Supporting Information

Isopropylmagnesium Chloride-promoted Unilateral Addition of Grignards to β-Diketones: One-pot Syntheses of β-Tertiary Alcohol Ketones or 3-Substituted Cyclic-2-Enones

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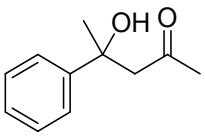
Content

1. General

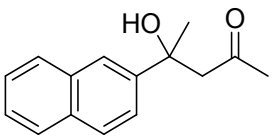
All reactions were performed under an argon atmosphere and solvents were dried according to the established procedures ahead of use. All reagents were commercial. The reactions were monitored by TLC (thin layer chromatography) method; column and preparative TLC purification were carried out using silica gel. Melting points were uncorrected and recorded on X-4 melting point apparatus. ^{1}H NMR and ^{13}C NMR spectra were measured on 400 MHz and 100 MHz spectrometers (NMR in $CDCl_3$ with TMS as an internal standard), respectively, and recorded as ppm. HR-MS were measured with Thermo Scientific Orbitrap Elite LTQ-06-ETD mass spectrometer.

2. General Procedure for the preparation of *β*-tertiary alcohol substrate.

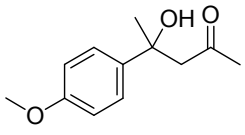
To a solution of *i*-PrMgCl (0.77 M, 0.13 mL, 0.1 mmol, 0.2 eq.) was dropwise added the 1,3-diketone (0.5 mmol, 1.0 eq.) in anhydrous THF (1 mL) at 0 °C. The mixture was stirred for 30 min at 0 °C and then the bromide Grignard reagent (1.25 mmol, 2.5 eq.) was introduced. The mixture was warmed to 40 °C. After stirring for 4 h at 40 °C, the reaction was carefully quenched with 25 mL 10% aqueous solution of acetic acid at 0 °C. The aqueous layer was extracted with ether (3×15 mL) and the combined organic layer was dried with anhydrous Na_2SO_4. The solvent was then evaporated under the reduced pressure and the residue was purified by column chromatography.



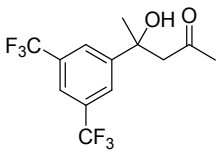
4-hydroxy-4-phenylpentan-2-one (1)[1]. Yield 165 mg, 93%; pale yellow oil; ^{1}H NMR (400MHz, $CDCl_3$) δ 7.44-7.20 (m, 5H), 4.54 (s, 1H), 3.19 (d, *J* = 16.8 Hz, 1H), 2.84 (d, *J* = 17.2 Hz, 1H), 2.07 (s, 3H), 1.58 (s, 3H).



4-hydroxy-4-(naphthalen-2-yl)pentan-2-one (2). Yield 207 mg, 91%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.24 (m, 7H), 4.71 (s, 1H), 3.28 (d, *J* = 16.8 Hz, 1H), 2.91 (d, *J* = 16.8 Hz, 1H), 2.06 (s, 3H), 1.59 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.6, 144.5, 133.1, 132.2, 128.1, 128.0, 127.4, 126.0, 125.7, 122.8, 73.4, 53.6, 31.8, 30.5; HRMS calcd for $C_{15}H_{16}NaO_2$ $[M+Na]^+$ 251.1048, found 251.1040.

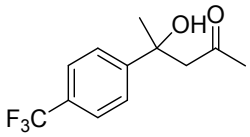


4-hydroxy-4-(4-methoxyphenyl)pentan-2-one (3)[2]. Yield 180 mg, 87%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-6.84 (m, 4H), 4.47 (s, 1H), 3.78 (s, 3H), 3.15 (d, *J* = 17.2 Hz, 1H), 2.82 (d, *J* = 16.8 Hz, 1H), 2.06 (s, 3H), 1.49 (s, 3H).

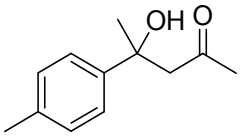


4-(3,5-bis(trifluoromethyl)phenyl)-4-hydroxypentan-2-one (4). Yield 292 mg, 93%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.77 (m, 3H), 4.78 (s, 1H), 3.17 (d, *J* = 17.6 Hz, 1H), 2.98 (d, *J* = 17.6 Hz, 1H), 2.16 (s, 3H), 1.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

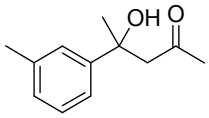
210.0, 150.2, 131.8, 131.4, 124.7, 122.0, 120.9, 72.9, 53.2, 31.6, 30.3; HRMS calcd for $C_{13}H_{12}F_6NaO_2$ $[M+Na]^+$ 337.0639, found 337.0637.



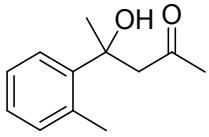
4-hydroxy-4-(4-(trifluoromethyl)phenyl)pentan-2-one (5)[2]. Yield 211 mg, 86%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.29 (m, 4H), 4.76 (s, 1H), 3.17 (d, *J* = 17.6 Hz, 1H), 2.98 (d, *J* = 17.6 Hz, 1H), 2.17 (s, 3H), 1.56 (s, 3H).



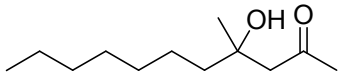
4-hydroxy-4-(*p*-tolyl)pentan-2-one (6)[3]. Yield 168 mg, 88%; yellow solid, mp 24.9-27.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.12 (m, 4H), 4.50 (s, 1H), 3.17 (d, *J* = 17.2 Hz, 1H), 2.82 (d, *J* = 17.2 Hz, 1H), 2.31 (s, 3H), 2.06 (s, 3H), 1.49 (s, 3H).



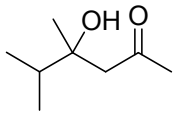
4-hydroxy-4-(*m*-tolyl)pentan-2-one (7). Yield 169 mg, 88%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.03 (m, 5H), 4.52 (s, 1H), 3.19 (d, *J* = 22.8 Hz, 1H), 2.84 (d, *J* = 22.8 Hz, 1H), 2.36 (s, 3H), 2.08 (s, 3H), 1.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.6, 147.1, 137.8, 128.1, 127.4, 125.0, 121.2, 73.2, 53.9, 31.8, 30.6, 21.5; HRMS calcd for $C_{12}H_{16}NaO_2$ $[M+Na]^+$ 215.1048, found 215.1048.



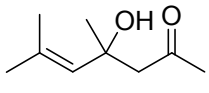
4-hydroxy-4-(*o*-tolyl)pentan-2-one (8). Yield 159 mg, 83%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.30 (m, 4H), 4.48 (s, 1H), 3.17 (d, *J* = 17.2 Hz, 1H), 2.82 (d, *J* = 17.2 Hz, 1H), 2.31 (s, 3H), 2.07 (s, 3H), 1.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.9, 144.0, 135.2, 133.0, 127.2, 125.9, 125.4, 74.8, 53.2, 31.8, 29.1, 22.5; HRMS calcd for $C_{12}H_{16}NaO_2$ $[M+Na]^+$ 215.1048, found 215.1045.



4-hydroxy-4-methylundecan-2-one (9). Yield 168 mg, 84%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 1H), 2.65 (d, *J* = 17.2 Hz, 1H), 2.57 (d, *J* = 17.2 Hz, 1H), 2.18 (s, 3H), 1.57-1.04 (m, 15H), 0.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 221.1, 71.5, 62.8, 42.1, 31.8, 30.0, 29.2, 26.6, 23.9, 22.5, 14.0; HRMS calcd for $C_{12}H_{24}NaO_2$ $[M+Na]^+$ 223.1674, found 223.1676.

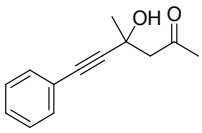


4-hydroxy-4,5-dimethylhexan-2-one (10)[3]. Yield 115 mg, 80%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.40 (s, 1H), 3.28 (d, *J* = 16.8 Hz, 1H), 2.87 (d, *J* = 16.8 Hz, 1H), 2.16 (s, 3H), 1.93-1.84 (m, 1H), 0.93-0.91 (d, *J* = 7.2 Hz, 3H), 0.78-0.76 (d, *J* = 6.8 Hz, 3H).

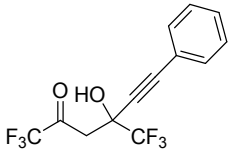


4-hydroxy-4,6-dimethylhept-5-en-2-one (11). Yield 94 mg, 60%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.28(s, 1H), 4.21(s, 1H), 3.41 (d, *J* = 17.2 Hz, 1H), 3.13 (d, *J* = 17.2 Hz, 1H), 2.58 (s, 3H), 2.08 (s, 3H), 2.58 (s, 3H), 1.91 (s, 3H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.6, 133.3,

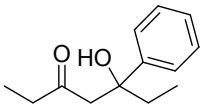
129.1, 70.7, 53.5, 30.7, 27.7, 26.4, 17.7; HRMS calcd for $C_9H_{16}NaO_2$ $[M+Na]^+$ 179.1048, found 179.1043.



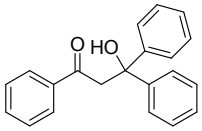
4-hydroxy-4-methyl-6-phenylhex-5-yn-2-one (12)[4]. Yield 163 mg, 81%; yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 - 7.26 (m, 5H), 4.54 (s, 1H), 3.09 (d, *J* = 16.8 Hz, 1H), 2.74 (d, *J* = 16.8 Hz, 1H), 2.26 (s, 3H), 1.59 (s, 3H).



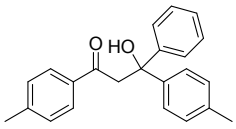
1,1,1-trifluoro-4-hydroxy-6-phenyl-4-(trifluoromethyl)hex-5-yn-2-one (13). Yield 245 mg, 79%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.55-7.33 (m, 5H), 3.72 (s, 1H), 3.41 (d, *J* = 17.8 Hz, 1H), 3.35 (d, *J* = 17.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.0, 132.1, 129.8, 128.5, 124.2, 121.4, 120.3, 88.6, 81.0, 69.4, 69.0, 41.4; HRMS calcd for $C_{13}H_8F_6O_2$ $[M]^+$ 310.0428, found 310.0422.



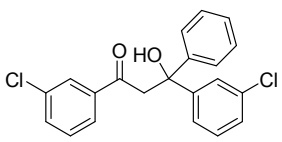
5-hydroxy-5-phenylheptan-3-one (14). Yield 198 mg, 96%; yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38-7.19 (m, 5H), 4.68 (s, 1H), 3.17 (d, *J* = 16.8 Hz, 1H), 2.79 (d, *J* = 16.8 Hz, 1H), 2.44-2.17 (m, 2H), 1.84- 1.72 (m, 2H), 0.92-0.84 (m, 3H), 0.76-0.72 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.7, 145.6, 128.1, 126.5, 124.9, 75.8, 51.5, 38.0, 35.8, 29.7, 7.6, 7.2; HRMS calcd for $C_{13}H_{18}NaO_2$ $[M+Na]^+$ 229.1204, found 229.1196.



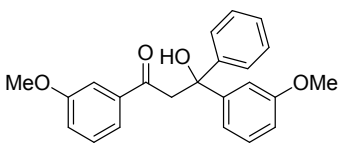
3-hydroxy-1,3,3-triphenylpropan-1-one (15)[5]. Yield 278 mg, 92%; white solid, mp 85.2-85.8 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.94-7.18 (m, 15H), 5.46 (s, 1H), 3.92 (s, 2H).



3-hydroxy-3-phenyl-1,3-di-*p*-tolylpropan-1-one (16). Yield 294 mg, 89%; yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85-7.07 (m, 13H), 5.52 (s, 1H), 3.90 (d, *J* = 17.8 Hz, 1H), 3.84 (d, *J* = 17.8 Hz, 1H), 2.43 (s, 3H) , 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.0, 147.1, 137.1, 132.4, 128.3, 127.9, 127.0, 125.7, 73.2, 51.7, 21.1, 20.2; HRMS calcd for $C_{23}H_{22}NaO_2$ $[M+Na]^+$ 353.1517, found 353.1520.

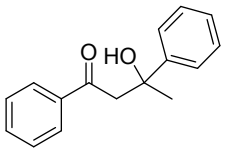


3-hydroxy-3-phenyl-1,3-di-*p*-tolylpropan-1-one (17). Yield 344 mg, 93%; yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.89-7.09 (m, 13H), 5.25 (s, 1H), 3.93 (d, *J* = 17.8 Hz, 1H), 3.82 (d, *J* = 17.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 148.4, 145.5, 138.1, 135.2, 134.4, 133.9, 130.2, 129.9, 128.4, 128.2, 127.6, 127.3, 126.4, 126.1, 125.6, 123.8, 48.3; HRMS calcd for $C_{21}H_{16}Cl_2NaO_2$ $[M+Na]^+$ 393.0425, found 393.0424.

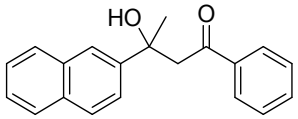


3-hydroxy-1,3-bis(3-methoxyphenyl)-3-phenylpropan-1-one (18). Yield 333 mg, 92%; yellow solid, mp 103.6-

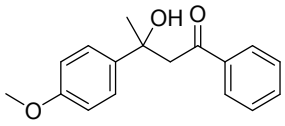
105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-6.95 (m, 13H), 5.44 (s, 1H), 3.92 (d, *J* = 18.0 Hz, 1H), 3.86 (d, *J* = 18.0 Hz, 1H), 3.80-3.45 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.7, 159.8, 159.5, 148.1, 146.2, 137.9, 129.7, 129.1, 128.1, 128.0, 126.9, 125.6, 120.6, 120.3, 118.2, 117.9, 112.1, 112.1,111.7, 55.3, 55.0; HRMS calcd for $C_{23}H_{22}NaO_4$ $[M+Na]^+$ 385.1416, found 385.1415.



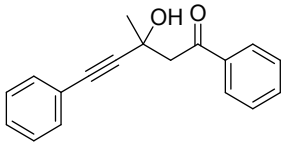
3-hydroxy-1,3-diphenylbutan-1-one (19)[6]. Yield 214 mg, 89%; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.20 (m, 10H), 4.87 (s, 1H), 3.79 (d, *J* = 17.6 Hz, 1H), 3.34 (d, *J* = 17.2 Hz, 1H), 1.62 (s, 3H).



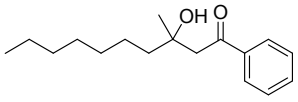
3-hydroxy-3-(naphthalen-2-yl)-1-phenylbutan-1-one (20). Yield 264 mg, 91%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.25 (m, 12H), 5.08 (s, 1H), 3.90 (d, *J* = 17.4 Hz, 1H), 3.43 (d, *J* = 17.4 Hz, 1H), 1.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.2, 144.9, 133.7, 128.7, 128.0, 127.4, 126.0, 125.7, 123.0, 73.8, 48.6, 30.9; HRMS calcd for $C_{20}H_{17}O$ { $[M-H_2O]+H\}^+$ 273.1274, found 273.1277.



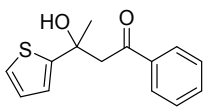
3-hydroxy-3-(4-methoxyphenyl)-1-phenylbutan-1-one (21). Yield 243 mg, 90%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-6.83 (m, 9H), 4.86 (s, 1H), 3.77 (s, 3H), 3.76 (d, *J* = 17.4 Hz, 1H), 3.31 (d, *J* = 17.4 Hz, 1H), 1.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.4, 158.2, 139.6, 136.8, 133.7, 128.6, 128.0, 125.5, 113.5, 73.3, 55.1, 48.7, 30.9; HRMS calcd for $C_{17}H_{18}NaO_3$ $[M+Na]^+$ 293.1154, found 293.1145.



3-hydroxy-3-methyl-1,5-diphenylpent-4-yn-1-one (22). Yield 211 mg, 80%; pale yellow solid, mp 45.2-46.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-7.22 (m, 10H), 4.88 (s, 1H), 3.73 (d, *J* = 17.0 Hz, 1H), 3.17 (d, *J* = 17.0 Hz, 1H), 1.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.3, 136.8, 133.8, 131.6, 128.7, 128.2, 128.0, 122.5, 91.9, 82.9, 66.2, 49.2, 29.9, 29.6; HRMS calcd for $C_{18}H_{16}NaO_2$ $[M+Na]^+$ 287.1048, found 287.1040.

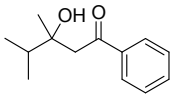


3-hydroxy-3-methyl-1-phenyldecan-1-one (23). Yield 223 mg, 85%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.19 (m, 5H), 4.52 (s, 1H), 3.20 (d, *J* = 16.8 Hz, 1H), 2.83 (d, *J* = 16.8 Hz, 1H), 1.78-1.18 (m, 12H), 0.88-0.82 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.1, 137.4, 133.5, 128.7, 128.1, 124.8, 72.0, 46.9, 42.4, 31.8, 30.1, 29.3, 27.0, 24.1, 22.6, 14.1; HRMS calcd for $C_{17}H_{26}NaO_2$ $[M+Na]^+$ 285.1830, found 285.1837.

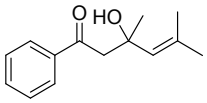


3-hydroxy-1-phenyl-3-(thiophen-2-yl)butan-1-one (24). Yield 214 mg, 87%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.07 (m, 8H), 4.99 (s, 1H), 3.70 (d, *J* = 17.2 Hz, 1H), 3.32 (d, *J* = 17.2 Hz, 1H), 1.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.3, 149.3, 136.9, 133.7,

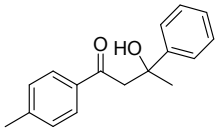
128.6, 128.0, 125.8, 125.1, 119.3, 72.4, 48.7, 30.4; HRMS calcd for $C_{14}H_{14}NaO_2S$ $[M+Na]^+$ 269.0612, found 269. 0608.



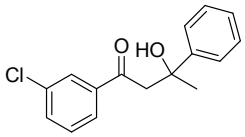
3-hydroxy-3,4-dimethyl-1-phenylpentan-1-one (25)[7]. Yield 165 mg, 80%; yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37-7.19 (m, 5H), 4.49 (s, 1H), 3.31 (d, *J* = 16.6 Hz, 1H), 2.82 (d, *J* = 16.6 Hz, 1H), 3.05 (s, 3H), 1.93-1.88 (m, 1H), 0.95-0.90 (m, 3H), 0.76-0.75 (m, 3H).



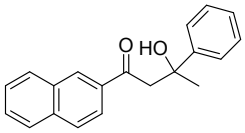
3-hydroxy-3,5-dimethyl-1-phenylhex-4-en-1-one (26)[8]. Yield 188 mg, 86%; yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.96-7.21 (m, 5H), 5.28 (s, 1H), 4.21 (s, 1H), 3.41 (d, *J* = 17.2 Hz, 1H), 3.12 (d, *J* = 17.2 Hz, 1H), 2.08 (s, 3H), 1.89 (s, 3H), 1.44 (s, 3H).



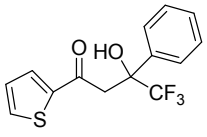
3-hydroxy-3-phenyl-1-(*p*-tolyl)butan-1-one (27). Yield 220 mg, 87%; yellow needle, 51.2-52.8 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81-7.09 (m, 9H), 4.98 (s, 1H), 3.76 (d, *J* = 17.4 Hz, 1H), 3.31 (d, *J* = 17.4 Hz, 1H), 2.40 (s, 3H), 1.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.0, 147.7, 144.7, 134.5, 129.6, 129.3, 128.2, 126.6, 124.4, 115.3, 73.6, 48.5, 30.9, 21.7; HRMS calcd for $C_{17}H_{18}NaO_2$ $[M+Na]^+$ 277.1204, found 277.1205.



1-(3-chlorophenyl)-3-hydroxy-3-phenylbutan-1-one (28). Yield 249 mg, 91%; pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85-7.19 (m, 9H), 4.63 (s, 1H), 3.76 (d, *J* = 17.4 Hz, 1H), 3.31 (d, *J* = 17.4 Hz, 1H), 1.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 147.3, 138.4, 135.0, 133.5, 129.9, 128.3, 126.7, 126.8, 126.1, 124.3, 73.5, 49.1, 30.8; HRMS calcd for $C_{16}H_{15}ClNaO_2$ $[M+Na]^+$ 297.0658, found 297.0660.



3-hydroxy-1-(naphthalen-2-yl)-3-phenylbutan-1-one (29). Yield 261 mg, 90%; yellow solid, 52.2-54.2 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.49-7.25 (m, 12H), 5.02 (s, 1H), 3.99 (d, *J* = 17.0 Hz, 1H), 3.53 (d, *J* = 17.0 Hz, 1H), 1.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2, 147.7, 135.8, 134.3, 132.4, 130.1, 129.6, 128.8, 128.6, 128.3, 127.8, 126.9, 126.7, 125.7, 124.4, 123.4, 73.7, 48.8, 30.9; HRMS calcd for $C_{20}H_{18}NaO_2$ $[M+Na]^+$ 313.1204, found 313.1200.

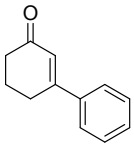


4,4,4-trifluoro-3-hydroxy-3-phenyl-1-(thiophen-2-yl)butan-1-one (30). Yield 231 mg, 77%; dark yellow solid, 51.3-51.8 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.83-7.16 (m, 8H), 5.72 (s, 1H), 3.89 (d, *J* = 16.6 Hz, 1H), 3.60 (d, *J* = 16.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.8, 143.1, 137.3, 135.9, 133.5, 128.8, 128.6, 128.4, 126.2, 40.9; HRMS calcd for $C_{14}H_{11}F_3NaO_2S$ $[M+Na]^+$, 323.0330, found 323.0325.

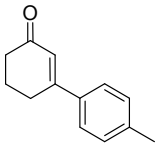
3. General Procedure for the preparation of 3-substituted enones.

To a solution *i*-PrMgCl (0.77 M, 0.13 mL, 0.1 mmol, 0.2 eq.) was dropwise added

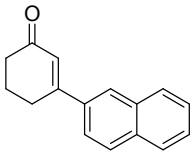
cyclic 1,3-diketones (0.5 mmol, 1.0 eq.) in anhydrous THF (1 mL) at 0 °C. The mixture was stirred for 30 min at 0 °C and then the bromide Grignard reagent (1.25 mmol, 2.5 eq.) was added. The mixture was warmed to 40 °C. After stirring for 4 h at 40 °C, the reaction was quenched with 25 mL 10% aqueous solution of acetic acid at 0 °C. The aqueous layer was extracted with ether (3×15 mL) and the combined organic layer was dried with anhydrous Na_2SO_4. The solvent was evaporated under the reduced pressure and the crude product was purified by column chromatography.



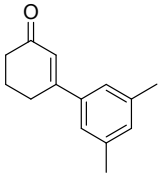
3-phenyl-2-cyclohexene-1-one (31)[9]. Yield 70.9 mg, 82%; yellow solid, 64-65 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.37 (m, 5H), 6.40 (s, 1H), 2.77-2.74 (m, 2H), 2.47-2.45 (m, 2H), 2.17-2.10 (m, 2H).



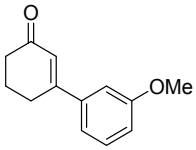
3-(4'-methyl)phenyl-2-cyclohexene-1one (32)[10]. Yield 83.8 mg, 90%; yellow solid, 43-44 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.20 (m, 4H), 6.40 (s, 1H), 2.77-2.73 (m, 2H), 2.48-2.44 (m, 2H), 2.34 (s, 3H), 2.17-2.10 (m, 2H).



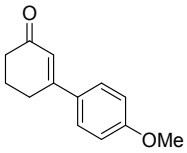
3-(naphthalen-2-yl)cyclohex-2-enone (33)[11]. Yield 98 mg, 88%; white solid, 89-90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-7.51 (m, 7H), 6.58 (s, 1H), 2.92-2.89 (m, 2H), 2.55-2.52 (m, 2H), 2.24-2.18 (m, 2H).



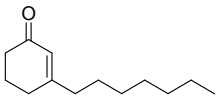
3-(3',5'-dimethyl)phenyl-2cyclohexene-1-one (34)[11]. Yield 70 mg, 70%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (s, 2H), 7.05 (s, 1H), 6.39 (s, 1H), 2.76-2.73 (m, 2H), 2.47-2.34 (m, 2H), 2.16 (s, 6H), 2.11-2.10 (m, 2H).



