Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Palladium-Catalyzed Ring-Opening [5+2] Annulation of Vinylethylene Carbonates (VECs) and C5-substituted Meldrum's acids: Rapid synthesis of 7-Membered Lactones

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Table of Contents

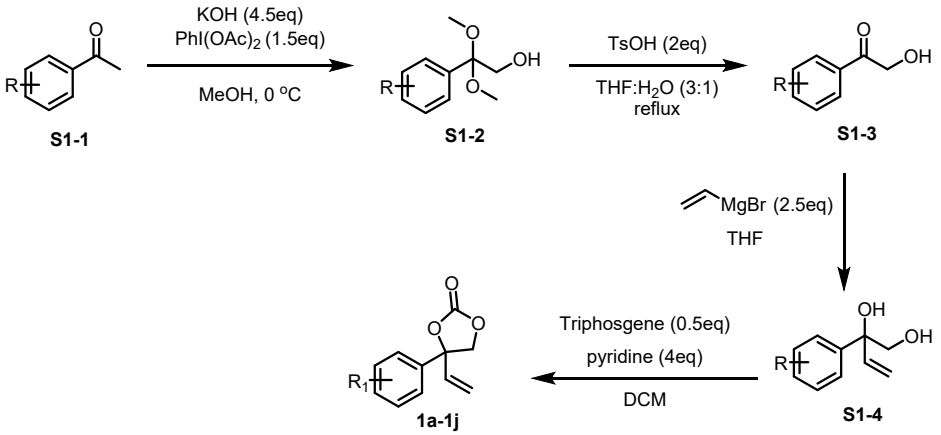
1. General Information and Materials

NMR spectra were recorded using Bruker AV-300 / AV-400/ AV-500 spectrometers. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets), coupling constants (Hz) and integration. High resolution mass spectra were acquired on an agilent 6230 spectrometer and were obtained by peak matching. Analytical thin layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV254 fluorescent indicator and/or by exposure to phosphormolybdic acid/cerium (IV) sulfate/ninhydrine followed by brief heating with a heat gun. Liquid chromatography (flash chromatography) was performed on 60Å (40-60 μm) mesh silica gel (SiO_2). All reactions were carried out under nitrogen with anhydrous solvents in oven-dried glassware, unless otherwise noted. All reagents were commercially obtained and, where appropriate, purified prior to use.

2. Preparation of Substrates

General proceduce for synthesis of 4-phenyl-4-vinyl-1,3-dioxolan-2-one 1a-1j:

Prepared according to a previous reported procedure[1-2]



Step 1: To a solution of $PhI(OAc)_2$ (1.5 equiv), KOH (2.5 equiv) in MeOH was added aryl acetophenone (1.0 equiv) under Ar at 0 ℃. The reaction mixture was allowed to stir at 0 ℃ for 3 h. The reaction mixture was quenched by H_2O and extracted with EA (x 3). The combined organic layers were washed with brine, and then dried over anhydrous Na_2SO_4 and concentrated. The crude residue was purified by column chromatography.

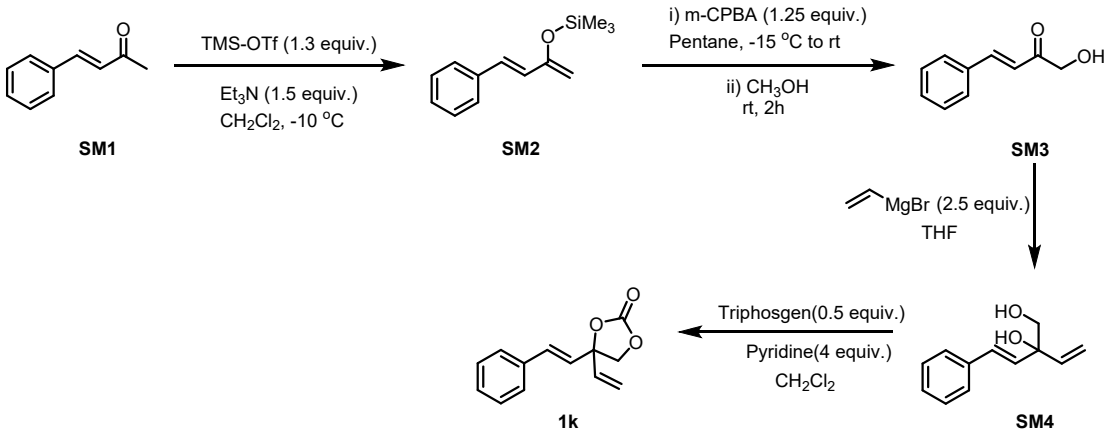
Step 2: S1-2 (1 equiv) was dissolved in THF: H_2O (3: 1) with the addition of *p*-TsOH

(2 equiv). The mixture was heated to reflux for 4.5 h, monitored the reaction with TLC. Quenched the reaction with sat. $NaHCO_3$ and extracted the product with EtOAc (x 3). The combined organic extracts were washed with brine and dried over Na_2SO_4[1]. After removal of the solvents under reduced pressure, the residue was purified by flash column chromatography (petroleum ether /EtOAc = 5/1 to 3/1) to afford substrates S1-3.

Step 3: To a solution of hydroxyl methyl ketone S1-3 (1 equiv.) in THF was added vinylmagnesium bromide (1.0 M in THF, 2.5 equiv.) at 0 °C. The reaction was stirred under N_2 atmosphere at room temperature for 2 h. The reaction mixture was then quenched with saturated aqueous NH_4Cl, and extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The crude residue was purified by column chromatography.

Step 4: To a solution of diol S1-3 (1 equiv.) and pyridine (4 equiv.) in CH_2Cl_2 was added triphosgene (0.5 equiv.) at 0 °C. The reaction was stirred under N_2 atmosphere at room temperature for 2 h. The reaction mixture was then quenched with saturated aqueous NH_4Cl, and extracted with CH_2Cl_2. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The crude residue was purified by column chromatograp[2].

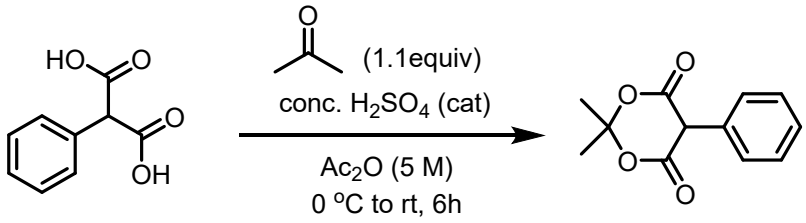
General proceduce for synthesis of (E)-4-styryl-4-vinyl-1,3-dioxolan-2-one 1k:



(E)-1-hydroxy-4-phenylbut-3-en-2-one (SM3) was synthesized according to the literature known proceure[3] starting from (E)-4-phenylbut-3-en-2-one (SM1).

General proceduce for synthesis of 2,2-dimethyl-5-phenyl-1,3-dioxane-4,6-dione (2s):

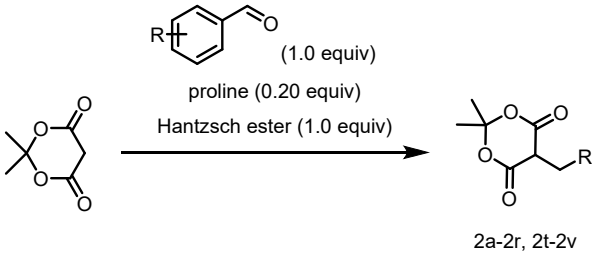
Prepared according to a previous reported procedure [4]



A round-bottom flask equipped with a stirring bar was charged with the malonic acid derivatives (1.0 equiv) and Ac_2O (5-8 M), and cooled to 0 °C (ice/water bath). After the addition of 2-3 drops of concentrated H_2SO_4, acetone (1.1 equiv) was added dropwise to the stirred mixture with a pressure-equalizing dropping funnel. The reaction was allowed to warm to room temperature and stirred for 6 h. Then, the resulting mixture was placed in the refrigerator for 2 h, and the resulting solid was collected by filtration on a fritted funnel and rinsed with cold water (2 times) and Et_2O (3 times). Traces of water were removed by addition of toluene (10 mL) and evaporation (3 times) to afford the desired product **2a**[4].

General proceduce for synthesis of 5-Aryl-2,2-dimethyl-1,3-dioxane-4,6-dione/ 5-alkyl-2,2-dimethyl-1,3-dioxane-4,6-dione 2a-2r,2t-2v

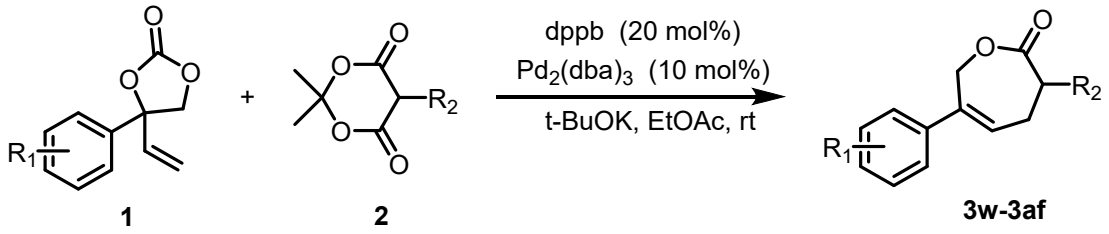
Prepared according to a previous reported procedure [5]



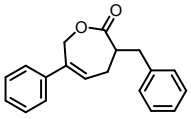
2a-2r, 2t-2v

A round-bottom flask with a stir bar was flame-dried under vacuum and cooled under inert atmosphere. Meldrum's acid (1.0 equiv), Hantzsch ester (1.0 equiv), and proline (0.20 equiv) were added on the benchtop. The flask was evacuated and backfilled with N_2 (x3). EtOH (0.3 M) was added, followed by the aldehyde (1.0 equiv) and the reaction was left to stir overnight at room temperature. Upon completion of the reaction (as determined by TLC), the solution was concentrated under reduced pressure, diluted with EtOAc, and washed with 1M HCl. The aqueous layer was extracted with EtOAc (x2) and the combined organic layer was washed with brine (x1), dried over $MgSO_4$, and concentrated. The crude residue was purified by column chromatography[5].

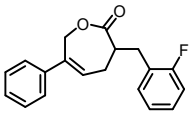
3. Preparation and Characterization of the products



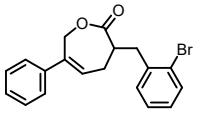
A 10 mL Schlenk tube containing a stirring bar was charged with $Pd_2(dba)_3$ (0.1 equiv., 0.015 mmol), dppb (0.2 equiv., 0.03 mmol), substituted Meldrum's acid **2** (0.3 mmol), t-BuOK (2.0 equiv., 0.3 mmol). The tube was then evacuated and back-filled with argon three times. Then substituted vinylethylene carbonate **1** (0.15 mmol in 1mL anhydrous EA) was added to the tube under nitrogen atmosphere, and stirred at room temperature for 10 h. After the reaction was completed (monitored by TLC), the reaction mixture was filtered with diatomite and purified by column chromatography on silica gel (PE : EA = 20:1) to give the desired product.



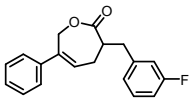
3-benzyl-6-phenyl-4,7-dihydrooxepin-2(3H)-one(3a) [6]: white solid, mp: 68-70ºC, 34.2 mg, 82%. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.25 (m, 4H), 7.22-7.14 (m, 6H), 5.81 (m, 1H), 5.32 (m, 1H), 4.71 (d, *J* = 15.6 Hz, 1H), 3.50 (m, 1H), 3.23 (m, 1H), 2.62 (m, 1H), 2.53 (m, 1H), 2.37 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ 175.7, 141.1, 138.9, 136.8, 129.3, 129.0, 128.6, 128.5, 127.6, 126.6, 126.2, 67.2, 41.3, 37.7, 32.1.



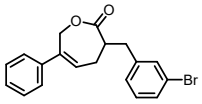
3-(2-fluorobenzyl)-6-phenyl-4,7-dihydrooxepin-2(3H)-one(3b): white solid, mp: 119-121ºC, 26.3 mg, 59%. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.44-7.22 (m, 7H), 7.12 (m, 2H), 5.94 (m, 1H), 5.44 (m, 1H), 4.83 (d, *J* = 15.2 Hz, 1H), 3.71 (m, 1H), 3.29 (m, 1H), 2.87 (m, 1H), 2.72-2.43 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-d) δ175.5, 162.6($^1J_{CF}$ = 243,2Hz), 141.1, 136.8, 132.3, 132.2, 128.9, 128.7, 128.6($^3J_{CF}$ = 8.2Hz), 127.7, 126.2, 125.8, 125.6, 124.3($^4J_{CF}$ = 3.5Hz), 115.3($^2J_{CF}$ = 21.8Hz), 67.2, 39.7, 32.2, 31.5. HRMS (ESI$^+$): calcd. for $[C_{19}H_{17}FNaO_2]^+$: 319.1110, found: 319.1111.



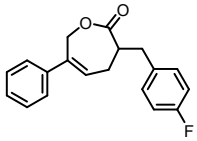
3-(2-bromobenzyl)-6-phenyl-4,7-dihydrooxepin-2(3H)-one(**3c**): white solid, mp: 103-105ºC, 32.7 mg, 61%. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.61 (m, 1H), 7.48-7.23 (m, 7H), 7.17 (m, 1H), 5.95 (m, 1H), 5.43 (m, 1H), 4.82 (d, J = 15.2 Hz, 1H), 3.82 (m, 1H), 3.42 (m, 1H), 2.90 (m, 1H), 2.75-2.47 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-d) δ 175.5, 141.1, 138.1, 136.8, 133.0, 132.5, 129.0, 128.7, 128.6, 127.7, 127.6, 126.2, 124.8, 67.2, 39.2, 38.0, 32.2. HRMS (ESI^{+}): calcd. for $[C_{19}H_{17}BrNaO_2]^{+}$: 379.0310, found: 379.0305.



3-(3-fluorobenzyl)-6-phenyl-4,7-dihydrooxepin-2(3H)-one(**3d**): white solid, mp: 96-98ºC, 27.8 mg, 63%.^{1}H NMR (400 MHz, Chloroform-d) δ 7.43-7.25 (m, 6H), 7.10 (d, J = 7.6 Hz, 1H), 7.07-6.95 (m, 2H), 5.94 (m, 1H), 5.44 (m, 1H), 4.84 (d, J = 15.6 Hz, 1H), 3.72-3.54 (m, 1H), 3.33 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ175.4, 164.1($^{1}J_{CF}$ = 244.4Hz), 141.5, 141.0, 136.9, 130.0($^{3}J_{CF}$ = 8.4Hz), 128.8, 128.7, 127.7, 126.2, 125.1($^{4}J_{CF}$ = 2.9Hz), 116.1($^{2}J_{CF}$ = 20.8Hz), 113.70, 113.5, 77.3, 67.2, 41.1, 37.5, 37.4, 32.2.HRMS (ESI^{+}): calcd. for $[C_{19}H_{17}FNaO_2]^{+}$: 319.1110, found: 319.1106.

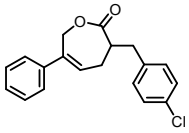


3-(3-bromobenzyl)-6-phenyl-2,3,4,7-tetrahydrooxepine(**3e**): white solid, mp: 84-86ºC, 37.5 mg, 70%. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.33 (d, J = 2.0 Hz, 1H), 7.32-7.02 (m, 8H), 5.80 (m, 1H), 5.30 (m, 1H), 4.70 (d, J = 15.6 Hz, 1H), 3.57-3.42 (m, 1H), 3.17 (m, 1H), 2.57 (m, 1H), 2.53-2.43 (m, 1H), 2.36 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ 175.4, 141.3, 141.0, 136.9, 132.3, 130.2, 129.8, 128.8, 128.7, 128.2, 127.7, 126.2, 122.6, 67.3, 41.2, 37.4, 32.2. HRMS (ESI^{+}): calcd. for $[C_{19}H_{17}BrNaO_2]^{+}$: 379.0310, found: 379.0306.

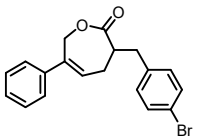


3-(4-fluorobenzyl)-6-phenyl-4,7-dihydrooxepin-2(3H)-one(**3f**): white solid, mp: 114-116ºC, 25.8 mg, 58%. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.38 (d, J = 7.2 Hz, 1H), 7.36-7.31 (m, 1H), 7.28 (m, 5H), 7.04 (m, 2H), 5.93 (m, 1H), 5.43(m, 1H), 4.82

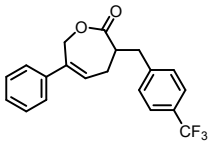
(d, J = 15.6 Hz, 1H), 3.57 (m, 1H), 3.30 (m, 1H), 2.71 (m, 1H), 2.63 (m, 1H), 2.49 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ 175.5, 162.9($^{1}J_{CF}$ = 243.1Hz), 141.0, 136.9, 134.6($^{4}J_{CF}$ = 3.3Hz), 130.8($^{3}J_{CF}$ = 8Hz), 128.7($^{2}J_{CF}$ = 18.6Hz), 127.7, 126.2, 115.5, 115.3, 67.2, 41.5, 36.9, 32.2. HRMS (ESI^{+}): calcd. for $[C_{19}H_{17}FNaO_2]^{+}$: 319.1110, found: 319.1110.



3-(4-chlorobenzyl)-6-phenyl-4,7-dihydrooxepin-2(3H)-one(**3g**): white solid, mp: 113-115ºC, 34.8 mg, 74%. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.34 (m, 5H), 7.26 (m, 4H), 5.93 (m, 1H), 5.43 (m, 1H), 4.83 (d, J = 15.2 Hz, 1H), 3.58 (m, 1H), 3.29 (m, 1H), 2.71 (m, 1H), 2.62 (m, 1H), 2.57-2.39 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ 175.4, 141.0, 137.4, 136.9, 132. 5, 130.7, 128.8, 128.7, 128.6, 127.7, 126.2, 67.2, 41.3, 37.1, 32.2. HRMS (ESI^{+}): calcd. for $[C_{19}H_{17}ClNaO_2]^{+}$: 335.0815, found: 335.0813.

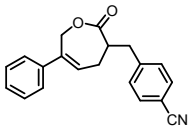


3-(4-bromobenzyl)-6-phenyl-4,7-dihydrooxepin-2(3H)-one(3h): white solid, mp: 98-100ºC, 40.2 mg, 75%. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.52-7.43 (m, 2H), 7.43-7.24 (m, 5H), 7.24-7.15 (m, 2H), 5.93 (m, 1H), 5.42 (m, 1H), 4.83 (d, J = 15.2 Hz, 1H), 3.64-3.51 (m, 1H), 3.28 (m, 1H), 2.70 (m, 1H), 2.66-2.57 (m, 1H), 2.49 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ 175.4, 141.0, 137.9, 136.9, 131.7, 131.1, 128.8, 128.7, 127.7, 126.2, 120.5, 67.2, 41.3, 37.2, 32.2. HRMS (ESI^{+}): calcd. for $[C_{19}H_{17}BrNaO_2]^{+}$: 379.0310, found: 379.0311.

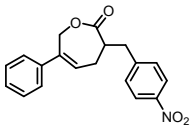


6-phenyl-3-(4-(trifluoromethyl)benzyl)-4,7-dihydrooxepin-2(3H)-one(3i): white solid, mp: 111-113ºC, 32.2 mg, 62%. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.62 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 7.41-7.25 (m, 5H), 5.93 (m, 1H), 5.42 (m, 1H), 4.83 (d, J = 15.6 Hz, 1H), 3.65 (m, 1H), 3.38 (m, 1H), 2.81 (m, 1H), 2.73-2.46 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-d) δ 175.2, 143.1(0), 140.92($^{1}J_{CF}$ = 216Hz), 136.9, 129.7, 129.1, 128.7($^{3}J_{CF}$ = 5.6Hz), 128.6($^{2}J_{CF}$ = 17.7Hz), 127.8, 126.2, 125.6($^{4}J_{CF}$ =

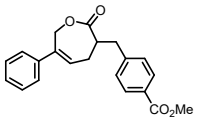
3.7Hz), 125.5(0), 125.4(6), 122.9, 67.2, 41.2, 37.6, 32.3. HRMS (ESI$^+$): calcd. for $[C_{20}H_{17}F_3NaO_2]^+$: 369.1078, found: 369.1081.



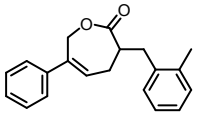
4-((2-oxo-6-phenyl-2,3,4,7-tetrahydrooxepin-3-yl)methyl)benzonitrile(**3j**): white solid, mp: 128-130ºC, 36.4 mg, 82%. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.57-7.48 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.29-7.12 (m, 5H), 5.82 (m, 1H), 5.31 (m, 1H), 4.71 (d, *J* = 15.6 Hz, 1H), 3.60-3.49 (m, 1H), 3.25 (m, 1H), 2.69 (m, 1H), 2.58-2.36 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-d) δ 175.0, 144.6, 140.8, 137.0, 132.4, 130.2, 128.7, 128.4, 127.8, 126.2, 118.9, 110.6, 67.3, 41.1, 37.9, 32.5. HRMS (ESI$^+$): calcd. for $[C_{20}H_{17}NNaO_2]^+$: 326.1157, found: 326.1154.



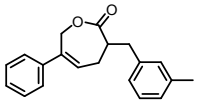
3-(4-nitrobenzyl)-6-phenyl-4,7-dihydrooxepin-2(3H)-one(**3k**): white solid, mp: 137-139ºC, 30.1 mg, 62%. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.21 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.42-7.24 (m, 5H), 5.94 (m, 1H), 5.42 (m, 1H), 4.84 (d, *J* = 15.2 Hz, 1H), 3.68 (m, 1H), 3.41 (m, 1H), 2.86 (m, 1H), 2.61 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-d) δ 174.9, 146.8, 146.7, 140.8, 137.0, 130.3, 128.7, 128.4, 127.8, 126.2, 123.8, 67.3, 41.2, 37.7, 32.5. HRMS (ESI$^+$): calcd. for $[C_{19}H_{17}NNaO_4]^+$: 346.1055, found: 346.1054.



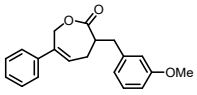
Methyl 4-((2-oxo-6-phenyl-2,3,4,7-tetrahydrooxepin-3-yl)-methyl)benzoate(**3l**): white solid, mp: 109-111ºC, 33.8 mg, 67%. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.04 (d, *J* = 8.0 Hz, 2H), 7.47-7.20 (m, 7H), 5.92 (m, 1H), 5.43 (m, 1H), 4.83 (d, *J* = 15.2 Hz, 1H), 3.95 (s, 3H), 3.66 (m, 1H), 3.37 (m, 1H), 2.80 (m, 1H), 2.71-2.42 (m, 2H). ^{13}C NMR (100MHz, Chloroform-d) δ 175.0, 167.0, 144.4, 140.9, 136.9, 129.9, 129.4, 128.7, 128.7, 128.6, 127.7, 126.2, 67.2, 52.2, 41.1, 37.8, 32.3. HRMS (ESI$^+$): calcd. for $[C_{21}H_{20}NaO_4]^+$: 359.1259, found: 359.1254.



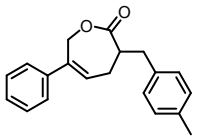
3-(2-methylbenzyl)-6-phenyl-4,7-dihydrooxepin-2(3H)-one(**3m**): white solid, mp: 138-140ºC, 30.4 mg, 67%. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.28-7.18 (m, 3H), 7.18-7.06 (m, 6H), 5.80 (m, 1H), 5.30 (m, 1H), 4.71 (d, *J* = 15.6 Hz, 1H), 3.48 (m, 1H), 3.20 (m, 1H), 2.66 (m, 1H), 2.52 (m, 1H), 2.40 (m, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 175.9, 141.1, 137.0, 136.7, 136.5, 130.6, 130.0, 129.1, 128.7, 127.7, 126.8, 126.2, 126.1, 67.3, 39.8, 34.7, 32.0, 19.8. HRMS (ESI^{+}): calcd. for $[C_{20}H_{20}NaO_2]^{+}$: 315.1361, found: 315.1362.



3-(3-methylbenzyl)-6-phenyl-4,7-dihydrooxepin-2(3H)-one(**3n**): white solid, mp: 91-93ºC, 26.6 mg, 60%. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.36 (m, 2H), 7.28 (m, 4H), 7.11 (d, *J* = 8.78Hz, 3H), 5.93 (m, 1H), 5.44 (m, 1H), 4.83 (d, *J* = 15.2 Hz, 1H), 3.60 (m, 1H), 3.31 (m, 1H), 2.74-2.66 (m, 1H), 2.62 (m, 1H), 2.57-2.42 (m, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 175.9, 141.1, 138.8, 138.3, 136.7, 130.2, 129.2, 128.7, 128.5, 127.7, 127.4, 126.4, 126.2, 67.3, 41.3, 37.7, 32.1, 21.5. HRMS (ESI^{+}): calcd. for $[C_{20}H_{20}NaO_2]^{+}$: 315.1361, found: 315.1359.

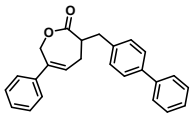


3-(3-methoxybenzyl)-6-phenyl-4,7-dihydrooxepin-2(3H)-one(**3o**): white solid, mp: 97-99ºC, 29.2 mg, 63%. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.30-7.11 (m, 6H), 6.81-6.67 (m, 3H), 5.80 (m, 1H), 5.31 (m, 1H), 4.70 (d, *J* = 15.2 Hz, 1H), 3.74 (s, 3H), 3.49 (m, 1H), 3.20 (m, 1H), 2.63-2.44 (m, 2H), 2.35 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ 175.8, 159.7, 141.1, 140.5, 136.7, 129.6, 129.1, 128.7, 127.7, 126.2, 121.7, 115.3, 111.7, 67.3, 55.3, 41.2, 37.7, 32.1. HRMS (ESI^{+}): calcd. for $[C_{20}H_{20}NaO_3]^{+}$: 331.1310, found: 331.1313.

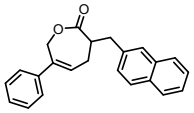


3-(4-methylbenzyl)-6-phenyl-4,7-dihydrooxepin-2(3H)-one(**3p**): white solid, mp: 92-94ºC, 27.7 mg, 63%. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.36 (m, 3H), 7.31-7.25 (m, 2H), 7.20 (m, 4H), 5.93 (m, 1H), 5.44 (m, 1H), 4.83 (d, *J* = 15.6 Hz, 1H), 3.60 (m 1H), 3.31 (m, 1H), 2.75-2.58 (m, 2H), 2.48 (m, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 175.9, 141.1, 136.7, 136.2, 135.8, 129.3, 129.2(5), 129.2, 128.7, 127.6, 126.2, 67.2, 41.4, 37.3, 32.1, 21.1. HRMS (ESI^{+}): calcd. for $[C_{20}H_{20}NaO_2]^{+}$: 315.1361,

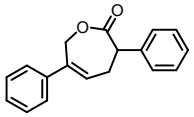
found: 315.1361.



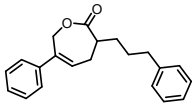
3-([1,1'-biphenyl]-4-ylmethyl)-6-phenyl-4,7-dihydrooxepin-2(3H)-one(**3q**): white solid, mp: 133-135ºC, 32.4 mg, 61%. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.72-7.62 (m, 4H), 7.56-7.25 (m, 10H), 5.97 (m, 1H), 5.48 (m, 1H), 4.86 (d, *J* = 15.2 Hz, 1H), 3.68 (m, 1H), 3.41 (m, 1H), 2.90-2.65 (m, 2H), 2.55 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ 175.7, 141.1, 140.8, 139.6, 138.0, 136.8, 129.8, 129.1, 128.8, 128.7, 127.7, 127.4, 127.3, 127.1, 126.2, 67.3, 41.3, 37.4, 32.2. HRMS (ESI^{+}): calcd. for $[C_{25}H_{22}NaO_2]^{+}$: 377.1517, found: 377.1518.



3-(naphthalen-2-ylmethyl)-6-phenyl-4,7-dihydrooxepin-2(3H)-one(**3r**): white solid, mp: 131-133ºC, 24.9 mg, 51%. ^{1}H NMR (400 MHz, Chloroform-d)δ 7.87 (m, 3H), 7.76 (s, 1H), 7.51 (m, 2H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.41-7.24 (m, 5H), 5.91 (m, 1H), 5.44 (m, 1H), 4.84 (d, *J* = 15.2 Hz, 1H), 3.71 (m, 1H), 3.51 (m, 1H), 2.91 (m, 1H), 2.67 (m, 1H), 2.54 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ 175.8, 141.1, 136.8, 136.4, 133.5, 132.3, 129.0, 128.67, 128.3, 127.9, 127.8, 127.7, 127.6(1), 127.6(0), 126.3, 126.2, 125.7, 67.3, 41.31, 37.9, 32.2. HRMS (ESI^{+}): calcd. for $[C_{23}H_{20}NaO_2]^{+}$: 351.1361, found: 351.1360.

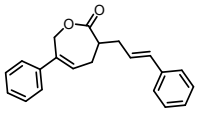


3,6-diphenyl-4,7-dihydrooxepin-2(3H)-one(**3s**): white solid, mp: 113-115ºC, 26.2 mg, 66%. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.31-7.21 (m, 10H), 5.96 (m, 1H), 5.42 (m, 1H), 4.81 (d, *J* = 15.6 Hz, 1H), 4.59-4.45 (m, 1H), 2.98 (m, 1H), 2.73 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ 174.3, 141.0, 137.7, 137.0, 128.8, 128.7, 128.6, 128.4, 127.8, 126.3, 117.7, 67.7, 45.5, 33.5. HRMS (ESI^{+}): calcd. for $[C_{18}H_{16}NaO_2]^{+}$: 287.1048, found: 287.1042.



