Supporting Information

Novel Palladium-Catalyzed Cascade Carboxylative Annulation to Construct Functionalized γ-Lactones in Ionic Liquids

Jianxiao Li, Shaorong Yang*, Wanqing Wu and Huanfeng Jiang*

School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, P. R. China

jianghf@scut.edu.cn; *lisryang@scut.edu.cn*

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I. General method

Melting points were measured with a BÜCHI B-545 melting point instrument and were uncorrected. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker Avance 400 MHz NMR spectrometer. The chemical shifts are referenced to signals at 7.24 and 77.0 ppm, respectively, and chloroform is solvent with TMS as the internal standard. IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Bruker Vector 22 spectrometer. GC–MS was obtained using electron ionization. HRMS (EI) was carried out on a MAT 95XP (Thermo). TLC was performed by using commercially prepared 100–400 mesh silica gel plates (GF254) and visualization was effected at 254 nm. The ionic liquids ([Bmim]Cl,[1] $[C_2OHmim]Cl$,[2] $[C_2O_2mim]Cl$[3]) were synthesized using reported procedures. The alkynoates[4] were prepared according to the literature. Other reagents were purchased as reagent grade and used without further purification.

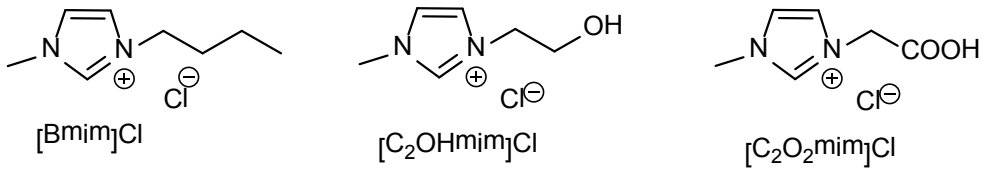

Fig. 1 Ionic liquids applied in this work.

II. General procedure for the synthesis of 3 and 6

Palladium chloride (1.3 mg, 3 mol%) and $CuCl_2 \cdot 2H_2O$ (79.0 mg, 2 equiv) were combined in an Schlenk tube equipped with a stir-bar. A balloon filled with CO and O_2 (the ratio is 3:1) was connected to the Schlenk tube via the side tube and purged 3 times. Then ionic liquid (1.0 mL), alkynoates **1** (0.25 mmol) and **2** (0.3 mmol) were then added to the tube and stirred at room temperature. After the reaction was completed, the balloon gas was released carefully and the reaction was quenched by water and extracted with CH_2Cl_2 three times. The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under vacuum. The desired products were

obtained in the corresponding yields after purification by flash chromatography on silica gel with hexane/ethyl acetate.

III. General procedure for the synthesis of 7 and 8

According to the reported procedure,[5] to a mixture of (4-ethylphenyl)boronic acid (112.5 mg, 0.75 mmol), $Pd(OAc)_2$ (2.8 mg, 0.0125 mmol), K_3PO_4 (0.75 mmol), and Xphos (11.9 mg, 0.025 mmol) in 1 mL of toluene was added a solution of (Z)-**3a** (73.5 mg, 0.25 mmol) in 1.0 mL of toluene under nitrogen. After stirring at 110 ^oC for 10 h, the reaction mixture was quenched with water, extracted with ethyl acetate, washed with brine, dried over $MgSO_4$, and concentrated. Column chromatography on silica (petroleum ether/ethyl acetate = 5/1) gave 63.7 mg (yield: 70%) of **7** as a yellow oil.

According to the reported procedure,[5] under nitrogen, $ZnCl_2$ (0.5 M solution in THF; 0.78 mL, 0.4 mmol) was added by syringe to a Schlenk tube. *o*-Tolylmagnesium chloride (1.0 M solution in THF; 1.0 mL, 1.0 mmol) was then added dropwise, and the resulting mixture was stirred at room temperature for 20 min. Next, NMP (1.0 mL) was added by syringe, followed after 5 min by $Pd(P(t\text{-}Bu)_3)_2$ (2.6 mg, 0.005 mmol) and (Z)-**3a** (73.5 mg, 0.25 mmol). The Schlenk tube was closed at the Teflon stopcock, and the reaction mixture was stirred in a 100 °C oil bath for 2 h. It was then allowed to cool to room temperature, and aqueous HCl was added (1.0 M; 5 mL). The resulting mixture was extracted with Et_2O (2 × 10 mL), and the organic extracts were combined, washed with water (2 × 10 mL), dried ($MgSO_4$), and concentrated, affording a yellow oil. Column chromatography on silica (petroleum ether/ethyl acetate = 5/1) furnished 52.9 mg (63%) of the title compound **8** as a yellow oil.

References

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Commun., 1998, 1765.

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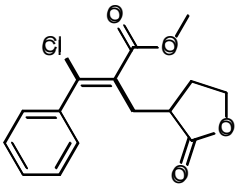
[3] C.-X. Miao, L.-N. He, J.-Q. Wang and J.-L. Wang, *Adv. Synth. Catal*., 2009, **351**, 2209.

[4] C. Pan, F. Luo, W. Wang, Z. Ye, J. Cheng, *Tetrahedron Lett.*, 2009, **50**, 5044.

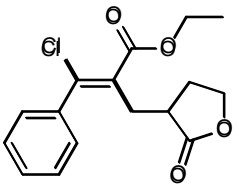
[5] A. F. Littke and G. C. Fu, *Angew. Chem. Int. Ed*., 2002, **41**, 4176.

IV. Analytical data for compounds 3 and 6



(Z)-methyl 3-chloro-2-((2-oxotetrahydrofuran-3-yl)methyl)-3-phenylacrylate (3a)

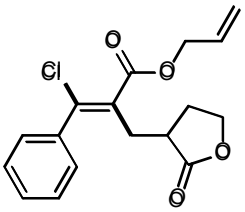
Yield: 86% (63.2 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.40 (m, 3H), 7.34-7.32 (m, 2H), 4.22 (td, J = 8.8, 2.2 Hz, 1H), 4.15-4.08 (m, 1H), 3.88 (s, 3H), 2.91 (dd, J = 14.4, 4.4 Hz, 1H), 2.66 (tdd, J = 10.8, 8.8, 4.4 Hz, 1H), 2.47 (dd, J = 14.4, 10.0 Hz, 1H), 2.40-2.33 (m, 1H), 1.78 (dtd, J = 12.4, 10.4, 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 167.6, 136.6, 134.6, 129.9, 129.5, 128.8, 128.4, 66.4, 52.5, 38.5, 31.8, 28.1 ppm; ν_{max}(KBr)/cm^{-1} 3040, 2965, 1716, 1635, 1541, 1507, 1104; MS (EI) m/z 115, 129, 149, 177, 208, 227, 259, 294; HRMS(EI) calcd for $C_{15}H_{15}NaClO_4$ 317.0551, found 317.0547.



(Z)-ethyl 3-chloro-2-((2-oxotetrahydrofuran-3-yl)methyl)-3-phenylacrylate (3b)

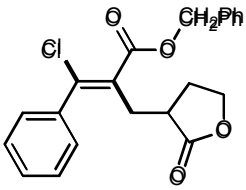
Yield: 83% (63.9 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.39 (m, 3H), 7.35-7.33 (m, 2H), 4.41-4.30 (m, 2H), 4.22 (td, J = 8.8, 2.0 Hz, 1H), 4.11 (td, J = 9.6, 6.4 Hz, 1H), 2.92 (dd, J = 14.4, 4.4 Hz, 1H), 2.67 (ddd, J = 19.6, 10.8, 4.4 Hz, 1H), 2.46 (dd, J = 14.4, 10.0 Hz, 1H), 2.42-2.34 (m, 1H), 1.78 (dt, J = 12.4, 10.4Hz,

1H), 1.39 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 167.2, 136.6, 134.1, 130.1, 129.5, 128.8, 128.5, 66.4, 61.7, 38.4, 31.8, 28.2, 14.1 ppm; ν_{max}(KBr)/cm^{-1} 3056, 2945, 1771, 1716, 1635, 1543, 1508, 1105; MS (EI) m/z 91, 115, 128, 141, 177, 199, 208, 227, 263, 308; HRMS(EI) calcd for $C_{16}H_{17}NaClO_4$ 331.0708, found 331.0709.



(Z)-allyl 3-chloro-2-((2-oxotetrahydrofuran-3-yl)methyl)-3-phenylacrylate (3c)

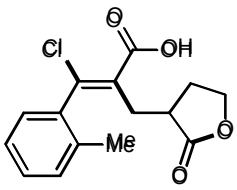
Yield: 71% (56.8 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.43 (m, 5H), 5.74-5.64 (m, 1H), 5.07-5.02 (m, 2H), 4.46-4.42 (m, 1H), 4.10-4.08 (m, 1H), 4.07-4.01 (m, 2H), 3.71 (ddd, J = 10.4, 7.2, 3.6 Hz, 1H), 2.38-2.34 (m, 1H), 2.31-2.28 (m, 2H), 2.19 (dd, J = 16.8, 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 167.1, 142.7, 137.6, 133.6, 130.3, 129.1, 127.5, 125.0, 117.5, 69.2, 63.9, 36.9, 36.8, 32.9 ppm; ν_{max}(KBr)/cm^{-1} 3057, 2948, 1762, 1733, 1637, 1542, 1508, 1102; MS (EI) m/z 115, 128, 141, 185, 207, 219, 249, 284, 320; HRMS(EI) calcd for $C_{17}H_{17}NaClO_4$ 343.0708, found 343.0708.



(Z)-benzyl 3-chloro-2-((2-oxotetrahydrofuran-3-yl)methyl)-3-phenylacrylate (3d)

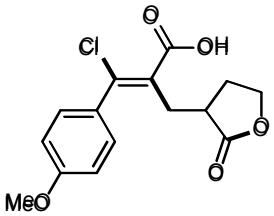
Yield: 76% (70.3 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.45 (m, 2H), 7.43-7.36 (m, 6H), 7.33-7.31 (m, 2H), 5.31 (q, J = 12.0 Hz, 2H), 4.15 (td, J = 8.8, 2.0 Hz, 1H), 4.04-3.96 (m, 1H), 2.92 (dd, J = 14.4, 4.0 Hz, 1H), 2.54 (tdd, J = 10.4, 8.4, 4.0 Hz, 1H), 2.44 (dd, J = 14.4, 10.4 Hz, 1H), 2.29-2.21 (m, 1H), 1.69 (dtd, J = 12.4, 10.4, 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 167.0, 136.6, 135.2, 134.6, 129.8, 129.5, 128.8, 128.7, 128.6, 128.6, 128.4, 67.5, 66.3, 38.3, 31.9, 28.2 ppm; ν_{max}(KBr)/cm^{-1} 3063, 3026, 2938, 1772, 1718, 1636, 1542, 1508, 1457, 1117; MS (EI) m/z 115, 128, 177, 191, 207, 263,

281, 335, 370; HRMS(EI) calcd for $C_{21}H_{19}NaClO_4$ 393.0864, found 393.0865.



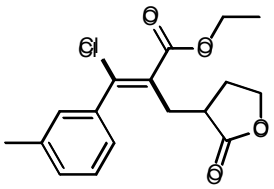
(Z)-3-chloro-2-((2-oxotetrahydrofuran-3-yl)methyl)-3-(o-tolyl)acrylic acid (3e)

Yield: 78% (57.3 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.43-7.36 (m, 3H), 4.55 (td, J = 12.4, 7.2 Hz, 1H), 4.25-4.20 (m, 1H), 3.16 (dd, J = 16.4, 7.2 Hz, 1H), 2.76 (dd, J = 16.4, 6.8Hz, 1H), 2.03 (s, 3H), 2.01-1.93 (m, 2H), 1.46-1.37 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 166.6, 139.3, 138.4, 134.7, 130.4, 129.9, 128.2, 126.2, 123.3, 73.1, 60.2, 36.9, 34.9, 20.8 ppm; ν_{max}(KBr)/cm^{-1} 3028, 2946, 1700, 1608, 1501, 1458, 1108; MS (EI) m/z 114, 149, 177, 189, 233, 268, 294; HRMS(EI) calcd for $C_{15}H_{14}ClO_4$[M-H] 293.0586, found 293.0583.



(Z)-3-chloro-3-(4-methoxyphenyl)-2-((2-oxotetrahydrofuran-3-yl)methyl)acrylic acid (3f)

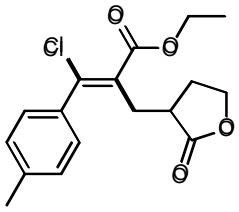
Yield: 71% (55.0 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 8.4 Hz, 2H), 4.79-4.72 (m, 1H), 4.91-4.86 (m, 2H), 3.84(s, 3H), 3.38 (dd, J = 17.6, 7.6 Hz, 1H), 2.89 (dd, J = 17.6, 6.4 Hz, 1H), 2.01-1.96 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 161.2, 146.3, 131.0, 130.0, 127.3, 122.3, 113.2, 73.7, 59.0, 55.3, 39.0, 37.4 ppm; ν_{max}(KBr)/cm^{-1} 3030, 2948, 1758, 1713, 1615, 1524, 1500, 1108; MS (EI) m/z 113, 145, 177, 191, 207, 237, 267, 281, 310; HRMS(EI) calcd for $C_{15}H_{14}ClO_5$[M-H] 309.0535, found 309.0528.



(Z)-ethyl 3-chloro-2-((2-oxotetrahydrofuran-3-yl)methyl)-3-(m-tolyl)acrylate

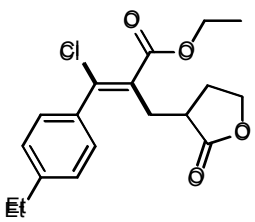
(3g)

Yield: 76% (61.2 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, J = 7.6 Hz, 1H), 7.20 (d, J = 7.6 Hz, 1H), 7.14-7.16 (m, 2H), 4.38-4.30 (m, 2H), 4.23 (td, J = 8.8, 2.0 Hz, 1H), 4.16-4.09 (m, 1H), 2.92 (dd, J = 14.4, 4.4 Hz, 1H), 2.66 (ddt, J = 14.8, 12.8, 4.4 Hz, 1H), 2.46 (dd, J = 14.4, 10.4 Hz, 1H), 2.40-2.35 (m, 4H), 1.79 (dtd, J = 12.4, 10.4, 8.8 Hz, 1H), 1.38 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8, 167.3, 138.7, 136.6, 134.2, 130.2, 129.9, 129.0, 128.7, 125.5, 66.4, 61.7, 38.5, 31.8, 28.1, 21.4, 14.2 ppm; ν_{max}(KBr)/cm^{-1} 3056, 2981, 1771, 1723, 1635, 1456, 1400, 1384, 1120; MS (EI) m/z 115, 129, 141, 163, 195, 220, 241, 277, 287, 322; HRMS(EI) calcd for $C_{17}H_{19}NaClO_4$ 345.0864, found 345.0864.



(Z)-ethyl 3-chloro-2-((2-oxotetrahydrofuran-3-yl)methyl)-3-(p-tolyl)acrylate (3h)

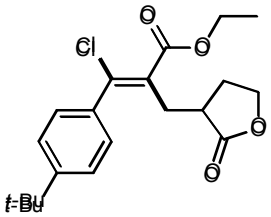
Yield: 81% (65.1 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.19 (m, 4H), 4.38-4.30 (m, 2H), 4.22 (td, J = 8.8, 2.0 Hz, 1H), 4.15-4.08 (m, 1H), 2.92 (dd, J = 14.4, 4.4 Hz, 1H), 2.71-2.61 (m, 1H), 2.47 (dd, J = 14.4, 10.0 Hz, 1H), 2.41-2.32 (m, 4H), 1.79 (dtd, J = 12.4, 10.4, 8.8 Hz, 1H), 1.38 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8, 167.4, 139.6, 134.4, 133.7, 129.8, 129.4, 128.4, 66.4, 61.7, 38.5, 31.8, 28.1, 21.3, 14.1 ppm; ν_{max}(KBr)/cm^{-1} 3056, 2946, 1772, 1716, 1635, 1541, 1507, 1106; MS (EI) m/z 115, 129, 141, 163, 191, 222, 241, 277, 287, 322; HRMS(EI) calcd for $C_{17}H_{19}NaClO_4$ 345.0864, found 345.0871.



(Z)-ethyl 3-chloro-3-(4-ethylphenyl)-2-((2-oxotetrahydrofuran-3-yl)methyl)acrylate (3i)

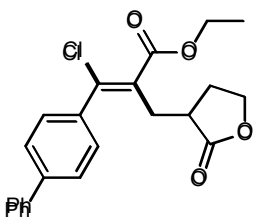
Yield: 83% (69.7 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ

7.24-7.22 (m, 4H), 4.38-4.30 (m, 2H), 4.23 (td, *J* = 8.8, 2.0 Hz, 1H), 4.15-4.08 (m, 1H), 2.93 (dd, *J* = 14.4, 4.4 Hz, 1H), 2.70-2.65 (m, 3H), 2.50-2.43 (m, 1H), 2.38 (dd, *J* = 14.4, 10.0 Hz, 1H), 1.79 (dtd, *J* = 12.4, 10.4, 8.8 Hz, 1H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.26 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8, 167.4, 145.8, 134.4, 133.9, 129.7, 128.5, 128.2, 66.4, 61.7, 38.5, 31.8, 28.7, 28.1, 15.2, 14.1 ppm; ν_{max}(KBr)/cm^{-1} 3057, 2967, 1772, 1719, 1637, 1450, 1021; MS (EI) m/z 115, 133, 153, 177, 236, 254, 301, 336; HRMS(EI) calcd for $C_{18}H_{21}NaClO_4$ 359.1021, found 359.1028.



(Z)-ethyl 3-(4-(tert-butyl)phenyl)-3-chloro-2-((2-oxotetrahydrofuran-3-yl)methyl)acrylate (3j)

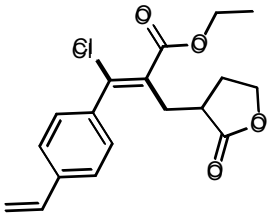
Yield: 79% (71.9 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 3.2 Hz, 2H), 4.38-4.30 (m, 2H), 4.23 (td, *J* = 8.8, 2.0 Hz, 1H), 4.15-4.09 (m, 1H), 2.94 (dd, *J* = 14.4, 4.4 Hz, 1H), 2.72-2.63 (m, 1H), 2.48 (dd, *J* = 14.4, 10.4 Hz, 1H), 2.43-2.35 (m, 1H), 1.81 (dtd, *J* = 12.4, 10.4, 8.8 Hz, 1H), 1.38 (t, *J* = 7.6 Hz, 3H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8, 167.4, 152.7, 134.3, 133.6, 129.7, 128.2, 125.7, 66.4, 61.7, 38.5, 34.8, 31.7, 31.2(3C), 28.1, 14.2 ppm; ν_{max}(KBr)/cm^{-1} 3055, 2959, 1771, 1723, 1634, 1505, 1458, 1384, 1105; MS (EI) m/z 115, 141, 153, 195, 217, 247, 262, 282, 303, 329, 349, 364; HRMS(EI) calcd for $C_{20}H_{25}NaClO_4$ 387.1334, found 387.1332.



(Z)-ethyl 3-([1,1'-biphenyl]-4-yl)-3-chloro-2-((2-oxotetrahydrofuran-3-yl)methyl)acrylate (3k)

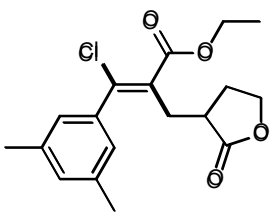
Yield: 74% (71.0 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ

7.64-7.60 (m, 4H), 7.48-7.37 (m, 5H), 4.40-4.32 (m, 2H), 4.25 (td, *J* = 8.8, 2.0 Hz, 1H), 4.17-4.09 (m, 1H), 2.98 (dd, *J* = 14.4, 4.4 Hz, 1H), 2.75-2.66 (m, 1H), 2.53 (dd, *J* = 14.4, 10.4 Hz, 1H), 2.46-2.36 (m, 1H), 1.79 (dtd, *J* = 12.4, 10.4, 8.8 Hz, 1H), 1.40 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 167.3, 142.4, 140.0, 135.4, 133.9, 130.2, 129.0, 128.9, 127.9, 127.4, 127.2, 66.4, 61.7, 38.5, 31.9, 28.2, 14.1 ppm; ν_{max}(KBr)/cm^{-1} 3060, 2927, 1753, 1637, 1500, 1450, 1104, 620; MS (EI) m/z 105, 133, 177, 191, 207, 253, 281, 302, 327, 361, 384; HRMS(EI) calcd for $C_{22}H_{21}NaClO_4$ 407.1021, found 407.1017.



(Z)-ethyl 3-chloro-2-((2-oxotetrahydrofuran-3-yl)methyl)-3-(4-vinylphenyl)acrylate (3l)

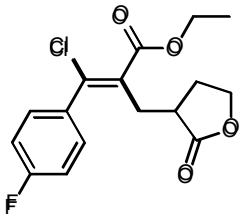
Yield: 68% (56.8 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 6.72 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.81 (d, *J* = 17.6 Hz, 1H), 5.34 (d, *J* = 10.8 Hz, 1H), 4.39-4.30 (m, 2H), 4.23 (td, *J* = 8.8, 2.0 Hz, 1H), 4.15-4.08 (m, 1H), 2.94 (dd, *J* = 14.4, 4.4 Hz, 1H), 2.72-2.62 (m, 1H), 2.48 (dd, *J* = 14.4, 10.0 Hz, 1H), 2.42-2.34 (m, 1H), 1.81 (dtd, *J* = 12.4, 10.4, 8.8 Hz, 1H), 1.39 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 167.3, 138.7, 135.8, 135.8, 133.9, 130.1, 128.8, 126.5, 115.6, 66.4, 61.7, 38.5, 31.9, 28.2, 14.1 ppm; ν_{max}(KBr)/cm^{-1} 3055, 2930, 1771, 1724, 1635, 1507, 1456, 1032; MS (EI) m/z 115, 131, 165, 207, 232, 252, 262, 289, 334; HRMS(EI) calcd for $C_{18}H_{19}NaClO_4$ 357.0864, found 357.0870.