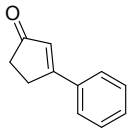
3-(3'-methoxy)phenyl-2-cyclohexene-1-one (35)[12]. Yield 79 mg, 79%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-6.95 (m, 4H), 6.42 (s, 1H), 3.84 (s, 3H), 2.78-2.75 (m, 2H), 2.51-2.47 (m, 2H), 2.19-2.12 (m, 2H).



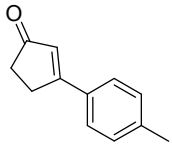
3-(4'-methoxy)phenyl-2-cyclohexene-1-one (36)[12]. Yield 85 mg, 84%; white solid, mp 84-85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-6.94 (m, 4H), 6.40 (s, 1H), 3.84 (s, 3H), 2.76-2.73 (m, 2H), 2.47-2.45 (m, 2H), 2.17-2.10 (m, 2H).



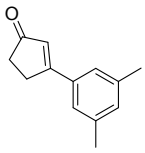
3-heptylcyclohex-2-enone (37)[13]. Yield 73 mg, 70%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (s, 1H), 2.36-2.21 (m, 17H), 0.88-0.84 (m, 3H).



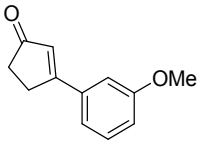
3-(3,5-dimethylphenyl)cyclopent-2-enone (38)[14]. Yield 82 mg, 76%; white solid, mp 82-83 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.44 (m, 5H), 6.59 (s, 1H), 3.08-3.05 (m, 2H), 2.61-2.59 (m, 2H).



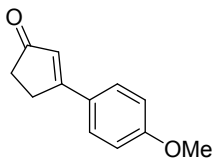
3-(*p*-tolyl)cyclopent-2-enone (39)[15]. Yield 67.4 mg, 78%; white solid, mp 100-101 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-2.26 (m, 4H), 6.55 (s, 1H), 3.06- 3.03 (m, 2H), 2.60-2.58 (m, 2H), 2.42 (s, 3H).



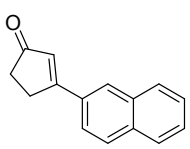
3-(3',5'-dimethylphenyl)cyclopent-2-enone (40). Yield 82 mg, 76%; yellow solid, mp 93-94 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.11 (m, 3H), 6.55 (s, 1H), 3.05-3.01 (m, 2H), 2.59-2.56 (m, 2H), 2.37 (s, 6H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.5, 174.1, 138.5, 134.1, 133.1, 127.4, 124.7,35.4, 28.8, 21.4; HRMS calcd for $C_{13}H_{15}O$ $[M+H]^+$, 187.1119, found 187.1123.



3-(3-methoxyphenyl)cyclopent-2-enone (41)[16]. Yield 68.9 mg, 73%; yellow solid, mp 95-96 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.00 (m, 4H), 6.57 (s, 1H), 3.86 (s, 3H), 3.06-3.02 (m, 2H), 2.61-2.58 (m, 2H).

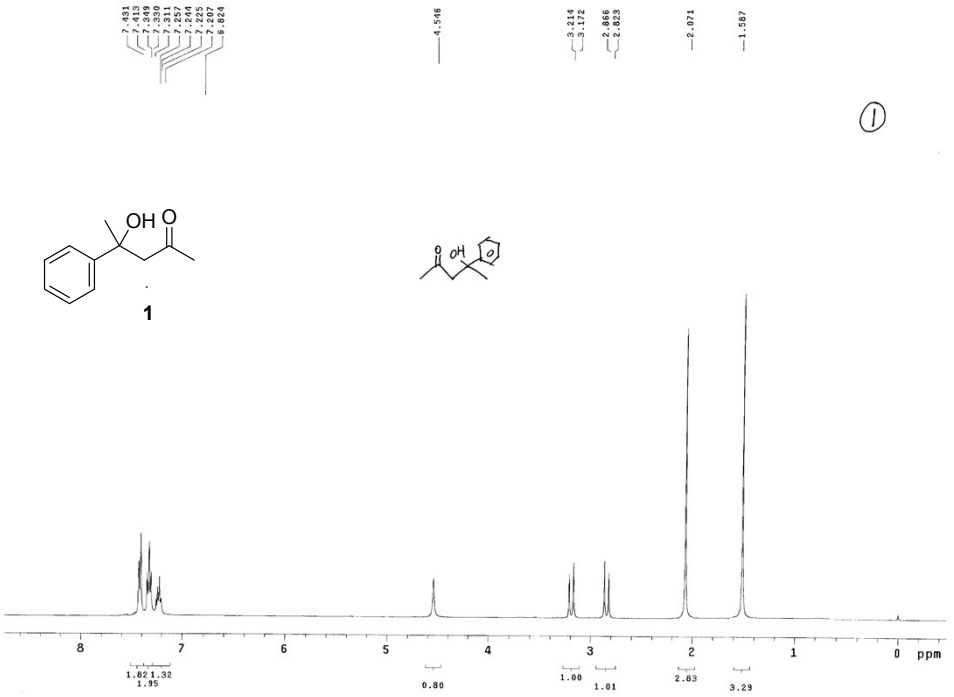


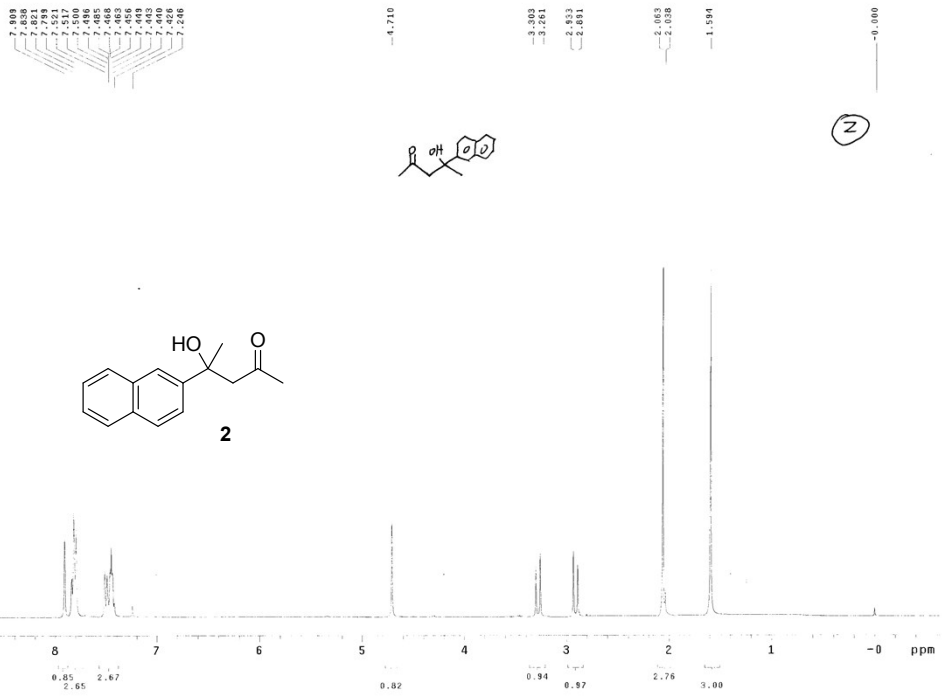
3-(4-methoxyphenyl)cyclopent-2-enone (42)[17]. Yield 68.9 mg, 73%; white solid, mp 140-141 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-6.95 (m, 4H), 6.48 (s, 1H), 3.87 (s, 3H), 3.04-3.01 (m, 2H), 2.59-2.56 (m, 2H).

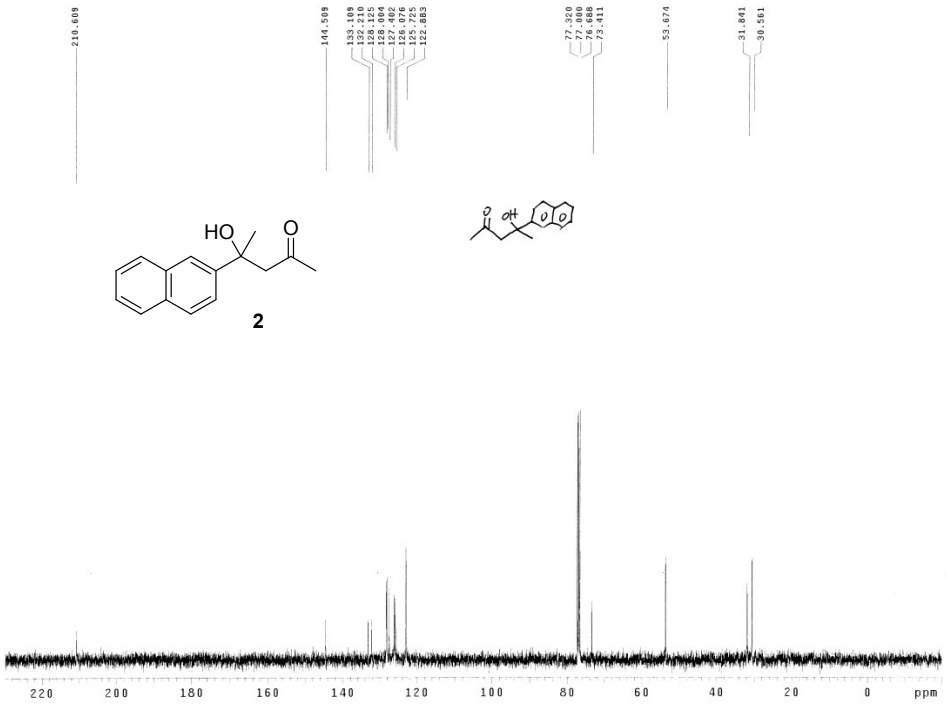


3-(naphthalen-2-yl)cyclopent-2-enone (43)[18]. Yield 76.6 mg, 74%; yellow solid, mp 126-127 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11-7.54 (m, 7H), 6.70 (s, 1H), 3.20-3.16 (m, 2H), 2.66-2.63 (m, 2H).

4. NMR Spectra



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31.841
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OH
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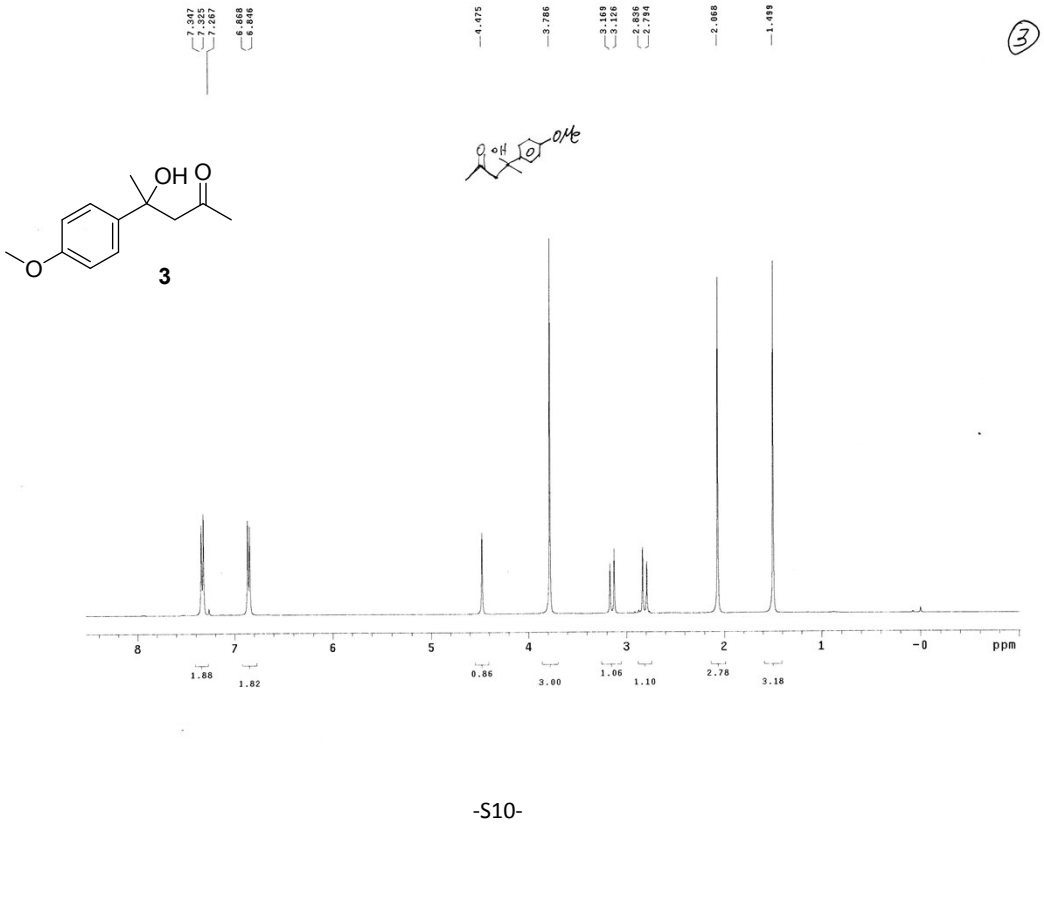
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2.794
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O
O
3
OH
O
OMe
8
7
6
5
4
3
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3.00
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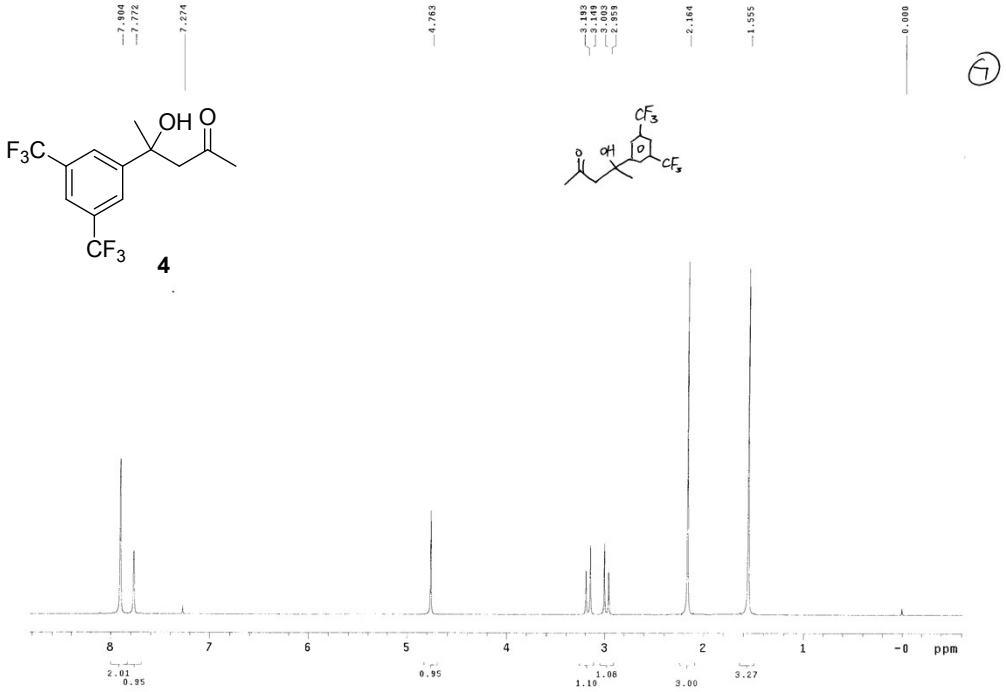
3.18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CF3
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CF3
OH
CF3
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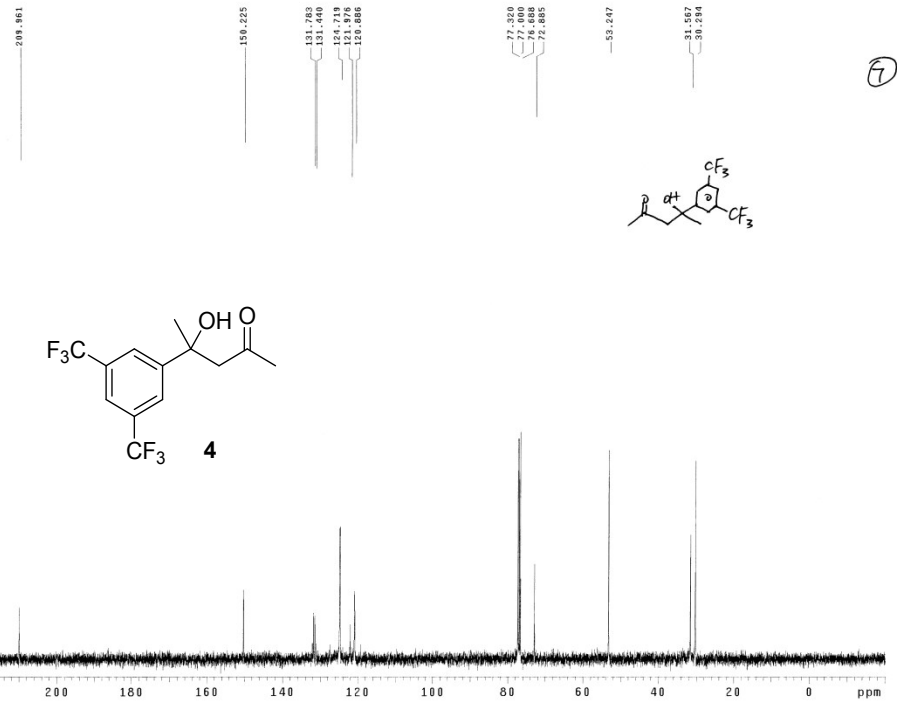
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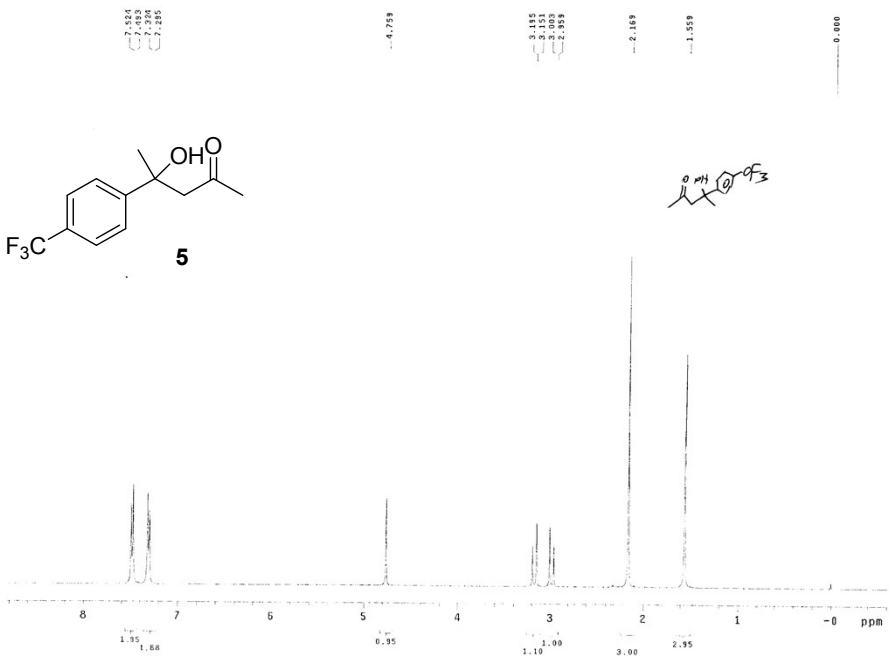
ppm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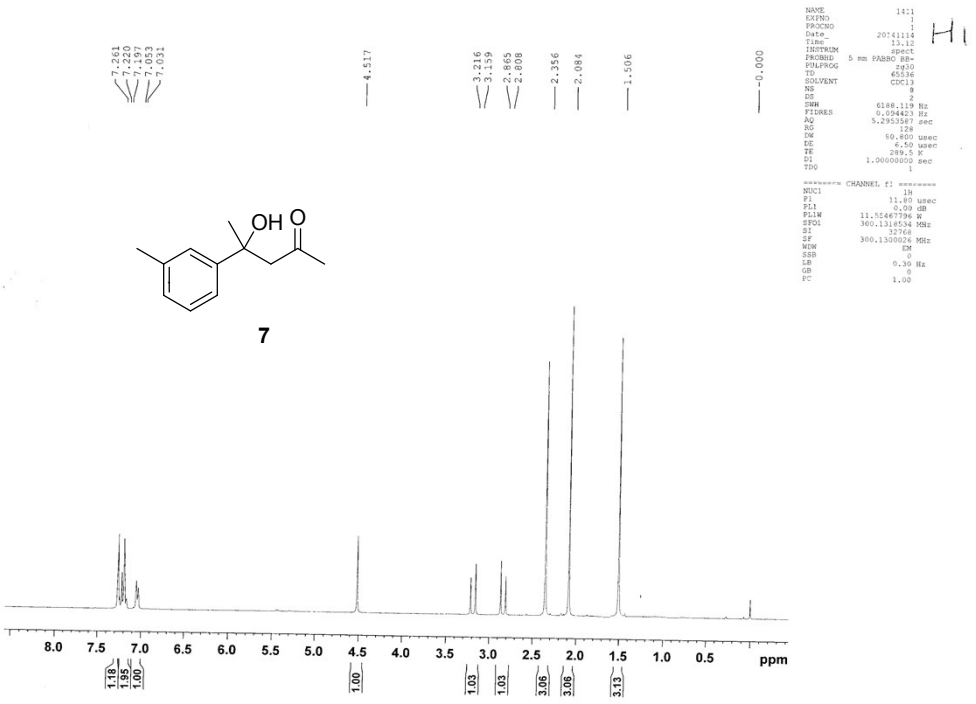
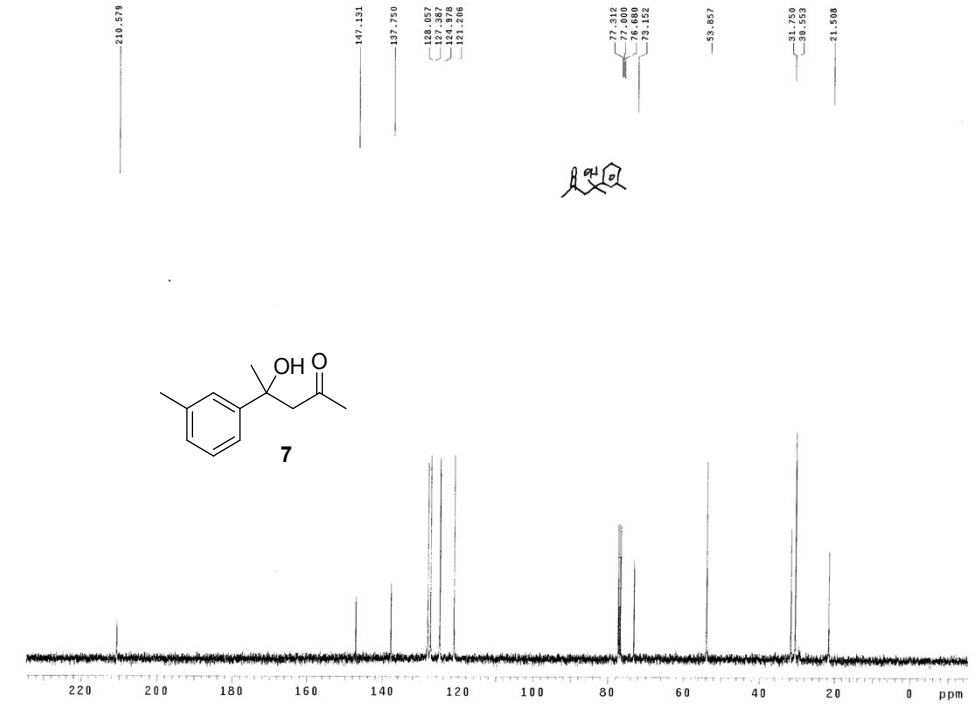
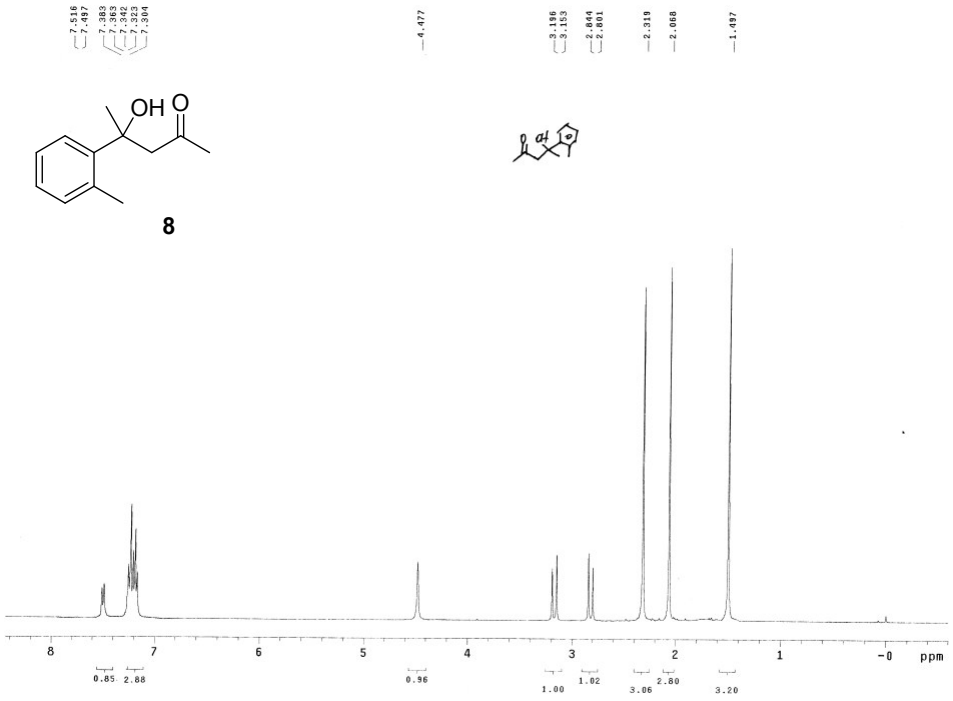
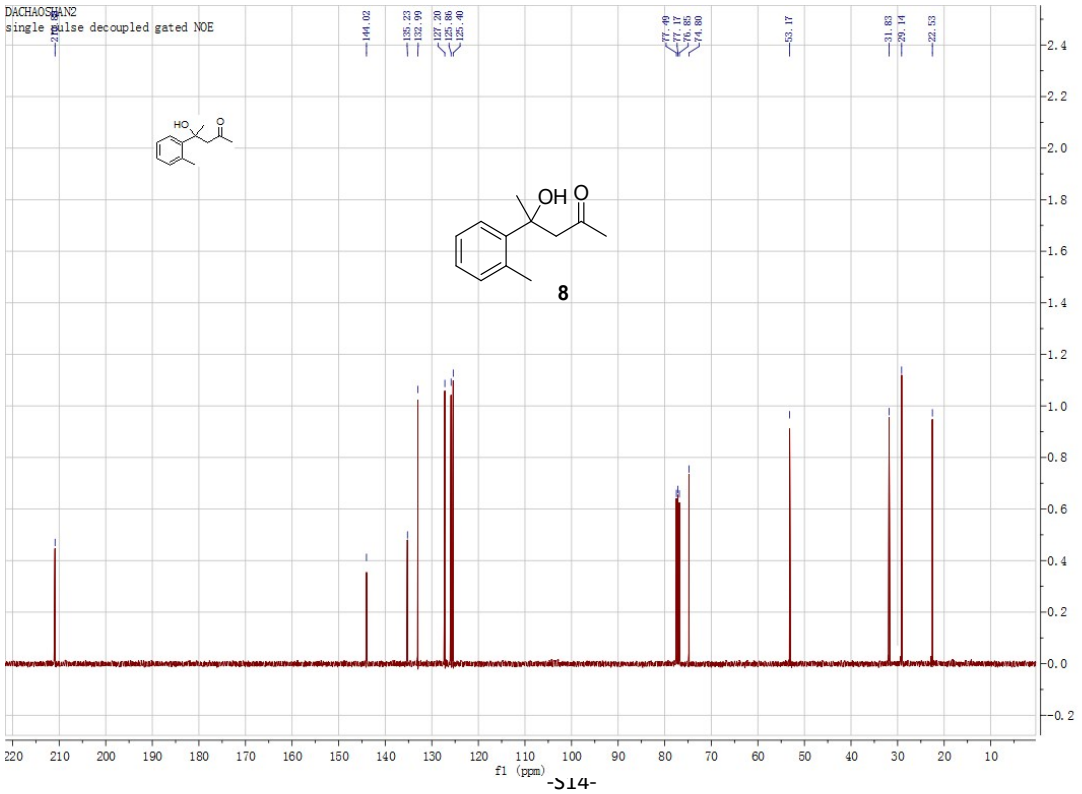
6
5
4
3
2
1
-0
ppm
1.95
1.88
0.95
1.10
1.00
3.00
2.95

