Supplementary Information (SI) for Chemical Communications.
This journal is © The Royal Society of Chemistry 2025

SUPPORTING INFORMATION

Merging Halogen Atom Transfer, Ring-Expansion and Oxidation by Electron-rich Arenediazonium Salts: Modular Assembly of Cyclohexenone Derivatives

Guodong Zhang,*[a] Xiaowen Teng,[a] Duo Zhang,*[b] Wei Tan,[a] Bingxin Xu,[b] Shuli Wang,[a] Xiang Li,*[c] Pan Gao,[a] and Feng Chen*[a]

[a]School of Chemistry and Chemical Engineering, Yangzhou University, Siwangting Road 180, 225002, Yangzhou (China). *Email: guodong.zhang@yzu.edu.cn; feng.chen@yzu.edu.cn.

[b]Medicine Center, Guangxi University of Science and Technology, Liushi Road 257, 545006, Liuzhou, Guangxi (China). *Email: duo.zhang@gxust.edu.cn.

[c]College of Chemistry and Chemical Engineering, Shaanxi University of Science and Technology, Xi'an, 710021, Shaanxi (China). E-mail: lix@sust.edu.cn

Table of Contents

Table of Contents 2

General Information 4

Preparation of the Starting Materials 5

Synthesis and Characterization of the Corresponding Products 8

Unsuccessful Substrates: 16

Control Experiments: 16

Gram Scale Reaction and Late-stage Modifications 17

Mechanistic Studies 18

References 19

Copies of ^{1}H, and ^{13}C spectra 20

General Information

Chemicals and solvents were either purchased (puriss p.A.) from commercial suppliers or purified by standard procedures prior to use. Reactions were performed in oven-dried glassware under an argon atmosphere containing a Teflon-coated stirring bar and dry septum. All reactions were monitored by GC using dodecane as an internal standard. Analytical TLC was performed with silica gel GF254 plates, and the products were visualized by UV detection. Flash column chromatography as performed over silica gel (200-300 mesh). NMR spectra were recorded on an Agilent DD2 400 MHz spectrometers using $CDCl_3$ or DMSO-d_6 as solvents with proton (400 MHz), and carbon (101 MHz) resonances. Chemical shifts (δ values) were reported in ppm relative to internal $CDCl_3$ (^{13}C NMR), and spin-spin coupling constants (*J*) were given in Hz. The High-resolution mass spectral (HRMS) data were obtained on Bruker Daltonics maXis Q-TOF (ESI).

All 0.2 mmol scale reactions were carried out in 10-mL vessels containing stirring bars, 5 mmol scale reaction was performed in a 200-mL vessel containing a stirring bar. Every vessel is sealed with a rubber stopper and connected with a balloon filled with argon gas.

Caution: a significant amount of nitrogen gas will be released during the reaction.

Figure S1 shows a 10-mL and a 200-mL reaction vessels.

Figure S1. reaction vessels and oil bath.

After each oven-dried reaction vessel was cooled to rt, the vessel was charged with all solid starting materials. After that, the vessel was sealed and flushed with three alternating vacuum and argon purge cycles. Then against a stream of argon, solvent was added via syringe, and then the vessel was stirred at room temperature.

Preparation of the Starting Materials

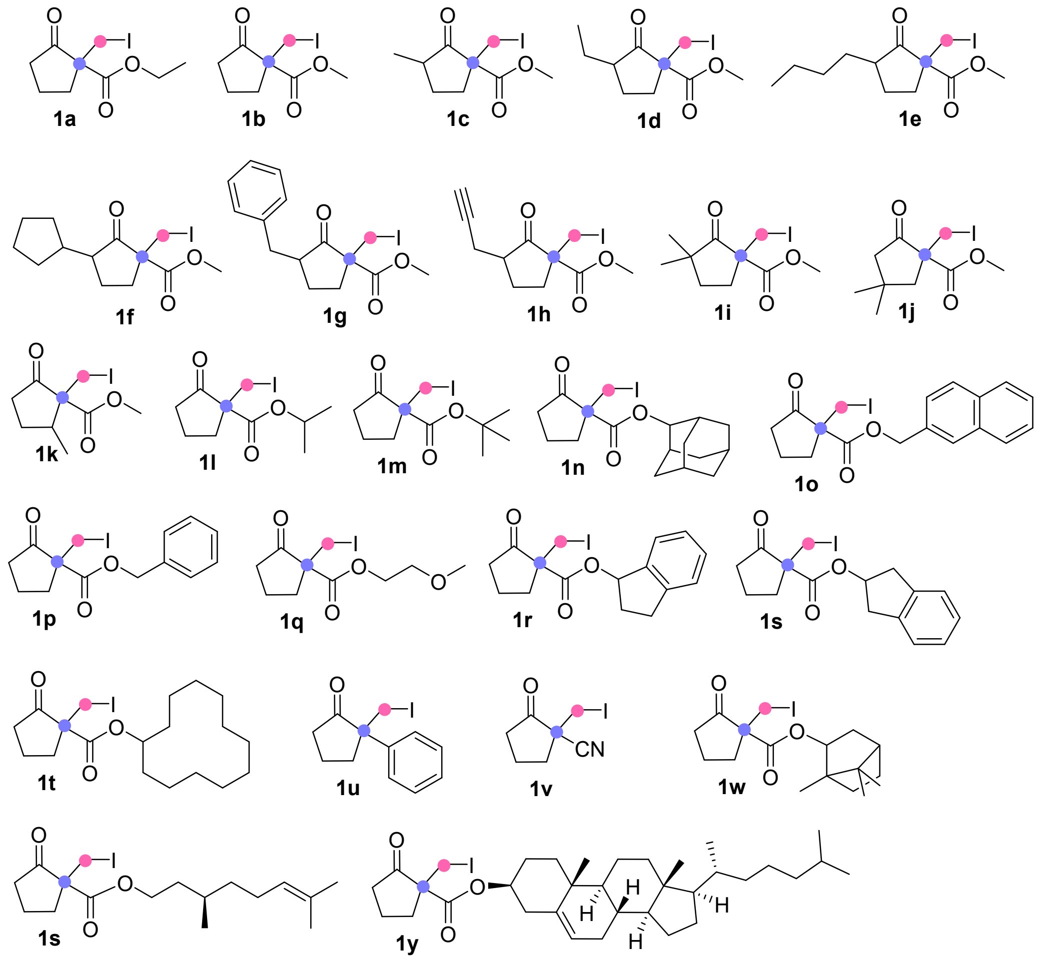
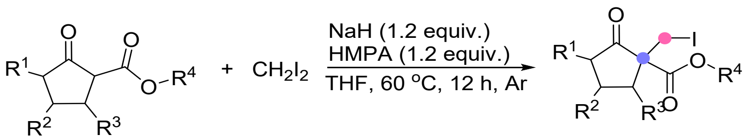


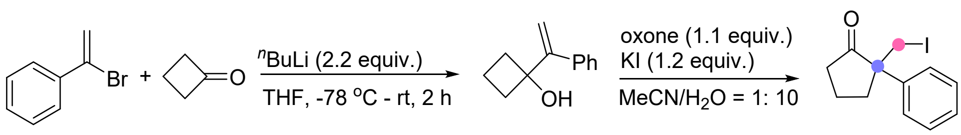
Figure S2. Starting materials.

Starting materials **1a-1t, 1w-1y** were prepared according to the following procedure.[1,2]



A solution of 5.0 mmol of 2 cyclic β-keto esters in 10 mL of dry THF was added slowly to a suspension of 0.24 g (6.0 mmol, 60% dispersion in mineral oil) of NaH in 5.0 mL of dry THF containing hexamethylphosphoramide (HMPA, 1.1 g, 6.0 mmol) at room temperature under argon. The reaction mixture was stirred at room temperature for 1.0 h, and then treated with 6.8 g (25.0 mmol) of diiodomethane. The reaction mixture was stired at 60 °C for 12 h, then washed with water (50.0 mL), extracted with ethyl acetate (50.0 mL × 3), dried over Na_2SO_4, filtered, and concentrated in vacuum. Purification of the residue by flash column chromatography (petroleum ether/ ethyl acetate) on silica gel provided target product.

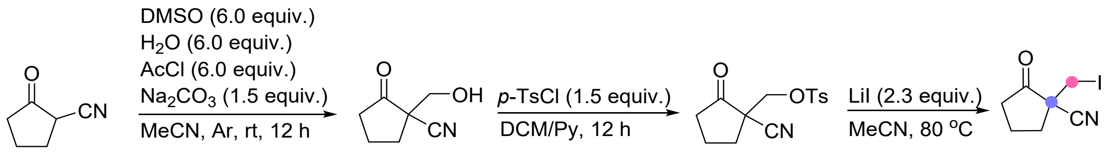
Starting material **1u** was prepared according to the following procedure.[3]



Step i：To a solution of α-bromostyrene (5.0 mmol, 1.0 equiv.) in dry THF (40 mL) at -78 °C was added slowly ^{n}BuLi (11 mmol, 2.2 equiv.) and the reaction mixture was stirred for 30 min at this temperature. Then, the cyclic ketone (5.5 mmol, 1.1 equiv.) was added slowly to the reaction mixture and the mixture was stirred for 30 min. The reaction was allowed to warm to room temperature and stirred for another 1.0 h, and then quenched with aqueous NH_4Cl. The organic phase was collected and the aqueous phase was extracted with ethyl acetate (3×30 mL). The combined organic fractions were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using eluents (petroleum ether/ethyl acetate = 20/1) to give the allylic alcohol.

Step ii: To a stirred solution of allylic alcohol substrate (2 mmol) in the MeCN/H_2O (1/10, 11 mL) at 0 °C were added KI (2.4 mmol, 1.2 equiv) and oxone (676 mg, 1.1 eq). After completion of the addition, the resulting mixture was stirred for 10 min before warmed to room temperature and stirred for an additional 1 h. When the allylic alcohol substrate was fully consumed as determined by TLC analysis, the reaction was quenched by addition of saturated aqueous Na_2SO_3 (20 mL). The organic layer was collected and the aqueous layer was extracted with ethyl acetate (3×30 mL). The combined organic fractions were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using eluents (petroleum ether/ethyl acetate = 20/1) to provide the compound **1s**.

Starting material **1v** was prepared according to the following procedure.[2]

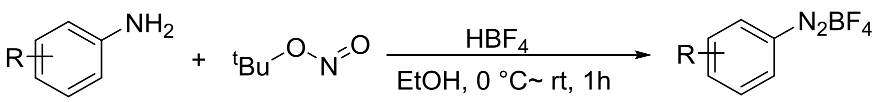


Step i：To a dry reaction tube was added freshly distilled dry MeCN (9 mL), AcCl (27.0 mmol, 3.0 equiv) under nitrogen atmosphere. Then the reaction mixture was stirred at room temperature. DMSO (54 mmol, 6.0 equiv) in dry MeCN (6 mL) was added dropwise to the above reaction mixture, and then H2 O (54.0 mmol, 6.0 equiv) and Na2 CO3 (13.5 mmol, 1.5 equiv.) were added successively. Finally, cyclic ketone (9.0 mmol) was added dropwise to the above reaction mixture. After the completion of the reaction as judged by TLC analysis, the reaction mixture was purified by column chromatography on silica gel to give desired products.[4]

Step ii: To a solution of the cyclic ketone derivative (5.3 mmol, 1.0 equiv.) in DCM\Pyridine = 1:1 (20 mL) at room temperature was added *p*-TsCl (3.0 g, 3.0 equiv.) and the reaction mixture was stirred for 12 h. When the allylic alcohol substrate was fully consumed as determined by TLC analysis, the reaction was diluted with DCM and washed with 1M HCl aqueous. The organic layer was collected and the aqueous layer was extracted with DCM (3×30 mL). The combined organic fractions were washed with brine, dried over Na 2 SO4 , and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using eluents (petroleum ether/ethyl acetate = 4/1) to provide the desired compound.[5]

Step iii: To a solution of cyclic ketone (1.0 g; 3.4 mmol) in dry MeCN (24 ml) was added 1.05 g (7.82 mmol) of dry lithium iodide. The reaction mixture was refluxed for 4 h and the solvent removed under reduced pressure. The residue was dissolved in dry diethyl ether (12 mL) and the organic layer was washed with water (2 x 6 mL), dried and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using eluents (petroleum ether/ethyl acetate = 10/1) to provide the desired compound **1v**.[5]

Arenediazonium salts were prepared according to the following procedure.[6]

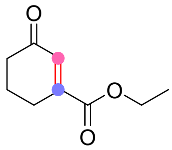


To The aniline (10 mmol) was dissolved in a mixture of absolute ethanol (3 mL) and an aqueous solution of HBF_4 (50%, 2.5 mL, 20 mmol) and *tert*-butyl nitrite (2.7 mL, 20 mmol) was added dropwise to the solution at 0 °C. The reaction was stirred at room temperature for 1 h and diethyl ether (20 mL) was added to precipitate the arenediazonium tetrafluoroborate that was filtered off and washed with diethyl ether (3 × 10 mL). The arenediazonium tetrafluoroborate was dried in vacuo for 10 minutes and was then directly used without further purification.

Synthesis and Characterization of the Corresponding Products

General Procedure: An oven-dried 10 mL glass vial was charged with starting material **1** (0.2 mmol, 1.0 equiv.), arenediazonium salt **2b** (103.4 mg, 0.44 mmol, 2.2 equiv.). Under an argon atmosphere, acetone (2 mL) and triethylamine (56 μL, 0.4 mmol, 2 equiv.) were added via syringe. The mixture was then stirred rapidly at room temperature for 12 h. After the reaction was completed, saturated sodium carbonate solution (10 mL) was added and the resulting mixture was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and the volatiles were removed under reduced pressure. The residue was purified by column chromatography to yield the corresponding product.

ethyl 3-oxocyclohex-1-ene-1-carboxylate (3a)



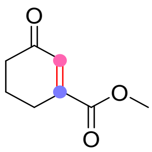
Compound **3a** was prepared following the above General Procedure, starting from **1a** (59.2 mg, 0.20 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 15: 1), **3a** was afforded as orange oil liquid (24.2 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.69 (t, *J* = 1.6 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 2.54 (td, *J* = 6.0, 1.6 Hz, 2H), 2.45 – 2.35 (m, 2H), 2.10 – 1.96 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 200.1, 166.4, 149.1, 132.7, 61.5, 37.6, 24.7, 22.0, 14.0 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_9H_{13}O_3^+$ 169.0859; Found 169.0856.

methyl 3-oxocyclohex-1-ene-1-carboxylate (3b)



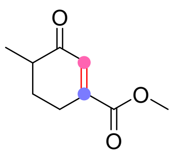
Compound **3b** was prepared following the above General Procedure, starting from **1b** (56.4 mg, 0.20 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 15: 1), **3b** was afforded as orange oil liquid (16.9 mg, 55%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.71 (t, *J* = 2.0 Hz, 1H), 3.81 (s, 3H), 2.56 (td, *J* = 6.0, 2.0 Hz, 2H), 2.47 – 2.39 (m, 2H), 2.08 – 2.00 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 200.0, 166.9, 148.7, 133.0, 52.6, 37.6, 24.8, 22.1 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_8H_{11}O_3^+$155.0703; Found 155.0712.

methyl 4-methyl-3-oxocyclohex-1-ene-1-carboxylate (3c)



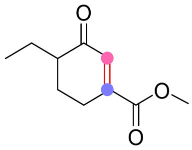
Compound **3c** was prepared following the above General Procedure, starting from **1c** (59.2 mg, 0.20 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 15: 1), **3c** was afforded as yellow oil liquid (22.8 mg, 68%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.70 (d, *J* = 2.4 Hz, 1H), 3.80 (s, 3H), 2.75 – 2.63 (m, 1H), 2.59 – 2.45 (m, 1H), 2.45 – 2.32 (m, 1H), 2.19 – 2.06 (m, 1H), 1.78 – 1.64 (m, 1H), 1.13 (d, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 202.5, 170.0, 147.9, 132.6, 52.5, 41.4, 30.1, 24.5, 14.6 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_9H_{13}O_3^+$ 169.0859; Found 169.0866.

methyl 4-ethyl-3-oxocyclohex-1-ene-1-carboxylate (3d)



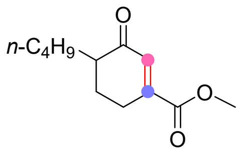
Compound **3d** was prepared following the above General Procedure, starting from **1d** (62.0 mg, 0.20 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 12: 1), **3d** was afforded as yellow oil liquid (15.6 mg, 43%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.72 – 6.68 (m, 1H), 3.82 (s, 3H), 2.75 – 2.63 (m, 1H), 2.57 – 2.45 (m, 1H), 2.26 – 2.11 (m, 2H), 1.91 – 1.71 (m, 2H), 1.51 – 1.36 (m, 1H), 0.94 (t, *J* = 7.6 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 202.1, 167.0, 147.6, 132.9, 52.5, 47.7, 26.7, 24.1, 21.9, 11.3 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{10}H_{15}O_3^+$ 183.1016; Found 183.1013.

methyl 4-butyl-3-oxocyclohex-1-ene-1-carboxylate (3e)



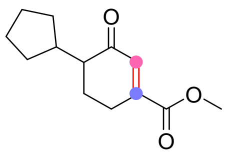
Compound **3e** was prepared following the above General Procedure, starting from **1e** (67.6 mg, 0.20 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 12: 1), **3e** was afforded as yellow oil liquid (26.1 mg, 62%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.71 (s, 1H), 3.82 (s, 3H), 2.76 – 2.63 (m, 1H), 2.59 – 2.45 (m, 1H), 2.34 – 2.23 (m, 1H), 2.23 – 2.12 (m, 1H), 1.91 – 1.71 (m, 2H), 1.43 – 1.29 (m, 5H), 0.90 (t, *J* = 6.4 Hz, 3H) ppm**.**

^{13}C NMR (101 MHz, $CDCl_3$): δ 202.3, 167.1, 147.6, 132.9, 52.5, 46.3, 29.0, 28.6, 27.2, 24.1, 22.7, 14.0 ppm.

HRMS (ESI-TOF) m/z: $[M+K]^+$ Calcd for $C_{12}H_{18}O_3K^+$ 249.0888; Found 249.0886.

methyl 4-cyclopentyl-3-oxocyclohex-1-ene-1-carboxylate (3f)



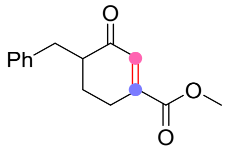
Compound **3f** was prepared following the above General Procedure, starting from **1f** (70.0 mg, 0.20 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 15: 1), **3f** was afforded as yellow oil liquid (20.4 mg, 46%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.68 (s, 1H), 3.82 (s, 3H), 2.71 – 2.61 (m, 1H), 2.57 – 2.47 (m, 1H), 2.26 – 2.18 (m, 1H), 2.17 – 2.07 (m, 2H), 1.99 – 1.88 (m, 1H), 1.84 – 1.69 (m, 2H), 1.68 – 1.60 (m, 2H), 1.57 – 1.47 (m, 2H), 1.29 – 1.23 (m, 1H), 1.22 – 1.14 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 202.4, 167.1, 147.3, 133.0, 52.5, 51.2, 38.4, 30.7, 30.2, 25.5, 25.1, 25.0, 23.5 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{19}O_3^+$ 223.1329; Found 223.1327.

methyl 4-benzyl-3-oxocyclohex-1-ene-1-carboxylate (3g)



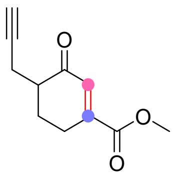
Compound **3g** was prepared following the above General Procedure, starting from **1g** (74.4 mg, 0.20 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 10: 1), **3g** was afforded as colorless oily liquid (21.0 mg, 43%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 – 7.22 (m, 2H), 7.22 – 7.10 (m, 3H), 6.73 (s, 1H), 3.79 (s, 3H), 3.31 – 3.26 (m, 1H), 2.70 – 2.60 (m, 1H), 2.58 – 2.45 (m, 2H), 2.45 – 2.33 (m, 1H), 2.07 – 1.95 (m, 1H), 1.68 – 1.59 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 201.0, 166.9, 148.0, 139.4, 132.8, 129.1, 128.4, 126.3, 52.6, 48.2, 35.0, 26.6, 24.4 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{17}O_3^+$ 245.1172; Found 245.1187.

methyl 3-oxo-4-(prop-2-yn-1-yl)cyclohex-1-ene-1-carboxylate (3h)



Compound **3h** was prepared following the above General Procedure, starting from **1h** (64.0 mg, 0.20 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 10: 1), **3h** was afforded as yellow solid (27.6 mg, 72%).

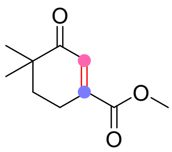
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.76 – 6.71 (m, 1H), 3.82 (s, 3H), 2.85 – 2.70 (m, 2H), 2.60 – 2.37 (m, 3H), 2.37 – 2.28 (m, 1H), 1.98 (t, J = 2.4 Hz, 1H), 1.92 – 1.80 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 199.4, 166.7, 148.5, 132.6, 81.5, 70.0, 52.6, 45.4, 27.1, 24.8, 18.7 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{11}H_{13}O_3^+$ 193.0859; Found 193.0855.

M.P.: 45 – 48 °C.

methyl 4,4-dimethyl-3-oxocyclohex-1-ene-1-carboxylate (3i)



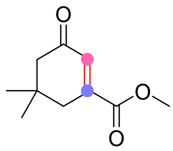
Compound **3i** was prepared following the above General Procedure, starting from **1i** (62.0 mg, 0.20 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 15: 1), **3i** was afforded as yellow oil liquid (24.8 mg, 68%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.64 (s, 1H), 3.81 (s, 3H), 2.58 (td, J = 6.4, 2.0 Hz, 2H), 1.85 (t, J = 6.0 Hz, 2H), 1.10 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 204.8, 166.9, 146.8, 131.8, 52.5, 41.1, 35.6, 23.7, 22.3 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{10}H_{15}O_3^+$ 183.1016; Found 183.1013.

methyl 5,5-dimethyl-3-oxocyclohex-1-ene-1-carboxylate (3j)



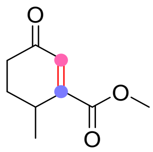
Compound **3j** was prepared following the above General Procedure, starting from **1j** (62.0 mg, 0.20 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 15: 1), **3j** was afforded as yellow oil liquid (22.5 mg, 62%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.75 (s, 1H), 3.82 (s, 3H), 2.47 (d, J = 2.0 Hz, 2H), 2.29 (s, 2H), 1.06 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 200.4, 167.1, 146.6, 132.2, 52.6, 51.4, 38.8, 33.5, 28.1 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{10}H_{15}O_3^+$ 183.1016; Found 183.1013.

methyl 6-methyl-3-oxocyclohex-1-ene-1-carboxylate (3k)



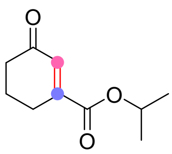
Compound **3k** was prepared following the above General Procedure, starting from **1k** (59.2 mg, 0.20 mmo). After column chromatography on silica (Petroleum Ether: EtOAc = 15: 1), **3k** was afforded as yellow oil liquid (12.8 mg, 38%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.61 (s, 1H), 3.82 (s, 3H), 3.02 – 2.93 (m, 1H), 2.63 – 2.51 (m, 1H), 2.40 (dt, J = 17.4, 4.5 Hz, 1H), 2.17 (tt, J = 13.4, 4.9 Hz, 1H), 1.88 (dq, J = 13.6, 4.4 Hz, 1H), 1.24 (d, J = 7.0 Hz, 3H) ppm。

^{13}C NMR (101 MHz, $CDCl_3$): δ 200.0, 166.8, 153.3, 131.9, 52.5, 33.4, 29.0, 28.7, 18.0 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_9H_{13}O_3^+$ 169.0859; Found 169.0866.

isopropyl 3-oxocyclohex-1-ene-1-carboxylate (3l)



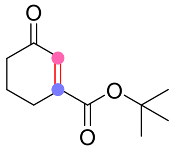
Compound **3l** was prepared following the above General Procedure, starting from **1l** (62.0 mg, 0.20 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 15: 1), **3l** was afforded as yellow oil liquid (21.8 mg, 60%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.76 – 6.68 (m, 1H), 5.20 – 5.05 (m, 1H), 2.63 – 2.52 (m, 2H), 2.50 – 2.38 (m, 2H), 2.13 – 1.99 (m, 2H), 1.40 – 1.22 (m, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 200.3, 166.0, 149.6, 132.6, 69.3, 37.7, 24.8, 22.2, 21.7 ppm.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{10}H_{14}O_3Na^+$ 205.0835; Found 205.0827.

tert-butyl 3-oxocyclohex-1-ene-1-carboxylate (3m)



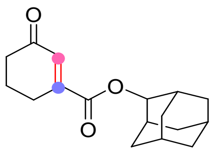
Compound **3m** was prepared following the above General Procedure, starting from **1m** (64.8 mg, 0.20 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 15: 1), **3m** was afforded as yellow oil liquid (29.8 mg, 76%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.65 (s, 1H), 2.56 – 2.48 (m, 2H), 2.45 – 2.37 (m, 2H), 2.07 – 1.98 (m, 2H), 1.50 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 200.6, 165.6, 150.9, 132.3, 82.2, 37.7, 27.9, 24.8, 22.1 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{11}H_{17}O_3^+$ 197.1172; Found 197.1167.

adamantan-2-yl 3-oxocyclohex-1-ene-1-carboxylate (3n)



Compound **3n** was prepared following the above General Procedure, starting from **1n** (80.4 mg, 0.20 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 15: 1), **3n** was afforded as white solid (18.1 mg, 33%).

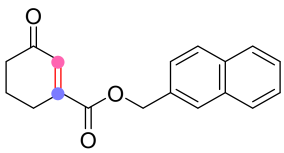
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.79 (t, J = 2.0 Hz, 1H), 5.09 – 5.03 (m, 1H), 2.61 (td, J = 6.0, 2.0 Hz, 2H), 2.49 – 2.42 (m, 2H), 2.13 – 1.97 (m, 6H), 1.91 – 1.83 (m, 4H), 1.82 – 1.72 (m, 4H), 1.63 – 1.56 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 200.4, 149.9, 132.6, 78.4, 37.7, 37.2, 36.2, 31.8, 27.1, 26.8, 24.9, 22.1 ppm.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{22}O_3Na^+$ 297.1461; Found 297.1462.