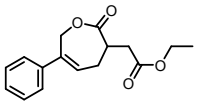
6-phenyl-3-(3-phenylpropyl)-4,7-dihydrooxepin-2(3H)-one(**3t**): white solid, mp: 70-72ºC, 22.4 mg, 52%. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.27-7.19 (m, 4H), 7.19-7.13 (m, 3H), 7.13-7.07 (m, 3H), 5.80 (m, 1H), 5.22 (m, 1H), 4.66 (d, *J* = 15.6 Hz, 1H),

3.16 (m, 1H), 2.68-2.43 (m, 3H), 2.29 (m, 1H), 1.87 (m, 1H), 1.73 (m, 1H), 1.67-1.44 (m, 1H), 1.36 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ 176.0, 142.1, 141.2, 136.8, 129.2, 128.7, 128.5, 128.4, 127.7, 126.2, 125.9, 67.1, 39.3, 36.0, 33.0, 31.6, 29.1. HRMS (ESI$^+$): calcd. for $[C_{21}H_{22}NaO_2]^+$: 329.1517, found: 329.1518.

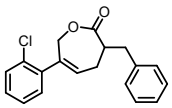


(Z)-6-phenyl-3-(3-phenylallyl)-4,7-dihydrooxepin-2(3H)-one(**3u**): white solid, mp: 113-115ºC, 26.4 mg, 63%. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.29 (m, 2H), 7.27-7.10 (m, 8H), 6.42 (d, *J* = 16.0 Hz, 1H), 6.19 (m, 1H), 5.85 (m, 1H), 5.41-5.26 (m, 1H), 4.72 (d, *J* = 15.2 Hz, 1H), 3.47-3.27 (m, 1H), 2.84-2.68 (m, 1H), 2.62 (m, 1H), 2.42-2.34 (m, 1H), 2.34-2.21 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ 175.7, 141.1, 137.2, 136.9, 133.0, 129.1, 128.7, 128.6, 127.7, 127.4, 126.8, 126.3, 126.2, 67.3, 39.6, 35.3, 32.3.

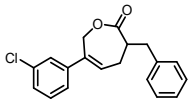
HRMS (ESI$^+$): calcd. for $[C_{21}H_{20}NaO_2]^+$: 327.1361, found: 327.1363.



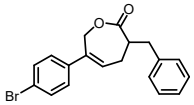
Ethyl 2-(2-oxo-6-phenyl-2,3,4,7-tetrahydrooxepin-3-yl)acetate(**3v**): white solid, mp: 69-71ºC, 30.6 mg, 74%. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.43-7.28 (m, 5H), 5.96 (m, 1H), 5.54 (m, 1H), 4.87 (d, *J* = 15.6 Hz, 1H), 4.21 (m, 2H), 3.94 (m, 1H), 2.99 (m, 1H), 2.65 (m, 1H), 2.57-2.42 (m, 2H), 1.32 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 175.3, 171.7, 141.0, 137.1, 128.7, 128.4, 127.7, 126.3, 67.4, 61.0, 36.5, 36.0, 32.0, 14.2. HRMS (ESI$^+$): calcd. for $[C_{16}H_{18}NaO_4]^+$: 297.1103, found: 297.1106.



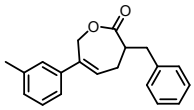
3-benzyl-6-(2-chlorophenyl)-4,7-dihydrooxepin-2(3H)-one(**3w**)**:** white solid, mp: 110-112ºC, 29.6 mg, 63%. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.38-7.30 (m, 3H), 7.30-7.24 (m, 3H), 7.24-7.16 (m, 3H), 5.78 (m, 1H), 5.42 (m, 1H), 4.51 (d, *J* = 15.2 Hz, 1H), 3.63 (m 1H), 3.31 (m, 1H), 2.70 (m, 1H), 2.62 (m, 1H), 2.42 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ 175.7, 140.8, 138.9, 136.2, 132.1, 131.9, 130.5, 129.6, 129.4, 129.1, 128.6, 127.1, 126.7, 66.8, 41.1, 37.8, 32.1. HRMS (ESI$^+$): calcd. for $[C_{19}H_{17}ClNaO_2]^+$: 335.0815, found: 335.0817.



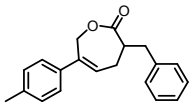
3-benzyl-6-(3-chlorophenyl)-4,7-dihydrooxepin-2(3H)-one(**3x**): white solid, mp: 70-72ºC, 32.8 mg, 70%. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.24 (m, 2H), 7.15 (m, 6H), 7.01 (m, 1H), 5.80 (m, 1H), 5.27 (m, 1H), 4.61 (d, *J* = 15.2 Hz, 1H), 3.47 (m, 1H), 3.20 (m, 1H), 2.66-2.43 (m, 2H), 2.43-2.25 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ 175.5, 142.8, 138.8, 135.7, 134.5, 130.3, 129.9, 129.4, 128.7, 127.7, 126.7, 126.5, 124.3, 66.8, 41.2, 37.7, 32.1. HRMS (ESI^{+}): calcd. for $[C_{19}H_{17}ClNaO_2]^{+}$: 335.0815, found: 335.0817.



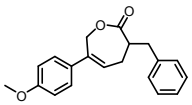
3-benzyl-6-(4-bromophenyl)-4,7-dihydrooxepin-2(3H)-one(**3y**) [6]: white solid, mp: 106-108ºC, 32.2 mg, 60%. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.49 (d, *J* = 8.4 Hz, 2H), 7.37 (m, 2H), 7.34-7.25 (m, 4H), 7.14 (d, *J* = 8.4 Hz, 2H), 5.93 (m, 1H), 5.42 (m, 1H), 4.75 (d, *J* = 15.2 Hz, 1H), 3.67-3.54 (m, 1H), 3.34 (m, 1H), 2.73 (m, 1H), 2.64 (m, 1H), 2.47 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ 175.5, 139.9, 138.8, 135.8, 131.8, 129.7, 129.3, 128.7, 127.9, 126.7, 121.7, 66.9, 41.2, 37.7, 32.1.



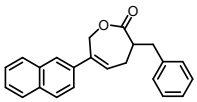
3-benzyl-6-(m-tolyl)-4,7-dihydrooxepin-2(3H)-one(**3z**) [6]: white solid, mp: 94-96ºC, 28.8 mg, 65%. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.41-7.26 (m, 5H), 7.18 (s, 4H), 5.89 (m, 1H), 5.42 (m, 1H), 4.82 (d, *J* = 15.2 Hz, 1H), 3.61 (m, 1H), 3.35 (m, 1H), 2.74 (m, 1H), 2.63 (m, 1H), 2.48 (m, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 175.9, 138.9, 138.2, 137.5, 136.5, 129.4, 129.3, 128.6, 128.2, 126.6, 126.1, 67.3, 41.3, 37.7, 32.1, 21.1.



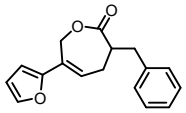
3-benzyl-6-(p-tolyl)-4,7-dihydrooxepin-2(3H)-one(**3aa**) [6]: white solid, mp: 94-96ºC, 34.1 mg, 77%. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.39 (m, 2H), 7.35-7.23 (m, 4H), 7.20-7.03 (m, 3H), 5.92 (m, 1H), 5.43 (m, 1H), 4.83 (d, *J* = 15.6 Hz, 1H), 3.72-3.55 (m, 1H), 3.36 (m, 1H), 2.75 (m, 1H), 2.65 (m, 1H), 2.49 (m, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 175.9, 141.1, 138.9, 138.3, 136.8, 129.4, 128.8, 128.6, 128.6, 128.4, 127.0, 126.7, 123.3, 67.3, 41.3, 37.8, 32.1, 21.5.



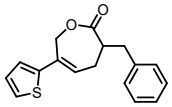
3-benzyl-6-(4-methoxyphenyl)-4,7-dihydrooxepin-2(3H)-one(3ab) [6]: white solid, mp: 93-95ºC, 34.6 mg, 75%. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.38 (m, 2H), 7.34-7.25 (m, 3H), 7.22 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 5.85 (m, 1H), 5.40 (m, 1H), 4.81 (d, *J* = 15.2 Hz, 1H), 3.84 (s, 3H), 3.69-3.52 (m, 1H), 3.34 (m, 1H), 2.73 (m, 1H), 2.62 (m, 1H), 2.48 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ 175.9, 159.2, 139.0, 136.2, 133.5, 129.4, 128.6, 127.6, 127.5, 126.6, 114.0, 67.3, 55.4, 41.3, 37.7, 32.1.



3-benzyl-6-(naphthalen-2-yl)-4,7-dihydrooxepin-2(3H)-one(3ac) [6]: white solid, mp: 113-115ºC, 30.0 mg, 61%. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.84-7.72 (m, 3H), 7.65 (d, *J* = 2.0 Hz, 1H), 7.507.42 (m, 2H), 7.40-7.30 (m, 3H), 7.26 (m, 3H), 5.99 (m, 1H), 5.44 (m, 1H), 4.90 (d, *J* = 15.2 Hz, 1H), 3.61 (m, 1H), 3.31 (m, 1H), 2.70 (m, 1H), 2.67-2.57 (m, 1H), 2.47 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ 175.8, 138.9, 138.3, 136.7, 133.3, 132.7, 129.6, 129.4, 128.7, 128.4, 128.0, 127.7, 126.7, 126.6, 126.2, 125.0, 124.4, 67.2, 41.3, 37.8, 32.2.

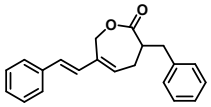


3-benzyl-6-(furan-2-yl)-4,7-dihydrooxepin-2(3H)-one(3ad) [6]**:** white solid, mp: 71-73ºC, 22.5 mg, 56%. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.36-7.29 (m, 2H), 7.24 (m, 3H), 7.16 (m, 1H), 7.00-6.89 (m, 2H), 6.09 (m, 1H), 5.32 (m, 1H), 4.89 (d, *J* = 15.2 Hz, 1H), 3.52 (m, 1H), 3.29 (m, 1H), 2.68 (m, 1H), 2.57 (m, 1H), 2.44 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ 175.5, 143.5, 138.8, 130.2, 129.3, 128.7, 127.7, 127.2, 126.7, 124.6, 123.0, 66.4, 41.2, 37.6, 31.8.

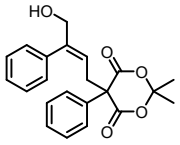


3-benzyl-6-(thiophen-2-yl)-4,7-dihydrooxepin-2(3H)-one(3ae) [6]**:** white solid, mp: 83-85ºC, 22.2 mg, 52%. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.26-7.20 (m, 3H), 7.18-7.14 (m, 3H), 6.29 (m, 1H), 6.18 (m, 1H), 6.15 (d, *J* = 3.6 Hz, 1H), 5.14 (m, 1H), 4.73 (d, *J* = 15.2 Hz, 1H), 3.44 (m, 1H), 3.20 (m, 1H), 2.60 (m, 1H), 2.56-2.48 (m, 1H), 2.41-2.31 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ 175.6, 152.1, 142.4, 138.8,

129.3, 128.6, 126.7, 126.3, 125.0, 111.4, 105.4, 64.0, 41.2, 37.7, 31.5.



(E)-3-benzyl-6-styryl-4,7-dihydrooxepin-2(3H)-one(3af) [6]**:** white solid, mp: 132--134ºC, 25.1 mg, 55%. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.39-7.35 (m, 2H), 7.32 (m, 4H), 7.26-7.21 (m, 4H), 6.65 (d, *J* = 16.4 Hz, 1H), 6.42 (d, *J* = 16.4 Hz, 1H), 5.88 (m, 1H), 5.13 (m, 1H), 4.92 (d, *J* = 14.8 Hz, 1H), 3.49 (m, 1H), 3.28 (m, 1H), 2.67 (m, 1H), 2.57 (m, 1H), 2.43 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ 175.8, 138.8, 136.8, 134.0, 131.7, 129.7, 129.3, 128.8, 128.6, 127.8, 126.8, 126.7, 126.4, 63.4, 41.2, 37.6, 32.0.



(*E*)-5-(4-hydroxy-3-phenylbut-2-en-1-yl)-2,2-dimethyl-5-phenyl-1,3-dioxane-4,6-dione(4s): white solid; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.47–7.32 (m, 7H), 7.29–7.24 (m, 2H), 7.22–7.19 (m, 1H), 5.72 (t, *J* = 8.0 Hz, 1H), 4.48 (s, 2H), 3.22 (d, *J* = 8.0 Hz, 2H), 2.53 (s, 1H), 1.63 (s, 3H), 1.21 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 166.6, 143.9, 141.0, 135.1, 130.0, 129.3, 128.4, 127.6, 126.5, 126.1, 124.2, 106.1, 60.8, 60.2, 40.5, 29.2, 27.6. HRMS (ESI^{+}): calcd. for $[C_{22}H_{22}NaO_5]^{+}$: 389.1365, found: 389.1366.

4. References

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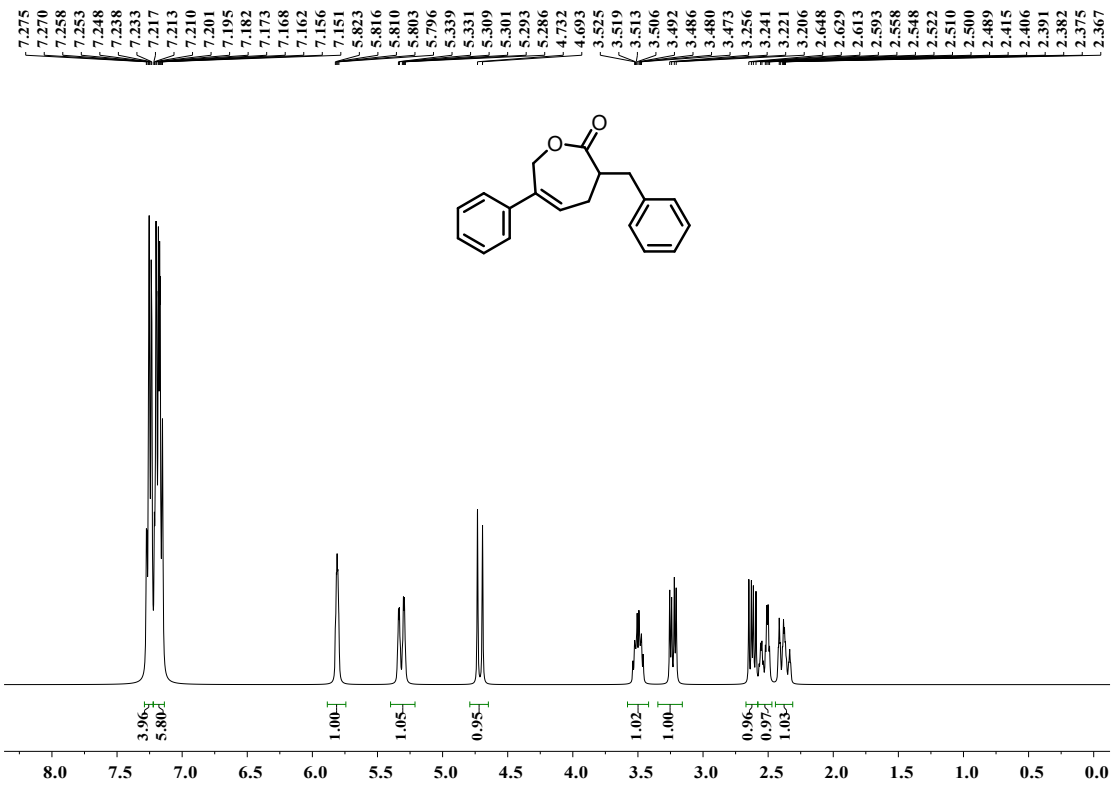
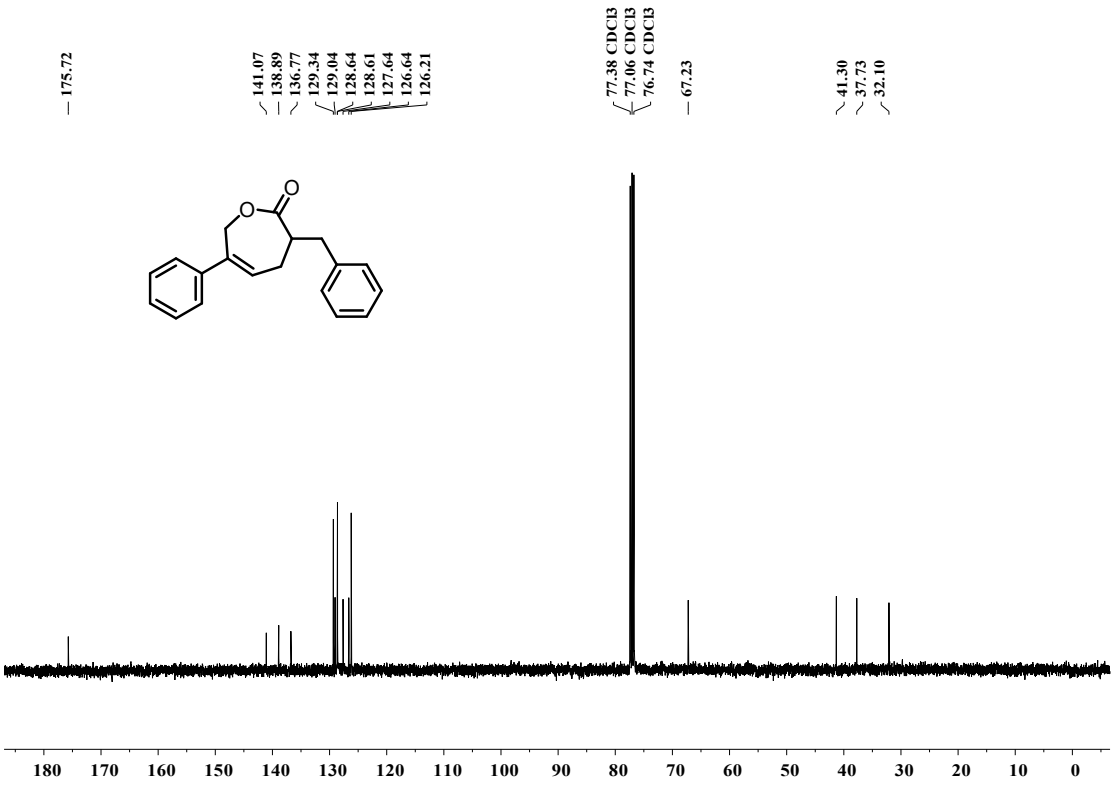
5. Copies of ^{1}H and ^{13}C NMR spectra

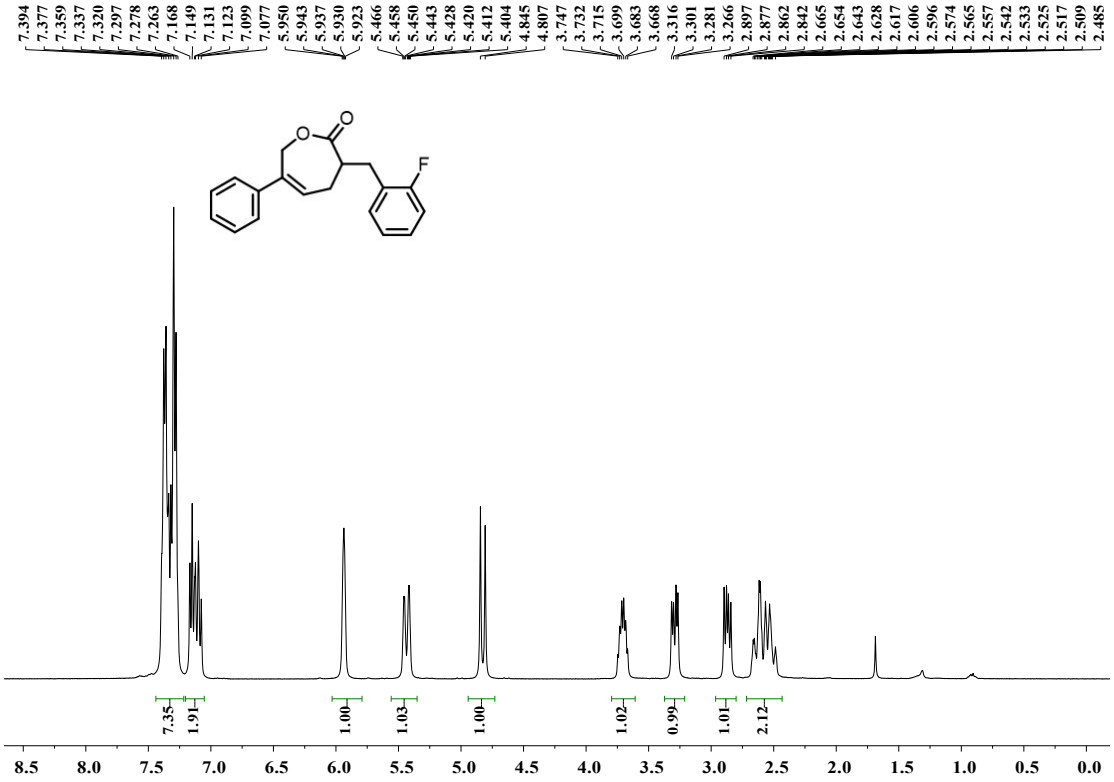
^{1}H NMR of 3a



^{13}C NMR of 3a



^{1}H NMR of 3b



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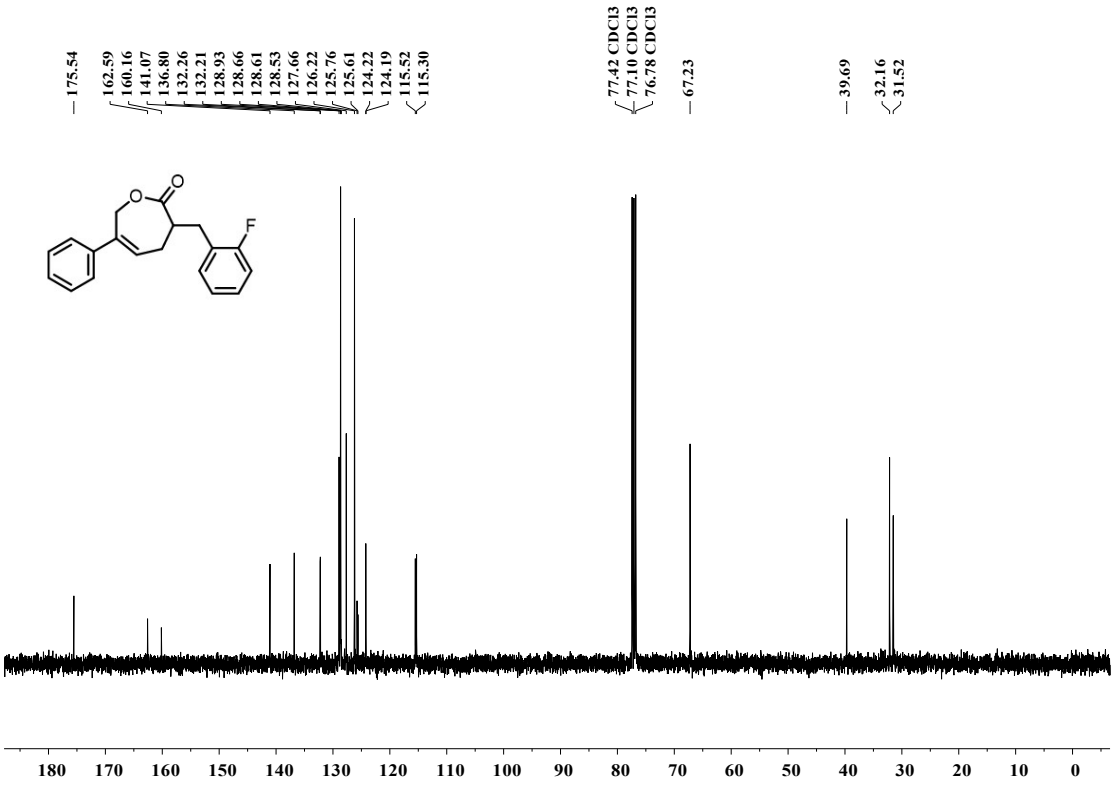
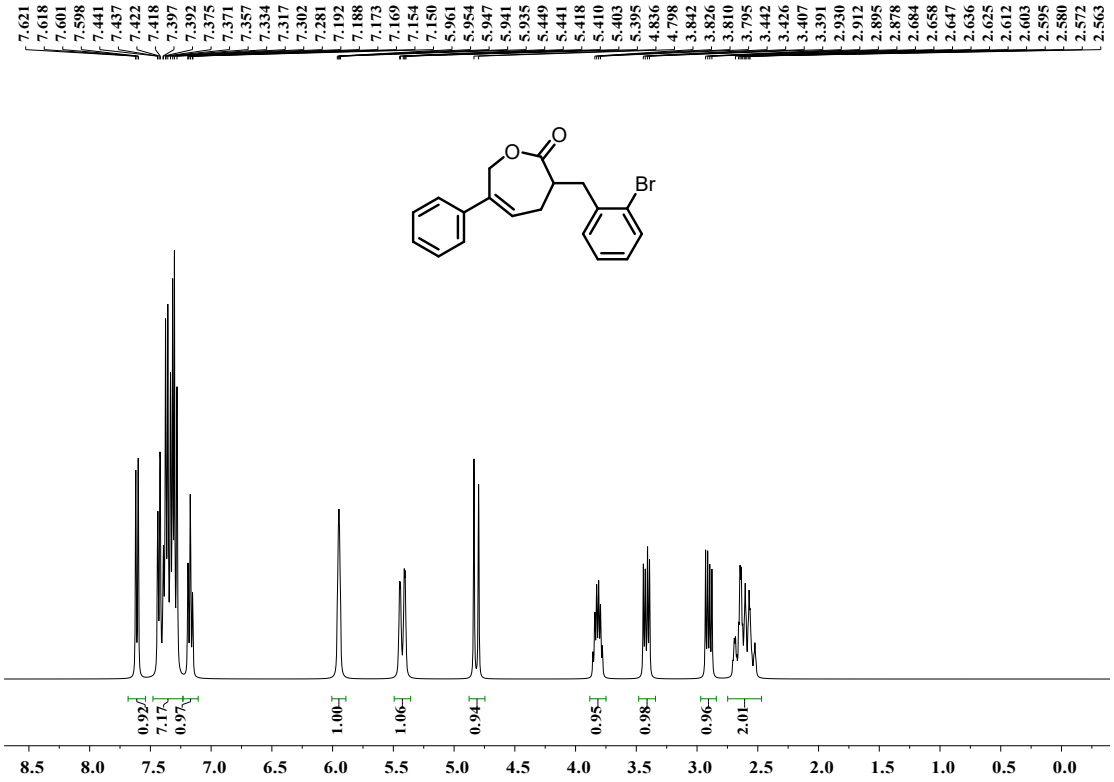
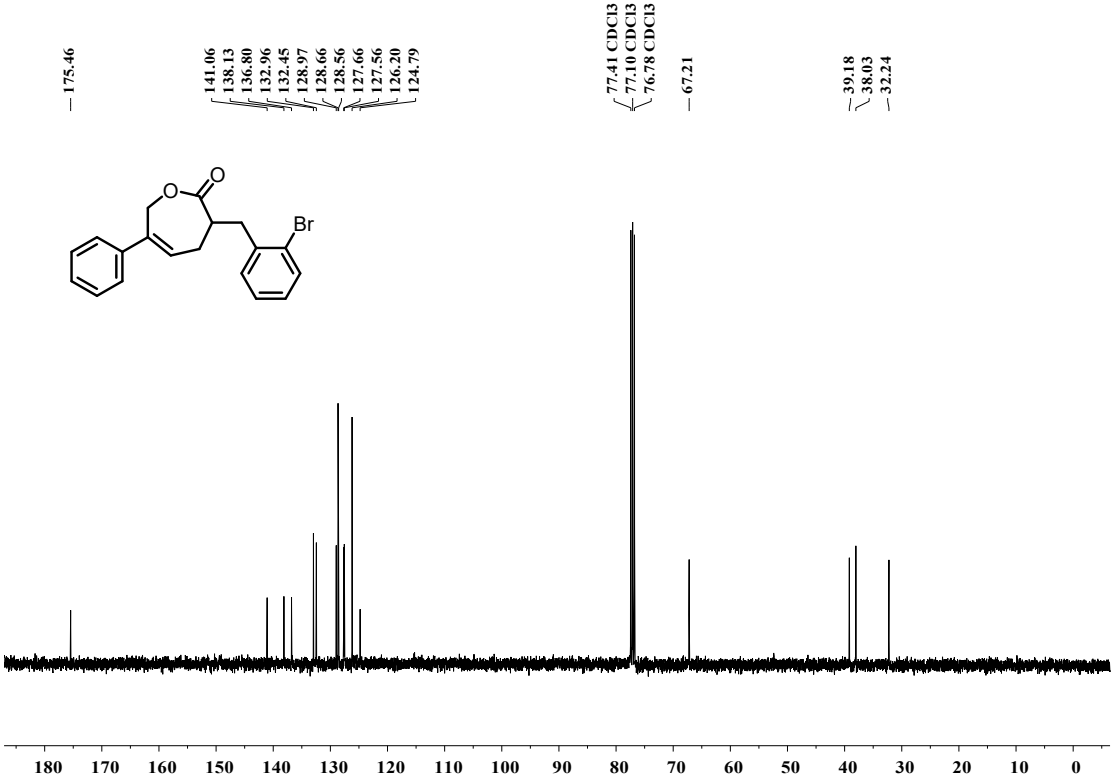