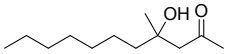

7.314
7.293
7.250
7.142
7.122
4.500
3.194
3.151
2.838
2.795
2.315
2.062
1.493
0.000
OH
O
6
8
7
6
5
4
3
2
1
-0
ppm
1.90
1.86
0.87
1.03
1.03
3.00
2.81
3.17


7.261
7.220
7.197
7.053
7.031
4.517
3.216
3.159
2.865
2.808
2.356
2.084
1.506
0.000
OH
O
7
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
1.18
1.95
1.00
1.00
1.03
1.03
3.06
3.05
3.13

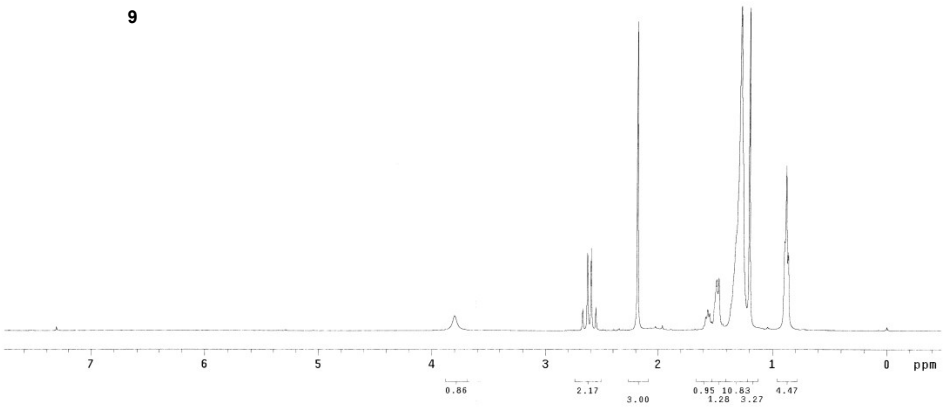

210.579
147.131
137.750
128.057
127.387
124.978
121.206
77.312
77.000
76.680
76.152
53.857
31.750
30.553
21.508
OH
O
7
220
200
180
160
140
120
100
80
60
40
20
0
ppm

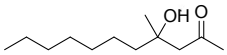

7.516
7.497
7.383
7.363
7.342
7.323
7.304
4.477
3.196
3.153
2.844
2.801
2.319
2.068
1.497
OH O
8
8 7 6 5 4 3 2 1 -0 ppm
0.85 2.88 0.96 1.00 1.02 3.06 2.80 3.20


DACHAOSHAN2
single pulse decoupled gated NOE
144.02
135.23
132.99
127.20
126.86
125.40
77.49
77.17
76.85
74.80
53.17
31.63
29.14
22.53
OH O
8
f1 (ppm)

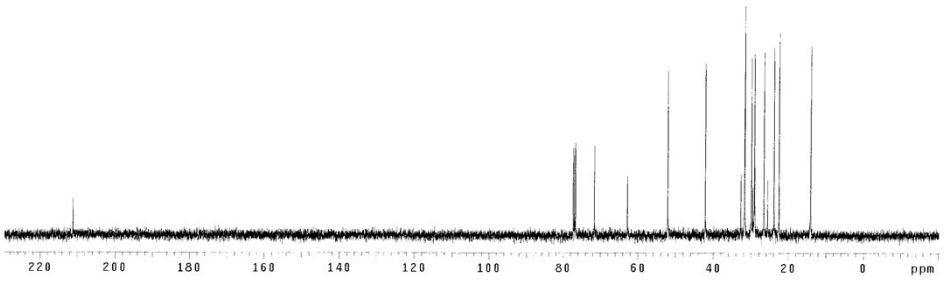


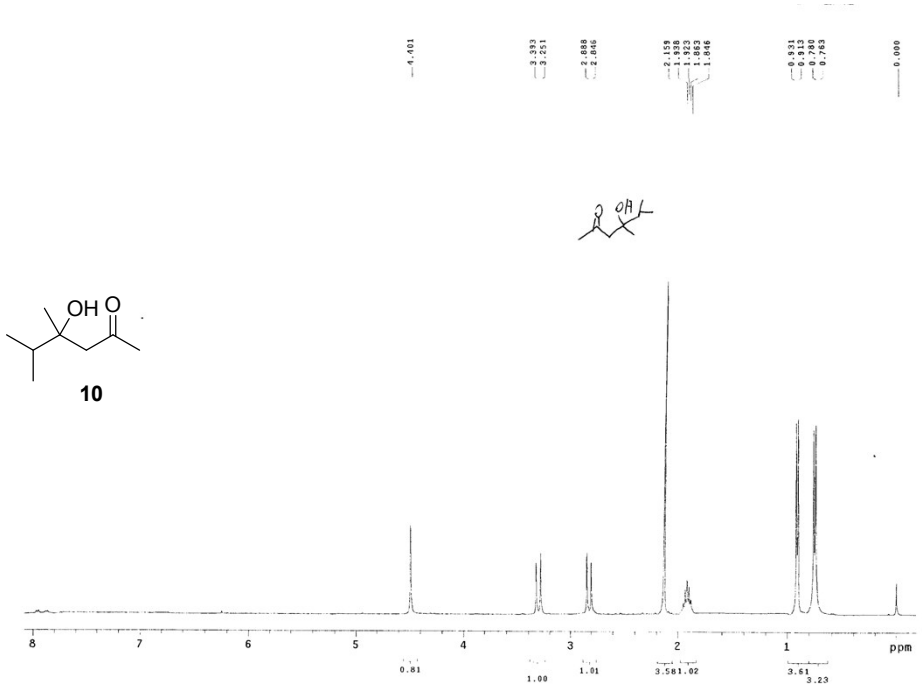
9



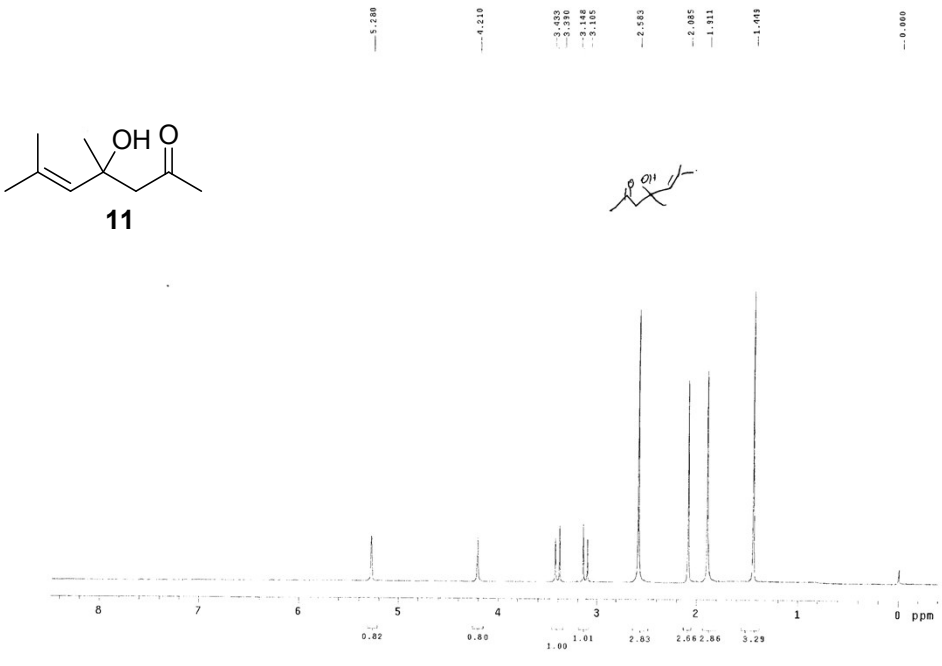


9

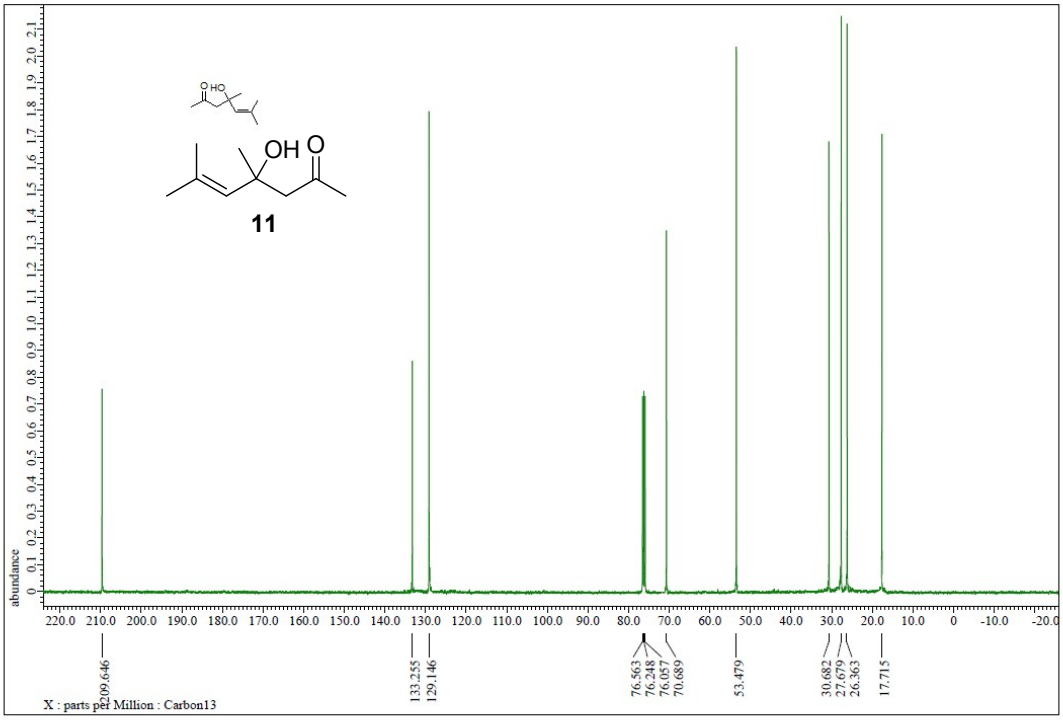


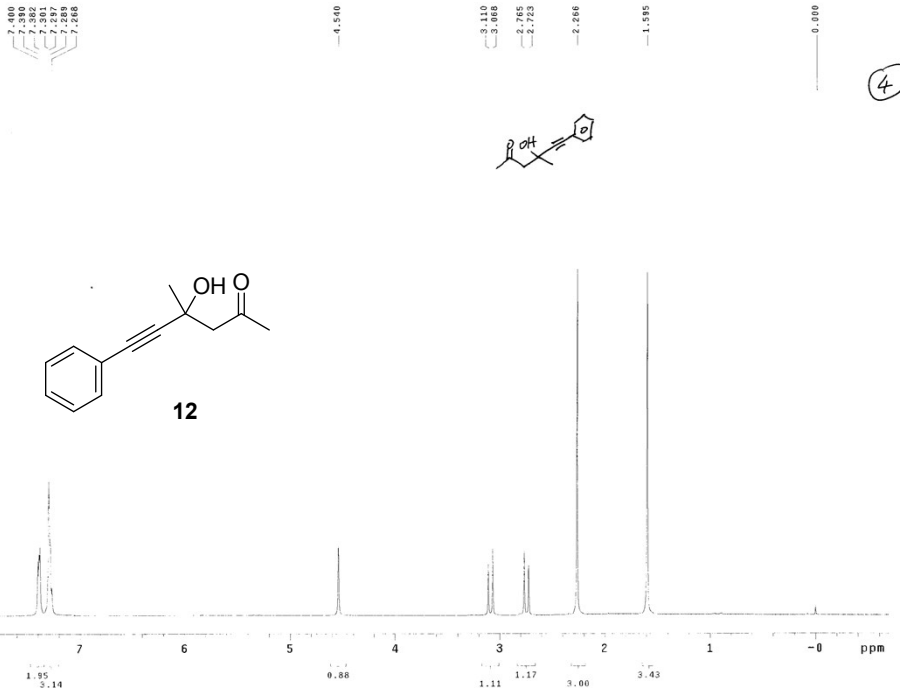

4.401
3.393
3.251
2.688
2.646
2.159
1.938
1.923
1.865
1.846
0.931
0.913
0.898
0.763
0.000
OH
O
8
7
6
5
4
3
2
1
ppm
0.81
1.00
1.01
3.58
1.02
3.61
3.23

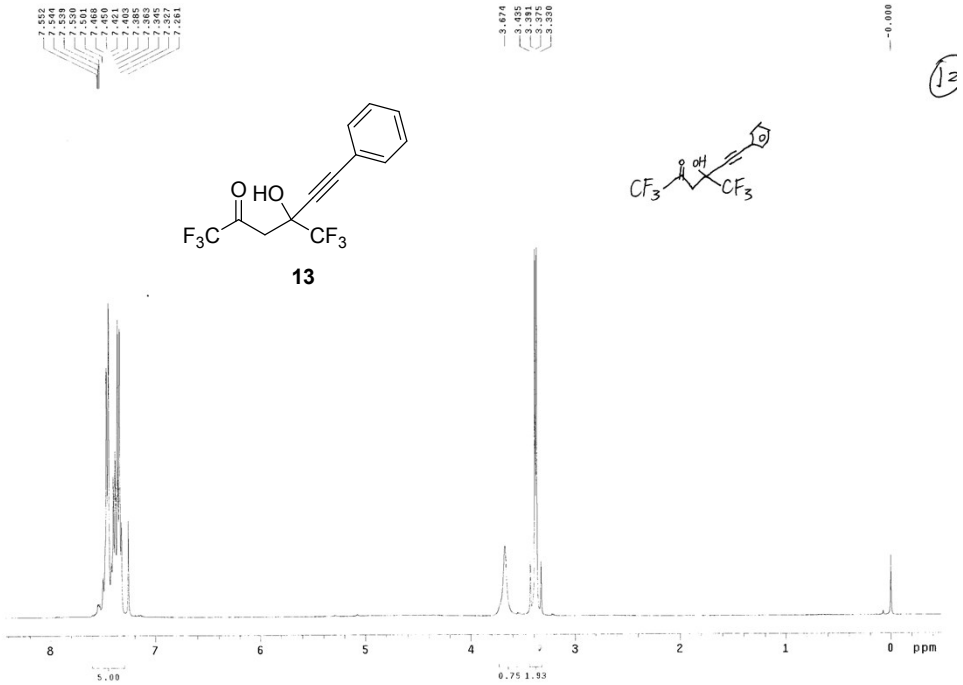
10

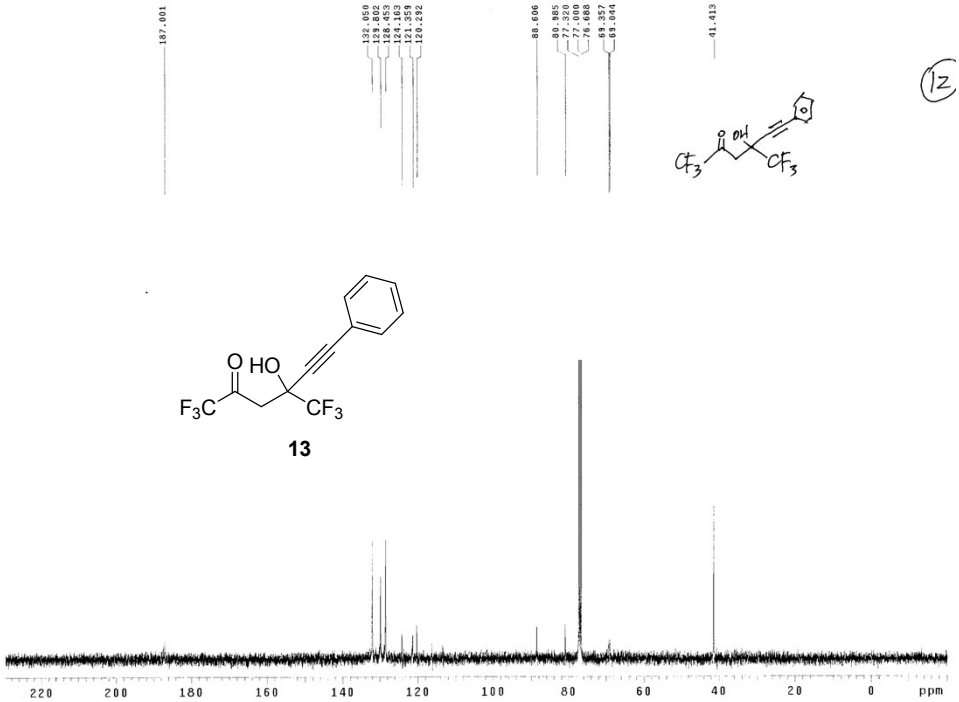

5.280
4.210
3.433
3.390
3.148
3.105
2.583
2.085
1.911
1.448
0.000
OH
O
8
7
6
5
4
3
2
1
0 ppm
0.82
0.80
1.00
1.01
2.83
2.66
2.86
3.29

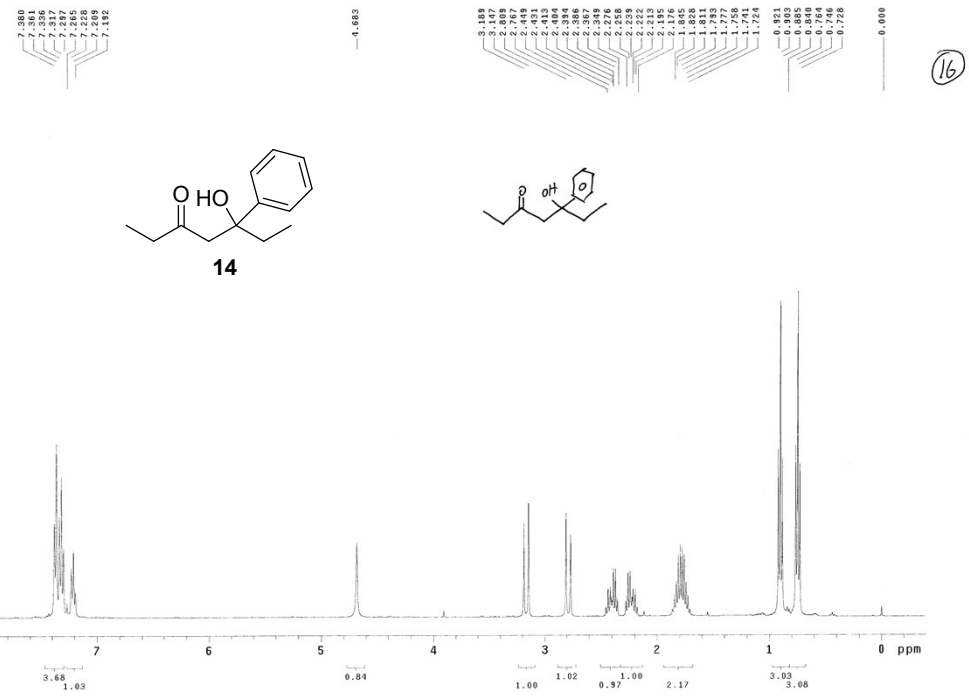
11

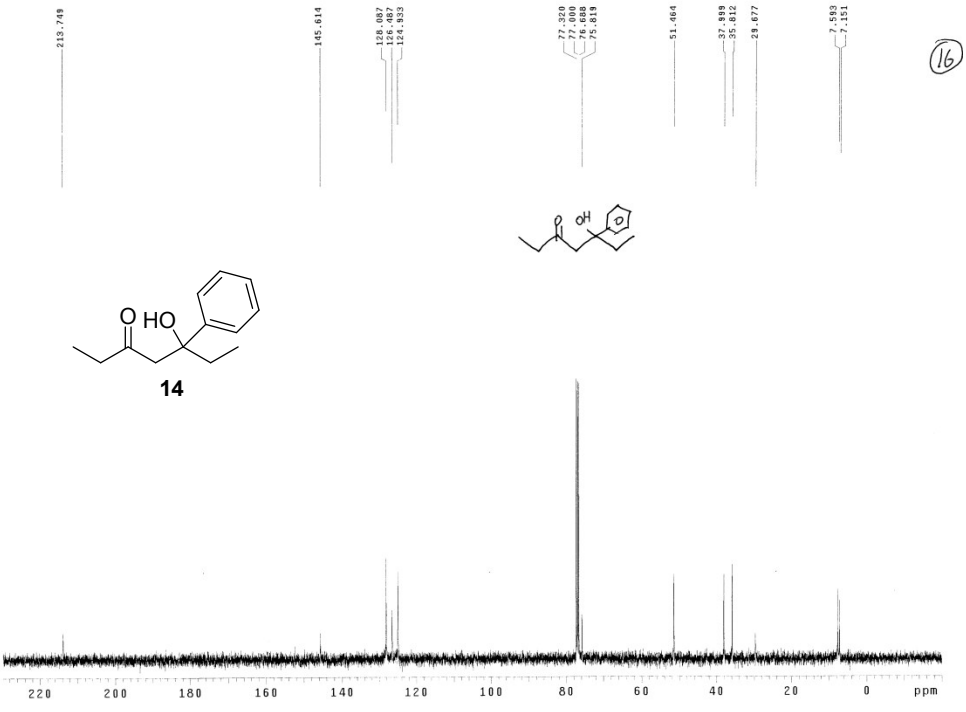

OH O
11
abundance
209.646
133.255
129.146
76.563
76.248
76.057
70.689
53.479
30.682
27.679
26.363
17.715
X : parts per Million : Carbon13

