Supporting Information

Access to ester-substituted -butyrolactones via photocatalyzed alkoxycarbonylation/lactonization of alkenoic acids

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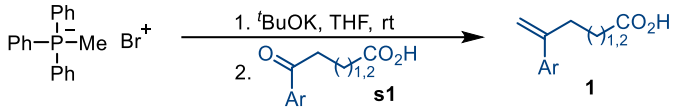
Contents

1. General information

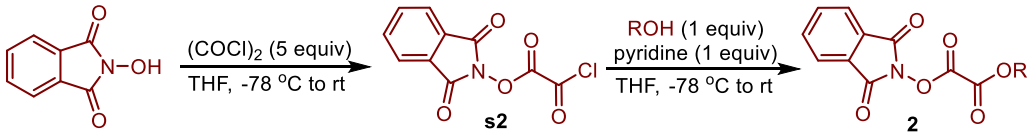
All glassware was thoroughly oven-dried. Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Thin-layer chromatography plates were visualized by exposure to ultraviolet light and/or staining with phosphomolybdic acid followed by heating on a hot plate. Flash chromatography was carried out using silica gel (200−300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-400 (400 MHz). The spectra were recorded in deuterochloroform ($CDCl_3$) as solvent at room temperature, ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to the residual solvent peak. The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.0 ppm). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet, br = broad), integration, coupling constant (Hz) and assignment. Data for ^{13}C NMR are reported as chemical shift. Electrospray–ionisation HRMS data were acquired on a Q–TOF mass spectrometer (Waters SYNAPT G2-Si) LC-MS TOF.

2. General procedure for the preparation of 1[1].



A suspension of potassium tert-butoxide (15.00 g, 2.6 equiv) in THF (69 mL) was added to a suspension of methyl triphenylphophonium bromide (34.29 g, 1.6 equiv) in THF (138 mL). The resulting yellow solution was stirred at room temperature for 1.5 h, upon which acid **s1** (60.0 mmol, 1.0 equiv) was added. The reaction was stirred at room temperature for 24 h and quenched with acetic acid (3.5 mL), followed by addition of EtOAc (100 mL). The organic layer was extracted with a saturated aqueous solution of $NaHCO_3$(200 mL x 3). The combined aqueous layers were acidified to pH 1 with concentrated HCl and the organic layer extracted with EtOAc (400 mL x 2). The combined organic layers were washed with water (200 mL), brine (200 mL), dried with Na_2SO_4, and concentrated in vacuo to afford the crude olefin product. Purification by column chromatography (25% EtOAc–hexanes) afforded **1**.

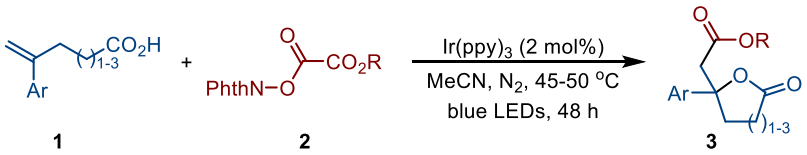
3. General procedure for the preparation of 2[2].



A round-bottom flask was charged with *N*-hydroxyphthalimide (3.3 g, 20 mmol, 1 equiv), followed by the addition of THF (200 mL). The resulting solution was then cooled to –78 °C and oxalyl chloride (8 mL, 100 mmol, 5 equiv) was added dropwise. The solution was then allowed to warm to room temperature and stirred for 20 h. The volatiles were removed under reduced pressure to yield **s2** as a colorless solid. Then a round-bottom flask was charged with the colorless solid followed by the addition of THF (200 mL). The mixture was cooled to −78 °C and a solution of ROH (1.0 equiv), pyridine (1.6 mL, 1.0 equiv) in THF (50 mL) was added dropwise. The resulting heterogeneous mixture was warmed to 0 ºC and allowed to stir for 1 h. The reaction was then allowed to warm to 23 ºC and stirred for another 30 min. The reaction mixture was concentrated under reduced pressure, and the resulting crude residue was

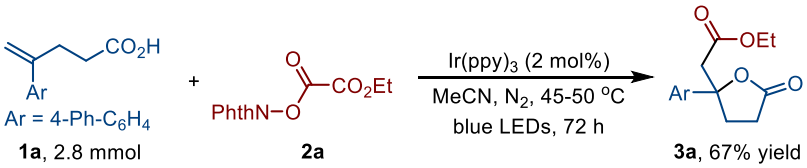
dissolved in CH_2Cl_2 (100 mL) and washed with sat. aq. $CuSO_4$ (3x 100 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The resulting crude residue was dissolved in CH_2Cl_2 (125 mL) then poured into pentanes (250 mL). The resulting heterogeneous mixture was filtered through a cotton plug that was then washed with pentanes (2 x 75 mL). The filtrate was concentrated under reduced pressure to yield **2**.

4. General procedure for the synthesis of 3.

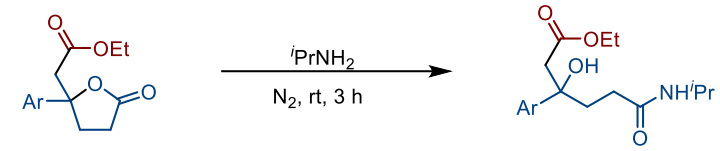


All optimization reactions were set up in a glove box under N_2 atmosphere. Substrate **1** (0.1 mmol, 1.0 equiv) and oxalate **2** (0.3 mmol, 3.0 equiv) were added to a solution of photocatalyst $Ir(ppy)_3$ (2 mol%) in dry MeCN (2 mL) at 20 °C. The heterogenous mixture was placed in the irradiation apparatus equipped with blue LEDs. The resulting mixture was stirred at 45-50 °C for 48 h. Upon completion of the reaction, the mixture was concentrated under reduced pressure and purified by column chromatography on silica gel to afford the desired product **3**.

5. Scale-up synthesis and further transformation[3].

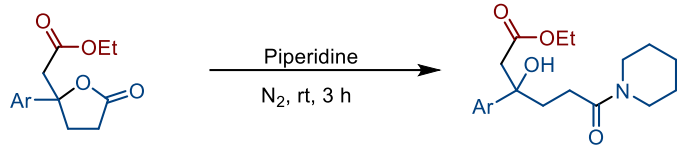


The reaction was set up in a glove box under N_2 atmosphere. Substrate **1a** (2.8 mmol, 1.0 equiv) and oxalate **2a** (8.4 mmol, 3.0 equiv) were added to a solution of photocatalyst $Ir(ppy)_3$ (2 mol%) in dry MeCN (50 mL) at 20 °C. The heterogenous mixture was placed in the irradiation apparatus equipped with blue LEDs. The resulting mixture was stirred at 45-50 °C for 72 h. Upon completion of the reaction, the mixture was concentrated under reduced pressure and purified by column chromatography onsilica gel to afford the desired product **3a** (607 mg, 67% yield).



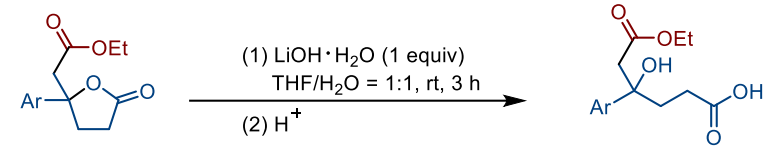
3a, Ar = 4-Ph-C$_6$H$_4$ **3a-I**, 69% yield

Isopropylamine (0.8 mL, 9.4 mmol) was added dropwise to **3a** (64.8 mg, 0.2 mmol) under nitrogen atmosphere. The mixture was allowed to react at room temperature for 3 h. Then the additional isopropylamine was removed under reduced pressure and the mixture was purified by silica gel chromatography (PE/EA= 2:1) to afford **3a-I** as a colorless oil (53 mg, 69% yield).



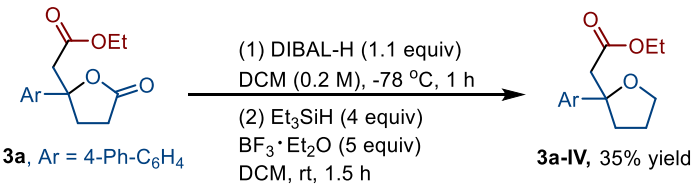
3a, Ar = 4-Ph-C$_6$H$_4$ **3a-II**, 45% yield

Piperidine (1.0 mL, 10.1 mmol) was added dropwise to **3a** (64.8 mg, 0.2 mmol) under nitrogen atmosphere. The mixture was allowed to react at room temperature for 3 h. Then the additional piperidine was removed under reduced pressure and the mixture was purified by silica gel chromatography (petroleum ether/ethyl acetate=2:1) to afford **3a-II** as a colorless oil (37 mg, 45% yield).



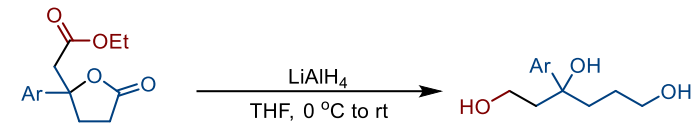
3a, Ar = 4-Ph-C$_6$H$_4$ **3a-III**, 63% yield

The **3a** (64.8 mg, 0.2 mmol) was dissolved in THF (1 mL). A solution of LiOH·H$_2$O (8.4 mg, 1.0 equiv) in H$_2$O (1 mL) was added, and the mixture stirred at room temperature for 3 h. Then the mixture was acidified with 1M HCl (5 mL) and was extracted with ethyl acetate (3×10 mL). Then the combined organic layers were washed with brine, dried over anhydrous Na$_2$SO$_4$, and concentrated under reduced pressure. The residue was purified through column chromatography on silica gel (PE/EA= 1:1) to afford to afford **3a-III** as a white solid (43 mg, 63% yield).



3a, Ar = 4-Ph-C$_6$H$_4$ **3a-IV**, 35% yield

To a solution of **3a** (64.8 mg, 0.2 mmol) in CH_2Cl_2 (1 mL) was added a solution of DIBAL-H (1M in toluene, 0.2 ml, 0.22 mmol) at -78 ºC and stirred for 1 h. The reaction was quenched by addition H_2O (0.4 mL) and NaOH (0.4 mL, 2N) and then the aqueous layer then extracted with CH_2Cl_2 (3 × 20 mL). The combined organics were then dried (Na_2SO_4) and concentrated in vacuo. Then adding Et_3SiH (63.3 mg, 0.4 mmol), $BF_3{\cdot}OEt_2$ (0.12 mL, 0.50 mmol) was added dropwise to mixture in dry CH_2Cl_2 (0.3 mL) at 0 °C under argon atmosphere. The mixture was allowed to warm to -10 °C during 1.5 h. Then saturated aqueous sodium bicarbonate solution (1 mL) was added and the mixture extracted with diethyl ether (10 mL) and dried ($MgSO_4$). The reaction mixture was purified by chromatography on silica gel to afford **3a-IV** as a colorless oil (22 mg, 35% yield).

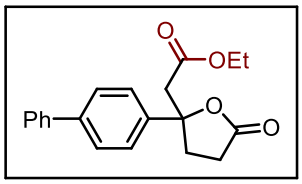


3a, Ar = 4-Ph-C_6H_4 **3a-V**, 86% yield

To a stirred solution of **3a** (64.8 mg, 0.2 mmol) in THF (2 mL) at 0 °C was added $LiAlH_4$ (40 mg, 1.06 mmol). After 3 h, the reaction mixture was quenched with brine and extracted with Et_2O. The combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The reaction mixture was purified directly by chromatography on silica gel to afford **3a-V** as a gray solid (49 mg, 86% yield).

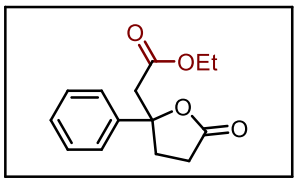
6. Characterization data for all new compounds.

Ethyl 2-(2-([1,1'-biphenyl]-4-yl)-5-oxotetrahydrofuran-2-yl)acetate (3a)



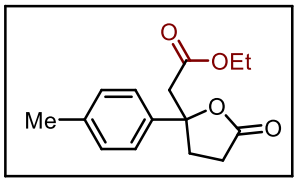
Purification by flash chromatography (PE/EA = 5/1). White solid; m.p. = 53–55 °C; 90% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.60–7.56 (m, 4H), 7.47–7.41 (m, 4H), 7.36–7.33 (m, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 3.05–2.97 (m, 2H), 2.97–2.86 (m, 1H), 2.73–2.58 (m, 2H), 2.55–2.45 (m, 1H), 1.17 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 176.1, 168.9, 141.7, 141.0, 140.2, 128.9, 127.6, 127.3, 127.1, 125.1, 85.9, 60.9, 46.4, 33.4, 28.6, 14.1. **HRMS (ESI)** calculated for $C_{20}H_{20}O_4Na$ $[M+Na]^+$: 347.1259, found: 347.1260.

Ethyl 2-(5-oxo-2-phenyltetrahydrofuran-2-yl)acetate (3b)



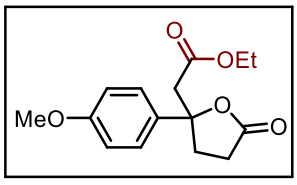
Purification by flash chromatography (PE/EA = 5/1). Colorless oil; 98% yield; **^{1}H NMR (400 MHz, CDCl$_3$)** δ (ppm) 7.32–7.27 (m, 4H), 7.25–7.20 (m, 1H), 3.99 (q, *J* = 7.2 Hz, 2H), 2.92 (d, *J* = 15.6 Hz, 1H), 2.88 (d, *J* = 15.2 Hz, 1H), 2.85–2.77 (m, 1H), 2.64–2.49 (m, 2H), 2.45–2.36 (m, 1H), 1.08 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ (ppm) 176.1, 168.9, 142.8, 128.6, 128.1, 124.5, 85.9, 60.8, 46.5, 33.3, 28.6, 14.0. **HRMS (ESI)** calculated for $C_{14}H_{16}O_4Na$ $[M+Na]^+$: 271.0946, found: 271.0955.

Ethyl 2-(5-oxo-2-(p-tolyl)tetrahydrofuran-2-yl)acetate (3c)



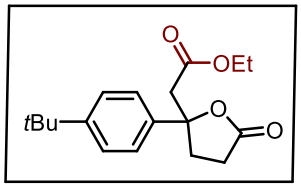
Purification by flash chromatography (PE/EA = 5/1). Colorless oil; 88% yield; **^{1}H NMR (400 MHz, CDCl$_3$)** δ (ppm) 7.28 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 4.10–4.05 (m, 2H), 2.99 (d, *J* = 15.6 Hz, 1H), 2.94 (d, *J* = 15.2 Hz, 1H), 2.89–2.82 (m, 1H), 2.70–2.56 (m, 2H), 2.52–2.44 (m, 1H), 2.34 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ (ppm) 176.2, 169.0, 139.7, 137.8, 129.3, 124.5, 86.0, 60.8, 46.5, 33.3, 28.6, 21.0, 14.0. **HRMS (ESI)** calculated for $C_{15}H_{18}O_4Na$ $[M+Na]^+$: 285.1103, found: 285.1109.

Ethyl 2-(2-(4-methoxyphenyl)-5-oxotetrahydrofuran-2-yl)acetate (3d)



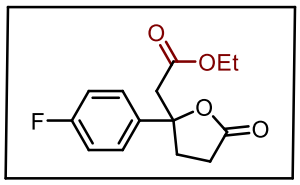
Purification by flash chromatography (PE/EA = 5/1). Colorless oil; 89% yield; **^{1}H NMR (400 MHz, CDCl$_3$)** δ (ppm) 7.31 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 4.10–4.05 (m, 2H), 3.80 (s, 3H), 2.98 (d, *J* = 15.2 Hz, 1H), 2.93 (d, *J* = 15.2 Hz, 1H), 2.89–2.81 (m, 1H), 2.70–2.57 (m, 2H), 2.53–2.43 (m, 1H), 1.17 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ (ppm) 176.1, 169.0, 159.3, 134.6, 126.0, 113.9, 85.9, 60.8, 55.3, 46.7, 33.2, 28.6, 14.0. **HRMS (ESI)** calculated for $C_{15}H_{18}O_5Na$ $[M+Na]^+$: 301.1052, found: 301.1060.

Ethyl 2-(2-(4-(tert-butyl)phenyl)-5-oxotetrahydrofuran-2-yl)acetate (3e)



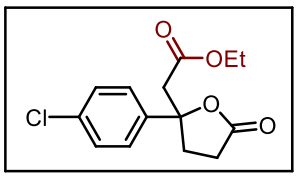
Purification by flash chromatography (PE/EA = 5/1). White solid; m.p. = 37−39 °C; 93% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.39 (d, *J* = 8.8 Hz, 2H), 7.31 (d, *J* = 8.8 Hz, 2H), 4.08 (q, *J* = 7.2 Hz, 2H), 3.00 (d, *J* = 15.6 Hz, 1H), 2.95 (d, *J* = 15.6 Hz, 1H), 2.91–2.84 (m, 1H), 2.71–2.58 (m, 2H), 2.54–2.45 (m, 1H), 1.31 (s, 9H), 1.15 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 176.2, 169.0, 151.0, 139.7, 125.5, 124.3, 86.0, 60.8, 46.5, 34.5, 33.2, 31.3, 28.7, 14.0. **HRMS (ESI)** calculated for $C_{18}H_{24}O_4Na$ $[M+Na]^+$: 327.1572, found: 327.1581.

Ethyl 2-(2-(4-fluorophenyl)-5-oxotetrahydrofuran-2-yl)acetate (3f)



Purification by flash chromatography (PE/EA = 5/1). Yellow oil; 92% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.40–7.37 (m, 2H), 7.09–7.05 (m, 2H), 4.13–4.02 (m, 2H), 2.98 (d, *J* = 15.6 Hz, 1H), 2.93 (d, *J* = 15.6 Hz, 1H), 2.89–2.84 (m, 1H), 2.74–2.66 (m, 1H), 2.63–2.56 (m, 1H), 2.54–2.45 (m, 1H), 1.17 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 175.8, 168.8, 162.4 (d, *J* = 245.9 Hz), 138.4 (d, *J* = 3.4 Hz), 126.6 (d, *J* = 8.1 Hz), 115.6 (d, *J* = 21.6 Hz), 85.6, 61.0, 46.6, 33.4, 28.5, 14.0. **^{19}F NMR (376 MHz, $CDCl_3$)** δ (ppm) -113.9 – -114.1 (m). **HRMS (ESI)** calculated for $C_{14}H_{15}O_4FNa$ $[M+Na]^+$: 289.0852, found: 289.0860.

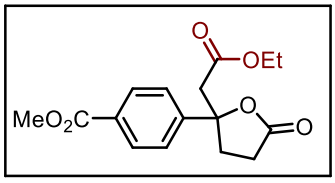
Ethyl 2-(2-(4-chlorophenyl)-5-oxotetrahydrofuran-2-yl)acetate (3g)



Purification by flash chromatography (PE/EA = 5/1). Yellow oil; 95% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.31–7.23 (m, 4H), 4.05–3.97 (m, 2H), 2.91 (d, *J* = 15.2 Hz, 1H), 2.86 (d, *J* = 15.6 Hz, 1H), 2.82–2.76 (m, 1H), 2.66–2.58 (m, 1H), 2.53–2.37 (m, 2H), 1.11 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 175.7, 168.7,

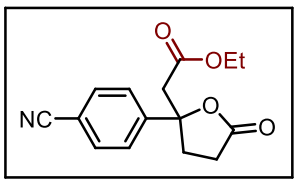
141.2, 134.1, 128.8, 126.2, 85.5, 61.0, 46.4, 33.4, 28.5, 14.0. **HRMS (ESI)** calculated for $C_{14}H_{15}O_4NaCl$ $[M+Na]^+$: 305.0557, found: 305.0560.

Methyl 4-(2-(2-ethoxy-2-oxoethyl)-5-oxotetrahydrofuran-2-yl)benzoate (3h)



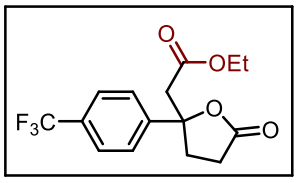
Purification by flash chromatography (PE/EA = 5/1). Yellow solid; m.p. = 67−69 °C; 87% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.05 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 2H), 4.12–4.04 (m, 2H), 3.93 (s, 3H), 3.02 (d, *J* = 15.6 Hz, 1H), 2.99–2.88 (m, 2H), 2.77 – 2.69 (m, 1H), 2.63–2.46 (m, 2H), 1.17 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 175.7, 168.6, 166.5, 147.6, 130.0, 124.7, 85.6, 61.0, 52.3, 46.1, 33.4, 28.4, 14.0. **HRMS (ESI)** calculated for $C_{16}H_{18}O_6Na$ $[M+Na]^+$: 329.1001, found: 329.1008.

Ethyl 2-(2-(4-cyanophenyl)-5-oxotetrahydrofuran-2-yl)acetate (3i)



Purification by flash chromatography (PE/EA = 5/1). Colorless oil; 66% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.70 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 4.12–4.05 (m, 2H), 3.01 (d, *J* = 15.6 Hz, 1H), 2.98–2.85 (m, 2H), 2.81–2.71 (m, 1H), 2.60–2.46 (m, 2H), 1.18 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 175.2, 168.4, 147.9, 132.6, 125.6, 118.3, 112.2, 85.1, 61.2, 46.0, 33.4, 28.3, 14.0. **HRMS (ESI)** calculated for $C_{15}H_{15}NO_4Na$ $[M+Na]^+$: 296.0899, found: 296.0906.

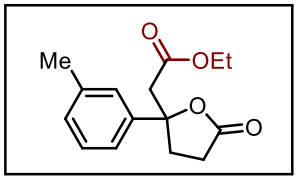
Ethyl 2-(5-oxo-2-(4-(trifluoromethyl)phenyl)tetrahydrofuran-2-yl)acetate (3j)



Purification by flash chromatography (PE/EA = 5/1). Colorless oil; 73% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.66 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 4.14–4.03 (m, 2H), 3.02 (d, *J* = 15.6 Hz, 1H), 2.99–2.88 (m, 2H), 2.77–2.69 (m, 1H), 2.65–2.46 (m, 2H), 1.17 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 175.5, 168.6, 146.7, 130.4 (q, *J* = 32.4 Hz) 125.7 (q, *J* = 3.5 Hz), 125.2, 123.8 (q, *J* =

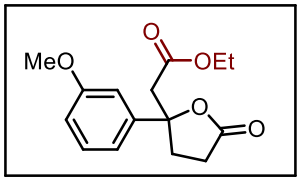
271.0 Hz), 85.4, 61.1, 46.2, 33.4, 28.4, 14.0. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.7 (s). **HRMS (ESI)** calculated for $C_{15}H_{15}O_4F_3Na$ $[M+Na]^+$: 339.0820, found: 339.0825.

Ethyl 2-(5-oxo-2-(m-tolyl)tetrahydrofuran-2-yl)acetate (3k)



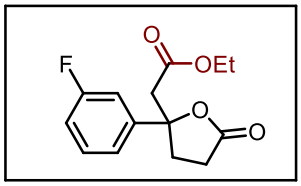
Purification by flash chromatography (PE/EA = 5/1). Yellow oil; 71% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.28–7.24 (m, 1H), 7.21 (s, 1H), 7.17–7.11 (m, 2H), 4.09 (q, *J* = 7.2 Hz, 2H), 3.01–2.84 (m, 3H), 2.71–2.56 (m, 2H), 2.53–2.45 (m, 1H), 2.36 (s, 3H), 1.18 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 176.2, 169.0, 142.8, 138.4, 128.8, 128.6, 125.2, 121.6, 86.0, 60.9, 46.5, 33.3, 28.6, 21.6, 14.0. **HRMS (ESI)** calculated for $C_{15}H_{18}O_4Na$ $[M+Na]^+$: 285.1103, found: 285.1111.

Ethyl 2-(2-(3-methoxyphenyl)-5-oxotetrahydrofuran-2-yl)acetate (3l)



Purification by flash chromatography (PE/EA = 5/1). Colorless oil; 70% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.31–7.27 (m, 1H), 6.95–6.93 (m, 2H), 6.86–6.83 (m, 1H), 4.09 (q, *J* = 7.2 Hz, 2H), 3.81 (s, 3H), 2.99 (d, *J* = 15.6 Hz, 1H), 2.94 (d, *J* = 15.6 Hz, 1H), 2.90–2.85 (m, 1H), 2.72–2.65 (m, 1H), 2.62–2.45 (m, 2H), 1.18 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 176.1, 168.9, 159.8, 144.5, 129.8, 116.7, 113.3, 110.5, 85.8, 60.9, 55.3, 46.4, 33.3, 28.6, 14.0. **HRMS (ESI)** calculated for $C_{15}H_{18}O_5Na$ $[M+Na]^+$: 301.1046, found: 301.1042.

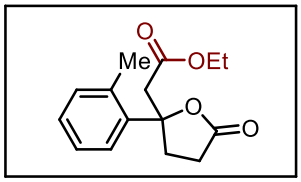
Ethyl 2-(2-(3-fluorophenyl)-5-oxotetrahydrofuran-2-yl)acetate (3m)



Purification by flash chromatography (PE/EA = 5/1). Colorless oil; 74% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.39–7.33 (m, 1H), 7.18–7.11 (m, 2H), 7.04–7.00 (m, 1H), 4.09 (q, *J* = 7.0 Hz, 2H), 2.99 (d, *J* = 15.2 Hz, 1H), 2.94 (d, *J* = 15.2 Hz, 1H), 2.90–2.85 (m, 1H), 7.74–7.67 (m, 1H), 2.61–2.46 (m, 2H), 1.18 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 175.7, 168.7, 162.8 (d,

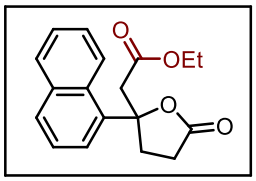
J = 245.5 Hz), 145.4 (d, J = 6.7 Hz), 130.4 (d, J = 8.3 Hz), 120.2 (d, J = 3.0 Hz), 115.1 (d, J = 20.9 Hz), 112.1 (d, J = 23.1 Hz), 85.3 (d, J = 1.9 Hz), 61.0, 46.3, 33.4, 28.4, 14.0. **^{19}F NMR (376 MHz, $CDCl_3$)** δ (ppm) -111.6 – -111.7 (m). **HRMS (ESI)** calculated for $C_{14}H_{15}O_4FNa$ $[M+Na]^+$: 289.0847, found: 289.0843.

Ethyl 2-(5-oxo-2-(o-tolyl)tetrahydrofuran-2-yl)acetate (3n)



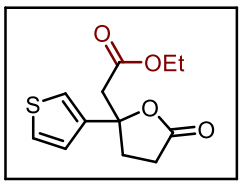
Purification by flash chromatography (PE/EA = 5/1). Colorless oil; 63% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.50–7.47 (m, 1H), 7.24–7.17 (m, 3H), 4.12–4.05 (m, 2H), 3.09 (d, J = 15.6 Hz, 1H), 3.00–2.93 (m, 2H), 2.82–2.72 (m, 1H), 2.65–2.49 (m, 2H), 2.45 (s, 3H), 1.18 (t, J = 7.0 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 176.1, 169.3, 141.0, 133.5, 132.6, 128.1, 126.1, 125.0, 86.6, 60.9, 44.6, 32.8, 28.7, 21.5, 14.0. **HRMS (ESI)** calculated for $C_{14}H_{18}O_4Na$ $[M+Na]^+$: 285.1097, found: 285.1093.

Ethyl 2-(2-(naphthalen-1-yl)-5-oxotetrahydrofuran-2-yl)acetate (3o)



Purification by flash chromatography (PE/EA = 5/1). Yellow solid; m.p. = 67−69 °C; 90% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.89–7.81 (m, 4H), 7.51–7.47 (m, 2H), 7.45–7.42 (m, 1H), 4.11–4.00 (m, 2H), 3.06 (s, 2H), 2.98–2.90 (m, 1H), 2.75–2.64 (m, 2H), 2.54–2.45 (m, 1H), 1.12 (t, J = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 176.2, 168.9, 140.0, 132.9, 132.8, 128.8, 128.3, 127.6, 126.7, 126.6, 123.5, 122.5, 86.1, 60.9, 46.3, 33.3, 28.6, 14.0. **HRMS (ESI)** calculated for $C_{18}H_{18}O_4Na$ $[M+Na]^+$: 321.1103, found: 321.1111.

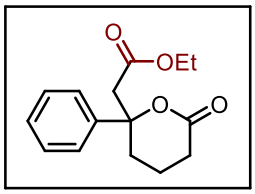
Ethyl 2-(5-oxo-2-(thiophen-3-yl)tetrahydrofuran-2-yl)acetate (3p)



Purification by flash chromatography (PE/EA = 5/1). Yellow oil; 90% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.36–7.34 (m, 1H), 7.28–7.26 (m, 1H), 7.06–7.05 (m, 1H), 4.10 (q, J = 7.2 Hz,

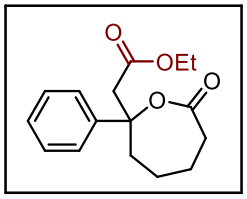
2H), 3.00 (s, 2H), 2.85–2.77 (m, 1H), 2.71–2.62 (m, 2H), 2.60–2.50 (m, 1H), 1.19 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ (ppm) 176.1, 168.9, 143.7, 127.0, 125.0, 121.1, 84.7, 60.9, 45.9, 33.3, 28.7, 14.0. **HRMS (ESI)** calculated for $C_{12}H_{14}O_4NaS$ $[M+Na]^+$: 277.0510, found: 277.0516.

Ethyl 2-(6-oxo-2-phenyltetrahydro-2H-pyran-2-yl)acetate (3q)



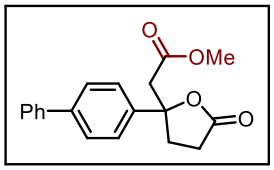
Purification by flash chromatography (PE/EA = 5/1). Yellow solid; m.p. = 52−54 °C; 65% yield; **^{1}H NMR (400 MHz, CDCl$_3$)** δ (ppm) 7.40–7.37 (m, 4H), 7.32–7.31 (m, 1H), 4.12–4.00 (m, 2H), 2.95 (d, *J* = 14.8 Hz, 1H), 2.90 (d, *J* = 15.2 Hz, 1H), 2.55–2.40 (m, 4H), 1.83–1.77 (m, 1H), 1.65–1.53 (m, 1H), 1.15 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ (ppm) 170.8, 168.9, 142.4, 128.7, 127.9, 125.0, 84.9, 60.7, 48.0, 31.1, 29.3, 16.3, 14.0. **HRMS (ESI)** calculated for $C_{15}H_{18}O_4Na$ $[M+Na]^+$: 285.1103, found: 285.1111.

Ethyl 2-(7-oxo-2-phenyloxepan-2-yl)acetate (3r)



Purification by flash chromatography (PE/EA = 5/1). Colorless oil; 27% yield; **^{1}H NMR (400 MHz, CDCl$_3$)** δ (ppm) 7.42–7.38 (m, 2H), 7.34–7.30 (m, 3H), 4.02–3.90 (m, 2H), 3.08 (d, *J* = 16.0 Hz, 1H), 2.87 (d, *J* = 13.6 Hz, 1H), 2.90 (d, *J* = 13.6 Hz, 1H), 2.54 (dd, *J* = 14.0, 6.8 Hz, 1H), 2.32–2.24 (m, 1H), 1.99–1.81 (m, 3H), 1.73–1.69 (m, 1H), 1.58–1.50 (m, 1H), 1.07 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ (ppm) 174.9, 169.0, 140.5, 128.9, 127.9, 125.9, 84.5, 60.6, 51.8, 36.8, 36.0, 24.1, 22.9, 14.0. **HRMS (ESI)** calculated for $C_{16}H_{20}O_4Na$ $[M+Na]^+$: 299.1254, found: 299.1249.

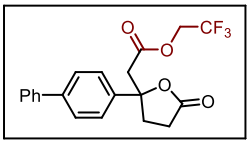
Methyl 2-(2-([1,1'-biphenyl]-4-yl)-5-oxotetrahydrofuran-2-yl)acetate (3s)



Purification by flash chromatography (PE/EA = 5/1). White solid; m.p. = 72−74 °C; 88% yield; **^{1}H NMR (400 MHz,**

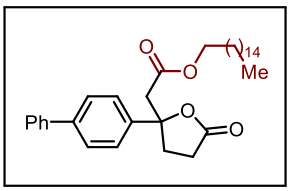
$CDCl_3$) δ (ppm) 7.52–7.48 (m, 4H), 7.38–7.33 (m, 4H), 7.28–7.24 (m, 1H), 3.54 (s, 3H), 2.96 (d, *J* = 15.6 Hz, 1H), 2.92 (d, *J* = 15.6 Hz, 1H), 2.85–2.77 (m, 1H), 2.65–2.51 (m, 2H), 2.46–2.37 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 176.1, 169.4, 141.7, 141.0, 140.2, 128.9, 127.7, 127.4, 127.1, 125.1, 85.8, 51.9, 46.1, 33.4, 28.6. **HRMS (ESI)** calculated for $C_{19}H_{18}O_4Na$ $[M+Na]^+$: 333.1103, found: 333.1106.

2,2,2-trifluoroethyl 2-(2-([1,1'-biphenyl]-4-yl)-5-oxotetrahydrofuran-2-yl)acetate (3t)



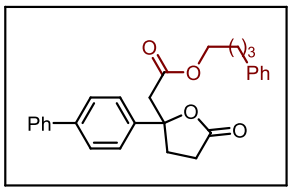
Purification by flash chromatography (PE/EA = 5/1). Colorless oil; 63% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.62–7.57 (m, 4H), 7.47–7.43 (m, 4H), 7.39–7.35 (m, 1H), 4.50–4.35 (m, 2H), 3.19 (d, *J* = 16.0 Hz, 1H), 3.13 (d, *J* = 16.0 Hz, 1H), 2.89–2.81 (m, 1H), 2.75–2.65 (m, 2H), 2.59–2.49 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 175.7, 167.3, 141.3, 140.9, 140.2, 128.9, 127.7, 127.5, 127.1, 125.4 (q, *J* = 275.9 Hz), 125.0, 85.3, 60.5 (q, *J* = 36.6 Hz), 45.7, 33.5, 28.4. **^{19}F NMR (376 MHz, $CDCl_3$)** δ (ppm) -73.7 (t, *J* = 8.3 Hz). **HRMS (ESI)** calculated for $C_{20}H_{17}O_4NaF_3$ $[M+Na]^+$: 401.0977, found: 401.0979.

Hexadecyl 2-(2-([1,1'-biphenyl]-4-yl)-5-oxotetrahydrofuran-2-yl)acetate (3u)



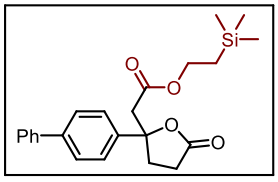
Purification by flash chromatography (PE/EA = 5/1). Yellow solid; m.p. = 55–57 °C; 78% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.52–7.47 (m, 4H), 7.38–7.32 (m, 4H), 7.27–7.23 (m, 1H), 3.92 (t, *J* = 6.8 Hz, 2H), 2.95 (d, *J* = 15.6 Hz, 1H), 2.90 (d, *J* = 15.2 Hz, 1H), 2.86–2.77 (m, 1H), 2.64–2.51 (m, 2H), 2.46–2.36 (m, 1H), 1.45–1.41 (m, 2H), 1.14 – 1.23 (m, 26H), 0.79 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 176.0, 169.0, 141.7, 141.0, 140.2, 128.9, 127.6, 127.3, 127.1, 125.1, 85.9, 65.1, 46.4, 33.4, 32.0, 29.7, 29.6, 29.5, 29.4, 29.2, 28.6, 28.5, 25.9, 22.7, 14.2. **HRMS (ESI)** calculated for $C_{34}H_{48}O_4Na$ $[M+Na]^+$: 543.3450, found: 543.3446.