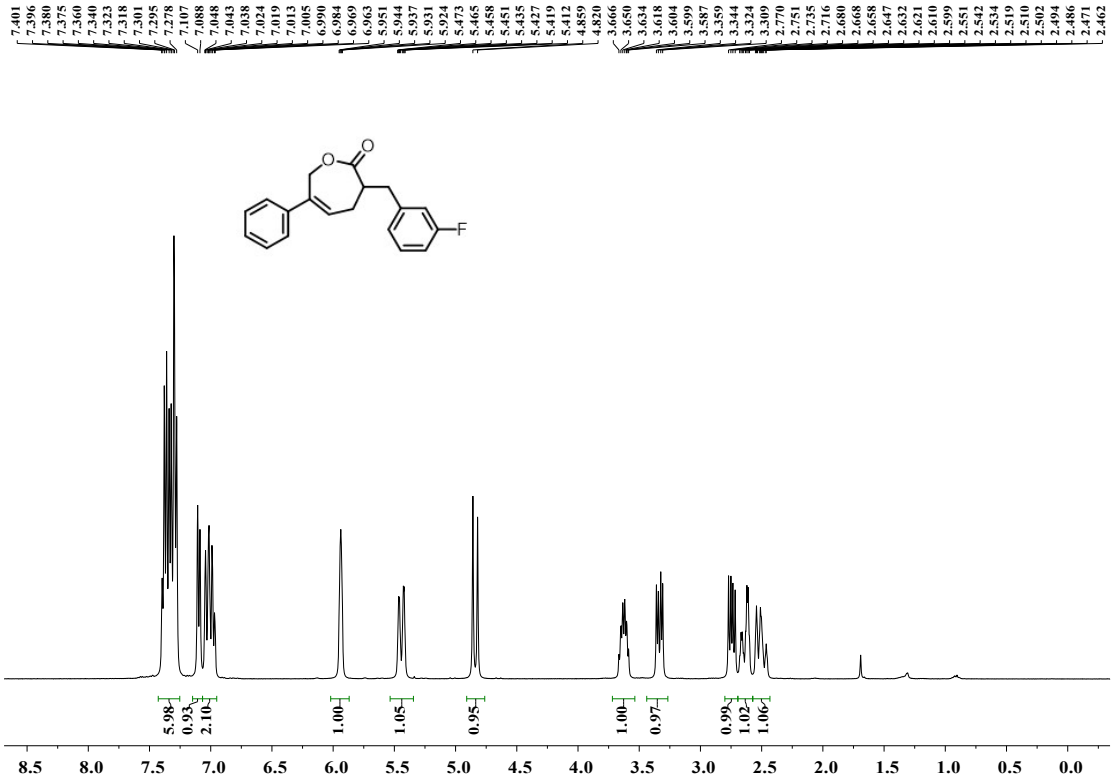
^{1}H NMR of 3c



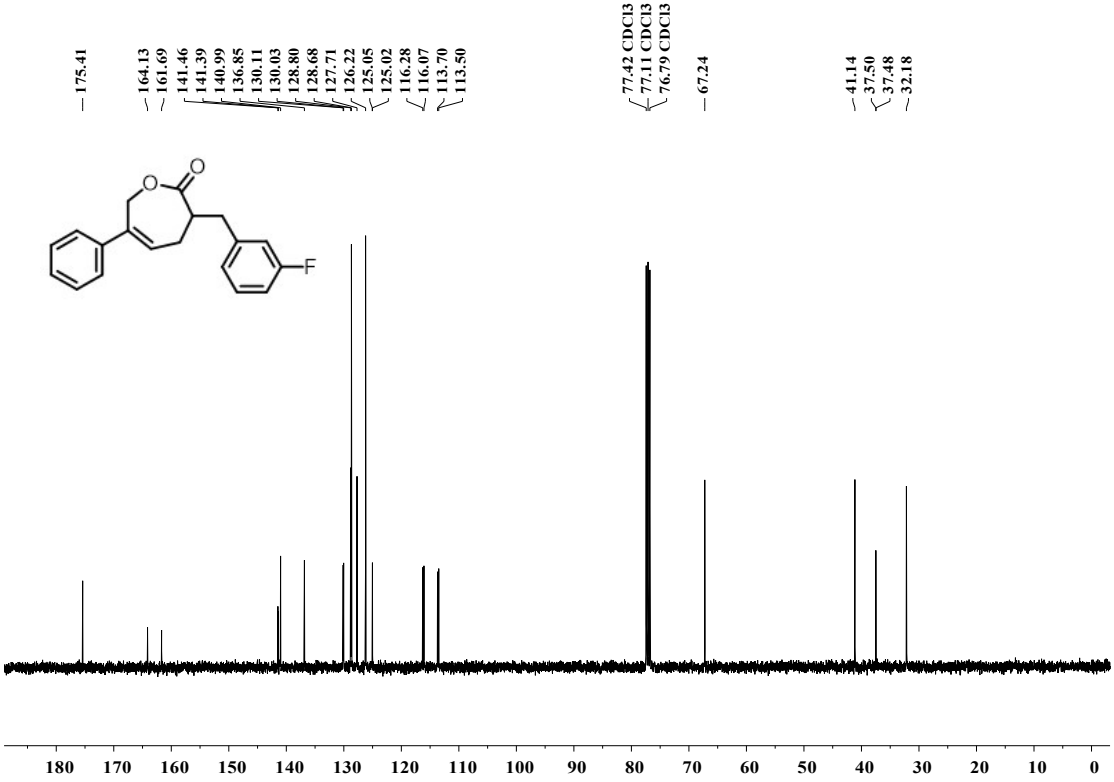
^{13}C NMR of 3c



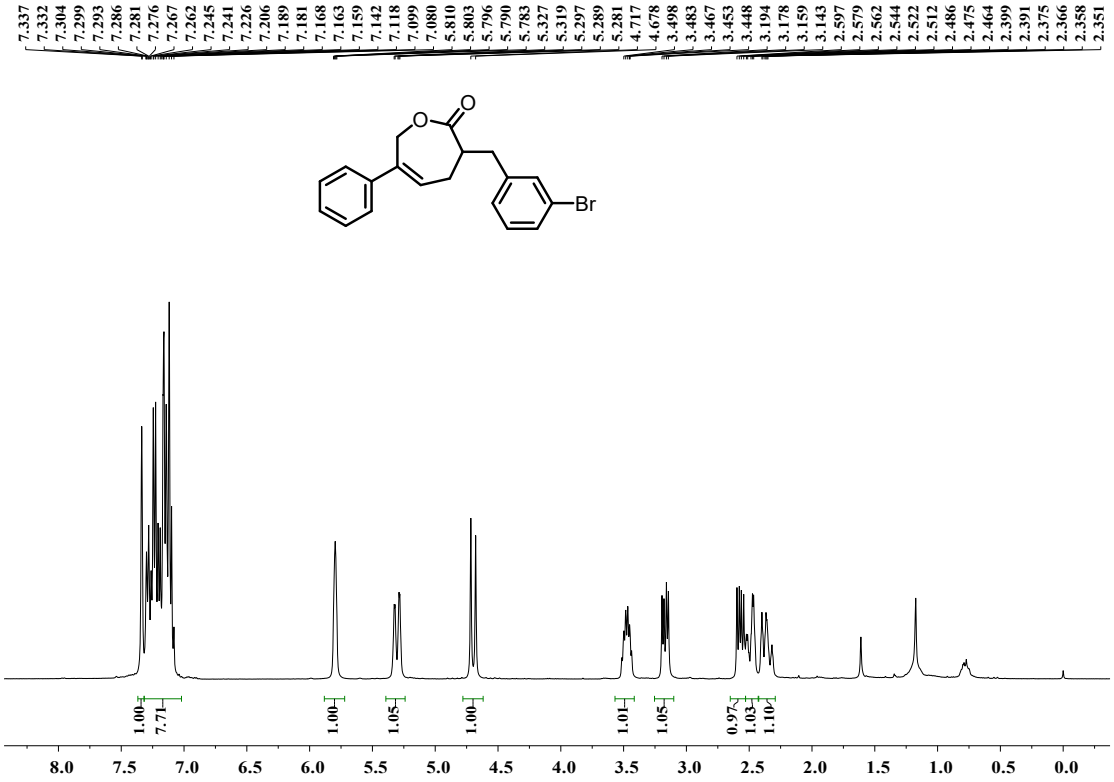
^{1}H NMR of 3d



^{13}C NMR of 3d



^{1}H NMR of 3e



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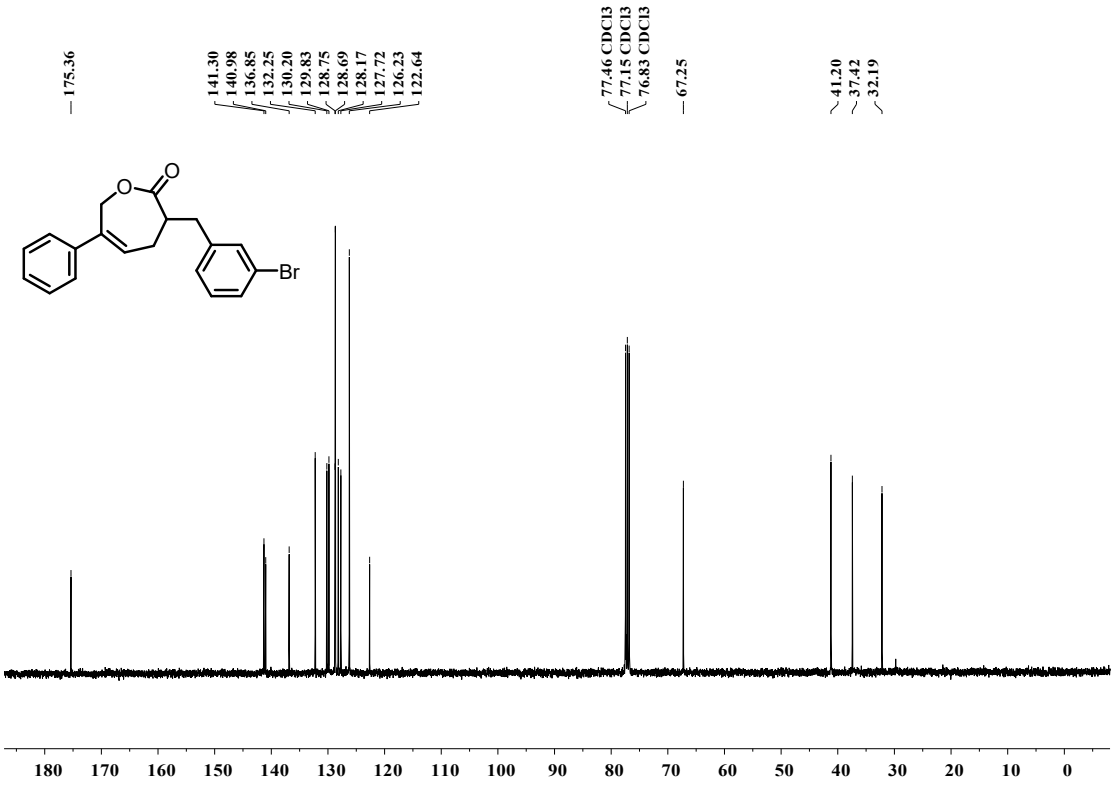
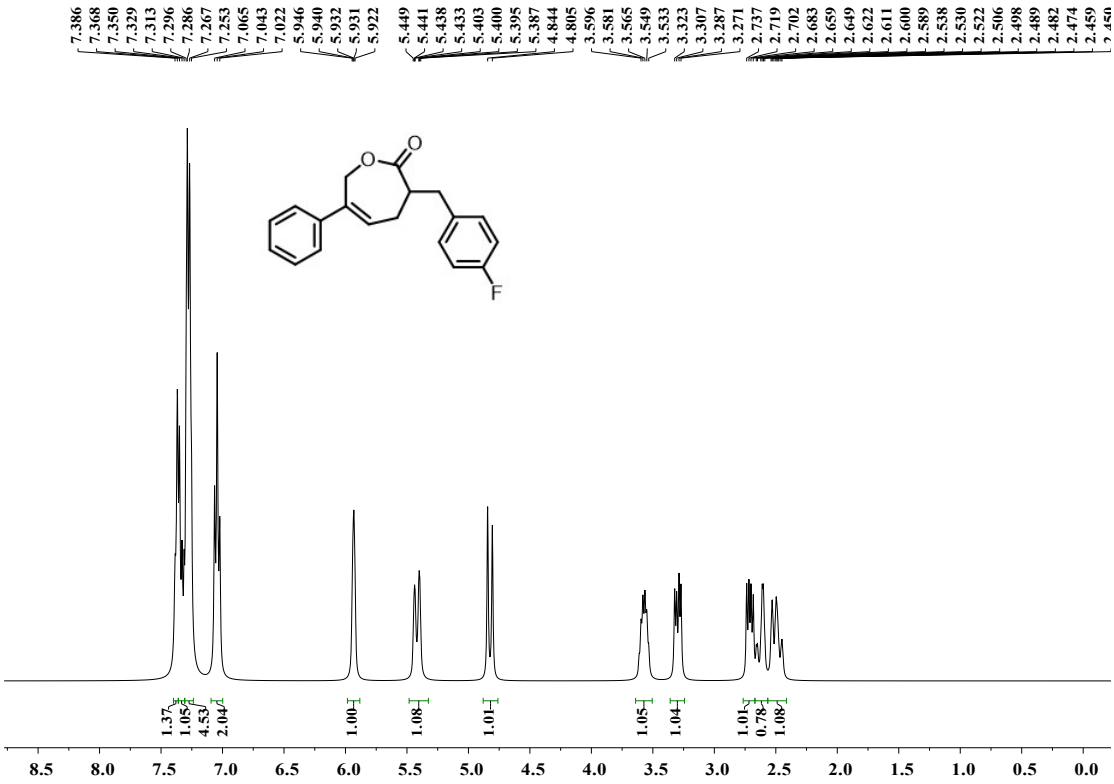
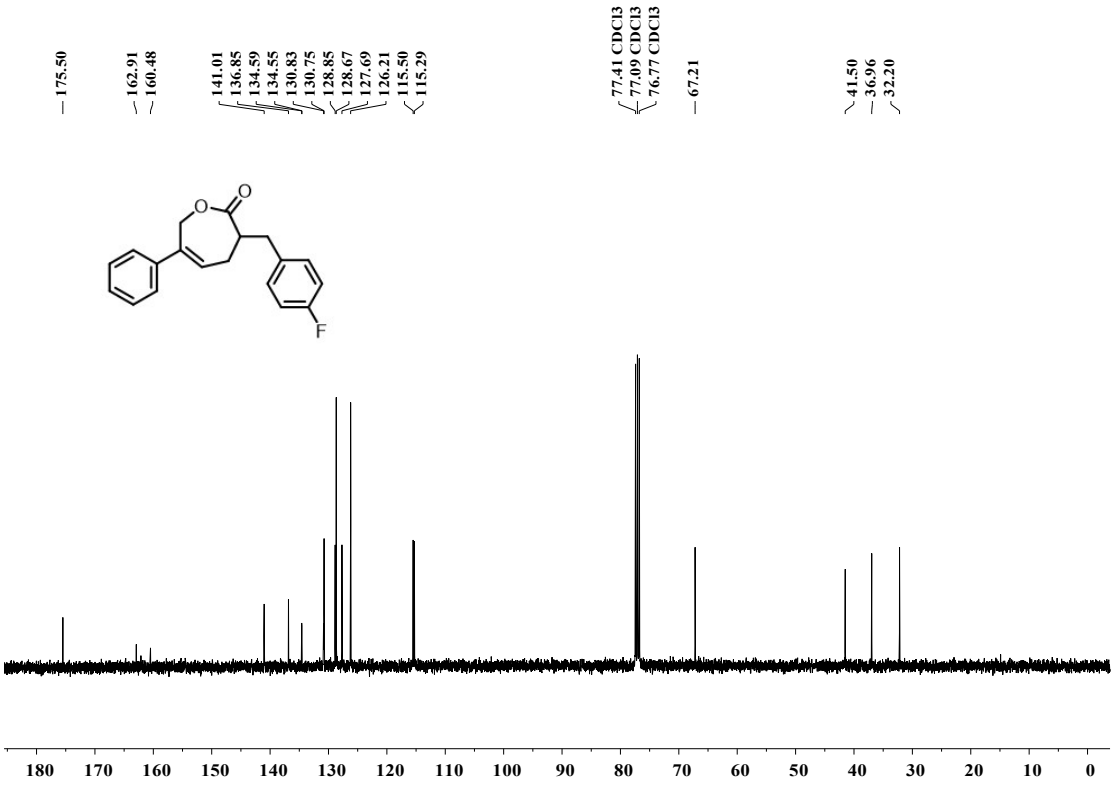


