

Copper-catalyzed formal O-H insertion reaction of α -diazo-1,3-dicarbonyl compounds to carboxylic acids with the assistance of isocyanide

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Electronic Supplementary Information

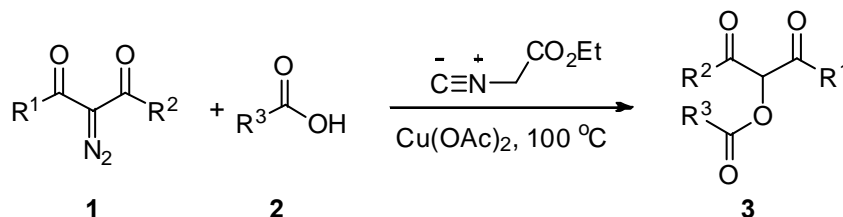
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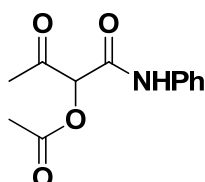
I. General information

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded at 25 °C on a Varian 300 MHz or 400 MHz and 100 MHz spectrometer, respectively, and TMS was used as internal standard. Mass spectra were recorded on BRUKER AutoflexIII Smartbeam MS-spectrometer. High resolution mass spectra (HRMS) were recorded on Bruker microTof by using ESI method.

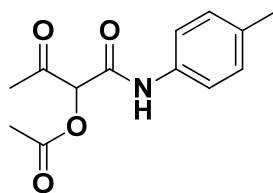
II. Synthesis and analytical data of compounds 3



Typical synthetic procedure (with **3a** as an example): To a solution of α -diazo- β -oxoamide (**1a**) (1.0 mmol) and ethyl isocyanoacetate (0.5 mmol) in acetic acid (4.0 mL) was added $\text{Cu}(\text{OAc})_2$ (0.1 mmol) in one portion at 100 °C under stirring. After being stirred for 5 hours, the reaction mixture was cooled to room temperature and saturated aqueous NaCl solution (20 mL) was added under stirring. The mixture was extracted with dichloromethane (3×20 mL) and the combined organic phase was washed with water (3×20 mL), dried over MgSO_4 , filtered, and concentrated under vacuum. Purification of the crude product by flash column chromatography (silica gel; petroleum ether: ethyl acetate = 8 : 1) gave **3a** in 83% yield as a white solid.

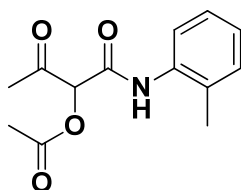


(3a) White solid, m.p. 66-68 °C; $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 2.25 (s, 3H), 2.44 (s, 3H), 5.62 (s, 1H), 7.13 (t, $J = 7.2$ Hz, 1H), 7.31 (t, $J = 7.8$ Hz, 2H), 7.50 (d, $J = 7.8$ Hz, 2H), 8.26 (s, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ 20.28, 27.46, 79.06, 120.12, 125.07, 128.91, 136.37, 161.08, 168.60, 199.86; **HRMS** (ESI) m/z calculated for $\text{C}_{12}\text{H}_{13}\text{NO}_4$ $[\text{M}+\text{Na}]^+$: 258.0740 found: 258.0742.

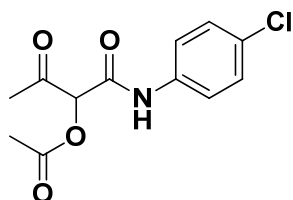


(3b) Yellowish solid, m.p. 43-45 °C; $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 2.23 (s, 3H), 2.26 (s, 3H), 2.40 (s, 3H), 5.56 (s, 1H), 7.08 (d, $J = 8.1$ Hz, 2H), 7.32 (d, $J = 8.1$ Hz, 2H), 7.90 (s, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100

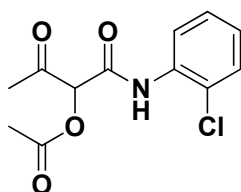
MHz) δ 20.40, 20.76, 27.60, 79.13, 120.20, 129.48, 133.80, 134.88, 160.87, 168.54, 199.82; **HRMS** (ESI) m/z calculated for $C_{13}H_{15}NO_4$ $[M+Na]^+$: 272.0903 found: 272.0899.