(Z)-ethyl 3-chloro-3-(3,5-dimethylphenyl)-2-((2-oxotetrahydrofuran-3-yl)methyl)acrylate (3m)

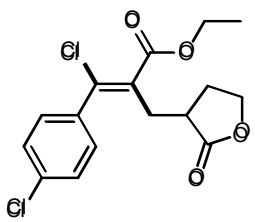
Yield: 70% (58.8 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ

7.01 (s, 1H), 6.94 (s, 1H), 4.37-4.30 (m, 2H), 4.23 (td, J = 8.8, 2.0 Hz, 1H), 4.13 (td, J = 9.6, 6.4 Hz, 1H), 2.91 (dd, J = 14.4, 4.4 Hz, 1H), 2.71-2.63 (m, 1H), 2.46 (dd, J = 14.4, 10.4 Hz, 1H), 2.40-2.30 (m, 8H), 1.80 (dt, J = 21.2, 10.4Hz, 1H), 1.38 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8, 167.3, 138.5, 136.5, 134.5, 131.1, 129.7, 126.1, 66.4, 61.6, 38.5, 31.9, 28.1, 21.3, 14.1 ppm; ν_{max}(KBr)/cm^{-1} 3054, 2949, 1774, 1711, 1637, 1543, 1500, 1438; MS (EI) m/z 115, 128, 142, 153, 177, 209, 234, 255, 291, 336; HRMS(EI) calcd for $C_{18}H_{21}NaClO_4$ 359.1021, found 359.1029.



(Z)-ethyl 3-chloro-3-(4-fluorophenyl)-2-((2-oxotetrahydrofuran-3-yl)methyl)acrylate (3n)

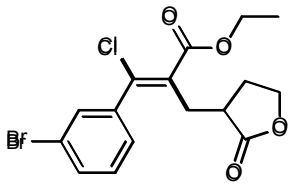
Yield: 77% (62.7 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.32 (m, 2H), 7.13-7.09 (m, 2H), 4.38-4.31 (m, 2H), 4.25 (td, J = 8.8, 2.0 Hz, 1H), 4.16-4.10 (m, 1H), 2.90 (dd, J = 14.4, 4.4 Hz, 1H), 2.71-2.62 (m, 1H), 2.49-2.35 (m, 2H), 1.78 (dt, J = 19.6, 10.8Hz, 1H), 1.39 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 167.1, 163.0 (J = 248.2 Hz), 133.0, 132.7 (J = 3.6 Hz), 130.6 (J = 8.4 Hz), 130.5, 116.0 (J = 21.8 Hz), 66.3, 61.8, 38.4, 31.9, 28.3, 14.1 ppm; ν_{max}(KBr)/cm^{-1} 3054, 2941, 1772, 1717, 1636, 1541, 1507, 1104; MS (EI) m/z 105,148, 162, 186, 204, 216, 253, 281, 308, 326; HRMS(EI) calcd for $C_{16}H_{16}ClFNaO_4$ 349.0613, found 349.0614.



(Z)-ethyl 3-chloro-3-(4-chlorophenyl)-2-((2-oxotetrahydrofuran-3-yl)methyl)acrylate (3o)

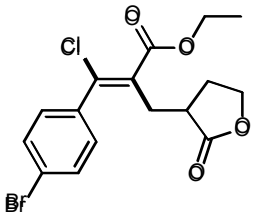
Yield: 75% (64.1 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40

(d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 4.39-4.31 (m, 2H), 4.25 (td, J = 8.8, 2.0 Hz, 1H), 4.16-4.10 (m, 1H), 2.90 (dd, J = 14.4, 4.4 Hz, 1H), 2.71-2.62 (m, 1H), 2.47-2.34 (m, 2H), 1.78 (dt, J = 19.6, 10.8Hz, 1H), 1.38 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 167.0, 135.6, 135.0, 132.8, 130.8, 129.9, 129.1, 66.3, 61.8, 38.4, 31.9, 28.3, 14.1 ppm; ν_{max}(KBr)/cm^{-1} 3060, 2925, 1772, 1718, 1636, 1541, 1508, 1103; MS (EI) m/z 115,125, 139, 151, 177, 205, 215, 240,242, 270, 299, 342; HRMS(EI) calcd for $C_{16}H_{16}Cl_2NaO_4$ 365.0318, found 365.0314.



(Z)-ethyl 3-(3-bromophenyl)-3-chloro-2-((2-oxotetrahydrofuran-3-yl)methyl)acrylate (3p)

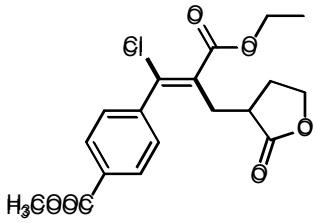
Yield: 64% (61.8 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.30 (m, 2H), 7.13-7.09 (m, 2H), 4.39-4.30 (m, 2H), 4.25 (td, J = 8.8, 2.0 Hz, 1H), 4.16-4.09 (m, 1H), 2.90 (dd, J = 14.4, 4.4 Hz, 1H), 2.71-2.62 (m, 1H), 2.48-2.42 (m, 1H), 2.41-2.35 (m, 1H), 1.78 (dt, J = 19.6, 10.8Hz, 1H), 1.38 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 167.3, 138.6, 136.5, 134.2, 130.2, 129.8, 128.9, 128.6, 125.5, 66.4, 61.5, 38.4, 31.8, 28.1, 14.1 ppm; ν_{max}(KBr)/cm^{-1} 3060, 2983, 1771, 1725, 1634, 1600, 1508, 1455, 1157; MS (EI) m/z 109,123, 146, 159, 195, 224, 244, 263, 291, 327, 357, 386; HRMS(EI) calcd for $C_{16}H_{16}BrClNaO_4$ 408.9813, found 408.9808.



(Z)-ethyl 3-(4-bromophenyl)-3-chloro-2-((2-oxotetrahydrofuran-3-yl)methyl)ac rylate (3q)

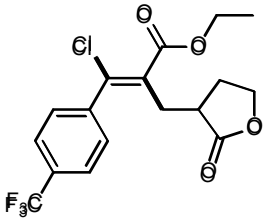
Yield: 71% (68.5 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 4.39-4.30 (m, 2H), 4.26 (td,

J = 8.8, 2.0 Hz, 1H), 4.16-4.10 (m, 1H), 2.90 (dd, *J* = 14.4, 4.4 Hz, 1H), 2.71-2.62 (m, 1H), 2.47-2.34 (m, 2H), 1.78 (dt, *J* = 21.2, 10.8Hz, 1H), 1.37 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.4, 167.0, 135.5, 132.8, 132.1, 130.7, 130.2, 123.8, 66.3, 61.8, 38.4, 31.9, 28.3, 14.1 ppm; ν_{max}(KBr)/cm^{-1} 3058, 2923, 1772, 1719, 1637, 1542, 1508, 1457, 1122; MS (EI) m/z 115,149, 183, 222, 257, 284, 288, 314, 351, 375, 386; HRMS(EI) calcd for $C_{16}H_{16}BrClNaO_4$ 408.9813, found 408.9805.



(Z)-methyl 4-(1-chloro-3-ethoxy-3-oxo-2-((2-oxotetrahydrofuran-3-yl)methyl)prop-1-en-1-yl)benzoate (3r)

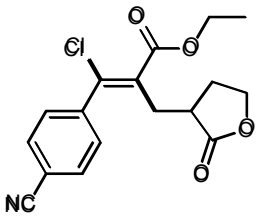
Yield: 81% (74.1 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 4.40-4.31 (m, 2H), 4.23 (td, *J* = 8.8, 2.0 Hz, 1H), 4.15-4.09 (m, 1H), 3.94 (s, 3H), 2.90 (dd, *J* = 14.4, 4.4 Hz, 1H), 2.71-2.62 (m, 1H), 2.46-2.36 (m, 2H), 1.75 (dt, *J* = 21.2, 10.8Hz, 1H), 1.39 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.4, 166.9, 166.2, 140.9, 132.8, 131.0, 131.0, 130.1, 128.6, 66.3, 62.0, 52.4, 38.4, 32.0, 28.2, 14.1 ppm; ν_{max}(KBr)/cm^{-1} 3061, 2956, 1770, 1723, 1638, 1434, 1104, 619; MS (EI) m/z 115, 128, 149, 163, 177, 207, 264, 285, 335, 337, 366; HRMS(EI) calcd for $C_{18}H_{19}ClNaO_6$ 389.0762, found 389.0768.



(Z)-ethyl 3-chloro-2-((2-oxotetrahydrofuran-3-yl)methyl)-3-(4-(trifluoromethyl)phenyl)acrylate (3s)

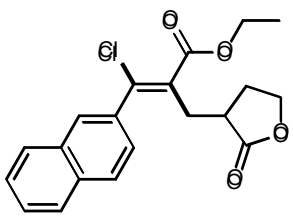
Yield: 84% (78.9 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 4.40-4.32 (m, 2H),

4.26 (td, J = 8.8, 2.0 Hz, 1H), 4.17-4.10 (m, 1H), 2.90 (dd, J = 14.4, 4.8 Hz, 1H), 2.72-2.63 (m, 1H), 2.46-2.36 (m, 2H), 1.78 (dt, J = 21.2, 10.8Hz, 1H), 1.40 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.4, 166.8, 140.1 (q, J = 1.4 Hz), 132.2, 131.4, 129.3 (q, J = 32.0 Hz), 129.1, 125.9 (q, J = 3.7), 124.4 (q, J = 268.8 Hz), 66.3, 62.0, 38.3, 32.0, 28.3, 14.1 ppm; ν_{max}(KBr)/cm^{-1} 3055, 2924, 1773, 1637, 1504, 1445, 1068; MS (EI) m/z 115, 133, 152, 173, 207, 245, 274, 341, 376; HRMS(EI) calcd for $C_{17}H_{16}ClF_3NaO_4$ 399.0581, found 399.0580.



(Z)-ethyl 3-chloro-3-(4-cyanophenyl)-2-((2-oxotetrahydrofuran-3-yl)methyl)acrylate (3t)

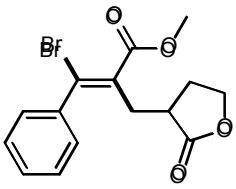
Yield: 78% (64.9 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 4.39-4.33 (m, 2H), 4.27 (td, J = 8.8, 2.0 Hz, 1H), 4.17-4.11 (m, 1H), 2.88 (dd, J = 14.4, 4.8 Hz, 1H), 2.71-2.62 (m, 1H), 2.45-2.35 (m, 2H), 1.78 (dt, J = 21.2, 10.8Hz, 1H), 1.39 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.3, 166.6, 140.9, 132.6, 131.8, 131.6, 129.4, 117.9, 113.4, 66.3, 62.0, 38.3, 32.0, 28.4, 14.1 ppm; ν_{max}(KBr)/cm^{-1} 3058, 2923, 2027, 1771, 1725, 1634, 1445, 1123; MS (EI) m/z 113,130, 153, 180, 202, 231, 252, 287, 298, 333; HRMS(EI) calcd for $C_{17}H_{16}ClNNaO_4$ 356.0660, found 356.0653.



(Z)-ethyl 3-chloro-3-(naphthalen-2-yl)-2-((2-oxotetrahydrofuran-3-yl)methyl)acrylate (3u)

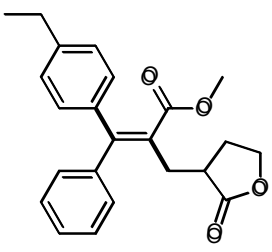
Yield: 71% (63.6 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.84 (m, 4H), 7.59-7.55 (m, 2H), 7.46 (dd, J = 8.4, 1.6 Hz, 1H),

4.43-4.35 (m, 2H), 4.21 (td, J = 8.8, 2.0 Hz, 1H), 4.15-4.09 (m, 1H), 3.01 (dd, J = 14.4, 4.4 Hz, 1H), 2.76-2.68 (m, 1H), 2.56 (dd, J = 14.4, 10.0 Hz, 1H), 2.45-2.38 (m, 1H), 1.80 (dtd, J = 12.4, 10.4, 8.8 Hz, 1H), 1.43 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 167.3, 134.2, 133.8, 133.3, 132.7, 130.4, 128.8, 128.4, 128.2, 127.8, 127.4, 126.9, 125.6, 66.4, 61.8, 38.4, 31.9, 28.2, 14.2 ppm; ν_{max}(KBr)/cm^{-1} 3058, 2966, 1772, 1716, 1635, 1545, 1505, 1102; MS (EI) m/z 125, 139, 152, 179, 215, 231, 249, 265, 298, 341, 358; HRMS(EI) calcd for $C_{20}H_{19}NaClO_4$ 381.0864, found 381.0868.



(Z)-methyl 3-bromo-2-((2-oxotetrahydrofuran-3-yl)methyl)-3-phenylacrylate (6a)

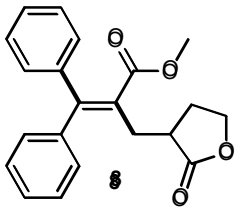
Yield: 81% (71.3 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.39 (m, 3H), 7.34-7.32 (m, 2H), 4.21 (td, J = 8.8, 2.0 Hz, 1H), 4.14-4.09 (m, 1H), 3.87 (s, 3H), 2.91 (dd, J = 14.4, 4.4 Hz, 1H), 2.71-2.61 (m, 1H), 2.47 (dd, J = 14.4, 10.0 Hz, 1H), 2.40-2.32 (m, 1H), 1.78 (dtd, J = 12.4, 10.4, 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 167.7, 136.6, 134.5, 129.8, 129.5, 128.7, 128.4, 66.3, 52.4, 38.4, 31.8, 28.1 ppm; ν_{max}(KBr)/cm^{-1} 3054, 2981, 1772, 1718, 1636, 1445, 1103; MS (EI) m/z 115, 133, 179, 207, 258, 281, 338; HRMS(EI) calcd for $C_{15}H_{15}BrNaO_4$ 361.0046, found 361.0038.



(Z)-methyl 3-(4-ethylphenyl)-2-((2-oxotetrahydrofuran-3-yl)methyl)-3-phenylacrylate (7)

Yield: 70% (63.7 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ

7.37-7.30 (m, 3H), 7.16-7.14 (m, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 4.21 (td, *J* = 8.8, 2.8 Hz, 1H), 4.13 (td, *J* = 9.6, 6.4 Hz, 1H), 3.50 (s, 3H), 2.93 (dd, *J* = 13.6, 4.8 Hz, 1H), 2.89-2.83 (m, 1H), 2.62 (q, *J* = 7.6 Hz, 2H), 2.54 (dd, *J* = 13.6, 10.0 Hz, 1H), 2.38 (tdd, *J* = 11.2, 6.4, 3.3 Hz, 1H), 1.93-1.83 (m, 1H), 1.21 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.3, 170.9, 149.0, 144.0, 140.3, 139.0, 129.0, 128.7, 128.5, 128.3, 127.9, 127.5, 66.4, 51.7, 39.0, 32.1, 28.5, 28.4, 15.2 ppm; ν_{max}(KBr)/cm^{-1} 3040, 2965, 1716, 1635, 1541, 1507, 1104; MS (EI) m/z 115, 128, 152, 165, 191, 219, 247, 276, 286, 304, 332, 364; HRMS(EI) calcd for $C_{23}H_{24}NaO_4$ 387.1567, found 387.1579.

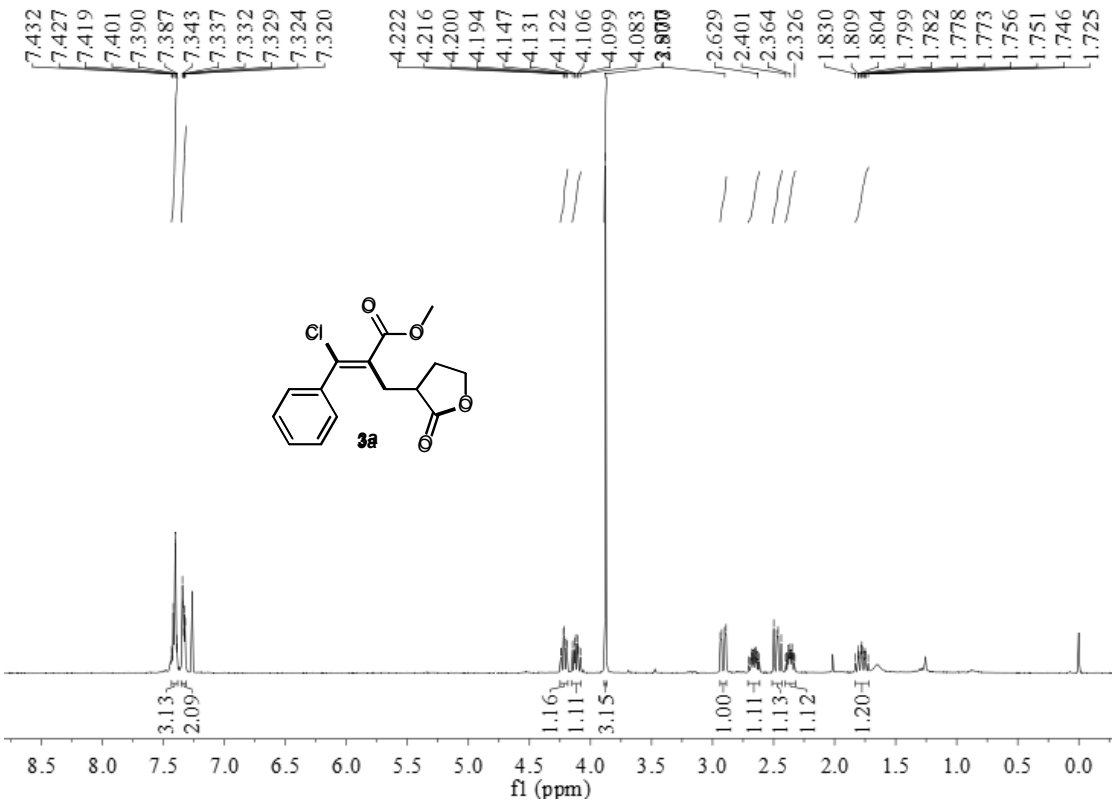


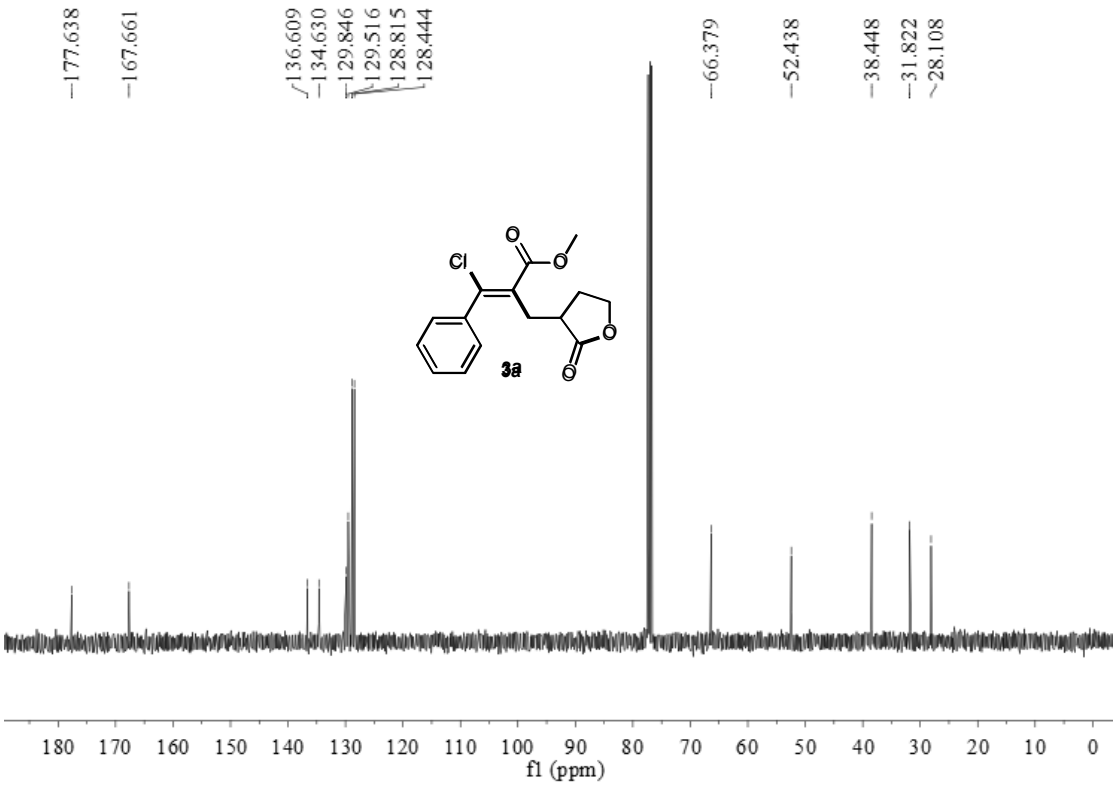
methyl 2-((2-oxotetrahydrofuran-3-yl)methyl)-3,3-diphenylacrylate (8)

Yield: 63% (52.9 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.21 (m, 6H), 7.09-7.05 (m, 4H), 4.15 (td, *J* = 8.8, 2.8 Hz, 1H), 4.08 (dd, *J* = 9.6, 2.4 Hz, 1H), 3.40 (s, 3H), 2.87 (dd, *J* = 13.6, 4.8 Hz, 1H), 2.82-2.76 (m, 1H), 2.50 (dd, *J* = 13.6, 10.0 Hz, 1H), 2.32 (dd, *J* = 14.8, 8.8 Hz, 1H), 1.80 (dd, *J* = 21.6, 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2, 169.7, 148.0, 140.8, 139.1, 128.3, 127.9, 127.6, 127.3, 127.1, 127.0, 126.8, 65.4, 50.7, 37.9, 31.0, 27.4 ppm; ν_{max}(KBr)/cm^{-1} 3043, 2966, 1716, 1630, 1542, 1500, 1110; MS (EI) m/z 115, 129, 152, 165, 191, 219, 248, 276, 286, 304, 336; HRMS(EI) calcd for $C_{21}H_{20}NaO_4$ 359.1254, found 359.1271.