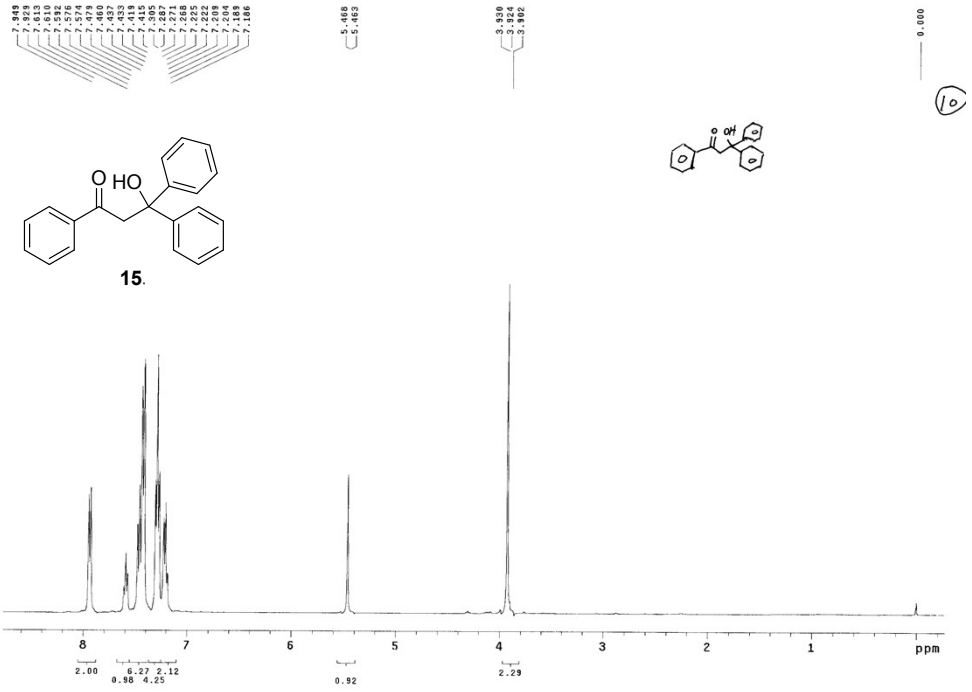

7.400
7.390
7.382
7.301
7.297
7.289
7.268
4.540
3.110
3.068
2.765
2.723
2.266
1.585
0.000
4
OH O
12
8
7
6
5
4
3
2
1
0
ppm
1.95
3.14
0.88
1.11
1.17
3.00
3.43

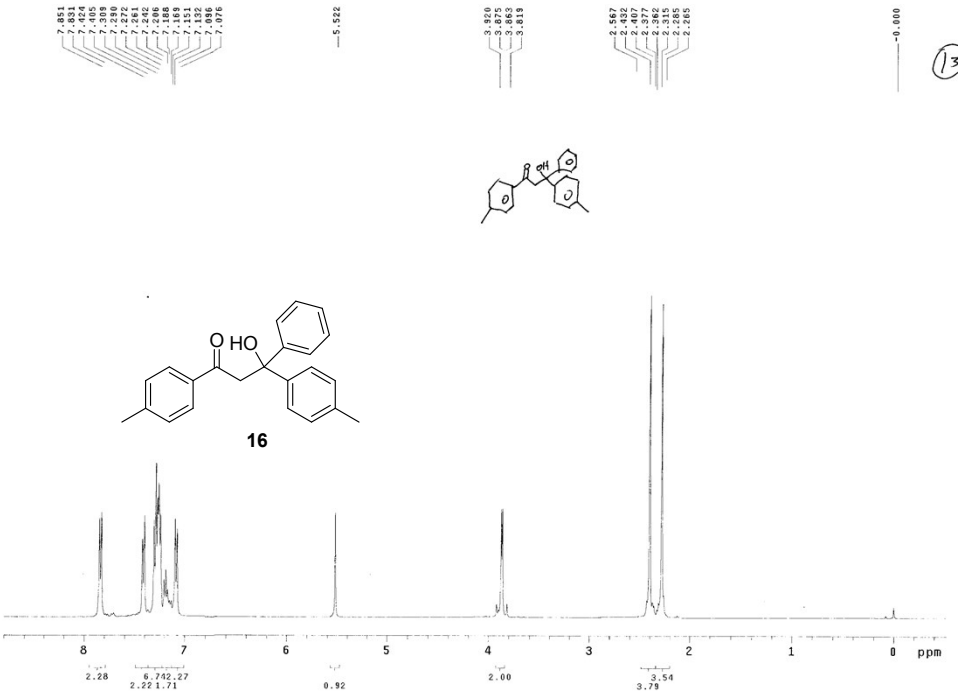

7.552
7.544
7.539
7.530
7.511
7.468
7.450
7.421
7.408
7.385
7.363
7.345
7.327
7.261
3.674
3.435
3.391
3.375
3.330
-0.000
O HO
F3C
CF3
13
CF3
OH
CF3
8
7
6
5
4
3
2
1
0 ppm
5.00
0.75 1.93

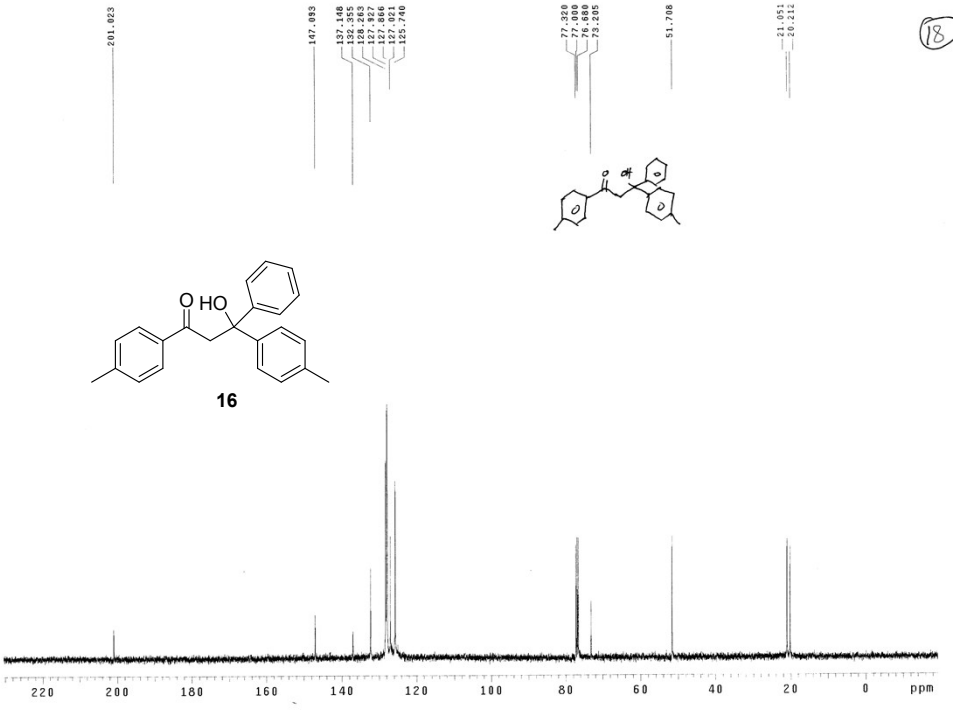

187.001
132.050
129.802
128.955
124.163
121.359
120.292
88.606
80.985
77.320
77.000
76.688
69.357
69.044
41.413
O HO
F3C
CF3
13
CF3
OH
CF3
220
200
180
160
140
120
100
80
60
40
20
0
ppm

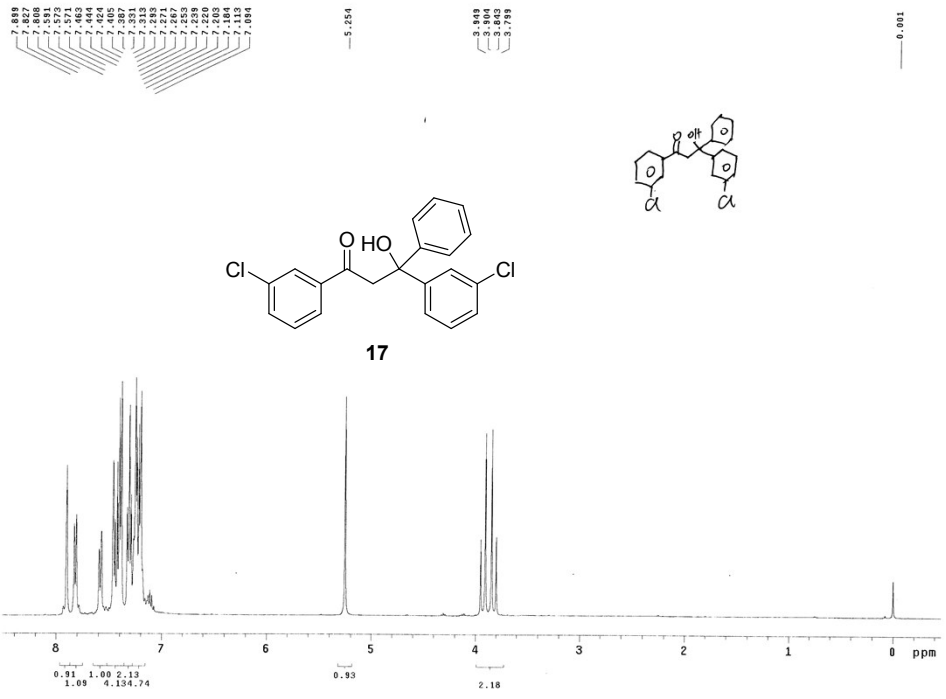

O HO
14
7 6 5 4 3 2 1 0 ppm

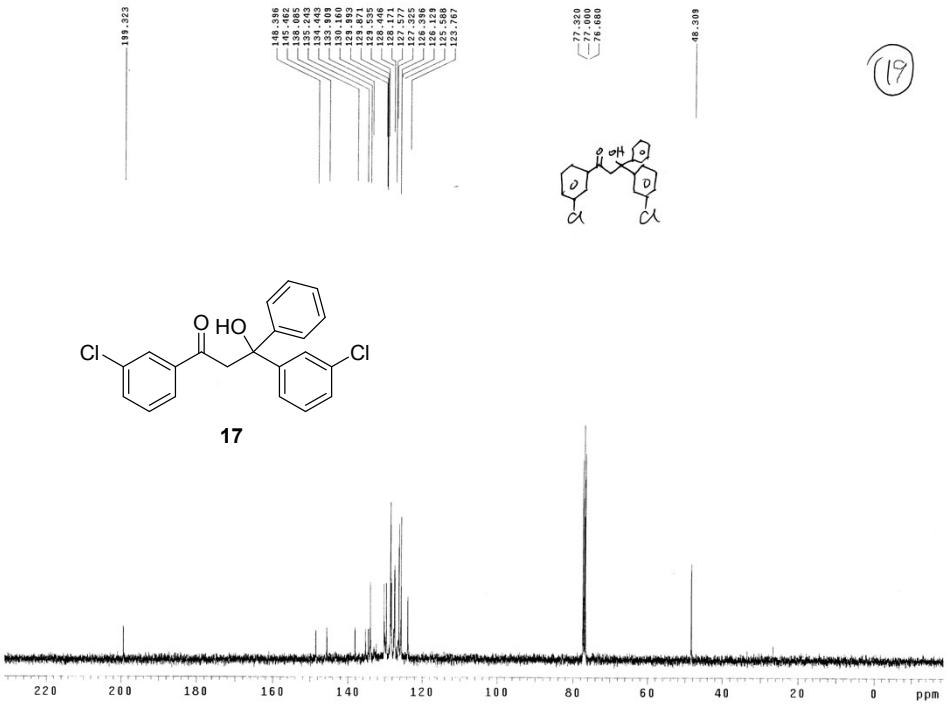

O HO
14
220 200 180 160 140 120 100 80 60 40 20 0 ppm

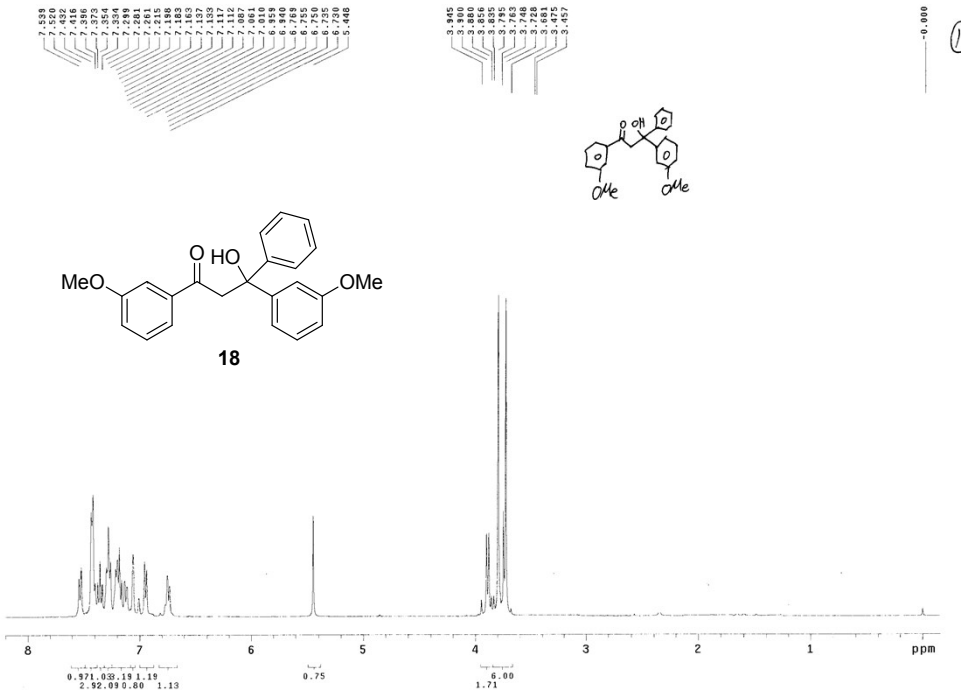

7.949
7.929
7.613
7.610
7.592
7.576
7.574
7.479
7.460
7.437
7.433
7.419
7.415
7.395
7.287
7.271
7.266
7.225
7.222
7.209
7.206
7.189
7.186
5.468
5.463
3.930
3.924
3.902
0.000
O HO
15.
2.00
6.27
0.98
4.25
2.12
0.92
2.29
8
7
6
5
4
3
2
1
ppm

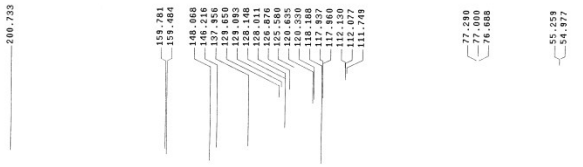

7.851
7.831
7.406
7.405
7.309
7.239
7.222
7.261
7.242
7.206
7.186
7.169
7.151
7.132
7.096
7.076
5.522
3.920
3.875
3.863
3.819
2.567
2.432
2.407
2.387
2.362
2.315
2.285
2.265
0.000
O HO
16
2.28
6.74
2.22
2.27
1.71
0.92
2.00
3.54
3.79
8
7
6
5
4
3
2
1
0
ppm

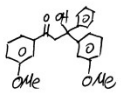

201.023
147.093
137.148
132.355
130.883
127.827
127.866
127.021
125.740
77.320
77.000
76.680
73.205
51.708
21.051
20.211
O HO
16
220
200
180
160
140
120
100
80
60
40
20
0
ppm

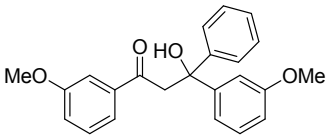

7.889
7.827
7.808
7.591
7.573
7.571
7.463
7.444
7.424
7.405
7.387
7.331
7.313
7.243
7.271
7.267
7.255
7.239
7.220
7.203
7.184
7.113
7.094
5.254
3.949
3.904
3.843
3.799
0.001
O HO
Cl
Cl
17
8
7
6
5
4
3
2
1
0
ppm
0.91
1.00
2.13
1.09
4.134.74
0.93
2.18


199.323
148.396
146.462
138.065
135.243
134.443
133.909
133.160
131.993
129.871
129.535
128.646
128.171
127.577
127.325
126.586
126.129
125.588
123.767
77.320
77.000
76.680
48.309
(19)
O HO
Cl
Cl
17
220
200
180
160
140
120
100
80
60
40
20
0
ppm

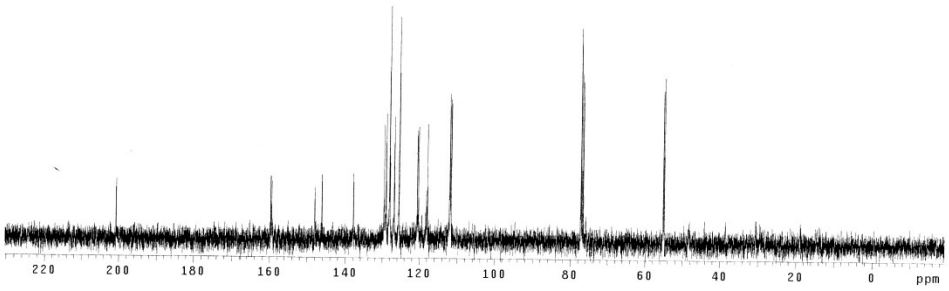

7.539
7.520
7.432
7.416
7.356
7.373
7.354
7.334
7.284
7.261
7.215
7.196
7.183
7.163
7.137
7.135
7.117
7.112
7.087
7.081
7.010
6.959
6.940
6.769
6.755
6.750
6.735
6.730
5.448
3.845
3.390
3.880
3.856
3.855
3.795
3.763
3.748
3.738
3.481
3.475
3.457
-0.000
(1)
O HO
MeO
OMe
18
8
7
6
5
4
3
2
1
ppm
0.97 1.03 2.19 1.19
2.92 2.09 0.80 1.13
0.75
6.00
1.71

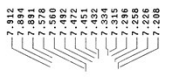


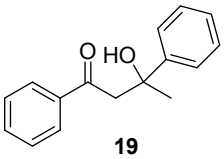




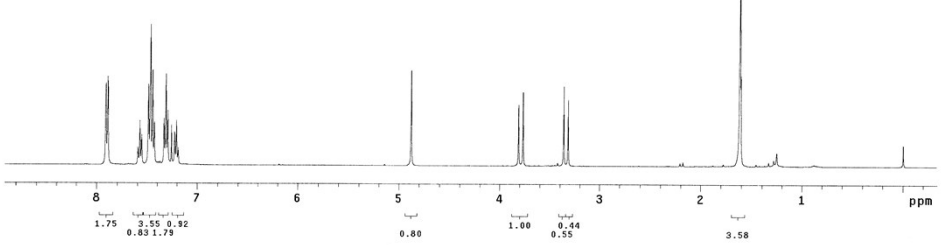
18





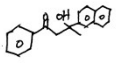


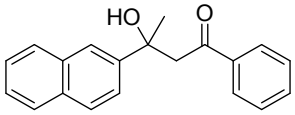
19



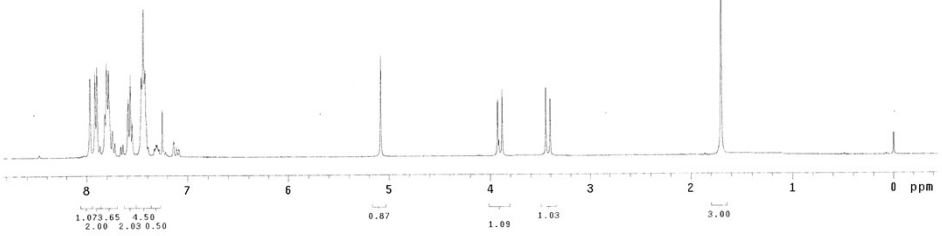

7.968
7.913
7.901
7.820
7.806
7.795
7.746
7.596
7.592
7.571
7.551
7.463
7.455
7.442
7.432
7.428
7.424
7.251
5.084
3.926
3.882
3.450
3.407
1.704
-0.000

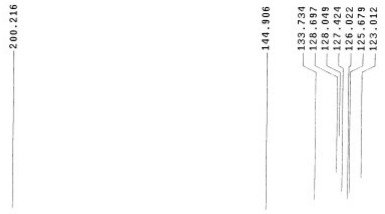
10



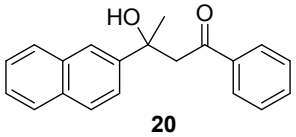

HO
O

20

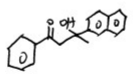

8
7
6
5
4
3
2
1
0 ppm
1.073.65 4.50
2.00 2.03 0.50
0.87
1.09
1.03
3.00

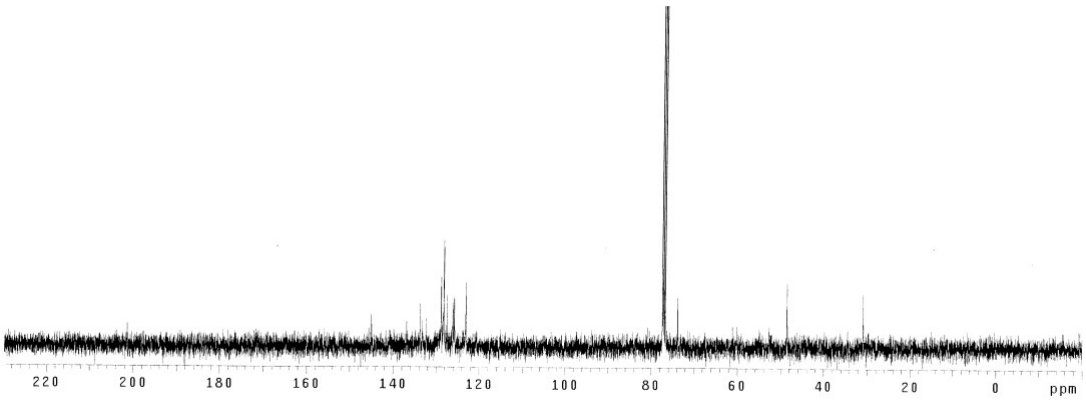

200.216
144.906
133.734
128.697
128.049
127.424
126.022
125.679
123.012
77.320
77.000
76.680
73.701
48.581
30.896