M.P.: 72 – 75 °C.

naphthalen-2-ylmethyl 3-oxocyclohex-1-ene-1-carboxylate (3o)



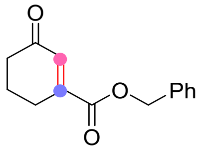
Compound **3o** was prepared following the above General Procedure, starting from **1o** (81.6 mg, 0.20 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 15: 1), **3o** was afforded as yellow oil liquid (27.5 mg, 49%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 8.4 Hz, 1H), 7.89 (t, J = 8.8 Hz, 2H), 7.61 – 7.51 (m, 3H), 7.49 – 7.44 (m, 1H), 6.78 – 6.73 (m, 1H), 5.72 (s, 2H), 2.59 (td, J = 6.0, 1.6 Hz, 2H), 2.46 – 2.39 (m, 2H), 2.09 – 1.98 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 200.1, 166.3, 148.8, 133.7, 133.2, 131.6, 130.7, 129.6, 128.8, 127.8, 126.8, 126.0, 125.2, 123.3, 65.7, 37.6, 24.8, 22.1 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{17}O_3^+$ 281.1172; Found 281.1186.

benzyl 3-oxocyclohex-1-ene-1-carboxylate (3p)



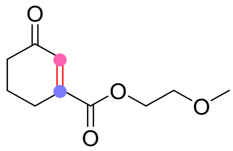
Compound **3p** was prepared following the above General Procedure, starting from **1p** (71.6 mg, 0.20 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 15: 1), **3p** was afforded as yellow oil liquid (26.7 mg, 58%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 – 7.32 (m, 5H), 6.79 (s, 1H), 5.25 (s, 2H), 2.64 – 2.57 (m, 2H), 2.49 – 2.41 (m, 2H), 2.12 – 1.99 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 200.1, 166.3, 148.8, 135.2, 133.2, 128.7, 128.5, 128.3, 67.3, 3767, 24.8, 22.1 ppm.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{14}O_3Na^+$ 253.0835; Found 253.0846.

2-methoxyethyl 3-oxocyclohex-1-ene-1-carboxylate (3q)



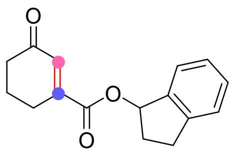
Compound **3q** was prepared following the above General Procedure, starting from **1q** (65.2 mg, 0.20 mmol) with arenediazonium salt **2b** (94 mg, 0.40 mmol, 2.0 equiv.). After column chromatography on silica (Petroleum Ether: EtOAc = 7: 1), **3q** was afforded as yellow oil liquid (30.5 mg, 77%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.77 (s, 1H), 4.38 – 4.34 (m, 2H), 3.67 – 3.63 (m, 2H), 3.39 (s, 3H), 2.59 (td, J = 6.0, 2.0 Hz, 2H), 2.48 – 2.42 (m, 2H), 2.10 – 2.02 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 200.1, 166.5, 148.7, 133.2, 70.1, 64.6, 59.0, 37.7, 24.8, 22.1 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{10}H_{15}O_3^+$ 199.0965; Found 199.0965.

2,3-dihydro-1H-inden-1-yl 3-oxocyclohex-1-ene-1-carboxylate (3r)



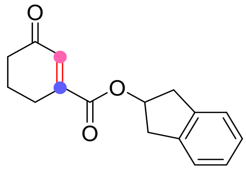
Compound **3r** was prepared following the above General Procedure, starting from **1r** (76.8 mg, 0.20 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 10: 1), **3r** was afforded as yellow oil liquid (28.2 mg, 55%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 – 7.36 (m, 1H), 7.32 – 7.15 (m, 3H), 6.73 – 6.61 (m, 1H), 6.33 – 6.17 (m, 1H), 3.17 – 3.04 (m, 1H), 2.94 – 2.82 (m, 1H), 2.59 – 2.45 (m, 3H), 2.43 – 2.35 (m, 2H), 2.20 – 2.07 (m, 1H), 2.07 – 1.94 (m, 2H) ppm.

^{13}C NMR 101 MHz, $CDCl_3$): δ 200.1, 166.4, 149.2, 144.5, 140.3, 133.0, 129.2, 126.7, 125.6, 124.8, 79.7, 37.6, 32.2, 30.2, 24.8, 22.1 ppm.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{16}O_3Na^+$ 279.0992; Found 279.1018.

2,3-dihydro-1H-inden-2-yl 3-oxocyclohex-1-ene-1-carboxylate (3s)



Compound **3s** was prepared following the above General Procedure, starting from **1s** (76.8 mg, 0.20 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 10: 1), **3s** was afforded as yellow solid (32.3 mg, 63%).

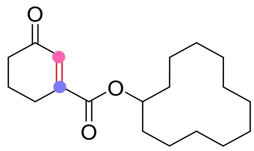
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 – 7.18 (m, 4H), 6.74 – 6.68 (m, 1H), 5.72 – 5.60 (m, 1H), 3.48 – 3.34 (m, 2H), 3.18 – 3.03 (m, 2H), 2.67 – 2.53 (m, 2H), 2.53 – 2.39 (m, 2H), 2.13 – 2.00 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 200.1, 166.4, 149.0, 139.9, 133.0, 126.9, 126.8, 124.6, 39.4, 37.6, 24.7, 22.1 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{17}O_3^+$ 257.1172; Found 257.1189.

M.P.: 75 – 78 °C.

cyclododecyl 3-oxocyclohex-1-ene-1-carboxylate (3t)



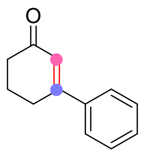
Compound **3t** was prepared following the above General Procedure, starting from **1t** (86.8 mg, 0.20 mmol) with arenediazonium salt **2b** (94 mg, 0.40 mmol, 2.0 equiv.). After column chromatography on silica (Petroleum Ether: EtOAc = 15: 1), **3t** was afforded as yellow oil liquid (36.1 mg, 59%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.71 (s, 1H), 5.16 – 5.05 (m, 1H), 2.58 – 2.54 (m, 2H), 2.46 – 2.40 (m, 2H), 2.08 – 2.01 (m, 2H), 1.79 – 1.72 (m, 2H), 1.57 – 1.53 (m, 2H), 1.39 – 1.33 (m, 18H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 200.3, 166.1, 149.7, 132.6, 74.0, 37.7, 28.9, 24.8, 24.1, 23.9, 23.3, 23.1, 22.1, 20.8 ppm.

HRMS (ESI-TOF) m/z: $[M+K]^+$ Calcd for $C_{19}H_{30}O_3K^+$ 345.1827; Found 345.1805.

5,6-dihydro-[1,1'-biphenyl]-3(4H)-one (3u)



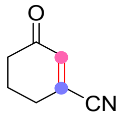
Compound **3u** was prepared following the above General Procedure, starting from **1u** (60.0 mg, 0.20 mmol) with arenediazonium salt **2b** (94 mg, 0.40 mmol, 2.0 equiv.). After column chromatography on silica (Petroleum Ether: EtOAc = 12: 1), **3u** was afforded as colorless oily liquid (12.4 mg, 36%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.51 (m, 2H), 7.44 – 7.38 (m, 3H), 6.45 – 6.38 (m, 1H), 2.78 (td, *J* = 6.0, 1.2 Hz, 2H), 2.52 – 2.45 (m, 2H), 2.20 – 2.12 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 199.9, 159.8, 138.8, 130.0, 128.7, 126.0, 125.4, 37.2, 28.1, 22.8 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{13}O^+$ 173.0961; Found 173.0972 ppm.

3-oxocyclohex-1-ene-1-carbonitrile (3v)



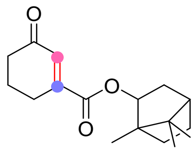
Compound **3v** was prepared following the above General Procedure, starting from **1v** (49.8 mg, 0.20 mmol) with arenediazonium salt **2b** (94 mg, 0.40 mmol, 2.0 equiv.). After column chromatography on silica (Petroleum Ether: EtOAc = 15: 1), **3v** was afforded as colorless oily liquid (7.3 mg, 30%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.53 – 6.50 (m, 1H), 2.61 – 2.45 (m, 4H), 2.18 – 2.06 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 196.3, 138.6, 131.0, 116.9, 37.2, 27.6, 22.0. ppm.

The data is consistent with the literature[7]

1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 3-oxocyclohex-1-ene-1-carboxylate (3w)



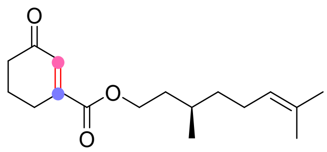
Compound **3w** was prepared following the above General Procedure, starting from **1w** (80.8 mg, 0.20 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 15: 1), **3w** was afforded as yellow oil liquid (36.0 mg, 65%).

^{1}H NMR (400 MHz, $CDCl_3$):δ 6.72 – 6.56 (m, 1H), 4.81 – 4.67 (m, 1H), 2.67 – 2.47 (m, 2H), 2.47 – 2.32 (m, 2H), 2.13 – 1.93 (m, 2H), 1.91 – 1.64 (m, 4H), 1.63 – 1.48 (m, 1H), 1.21 – 1.04 (m, 2H), 0.98 (s, 3H), 0.83 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 200.2, 165.9, 149.6, 132.5, 82.4, 48.9, 46.9, 44.9, 38.7, 37.7, 33.6, 26.9, 24.8, 22.1, 20.0, 19.9, 11.5 ppm.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{24}O_3Na^+$ 299.1618; Found 299.1602.

(R)-3,7-dimethyloct-6-en-1-yl 3-oxocyclohex-1-ene-1-carboxylate (3x)



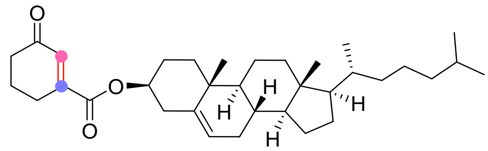
Compound **3x** was prepared following the above General Procedure, starting from **1x** (81.2 mg, 0.20 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 10: 1), **3x** was afforded as yellow oil liquid (30.0 mg, 53%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.73 (s, 1H), 5.08 (t, *J* = 7.2 Hz, 1H), 4.31 – 4.19 (m, 2H), 2.58 (td, *J* = 6.0, 1.6 Hz, 2H), 2.49 – 2.42 (m, 2H), 2.11 – 1.90 (m, 4H), 1.78 – 1.66 (m, 4H), 1.61 – 1.45 (m, 5H), 1.41 – 1.32 (m, 1H), 1.23 – 1.14 (m, 1H), 0.93 (d, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 200.2, 166.6, 149.2, 132.8, 131.5, 124.4, 64.2, 37.7, 36.9, 35.2, 29.4, 25.7, 25.32, 24.8, 22.1, 19.4, 17.7 ppm.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{26}O_3Na^+$301.1774; Found 301.1791.

(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 3-oxocyclohex-1-ene-1-carboxylate (3y)



Compound **3y** was prepared following the above General Procedure, starting from **1y** (127.3 mg, 0.20 mmol). After column chromatography on silica (Petroleum Ether: EtOAc = 12: 1), **3y** was afforded as white solid (43.6 mg, 43%).

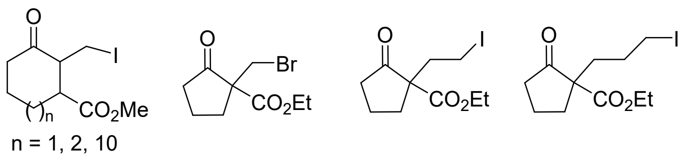
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.74 (s, 1H), 5.46 – 5.36 (m, 1H), 4.82 – 4.62 (m, 1H), 2.60 – 2.55 (m, 1H), 2.52 – 2.41 (m, 2H), 2.41 – 2.32 (m, 2H), 2.09 – 1.98 (m, 3H), 1.93 – 1.80 (m, 3H), 1.63 – 1.44 (m, 8H), 1.29 (s, 6H), 1.18 – 1.08 (m, 6H), 1.05 – 0.99 (m, 5H), 0.95 – 0.89 (m, 4H), 0.88 – 0.84 (m, 6H), 0.68 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 200.3, 165.9, 149.6, 139.2, 132.7, 123.1, 75.4, 56.7, 56.1, 50.0, 42.3, 39.7, 39.5, 37.9, 37.7, 36.9, 36.6, 36.2, 35.8, 31.9, 31.8, 29.7, 28.2, 28.0, 27.6, 24.8, 24.3, 23.8, 22.8, 22.6, 22.2, 21.0, 19.3, 18.7, 11.8 ppm.

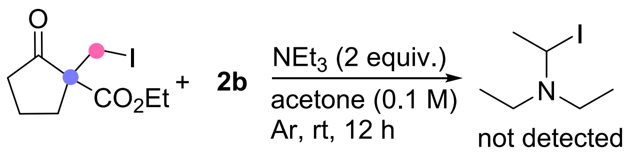
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{34}H_{53}O_3^+$ 509.3989; Found 509.3963.

M.P.: 95 – 98 °C.

Unsuccessful Substrates:



Control Experiments:



The possibility of XAT from alpha-amino radicals was excluded by the above experiments.

Gram Scale Reaction and Late-stage Modifications

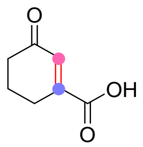
Gram-scale synthesis

An oven-dried 200 mL glass vial was charged with starting material **1** (5 mmol, 1.0 equiv.), arenediazonium salt **2b** (2.58 g, 11 mmol, 2.2 equiv.). Under an argon atmosphere, acetone (50 mL) and triethylamine (1.4 mL, 10 mmol, 2 equiv.) were added via syringe. The mixture was then stirred rapidly at room temperature for 12 h. After the reaction was completed, saturated sodium carbonate solution (10 mL) was added and the resulting mixture was extracted with EtOAc (3 × 50 mL). The combined organic layers were dried over Na_2SO_4, filtered, and the volatiles were removed under reduced pressure. The residue was purified by column chromatography to yield the corresponding product. **3a** was selected as an example in 63% yield (0.53 g).

Caution: a significant amount of nitrogen gas will be released.

Synthesis of 3-oxocyclohex-1-ene-1-carboxylic acid (4)

To a reaction tube was added the compoud **3m** (39.2 mg, 0.2 mmol), CH_2Cl_2 (2 mL), TFA (2 mmol, 10 equiv.) under air atmosphere, and the reaction was stirred at room temperature for 24 h. Upon completion, the mixture was concentrated under reduced pressure. The crude product **4** was obtained as a white solid.[8]



^{1}H NMR (400 MHz, DMSO-d_6) : δ 6.45 (s, 1H), 3.36 (s, 1H), 2.50 – 2.46 (m, 2H), 2.39 – 2.33 (m, 2H), 1.98 – 1.89 (m, 2H) ppm.

^{13}C NMR (101 MHz, DMSO-d_6) :δ 201.1, 170.4, 156.6, 129.7, 37.7, 25.8, 22.6 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_7H_9O_3^+$ 141.0546; Found 141.0558.

M.P.: 127 – 129 °C.

Modification of epiandrosterone derivative

Step i:[9,10] To a dried three-necked flask equipped with a dropping funnel, a condenser, and a magnetic stirrer was added NaH (6 mmol), dimethyl carbonate (5 mL), and toluene (2 mL). The mixture was heated to 110 °C. A solution of epiandrosterone derivative **5** (2.5 mmol) in toluene (2 mL) was added slowly dropwise via syringe. After the addition, the mixture was heated to reflux at 110 °C until the evolution of hydrogen ceased. When the reaction was cooled to room temperature, glacial acetic acid (2 mL) was added dropwise and a heavy, pasty solid appeared. Ice-water was added until the solid was dissolved completely. The toluene layer was separated, and the water layer was washed with toluene (3×10 mL). The combined toluene solution was washed with water (10 mL) and brine (10 mL), then dried over Na_2SO_4. After evaporation of the solvent, The residue was purified by column chromatography to yield the product **6** in 90% yield (0.87 g) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.46 – 5.39 (m, 1H), 4.53 – 4.40 (m, 1H), 3.76 (s, 3H), 3.74 (s, 3H), 3.20 – 3.10 (m, 1H), 2.48 – 2.33 (m, 2H), 2.29 – 2.18 (m, 1H), 2.17 – 2.06 (m, 1H), 2.06 – 1.92 (m, 2H), 1.92 – 1.83 (m, 2H), 1.72 – 1.60 (m, 4H), 1.54 – 1.44 (m, 1H), 1.36 – 1.22 (m, 3H), 1.19 – 1.10 (m, 1H), 1.04 (s, 3H), 0.95 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 212.1, 169.9, 155.1, 139.6, 121.9, 77.5, 54.5, 54.0, 52.5, 50.1, 49.2, 48.4, 37.9, 36.8, 36.7, 31.7, 31.1, 30.7, 27.6, 26.7, 20.2, 19.3, 12.9 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{33}O_5^+$ 389.2323; Found 389.2316.

M.P.: 128 – 130 °C.

Step ii:[1] A solution of 2.0 mmol of the compound **6** in 2 mL of dry THF was added slowly to a suspension of 2.5 mmol of NaH in 2 mL of dry THF containing hexamethylphosphoramide (2.5 mmol) at room temperature under argon. The reaction mixture was stirred at room temperature for 1.0 h, and then treated with 10 mmol of diiodomethane. The reaction mixture was stired at 60 °C for 12 h, then washed with water (20.0 mL), extracted with ethyl acetate (20.0 mL × 3), dried over Na_2SO_4, filtered, and concentrated in vacuum. Purification of the residue by flash column chromatography (petroleum ether/ ethyl acetate) on silica gel provided the product **7** in 70% yield (0.74 g) as a white solid (d.r. = 4.3:1 base on ^{1}H NMR).

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.42 (d, *J* = 5.2 Hz, 1H), 4.55 – 4.41 (m, 1H), 3.81 – 3.74 (m, 7H), 3.20 (d, *J* = 10.1 Hz, 0.17 H), 3.15 (d, *J* = 10.1 Hz, 0.73 H), 2.54 – 2.36 (m, 2H), 2.23 – 2.04 (m, 2H), 1.98 – 1.82 (m, 3H), 1.74 – 1.61 (m, 5H), 1.55 – 1.45 (m, 1H), 1.43 – 1.21 (m, 3H), 1.17 – 1.09 (m, 1H), 1.03 (s, 3H), 0.99 – 0.96 (m, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 209.7, 169.3, 155.1, 139.6, 121.9, 77.5, 61.9, 54.5, 53.3, 50.2, 50.1, 47.5, 37.9, 36.7, 36.6, 32.7, 32.2, 31.0, 30.6, 27.6, 20.1, 19.2, 13.7, 9.0 ppm.

HRMS (ESI-TOF) m/z: $[M+K]^+$ Calcd for $C_{24}H_{35}O_5K^+$ 569.1161; Found 569.1186.

M.P.: 152 – 155 °C.

Step iii: An oven-dried 10 mL glass vial was charged with the compound **7** (0.2 mmol), arenediazonium salt **2e** (0.4 mmol). Under an argon atmosphere, acetone (2 mL) and triethylamine (56 μL, 0.4 mmol, 2 equiv.) were added via syringe. The mixture was then stirred rapidly at room temperature for 12 h. After the reaction was completed, saturated sodium carbonate solution (10 mL) was added and the resulting mixture was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and the volatiles were removed under reduced pressure. The residue was purified by column chromatography to yield the the product **3x** in 68% yield (54 mg) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) : δ 6.73 – 6.61 (m, 1H), 5.48 – 5.36 (m, 1H), 4.56 – 4.40 (m, 1H), 3.82 (s, 3H), 3.77 (s, 3H), 2.83 – 2.72 (m, 1H), 2.50 – 2.32 (m, 2H), 2.31 – 2.21 (m, 1H), 2.16 – 2.01 (m, 2H), 2.00 – 1.87 (m, 2H), 1.69 – 1.50 (m, 6H), 1.45 – 1.32 (m, 2H), 1.20 – 1.09 (m, 1H), 1.04 – 0.99 (m, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) : δ 205.4, 167.0, 155.1, 146.1, 139.2, 131.4, 121.9, 77.5, 54.5, 52.6, 48.7, 46.6, 44.1, 37.8, 36.7, 36.4, 32.1, 31.6, 31.1, 27.5, 26.3, 19.8, 19.2, 15.1 ppm.

HRMS (ESI-TOF) m/z: $[M+K]^+$ Calcd for $C_{24}H_{32}O_5K^+$ 439.1881; Found 439.1901.

M.P.: 174 – 177 °C.

Mechanistic Studies

Radical trapping experiments

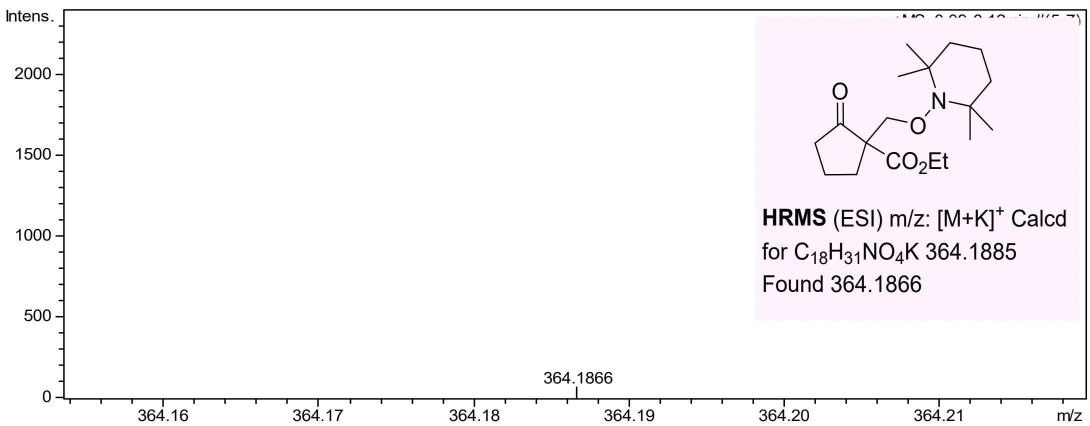


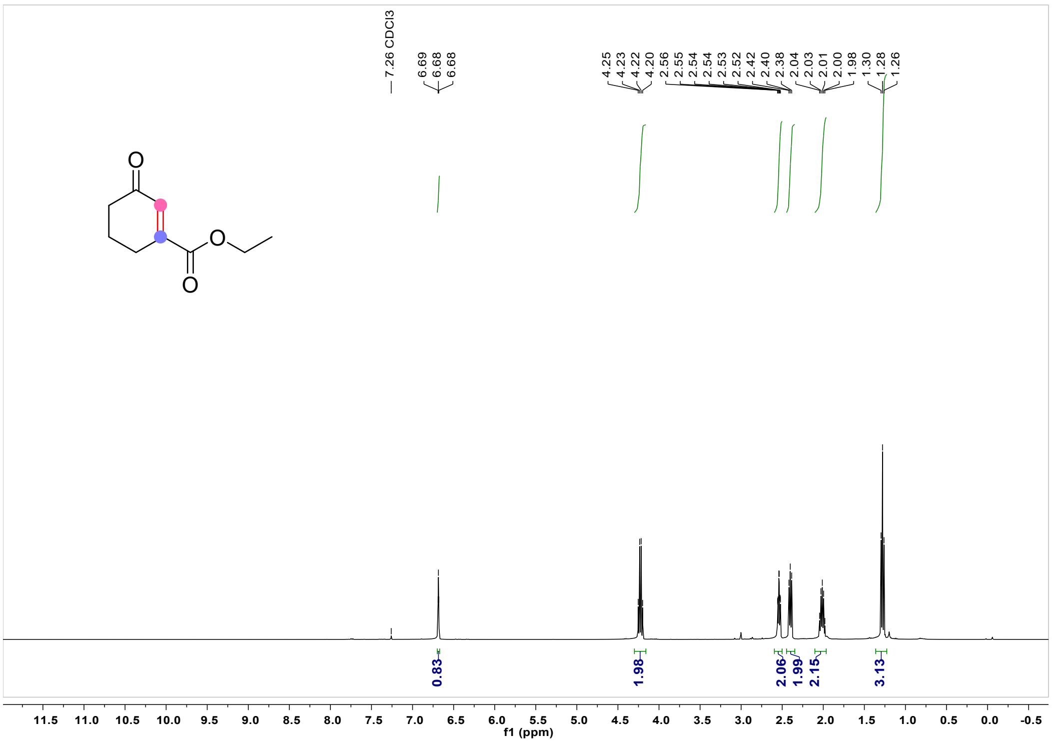
Figure S3. HRMS profiles after adding TEMPO.

