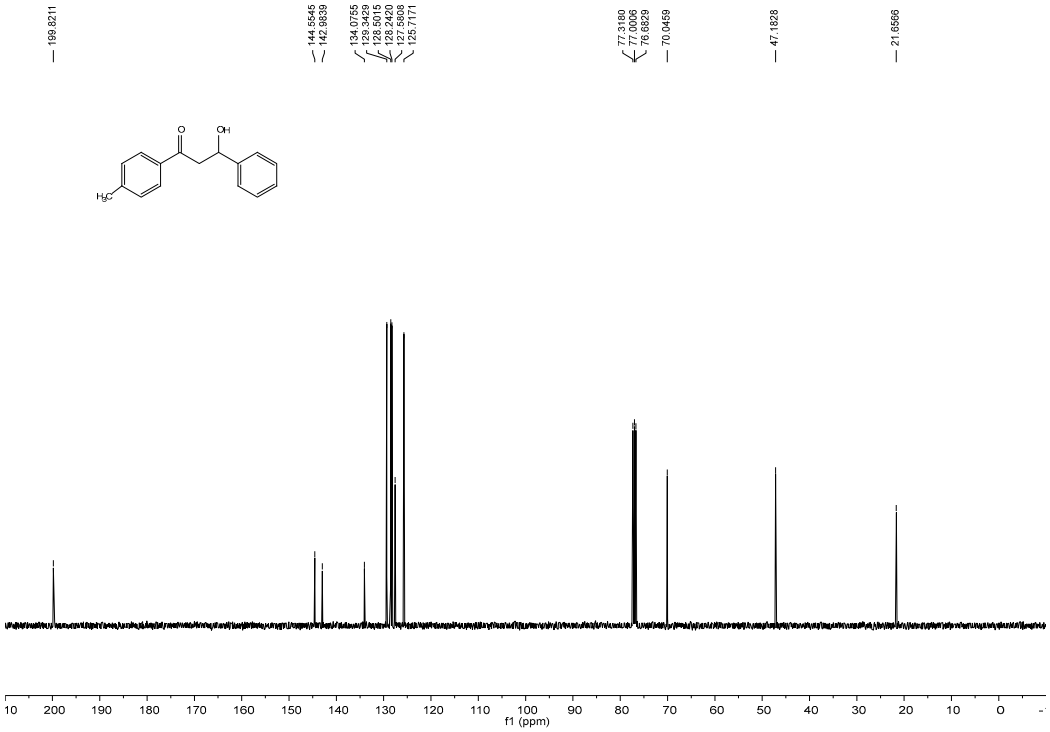
6a



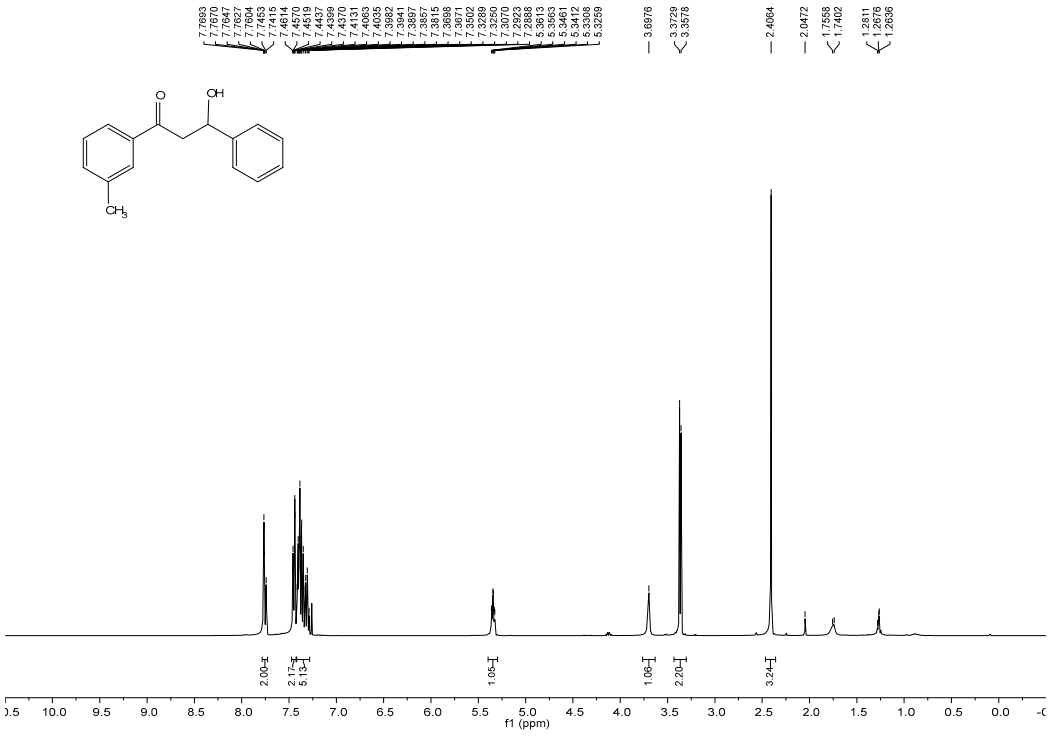

199.8843
142.9633
136.4687
133.4966
128.5269
128.3936
128.0300
127.4857
125.6386
77.3182
77.0000
76.6813
69.8717
47.2858
O
HO
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

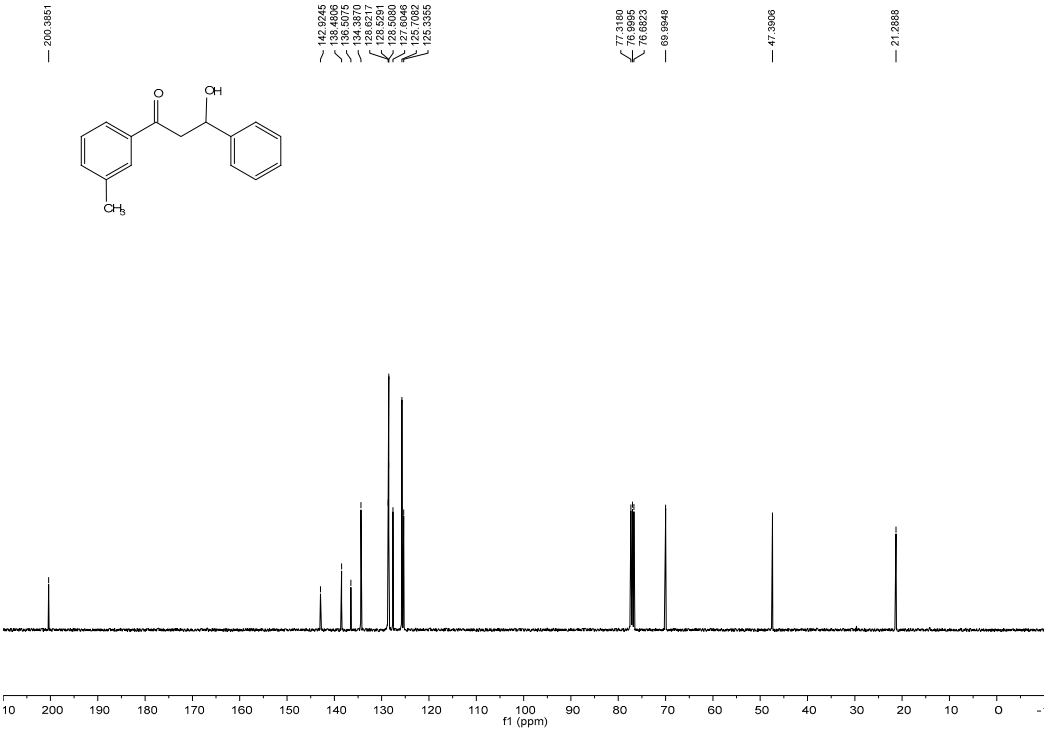
6b


7.8664
7.8457
7.4686
7.4477
7.4387
7.4348
7.4321
7.4014
7.3988
7.3852
7.3811
7.3770
7.3617
7.3197
7.3015
7.2709
7.2715
7.2674
7.2597
7.2524
7.2504
6.8874
5.3502
5.3469
5.3386
5.3305
5.3272
5.3198
3.6582
3.6520
3.3589
3.3559
3.3480
3.3363
2.4159
O
OH
H3C
2.00
2.09
2.10
0.99
4.24
1.09
1.11
2.07
3.23
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


199.8211
144.5545
142.9839
134.0755
129.3429
128.5015
128.2420
127.5808
125.7171
77.3180
77.0965
76.6829
70.0459
47.1828
21.6566
O
OH
H3C
f1 (ppm)

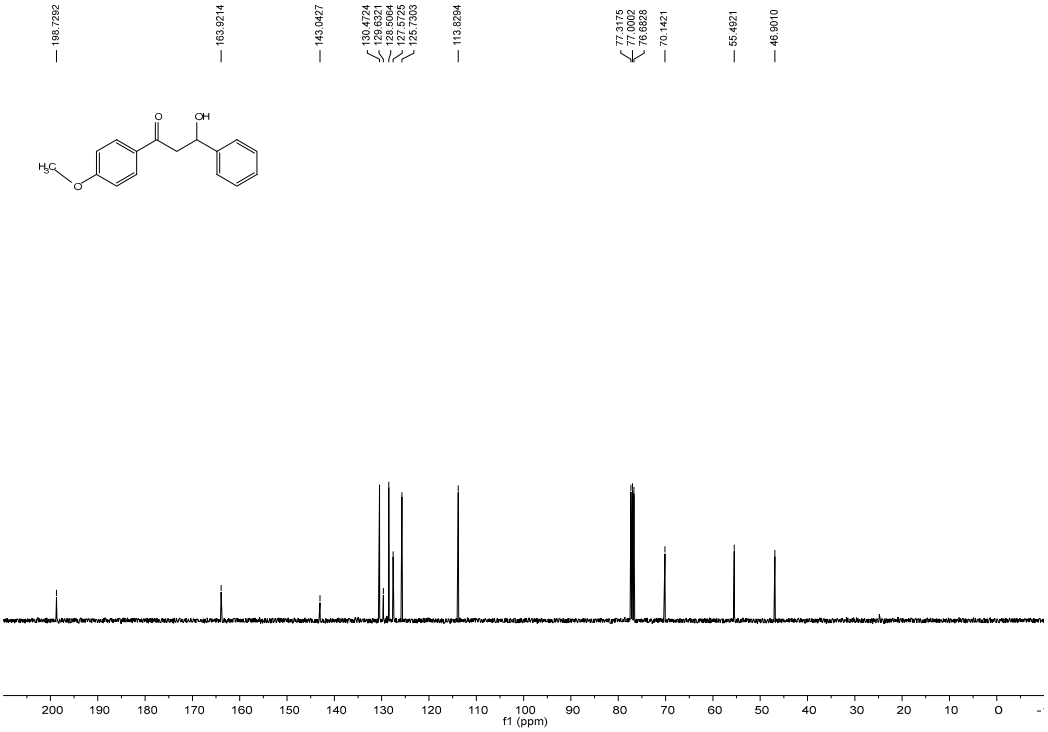
6c


7.7693
7.7670
7.7647
7.7627
7.7604
7.7453
7.7415
7.4464
7.4570
7.4519
7.4437
7.4399
7.4370
7.4311
7.4063
7.4035
7.3982
7.3941
7.3897
7.3857
7.3815
7.3698
7.3671
7.3502
7.3289
7.3259
7.3070
7.2923
7.2888
5.3813
5.3463
5.3461
5.3412
5.3308
5.3259
3.6976
3.3729
3.3578
2.4064
2.0472
1.7558
1.7402
1.2811
1.2676
1.2636
O
OH
CH3
2.00
2.17
5.13
1.05
1.06
2.20
3.24
f1 (ppm)

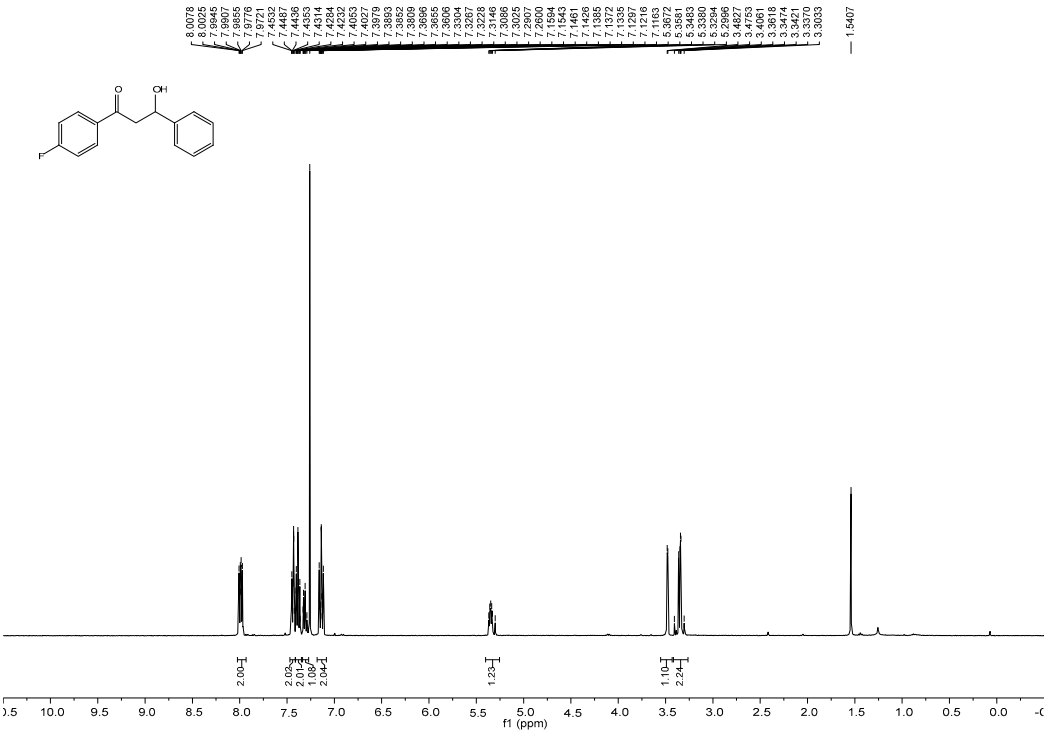

200.3851
142.9245
138.4806
136.5075
134.3870
128.6217
128.5931
128.5080
127.6046
125.7082
125.3355
77.3180
76.9995
76.6823
69.9948
47.3906
21.2888
O
OH
CH3
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

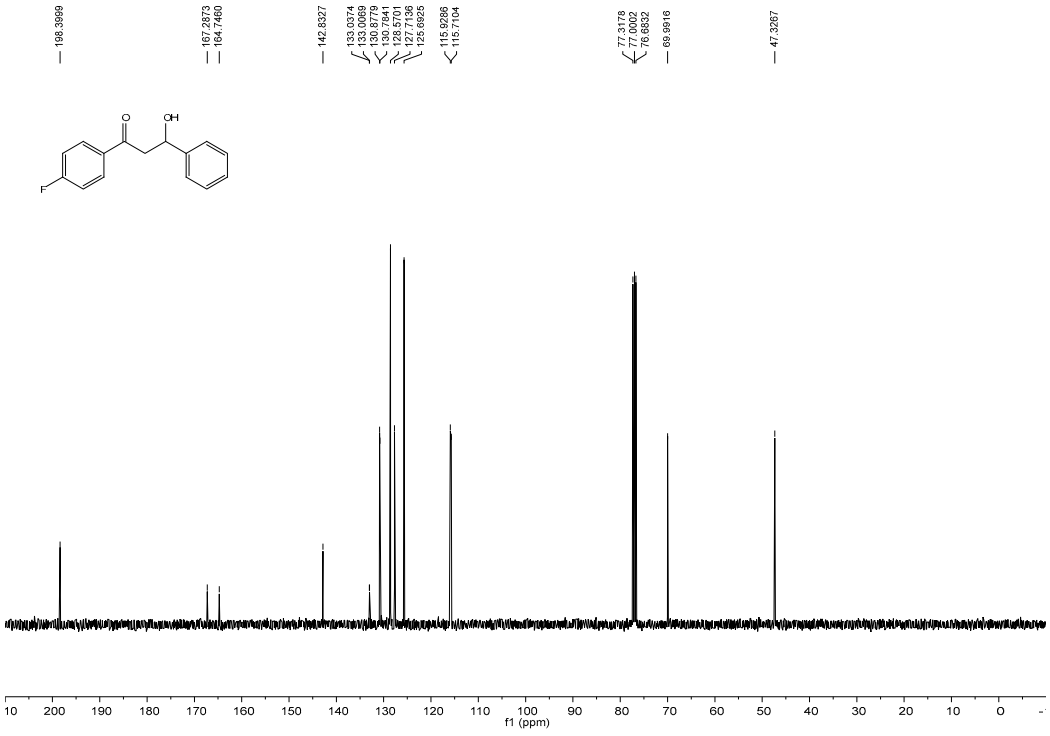
6d


7.9467
7.9415
7.9296
7.9246
7.4557
7.4520
7.4507
7.4378
7.4350
7.4333
7.4312
7.4299
7.3988
7.3964
7.3832
7.3806
7.3784
7.3745
7.3692
7.3168
7.2857
7.2044
6.9417
6.9194
5.3443
5.3379
5.3337
5.3282
5.3246
5.3179
5.3138
5.3080
3.8711
3.7703
3.7664
3.7607
3.3287
3.3238
3.3186
3.3033
O
OH
H3C
O
2.00
2.00
1.94
0.96
1.98
1.02
3.12
0.92
2.09
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