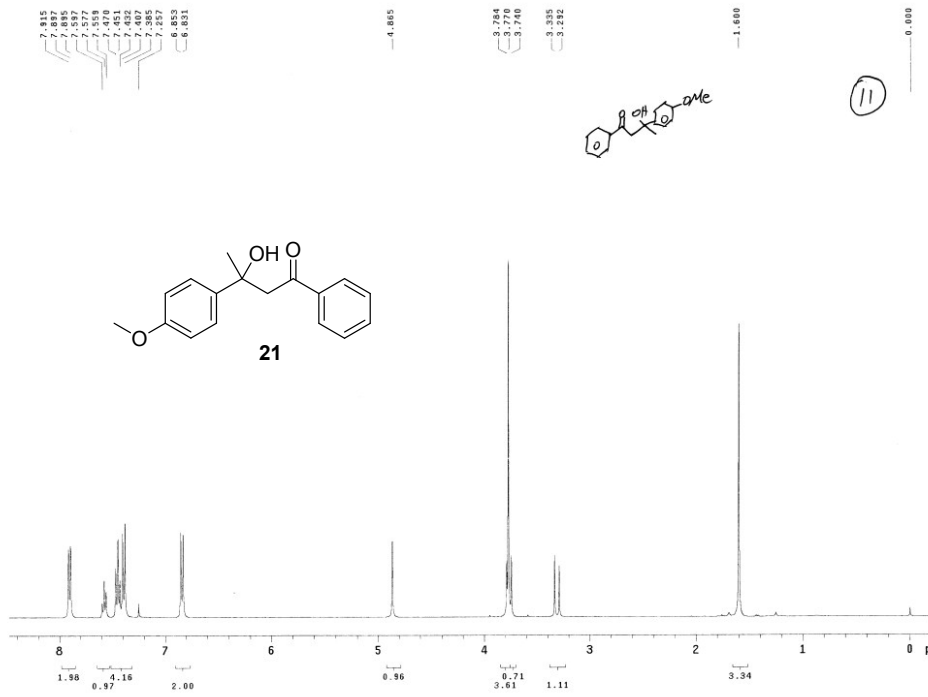
10


HO
O

20




220
200
180
160
140
120
100
80
60
40
20
0
ppm


7.915
7.897
7.895
7.597
7.577
7.559
7.470
7.451
7.428
7.407
7.385
7.257
6.853
6.831
4.865
3.784
3.770
3.740
3.335
3.252
1.600
0.000
OH
O
O
21
8
7
6
5
4
3
2
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1.98
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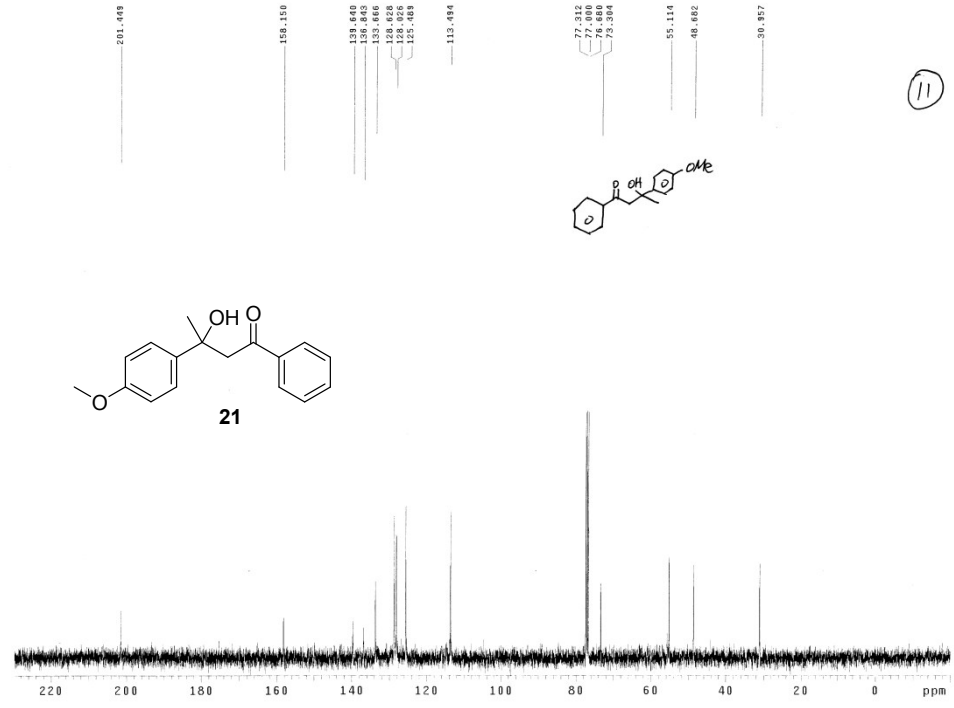
2.00
0.96
0.71
3.61
1.11
3.34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139.640
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133.666
128.628
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125.489
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77.000
76.680
73.304
55.114
48.682
30.957
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O
O
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200
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160
140
120
100
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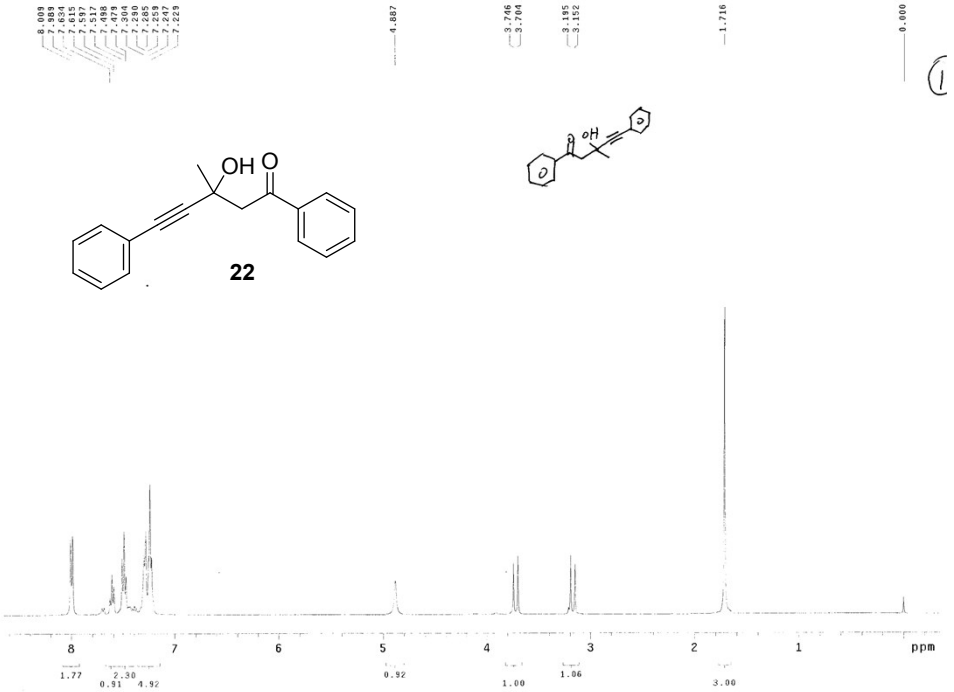
60
40
20
0
ppm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7.984
7.834
7.615
7.597
7.512
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7.479
7.304
7.280
7.265
7.259
7.207
7.225
4.887
3.746
3.704
3.195
3.152
1.716
0.000
OH
O
22
8
7
6
5
4
3
2
1
ppm
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4.92
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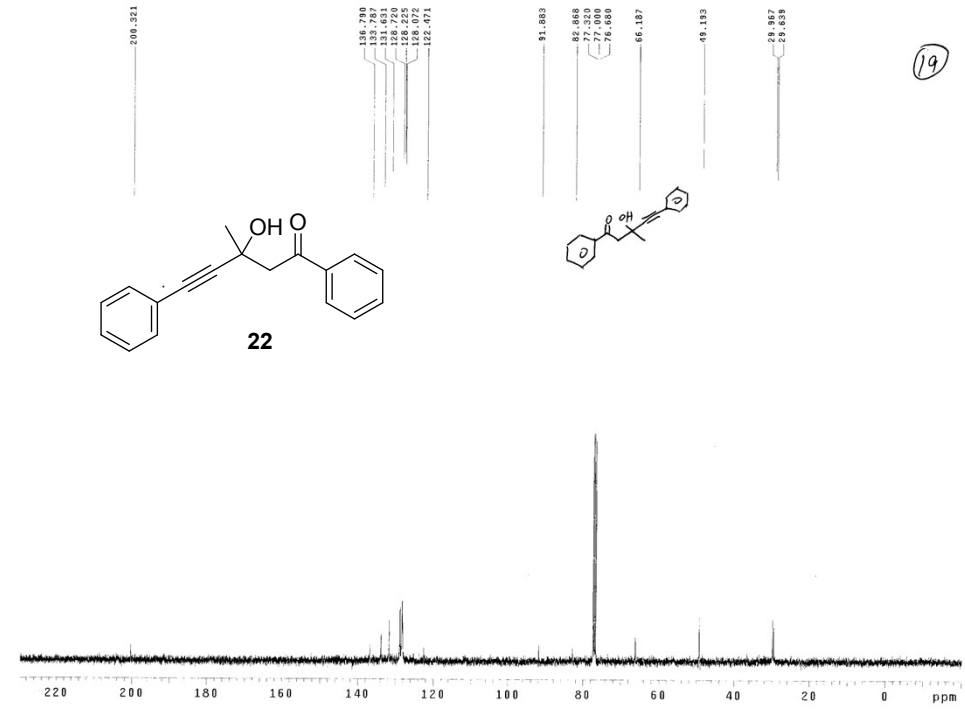
1.00
1.06
3.00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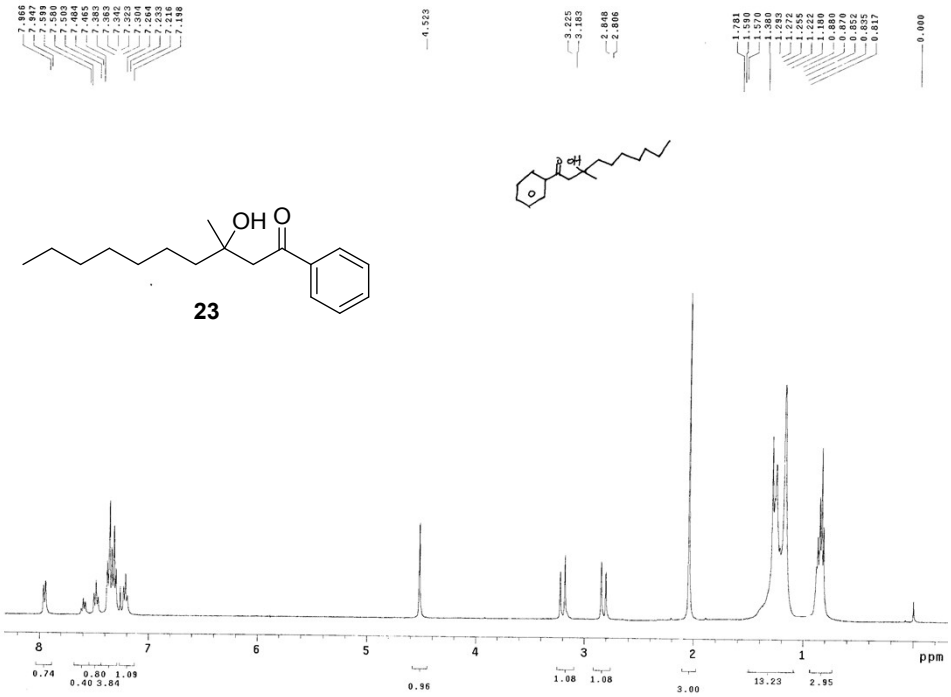
136.790
132.737
131.631
128.720
128.225
127.072
122.471
91.883
82.868
77.320
77.000
76.680
66.187
49.193
29.967
29.639
OH
O
22
220
200
180
160
140
120
100
80
60
40
20
0
ppm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7.947
7.580
7.503
7.484
7.465
7.383
7.363
7.342
7.322
7.304
7.264
7.233
7.213
7.198
4.523
3.225
3.183
2.848
2.806
1.701
1.590
1.570
1.380
1.293
1.272
1.255
1.222
1.180
0.880
0.859
0.852
0.835
0.817
0.000
OH
O
23
8
7
6
5
4
3
2
1
ppm
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0.40
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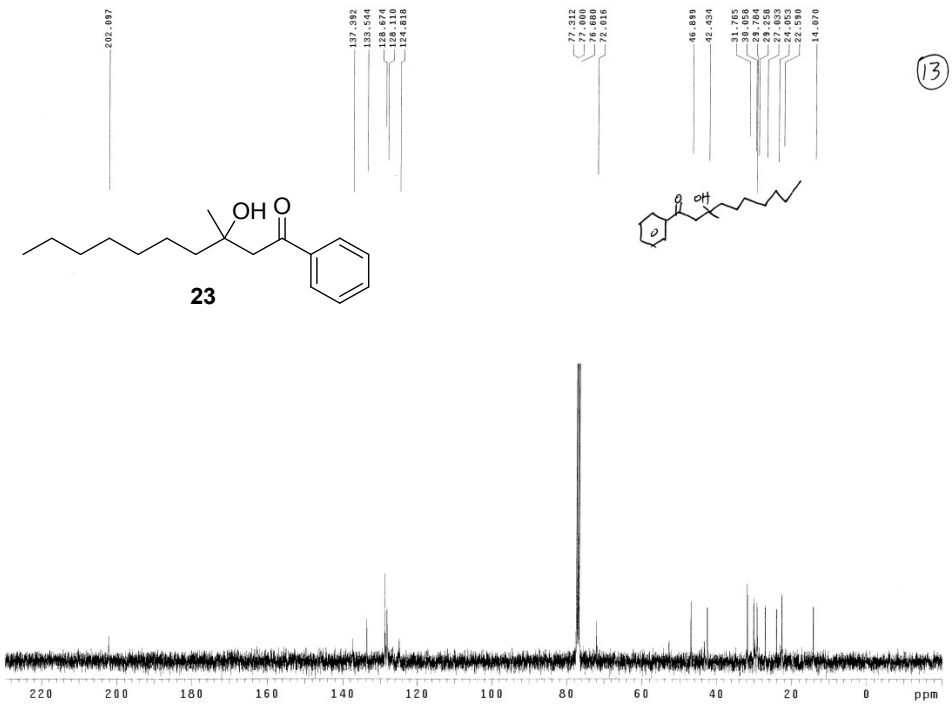
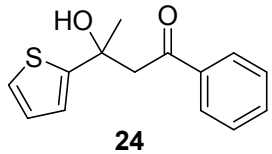
0.96
1.08
1.08
3.00
13.23
2.95

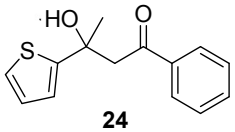

202.097
137.392
133.544
128.674
128.110
124.818
77.312
77.000
76.680
72.016
46.899
42.434
31.765
31.068
29.764
29.258
27.033
24.053
22.590
14.070
OH
O
23
220
200
180
160
140
120
100
80
60
40
20
0
ppm

21



24

21



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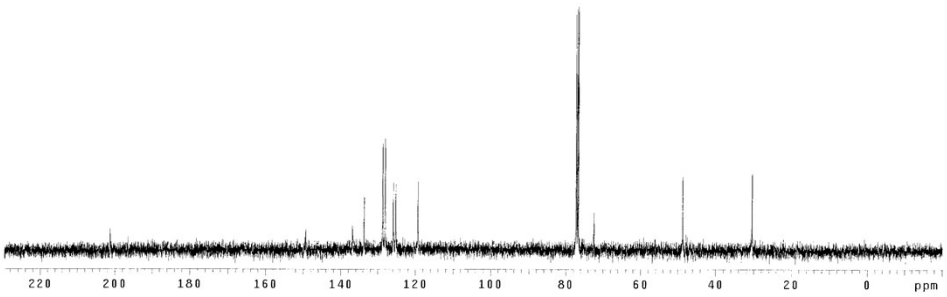
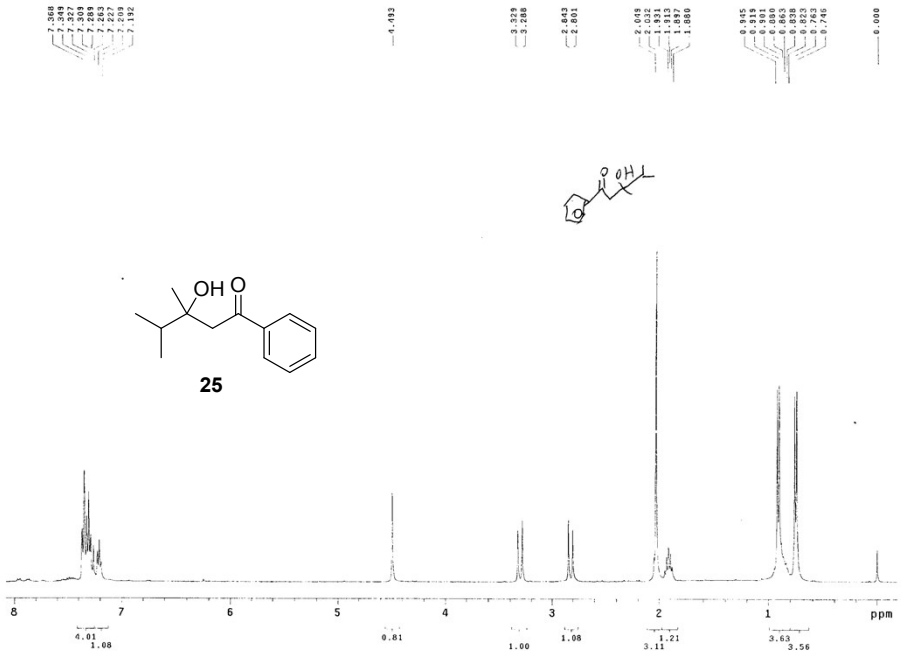
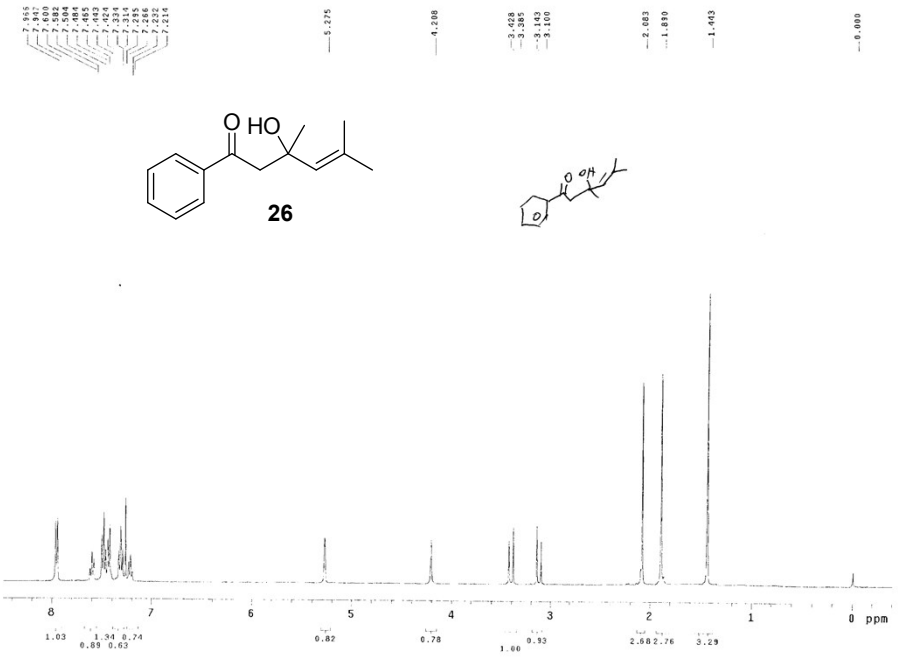
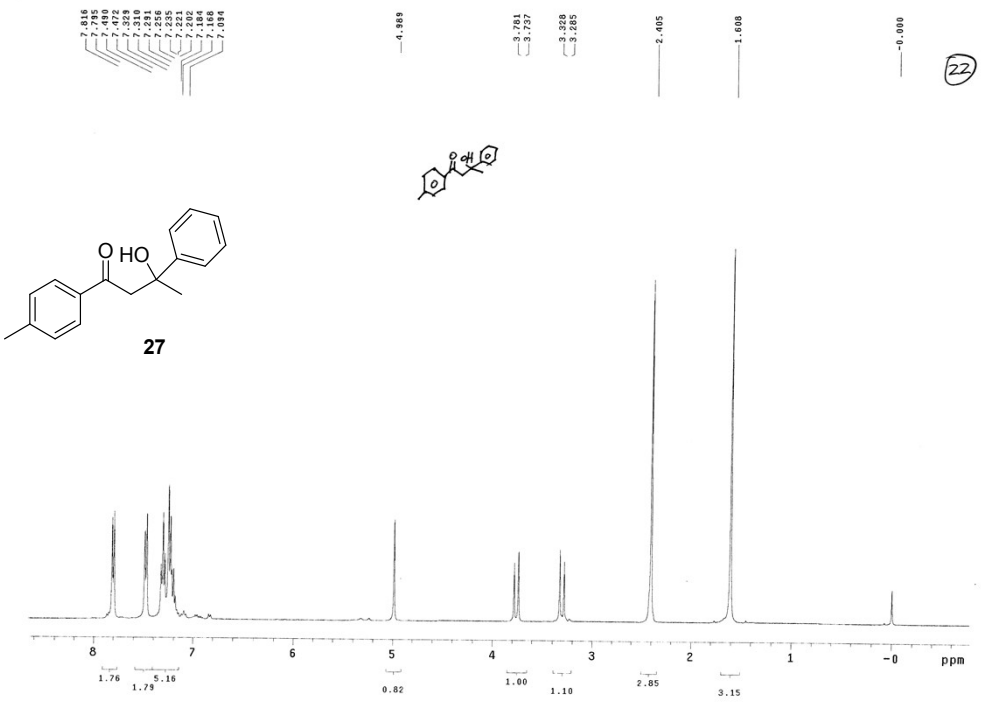
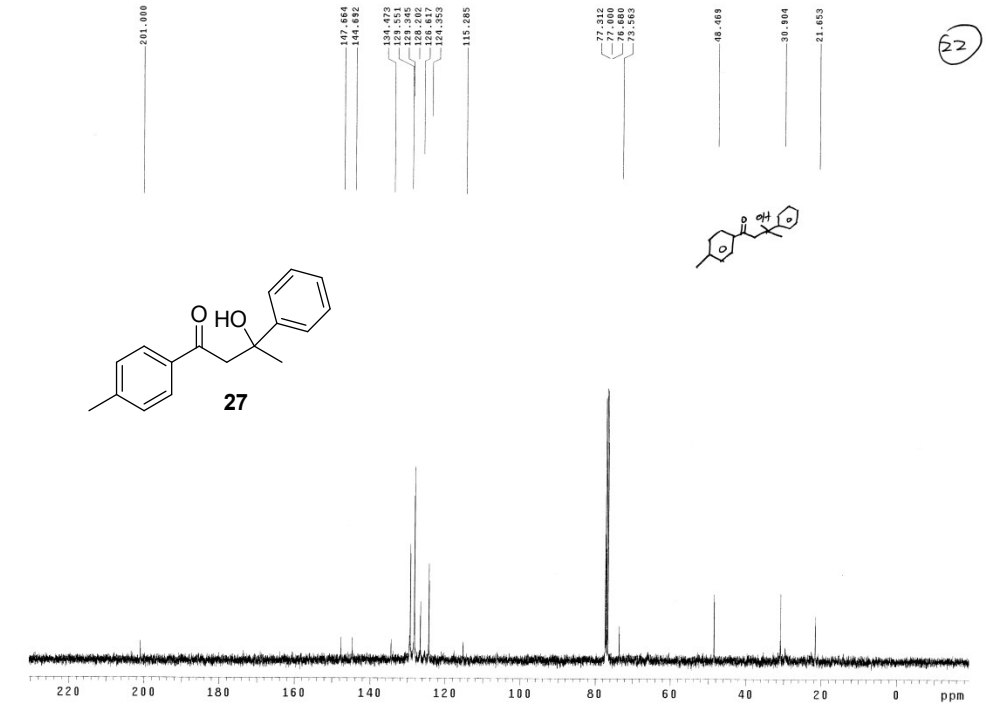



