

Borylation of α,β -Unsaturated Acceptors by Chitosan Composite Film Supported Copper Nanoparticles

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Supporting Information

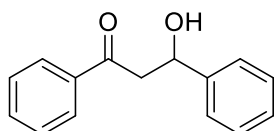
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1. Characterization Data for β -Hydroxyl Products

All of adducts are literature-known; obtained characterization data for these compounds is in full agreement with reported data.

3-Hydroxy-1,3-diphenylpropan-1-one (**3a**)



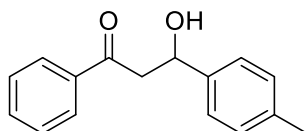
Colorless oil

^1H NMR (400 MHz); δ = 7.97 (d, J = 7.1 Hz, 2H), 7.61-7.57 (m, 1H), 7.49-7.44 (m, 4H), 7.40-7.37 (m, 2H), 7.33-7.29 (m, 1H), 5.37 (t, J = 6.1 Hz, 1H), 3.39 (d, J = 6.1 Hz, 2H).

^{13}C NMR (100 MHz); δ = 200.0, 142.9, 136.5, 133.6, 128.6, 128.5, 128.1, 127.6, 125.7, 69.9, 47.3.

MS (ESI): m/z 227 $[\text{M}+\text{H}]^+$.

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



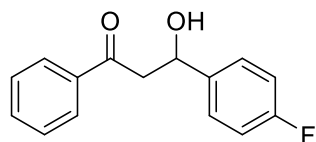
White solid

^1H NMR (400 MHz); δ = 7.97 (d, J = 7.0 Hz, 2H), 7.61 (m, J = 7.4 Hz, 1H), 7.49-7.45 (m, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 7.8 Hz, 2H), 5.34-5.30 (m, 1H), 3.64 (d, J = 2.3 Hz, 1H), 3.38-3.35 (m, 2H), 2.37 (s, 3H).

^{13}C NMR (100 MHz); δ = 200.1, 139.9, 137.2, 136.5, 133.5, 129.1, 128.6, 128.1, 125.6, 69.8, 47.3, 21.1.

MS (ESI): m/z 241 $[\text{M}+\text{H}]^+$.

3-(4-Fluorophenyl)-3-hydroxy-1-phenylpropan-1-one (**3c**)



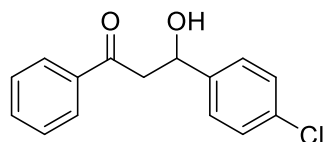
White solid

^1H NMR (400 MHz); δ = 7.96 (d, J = 7.0 Hz, 2H), 7.62-7.58 (m, 2H), 7.49-7.40 (m, 4H), 7.06 (t, J = 8.7 Hz, 2H), 5.34-5.32 (m, 1H), 3.36-3.34 (m, 2H).

^{13}C NMR (100 MHz); δ = 200.0, 163.4, 160.9, 138.69, 138.66, 136.4, 133.7, 128.7, 128.1, 127.44, 127.36, 115.4, 115.2, 69.4, 47.3.

MS (ESI): m/z 245 $[\text{M}+\text{H}]^+$.

3-(4-Chlorophenyl)-3-hydroxy-1-phenylpropan-1-one (**3d**)



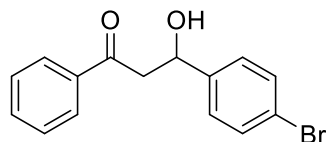
White solid

^1H NMR (400 MHz); δ = 7.96 (d, J = 7.0 Hz, 2H), 7.62 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.9 Hz, 2H), 7.39-7.34 (m, 4H), 5.34 (m, 1H), 3.35-3.33 (m, 2H).

^{13}C NMR (100 MHz); δ = 199.8, 141.4, 136.3, 133.7, 133.2, 128.64, 128.56, 128.1, 127.1, 69.3, 47.2.

MS (ESI): m/z 262 $[\text{M}+\text{H}]^+$.

3-(4-Bromophenyl)-3-hydroxy-1-phenylpropan-1-one (**3e**)



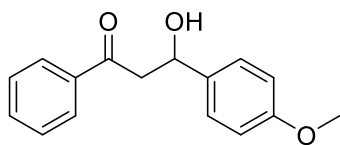
White solid

^1H NMR (400 MHz); δ = 7.95 (d, J = 7.0 Hz, 2H), 7.62 (t, J = 7.4 Hz, 1H), 7.51-7.45 (m, 4H), 7.33 (d, J = 8.4 Hz, 2H), 5.32 (dd, J = 7.4, 4.8 Hz, 1H), 3.68 (br, 1H), 3.38-3.28 (m, 2H).

^{13}C NMR (100 MHz); δ = 199.9, 141.9, 136.3, 133.8, 131.6, 128.7, 128.1, 127.5, 121.4, 69.4, 47.2.

MS (ESI): m/z 306 $[M+H]^+$.

3-Hydroxy-3-(4-methoxyphenyl)-1-phenylpropan-1-one (**3f**)



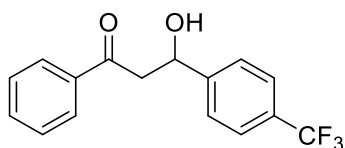
White solid

^1H NMR (400 MHz); δ = 7.97 (d, J = 7.0 Hz, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.49-7.45 (m, 2H), 7.38 (t, J = 8.5 Hz, 2H), 6.93-6.91 (m, 2H), 5.32 (dd, J = 7.1, 5.0 Hz, 1H), 3.82 (s, 3H), 3.38-3.33 (m, 2H).

^{13}C NMR (100 MHz); δ = 200.2, 159.0, 136.5, 135.1, 133.6, 128.6, 128.1, 127.0, 113.9, 69.6, 55.2, 47.3.

MS (ESI): m/z 257 $[M+H]^+$.

3-Hydroxy-1-phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one (**3g**)



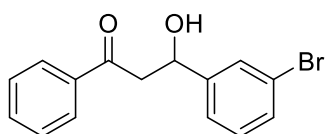
White solid

^1H NMR (400 MHz); δ = 7.96 (d, J = 7.4 Hz, 2H), 7.65-7.57 (m, 5H), 7.50 (t, J = 7.7 Hz, 2H), 5.43 (dd, J = 8.6, 3.4 Hz, 1H), 3.38-3.35 (m, 2H).

^{13}C NMR (100 MHz); δ = 199.8, 146.9, 136.3, 133.9, 130.0, 129.6, 128.8, 128.1, 126.0, 125.499, 125.495, 125.46, 125.42, 122.7, 68.4, 47.2.

MS (ESI): m/z 295 $[M+H]^+$.

3-(3-Bromophenyl)-3-hydroxy-1-phenylpropan-1-one (**3h**)



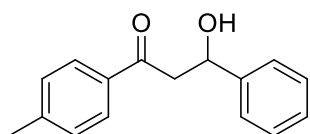
White solid

^1H NMR (400 MHz); δ = 7.95 (d, J = 7.5 Hz, 2H), 7.61-7.57 (m, 2H), 7.48-7.21 (m, 5H), 5.37 (m, 1H), 3.82 (br, 1H), 3.34-3.32 (m, 2H).

^{13}C NMR (100 MHz); δ = 199.7, 145.2, 136.2, 133.7, 130.6, 130.0, 128.8, 128.6, 128.1, 124.3, 122.6, 69.1, 47.1.

MS (ESI): m/z 306 $[\text{M}+\text{H}]^+$.

3-Hydroxy-3-phenyl-1-(*p*-tolyl)propan-1-one (**3i**)



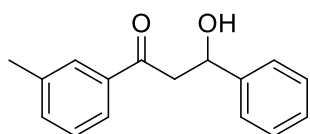
White solid

^1H NMR (400 MHz); δ = 7.84 (d, J = 8.3 Hz, 2H), 7.43 (d, J = 6.8 Hz, 2H), 7.37-7.34 (m, 2H), 7.30-7.23 (m, 3H), 5.33-5.29 (m, 1H), 3.76 (d, J = 2.9 Hz, 1H), 3.33 (d, J = 6.0 Hz, 2H), 2.39 (s, 3H).

^{13}C NMR (100 MHz); δ = 199.8, 144.5, 142.9, 134.0, 129.3, 128.4, 128.2, 127.5, 125.7, 70.0, 47.1, 21.6.

MS (ESI): m/z 241 $[\text{M}+\text{H}]^+$.

3-Hydroxy-3-phenyl-1-(*m*-tolyl)propan-1-one (**3j**)



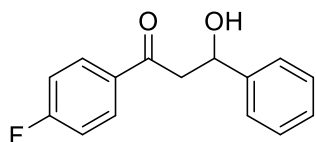
White solid

^1H NMR (400 MHz); δ = 7.76 (d, J = 8.3 Hz, 2H), 7.46-7.29 (m, 7H), 5.36-5.33 (m, 1H), 3.37 (br, 2H), 2.40 (s, 3H).

^{13}C NMR (100 MHz); δ = 200.3, 142.9, 138.4, 136.5, 134.2, 128.6, 128.5, 128.4, 127.5, 125.7, 125.3, 69.9, 47.4, 21.2.

MS (ESI): m/z 241 $[\text{M}+\text{H}]^+$.

1-(4-Fluorophenyl)-3-hydroxy-3-phenylpropan-1-one (**3k**)



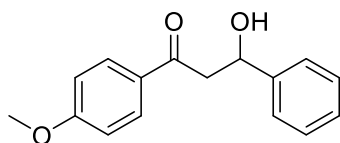
White solid

^1H NMR (400 MHz); δ = 7.99-7.96 (m, 2H), 7.44-7.42 (m, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.32 (t, J = 7.2 Hz, 1H), 7.15-7.10 (m, 2H), 5.35-5.32 (m, 1H), 3.63 (d, J = 3.0 Hz, 1H), 3.40-3.27 (m, 2H).

^{13}C NMR (100 MHz); δ = 198.3, 167.2, 164.7, 142.8, 133.0, 132.9, 130.8, 130.7, 128.5, 127.7, 125.7, 115.9, 115.6, 69.9, 47.3.

MS (ESI): m/z 245 $[\text{M}+\text{H}]^+$.

3-Hydroxy-1-(4-methoxyphenyl)-3-phenylpropan-1-one (**3l**)



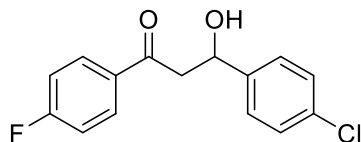
White solid

^1H NMR (400 MHz); δ = 7.95 -7.93 (m, 2H), 7.45-7.26 (m, 5H), 6.94 (d, J = 9.0 Hz, 2H), 5.34 (dd, J = 8.4, 3.7 Hz, 1H), 3.87 (s, 3H), 3.33-3.30 (m, 2H).

^{13}C NMR (100 MHz); δ = 198.7, 163.8, 143.0, 130.4, 129.5, 128.4, 127.5, 125.7, 113.7, 70.0, 55.4, 46.8.

MS (ESI): m/z 257 $[\text{M}+\text{H}]^+$.

3-(4-Chlorophenyl)-1-(4-fluorophenyl)-3-hydroxypropan-1-one (**3m**)



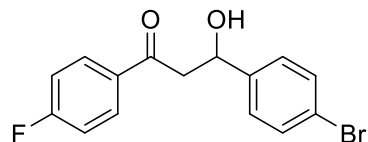
White solid

^1H NMR (400 MHz); δ = 7.99 (dd, J = 8.9, 5.3 Hz, 2H), 7.38 (dd, J = 12.2, 8.7 Hz, 4H), 7.14 (t, J = 8.6 Hz, 2H), 5.33-5.30 (m, 1H), 3.31-3.30 (m, 2H).

^{13}C NMR (100 MHz); δ = 198.2, 167.4, 164.8, 141.3, 133.4, 132.9, 132.8, 130.9, 130.8, 128.7, 127.1, 116.0, 115.8, 69.3, 47.2.

MS (ESI): m/z 280 $[M+H]^+$.

3-(4-Bromophenyl)-1-(4-fluorophenyl)-3-hydroxypropan-1-one (**3n**)



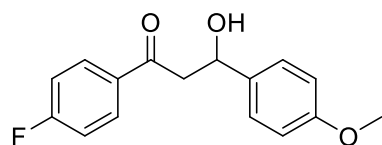
White solid

^1H NMR (400 MHz); δ = 7.99 (dd, J = 8.9 Hz, 5.4 Hz, 2H), 7.51 (d, J = 8.4 Hz, 1H), 7.32 (d, J = 8.4 Hz, 2H), 7.14 (t, J = 8.6 Hz, 2H), 5.31-5.28 (m, 1H), 3.59 (br, 1H), 3.30 (d, J = 5.9 Hz, 2H).

^{13}C NMR (100 MHz); δ = 198.2, 167.4, 164.8, 141.8, 132.83, 132.81, 131.7, 130.9, 130.8, 127.4, 121.5, 116.0, 115.8, 69.4, 47.1.

MS (ESI): m/z 324 $[M+H]^+$.

1-(4-Fluorophenyl)-3-hydroxy-3-(4-methoxyphenyl)propan-1-one (**3o**)



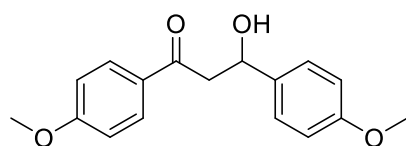
White solid

^1H NMR (400 MHz); δ = 8.00-7.97 (m, 2H), 7.37 (d, J = 8.6 Hz, 2H), 7.16 (t, J = 8.6 Hz, 2H), 6.92 (d, J = 8.7 Hz, 2H), 5.31-5.27 (m, 1H), 3.81 (s, 3H), 3.45 (br, 1H), 3.35-3.31 (m, 2H).

^{13}C NMR (100 MHz); δ = 198.4, 167.2, 164.6, 159.0, 135.0, 133.0, 132.98, 130.8, 130.7, 126.9, 115.8, 115.6, 113.8, 69.6, 55.2, 47.2.

MS (ESI): m/z 275 $[M+H]^+$.

3-Hydroxy-1,3-bis(4-methoxyphenyl)propan-1-one (**3p**)



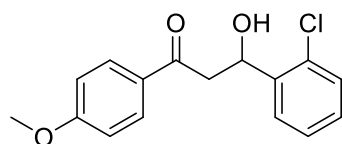
White solid

^1H NMR (400 MHz); δ = 7.95 (d, J = 8.9 Hz, 2H), 7.37 (d, J = 8.6 Hz, 2H), 6.94 (t, J = 8.3 Hz, 4H), 5.29-5.26 (m, 1H), 3.87 (s, 3H), 3.81 (s, 3H), 3.31-3.29 (m, 2H).

^{13}C NMR (100 MHz); δ = 198.8, 163.9, 159.0, 135.2, 130.5, 129.6, 127.0, 113.9, 113.8, 69.8, 55.5, 55.3, 46.8.

MS (ESI): m/z 287 $[\text{M}+\text{H}]^+$.

3-(2-Chlorophenyl)-3-hydroxy-1-(4-methoxyphenyl)propan-1-one (**3q**)



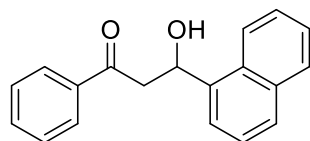
White solid

^1H NMR (400 MHz); δ = 7.93 (d, J = 9.0 Hz, 2H), 7.71.-7.68 (dd, J = 7.5, 1.6 Hz, 1H), 7.33-7.29 (m, 2H), 7.24-7.18 (m, 1H), 6.93 (d, J = 9.0 Hz, 2H), 5.66-5.62 (m, 1H), 4.06 (br, 1H), 3.84 (s, 3H), 3.52-3.47 (dd, J = 17.5, 2.2 Hz, 1H), 3.08-3.02 (dd, J = 17.5, 9.6 Hz, 1H).

^{13}C NMR (100 MHz); δ = 198.8, 163.9, 140.4, 131.1, 130.5, 129.4, 129.2, 128.4, 127.23, 127.18, 113.8, 66.9, 55.5, 44.8.

MS (ESI): m/z 292 $[\text{M}+\text{H}]^+$.

3-Hydroxy-3-(naphthalen-1-yl)-1-phenylpropan-1-one (**3r**)



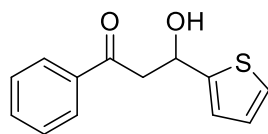
White solid

^1H NMR (400 MHz); δ = 8.07-8.05 (m, 1H), 8.00-7.90 (m, 3H), 7.83 (d, J = 7.6 Hz, 2H), 7.60-7.43 (m, 6H), 6.19-6.15 (m, 1H), 3.86 (br, 1H), 3.58-3.45 (m, 2H).

^{13}C NMR (100 MHz); δ = 200.2, 138.4, 136.4, 133.7, 133.6, 129.8, 129.0, 128.6, 128.1, 128.0, 126.1, 125.6, 125.5, 123.1, 122.7, 66.7, 46.7.

MS (ESI): m/z 277 $[\text{M}+\text{H}]^+$.

3-Hydroxy-1-phenyl-3-(thiophen-2-yl)propan-1-one (**3s**)



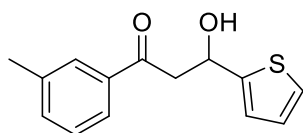
White solid

^1H NMR (400 MHz); δ = 7.99-7.97 (m, 2H), 7.61-7.50 (m, 1H), 7.50-7.46 (m, 2H), 7.29-7.26 (m, 1H), 7.04-6.98 (m, 2H), 5.62 (m, 1H), 3.79 (s, 1H), 3.53-3.50 (m, 2H).

^{13}C NMR (100 MHz); δ = 199.6, 146.6, 136.4, 133.8, 128.7, 128.1, 126.7, 124.7, 123.5, 66.4, 47.1.

MS (ESI): m/z 233 $[\text{M}+\text{H}]^+$.

3-Hydroxy-3-(thiophen-2-yl)-1-(*m*-tolyl)propan-1-one (**3t**)



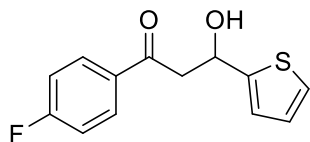
White solid

^1H NMR (400 MHz); δ = 7.78 (d, J = 7.9 Hz, 2H), 7.42-7.35 (m, 2H), 7.28 (dd, J = 5.0, 1.2 Hz, 2H), 7.05 (d, J = 3.5 Hz, 1H), 7.00 (dd, J = 5.0, 3.5 Hz, 1H), 5.60 (t, J = 5.8 Hz, 1H), 3.50 (d, J = 5.9 Hz, 2H), 2.42 (s, 3H).

^{13}C NMR (100 MHz); δ = 199.9, 146.7, 138.6, 136.4, 134.5, 128.63, 128.59, 126.7, 125.4, 124.7, 123.5, 66.5, 47.2, 21.3.

MS (ESI): m/z 247 $[\text{M}+\text{H}]^+$.

1-(4-Fluorophenyl)-3-hydroxy-3-(thiophen-2-yl)propan-1-one (**3u**)



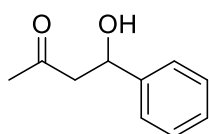
White solid

^1H NMR (400 MHz); δ = 8.01-7.98 (dd, J = 7.6, 5.4 Hz, 2H), 7.28-7.26 (m, 1H), 7.17-7.13 (m, 2H), 7.03-6.97 (m, 2H), 5.61-5.58 (m, 1H), 3.70 (br, 1H), 3.54-3.41 (m, 2H).

^{13}C NMR (100 MHz); $\delta = 197.9, 167.4, 164.8, 146.5, 132.9, 132.8, 130.9, 130.8, 126.7, 124.7, 123.6, 116.0, 115.8, 66.4, 47.1.$

MS (ESI): m/z 251 $[\text{M}+\text{H}]^+$.

4-Hydroxy-4-phenylbutan-2-one (**3v**)



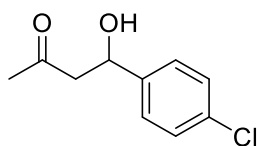
Colorless oil

^1H NMR (400 MHz); $\delta = 7.37$ (d, $J = 4.4$ Hz, 4H), 7.31-7.28 (m, 1H), 5.18-5.14 (m, 1H), 3.41 (br, 1H), 2.93-2.78 (m, 2H), 2.20 (s, 3H).

^{13}C NMR (100 MHz); $\delta = 209.1, 142.6, 128.5, 127.7, 125.6, 69.8, 51.9, 30.8.$

MS (ESI): m/z 165 $[\text{M}+\text{H}]^+$.

4-(4-Chlorophenyl)-4-hydroxybutan-2-one (**3w**)



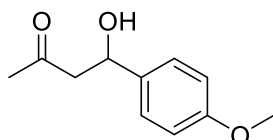
White solid

^1H NMR (400 MHz); $\delta = 7.38$ -7.32 (m, 4H), 5.19-5.16 (m, 1H), 3.2 (br, 1H), 2.89-2.85 (m, 2H), 2.25 (s, 3H).

^{13}C NMR (100 MHz); $\delta = 209.0, 141.2, 133.2, 128.6, 127.0, 69.1, 51.7, 30.7.$

MS (ESI): m/z 200 $[\text{M}+\text{H}]^+$.

4-Hydroxy-4-(4-methoxyphenyl)butan-2-one (**3x**)



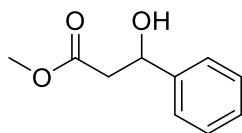
White solid

^1H NMR (400 MHz); $\delta = 7.29$ -7.26 (m, 2H), 6.89 (d, $J = 8.7$ Hz, 2H), 5.12-5.08 (m, 1H), 3.80 (s, 3H), 3.23 (br, 1H), 2.89-2.76 (m, 2H), 2.19 (s, 3H).

^{13}C NMR (100 MHz); $\delta = 209.2, 159.1, 134.8, 126.9, 113.9, 69.5, 55.3, 51.9, 30.8$.

MS (ESI): m/z 195 $[\text{M}+\text{H}]^+$.

Methyl-3-hydroxy-3-phenylpropanoate (**3y**)



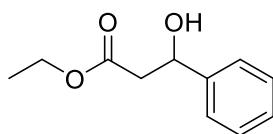
Colorless oil

^1H NMR (400 MHz); $\delta = 7.39\text{-}7.29$ (m, 5H), 5.16 (dd, $J = 8.9, 3.3$ Hz, 1H), 3.73 (s, 3H), 2.81-2.89 (m, 2H).

^{13}C NMR (100 MHz); $\delta = 172.8, 142.4, 128.6, 127.6, 125.6, 70.3, 51.9, 43.1$.

MS (ESI): m/z 181 $[\text{M}+\text{H}]^+$.

Ethyl-3-hydroxy-3-phenylpropanoate (**3z**)



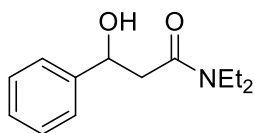
Colorless oil

^1H NMR (400 MHz); $\delta = 7.39\text{-}7.29$ (m, 5H), 5.16 (m, 1H), 4.22 (q, $J = 7.2$ Hz, 2H), 2.80-2.68 (m, 2H), 1.29 (t, $J = 7.0$ Hz, 3H).