References

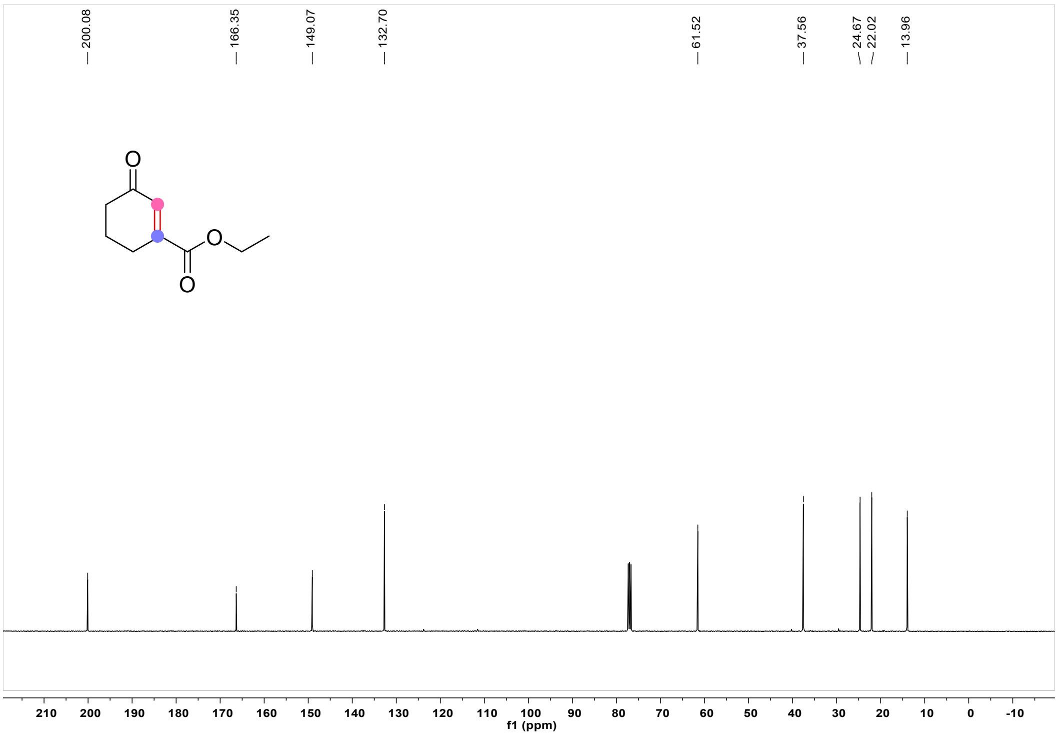
1 M. Deguchi, A. Fujiya, E. Yamaguchi, N. Tada, B. Unoa and A. Itoh, *RSC Adv.,* 2018, **8**, 15825–15830.
2 Y.-F. Ren, X.-Y. Chen, H.-W. Du and W. Shu, *ChemRxiv*., 2023, 10.26434/chemrxiv-2023-cq8jz.
3 L. Song, Y. Zhou, H. Liang, H. Li, Y. Lai, H. Yao, R. Lin and R. Tong, *J. Org. Chem*., 2023, **88**, 504–512.
4 L. Zhang, S. Liu, Y. Lin and Y. Wang, *Tetrahedron Lett.,* 2022, **93**, 153663.
5 P. A. van Elburg and D. N. Reinhoudt, *Recueil des Travaux Chimiques des Pays-Bas,* 1988, **107**, 381–387.
6 B. Bayarmagnai, C. Matheis, K. Jouvin and L. J. Goossen, *Angew. Chem., Int. Ed.,* 2015, **54**, 5753–5756.
7 Y. Li, T. B. Lee, T. Wang, A. V. Gamble and A. E. V. Gorden, *J. Org. Chem.,* 2012, **77**, 4628–4633.
8 J. M. Kaplan, D. P. Hruszkewycz, I. I. Strambeanu, C. J. Nunn, K. F. Van Gelder, A. L. Dunn, D. I. Wozniak, G. E. Dobereiner and D. C. Leitch, *Organometallics,* 2019, **38**, 85–96.
7 H.-J. Zheng, W.-B. Chen, Z.-J. Wu, J.-G. Deng, W.-Q. Lin, W.-C. Yuan and X.-M. Zhang, *Chem. Eur. J*., 2008, **14**, 9864–9867.
8 W. Tang, W. Wang, Y. Chi and X. Zhang, *Angew. Chem., Int. Ed.,* 2003, **42**, 3509–3511.

Copies of ^{1}H, and ^{13}C spectra

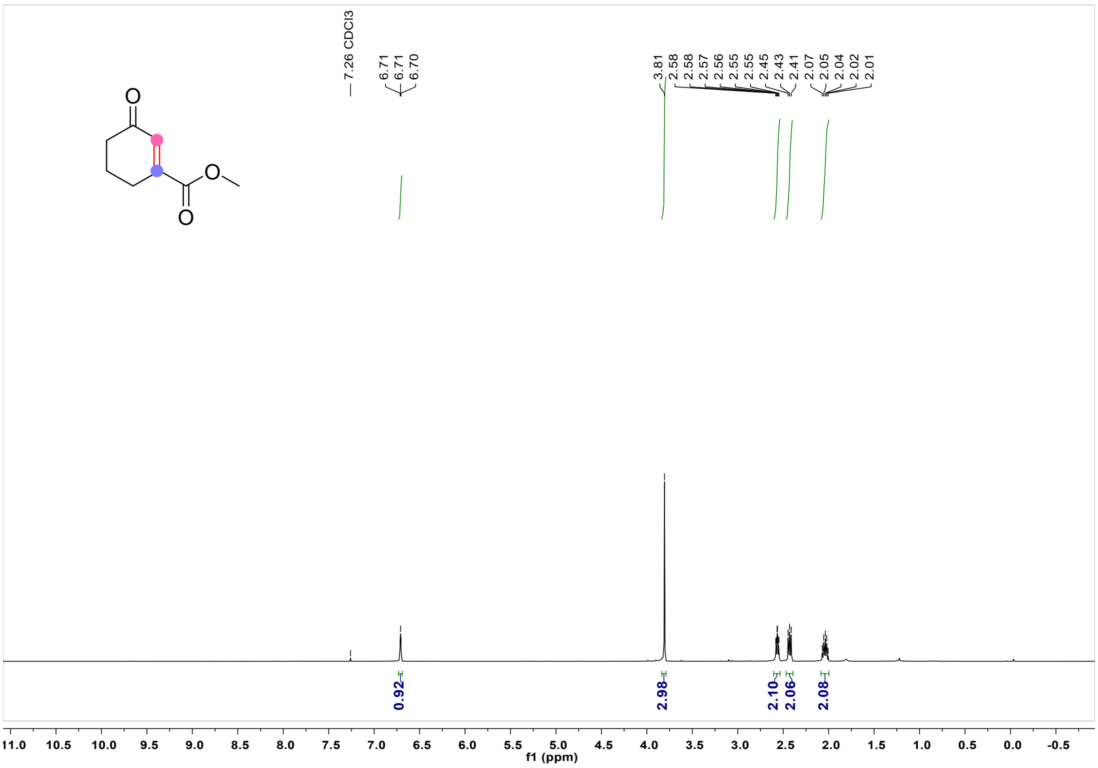
^{1}**H NMR** spectra (400 MHz) of **3a** in $CDCl_3$.



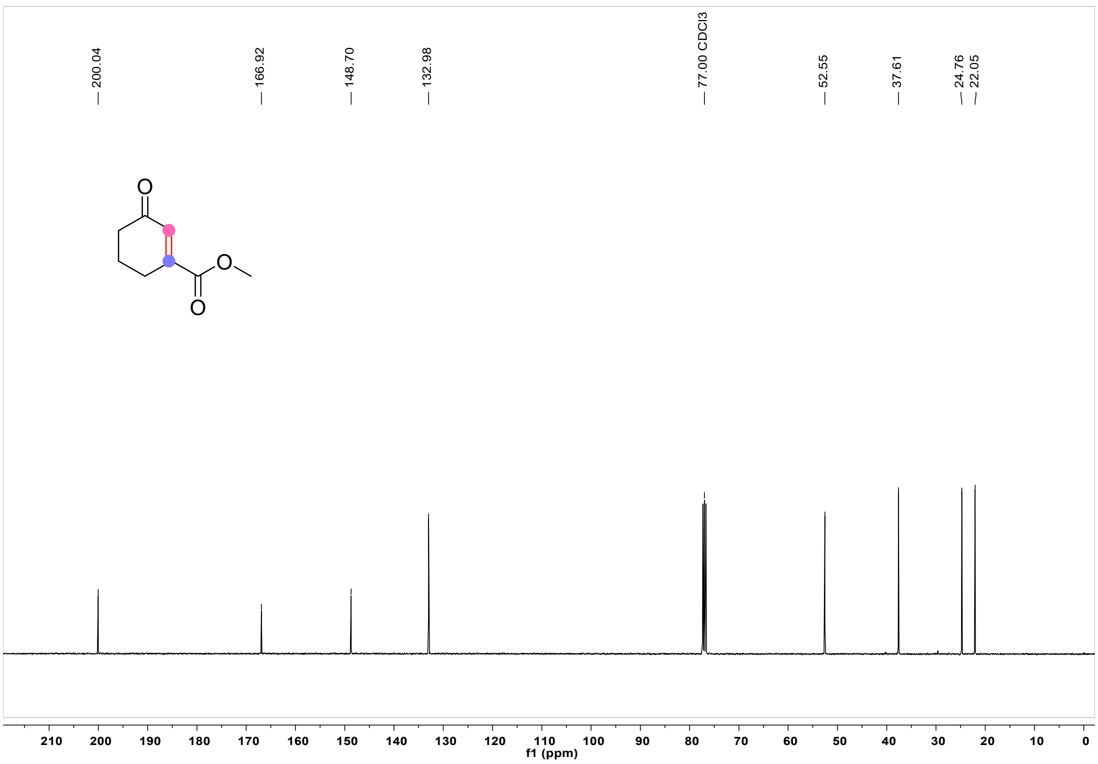
^{13}**C NMR** spectra (101 MHz) of **3a** in $CDCl_3$.



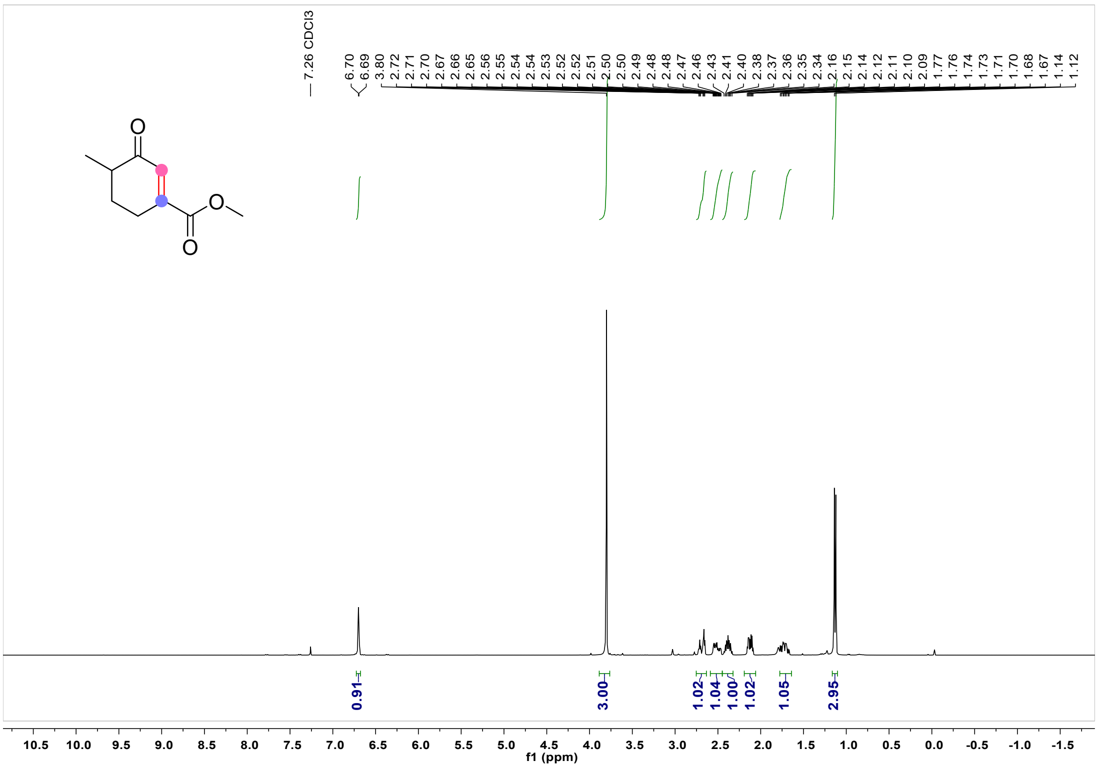
^{1}H NMR spectra (400 MHz) of **3b** in $CDCl_3$.



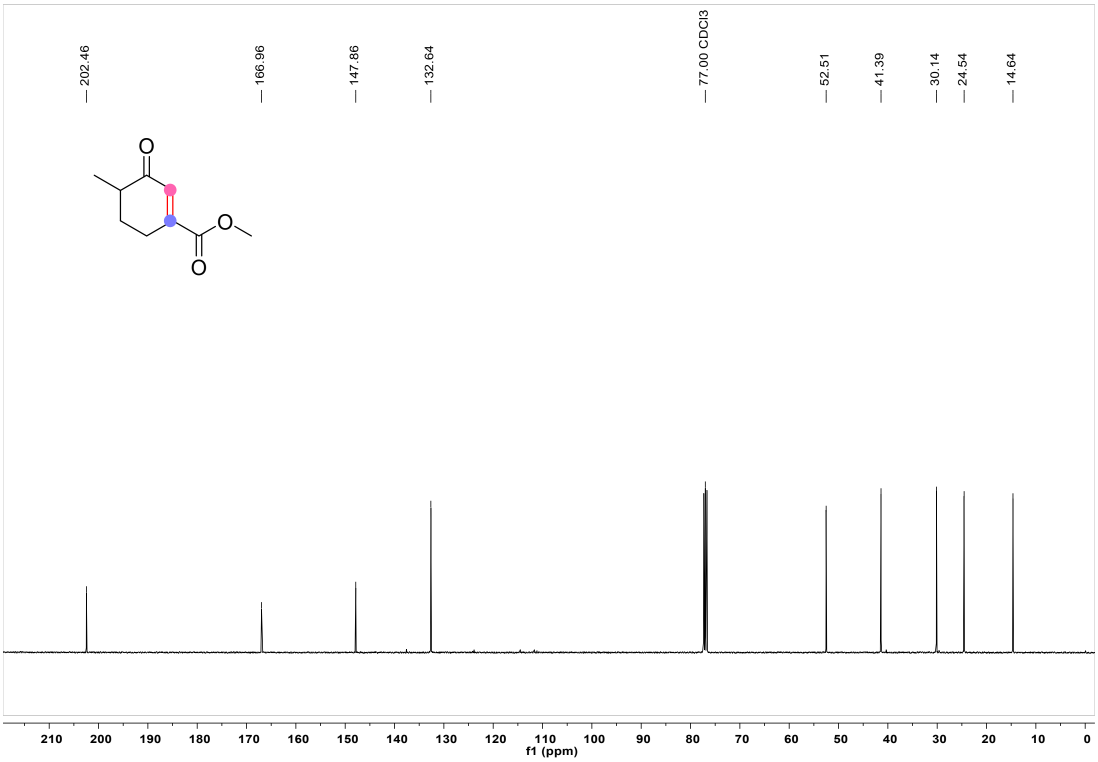
^{13}C NMR spectra (101 MHz) of **3b** in $CDCl_3$.



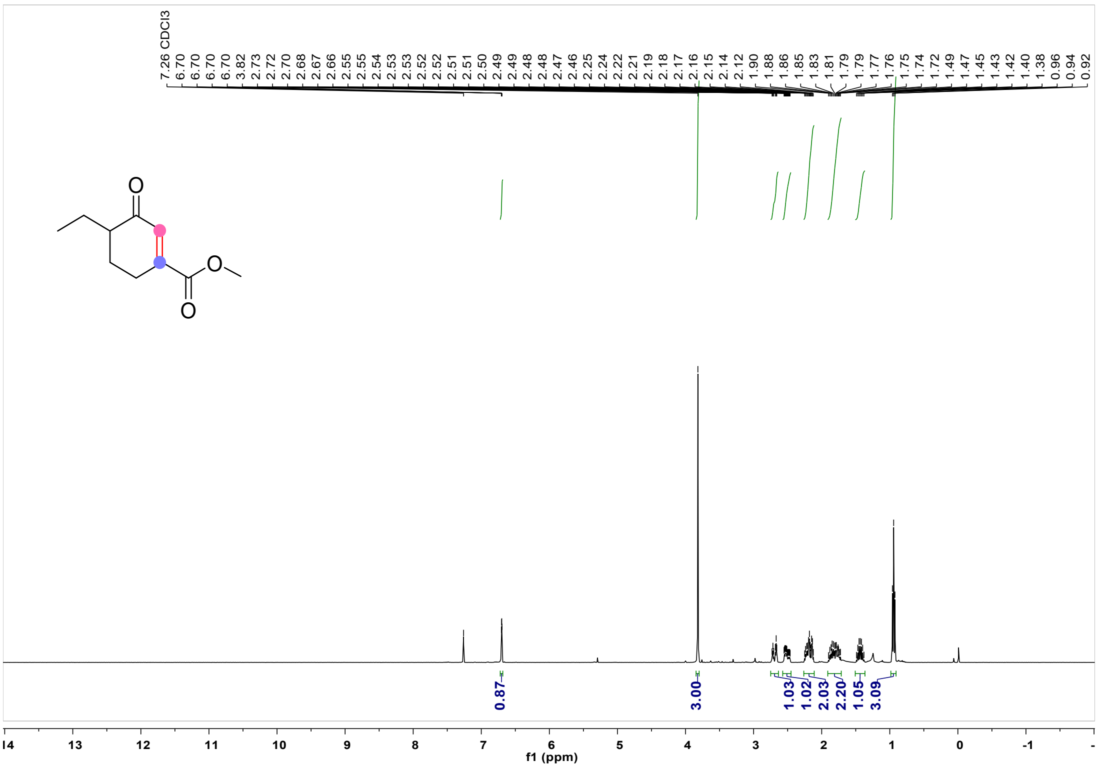
^{1}H NMR spectra (400 MHz) of **3c** in $CDCl_3$.



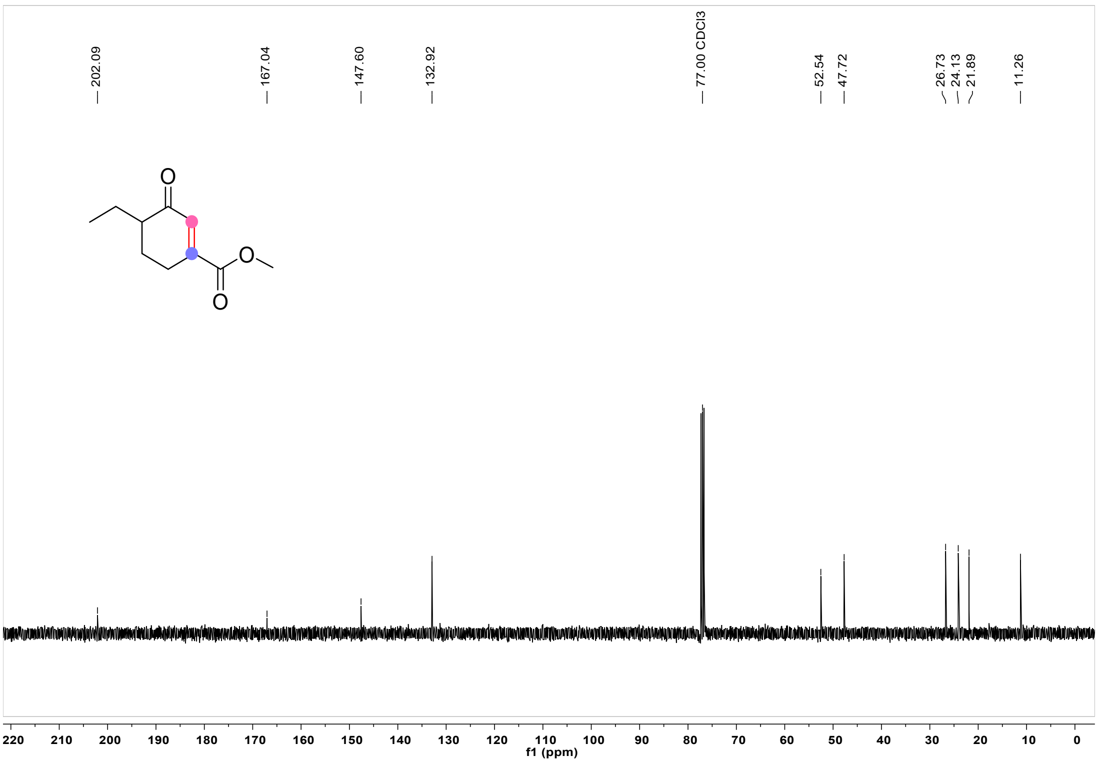
^{13}C NMR spectra (101 MHz) of **3c** in $CDCl_3$.



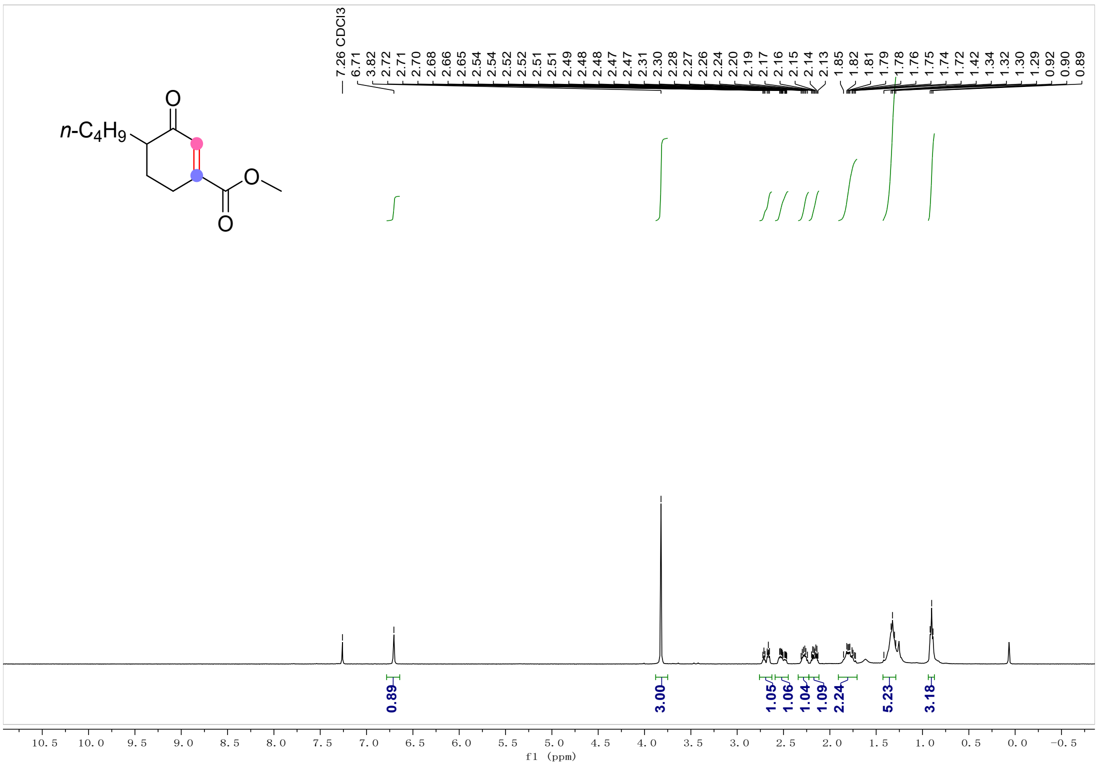
^{1}H NMR spectra (400 MHz) of **3d** in $CDCl_3$.



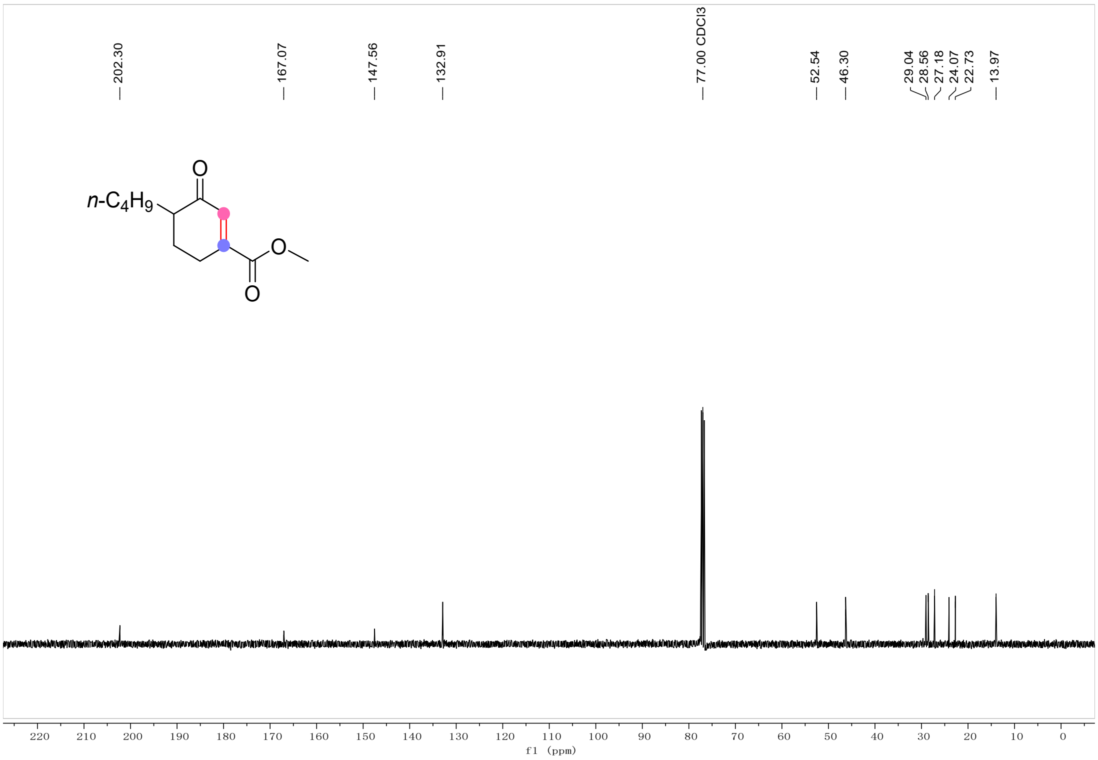
^{13}C NMR spectra (101 MHz) of **3d** in $CDCl_3$.