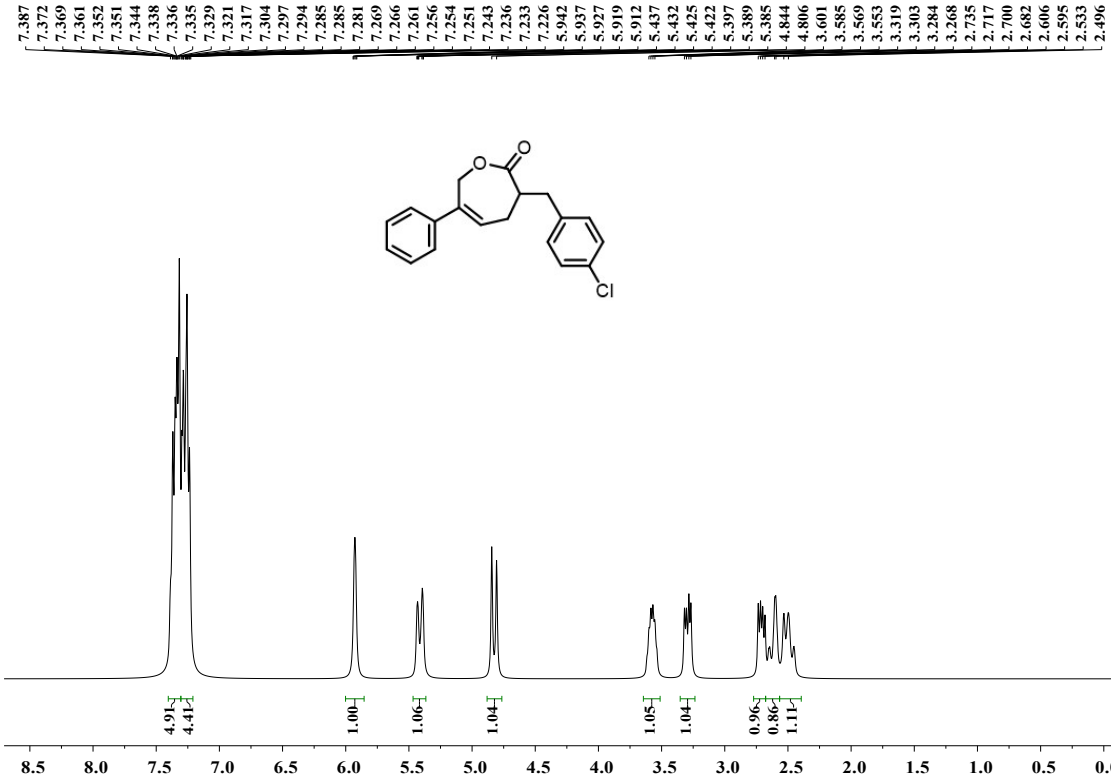
^{1}H NMR of 3f



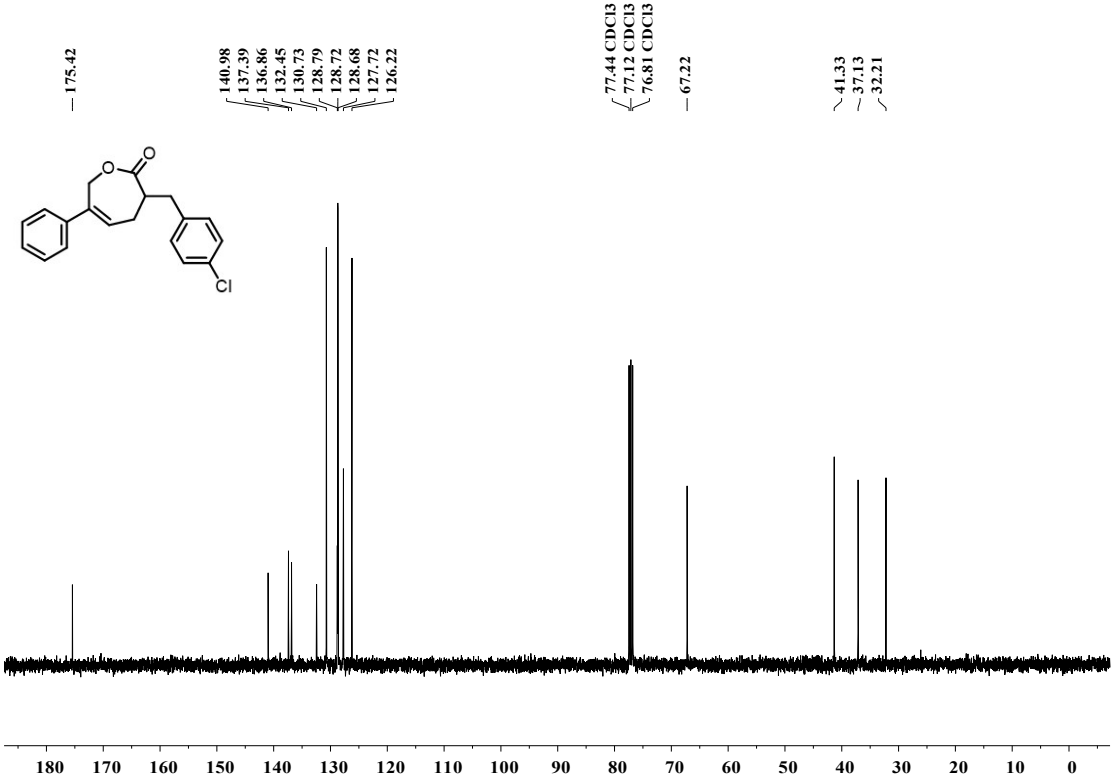
^{13}C NMR of 3f



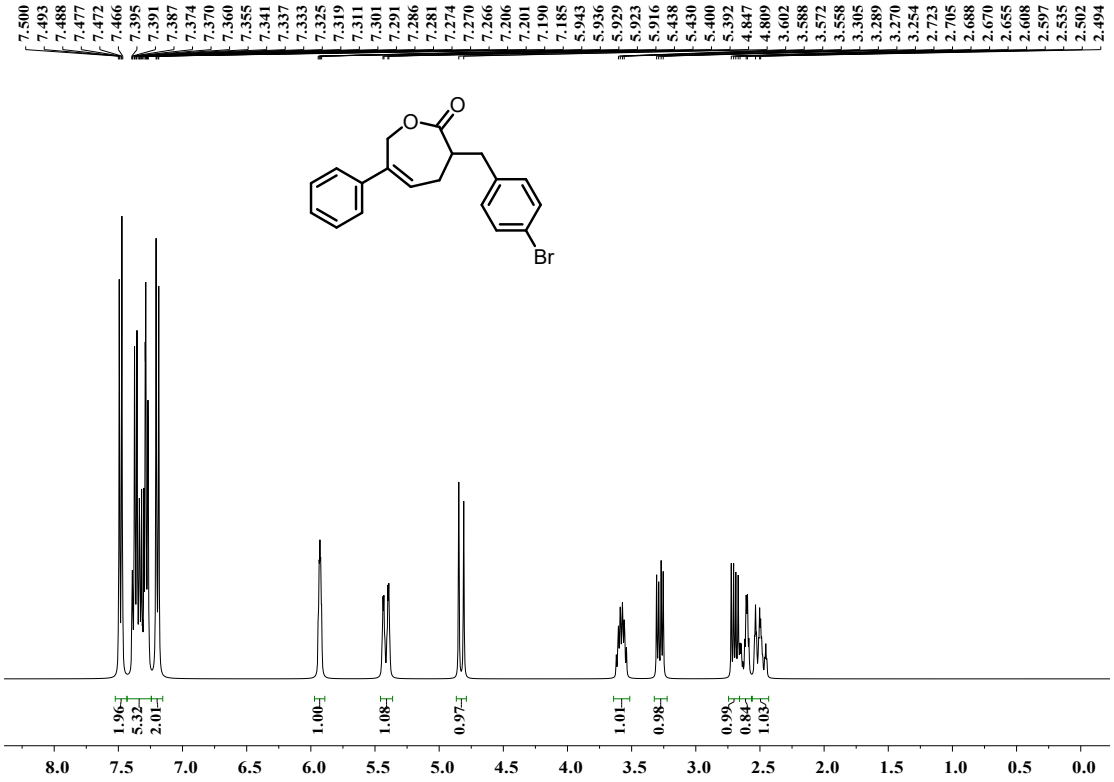
^{1}H NMR of 3g



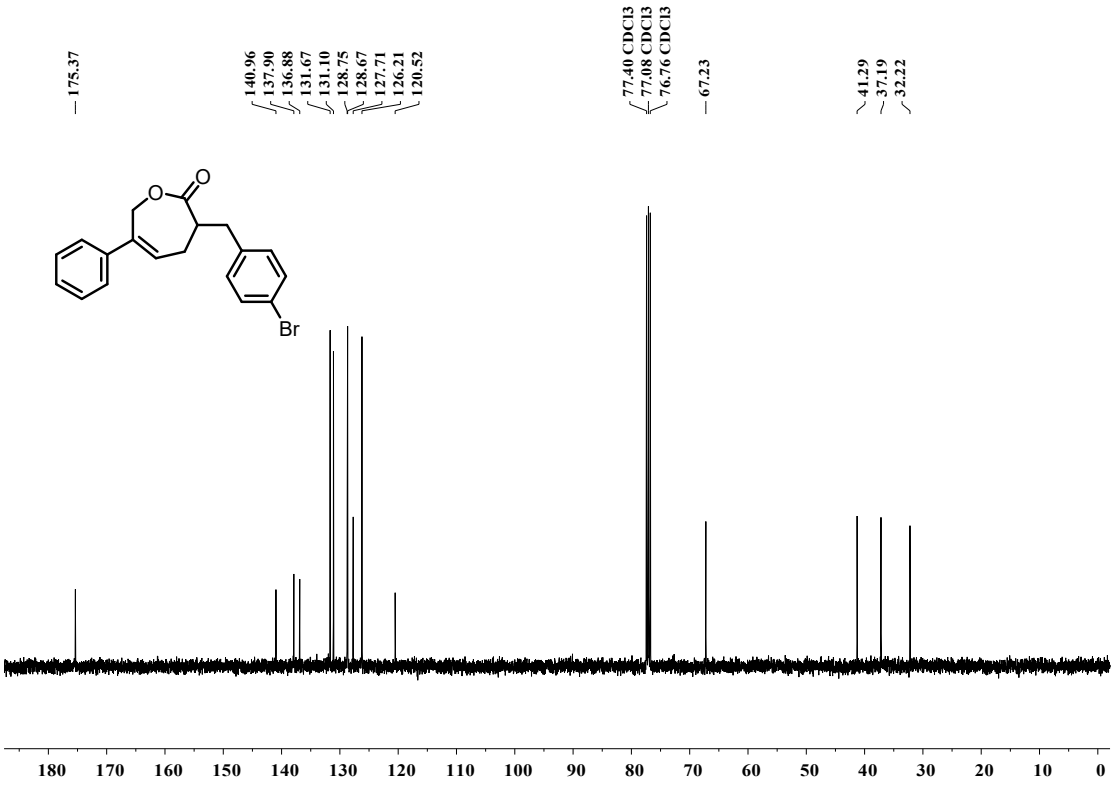
^{13}C NMR of 3g



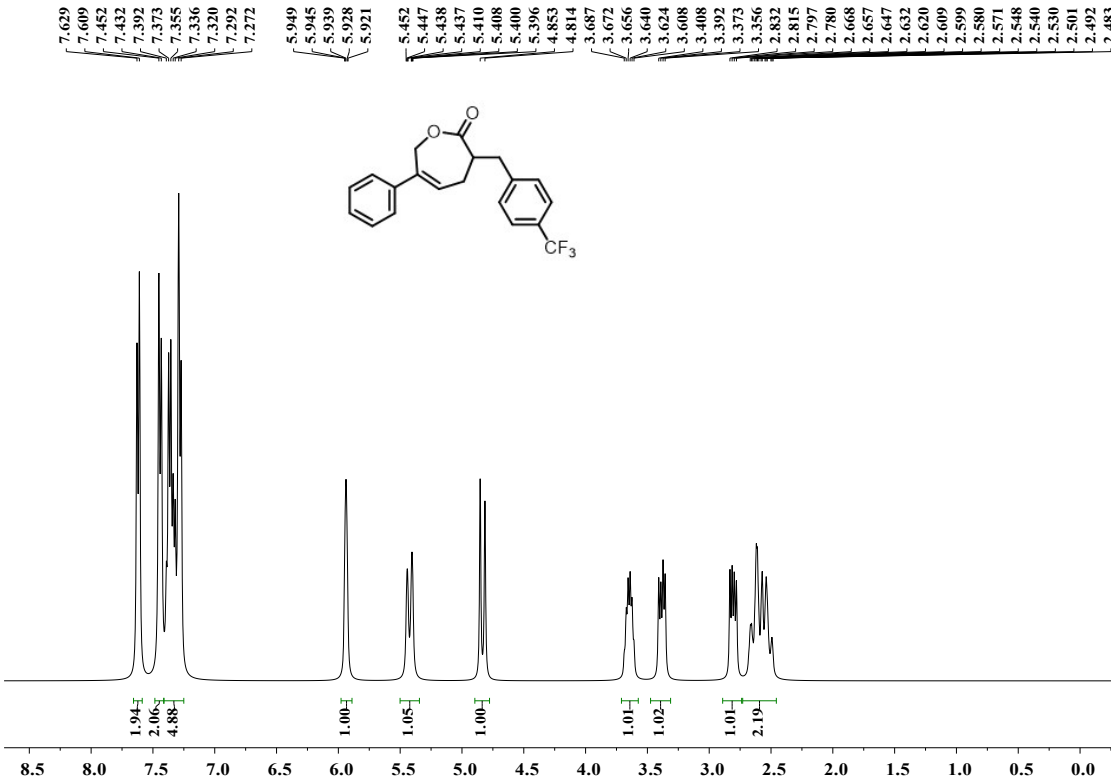
^{1}H NMR of 3h



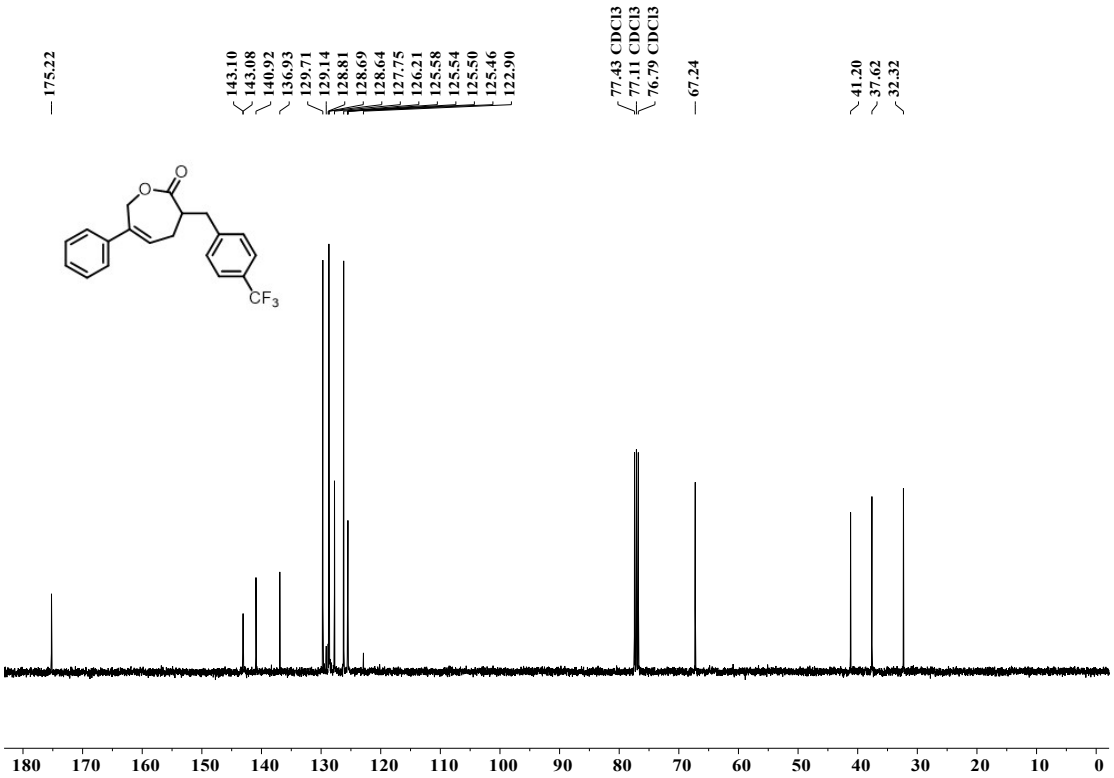
^{13}C NMR of 3h



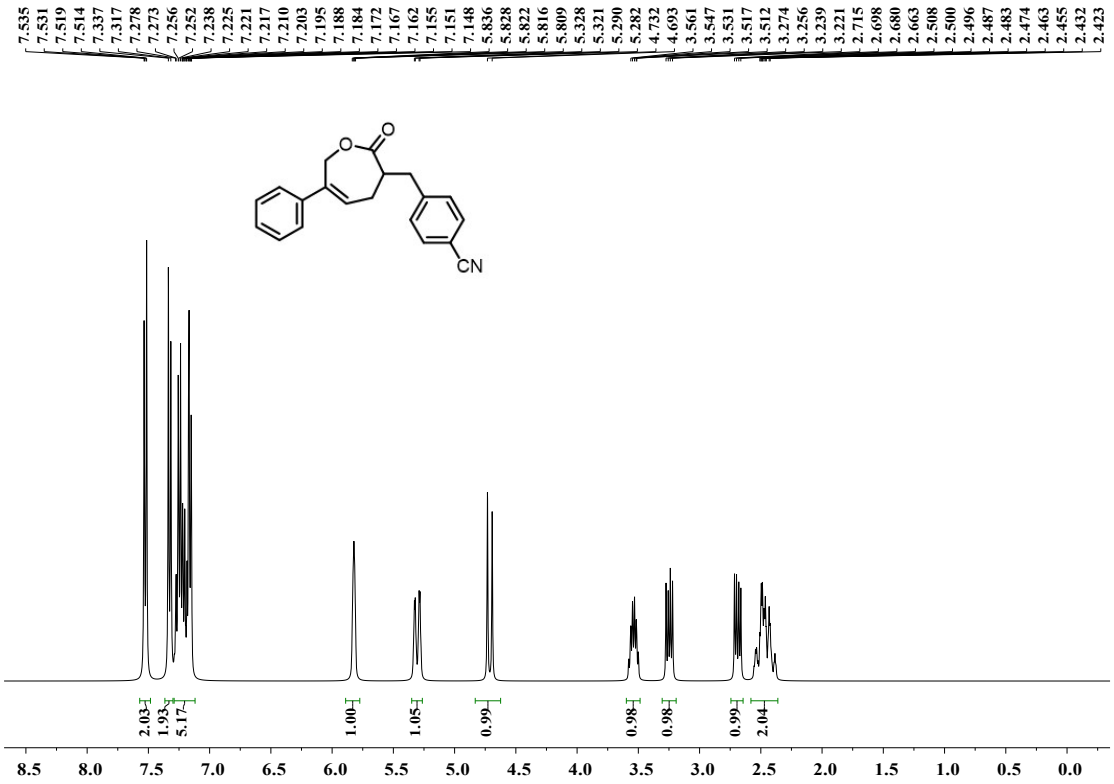
^{1}H NMR of 3i



^{13}C NMR of 3i



^{1}H NMR of 3j



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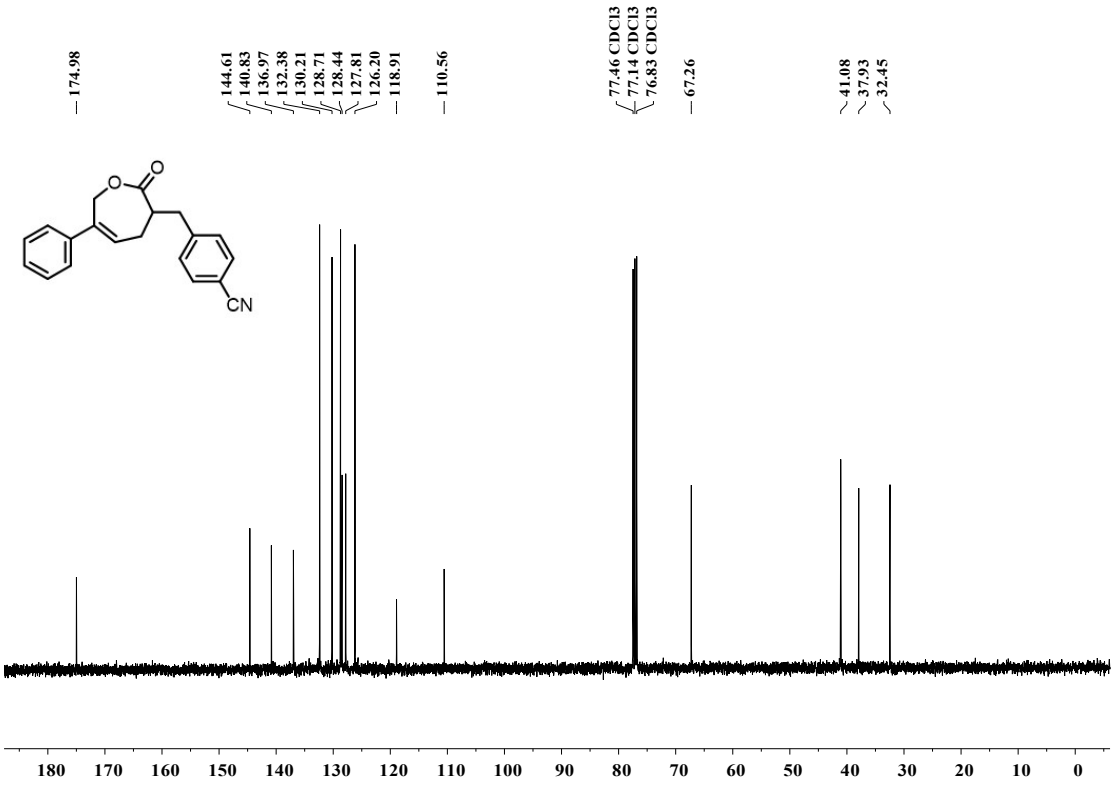
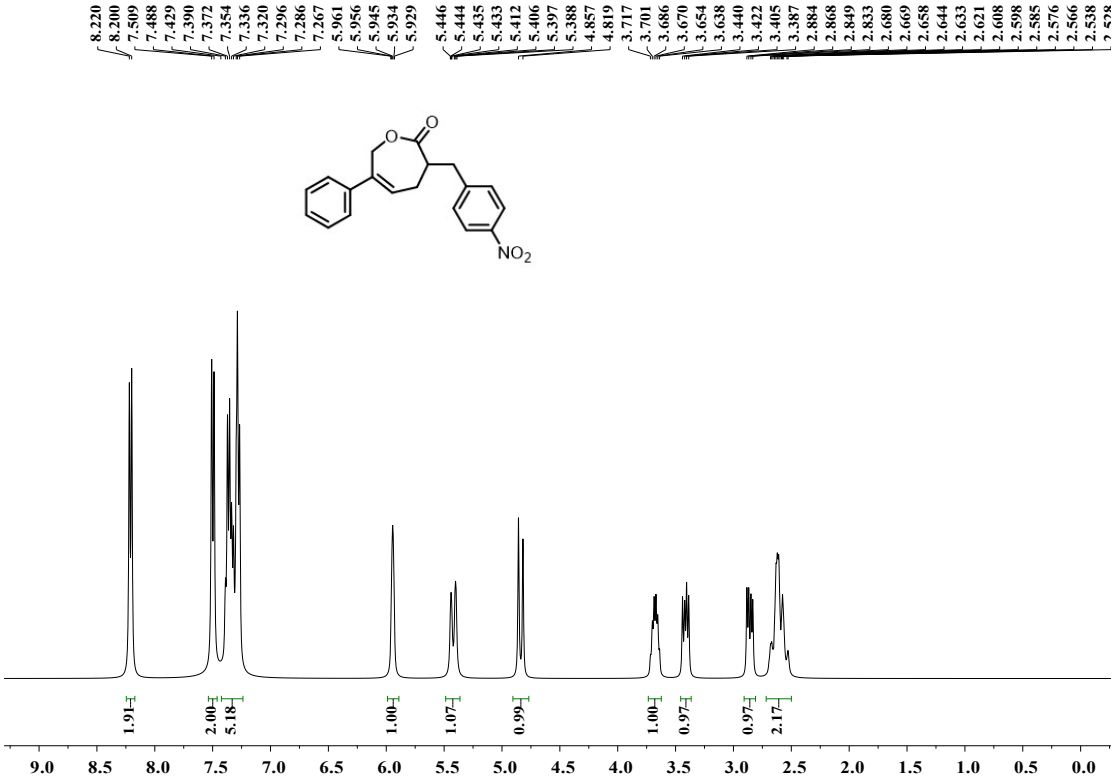


^{1}H NMR of 3k



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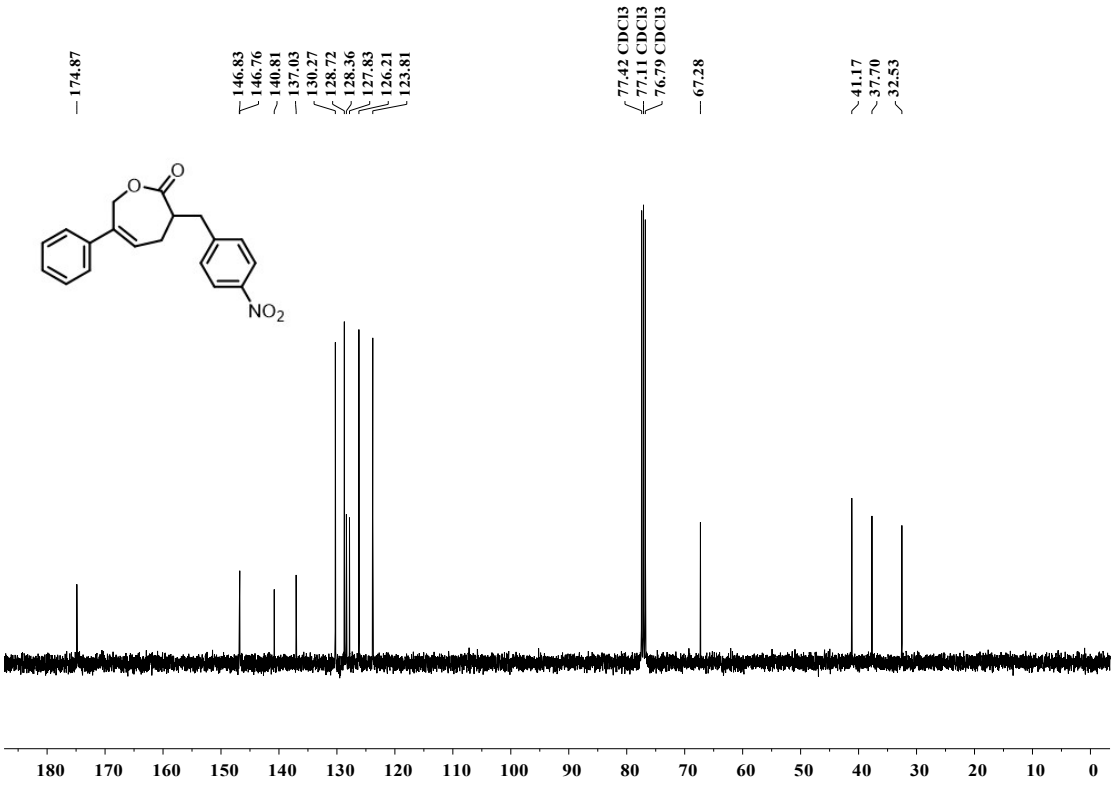
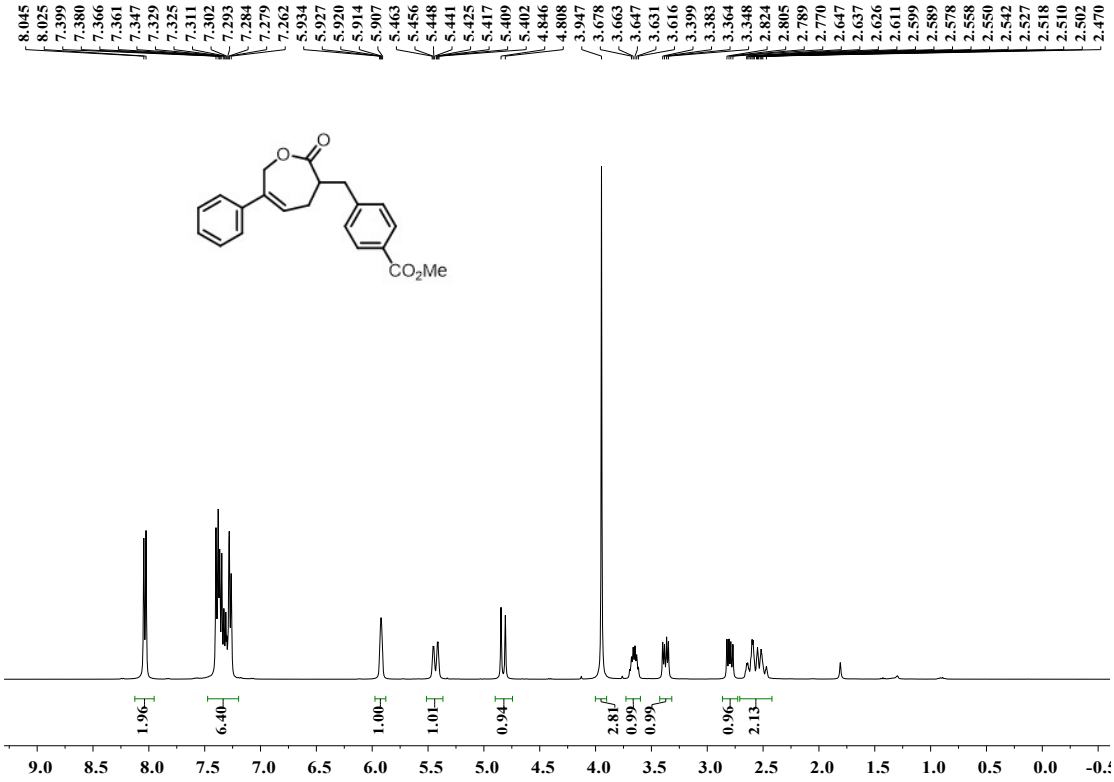
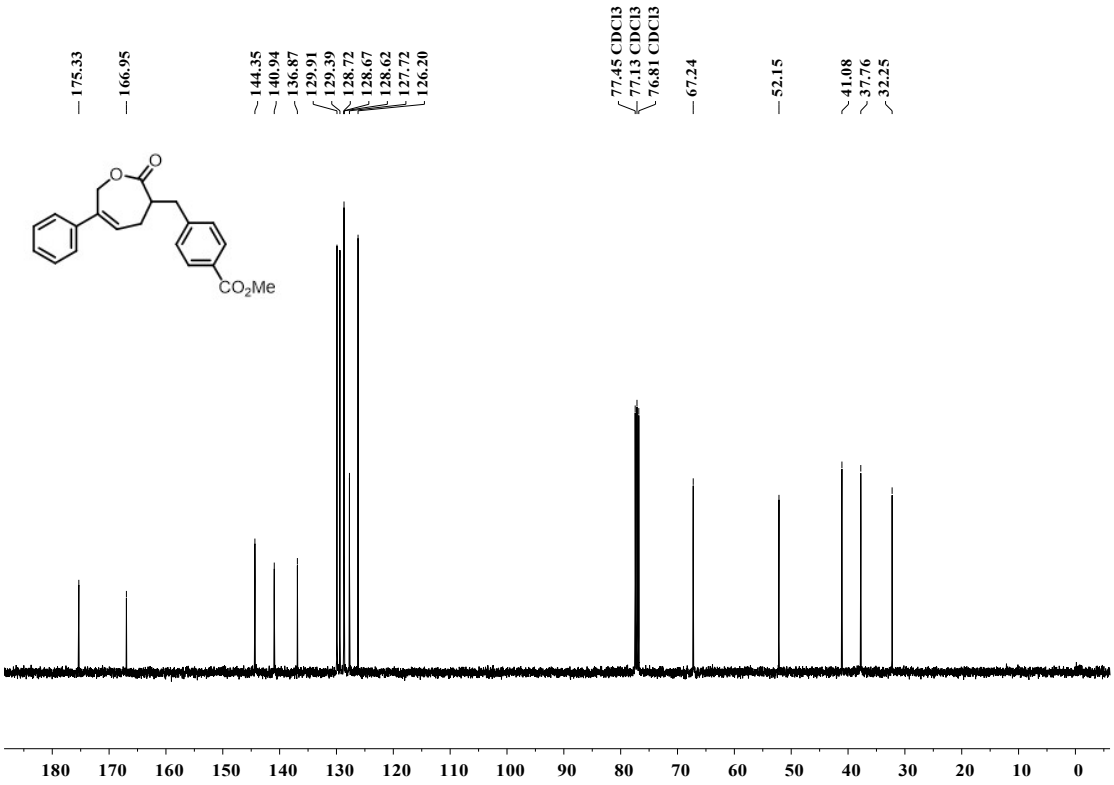


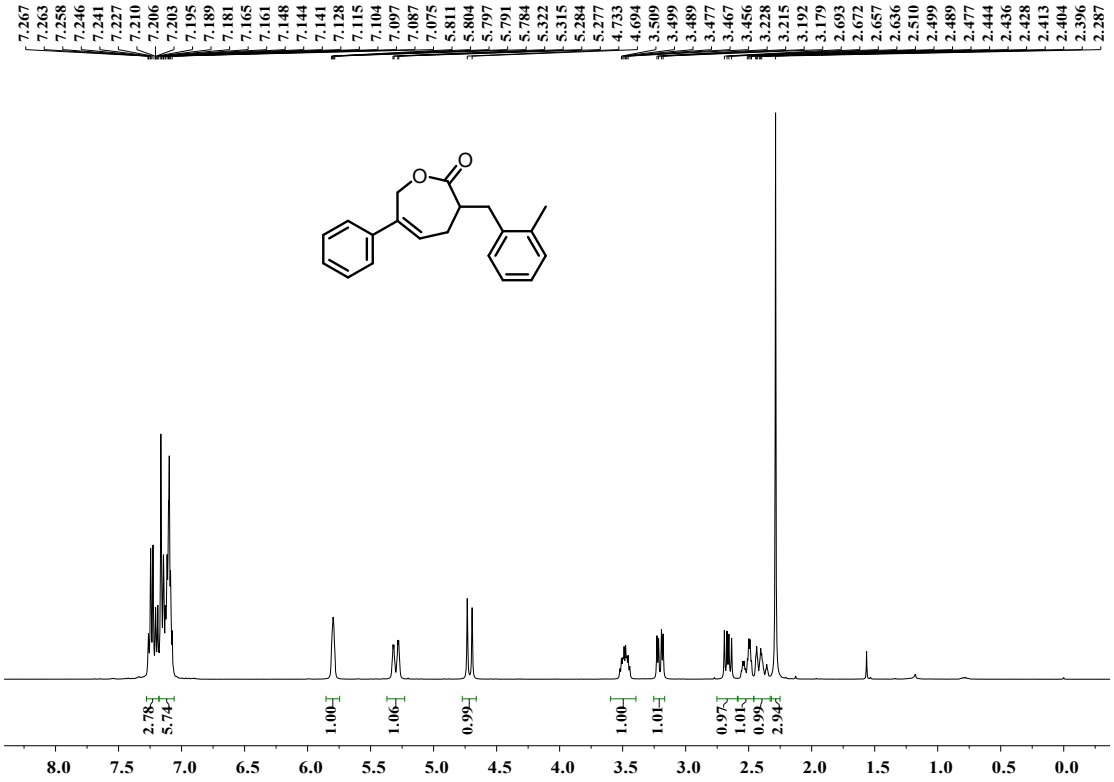
^{1}H NMR of 3l



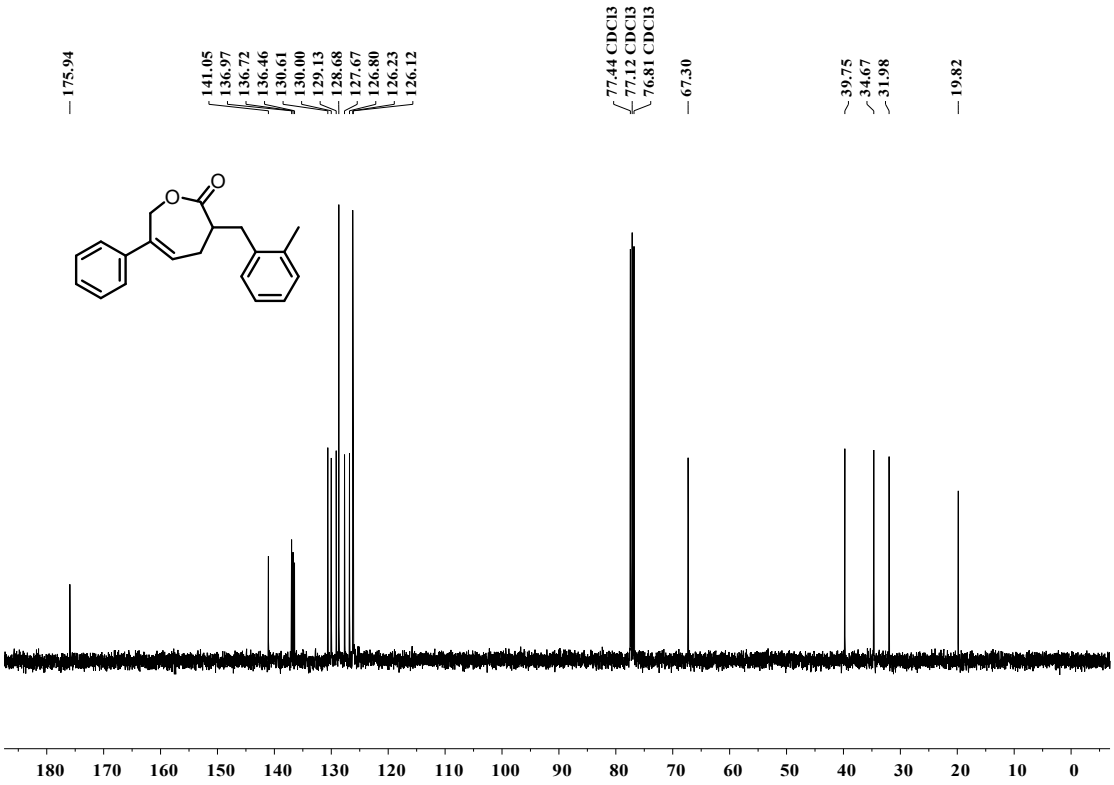
^{13}C NMR of 3l



^{1}H NMR of 3m



^{13}C NMR of 3m



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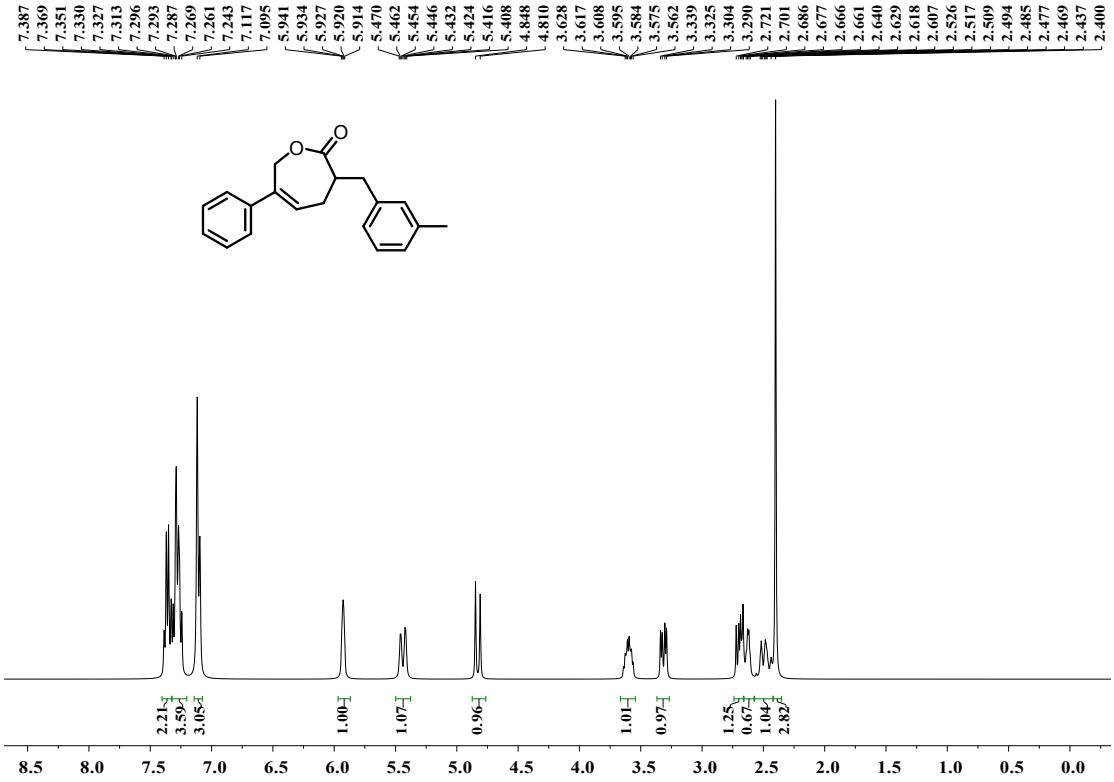