^{13}C NMR (100 MHz); $\delta = 172.5, 142.4, 128.5, 127.8, 125.6, 70.3, 60.9, 43.3, 14.1$.

MS (ESI): m/z 195 $[\text{M}+\text{H}]^+$.

N,N-diethyl-3-hydroxy-3-phenylpropanamide (**3aa**)



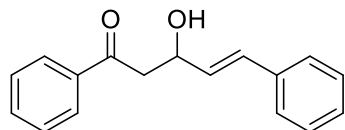
A little bit yellow oil

^1H NMR (400 MHz); $\delta = 7.41\text{-}7.26$ (m, 5H), 5.16-5.13 (m, 1H), 3.44-3.34 (m, 2H), 3.26-3.20 (m, 2H), 2.71-2.57 (m, 2H), 1.16-1.10 (m, 6H)

^{13}C NMR (100 MHz); $\delta = 171.5, 143.1, 128.4, 127.5, 125.7, 70.6, 41.9, 41.5, 40.2, 14.1, 13.0$

MS (ESI): m/z 222 $[M+H]^+$.

(*E*)-3-Hydroxy-1,5-diphenylpent-4-en-1-one (**3ab**)



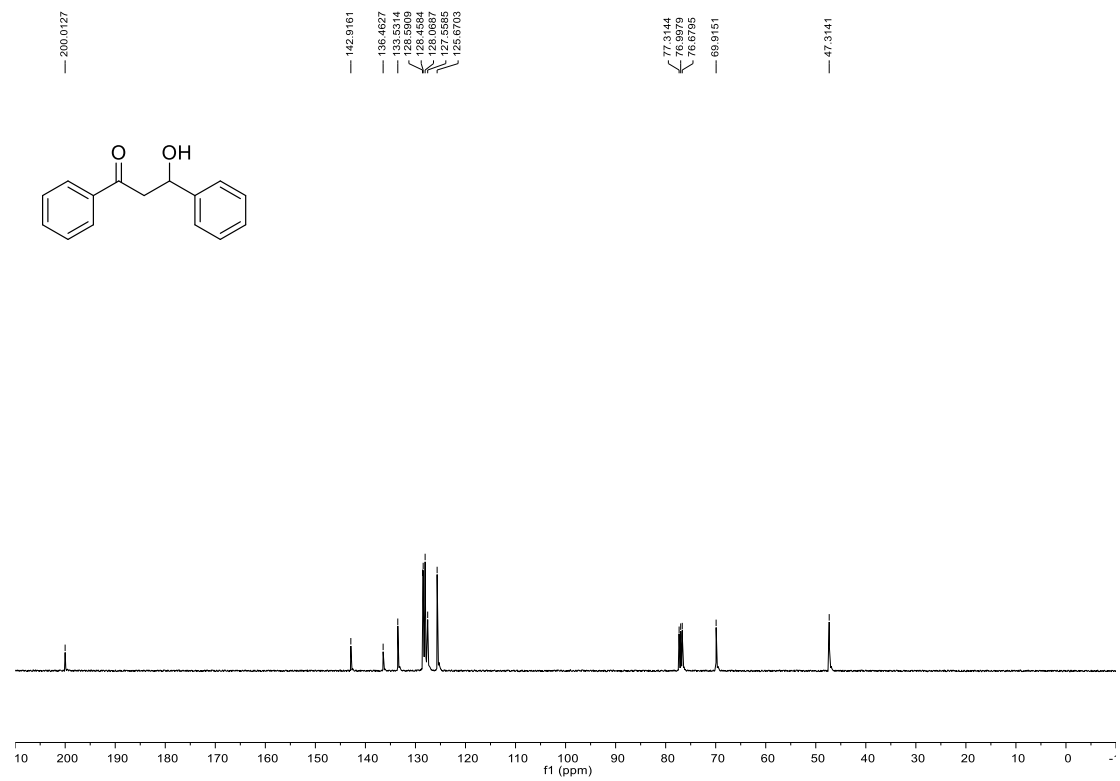
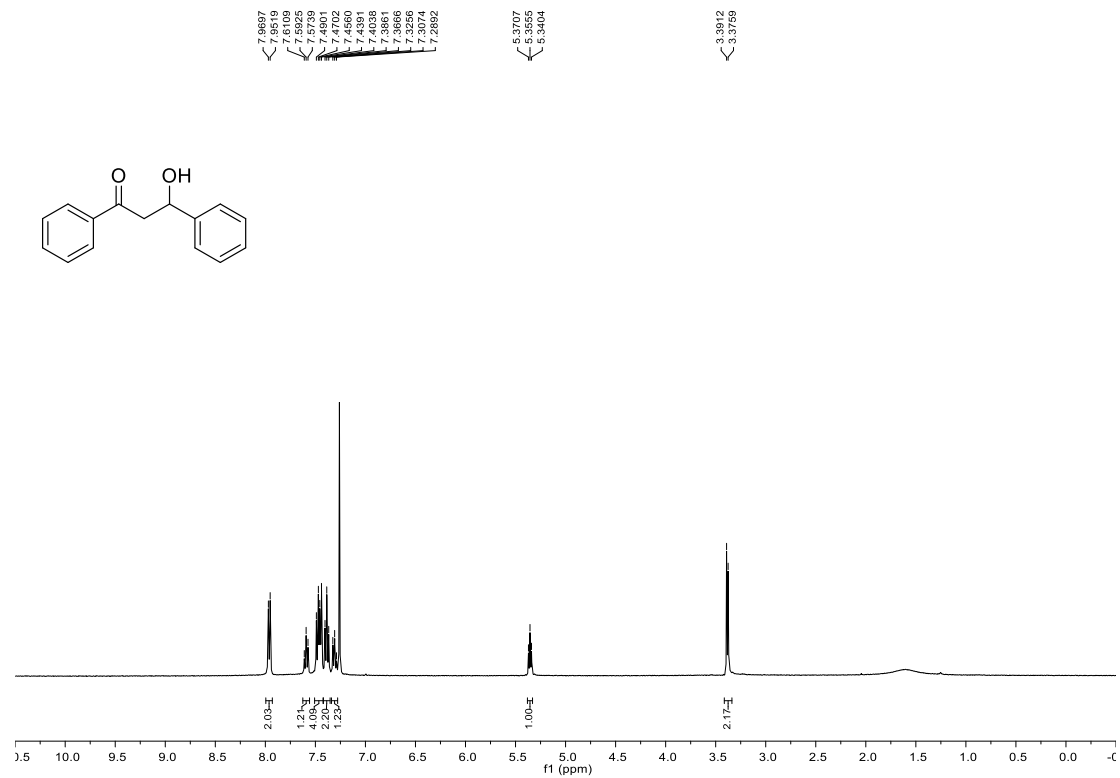
White solid

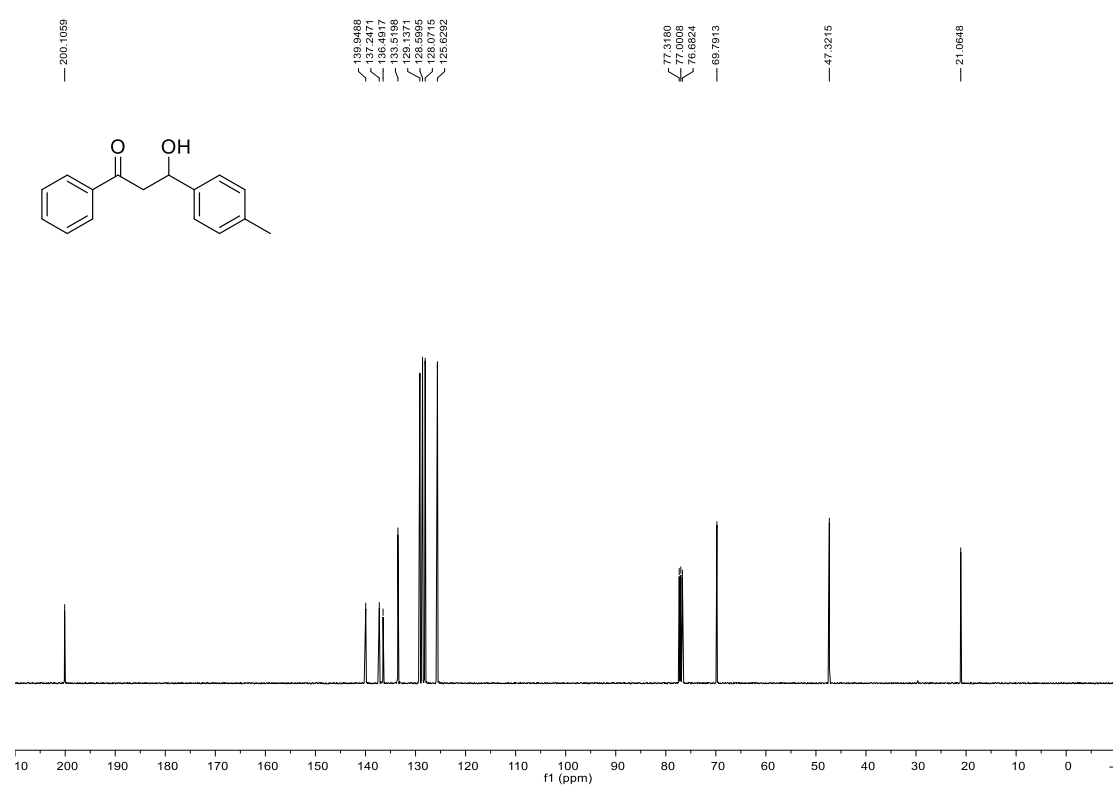
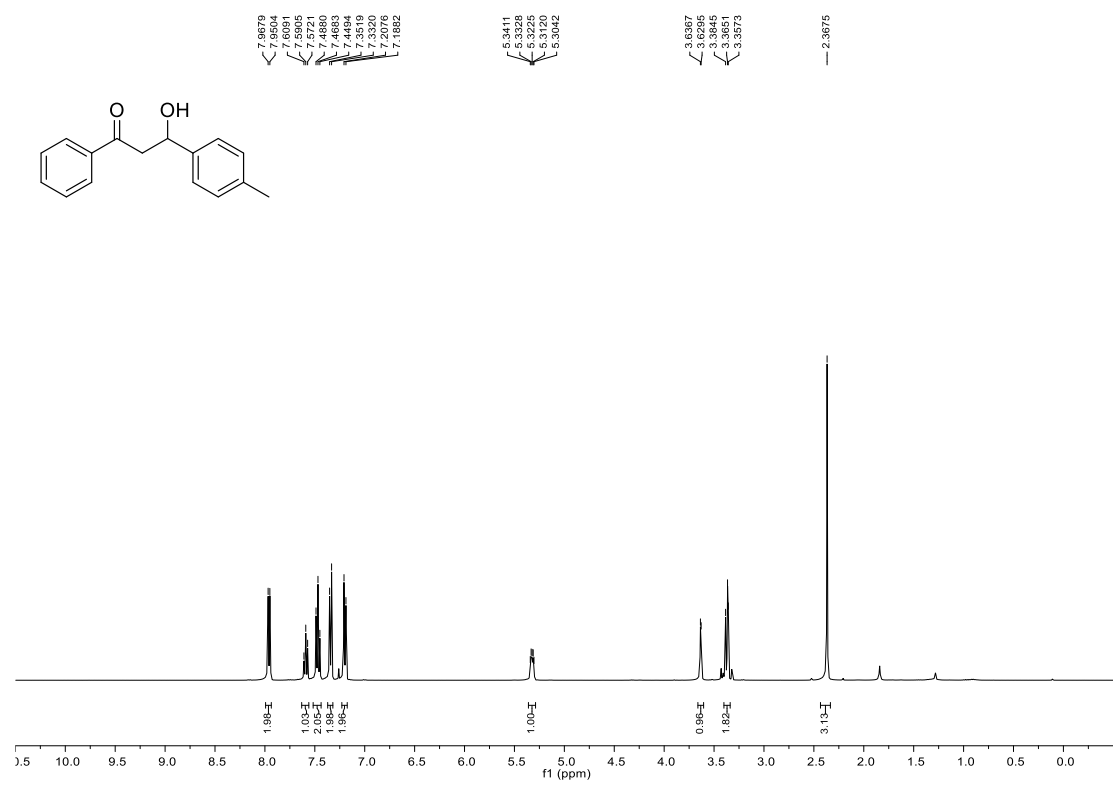
^1H NMR (400 MHz); δ = 7.90 (d, J = 7.2 Hz, 2H), 7.54 (t, J = 7.3 Hz, 1H), 7.42 (t, J = 7.6 Hz, 2H), 7.33 (d, J = 7.0 Hz, 2H), 7.26-7.22 (m, 2H), 7.18-7.15 (m, 1H), 6.65 (d, J = 15.8 Hz, 1H), 6.27 (dd, J = 15.9 Hz, 6.0 Hz, 1H), 4.89-4.86 (m, 1H), 3.38 (d, J = 3.7 Hz, 1H), 3.22-3.19 (m, 2H).

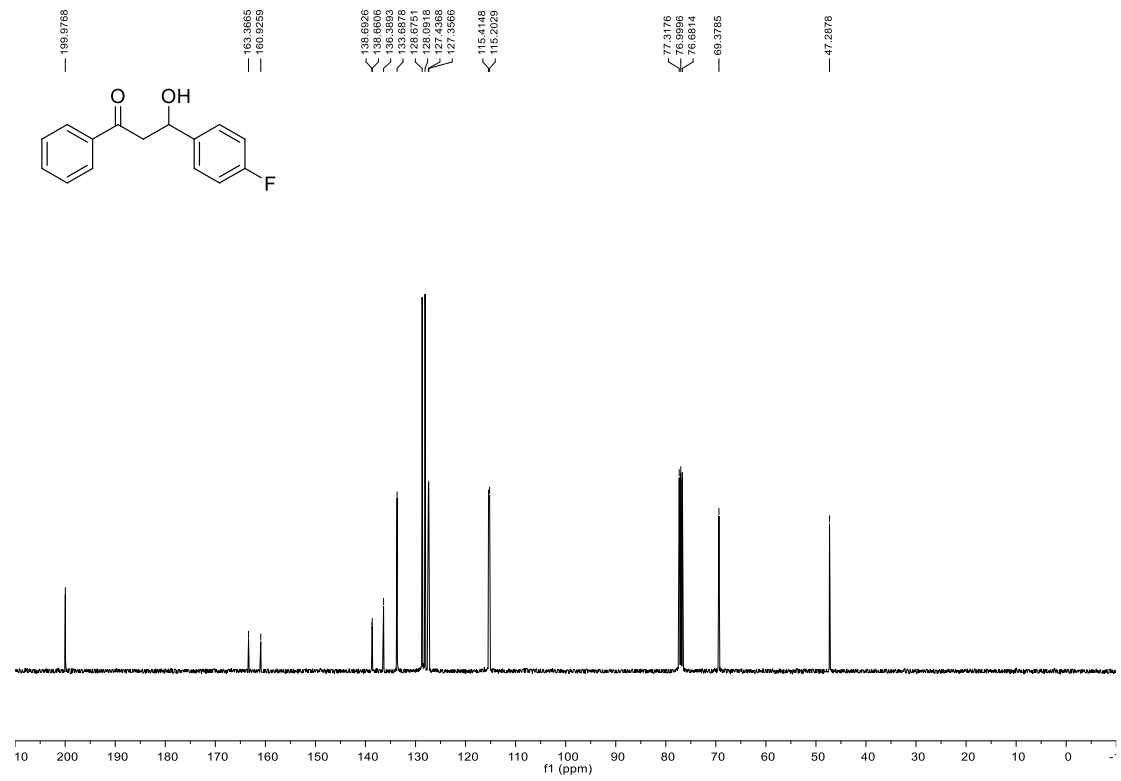
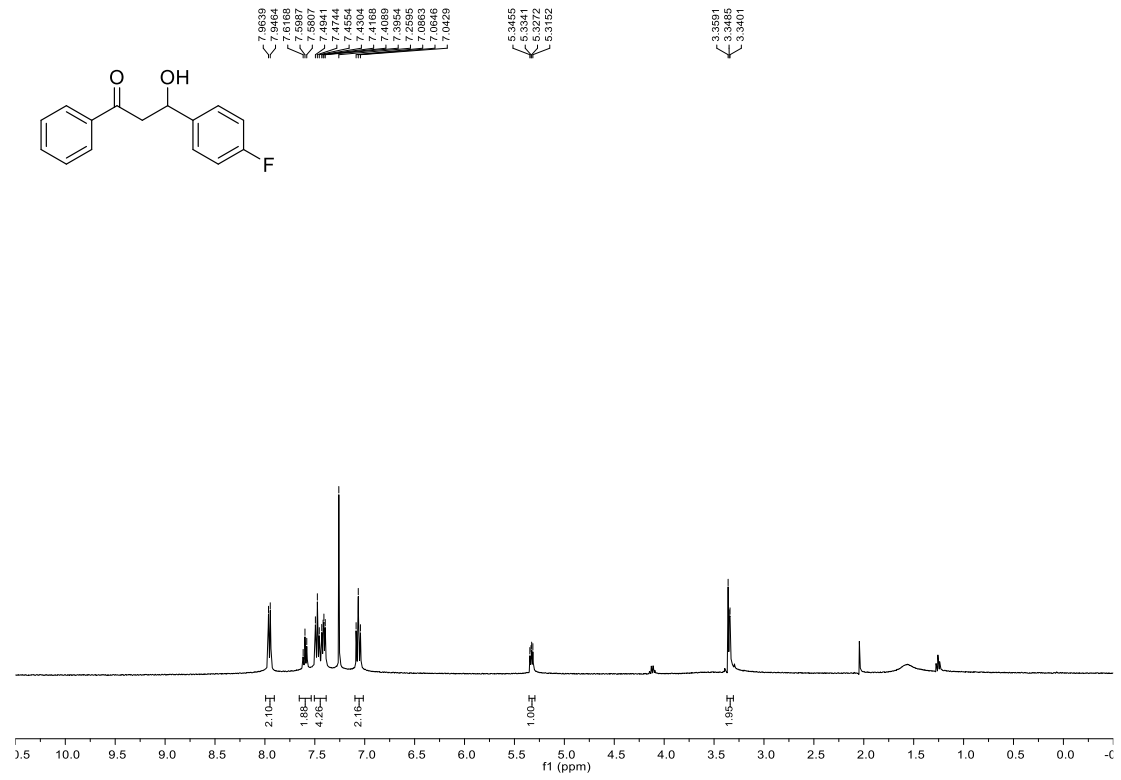
^{13}C NMR (100 MHz); δ = 200.0, 136.5, 133.6, 130.4, 130.2, 128.7, 128.5, 128.1, 127.7, 126.5, 68.6, 45.2.

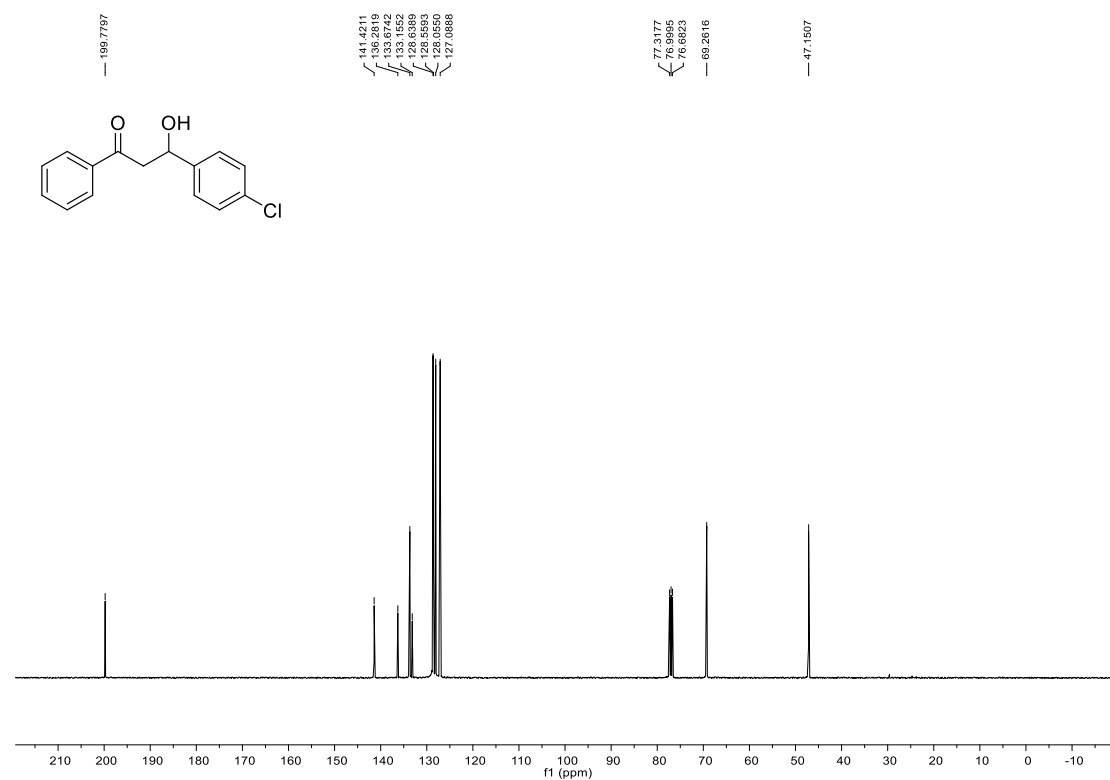
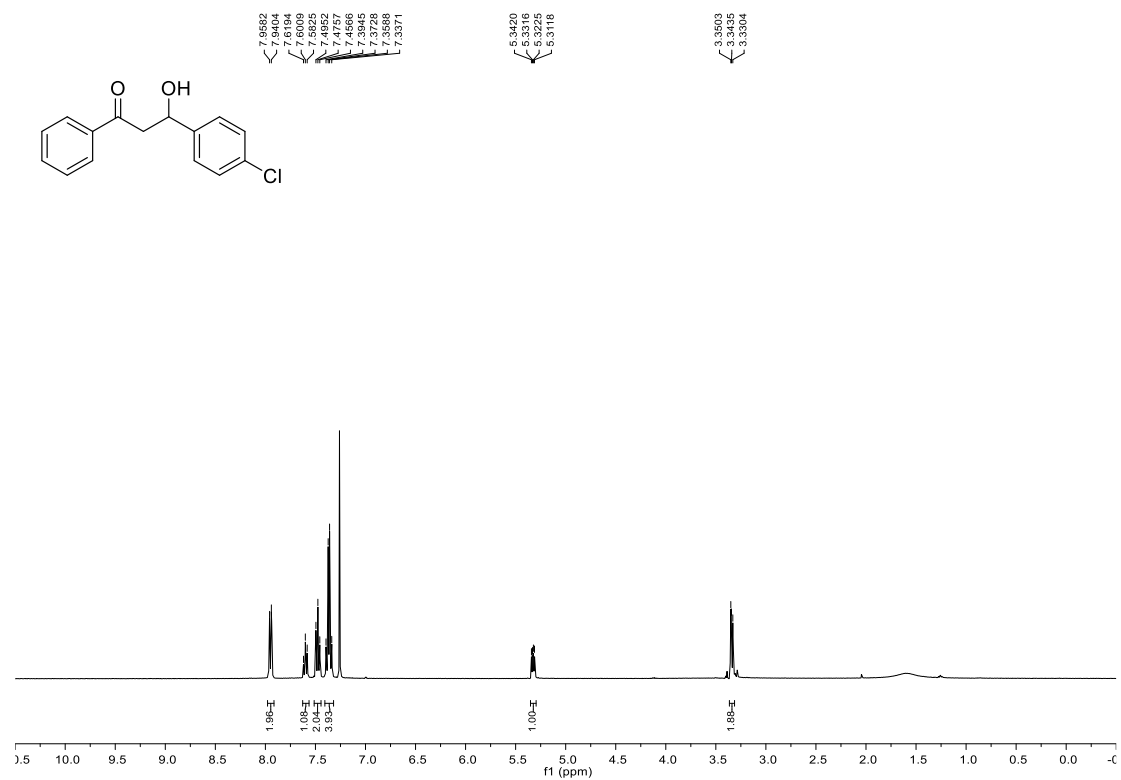
MS (ESI): m/z 253 $[M+H]^+$.