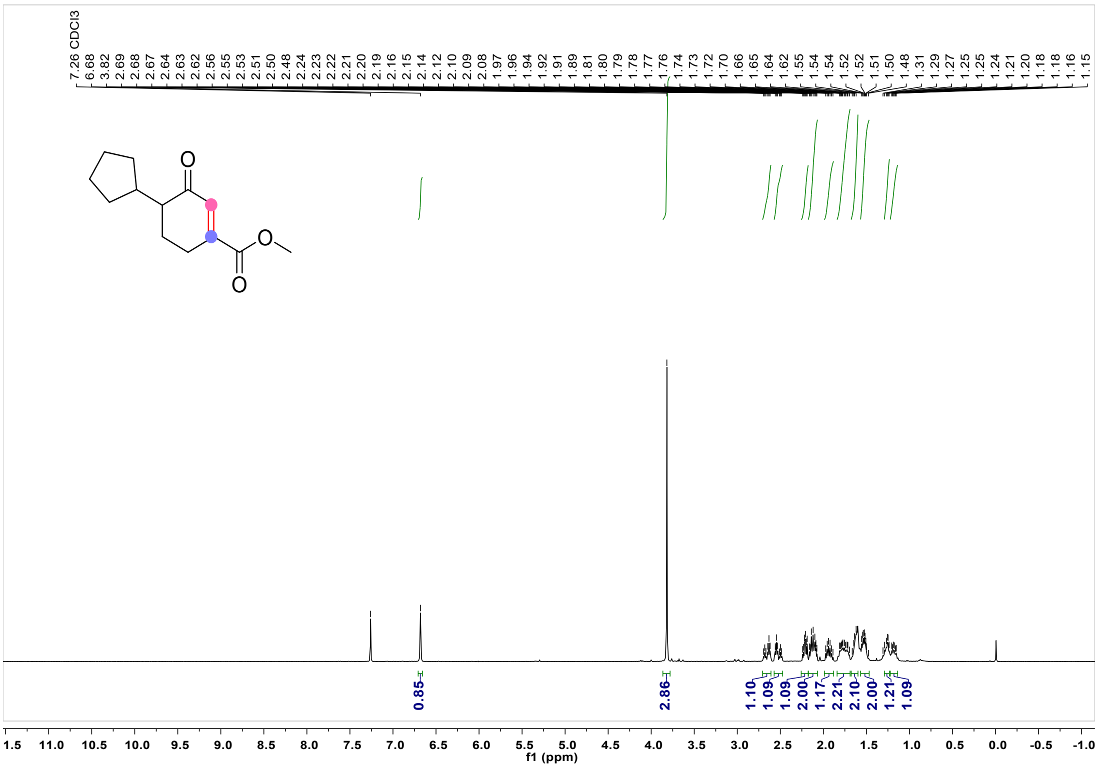
^{1}H NMR spectra (400 MHz) of **3e** in $CDCl_3$.



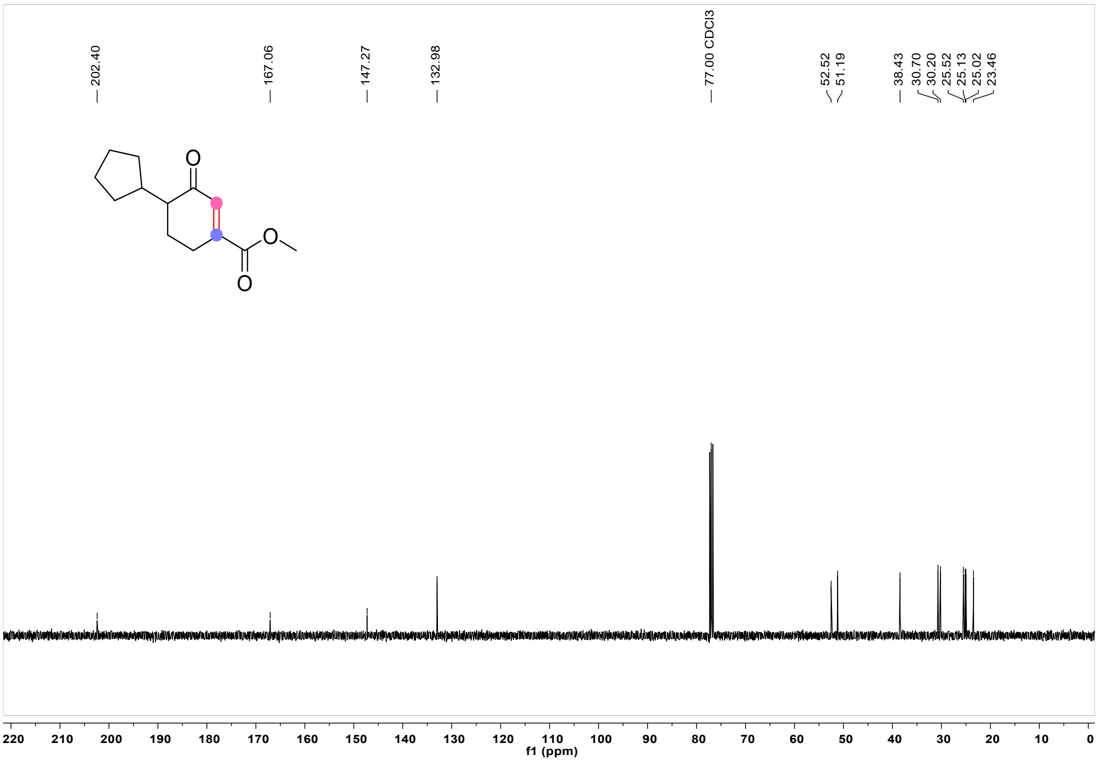
^{13}C NMR spectra (101 MHz) of **3e** in $CDCl_3$.



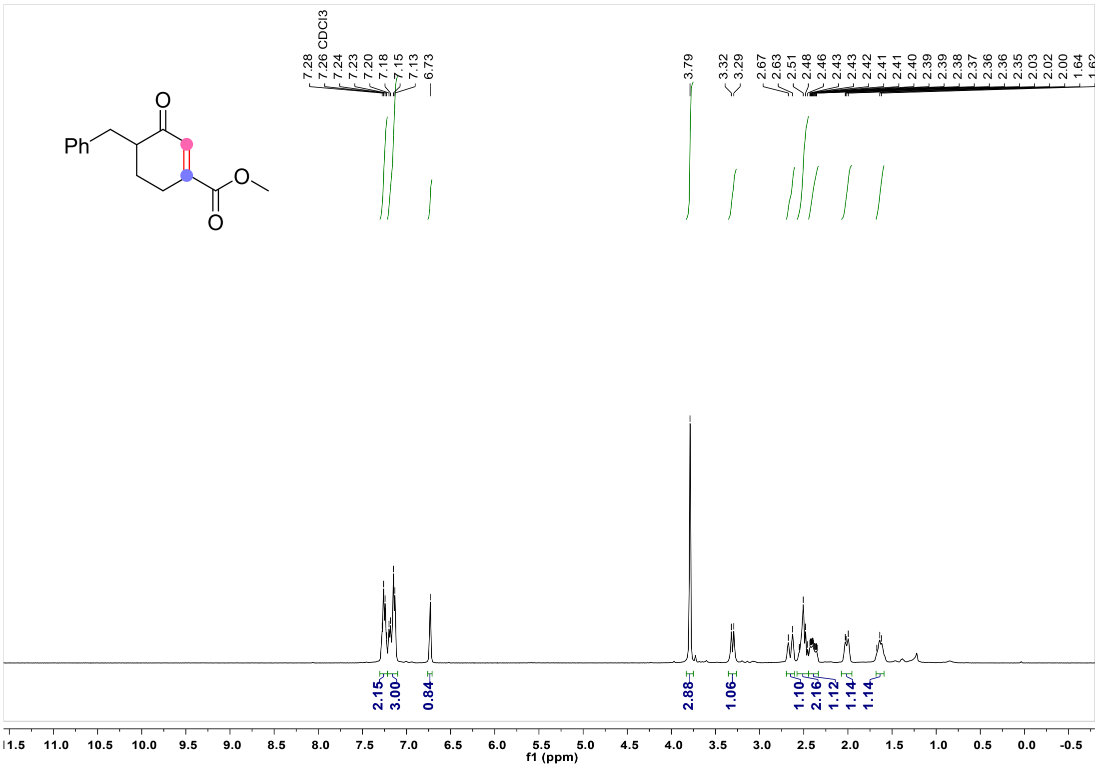
^{1}**H NMR** spectra (400 MHz) of **3f** in $CDCl_3$.



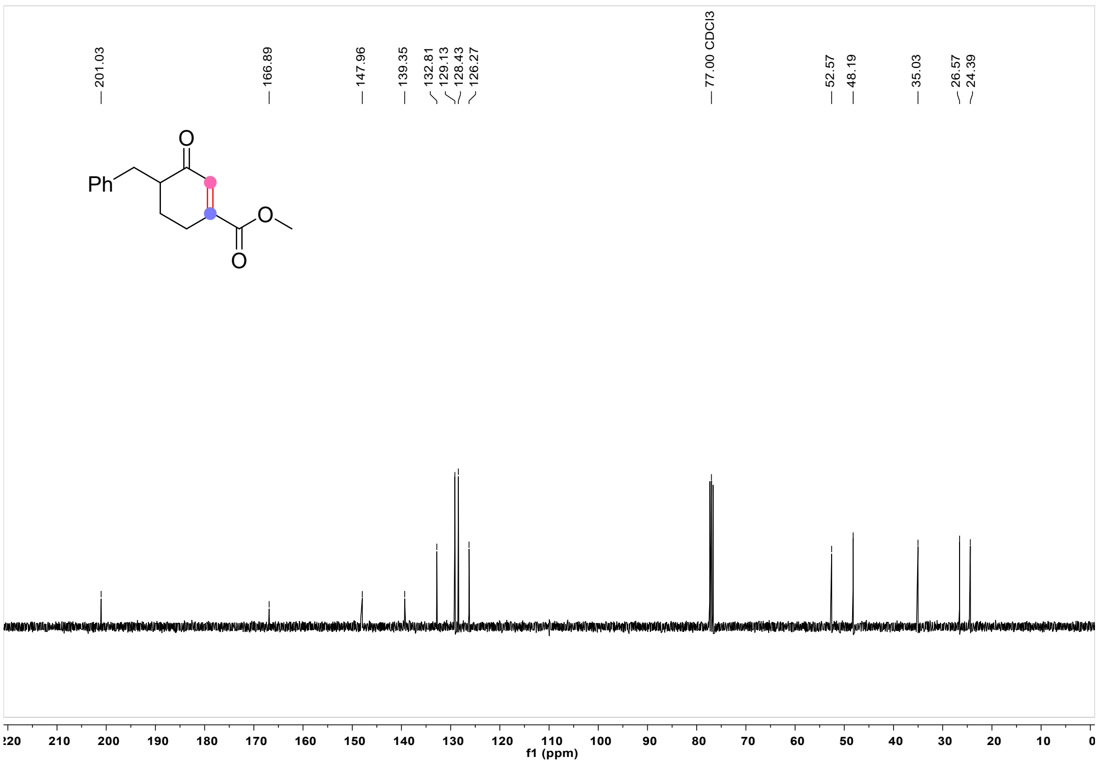
^{13}**C NMR** spectra (101 MHz) of **3f** in $CDCl_3$.



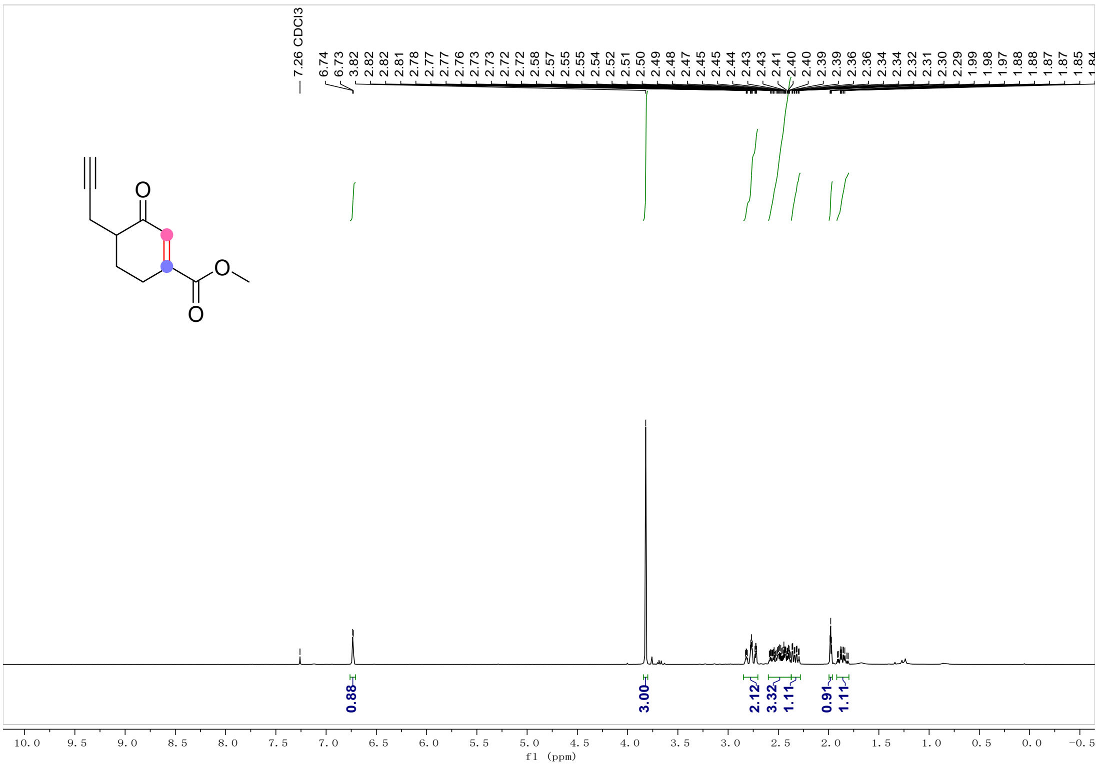
^{1}H NMR spectra (400 MHz) of **3g** in $CDCl_3$.



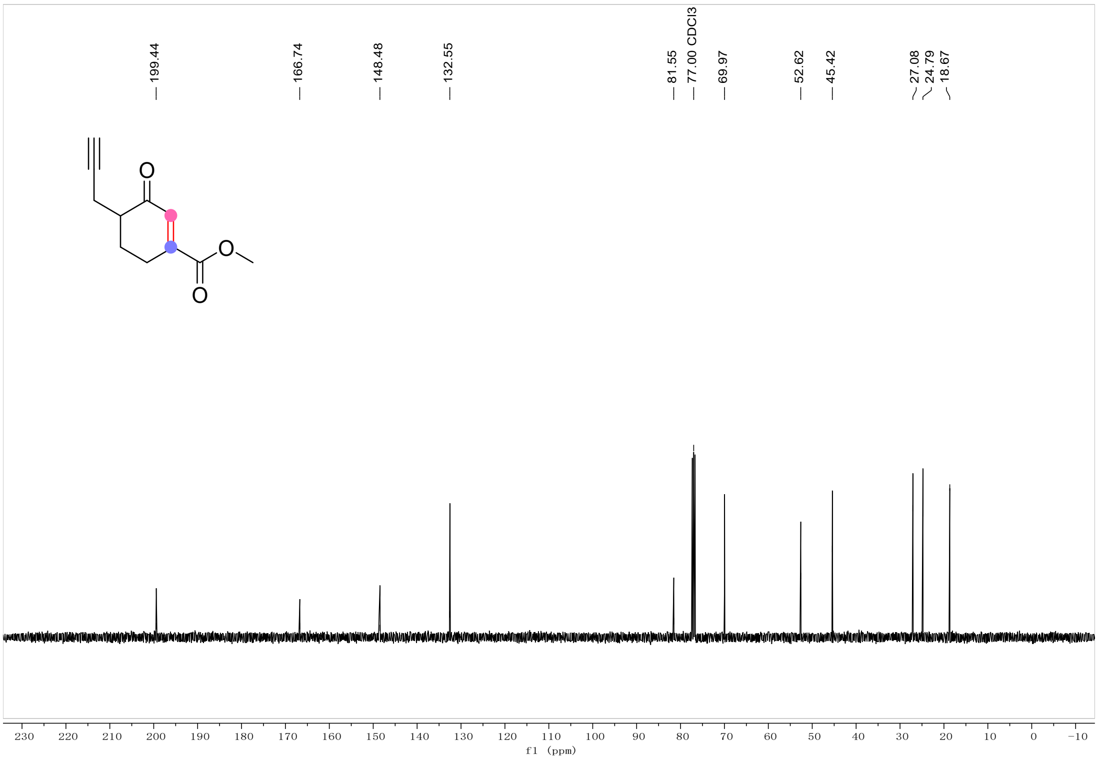
^{13}C NMR spectra (101 MHz) of **3g** in $CDCl_3$.



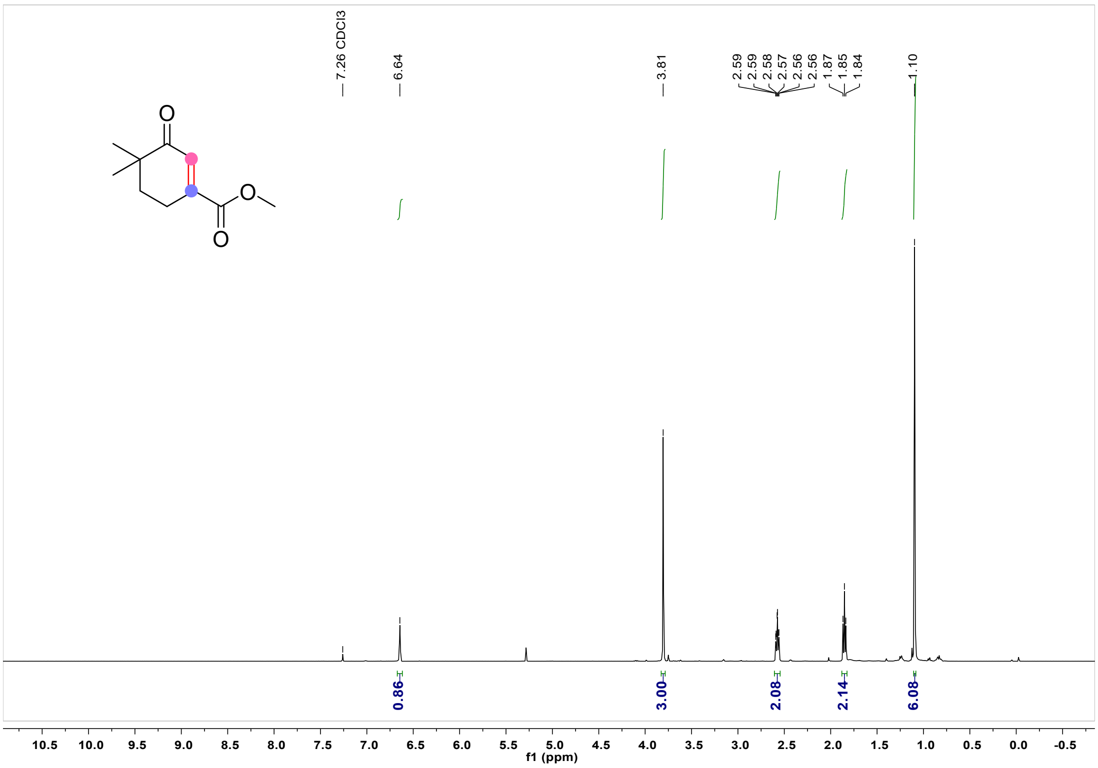
[1]H NMR spectra (400 MHz) of **3h** in $CDCl_3$.



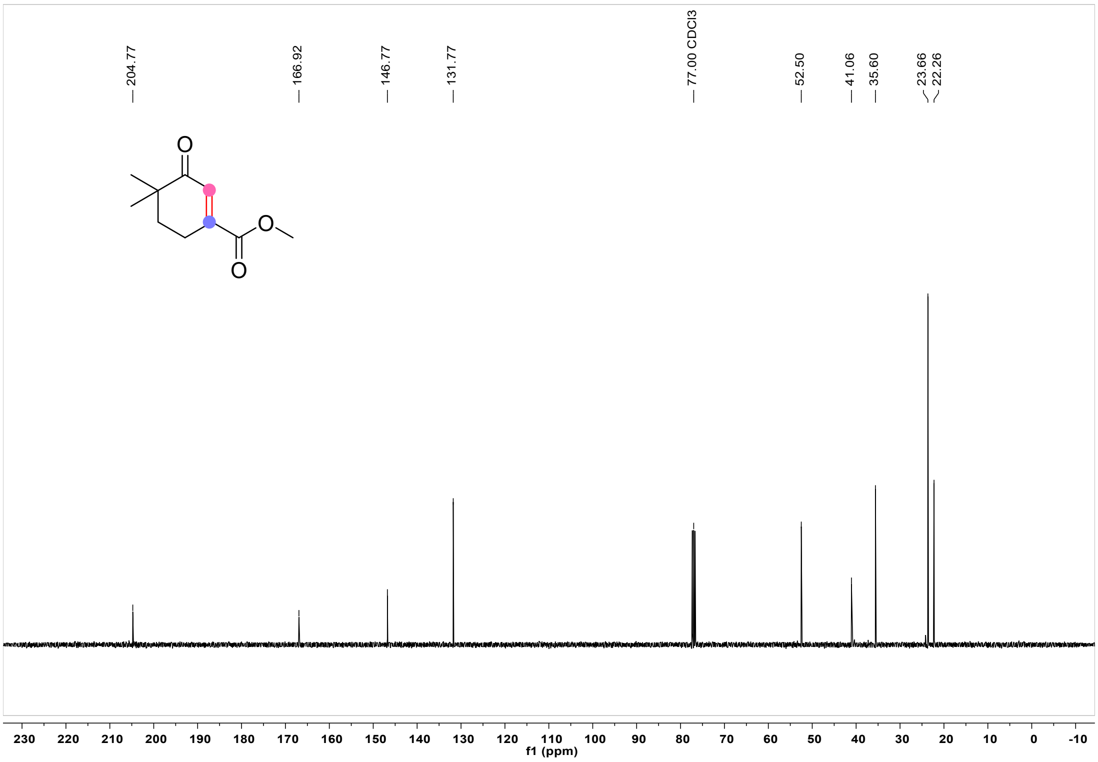
[13]C NMR spectra (101 MHz) of **3h** in $CDCl_3$.



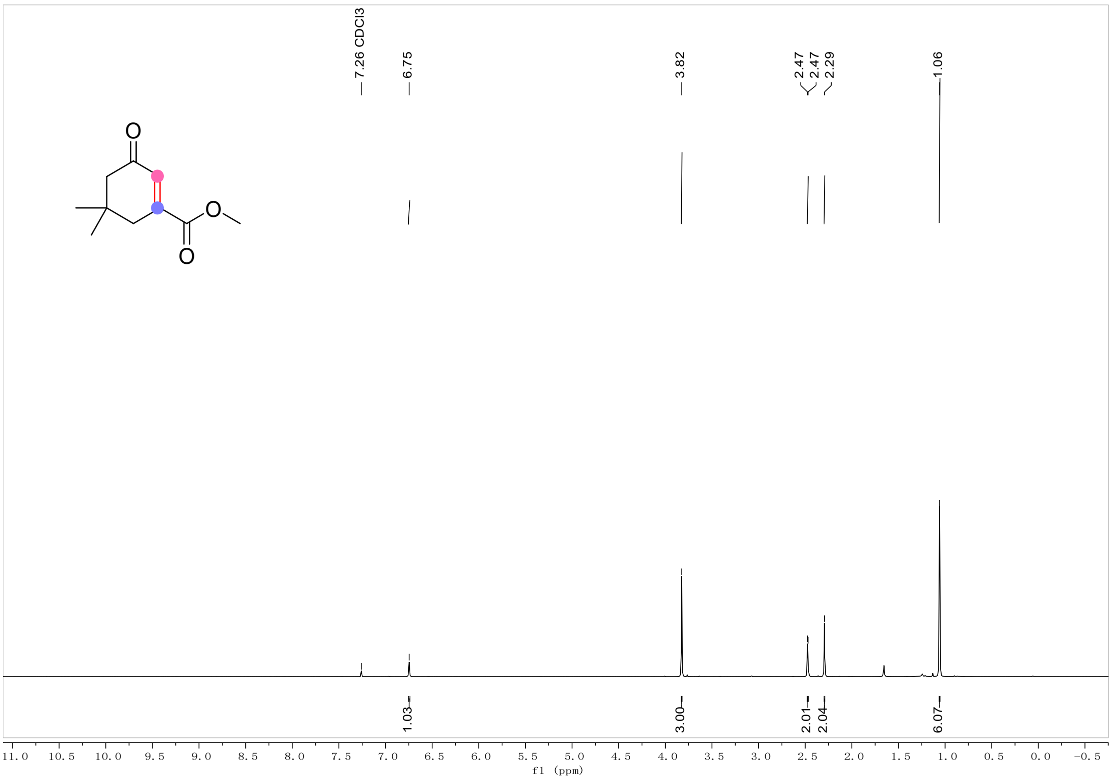
¹H NMR spectra (400 MHz) of **3i** in $CDCl_3$.



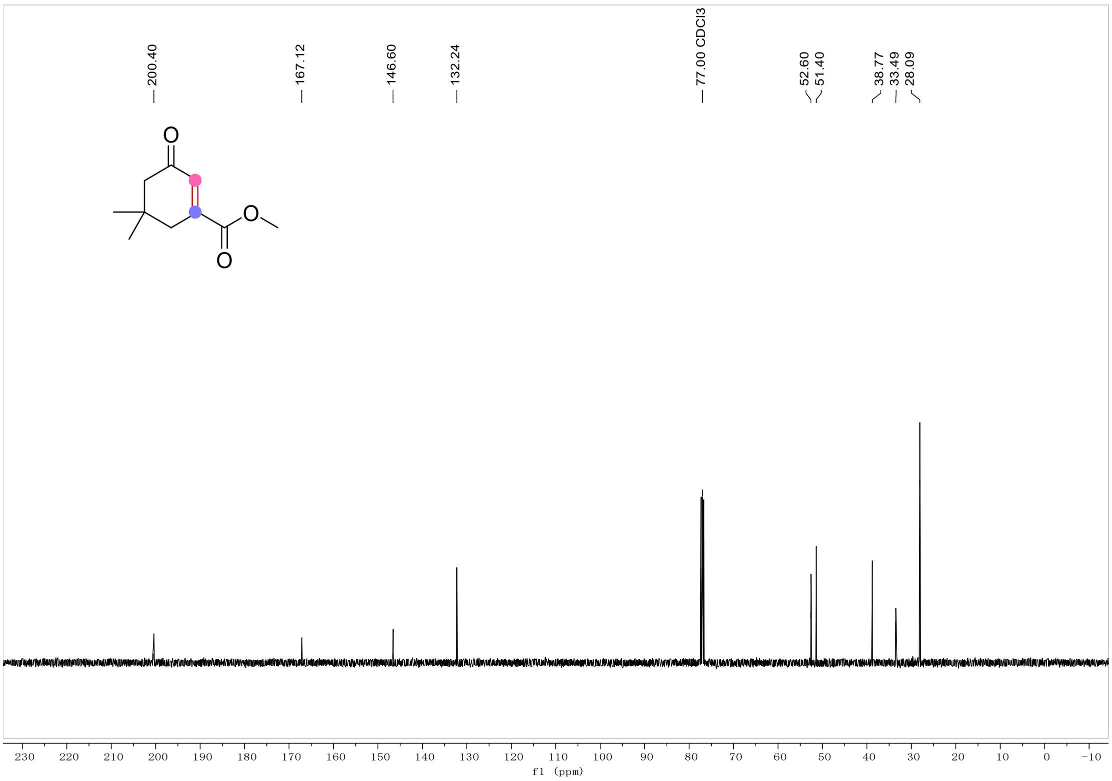
¹³C NMR spectra (101 MHz) of **3i** in $CDCl_3$.