OH O
25
ppm


O HO
26
ppm


7.816
7.795
7.490
7.472
7.329
7.310
7.281
7.256
7.235
7.223
7.202
7.184
7.166
7.084
4.989
3.781
3.757
3.328
3.285
2.405
1.608
0.000
22
O HO
27
8
7
6
5
4
3
2
1
0
ppm
1.76
5.16
1.79
0.82
1.00
1.10
2.85
3.15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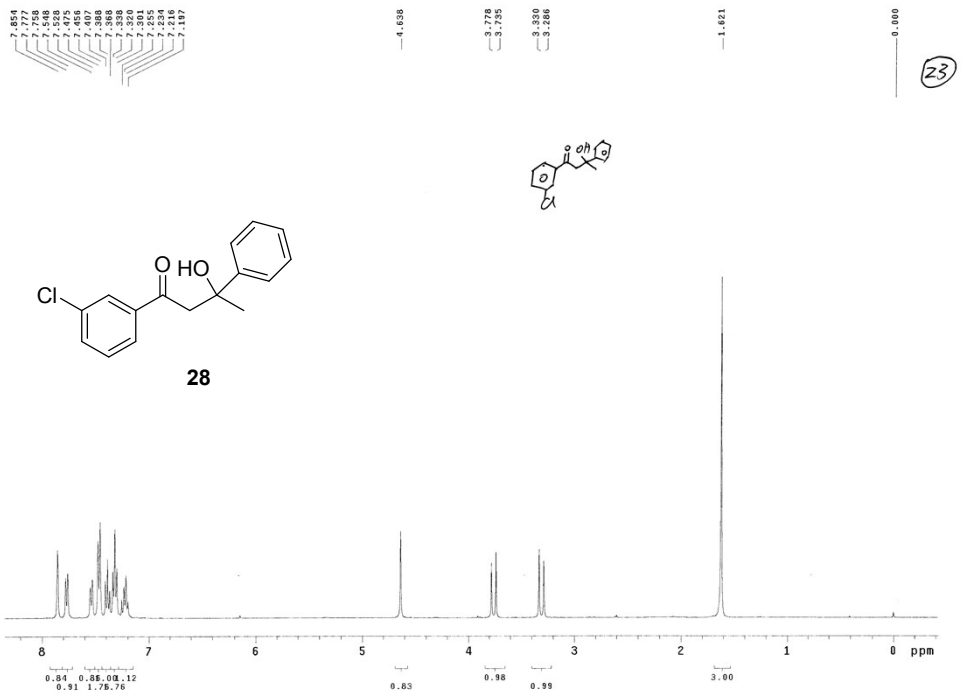
147.664
144.692
134.473
129.551
128.345
128.202
126.617
124.353
115.285
77.312
77.000
76.680
73.563
48.469
30.904
21.653
22
O HO
27
220
200
180
160
140
120
100
80
60
40
20
0
ppm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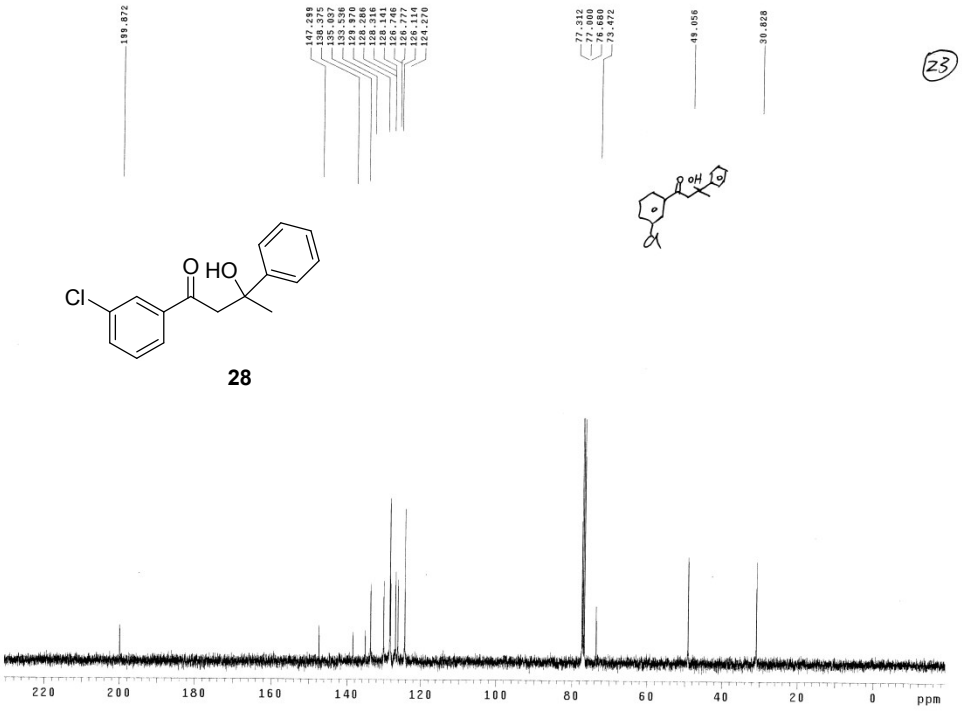
7.777
7.758
7.548
7.526
7.475
7.456
7.407
7.388
7.368
7.338
7.320
7.301
7.255
7.234
7.216
7.197
4.638
3.778
3.735
3.330
3.286
1.621
0.000
Z3
O HO
Cl
28
8
7
6
5
4
3
2
1
0 ppm
0.84
0.91
1.75
5.76
1.12
0.83
0.98
0.99
3.00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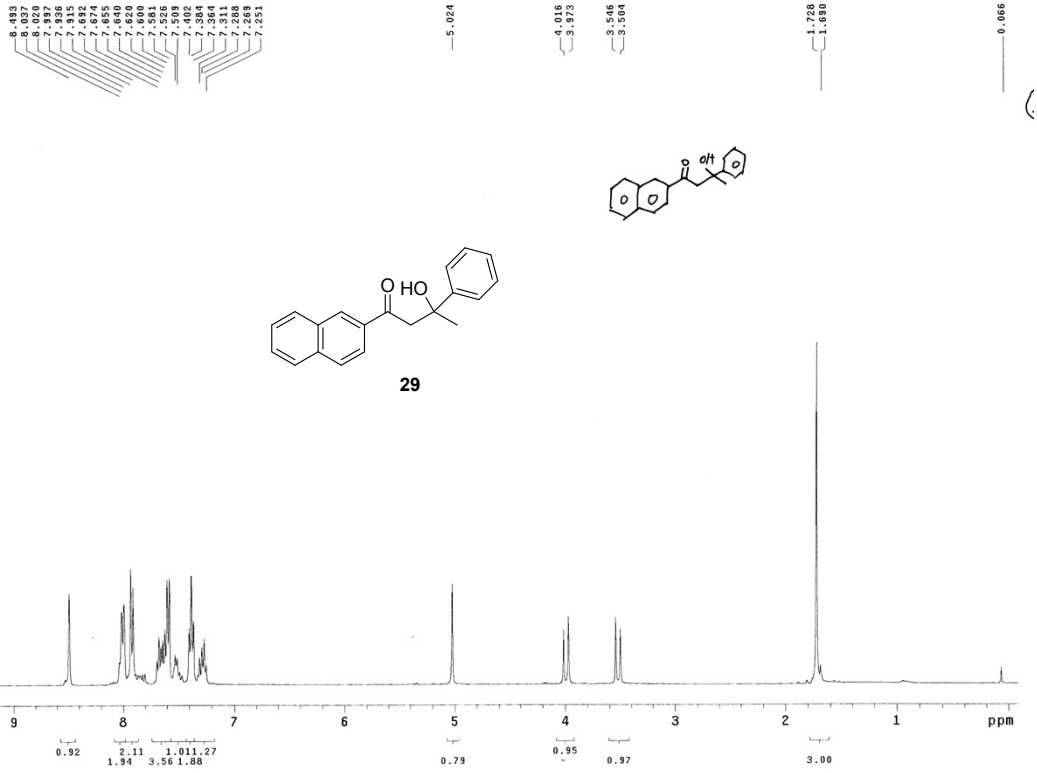
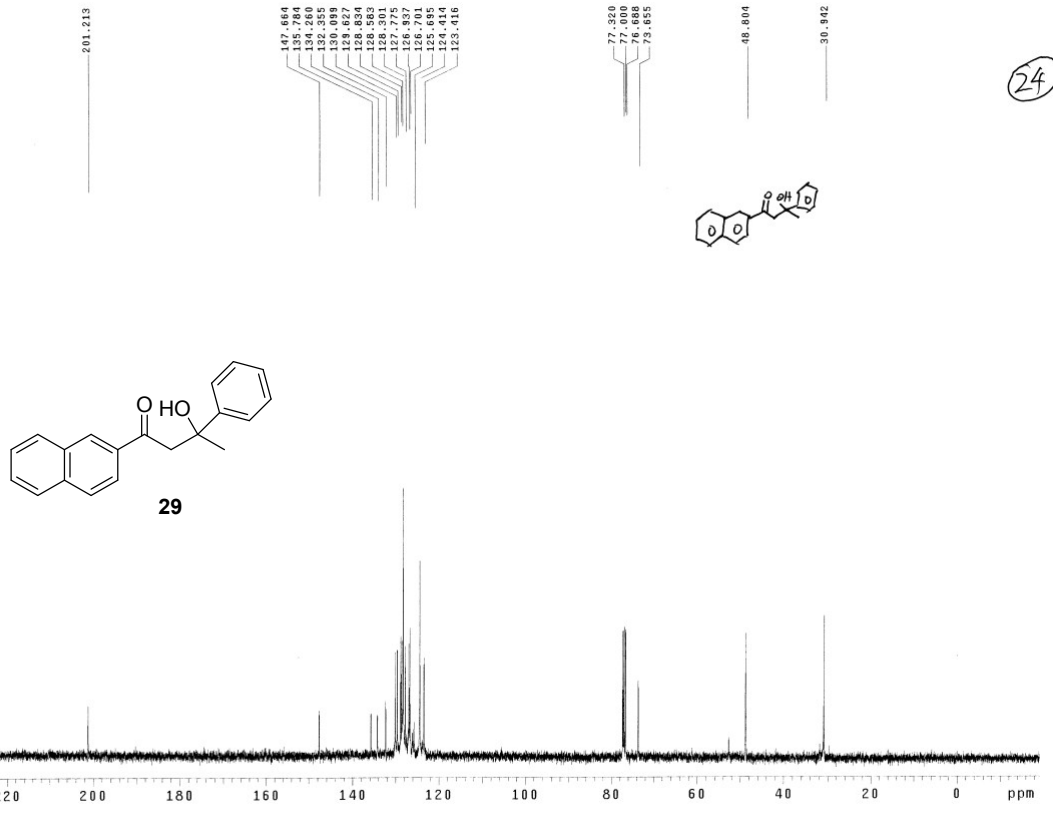
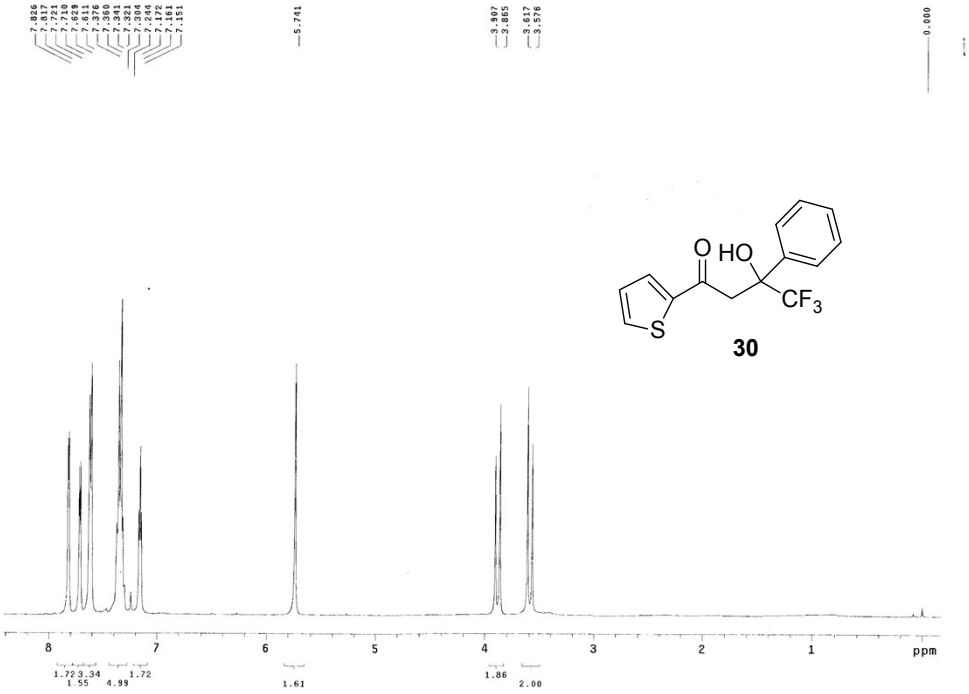
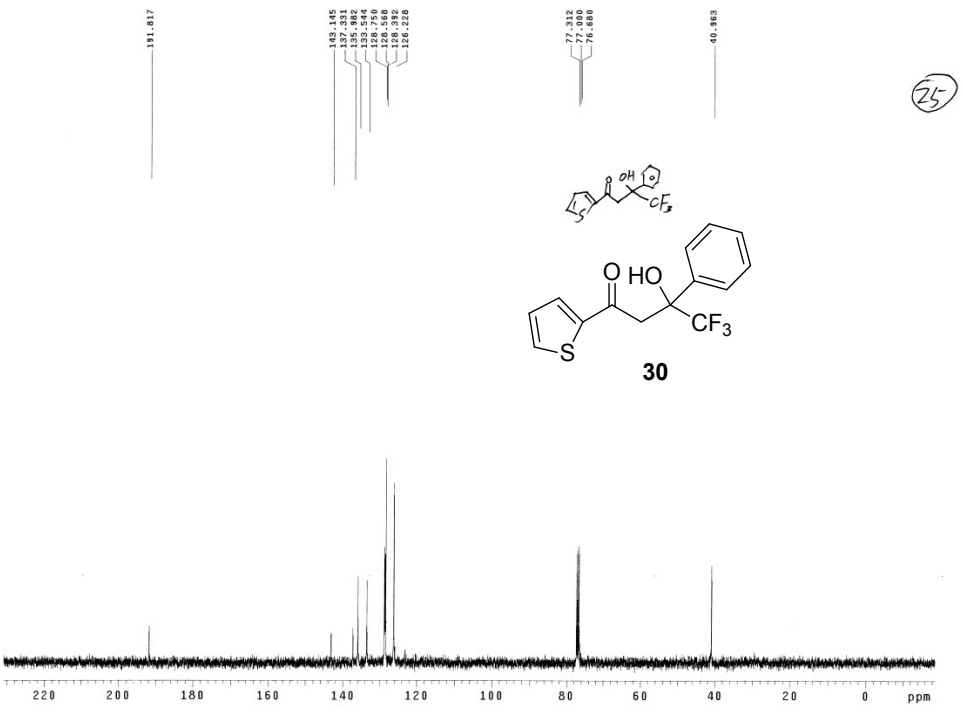
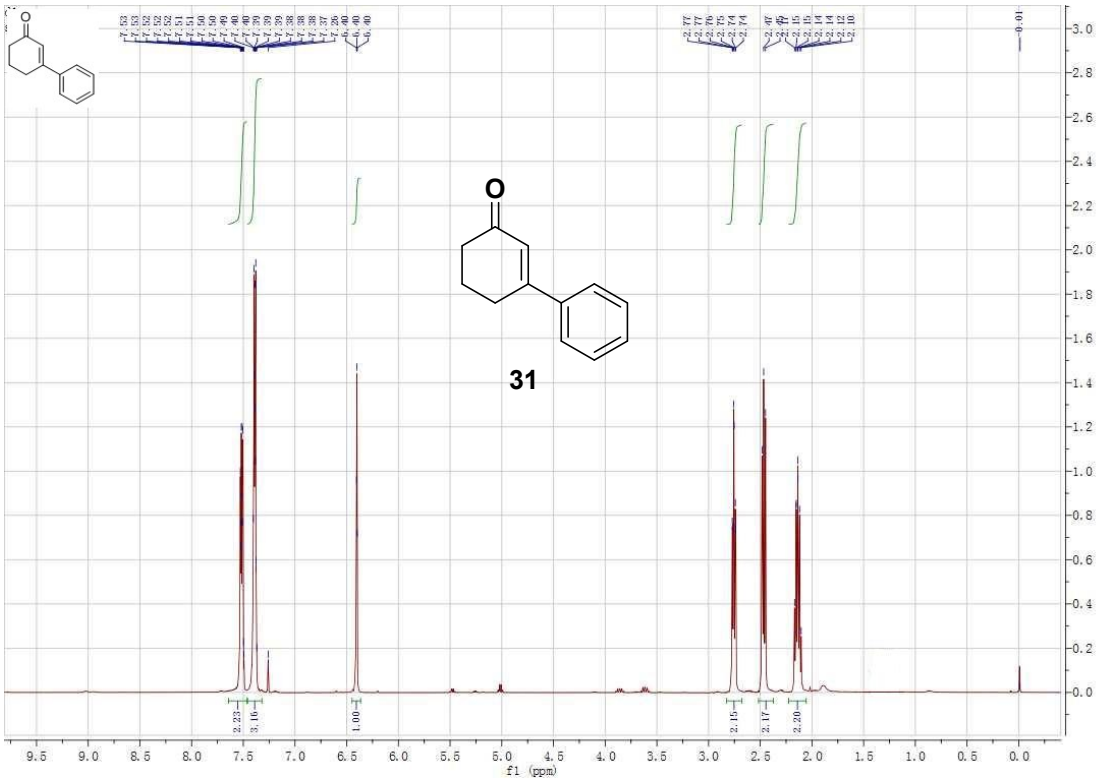
138.375
135.037
133.536
129.370
128.280
128.316
128.141
126.946
126.777
126.114
124.270
77.312
77.000
76.688
73.472
49.056
30.828
Z3
O HO
Cl
28
220
200
180
160
140
120
100
80
60
40
20
0 ppm

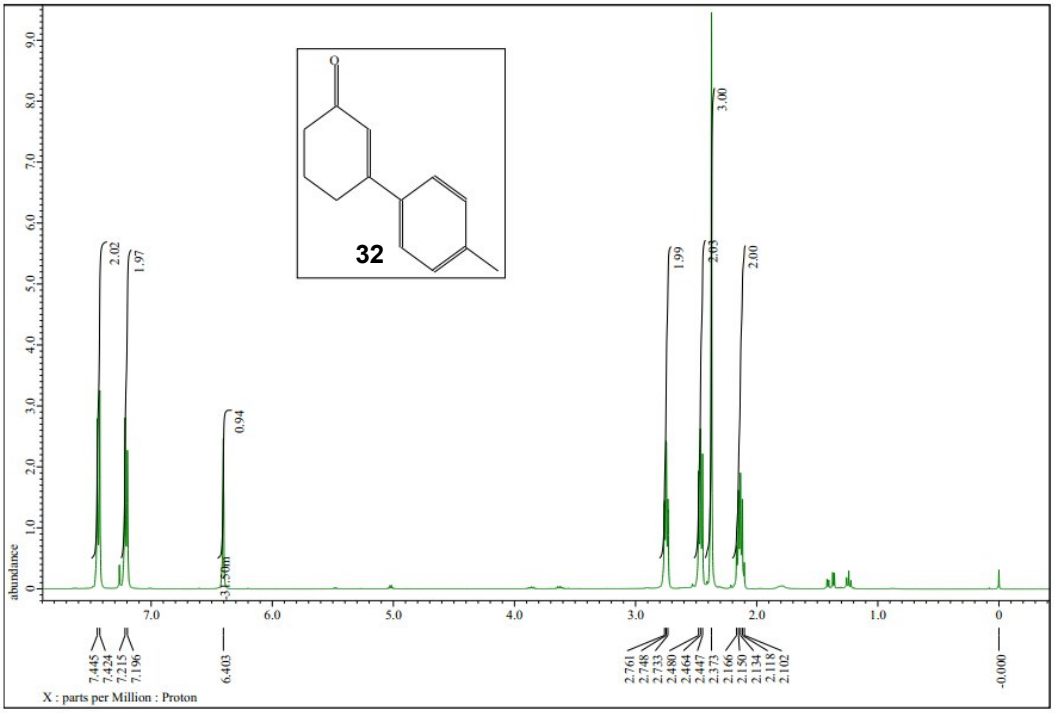

8.483
8.037
8.020
7.997
7.938
7.915
7.898
7.674
7.655
7.640
7.620
7.600
7.581
7.526
7.509
7.402
7.384
7.364
7.311
7.288
7.269
7.251
5.024
4.016
3.973
3.546
3.504
1.728
1.690
0.066
O HO
29
9
8
7
6
5
4
3
2
1
ppm
0.92
2.11
1.94
3.56
1.011.27
1.88
0.79
0.95
0.97
3.00

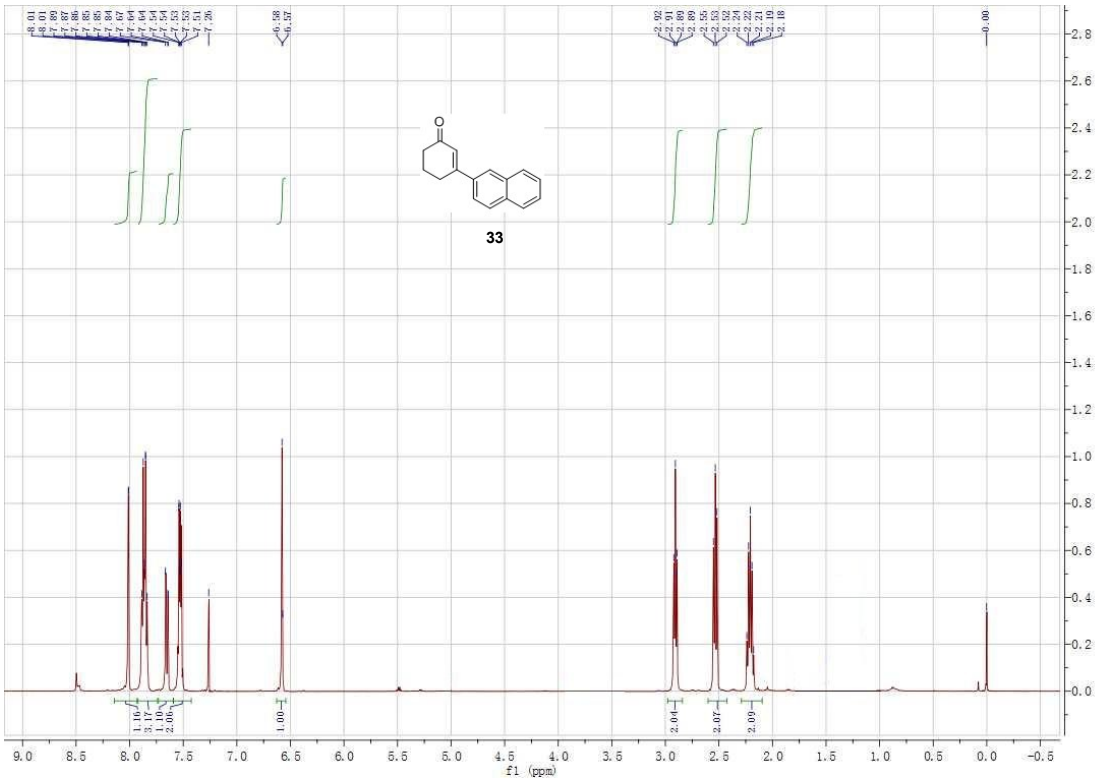

201.213
147.664
135.784
134.240
132.355
130.099
129.627
128.834
128.583
128.301
127.775
126.937
126.701
125.695
124.414
123.416
77.320
77.000
76.688
73.655
48.804
30.942
O HO
29
220
200
180
160
140
120
100
80
60
40
20
0
ppm


7.826
7.817
7.721
7.710
7.629
7.621
7.528
7.360
7.341
7.321
7.304
7.244
7.172
7.161
7.151
5.741
3.907
3.865
3.617
3.576
0.000
O HO
CF3
S
30
8
7
6
5
4
3
2
1
ppm
1.72 3.34
1.55
4.99
1.72
1.61
1.86
2.00

