Supporting Information

Electrochemical α-Thiolation and Azidation of 1,3-Dicarbonyls

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Contents

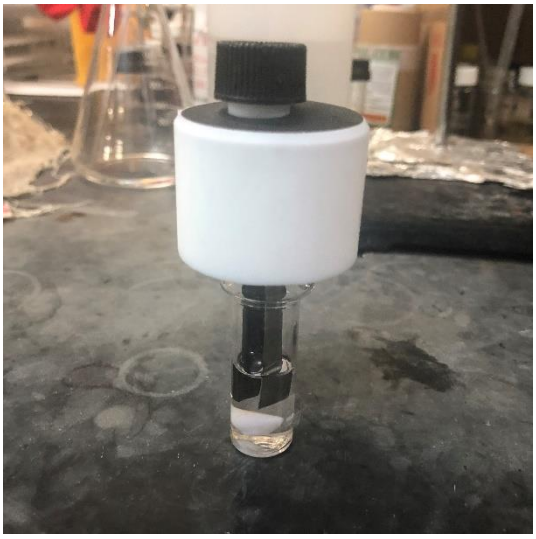
1. General Information

Regular reactions were carried out under ambient atmosphere with magnetic stirring. Electrolysis reactions were performed in colorless 5 mL ElectraSyn Vial from IKA under room temperature. Anhydrous solvents were obtained from Inert Pure Solv solvent purification system (acetonitrile). TLC were performed on silica gel Huanghai HSGF254 plates and visualization of the developed chromatogram was performed by fluorescence quenching (λ_{max} = 254 nm). Silica gel column chromatography was performed using GENERAL-REAGENT silica gel (200-300 mesh). Unless otherwise specified, all reagents were purchased from commercial suppliers (Adamas-beta, Bide Pharmatech, Energy Chemical, TCI, Aldrich, Alfa and J&K) and directly used without further purification.

NMR spectra were recorded on Bruker DRX-400 and DPX-600 spectrometers at 400 or 600 MHz for ^{1}H NMR, 101 or 151 MHz for ^{13}C NMR and 376 MHz or 565 MHz for ^{19}F NMR respectively, at ambient temperature. NMR standards were used as follows: (^{1}H NMR) $CDCl_3$ = 7.26 ppm; (^{13}C NMR) $CDCl_3$ = 77.16 ppm. Chemical shifts (δ) were reported in ppm and coupling constants (J) were quoted in Hertz (Hz). ^{1}H NMR data were recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet; d = doublet; dd = doublet of doublets; t = triplet; td = triplet of doublets; q = quartet; m = multiplet), coupling constant (Hz), integration. ^{13}C NMR data were reported in terms of chemical shift (δ, ppm). High-resolution mass spectra (HRMS) were performed on an Agilent Technologies 6230 TOF LC/MS spectrometer by electrospray ionization (ESI). X-ray single-crystal diffraction data were collected on Bruker D8 VENTURE.

The electrochemical reactions were carried out in a constant current mode using IKA ElectraSyn 2.0 equipped with IKA Carousel (six parallel reactions module). Graphite electrode (C, 2 mm × 8 mm × 52 mm, the purity of carbon: 99.99%, purchased from the shop of Shanghai Yueci Electronic Technology Co., Ltd. In Taobao.com) and Platinum plate electrode (Pt, 0.1 mm × 8 mm × 52 mm, the purity of platinum: 99.99%, purchased from the shop of Shanghai Yueci Electronic Technology Co., Ltd. In Taobao.com) were both commercially available. The cell assembly process is depicted

below:

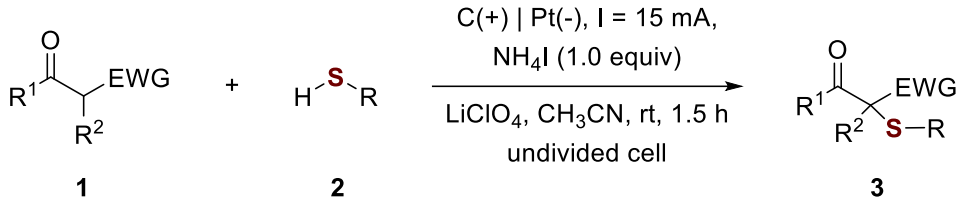


(***Left***) Graphite electrode (2 mm × 8 mm × 52 mm) and Platinum electrode (0.1 mm × 8 mm × 52 mm) were inserted into the holders on the connector; Platinum plate electrode was stuck with a section of graphite (***Right***) The electrode connector was plugged into the ElectraSyn Vial cap. (The distance between two electrodes is 0.5 cm)

The electrochemical cell was plugged into ElectraSyn 2.0 equipped with IKA Carousel (six parallel reactions module available).

(Left) Graphite electrode (30 mm × 30 mm × 3 mm) and Platinum plate electrode (30 mm × 30 mm × 0.1 mm); ***(Right)*** The setup for the gram-scale reaction.

2. Electrochemical α-Thiolation of 1,3-Dicarbonyls



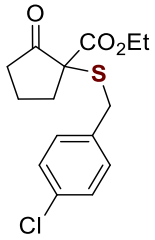
1 **2** **3**

Procedure A: Inside of an oven-dried 5 mL ElectraSyn Vial was charged with NH_4I (28.9 mg, 0.2 mmol, 1.0 equiv), $LiClO_4$ (21.3 mg, 0.2 mmol, 1.0 equiv), **1** (0.2 mmol, 1.0 equiv) and **2** (0.4 mmol, 2.0 equiv). Acetonitrile (3.0 mL) were added and stirred with a stir bar to form a homogeneous solution. The vial was equipped with graphite electrode as anode and platinum electrode as cathode (contacting area: 1.0 × 1.0 cm^2) with the electric connector under open air. The vial was stirred and electrolyzed at constant current of 15 mA for 1.5 or 3 hours at room temperature. When the electrolysis was terminated, the mixture was transferred into a separation funnel by dichloromethane or ethyl acetate. The combined organic layer was washed with water (5 mL × 3), saturated sodium thiosulfate and brine, and then dried over with anhydrous Na_2SO_4. After concentrated under *vacuo*, the crude product was purified by silica gel column chromatography or preparative TLC on a silica gel to afford the desired α-thiolated carbonyl compounds.

Procedure B: Inside of an oven-dried 20 mL ElectraSyn Vial was charged with NH_4I (144.5 mg, 1.0 mmol, 1.0 equiv), $LiClO_4$ (106.5 mg, 1.0 mmol, 1.0 equiv), **1** (1.0 mmol, 1.0 equiv) and **2** (2.0 mmol, 2.0 equiv). Acetonitrile (10.0 mL) were added and stirred with a stir bar to form a homogeneous solution. The vial was equipped with graphite electrode as anode and platinum electrode as cathode with the electric connector under open air. The vial was stirred and electrolyzed at constant current of 15 mA for 12 hours at room temperature. When the electrolysis was terminated, the mixture was transferred into a separation funnel by dichloromethane or ethyl acetate. The combined organic layer was washed with water (25 mL × 3), saturated sodium thiosulfate and brine, and then dried over with anhydrous Na_2SO_4. After concentrated under *vacuo*, the crude product was purified by silica gel column chromatography or preparative TLC on a

silica gel to afford the desired α-thiolated carbonyl compounds.

Ethyl 1-((4-chlorobenzyl)thio)-2-oxocyclopentane-1-carboxylate (**3a**)



3a

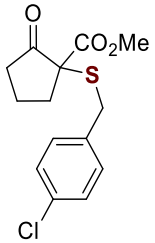
The reaction was performed according to **Procedure A,** then the product **3a** was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30:1 to 20:1) as a brown oil, 56.2 mg, 90% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 4H), 4.21 (q, J = 7.1 Hz, 2H), 4.05 (d, J = 12.2 Hz, 1H), 3.77 (d, J = 12.2 Hz, 1H), 2.67 – 2.57 (m, 2H), 2.43 – 2.36 (m, 1H), 2.16 – 1.99 (m, 3H), 1.29 (t, J = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 206.7, 169.4, 135.2, 133.2, 130.8, 128.8, 62.4, 60.3, 36.6, 35.5, 34.3, 19.4, 14.2.

HRMS (ESI, *m*/*z*) $[M + H]^+$calcd for $[C_{15}H_{18}ClO_3S]^+$: 313.0660; found: 313.0658.

Methyl 1-((4-chlorobenzyl)thio)-2-oxocyclopentane-1-carboxylate (**3b**)



3b

The reaction was performed according to **Procedure A,** then the product **3b** was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30:1 to 20:1) as a light-yellow oil, 50.1 mg, 84% yield.

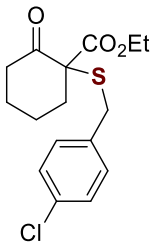
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.25 (m, 4H), 4.03 (d, J = 12.3 Hz, 1H), 3.76 (d, J = 12.3 Hz, 1H), 3.73 (s, 3H), 2.70 – 2.54 (m, 2H), 2.44 – 2.33 (m, 1H), 2.16 – 1.99

(m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.5, 169.9, 135.2, 133.3, 130.8, 128.8, 60.2, 53.2, 36.6, 35.5, 34.3, 19.4.

HRMS (ESI, *m/z*) $[M + H]^+$calcd for $[C_{14}H_{16}ClO_3S]^+$: 299.0503; found: 299.0503.

Ethyl 1-((4-chlorobenzyl)thio)-2-oxocyclohexane-1-carboxylate (**3c**)



3c

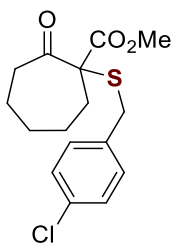
The reaction was performed according to **Procedure A,** then the product **3c** was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30:1 to 20:1) as a yellow oil, 46.3 mg, 71% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.25 (m, 4H), 4.31 – 4.17 (m, 2H), 3.87 (d, *J* = 12.4 Hz, 1H), 3.73 (d, *J* = 12.4 Hz, 1H), 2.81 – 2.73 (m, 1H), 2.71 – 2.64 (m, 1H), 2.45 – 2.38 (m, 1H), 1.97 – 1.90 (m, 2H), 1.90 – 1.82 (m, 2H), 1.72 – 1.63 (m, 1H), 1.31 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.3, 169.4, 135.5, 133.0, 130.6, 128.7, 64.6, 62.1, 39.4, 36.4, 33.8, 26.8, 22.1, 14.1.

HRMS (ESI, *m/z*) $[M + H]^+$calcd for $[C_{16}H_{20}ClO_3S]^+$: 327.0816; found: 327.0814.

Methyl 1-((4-chlorobenzyl)thio)-2-oxocycloheptane-1-carboxylate (**3d**)



3d

The reaction was performed according to **Procedure A,** then the product **3d** was

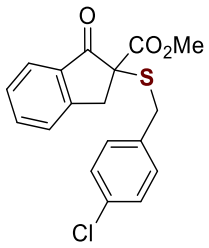
purified by silica gel column chromatography (petroleum ether/ethyl acetate = 40:1 to 20:1) as a white foam, 39.1 mg, 60% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.22 (m, 4H), 3.88 (d, J = 12.4 Hz, 1H), 3.74 (s, 3H), 3.68 (d, J = 12.5 Hz, 1H), 2.89 (ddd, J = 12.3, 11.1, 2.6 Hz, 1H), 2.48 (ddd, J = 12.3, 8.3, 2.3 Hz, 1H), 2.33 – 2.25 (m, 1H), 1.84 – 1.74 (m, 4H), 1.64 – 1.52 (m, 2H), 1.52 – 1.43 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.8, 170.6, 135.4, 133.2, 130.8, 128.8, 66.1, 53.0, 40.7, 35.2, 34.1, 30.4, 25.8, 25.3.

HRMS (ESI, *m*/*z*) $[M + H]^+$calcd for $[C_{16}H_{20}ClO_3S]^+$: 327.0816; found: 327.0814.

Methyl 2-((4-chlorobenzyl)thio)-1-oxo-2,3-dihydro-*1H*-indene-2-carboxylate (**3e**)



3e

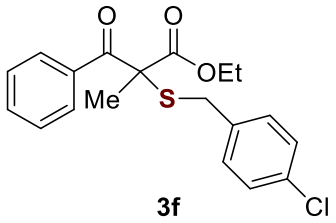
The reaction was performed according to **Procedure A** then the product **3e** was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30:1 to 20:1) as a white foam, 66.4 mg, 96% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.7 Hz, 1H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.49 – 7.41 (m, 2H), 7.29 – 7.23 (m, 4H), 4.19 (d, *J* = 12.4 Hz, 1H), 4.06 (d, *J* = 12.4 Hz, 1H), 3.89 (d, *J* = 17.9 Hz, 1H), 3.76 (s, 3H), 3.14 (d, *J* = 17.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 169.8, 150.5, 135.7, 135.1, 133.9, 133.2, 130.9, 128.8, 128.5, 126.3, 125.7, 58.9, 53.4, 40.1, 34.3.

HRMS (ESI, *m*/*z*) $[M + H]^+$calcd for $[C_{18}H_{16}ClO_3S]^+$: 347.0503; found: 347.0502.

Ethyl 2-((4-chlorobenzyl)thio)-2-methyl-3-oxo-3-phenylpropanoate (**3f**)



3f

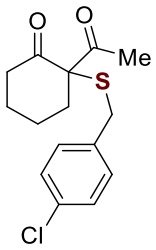
The reaction was performed according to **Procedure A,** and the reaction time was prolonged to 3 hours then the product **3f** was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 40:1 to 30:1) as a colorless oil, 14.5 mg, 20% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 8.4, 1.1 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 7.15 (d, *J* = 8.6 Hz, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.73 (d, *J* = 12.3 Hz, 1H), 3.60 (d, *J* = 12.4 Hz, 1H), 1.85 (s, 3H), 1.05 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.5, 171.2, 135.0, 135.0, 133.2, 133.2, 130.7, 129.2, 128.7, 128.5, 62.5, 61.4, 33.7, 23.2, 13.8.

HRMS (ESI, *m*/*z*) $[M + H]^+$calcd for $[C_{19}H_{20}ClO_3S]^+$: 363.0816; found: 363.0809.

2-Acetyl-2-((4-chlorobenzyl)thio)cyclohexan-1-one (**3g**)



3g

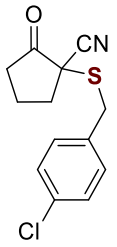
The reaction was performed according to **Procedure A,** then the product **3g** was purified by silica gel column chromatography (petroleum ether/ethyl acetate =30:1 to 20:1) as a white foam, 44.4 mg, 75% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 3.57 – 3.47 (m, 2H), 2.71 (dt, *J* = 14.1, 4.8 Hz, 1H), 2.63 – 2.55 (m, 1H), 2.34 (ddd, *J* = 14.3, 11.0, 5.7 Hz, 1H), 2.28 (s, 3H), 2.03 – 1.94 (m, 1H), 1.92 – 1.85 (m, 1H), 1.85 – 1.73 (m, 2H), 1.69 – 1.60 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.3, 200.5, 135.4, 133.2, 130.6, 128.8, 71.5, 41.1, 35.2, 33.1, 27.1, 25.6, 22.6.

HRMS (ESI, *m*/*z*) $[M + H]^+$calcd for $[C_{15}H_{18}ClO_2S]^+$: 297.0711; found: 297.0710.

1-((4-Chlorobenzyl)thio)-2-oxocyclopentane-1-carbonitrile (**3h**)



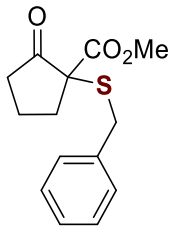
3h

The reaction was performed according to **Procedure A,** then the product **3h** was purified by silica gel column chromatography (petroleum ether/ethyl acetate =30:1 to 20:1) as a white foam, 28.6 mg, 54% yield.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.31 – 7.25 (m, 4H), 4.05 (d, *J* = 12.0 Hz, 1H), 3.89 (d, *J* = 12.0 Hz, 1H), 2.78 – 2.69 (m, 1H), 2.53 (ddd, *J* = 13.9, 11.4, 7.9 Hz, 1H), 2.44 – 2.33 (m, 1H), 2.33 – 2.25 (m, 1H), 2.20 – 2.05 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) *δ* 201.5, 134.0, 133.1, 131.0, 129.1, 116.6, 47.7, 35.2, 34.9, 34.4, 18.9. **HRMS** did not ionize using ESI.

Methyl 1-(benzylthio)-2-oxocyclopentane-1-carboxylate (**3i**)



3i

The reaction was performed according to **Procedure A,** then the product **3i** was purified by silica gel column chromatography (petroleum ether/ethyl acetate =50:1 to 30:1) as a yellow oil, 47.0 mg, 89% yield.

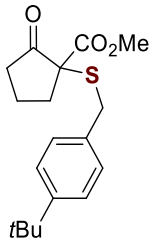
^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.33 – 7.26 (m, 4H), 7.26 – 7.21 (m, 1H), 4.06 (d, *J* =

12.1 Hz, 1H), 3.79 (d, *J* = 12.1 Hz, 1H), 3.73 (s, 3H), 2.70 – 2.55 (m, 2H), 2.44 – 2.33 (m, 1H), 2.19 – 1.97 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.5, 170.0, 136.6, 129.5, 128.7, 127.5, 60.3, 53.2, 36.5, 35.5, 35.0, 19.4.

HRMS (ESI, *m*/*z*) $[M + H]^+$calcd for $[C_{14}H_{17}O_3S]^+$: 265.0893; found: 265.0894.

Methyl 1-((4-(*tert*-butyl)benzyl)thio)-2-oxocyclopentane-1-carboxylate (**3j**)



3j

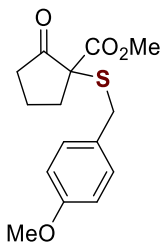
The reaction was performed according to **Procedure A,** then the product **3j** was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30:1) as a light-yellow oil, 45.4 mg, 71% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.4 Hz, 2H), 7.24 (d, *J* = 7.7 Hz, 2H), 4.04 (d, *J* = 12.0 Hz, 1H), 3.76 (d, *J* = 12.0 Hz, 1H), 3.73 (s, 3H), 2.69 – 2.55 (m, 2H), 2.42 – 2.34 (m, 1H), 2.15 – 2.06 (m, 2H), 2.00 (q, *J* = 9.3 Hz, 1H), 1.29 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 206.4, 170.1, 150.4, 133.4, 129.1, 125.7, 60.3, 53.1, 36.5, 35.5, 34.6, 34.6, 31.4, 19.3.

HRMS (ESI, *m*/*z*) $[M+Na]^+$calcd for $[C_{18}H_{24}NaO_3S]^+$: 343.1338; found: 343.1337.

Methyl 1-((4-methoxybenzyl)thio)-2-oxocyclopentane-1-carboxylate (**3k**)



3k

The reaction was performed according to **Procedure A,** then the product **3k** was

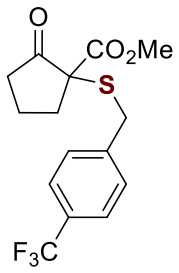
purified by silica gel column chromatography (petroleum ether/ethyl acetate = 50:1 to 40:1) as a light-yellow oil, 52.9 mg, 90% yield. When the reaction was performed according to **Procedure B**, the product **3k** was obtained in 85% yield, 250 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 8.6 Hz, 2H), 6.82 (d, J = 8.7 Hz, 2H), 4.01 (d, J = 12.0 Hz, 1H), 3.78 (s, 3H), 3.76 – 3.72 (m, 4H), 2.68 – 2.54 (m, 2H), 2.43 – 2.32 (m, 1H), 2.17 – 1.97 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.4, 170.1, 159.0, 130.6, 128.3, 114.1, 60.4, 55.4, 53.2, 36.5, 35.5, 34.4, 19.3.

HRMS (ESI, *m*/*z*) $[M+Na]^+$calcd for $[C_{15}H_{18}NaO_4S]^+$: 317.0818; found: 317.0813.

Methyl 2-oxo-1-((4-(trifluoromethyl)benzyl)thio)cyclopentane-1-carboxylate (**3l**)



3l

The reaction was performed according to **Procedure A,** then the product **3l** was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 40:1 to 30:1) as a colorless oil, 58.4 mg, 88% yield. When the reaction was performed according to **Procedure B,** the product **3l** was obtained in 84% yield, 278.9 mg.

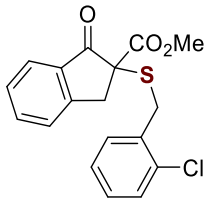
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.1 Hz, 2H), 7.43 (d, J = 8.1 Hz, 2H), 4.10 (d, J = 12.5 Hz, 1H), 3.84 (d, J = 12.5 Hz, 1H), 3.71 (s, 3H), 2.68 – 2.55 (m, 2H), 2.45 – 2.34 (m, 1H), 2.17 – 1.99 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 206.5, 169.9, 141.0, 129.8, 129.7 (q, J = 32.4 Hz), 125.6 (q, J = 3.8 Hz), 124.2 (q, J = 272.0 Hz), 60.1, 53.2, 36.6, 35.5, 34.5, 19.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.56.

HRMS (ESI, *m*/*z*) $[M+Na]^+$calcd for $[C_{15}H_{15}F_3NaO_3S]^+$: 355.0586; found: 355.0579.

Methyl 2-((2-chlorobenzyl)thio)-1-oxo-2,3-dihydro-*1H*-indene-2-carboxylate (**3m**)



3m

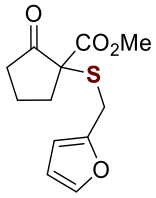
The reaction was performed according to **Procedure A,** and the reaction time was prolonged to 3 hours, then the product **3m** was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 40:1 to 20:1) as a white foam, 59.7 mg, 86% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 7.7 Hz, 1H), 7.63 (t, J = 8.0 Hz, 1H), 7.47 – 7.39 (m, 3H), 7.34 – 7.30 (m, 1H), 7.18 (t, J = 3.9 Hz, 2H), 4.34 (d, J = 12.2 Hz, 1H), 4.21 (d, J = 12.2 Hz, 1H), 3.91 (d, J = 17.9 Hz, 1H), 3.76 (s, 3H), 3.16 (d, J = 17.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 169.9, 150.5, 135.6, 134.6, 134.6, 134.0, 131.7, 129.8, 128.9, 128.4, 127.1, 126.3, 125.7, 58.7, 53.5, 40.1, 32.7.

HRMS (ESI, *m/z*) $[M + H]^+$calcd for $[C_{18}H_{16}ClO_3S]^+$: 347.0503; found: 347.0500.

Methyl 1-((furan-2-ylmethyl)thio)-2-oxocyclopentane-1-carboxylate (**3n**)



3n

The reaction was performed according to **Procedure A,** then the product **3n** was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30:1 to 20:1) as a yellow oil, 39.6 mg, 78% yield.

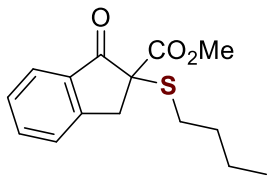
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 1H), 6.31 – 6.26 (m, 1H), 6.20 (d, J = 2.8 Hz, 1H), 4.11 (d, J = 14.0 Hz, 1H), 3.86 (d, J = 14.0 Hz, 1H), 3.74 (s, 3H), 2.67 – 2.55 (m, 2H), 2.42 – 2.32 (m, 1H), 2.16 – 1.97 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.5, 170.0, 150.2, 142.5, 110.6, 108.4, 59.5, 53.3,

36.5, 35.5, 27.2, 19.3.

HRMS (ESI, *m*/*z*) [M + H]$^+$calcd for [$C_{12}H_{15}O_4S$]$^+$: 255.0686; found: 255.0683.

Methyl 2-(butylthio)-1-oxo-2,3-dihydro-*1H*-indene-2-carboxylate (**3o**)



3o

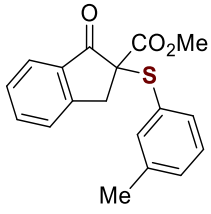
The reaction was performed according to **Procedure A,** then the product **3o** was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30:1) as a yellow oil, 47.8 mg, 86% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 7.9 Hz, 1H), 7.62 (t, J = 7.0 Hz, 1H), 7.46 – 7.40 (m, 2H), 3.89 (d, J = 17.8 Hz, 1H), 3.80 (s, 3H), 3.16 (d, J = 17.8 Hz, 1H), 2.93 – 2.81 (m, 2H), 1.55 – 1.46 (m, 2H), 1.43 – 1.35 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 170.2, 150.5, 135.5, 134.1, 128.3, 126.3, 125.7, 58.6, 53.4, 40.4, 30.9, 29.9, 22.2, 13.8.

HRMS (ESI, *m*/*z*) [M + H]$^+$calcd for [$C_{15}H_{19}O_3S$]$^+$: 279.1049; found: 279.1050.

Methyl 1-oxo-2-(*m*-tolylthio)-2,3-dihydro-*1H*-indene-2-carboxylate (**3p**)



3p

The reaction was performed according to **Procedure A,** then the product **3p** was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30:1 to 20:1) as a yellow oil, 56.2 mg, 90% yield.

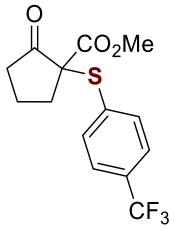
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, J = 7.7 Hz, 1H), 7.55 (t, J = 7.4 Hz, 1H), 7.35 (t, J = 7.5 Hz, 1H), 7.31 (d, J = 7.7 Hz, 1H), 7.27 – 7.24 (m, 2H), 7.14 – 7.06 (m, 2H),

3.88 (d, *J* = 17.7 Hz, 1H), 3.76 (s, 3H), 3.31 (d, *J* = 17.7 Hz, 1H), 2.24 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.0, 169.4, 151.2, 138.7, 136.7, 135.6, 134.4, 133.1, 130.5, 129.8, 128.7, 128.1, 126.1, 125.2, 63.9, 53.6, 39.4, 21.2.

HRMS (ESI, *m*/*z*) $[M + H]^+$calcd for $[C_{18}H_{17}O_3S]^+$: 313.0893; found: 313.0892.

Methyl 2-oxo-1-((4-(trifluoromethyl)phenyl)thio)cyclopentane-1-carboxylate (**3q**)



3q

The reaction was performed according to **Procedure A,** then the product **3q** was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30:1 to 20:1) as a dark oil, 43.2 mg, 68% yield.

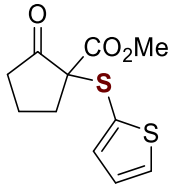
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, J = 7.9 Hz, 2H), 7.56 (d, J = 7.9 Hz, 2H), 3.75 (s, 3H), 2.65 – 2.59 (m, 1H), 2.57 – 2.51 (m, 1H), 2.44 – 2.37 (m, 1H), 2.20 – 2.12 (m, 2H), 2.07 – 1.99 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 206.7, 169.6, 135.6, 135.3, 131.3 (d, J = 32.8 Hz), 125.8 (q, J = 3.6 Hz), 123.9 (q, J = 272.4 Hz), 64.6, 53.5, 36.8, 35.3, 19.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.87.