4-Phenylbutyl 2-(2-([1,1'-biphenyl]-4-yl)-5-oxotetrahydrofuran-2-yl)acetate (3v)



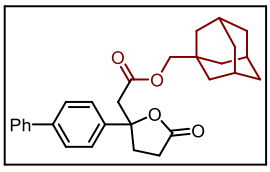
Purification by flash chromatography (PE/EA = 5/1). Yellow solid; m.p. = 53−55 °C; 64% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.60–7.55 (m, 4H), 7.46–7.42 (m, 4H), 7.38–7.34 (m, 1H), 7.27–7.24 (m, 2H), 7.19–7.12 (m, 3H), 4.04 (t, *J* = 6.2 Hz, 2H), 3.04 (d, *J* = 15.6 Hz, 1H), 3.00 (d, *J* = 15.6 Hz, 1H), 2.93–2.85 (m, 1H), 2.74–2.63 (m, 2H), 2.62–2.47 (m, 3H), 1.59–1.57 (m, 4H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 176.0, 169.0, 141.9, 141.6, 141.0, 140.2, 128.9, 128.4, 128.3, 127.6, 127.4, 127.1, 125.9, 125.1, 85.9, 64.8, 46.4, 35.3, 33.4, 28.6, 28.0, 27.6. **HRMS (ESI)** calculated for $C_{28}H_{28}O_4Na$ $[M+Na]^+$: 451.1885, found: 451.1887.

2-(Trimethylsilyl)ethyl 2-(2-([1,1'-biphenyl]-4-yl)-5-oxotetrahydrofuran-2-yl)acetate (3w)



Purification by flash chromatography (PE/EA = 5/1). Colorless oil; 65% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.61–7.56 (m, 4H), 7.47–7.42 (m, 4H), 7.37–7.34 (m, 1H), 4.19–4.06 (m, 2H), 3.02 (d, *J* = 15.6 Hz, 1H), 3.00–2.88 (m, 2H), 2.75–2.61 (m, 2H), 2.57–2.47 (m, 1H), 0.93–0.88 (m, 2H), 0.00 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 177.6, 170.7, 143.3, 142.6, 141.8, 130.4, 129.2, 128.9, 128.6, 126.7, 87.5, 64.8, 48.1, 34.8, 30.2, 18.8, 0.0. **HRMS (ESI)** calculated for $C_{23}H_{28}O_4SiNa$ $[M+Na]^+$: 419.1649, found: 419.1645.

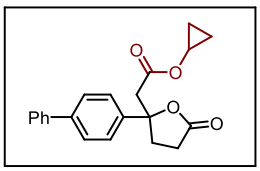
((3r,5r,7r)-Adamantan-1-yl)methyl 2-(2-([1,1'-biphenyl]-4-yl)-5-oxotetrahydrofuran -2-yl)acetate (3x)



Purification by flash chromatography (PE/EA = 5/1). White solid; m.p. = 98−100 °C; 61% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.61–7.56 (m, 4H), 7.48–7.42 (m, 4H), 7.38–7.34 (m, 1H), 3.63 (d, *J* = 10.8 Hz, 1H), 3.60 (d, *J* = 10.8 Hz, 1H), 3.08 (d, *J* =

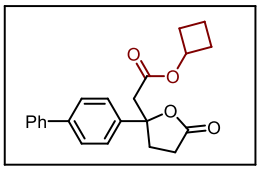
15.2 Hz, 1H), 3.03 (d, *J* = 15.6 Hz, 1H), 2.96–2.87 (m, 1H), 2.75–2.61 (m, 2H), 2.58–2.48 (m, 1H), 1.91 (s, 3H), 1.67 (d, *J* = 12.0 Hz, 3H), 1.58 (d, *J* = 11.6 Hz, 3H), 1.43–1.36 (m, 6H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ (ppm) 176.1, 169.2, 141.5, 141.1, 140.3, 128.9, 127.6, 127.4, 127.1, 125.2, 86.0, 74.6, 46.4, 39.1, 36.8, 33.5, 32.9, 28.6, 27.9. **HRMS (ESI)** calculated for $C_{29}H_{32}O_4Na$ $[M+Na]^+$: 467.2193, found: 467.2187.

Cyclopropyl 2-(2-([1,1'-biphenyl]-4-yl)-5-oxotetrahydrofuran-2-yl)acetate (3y)



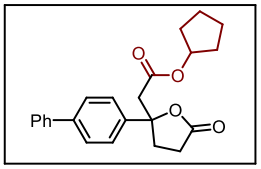
Purification by flash chromatography (PE/EA = 5/1). White solid; m.p. = 62−64 °C; 38% yield; **^{1}H NMR (400 MHz, CDCl$_3$)** δ (ppm) 7.61–7.57 (m, 4H), 7.46–7.42 (m, 4H), 7.37–7.34 (m, 1H), 4.10–4.05 (m, 1H), 3.01 (d, *J* = 15.2 Hz, 1H), 2.97 (d, *J* = 15.6 Hz, 1H), 2.92–2.85 (m, 1H), 2.74–2.60 (m, 2H), 2.56–2.46 (m, 1H), 0.69–0.50 (m, 4H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ (ppm) 176.0, 169.8, 141.5, 141.1, 140.2, 128.9, 127.7, 127.4, 127.1, 125.1, 85.8, 49.4, 46.3, 33.4, 28.6, 5.0. **HRMS (ESI)** calculated for $C_{21}H_{20}O_4Na$ $[M+Na]^+$: 359.1254, found: 359.1248.

Cyclobutyl 2-(2-([1,1'-biphenyl]-4-yl)-5-oxotetrahydrofuran-2-yl)acetate (3z)



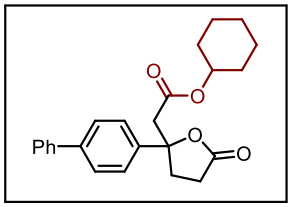
Purification by flash chromatography (PE/EA = 5/1). White solid; m.p. = 85−87 °C; 46% yield; **^{1}H NMR (400 MHz, CDCl$_3$)** δ (ppm) 7.56–7.61 (m, 4H), 7.47–7.42 (m, 4H), 7.37–7.33 (m, 1H), 4.97–4.89 (m, 1H), 3.01 (d, *J* = 15.2 Hz, 1H), 2.96 (d, *J* = 15.6 Hz, 1H), 2.92–2.85 (m, 1H), 2.73–2.59 (m, 2H), 2.55–2.45 (m, 1H), 2.31–2.24 (m, 2H), 2.03–1.88 (m, 2H), 1.78–1.70 (m, 1H), 1.62–1.51 (m, 1H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ (ppm) 176.1, 168.3, 141.7, 141.0, 140.3, 128.9, 127.6, 127.3, 127.1, 125.1, 85.9, 69.3, 46.4, 33.4, 30.1, 28.6, 13.6. **HRMS (ESI)** calculated for $C_{22}H_{22}O_4Na$ $[M+Na]^+$: 373.1410, found: 373.1406.

Cyclopentyl 2-(2-([1,1'-biphenyl]-4-yl)-5-oxotetrahydrofuran-2-yl)acetate (3aa)



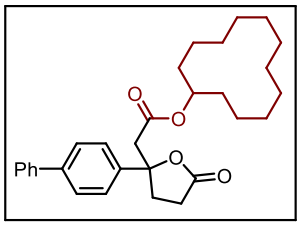
Purification by flash chromatography (PE/EA = 5/1). White solid; m.p. = 93−95 °C; 55% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.61–7.56 (m, 4H), 7.47–7.43 (m, 4H), 7.38–7.34 (m, 1H), 5.13–5.10 (m, 1H), 3.01 (d, *J* = 15.2 Hz, 1H), 2.96 (d, *J* = 15.2 Hz, 1H), 2.93–2.86 (m, 1H), 2.74–2.60 (m, 2H), 2.57–2.47 (m, 1H), 1.81–1.69 (m, 2H), 1.64–1.51 (m, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 176.1, 168.7, 141.6, 141.0, 140.3, 128.9, 127.6, 127.3, 127.1, 125.1, 86.7, 77.9, 46.8, 33.4, 32.6, 32.5, 28.6, 23.6. **HRMS (ESI)** calculated for $C_{23}H_{24}O_4Na$ $[M+Na]^+$: 387.1567, found: 387.1562.

Cyclohexyl 2-(2-([1,1'-biphenyl]-4-yl)-5-oxotetrahydrofuran-2-yl)acetate (3ab)



Purification by flash chromatography (PE/EA = 5/1). Yellow solid; m.p. = 115−117 °C; 65% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.61–7.56 (m, 4H), 7.47–7.43 (m, 4H), 7.38–7.34 (m, 1H), 4.75–4.71 (m, 1H), 3.03 (d, *J* = 15.2 Hz, 1H), 2.98 (d, *J* = 15.2 Hz, 1H), 2.96–2.88 (m, 1H), 2.75–2.61 (m, 2H), 2.57–2.47 (m, 1H), 1.79–1.62 (m, 4H), 1.51–1.48 (m, 1H), 1.40–1.19 (m, 5H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 176.1, 168.4, 141.7, 141.0, 140.3, 128.9, 127.6, 127.3, 127.1, 125.1, 86.0, 73.5, 46.8, 33.4, 31.5, 28.7, 25.3, 23.7. **HRMS (ESI)** calculated for $C_{24}H_{26}O_4Na$ $[M+Na]^+$: 401.1729, found: 401.1734.

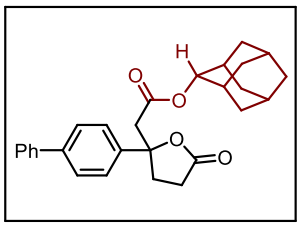
Cyclododecyl 2-(2-([1,1'-biphenyl]-4-yl)-5-oxotetrahydrofuran-2-yl)acetate (3ac)



Purification by flash chromatography (PE/EA = 5/1). White solid; m.p. = 124−126 °C; 57% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.60–7.56 (m, 4H), 7.47–7.43 (m, 4H), 7.38–7.34 (m, 1H), 4.99–4.93 (m, 1H), 3.02 (d, *J* = 15.2 Hz, 1H), 3.00–2.89 (m, 2H), 2.74–2.62 (m, 2H), 2.57–2.47 (m, 1H), 1.67–1.53 (m, 2H), 1.47–1.17 (m, 20H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 176.1, 168.6, 141.5, 141.0, 140.3, 128.9, 127.6, 127.3, 127.1, 125.2, 86.1, 73.2, 46.8, 33.4, 29.0, 28.8, 28.6,

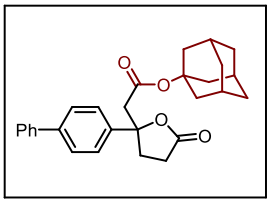
24.1, 23.9, 23.4, 23.3, 23.2, 23.1, 20.8, 20.7. **HRMS (ESI)** calculated for $C_{30}H_{38}O_4Na$ $[M+Na]^+$: 485.2668, found: 485.2665.

(1R,3S,5r,7r)-Adamantan-2-yl 2-(2-([1,1'-biphenyl]-4-yl)-5-oxotetrahydrofuran-2-yl)acetate (3ad)



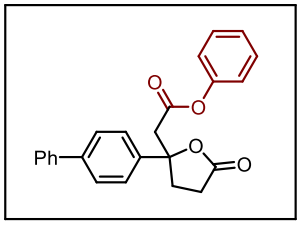
Purification by flash chromatography (PE/EA = 5/1). White solid; m.p. = 163−165 °C; 70% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.60–7.56 (m, 4H), 7.48–7.43 (m, 4H), 7.38–7.34 (m, 1H), 4.90 (s, 1H), 3.09 (d, *J* = 15.2 Hz, 1H), 3.04 (d, *J* = 14.8 Hz, 1H), 2.98–2.90 (m, 1H), 2.76–2.60 (m, 2H), 2.58–2.48 (m, 1H), 1.90–1.65 (m, 12H), 1.51–1.42 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 176.1, 168.4, 141.6, 141.1, 140.4, 128.9, 127.6, 127.4, 127.1, 125.1, 86.1, 77.9, 46.8, 37.3, 36.3, 33.5, 31.8, 31.6, 28.6, 27.1, 26.9. **HRMS (ESI)** calculated for $C_{28}H_{30}O_4Na$ $[M+Na]^+$: 453.2042, found: 453.2041.

(3s,5s,7s)-Adamantan-1-yl 2-(2-([1,1'-biphenyl]-4-yl)-5-oxotetrahydrofuran-2-yl) acetate (3ae)



Purification by flash chromatography (PE/EA = 5/1). Colorless oil; 58% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.61–7.57 (m, 4H), 7.47–7.43 (m, 4H), 7.38–7.34 (m, 1H), 2.98–2.86 (m, 3H), 2.74–2.67 (m, 1H), 2.65–2.58 (m, 1H), 2.56–2.48 (m, 1H), 2.12 (s, 3H), 2.06–1.96 (m, 6H), 1.67–1.52 (m, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 176.2, 167.9, 141.9, 140.9, 140.4, 128.9, 127.6, 127.3, 127.1, 125.2, 86.2, 81.8, 47.8, 41.2, 36.1, 33.3, 30.8, 28.7. **HRMS (ESI)** calculated for $C_{28}H_{30}O_4Na$ $[M+Na]^+$: 453.2036, found: 453.2036.

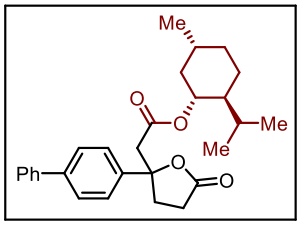
Phenyl 2-(2-([1,1'-biphenyl]-4-yl)-5-oxotetrahydrofuran-2-yl)acetate (3af)



Purification by flash chromatography (PE/EA = 5/1). White solid; m.p. = 90−92 °C; 43% yield; **^{1}H NMR (400 MHz,**

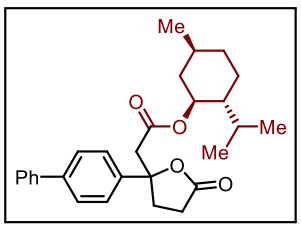
$CDCl_3$) δ (ppm) 7.64 (d, *J* = 8.8 Hz, 2H), 7.59–7.61 (m, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.48–7.44 (m, 2H), 7.39–7.32 (m, 3H), 7.23–7.19 (m, 1H), 6.96–6.94 (m, 2H), 3.31 (d, *J* = 15.6 Hz, 1H), 3.26 (d, *J* = 15.6 Hz, 1H), 3.01–2.93 (m, 1H), 2.78–2.68 (m, 2H), 2.62–2.51 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 175.9, 167.6, 150.2, 141.3, 140.2, 129.5, 128.9, 127.7, 127.5, 127.1, 126.2, 125.2, 121.4, 85.8, 46.5, 33.5, 28.5. **HRMS (ESI)** calculated for $C_{24}H_{20}O_4Na$ $[M+Na]^+$: 395.1259, found: 395.1257.

(1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl 2-(2-([1,1'-biphenyl]-4-yl)-5-oxotetrahydrofuran-2-yl)acetate (3ag)



Purification by flash chromatography (PE/EA = 5/1). White solid; m.p. = 127−129 °C; 45% yield; 1:1 dr; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.53–7.49 (m, 4H), 7.40–7.34 (m, 4H), 7.30–7.26 (m, 1H), 4.61–4.53 (m, 1H), 2.99–2.90 (m, 2H), 2.88–2.79 (m, 1H), 2.66–2.53 (m, 2H), 2.51–2.39 (m, 1H), 1.85–1.15 (m, 7H), 0.97–0.73 (m, 8H), 0.69 (d, *J* = 7.2 Hz, 1H), 0.63 (d, *J* = 7.2 Hz, 1H), 0.55 (d, *J* = 6.8 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 176.0, 168.5, 141.5, 141.4, 141.0, 140.3, 128.9, 127.6, 127.3, 127.1, 125.3, 125.2, 86.1, 86.0, 75.0, 46.8, 46.7, 46.6, 40.7, 34.1, 33.4, 33.3, 31.4, 28.6, 26.1, 26.0, 23.3, 22.0, 20.8, 20.7, 16.2, 16.1. **HRMS (ESI)** calculated for $C_{28}H_{34}O_4Na$ $[M+Na]^+$: 457.2355, found: 457.2356.

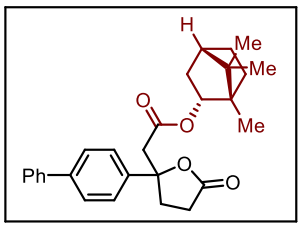
(1S,2R,5S)-2-Isopropyl-5-methylcyclohexyl 2-(2-([1,1'-biphenyl]-4-yl)-5-oxotetrahydrofuran-2-yl)acetate (3ah)



Purification by flash chromatography (PE/EA = 5/1). Yellow solid; m.p. = 115−117 °C; 50% yield; 1:1 dr; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.52–7.48 (m, 4H), 7.40–7.34 (m, 4H), 7.29–7.25 (m, 1H), 4.61–4.52 (m, 1H), 2.98–2.90 (m, 2H), 2.87–2.78 (m, 1H), 2.66–2.53 (m, 2H), 2.50–2.39 (m, 1H), 1.85–1.16 (m, 7H), 0.96–0.72 (m, 8H), 0.68 (d, *J* = 7.2 Hz, 1H), 0.63 (d, *J* = 7.2 Hz, 1H), 0.54 (d, *J* = 7.2 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 176.0, 168.5,

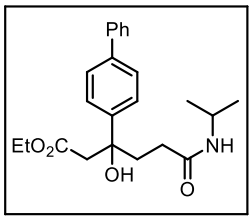
141.6, 141.0, 140.3, 128.9, 127.6, 127.3, 127.1, 125.3, 125.2, 86.1, 86.0, 75.0, 46.8, 46.7, 46.6, 40.7, 34.1, 33.4, 31.4, 28.6, 26.1, 26.0, 23.3, 22.0, 20.8, 20.7, 16.2. **HRMS (ESI)** calculated for $C_{28}H_{34}O_4Na$ $[M+Na]^+$: 457.2355, found: 457.2362.

(1S,2R,4S)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl 2-(2-([1,1'-biphenyl]-4-yl)-5-oxotetrahydrofuran-2-yl)acetate (3ai)



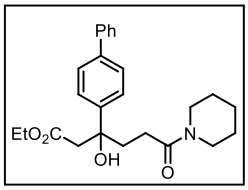
Purification by flash chromatography (PE/EA = 5/1). Yellow solid; m.p. = 54−56 °C; 67% yield; 1.1:1 dr; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.61–7.55 (m, 4H), 7.48–7.42 (m, 4H), 7.37–7.34 (m, 1H), 4.83–4.80 (m, 1H), 3.10–3.00 (m, 2H), 2.94–2.86 (m, 1H), 2.75–2.60 (m, 2H), 2.57–2.47 (m, 1H), 2.33–2.19 (m, 1H), 1.78–1.59 (m, 3H), 1.34–0.98 (m, 3H), 0.85 (s, 3H), 0.83 (s, 3H), 0.77 (s, 2H), 0.68 (s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 176.0, 169.2, 141.5, 141.4, 141.1, 140.3, 128.9, 127.6, 127.4, 127.1, 125.2, 125.1, 86.1, 86.0, 80.9, 48.7, 47.8, 46.8, 46.7, 44.8, 36.6, 33.5, 28.6, 27.9, 27.0, 19.7, 18.8, 13.4. **HRMS (ESI)** calculated for $C_{28}H_{32}O_4Na$ $[M+Na]^+$: 455.2198, found: 455.2202.

Ethyl 3-([1,1'-biphenyl]-4-yl)-3-hydroxy-6-(isopropylamino)-6-oxohexanoate (3a-I)



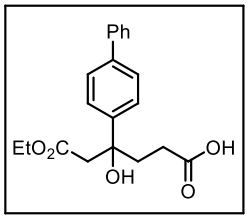
Purification by flash chromatography (PE/EA = 2/1). White solid; m.p. = 80−82 °C; 69% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.59–7.55 (m, 4H), 7.48–7.41 (m, 4H), 7.36–7.32 (m, 1H), 5.31 (d, *J* = 6.8 Hz, 1H), 4.87 (s, 1H), 4.04 (q, *J* = 7.2 Hz, 2H), 3.99–3.92 (m, 1H), 2.96 (d, *J* = 15.6 Hz, 1H), 2.82 (d, *J* = 15.6 Hz, 1H), 2.27–2.13 (m, 3H), 1.98–1.90 (m, 1H), 1.12–1.05 (m, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 172.6, 172.1, 143.5, 140.6, 139.8, 128.8, 127.3, 127.0, 125.7, 74.6, 60.8, 46.3, 41.3, 37.8, 31.0, 22.7, 14.0. **HRMS (ESI)** calculated for $C_{23}H_{29}NO_4Na$ $[M+Na]^+$: 406.1994, found: 406.1991.

Ethyl 3-([1,1'-biphenyl]-4-yl)-3-hydroxy-6-oxo-6-(piperidin-1-yl)hexanoate (3a-II)



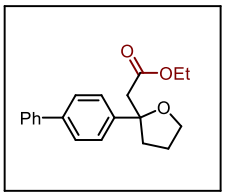
Purification by flash chromatography (PE/EA = 2/1). Colorless oil; 45% yield; **^{1}H NMR (400 MHz, CDCl$_3$)** δ (ppm) 7.60–7.56 (m, 4H), 7.50–7.48 (m, 2H), 7.45–7.41 (m, 2H), 7.35–7.32 (m, 1H), 4.96 (br, 1H), 4.04 (q, *J* = 6.8 Hz, 2H), 3.58–3.52 (m, 1H), 3.46–3.40 (m, 1H), 3.32–3.19 (m, 2H), 2.96 (d, *J* = 15.2 Hz, 1H), 2.84 (d, *J* = 15.6 Hz, 1H), 2.49–2.41 (m, 1H), 2.32–2.17 (m, 2H), 2.11–2.04 (m, 1H), 1.61–1.54 (m, 2H), 1.49–1.44 (m, 4H), 1.11 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ (ppm) 172.6, 171.3, 143.8, 140.7, 139.6, 128.8, 127.3, 127.0, 126.9, 125.7, 74.5, 60.8, 46.7, 46.5, 42.8, 37.4, 27.5, 26.3, 25.5, 24.5, 14.0. **HRMS (ESI)** calculated for $C_{25}H_{31}NO_4Na$ $[M+Na]^+$: 432.2145, found: 432.2139.

4-([1,1'-Biphenyl]-4-yl)-6-ethoxy-4-hydroxy-6-oxohexanoic acid (3a-III)



Purification by flash chromatography (PE/EA = 1/1). White solid; m.p. = 102−104 °C; 63% yield; **^{1}H NMR (400 MHz, CDCl$_3$)** δ (ppm) 7.58–7.54 (m, 4H), 7.45–7.40 (m, 4H), 7.34–7.30 (m, 1H), 4.60 (br, 1H), 4.03 (q, *J* = 6.8 Hz, 2H), 2.98 (d, *J* = 15.6 Hz, 1H), 2.82 (d, *J* = 16.0 Hz, 1H), 2.51–2.43 (m, 1H), 2.24–2.05 (m, 3H), 1.09 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ (ppm) 179.6, 172.6, 143.0, 140.6, 140.0, 128.8, 127.4, 127.1, 125.6, 74.3, 61.0, 45.7, 37.2, 28.5, 14.0. **HRMS (ESI)** calculated for $C_{20}H_{22}O_5Na$ $[M+Na]^+$: 365.1365, found: 365.1371.

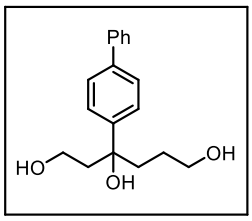
Ethyl 2-(2-([1,1'-biphenyl]-4-yl)tetrahydrofuran-2-yl)acetate (3a-IV)



Purification by flash chromatography (PE/EA = 8/1). Colorless oil; 35% yield; **^{1}H NMR (400 MHz, CDCl$_3$)** δ (ppm) 7.59–7.54 (m, 4H), 7.48–7.41 (m, 4H), 7.35–7.31 (m, 1H), 4.04 (q, *J* = 7.6 Hz, 3H), 3.96–3.90 (m, 1H), 2.88 (d, *J* = 14.0 Hz, 1H), 2.83 (d, *J* = 13.6 Hz, 1H), 2.48–2.41 (m, 1H), 2.38–2.31 (m, 1H), 2.04–1.95 (m, 1H), 1.89–1.78 (m, 1H), 1.12 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ (ppm) 170.3, 144.8,

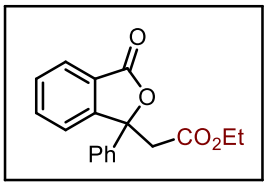
140.9, 139.7, 128.8, 127.2, 127.1, 126.8, 125.7, 84.6, 68.0, 60.3, 47.1, 37.4, 25.4, 14.1. **HRMS (ESI)** calculated for $C_{20}H_{22}O_3Na$ $[M+Na]^+$: 333.1461, found: 333.1456.

3-([1,1'-Biphenyl]-4-yl)hexane-1,3,6-triol (3a-V)



Purification by flash chromatography (PE/EA = 1/1). Gray solid; m.p. = 134−136 °C; 86% yield; **^{1}H NMR (400 MHz, DMSO)** δ (ppm) 7.68 (d, *J* = 7.2 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.50–7.44 (m, 4H), 7.37–7.33 (m, 1H), 4.97 (s, 1H), 4.48 (t, *J* = 4.2 Hz, 1H), 4.39 (t, *J* = 4.6 Hz, 1H), 3.51–3.46 (m, 1H), 3.32–3.28 (m, 3H), 2.01 (t, *J* = 7.2 Hz, 2H), 1.85–1.72 (m, 2H), 1.53–1.42 (m, 1H), 1.20–1.09 (m, 1H). **^{13}C NMR (100 MHz, DMSO)** δ (ppm) 146.9, 140.6, 138.0, 129.4, 127.6, 127.0, 126.4, 75.4, 61.8, 58.1, 45.1, 27.3. **HRMS (ESI)** calculated for $C_{18}H_{22}O_3Na$ $[M+Na]^+$: 309.1467, found: 309.1476.

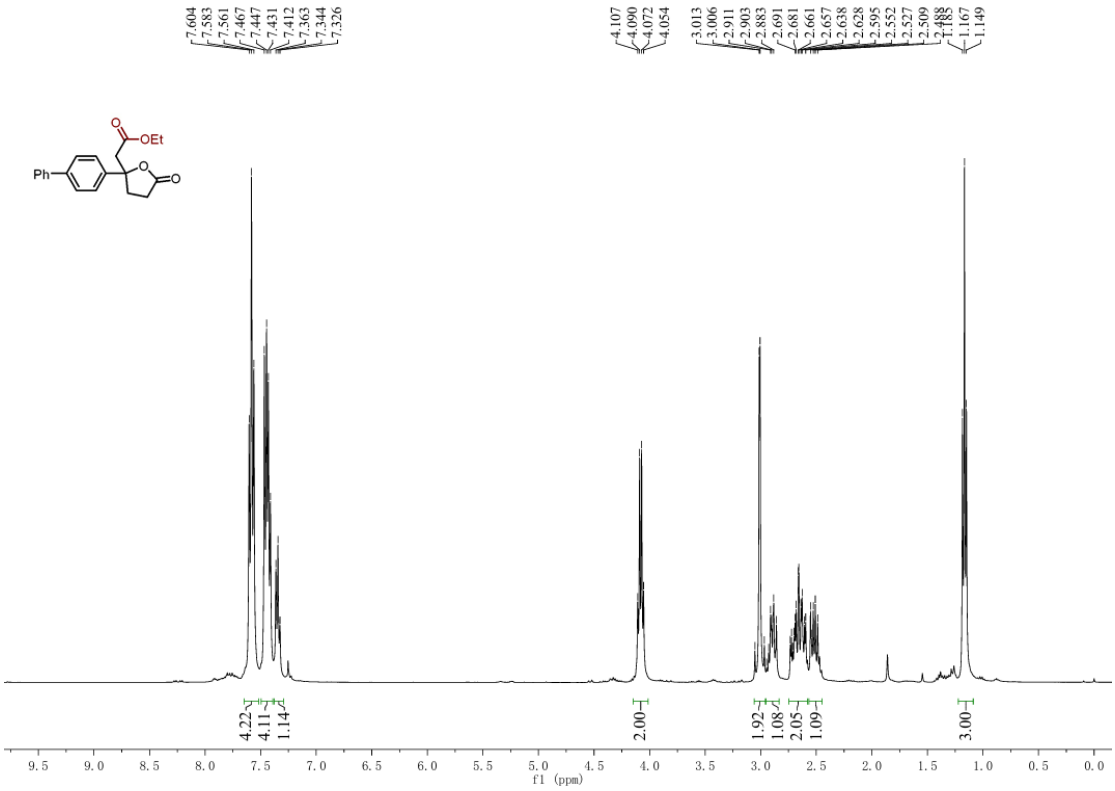
Ethyl 2-(3-oxo-1-phenyl-1,3-dihydroisobenzofuran-1-yl)acetate (5a)

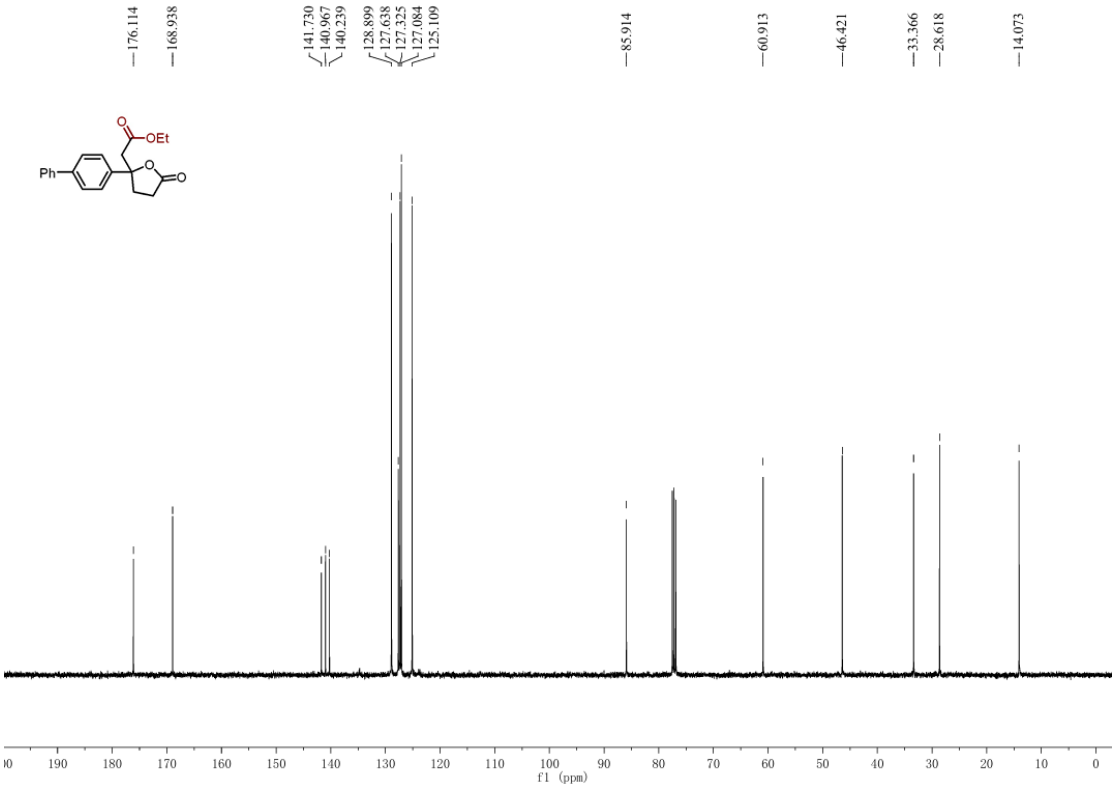


Purification by flash chromatography (PE/EA = 5/1). Colorless oil; 59% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.90 (d, *J* = 7.6 Hz, 1H), 7.71–7.63 (m, 2H), 7.56–7.50 (m, 3H), 7.39–7.30 (m, 3H), 3.93 (q, *J* = 7.2 Hz, 2H), 3.47 (d, *J* = 16.0 Hz, 1H), 3.40 (d, *J* = 16.0 Hz, 1H), 1.01 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 169.5, 168.0, 151.2, 139.7, 134.2, 129.5, 128.9, 128.6, 126.0, 125.8, 125.0, 122.8, 86.5, 60.9, 44.3, 13.8. **HRMS (ESI)** calculated for $C_{18}H_{16}O_4Na$ $[M+Na]^+$: 319.0941, found: 319.0941.