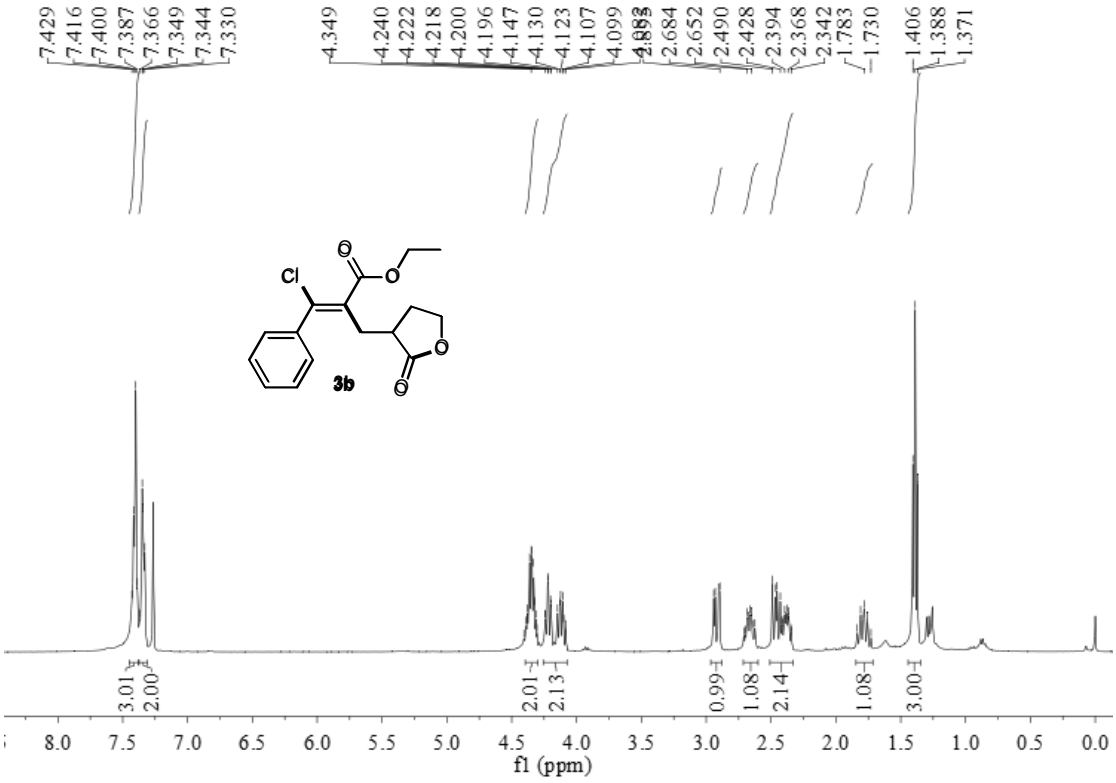
V. ^{1}H and ^{13}C NMR spectra of compounds 3 and 6

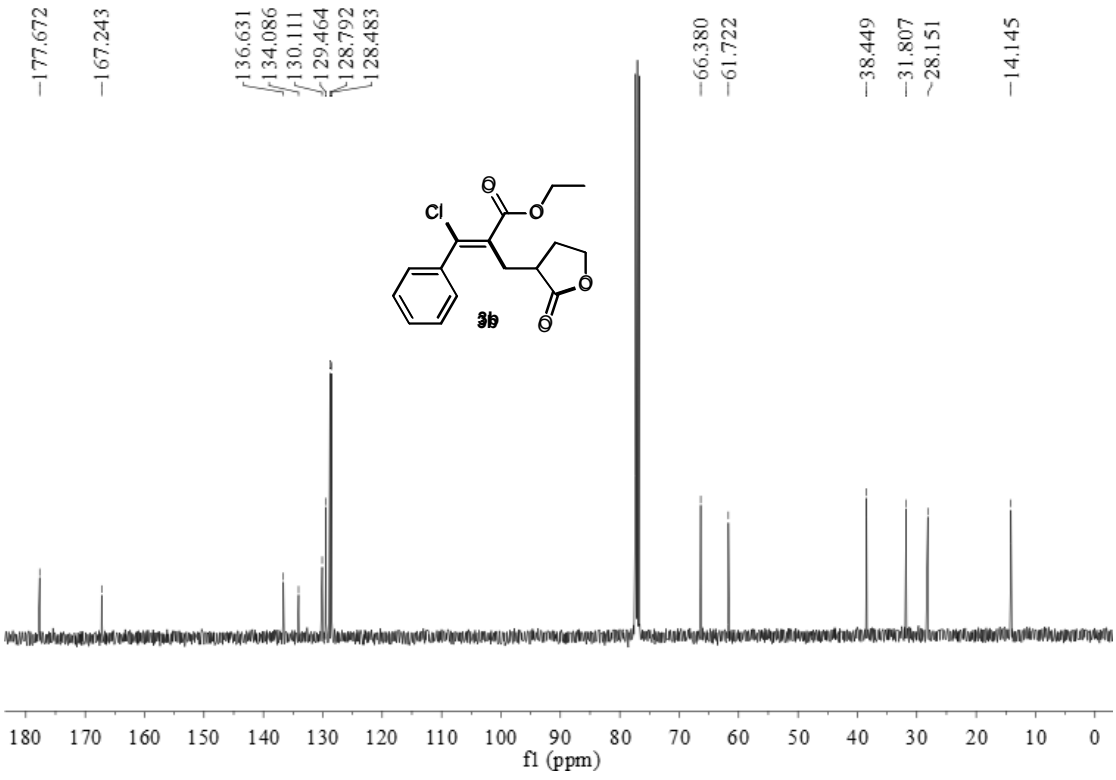
^{1}H NMR and ^{13}C NMR of (Z)-methyl 3-chloro-2-((2-oxotetrahydrofuran-3-yl)methyl)-3-phenylacrylate (3a)



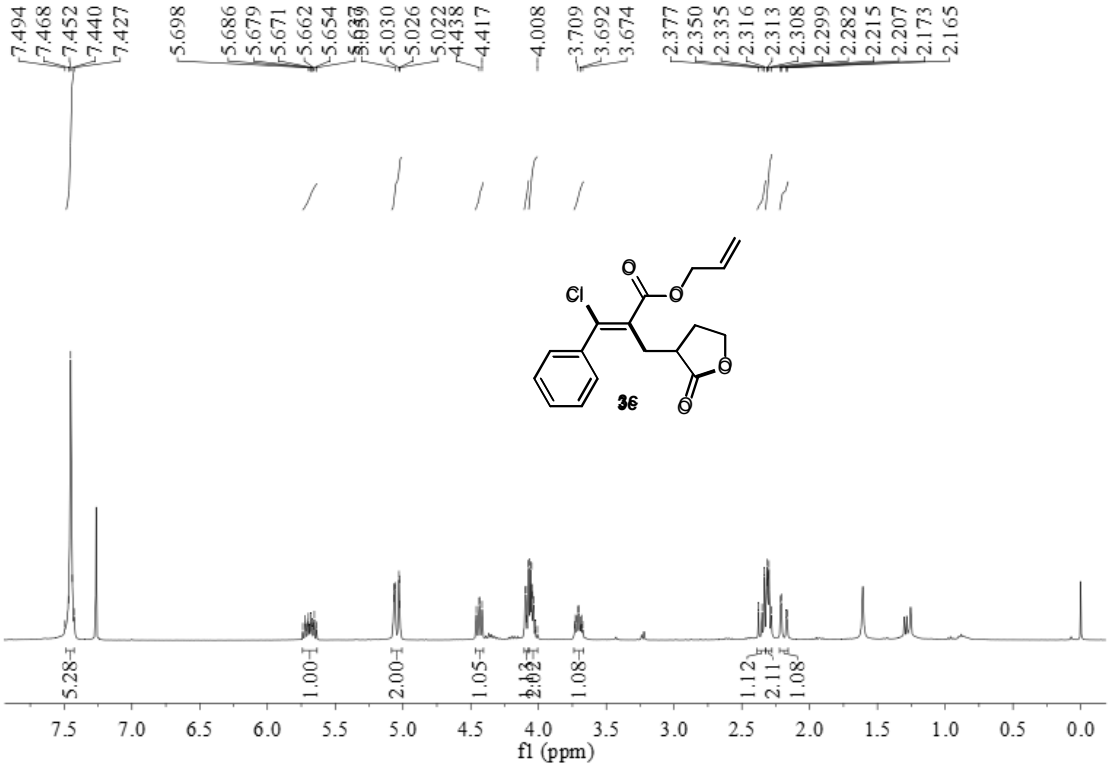


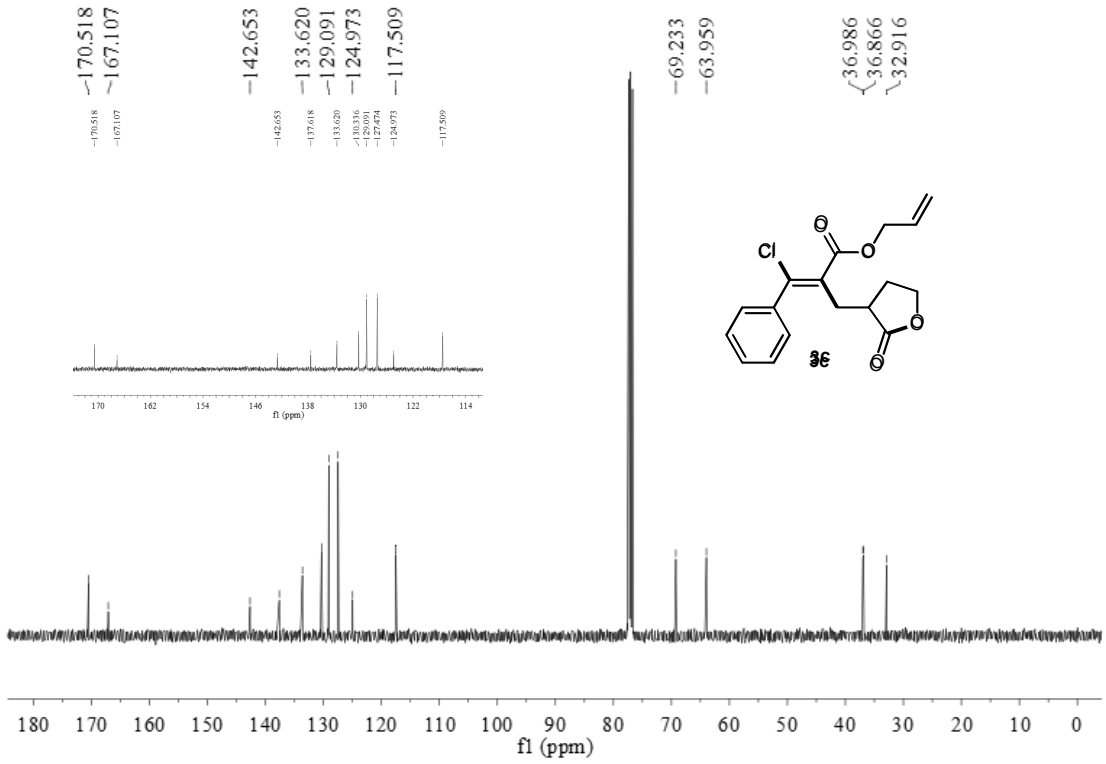
^{1}H NMR and ^{13}C NMR of (Z)-ethyl 3-chloro-2-((2-oxotetrahydrofuran-3-yl)methyl)-3-phenylacrylate (3b)



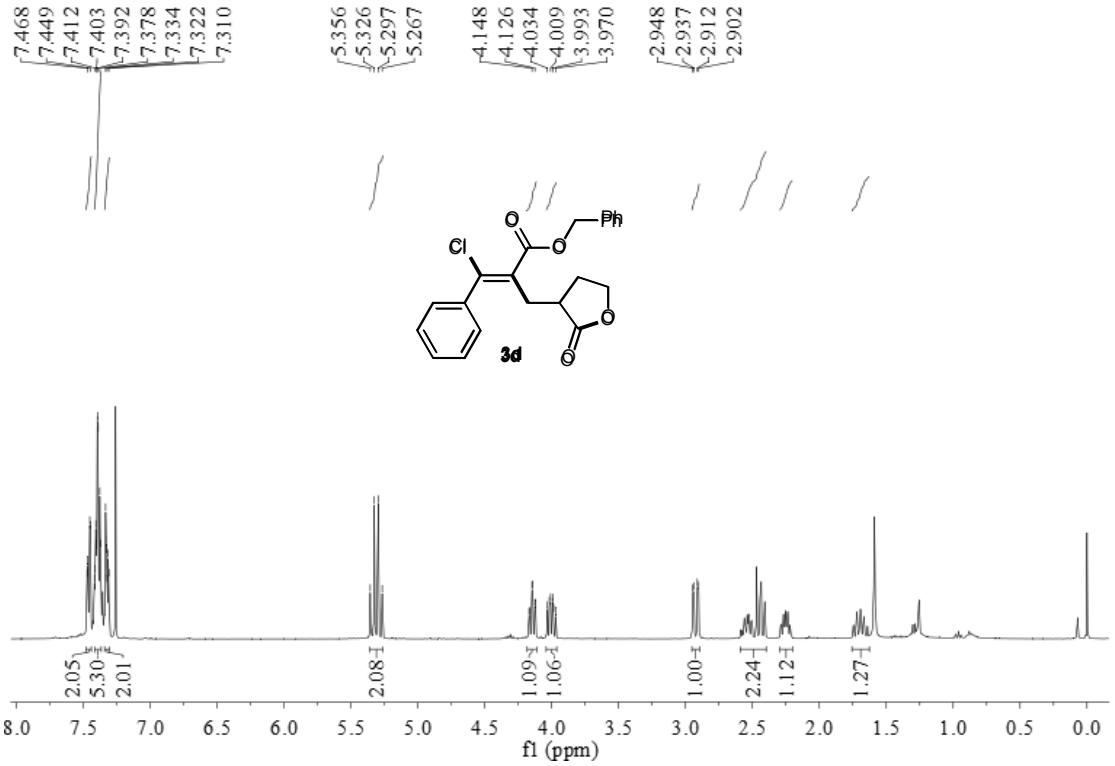


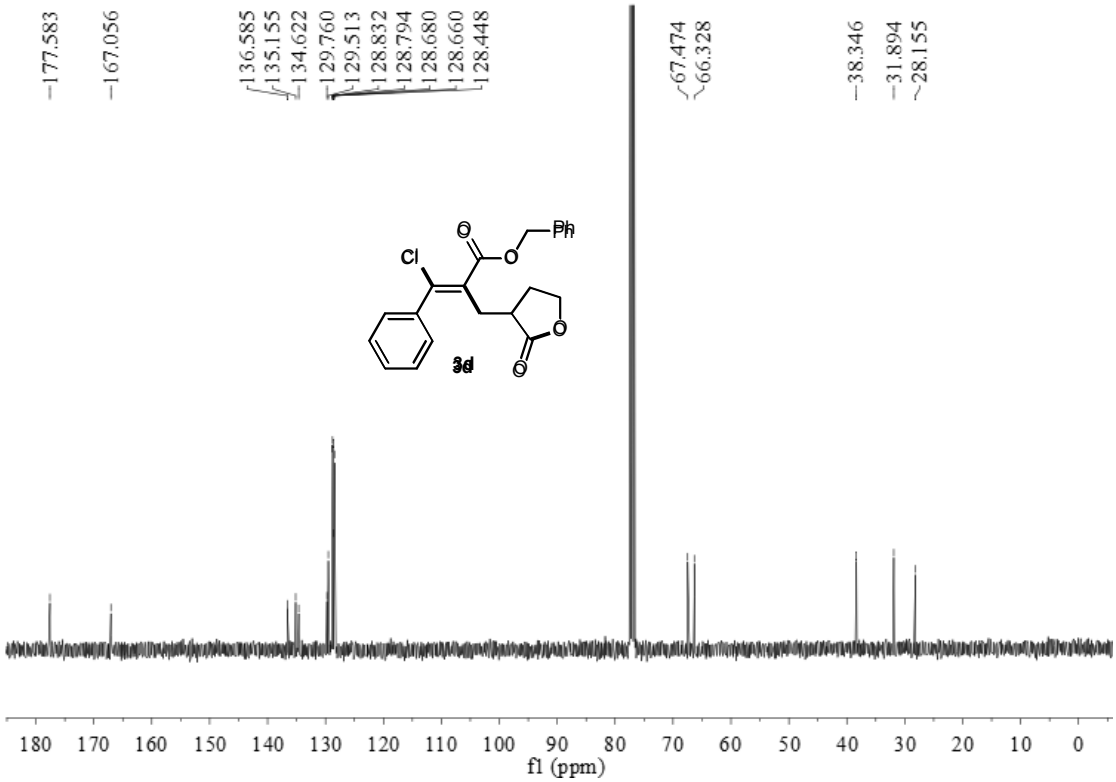
^{1}H NMR and ^{13}C NMR of (Z)-allyl 3-chloro-2-((2-oxotetrahydrofuran-3-yl)methyl)-3-phenylacrylate (3c)



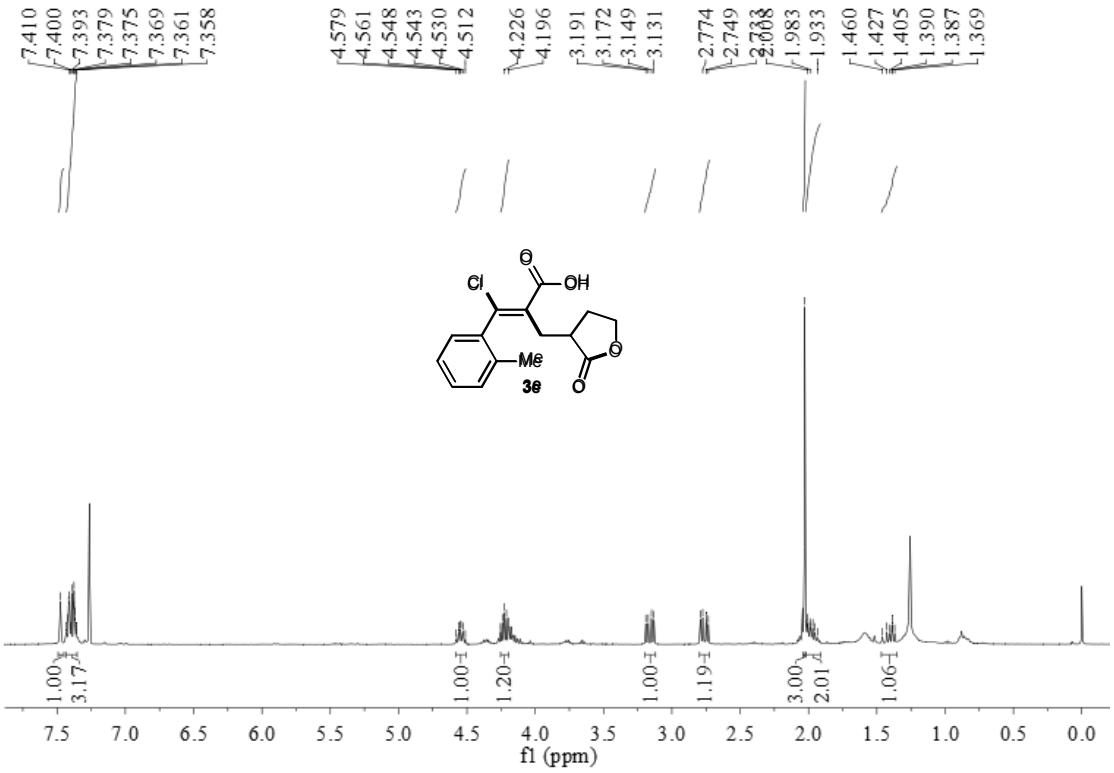


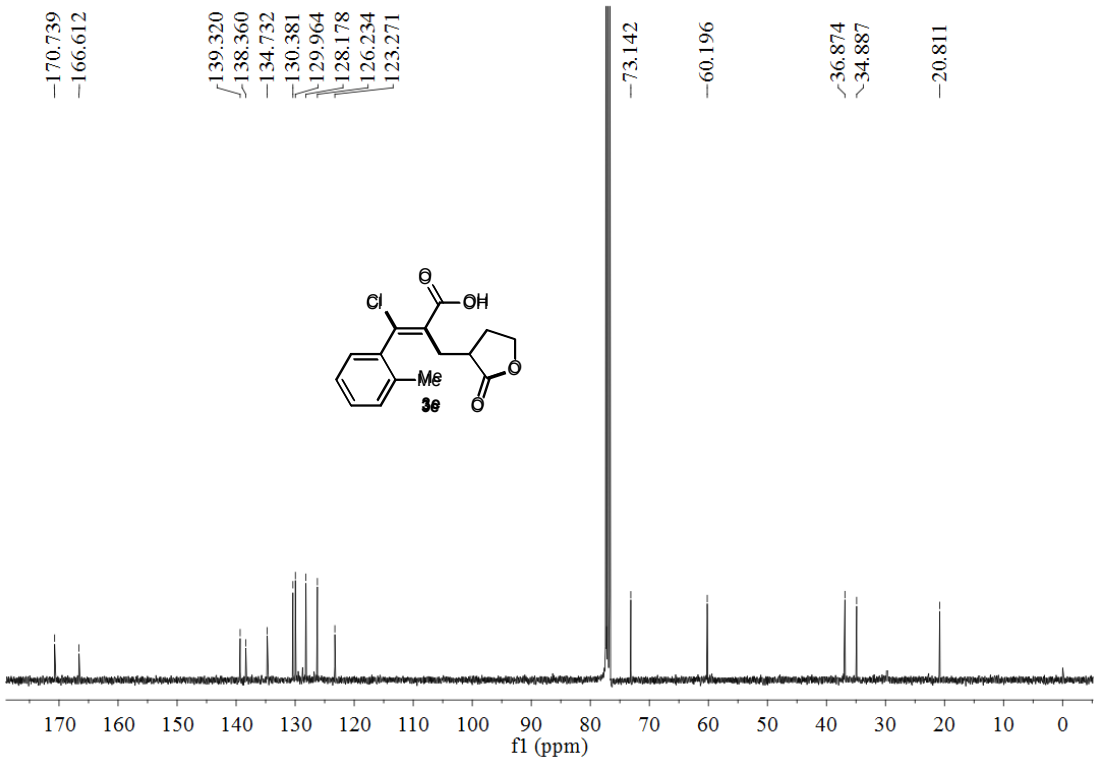
^{1}H NMR and ^{13}C NMR of Z)-benzyl 3-chloro-2-((2-oxotetrahydrofuran-3-yl)methyl)-3-phenylacrylate (3d)