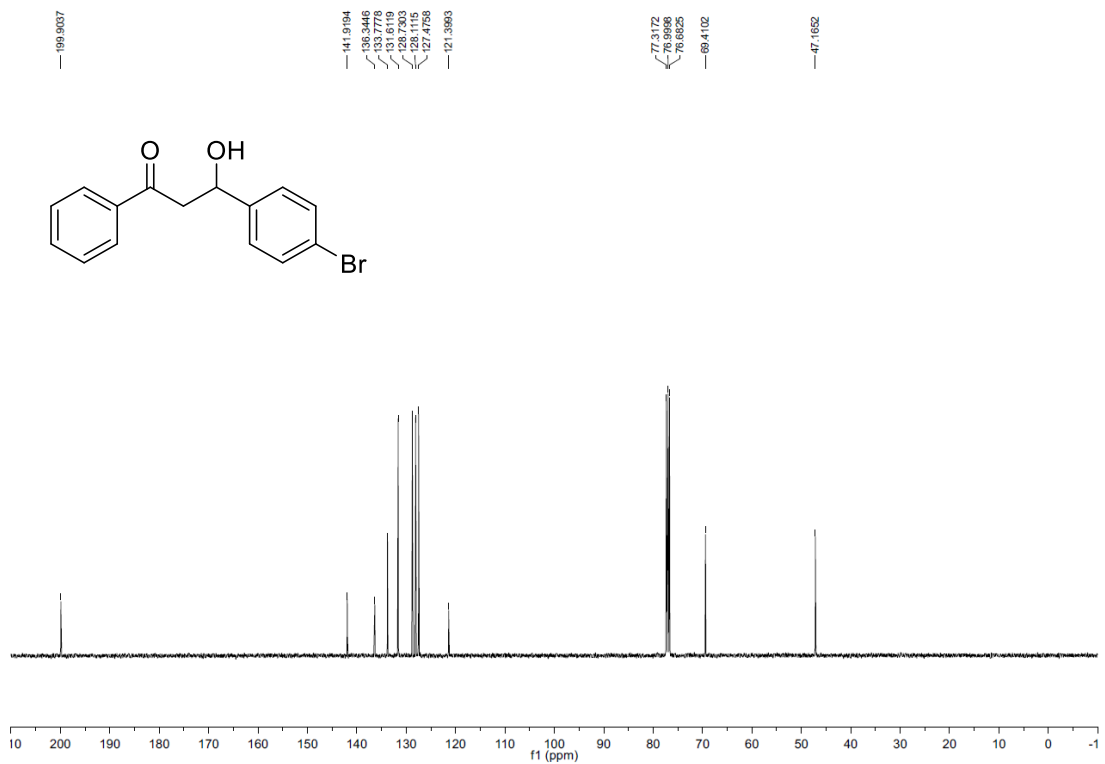
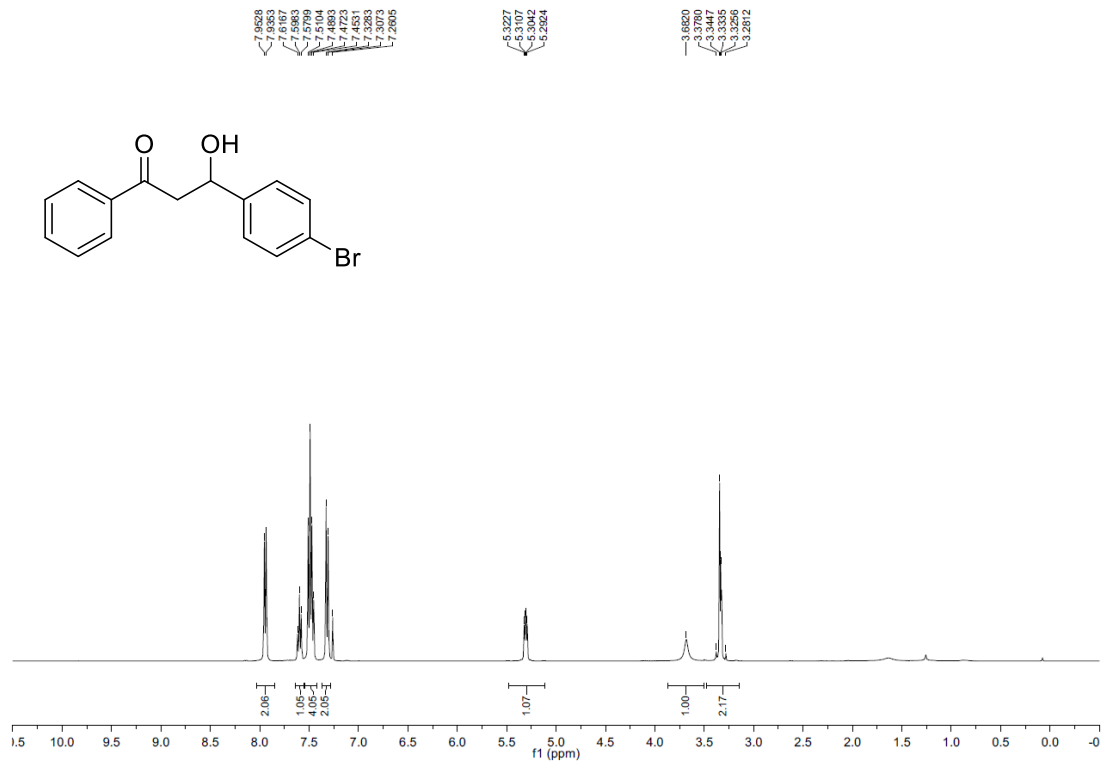
2. ^1H and ^{13}C NMR spectra

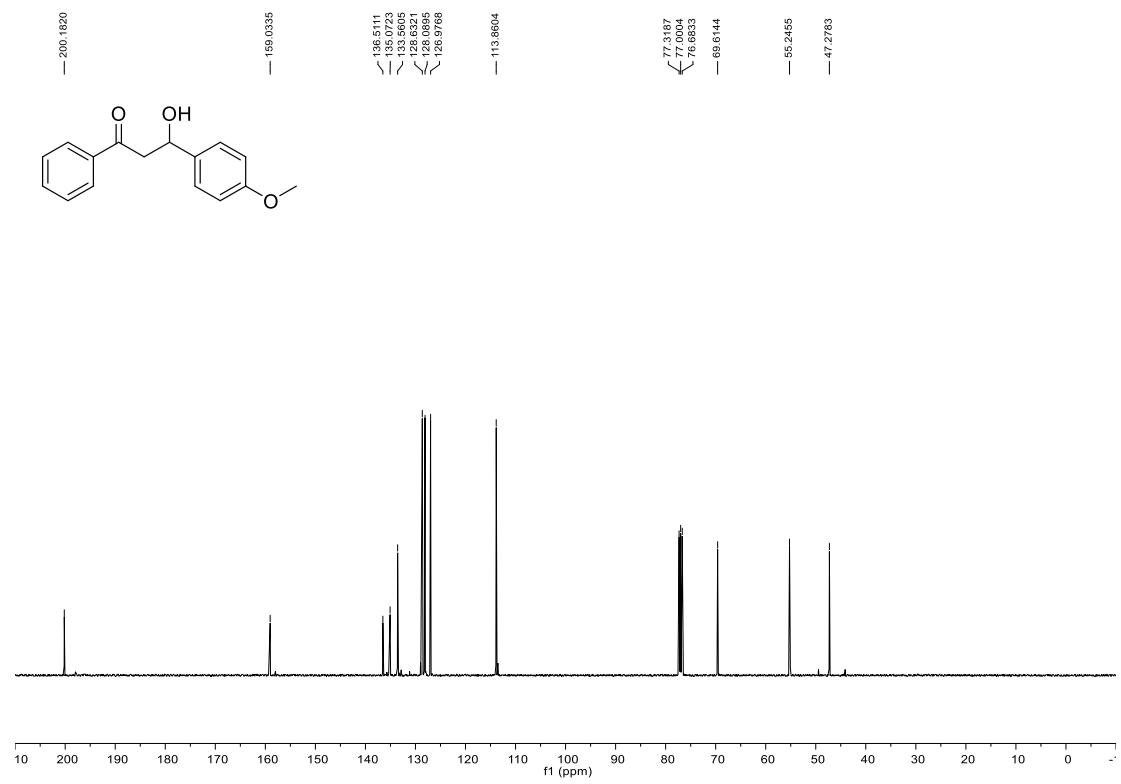
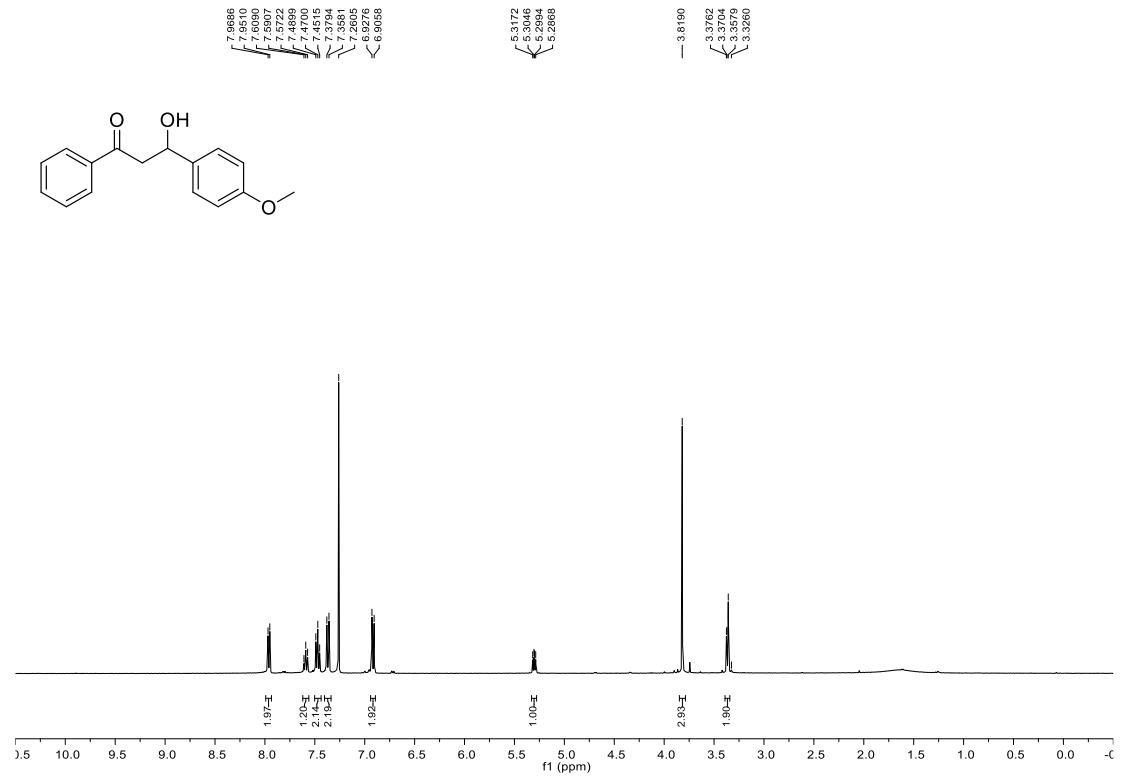


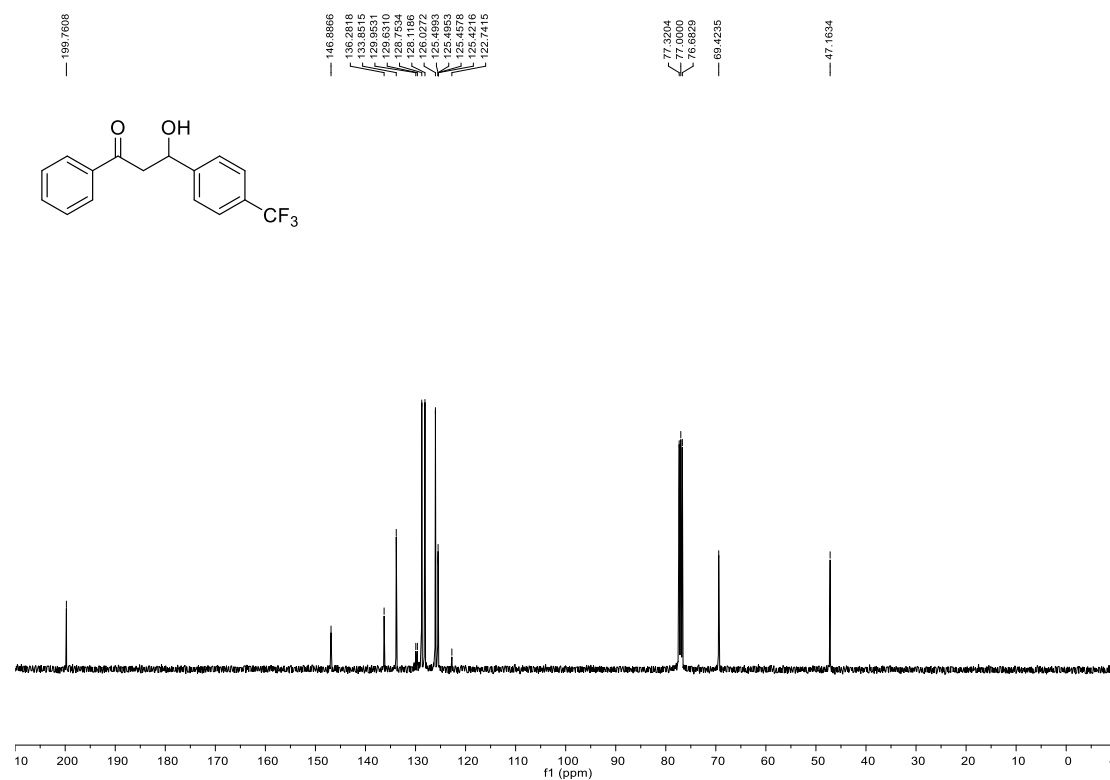
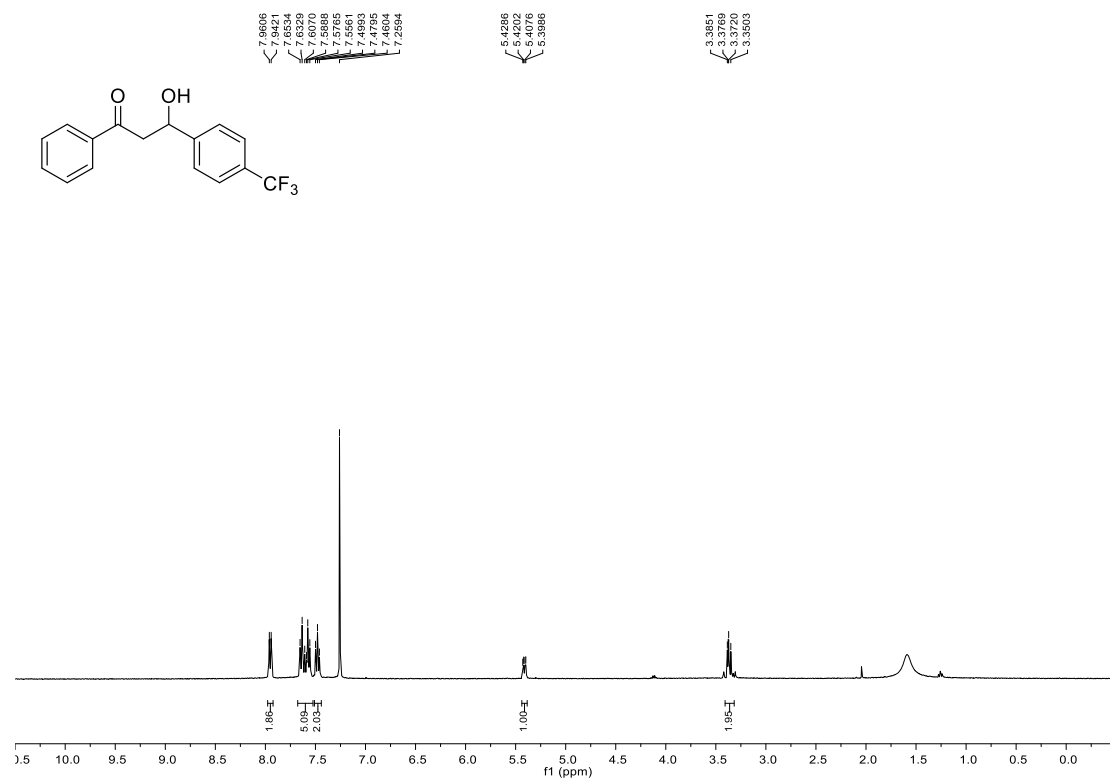


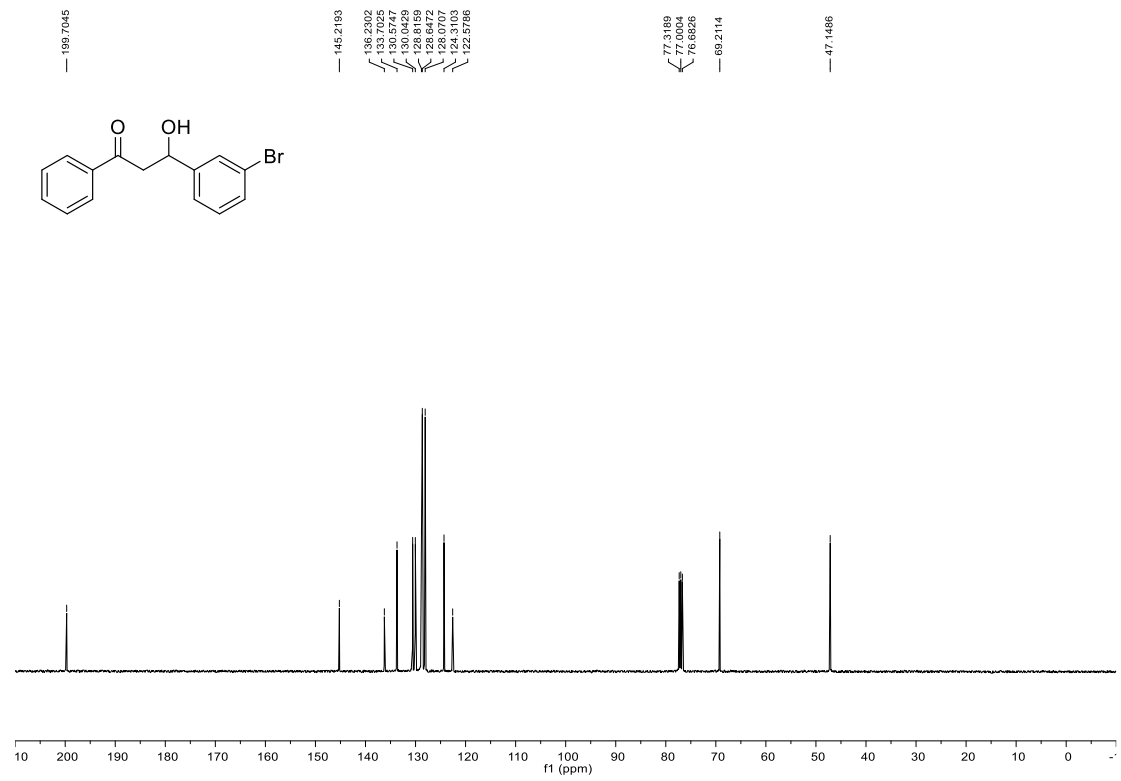
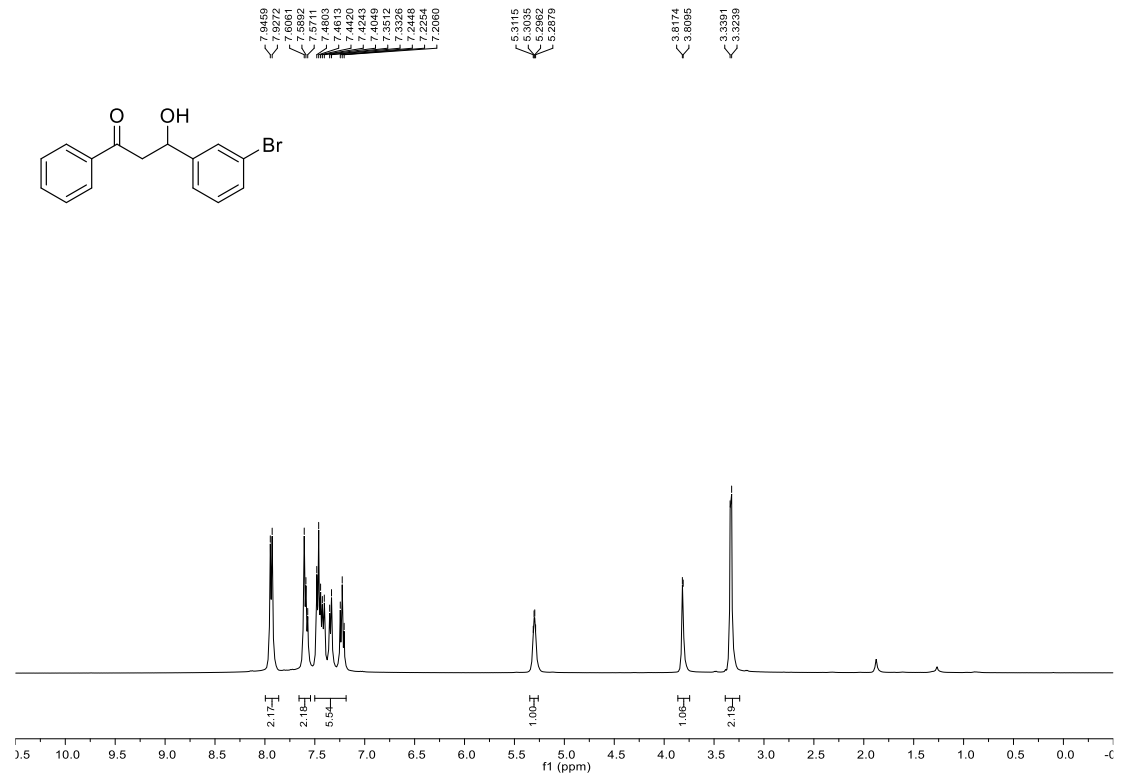