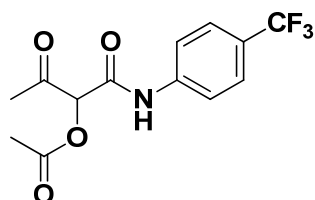
(3c) White solid, m.p. 68-70 °C; **1H -NMR** (300 MHz, $CDCl_3$) δ 2.27 (s, 3H), 2.31 (s, 3H), 5.67 (s, 1H), 7.11 (t, $J = 7.5$ Hz, 1H), 7.21 (d, $J = 7.5$ Hz, 2H), 7.81 (d, $J = 7.8$ Hz, 1H), 8.03 (s, 1H); **^{13}C -NMR** ($CDCl_3$, 100 MHz) δ 17.35, 20.42, 27.67, 79.19, 122.69, 125.83, 126.80, 129.21, 130.55, 134.27, 161.00, 168.51, 200.09; **HRMS** (ESI) m/z calculated for $C_{13}H_{15}NO_4$ $[M+Na]^+$: 272.0905 found: 272.0899.



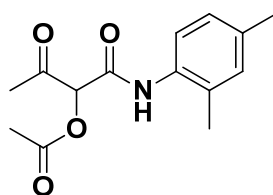
(3d) Yellowish solid, m.p. 66-67 °C; **1H -NMR** (400 MHz, $CDCl_3$) δ 2.26 (s, 3H), 2.44 (s, 3H), 5.61 (s, 1H), 7.28 (d, $J = 8.4$ Hz, 2H), 7.46 (d, $J = 8.4$ Hz, 2H), 8.24 (s, 1H) ; **^{13}C -NMR** ($CDCl_3$, 100 MHz) δ 20.36, 27.58, 78.99, 121.40, 129.03, 130.20, 135.00, 161.07, 168.54, 199.98; **HRMS** (ESI) m/z calculated for $C_{12}H_{12}ClNO_4$ $[M+Na]^+$: 292.0338 found: 292.0353.



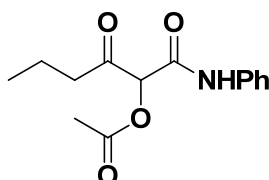
(3e) White solid, m.p. 77-79 °C; **1H -NMR** (300 MHz, $CDCl_3$) δ 2.32 (s, 3H), 2.49 (s, 3H), 5.68 (s, 1H), 7.07-7.13 (m, 1H), 7.29-7.32 (m, 1H), 7.38-7.41 (m, 1H), 8.76 (s, 1H) ; **^{13}C -NMR** ($CDCl_3$, 100 MHz) δ 20.36, 27.68, 79.03, 121.42, 123.32, 125.51, 127.75, 129.15, 133.33, 161.07, 168.32, 198.99; **HRMS** (ESI) m/z calculated for $C_{12}H_{12}ClNO_4$ $[M+Na]^+$: 292.0348 found: 292.0353.



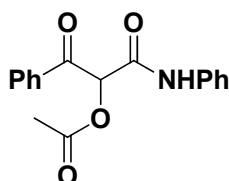
(**3f**) White solid, m.p. 74-75 °C; **¹H-NMR** (400 MHz, CDCl₃) δ 2.27 (s, 3H), 2.44 (s, 3H), 5.62 (s, 1H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 8.34 (s, 1H); **¹³C-NMR** (CDCl₃, 100 MHz) δ 20.40, 27.62, 79.00, 119.83, 123.86 (q, ¹*J*_{CF} = 270.0 Hz), 126.31, 126.98 (q, ²*J*_{CF} = 32.9 Hz), 139.53, 161.33, 168.58, 200.12; **HRMS** (ESI) *m/z* calculated for C₁₃H₁₂F₃NO₄ [M+Na]⁺ : 326.0621 found: 326.0616.



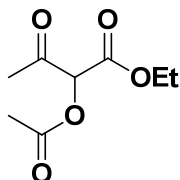
(**3g**) Yellow solid, m.p. 71-74 °C; **¹H-NMR** (300 MHz, CDCl₃) δ 2.21 (s, 3H), 2.28 (s, 6H), 2.45 (s, 3H), 5.64 (s, 1H), 7.01 (s, 2H), 7.57-7.60 (m, 1H), 7.97 (s, 1H); **¹³C-NMR** (CDCl₃, 100 MHz) δ 17.27, 20.37, 20.75, 27.61, 79.18, 123.00, 127.24, 129.58, 131.17, 131.55, 135.65, 161.03, 168.50, 199.98; **HRMS** (ESI) *m/z* calculated for C₁₄H₁₇NO₄ [M+Na]⁺ : 286.1057 found: 286.1055.