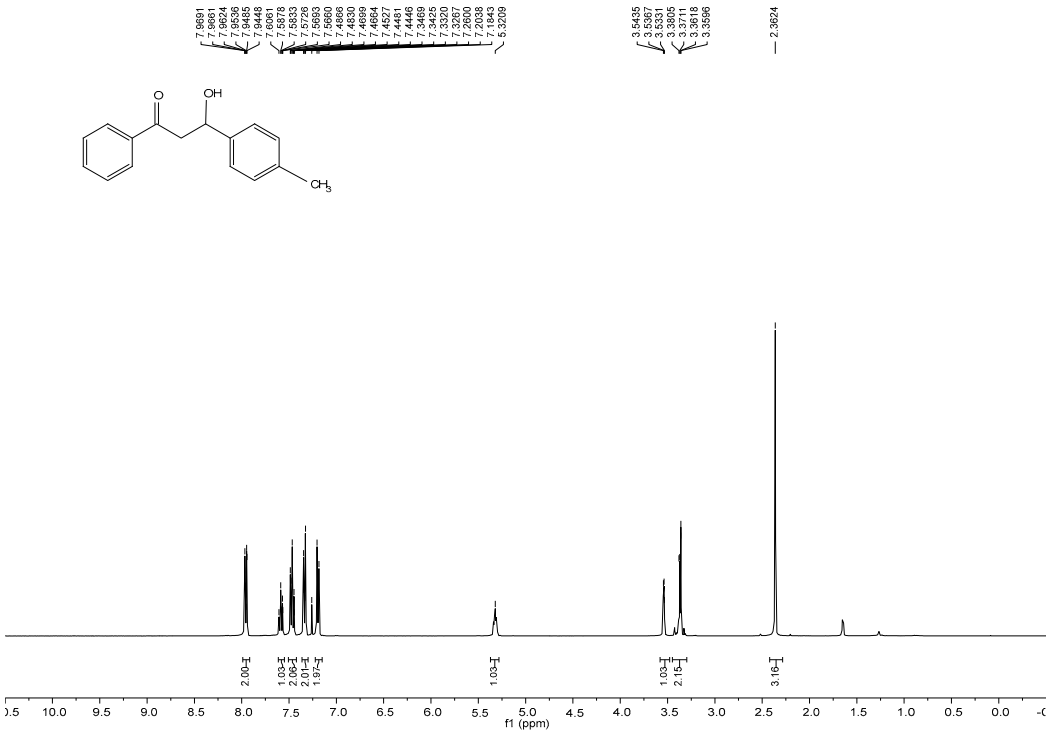

198.7292
163.9214
143.0427
130.4724
129.6321
128.5064
127.5725
125.7303
113.8294
77.3175
77.0002
76.6828
70.1421
55.4921
46.9010
O
OH
H3C
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

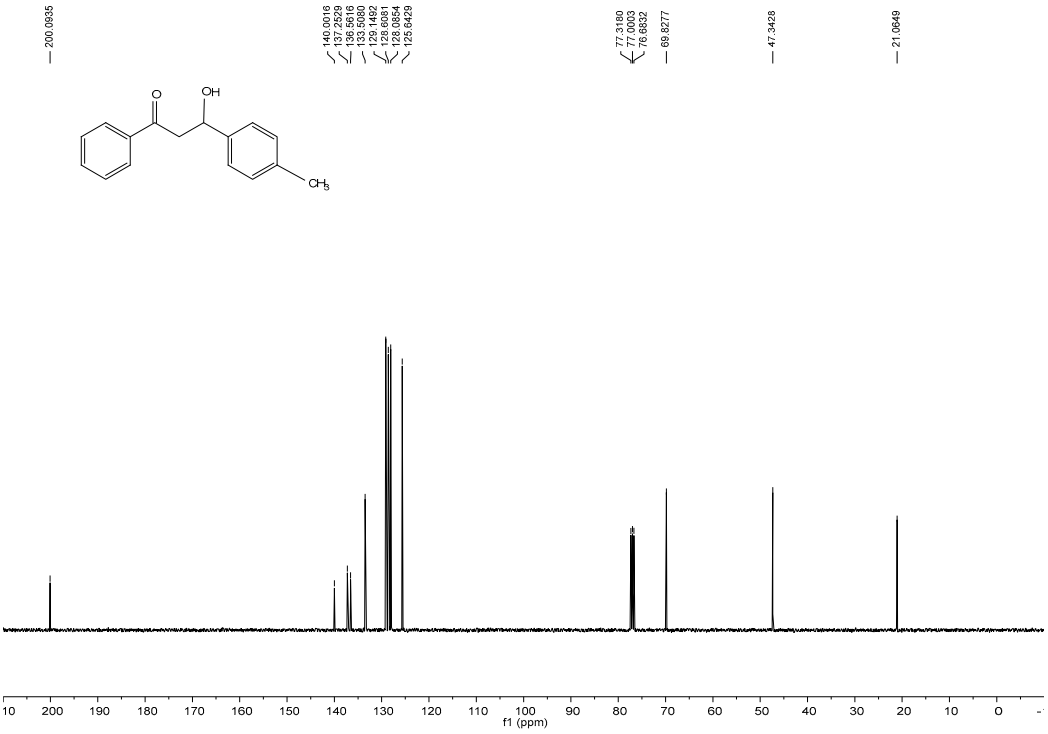
6e.


8.0078
8.0025
7.9946
7.9907
7.9855
7.9776
7.9721
7.4532
7.4497
7.4446
7.4353
7.4314
7.4284
7.4232
7.4053
7.4027
7.3979
7.3893
7.3852
7.3809
7.3696
7.3655
7.3606
7.3304
7.3287
7.3228
7.3146
7.3086
7.3025
7.2907
7.2600
7.1594
7.1543
7.1491
7.1426
7.1385
7.1372
7.1335
7.1297
7.1216
7.1163
5.3672
5.3581
5.3483
5.3394
5.3294
5.2996
3.4827
3.4763
3.4061
3.3918
3.3814
3.3474
3.3421
3.3370
3.3033
1.5407
O
OH
F
2.00
2.02
2.01
1.08
2.04
1.23
1.10
2.24
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

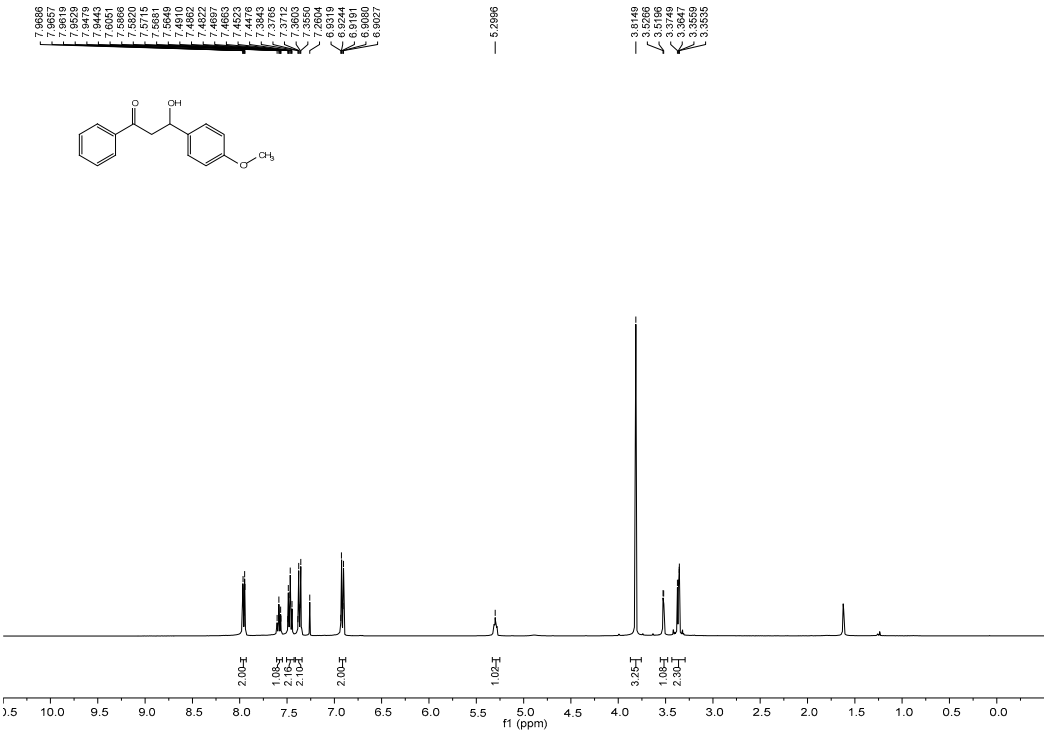

198.3969
167.2873
164.7460
142.8327
133.0374
133.0069
130.8779
130.7841
128.5791
127.7738
125.6925
115.9286
115.7104
77.3178
77.0002
76.6832
69.9916
47.3267
O
OH
F
f1 (ppm)

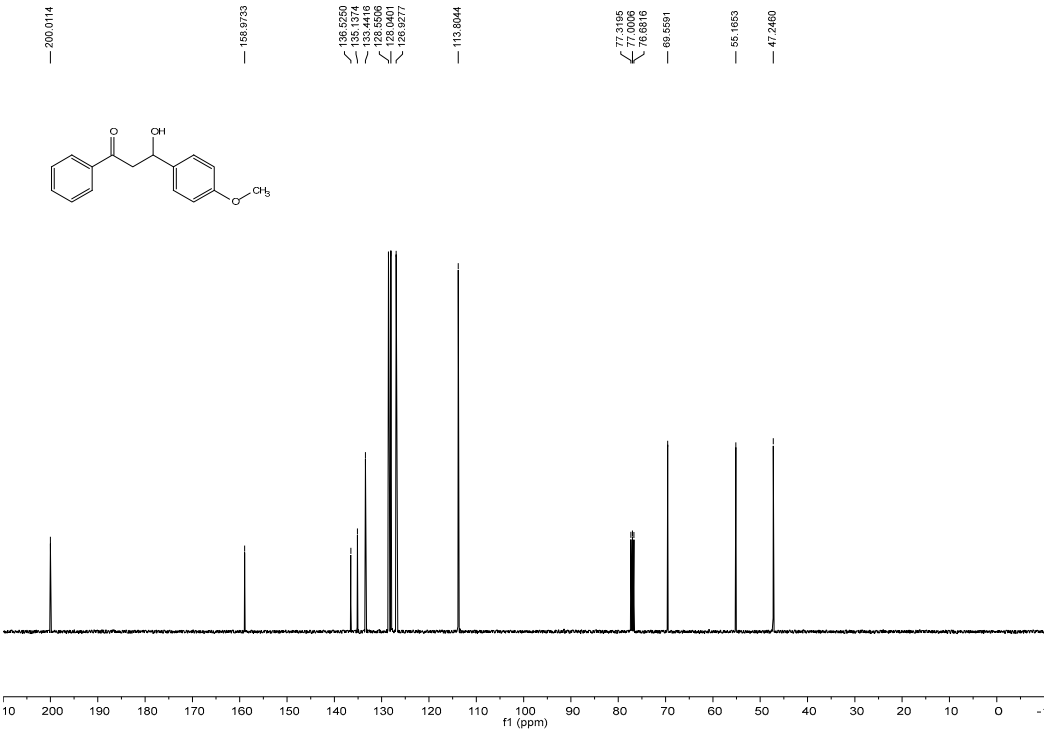
6f


7.9691
7.9661
7.9624
7.9536
7.9455
7.9448
7.9361
7.5878
7.5833
7.5726
7.5693
7.5660
7.4696
7.4830
7.4689
7.4664
7.4527
7.4491
7.4446
7.3469
7.3425
7.3320
7.3267
7.2800
7.2038
7.1843
5.3209
3.5435
3.5357
3.5331
3.3805
3.3711
3.3618
3.3596
2.3624
O
OH
CH3
2.00
1.03
2.06
2.01
1.97
1.03
1.03
2.16
3.16
f1 (ppm)

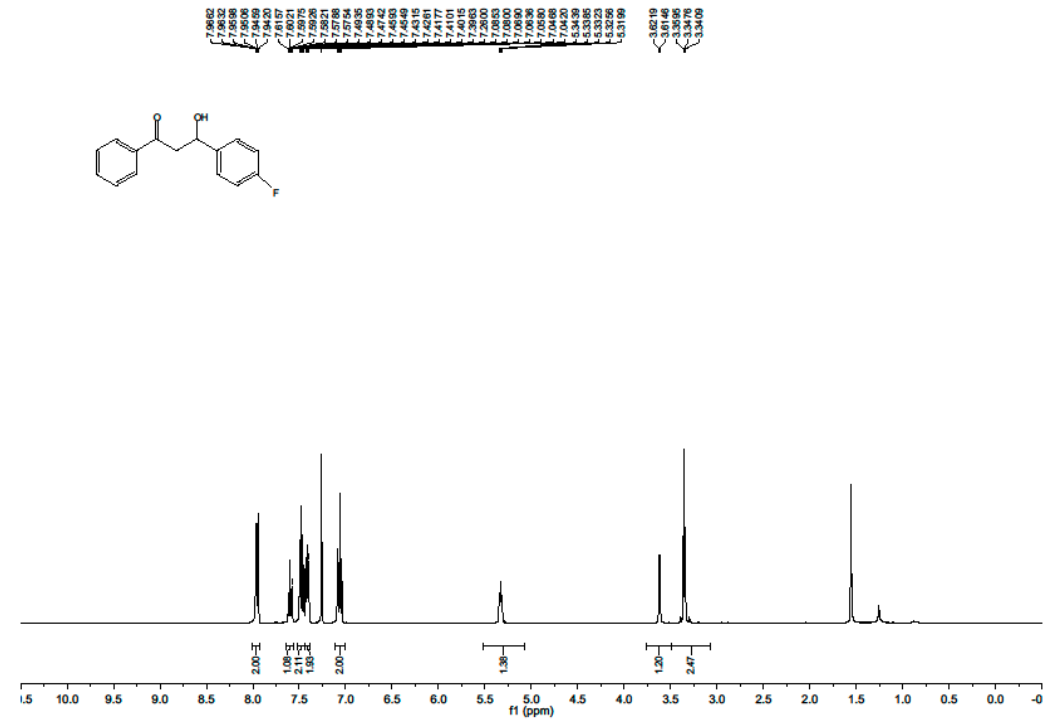

200.0935
140.0016
137.2938
136.5615
133.5080
129.1492
128.6081
128.0854
125.6429
77.3160
77.0003
76.6832
69.8277
47.3428
21.0649
O
OH
CH3
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