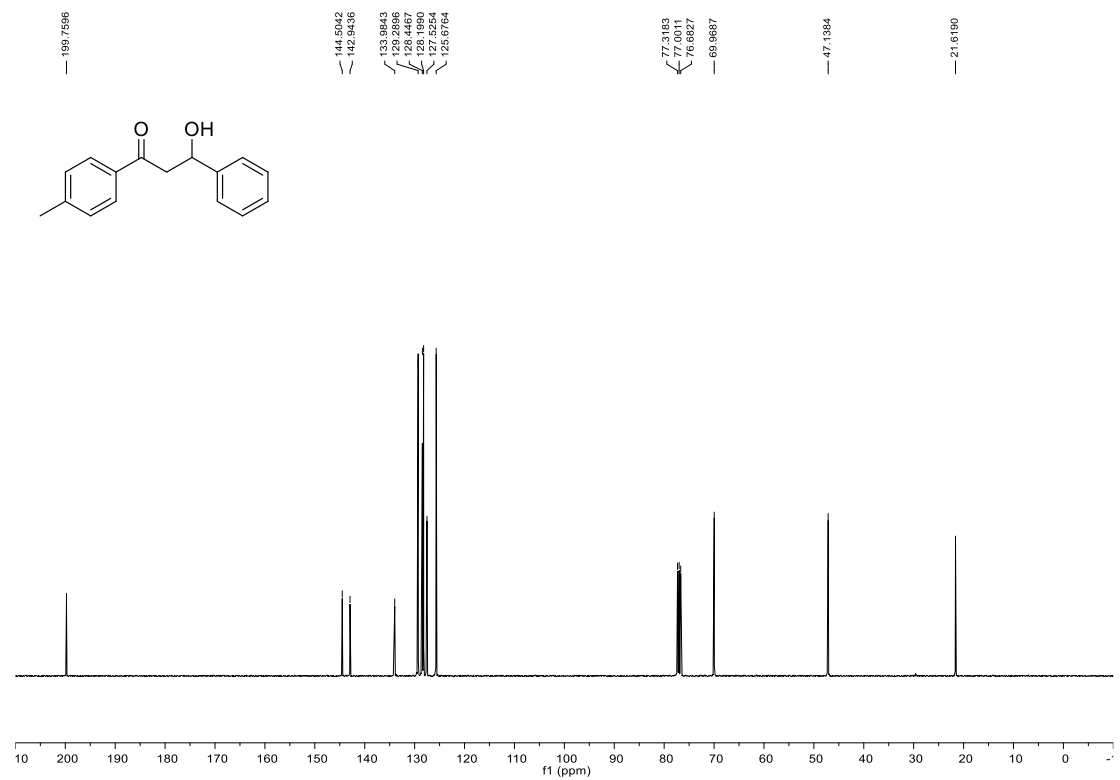
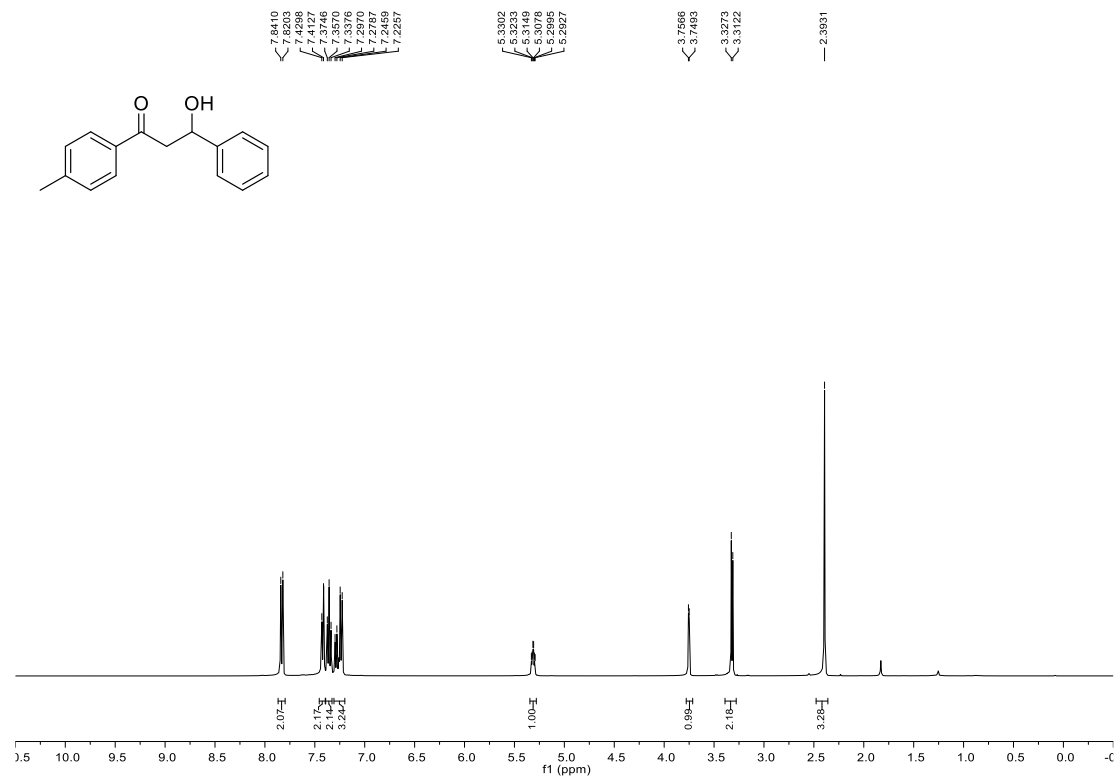


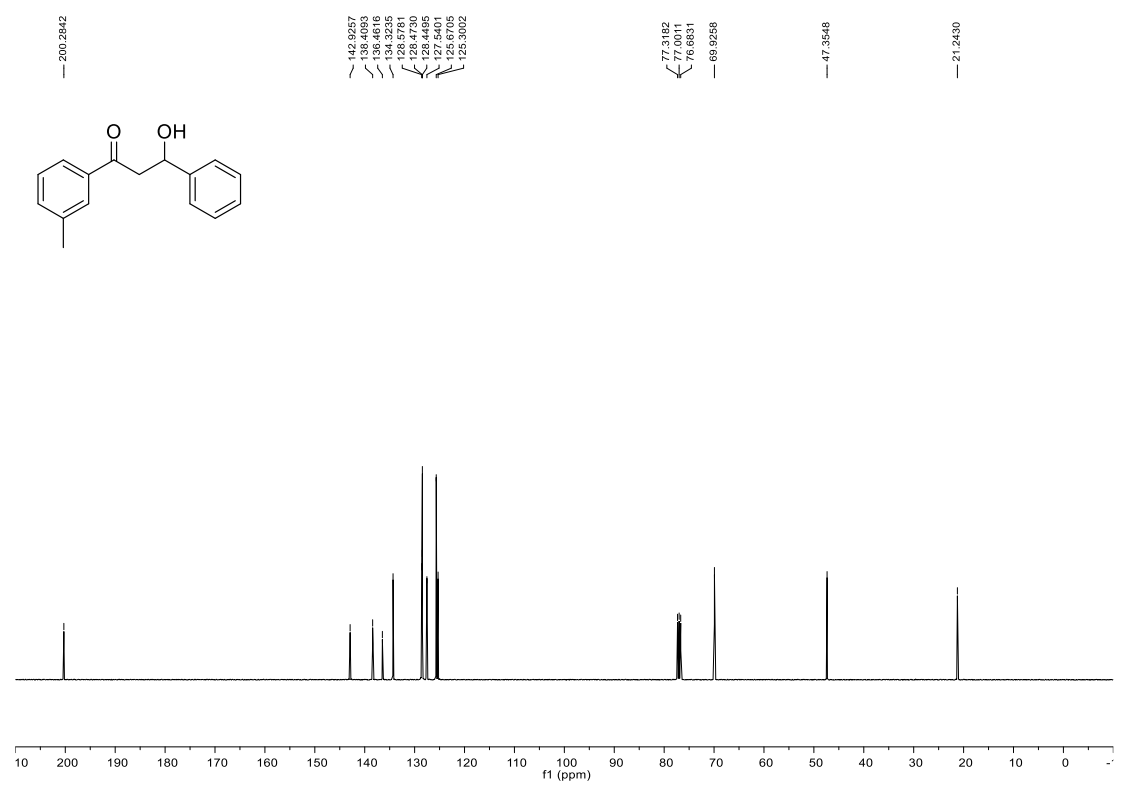
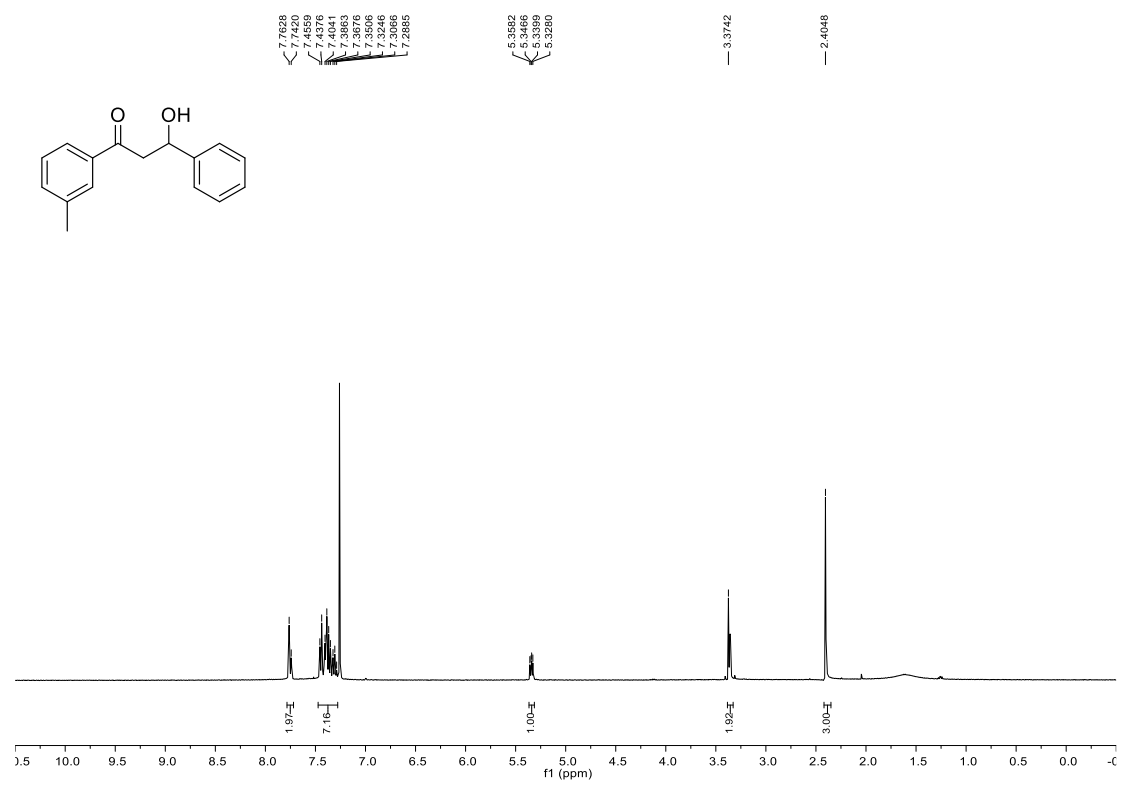


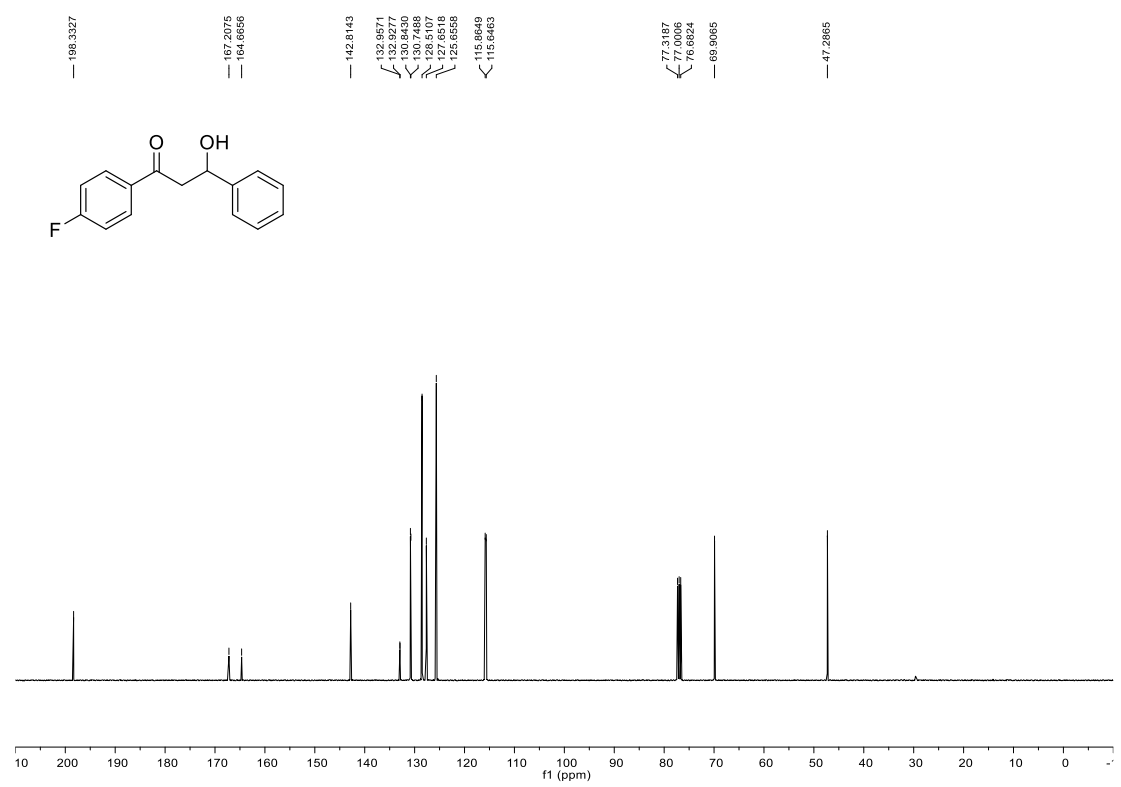
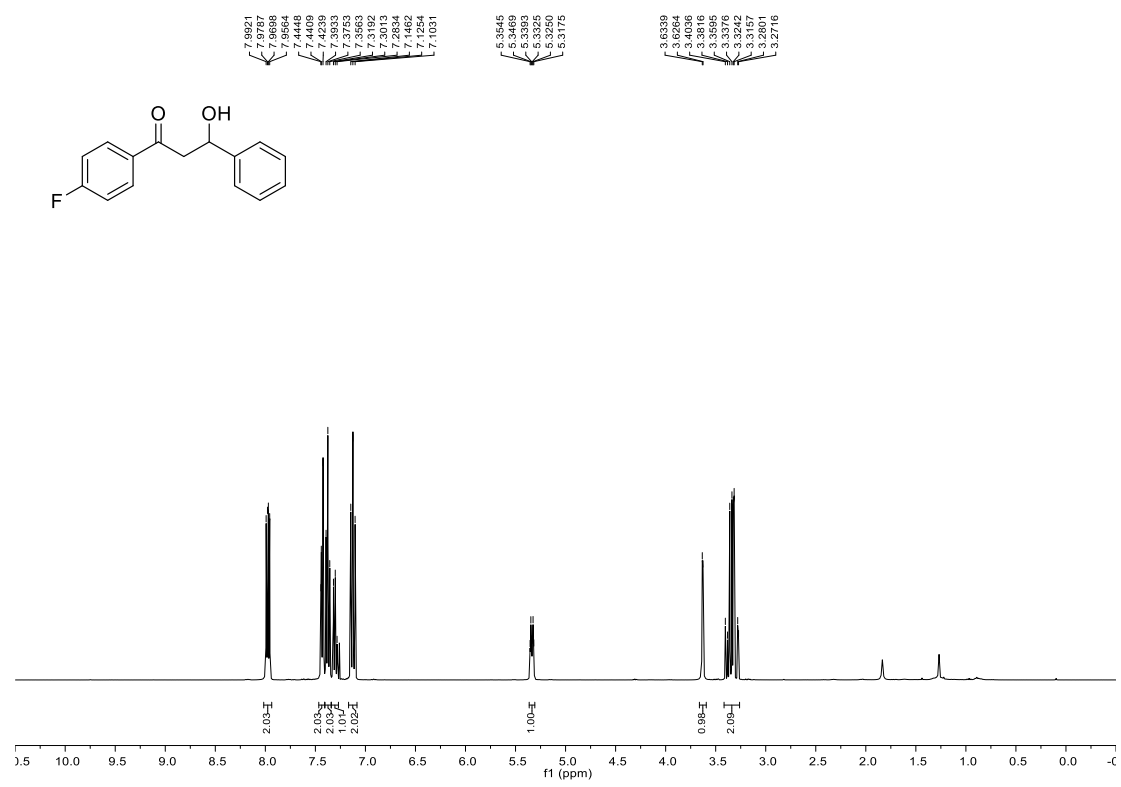


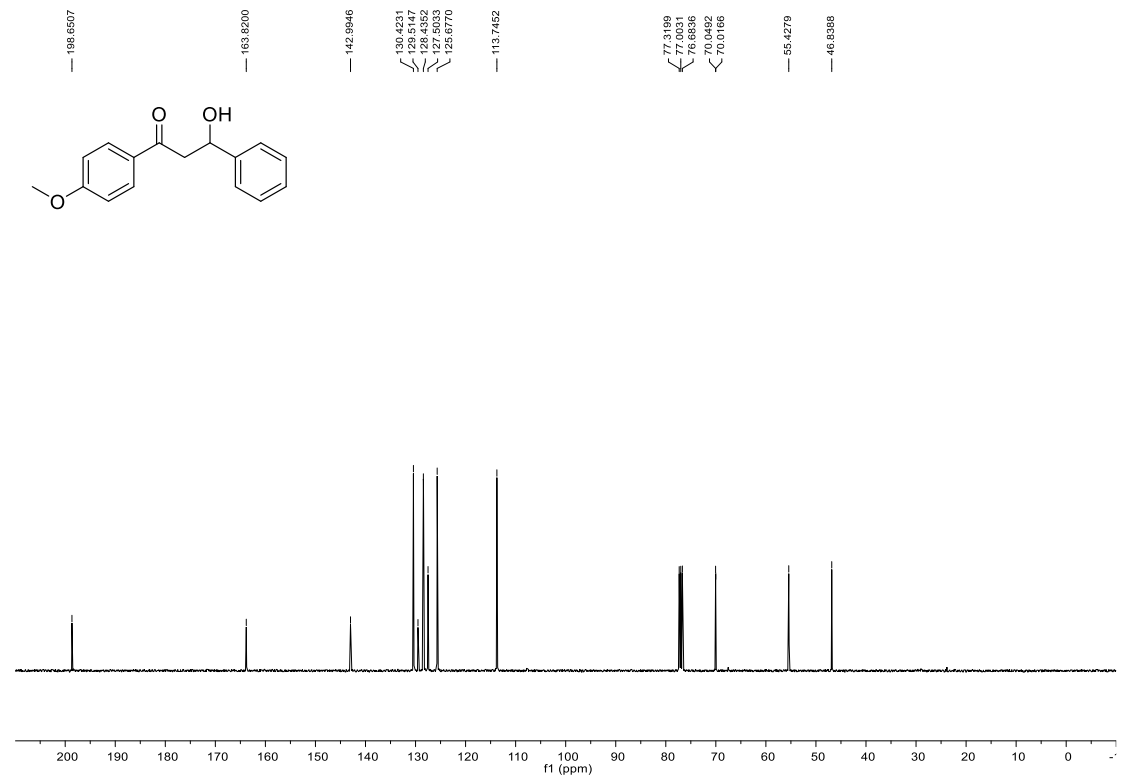
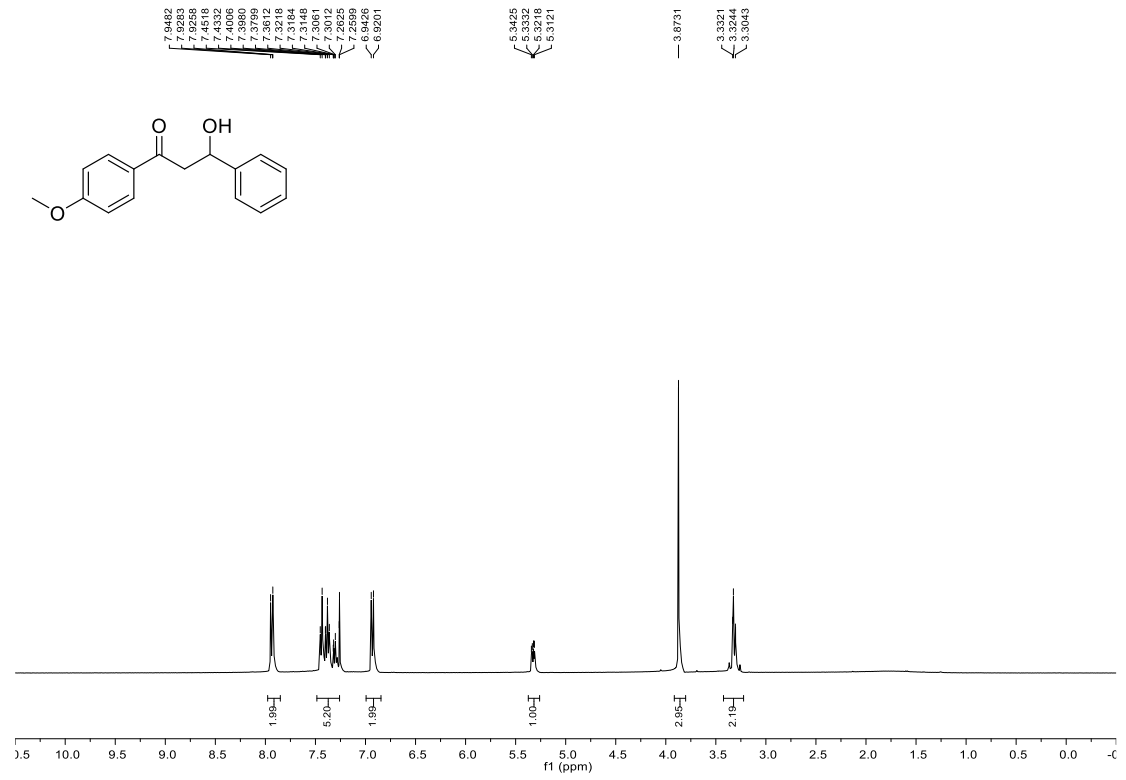