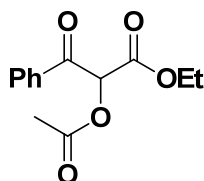
(**3h**) Yellow-oil liquid; **¹H-NMR** (300 MHz, CDCl₃) δ 0.92 (t, *J* = 7.5 Hz, 3H), 1.58-1.70 (m, 2H), 2.25 (s, 3H), 2.67-2.92 (m, 2H), 5.60 (s, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.51 (d, *J* = 7.8 Hz, 2H), 8.18 (s, 1H); **¹³C-NMR** (CDCl₃, 100 MHz) δ 13.26, 16.33, 20.32, 41.89, 78.89, 120.11, 125.04, 128.92, 136.42, 161.19, 168.56, 202.16; **HRMS** (ESI) *m/z* calculated for C₁₄H₁₇NO₄ [M+Na]⁺ : 286.1048 found: 286.1055.



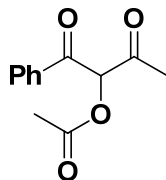
(3i) Yellow solid, m.p. 126-128 °C; $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 2.29 (s, 3H), 6.45 (s, 1H), 7.13 (t, $J = 7.5$ Hz, 1H), 7.31 (t, $J = 7.5$ Hz, 2H), 7.48-7.53 (m, 4H), 7.63 (t, $J = 7.5$ Hz, 1H), 8.11 (s, 1H), 8.18 (d, $J = 7.5$ Hz, 2H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ 20.49, 76.51, 120.08, 125.12, 128.63, 128.98, 129.71, 134.17, 134.30, 136.49, 161.47, 168.59, 191.59; **HRMS** (ESI) m/z calculated for $\text{C}_{17}\text{H}_{15}\text{NO}_4$ $[\text{M}+\text{Na}]^+$: 320.0891 found: 320.0899.



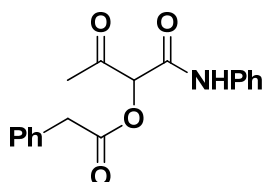
(3j) Yellow-oil liquid; $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 1.24 (t, $J = 7.2$ Hz, 3H), 2.15 (s, 3H), 2.27 (s, 3H), 4.21 (q, $J = 7.2$ Hz, $J = 14.4$ Hz, 2H), 5.42 (s, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ 13.65, 20.02, 26.82, 62.14, 77.62, 164.25, 169.14, 197.27; **HRMS** (ESI) m/z calculated for $\text{C}_8\text{H}_{12}\text{O}_5$ $[\text{M}+\text{Na}]^+$: 211.0586 found: 211.0582.



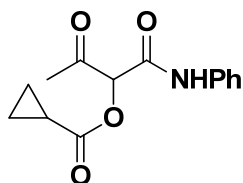
(3k) Yellow-oil liquid; $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 1.21 (t, $J = 7.2$ Hz, 3H), 2.23 (s, 3H), 4.24 (q, $J = 7.2$ Hz, $J = 14.4$ Hz, 2H), 6.32 (s, 1H), 7.50 (t, $J = 7.5$ Hz, 2H), 7.63 (t, $J = 7.5$ Hz, 1H), 7.99 (d, $J = 7.5$ Hz, 2H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ 13.72, 20.30, 62.30, 74.37, 128.31, 128.64, 129.03, 134.06, 165.01, 169.35, 189.55; **HRMS** (ESI) m/z calculated for $\text{C}_{13}\text{H}_{14}\text{O}_5$ $[\text{M}+\text{Na}]^+$: 273.0731 found: 273.0739.



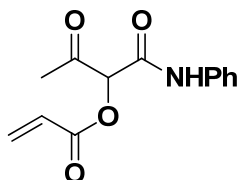
(3l) Yellow-oil liquid; $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 2.23 (s, 3H), 2.29 (s, 3H), 6.26 (s, 1H), 7.48 (t, $J = 7.5$ Hz, 2H), 7.62 (t, $J = 7.5$ Hz, 1H), 8.00 (d, $J = 7.5$ Hz, 2H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ 20.47, 26.79, 82.15, 128.72, 129.42, 131.52, 134.22, 169.24, 190.84, 199.40; **HRMS** (ESI) m/z calculated for $\text{C}_{12}\text{H}_{12}\text{O}_4$ $[\text{M}+\text{Na}]^+$: 243.0622 found: 243.0633.