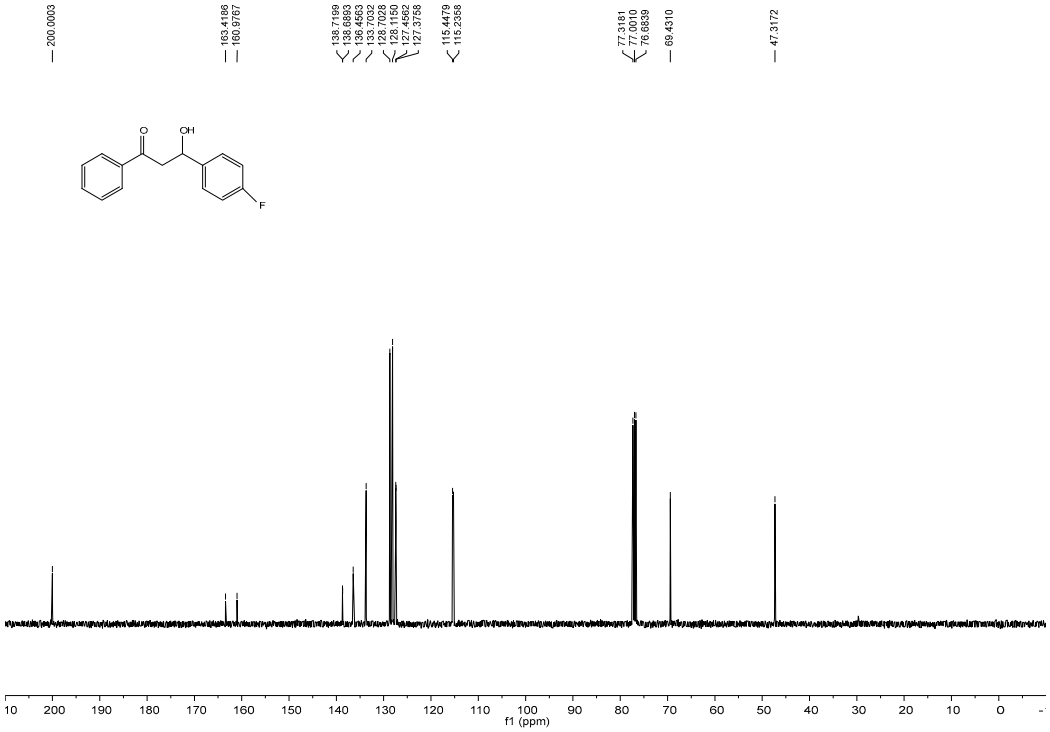
6g


7.9686
7.9657
7.9619
7.9529
7.9443
7.9443
7.6051
7.5866
7.5820
7.5715
7.5681
7.5649
7.4910
7.4882
7.4822
7.4697
7.4653
7.4523
7.4476
7.3843
7.3765
7.3712
7.3693
7.3550
7.2604
6.9319
6.9244
6.9181
6.9060
6.9027
5.2996
3.8149
3.5196
3.5196
3.3749
3.3647
3.3559
3.3535
O
OH
O
CH3
2.00
1.08
2.16
2.16
2.00
1.00
3.25
1.08
2.30
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

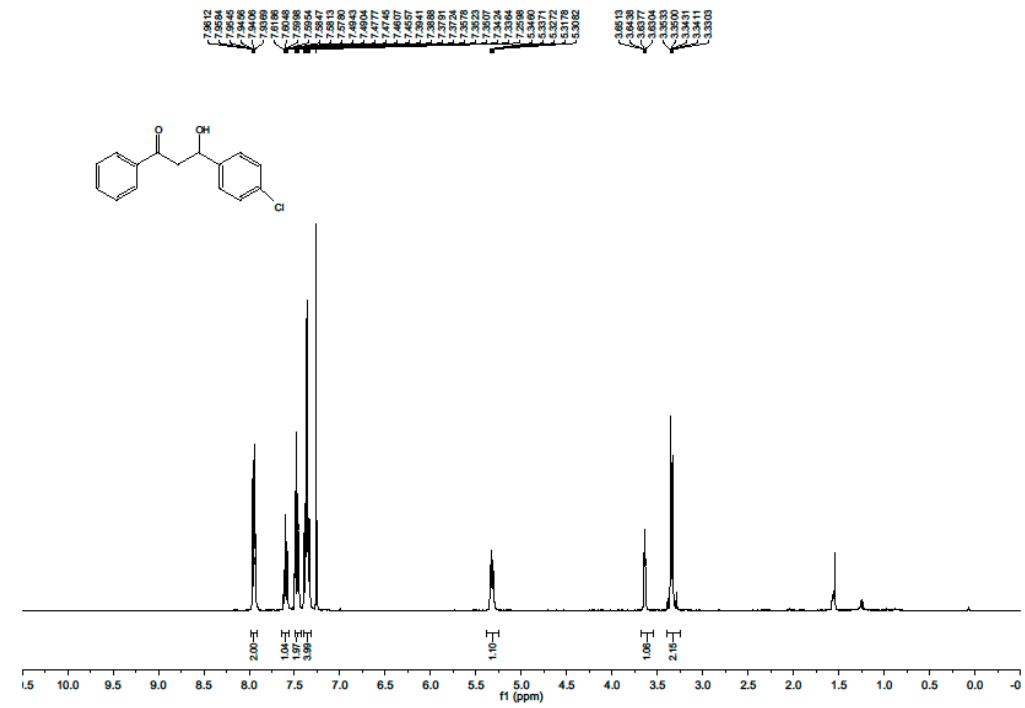

200.0114
158.9733
136.5260
135.1374
130.4446
128.5536
128.0401
126.9277
113.8044
77.3195
77.0066
76.6816
69.5591
55.1653
47.2460
O
OH
O
CH3
f1 (ppm)

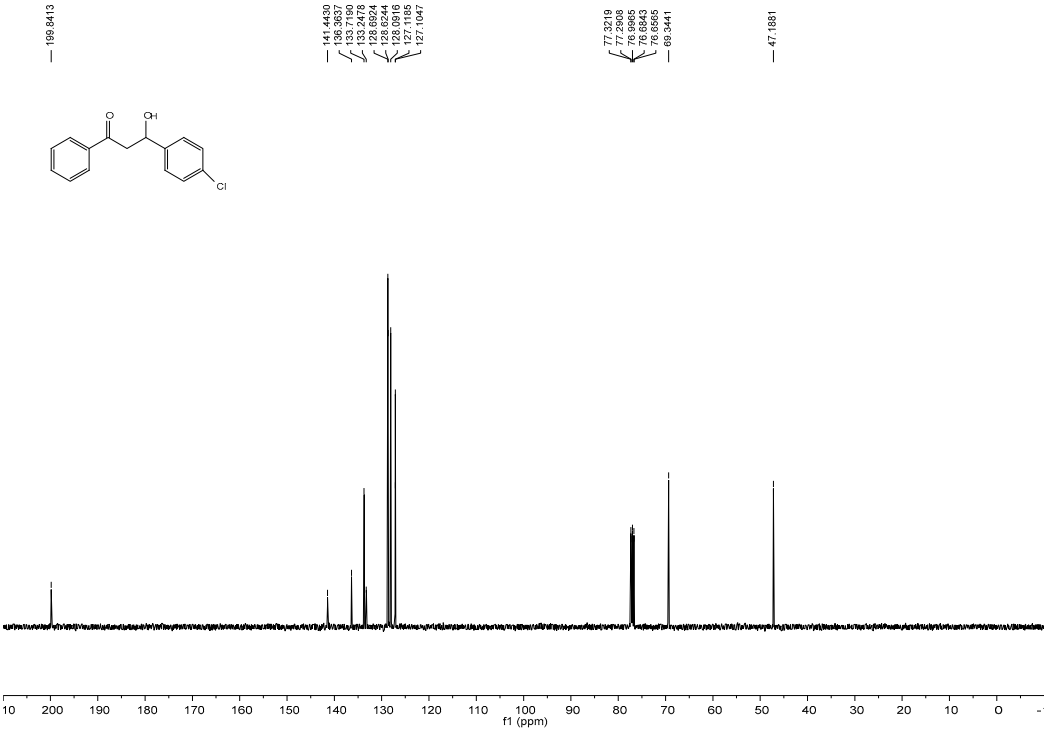
6h


O
OH
F
2.00
1.09
2.11
1.93
2.00
1.39
1.20
2.47
f1 (ppm)

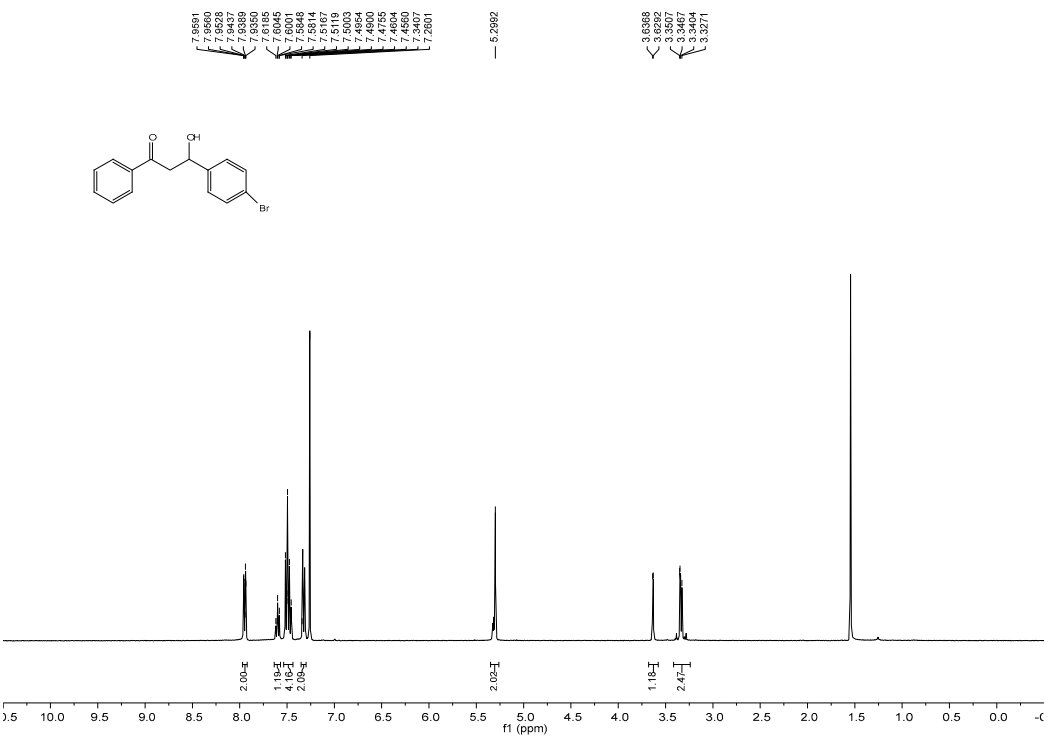

200.0003
163.4186
160.9767
138.7199
138.6893
136.4563
133.7032
133.7028
128.1150
127.4582
127.3758
115.4479
115.2356
77.3161
77.0010
76.6839
69.4310
47.3172
O
OH
F
f1 (ppm)

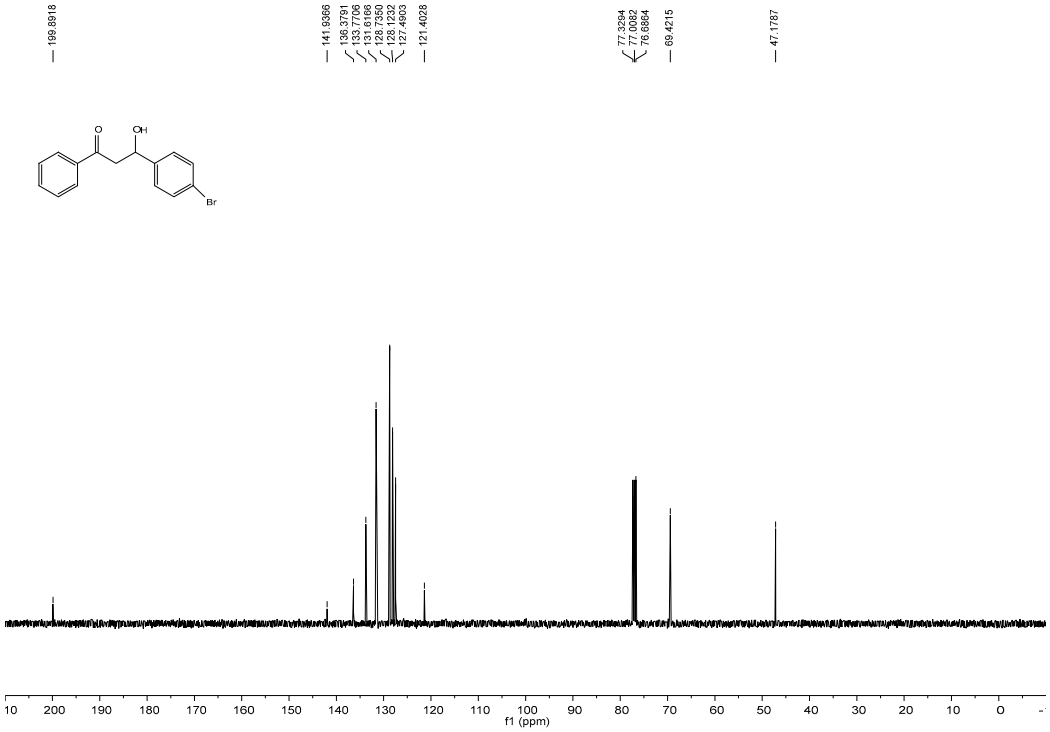
6i


O
OH
Cl
2.00
1.04
1.97
3.99
1.10
1.06
2.15
f1 (ppm)

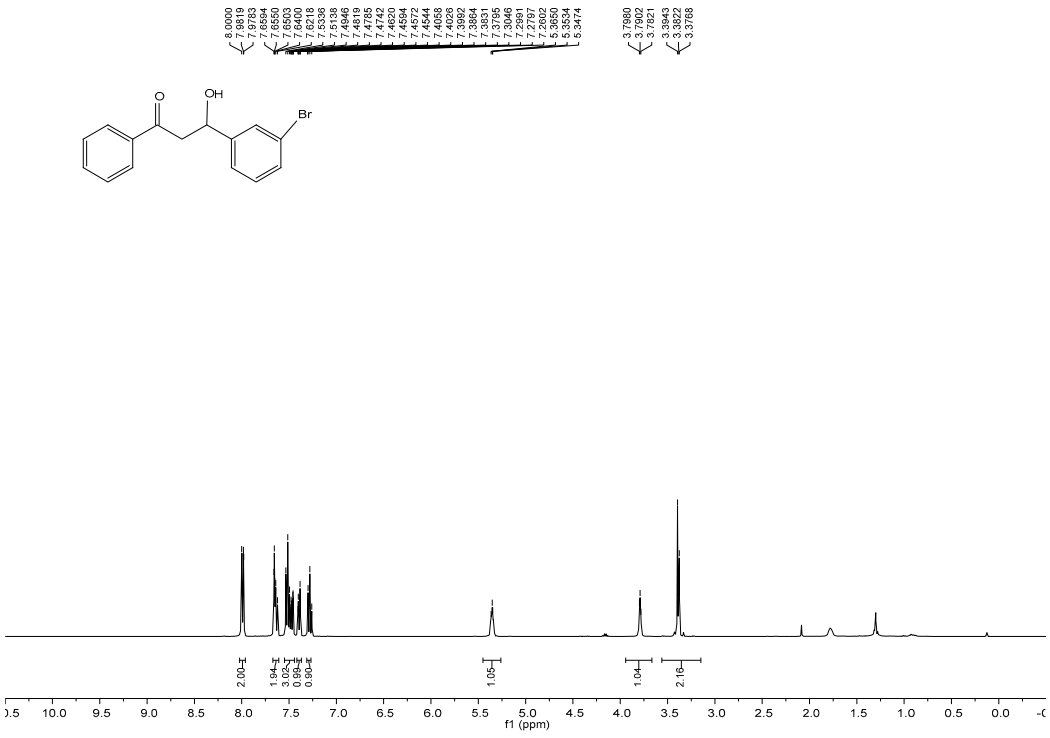

199.8413
141.4430
135.9527
133.7190
133.2478
128.6924
128.6244
128.0916
127.7185
127.1047
77.3219
77.2908
76.9595
76.6843
76.6565
69.3441
47.1881
O
OH
Cl
f1 (ppm)

