Palladium-catalysed fragmentary esterification-induced allylic alkylation of allyl carbonates and cyclic vinylogous anhydrides

Shu-Yi Wu, Yang Li, Peng Shen, Xin-Han Yang, Guang-Yao Ran*

Department of Medicinal Chemistry, College of Pharmacy, Chongqing Medical University, Chongqing 400016, China.

Email: gyran@cqmu.edu.cn

Supporting Information

Table of Contents

1. General information

^{1}H NMR (600 MHz), ^{13}C NMR (150 MHz) spectra were recorded on Bruker AVANCE III 600 instrument, chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in $CDCl_3$ solution. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, dd = double doublet, m = multiplet, and coupling constants (*J*) are reported in Hertz (Hz). ESI-HRMS was recorded on Waters XEAO G2-XS QT of using a time-of-flight mass spectrometer equipped with an ESI resource. X-ray single-crystal diffraction experiments were carried out on a Rigaku XtaLAB P200 diffractometer. Enantiomeric ratio was determined by HPLC analysis on a chiral column in comparison with authentic racemate, using a Chiralpak IA Column (250 × 4.6 mm). UV detection was monitored at 254 nm. Optical rotation was measured on Rudolph Research Analytical Autopol I automatic polarimeter in $CHCl_3$ solution at 20 °C. The melting point was obtained from WRS-2C Mel-Temp apparatus. Column chromatography was performed on silica gel (300-400 mesh) eluting with ethyl acetate (EtOAc) and petroleum ether. TLC was performed on glass-backed silica plates. UV light, I_2, and a solution of potassium permanganate were used to visualize products or starting materials. All chemicals were used without purification as commercially available unless otherwise noted. Toluene, petroleum ether and tetrahydrofuran (THF) were re-distilled. CVA **1 (1c, 1l, 1m, 1r)** were obtained from the corresponding phthalic anhydrides according to the published method.[1] Allyl methyl carbonate **2** were prepared according to the reported procedure.[2] The substituted cyclic allyl carbonates **5** were prepared according to the reported procedure.[3]

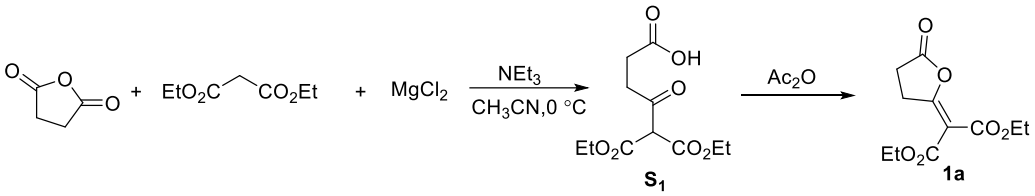
[1] (a) Liu Shi; Qiang Xiong; Shu-Yi Wu; Yang Li; Peng Shen; Ji Lu; and Guang-Yao Ran. *Org. Lett.* **2023**, 25, 12, 2030-2035. (b) Qiang Xiong; Ji Lu; Liu Shi; and Guang-Yao Ran. *Org. Lett.* **2022**, 24, 18, 3363-3367. (c) Yosefdad, S.; Valadbeigi, Y.; and Bayat M. *Journal of Molecular Structure*. **2019**, 127105.

[2] (a) Barry M. Trost; John R. Miller; and Christopher M. Hoffman. *J. Am. Chem. Soc.* **2011**, 133, 21, 8165-8167. (b) Jia-Hao Xie; Chao Zheng; and Shu-Li You. *Angew. Chem. Int. Ed.* **2011**, 60, 22184-22188. (c) Peter Vertesaljai ; Primali V. Navaratne and Alexander J. Grenning. *Angew. Chem. Int. Ed.* **2016**, 128, 325-328.

[3] (a) Jinjin Yun; Xuanyu Liu; Wei Deng; Xueqiang Chu; Zhiliang Shen; and Teckpeng Loh. *J. Org. Chem.* **2018**, 83, 10898-10907. (b) Hang Xu; Sardaraz Khan; Hongfang Li; Xue Wu; and YongJian Zhang. *Org. Lett.* **2019**, 21, 214-217.

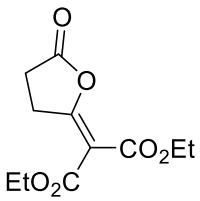
2. General procedure for preparation of CVAs 1

General procedure A

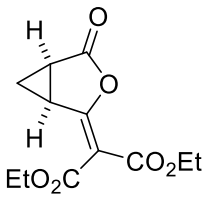


Synthesis of 1a: To a solution of $MgCl_2$ (952.0 mg, 10.0 mmol) in CH_3CN (15 mL) was added diethyl malonate (1.60 mL, 10.0 mmol) and Et_3N (2.78 mL, 20.0 mmol) at 0 °C. After stirring for 15 min, a solution of succinic anhydride (1.00 g, 10.0 mmol) in CH_3CN (10 mL) was added to the mixture and stirred for 30 min at 0 °C. After that, the reaction was moved to room temperature and stirred for 4 h. After completion, the reaction was acidified with 1N HCl. The aqueous layer was extracted with EtOAc (40 mL), and the combined organic layer was washed with 10% HC1 (20 mL) and brine (20 mL). The combined organic layers were dried over Na_2SO_4 and then concentrated to give a colorless oil **S1**.

After that, **S1** was dissolved in acetic anhydride (5 mL) and stirred for 3 h at room temperature. The reaction mixture was concentrated under reduced pressure and purified by flash chromatography on silica gel (petroleum ether/EtOAc/acetic acid = 30/10/1) to give crude product. The crude product was recrystallized from PE/EA to afford **1a**.

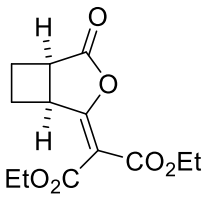


Synthesis of 1a: According to general procedure A from succinic anhydride (1.00 g, 10.0 mmol) and diethyl malonate (1.60 mL, 10.0 mmol) to provide **1a** as a white solid (1.58 g, 65% yield); mp 61–64 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 4.31 (q, J = 7.1 Hz, 2H), 4.24 (q, J = 7.1 Hz, 2H), 3.43-3.38 (m, 2H), 2.77-2.71 (m, 2H), 1.33 (t, J = 7.1 Hz, 3H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 172.3, 165.9, 163.7, 163.4, 106.8, 61.8, 61.2, 26.6, 25.5, 14.1, 14.0; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{14}O_6Na^+$ 265.0683; Found 265.0692.

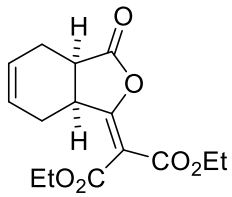


Synthesis of 1e: According to general procedure A from 1,2-cyclopropanedicarboxylic anhydride (1.13 g, 10.0 mmol) and diethyl malonate (1.60 mL, 10.0 mmol) to provide **1e** as a white solid (1.92 g, 76% yield); mp 43–46 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 4.33-4.22 (m, 4H), 3.76-3.71 (m, 1H), 2.55-2.50 (m, 1H), 1.71-1.62 (m, 1H), 1.41-1.36 (m, 1H), 1.35-1.28 (m, 6H). ^{13}C NMR (150

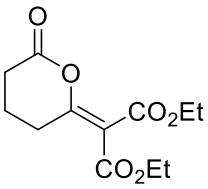
MHz, $CDCl_3$): δ (ppm) 169.7, 163.8, 163.7, 163.2, 106.5, 61.8, 61.4, 21.8, 18.7, 16.7, 14.1, 14.0; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{14}O_6Na^+$ 277.0683; Found 277.0689.



Synthesis of 1f: According to general procedure A from cyclobutane-1,2-dicarboxylic anhydride (1.26 g, 10.0 mmol) and diethyl malonate (1.60 mL, 10.0 mmol) to provide **1f** as a colourless oil (1.27 g, 48% yield); ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 4.38-4.27 (m, 2H), 4.26-4.17 (m, 3H), 3.35-3.28 (m, 1H), 2.90-2.81 (m, 1H), 2.73-2.63 (m, 1H), 2.35-2.21 (m, 2H), 1.35 (t, J = 7.1 Hz, 3H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 175.1, 169.6, 163.6, 163.4, 105.5, 61.8, 61.2, 38.3, 35.2, 26.3, 22.8, 14.1, 14.1; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{16}O_6Na^+$ 291.0849; Found 291.0849.

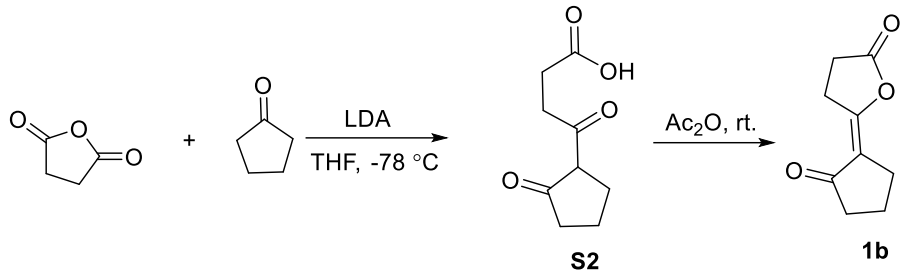


Synthesis of 1g: According to general procedure A from cis-1,2,3,6-Tetrahydrophthalic anhydride (1.52 g, 10.0 mmol) and diethyl malonate (1.60 mL, 10.0 mmol) to provide **1g** as a colourless oil (2.60 g, 88% yield); ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 5.85 (s, 2H), 4.35-4.28 (m, 2H), 4.28-4.19 (m, 2H),4.05-3.97 (m, 1H), 3.10 (td, J = 8.5, 2.3 Hz, 1H), 2.68-2.57 (m, 2H), 2.42-2.34 (m, 1H), 2.12-2.04 (m, 1H), 1.31-1.29 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 174.4, 169.2, 163.5, 163.3, 125.9, 125.8, 106.7, 61.8, 61.3, 37.0, 36.4, 25.4, 21.6, 14.1, 14.0; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{18}O_6Na^+$ 317.0996; Found 317.1003.



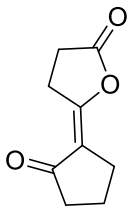
Synthesis of 1n: According to general procedure A from glutaric anhydride (1.14 g, 10.0 mmol) and diethyl malonate (1.60 mL, 10.0 mmol) to provide **1n** as a white solid (1.66 g, 65% yield); mp 62–65 °C; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 4.32 (q, J = 7.1 Hz, 2H), 4.22 (q, J = 7.1 Hz, 2H), 3.15 (t, J = 6.5 Hz, 2H), 2.70 (t, J = 6.7 Hz, 2H), 1.97 (p, J = 6.7 Hz, 2H), 1.33 (t, J = 7.1 Hz, 3H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 164.9, 164.0, 164.0, 163.7, 110.8, 61.8, 61.2, 30.6, 24.5, 17.2, 14.0; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{16}O_6Na^+$ 279.0839; Found 279.0848.

General procedure B

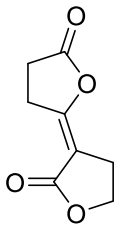


Synthesis of 1b: To a solution of cyclopentanone (1.70 mL, 20.0 mmol) in dry THF (8 mL) was added 2M LDA (10.0 mL, 20.0 mmol) at -78 °C. After stirring for 1 h, a solution of succinic anhydride (1.00 g, 10.0 mmol) in dry THF (10 mL) was further dropped into the reaction and continued stirring for 3 h at -78 °C. After that, the reaction was moved to room temperature and stirred for 1 h. After completion, the reaction was quenched with 1N HCl, and the reaction was extracted with EtOAc. The combined organic layers were dried over Na_2SO_4. The reaction mixture was concentrated under reduced pressure to get yellow oil product **S2**.

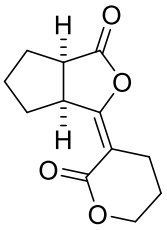
S2 was dissolved in acetic anhydride (5 mL) and stirred for 3 h at room temperature. After completion, the reaction mixture was concentrated under reduced pressure and purified by flash chromatography on silica gel (petroleum ether/EtOAc/acetic acid = 30/10/1) to give crude product. The crude product was recrystallized from PE/EA to afford **1b.**



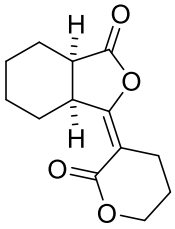
Synthesis of 1b: According to general procedure B to provide **1b** as a white solid (512.8 mg, 31% yield); mp 89–91 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 3.38-3.31 (m, 2H), 2.77-2.69 (m, 4H), 2.36 (t, J = 7.8 Hz, 2H), 1.97 (p, J = 7.6 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 208.2, 174.2, 158.0, 113.3, 39.9, 26.6, 26.2, 25.5, 20.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_9H_{11}O_3^+$ 167.0703; Found 167.0708.



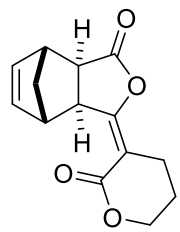
Synthesis of 1d: According to general procedure B from γ-butyrolactone (1.54 mL, 20 mmol) and succinic anhydride (1.00 g, 10.0 mmol) to provide **1d** as a white solid (518.6 mg, 31% yield); mp 92–95 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 4.40 (t, J = 7.6 Hz, 2H), 3.44-3.37 (m, 2H), 3.05-2.98 (m, 2H), 2.81-2.75 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 173.5, 171.3, 160.0, 101.3, 65.8, 26.2, 25.1, 24.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_8H_9O_4^+$ 169.0495; Found 169.0503.



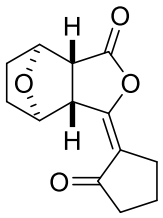
Synthesis of 1h: According to general procedure B from cis-cyclopentane-1,2-dicarboxylic acid anhydride (273.9 mg, 1.95 mmol) and δ-valerolactone (0.37 mL, 3.91 mmol) to provide **1h** as a white solid (136.5 mg, 32% yield); mp 125–128 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 4.32-4.24 (m, 2H), 3.51 (td, J = 9.4, 3.5 Hz, 1H), 3.22 (td, J = 9.0, 2.5 Hz, 1H), 2.54 (t, J = 6.7 Hz, 2H), 2.25-2.18 (m, 1H), 2.13-2.03 (m, 1H), 2.03-1.93 (m, 3H), 1.92-1.85 (m, 1H), 1.84-1.78 (m, 1H), 1.59-1.48 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 176.9, 163.9, 162.9, 100.7, 68.2, 43.6, 42.9, 32.8, 31.2, 25.8, 23.8, 22.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{14}O_4Na^+$ 245.0784; Found 245.0794.



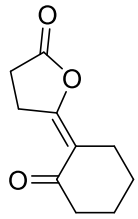
Synthesis of 1i: According to general procedure B cis-1,2-cyclohexanedicarboxylic anhydride (770.8 mg, 5.0 mmol) and δ-valerolactone (0.94 mL, 10.0 mmol) to provide **1i** as a white solid (425.0 mg, 36% yield); mp 161–164 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 4.29 (t, J = 5.3 Hz, 2H), 3.14 (dt, J = 11.1, 6.7 Hz, 1H), 2.88 (t, J = 7.0 Hz, 1H), 2.64-2.57 (m, 1H), 2.56-2.49 (m, 1H), 2.29 (d, J = 12.9 Hz, 1H), 2.10-2.02 (m, 1H), 2.02-1.94 (m, 2H), 1.80-1.74 (m, 1H), 1.71 (t, J = 5.6 Hz, 1H), 1.64-1.57 (m, 1H), 1.24-1.13 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 174.1, 162.7, 162.4, 100.6, 68.2, 38.4, 38.3, 26.7, 23.0, 23.0, 22.7, 22.0, 21.7; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{14}O_6Na^+$ 265.0683; Found 265.0692.



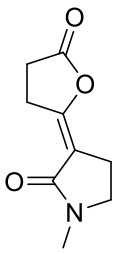
Synthesis of 1j: According to general procedure B from cis-5-norbornene-exo-2,3-dicarboxylic anhydride (328.3 mg, 2.0 mmol) and δ-valerolactone (0.38 mL, 4.0 mmol) to provide **1j** as a white solid (147.7 mg, 30% yield); mp 142–145 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 6.36-6.32 (m, 1H), 6.32-6.27 (m, 1H), 4.35-4.26 (m, 2H), 3.41 (s, 1H), 3.24 (s, 1H), 3.09 (d, J = 7.7 Hz, 1H), 2.84-2.80 (m, 1H), 2.70-2.56 (m, 2H), 2.07-1.94 (m, 2H), 1.61-1.56 (m, 1H), 1.45 (d, J = 9.9 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 173.6, 162.6, 160.8, 138.2, 137.9, 101.6, 68.2, 47.3, 46.7, 46.5, 46.3, 43.9, 23.8, 22.7; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{14}O_4Na^+$ 269.0784; Found 269.0791.



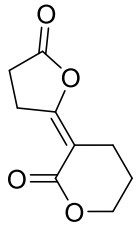
Synthesis of 1k: According to general procedure B from norcantharidine (500 mg, 2.97 mmol) and cyclopentanone (0.51 mL, 5.95 mmol) to provide **1k** as a white solid (159.9 mg, 23% yield); mp 143–148 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 4.98 (d, J = 4.9 Hz, 1H), 4.79 (d, J = 4.9 Hz, 1H), 3.15-3.11 (m, 1H), 2.95 (d, J = 7.8 Hz, 1H), 2.76-2.68 (m, 1H), 2.66-2.59 (m, 1H), 2.40-2.34 (m, 2H), 2.12-2.03 (m, 1H), 1.96 (dd, J = 20.9, 8.2 Hz, 1H), 1.91-1.80 (m, 2H), 1.67-1.63 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 202.8, 174.1, 153.4, 112.7, 80.2, 80.0, 48.6, 47.8, 39.5, 28.4, 28.3, 27.0, 20.5; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{14}O_4Na^+$ 257.0784; Found 257.0792.



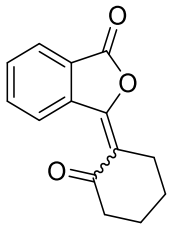
Synthesis of 1o: According to general procedure B from cyclohexanone (2.44 mL, 20.0 mmol) and succinic anhydride (1.00 g, 10.0 mmol) to provide **1o** as a white solid (576.0 mg, 32% yield); mp 61–63 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 3.35-3.29 (m, 2H), 2.76-2.68 (m, 2H), 2.64-2.58 (m, 2H), 2.40 (t, J = 6.7 Hz, 2H), 1.88-1.81 (m, 2H), 1.76-1.69 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 201.2, 174.2, 160.5, 113.3, 40.8, 27.5, 26.5, 25.4, 23.0, 22.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{10}H_{13}O_3^+$ 181.0859; Found 181.0863.



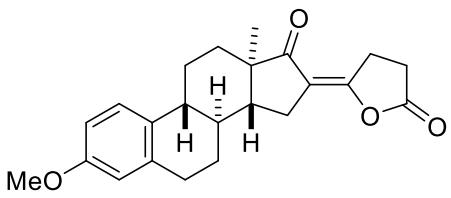
Synthesis of 1p: According to general procedure B from N-methylpyrrolidone (0.96 mL, 10.0 mmol) and succinic anhydride (500 mg, 5.0 mmol) to provide **1p** as a white solid (226.3 mg, 25% yield); mp 151–153 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 3.46-3.40 (m, 2H), 2.90 (s, 3H), 2.87-2.80 (m, 2H), 2.73-2.66 (m, 2H), 2.65-2.59 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 173.9, 165.7, 149.6, 106.8, 46.4, 29.9, 25.8, 25.2, 21.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_9H_{11}NO_3Na^+$ 204.0631; Found 204.0638.



Synthesis of 1q: According to general procedure B from succinic anhydride (1.00 g, 10.0 mmol) and δ-valerolactone (1.88 mL, 20.0 mmol) to provide **1q** as a white solid (546.2 mg, 30% yield); mp 142–148 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 4.35-4.29 (m, 2H), 3.45-3.38 (m, 2H), 2.78-2.72 (m, 2H), 2.66-2.61 (m, 2H), 1.94-1.84 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 173.7, 165.7, 163.8, 103.1, 68.9, 27.4, 26.4, 22.8, 21.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_9H_{11}O_4^+$ 183.0652; Found 183.0660.

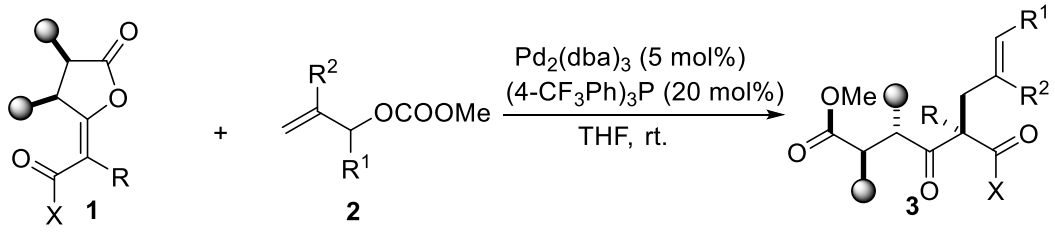


Synthesis of 1s: According to general procedure B from phthalic anhydride (1.48 g, 10.0 mmol) and cyclohexanone (2.44 mL, 20.0 mmol) to provide **1s** as a white solid (524.4 mg, 23% yield), 2.8:1 *E/Z*, determined by ^{1}H NMR analysis; mp 135–141 ℃; ^{1}H NMR (600 MHz, $CDCl_3$, major isomer): δ (ppm) 8.01 (d, J = 7.6 Hz, 1H), 7.88 (d, J = 7.9 Hz, 1H), 7.77 (td, J = 7.7, 1.2 Hz, 1H), 7.65 (td, J = 7.5, 0.9 Hz, 1H), 3.05 (t, J = 6.3 Hz, 2H), 2.65-2.61 (m, 1H), 2.01-1.92 (m, 5H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 200.0, 166.2, 145.4, 138.5, 134.6, 131.0, 126.2, 125.9, 124.9, 119.8, 42.3, 28.5, 24.2, 24.0; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{12}O_3Na^+$ 251.0679; Found 251.0688.



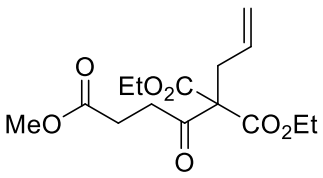
Synthesis of 1t: According to general procedure B from estrone 3-methyl ether (1.40 g, 5.0 mmol) and succinic anhydride (251.6 mg, 2.5 mmol) to provide **1t** as a white solid (143.7 mg, 16 % yield); mp 277–281 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.20 (d, J = 8.6 Hz, 1H), 6.72 (dd, J = 8.6, 2.8 Hz, 1H), 6.65 (d, J = 2.8 Hz, 1H), 3.78 (s, 3H), 3.46-3.36 (m, 2H), 2.97-2.86 (m, 2H), 2.82 (dd, J = 15.0, 6.3 Hz, 1H), 2.77-2.71 (m, 2H), 2.45-2.38 (m, 1H), 2.32-2.20 (m, 2H), 1.99 (dd, J = 9.2, 2.7 Hz, 2H), 1.67-1.52 (m, 4H), 1.52-1.40 (m, 1H), 0.93 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 210.3, 174.0, 158.5, 157.7, 137.7, 132.0, 126.2, 113.9, 112.8, 111.7, 55.2, 49.3, 48.6, 44.0, 37.9, 31.6, 29.6, 26.7, 26.3, 26.2, 26.0, 25.6, 14.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{27}O_4^+$ 367.1904; Found 367.1912.

3. General procedure of FEAA

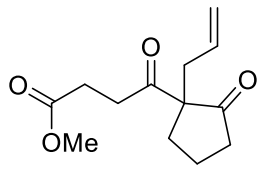


To a dried 10 mL schlenk tube equipped with a stirring bar were added $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol), and $(4\text{-}CF_3Ph)_3P$ (9.3 mg, 0.02 mmol, 20 mol%). The tube was evacuated and back-filled with argon for three times. Redistilled THF (1 mL) was added via a syringe under argon atmosphere. The mixture was stirred at room temperature for 30 min to give a clear solution, and then transferred to

another schlenk tube containing **1** (0.1 mmol, 1.0 equiv.) and allyl carbonate **2** (0.1 mmol, 1.0 equiv.) under argon atmosphere. Next, the tube was evacuated and back-filled with argon for three times. The reaction was stirred at room temperature for 12 h and monitored by TLC. After completion, the reaction mixture was concentrated under reduced pressure and purified by flash chromatography on silica gel (petroleum ether/EtOAc = 6:1) to give product **3**.

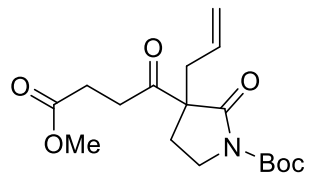


Synthesis of 3a: According to general procedure from **1a** (24.2 mg, 0.1 mmol) and **2a** (11.6 mg, 0.1 mmol) to provide **3a** as a colourless oil (26.7 mg, 85% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 5.91-5.81 (m, 1H), 5.13-5.10 (m, 1H), 5.09 (t, J = 1.3 Hz, 1H), 4.30-4.20 (m, 4H), 3.68 (s, 3H), 3.05 (t, J = 6.8 Hz, 2H), 2.86 (d, J = 7.2 Hz, 2H), 2.60 (t, J = 6.8 Hz, 2H), 1.29 (t, J = 7.1 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 200.5, 172.8, 167.1, 132.6, 119.3, 70.8, 62.2, 51.8, 37.0, 35.8, 28.2, 14.0; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{22}O_7Na^+$ 337.1258; Found 337.1266.

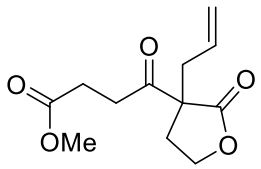


Synthesis of 3b: To a dried 10 mL schlenk tube equipped with a stirring bar were added $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol, 5 mol%), **1b** (16.6 mg, 0.1 mmol, 1.0 equiv.) and allyl carbonate **2a** (11.6 μL, 0.1 mmol, 1.0 equiv.). The tube was evacuated and back-filled with argon for three times. Redistilled THF (1 mL) was added via a syringe under argon atmosphere. Next, the tube was evacuated and back-filled with argon for three times. The reaction was stirred at room temperature for 12 h and monitored by TLC. After completion, product **3b** was obtained by flash chromatography on silica gel (petroleum ether/EtOAc = 6/1): 23.4 mg, as a colourless oil, 98% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 5.64-5.54 (m, 1H), 5.18-5.16 (m, 1H), 5.14 (t, J = 1.3 Hz, 1H), 3.65 (s, 3H), 3.04-2.96 (m, 1H), 2.76-2.65 (m, 3H), 2.64-2.58 (m, 1H), 2.57-2.49 (m, 1H), 2.47-2.42 (m, 1H), 2.41-2.35 (m, 1H), 2.28-2.19 (m, 1H), 1.94-1.83 (m, 2H), 1.82-1.74 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 215.6, 204.4, 173.1, 132.5, 119.1, 67.9, 51.8, 39.1, 38.6, 32.9, 30.5, 28.1, 19.3; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{18}O_4Na^+$ 261.1097; Found 261.1104.

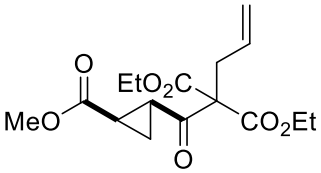
Synthesis of 3c: According to general procedure from **1c** (26.7 mg, 0.1 mmol) and allyl carbonate **2a**



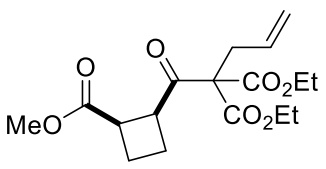
(14.0 μL, 0.12 mmol) to provide **3c** as a colourless oil (20.8 mg, 61% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 5.68-5.58 (m, 1H), 5.19-5.13 (m, 2H), 3.71-3.67 (m, 1H), 3.65 (s, 3H), 3.58 (ddd, J = 10.8, 8.8, 7.6 Hz, 1H), 3.16-3.08 (m, 1H), 2.91-2.78 (m, 2H), 2.68-2.54 (m, 4H), 1.83 (dt, *J* = 13.2, 8.9 Hz, 1H), 1.52 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 204.3, 173.0, 171.9, 149.9, 131.7, 119.9, 83.3, 63.8, 51.8, 43.90, 39.1, 32.9, 28.0, 28.0, 24.7; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{25}NO_6Na^+$ 362.1574; Found 362.1582.



Synthesis of 3d: According to general procedure from **1d** (16.8 mg, 0.1 mmol) and **2a** (11.6 μL, 0.1 mmol) to provide **3d** as a colourless oil (14.7 mg, 61% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 5.69-5.60 (m, 1H), 5.21-5.19 (m, 1H),5.19-5.17 (m, 1H), 4.30 (td, *J* = 8.9, 3.4 Hz, 1H), 4.24-4.17 (m, 1H), 3.67 (s, 3H), 3.15-3.07 (m, 1H), 2.94-2.84 (m, 2H), 2.82-2.75 (m, 1H), 2.71-2.57 (m, 3H), 2.19-2.11 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 203.1, 175.4, 172.8, 131.3, 120.4, 66.4, 60.6, 51.9, 38.9, 32.7, 29.1, 28.0; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{16}O_5Na^+$ 263.0890; Found 263.0899.

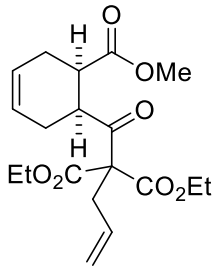


Synthesis of 3e: According to general procedure from **1e** (25.4 mg, 0.1 mmol) and **2a** (11.6 μL, 0.1 mmol) to provide **3e** as a colourless oil (23.6 mg, 73% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 5.88-5.78 (m, 1H), 5.14-5.09 (m, 1H), 5.08-5.05 (m, 1H), 4.32-4.19 (m, 4H), 3.66 (s, 3H), 2.93-2.86 (m, 1H), 2.84-2.77 (m, 1H), 2.70-2.63 (m, 1H), 2.20-2.12 (m, 1H), 1.87-1.81 (m, 1H), 1.34-1.24 (m, 7H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 196.4, 169.2, 167.2, 166.9, 132.7, 118.9, 71.4, 62.2, 62.0, 52.0, 36.6, 27.1, 25.9, 13.9, 13.9, 13.8; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{22}O_7Na^+$ 349.1258; Found 349.1266.

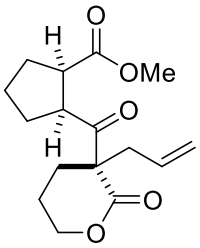


Synthesis of 3f: According to general procedure from **3f** (26.8 mg, 0.1 mmol) and **2a** (11.6 μL, 0.1 mmol) to provide **3f** as a colourless oil (22.8 mg, 67% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 5.85-5.75 (m, 1H), 5.12-5.07 (m, 1H), 5.07-5.03 (m, 1H), 4.29-4.15 (m, 4H), 4.13-4.06 (m, 1H), 3.60 (s, 3H), 3.35-3.26

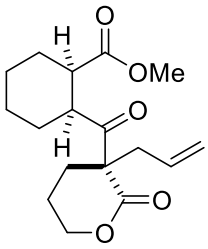
(m, 1H), 2.90 (dd, J = 14.2, 6.9 Hz, 1H), 2.79 (dd, J = 14.2, 7.6 Hz, 1H), 2.54-2.43 (m, 1H), 2.29-2.21 (m, 1H), 2.19-2.11 (m, 2H), 1.30 (t, J = 7.1 Hz, 3H), 1.26 (t, J = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 201.4, 173.1, 167.3, 166.5, 132.8, 118.8, 71.3, 62.1, 61.9, 51.5, 46.3, 40.9, 36.5, 23.6, 21.3, 14.0, 13.9; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{24}O_7Na^+$ 363.1414; Found 363.1420.



Synthesis of 3g: According to general procedure from **1g** (29.4 mg, 0.1 mmol) and **2a** (11.6 μL, 0.1 mmol) to provide **3g** as a colourless oil (24.3 mg, 66% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.90-5.80 (m, 1H), 5.68 (s, 2H), 5.15-5.04 (m, 2H), 4.29-4.18 (m, 4H), 3.66 (s, 3H), 3.66-3.60 (m, 1H), 2.94-2.89 (m, 1H), 2.90-2.82 (m, 2H), 2.58-2.46 (m, 2H), 2.40-2.31 (m, 1H), 2.30-2.21 (m, 1H), 1.30 (t, J = 7.1 Hz, 3H), 1.26 (t, J = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 202.1, 173.7, 167.5, 167.2, 132.7, 124.7, 124.6, 119.0, 70.9, 62.0, 62.0, 51.5, 44.9, 39.4, 38.1, 26.5, 25.7, 13.9, 13.9; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{26}O_7Na^+$ 389.1571; Found 389.1574.

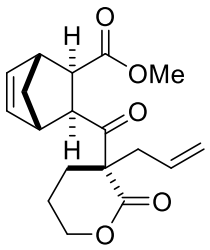


Synthesis of 3h: According to general procedure from **1h** (22.2 mg, 0.1 mmol) and **2a** (11.6 μL, 0.1 mmol) to provide **3h** as a colourless oil (19.7 mg, 67% yield), 14:1 dr, determined by ^{1}H NMR analysis; ^{1}H NMR (600 MHz, $CDCl_3$, major isomer): δ (ppm) 5.73-5.63 (m, 1H), 5.21-5.10 (m, 2H), 4.34-4.22 (m, 2H), 3.98-3.91 (m, 1H), 3.63 (s, 3H), 3.02 (dd, J = 13.8, 6.3 Hz, 1H), 2.92 (q, J = 8.3 Hz, 1H), 2.49-2.41 (m, 1H), 2.27 (dd, J = 13.8, 8.1 Hz, 1H), 2.18-2.10 (m, 1H), 2.02-1.91 (m, 2H), 1.85-1.61 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$, major isomer): δ (ppm) 206.7, 174.0, 171.0, 132.3, 120.0, 70.2, 60.4, 51.6, 48.4, 47.9, 40.8, 30.6, 28.1, 25.4, 24.3, 21.1; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{12}O_5Na^+$ 317.1359; Found 317.1367.

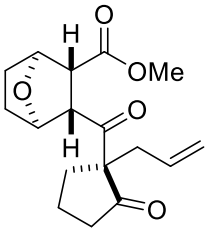


Synthesis of 3i: According to general procedure from **1i** (23.6 mg, 0.1 mmol) and **2a** (14.0 μL, 0.12 mmol) to provide **3i** as a colourless oil (23.4 mg, 76% yield), 13:1 dr, determined by ^{1}H NMR analysis; ^{1}H NMR (600 MHz, $CDCl_3$, major isomer): δ (ppm) 5.70-5.59 (m, 1H), 5.18-5.06 (m, 2H), 4.35-4.25 (m, 2H), 3.65 (s, 3H), 2.95 (dd, J = 13.9, 6.4 Hz, 1H), 2.65-2.56 (m, 1H), 2.53-2.39 (m, 1H), 2.34 (dd, J = 13.9, 8.0

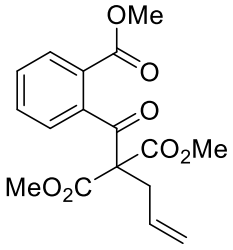
Hz, 1H), 2.16-2.06 (m, 1H), 2.02-1.91 (m, 1H),1.90-1.65 (m, 6H), 1.64-1.56 (m, 1H), 1.50-1.41 (m, 1H), 1.39-1.30 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, major isomer): δ (ppm) 207.1, 174.3, 171.6, 132.6, 119.9, 70.1, 60.1, 51.5, 44.5, 42.8, 41.7, 26.2, 26.0, 25.7, 23.6, 22.6, 21.0; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{24}O_5Na^+$ 331.1516; Found 331.1523.



Synthesis of 3j: According to general procedure from **1j** (24.6 mg, 0.1 mmol) and **2a** (11.6 μL, 0.1 mmol) to provide **3j** as a colourless oil (18.2 mg, 57% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 6.22 (s, 2H), 5.74-5.64 (m, 1H), 5.20-5.07 (m, 2H), 4.35-4.23 (m, 2H), 3.62 (s, 3H), 3.58 (d, J = 9.0 Hz, 1H), 3.22 (d, J = 1.8 Hz, 1H), 2.99 (dd, J = 13.9, 6.5 Hz, 1H), 2.76 (d, J = 1.8 Hz, 1H), 2.47-2.39 (m, 2H), 2.29 (dd, J = 13.9, 8.0 Hz, 1H), 1.95 (d, J = 9.2 Hz, 1H), 1.88-1.74 (m, 2H), 1.74-1.66 (m, 1H), 1.42 (d, J = 9.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 205.1, 173.9, 170.8, 138.3, 137.4, 132.0, 120.1, 70.2, 60.8, 51.5, 49.0, 48.1, 47.8, 44.4, 44.2, 40.8, 25.3, 21.1; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{22}O_5Na^+$ 341.1359; Found 341.1369.

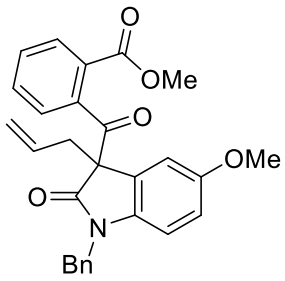


Synthesis of 3k: According to general procedure from **1k** (23.4 mg, 0.1 mmol) and **2a** (11.6 μL, 0.1 mmol) to provide **3k** as a colourless oil (25.1 mg, 82% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 5.63-5.54 (m, 1H), 5.12 (d, J = 1.1 Hz, 1H), 5.11-5.08 (m, 2H), 4.08 (d, J = 4.4 Hz, 1H), 3.90 (d, J = 9.3 Hz, 1H), 3.63 (s, 3H), 2.79 (d, J = 9.3 Hz, 1H), 2.70-2.62 (m, 1H), 2.64-2.59 (m, 1H), 2.54-2.47 (m, 1H), 2.39-2.31 (m, 1H), 2.26-2.18 (m, 1H), 1.92-1.85 (m, 1H), 1.83-1.72 (m, 4H), 1.67-1.58 (m, 1H), 1.55-1.45 (m, 1H).; ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 216.6, 201.6, 171.7, 132.1, 119.4, 79.0, 77.9, 68.2, 54.1, 52.2, 51.8, 39.4, 39.2, 29.5, 29.4, 28.6, 19.1; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{22}O_5Na^+$ 329.1359; Found 329.1370.

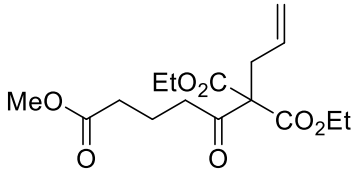


Synthesis of 3l: According to general procedure from **1l** (26.2 mg, 0.1 mmol) and **2a** (11.6 μL, 0.1 mmol) to provide **3l** as a colourless oil (31.2 mg, 86% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.94 (d, J = 7.8 Hz, 1H), 7.56 (t, J = 7.6 Hz, 1H), 7.52-7.44 (m, 2H), 6.08-5.98 (m, 1H), 5.16-5.06 (m, 2H), 3.86 (s, 3H), 3.65 (s, 6H), 3.08 (d, J = 7.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 197.1, 167.7, 166.5, 141.7,

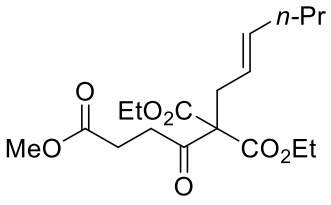
133.3, 132.3, 129.8, 129.5, 128.2, 126.4, 118.9, 72.2, 52.8, 52.6, 38.2; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{19}H_{22}O_7Na^+$ 385.1258; Found 385.1256.



Synthesis of 3m: According to general procedure from **1m** (38.3 mg, 0.1 mmol) and **2a** (11.6 μL, 0.1 mmol) to provide **3m** as a colourless oil (44.1 mg, 97% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, J = 7.7 Hz, 1H), 7.41 (t, J = 7.5 Hz, 1H), 7.34 (t, J = 7.4 Hz, 1H), 7.23-7.18 (m, 3H), 7.08 (d, J = 2.6 Hz, 1H), 7.03 (dd, J = 6.7, 2.7 Hz, 2H), 6.81 (d, J = 7.4 Hz, 1H), 6.70 (dd, J = 8.5, 2.6 Hz, 1H), 6.54 (d, J = 8.5 Hz, 1H), 5.40-5.30 (m, 1H), 5.08 (d, J = 16.7 Hz, 1H), 4.92 (d, J = 9.9 Hz, 1H), 4.81 (d, J = 15.5 Hz, 1H), 4.66 (d, J = 15.6 Hz, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 3.26 (dd, J = 13.6, 6.8 Hz, 1H), 3.18 (dd, J = 13.5, 8.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 200.4, 173.6, 166.2, 156.0, 141.2, 136.6, 135.6, 132.3, 131.4, 129.8, 129.3, 128.6, 128.3, 127.9, 127.5, 127.5, 125.6, 119.8, 113.8, 112.0, 109.3, 66.6, 55.8, 52.6, 44.0, 40.0; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{28}H_{25}NO_5Na^+$ 478.1625; Found 478.1635.

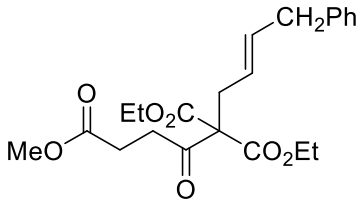


Synthesis of 3n: According to general procedure from **1n** (25.6 mg, 0.1 mmol) and **2a** (11.6 μL, 0.1 mmol) to provide **3n** as a colourless oil (22.9 mg, 70% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 5.92-5.83 (m, 1H), 5.14-5.05 (m, 2H), 4.24 (q, J = 7.1 Hz, 4H), 3.67 (s, 3H), 2.86-2.81 (m, 2H), 2.73 (t, J = 7.0 Hz, 2H), 2.34 (t, J = 7.3 Hz, 2H), 1.93 (p, J = 7.2 Hz, 2H), 1.28 (t, J = 7.1 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 201.3, 173.5, 167.3, 132.7, 119.2, 70.9, 62.1, 51.6, 39.7, 37.0, 32.8, 19.0, 14.0; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{16}H_{24}O_7Na^+$ 351.1414; Found 351.1412.



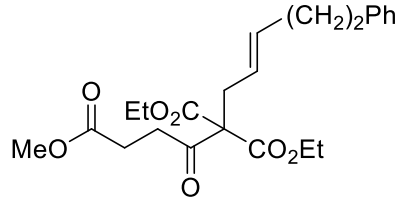
Synthesis of 3o: According to general procedure from **1a** (24.2 mg, 0.1 mmol) and allyl carbonate **2b** (15.8 mg, 0.1 mmol) to provide **3o** as a colourless oil (29.1 mg, 82% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 5.56-5.42 (m, 2H), 4.24 (q, J = 7.2 Hz, 4H), 3.67 (s, 3H), 3.04 (t, J = 6.9 Hz, 2H), 2.80 (d, J = 6.8 Hz, 2H), 2.60 (t, J = 6.9 Hz, 2H), 1.94 (q, J = 6.9 Hz, 2H), 1.33 (q, J = 7.4

Hz, 2H), 1.28 (t, J = 7.1 Hz, 6H), 0.86 (t, J = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 200.8, 172.8, 167.3, 135.6, 123.8, 71.2, 62.0, 51.8, 36.1, 35.8, 34.6, 28.2, 22.4, 14.0, 13.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{28}O_7Na^+$ 379.1727; Found 379.1734.

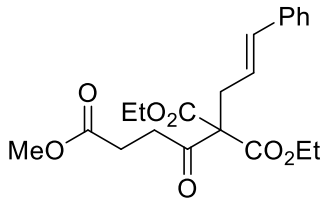


Synthesis of 3p: According to general procedure from **1a** (24.2 mg, 0.1 mmol) and allyl carbonate **2c** (20.6 mg, 0.1 mmol) to provide **3p** as a colourless oil (28.5 mg, 71% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.29-7.23 (m, 2H), 7.17 (t, J = 7.4 Hz, 1H), 7.13 (d, J = 6.7 Hz, 2H), 5.71-5.63 (m, 1H), 5.63-5.55 (m, 1H), 4.19 (q, J = 7.1 Hz, 4H), 3.67 (s, 3H), 3.30 (d, J = 6.7 Hz, 2H), 3.03 (t, J = 6.9 Hz, 2H), 2.86-2.81 (m, 2H), 2.57 (t, J = 6.8 Hz, 2H), 1.23 (t, J = 7.1 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 200.7, 172.8, 167.2, 140.3, 134.2, 128.5, 128.4, 126.0, 125.2, 71.1, 62.1, 51.8, 39.1, 35.9, 35.8, 28.2, 13.9; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{28}O_7Na^+$ 427.1727; Found 427.1735.

Synthesis of 3q: According to general procedure from **1a** (24.2 mg, 0.1 mmol) and allyl carbonate

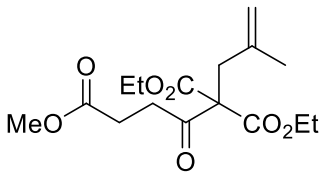


2d (22.0 mg, 0.1 mmol) to provide **3q** as a colourless oil (30.9 mg, 74% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.26 (t, J = 7.6 Hz, 2H), 7.21-7.12 (m, 3H), 5.61-5.48 (m, 2H), 4.22 (q, J = 7.1 Hz, 4H), 3.67 (s, 3H), 3.01 (t, J = 6.9 Hz, 2H), 2.80 (d, J = 6.6 Hz, 2H), 2.65-2.61 (m, 2H), 2.58 (d, J = 6.9 Hz, 2H), 2.33-2.26 (m, 2H), 1.27 (t, J = 7.1 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 200.7, 172.8, 167.2, 141.7, 134.7, 128.4, 128.3, 125.8, 124.4, 71.1, 62.1, 51.8, 36.0, 35.8, 35.7, 34.2, 28.2, 14.0; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{30}O_7Na^+$ 441.1884; Found 441.1893.



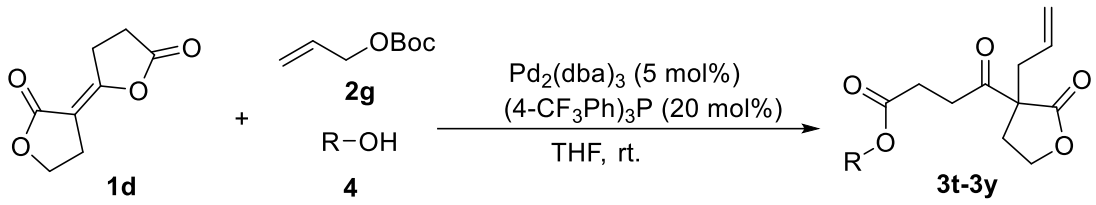
Synthesis of 3r: According to general procedure from **1a** (24.2 mg, 0.1 mmol) and allyl carbonate **2e** (19.2 mg, 0.1 mmol) to provide **3r** as a colourless oil (24.1 mg, 62% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.24 (d, J = 6.8 Hz, 2H), 7.22-7.18 (m, 2H), 7.13 (t, J = 7.2 Hz, 1H), 6.37 (d, J = 15.8 Hz, 1H), 6.22-6.13 (m, 1H), 4.23-4.13 (m, 4H), 3.59 (s, 3H), 3.00 (t, J = 6.8 Hz, 2H), 2.94 (dd, J = 7.4, 1.4 Hz, 2H), 2.54 (t, J = 6.8 Hz, 2H), 1.20 (t, J = 7.1 Hz, 6H); ^{13}C NMR (150 MHz,

$CDCl_3$): δ (ppm) 200.5, 172.8, 167.2, 137.0, 134.2, 128.5, 127.4, 126.3, 124.1, 71.1, 62.3, 51.8, 36.4, 35.8, 28.3, 14.0; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{26}O_7Na^+$ 413.1571; Found 413.1581.

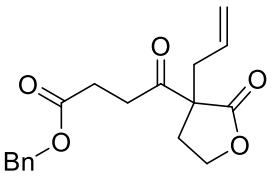


Synthesis of 3s: According to general procedure from **1a** (24.2 mg, 0.1 mmol) and allyl carbonate **2f** (13.0 mg, 0.1 mmol) to provide **3s** as a colourless oil (22.2 mg, 68% yield); ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 4.81 (s, 1H), 4.69 (d, J = 1.0 Hz, 1H), 4.23 (td, J = 7.2, 0.7 Hz, 4H), 3.67 (s, 3H), 3.16 (t, J = 6.8 Hz, 2H), 2.96 (d, J = 1.2 Hz, 2H), 2.60 (t, J = 6.8 Hz, 2H), 1.66 (s, 3H), 1.28 (t, J = 7.2 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 200.5, 172.7, 167.0, 140.8, 115.2, 70.8, 62.1, 51.7, 40.1, 36.1, 28.4, 23.3, 13.8; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{24}O_7Na^+$ 351.1414; Found 351.1424.

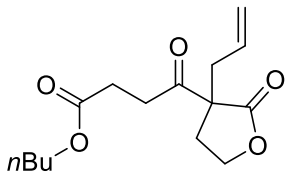
4. General procedure of three-component FEAA



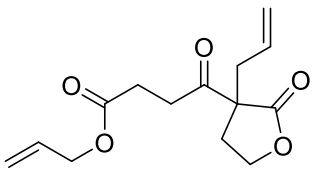
To a dried 10 mL schlenk tube equipped with a stirring bar were added $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol), and $(4\text{-}CF_3Ph)_3P$ (9.3 mg, 0.02 mmol, 20 mol%). The tube was evacuated and back-filled with argon for three times. Redistilled THF (1 mL) was added via a syringe under argon atmosphere. The mixture was stirred at room temperature for 30 min to give a clear solution, and then transferred to another schlenk tube containing **1d** (16.8 mg, 0.1 mmol, 1.0 equiv.), allyl tert-butyl carbonate **2g** (17.0 mg, 0.12 mmol, 1.2 equiv.), alcohol **4** (0.1 or 0.2 mmol, 1.0 or 2.0 equiv.). Next, the tube was evacuated and back-filled with argon for three times. The reaction was stirred at room temperature for 12 h and monitored by TLC. After completion, the reaction mixture was concentrated under reduced pressure and purified by flash chromatography on silica gel (petroleum ether/EtOAc = 5:1) to give product **3t-3y**.



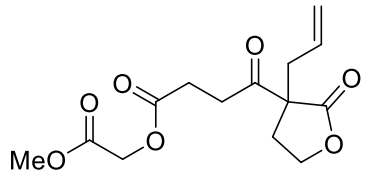
Synthesis of 3t: According to general procedure from **1d** (16.8 mg, 0.1 mmol), **2g** (17.0 mg, 0.12 mmol) and **4a** (10.4 μL, 0.1 mmol) to provide **3t** as a colourless oil (13.7 mg, 87% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.44-7.29 (m, 5H), 5.68-5.58 (m, 1H), 5.22-5.15 (m, 2H), 5.11 (d, J = 2H), 4.27 (td, J = 8.8, 3.5 Hz, 1H), 4.20-2.13 (m, 1H), 3.15-3.07 (m, 2H), 2.95-2.84 (m, 1H), 2.76 (dd, J = 14.3, 7.8 Hz, 3H), 2.74-2.62 (m, 1H), 2.18-2.09 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 203.1, 175.4, 172.2, 135.7, 131.3, 128.6, 128.3, 128.3, 120.4, 66.7, 66.4, 60.6, 38.9, 32.7, 29.1, 28.2; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{20}O_5Na^+$ 339.1203; Found 339.1212.



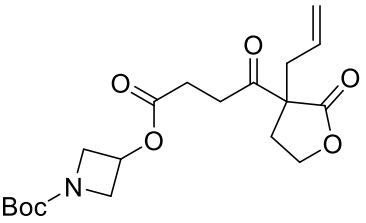
Synthesis of 3u: According to general procedure from **1d** (16.8 mg, 0.1 mmol), **2g** (17.0 mg, 0.12 mmol) and **4b** (18.3 μL, 0.2 mmol) to provide **3u** as a colourless oil (15.3 mg, 53% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 5.70-5.60 (m, 1H), 5.21-5.19 (m, 1H), 5.19-5.17 (m, 1H), 4.29 (td, J = 8.9, 3.5 Hz, 1H), 4.21 (td, J = 8.9, 7.3 Hz, 1H), 4.06 (t, J = 6.7 Hz, 2H), 3.13-3.05 (m, 1H), 2.93-2.84 (m, 2H), 2.82-2.74 (m, 1H), 2.70-2.66 (m, 1H), 2.65-2.57 (m, 2H), 2.15 (dt, J = 13.2, 8.8 Hz, 1H), 1.62-1.59 (m, 1H), 1.59-1.57 (m, 1H), 1.44-1.32 (m, 2H), 0.93 (t, J = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 203.2, 175.4, 172.5, 131.4, 120.4, 66.4, 64.7, 60.6, 38.9, 32.7, 30.6, 29.1, 28.2, 19.1, 13.7; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{22}O_5Na^+$ 305.1359; Found 305.1367.



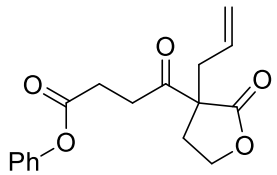
Synthesis of 3v: According to general procedure from **1d** (16.8 mg, 0.1 mmol), **2g** (17.0 mg, 0.12 mmol) and **4c** (14.1 μL, 0.2 mmol) to provide **3v** as a colourless oil (16.6 mg, 62% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 5.95-5.85 (m, 1H), 5.70-5.60 (m, 1H), 5.31 (dd, J = 17.2, 1.5 Hz, 1H), 5.24 (dd, J = 10.5, 1.3 Hz, 1H), 5.22-5.18 (m, 1H), 5.18 (s, 1H), 4.57 (dd, J = 5.8, 1.4 Hz, 2H), 4.33-4.26 (m, 1H), 4.20 (td, J = 8.9, 7.3 Hz, 1H), 3.15-3.07 (m, 1H), 2.95-2.86 (m, 2H), 2.78 (dd, J = 14.4, 7.8 Hz, 1H), 2.72-2.60 (m, 3H), 2.15 (dt, J = 13.2, 8.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 203.1, 175.4, 172.0, 132.0, 131.3, 120.4, 118.4, 66.4, 65.5, 60.6, 38.9, 32.7, 29.1, 28.1; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{18}O_5Na^+$ 289.1046; Found 289.1056.



Synthesis of 3w: According to general procedure from **1d** (16.8 mg, 0.1 mmol), **2g** (17.0 mg, 0.12 mmol) and **4d** (15.8 μL, 0.2 mmol) to provide **3w** as a colourless oil (24.7 mg, 83% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 5.69-5.59 (m, 1H), 5.20 (d, J = 3.6 Hz, 1H), 5.18 (s, 1H), 4.62 (s, 2H), 4.29 (td, J = 8.9, 3.6 Hz, 1H), 4.24-4.17 (m, 1H), 3.76 (s, 3H), 3.18-3.10 (m, 1H), 2.99-2.91 (m, 1H), 2.92-2.85 (m, 1H), 2.82-2.75 (m, 1H), 2.77-2.70 (m, 2H), 2.68 (dd, J = 14.4, 6.7 Hz, 1H), 2.15 (dt, J = 13.2, 8.7 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 202.8, 175.3, 171.8, 168.1, 131.3, 120.4, 66.4, 60.8, 60.5, 52.3, 38.9, 32.6, 29.0, 27.7; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{18}O_7Na^+$ 321.0945; Found 321.0955.

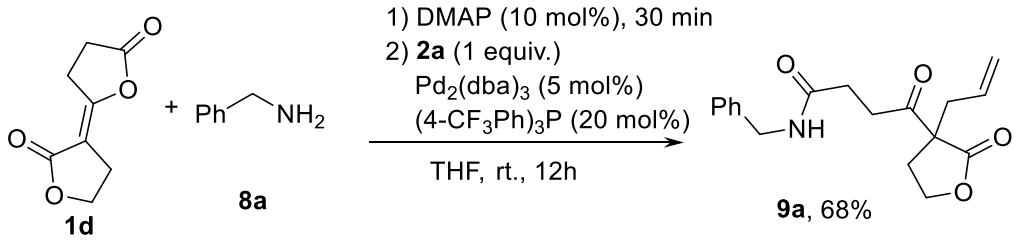


Synthesis of 3x: According to general procedure from **1d** (16.8 mg, 0.1 mmol), **2g** (17.0 mg, 0.12 mmol) and **4e** (29.3 μL, 0.2 mmol) to provide **3x** as a colourless oil (25.3 mg, 66% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 5.68-5.58 (m, 1H), 5.21 (d, J = 1.3 Hz, 1H), 5.19-5.17 (m, 1H), 5.14-5.07 (m, 1H), 4.30 (td, J = 8.9, 3.6 Hz, 1H), 4.24-4.16 (m, 3H), 3.88 (dd, J = 10.3, 4.2 Hz, 2H), 3.17-3.09 (m, 1H), 2.95-2.85 (m, 2H), 2.78 (dd, J = 14.4, 7.8 Hz, 1H), 2.71-2.59 (m, 3H), 2.15 (dt, J = 13.1, 8.7 Hz, 1H), 1.44 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 203.0, 175.3, 171.8, 156.0, 131.2, 120.5, 79.9, 66.4, 63.7, 60.5, 56.7, 38.9, 32.6, 29.0, 28.3, 27.9; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{27}NO_7Na^+$ 404.1680; Found 404.1688.

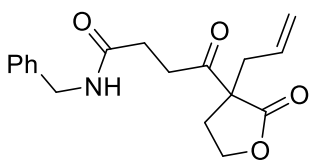


Synthesis of 3y: According to general procedure from **1d** (16.8 mg, 0.1 mmol), **2g** (17.0 mg, 0.12 mmol) and **4f** (9.4 mg, 0.1 mmol) to provide **3y** as a colourless oil (27.6 mg, 91% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.37 (dd, J = 8.5, 7.4 Hz, 2H), 7.23 (t, J = 7.4 Hz, 1H), 7.08 (dd, J = 8.6, 1.1 Hz, 2H), 5.70-5.60 (m, 1H), 5.23-5.16 (m, 2H), 4.29 (td, J = 8.8, 3.7 Hz, 1H), 4.20 (td, J = 8.8, 7.4 Hz, 1H), 3.18 (dt, J = 18.8, 5.9 Hz, 1H), 3.08-3.01 (m, 1H), 2.92-2.87 (m, 3H), 2.80 (dd, J = 14.4, 7.8 Hz, 1H), 2.70 (dd, J = 14.3, 6.7 Hz, 1H), 2.16 (dt, J = 13.2, 8.7 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 203.1, 175.4, 171.2, 150.6, 131.2, 129.5, 126.0, 121.5, 120.6, 66.4, 60.5, 38.9, 32.9, 29.1, 28.2; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{18}O_5Na^+$ 325.1046; Found 325.1043.

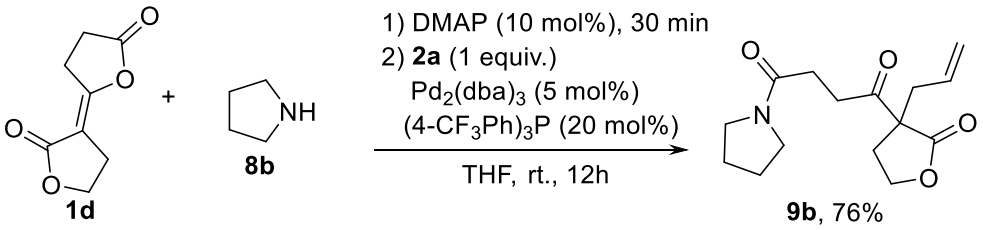
5. General procedure of N-pronucleophiles-involved three-component FEAA



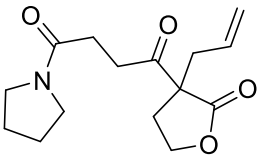
To a dried 10 mL schlenk tube **A** equipped with a stirring bar were added **1d** (16.8 mg, 0.1 mmol), benzylamine **8a** (11.0 μL, 0.1 mmol) and DMAP (1.2 mg, 10 mol%). Redistilled THF (0.5 ml) was added via a syringe under argon atmosphere, and the reaction mixture was stirred at room temperature for 30 minutes. To another dried 10 mL schlenk tube **B** equipped with a stirring bar were added $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol, 5 mol%), and $(4\text{-}CF_3Ph)_3P$ (9.3 mg, 0.02 mmol, 20 mol%). The tube was evacuated and back-filled with argon for three times. Redistilled THF (0.5 ml) was added via a syringe under argon atmosphere. The mixture was stirred at room temperature for 30 min to give a clear solution, and then transferred to above schlenk tube **A** under argon atmosphere. **2a** (11.6 μL, 0.1 mmol) was added subsequently, the tube **A** was evacuated and back-filled with argon for three times. The reaction was stirred at room temperature for 12 h and monitored by TLC. After completion, the mixture was concentrated under reduced pressure and purified by column chromatography on silica gel (petrol ether/EtOAc = 1/1) to give product **9a** as a colourless oil (21.3 mg, 68% yield).



9a: as a colourless oil (21.3 mg, 68% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.33 (t, J = 7.2 Hz, 2H), 7.30-7.23 (m, 3H), 5.91 (s, 1H), 5.71-5.61 (m, 1H), 5.22-5.14 (m, 2H), 4.41 (d, J = 5.7 Hz, 2H), 4.27 (td, J = 8.8, 3.8 Hz, 1H), 4.25-4.18 (m, 1H), 3.13-3.04 (m, 1H), 3.01-2.92 (m, 1H), 2.91-2.83 (m, 1H), 2.79-2.72 (m, 1H), 2.72-2.65 (m, 1H), 2.57-2.47 (m, 2H), 2.16 (dt, J = 13.2, 8.7 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 204.0, 175.7, 171.1, 138.1, 131.5, 128.7, 127.7, 127.5, 120.4, 66.4, 60.5, 43.7, 38.6, 33.1, 29.9, 29.2; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{21}NO_4Na^+$ 338.1363; Found 338.1365.

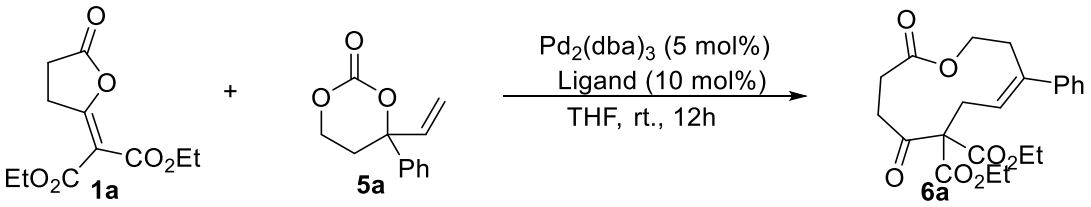


According to the procedure to synthesize **9a**, **9b** was prepared from **1d** (16.8 mg, 0.1 mmol) and pyrrolidine **8b** (8.4 μL, 0.1mmol).