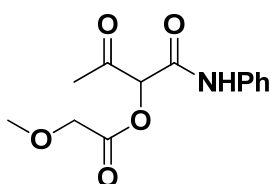
(**3m**) White solid, m.p. 62-64 °C; $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 2.44 (s, 3H), 3.89 (d, $J = 2.1$ Hz, 2H), 5.63 (s, 1H), 7.12-7.16 (m, 1H), 7.28-7.43 (m, 9H), 7.70 (s, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ 27.72, 40.81, 79.08, 119.95, 125.14, 127.59, 128.90, 129.01, 129.38, 133.01, 136.34, 160.82, 168.88, 199.14; **HRMS** (ESI) m/z calculated for $\text{C}_{18}\text{H}_{17}\text{NO}_4$ $[\text{M}+\text{Na}]^+$: 334.1049 found: 334.1055.



(**3n**) Yellow-oil liquid; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 1.00-1.10 (m, 4H), 1.82-1.83 (m, 1H), 2.43 (s, 3H), 5.63 (s, 1H), 7.15 (t, $J = 7.8$ Hz, 1H), 7.32 (t, $J = 7.8$ Hz, 2H), 7.51 (d, $J = 7.8$ Hz, 2H), 8.30 (s, 1H) ; $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ 9.38, 9.51, 12.42, 27.54, 78.94, 120.16, 125.07, 128.94, 136.45, 161.23, 172.77, 200.13; **HRMS** (ESI) m/z calculated for $\text{C}_{14}\text{H}_{15}\text{NO}_4$ $[\text{M}+\text{Na}]^+$: 284.0899 found: 284.0899.

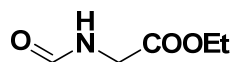


(**3o**) Red-oil liquid; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 2.48 (s, 3H), 5.71 (s, 1H), 6.03 (d, $J = 10.4$ Hz, 1H), 6.30-6.36 (m, 1H), 6.59 (d, $J = 17.2$ Hz, 1H), 7.16 (t, $J = 7.2$ Hz, 1H), 7.34 (t, $J = 7.6$ Hz, 2H), 7.51 (d, $J = 7.6$ Hz, 2H), 8.12 (s, 1H) ; $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ 27.64, 79.06, 120.20, 125.20, 126.46, 129.04, 133.57, 136.41, 160.97, 163.78, 199.91; **HRMS** (ESI) m/z calculated for $\text{C}_{13}\text{H}_{13}\text{NO}_4$ $[\text{M}+\text{Na}]^+$: 270.0733 found: 270.0742.



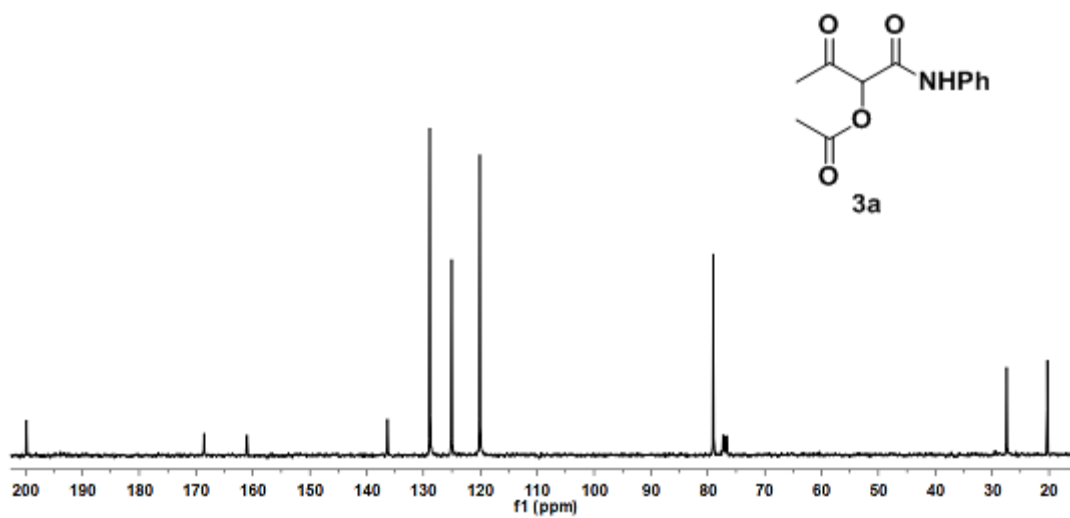
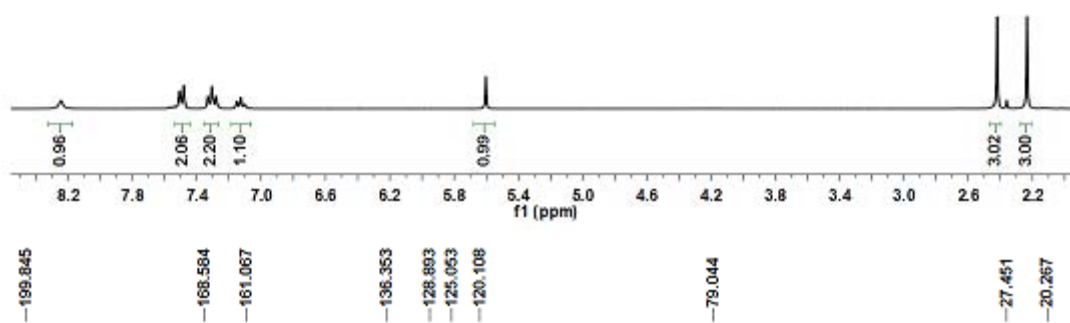
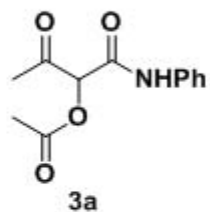
(**3p**) Yellow-oil liquid; $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 2.46 (s, 3H), 3.50 (s, 3H), 4.28 (s, 2H), 5.72 (s, 1H), 7.15 (t, $J = 7.5$ Hz, 1H), 7.33 (t, $J = 7.5$ Hz, 2H), 7.50 (d, $J = 8.1$ Hz, 2H), 8.22 (s, 1H) ; $^{13}\text{C-NMR}$