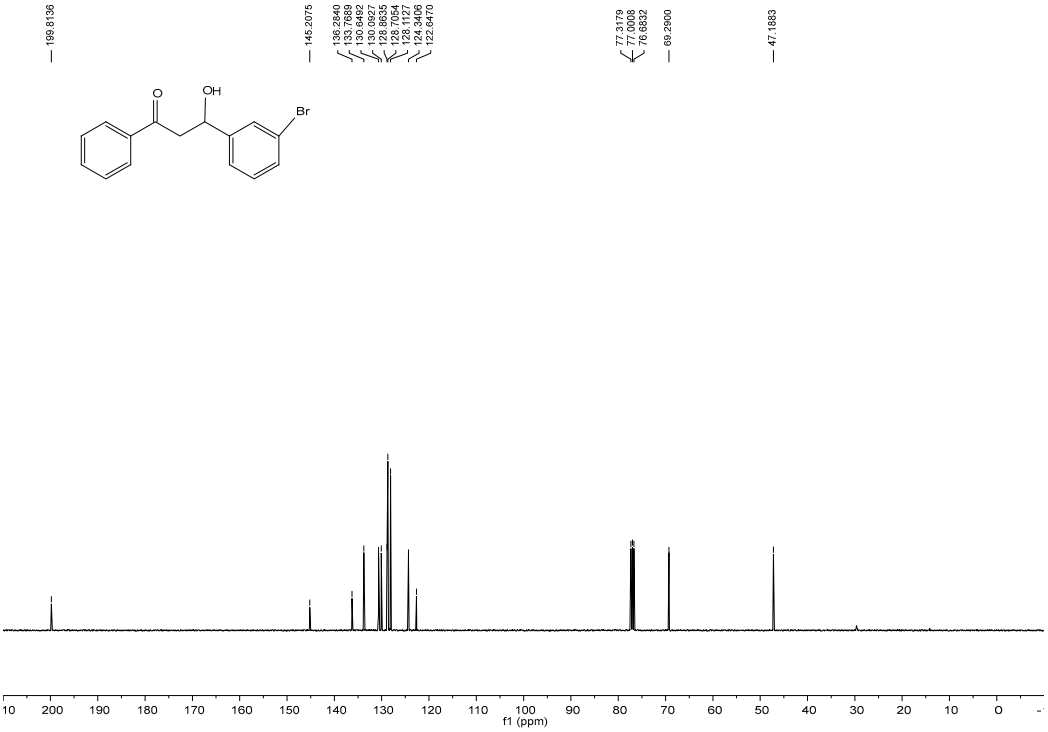
6j


7.9591
7.9560
7.9528
7.9437
7.9389
7.9350
7.6185
7.6045
7.6001
7.5848
7.5814
7.5165
7.5119
7.5003
7.4954
7.4900
7.4755
7.4664
7.4560
7.3407
7.2601
5.2992
3.6368
3.6292
3.3507
3.3467
3.3404
3.3271
O
OH
Br
2.00
1.19
4.16
2.09
2.02
1.18
2.47
f1 (ppm)

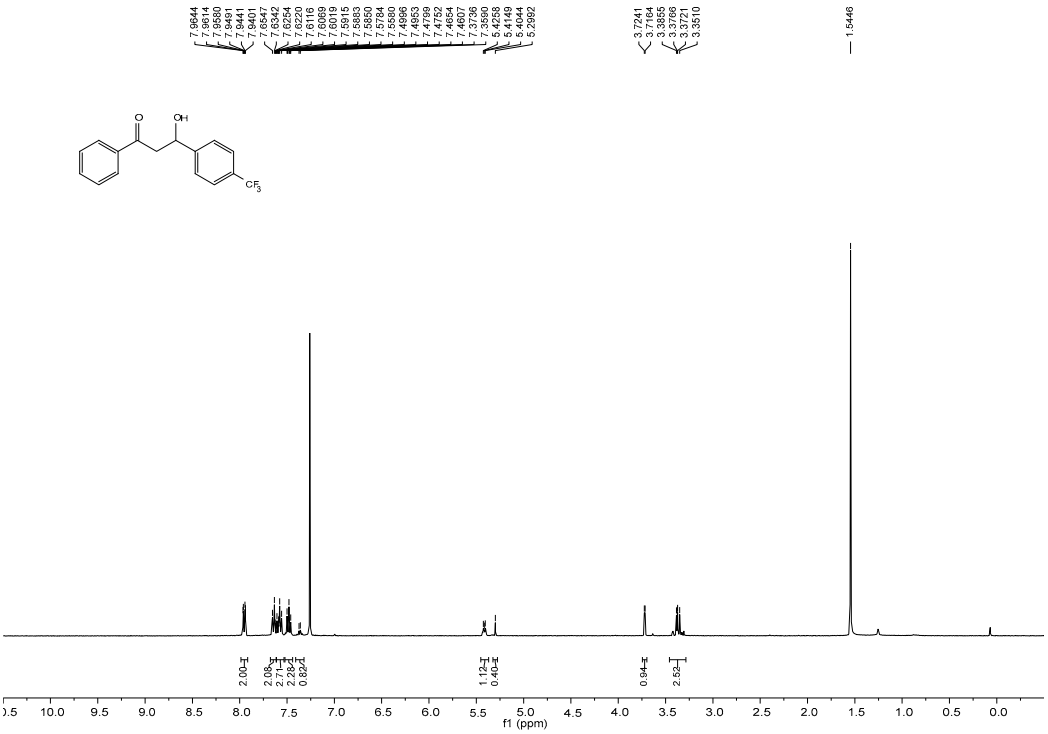

199.8918
141.9366
138.3791
133.7706
131.6666
128.7350
128.1232
127.4903
121.4028
77.3284
77.0082
76.6864
69.4215
47.1787
O
OH
Br
f1 (ppm)

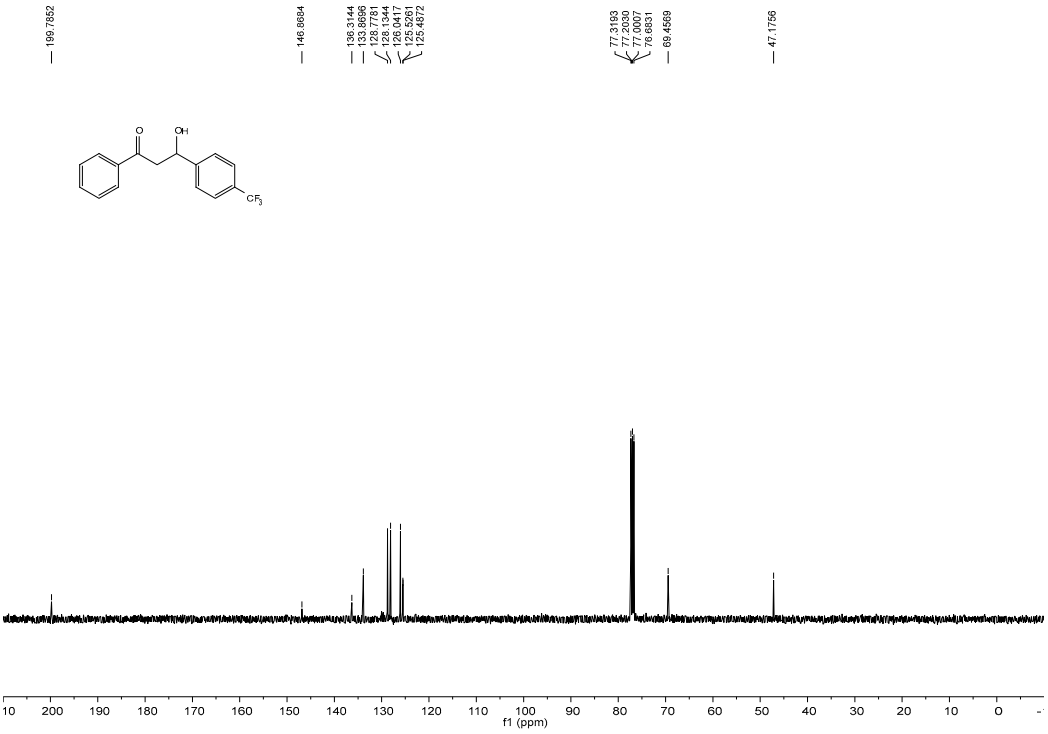
6k


8.0090
7.9819
7.9783
7.6594
7.6550
7.6503
7.6440
7.6218
7.5338
7.5138
7.4946
7.4819
7.4785
7.4742
7.4620
7.4594
7.4572
7.4544
7.4468
7.4026
7.3992
7.3864
7.3831
7.3795
7.3046
7.2991
7.2797
7.2602
5.3650
5.3534
5.3414
3.7980
3.7902
3.7821
3.3943
3.3822
3.3768
O
OH
Br
2.00
1.94
3.02
0.94
0.90
1.05
1.04
2.16
f1 (ppm)

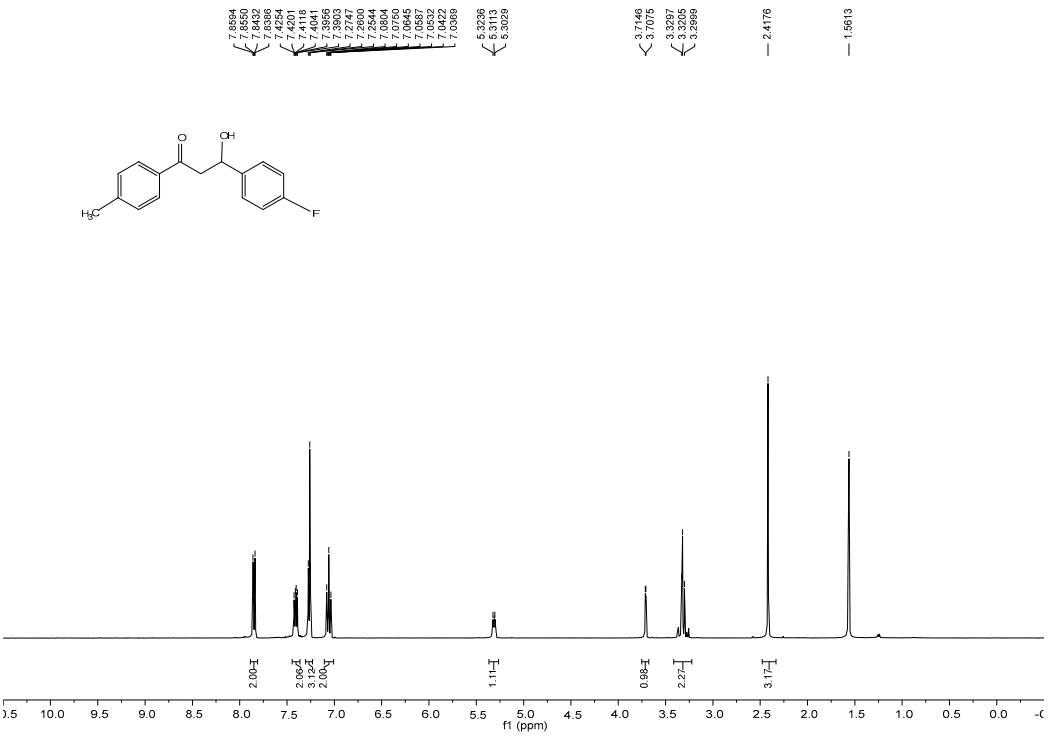

199.8136
145.2075
136.2840
133.7689
130.6492
130.0927
128.8635
128.7054
128.1127
124.3406
122.6470
77.3179
77.0998
76.6832
69.2900
47.1683
O
OH
Br
f1 (ppm)

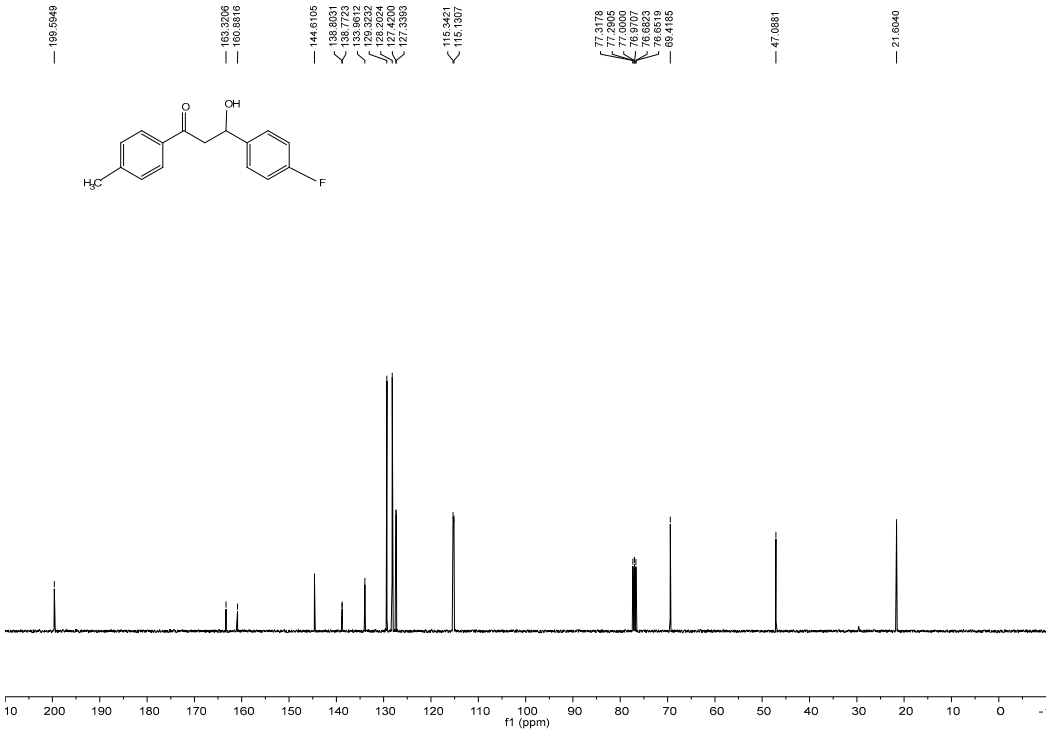
6l


7.9644
7.9614
7.9580
7.9491
7.9441
7.9401
7.6547
7.6342
7.6254
7.6220
7.6116
7.6069
7.6019
7.5915
7.5883
7.5850
7.5784
7.5694
7.5590
7.4996
7.4953
7.4799
7.4752
7.4654
7.4607
7.3736
7.3590
5.4258
5.4149
5.4044
5.2992
3.7241
3.7164
3.3885
3.3806
3.3721
3.3510
1.5446
O
OH
CF3
2.00
2.08
2.71
2.28
0.82
1.12
0.40
0.94
2.62
f1 (ppm)

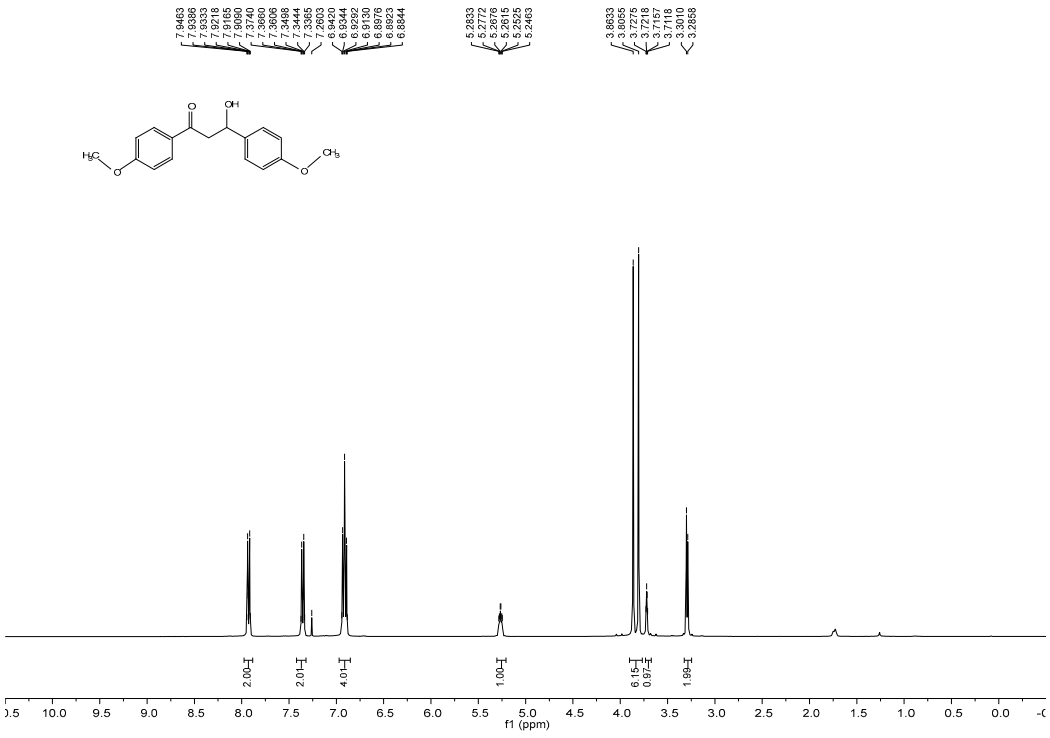

199.7852
146.6684
136.3144
133.8696
128.7781
128.1344
126.0417
125.5251
125.4672
77.3193
77.2030
77.0007
76.6831
69.4569
47.1756
O
OH
CF3
f1 (ppm)