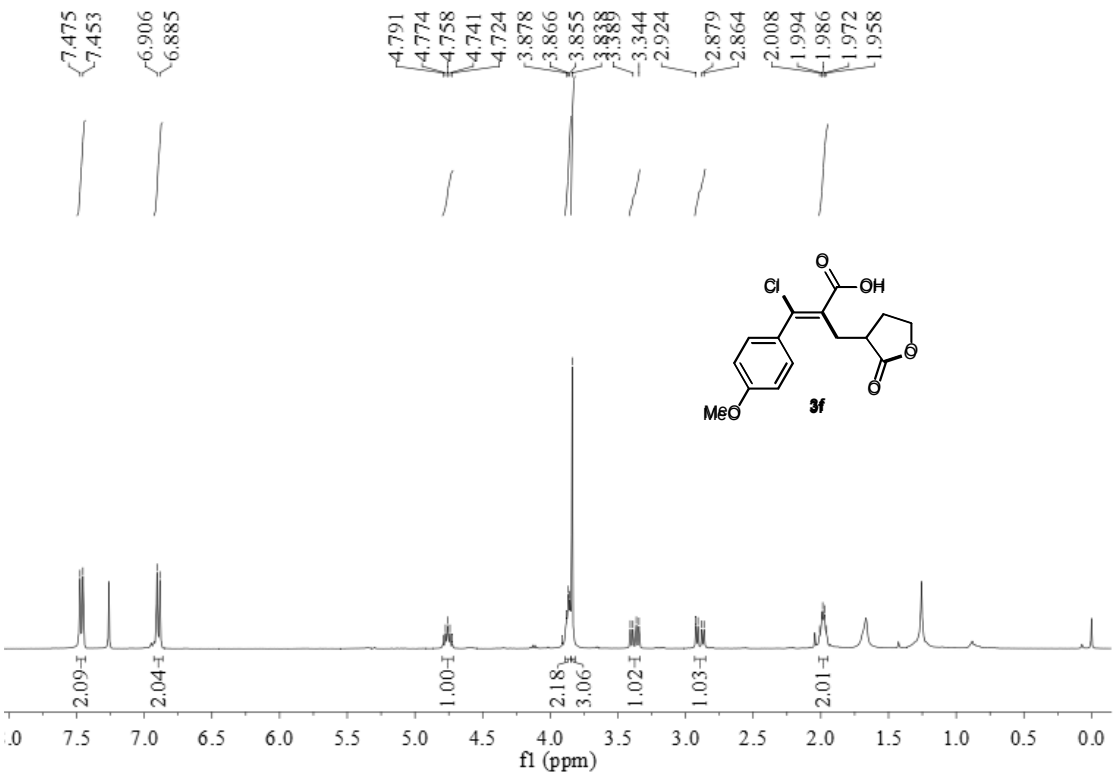


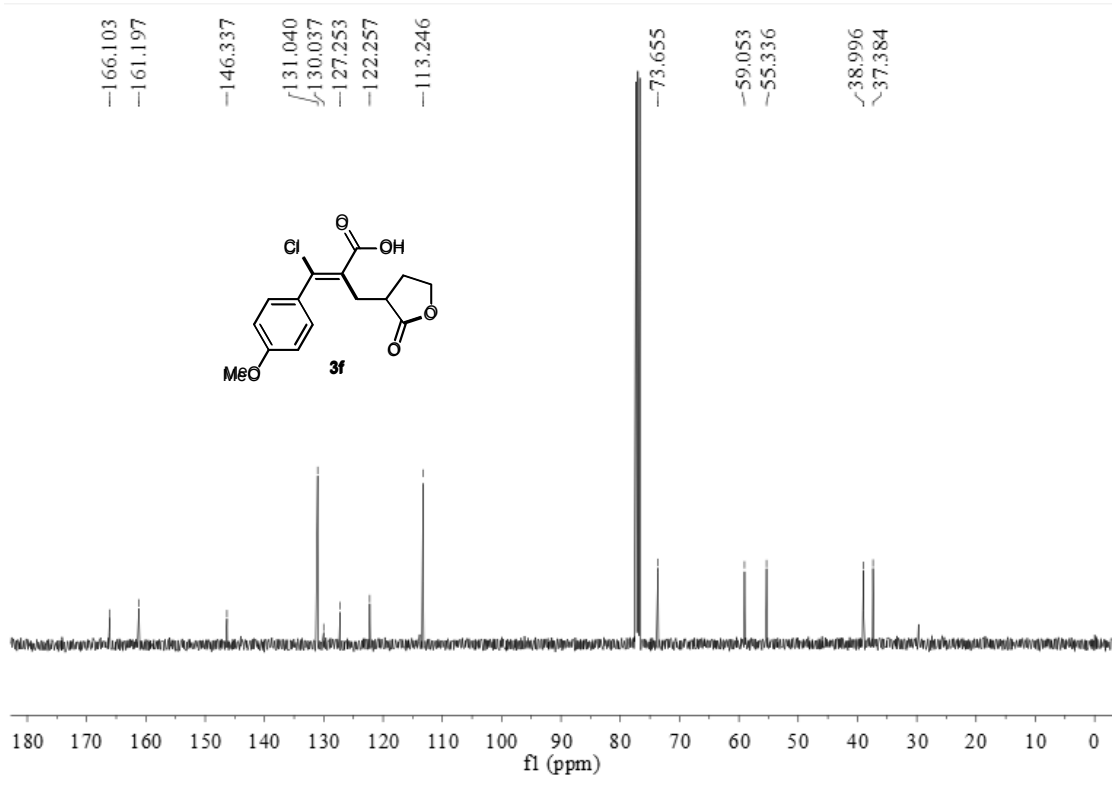
^{1}H NMR and ^{13}C NMR of (Z)-3-chloro-2-((2-oxotetrahydrofuran-3-yl)methyl)-3-(o-tolyl)acrylic acid (3e)



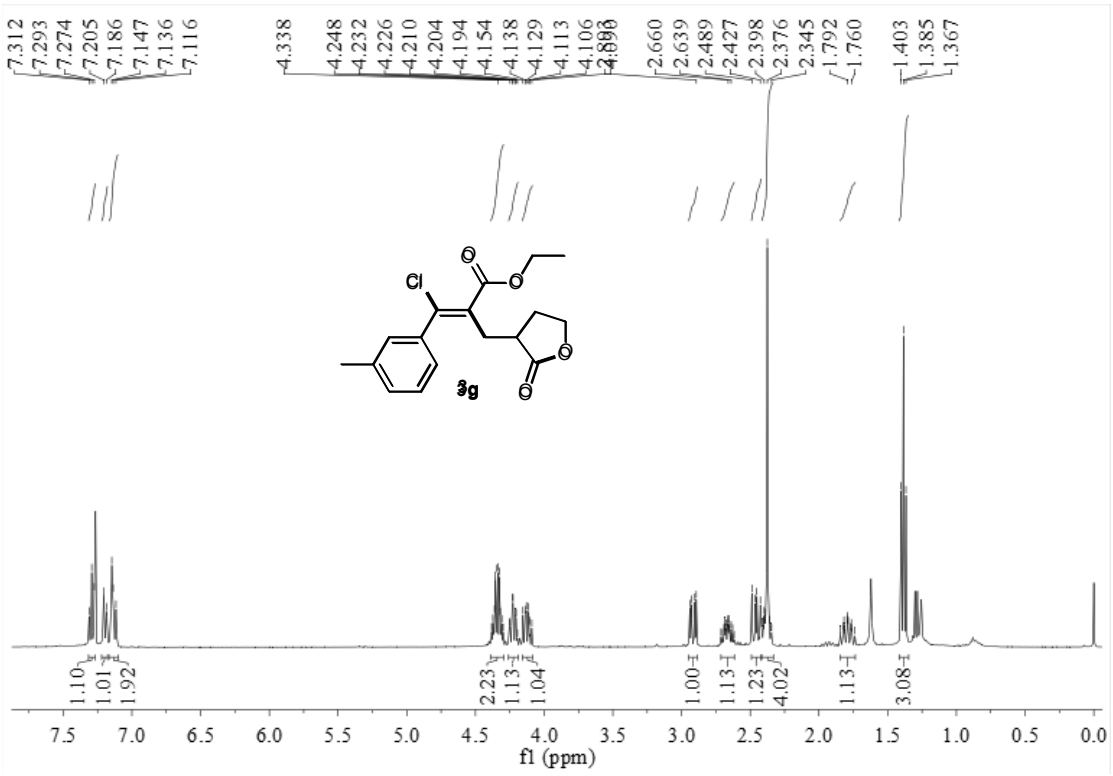


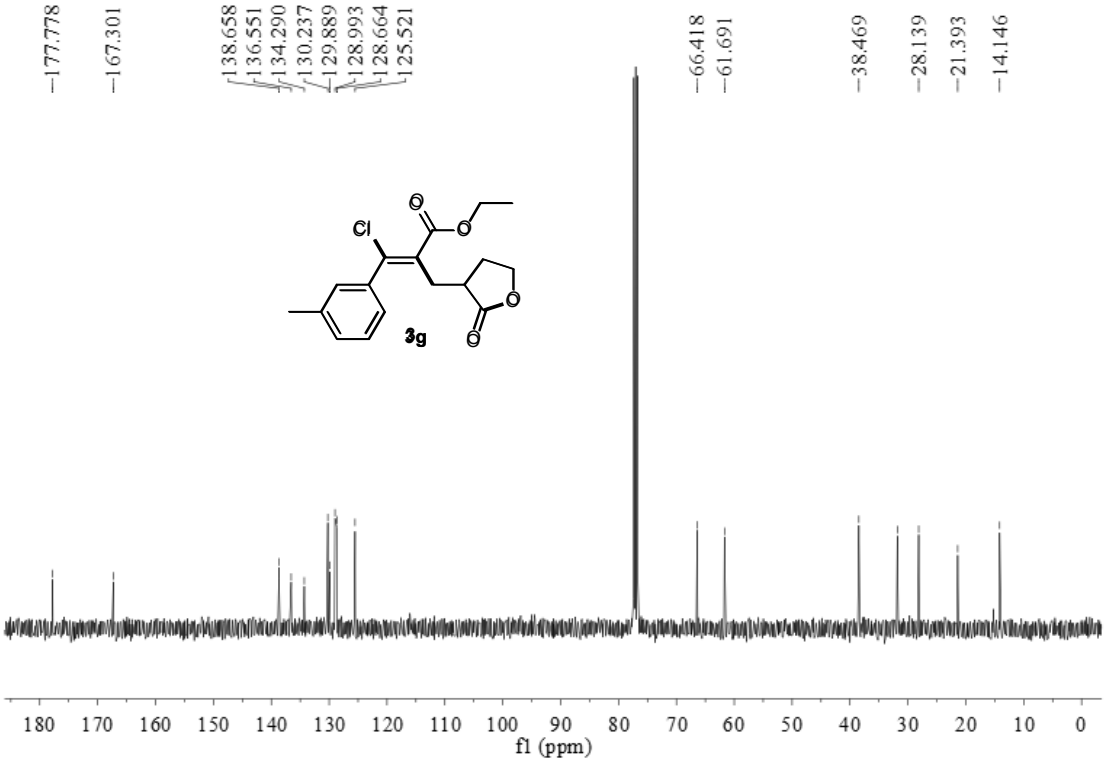
^{1}H NMR and ^{13}C NMR of (Z)-3-chloro-3-(4-methoxyphenyl)-2-((2-oxotetrahydrofuran-3-yl)methyl)acrylic acid (3f)



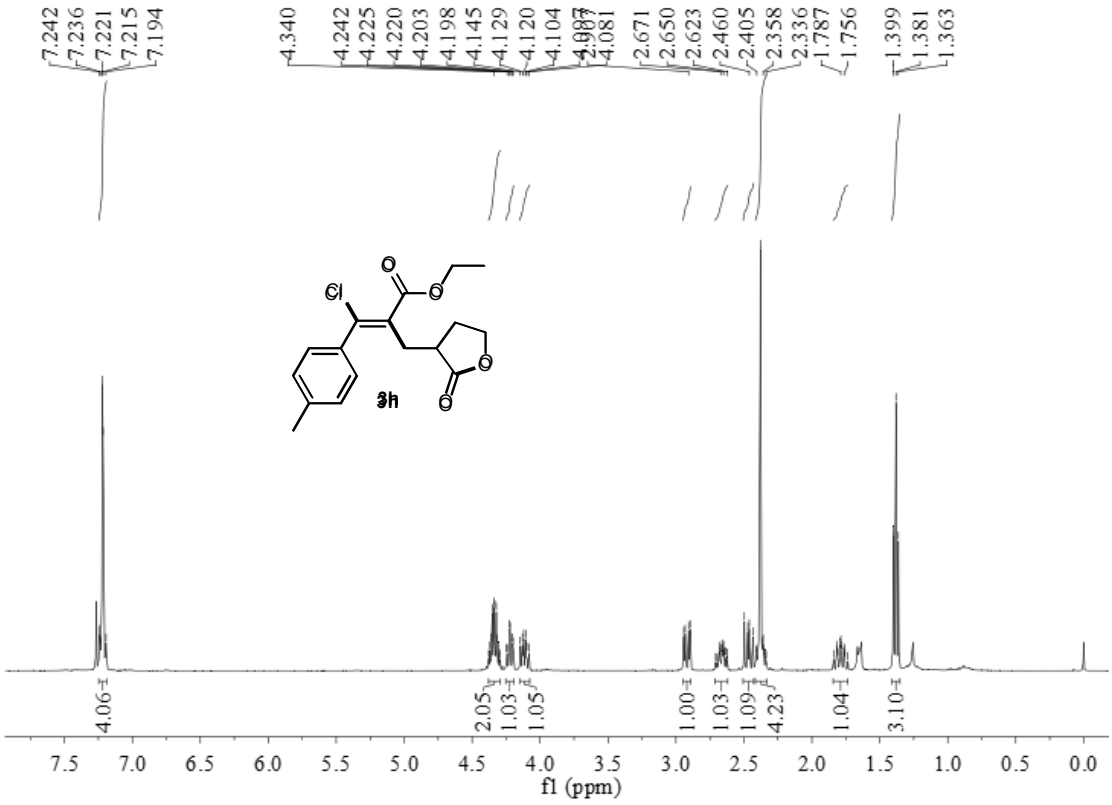


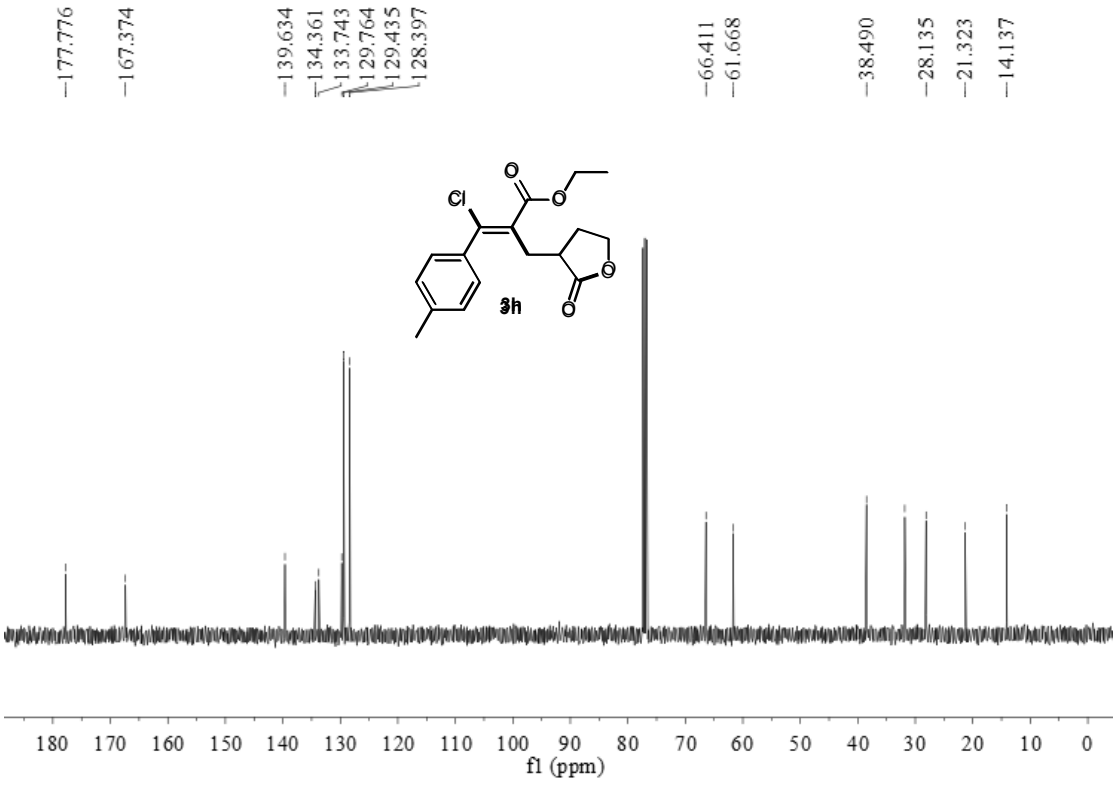
^{1}H NMR and ^{13}C NMR of (Z)-ethyl 3-chloro-2-((2-oxotetrahydrofuran-3-yl)methyl)-3-(m-tolyl)acrylate (3g)



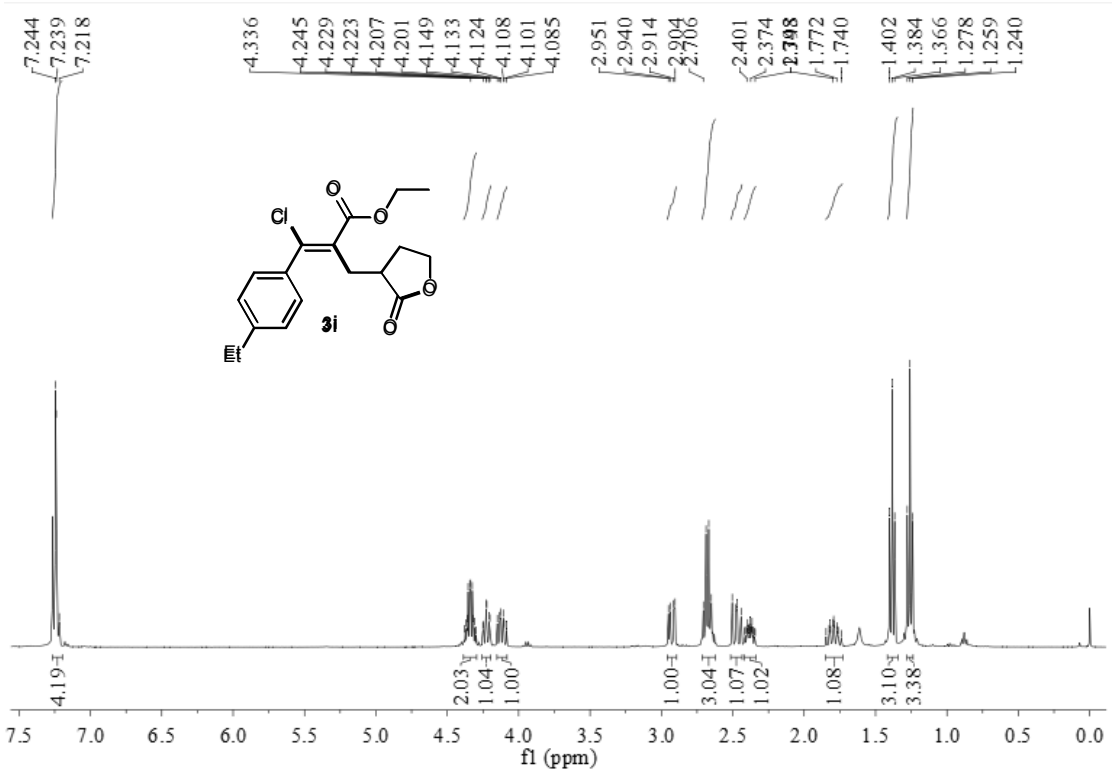


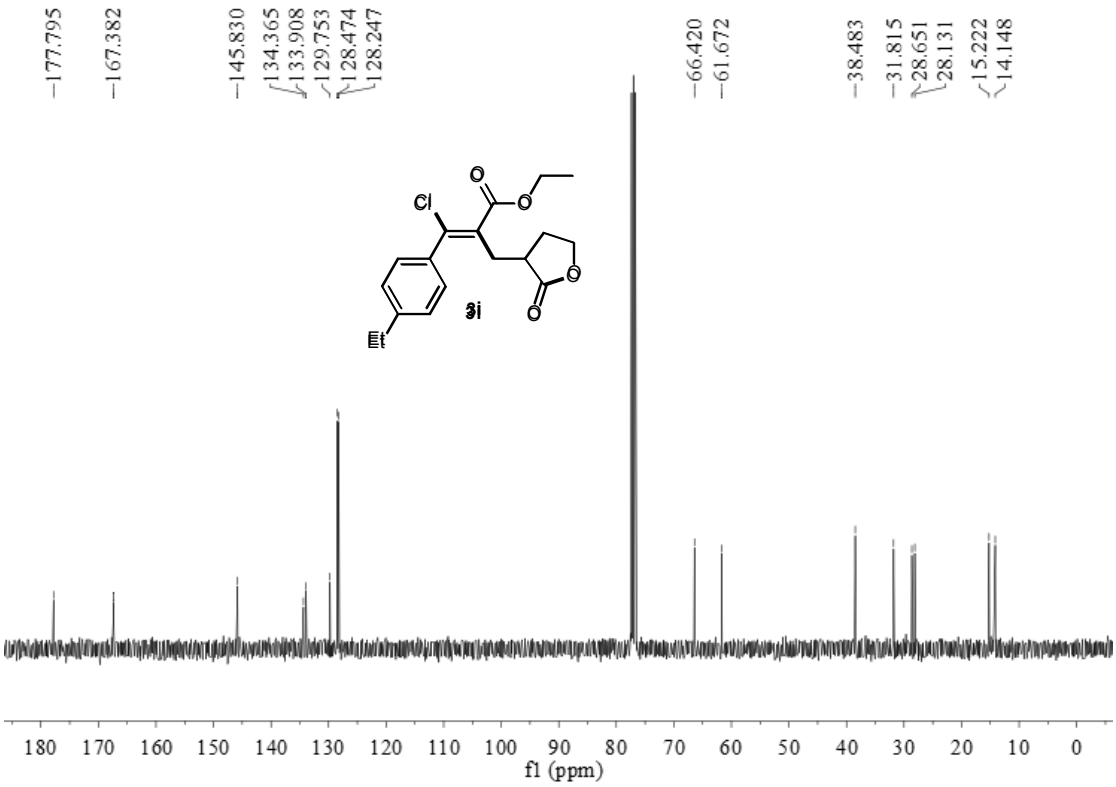
^{1}H NMR and ^{13}C NMR of (Z)-ethyl 3-chloro-2-((2-oxotetrahydrofuran-3-yl)methyl)-3-(p-tolyl)acrylate (3h)