9b: as a colourless oil (21.1mg, 76% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 5.75-5.65 (m, 1H), 5.22-5.15 (m, 2H), 4.32-4.23 (m, 2H), 3.47-3.37 (m, 4H), 3.09-3.01 (m, 1H), 2.98-2.91 (m, 1H), 2.91-2.83 (m, 1H), 2.79-2.67 (m, 2H), 2.66-2.54 (m, 2H), 2.18 (dt, J = 13.2, 8.7 Hz, 1H), 1.96 (p, J = 6.8 Hz, 2H), 1.85 (p, J = 6.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 204.3, 176.0, 169.5, 131.8, 120.2, 66.4, 60.6, 46.5, 45.7, 38.6, 32.7, 29.3, 28.9, 26.0, 24.4; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{21}NO_4Na^+$ 302.1363; Found 302.1367.

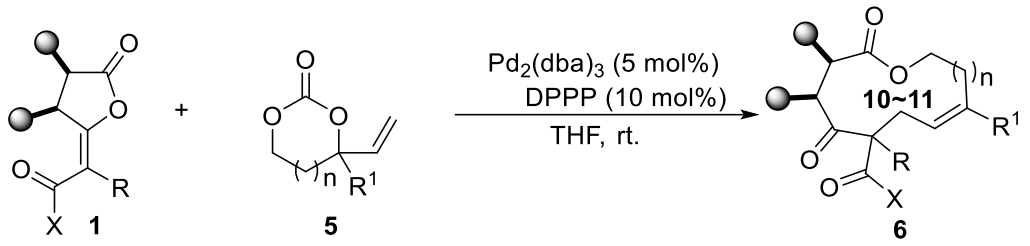
6. Screening reaction conditions of cyclic allyl carbonates-involved FEAA



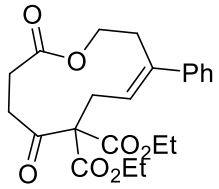
Entry	Ligand	solvent	time (h)	yield (%)[b]
1	DPPE	THF	12	64
2	DPPP	THF	12	75
3	$(4\text{-}CF_3Ph)_3P$	THF	12	55
4	$(2\text{-furyl})_3P$	THF	12	61
5	$(4\text{-}MeOPh)_3P$	THF	12	44
6	BINAP(+/−)	THF	12	54
7	DPPP	Tol	12	52
8	DPPP	DCM	12	Trace
9[c]	DPPP	THF	12	74
10[d]	DPPP	THF	12	75
11[e]	$Pd(PPh_3)_4$	THF	12	39

[a] Unless noted otherwise, reactions were performed with **1a** (0.1 mmol), **2a** (0.1 mmol), $Pd_2(dba)_3$ (5 mol%), ligand **L** (10 or 20 mol%) in solvent (1 mL) at room temperature. [b] Isolated yield. [c] with **2a** (0.12 mmol). [d]with **2a** (0.15 mmol). [e] With Pd $(PPh_3)_4$ (5 mol%).

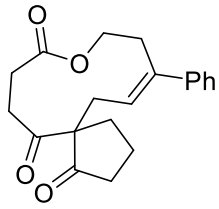
7. General procedure for the synthesis of medium-sized rings



To a dried 10 mL schlenk tube equipped with a stirring bar were added $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol, 5 mol%), and DPPP (4.1 mg, 0.01 mmol, 10 mol%). The tube was evacuated and back-filled with argon for three times. Redistilled THF (1.0 mL) was added via a syringe under argon atmosphere. The mixture was stirred at room temperature for 30 min to give a clear solution, and then transferred to another schlenk tube containing **1** (0.1 mmol, 1.0 equiv.) and cyclic allyl carbonates **5** (0.1 mmol, 1.0 equiv.). Next, the tube was evacuated and back-filled with argon for three times. The reaction was stirred at room temperature for 12 hours and monitored by TLC. After completion, product **6** was obtained by flash chromatography on silica gel (petroleum ether/EtOAc).

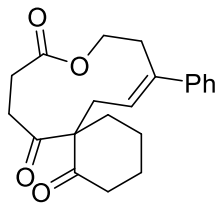


Synthesis of 6a: According to general procedure from **1a** (24.2 mg, 0.1 mmol) and **5a** (20.4 mg, 0.1 mmol) to provide **6a** as a white solid (30.0 mg, 75% yield); mp 109–112 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.33-7.28 (m, 2H), 7.27-7.24 (m, 3H), 5.75-5.69 (m, 1H), 4.29 (q, J = 7.2 Hz, 4H), 4.06 (s, 1H), 3.90 (s, 1H), 3.16 (d, J = 7.1 Hz, 3H), 3.05 (s, 1H), 2.87-2.80 (m, 2H), 2.56 (s, 2H), 1.29 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 201.0, 170.1, 170.1, 167.6, 141.9, 139.1, 128.4 127.4, 127.1, 125.5, 70.6, 62.5, 62.1, 61.7, 36.3, 32.7, 29.2, 28.7, 14.0, 14.0; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{26}O_7Na^+$ 425.1571; Found 425.1574.

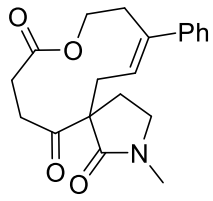


Synthesis of 6b: According to general procedure from **1b** (16.6 mg, 0.1 mmol) and **5a** (20.4 mg, 0.1 mmol) to provide **6b** as a white solid (30.4 mg, 93% yield); mp 142–143 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.32-7.27 (m, 2H), 7.26-7.22 (m, 3H), 5.51 (d, J = 11.2 Hz, 1H), 4.04-3.98 (m, 1H), 3.92-3.86 (m, 1H), 3.72-3.63 (m, 1H), 3.36 (s, 1H), 3.10-3.01 (m, 2H),3.00-2.94 (m, 1H), 2.55 (d, J = 14.6 Hz, 1H), 2.43-2.34 (m, 2H), 2.32-2.23 (m, 1H), 2.14 (d, J = 13.3 Hz, 1H), 2.06-1.97 (m, 1H), 1.80-1.72 (m, 2H), 1.66-1.59 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 217.2, 203.2, 170.2, 142.3, 138.8, 128.4,

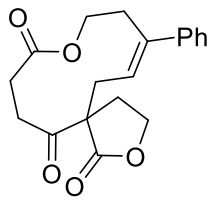
127.4, 127.2, 125.9, 68.6, 62.4, 38.2, 34.5, 34.5, 31.5, 29.5, 28.8, 19.4; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{20}H_{22}O_4Na^+$ 349.1410; Found 349.1418.



Synthesis of 6c: According to general procedure from **1o** (18.0 mg, 0.1 mmol) and **5a** (20.4 mg, 0.1 mmol) to provide **6c** as a white solid (20.1 mg, 59% yield); mp 150–153 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.24-7.19 (m, 2H), 7.18-7.09 (m, 3H), 5.48 (d, J = 12.4 Hz, 1H), 3.95 (t, J = 11.8 Hz, 1H), 3.79 (d, J = 9.9 Hz, 1H), 3.26 (t, J = 12.7 Hz, 1H), 3.15-2.97 (m, 4H), 2.50 (dd, J = 46.8, 14.5 Hz, 2H), 2.37-2.15 (m, 3H), 2.02-1.94 (m, 2H), 1.74 (d, J = 13.8 Hz, 1H), 1.66-1.55 (m, 1H), 1.55-1.44 (m, 1H), 1.37-1.28 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 209.3, 202.6, 169.0, 141.6, 137.8, 127.3, 126.3, 126.2, 124.3, 66.5, 61.3, 41.7, 32.9, 32.5, 32.3, 28.3, 27.5, 26.2, 21.5; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{21}H_{24}O_4Na^+$ 363.1567; Found 363.1577.

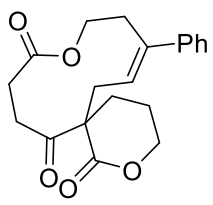


Synthesis of 6d: According to general procedure from **1p** (18.1 mg, 0.1 mmol) and **5a** (20.4 mg, 0.1 mmol) to provide **6d** as a white solid (21.9 mg, 78% yield); mp 159–163 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.30 (t, J = 7.2 Hz, 2H), 7.26-7.21 (m, 3H), 5.51 (dd, J = 12.2, 3.1 Hz, 1H), 4.06-3.99 (m, 1H), 3.95-3.85 (m, 2H), 3.47 (t, J = 13.3 Hz, 1H), 3.29-3.19 (m, 2H), 3.13-3.02 (m, 2H), 3.01-2.94 (m, 1H), 2.90 (s, 3H), 2.55 (d, J = 14.5 Hz, 1H), 2.43-2.34 (m, 1H), 2.27 (dd, J = 14.6, 3.1 Hz, 1H), 2.02-1.93 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 205.0, 172.8, 170.5, 142.3, 138.9, 128.4, 127.4, 127.2, 125.5, 62.3, 61.7, 46.3, 34.8, 33.9, 30.2, 29.6, 28.8, 27.1; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{20}H_{23}NO_4Na^+$ 364.1519; Found 364.1521.

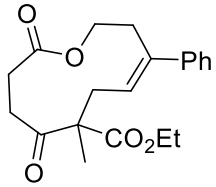


Synthesis of 6e: According to general procedure from **1d** (16.8 mg, 0.1 mmol) and **5a** (20.4 mg, 0.1 mmol) to provide **6e** as a white solid (27.6 mg, 84% yield); mp 153–155 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.31 (t, J = 7.2 Hz, 2H), 7.29-7.26 (m, 1H), 7.23 (d, J = 7.0 Hz, 2H), 5.44 (d, J = 11.1 Hz, 1H), 4.36 (t, J = 9.0 Hz, 1H), 4.10-3.99 (m, 2H), 3.90 (d, J = 10.8 Hz, 1H), 3.84-3.75 (m, 1H), 3.48 (t, J = 12.5 Hz, 1H), 3.25-3.19 (m, 1H), 3.11-2.96 (m, 2H), 2.60-2.55 (m, 1H), 2.45 (dt, J = 17.5, 3.7 Hz, 1H),2.39 (d, J = 14.1 Hz, 1H), 2.27-2.19 (m, 1H), 2.11-2.02 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 202.0,

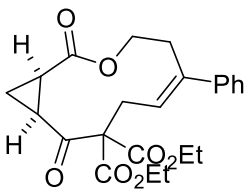
176.1, 170.0, 142.0, 139.8, 128.4,, 127.6, 127.2, 124.6, 66.2, 62.4, 60.6, 34.6, 34.0, 30.4, 29.6, 28.7; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{20}O_5Na^+$ 351.1230; Found 351.1209.



Synthesis of 6f: According to general procedure from **1q** (18.2 mg, 0.1 mmol) and **5a** (20.4 mg, 0.1 mmol) to provide **6f** as a white solid (29.4 mg, 86% yield); mp 171–174 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.34-7.28 (m, 2H), 7.28-7.23 (m, 3H), 5.51 (d, J = 9.6 Hz, 1H), 4.63-4.29 (m, 1H), 4.07-3.98 (m, 2H), 3.87 (dt, J = 10.8 Hz, 1H), 3.64-3.49 (m, 2H), 3.20 (dt, J = 13.2, 6.2 Hz 1H), 3.10 (t, J = 15.4 Hz, 1H), 3.04-2.96 (m, 1H), 2.55 (d, J = 14.5 Hz, 1H), 2.44 (t, J = 13.9 Hz, 2H), 2.11 (dt, J = 18.9 Hz, 3.7Hz, 1H), 1.96-1.89 (m, 1H), 1.89-1.81 (m, 1H), 1.65 (dt, J = 14.5, 7.6 Hz, 1H) ; ^{13}C NMR (150 MHz, $CDCl_3$) δ 202.5, 172.7, 170.0, 142.4, 139.7, 128.4, 127.5 127.3, 124.3, 68.5, 62.6, 59.9, 35.2, 33.6, 29.4, 28.6, 25.3, 20.7; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{22}O_5Na^+$ 365.1359; Found 365.1368.

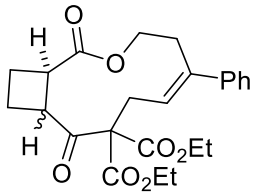


Synthesis of 6g: According to general procedure from **1r** (18.4 mg, 0.1 mmol) and **5a** (20.4 mg, 0.1 mmol) with $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol, 5 mol%), and DPPP (4.1 mg, 0.01 mmol, 10 mol%) to provide **6f** as a white solid (35.1 mg, 92% yield); mp 93–95 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.32-7.27 (m, 2H), 7.27-7.21 (m, 3H), 5.63 (d, J = 12.1 Hz, 1H), 4.26 (q, J = 7.2 Hz, 2H), 4.04 (d, J = 12.2 Hz, 1H), 3.87 (d, J = 10.3 Hz, 1H), 3.22 (t, J = 13.6 Hz, 1H), 3.11-2.96 (m, 3H), 2.54 (d, J = 14.8 Hz, 2H), 2.39 (d, J = 15.7 Hz, 2H), 1.56 (s, 3H), 1.31 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 204.7, 173.9, 170.2, 142.4, 138.7, 128.4, 127.3, 127.2, 125.5, 62.2, 61.6, 59.3, 34.1, 33.3, 29.5, 28.9, 18.7, 14.1; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{24}O_5Na^+$ 367.1516; Found 367.1525.

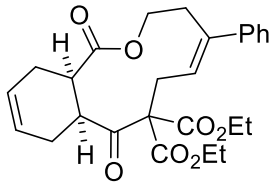


Synthesis of 6h: According to general procedure from **1e** (25.4 mg, 0.1 mmol) and **5a** (20.4 mg, 0.1 mmol) to provide **6h** as a colourless oil (25.5mg, 62% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.35-7.28 (m, 4H), 7.26-7.22 (m, 1H), 5.61 (s, 1H), 4.40-4.33 (m, 2H), 4.32-4.27 (m, 1H), 4.27-4.12 (m, 2H), 3.92 (s, 1H), 3.05 (d, J = 10.4 Hz, 3H), 2.51 (s, 2H), 2.23 (s, 1H), 1.99-1.92 (m, 1H), 1.35 (t, J = 7.1 Hz, 3H), 1.28 (t, J = 7.1 Hz, 3H), 1.21 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 194.2, 168.4, 167.7, 142.3, 137.9, 128.3, 127.4, 127.2, 125.6, 70.8, 62.3, 32.9, 29.1, 28.0, 26.3, 14.0, 13.9, 10.7;

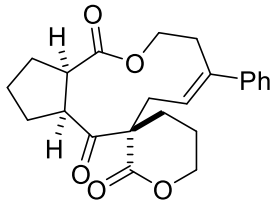
HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{26}O_7Na^+$ 437.1571; Found 437.1577.



Synthesis of 6i: According to general procedure from **1f** (26.8 mg, 0.1 mmol) and **5a** (20.4 mg, 0.1 mmol) to provide **6i** as a colourless oil (31.3mg, 73% yield), 5:1 dr , determined by ^{1}H NMR analysis; ^{1}H NMR (600 MHz, $CDCl_3$, major isomer): δ (ppm) 7.28 (t, J = 7.6 Hz, 1H), 7.23 (t, J = 7.2 Hz, 3H), 7.18-7.15 (m, 1H), 5.56 (s, 1H), 4.27-4.09 (m, 5H), 4.04-3.81 (m, 1H), 3.67 (d, J = 42.0 Hz, 1H), 3.47-3.16 (m, 2H), 3.01 (s, 1H), 2.94-2.70 (m, 1H), 2.66-2.36 (m, 2H), 2.32-2.18 (m, 1H), 2.14-2.04 (m, 1H), 2.04-1.94 (m, 1H), 1.25 (t, J = 7.2 Hz, 3H), 1.17 (t, J = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 201.8, 171.0, 165.8, 165.6, 138.9, 137.8, 127.3, 127.2, 126.2, 125.9, 69.6, 61.2, 61.1,61.1 58.9, 40.9, 37.6, 32.9, 28.5, 13.0, 12.9, 12.8; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{28}O_7Na^+$ 451.1727; Found 451.1731.

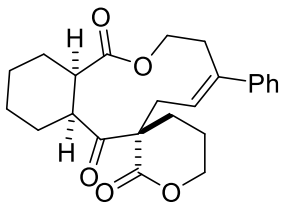


Synthesis of 6j: According to general procedure from **1g** (29.4 mg, 0.1 mmol) and **5a** (20.4 mg, 0.1 mmol) to provide **6j** as a colourless oil (33.2mg, 73% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.36-7.27 (m, 4H), 7.23 (d, J = 7.2 Hz, 1H), 5.87-5.68 (m, 2H), 5.52 (dd, J = 10.1, 1.5 Hz, 1H), 4.30 (d, J = 32.2 Hz, 4H), 4.17 (d, J = 18.0 Hz, 2H), 3.80 (d, J = 10.3 Hz, 1H), 3.27 (t, J = 13.0 Hz, 1H), 3.19-2.89 (m, 2H), 2.83 (d, J = 14.7 Hz, 1H), 2.70 (s, 1H), 2.58-2.46 (m, 1H), 2.38 (t, J = 21.0 Hz, 2H), 2.16 (d, J = 18.5 Hz, 1H), 1.34 (t, J = 7.1 Hz, 3H), 1.27-1.18 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 200.8, 172.6, 169.2, 167.8, 142.2, 138.3, 128.3, 127.3, 126.9, 126.4, 124.4, 121.2, 71.1, 62.5, 62.3, 61.8, 40.2, 39.4, 34.2, 29.3, 25.5, 24.4, 14.0, 13.8; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{30}O_7Na^+$ 477.1884; Found 477.1891.

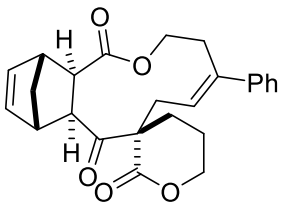


Synthesis of 6k: According to general procedure from **1h** (22.2 mg, 0.1 mmol) and **5a** (20.4 mg, 0.1 mmol) to provide **6k** as a white solid (38.0 mg, 99% yield); mp 144–147 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.33-7.28 (m, 2H), 7.29-7.22 (m, 3H), 5.47 (d, J = 11.4 Hz, 1H), 4.43 (d, J = 13.3 Hz, 1H), 4.37-4.27 (m, 2H), 4.18-4.12 (m, 1H), 3.66 (d, J = 10.9 Hz, 1H), 3.52 (t, J = 13.5 Hz, 1H), 3.09-2.99 (m, 2H), 2.89-2.82 (m, 1H), 2.52 (dd, J = 14.6, 3.7 Hz, 1H), 2.42-2.36 (m, 1H), 2.32-2.22 (m, 1H),

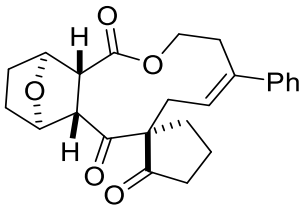
2.02-1.91 (m, 1H), 1.91-1.81 (m, 2H), 1.76-1.65 (m, 2H), 1.67-1.57 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 204.4, 172.4, 172.1, 143.1, 140.2, 128.3, 127.4, 127.3, 124.1, 70.4, 61.8, 60.3, 48.0, 48.0, 35.2, 29.9, 29.6, 26.7, 26.2, 23.3, 21.3; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{26}O_5Na^+$ 405.1672; Found 405.1678.



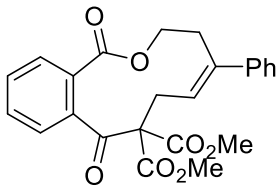
Synthesis of 6l: According to general procedure from **1i** (23.6 mg, 0.1 mmol) and **5a** (20.4 mg, 0.1 mmol) to provide **6l** as a white solid (39.5 mg, 99% yield); mp 171–174 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.33-7.28 (m, 2H), 7.26-7.22 (m, 3H), 5.47 (d, J = 12.3 Hz, 1H), 4.44-4.30 (m, 3H), 4.06 (s, 1H), 3.71 (d, J = 10.9 Hz, 1H), 3.67-3.60 (m, 1H), 3.12 (t, J = 15.4 Hz, 2H), 2.52 (d, J = 14.4 Hz, 1H), 2.41-2.32 (m, 2H), 2.24 (qd, J = 13.2, 4.1 Hz, 1H), 1.97 (dd, J = 13.4, 3.8 Hz, 1H), 1.92-1.81 (m, 3H), 1.64-1.50 (m, 4H), 1.27-1.17 (m, 1H), 1.10-1.00 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 204.5, 172.4, 172.4, 142.6, 139.5, 128.3, 127.4, 127.3, 124.2, 70.0, 61.6, 60.1, 43.7, 42.0, 36.6, 29.9, 26.8, 26.7, 25.3, 24.3, 21.2, 21.0; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{28}O_5Na^+$ 419.1829; Found 419.1835.



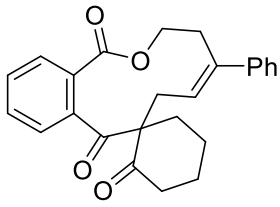
Synthesis of 6m: According to general procedure from **1j** (24.6 mg, 0.1 mmol) and **5a** (20.4 mg, 0.1 mmol) to provide **6m** as a white solid (34 mg, 84% yield); mp 142–148 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.35-7.28 (m, 4H), 7.25 (d, J = 6.3 Hz, 1H), 6.28-6.23 (m, 1H), 6.16-6.10 (m, 1H), 5.57 (dd, J = 12.3, 3.8 Hz, 1H), 4.54 (d, J = 11.0 Hz, 1H), 4.43-4.34 (m, 1H), 4.21 (t, J = 11.2 Hz, 1H), 3.71 (d, J = 8.6 Hz, 1H), 3.38 (d, J = 9.3 Hz, 2H), 3.20 (s, 1H), 2.96 (dd, J = 28.3, 15.3 Hz, 2H), 2.82 (s, 1H), 2.53 (dd, J = 14.8, 4.8 Hz, 1H), 2.49 (d, J = 9.3 Hz, 1H), 2.45-2.26 (m, 1H), 2.18 (d, J = 9.1 Hz, 1H), 1.89 (d, J = 10.0 Hz, 1H), 1.80-1.63 (m, 2H), 1.42-1.36 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 205.2, 173.6, 172.0 143.5, 140.1, 139.5, 136.7, 128.3, 127.4, 127.2, 124.2, 70.7, 62.9, 61.7, 49.7, 48.5, 47.7, 44.1, 43.1, 34.6, 29.7, 28.9, 21.5; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{26}O_5Na^+$ 429.1672 Found 429.1682.



Synthesis of 6n: According to general procedure from **1k** (23.4 mg, 0.1 mmol) and **5a** (20.4 mg, 0.1 mmol) to provide **6n** as a white solid (39.3 mg, 99% yield), 10:1 dr , determined by ^{1}H NMR analysis; mp 242–253 °C; ^{1}H NMR (600 MHz, $CDCl_3$, major isomer): δ (ppm) 7.35-7.30 (m, 2H), 7.32-7.26 (m, 2H), 7.27-7.21 (m, 1H), 5.48 (dd, *J* = 12.0, 3.9 Hz, 1H), 5.09 (s, 1H), 4.21-4.13 (m, 2H), 3.88 (d, *J* = 9.0 Hz, 1H), 3.69-3.60 (m, 1H), 3.05-2.98 (m, 1H), 2.93-2.82 (m, 2H), 2.73 (d, *J* = 8.9 Hz, 1H), 2.54 (dd, *J* = 14.7, 4.9 Hz, 1H), 2.50-2.43 (m, 1H), 2.43-2.32 (m, 1H), 2.17 (d, *J* = 11.8 Hz, 1H), 2.12-2.03 (m, 1H), 1.89-1.79 (m, 2H), 1.78-1.66 (m, 2H), 1.54-1.43 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 219.4, 201.2, 169.7, 143.3, 139.8, 128.3, 127.6, 127.3, 125.5, 77.7, 76.4, 68.8, 62.7, 54.2, 52.5, 38.8, 33.5, 33.3, 30.2, 29.7, 28.7, 19.8; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{28}O_5Na^+$ 417.1672; Found 417.1682.

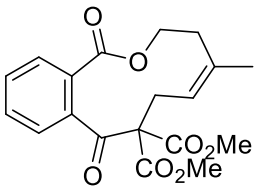


Synthesis of 6o: According to general procedure from **1l** (26.2 mg, 0.1 mmol) and **5a** (20.4 mg, 1.0 mmol) to provide **6o** as a white solid (41.9. mg, 99% yield); mp 127–130 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.92 (d, *J* = 7.7 Hz, 1H), 7.47-7.42 (m, 1H), 7.44-7.37 (m, 3H), 7.32 (d, *J* = 6.9 Hz, 1H), 7.24 (t, *J* = 7.6 Hz, 2H), 7.20-7.14 (m, 1H), 5.92 (d, *J* = 11.1 Hz, 1H), 4.40 (d, *J* = 10.2 Hz, 1H), 3.93 (t, *J* = 12.0 Hz, 1H), 3.85 (s, 3H), 3.54 (t, *J* = 12.9 Hz, 1H), 3.40 (s, 3H), 3.15 (t, *J* = 12.2 Hz, 2H), 2.56 (d, *J* = 14.7 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 195.4, 168.6, 167.1, 164.8, 141.4, 140.6, 137.8, 130.5, 130.2, 128.5, 127.3, 127.0, 126.3, 126.2, 125.2, 122.8, 71.3, 64.9, 52.5, 52.0, 34.6, 27.9 ; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{22}O_7Na^+$ 445.1258; Found 445.1266.

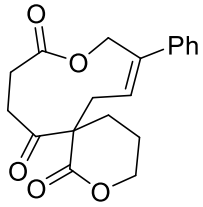


Synthesis of 6p: According to general procedure from **1s** (22.8 mg, 0.1 mmol) and **5a** (20.4 mg, 0.1 mmol) to provide **6p** as a white solid (30.4 mg, 78% yield); mp 185–187 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.97 (s, 1H), 7.49 (d, *J* = 49.8 Hz, 2H), 7.30 (d,, *J* = 21.8 Hz, 5H), 7.13 (d, *J* = 60.7 Hz, 1H), 6.04 (s, 1H), 4.41 (s, 1H), 3.94 (d, *J* = 34.4 Hz, 2H), 3.01 (d, *J* = 139.6 Hz, 2H),2.51 (t, *J* = 73.5 Hz, 4H), 2.15 (s, 1H), 1.78 (d, *J* = 60.0 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 208.7, 203.5, 164.6, 142.0, 141.7, 140.8, 131.4, 129.9, 127.9, 127.5, 126.6, 126.4, 125.8, 124.4, 123.9, 67.0, 63.7,

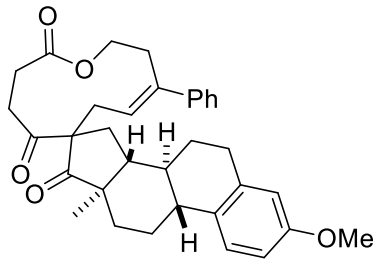
37.9, 31.9, 28.8, 27.7, 25.9, 20.8; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{24}O_4Na^+$ 411.1567; Found 411.1569.



Synthesis of 6q: According to general procedure from **1l** (26.2 mg, 0.1 mmol) and **5b** (20.4 mg, 0.1 mmol) with $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol, 10 mol%), and DPPP (8.2 mg, 0.02 mmol, 20 mol%) to provide **6q** as a colorless oil (20.4 mg, 57% yield); ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.92 (dd, J = 7.5, 1.6 Hz, 1H), 7.64-7.34 (m, 2H), 7.30 (s, 1H), 5.47 (s, 1H), 4.37 (s, 1H), 4.05 (d, J = 7.0 Hz, 1H), 3.84 (s, 3H), 3.39 (s, 3H), 3.34 (s, 1H), 2.92 (d, J = 15.6 Hz, 2H), 1.84 (d, 1H), 1.76 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$)δ (ppm) 195.0, 168.8, 167.2, 164.9, 140.7, 133.8, 130.4, 130.2, 128.5, 128.5, 122.8, 121.6, 70.7, 64.2, 52.4, 51.9, 34.5, 29.2, 23.0; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{20}O_7Na^+$ 383.1101; Found 383.1108.

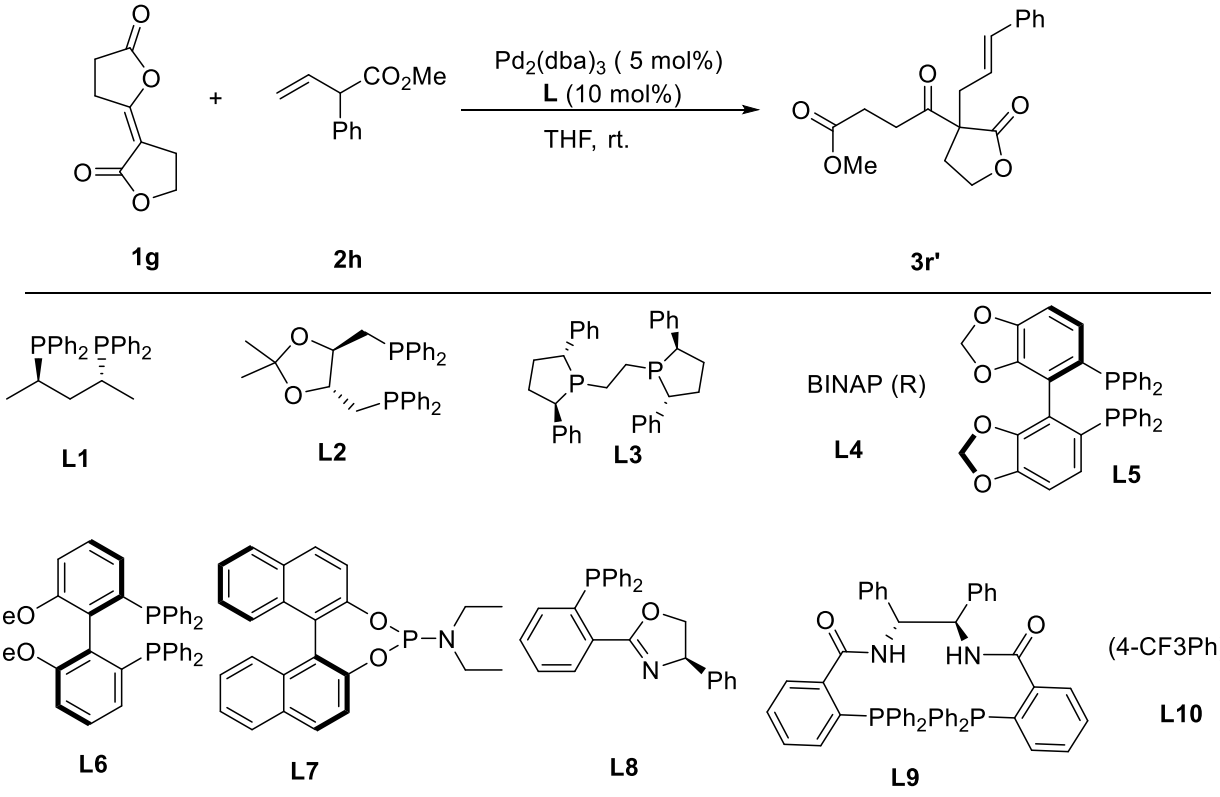


Synthesis of 6r: According to general procedure, to a dried 10 mL schlenk tube equipped with a stirring bar were added $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol), and (2-furyl)$_3$P (4.6 mg, 0.02 mmol, 20 mol%). The tube was evacuated and back-filled with argon for three times. Redistilled THF (1.0 mL) was added via a syringe under argon atmosphere. The mixture was stirred at room temperature for 30 min to give a clear solution, and then transferred to another schlenk tube containing **1q** (18.2 mg, 0.1 mmol, 1.0 equiv.) and **5c** (19.0 mg, 0.1 mmol, 1.0 equiv.). Next, the tube was evacuated and back-filled with argon for three times. The reaction was stirred at room temperature for 12 h and monitored by TLC. After completion, product **6r** was obtained by flash chromatography on silica gel (petroleum ether/EtOAc = 6/1): 22.2 mg, as a white solid, 69% yield) ; mp 179–181 °C; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.38 (d, J = 7.4 Hz, 2H), 7.32 (t, J = 7.5 Hz, 2H), 7.28 (d, J = 7.2 Hz, 1H), 5.56 (d, J = 7.1 Hz, 1H), 5.40 (d, J = 14.1 Hz, 1H), 4.69 (d, J = 13.5 Hz, 1H), 4.34-4.27 (m, 1H), 4.06-3.99 (m, 1H), 3.77-3.69 (m, 2H), 2.97-2.88 (m, 2H), 2.60-2.54 (m, 1H), 2.41 (dd, J = 14.0, 3.6 Hz, 1H), 2.12 (d, J = 16.7 Hz, 1H), 1.91-1.77 (m, 2H), 1.65-1.59 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 202.9, 172.1, 169.6, 141.3, 140.9, 128.4, 127.8, 127.0, 125.6, 68.5, 63.1, 61.8, 36.6, 33.2, 29.7, 24.7, 20.4; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{20}O_5Na^+$ 351.1203; Found 351.1212.



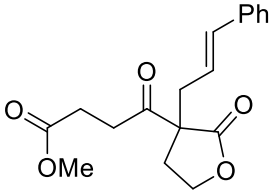
Synthesis of 6s: According to general procedure from **1t** (35.2 mg, 0.1 mmol) and **5a** (20.4 mg, 0.1 mmol) to provide **6s** as a white solid (33.3 mg, 63% yield), 7.5:1 dr, determined by ^{1}H NMR analysis; mp 197–205 °C; ^{1}H NMR (600 MHz, $CDCl_3$, major isomer): δ (ppm) 7.31 (t, J = 7.3 Hz, 2H), 7.28-7.22 (m, 3H), 7.19 (d, J = 8.6 Hz, 1H), 6.72 (dd, J = 8.6, 2.8 Hz, 1H), 6.64 (d, J = 2.7 Hz, 1H), 5.63 (s, 1H), 4.18-4.11 (m, 1H), 3.89-3.80 (m, 2H), 3.77 (s, 3H), 3.37-3.21 (m, 1H), 3.07 (d, *J* = 12.7 Hz, 1H), 2.99 (t, *J* = 15.0 Hz, 1H), 2.93-2.87 (m, 2H), 2.57 (d, *J* = 14.3 Hz, 1H), 2.44-2.32 (m, 3H), 2.31-2.14 (m, 3H), 2.07-2.00 (m, 1H), 2.02-1.94 (m, 1H), 1.81 (d, *J* = 18.1 Hz, 1H), 1.58-1.44 (m, 4H), 1.44-1.36 (m, 1H), 0.84 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 216.7, 205.9, 170.2, 157.7, 142.3, 138.9, 137.7, 131.7, 128.4, 127.5 127.3, 126.3, 126.0, 113.9, 111.7, 66.3, 61.8, 55.2, 49.9, 44.6, 43.9, 38.0, 37.8, 33.8, 31.7, 29.8, 29.6, 29.2, 28.8, 26.4, 25.8, 13.7; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{28}O_5Na^+$ 549.2611; Found 549.2620.

8. More screening reaction conditions for asymmetric synthesis[a]



Entry	L	Time	Yield (%)[b]	ee (%)[c]
1	**L1**	12h	76%	6
2	**L2**	12h	47%	1
3	**L3**	12h	70%	35
4	**L4**	12h	49%	-13
5	**L5**	12h	trace	/
6	**L6**	12h	trace	/
7[d]	**L7**	12h	74%	-11
8	**L8**	12h	75%	14
9	**L9**	12h	/	/
10[d]	**L10**	12h	62%	/

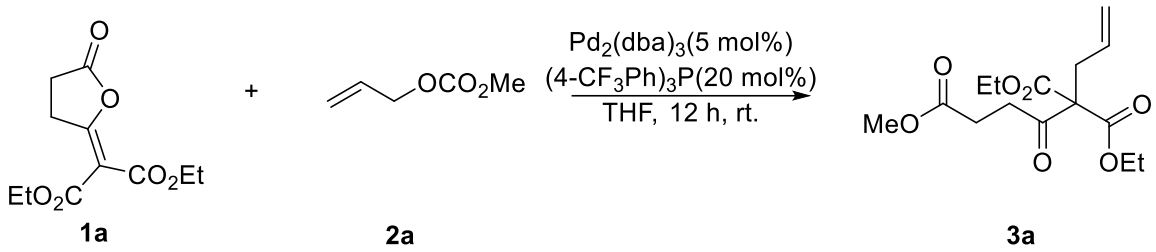
[a] Unless noted otherwise, reactions were performed with **1a** (0.1 mmol), **2a** (0.1 mmol), $Pd_2(dba)_3$ (5 mol%), **L** (10 mol%) in THF (1 mL). [b] Isolated yield. [c] The value of ee was determined by HPLC. [d] With $Pd_2(dba)_3$ (5 mol%) and **L** (20 mol%).



To a dried 10 mL schlenk tube equipped with a stirring bar were added $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol), and **L3** (5.0 mg, 0.01 mmol, 10 mol%). The tube was evacuated and back-filled with argon for three times. Redistilled THF (1 mL) was added via a syringe under argon atmosphere. The mixture was stirred at room temperature for 30 min to give a clear solution, and then transferred to another schlenk tube containing **1g** (16.8 mg, 0.1 mmol) and allyl carbonate **2h** (21.1 mg, 0.12 mmol) under argon atmosphere. Next, the tube was evacuated and back-filled with argon for three times. The reaction was stirred at room temperature for 12 hours and monitored by TLC. After completion, the reaction mixture was concentrated under reduced pressure and purified by flash chromatography on silica gel (petroleum ether/EtOAc = 5:1) to give product **3r'** as a colorless oil, (22.0 mg, 70% yield); $[\alpha]_D^{20}$= -1.8 (*c* = 0.48 in $CHCl_3$); 35% ee, determined by HPLC analysis [Chralpak IA, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 254 nm, t (minor) = 27.99 min, t (major) = 30.76 min]; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.42-7.28 (m, 4H), 7.28-7.21 (m, 1H), 6.51 (d, *J* = 15.7 Hz, 1H), 6.02 (dt, *J* = 15.2, 7.4 Hz, 1H), 4.29 (td, *J* = 8.8, 3.4 Hz, 1H), 4.21 (q, *J* = 8.6 Hz, 1H), 3.67 (s, 3H), 3.22-3.07 (m, 1H), 2.98-2.83 (m, 4H), 2.72-2.59 (m, 2H), 2.26-2.17 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm)

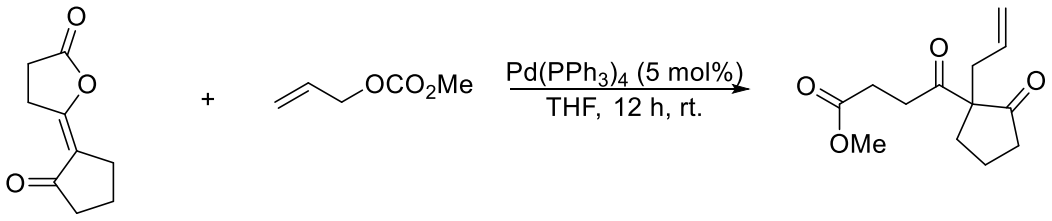
203.2, 175.5, 172.8, 136.4, 135.2, 128.6, 122.4, 66.4, 60.9, 51.9, 38.1, 32.8, 29.1, 28.0; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{21}O_5^+$ 317.1384; Found 317.1382.

9. Reaction on a 1.0 mmol scale



1a **2a** **3a**

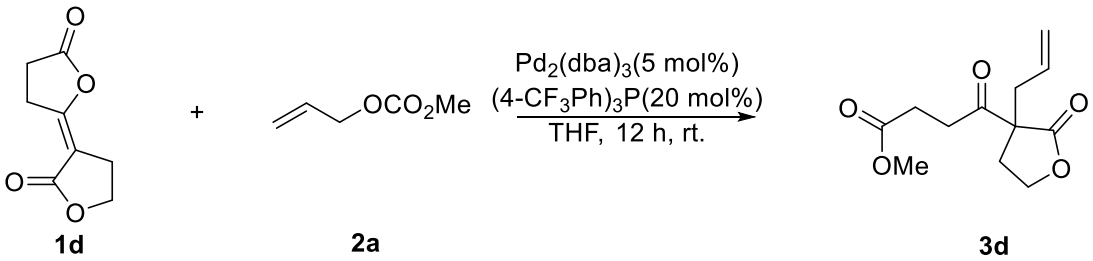
To a dried 20 mL schlenk tube equipped with a stirring bar were added $Pd_2(dba)_3$ (45.8 mg, 0.05 mmol, 5 mol%), and $(4\text{-}CF_3Ph)_3P$ (93.3 mg, 0.2 mmol, 20 mol%). The tube was evacuated and back-filled with argon for three times. Redistilled THF (10 mL) was added via a syringe under argon atmosphere. The mixture was stirred at room temperature for 30 min to give a clear solution, and then transferred to another schlenk tube containing **1a** (242.1 mg, 1.0 mmol, 1.0 equiv.) and allyl carbonate **2a** (116.0 μL, 1.0 mmol, 1.0 equiv.). Next, the tube was evacuated and back-filled with argon for three times. The reaction was stirred at room temperature for 12 h and monitored by TLC. After completion, product **3a** was obtained by flash chromatography on silica gel (petroleum ether/EtOAc = 5/1): 265.8 mg as a colorless oil, 82% yield.



1b **2a** **3b**

To a dried 20 mL schlenk tube equipped with a stirring bar were added $Pd(PPh_3)_4$ (57.8 mg, 5 mol%). The tube was evacuated and back-filled with argon for three times. Redistilled THF (10 mL) was added via a syringe under argon atmosphere. The mixture was stirred at room temperature for 30 min to give a clear solution, and then transferred to another schlenk tube containing **1b** (166.1 mg, 1.0 mmol, 1.0 equiv.) and allyl carbonate **2a** (116.0 μL, 1.0 mmol, 1.0 equiv.). Next, the tube was evacuated and back-filled with argon for three times. The reaction was stirred at room temperature

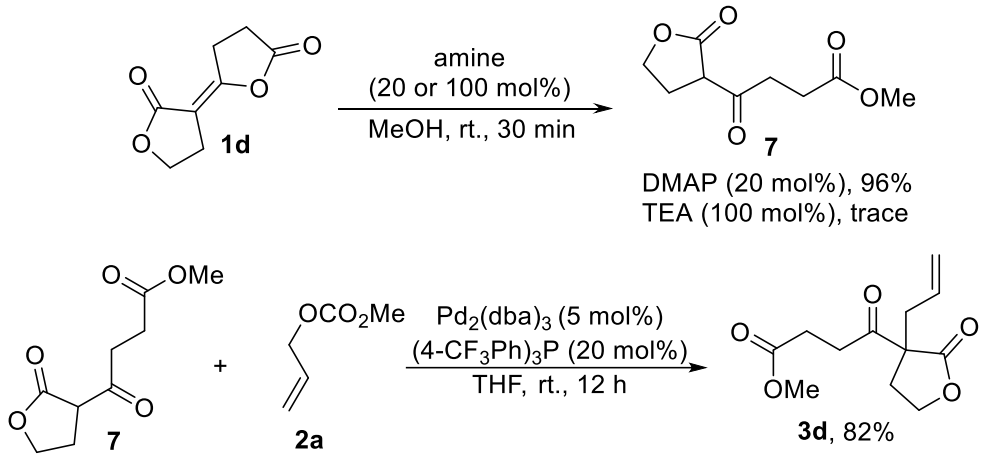
for 12 h and monitored by TLC. After completion, product **3b** was obtained by flash chromatography on silica gel (petroleum ether/EtOAc = 5/1): 221.3 mg as a colorless oil, 93% yield.



1d **2a** **3d**

To a dried 20 mL schlenk tube equipped with a stirring bar were added $Pd_2(dba)_3$ (45.8 mg, 0.05 mmol, 5 mol%), and $(4\text{-}CF_3Ph)_3P$ (93.3 mg, 0.2 mmol, 20 mol%). The tube was evacuated and back-filled with argon for three times. Redistilled THF (10 mL) was added via a syringe under argon atmosphere. The mixture was stirred at room temperature for 30 min to give a clear solution, and then it was transferred to another schlenk tube containing **1d** (168.0 mg, 1.0 mmol, 1.0 equiv.) and allyl carbonate **2a** (116.0 μL, 1.0 mmol, 1.0 equiv.). Next, the tube was evacuated and back-filled with argon for three times. The reaction was stirred at room temperature for 12 h and monitored by TLC. After completion, product **3d** was obtained by flash chromatography on silica gel (petroleum ether/EtOAc = 5/1): 143.9 mg as a colorless oil, 60% yield.

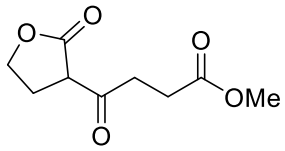
10. Studies of reaction mechanism



1d **7** **2a**

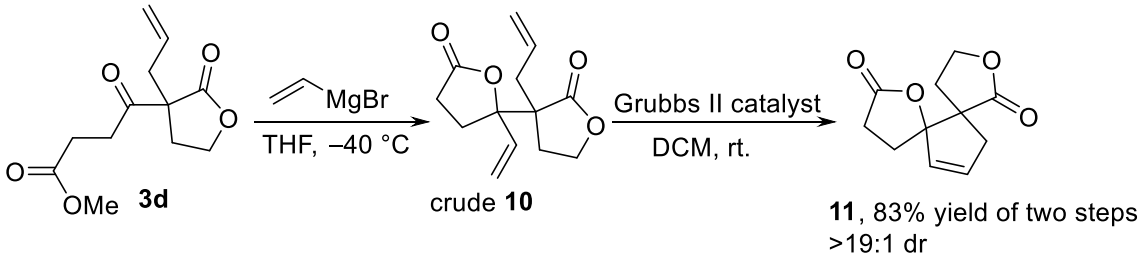
Synthesis of intermediate 7: To a solution of CVA **1d** (16.8 mg, 0.1 mmol) in MeOH (1 mL) under N_2 was added DMAP (2.4 mg, 20 mol%) at room temperature. The reaction was stirred at room temperature for 0.5 h and monitored by TLC. The reaction mixture was concentrated and the residue was chromatographed on silica gel with petroleum ether/ EtOAc (2:1) to give intermediate **7** (19.2 mg, 96%) as a colorless oil.

Synthesis of 3d from 7: To a dried 10 mL schlenk tube equipped with a stirring bar were added $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol), and $(4\text{-}CF_3Ph)_3P$ (9.3 mg, 0.02 mmol, 20 mol%). The tube was evacuated and back-filled with argon for three times. Redistilled THF (1 mL) was added via a syringe under argon atmosphere. The mixture was stirred at room temperature for 30 min to give a clear solution, and then transferred to another schlenk tube containing **7** (20.0 mg, 0.1 mmol, 1.0 equiv.) and **2a** (11.6 μL, 0.1 mmol, 1.0 equiv.). Next, the tube was evacuated and back-filled with argon for three times. The reaction was stirred at room temperature for 12 h and monitored by TLC. After completion, product **3d** was obtained by flash chromatography on silica gel (petroleum ether/EtOAc = 3/1): 19.4 mg, as a colourless oil, 82% yield.



7: ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 4.39 (td, J = 8.5, 6.0 Hz, 1H), 4.34 (td, J = 8.5, 6.5 Hz, 1H), 3.76 (dd, J = 9.3, 6.8 Hz, 1H), 3.68 (s, 3H), 3.28-3.20 (m, 1H), 2.99-2.91 (m, 1H), 2.85-2.77 (m, 1H), 2.77-2.65 (m, 1H), 2.64-2.55 (m, 1H), 2.39-2.30 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 201.0, 172.9, 172.7, 67.5, 52.5, 51.9, 36.6, 27.8, 23.9; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_9H_{12}O_5Na^+$ 223.0577; Found 223.0586.

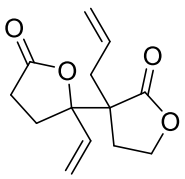
11. Synthetic transformations of product 3d



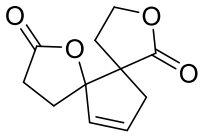
To a solution of **3d** (24 mg, 0.1 mmol) in THF (0.6 mL) was added vinylmagnesium bromide (0.27M in THF, 0.4 mL) at -40°C. The reaction was stirred under argon atmosphere at -40°C for 8.5 h. The reaction mixture was then quenched with 1N HCl, and extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography on silica (petroleum ether/EtOAc = 4/1) to afford crude **10** (20.5mg, 87% yield) with trace of inseparable impurity.

To a stirred solution of **10** (11.8 mg, 0.05 mmol) in degassed CH_2Cl_2 (0.5 ml) was added 2nd generation Grubbs'catalyst (2.1 mg, 0.0025 mmol) at room temperature, and stirring was continued

for 4 h. The reaction mixture was concentrated and the residue was chromatographed on silica gel (petroleum ether/EtOAc = 4/1) to give **11** (10.0 mg, 96% yield) as a colorless oil.

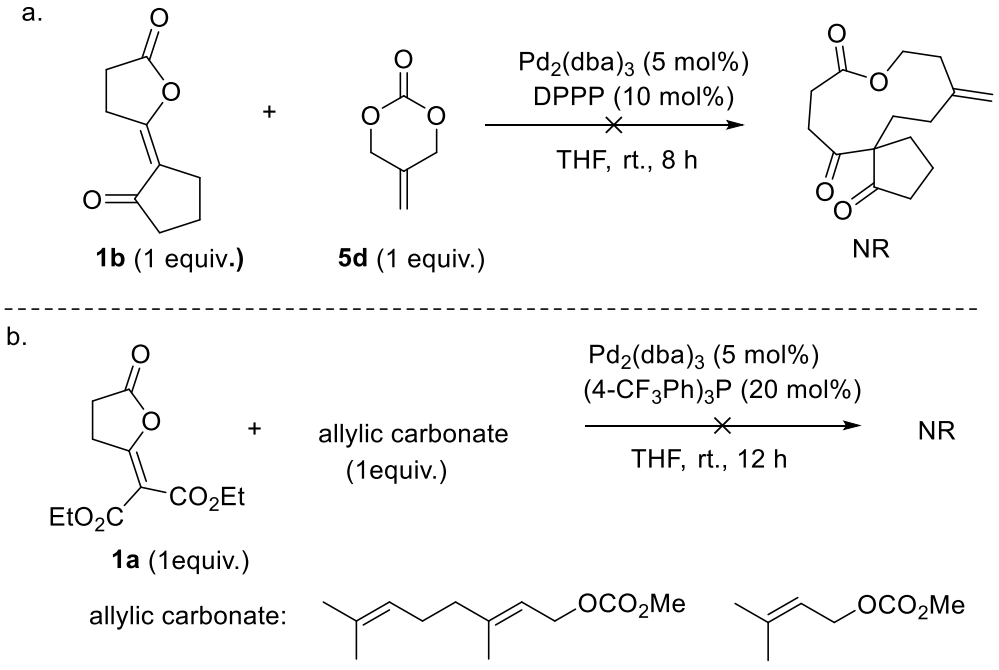


10: ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 6.00 (dd, J = 17.1, 10.9 Hz, 1H), 5.76-5.65 (m, 1H), 5.46-5.35 (m, 2H), 5.24 (s, 1H), 5.21 (d, J = 6.3 Hz, 1H), 4.32 (td, J = 9.0, 5.9 Hz, 1H), 4.15 (td, J = 8.9, 6.2 Hz, 1H), 3.09 (dt, J = 12.7, 10.5 Hz, 1H), 2.64 (dd, J = 13.5, 5.8 Hz, 1H), 2.55-2.48 (m, 2H), 2.50-2.41 (m, 1H), 2.26-2.14 (m, 2H), 2.07-2.00 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 177.4, 175.6, 135.3, 131.6, 120.9, 117.2, 89.4, 65.7, 52.0, 37.8, 28.6, 27.6, 27.0; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{16}O_4Na^+$ 259.0941; Found 259.0949.

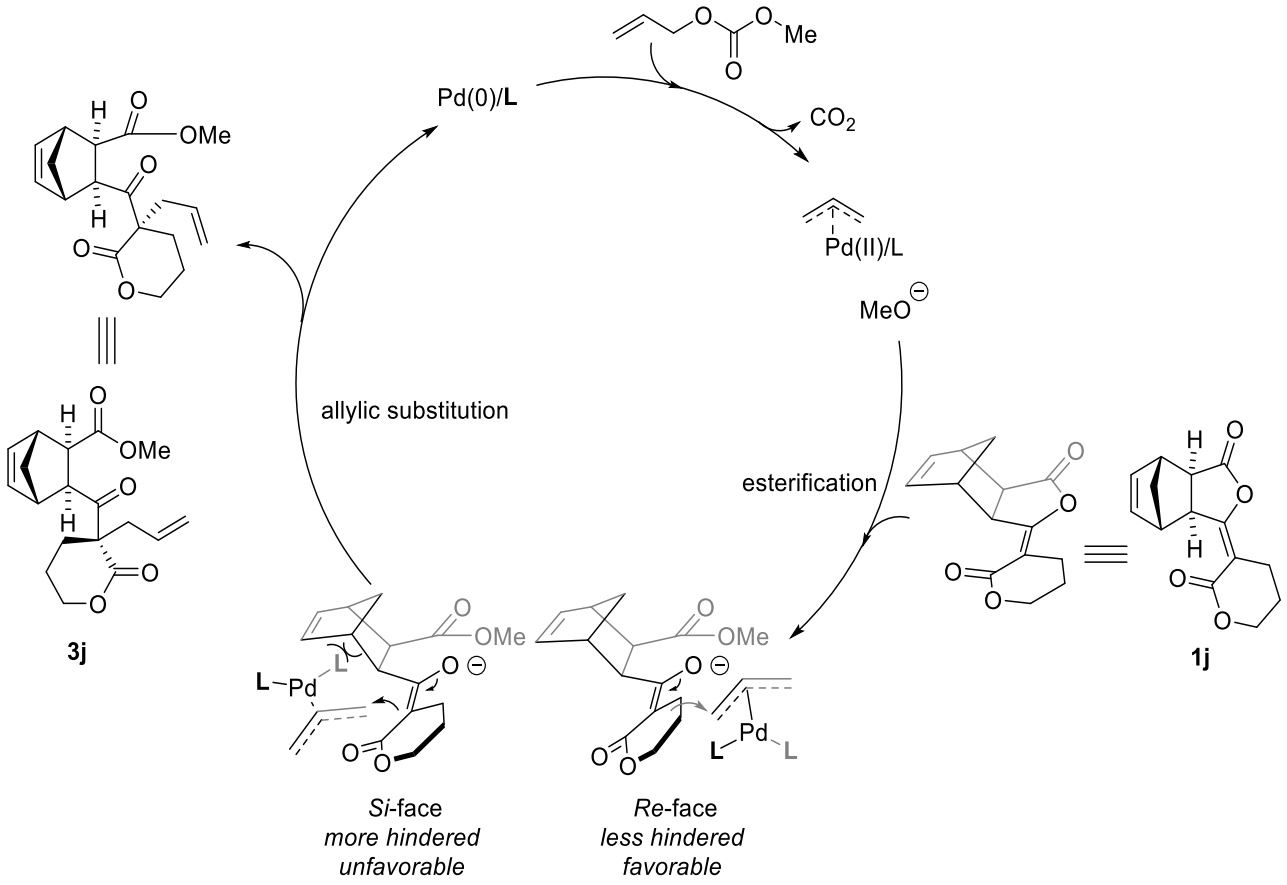


11: ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 6.16-6.11 (m, 1H), 5.82 (dt, J = 5.8, 2.1 Hz, 1H), 4.32 (t, J = 7.0 Hz, 2H), 2.95 (dt, J = 16.9, 2.3 Hz, 1H), 2.78-2.70 (m, 1H), 2.70-2.54 (m, 3H), 2.45-2.33 (m, 2H), 2.29-2.21 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 178.2, 175.9, 134.2, 131.4, 97.4, 66.3, 54.5, 42.7, 31.8, 29.2, 28.8; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{14}O_4Na^+$ 231.0628; Found 231.0631.

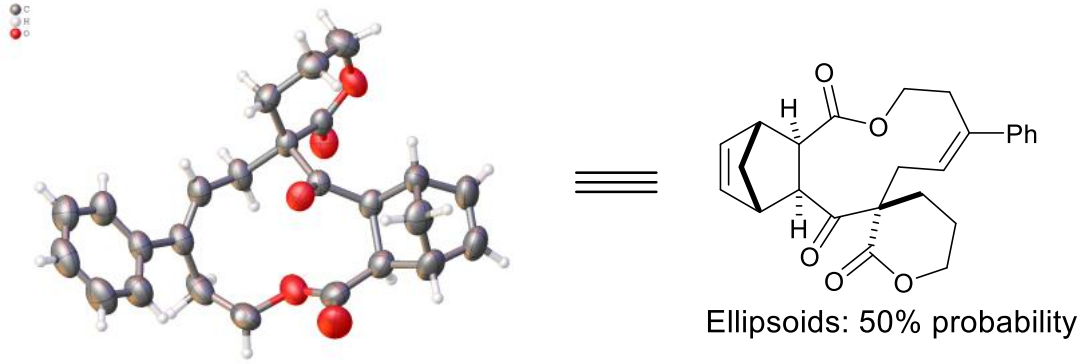
12. Additional unsuccessful exploration



13. Proposed mechanism



14. Single-crystal X-ray diffraction data of 6m



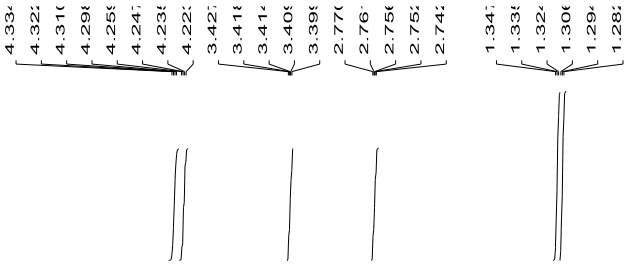
Procedure for the recrystallization of **6m**: To a 10 mL tube containing **6m** (25 mg) was added a 5:1 mixture of n-hexane and EtOAc (2 mL). The mixture was heated until complete dissolution, which was allowed to stand at room temperature to obtain crystals. These crystals were subjected for single crystal XRD to determine the relative configuration of **6m**. The data were collected by a Rigaku XtaLAB P200 equipped with a Cu radiation source (Kα = 1.54184 Å) at 293 K. CCDC 2303781 (**6m**) contains the supplementary crystallographic data for this paper. These data can be obtained free of

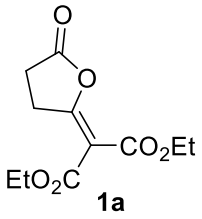
charge via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data and structure refinement for 6m.