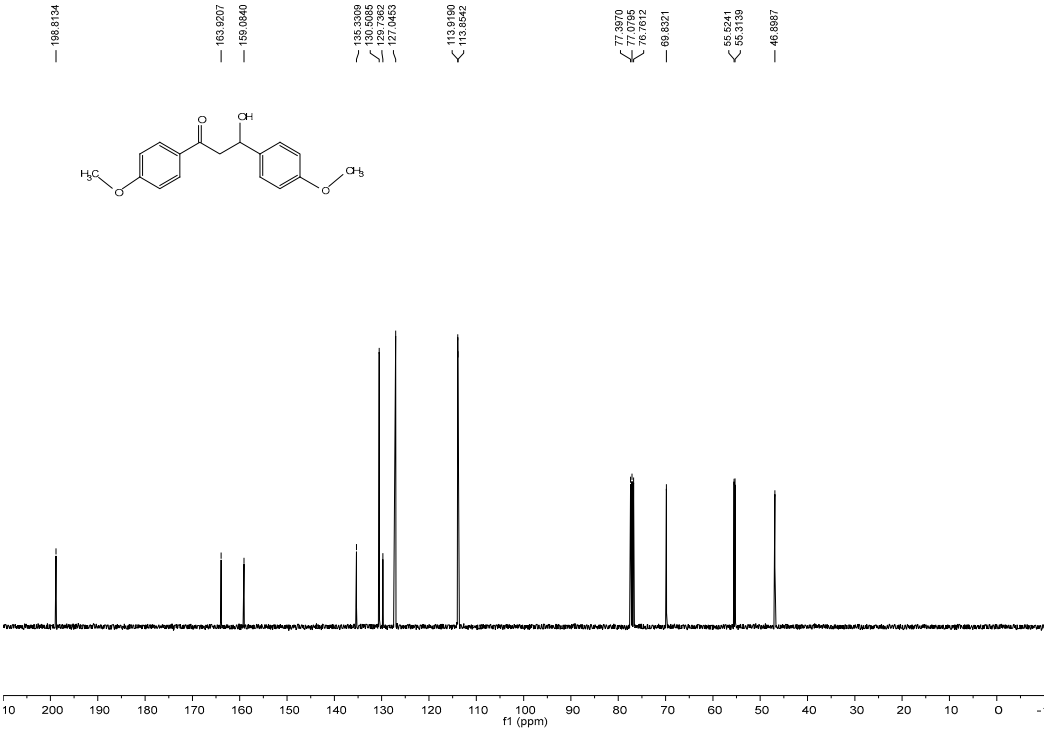
6m


7.8594
7.8550
7.8432
7.8388
7.4254
7.4201
7.4118
7.4041
7.3956
7.3903
7.2747
7.2600
7.2544
7.0804
7.0750
7.0645
7.0587
7.0532
7.0422
7.0369
5.3236
5.3113
5.3029
3.7146
3.7075
3.3297
3.3205
3.2899
2.4176
1.5613
O
OH
H3C
F
2.00
2.08
2.12
2.05
1.11
0.98
2.27
3.17
f1 (ppm)

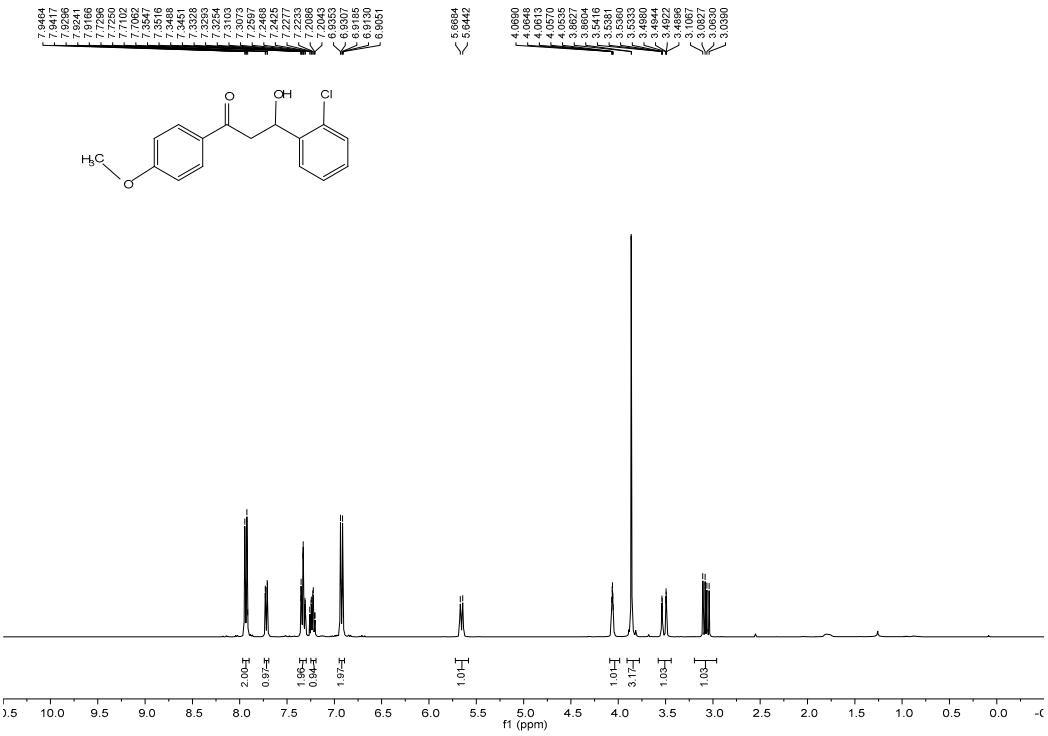

199.5949
163.3206
160.8816
144.6105
138.8031
138.7723
133.9612
133.9577
128.2024
127.4200
127.3393
115.3421
115.1307
77.3178
77.2905
77.0000
76.6877
76.6823
76.6519
69.4185
47.0881
21.6040
O
OH
H3C
F
f1 (ppm)

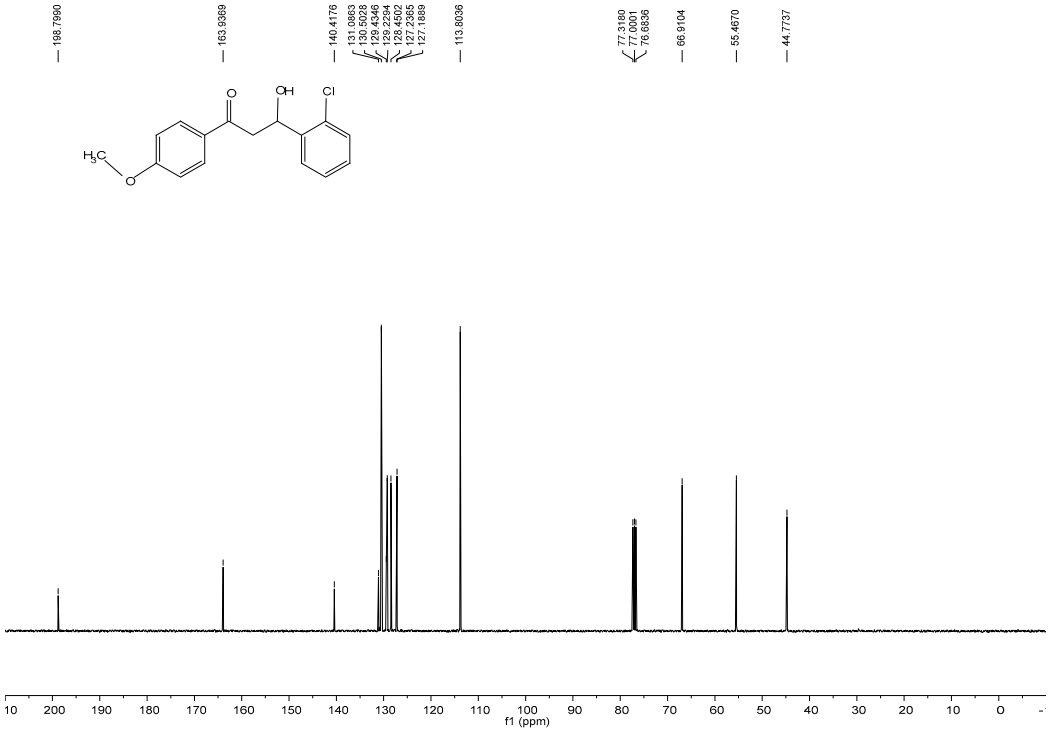
6n


7.9463
7.9386
7.9333
7.9218
7.9165
7.9090
7.3740
7.3660
7.3606
7.3498
7.3444
7.3365
7.2603
6.9420
6.9344
6.9292
6.9130
6.8976
6.8923
6.8844
5.2833
5.2772
5.2668
5.2615
5.2525
5.2463
3.8633
3.8055
3.7775
3.7218
3.7157
3.7118
3.3010
3.2858
O
OH
H3C
CH3
2.00
2.01
4.01
1.00
6.15
0.87
1.99
f1 (ppm)

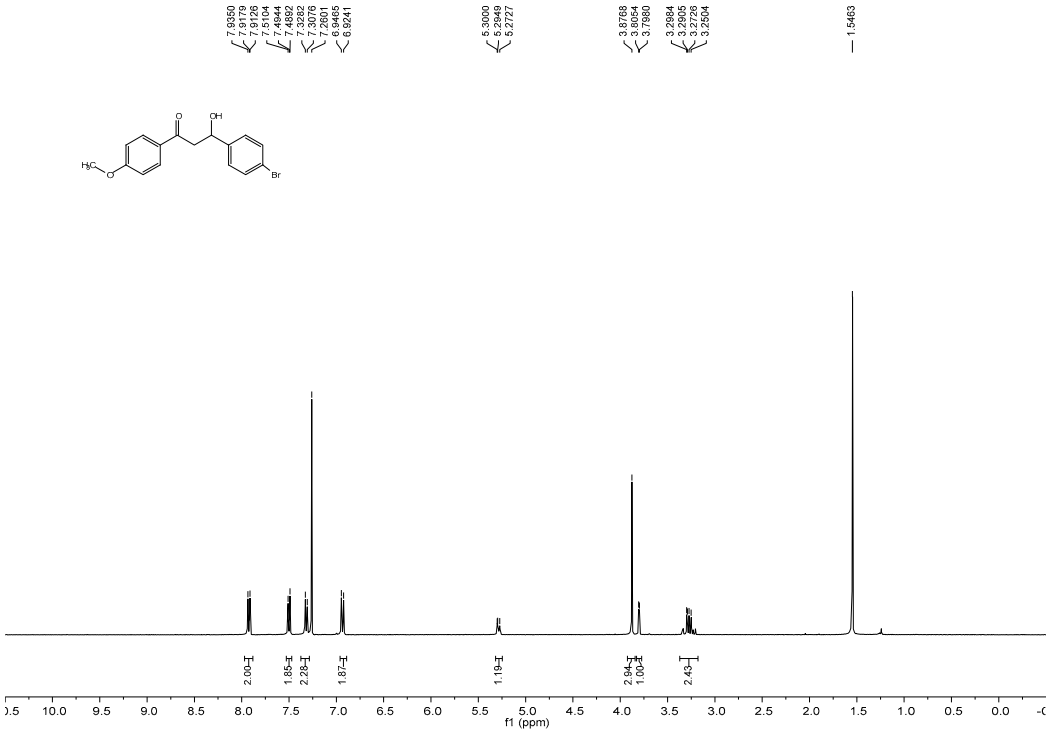

198.8134
163.9207
159.0840
135.3309
130.5085
129.7982
127.0453
113.9190
113.8542
77.3970
77.0755
76.7612
69.8321
55.5241
55.3139
46.8987
O
OH
H3C
O
O
CH3
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

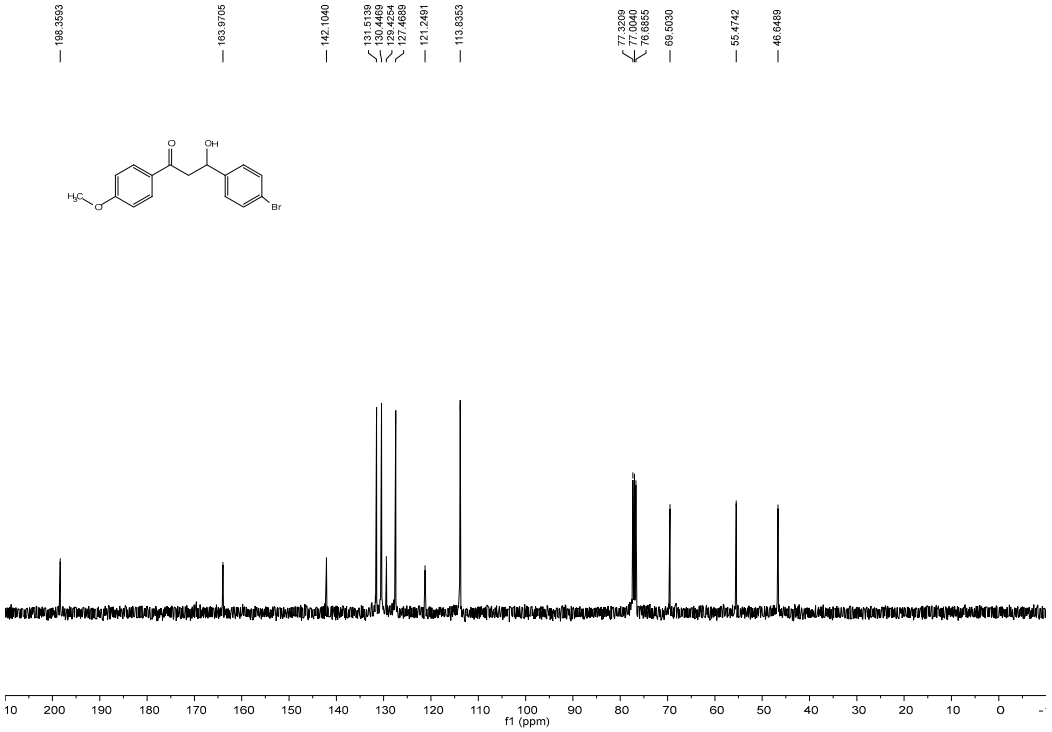
6o


7.9464
7.9417
7.9296
7.9241
7.9166
7.7996
7.7250
7.7102
7.7062
7.3547
7.3516
7.3468
7.3451
7.3328
7.3293
7.3254
7.3103
7.2977
7.2597
7.2468
7.2425
7.2277
7.2233
7.2086
7.2043
6.9353
6.9307
6.9185
6.9130
6.9051
5.6684
5.6442
4.0690
4.0648
4.0613
4.0570
4.0535
3.8827
3.8604
3.5416
3.5381
3.5360
3.5333
3.4980
3.4944
3.4922
3.4896
3.1867
3.1827
3.0630
3.0390
O
OH
Cl
H3C
O
2.00
0.97
1.96
0.94
1.97
1.01
1.01
3.17
1.03
1.03
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