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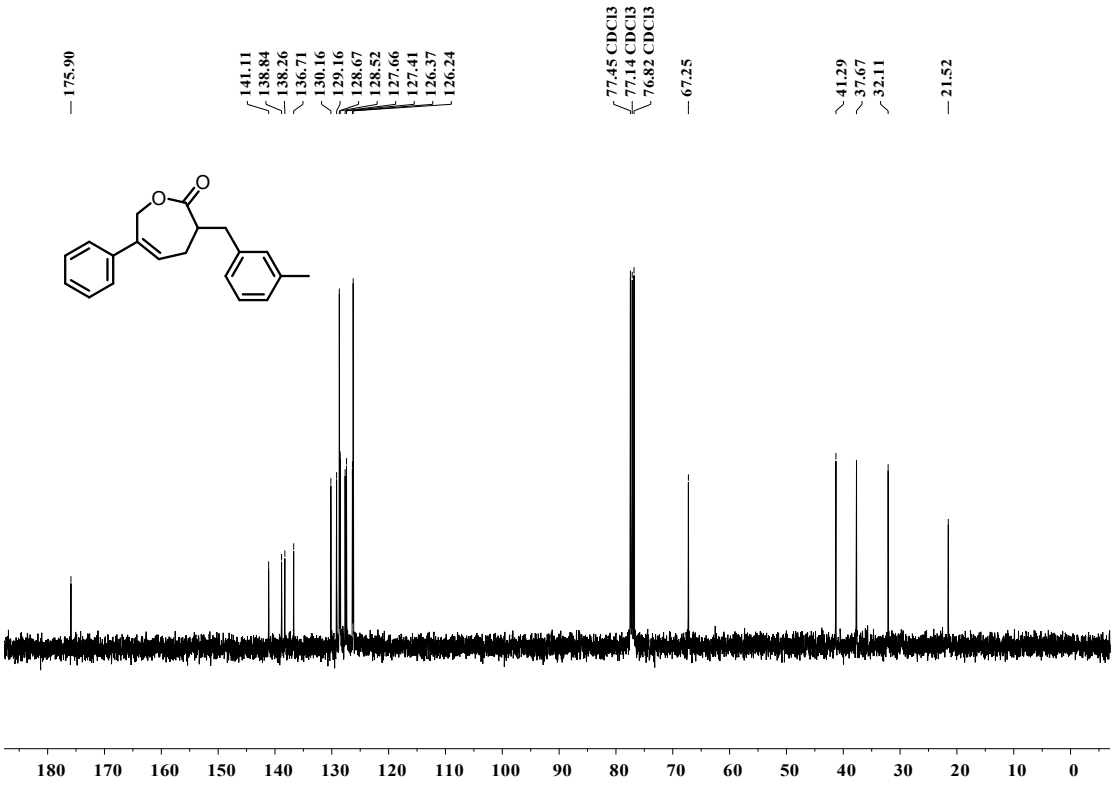
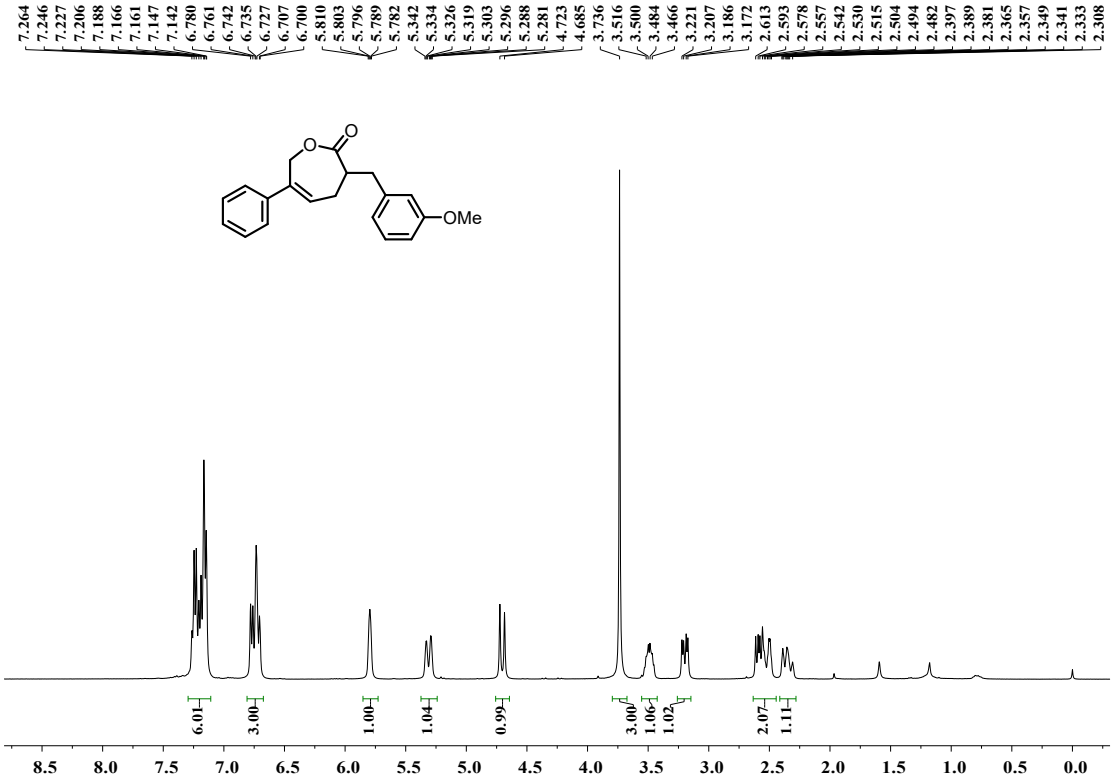


^{1}H NMR of 3o



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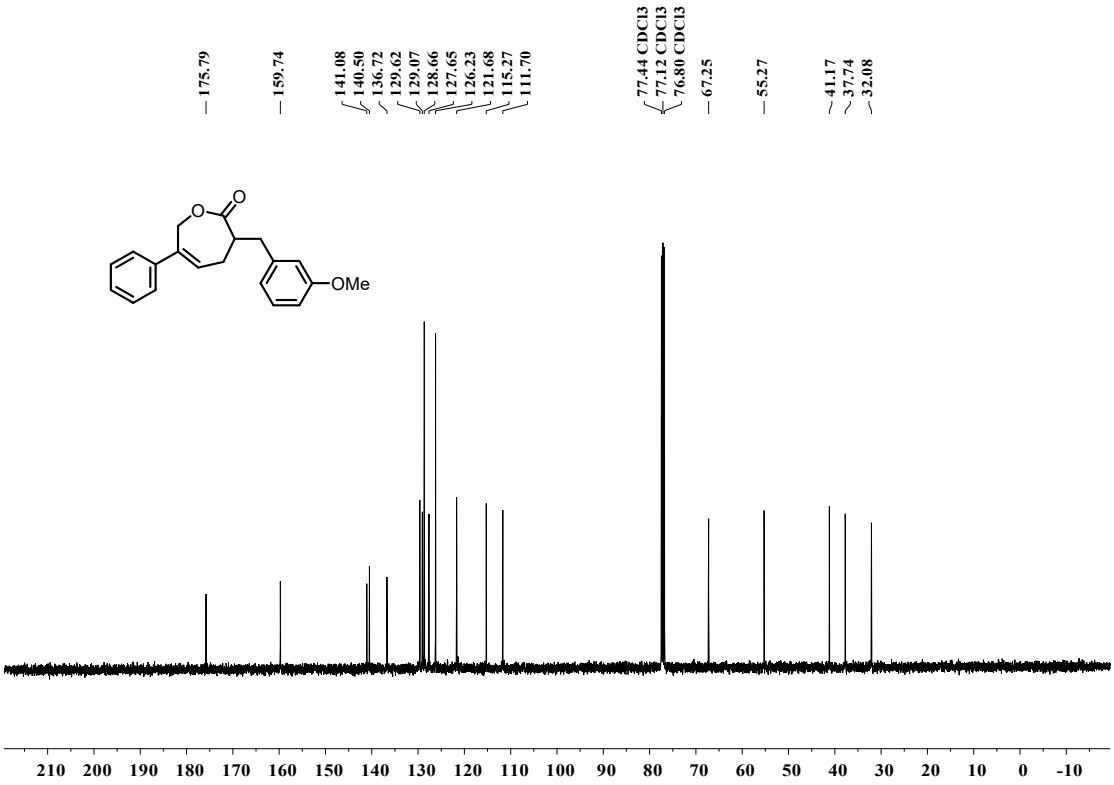
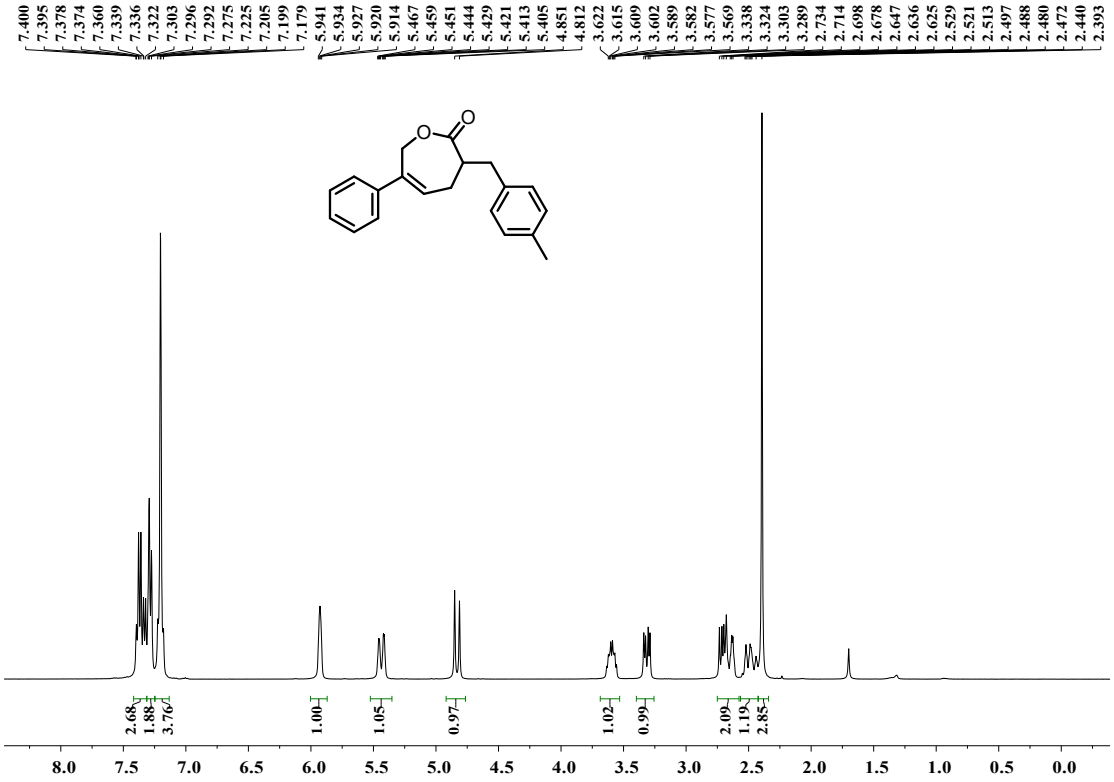
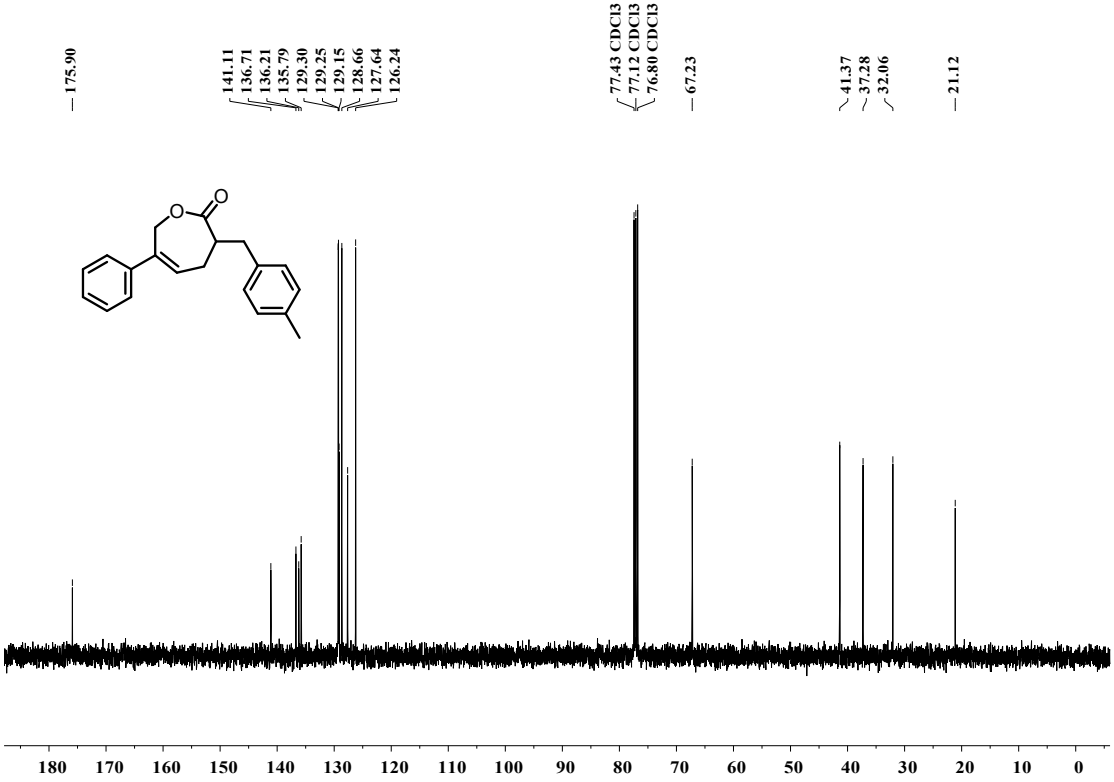


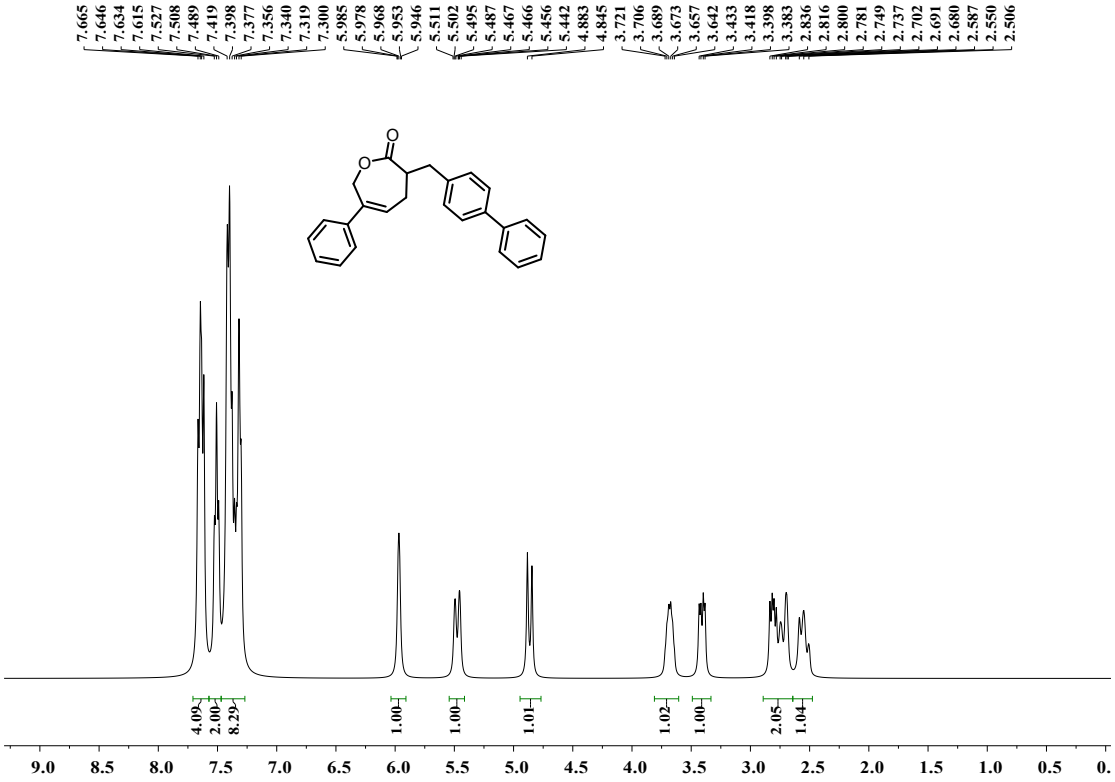
^{1}H NMR of 3p



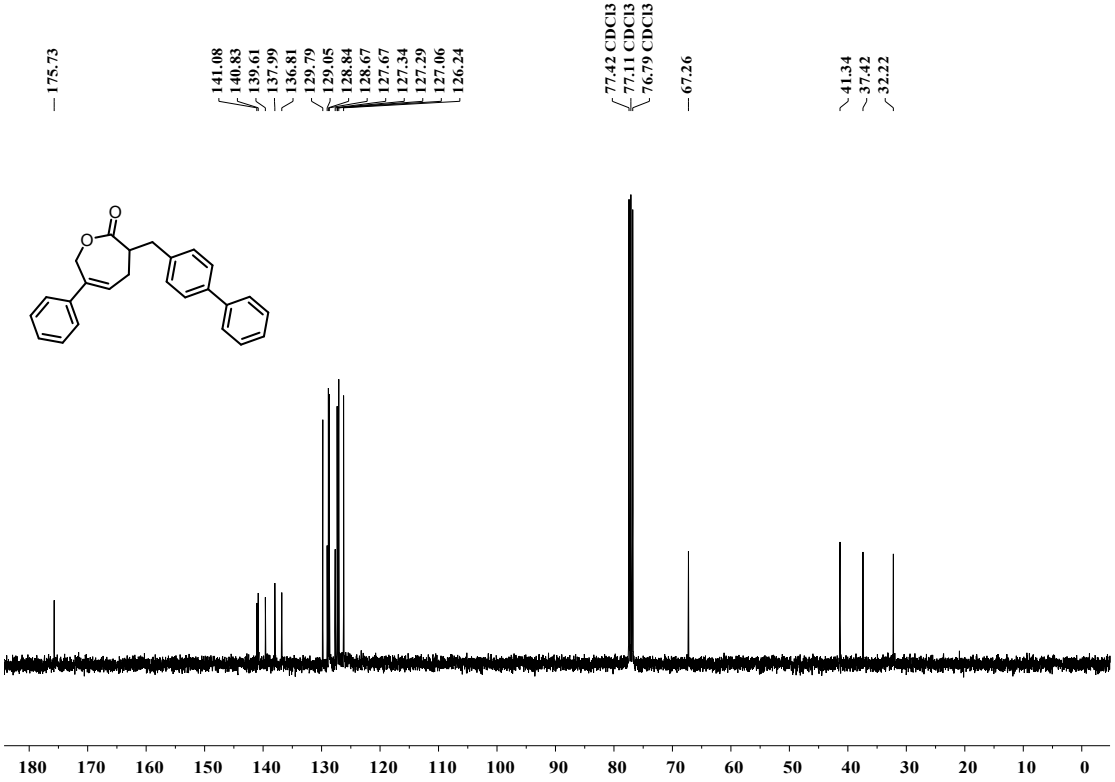
^{13}C NMR of 3p



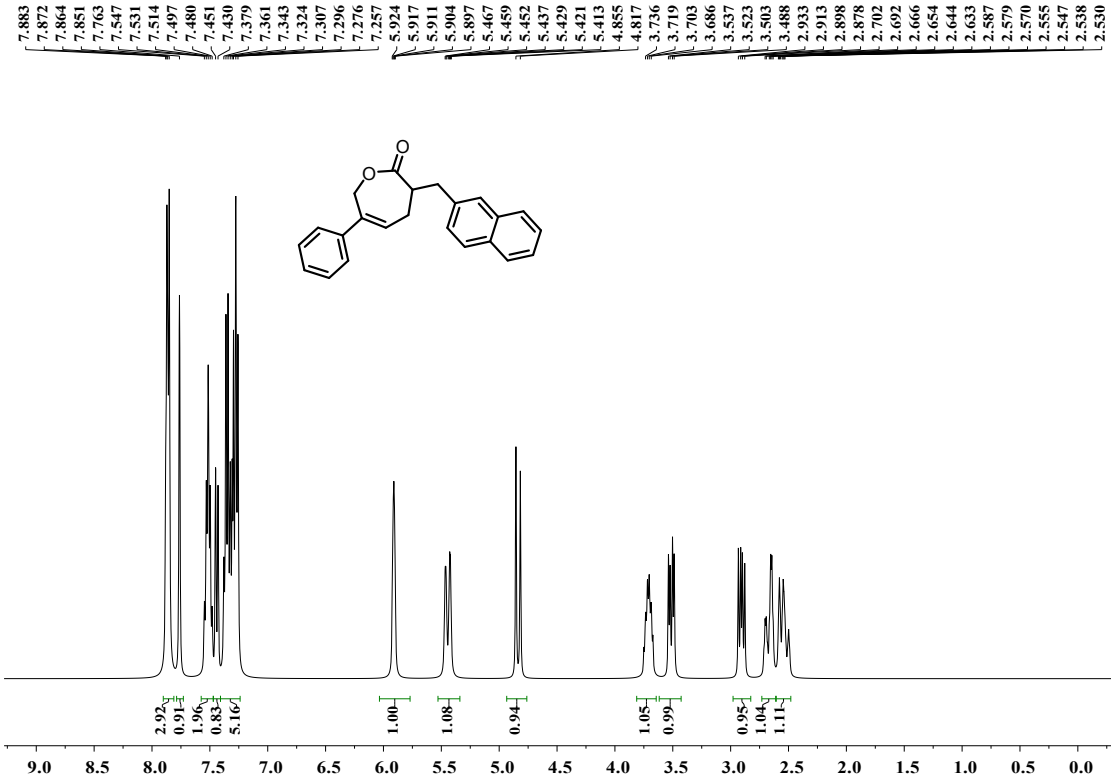
^{1}H NMR of 3q



^{13}C NMR of 3q



^{1}H NMR of 3r



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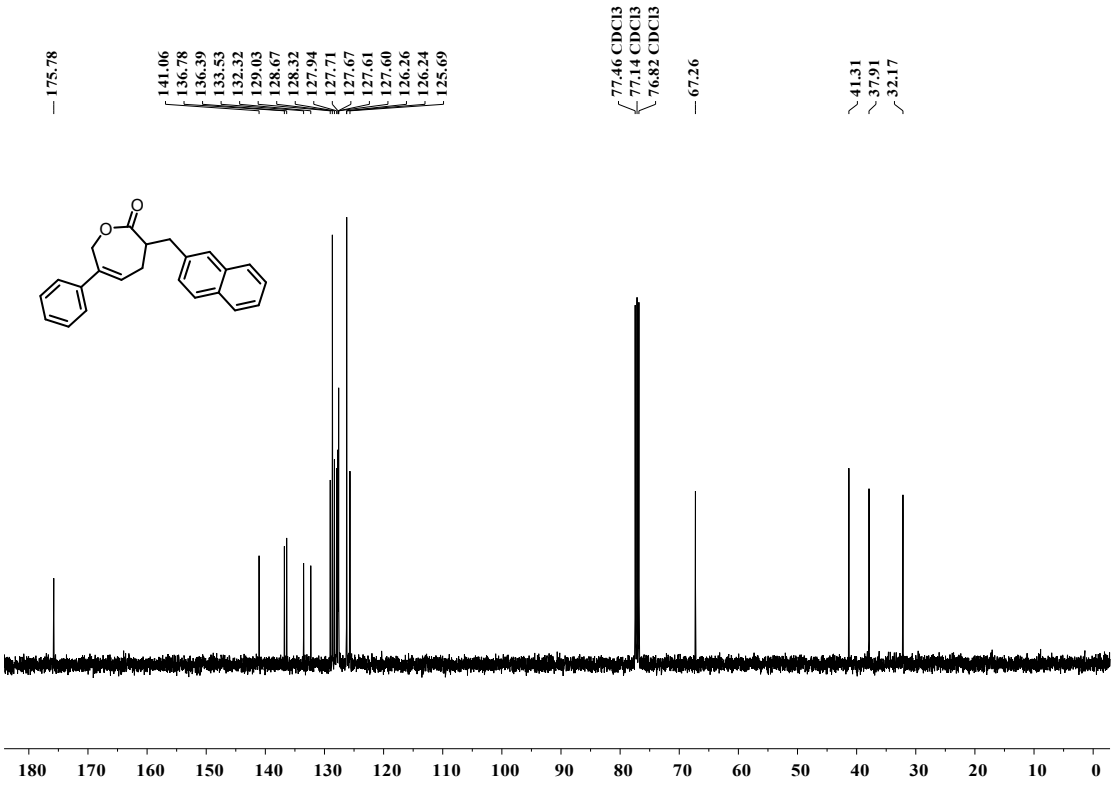

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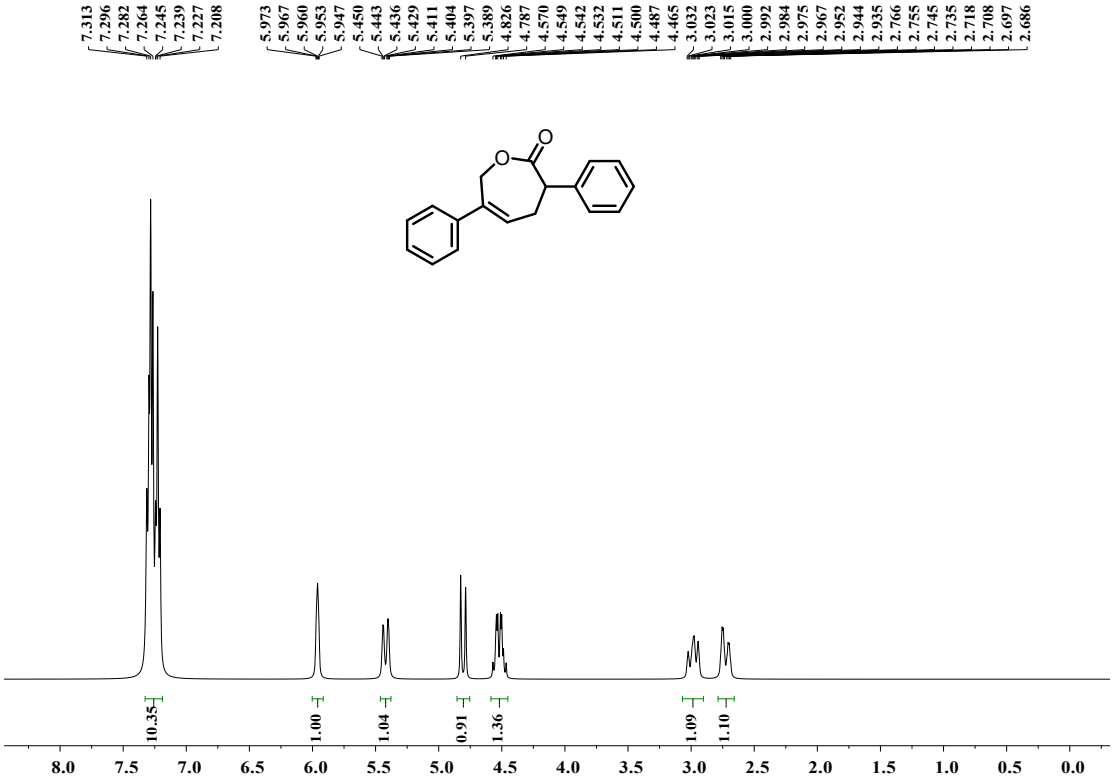