Identification code	**6m** (CCDC: 2303781)
Empirical formula	$C_{25}H_{26}O_5$
Formula weight	406.46
Temperature/K	293
Crystal system	triclinic
Space group	P-1
a/Å	10.1019(2)
b/Å	10.7180(3)
c/Å	11.1905(2)
α/°	64.873(2)
β/°	69.562(2)
γ/°	83.168(2)
Volume/Å^3	1027.30(4)
Z	2
ρ_{calc}g/cm^3	1.314
μ/mm^{-1}	0.737
F(000)	432.0
Crystal size/mm^3	0.06 × 0.05 × 0.03
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.118 to 136.542
Index ranges	$-11 \leq h \leq 12$, $-12 \leq k \leq 12$, $-10 \leq l \leq 13$
Reflections collected	8925
Independent reflections	3616 [R_{int} = 0.0348, R_{sigma} = 0.0428]
Data/restraints/parameters	3616/0/271
Goodness-of-fit on F^2	1.073
Final R indexes [I>=2σ (I)]	R_1 = 0.0574, wR_2 = 0.1593
Final R indexes [all data]	R_1 = 0.0647, wR_2 = 0.1698
Largest diff. peak/hole / e Å^{-3}	0.38/-0.25

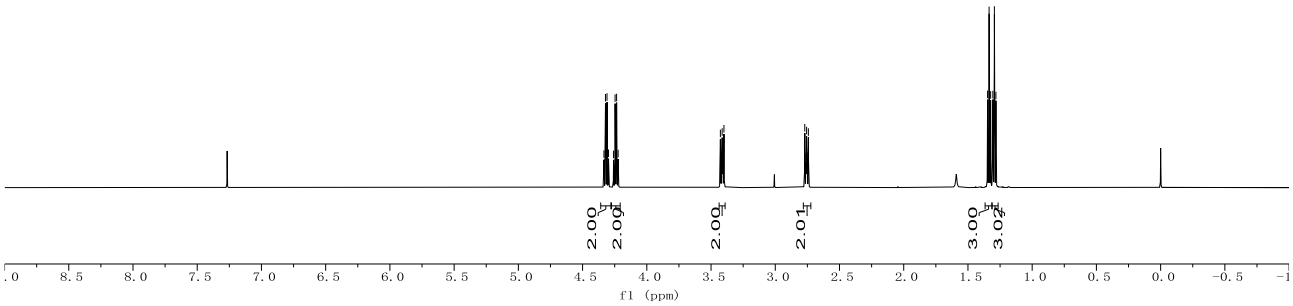
15. ^{1}H and ^{13}C NMR spectra and HPLC chromatograms

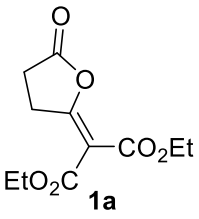




1a

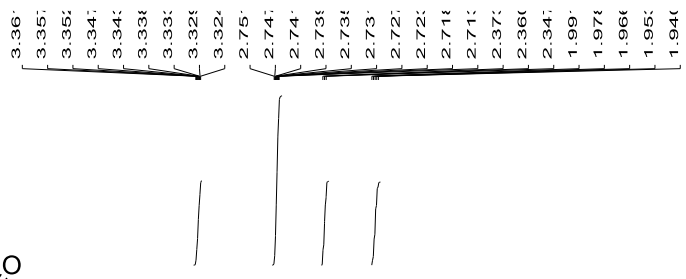
^{1}H NMR (600 MHz, $CDCl_3$)

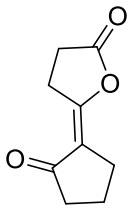




1a

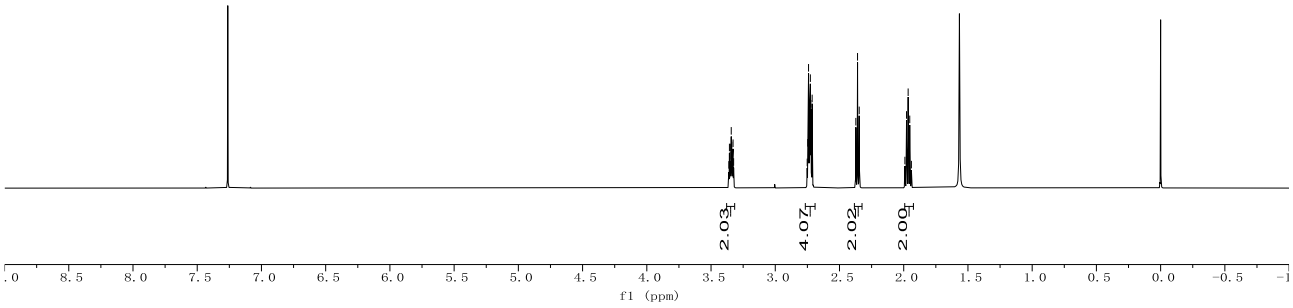
^{13}C NMR (150 MHz, $CDCl_3$)

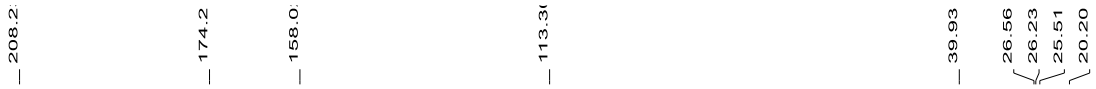


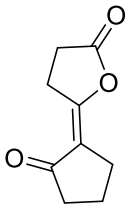


1b

^{1}H NMR (600 MHz, $CDCl_3$)

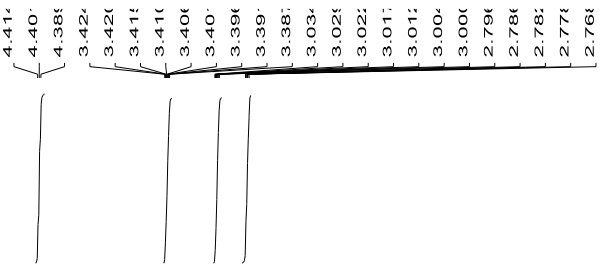


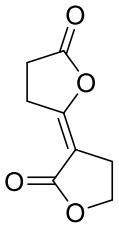




1b

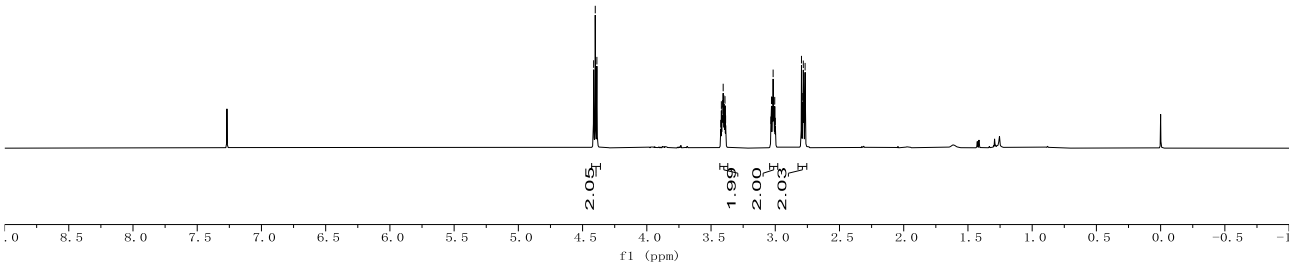
^{13}C NMR (150 MHz, $CDCl_3$)

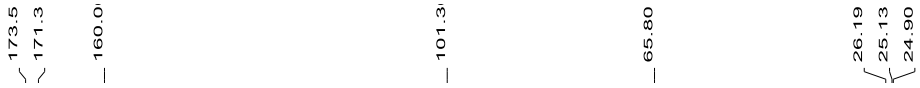


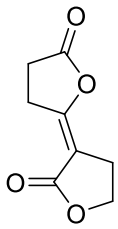


1d

^{1}H NMR (600 MHz, $CDCl_3$)

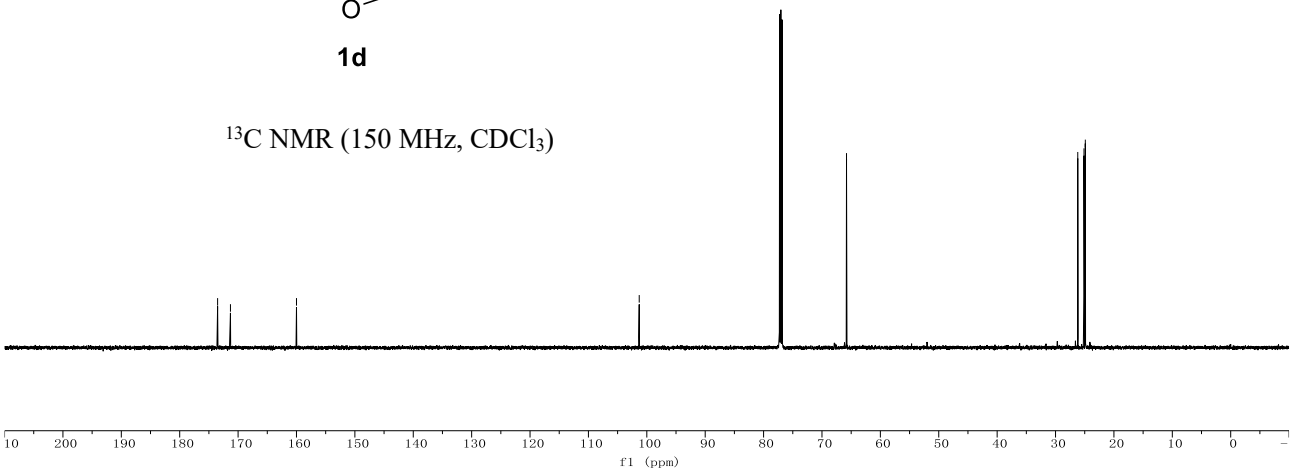


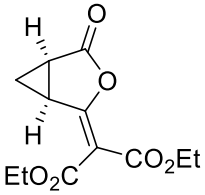




1d

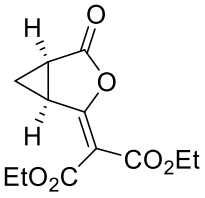
^{13}C NMR (150 MHz, $CDCl_3$)





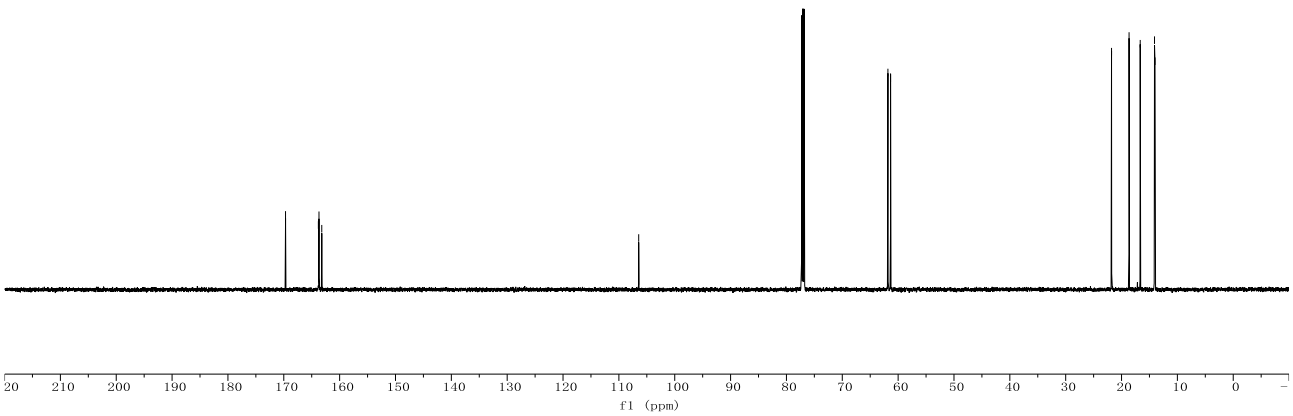
1e

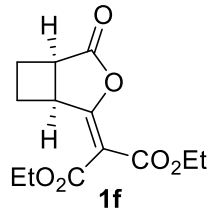
^{1}H NMR (600 MHz, $CDCl_3$)



1e

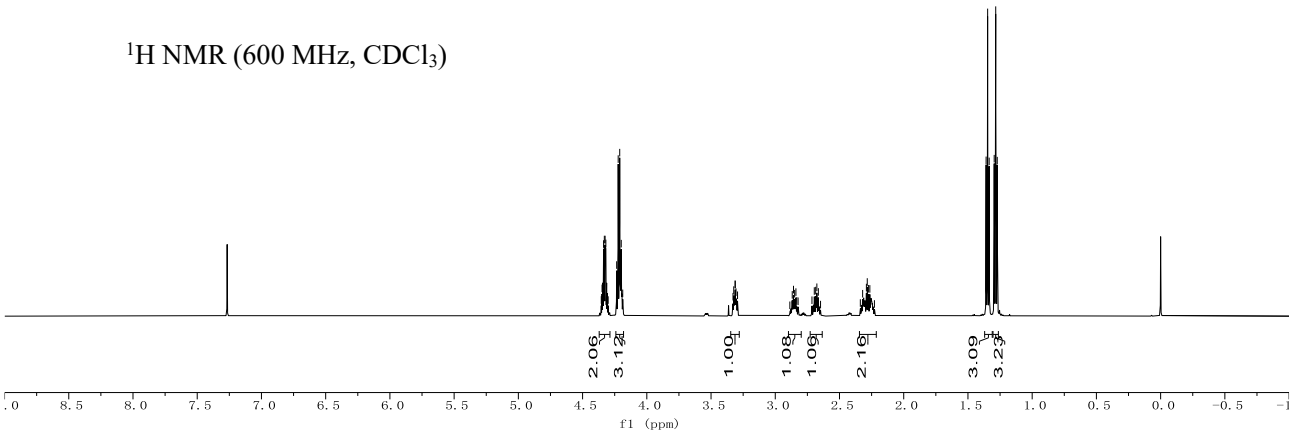
^{13}C NMR (150 MHz, $CDCl_3$)

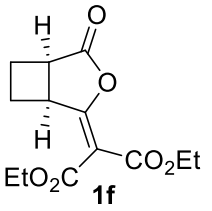




1f

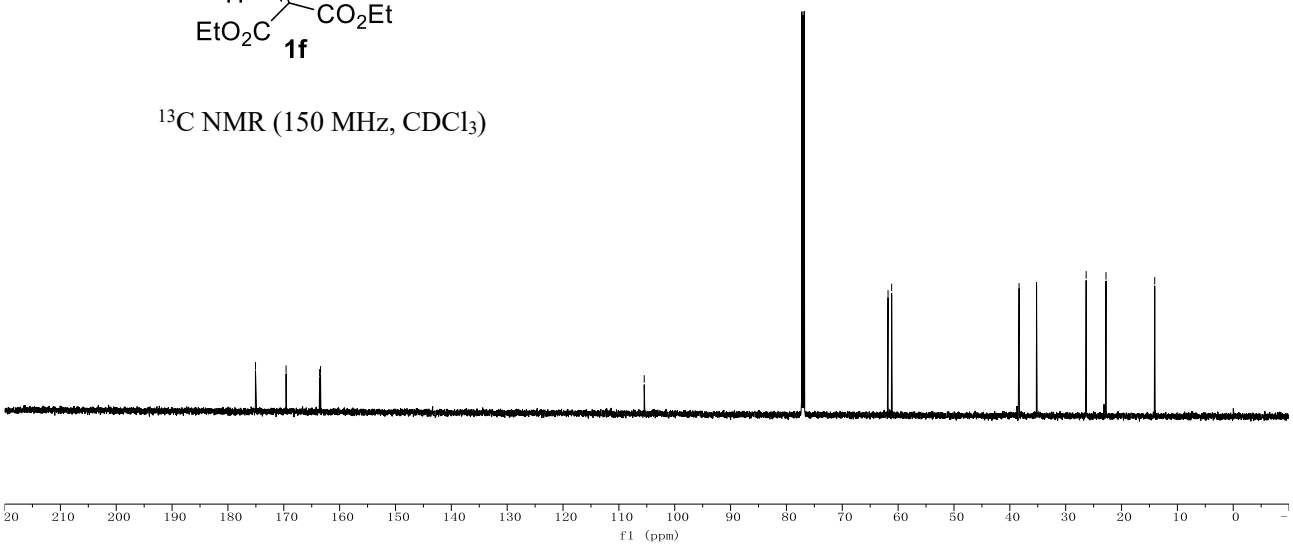
^{1}H NMR (600 MHz, $CDCl_3$)

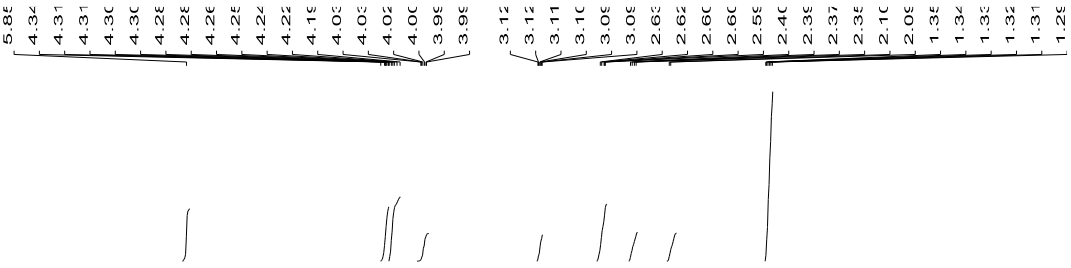


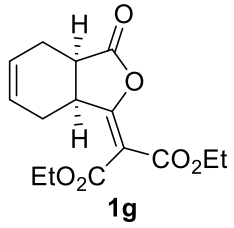


1f

^{13}C NMR (150 MHz, $CDCl_3$)

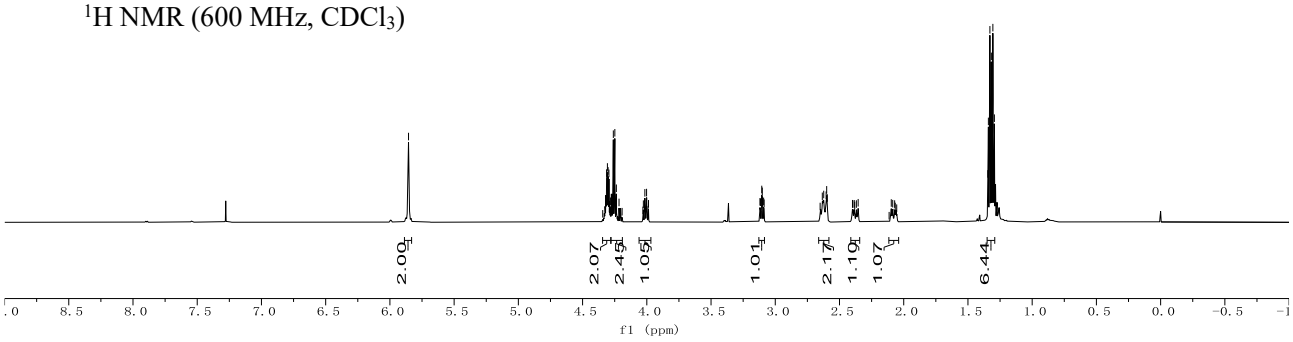


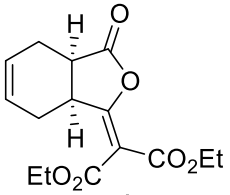




1g

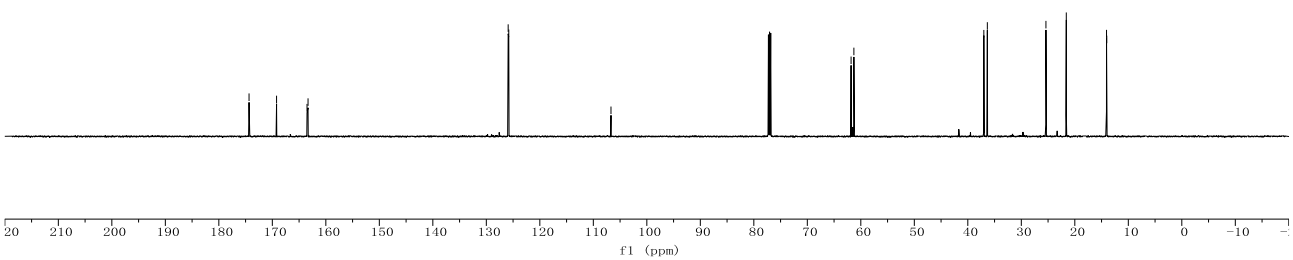
^{1}H NMR (600 MHz, $CDCl_3$)

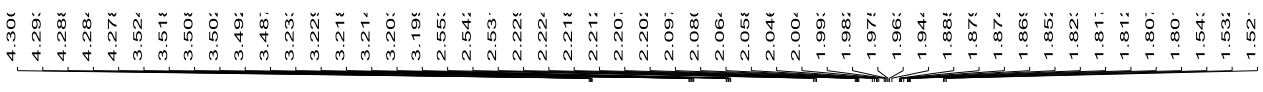


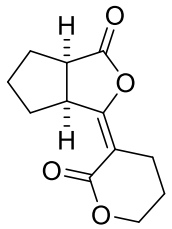


1g

^{13}C NMR (150 MHz, $CDCl_3$)

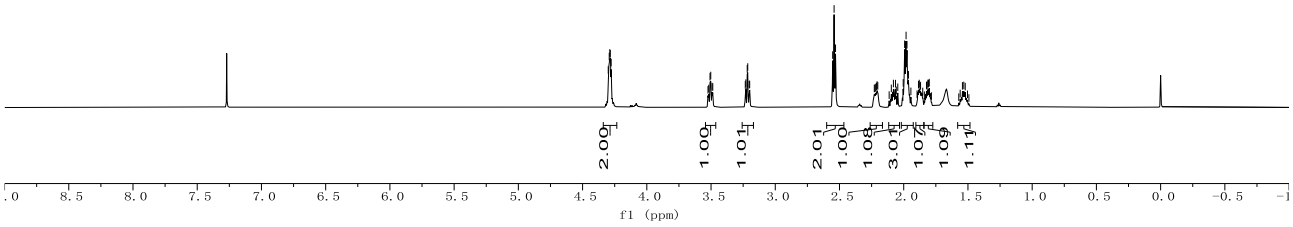


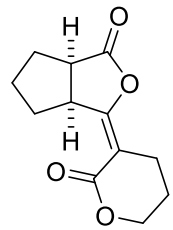




1h

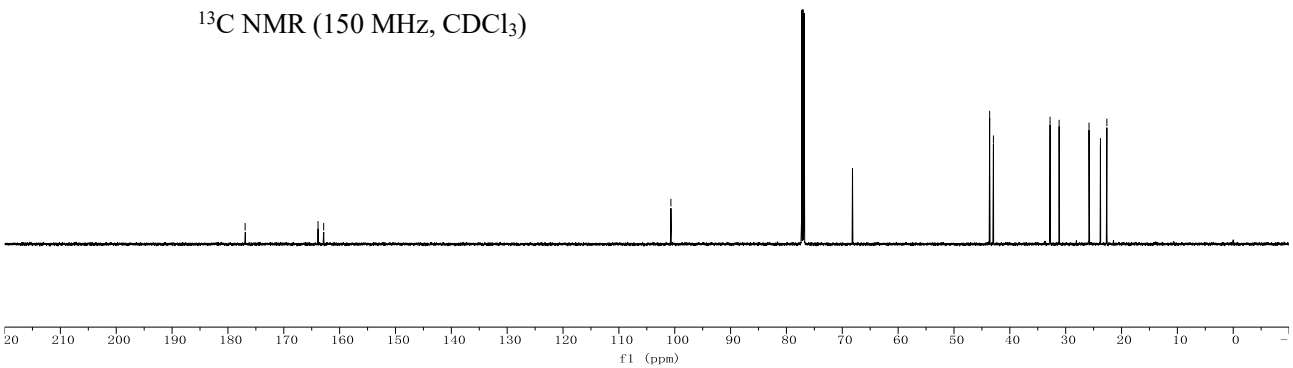
^{1}H NMR (600 MHz, $CDCl_3$)

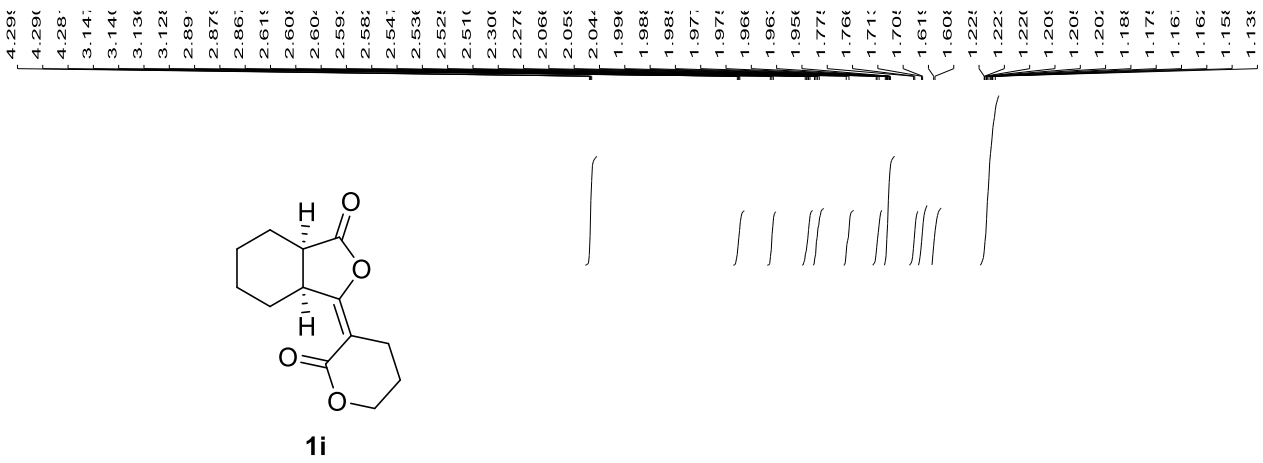




1h

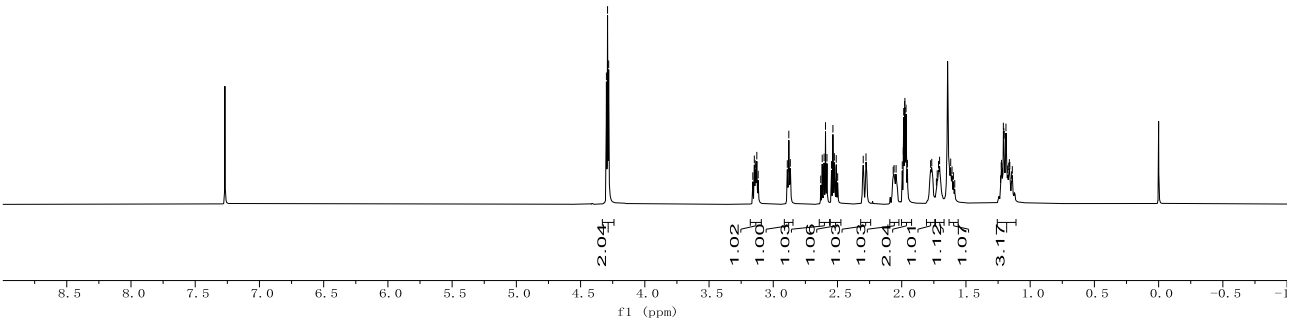
^{13}C NMR (150 MHz, $CDCl_3$)

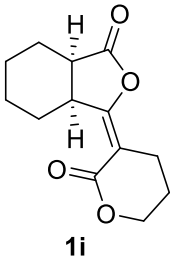




1i

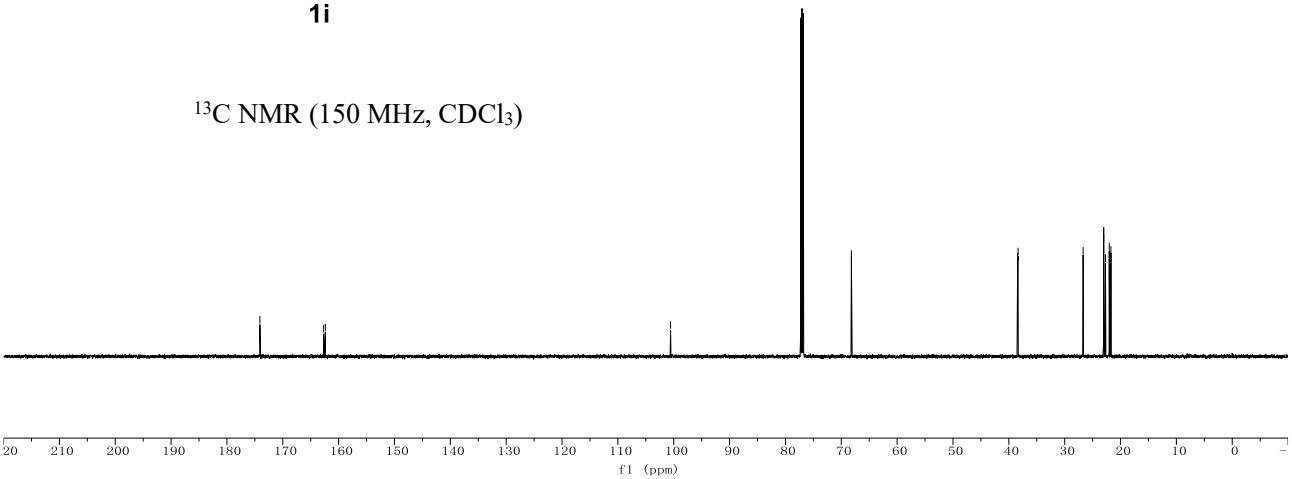
^{1}H NMR (600 MHz, $CDCl_3$)

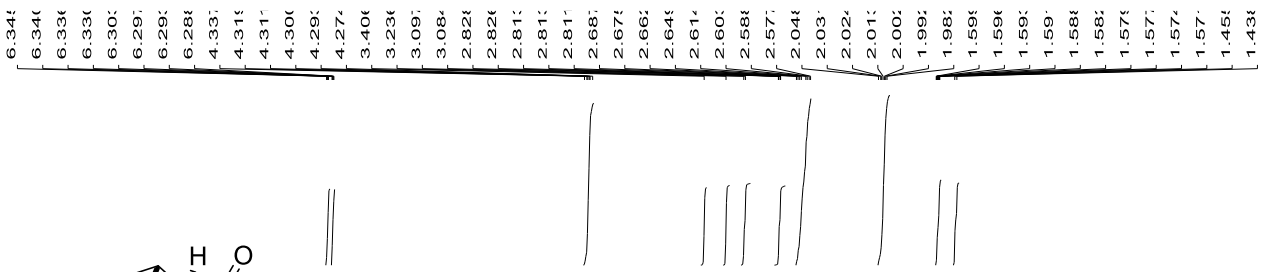


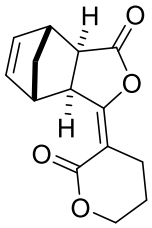


1i

^{13}C NMR (150 MHz, $CDCl_3$)

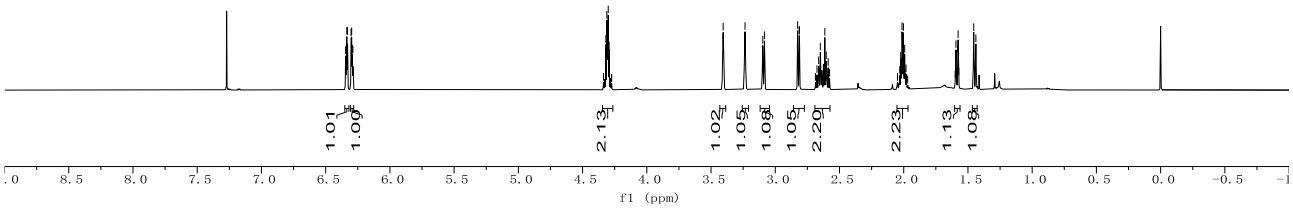


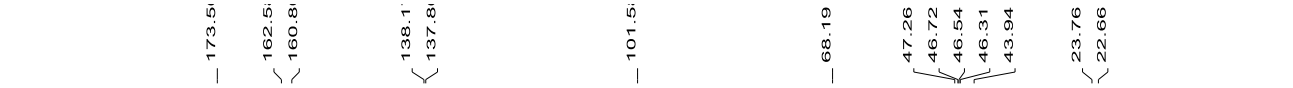


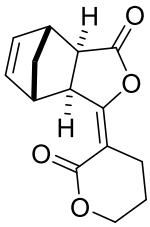


1j

^{1}H NMR (600 MHz, $CDCl_3$)

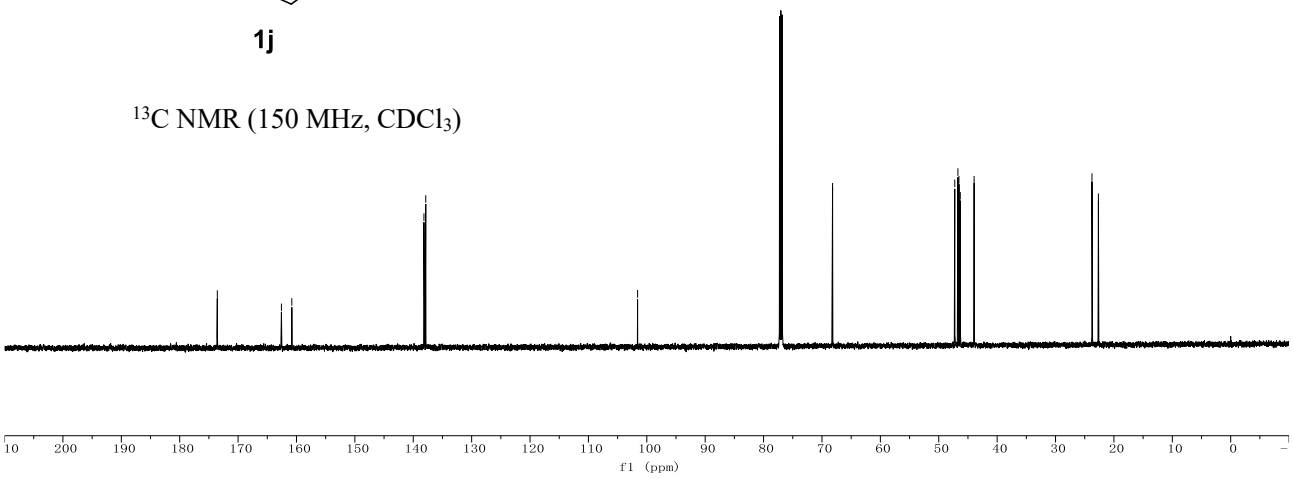


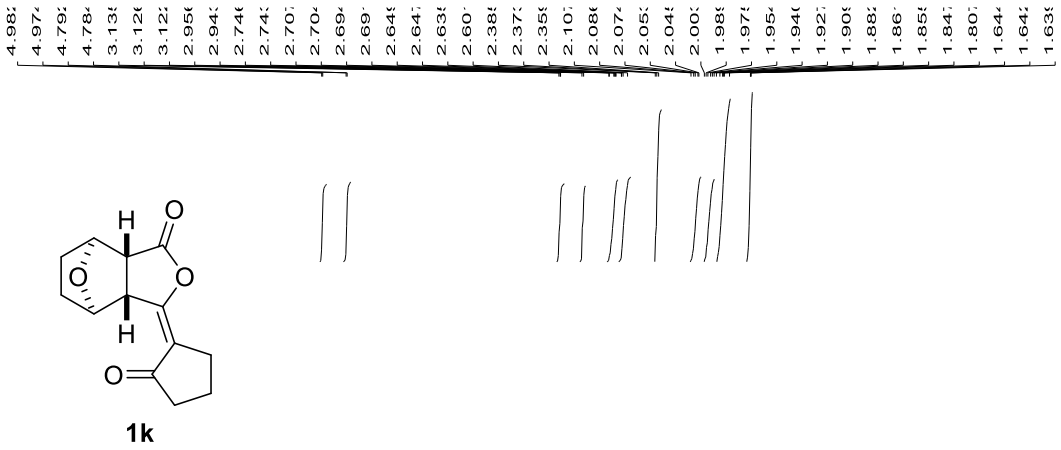




1j

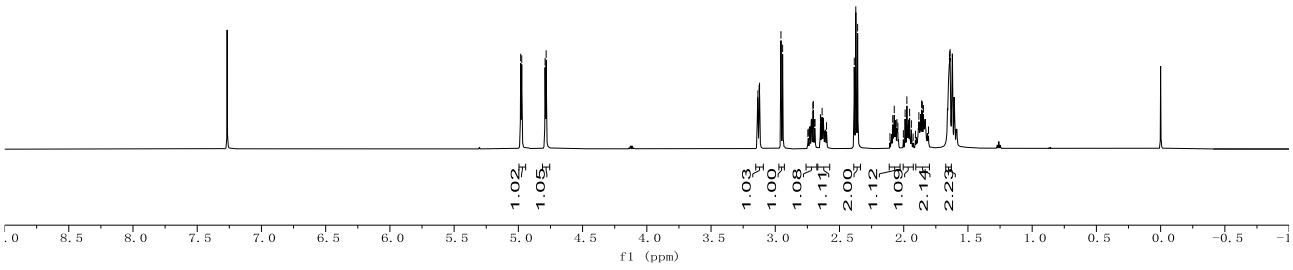
^{13}C NMR (150 MHz, $CDCl_3$)

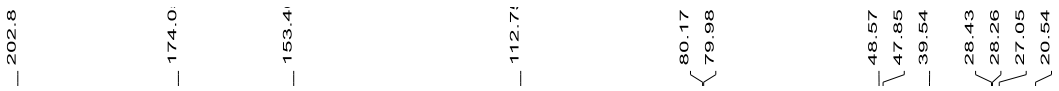


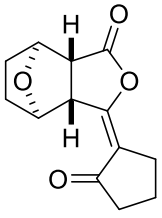


1k

^{1}H NMR (600 MHz, $CDCl_3$)

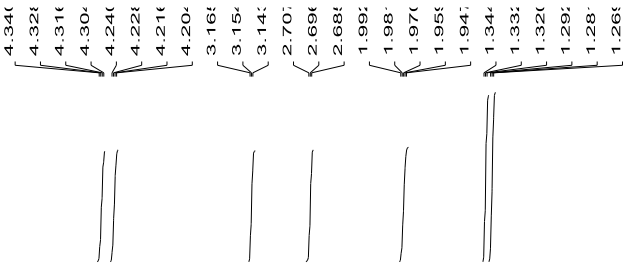


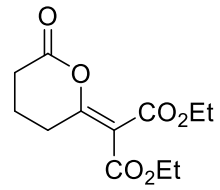




1k

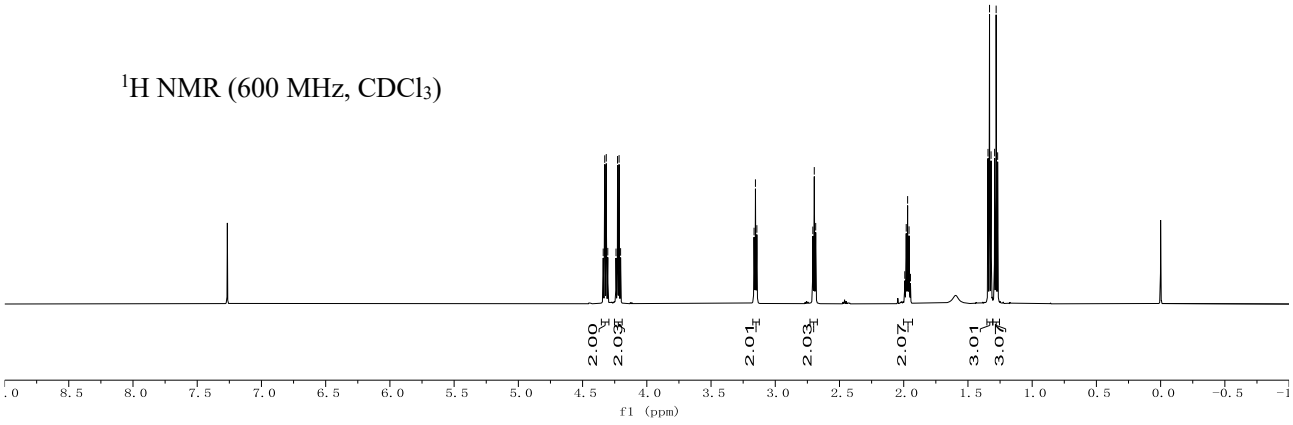
^{13}C NMR (150 MHz, $CDCl_3$)

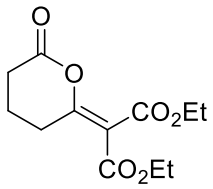




1n

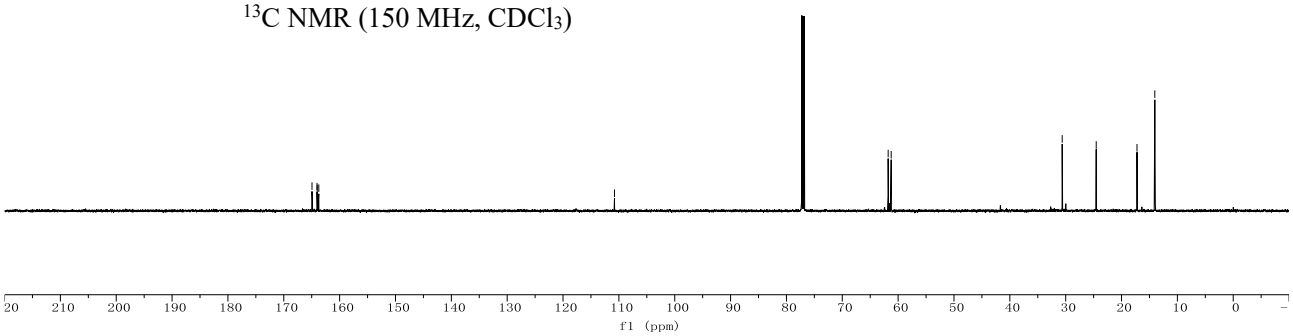
^{1}H NMR (600 MHz, $CDCl_3$)

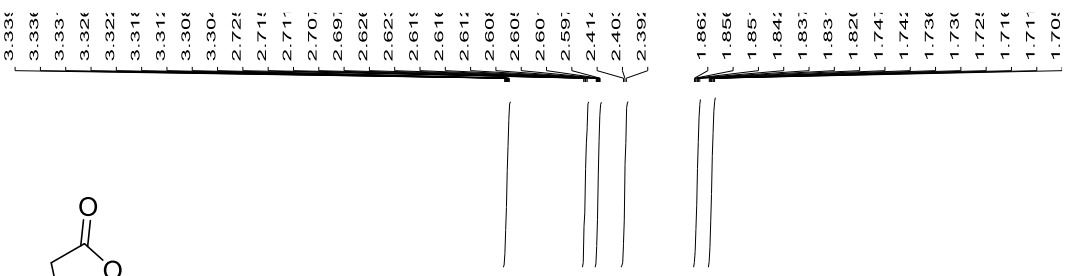


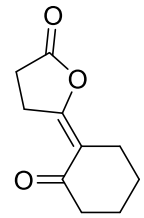


1n

^{13}C NMR (150 MHz, $CDCl_3$)

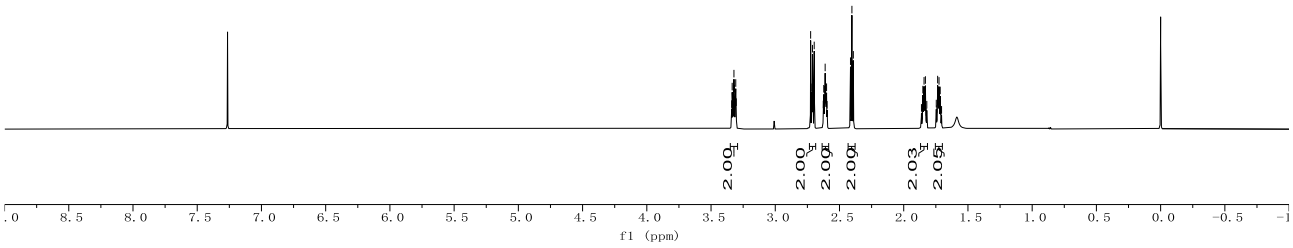


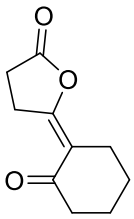




1o

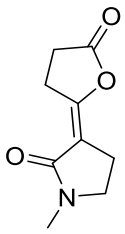
^{1}H NMR (600 MHz, $CDCl_3$)





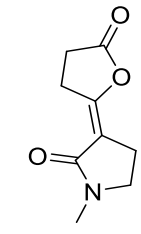
1o

^{13}C NMR (150 MHz, $CDCl_3$)



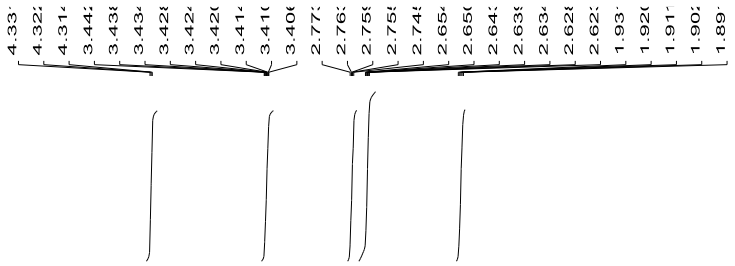
1p

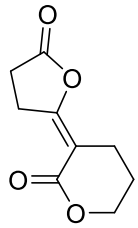
^{1}H NMR (600 MHz, $CDCl_3$)



1p

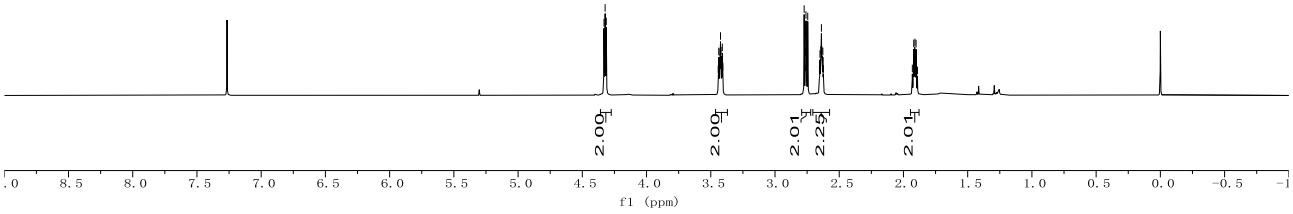
^{13}C NMR (150 MHz, $CDCl_3$)

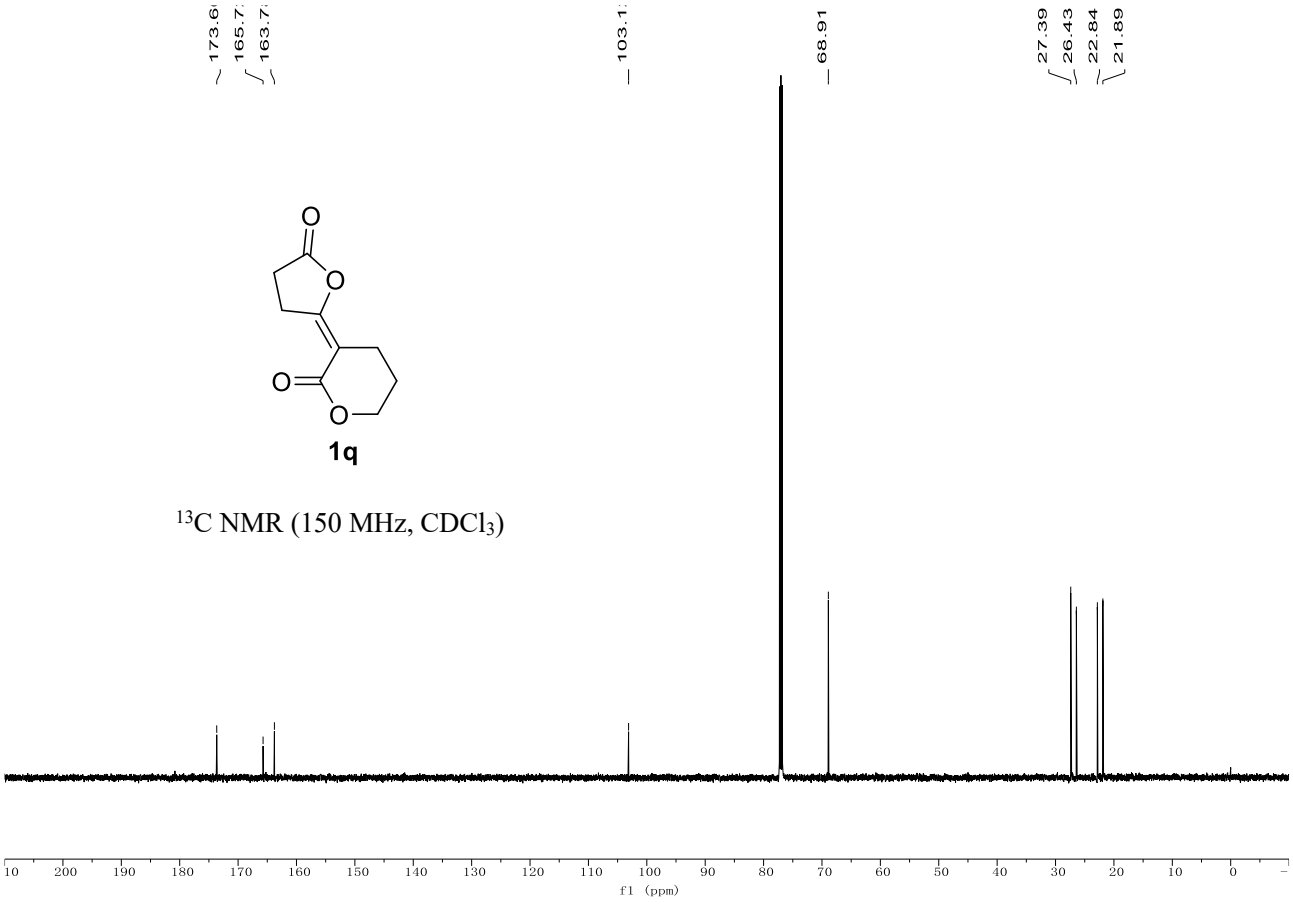




1q

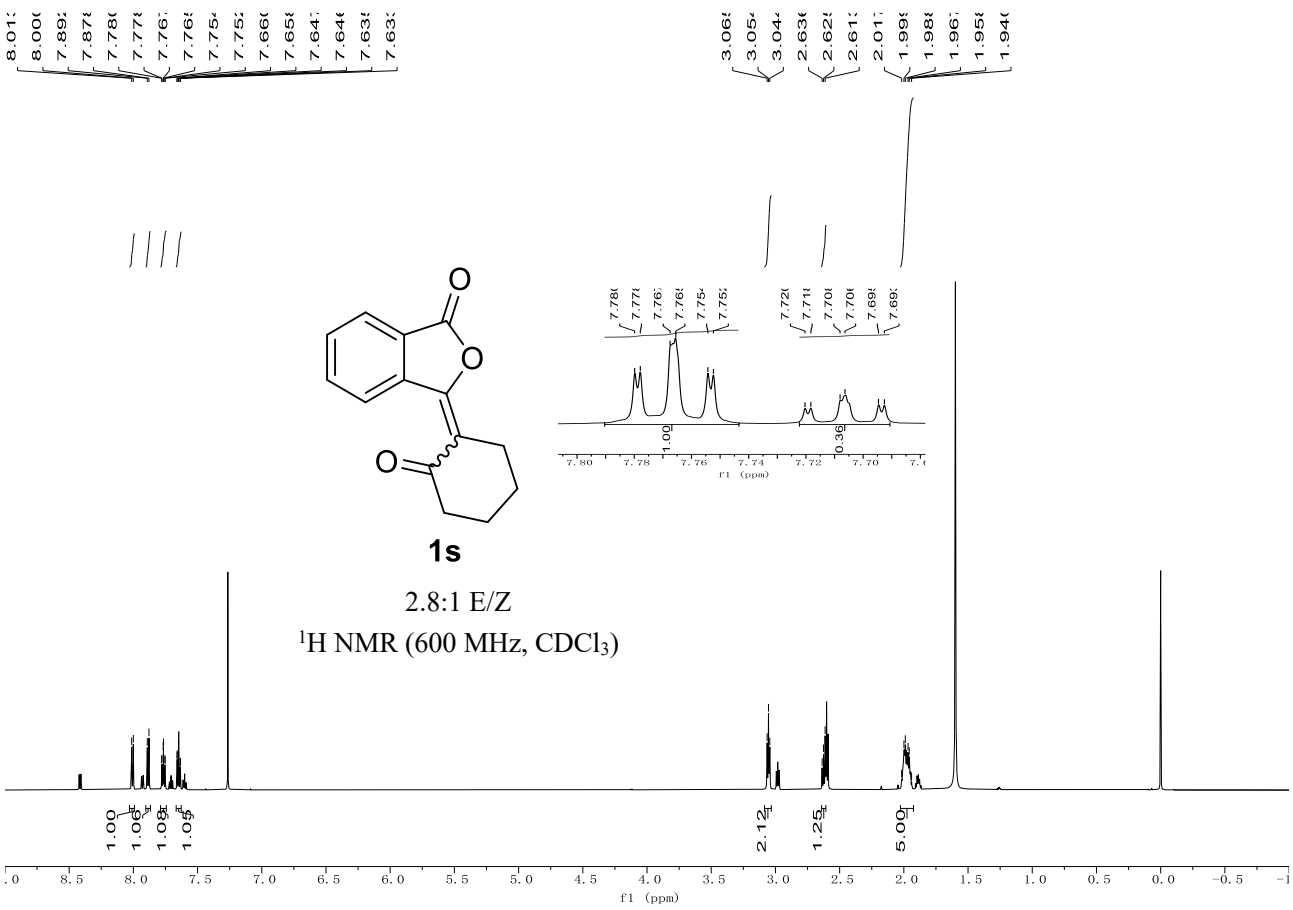
^{1}H NMR (600 MHz, $CDCl_3$)





1q

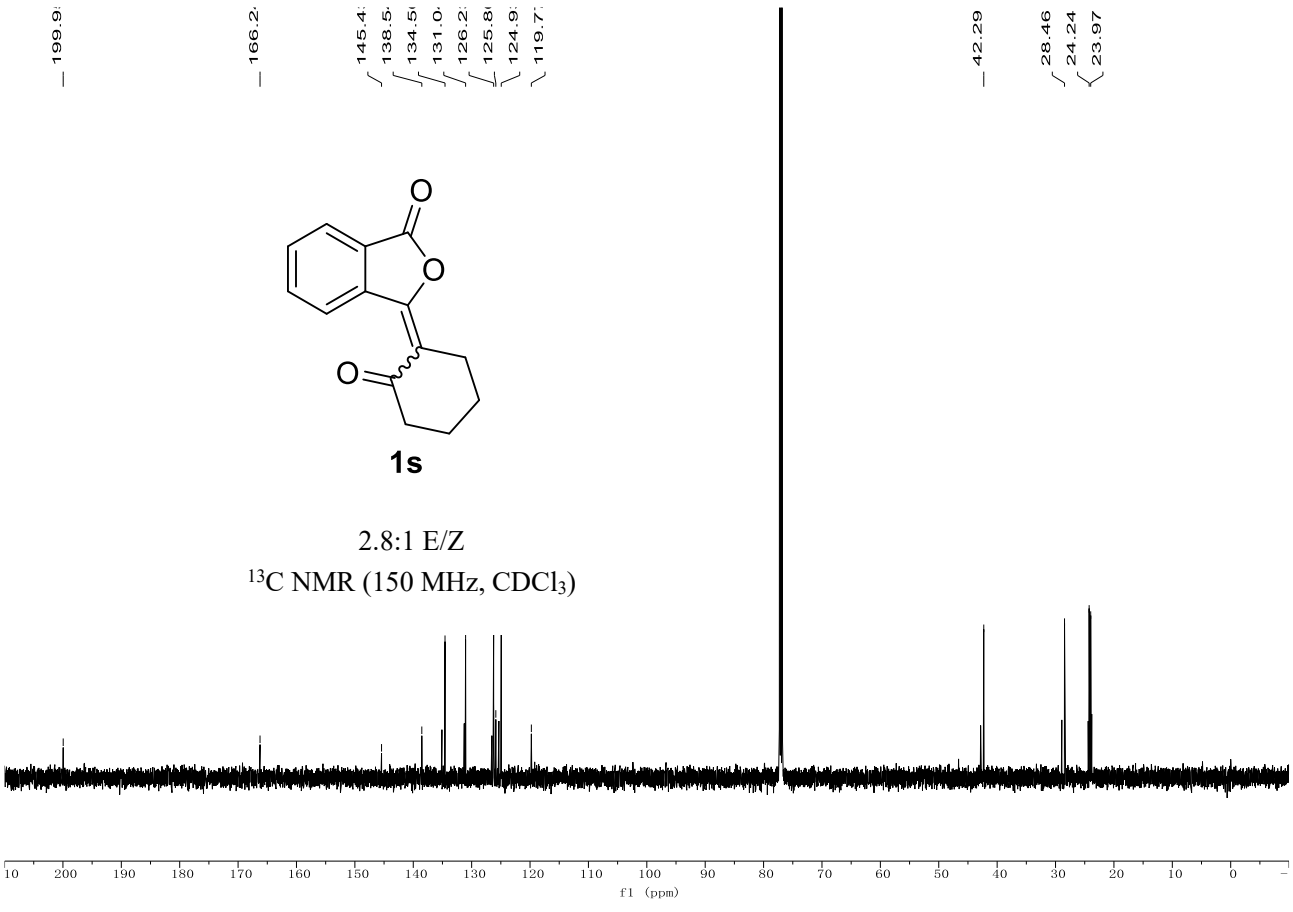
^{13}C NMR (150 MHz, $CDCl_3$)



1s

2.8:1 E/Z

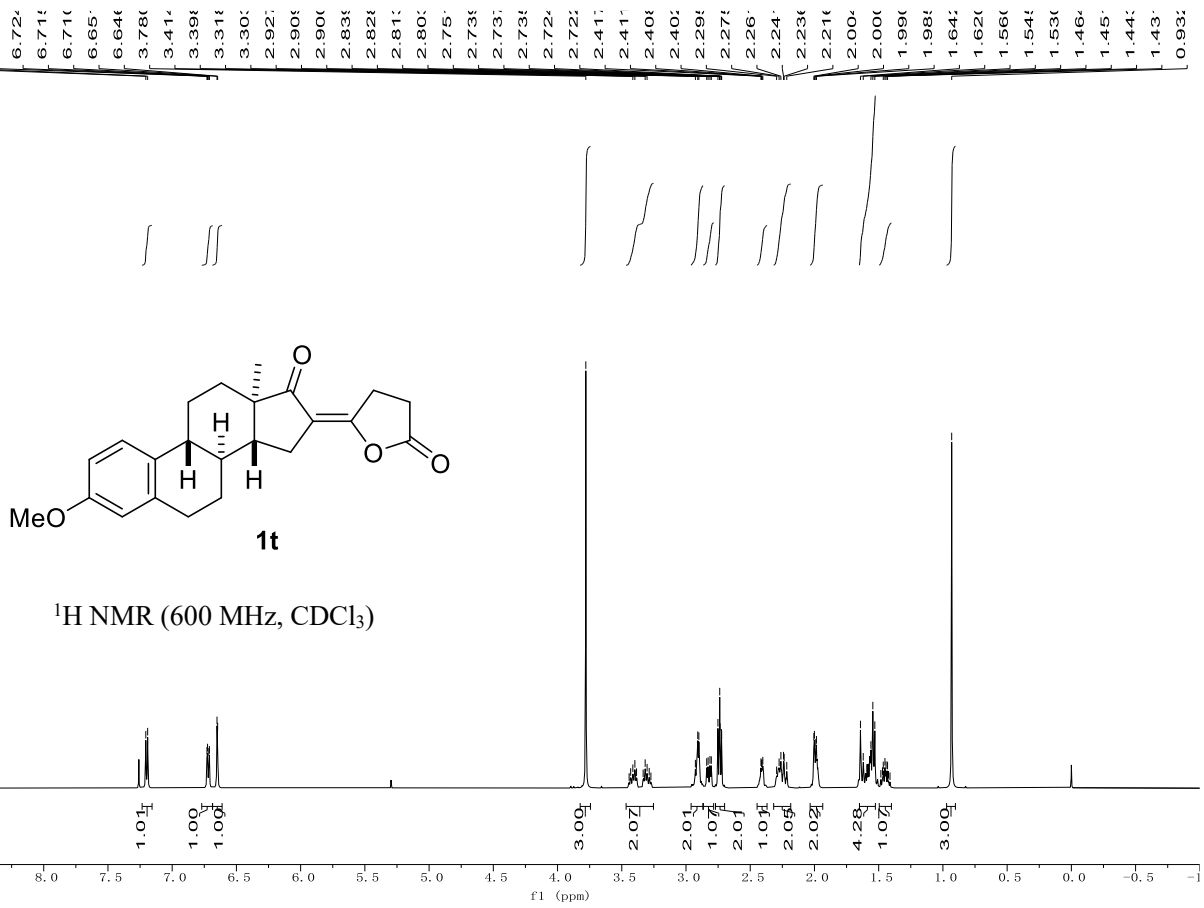
^{1}H NMR (600 MHz, $CDCl_3$)



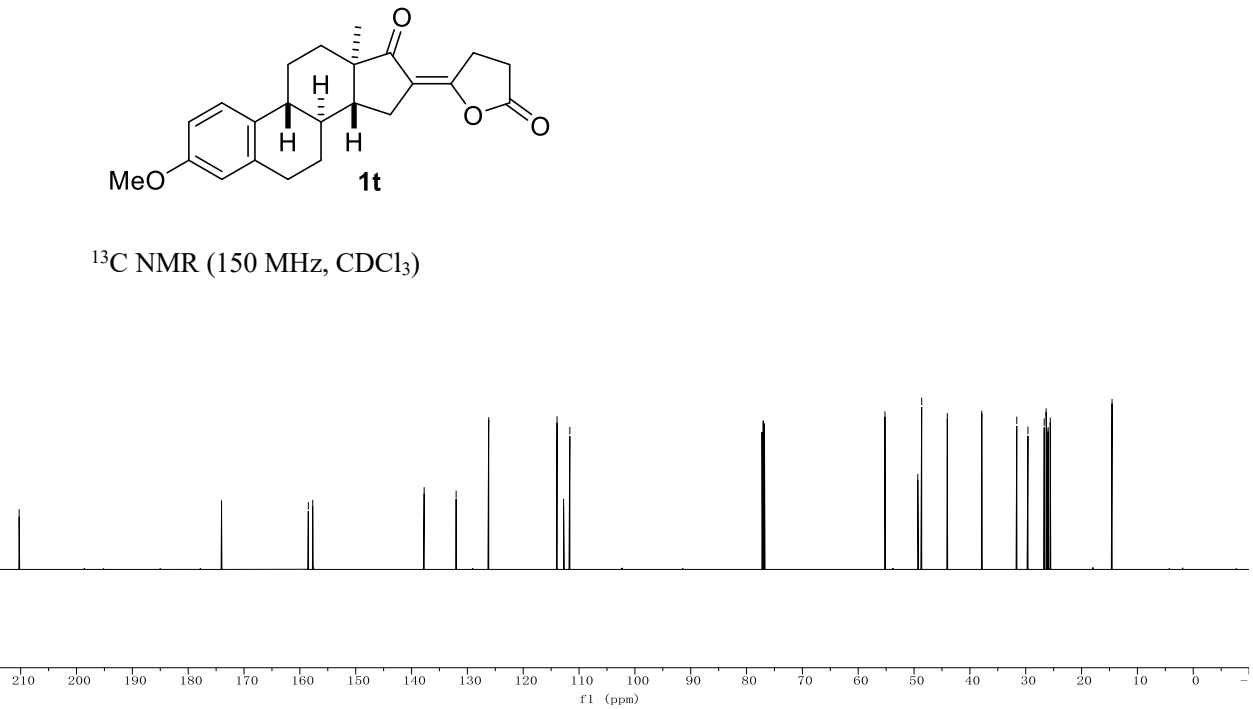
1s

2.8:1 E/Z

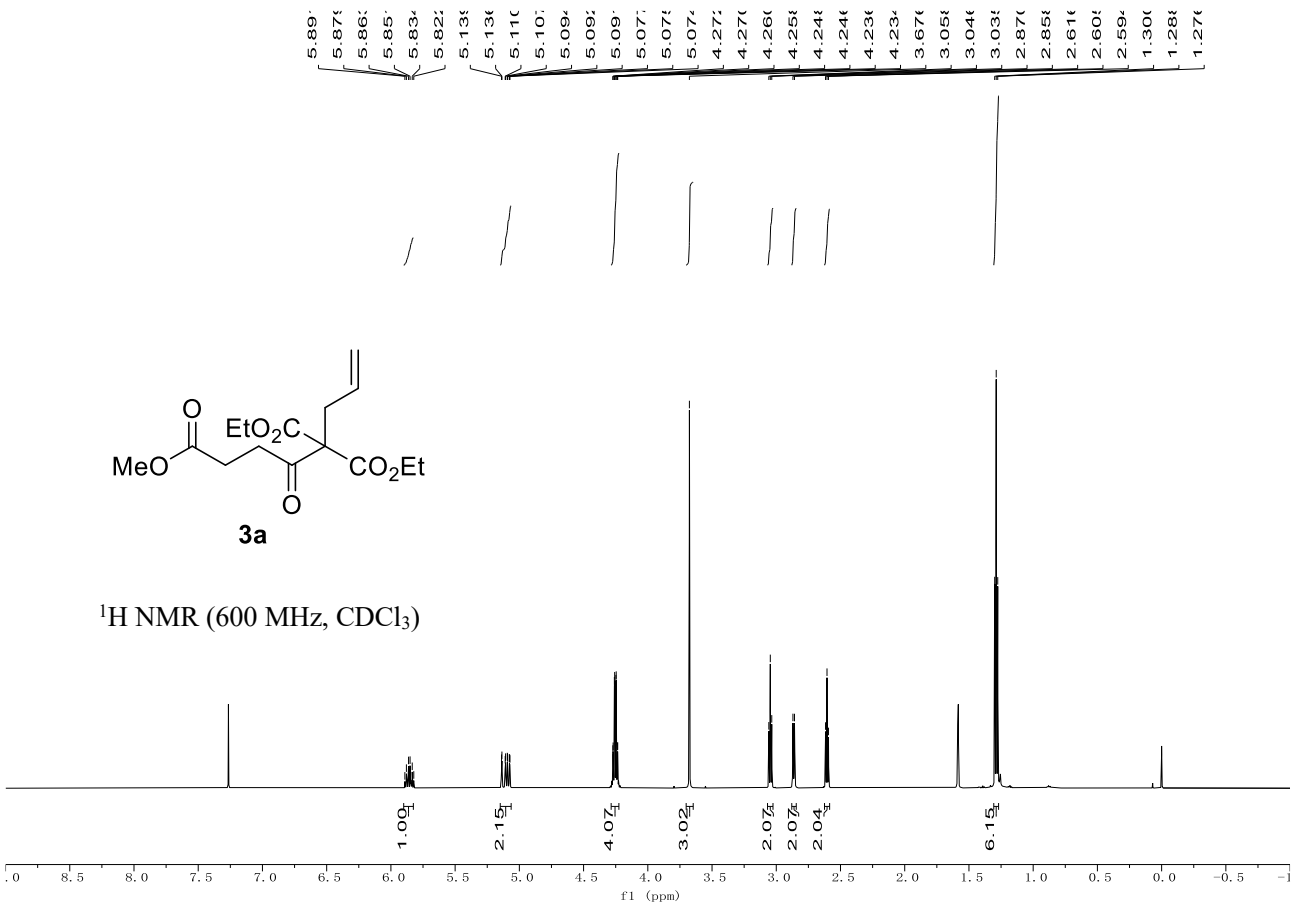
^{13}C NMR (150 MHz, $CDCl_3$)