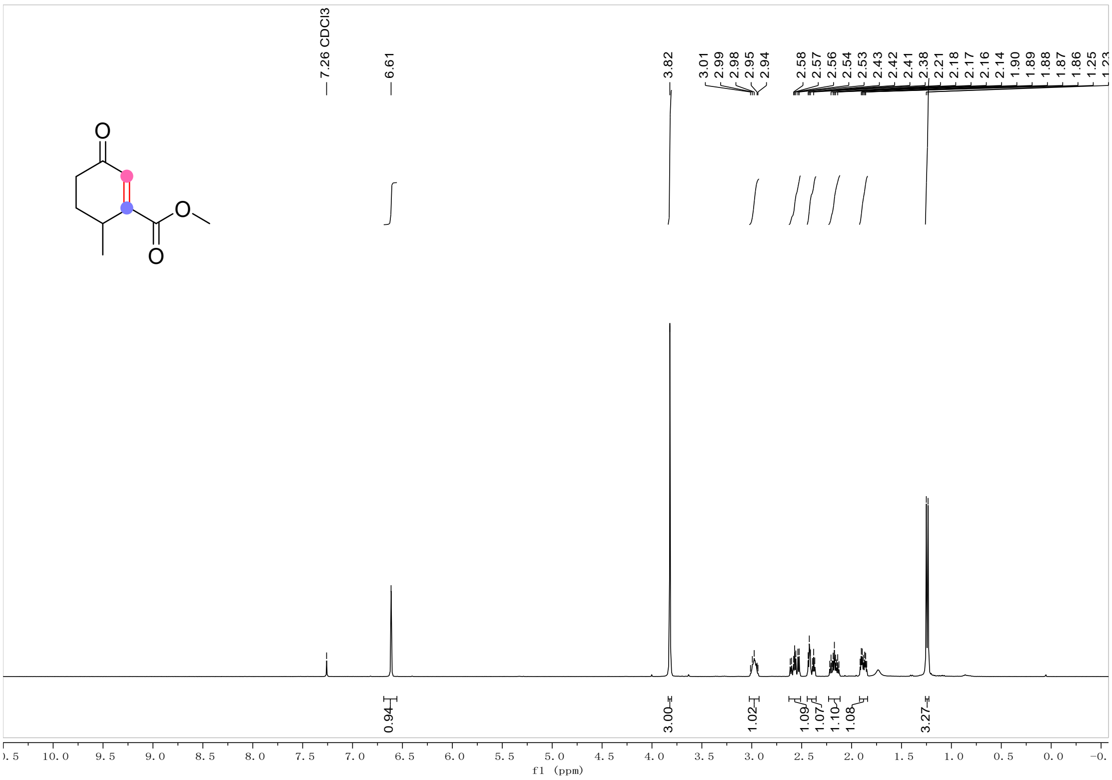
[1]H NMR spectra (400 MHz) of **3j** in $CDCl_3$.



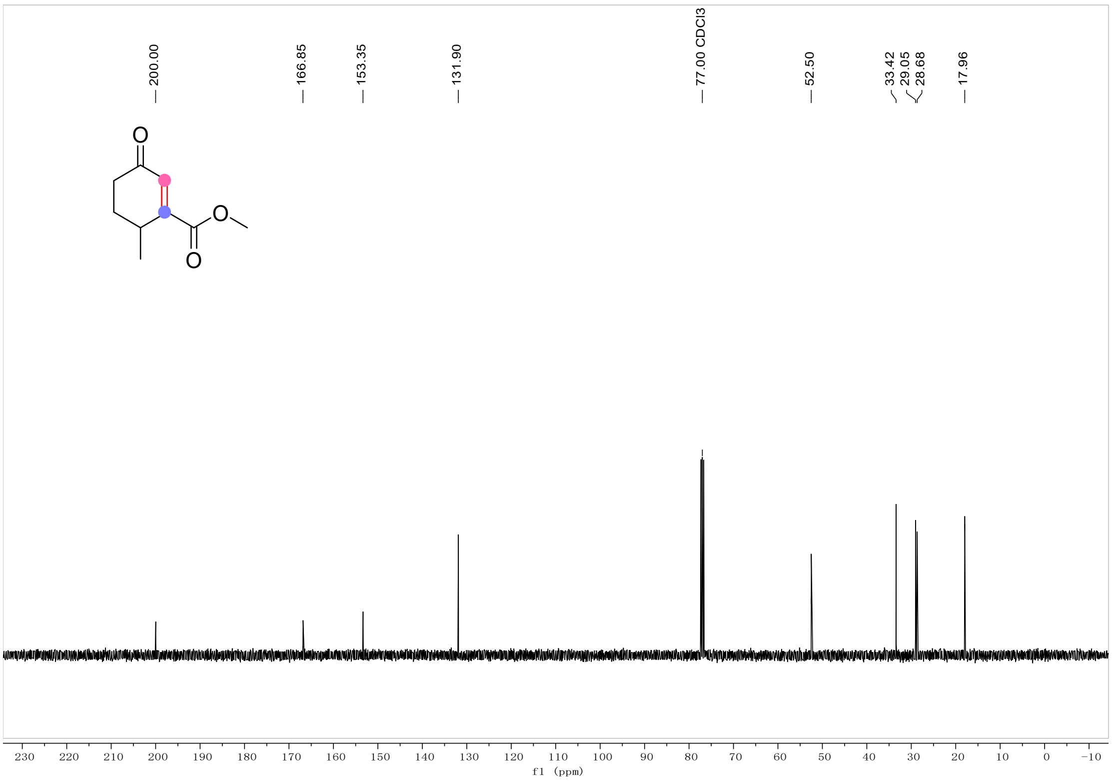
[13]C NMR spectra (101 MHz) of **3j** in $CDCl_3$.



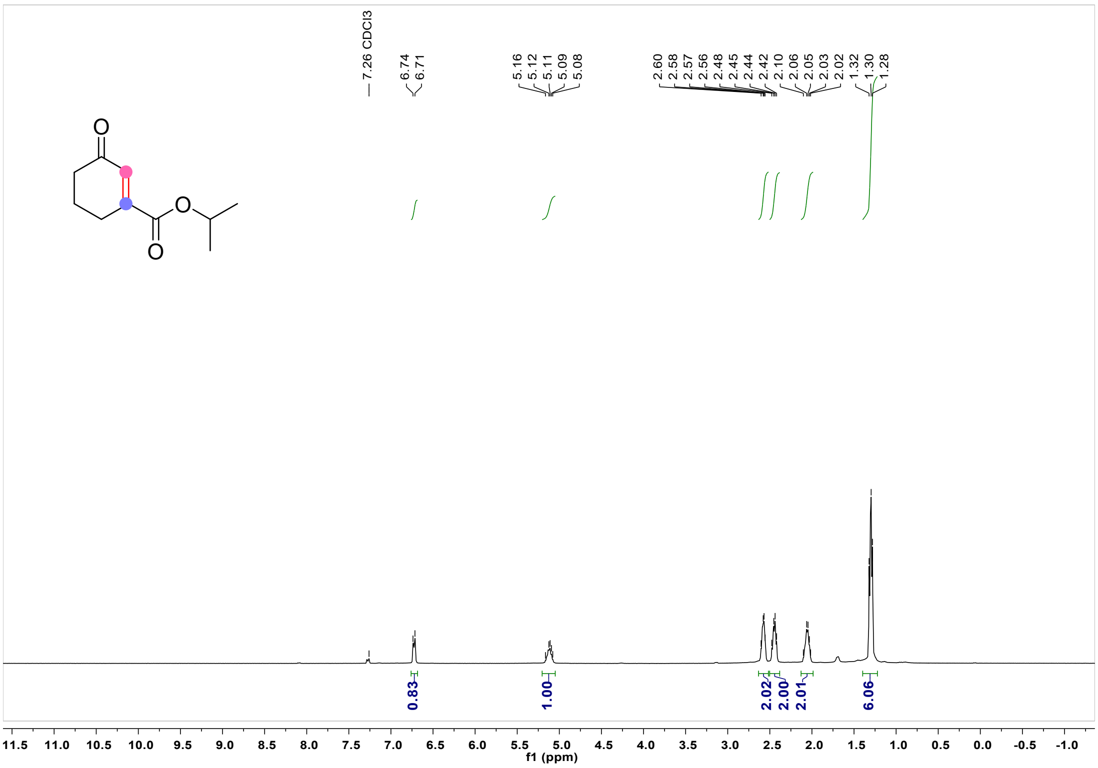
^{1}H NMR spectra (400 MHz) of **3k** in $CDCl_3$.



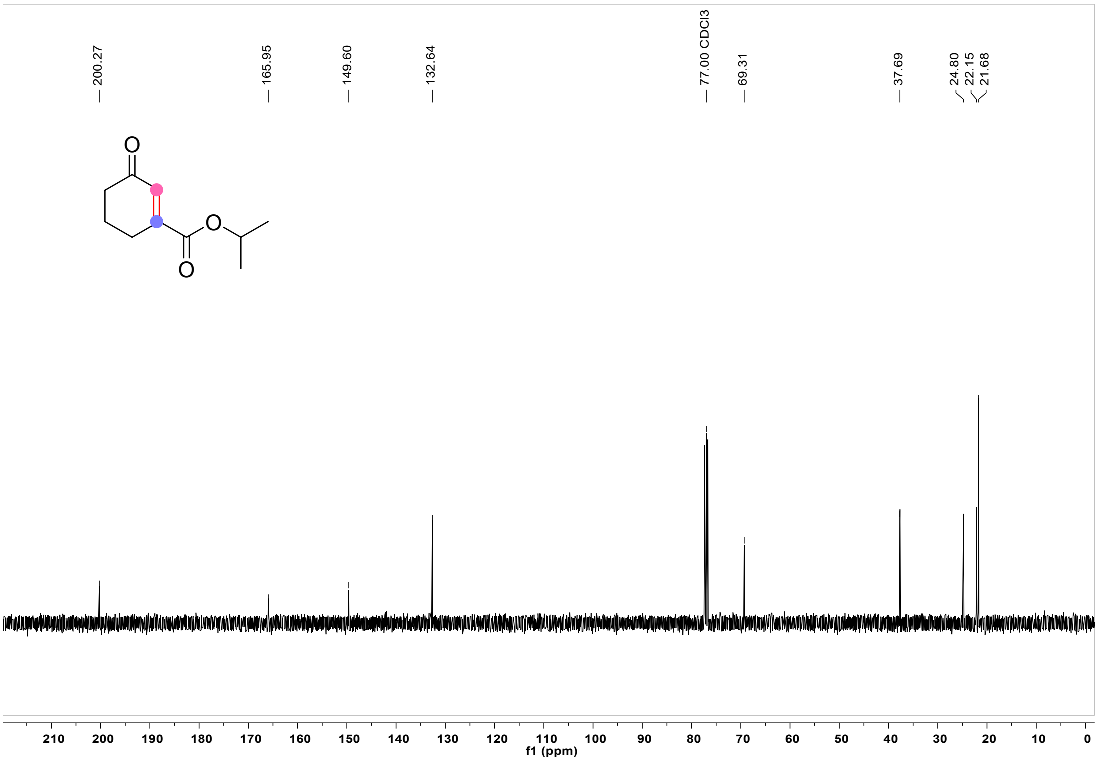
^{13}C NMR spectra (101 MHz) of **3k** in $CDCl_3$.



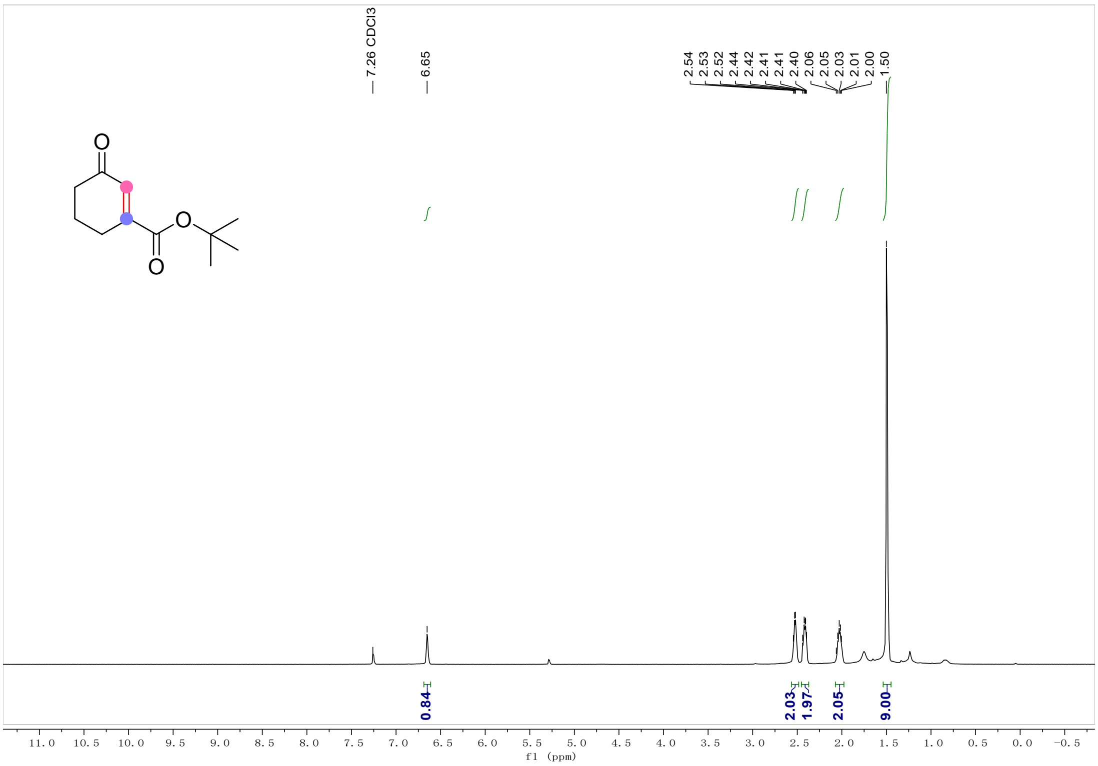
^{1}H NMR spectra (400 MHz) of **3l** in $CDCl_3$.



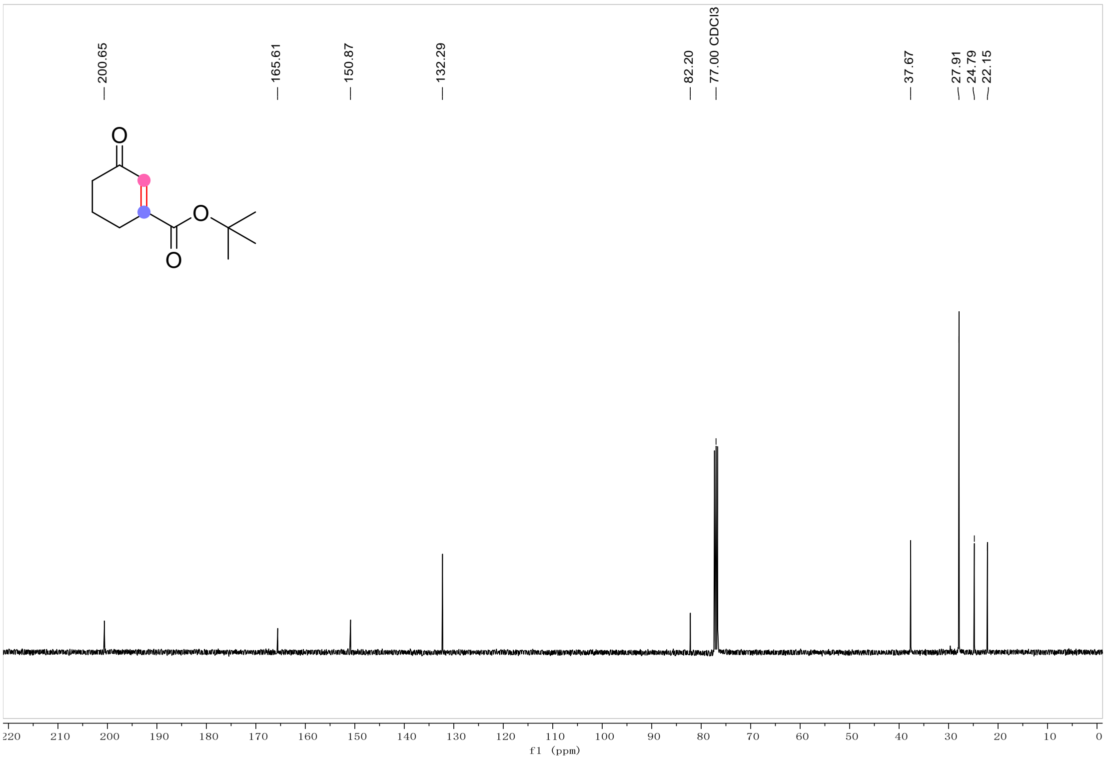
^{13}C NMR spectra (101 MHz) of **3l** in $CDCl_3$.



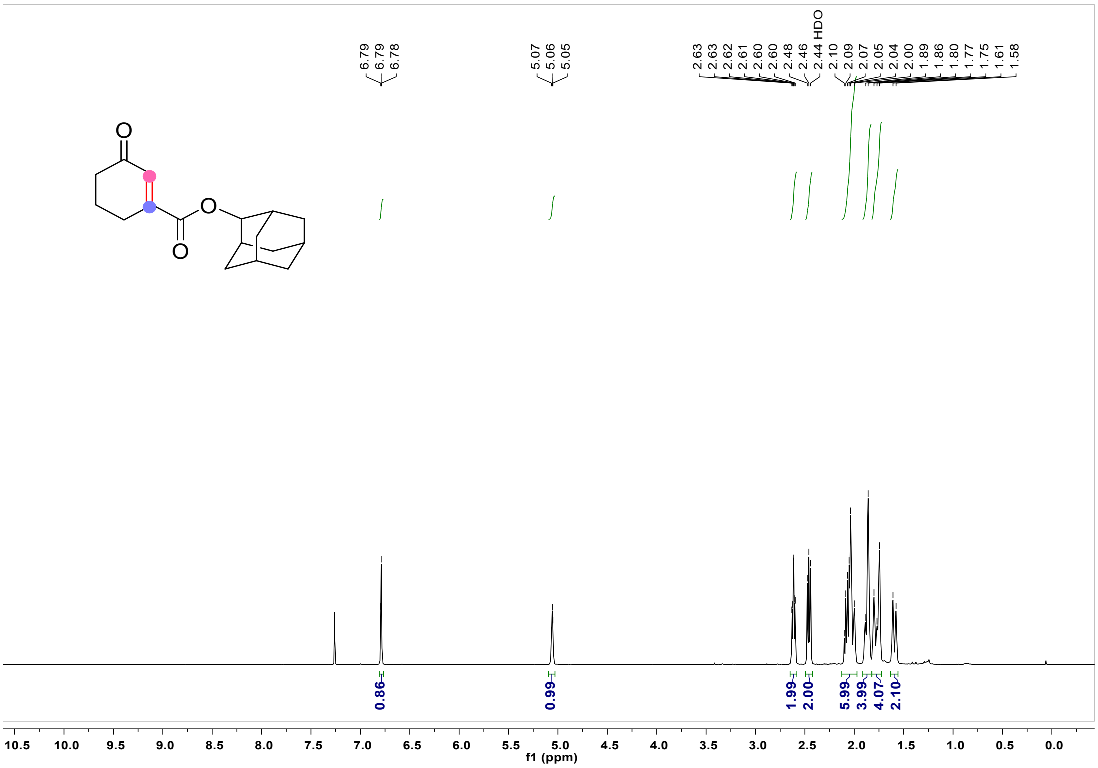
^{1}H NMR spectra (400 MHz) of **3m** in $CDCl_3$.



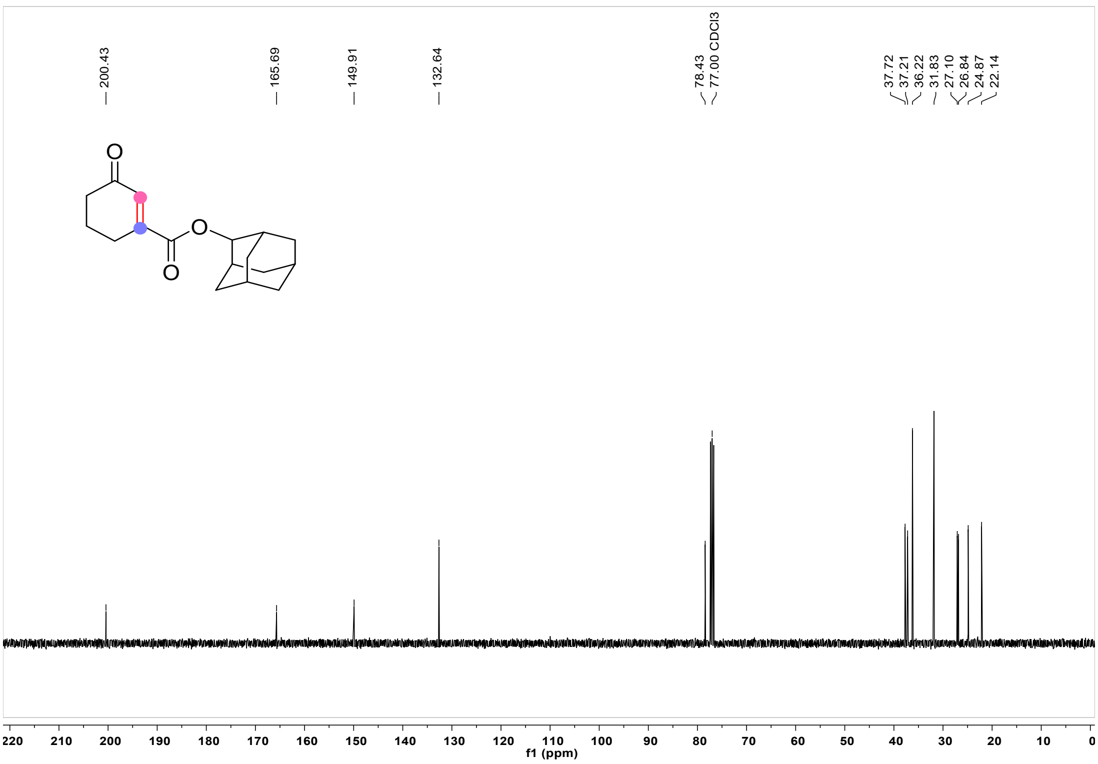
^{13}C NMR spectra (101 MHz) of **3m** in $CDCl_3$.



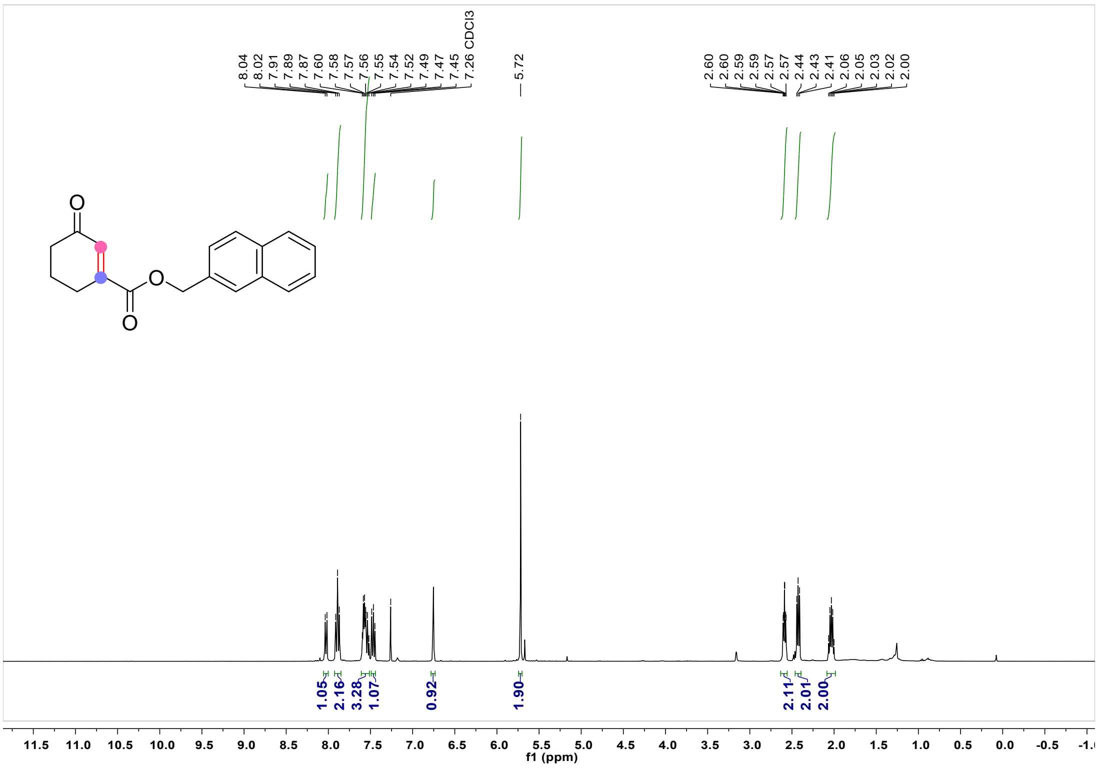
[1]**H NMR** spectra (400 MHz) of **3n** in $CDCl_3$.