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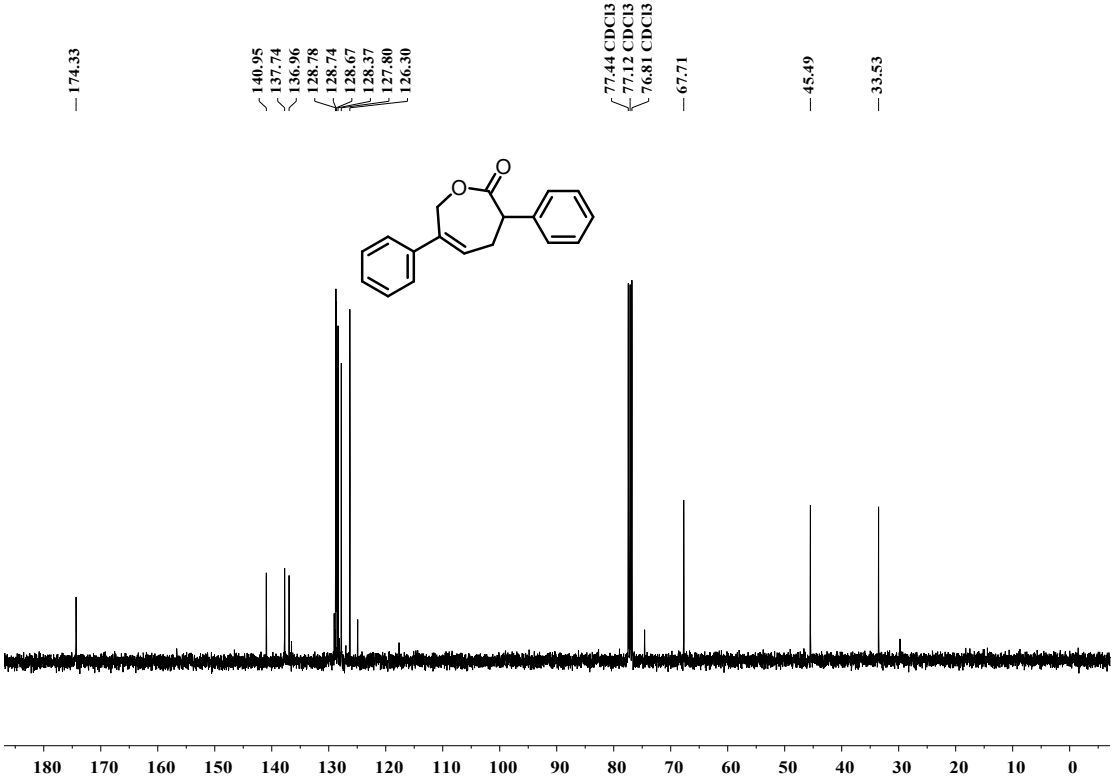
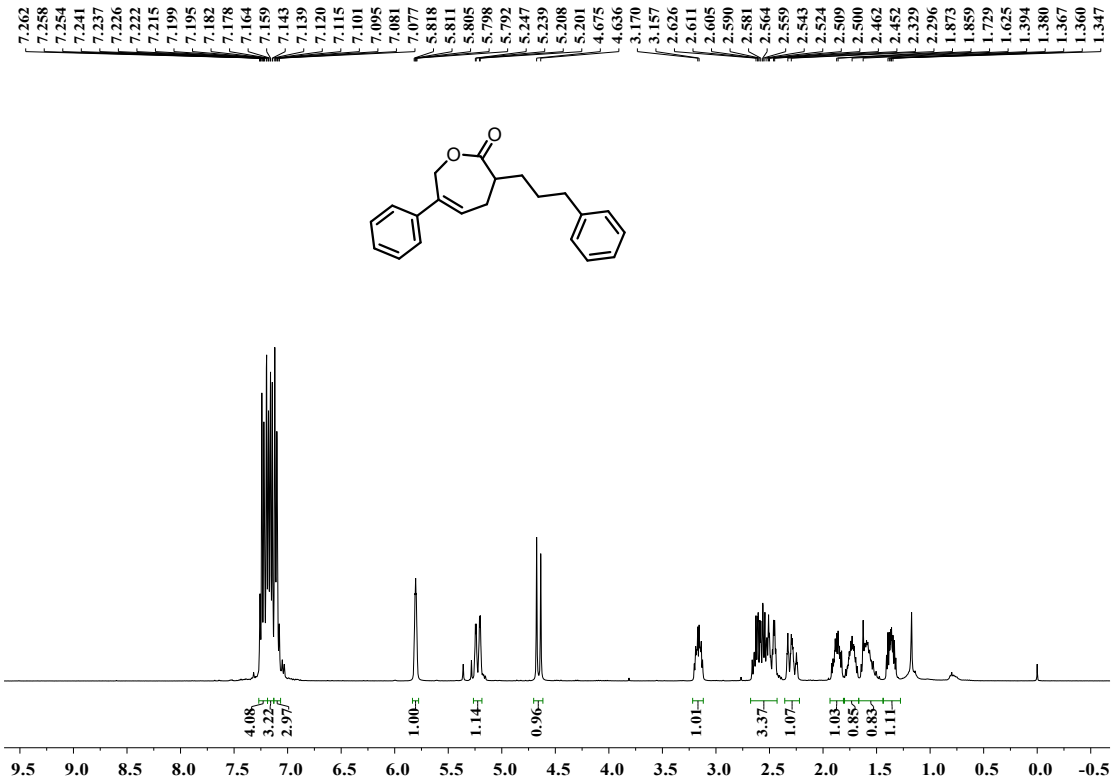
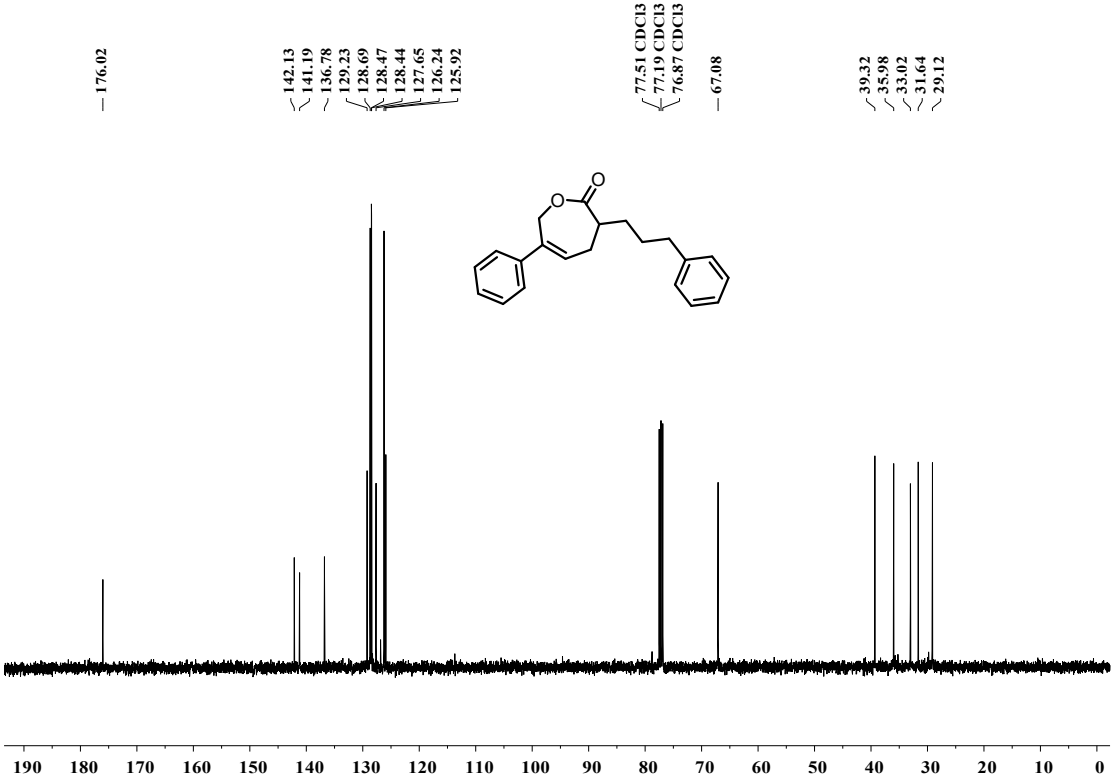