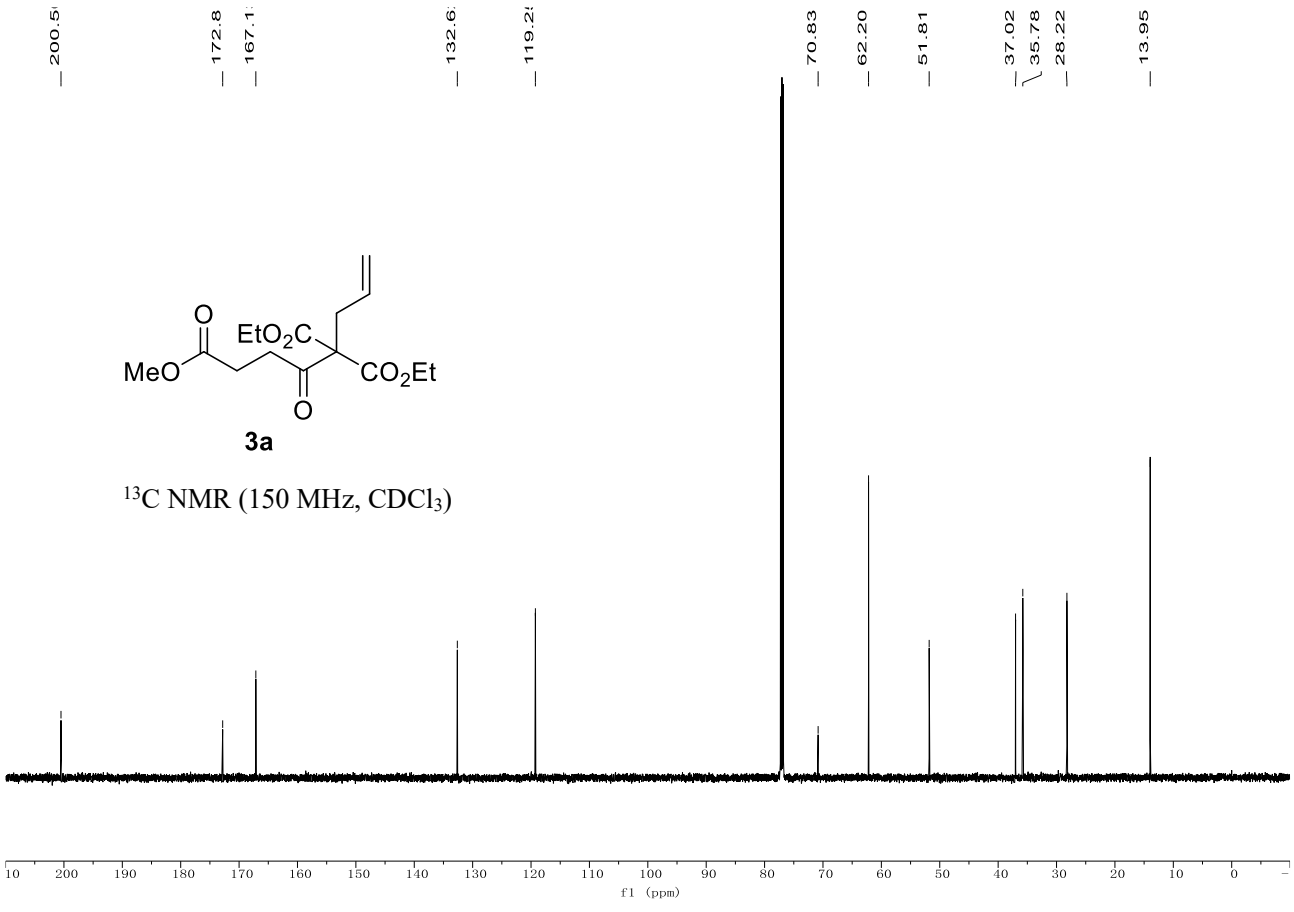


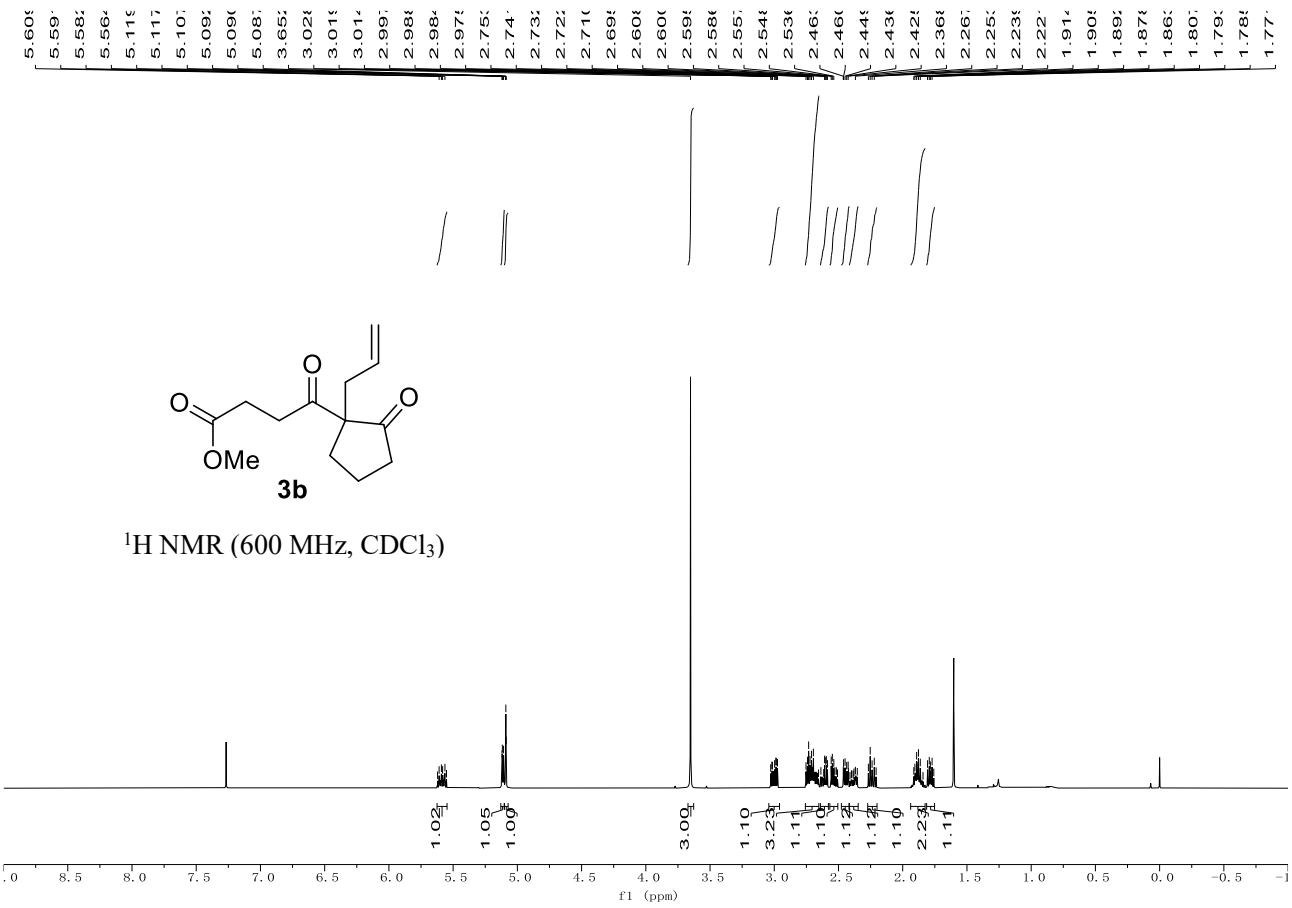
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (150 MHz, $CDCl_3$)

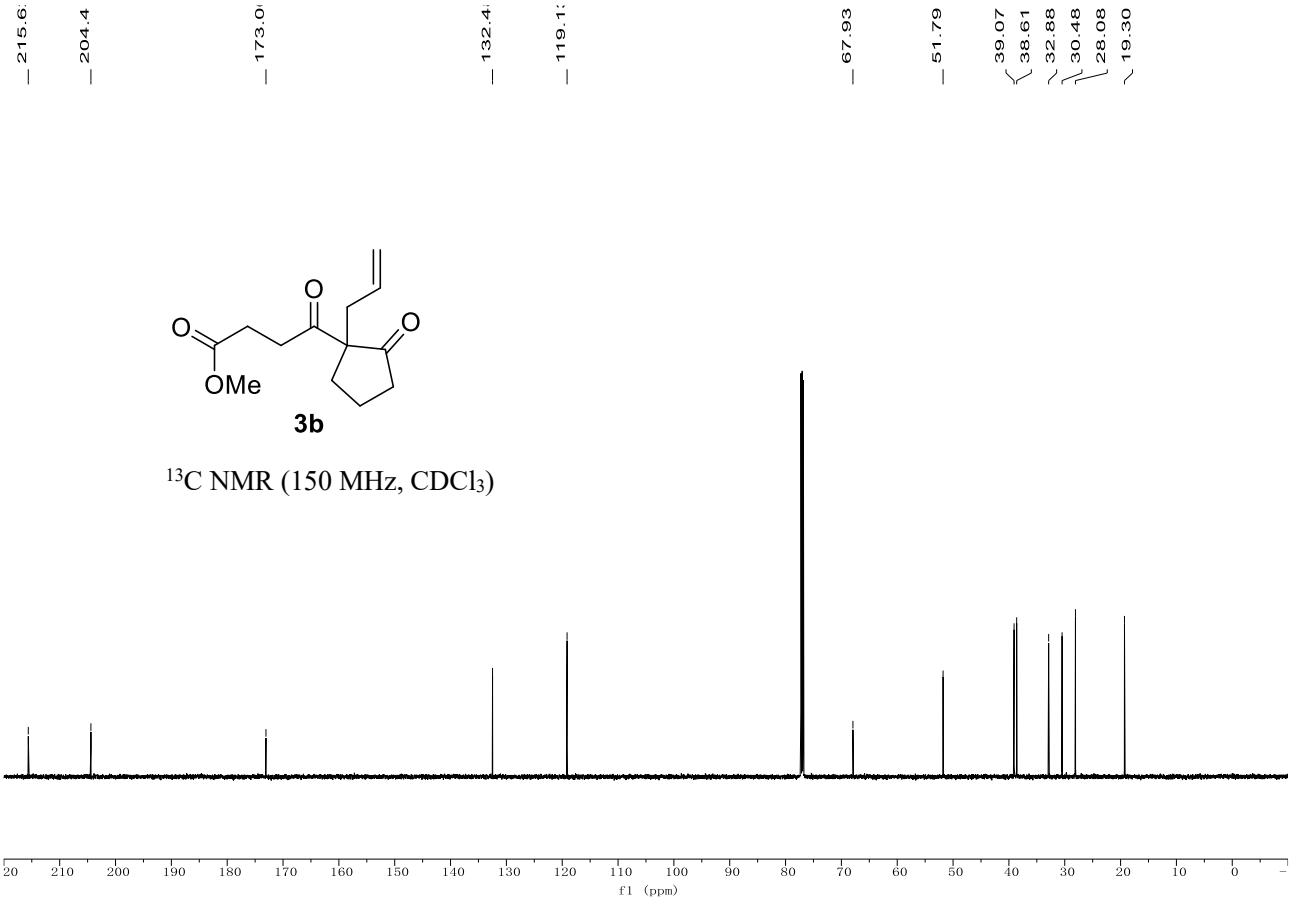

MeO
EtO2C
CO2Et
O
3a
1H NMR (600 MHz, CDCl3)
f1 (ppm)


MeO
EtO2C
CO2Et
O
3a
13C NMR (150 MHz, CDCl3)
f1 (ppm)



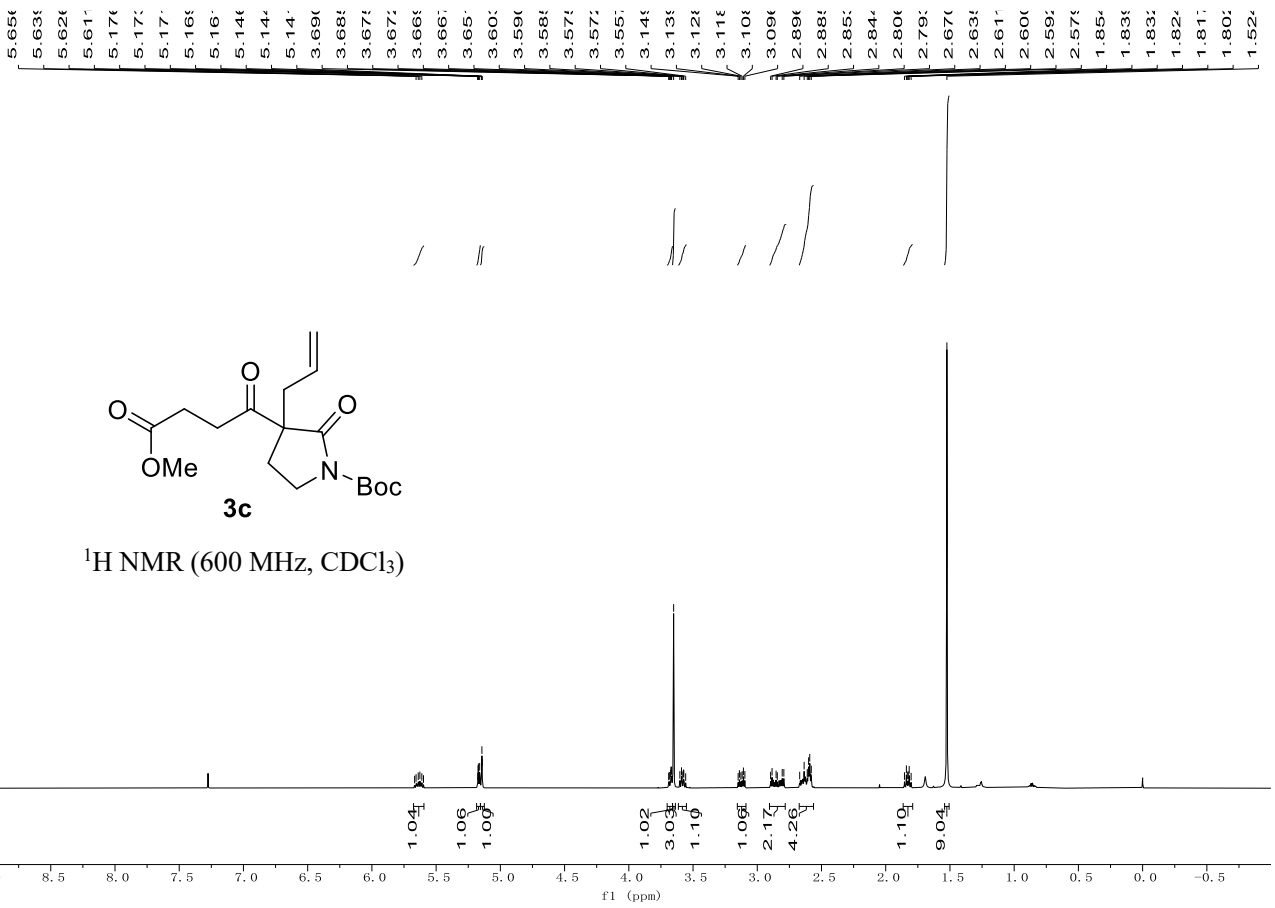
3b

^{1}H NMR (600 MHz, $CDCl_3$)



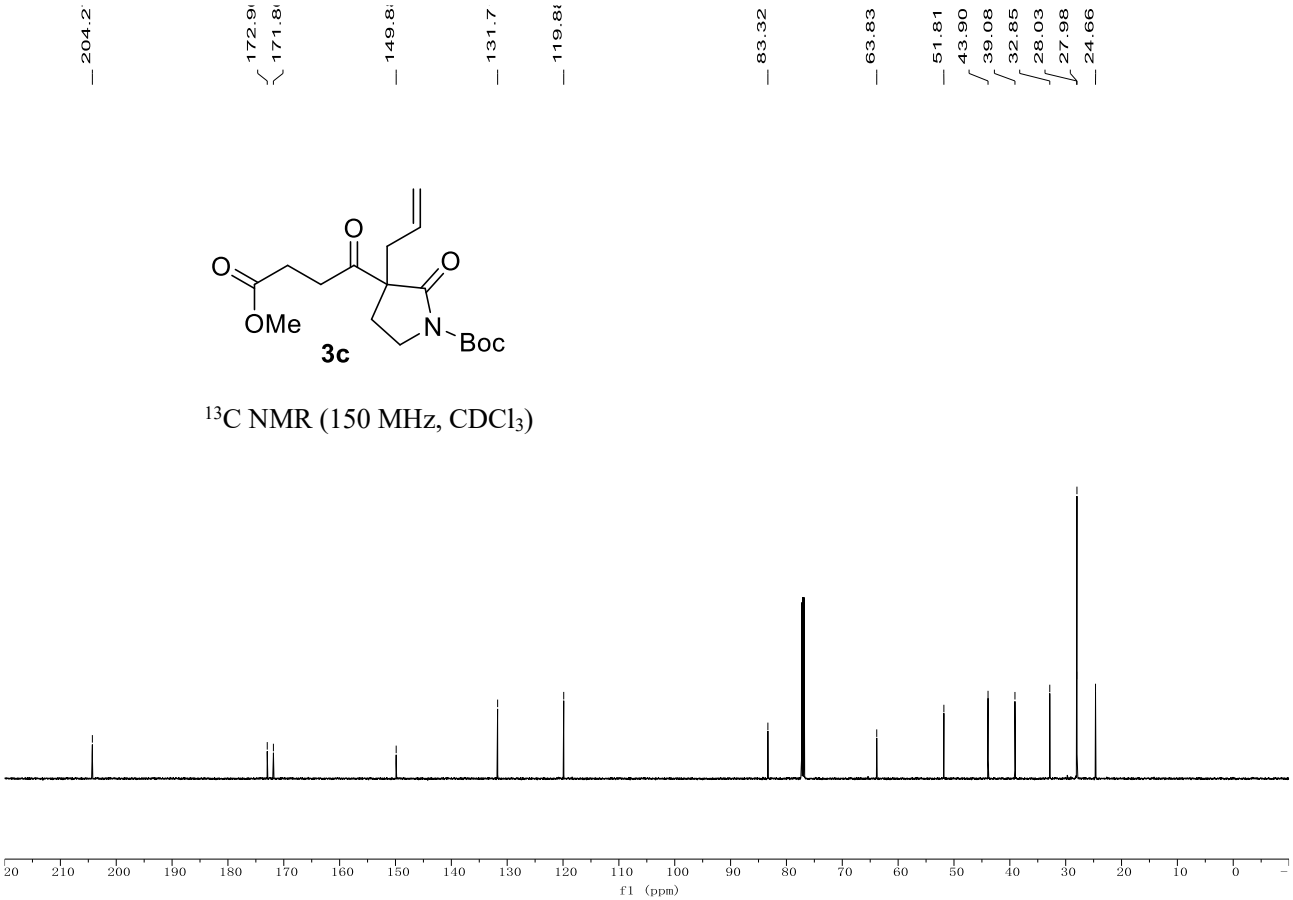
3b

^{13}C NMR (150 MHz, $CDCl_3$)



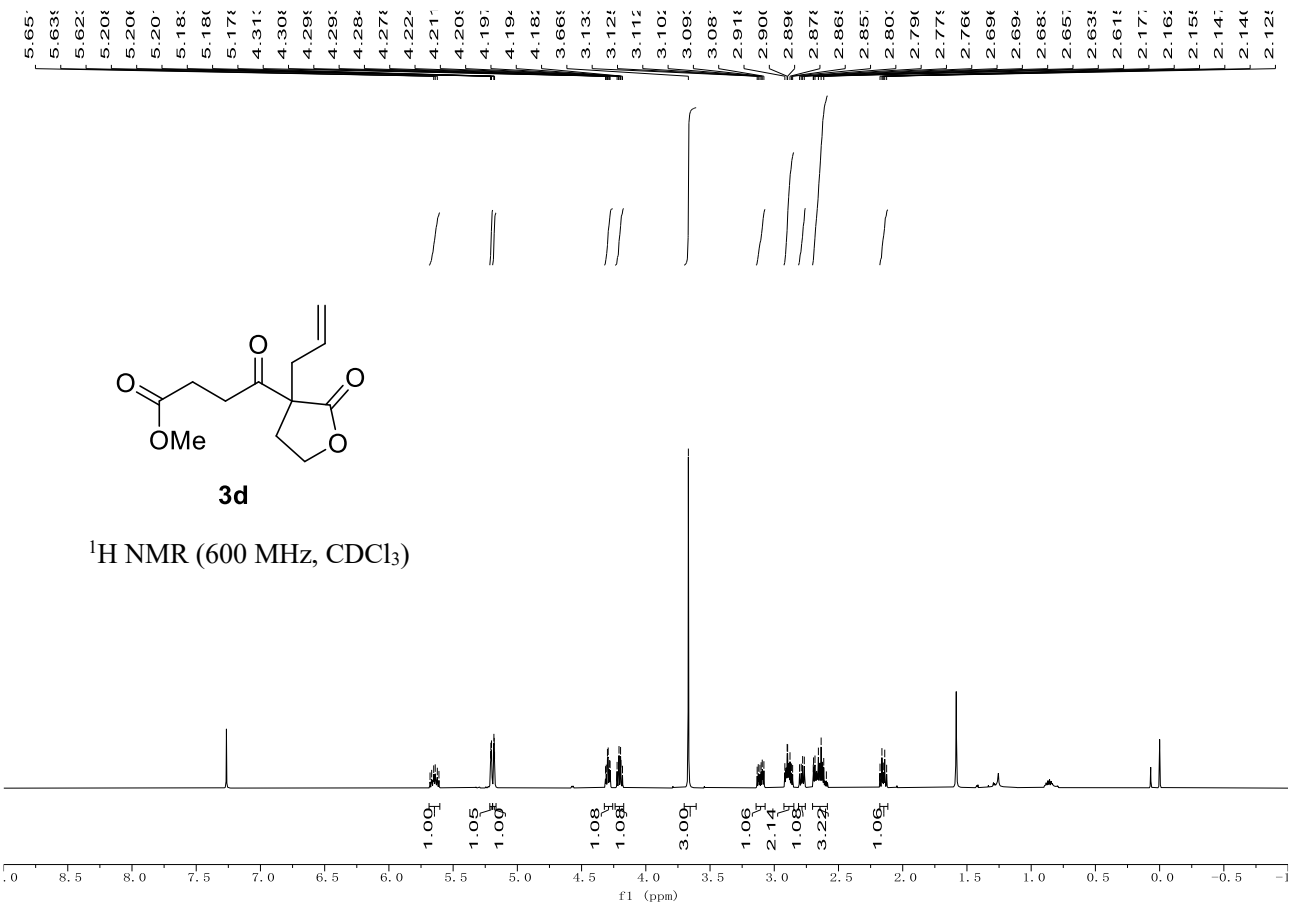
3c

^{1}H NMR (600 MHz, $CDCl_3$)



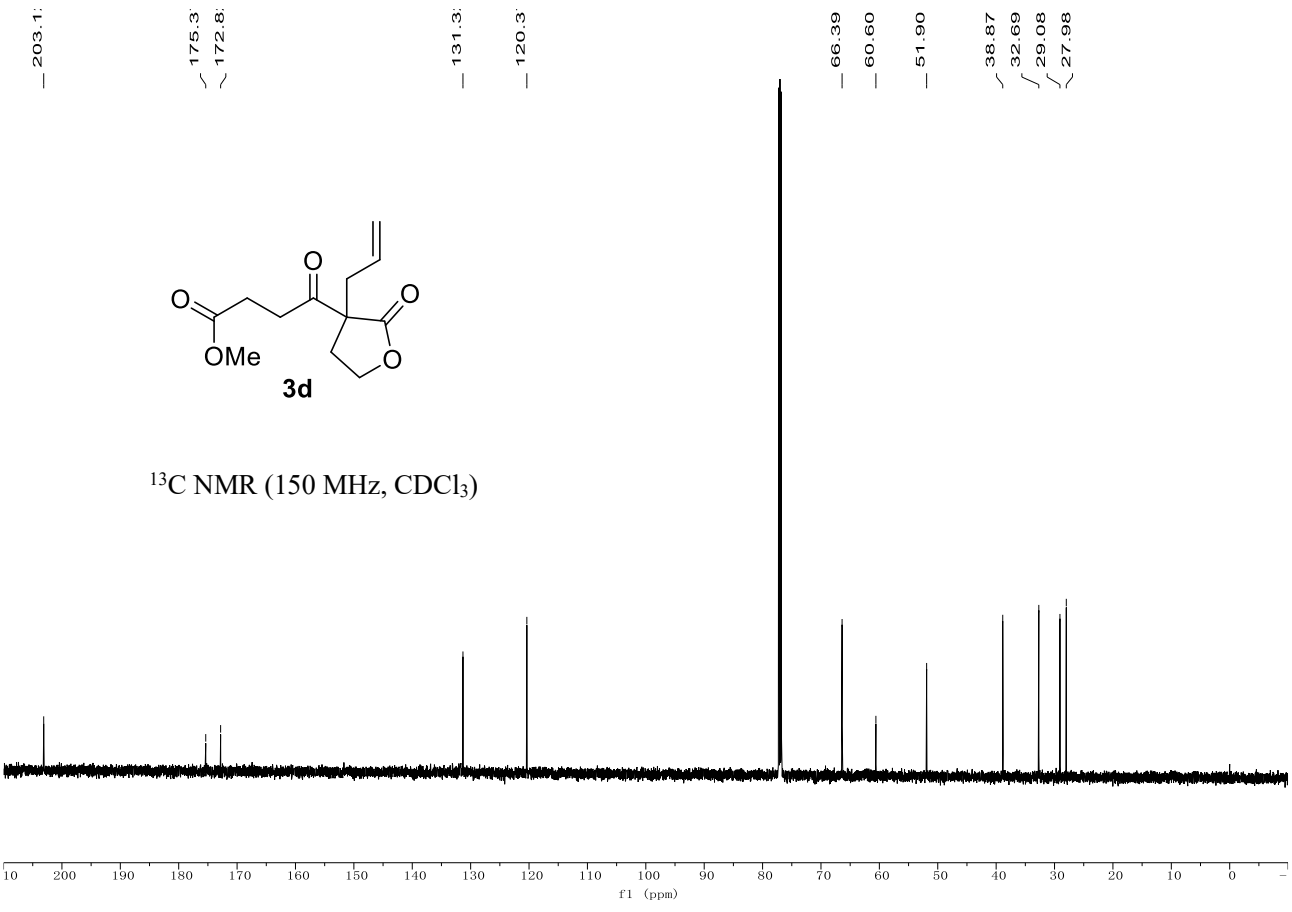
3c

^{13}C NMR (150 MHz, $CDCl_3$)



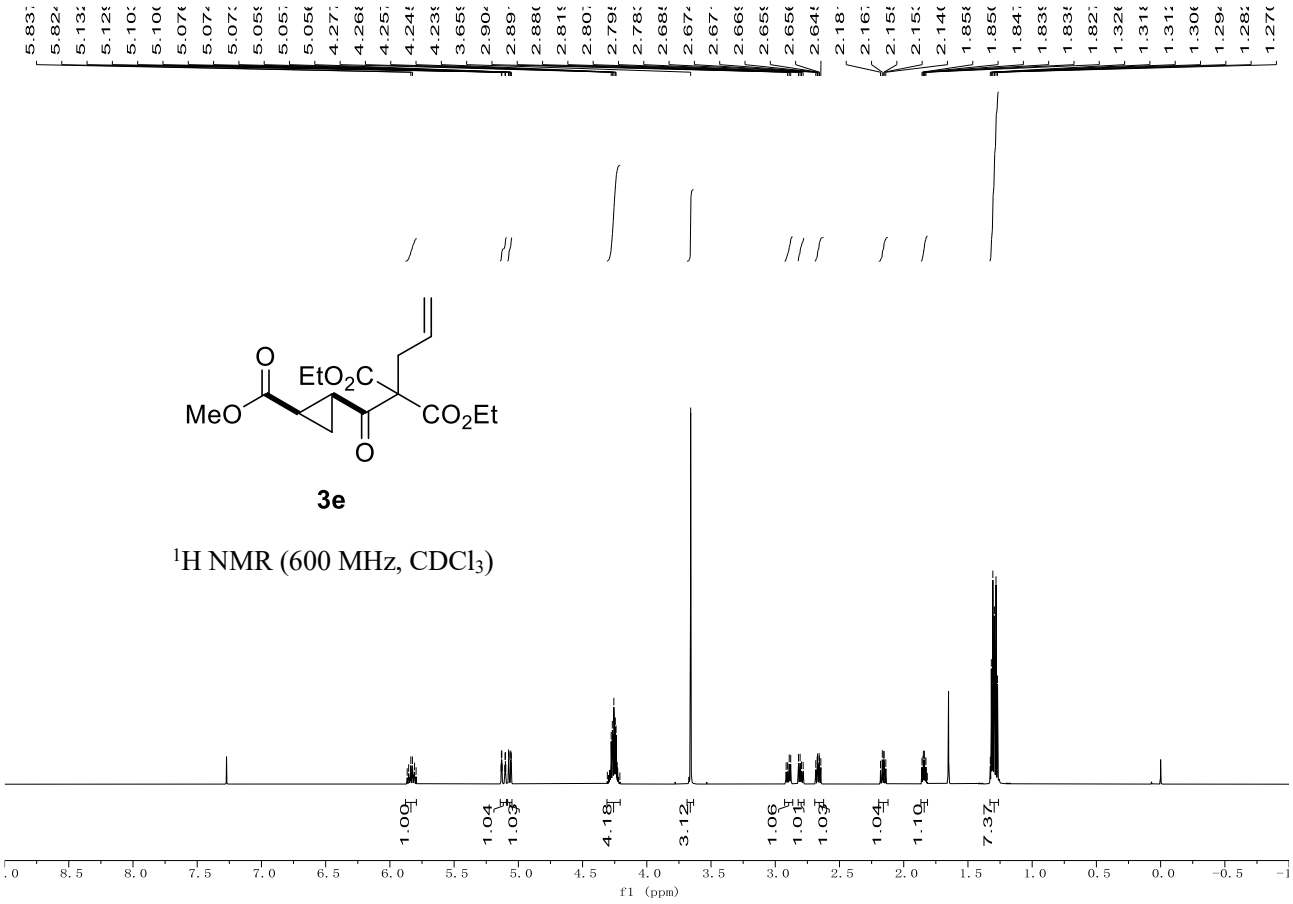
3d

^{1}H NMR (600 MHz, $CDCl_3$)



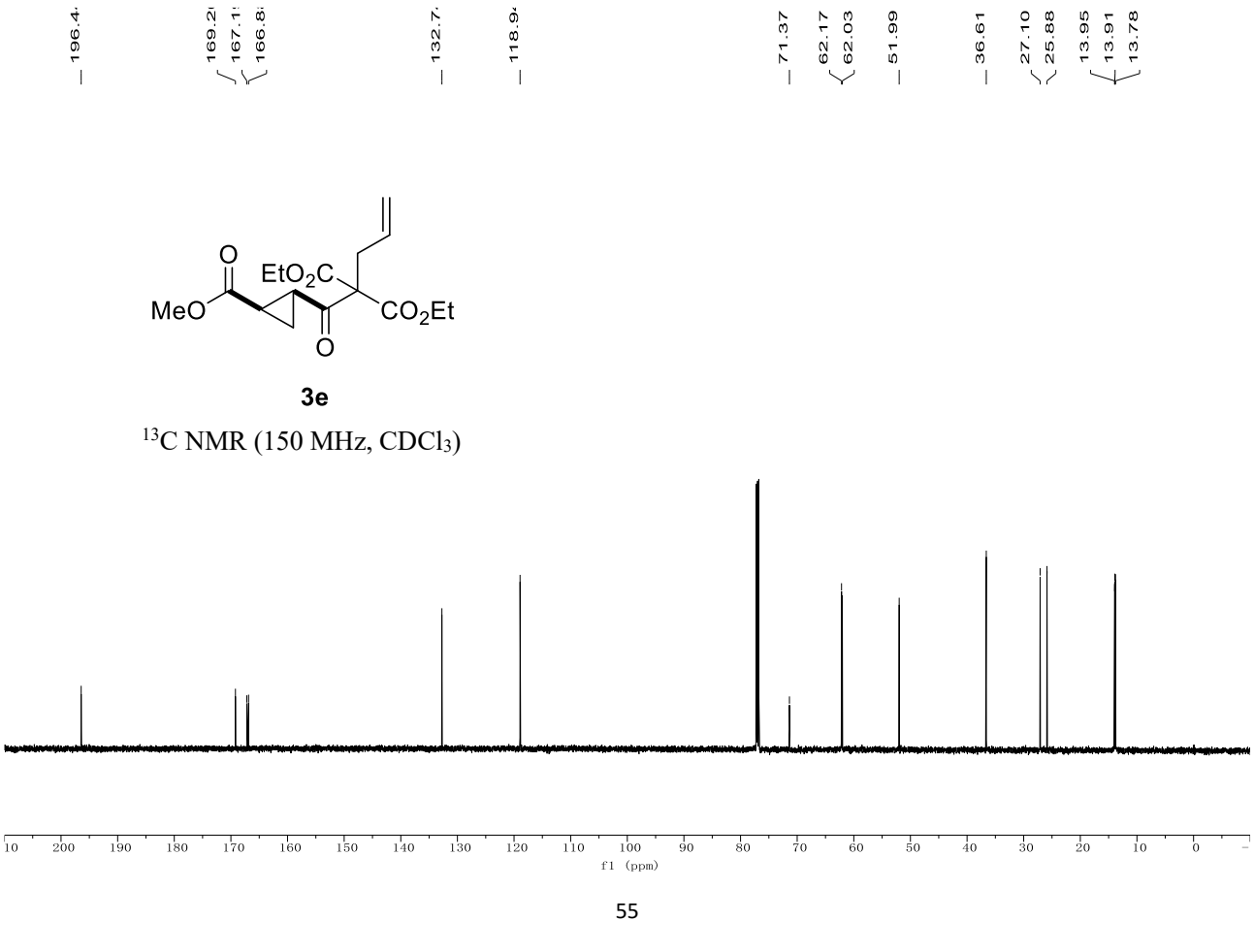
3d

^{13}C NMR (150 MHz, $CDCl_3$)



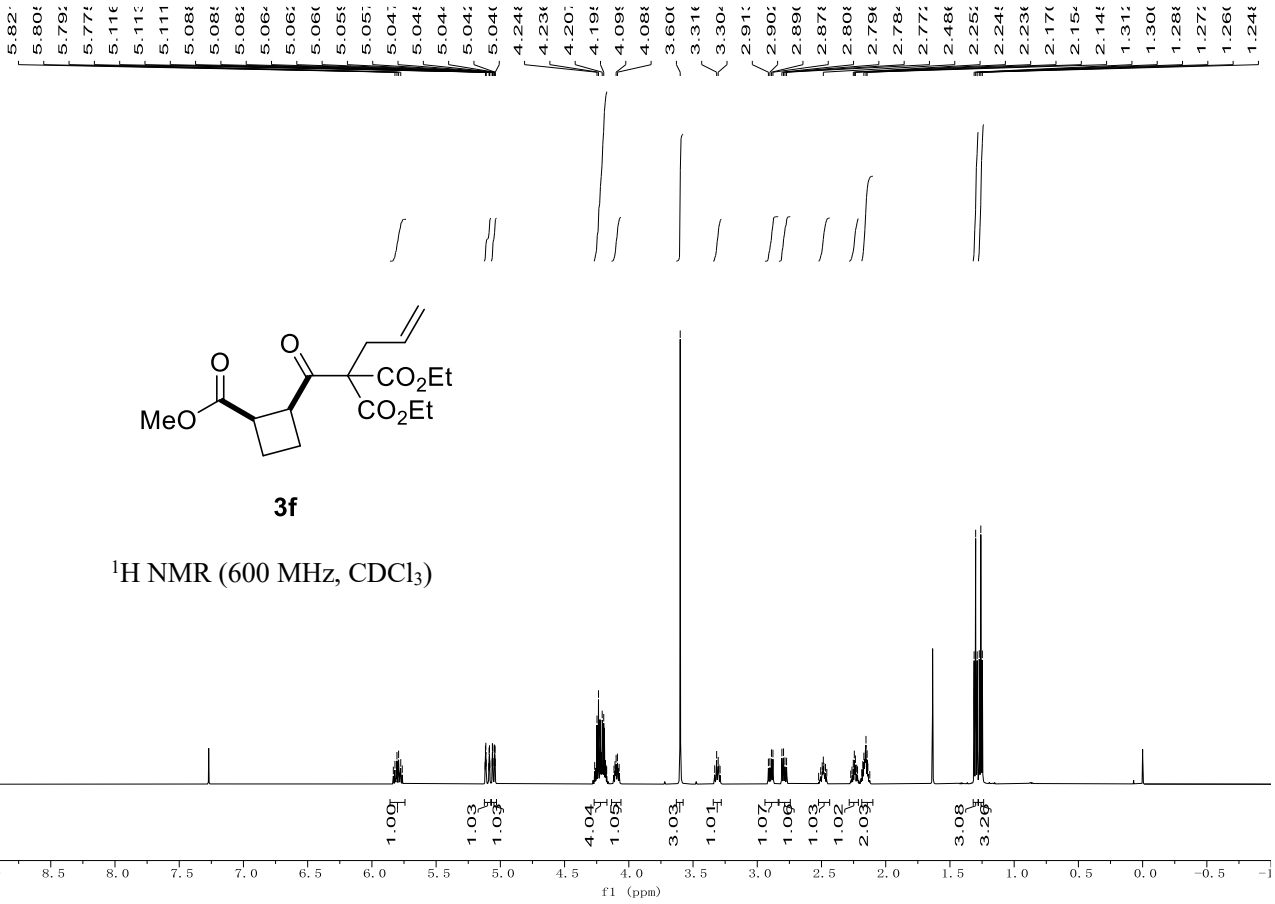
3e

^{1}H NMR (600 MHz, $CDCl_3$)



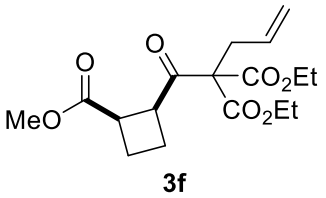
3e

^{13}C NMR (150 MHz, $CDCl_3$)



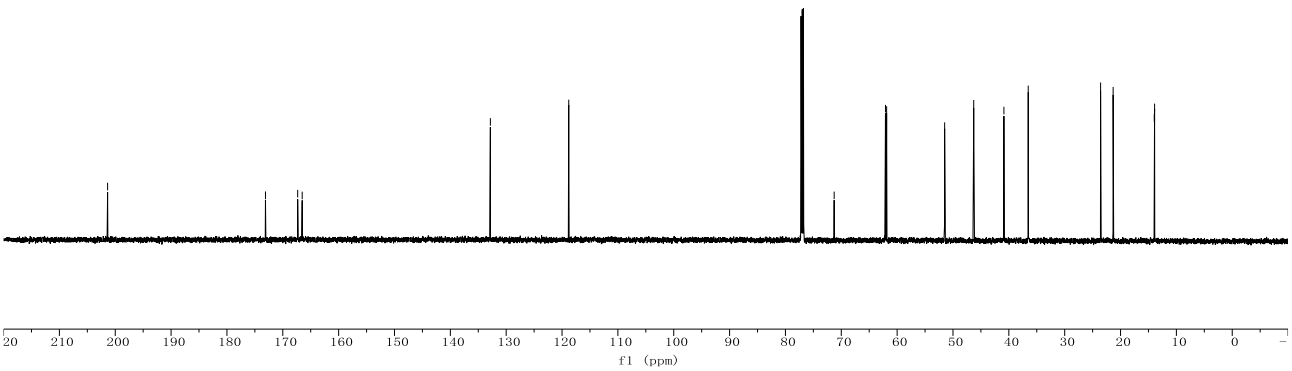
3f

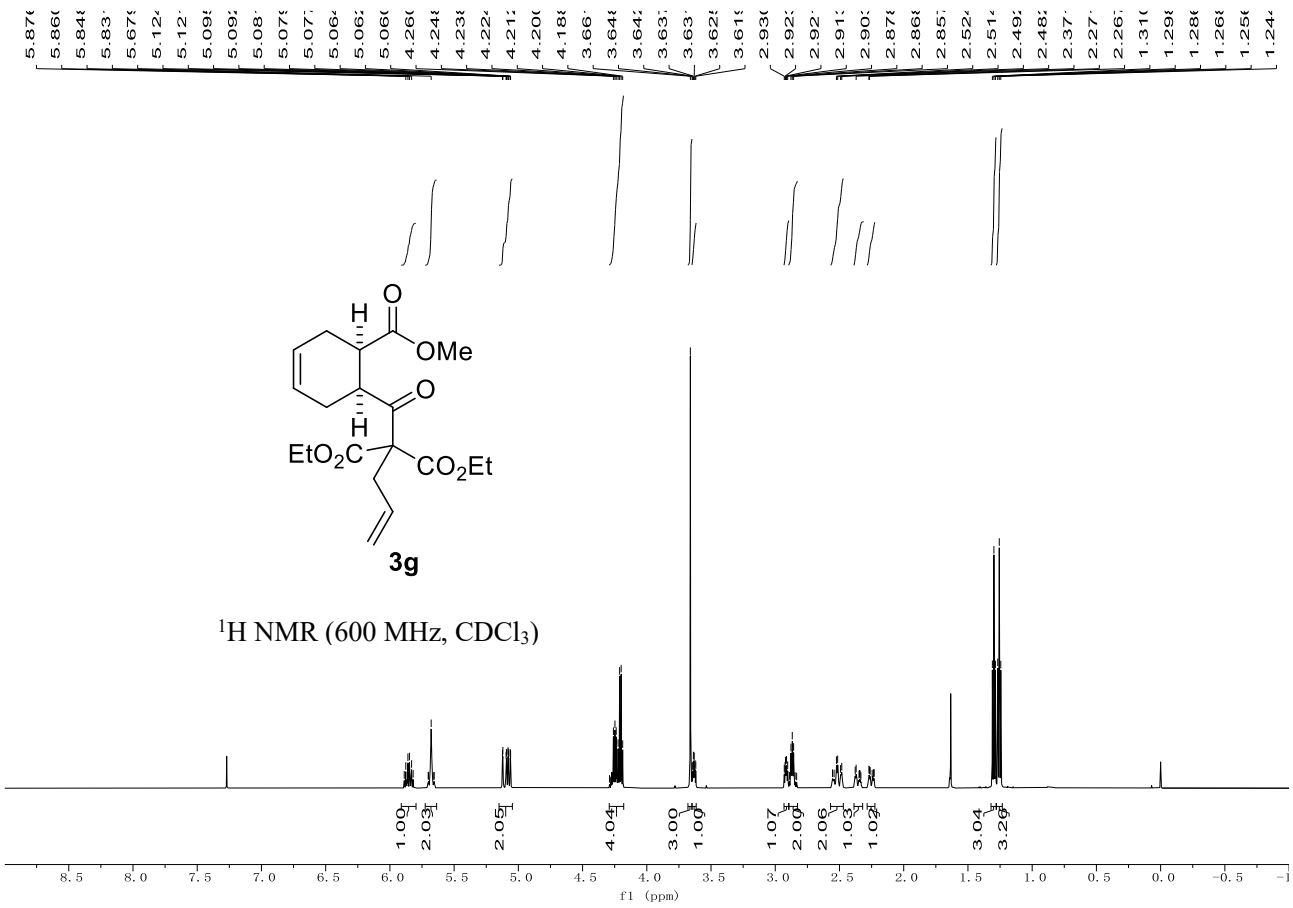
^{1}H NMR (600 MHz, $CDCl_3$)



3f

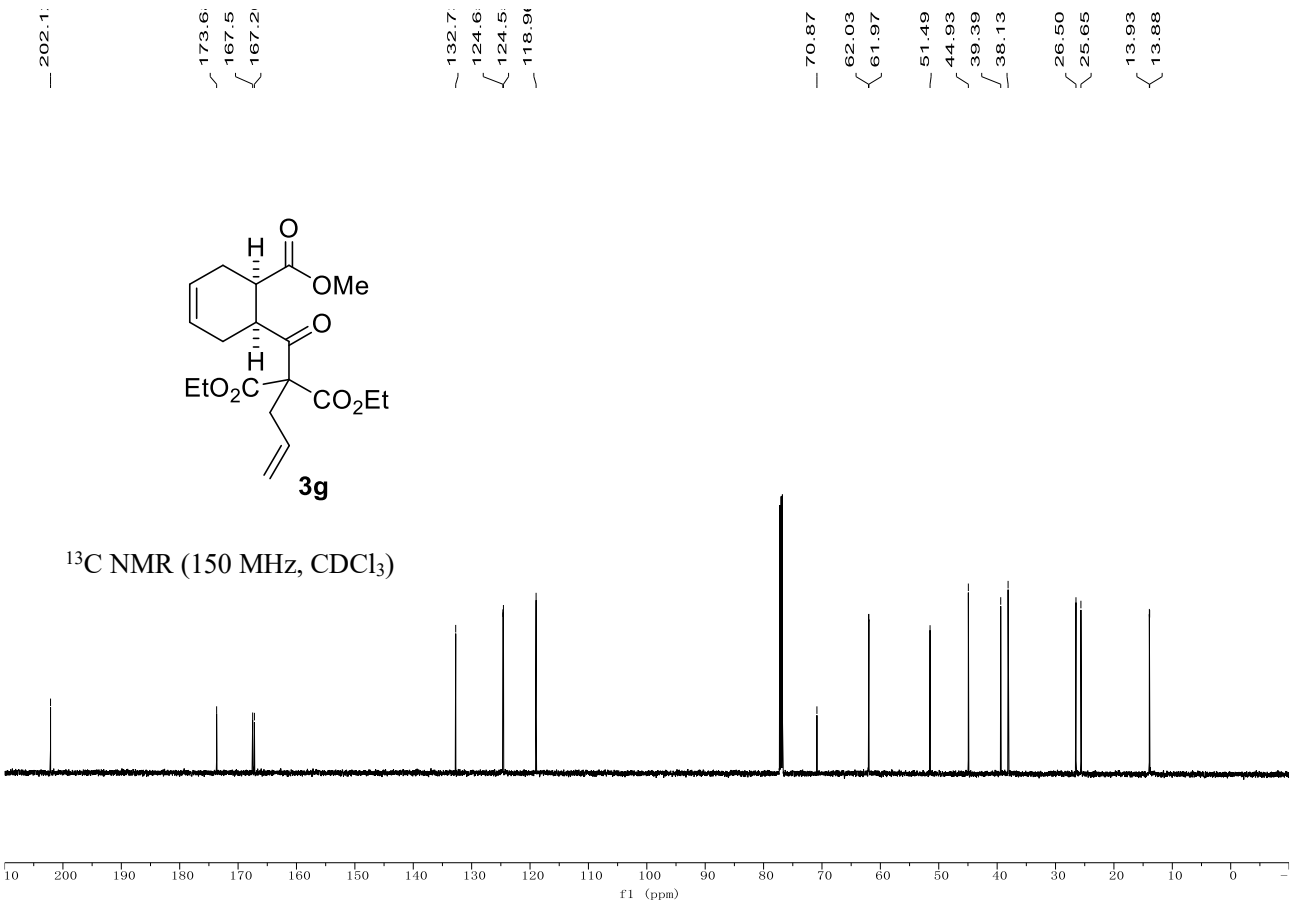
^{13}C NMR (150 MHz, $CDCl_3$)





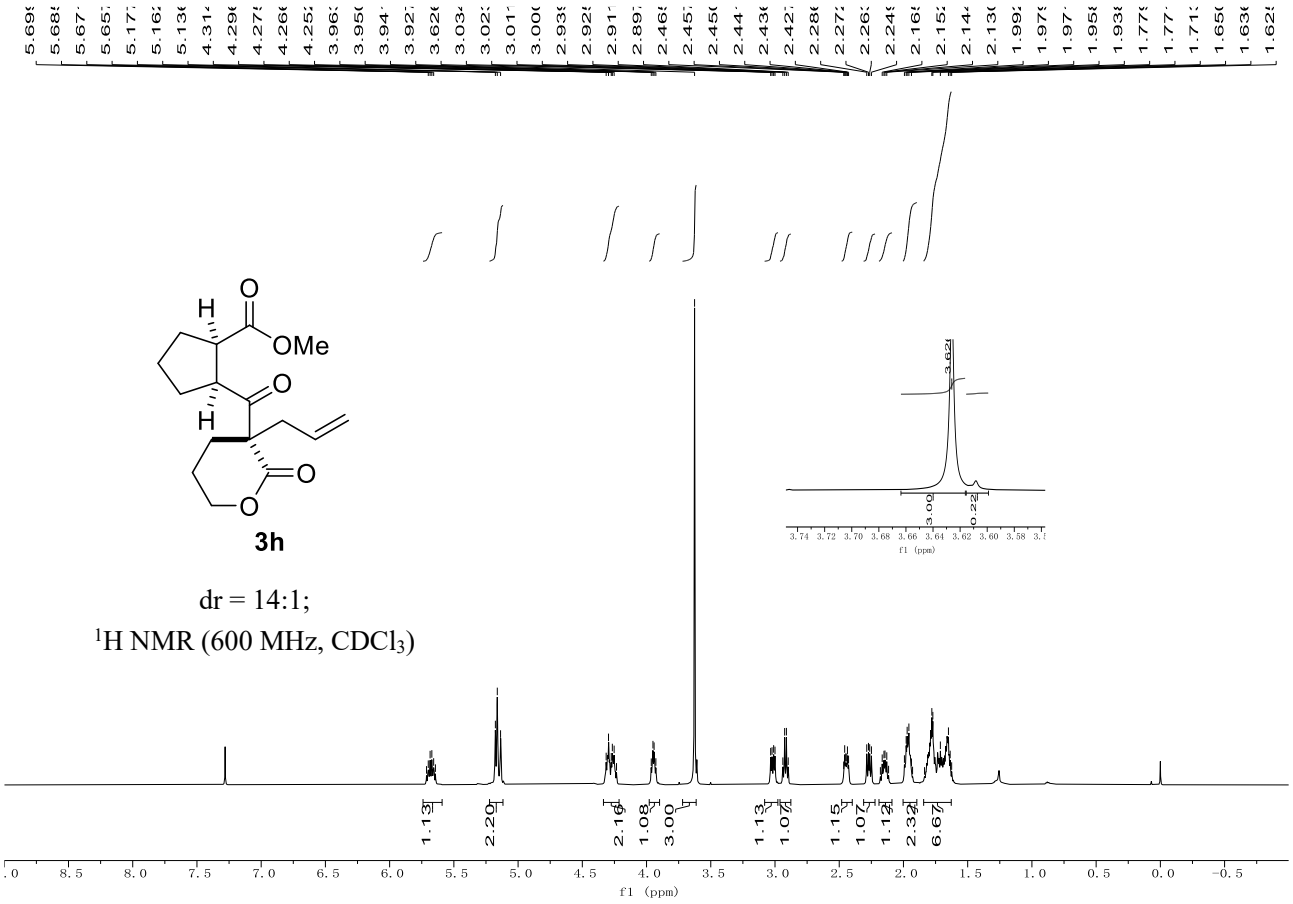
3g

^{1}H NMR (600 MHz, $CDCl_3$)



3g

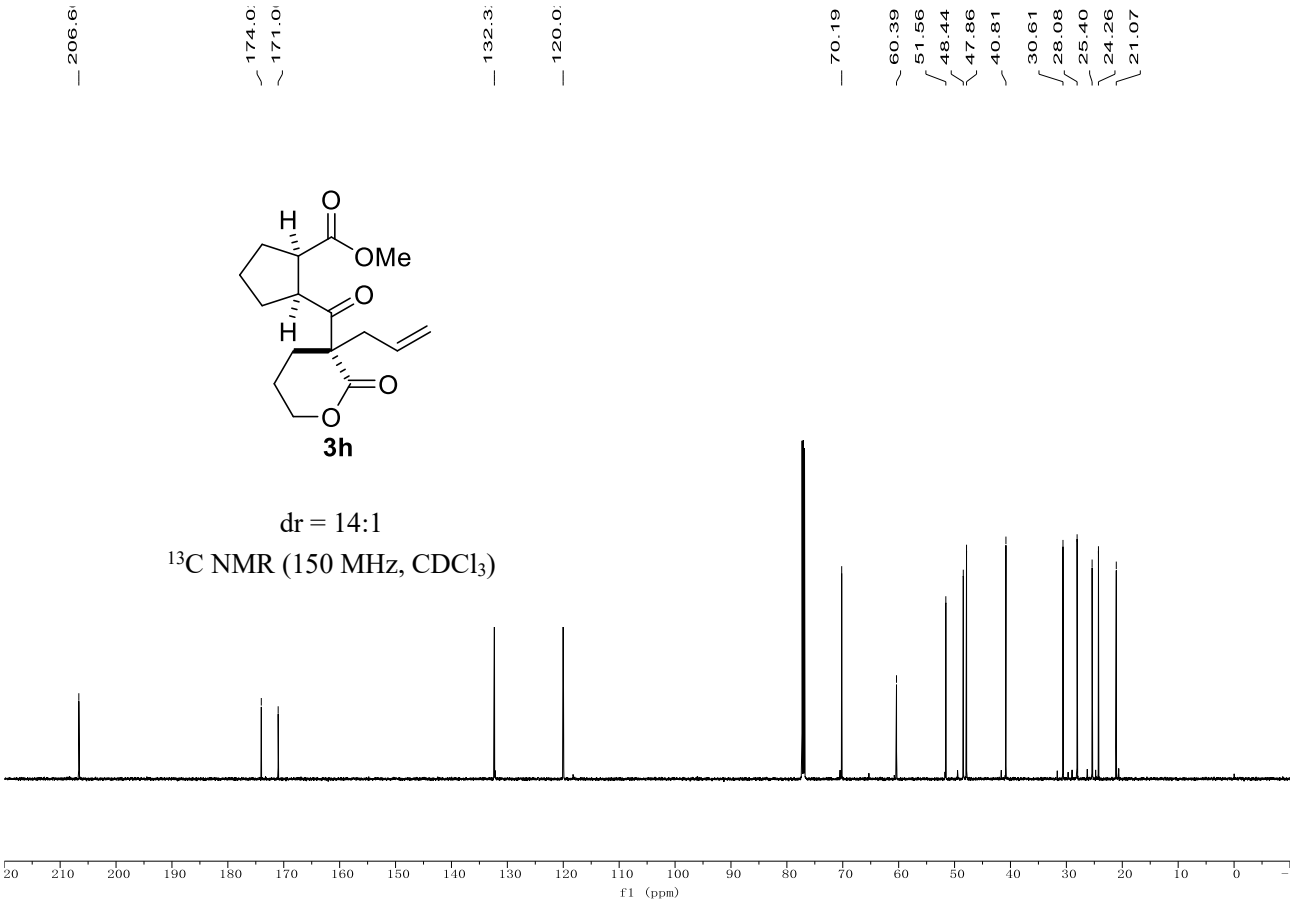
^{13}C NMR (150 MHz, $CDCl_3$)



3h

dr = 14:1;

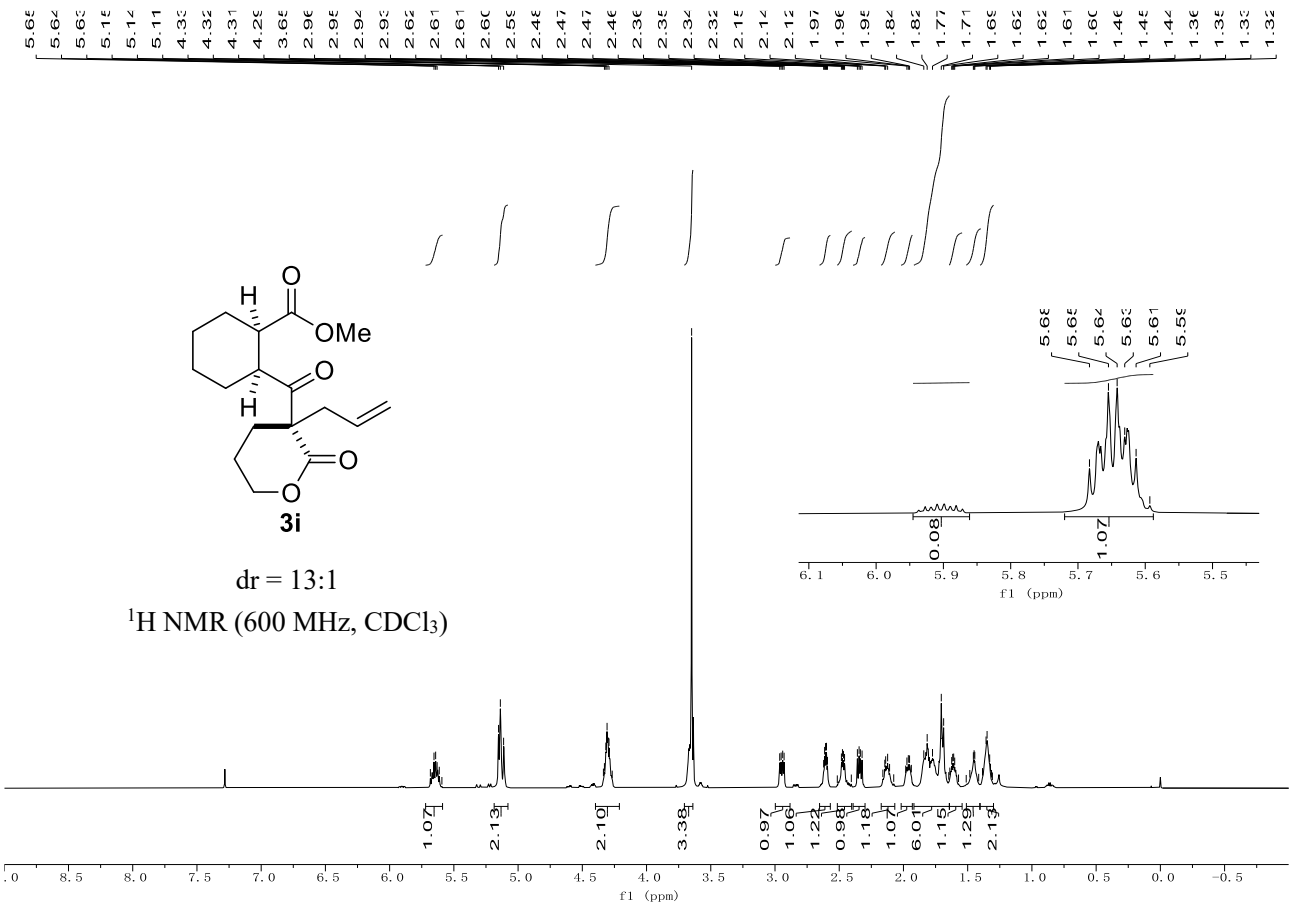
^{1}H NMR (600 MHz, $CDCl_3$)



3h

dr = 14:1

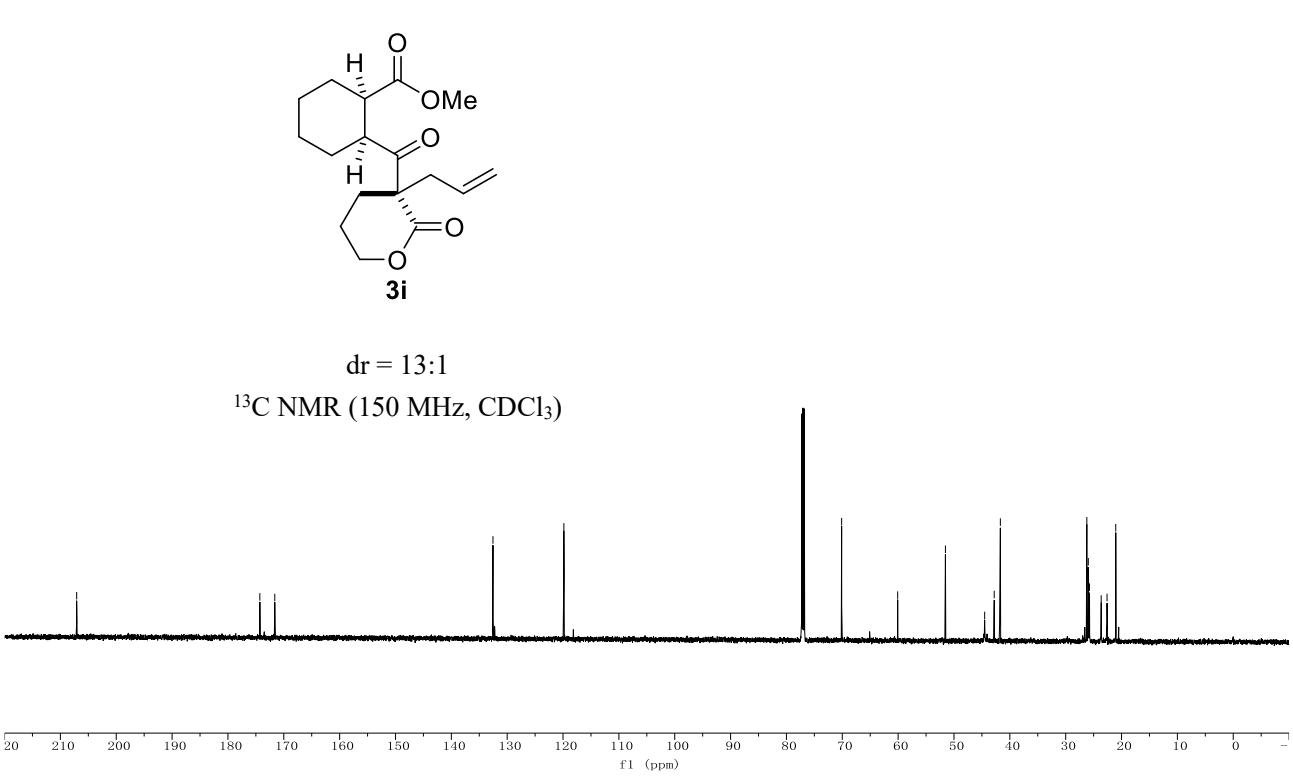
^{13}C NMR (150 MHz, $CDCl_3$)