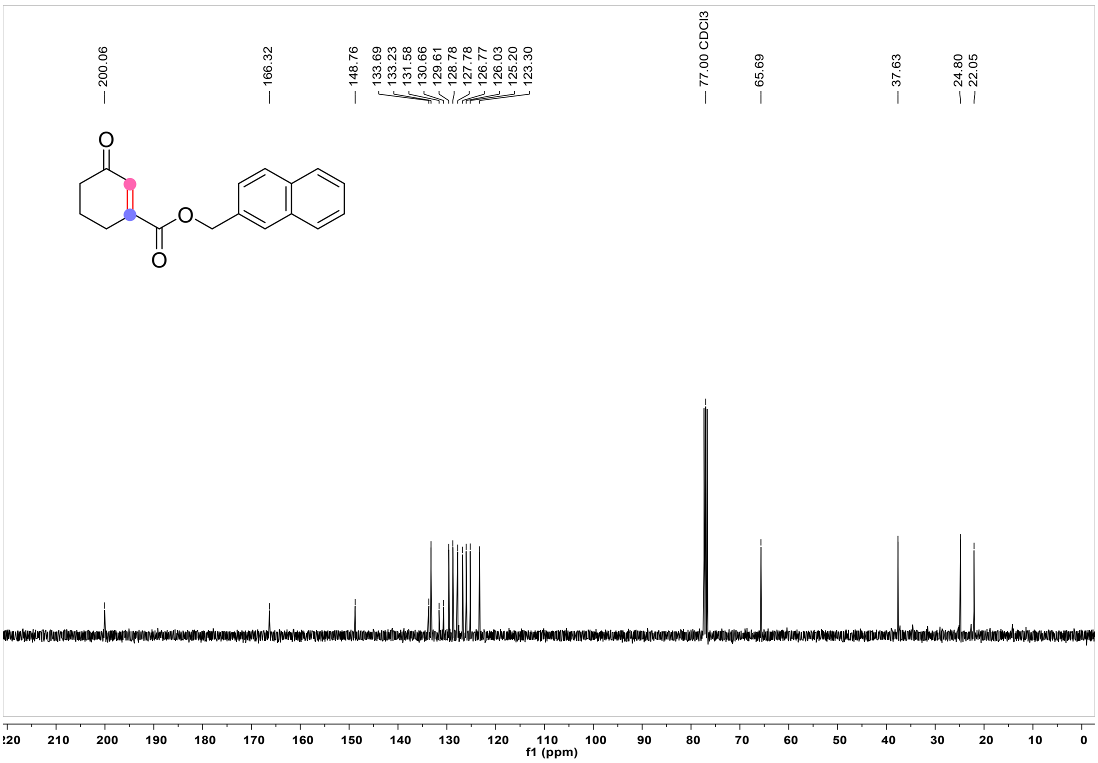
[13]**C NMR** spectra (101 MHz) of **3n** in $CDCl_3$.



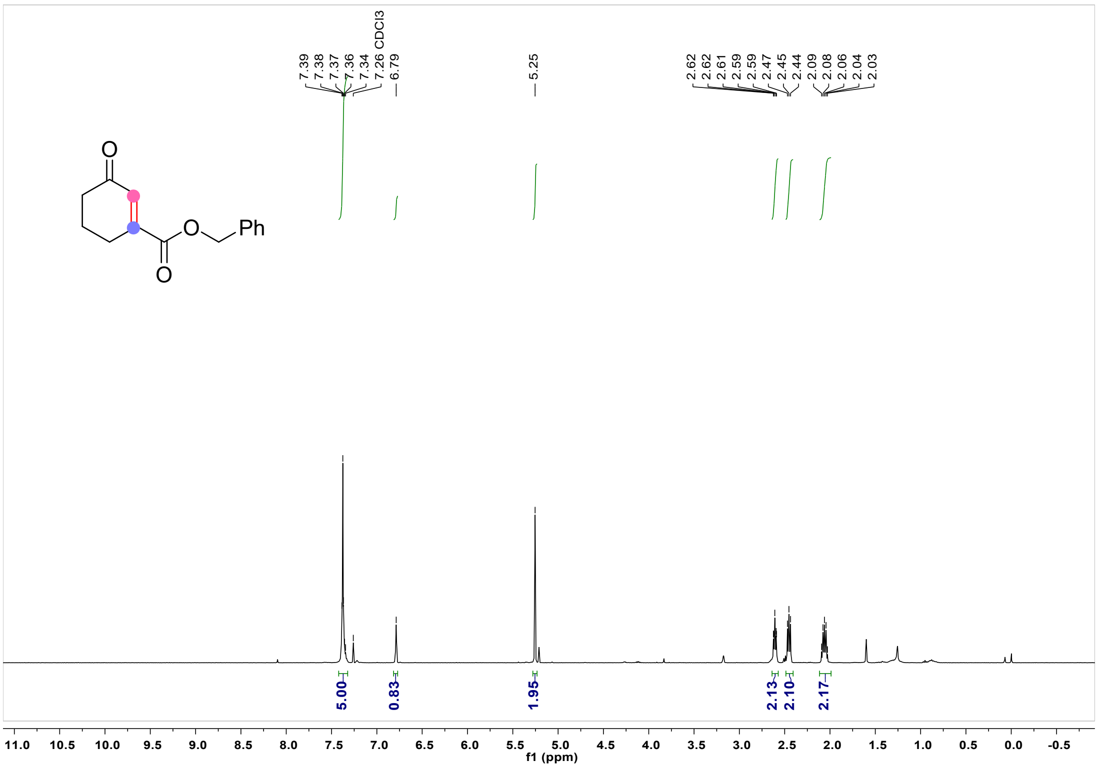
¹H NMR spectra (400 MHz) of **3o** in $CDCl_3$.



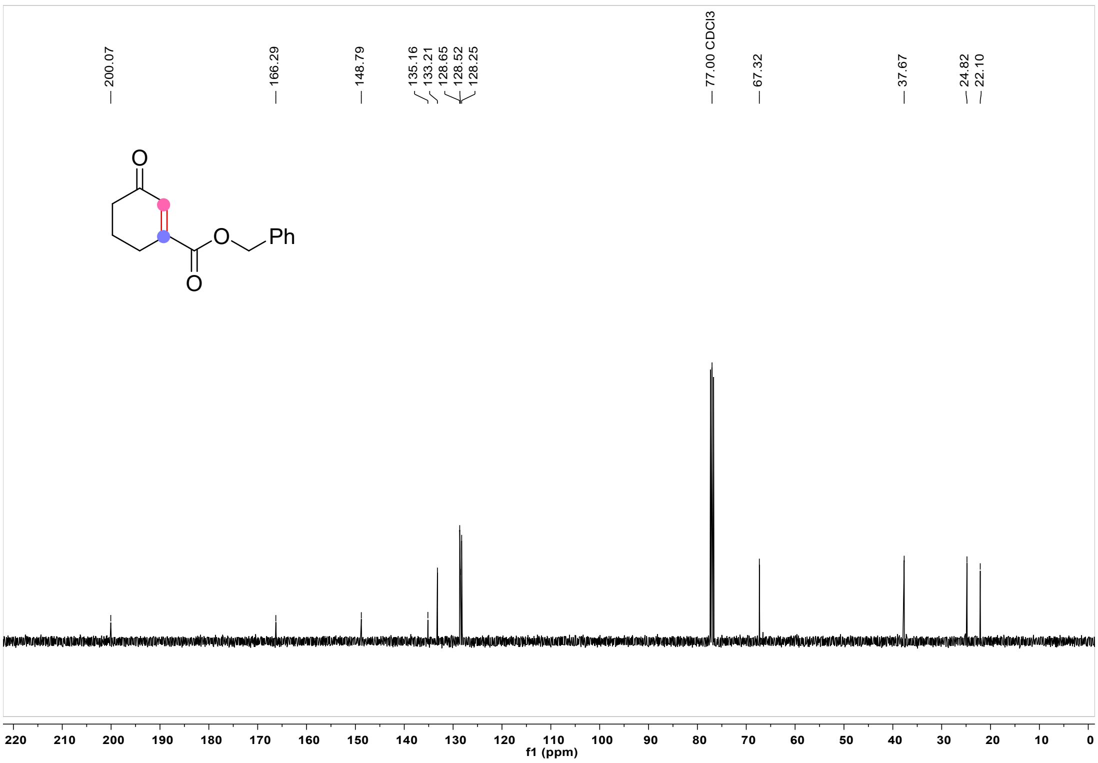
¹³C NMR spectra (101 MHz) of **3o** in $CDCl_3$.



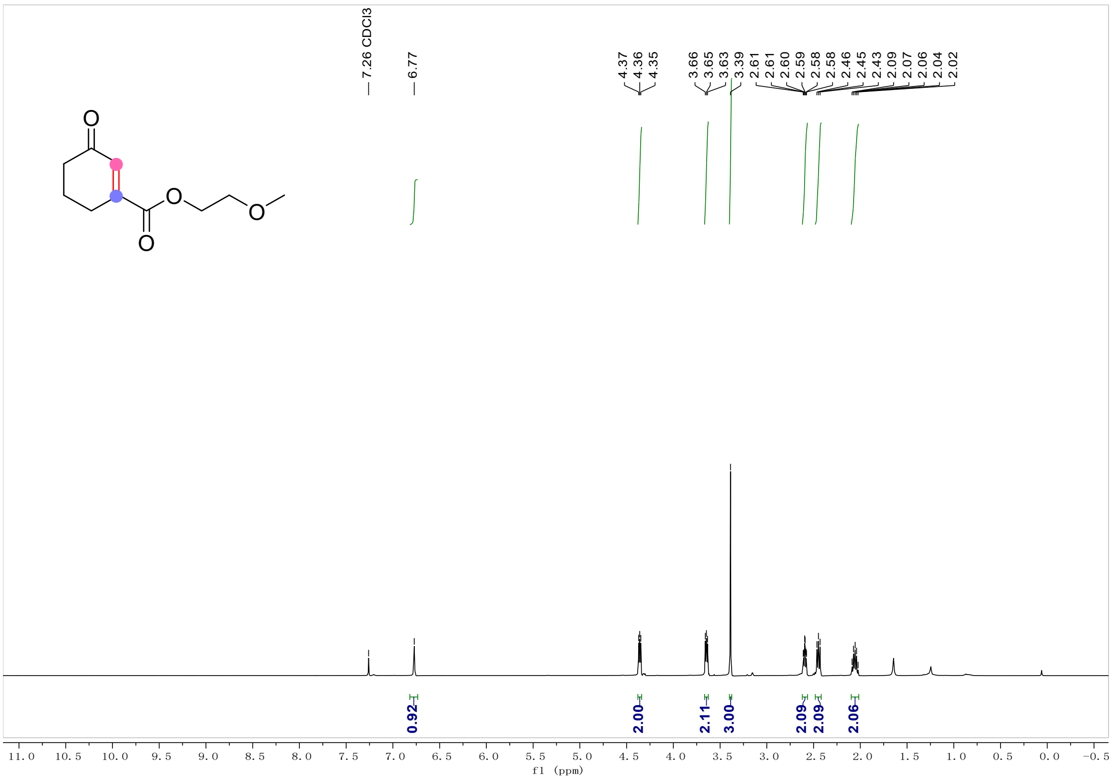
^{1}**H NMR** spectra (400 MHz) of **3p** in $CDCl_3$.



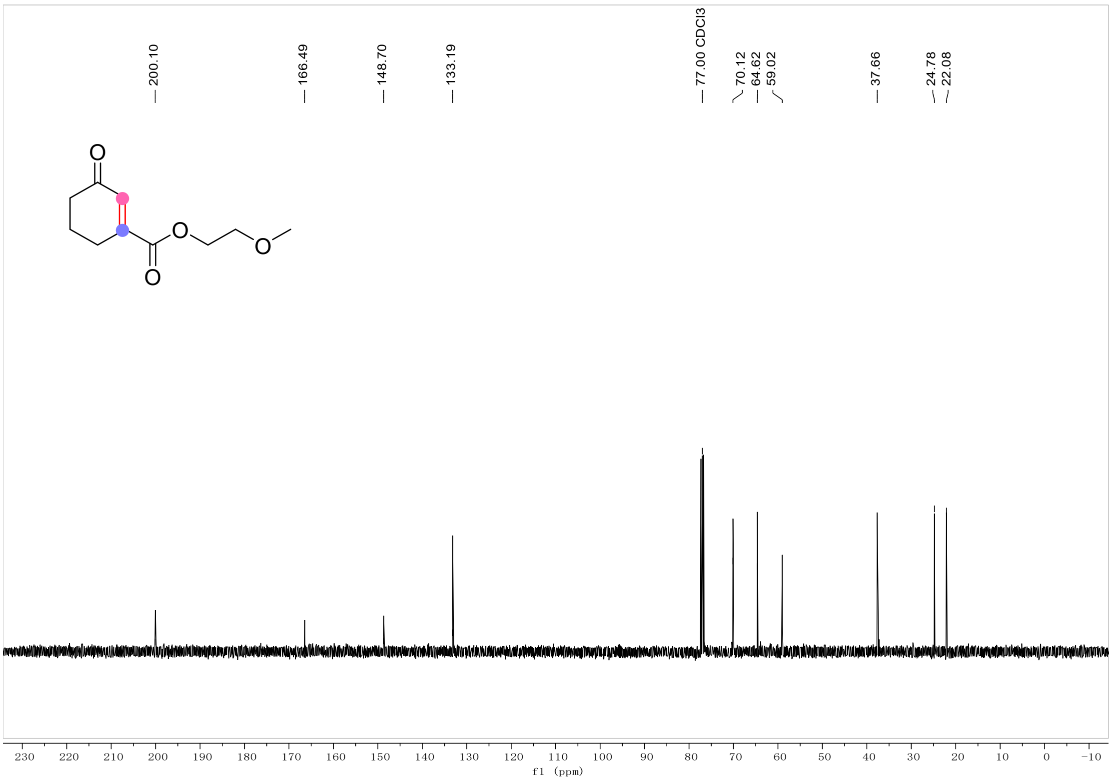
^{13}**C NMR** spectra (101 MHz) of **3p** in $CDCl_3$.



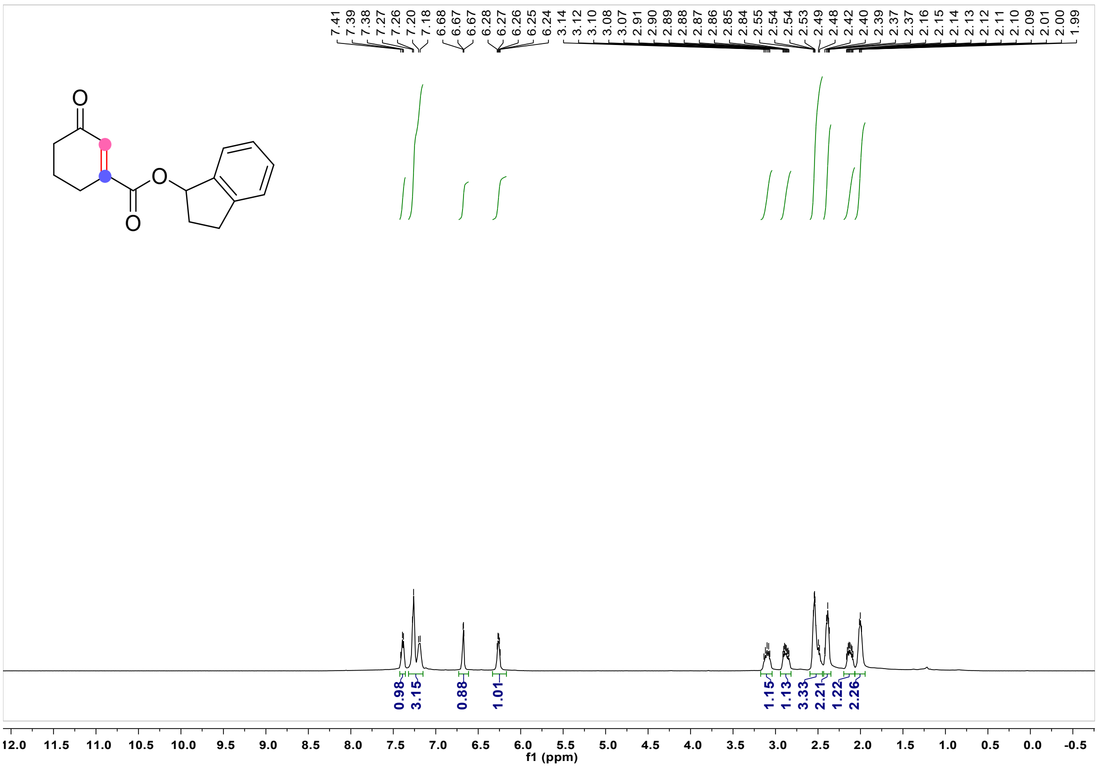
^{1}**H NMR** spectra (400 MHz) of **3q** in $CDCl_3$.



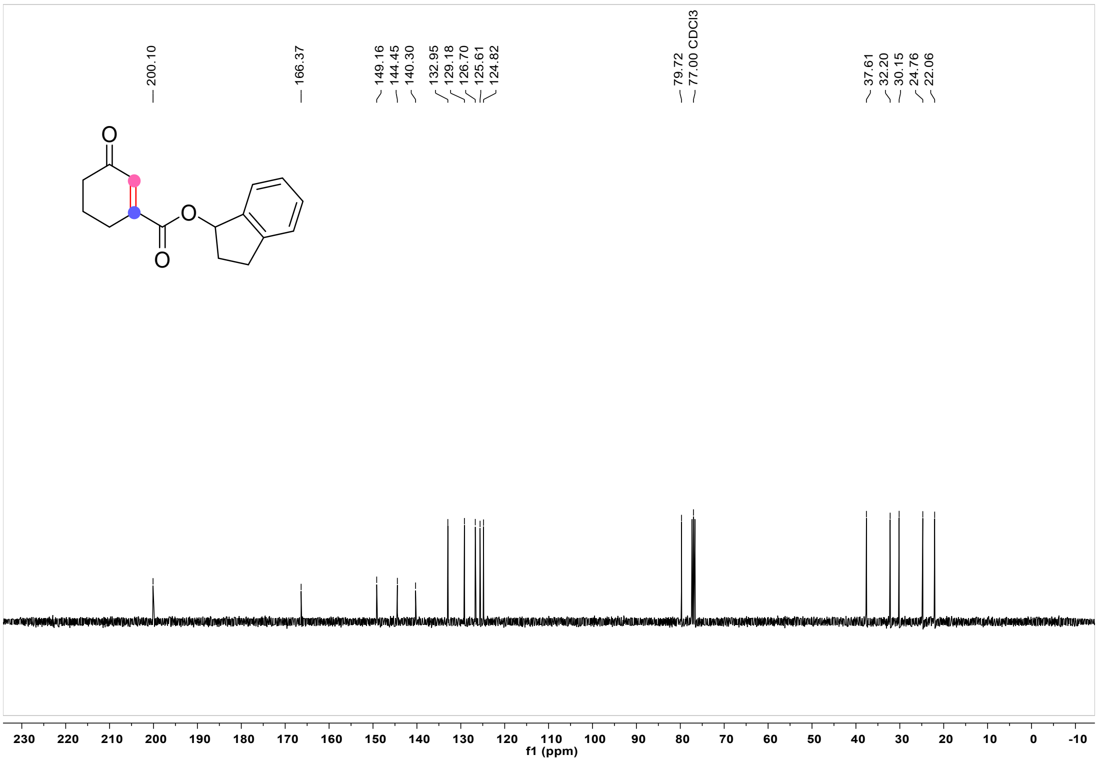
^{13}**C NMR** spectra (101 MHz) of **3q** in $CDCl_3$.



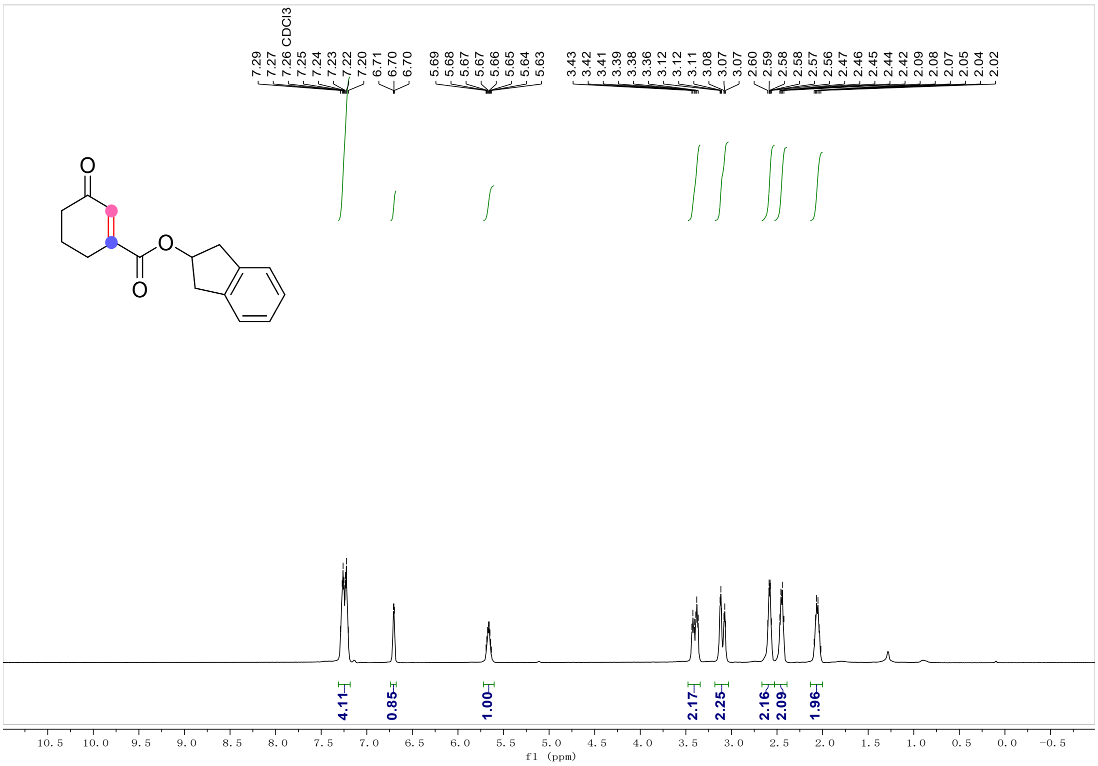
^{1}H NMR spectra (400 MHz) of **3r** in $CDCl_3$.



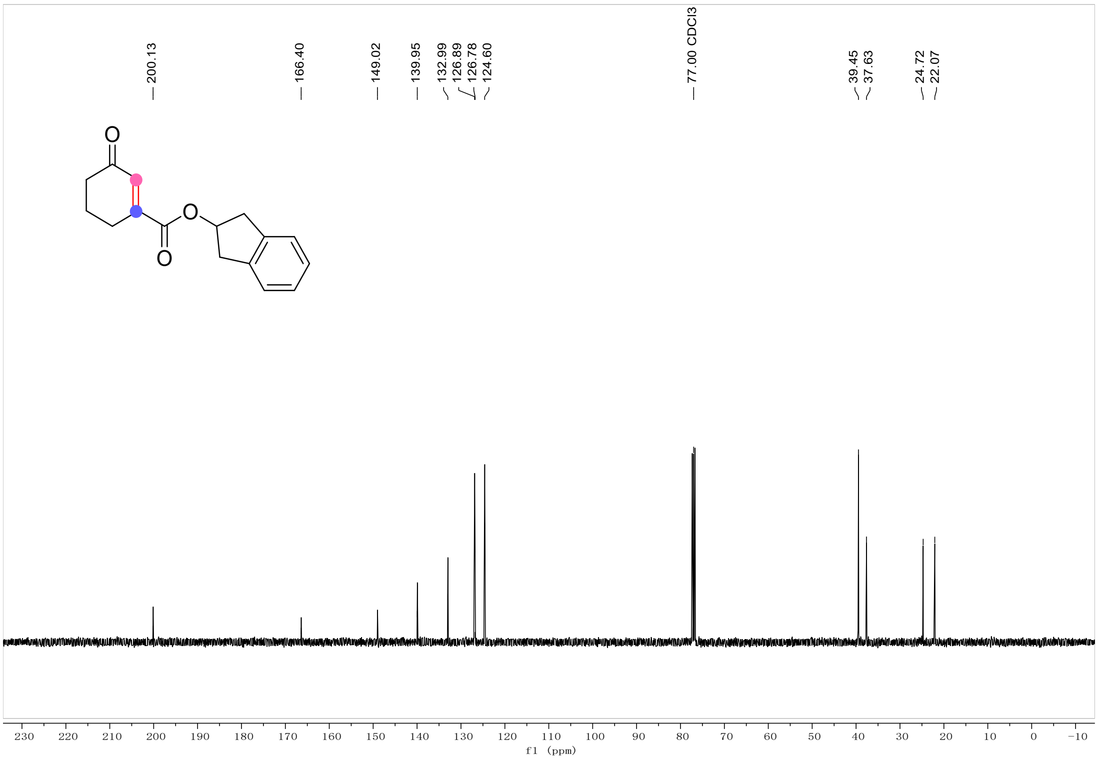
^{13}C NMR spectra (101 MHz) of **3r** in $CDCl_3$.