HRMS (ESI, *m*/*z*) $[M + H]^+$calcd for $[C_{14}H_{14}F_3O_3S]^+$: 319.0610; found: 319.0612.

Methyl 2-oxo-1-(thiophen-2-ylthio)cyclopentane-1-carboxylate (**3r**)



3r

The reaction was performed according to **Procedure A,** and the reaction time was prolonged to 3 hours, then the product **3r** was purified by silica gel column

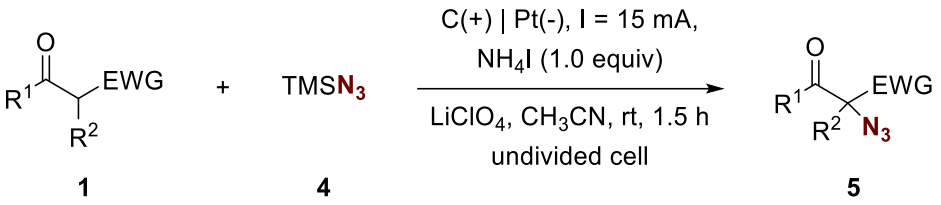
chromatography (petroleum ether/ethyl acetate = 30:1 to 20:1) as a brown oil, 38.4 mg, 75% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (dd, J = 5.4, 1.2 Hz, 1H), 7.26 (d, J = 3.5 Hz, 1H), 7.02 (dd, J = 5.4, 3.6 Hz, 1H), 3.79 (s, 3H), 2.63 – 2.54 (m, 1H), 2.52 – 2.43 (m, 1H), 2.42 – 2.32 (m, 1H), 2.22 – 2.06 (m, 2H), 2.05 – 1.95 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 207.0, 169.4, 138.7, 132.8, 128.1, 127.8, 66.1, 53.4, 37.0, 34.4, 19.2.

HRMS (ESI, *m*/*z*) $[M + H]^+$calcd for $[C_{11}H_{13}O_3S_2]^+$: 257.0301; found: 257.0300.

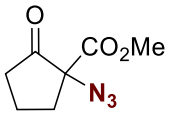
3. Electrochemical α-Azidation of 1,3-Dicarbonyls



1 **4** **5**

Procedure C: Inside of an oven-dried 5 mL ElectraSyn Vial was charged with NH_4I (28.9 mg, 0.2 mmol, 1.0 equiv), $LiClO_4$ (21.3 mg, 0.2 mmol, 1.0 equiv), **1** (0.2 mmol, 1.0 equiv) and trimethylsilyl azide **4** (0.4 mmol, 2.0 equiv). Acetonitrile (3.0 mL) were added and stirred with a stir bar to form a homogeneous solution The vial was equipped with graphite electrode as anode and platinum electrode as cathode (contacting area: 1.0 × 1.0 cm^2) with the electric connector under open air. The vial was stirred and electrolyzed at constant current of 15 mA for 1.5 or 3 hours at room temperature. When the electrolysis was terminated, the mixture was transferred into a separation funnel by dichloromethane or ethyl acetate. The combined organic layer was washed with water (5 mL × 3), saturated sodium thiosulfate and brine, and then dried over with anhydrous Na_2SO_4. After concentrated under *vacuo*, the crude product was purified by silica gel column chromatography or preparative TLC on a silica gel to afford the desired α-azido carbonyl compounds.

Methyl 1-azido-2-oxocyclopentane-1-carboxylate (**5a**)



5a

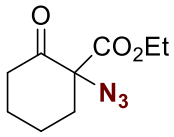
The reaction was performed according to **Procedure C** then the product **5a** was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) as a yellow oil, 31.1 mg, 85% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.83 (s, 3H), 2.50 – 2.41 (m, 3H), 2.12 – 2.07 (m, 1H), 2.04 – 1.98 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 209.1, 169.2, 71.0, 53.5, 36.7, 34.3, 19.3.

HRMS (ESI, *m*/*z*) $[M + H]^+$calcd for $[C_7H_{10}N_3O_3]^+$: 184.0717; found: 184.0710.

Ethyl 1-azido-2-oxocyclohexane-1-carboxylate (**5b**)



5b

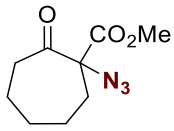
The reaction was performed according to **Procedure C** and the reaction time was prolonged to 3 hours then the product **5b** was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30:1) as an orange oil, 33.3 mg, 79% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.36 – 4.27 (m, 2H), 2.65 – 2.60 (m, 1H), 2.51 – 2.42 (m, 2H), 1.99 – 1.93 (m, 1H), 1.86 – 1.74 (m, 4H), 1.32 (t, J = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 202.6, 167.7, 74.1, 62.8, 39.8, 35.6, 26.6, 21.5, 14.3.

HRMS (ESI, *m*/*z*) $[M + H - N_2]^+$calcd for $[C_9H_{14}NO_3]^+$: 184.0968; found: 184.0968.

Methyl 1-azido-2-oxocycloheptane-1-carboxylate (**5c**)



5c

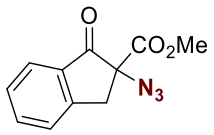
The reaction was performed according to **Procedure C,** then the product **5c** was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30:1) as a yellow oil, 32.1 mg, 76% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.79 (s, 3H), 2.93 – 2.86 (m, 1H), 2.70 – 2.62 (m, 1H), 2.62 – 2.51 (m, 2H), 1.80 – 1.67 (m, 4H), 1.66 – 1.59 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.8, 170.6, 54.0, 53.8, 40.7, 38.9, 29.5, 26.8, 25.9.

HRMS (ESI, *m*/*z*) $[M + H - N_2]^+$calcd for $[C_9H_{14}NO_3]^+$: 184.0968; found: 184.0970.

Methyl 2-azido-1-oxo-2,3-dihydro-*1H*-indene-2-carboxylate (**5d**)



5d

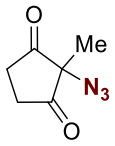
The reaction was performed according to **Procedure C,** then the product **5d** was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) as a yellow foam, 45.3 mg, 98% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 7.7 Hz, 1H), 7.68 (d, J = 7.2 Hz, 1H), 7.46 (t, J = 8.0 Hz, 2H), 3.81 (s, 3H), 3.68 (d, J = 17.4 Hz, 1H), 3.05 (d, J = 17.4 Hz, 1H).

^{13}C NMR (101 MHz, CDCl3) δ 197.5, 169.1, 152.2, 136.6, 133.1, 128.6, 126.6, 125.8, 70.3, 53.7, 38.7.

HRMS (ESI, *m*/*z*) $[M + H - N_2]^+$calcd for $[C_{11}H_{10}NO_3]^+$: 204.0655; found: 204.0655.

2-Azido-2-methylcyclopentane-1,3-dione (**5e**)



5e

The reaction was performed according to **Procedure C** only with an alternation as changing solvent into dimethyl sulfoxide to completely dissolve the substrate**,** then the product **5e** was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) as a yellow green foam, 26.0 mg, 85% yield.

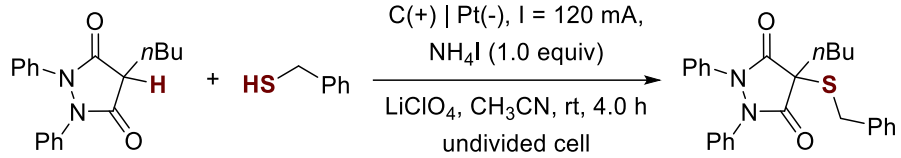
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.00 – 2.79 (m, 4H), 1.51 (s, 3H).

^{13}C NMR (101 MHz, CDCl3) δ 207.8, 66.7, 34.0, 18.0.

HRMS (ESI, *m*/*z*) $[M + H - N_2]^+$calcd for $[C_6H_8NO_2]^+$: 126.0555; found:126.0551.

4. Synthetic Applications

Gram-scale synthesis:



phenylbutazone, **6** — **7**, 1.2 g, 73%

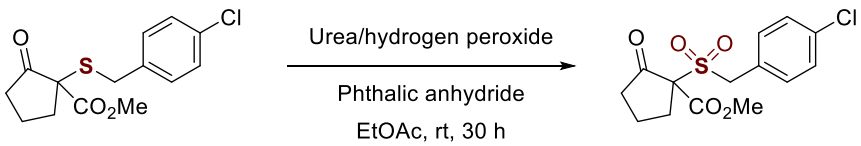
To a flat-bottom flask (50 mL) with a stir bar was added phenylbutazone (**6**) (1.23 g, 4 mmol, 1.0 equiv), benzyl thiol (0.96 mL, 8 mmol, 2.0 equiv), $LiClO_4$ (0.43 g, 4 mmol, 1.0 equiv), NH_4I (0.58 g, 4 mmol, 1.0 equiv) and acetonitrile (30 mL). Then a cap equipped with anode (graphite) and cathode (platinum) was inserted into the mixture. The reaction mixture was electrolyzed under the constant current of 120 mA (j = 20 mA/cm^2) for 4 h in the open air under room temperature. When the electrolysis was terminated, the mixture was transferred into a separation funnel by dichloromethane. The combined organic layer was washed with water (15 mL × 3), saturated sodium thiosulfate and brine, and then dried over with anhydrous Na_2SO_4. After concentrated under *vacuo*, the crude product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 50:1 to 30:1) to provide **7** as light-yellow oil. (1.21 g, 2.8 mmol, 73% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 13H), 7.22 – 7.16 (m, 2H), 3.98 (s, 2H), 2.17 – 2.10 (m, 2H), 1.37 – 1.28 (m, 4H), 0.86 (t, J = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 135.8, 135.5, 129.5, 129.2, 128.7, 127.7, 127.2, 122.9, 54.1, 34.4, 34.1, 27.4, 22.7, 13.7.

HRMS (ESI, *m*/*z*) [M + H]$^+$calcd for $[C_{26}H_{27}N_2O_2S]^+$: 431.1788; found: 431.1792.

Derivatizations



3b — **8**, 81%

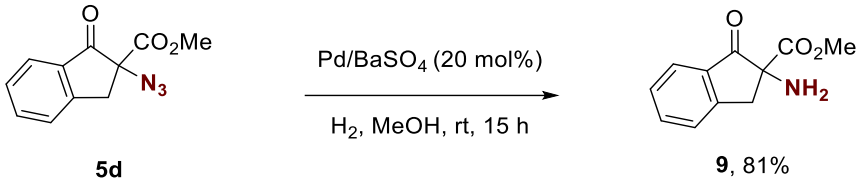
The synthesis was adapted from the reported literature.[1] To a 25 mL round bottom flask,

urea hydrogen peroxide (28.2 mg, 0.3 mmol, 3.0 equiv) and phthalic anhydride (44.4 mg, 0.3 mmol, 3.0 equiv) was added a solution of sulfide (29.9 mg, 0.1 mmol, 1.0 equiv) in ethyl acetate (5 mL) and the solution was stirred for 16 hours under room temperature. Additional urea hydrogen peroxide (28.2 mg, 0.3 mmol, 3.0 equiv) and phthalic anhydride (44.4 mg, 0.3 mmol, 3.0 equiv) were added in to the mixture and reacted for further 14 hours to complete the consumption of sulfide. The reaction slurry was quenched with Na_2SO_3 (1 mL) and the mixture was extracted with ethyl acetate (5 mL × 3). The combined organic layer was washed with brine and then dried over anhydrous Na_2SO_4. After the concentration *in vacuo*, the crude product was purified by preparative TLC (petroleum ether/ethyl acetate = 4:1) to afford **8** as a white foam, (26.7 mg, 81% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 4.00 (d, J = 12.9 Hz, 1H), 3.76 – 3.68 (m, 4H), 2.82 – 2.72 (m, 1H), 2.63 – 2.44 (m, 2H), 2.35 – 2.07 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 166.7, 135.7, 132.7, 129.4, 125.3, 66.5, 57.3, 53.7, 33.2, 25.0, 22.3.

HRMS (ESI, *m/z*) $[M + H]^+$calcd for $[C_{14}H_{16}ClO_5S]^+$: 331.0401; found: 331.0397.



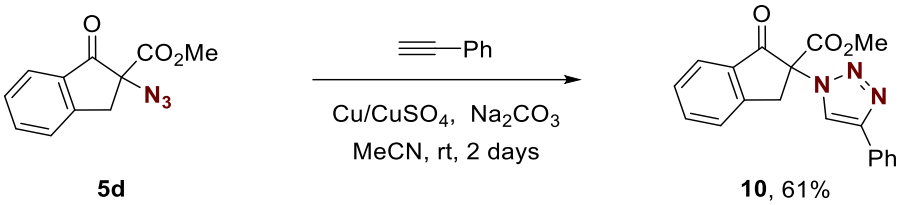
5d **9**, 81%

The synthesis was adapted from the reported literature.[2] A flame-dried flask under H_2 was charged with **5d** (23.1 mg, 0.1 mmol, 1.0 equiv) and methanol (1.5 mL). $Pd/BaSO_4$ (20 mol%) was added to this solution at room temperature, and the mixture was stirred for 15 h. The mixture was filtered through celite, and the filtrate was concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (dichloromethane: methanol = 40:1) to give of **9** as a colorless oil, 16.7 mg, 81% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, J = 7.7 Hz, 1H), 7.65 (t, J = 7.4 Hz, 1H), 7.48 (d, J = 7.7 Hz, 1H), 7.42 (t, J = 7.5 Hz, 1H), 3.76 (d, J = 45.3 Hz, 1H), 3.69 (s, 3H),

3.09 (d, *J* = 17.0 Hz, 1H), 2.17 (br, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 202.3, 173.1, 152.6, 136.0, 134.1, 128.2, 126.6, 125.5, 67.2, 53.2, 41.3. The spectroscopic data are in agreement with the literature.[3]



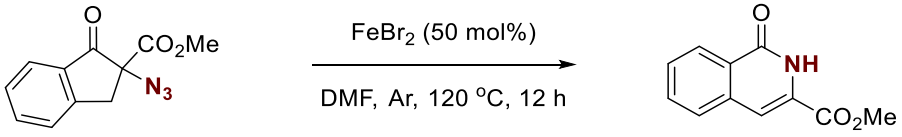
5d **10**, 61%

The synthesis was adapted from the reported literature.[4] To a 5 mL test tube was placed azide **5d** (23.3 mg, 0.1 mmol, 1.0 equiv) in acetonitrile (0.15 mL) and $NaHCO_3$ (0.2 M, 0.15 mL) solution, then the alkyne (10.2 mg, 0.1 mmol, 1.0 equiv) was added to the mixture. Copper sulfate (1.0 M, 0.01 mL) was added to the above suspension followed by copper powder (6.4 mg, 0.1 mmol, 1.0 equiv). The resulting mixture was stirred at 25 ℃ for 2 days and monitored by TLC plate to confirm the consumption of azide. Upon completion, the suspension was extracted with ethyl acetate (5 mL × 3). The combined organic layer was washed with brine and then dried over anhydrous Na_2SO_4. After the concentration *in vacuo*, the crude product was purified by preparative TLC (petroleum ether/ethyl acetate = 8:1) to afford **10** as a white foam, (20.3 mg, 61% yield)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.88 (t, *J* = 7.4 Hz, 3H), 7.75 (t, *J* = 7.5 Hz, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 4.83 (d, *J* = 17.8 Hz, 1H), 4.20 (d, *J* = 17.8 Hz, 1H), 3.78 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 195.0, 167.5, 152.7, 137.3, 132.9, 130.6, 128.9, 128.8, 128.4, 126.7, 126.1, 126.0, 121.1, 73.7, 54.2, 37.6.

HRMS (ESI, *m*/*z*) $[M+H]^+$calcd for $[C_{19}H_{16}N_3O_3]^+$: 334.1186; found: 334.1185.



5d **11**, 72%

The synthesis was adapted from the reported literature.[5] The azide **5d** (23.1 mg, 0.1

mmol, 1.0 equiv) and $FeBr_2$ (10.8 mg, 0.05 mmol, 0.5 equiv) were dissolved in 1.0 mL DMF, then the mixture was stirred at 120 ºC in oil bath under an argon atmosphere for 12 h. After the reaction completed as indicated by TLC, the mixture was cooled to room temperature. The solution was filtered through silica gel, which was then eluted with EtOAc (30 mL × 3). The combined organic phases were washed with brine (50 mL × 6), dried over anhydrous Na_2SO_4, and then concentrated under reduced pressure on a rotary evaporator. The residual was treated with silica gel column chromatography (petroleum ether/ethyl acetate = 4:1) to yield product **11** as a yellow solid, 11.6 mg, 57% yield.

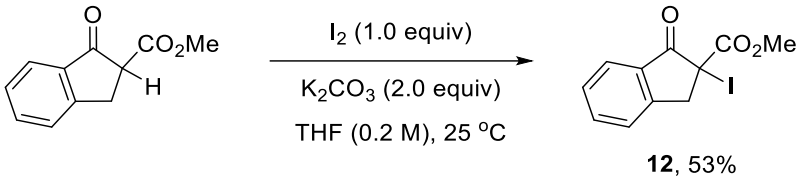
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (br, 1H), 8.46 (d, J = 8.0 Hz, 1H), 7.76 – 7.70 (m, 1H), 7.68 (d, J = 7.1 Hz, 1H), 7.66 – 7.60 (m, 1H), 7.38 (s, 1H), 3.99 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4, 161.9, 136.1, 133.2, 129.6, 128.5, 128.3, 128.1, 127.8, 111.5, 53.3.

HRMS (ESI, *m*/*z*) $[M+H]^+$calcd for $[C_{11}H_{10}NO_3]^+$: 204.0655; found: 204.0656.

5. Mechanistic Studies

Control experiments:



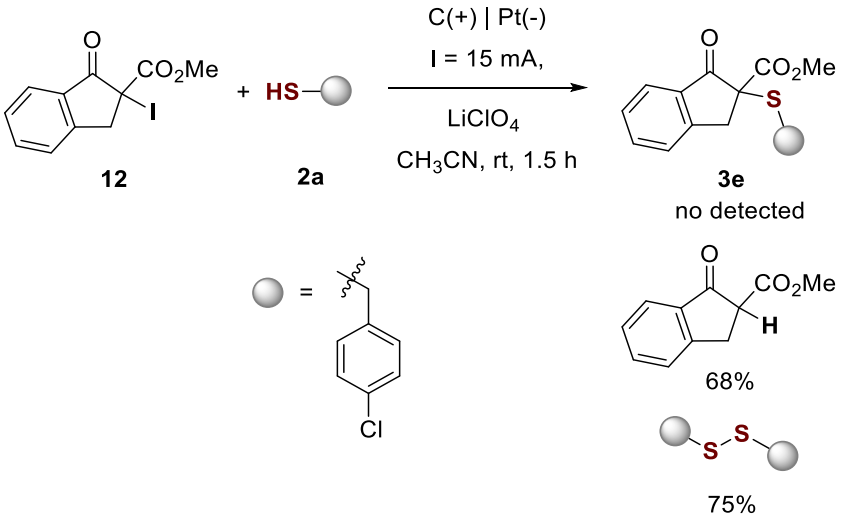
12, 53%

According to the reported literature,[6] to a solution of Methyl 1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (114.0 mg, 0.6 mmol) and K_2CO_3 (165.6 mg, 1.2 mmol) in THF (3.0 mL) was added iodine (152.3 mg, 0.6 mmol) at room temperature. After the starting material was consumed, the reaction mixture was poured into saturated H_2O (5 mL), extracted with ethyl acetate, and washed with brine. The combined organic layers were dried over Na_2SO_4 and solvents were removed in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30:1) to give **12** as a brown oil, 100.5 mg, 53% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 7.3 Hz, 1H), 7.67 (t, J = 7.5 Hz, 1H), 7.43 (d, J = 7.6 Hz, 2H), 4.33 (d, J = 18.4 Hz, 1H), 3.81 (s, 3H), 3.73 (d, J = 18.4 Hz, 1H).

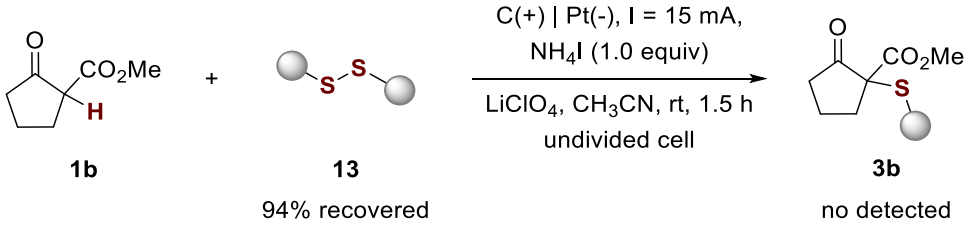
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 169.2, 149.7, 136.2, 131.7, 128.6, 126.4, 126.0, 54.4, 45.8, 36.3.

HRMS (ESI, *m*/*z*) [M-I]$^+$calcd for $[C_{11}H_9O_3]^+$: 189.0546; found: 189.0544.



Inside of an oven-dried 5 mL ElectraSyn Vial was charged with NH_4I (28.9 mg, 0.2

mmol, 1.0 equiv), $LiClO_4$ (21.3 mg, 0.2 mmol, 1.0 equiv), **12** (63.2 mg, 0.2 mmol, 1.0 equiv) and **2a** (63.2 mg, 0.4 mmol, 2.0 equiv). Acetonitrile (3.0 mL) were added and stirred with a stir bar to form a homogeneous solution. The vial was equipped with graphite electrode as anode and platinum electrode as cathode (contacting area: 1.0 × 1.0 cm^2) with the electric connector under open air. The vial was stirred and electrolyzed at constant current of 15 mA for 1.5 hours at room temperature. When the electrolysis was terminated, the mixture was transferred into a separation funnel by dichloromethane or ethyl acetate. The combined organic layer was washed with water (5 mL × 3), saturated sodium thiosulfate and brine, and then dried over with anhydrous Na_2SO_4. Base on the analysis of the crude ^1H NMR, we found that no desired product **3e** was detected. 68% of **12** was converted to methyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate and 75% of **2a** was converted to disulfide **13**.



1b **13** **3b**

94% recovered no detected

Inside of an oven-dried 5 mL ElectraSyn Vial was charged with NH_4I (28.9 mg, 0.2 mmol, 1.0 equiv), $LiClO_4$ (21.3 mg, 0.2 mmol, 1.0 equiv), **1b** (28.4 mg, 0.2 mmol, 1.0 equiv) and **13** (62.8 mg, 0.2 mmol, 1.0 equiv). Acetonitrile (3.0 mL) were added and stirred with a stir bar to form a homogeneous solution. The vial was equipped with graphite electrode as anode and platinum electrode as cathode (contacting area: 1.0 × 1.0 cm^2) with the electric connector under open air. The vial was stirred and electrolyzed at constant current of 15 mA for 1.5 hours at room temperature. When the electrolysis was terminated, the mixture was transferred into a separation funnel by dichloromethane or ethyl acetate. The combined organic layer was washed with water (5 mL × 3), saturated sodium thiosulfate and brine, and then dried over with anhydrous Na_2SO_4. Base on the analysis of the crude ^1H NMR, we found that no desired product **3e** was detected. 94% of disulfide **13** was recovered.

Cyclic voltammetry analysis：

Cyclic voltammetry was recorded on the CHI 660E instrument. A 3 mm diameter glassy carbon disc electrode was used as the working electrode; a platinum plated electrode was used as the counter electrode; SCE was used as reference electrode. A CH_3CN solution (5.0 mL) of sample including 10 mM of each sample and 0.1 M of $LiClO_4$ was prepared as an electrochemical solution. The spectra were recorded with the scan rate of 100 mVs^{-1} or 200 mVs^{-1}.

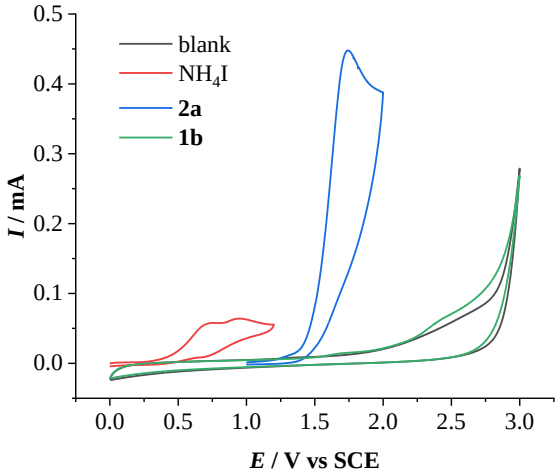


Figure S1. Cyclic voltammetry experiments.

Proposed mechanism:

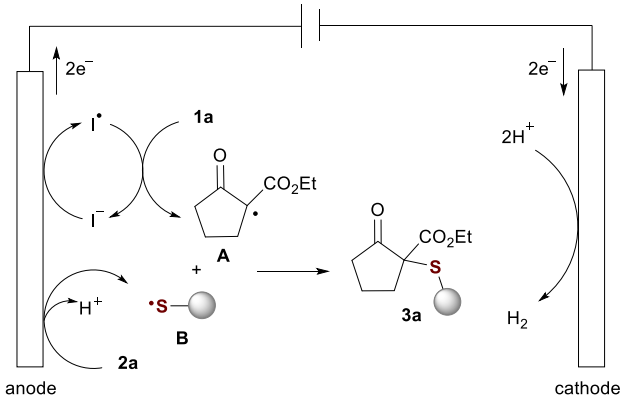


Figure S2. Proposed mechanism

Based on the above results, a radical mechanism was proposed for this electrochemical transformation. First, the iodide is oxidized to the iodine radical at the anode, which

then abstracts a hydrogen atom from **1a** to produce the radical intermediate **A**. Meanwhile, thiol **2a** undergoes oxidation at anode to afford sulfur radical intermediate **B**, which can couple with radical intermediate **A** to give the product **3a**.

6. X-Ray Crystallographic Data

Single crystal suitable for X-ray diffraction of compound **5d** was obtained from a solution of the compound **5d** in dichloromethane layered with petroleum ether. The X-ray crystal structure is deposited in the Cambridge Crystallographic Data Center under reference number CCDC 2115172.

Diffraction Data were collected on a Bruker D8 venture employing CuKα radiation (λ = 1.54178 Å).