3i

dr = 13:1

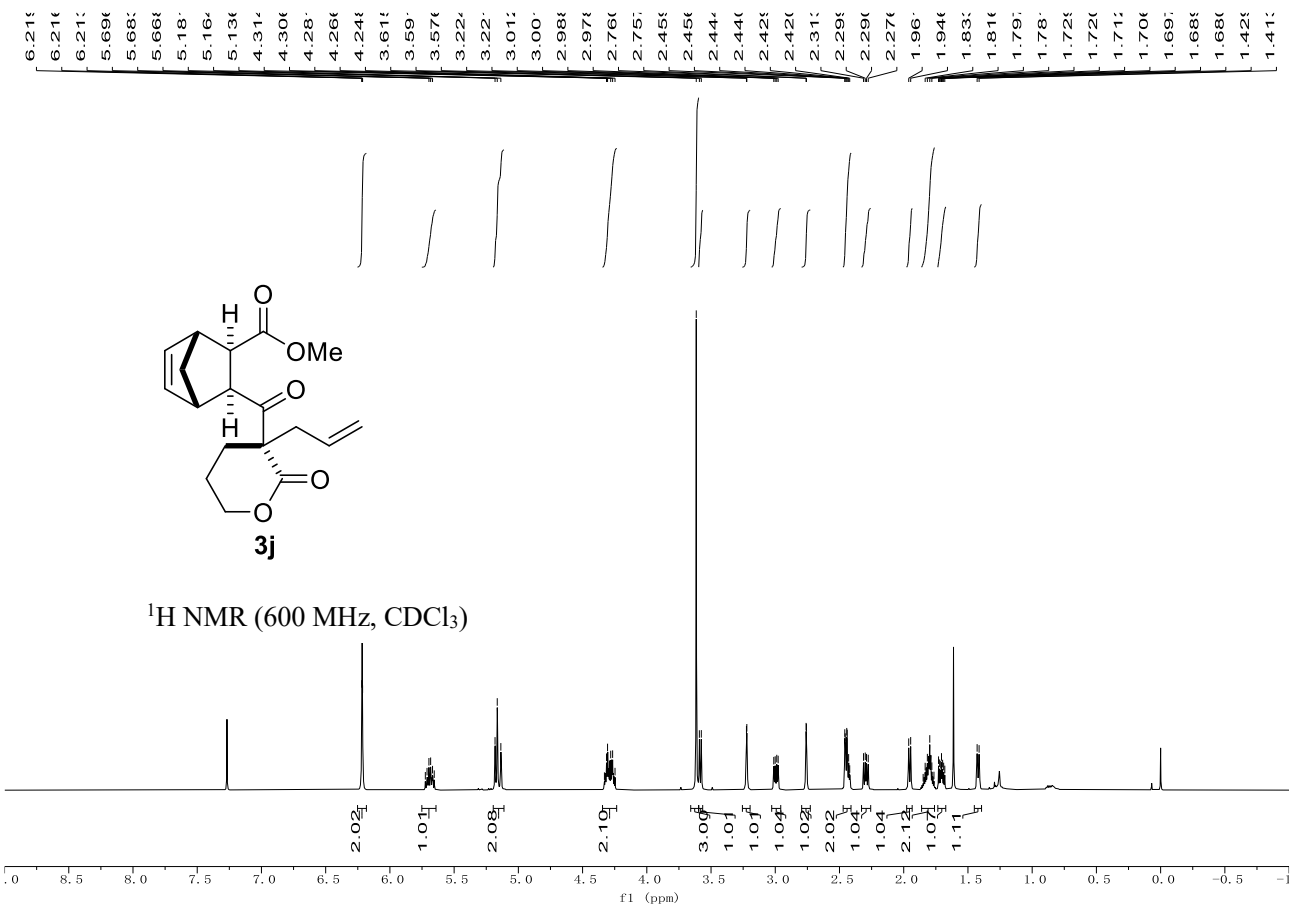
^{1}H NMR (600 MHz, $CDCl_3$)



3i

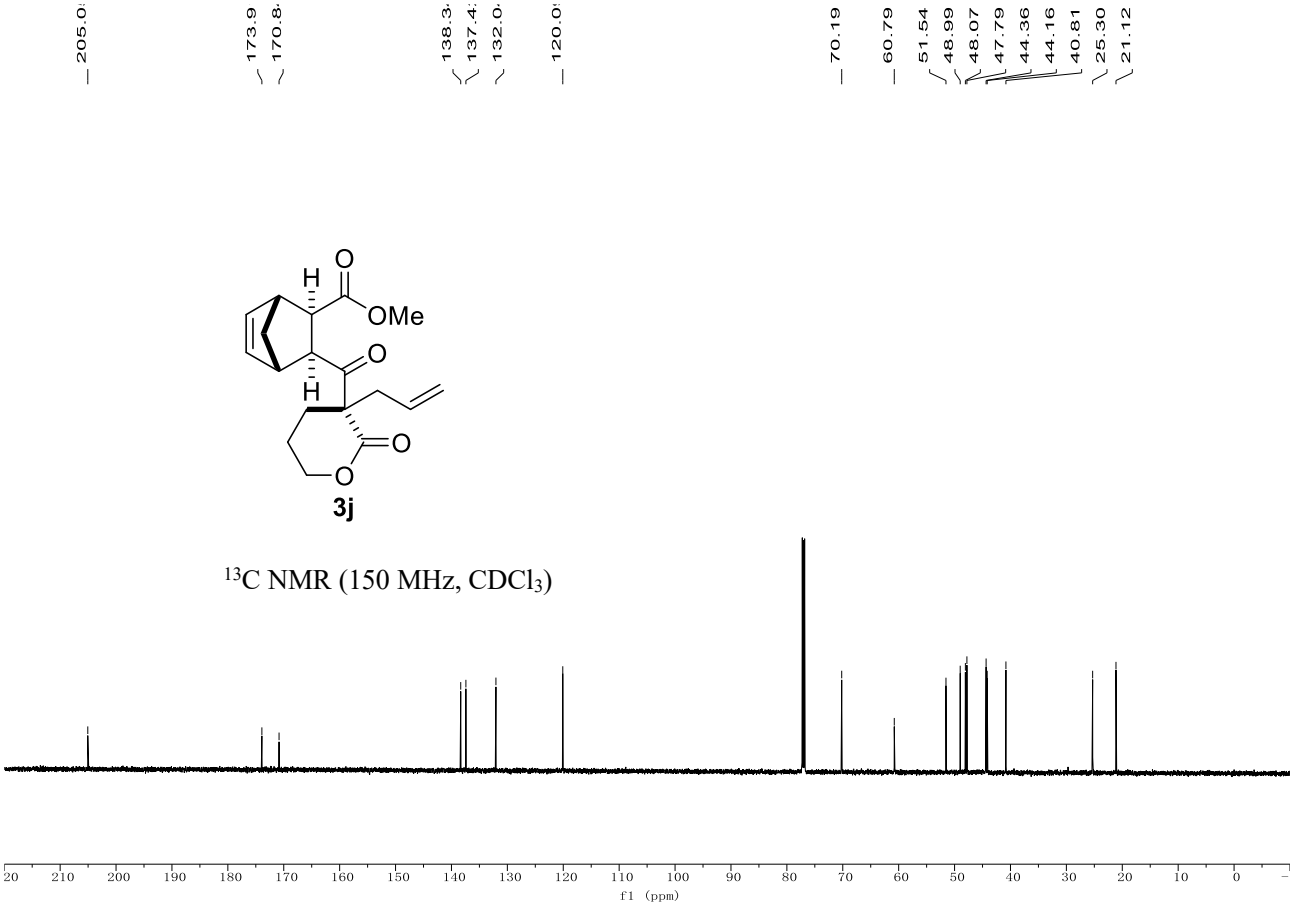
dr = 13:1

^{13}C NMR (150 MHz, $CDCl_3$)



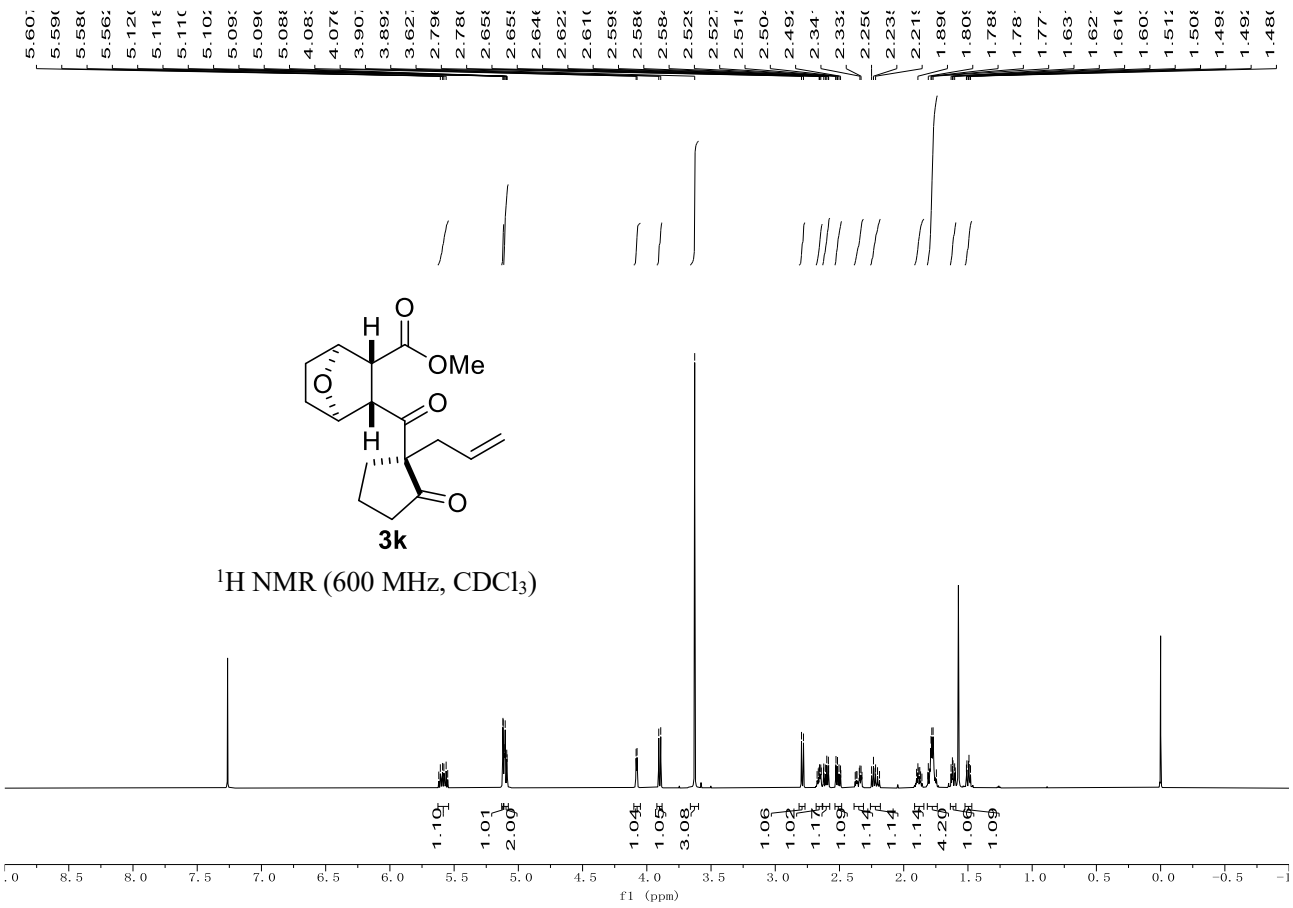
3j

^{1}H NMR (600 MHz, $CDCl_3$)



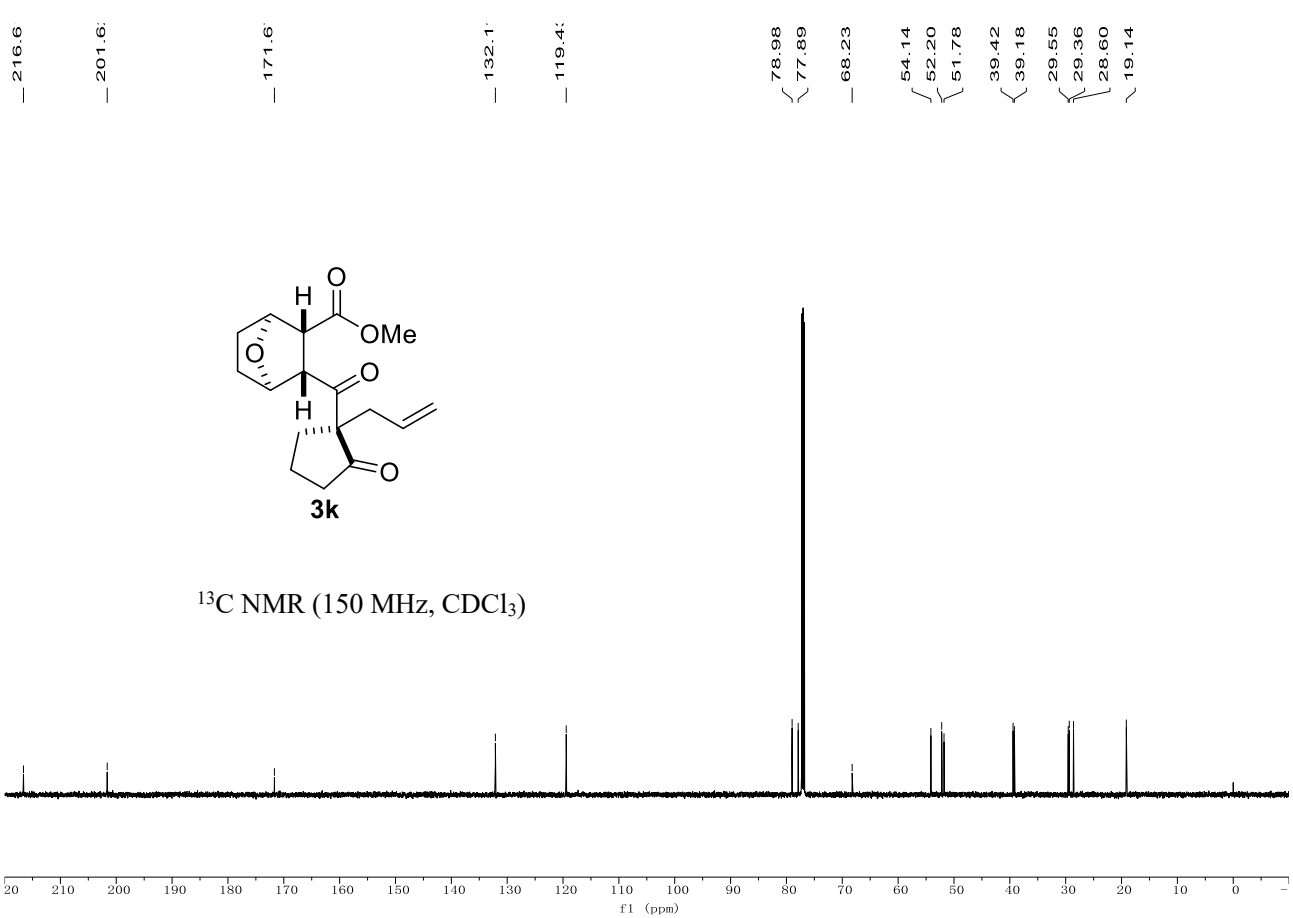
3j

^{13}C NMR (150 MHz, $CDCl_3$)



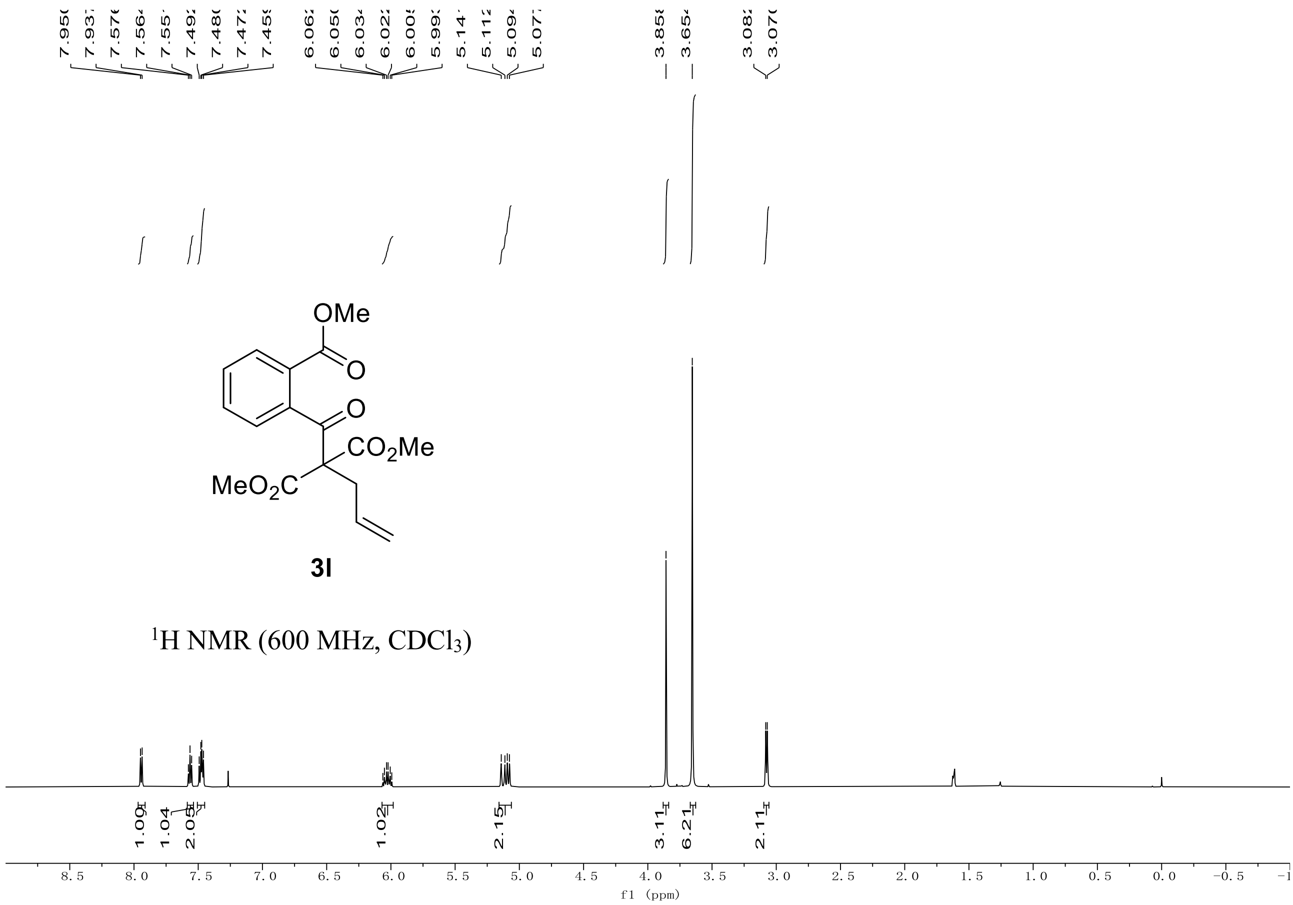
3k

^{1}H NMR (600 MHz, $CDCl_3$)

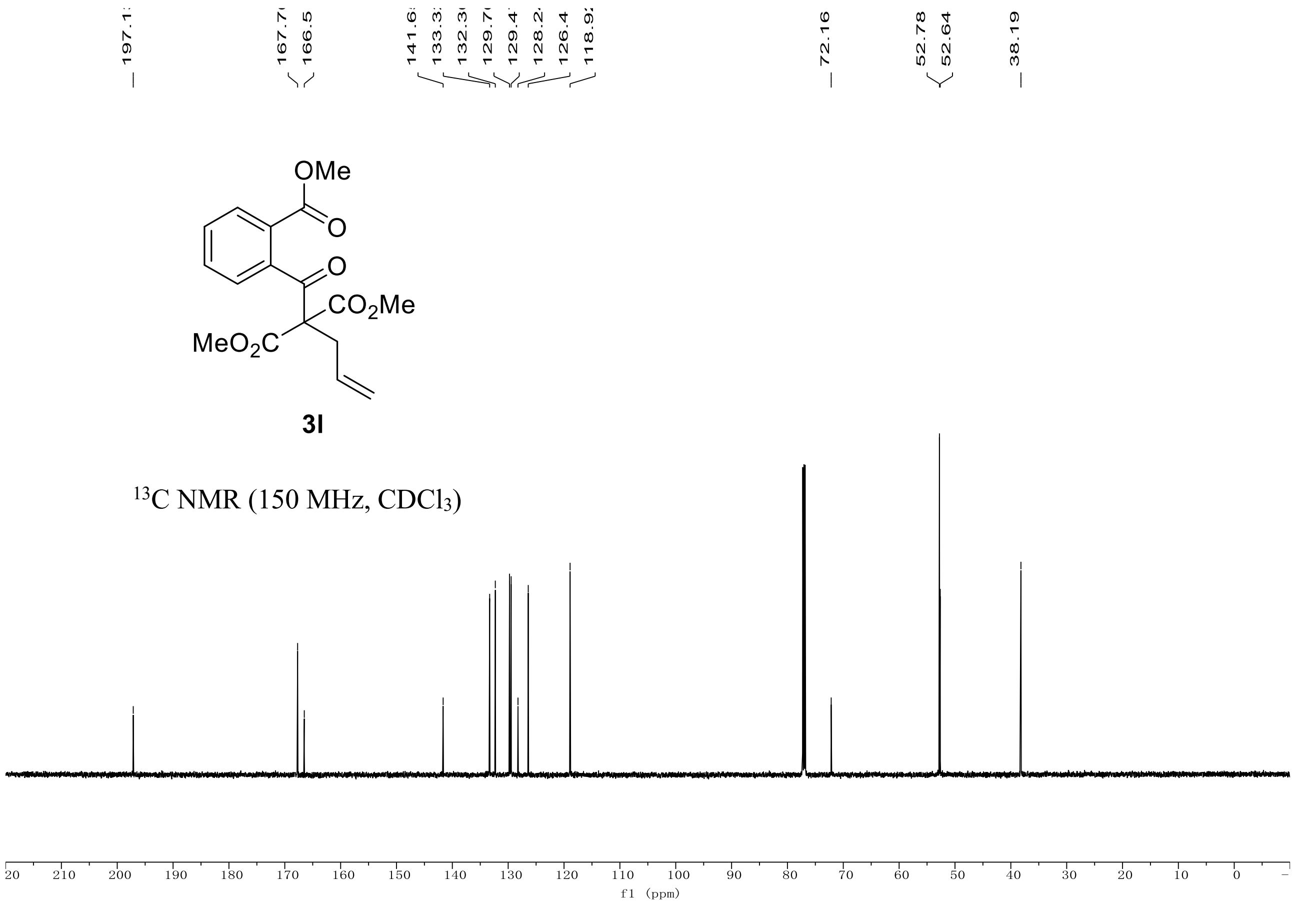


3k

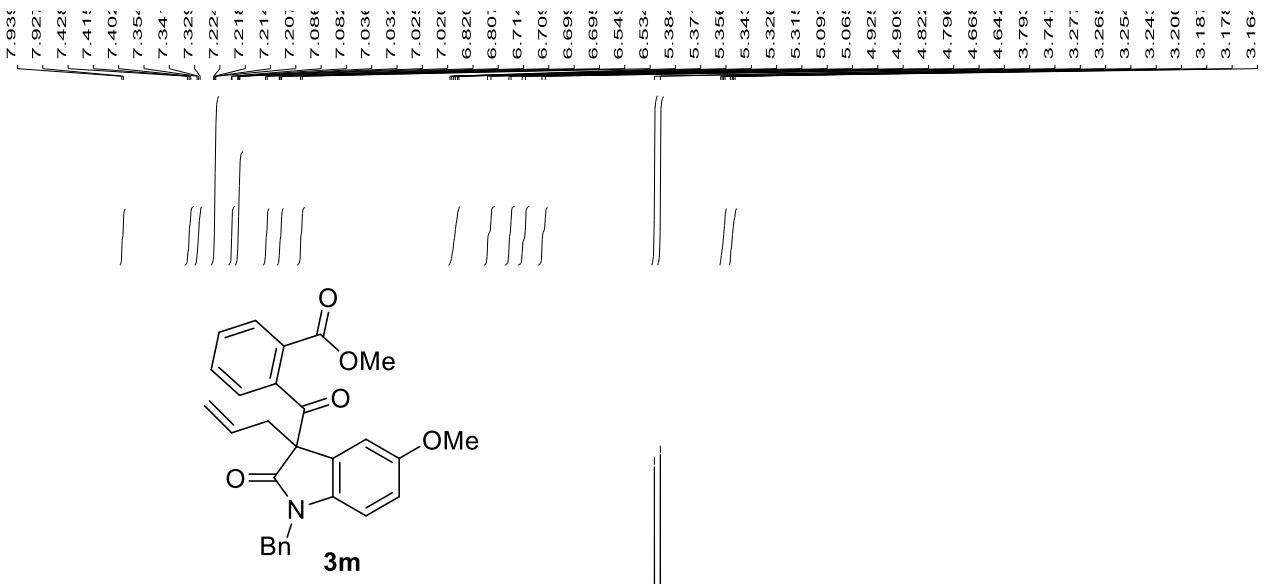
^{13}C NMR (150 MHz, $CDCl_3$)



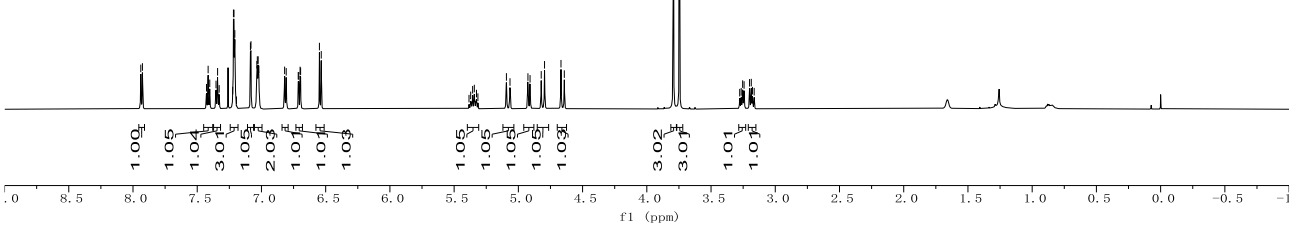
OMe
O
O
CO_2Me
MeO_2C
3l
^{1}H NMR (600 MHz, $CDCl_3$)
f1 (ppm)

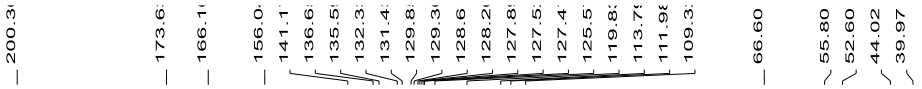


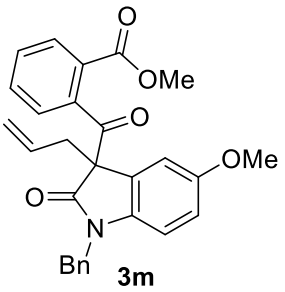
197.1
167.7
166.5
141.6
133.3
132.3
129.7
129.4
128.2
126.4
118.9
72.16
52.78
52.64
38.19
OMe
O
O
CO_2Me
MeO_2C
3l
^{13}C NMR (150 MHz, $CDCl_3$)
f1 (ppm)



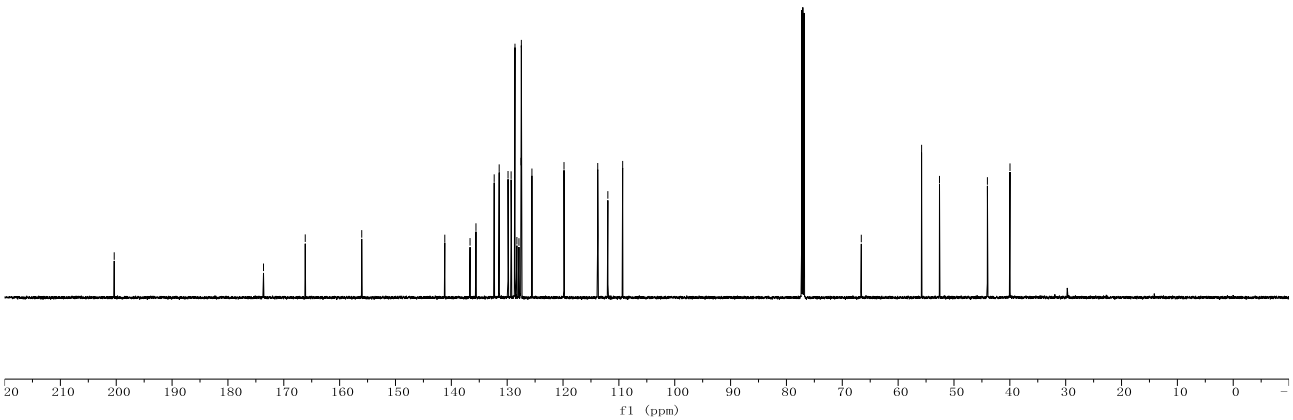
^{1}H NMR (600 MHz, $CDCl_3$)

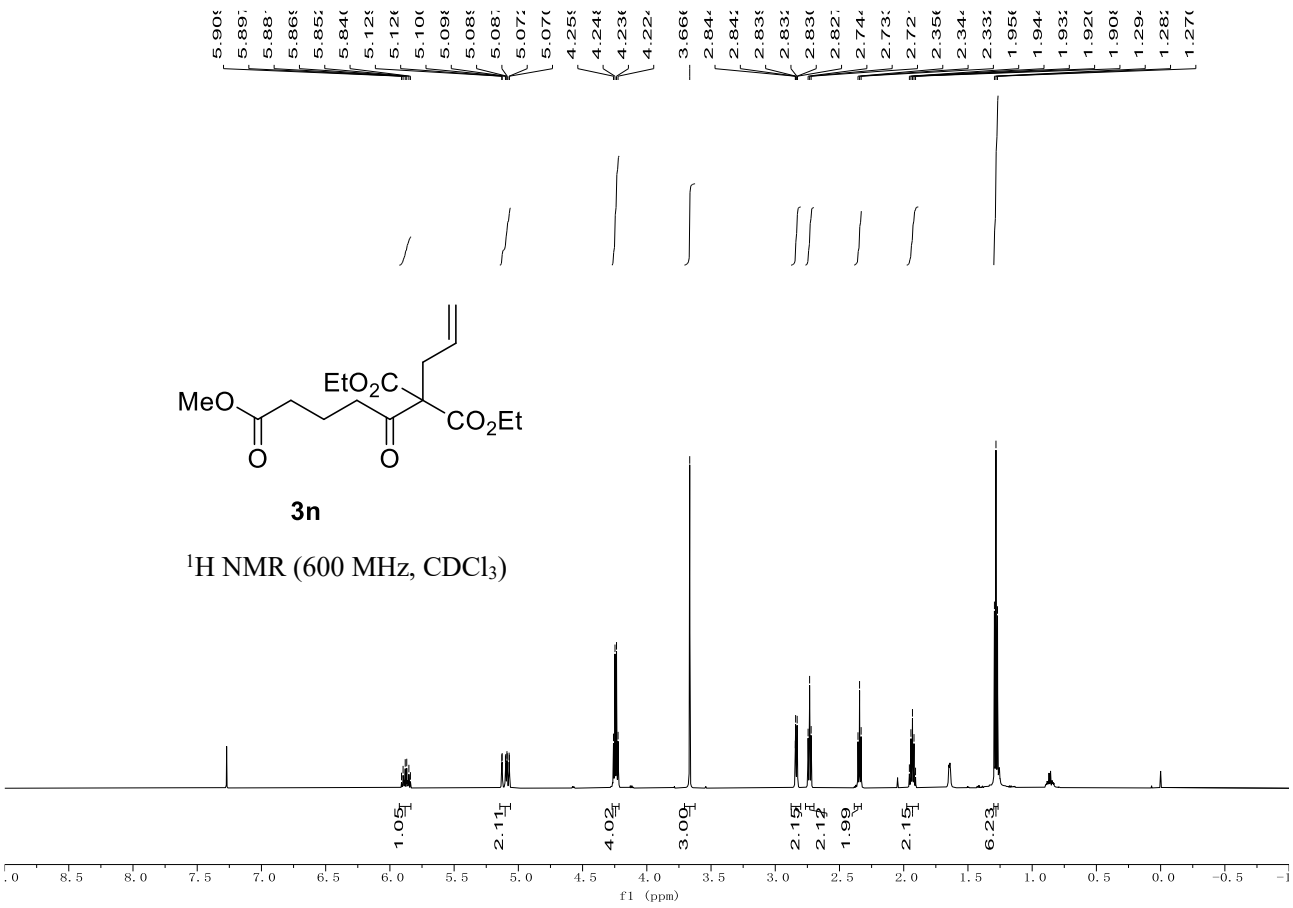






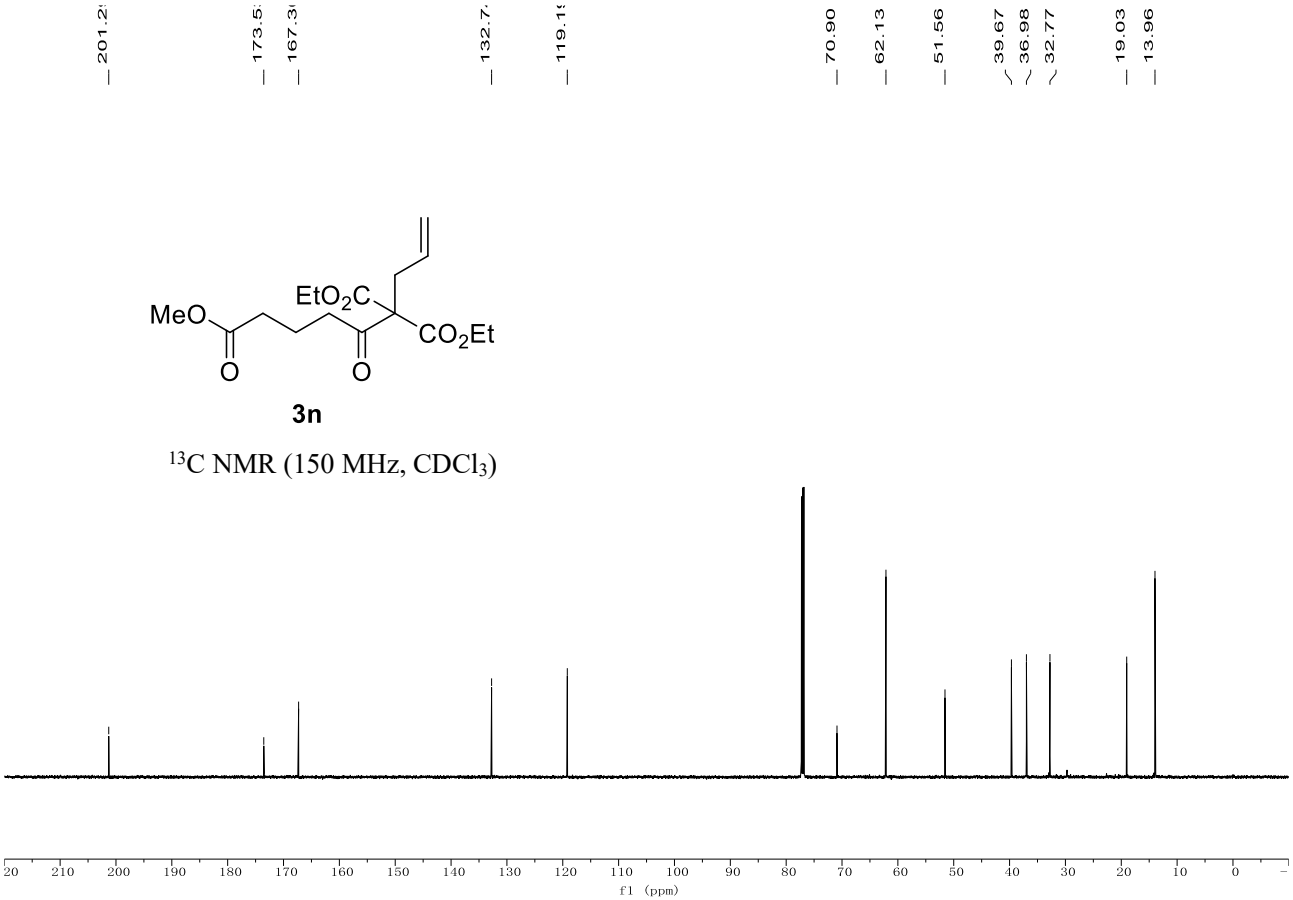
^{13}C NMR (150 MHz, $CDCl_3$)





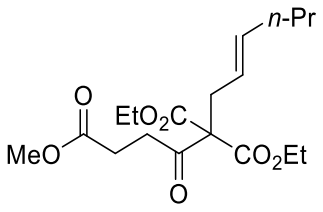
3n

^{1}H NMR (600 MHz, $CDCl_3$)



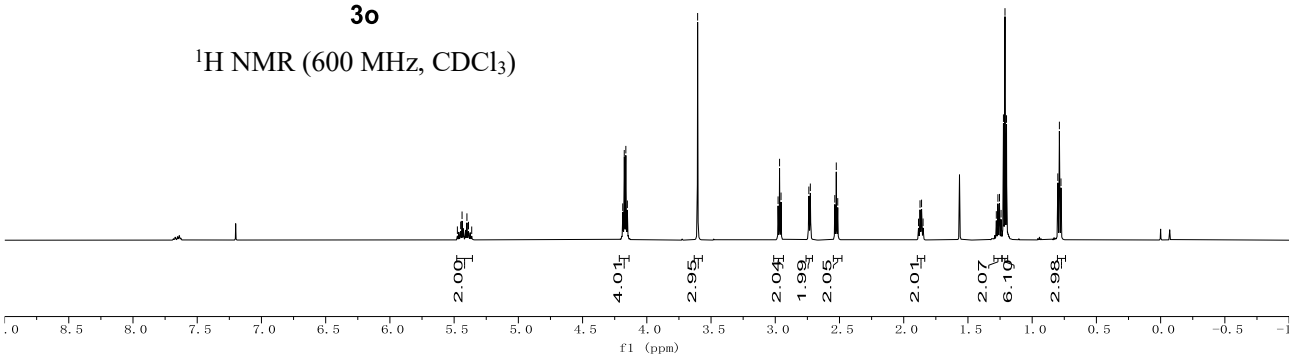
3n

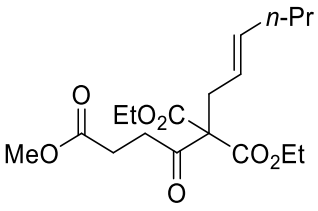
^{13}C NMR (150 MHz, $CDCl_3$)



3o

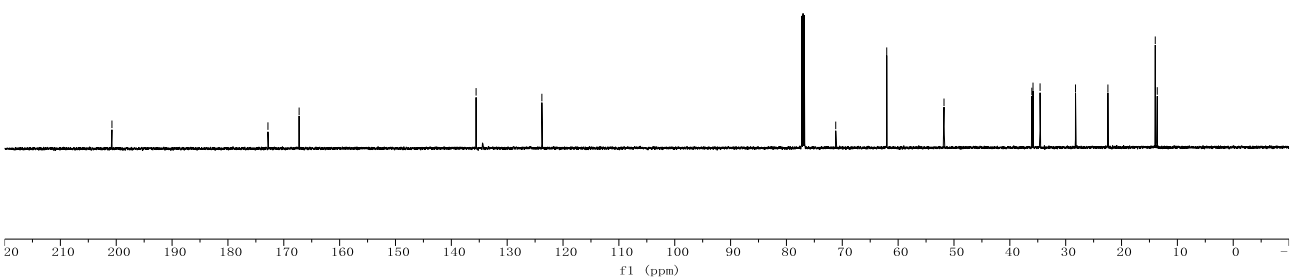
^{1}H NMR (600 MHz, $CDCl_3$)

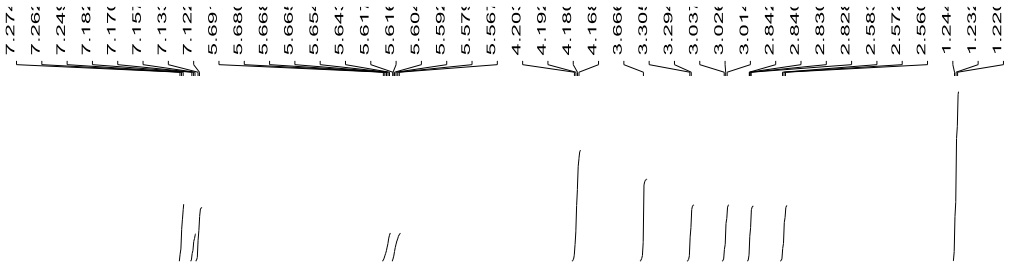


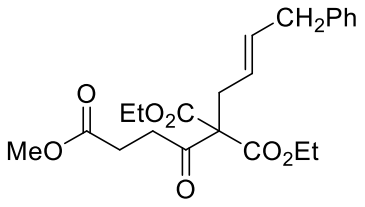


3o

^{13}C NMR (150 MHz, $CDCl_3$)

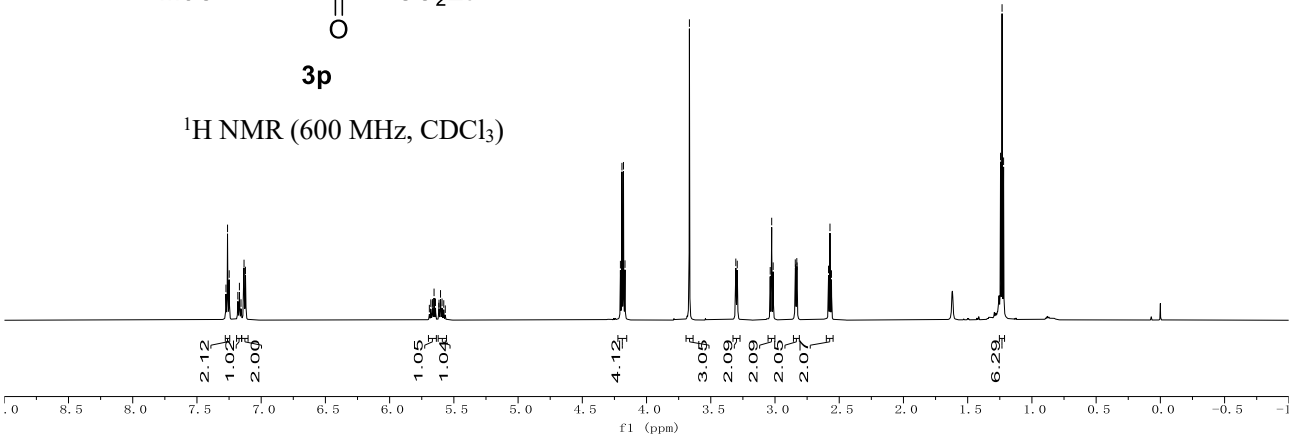


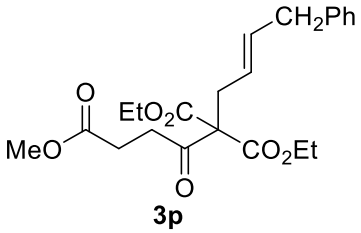




3p

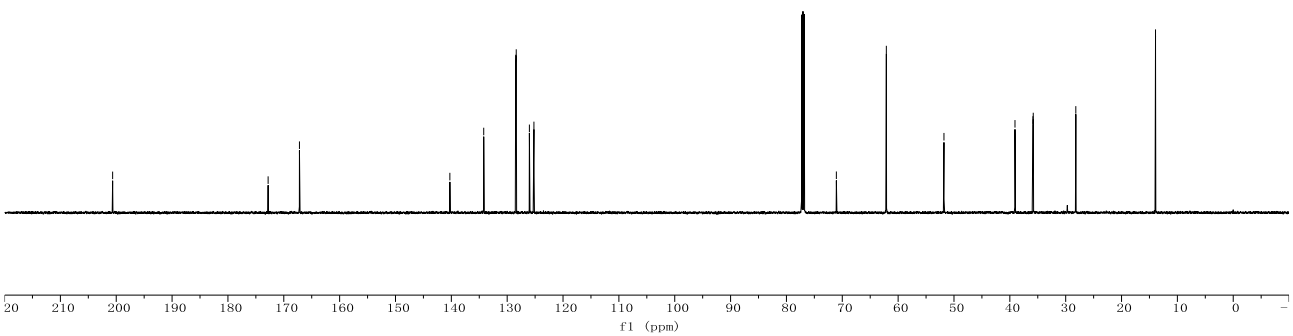
^{1}H NMR (600 MHz, $CDCl_3$)

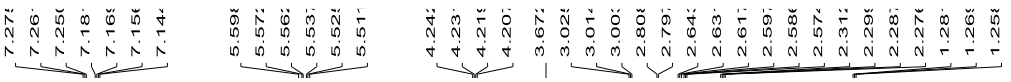


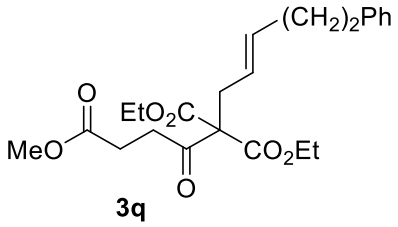


3p

^{13}C NMR (150 MHz, $CDCl_3$)

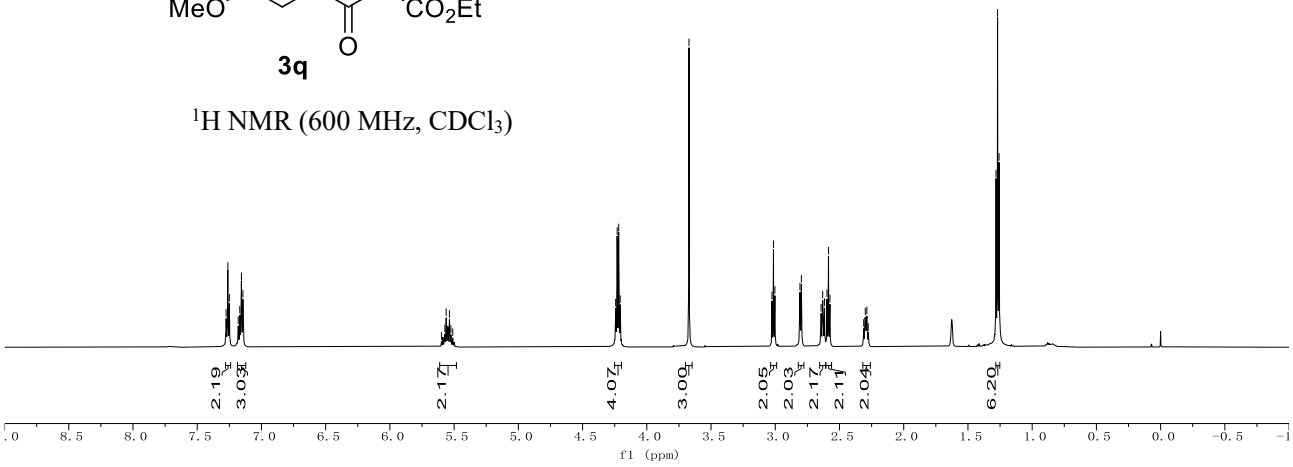


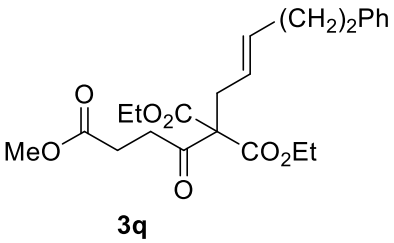




3q

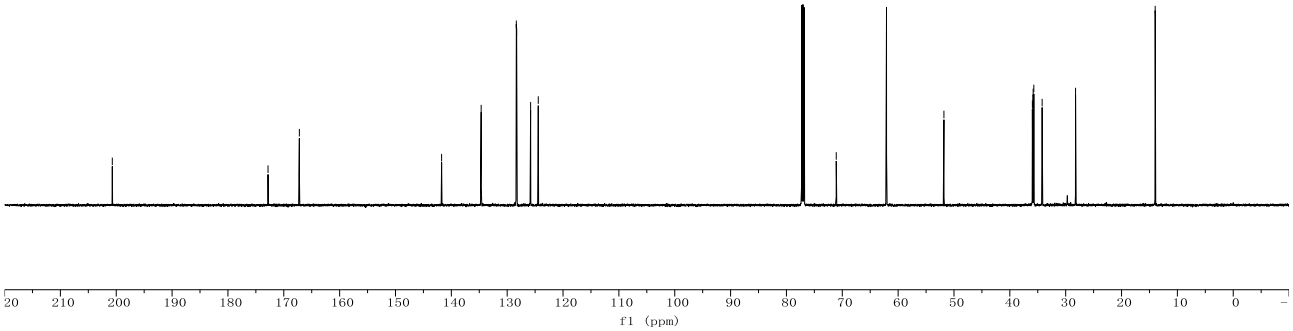
^{1}H NMR (600 MHz, $CDCl_3$)

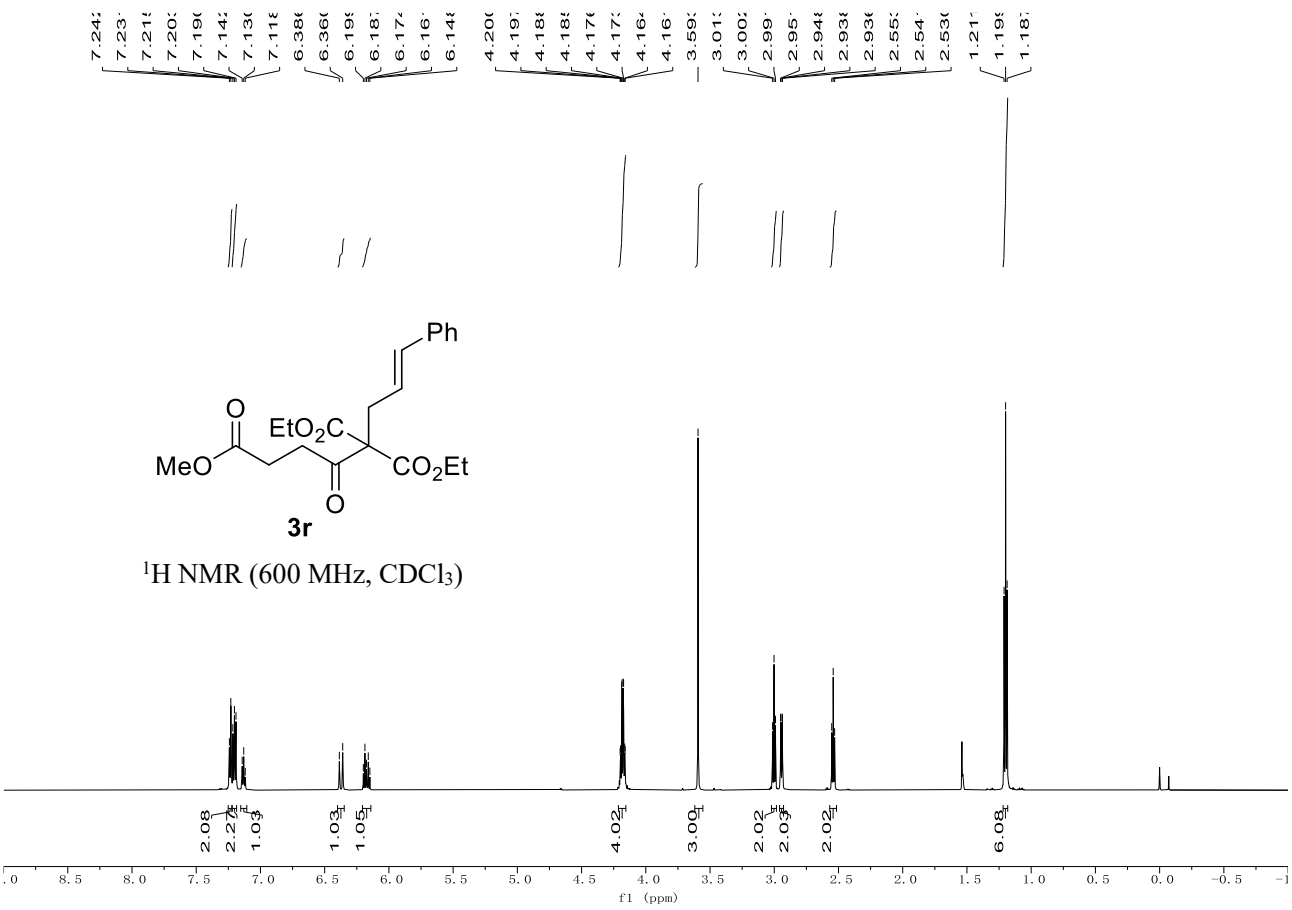




3q

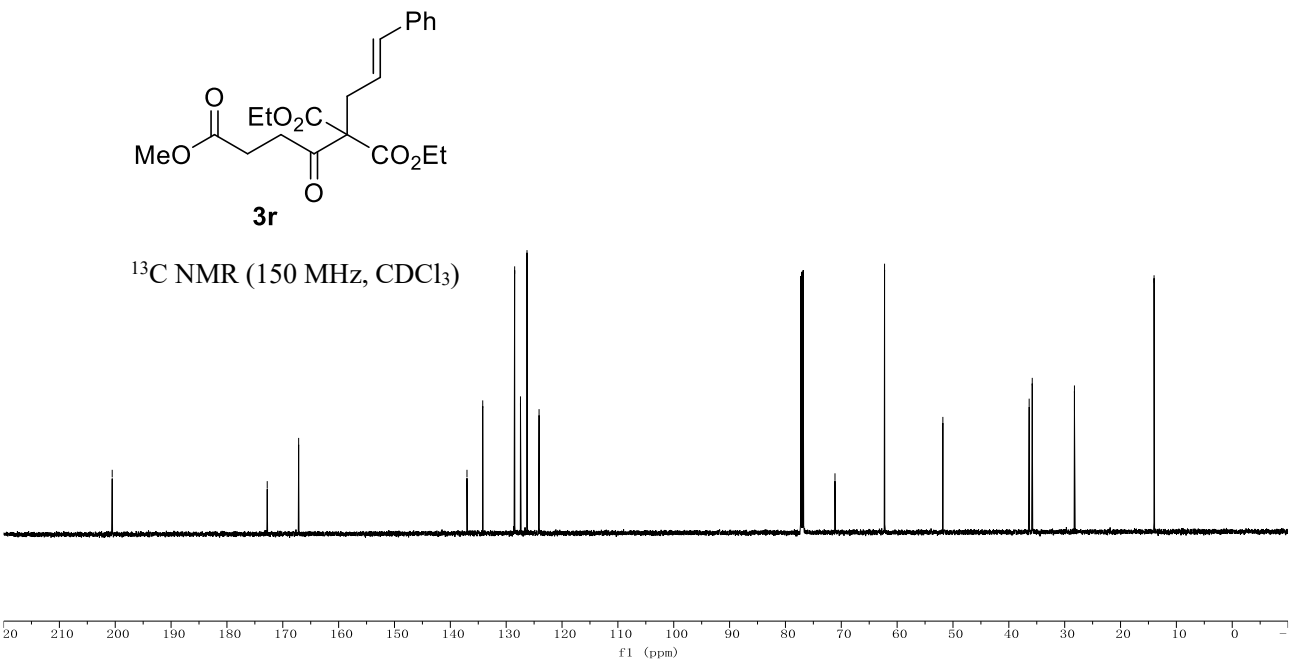
^{13}C NMR (150 MHz, $CDCl_3$)





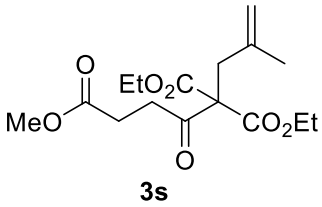
3r

^{1}H NMR (600 MHz, $CDCl_3$)



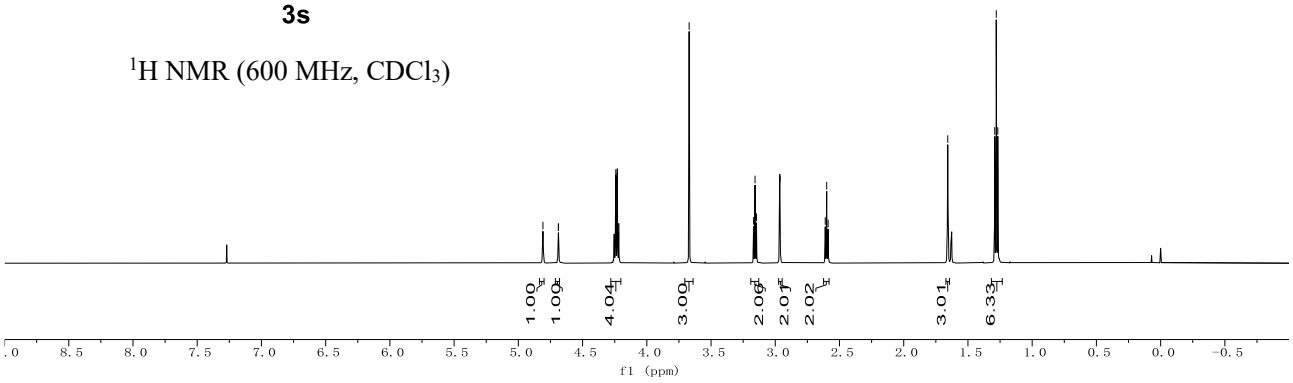
3r

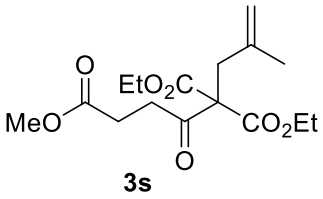
^{13}C NMR (150 MHz, $CDCl_3$)



3s

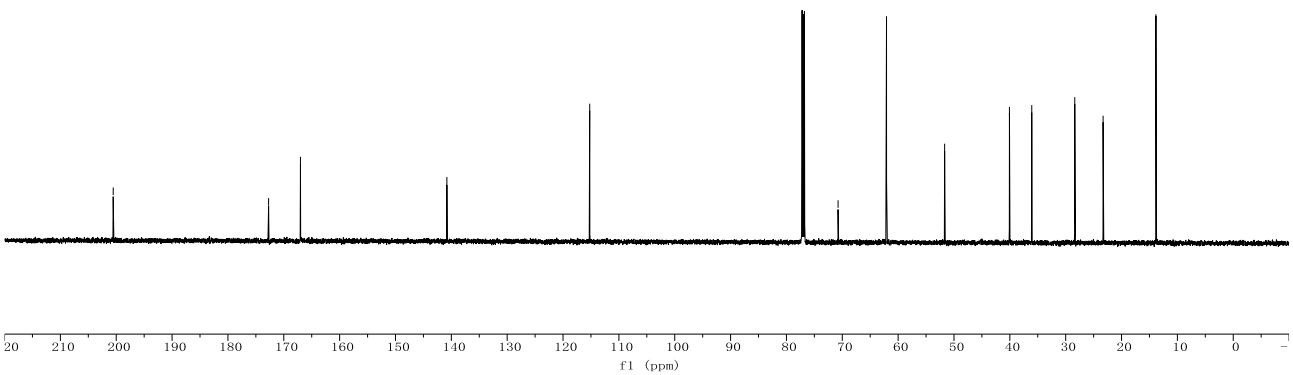
^{1}H NMR (600 MHz, $CDCl_3$)

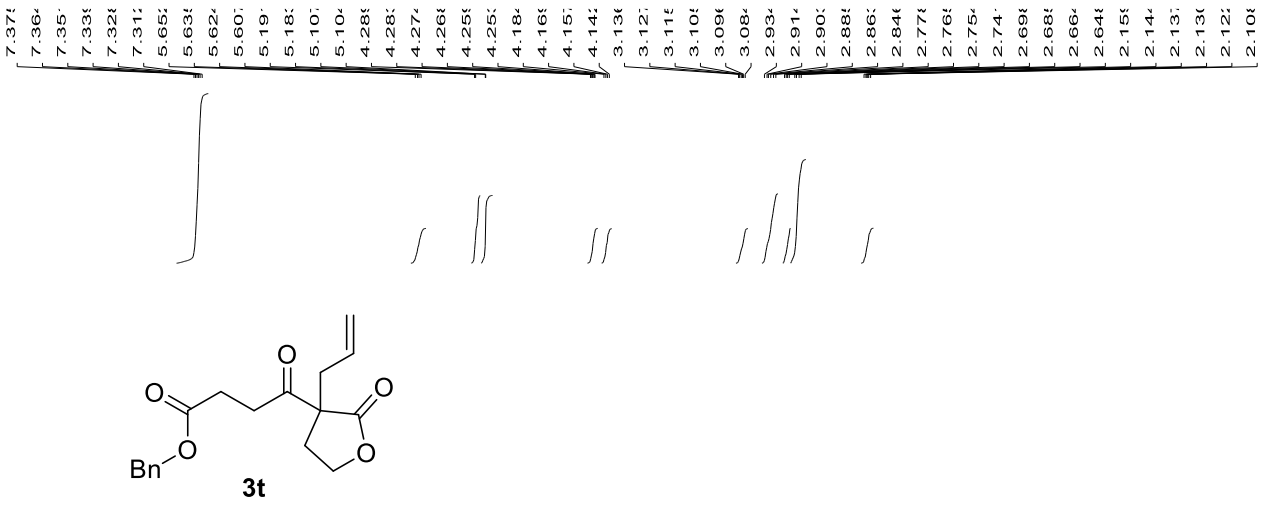




3s

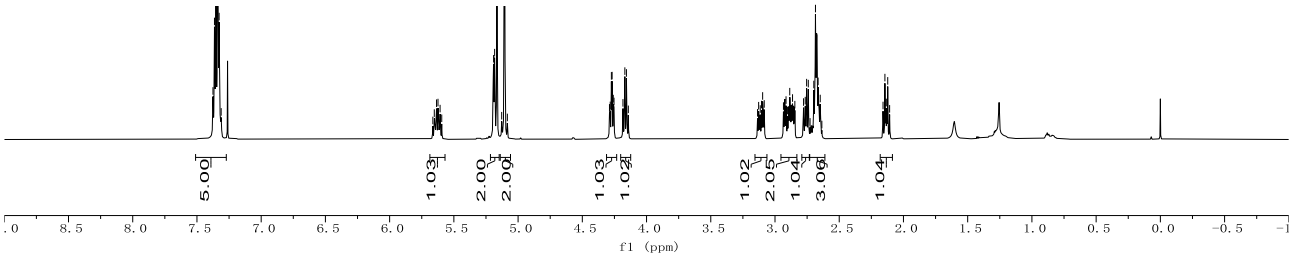
^{13}C NMR (150 MHz, $CDCl_3$)

