SUPPORTING INFORMATION

Expedient approach for trans-esterification of β-keto esters under solvent free condition using silica supported boric acid (SiO_2-H_3BO_3) as recyclable catalyst

Kamal Das and Swapan Majumdar*

Department of Chemistry
Tripura University Suryamaninagar 799 022,
Tripura INDIA
E-mail: smajumdar@tripurauniv.ac.in

Contents

	Pages
Experimental: General	S2
General experimental procedure for the synthesis of **3a-p, 4a-d and 5a-c**	S2
Spectral data of **3a-p**	S2-S6
Spectral data of **4a-d**	S7-S8
Spectral data of **5a-c**	S8-S9
^{1}H and ^{13}C NMR Spectra of **3a-p, 4a-d and 5a-c**	S10-S32
HRMS of **3f**	S33
SEM images related characterization of catalyst	S34
References	S35

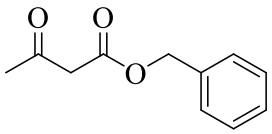
Experimental Section

General: All reactions were monitored by thin-layer chromatography carried out on silica coated aluminium plates using UV-light and iodine or Lieberman–Burchard reagent for visualization. Unless otherwise noted, all utilizing reagents were used exactly as received and solvents were freshly distilled before use. Column chromatography was performed on silica gel (60–120 mesh and 100-200) using n-hexane and ethyl acetate as eluent. Evaporation of solvents was conducted under reduced pressure at temperatures less than 50°C. FTIR spectra (Bruker Alpha FTIR) were recorded in neat. SEM image are recoded on model-Sigma 300 (Carl Zeiss). ^{1}H NMR and ^{13}C NMR spectra (Bruker Ascend^{TM} 400 MHz) were recorded in $CDCl_3$ solvent. Chemical shifts δ and coupling constants J are given in ppm (parts per million) and Hz (hertz) respectively. Chemical shifts are reported relative to residual solvent as an internal standard for ^{1}H and ^{13}C ($CDCl_3$: δ 7.28 ppm for ^{1}H and 77.04 ppm for ^{13}C. Mass spectra (HRMS) were obtained from XEVO G2-XS QTOF (Waters) using 70 ev in positive ion mode.

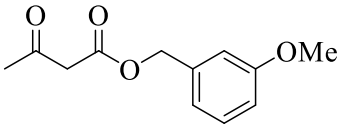
General procedure for trans-esterification reaction

A mixture of β-keto- esters (1 mmol), alcohols (1.1 mmol) and silica supported boric acid (SiO_2-H_3BO_3) (50mg, 8.3 mol%), were charged into a clean reaction vessel equipped with a magnetic stir bar and heated for 5-7 hours at 100 °C temperature. After completion of reaction (TLC), the mixture was cooled, diluted with diethyl ether or ethyl acetate and filtered to remove the catalyst and the crude product was purified using column chromatography with silica gel (100-200 mesh) EtOAc/hexane (1:9, 1:4). Melting point, FTIR data, ^{1}H NMR, ^{13}C NMR and HRMS analyses were used to determine the products identities.

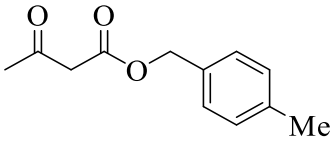
Spectral data



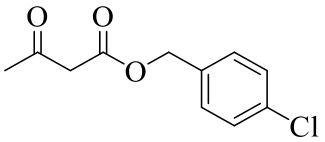
Benzyl 3-oxobutanoate (3a)[1]: Yield: 95%, colourless oil; IR (neat) ν_{max} 1716, 1261, 1146, 1025, 744 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.36 (m, 5H), 5.20 (s, 2H), 3.53 (s, 2H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.4, 167.0, 135.3, 128.6, 128.5, 128.4, 128.1, 67.2, 50.1, 30.2.



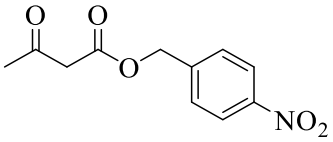
3-Methoxybenzyl 3-oxobutanoate (3b)[1]: Yield: 94%, colourless oil; IR (neat) ν_{max} 2951, 1717, 1596, 1453, 1262, 1148, 1036, 782 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.0 Hz, 1H), 6.97-6.89 (m, 3H), 5.18 (s, 2H), 3.84 (s, 3H), 3.53 (s, 2H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.4, 166.9, 159.8, 136.8, 129.7, 120.5, 114.1, 113.7, 67.0, 55.3, 50.1, 30.2.



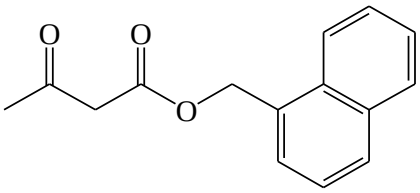
4-Methylbenzyl 3-oxobutanoate (3c)[2]: Yield: 94%, colourless oil; IR (neat) ν_{max} 1718, 1643, 1516, 1312, 1262, 1146, 1026, 966 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 1.6 Hz, 2H), 7.20 (d, *J* = 8 Hz, 2H), 5.16 (s, 2H), 3.50 (s, 2H), 2.38 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.5, 167.0, 138.4, 132.3, 129.3, 128.6, 128.3, 89.7, 67.1, 65.7, 50.1, 30.2, 21.2.



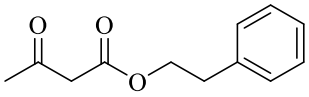
4-Chlorobenzyl 3-oxobutanoate (3d)[3]: Yield: 93%, colourless oil; IR (neat) ν_{max} 1717, 1492, 1410, 1363, 1261, 1145, 1091, 1013, 805 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37-7.28 (m, 4H), 5.15 (s, 2H), 3.52 (s, 2H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.3, 166.8, 134.4, 133.8, 129.5, 128.8, 89.5, 66.3, 64.8, 50.0. 30.2.



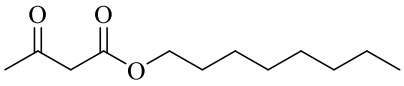
4-Nitrobenzyl 3-oxobutanoate (3e)[4]: Yield: 92%, reddish oil; IR (neat) ν_{max} 1714, 1606, 1519, 1411, 1345, 1257, 1143, 1036, 847 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 2H), 5.29 (s, 2H), 3.59 (s, 2H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 176.8, 166.6, 147.8, 142.2, 128.5, 128.2, 123.9, 89.2, 65.5, 64.1, 49.8, 30.3, 21.3.



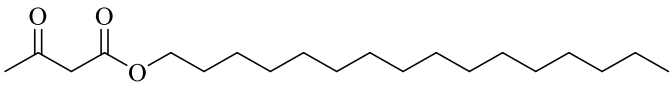
Naphthalen-1-ylmethyl 3-oxobutanoate (3f): Yield: 87% colour -less oil; IR (neat) ν_{max} 1717, 1643, 1511, 1410, 1359, 1309, 1250, 1145, 962, 861, 786 cm^{-1}**;** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.0 Hz, 1H), 7.90 (t, *J* = 8.8 Hz, 2H), 7.62-7.54 (m, 3H), 7.50-7.28 (m, 1H), 5.67 (s, 2H), 3.52 (s, 2H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.4, 176.0, 172.4, 167.1, 133.7, 131.6, 130.8, 129.6, 129.3, 128.8, 127.9, 127.4, 126.7, 126.6, 126.1, 126.0, 125.3, 123.5, 89.7, 65.5, 64.0, 50.1, 30.2, 21.3; HRMS calcd for $C_{15}H_{14}O_3$ + Na (M + Na) 265.0841; found: 265.0840.



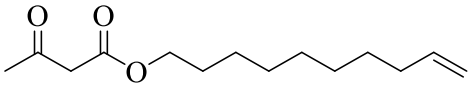
Phenethyl 3-oxobutanoate (3g)[5]: Yield: 90%, colourless oil; IR (neat) ν_{max} 1717, 1644, 1413, 1313, 1245, 1148, 1031, 744 cm^{-1}**;** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.23 (m, 5H), 4.41-4.35 (m, 2H), 3.45 (s, 2H), 2.99 (t, *J* = 7.2 Hz, 2H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.6, 167.1, 137.4, 128.9, 128.6, 128.5, 126.7, 65.8, 64.5, 50.1, 34.9, 30.1.



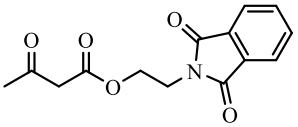
Octyl 3-oxobutanoate (3h)[6]: Yield: 91% colourless oil; IR (neat) ν_{max} 2926, 2858, 1720, 1643, 1459, 1361, 1313, 1237, 1150, 1034, 728 cm^{-1}**;** ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.15 (t, *J* = 6.8 Hz, 2H), 3.46 (s, 2H), 2.29 (s, 3H), 1.69-1.62 (m, 2H), 1.29 (s, 6H), 0.89 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.7, 167.2, 89.8, 65.6, 64.1, 50.2, 31.8, 30.1, 29.2, 28.7, 28.5, 25.9, 22.6, 21.2, 14.1.



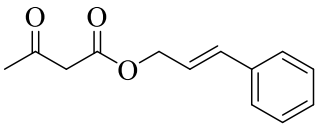
Hexadecyl 3-oxobutanoate (3i)[7]: Yield: 88%, colourless oil; IR (neat) ν_{max} 2916, 2848, 1739, 1707, 1465, 1411, 1368, 1315, 1260, 1153, 1153 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.15 (t, *J* = 6.8 Hz, 2H), 3.47 (s, 2H), 2.30 (s, 3H), 1.66-1.62 (m, 7H), 1.27 (s, 36H), 0.90 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.6, 167.2, 89.8, 65.6, 64.1, 50.2, 31.9, 30.9, 30.1, 29.7, 29.7, 29.6, 29.5, 29.4, 29.2, 28.7, 28.5, 25.9, 25.8, 22.7, 21.2, 14.1.



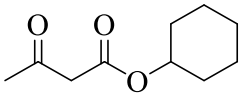
Dec-9-en-1-yl 3-oxobutanoate (3j)[5]: Yield: 95%, colourless oil; IR (neat) ν_{max} 2926, 2855, 1722, 1641, 1312, 1237, 1151, 1035, 993, 909, 727 cm^{-1}**;** ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88-5.78 (m, 1H), 5.03-4.94 (m, 2H), 4.15 (t, *J* = 6.4 Hz, 2H), 3.47 (s, 2H), 2.29 (s, 3H), 2.08-2.02 (m, 2H), 1.66 (t, *J* = 7.2 Hz, 3H), 1.32 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.6, 167.2, 139.2, 129.1, 114.2, 89.8, 65.6, 64.1, 50.2, 33.8, 30.1, 29.3, 29.1, 29.0, 28.8, 28.7, 28.5, 25.9, 25.8, 21.2.



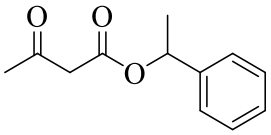
2-(1,3-Dioxoisoindolin-2-yl)ethyl 3-oxobutanoate (3k)[8]: Yield: 90%, white solid, m. p. 120°C [lit = 88-89°C]; IR (neat) ν_{max} 1701, 1391, 1316, 1145, 997, 795, 714 cm^{-1}**;** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 2.4 Hz, 2H), 7.75 (t, *J* = 2.4 Hz, 2H), 4.39 (t, *J* = 4.8 Hz, 2H), 3.98 (t, *J* = 5.2 Hz, 2H), 3.44 (s, 2H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.4, 168.1, 167.0, 134.2, 131.9, 123.4, 89.4, 62.5, 45.7, 37.1, 30.2, 21.3.



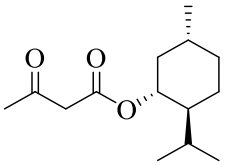
Cinnamyl 3-oxobutanoate (3l)[3]: Yield: 90% colourless oil; IR (neat) ν_{max} 1716, 1257, 1146, 962, 741 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.28 (m, 5H), 6.67 (d, *J* = 16.0 Hz, 1H), 6.34-6.23 (m, 1H), 4.82 (d, *J* = 6.8 Hz, 2H), 3.53 (s, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.5, 166.9, 136.0, 134.9, 128.7, 128.3, 126.7, 123.1, 122.4, 89.6, 66.0, 50.0, 30.2.



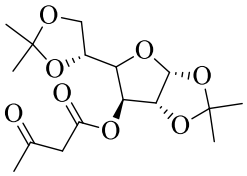
Cyclohexyl 3-oxobutanoate (3m)[4]: Yield: 88%, colourless oil; IR (neat) ν_{max} 2935, 2860, 1716, 1643, 1448, 1412, 1241, 1151, 1023, 961, 907, 803 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.84 (m, 1H), 3.43 (s, 2H), 2.27 (s, 3H), 1.88-1.85 (m, 2H), 1.78-1.72 (m, 2H), 1.56-1.47 (m, 1H), 1.45-1.27 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.8, 166.6, 90.1, 73.8, 72.2, 31.6, 31.4, 25.2, 23.7, 21.1.



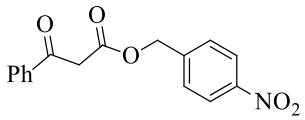
1-phenylethyl 3-oxobutanoate (3n)[9]: Yield: 92%, colourless oil; IR (neat) ν_{max} 2982, 2933, 1717, 1644, 1495, 1448, 1411, 1358, 1252, 1150, 1061, 1026, 945, 858, 803 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38-7.28 (m, 5H), 5.99 (q, *J* = 6.4 Hz, 1H), 3.49 (s, 2H), 2.26 (s, 3H), 1.60 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.5, 166.4, 140.9, 129.0, 128.6, 128.5, 128.1, 126.2, 124.5, 90.0, 73.6, 50.4, 30.9, 30.1, 22.0.



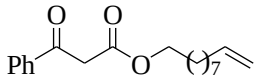
(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 3-oxobutanoate (3o)[10] : Yield: 93%, colourless oil; IR (neat) ν_{max} 2952, 2867, 1718, 1643, 1454, 1240, 1149, 1029, 975, 913, 843 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.79-4.73 (m, 1H), 3.45 (s, 2H), 2.29 (s, 2H), 2.04 (d, *J* = 15.2 Hz, 1H), 1.90-1.88 (m, 1H), 1.70 (d, *J* = 12.0 Hz, 2H), 1.61 (s, 3H), 1.52-1.37 (m, 2H), 1.09-0.97 (m, 3H), 0.92 (t, *J* = 6.8 Hz, 7H), 0.78 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.7, 166.7, 73.7, 50.6, 46.9, 40.7, 34.2, 31.4, 30.1, 26.2, 23.6, 22.0, 20.7, 16.2.



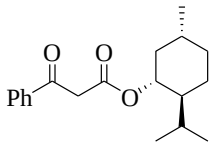
(3aR,5R,6S,6aR)-5-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydro furo[2,3-d][1,3]dioxol-6-yl 3-oxobutanoate (3p)[11]: Yield: 92%, colourless syryp; IR (neat) ν_{max} 2987, 1751, 1718, 1373, 1214, 1152, 1070, 1017, 846, 731 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 11.90 (s, enol-OH), 5.90 (s, 1H), 5.33 (s, 1H), 4.60 (d, *J* = 3.6 Hz, 1H), 4.21 (s, 2H), 4.10-4.02 (m, 2H), 3.53 (d, *J* = 4.4 Hz, 2H), 2.30 (s, 3H), 1.68 (s, 4H), 1.54 (s, 4H), 1.23 (s, 3H), 1.34 (s, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 166.2, 165.8, 112.4, 112.3, 109.5, 109.3, 105.1, 105.0, 89.2, 83.4, 83.2, 83.1, 79.7, 79.6, 79.2, 75.7, 72.4, 72.3, 68.4, 67.4, 67.0, 64.4, 50.0, 50.0, 30.9, 30.4, 30.1, 30.0, 26.9, 26.7, 26.7, 26.2, 25.2, 21.3.



4-nitrobenzyl 3-oxo-3-phenylpropanoate (4a)[3]: Yield: 90%, reddish oil; IR (neat) ν_{max} 1742, 1683, 1605, 1518, 1449, 1339, 1262, 1181, 1141, 986, 846, 744, 686 cm^{-1}**;** ^1H NMR (400 MHz, $CDCl_3$) δ (s, enol-OH), two sets of doublets 8.26 and 8.21 (*J* = 8.8 Hz, 2H), 7.96-7.94 (m, 2H), two sets of multiplets 7.82-7.80 and 7.66 – 7.58 (m, 2H), 7.53-7.44 (m, 5H), 5,79 (s, enol-CH), 5.36 and 5.32 (s, 2H), 4.13 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 172.5, 167.1, 147.7, 143.2, 142.6, 135.8, 134.0, 133.1, 131.7, 128.9, 128.6, 128.5, 128.4, 128.3, 126.2, 123.9, 123.8, 86.6, 65.5, 64.5, 45.8.

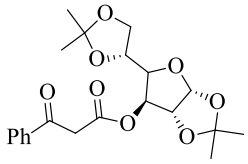


dec-9-en-1-yl 3-oxo-3-phenylpropanoate (4b)[12]: Yield: 91%, colourless oil; IR (neat) ν_{max} 2926, 2854, 1740, 1687, 1631, 1455, 1412, 1263, 1190, 1076, 993, 910, 764, 688 cm^{-1}**;** ^1H NMR (400 MHz, $CDCl_3$) δ 12.61 (enol-OH), 7.97-7.95 (m, 2H), 7.81-7.79 (m), 7.61 (t, *J* = 6.4 Hz, 1H), 7.52-7.42 (m, 3H), 5.86-5.77 (m, 1H), 5.69 (s, due enol-CH), 5.03-4.96 (m, 2H), two sets of triplet at 4.21 and 4.16 (*J* = 6.4 Hz, 2H), 4.01 (s, 2H), 2.06 (q, *J* = 6.8 Hz, 2H), 1.73 (s, 1H), 1.27 (s, 14H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 167.6, 139.2, 136.0, 133.5, 131.2, 128.8, 128.5, 126.1, 114.2, 87.4, 65.7, 64.5, 46.1, 33.8, 29.4, 29.3, 29.2, 29.1, 29.0, 28.9, 28.7, 28.4, 25.7.

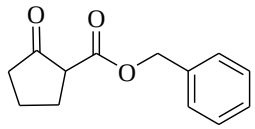


(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 3-oxo-3-phenyl pro-panoate (4c)[13]: Yield: 92%, colourless oil; IR (neat) ν_{max} 2952, 2866, 1734, 1687, 1631, 1453, 1408, 1263, 1193, 1147, 1085, 975, 763, 687 cm^{-1}**;** ^1H NMR (400 MHz, $CDCl_3$) δ 12.70 (s, enol 1H, OH), 7.96 (d, *J* = 7.2 Hz, keto 2H, Ar), 7.79 (d, *J* = 6.8 Hz, enol 2H, Ar), 7.60 (t, *J* = 8.0, keto 1H, Ar), 7.51-7.41 (m, keto 2H + enol 3H, Ar), 5.67 (s, enol 1H, C(OH)CHCO), 4.88-4.70 (m, keto 1H + enol 1H, OCH), 4.02 (d, *J* = 15.6 Hz, 1H, keto 1H, $COCH_2CO$)), 3.96 (d, *J* = 15.6 Hz, 1H, keto 1H, $COCH_2CO$), 2.11-1.30 (m, keto 4H + enol 4H, OCHCHCH, OCHCH2), 1.13-0.07 (m, keto 14H + enol 14H, $OCHCH_2CHCH_2CH_2$, $CH(CH_3)_2$, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.6 (keto), 172.9 (enol), 171.3 (enol), 167.1 (keto), 136.1 (keto), 133.6 (keto + enol), 131.2 (enol), 128.7 (keto), 128.5 (keto + enol), 126.0 (enol), 87.7 (enol), 75.6 (keto),

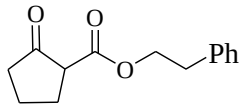
74.2 (enol), 47.1 (enol), 46.8 (keto), 46.6 (keto), 41.1 (enol), 40.6 (keto), 34.2 (enol), 34.1 (keto), 31.4 (keto + enol), 26.3 (enol), 25.9 (keto), 23.5 (enol), 23.2 (keto), 22.0 (enol), 21.9 (keto), 20.7 (keto + enol), 16.4 (enol), 16.0 (keto).