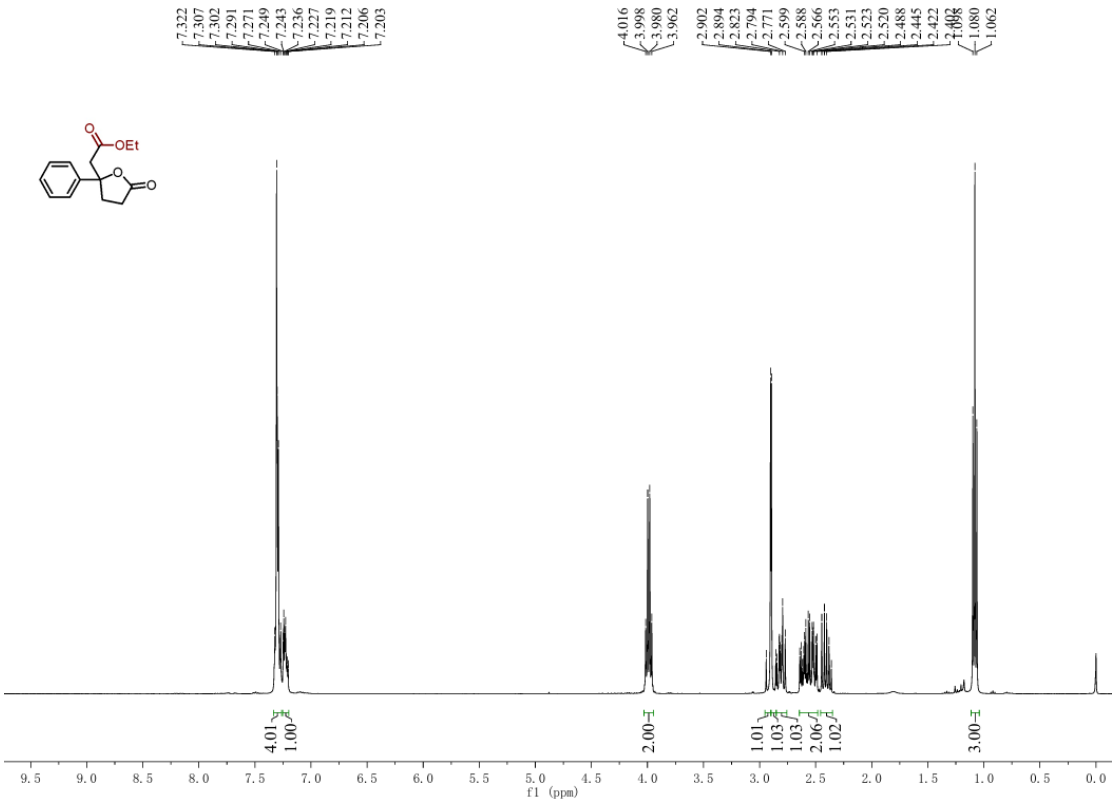
7. NMR spectra of compounds

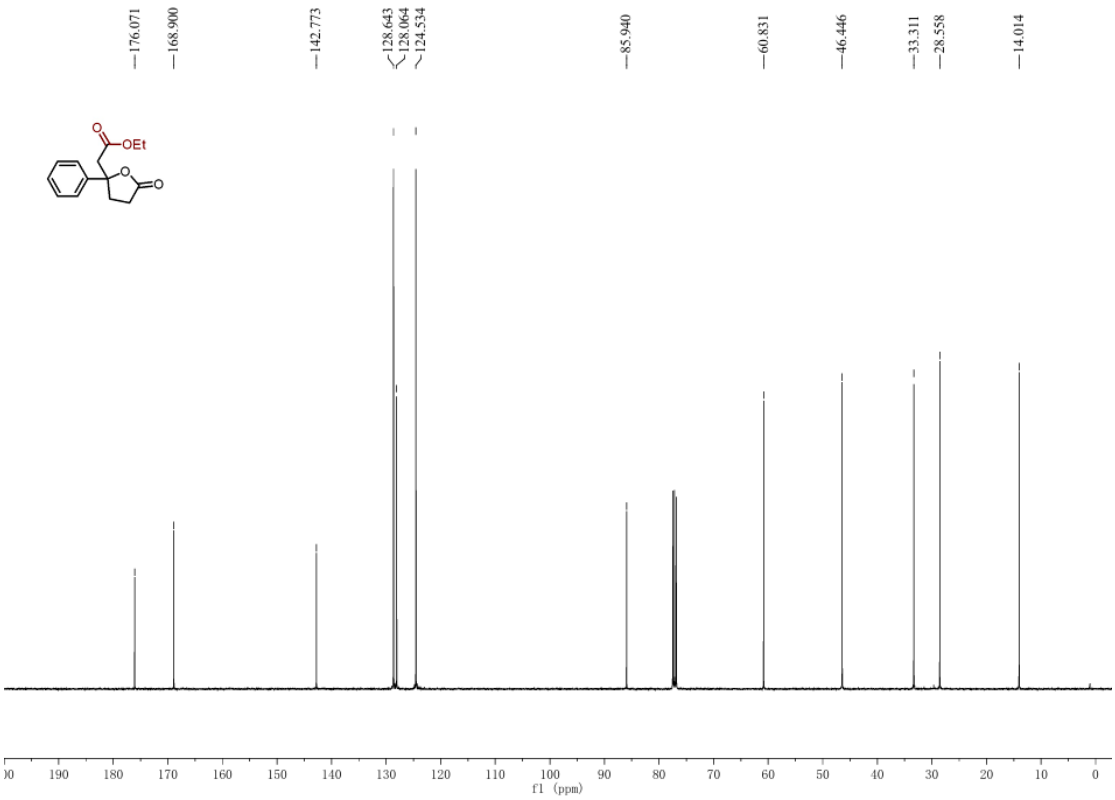
Ethyl 2-(2-([1,1'-biphenyl]-4-yl)-5-oxotetrahydrofuran-2-yl)acetate (3a)



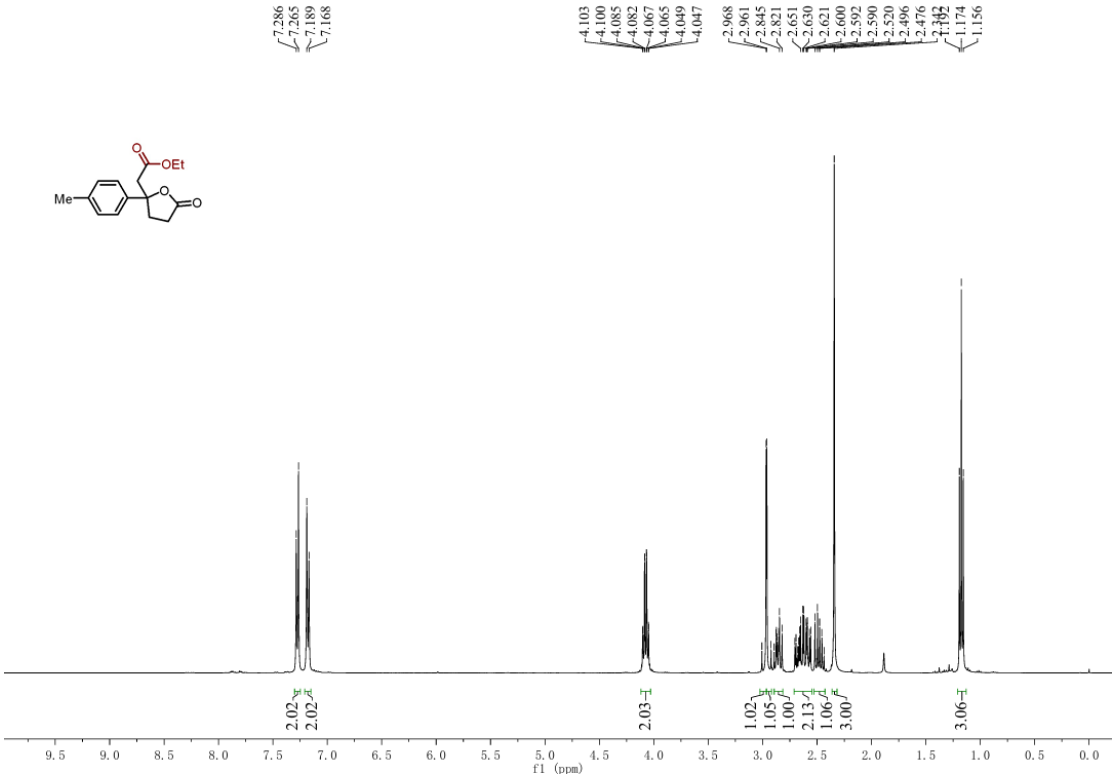


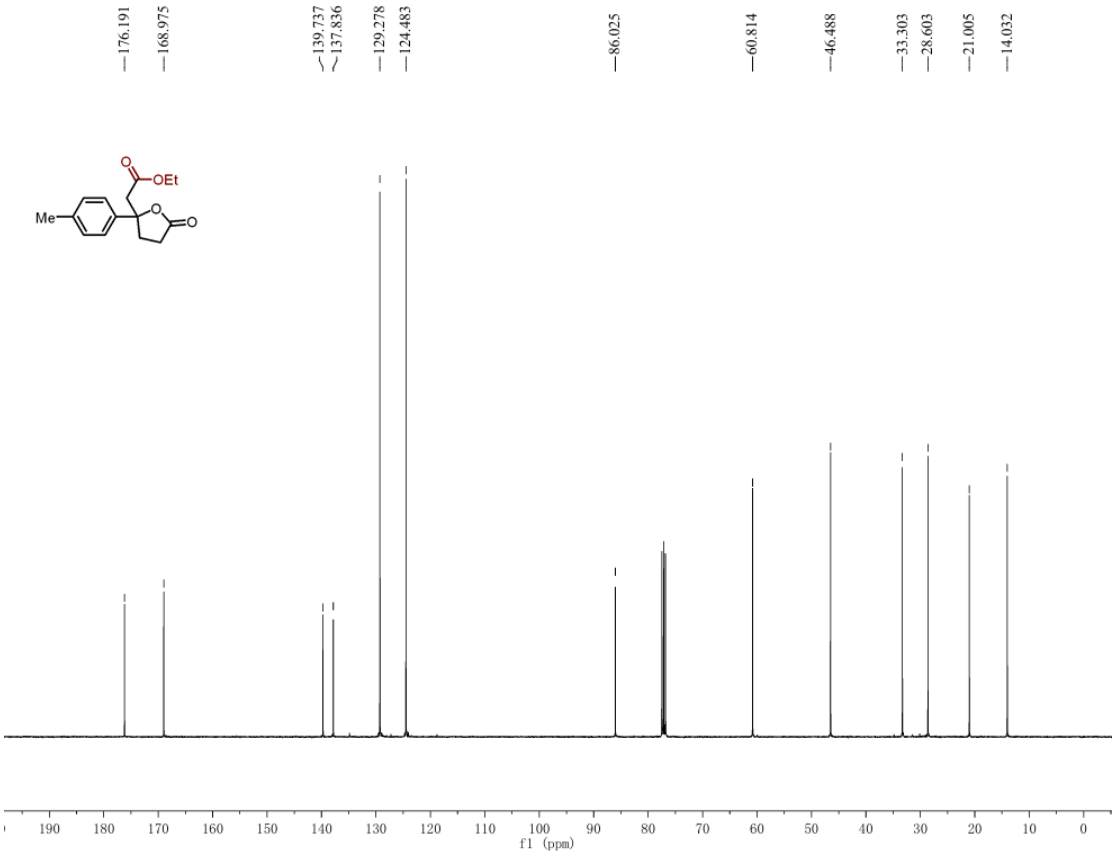
Ethyl 2-(5-oxo-2-phenyltetrahydrofuran-2-yl)acetate (3b)



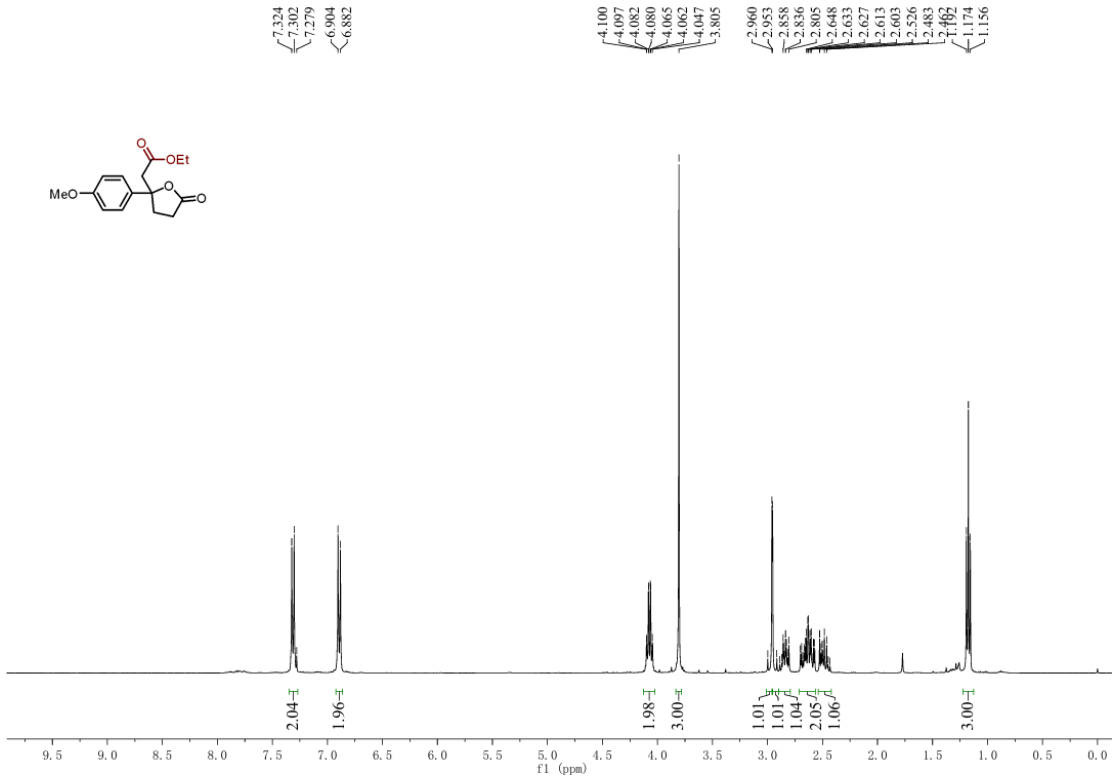


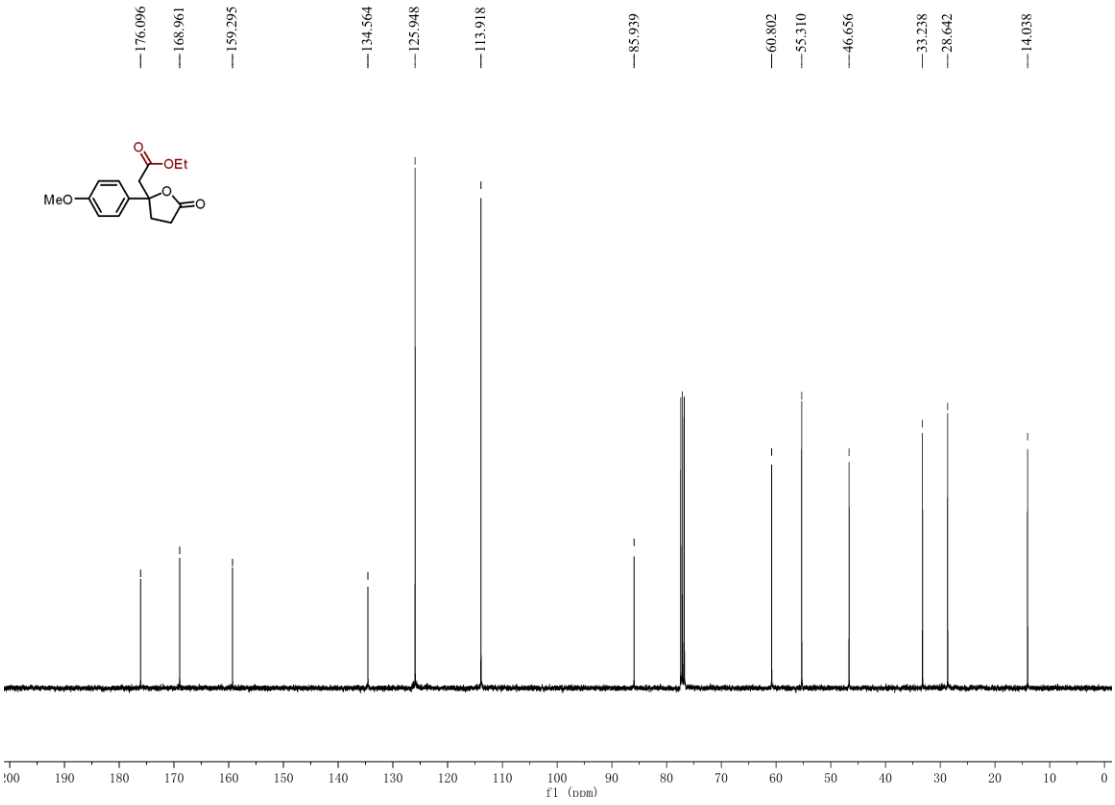
Ethyl 2-(5-oxo-2-(p-tolyl)tetrahydrofuran-2-yl)acetate (3c)



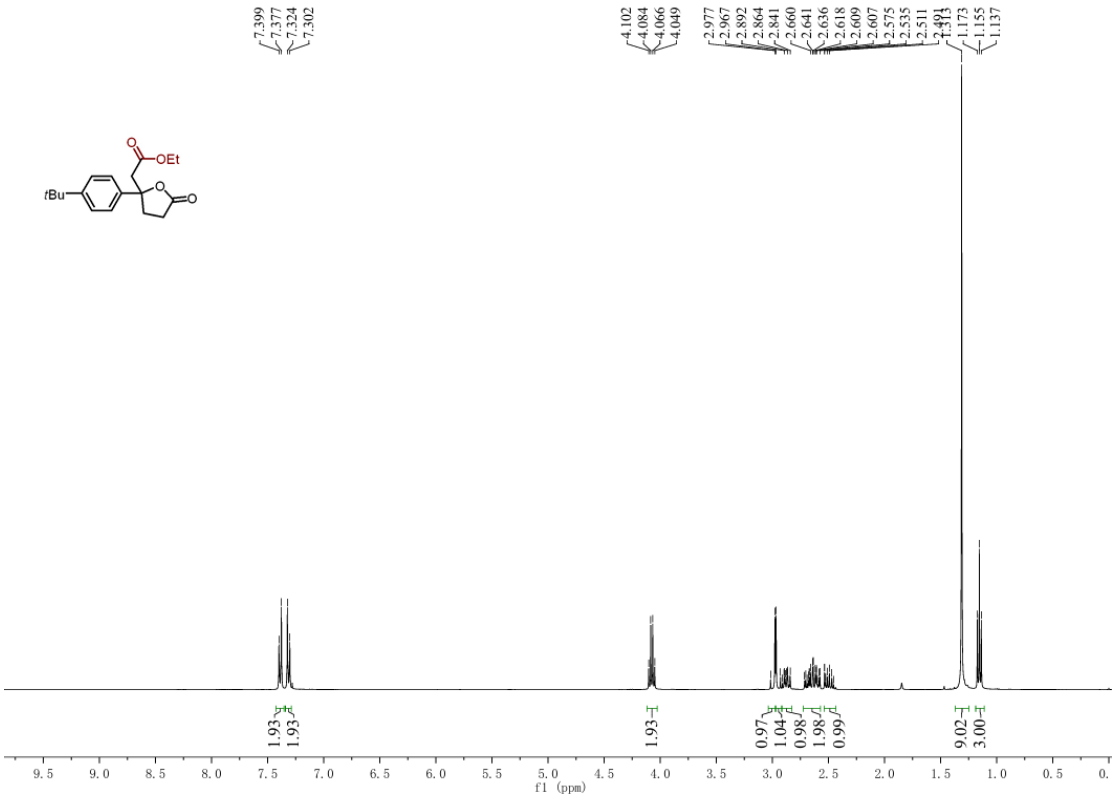


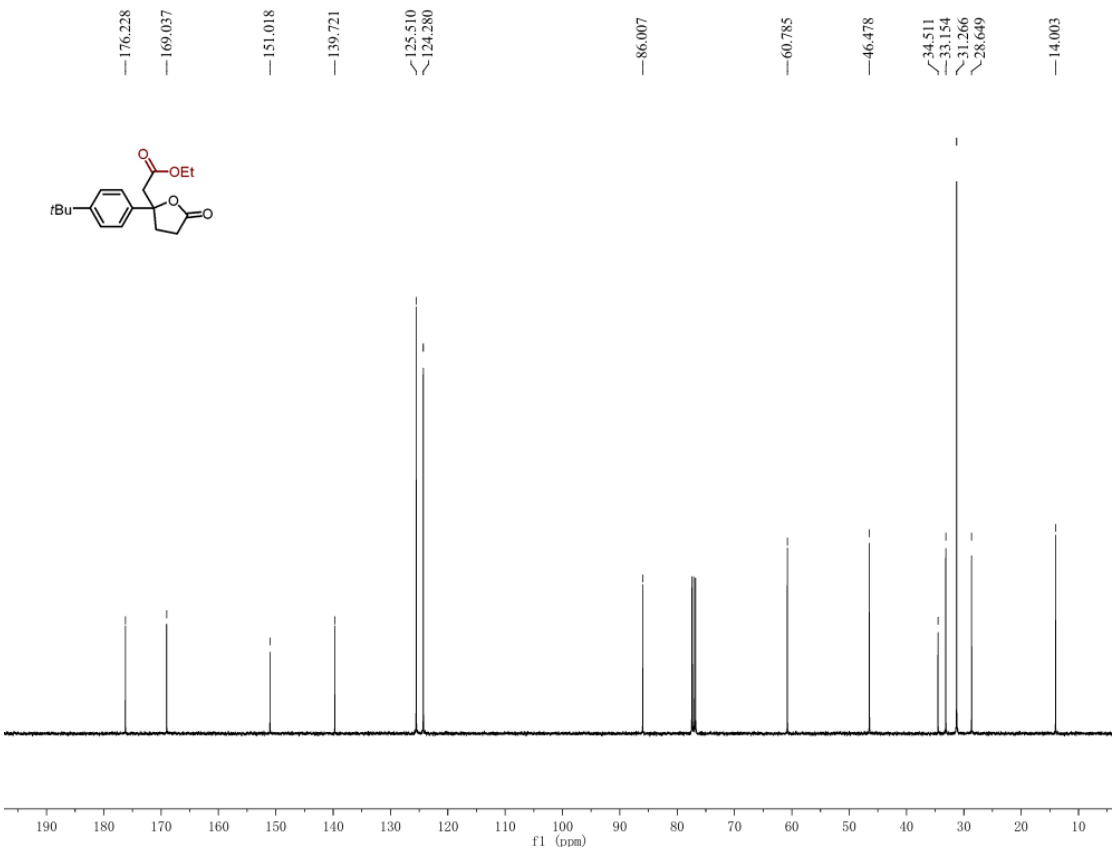
Ethyl 2-(2-(4-methoxyphenyl)-5-oxotetrahydrofuran-2-yl)acetate (3d)



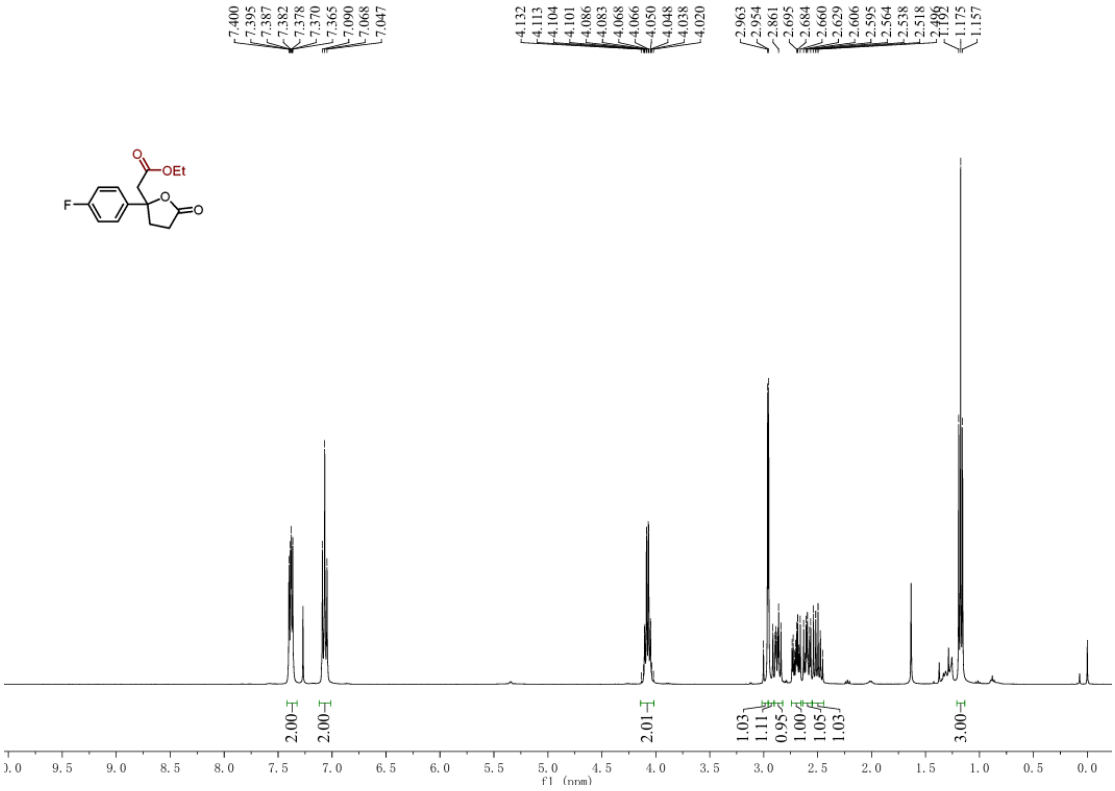


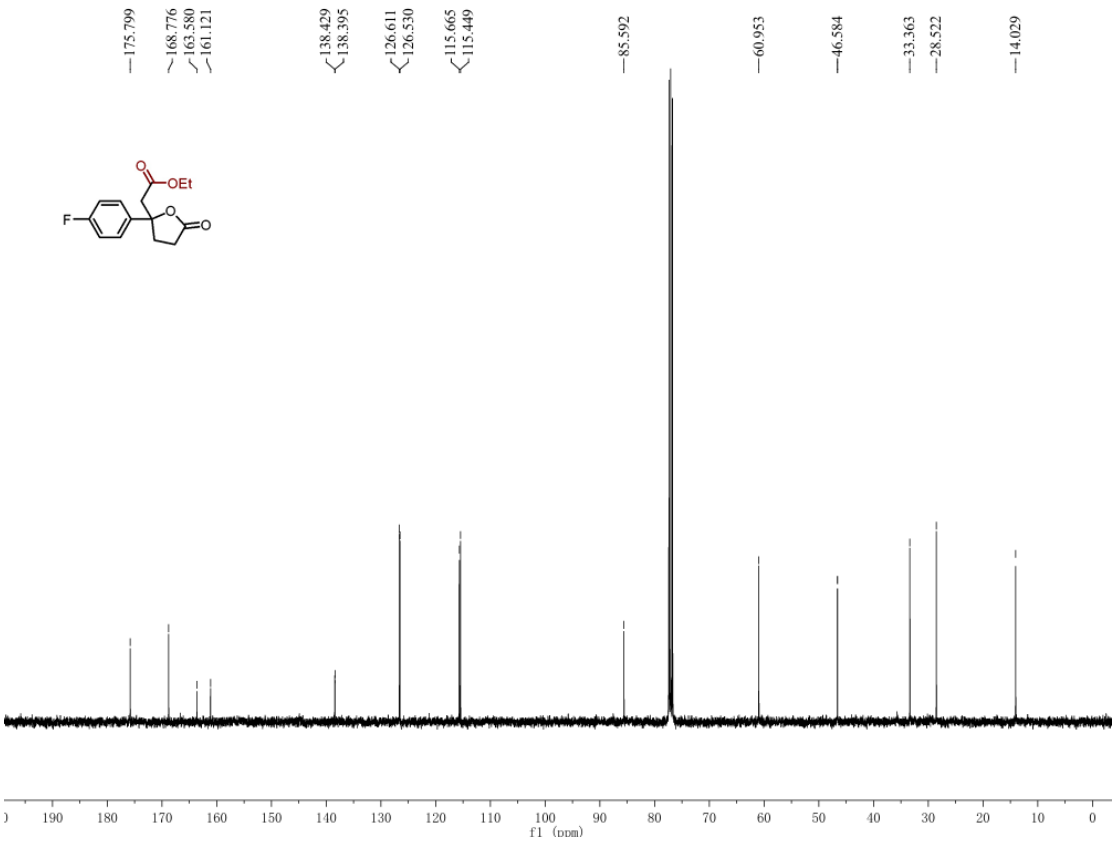
Ethyl 2-(2-(4-(tert-butyl)phenyl)-5-oxotetrahydrofuran-2-yl)acetate (3e)

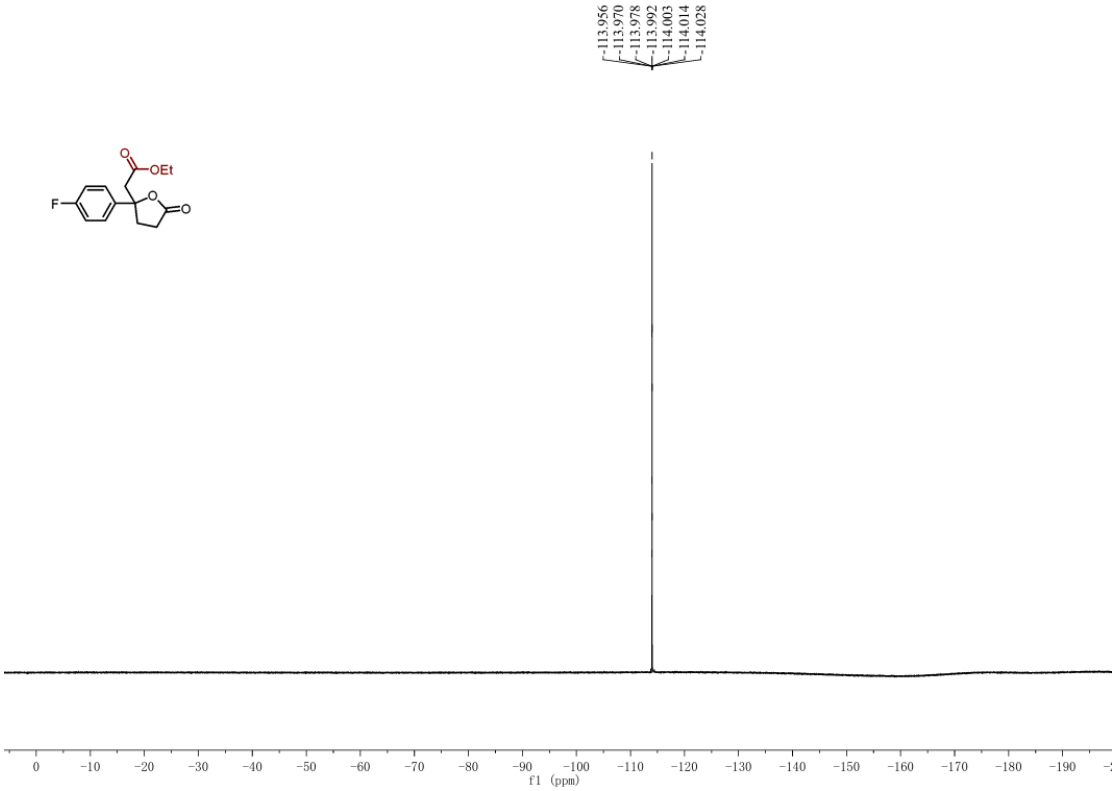




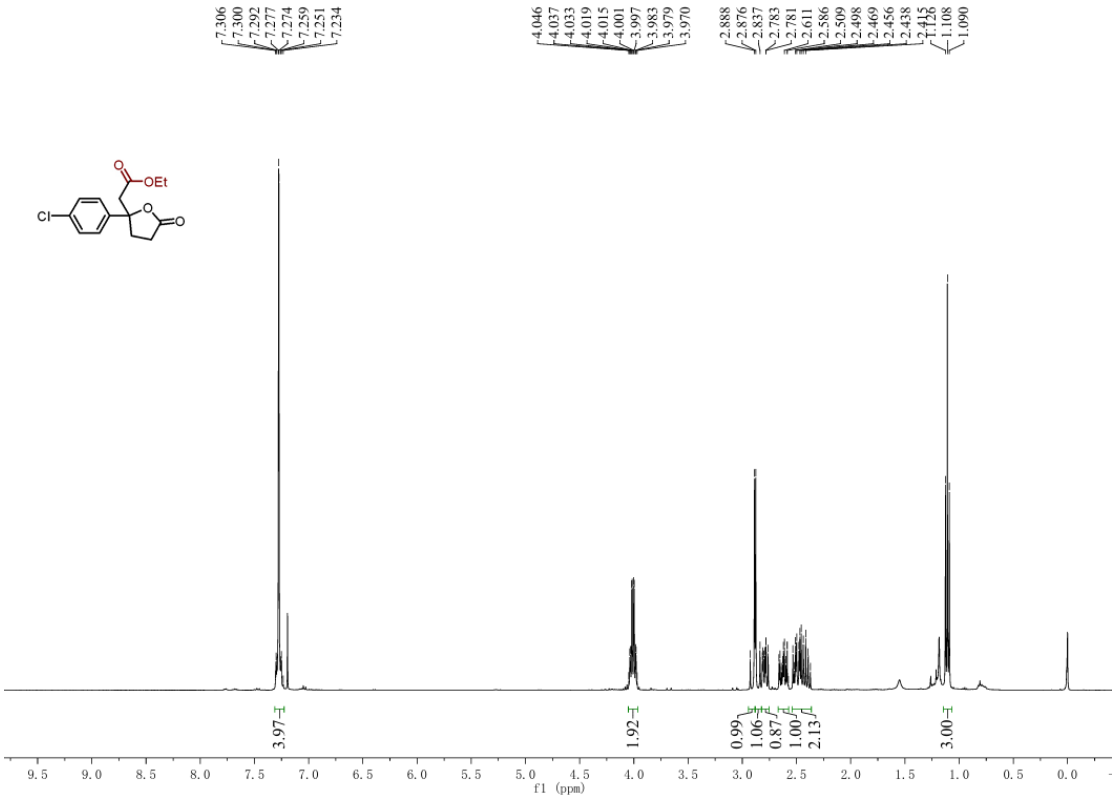
Ethyl 2-(2-(4-fluorophenyl)-5-oxotetrahydrofuran-2-yl)acetate (3f)

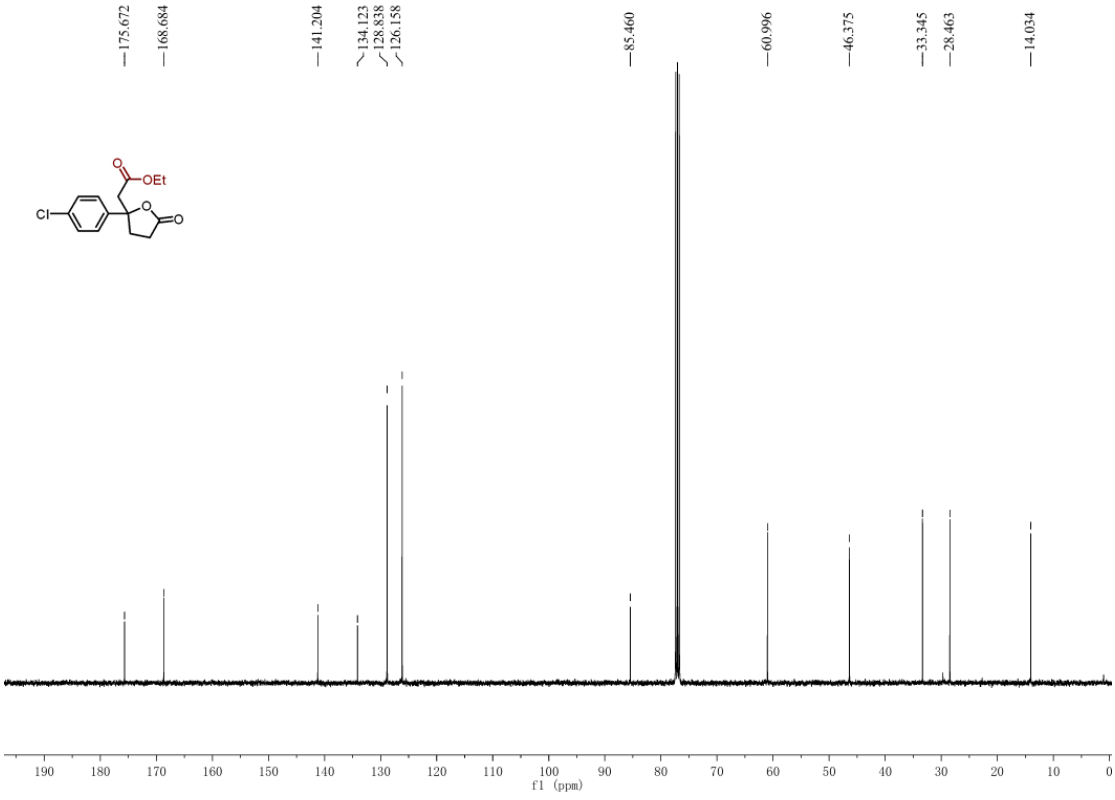




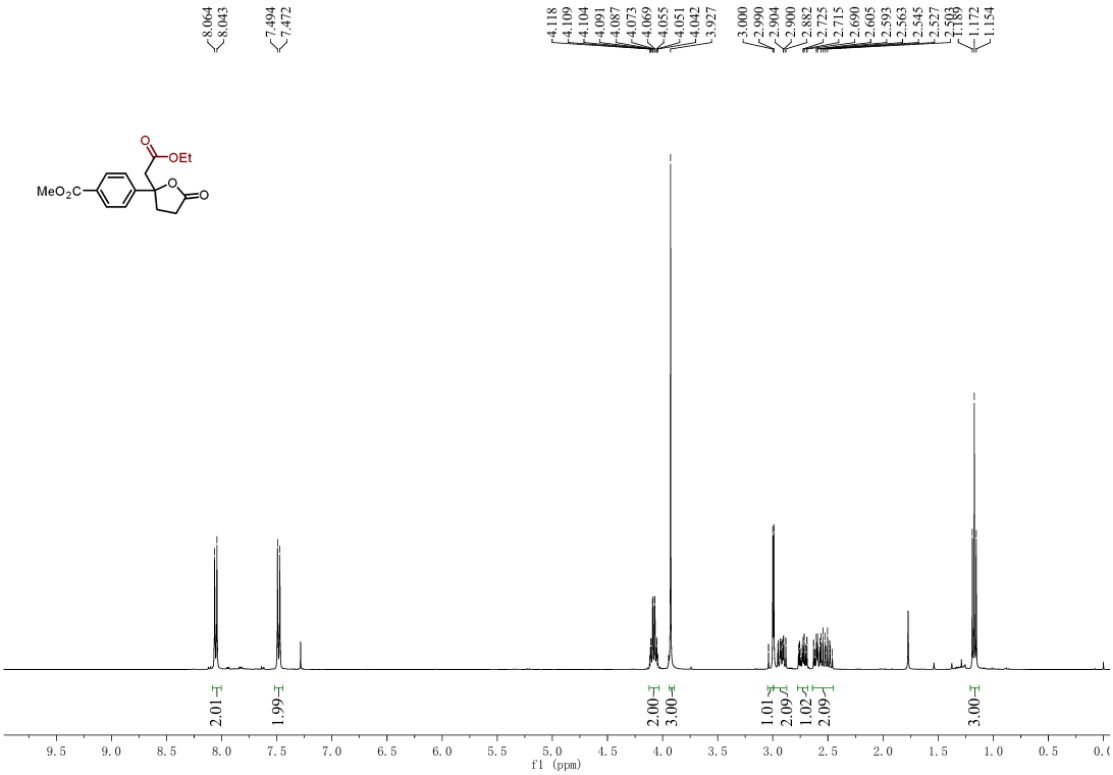

-113.956
-113.970
-113.978
-113.992
-114.003
-114.014
-114.028
O
OEt
F
O
O
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
f1 (ppm)