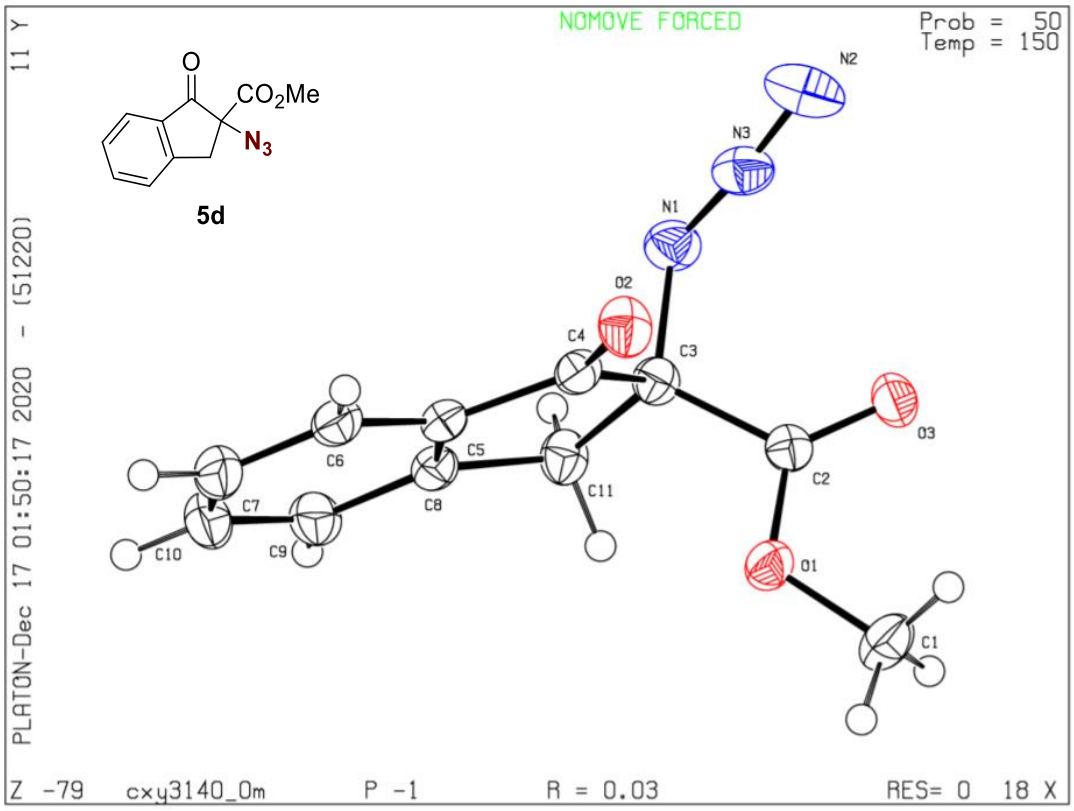


Figure S3. Crystal Structure of **5d** (CCDC 2115172, 50% probability level shown).

Table S1 Crystal data and structure refinement for **5d.**

Identification code	cxy3140_0m
Empirical formula	$C_{12}H_9N_2O_3$
Formula weight	229.21
Temperature/K	150.0
Crystal system	triclinic
Space group	P-1
a/Å	7.8656(4)
b/Å	8.0258(4)
c/Å	9.6858(5)
α/°	88.672(2)
β/°	79.601(2)
γ/°	65.232(2)
Volume/Å^3	545.14(5)
Z	2
ρ_{calc}g/cm^3	1.396
μ/mm^{-1}	0.859
F(000)	238
Crystal size/mm^3	0.32 × 0.31 × 0.25
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	12.166 to 136.788
Index ranges	-9 ⩽ h ⩽ 9, -8 ⩽ k ⩽ 9, -11 ⩽ l ⩽ 11
Reflections collected	6663
Independent reflections	2001 [R_{int} = 0.0319, R_{sigma} = 0.0293]
Data/restraints/parameters	2001/0/155
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0328, wR_2 = 0.0813
Final R indexes [all data]	R_1 = 0.0350, wR_2 = 0.0826
Largest diff. peak/hole / e Å^{-3}	0.27/-0.16

Table S2 Bond lengths for **5d**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C1	1.4521(14)	C3	C11	1.5388(16)
O1	C2	1.3250(14)	C4	C5	1.4645(16)
O2	C4	1.2098(14)	C5	C6	1.3927(17)
O3	C2	1.2000(14)	C5	C8	1.3869(17)
N1	C3	1.4789(15)	C6	C7	1.3809(18)
N1	N3	1.2447(16)	C7	C10	1.395(2)
N2	N3	1.1315(17)	C8	C9	1.3900(17)
C2	C3	1.5224(15)	C8	C11	1.5089(17)
C3	C4	1.5582(16)	C9	C10	1.385(2)

Table S3 Bond angles for **5d**.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C2	O1	C1	116.55(9)	C5	C4	C3	107.36(9)
N3	N1	C3	115.36(10)	C6	C5	C4	127.94(11)
O1	C2	C3	109.35(9)	C8	C5	C4	109.88(10)
O3	C2	O1	125.77(10)	C8	C5	C6	122.17(11)
O3	C2	C3	124.86(10)	C7	C6	C5	117.88(12)
N1	C3	C2	111.63(9)	C6	C7	C10	120.29(12)
N1	C3	C4	108.23(9)	C5	C8	C9	119.69(11)
N1	C3	C11	107.83(9)	C5	C8	C11	112.34(10)
C2	C3	C4	109.65(9)	C9	C8	C11	127.96(11)
C2	C3	C11	114.06(9)	C10	C9	C8	118.40(12)
C11	C3	C4	105.10(9)	C9	C10	C7	121.57(12)
O2	C4	C3	123.15(10)	C8	C11	C3	104.55(9)
O2	C4	C5	129.45(11)	N2	N3	N1	170.80(13)

7. References

1. M. Lutz, M. Wenzler and I. Likhotvorik, *Synthesis*, 2018, **50**, 2231.
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5. T. Yang, X. Fan, X. Zhao and W. Yu, *Org. Lett.*, 2018, **20**, 1875.
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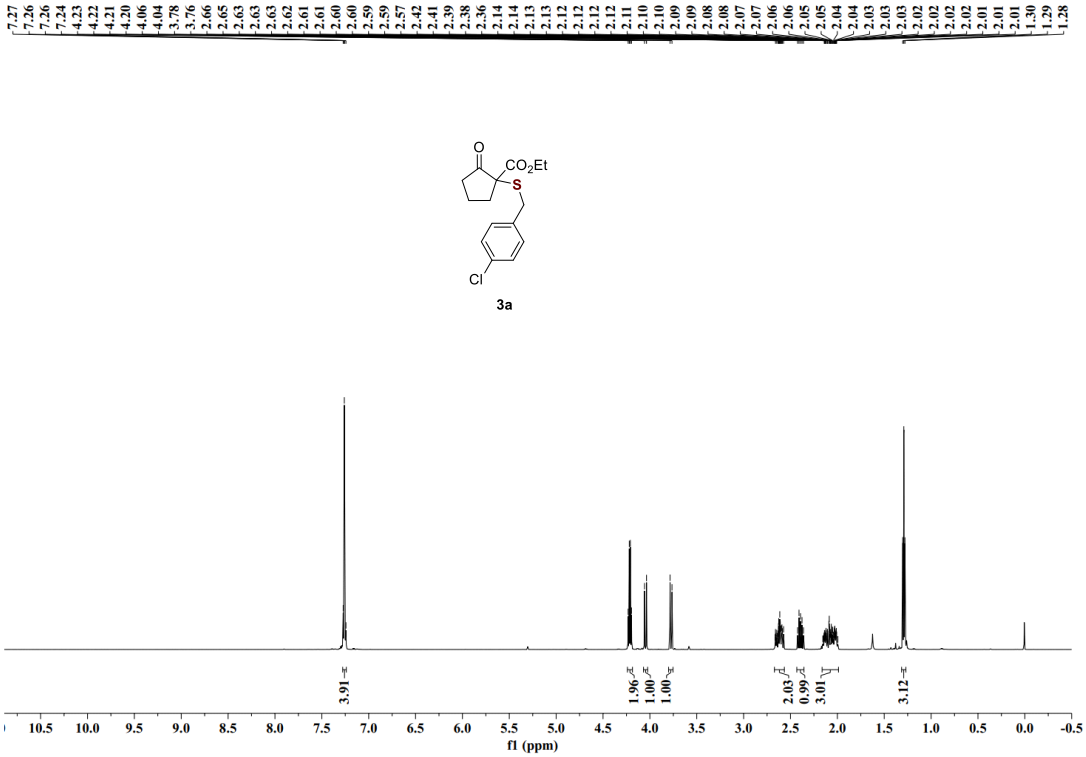
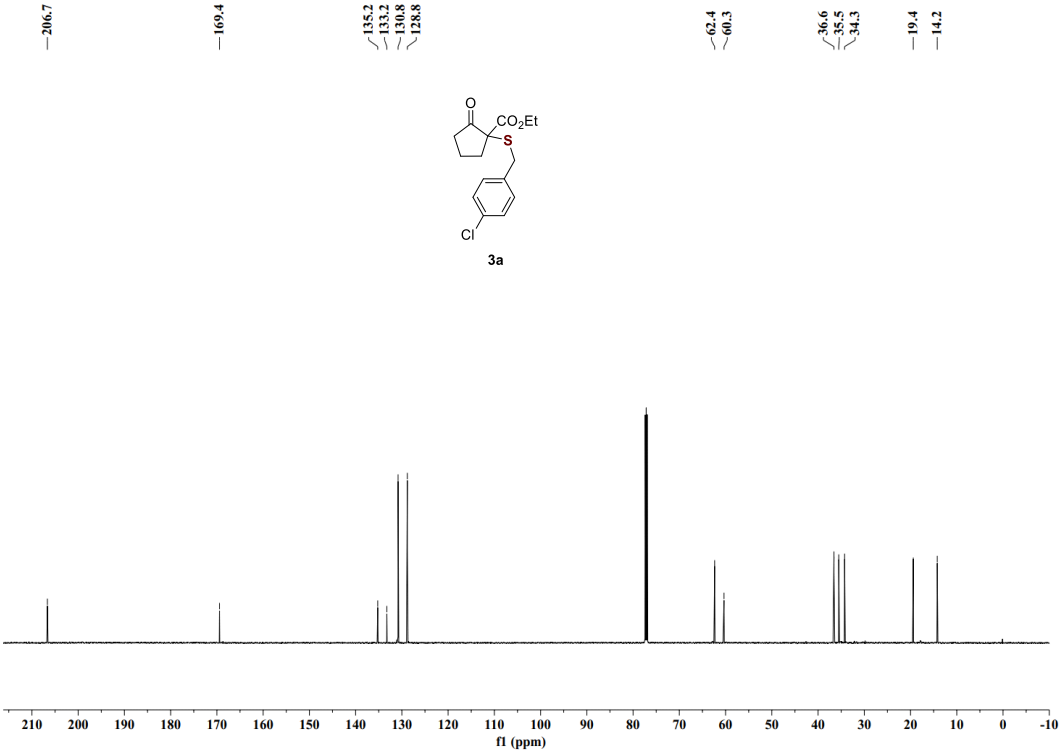
8. NMR Spectra

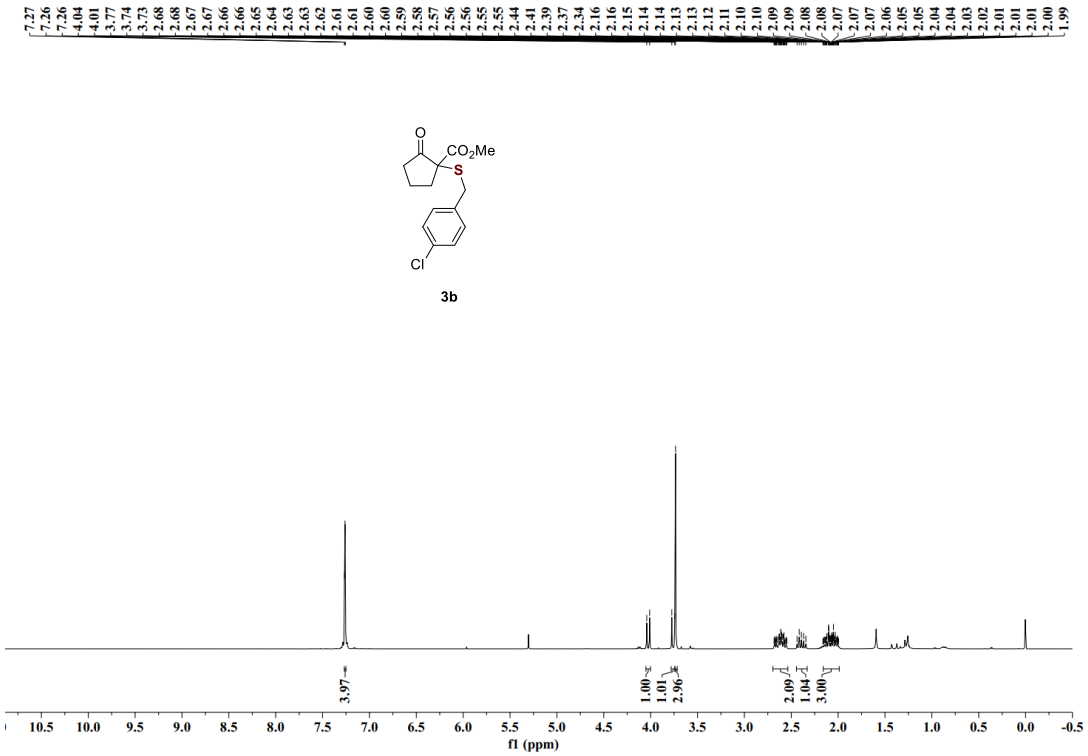
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



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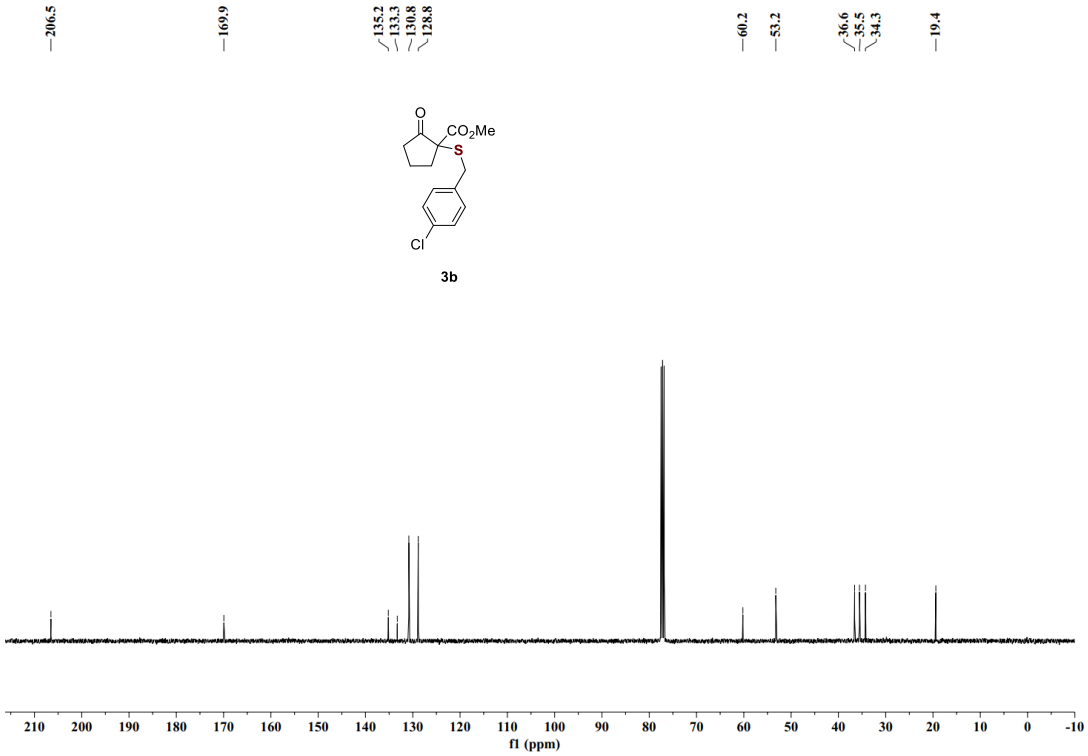
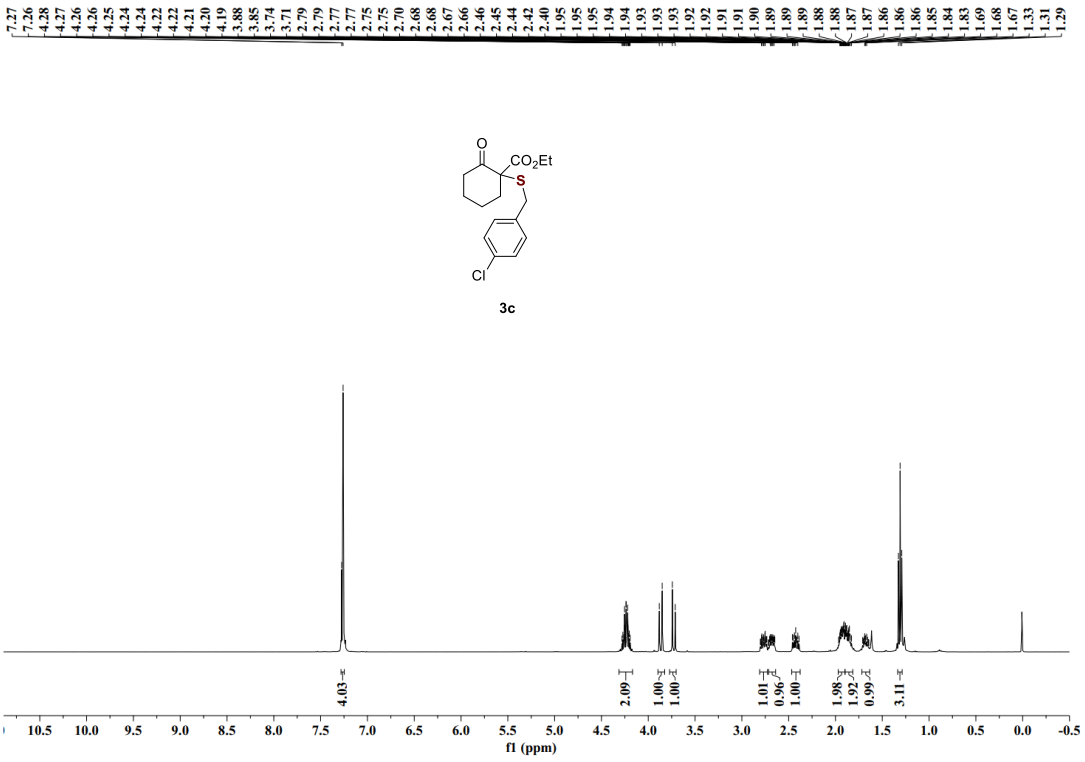


^{1}H NMR (400 MHz, $CDCl_3$)



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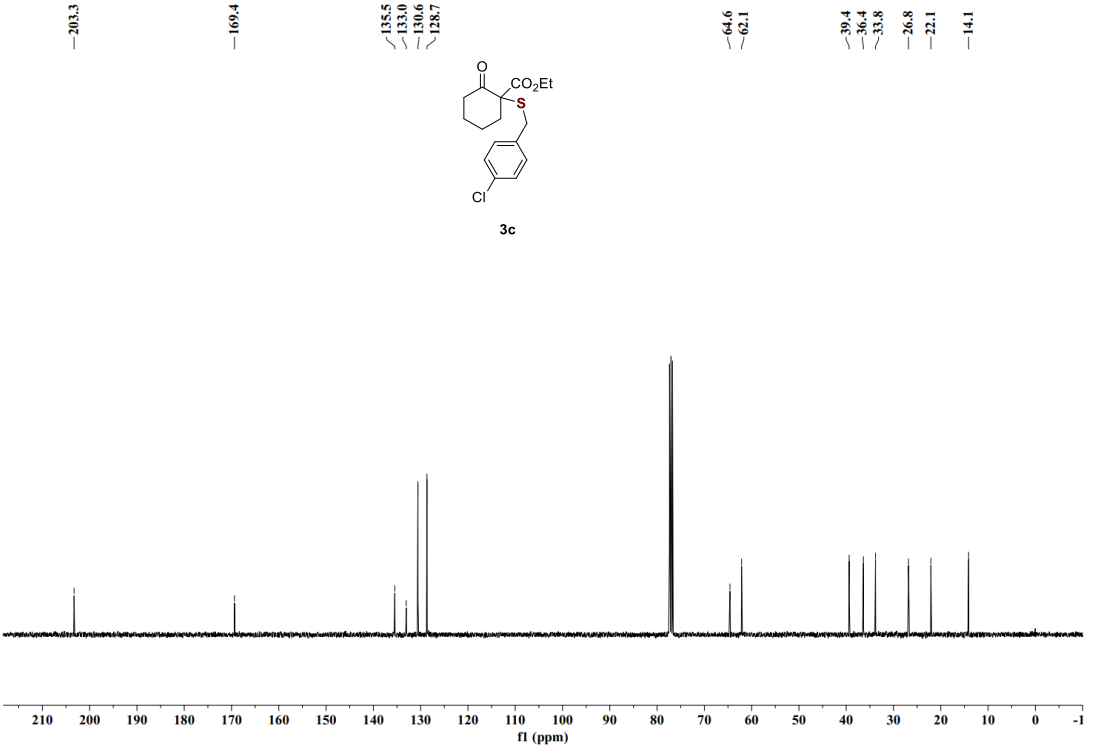

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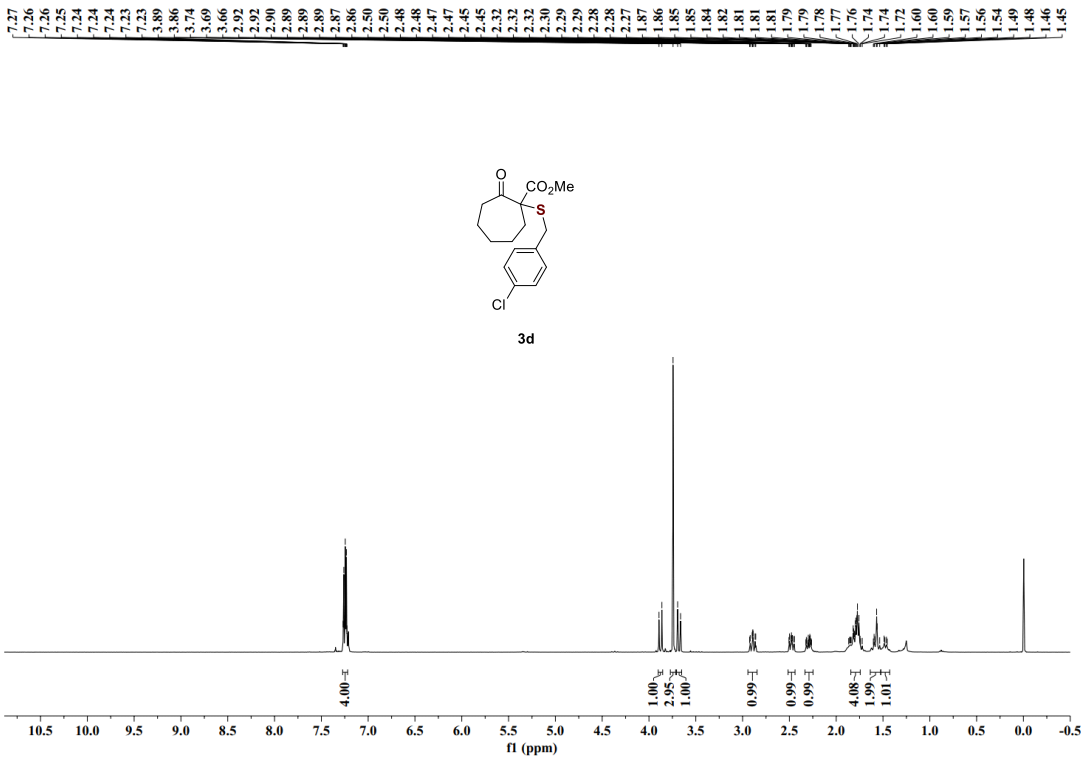

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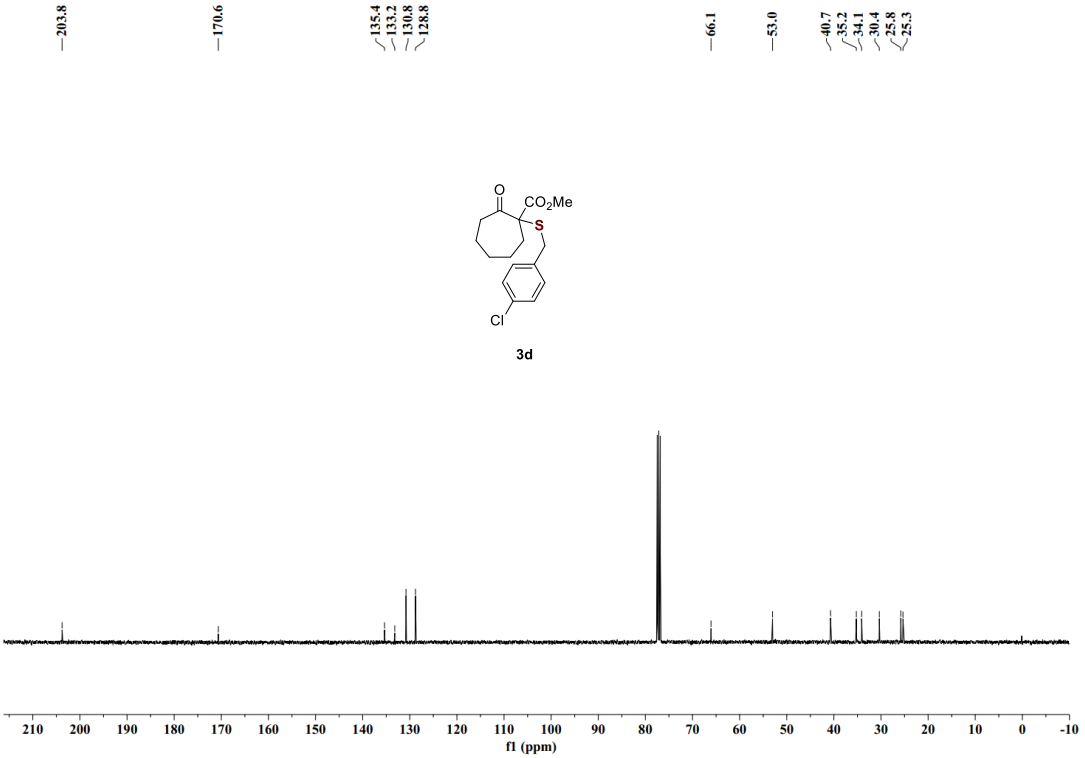