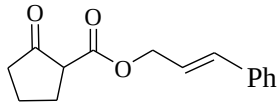
(3aR,5R,6S,6aR)-5-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl tetrahydrofuro [2,3-d][1,3]dioxol-6-yl 3-oxo-3-phenyl propanoate (4d)[11]: Yield: 89% colourless syrup; IR (neat) ν_{max} 2987, 1750, 1686, 1376, 1256, 1212, 1153, 1069, 1013, 947, 844, 765, 689 cm^{-1}**;** ^1H NMR (400 MHz, $CDCl_3$) δ 12.37 (enol-OH), 7.94 (d, *J* = 7.6 Hz) and 7.80 (d, J = 7.2 Hz) 7.64 (t, *J* = 8.0 Hz, 1H), 7.54-7.43 (m, 3H), 5.94 and 5.83 (d, *J* = 4.0 and 3.2 Hz, 1H), 5.71 (enol-CH) 5.39 and 5.34 (d, *J* = 2.4 Hz, 1H), 4.61 (m, 1H), 4.22-3.77 (m, 7H), 1.56 and 1.53 (two s, 3H), 1.45 and 1.42 (two s, 3H), 1.34, 1.33 and 1.31 (three s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 172.7, 171.9, 166.3, 135.8, 134.0, 133.0, 131.7, 128.9, 128.6, 128.5, 128.4, 126.2, 112.4, 109.4, 105.1, 86.7, 83.4, 83.1, 79.6, 76.1, 72.4, 72.3, 67.2, 67.1, 45.8, 26.9, 26.7, 26.2, 25.3.



Benzyl 2-oxocyclopentane-1-carboxylate (5a)[5]: Yield: 93%, colourless oil; IR (neat) ν_{max} 2962, 2887, 1720, 1497, 1453, 1380, 1335, 1249, 1175, 1109, 996, 831, 742, 696 cm^{-1}**;** ^1H NMR (400 MHz, $CDCl_3$) δ 7.39-7.34 (m, 5H), 5.20 (s, 2H), 3.23 (t, *J* = 9.2 Hz, 1H), 2.34-2.26 (m, 4H), 2.19-2.10 (m, 1H), 1.94-1.82 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.2, 169.3, 135.6, 128.6, 128.3, 128.1, 67.0, 54.8, 38.1, 27.4, 21.0.



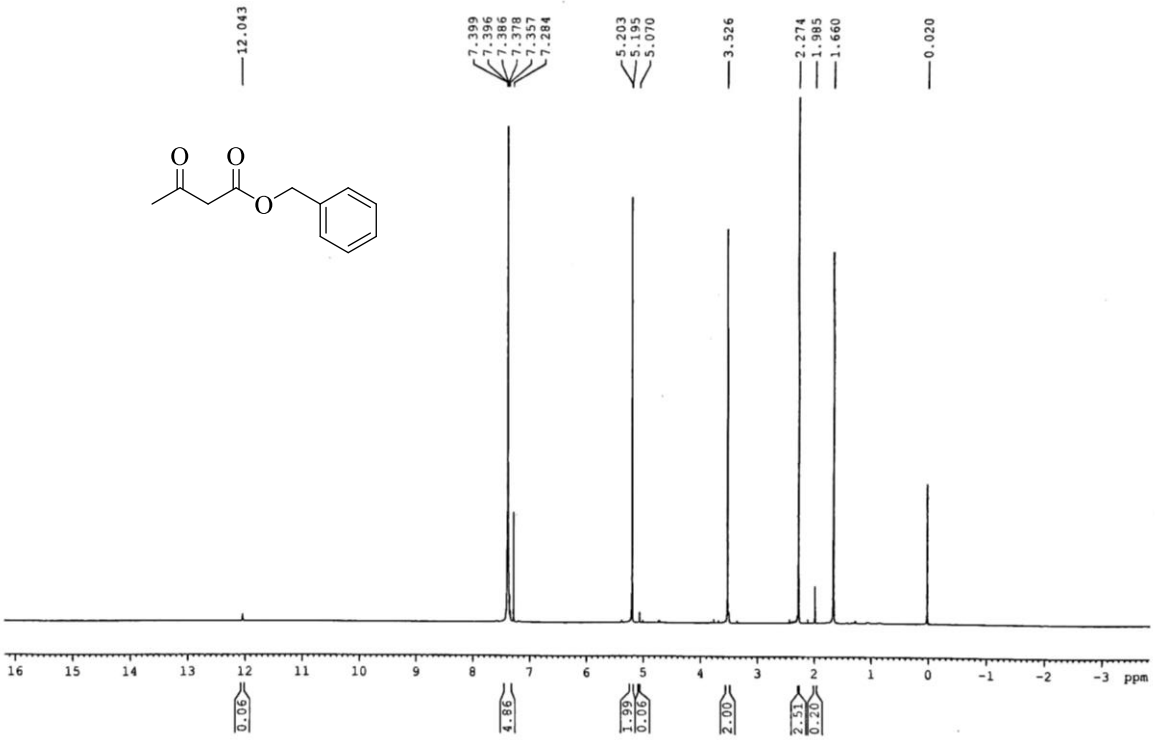
Phenethyl 2-oxocyclopentane-1-carboxylate (5b)[14]: Yield: 92%, colourless oil; IR (neat) ν_{max} 2961, 1719, 1454, 1335, 1248, 1172, 1109, 831,744, 697 cm^{-1}**;** ^1H NMR (400 MHz, $CDCl_3$) δ 7.35-7.23 (m, 5H), 4.47-4.32 (m, 2H), 3.16 (t, *J* = 8.8 Hz, 1H), 3.06-2.90 (m, 2H), 2.43-2.24 (m, 4H), 2.14-2.08 (m, 1H), 1.92-1.83 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.4, 169.4, 137.6, 129.0, 128.5, 126.6, 65.8, 54.8, 38.1, 35.0, 27.4, 21.0.



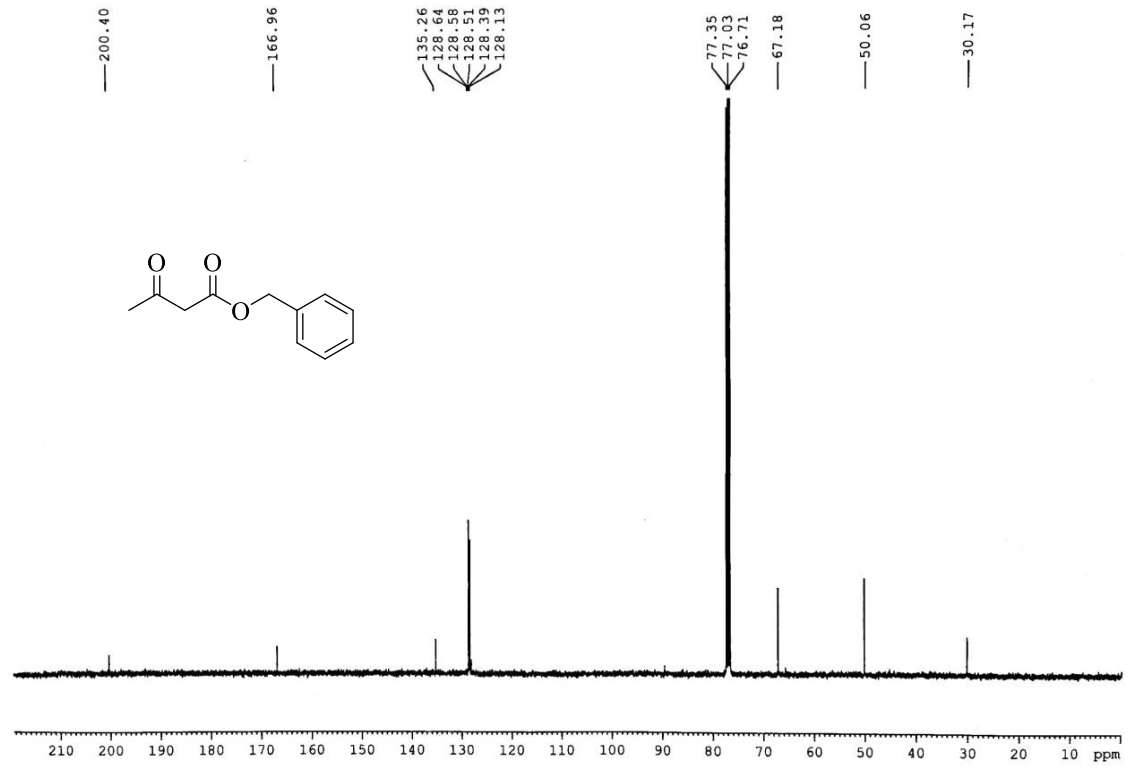
Cinnamyl 2-oxocyclopentane-1-carboxylate (5c)[12]: Yield: 90%, colourless oil; IR (neat) ν_{max} 2962, 1719, 1661, 1449, 1389, 1334, 1246, 1176, 1109, 966, 831, 741 cm^{-1}**;** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.26 (m, 5H), 6.70 (d, *J* = 15.6 Hz, 1H), 6.34-6.27 (m, 1H), 4.84-4.82 (m, 2H), 3.23 (t, *J* = 9.2 Hz, 1H), 2.38-2.32 (m, 4H), 2.18-2.15 (m, 1H), 1.93-1.89 (m, 1H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.3, 169.2, 136.1, 134.5, 128.6, 128.1, 126.7, 122.7, 65.9, 54.8, 38.1, 27.4, 21.0.

NMR Spectra

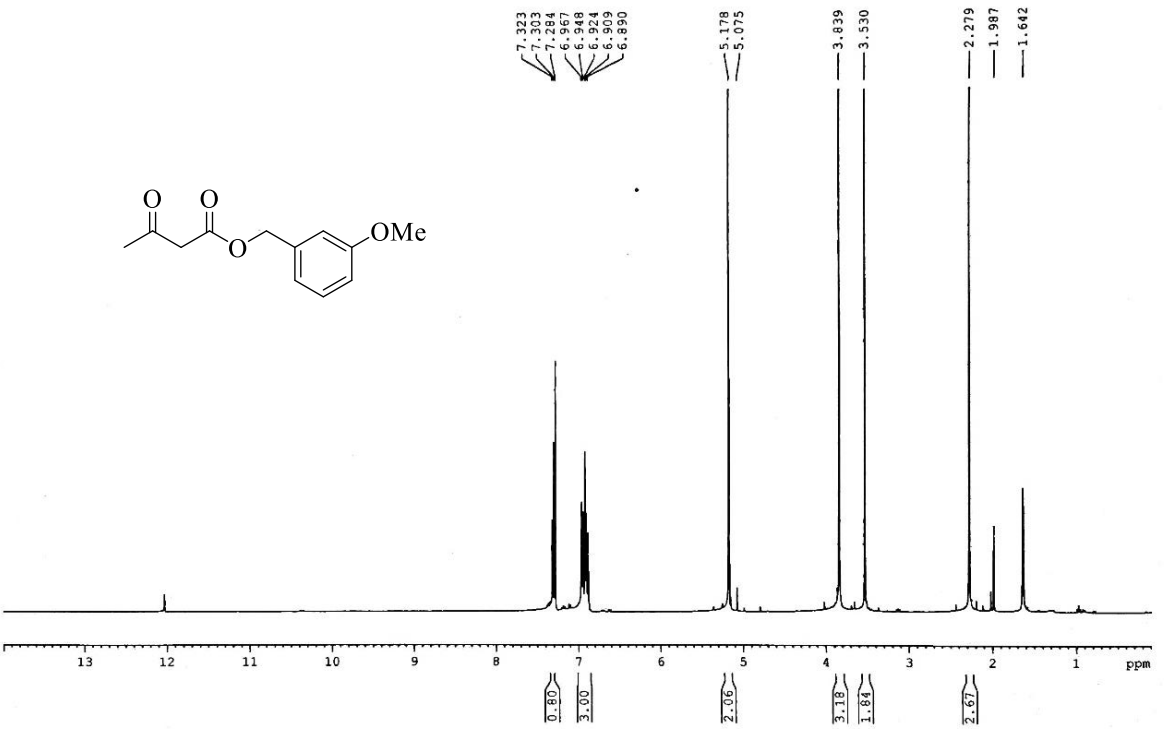
^{1}H NMR of **3a** (400 MHz, $CDCl_3$)



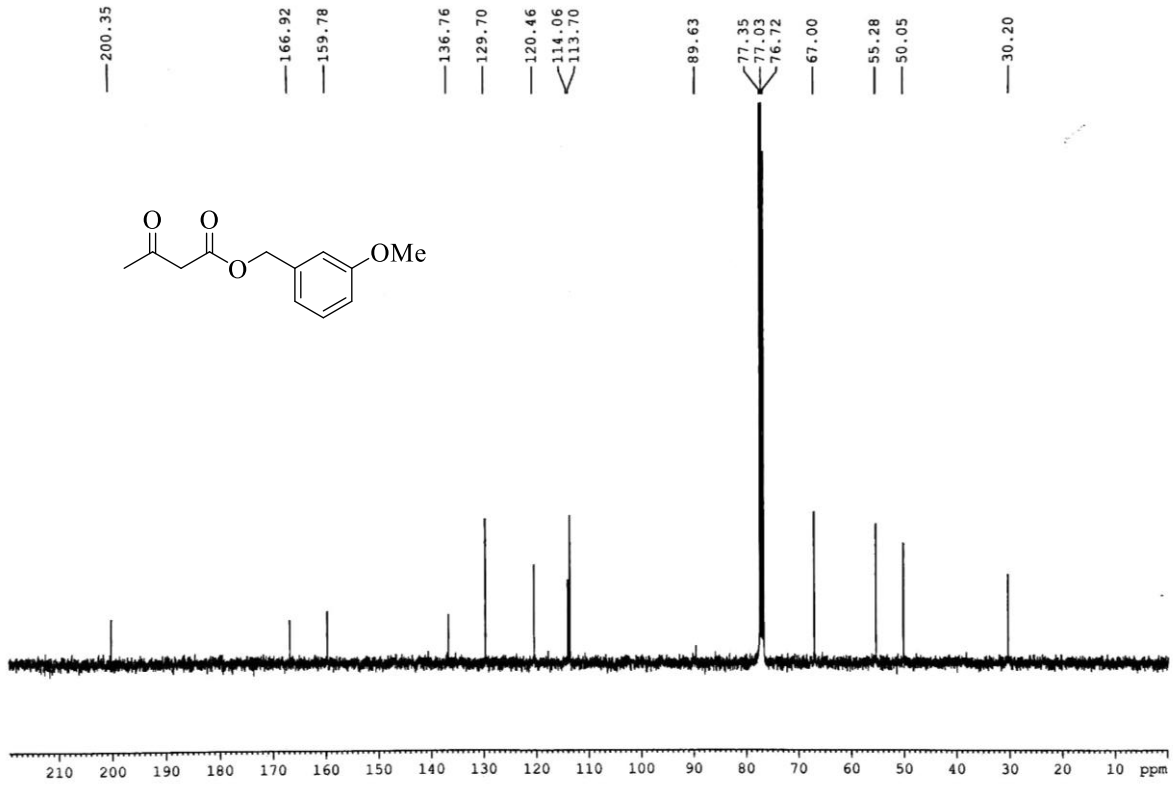
^{13}C NMR of **3a** (100 MHz, $CDCl_3$)



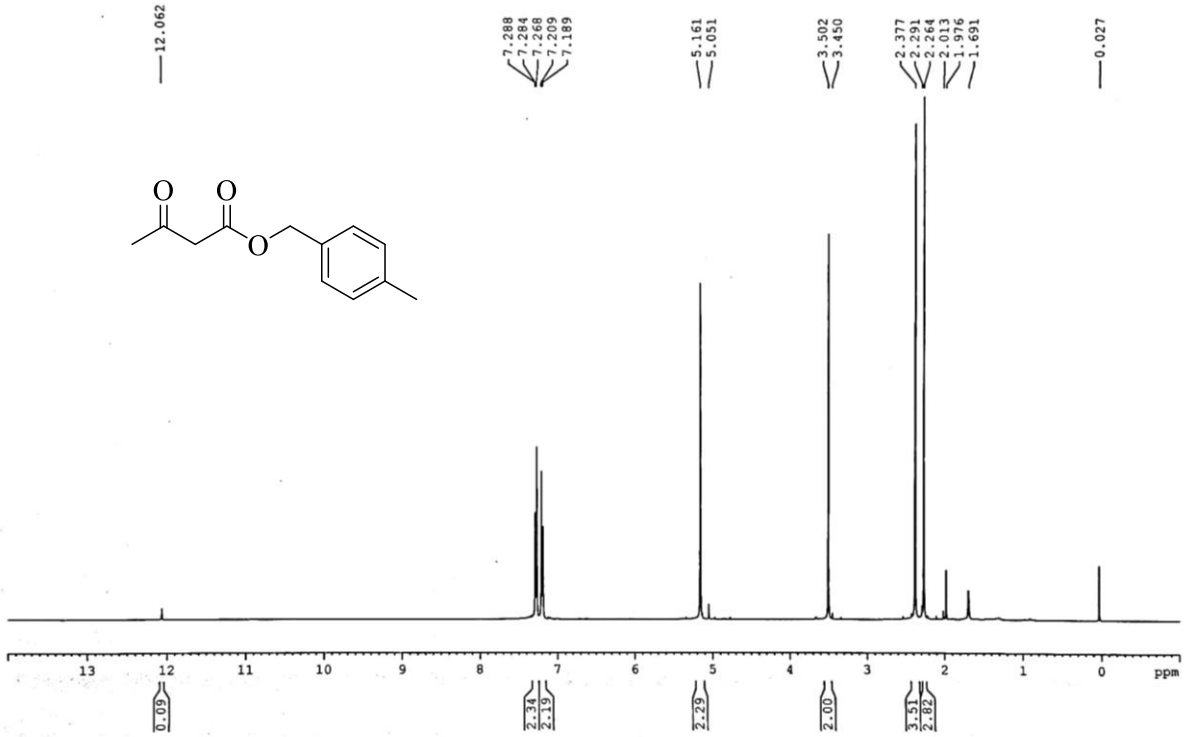
^{1}H NMR of **3b** (400 MHz, $CDCl_3$)



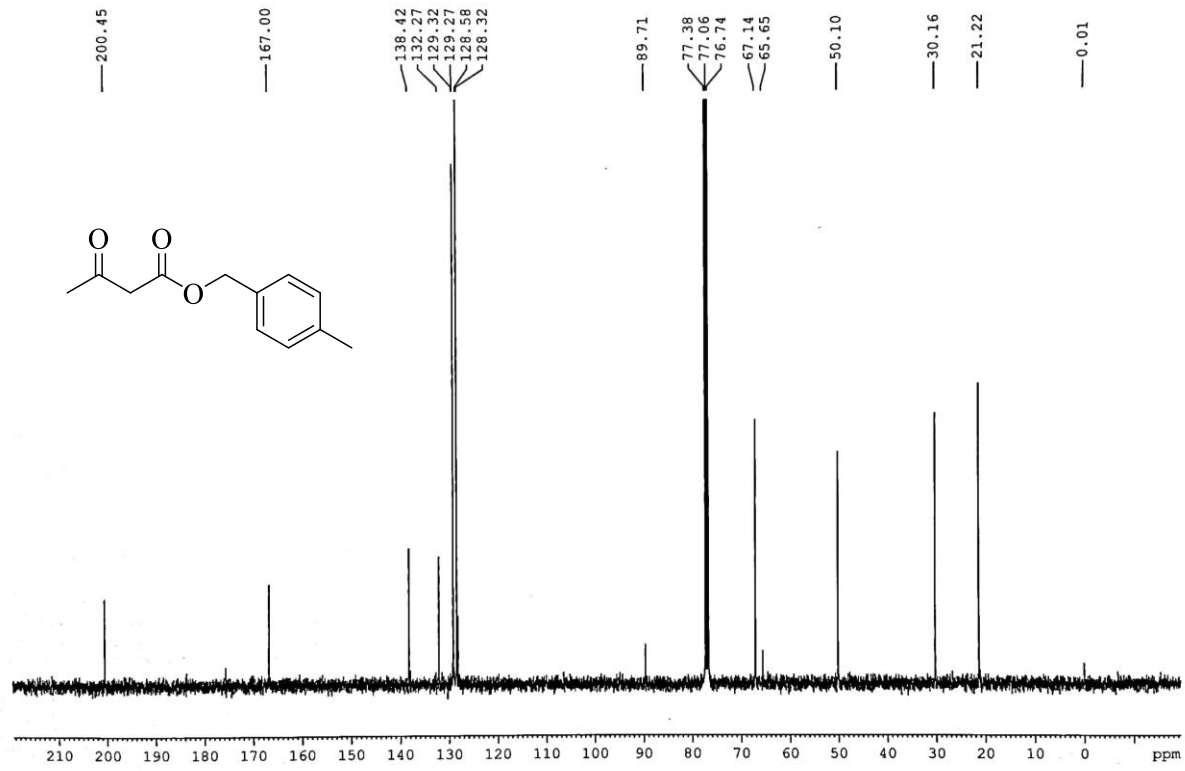
^{13}C NMR of **3b** (100 MHz, $CDCl_3$)