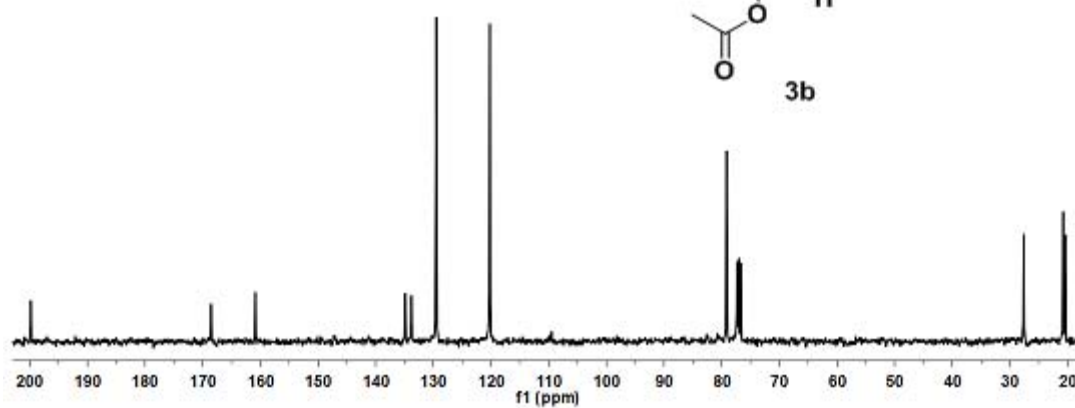
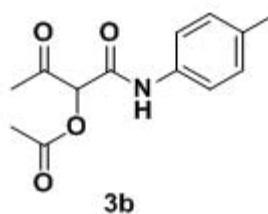
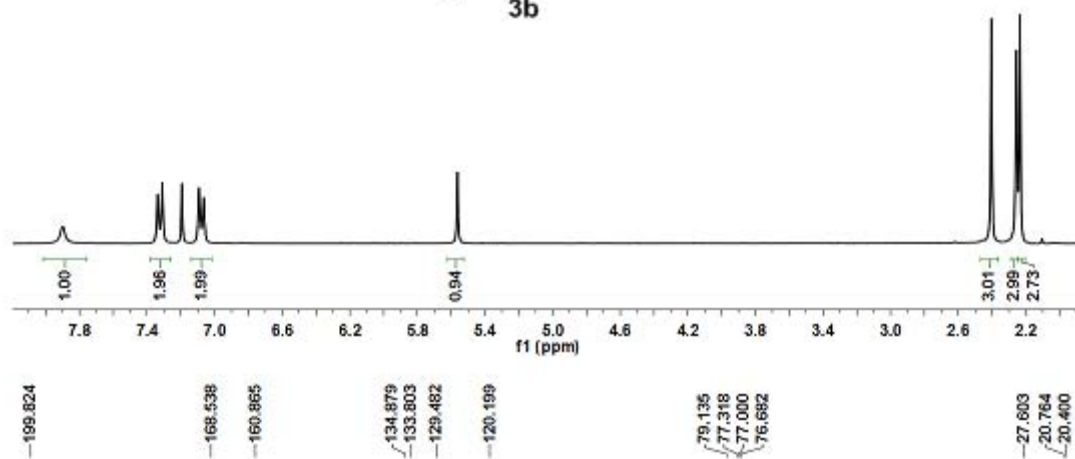
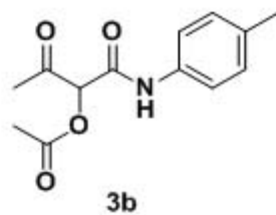
(CDCl₃, 100 MHz) δ 27.56, 59.52, 69.40, 79.07, 120.25, 125.28, 129.07, 136.36, 160.67, 168.26, 199.44;
HRMS (ESI) m/z calculated for C₁₃H₁₅NO₅ [M+Na]⁺ : 288.0841 found: 288.0848.