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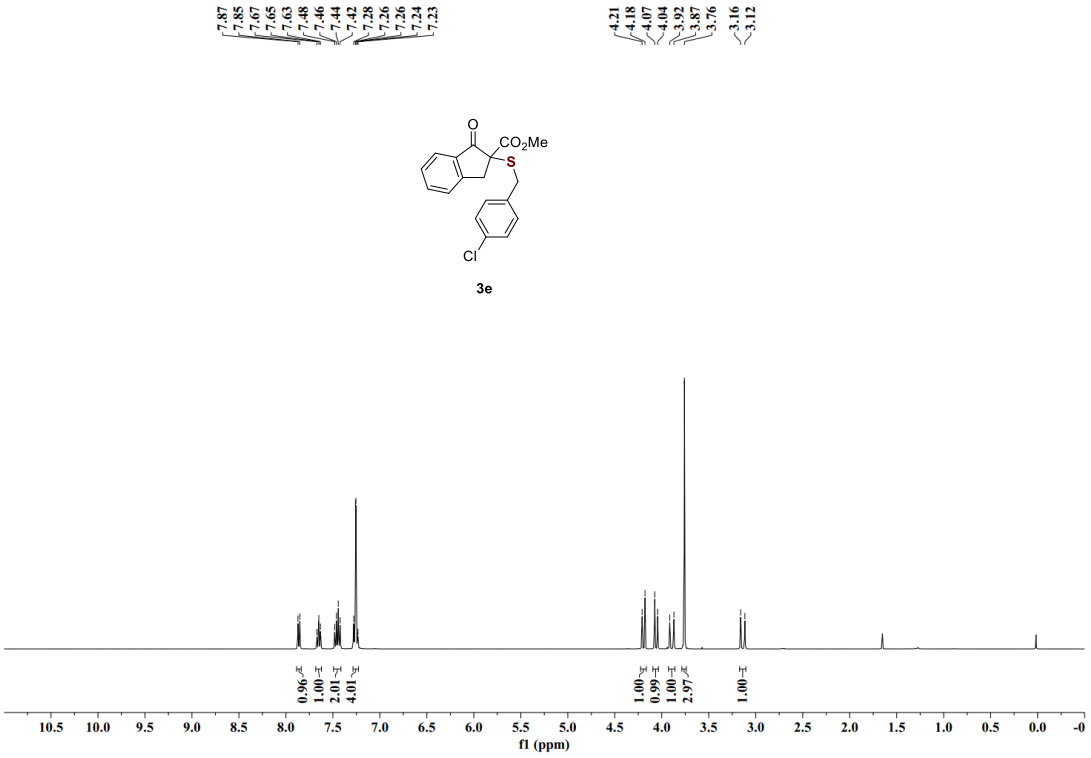

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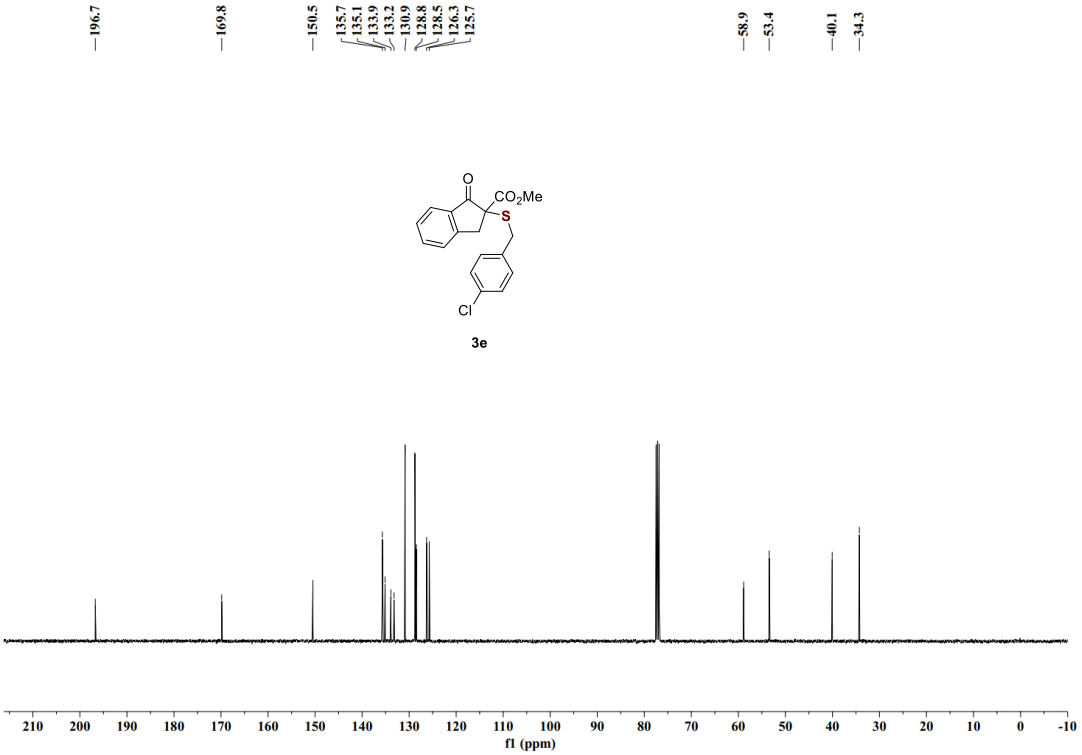

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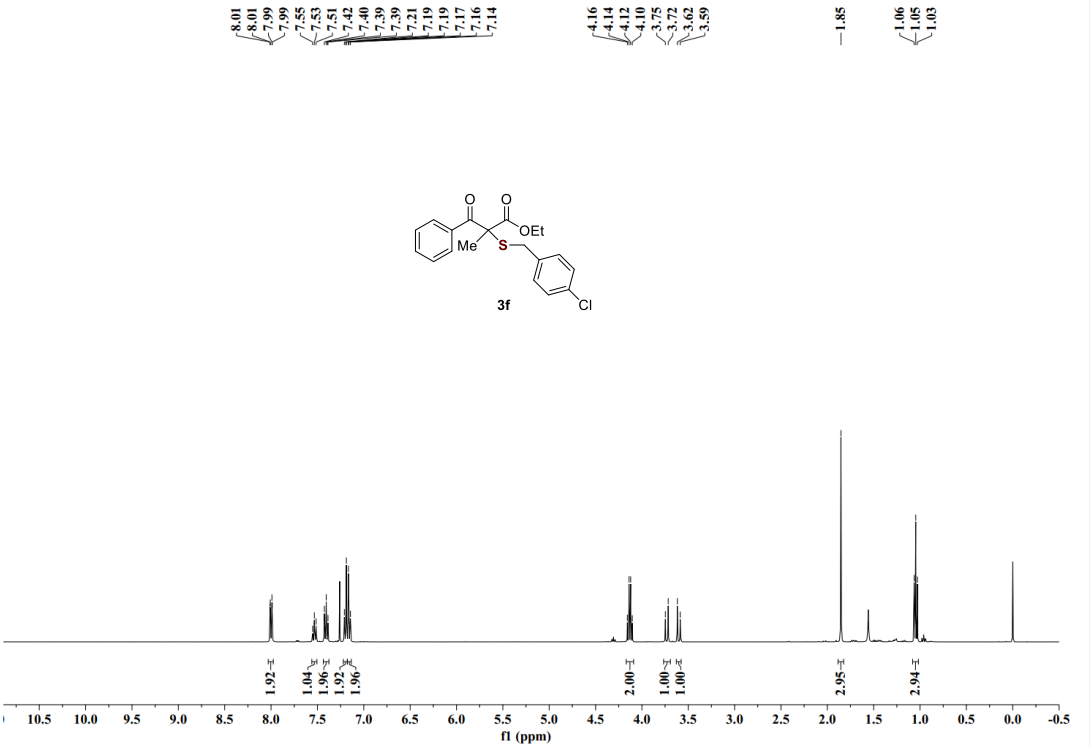

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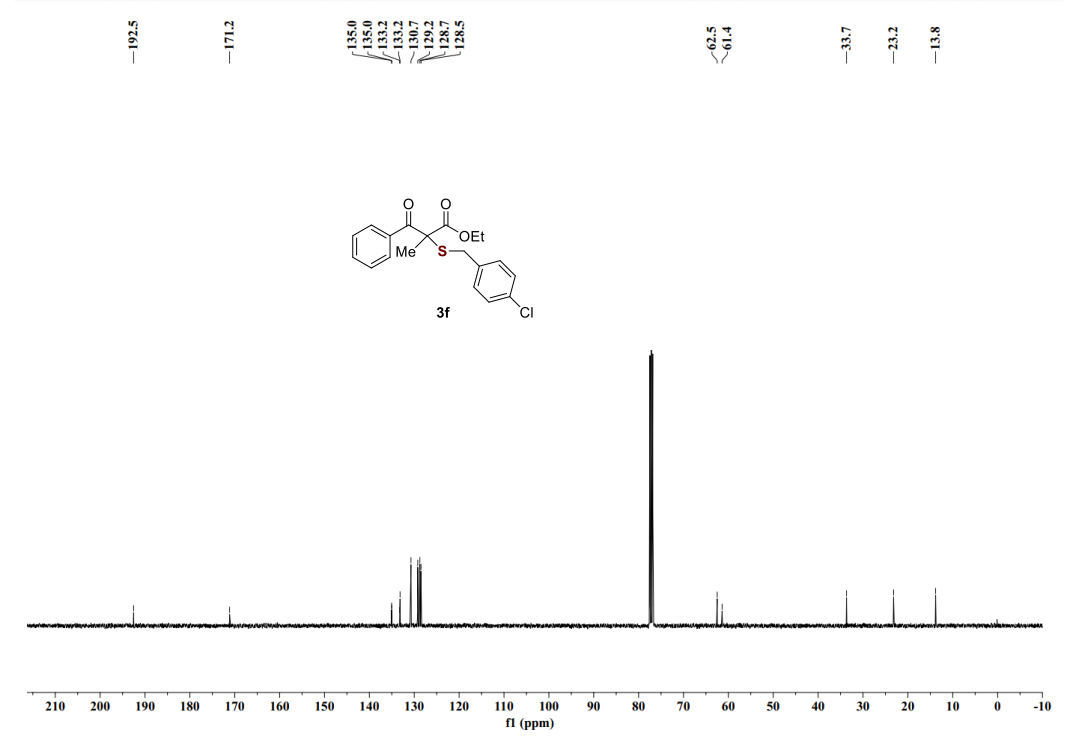

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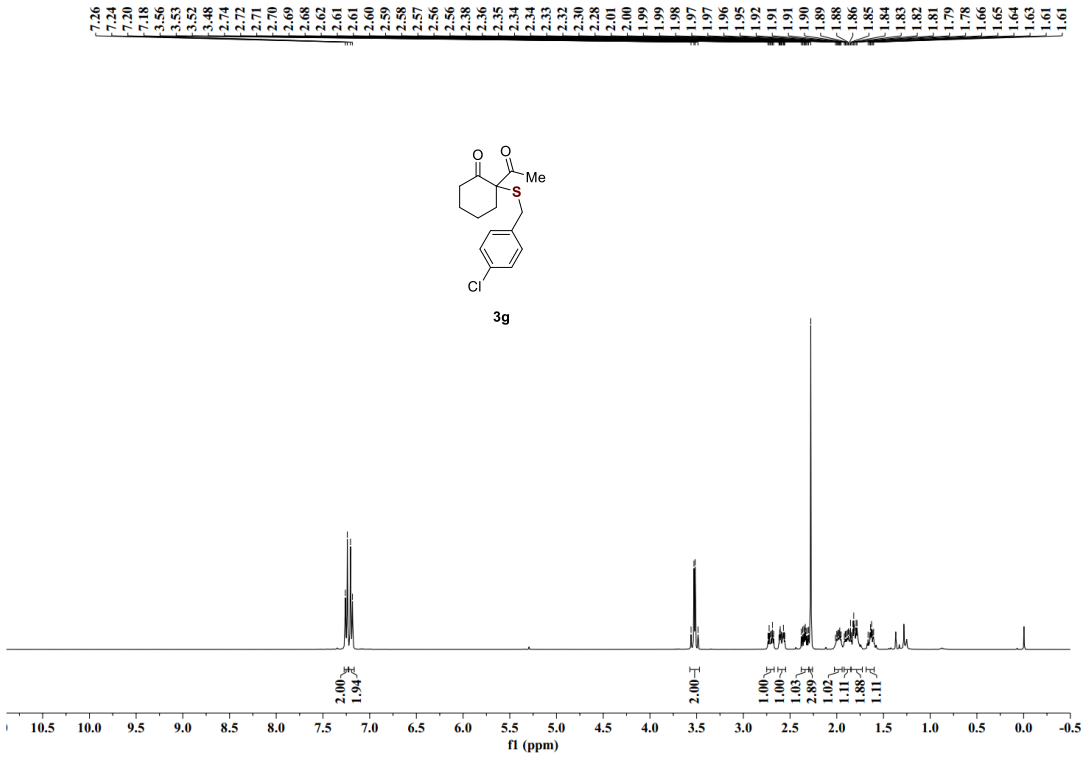

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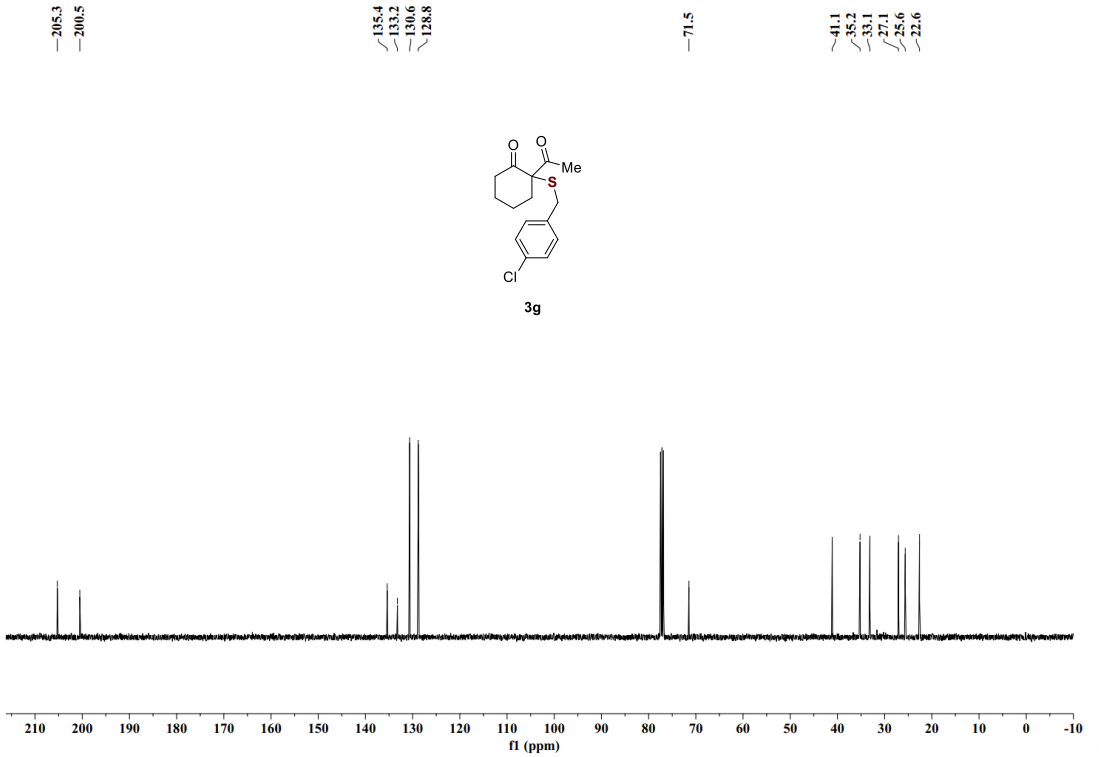

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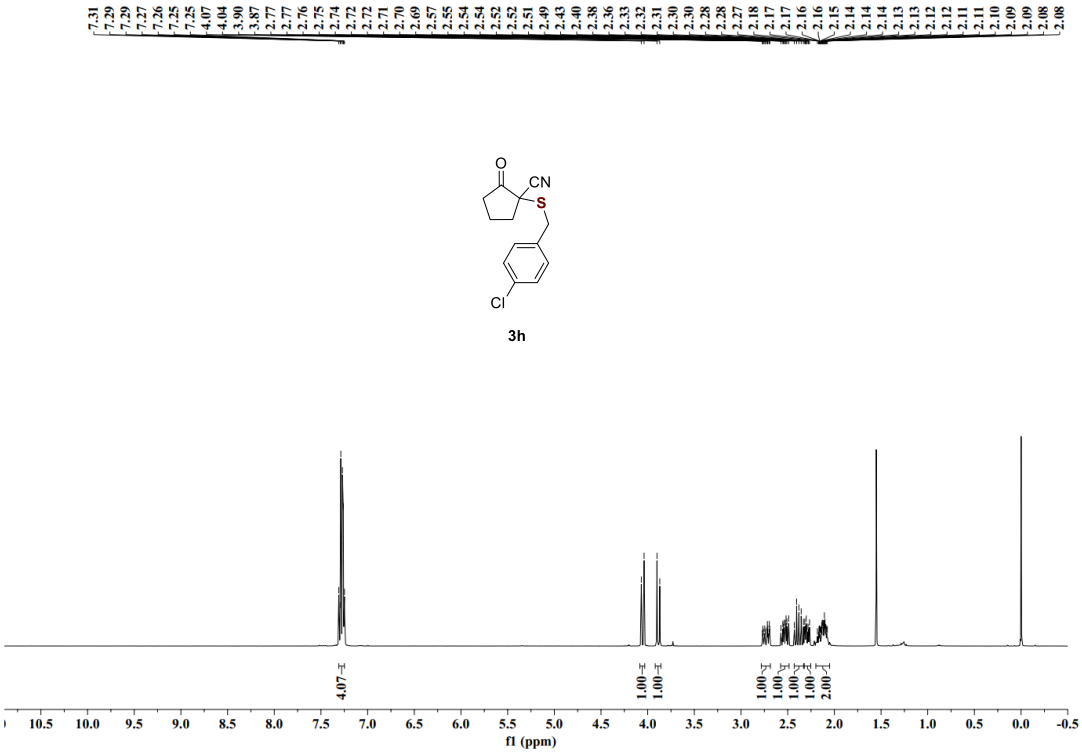

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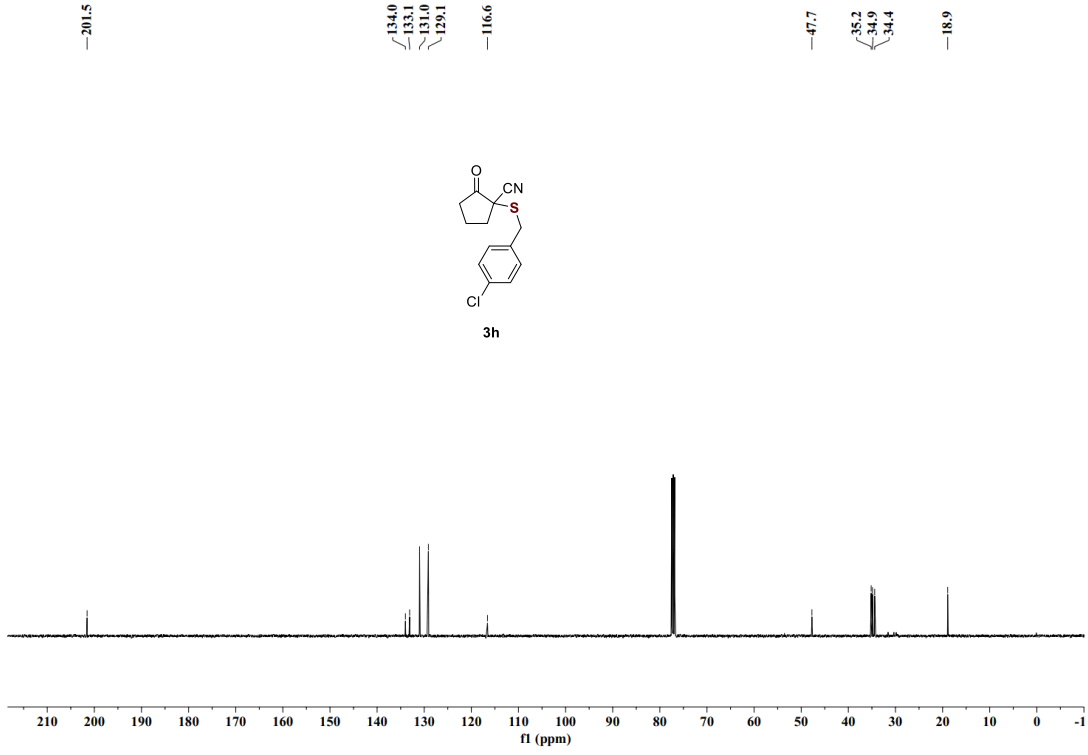

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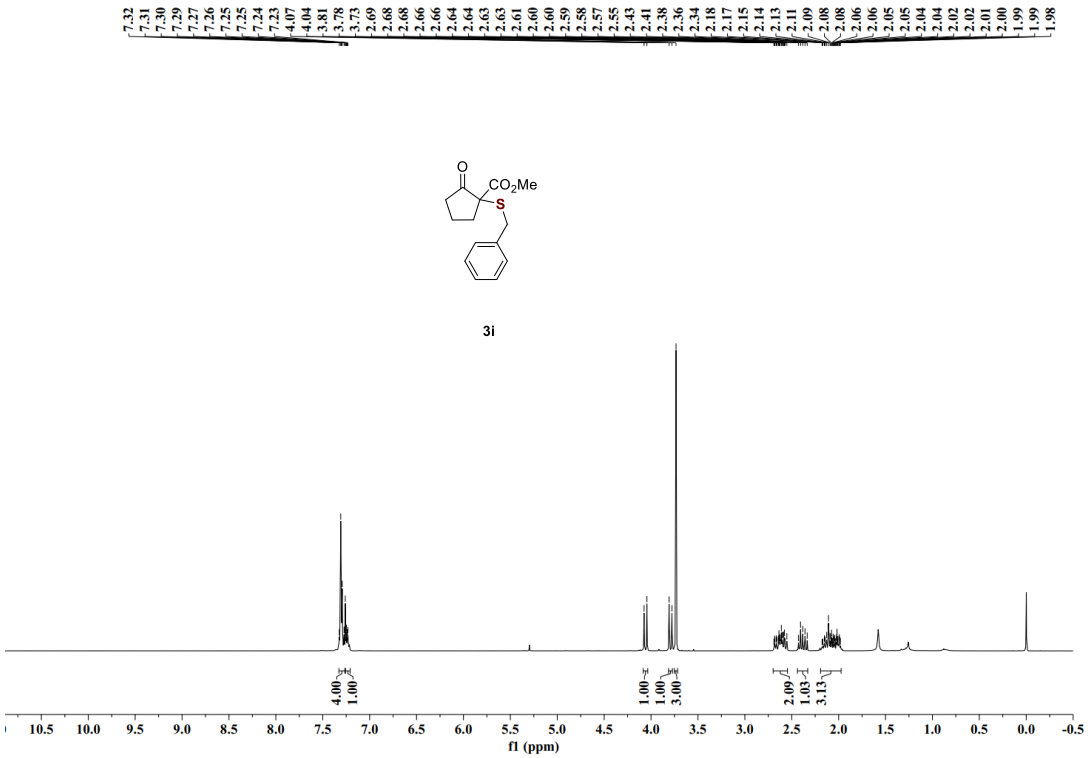

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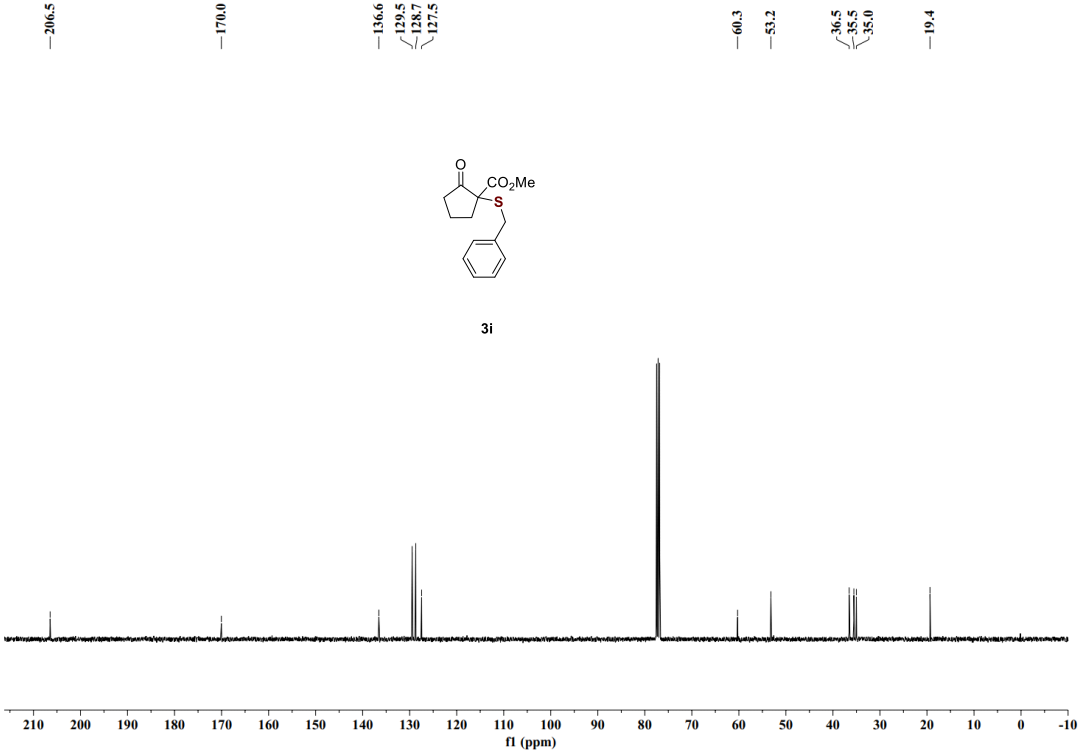