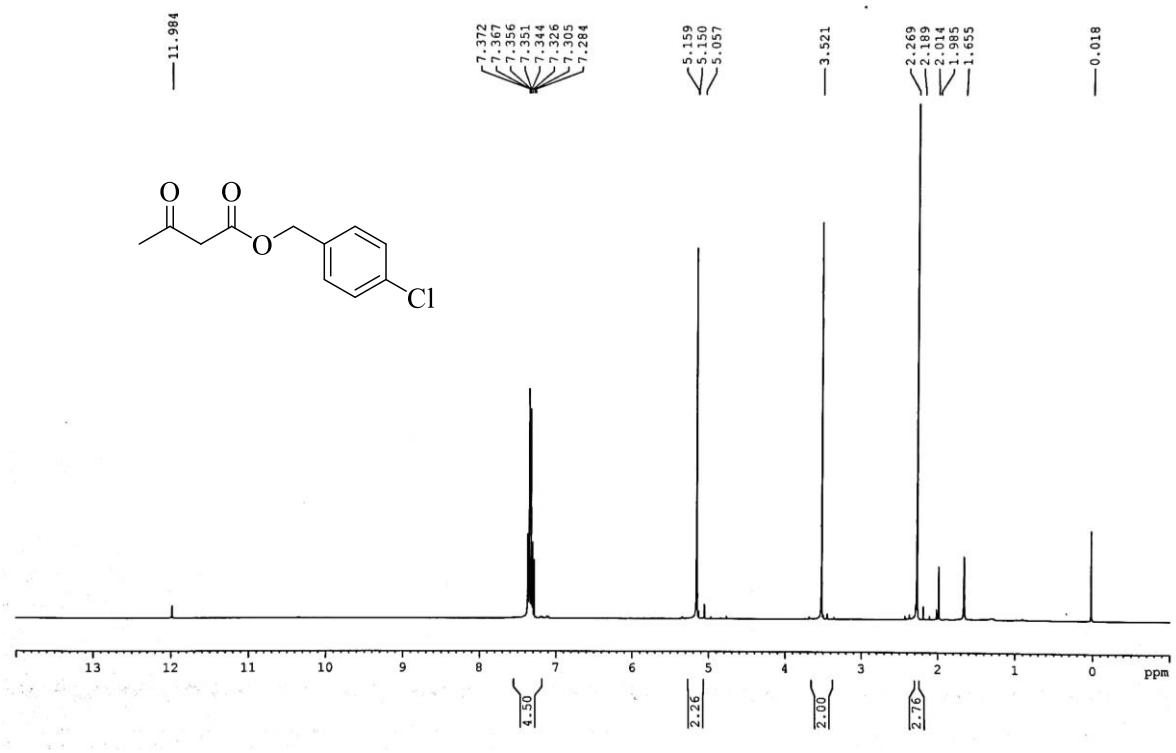
^{1}H NMR of **3c** (400 MHz, $CDCl_3$)



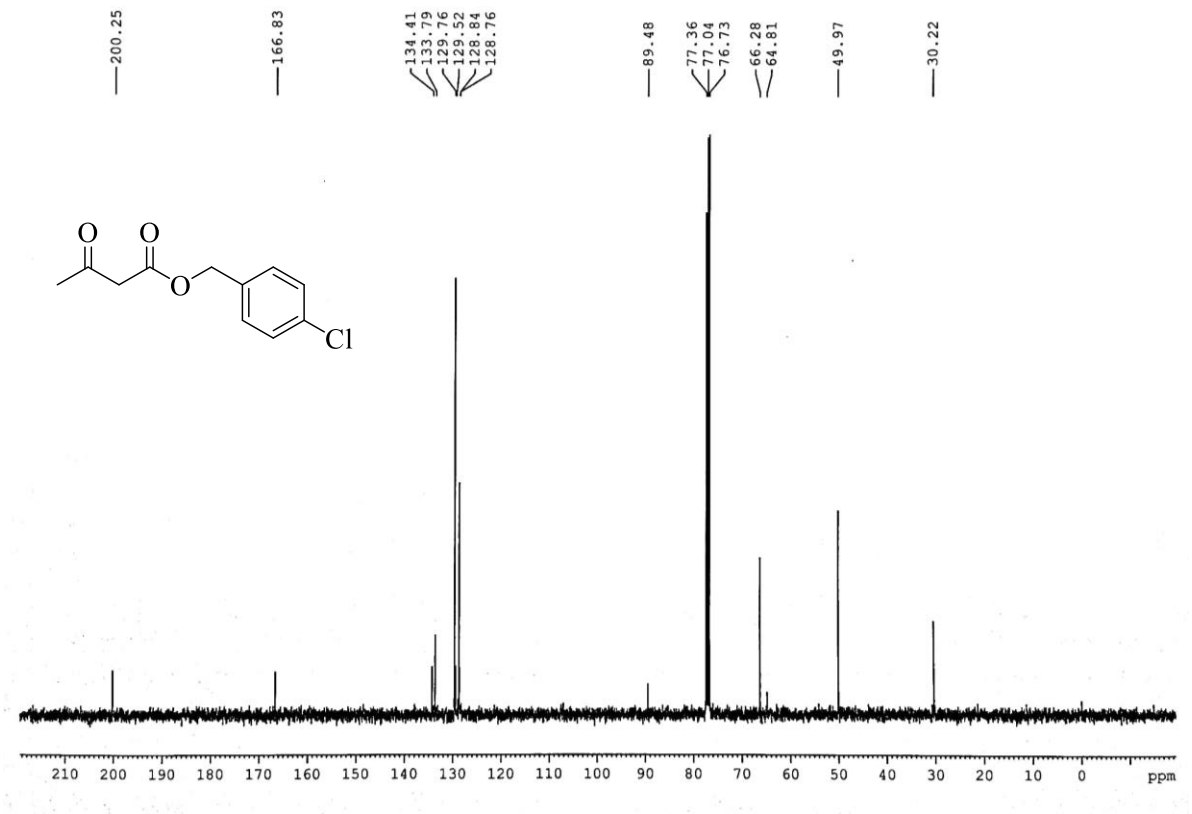
^{13}C NMR of **3c** (100 MHz, $CDCl_3$)



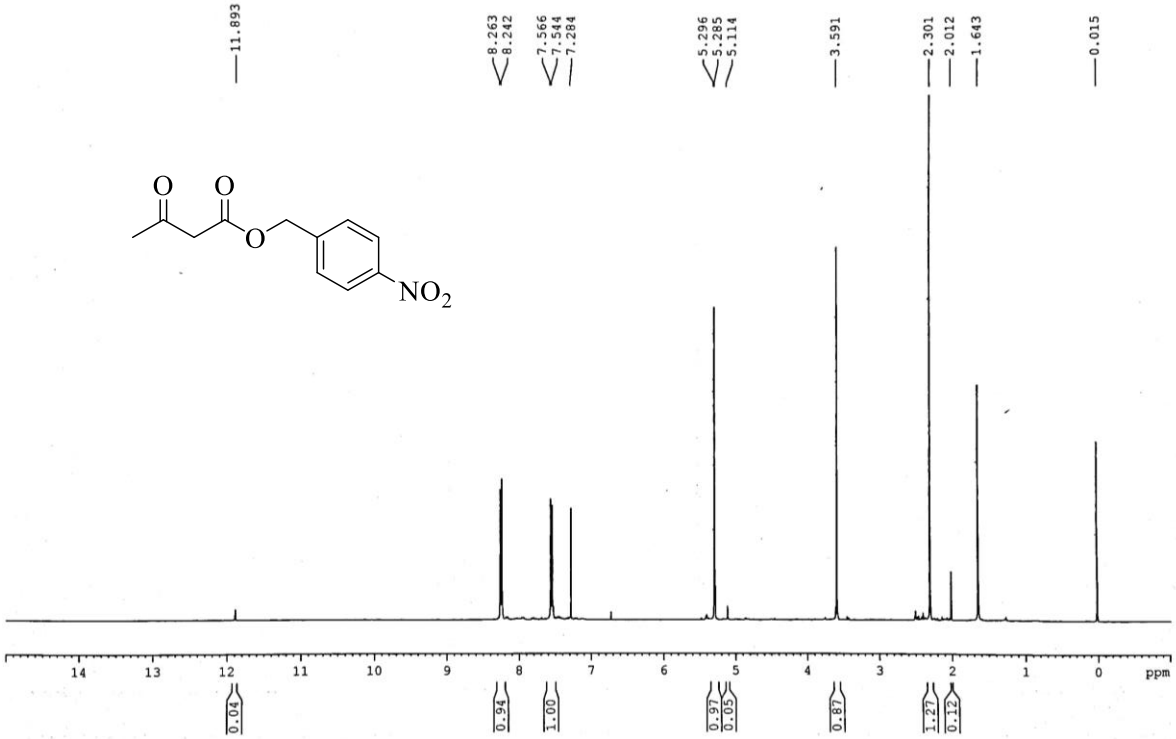
^{1}H NMR of **3d** (400 MHz, $CDCl_3$)



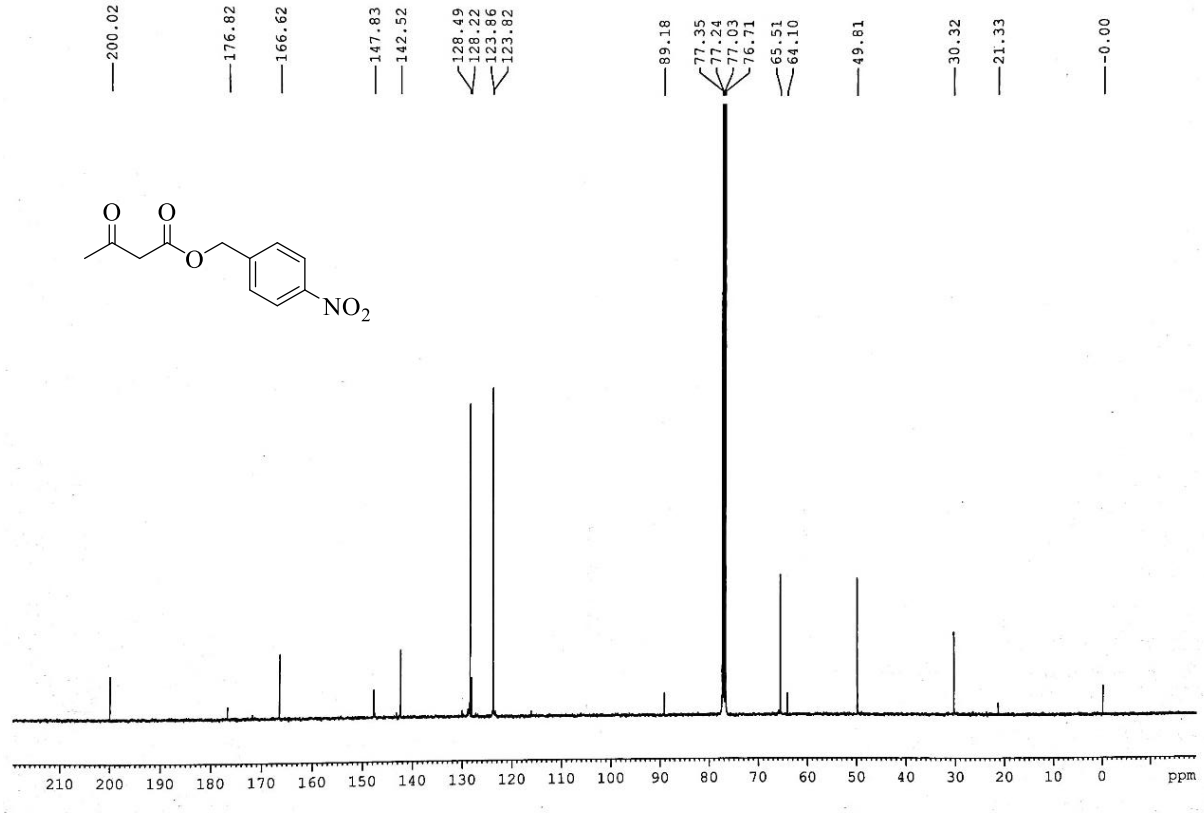
^{13}C NMR of **3d** (100 MHz, $CDCl_3$)



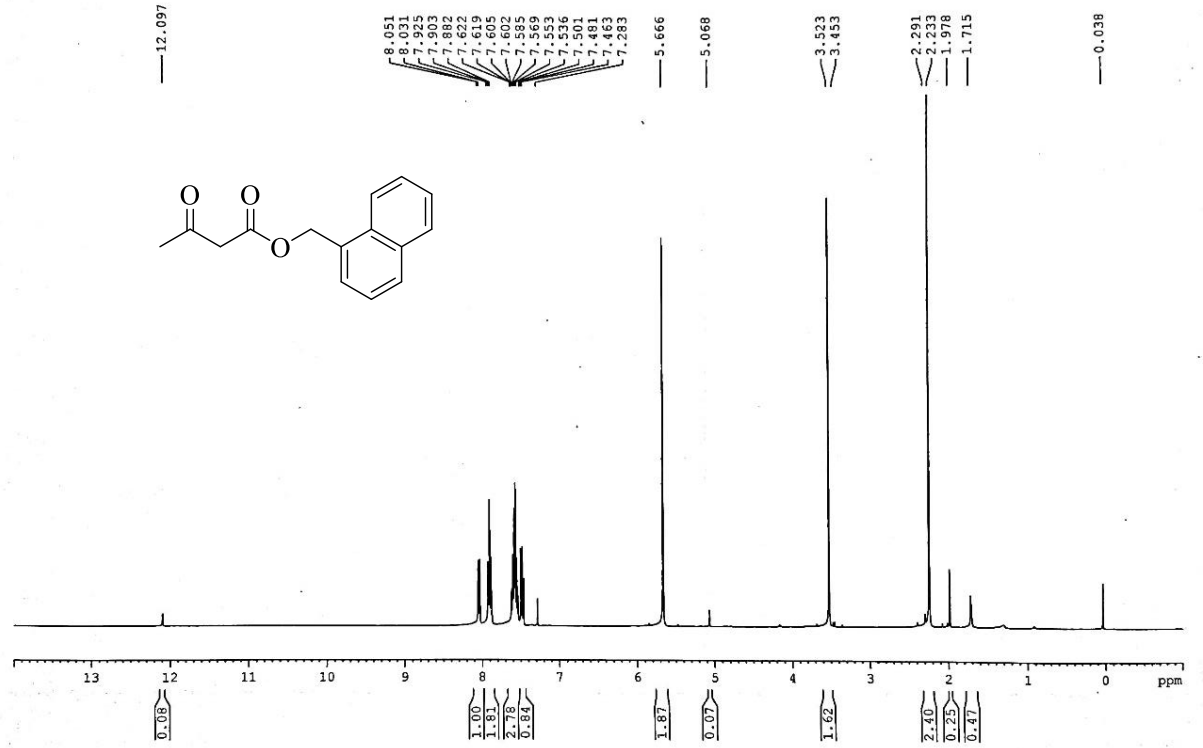
^{1}H NMR of **3e** (400 MHz, $CDCl_3$)



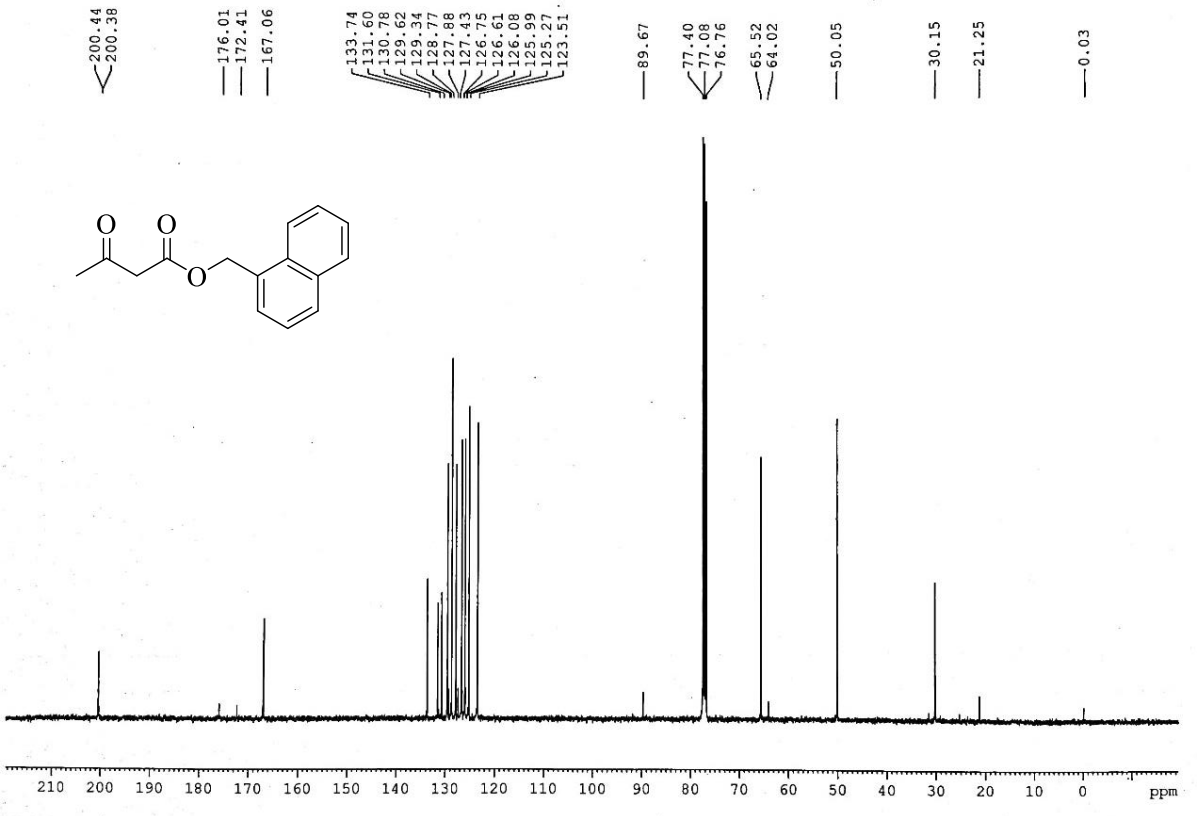
^{13}C NMR of **3e** (100 MHz, $CDCl_3$)