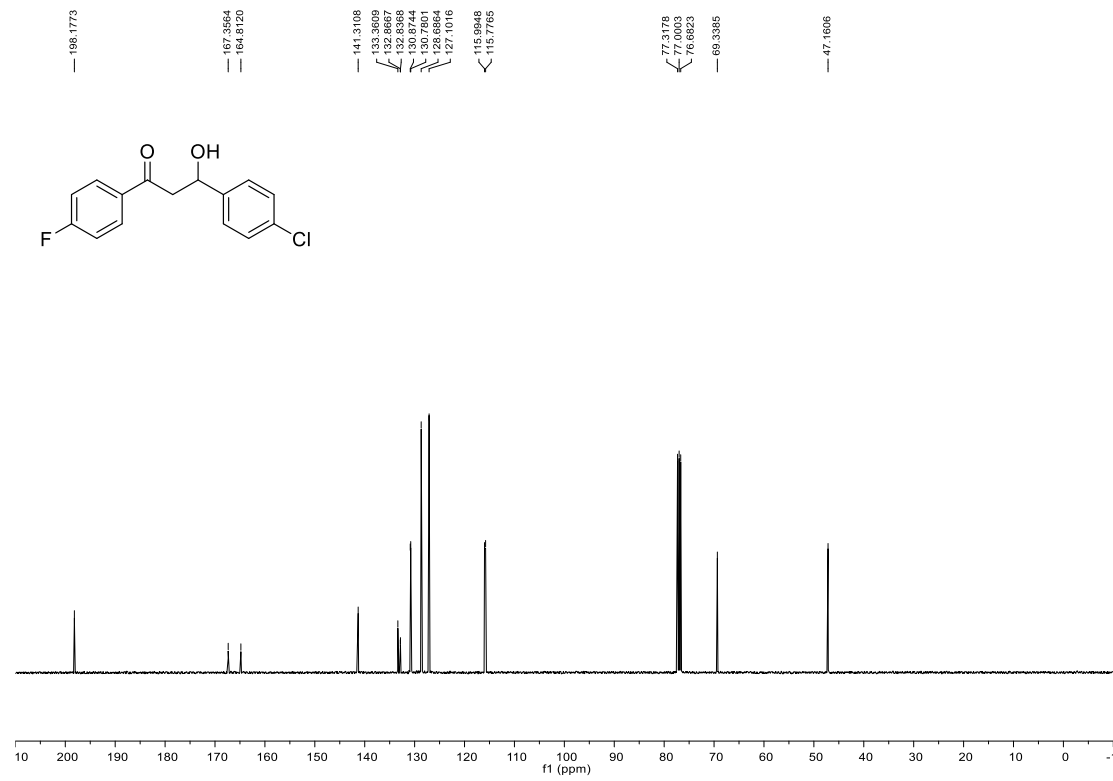
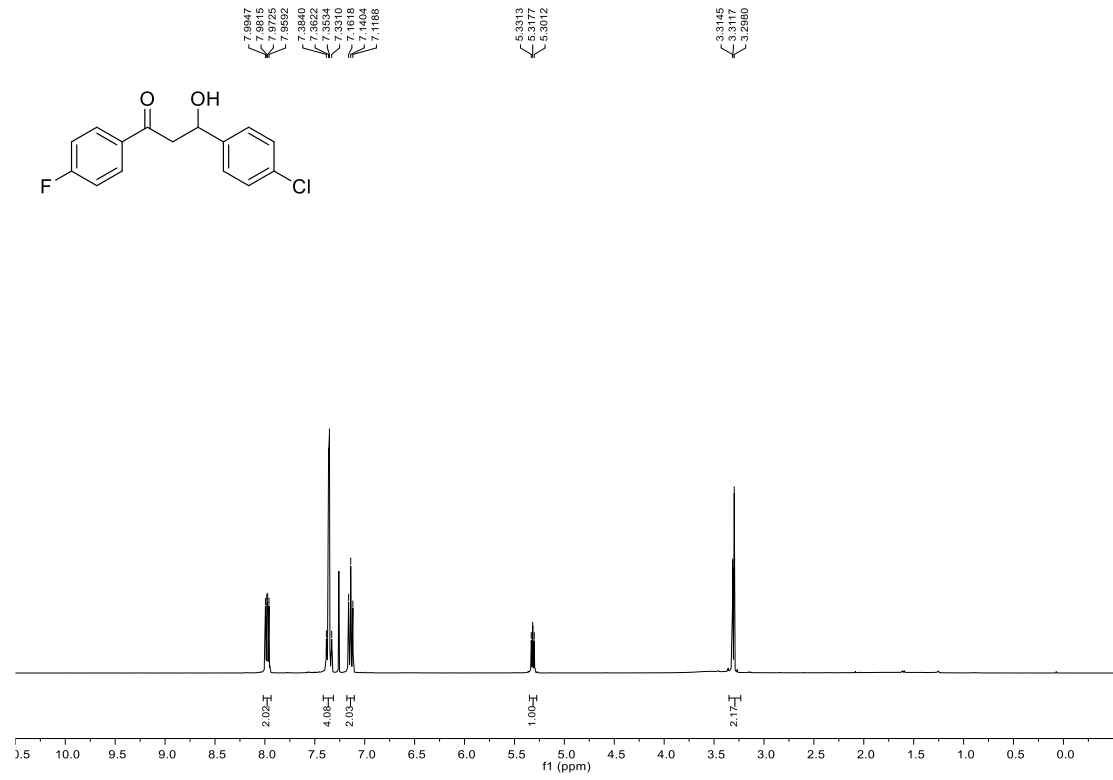


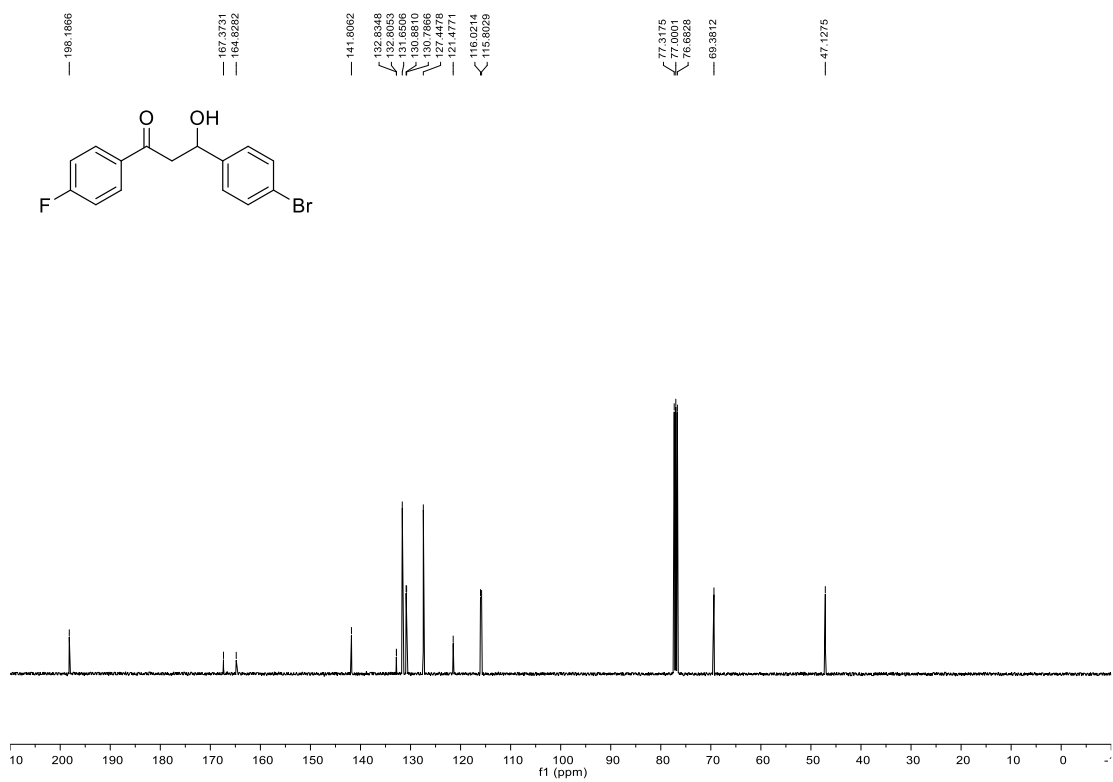
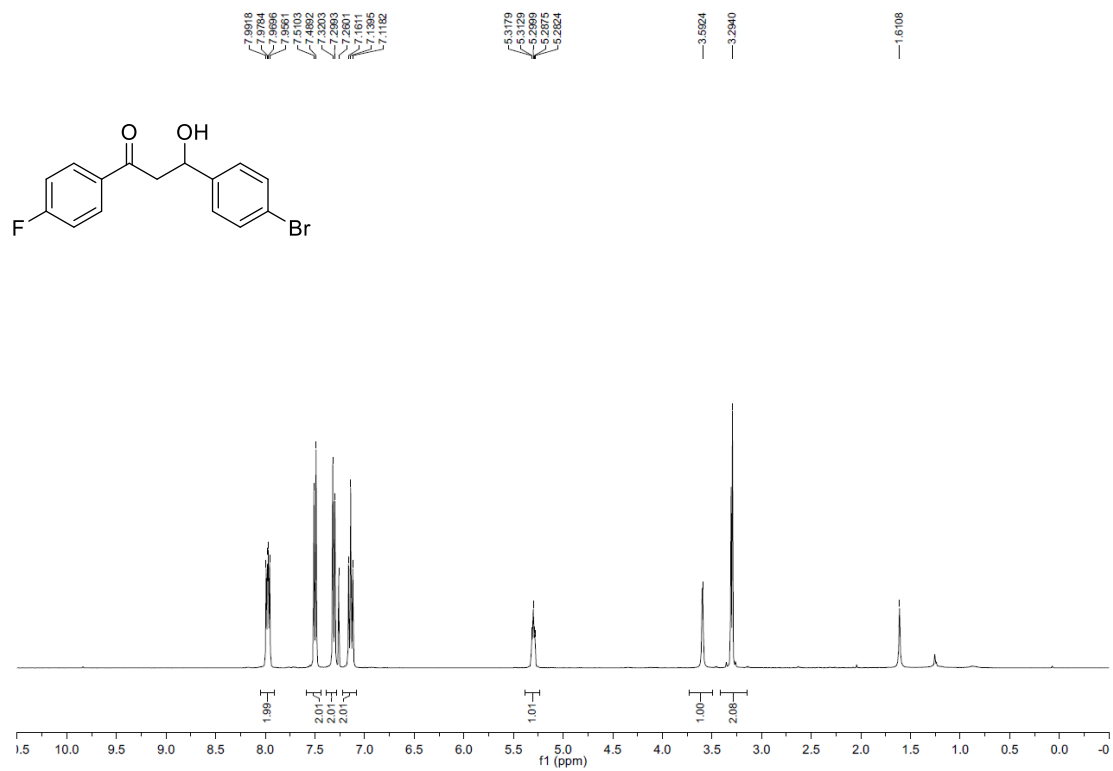


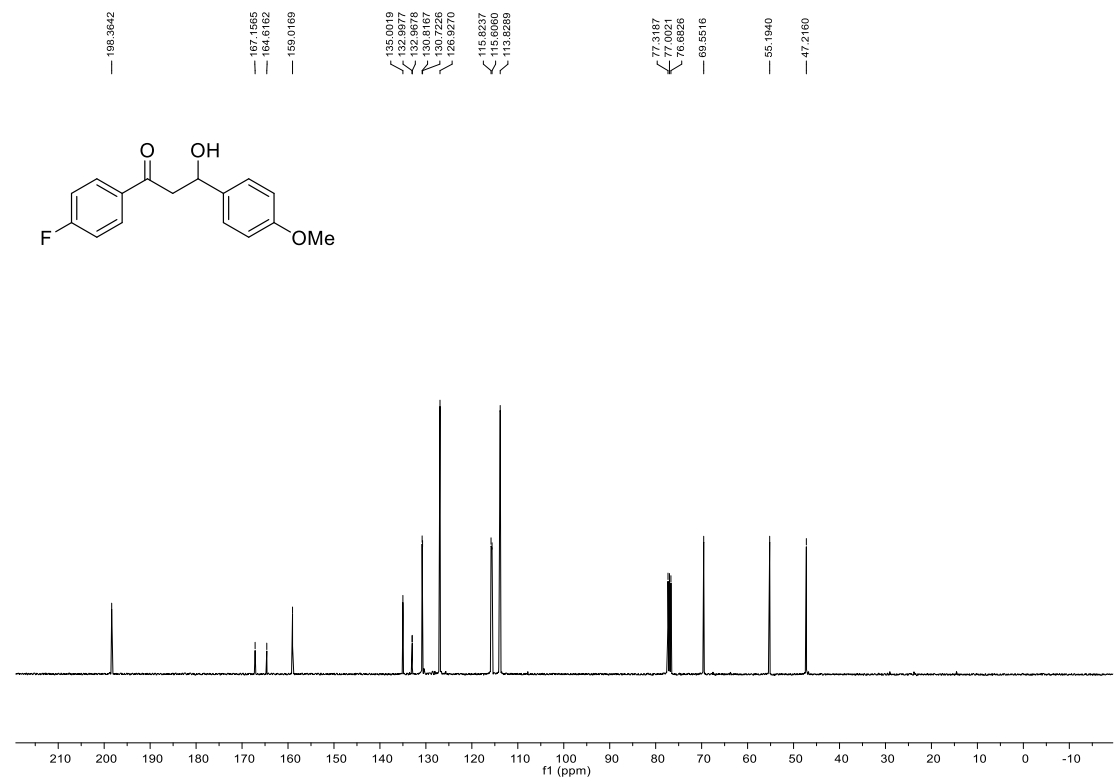
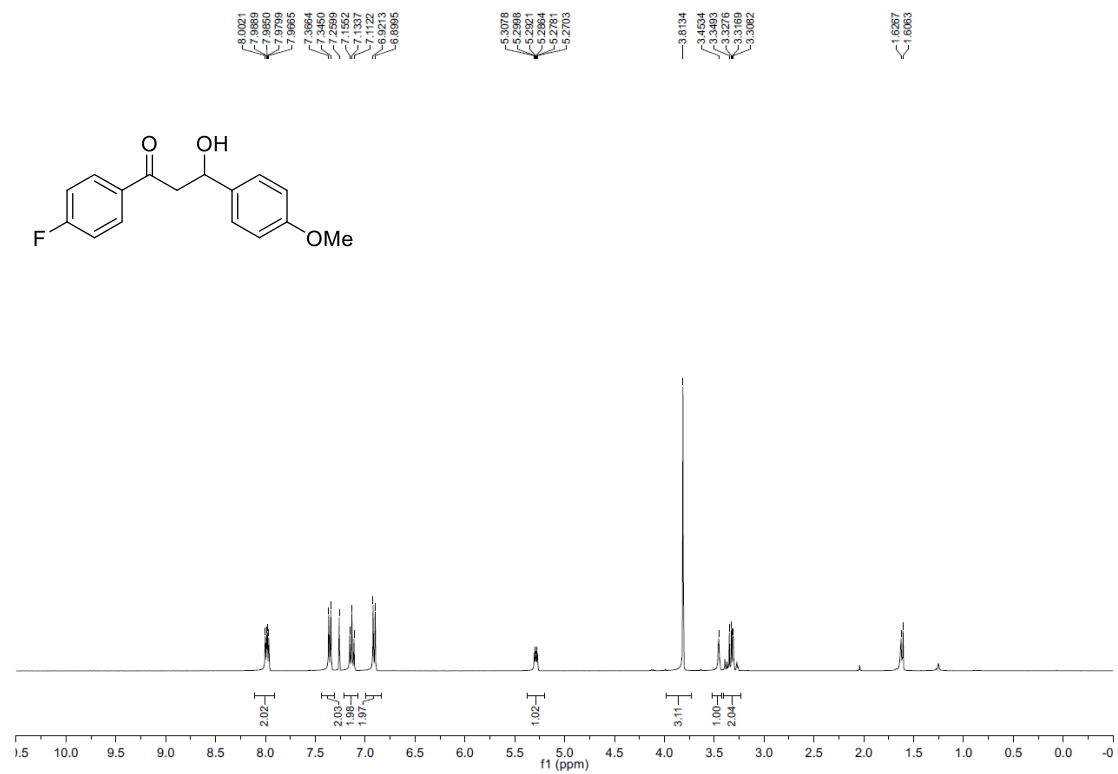


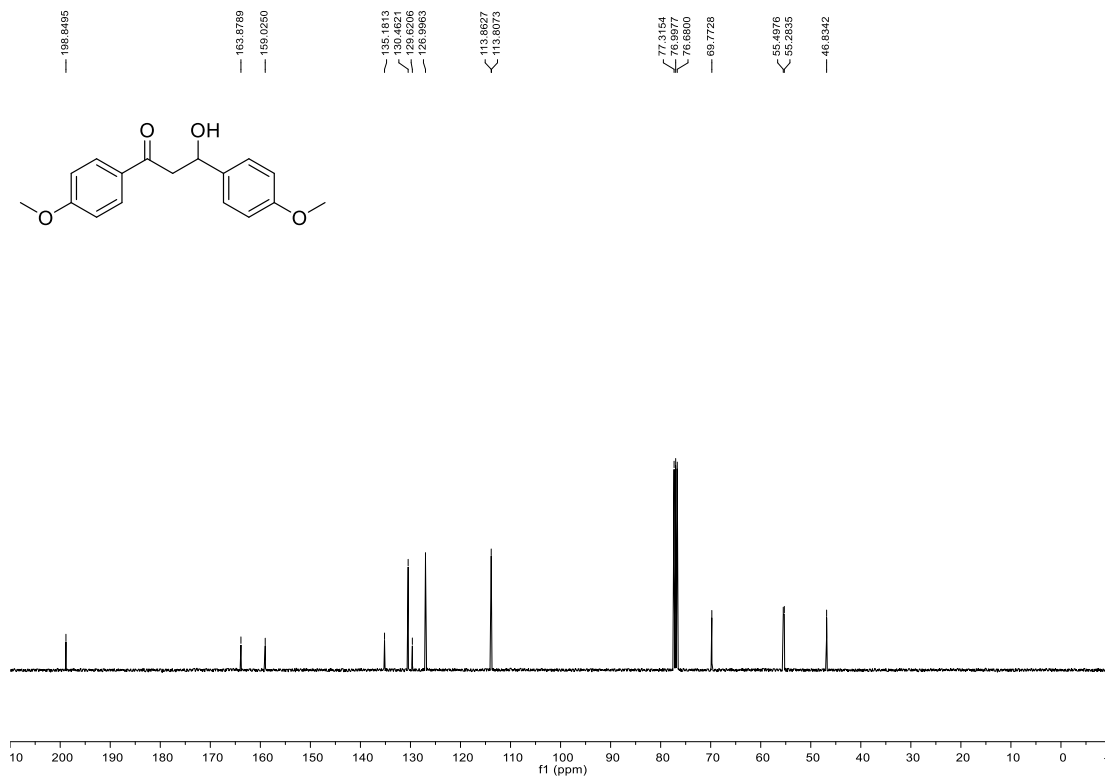
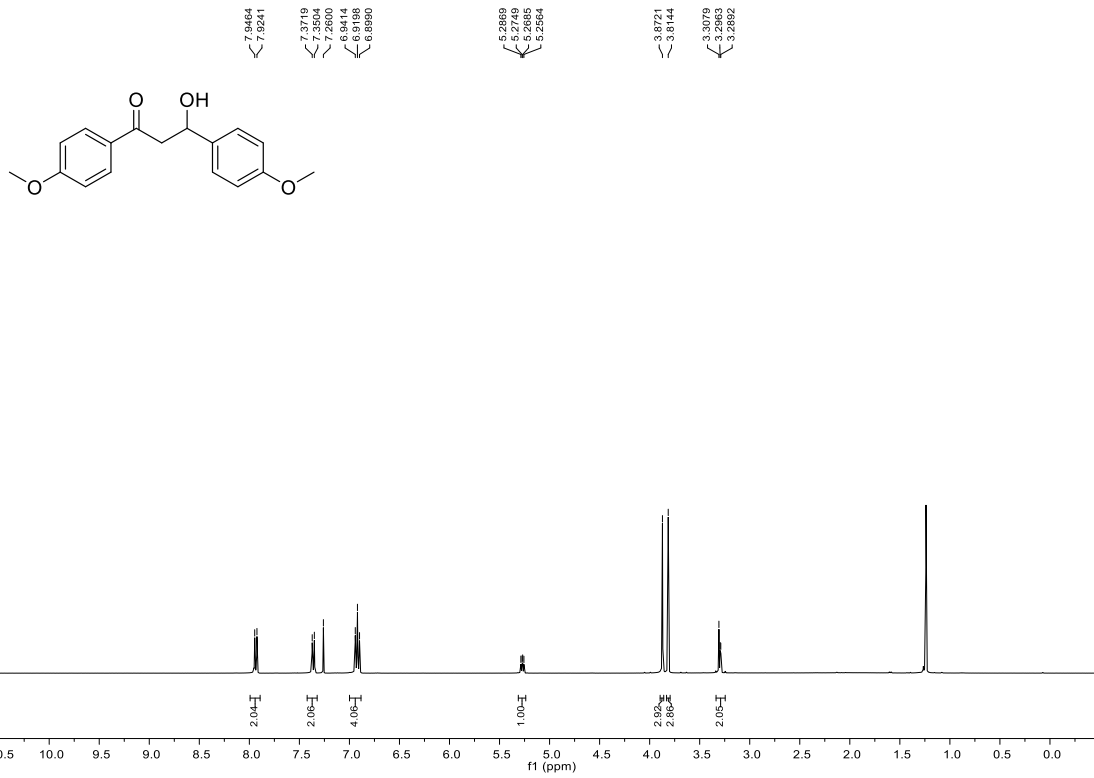