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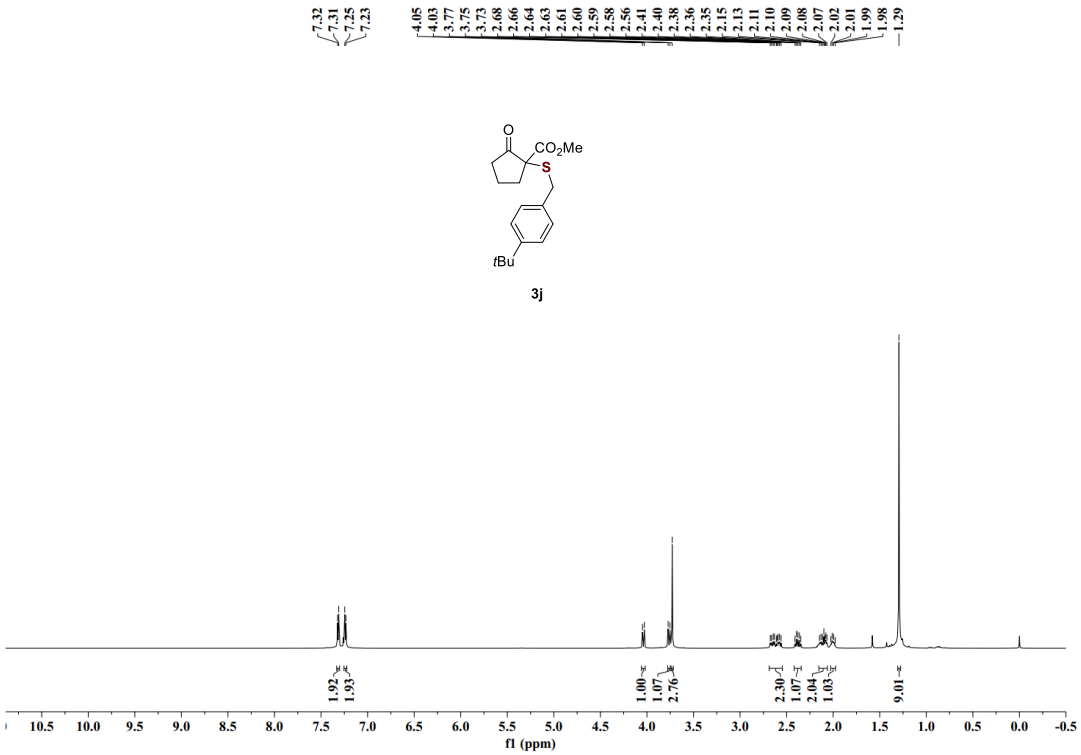
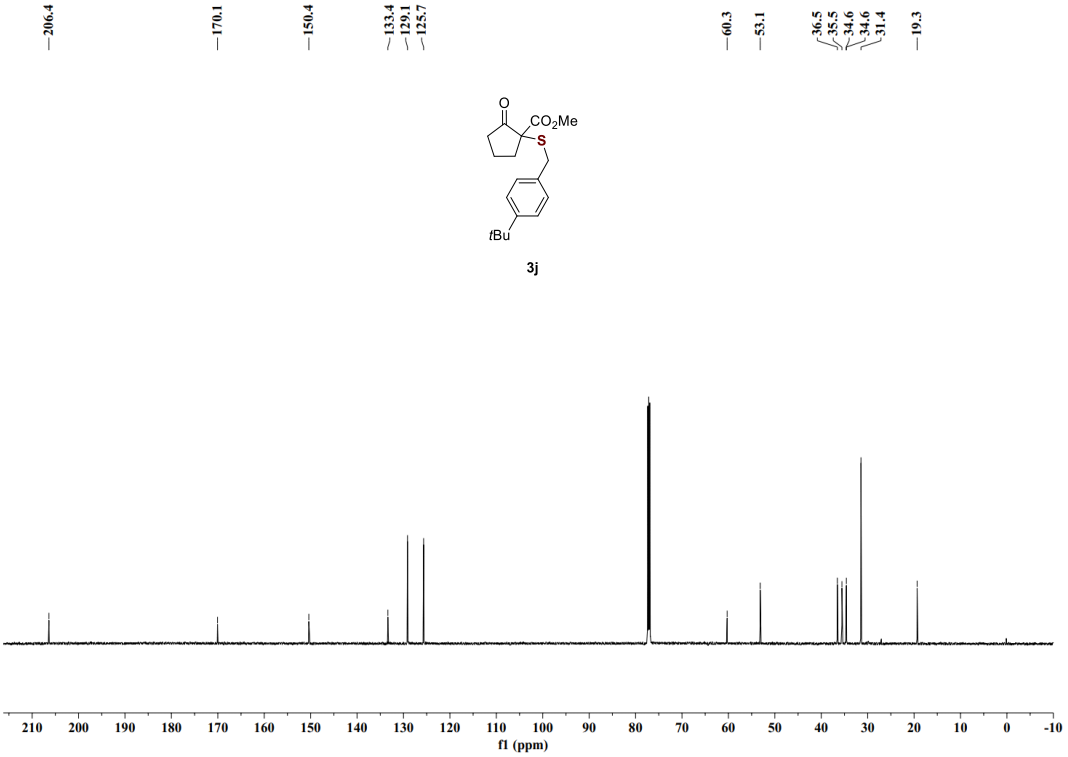


^{13}C NMR (151 MHz, $CDCl_3$)



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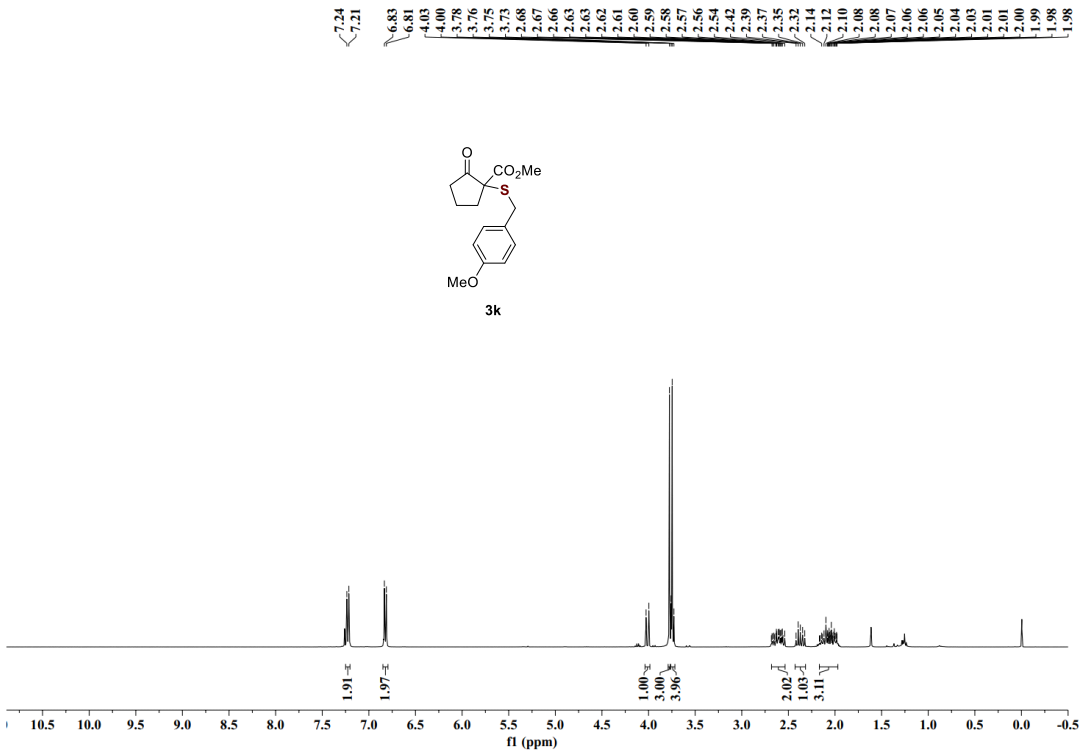

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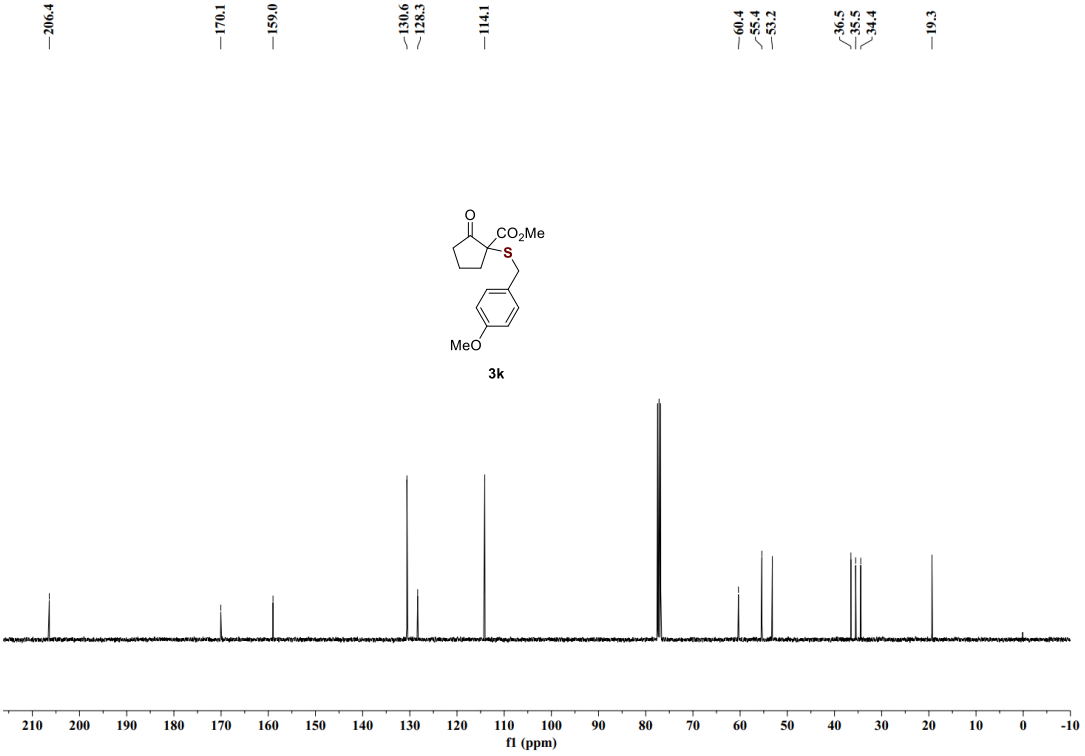

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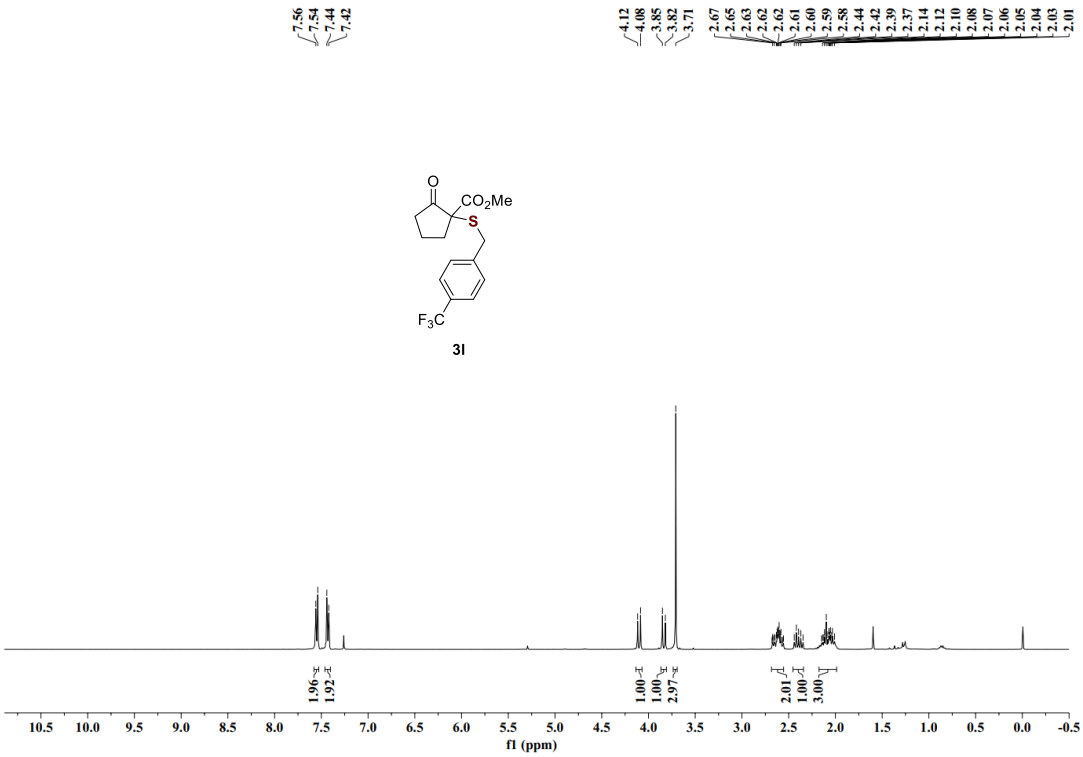

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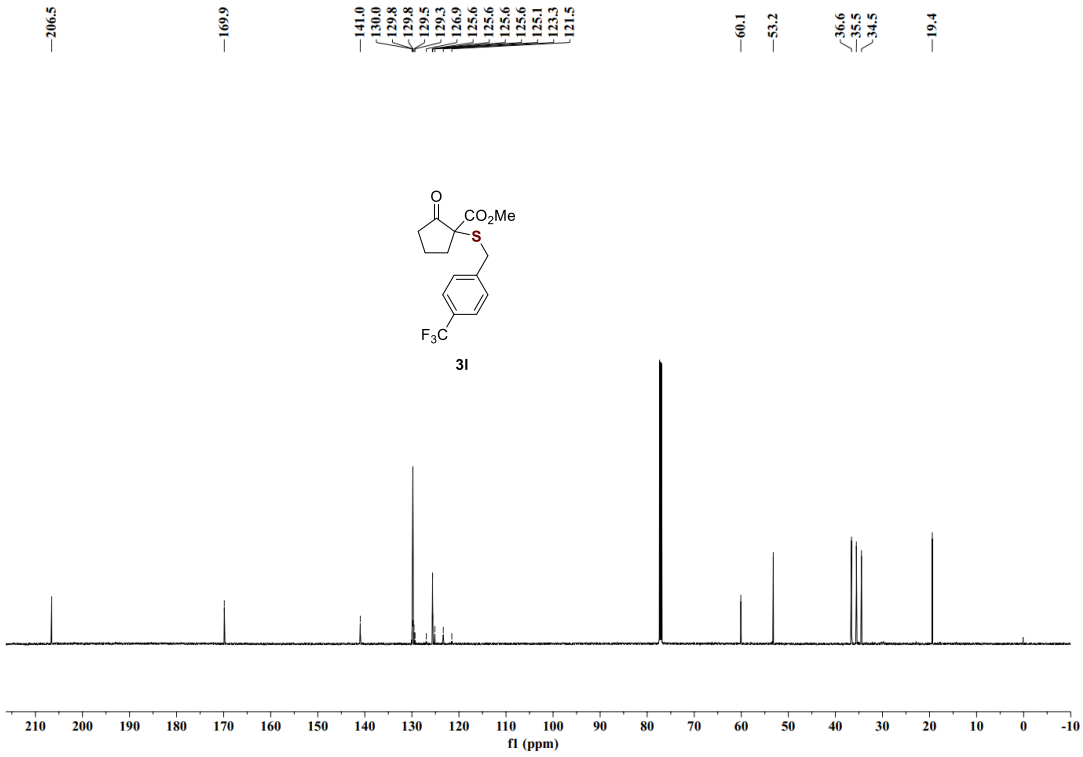
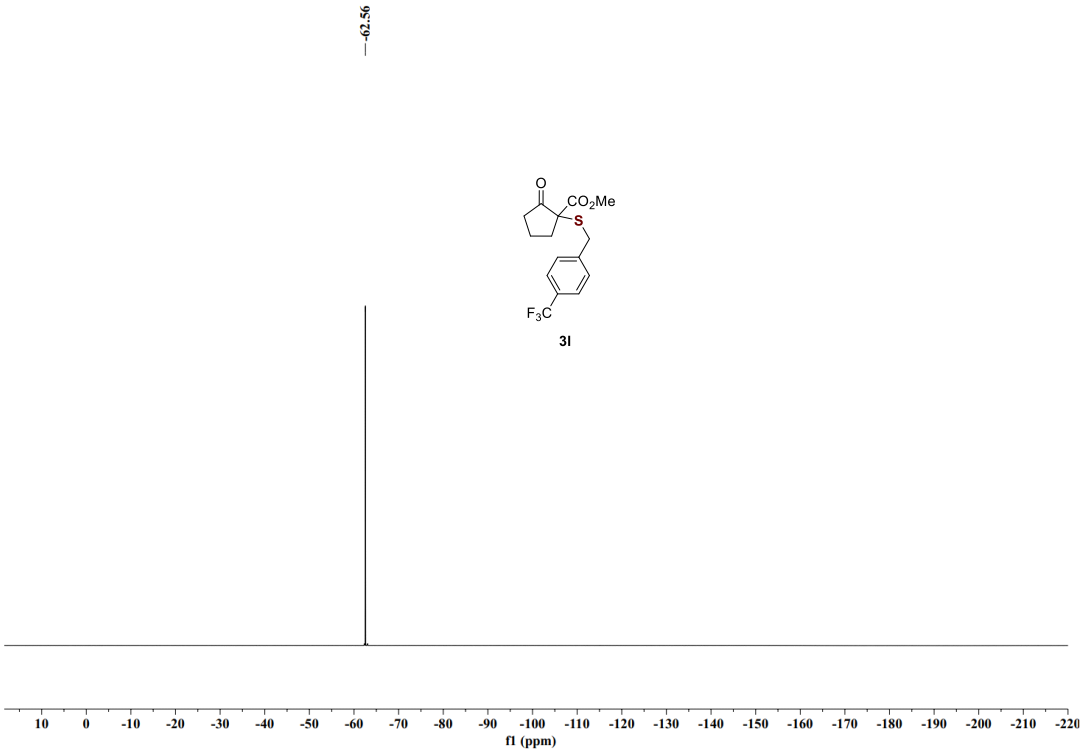


^{19}F NMR (376 MHz, $CDCl_3$)



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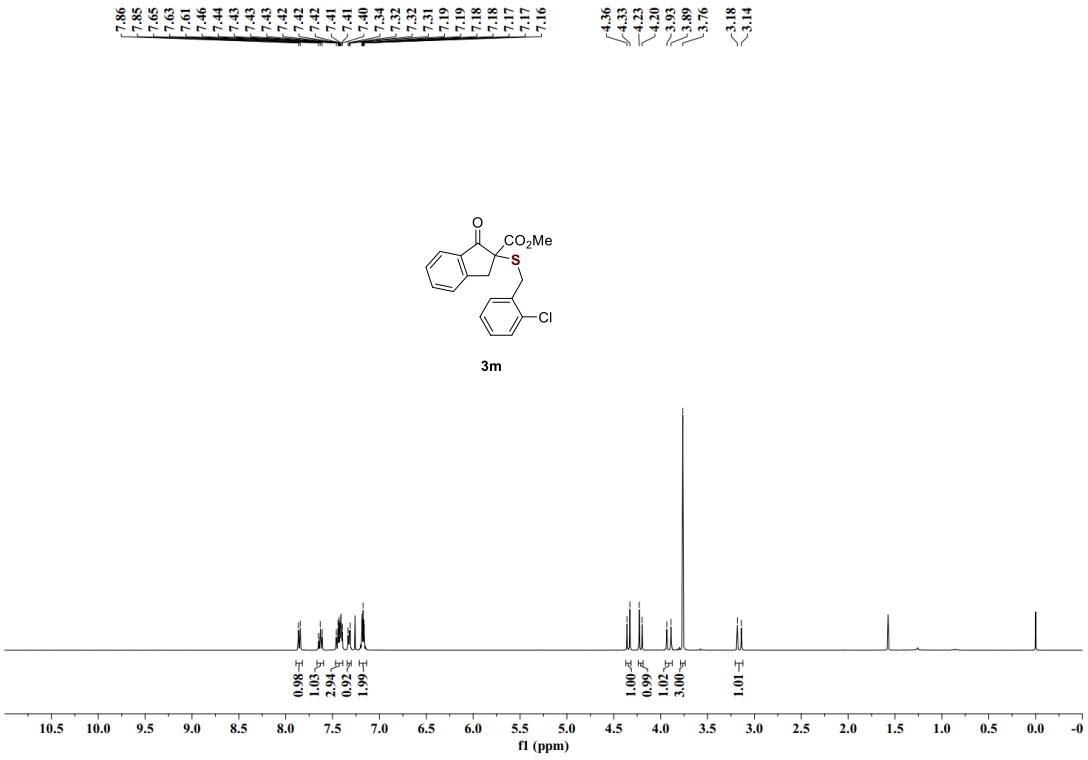

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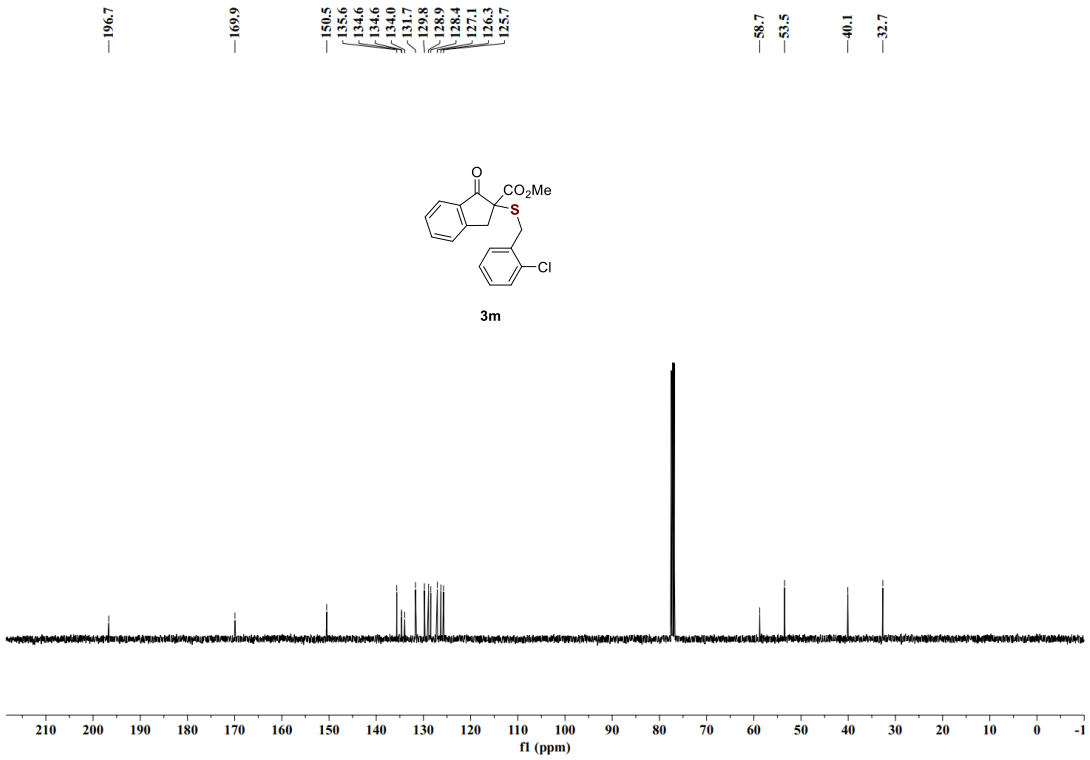
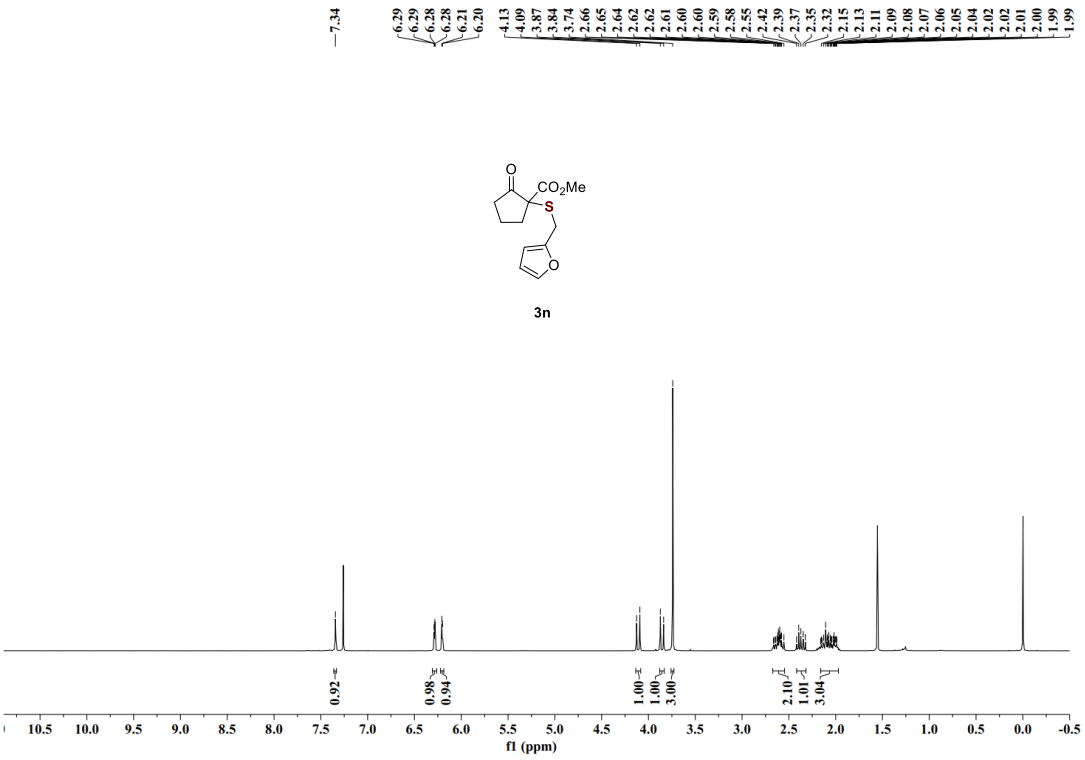
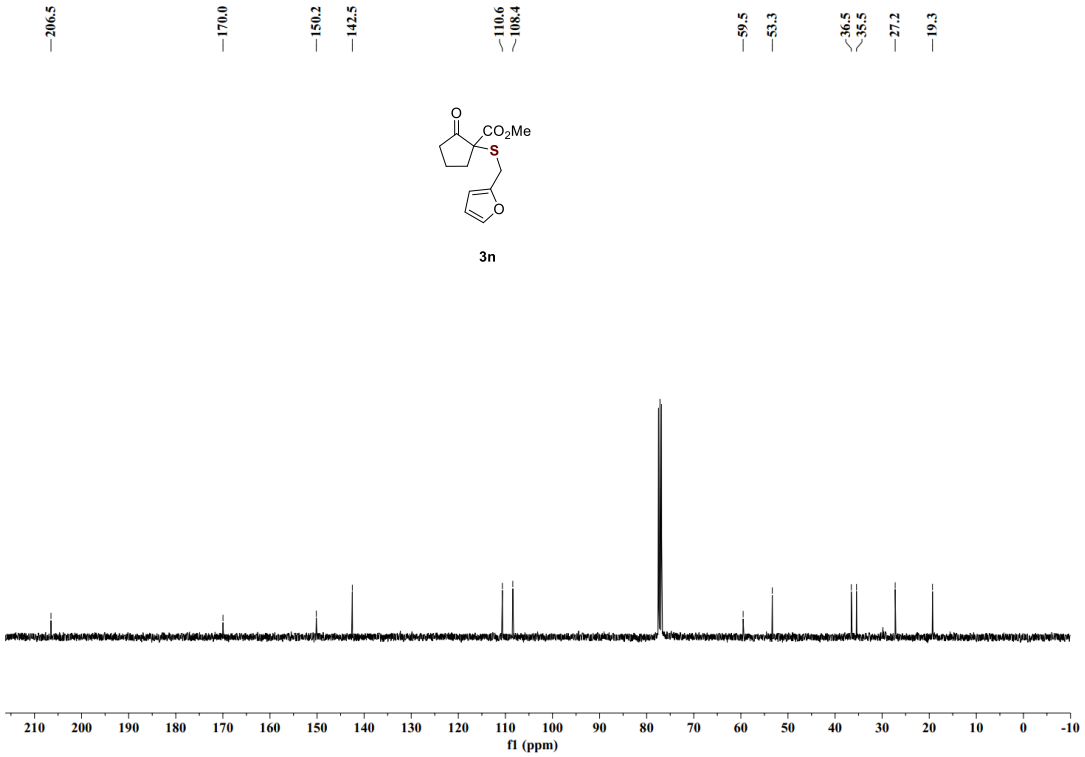