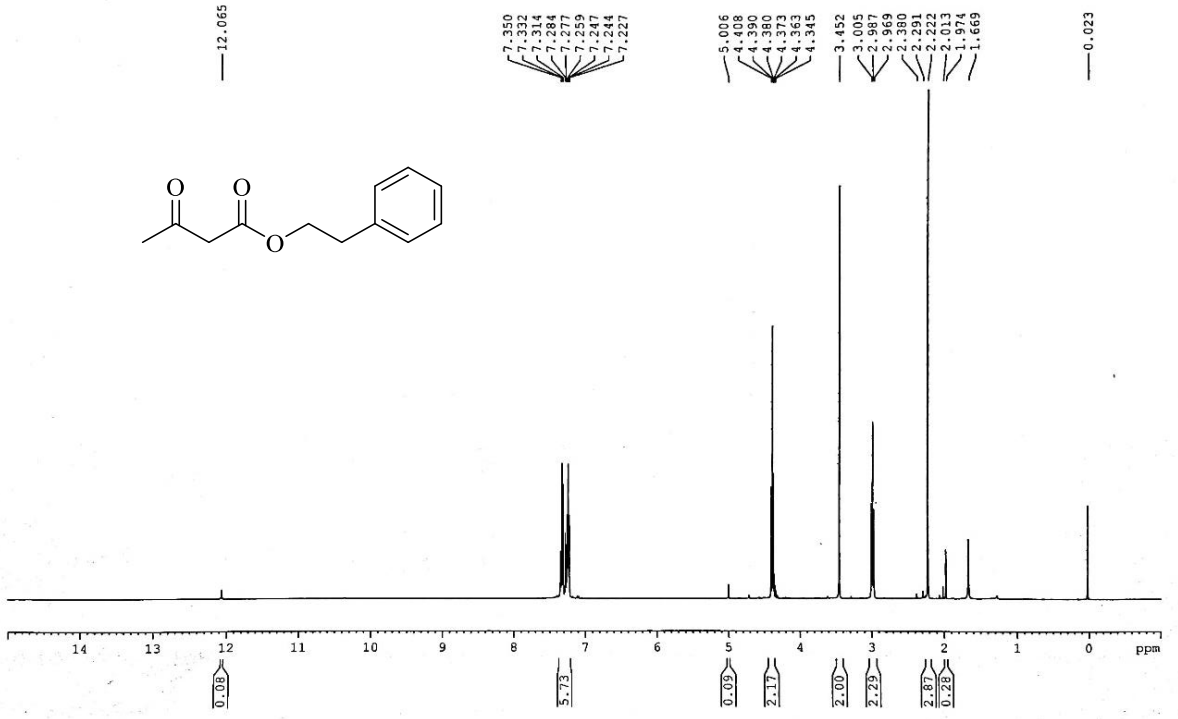
^{1}H NMR of **3f** (400 MHz, $CDCl_3$)



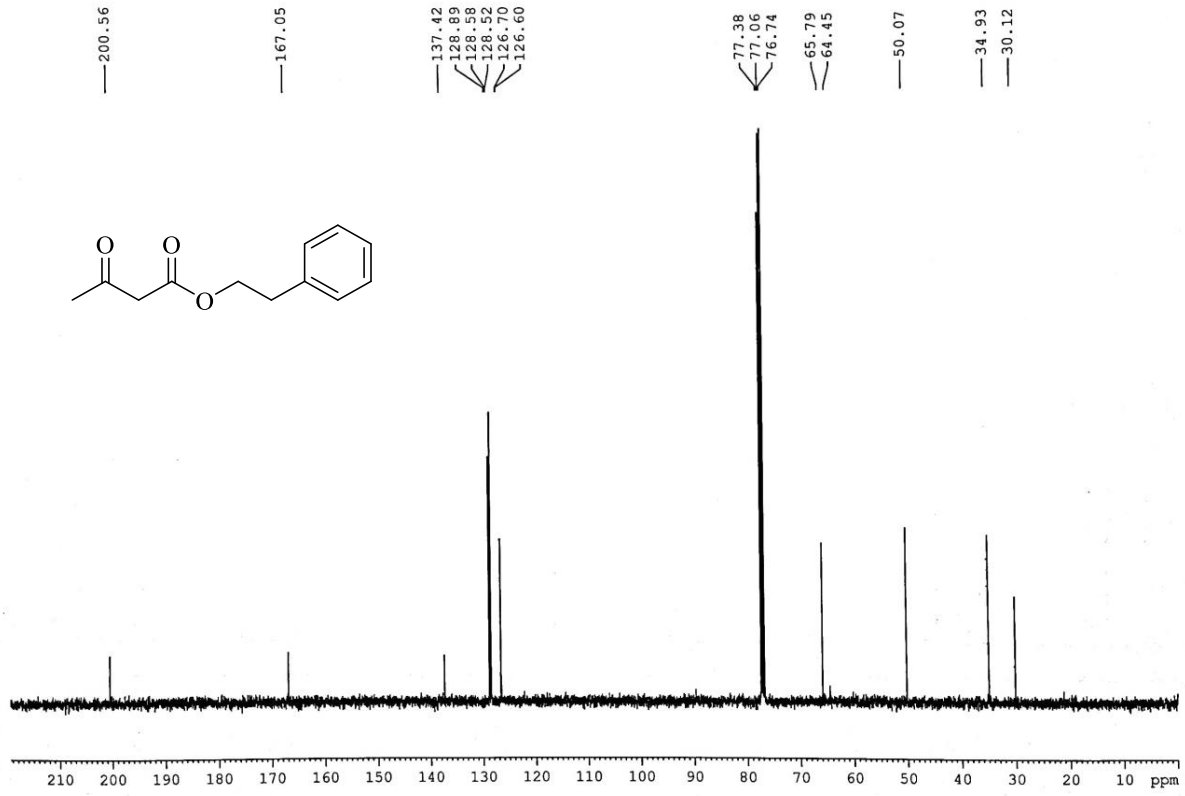
^{13}C NMR of **3f** (100 MHz, $CDCl_3$)



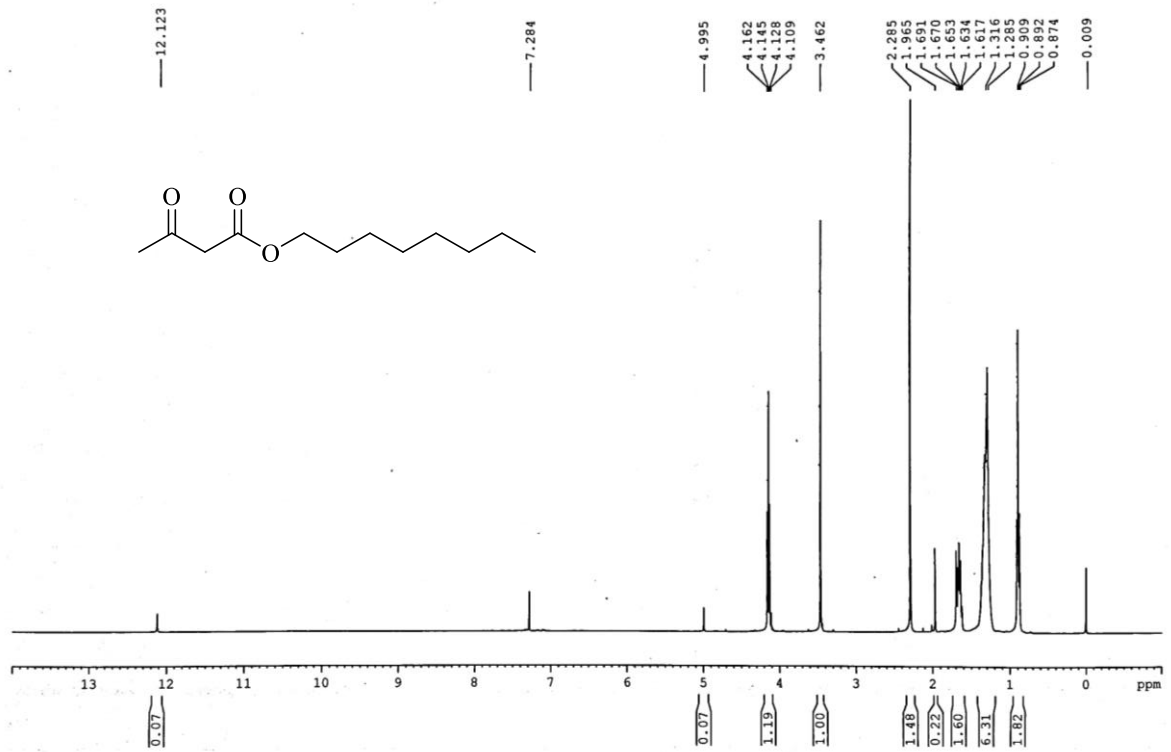
^{1}H NMR of **3g** (400 MHz, $CDCl_3$)



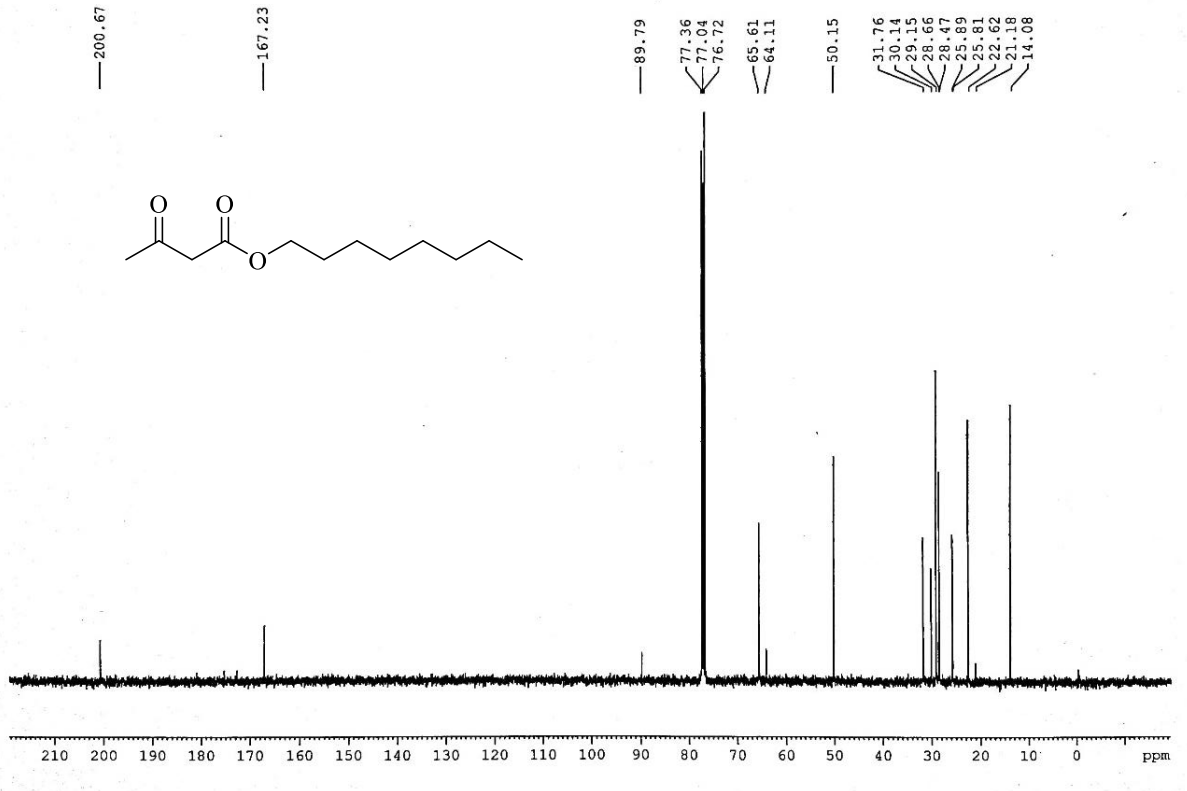
^{13}C NMR of **3g** (100 MHz, $CDCl_3$)



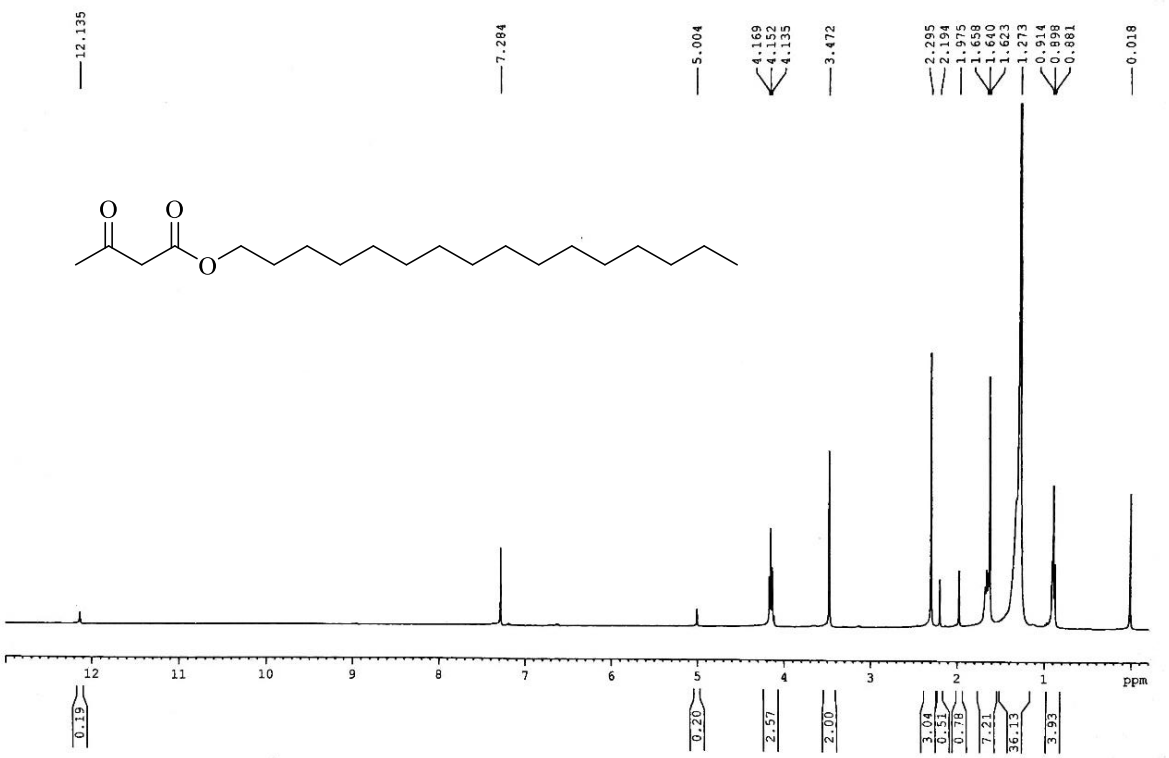
^{1}H NMR of **3h** (400 MHz, $CDCl_3$)



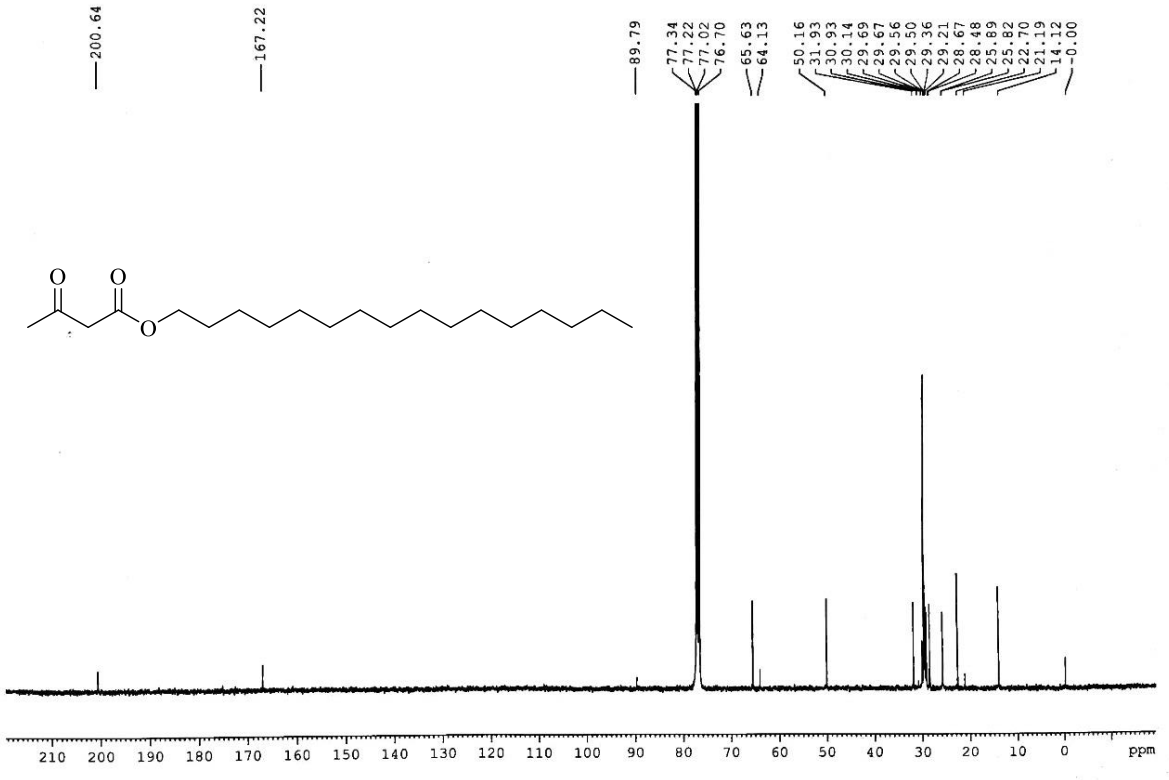
^{13}C NMR of **3h** (100 MHz, $CDCl_3$)



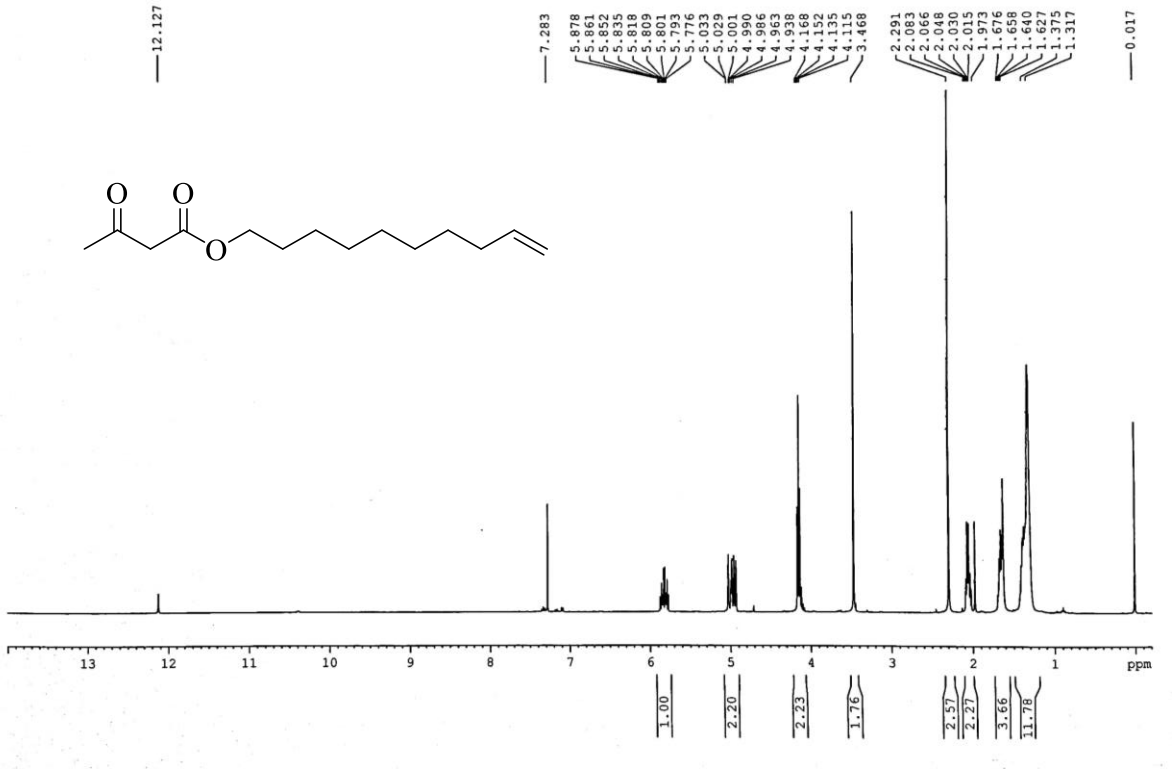
^{1}H NMR of **3i** (400 MHz, $CDCl_3$)