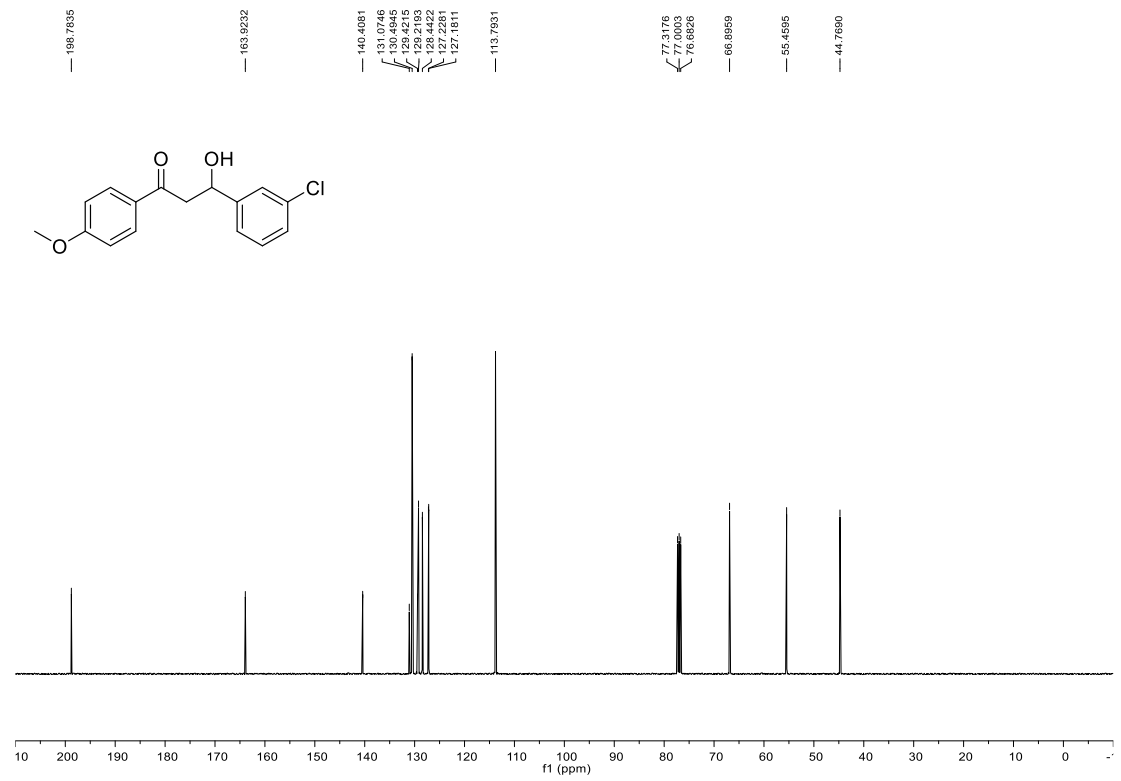
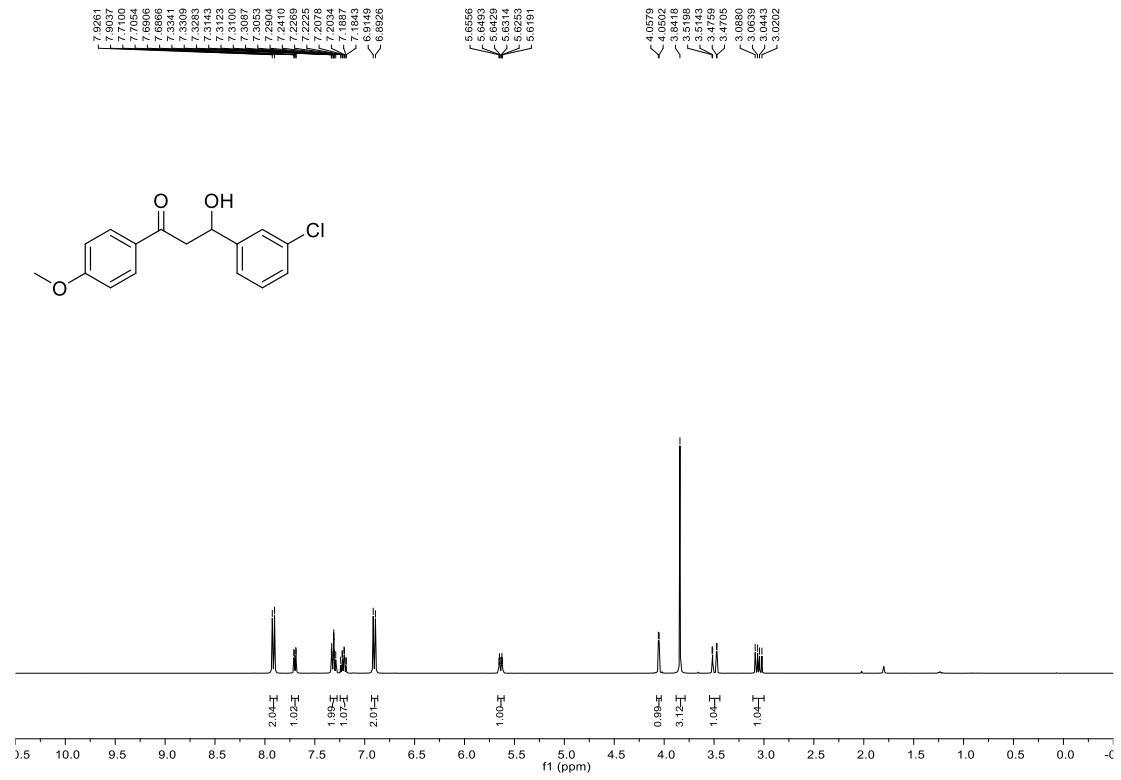


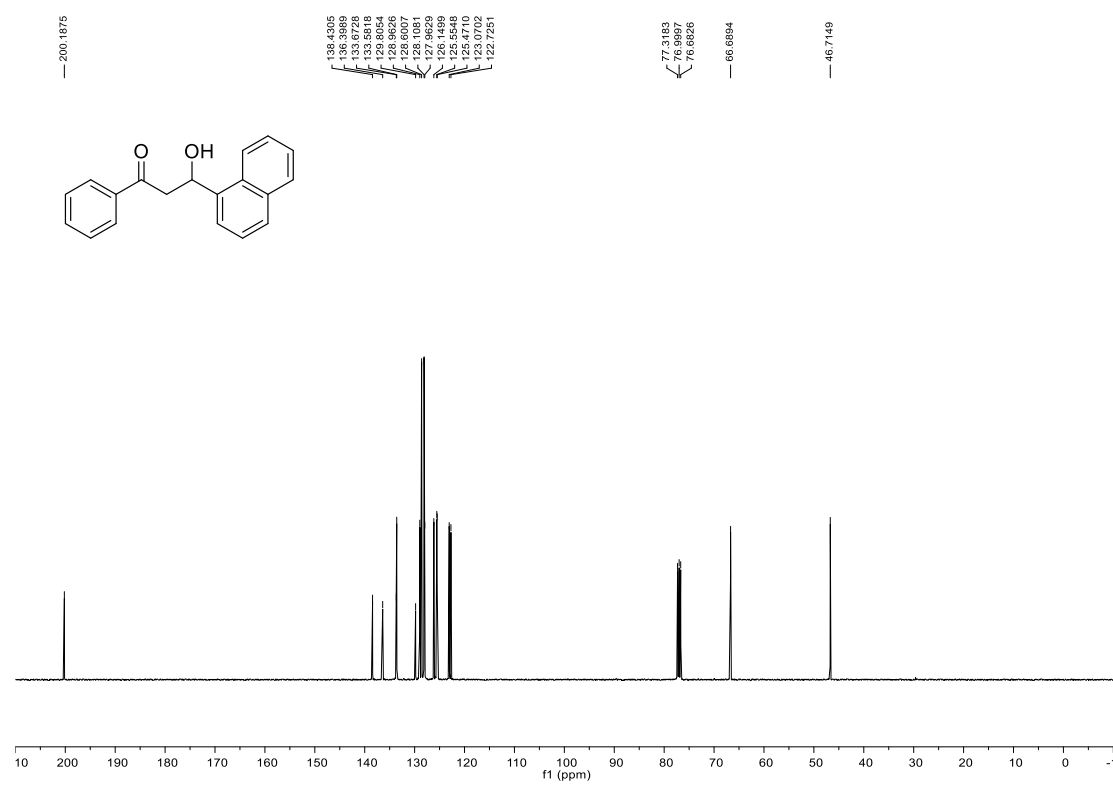
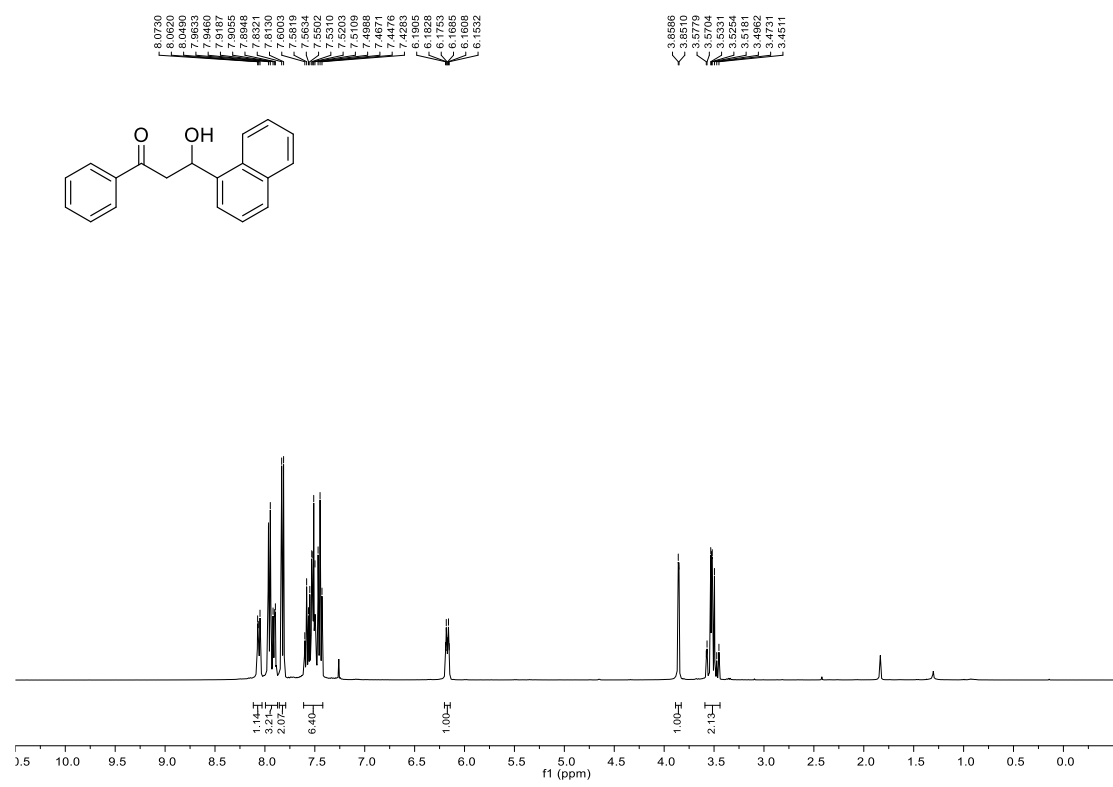


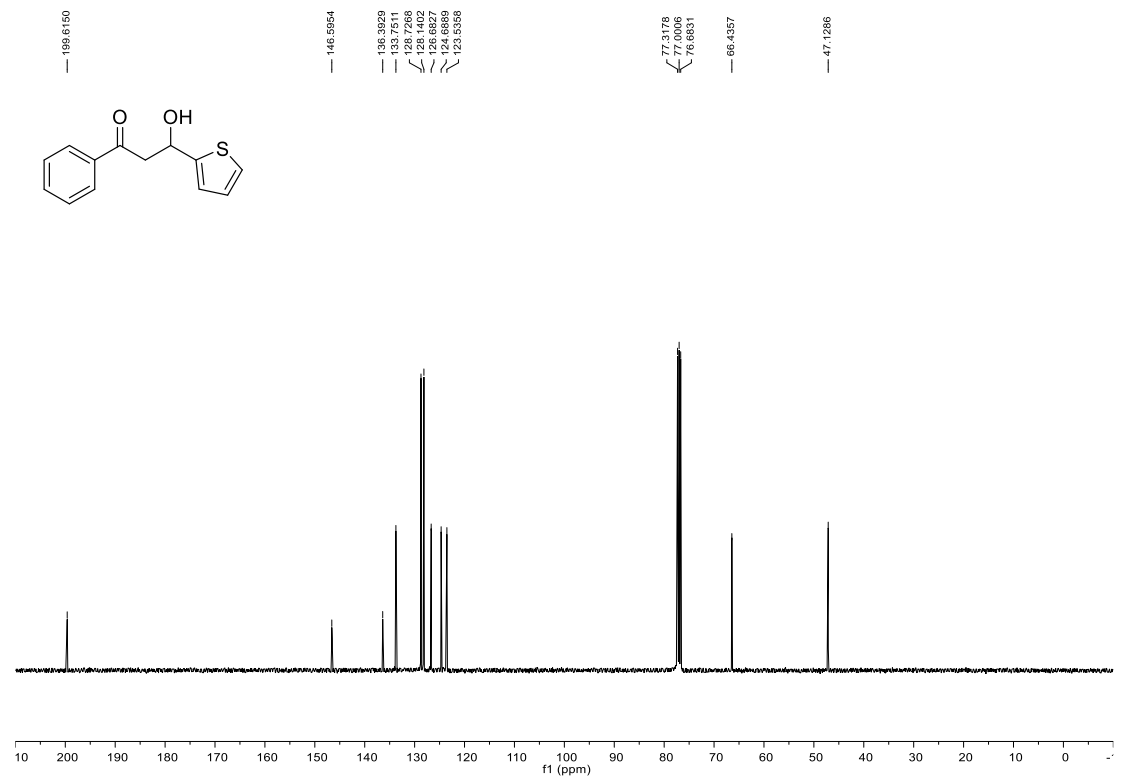
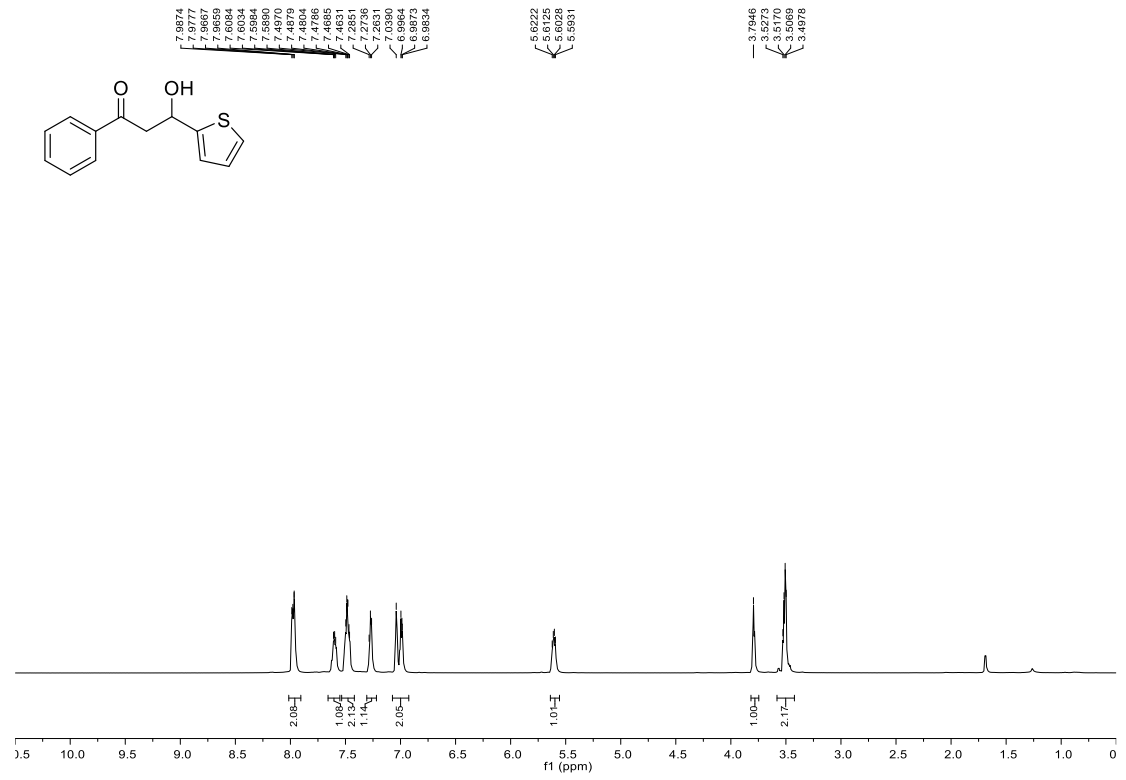


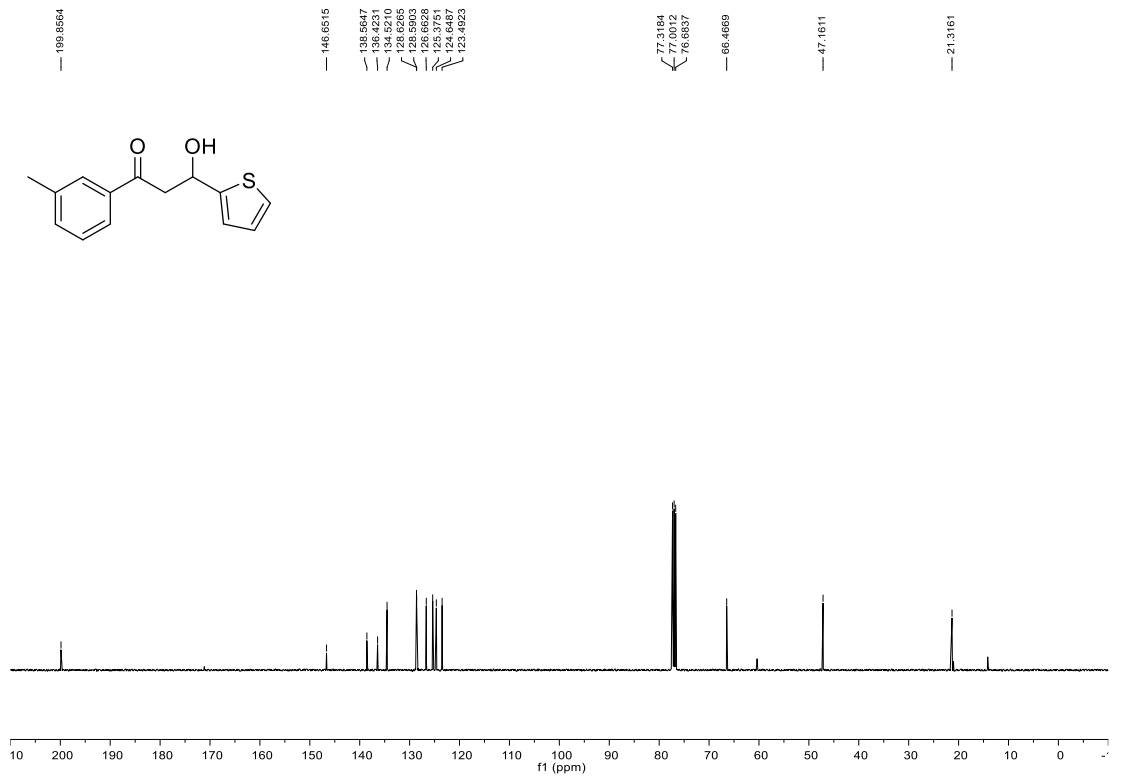
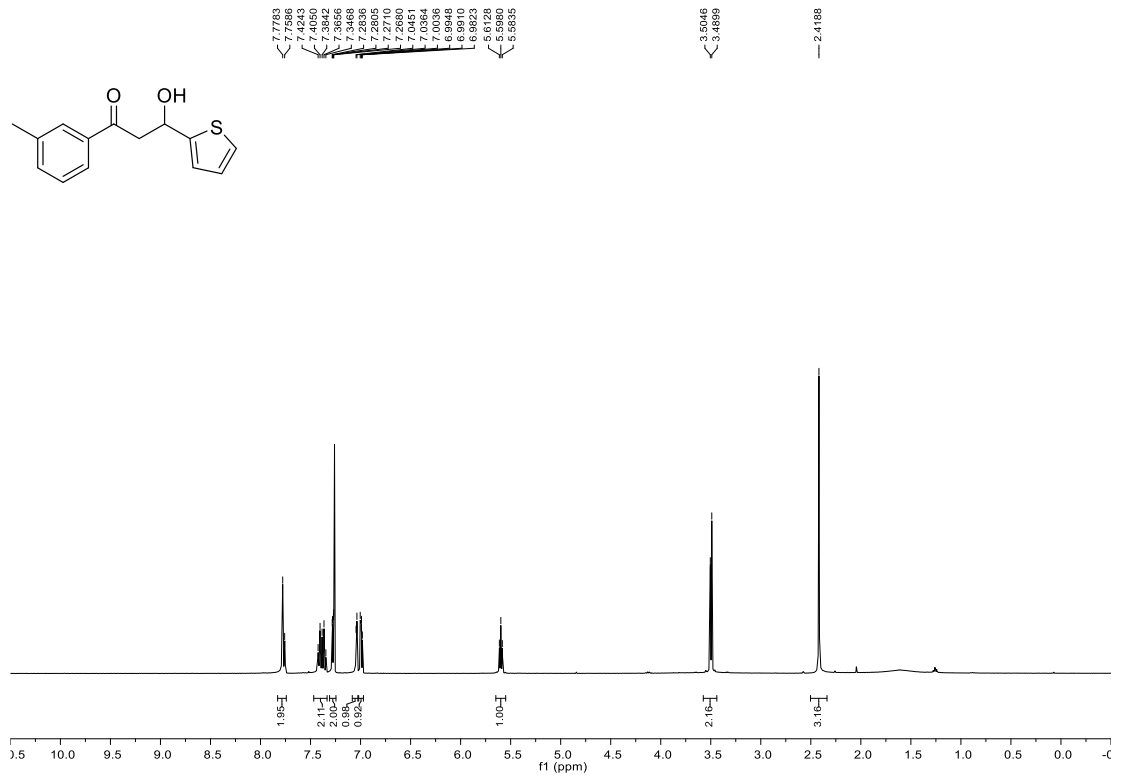