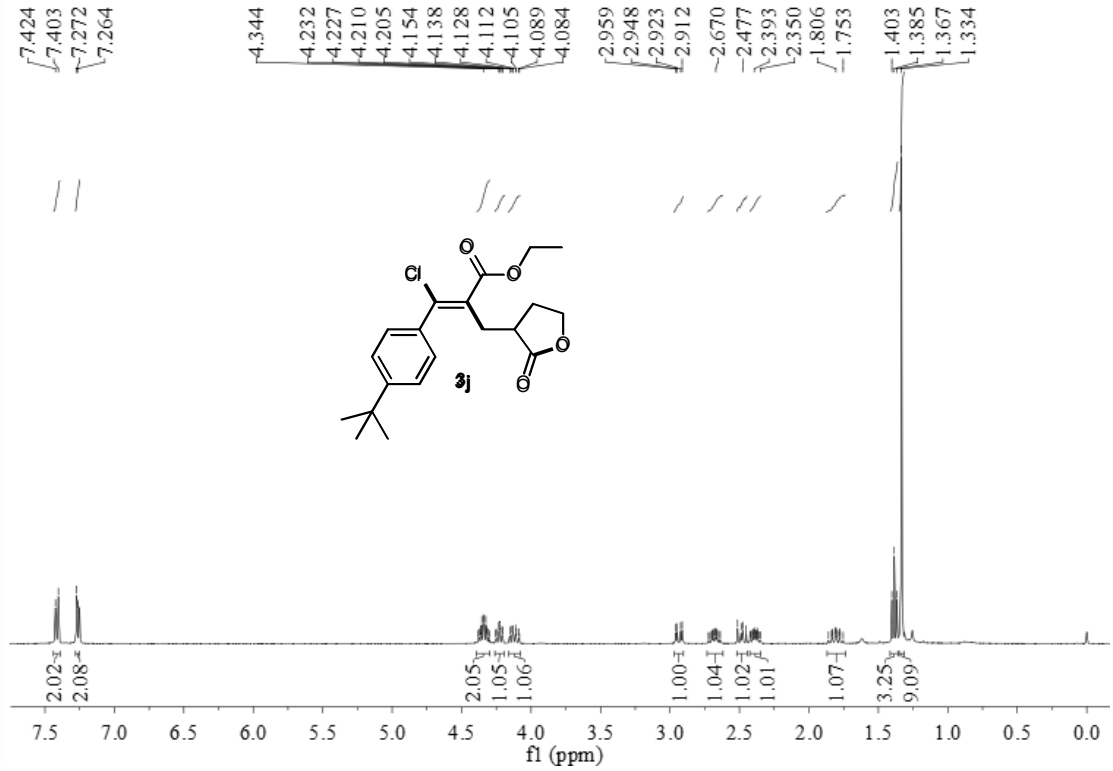


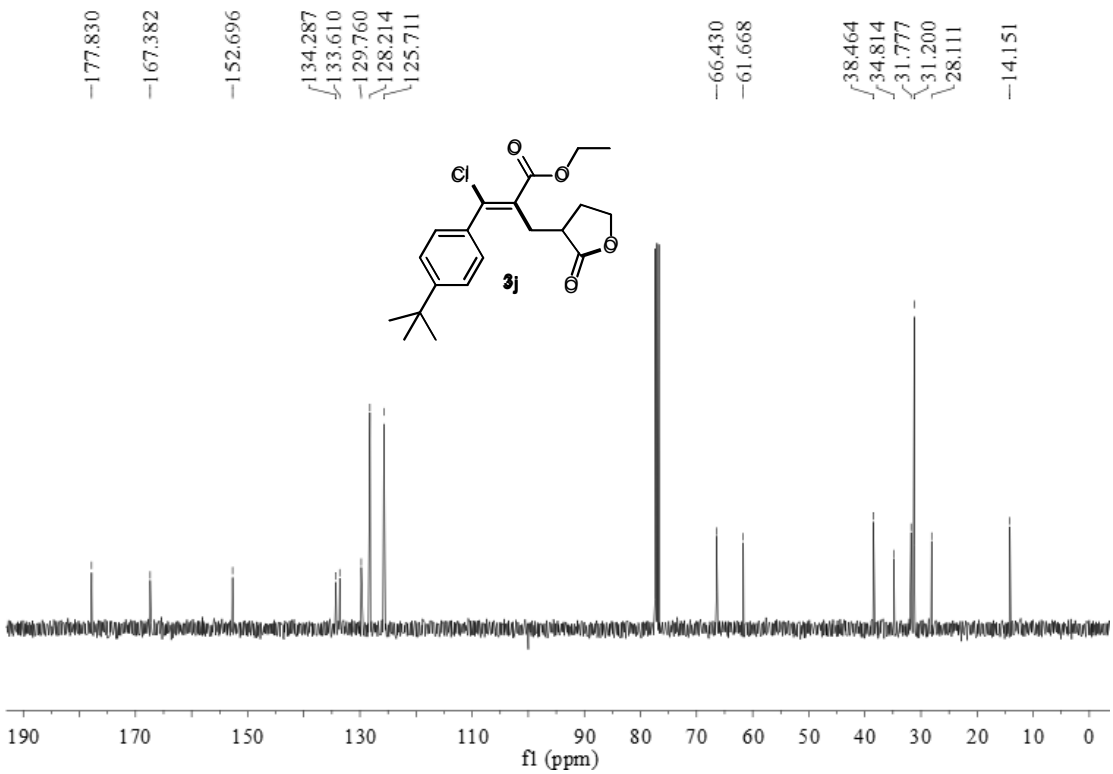
^{1}H NMR and ^{13}C NMR of (Z)-ethyl 3-chloro-3-(4-ethylphenyl)-2-((2-oxotetrahydrofuran-3-yl)methyl) -acrylate (3i)



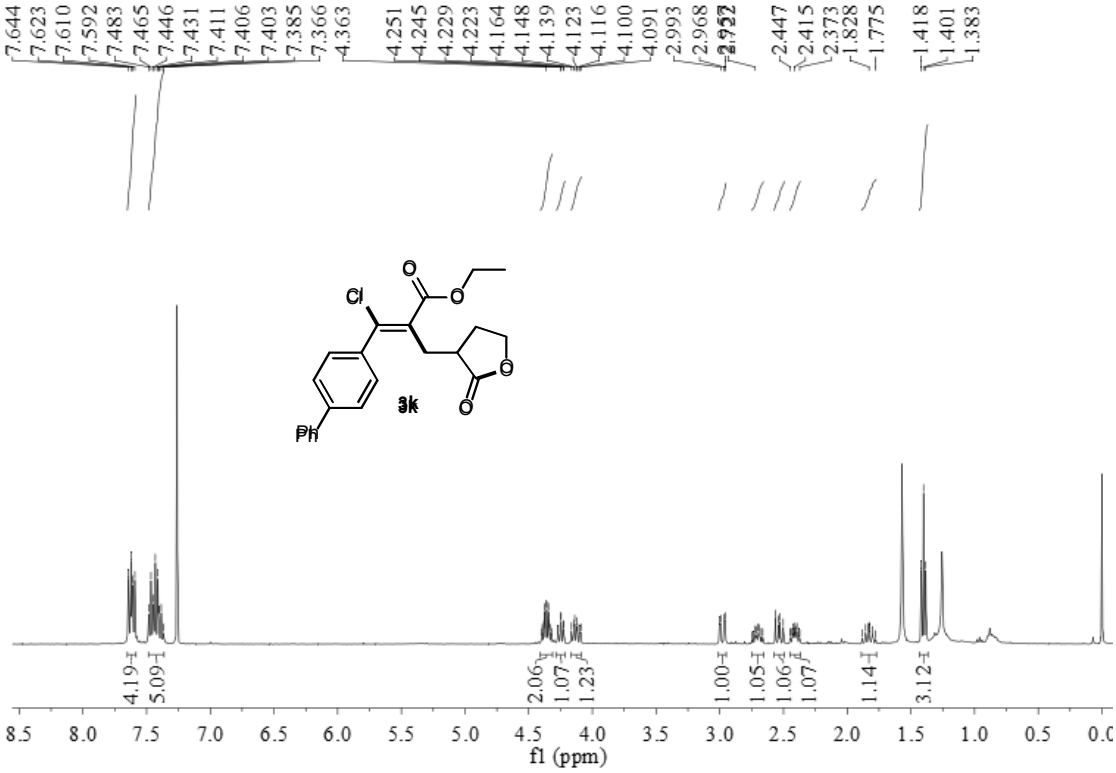


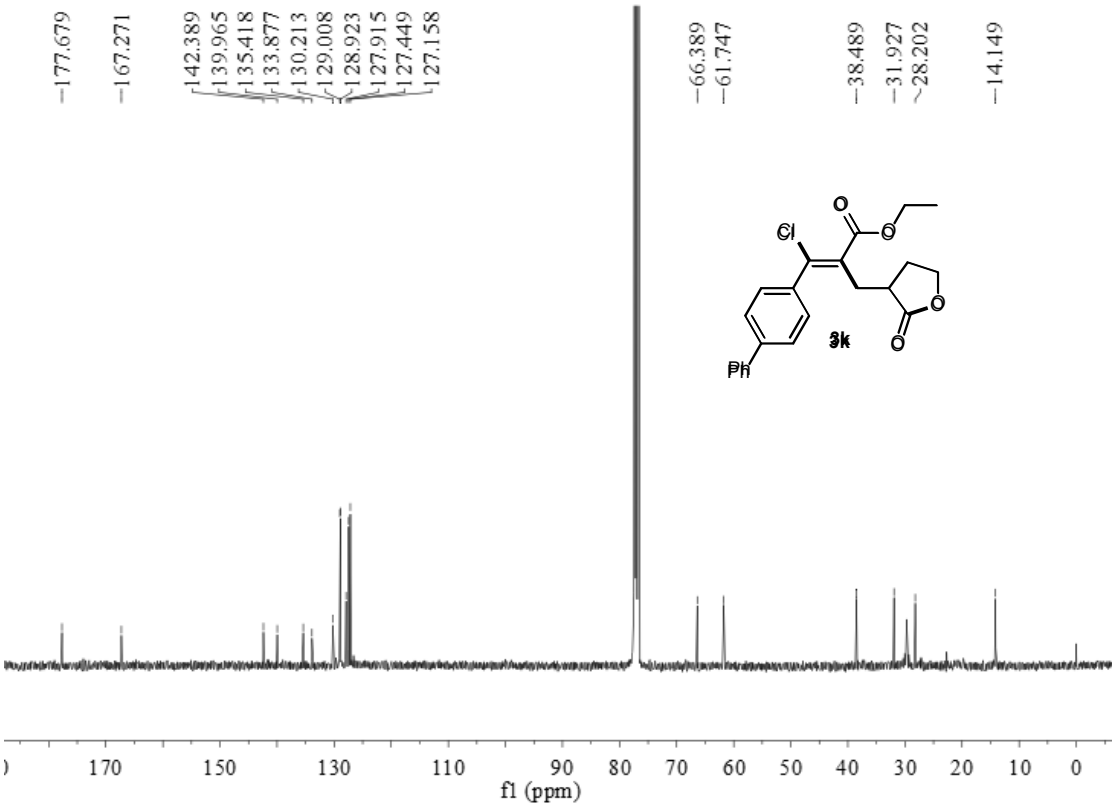
^{1}H NMR and ^{13}C NMR of (Z)-ethyl 3-(4-(tert-butyl)phenyl)-3-chloro-2-((2-oxotetrahydrofuran-3-yl)methyl) -acrylate (3j)



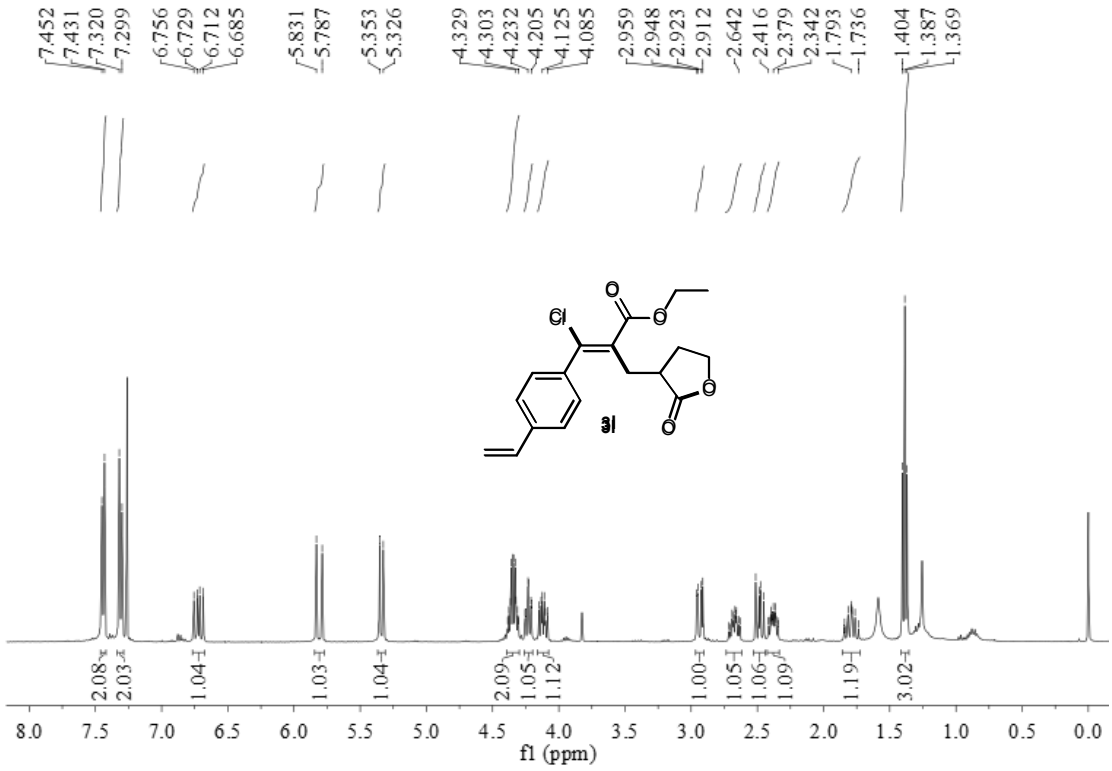


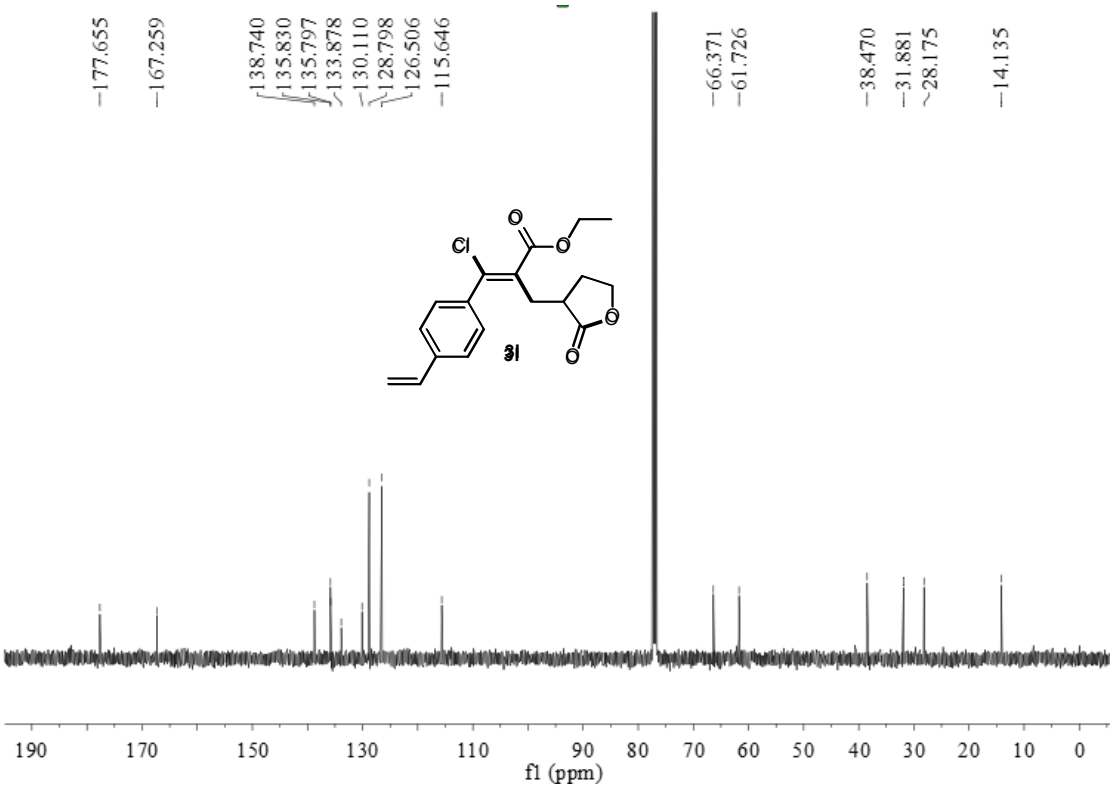
^{1}H NMR and ^{13}C NMR of (Z)-ethyl 3-([1,1'-biphenyl]-4-yl)-3-chloro-2-((2-oxotetrahydrofuran-3-yl)methyl)-acrylate (3k)