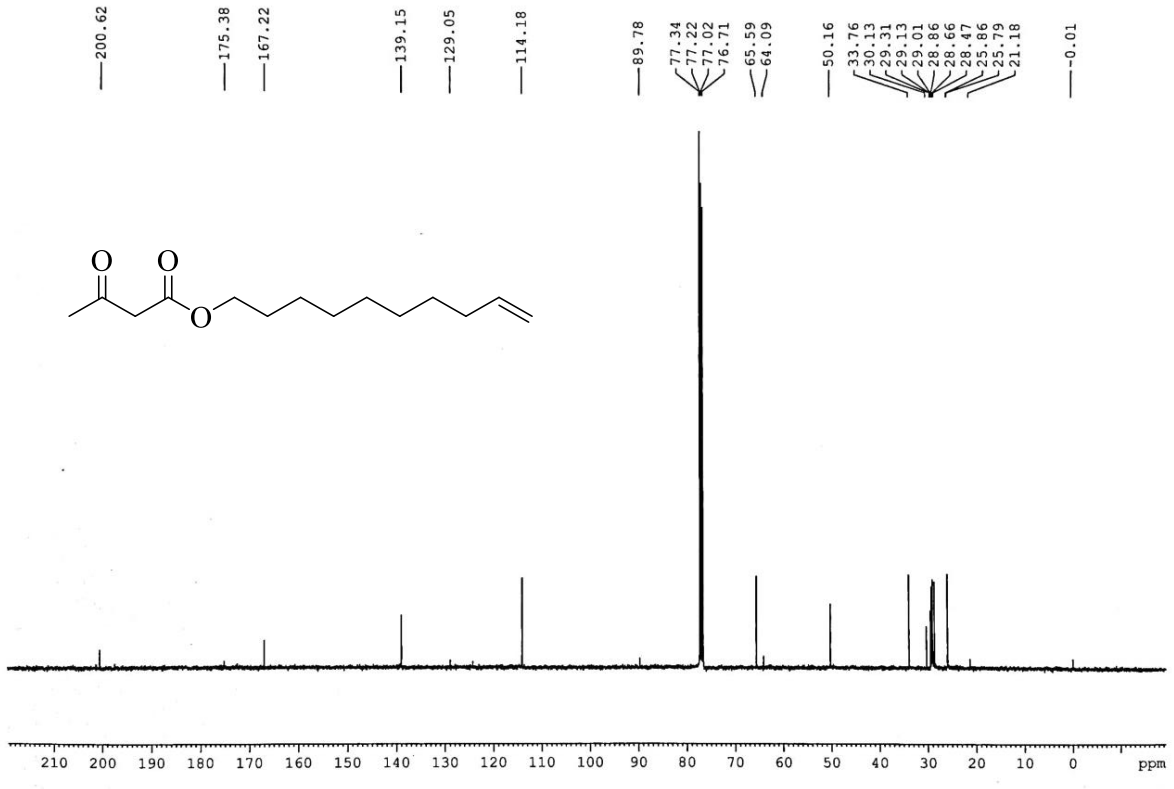
^{13}C NMR of **3i** (100 MHz, $CDCl_3$)



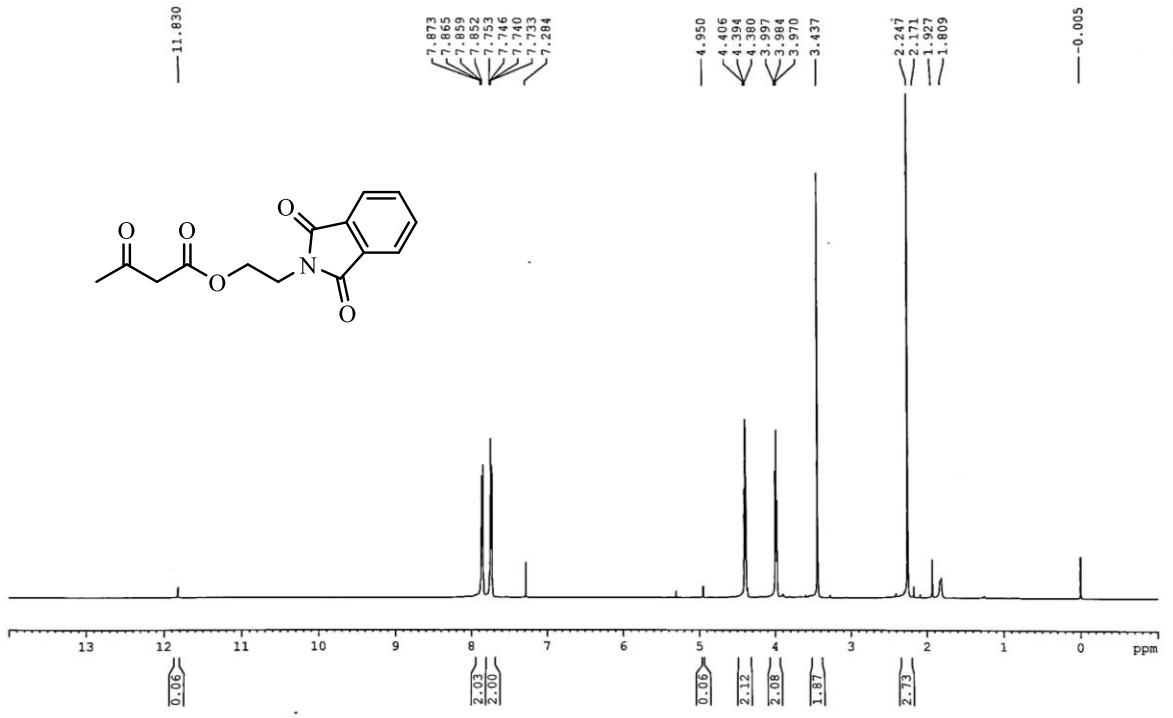
^{1}H NMR of **3j** (400 MHz, $CDCl_3$)



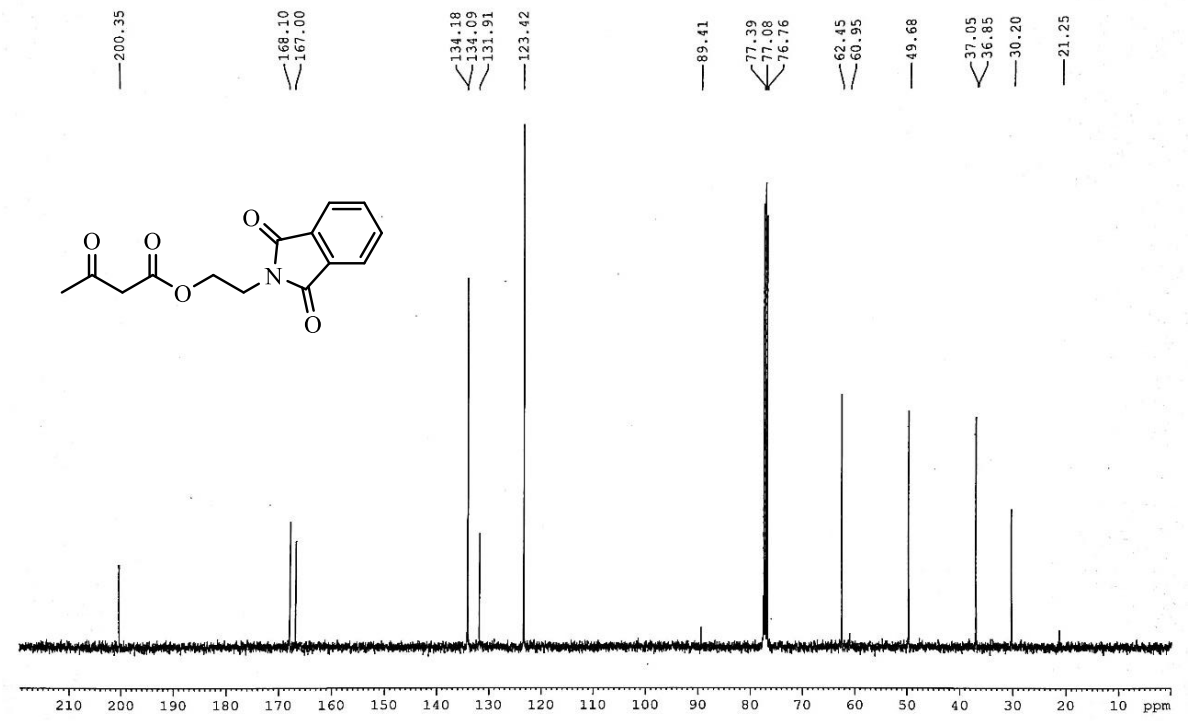
^{13}C NMR of **3j** (100 MHz, $CDCl_3$)



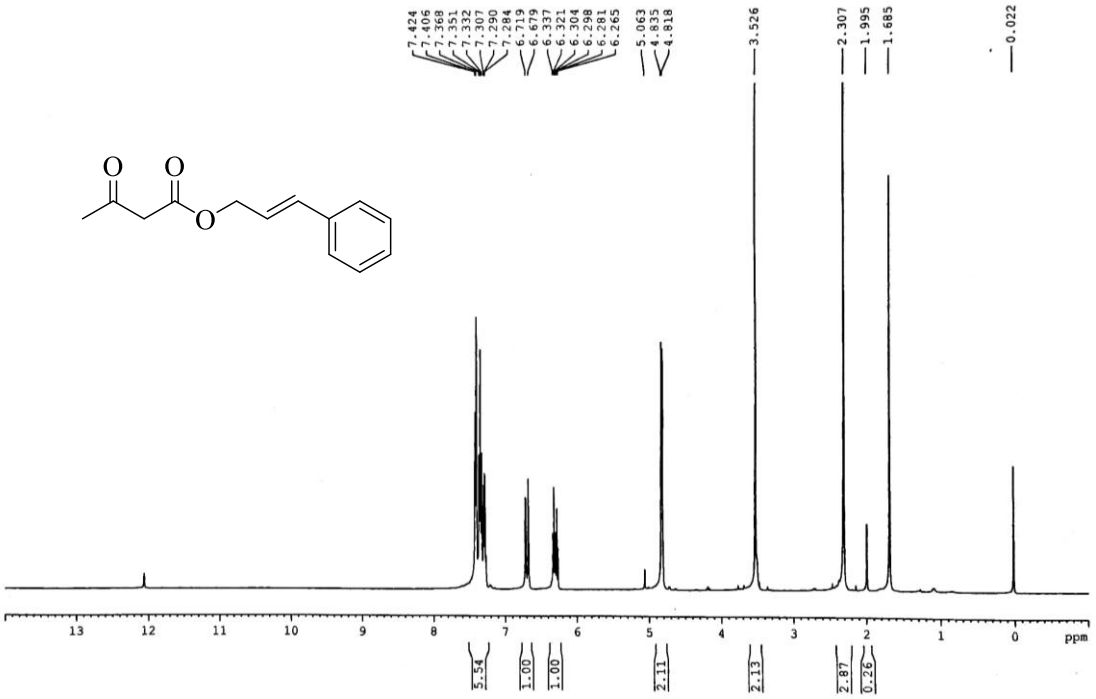
^{1}H NMR of **3k** (400 MHz, $CDCl_3$)



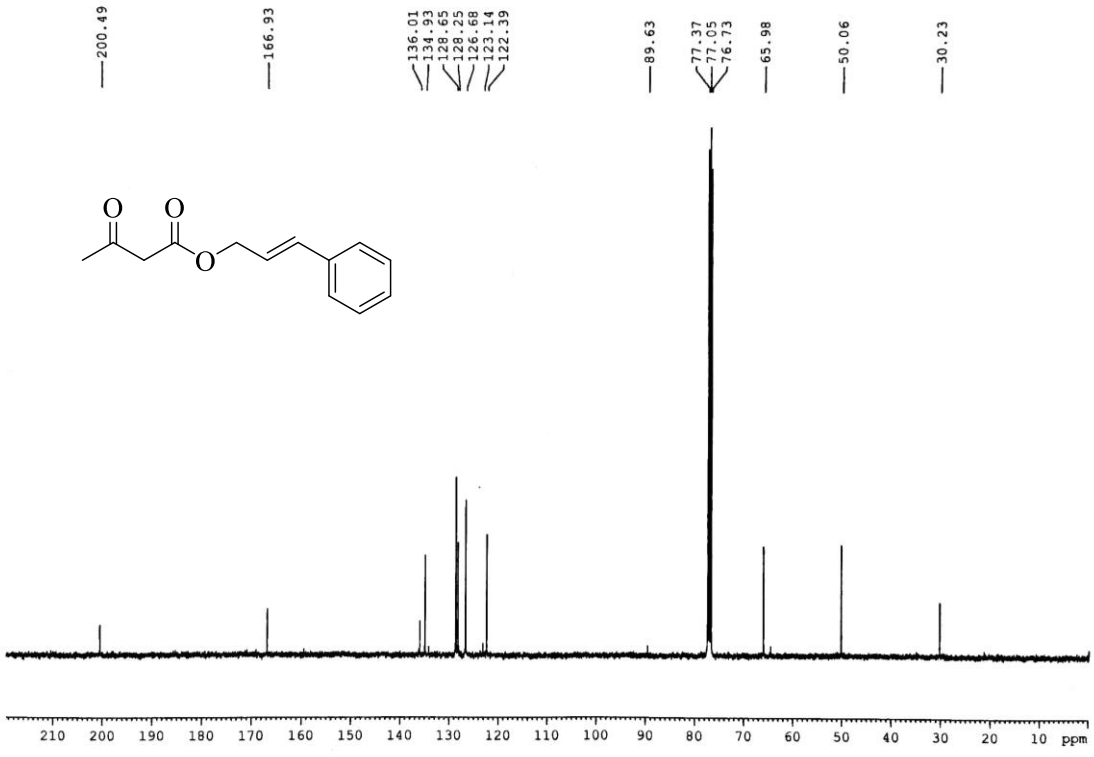
^{13}C NMR of **3k** (100 MHz, $CDCl_3$)



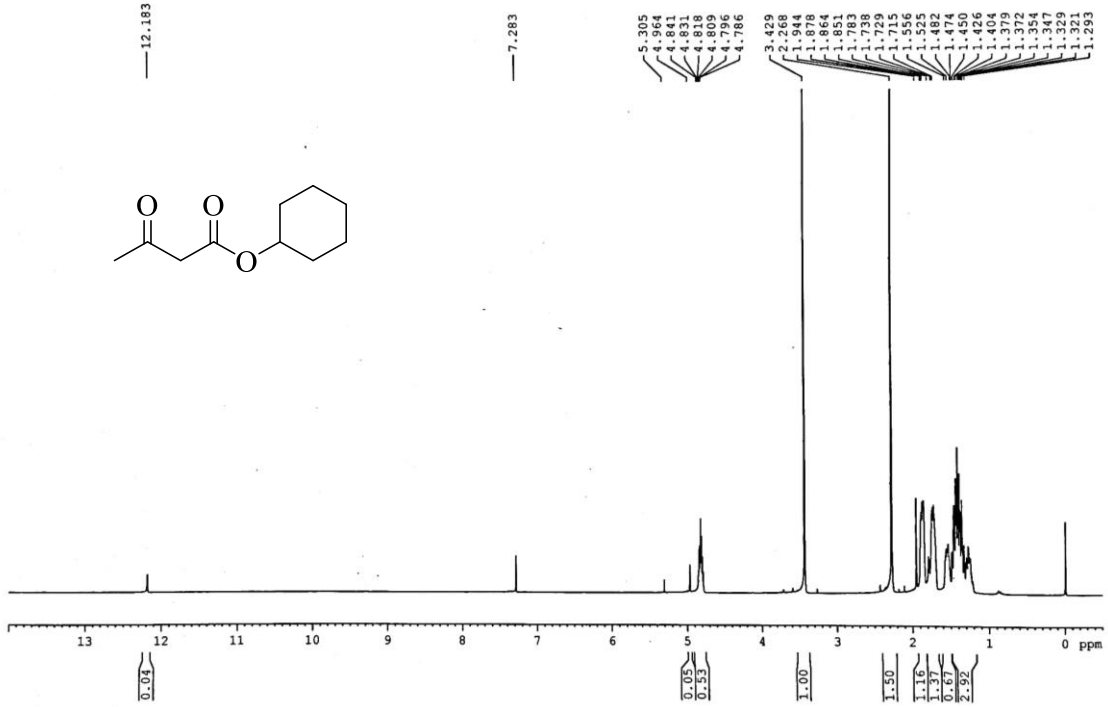
^{1}H NMR of **3l** (400 MHz, $CDCl_3$)



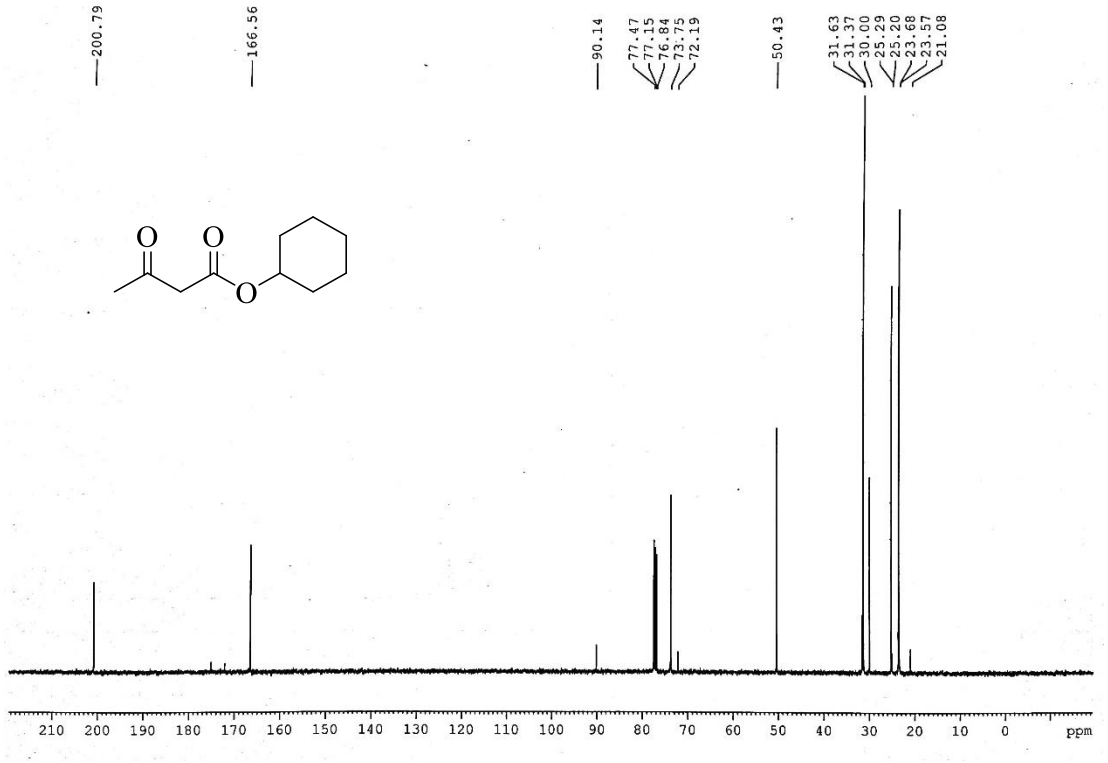
^{13}C NMR of **3l** (100 MHz, $CDCl_3$)