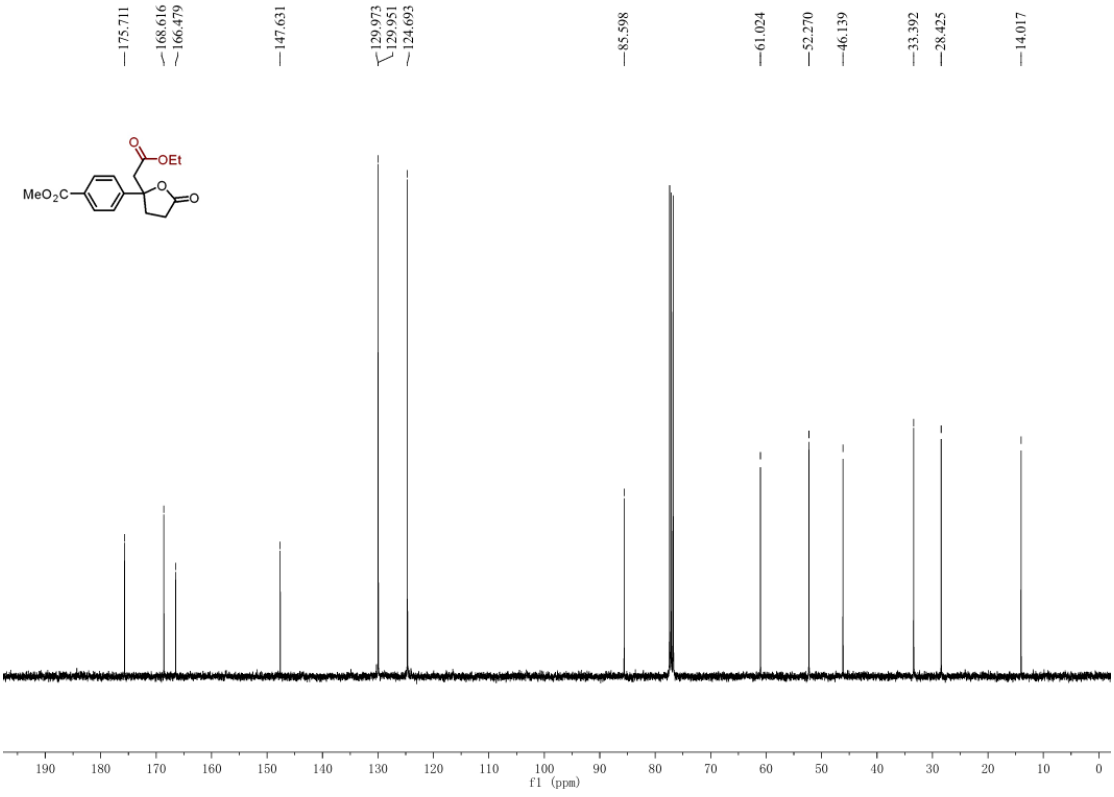
Ethyl 2-(2-(4-chlorophenyl)-5-oxotetrahydrofuran-2-yl)acetate (3g)



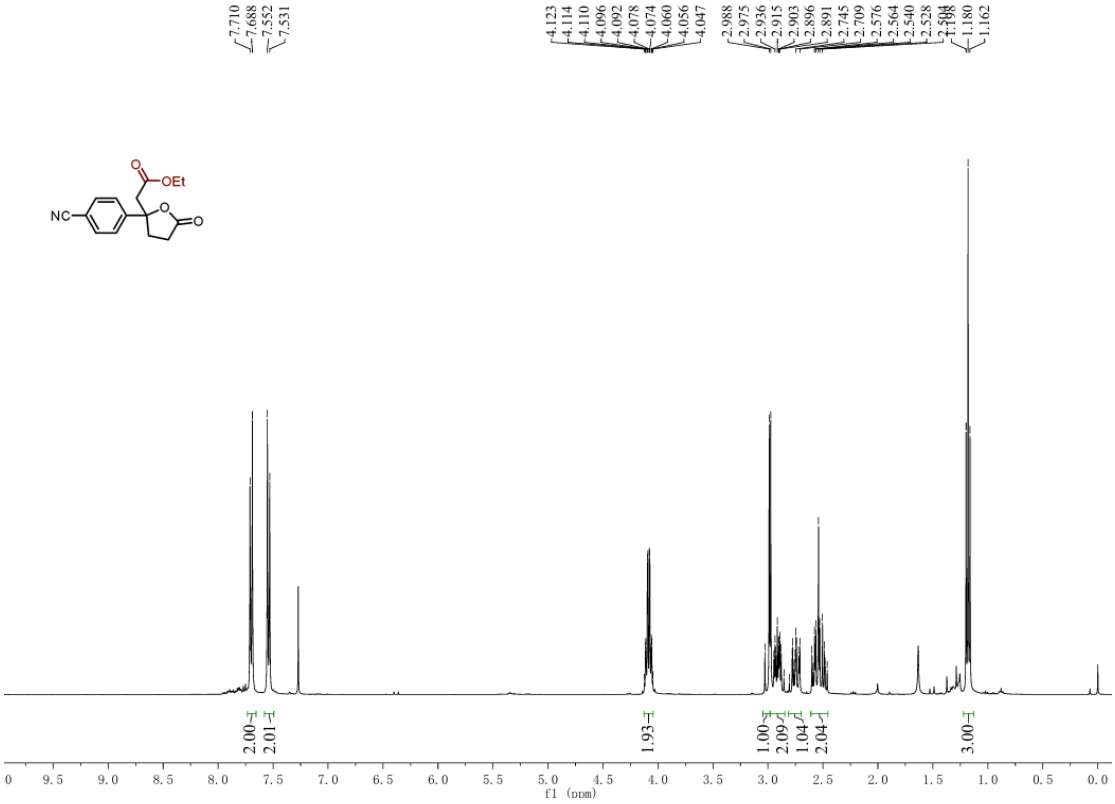


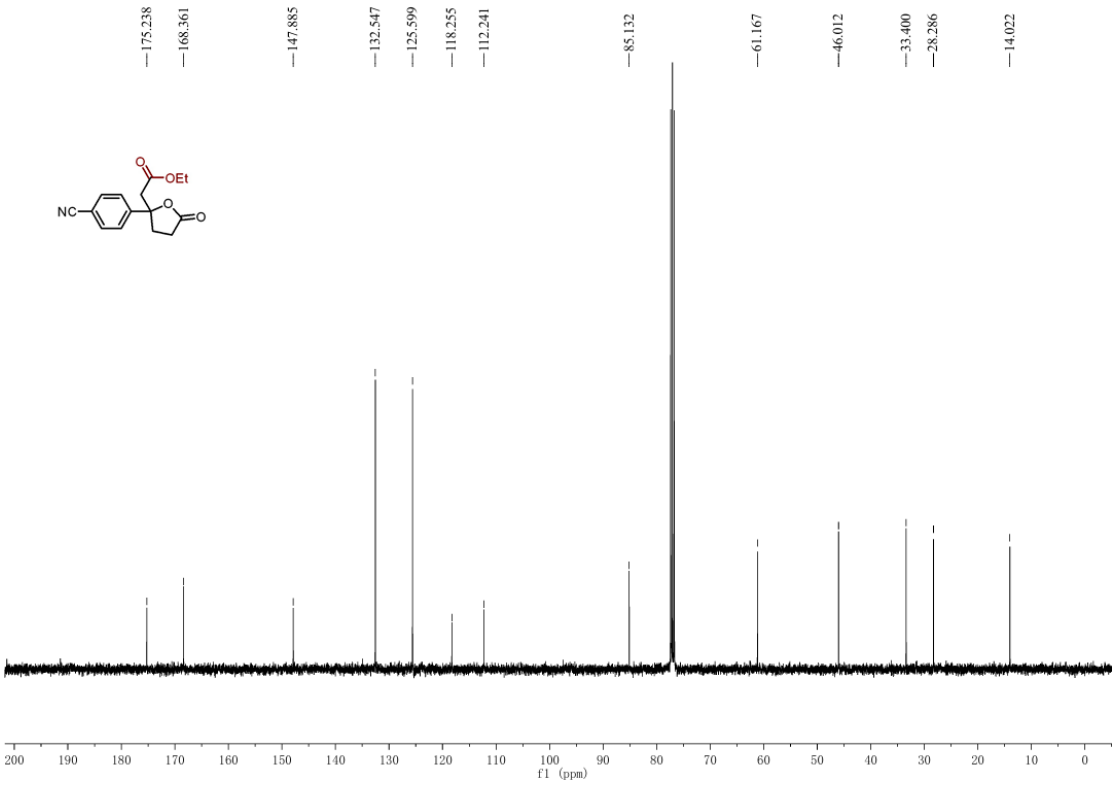
Methyl 4-(2-(2-ethoxy-2-oxoethyl)-5-oxotetrahydrofuran-2-yl)benzoate (3h)



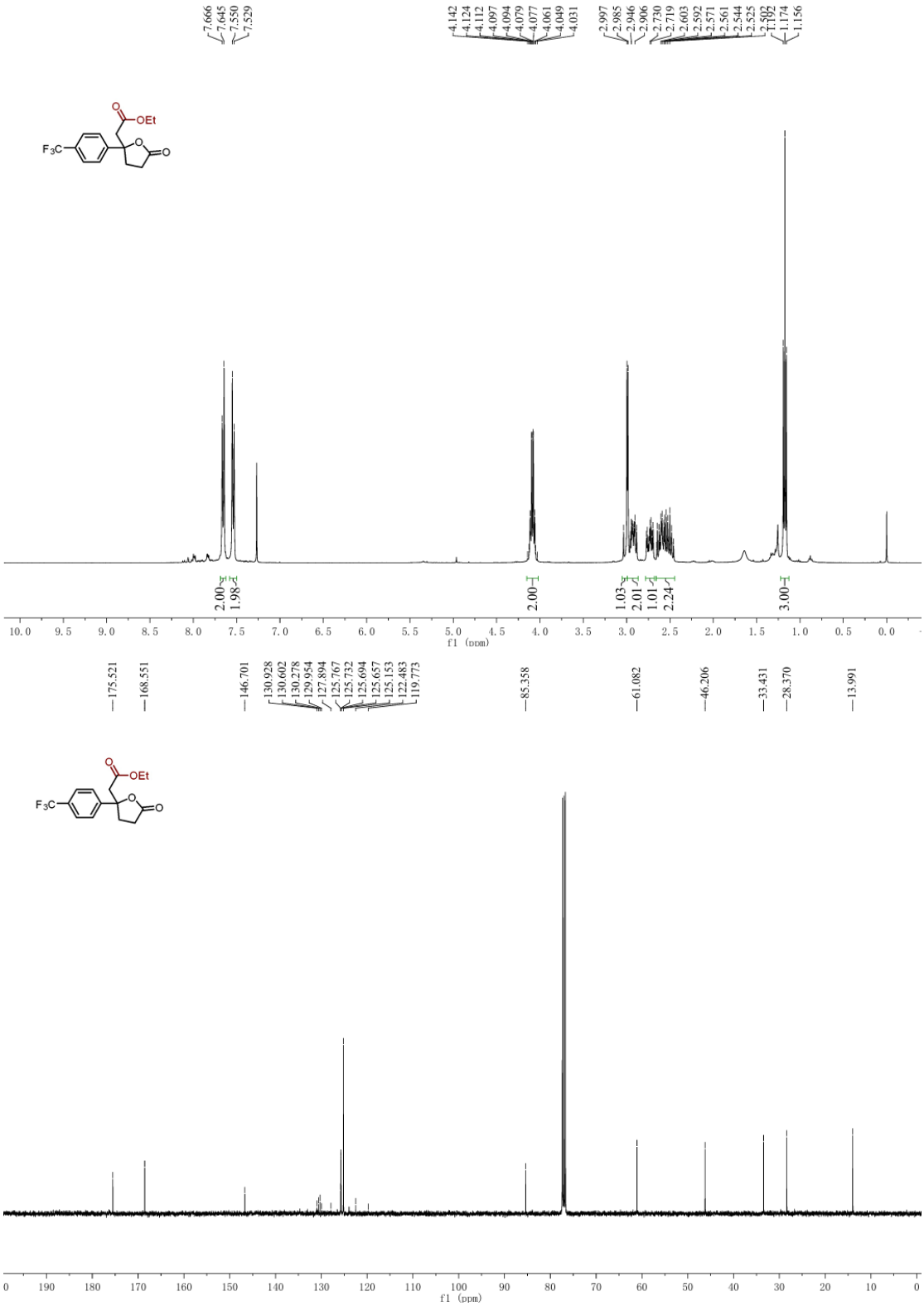


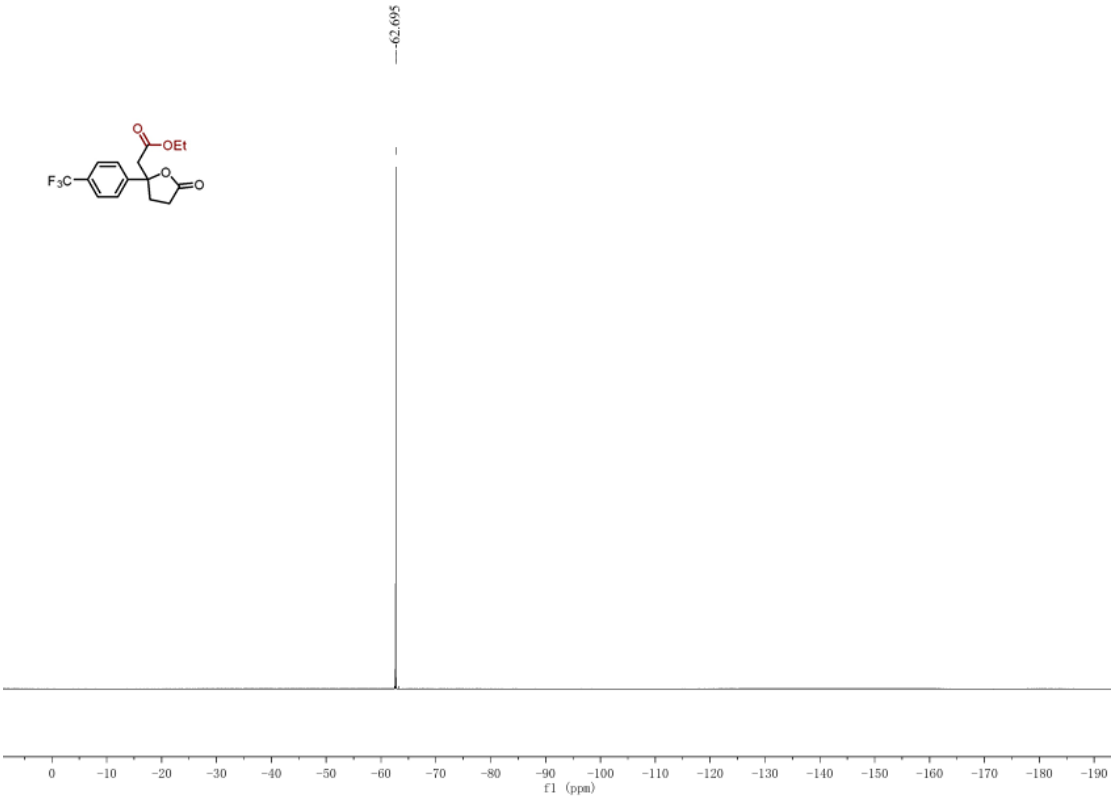
Ethyl 2-(2-(4-cyanophenyl)-5-oxotetrahydrofuran-2-yl)acetate (3i)



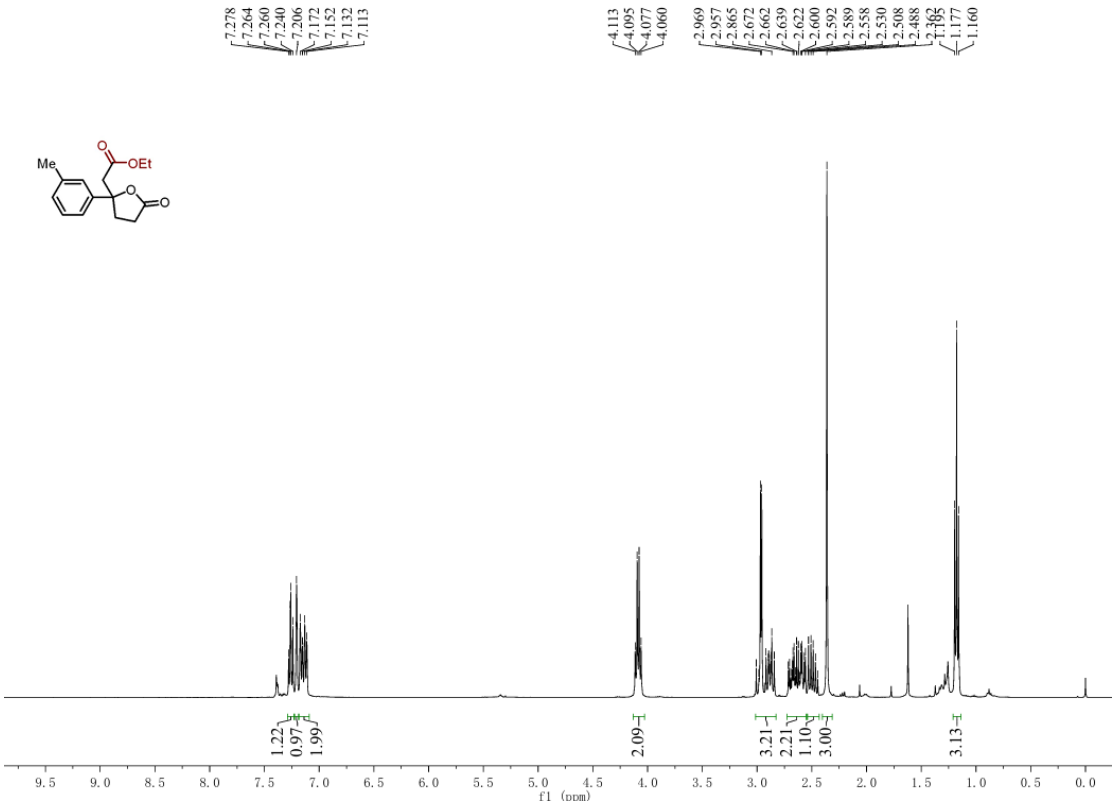


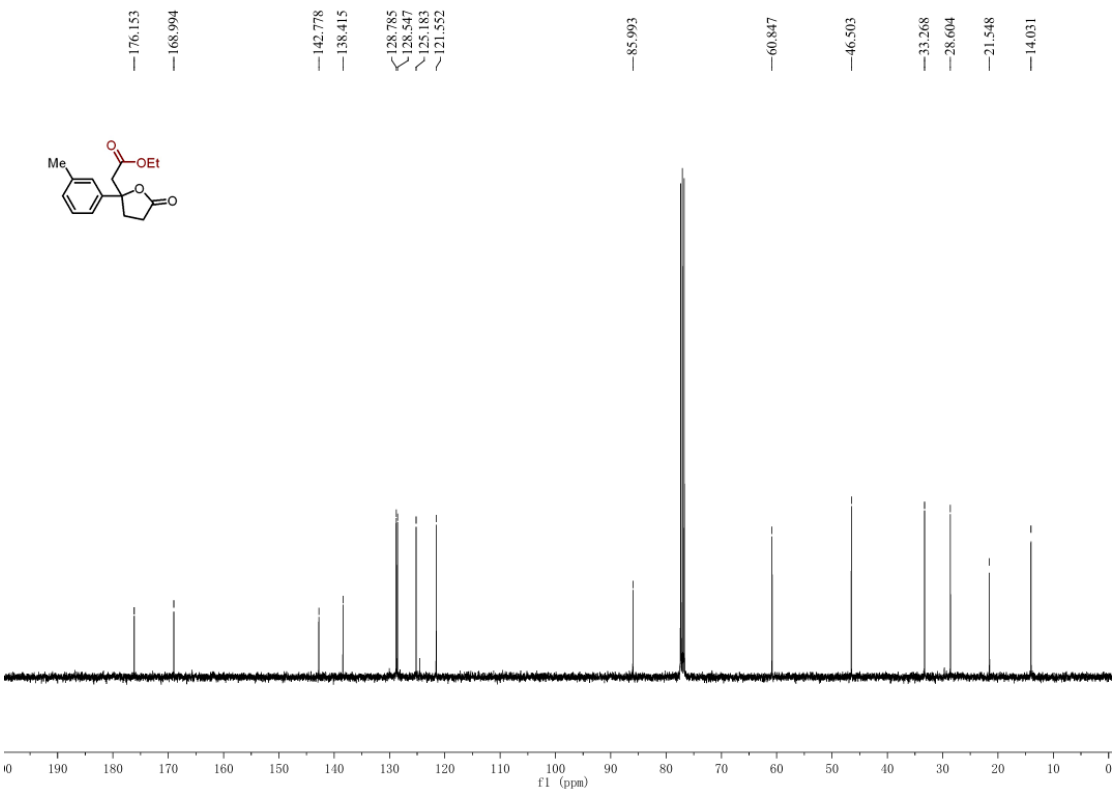
Ethyl 2-(5-oxo-2-(4-(trifluoromethyl)phenyl)tetrahydrofuran-2-yl)acetate (3j)



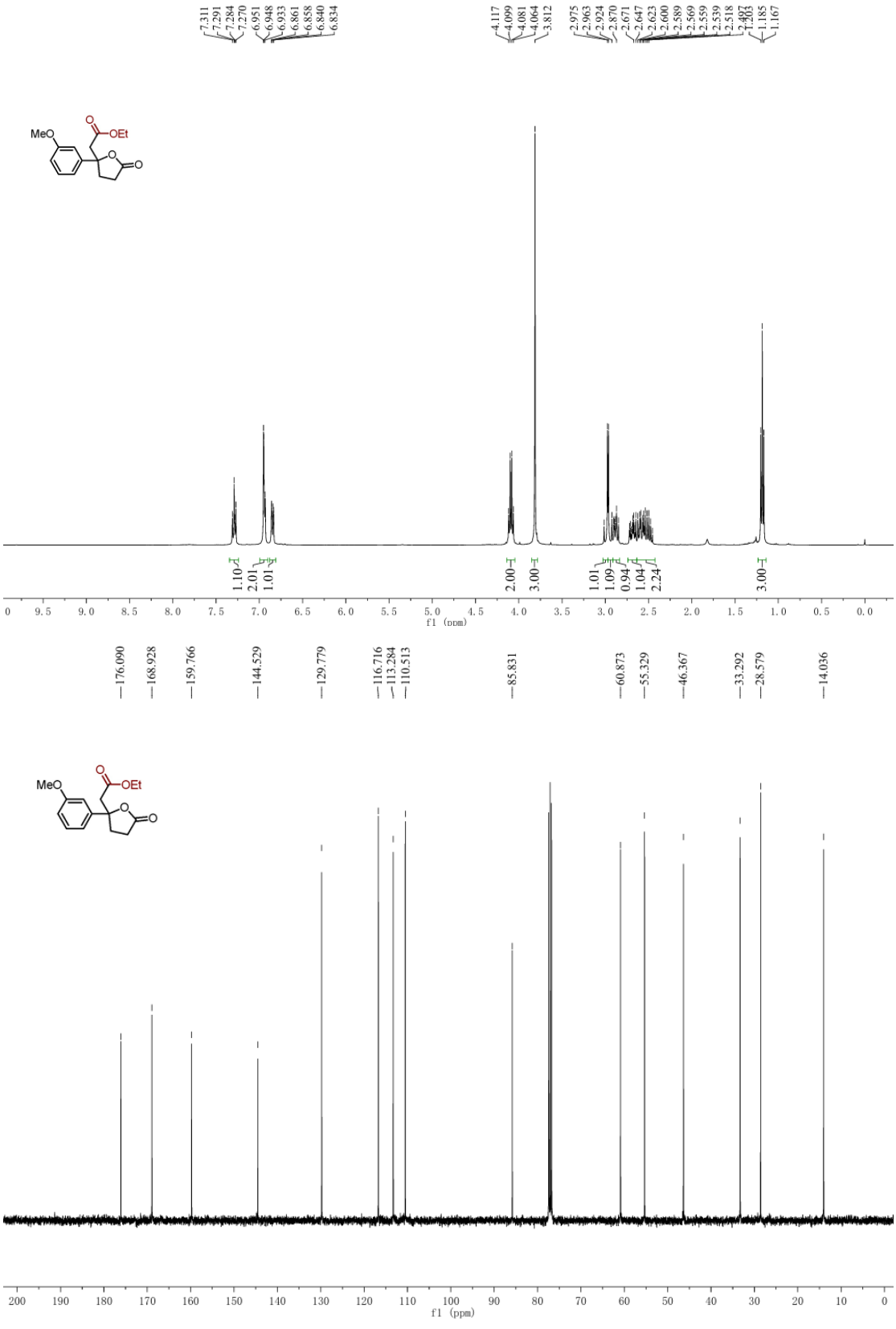

-62.695
OEt
F3C
O
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

Ethyl 2-(5-oxo-2-(m-tolyl)tetrahydrofuran-2-yl)acetate (3k)

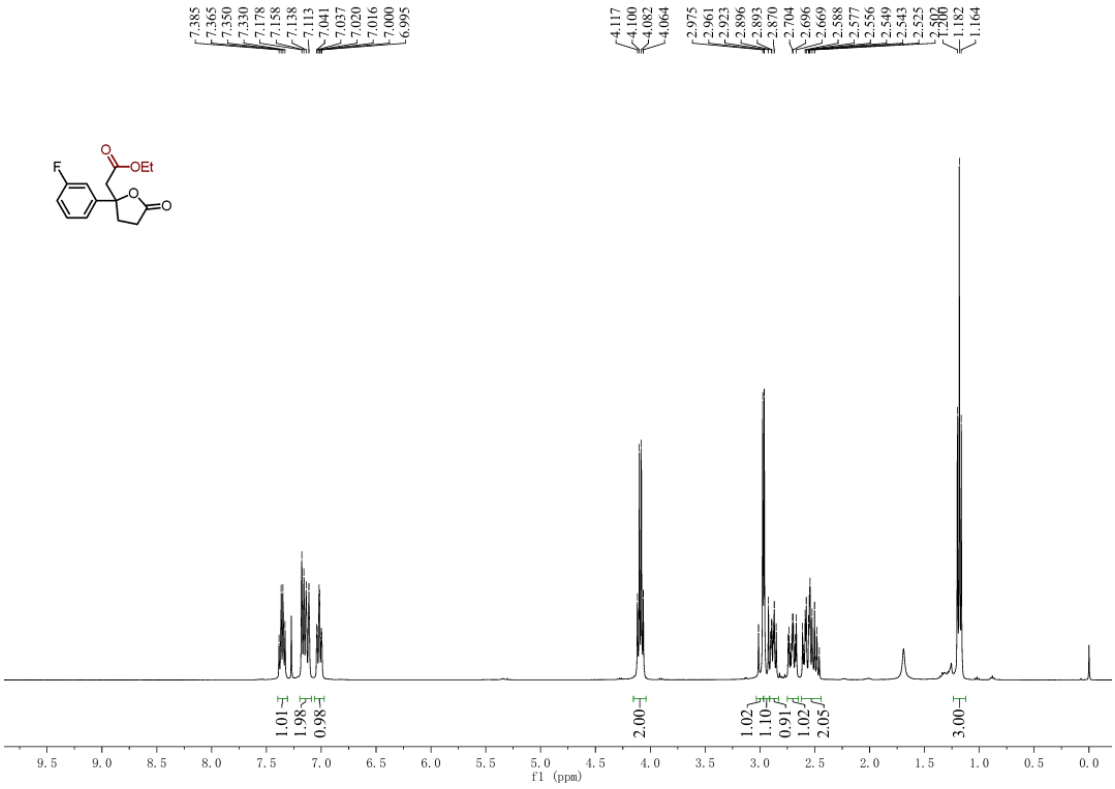


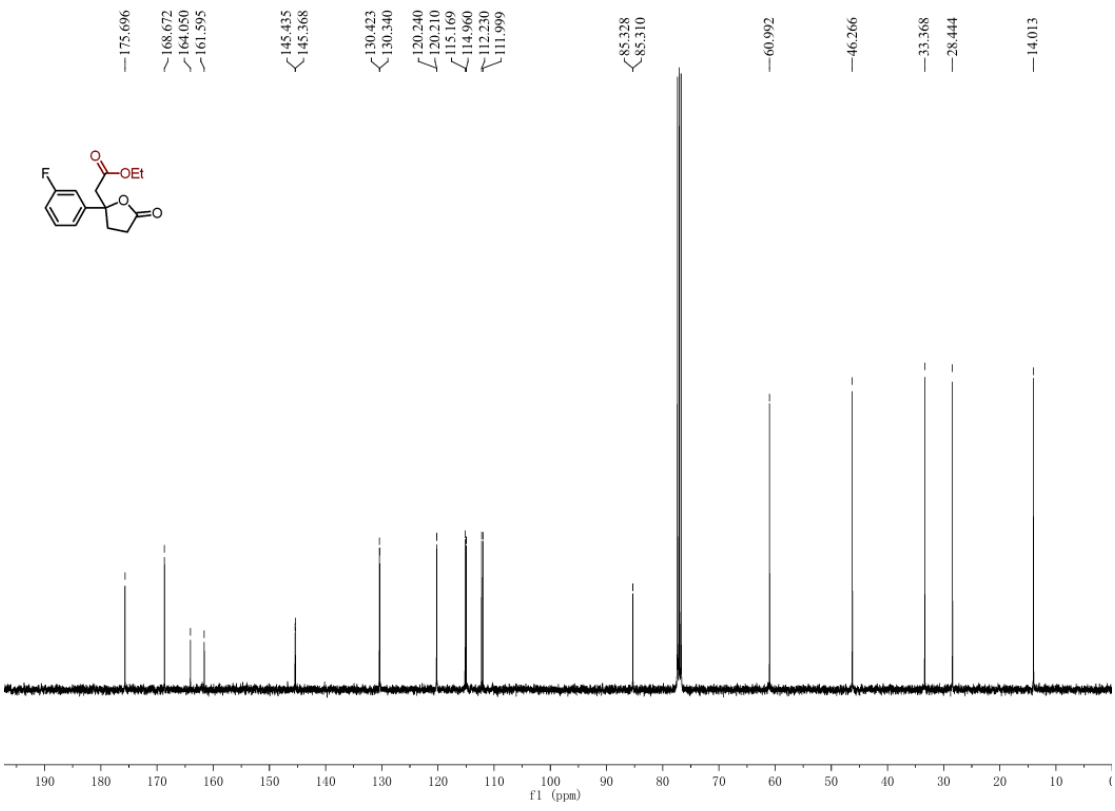


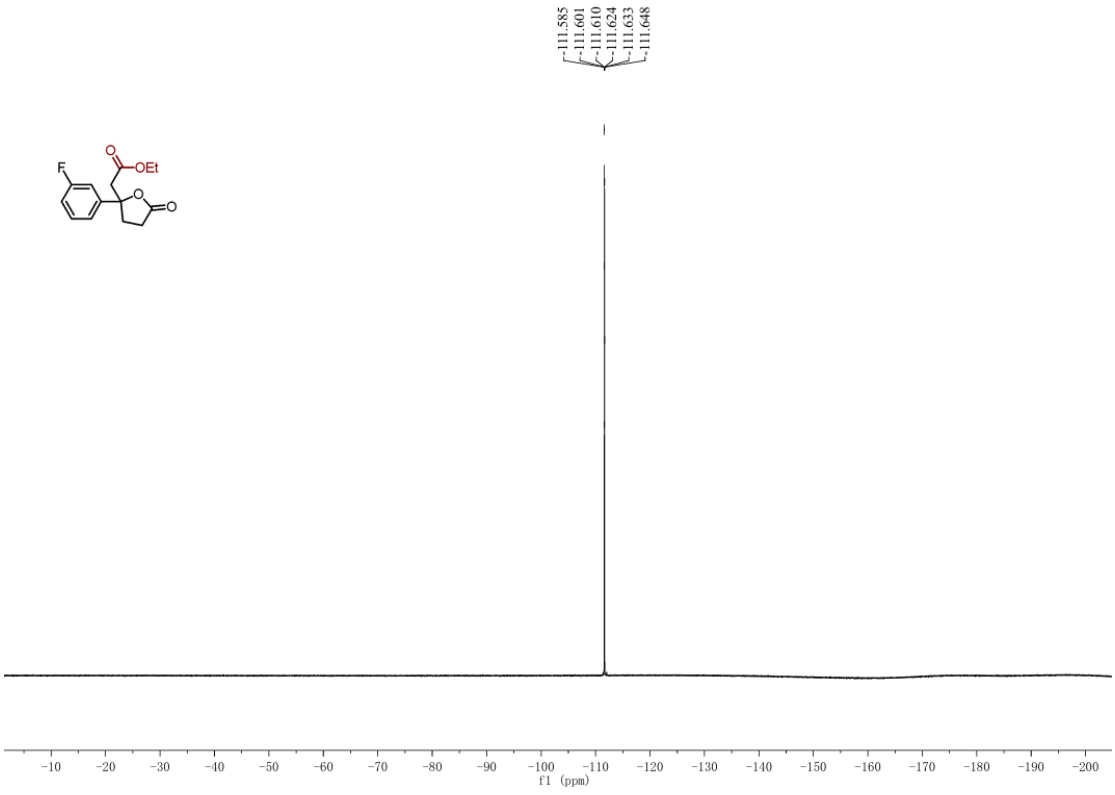
Ethyl 2-(2-(3-methoxyphenyl)-5-oxotetrahydrofuran-2-yl)acetate (3l)