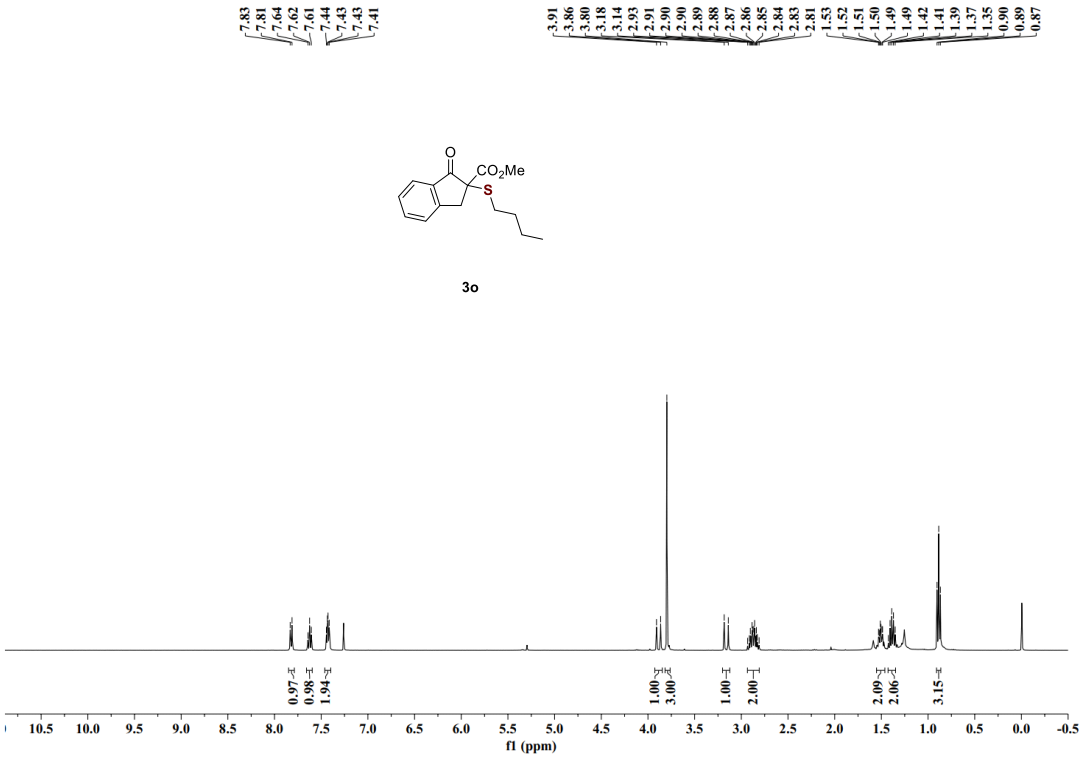
^{1}H NMR (400 MHz, $CDCl_3$)



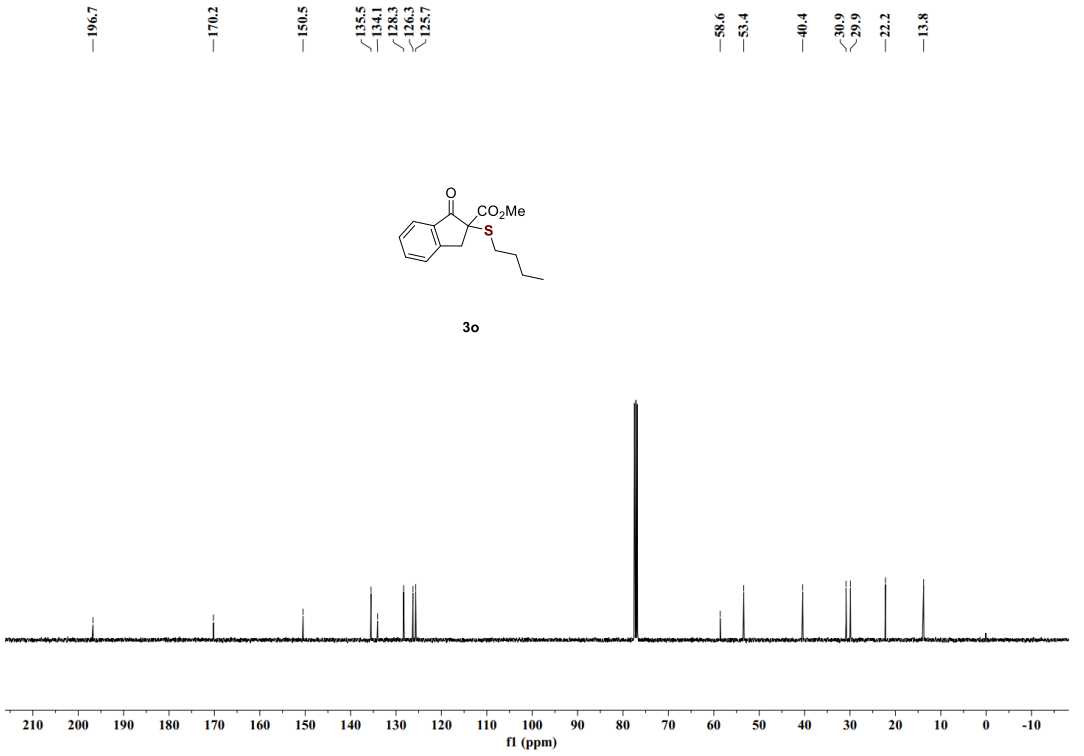
^{13}C NMR (101 MHz, $CDCl_3$)



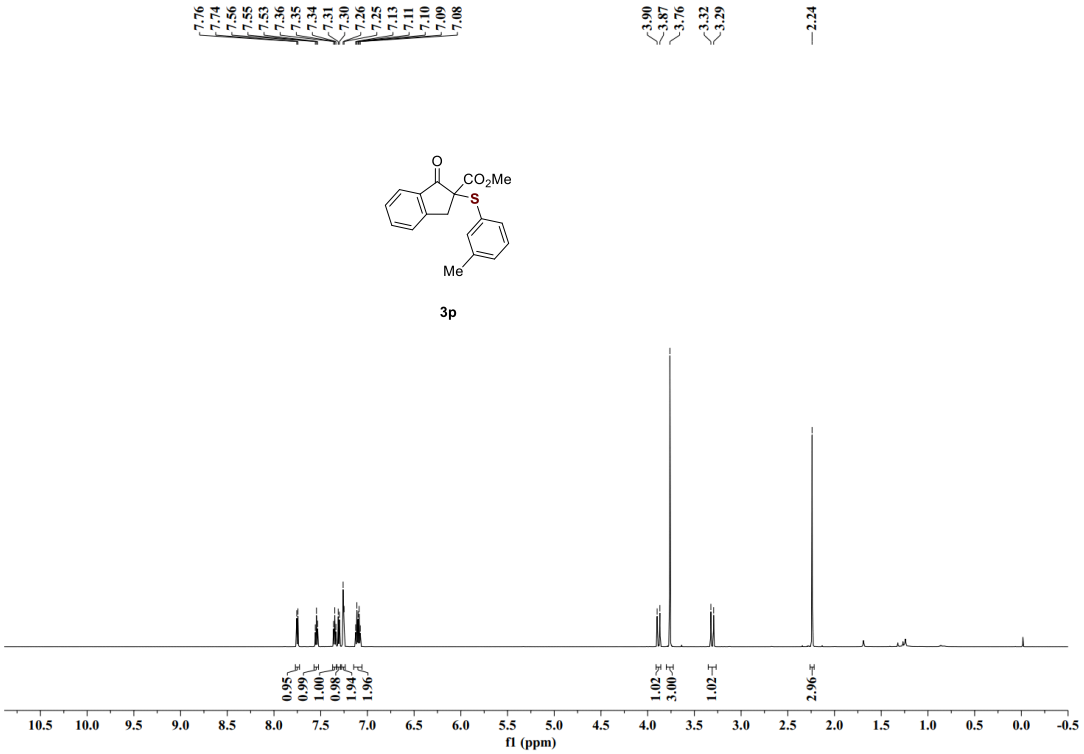
^{1}H NMR (400 MHz, $CDCl_3$)



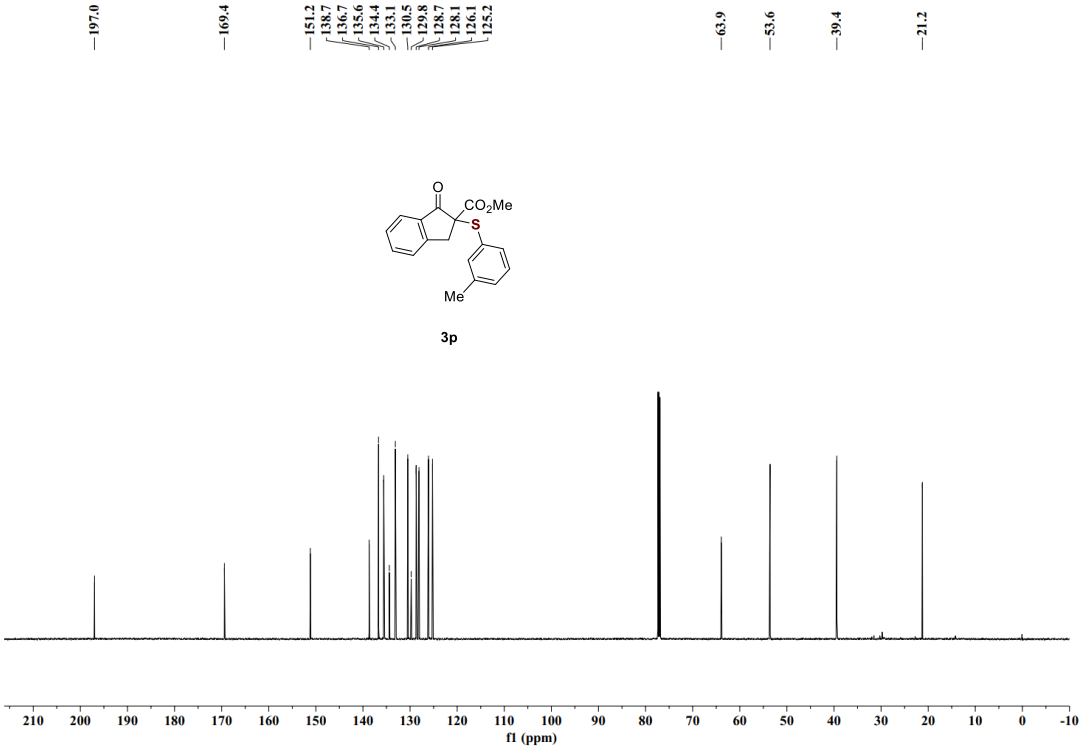
^{13}C NMR (101 MHz, $CDCl_3$)



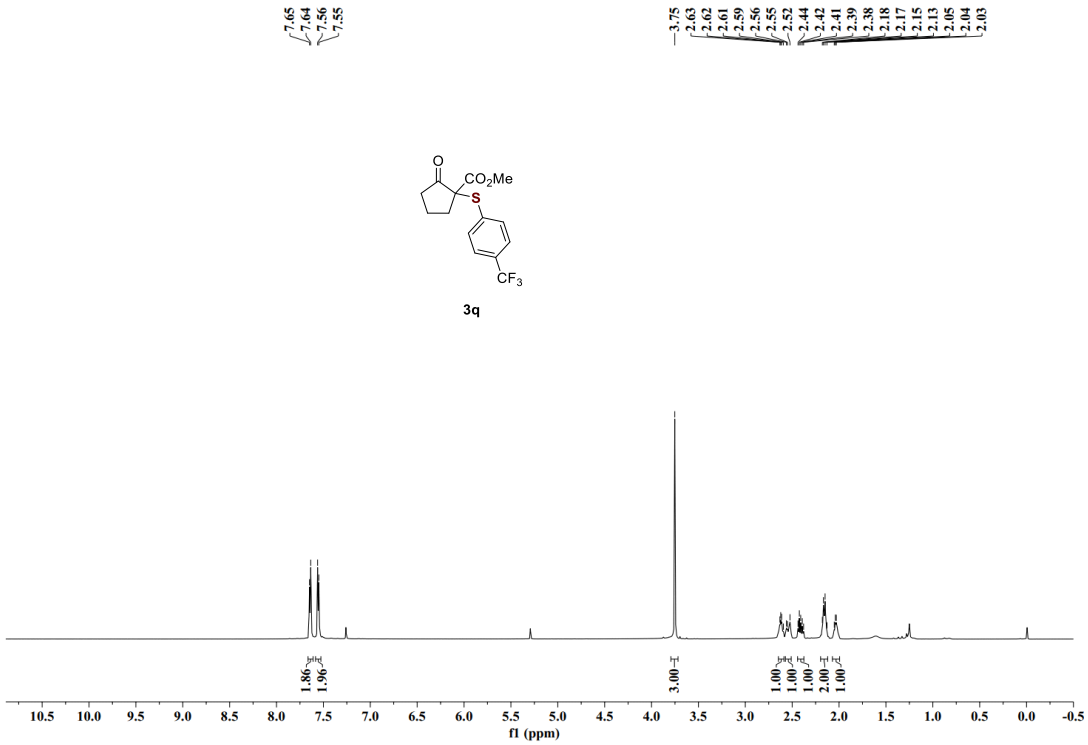
^{1}H NMR (600 MHz, $CDCl_3$)



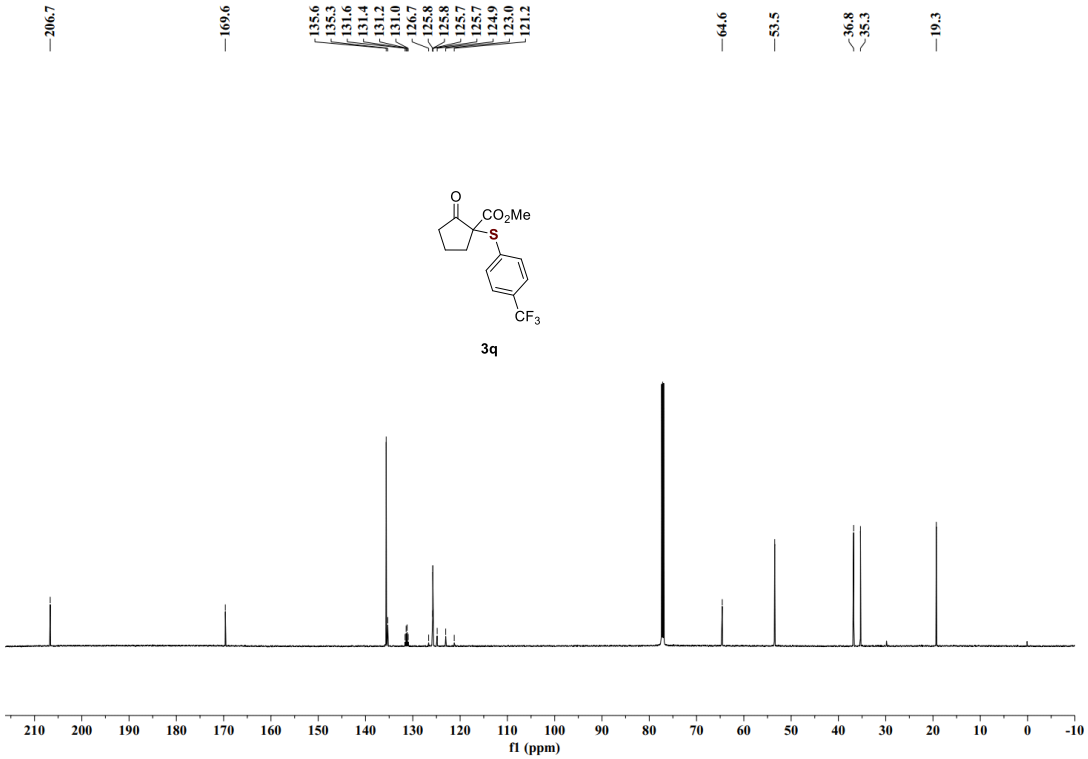
^{13}C NMR (151 MHz, $CDCl_3$)



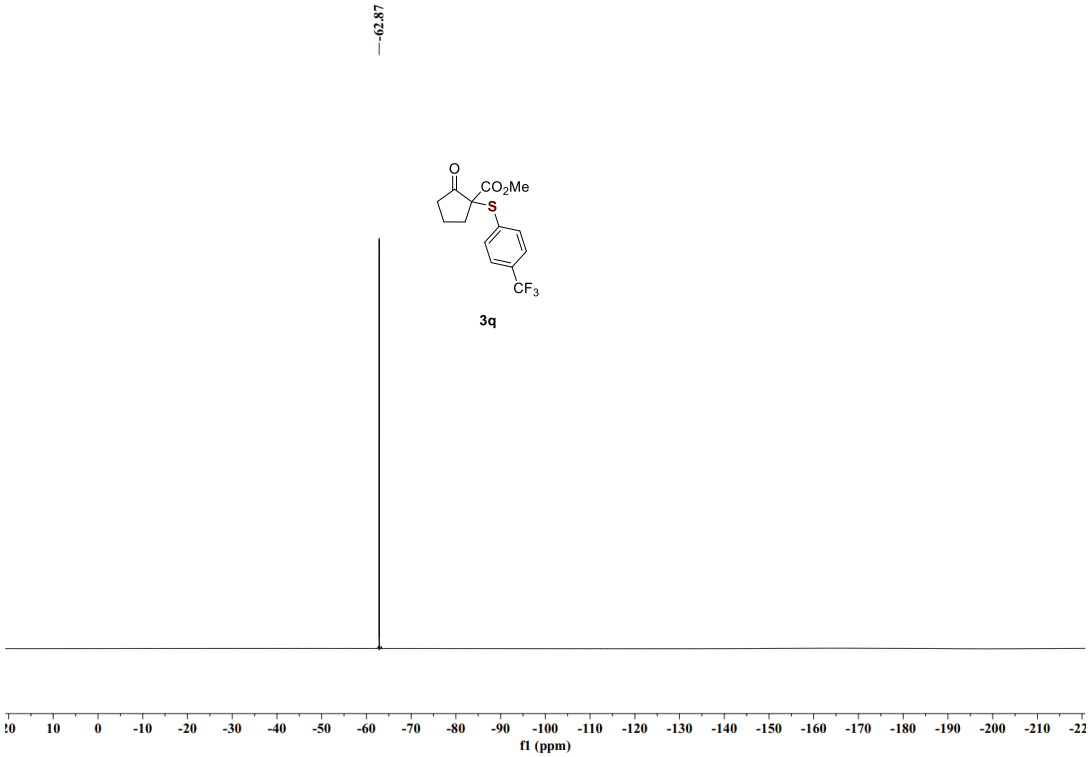
^{1}H NMR (600 MHz, $CDCl_3$)



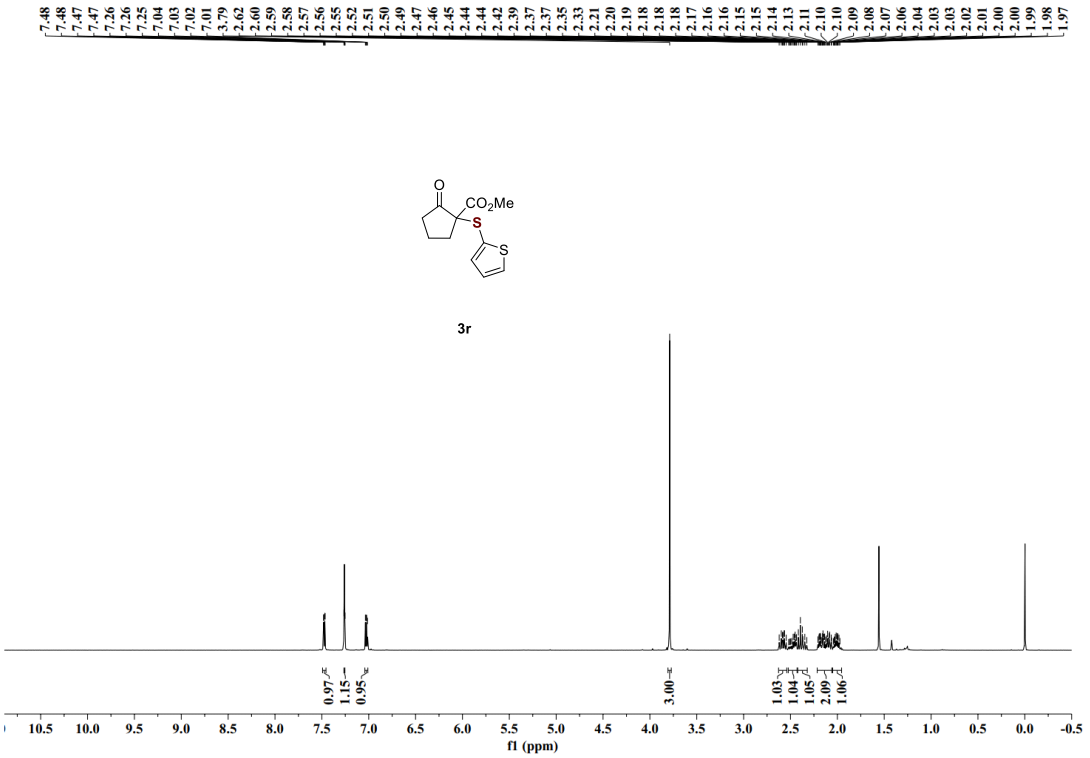
^{13}C NMR (151 MHz, $CDCl_3$)



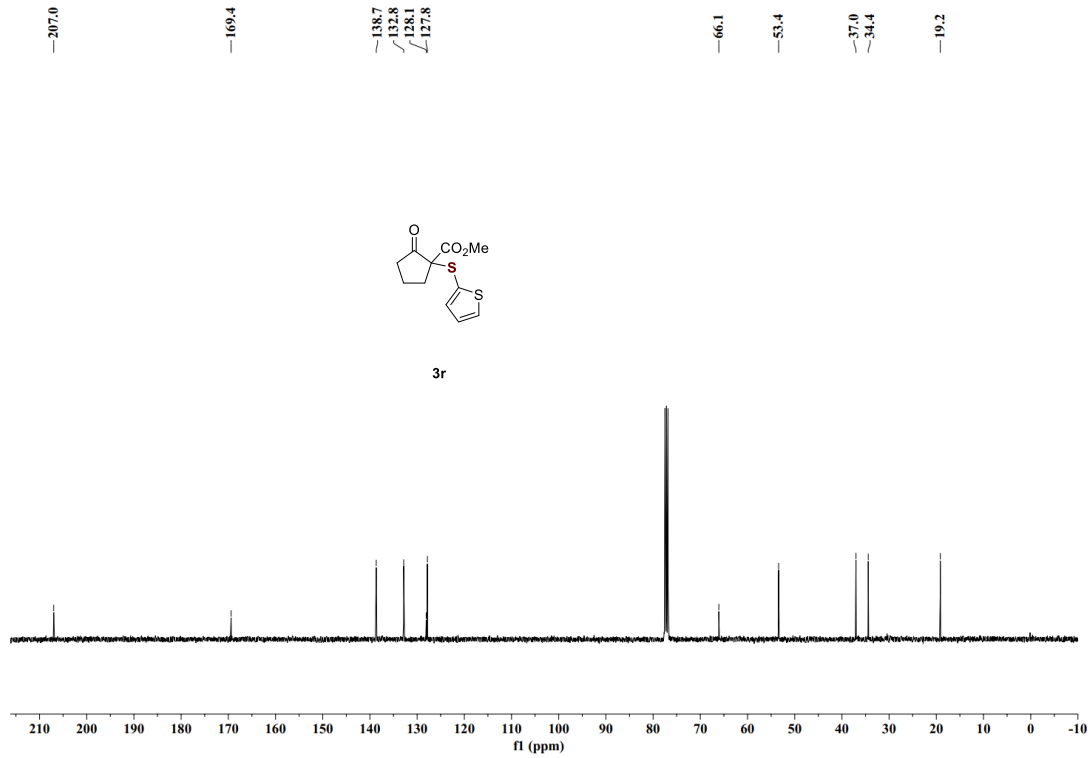
^{19}F NMR (376 MHz, $CDCl_3$)



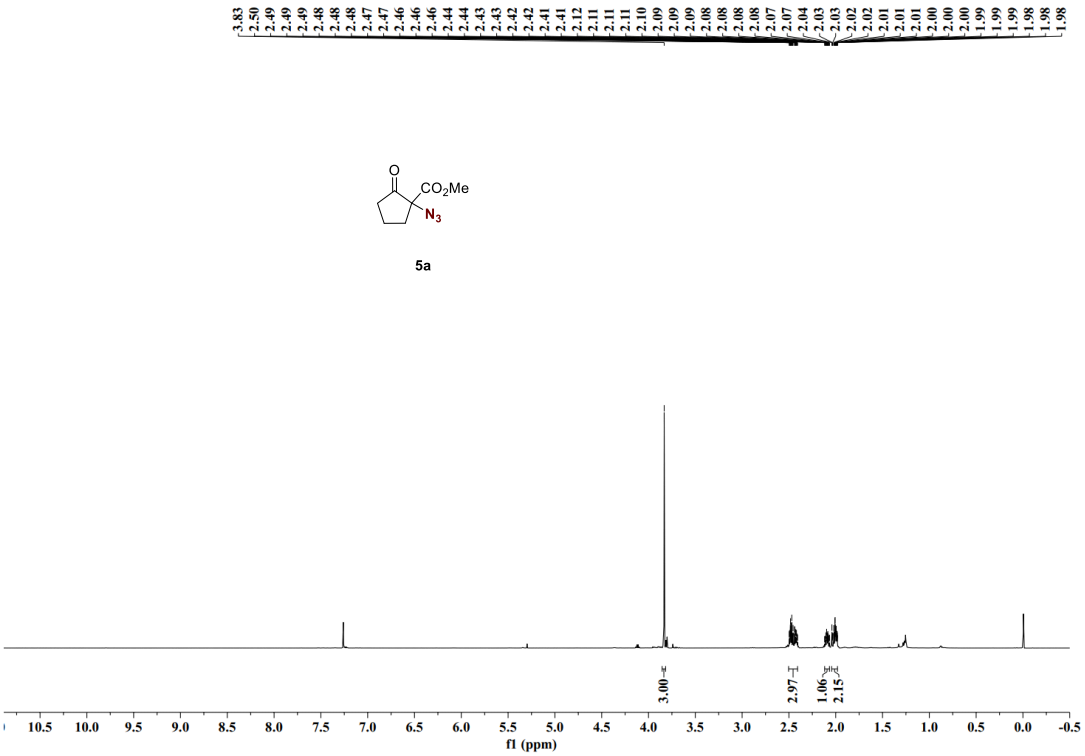
^{1}H NMR (400 MHz, $CDCl_3$)