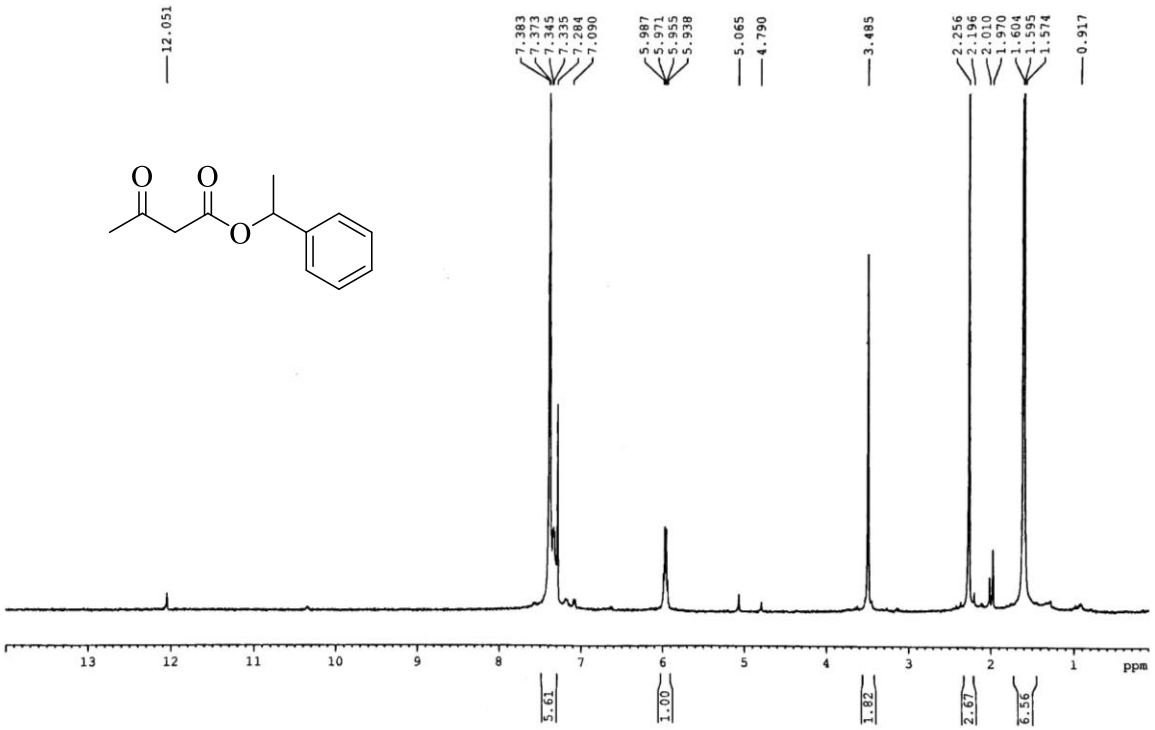
^{1}H NMR of **3m** (400 MHz, $CDCl_3$)



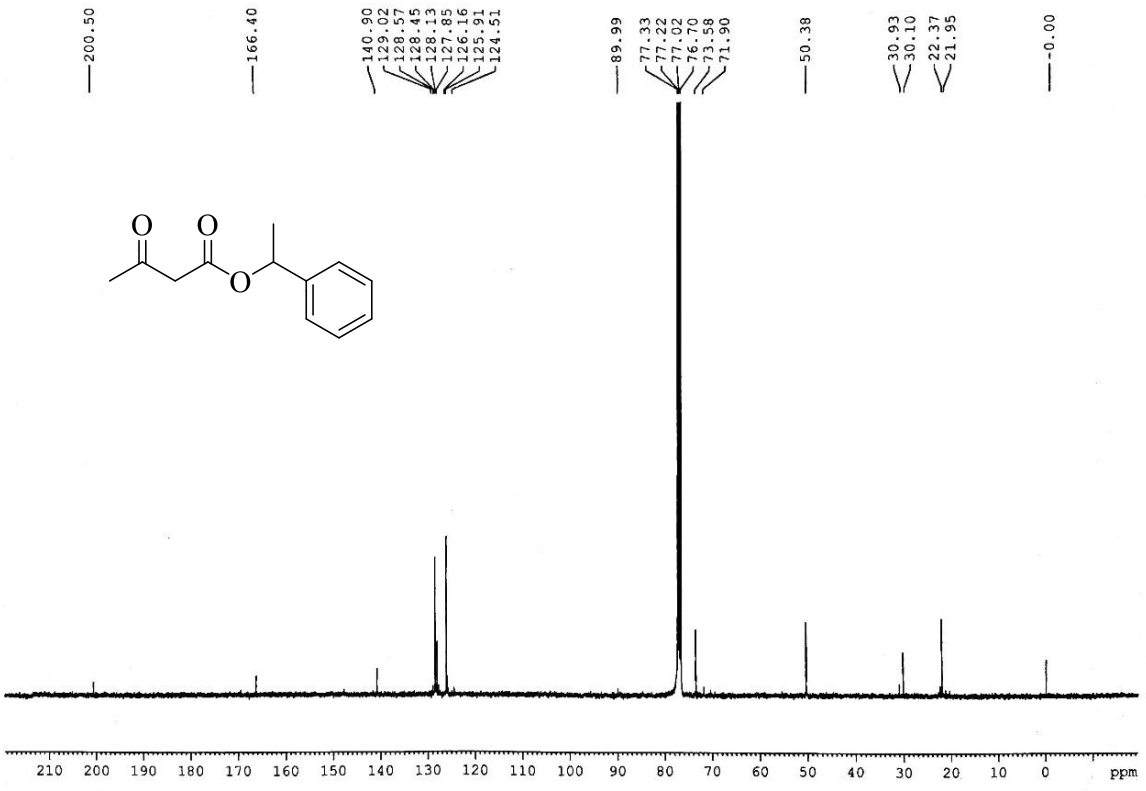
^{13}C NMR of **3m** (100 MHz, $CDCl_3$)



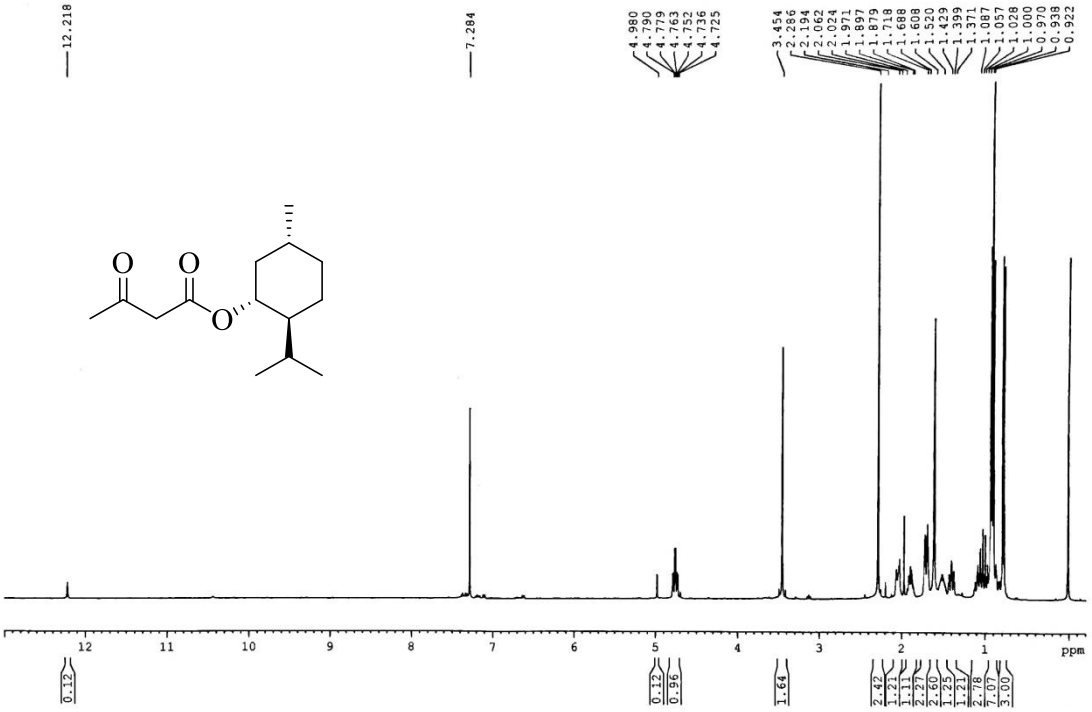
^{1}H NMR of **3n** (400 MHz, $CDCl_3$)



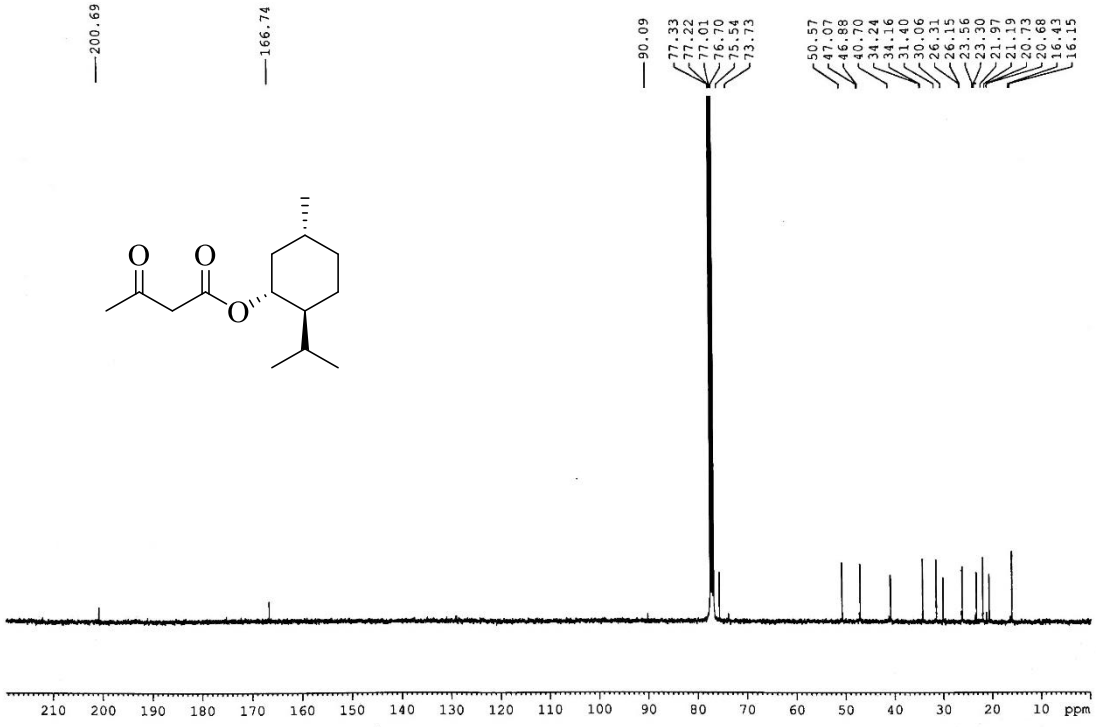
^{13}C NMR of **3n** (100 MHz, $CDCl_3$)



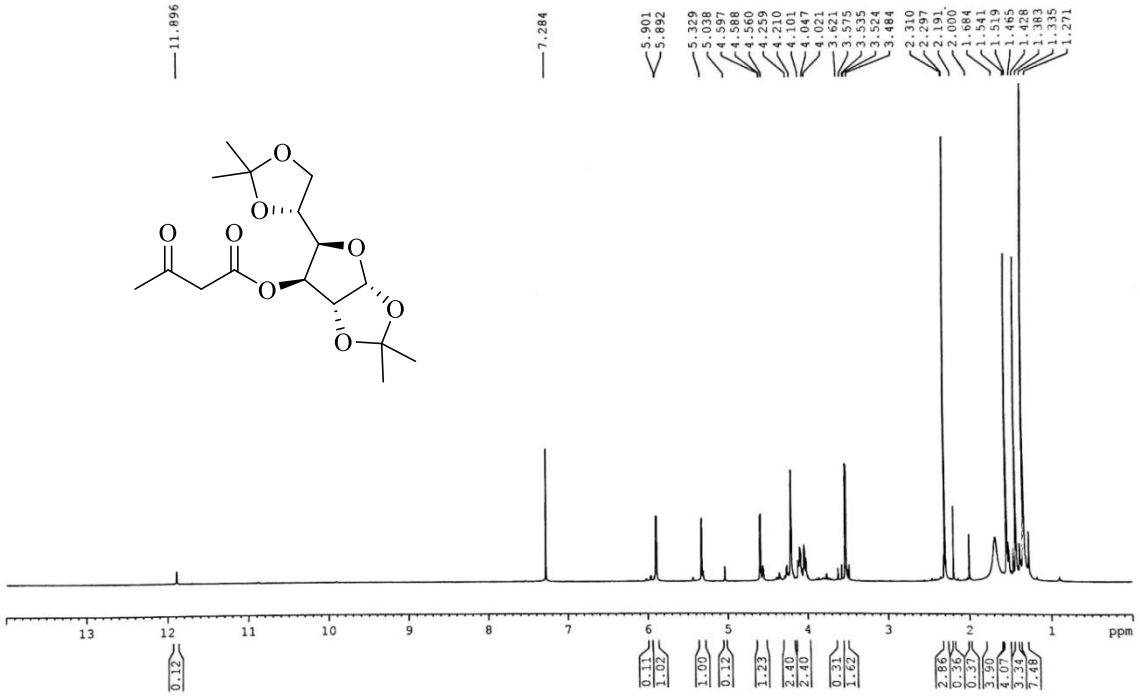
^{1}H NMR of **3o** (400 MHz, $CDCl_3$)



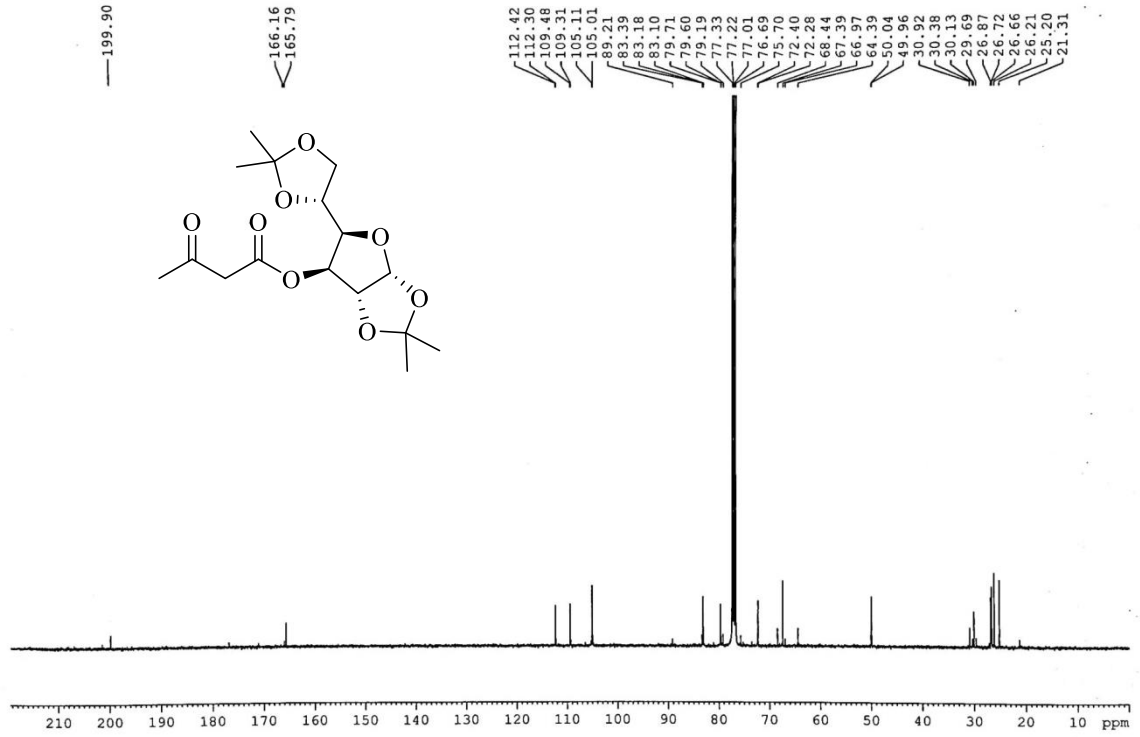
^{13}C NMR of **3o** (100 MHz, $CDCl_3$)



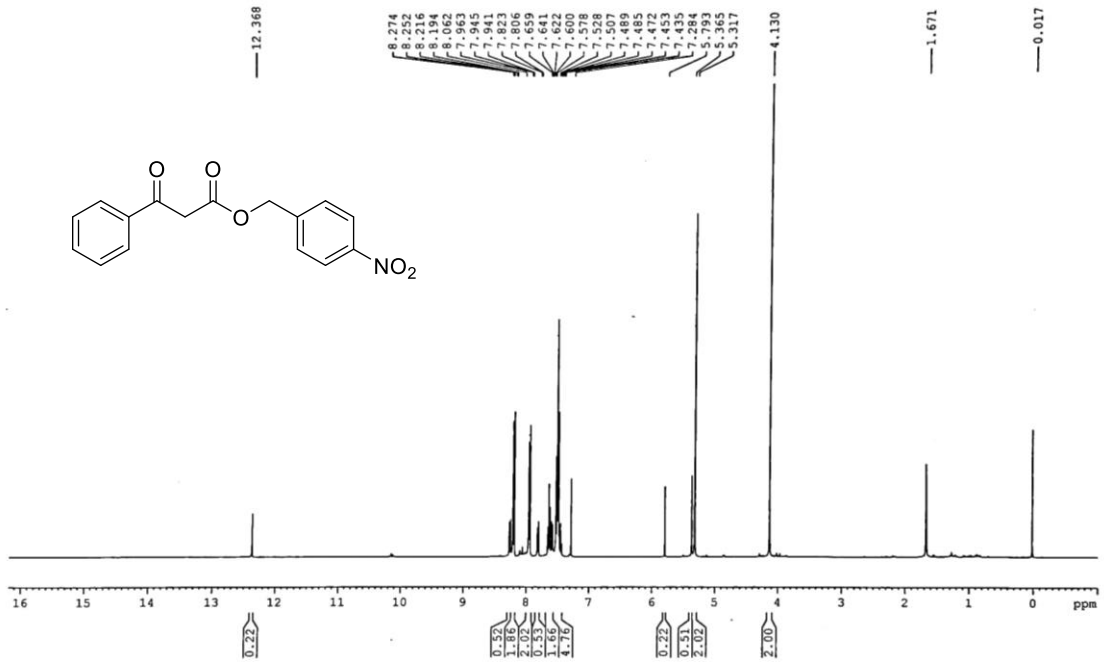
^{1}H NMR of **3p** (400 MHz, $CDCl_3$)



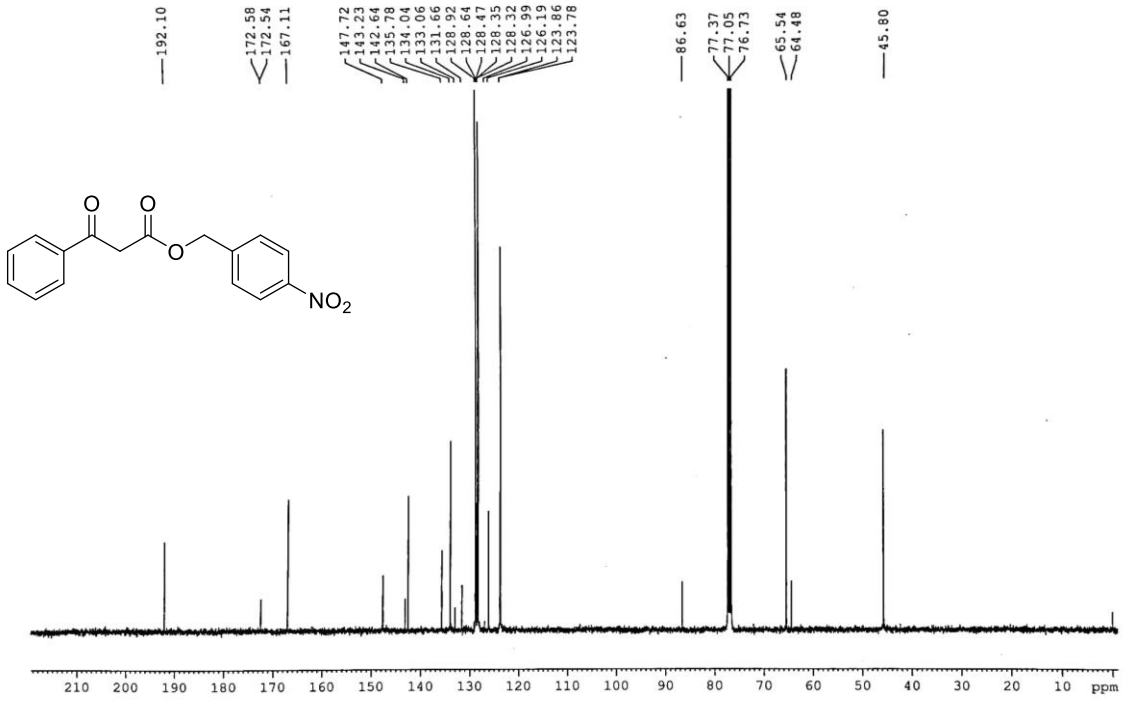
^{13}C NMR of **3p** (100 MHz, $CDCl_3$)