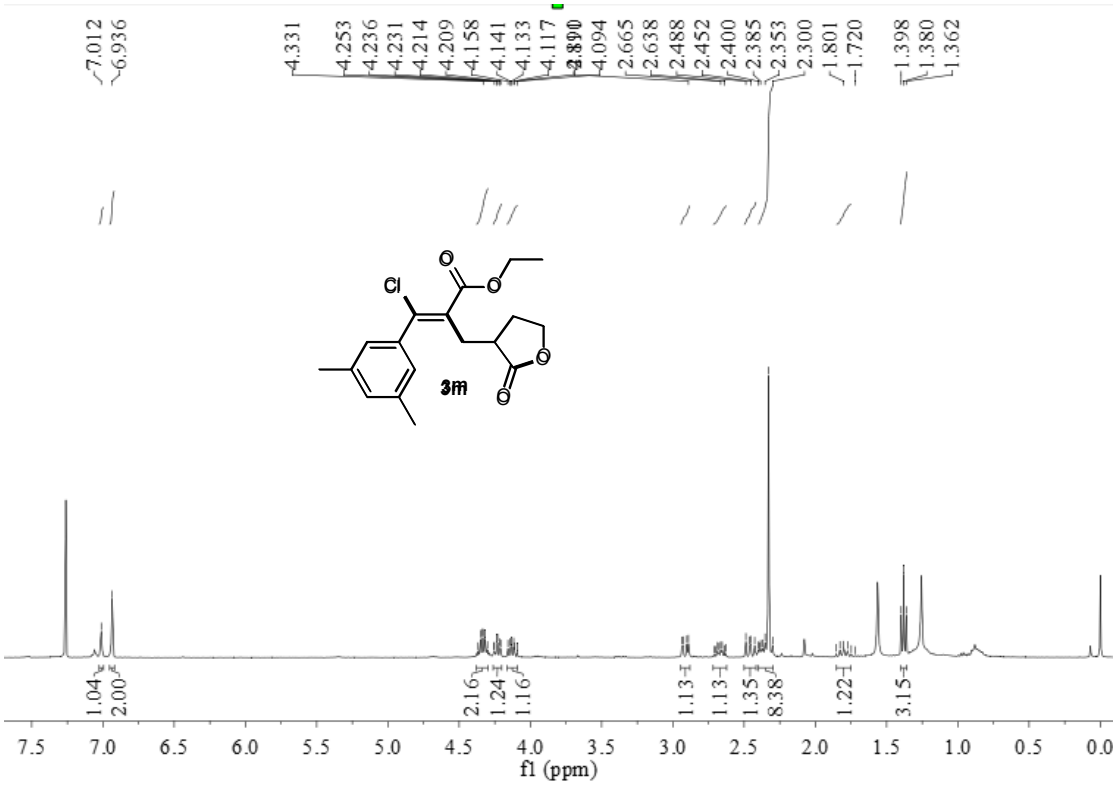


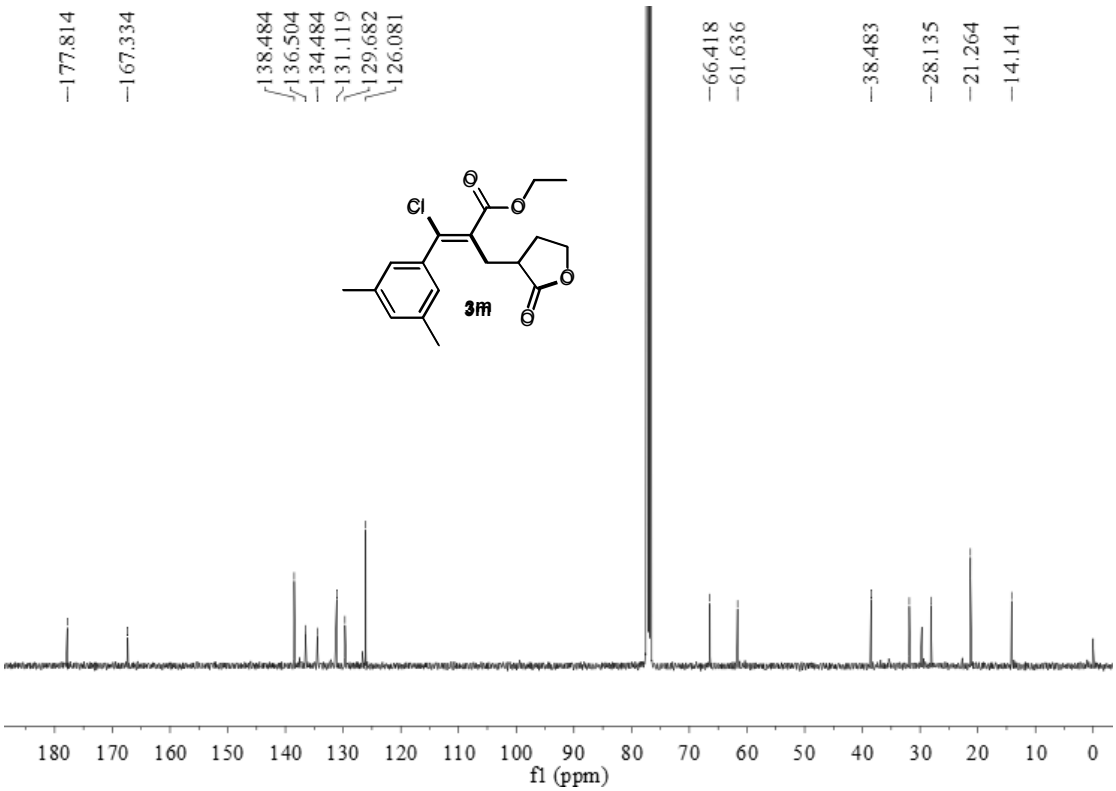
^{1}H NMR and ^{13}C NMR of (Z)-ethyl 3-chloro-2-((2-oxotetrahydrofuran-3-yl)methyl)-3-(4-vinylphenyl)-acrylate (3l)



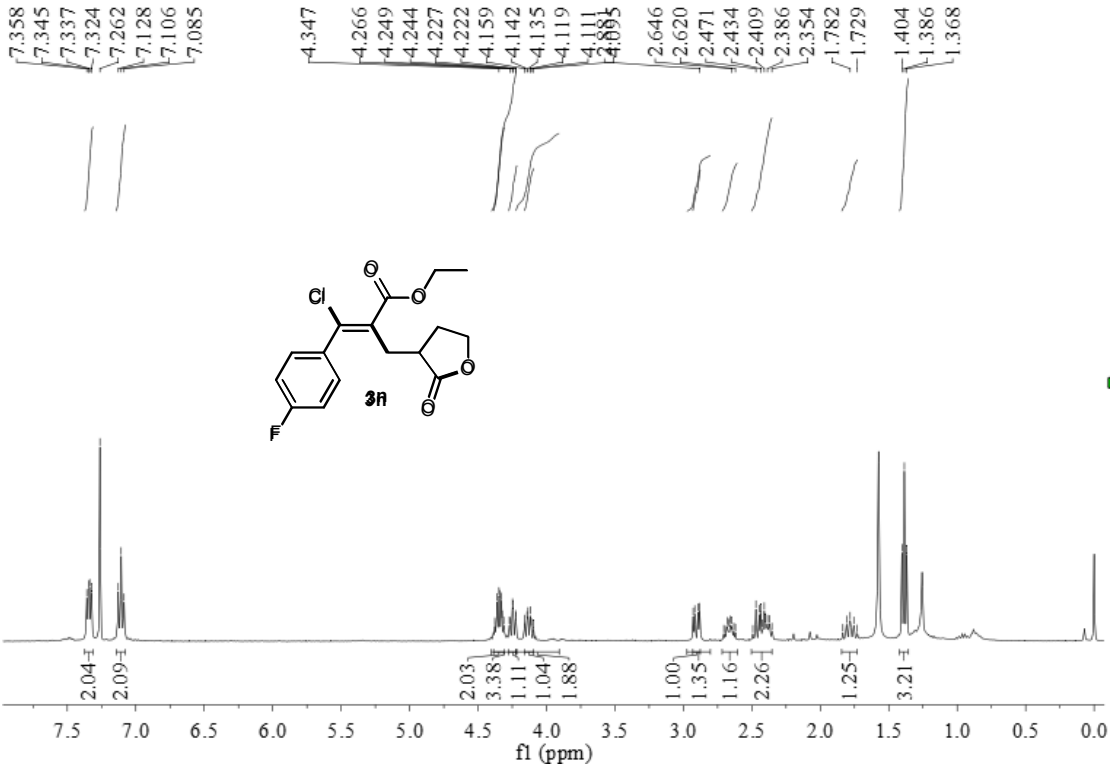


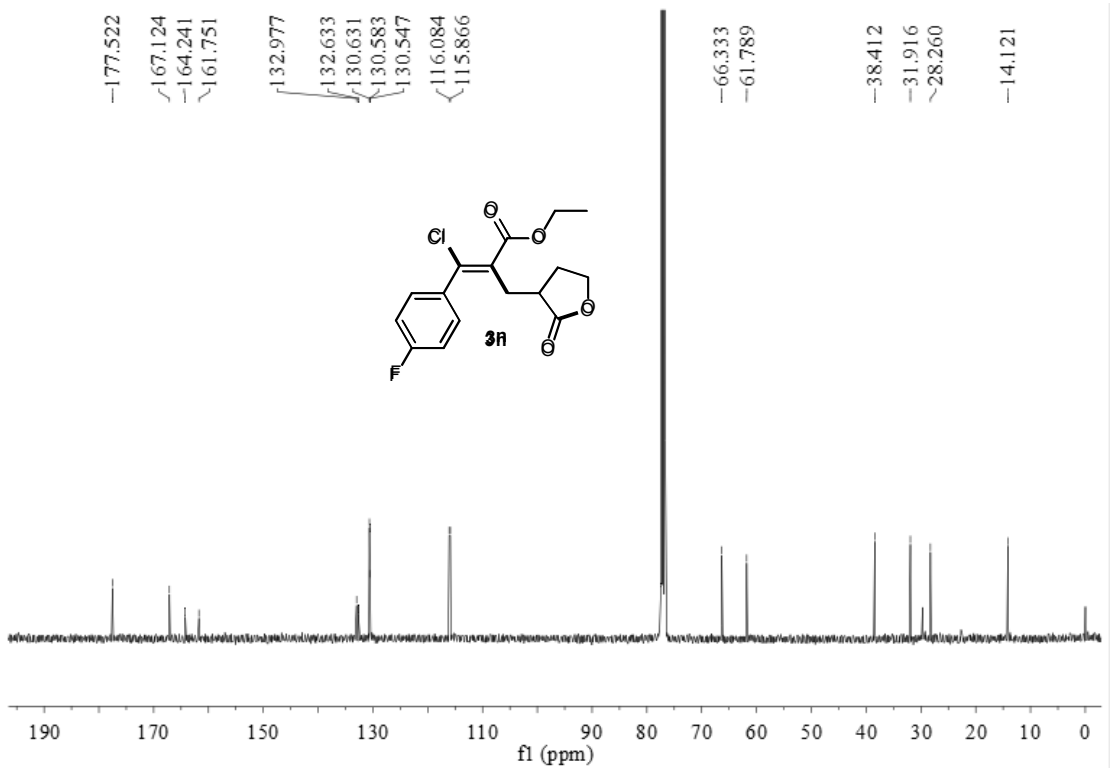
^{1}H NMR and ^{13}C NMR of (Z)-ethyl 3-chloro-3-(3,5-dimethylphenyl)-2-((2-oxotetrahydrofuran-3-yl)methyl)-acrylate (3m)



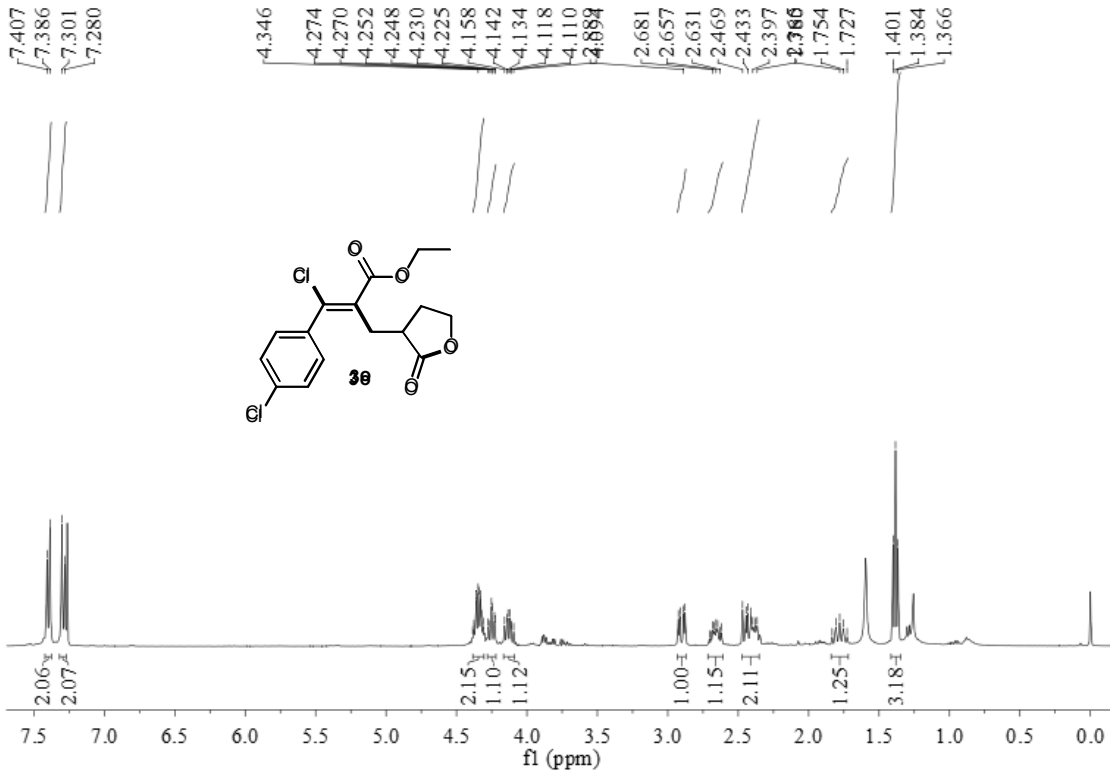


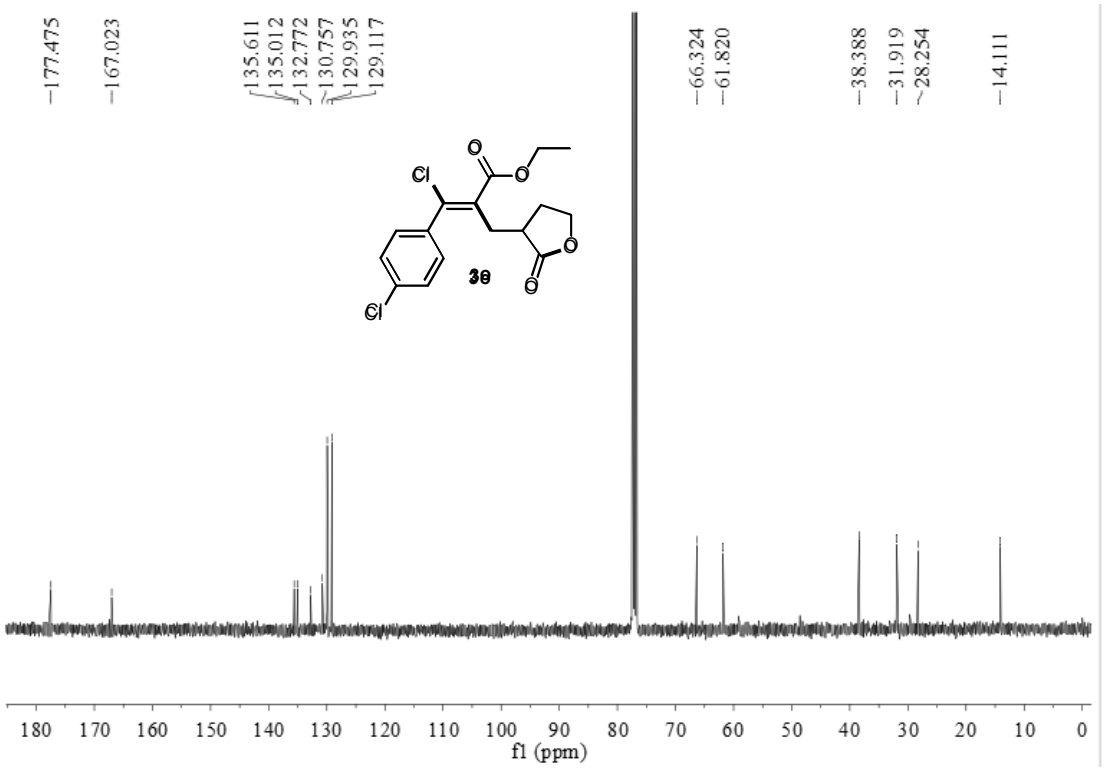
^{1}H NMR and ^{13}C NMR of (Z)-ethyl 3-chloro-3-(4-fluorophenyl)-2-((2-oxotetrahydrofuran-3-yl)methyl)-acrylate (3n)



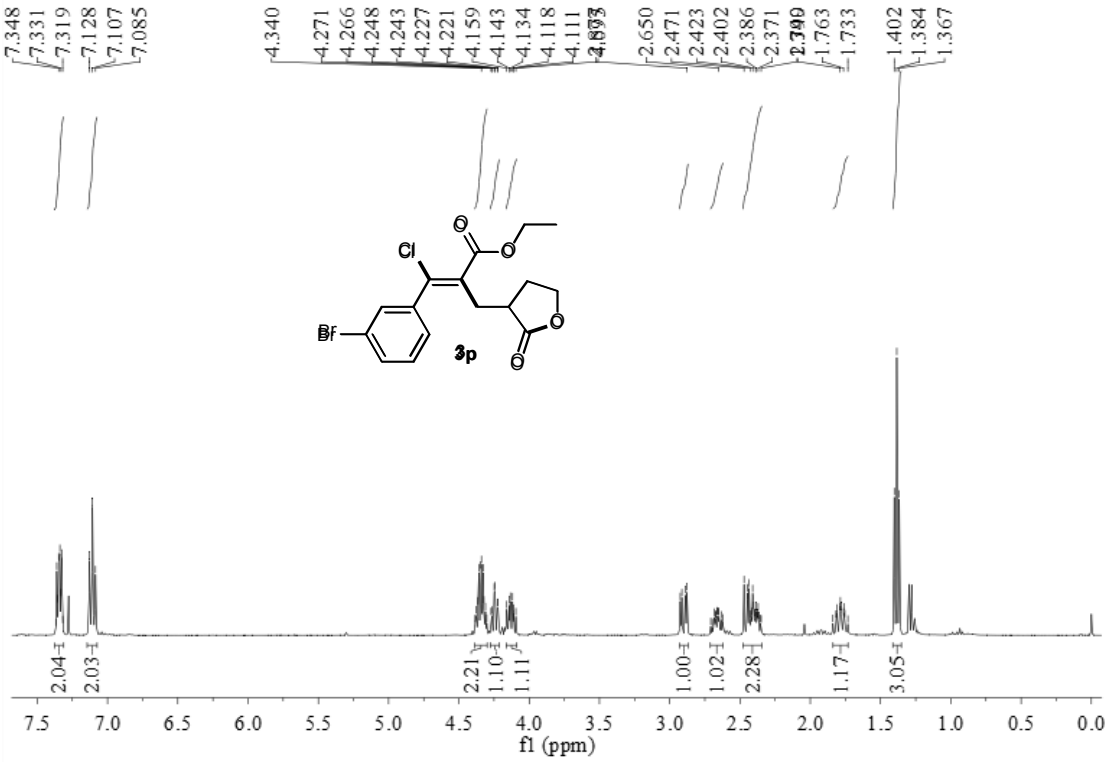


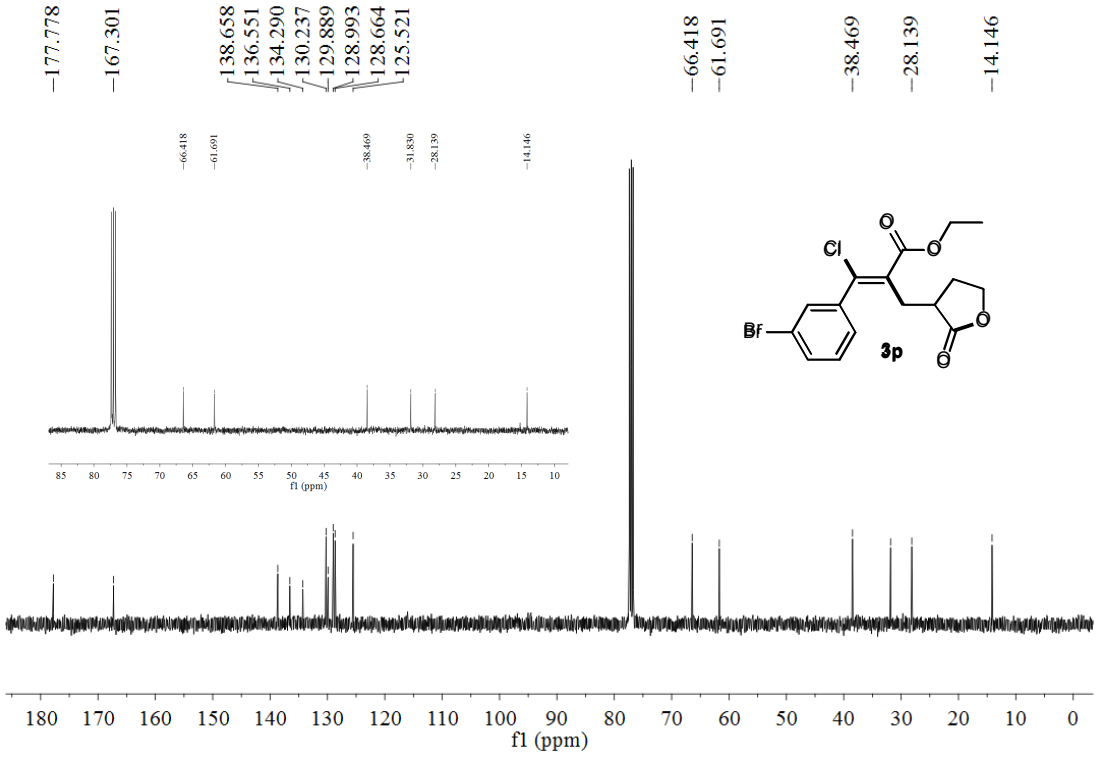
^{1}H NMR and ^{13}C NMR of (Z)-ethyl 3-chloro-3-(4-chlorophenyl)-2-((2-oxotetrahydrofuran-3-yl)methyl)-acrylate (3o)