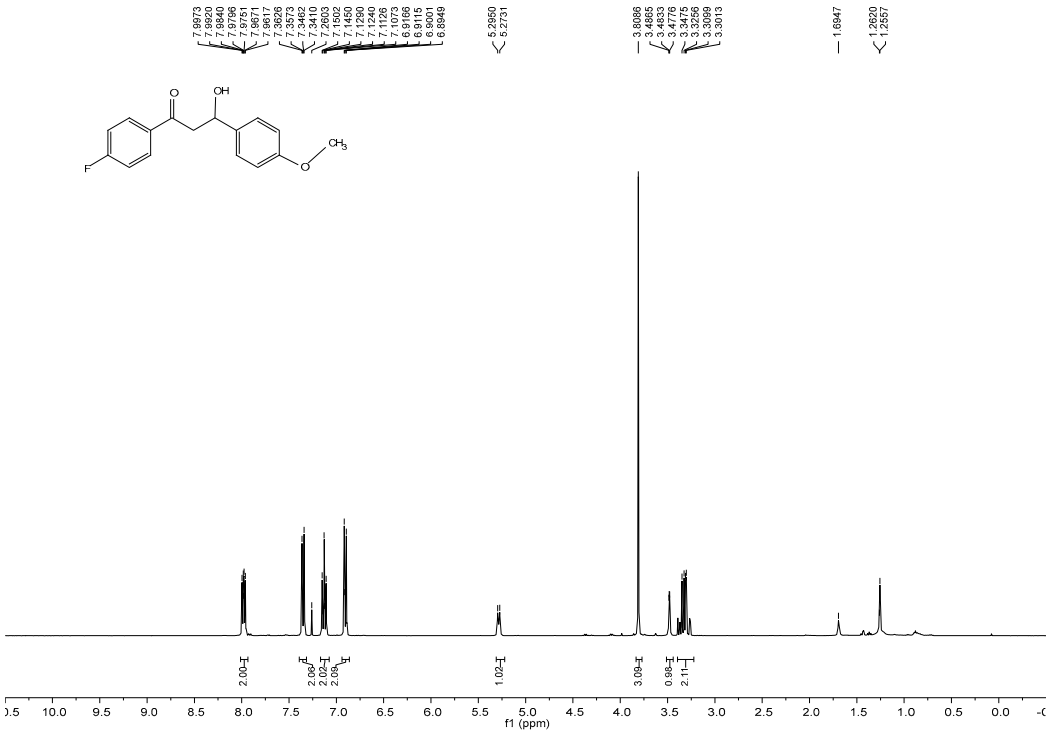

198.7990
163.9369
140.4176
131.0863
130.5028
129.4346
128.2294
128.4562
127.2985
127.1689
113.8036
77.3180
77.0001
76.6838
66.9104
55.4670
44.7737
O
OH
Cl
H3C
O
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

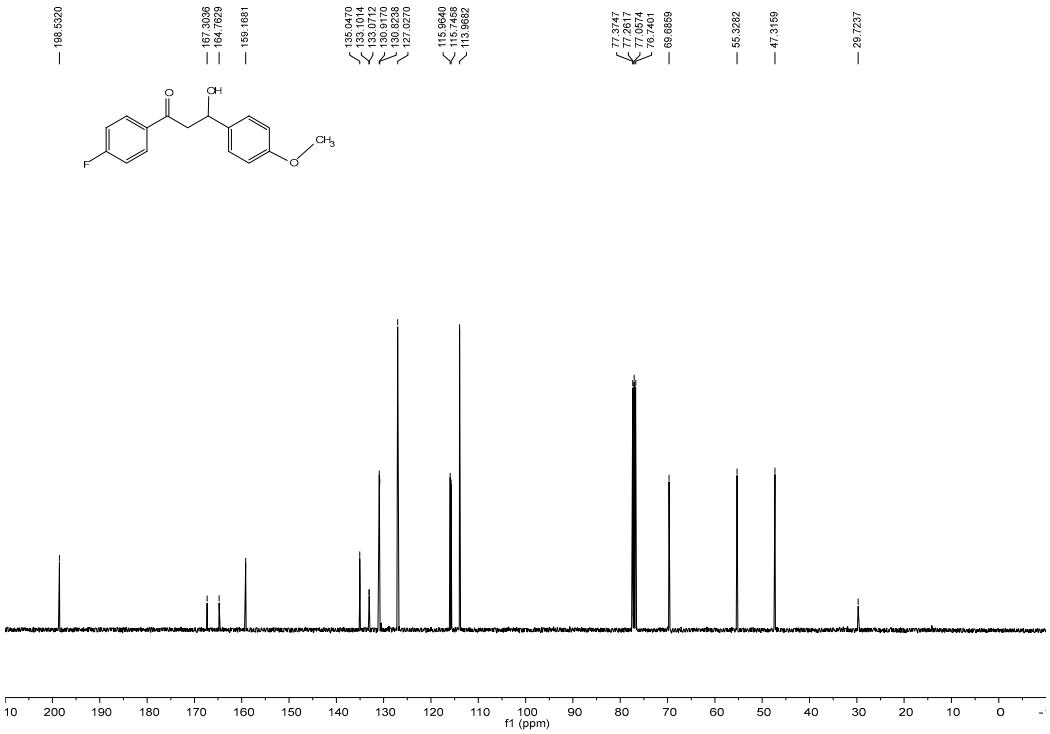
6p


7.9350
7.9179
7.9126
7.5104
7.4944
7.4892
7.3282
7.2976
7.2601
6.9465
6.9241
5.3000
5.2949
5.2727
3.8768
3.8654
3.7980
3.2984
3.2905
3.2726
3.2504
1.5463
O
OH
H3C
O
Br
2.00
1.85
2.28
1.87
1.19
2.94
1.00
2.43
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

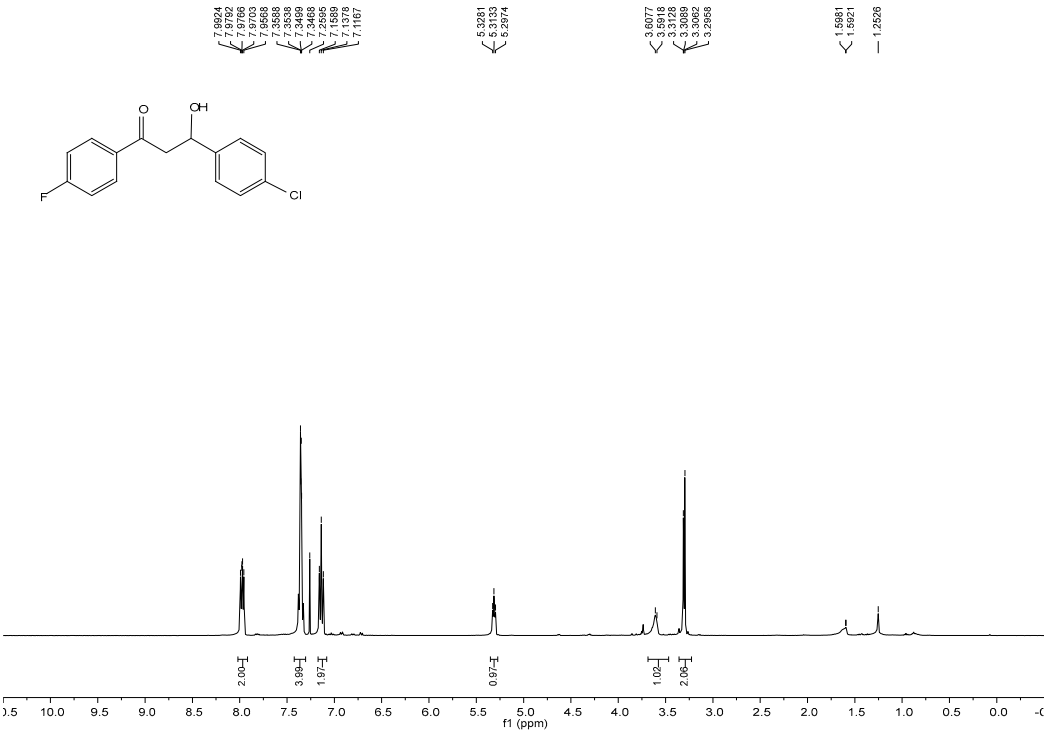

198.3593
163.9705
142.1040
131.5139
130.4469
129.4254
127.4689
121.2491
113.8353
77.3269
77.0040
76.6855
69.5030
55.4742
46.6489
O
OH
H3C
O
Br
f1 (ppm)

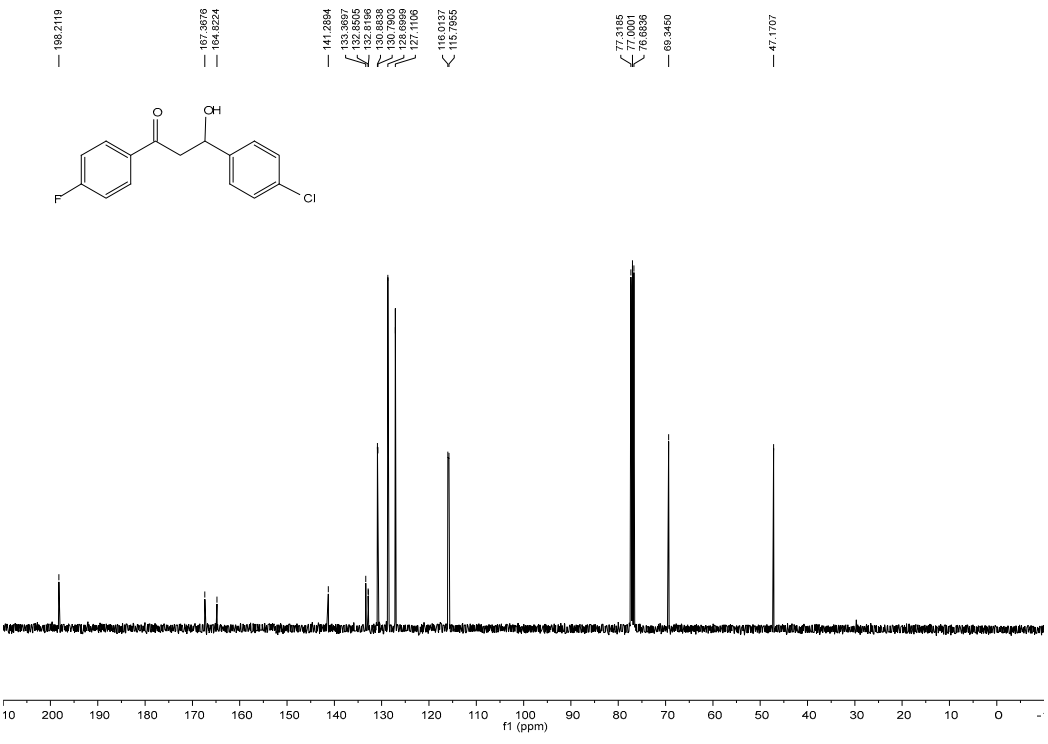
6q


7.9973
7.9920
7.9840
7.9796
7.9751
7.9677
7.9617
7.3828
7.3573
7.3462
7.3410
7.2983
7.1502
7.1450
7.1290
7.1240
7.1178
7.1073
6.9166
6.9115
6.9001
6.8949
5.2950
5.2731
3.8088
3.4885
3.4453
3.4776
3.3475
3.3256
3.3089
3.3013
1.6947
1.2620
1.2557
O
OH
F
CH3
O
2.00
2.06
2.02
2.09
1.02
3.09
0.98
2.11
f1 (ppm)

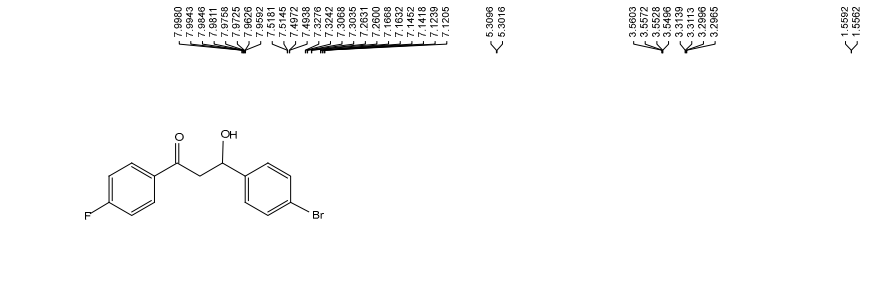

198.5320
167.3036
164.7629
159.1681
135.0470
133.1014
133.0712
130.8170
130.8028
127.0270
115.9640
115.7468
115.5662
77.3747
77.2617
77.0574
76.7401
69.6859
55.3282
47.3159
29.7237
O
OH
F
O
CH3
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

6r

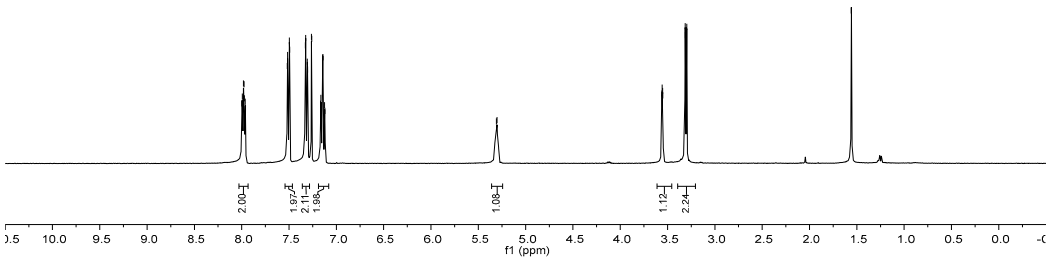

7.9924
7.9792
7.9766
7.9703
7.9568
7.3588
7.3538
7.3499
7.3468
7.2965
7.1589
7.1378
7.1167
5.3281
5.3153
5.2974
3.6077
3.5918
3.3218
3.3089
3.3062
3.2958
1.5981
1.5921
1.2526
O
OH
F
Cl
2.00
3.99
1.97
0.97
1.02
2.06
f1 (ppm)

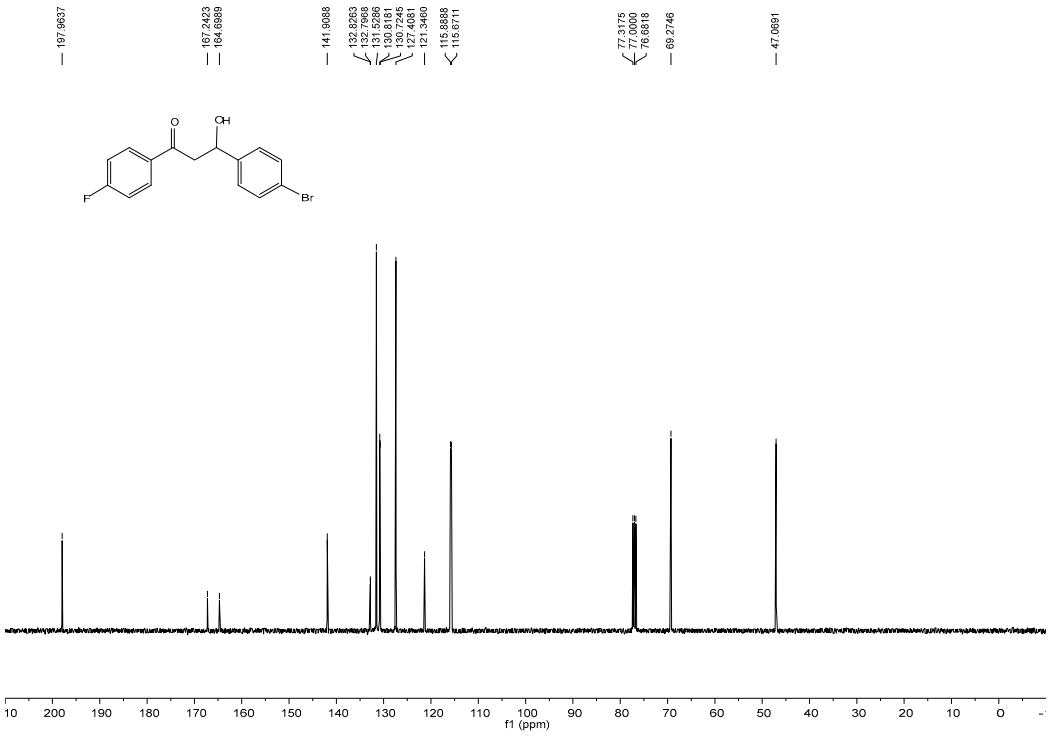

198.2119
167.3676
164.8224
141.2884
133.3687
132.8505
132.8196
130.9838
130.7903
128.8999
127.1106
116.0137
115.7955
77.3185
77.0001
76.6838
69.3450
47.1707
O
OH
F
Cl
f1 (ppm)