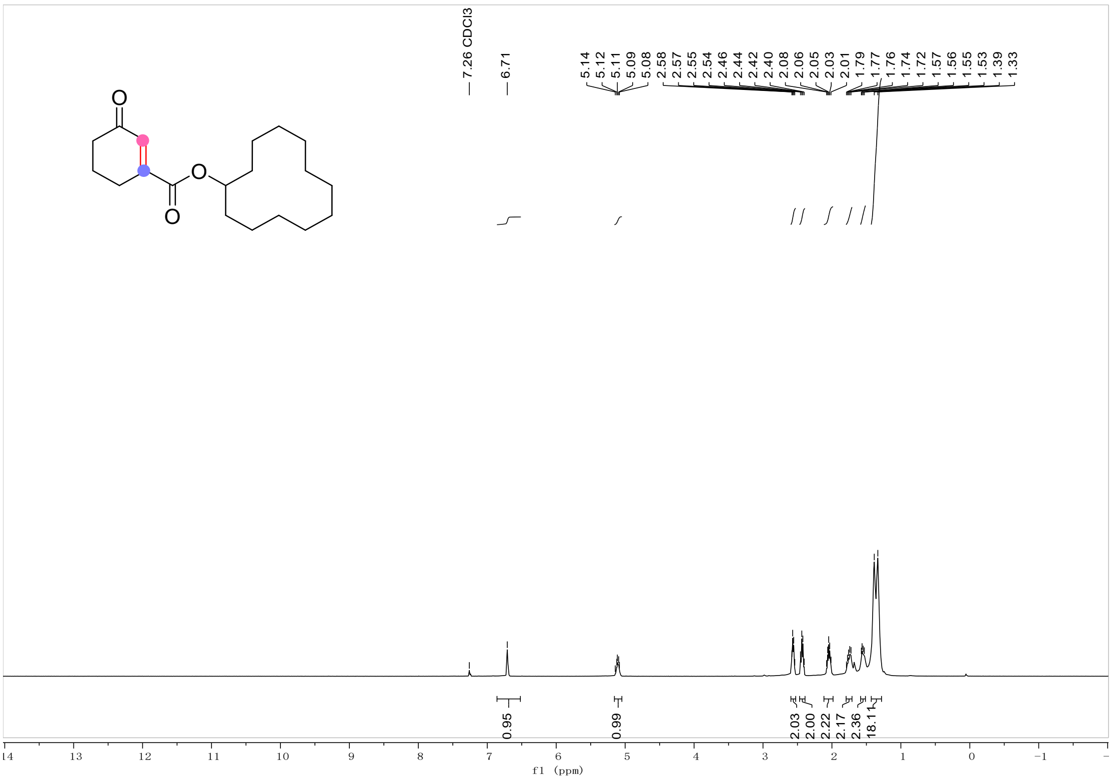
¹H NMR spectra (400 MHz) of **3s** in $CDCl_3$.



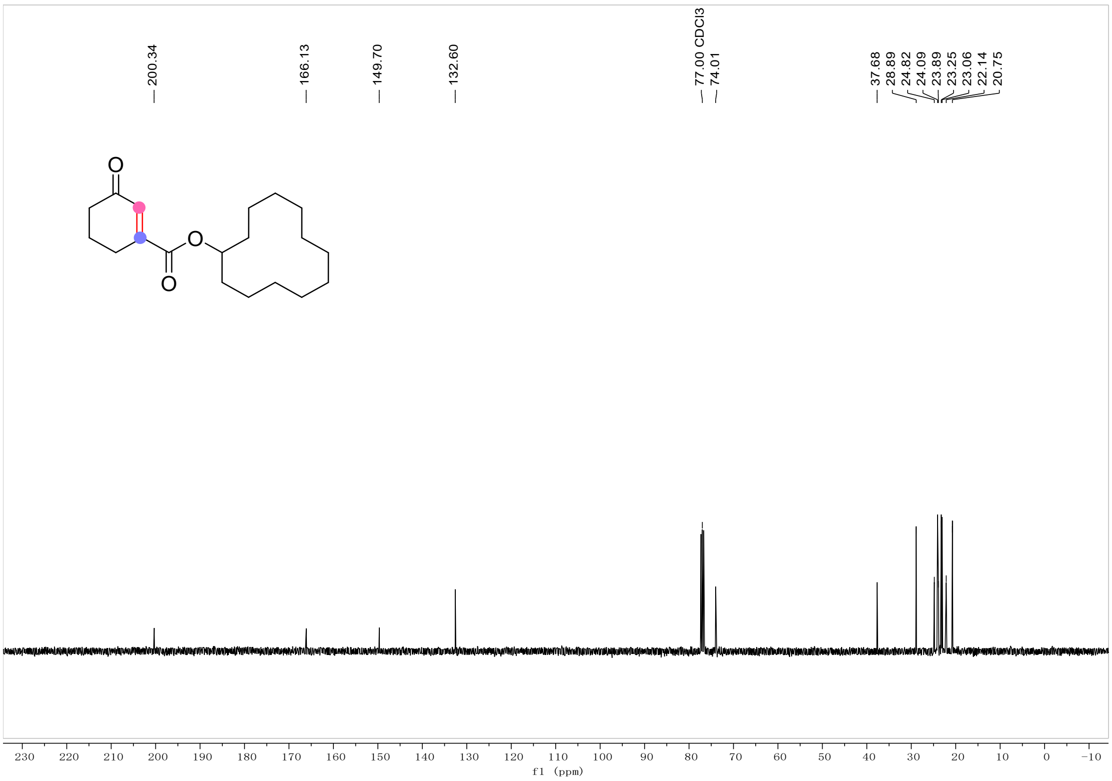
¹³C NMR spectra (101 MHz) of **3s** in $CDCl_3$.



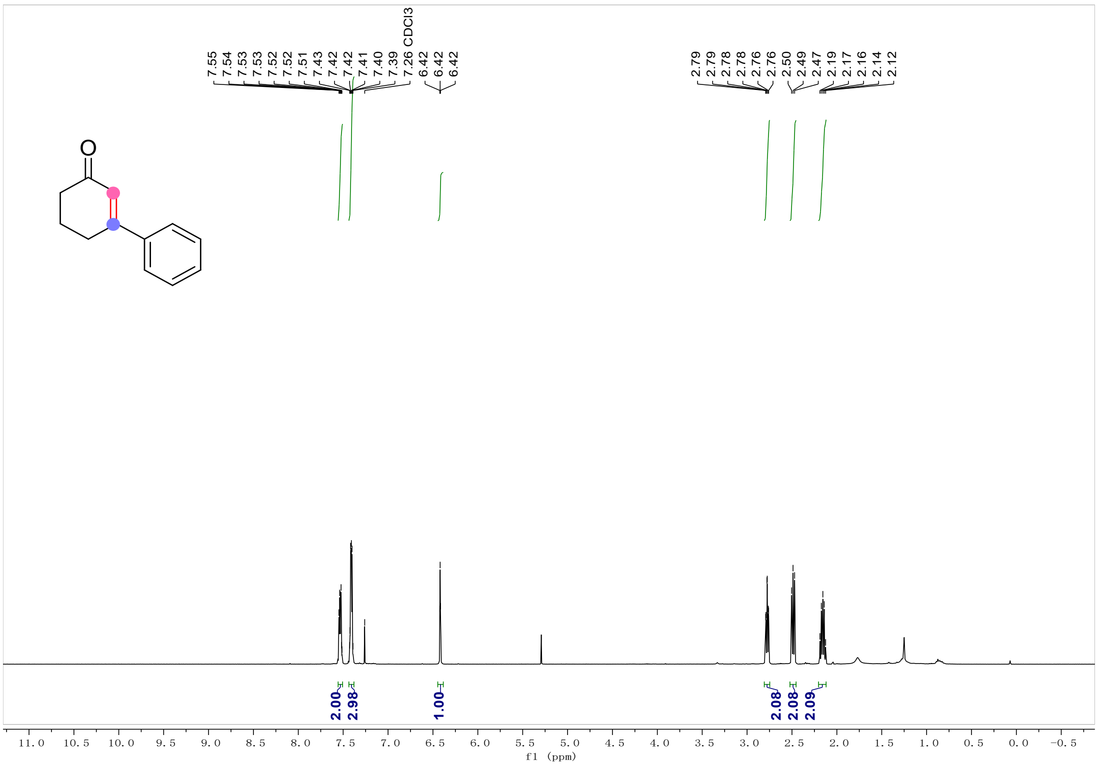
^{1}H NMR spectra (400 MHz) of **3t** in $CDCl_3$.



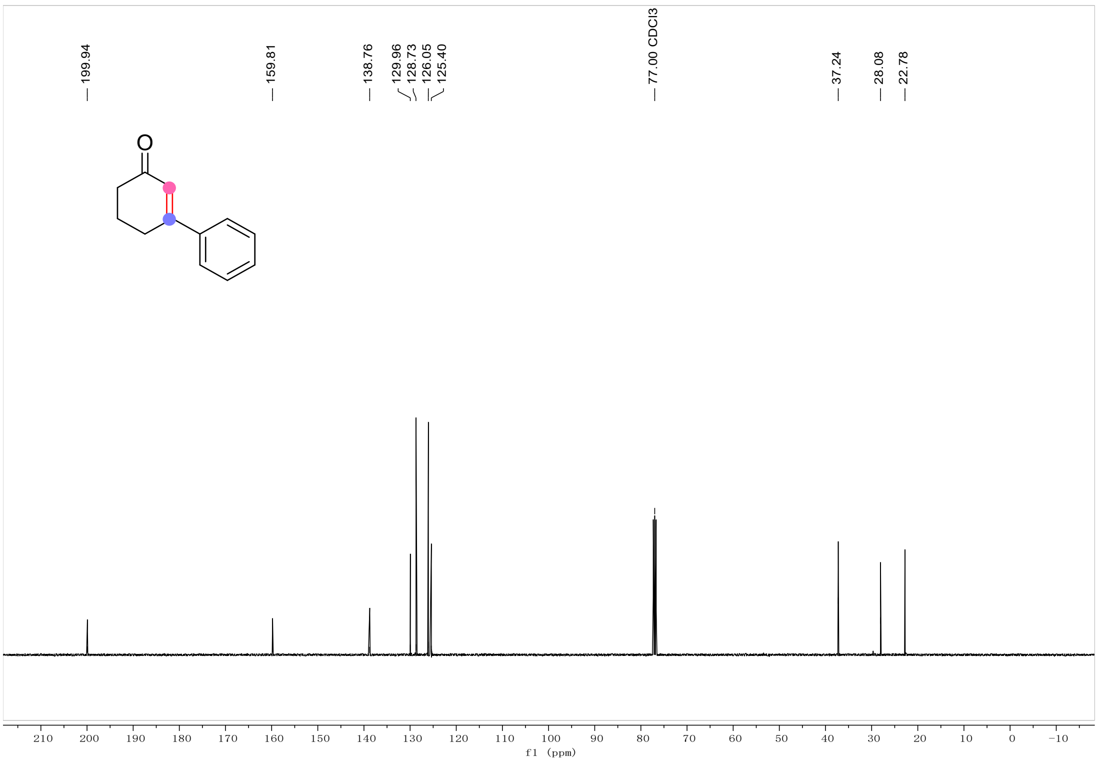
^{13}C NMR spectra (101 MHz) of **3t** in $CDCl_3$.



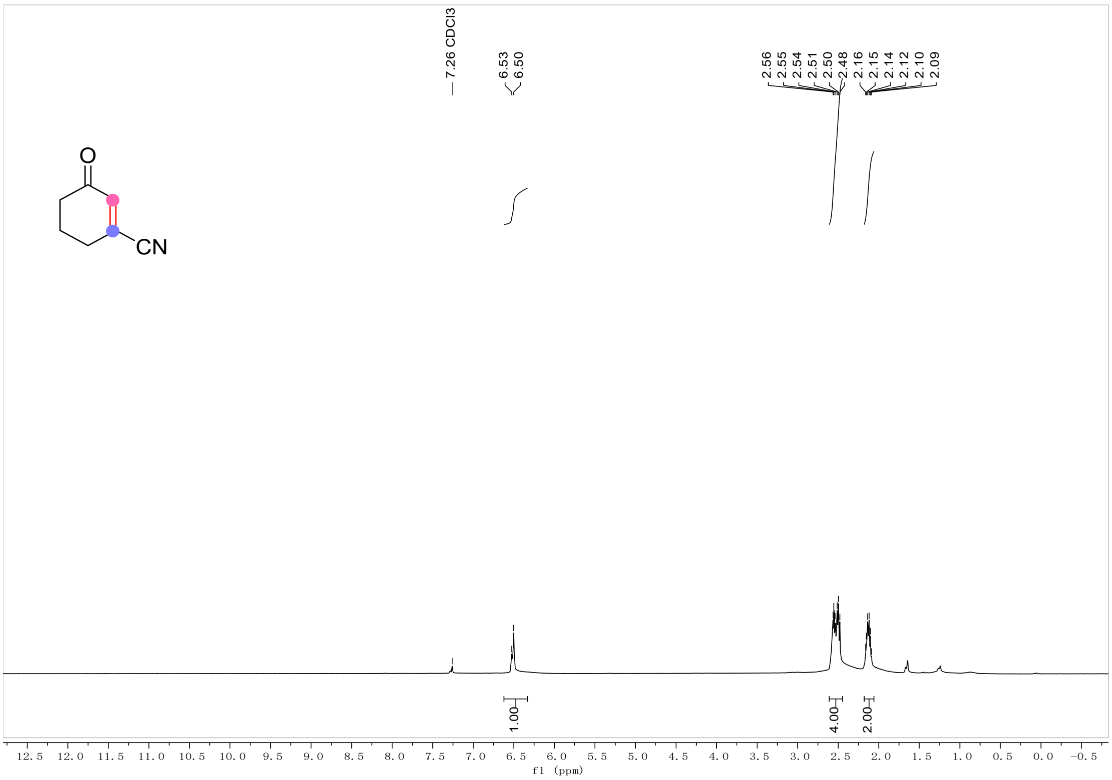
^{1}H NMR spectra (400 MHz) of **3u** in $CDCl_3$.



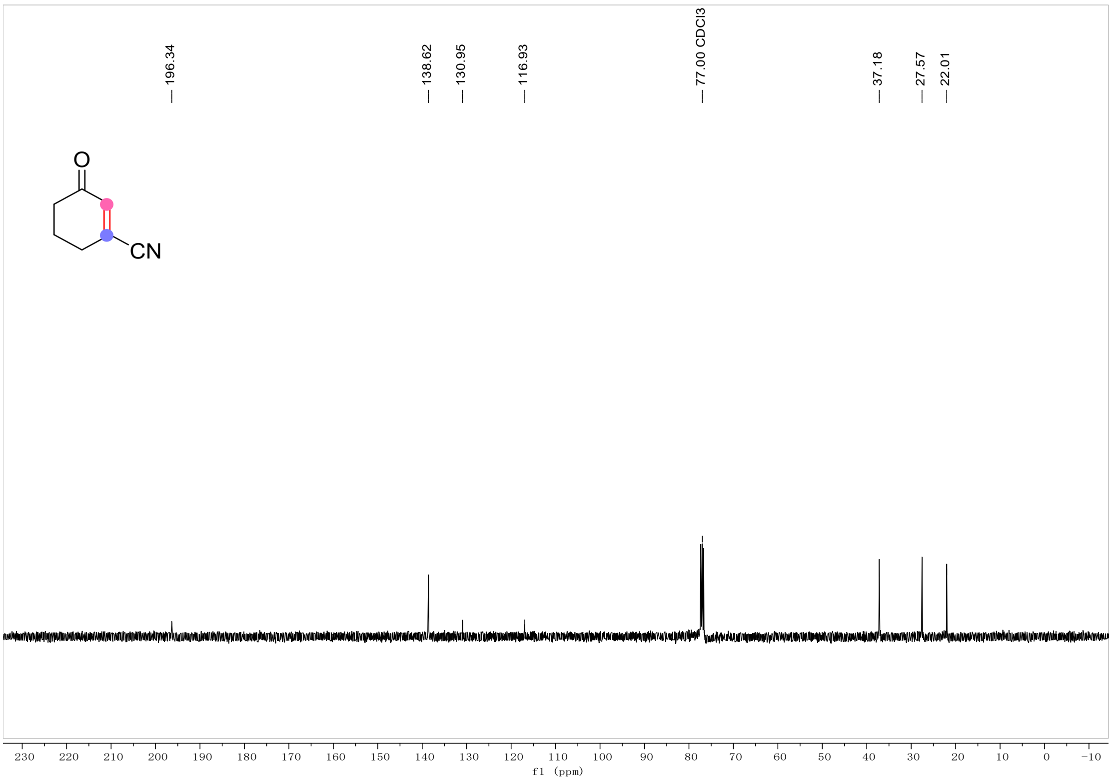
^{13}C NMR spectra (101 MHz) of **3u** in $CDCl_3$.



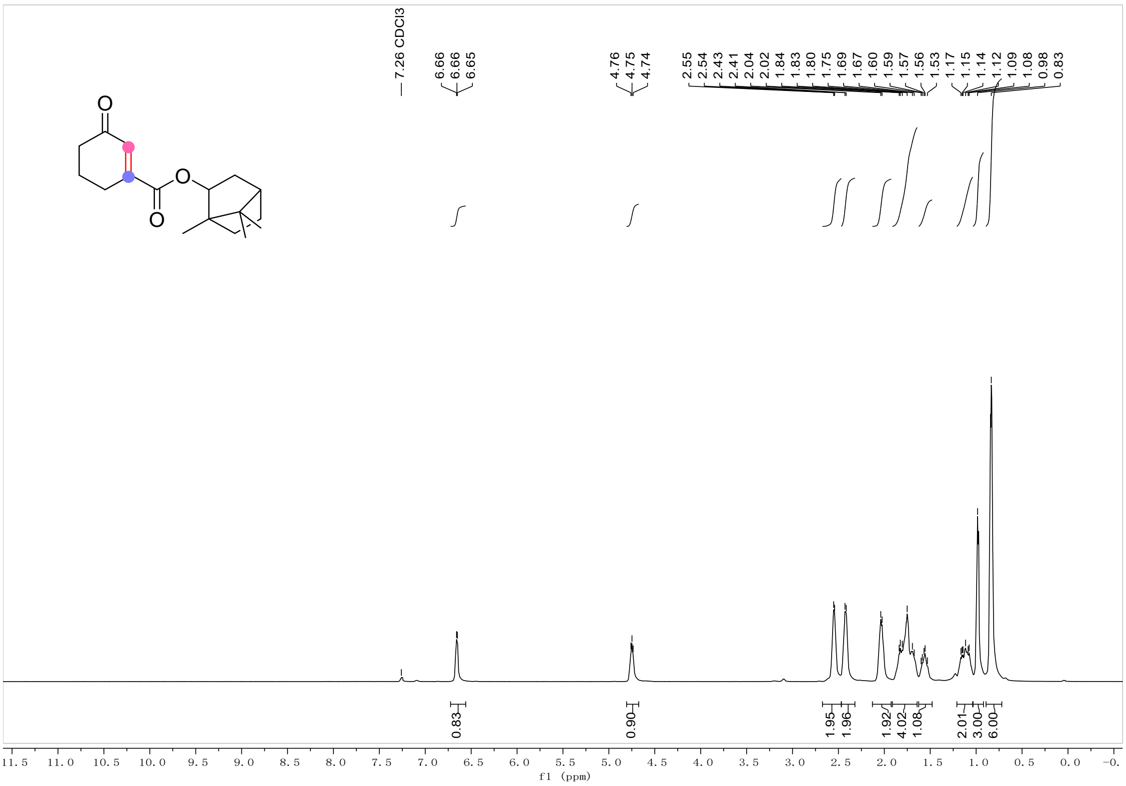
^{1}**H NMR** spectra (400 MHz) of **3v** in $CDCl_3$.



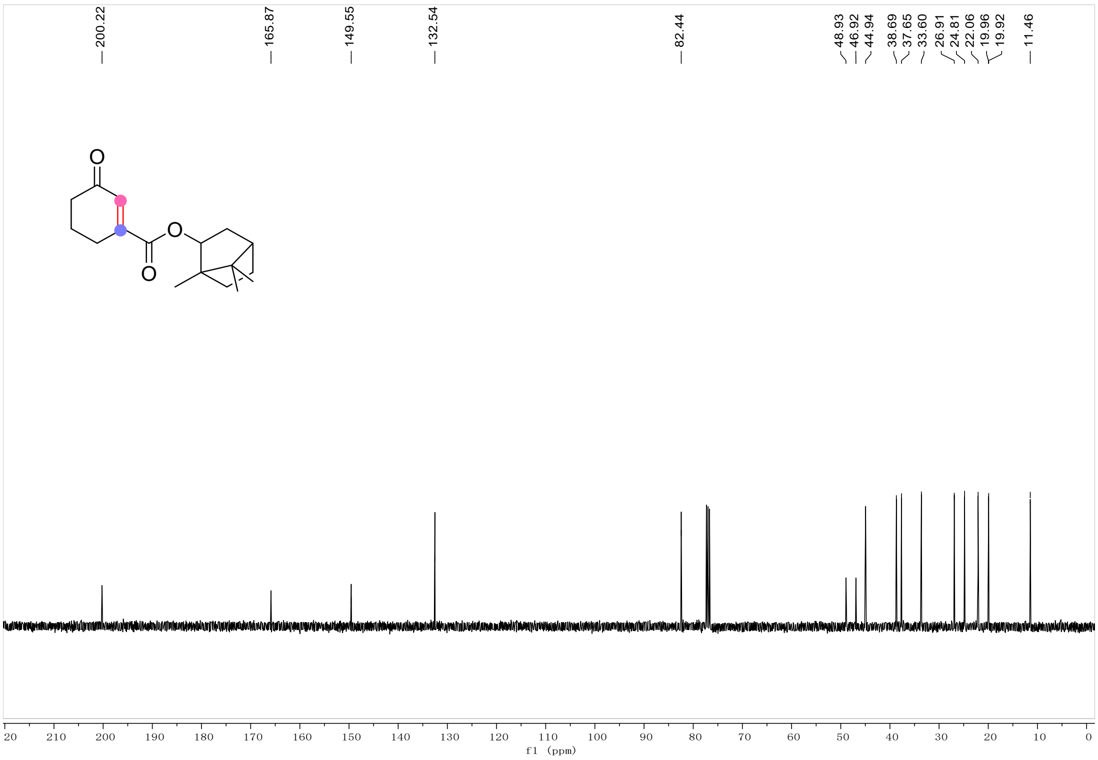
^{13}**C NMR** spectra (101 MHz) of **3u** in $CDCl_3$.



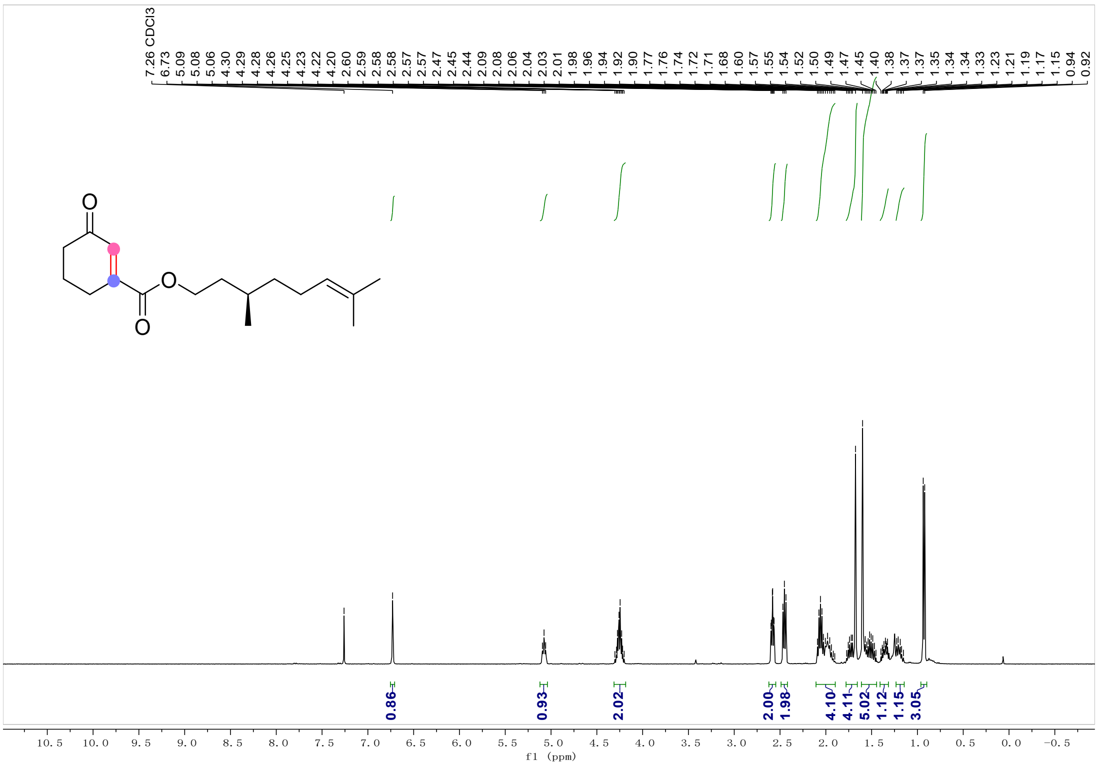
^{1}H NMR spectra (400 MHz) of **3w** in $CDCl_3$.



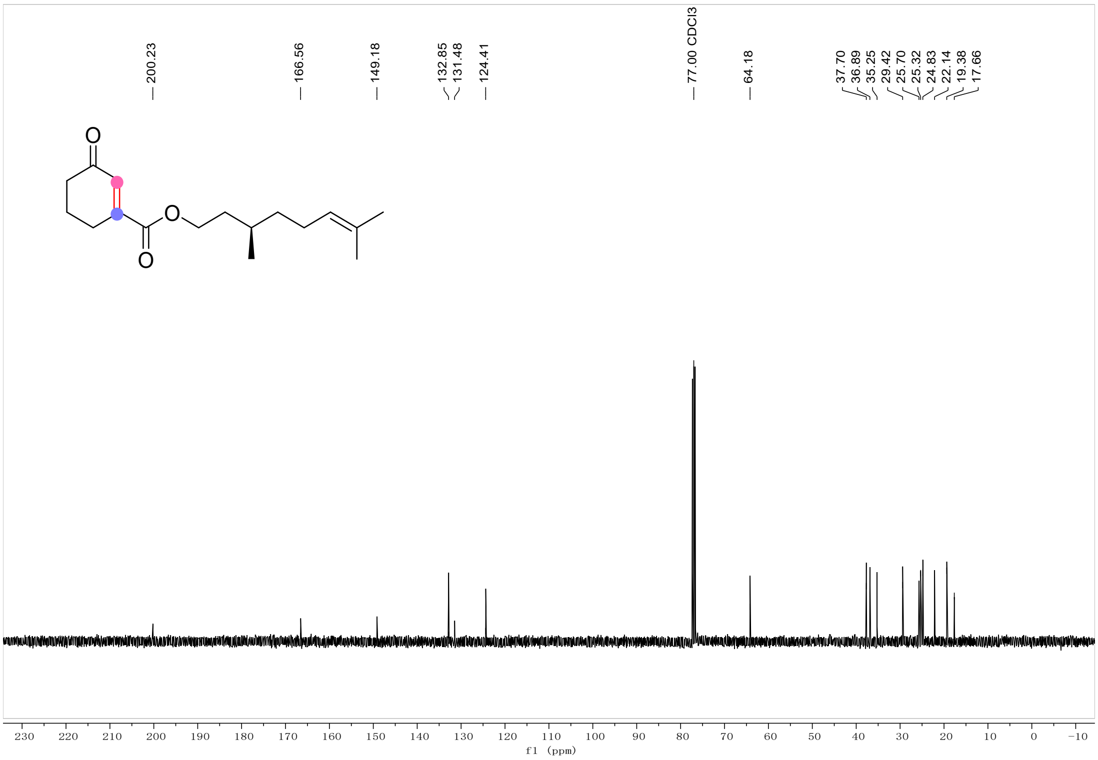
^{13}C NMR spectra (101 MHz) of **3w** in $CDCl_3$.