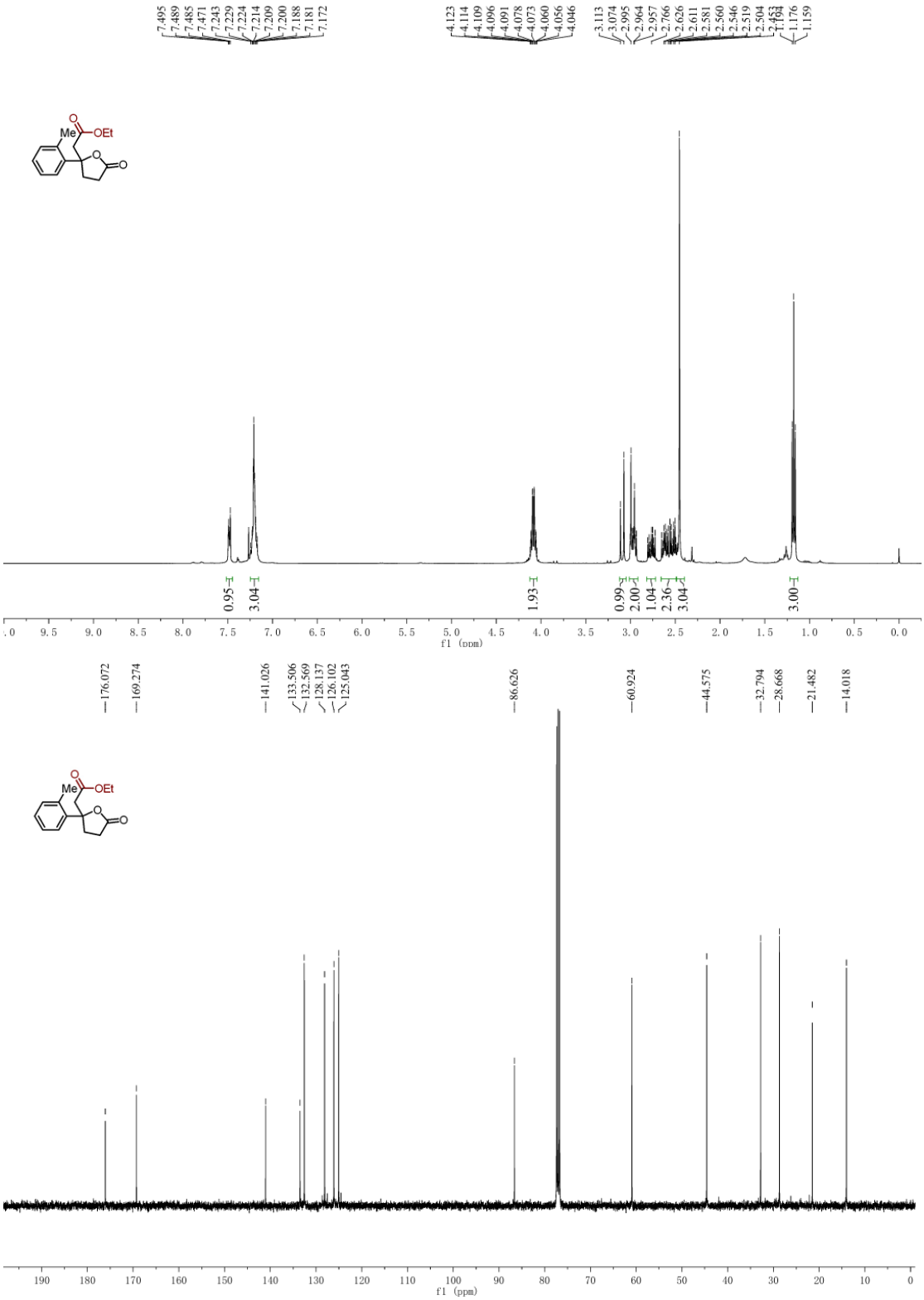
Ethyl 2-(2-(3-fluorophenyl)-5-oxotetrahydrofuran-2-yl)acetate (3m)



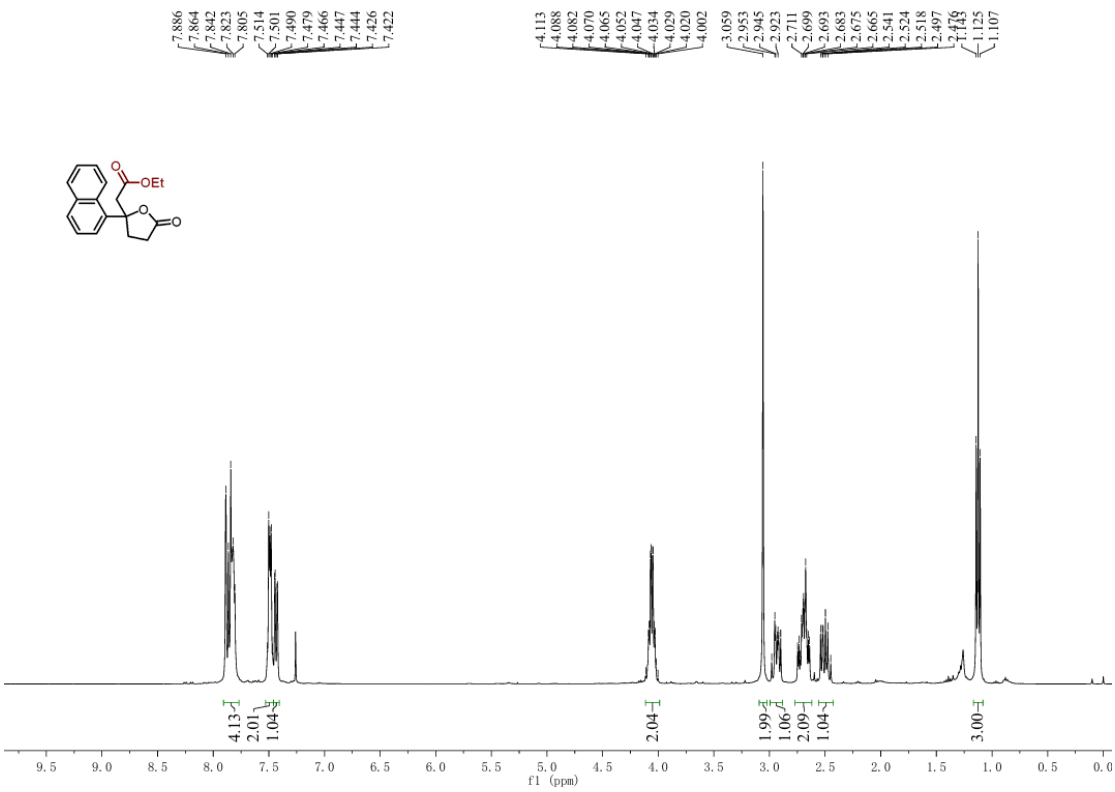


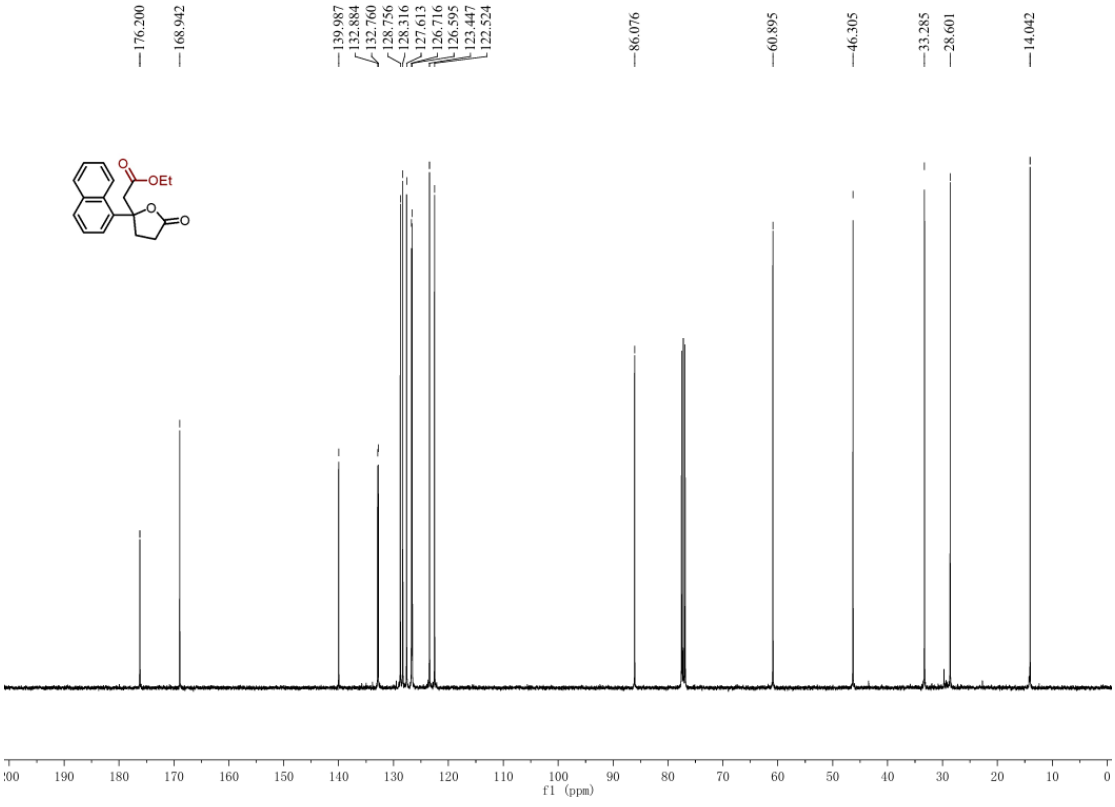

-111.585
-111.601
-111.610
-111.624
-111.633
-111.648
F
O
OEt
O
O
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

Ethyl 2-(5-oxo-2-(o-tolyl)tetrahydrofuran-2-yl)acetate (3n)

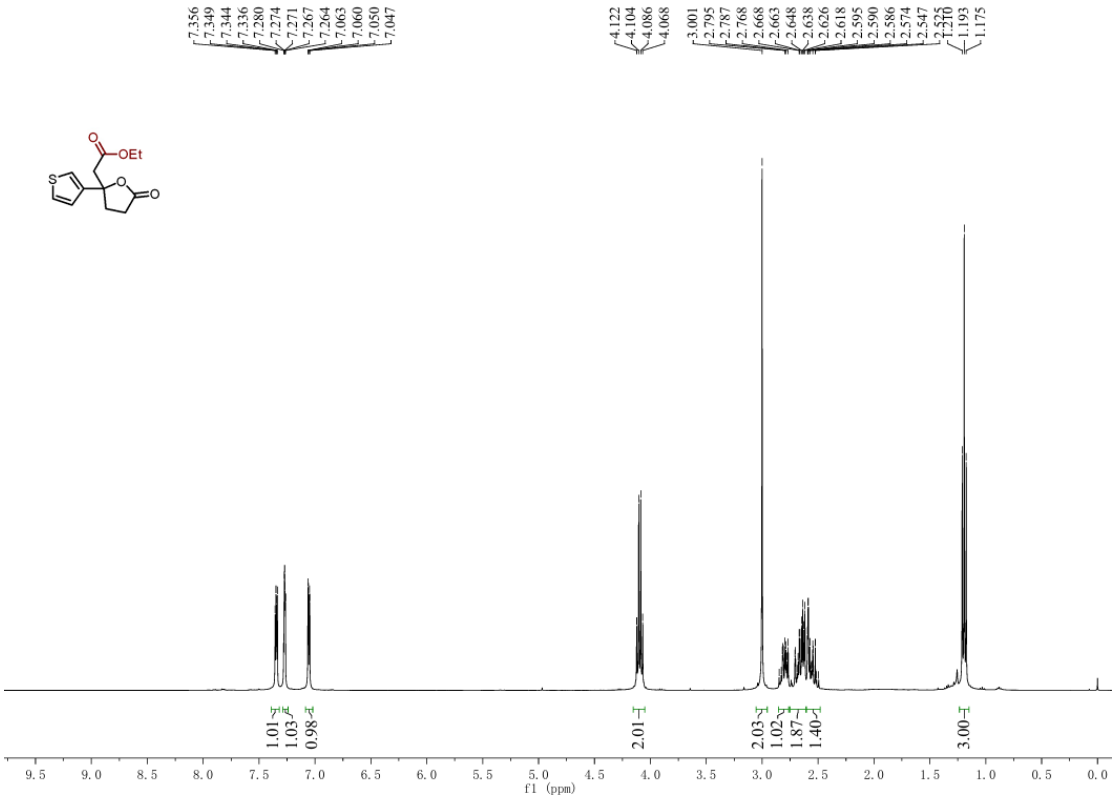


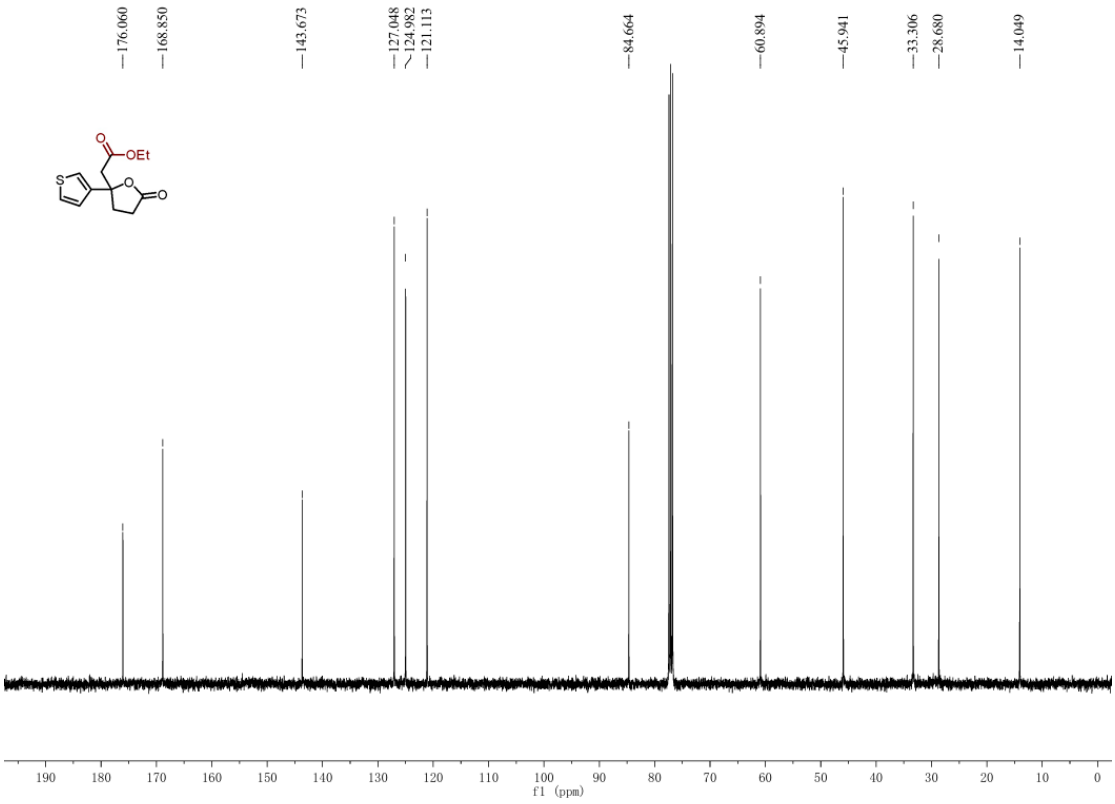
Ethyl 2-(2-(naphthalen-1-yl)-5-oxotetrahydrofuran-2-yl)acetate (3o)



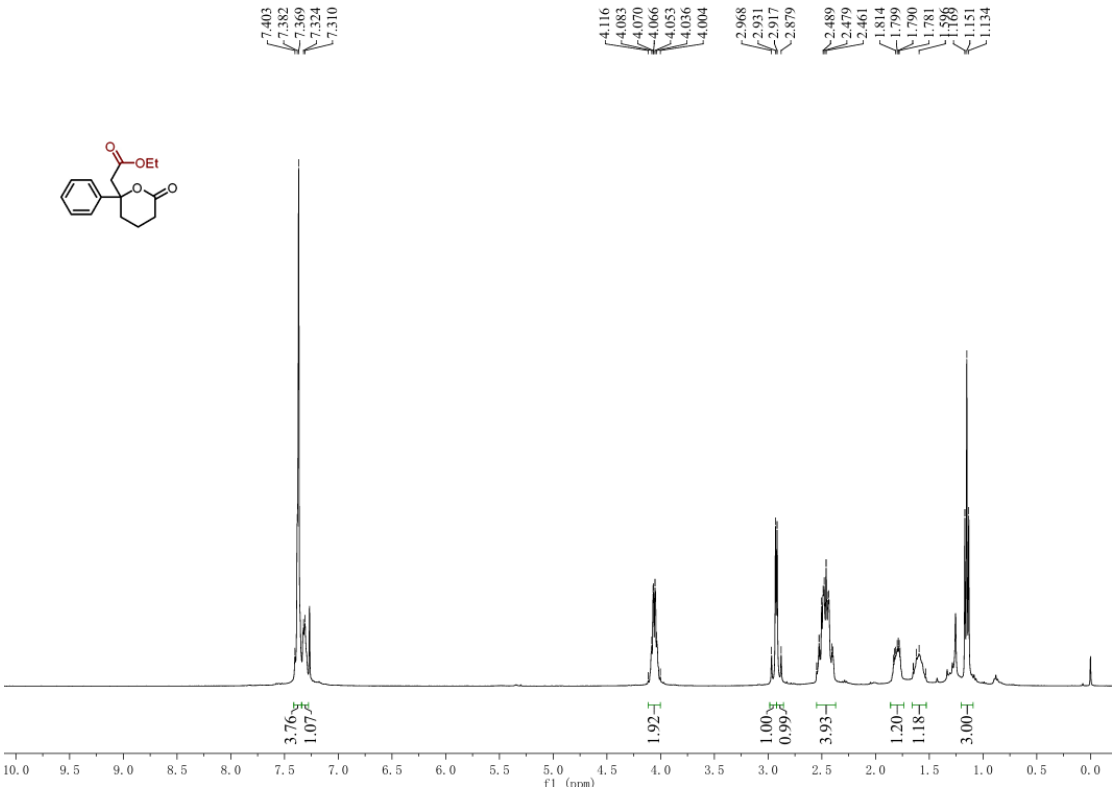


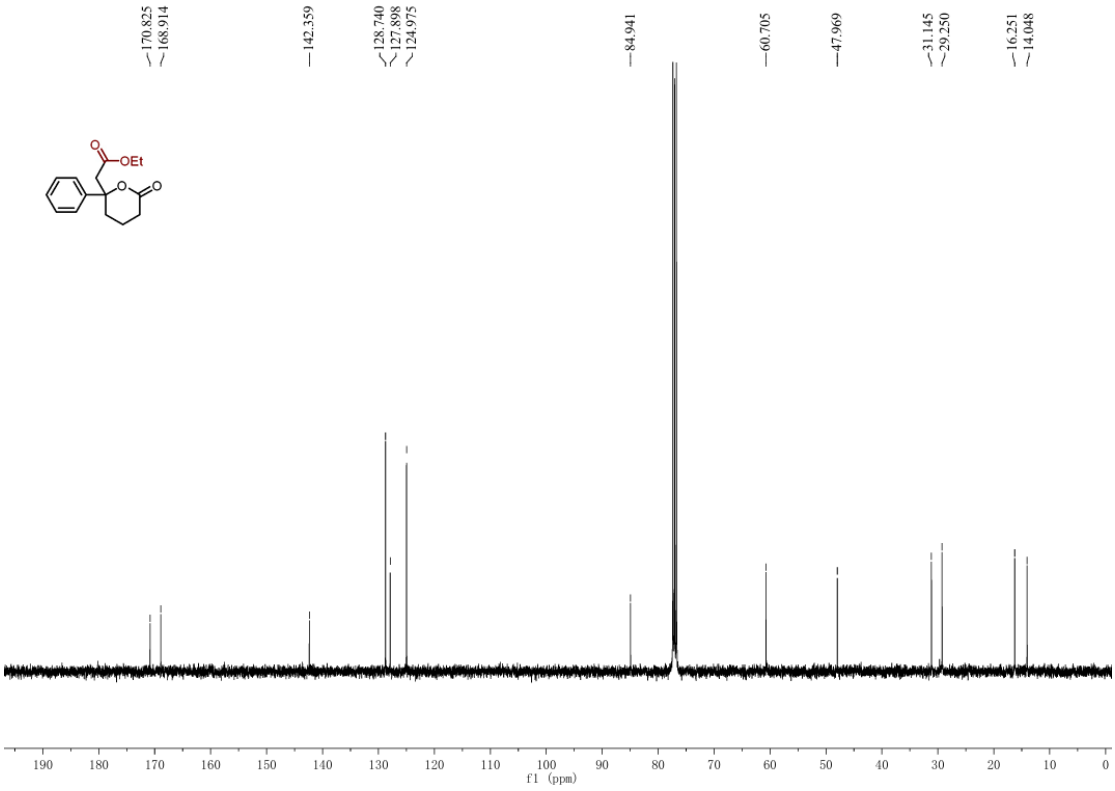
Ethyl 2-(5-oxo-2-(thiophen-3-yl)tetrahydrofuran-2-yl)acetate (3p)



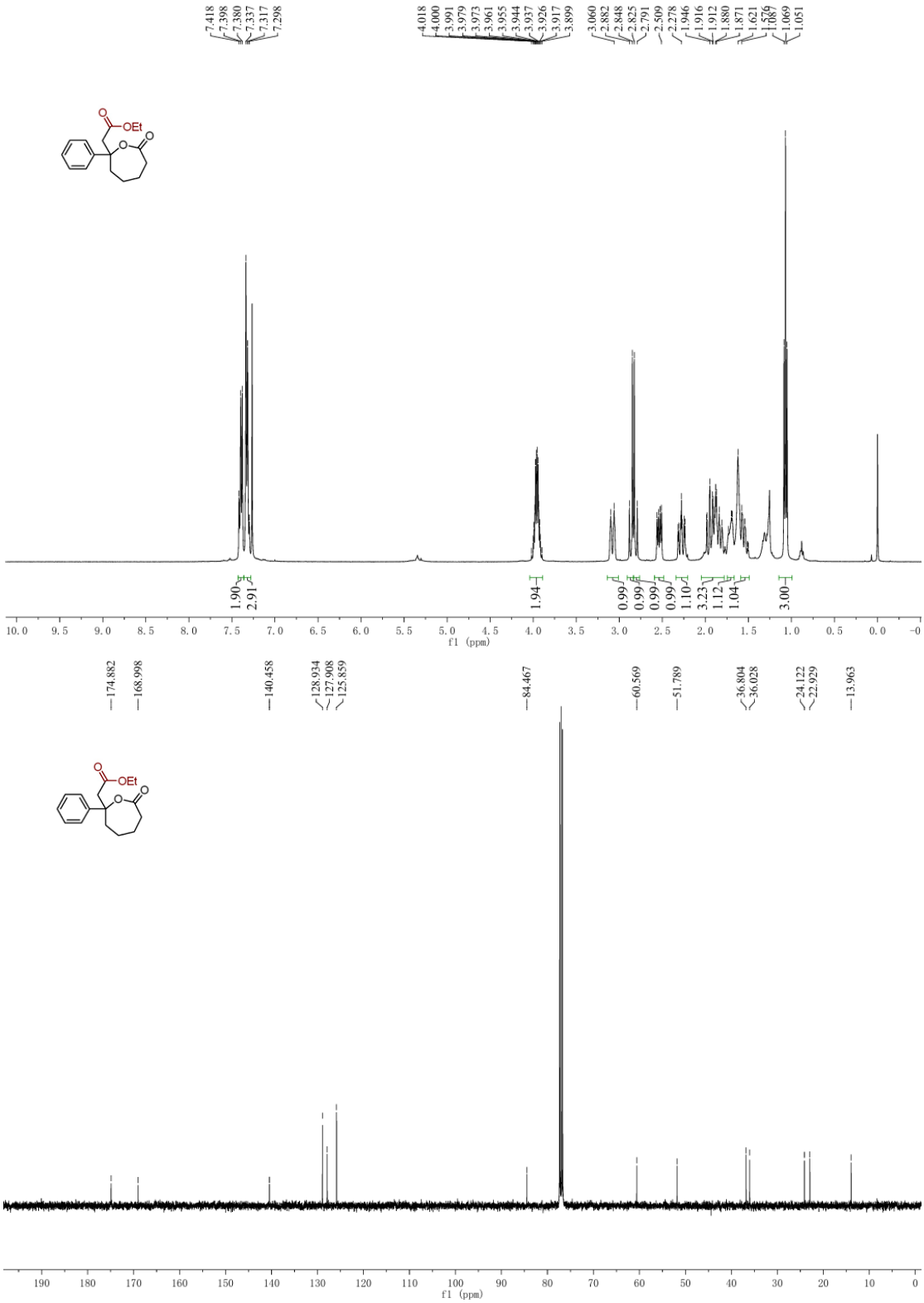


Ethyl 2-(6-oxo-2-phenyltetrahydro-2H-pyran-2-yl)acetate (3q)

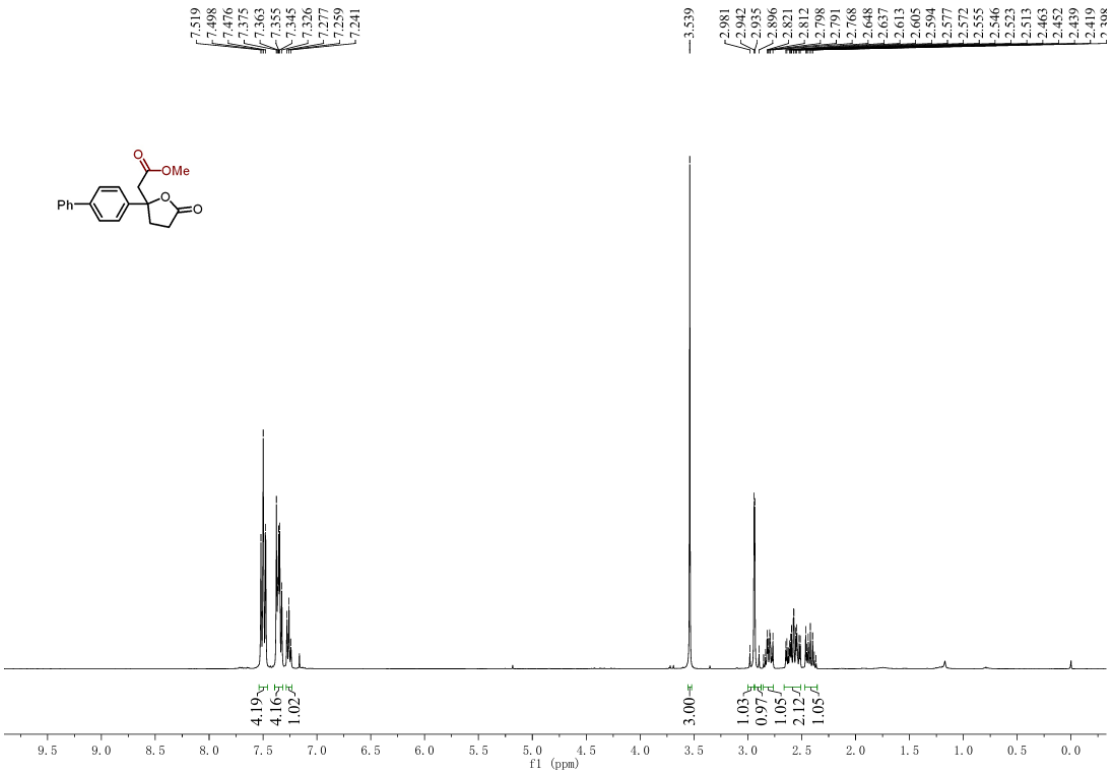


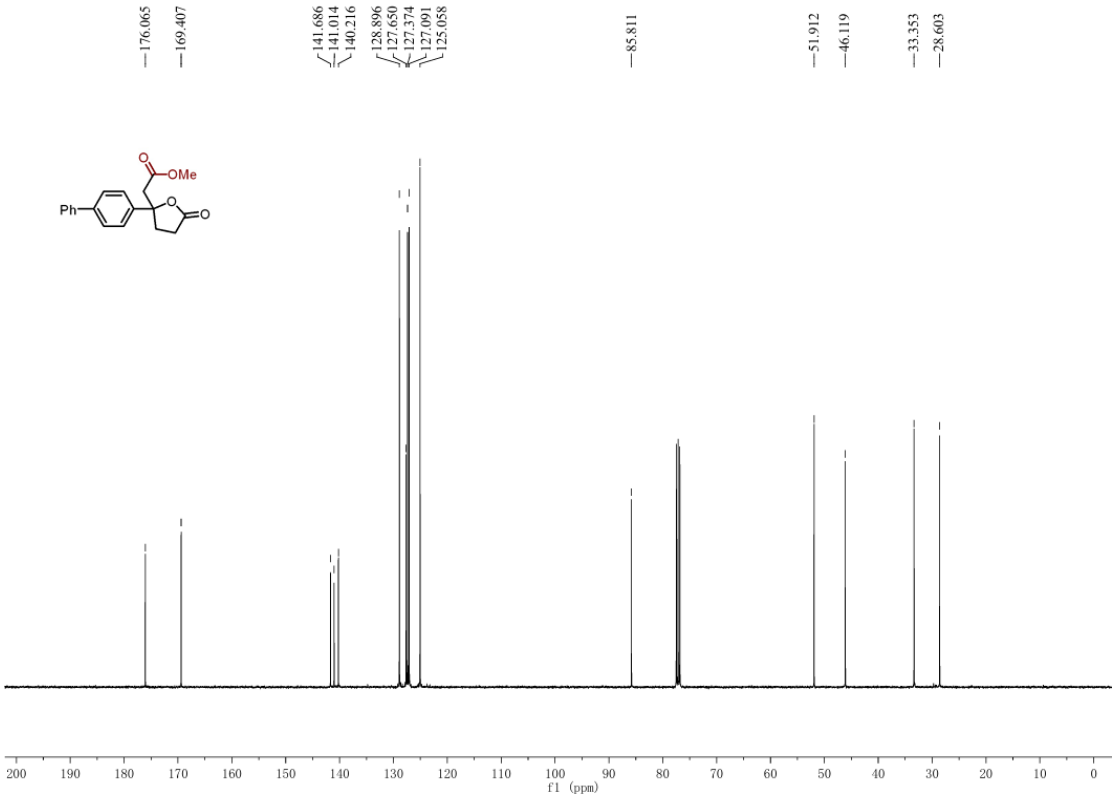


Ethyl 2-(7-oxo-2-phenyloxepan-2-yl)acetate (3r)

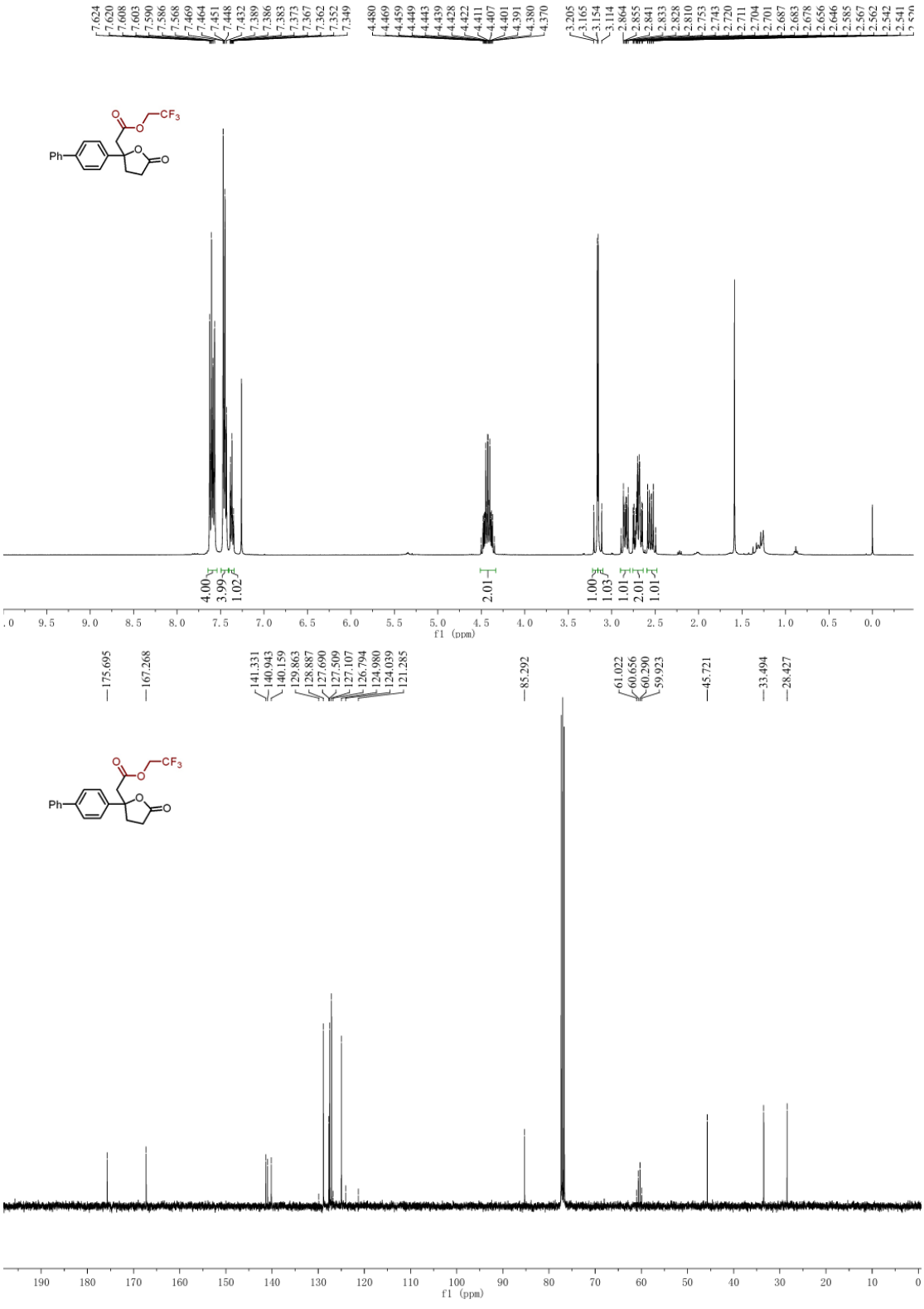


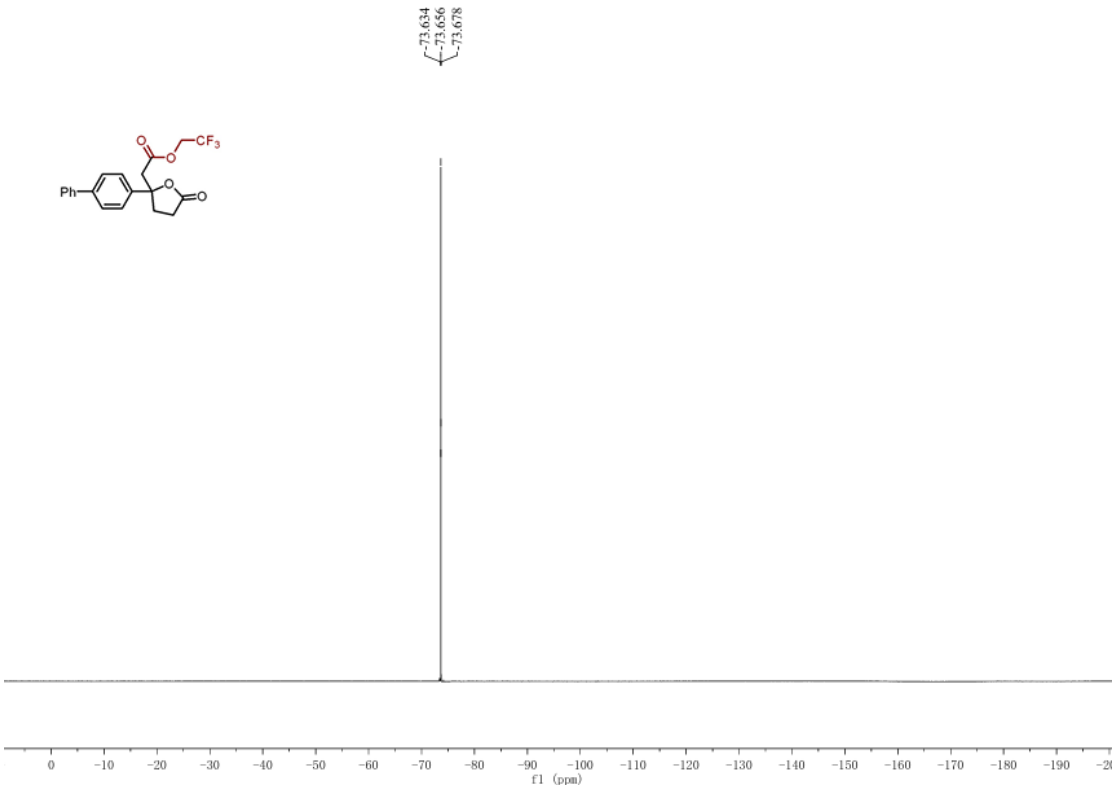
Methyl 2-(2-([1,1'-biphenyl]-4-yl)-5-oxotetrahydrofuran-2-yl)acetate (3s)