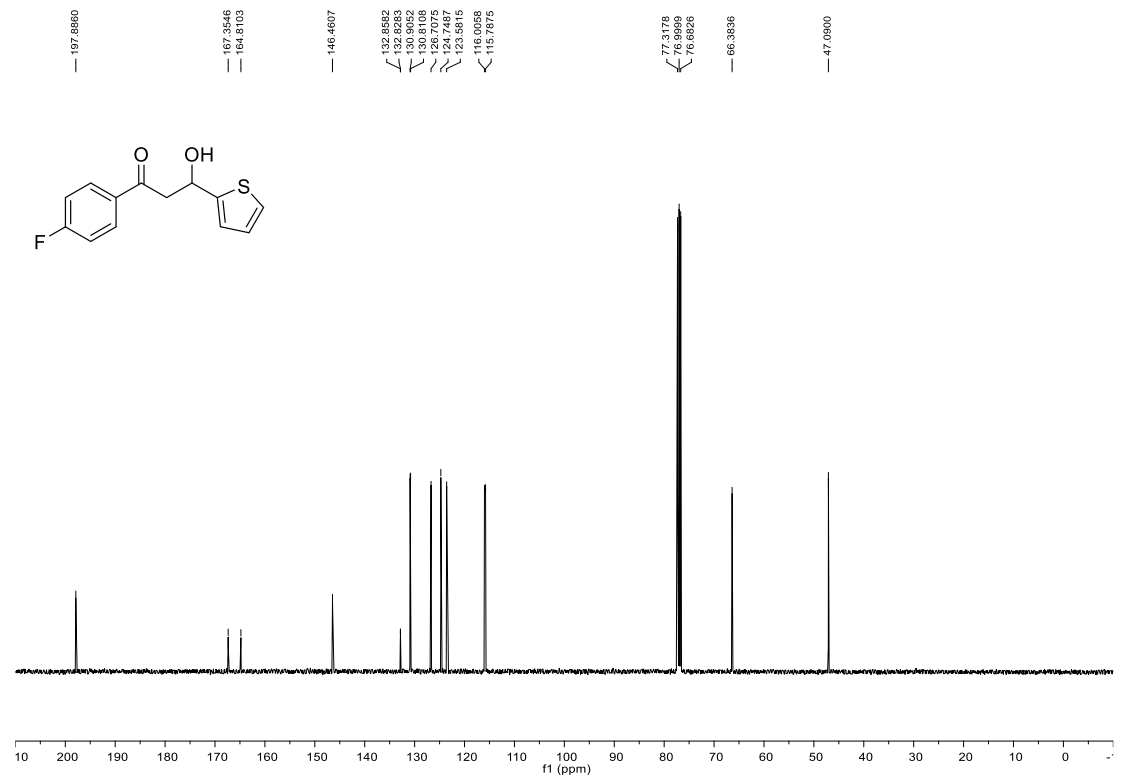
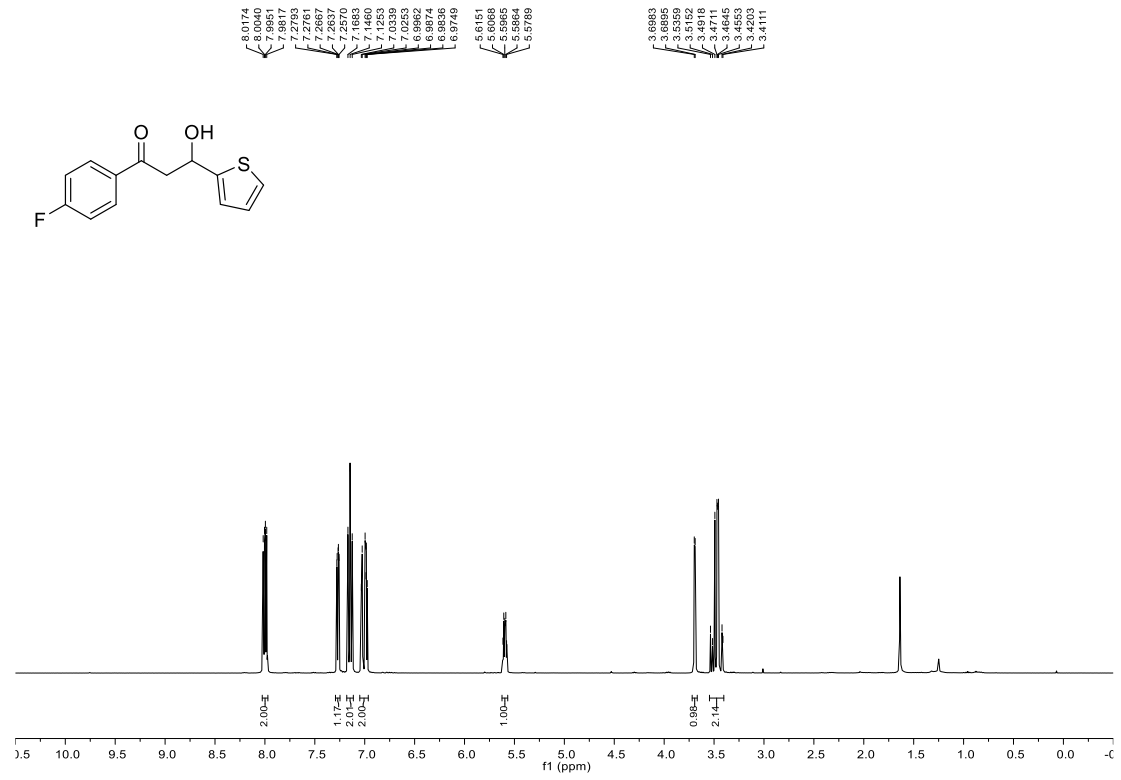


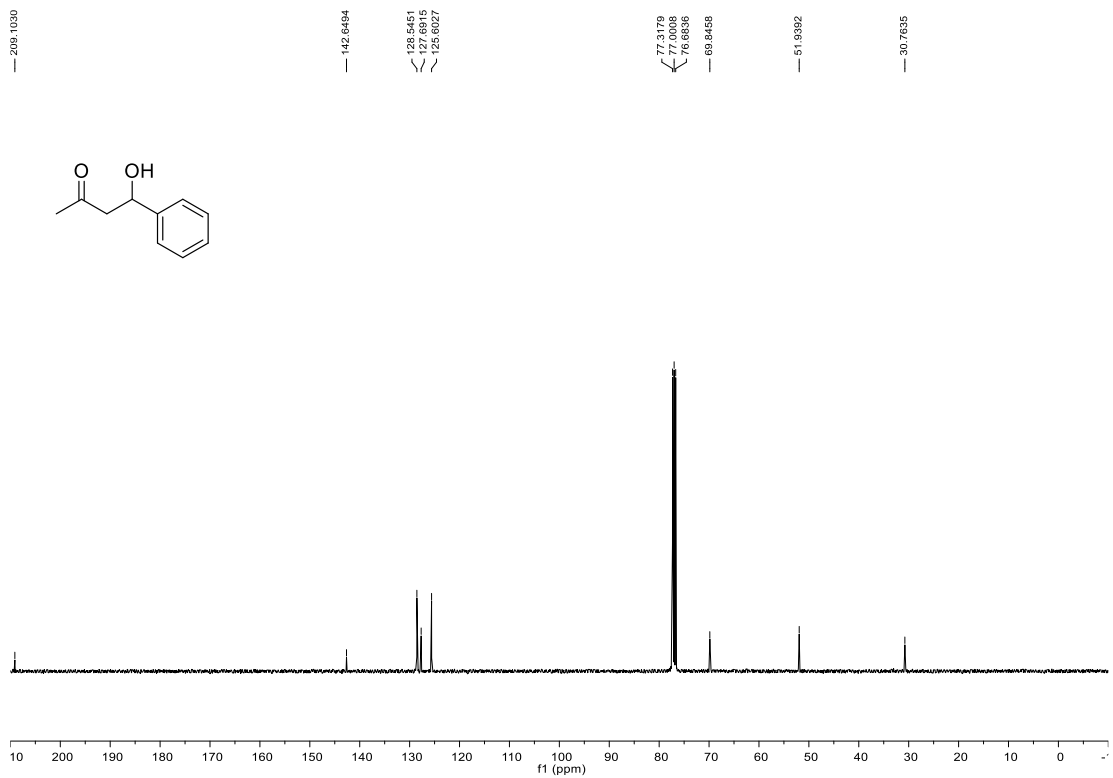
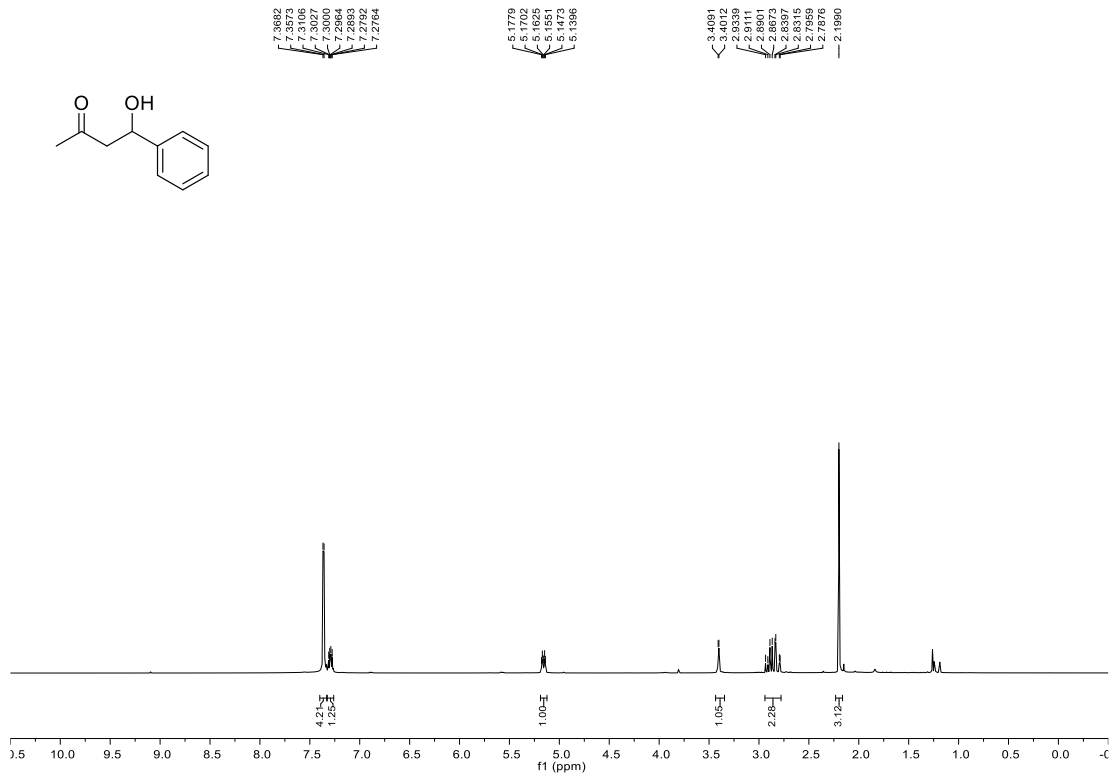


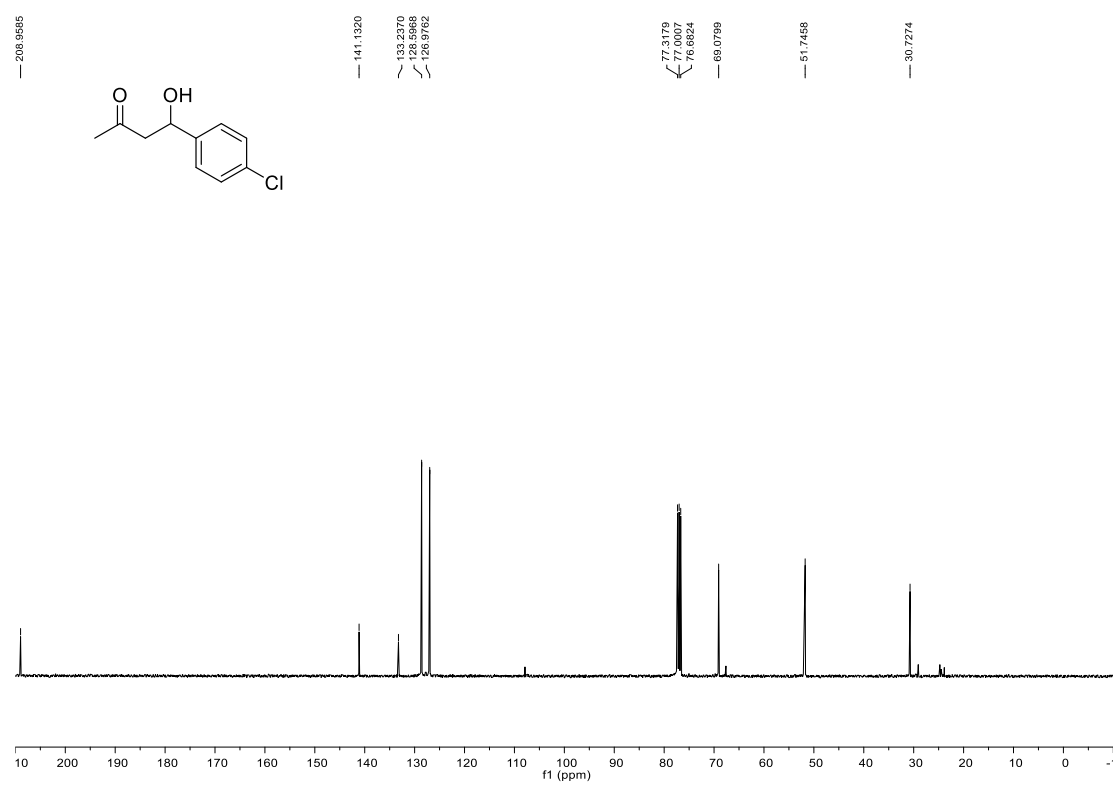
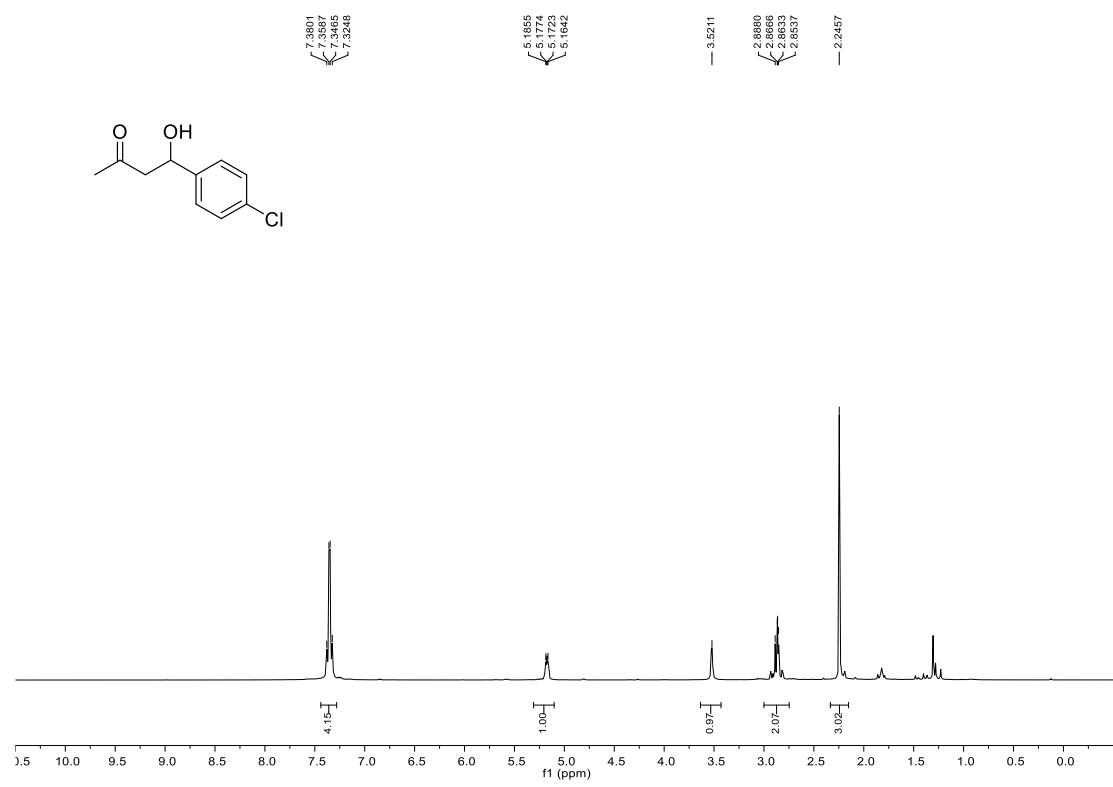


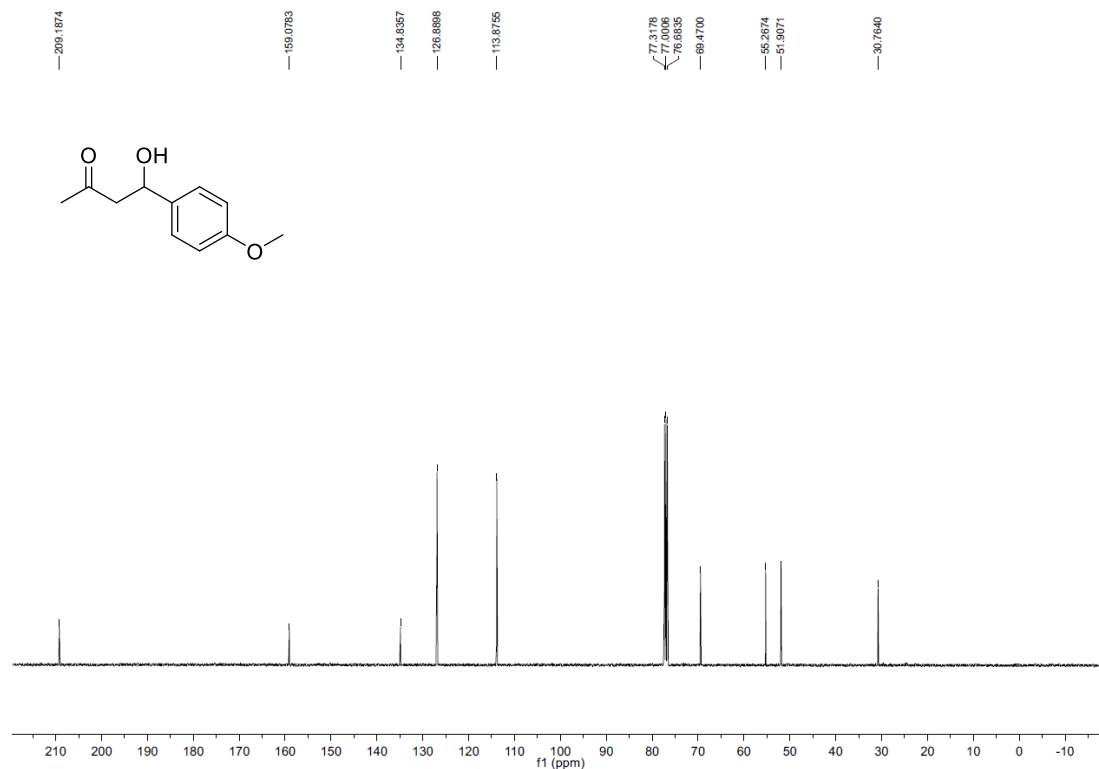
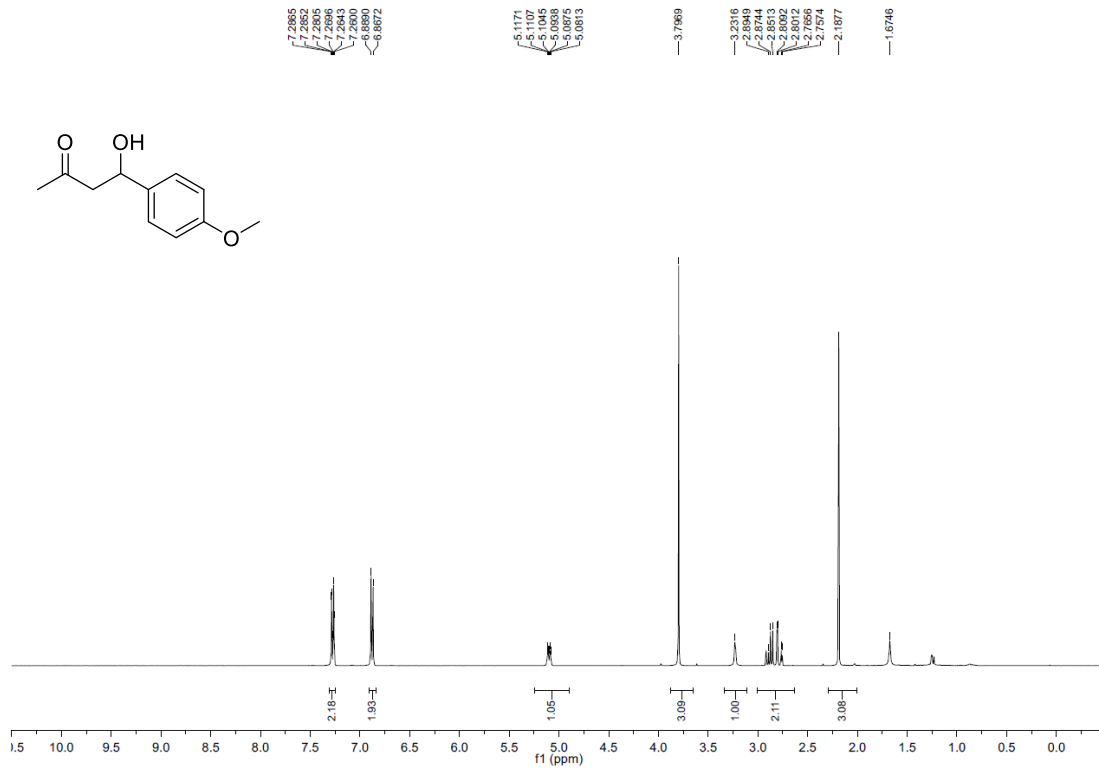


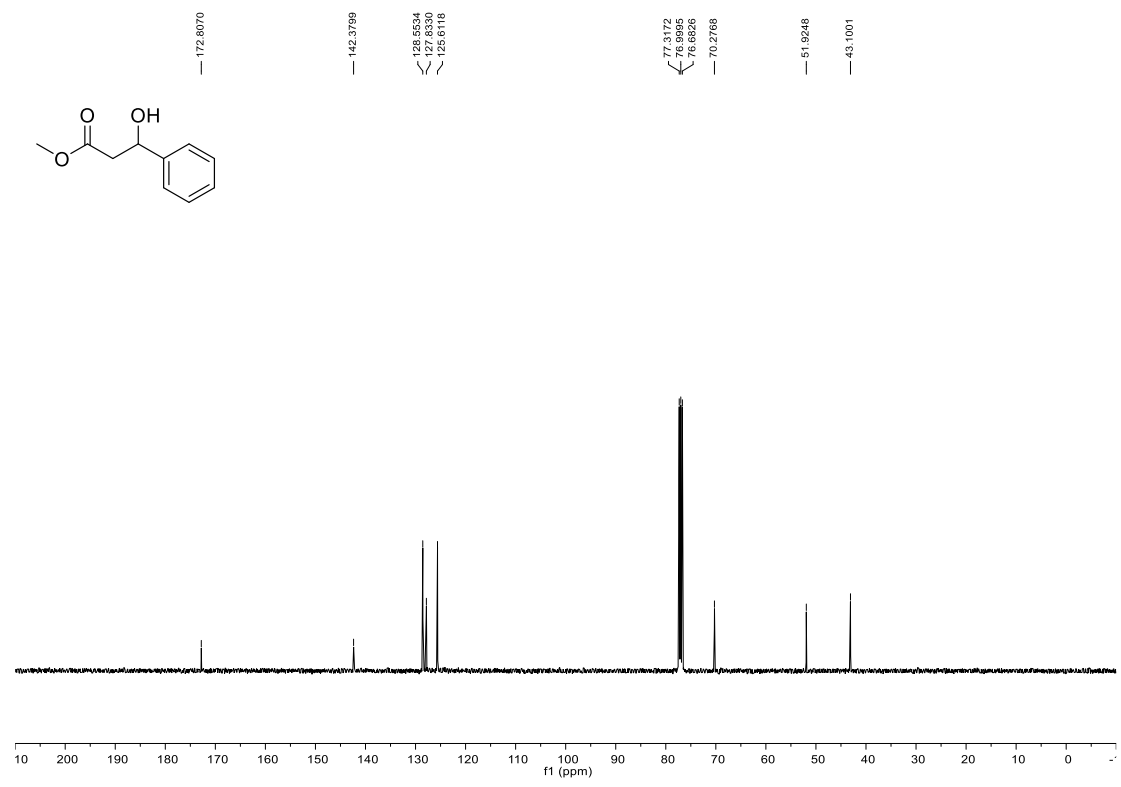
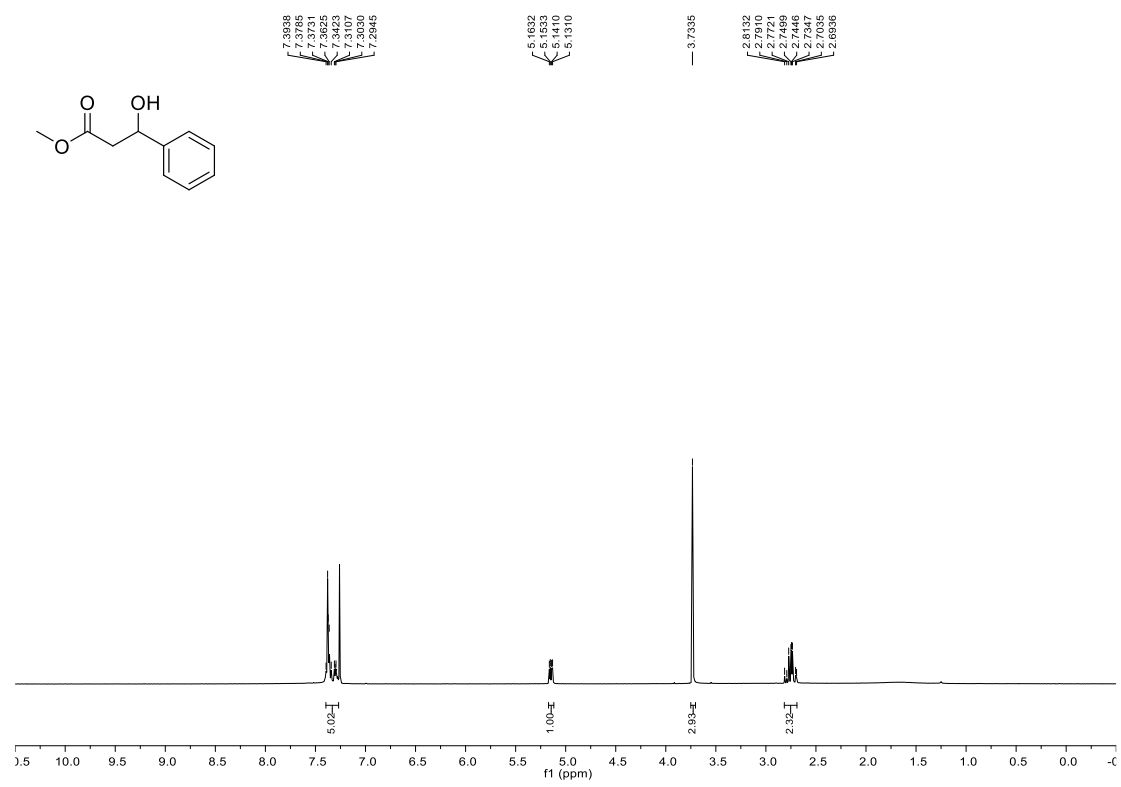