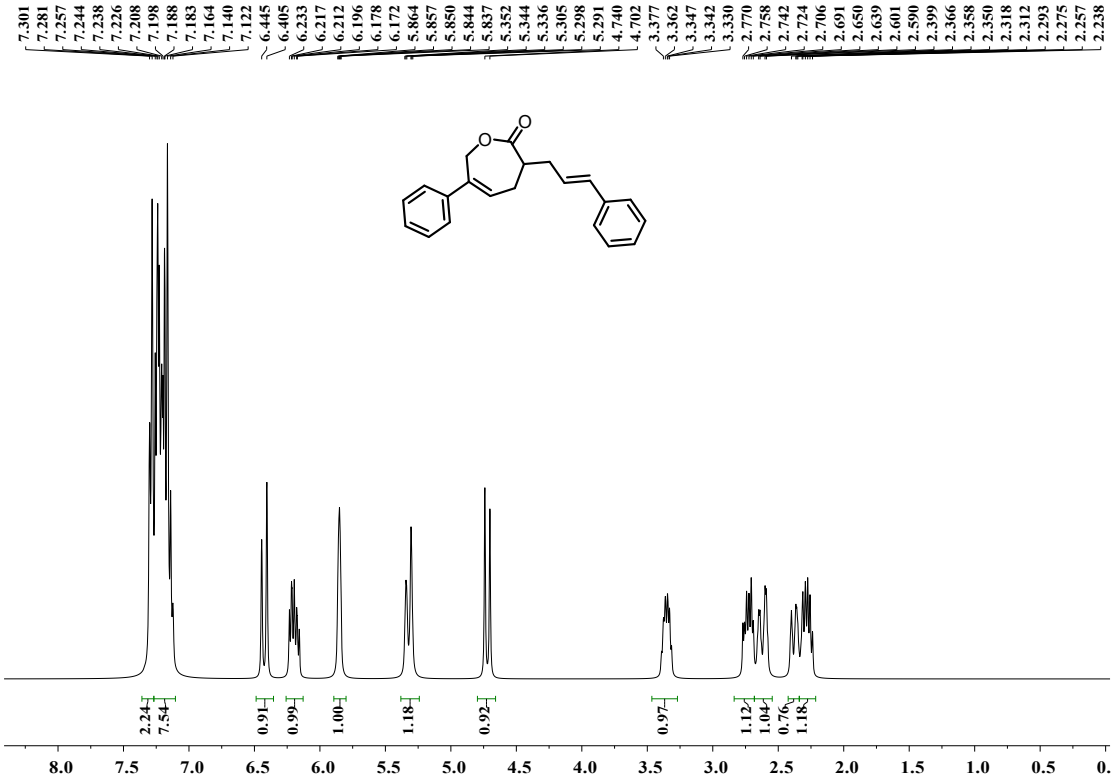
^{1}H NMR of 3t



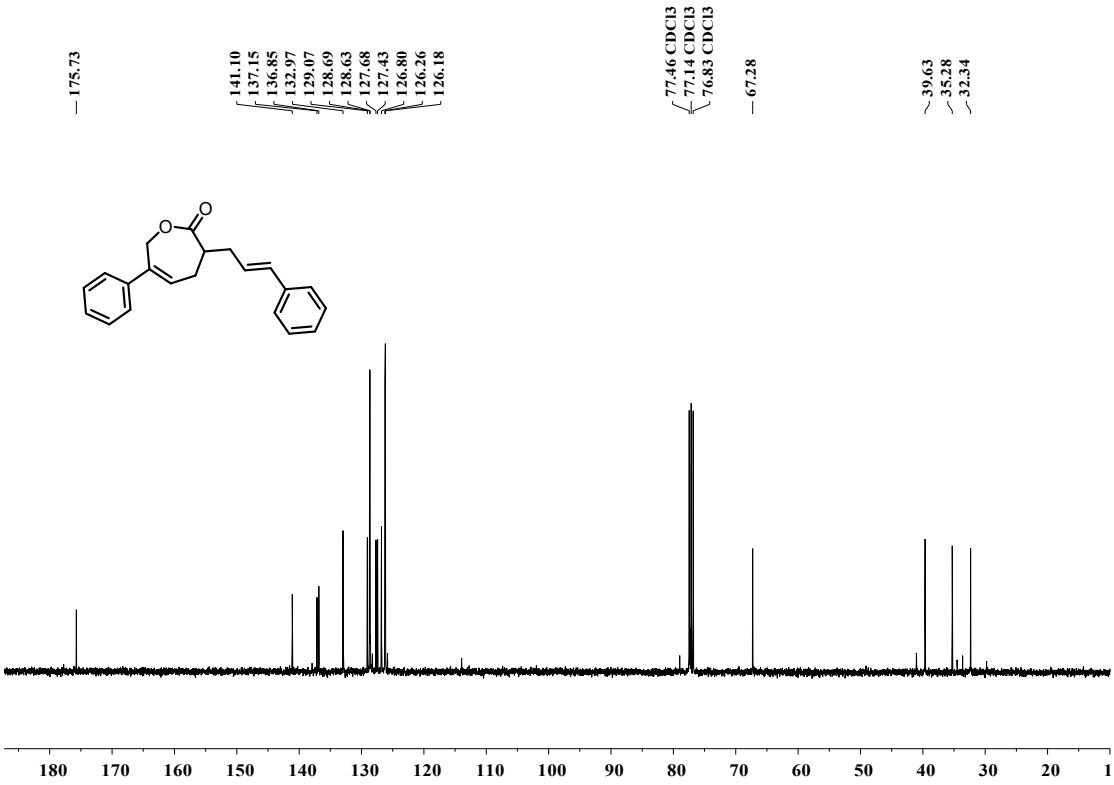
^{13}C NMR of 3t



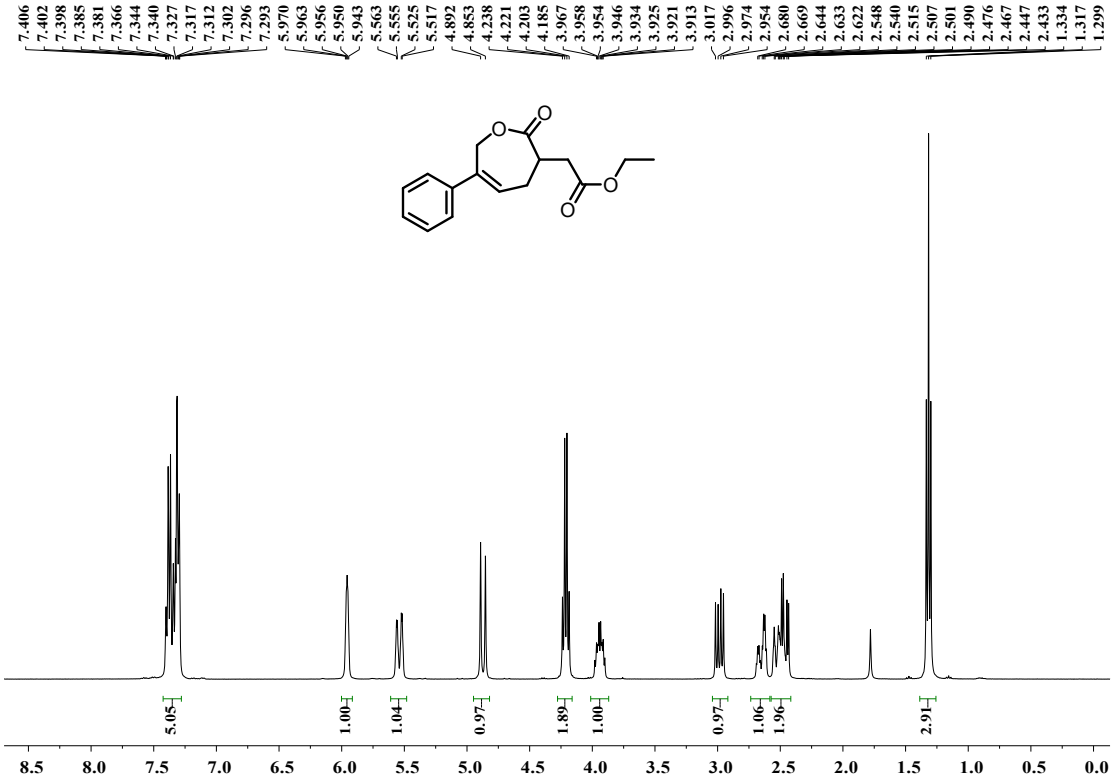
^{1}H NMR of 3u



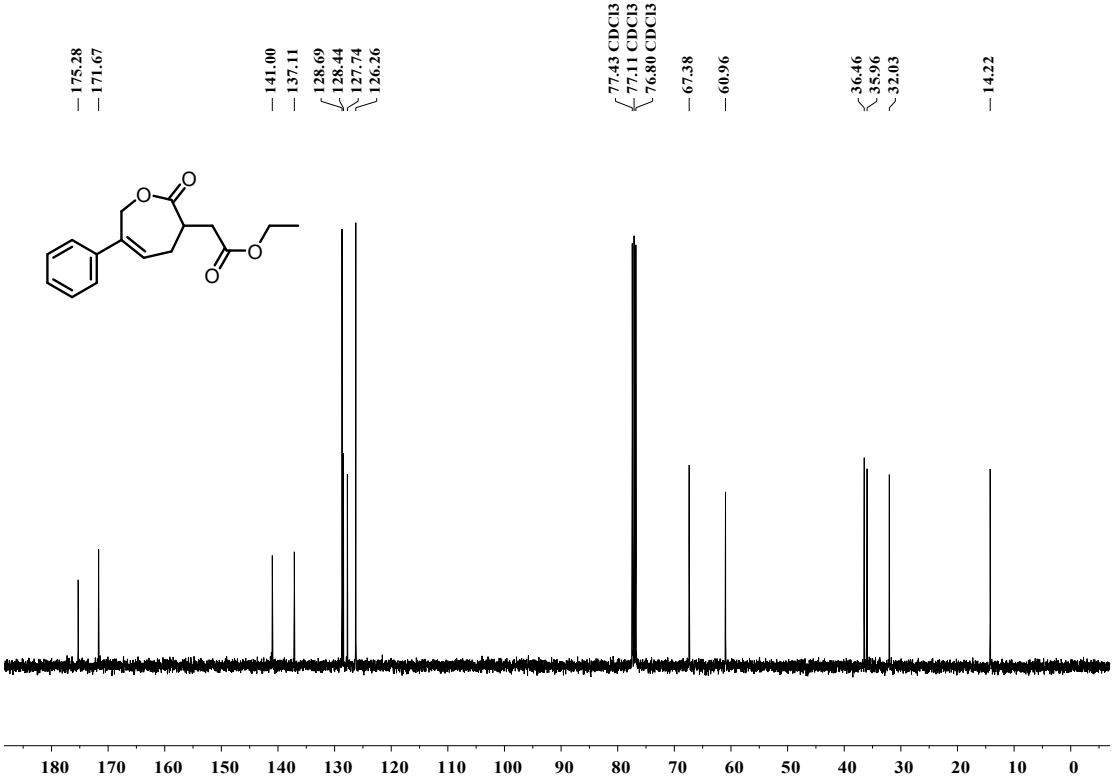
^{13}C NMR of 3u



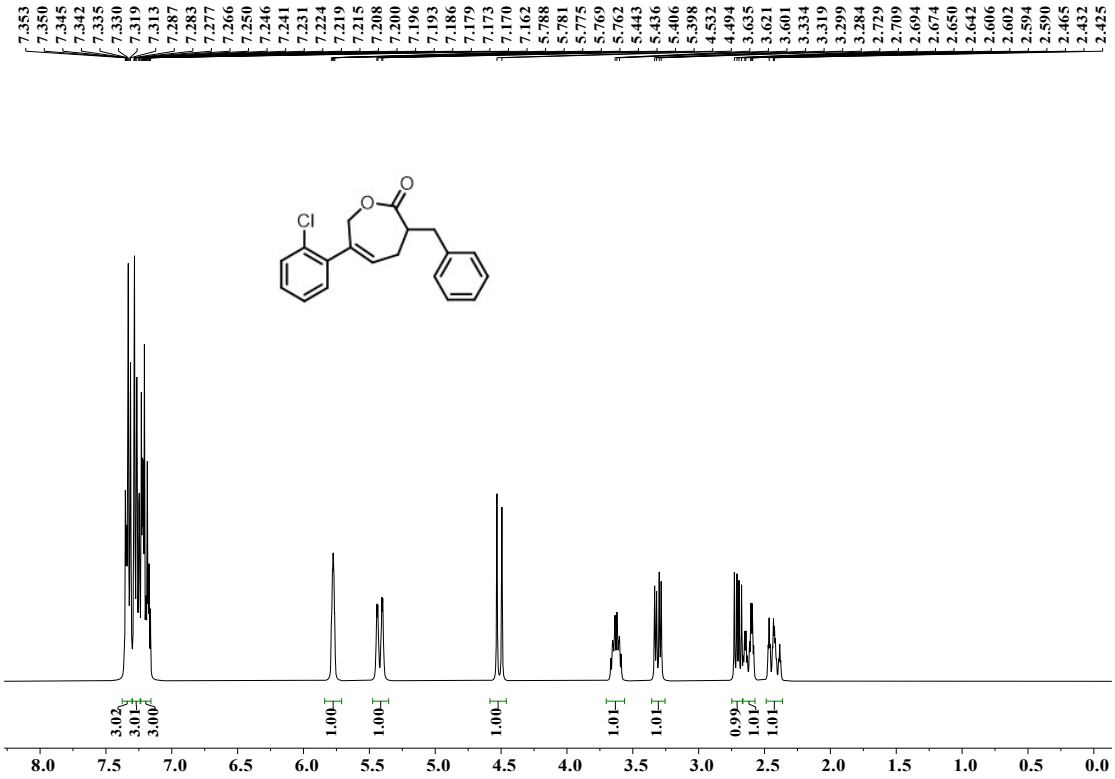
^{1}H NMR of 3v



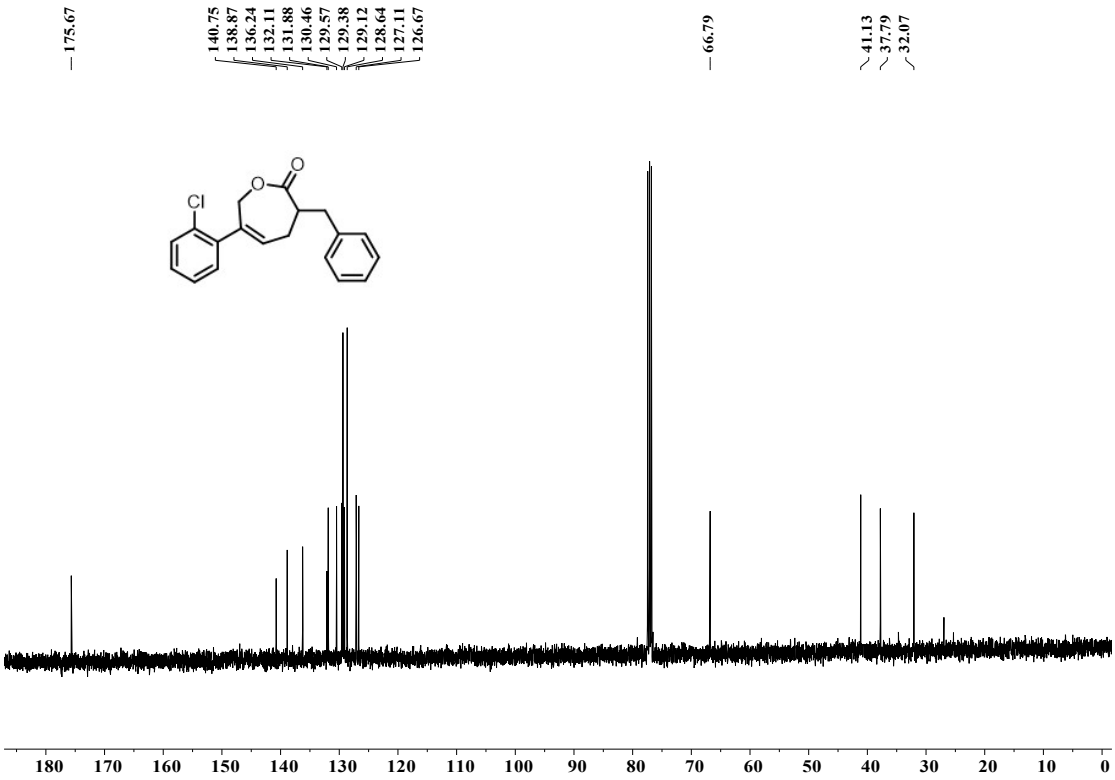
^{13}C NMR of 3v



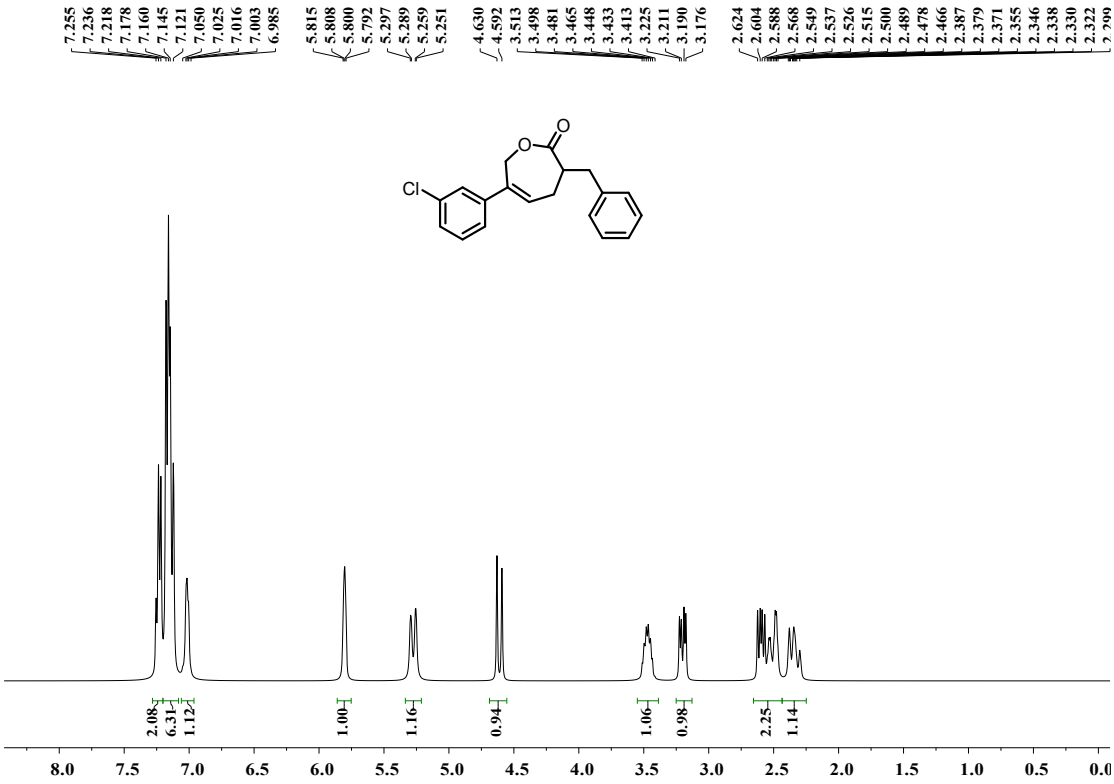
^{1}H NMR of 3w



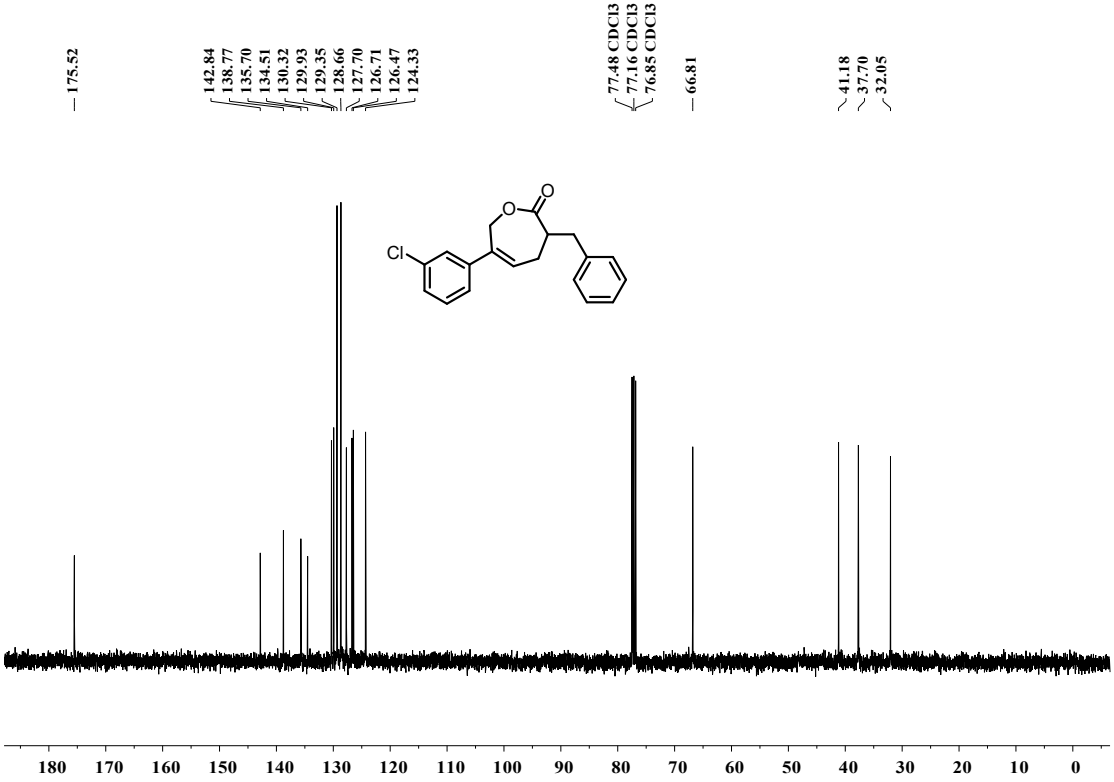
^{13}C NMR of 3w



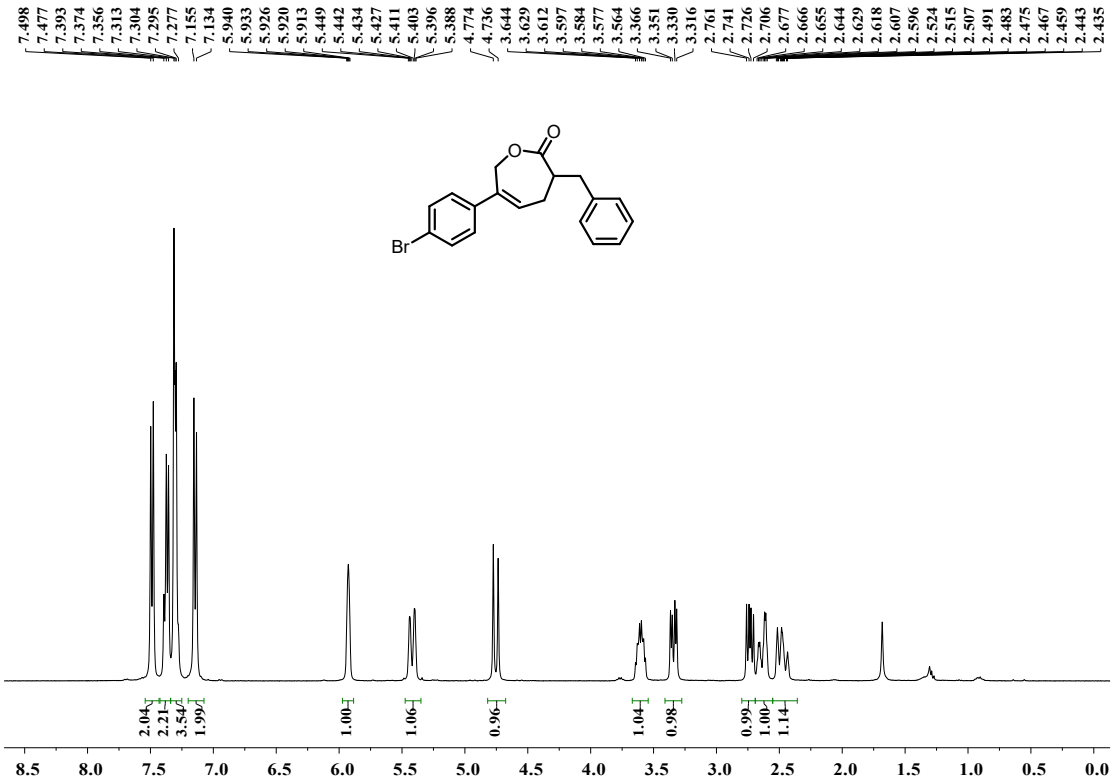
^{1}H NMR of 3x



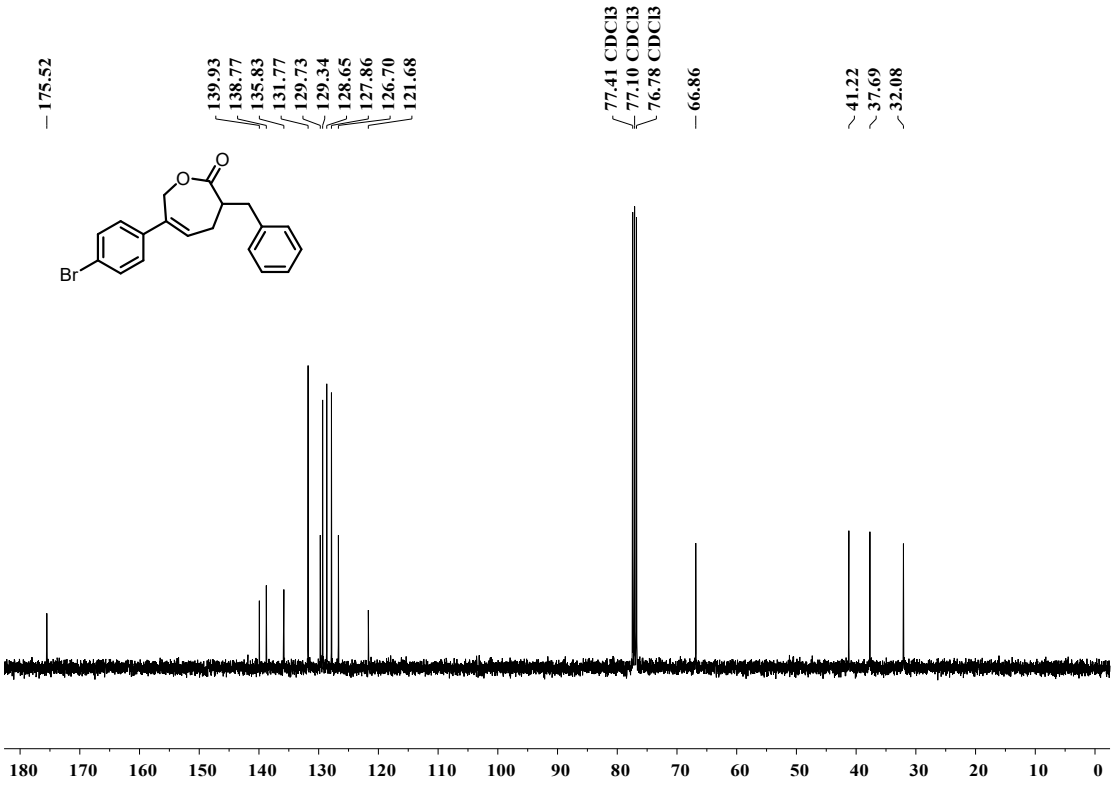
^{13}C NMR of 3x



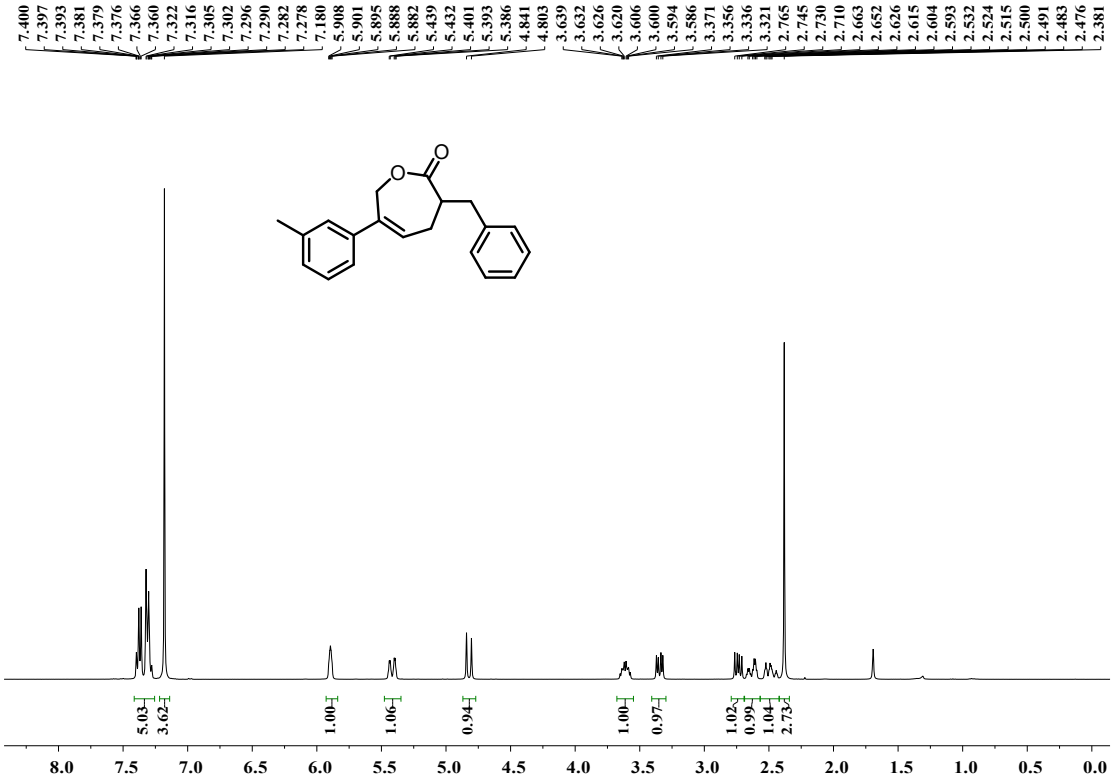
^{1}H NMR of 3y



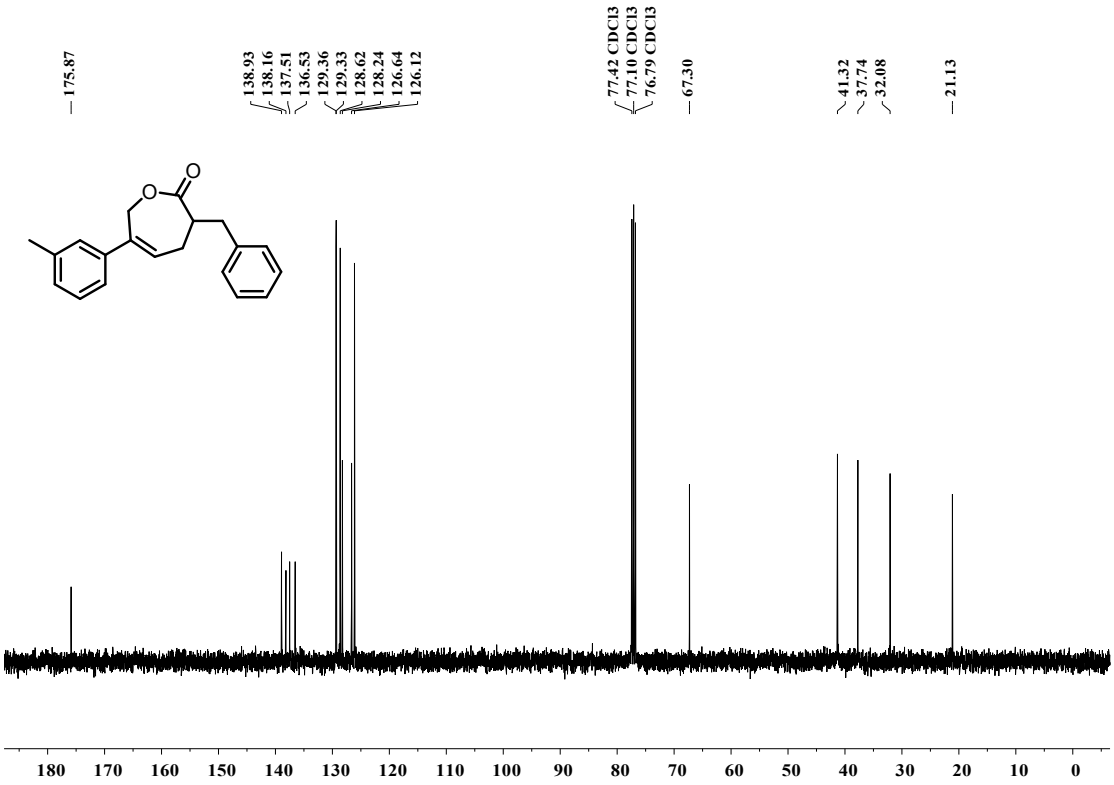
^{13}C NMR of 3y



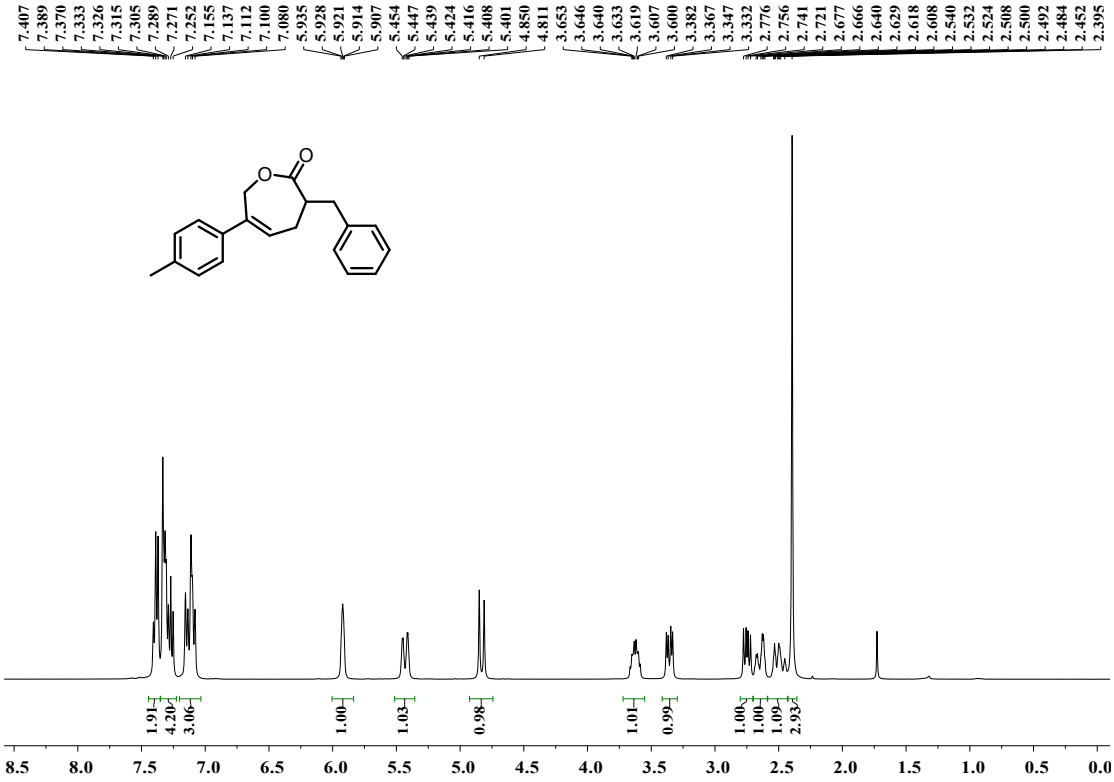
^{1}H NMR of 3z



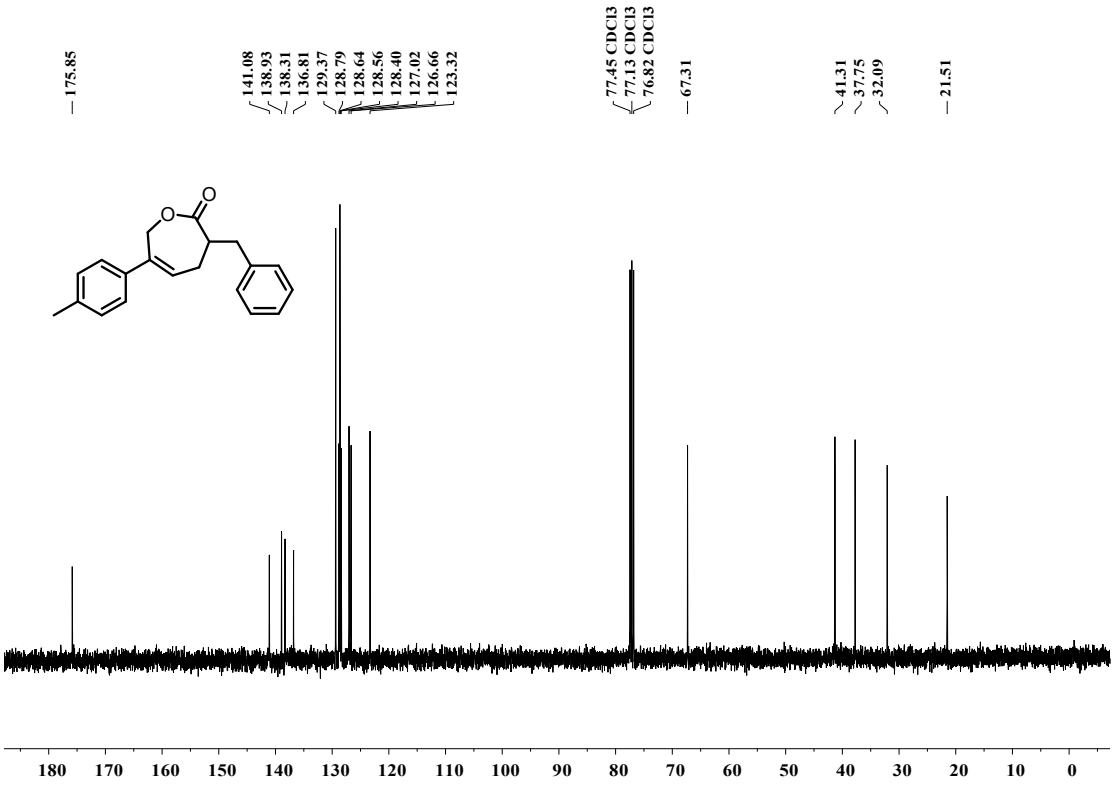
^{13}C NMR of 3z



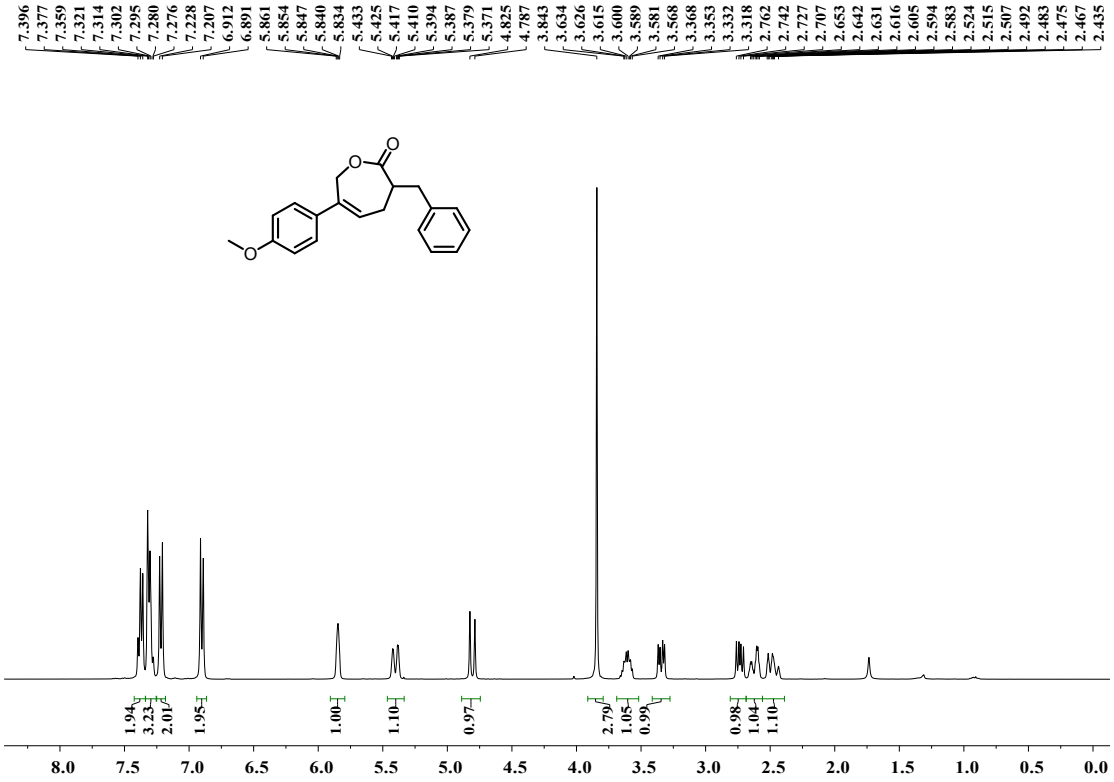
^{1}H NMR of 3aa



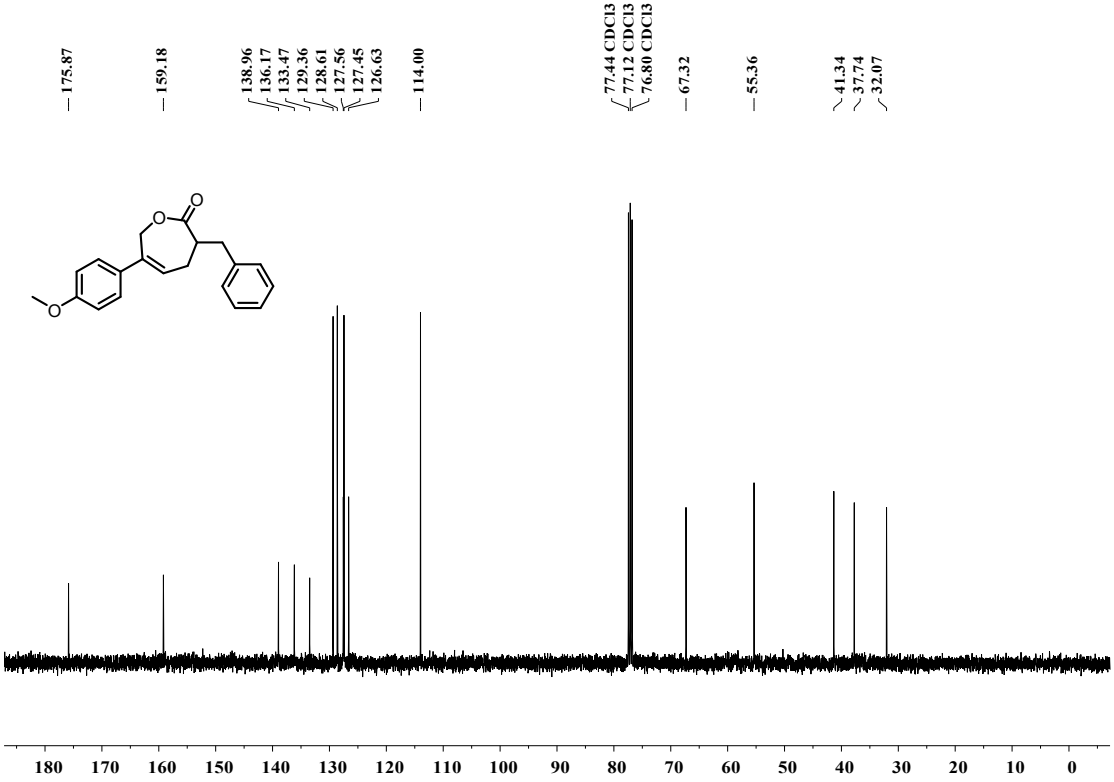
^{13}C NMR of 3aa



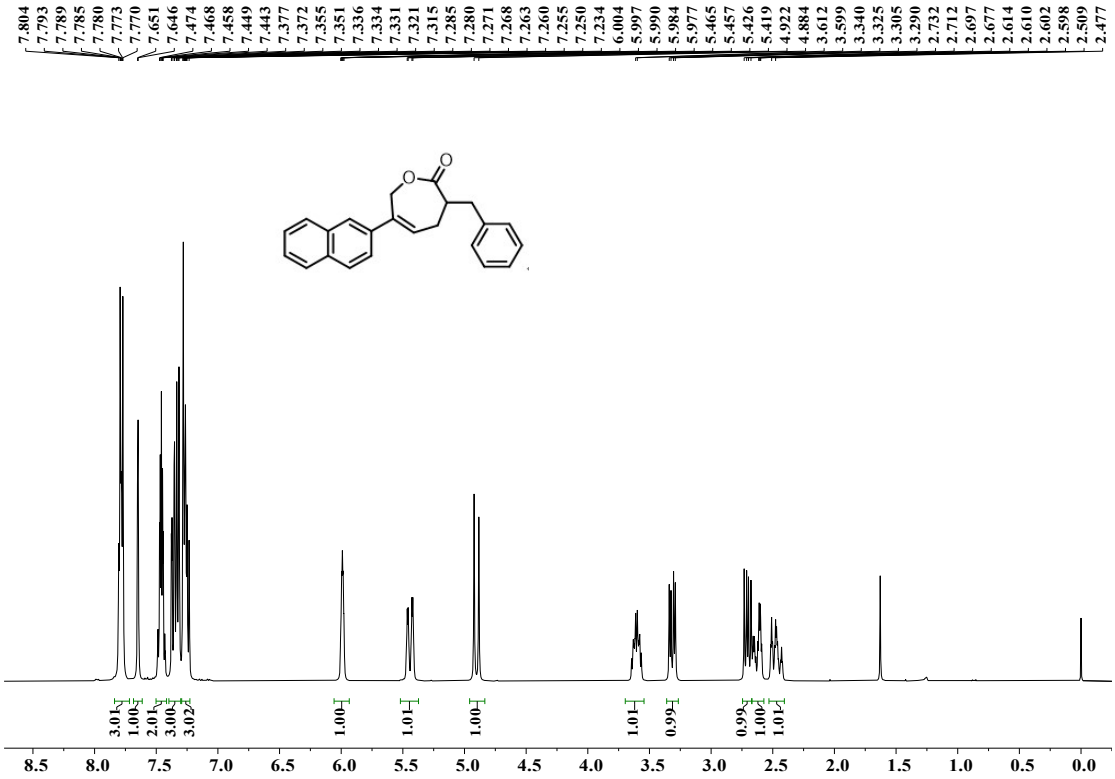
^{1}H NMR of 3ab



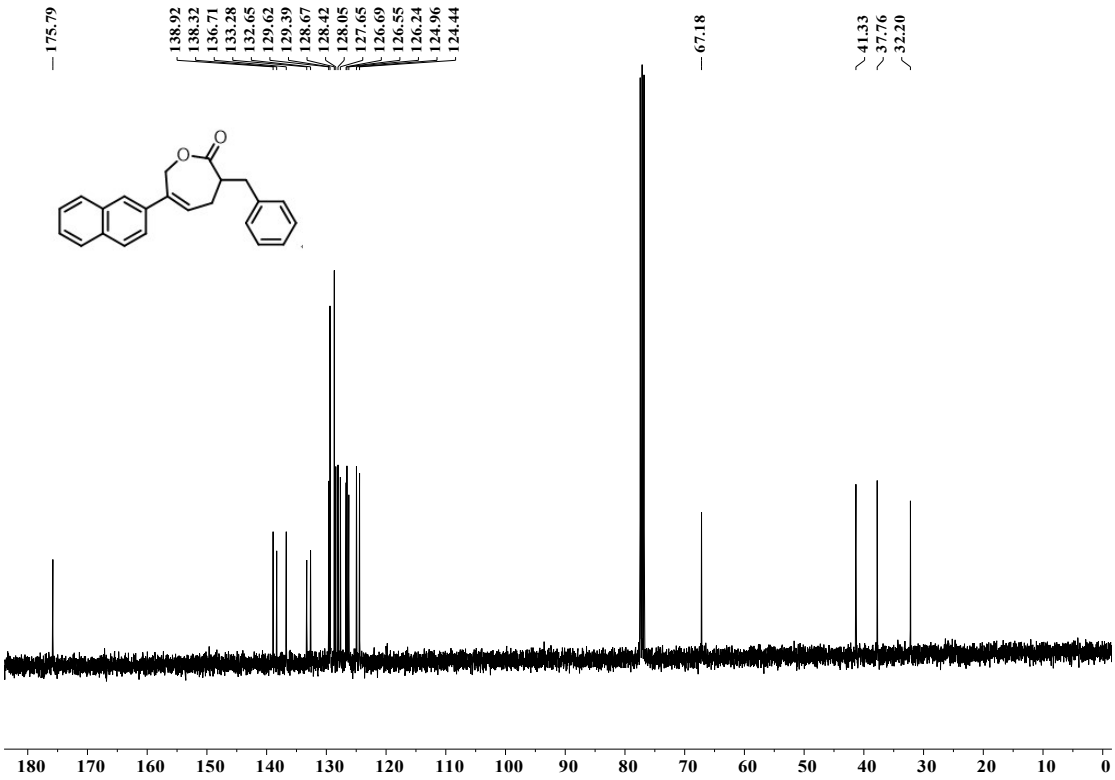
^{13}C NMR of 3ab



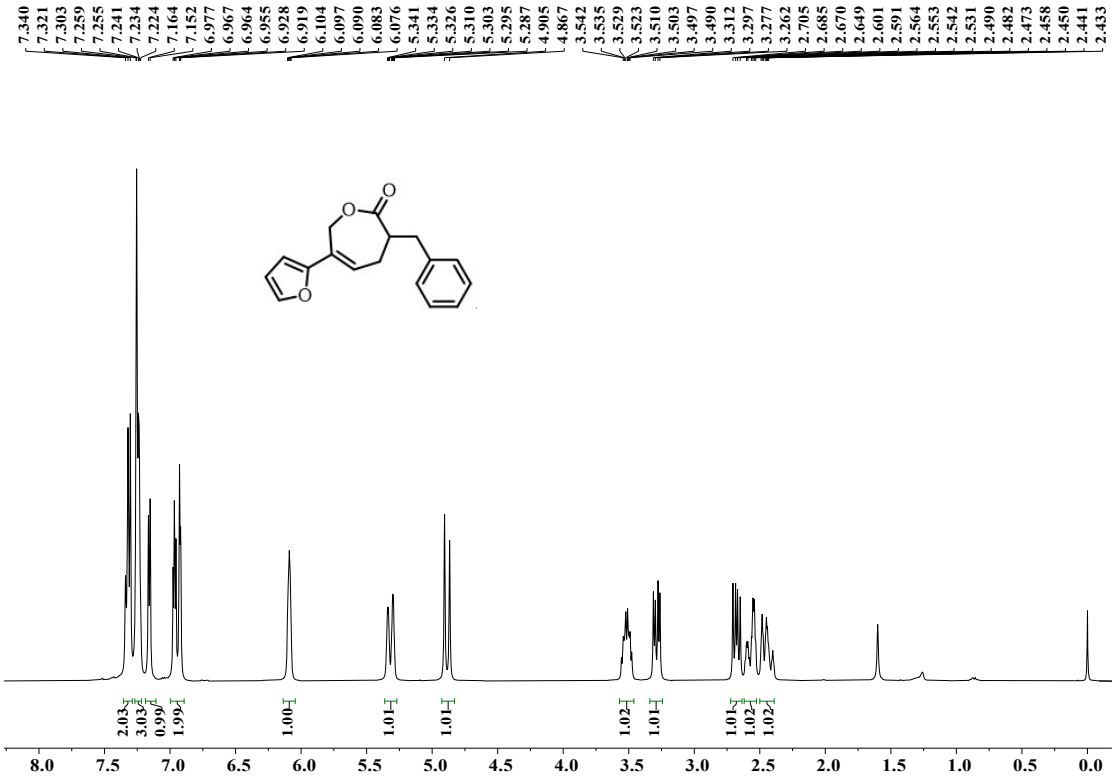
^{1}H NMR of 3ac



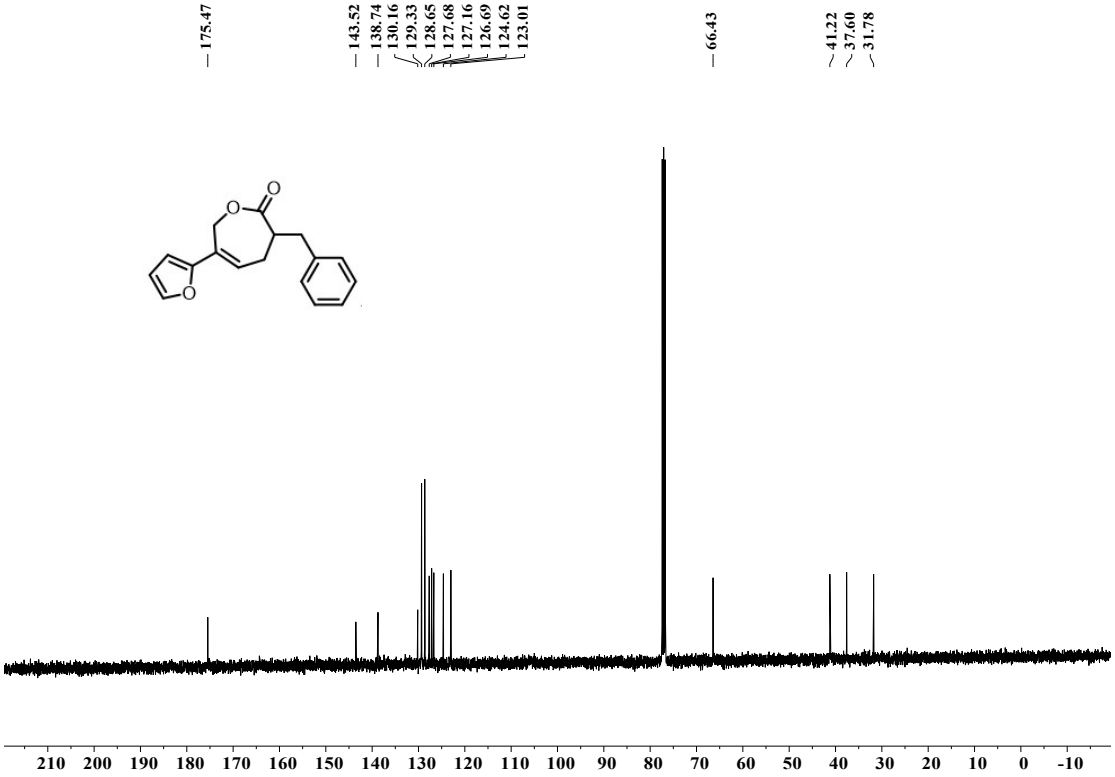
^{13}C NMR of 3ac



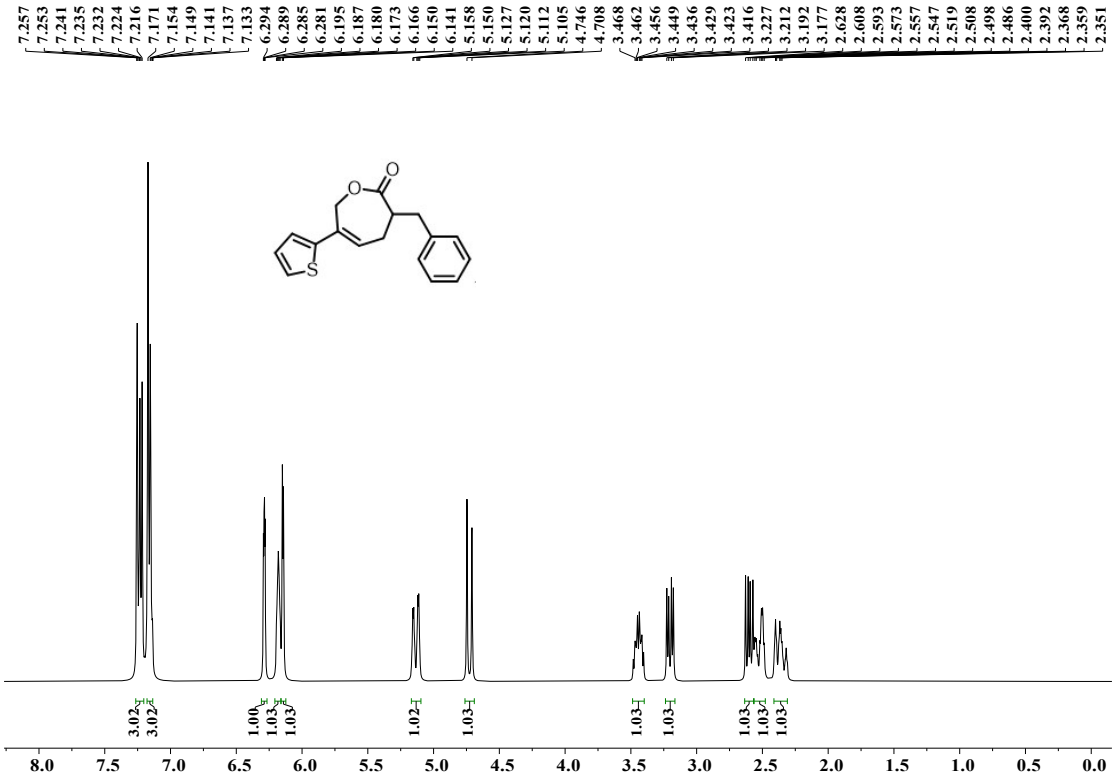
^{1}H NMR of 3ad



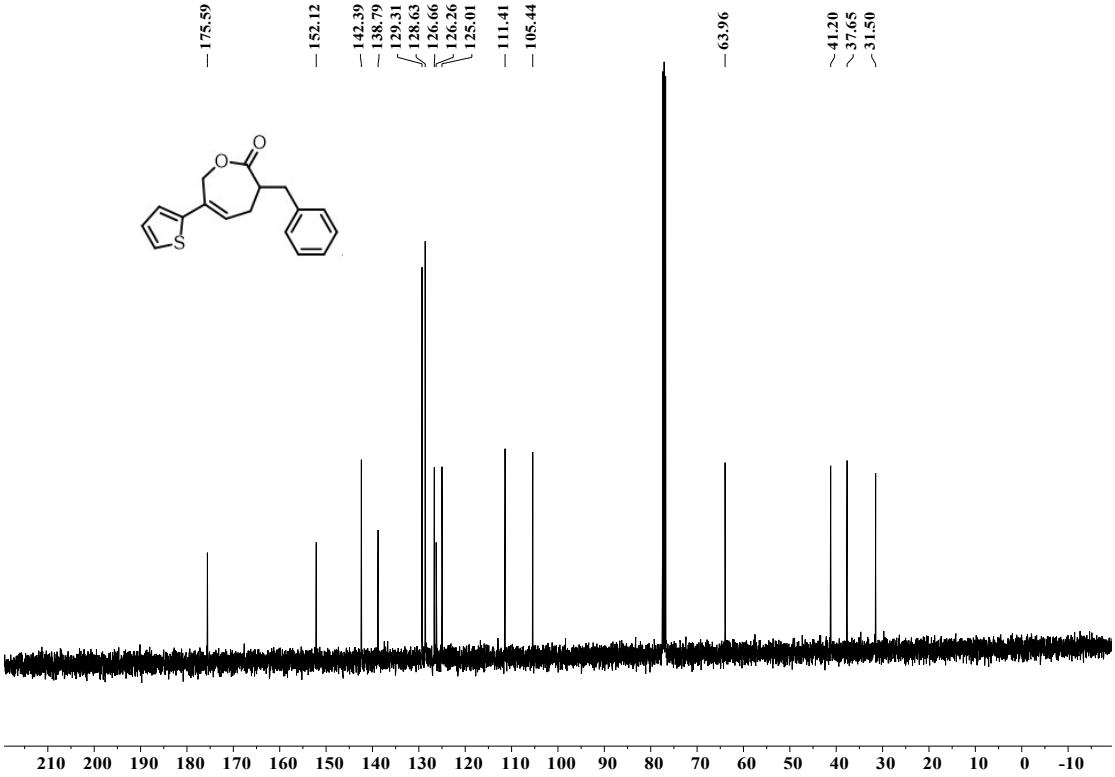
^{13}C NMR of 3ad



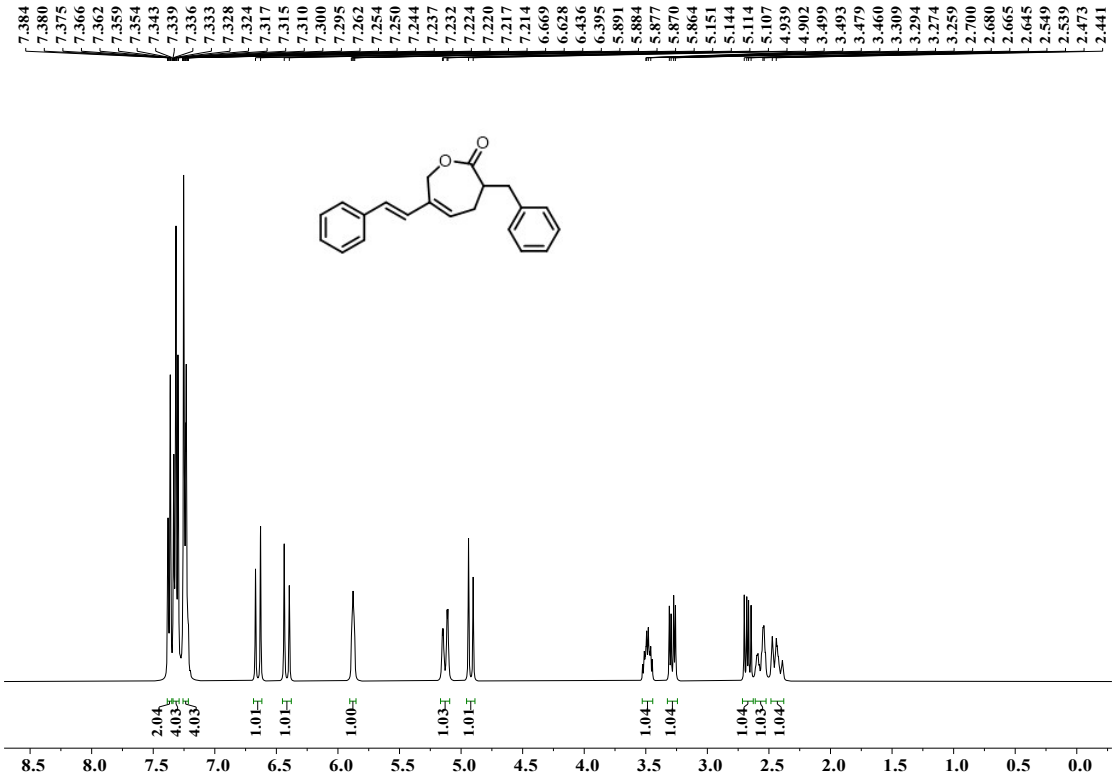
^{1}H NMR of 3ae



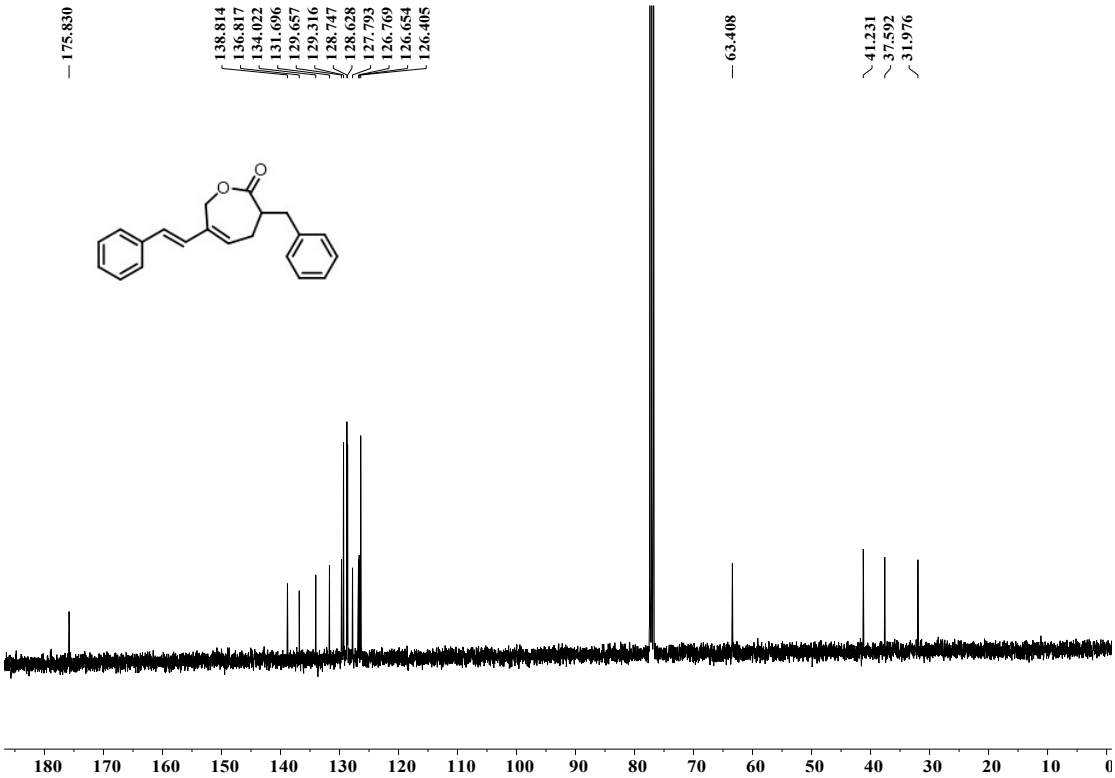
^{13}C NMR of 3ae



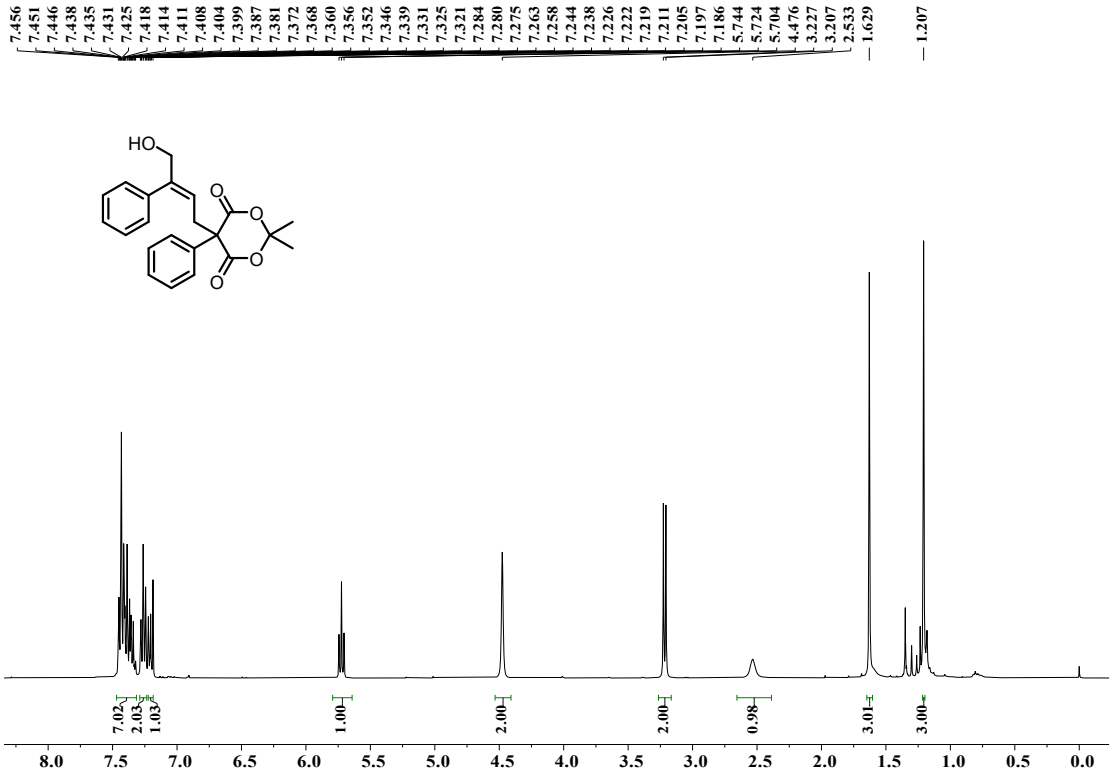
^{11}H NMR of 3af



^{13}C NMR of 3af



^{1}H NMR of 4s



^{13}C NMR of 4s

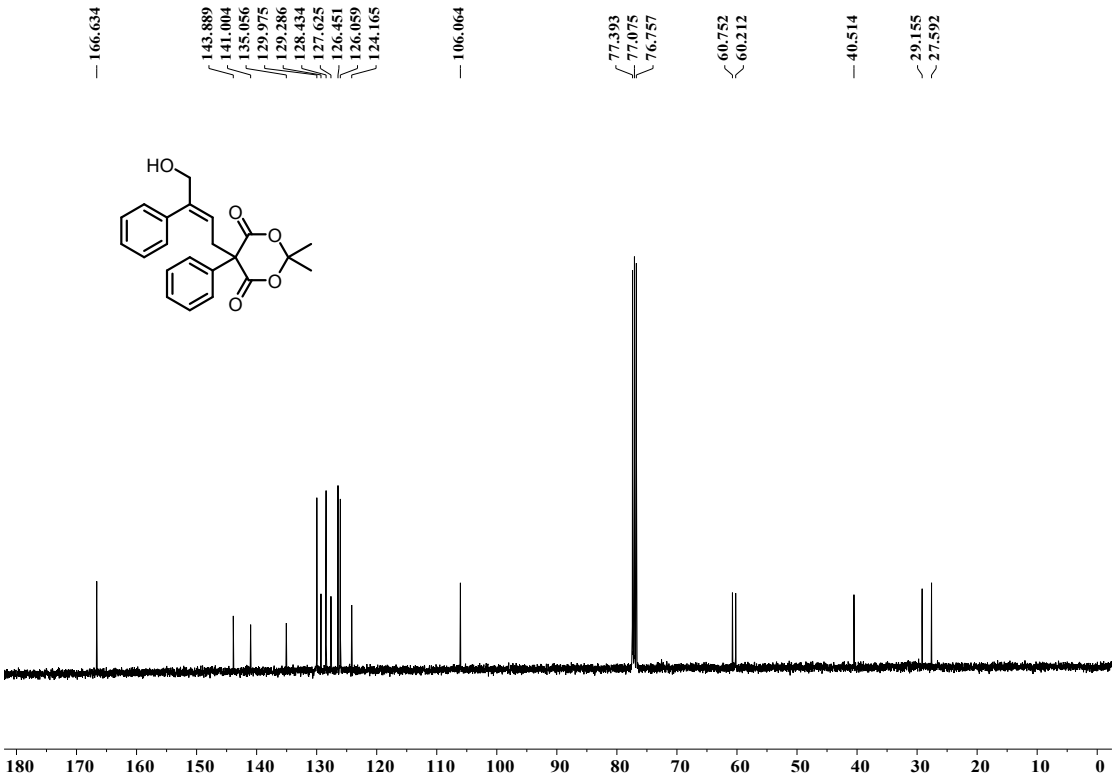
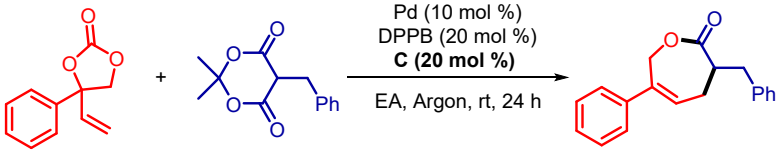
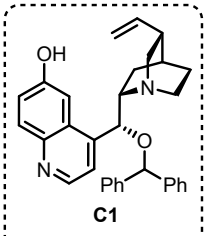


Table S1. Chiral Brønsted bases Screening



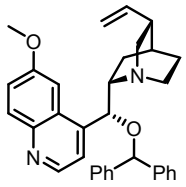
1a (0.15 mmol) **2a (0.3 mmol)** **3a**

Chiral Brønsted bases



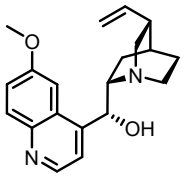
C1

46% yield, 45% ee



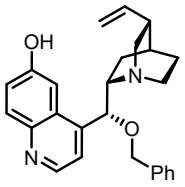
C2

40% yield, 25% ee



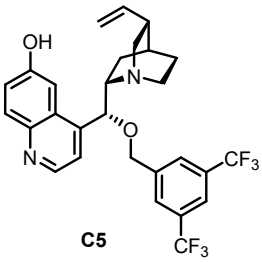
C3

44% yield, 15% ee



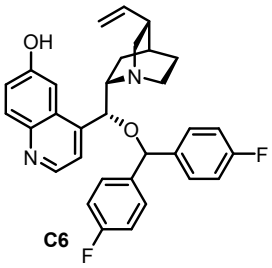
C4

31% yield, 5% ee



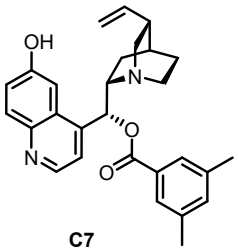
C5

40% yield, 29% ee



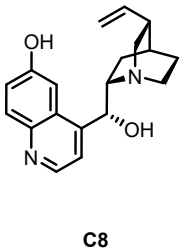
C6

48% yield, 43% ee



C7

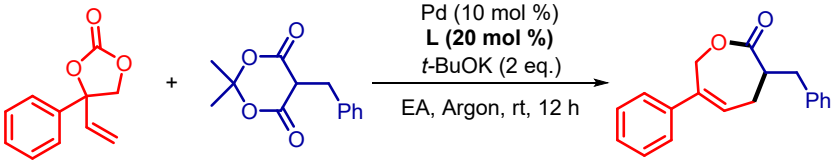
36% yield, 25% ee



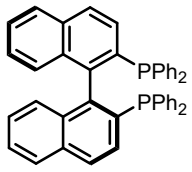
C8

29% yield, 3% ee