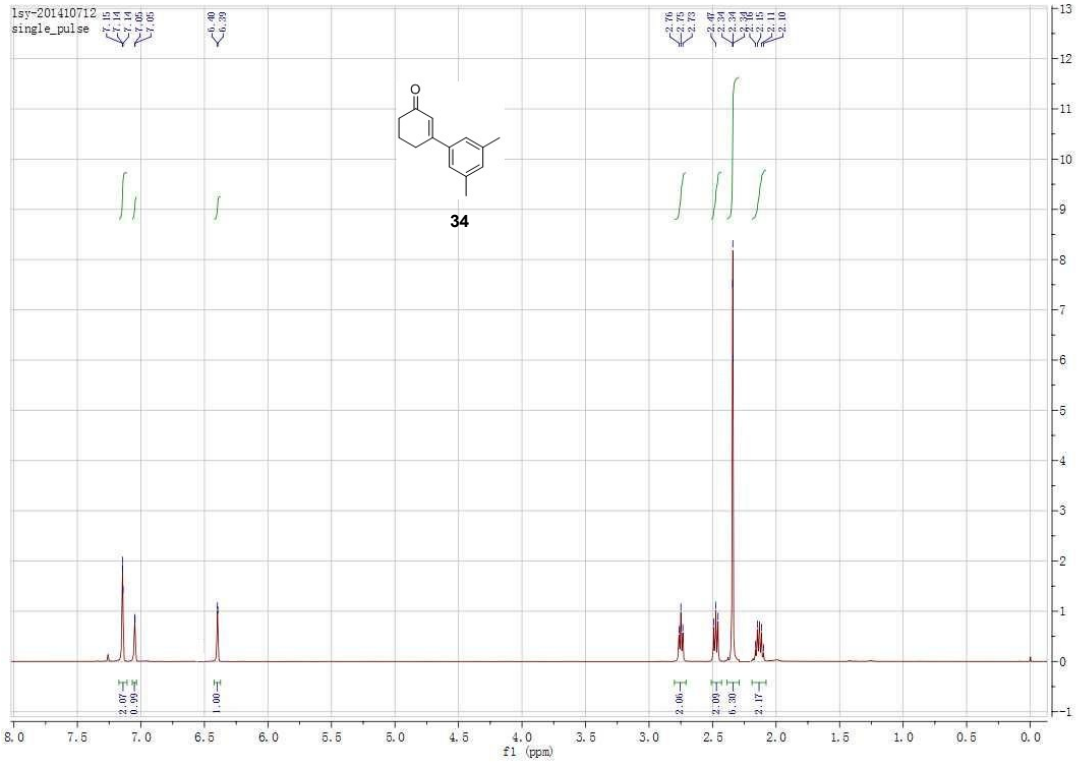

191.817
143.145
137.331
135.982
133.554
128.750
128.568
128.392
126.228
77.312
77.000
76.680
40.963
25
O HO
CF3
S
30
220
200
180
160
140
120
100
80
60
40
20
0
ppm


O
31
f1 (ppm)

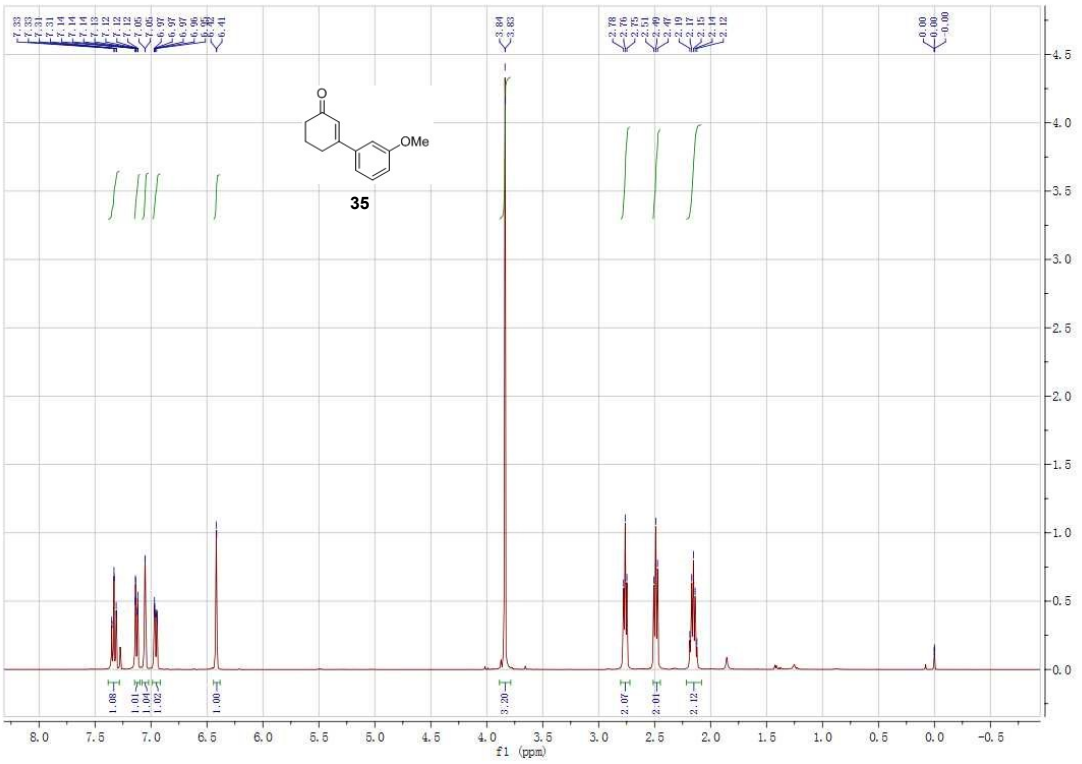

O
32
abundance
X : parts per Million : Proton

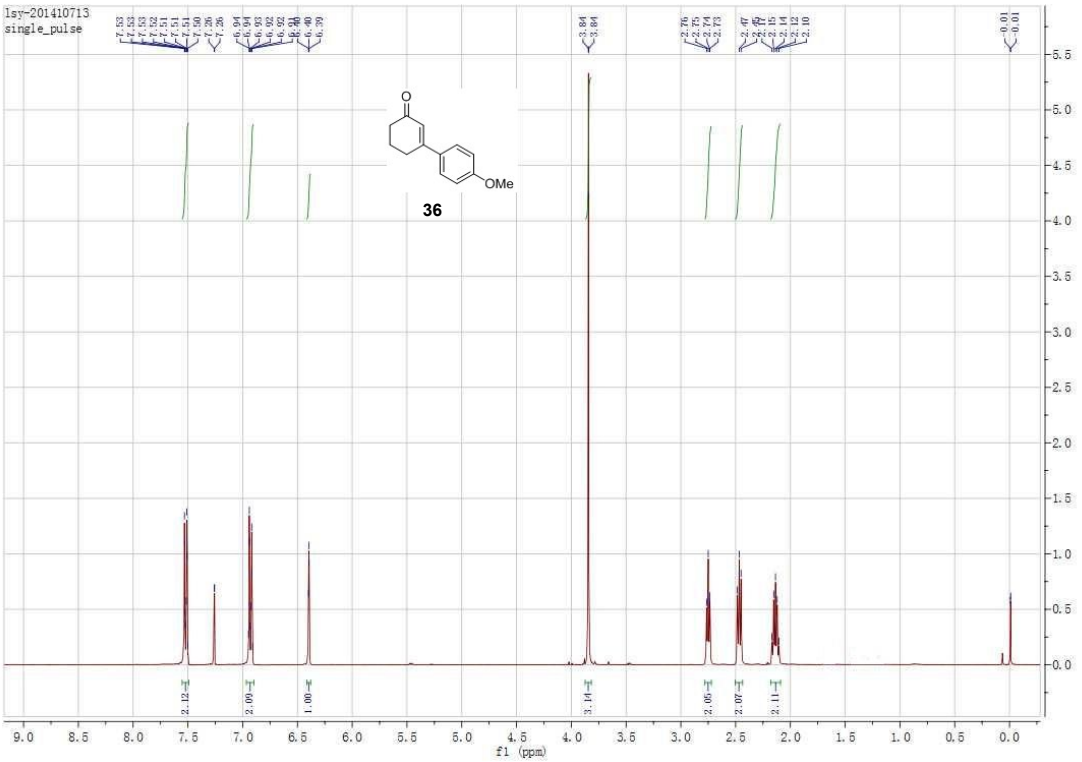


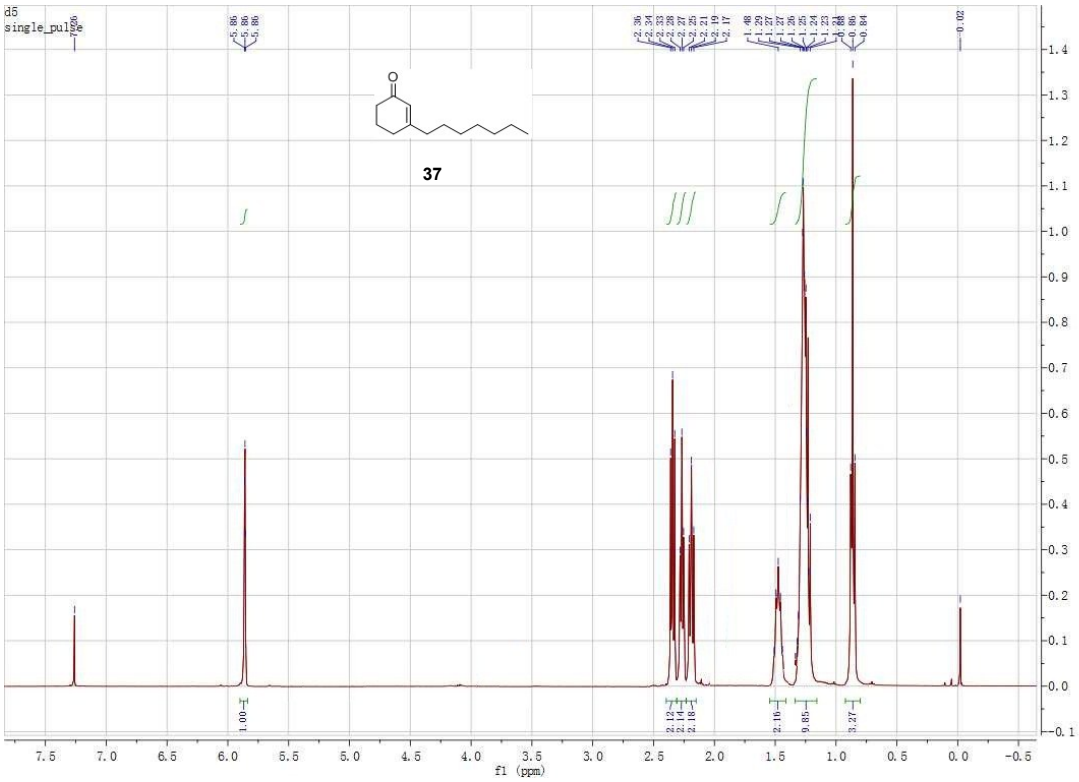
33

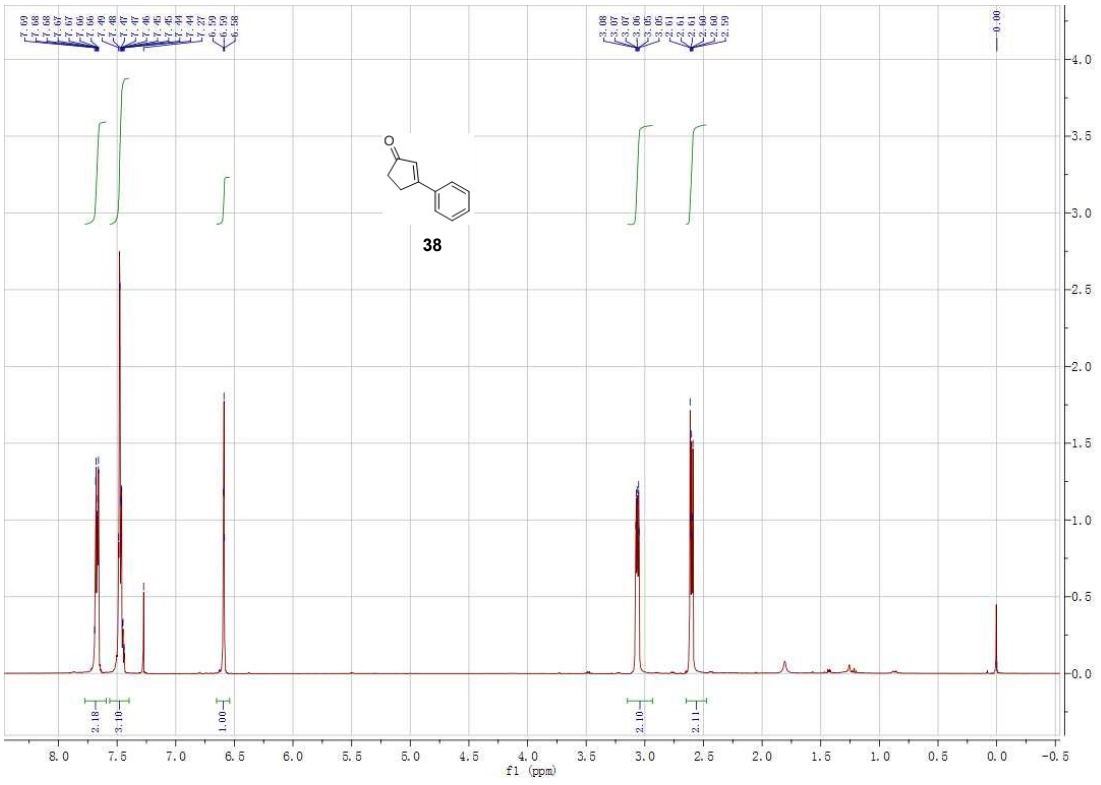


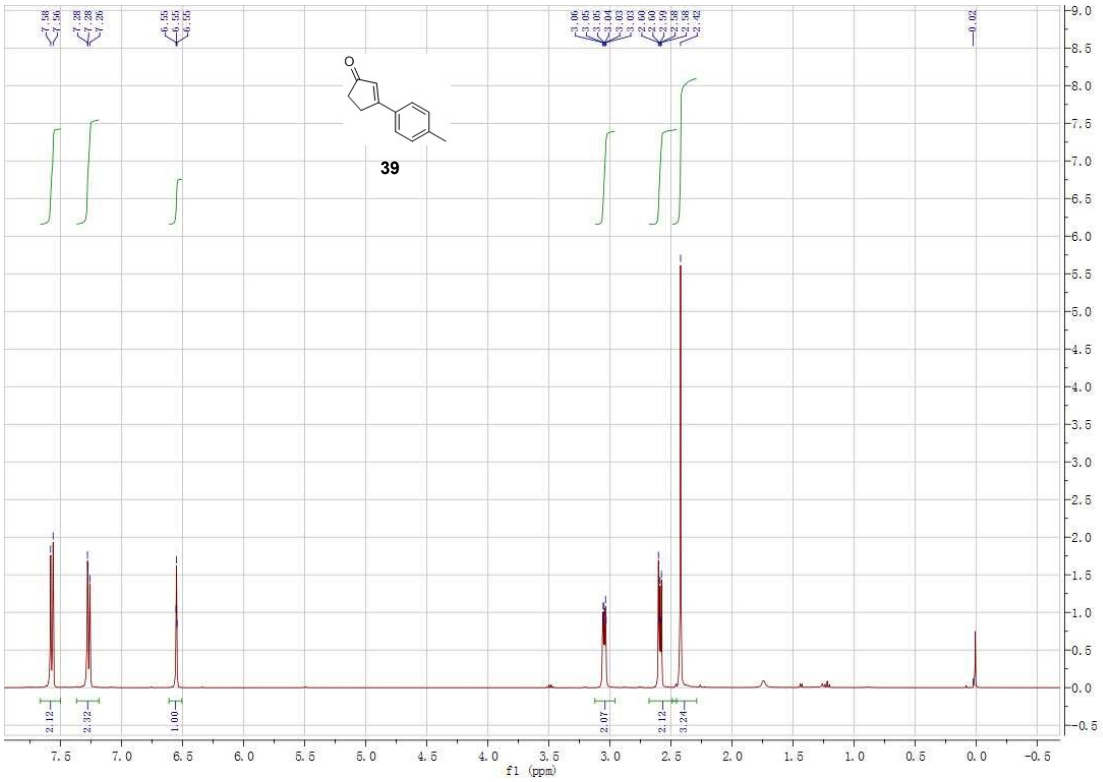
34

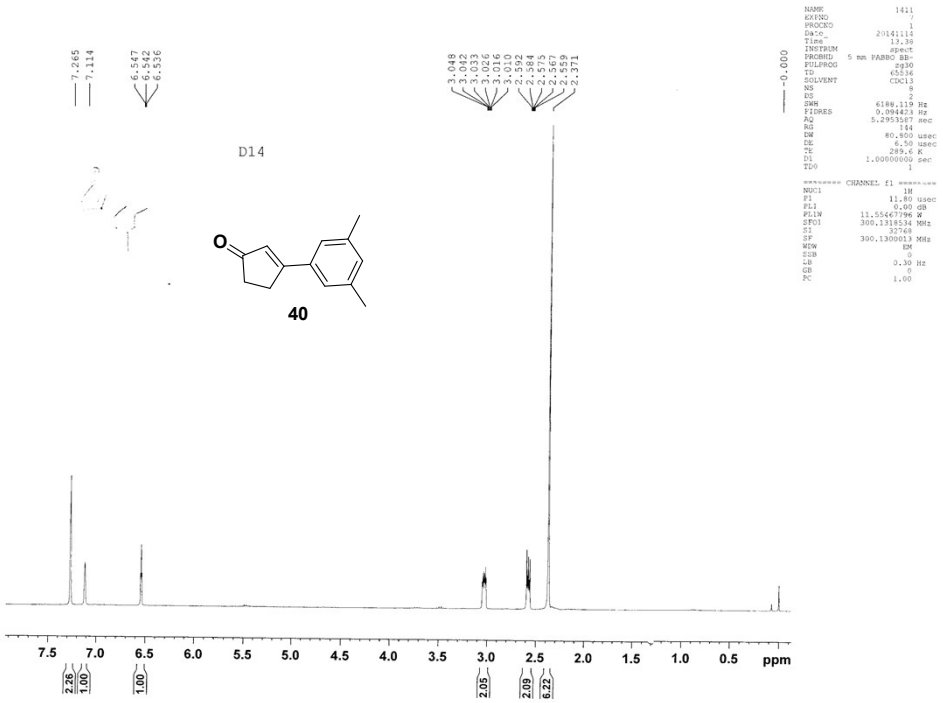

OMe
35
f1 (ppm)

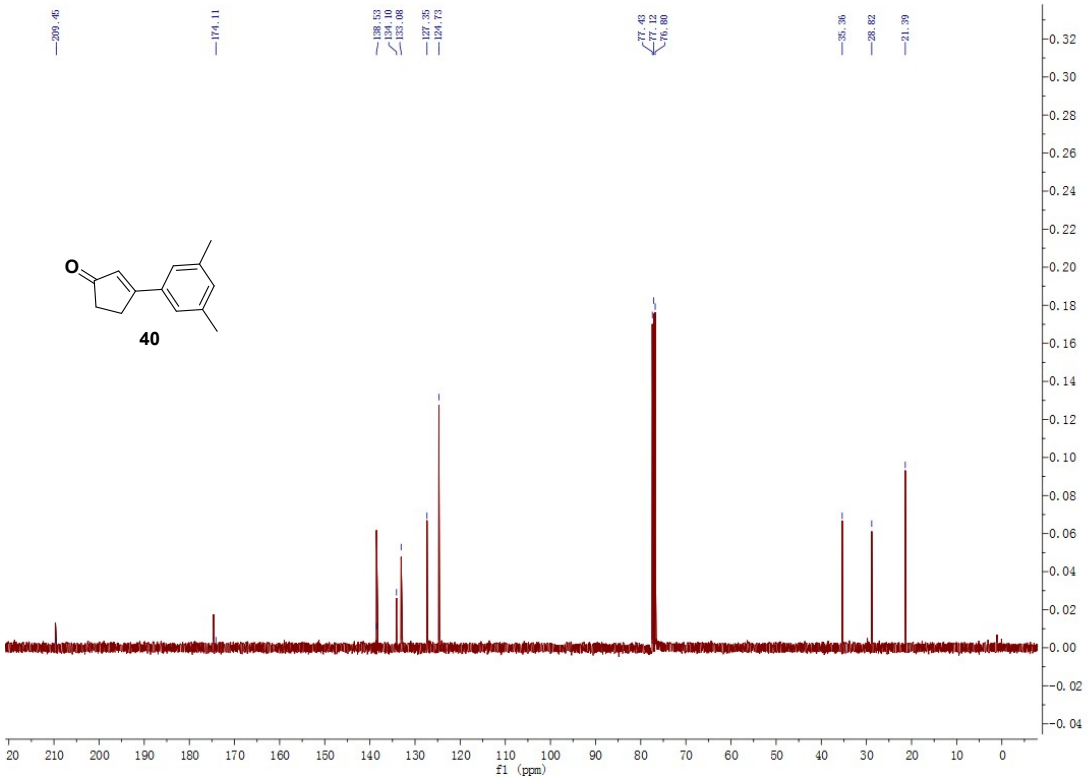

lsy-201410713
single_pulse
OMe
36
f1 (ppm)

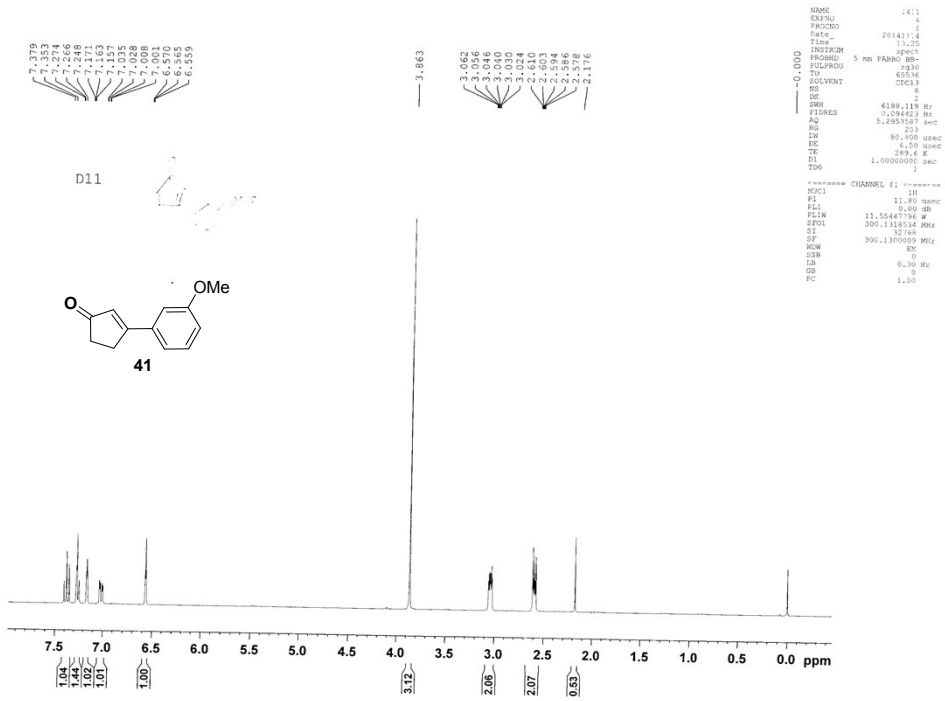

d5
single_pulse
37
f1 (ppm)

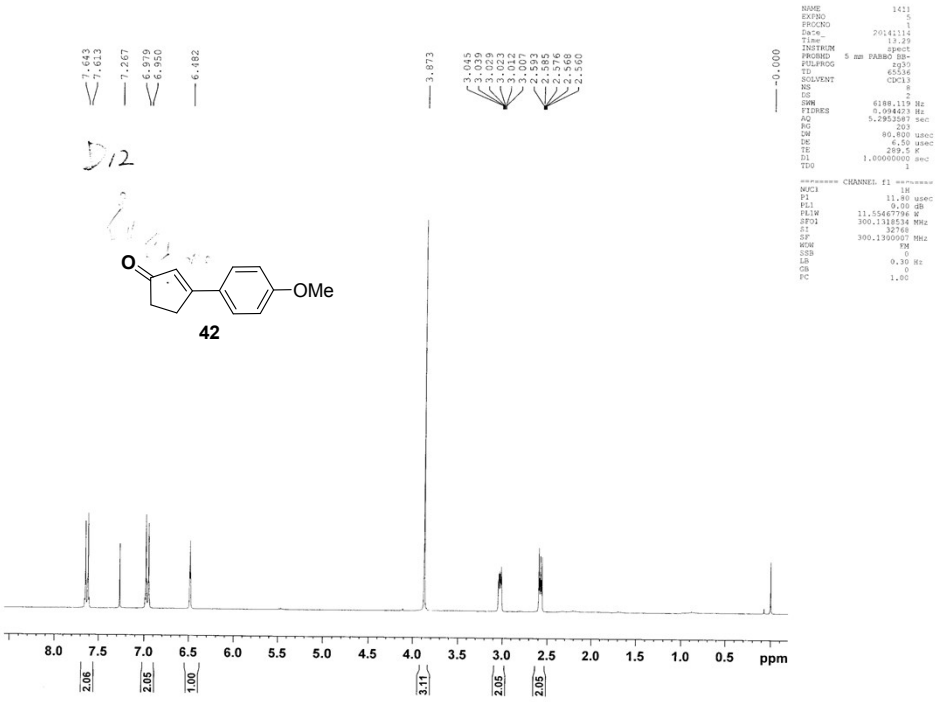

38
f1 (ppm)