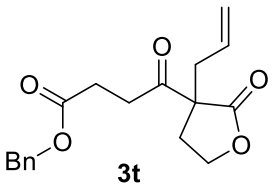




3t

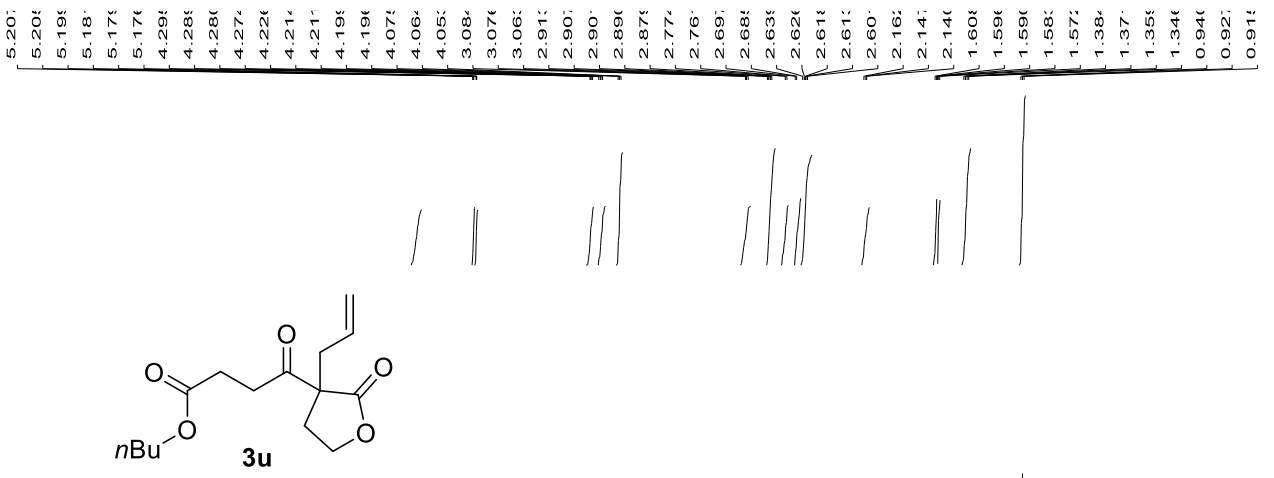
^{1}H NMR (600 MHz, $CDCl_3$)



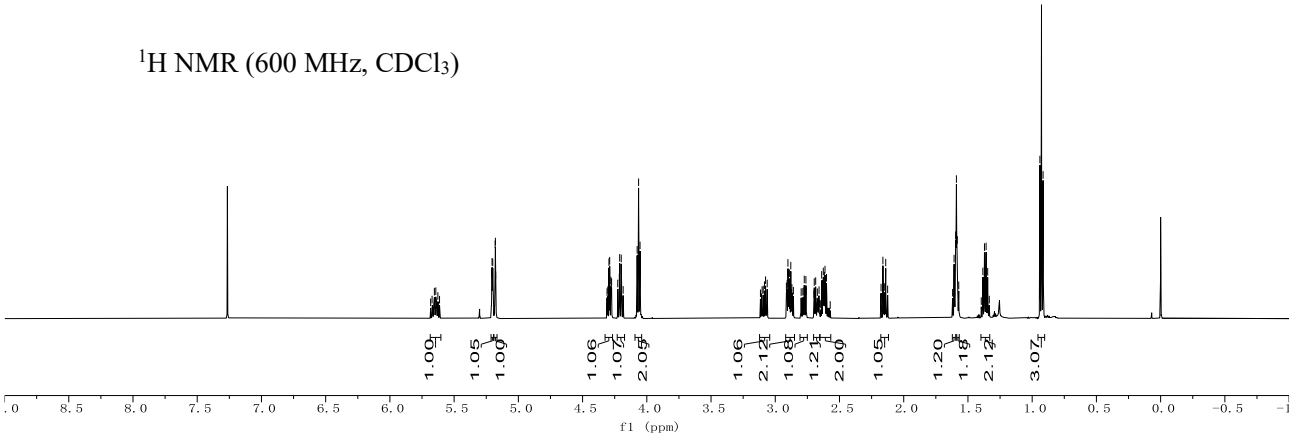


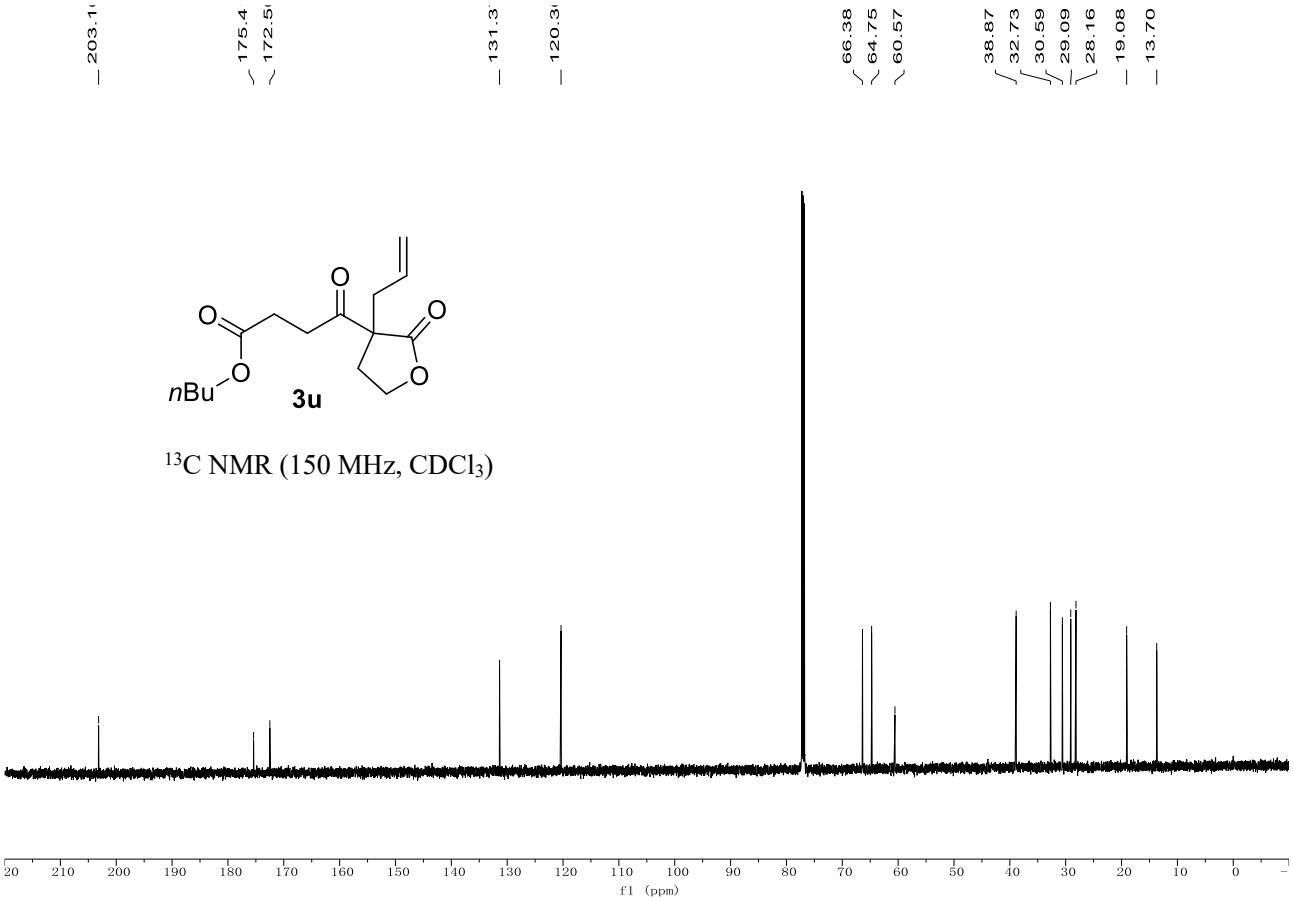
3t

^{13}C NMR (150 MHz, $CDCl_3$)

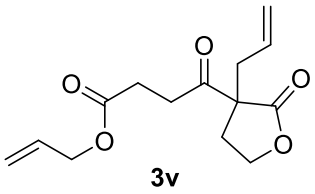


^{1}H NMR (600 MHz, $CDCl_3$)



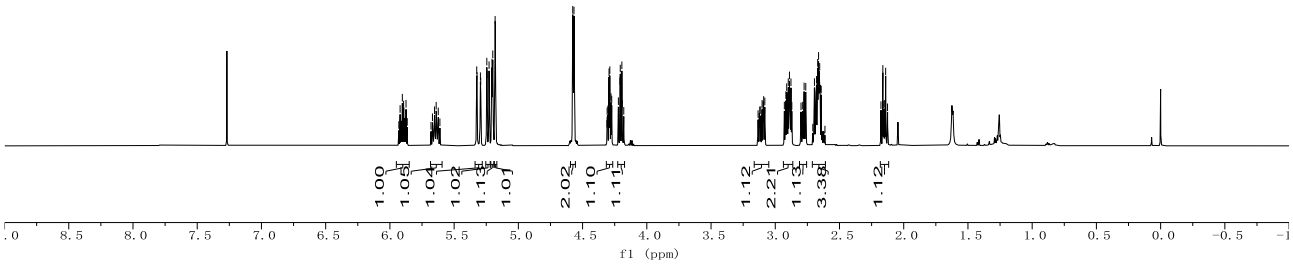


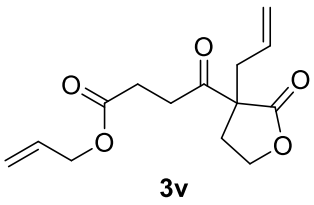
^{13}C NMR (150 MHz, $CDCl_3$)



3v

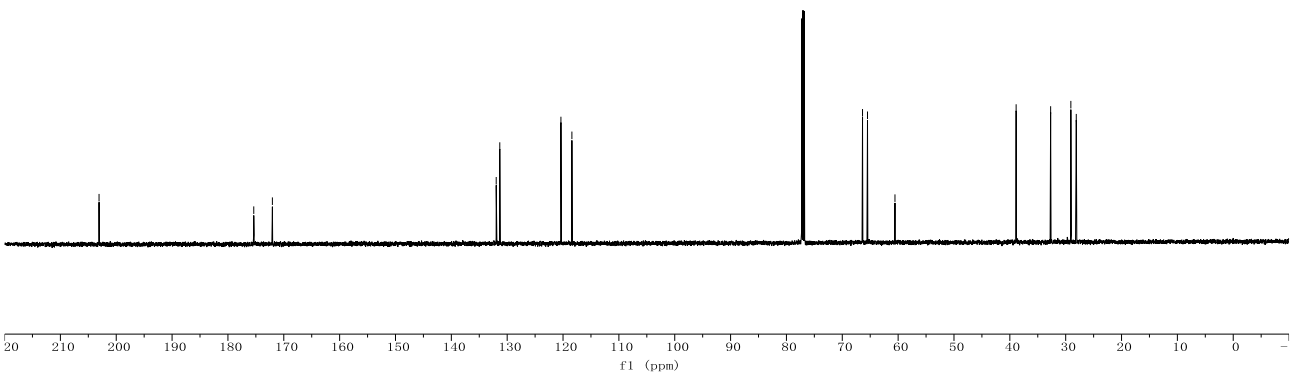
^{1}H NMR (600 MHz, $CDCl_3$)

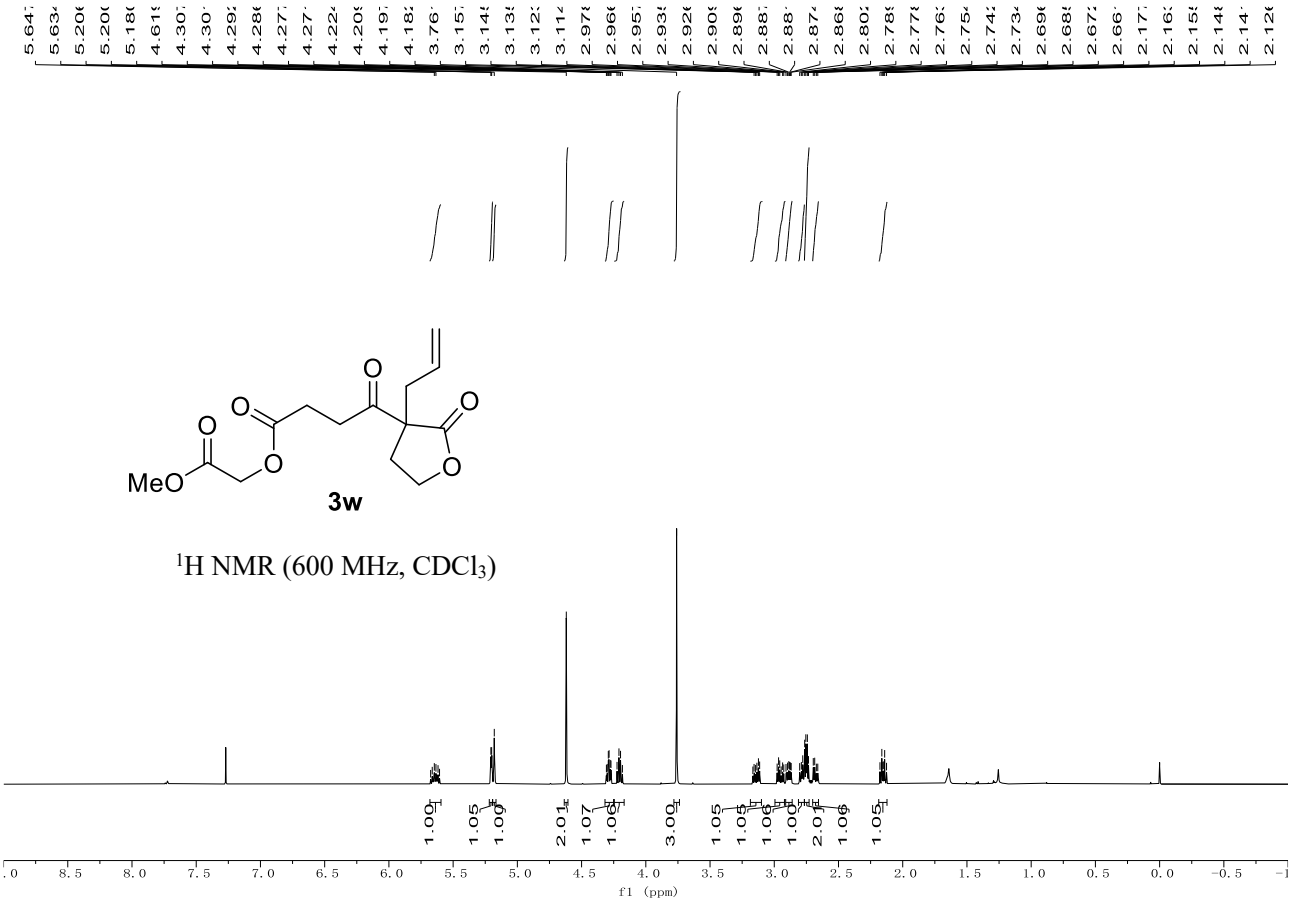




3v

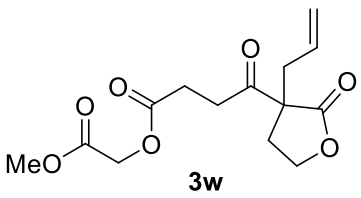
^{13}C NMR (150 MHz, $CDCl_3$)





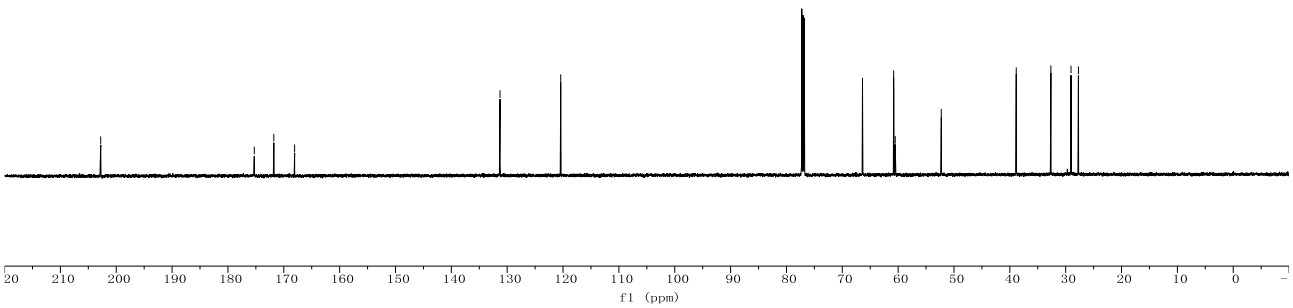
3w

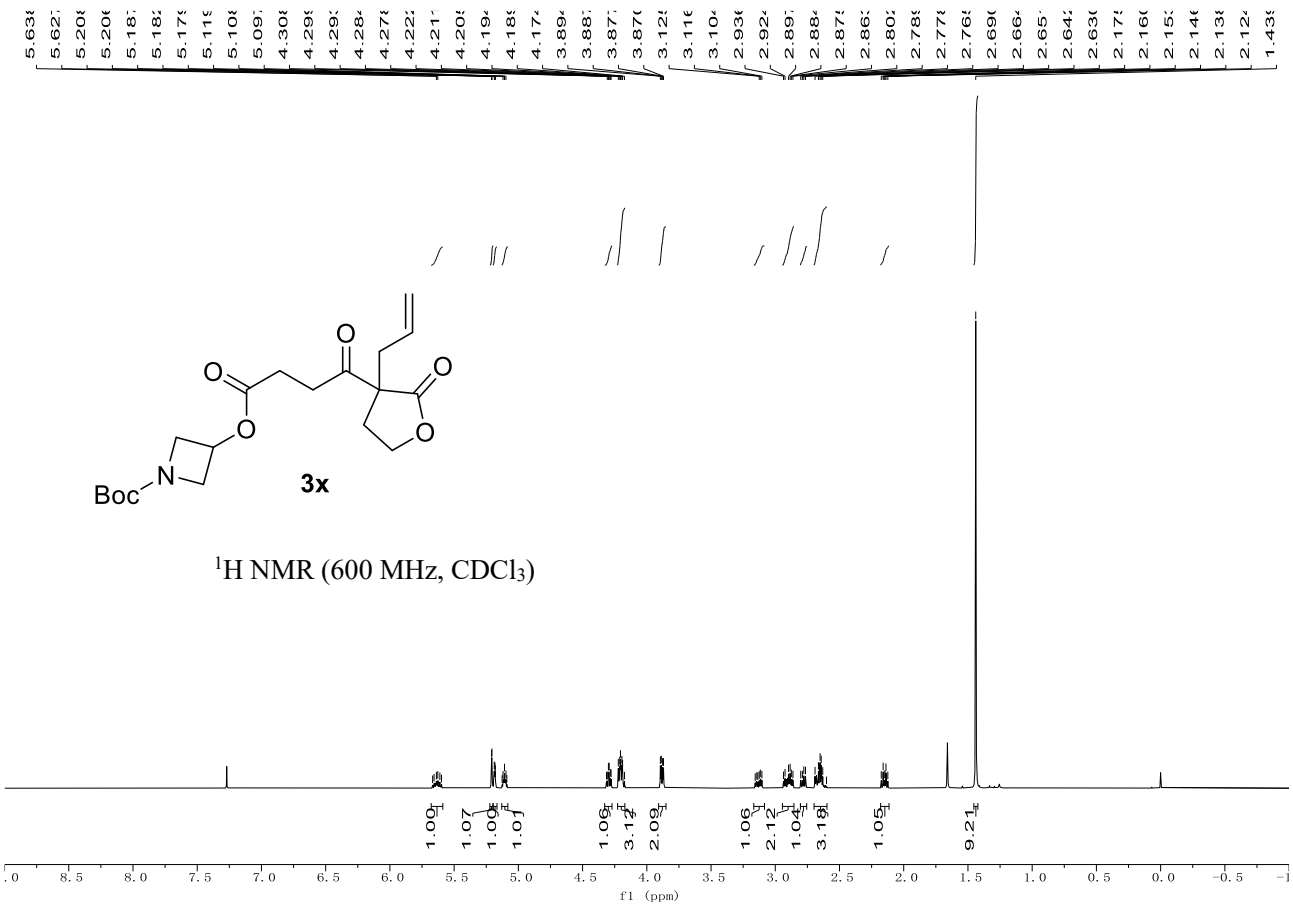
^{1}H NMR (600 MHz, $CDCl_3$)



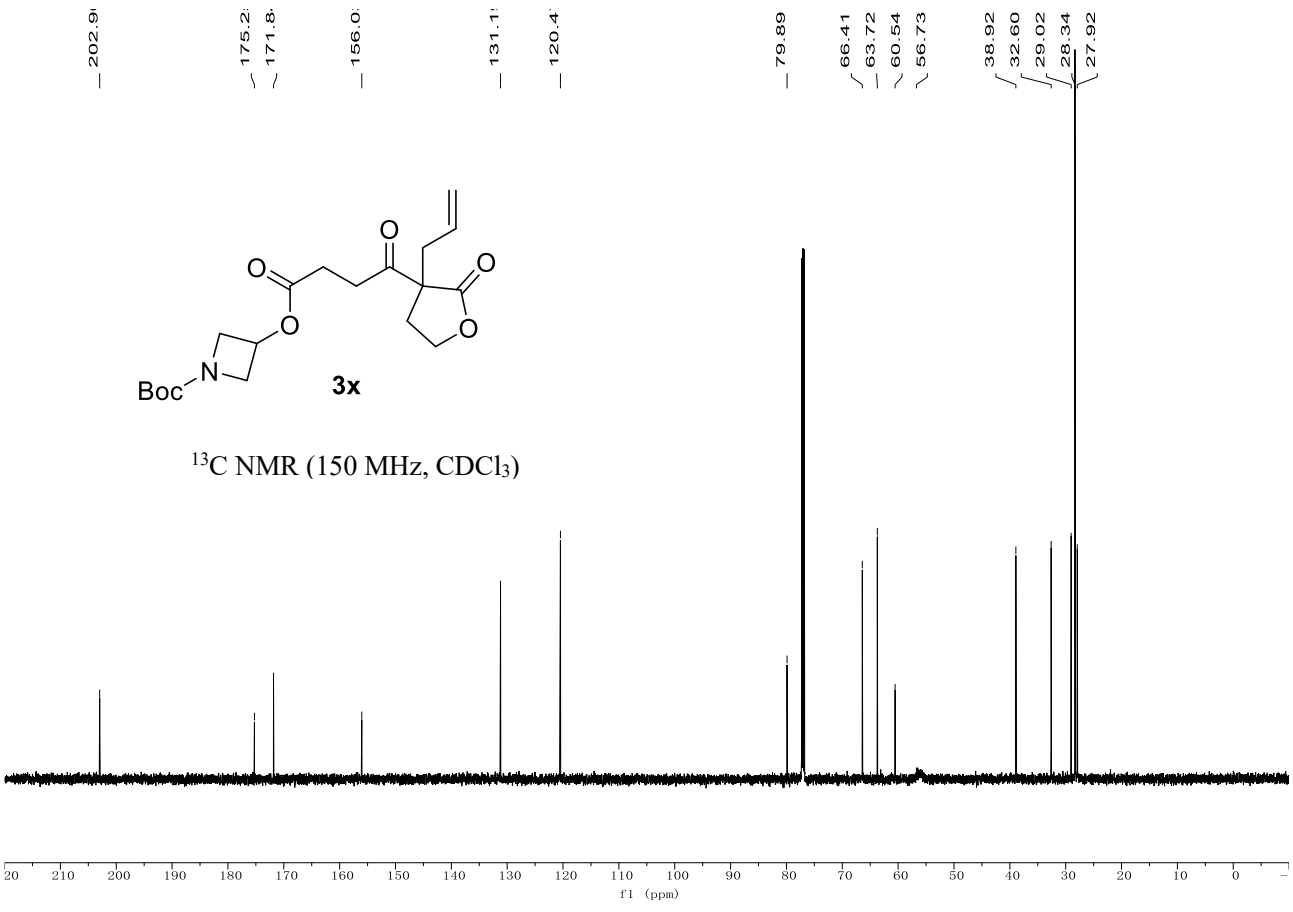
3w

^{13}C NMR (150 MHz, $CDCl_3$)

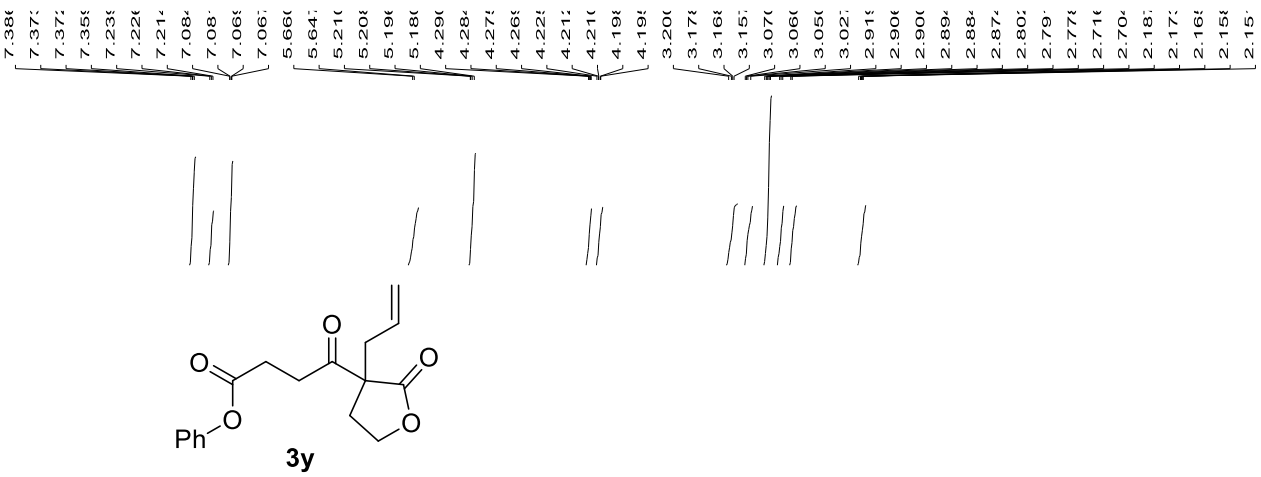




^{1}H NMR (600 MHz, $CDCl_3$)

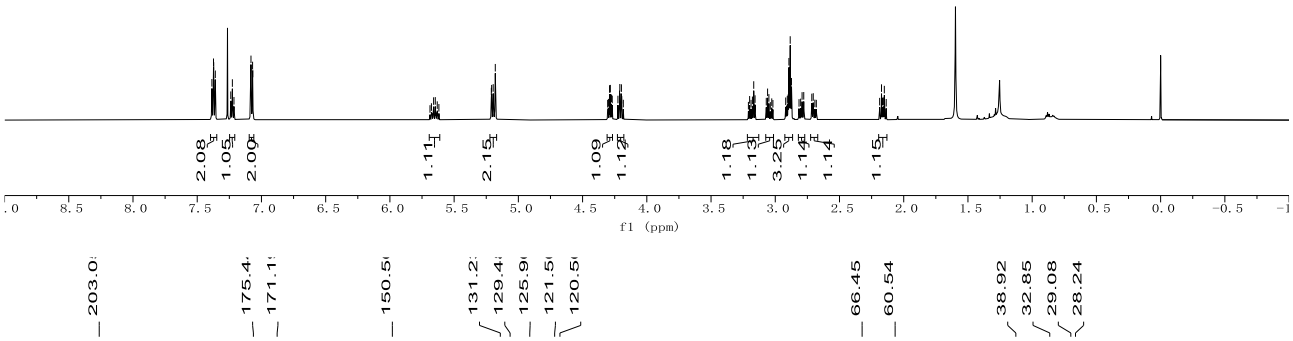


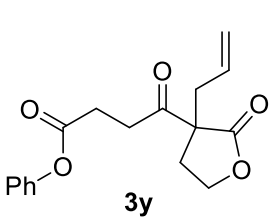
^{13}C NMR (150 MHz, $CDCl_3$)



3y

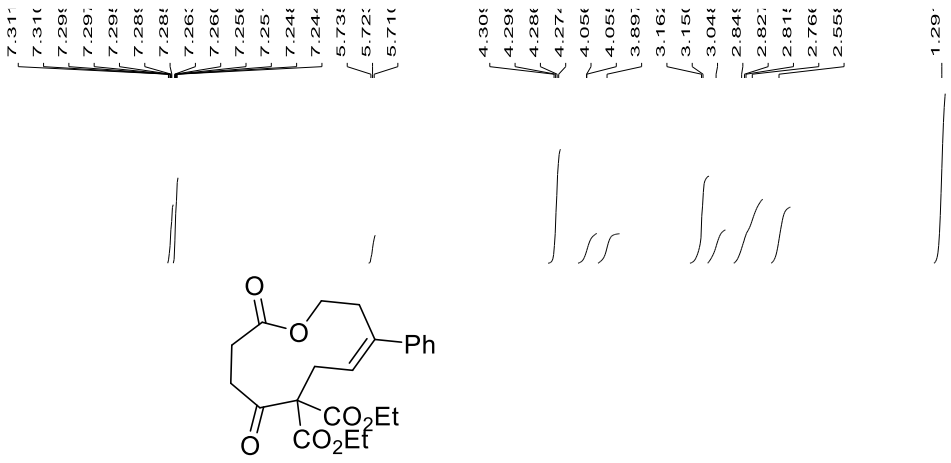
^{1}H NMR (600 MHz, $CDCl_3$)





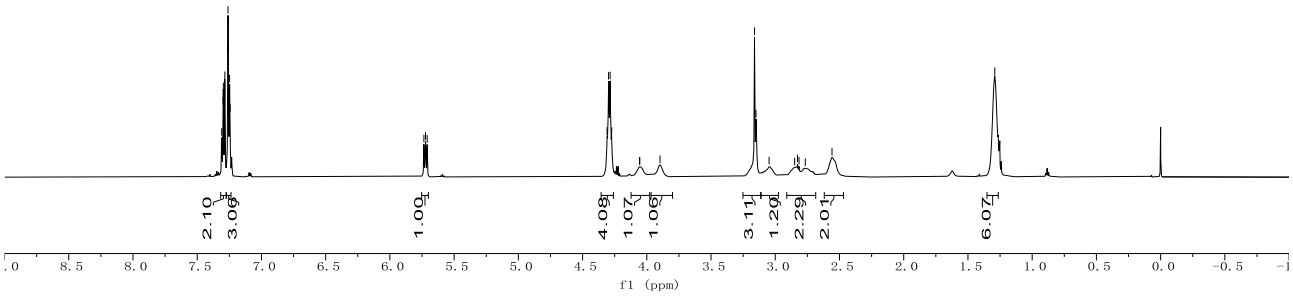
3y

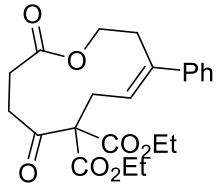
^{13}C NMR (150 MHz, $CDCl_3$)



6a

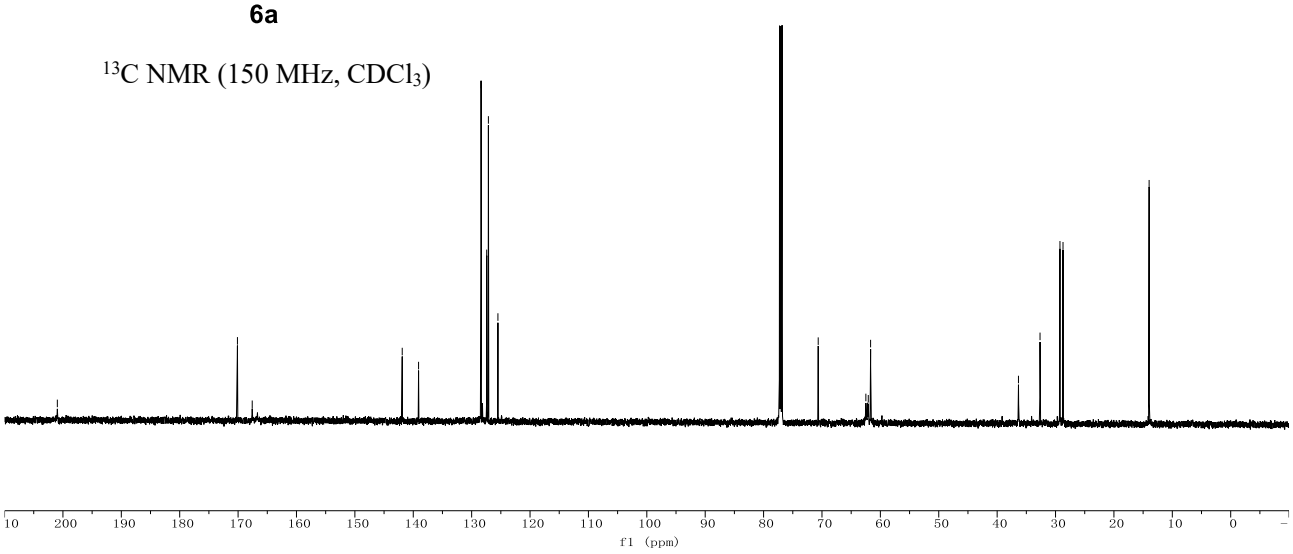
^{1}H NMR (600 MHz, $CDCl_3$)

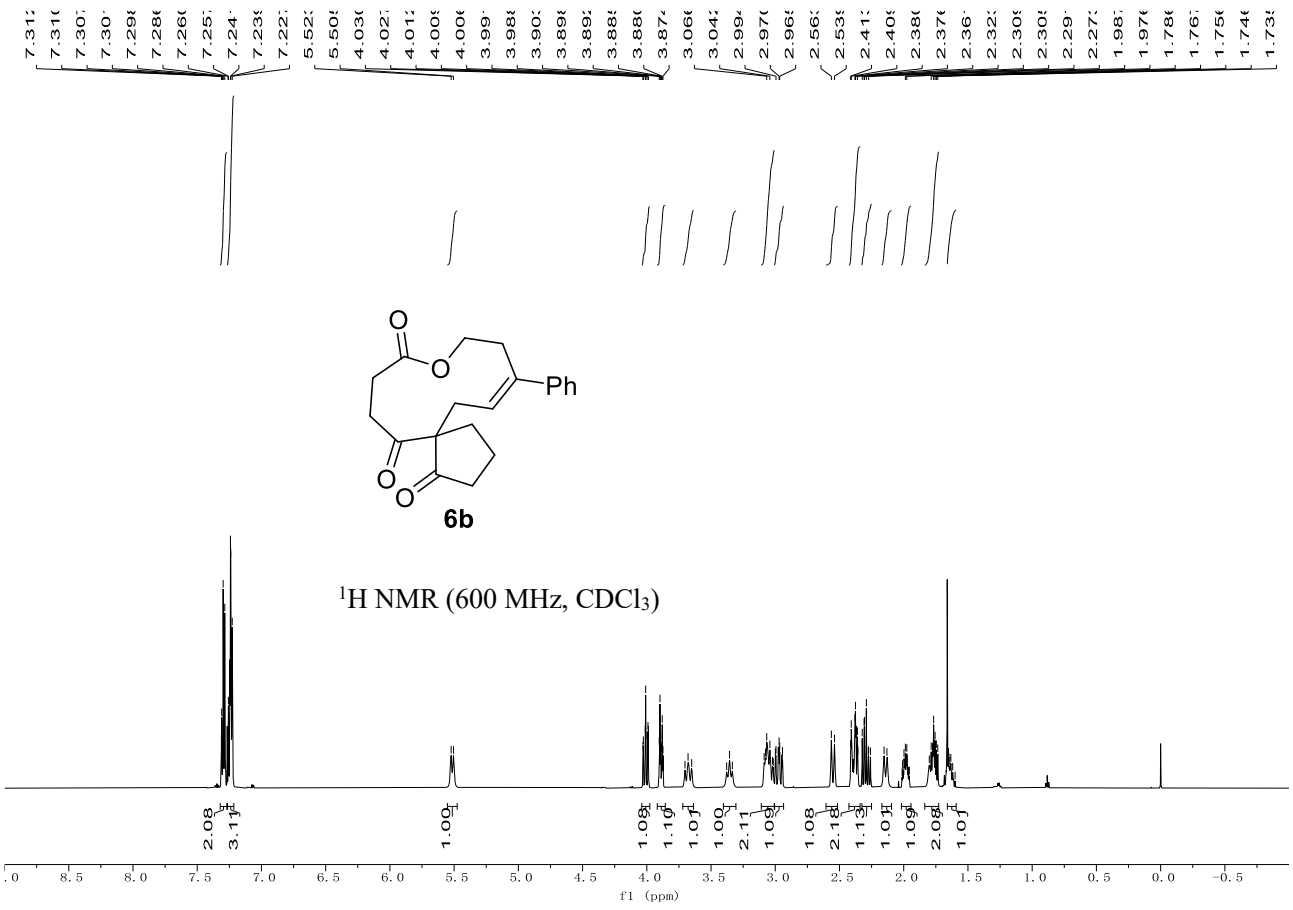


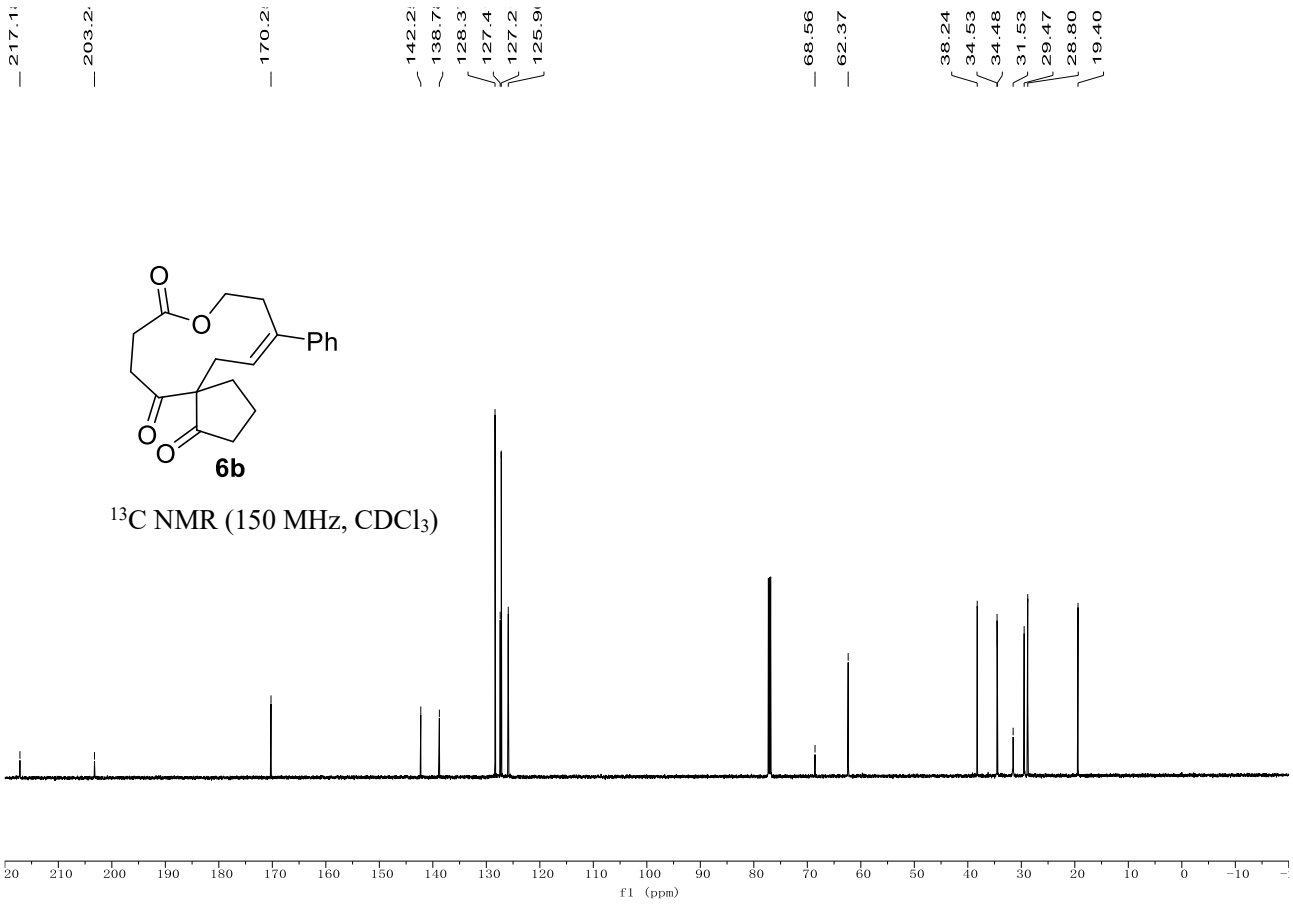


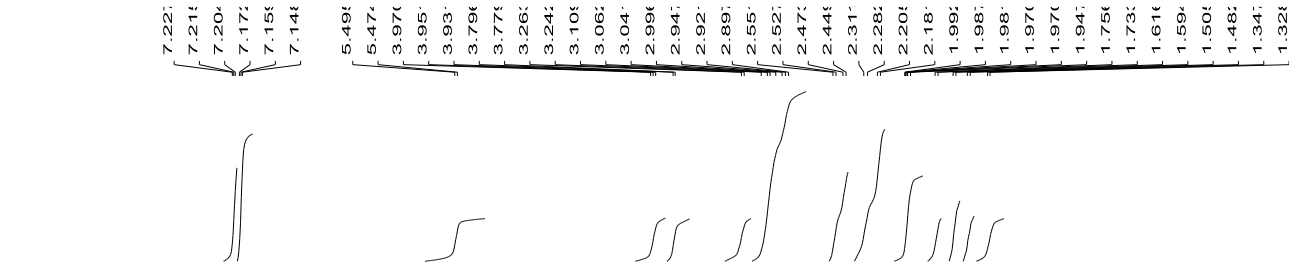
6a

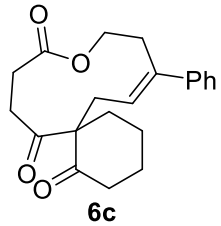
^{13}C NMR (150 MHz, $CDCl_3$)




Ph
6b
1H NMR (600 MHz, CDCl3)
f1 (ppm)

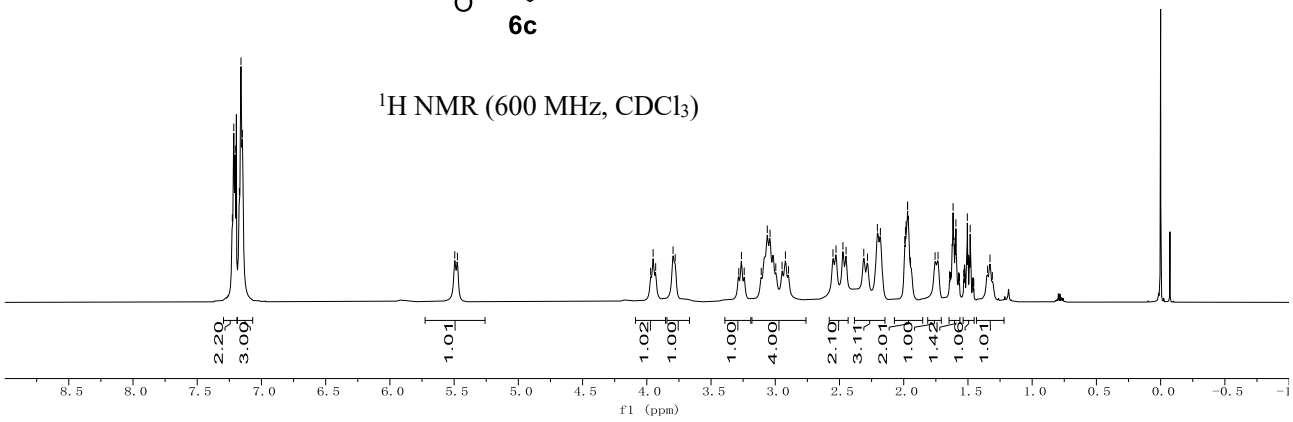

Ph
6b
13C NMR (150 MHz, CDCl3)
f1 (ppm)

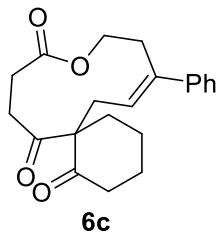




6c

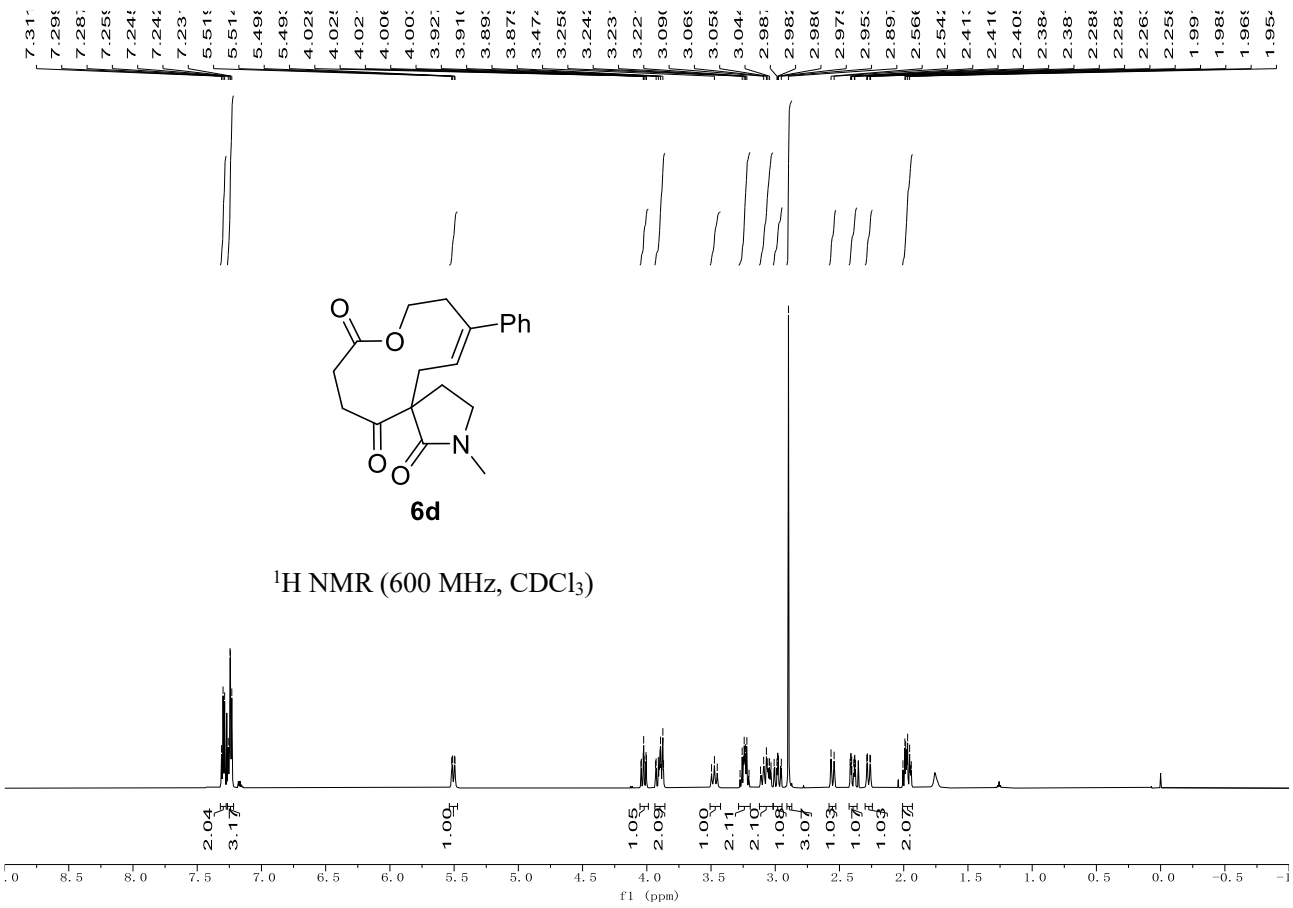
^{1}H NMR (600 MHz, $CDCl_3$)



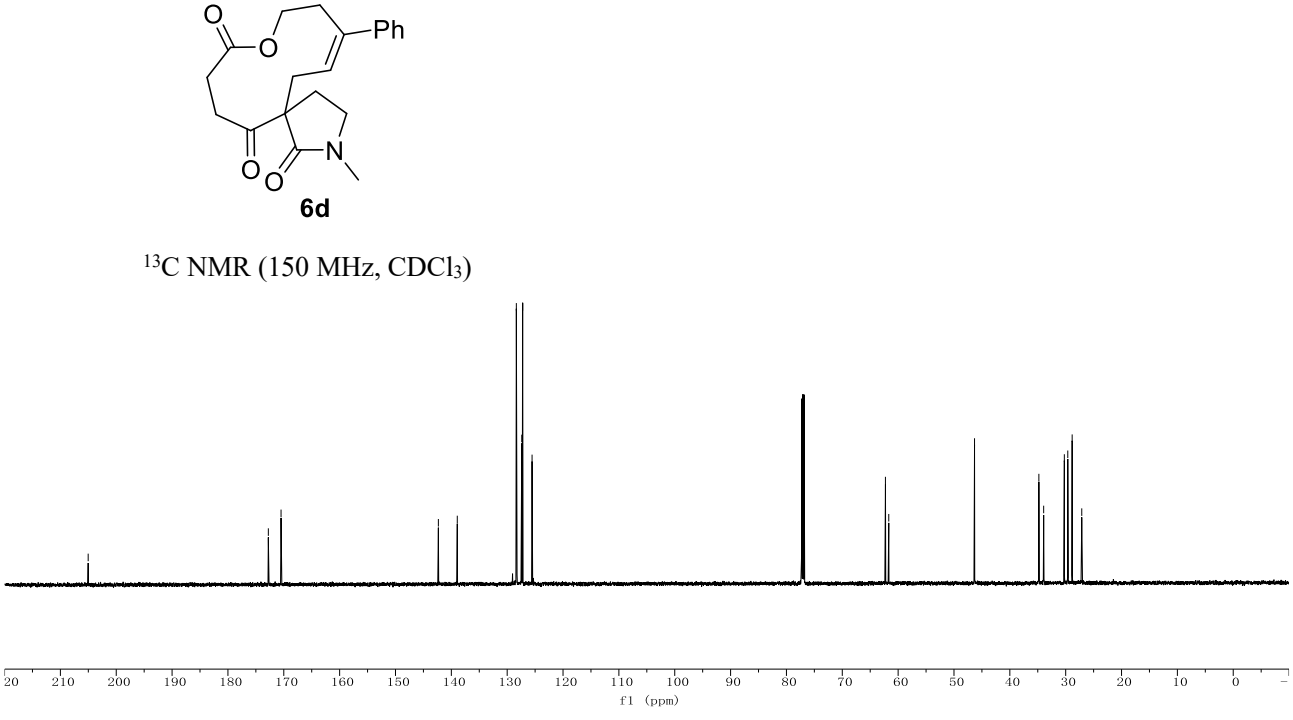


6c

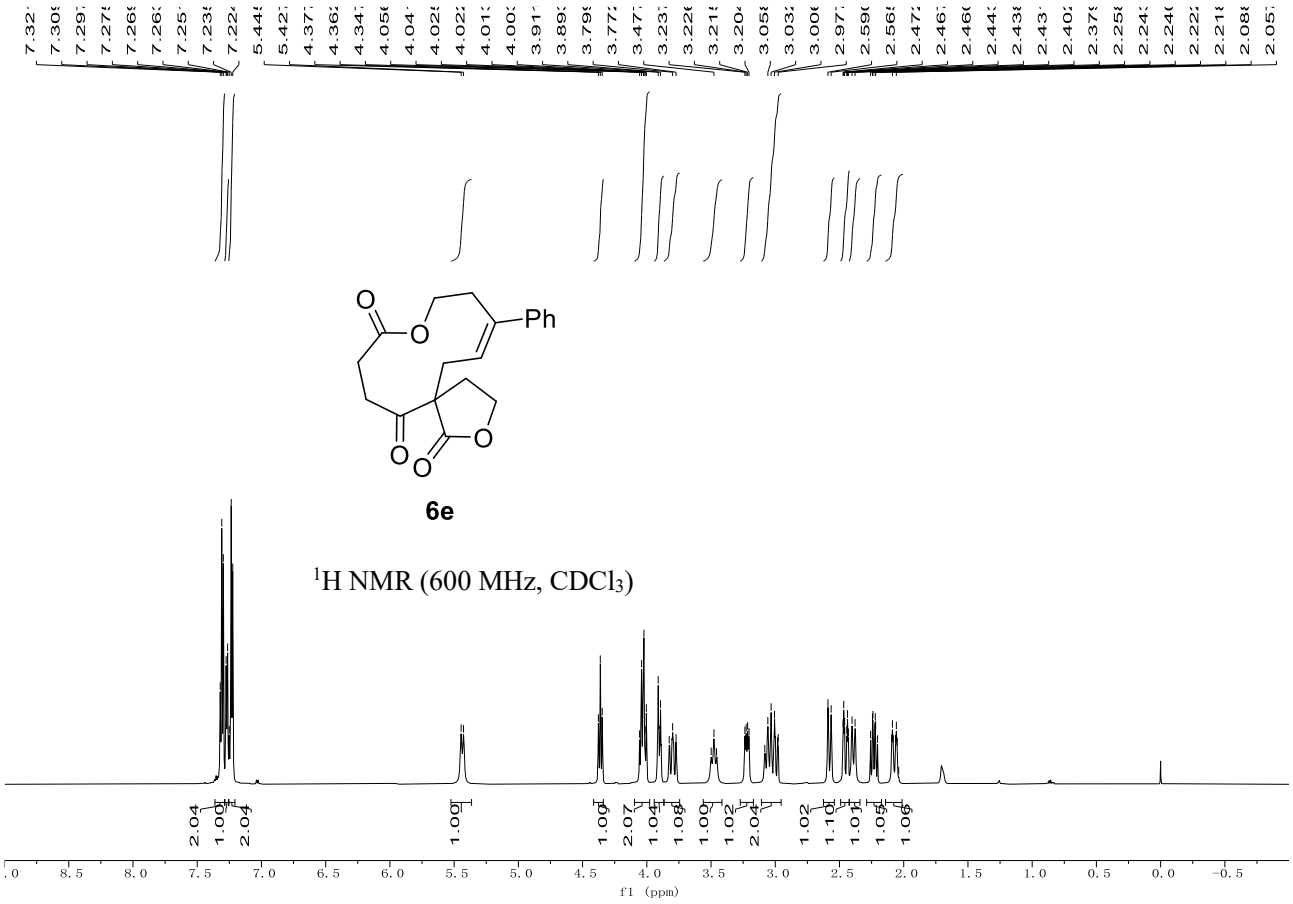
^{13}C NMR (150 MHz, $CDCl_3$)



^{1}H NMR (600 MHz, $CDCl_3$)

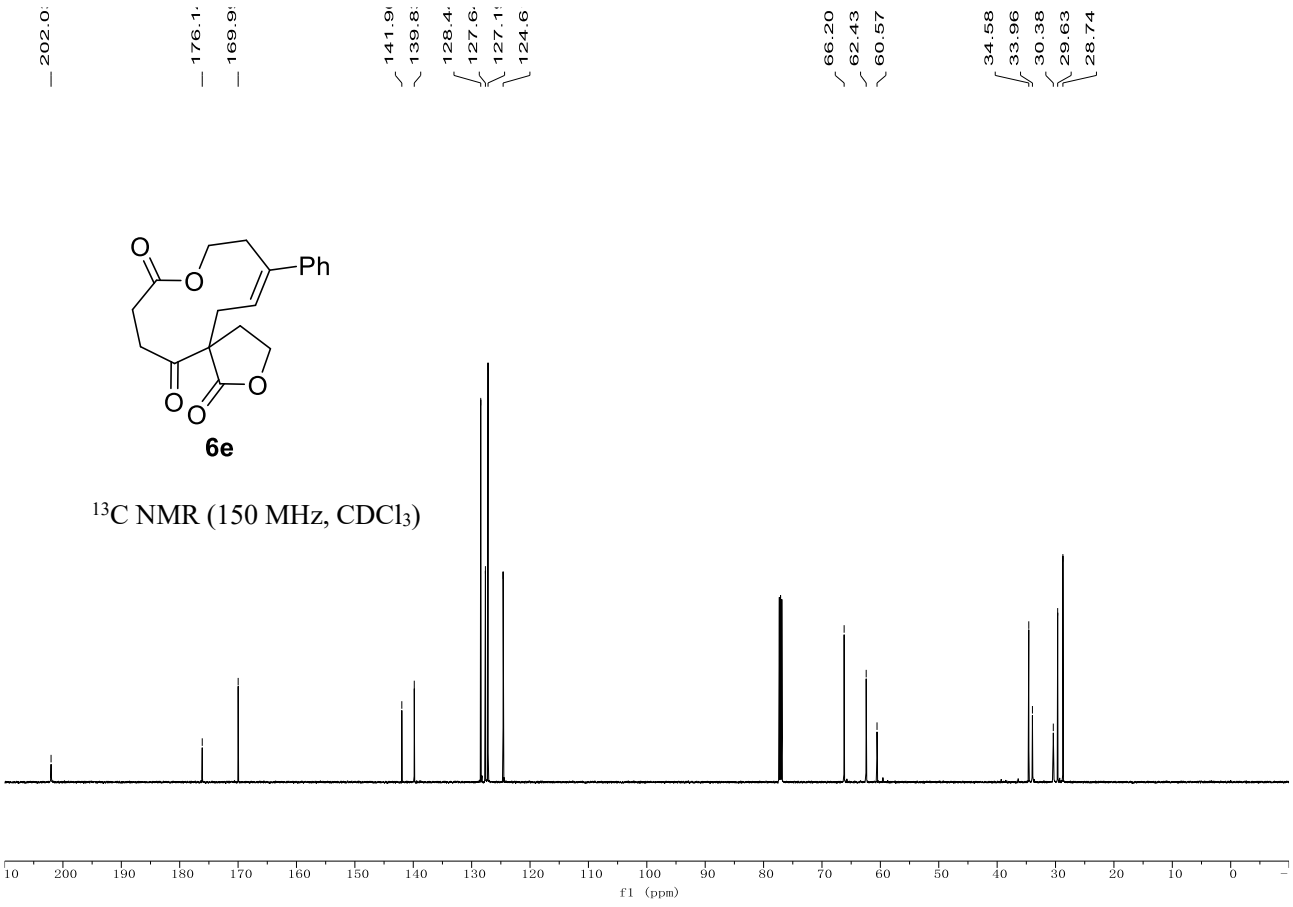


^{13}C NMR (150 MHz, $CDCl_3$)