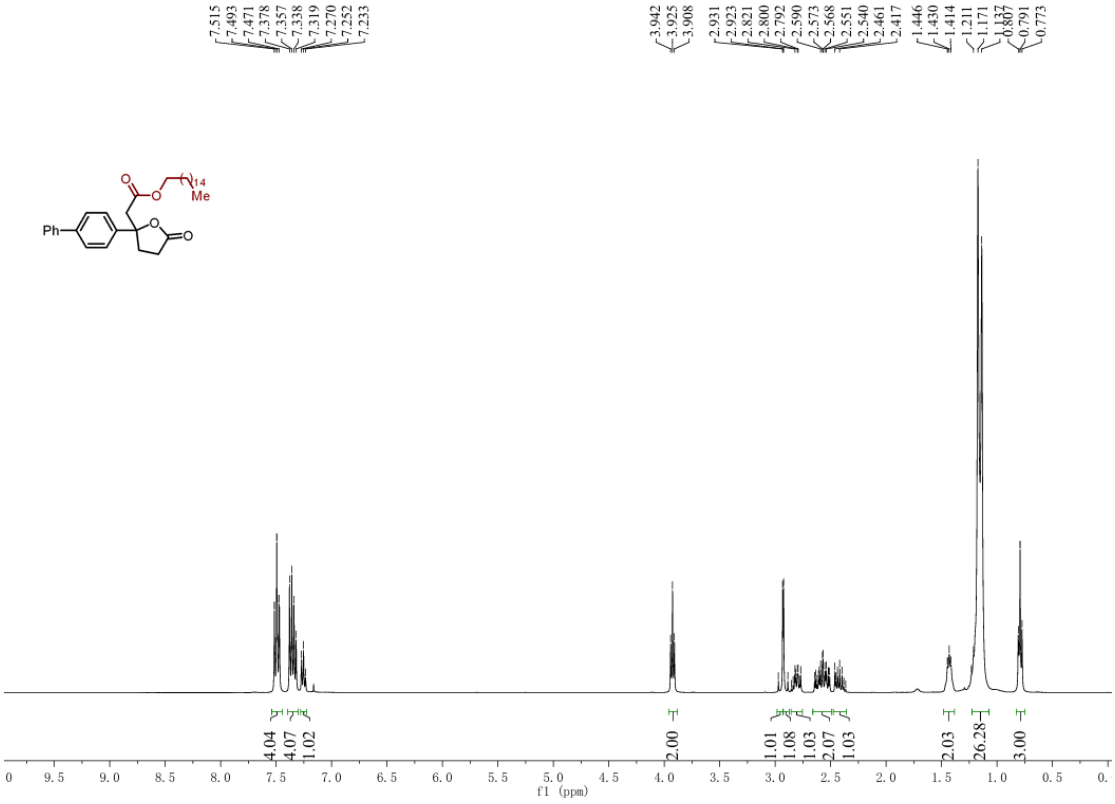


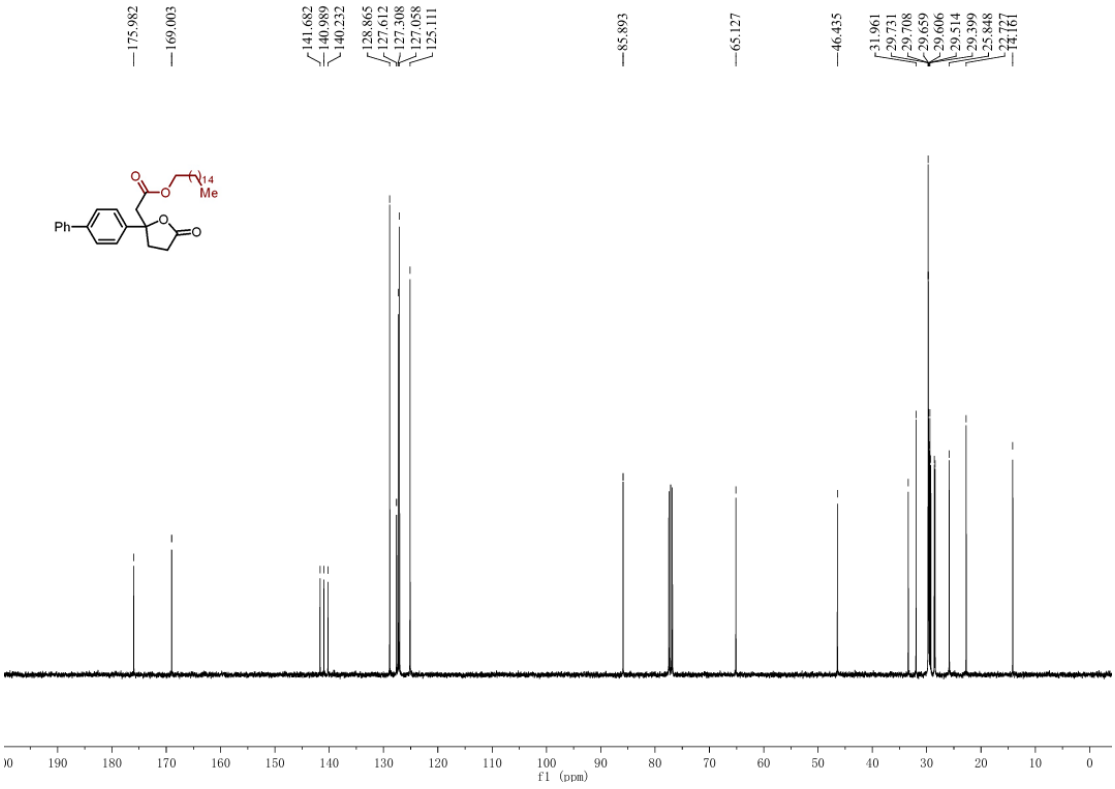
2,2,2-trifluoroethyl 2-(2-([1,1'-biphenyl]-4-yl)-5-oxotetrahydrofuran-2-yl)acetate (3t)



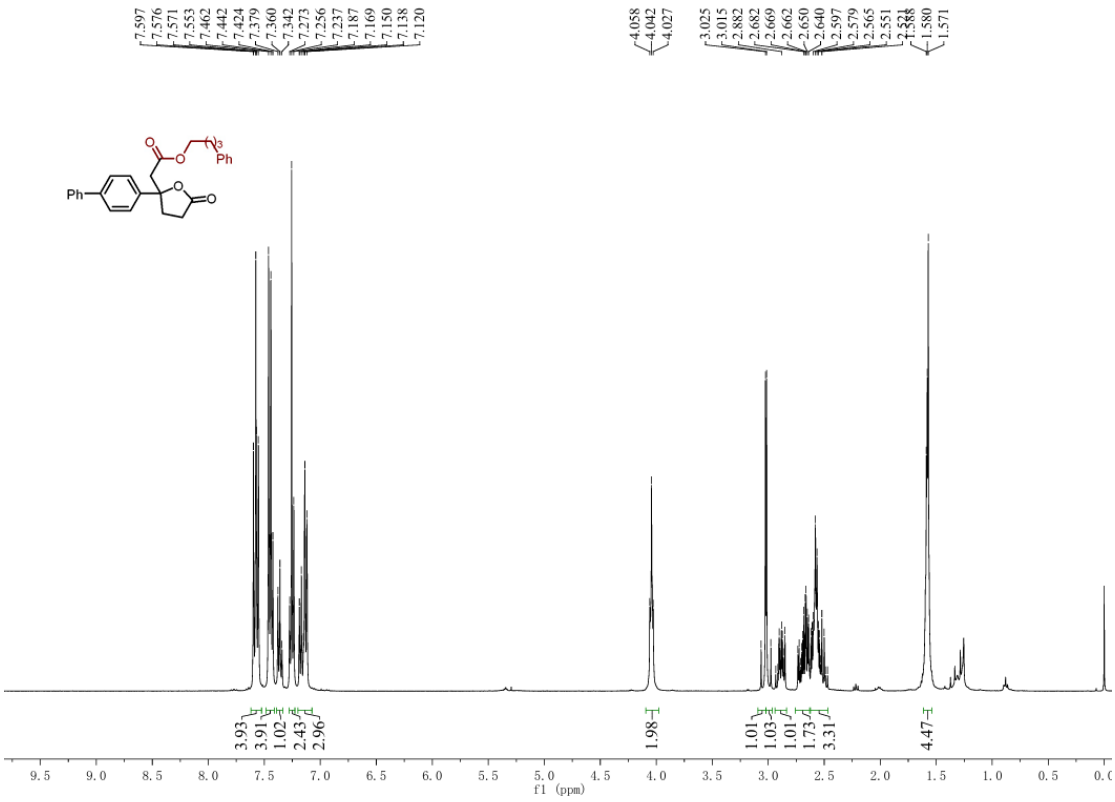

-73.634
-73.656
-73.678
Ph
O
O
O
O
CF3
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

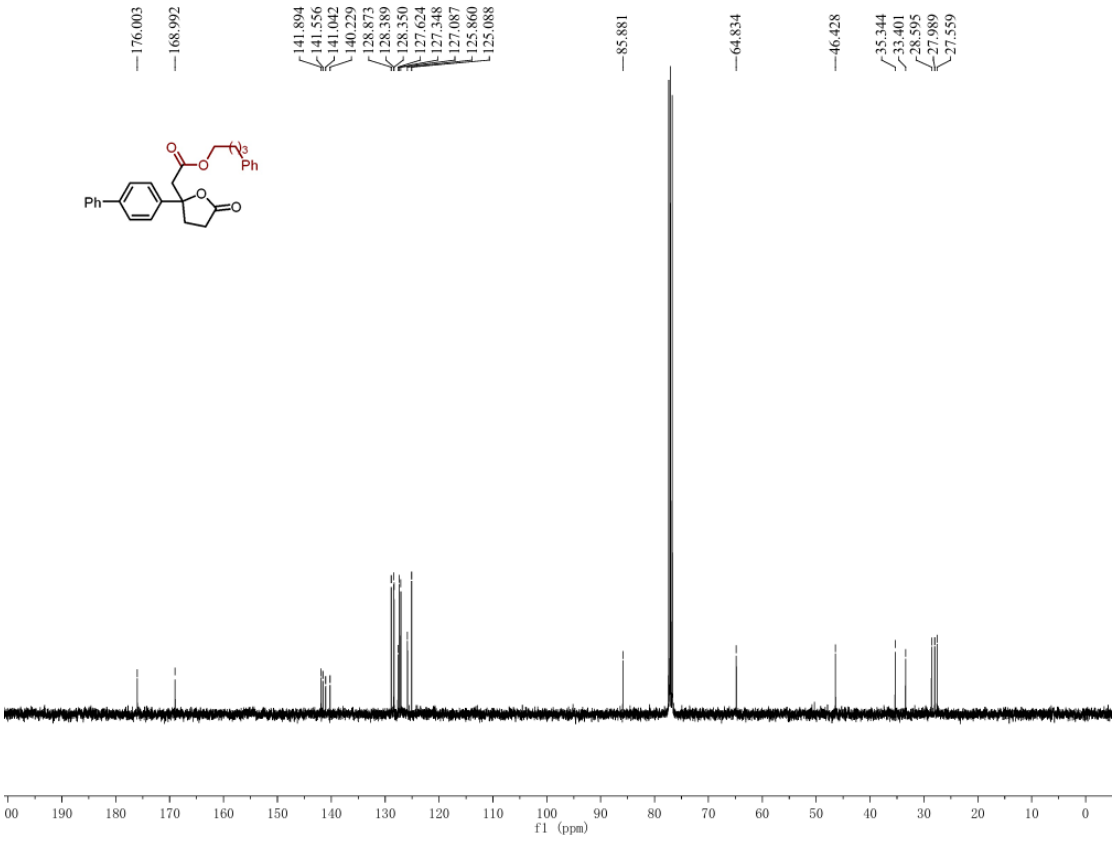
Hexadecyl 2-(2-([1,1'-biphenyl]-4-yl)-5-oxotetrahydrofuran-2-yl)acetate (3u)



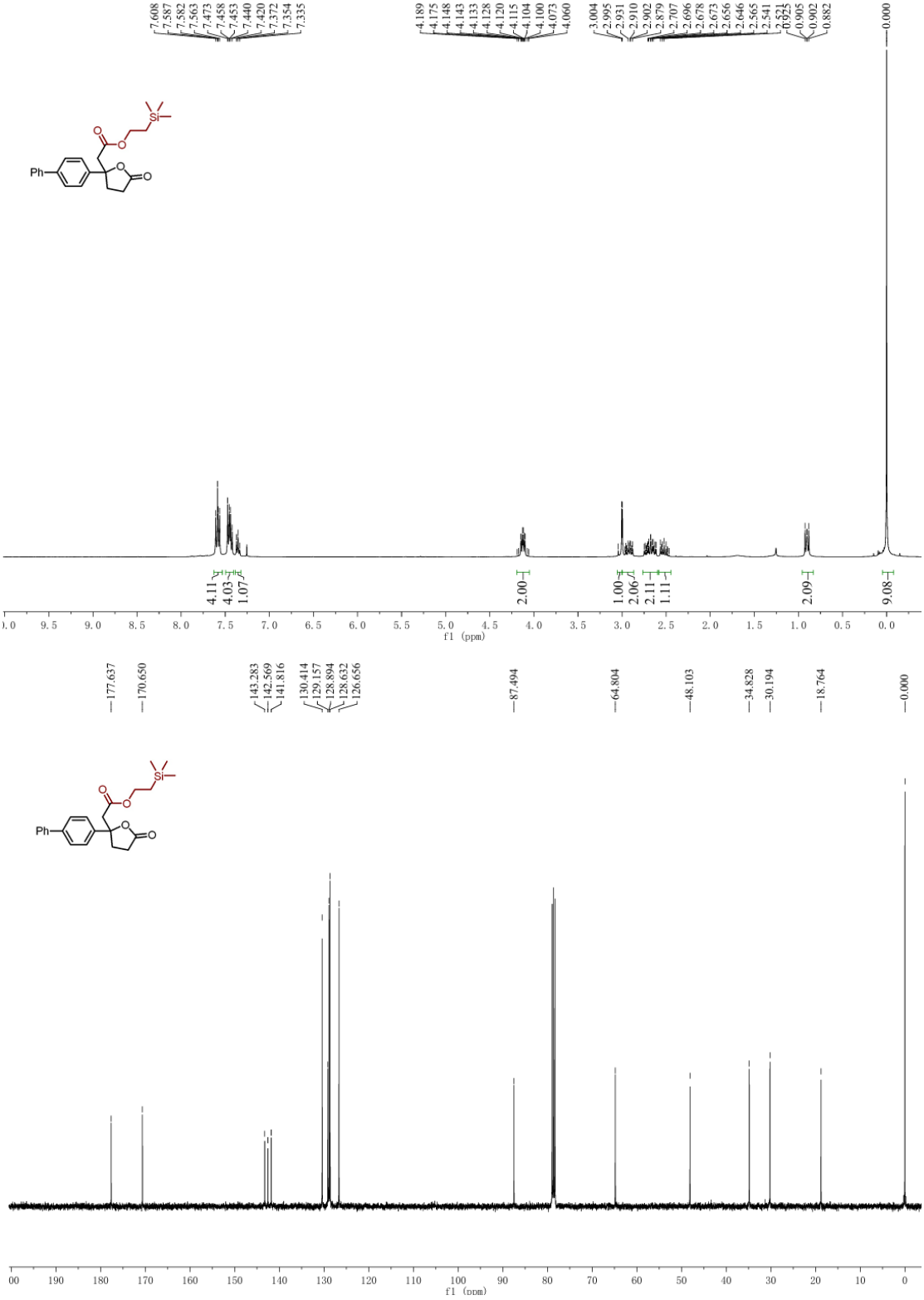


4-Phenylbutyl 2-(2-([1,1'-biphenyl]-4-yl)-5-oxotetrahydrofuran-2-yl)acetate (3v)

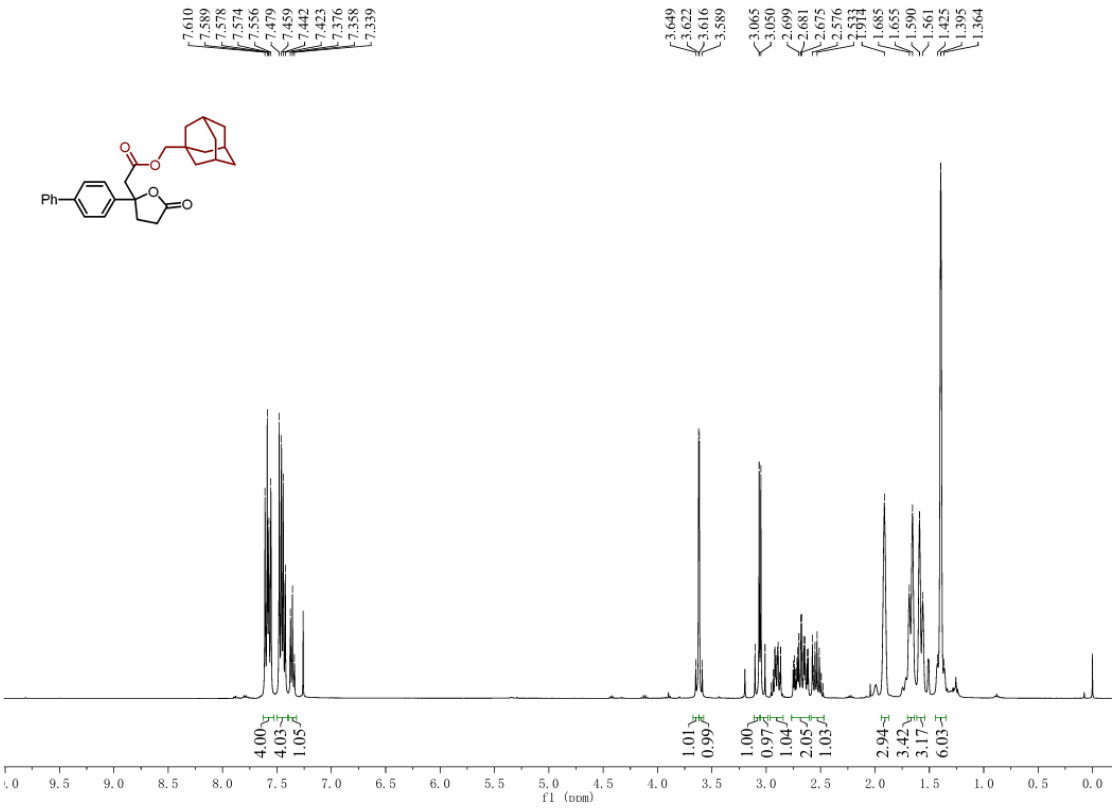


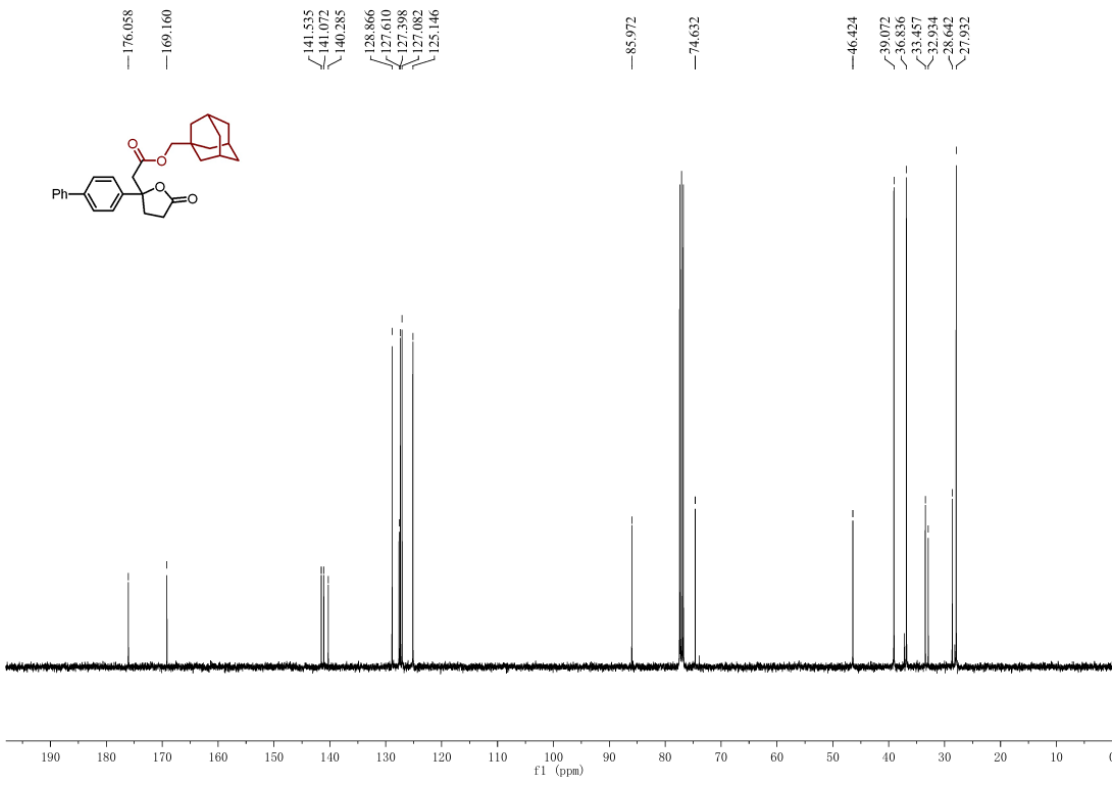


2-(Trimethylsilyl)ethyl 2-(2-([1,1'-biphenyl]-4-yl)-5-oxotetrahydrofuran-2-yl)acetate (3w)

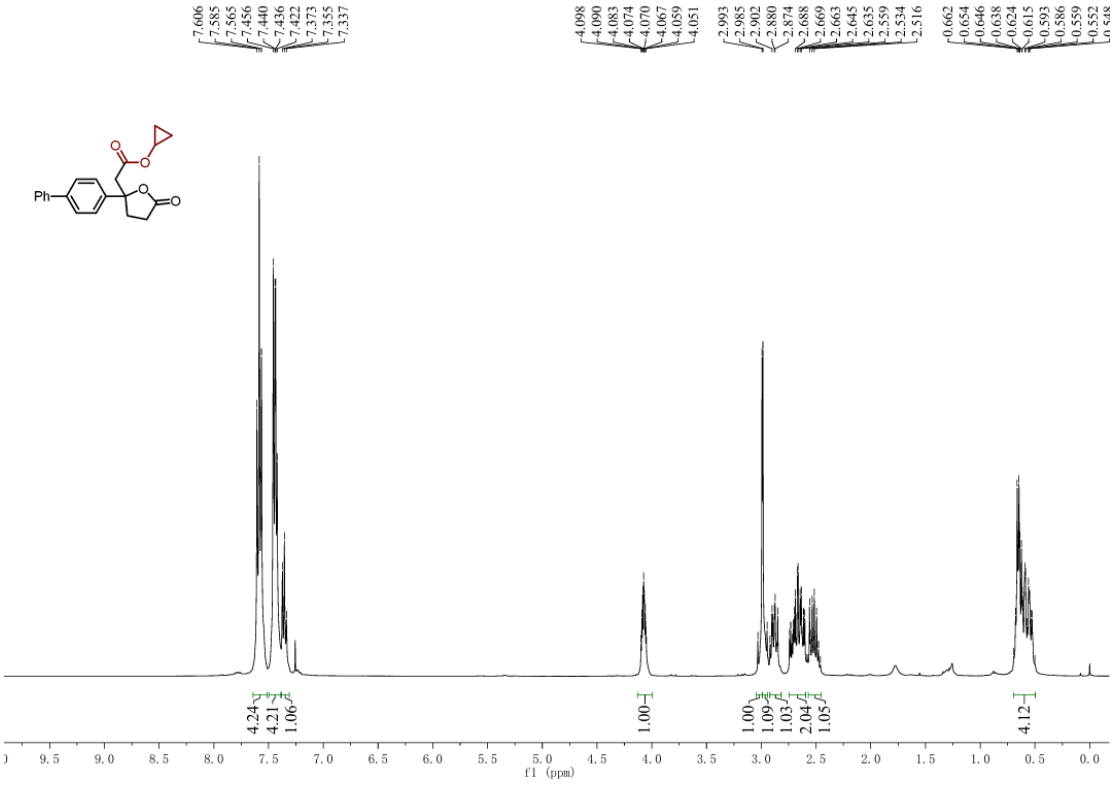


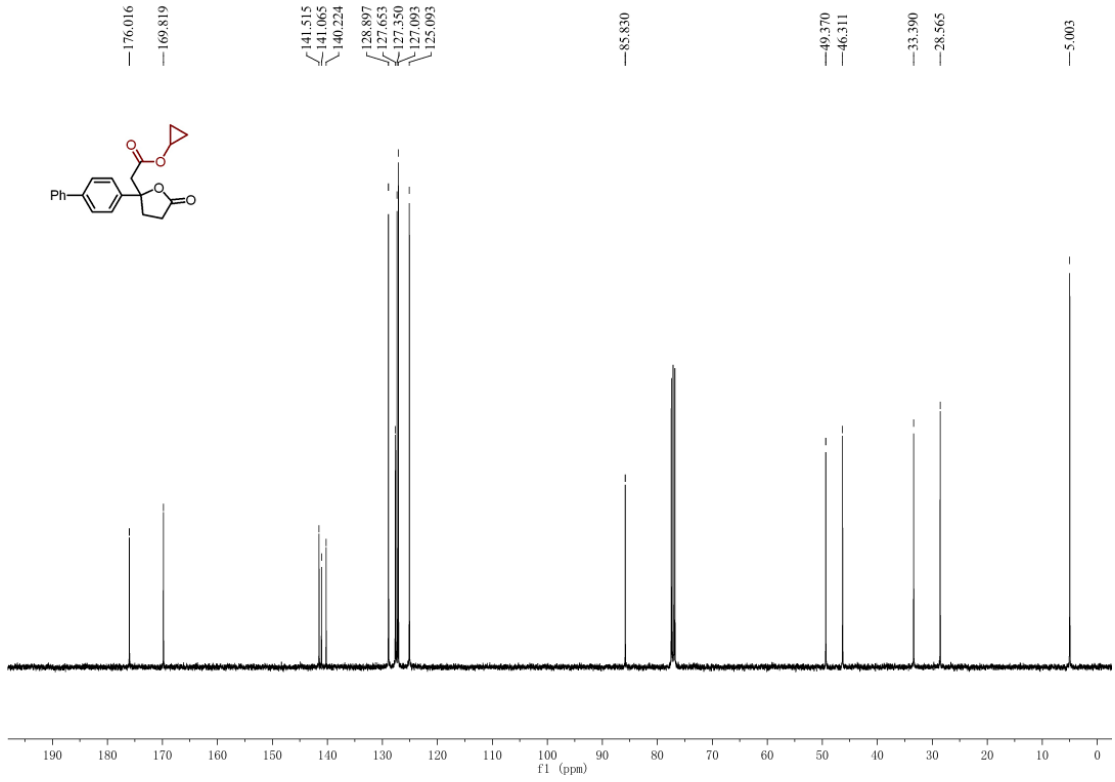
((3r,5r,7r)-Adamantan-1-yl)methyl 2-(2-([1,1'-biphenyl]-4-yl)-5-oxotetrahydrofuran -2-yl)acetate (3x)



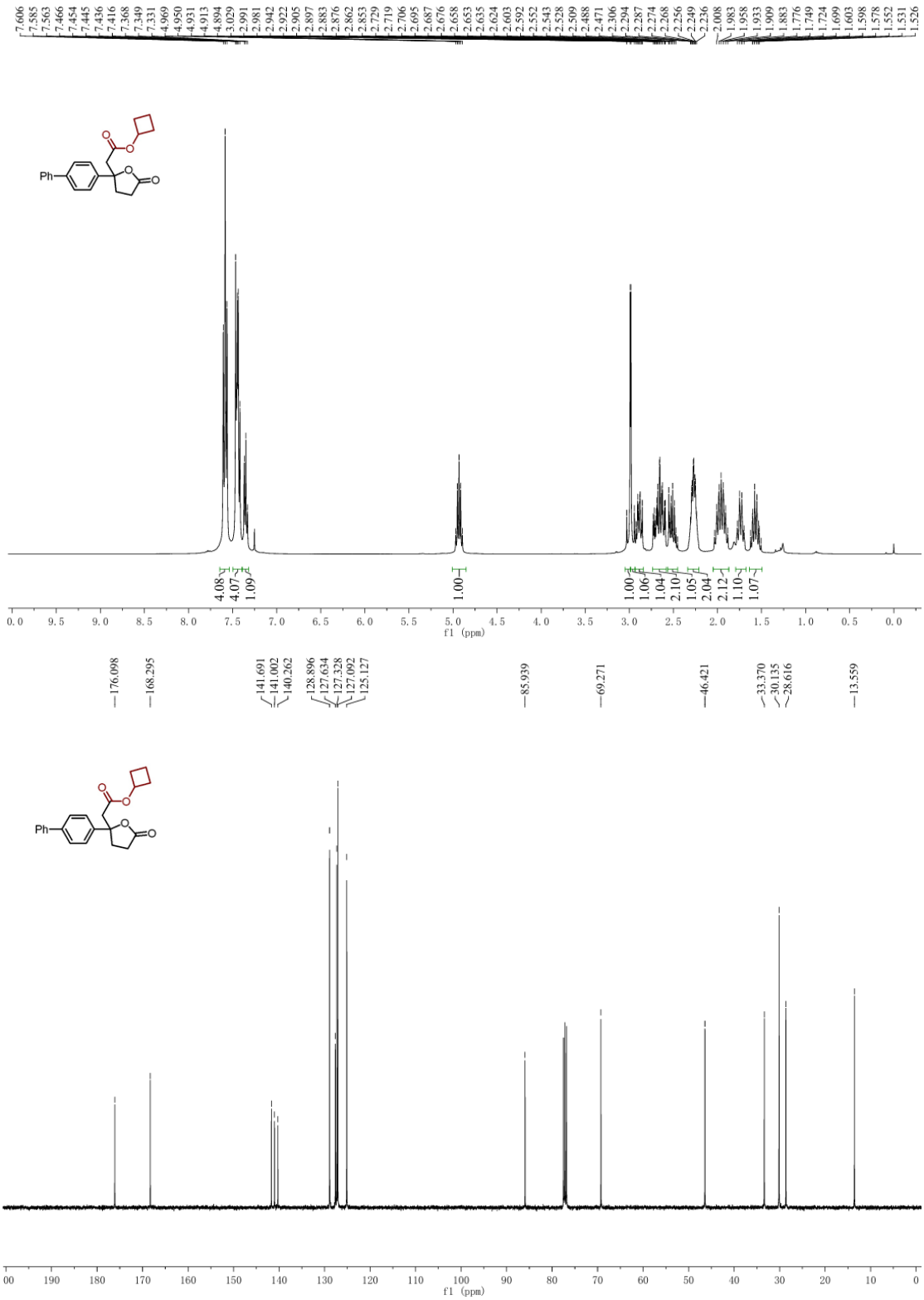


Cyclopropyl 2-(2-([1,1'-biphenyl]-4-yl)-5-oxotetrahydrofuran-2-yl)acetate (3y)

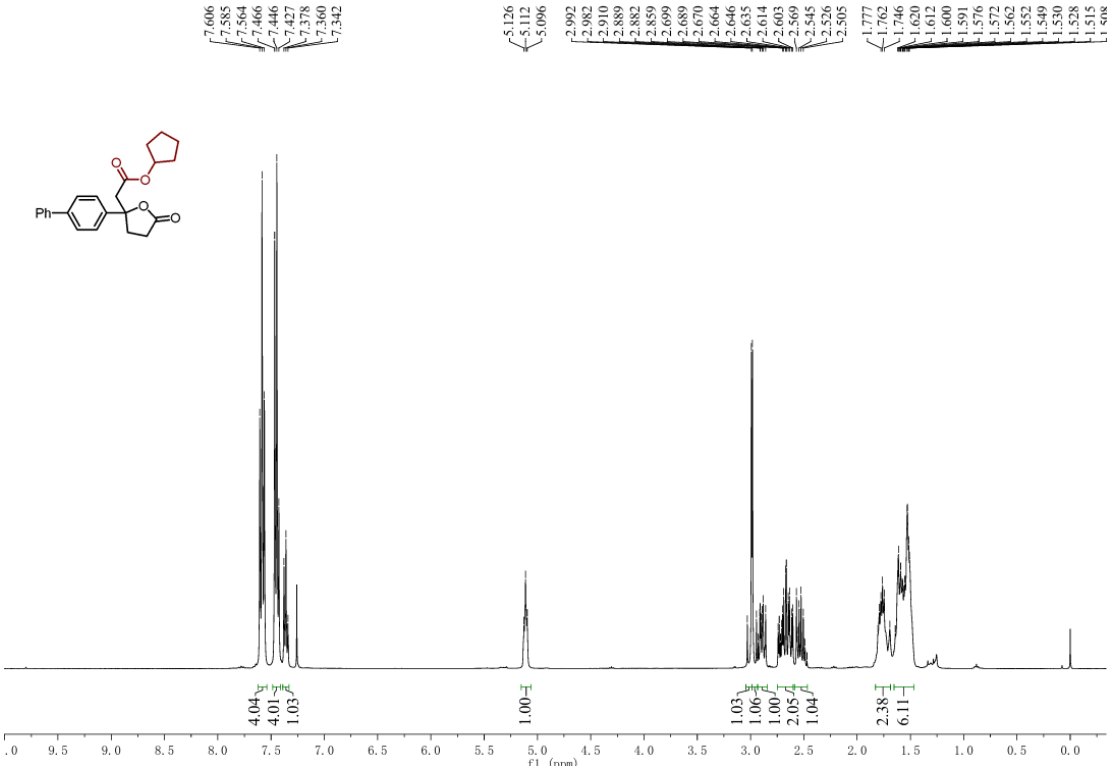


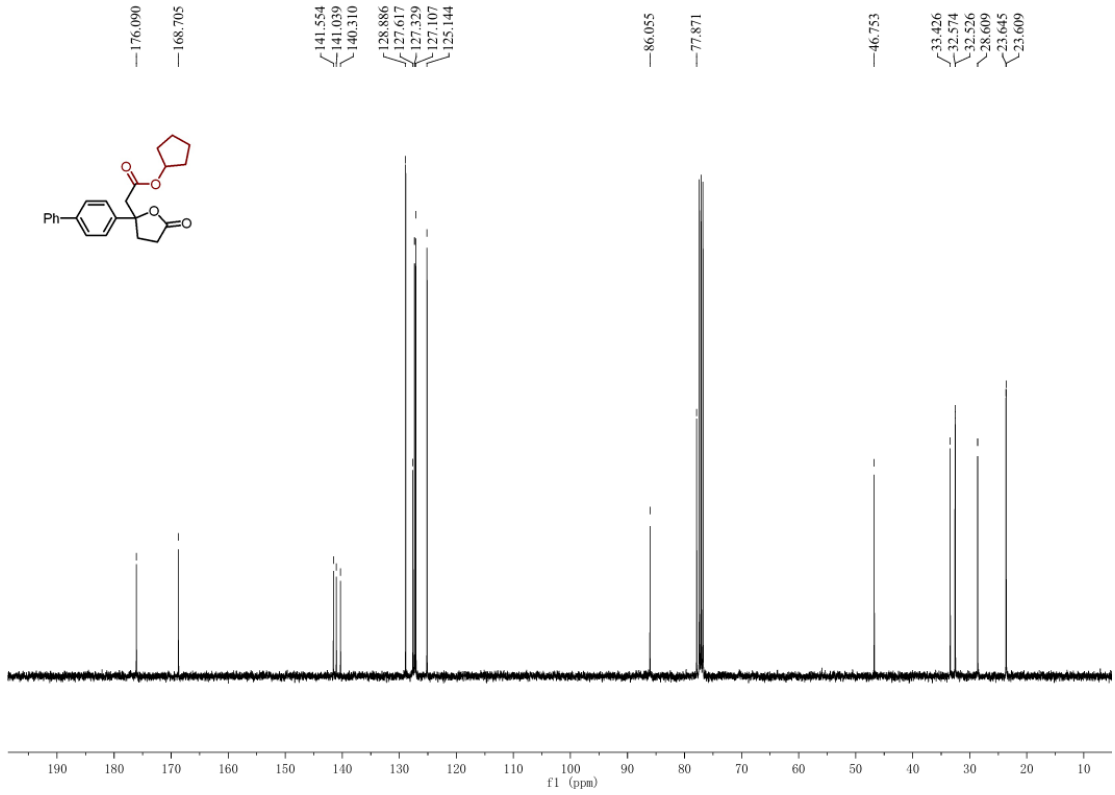


Cyclobutyl 2-(2-([1,1'-biphenyl]-4-yl)-5-oxotetrahydrofuran-2-yl)acetate (3z)