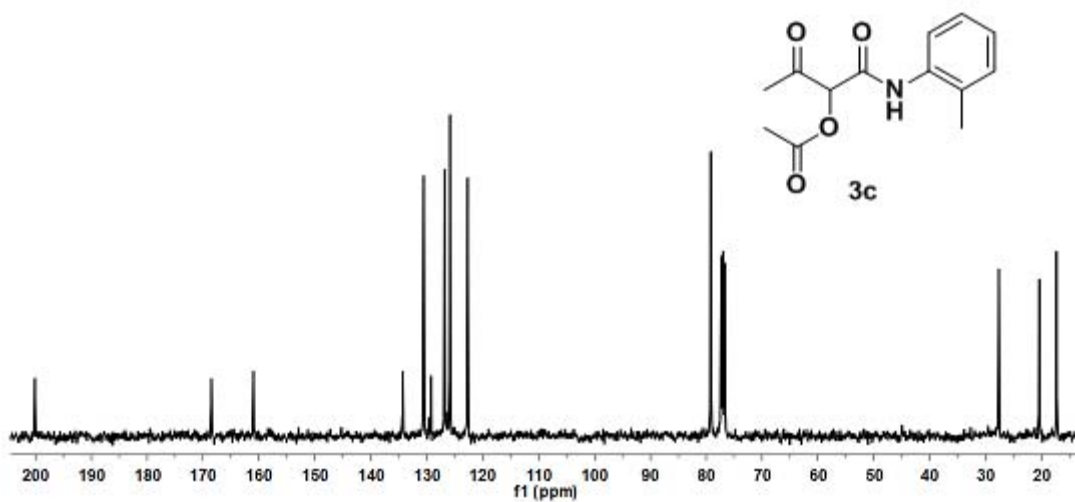
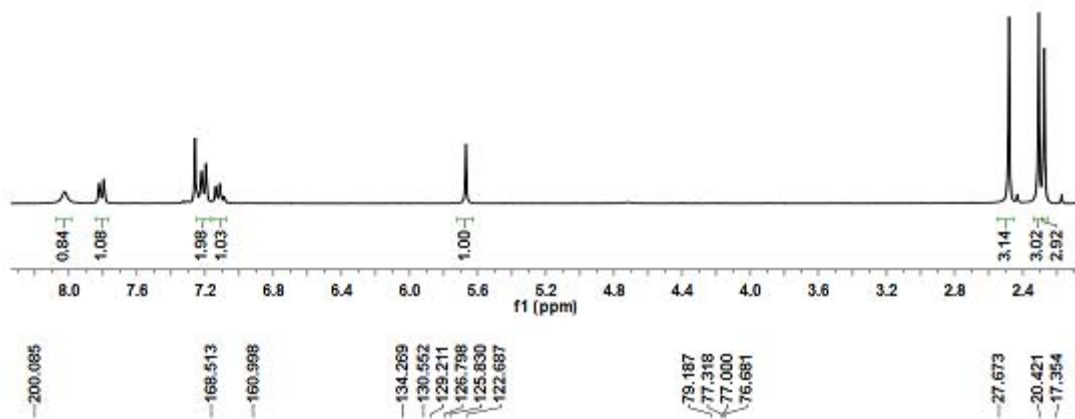
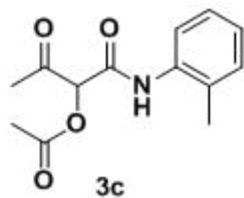