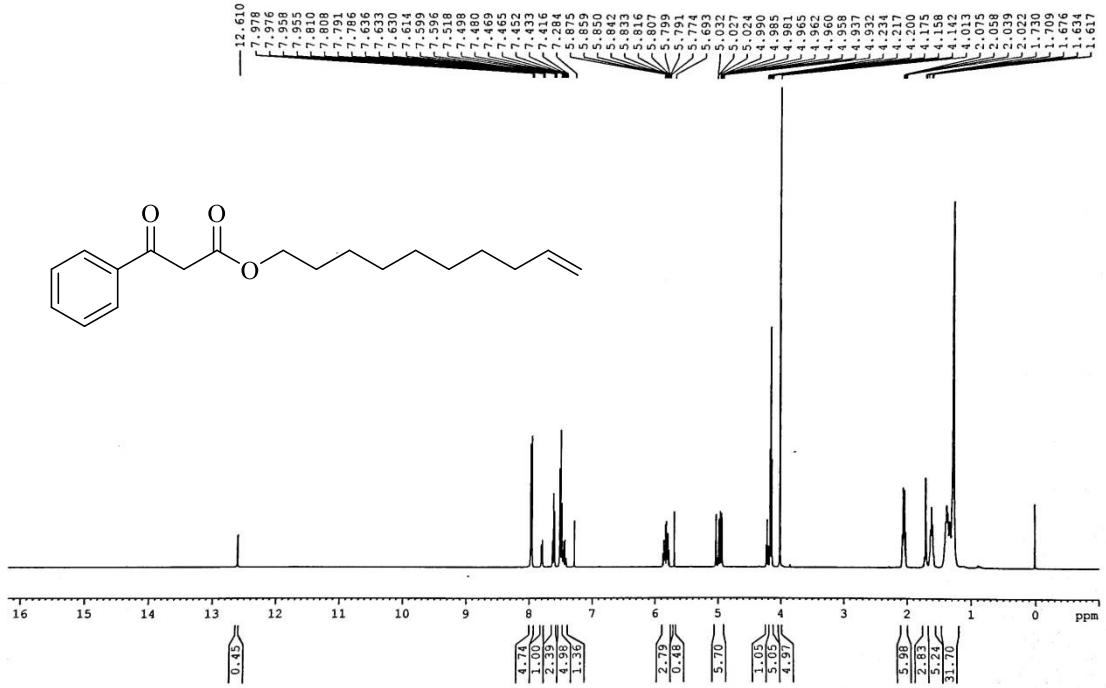
^{1}H NMR of **4a** (400 MHz, $CDCl_3$)



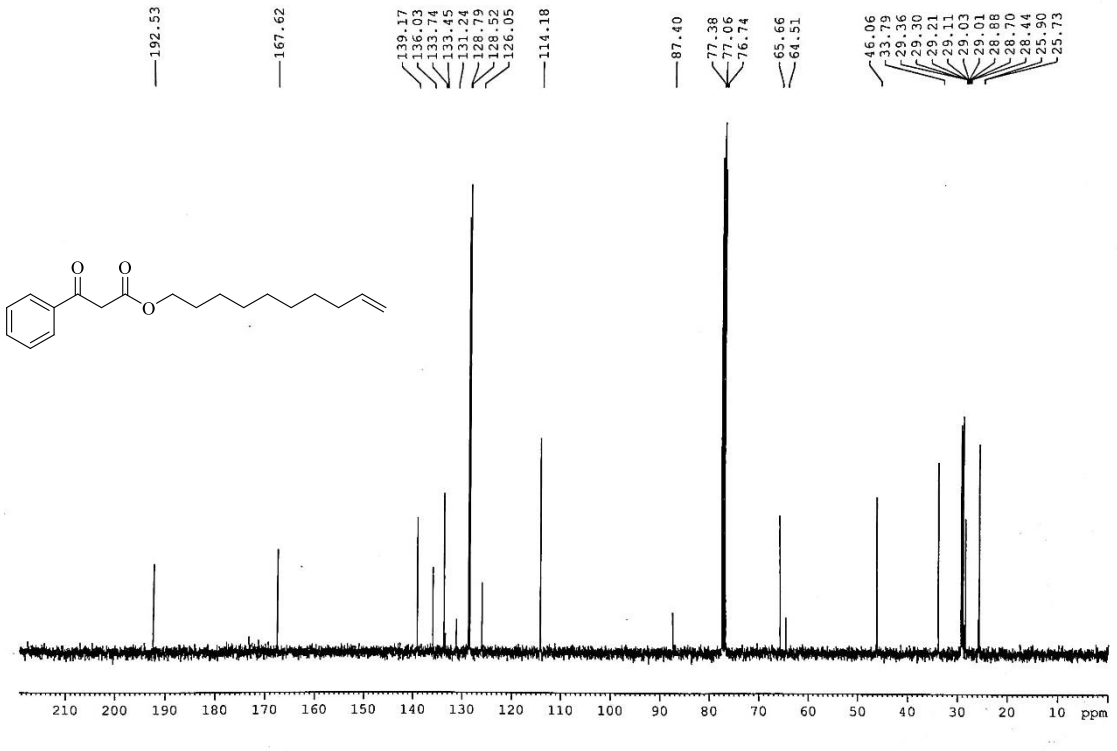
^{13}C NMR of **4a** (100 MHz, $CDCl_3$)



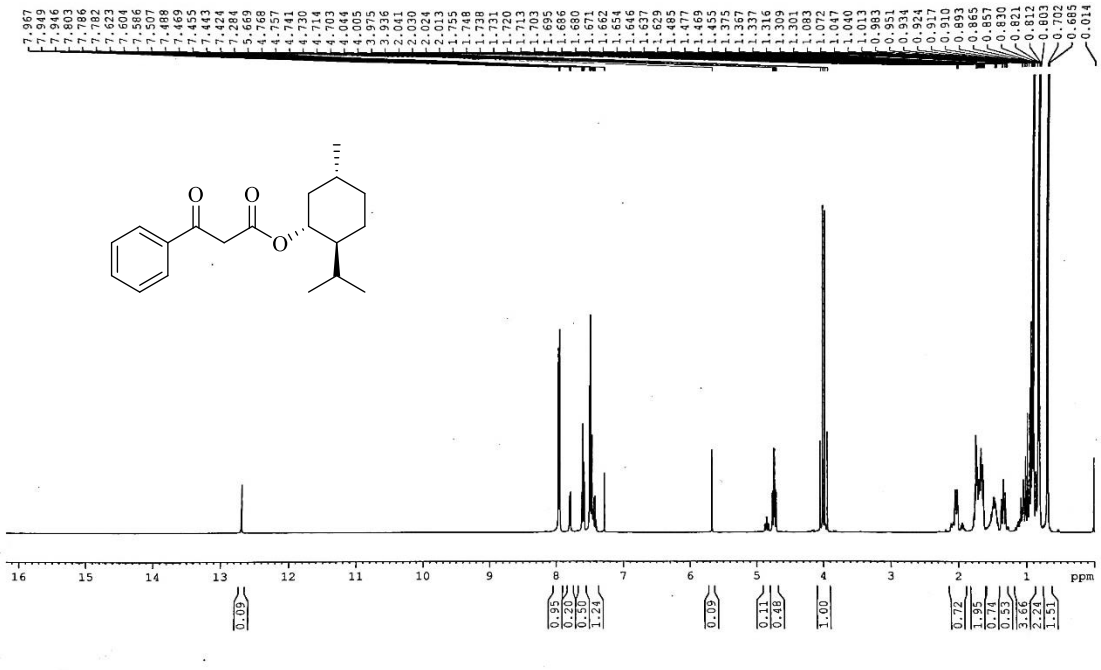
^{1}H NMR of **4b** (400 MHz, $CDCl_3$)



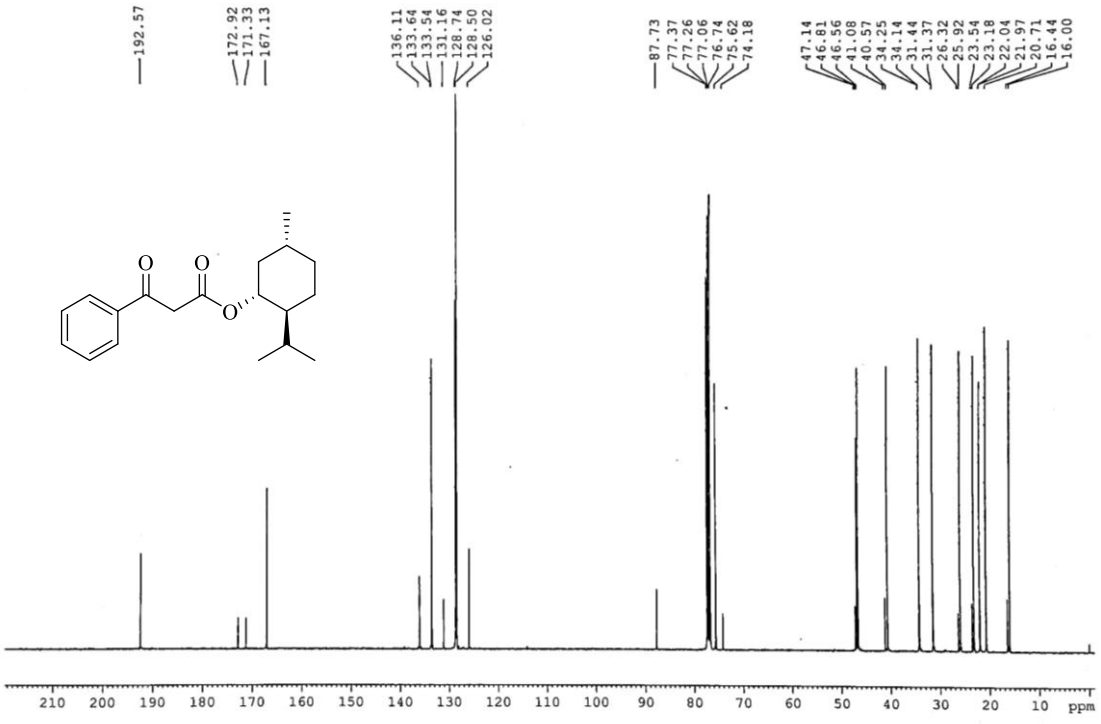
^{13}C NMR of **4b** (100 MHz, $CDCl_3$)



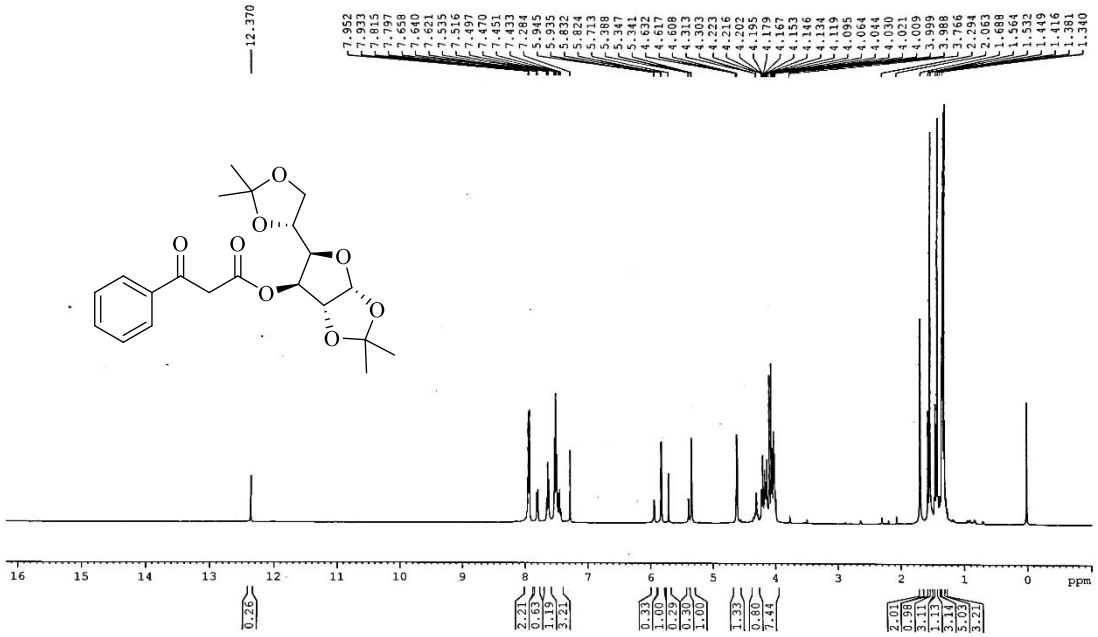
^{1}H NMR of **4c** (400 MHz, $CDCl_3$)



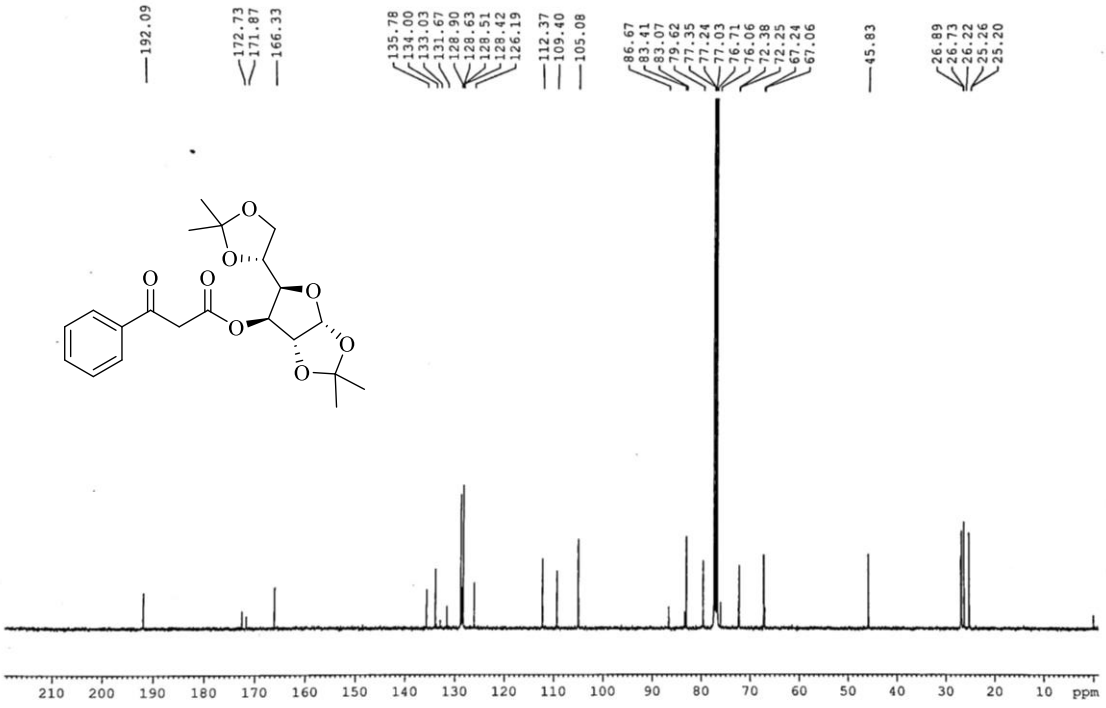
^{13}C NMR of **4c** (100 MHz, $CDCl_3$)



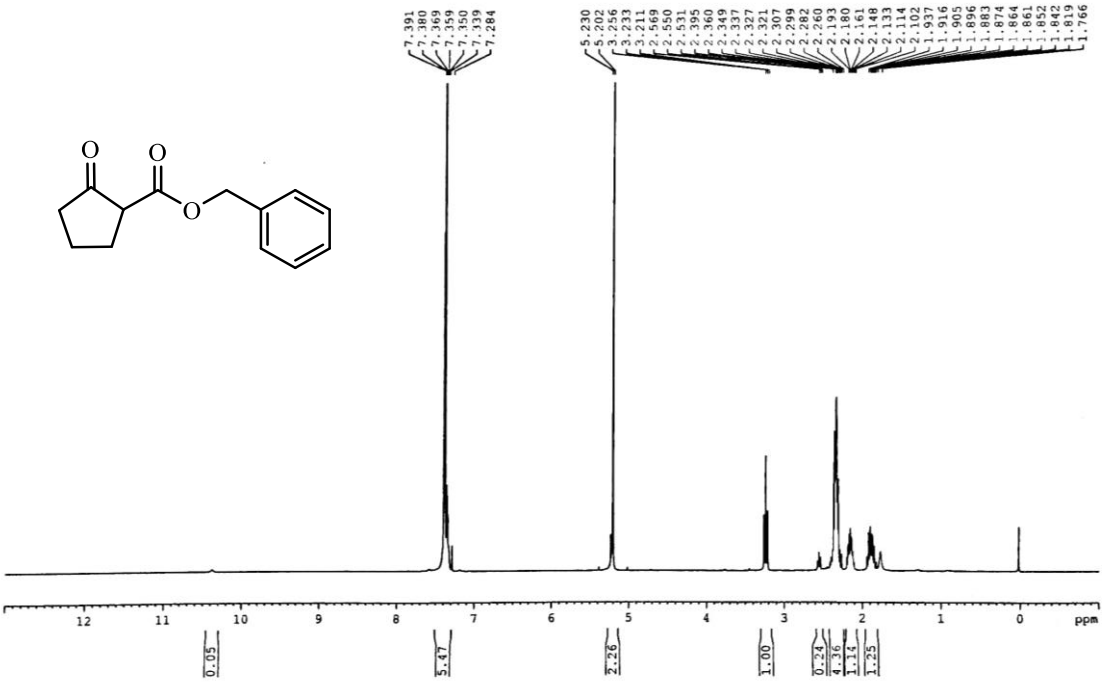
^{1}H NMR of **4d** (400 MHz, $CDCl_3$)