6s


7.9880
7.9843
7.9846
7.9651
7.9758
7.9725
7.9626
7.9592
7.5181
7.5145
7.4972
7.4838
7.3276
7.3242
7.3068
7.3035
7.2631
7.2600
7.1668
7.1632
7.1418
7.1418
7.1239
7.1205
5.3096
5.3016
3.5603
3.5572
3.5528
3.5496
3.3139
3.3115
3.2998
3.2965
1.5592
1.5562

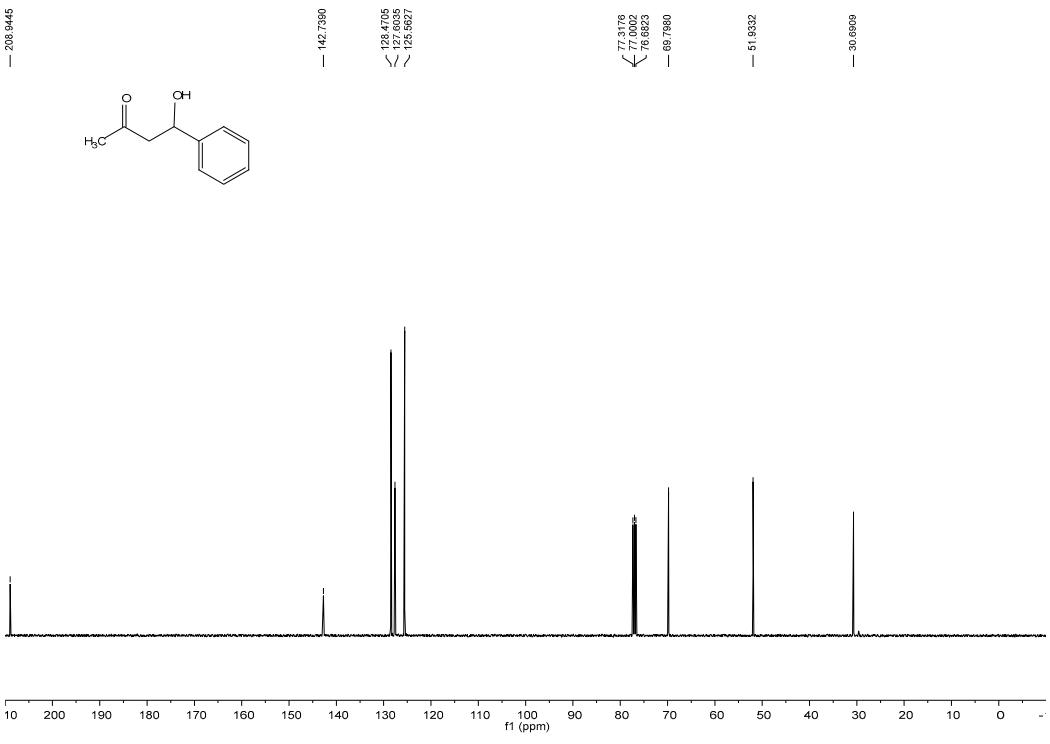
O
OH
F
Br


2.00
1.97
2.11
1.98
1.08
1.12
2.24
f1 (ppm)

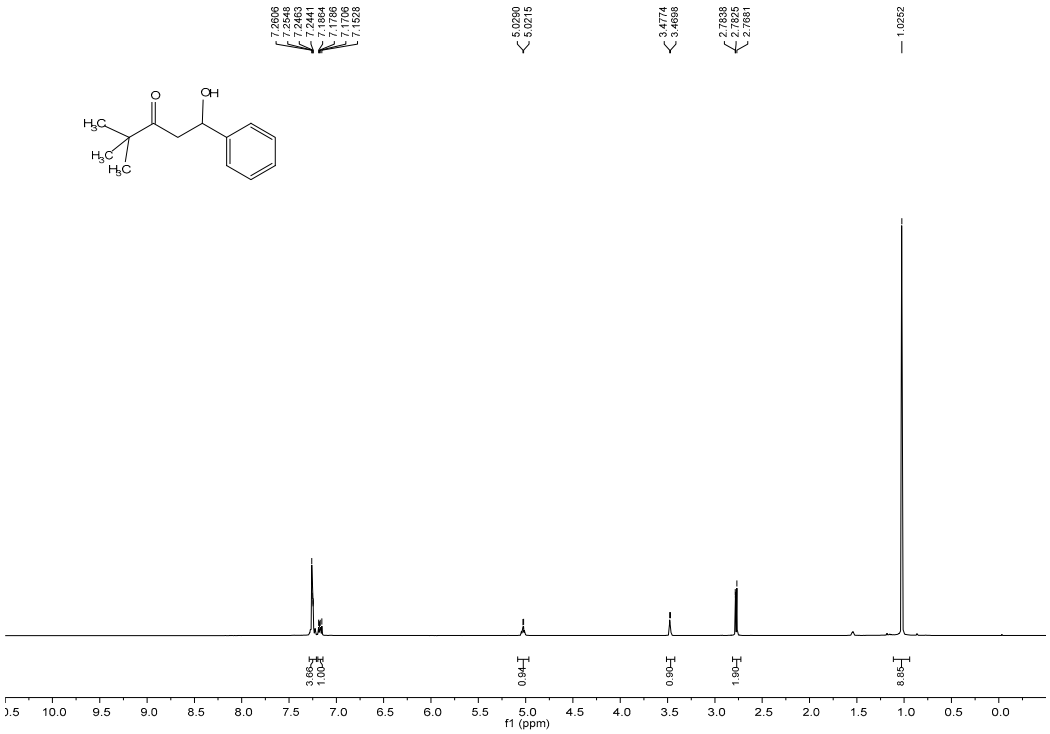

197.9637
167.2423
164.6989
141.9068
132.8263
132.7968
131.5286
130.8181
130.7245
127.4081
121.3460
115.8888
115.6711
77.3175
77.0000
76.6818
69.2746
47.0691
O
OH
F
Br
f1 (ppm)

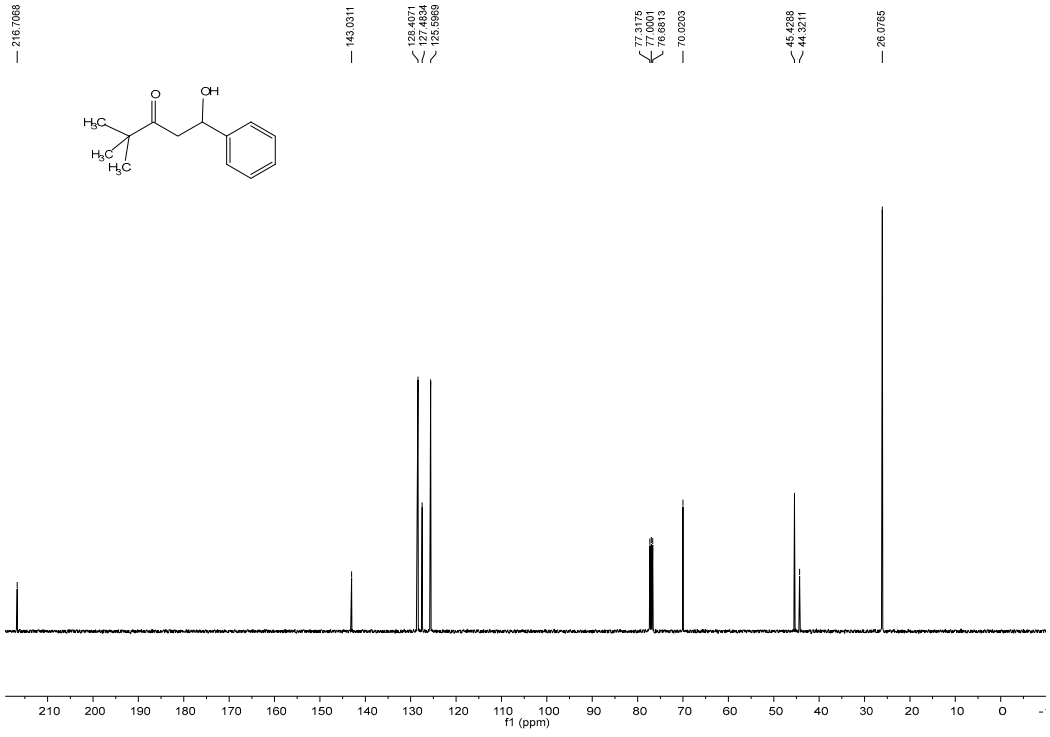
6t


7.2823
7.2712
7.2690
7.2590
7.2125
7.2040
7.2012
7.1977
7.1911
7.1790
5.0767
5.0683
5.0540
5.0456
3.2555
2.8351
2.7915
2.7688
2.7424
2.7340
2.6888
2.0992
O
OH
H3C
3.93
1.00
1.05
1.03
2.23
3.21
f1 (ppm)

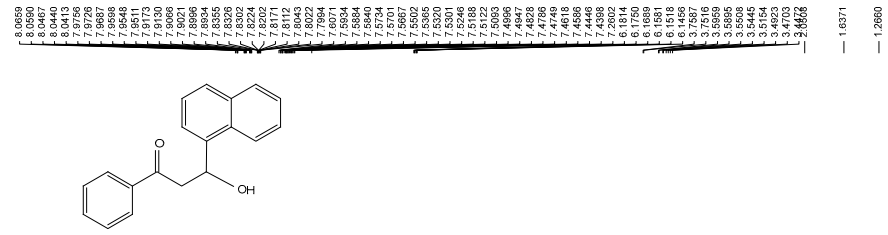

208.9445
142.7390
128.4705
127.8095
126.5827
77.3178
77.0002
76.6823
69.7980
51.9332
30.6909
O
OH
H3C
f1 (ppm)

6u

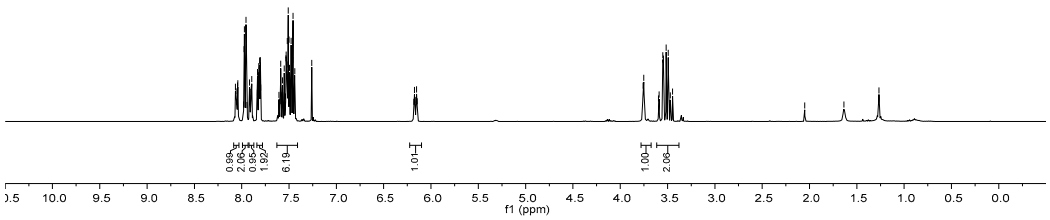

7.2606
7.2548
7.2463
7.2441
7.1864
7.1786
7.1706
7.1528
5.0290
5.0215
3.4774
3.4698
2.7838
2.7825
2.7681
1.0252
O
OH
H3C
H3C
H3C
3.66
1.00
0.94
0.90
1.90
8.85
f1 (ppm)

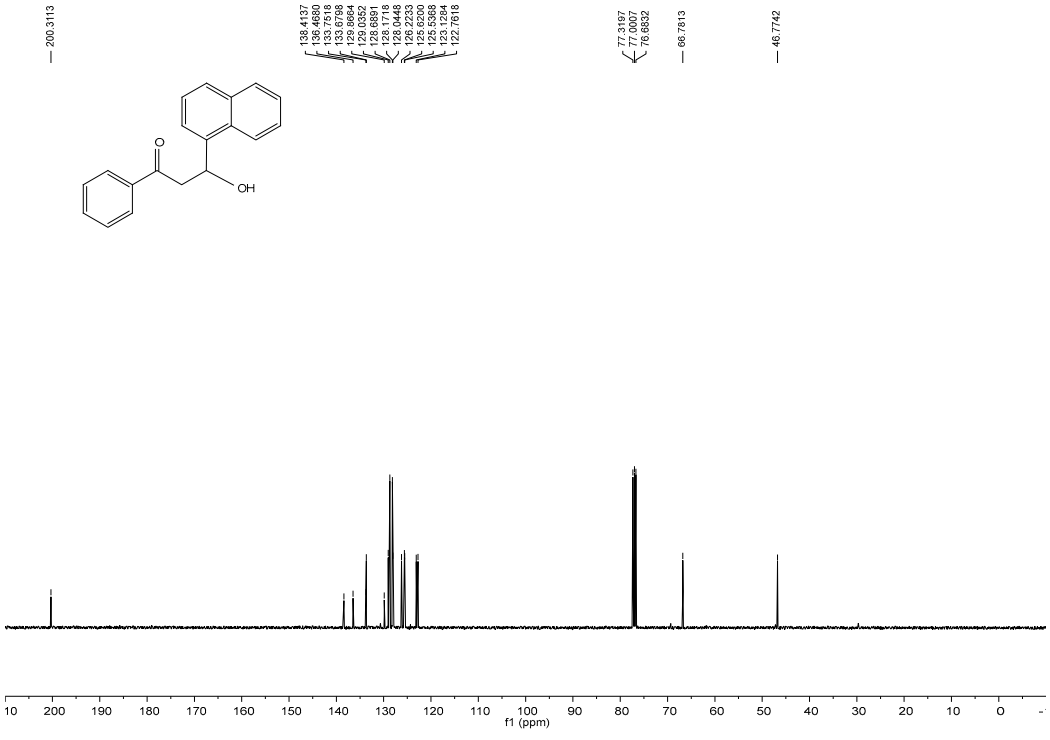

216.7068
143.0311
128.4671
127.4834
125.5969
77.3175
77.0001
76.6813
70.0203
45.4288
44.3211
26.0765
O
OH
H3C
H3C
H3C
f1 (ppm)

6v.