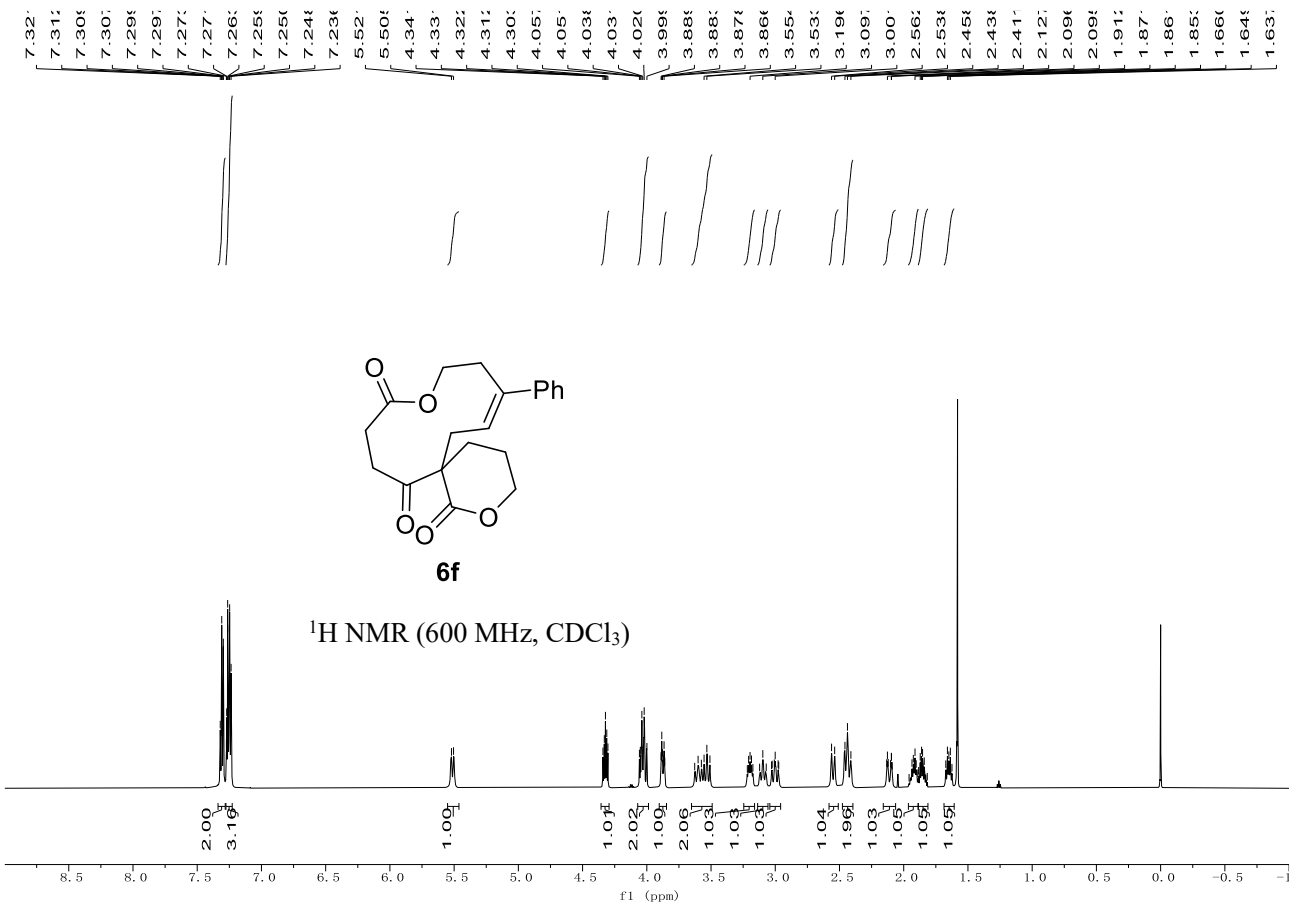
6e

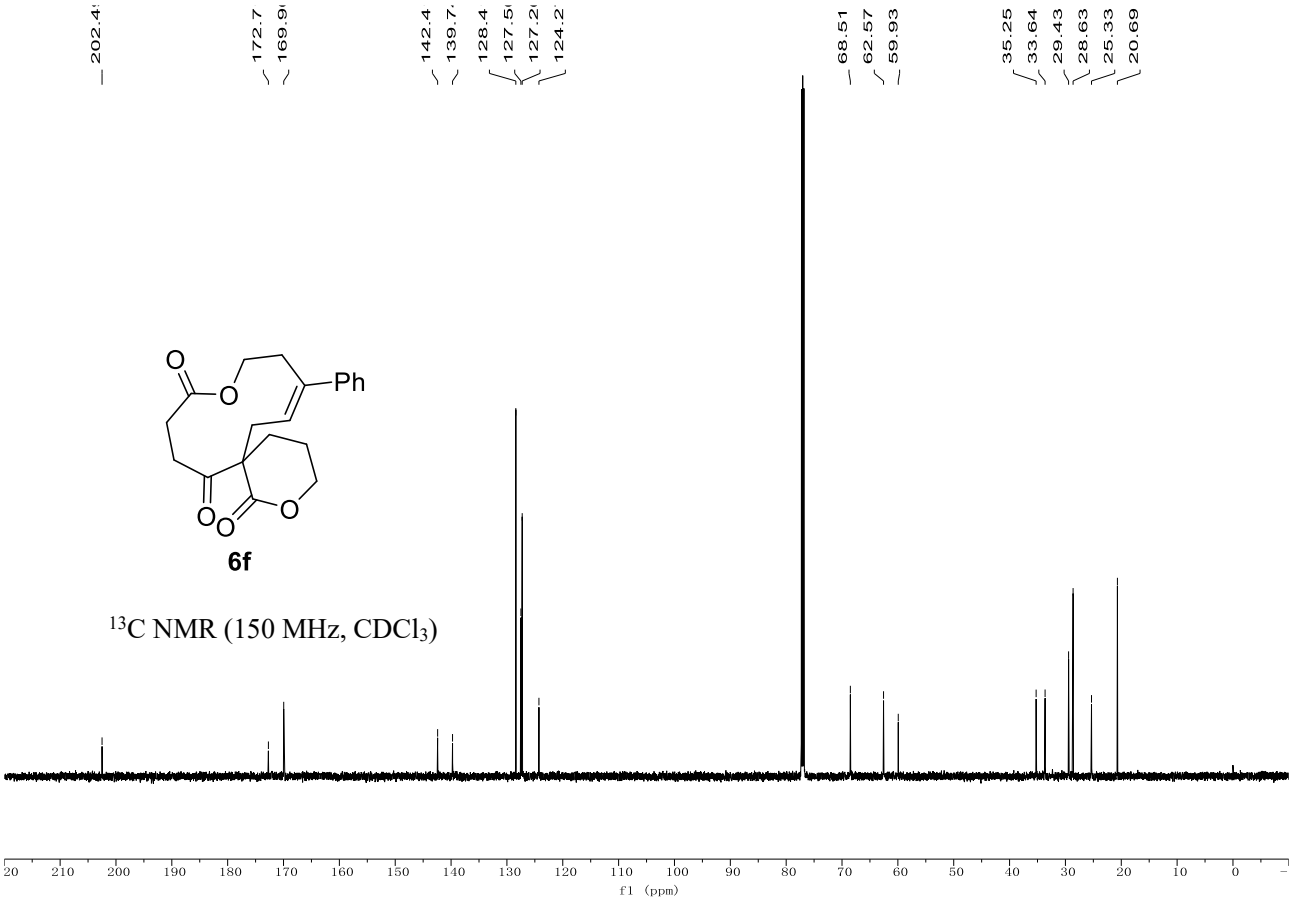
^{1}H NMR (600 MHz, $CDCl_3$)

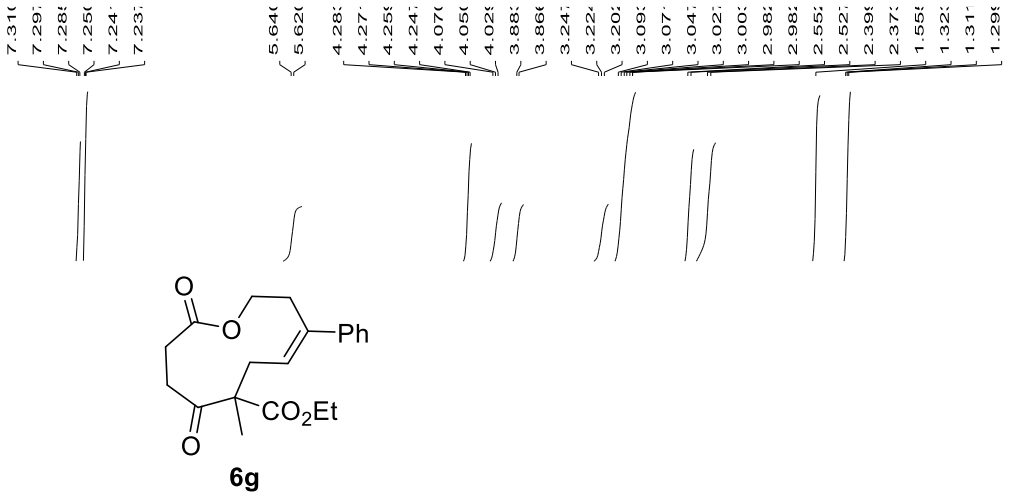


6e

^{13}C NMR (150 MHz, $CDCl_3$)

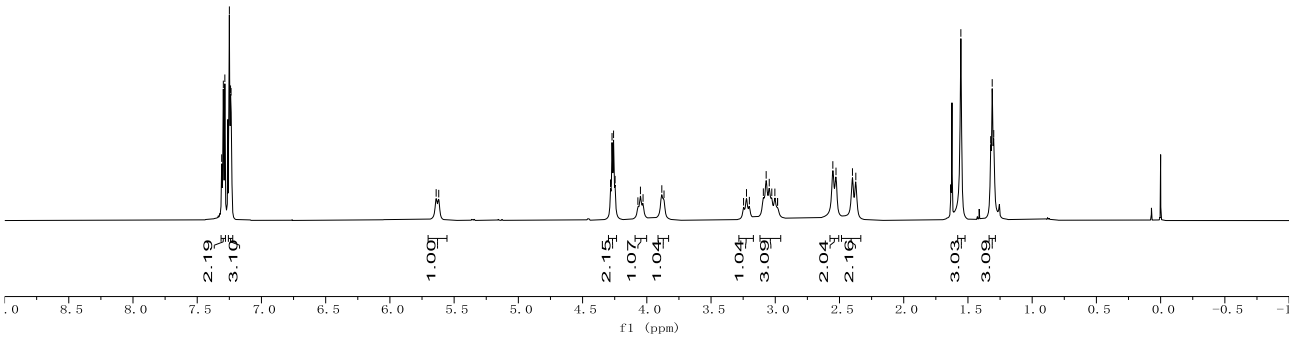

Ph
6f
1H NMR (600 MHz, CDCl3)
f1 (ppm)

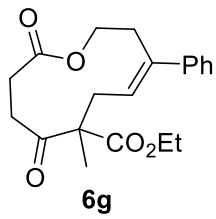

Ph
6f
13C NMR (150 MHz, CDCl3)
f1 (ppm)



6g

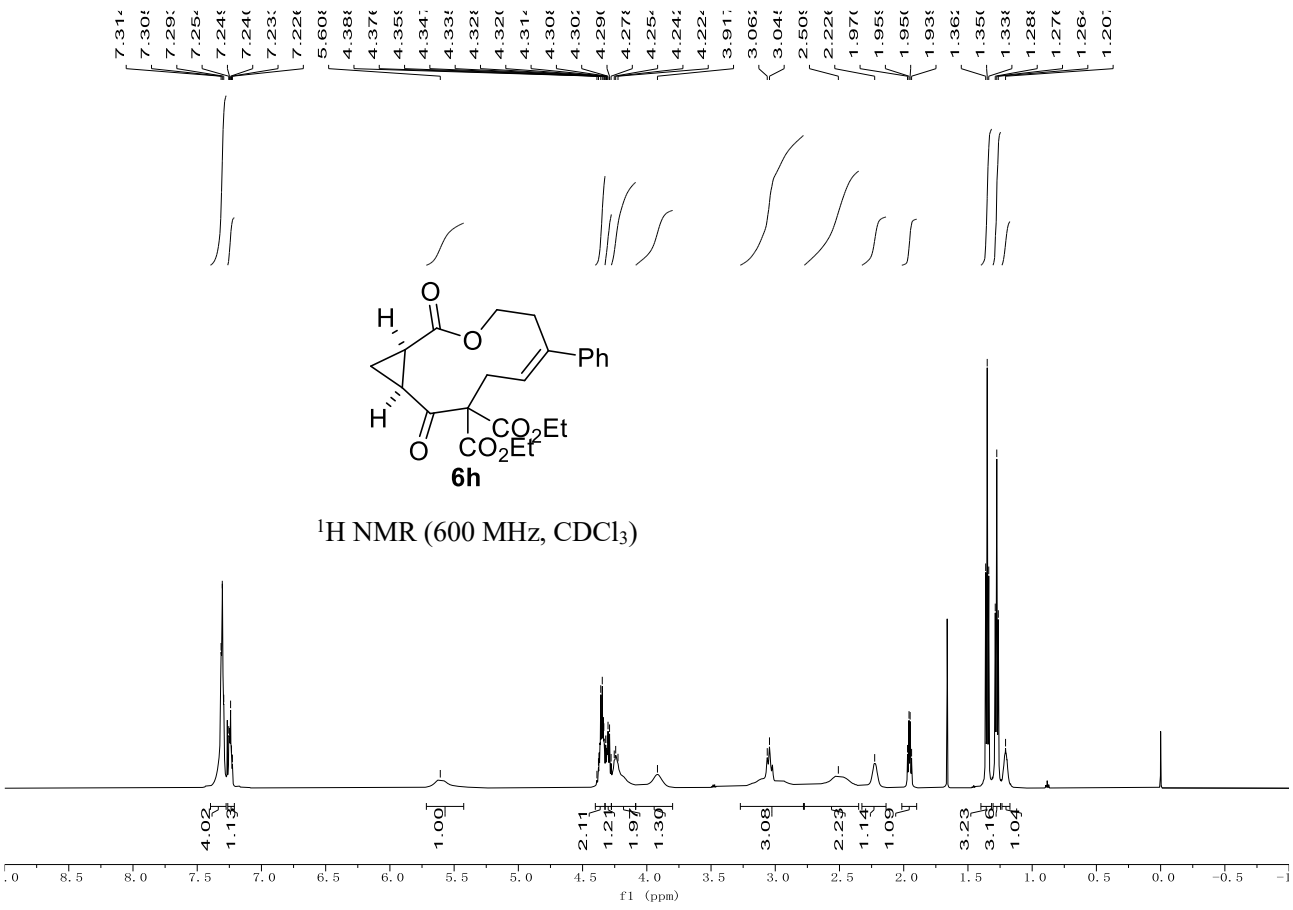
^{1}H NMR (600 MHz, $CDCl_3$)



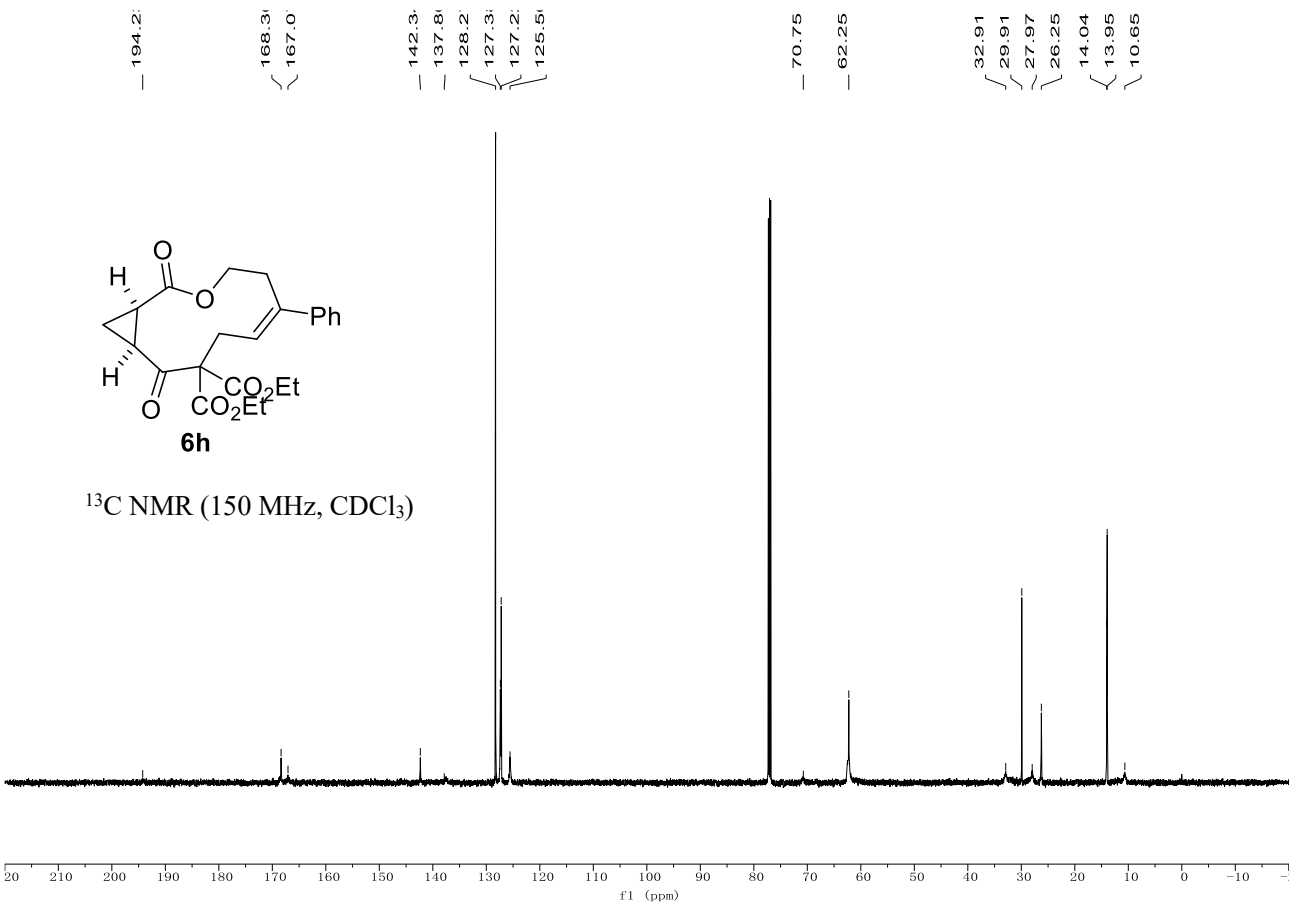


6g

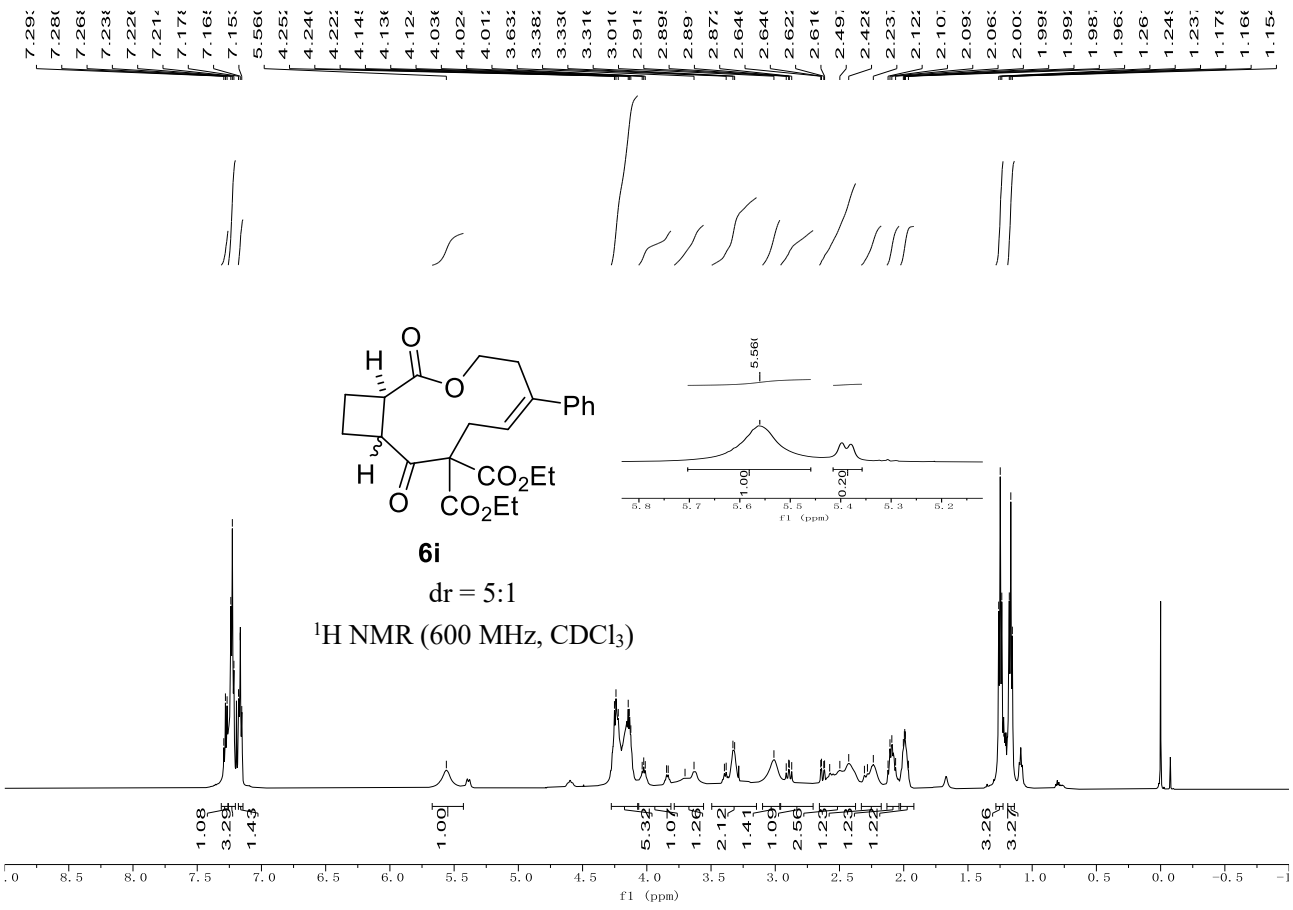
^{13}C NMR (150 MHz, $CDCl_3$)

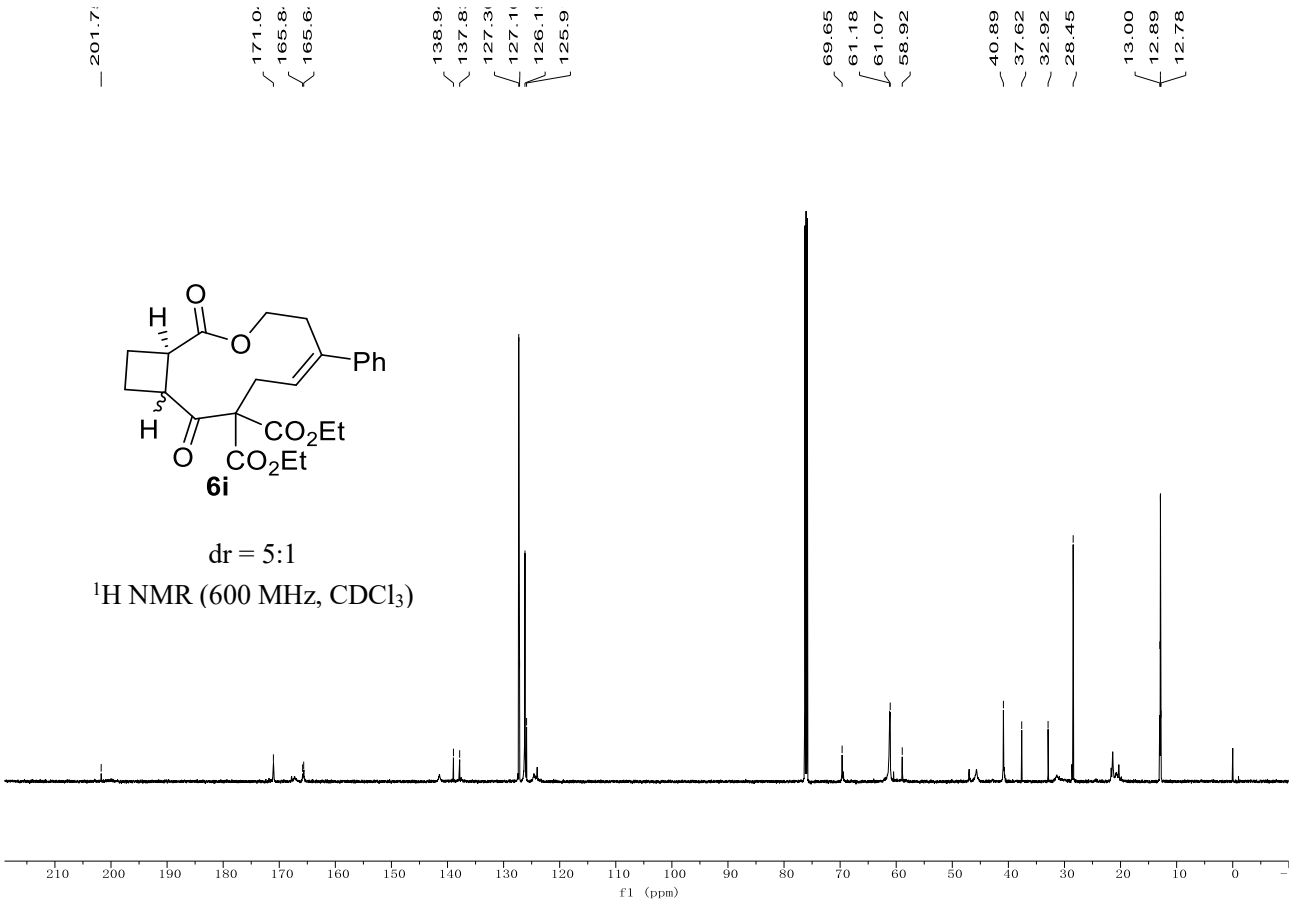


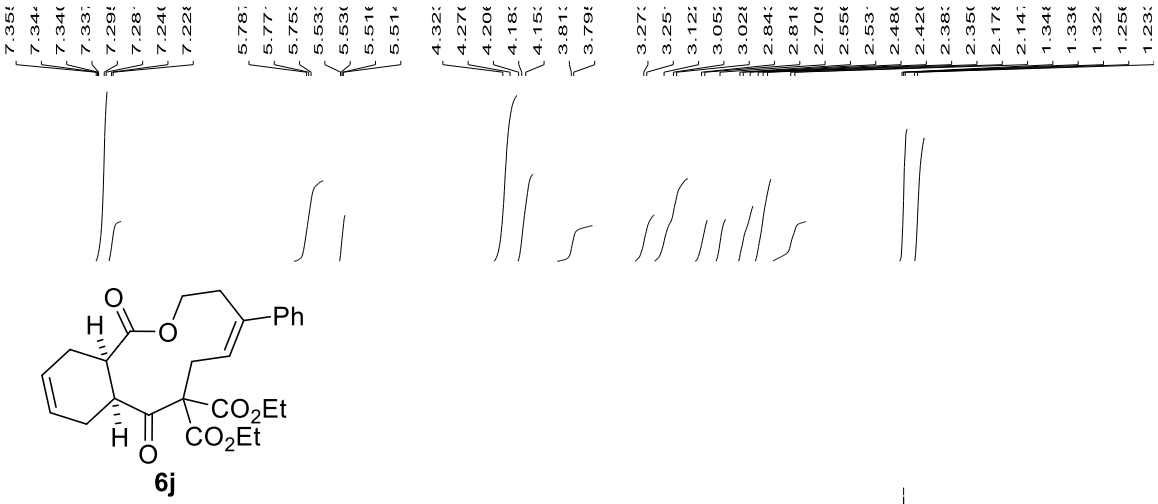
^{1}H NMR (600 MHz, $CDCl_3$)



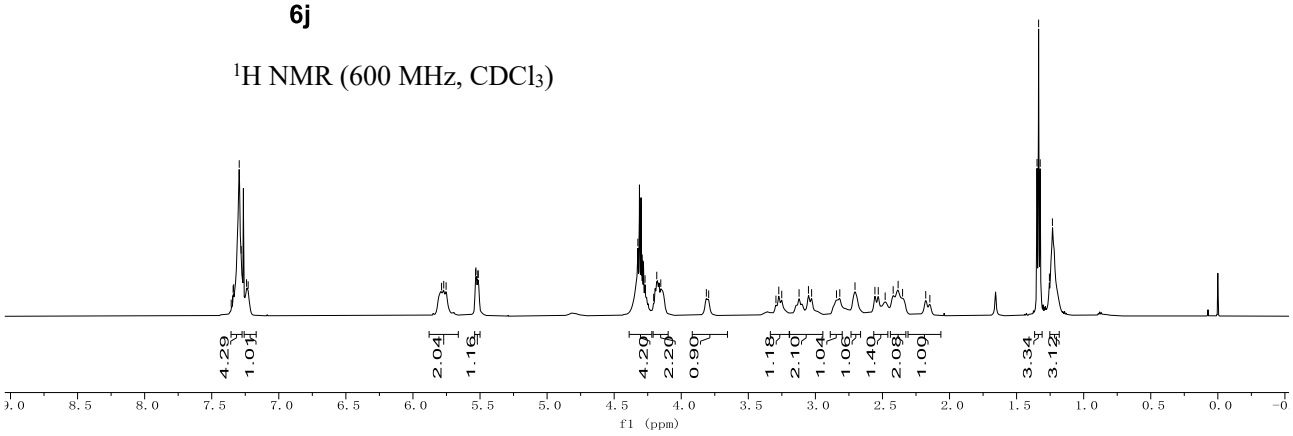
^{13}C NMR (150 MHz, $CDCl_3$)

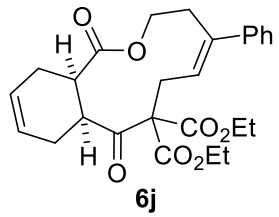

Ph
CO2Et
CO2Et
6i
dr = 5:1
1H NMR (600 MHz, CDCl3)
f1 (ppm)


Ph
CO2Et
CO2Et
6i
dr = 5:1
1H NMR (600 MHz, CDCl3)
f1 (ppm)

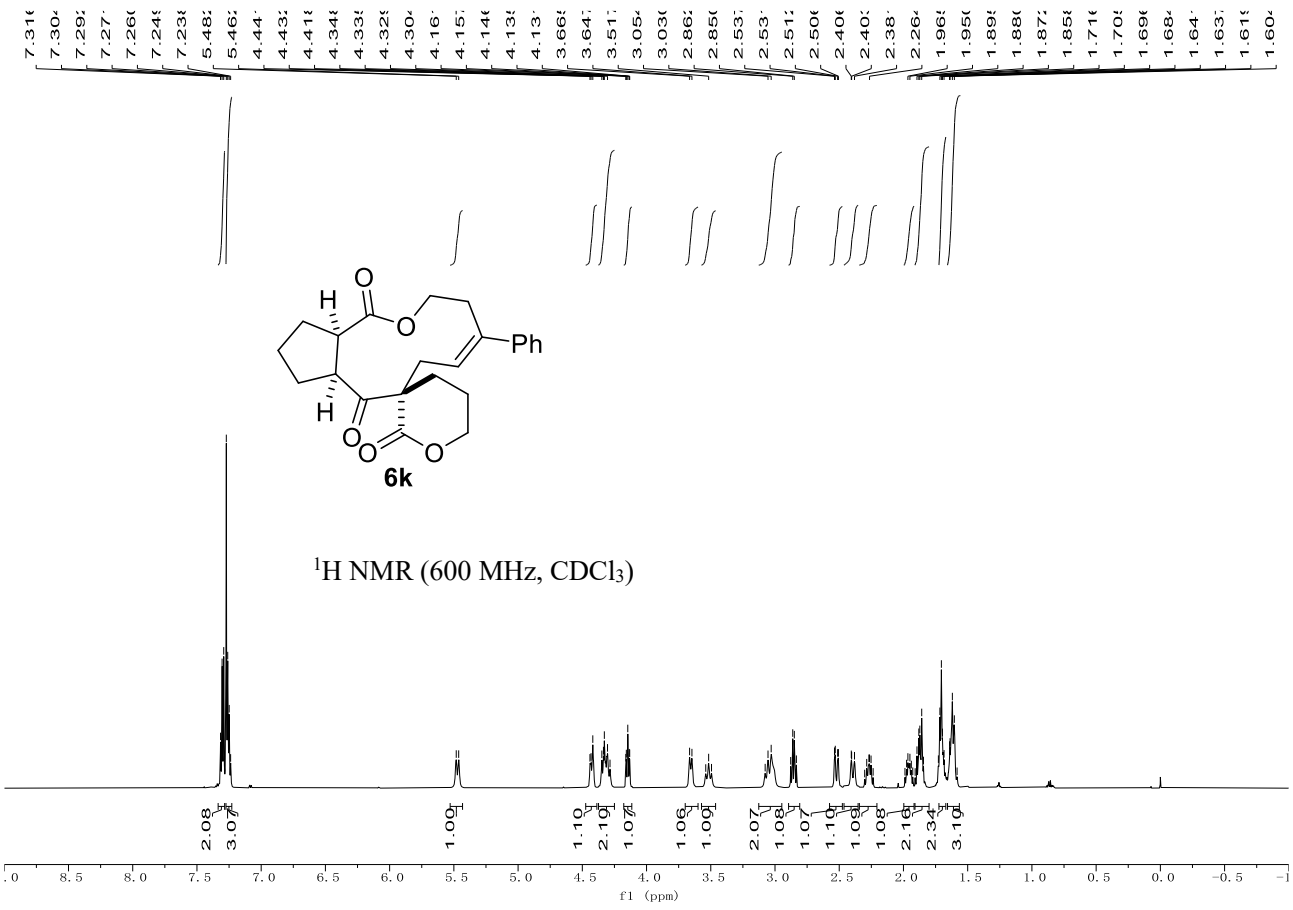


^{1}H NMR (600 MHz, $CDCl_3$)

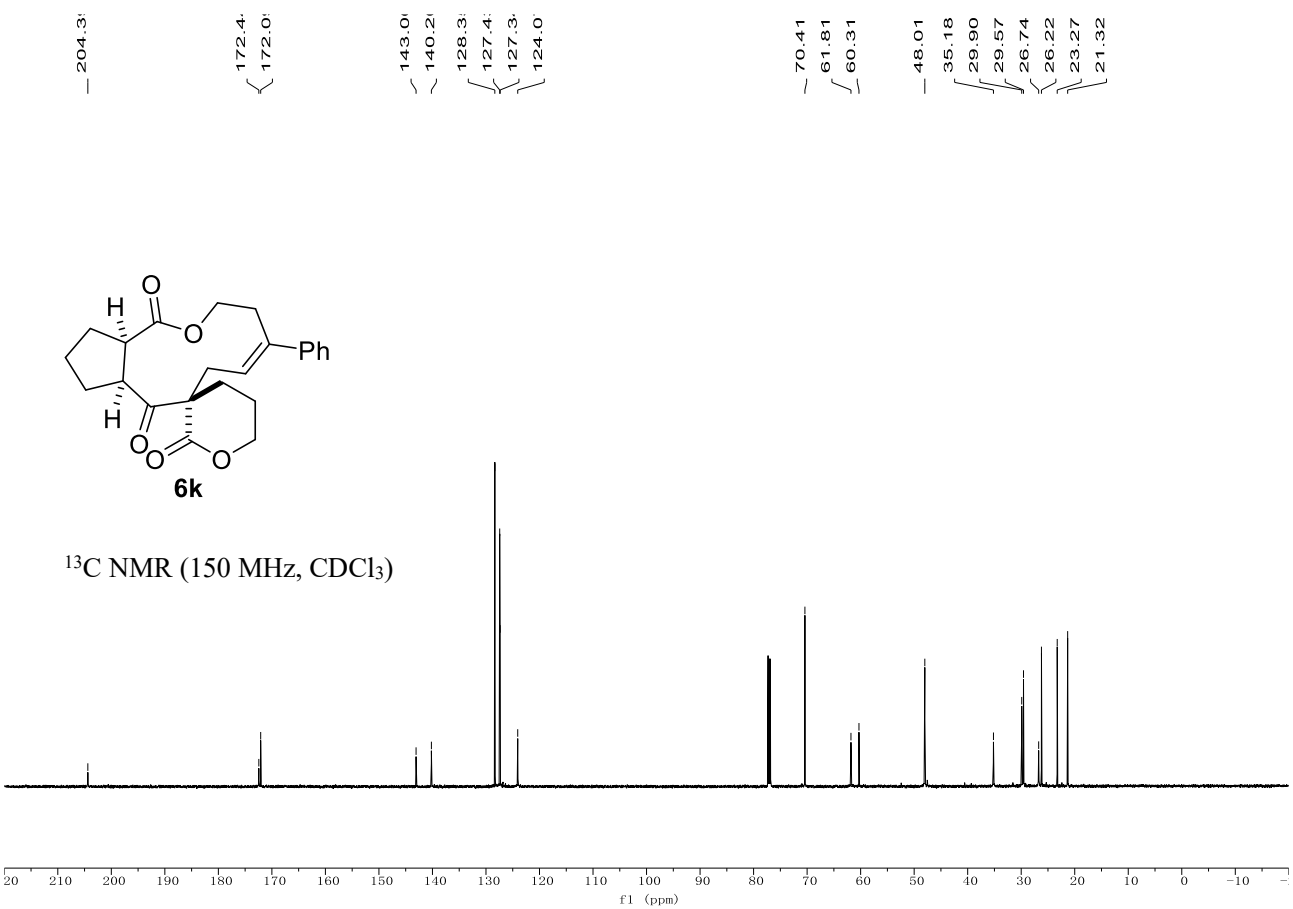




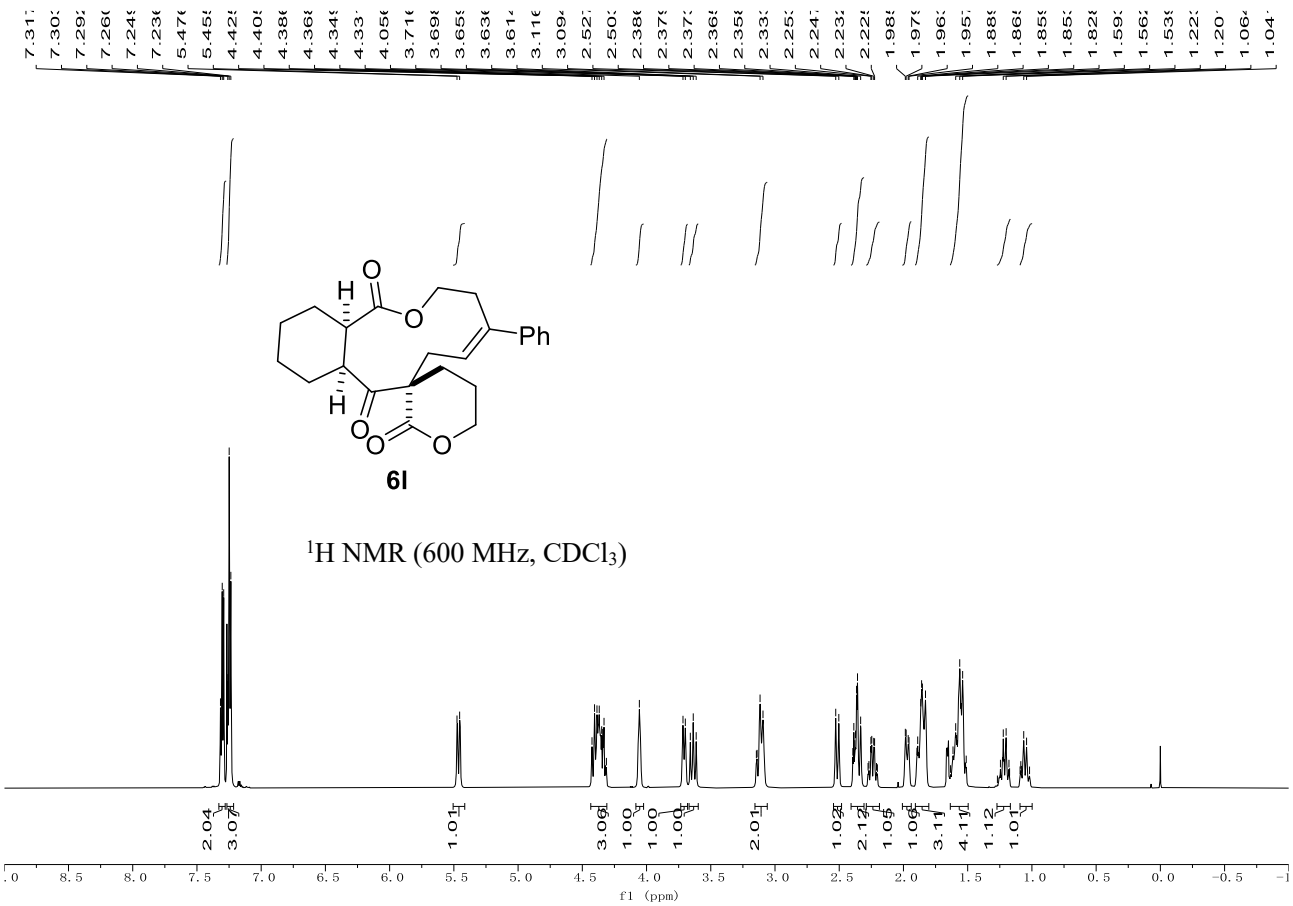
^{13}C NMR (150 MHz, $CDCl_3$)



^{1}H NMR (600 MHz, $CDCl_3$)

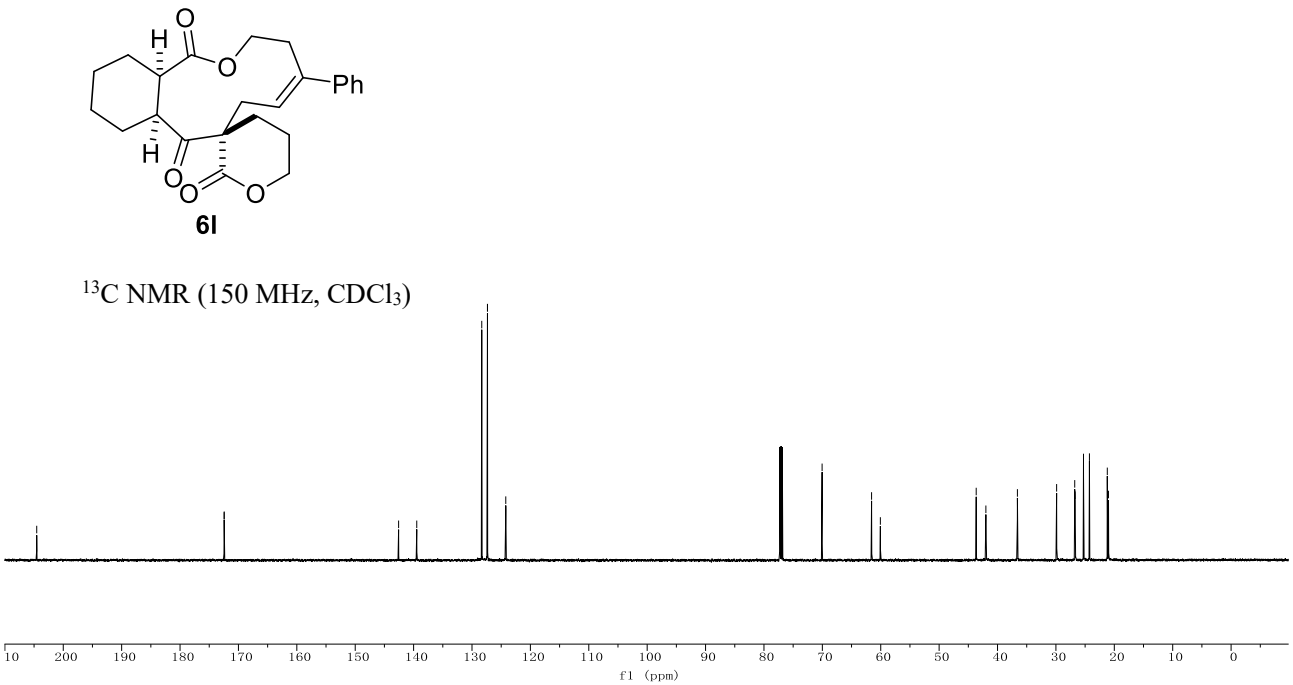


^{13}C NMR (150 MHz, $CDCl_3$)



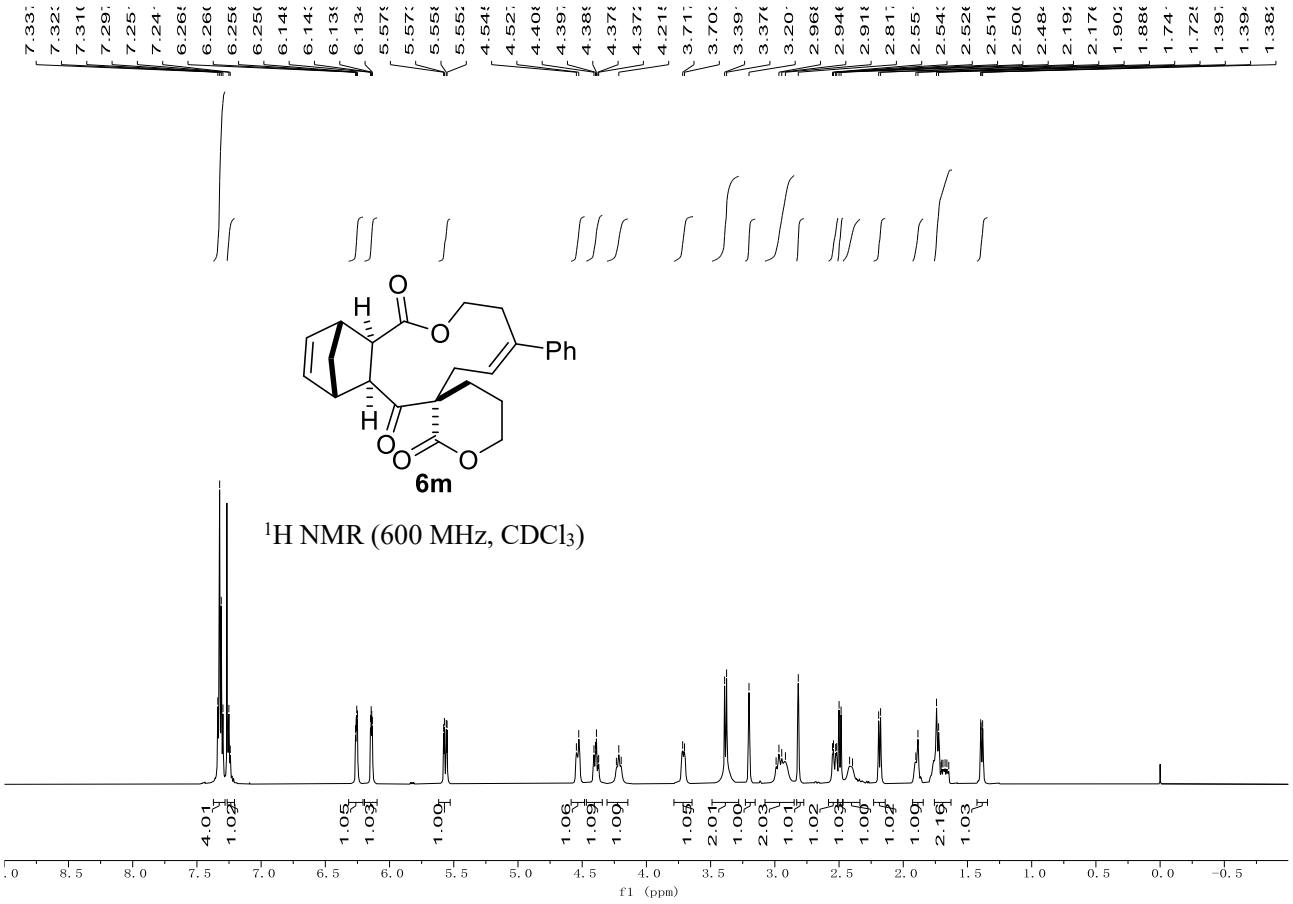
6l

^{1}H NMR (600 MHz, $CDCl_3$)

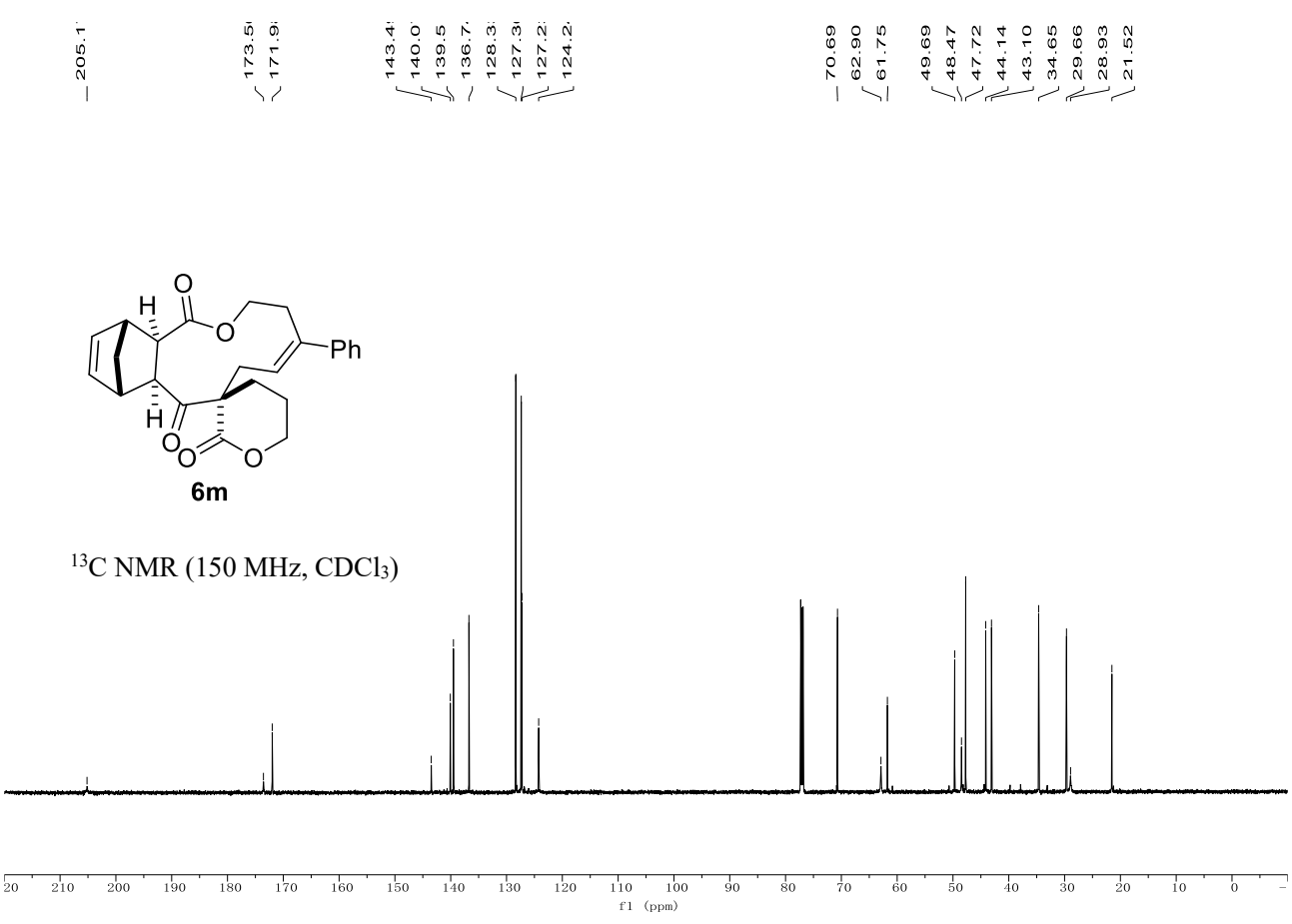


6l

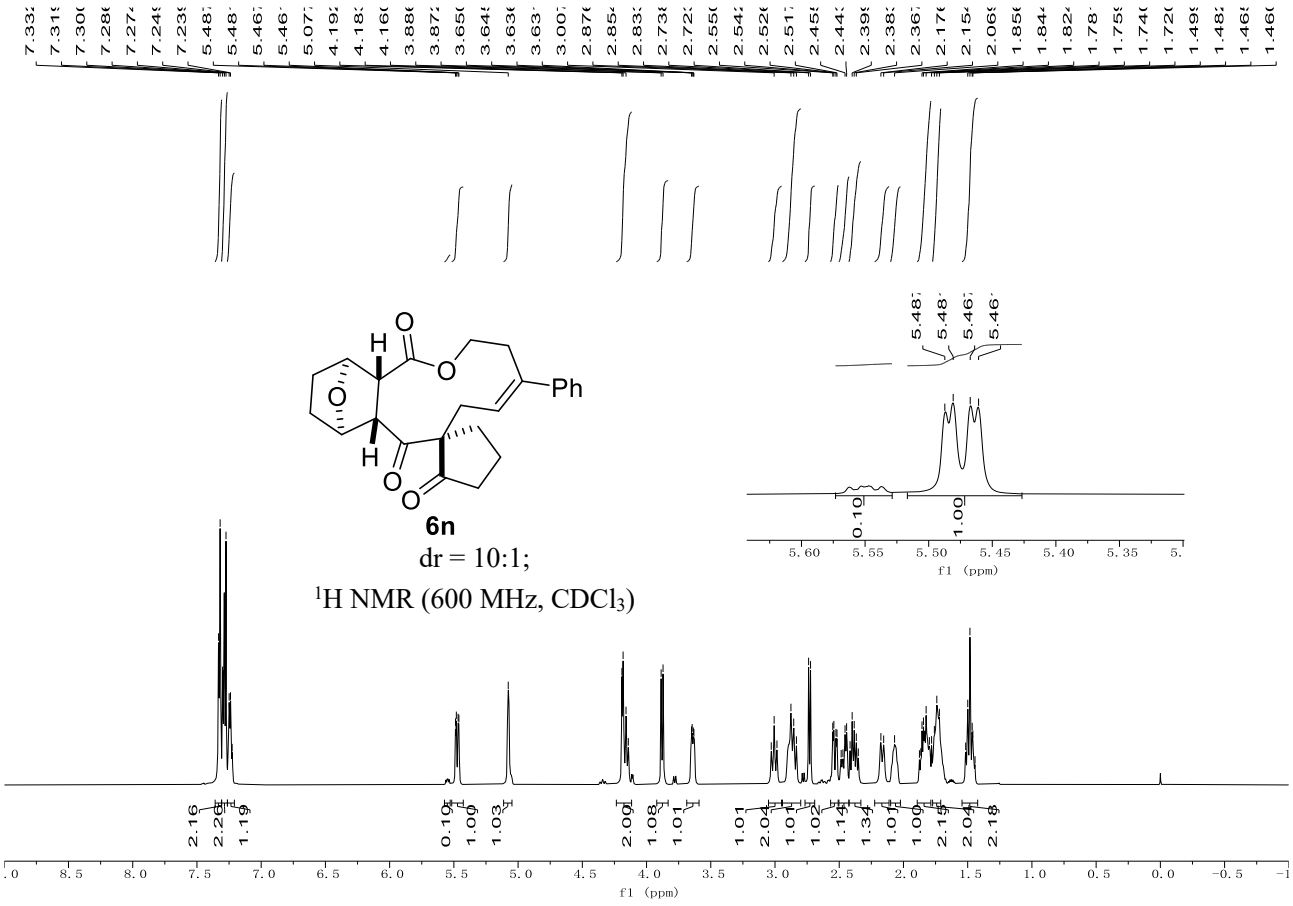
^{13}C NMR (150 MHz, $CDCl_3$)



^{1}H NMR (600 MHz, $CDCl_3$)



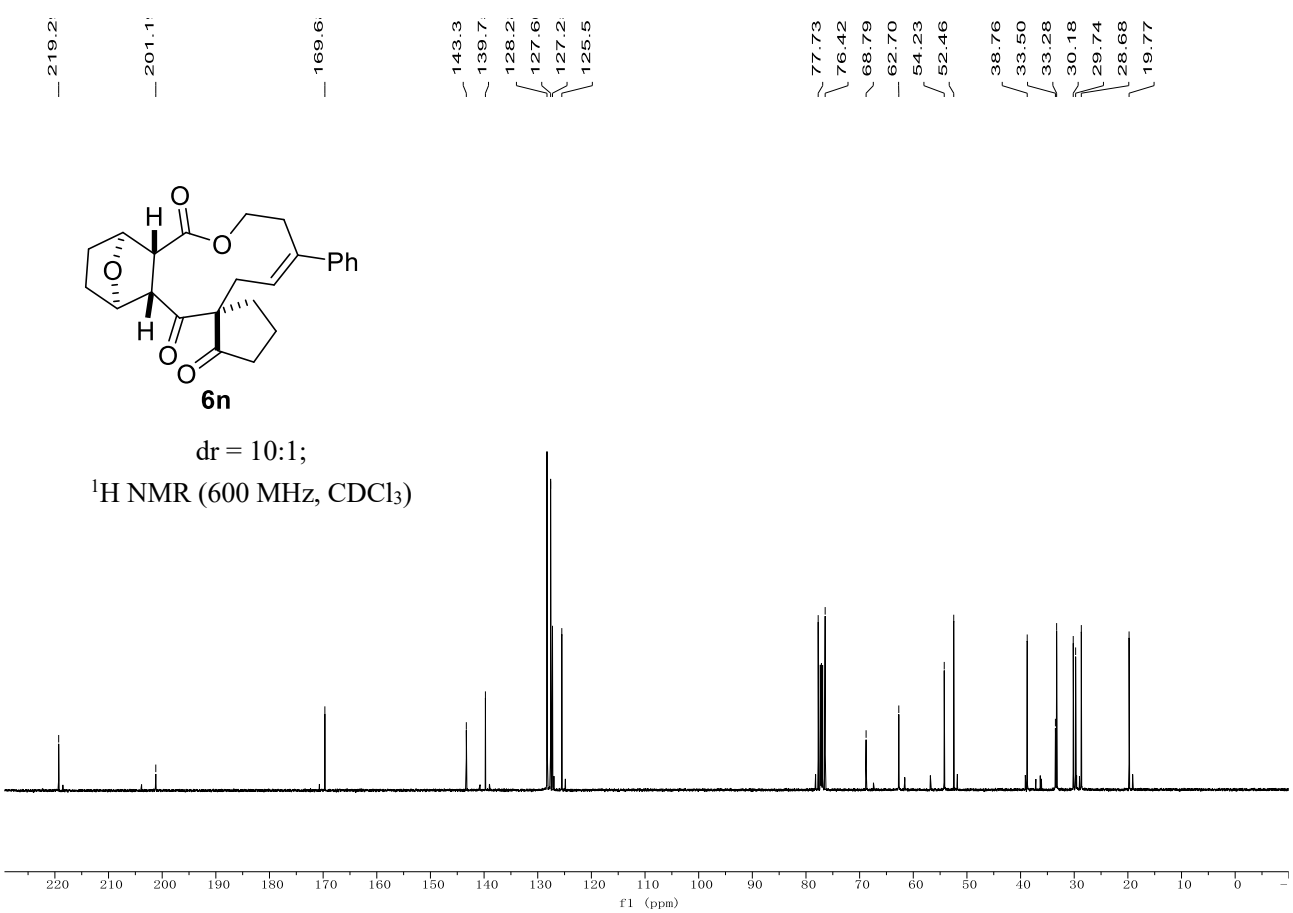
^{13}C NMR (150 MHz, $CDCl_3$)



6n

dr = 10:1;

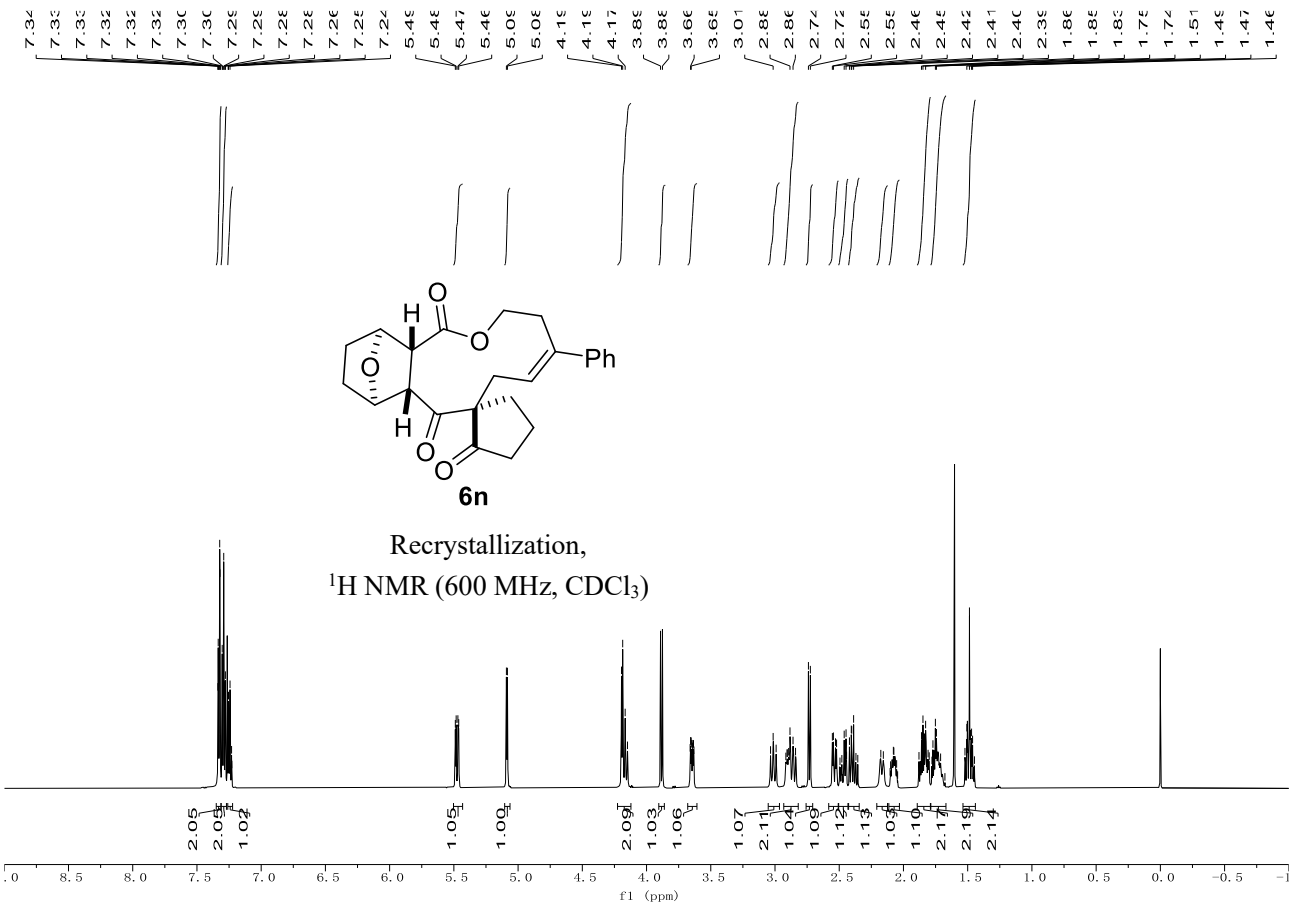
^{1}H NMR (600 MHz, $CDCl_3$)