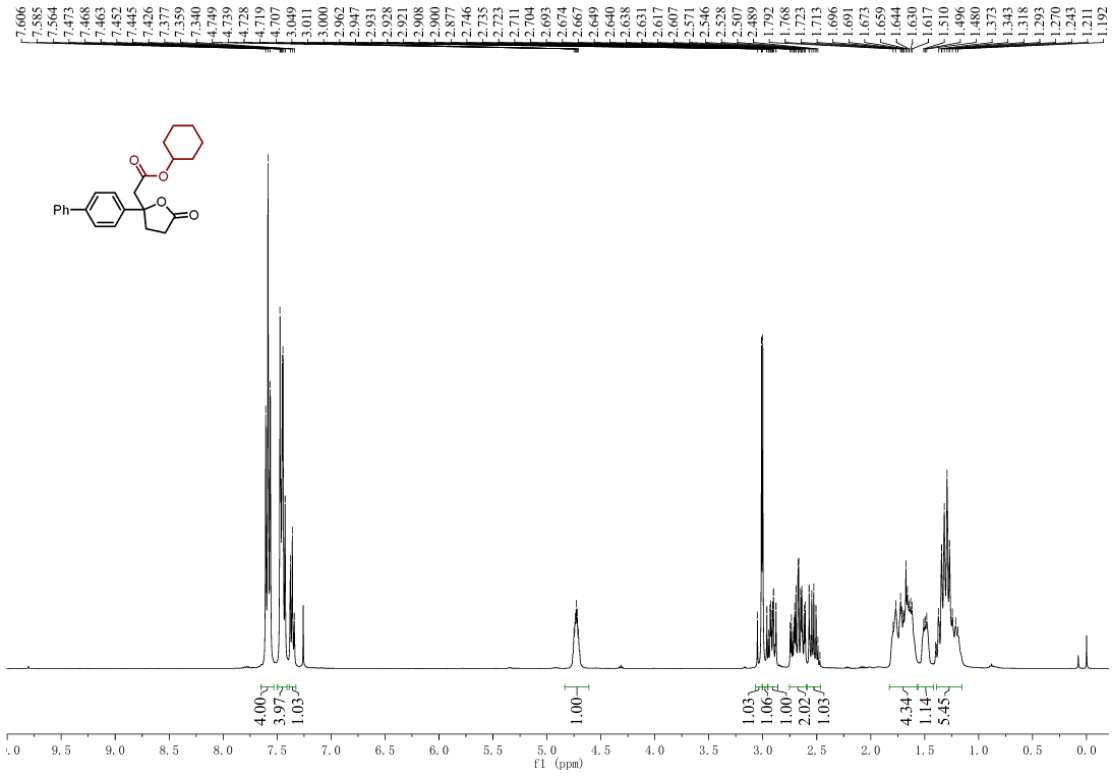


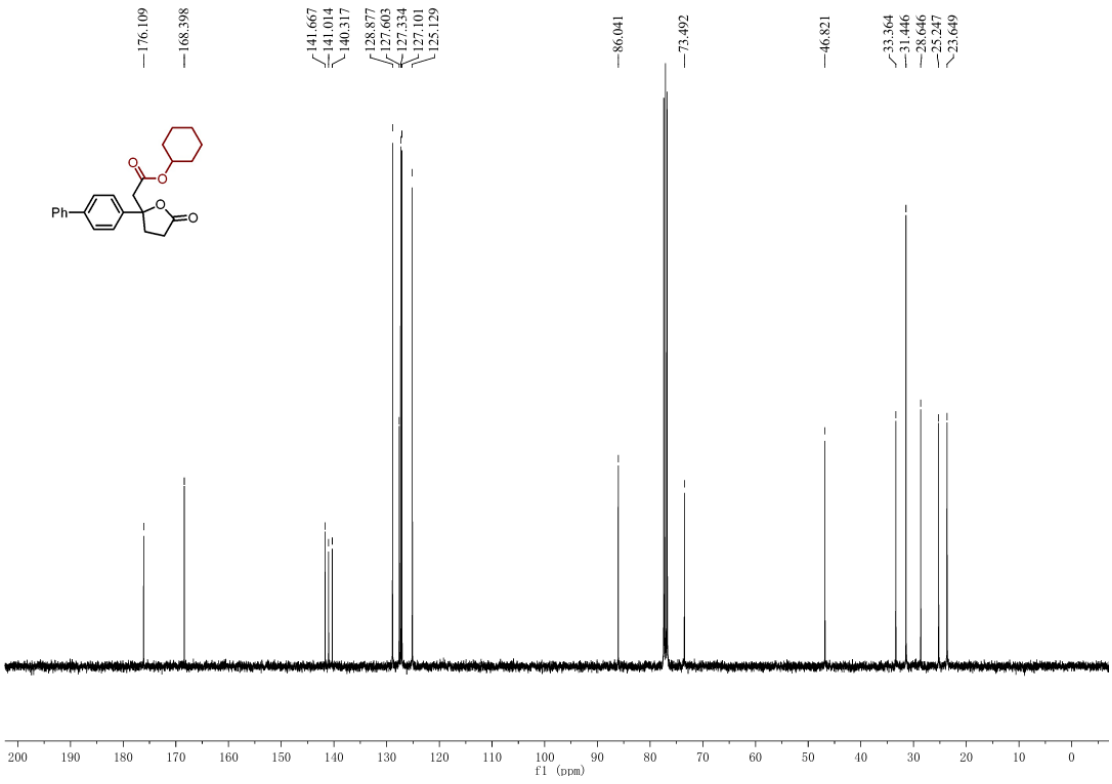
Cyclopentyl 2-(2-([1,1'-biphenyl]-4-yl)-5-oxotetrahydrofuran-2-yl)acetate (3aa)



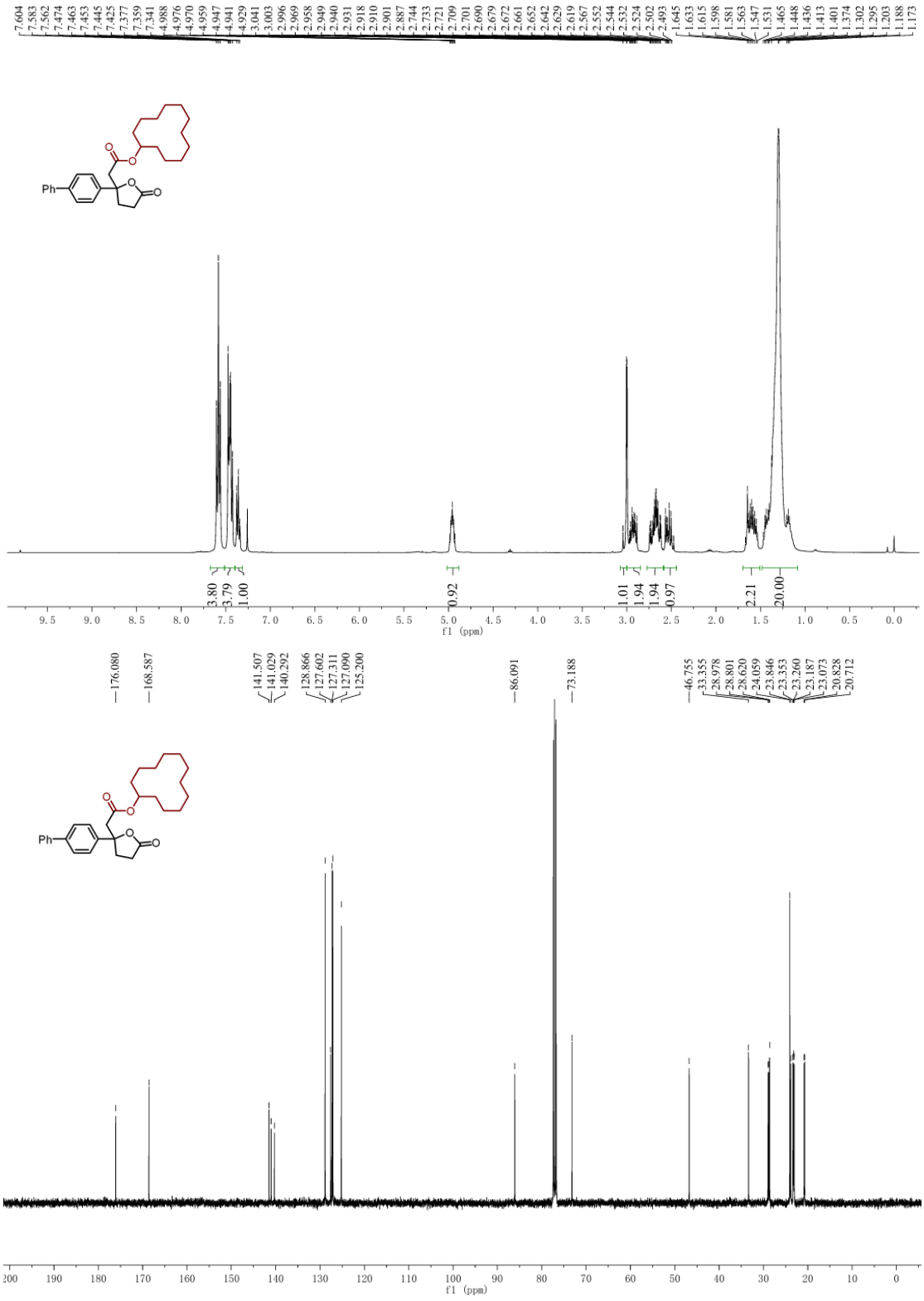


Cyclohexyl 2-(2-([1,1'-biphenyl]-4-yl)-5-oxotetrahydrofuran-2-yl)acetate (3ab)

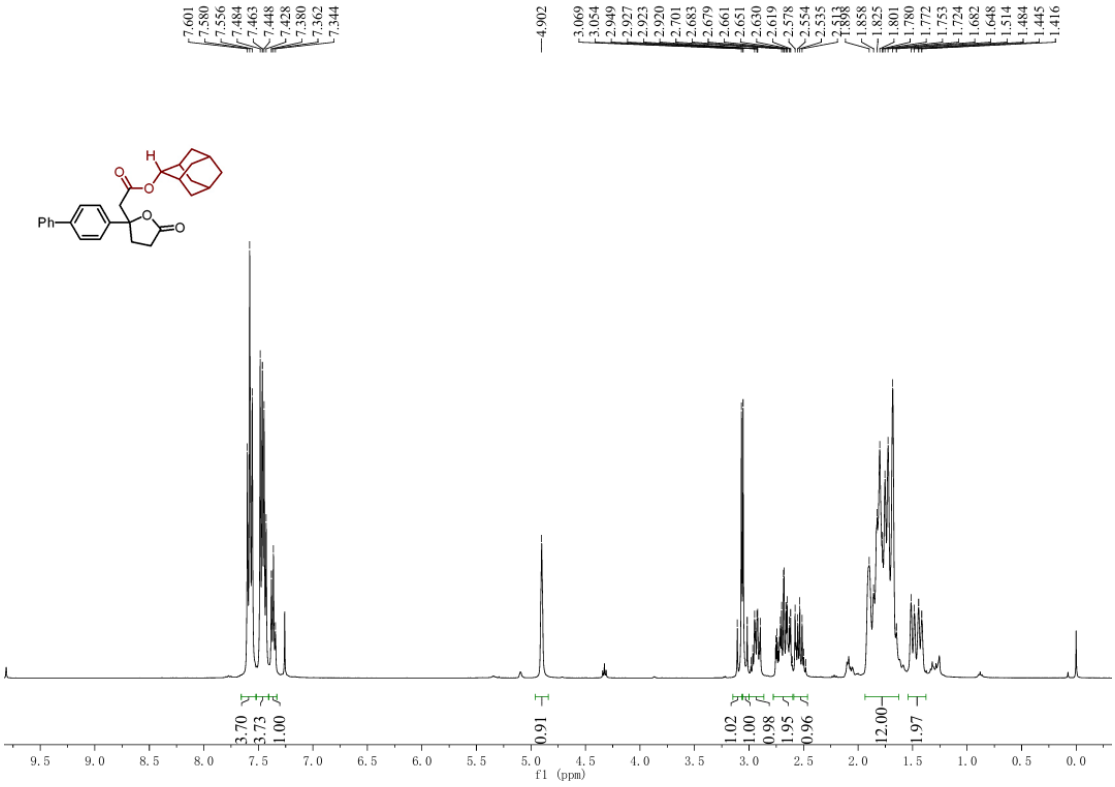


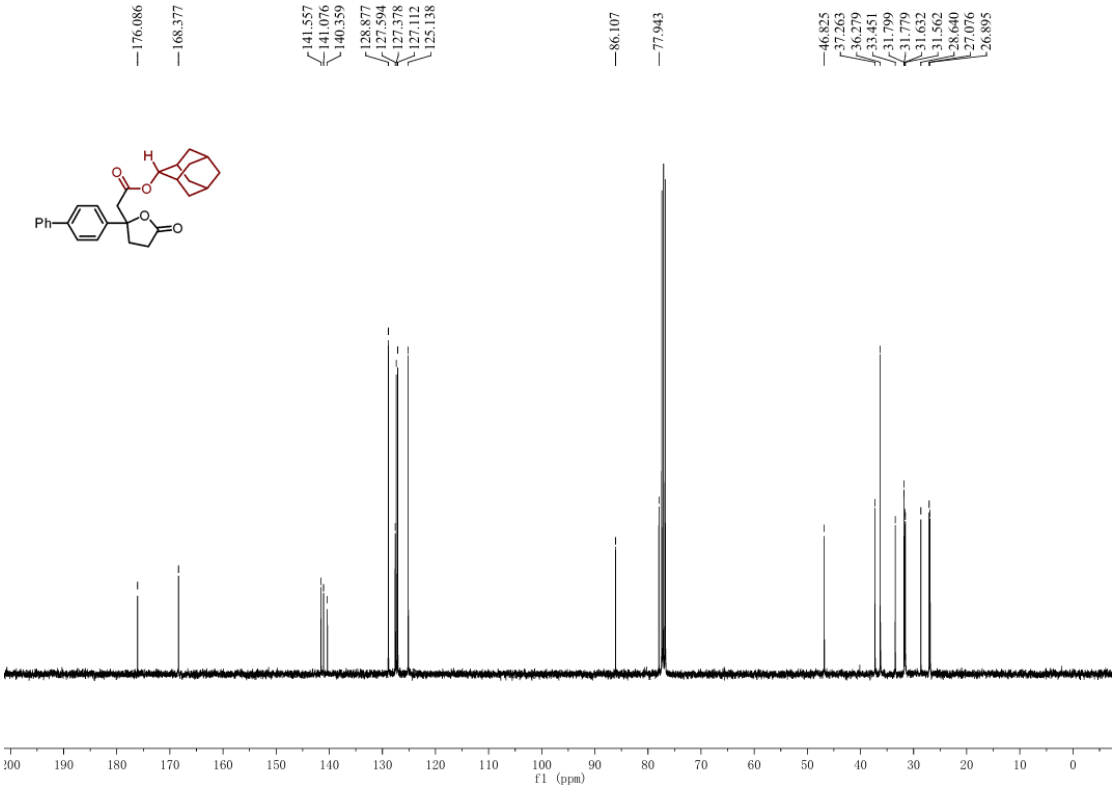


Cyclododecyl 2-(2-([1,1'-biphenyl]-4-yl)-5-oxotetrahydrofuran-2-yl)acetate (3ac)

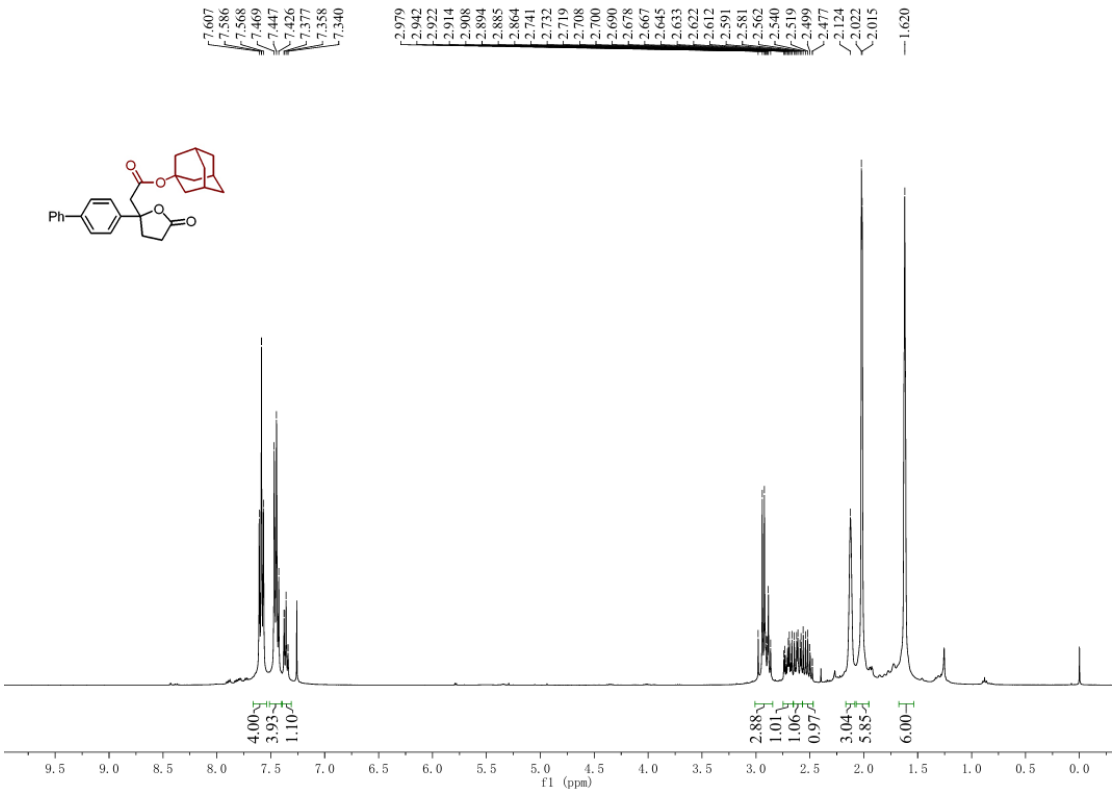


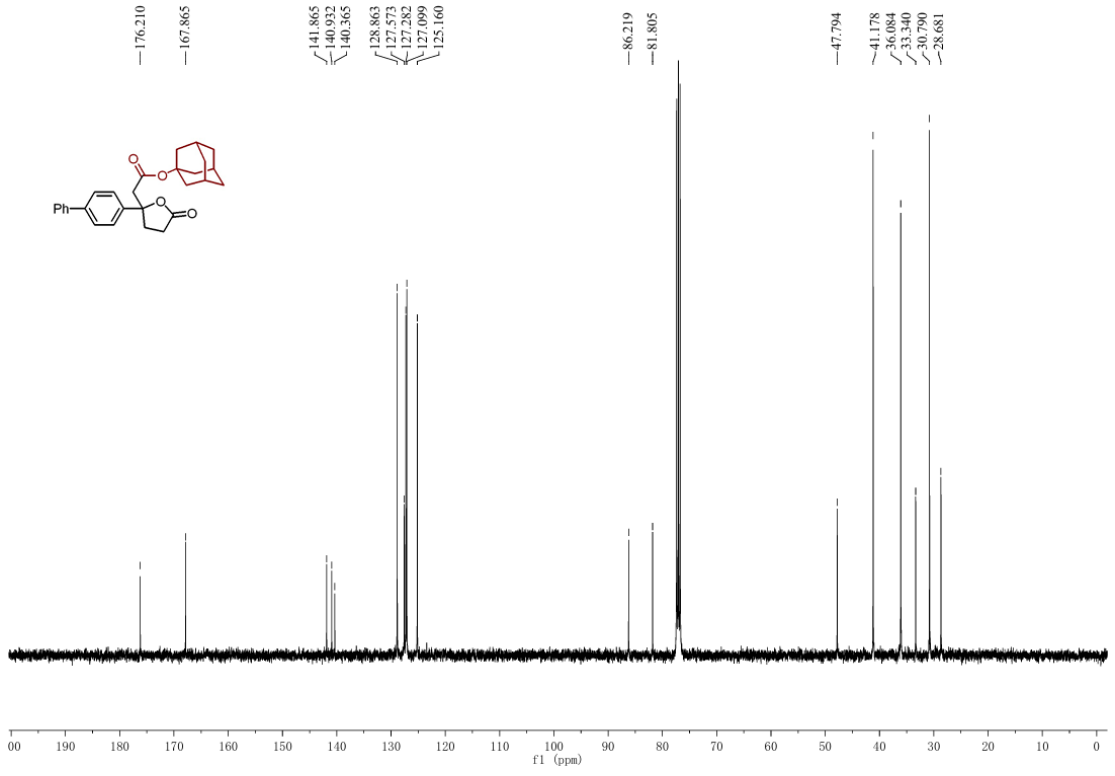
(1R,3S,5r,7r)-Adamantan-2-yl 2-(2-([1,1'-biphenyl]-4-yl)-5-oxotetrahydrofuran -2-yl)acetate (3ad)



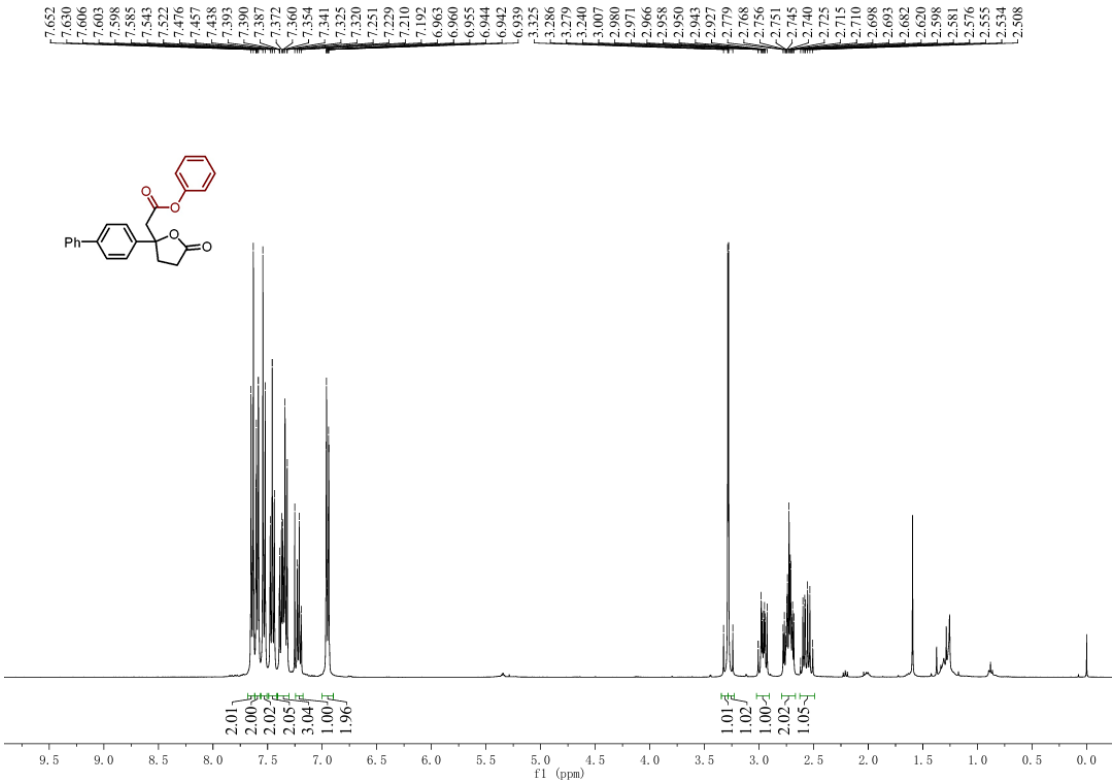


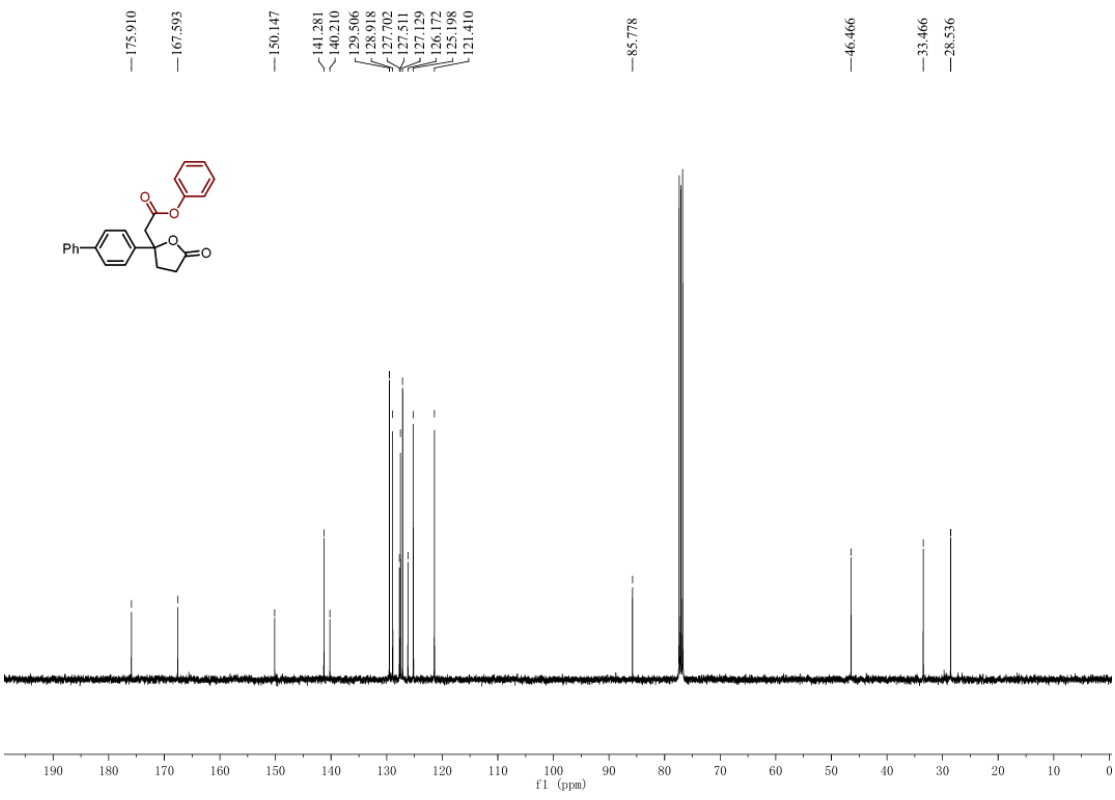
(3s,5s,7s)-Adamantan-1-yl 2-(2-([1,1'-biphenyl]-4-yl)-5-oxotetrahydrofuran-2-yl)acetate (3ae)



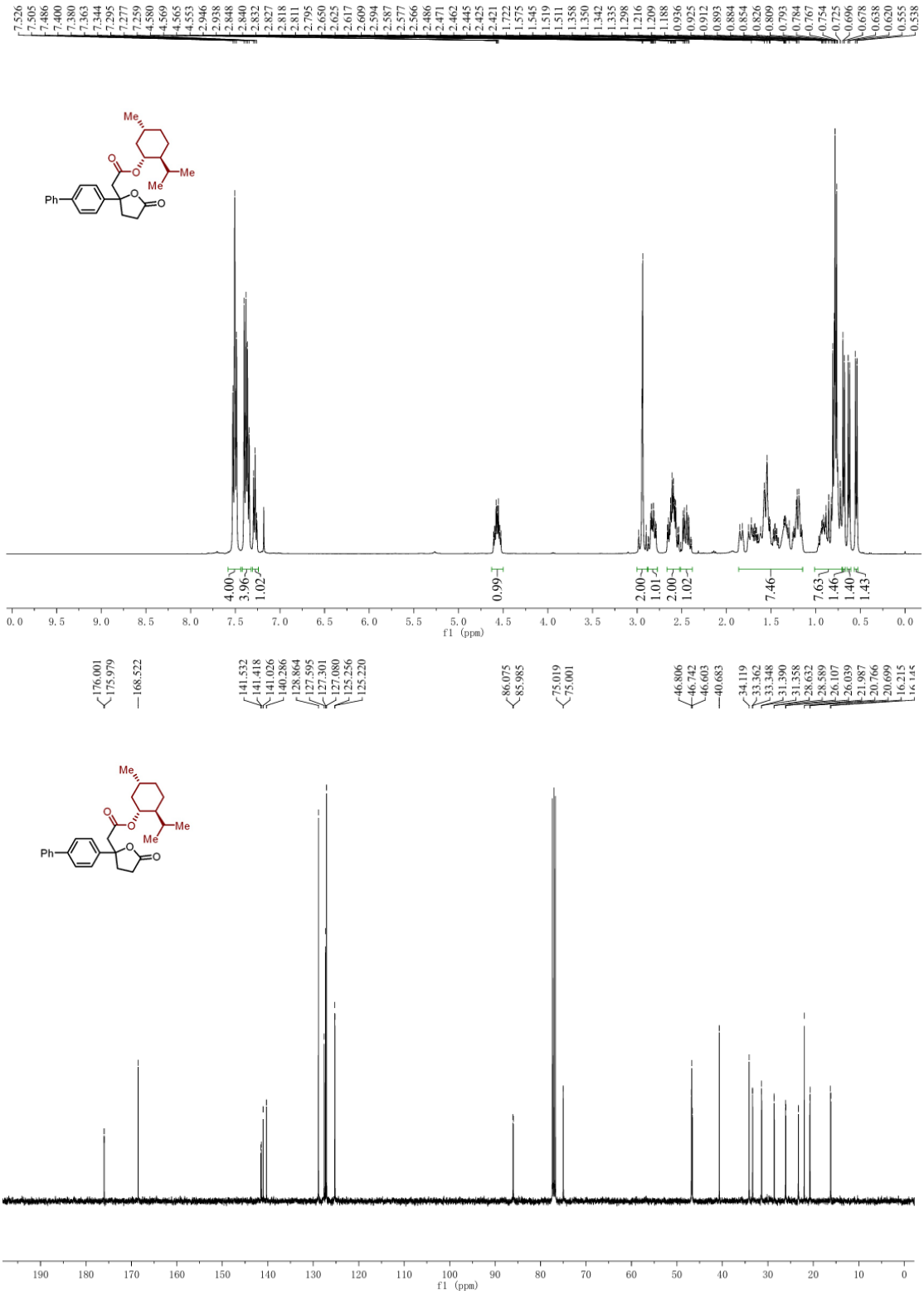


Phenyl 2-(2-([1,1'-biphenyl]-4-yl)-5-oxotetrahydrofuran-2-yl)acetate (3af)

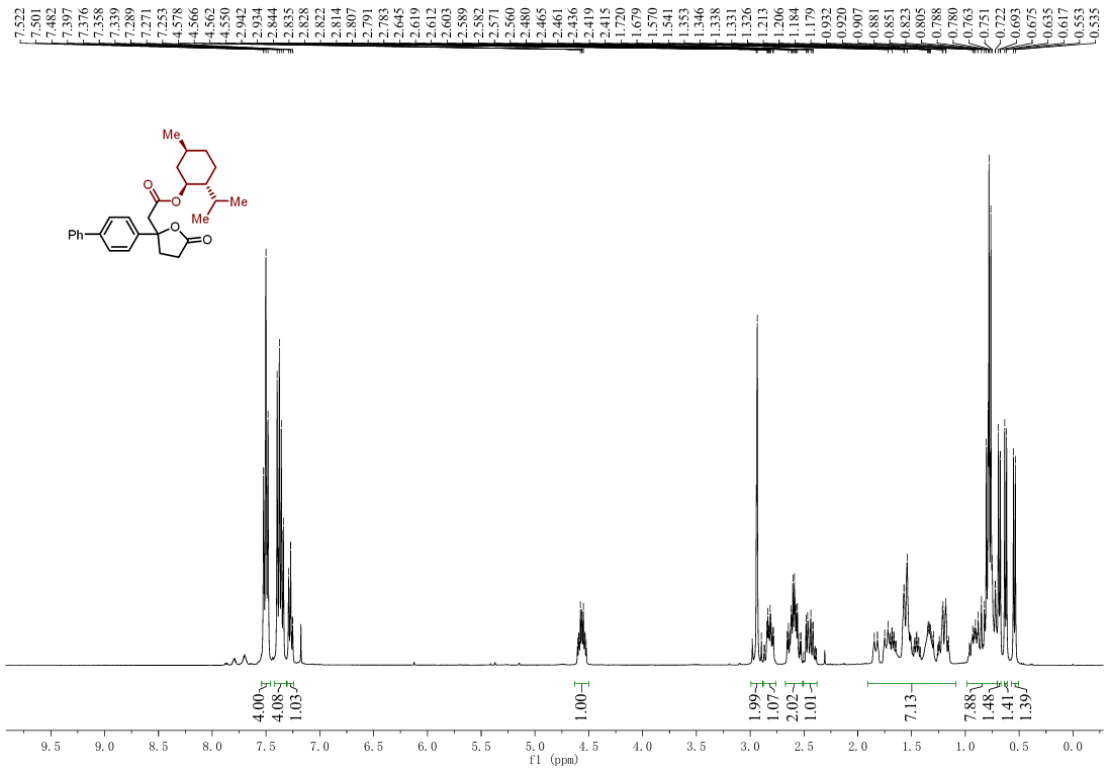


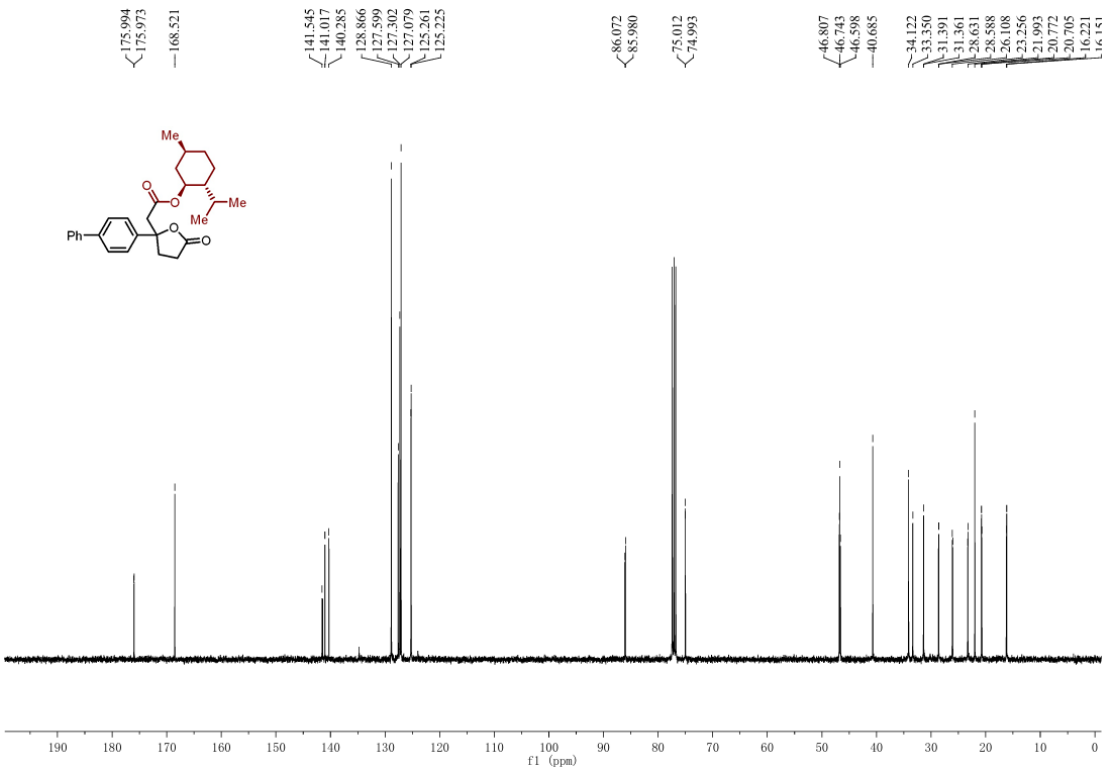


(1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl 2-(2-([1,1'-biphenyl]-4-yl)-5-oxotetrahydrofuran-2-yl)acetate (3ag)