Table S2. Chiral phosphine ligands Screening

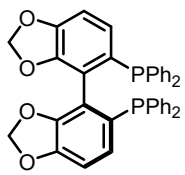


1a (0.15 mmol) **2a (0.3 mmol)** **3a**



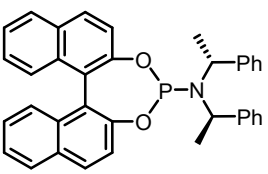
L1

61% yield, 0% ee



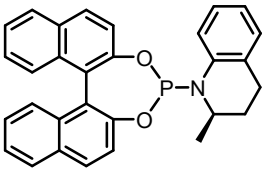
L2

55% yield, 0% ee



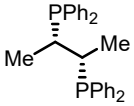
L3

68% yield, 0% ee



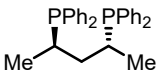
L4

63% yield, 0% ee



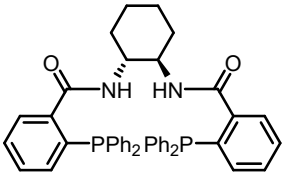
L5

72% yield, 0% ee



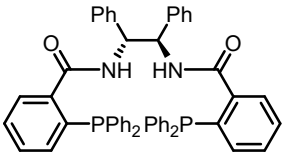
L6

70% yield, 0% ee



L7

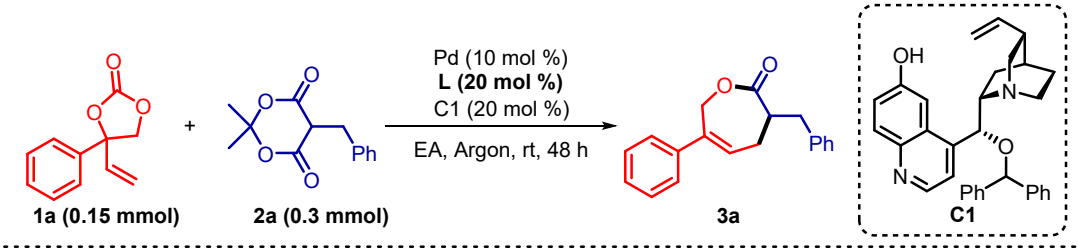
64% yield, 0% ee



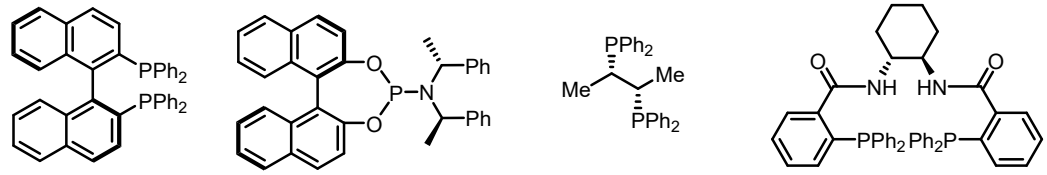
L8

66% yield, 0% ee

Table S3. Screening for the combination of Chiral Brønsted bases and phosphine ligands



1a (0.15 mmol) 2a (0.3 mmol) 3a C1



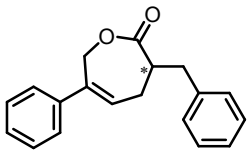
L1	L3	L5	L7
57% yield, 42% ee	53% yield, 41% ee	68% yield, 45% ee	61% yield, 45% ee

Example for the enantioselective synthesis of **3a**:

A 10 mL Schlenk tube containing a stirring bar was charged with $Pd_2(dba)_3$ (0.1 equiv., 0.015 mmol), dppb (0.2 equiv., 0.03 mmol), substituted Meldrum's acid 2 (0.3 mmol), chiral Brønsted base C1 (20 mol %, 0.03 mmol). The tube was then evacuated and back-filled with argon three times. Then substituted vinylethylene carbonate 1 (0.15 mmol in 1mL anhydrous EA) was added to the tube under nitrogen atmosphere, and stirred at room temperature for 10 h. After the reaction was completed (monitored by TLC), the reaction mixture was filtered with diatomite and purified by column chromatography on silica gel (PE : EA = 20:1) to give the desired product.

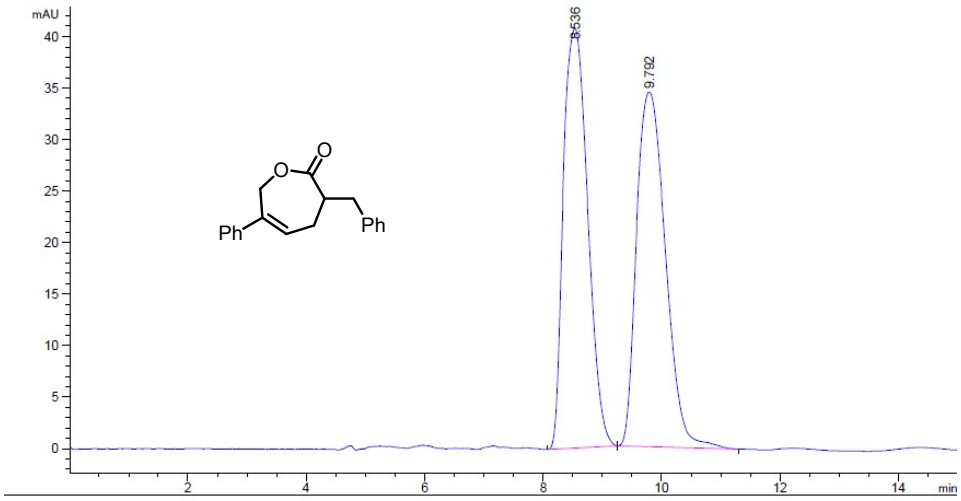
6. Spectroscopic Data of **3a** (HPLC Trace)

3-benzyl-6-phenyl-4,7-dihydrooxepin-2(3H)-one(3a)



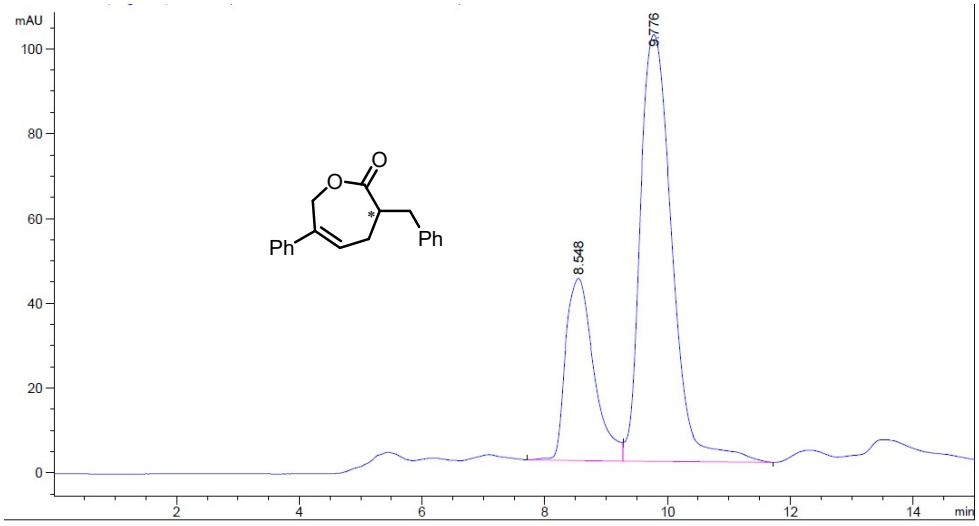
19.2 mg, 46% yield;

HPLC 45% ee, analysis: (Chiralcel OD-H, hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 254 nm), t_R = 8.5 min (minor), t_R = 9.7 min(major).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.536	BB	0.4587	1162.77771	40.77131	49.8432
2	9.792	BB	0.5461	1170.09302	34.46396	50.1568
totals				2332.87073	75.23528	

Chiral HPLC spectrum of racemic 3a



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.548	BV	0.5026	1373.44324	43.00070	27.5373
2	9.776	VB	0.5687	3614.12305	100.70448	72.4627
totals				4987.56628	143.70518	

Chiral HPLC spectrum of 3a