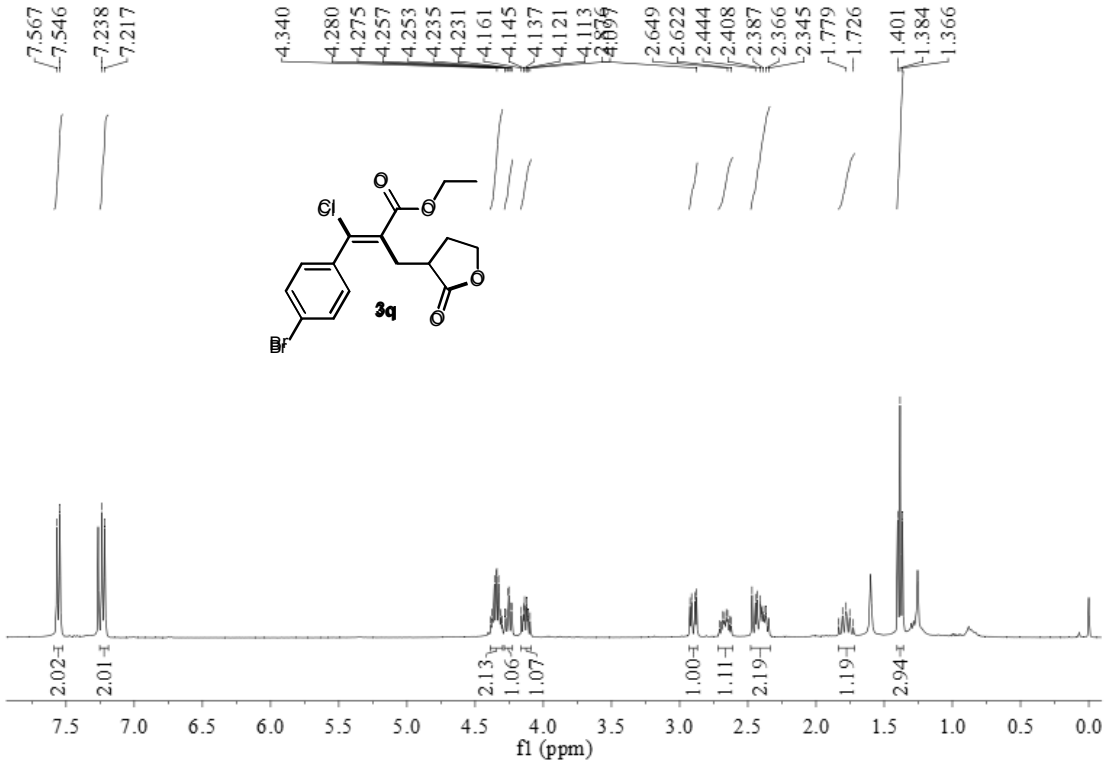


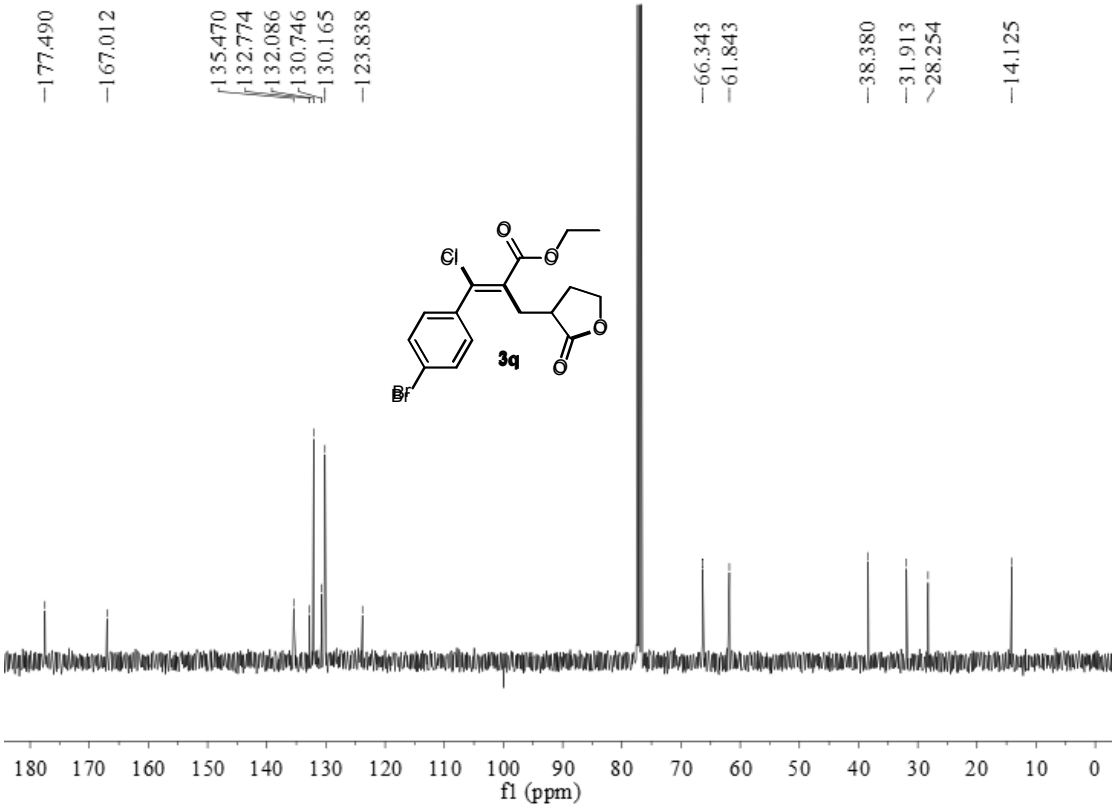
^{1}H NMR and ^{13}C NMR of (Z)-ethyl 3-(3-bromophenyl)-3-chloro-2-((2-oxotetrahydrofuran-3-yl)methyl)-acrylate (3p)



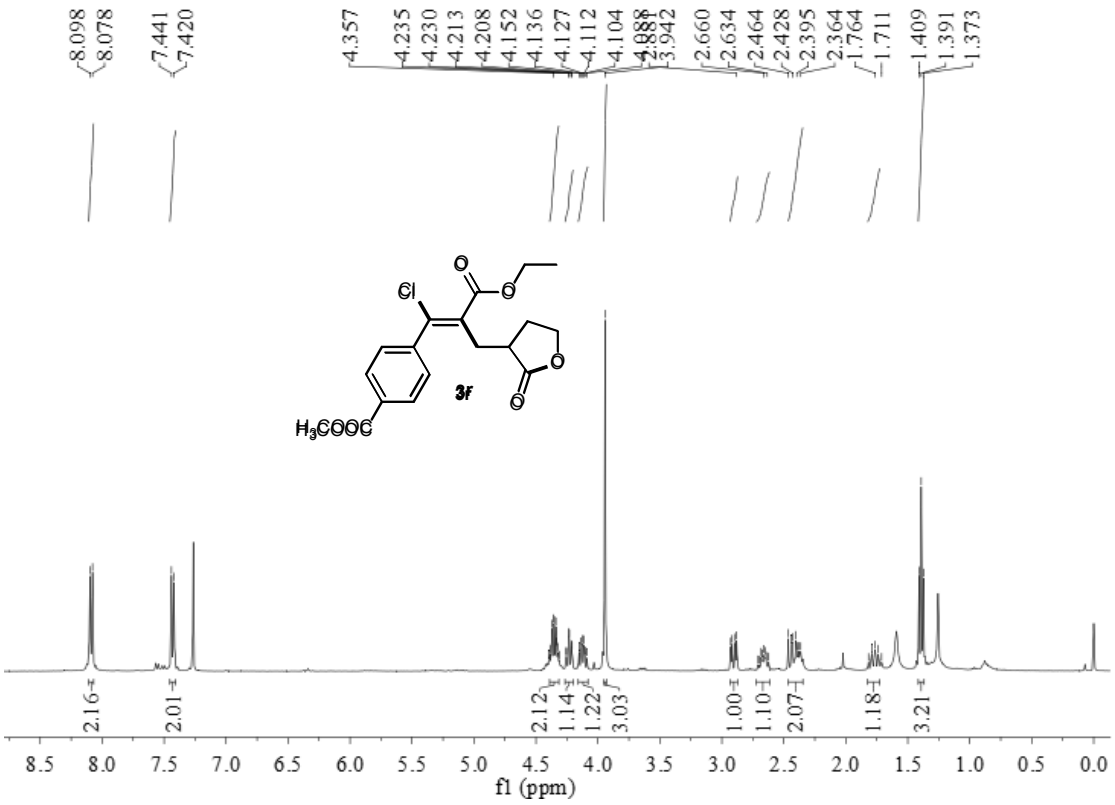


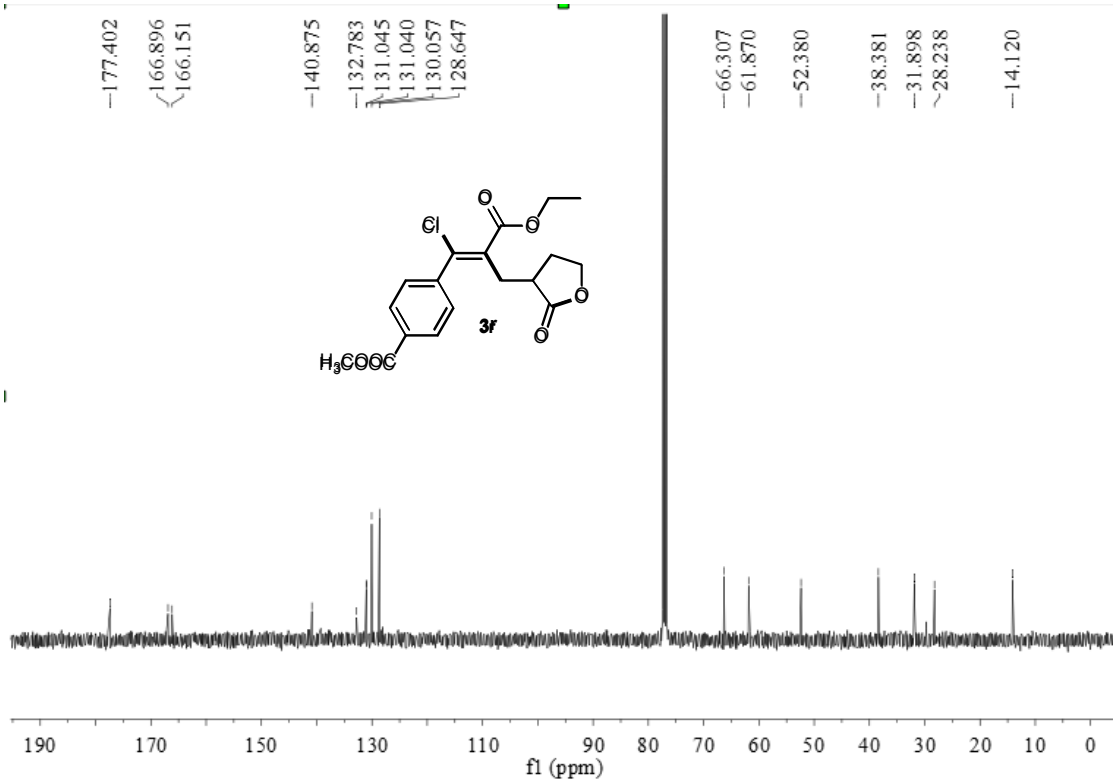
^{1}H NMR and ^{13}C NMR of (Z)-ethyl 3-(4-bromophenyl)-3-chloro-2-((2-oxotetrahydrofuran-3-yl)methyl)-acrylate (3q)



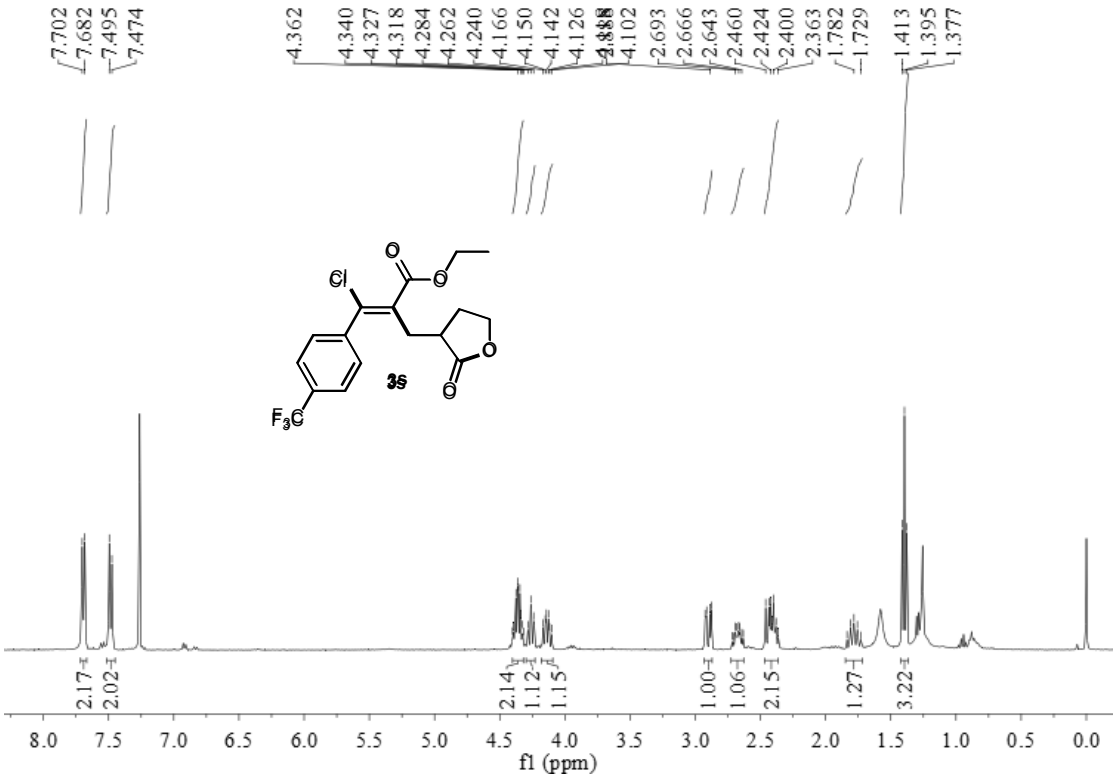


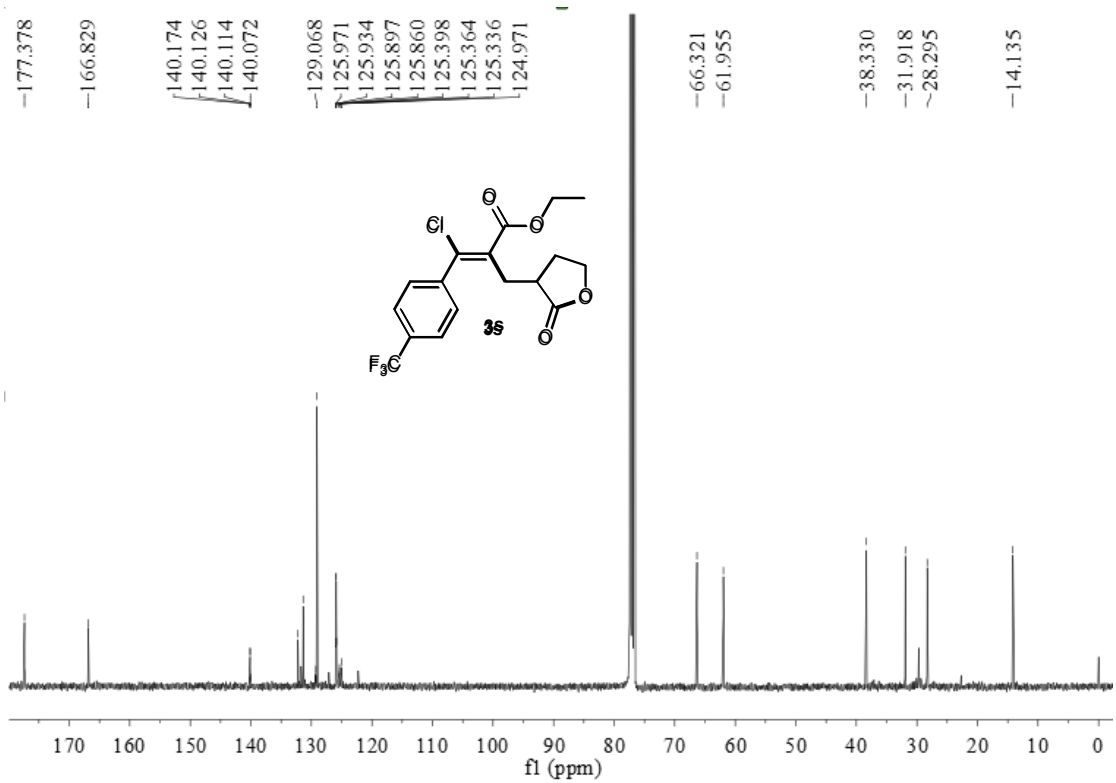
^{1}H NMR and ^{13}C NMR of (Z)-methyl 4-(1-chloro-3-ethoxy-3-oxo-2-((2-oxotetrahydrofuran-3-yl)methyl)-prop-1-en-1-yl)benzoate (3r)



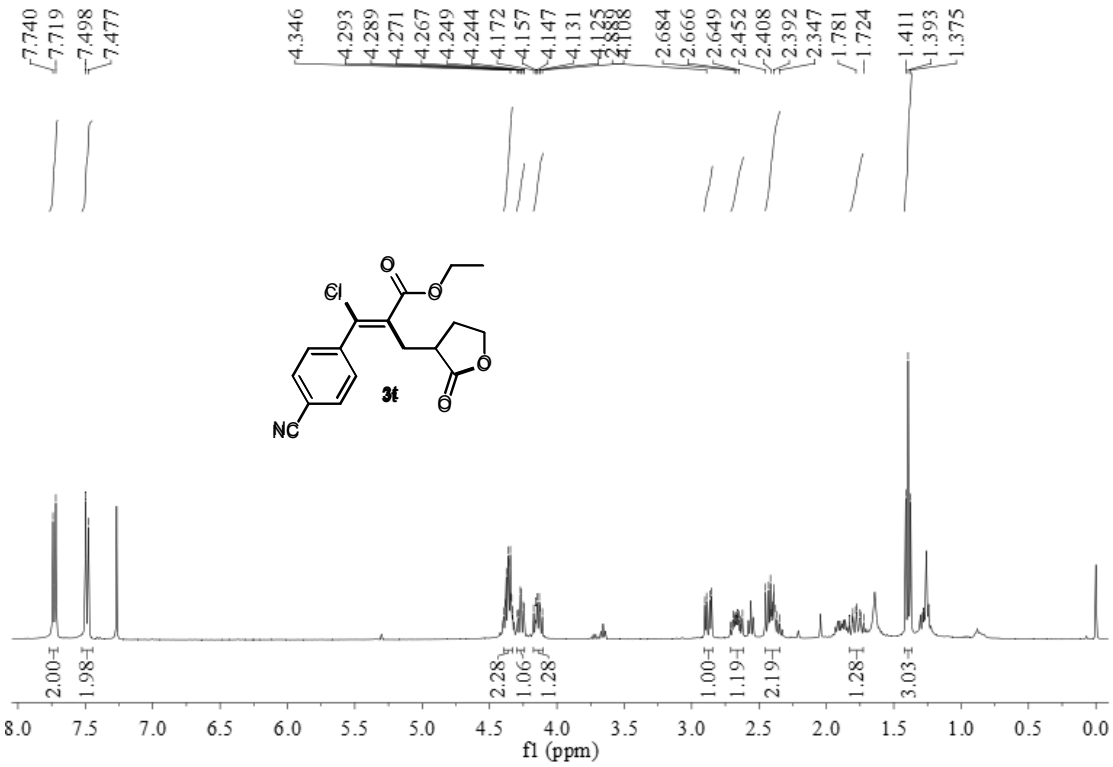


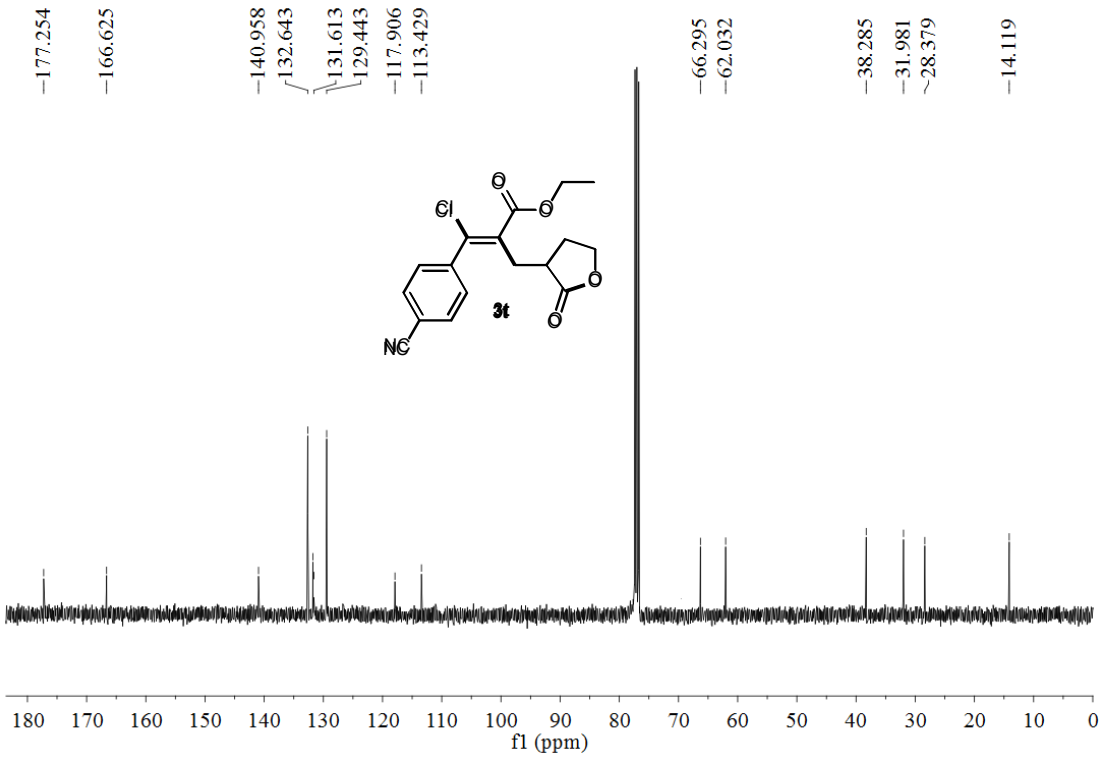
^{1}H NMR and ^{13}C NMR of (Z)-ethyl 3-chloro-2-((2-oxotetrahydrofuran-3-yl)methyl)-3-(4-(trifluoromethyl)phenyl)acrylate (3s)