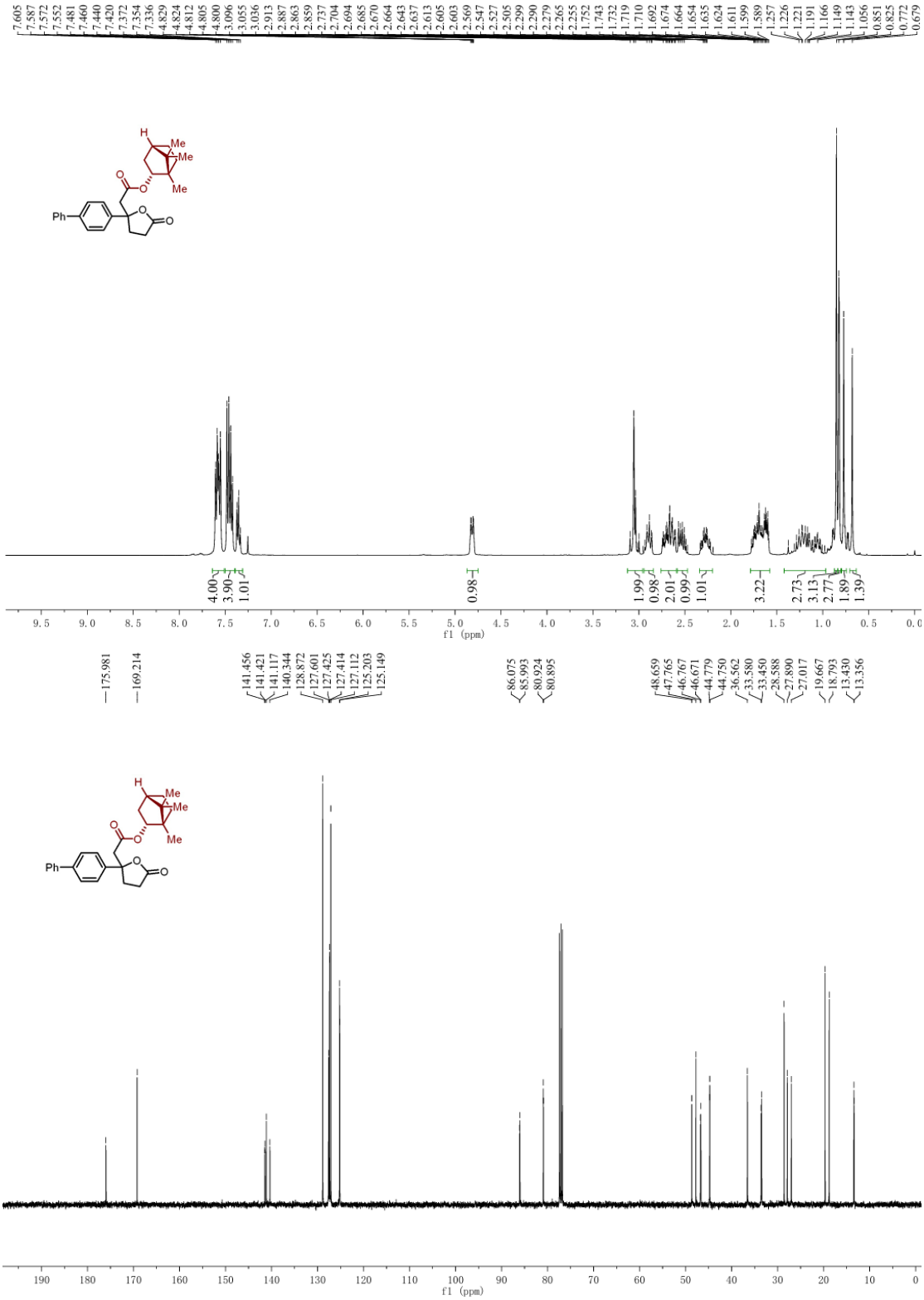


(1S,2R,5S)-2-Isopropyl-5-methylcyclohexyl 2-(2-([1,1'-biphenyl]-4-yl)-5-oxotetrahydrofuran-2-yl)acetate (3ah)

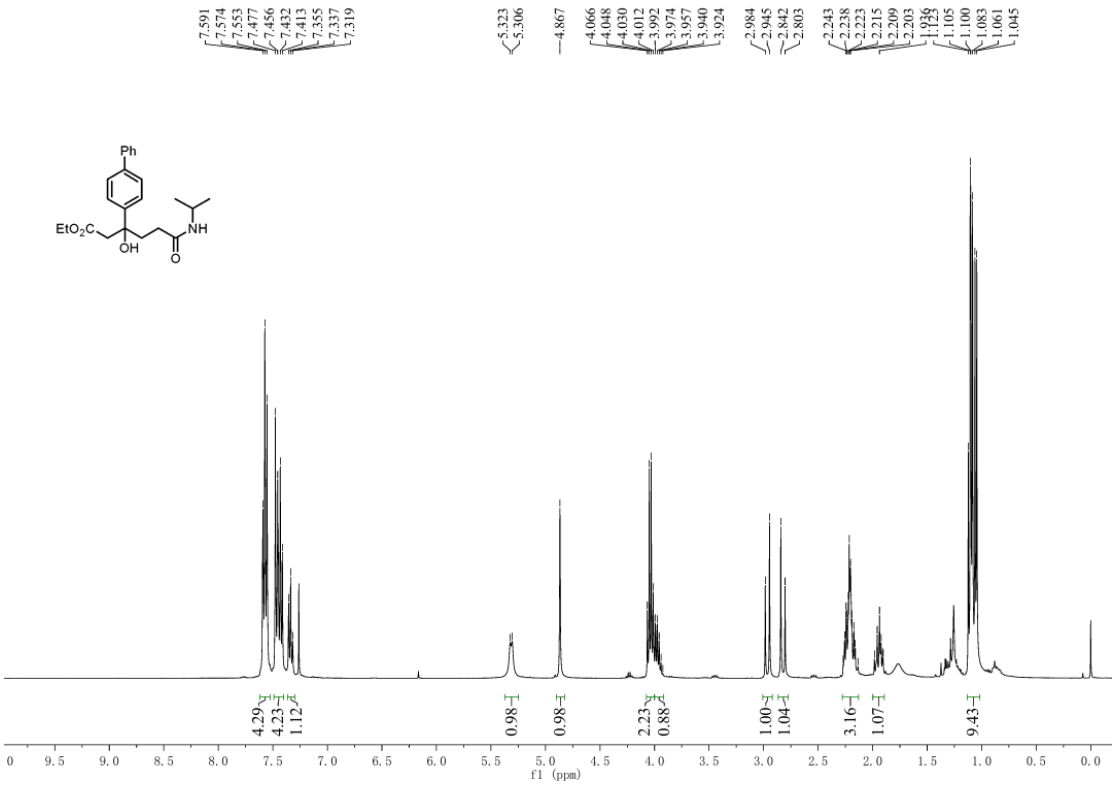


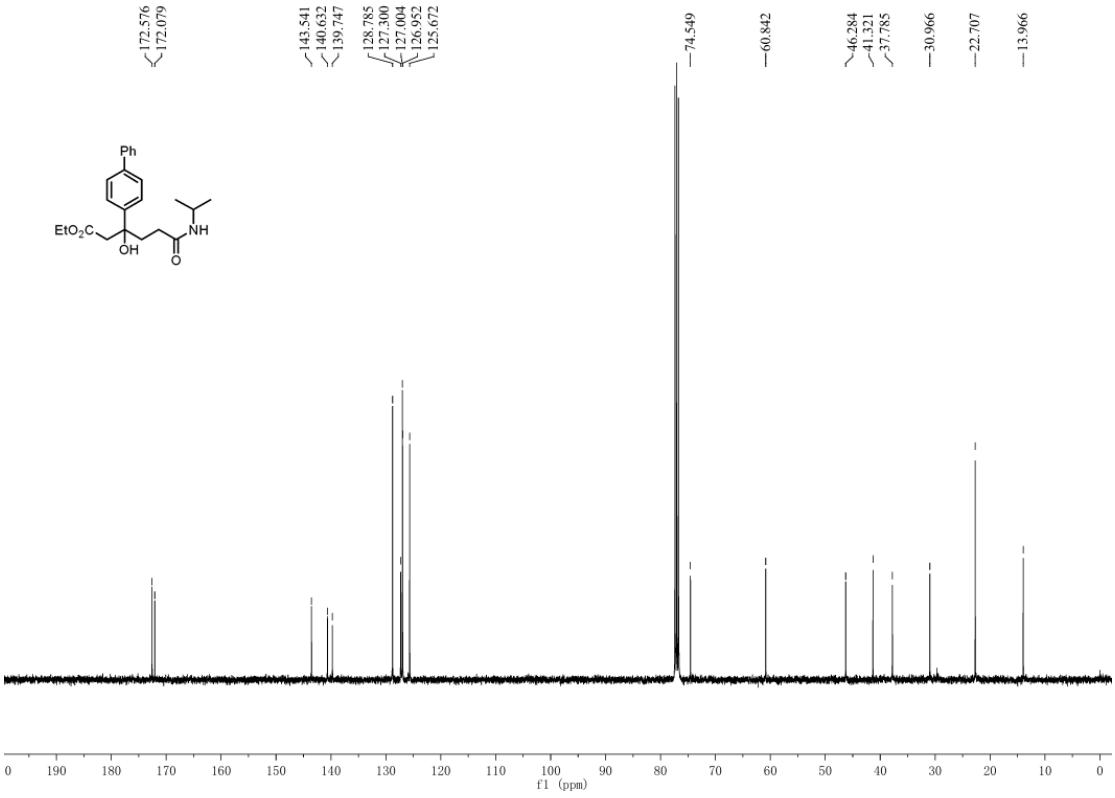


(1S,2R,4S)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl 2-(2-([1,1'-biphenyl]-4-yl)-5-oxotetrahydrofuran-2-yl)acetate (3ai)

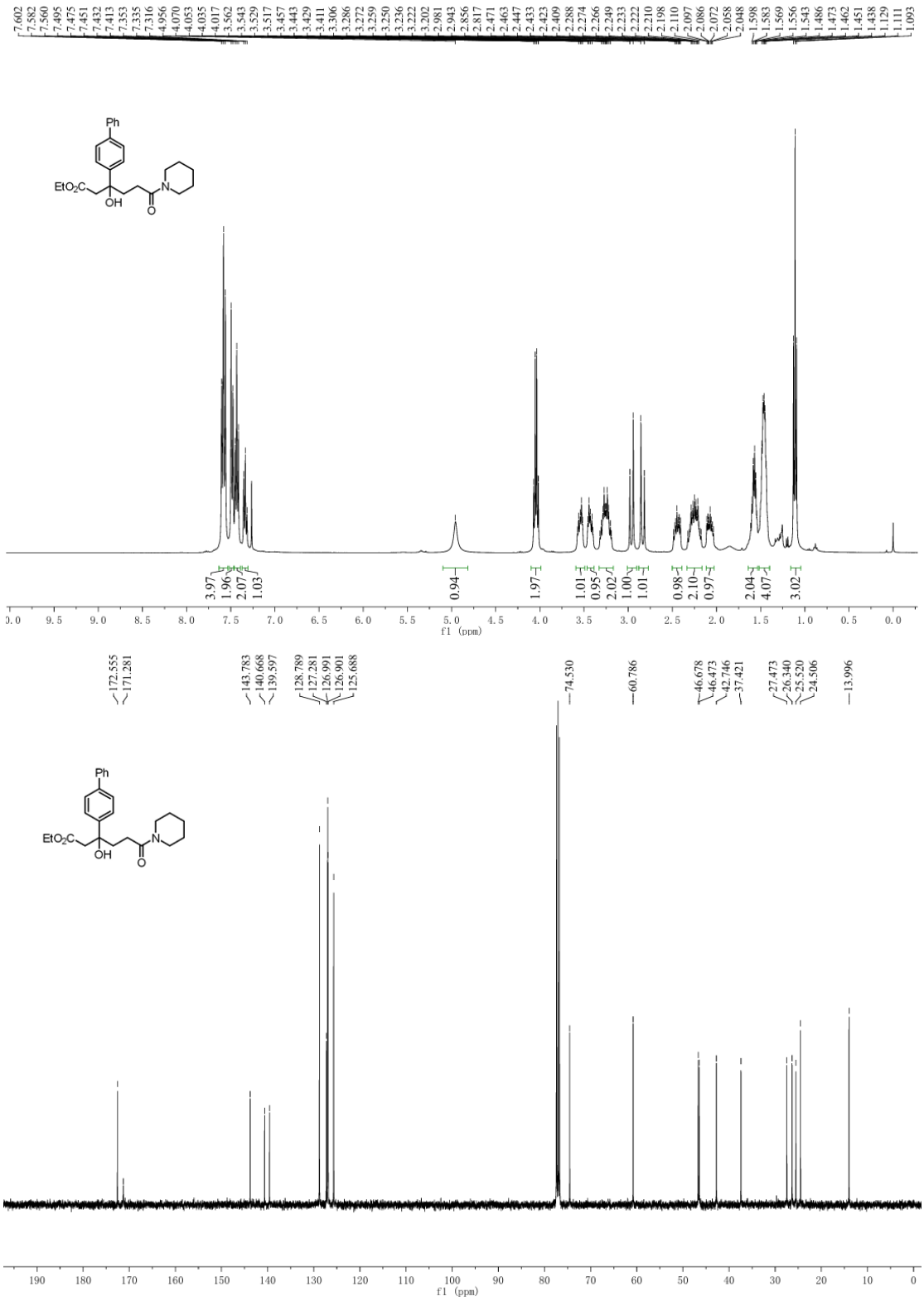


Ethyl 3-([1,1'-biphenyl]-4-yl)-3-hydroxy-6-(isopropylamino)-6-oxohexanoate (3a-I)

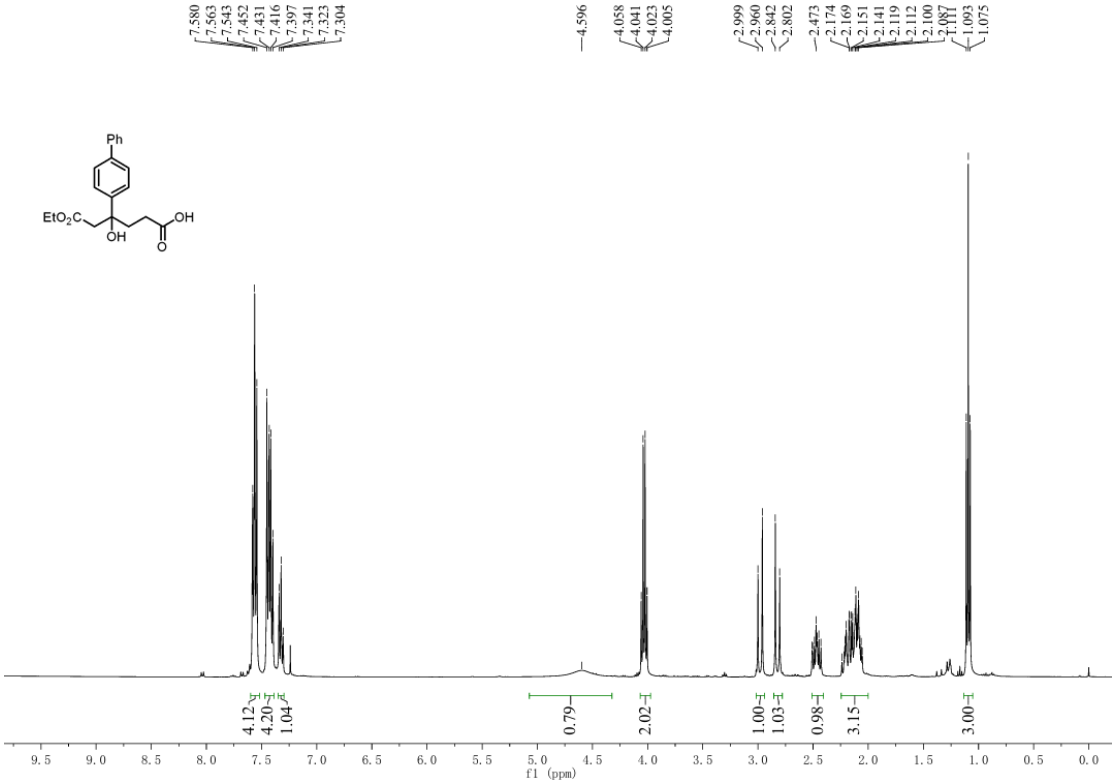


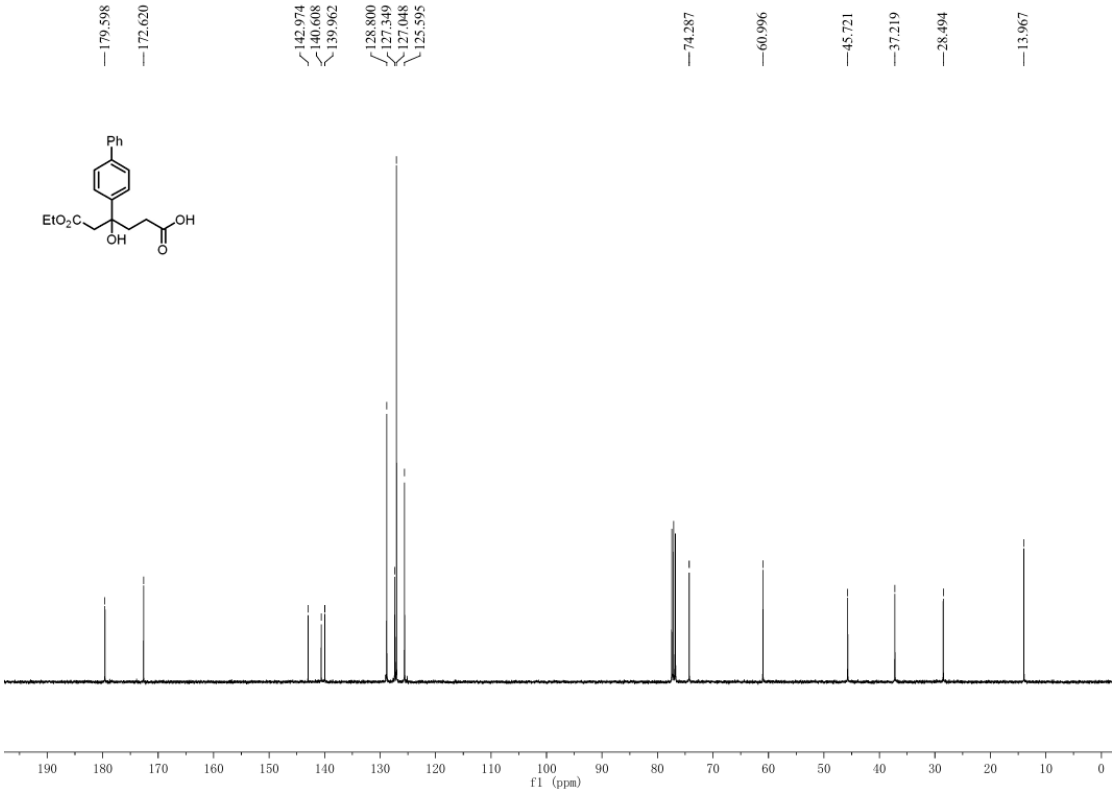


Ethyl 3-([1,1'-biphenyl]-4-yl)-3-hydroxy-6-oxo-6-(piperidin-1-yl)hexanoate (3a-II)

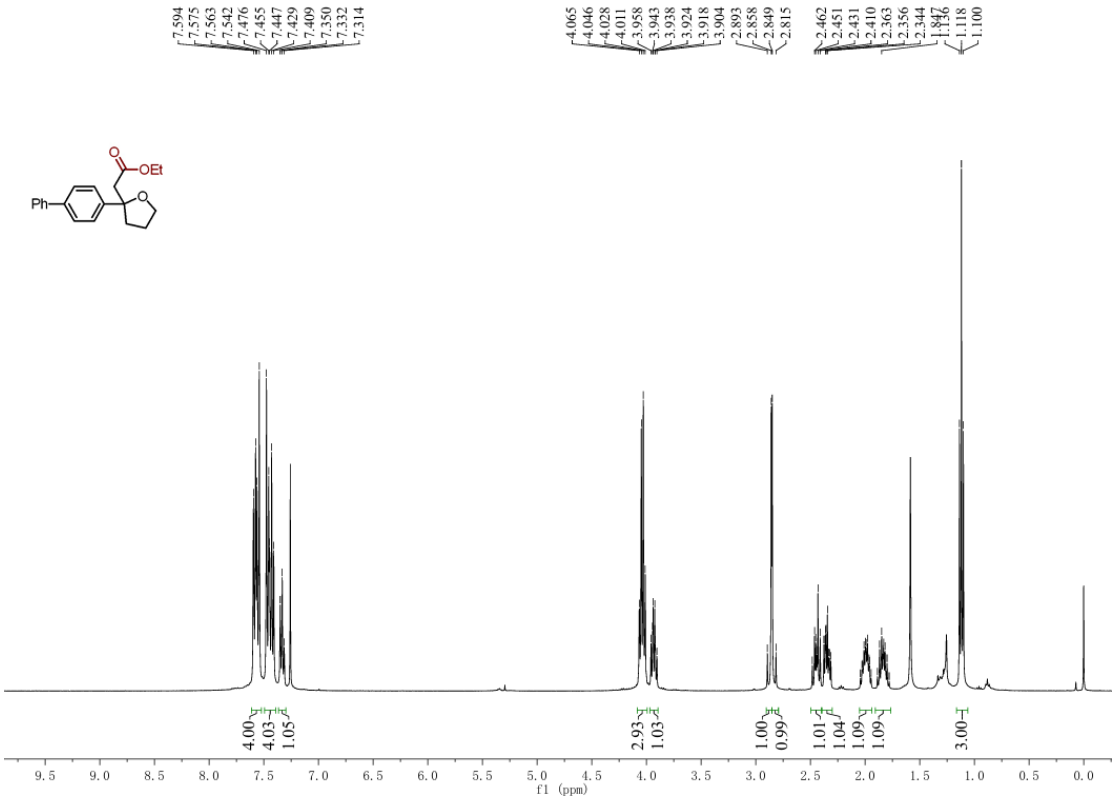


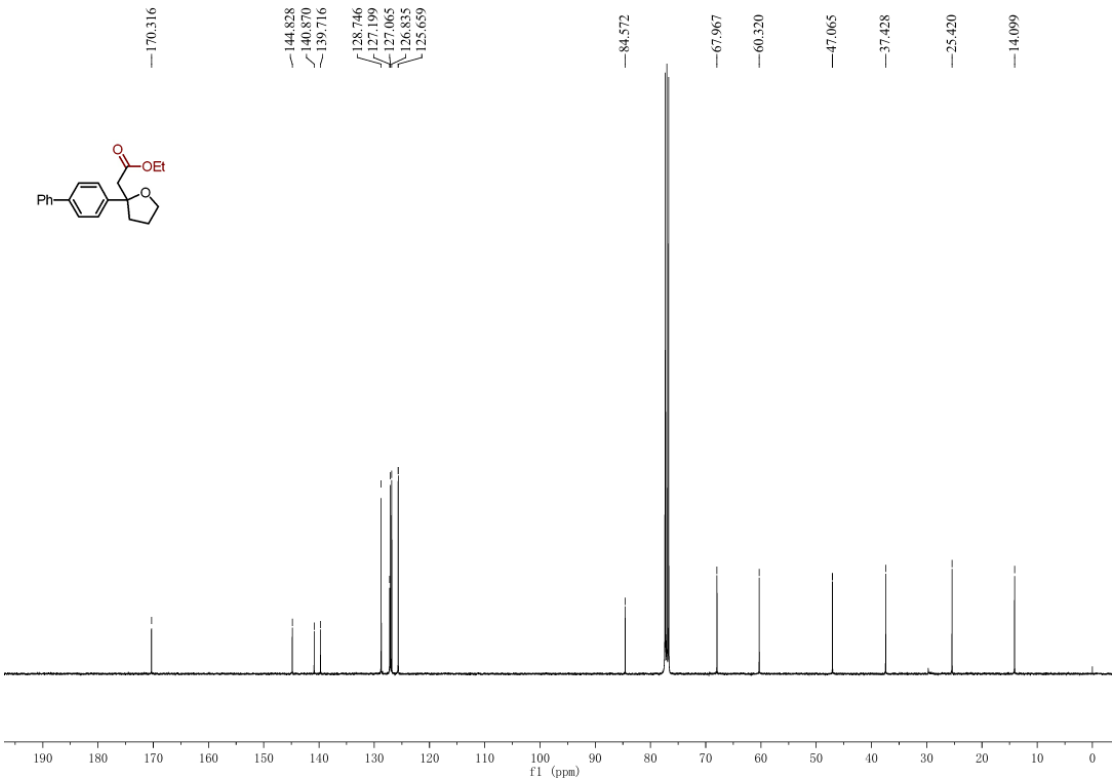
4-([1,1'-Biphenyl]-4-yl)-6-ethoxy-4-hydroxy-6-oxohexanoic acid (3a-III)



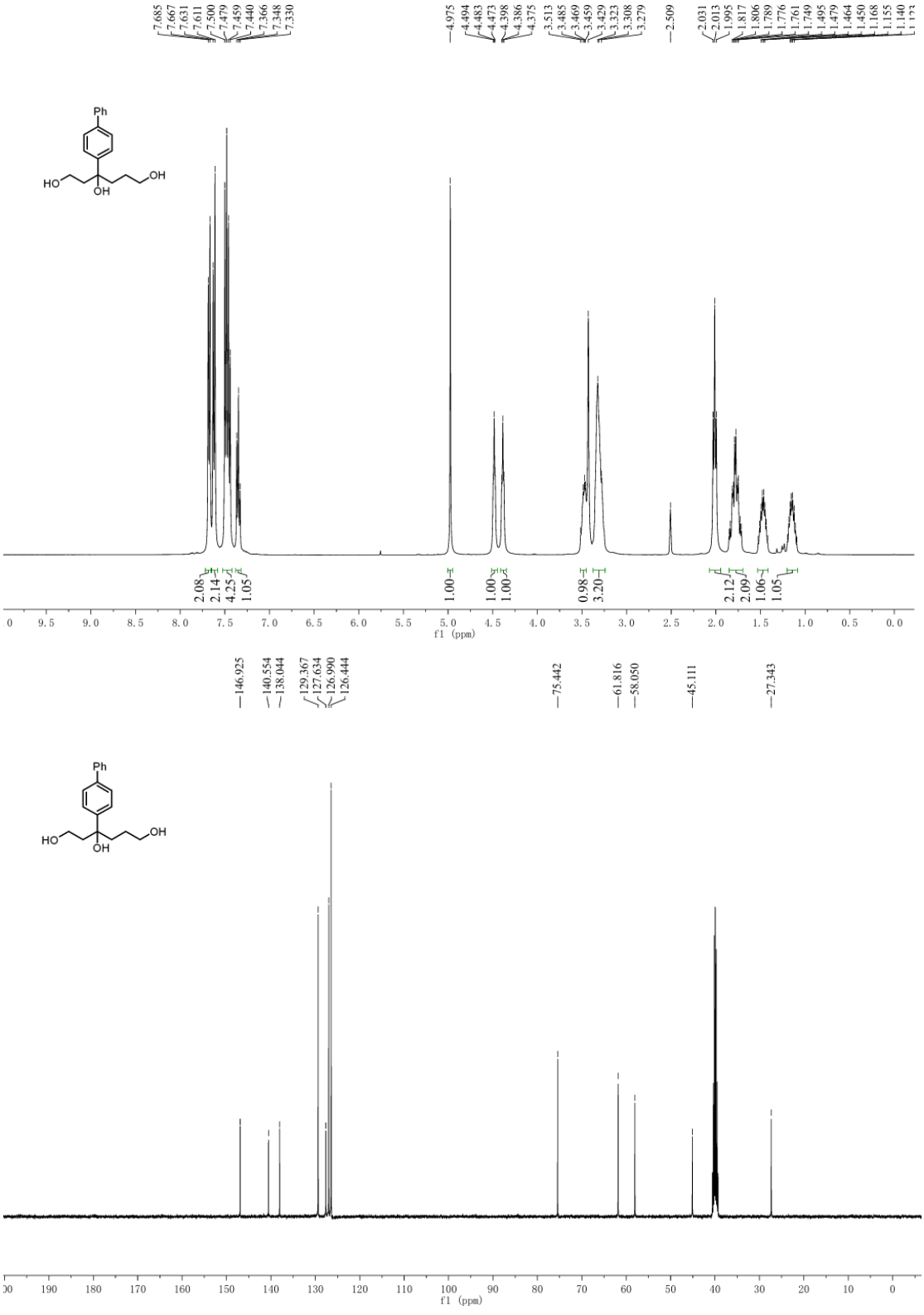


Ethyl 2-(2-([1,1'-biphenyl]-4-yl)tetrahydrofuran-2-yl)acetate (3a-IV)

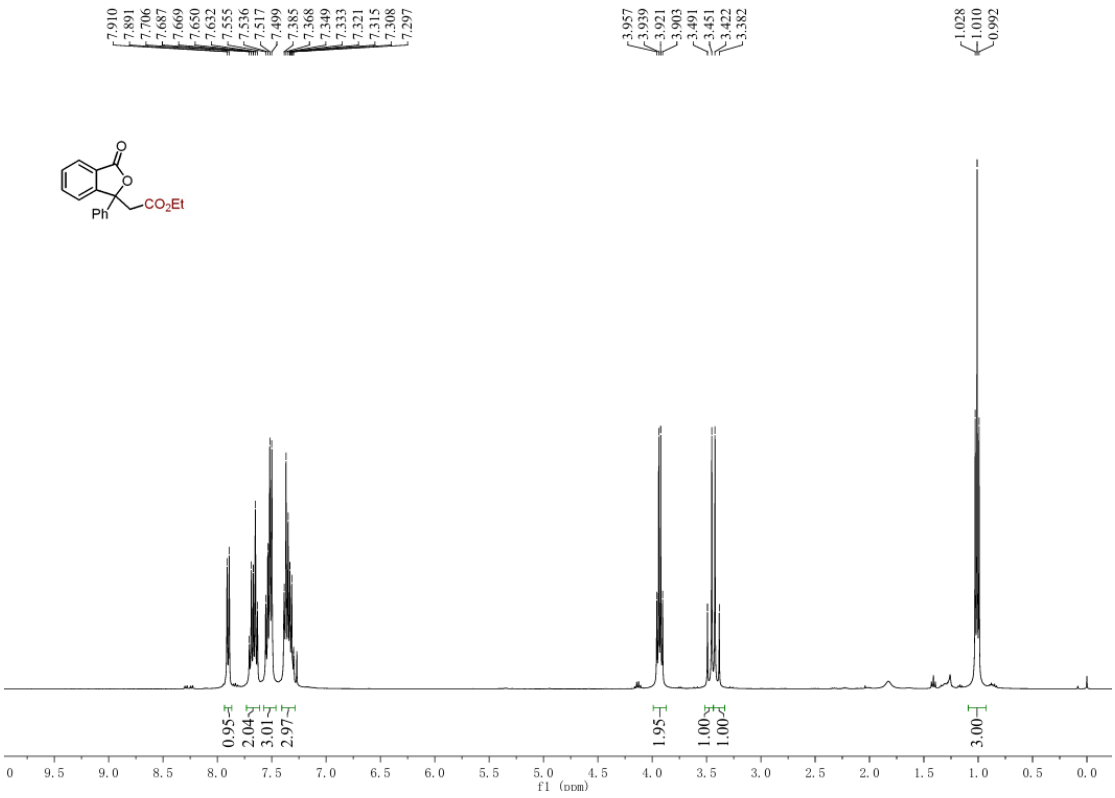


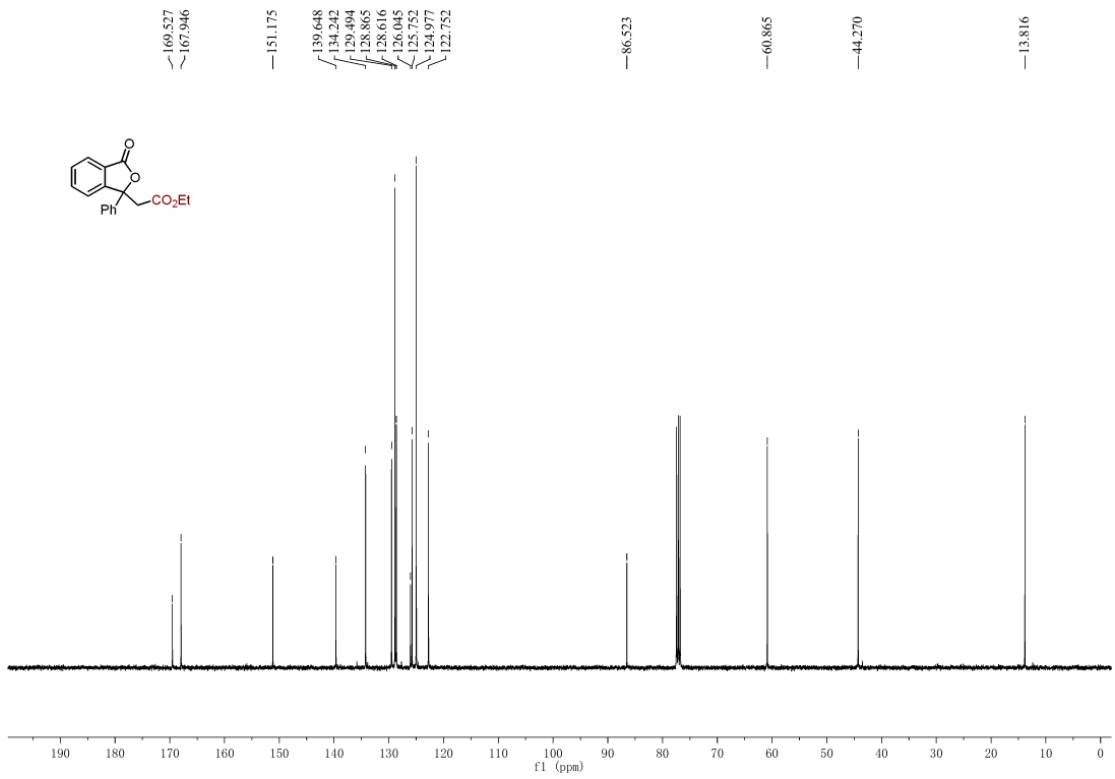


3-([1,1'-Biphenyl]-4-yl)hexane-1,3,6-triol (3a-V)



Ethyl 2-(3-oxo-1-phenyl-1,3-dihydroisobenzofuran-1-yl)acetate (5a)





8. References.

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2 (a) Y. Slutskyy and L. E. Overman, Generation of the methoxycarbonyl radical by visible-light photoredox catalysis and its conjugate addition with electron-deficient olefins, *Org. Lett.*, 2016, **18**, 2564–2567; (b) G. L. Lackner, K. W. Quasdorf and L. E. Overman, Direct construction of quaternary carbons from tertiary alcoholsvia photoredox-catalyzed fragmentation of tert-alkyl *N*-phthalimidoyl oxalates, *J. Am. Chem. Soc.*, 2013, **135**, 15342−15345.

3 (a) S. Li, Q. Chen, J. Yang and J. Zhang, Palladium-catalyzed enantioselective γ-arylation of β,γ-unsaturated butenolides, *Angew. Chem., Int. Ed.,* 2022, **61**, e202202046; (b) Y. Jin, L. Fan, E. W. H. Ng, L. Yu, H. Hirao and L. Gong, Atom transfer radical coupling enables highly enantioselective carbo-oxygenation of alkenes with hydrocarbons, *J. Am. Chem. Soc.*, 2023, **145**, 22031−22040; (c) M. Xue, J. Cui, X. Zhu, F. Wang, D. Lv, Z. Nie, Y. Li and H. Bao, Copper-catalyzed radical enantioselective synthesis of *γ*-butyrolactones with two non-vicinal carbon stereocenters, *Angew. Chem., Int. Ed.,* 2023, **62**, e202304275.