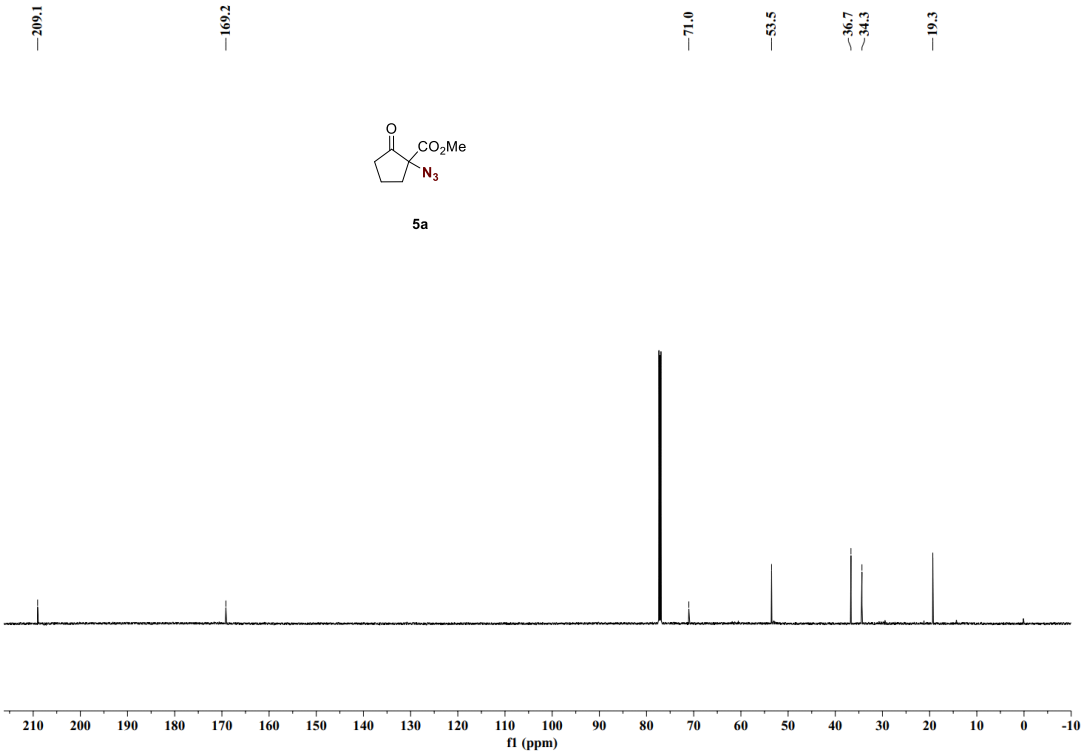
^{13}C NMR (101 MHz, $CDCl_3$)



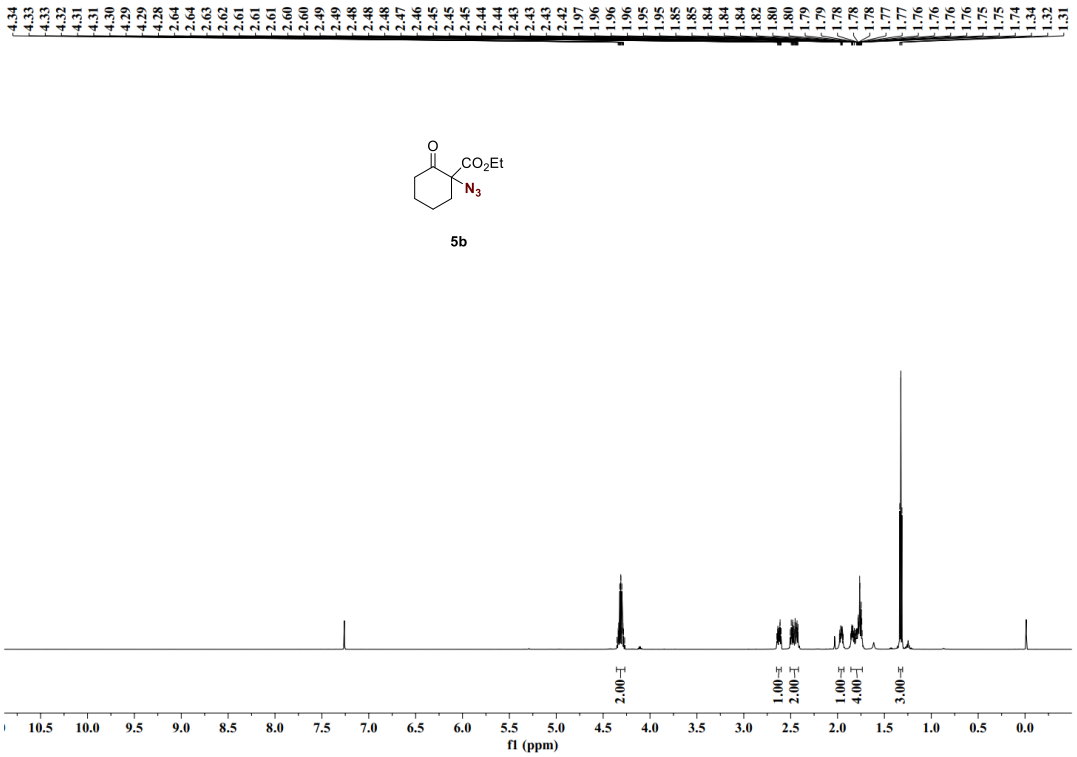
^{1}H NMR (600 MHz, $CDCl_3$)



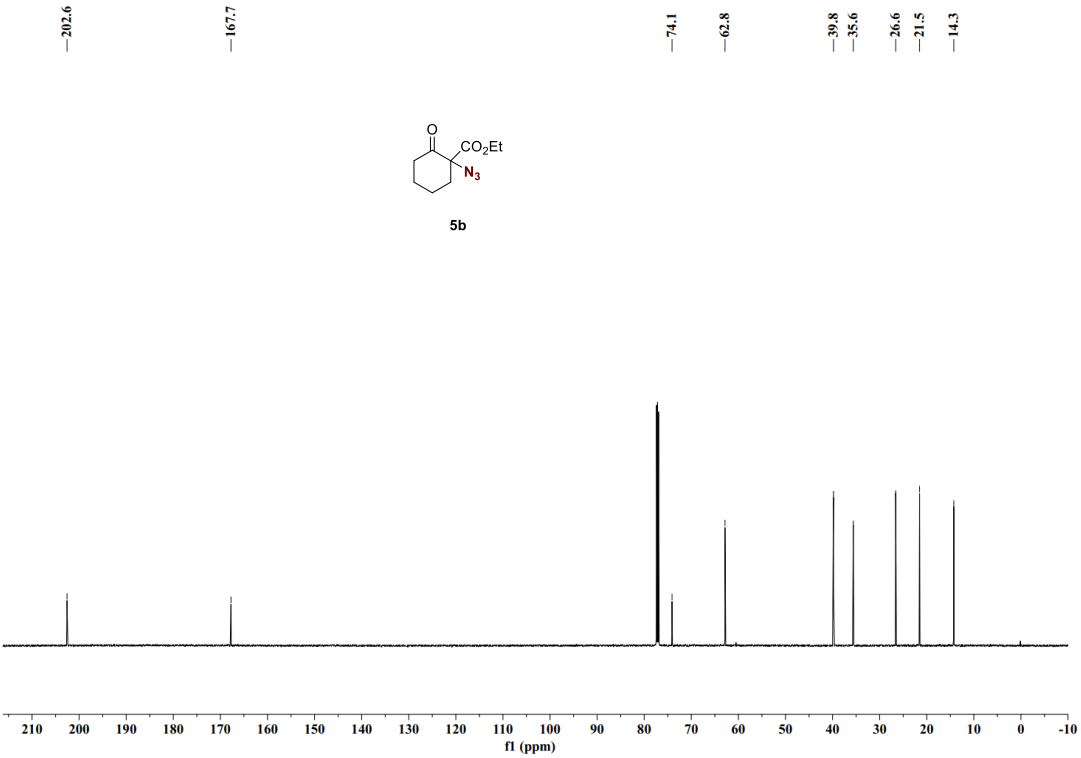
^{13}C NMR (151 MHz, $CDCl_3$)



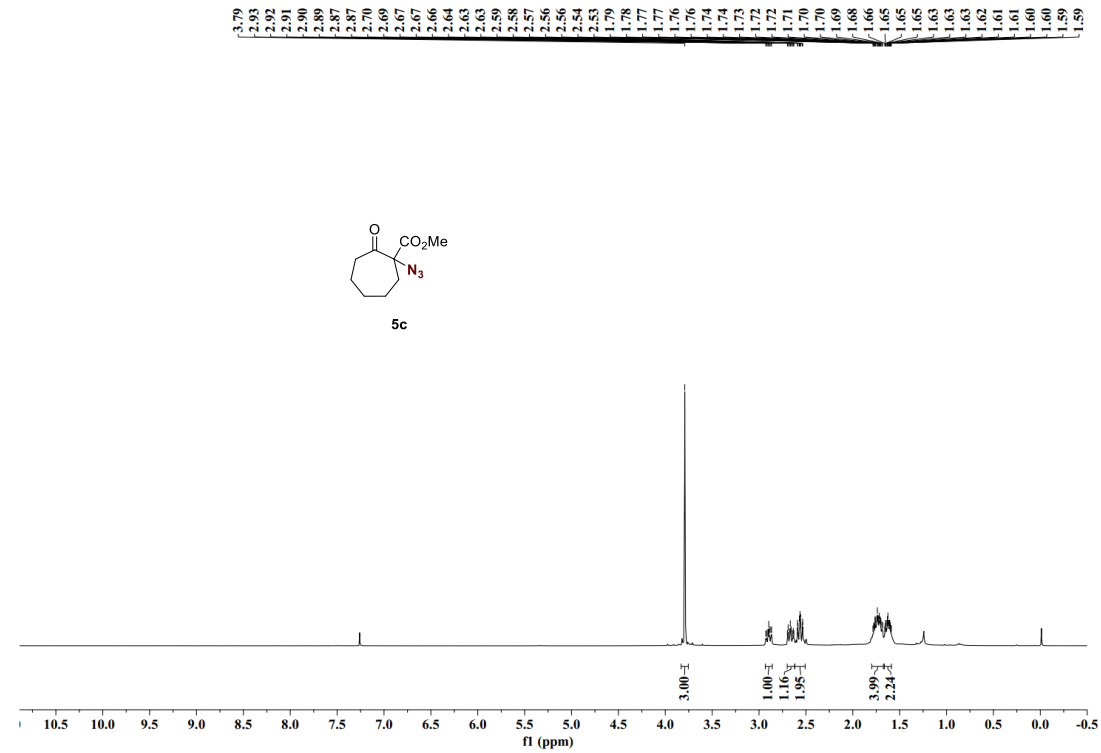
^{1}H NMR (600 MHz, $CDCl_3$)



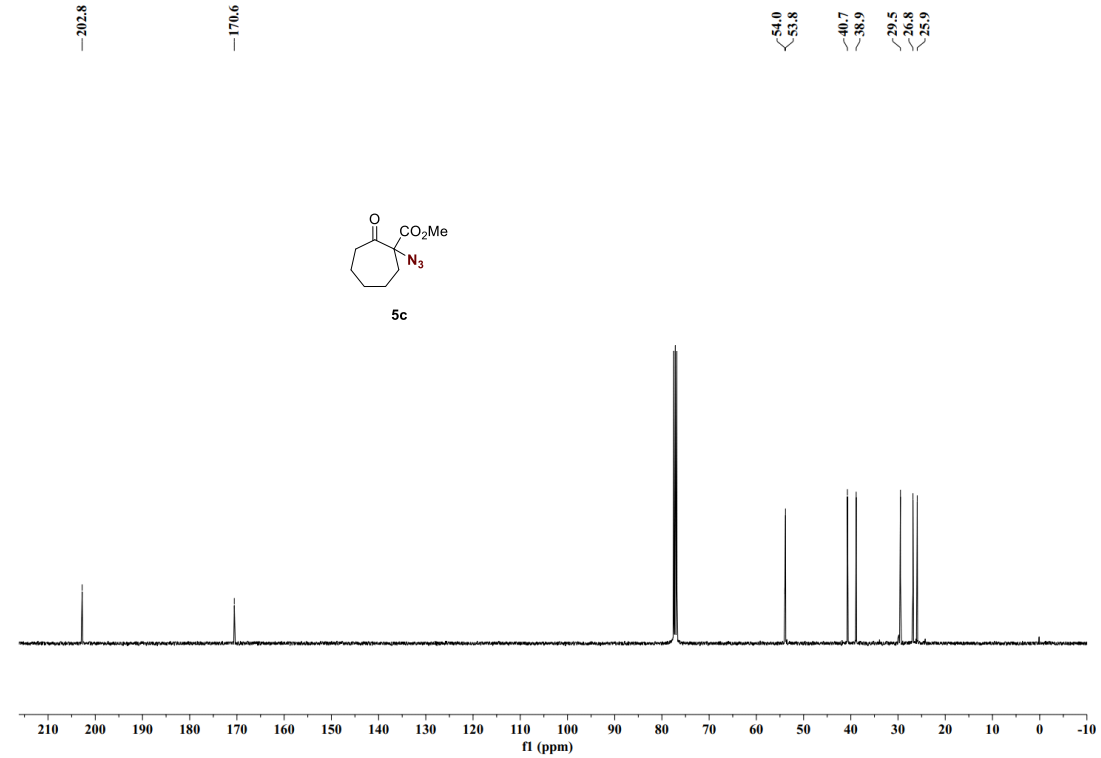
^{13}C NMR (151 MHz, $CDCl_3$)



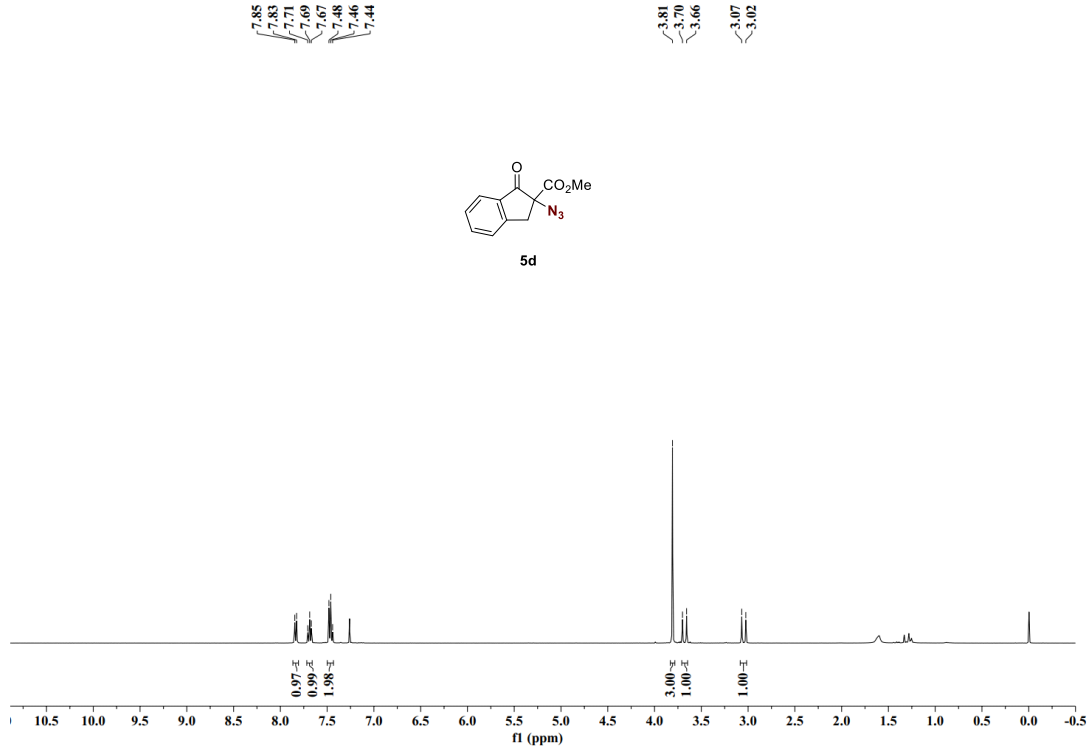
^{1}H NMR (400 MHz, $CDCl_3$)



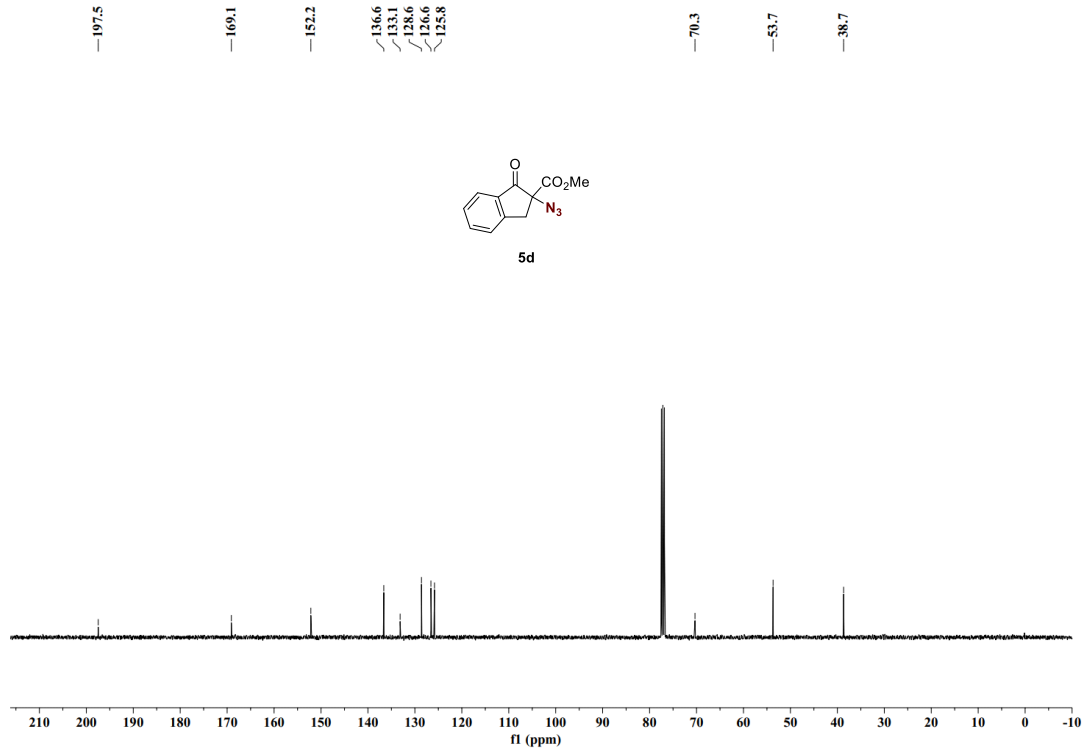
^{13}C NMR (101 MHz, $CDCl_3$)



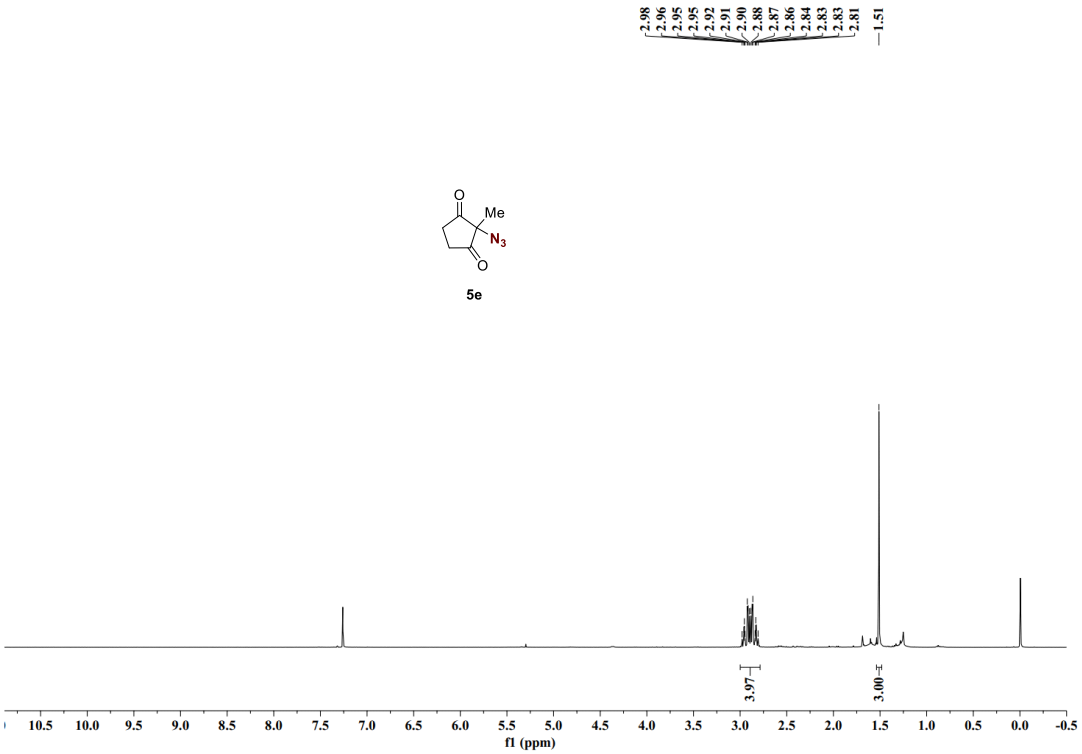
^{1}H NMR (400 MHz, $CDCl_3$)



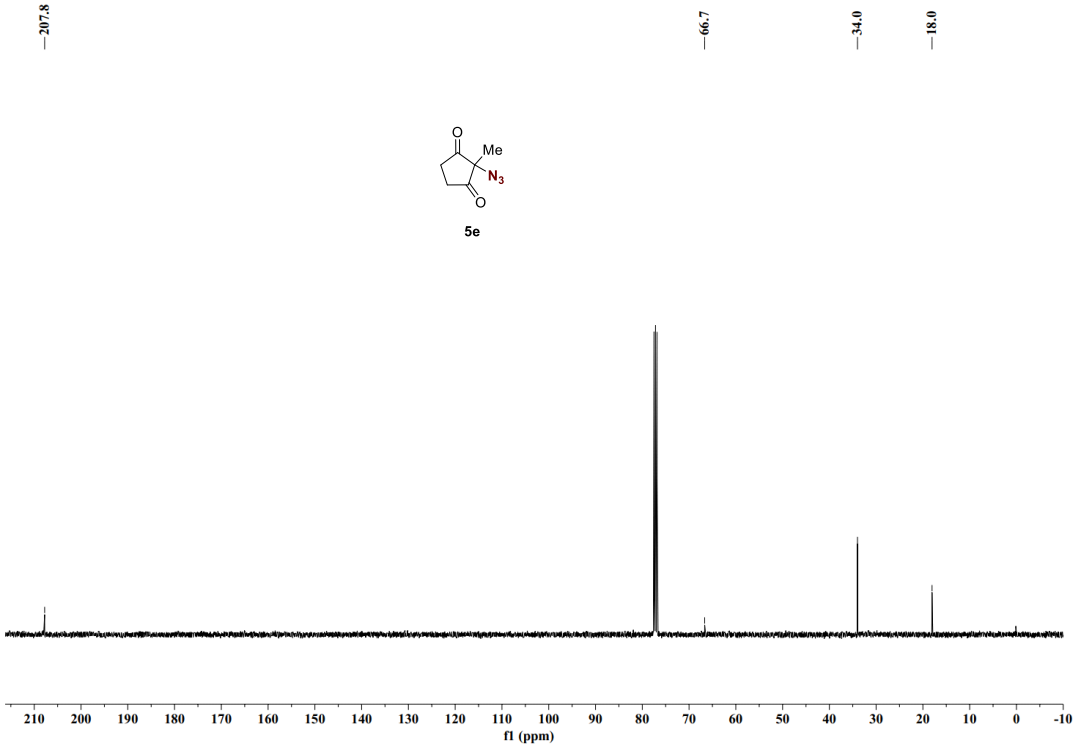
^{13}C NMR (101 MHz, $CDCl_3$)



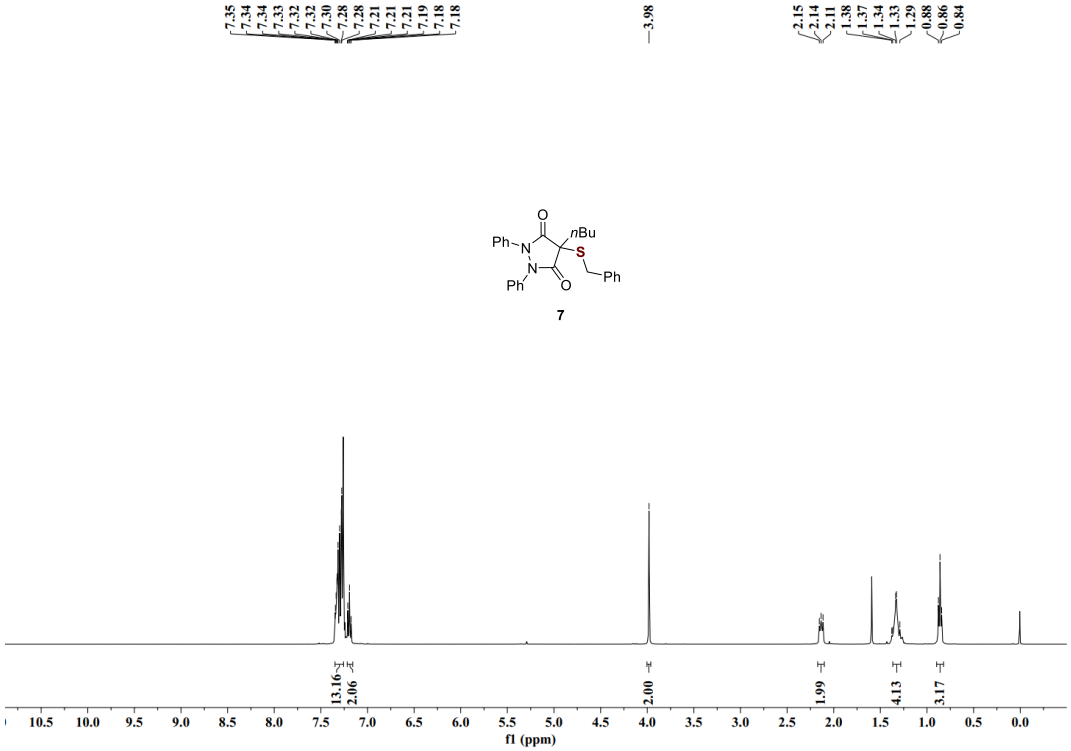
^{1}H NMR (400 MHz, $CDCl_3$)