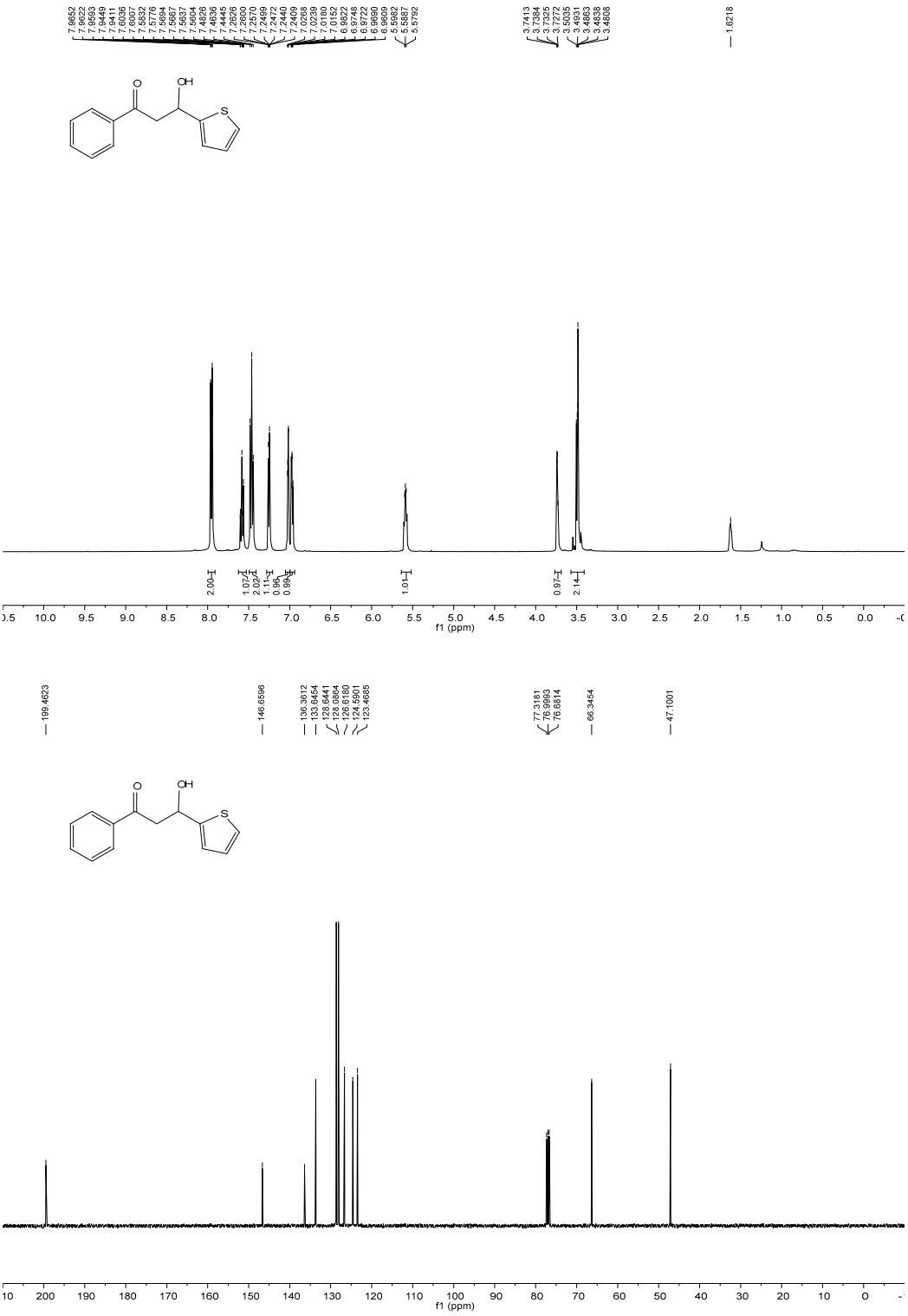


O
OH

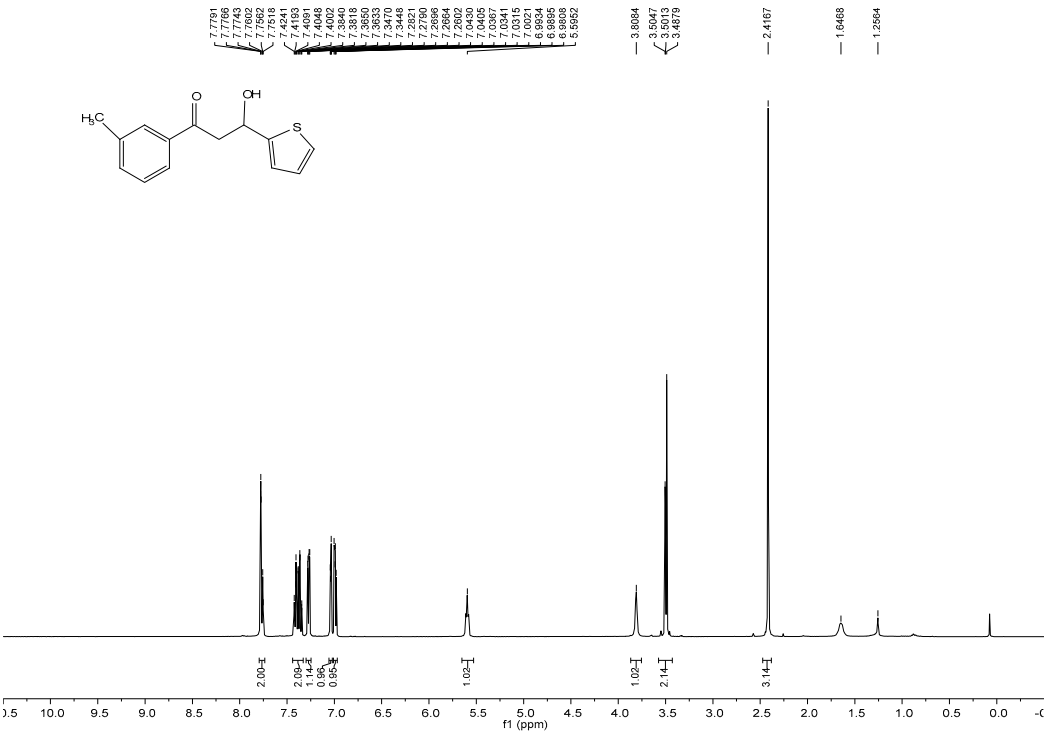

0.66
2.85
0.95
1.92
6.19
1.01
1.00
2.06
f1 (ppm)

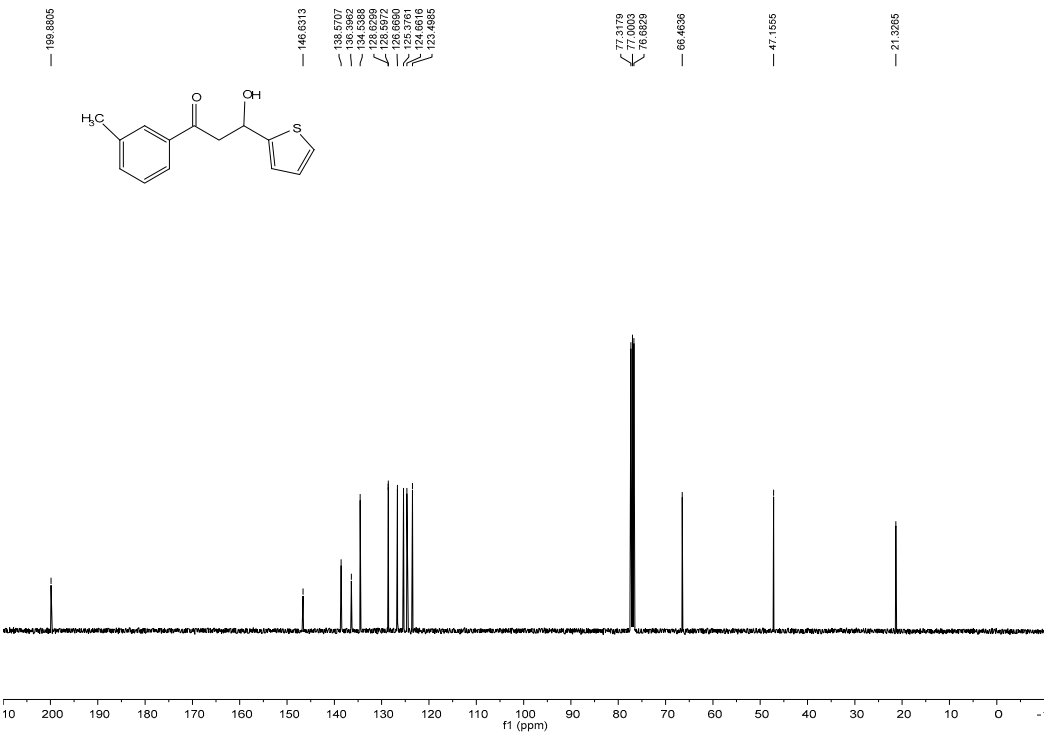

200.3113
138.4137
136.4680
133.7518
133.3598
129.8664
129.0352
128.6891
128.1718
128.0448
126.2233
125.6200
125.5368
123.1284
122.7618
77.3167
77.0007
76.6832
66.7813
46.7742
O
OH
f1 (ppm)

6w


7.9652
7.9622
7.9593
7.9449
7.9411
7.8098
7.6007
7.5832
7.5776
7.5684
7.5657
7.5627
7.5604
7.4826
7.4636
7.4445
7.2828
7.2800
7.2570
7.2499
7.2472
7.2440
7.2408
7.2068
7.0239
7.0180
7.0152
6.9822
6.9758
6.9727
6.9660
6.9609
5.5982
5.5887
5.5792
3.7413
3.7394
3.7325
3.7272
3.5035
3.4931
3.4863
3.4838
3.4808
1.6218
O
OH
S
2.00
1.07
2.04
1.11
0.96
0.99
1.01
0.97
2.14
f1 (ppm)
199.4623
146.6596
136.3612
133.6454
128.6441
128.0864
126.6180
124.5901
123.4685
77.3181
76.9983
76.6814
66.3454
47.1001
O
OH
S
f1 (ppm)

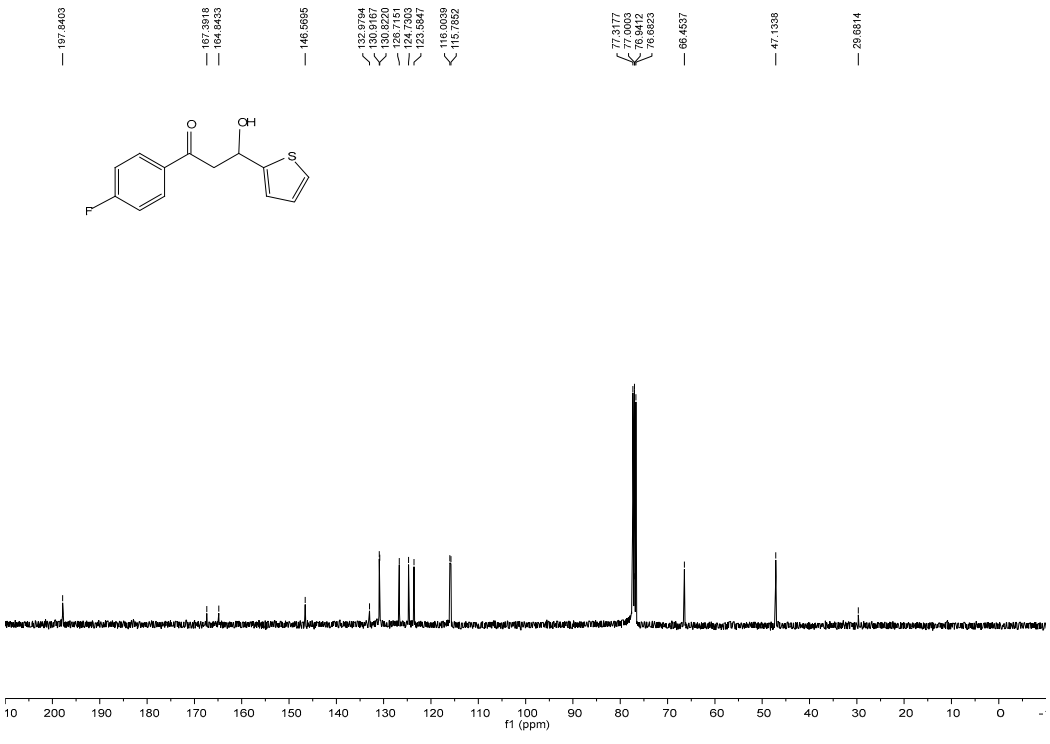
6x


7.7791
7.7766
7.7743
7.7602
7.7582
7.7518
7.4241
7.4163
7.4091
7.4048
7.4002
7.3840
7.3818
7.3659
7.3633
7.3470
7.3448
7.2821
7.2690
7.2666
7.2664
7.2602
7.0430
7.0405
7.0357
7.0341
7.0315
7.0021
6.9934
6.9895
6.9868
6.9852
3.8084
3.5047
3.5013
3.4879
2.4167
1.6458
1.2564
O
OH
H3C
S
2.00
2.09
1.14
0.96
0.95
1.03
1.00
2.14
3.14
f1 (ppm)

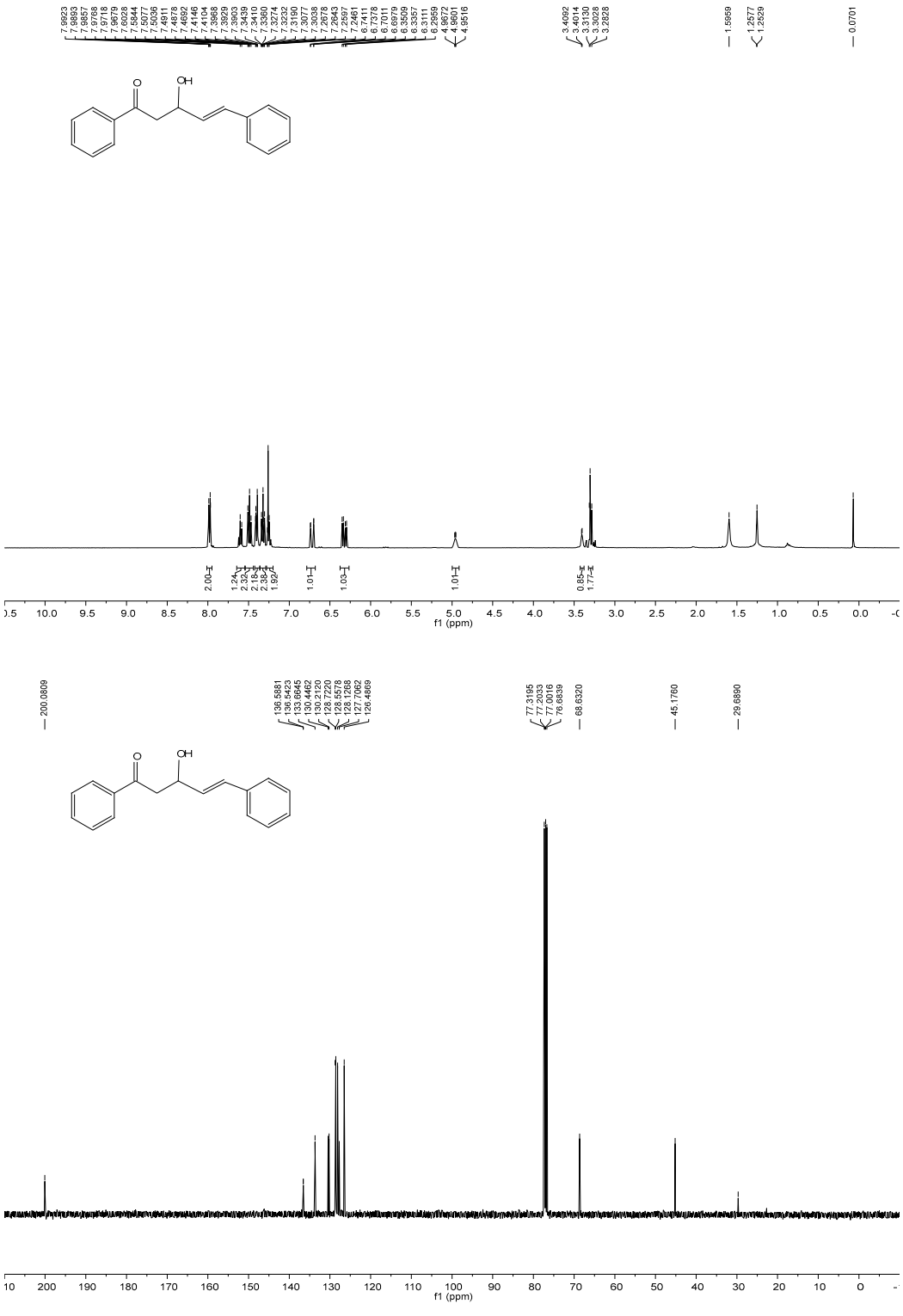

199.8805
146.6313
138.5707
136.3962
134.5388
128.6299
128.5972
126.6690
125.3701
124.6616
123.4985
77.3179
77.0003
76.6829
66.4636
47.1555
21.3265
O
OH
H3C
S
f1 (ppm)

6y


8.0219
8.0082
8.0002
7.9865
7.9815
7.2786
7.2691
7.2657
7.2598
7.1721
7.1668
7.1508
7.1339
7.1293
7.0394
7.0308
7.0092
6.9912
6.9874
6.9785
5.6096
5.5917
3.6428
3.6352
3.4951
3.4744
3.4682
3.4581
1.2571
O
OH
S
F
2.00
1.41
2.16
1.06
1.02
1.02
1.01
2.22
1.16
f1 (ppm)


197.8403
167.3918
164.8433
146.5695
132.9764
130.9167
130.8220
129.7751
124.7303
123.5847
116.0039
115.7862
77.3177
77.0003
76.8412
76.6823
66.4537
47.1338
29.6814
O
OH
S
F
f1 (ppm)

6z


7.9923
7.9863
7.9857
7.9798
7.9718
7.9679
7.9679
7.9028
7.6944
7.5077
7.5036
7.4911
7.4878
7.4690
7.4146
7.4104
7.3988
7.3929
7.3903
7.3418
7.3410
7.3380
7.3274
7.3232
7.3190
7.3077
7.3008
7.2678
7.2643
7.2597
7.2461
6.7411
6.7378
6.7011
6.6979
6.3509
6.3357
6.3151
6.2959
4.9672
4.9601
4.9516
3.4092
3.4014
3.3130
3.3028
3.2828
1.5869
1.2577
1.2269
0.0701
O
OH
2.00
1.24
2.15
2.38
1.92
1.01
1.03
1.01
0.85
1.77
f1 (ppm)
200.0809
136.5881
136.5423
133.6645
130.4462
130.2120
128.7220
128.5578
128.1288
127.7062
126.4869
77.3195
77.2033
77.0016
76.6839
68.6320
45.1760
29.6890
f1 (ppm)