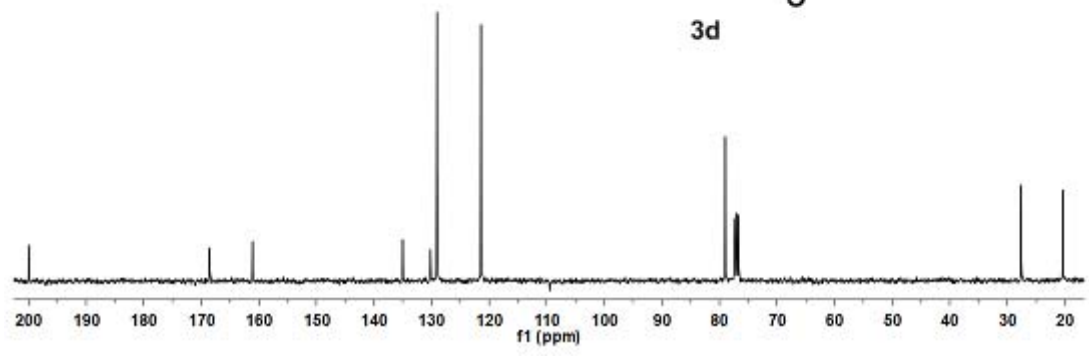
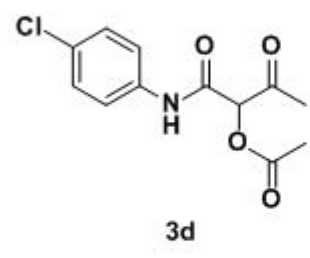
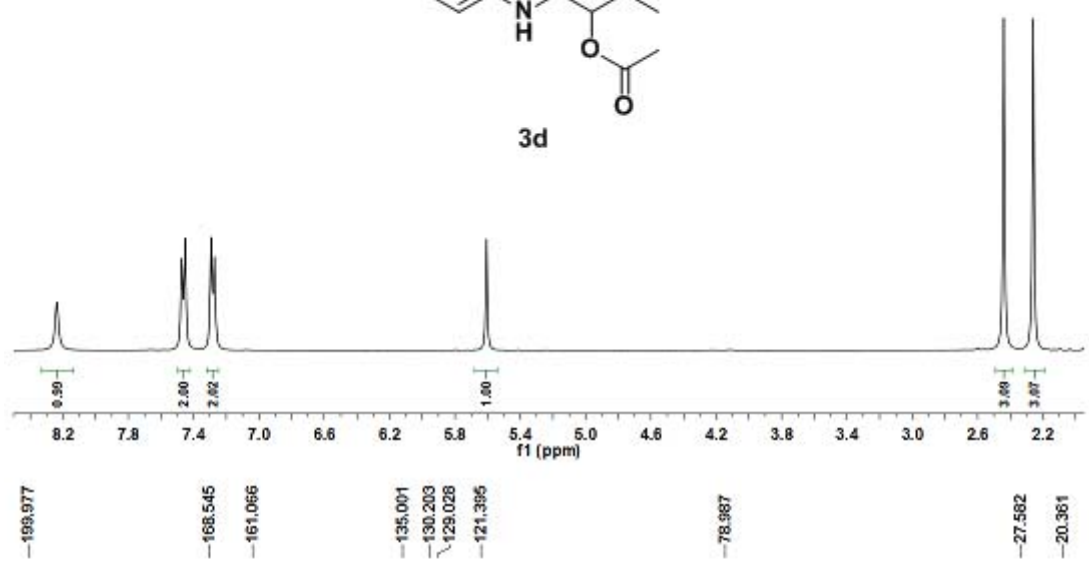
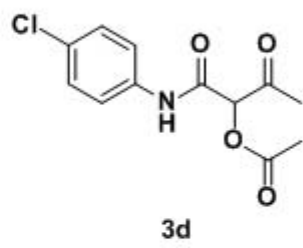
Yellow-oil liquid; **¹H-NMR** (400 MHz, CDCl₃) δ 1.15 (t, J = 7.2 Hz, 3H), 3.91 (d, J = 5.6 Hz, 2H), 4.07 (q, J = 7.2 Hz, 14.0 Hz, 2H), 7.08 (s, 1H), 8.10 (s, 1H) ; **¹³C-NMR** (CDCl₃, 100 MHz) δ 13.67, 39.53, 61.10, 161.58, 169.26; **HRMS** (ESI) m/z calculated for C₅H₁₀NO₃ [M+H]⁺ : 132.0800 found: 132.0661.