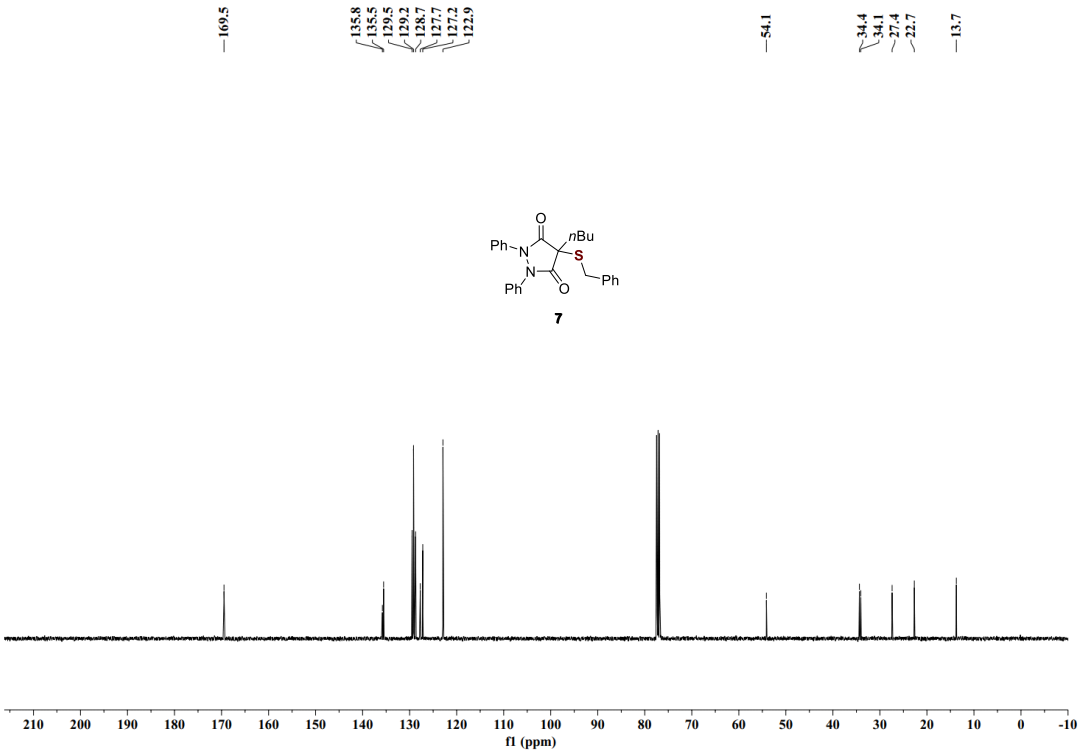
^{13}C NMR (101 MHz, $CDCl_3$)



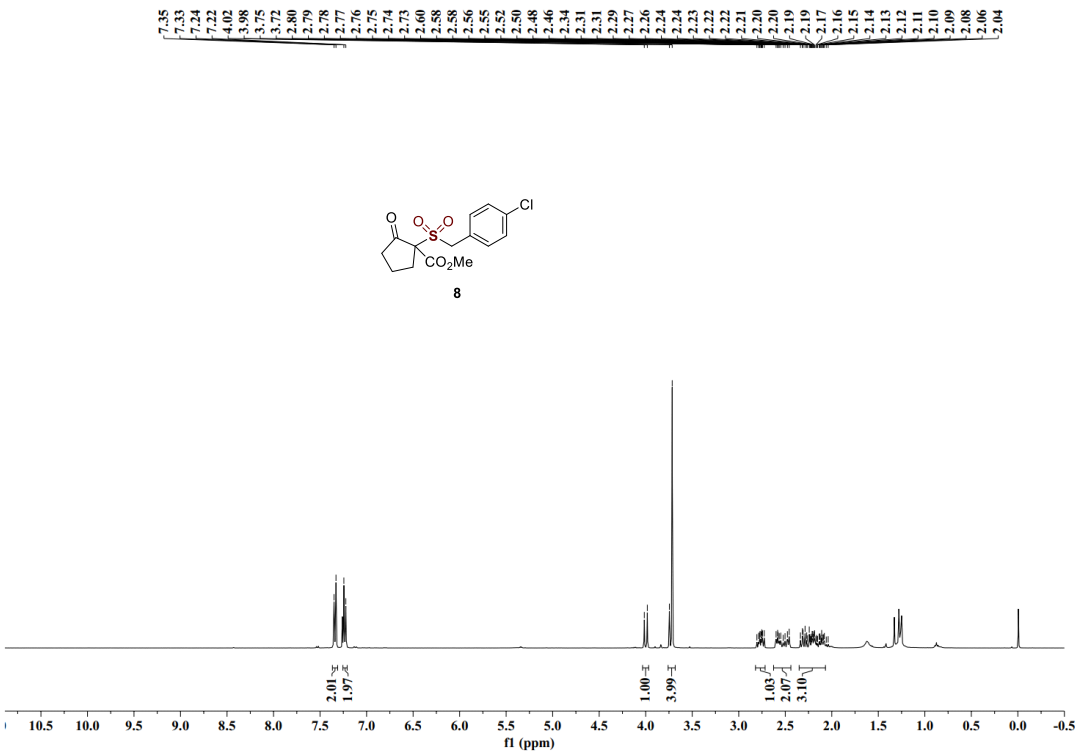
^{1}H NMR (400 MHz, $CDCl_3$)



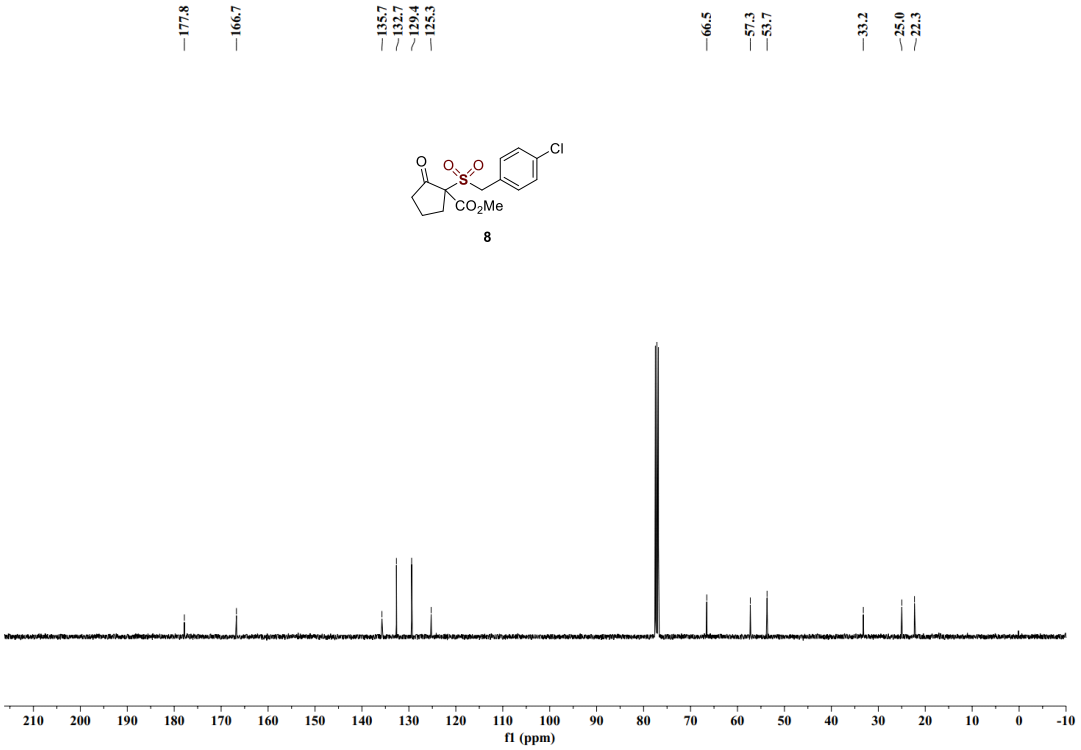
^{13}C NMR (101 MHz, $CDCl_3$)



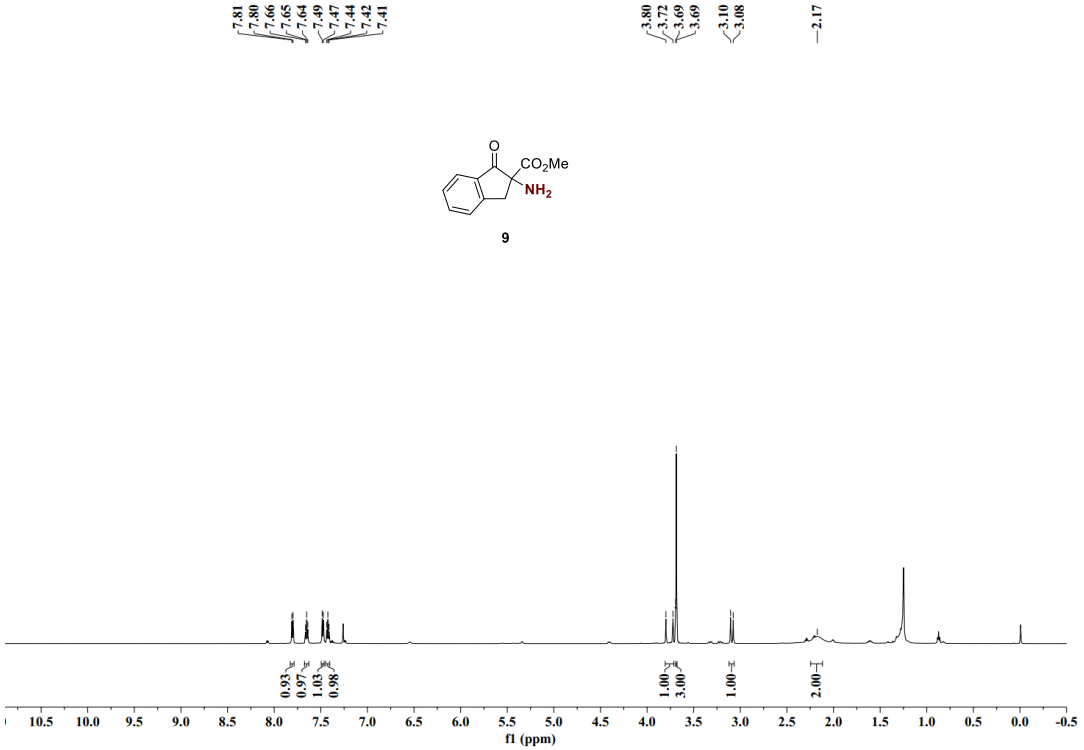
^{1}H NMR (400 MHz, $CDCl_3$)



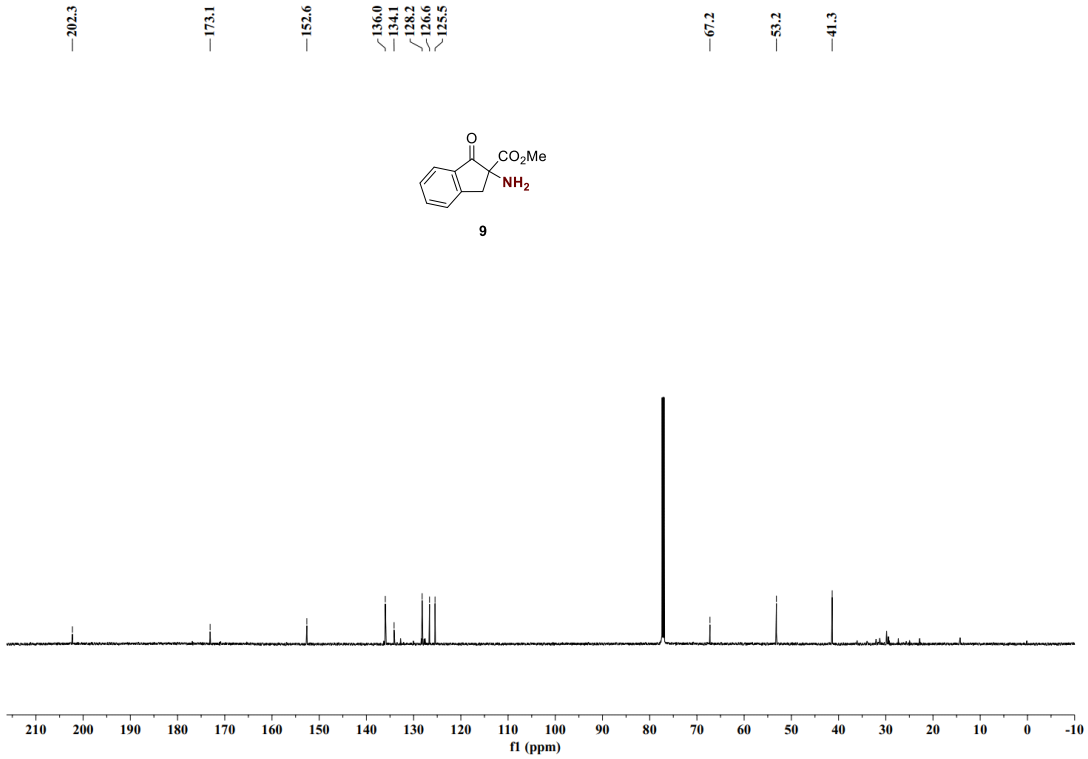
^{13}C NMR (101 MHz, $CDCl_3$)



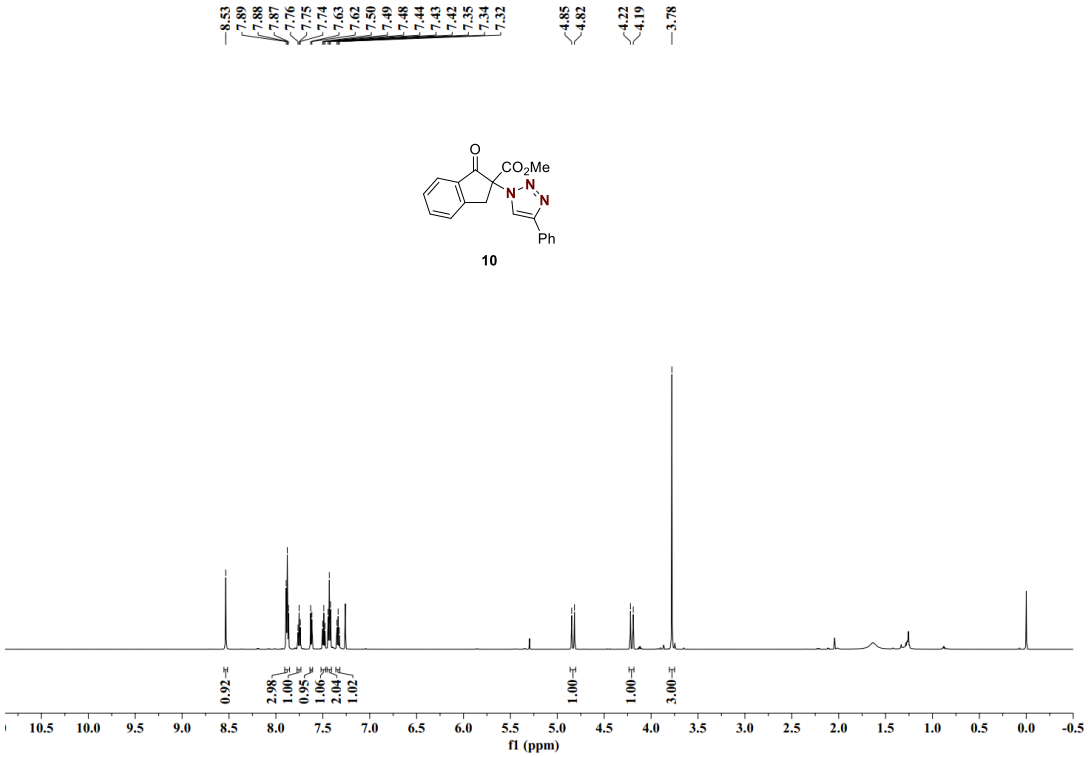
^{1}H NMR (600 MHz, $CDCl_3$)



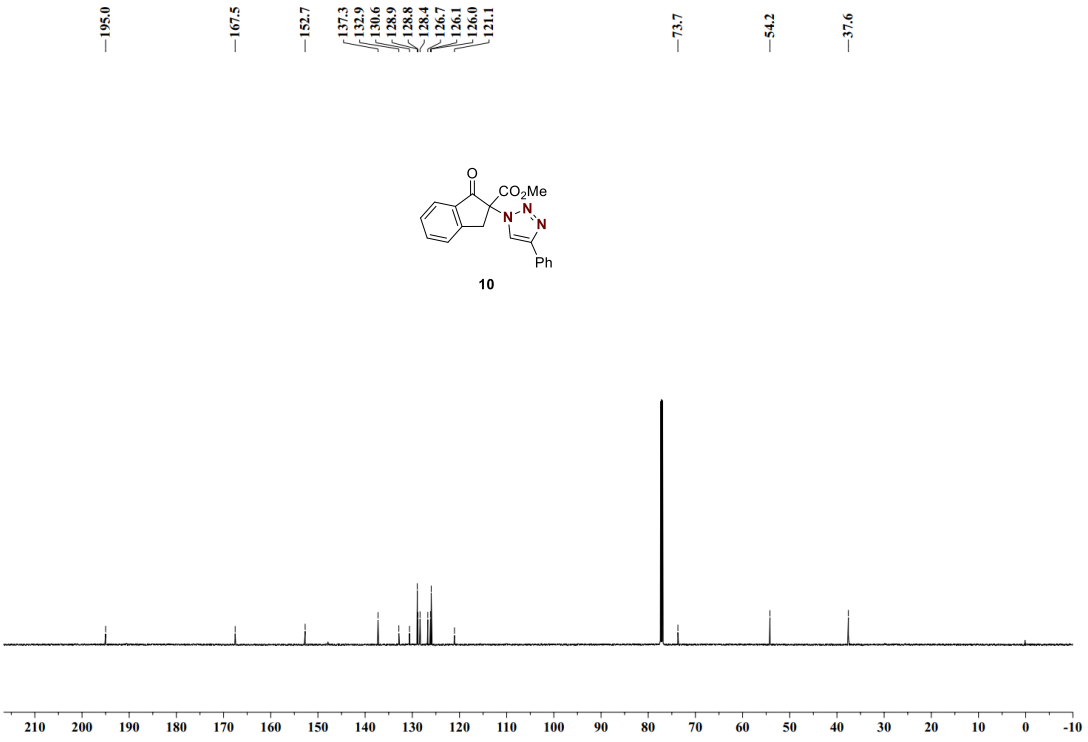
^{13}C NMR (151 MHz, $CDCl_3$)



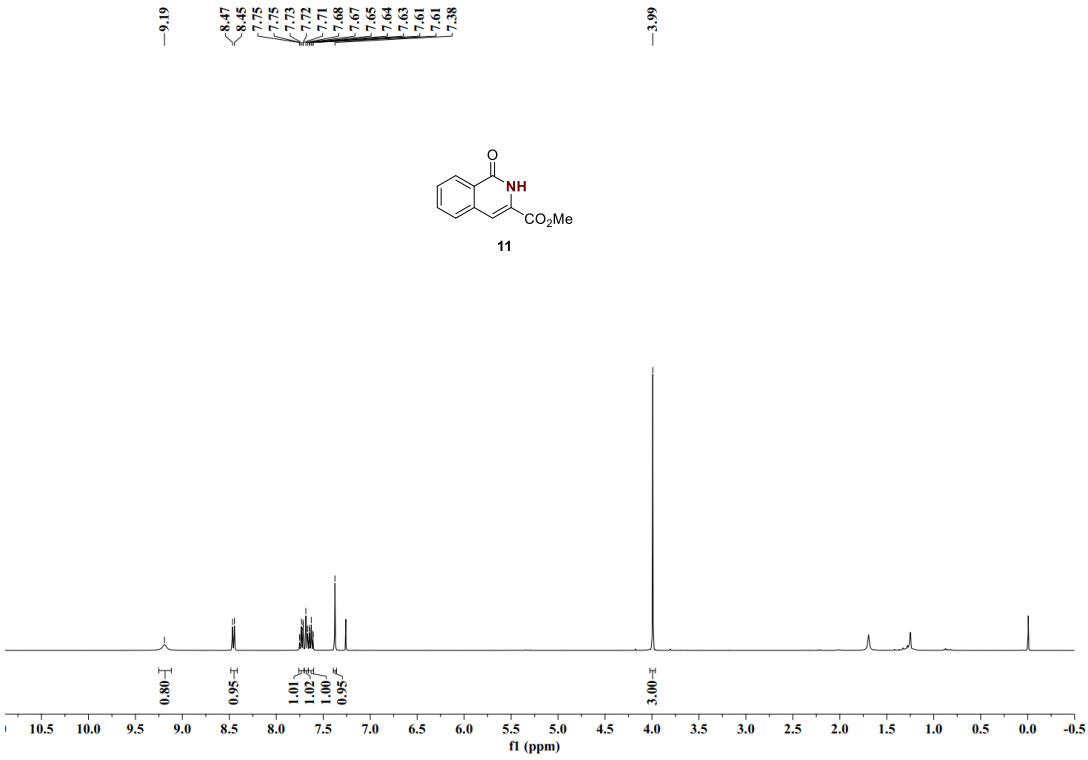
^{1}H NMR (600 MHz, $CDCl_3$)



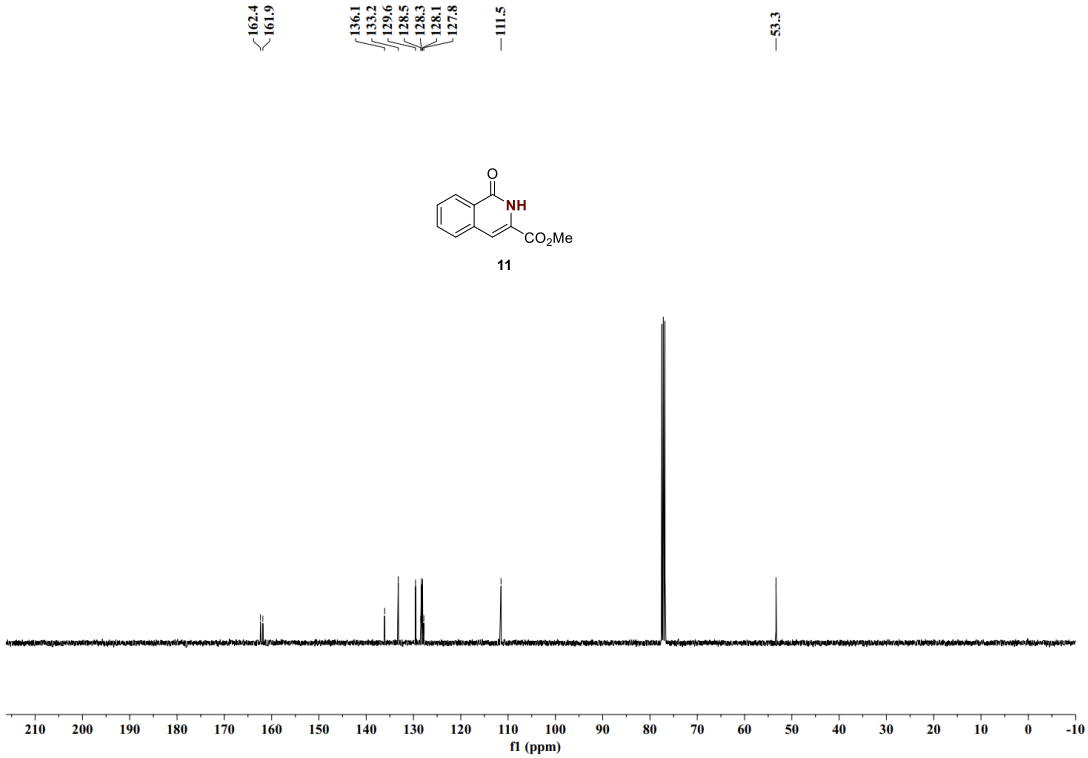
^{13}C NMR (151 MHz, $CDCl_3$)



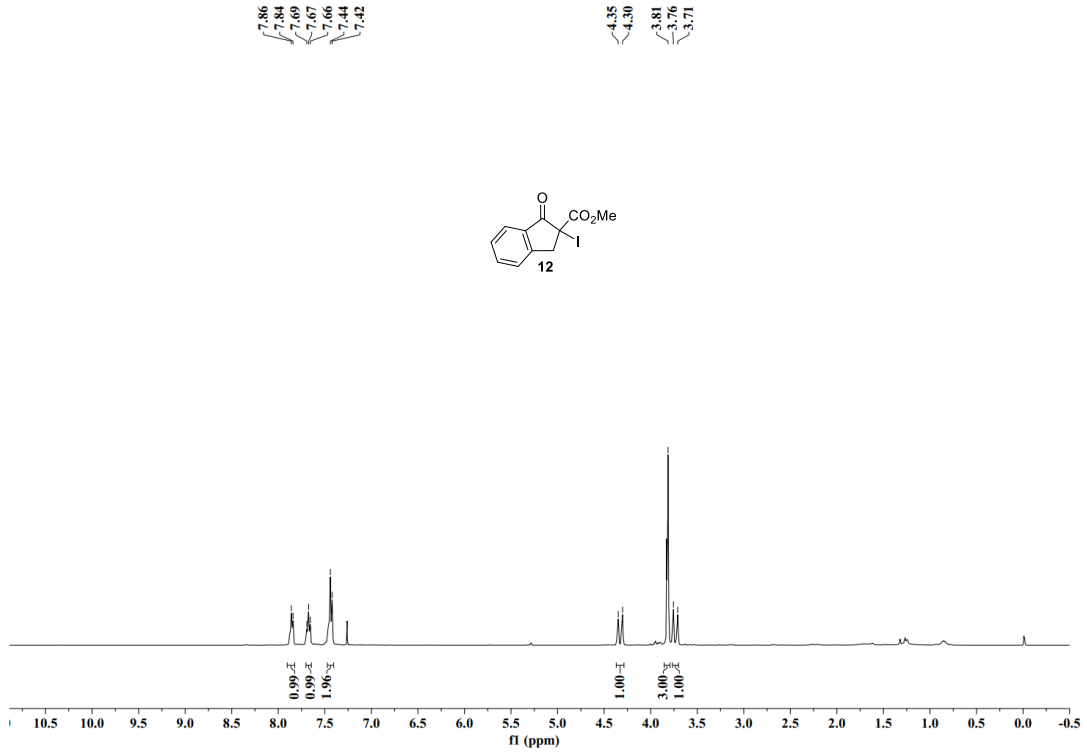
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)