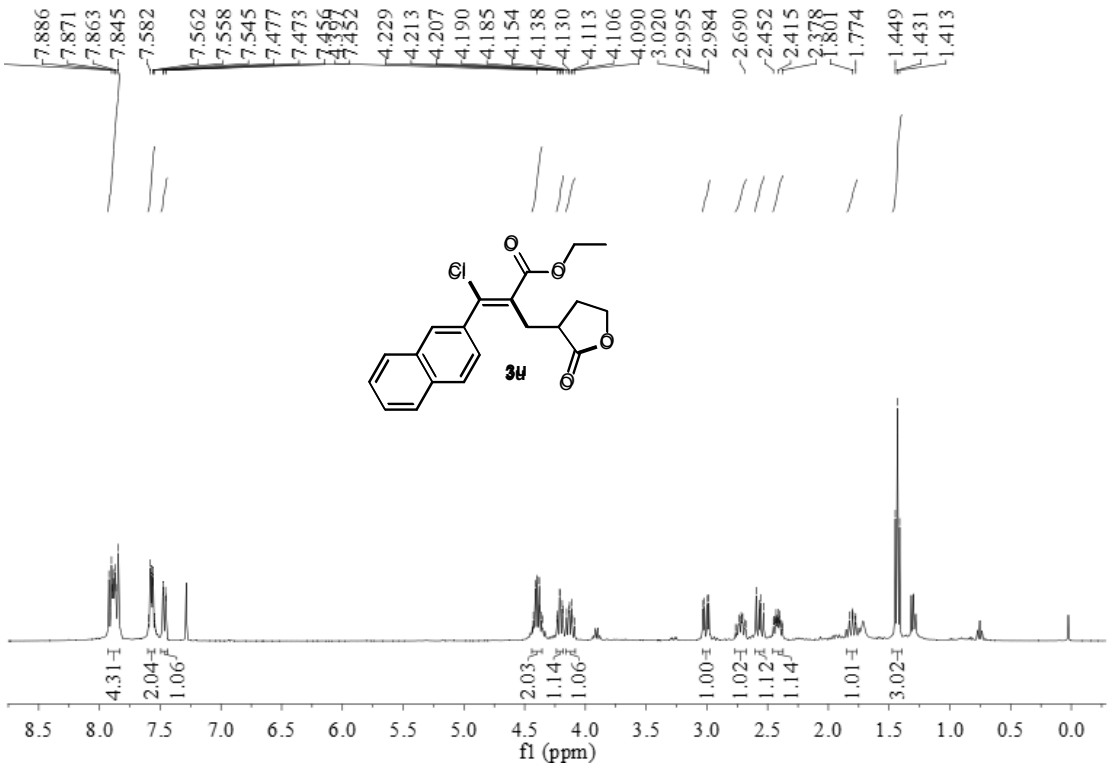


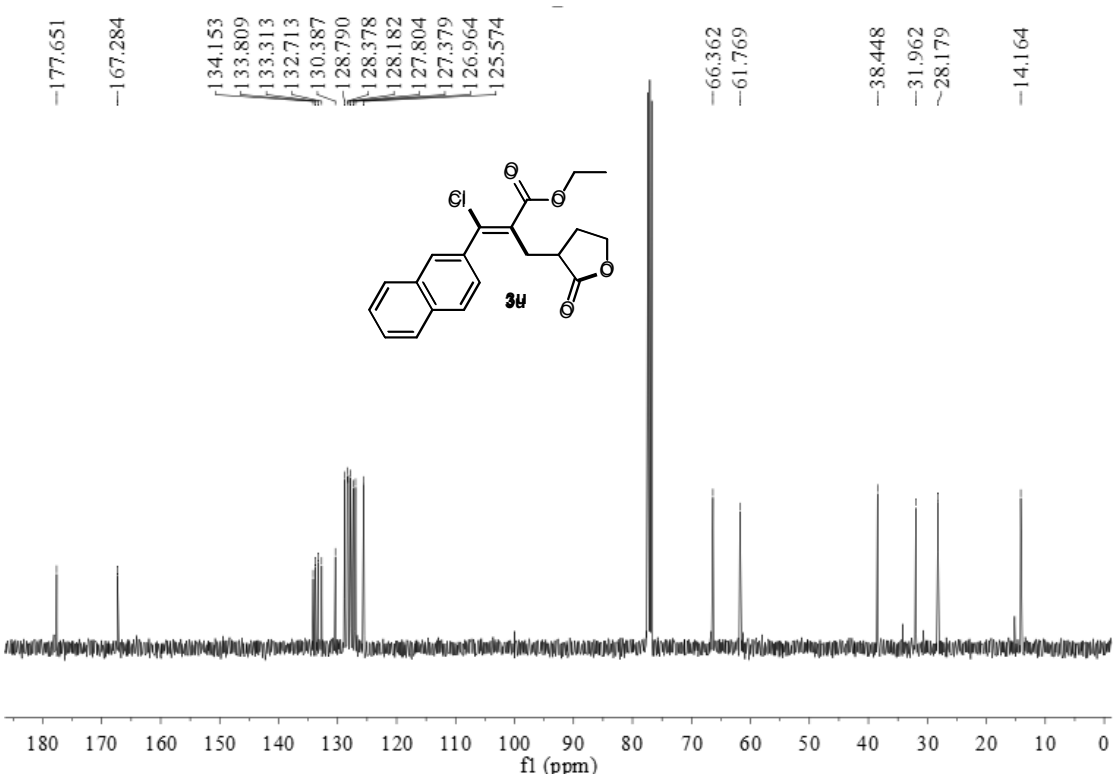
^{1}H NMR and ^{13}C NMR of (Z)-ethyl 3-chloro-3-(4-cyanophenyl)-2-((2-oxotetrahydrofuran-3-yl)methyl)-acrylate (3t)



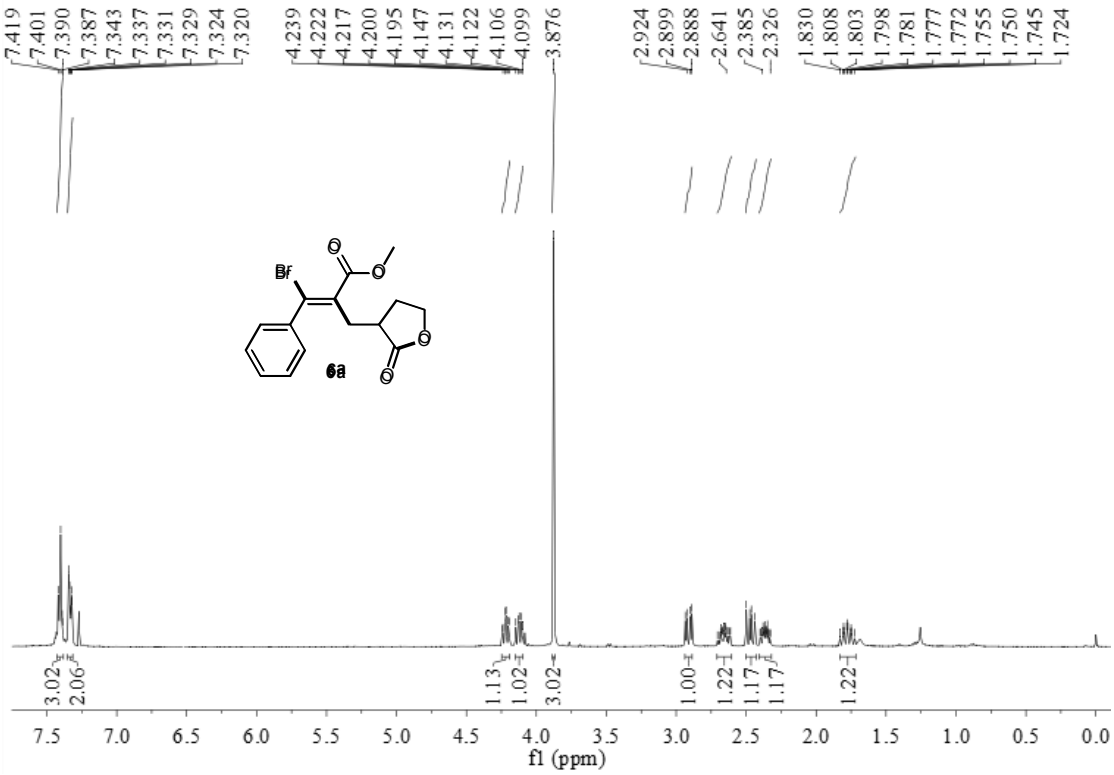


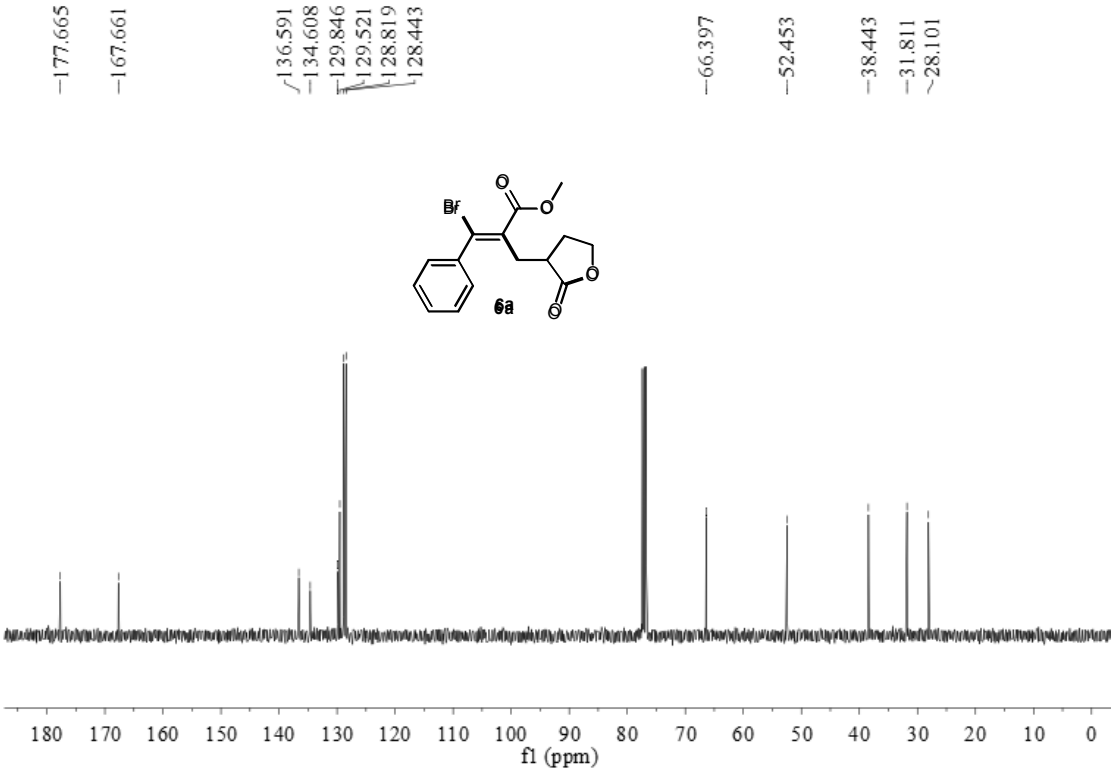
^{1}H NMR and ^{13}C NMR of (Z)-ethyl 3-chloro-3-(naphthalen-2-yl)-2-((2-oxotetrahydrofuran-3-yl)methyl)-acrylate (3u)



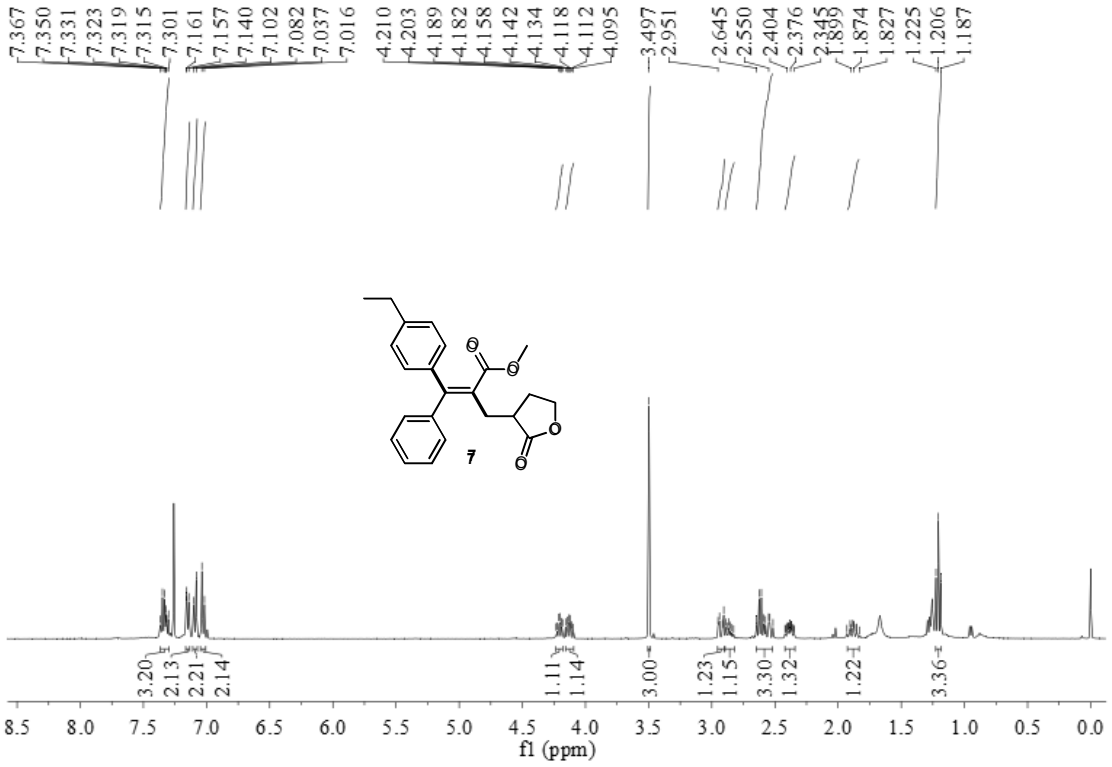


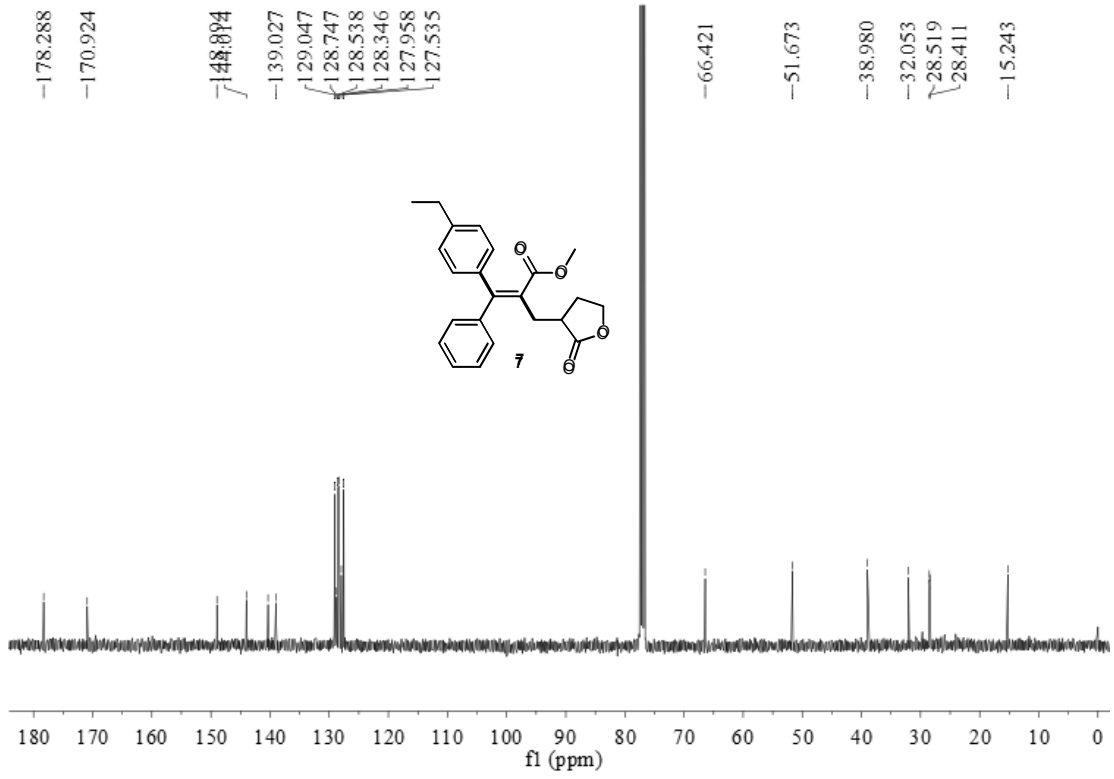
^{1}H NMR and ^{13}C NMR of (Z)-methyl 3-bromo-2-((2-oxotetrahydrofuran-3-yl)methyl)-3-phenylacrylate (6a)



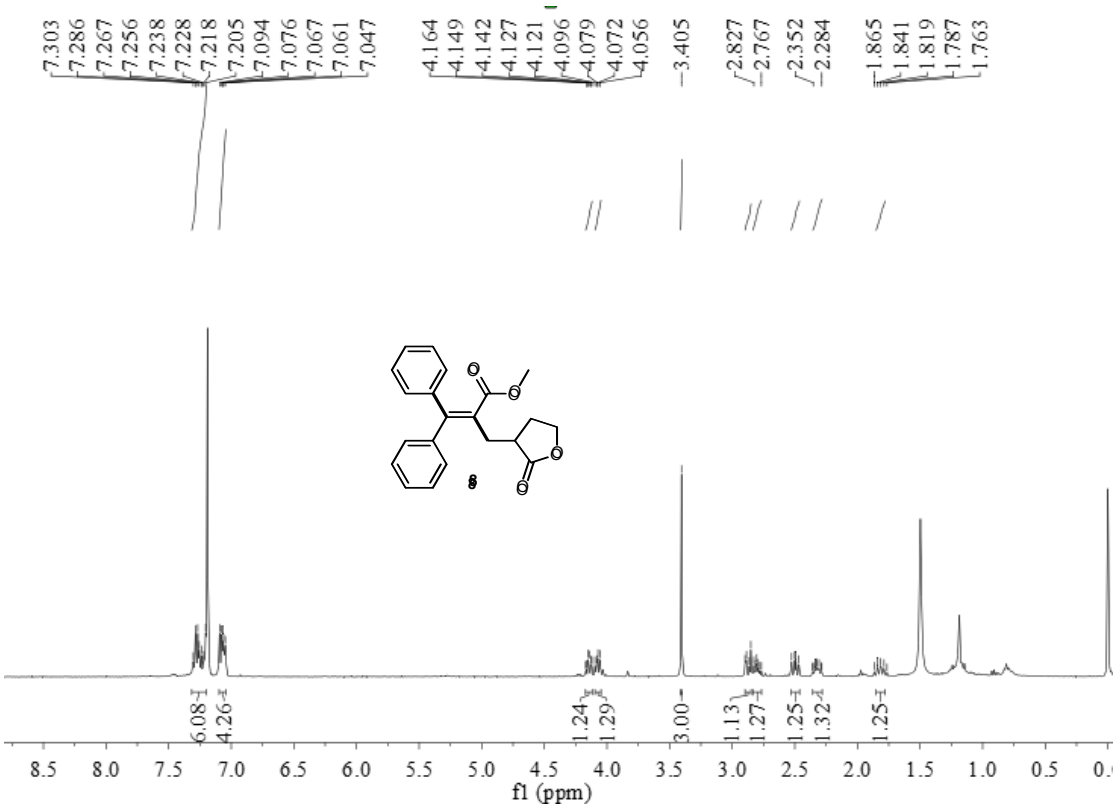


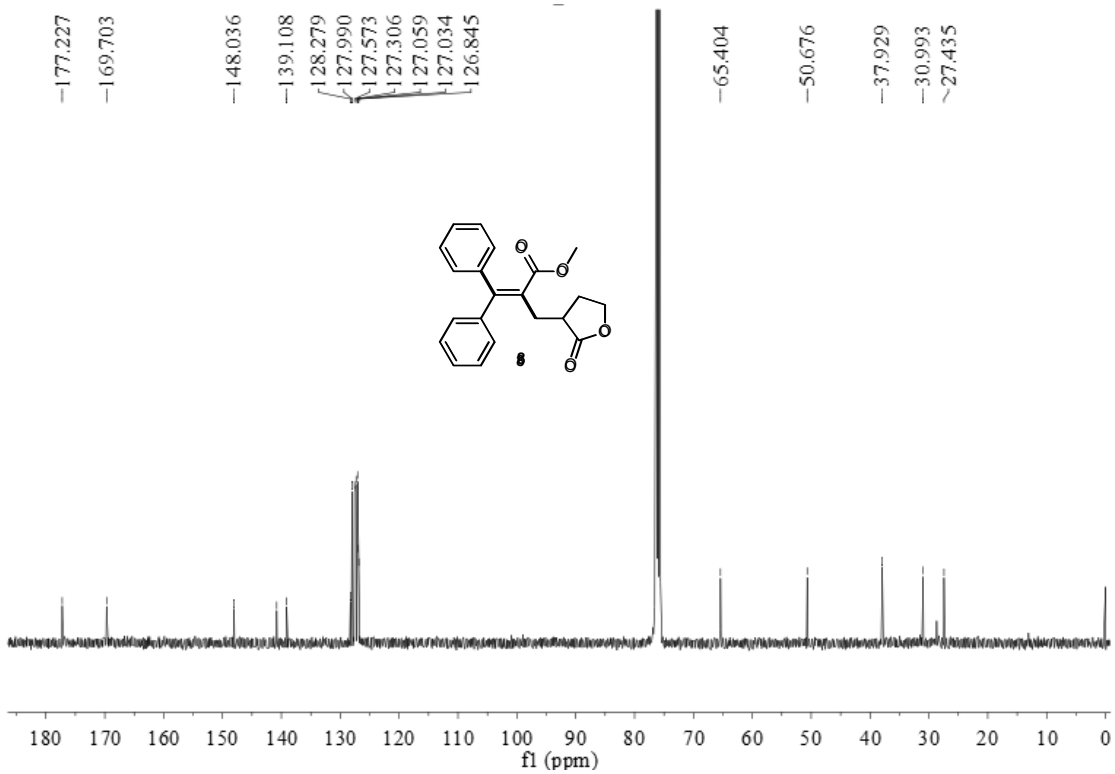
^{1}H NMR and ^{13}C NMR of (Z)-methyl 3-(4-ethylphenyl)-2-((2-oxotetrahydrofuran-3-yl)methyl)-3-phenylacrylate (7)





^{1}H NMR and ^{13}C NMR of methyl 2-((2-oxotetrahydrofuran-3-yl)methyl)-3,3-diphenylacrylate (8)





VI. Studies on stereochemistry of 3a

The noesy spectrum of 3a