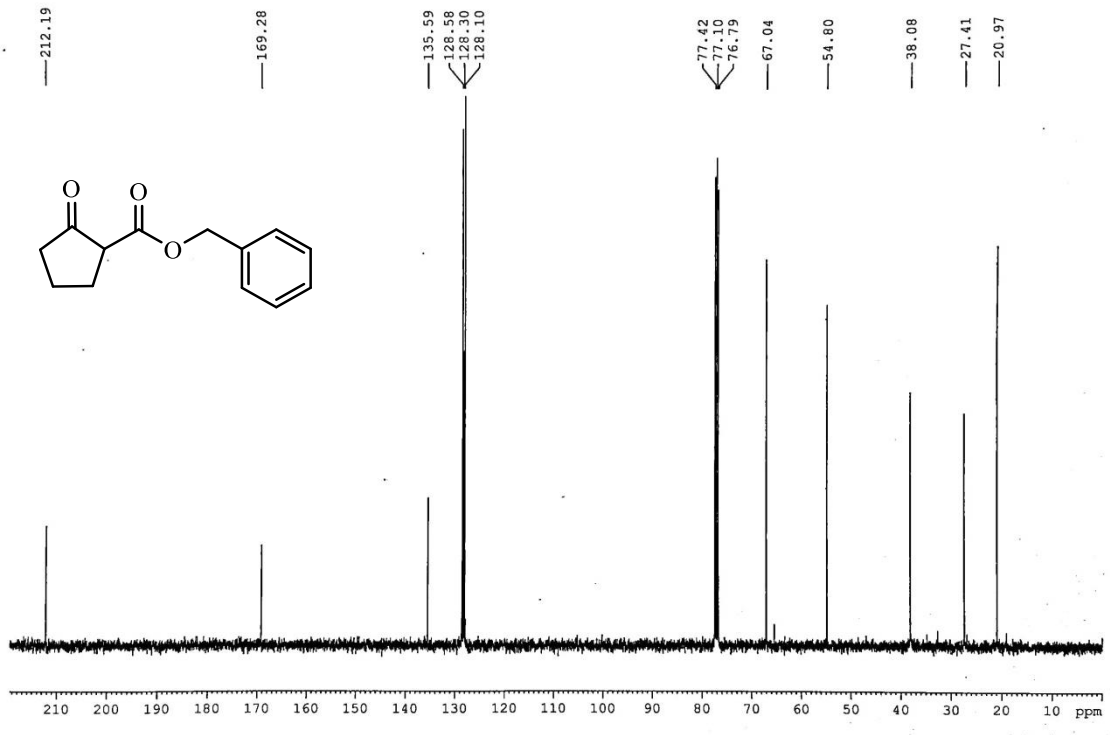
^{13}C NMR of **4d** (100 MHz, $CDCl_3$)



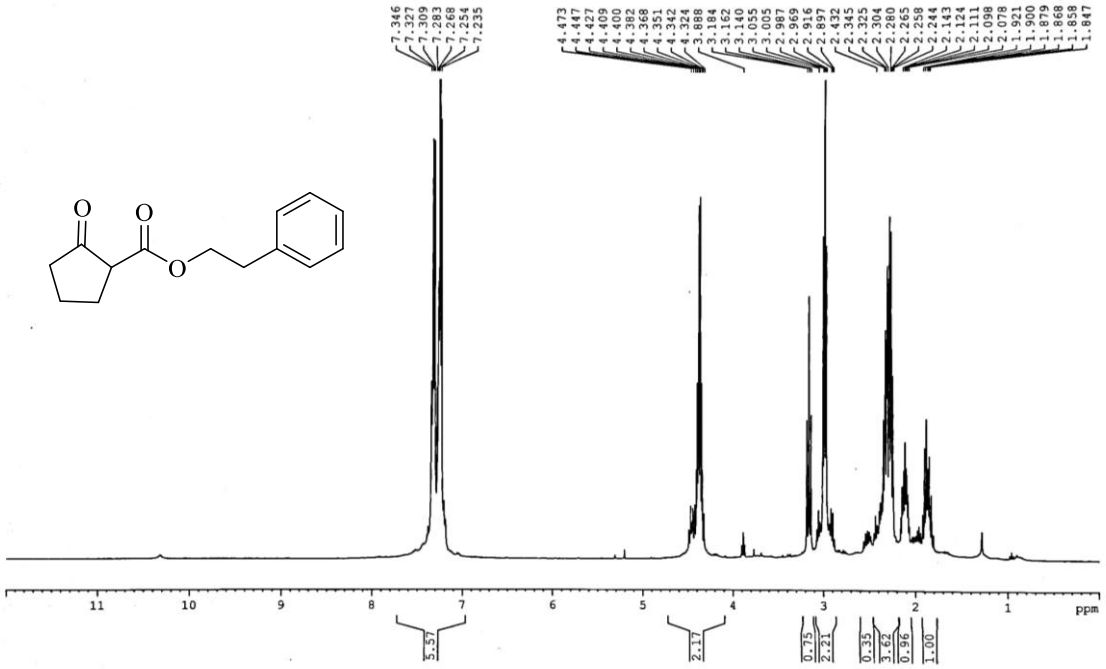
^{1}H NMR of **5a** (400 MHz, $CDCl_3$)



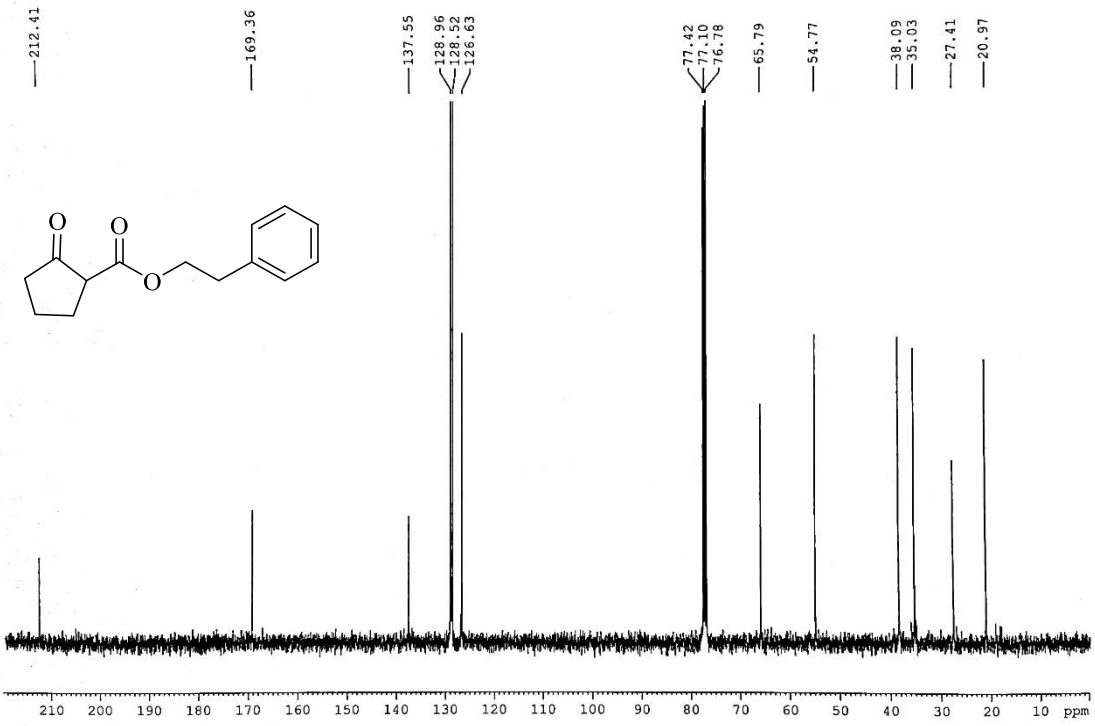
^{13}C NMR of **5a** (100 MHz, $CDCl_3$)



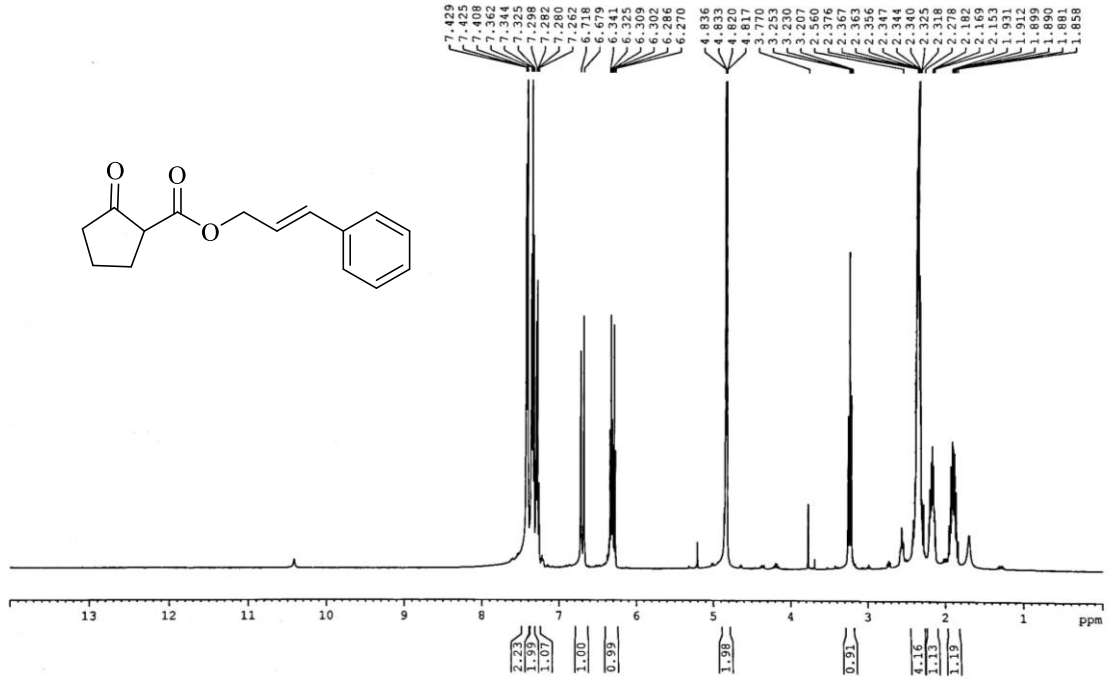
^{1}H NMR of **5b** (400 MHz, $CDCl_3$)



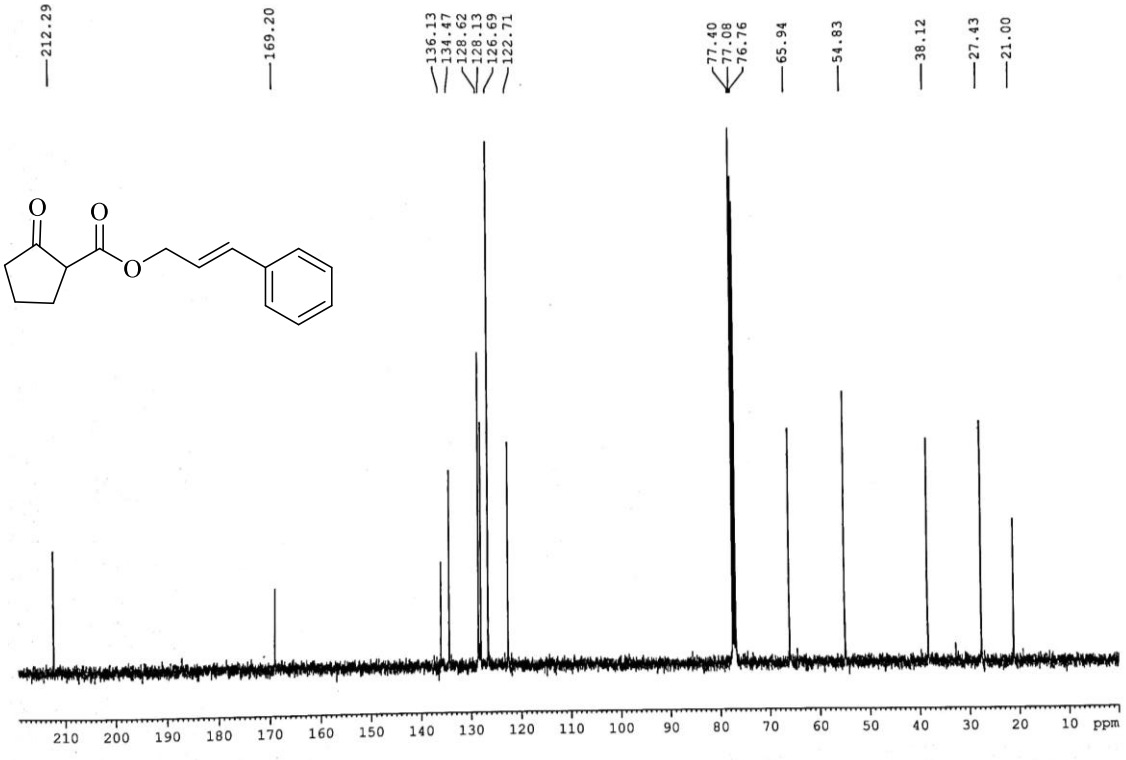
^{13}C NMR of **5b** (100 MHz, $CDCl_3$)



^{1}H NMR of **5c** (400 MHz, $CDCl_3$)



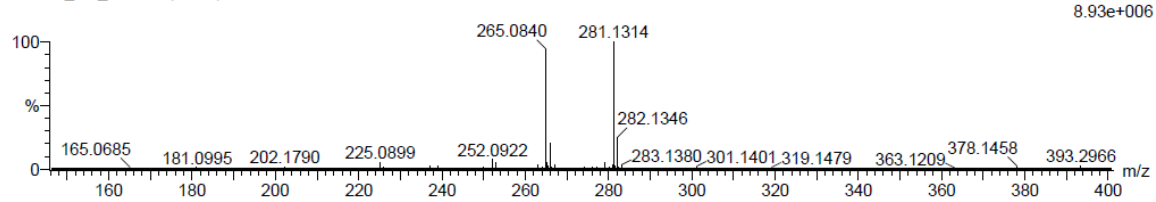
^{13}C NMR of **5c** (100 MHz, $CDCl_3$)



HRMS spectra of 3f

Monoisotopic Mass, Even Electron Ions
265 formula(e) evaluated with 1 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-50 H: 0-50 N: 0-10 O: 0-10 Na: 1-1

Sample Name : KD_135 IITRPR XEVO G2-XS QTOF
Test Name :
190522_KD_135 27 (0.294) 1: TOF MS ES+
8.93e+006



Minimum:				-1.5				
Maximum:		2.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
265.0840	265.0841	-0.1	-0.4	8.5	2006.3	n/a	n/a	C15 H14 O3 Na

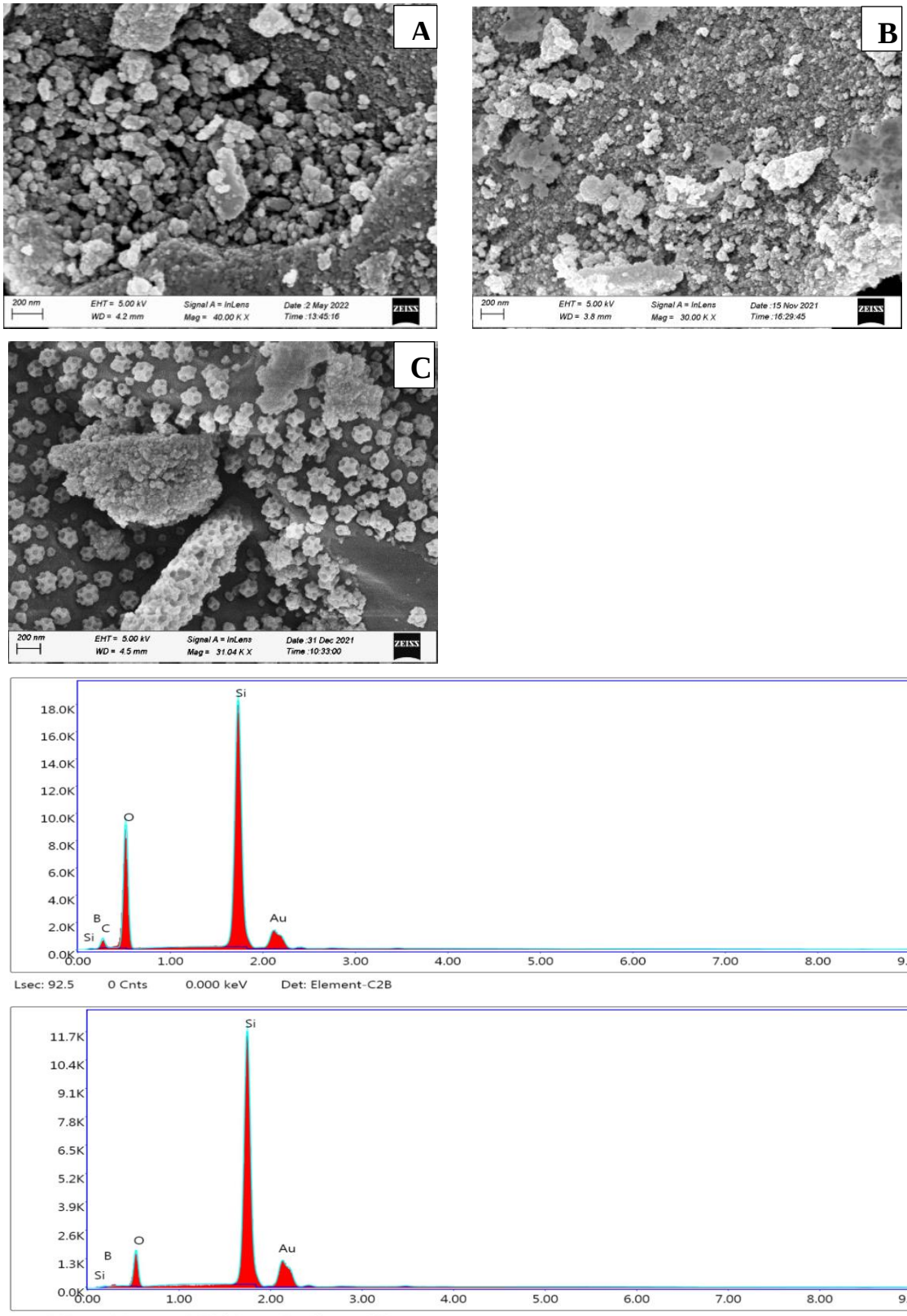


Figure 2: Characterization of the SiO_2-boric acid catalyst: [A] and [B] SEM images of freshly prepared silica-boric acid 60-120 and 230-400 respectively; [C], SEM images of recycled silica(230-400 mesh)-boric acid and [D] and [E] EDAX spectrum of silica (230-400 mesh)-boric acid and silica (60-120 mesh)-boric acid showing absorption peaks for B, Si and O.

References

1. M. Gohain, V. Kumar, J. H. V. Tonder, H. C. Swart, O. M. Ntwaeaborwa, B. C. B. Bezuidenhoudt, *RSC Adv*., 2015, **5**, 18972–18976.
2. T. Raja Mani, Y. Hemanth Sriram, K. Bhaskar, A. K. Kumar, K. R. Kudle, *Chem. Methodol*., 2018, **2**, 83–92.
3. R. H. Tale, A. D. Sagar, H. D. Santan, R. N. Adude, *Synlett* 2006, **3**, 415–418.
4. B. P. Bandgar, V. S. Sadavarte, L. S. Uppalla, *Synth.Commun*., 2001, **31**, 2063–2066.
5. J. S. Yadav, B. V. S. Reddy, A. D. Krishna, C. S. Reddy, A. V. Narsaiah, *J. Mol. Catal. A: Chem*., 2007, **261**, 93–97.
6. M. Lakshmi Kantam, P. Sreekanth, *Catal. Lett*., 2001, **77**, 241–243.
7. A. C. H. Weber, T. C. Batista, B. Gonçalves, C. R. L. Hack, L. M. Porciuncula, T. G. M. Treptow, C. D. R. M. D'Oca, D. Russowsky, M. G. M. D'Oca, *J. Am. Oil Chem. Soc*., 2016, **93**, 1399–1406.
8. S. P. Chavan, Y. T. Subbarao, S. W. Dantale, R. Sivappa, *Synth. Commun*., 2001, **31**, 289–294.
9. H. Yue, H. Yu, S. Liu, C. Xu, *RSC Adv*., 2016, **6**, 19041–19051.
10. B. R. Madje, P. T. Patil, S. S. Shindalkar, S. B. Benjamin, M. S. Shingare, M. K. Dongare, *Catal. Commun*., 2004, **5**, 353–357.
11. F. C. da Silva, V. F. Ferreira, R. S. Rianelli and W. C. Perreira, *Tetrahedron Letts*., 2002, **43**, 1165–1168.
12. B. P. Bandgar, S. S. Pandit, L. S. Uppalla, *Org. Prep. Proced. Int*., 2003, **35**, 219–222.
13. K. Agura, Y. Hayashi, M. Wada, D. Nakatake, K. Mashima, T. Ohshima, *Chem.–Asian J*., 2016, **11**, 1548–1554.
14. H. Hagiwara, A. Koseki, K. Isobe, K.-ichi Shimizu, T. Hoshi, T. Suzuki, *Synlett* 2004, **12**, 2188-2190.