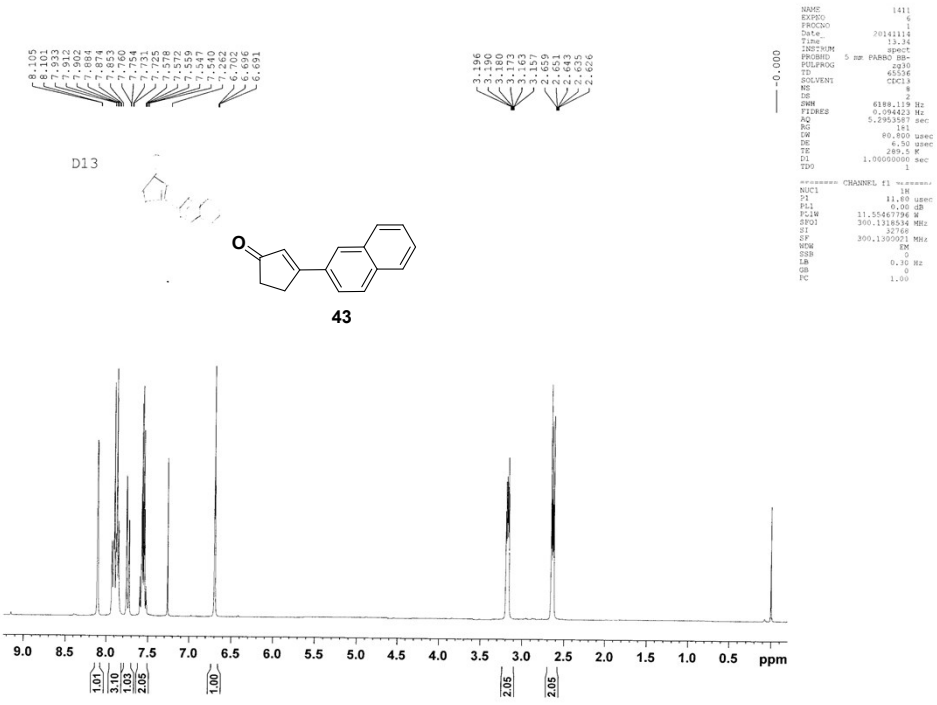

39
f1 (ppm)


D14
40
ppm


209.45
174.11
138.53
134.10
133.08
127.35
124.73
77.43
77.12
76.80
35.36
28.82
21.39
O
40
f1 (ppm)

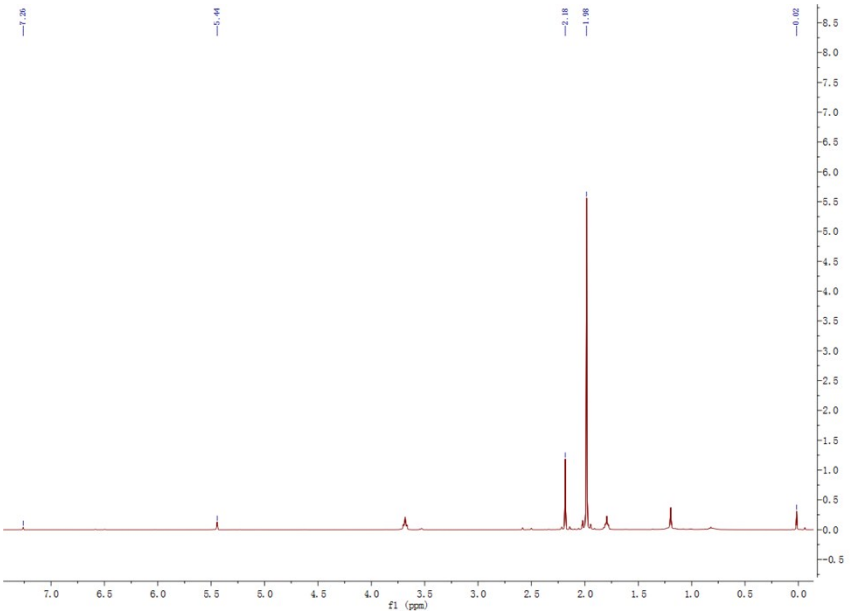

7.379
7.353
7.274
7.266
7.248
7.171
7.163
7.137
7.035
7.028
7.008
7.001
6.570
6.565
6.559
3.863
3.062
3.056
3.046
3.040
3.030
3.024
2.610
2.603
2.594
2.586
2.578
2.176
D11
OMe
O
41
ppm


7.643
7.613
7.267
6.979
6.950
6.482
3.873
3.045
3.039
3.029
3.023
3.012
3.007
2.593
2.585
2.576
2.568
2.560
-0.000
D12
O
OMe
42
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
2.06
2.05
1.00
3.11
2.05
2.05

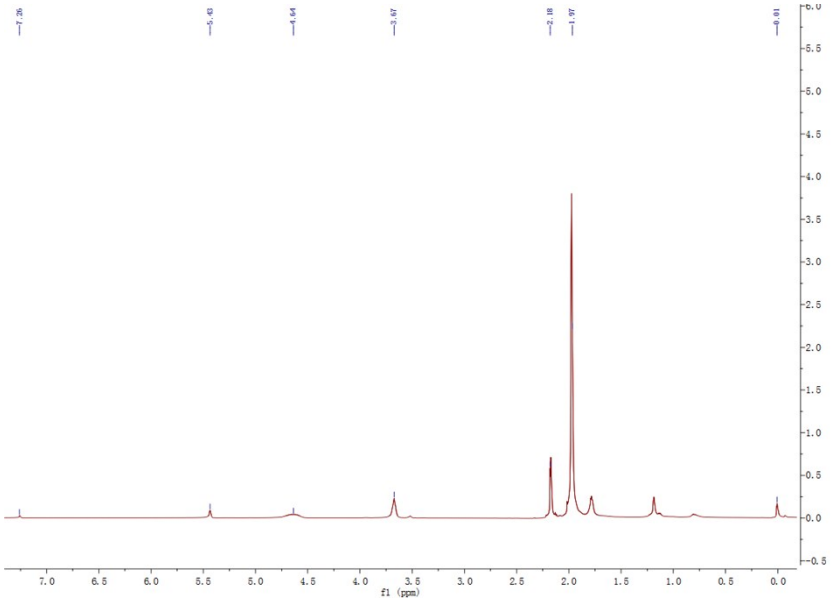

8.105
8.101
7.933
7.912
7.902
7.884
7.874
7.853
7.760
7.754
7.731
7.725
7.578
7.572
7.559
7.547
7.540
7.262
6.702
6.696
6.691
3.196
3.190
3.180
3.173
3.163
3.157
2.659
2.651
2.643
2.635
2.626
-0.000
D13
O
43
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.01
3.10
1.03
2.05
1.00
2.05
2.05

5. ^{1}H NMR and mass spectrometry for reaction mechanism.

5.1 ^{1}H NMR

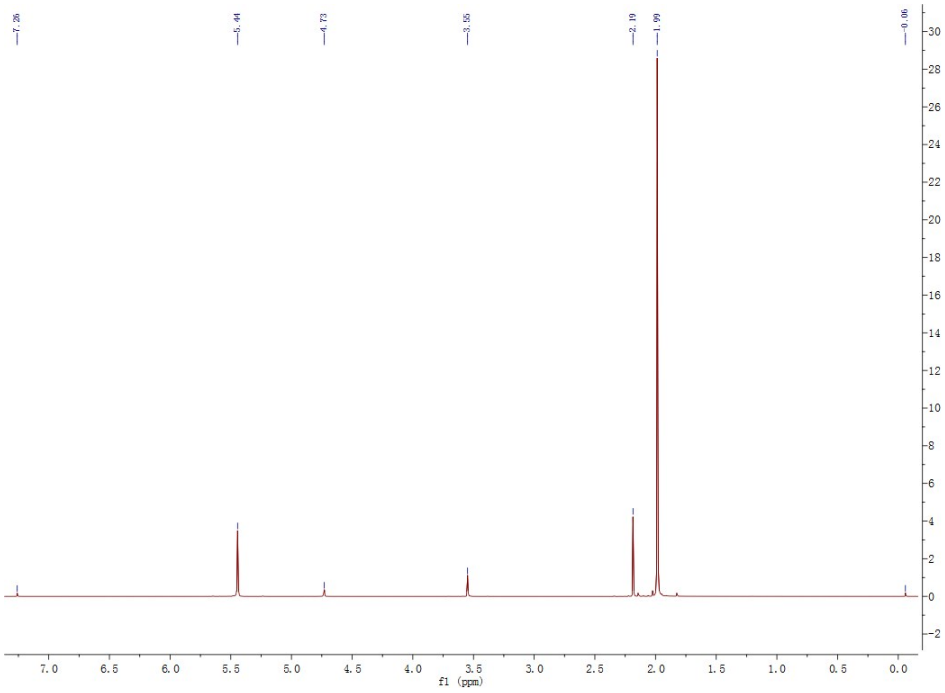


(1) ^{1}H NMR of deuterated acetylacetone. 20 mol% ***i*-PrMgCl** (0.77 M, 0.13 mL, 0.1 mmol, 0.2 eq.) was added to acetylacetone (0.0050 g, 0.5 mmol, 1.0 eq.) in anhydrous THF (1 mL) at 0 °C. After 30 min, the reaction was directly condensed to dryness in vacuum and the reaction mixture was directly characterized with ^{1}H NMR, with a drop of D_2O added.



(2) ^{1}H NMR of deuterated acetylacetone. 20 mol% ***i*-PrMgBr** (0.70 M, 0.14 mL, 0.1 mmol, 0.2 eq.) was added to acetylacetone (0.0050 g, 0.5 mmol, 1.0 eq.) in anhydrous THF (1 mL) at 0 °C. After 30 min, the reaction was

directly condensed to dryness in vacuum and the reaction mixture was directly characterized with ^{1}H NMR, with a drop of D_2O added.



(3) ^{1}H NMR of acetylacetone in $CDCl_3$ in the addition of one drop of D_2O.

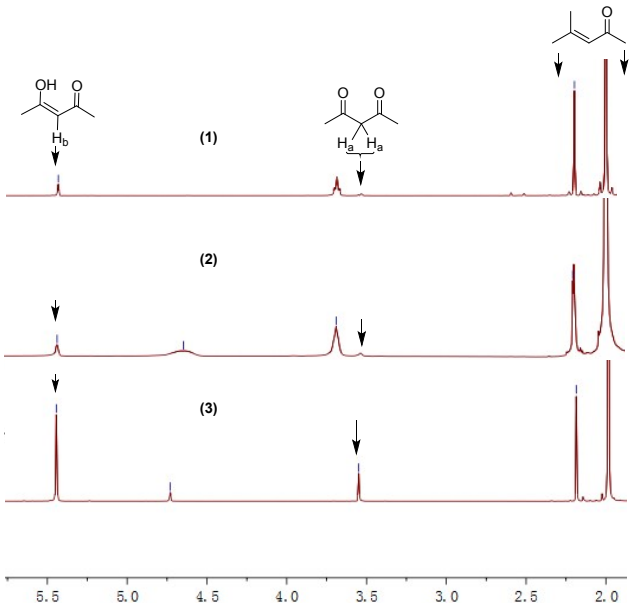
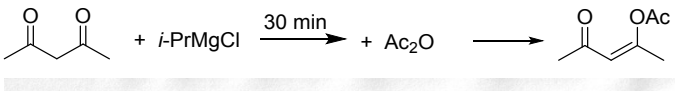


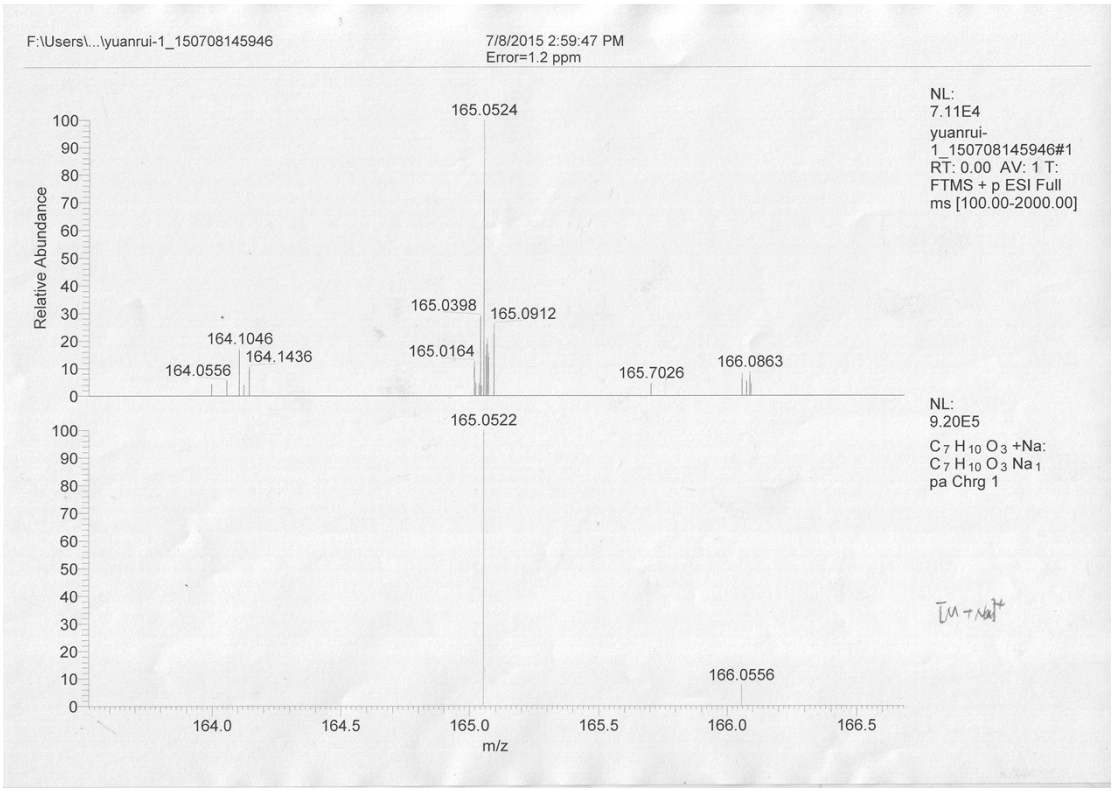
Figure 1. The comparison of ^{1}H NMR (400 MHz) spectrum of deuterated acetylacetone in $CDCl_3$. **(1)** the deuterated acetylacetone after reacted with 20 mol% *i*-PrMgCl. **(2)** the deuterated acetylacetone after reacted with 20 mol% *i*-PrMgBr. **(3)** the deuterated acetylacetone.

5.2 Mass spectrometry

5.2.1

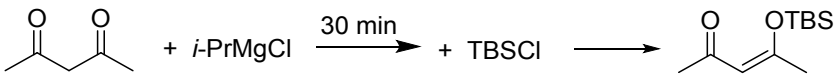
To a solution *i*PrMgCl (0.77 M, 0.13 mL, 0.1 mmol, 0.2 eq.) was dropwise added acetylacetone (0.0050 g, 0.5 mmol, 1.0 eq.) in anhydrous THF (1 mL) at 0 °C. The mixture was stirred for 15 min at 0 °C and then acetic anhydride (12 μL, 0.125 mmol, 0.25 eq.) was added. The reaction was directly was analyzed with HR-MS. HRMS calcd for $[C_7H_{10}+Na]^+$ 165.0528, found 165.0522.

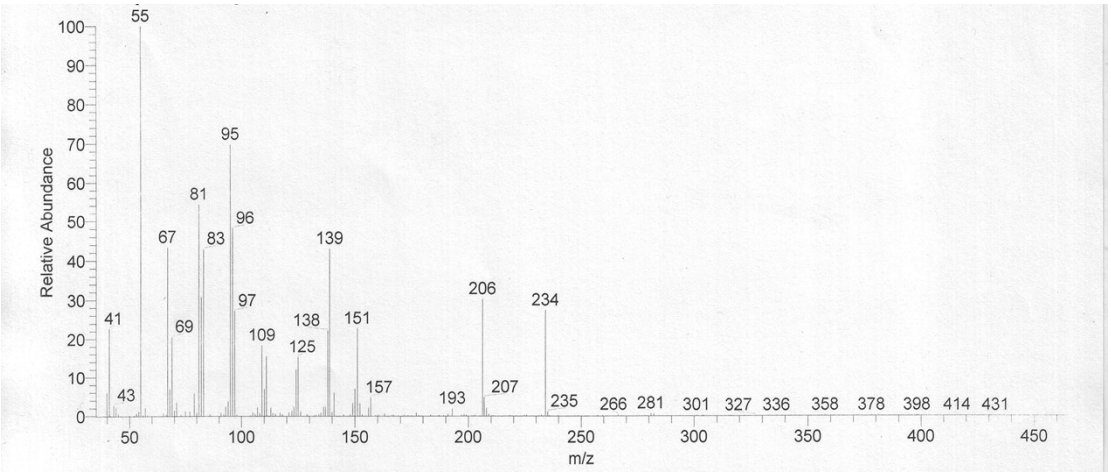




5.2.2

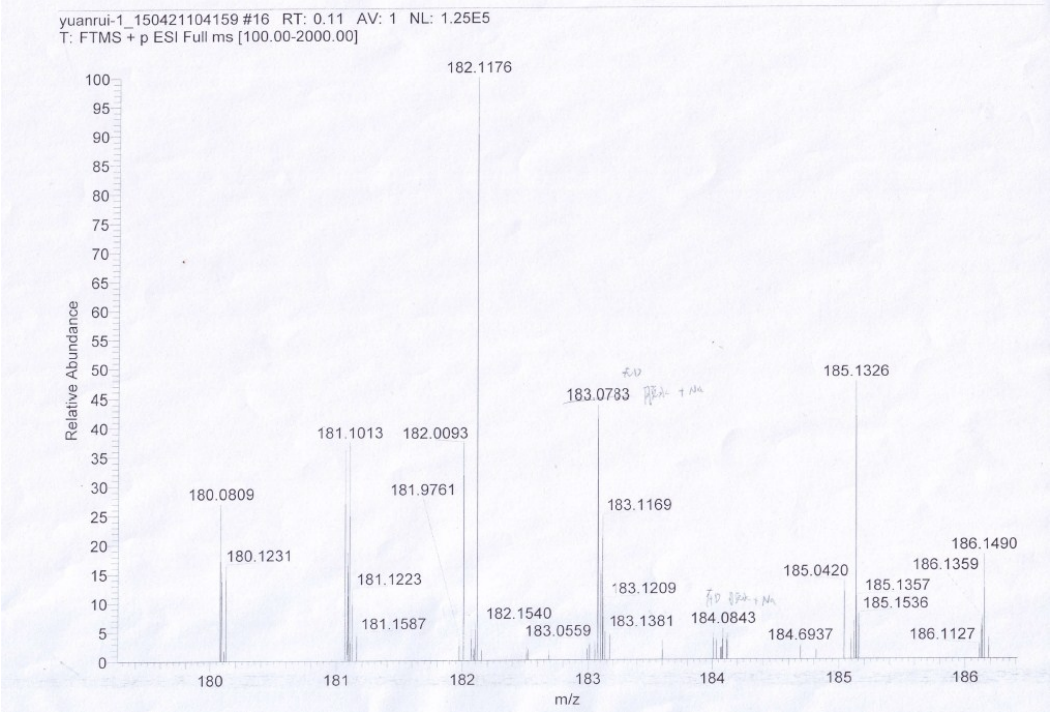
To a solution *i*PrMgCl (0.77 M, 0.13 mL, 0.1 mmol, 0.2 eq.) was dropwise added acetylacetone (0.0050 g, 0.5 mmol, 1.0 eq.) in anhydrous THF (1 mL) at 0 °C. The mixture was stirred for 15 min at 0 °C and then *t*-butyldimethylsilyl chloride (0.0188 g, 0.125 mmol, 0.25 eq.) was added. The reaction was directly was analyzed with GC-MS. Fragment peak that without tertiary butyl were determined at 157.





5.2.3

To a solution *i*-PrMgCl (0.77 M, 0.13 mL, 0.1 mmol, 0.2 eq.) was dropwise added acetylacetone (0.0050 g, 0.5 mmol, 1.0 eq.) in anhydrous THF (1 mL) at 0 °C. The mixture was stirred for 0.5 h at 0 °C and then PhMgBr (0.9 M, 1.4 mL, 1.25 mmol, 2.5 eq.) was added. The mixture was warmed to 40 °C. After stirring for 4 h at 40 °C, the reaction was quenched with D_2O. The purified product was analyzed with HR-MS. HRMS calcd for $[C_{11}H_{12}D_2O–D_2O+Na]^+$ 183.0786, found 184.0783, and for $[C_{11}H_{12}D_2O_2–DHO+Na]^+$ 184.0849, found 184.0843.



6. General Procedure for the sequential Grignard reactions

To a solution of *i*-PrMgCl (0.77 M, 0.05 mL, 0.04 mmol, 0.2 eq.) was dropwise added the linear 1,3-diketone (0.2 mmol, 1.0 eq.) in anhydrous THF (1 mL) at 0 ^{o}C. The mixture was stirred for 30 min at 0 ^{o}C and then the bromide Grignard reagent (0.5 mmol, 2.5 eq.) was introduced. The mixture was warmed to 40 ^{o}C. After stirring for 4 h at 40 ^{o}C, the mixture was cooled to 0 ^{o}C and then another quantum of bromide Grignard reagent (0.5 mmol, 2.5 eq.) was added, then cyclic 1,3-diketones (0.2 mmol, 1.0 eq.) in anhydrous THF (1 mL) was dropwise added. The mixture was warmed to 40 ^{o}C and stirred overnight. The reaction was carefully quenched with 25 mL 10% aqueous solution of acetic acid at 0 ^{o}C. The aqueous layer was extracted with ether (3×15 mL) and the combined organic layer was dried with anhydrous Na_2SO_4. The solvent was then evaporated under the reduced pressure and the residue was purified by column chromatography. The results are listed in the below.

(1) (Table 4, entry 1), 4-hydroxy-4-phenylpentan-2-one, **1**, yield 32.2 mg, 90%; and 3-phenyl-2-cyclohexene-1-one, **31**, yield 28.9 mg, 82%.

(2) (Table 4, entry 2), 4-hydroxy-4-(naphthalen-2-yl)pentan-2-one, **2**, yield 40.8 mg, 89%; 3-(naphthalen-2-yl)cyclohex-2-enone, **33**, yield 37.9 mg, 85%.

(3) (Table 4, entry 3), 4-hydroxy-4-(4-methoxyphenyl)pentan-2-one, **3**, yield 35.4 mg, 85%; 3-(4'-methoxy)phenyl-2-cyclohexene-1-one, **36**, yield 31.9 mg, 79%.

(4) (Table 4, entry 4), 3-hydroxy-1,3-diphenylbutan-1-one, **19**, yield 42.3 mg, 88%; 3-phenyl-2-cyclohexene-1-one), **31**, yield 27.9 mg, 81%.

(5) (Table 4, entry 5), 3-hydroxy-3-(naphthalen-2-yl)-1-phenylbutan-1-one, **20**, yield 51.3 mg, 88%; 3-(naphthalen-2-yl)cyclohex-2-enone, **33**, yield 38.4 mg, 86%.

(6) (Table 4, entry 6), 3-hydroxy-3-methyl-1-phenyldecan-1-one, **23**, yield 39.7 mg, 76%; 3-heptylcyclohex-2-enone, **37**, yield 26.4 mg, 68%.

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