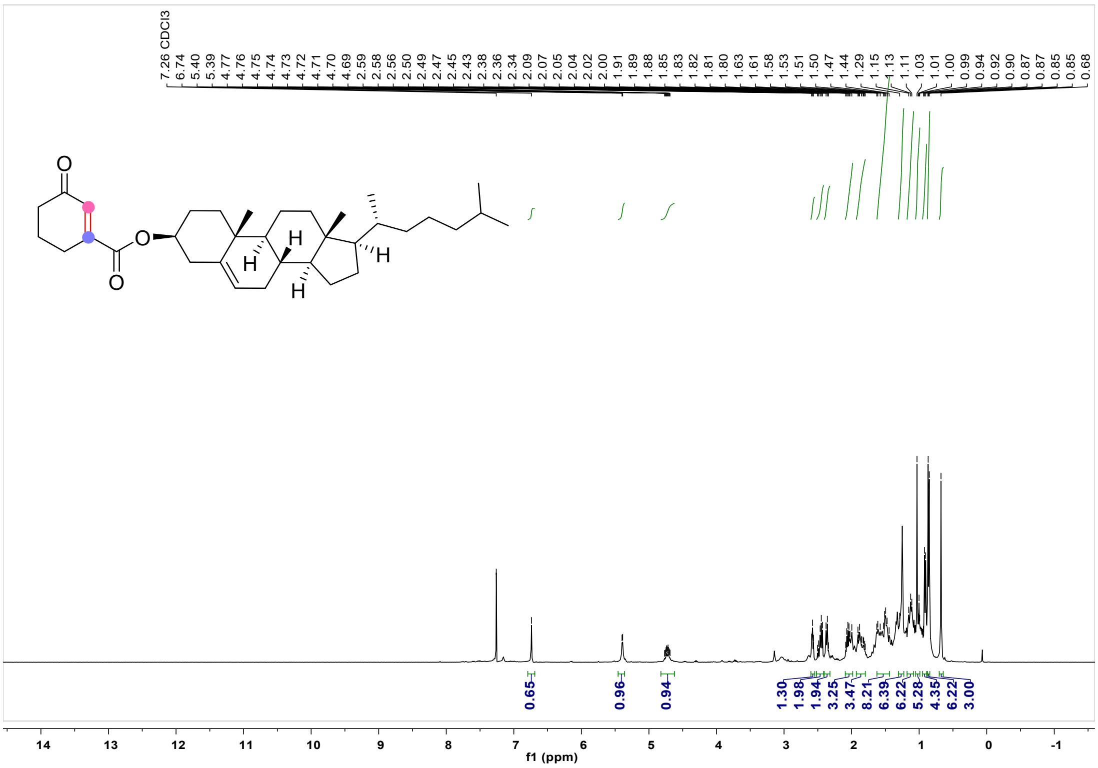
^{1}H NMR spectra (400 MHz) of **3x** in $CDCl_3$.



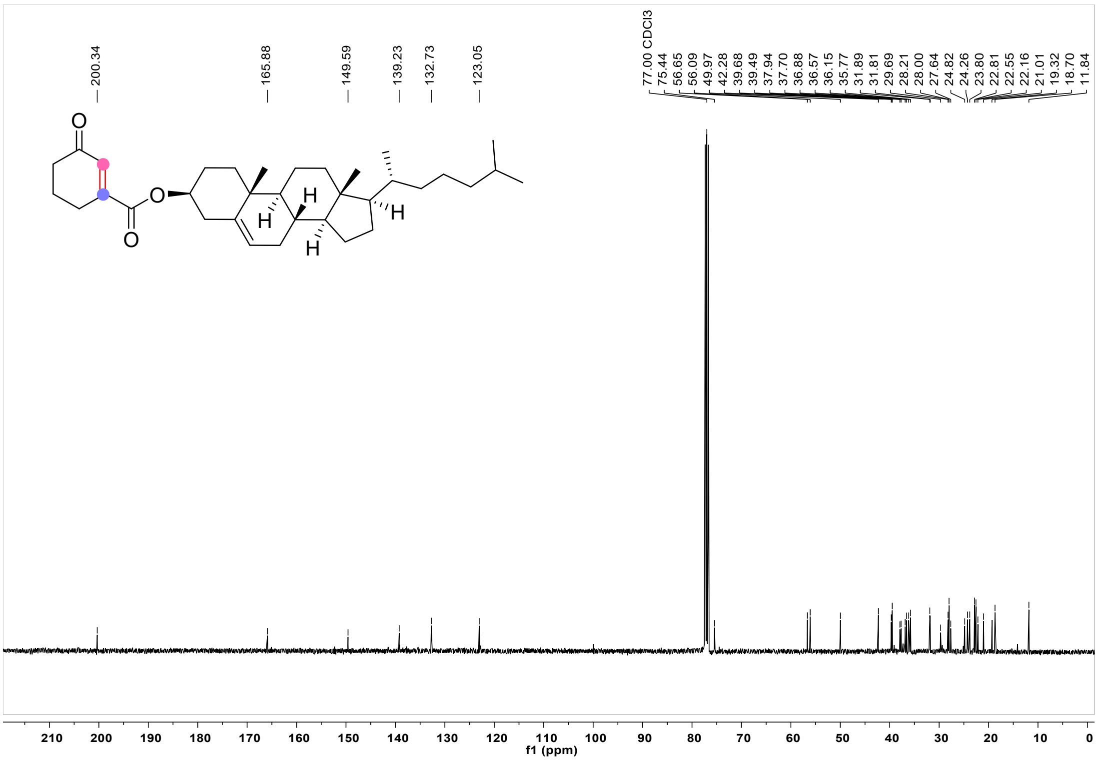
^{13}C NMR spectra (101 MHz) of **3x** in $CDCl_3$.



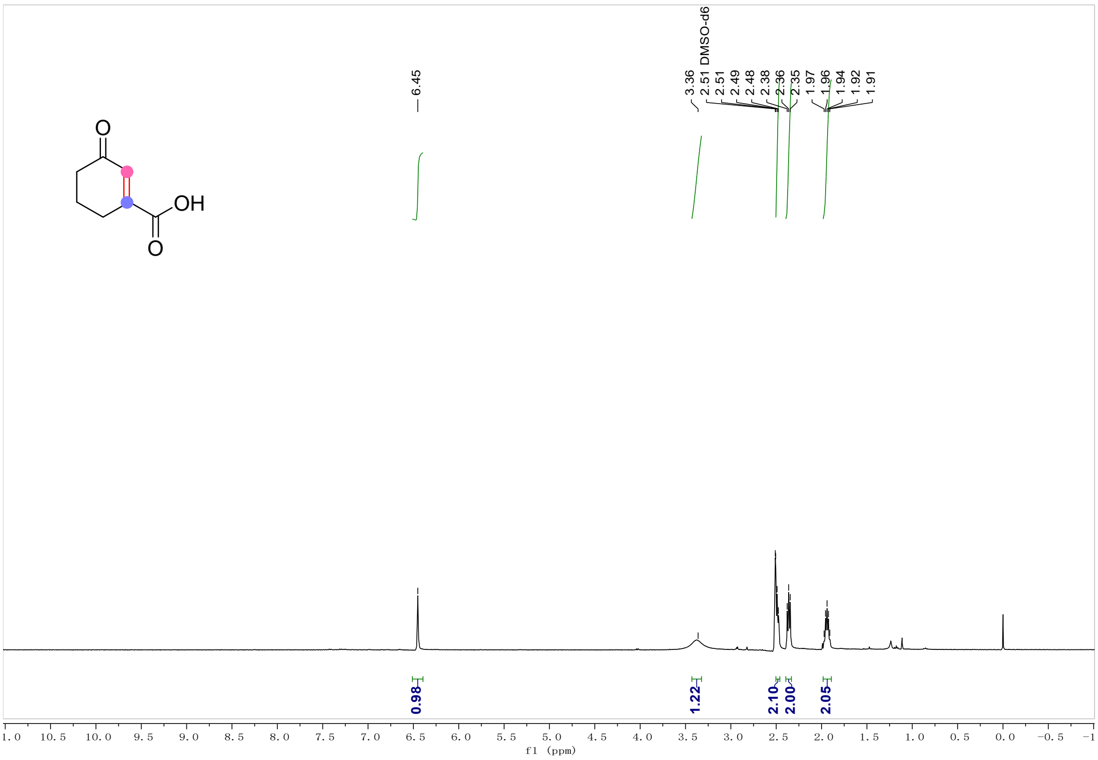
^{1}H NMR spectra (400 MHz) of **3y** in $CDCl_3$.



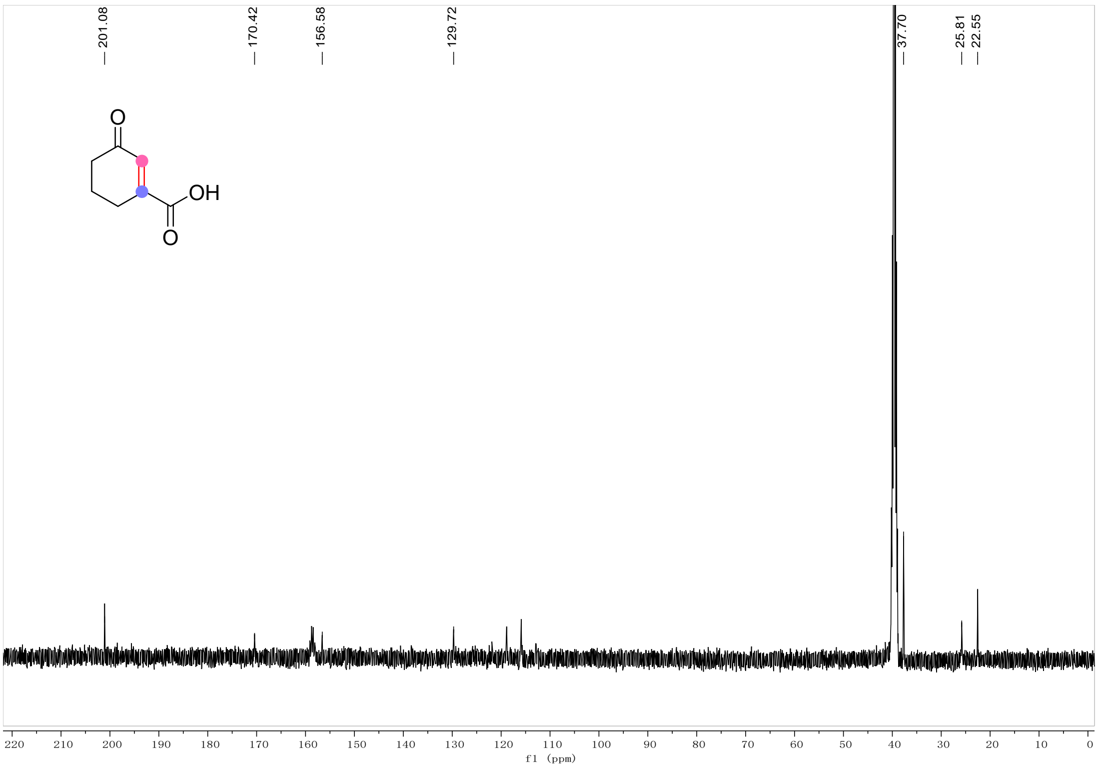
^{13}C NMR spectra (101 MHz) of **3y** in $CDCl_3$.



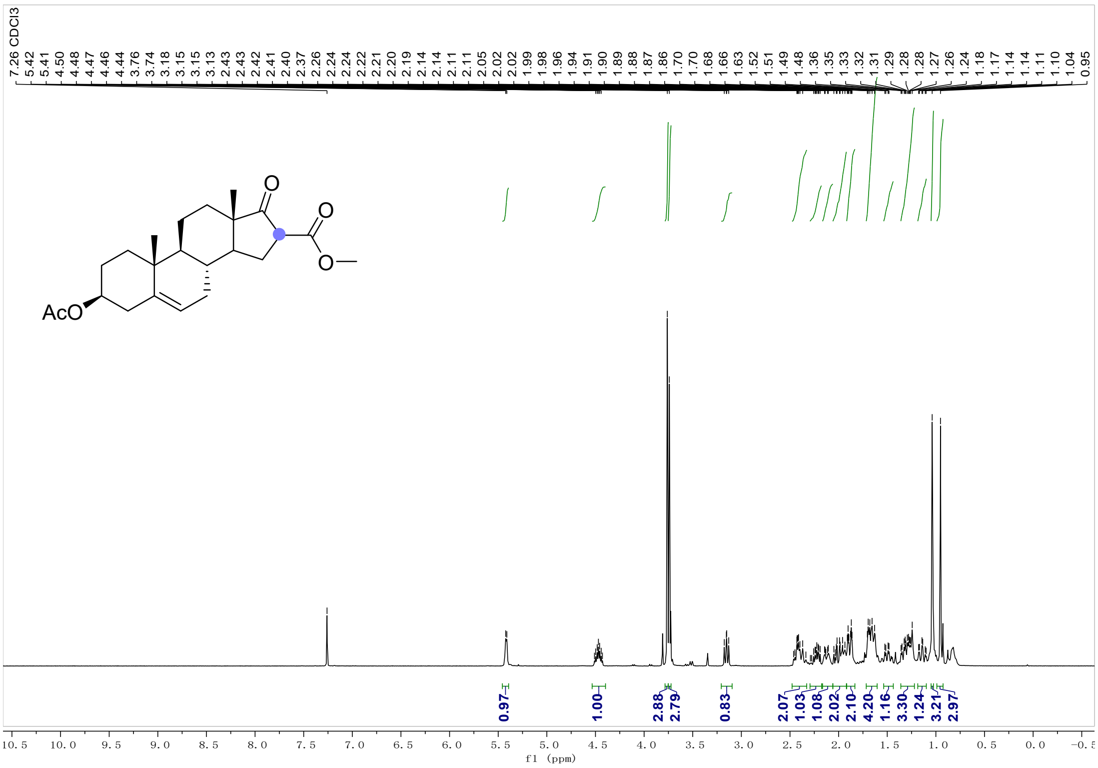
Crude ^{1}**H NMR** spectra (400 MHz) of **4** in DMSO-d_6.



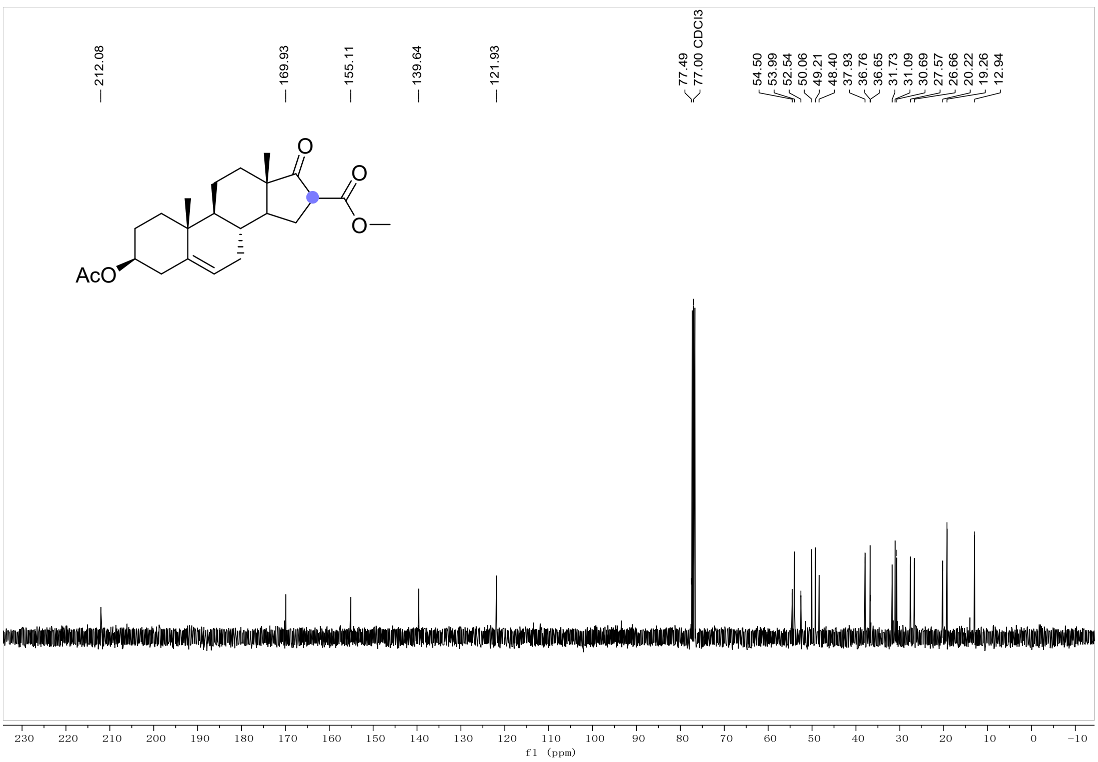
Crude ^{13}**C NMR** spectra (101 MHz) of **4** in DMSO-d_6.



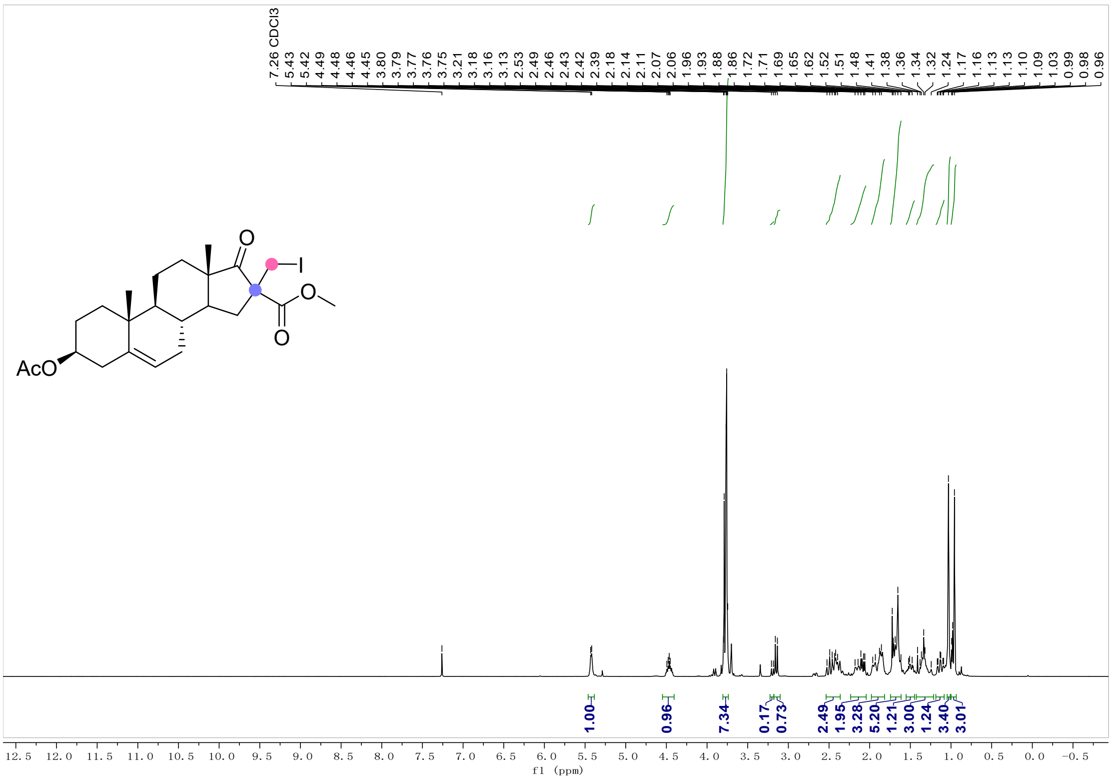
¹H NMR spectra (400 MHz) of **6** in $CDCl_3$.



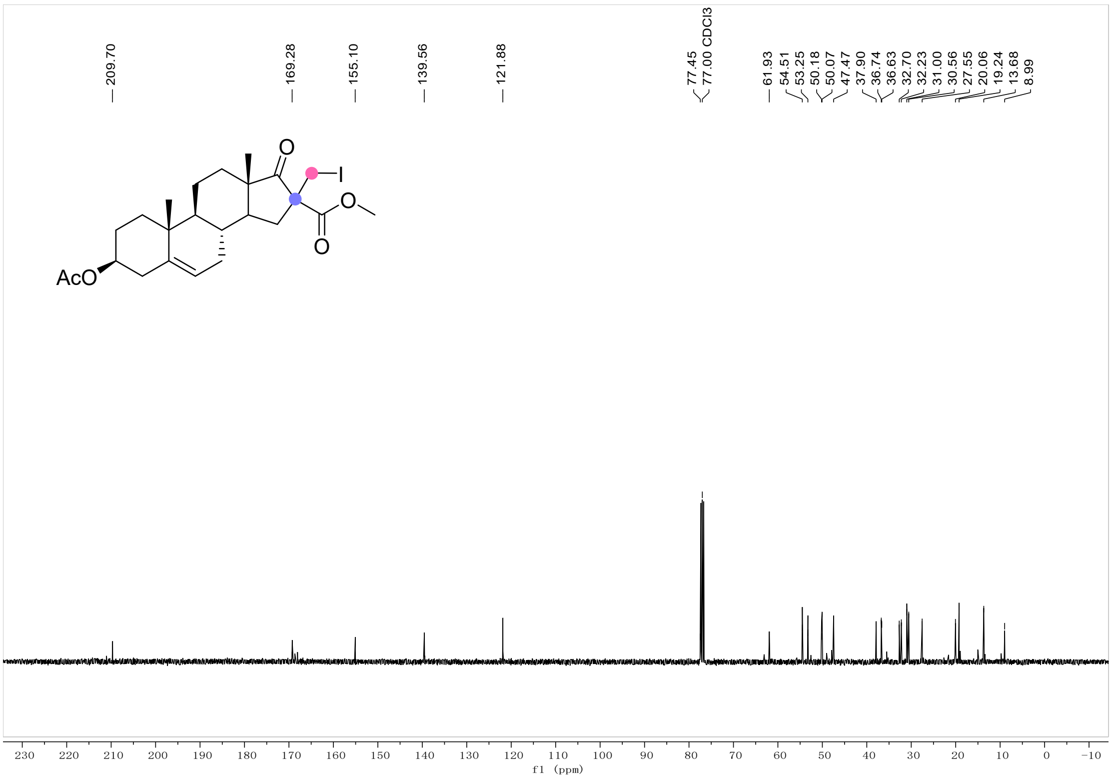
¹³C NMR spectra (101 MHz) of **6** in $CDCl_3$.



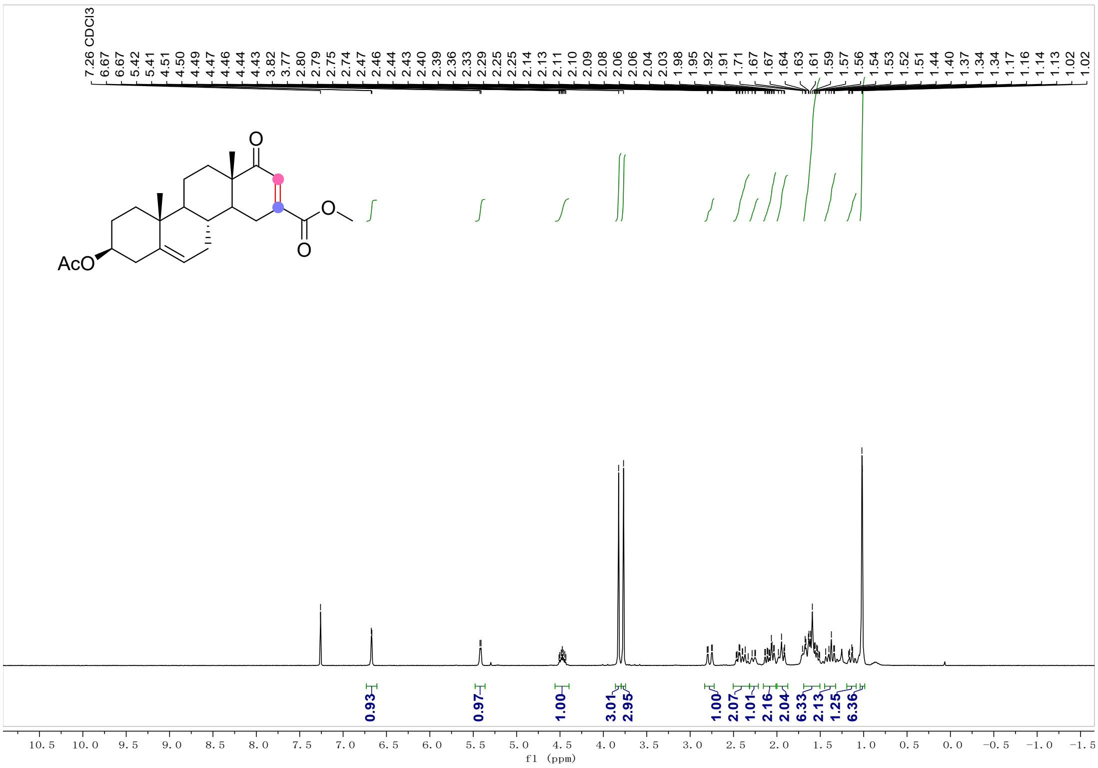
^{1}H NMR spectra (400 MHz) of **7** in $CDCl_3$.



^{13}C NMR spectra (101 MHz) of **7** in $CDCl_3$.



^{1}H NMR spectra (400 MHz) of **3z** in $CDCl_3$.



^{13}C NMR spectra (101 MHz) of **3z** in $CDCl_3$.