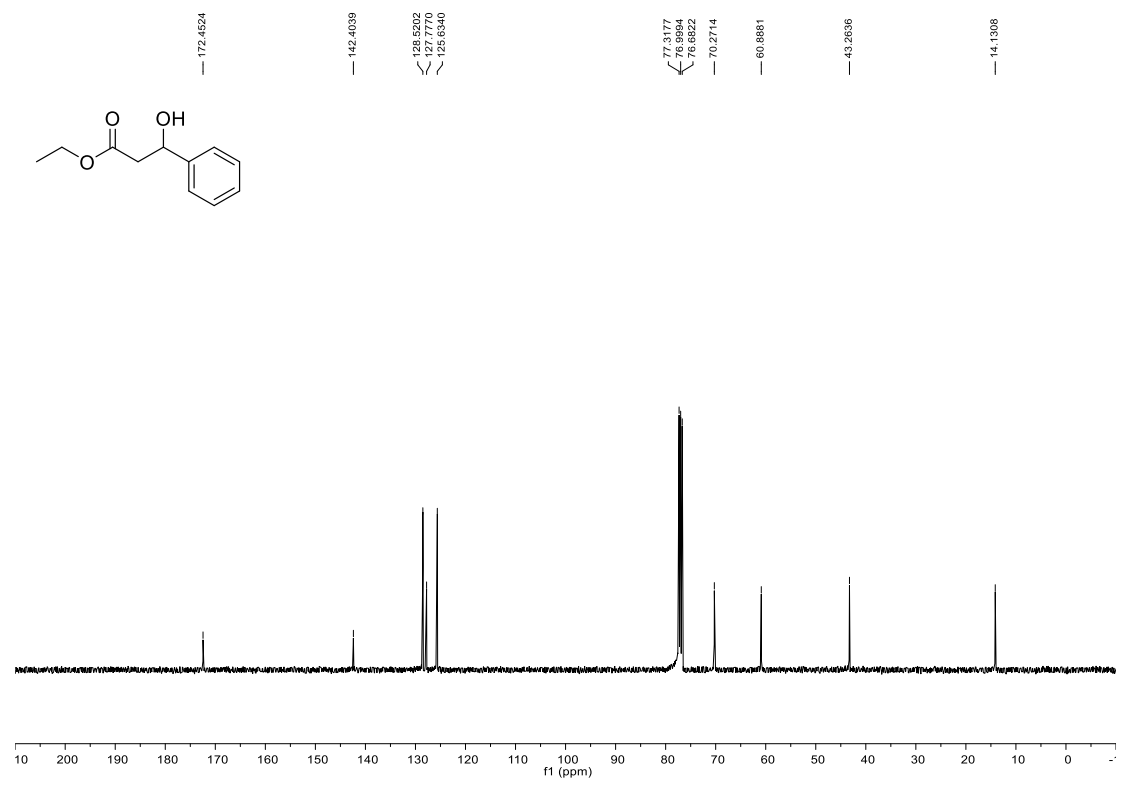
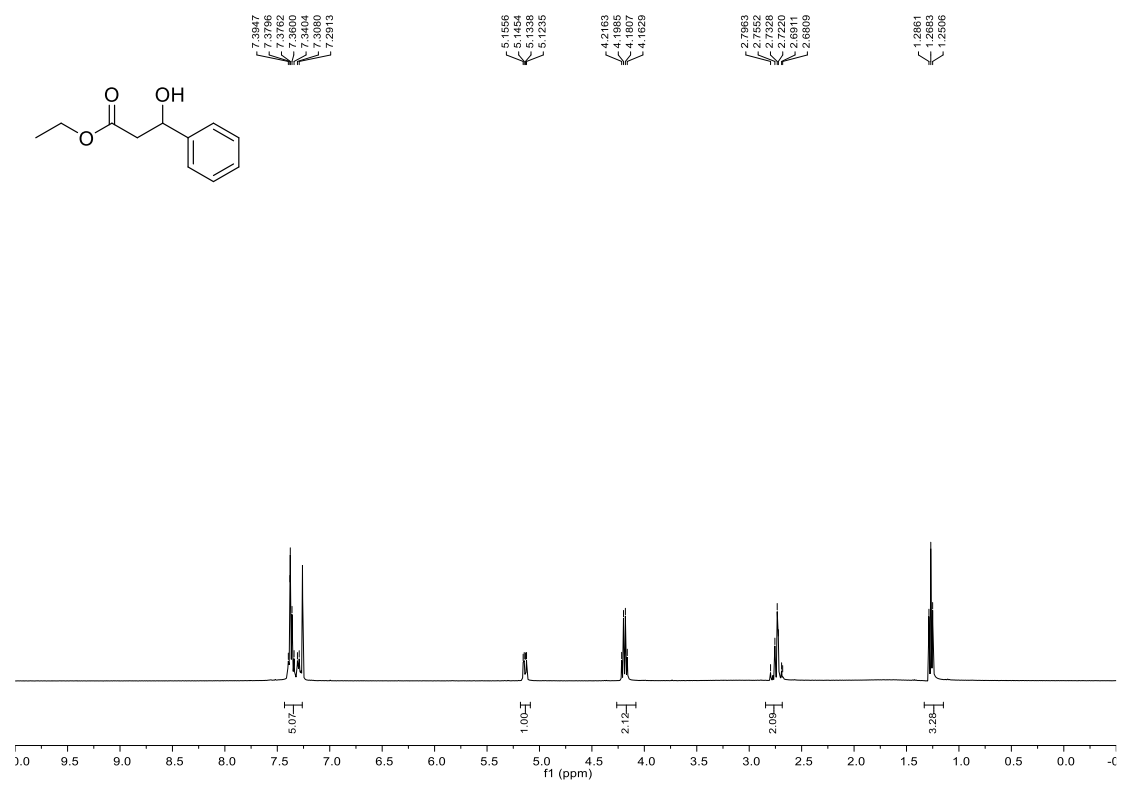


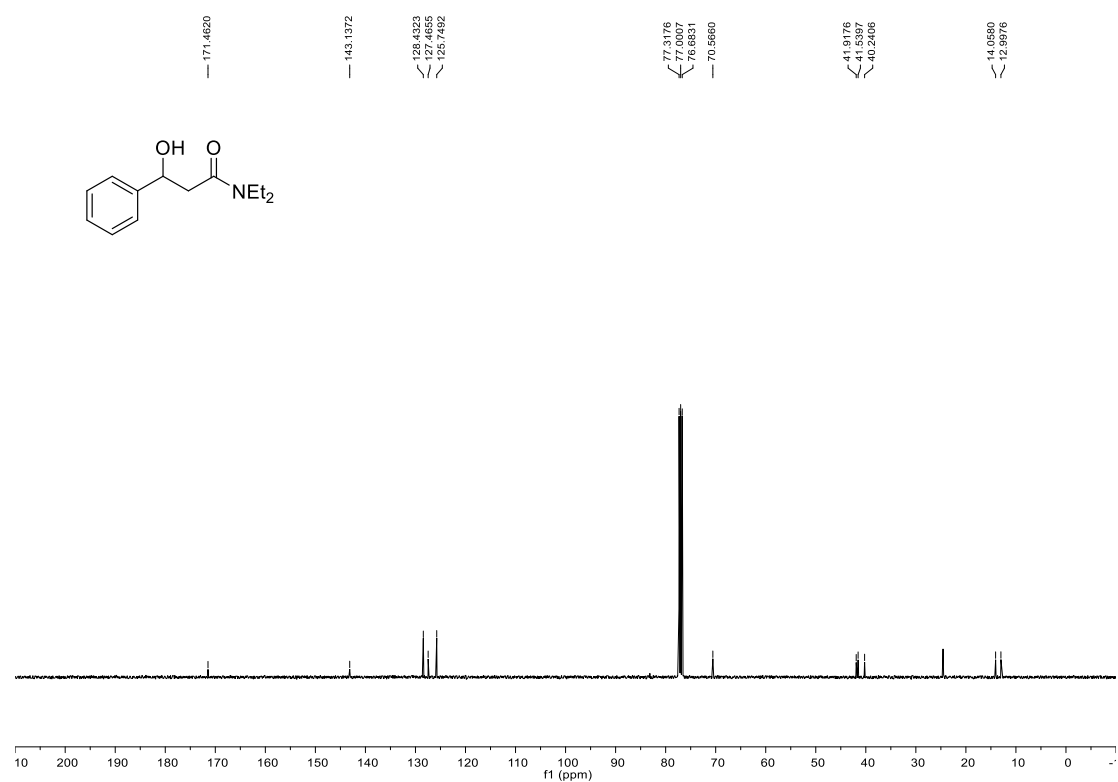
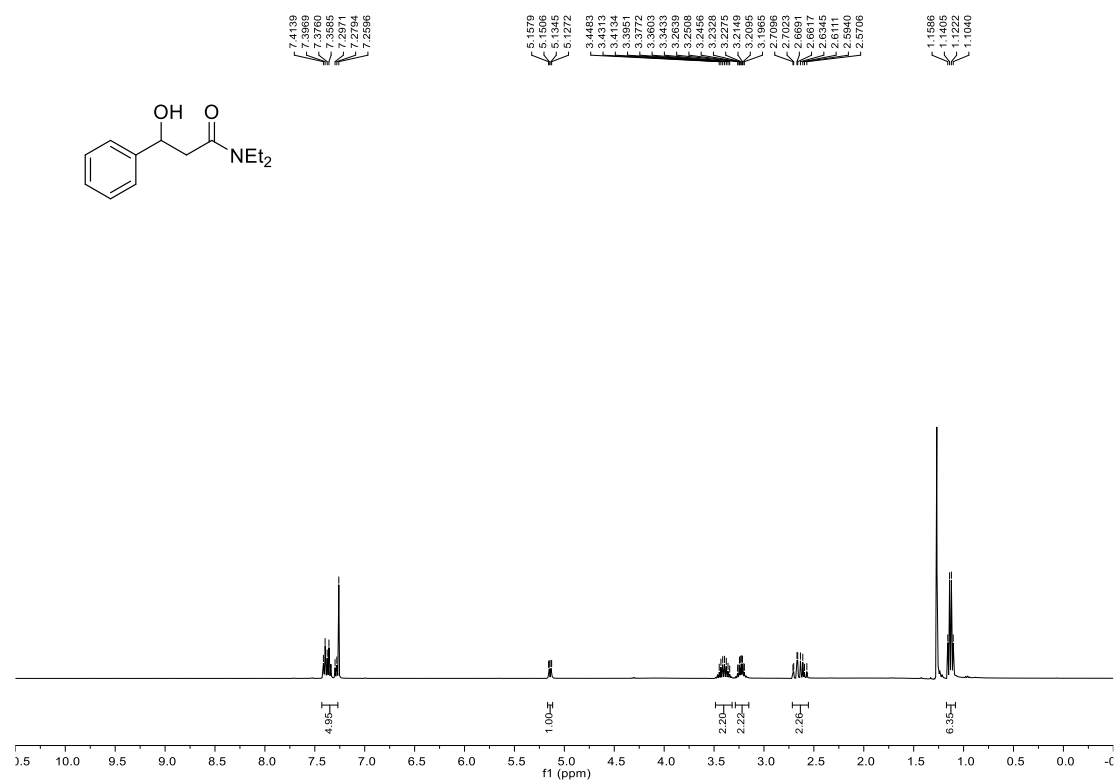


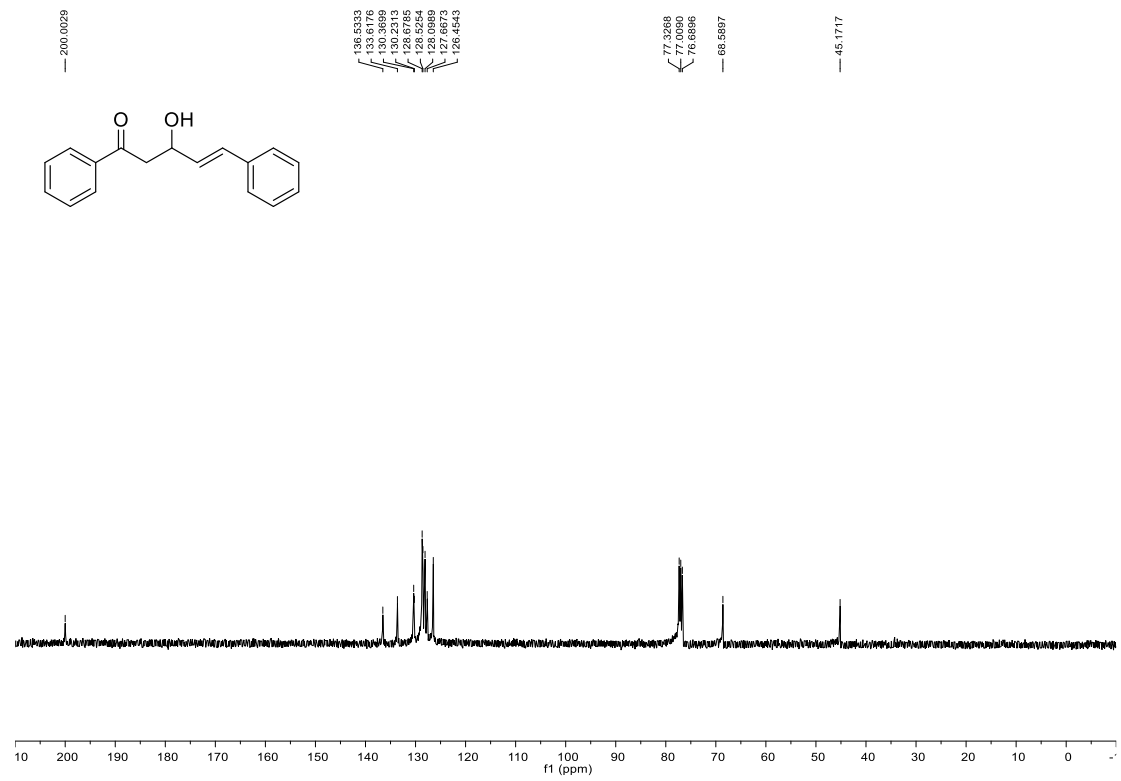
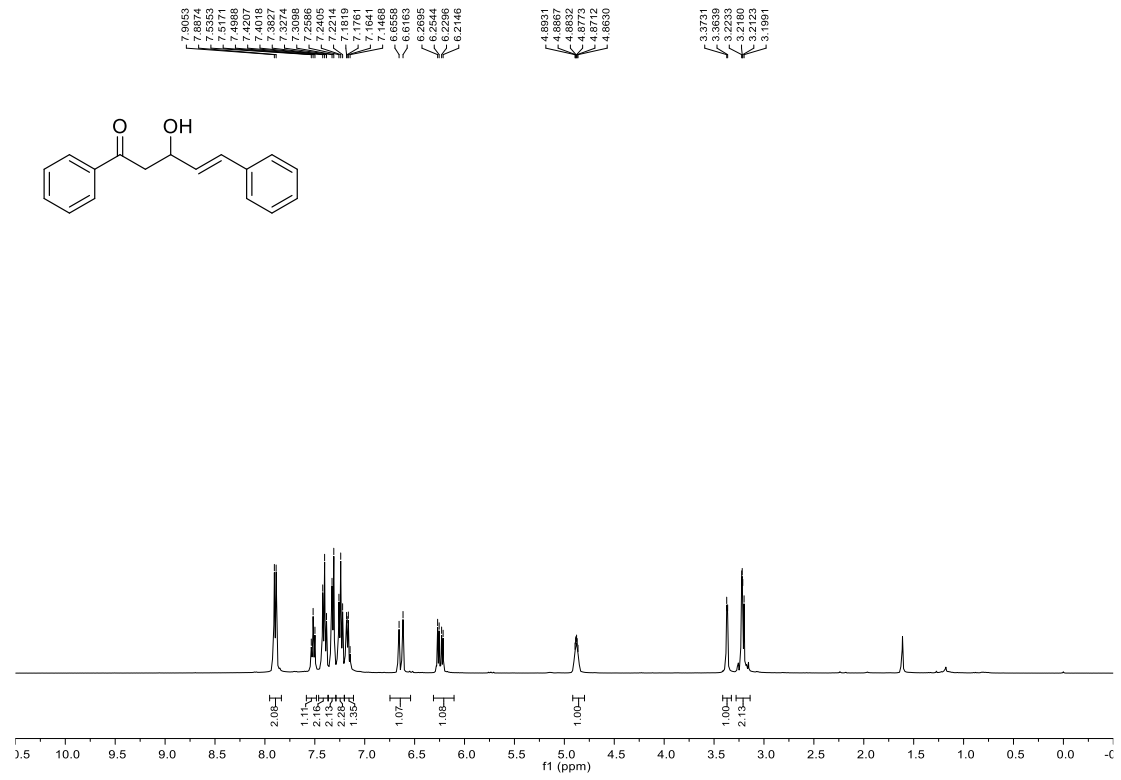












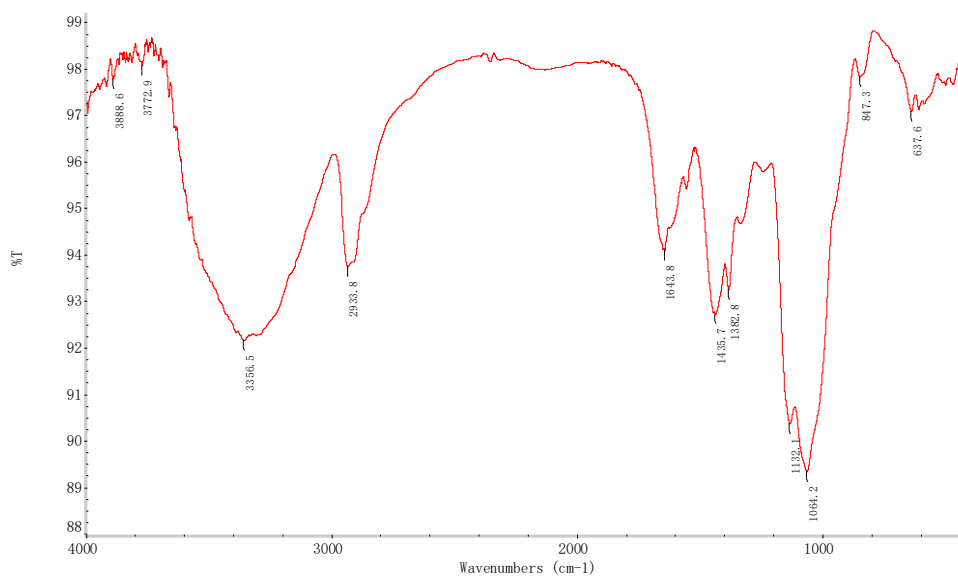


Figure S1. IR spectra of CP@Cu nanoparticles

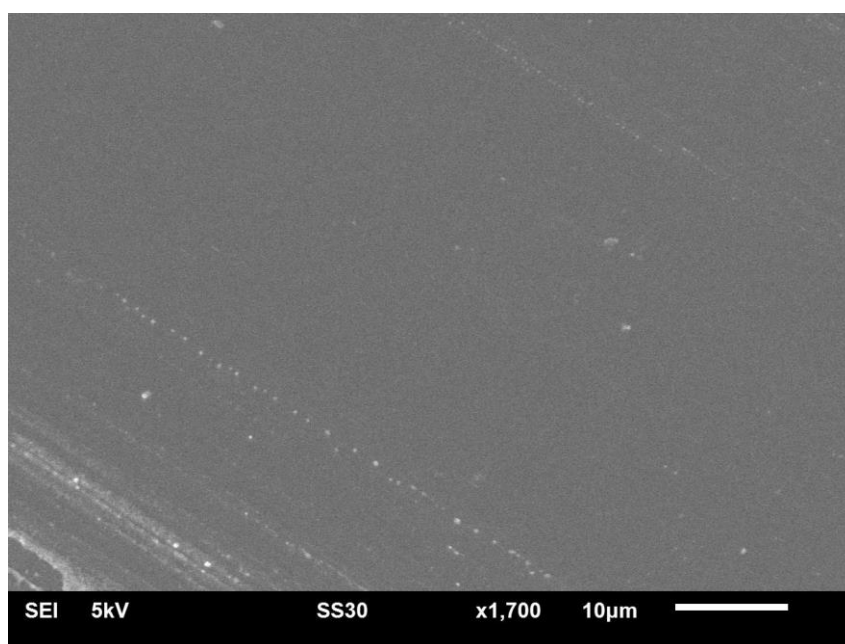


Figure S2. SEM image of CP@Cu nanoparticles