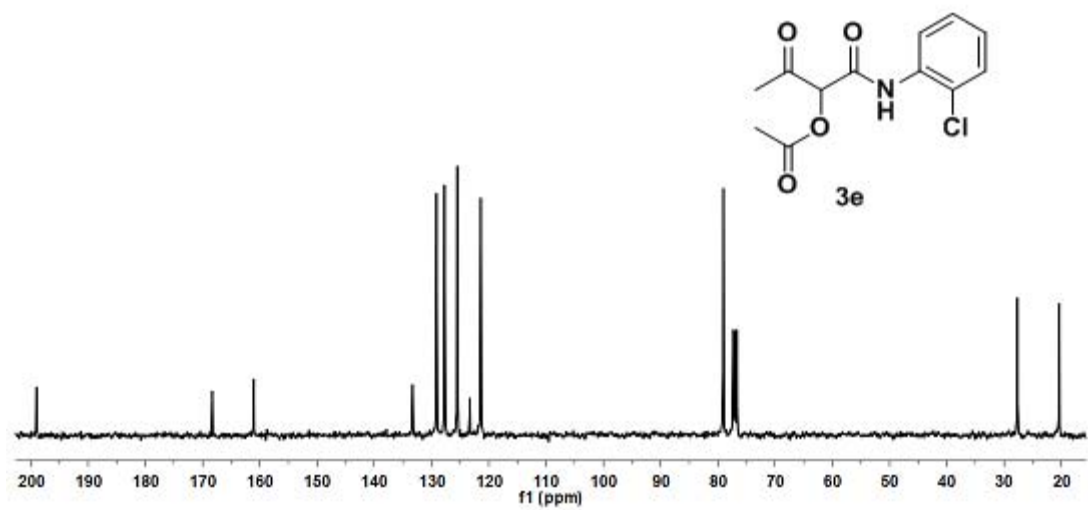
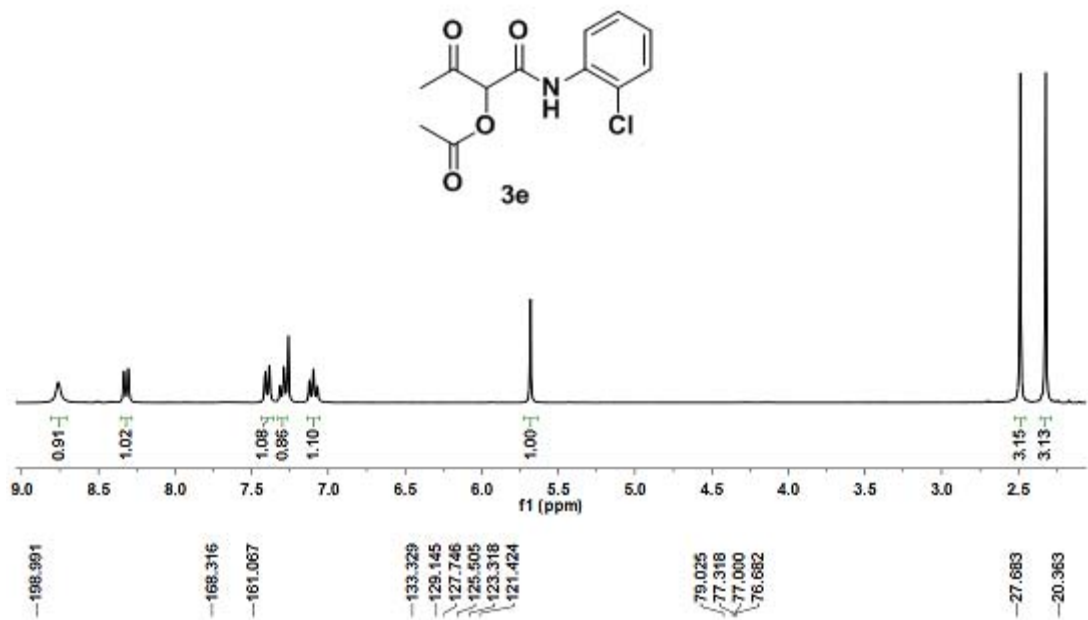
III. NMR spectra copies

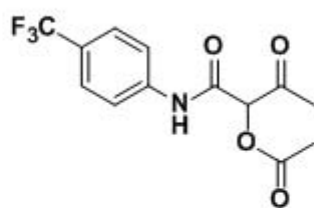












3f