6n

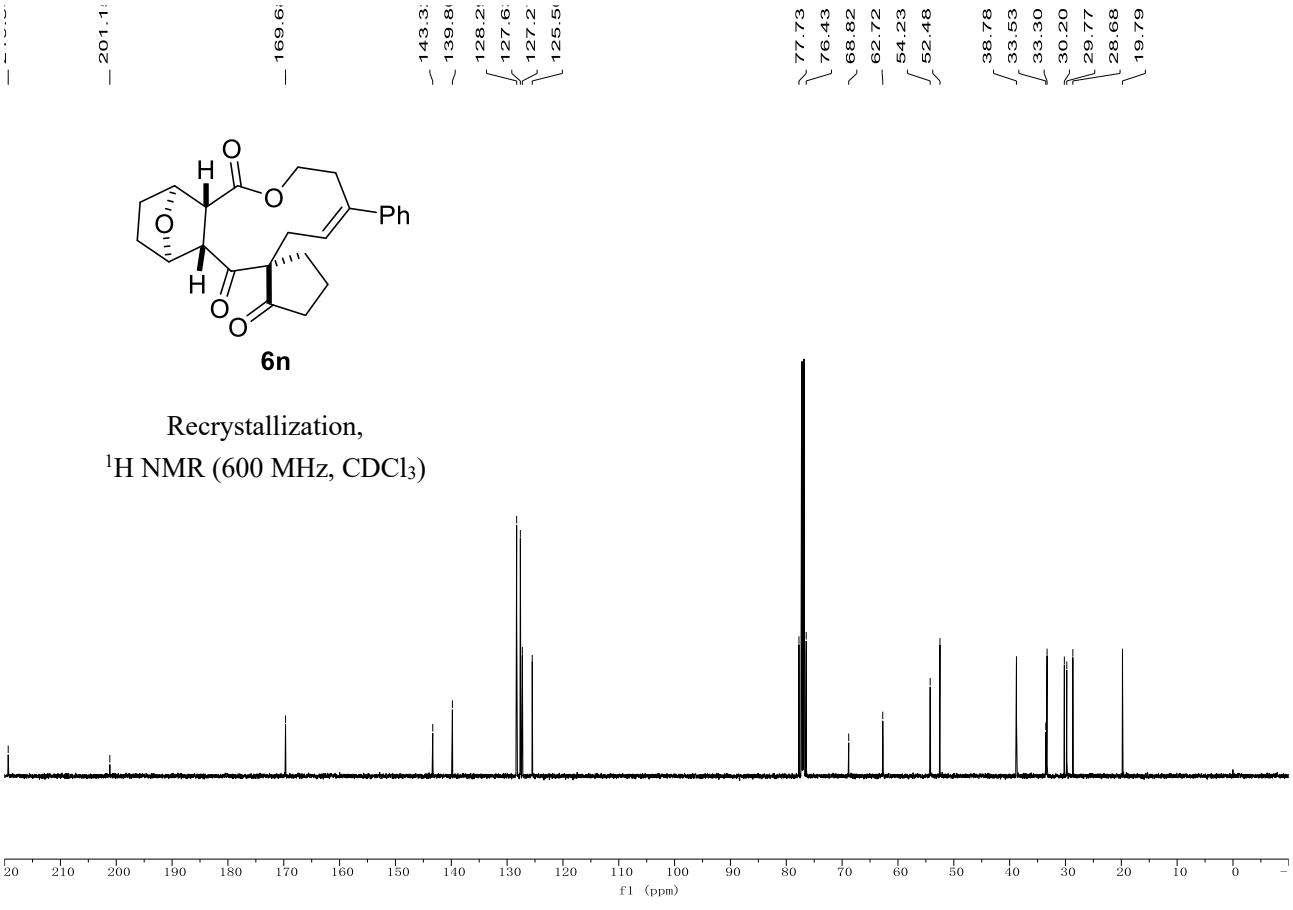
dr = 10:1;

^{1}H NMR (600 MHz, $CDCl_3$)



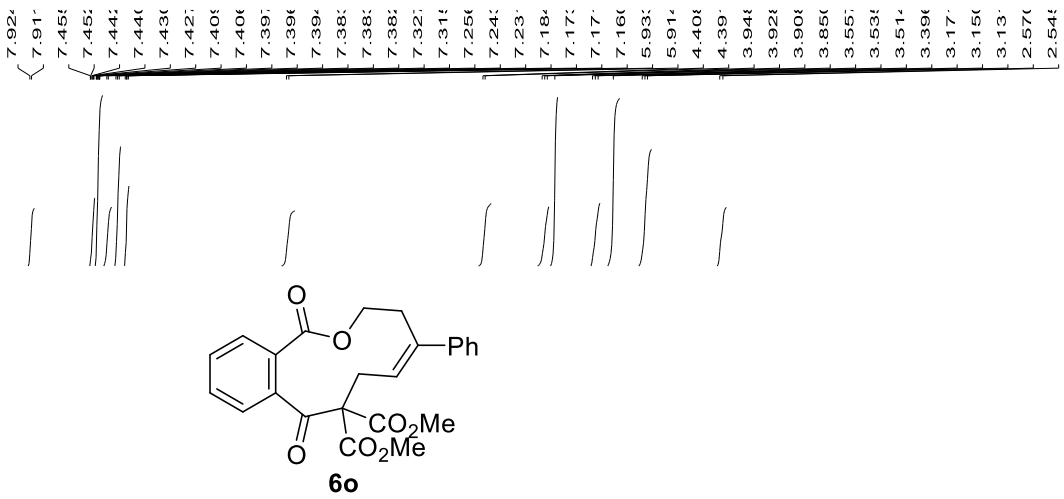
6n

Recrystallization,
^{1}H NMR (600 MHz, $CDCl_3$)



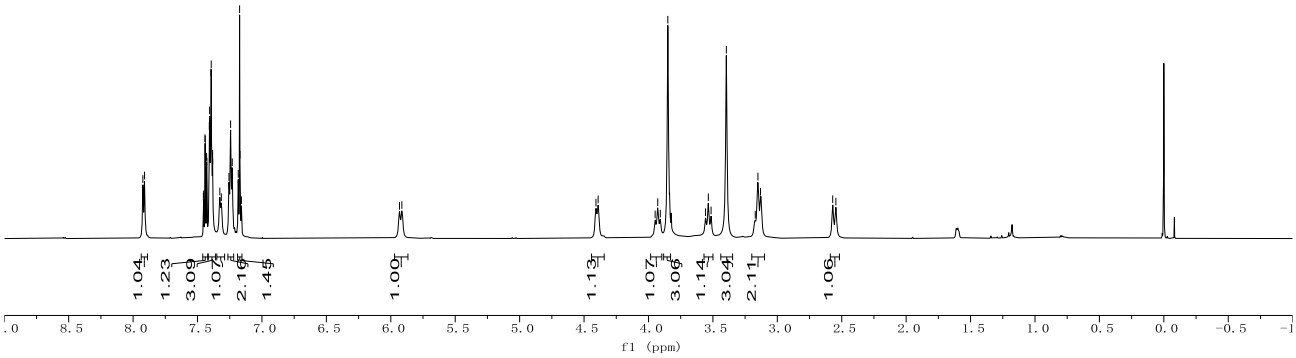
6n

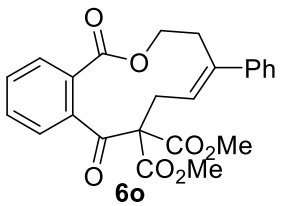
Recrystallization,
^{1}H NMR (600 MHz, $CDCl_3$)



6o

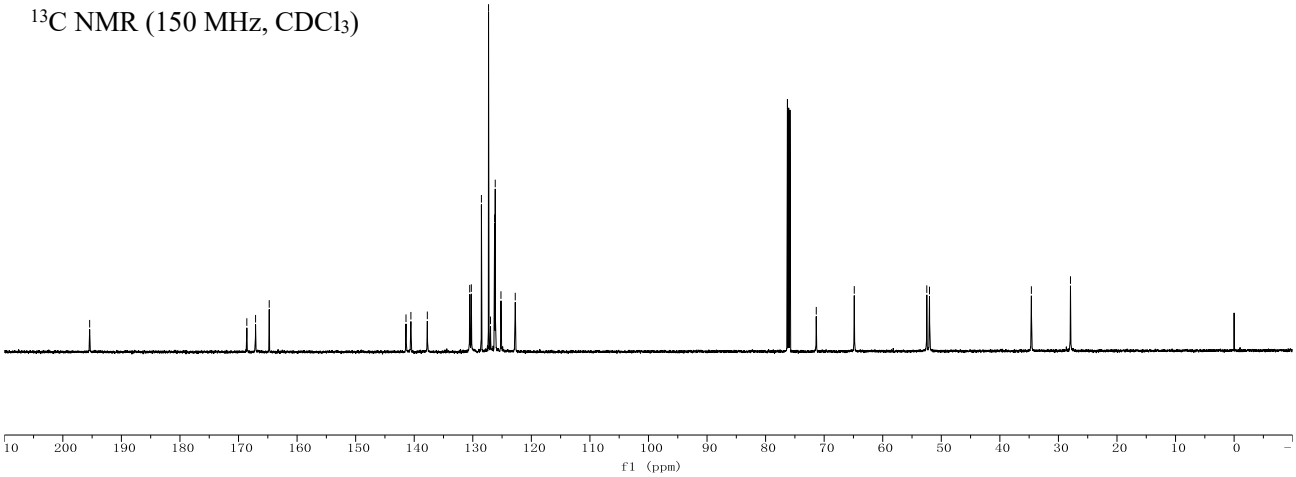
^{1}H NMR (600 MHz, $CDCl_3$)

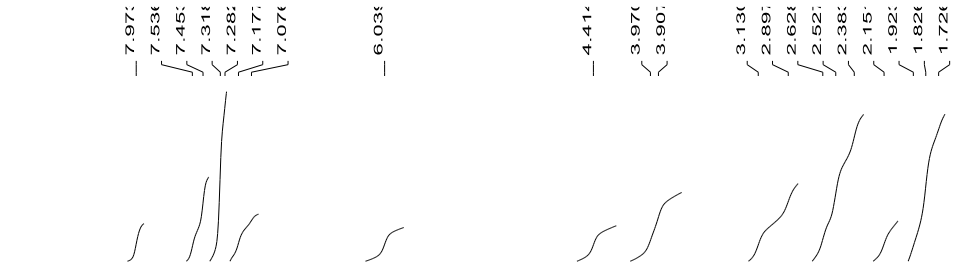


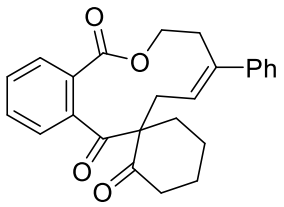


6o

^{13}C NMR (150 MHz, $CDCl_3$)

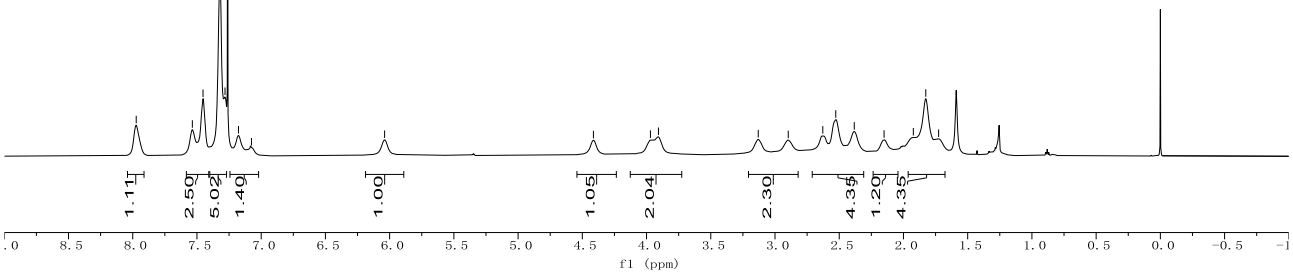


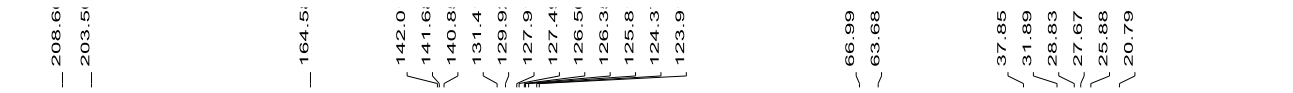


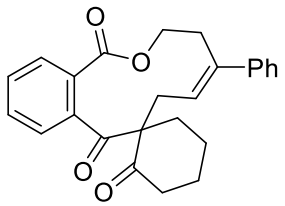


6p

^{1}H NMR (600 MHz, $CDCl_3$)

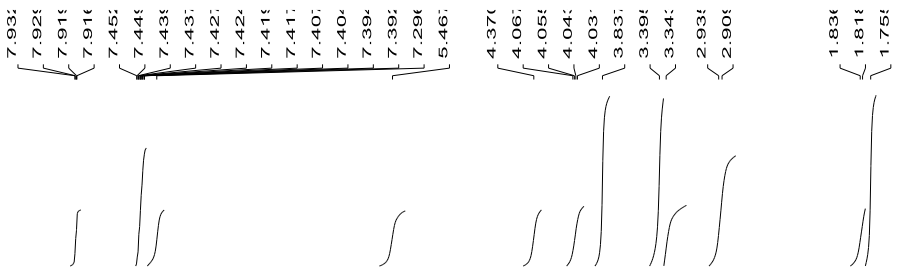


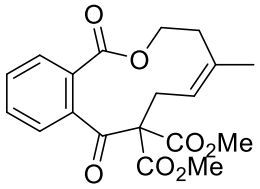




6p

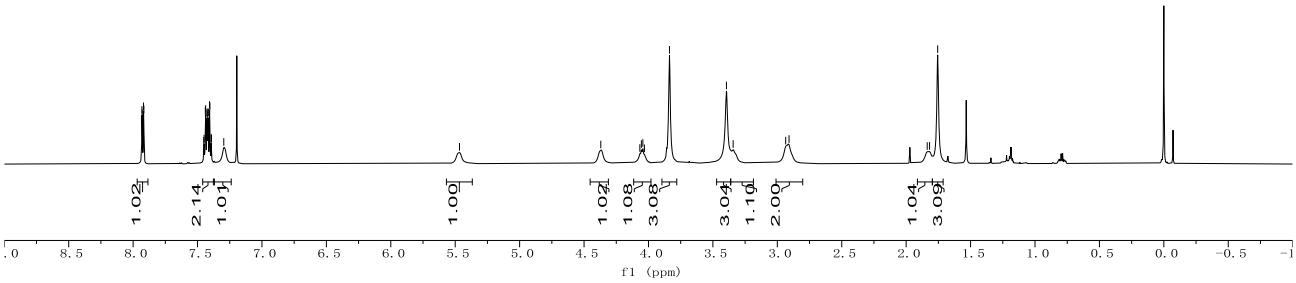
^{13}C NMR (150 MHz, $CDCl_3$)

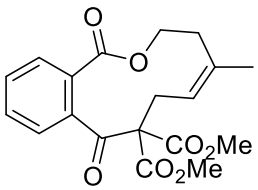




6q

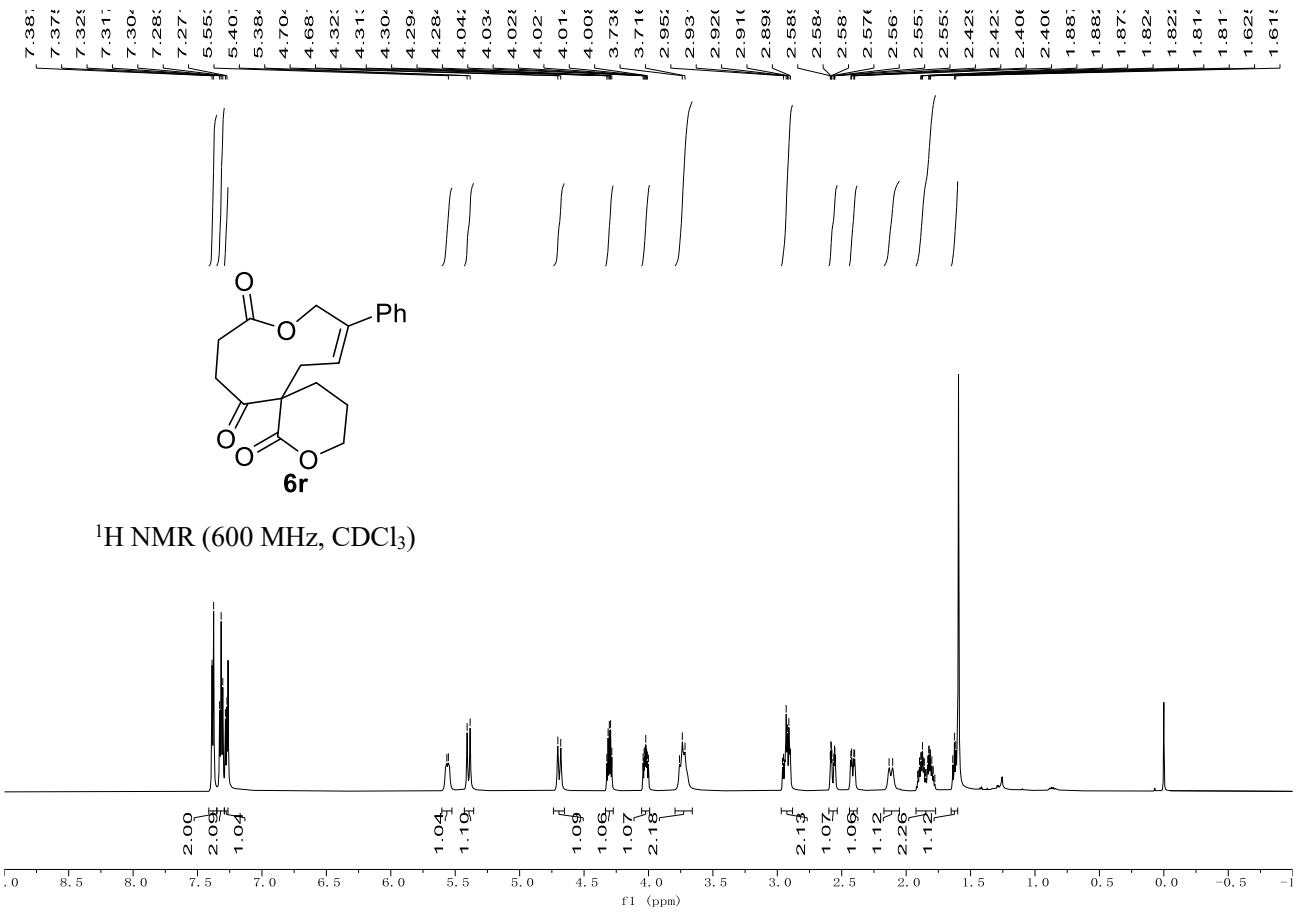
^{1}H NMR (600 MHz, $CDCl_3$)



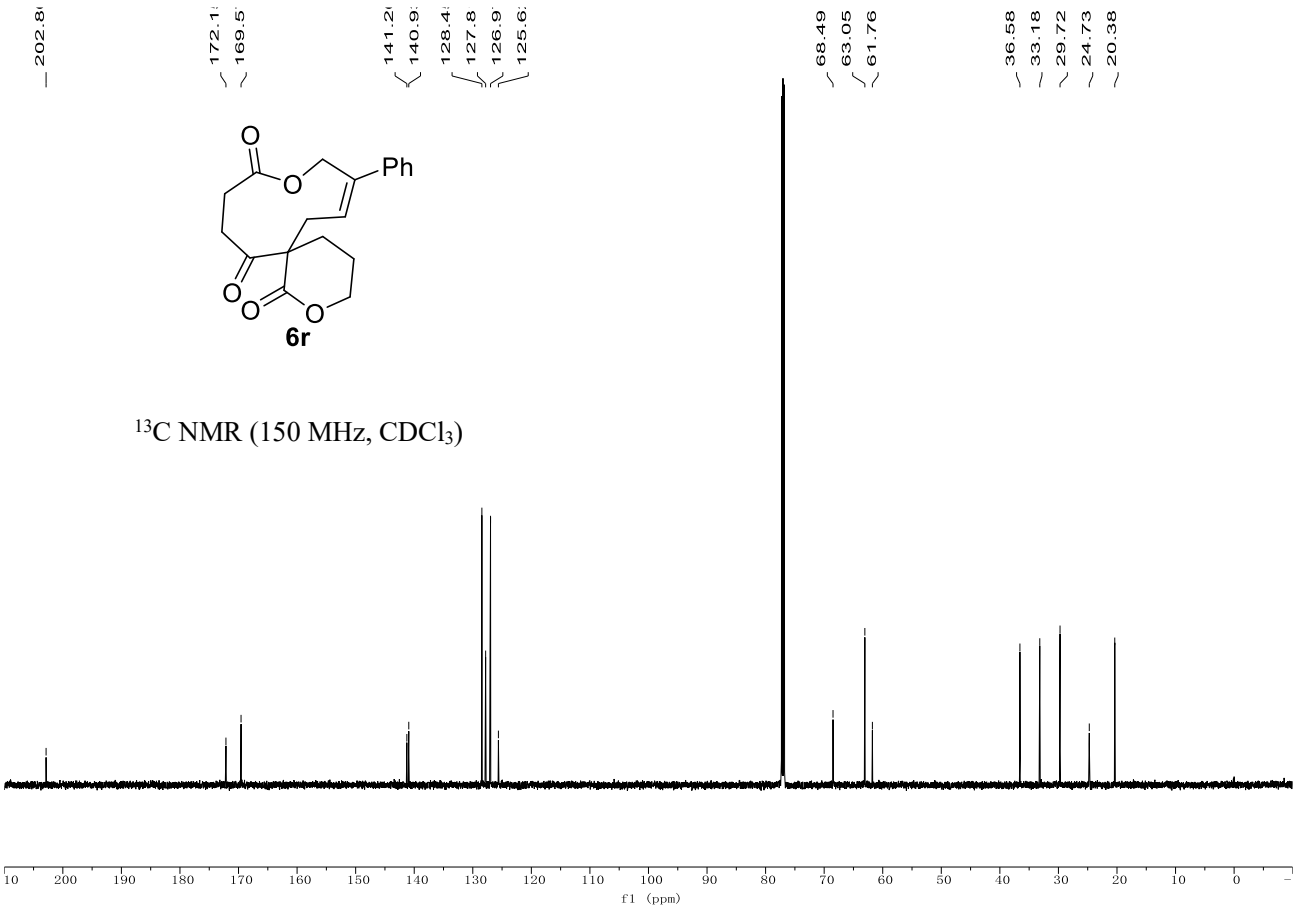


6q

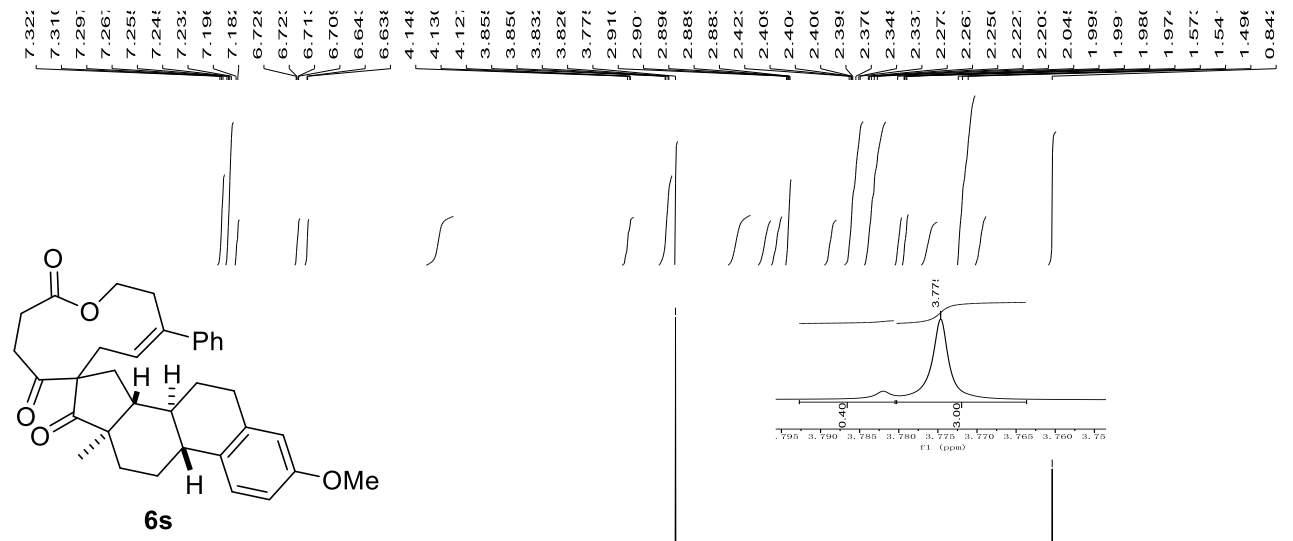
^{13}C NMR (150 MHz, $CDCl_3$)



^{1}H NMR (600 MHz, $CDCl_3$)



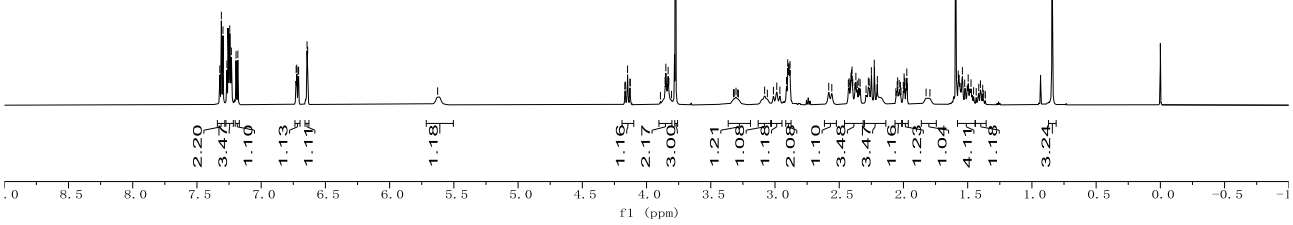
^{13}C NMR (150 MHz, $CDCl_3$)

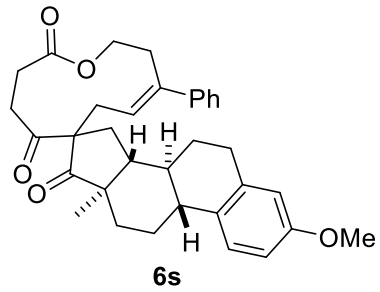


6s

dr = 7.5:1

^{1}H NMR (600 MHz, $CDCl_3$)

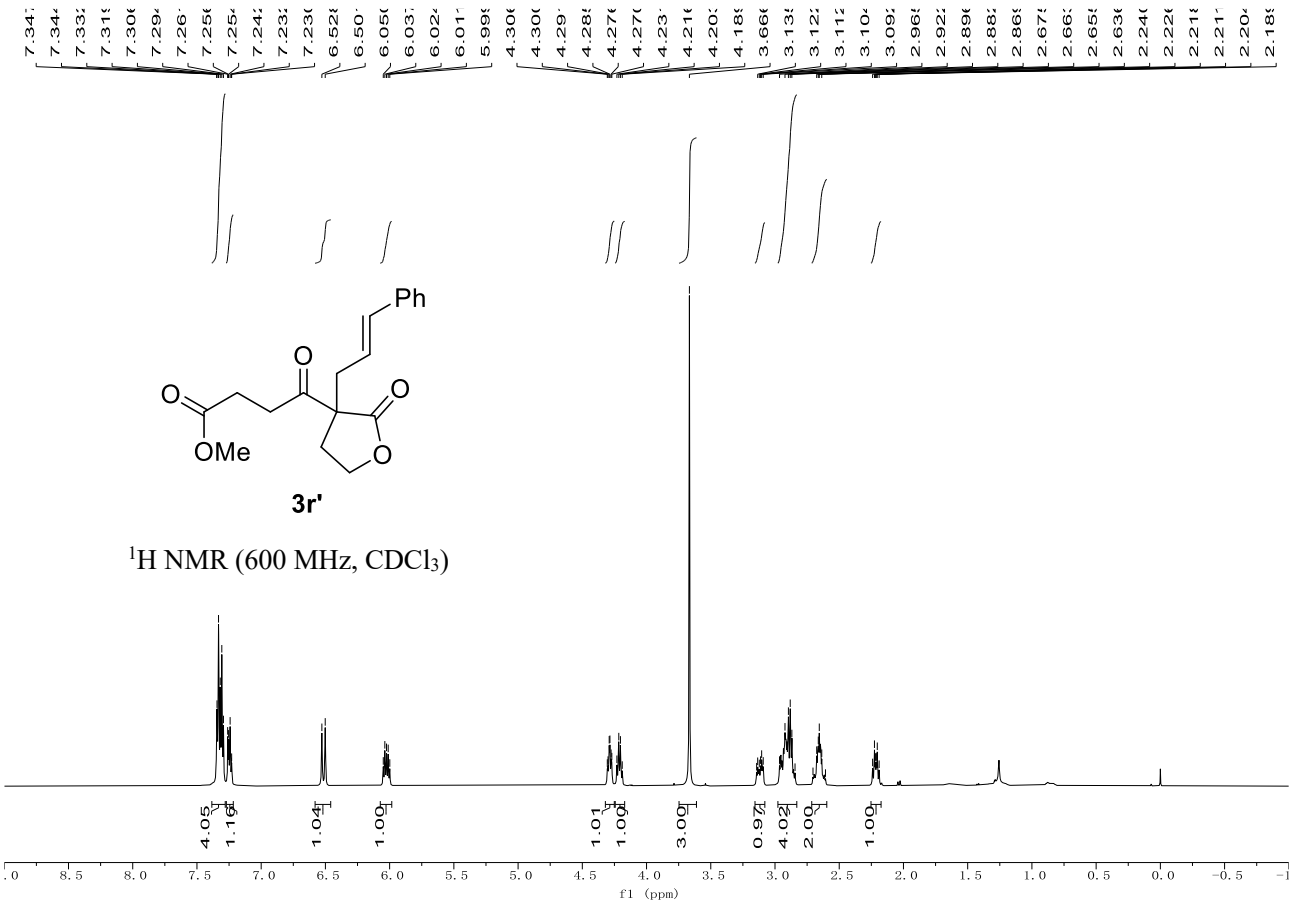




6s

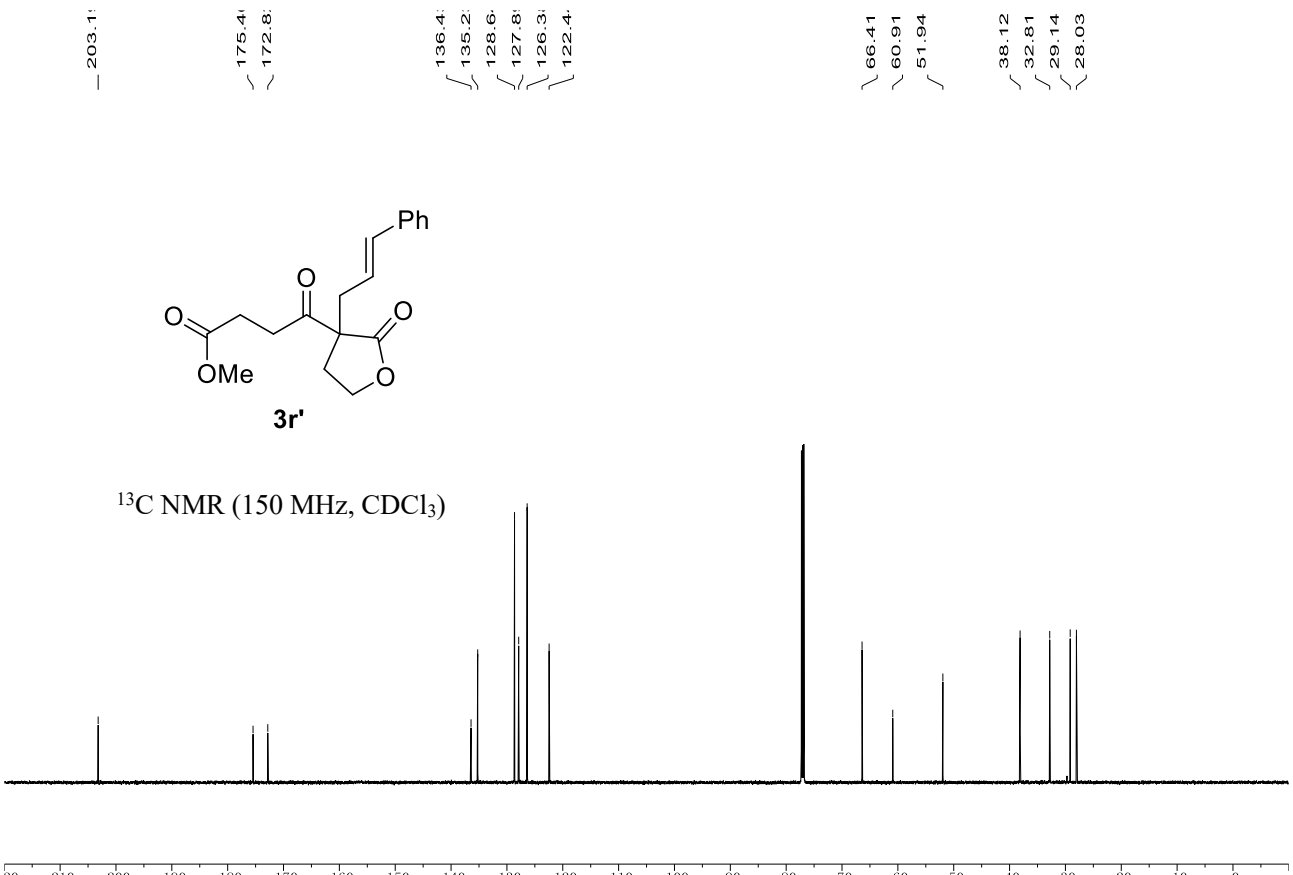
dr = 7.5:1

^{13}C NMR (150 MHz, $CDCl_3$)



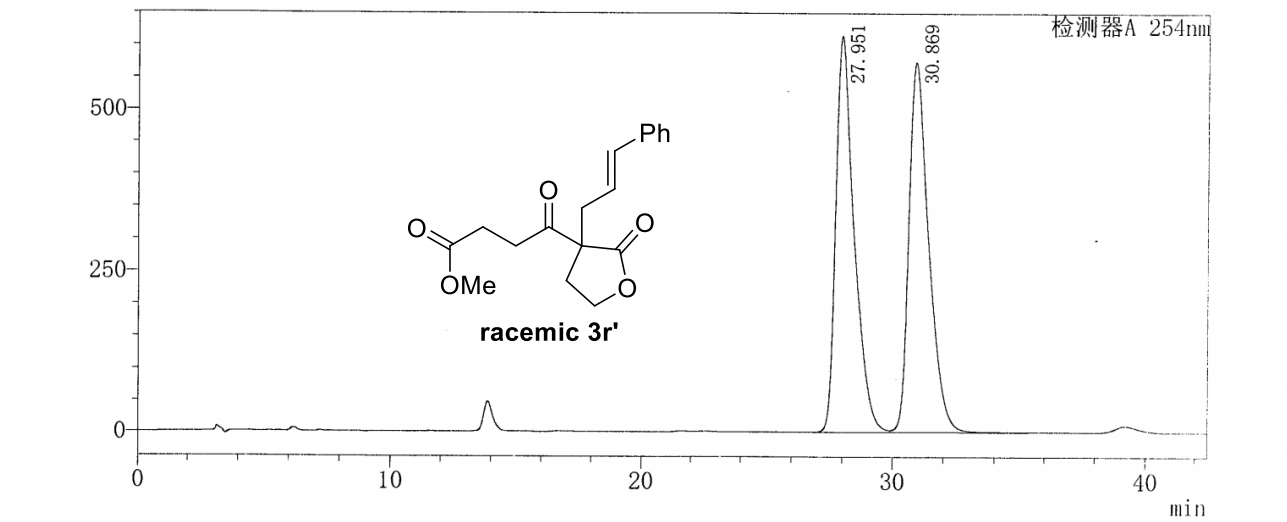
3r'

^{1}H NMR (600 MHz, $CDCl_3$)

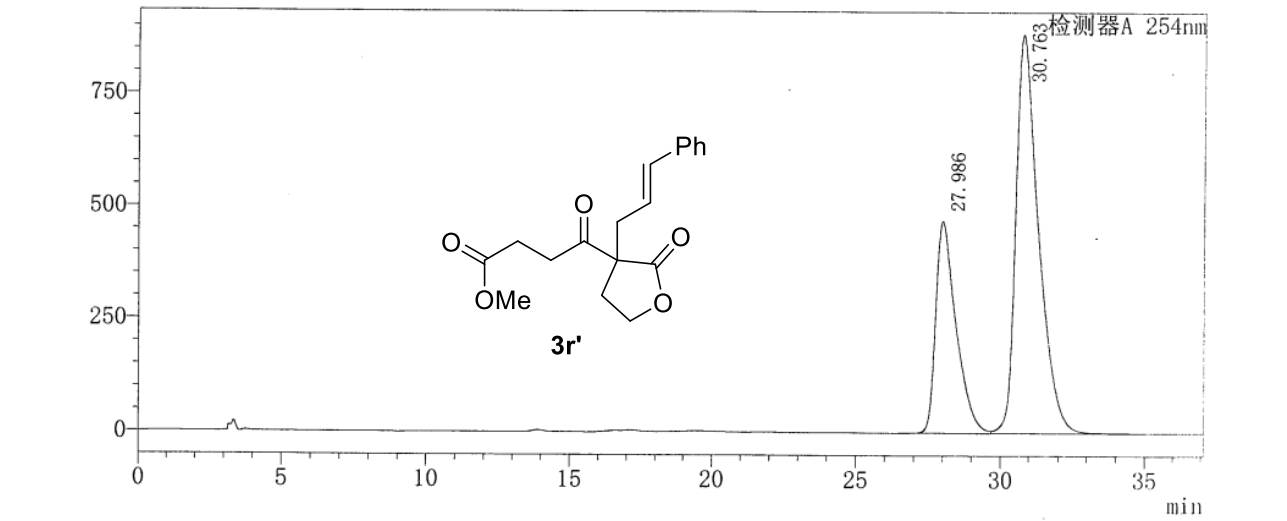


3r'

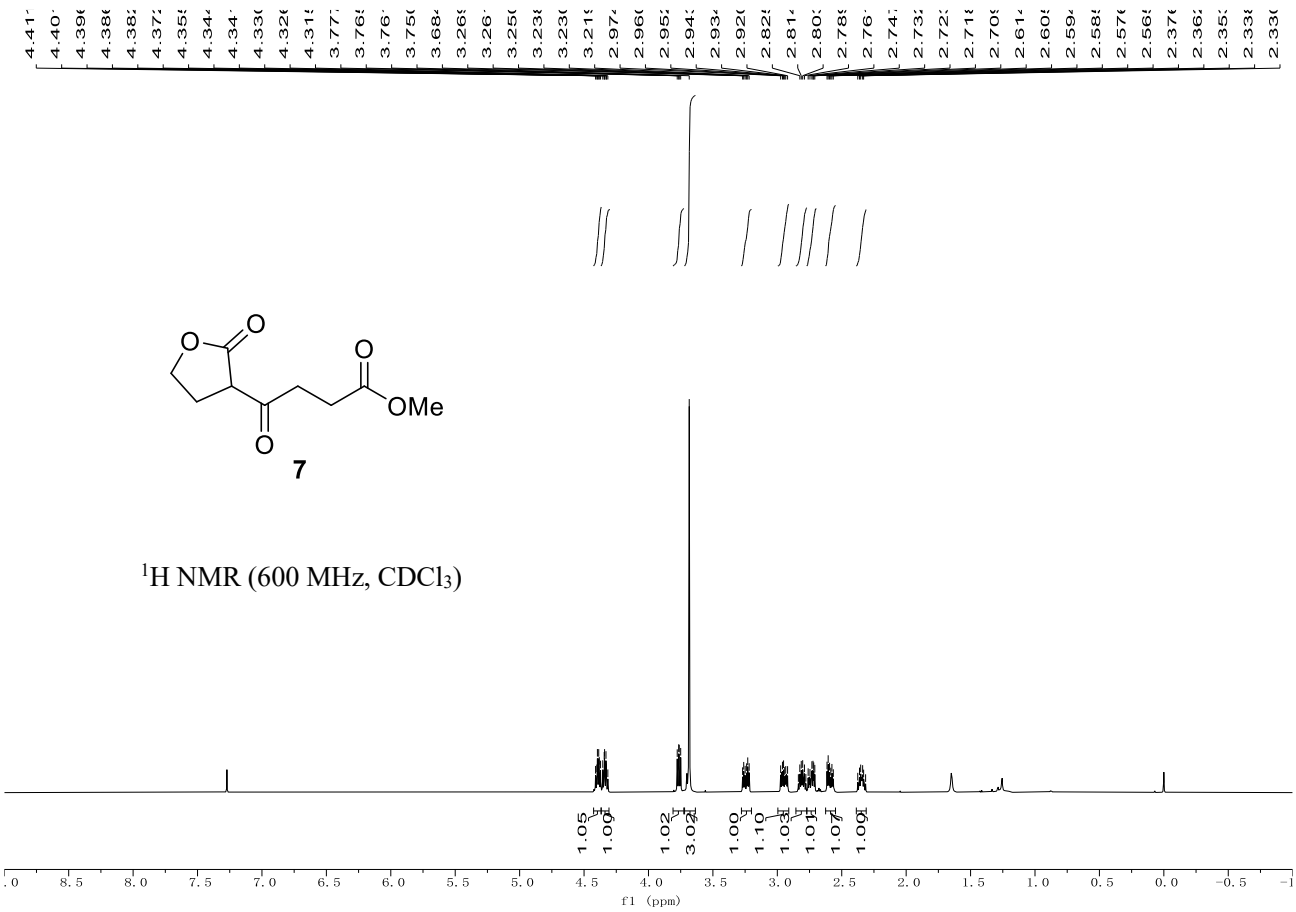
^{13}C NMR (150 MHz, $CDCl_3$)



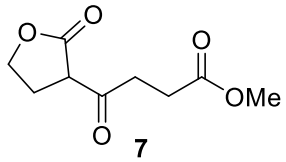
	Retention Time	Area	Height	Area%
1	27.951	31184948	615007	49.924
2	30.869	31280265	574172	50.076
Total		62465213	1189179	100.000



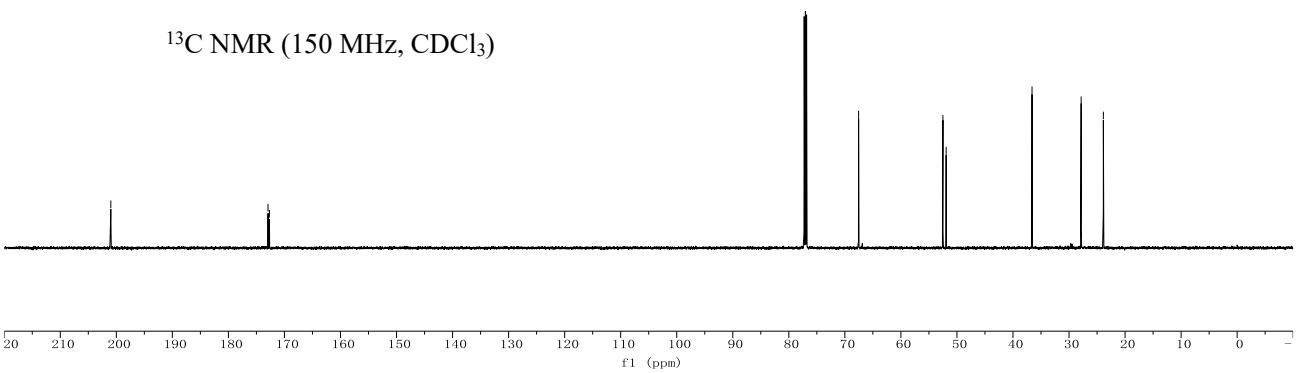
	Retention Time	Area	Height	Area%
1	27.986	23438811	469749	32.490
2	30.763	48702745	885193	67.510
Total		72141556	1354943	100.000

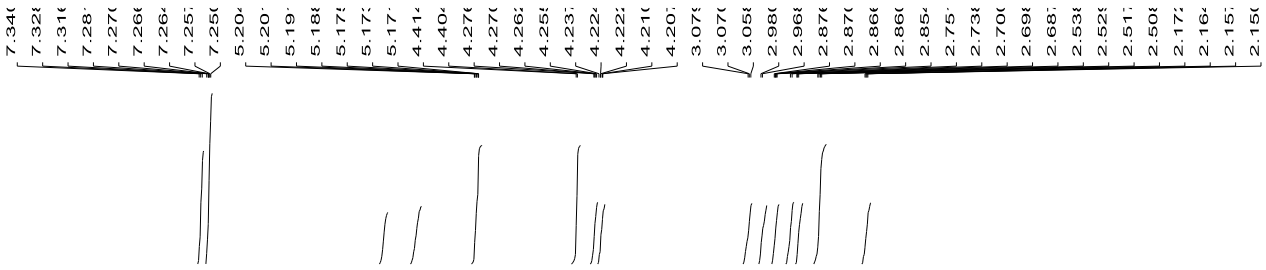


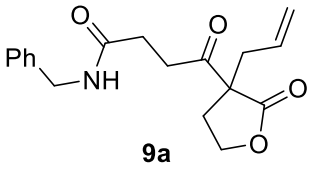
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (150 MHz, $CDCl_3$)

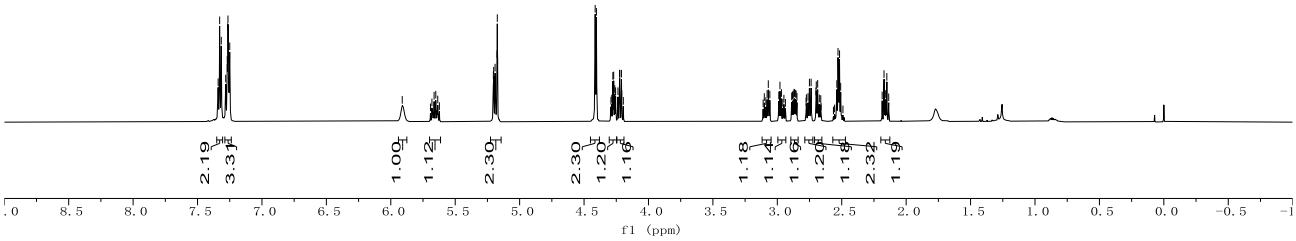


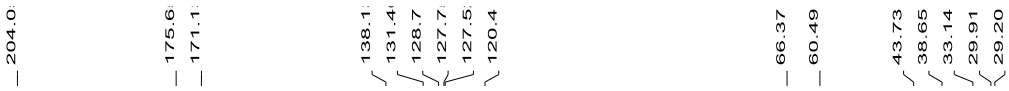


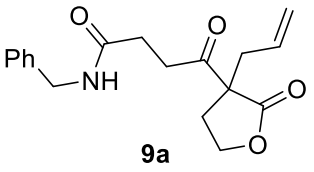


9a

^{1}H NMR (600 MHz, $CDCl_3$)

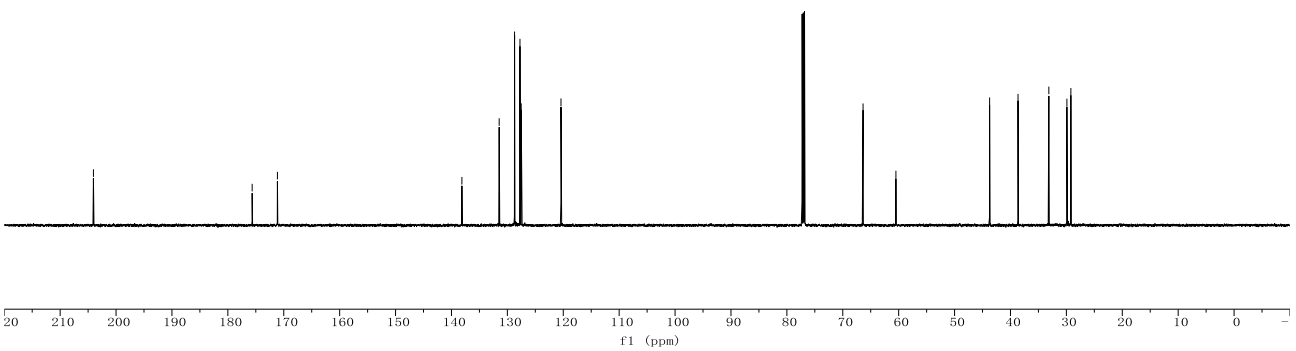


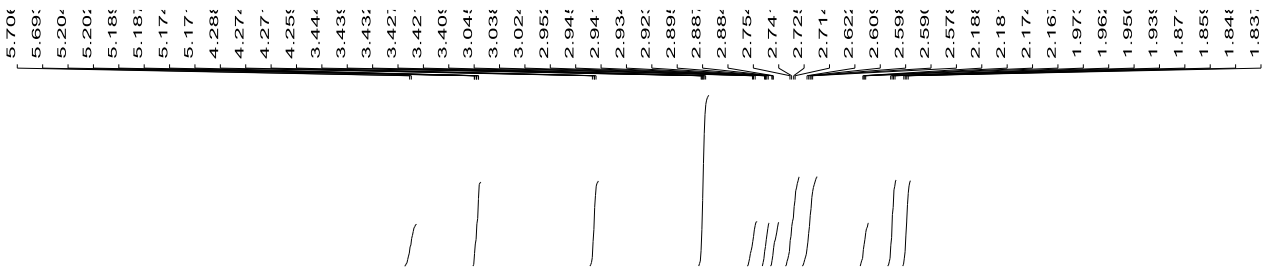


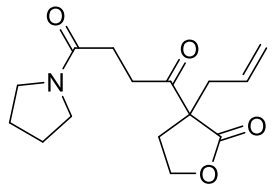


9a

^{13}C NMR (150 MHz, $CDCl_3$)

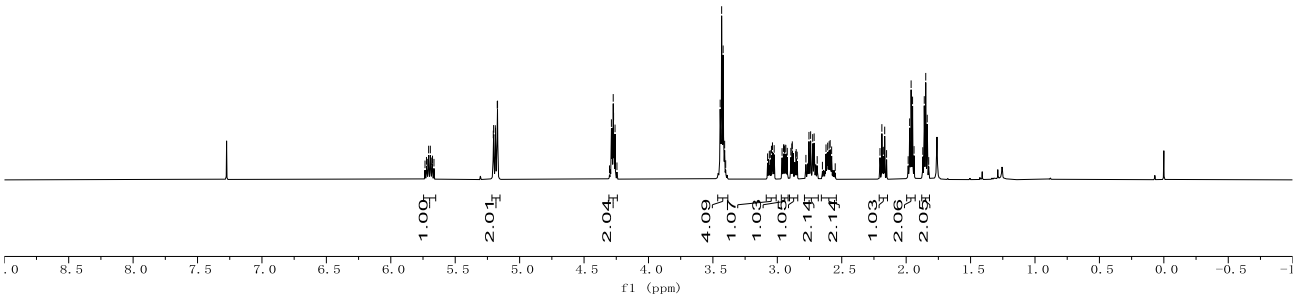


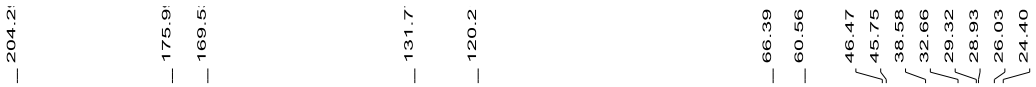


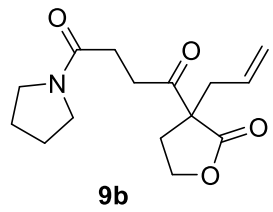


9b

^{1}H NMR (600 MHz, $CDCl_3$)

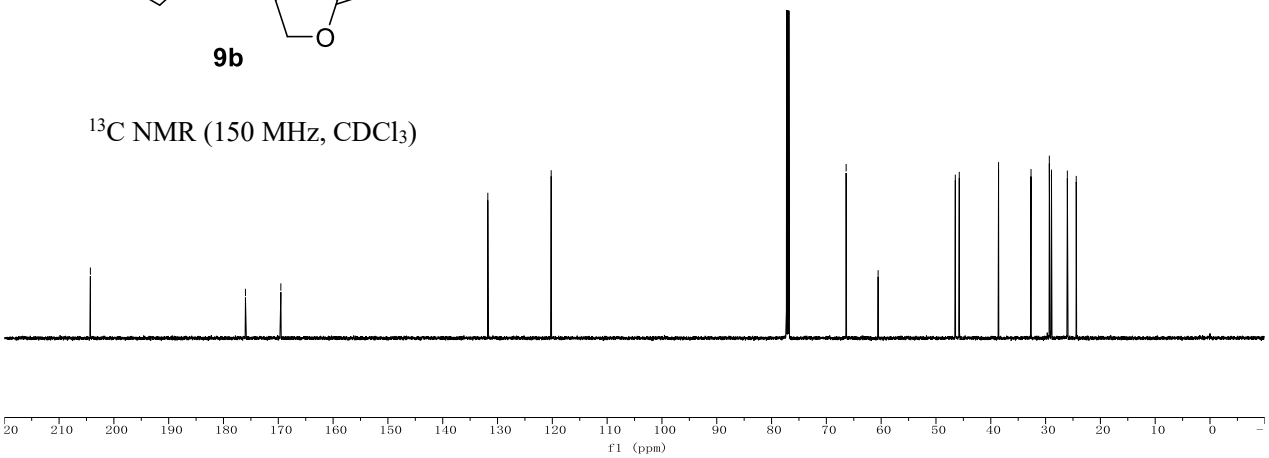


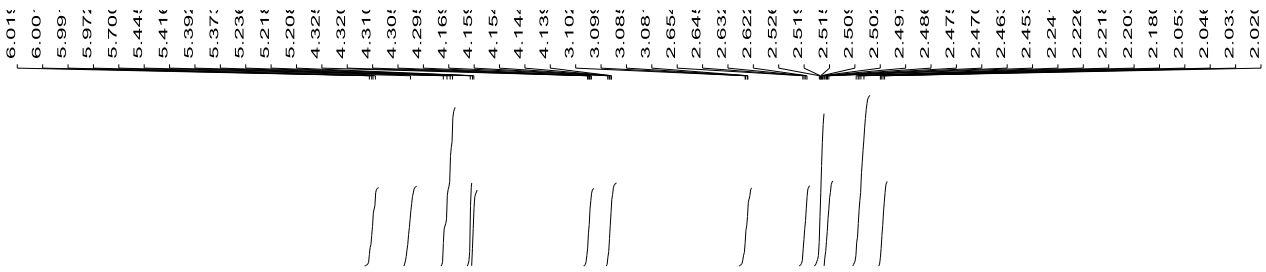


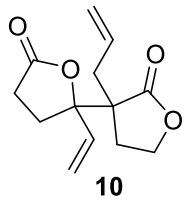


9b

^{13}C NMR (150 MHz, $CDCl_3$)

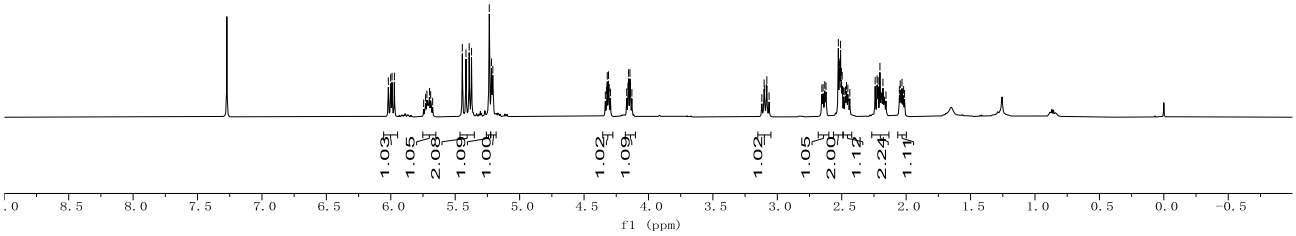


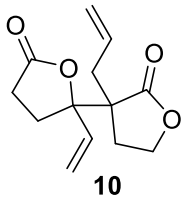




10

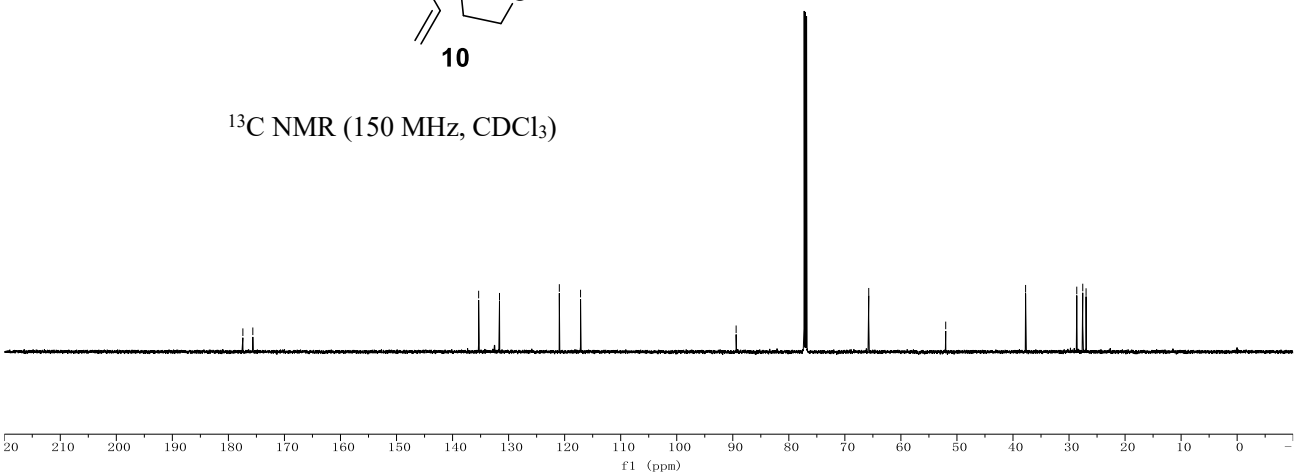
^{1}H NMR (600 MHz, $CDCl_3$)

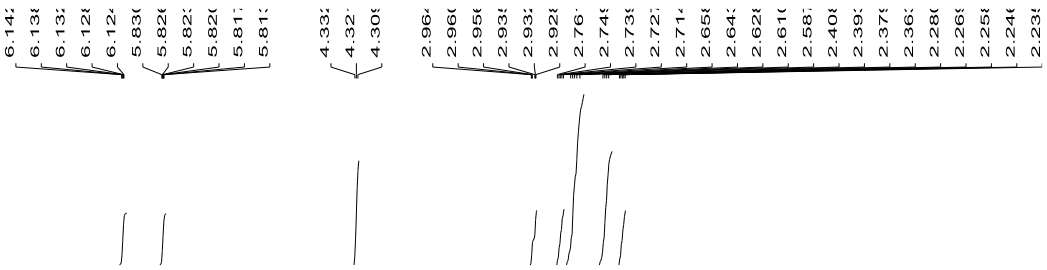


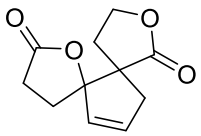


10

^{13}C NMR (150 MHz, $CDCl_3$)

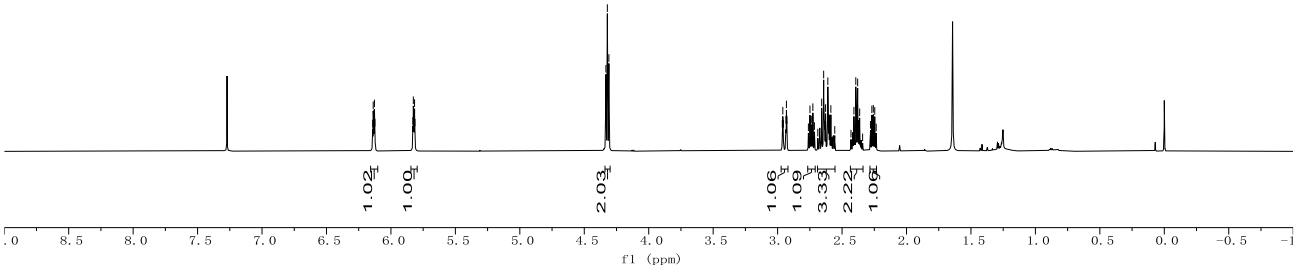


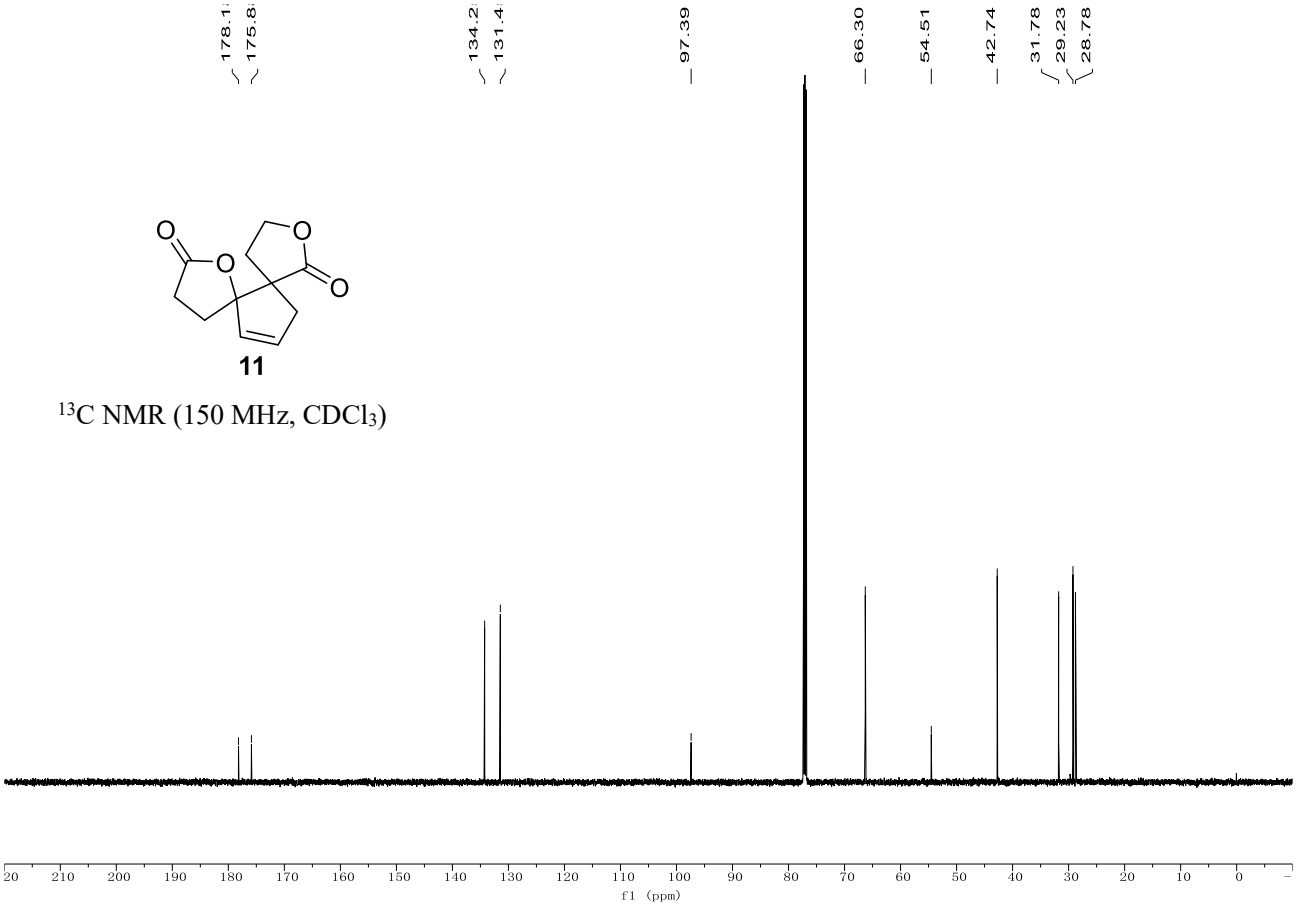




11

^{1}H NMR (600 MHz, $CDCl_3$)





11

^{13}C NMR (150 MHz, $CDCl_3$)